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Synthetic Investigations Towards Substituted Pentacenes for Thin-Film Electronics

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Synthetic Investigations Towards Substituted Pentacenes for Thin-Film Electronics

Kelly VanCrey

B.Sc. (Honours, Co-Op), McMaster University, 2003

Thesis Submitted to the
School of Graduate Studies and Research
University of Ottawa
In Partial Fulfillment of the Requirements for the
Degree of Master of Science

Ottawa-Carelton Chemistry Institute
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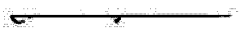

Professor A.G. Fallis

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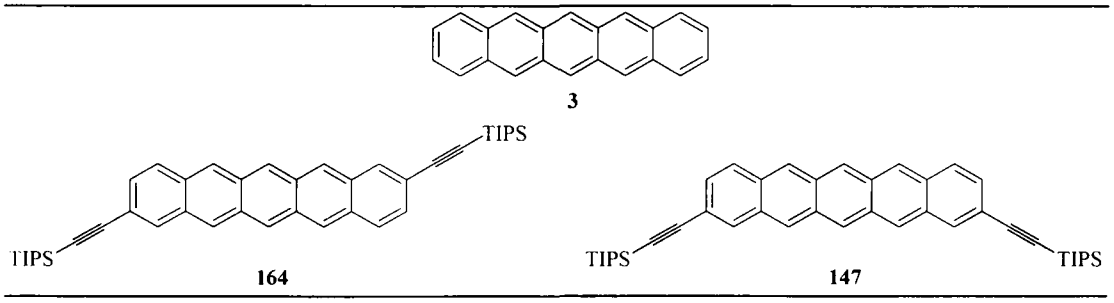
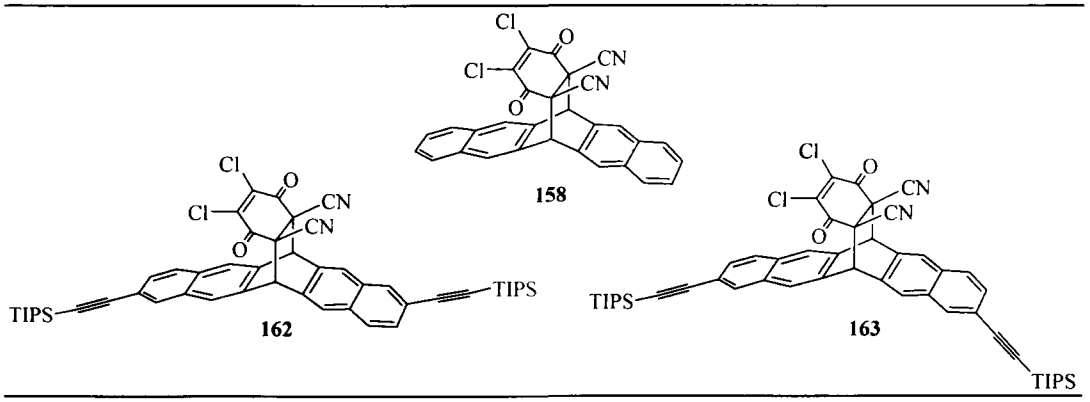
Abstract

The purpose of this project was to design a new and efficient synthetic route to 2,9 and 2,10 disubstituted pentacenes (**164** and **147**). The original route that was developed for these compounds in the Fallis Lab was lengthy and low yielding. A new and improved synthesis was developed; however, the tandem double Diels-Alder/aromatization reaction was not regioselective. In despite of this, both isomers were easily separated by fractional recrystallization. The 2,9 and 2,10 disubstituted pentacenes and pentacene were synthesized and trapped *in situ* with DDQ (**162**, **163** and **158**) to afford an air stable, soluble pentacene precursor. We believe that these adducts have the capability for casting into thin-films. Subsequent heating should allow for a retro-Diels-Alder reaction to afford disubstituted pentacenes **164** and **147** and unsubstituted pentacene (**3**). In addition, a new route to unsubstituted pentacene (**3**) was developed, which has several benefits over the existing literature procedures.





Abstract

In recent years, the demand for mobile telephone services has been increasing rapidly. However, the electro-magnetic spectrum of frequencies allocated for this purpose is limited and many constraints have to be respected in order to avoid channel interferences.

The main contributions of this thesis are

1. to provide a classification of channel allocation algorithms based upon their characteristics.

2. to enhance the distributed algorithm for dynamic channel allocation developed by A. Boukerche *et al.*, by adding an efficient adaptive channel reservation schema in order to provide continuous QoS support.

3. to propose a distributed fault-tolerant channel allocation scheme which can work well under the *mobile host failures*, *base station failures* and *communication link failures*.

4. to enhance further our dynamic channel allocation by integrating both QoS and fault tolerant components.

Our algorithms are based upon mutual exclusion model where the channels are grouped by the number of cells in a cluster and each group of channels cannot be shared concurrently within the cluster. We describe our algorithms and discuss their implementation. Finally, we present the main results of the extensive set of simulation experiments that have been used in order to evaluate their performance.

Acknowledgements

There are several people that I would like to thank that have been apart of my life the past two years that have helped me develop as a person and as a good chemist.

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I owe thanks to my co-workers in the Fallis Lab. Matt, you took me under your wing when I arrived and to this day I think of you as my second supervisor. Our blackboard sessions with Classics and all of your help with my seminar and thesis is greatly appreciated - I owe most of my chemistry knowledge to you. Natalie, you are a good friend, the few beers that we have shared and kilometers that we ran were a well needed component of this degree. Christophe and Sara, the "french post-docs". I enjoyed your company in the lab (even though Sara always got in my way!) and thanks for your help with my project – Christophe, one day we will know that mechanism!

I would also like to thank the people across the hall, the Ogilivie Lab and Joe #2, for there help when I wondered over there and their friendship. Pat Bazinet and Jen Scott, thanks for your friendship and being my short distance running buddies. The volleyball team (you know who you are) I had a blast playing with you guys and I will be thinking of you this year. Go team!

Finally, I could not have done this without my friends, family and Darren. My high school and Mac friends gave me my well needed breaks on the weekends. My parents and sisters gave me endless support and encouragement from the beginning. Finally, Darren, thank you for moving to Ottawa with me, I know I could not have done this without you. Thank you for your patience, love and support.

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List of Schemes

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List of Abbreviations

AIBN	azobisisobutyronitrile
*n*BuLi	*n*-butyllithium
CAN	ceric ammonium nitrate
DBH	1,3-dibromo-5,5-dimethylhydantoin
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMF	*N,N*-dimethylformamide
DMA	*N,N*-dimethacetamide
DMSO	dimethyl sulfoxide
EA	ethyl acetate
EI	electron impact
eq.	equivalents
g	grams
H_2O	distilled water
h	hour
HRMS	high resolution mass spectroscopy
Hz	hertz
IBX	*o*-iodoxybenzoic Acid
IR	infrared
J	coupling constant
LAH	lithium aluminum hydride
m	multiplet
mmol	millimole
mL	milliliter
mp.	melting point
NBS	*N*-bromosuccinimide
NMR	Nuclear Magnetic Resonance
PCC	pyridinium chlorochromate
PE	petroleum ether
pTSA	*para*-toluenesulfonic acid

rongalite	sodium hydroxymethanesulfinate
rt	room temperature
s	singlet
SM	starting material
t	triplet
TBAB	tetrabutylammonium bromide
TBAF	tetrabutylammonium fluoride
TBS	*t*-butyldimethylsilyl
TBSCl	*t*-butyldimethylsilyl chloride
TCNE	tetracyanoethylene
Tf	triflate
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromotography
TMEDA	*N,N,N',N'*-tetramethylethylenediamine
TMS	trimethylsilyl

1 Introduction

A previous research project in the Fallis lab was directed toward the synthesis of pentaceneophane **1**, with the goal of preparing a planar cyclophane (Figure 1). It is known that by having *meta*-substituted capping rings and the appropriate bridges, planarity could be achieved. This would require the synthesis of a 2,10 disubstituted pentacene **2**.

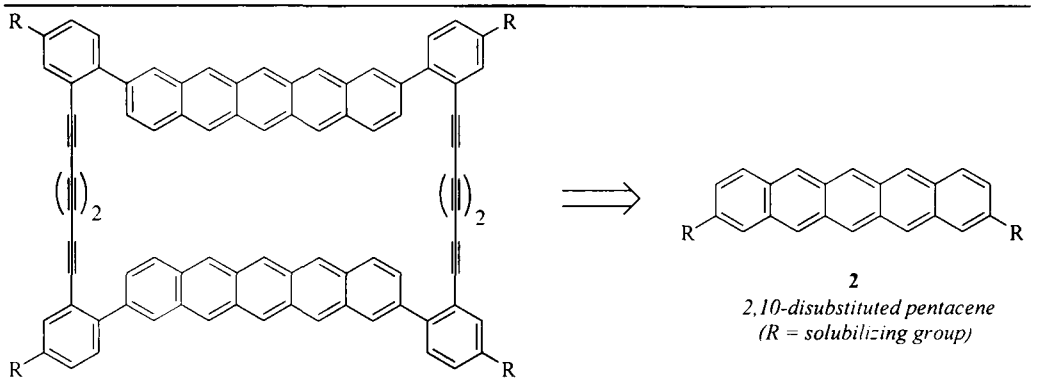


Figure 1 2,10 Disubstituted pentacene 2 as a capping group for cyclophane 1

During the course of the synthetic investigations, the promising capabilities and properties of substituted pentacenes as organic field effect transistors was realized. The research focus thus shifted from the planar cyclophane project to the synthesis of substituted pentacenes (**3**, with substituents at 2,9 and 2,10 positions, Figure 2). A preliminary, lengthy synthesis was proposed and completed; however, a more efficient synthesis was needed if an industrial application were to be considered. There is great interest, industrially and academically, in the synthesis of substituted pentacenes. This is due to their semiconductive properties which enable their use in organic field effect transistors (OFETS), organic thin-film transistors (OTFTs) and organic light-emitting diodes (OLEDs).

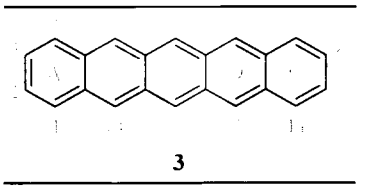


Figure 2 - Numbering of pentacene (3)

1.1 Introduction to Semiconductors

Semiconductors are predominantly used as field effect transistors (FETs), which play an important part in many modern technological devices (*e.g.* computer chips). They have revolutionized the microelectronic industry. Out of all the elements that exist, only a few have semiconductive properties when the proper conditions are employed (*e.g.* temperature). Basically, semiconductors are materials whose electrical conductivities lie between that of conductors and insulators. This is essentially due to their electron mobility - free electrons mean high conductivity and tightly bound electrons mean no conductivity.[1] Silicon (Si) and germanium (Ge) are among the most commonly used semiconductive elements. However, increasing the temperature to such a degree to allow them to conduct would make them impractical for general use (could require >1000 K).[2] Instead, impurities are used to introduce free electrons into the conduction band. This process, known as doping, allows a relatively non-conductive element to become a semiconductor. This important feature has contributed to the success of silicon and germanium as semiconductive substrates. They could be prepared with an impurity of only one part in 10^{10}.[1] This is essential because it allows for the controlled introduction of the dopants. There is a minimum ionization energy associated with pure silicon that can be changed significantly with the introduction of a dopant. This is because the electron belonging to the dopant requires far less energy to become available for conduction than the electron of pure silicon.[1] In the end, the semiconductor becomes much more practical and energy efficient.

There are two types of impurities or dopants, N-type and P-type, the latter being pertinent to this discussion. In P-type doping, elements such as gallium or boron are used because they have three electrons in their outer shell. When a small quantity of these impurities/dopants are placed in the crystal lattice of silicon, they form "holes" in the lattice. Holes facilitate conduction because they can accept an electron from a neighbouring atom, in effect 'moving' the hole over a space in the lattice, and thus create a current of electrons moving opposite to the holes.

---

[1] Solymar, L.; Walsh, D. Electrical Properties of Materials, 6th Ed. Oxford University Press, New York, 1998.
[2] White, M. A. Properties of Materials, Oxford University Press, New York, 1999.

A typical FET is composed of three electrodes (gate, source and drain), a semiconductor layer and a dielectric layer (Figure 3).[3] The current between the source and the drain (the channel) is controlled by the voltage applied to the gate electrode. If there is no voltage applied to the gate then there is little or no current flowing from the source to the drain and the transistor is 'off.' The transistor is considered 'on' when there is a voltage applied to the gate electrode. The value of the gate voltage determines the value of the output current in the channel. When a voltage is applied, the electrons of the semiconducting material are promoted to the conduction band, where they become charge carriers for the FET. The efficiency of the FET mainly relies on the ability of the semiconductor to conduct: how easily the electron and hole can move through the material (characterized by the electron mobility, μ_e, and hole mobility, μ_h); and the on/off ratio: the drain-source current ratio between the 'on' and 'off' states.

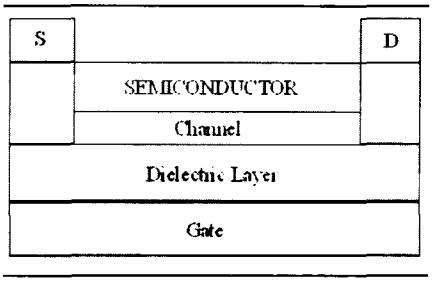


Figure 3 - Diagram of a typical FET device

1.2 Organic Semiconductors

Until now, this discussion has been limited to inorganic semiconductors. While they have excellent electron and hole mobilities, their processing methods are not cost effective, often involving high temperature, high pressure, and other undesirable processing environments.[3] Largely due to these reasons, there is great interest in organic and polymeric semiconducting materials. While they do not have electron or hole mobilities as good as single-crystalline silicon (Table 1), they potentially offer numerous advantages for easy, less expensive processing.[4] Organic semiconductors are therefore desirable for single use devices such as smartcards, luggage tags, and anti-theft devices.

[3] Bao, Z.; Rogers, J.A.; Katz, H.E. *J. Mater. Chem.* **1999**, *9*, 1895.
[4] Kraft, A. *Chem. Phys. Chem.* **2001**, *2*, 163.

Table 1 - Electron (μ_e) and hole (μ_h) mobilities of semiconductors

Semiconductor	μ_e / $cm^2V^{-1}s^{-1}$	μ_h / $cm^2V^{-1}s^{-1}$
single-crystalline silicon	**1500**	**480**
amorphous silicon	0.1 - 1	< 0.1
tetracene (**4**)	~2	~2
pentacene (3)	**1.7**	**2.7**
α-sexithiophene (**5**)	0.7	1.1
perfluorinated copper phthalocyanine (**6**)	1.7	-
C_{60}	2.1	1.8

As mentioned previously, electrons are required in the conduction band to act as charge carriers. In inorganic materials, they are available from dopants. Organic materials must meet three criteria in order to conduct: 1) the frontier orbital energies must be at levels where electrons may be added or removed at accessible applied voltages; 2) sufficient overlap of the frontier orbitals must exist to allow charge to migrate among neighbouring molecules; and 3) the crystal structure must be continuous and arranged in the direction of the current flow.[3]

Linear acenes (tetracene (**4**) and pentacene (**3**)), oligothiophenes (α-sexithiophene (**5**)), copper phthalocyanines (**6**), and naphthalenebisimides (**7**) are the current leading classes of molecular organic semiconductors (Figure 4).[5] These compounds are all electron-rich and highly conjugated. However, pentacene (**3**) has the highest electron and hole mobility among organic semiconductors, consequently it is widely investigated.

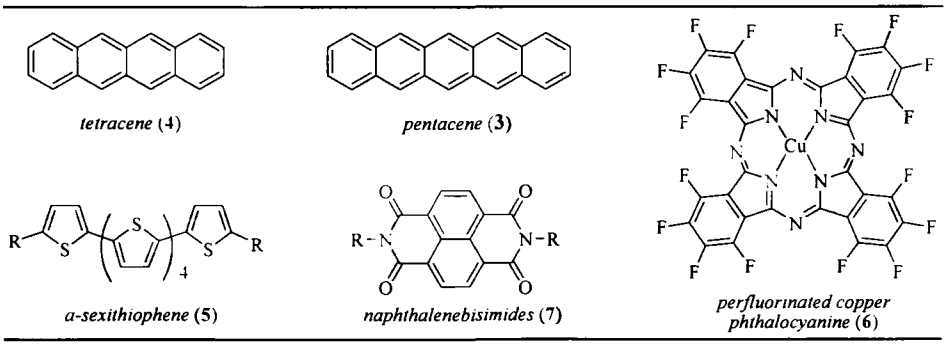
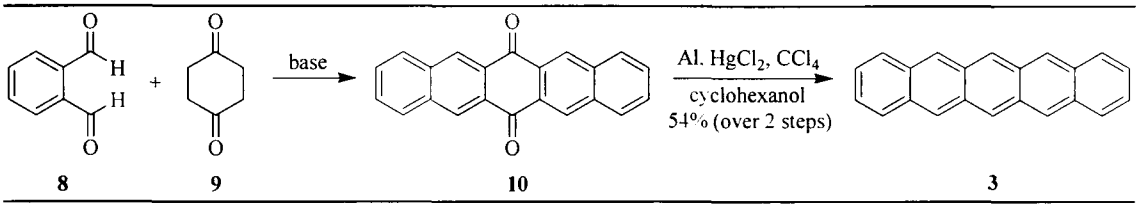


Figure 4 - Organic semiconductors

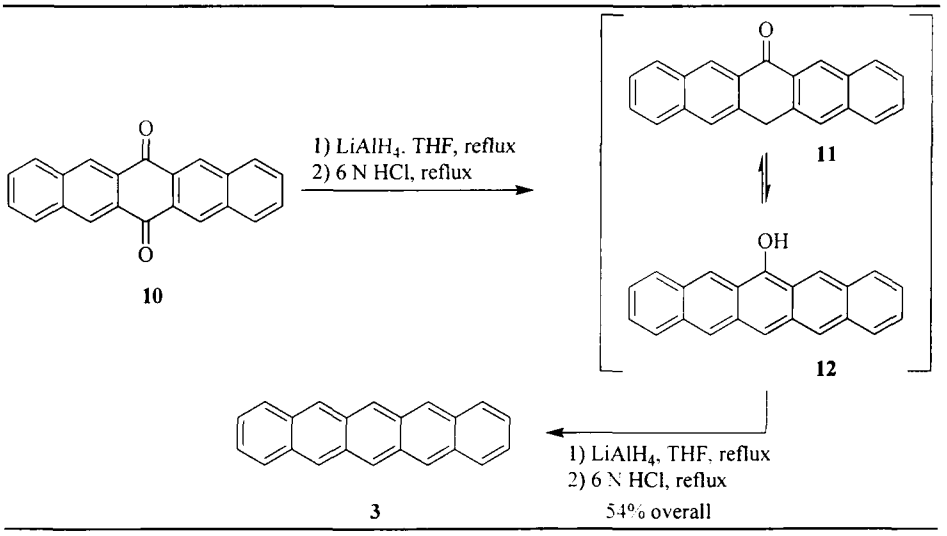
[5] Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359.

One of the more common syntheses of pentacene (**3**) begins with the condensation of phthalaldehyde (**8**) and 1,4-cyclohexanone (**9**) using a base, followed by reduction of quinone **10** with aluminum and mercuric chloride to afford **3** (Scheme 1).[6]



Scheme 1 - Synthesis of pentacene (3)

In 2004, a more environmentally friendly procedure was reported that did not involve the toxic reagents in the previous procedure. Dehaen *et al* devised a route that started with the $LiAlH_4$-mediated reduction of pentacenequinone (**10**) to the diol.[7] Acidification with 6 N HCl to expel water afforded a mixture of ketone (**11**) and the corresponding phenol (**12**), which was further reduced under the same reaction conditions to provide pentacene (**3**).



Scheme 2 - Improved route to pentacene (3)

[6] Goodings, E. P.; Mitchad, D. A.: Owen, G. *J. Chem. Soc., Perkin I* **1972**. 1310.
[7] Vets, N.; Smet, M.; Dehaen, W. *Tetrahedron Lett.* **2004**, *45*, 7287.

After the first synthesis of pentacene (**3**), it was discovered that pentacene had three main drawbacks: it was sensitive to light and oxygen; the non-ideal crystal packing, which negatively affects the electron and hole mobilities; and most importantly, lack of solubility in common organic solvents. These cause major inconveniences when handling pentacene in the conventional laboratory environment and in their use as OFETs.

1.2.1 Pentacene's Sensitivity to Light and Air

The instability of pentacene to light an air can be explained by the exceptionally reactive, electron-rich center ring. This was made evident by nucleus-independent chemical shifts (NICS) investigations (Figure 5, NICS(0) data obtained – illustrated visually).[8] The inner rings of anthracene, tetracene and pentacene exhibit greater diatropic rings currents than the outer rings. In a sense, the inner rings are more aromatic than benzene. The data obtained is consistent with the regioselectivity of Diels-Alder reactions that prefer the middle rings of linear acenes (despite their greater aromaticity) to an increasing extent.[9] This reactivity allows pentacene to react with very poor dienophiles, such as oxygen. This problem can be overcome if it is handled in an inert atmosphere or the center ring is 'protected' to create a pentacene precursor (as described in Section 1.3).

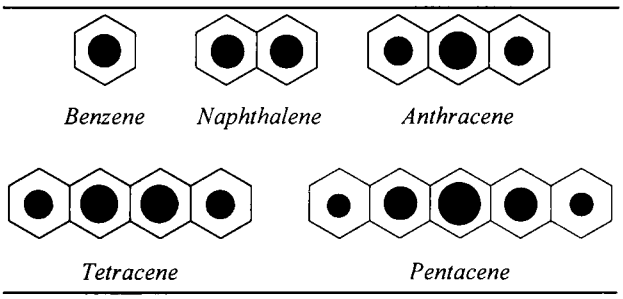


Figure 5 - Nucleus-independent chemical shifts

1.2.2 Crystal Packing of Pentacene

The second concern is the crystal packing. In order to achieve optimum electron and hole mobilities the organic molecules must have a good solid state order. However, pentacene packs

[8] Schleyer, P.V.R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643.
[9] Herdon, W.C. *J. Chem. Soc. Chem. Commun.* **1977**, 817.

in a herringbone fashion, having both edge-to-face and face-to-face interactions among the molecules in their crystal packing lattice (Figure 6).[10] The edge-to-face packing arrangement yields limited π-orbital overlap and likely limits the hole and electron mobilities of pentacene. Greater charge transport could be achieved if the molecules had increased face-to-face π-stacking.[11] The crystal packing can be greatly influenced by strategically adding substituents to pentacene. This could lead to the disruption of the undesired edge-to-face interactions (as described in Section 1.3).

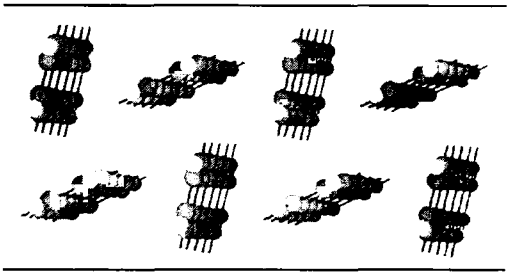


Figure 6 - Herringbone motif found in pentacene (3) crystals

1.2.3 Solubility of Pentacene

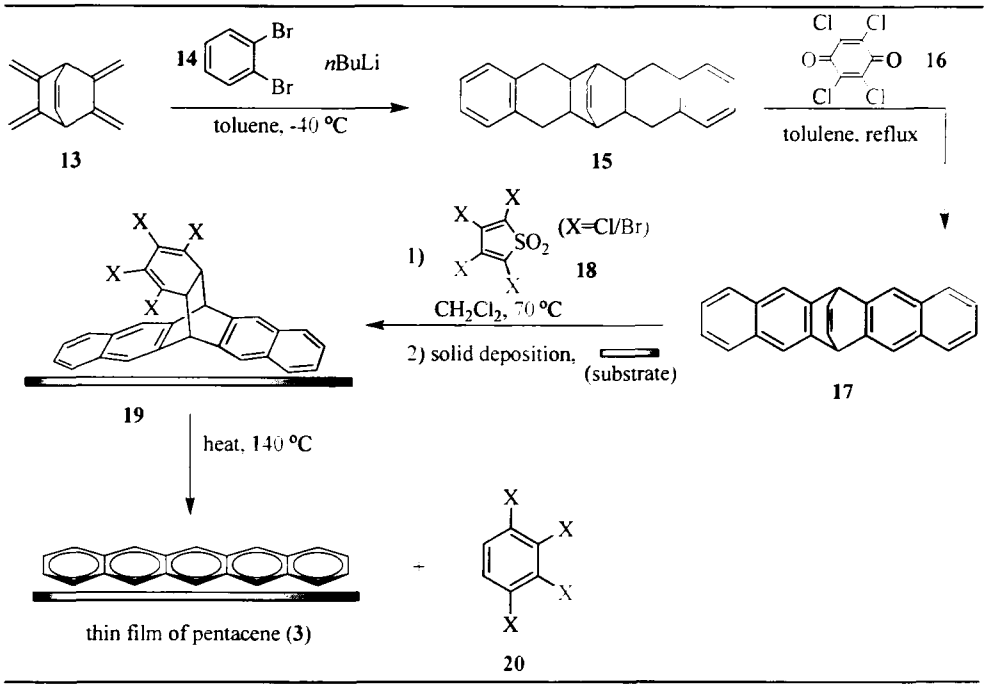
Pentacene is virtually insoluble in common organic solvents, which creates a substantial problem for industrial application. The primary reason why organic semiconductors can compete with their inorganic counterparts are their cost-effective processing techniques. These techniques, such as spin-coating, dip-coating, and printable/lithographic processing all require the semiconducting compound to be in solution. As a result, pentacene thin films are prepared by the less desirable methods, such as evaporation/deposition. This problem could be circumvented by incorporating solubilizing groups onto the structure of pentacene.

1.3 Routes to Improved Pentacene

The aforementioned undesirable characteristics prompted researchers to synthesize and investigate both 'pentacene precursors' and functionalized pentacene derivatives to remedy the issues.

[10] Anthony, J.E.; Eaton, D.L.; Parkin, S.R. *Org. Lett.* **2002**, *4*, 15.
[11] McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93.

In synthesizing a pentacene precursor one can take advantage of the reactive center ring. The center ring is reacted with a dienophile to create a substrate that is more soluble and light and air stable. The pentacene precursor is spin-coated onto the thin-film and then heated to perform a retro Diels-Alder reaction to generate pentacene. Müllen *et al* used this strategy and synthesized the soluble pentacene precursor (**19**).[12] After **19** was cast into thin films by solution deposition the substrate was heated at 140 °C to yield pentacene (**3**) *via* a retro Diels-Alder reaction. The main limitations to this approach were the lengthy synthesis of the pentacene precursor and the overall low yield, as well as the wasted tetra-halo by-product (**20**).

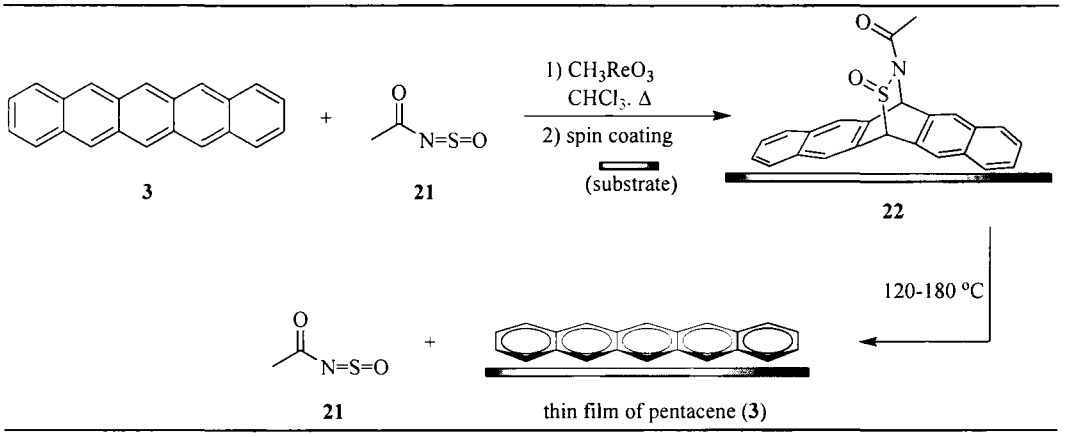


Scheme 3 - 'Precursor route' to pentacene (3)

Shortly after Müllen's synthesis was published, Alzali *et al* prepared a pentacene precursor directly from pentacene (Scheme 4).[13] *N*-Sulfinylacetamide (**21**) underwent a rhenium-catalyzed Diels-Alder reaction with the center ring of pentacene (**3**) to give adduct **22**. Not only is this approach much shorter than Müllen's, but precursor **22** also has a lower conversion temperature to pentacene (**3**), which makes the processing compatible with plastic

[12] Herwig, P.; Müllen, K. *Adv. Mater.* **1999**, *11*, 480.
[13] Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812.

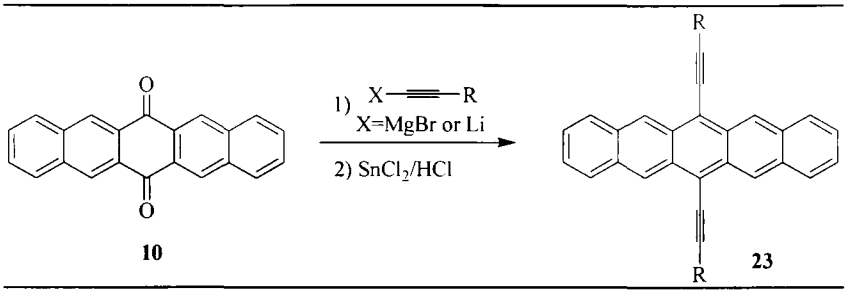
substrates. Plastic substrates are important for the fabrication of low-cost and high-performance OTFTs that are typically used in large area electronic applications.[13] Other *N*-sulfinyl derivatives have also been used in the Diels-Alder reaction, such as *N*-sulfinylbenzamide,[14] *N*-sulfinylmethacrylamide[15] and *N*-sulfinyl-*tert*-butylcarbamate.[16] The latter two provide more flexibility in the processing of transistors because they are photosensitive and acid-sensitive precursors, respectively, which allow for lower temperatures.



Scheme 4 - Improved 'precursor route' to pentacene (3)

The previous solutions all addressed the processing problems associated with the lack of solubility of pentacene. However, they did not improve the crystal packing or the electronics of pentacene. Therefore, research interests were directed towards making substituted pentacenes that will not only encourage better packing, but the added substituents will also act as solubilizing groups. Anthony *et al* were one of the more recent groups to design such a molecule (Scheme 5).[17,10] Their goal was to place substituents at one or more of the central positions of the acene. This would disrupt edge-to-face interactions and thus favour the desirable face-to-face interactions.[10] To allow the closest possible contact between the aromatic rings, a rigid spacer (an alkyne) was used to hold the bulky solubilizing groups well away from the aromatic core to prevent interference with the π-stacking interactions. Several different R groups were tested in order to optimize the packing.

[14] Zander, D.; Hoffmann, N.; Lmimouni, K.; Lenfant, S.; Petit, C.; Vuillaume, D. *Microelectronic Engineering* **2005**, *80*, 394.
[15] Alfzali, A; Dimitrakopoulos, C. D.; Graham, T. O. *Adv. Mater.* **2003**, *15*, 2066.
[16] Weidkamp, K. P.; Afzali, A.; Tromp R. M.; Hamers, R. J. *J. Amer. Chem. Soc.* **2004**, *126*, 12740.
[17] 1) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482.



Scheme 5 - Synthesis of 6,13-disubstituted pentacenes

The R substituents were chosen carefully as their size dictates the distance between adjacent molecules and hence the amount of π-orbital overlap between each molecule. If R is spherical, then a ~7 Å diameter is required so that two of these units occupy the same in-plane area as one pentacene unit (length ~14 Å) (Figure 7a). Their size also influences the amount of π-orbital overlap along the pentacene long axis between any two adjacent acenes (Figure 7b).[10] The 6,13-disubstituted pentacenes (**23**) were found to be soluble in many organic solvents, oxidatively stable in the solid state and exhibited significantly more face-to-face π-stacking in the crystal state than unsubstituted pentacene (**3**). Unfortunately, evaporated thin-films of these compounds did not show a high degree of crystalline order or a better mobility (0.38 $cm^2V^{-1}s^{-1}$) than pentacene (2.7 $cm^2V^{-1}s^{-1}$). However, their applicability to electronic device fabrication is still being investigated.

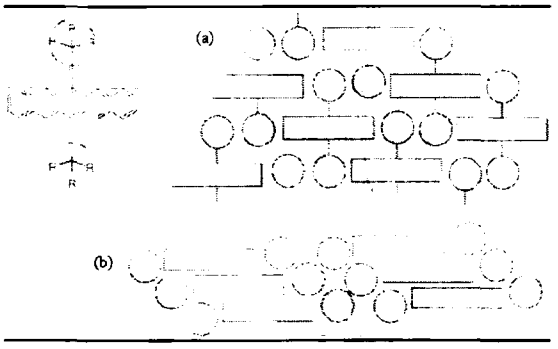
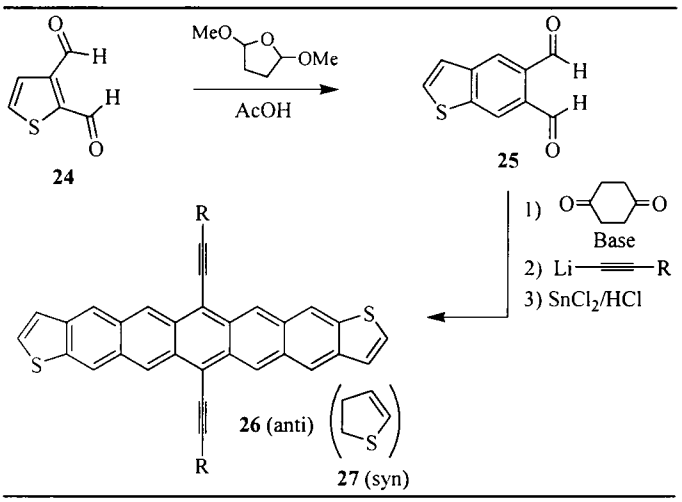


Figure 7 - a) side view; b) top view

Further investigations of 6,13-disubstituted pentacenes are ongoing and have been applied to other fused acene systems to obtain more information on structure-property relationships. Substitution of a thiophene ring on the terminal positions is an attractive way to

increase the length of the acene without perturbing the basic molecular geometry. Anthony *et al* designed a three step synthesis of functionalized acenedithiophenes (Scheme 6).[18] The final compounds, **26** and **27**, exist as a mixture of inseparable *syn*- and *anti*-isomers; however, it did not interfere with crystallization or X-ray diffraction studies. The solid-state arrangement minimizes the distortion of the aromatic core and has close π-face contacts. The average interplanar spacing for **26/27** and **23** is 3.42 Å[18] and 3.47 Å[17]; whereas unsubstituted pentacene (**3**) is 6.27 Å[17]. It has been shown that charge-carrier mobility is strongly dependent on the spacing between aromatic faces in the solid.[19]

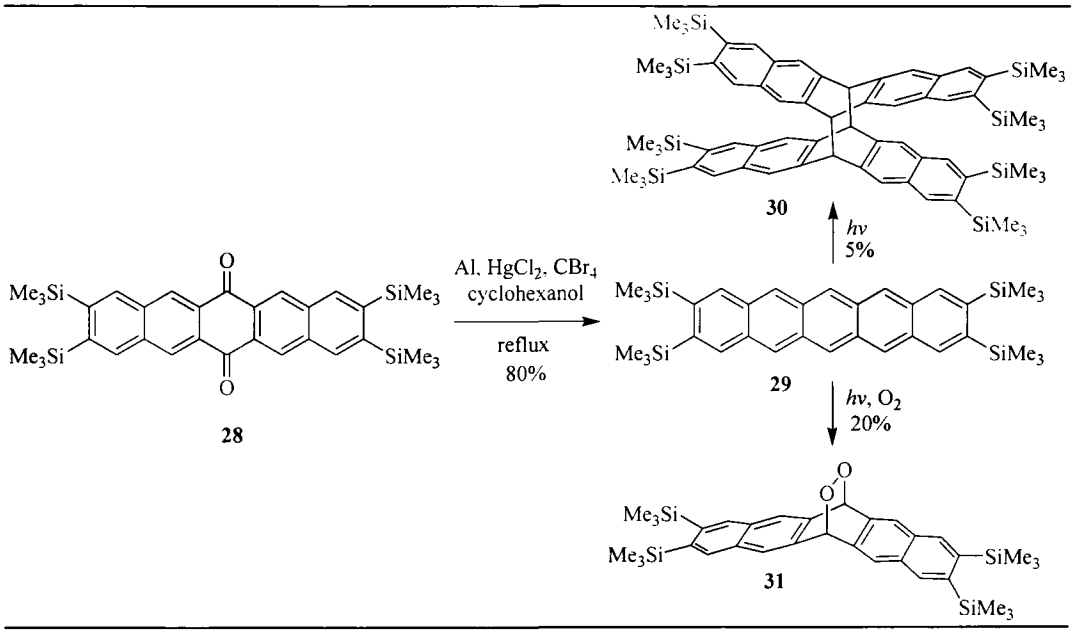


Scheme 6 - Synthesis of acenedithiophenes (26 and 27)

Pentacene has also been synthesized with substitution patterns other than the previously mentioned 6,13 disubstituted pentacene. Recently, pentacene has been prepared with trimethylsilyl groups at the 2, 3, 9 and 10 positions (Scheme 7).[20] The reason for introducing these groups was to enhance the solubility of pentacene. The preparation of **29** involved a carbon tetrabromide-promoted Meerwin-Ponndorf-Verley reduction of **28** with complete exclusion of air and light. It was found that upon exposure of a concentrated solution of **29** to light dimer **30** was produced in low yield *via* a [4+4] photocycloaddition. Alternatively, peroxide **31** was formed when **29** was exposed to light and oxygen. During the investigations, it was discovered that **29** has radical cationic character in the presence of light. This has provided

[18] Payne, M. M.; Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 3325.
[19] Brédas, J. L.; Calbert, J. P.; da Silva Filho, D. A.; Cornil, J. *Proc. Nat. Acad. Sci. U.S.A.* **2002**, *99*, 5804.
[20] Chan, S. H.; Lee, J. K.; Wang, M.; Fu, N. Y.; Chen, X. M.; Cai, Z. W.; Wong H. N. C. *Chem. Commun.* **2005**, 66.

some insight into the sensitivity of pentacene to light and air. Investigations into the hole and electron mobilities are currently underway.



Scheme 7 - Synthesis of soluble pentacene 29, dimer 30 and endoperoxide 31

1.4 2,9 and 2,10 Disubstituted Pentacene

As discussed in section 1.3, substituents have been placed on pentacene in various positions to increase the solubility and improve the solid-state packing. However, until now no substituents have been placed selectively on the 2 and 9 positions. Using Anthony's rationale[10], it was deduced that by placing substituents at the 2 and 9 positions the edge-to-face packing would be disrupted, thereby favouring the face-to-face packing in the solid state. This would increase the solubility and maximize the π-orbital overlap, which would increase the electron and hole mobilities (Figure 8).

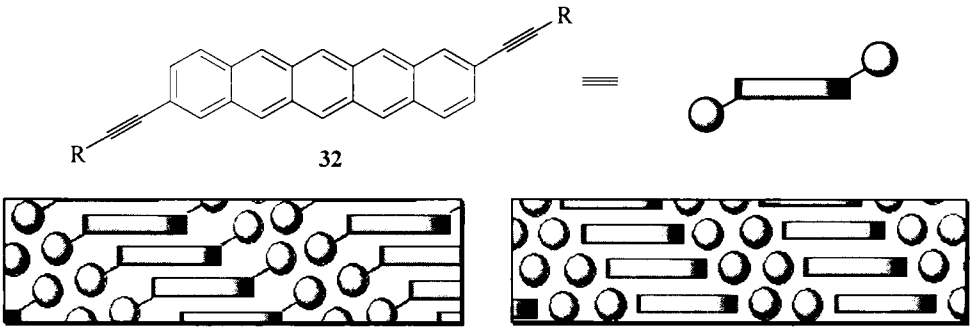


Figure 8 - Packing diagrams of 2,9 disubstituted pentacene derivatives; side view (left); top view (right)

The functionalization of the A and E rings of pentacene required a new synthetic approach. A first generation approach was designed in the Fallis Lab.[21] The goal was to synthesize a functionalized pentacylic scaffold that could be easily manipulated before converting it to pentacene. The proposed retrosynthetic route is shown in Figure 9. Pentacene (**32**) can be obtained through the reduction of diquinone **33**. Through the palladium-mediated coupling reaction with triflate **34**, a variety of substituents can be introduced to yield **33**. Simple desilyation and triflation of **35/36** would afford triflate **34**. Finally, a double Diels-Alder reaction with Danishefsky's diene **37** and known anthradiquinone **38** would give silyl ethers **35/36**.

[21] Dr. Matthew A. Heuft, *Ph.D. Thesis*

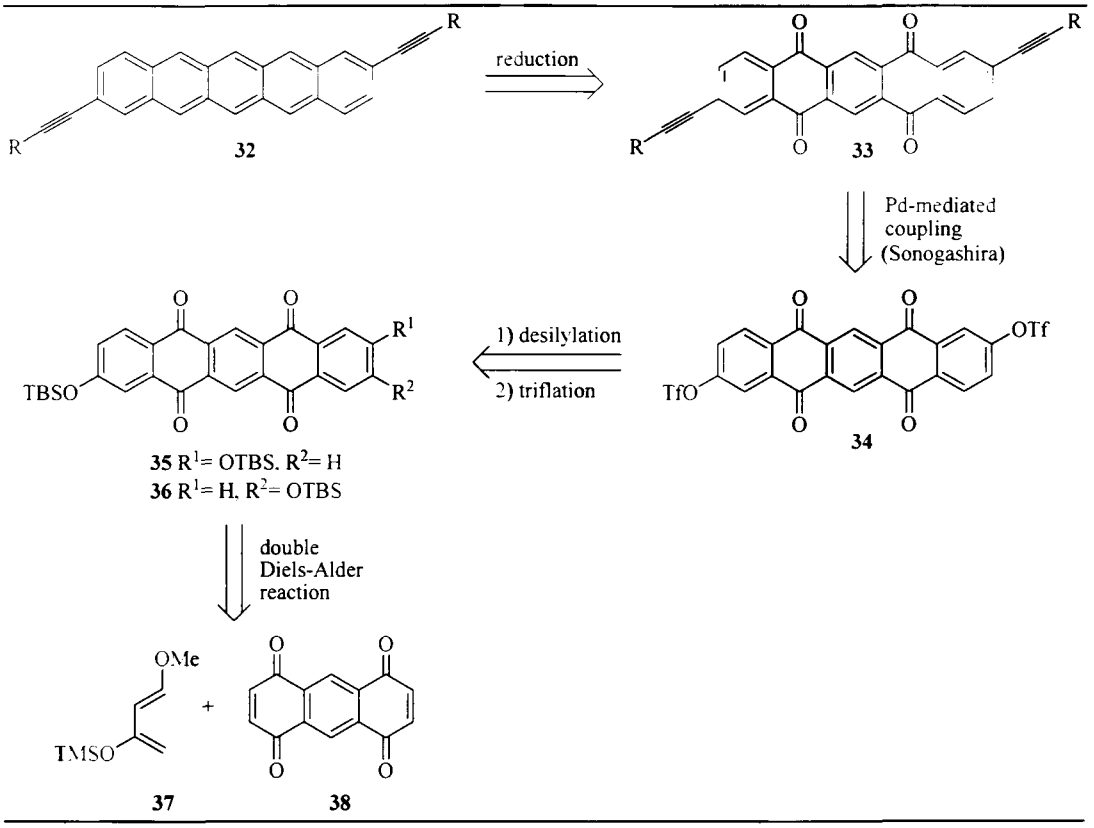
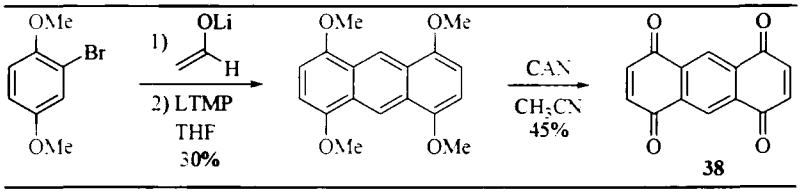


Figure 9 - First generation retrosynthetic plan for 2,9 disubstituted pentacenes (32)

Although this route yielded 2.9 disubstituted pentacene, there were several drawbacks. The first was that the Diels-Alder reaction was not regioselective. Two isomers were produced (**35** 2,9 and **36** 2.10 disubstituted) and had to be separated by repeated fractional recrystallization. Secondly, Danishefsky's diene (**37**) is an expensive starting material and would not be considered for industrial application. Finally, the synthesis of anthradiquinone **38** is very low yielding, and would not be a viable reaction for scale up (Scheme 8).[22]



Scheme 8 - Preparation of 1,4,5,8-anthradiquinone (38)

[22] Cory, R. M.; McPhail, C. L.; Dikmans, A. J. *Tetrahedron Lett.* **1993**, *34*, 7533

1.5 The New and Efficient Route to 2,9 and 2,10 Disubstituted Pentacenes

In order to circumvent the issues with the first generation synthesis, a new approach was designed. This route needed to be a shorter and less expensive, and if possible, regioselective with respect to the substituents on the A and E rings of pentacene. The 2,9 disubstituted pentacene **32** would be obtained through the reduction of 6,13 quinone **39** (Figure 10). We envisioned using the same functionalizing transformations on the A and E rings as in the first generation route. A palladium-mediated coupling reaction with a terminal acetylene and **40** would afford **39**. 2,9 Disubstituted pentacenequinone **40** would be produced through a regioselective, double Diels-Alder/tandem aromatization reaction. The *o*-quinodimethane intermediate **41** is available through several easily prepared precursors starting from **42**.

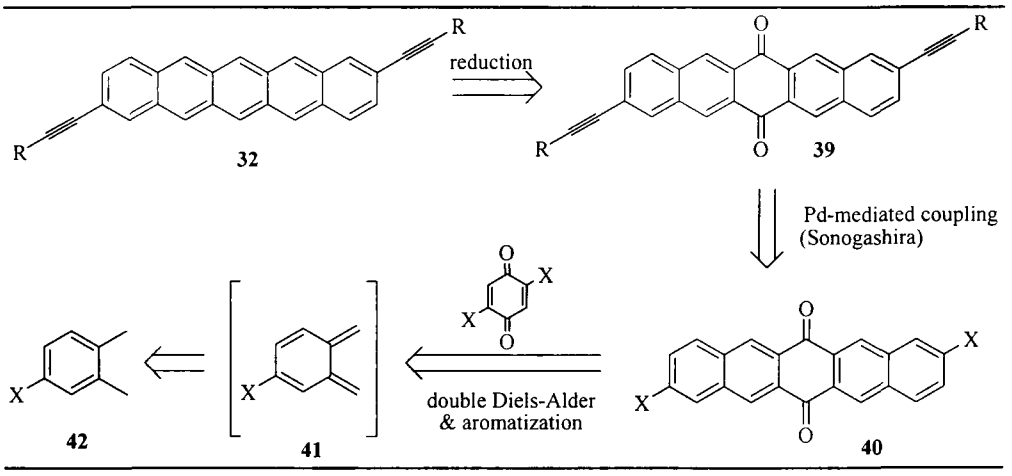
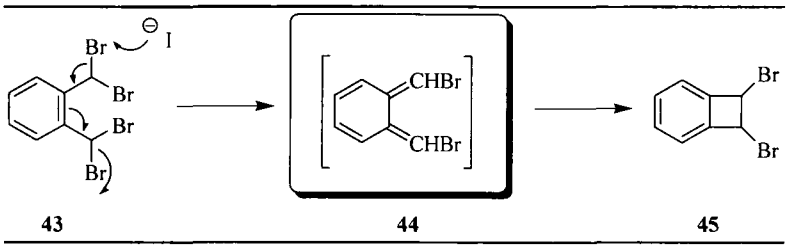


Figure 10 - Second generation retrosynthetic plan for 2,9 disubstituted pentacenes (32)

The Diels-Alder reaction is one of the most widely used reactions in organic synthesis. It is a concerted [4+2] cycloaddition that can be diastereo-, regio- and stereoselective. The diene used in the proposed retrosynthetic route (Figure 10) is an *o*-quinodimethane **41** (initially termed an *o*-xylylene). It is a reactive intermediate widely used for the synthesis of polycyclic compounds *via* inter- and intramolecular Diels-Alder reactions. Due to their high reactivity and thermal instability they must be generated *in situ*. In 1910, Finkelstein prepared 1,2-dibromobenzocyclobutane (**45**) by reduction of α,α,α',α'-tetrabromo-*o*-xylene (**43**) with ethanolic sodium iodide (Scheme 9).[23] However, the involvement of the dibromo-*o*-

[23] Finkelstein, H. *Dissertation* Strassbourg, **1910**.

quinodimethane intermediate (**44**) was first recognized by Cava *et al* who successfully trapped the intermediate with typical dienophiles.[24] Compound **45** is produced *via* a conrotatory electrocyclic ring closer of **44**.



Scheme 9 - Finkelstien's preparation of 45

Several different precursors, in addition to **43**, exist to generate the intermediate *o*-quinodimethane **46** (Figure 11). Thermal cleavage of benzocylobutane (**47**) is an attractive method if the substrates are stable at high temperatures.[25] The dihalide **48** (when X = Br) can undergo a 1,4-dehalogenation with zinc and sonic waves,[26] nickel,[27] copper,[28] iron[29] and chromium,[30] or with potassium hydroxide and heat when X = Cl.[31] Lithium dialkylamide or fluoride ion induced elimination of methyl *o*-methylbenzyl (**49**)[32] and *o*-(α-trimethylsilylalkyl)benzyltrimethylammonium halides (**50**),[33] respectively also generate **46**. Finally, heating sultine **52** affords **46**.[34] Diene **46** is typically generated in the presence of a dienophile, in which the addition occurs by a *supra-supra*-facial addition to afford **53**.

[24] Cava, M. P.; Napier, D. R. *J. Amer. Chem. Soc.* **1957**, *79*, 1701.
[25] (a) Kametani, T.; Tsubuki, M.; Nemoto, H. *J. Org. Chem.* **1980**, *45*, 4391. (b) For a review see Oppolzer, W. *Synthesis* **1978**, *11*, 793.
[26] (a) Kruizinga, W. H.; Strigtveen, B.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4323. (b) Hee Han, B.: Boudjouk, P. *J. Org. Chem.* **1982**, *47*, 752. (c) Heffner, R.: Safaryn, J. E.; Joullie, M. M.; *Tetrahedron Lett.* **1987**, *28*, 6539.
[27] Inaba, S. I.; Wehmeyer, R. M.; Forkner, M. W.; Rieke. R. D. *J. Org. Chem.* **1988**, *53*, 339.
[28] Ito, Y.; Yonezawa, K.; Saegusa, T. *J. Org. Chem.* **1974**, *39*, 2769.
[29] Nozaki, J.; Noyori, R.; *Tetrahedron* **1966**, *22*, 2163.
[30] Stephan, D.; Gorgues, A.; Le Coq. A. *Tetrahedron Lett.* **1984**, *25*, 5649.
[31] Klarner, F. G.; Lobert, M.; Naatz, U.; Bandmann, H.: Boese. R. *Chem. Eur. J.* **2003**, *9*, 5036.
[32] Tuschka, T.; Naito, K.; Rickborn, B. *J. Org. Chem.* **1983**, *48*, 70.
[33] Ito, Y.; Nakatsuka, M. Saegusa, T. *J. Amer. Chem. Soc.* **1980**, *102*, 863.
[34] Martin, N.; Behnisch, R.; Hanack, M. *J. Org. Chem.* **1989**, *54*, 2563.

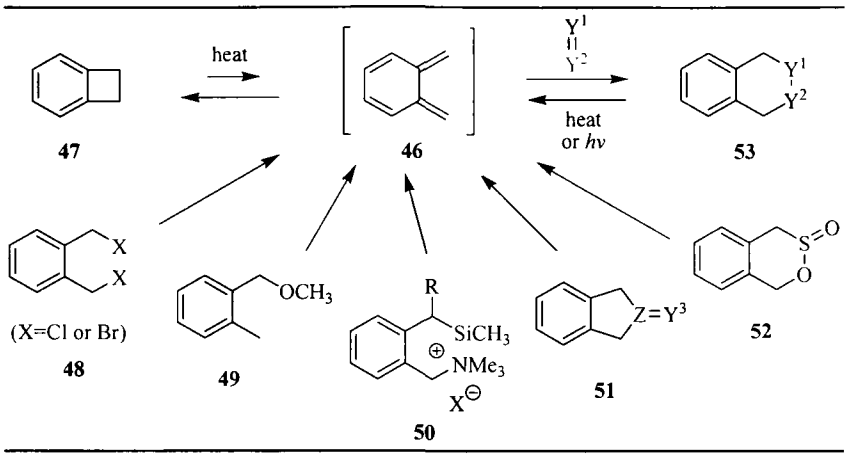


Figure 11 - Generation of *o*-quinodimethane 46

The Diels-Alder reaction is often regioselective when unsymmetric dienes and dienophiles are used if the coefficients (determined by Hückel MO Theory) of the atoms are appropriately influenced by electron donating or withdrawing groups. The reasoning behind this selectivity can be explained using frontier molecular orbital theory (FMO).[35] In the example given in Figure 12, the diameter of the 'orbitals' is roughly proportional to the size of the coefficients. The sign (positive = white or negative = shaded) of the coefficient directs the orbitals in the transition state, leading to the major regioisomer. In this example, the energetically favoured combination results in the highest occupied molecular orbital (HOMO) of the diene reacting with lowest unoccupied molecular orbital (LUMO) of the dienophile. The electron donating group on C1 of the diene generates a larger coefficient at C4 while the electron withdrawing group on the dienophile produces a larger coefficient at C3. The sizes of the coefficients are matched in the transition state, resulting in the major product with the *ortho* substituents.

[35] Fleming, I. *Frontier Orbitals and Organic Chemical Reactions* John Wiley & Sons 1976.

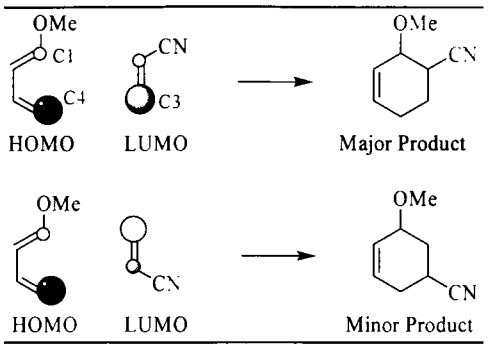
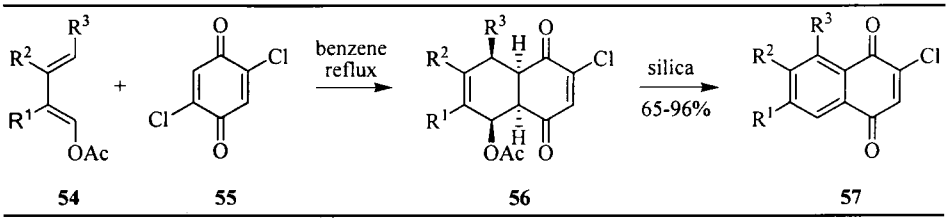


Figure 12 - An example of a regioselective Diels-Alder reaction using FMO

One of the main challenges in synthesizing asymmetric linearly fused compounds is controlling the regiochemistry on the terminal carbon rings. There have been a few different approaches to addressing this, including using steric hindrance[36], or more commonly manipulating the orbital coefficients on the diene and dienophile with the appropriate substituents. One of the main problems is the extra functionality required, which may not be desirable in the final product. Two approaches have been developed to overcome this problem. The methods incorporate a transient directing group onto the diene or dienophile. The first example shows that simple dienes (**54**) can react regiospecifically with haloquinones (**55**) (Scheme 10).[37] This method is doubly advantageous in that the regiochemistry depends only on the position of the halogen, which is eliminated later in the process. However, an additional step is required to remove the directing acetate group from the diene to yield **57**.

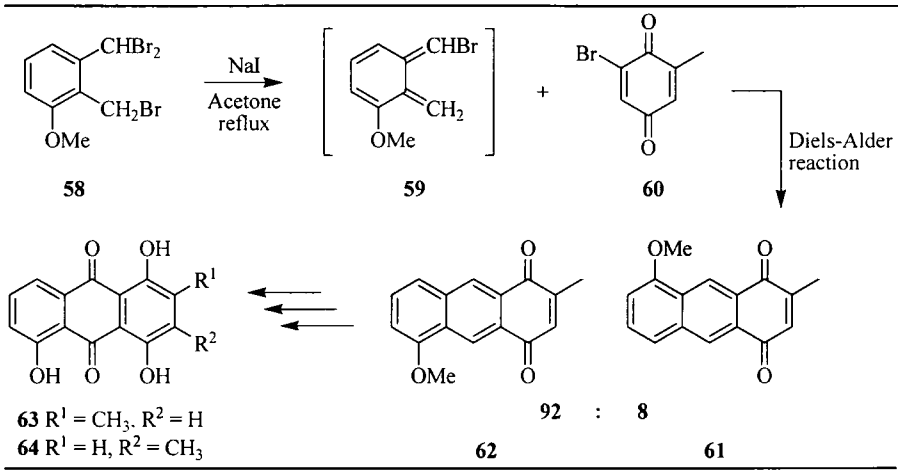


Scheme 10 - Regioselective Diels-Alder reaction with haloquinones (55)

Alternatively, strategic placement of bromine substituents on the precursors to the *o*-quinodimethane **58** and quinone **60** provide excellent regio-control in the cycloaddition reaction

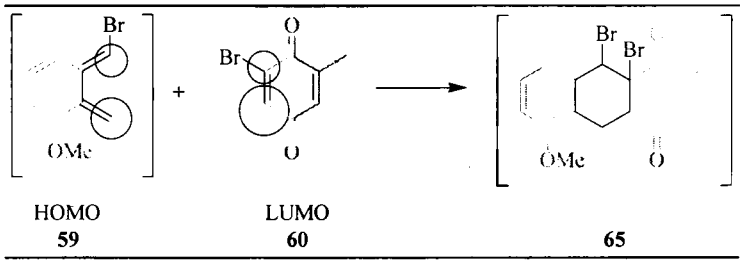
[36] Kraus, G. A.; Zhang, N.; Wei, J. Q.; Jensen, J. H. *Eur. J. Org. Chem.* **2005**, 3040.
[37] Boisvert, L.; Brassard, P. *Tetrahedron Lett.* **1983**, *24*, 2453.

(Scheme 11).[38] This is a tandem Diels-Alder/aromatization reaction as elimination of the bromines aromatizes the product *in situ*. The 92:8 isomeric ratio favouring **62** can be reversed if the substituents on the quinone are *para* to each other instead of *meta*. Through a multistep sequence, compound **61** can be converted to islandicin (**63**) and compound **62** to digitopurpone (**64**).



Scheme 11 - Regioselective tandem Diels-Alder/aromatization reaction

The regioselectivity in the above Diels-Alder reaction is dictated by the electron withdrawing nature of the bromine atoms, which favour formation of *ortho* adduct **65** (Scheme 12).

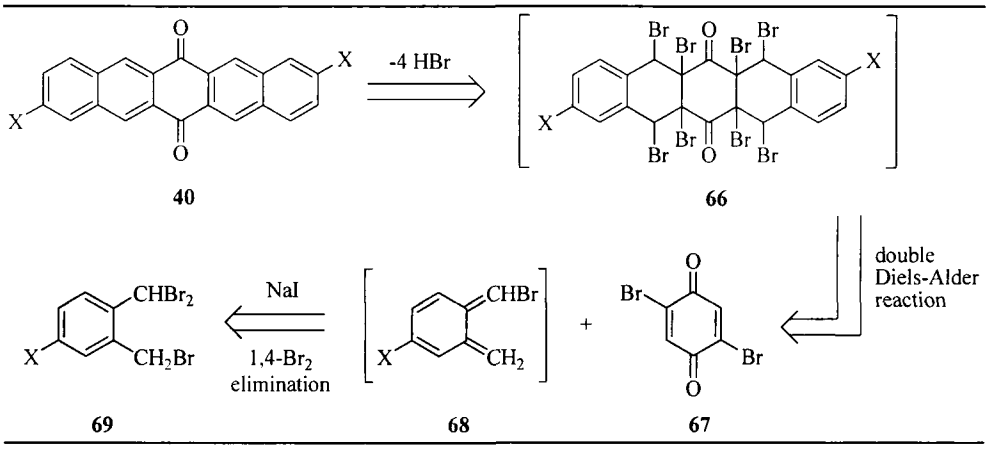


Scheme 12 - Influence of bromine on the orbital coefficients

Based on these previous examples, a regioselective tandem double Diels-Alder/aromatization reaction was designed for the synthesis of the 2,9 disubstituted pentacene **40** (Scheme 13). The transient directing bromine atoms are advantageous as it allows for a very

[38] Wiseman, J. R.; Pendery, J. J.; Otto, C. A.; Chiong, K. G. *J. Org. Chem.* **1980**, *45*, 516.

short regioselective synthetic route. Loss of hydrogen bromide from intermediate **66** would afford quinone **40**. Strategic placement of the bromine atoms on dienophile **67** and diene **68** should result in a regioselective Diels-Alder reaction to yield **40**. Finally, reactive *o*-quinodimethane intermediate **68** could be produced through 1.4-Br_2 elimination of **69**.



Scheme 13 - Proposed regioselective tandem Diels-Alder/aromatization reaction

The last key step proposed in the retrosynthesis is the Sonogashira reaction, which couples a substituted alkyne to an aryl triflate/halide. Over the last twenty years the development of palladium catalysts for the formation of new carbon-carbon bonds has revolutionized synthetic organic chemistry. This reaction will be used in the functionalization of the substituted pentacenes. The Sonogashira reaction involves the coupling of terminal alkynes with aryl or vinyl halides/triflates in the presence of a copper co-catalyst and an amine base, normally used as a co-solvent. Palladium has two common oxidation states, Pd(II) and Pd(0), and in the Sonogashira, Pd(0) is the active catalyst. Palladium(0) **70** is generated from successive transmetallation reactions with copper acetylide (**71**) to give the Pd(II) complex **72**, followed by reductive elimination (Figure 13). This process forms dimer **73**, so it is necessary to use an excess of the terminal alkyne. The first step of the catalytic cycle is the oxidative addition of Pd(0) to an organic halide **74**, which affords the Pd(II) complex **75**. Transmetallation with the copper acetylide **76** affords complex **77**. Copper acetylide **76** is generated from a catalytic amount of copper iodide, the terminal alkyne and the amine base. *Trans-cis* isomerization affords complex **78**. Finally, reductive elimination affords the coupled product **79** and regenerates the active catalyst.

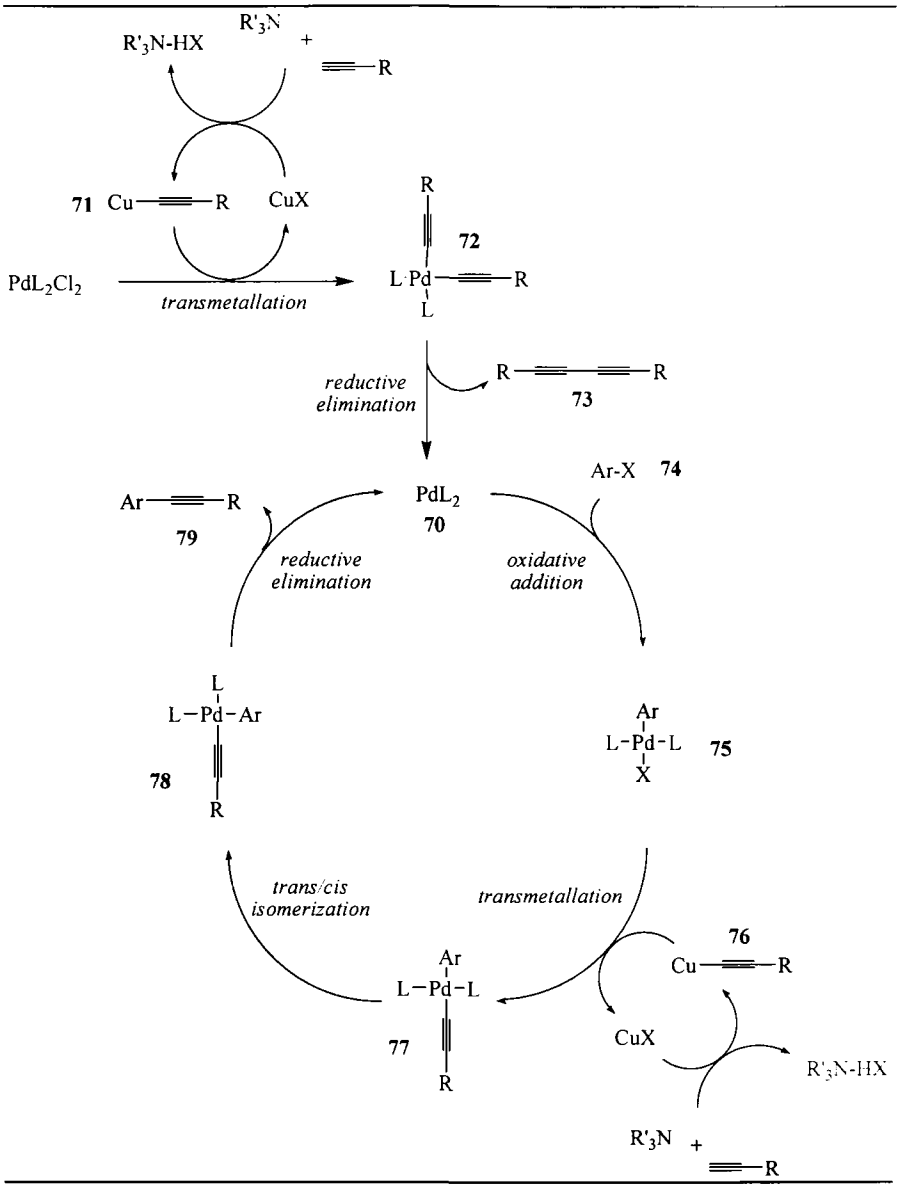


Figure 13 - Sonogashira reaction - catalytic cycle

2 Results and Discussion

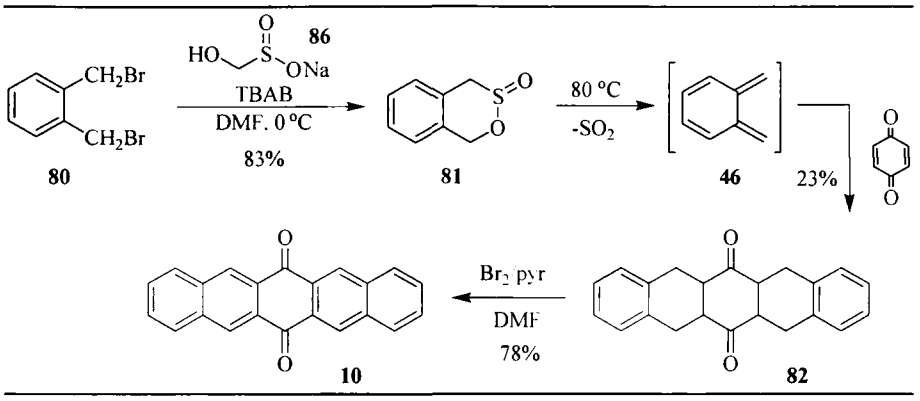
2.1 Investigations into Possible *o*-Quinodimethane Precursors and Dienes

Our design for the second generation synthesis involved incorporation of the necessary functionality on the A and E rings of pentacene from the beginning. Initial investigations screened for possible precursors to the 4-substituted *o*-quinodimethane, but revealed no literature examples with the required substitution pattern. Therefore, the literature search was limited to the *unsubstituted* *o*-quinodimethane. The two main goals for this research project were a regioselective double Diels-Alder reaction and a shorter and higher yielding synthesis than the first generation route (see Section 1.4, Figure 9). Accomplishing both goals would be ideal; however, we did not want to limit other possible successful routes, which may not be regioselective, but may circumvent the other problems that were involved in the first generation synthetic route.

2.1.1 Attempted Formation of the Substituted *o*-Quinodimethane *via* a Sultine

The first viable synthesis found in the literature involved starting with the commercially available 1,2-dibromo-*o*-xylene (**80**), which was easily transformed into sultine **81** (Scheme 14).[39] Upon heating, sulfur dioxide was liberated and *o*-quinodimethane (**44**) was generated and trapped *in situ* with 1,4-benzoquinone.[34] Aromatization of **82** with bromine and pyridine afforded 6,13-pentacenedione (**10**) in 78% yield. This literature reaction sequence was repeated up to **82**, and the formation of the sultine **81** was obtained in only 22% yield, and **82** in an improved 32% yield (not optimized).

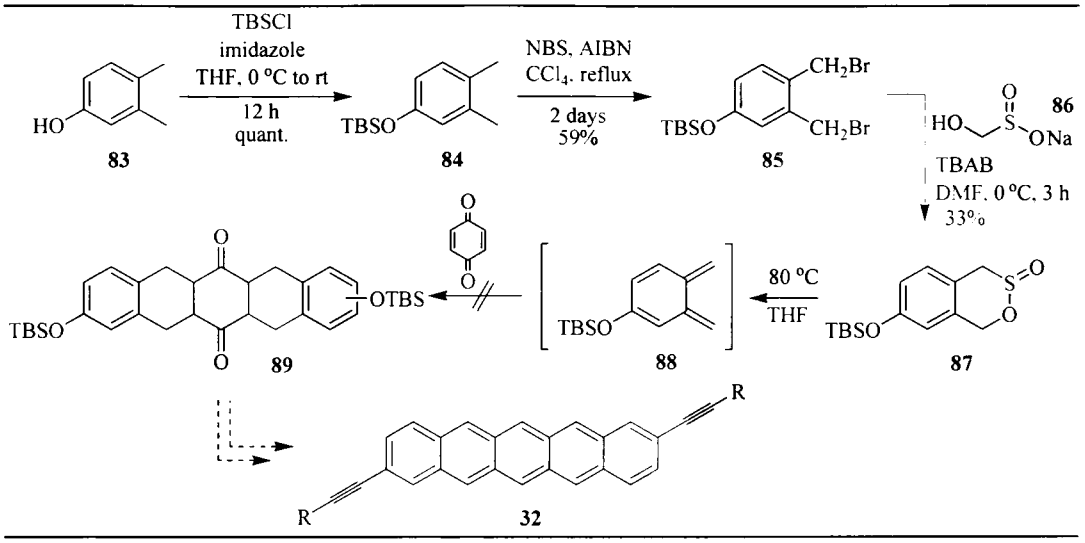
[39] Hoey, M. D.; Dittmer, D. C. *J. Org. Chem.* **1991**, *56*, 1947.



Scheme 14 - Double Diels-Alder reaction with sultine 81[39]

The same chemical transformations were attempted on the substituted 3,4-dibromo-*o*-xylene **84** (Scheme 15). The commercially available 3,4-dimethylphenol (**83**) was easily protected as *tert*-butyldimethylsilyl ether in quantitative yield to afford **84**. Radical bromination of **84** with NBS afforded dibrominated compound **85** in 59% yield. Subsequent treatment with rongalite (**86**) and tetrabutylammonium bromide (TBAB) in DMF yielded sultine **87** in 33% yield. This compound was extremely unstable and decomposed at room temperature and -20 °C over a short period of time. Thus, the double Diels-Alder reaction was attempted immediately after sultine **87** was isolated, and without purification as it would decompose. This reaction produced a black insoluble material, which may have resulted from the polymerization of the substituted *o*-quinodimethane intermediate **88**.

Unsubstituted sultine **81** was stable, and in the presence of heat was able to produce diene **46**, which successfully underwent a Diels-Alder reaction. Unfortunately, the silyl ether substituent on sultine **81** was neither a neutral nor enhancing addition to the diene as it was extremely unstable and no Diels-Alder adduct **89** was produced.

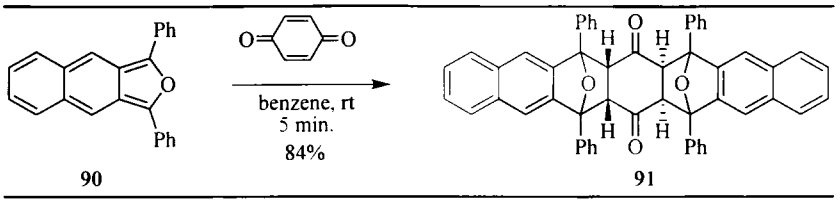


Scheme 15 - Attempted synthetic route using substituted sultine 87 as the diene precursor

2.1.2 Substituted Benzofuran as a Possible Diene

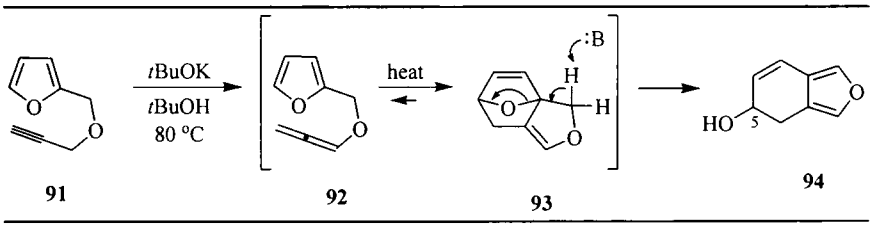
An alternate route that was attempted towards the end of these synthetic investigations used a different diene source. Benzofuran, also known as isobenzofuran, is a reactive diene that readily undergoes Diels-Alder reactions with alkynes and other dienophiles to form the corresponding *endo*-oxide adducts. However, this diene is only stable at low temperatures; therefore, extra functionality is normally incorporated so it can be isolated and used in a convenient way. A relevant literature example is a double Diels-Alder reaction between 1,4-benzoquinone and 1,3-diphenylnaphtho[2,3-*c*]-furan (**90**)[40], which was prepared using a modified Cava procedure (Scheme 16).[41] The ^{1}H and ^{13}C NMR suggested that a single diastereomer, **91**, formed *via* an *endo,exo* Diels-Alder sequence. Further transformations on **91** were conducted to eliminate the oxide bridges *via* a double dehydration, and the center ring was deoxygenated to give a 6,13-dihydro species. When the unsaturated center ring was aromatized and trapped *in situ*, a *cis,cis*-tris[60]fullerene adduct of 6,8.15.17-tetraphenylheptacene was isolated.

[40] Miller, G. P.; Briggs, J. *Org. Lett.* **2003**, *5*, 4203.
[41] Cava, M. P.; VanMeter, J. P. *J. Org. Chem.* **1969**, *34*, 538.



Scheme 16 - An example of a Diels-Alder reaction between furan 90 and 1,4-benzoquinone

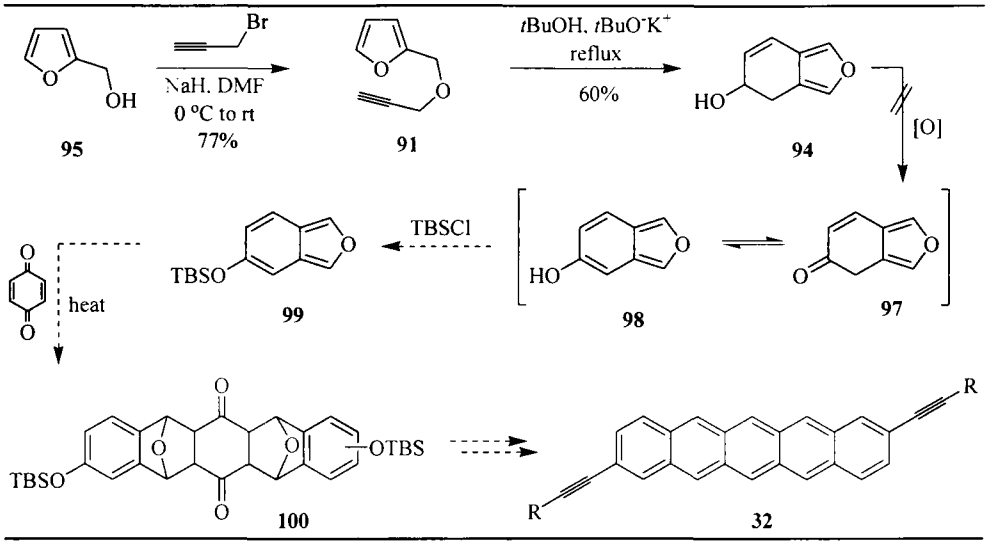
In order to exploit this synthetic strategy, a benzofuran with a substituent at carbon five was required (eventually resulting in the 2,9 and 2,10 disubstituted pentacenes). In 1985, Kanematsu *et al* prepared a possible precursor to such a molecule (**94**) (Scheme 17).[42] They synthesized 5-hydroxy-4,5-dihydroisobenzofuran (**94**) *via* an intramolecular Diels-Alder reaction between the allenyl ether and furan moieties of **92**, followed by a base-catalyzed ring opening of the strained oxa-bicyclo[2.2.1]hexane (**93**).



Scheme 17 - Intramolecular Diels-Alder reaction with allenyl ether and furan

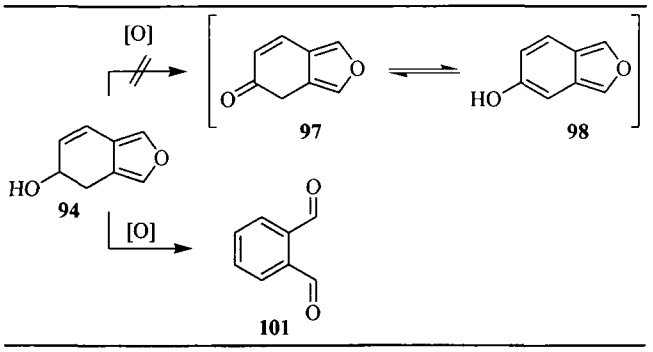
We anticipated that oxidation of 5-hydroxy-4,5-dihydroisobenzofuran (**94**) would produce an α,β-unsaturated ketone **97** that would be in equilibrium with its enol **98** (Scheme 18). The latter compound would be a suitably substituted benzofuran needed in our synthesis. Then, enol **98** could be trapped with a silyl group to afford diene **99**.

[42] Hayakawa, K.; Yamaguchi, Y.; Kanematsu, K. *Tetrahedron Let.* **1985**, *26*, 2689.



Scheme 18 - Attempted synthetic route using substituted isobenzofuran as the diene

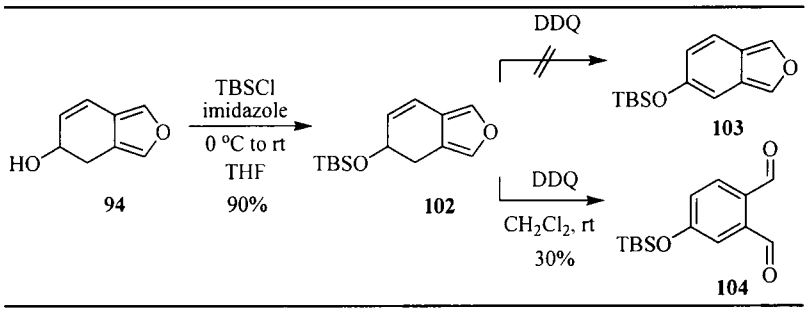
Unfortunately, attempts to prepare ketone **97** were unsuccessful. Using a variety of oxidizing agents: Dess-Martin, MnO_2, PCC, SO_3-py, DMAP-$HCrO_3Cl$[43], IBX, Swern and aluminum isopropoxide, we observed dehydration of the alcohol rather than the anticipated oxidation of allylic alcohol **94** to ketone **97**. Further oxidation of the furan to *bis*-aldehyde **101** also occurred (Scheme 19). Aromatization of **94** with DDQ was also attempted to afford **98**, but the same result was afforded. It was not until after these reactions were completed was a paper received (by interlibrary loan) titled, "An Unusual Synthesis of Phthalaldehyde."[44] They found the same results using CAN, *t*BuOCl/py, Swern, *m*-CPBA, *t*BuOOH/$VO(acac)_2$, and SeO_2.



Scheme 19 - Attempted oxidation of allylic alcohol 94

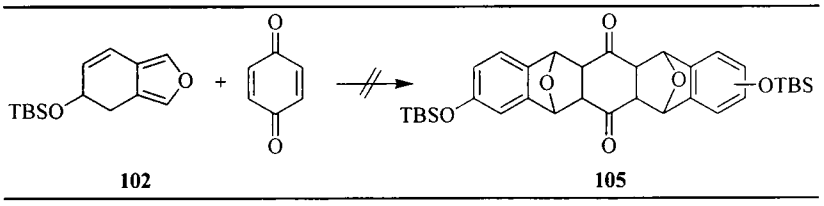
[43] Synthesis of reagent: Guziec, F. S. Jr.; Luzzio, F. A. *J. Org. Chem.* **1982**, *47*, 1787.
[44] Wenkert, E.; Khatuya, H. *Syn. Comm.* **1999**, *29*, 2413.

We believed that this issue could potentially be resolved by removing the oxidation step. Protection of alcohol **94** with a silyl group would prevent dehydration; hence, water would not be able to aid in the oxidation of the furan (Scheme 20). Simple aromatization of **102** with DDQ should have afforded **103**, but instead, both aromatization and oxidation to the substituted phthalaldehyde **104** occurred. It was discovered by a premature work-up using ^{1}H NMR that the oxidation of the furan takes place before the aromatization of the ring, as a mixture of the *bis*-aldehydes (aromatized **104** and unaromatized) were obtained.



Scheme 20 - Attempted aromatization of 102 with DDQ

In a final effort to use this synthetic route, a Diels-Alder reaction was attempted between the unaromatized furan **102** and 1,4-benzoquinone to afford **105** (Scheme 21). Unfortunately, using a variety of conditions (including microwave) no reaction occurred and only starting materials were isolated.



Scheme 21 - Attempted Diels-Alder reaction between furan 102 and 1,4-benzoquinone

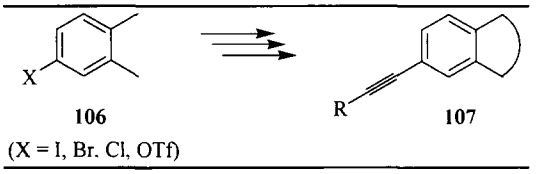
2.2 Synthesis of 2,9 and 2,10 Disubstituted Pentacene

Section 2.1 detailed the difficulties that were associated with a few of our selected routes. This section involves a detailed look into our successful synthetic route. Referring back to Section 1.5 and Figure 10, the retrosynthesis involved an *o*-quinodimethane intermediate (as the

diene) for the double Diels-Alder reaction. The precursor chosen for this reactive intermediate was Finkelstein's and Cava's α,α,α',α'-tetrabromo-*o*-xylene (**43**). The first part of this discussion will entail the preparation of the *substituted o*-quinodimethane precursor.

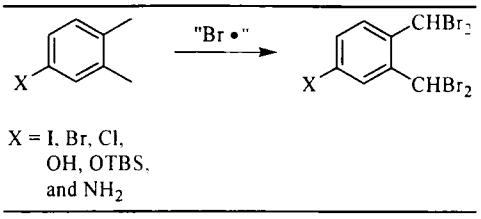
2.2.1 Preparation of the Substituted Tetrabromo-*o*-Xylene

The synthesis began with an aryl substituted compound (**106**). We would have to incorporate the appropriate substituent (X=I, Br, Cl, OTf), as later functionalization with a substituted terminal alkyne *via* a Sonogashira reaction would be required (Scheme 22).



Scheme 22 - Possible substrates for the Sonogashira reaction

Our synthesis commenced with the tetra-bromination of a substituted *o*-xylene (Scheme 23). The potential substituents that were selected were halogens (I, Br and Cl), OH, OTBS, and NH_2. The first compound that was subjected to the bromination was 4-iodo-*o*-xylene (**108**). This was chosen as aryl iodides are a more reactive species in palladium-mediated coupling reactions, which would be a future transformation. The reaction sequence to substituted pentacene is the shortest when X is a halogen. One or two more steps are required to obtain the precursor to the Sonogashira reaction when X is a hydroxyl or silyl protected hydroxyl, as it needs to be converted to the aryl triflate. When X is an amine, treatment with sodium nitrate would afford the diazonium salt, and subsequent treatment with potassium bromide would afford the aryl bromide. Radical halogen substitution at the benzylic position is normally an easy task due to the enhanced reactivity. However, the main challenge in our case is the addition of four bromine atoms. The steric encumbrance created after the addition of two to three bromine atoms makes it difficult to add the remaining, and mixtures of tri-, tetra- and penta-brominated that result could not be separated by flash column chromatography.



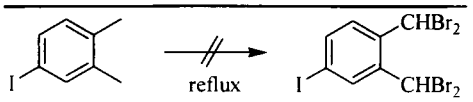
Scheme 23 - Viable substrates for tetra-bromination

The reaction conditions that were screened during the optimization were solvent (CCl_4, $CHCl_3$ and benzene), radical initiator (AIBN, Bz_2O_2, light) and bromine source (NBS, DBH, Br_2, and NaBr). Metres *et al* have shown that chlorinated solvents allow for the maximum amount of 'available bromine,' and hence higher bromination yields.[45] They also demonstrated that non-halogenated solvents gave moderate to poor yields, with benzene giving the highest. Both benzoyl peroxide (Bz_2O_2) and AIBN behaved similarly in yields; whereas, light gave the lowest yields of tetra-brominated *o*-xylene and a large mixture of di- to penta-brominated *o*-xylenes. Finally, the best bromine source was determined to be NBS. The slow release of bromine from NBS played a crucial role during the addition of four bromine atoms to one molecule. Molecular bromine and 1,3-dibromo-5,5-dimethylhydantoin (DBH) gave mixtures and lower yields.

Several different reaction conditions were employed to achieve tetra-bromination on **108**, as this substituent would allow for the shortest overall synthetic sequence and facile functionalization using the Sonogashira reaction. Tetra-bromination of 4-iodo-*o*-xylene (**108**) was not achieved, even with lengthy reaction times (Table 2). Benzylic bromination is known to be difficult when the aromatic ring bares an iodide substituent.[46]

[45] Mestres, R.; Palenzuela, J. *Green Chemistry* **2002**, *4*, 314.
[46] Bodwell, G. J. Personal Communication.

Table 2 - Tetrabromination of 4-iodo-*o*-xylene (108)



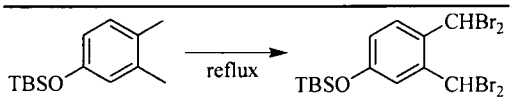
108 109

Entry	Bromine Source	Initiator	Solvent	Time (days)	Crude Yield (%)
1	10 eq. Br_2	*hv*	CCl_4	7	86 – mixture
2	9 eq. Br_2	AIBN	CCl_4	7	73 – mixture
3	2.2 eq. DBH	Bz_2O_2	CCl_4	5	45 – mixture
4	4 eq. NBS	Bz_2O_2	benzene	10	50 – mixture
5	12 eq. NBS*	*hv*	benzene	12	65 – mixture
6	4.4 eq. NaBr. H_2SO_4, H_2O_2	*hv*	$CHCl_3$	3	30 – mixture

* NBS was continuously added over a period of 10 days

These discouraging results directed our efforts towards substrate **84** where X = OTBS. Several different reaction conditions were employed, and it was found that entry three gave the best result. The yield was good (61%), but more importantly, **110** was obtained as the sole product. Entries 1, 2, 4 and 5 gave good yields; however, mixtures were obtained in varying degrees.

Table 3 - Tetra-bromination of 84



84 110

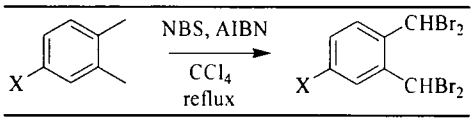
Entry	Bromine Source	Initiator	Solvent	Time (days)	Crude Yield (%)*
1	4.1 eq. NBS	*hv*	benzene	1*	58 - mix
2	4.1 NBS	*hv*	benzene	4	85 - mix
3	**4.3 eq. NBS**	**AIBN**	**CCl_4**	**4.5**	**61**
4	4.5 eq. Br_2	AIBN	CCl_4	5	80 – mix
5	2.1 eq. DBH	Bz_2O_2	CCl_4	5	77 - mix

* small scale (30 mg)

The optimized conditions (for X = OTBS) were attempted on the remaining substrates (X = Br, Cl, OH and NH_2). Unlike the aryl iodide, bromination was easily accomplished when X was either a bromide (entry 2) or chloride (entry 3) (Table 4). The tetra-brominated products **111** (X = Br) and **112** (X = Cl) were obtained in great yields and as the sole product. Unfortunately, difficulties were encountered when X was a hydroxyl (entry 4) or an amine

substituent (entry 6). In addition to benzylic bromination, electrophilic aromatic substitution was also observed, likely due to the activation of the benzene ring by the electron donating groups. On average, the reactions in entries 2, 3 and 5 (Table 4) gave entirely tetra-brominated product. However, on some occasions a mixture (normally ~4:1; tetra:tri) was obtained. Luckily, they could be separated by recrystallization from acetone, as the tri-brominated was a yellow oil while the tetra-brominated product was a white solid. However, the tetra- and penta-brominated substrates could not be separated *via* recrystallization as they are both white solids.

Table 4 - Summary - optimized bromination reactions



Entry	X	Time (days)	Yield (%)
1	I	12	0*
2	**Br**	4.5	**80**
3	**Cl**	4.5	**75**
4	OH	1	0**
5	**OTBS**	5	**61**
6	NH_2	1	0**

* mixture of mono-, di- and tri-brominated
** bromination of aromatic ring

Tetra-bromination of the selected substrates required prolonged reaction times. The addition of the first three bromine atoms occurred within the first few days; however, the introduction of the fourth bromine was inhibited due to the steric hindrance created by the surrounding bromine atoms. This congestion was evident in the ^{1}H NMR spectrum of 4-chloro-tetrabromo-*o*-xylene (**112**) (Figure 14). The broad signals at δ 7.79, 7.85 and 7.86 for Ha and Hc demonstrates the restricted rotation of the adjacent dibromomethyl groups (298 K). The broad signal is a result of the nuclei's chemical environment. A slow rotation of the dibromomethyl groups or a combination of several different rotamers existing with no rotation could be the cause for a broad signal. Free rotation of the dibromomethyl groups is observed when the temperature is raised to 348 K (DMSO-d_6) as the signals become sharper for Ha and Hc.

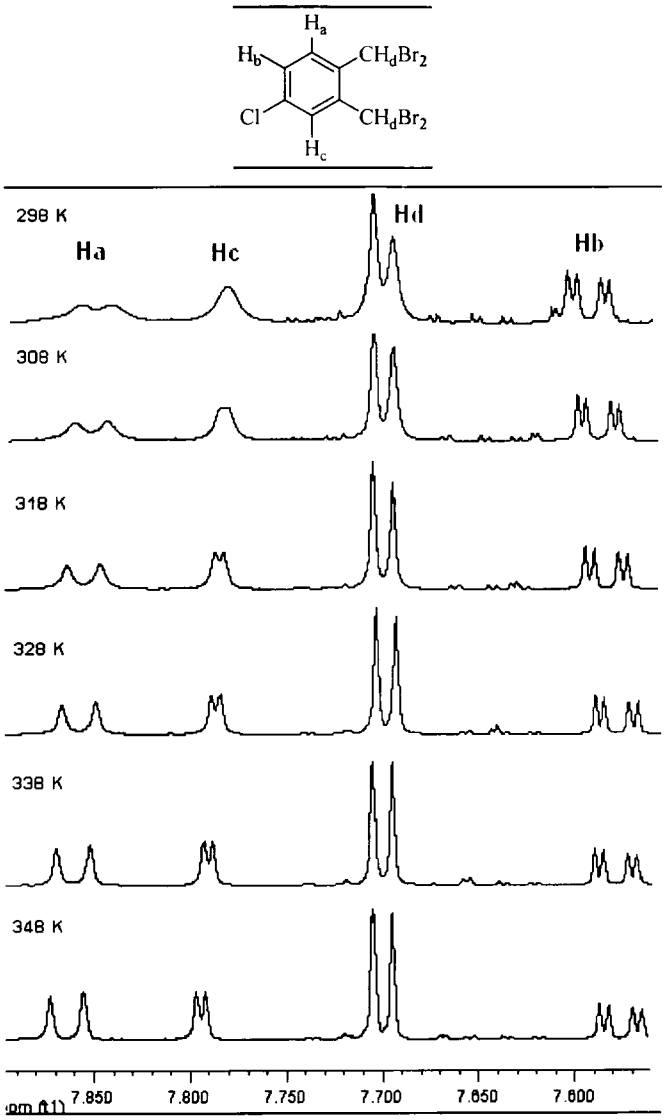


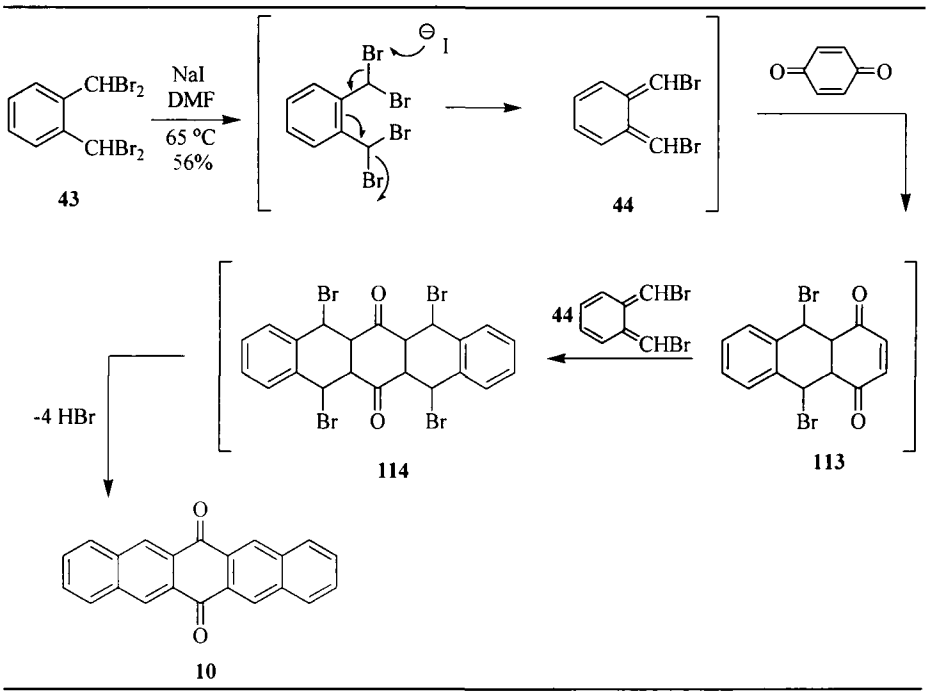
Figure 14 - Variable Temperature ^{1}H NMR of 112

2.2.2 Tandem Double Diels-Alder/Aromatization Reaction

2.2.2.1 Model Studies

To the best of our knowledge, the tandem double Diels-Alder/aromatization reaction between the *unsubstituted* tetrabromo-*o*-xylene (**43**) and 1.4-benzoquinone (Scheme 24), as well as generation of a 4-*substituted* *o*-quinodimethane intermediate have never been reported. Therefore, initial model studies were conducted on the *unsubstituted* compounds to determine

the ideal reaction conditions. The proposed mechanism for the tandem double Diels-Alder/aromatization reaction begins with a 1,4-Br_2 elimination from tetrabromo-*o*-xylene (**43**) using NaI as the nucleophile to produce reactive intermediate **44**, which rapidly undergoes a Diels-Alder reaction with 1,4-benzoquinone (Scheme 24). Mono-adduct **113** is not observed (by TLC or ^{1}H NMR) as the second addition of diene **44** to **113** rapidly occurs. Spontaneous and facile elimination of hydrogen bromide then affords 6,13-pentacenedione (**10**). The stage at which the aromatization occurs, either at the *mono*-addition product **113** or the di-addition **114**, is unknown.



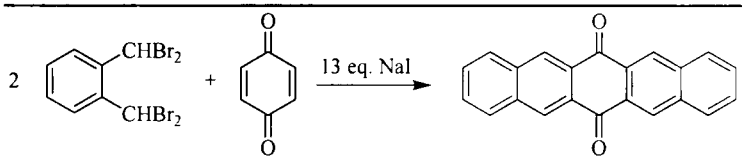
Scheme 24 - Tandem double Diels-Alder/aromatization reaction

A variety of conditions were employed for this reaction in order to achieve the optimum yield. This reaction was first attempted using the original conditions developed by Cava (entry 1) (Table 5).[47] A reasonable 45% yield was obtained; however, by increasing the temperature to 80 °C the best yield (55%) was achieved (entry 2). It was discovered after attempting a range of different temperatures (entries 3 and 4), the ideal temperature was between 65-80 °C. The conditions in entry 5 were discovered through the optimization of a similar reaction (different

[47] Cava, M. P.; Deana, A. A.; Muth, K. *Org. Lett.* **1959**, *81*, 6458.

dienophile) by Klärner *et al.*[48] Their repetition of Cava's procedure resulted in a yield of 5%. They claimed that the generation of HBr led to decomposition of their dienophile. Addition of triethylamine to the reaction to neutralize the HBr afforded their adduct in 63%. Their optimized conditions (83% yield) used $CaCO_3$, a large excess of reagents, a temperature of 55 °C and a vacuum of 100 mbar. Unfortunately, these reaction conditions did not improve the yield (50%) (entry 5). Investigations into other solvents in which NaI was soluble, such as acetone (entry 7) and CH_3CN (entry 8), afforded the lowest yields.

Table 5 - Optimization of the Diels-Alder reaction with diene 44



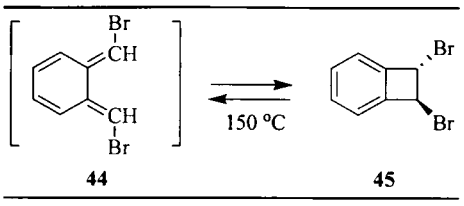
43 **10**

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	DMF	65	24	45
2	**DMF**	**25 → 80**	**45.5**	**55**
3	DMF	25 → 125	30.5	25
4	DMF	40	23	20
5*	**DMF**	**55, 100 mbar**	**7**	**50**
6	**DMA**	**70**	**6**	**50**
7	Acetone	75	46	5
8	CH_3CN	25 → 85	24	10

* 16 eq. of $CaCO_3$, 53 eq. of NaI and 7.7 eq. of **43**

Unfortunately, the yield of this reaction never exceeded 55% (30-50%). This was mainly due to a competing reaction that was discovered during an in depth analysis of the final reaction mixture. In the absence of a trapping reagent, the highly reactive dibromo-*o*-quinodimethane (**44**) underwent a conrotatory electrocyclic ring closure to yield 3,4-dibromo-1,2-benzocyclobutene (**45**) (Scheme 25). The formation of benzocyclobutene **45** during the reaction was visible on TLC, as it was slightly less polar than tetra-brominated *o*-xylene **43**. However, benzocyclobutene **45** was not produced until after the concentration of the dienophile diminished (monitored by TLC).

[48] Klärner, F. G.; Panitzky, J.; Bläser, D.; Boese, R. *Tetrahedron* **2001**, *57*, 3673.



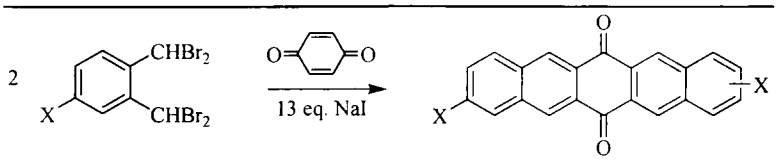
Scheme 25 - Electrocyclic ring closure of *o*-quinodimethane (44)

With this information in hand, the reaction conditions were modified to try to limit the amount of benzocyclobutene **45** that was being produced. First, the concentration of the reaction mixture was increased in the hopes of favouring the intermolecular Diels-Alder reaction as opposed to the intramolecular ring closing reaction. Unfortunately, this did not prevent the formation of **45** nor increase the yield of 6,13-pentacenequinone (**10**). To control the rate of formation of the diene, it was added slowly *via* syringe pump over 3 to 15 h. Also, NaI was added in aliquots over a period of time. Neither method increased the yield of **10**. Finally, increasing the number of equivalents of diene had no effect. All of these attempts resulted in the normal yield range of 30-50%. At this time, the best reaction conditions, 70 °C and DMA (Table 5, entry 6), were attempted on the halide substituted tetrabromo-*o*-xylene.

2.2.2.2 Substituted Tetrabromo-o-Xylene

Next, we attempted the tandem double Diels-Alder/aromatization reaction on the three substrates that were successfully tetra-brominated (X = Cl, Br and OTBS). The bromo- and chloro- substituted tetrabromo-*o*-xylenes (**111** and **112**) were subjected to the optimum conditions found for the unsubstituted diene (Table 6). It was quickly discovered that the halide (X = Cl and Br) had a negative effect on the stability of the reactive intermediate **44** as no Diels-Alder adduct (**115** or **116**) was obtained while all starting material had decomposed. The resulting reaction mixture was insoluble and uncharacterizable.

Table 6 - Diels-Alder reaction with the halide substituted tetrabromo-*o*-xylene (111 and 112)



111 X = Br
112 X = Cl

115 X = Br
116 X = Cl

Entry	X	Conditions	Time (h)	Yield (%)
1	Cl	70 °C, DMA, $CaCO_3$	3.5	0
2	Br	70 °C, DMA	4	0
3	Br	70 °C, DMA, $CaCO_3$	5.5	0
4*	Br	70 °C, DMA, $CaCO_3$	15	0
5	Br	55 °C, DMA, $CaCO_3$, 100 mbar	8	0

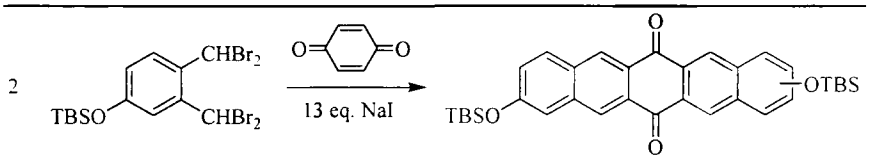
* Diene was added over a period of 15 h

The only successful tandem double Diels-Alder/aromatization reaction was between silyloxy substituted tetrabromo-*o*-xylene **110** and 1,4-benzoquinone (Table 7). It was found that DMA and DMF were the only suitable solvents, as acetone (entry 3) resulted in decomposition with no sign of product. There was an inverse relationship between the yield of **117/118** and the reaction time. Entries 2 and 4 have an extended reaction time with the lowest yields. We believe this is due to the harsh reaction conditions (specifically the generation of HBr) and the stability of the product and starting materials. There is also an inverse relationship between the reaction time, yield and temperature. Increasing the temperature increases the rate at which the reactive diene is produced, hence decreasing the reaction time and the yield, as production of the four-membered ring is accelerated. The conditions in entry 11 were taken from a literature procedure and used **43** as the diene and 2-cyclohexene-1-one as the dienophile; however, they were able to reach a pressure of 6 kbar and obtain a yield of 32%.[49] We found, the best reaction conditions were a temperature of 65 °C, 0.1 eq. $Cu(OTf)_2$ and a reaction time of 6 h (entry 8). We suspected that 1,4-benzoquinone was decomposing/aromatizing. Thus, as the reaction progressed, the addition of excess equivalents (0.25 X 4) of dienophile assisted with the reproducibility of this reaction. Even though the highest yield was 50% (30-50%). this reaction is still outstanding as eight reactions (two 1,4-Br_2 eliminations, two Diels-Alder reactions, and four eliminations of HBr) take place in one-pot. A highlight of this reaction is the work up. The

[49] Minuti, L.; Taticchi, A.; Gacs-Baitz, E.; Marrocchi, A. *Tetrahedron* **1998**, *54*, 10891.

reaction mixture is added to an ice cold solution of 1 M $Na_2S_2O_3$ and the precipitate is collected. The impurities and side products that exist are soluble in acetone, whereas the product is not. Once again, the yellow precipitate is filtered and collected to give pure **117/118** as a 50:50 mixture of the 2,9 and 2,10 disubstituted pentacenequinones.

Table 7 - Optimization of the Diels-Alder reaction with diene precursor 110



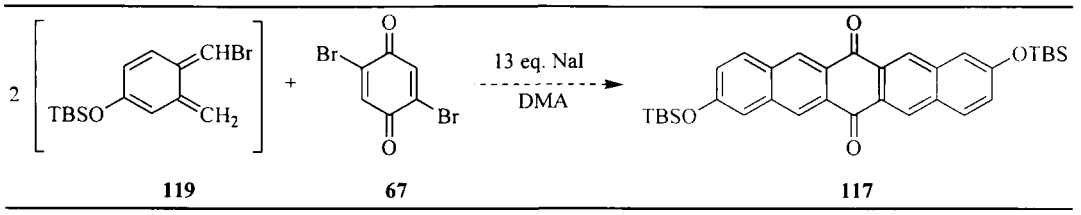
110

117 (2,9 isomer)
118 (2,10 isomer)

Entry	Solvent	Conditions	Time (h)	Yield (%)
1	DMF	85 °C	7.5	30
2	DMF	80 °C	18.5	12
3	Acetone	75 °C	23.5	0
4	DMA	70 °C	22	10
5	DMA	75 °C	6.5	30
6	DMA	75 °C, 4 eq. $CaCO_3$	3	36
7	DMA	50 °C, 0.1 eq. $Cu(OTf)_2$	8.5	36
8	**DMA**	**65 °C, 0.1 eq. $Cu(OTf)_2$**	**6**	**50 (30-50)**
9	DMA	70 °C, 0.1 eq. $Cu(OTf)_2$	6	33
10	DMA	80 °C, 0.1 eq. $Cu(OTf)_2$	4.5	17
11	DMA	65 °C, 800 psi	23	20

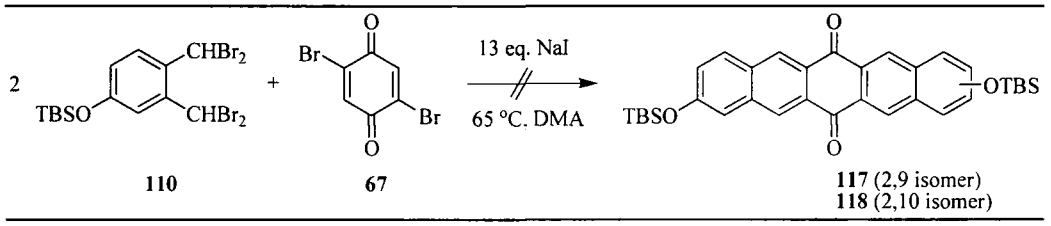
2.2.2.3 Attempts Towards a Regioselective Double Diels-Alder Reaction

We have shown that the tandem double Diels-Alder/aromatization reaction successfully afforded the 2,9 and 2,10 disubstituted pentacenquinones in a 50:50 mixture; however, this reaction must still be done regioselective. The design for the regioselective Diels-Alder reaction involved incorporating transient directing groups on the diene and dienophile (Scheme 26). The *o*-quinodimethane intermediate (**119**) could be generated from a tribrominated *o*-xylene. It has been shown that the tribromination of substituted *o*-xylenes can be achieved regioselectively (see Section 1.5, Scheme 11).[38]



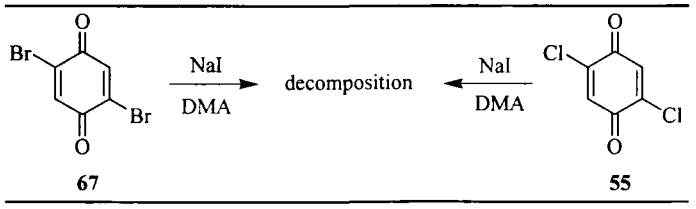
Scheme 26 - Proposed regioselective tandem double Diels-Alder/aromatization reaction

Instead of introducing two new parameters to the system, the reaction between the known substituted tetrabromo-*o*-xylene **110** and substituted benzoquinone **67** was performed (Scheme 27). If this reaction was successful, then the synthesis of substituted tribromo-*o*-xylene would be attempted to achieve a regioselective Diels-Alder reaction. Unfortunately, this reaction did not succeed and decomposition of the starting materials was observed. Despite the use of a variety of conditions and Lewis acids ($ZnCl_2$, $Yb(OTf)_3 \cdot H_2O$, $MgBr_2 \cdot OEt_2$, $Cu(OTf)_2$, $BF_3 \cdot OEt_2$, $SnCl_2$) compounds **117/118** were not formed.



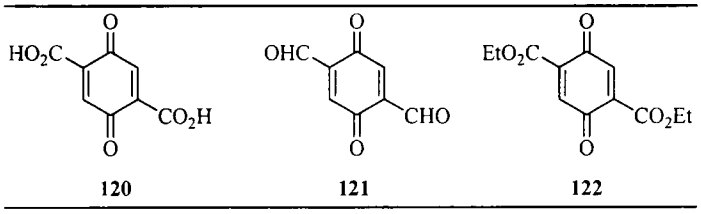
Scheme 27 - Attempted Diels-Alder reaction with new dienophile 67

To gain some insight as to why to the halide substituted dienophile was decomposing, **67** and **55** were subjected to NaI in the absence of diene precursor **110** (Scheme 28). It was discovered that the halide substituted benzoquinones, **67** and **55** decomposed to an insoluble brown solid in the presence of NaI. Therefore, we required an alternative dienophile.



Scheme 28 - Decomposition of halide substituted 1,4-benzoquinone with NaI

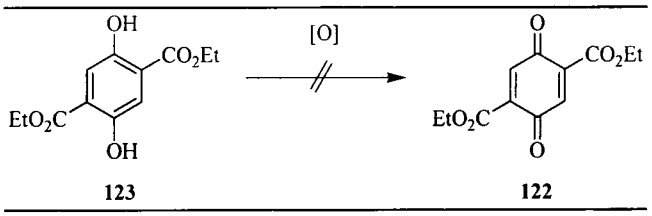
An alternate directing group could be an acid, aldehyde or ester (Figure 15). Unlike dienophile **67**, these groups would need to be eliminated later in the synthesis. After compound **120** had undergone a Diels-Alder reaction, it could easily be decarboxylated to afford aromatized pentacylic compound **117**. Similar functional group transformations of compounds **121** and **122** would have to be carried out after the Diels-Alder reaction to afford **117**. These compounds needed to be synthesized as they are not commercially available.



120 **121** **122**

Figure 15 - Possible substituted dienophiles

The oxidation of commercially available diethyl-2.5-dihydroxyterephthalate (**123**) to quinone **122** was unsuccessful when either ceric ammomium nitrate (CAN) in CH_3CN/H_2O or MnO_2 in refluxing CH_2Cl_2 and toluene were used (Scheme 29).



123 **122**

Scheme 29 - Oxidation of 123 to quinone 122

We attribute the difficultly in oxidizing compound **123** to the hydrogen bonds that exist between the phenolic hydrogen and the carbonyl of the ester (Figure 16).

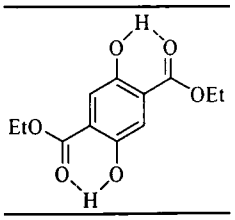
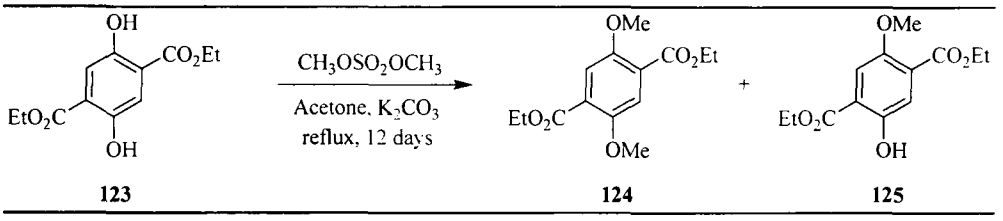


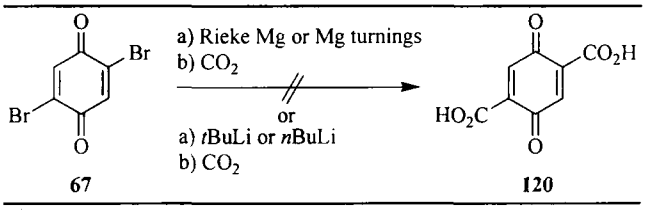
Figure 16 - Hydrogen bonding

This problem could be circumvented if the hydrogen bonding did not exist. This could be accomplished by treatment of **123** with base and a methylating agent (Scheme 30). Unfortunately, after 12 days at reflux, the reaction was stopped and a mixture of mono- **125** and di-methylated **124** was obtained. In addition, NaH and MeI were used, but did not improve the result. Compounds **124** and **125** were not separated, but were treated with CAN. Sadly, no oxidation occurred, and only starting material was isolated.



Scheme 30 - Methylation of 123

A new approach to a substituted quinone was required. Instead of oxidizing the aromatic ring, we decided to begin with quinone **67** and functionalize the bromine (Scheme 31). Quinone **120** could be formed by an oxidative insertion with Mg or lithium-halogen exchange to 2,5-dibromo-1,4-benzoquinone (**67**), followed by the appropriate work-up. Magnesium turnings and reactive Rieke Mg were used followed by the addition of CO_2 (dry ice). Unfortunately, only starting material with additional impurities were obtained. The same result was afforded with lithium-halogen exchange using *n*BuLi and *t*BuLi with subsequent treatment of CO_2 (dry ice).



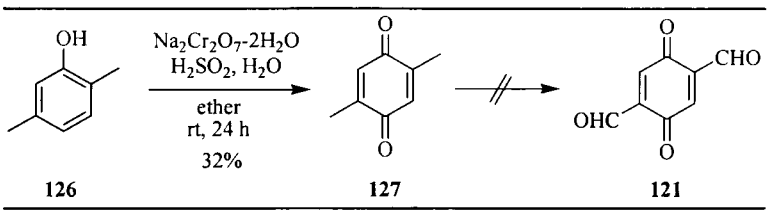
Scheme 31 - Attempted functionalization of 67

One of the final attempts involved the allylic oxidation of the methyl groups on 2,5-dimethyl-1,4-benzoquinone (**127**) (Table 8). This compound was prepared in 32% yield from **126** *via* a literature procedure using the Jones oxidation.[50] Unfortunately, despite the use of

[50] Liotta, D.; Arbiser, J.; Short, J. W.; Saindane, M. *J. Org. Chem.* **1983**, *48*, 2932.

several oxidizing agents, compound **121** could not be synthesized. In most cases starting material was obtained.

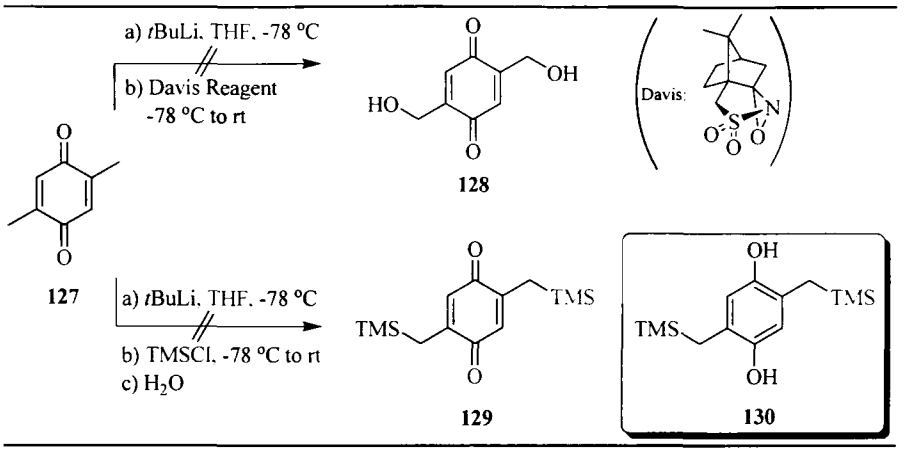
Table 8 - Oxidation of 127



126 **127** **121**

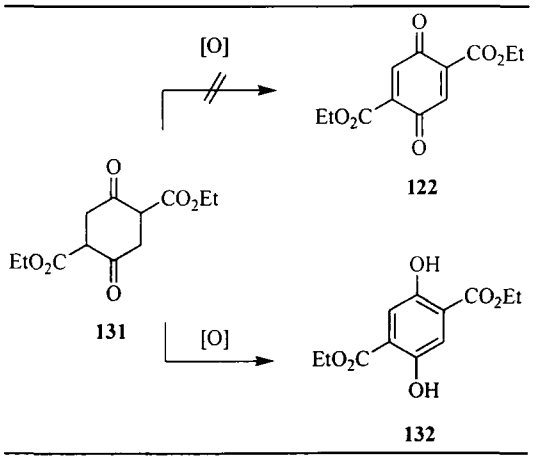
Entry	Reagents (Solvent)	Temperature (°C)	Time (h)	Yield (%)
1	SeO_2 (dioxane)	reflux	2	SM
2	CAN (CH_3CN/H_2O)	rt then reflux	24	decomposition
3	CuI, *t*BuOOH (CH_3CN)	55	24	SM
4	Jones	reflux	48	SM
5	IBX (DMSO)	80	24	SM
6	$KMnO_4$, silica (benzene)	rt then reflux	24	SM
7	SeO_2, sealed tube (dioxane)	150	22	SM and decomposition

A few additional functionalization reactions were performed on **127** in attempt to create the required dienophile (Scheme 32). Conversion of **127** *via* allylic deprotonation followed by quenching with Davis' reagent could produce a precursor to the desired aldehyde or carboxylic acid. An inseparable mixture was obtained without any indication of product **128**. This reaction was also attempted with a better electrophile, TMSCl, to determine if the generation of the allylic anion or Davis' reagent was the problem. Allylic deprotonation with *t*BuLi and subsequent addition of TMSCl should have afforded **129**. This reaction also produced several impurities; however, it was discovered that the aromatized equivalent (**130**) of **129** was the major product. Based on these results, this synthetic approach was discontinued.



Scheme 32 - Attempted functionalization of 2,5-dimethyl-1,4-benzoquinone (127)

The very last attempt to synthesize a substituted dienophile for a regioselective Diels-Alder reaction was the transformation of diethyl-1.4-cyclohexadione-2.5-dicarboxaldehyde (**131**) to quinone **122** (Scheme 33). Several oxidizing agents were used including, IBX (80 °C, toluene:DMSO;2:1); NaH and PhSeCl (without H_2O_2); pyridine and PhSeCl, then H_2O_2 at 0 °C; DDQ (reflux, benzene). None of these reactions afforded the desired quinone **122**, but rather aromatized product **132**. This clearly indicates of the poor stability of these quinones substituted with two electron-withdrawing substituents. No further attempts were made to prepare a substituted dienophile.



Scheme 33 - Attempts to prepare quinone 122

We chose to continue with this synthetic route, which involves the tandem double Diels-Alder aromatization reaction, as it was still more efficient than the first generation synthesis. However, because it was not regioselective, we had to separate the 2,9 and 2,10 disubstituted compounds, **117** and **118**, that were formed from the Diels-Alder reaction (Figure 17). Several attempts to separate them *via* flash column chromatography were unsuccessful as only the first few fractions afforded pure 2,9 isomer **117** with the remaining fractions containing both isomers. The first compound that eluted was characterized as the 2,9 isomer as the C_{2h} symmetry afforded only one carbonyl peak in the ^{13}C NMR, whereas the 2,10 isomer had two carbonyl peaks due to its C_{2v} symmetry. We decided to proceed to the next step in hopes that a better separation could be achieved.

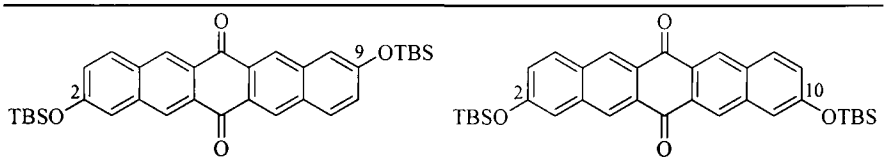


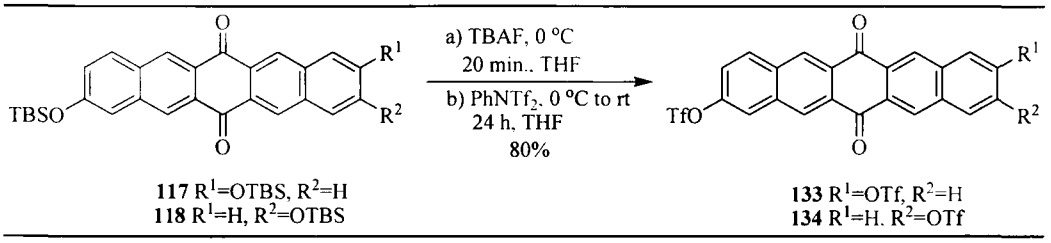
Figure 17 - 2,9 and 2,10 Disubstituted 6,13-pentacenedione 117 and 118

2.2.3 Preparation of Ditriflates and the Sonogashira Reaction

The next two steps in this synthetic design were previously developed on a different molecule in the Fallis Lab.[21] Preparation of ditriflates **133** and **134** would allow for a large assortment of 2,9 and 2,10 disubstituted pentacene derivatives *via* Sonogashira reaction. This would permit an in-depth investigation into the effect that different substituents have on the electron and hole mobilities, crystal packing and solubility.

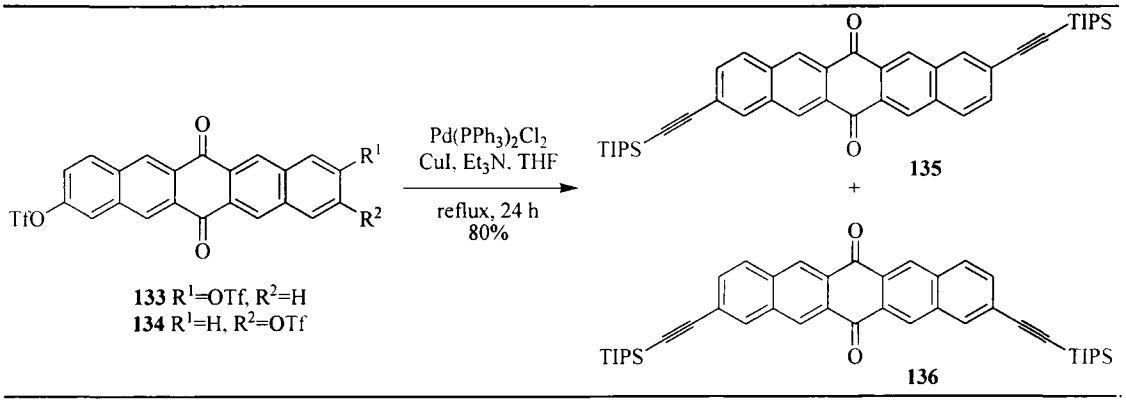
Desilylation and triflation of **117** and **118** were conducted in one-pot to overcome the problems with the solubility of the intermediate diphenol. The optimum conditions previously found[21] were conducted on the mixture of silyl ethers **117** and **118** (Scheme 34). Desilylation with TBAF at 0 °C produced the dianion, which was subsequently quenched with *N*-Phenyltrifluoromethanesulfonimide ($PhNTf_2$). After warming to room temperature the resulting yellow ditriflates **133** and **134** were isolated and found to be sparingly soluble in THF and could

not be characterized. They were used without further purification in the following Sonogashira reaction.



Scheme 34 - Deprotection/triflation of silyl ethers 117 and 118

The first attempted palladium-mediated coupling reaction was with tri*iso*propylsilyl acetylene. As mentioned previously (Sections 1.3 and 1.4), this substituent could allow for optimum intermolecular crystal packing, and hence increased electron and hole mobilities. A Sonogashira reaction on the mixture of ditriflates, **133** and **134** with tri*iso*propylsilyl acetylene using $Pd(PPh_3)_2Cl_2$ as the catalyst and CuI as co-catalyst in Et_3N and THF afforded quinones **135** and **136** (Scheme 35). Purification was accomplished by filtering through a pad of silica with pet ether to elute the tri*iso*propylsilyl acetylene dimer, followed by 10% ethyl acetate in pet ether to afford pure isomers, **135** and **136** in 80% yield.



Scheme 35 - Sonogashira reaction with TIPS-acetylene and ditriflates 133 and 134

The separation of isomers **135** and **136** by flash column chromatography proved as difficult as with silyl ethers **117** and **118**. Other chromatographic techniques were utilized, such as normal and reverse phase high pressure liquid chromatography (HPLC) (with and without a gradient), automatic flash column purification (Biotage Inc. with Horizon^{TM} detector),

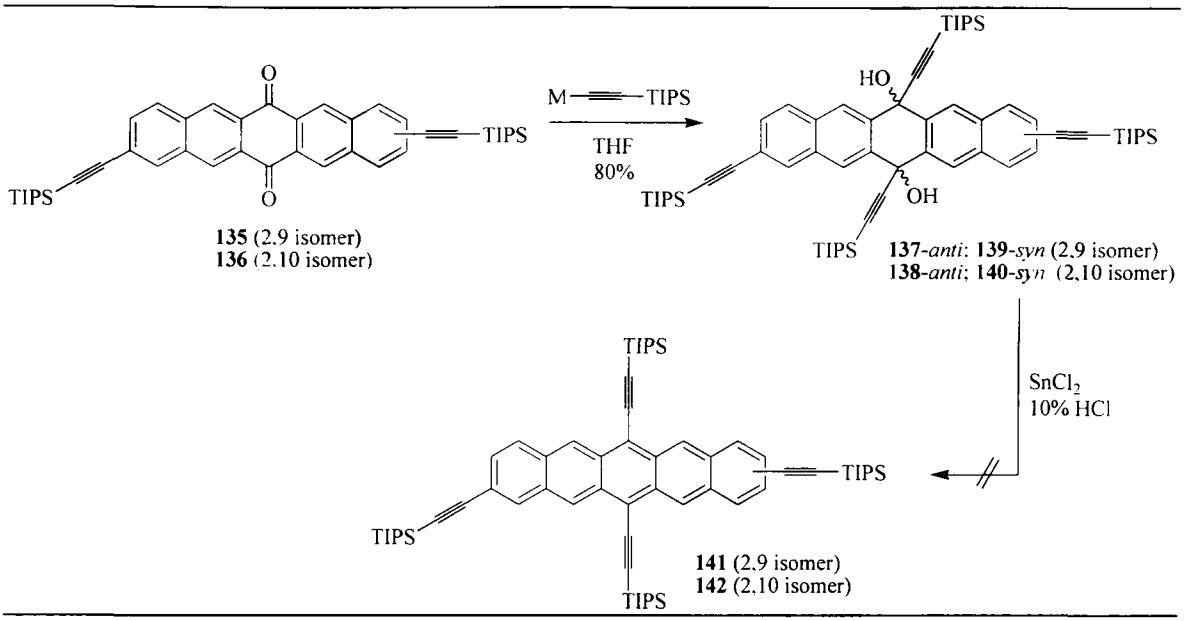
preparative TLC, and a Chromatotron (preparative, centrifugally accelerated, radial, thinlayer chromatograph). No separation was achieved by HPLC. The automated flash column eluted both isomers simultaneously. Preparative TLC was an extremely lengthy and tedious process as the isomers had a very small loading capacity on the silica plate. The Chromatotron was somewhat successful and gave pure fractions of each in addition to several mixed fractions. However, vast quantities of solvent were required as an extremely small gradient and slow elution time was needed for optimal separation. Also, similar to preparative TLC, at most 20-30 mg could be loaded onto the plate.

After all of these attempts to separate the regio-isomers, it was found that repeated fractional recrystallization from CH_2Cl_2 afforded pure isomers **135** and **136**. It was discovered that the 2,10 isomer **136** was slightly less soluble than the 2,9 isomer **135** as it was the first to precipitate at -20 °C. As an afterthought, we attempted fractional recrystallization on silyl ethers **117** and **118** from CH_2Cl_2. This was also found be successful, and it was discovered that the 2,9 isomer **117** was the first to precipitate at -20 °C and was much less soluble than the 2,10 isomer **118**. Fractional recrystallization (of **117** and **118**) at this stage in the synthesis was more advantageous as fewer recrystallizations needed to be performed.

2.2.4 Preparation of 2,9 and 2,10 Disubstituted Pentacenes

There are a few known procedures to reduce 6,13-pentacenediones to pentacene. This section involves a detailed discussion of the literature procedures that were conducted on 2,9 and 2,10 disubstituted pentacenequinones **135** and **136**. Furthermore, new synthetic routes to pentacene were designed and conducted on the unsubstituted and substituted pentacenequinones.

We initially added tri*iso*propylsilyl acetylide to the mixture of isomers, **135** and **136**, to give a mixture of *anti*- and *syn*-diols **137/138** and **139/140** in 80% yield (Scheme 36). The diols were isolated and treated with 10% HCl saturated with $SnCl_2$. This should have afforded an air stable pentacene (**141/142**) that could be handled and purified in the presence of light and air. However, a green solution, uncharacteristic of pentacene was obtained. Thin layer chromatography analysis displayed several different products, while ^1H NMR analysis did not indicate the presence of pentacene product.



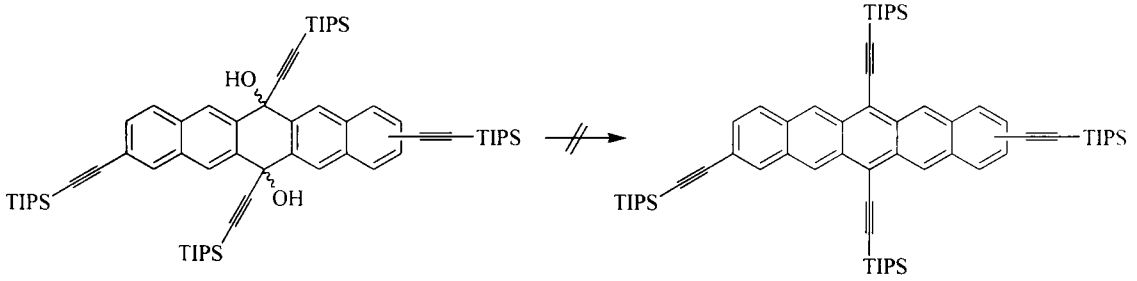
Scheme 36 - Addition of TIPS-acetylide to pentacenequinones 135 and 136

Anthony *et al* have reported several sets of conditions to remove the diols from their cyclic thiophene and cyclic ether containing pentacenes using $SnCl_2$.[18,51] These conditions were employed on 2,9 and 2,10 disubstituted diols **137/139** and **138/140** (entries 1 and 2, Table 9). Several products were obtained and preparative TLC was used in an attempt to determine the products. Unfortunately, no conclusions could be drawn from this analysis as there were a vast number of products in very small quantities. It was later discovered through personal communication with one of Anthony's colleagues at the Canadian Society of Chemistry Conference at Saskatoon 2005 that the published experimental procedures were not accurately reported. Unfortunately, his colleague possessed a competitive trait and would not share the correct procedure. Repeating the procedure with compound **23** was likewise unsuccessful (Section 1.3, Scheme 5). The dehydration was also attempted using a catalytic amount of concentrated HCl; however, a complex mixture was obtained (entry 4). Finally, KI and $Na_2S_2O_3 \cdot 5H_2O$ in refluxing acetic acid was employed as it has previously been shown to dehydrate a similarly substituted diol.[52] The reaction was conducted both in the dark, as in the reported procedure, and in the light to see if any differences existed between the two methods.

[51] Payne, M. M.; Delcamp, J. H.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 1609.
[52] Sparfel D.; Gobert, F.; Rigaudy, J. *Tetrahedron* **1980**, *36*, 2225.

Both procedures gave a mixture of products, although the reaction conducted in the dark had fewer products (TLC analysis). Unfortunately, the mixture of products obtained in each reaction discouraged us from further pursuing this route.

Table 9 - Attempts to form 2,6,9,13 and 2,6,10,13 tetra-substituted pentacenes 141 and 142



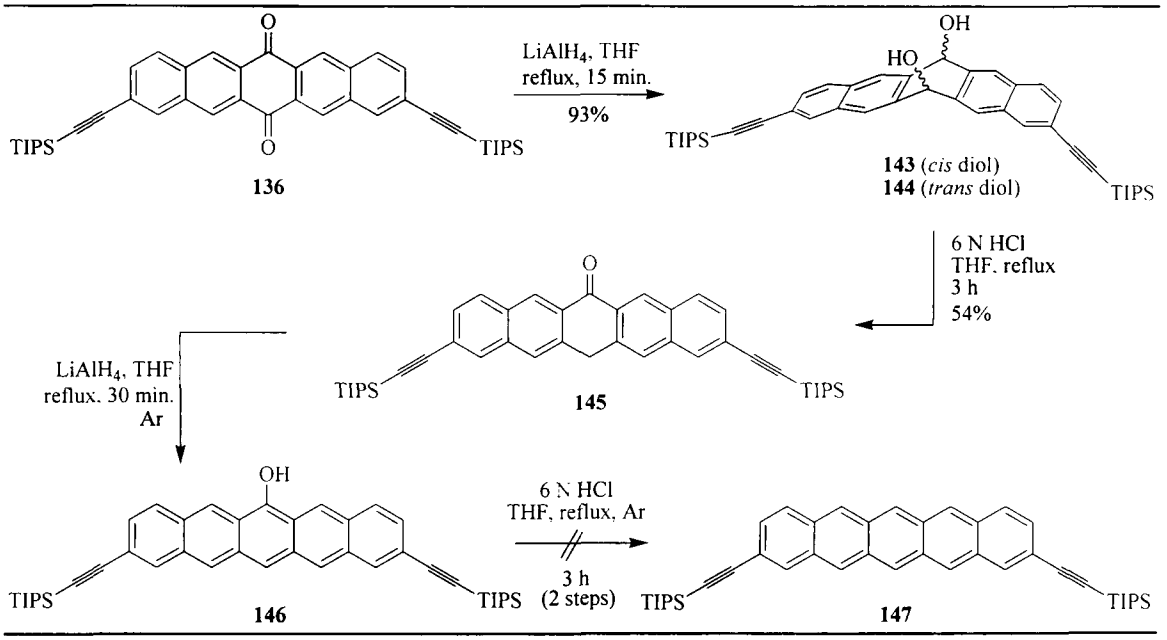
137-*anti*; **139**-*syn* (2,9 isomer)
138-*anti*; **140**-*syn* (2,10 isomer)

141 (2,9 isomer)
142 (2,10 isomer)

Entry	Reagents	Solvent	Time (h)	Yield (%)
1	2 eq. $SnCl_2 \cdot 2H_2O$	THF:CH_3CN; 2:3	2	0
2	3 eq. $SnCl_2 \cdot 2H_2O$	THF:CH_3CN; 2:3	2	0
3	10% HCl/$SnCl_2$	THF (60 °C)	1	0
4	conc. HCl	THF	1	0
5	KI, $Na_2S_2O_3 \cdot 5H_2O$ (light)	Acetic Acid (reflux)	1	0
6	KI, $Na_2S_2O_3 \cdot 5H_2O$ (dark)	Acetic Acid (reflux)	1	0

We tried the literature procedure that used $LiAlH_4$ and 6 N HCl (repeated) to reduce pentacenequinone (**10**) to pentacene (**3**) next (Section 1.2, Scheme 2). Formation of diols **143** and **144** in 93% yield was accomplished by treatment of pentacenequinone **136** with $LiAlH_4$ in refluxing THF (Scheme 37). The resulting mixture of *trans* and *cis* diols (**144** and **143**) were separated by column chromatography and their ratio was determined to be 63:37, *trans:cis*. It was discovered by NMR analysis that when diols **143** and **144** were dissolved in $CDCl_3$, they would convert back into pentacenequinone **136** over a period of a few hours. Treatment of diols **143** and **144** with 6 N HCl in refluxing THF afforded ketone **145** in 54% yield. Interestingly, the ^1H and ^{13}C NMR and TLC analysis all suggested that only one isomer existed. To the best of our knowledge, both protonated hydroxyl groups should have an equal chance of being expelled, therefore a 50:50 mixture was expected (ketone alternatively at the 6 or 13 position). Thus, ketone **145** shown may not be the correct isomer or a mixture may exist. Nevertheless, ketone **145** was treated with $LiAlH_4$ in refluxing THF under argon to afford a dark red solution. The

addition of 6 N HCl should have afforded a dark purple solution of pentacene **147**; however, the solution remained red. Unfortunately, the resulting mixture of products could not be separated or characterized.



Scheme 37 - Attempt to synthesis 2,10 disubstituted pentacene 147 *via* literature procedure

The transformation of 6,13-diol **143/144** to mono-ketone **145** is of some mechanistic interest (Figure 18). It is proposed that after the loss of water a proton is abstracted (by H_2O or Cl^-) to quench the carbocation to form an enol, which then tautomerizes to the ketone. Proton abstraction allows for the re-aromatization of ring D, which then yields the final mono-ketone **145**.

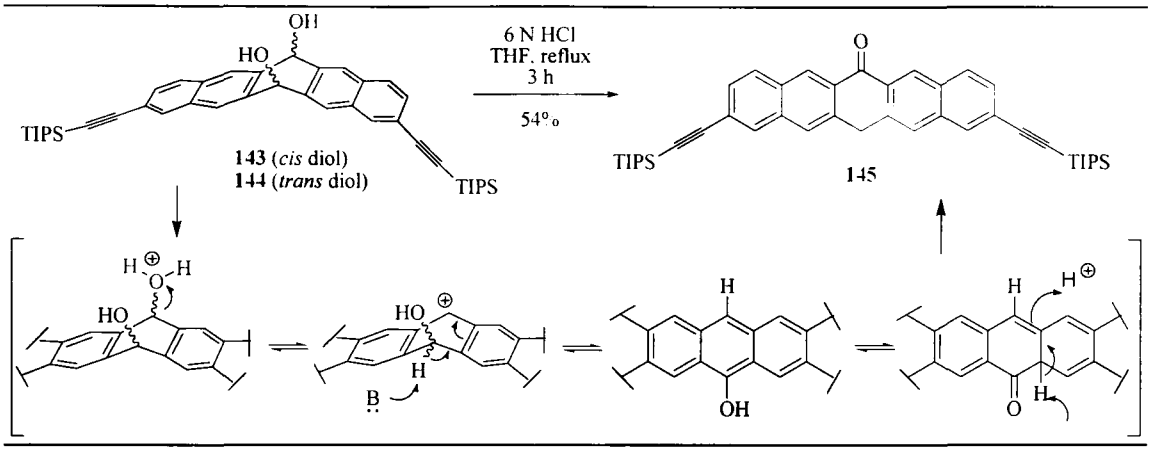


Figure 18 - Proposed mechanism for the formation of 145

The next section entails the new synthetic designs that were created and pursued on the 2,9 and 2,10 disubstituted pentacenequinones **135** and **136**. In addition, some model studies were conducted on 6,13-pentacenequinone **10**. Most syntheses of pentacene reduce the carbonyl groups and aromatize in one pot. We wanted to progress stepwise so that any issues could more easily be recognized and solved. Retrosynthetically, disubstituted pentacene **148** could be obtained by the aromatization of the center ring of **149** (Figure 19). The removal of the carbonyl groups from **150** to yield **149** should be an easy transformation as a vast number of reagents exist to accomplish such a task.

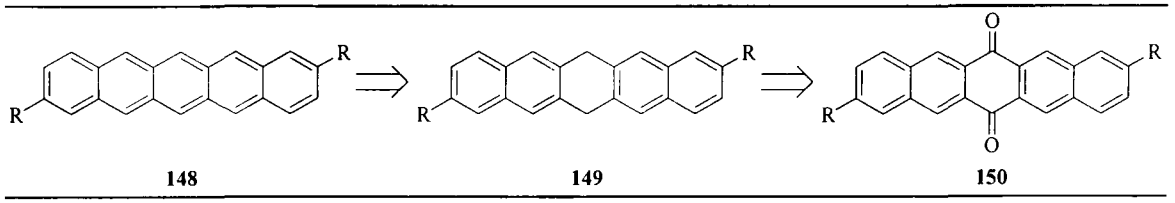
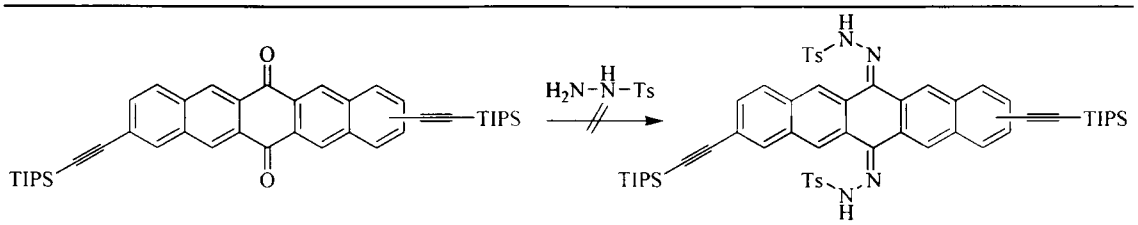


Figure 19 - Retrosynthetic route of pentacene 148 from pentacenequinone 150

The Wolff-Kishner reduction is a traditional and well-known reaction used to remove carbonyl groups in two steps. However, before the reduction can occur, the hydrazone must first form. Unfortunately, using numerous acids and solvents, hydrazones **151/152** resulting from the condensation of **135/136** with tosylhydrazine did not form (Table 10). This could be due to the poor electrophilicity of the carbonyls, as it is an extremely conjugated molecule.

Table 10 -Attempts to form hydrazones 151 and 152

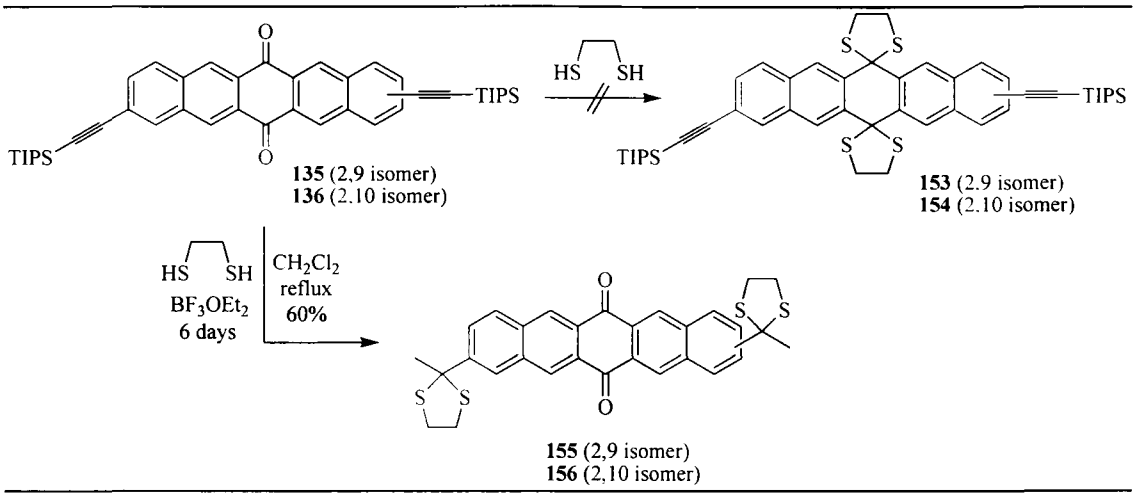


135 (2,9 isomer)
136 (2,10 isomer)

151 (2.9 isomer)
152 (2.10 isomer)

Entry	Acid	Solvent	Temperature (°C)	Yield (%)
1	*p*TSA	CH_2Cl_2	rt then reflux	SM
2	*p*TSA	THF	reflux	SM
3	H_3PO_4	EtOH	reflux	SM
4	H_2SO_4	*i*-PrOH	reflux	SM
5	AcOH	CH_2Cl_2	reflux	SM
6	*p*TSA	toluene	reflux	SM

An alternative method to remove carbonyls is *via* the generation of thioacetals. They are often easily reduced with Raney nickel to form the desired deoxygenated product. One attempt was made to form thioacetals **153** and **154** from pentacenequinones **135** and **136** with dithiol and BF_3OEt_2 (Scheme 38). Unfortunately, thioacetals **153** and **154** were not produced. However, given a lengthy reaction time the alkynes were reduced and deprotected, with the formation of the thioacetals, affording **155** and **156** in 60% yield. With this discouraging result, we directed our focus towards the removal of carbonyls using a different approach.

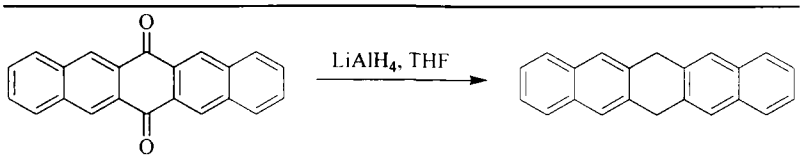


Scheme 38 - Formation of thioacetals 155 and 156

The well-known two step methods were abandoned and investigations were directed towards the removal of the carbonyls in one step. A substituted anthraquinone has been reported to undergo reduction to its dihydro equivalent using $AlCl_3$ and $LiAlH_4$.[53] The reaction time and temperature were not reported; therefore this reaction was first conducted on pentacenequinone (**10**) at room temperature (entry 1, Table 11). Gratifyingly, 6,13-Dihydropentacene (**157**) was obtained in 34% yield. In order to increase the yield, additional Lewis acids were employed; however, the yield remained low (entries 2 to 4). As a final attempt, The original reaction was repeated at reflux instead of room temperature (entry 5), and the yield was greatly improved to 93%.

[53] Shahlai, K.; Hart, H. *J. Amer. Chem. Soc.* **1990**, *112*, 3697.

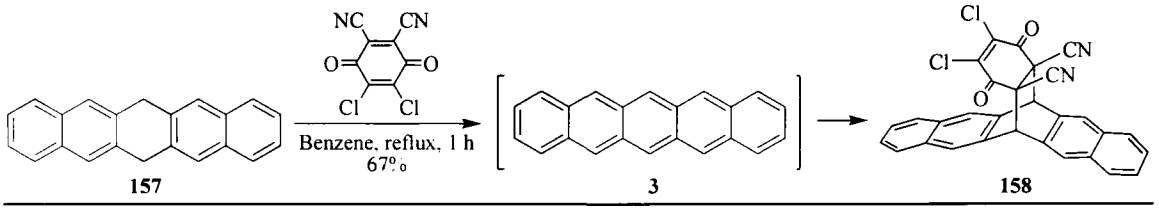
Table 11 - Reduction of pentacenequinone (10)



10 157

Entry	Lewis Acid	Temperature (°C)	Time (h)	Yield (%)
1	$AlCl_3$	23	10	34
2	$SnCl_2 \cdot 2H_2O$	23	24	SM
3	$ZnCl_2$	23	10	26
4	Al tri-*sec*butoxide	23	10	6
5	**$AlCl_3$**	**reflux**	**21**	**93**

With 6,13-dihydropentacene (**157**) at hand, simple aromatization should afford pentacene (**3**). As expected, treatment of **157** with DDQ in refluxing benzene aromatized the center ring to afford pentacene **3** (Scheme 39). However, it was not isolated nor detected by TLC as the reactive center ring underwent a cycloaddition with excess DDQ to afford **158** in 67%. It was confirmed by X-ray crystallography that the addition of the dienophile occurred at the dicyano side of DDQ (Figure 20). Pentacene was successfully prepared and 'trapped' *in situ* to form a stable and soluble pentacene precursor. Müllen's synthesis of pentacene (Scheme 3, Section 1.3), was lengthy and low yielding and trapped pentacene with a tetrahalo dienophile. This synthetic route is much shorter and higher yielding and **158** could possibly be used as a pentacene precursor, similar to Müllen's.



157 3 158

Scheme 39 - Formation of pentacene-DDQ adduct 158

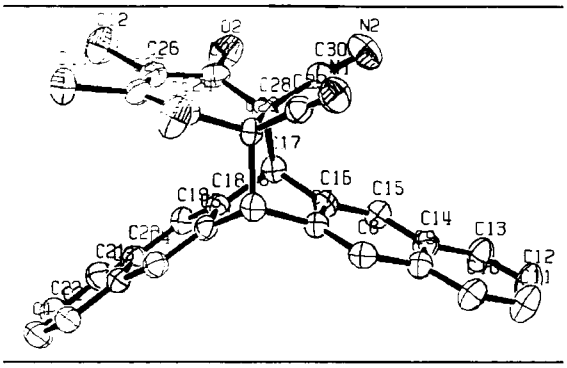
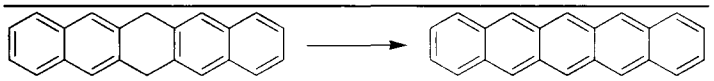


Figure 20 - Crystal Structure of pentacene-DDQ adduct 158

Despite the success of the synthesis of a pentacene precursor (**158**) *via* a new route, we still wanted a method to prepare and isolate pentacene (**3**). It was previously reported that 5,14-dihydropentacene (**157**) was aromatized with Pd/C in refluxing xylene to produce pentacene in 100% yield.[54] Thus, 6,13-Dihydropentacene (**157**) was treated with Pd/C in ethyl acetate (entry 1), toluene (entry 2) and mesitylene (entry 3) for several days at reflux (Table 12). The purple colour of the solution was indicative of pentacene; however, only starting material was isolated from the reaction. We next tried the same conditions that were successful in the dehydrogenation of 9,10-dihydroanthracene.[55] Triphenylmethanol and trifluoroacetic acid produced the active species, trityl trifluoroacetate, which abstracts hydride ions. Unfortunately, when these reagents were used for the dehydrogenation of **157**, only decomposition was observed (entry 4). When **157** was treated with MnO_2, pentacenequinone **10** was produced, in addition to recovered starting material (entry 5). Finally, when **157** was treated with *n*BuLi/TMEDA in refluxing hexanes followed by subsequent treatment with $CdCl_2$, pentacene (**3**) was successfully produced and later trapped with tetracyanoethylene to afford **159** (Scheme 40) in 27% yield (over two steps, unoptimized). Deprotonation at carbons 6 and 13 with *n*BuLi produced a dianionic intermediate which was stabilized by the formation of a TMEDA complex.[56] Aromatization was achieved *via* electron transfer from $CdCl_2$. The second Diels-Alder step was necessary to prove that pentacene (**3**) had formed, as it can not be characterized due to its lack of solubility.

[54] Luo, J.; Hart, H. *J. Org. Chem.* **1987**, *52*, 4836.
[55] Fu, P. P.; Harvey, R. G. *Tet. Lett.* **1974**, *36*, 3217.
[56] Harvey, R. G.; Cho, H. *J. Amer. Chem. Soc.* **1974**, *96*, 2434.

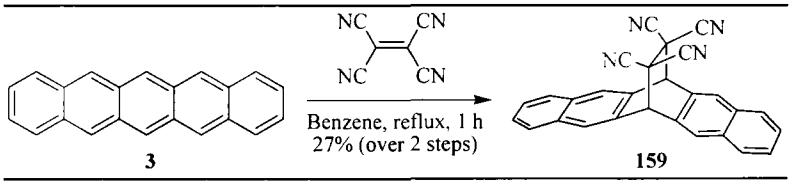
Table 12 - Aromatization to pentacene (3)



157 3

Entry	Reagents	Solvent	Temperature (°C)	Yield (%)
1	Pd/C	ethyl acetate	rt then reflux	SM
2	Pd/C	toluene	reflux	SM
3	Pd/C	mesitylene	reflux	SM
4	Ph_3COH	CF_3CO_2H	reflux	Decomposed
5	MnO_2	toluene	reflux	SM + **10**
6	a) *n*BuLi/TMEDA b) $CdCl_2$	hexanes	a) reflux b) rt	27*

* not optimized; yield over two steps, see Scheme 40

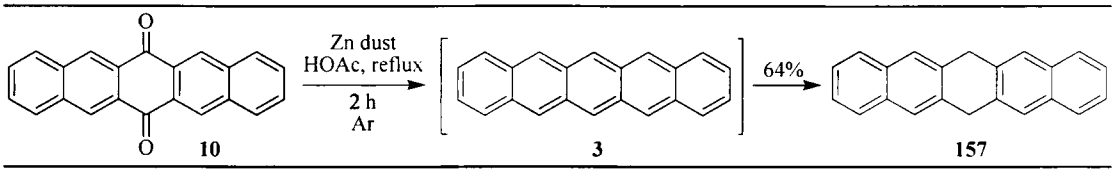


3 159

Scheme 40 - Diels-Alder reaction to prove the formation of 3 *via* *n*BuLi/TMEDA and $CdCl_2$

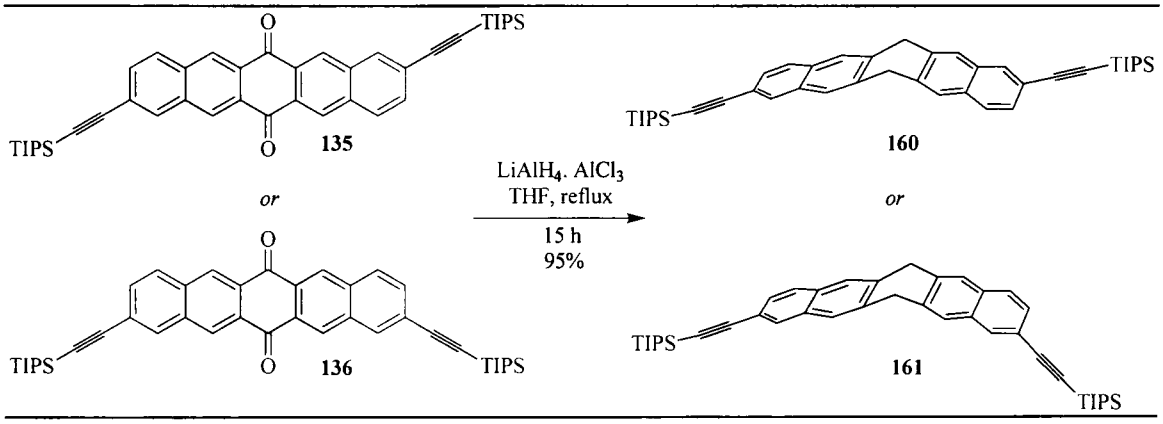
One final reaction was conducted on 6,13-pentacenequinone (**10**). It has been previously reported that when 9,10-anthraquinone is treated with Zn dust in HOAc, the dihydro equivalent is obtained.[57] In addition, an intermediate was discovered to be anthracene. The reaction times between the intermediate and product were long enough, 12 h for anthracene and 24 h for 9,10-dihyroanthracene, that the reaction could be stopped and the intermediate isolated (anthracene). The same reaction conditions were employed on **10** (Scheme 41). After 30 minutes, a purple precipitate had formed, indicating that pentacene had formed. Unfortunately, the formation of dihydro **157** quickly followed and was obtained in 64% yield. This reaction did not seem viable on our substrates due to the small window that existed to isolate the pentacene intermediate (**3**).

[57] Lu, L.; Chen, Q.; Zhu, X.; Chen, C. *Synthesis* **2003**, *16*, 2464.



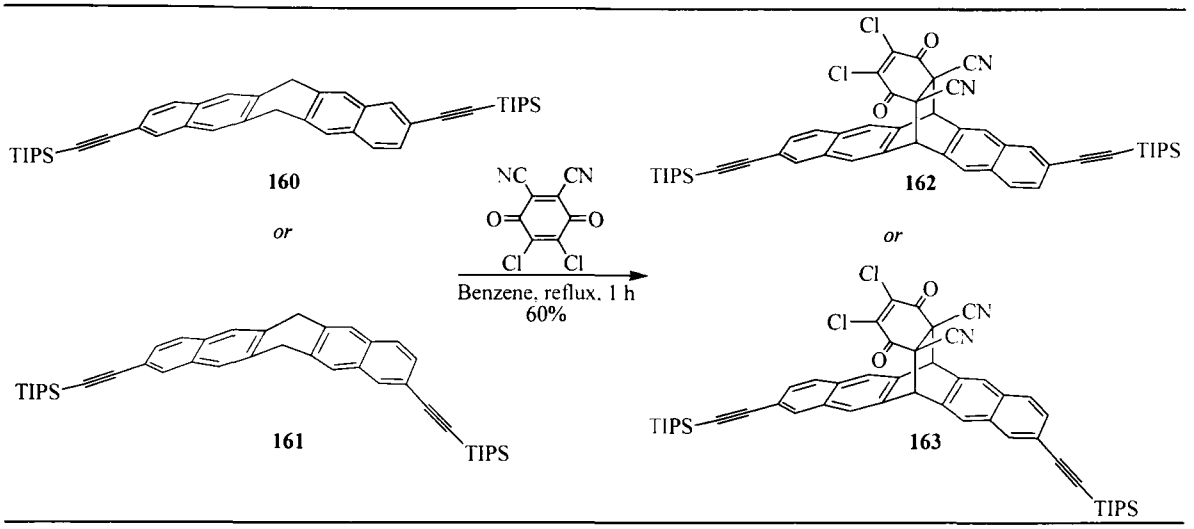
Scheme 41 - Formation of 157 *via* Zn dust

The reactions that were successful on unsubstituted pentacenequinone **10** were repeated on 2,9 and 2,10 disubstituted pentacenequinones, **135** and **136**. Treatment of either isomer with $LiAlH_4$ and $AlCl_3$ in refluxing THF easily afforded **160** and **161**, both in 95% yield (Scheme 42).



Scheme 42 - Reduction of 2,9 and 2,10 disubstituted pentacenequinones

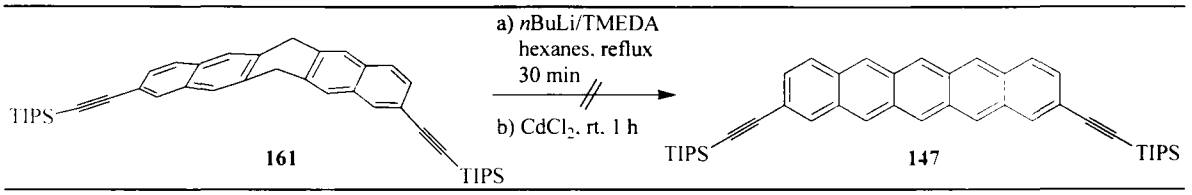
Each dihydro isomer, **160** and **161**, were treated with DDQ (Scheme 43). The results were analogous to when unsubstituted 6,13-dihydropentacene (**157**) was treated with DDQ. The disubstituted pentacenes were successfully produced and trapped *in situ* to form the DDQ adducts **162** and **163**, in both 60% yield. These compounds could be used as an air stable, soluble pentacene precursor, similar to Müllen's approach (Scheme 3, Section 1.3).



Scheme 43 - 2,9 and 2,10 Disubstituted pentacene-DDQ adducts (162 and 163)

Finally, the last reaction that was attempted to generate the disubstituted pentacenes was found to be successful during the model studies on 6,13-dihydropentacene (**157**). Aromatization of 2,10 disubstituted 6,13-dihydropentacene **161** was attempted several times using *n*BuLi/TMEDA followed by $CdCl_2$ to afford 2,10 disubstituted pentacene **147**. The conditions, such as time, temperature and equivalents of *n*BuLi were altered, but unfortunately only starting material was obtained. Upon the addition of *n*BuLi, the solution instantly turned dark red, and then dark green/purple. The dark red colour is normally indicative of the mono-anion, and once heated the di-anion is produced, giving a purple solution (with 6,13-dihyroanthracene).[56] After an hour of stirring at reflux in hexanes and TMEDA, the dark green/purple solution faded to a faint pink colour. Addition of $CdCl_2$ never afforded pentacene **147**, and only starting material was recovered. We thought that the tri*iso*proylsilyl groups were causing the interference as this reaction was successful with the unsubstituted 6,13-dihydropentacene (**157**). It has been reported that α-silyl carbanions are generated when treated with *n*BuLi at room temperature.[58] To account for this, the number of equivalents of *n*BuLi was increased. Once again, only starting material was recovered. Although these reagents were not successful in producing disubstituted pentacene **147**, they were successful in a new synthesis of pentacene (**3**). Investigations into the generation of 2,9 and 2,10 disubstituted pentacenes **164** and **147** *via* 6,13-pentacenequinones **117** and **118** using an alternate route are currently underway.

[58] Van der Leij, M.; Porskamp, P.A.T.W.; Lammerink, B.H.M.; Zwanenburg, B. *Tet. Lett.* **1978**, *9*, 811.



161 147

Scheme 44 - Attempted formation of 2,10-disubstituted pentacene 147

3 Summary

The goal for this project was to develop a shorter and more efficient route to 2,9 and 2,10 disubstituted pentacenes (**164** and **147**). The double Diels-Alder reaction between a substituted *o*-quinodimethane and 1,4-benzoquinone was the key step in this synthetic route. First, we attempted the synthesis of sultine **87**, which upon heating liberates SO_2 and generates the diene. We found that silyloxy substituted sultine **87** was very unstable and could not be used in the double Diels-Alder reaction (Figure 21). Next, we attempted the synthesis of a substituted *iso*benzofuran (**98**). Allylic oxidation of **94** to afford **97** was unsuccessful; instead, dehydration followed by oxidation of the furan to *bis*-aldehyde **101** occurred.

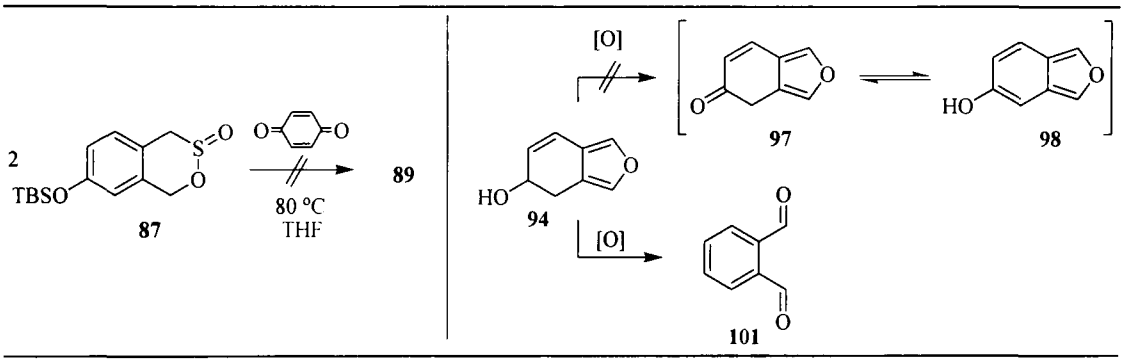
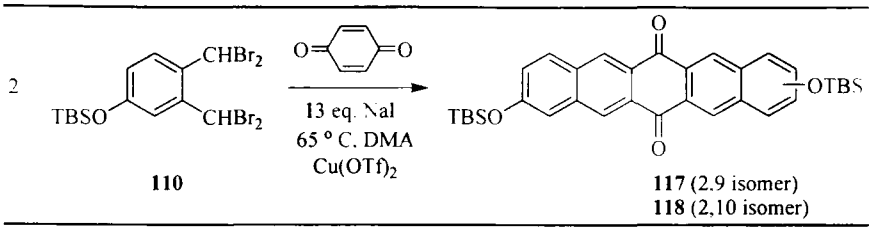


Figure 21 - Unsuccessful dienes

Literature examples have shown that tetrabromo-*o*-xylene **43** is a suitable precursor to *o*-quinodimethane **44**. Tetra-bromination of several possible 4-substituted *o*-xylenes was attempted. It was found that when the substituent was an iodide (**108**) only a mixture of mono-, di- and tri-brominated *o*-xylene was obtained. When the substituent was NH_2 or OH, aromatic substitution occurred. Tetra-bromination successfully occurred when the substituent was a Br (**111**), Cl (**112**) or OTBS (**110**). These three compounds were used in the tandem double Diels-Alder/aromatization reaction with 1,4-benzoquinone. Only **110** was successful, as the halide substituted tetrabromo-*o*-xylenes (**111** and **112**) resulted in decomposition. 2,9 and 2,10 Disubstituted pentacenequinones **117** and **118** were obtained in 50% yield in an isomeric ratio of 50:50 (Scheme 45).



Scheme 45 - Successful tandem double Diels-Alder/aromatization reaction

The tandem double Diels-Alder/aromatization reaction was anticipated to have some regioselectivity towards 2,9 disubstituted pentacenequinone **117,** by placing substituents on the dienophile and synthesizing a 4-substituted tribromo-*o*-xylene. It was found that halide substituted benzoquinones (**67** and **55**) were not stable to the reaction conditions. In addition, synthesis of a 2,5 disubstituted (acid, ester or aldehyde) benzoquinone was not achieved as each synthetic route resulted in either recovered starting material or aromatization to the phenol. The regioselective reaction was abandoned; therefore, we needed to find a way to separate regio-isomers **117** and **118**. Fractional recrystallization with CH_2Cl_2 successfully separated both isomers. Desilylation/triflation of **117/118** followed by a Sonogashira reaction successfully afforded **135** and **136** (Figure 22).

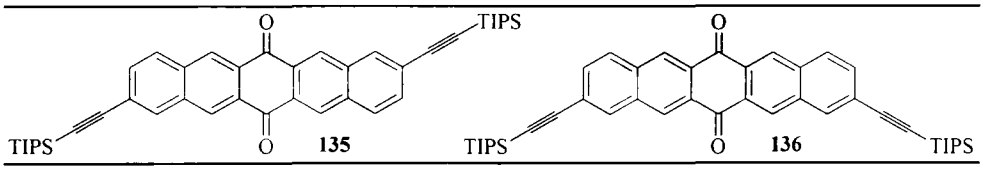
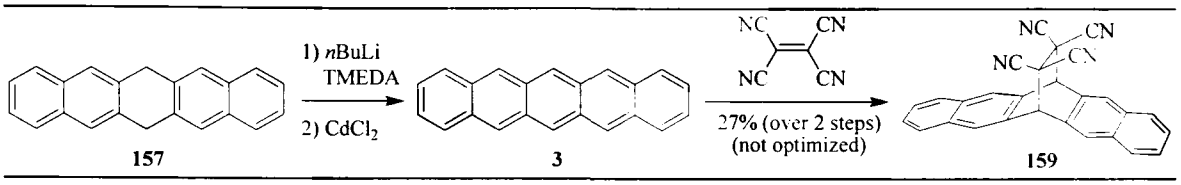


Figure 22 - 2,9 and 2,10 Disubstituted pentacenequinones 135 and 136

The final transformation, reduction of **135** or **136** to pentacene, proved to be a difficult task. Literature procedures were employed on pentacenequinones **135** or **136**. Unfortunately, they did not produce disubstituted pentacenes **164** or **147**. A new route was developed and first conducted on 6,13-pentacenequinone (**10**). Instead of reducing the carbonyls and aromatization in one-pot, we conducted these transformations stepwise. 6,13-Pentacenequinone (**10**) was reduced to 6,13-dihydropentacene (**157**) in an excellent 93% yield. Dehydrogenation of **157** to afford pentacene **3** was challenging. Several reagents were unsuccessful; however, treatment of **157** with *n*BuLi/TMEDA followed by $CdCl_2$ produced **3** (Scheme 46). Pentacene (**3**) was

subsequently 'trapped' with tetracyanoethylene to afford an air stable, soluble pentacene precursor **159**.



Scheme 46 - New route to pentacene (3)

Alternatively, **157** was aromatized to **3** and trapped *in situ* with DDQ (Figure 23). These same reaction conditions were conducted on the 2,9 and 2,10 disubstituted pentacenequinones **135** and **136**. Their dihydro equivalents **160** and **161** were each easily produced in 95% yield. Unfortunately, treatment of **160** or **161** with *n*BuLi/TMEDA followed by $CdCl_2$ was not successful. However, **160** and **161** were aromatized and trapped *in situ* with DDQ to afford **162** and **163**. We believe that these adducts have the capability for casting into thin-films. Subsequent heating should allow for a retro-Diels-Alder reaction to afford disubstituted pentacenes **164** and **147** and unsubstituted pentacene (**3**).

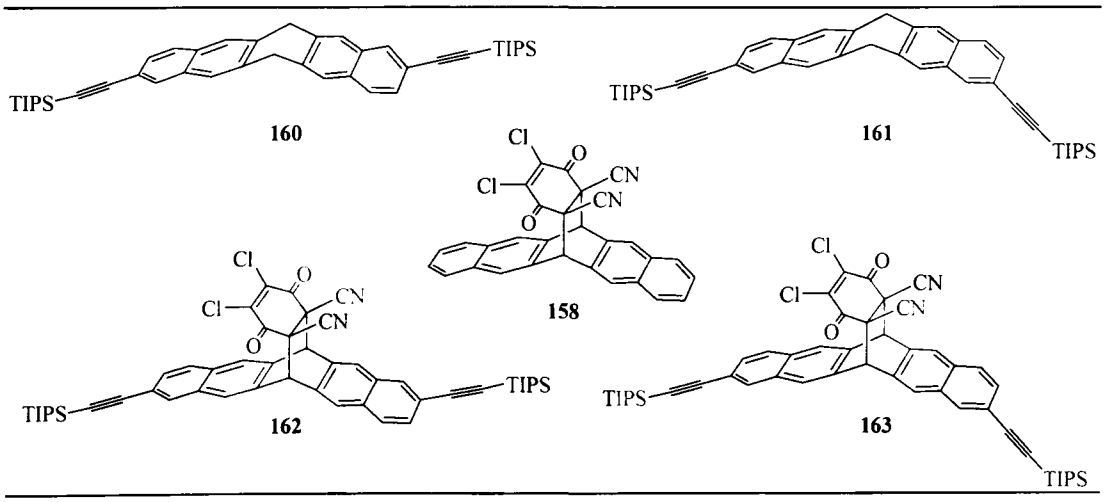


Figure 23 - Pentacene-DDQ adducts 158, 162 and 163

4 Future Work

There are some areas within this project that require additional investigation and other target molecules that could to be synthesized. First, the reaction conditions and reagents to prepare 2,9 disubstituted pentacene **164** from quinone **135** should be determined (Figure 24). It has been recently shown in the Fallis Lab, with the first generation route, that **164** undergoes a [4+4] cycloaddition in the presence of light to afford two isomers, dimers **165** and **166**, which can be separated by column chromatography. The pentacene dimers are soluble and air stable. Investigations into the reverse reaction are currently underway. We hope that the dimers will be suitable pentacene precursors once they have been examined on a semiconductor substrate. The next step would be to test the 2,9 and 2,10 disubstituted pentacenes **164** and **147** and dimers for their potential as organic field effect transistors.

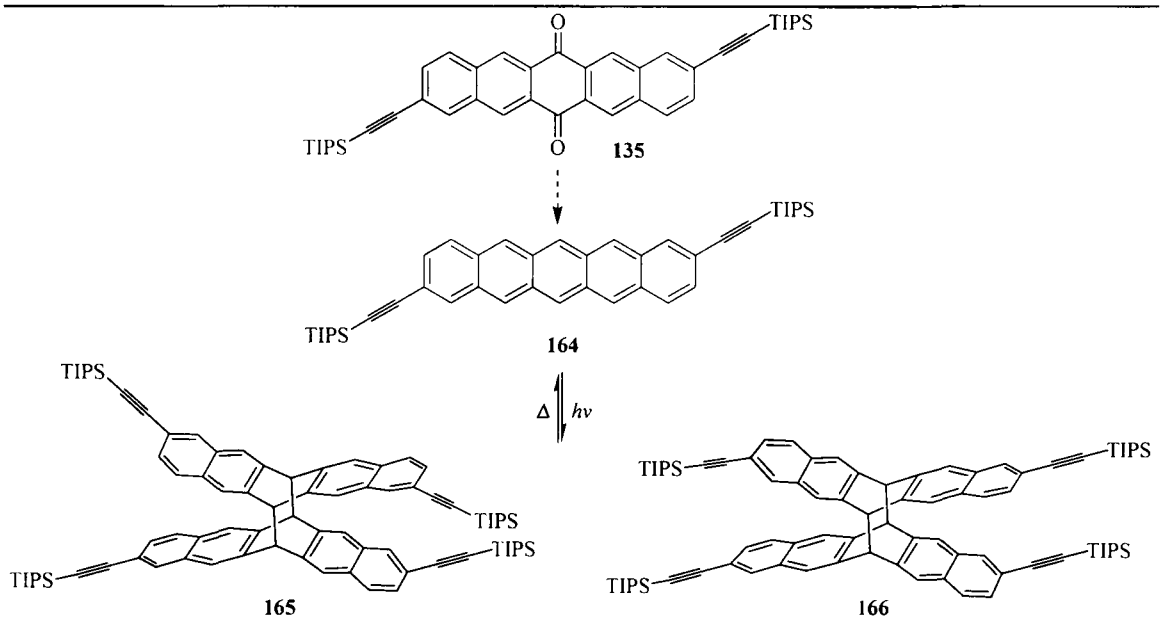


Figure 24 - Generation of dimers 165 and 166 from 2,9 disubstituted pentacene 164

The synthesis of disubstituted diazaheptacene **167** has been designed and is currently underway (Figure 25). The substituents would allow for solubility and the desired solid state packing. In addition, sensitivity to oxygen no longer exists by replacing the central carbon atoms with nitrogen. Also, placing different substituents, such on the acetylenes (at carbon 2 and 9) of

pentacene **32** would allow for an in-depth investigation into the effects the substituents have on electron and hole mobility, solid state packing, and solubility.

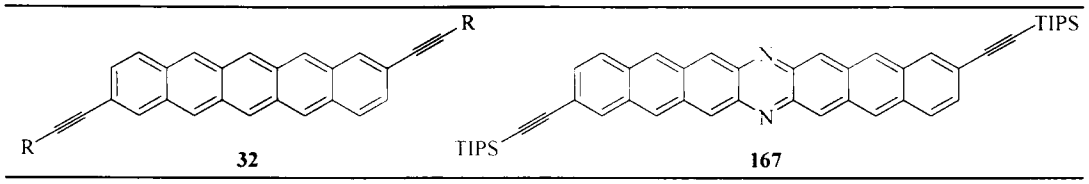


Figure 25 - Diazaheptacene 167 as an air stable alternative to pentacene and investigations into new R substituents on 32

With the 2,10 disubstituted pentacene in hand, the originally proposed *meta*-capped, planar cyclophane could be synthesized (Figure 26). This would continue the Fallis' Lab research on cyclophanes.

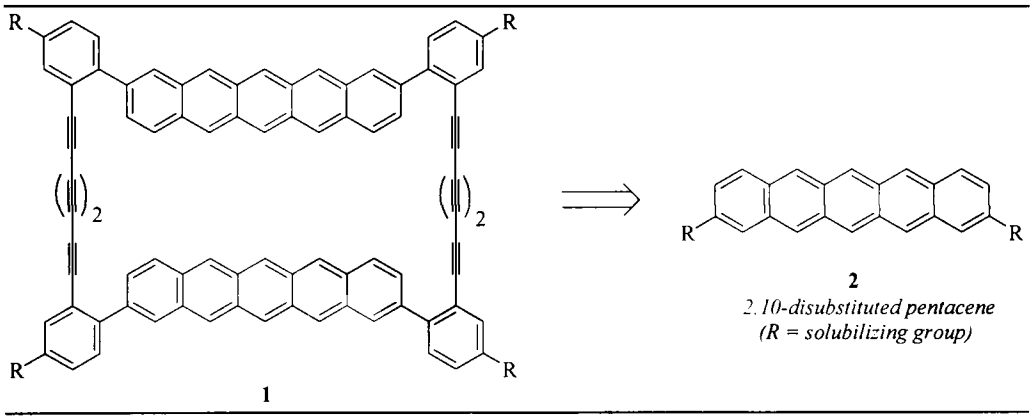


Figure 26 – *meta*-Capped planar cyclophane 1

5 Claims to Original Research

1. Designed and completed a shorter and more efficient route to 2,9 and 2,10 disubstituted pentacenes.
2. Successfully conducted the first tandem double Diels-Alder/aromatization reaction between a silyloxy substituted *o*-quinodimethane and 1,4-benzoquinone.
3. Generated new DDQ-pentacene adducts (**158**, **162** and **163)** *in situ* from their 6,13 dihydro equivalents. These compounds have the potential to be used as pentacene precursors for OFETs.
4. A new approach to unsubstituted pentacene (**3**) was developed using *n*BuLi/TMEDA followed by $CdCl_2$. This route has many benefits over the existing literature procedures.

6 Experimental Section

6.1 General Experimental

All non-aqueous reactions were performed under a positive pressure of dry nitrogen in flame-dried glassware using dry solvents. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone. Dichloromethane, toluene and triethylamine were distilled from calcium hydride. Standard inert atmosphere techniques were employed in handling air and moisture sensitive reagents. *n*BuLi and *t*BuLi was used as commercially available solutions in hexanes from Aldrich Chemical Company and titrated prior to use against diphenylacetic acid. Grignard reagents were titrated prior to use against diphenyl ditelluride. All TBAF solutions were in THF solvent. All starting materials were purchased from Aldrich Chemical Company and used without further purification unless otherwise stated.

Reactions were monitored by thin layer chromatography (TLC) using commercial aluminum-backed silica gel sheets coated with silica gel 60 F_{254} (E. Merck). TLC spots were visualized under ultraviolet light and developed by heating the plate after treatment with a 5% solution of ammonium molybdate in 10% aqueous sulphuric acid. Room temperature (rt) corresponds to 23 °C. Anhydrous magnesium sulfate ($MgSO_4$) was used to dry solutions in organic solvents, and in the experimental this is referred to "dried and filtered." Excess solvents were removed (concentrated) *in vacuo* at pressures obtained by a water or air aspirator connected to a Büchi rotary evaporator. Trace solvents were removed on a vacuum pump. "Degassed" refers to bubbling argon through the necessary solutions for a minimum of 15 minutes. Product purification by flash chromatography was performed with E. Merck Silica Gel 60 (230-400 mesh). Petroleum ether refers to a mixture of hydrocarbons with a boiling range of 30-60 °C.

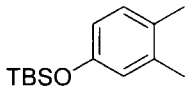
Microwave reactions were performed in a CEM Model ESP-1500 Plus oven equipped with a pressure monitoring device and an EST-300 Plus fiber optic temperature probe. All reactions were heated in a quartz tube.

Melting points were determined with a Thomas-Hoover Unit melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained as neat thin films or as a solution of the sample in CH_2Cl_2 in a sodium chloride solution cell. All IR spectra were recorded on a Bomem Michelson 100 Fourier transform infrared spectrometer (FTIR). ^1H NMR (200, 300 or 500 MHz) and ^{13}C NMR (75 or 125 MHz) spectra were run on a Gemini 200 spectrometer, Bruker

AMX300 spectrometer or Brucker AMX500 spectrometer. Chemical shifts are reported downfield from tetramethylsilane (δ scale) in ppm. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet), coupling constants (Hz), and integration. Low resolution mass spectroscopy (MS), using either electron impact (EI) or chemical ionization (CI), was performed on a V.G. Micromass 7070 HS mass spectrometer with an electron beam energy of 70 eV (for EI). High resolution mass spectroscopy (HRMS) was performed on a Kratos Concept-11A mass spectrometer with an electron beam energy of 70 eV. Electrospray mass spectra ES (MS) were determined on a Micromass Quattro LC with a pump rate of 20 μL/min. The purity of all title compounds was judged to be > 95% as determined by a combination of ^{1}H NMR and ^{13}C NMR analyses.

6.2 Detailed Experimental

tert-Butyl(3,4-dimethylphenoxy)dimethylsilane (84)

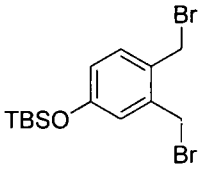


$C_{14}H_{24}OSi$
Mol. Wt.: 236.43

3,4-Dimethylphenol (25.02 g, 204.8 mmol) was added to THF (400 mL) and cooled to 0 °C. Imidazole (27.89 g, 409.6 mmol, 2 eq.) was added followed by TBSCl (37.08 g, 245.7 mmol, 1.2 eq.). It was stirred for 24 h, during which it was warmed to rt. The reaction was quenched with sat. NH_4Cl and any remaining precipitate was dissolved with distilled H_2O. The organics were extracted with ether, dried, filtered and concentrated. Filtration through a silica gel plug (10 cm high) using 10:1 PE:EA as eluent, provided the title compound as a clear oil (47.20 g, 98%).

^1H NMR (300 MHz, $CDCl_3$) δ 6.94 (d, J = 8.1 Hz, 1H), 6.62 (d, J = 2.4 Hz, 1H), 6.56 (dd, J = 8.1 and 2.5 Hz, 1H), 2.17 (d, J = 5.9 Hz, 1H), 0.96 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9 (C), 137.9 (C), 130.6 (CH), 129.5 (C), 121.7 (CH), 117.4 (CH), 26.1 (CH_3), 20.3 (C), 19.3 (CH_3), 18.6 (CH_3), -4.1 (CH_3); IR (neat): ν = 3022, 2957; MS (EI) *m/z* 236 (M^+) (40), 179 (100), 105 (9); HRMS calculated for $C_{14}H_{24}OSi$ (M^+) 236.15964, found 236.15986.

(3,4-Bis(bromomethyl)phenoxy)(*tert*-butyl)dimethylsilane (85)



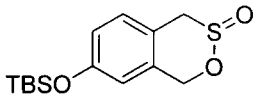
$C_{14}H_{22}Br_2OSi$
Mol. Wt.: 394.22

tert-Butyl(3,4-dimethylphenoxy)dimethylsilane (**84**) (0.519 g, 2.195 mmol) and NBS (0.977 g, 5.488 mmol, 2.5 eq.) were added to benzene and heated at a gentle reflux. A catalytic amount of AIBN was added and the solution gradually turned from colourless to a pale red. After 2 days, the reaction was cooled to rt and the organics were washed with sat. $NaHCO_3$ (3X), dried, filtered and concentrated. Purification by column chromatography (95:5; PE:EA) afforded the

title compound as a colourless oil (0.546 g, 59%). This compound was carried on to the next step as it could not be sufficiently purified.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 0.6 Hz, 1H), 6.77 (dd, J = 8.4 and 2.4 Hz, 1H), 4.66 (s, 2H), 4.61 (s, 2H), 1.00 (s, 9H), 0.23 (s, 6H).

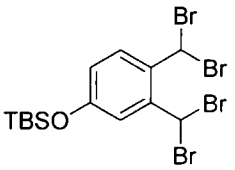
7-(*tert*-butyl-dimethyl-silanyloxy)-1,4-dihydro-2,3-benzoxathiin-3-oxide (87)



$C_{14}H_{22}O_3SSi$
Mol. Wt.: 298.47

A suspension of rongalite (0.180 g, 1.168 mmol) in DMF (5 mL) was added to **85** (0.149 g, 0.354 mmol) and TBAB (0.023 g, 0.071 mmol) at 0 °C. The resulting suspension was stirred for 3 h at 0 °C and then warmed to rt. Water was added to the reaction and then extracted with ether (3X). The organics were dried, filtered and concentrated to give the title compound as a yellow oil (0.035g, 33%). This compound was carried on to the next step as it could not be sufficiently purified or easily handled due to decomposition.

(3,4-Bis(dibromomethyl)phenoxy)(*tert*-butyl)dimethylsilane (110)



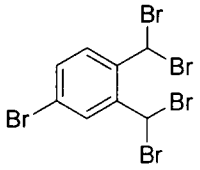
$C_{14}H_{20}Br_4OSi$
Mol. Wt.: 552.01

tert-Butyl(3,4-dimethylphenoxy)dimethylsilane (**84**) (9.747 g, 41.23 mmol) and NBS (31.56 g, 177.3 mmol, 4.3 eq.) were added to CCl_4 and heated at a gentle reflux. A catalytic amount of AIBN was added and the solution gradually turned from colourless to red. After 5 days the reaction was cooled to rt and the organics were washed with sat. $NaHCO_3$ (3X), dried, filtered and concentrated. The crude product was filtered through a silica gel plug (10 cm high) using 10:1 PE:EA as eluent, which provided the title compound as a white solid (14.71 g, 60%).

mp: 81-82°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (b, 1H), 7.11 (d, J = 8.4 Hz, 2H), 7.00 (s, 1H), 6.77 (dd, J = 8.4 and 2.7 Hz, 1H), 0.97 (s, 9H), 0.24 (s, 6H): ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5

(C), 139.8 (C), 130.9 (CH), 130.4 (C), 122.1 (CH), 121.3 (CH), 36.7 (CH), 36.7 (CH), 25.8 (CH_3), 18.6 (C), -3.9 (CH_3); IR (thin-film): ν = 3052, 2954; MS (EI) *m/z* 551 (M^+) (9), 473 (100), 392 (8), 335 (19), 254 (10), 139 (4), 73 (46): HRMS calculated for $C_{14}H_{20}{}^{79}Br_4OSi$ (M^+) 547.80169, found 547.79231.

4-Bromo-1,2-bis(dibromomethyl)benzene (111)

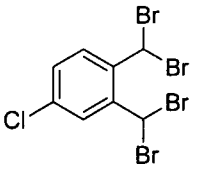


$C_8H_5Br_5$
Mol. Wt.: 500.65

4-Bromo-1,2-dimethylbenzene (0.556 g, 3.003 mmol) and NBS (2.673 g, 15.02 mmol, 5 eq.) were added to CCl_4 (100 mL) and heated at a gentle reflux. A catalytic amount of AIBN was added and the solution gradually turned from colourless to red. After 6 days, the reaction was cooled to rt and the organics were washed with sat. $NaHCO_3$, dried, filtered and concentrated. The crude product was recrystallized from acetone to afford the title compound as a white solid (1.182 g, 79%).

mp: 102-103 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.51 (m, 2H), 7.02 (d, J = 9.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0 (b), 136.6 (b), 133.5 (CH), 132.1 (b), 131.2 (b), 124.1 (C), 35.2 (CH), 34.8 (CH); IR (thin-film): ν = 3047, 3007; MS (EI) *m/z* 500.6 (M^+) (4), 420.7 (100), 339.8 (18), 262.9 (16), 182.0 (19); HRMS calculated for $C_8H_5{}^{79}Br_5$ (M^+) 495.63080, found 495.63292.

4-Chloro-1,2-bis(dibromomethyl)benzene (112)



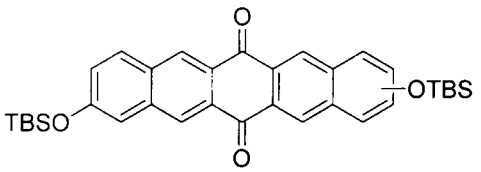
$C_8H_5Br_4Cl$
Mol. Wt.: 456.19

4-Chloro-1,2-dimethylbenzene (0.712 g, 5.07 mmol) and NBS (4.508 g, 25.32 mmol, 5 eq.) were added to CCl_4 (150 mL) and heated at gentle reflux. A catalytic amount of AIBN was

added the solution gradually turned form colourless to red. After 6 days, the reaction was cooled to rt and the organics were washed with $NaHCO_3$, dried, filtered and concentrated. The crude product was recrystallized from acetone to afford the title compound as a white solid (1.764 g, 76%).

mp: 105-7°C; ^{1}H NMR (500 MHz, *d*-DMSO, 25 °C) δ 7.85 (d, J = 8.5 Hz, 1H), 7.79 (s, 1H), 7.71 (s, 1H), 7.70 (s, 1H), 7.60 (dd, J = 8.5 and 2 Hz, 1H); ^{1}H NMR (500 MHz, *d*-DMSO, 35 °C) δ 7.86 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 1.5 Hz, 1H), 7.71 (s, 1H), 7.70 (s, 1H), 7.59 (dd, J = 8.5 and 2 Hz, 1H); ^{1}H NMR (500 MHz, *d*-DMSO, 45 °C) δ 7.86 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 2 Hz, 1H), 7.71 (s, 1H), 7.70 (s, 1H), 7.59 (dd, J = 8.5 and 2 Hz, 1H); ^{1}H NMR (500 MHz, *d*-DMSO, 55 °C) δ 7.86 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 2.5 Hz, 1H), 7.71 (s, 1H), 7.70 (s, 1H), 7.59 (dd, J = 8.5 and 2.5 Hz, 1H); ^{1}H NMR (500 MHz, *d*-DMSO, 65 °C) δ 7.86 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 2.5 Hz, 1H), 7.71 (s, 1H), 7.70 (s, 1H), 7.58 (dd, J = 9.0 and 2.5 Hz, 1H); ^{1}H NMR (500 MHz, *d*-DMSO, 75 °C) δ 7.86 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 2.5 Hz, 1H), 7.71 (s, 1H), 7.70 (s, 1H), 7.58 (dd, J = 8.5 and 2 Hz, 1H); ^{13}C NMR (125 MHz, *d*-DMSO, 75 °C) δ 138.1, 135.6, 134.6, 131.5, 130.6, 128.3, 36.3, 36.0; IR (thin-film): ν = 3047, 3009; MS (EI) *m/z* 455 (M^+) (2), 377 (100), 296 (23), 217 (40), 136 (26), 68 (9); HRMS calculated for $C_8H_5{}^{79}Br_4{}^{37}Cl$ (M^+) 453.67838, found 453.67146.

2,9 and 2,10-Bis-(*tert*-butyl-dimethyl-silanyloxy)-pentacene-6,13-dione (117 and 118)



$C_{34}H_{40}O_4Si_2$
Mol. Wt.: 568.85

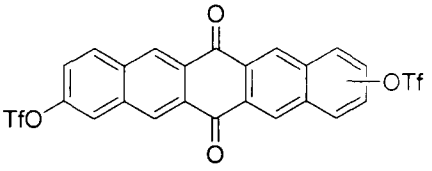
1,4-Benzoquinone (0.040 g, 0.368 mmol) was dissolved in dry DMA (20 mL) and **110** (0.407 g, 0.736 mmol, 2 eq.) was added, followed by $Cu(OTf)_2$ (0.013 g, 0.037 mmol, 0.1 eq.) and NaI (0.717 g, 4.786 mmol, 13 eq.), respectively. The reaction was stirred at 65 °C for 8 h (reaction time varied). When benzoquinone was no longer detected by TLC during the reaction, further equivalents were added (0.010 g, 0.093 mmol, 0.25 eq., 3X over duration of reaction) until complete consumption of **110** was observed. Reaction was cooled to rt and the solution turned from brown to yellow upon the addition of cold sat. $Na_2S_2O_3$. The yellow precipitate that formed

was filtered and washed with H_2O, then taken up with CH_2Cl_2 and concentrated. The impurities were dissolved in acetone and the product was filtered through a sintered glass funnel, which provided the title compound as a yellow solid (0.106 g, 50% (30%-50%)).

117 mp: >270 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.83 (s, 2H), 8.73 (s, 2H), 7.98 (d, J = 9 Hz, 2H), 7.41 (d, J = 2.1 Hz, 2H), 7.27 (m, 2H), 1.02, (s, 18H), 0.29 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.5 (C=O), 157.1 (C), 137.4 (C), 132.2 (CH), 131.4 (C), 131.2 (C), 130.0 (CH), 129.3 (C), 128.4 (CH), 126.2 (CH), 116.9 (CH), 26.0 (CH_3), 18.7 (C), -3.9 (CH_3); IR (CH_2Cl_2): ν = 3055, 3005, 1712; MS (EI) *m/z* 568 (M^+) (63), 545 (4.6), 511 (100), 455 (14), 227 (28); HRMS calculated for (M^+) 568.24651, found 568.24548.

118 mp: >270 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 2H), 8.73 (s, 2H), 7.99 (d, J = 9 Hz, 2H), 7.42 (d, J = 2.1 Hz, 2H), 7.27 (m, 2H), 1.06 (s, 18H), 0.33 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.8 (C=O), 183.1 (C=O), 157.1 (C), 137.3 (C), 132.2 (CH), 131.3 (C), 131.2 (C), 129.9 (CH), 129.4 (C), 128.5 (CH), 126.3 (CH), 117.0 (CH), 26.1 (CH_3), 18.8 (C), -3.8 (CH_3); IR (thin-film): ν = 2955, 2857, 1672, 1619, 829; MS (EI) *m/z* 568 (M^+) (54), 511 (100), 227 (28), 143 (12); HRMS calculated for (M^+) 568.24651, found 568.24910.

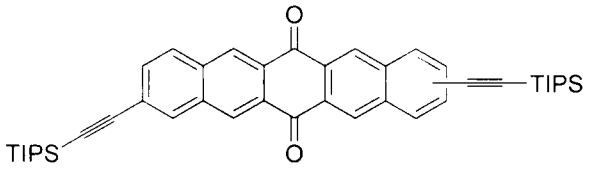
2,9 and 2,10-Bis(trifluoromethylsulfonyloxy)-6,13-pentacenequinone (133 and 134)



$C_{24}H_{10}F_6O_8S_2$
Mol. Wt.: 604.45

2,9 and 2,10-Bis-(*tert*-butyl-dimethyl-silanyloxy)-pentacene-6,13-dione (**117** and **118**) (0.177 g, 0.312 mmol) were dissolved in THF (100 mL) and cooled to 0 °C. A solution of TBAF in THF (1.0 M, 0.69 mL, 0.686 mmol, 2.2 eq.) was added and the reaction turned from yellow to deep blue. After 15 min., Tf_2NPh (0.334 g, 0.936 mmol, 3 eq.) dissolved in THF (5 mL) was cannulated into the reaction flask and then warmed to rt. The reaction turned from deep blue to red to yellow. After 24 h, the reaction was concentrated to 50 mL, diluted with ether, washed with 10% HCl, 5% $NaHCO_3$ and H_2O. It was concentrated to 20 mL and filtered through a sintered glass funnel to obtain the title compounds (0.150 g, 80%).

2,9 and 2,10-Bis-[(tri*iso*propylsilanyl)-ethynyl]-pentacene-6,13-dione (135 and 136)



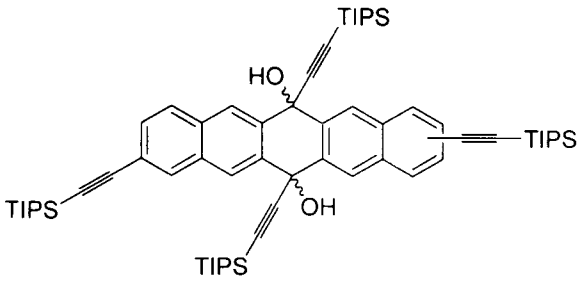
$C_{44}H_{52}O_2Si_2$
Mol. Wt.: 669.05

2,9 and 2,10-Bis(trifluoromethylsulfonyloxy)-6,13-pentacenequinone (**133** and **134**) (0.070 g, 0.116 mmol) were dissolved in THF (20 mL), followed by CuI (0.004 g, 0.023 mmol, 0.2 eq.), $Pd(PPh_3)Cl_2$ (0.008 g, 0.012 mmol, 0.1 eq.) and NEt_3 (2 mL). After degassing, TIPS-acetylene (65 µL, 0.290 mmol, 2.5 eq.) was added and heated at reflux for 12 h. The reaction was cooled to rt and filtered through a pad of silica (95:5, PE/EA) which afforded the title compounds (0.057 g, 66%). The isomers were separated by fractional recrystallization to give the 2,9 isomer as yellow needles and the 2,10 isomer as a pale yellow powder.

135 mp: >270 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (s, 4H), 8.21 (s, 2H), 8.01 (d, J = 8.3, 2H), 7.69 (d, J = 7.8 Hz, 2H), 1.16 (s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.9 (C=O), 135.2 (C), 134.8 (C), 133.9 (CH), 132.7 (CH), 131.5 (C), 131.2 (C), 130.3 (CH), 129.9 (CH), 129.8 (CH), 125.2 (C), 106.7 (C), 95.1 (C), 19.1 (CH_3), 11.7 (CH); IR (CH_2Cl_2): ν = 3058, 2929, 2150, 1713; MS (EI) *m/z* 668 (M^+) (2), 625 (28), 555 (8), 162 (22), 69 (100); HRMS calculated for (M^+) 668.35058, found 668.35000.

136 mp: >270 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (s, 4H), 8.20 (s, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.68 (dd, J = 8.4 and 1.5 Hz, 2H), 1.16 (s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.9 (C=O), 182.9 (C=O), 135.2 (C), 134.8 (C), 133.9 (CH), 132.7 (CH), 131.4 (C), 131.2 (C), 130.3 (CH), 129.8 (CH), 129.8 (CH), 125.1 (C), 106.6 (C), 95.1 (C), 19.1 (CH_3), 11.7 (CH); IR (CH_2Cl_2): ν = 3054, 2933, 2154, 1678; MS (EI) *m/z* 668 (M^+) (9), 625 (100), 583 (23), 555 (34), 419 (5), 162 (12), 70 (15); HRMS calculated for (M^+) 668.35058, found 668.34877.

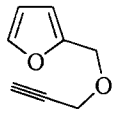
2,6,9,13 and 2,6,10,13-Tetra-(tri*iso*propylsilylethynyl)pentacene-6,13-diol (137,138,139,140)



$C_{66}H_{96}O_2Si_4$
Mol. Wt.: 1033.81

*iso*Propyl magnesium chloride (2.0 M in THF, 0.42 mL,0.833 mmol, 6 eq.) was added to tri*iso*propylsilyl acetylene (19 mL, 0.833 mmol, 6 eq.) in THF (2 mL) and stirred for 15 min. at 65 °C then cooled to rt. 2,9 and 2,10-Bis-[(tri*iso*propylsilanyl)-ethynyl]-pentacene-6,13-dione (**135** and **136**) (0.105 g, 0.139 mmol) dissolved in THF (3 mL) were cannulated into the solution and stirred at 65 °C for 1 h then cooled to rt. Water and CH_2Cl_2 were added and the organics were washed with water (3X), dried, filtered and concentrated. The crude products were filtered through a pad of silica with hexanes to elute the excess TIPS-acetylene followed by CH_2Cl_2 to afford the title compounds as a yellow foam (0.101 g, 71%). The four isomers were carried onto the next step as they could not be separated.

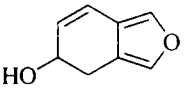
2-((Prop-2-ynyloxy)methyl)furan (91)



$C_8H_8O_2$
Mol. Wt.: 136.15

Furfuryl alcohol (25.05 g, 255.4 mmol) was added dropwise to a solution of NaH (60% in mineral oil, 11.24 g, 280.9 mmol, 1.1 eq.) in DMF (250 mL) at 0 °C. After 10 min. propargyl bromide (41.78 g, 280.9 mmol, 1.1 eq.) was added and then warmed to rt and stirred for 4.5 h. Water was added to the solution and then extracted with ether (3X), dried and concentrated. Filtration through a pad of silica (9:1: PE:EA) afforded the title compound as a yellow oil (26.78 g, 77%). Characterization of this compound can be found in: Martin-Matute, B.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Amer. Chem. Soc.* **2003**, *125*, 5757.

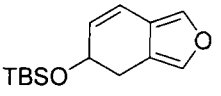
4,5-Dihydroisobenzofuran-5-ol (94)



$C_8H_8O_2$
Mol. Wt.: 136.15

Potassium *tert*-butoxide (48.56 g, 432.7 mmol, 2.2 eq.) was added to a solution of **91** (26.78 g, 196.7 mmol) and *t*-BuOH (400 mL) and heated at reflux overnight. The reaction was cooled to rt and H_2O was added. The solution was extracted with ether (3X), washed with brine, dried and concentrated. Purification by column chromatography (2:1: PE:EA) afforded the title compound as a yellow oil (35.35 g, 60%). Characterization of this compound can be found in: Hayakawa, K.; Yamaguchi, Y.; Kanematsu, K. *Tetrahedron Lett.* **1985**, *26*, 2689.

***tert*-Butyl(4,5-dihyroisobenzofuran-5-yloxy)dimethylsilane (102)**

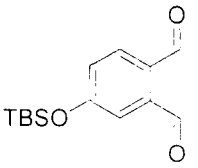


$C_{14}H_{22}O_2Si$
Mol. Wt.: 250.41

4,5-Dihydroisobenzofuran-5-ol (**94**) (5.080 g, 37.31 mmol) was dissolved in THF (100 mL) and cooled to 0 °C. Imidazole (5.080 g, 74.62 mmol, 2 eq.) was then added followed by TBSCl (6.741 g, 44.77 mmol, 1.2 eq.). The reaction was stirred overnight at rt. It was quenched with sat. NH_4Cl and any remaining precipitate was dissolved with distilled H_2O. The organics were extracted with ether, dried, filtered and concentrated. Filtration through a silica gel plug (10 cm high) using PE as eluent, provided the title compound as a clear oil (8.411 g, 90%).

^{1}H NMR (300 MHz, C6D6) δ 6.97 (s, 1H), 6.85 (s, 1H), 6.18 (dd, J = 9.9 and 2.0 Hz, 1H), 5.73 (dd, J = 9.8 and 2.5 Hz, 1H), 4.45 (m, 1H), 2.60 (m, 2H), 0.94 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (75 MHz, C6D6) δ 137.9 (CH), 137.2 (CH), 133.1 (CH), 121.3 (C), 118.7 (C), 118.4 (CH), 68.3 (CH), 29.0 (CH_2), 26.1 (CH_3), 18.3 (C), -4.5 (CH_3); IR (neat): ν = 3438, 3045, 2954, 1770; MS (EI) *m/z* 250 (M^+) (2), 193 (33), 119 (15), 91 (11), 75 (100); HRMS calculated for (M^+) 250.13891, found 250.13873.

4-(*tert*-Butyldimethylsiloxy)phthalaldehyde (104)

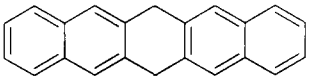


$C_{14}H_{20}O_3Si$
Mol. Wt.: 264.39

tert-Butyl(4,5-dihyroisobenzofuran-5-yloxy)dimethylsilane (**102**) (0.506 g, 2.022 mmol) and DDQ (1.115 g, 5.055 mmol, 2.5 eq.) were dissolved in CH_2Cl_2 (30 mL) and stirred at rt. After 4.5 h, the reaction was concentrated and filtered through a pad of silica (10:1; PE:EA) to afford the title compound as a yellow oil (0.160 g, 30%).

^1H NMR (300 MHz, $CDCl_3$) δ 10.56 (s, 1H), 10.30 (s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.12 (dd, J = 8.4 and 2.5 Hz, 1H), 0.96 (s, 9H), 0.24 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4 (CH), 191.5 (CH), 161.3 (C), 139.0 (C), 134.9 (CH), 130.3 (C), 124.8 (CH), 121.7 (CH), 25.8 (CH_3), 18.6 (C), -4.0 (CH_3); IR (neat): ν = 3367, 3066, 1844, 1775; MS (EI) *m/z* 264 (M^+) (31), 221 (10), 179 (100), 151 (7), 75 (10); HRMS calculated for (M^+) 264.11817, found 264.11785.

6,13-Dihydropentacene (157)



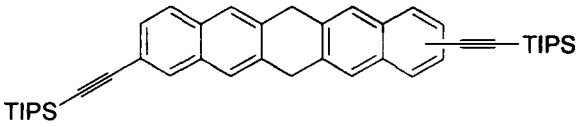
$C_{22}H_{16}$
Mol. Wt.: 280.36

6,13-Pentacenequinone (**10**) (0.046 g, 0.144 mmol) was dissolved THF (5 mL) and $AlCl_3$ (0.096 g, 0.719 mmol, 5 eq.) and LAH (0.055 g, 1.438 mmol, 10 eq.) were added at 0 °C. The reaction was heated at reflux overnight. It was cooled to rt and purified by column chromatography (95:5; PE:EA) to afford the title compound as a yellow solid. The product was recrystallized in PE to give a white solid (0.038 g, 93%).

mp: decomposed 137 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (t, 8H), 7.41 (dd, J = 6.2 and 3.2 Hz, 4H), 4.23 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2 (C), 132.8 (C), 127.6 (CH), 125.7 (CH), 125.5 (CH), 37.7 (CH_2); IR (thin-film): ν = 3051, 2921, 2800; MS (EI) *m/z* 280 (M^+)

(100), 278 (42), 196 (15), 150 (6), 70 (7); HRMS calculated for (M^+) 280.12520, found 280.12392.

2,9 & 2,10-Bis(2-(tri*iso*propylsily)ethynyl)-6,13-dihydropentacene (160 and 161)



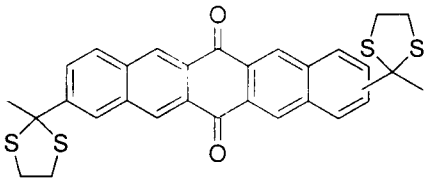
$C_{44}H_{56}Si_2$
Mol. Wt.: 641.09

2,9 or 2,10-Bis-[(tri*iso*propylsilanyl)-ethynyl]-pentacene-6,13-dione (**135** or **136**) (0.025 g, 0.038 mmol) was dissolved in THF (10 mL) and degassed. At 0 °C, $AlCl_3$ (0.051 g, 0.379 mmol, 10 eq.) and LAH (0.007 g, 0.189 mmol, 5 eq.) were added and the reaction was heated at reflux for 15 h. The reaction was cooled to rt and EA was added to quench the excess LAH. The salts were precipitated and filtered after dropwise addition of sat. NaCl. The organics were dried, filtered and concentrated. Recrystallization in PE afforded the title compound as a white solid (0.023 g, 95%).

160 mp: 73-75°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (2H), 7.71 (m, 6H), 7.46 (d, J = 1.5 Hz, 1H), 7.43 (d, J = 1.8 Hz, 1H), 4.19 (s, 4H), 1.14 (s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9 (C), 136.6 (C), 132.3 (C), 132.2 (C), 131.6 (CH), 128.9 (CH), 127.5 (CH), 125.5 (CH), 125.4 (CH), 120.7 (C), 108.0 (C), 91.0 (C), 37.7 (CH_2), 19.1 (CH_3), 11.8 (CH); IR (thin-film): ν = 2941, 2864, 2150, 1458; MS (EI) *m/z* 640 (M^+) (38), 597 (100), 555 (36), 162 (51); HRMS calculated for (M^+) 640.39205, found 640.39153.

161 mp: 73-5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.69 (m, 6H), 7.45 (d, J = 8.3 Hz, 2H), 4.19 (s, 4H), 1.15 (s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9 (C), 136.7 (C), 132.3 (C), 132.2 (C), 131.6 (CH), 128.8 (CH), 127.5 (CH), 125.5 (CH), 125.4 (CH), 120.7 (C), 108.0 (C), 91.0 (C), 37.8 (CH_2), 37.7 (CH_2), 19.1 (CH_3), 11.7 (CH); IR (thin-film): ν = 2942, 2864, 2152, 1462; MS (EI) *m/z* 640 (M^+) (42), 597 (100), 555 (22), 415 (6), 277 (8), 214 (25); HRMS calculated for (M^+) 640.39205, found 640.38938.

2,9 & 2,10-Bis(2-methyl-1,3-dithiolan-2-yl)pentacene-3,16-dione (155 and 156)

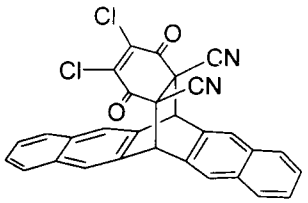


$C_{30}H_{24}O_2S_4$
Mol. Wt.: 544.77

2.9 and 2,10-Bis-[(tri*iso*propylsilanyl)-ethynyl]-pentacene-6,13-dione (**135** and **136**) (0.028 g, 0.041 mmol), BF_3-OEt_2 (0.10 mL, 0.825 mmol, 20 eq.) and 1,2-ethanedithiol (0.04 mL, 0.413 mmol, 10 eq.) were dissolved in CH_2Cl_2 and heated at reflux for 6 days. The solution was cooled to rt, concentrated and filtered through a pad of silica (4:1: PE:EA) to afford the title compound as a yellow solid (0.017 g, 60%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 2H), 8.86 (s, 2H), 8.41 (s, 2H), 8.05 (s, 4H), 3.47 (m, 8H), 2.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.35 (C), 183.31 (C), 183.25 (C), 147.8 (C), 135.1 (C), 134.7 (C), 131.4 (C), 131.3 (C), 131.22 (C), 131.19 (C), 130.41 (CH), 130.37 (CH), 129.4 (CH), 126.9 (CH), 68.6 (C), 41.1 (CH_2), 33.3 (CH_3); IR (CH_2Cl_2): ν = 2963, 2925, 2853, 1678 ; MS (EI) *m/z* 544 (M^+) (68), 529 (100), 516 (77), 501 (15), 409 (19), 218 (14), 161 (33); HRMS calculated for (M^+) 544.06591, found 544.06625.

6,13-(4,5-Dichloro-1,2-dicyano-3,6-dioxocyclohex-4-ene)pentacene (158)



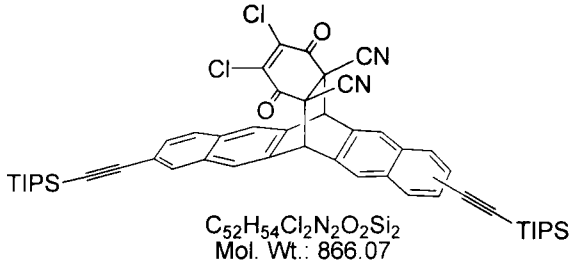
$C_{30}H_{14}Cl_2N_2O_2$
Mol. Wt.: 505.35

In separate flasks, **157** (0.046 g, 0.165 mmol) and DDQ (0.112 g, 0.494 mmol, 3 eq.) were dissolved in benzene (5 mL each) and degassed. The solution of DDQ was cannulated into the solution of **157** and heated at reflux. After 1 h, the solution was cooled to rt and concentrated.

Purification by column chromatography (9:1; PE:EA) afforded the title compound as an orange/yellow solid (0.056 g, 67%).

mp: decomposed 185 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.91 (dd, J = 6.3 and 3.0 Hz, 2H), 7.78 (dd, J = 6.6 and 3.6 Hz, 2H), 7.74 (s, 2H), 7.58 (m, 4H), 5.22 (s, 2H); ^{13}C NMR (75 MHz, acetone-d_6) δ 180.6 (C), 142.8 (C), 134.0 (C), 133.6 (C), 133.5 (C), 132.4 (C), 128.6 (CH), 128.5 (CH), 128.0 (CH), 127.5 (CH), 126.6 (CH), 126.0 (CH), 115.9 (CN), 58.4 (C), 55.7 (CH); IR (thin-film): ν = 3062, 2959, 1707; MS (EI) *m/z* 278 (M^+-227) (84), 228 (100), 170 (8), 91 (25). HRMS calculated for (M^+-227) 278.10995, found 278.11016. X-ray structural analyses: Crystal size 0.25 x 0.15 x 0.10 mm, triclinic, space group P-1, scan range1.80<2θ<26.43°, a = 10.431(2), b = 12.194(3), c = 12.972(3) Å, V = 1457.3(5) Å^3, Z = 2, r_{calcd} = 1.337 mg/m^3, u = 0.263 mm^{-1}, 5910 unique reflections at 213 K, R = 0.0713, R_w = 0.1356.

2,9 & 2,10-Bis(2-(tri*iso*propylsily)ethynyl)-6,13-(4,5-dichloro-1,2-dicyano-3,6-dioxocyclohex-4-ene)pentacene (162 and 163)



$C_{52}H_{54}Cl_2N_2O_2Si_2$
Mol. Wt.: 866.07

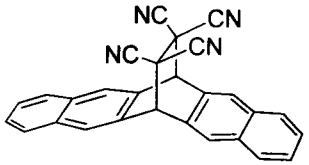
In separate flasks, **160** or **161** (0.023 g, 0.036 mmol) and DDQ (0.0172 g, 0.076 mmol. 2.1 eq.) were dissolved in benzene (7.5 mL each) and degassed. The solution of DDQ was cannulated into the solution of **160** or **161** and heated at reflux. After 1 h, the solution was cooled to rt and concentrated. Purification by column chromatography (9:1; PE:EA) afforded the title compound as an yellow solid (0.0185 g, 60%).

162 mp: turned brown 195 °C, turned black 204 °C, melted 216 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.03 (s, 2H), 7.90 (s, 1H), 7.82 (d, J = 8.5 Hz, 2H), 7.71 (s, 2H), 7.68 (d, J = 8.5 Hz, 1H), 7.59 (dd, J = 1.5 and 8.5 Hz, 1H), 7.56 (dd, J = 1.5 and 8.5 Hz, 1H), 5.20 (s, 2H), 1.14 (s, 21H), 1.13 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1 (C), 179.0 (C), 144.4 (C), 144.3 (C), 132.8 (C), 132.6 (C), 132.5 (C), 132.5 (C), 132.5 (C), 132.2 (C), 132.0 (CH), 131.6 (CH), 131.5 (C), 131.1 (CH), 130.5 (CH), 128.2 (CH), 127.9 (CH), 125.8 (CH), 125.7 (CH), 125.6 (CH), 125.5 (CH), 123.2 (C), 122.7 (C), 114.2 (CN), 114.2 (CN), 106.6 (C), 106.2 (C), 93.4 (C),

92.7 (C), 57.1 (C), 55.5 (CH), 18.7 (CH_3), 18.7 (CH_3), 11.3 (CH), 11.3 (CH); IR (CH_2Cl_2): ν = 2992, 2944, 2153, 1709. MS could not be obtained for this compound.

163 mp: turned brown 197 °C, turned black 205 °C, melted 218 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (m, 3H), 7.90 (s, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.70 (m, 3H), 7.57 (m, 2H), 5.19 (s, 2H), 1.13 (m, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.5 (C), 179.5 (C), 144.9 (C), 144.7 (C), 133.2 (C), 133.0 (C), 132.8 (C), 132.8 (C), 132.6 (C), 132.5 (CH), 132.0 (C), 131.9 (CH), 131.5 (CH), 130.9 (CH), 128.7 (C), 128.6 (CH), 128.3 (CH), 126.2 (CH), 126.1 (CH), 126.0 (CH), 125.9 (CH), 123.6 (C), 123.1 (C), 114.6 (CN), 114.6 (CN), 107.0 (C), 106.5 (C), 93.8 (C), 93.1 (C), 57.5 (C), 57.5 (C), 56.2 (CH), 56.1 (CH), 19.1 (CH_3), 19.1 (CH_3), 11.7 (CH), 11.7 (CH); IR (CH_2Cl_2): ν = 2993, 2944, 2157, 1707. MS could not be obtained for this compound.

6,13-(1,1,2,2-Tetracarbonitrile-ethane)pentacene (159)



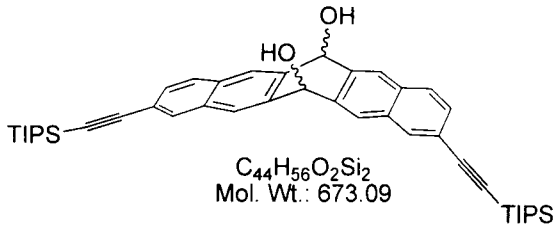
$C_{28}H_{14}N_4$
Mol. Wt.: 406.44

6,13-Dihydropentacene (**157**) (0.100 g, 0.358 mmol), TMEDA (5 mL) and hexanes (10 mL) were degassed in a schlenk tube. Upon the addition of *n*BuLi (2.23 M, 0.40 mL, 2.5 eq.) the solution turned dark green. The reaction was heated at reflux for 1.5 h and then cooled to RT. Cadmium chloride (0.130 g, 0.715 mmol, 2 eq.) was added and stirred at rt for 1 h. The purple precipitate that formed was filtered and washed with H_2O (2 x 10 mL), CH_2Cl_2 (2 x 10 mL), MeOH (2 x 10 mL) and ether (2 x 10 mL). The washing sequence was repeated. The purple residue, pentacene, was dried under vacuum. (All solvents were degassed, the reactions were carried out in an Ar atmosphere, TMEDA and hexanes were distilled over LAH and $CdCl_2$ was dried under vacuum at 100 °C).

Tetracyanoethylene (0.092 g, 0.716 mmol, 2 eq.) was dissolved in benzene (15 mL), degassed and cannulated into the schlenk flask containing pentacene. The solution turned yellow/brown immediately and was then heated at reflux for 3 h to react the remaining insoluble material. The solvent was evaporated and the residue was purified by column chromatography (4:1; PE:EA) and then recrystallized in CH_2Cl_2 to afford the title compound as a white solid (0.039 g, 27%).

mp: turned brown 170 °C, >270 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 8.33 (s, 4H), 8.05 (m, 4H), 7.63 (m, 4H), 6.04 (s, 2H); ^{13}C NMR (125 MHz, acetone-d_6) δ 133.2 (C), 131.4 (C), 128.2 (CH), 127.5 (CH), 126.4 (CH), 111.7 (CN), 52.0 (CH), 46.8 (C); IR (CH_2Cl_2): ν = 3066, 2997, 2933, 1458; MS (EI) *m/z* retro Diels-Alder 278.1 (M^+ - 128.0) (100).

2,10-Bis(2-(tri*iso*propylsilyl)ethynyl)-6,13-dihydropentacene-6,13-diol (143 and 144)



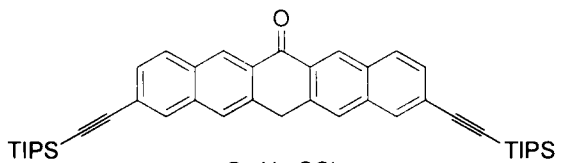
$C_{44}H_{56}O_2Si_2$
Mol. Wt.: 673.09

Lithium aluminum hydride (0.005 g, 0.143 mmol, 4 eq.) was added to a solution of **135** or **136** (0.0234 g, 0.036 mmol) in THF (10 mL). The reaction was gently refluxed for 15 min. then cooled to rt. Ethyl acetate (5 mL) and ether (15 mL) were added followed by dropwise addition of sat. NaCl until the salts precipitated. The solution was filtered and concentrated to give the title compound as a mixture of *trans* and *cis*-isomers (*trans*:*cis*; 63:37) (93%, 0.022 g). Separation of the isomers by column chromatography (5:1; PE:EA then 10:1; PE:EA) afforded each as a white solid.

143 (cis): ^{1}H NMR (300 MHz, C6D6) δ 8.19 (s, 2H), 7.81 (s, 2H), 7.72 (m, 4H), 7.60 (d, J = 8.4 Hz, 2H), 5.89 (s, 1H), 5.83 (s, 1H), 1.38 (s, 42H); ^{13}C NMR (75 MHz, acetone-d_6) δ 140.3 (C), 139.9 (C), 132.8 (C), 132.8 (C), 132.0 (CH), 129.0 (CH), 128.5 (CH), 124.9 (CH), 124.8 (CH), 121.0 (C), 108.2 (C), 90.6 (C), 70.4 (CH), 70.3 (CH), 18.6 (CH_3), 11.6 (CH); IR (thin-film): ν = 3332, 2944, 2864, 2153; MS (EI) *m/z* 654 (M^+ - H_2O) (11), 638 (23), 541 (19), 57 (100).

144 (trans): ^{1}H NMR (300 MHz, C6D6) δ 8.09 (s, 2H), 7.75 (s, 2H), 7.69 (s, 2H), 7.60 (dd, J = 8.4 and 1.5 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 5.26 (dd, J = 15.9 and 6.3 Hz, 2H), 1.26 (s, 42H); ^{13}C NMR (75 MHz, acetone-d_6) δ 139.7 (C), 139.5 (C), 132.5 (C), 132.5 (C), 132.0 (CH), 128.7 (CH), 128.5 (CH), 122.1 (CH), 120.7 (C), 108.3 (C), 90.4 (C), 68.5 (CH), 68.4 (CH), 18.6 (CH_3), 11.6 (CH); IR (thin-film): ν = 3332, 2944, 2864, 2153; MS (EI) *m/z* 654 (M^+ - H_2O) (8), 625 (36), 555 (26), 69 (100).

2,10-Bis(2-(tri*iso*propylsilyl)ethynyl)pentacen-6(13*H*)-one (145)

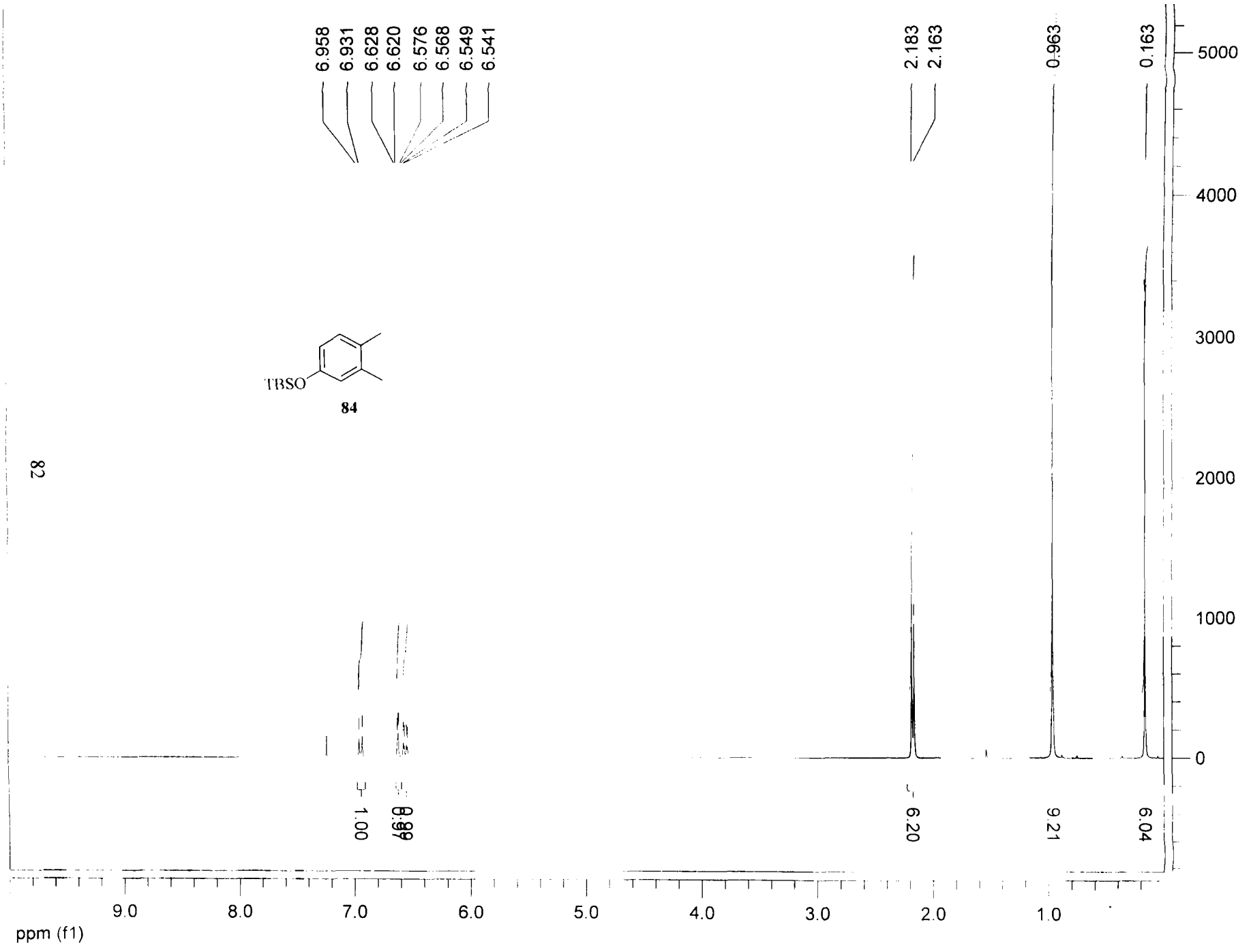


$C_{44}H_{54}OSi_2$
Mol. Wt.: 655.07

6N Hydrochloric acid (1 mL) was added to a solution of **143** and **144** (0.038 g, 0.057 mmol) and THF (7 mL). The solution was heated at reflux for 3 h, and then cooled to rt. Ether was added and the organics were washed with H_2O (3X), dried and concentrated. Purification by column chromatography (97:3: PE:EA) afforded the title compound as a pale orange solid (0.020 g, 54%).

mp: 228-230 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (s, 2H), 8.21 (s, 2H), 7.90 (s, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.63 (dd, J = 8.4 and 1.2 Hz, 2H), 4.67 (s, 2H), 1.20 (s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.3 (C), 136.7 (C), 135.2 (C), 134.0 (CH), 132.0 (CH), 131.8 (C), 131.2 (C), 129.6 (CH), 127.5 (CH), 127.2 (CH), 121.7 (C), 107.2 (C), 92.5 (C), 33.0 (CH_2), 19.1 (CH_3), 11.8 (CH); IR (thin-film): ν = 2937, 2870, 2154, 1669; MS (EI) *m/z* 654 (M^+) (22), 611 (100), 541 (33), 221 (43). HRMS calculated for $C_{44}H_{54}OSi_2$ 654.37132, found 654.36999.

Appendix I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6.620
6.576
6.568
6.549
6.541
2.183
2.163
0.963
0.163
TBSO
84
82
1.00
0.89
0.89
6.20
9.21
6.04
5000
4000
3000
2000
1000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

83
TBSO
84
153.875
137.943
130.567
129.481
121.704
117.410
26.118
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19.284
-4.029
ppm (f1)
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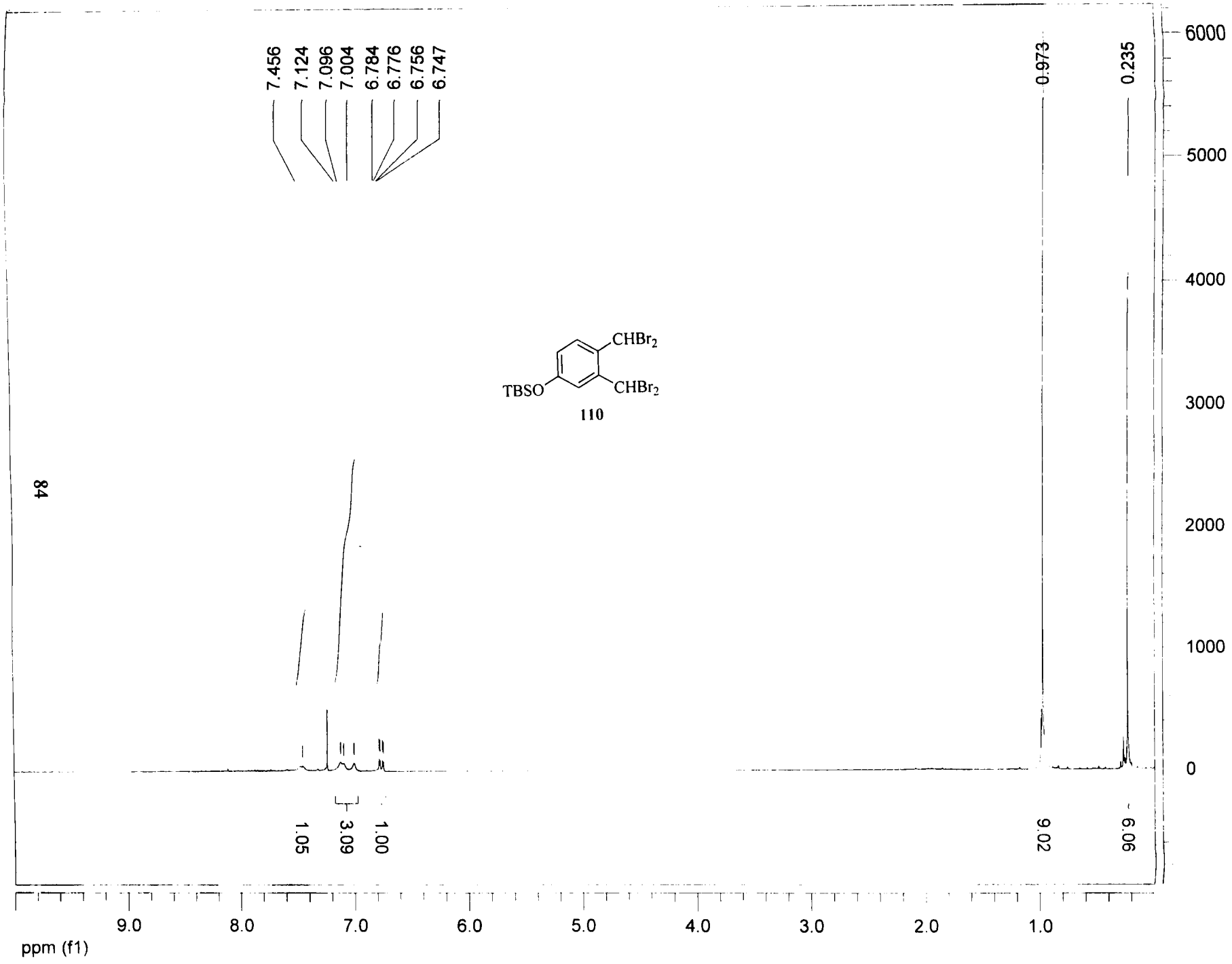
100
50
0
0
500
1000
1500
2000
2500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7.004
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6.776
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6.747
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0.235
CHBr2
TBSO
CHBr2
110
84
1.05
3.09
1.00
9.02
6.06
6000
5000
4000
3000
2000
1000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

157.504
139.791
130.936
130.430
122.078
121.302
36.741
36.714
26.000
18.602
-3.949
TBSO
CHBr2
CHBr2
110
ppm (f1)
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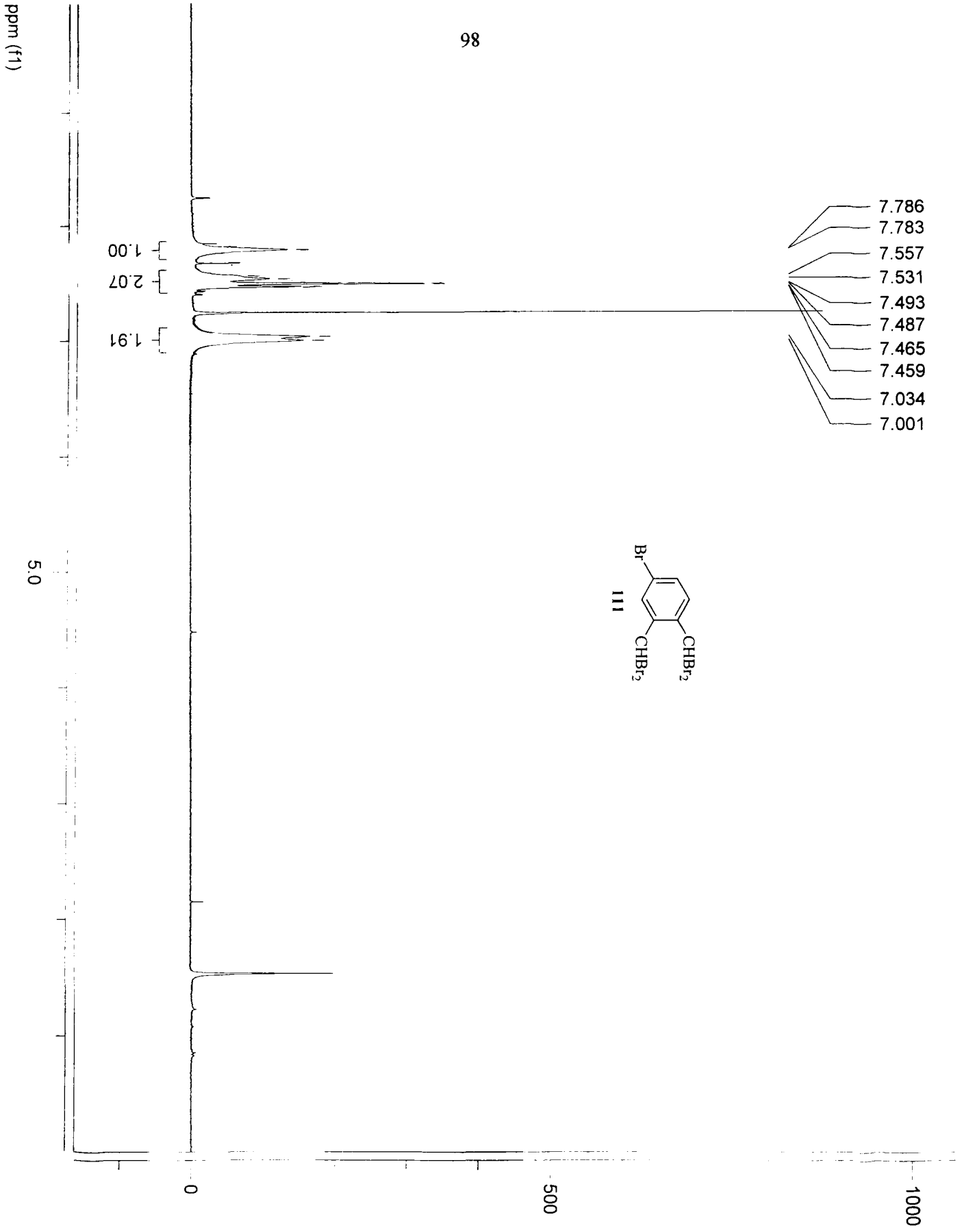
100
50
0
0
1000
2000
3000
4000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7.487
7.465
7.459
7.034
7.001
Br
CHBr2
CHBr2

111

ppm (f1)
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100
50
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1000
2000
3000
4000
5000
6000
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8000
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CHBr2
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136.761
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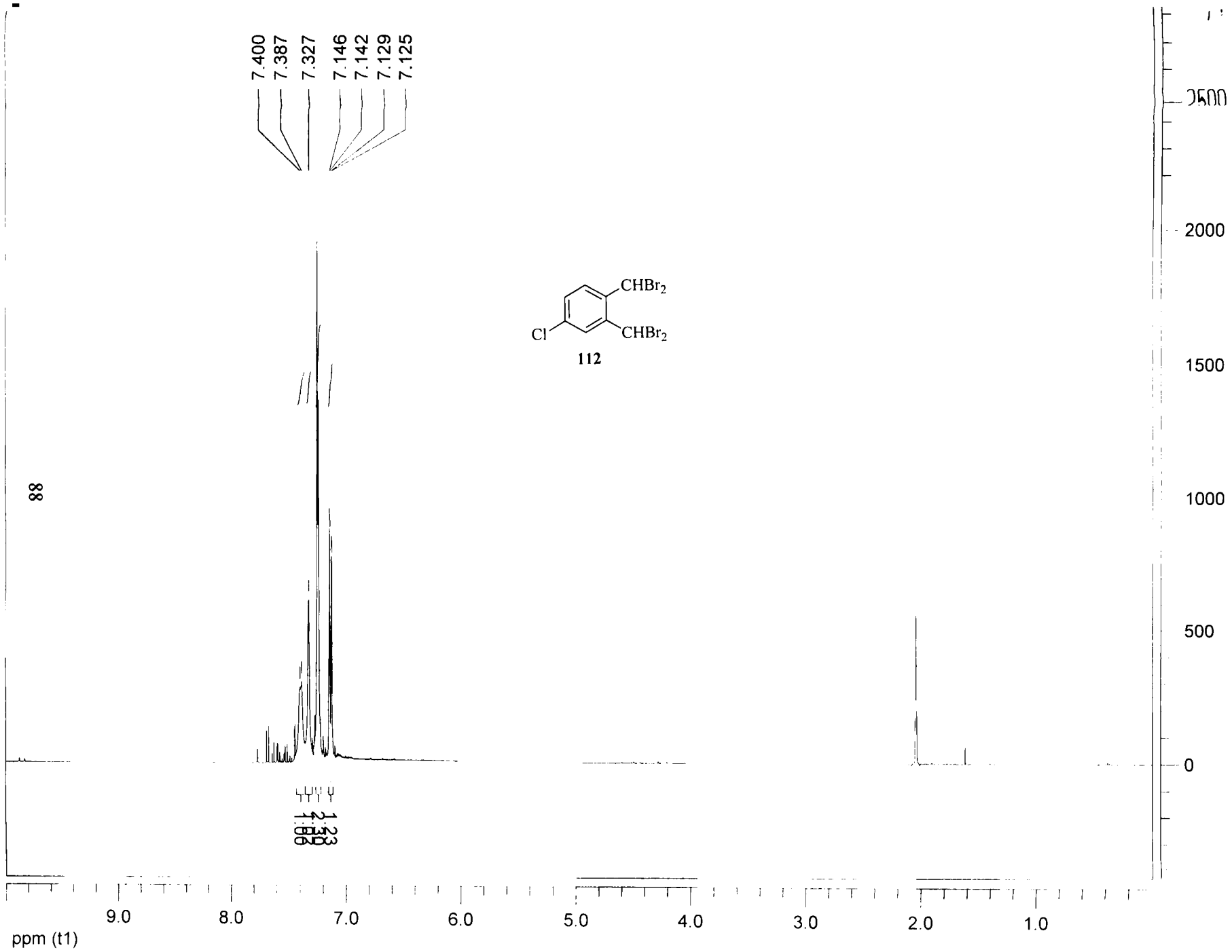
132.338
131.227
124.125
35.238
34.801


7.400
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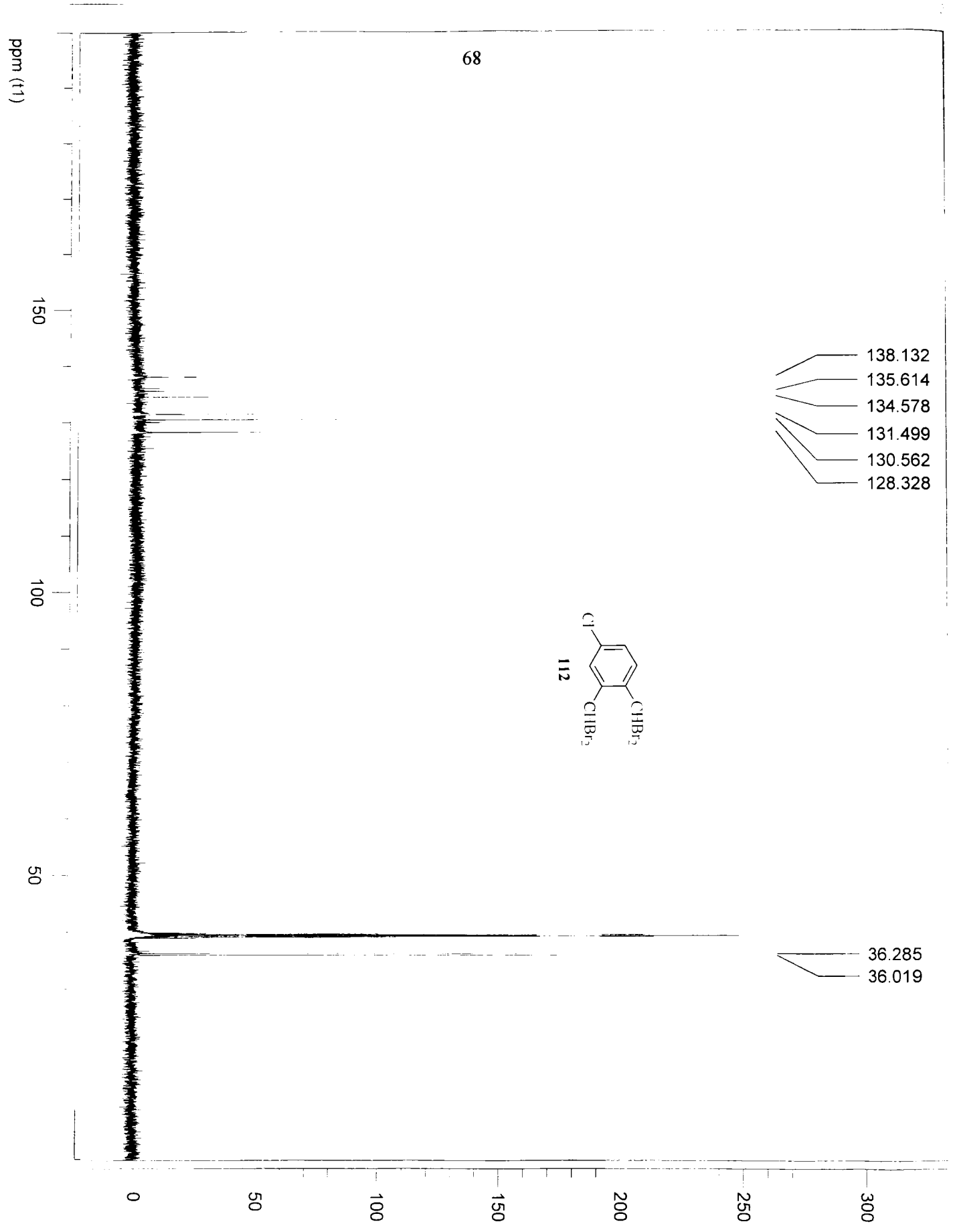
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


ppm (t1)
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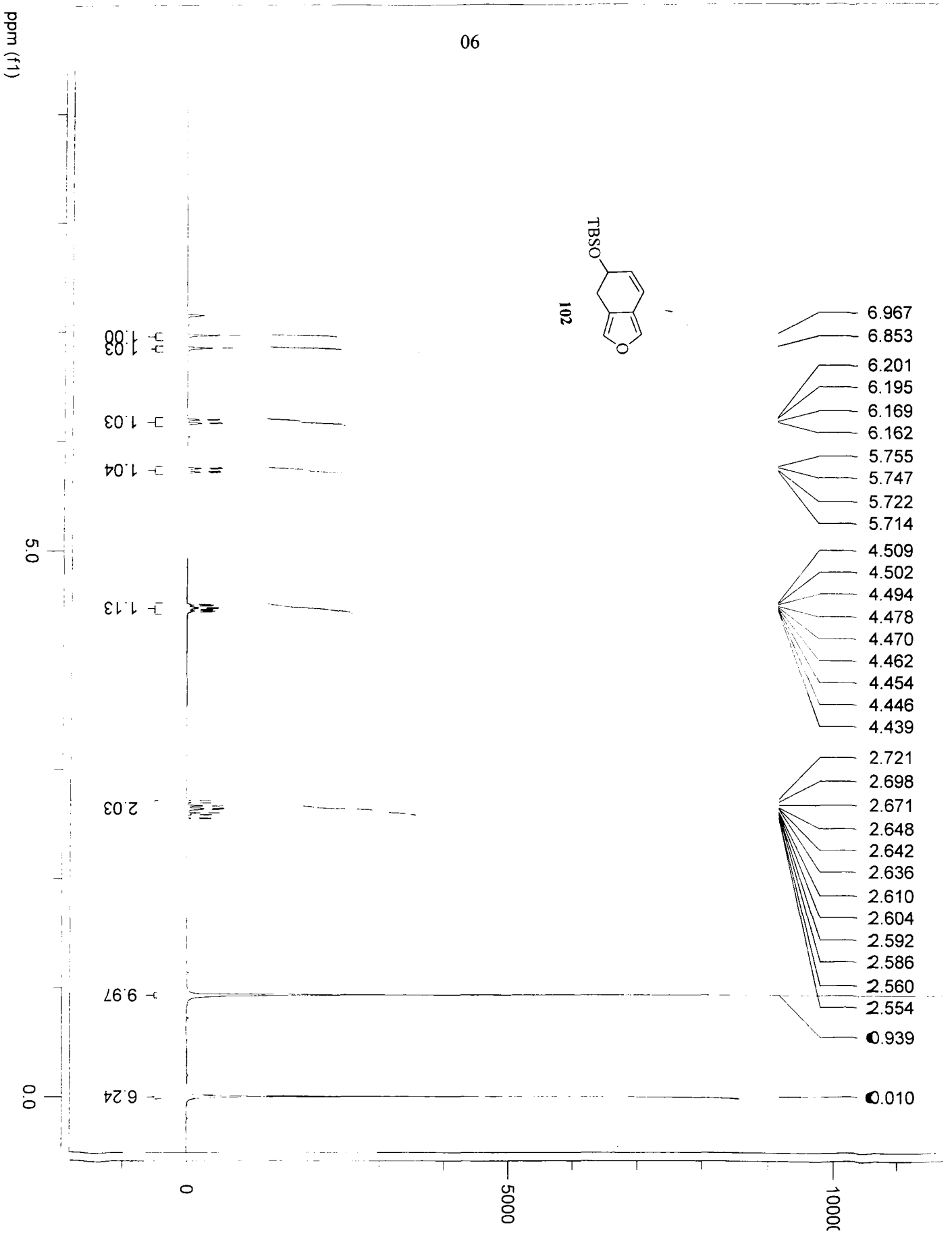
36.019
Cl
CHBr2
CHBr2

112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6.201
6.195
6.169
6.162
5.755
5.747
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2.698
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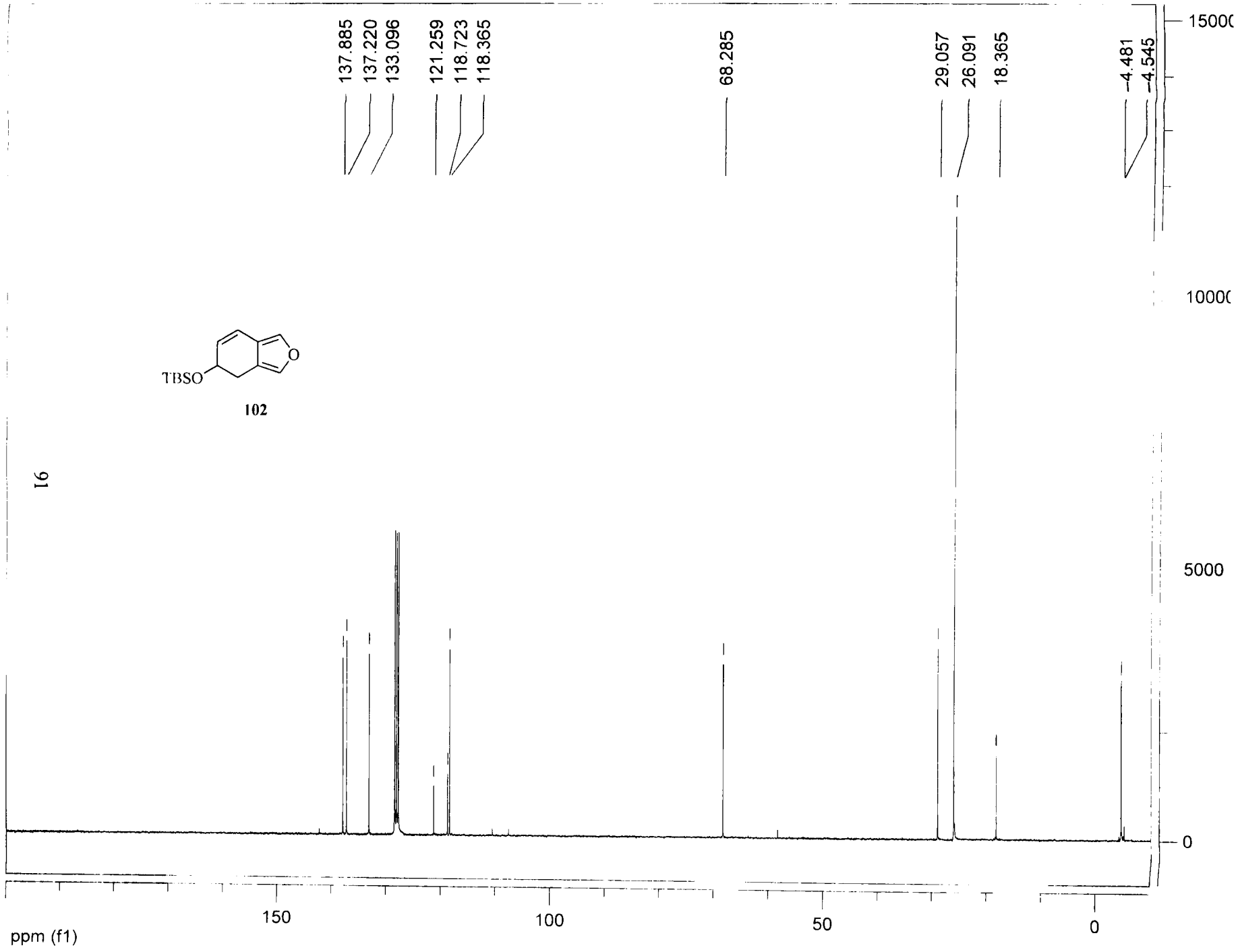
2.560
2.554
0.939
0.010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O
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91
15000
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5000
0
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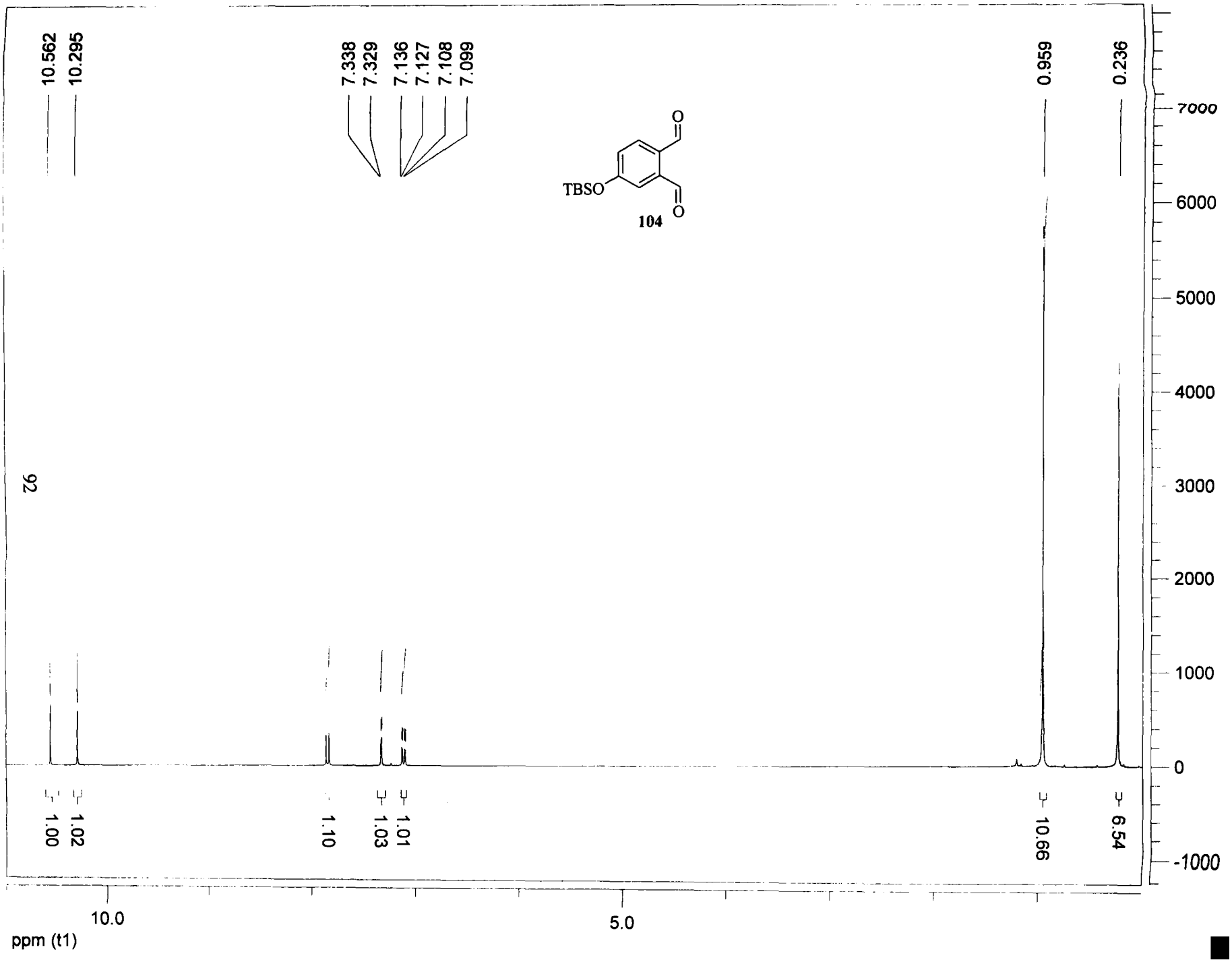
100
50
0
ppm (f1)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O
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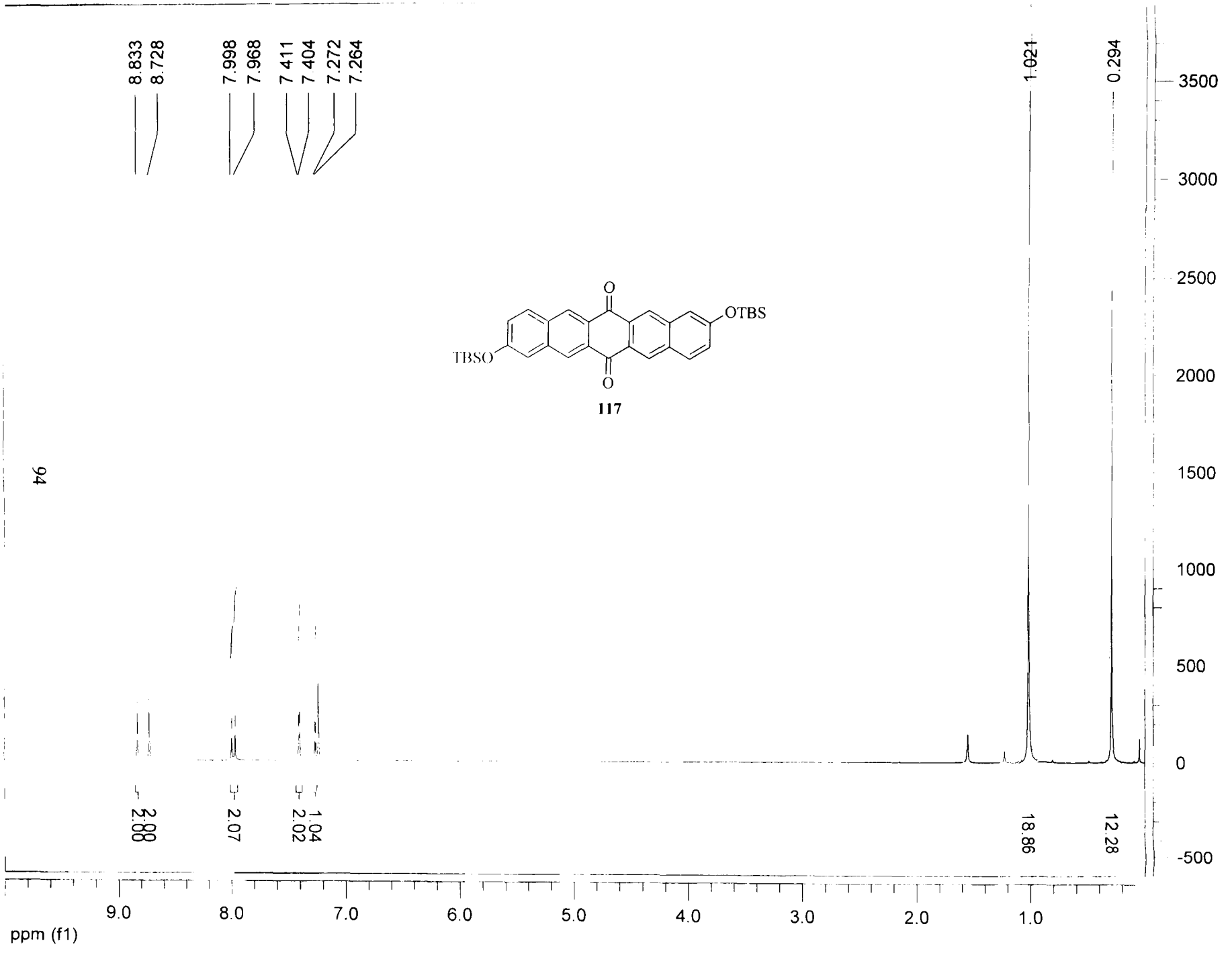
92
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
1.02
1.10
1.03
1.01
10.66
6.54
10.0
5.0
ppm (t1)

ppm (f1)
150
100
50
0
192.393
191.482
161.273
139.026
134.915
130.281
124.827
121.701
25.864
18.611
-3.988
TBSO
O
O
104
0
5000
10000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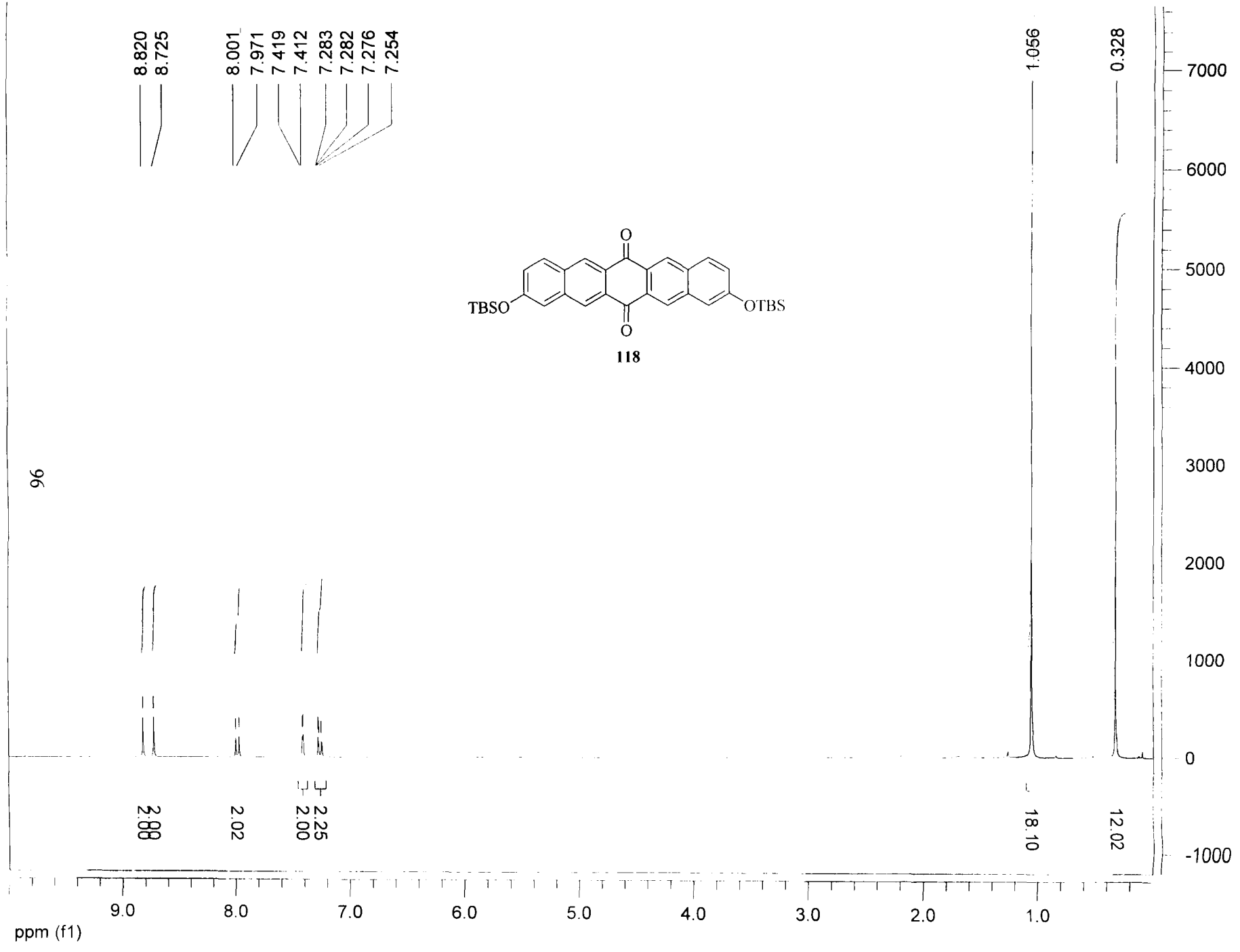
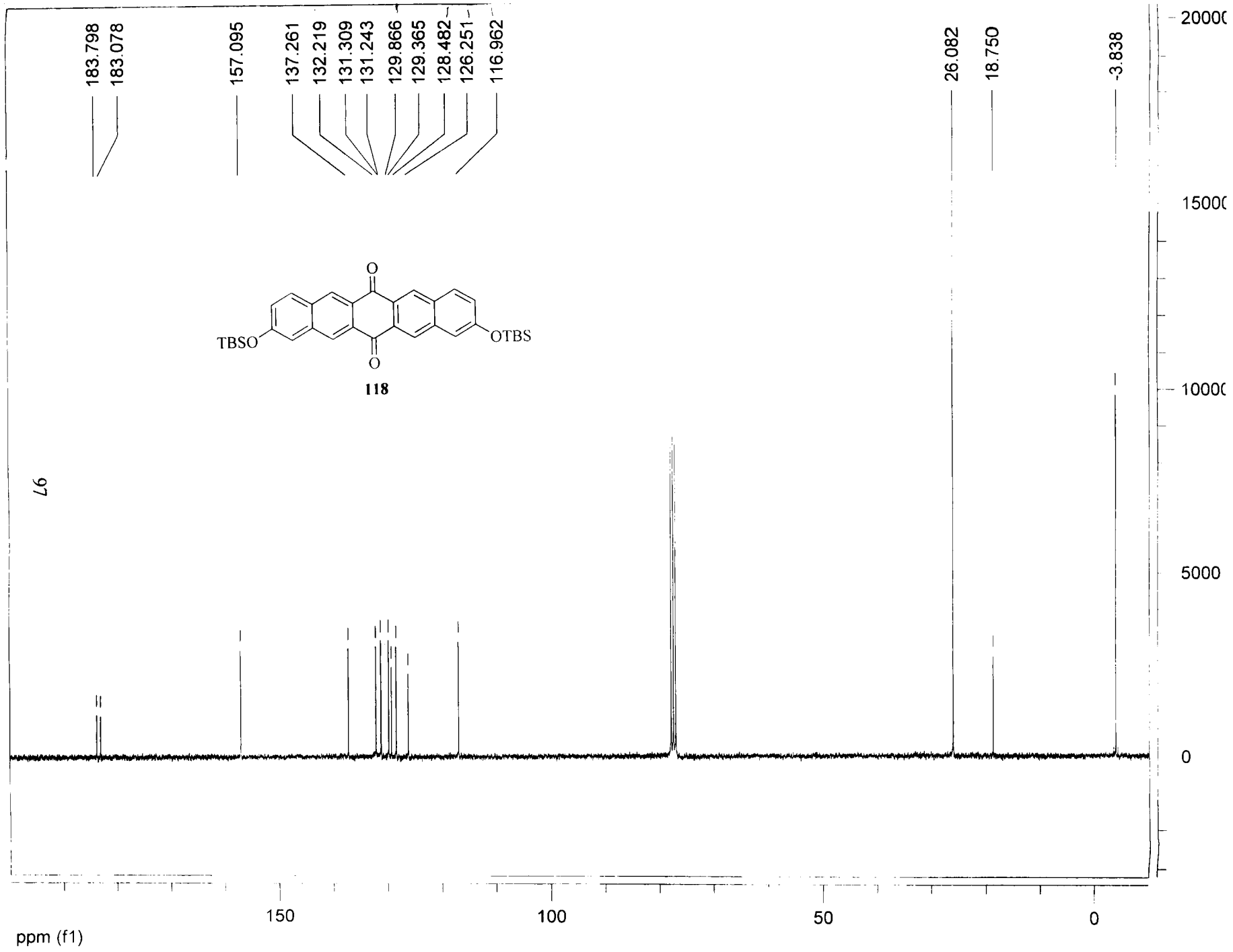
8.728
7.998
7.968
7.411
7.404
7.272
7.264
1.00
0.294
3500
3000
2500
2000
1500
1000
500
0
-500
O
OTBS
TBSO
O
117
94
2.88
2.07
1.04
2.02
18.86
12.28
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

95
183.503
157.153
137.373
132.234
131.361
131.226
129.972
129.288
128.427
126.220
116.958
26.042
18.719
-3.872
TBSO
OTBS
O
O
117
ppm (f1)
150
100
50
0
0
5000
1000


8.820
8.725
8.001
7.971
7.419
7.412
7.283
7.282
7.276
7.254
1.059
0.328
TBSO
OTBS
O
O
118
96
2.08
2.02
2.00
2.25
18.10
12.02
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)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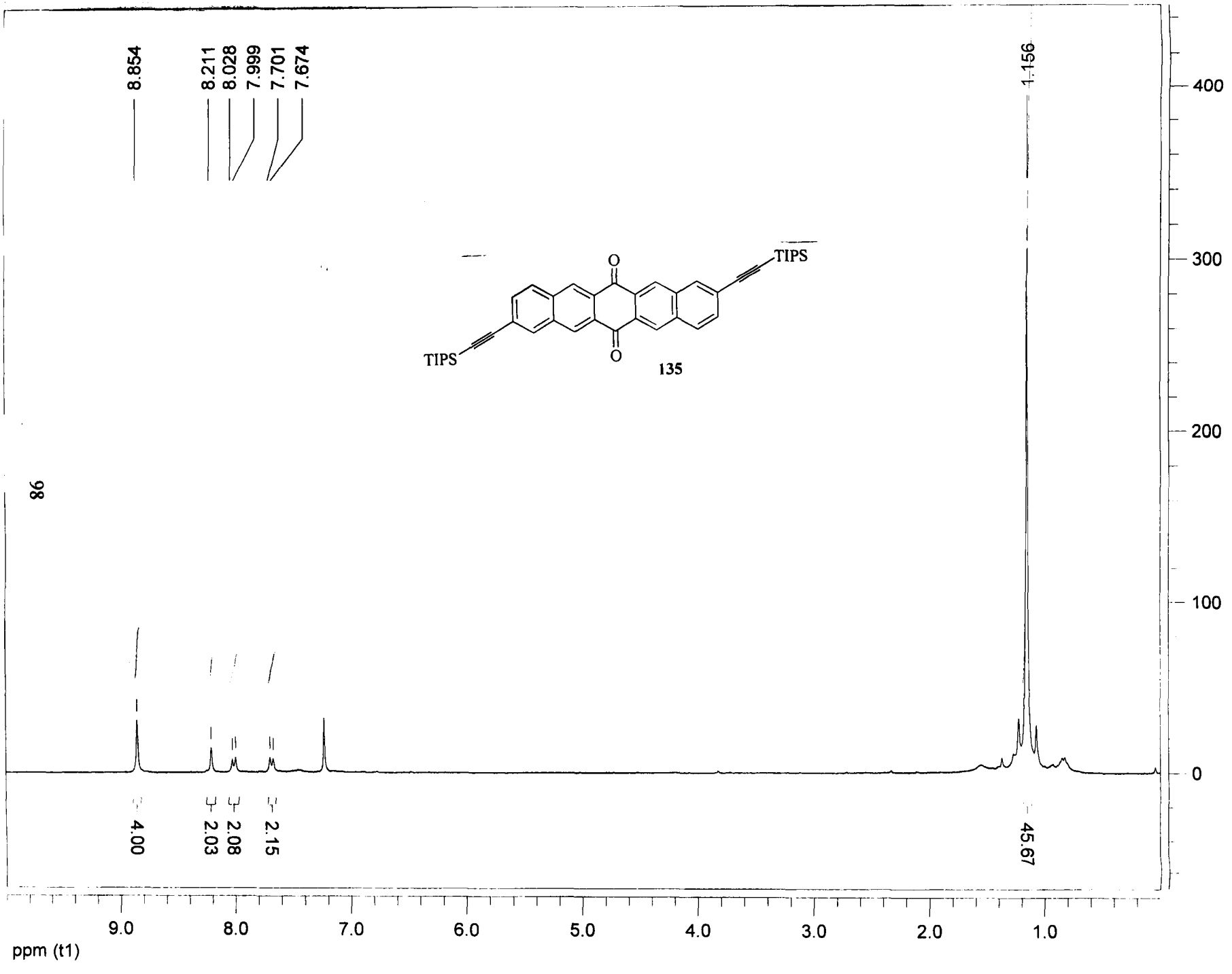
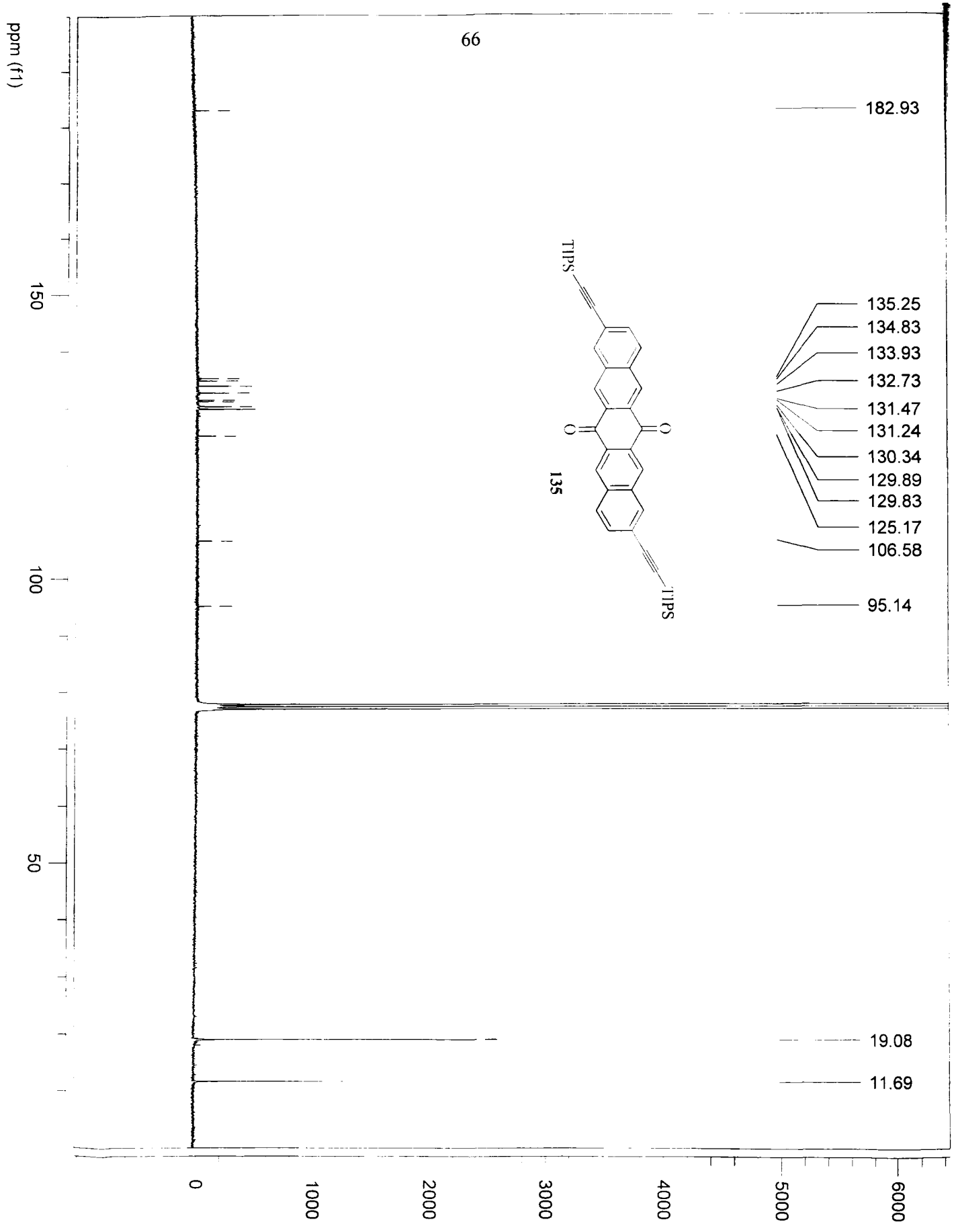
183.078
157.095
137.261
132.219
131.309
131.243
129.866
129.365
128.482
126.251
116.962
26.082
18.750
-3.838
TBSO
OTBS
O
O
118
97
20000
15000
10000
5000
0
150
100
50
0
ppm (f1)


8.854
8.211
8.028
7.999
7.701
7.674
1.156
TIPS
TIPS
O
O
135
98
4.00
2.03
2.08
2.15
45.67
400
300
200
100
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


ppm (f1)
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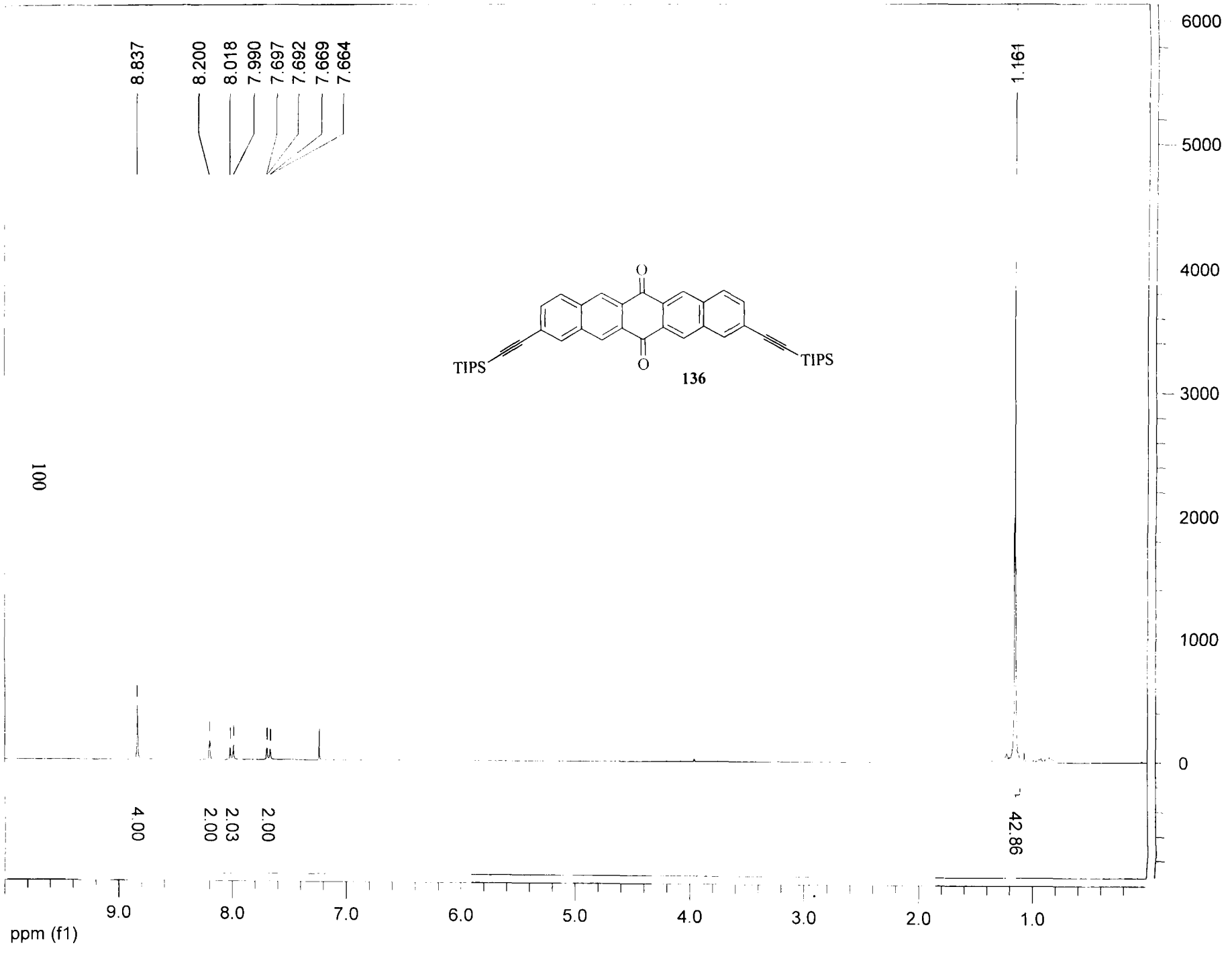
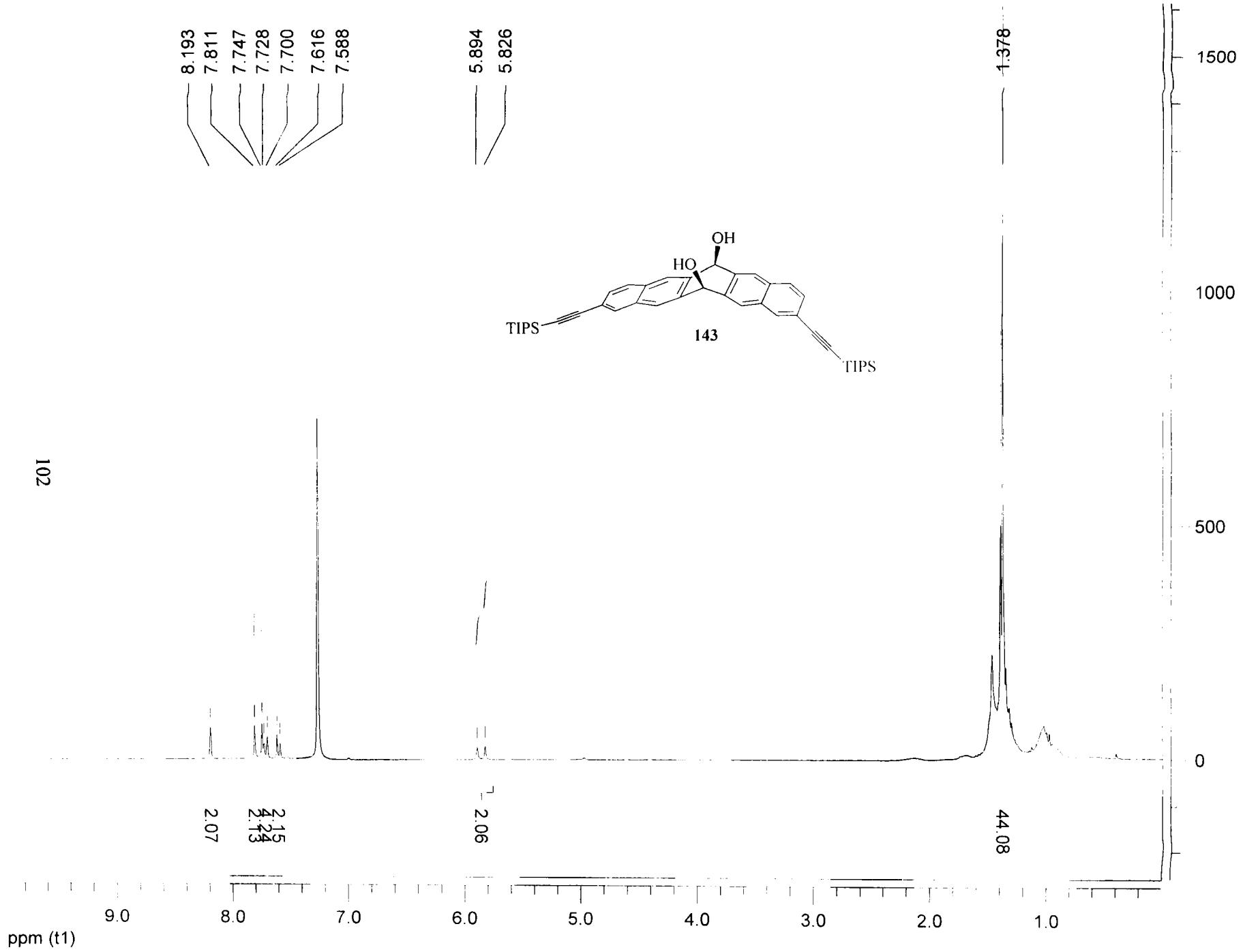
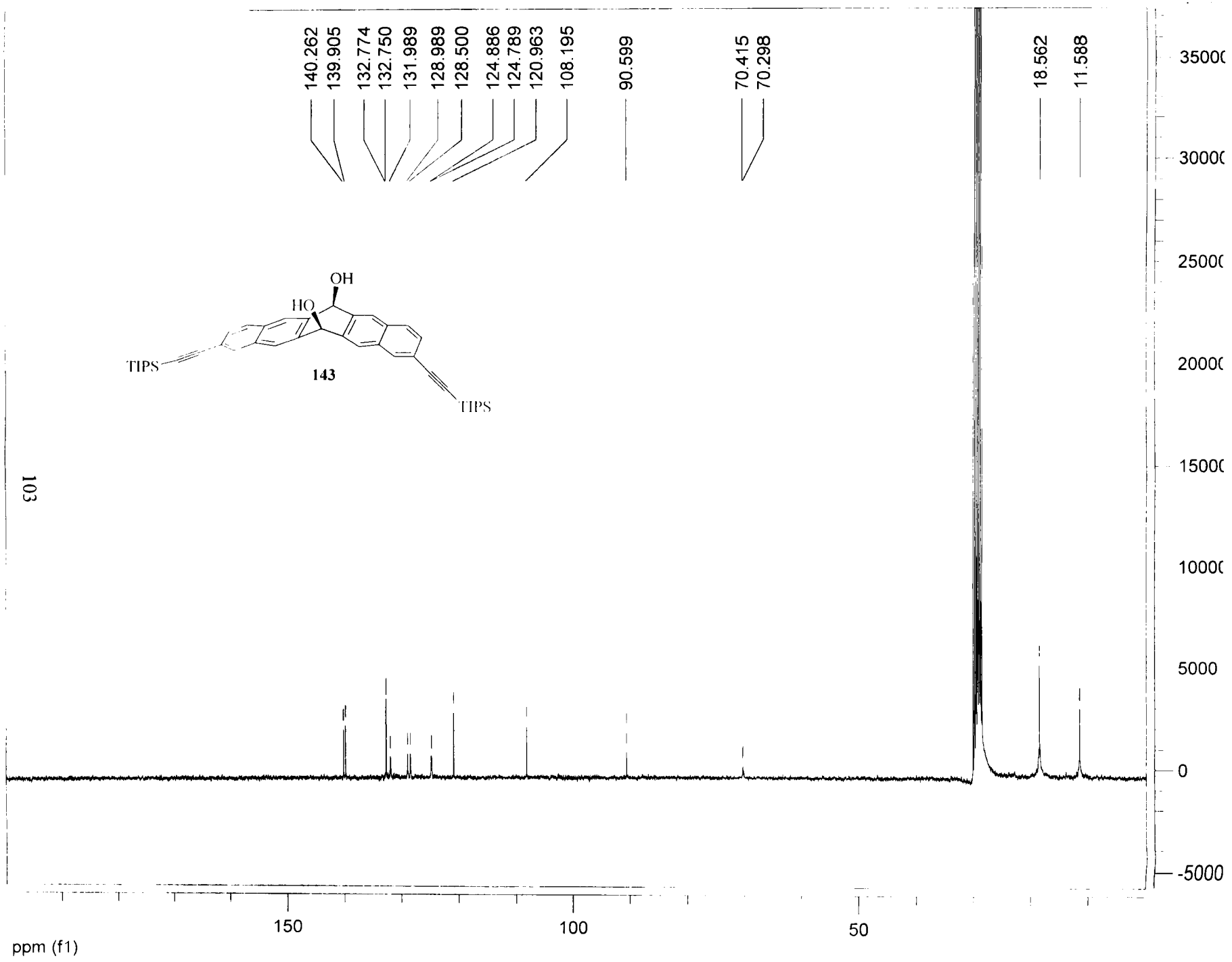
100
50
0
1000
2000
3000
4000
5000
6000
182.93
135.25
134.83
133.93
132.73
131.47
131.24
130.34
129.89
129.83
125.17
106.58
95.14
19.08
11.69
TIPS
TIPS
O
O
135


8.837
8.200
8.018
7.990
7.697
7.692
7.669
7.664
1.161
TIPS
TIPS
O
O
136
100
4.00
2.00
2.03
2.00
42.86
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
6000
5000
4000
3000
2000
1000
0

ppm (f1)
150
100
50
-1000
0
1000
2000
3000
4000
5000
6000
7000
182.894
182.865
135.221
134.820
133.911
132.730
131.414
131.253
130.324
129.852
129.822
125.154
106.577
95.141
19.085
11.695
TIPS
TIPS
O
O
136


8.193
7.811
7.747
7.728
7.700
7.616
7.588
5.894
5.826
1.378
1500
1000
500
0
OH
HO
TIPS
TIPS
143
102
2.07
2.15
2.24
2.13
2.06
44.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


140.262
139.905
132.774
132.750
131.989
128.989
128.500
124.886
124.789
120.963
108.195
90.599
70.415
70.298
18.562
11.588
OH
HO
TIPS
TIPS
143
103
35000
30000
25000
20000
15000
10000
5000
0
-5000
150
100
50
ppm (f1)

104
8.093
7.750
7.693
7.614
7.609
7.586
7.580
7.512
7.484
5.298
5.277
5.245
5.226
1.261
48.66
2.00
1.91
TIPS
HO
OH
TIPS
144
ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
500
1000
1500
2000

TIPS
HO
OH
TIPS
144
139.670
139.481
132.480
132.463
131.995
128.694
128.450
122.054
120.680
108.323
90.371
68.509
68.392
18.558
11.591
ppm (f1)
150
100
50
0
5000
10000

8.905
8.206
7.900
7.819
7.791
7.650
7.646
7.622
7.618
4.665
1.195
O
TIPS
TIPS
145
106
2.00
1.99
2.00
1.99
43.47
500
400
300
200
100
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

185.252
136.675
135.206
134.022
131.971
131.830
131.161
129.570
127.489
127.160
121.719
107.209
92.499
32.987
19.143
11.768
TIPS
TIPS
O
145
ppm (f1)
150
100
50
-1000
0
1000
2000
3000
4000
5000
6000
7000

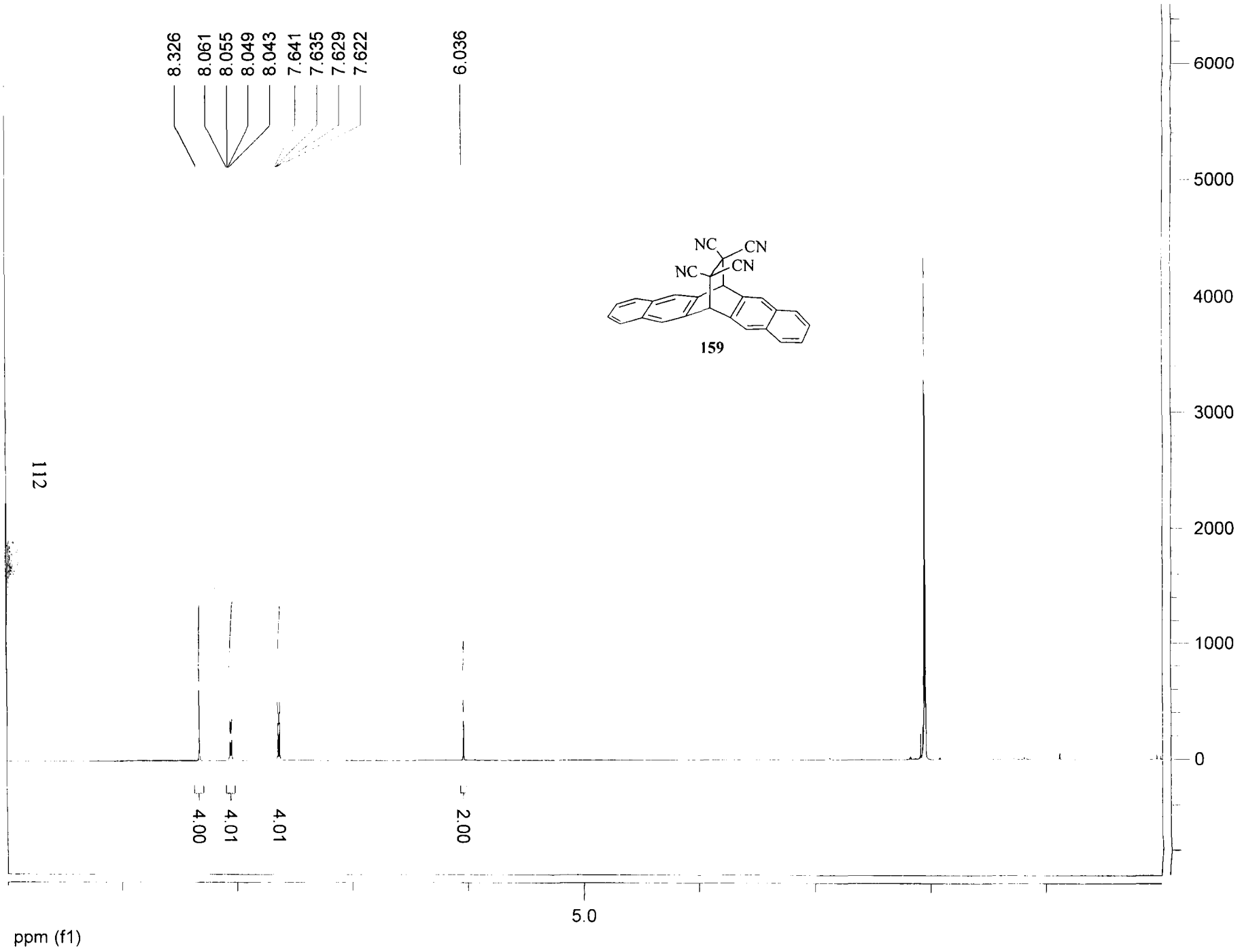
ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
500
1000
8.00
4.00
4.00
7.781
7.421
7.410
7.400
7.390
4.230
157

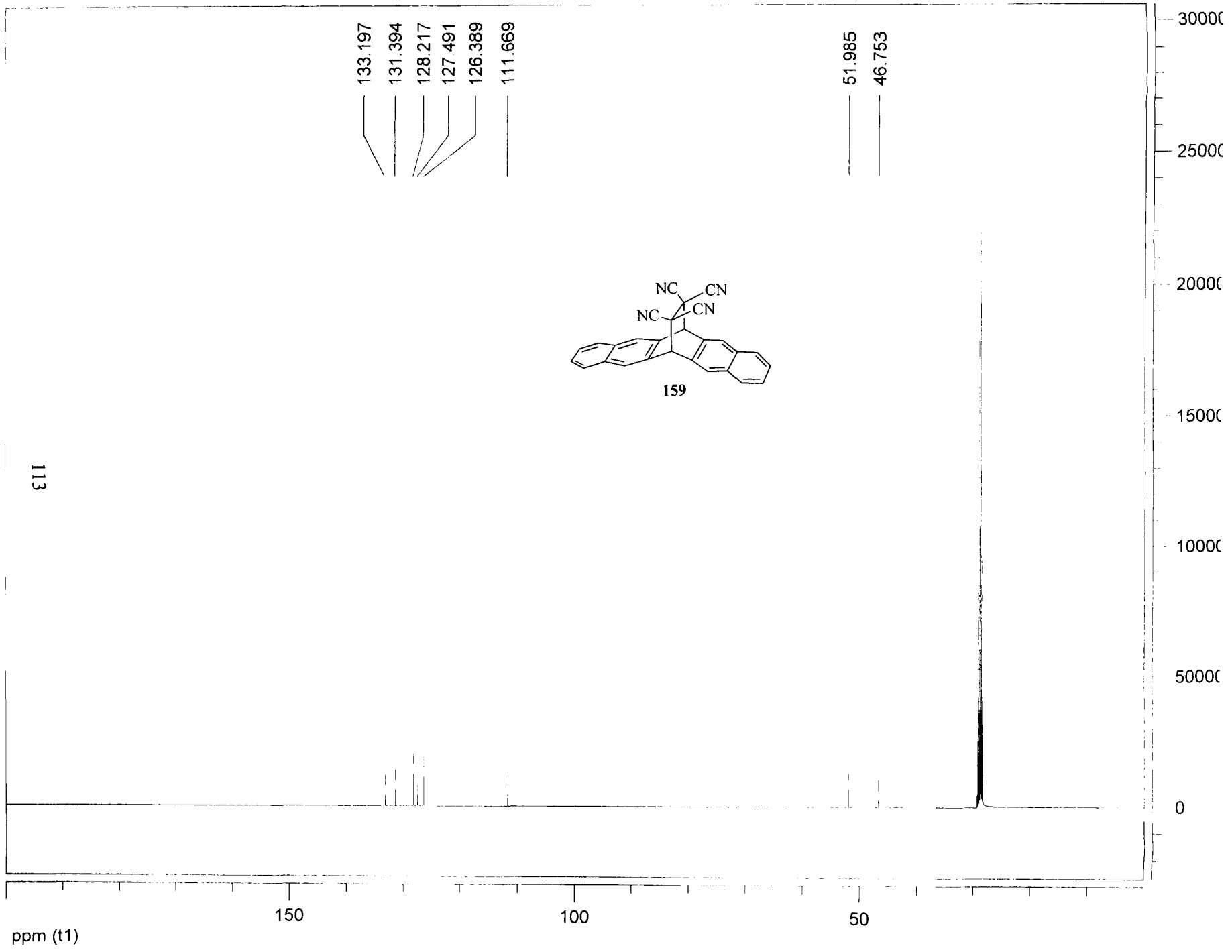
ppm (f1)
150
100
50
0
5000
10000
136.239
132.814
127.612
125.728
125.489
37.737

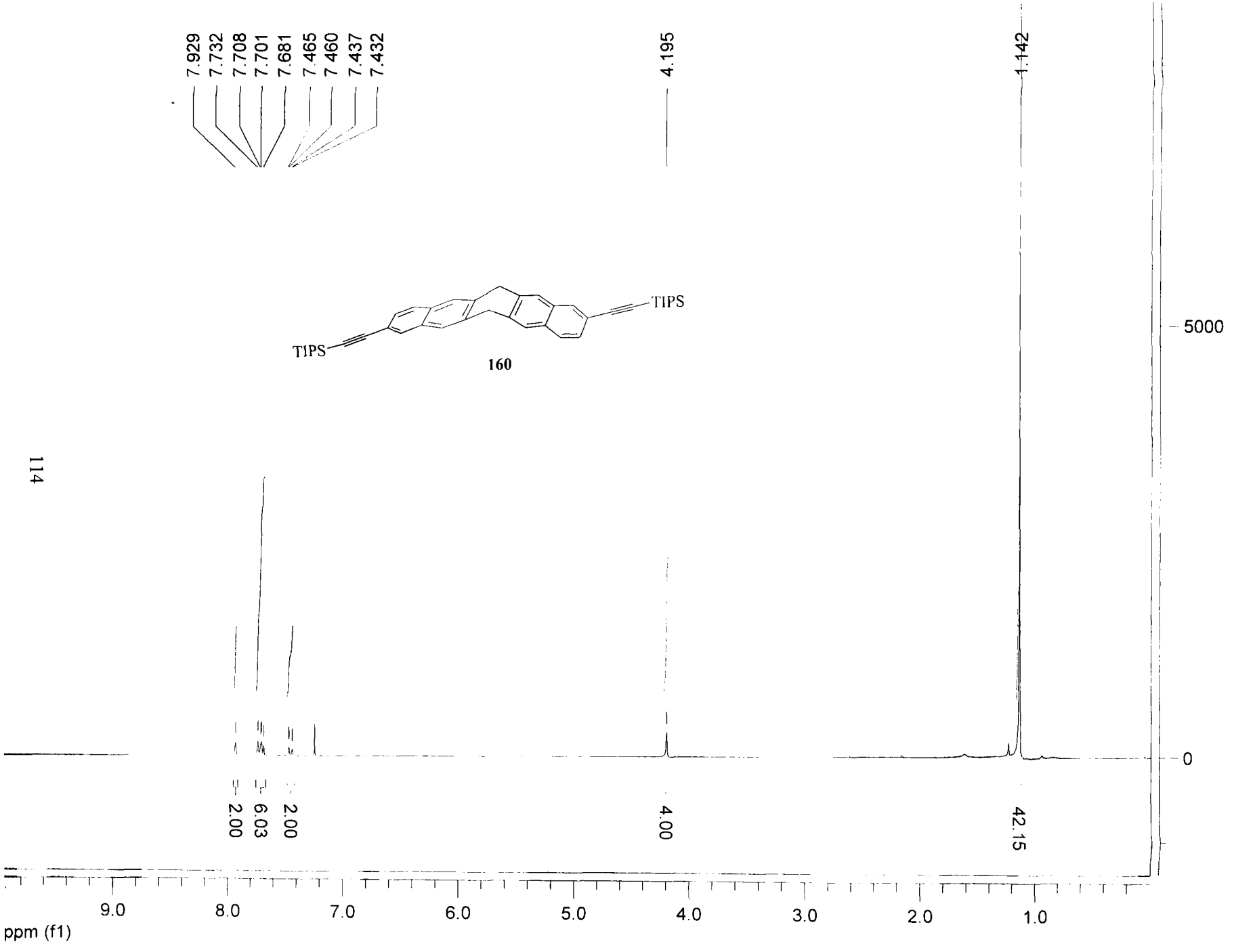
157

110
8.103
7.922
7.912
7.901
7.890
7.796
7.784
7.774
7.764
7.742
7.577
7.566
7.556
7.545
7.534
7.523
5.216
2.13
3.98
3.82
2.07
2.00
158
Cl
Cl
O
O
CN
CN
ppm (f1)
5.0
0
500
1000
1500

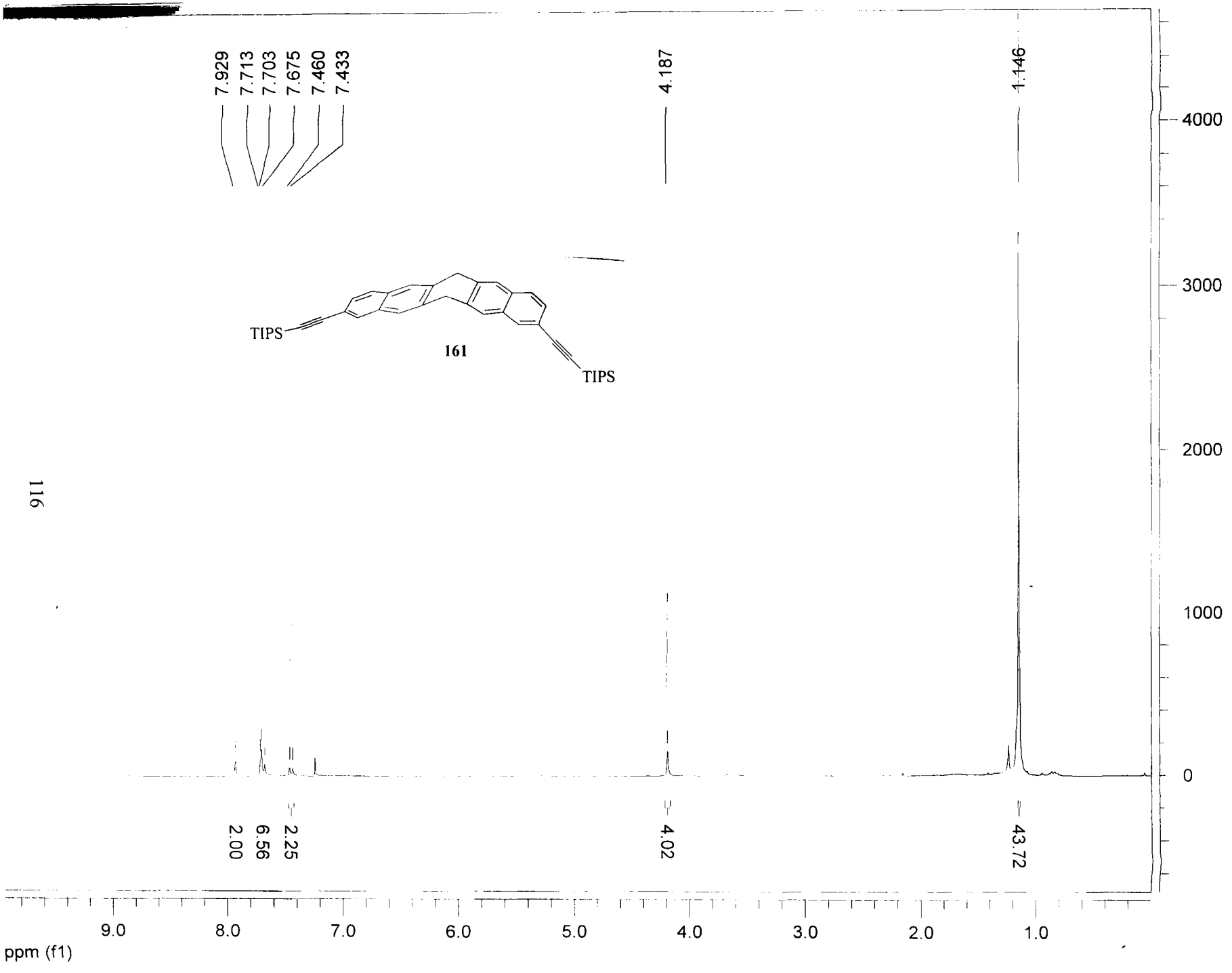
111
ppm (f1)
150
100
50
0
5000
180.561
142.798
134.026
133.642
133.493
132.382
128.613
128.491
128.036
127.506
126.560
125.967
115.896
58.406
55.695
158
Cl
Cl
O
O
CN
CN


8.326
8.061
8.055
8.049
8.043
7.641
7.635
7.629
7.622
6.036
NC
CN
NC
CN
159
112
6000
5000
4000
3000
2000
1000
0
4.00
4.01
4.01
2.00
5.0
ppm (f1)


133.197
131.394
128.217
127.491
126.389
111.669
51.985
46.753
NC
CN
NC
CN
159
30000
25000
20000
15000
10000
5000
0
150
100
50
ppm (t1)

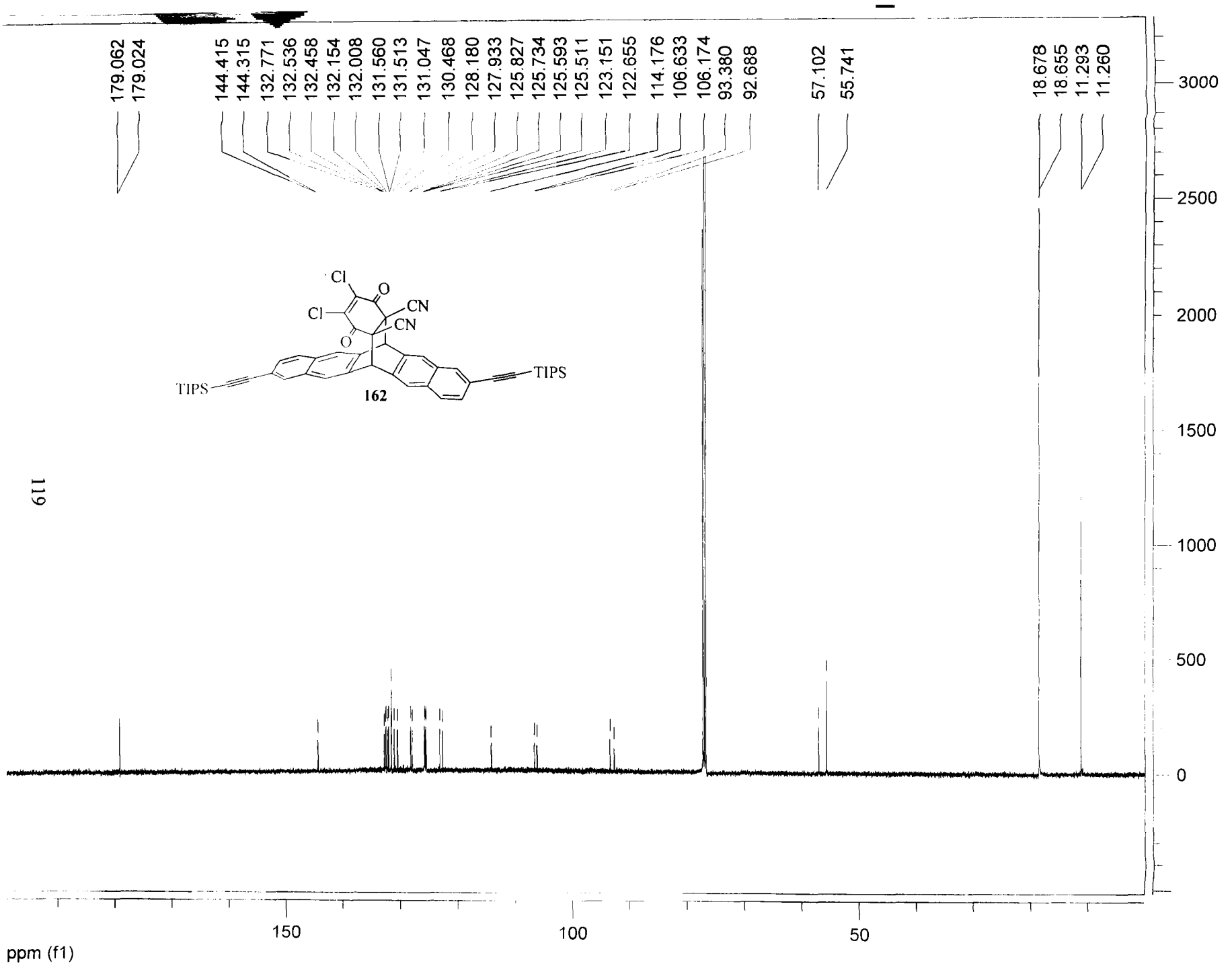

7.929
7.732
7.708
7.701
7.681
7.465
7.460
7.437
7.432
4.195
1.142
TIPS
TIPS
160
114
5000
0
2.00
6.03
2.00
4.00
42.15
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

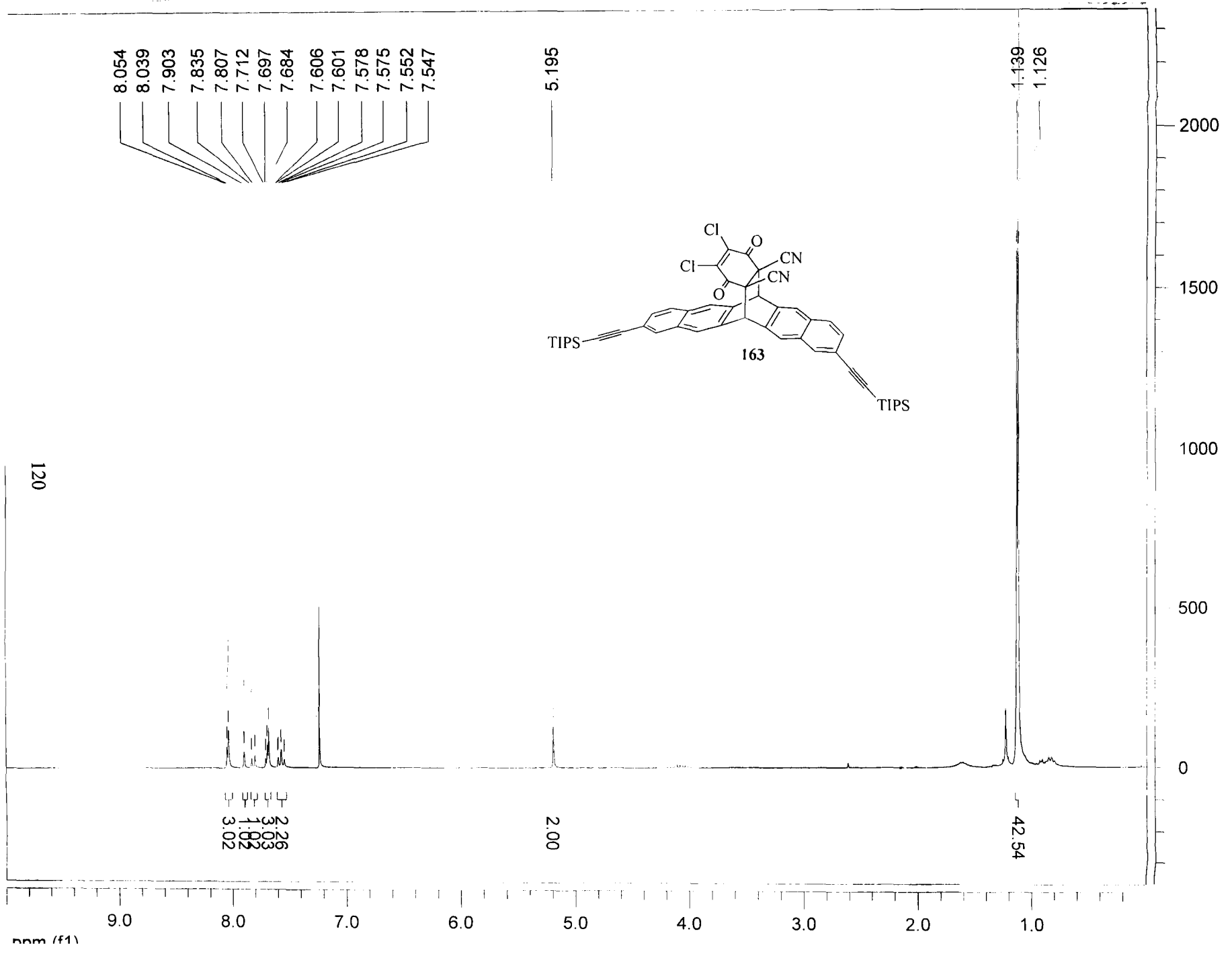
TIPS
TIPS
160
136.940
136.644
132.292
132.242
131.647
128.858
127.548
125.506
125.355
120.656
108.024
90.994
37.725
19.119
11.752
ppm (f1)
150
100
50
0
5000
1000

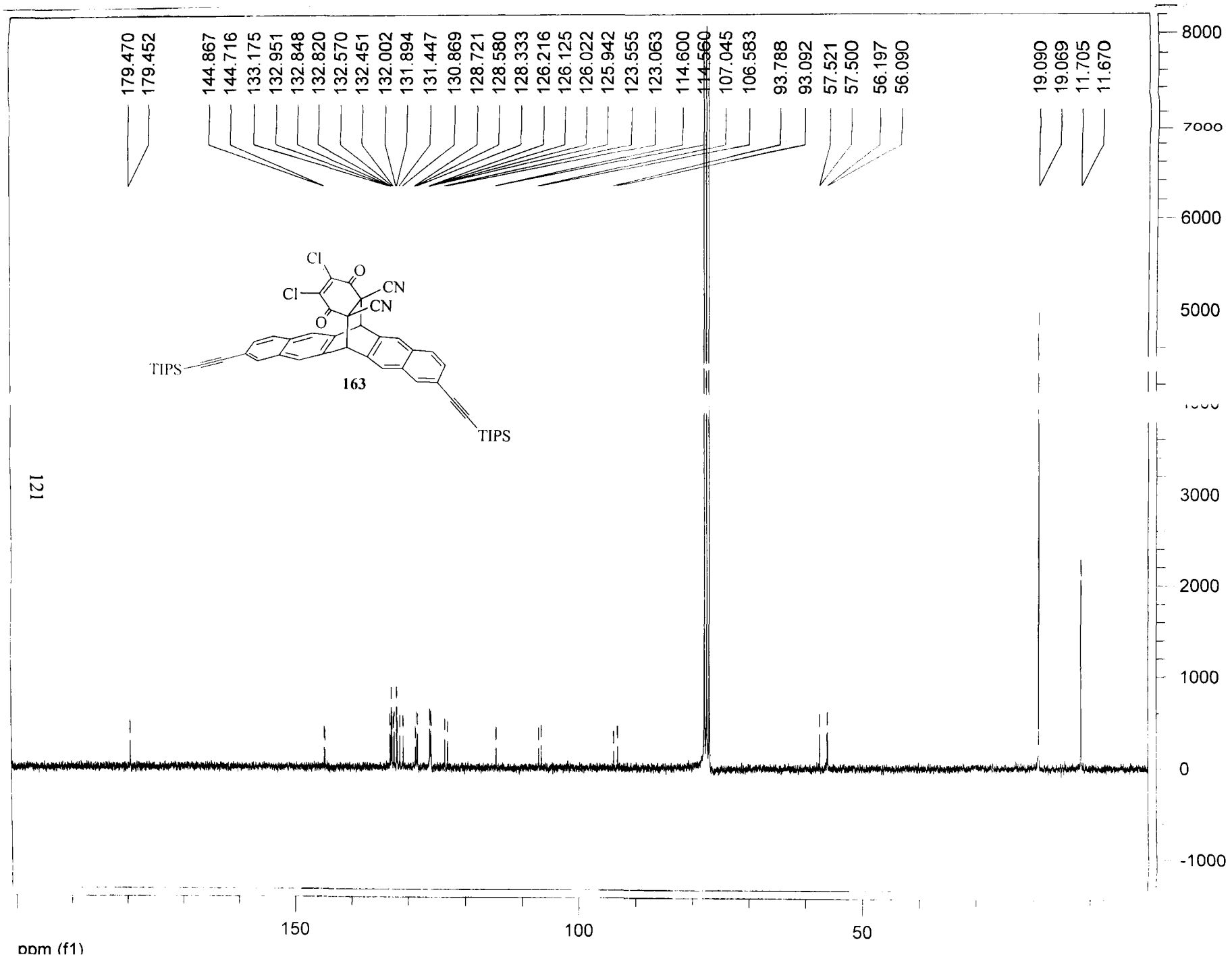

7.929
7.713
7.703
7.675
7.460
7.433
4.187
1.146
TIPS
TIPS
161
4000
3000
2000
1000
0
2.00
6.56
2.25
4.02
43.72
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

TIPS
TIPS
161
136.888
136.685
132.291
132.243
131.658
128.847
127.544
125.476
125.379
120.663
108.034
90.999
19.122
11.757
ppm (f1)
150
100
50
0
1000
2000
3000
4000
5000

8.065
8.028
7.898
7.830
7.813
7.709
7.692
7.675
7.598
7.595
7.581
7.578
7.574
7.571
7.557
7.554
5.197
1.141
1.127
42.20
1.93
TIPS
TIPS
Cl
Cl
O
O
CN
CN
162
ppm (f1)


179.062
179.024
144.415
144.315
132.771
132.536
132.458
132.154
132.008
131.560
131.513
131.047
130.468
128.180
127.933
125.827
125.734
125.593
125.511
123.151
122.655
114.176
106.633
106.174
93.380
92.688
57.102
55.741
18.678
18.655
11.293
11.260
Cl
O
CN
Cl
CN
O
TIPS
TIPS
162
119
3000
2500
2000
1500
1000
500
0
150
100
50
ppm (f1)


8.054
8.039
7.903
7.835
7.807
7.712
7.697
7.684
7.606
7.601
7.578
7.575
7.552
7.547
5.195
1.139
1.126
Cl
Cl
O
O
CN
CN
TIPS
TIPS
163
120
2000
1500
1000
500
0
3.02
1.02
3.03
2.26
2.00
42.54
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


179.470
179.452
144.867
144.716
133.175
132.951
132.848
132.820
132.570
132.451
132.002
131.894
131.447
130.869
128.721
128.580
128.333
126.216
126.125
126.022
125.942
123.555
123.063
114.600
114.560
107.045
106.583
93.788
93.092
57.521
57.500
56.197
56.090
19.090
19.069
11.705
11.670
Cl
Cl
O
O
CN
CN
TIPS
TIPS
163
121
8000
7000
6000
5000
3000
2000
1000
0
-1000
150
100
50
ppm (f1)

Appendix II

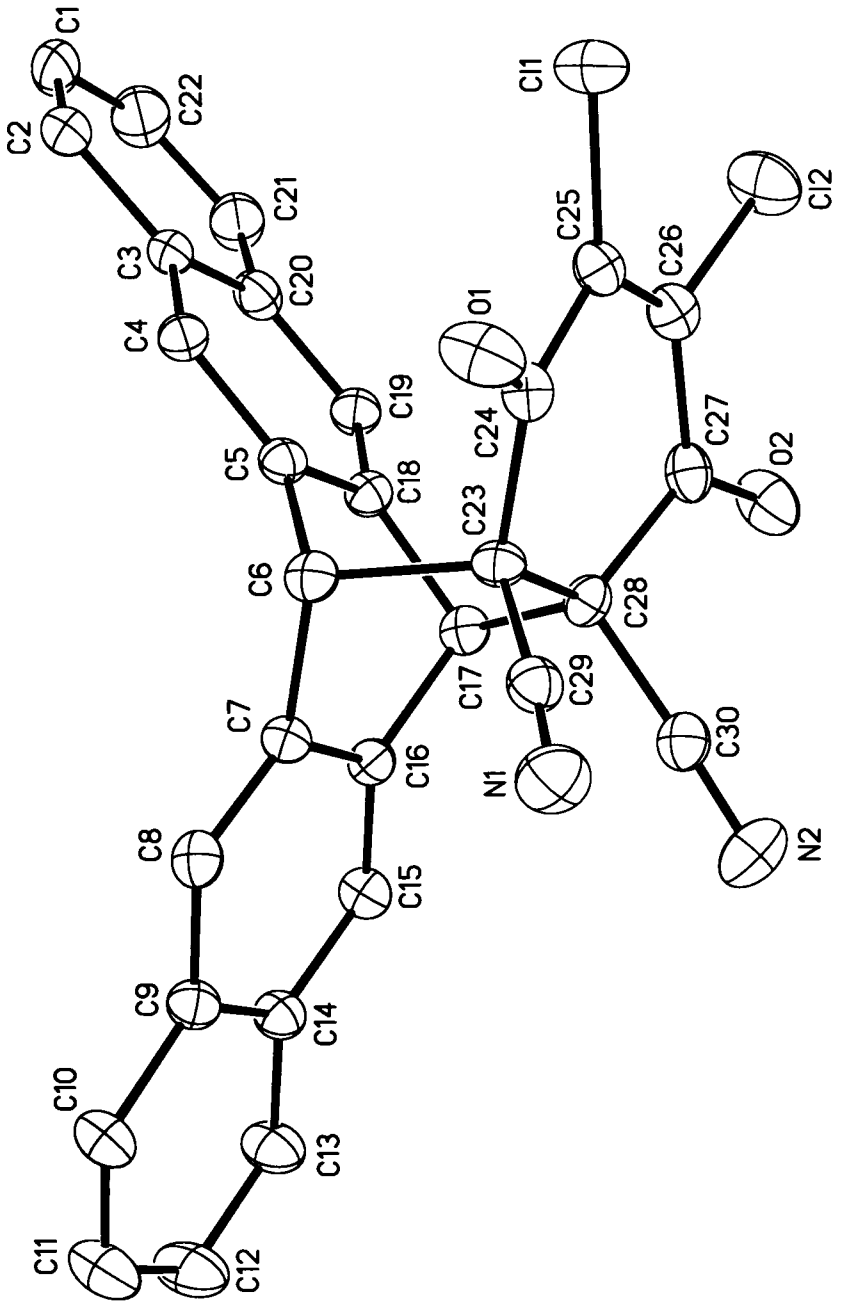

C1
C22
C2
C21
C3
C20
C4
C19
C5
C18
C6
C17
C7
C16
C8
C15
C9
C14
C10
C13
C11
C12
Cl1
C25
Cl2
C26
O1
C24
C27
O2
C23
C28
C29
C30
N1
N2

Table 1. Crystal data and structure refinement for 158.

Identification code	158
Empirical formula	C34.20 H22.40 Cl2 N2 O3.40
Formula weight	586.64
Temperature	213(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.431(2) A alpha = 105.956(4) deg. b = 12.194(3) A beta = 107.403(4) deg. c = 12.972(3) A gamma = 99.551(4) deg.
Volume	1457.3(5) A^3
Z, Calculated density	2, 1.337 Mg/m^3
Absorption coefficient	0.263 mm^-1
F(000)	606
Crystal size	0.25 x 0.15 x 0.10 mm
Theta range for data collection	1.80 to 26.43 deg.
Limiting indices	-13<=h<=13, -15<=k<=15, -16<=l<=16
Reflections collected / unique	15419 / 5910 [R(int) = 0.0765]
Completeness to theta = 26.43	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9742 and 0.9373
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5910 / 0 / 397
Goodness-of-fit on F^2	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0713, wR2 = 0.1356
R indices (all data)	R1 = 0.1609, wR2 = 0.1642
Largest diff. peak and hole	0.272 and -0.248 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 158.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	6588(1)	1090(1)	2258(1)	50(1)
Cl(2)	3865(1)	-972(1)	603(1)	59(1)
N(1)	3781(4)	3226(3)	5309(3)	53(1)
N(2)	453(4)	858(3)	3293(3)	63(1)
O(1)	6010(3)	2799(2)	3949(2)	52(1)
O(2)	1448(3)	-587(2)	1123(2)	54(1)
C(1)	4909(5)	3248(4)	-1661(4)	57(1)
C(2)	5197(4)	3649(3)	-503(4)	46(1)

C(3)	4244(4)	3176(3)	-51(3)	35(1)
C(4)	4462(4)	3621(3)	1142(3)	34(1)
C(5)	3496(3)	3178(3)	1543(3)	30(1)
C(6)	3552(3)	3575(3)	2772(3)	31(1)
C(7)	2229(3)	3895(3)	2801(3)	28(1)
C(8)	2136(4)	4900(3)	3526(3)	33(1)
C(9)	805(4)	5054(3)	3497(3)	33(1)
C(10)	651(4)	6062(3)	4253(3)	42(1)
C(11)	-643(4)	6192(4)	4197(4)	54(1)
C(12)	-1847(4)	5314(4)	3404(4)	57(1)
C(13)	-1738(4)	4315(4)	2664(4)	48(1)
C(14)	-428(4)	4146(3)	2683(3)	35(1)
C(15)	-277(4)	3115(3)	1965(3)	35(1)
C(16)	1014(4)	2983(3)	2025(3)	30(1)
C(17)	1339(3)	1906(3)	1381(3)	32(1)
C(18)	2287(3)	2256(3)	776(3)	31(1)
C(19)	2057(4)	1796(3)	-364(3)	35(1)
C(20)	3021(4)	2267(3)	-804(3)	38(1)
C(21)	2778(5)	1875(4)	-2002(4)	52(1)
C(22)	3697(5)	2374(4)	-2406(4)	61(1)
C(23)	3557(3)	2442(3)	3159(3)	29(1)
C(24)	4940(4)	2158(3)	3190(3)	33(1)
C(25)	4969(4)	1144(3)	2268(3)	33(1)
C(26)	3808(4)	275(3)	1564(3)	37(1)
C(27)	2427(4)	275(3)	1643(3)	36(1)
C(28)	2194(4)	1430(3)	2320(3)	31(1)
C(29)	3635(4)	2839(3)	4363(3)	35(1)
C(30)	1251(4)	1103(3)	2902(3)	39(1)
O(3)	3668(3)	10253(3)	3902(3)	70(1)
C(31)	3178(7)	8194(5)	3441(5)	104(2)
C(32)	3144(5)	9389(4)	4066(3)	53(1)
C(33)	2451(7)	9467(5)	4912(5)	97(2)
O(4)	1625(13)	5517(15)	796(12)	150(6)
C(34)	-130(40)	4110(30)	-660(20)	121(16)
C(35)	489(19)	5130(20)	220(20)	69(5)
C(36)	-590(30)	5710(30)	560(40)	99(14)

Table 3. Bond lengths [A] and angles [deg] for 158.

Cl(1)-C(25)	1.704(4)
Cl(2)-C(26)	1.704(4)
N(1)-C(29)	1.140(4)
N(2)-C(30)	1.138(4)
O(1)-C(24)	1.206(4)
O(2)-C(27)	1.202(4)
C(1)-C(2)	1.365(5)
C(1)-C(22)	1.388(6)
C(2)-C(3)	1.417(5)
C(3)-C(20)	1.415(5)
C(3)-C(4)	1.424(5)
C(4)-C(5)	1.366(4)
C(5)-C(18)	1.417(5)
C(5)-C(6)	1.514(4)
C(6)-C(7)	1.503(4)
C(6)-C(23)	1.594(5)
C(7)-C(8)	1.362(4)
C(7)-C(16)	1.418(5)
C(8)-C(9)	1.422(5)
C(9)-C(10)	1.413(5)
C(9)-C(14)	1.438(5)
C(10)-C(11)	1.368(5)
C(11)-C(12)	1.399(5)
C(12)-C(13)	1.373(5)
C(13)-C(14)	1.410(5)
C(14)-C(15)	1.408(5)
C(15)-C(16)	1.364(5)
C(16)-C(17)	1.501(5)
C(17)-C(18)	1.512(4)
C(17)-C(28)	1.590(5)

C(18)-C(19)	1.358(4)
C(19)-C(20)	1.414(5)
C(20)-C(21)	1.423(5)
C(21)-C(22)	1.358(5)
C(23)-C(29)	1.474(5)
C(23)-C(24)	1.531(5)
C(23)-C(28)	1.575(5)
C(24)-C(25)	1.477(5)
C(25)-C(26)	1.344(5)
C(26)-C(27)	1.474(5)
C(27)-C(28)	1.541(5)
C(28)-C(30)	1.475(5)
O(3)-C(32)	1.207(5)
C(31)-C(32)	1.472(6)
C(32)-C(33)	1.475(6)
O(4)-C(35)	1.131(16)
C(34)-C(35)	1.33(5)
C(35)-C(36)	1.53(5)

C(2)-C(1)-C(22)	120.9(4)
C(1)-C(2)-C(3)	119.9(4)
C(2)-C(3)-C(20)	119.5(3)
C(2)-C(3)-C(4)	121.6(3)
C(20)-C(3)-C(4)	118.8(3)
C(5)-C(4)-C(3)	120.2(3)
C(4)-C(5)-C(18)	120.0(3)
C(4)-C(5)-C(6)	126.7(3)
C(18)-C(5)-C(6)	113.3(3)
C(7)-C(6)-C(5)	109.4(3)
C(7)-C(6)-C(23)	106.4(3)
C(5)-C(6)-C(23)	106.2(3)
C(8)-C(7)-C(16)	120.9(3)
C(8)-C(7)-C(6)	126.3(3)
C(16)-C(7)-C(6)	112.7(3)
C(7)-C(8)-C(9)	120.0(3)
C(8)-C(9)-C(10)	122.3(3)
C(8)-C(9)-C(14)	119.0(3)
C(10)-C(9)-C(14)	118.7(3)
C(11)-C(10)-C(9)	120.9(4)
C(10)-C(11)-C(12)	120.7(4)
C(13)-C(12)-C(11)	120.1(4)
C(12)-C(13)-C(14)	121.4(4)
C(15)-C(14)-C(13)	122.9(3)
C(15)-C(14)-C(9)	118.8(3)
C(13)-C(14)-C(9)	118.3(3)
C(16)-C(15)-C(14)	120.8(3)
C(15)-C(16)-C(7)	120.4(3)
C(15)-C(16)-C(17)	126.7(3)
C(7)-C(16)-C(17)	112.8(3)
C(16)-C(17)-C(18)	109.7(3)
C(16)-C(17)-C(28)	106.6(3)
C(18)-C(17)-C(28)	107.1(3)
C(19)-C(18)-C(5)	121.4(3)
C(19)-C(18)-C(17)	126.7(3)
C(5)-C(18)-C(17)	111.9(3)
C(18)-C(19)-C(20)	119.5(3)
C(19)-C(20)-C(3)	120.0(3)
C(19)-C(20)-C(21)	121.7(4)
C(3)-C(20)-C(21)	118.2(3)
C(22)-C(21)-C(20)	120.5(4)
C(21)-C(22)-C(1)	121.0(4)
C(29)-C(23)-C(24)	106.2(3)
C(29)-C(23)-C(28)	113.3(3)
C(24)-C(23)-C(28)	116.0(3)
C(29)-C(23)-C(6)	105.9(3)
C(24)-C(23)-C(6)	106.3(3)
C(28)-C(23)-C(6)	108.5(3)
O(1)-C(24)-C(25)	120.5(3)
O(1)-C(24)-C(23)	119.3(3)
C(25)-C(24)-C(23)	120.2(3)
C(26)-C(25)-C(24)	121.6(3)

C(26)-C(25)-Cl(1)	122.9(3)
C(24)-C(25)-Cl(1)	115.2(3)
C(25)-C(26)-C(27)	122.7(3)
C(25)-C(26)-Cl(2)	121.7(3)
C(27)-C(26)-Cl(2)	115.3(3)
O(2)-C(27)-C(26)	121.3(3)
O(2)-C(27)-C(28)	118.8(3)
C(26)-C(27)-C(28)	119.7(3)
C(30)-C(28)-C(27)	107.2(3)
C(30)-C(28)-C(23)	113.1(3)
C(27)-C(28)-C(23)	115.7(3)
C(30)-C(28)-C(17)	106.0(3)
C(27)-C(28)-C(17)	106.0(3)
C(23)-C(28)-C(17)	108.2(3)
N(1)-C(29)-C(23)	174.3(4)
N(2)-C(30)-C(28)	175.4(4)
O(3)-C(32)-C(31)	121.7(4)
O(3)-C(32)-C(33)	122.2(4)
C(31)-C(32)-C(33)	116.1(4)
O(4)-C(35)-C(34)	130(4)
O(4)-C(35)-C(36)	118(3)
C(34)-C(35)-C(36)	111(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 158. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(1)	41(1)	57(1)	53(1)	13(1)	23(1)	17(1)
Cl(2)	62(1)	45(1)	53(1)	-5(1)	18(1)	14(1)
N(1)	63(2)	61(2)	37(2)	16(2)	21(2)	19(2)
N(2)	56(3)	72(3)	67(3)	32(2)	29(2)	4(2)
O(1)	29(2)	52(2)	47(2)	-7(1)	-1(1)	8(1)
O(2)	38(2)	32(2)	66(2)	0(1)	4(1)	1(1)
C(1)	85(4)	39(3)	73(3)	26(2)	57(3)	23(3)
C(2)	56(3)	36(2)	63(3)	20(2)	38(2)	19(2)
C(3)	43(2)	30(2)	42(2)	15(2)	25(2)	16(2)
C(4)	27(2)	33(2)	43(2)	13(2)	13(2)	8(2)
C(5)	25(2)	30(2)	35(2)	10(2)	10(2)	9(2)
C(6)	23(2)	30(2)	31(2)	5(2)	6(2)	1(2)
C(7)	23(2)	30(2)	26(2)	9(2)	6(2)	7(2)
C(8)	26(2)	31(2)	33(2)	10(2)	4(2)	2(2)
C(9)	31(2)	36(2)	33(2)	12(2)	11(2)	11(2)
C(10)	41(2)	36(2)	41(2)	6(2)	11(2)	14(2)
C(11)	47(3)	46(3)	59(3)	1(2)	16(2)	19(2)
C(12)	36(3)	60(3)	64(3)	4(2)	17(2)	16(2)
C(13)	31(2)	48(3)	57(3)	8(2)	15(2)	12(2)
C(14)	29(2)	37(2)	37(2)	12(2)	11(2)	10(2)
C(15)	31(2)	35(2)	32(2)	7(2)	6(2)	7(2)
C(16)	30(2)	29(2)	27(2)	7(2)	10(2)	5(2)
C(17)	26(2)	30(2)	30(2)	5(2)	6(2)	1(2)
C(18)	28(2)	33(2)	30(2)	11(2)	10(2)	8(2)
C(19)	36(2)	36(2)	33(2)	10(2)	13(2)	10(2)
C(20)	49(3)	34(2)	36(2)	12(2)	19(2)	17(2)
C(21)	66(3)	47(3)	47(3)	17(2)	27(2)	16(2)
C(22)	92(4)	56(3)	53(3)	21(3)	45(3)	26(3)
C(23)	25(2)	32(2)	27(2)	6(2)	9(2)	7(2)
C(24)	33(2)	30(2)	29(2)	10(2)	6(2)	6(2)
C(25)	35(2)	31(2)	30(2)	10(2)	8(2)	10(2)
C(26)	42(2)	37(2)	29(2)	12(2)	10(2)	12(2)
C(27)	36(2)	28(2)	35(2)	11(2)	4(2)	4(2)
C(28)	30(2)	31(2)	29(2)	10(2)	9(2)	3(2)
C(29)	33(2)	36(2)	38(2)	13(2)	12(2)	11(2)

C(30)	36(2)	36(2)	39(2)	13(2)	9(2)	6(2)
O(3)	75(2)	67(2)	75(2)	46(2)	22(2)	16(2)
C(31)	163(6)	75(4)	104(5)	31(4)	79(4)	49(4)
C(32)	67(3)	55(3)	38(2)	21(2)	14(2)	20(2)
C(33)	157(6)	81(4)	92(4)	47(3)	78(4)	47(4)
O(4)	59(8)	195(15)	152(12)	44(10)	18(8)	-9(9)
C(34)	160(40)	110(20)	65(14)	48(14)	18(19)	0(30)
C(35)	57(13)	67(12)	82(14)	37(11)	22(13)	1(14)
C(36)	100(19)	120(30)	170(30)	120(30)	90(20)	80(20)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 158.

	x	y	z	U(eq)
H(1A)	5541	3569	-1958	68
H(2A)	6025	4238	-7	56
H(4A)	5273	4222	1655	41
H(6A)	4386	4240	3282	37
H(8A)	2951	5491	4045	39
H(10A)	1450	6652	4803	50
H(11A)	-724	6877	4696	65
H(12A)	-2732	5409	3377	68
H(13A)	-2555	3732	2134	57
H(15A)	-1076	2510	1438	42
H(17A)	473	1295	828	38
H(19A)	1263	1169	-856	42
H(21A)	1976	1268	-2518	62
H(22A)	3508	2123	-3202	73
H(31A)	3650	8240	2908	156
H(31B)	2231	7692	3018	156
H(31C)	3674	7860	3985	156
H(33A)	2485	10287	5272	145
H(33B)	2925	9166	5495	145
H(33C)	1485	8999	4525	145
H(34A)	579	3750	-844	181
H(34B)	-695	4250	-1328	181
H(34C)	-714	3572	-449	181
H(36A)	-106	6458	1184	149
H(36B)	-1137	5189	811	149
H(36C)	-1192	5843	-95	149

Table 6. Torsion angles [deg] for 158.

C(22)-C(1)-C(2)-C(3)	-0.5(6)
C(1)-C(2)-C(3)-C(20)	1.8(5)
C(1)-C(2)-C(3)-C(4)	-176.1(4)
C(2)-C(3)-C(4)-C(5)	177.4(3)
C(20)-C(3)-C(4)-C(5)	-0.5(5)
C(3)-C(4)-C(5)-C(18)	1.3(5)
C(3)-C(4)-C(5)-C(6)	-178.2(3)
C(4)-C(5)-C(6)-C(7)	125.7(4)
C(18)-C(5)-C(6)-C(7)	-53.8(4)
C(4)-C(5)-C(6)-C(23)	-119.8(4)
C(18)-C(5)-C(6)-C(23)	60.7(4)
C(5)-C(6)-C(7)-C(8)	-131.8(4)
C(23)-C(6)-C(7)-C(8)	113.9(4)
C(5)-C(6)-C(7)-C(16)	52.5(4)
C(23)-C(6)-C(7)-C(16)	-61.8(3)
C(16)-C(7)-C(8)-C(9)	-1.1(5)
C(6)-C(7)-C(8)-C(9)	-176.5(3)
C(7)-C(8)-C(9)-C(10)	178.1(3)
C(7)-C(8)-C(9)-C(14)	-1.0(5)
C(8)-C(9)-C(10)-C(11)	179.3(4)
C(14)-C(9)-C(10)-C(11)	-1.7(6)

C(9)-C(10)-C(11)-C(12)	1.5(6)
C(10)-C(11)-C(12)-C(13)	-0.6(7)
C(11)-C(12)-C(13)-C(14)	0.1(7)
C(12)-C(13)-C(14)-C(15)	177.8(4)
C(12)-C(13)-C(14)-C(9)	-0.4(6)
C(8)-C(9)-C(14)-C(15)	2.0(5)
C(10)-C(9)-C(14)-C(15)	-177.1(3)
C(8)-C(9)-C(14)-C(13)	-179.8(3)
C(10)-C(9)-C(14)-C(13)	1.2(5)
C(13)-C(14)-C(15)-C(16)	-179.1(3)
C(9)-C(14)-C(15)-C(16)	-1.0(5)
C(14)-C(15)-C(16)-C(7)	-1.1(5)
C(14)-C(15)-C(16)-C(17)	175.3(3)
C(8)-C(7)-C(16)-C(15)	2.2(5)
C(6)-C(7)-C(16)-C(15)	178.1(3)
C(8)-C(7)-C(16)-C(17)	-174.6(3)
C(6)-C(7)-C(16)-C(17)	1.3(4)
C(15)-C(16)-C(17)-C(18)	128.4(4)
C(7)-C(16)-C(17)-C(18)	-54.9(4)
C(15)-C(16)-C(17)-C(28)	-115.9(4)
C(7)-C(16)-C(17)-C(28)	60.7(3)
C(4)-C(5)-C(18)-C(19)	-0.1(5)
C(6)-C(5)-C(18)-C(19)	179.4(3)
C(4)-C(5)-C(18)-C(17)	-178.9(3)
C(6)-C(5)-C(18)-C(17)	0.7(4)
C(16)-C(17)-C(18)-C(19)	-125.2(4)
C(28)-C(17)-C(18)-C(19)	119.5(4)
C(16)-C(17)-C(18)-C(5)	53.5(4)
C(28)-C(17)-C(18)-C(5)	-61.8(4)
C(5)-C(18)-C(19)-C(20)	-1.8(5)
C(17)-C(18)-C(19)-C(20)	176.8(3)
C(18)-C(19)-C(20)-C(3)	2.6(5)
C(18)-C(19)-C(20)-C(21)	-175.4(3)
C(2)-C(3)-C(20)-C(19)	-179.4(3)
C(4)-C(3)-C(20)-C(19)	-1.5(5)
C(2)-C(3)-C(20)-C(21)	-1.3(5)
C(4)-C(3)-C(20)-C(21)	176.6(3)
C(19)-C(20)-C(21)-C(22)	177.6(4)
C(3)-C(20)-C(21)-C(22)	-0.5(6)
C(20)-C(21)-C(22)-C(1)	1.9(7)
C(2)-C(1)-C(22)-C(21)	-1.4(7)
C(7)-C(6)-C(23)-C(29)	-64.4(3)
C(5)-C(6)-C(23)-C(29)	179.1(3)
C(7)-C(6)-C(23)-C(24)	-177.1(3)
C(5)-C(6)-C(23)-C(24)	66.4(3)
C(7)-C(6)-C(23)-C(28)	57.5(3)
C(5)-C(6)-C(23)-C(28)	-59.0(3)
C(29)-C(23)-C(24)-O(1)	-40.2(4)
C(28)-C(23)-C(24)-O(1)	-167.1(3)
C(6)-C(23)-C(24)-O(1)	72.3(4)
C(29)-C(23)-C(24)-C(25)	142.8(3)
C(28)-C(23)-C(24)-C(25)	15.9(4)
C(6)-C(23)-C(24)-C(25)	-104.8(3)
O(1)-C(24)-C(25)-C(26)	165.2(4)
C(23)-C(24)-C(25)-C(26)	-17.8(5)
O(1)-C(24)-C(25)-Cl(1)	-8.7(5)
C(23)-C(24)-C(25)-Cl(1)	168.3(2)
C(24)-C(25)-C(26)-C(27)	1.1(5)
Cl(1)-C(25)-C(26)-C(27)	174.6(3)
C(24)-C(25)-C(26)-Cl(2)	-172.8(3)
Cl(1)-C(25)-C(26)-Cl(2)	0.6(5)
C(25)-C(26)-C(27)-O(2)	-168.9(4)
Cl(2)-C(26)-C(27)-O(2)	5.4(5)
C(25)-C(26)-C(27)-C(28)	16.3(5)
Cl(2)-C(26)-C(27)-C(28)	-169.4(2)
O(2)-C(27)-C(28)-C(30)	41.8(4)
C(26)-C(27)-C(28)-C(30)	-143.2(3)
O(2)-C(27)-C(28)-C(23)	169.0(3)
C(26)-C(27)-C(28)-C(23)	-16.1(4)
O(2)-C(27)-C(28)-C(17)	-71.1(4)
C(26)-C(27)-C(28)-C(17)	103.8(3)

C(29)-C(23)-C(28)-C(30)	1.5(4)
C(24)-C(23)-C(28)-C(30)	124.7(3)
C(6)-C(23)-C(28)-C(30)	-115.9(3)
C(29)-C(23)-C(28)-C(27)	-122.7(3)
C(24)-C(23)-C(28)-C(27)	0.5(4)
C(6)-C(23)-C(28)-C(27)	120.0(3)
C(29)-C(23)-C(28)-C(17)	118.6(3)
C(24)-C(23)-C(28)-C(17)	-118.1(3)
C(6)-C(23)-C(28)-C(17)	1.3(3)
C(16)-C(17)-C(28)-C(30)	62.3(3)
C(18)-C(17)-C(28)-C(30)	179.6(3)
C(16)-C(17)-C(28)-C(27)	176.0(3)
C(18)-C(17)-C(28)-C(27)	-66.6(3)
C(16)-C(17)-C(28)-C(23)	-59.3(3)
C(18)-C(17)-C(28)-C(23)	58.0(3)
C(24)-C(23)-C(29)-N(1)	67(4)
C(28)-C(23)-C(29)-N(1)	-165(4)
C(6)-C(23)-C(29)-N(1)	-46(4)
C(27)-C(28)-C(30)-N(2)	-101(5)
C(23)-C(28)-C(30)-N(2)	131(5)
C(17)-C(28)-C(30)-N(2)	12(5)

Symmetry transformations used to generate equivalent atoms: