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AN APPROACH TOWARD THE SYNTHESIS AND INVESTIGATION OF DI- AND TRI-BENZO-13-METHYLPHENALENE

by

Derek Warren Keith Levison

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

1995

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Abstract

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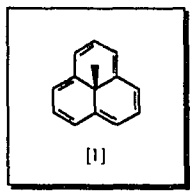
by

Derek Levison

Adviser: Professor Klaus Grohmann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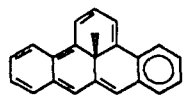
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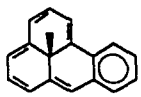
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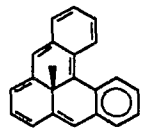
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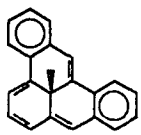
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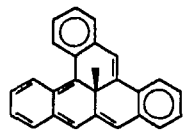
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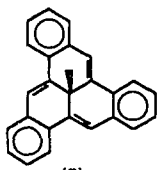
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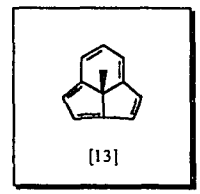
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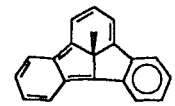
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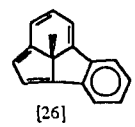
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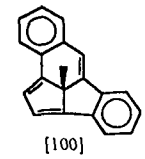
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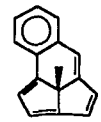
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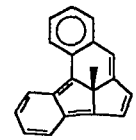
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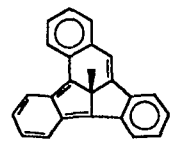
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Theoretical and synthetic investigations have been undertaken on 13-Methylphenalene, a long-sought bridged [*12*]-annulene, and its mono-, di-, and tri-benzannelated derivatives [1-7]. Using AM1 calculation methodology, the bond-dissociation energies of the central sp^3 carbon/methyl bond have been found to range from a high of 33.37 kcal/mole for [7], to a low of 1.03 kcal/mole for [3]. A trend of increasing stability of these anti-aromatic systems with respect to increasing benzannelation has been observed. Exceptions noted

are only for those derivatives which are benzannelated in an anthracene-like fashion [3, 5 and 6], whereby no resonance structure can exist in which all external benzenoid rings simultaneously contain a closed sextet of π-electrons. Transition state calculations suggest an inherent minimum barrier to dissociation of 24.36 kcal/mole for [3], and increase as high as 40.30 kcal/mole. Comparative studies of a corresponding [*10*]-annulene series, 7b-methyl-7bH-cyclopent-[*c,d*]-indene [13] and its mono-, di- and tri-benzannelated derivatives, suggest an opposite trend, with decreasing stability of the central sp^3 carbon/methyl bond upon increasing benzannelation.

Synthetic investigation of three benzannelated derivatives of 13-methylphenalene, [3], [4] and [7], have been pursued. The first approach is toward [7], the most stable derivative of the 13-methylphenalene series. This involves a simultaneous functionalization of the benzylic positions of tribenzylcarbinol, the key step being a three-fold ring-closing intramolecular Friedel-Crafts acylation. The second approach, towards [4], the second most stable derivative of this series, is based on an intramolecular Diels-Alder approach to the formation of its carbon skeleton. A novel and exciting third approach towards the synthesis of [3], the least stable and therefore the most interesting of the entire series, has been conceived, using Hart's elegant synthesis of *meta*-terphenyls. Several attempts at modification and cyclization of *meta*-terphenyls to form the as yet unknown dibenz-metacyclophane-1,3,4,6-tetraene have been undertaken. In a key step, the low-temperature (0°C) Ramberg-Bäcklund rearrangement of 8*H*,10*H*-tribenzo-[*c,ef,h*]-[*1*]-thiecine-9,9-dioxide to dibenz-6-metacyclophane-3-ene has resulted in the formation of benz[*e*]acephenathrylene only, with no observable trace of the alkene. Presumably the alkene undergoes immediate Cope-rearrangement, followed by oxidization and aromatization. This promising result suggests that the last cyclophane-allene will also be able to undergo Cope-rearrangement to form [7]. Alternate routes toward dibenz-metacyclophane-1,3,4,6-tetraene, avoiding the formation of the alkene, are proposed.

ACKNOWLEDGEMENTS

I would like to extend my first and foremost my deepest gratitudes to Dr. K. Grohmann for his support, guidance, protection, and a thorough education during my years at Hunter College of the City University of New York. I would like to also thank Drs. R. Franck (Hunter) and N. McKelvie (City College) for their time, effort, and inspiration as members of the Thesis Review Committee.

I would like to thank Dr. C. Soll for all Gas Chromatography/Mass Spectra; Dr. M. Blumenstein for his assistance and interpretation with ^{1}H NMR and ^{13}C NMR spectra, as well as all dynamic and decoupling investigations; Dr. J. J. Dannenberg for his assistance with and interpretation of AM1 results (all of Hunter College); and Dr. L. Todaro of Hoffman-La Roche Pharmaceuticals for all X-ray spectra.

I would like to thank the following for their support, advice, and good humour: Dr. S. Karimi, Dr. R. Bizanek, M. Pencak, Dr. M. Connelly, Dr. C. Alva, Dr. W. Win, Dr. T. Karydas, Dr. P. Longo, R. Benshafrut, X. Qian, K. Hagloff, R. Belgrave, and all my students.

Lastly, I would like to thank my father and mother for all they have done throughout the years in support of all aspects of my education and rearing, my brother Greg and sister Rebecca for their everlasting friendship, and especially Ulla Dahmen for her caring, thousands of miles away.

for Stuart my dad my friend

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Introduction and Summary

In order to further the understanding of antiaromaticity, attempts have been undertaken by the Grohmann group to synthesize and investigate 13-methylphenalene [1] and its mono-benzannelated derivative [2], both bridged [12]-annulenes. This investigation seeks to further these previous efforts by attempting to synthesize di- and tri-benzannelated 13-methylphenalene derivatives, with a focus on compounds [3] and [7].

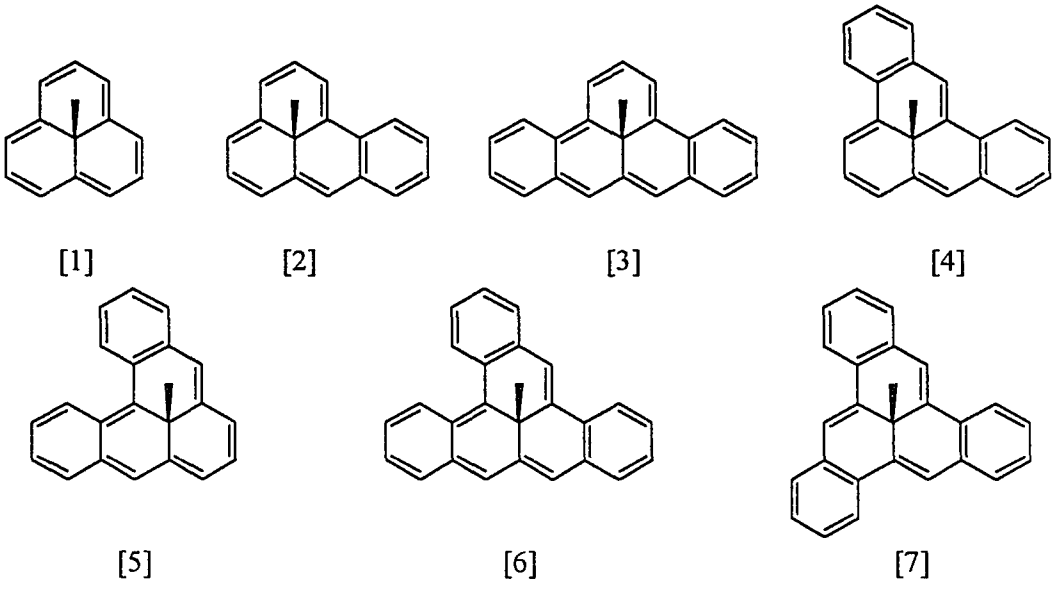


Figure 1. Target Compounds of this Investigation: 13-Methylphenalene and Selected Di- and Tri-benzo-derivatives

While several bridged [12]-annulenes have been previously investigated by other groups,[1] none of these systems contain the optimal properties for the study of paratropicity as does 13-methylphenalene. Geometry optimization of 13-methylphenalene using MM-2, AM1, and Dreiding model considerations suggest a nearly planar [12π]-perimeter, with a maximum torsional angle of 12°. The compound has a highly symmetrical propeller-type structure; the pseudo Jahn-Teller distortion should therefore be quite small, and a very strong paramagnetic ring current, if not a triplet-state, would be expected. 13-Methylphenalene and its benzannelated derivatives will be fairly rigid, regular hexagonal structures, sharing many of the advantages of 15,16-dimethyldihydropyrene for the studying of ring currents, such as reduced ring strain relative to other bridged annulenes and only small perturbations introduced by the internal sp^3-carbon bearing the methyl group. This single methyl group located within the π-electron cloud of the 13-methylphenalene series will serve as an important NMR probe for the paratropicity of the ring, and will be useful in the comparative study of the ring currents of mono-, di-, and tri-benzannelated derivatives. Taken together, these considerations make 13-methylphenalene and its benzannelated derivatives an ideal series for the study of planar, rigid [4*n*]-annulenes, one which is complementary and analogous to the Boekelheide/Mitchell [4*n* + 2] 15,16-dimethyldihydropyrene series.[2]

Additionally, this investigation seeks to establish a correlation between the calculated bond dissociation energy (BDE) of the central methyl group and a decrease in the paramagnetic ring current of the macroring. This work extends and enhances earlier theoretical studies begun by W. Huang[3] and C. Alva[4] on 13-methylphenalene and its monobenzannulated derivative. Current AM1 calculations predict an increase in the bond strength between the central sp^3-carbon and the central methyl group as 13-methylphenalene is increasingly benzannelated. Dibenzannelation in a phenanth-like configuration furthers this BDE increase, while a decrease is observed upon benzannelation in an anthracene-like configuration. Entirely opposite results are obtained upon benzannelation of an analogous [10]-annulene system, with an observed overall decrease in the calculated BDE of this aromatic $[4n + 2]$ π-system as it is increasingly benzannelated. The investigation of calculated homolytic bond dissociation energies, along with their calculated barriers of dissociation, should bring both insight toward the understanding of paratropic annulenes and be extremely useful in the selection of appropriate targets for synthetic investigation. Synthesis of one or more of the benzannelated 13-methylphenalenes will provide a direct means for the investigation of antiaromatic annulenes.

1. Theoretical Aspects of and Criteria for Aromaticity and Antiaromaticity

1.1 Definition of Aromaticity and Antiaromaticity

The concepts and definitions of aromaticity and antiaromaticity continue to present a theoretical problem of interest to the physical organic chemist. The simplest and most straight-forward example of an aromatic compound is Benzene, yet the nature of its electronic structure is still debated to this day.[5] In general, organic molecules can be divided into two broad classes of compounds: aliphatic (fatty) and aromatic (fragrant.) Aromatic compounds are distinguished from normal alkenes by their chemical, thermodynamic and electromagnetic properties. In general, they are relatively planar, ringed compounds containing alternating single and double bonds and, unlike alkenes, undergo substitution rather than addition with electrophiles. An aromatic compound also possesses enhanced thermodynamic stability relative to its corresponding open-chained polyene and must have an odd number of double bonds in the ring.[6] Planar, ringed compounds having an even number of double bonds have been observed to have a decreased stability relative to their linear open-chained form, are therefore not aromatic, and are defined as antiaromatic.[7] Taken together, both groups form a separate class of compounds which are termed annulenes.[8]

Aromatic and antiaromatic annulenes are further distinguished by their electromagnetic properties. Aromatic annulenes are diatropic and are pulled toward an electromagnet when placed within its magnetic field, while paratropic antiaromatic annulenes are pushed away from an electromagnet when placed within its magnetic field. The diamagnetic and paramagnetic characteristics of these compounds arise from the electron configuration of the double bonds in the ring. Strong diamagnetism in aromatic annulenes result from an electric circuit of paired, opposite-spin electrons, while paramagnetism results from an electric circuit of unpaired, same-spin electrons, similar to the paramagnetism observed in the oxygen molecule. The electromagnetic properties of aromatic and antiaromatic compounds may be explained and understood by the use of the Hückel molecular orbital theory.

1.2 Hückel (HMO) Theory

In 1925, Robinson coined the term "aromatic sextet" to describe the six π-electrons in benzene to explain the enhanced stability responsible for its aromatic chemical behavior.[9] Robinson was the first to symbolize the aromatic sextet by drawing a circle within the six-membered ring of benzene. Likewise, the circle came to symbolize the aromatic sextet of similar compounds such as pyrrole, thiophene, and other similar heterocycles. [Figure 2.]

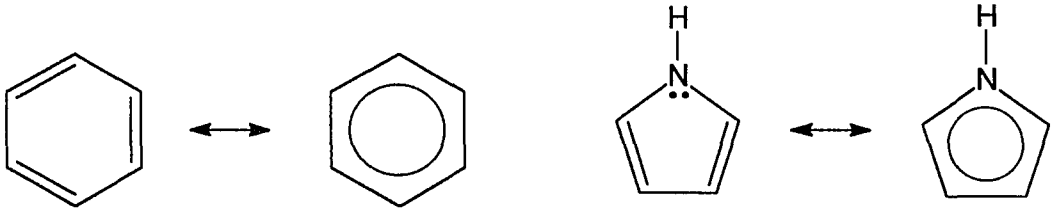


Figure 2. Aromatic Sextet of Benzene and Pyrrole

However, valence bond theory and Lewis structures do not provide an adequate description or explanation of aromaticity. Although Kekulé's[10] alternating resonance structures, which form a resonance hybrid from the three π-pairs of electrons, may account for many of the properties of aromatic benzene, they still do not explain the lack of stability and difference in chemical reactivity as observed in the antiaromatic cyclobutadiene or cycloöctatetraene. The Hückel Molecular Orbital theory (HMO)[11] was developed to explain experimental findings of why the "magic number" of 6 π-electrons in an aromatic sextet was responsible for the aromatic character of particular ringed

compounds, while 4 and 8 π-electrons were responsible for antiaromatic character. This model of the π-electron system was determined by using the approximation that the σ-electrons were localized and could be treated separately from the π-electrons. All electronic interactions (overlap integrals) other than those between adjacent atoms are also neglected. The reason for this approximation is clear; the matrix determinants required for these calculations are extremely complicated to solve without most of the matrix elements (those representing overlap integrals, $*ij$, on non-adjacent carbons) assuming a value of zero.

$$\begin{vmatrix} x & * & * & \cdots \\ * & x & * & \cdots \\ * & * & x & \cdots \\ \cdots & \cdots & \cdots & \end{vmatrix} = 0$$

Equation 1

where $x = \dfrac{\alpha - E}{\beta}$, $E = \alpha - x\beta$ and $*ij = 0$ if $i \neq j$ $*ij = 1$ if $i = j$

The Energy levels of each molecular orbitals (MO) are given in terms of ß units, the Hamiltonian integral representing the interaction energy between two p-orbitals, each on a carbon which are directly bonded to each other. This is roughly equal in energy to a π-electron in an ethylene bonding molecular orbital.[12] α is the energy of an electron in a basis orbital with no interactions. Although the assumptions made are not completely accurate and lead in some cases to unreliable results, the HMO theory's predictive power remains quite impressive, as it is able to qualitatively account for both aromatic, non-

aromatic and antiaromatic behavior, including that of systems such as cyclopentadiene anion and the tropylium cation.

The aromatic or antiaromatic character of any simple annulene may be described by comparing the π-orbital energies and MOs of an open-chained conjugated polyene with its corresponding closed conjugated polyene. As an example, consider butadiene and cyclobutadiene [Figure 3]:

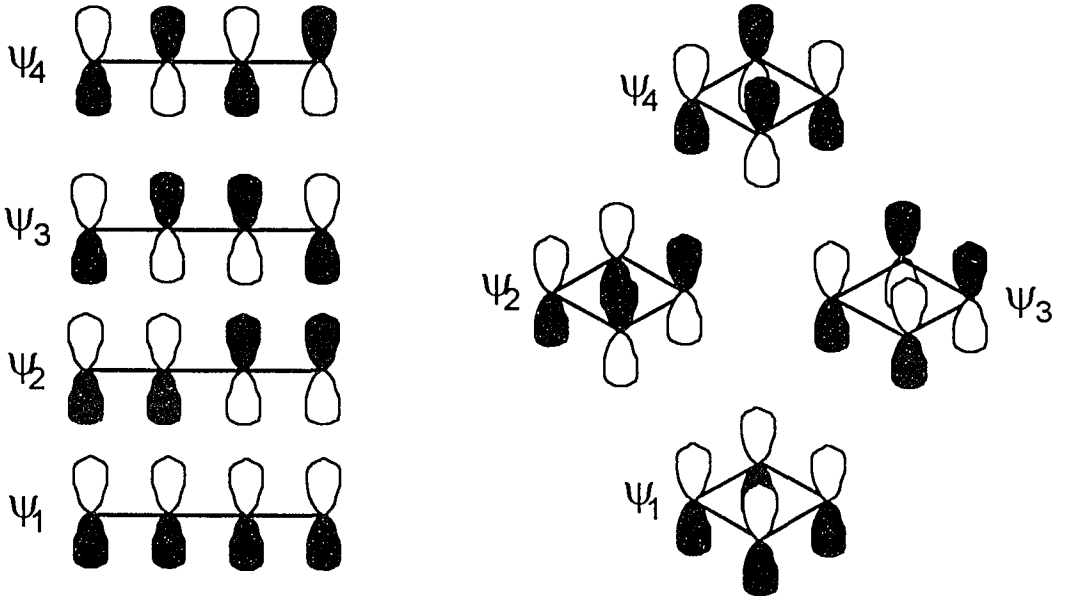


Figure 3. The molecular orbitals of butadiene and cyclobutadiene.

The four π atomic orbitals (basis orbitals) of butadiene are combined to form four molecular orbitals using the linear combination of atomic orbitals (LCAO) approximation. Each MO is ordered in terms of increasing energy and increasing number of nodes; the

lowest-energy MO, Ψ_1, having zero nodes, the next MO, Ψ_2, one node, and so on. Two adjacent basis orbitals having the same sign on top and bottom symbolize a bonding interaction between the two atoms; two adjacent basis orbitals having differing signs indicate the presence of a node or an antibonding interaction. Nodes are regions of zero electron density and are recognized by a change in sign of the wave function between two carbons, here represented by the grey or white color of the lobes of the π basis orbitals.

In order to obtain the MOs of cyclobutadiene, the ends of the open-chained polyene are brought together for each MO, any new nodes arising from the formation of the ring are noted, and the new MOs are ordered from lowest to highest energy. For example, the Ψ_2 MO of cyclobutadiene forms a new node by the attachment of the ends of the Ψ_2 of butadiene, for a total of two nodes. The Ψ_3 MO of cyclobutadiene does not form a new node by the ring formation and remains with two nodes. Ψ_2 and Ψ_3, having the same number of nodes, form a degenerate pair of MOs. With benzene, two pairs of degenerate MOs are created. By adding electrons into the MOs according to the Aufbau principle and following Hund's rule, it is found that for benzene, the HOMO (consisting of a degenerate pairs of bonding MOs) is completely filled, whereas for cyclobutadiene, the HOMO in the ground state is a degenerate pair of non-bonding half-filled MOs, forming a diradical. [Figure 4.] The conclusions of HMO theory are summarized by the Hückel Rule.

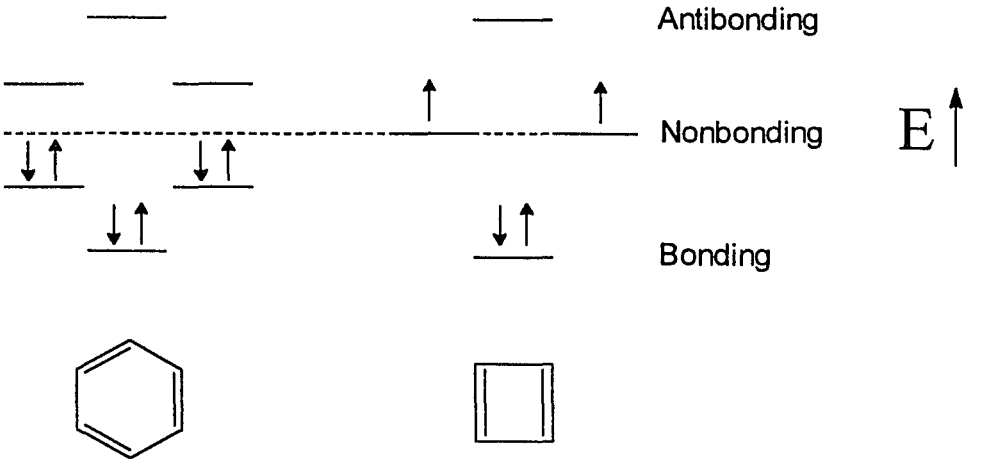


Figure 4. Benzene and Cyclobutadiene HMO π-Electron Energies

The Hückel Rule predicts that planar, cyclic, conjugated polyenes (annulenes) containing [4*n* + 2] π-electrons (*n* = 0, 1, 2..) are aromatic, while those containing [4*n*] π-electrons are antiaromatic. A cyclic compound which is either not planar, or has one or more points of saturation in the ring preventing cyclic conjugation of all π-electrons is defined as non-aromatic. Annulenes are predicted to be aromatic provided they are reasonably planar, contain [4*n* +2] out-of-plane π-electrons, and have a ring-size that is below a certain limit of about 30 carbons,[13] while a triplet configuration is predicted for all planar and symmetric annulenes possessing a [4*n*] number of π-electrons. Based on HMO theory, all aromatic annulenes are predicted to exhibit diamagnetism and all antiaromatic annulenes are predicted to exhibit paramagnetism.

1.3 Planarity and the Pseudo Jahn-Teller Effect

Planarity is an important requirement for the π-system conjugation in aromatic and antiaromatic ring circuits. It allows maximum overlap of the π-orbitals and results in maximum resonance energy for the annulene systems, be it a positive or negative gain. For aromatic [4*n* + 2] systems, this corresponds to a flattening of the ring sometimes at the expense of increased strain or steric crowding, as is observed with [10]-annulene and in many bridged systems. Conversely, [4*n*]-annulenes are likely to bend or twist out of plane in order to avoid the destabilization associated with the triplet ground state that exists as a consequence of planarity. Loss of conjugation localizes the π-system into alternating double and single bonds, distorting the ring system and thereby decreasing the symmetry of the molecule.[14] This distortion causes the removal the degeneracy of the two HOMOs by a process known as the pseudo Jahn-Teller effect.[15] [Figure 5.]

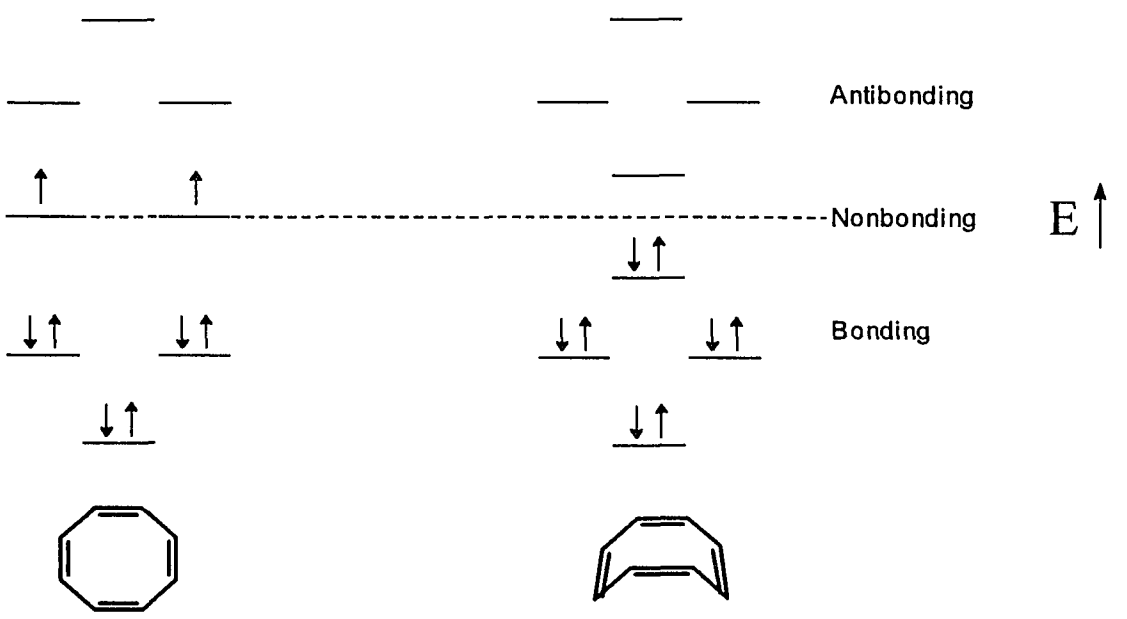
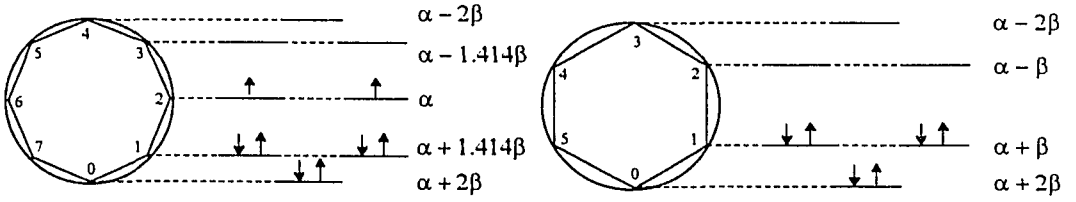


Figure 5. HMO of Cycloöctatetraene and the Pseudo-Jahn-Teller Effect.

Cycloöctatetraene,[16] [12]-annulene,[17] and [16]-annulene[18] are found experimentally to be twisted out of planarity and to contain alternating double and single bonds. Cyclobutadiene, unable to twist itself far from planarity, is highly unstable and therefore experimentally elusive, being isolated only in a frozen argon-matrix at 10 K.[19]

1.4 Resonance Energy

The difference in π-electron energy between a conjugated C_nH_n ring and an open-chain C_nH_{n+2} conjugated polyene is known as the resonance energy. For aromatic, [$4n$ + 2] annulenes, the resonance energy is positive and the compounds are stabilized relative to the open-chained compound. For [$4n$] annulenes, the resonance energy is negative and the compounds are destabilized. A simple, geometrical description of annulenes and their resonance energies is accomplished by the method of Frost and Musulin.[20] [Figure 6.]



$$\Delta E_{cyclooct.} = \left[2(2\beta) + 4(\sqrt{2}\beta)\right] - 8\beta = 1.656\beta \qquad \Delta E_{benzene} = \left[2(2\beta) + 4\beta\right] - 6\beta = 2\beta$$

Figure 6. Frost and Musulin Diagrams of Cycloöctatetraene and Benzene

Without the solving of many secular determinants, a similar result as HMO theory is obtained by inscribing a regular polygon in a circle of radius 2ß with the center at zero of the vertical energy axis and a vertex of the polygon at the lowest MO energy level. ß is the energy of one electron in an ethylene π-orbital, that is, it represents the energy of an

electron in a molecular orbital derived from a pair of adjacent, bonded basis orbitals. The heights of all vertices of the polygon are the same as the energy of each MO. The π-electron energy of each orbital is determined by the formula:

$$E_j = \alpha + 2\beta \cos\left(\frac{2\pi}{N} J\right) \quad J = 0,\ 1,\ 2,\ldots,\ N-1. \qquad \textbf{Equation 2.}$$

where each vertix is numbered J, starting from the lowest vertix $J = 0$; α is the energy of an electron in a basis orbital with no interactions; an isolated π-orbital in this approximation. The total energy of the individual electrons in the molecular orbitals is simply $N\beta$, and by subtracting this energy from the total π-electron energy contributions, E_π, the Hückel delocalization energy (DE) is obtained. As a reference, cyclobutadiene is calculated to have a Hückel DE of 0 ß, cycloöctatetraene 1.66 ß, and benzene 2 ß.

1.5 Dewar Resonance Energy

The Hückel DE overestimates the amount of stabilization energy, especially of the [4*n*] antiaromatic compounds, which are calculated by the HMO method as having reduced DE rather than negative stabilization, as is observed experimentally with cyclobutadiene. A further refinement of the Hückel DE is the Dewar Resonance Energy (DRE),[21] which is based on a combination of the perturbational molecular orbital theory (PMO) of Longuet-Higgins[22] and the Self-Consistent Field Molecular Orbital method of Pople.[23] The DRE gives a more accurate description for the [*n*]-annulenes, showing destabilization and antiaromaticity for the [4*n*]-annulenes and stabilization and aromaticity for the [4*n* + 2]-annulenes. [Figure 7.]

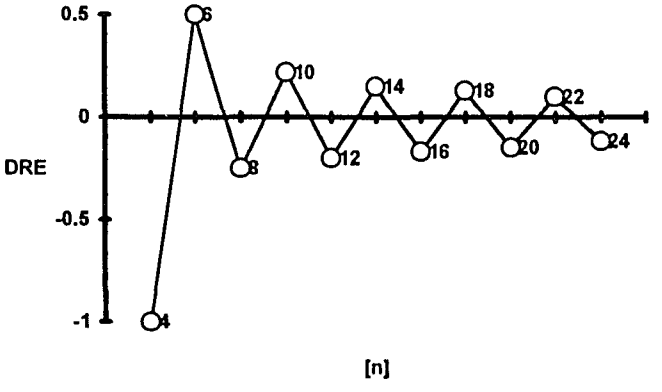


Figure 7. Dewar Resonance Energies (DRE) for [*n*]-annulenes[24]

1.6 Ab initio and Semi-Empirical Calculation Methods

A fundamental difficulty in the attempt to solve the Schrödinger equation for larger molecules is the exceptionally large number of two-electron integrals which must be calculated. Propane, for example, requires 38,226 two-electron integral calculations (although many may be neglected due to symmetry considerations.)[25] These overlap integrals, principally electron-electron repulsion interactions called exchange integrals, consist of two-center charge-distribution functions and may be approximated in several ways. The simplest, CNDO[26] (Complete Neglect of Differential Overlap) treats electron-electron repulsion very approximately, ignoring most of the exchange integrals. Other treatments, such as INDO (Intermediate NDO) and MINDO[27] (Modified INDO) correct many of the severest problems arising from the approximations of CNDO. AM1, the Austin Model 1, is a modified version of the MNDO[28] (modified neglect of diatomic overlap) and, generally speaking, is usually one of the most accurate of the semi-empirical computational methods. It includes the extra corrections of INDO and MINDO, plus additional electron-electron repulsion integrals.[29]

1.7 Nuclear Magnetic Resonance Spectroscopy

Another important criteria for the determination of aromaticity and antiaromaticity is through the use of Nuclear magnetic resonance spectroscopy (NMR.) The strong diamagnetism or paramagnetism of annulenes, resulting from the ability of annulenes to sustain a ring current[30] of circulating electrons in their π-systems, is easily detected by NMR. This method allows the easy, convenient study and identification of these compounds, and NMR has become an important tool for routine classification of numerous compounds as aromatic or antiaromatic.[31]

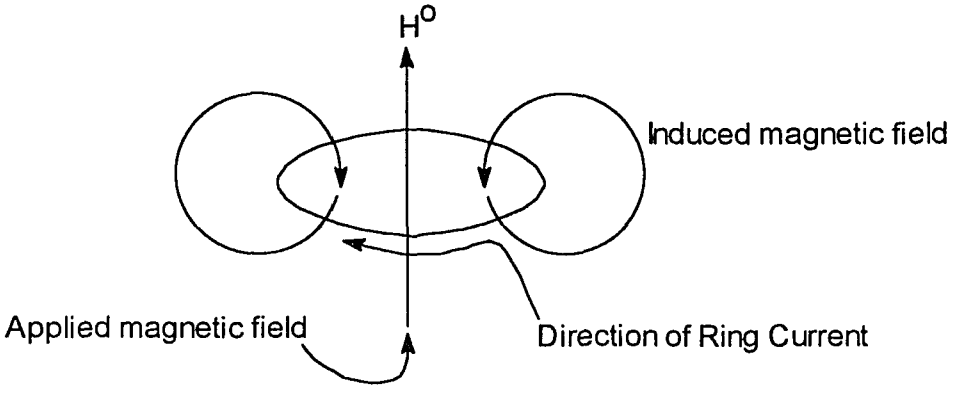


Figure 8. Representation of an induced Ring Current and induced Magnetic Field of an Annulene by an applied Magnetic Field

As an analyte is placed within a magnetic field, an electric ring current is induced within the annulene π-system. This tiny circuit in turn creates its own magnetic field, one which is in opposition to the applied field. The induced magnetic field is anisotropic, stronger in

one direction than in another. With [4*n* + 2] systems, the point of opposition to the applied field is at the center of the ring (diamagnetic anisotropy), while in the region outside of the ring the applied magnetic field is reinforced. In [4*n*] systems, these directions of opposition to the magnetic field are reversed (paramagnetic anisotropy.) The chemical shift of nearby atoms is thus determined by their orientation with respect to the π-bonds in the ring. In [4*n* + 2] systems, this means that hydrogens located on the outside of the ring come into resonance downfield at about 1.5-2.00 ppm from the corresponding olefinic signal (ethylene δ = 5.28 ppm), while any interior hydrogens, such as those found on [18]-annulene, are shifted substantially upfield.[32] In antiaromatic annulenes, the situation is reversed. For example, [12]-annulene has a temperature-dependent ^{1}H NMR of two bands at δ = 7.83 (3H, inner three protons) and 5.88 (9H, nine outer protons) measured at -170°C.[33]

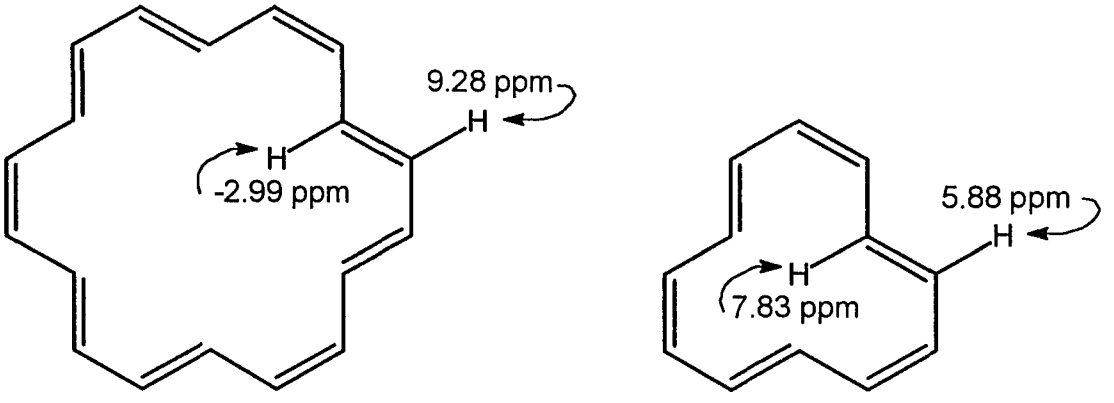


Figure 9. Shielding and Deshielding Effects of [4*n*+2]- and [4*n*]-annulenes.

1.8 Benzoannulenes and Local Aromaticity

Ring currents can be significantly reduced by the fusion of one or more benzene rings with an [*n*]-annulene. Benzannelation has been shown to reduce the diatropicity or paratropicity of the ring by both reducing the symmetry of the molecule and enhancing bond localization of the π-system. This also effects pseudo Jahn-Teller distortion, whereby aromatic systems will be destabilized by the increased bond-alternation, and antiaromatic systems will be stabilized by increased bond-alternation. The degree of perturbation also depends on the point of annelation,[34] as in the observation of the increased aromatic character of phenanthrene over anthracene. Simple resonance structures show that phenanthrene may contain up to two aromatic sextets among three rings, while in anthracene there is a maximum of only one aromatic sextet. [Figure 10.] This was first described in quantitative quantum-mechanical terms by Polansky and Derflinger,[35] and later by several other authors.[36] It has also been demonstrated through calculations that the aromaticity of benzoannulenes is characterized more by the separate contributions of each ring rather than that of the entire π-system periphery.[37]

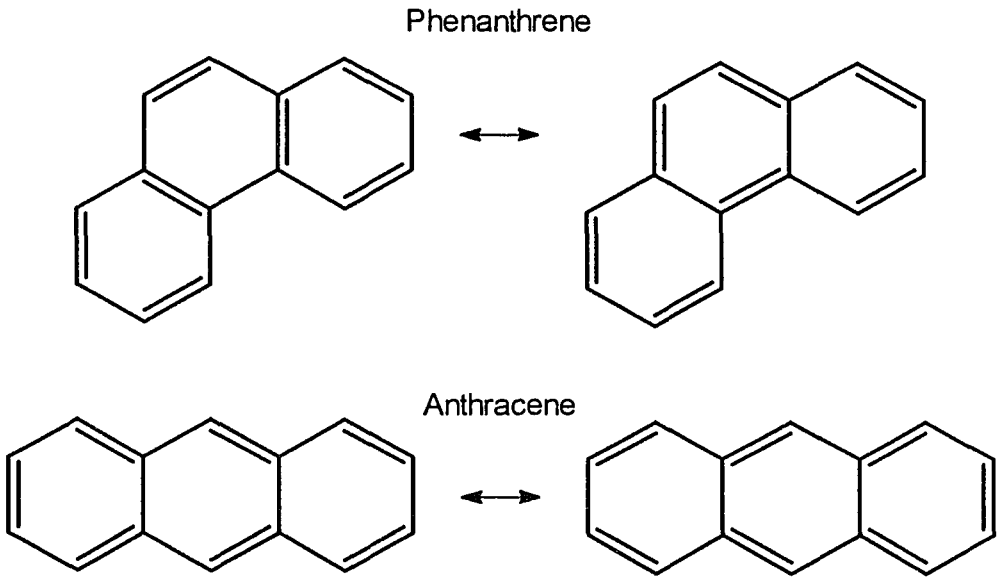


Figure 10. Resonance structures of Phenanthrene and Anthracene

Another interesting probe into the π-electronic structure of benzo-[*n*]-annulenes can also be determined by examination of experimentally obtained NMR vicinal coupling constants.[38] The Günther alternance parameter, Q, allows the differentiation between aromatic [4*n* + 2] π-systems and antiaromatic [4*n*] systems. Q is a ratio of the π-bond orders in the benzo-fused ring of a benzo-[*n*]-annulene, where the π-bond orders are related to the experimentally determined vicinal $^{3}J_{H\text{-}H}$ coupling constants by the equation:

$$P_{\mu,\nu} = (0.104)\ {}^{3}J_{\mu,\nu} - 0.12 \qquad \textbf{Equation 3}$$

where $P_{\mu,\nu}$ is the bond order between H atoms μ and ν, and $Q = P_{\mu',\nu'} / P_{\mu'',\nu''}$. Annulenes may be classified into three groups based on their Q-value: delocalized [$4n$] π-systems ($Q < 1.04$), delocalized [$4n + 2$] π-systems ($Q > 1.10$), and localized π-systems ($1.04 < Q < 1.10$.) The results obtained from Q-values are in close agreement with experimental results and those derived from SCF calculations.[39]

$$Q^1 = \frac{8.28 \times 0.104 - 0.12}{6.85 \times 0.104 - 0.12} = 1.252 \qquad Q^2 = \frac{6.89 \times 0.104 - 0.12}{8.23 \times 0.104 - 0.12} = 0.811$$

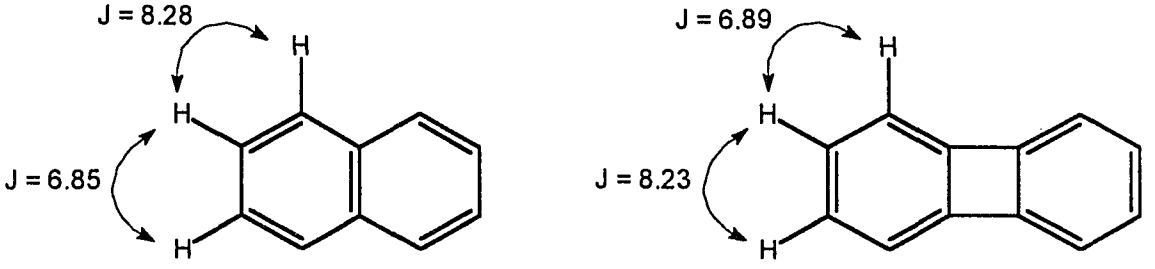


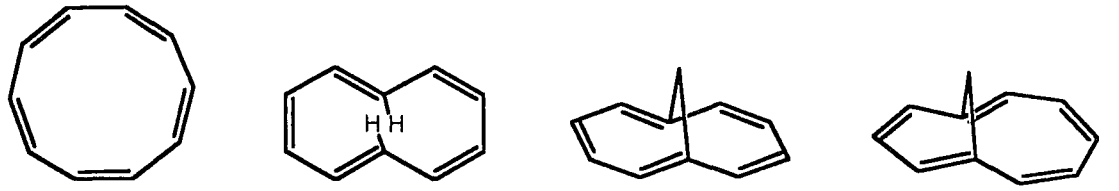
Figure 11. Q-values for Naphthalene (benzo[6]annulene) and Biphenylene (benzo[4]annulene.)[40]

Antiaromatic character is also found to be reduced by benzannelation. For example, biphenylene, a dibenzannelated derivative of cyclobutadiene, is a stable crystalline compound with a melting point of 110-111°C. [12]-annulene is also a very thermally unstable compound, while its derivative tribenz-[12]-annulene is a crystalline solid. NMR studies on dibenzo-[12]-annulenes suggest that with two benzene rings there is still greatly reduced paratropicity, although some [12]-annulene character is shown to remain.[41]

1.9 Bridged Annulenes

1.9.1 [10]-annulenes

Although all [4n + 2]-annulenes are predicted to be aromatic, other constraints may either outweigh any energy-lowering due to bond delocalization or prevent it altogether. For example, the *all-cis* isomer of [10]-annulene [8], with bond angles of 144°, suffers from too much strain energy and is found to have properties similar to a polyolefin.[42] Likewise, the *di-trans* isomer of [10]-annulene [9] would contain substantial steric strain caused by internal H-H repulsion, and has not been isolated.

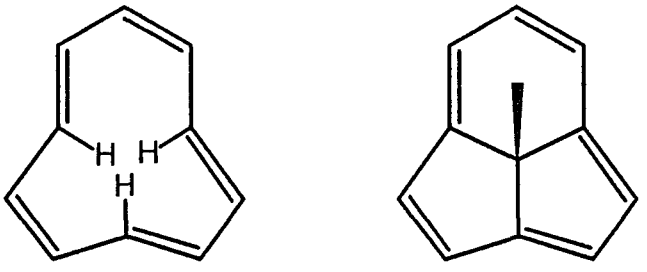


all-cis-[10]-annulene [8] *di-trans*-[10]-annulene [9] 1,6-methano-[10]-annulene [10] 1,7-methano-[10]annulene [11]

Figure 12. Comparison of isomers of [10]-annulene with two bridged [10]-annulenes

The best strategy to eliminate internal hydrogen-hydrogen repulsion, to reduce conformational mobility, and to force π-systems into (near) planarity involves the introduction of bridges inside the π-perimeter of [*n*]-annulenes. Vogel's bicyclic

compound [10], 1,6-methano-[10]-annulene [Figure 12], first achieved this goal by replacing the 1,6-hydrogens with a methylene bridge, which removed the distortion caused by the 1,6-hydrogen interaction and allowed the ring periphery to become almost planar. The ^{1}H-NMR spectrum revealed a singlet at -0.5 ppm, representing the methylene hydrogens, and a multiplet of the eight olefinic hydrogens between 6.8-7.5 ppm. The downfield shift of the ring hydrogens, the shielding of the interior protons on the bridge, and the fact that the NMR spectra was temperature-independent indicated that a diamagnetic ring current was present.[43] Scott's somewhat more unstable 1,5-methano-[10]-annulene [11] has a proton NMR shift of -1.23 and -0.74 ppm for its two internal hydrogens.



"tri-trans"-[10]-annulene [12] Rees (1981) [13]

Figure 13. Comparison of the Hypothetical *tri-trans*-[10]-Annulene and a Bridged Version

Another example, Rees' tricyclic compound 7b-methyl-7bH-cyclopent-[c,d]-indene [13], is a methine-bridged *tri-trans*-[10]-annulene. This compound exhibits an induced diamagnetic ring current with an internal methyl group NMR spectrum at -1.67 ppm (3H) and external hydrogens between 7.53-7.92 ppm (7H.)[44]

1.9.2 [12]-annulenes

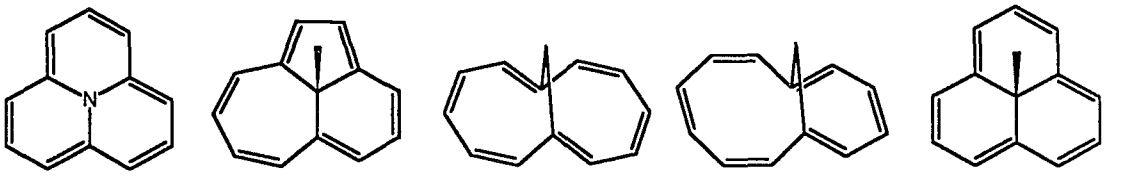


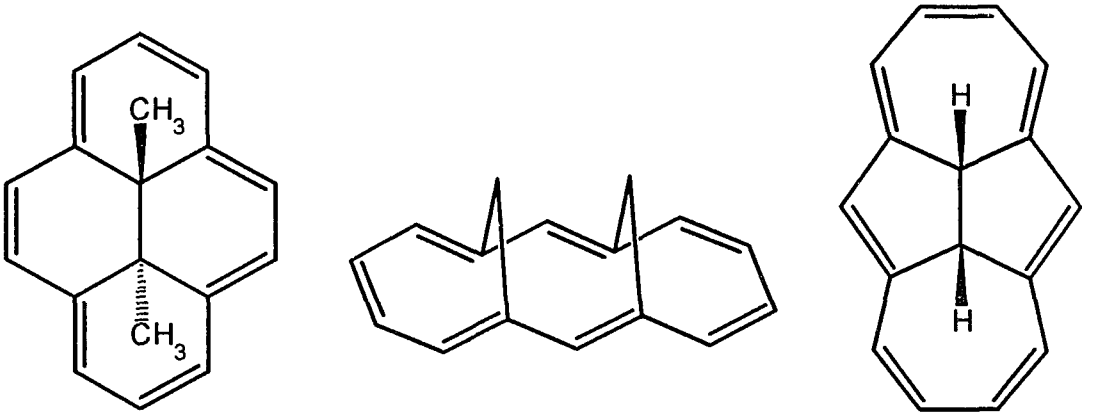
Figure 14. Selected bridged [12]-annulenes

The introduction of bridges to reduce conformational mobility and to force the π-system towards planarity has also been successful with [12]-annulene. Leaver's[45] [3.3.3]-cyclazine [14] is a nitrogen-bridged [12]-annulene exhibiting NMR proton resonances at 3.65 ppm (3H) and 2.07 ppm (6H.) The external protons are shielded relative to ethylene, demonstrating the presence of an induced paramagnetic ring circuit, and the compound is considered antiaromatic. However, there are no internal hydrogens. Hafner's[46] compound [15], 9b-methyl-9bH-benzo[cd]azulene, exhibits a substantial downfield shift to 4.75 ppm for the internal methyl group, while the external perimeter protons are shifted upfield in a range between 3.88-4.69 ppm. The first all-carbon tricyclic [12]-annulene, this compound undergoes a presumed [1,5] sigmatropic methyl shift quantitatively within 15 minutes upon reflux in xylene. Vogel's[47] compound [16], 1,7-methano-[12]-annulene, has a ^{1}H-NMR spectrum of 6.0 ppm for the methylene bridge (2H) and 5.2-5.5 ppm for the external

hydrogens on the ring periphery (10H.) The NMR spectrum is in opposition to that of 1,6-methano-[10]-annulene, showing paratropicity and bond alternation below -60°C. 1,6-Methano-[12]-annulene [17],[48] also by Vogel, has been shown by NMR analysis of its proton coupling constants to exist exclusively as the valence tautomer shown above.

One compound which would be highly symmetrical, rigid, and planar is the bridged tricylic-[12]-annulene 13-methylphenalene [1]. High symmetry, rigidity and planarity of this compound would allow degeneracy of the HOMO, may prohibit any significant pseudo Jahn-Teller distortion and, as a result, would exhibit extremely strong paramagnetism. This interior methyl group would be predicted to be extremely deshielded and the external protons would resonate far upfield, even more dramatically than the [12]-annulenes shown.

1.9.3 [14]-Annulenes



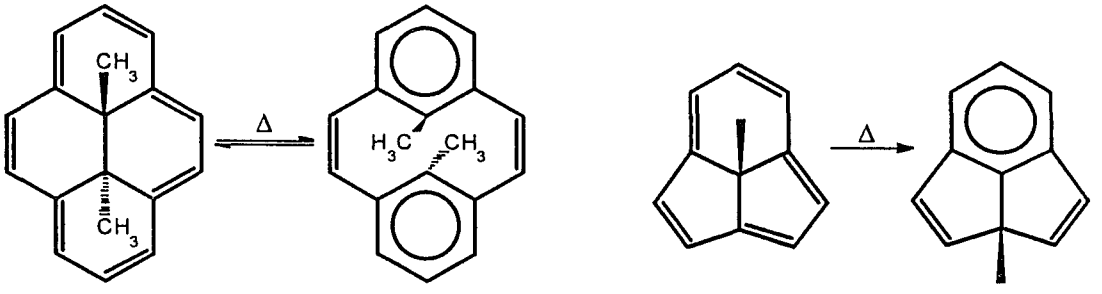
Boekelheide (1967) [18] Vogel (1975) [19] Vogel (1972) [20]

Figure 15. Selected bridged [14]-annulenes

Bridging of [14]-annulene has also been investigated with similarly successful results as [10]- and [12]-annulene. Boekelheide's compound [18], trans-15,16-dimethyldihydropyrene,[49] is a doubly carbon-bridged [14]-annulene, with an internal methyl proton NMR resonance at -4.25 ppm (6H, singlet) and external protons coming into resonance between 7.98 and 8.67 ppm (12H.) This compound was the first example of an aromatic annulene having a substituent other than hydrogen within the cavity of the π-electron ring. The six protons of the two methyl groups are substantially shielded, indicating a strongly induced diamagnetic ring current. Vogel's compound [19],[50] *syn*-1,6:8,13-bismethano-[14]-annulene, has internal protons at -1.2 (2H) and 0.9 (2H) ppm, corresponding to the outward- and inward-pointing hydrogens on the methylene bridges,

respectively. The external protons come into resonance between 7-8 ppm (10), all together indicating a diatropic aromatic π-system. 1,6:8,13-Ethanediylidene-[14]-annulene [20],[51] another of Vogel's [14]-annulenes shown in this series, is similar, having internal ethyl bridge protons at -1.2 ppm (2H) and external proton resonances between 7.82-8.17 ppm (10H.)

The [14]-annulenes shown in Figure 15 all exhibit strong diamagnetism and aromatic character directly as a result of the carbon-bridges. The carbon-bridges impose rigidity, symmetry to the π-system and causes only small deviations from planarity, allowing maximum overlap and conjugation of the π-orbitals, all of which is not observed in the corresponding unbridged [14]-annulenes. Furthermore, the bridged [14]-annulenes have a slight advantage over the bridged [10]-annulenes in that there is somewhat less strain energy due to the larger ring size. This is especially true in the comparison of chemical reactivity between Rees' compound [13] with Boekelheide's compound [18.]



[18] [18b] [13] [13b]

Figure 16. Thermal rearrangements of selected bridged [4n+2]-annulenes

Although both [4n + 2] compounds undergo characteristic aromatic substitutions such as nitration and acylation, upon heating at 70°C Boekelheide's compound [18] will reversibly rearrange to the metacyclophane [18b], while Rees' compound irreversibly rearranges through a [1,5] sigmatropic shift to the 2aH isomer [13b] at 138°C.[52] At 200°C, Boekelheide's [18] also undergoes a similar [1,5] sigmatropic rearrangement.[53] Relief of strain energy could account for this difference.

1.9.4 Bridged Annulene Dianions

The importance of the effect of ring currents on the chemical shifts of both internal and external protons of annulenes is reflected by the large chemical shift differences between these annulenes and their respective dianions.

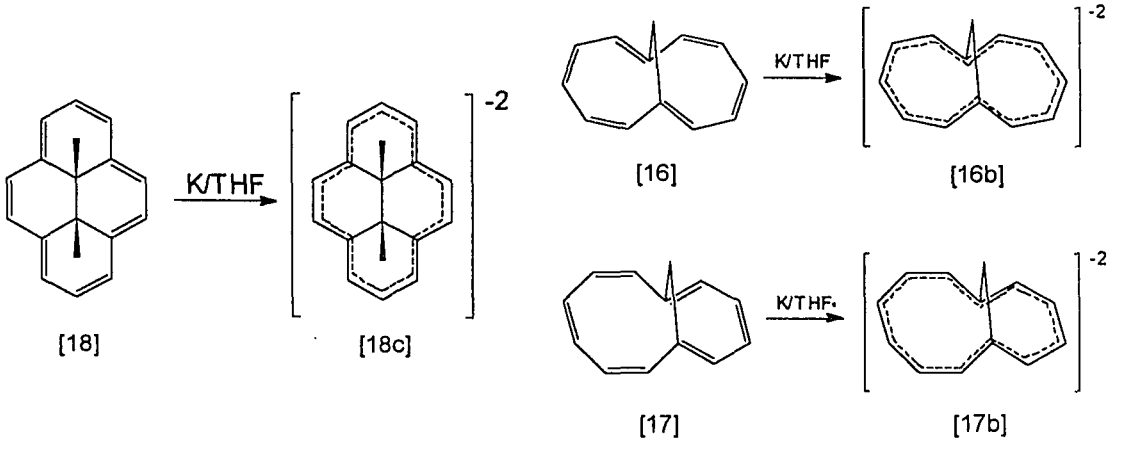


Figure 17. Dianions of Selected Bridged Annulenes

The dianion of *trans*-15,16-dimethyldihydropyrene [18c] was obtained by reduction with potassium in tetrahydrofuran. The diamagnetic ring current of the parent compound [18] is converted into a paramagnetic ring upon the introduction of two additional electrons, and the effect upon the proton NMR spectra is dramatic. The internal methyl groups of [18] are shifted from -4.25 ppm to about +21 ppm, the greatest δ value that has been so far observed for a carbon proton. The external protons are shifted from a range of +7.95 through +8.67 ppm to -3.19 through -3.96 ppm.[54] The dianions of 1,6- and 1,7-methano-[12]-annulene have also been investigated.[55] Proton NMR of the dianion of 1,6-methano-[12]-annulene [16b] at -80°C (THF, d_8) reveal a shift of -6.44 ppm for the methano-bridged protons and a range of 6.28 to 7.16 ppm for the external protons. These values clearly indicate a diamagnetic ring current and consequently aromatic character. Similarly, the bridged protons of the dianion of 1,7-methano-[12]-annulene [17b] come into resonance at -6.08 and -5.52, while the external protons are at a range of +6.51 to 7.56 ppm. It is interesting to note that the chemical shift difference between the protons on the bridge of the dianion (0.44 ppm) is much smaller than that of the parent compound [17] (4.7 ppm) suggesting a significant reduction in the bond localization over the parent compound.

1.10 Bridged Benzoannulenes

The observation of the effects of the benzannelation of [*n*]-annulenes on the ring currents of these systems is complicated by angle strain, steric interactions, and, especially in 4*n* systems, a lack of planarity. Because bridged annulenes are rigid, they are less prone to torsional distortion and have a relatively planar π-electron perimeter. They also contain an interior methyl group, within the π-electron cavity, which is useful as an NMR probe for the evaluation of changes in the ring currents. As a consequence, the fusing of a benzene ring on a bridged annulene is free from the interferences associated with the unbridged π-systems, and should provide a clearer picture of its effect upon ring currents of annulenes than from benzannelation of unbridged systems. Furthermore, the increased effect of the fusion of two or even three benzene rings upon the π-system may be investigated. The separate fusing of two benzene rings at key locations on the annulene perimeter can have varying effects. For example, one of either enhanced interference in the π-system, or an effective canceling of any interference at all.

1.10.1 Benzo-[10]-annulenes

The Benzannelation of 1,6-methano-[10]-annulene [10] by Vogel's[56] group shows a greatly reduced diamagnetic ring current, with the two protons of the methylene bridge serving as a convenient NMR probe. The internal protons of 2,3-benzo-1,6-methano-

[10]-annulene [21] are shifted downfield relative to the parent compound, from -0.5 ppm to 1.9 and 0.5 ppm. Considering that the methylene group of norboradiene [22] is 2.0 ppm[57], it appears as if benzannelation of this compound may completely localize the double bonds of the π-system.

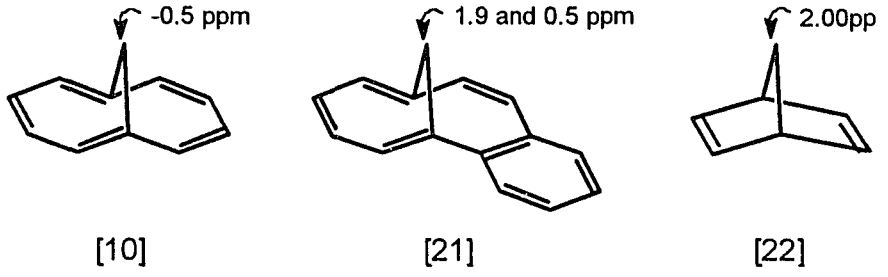
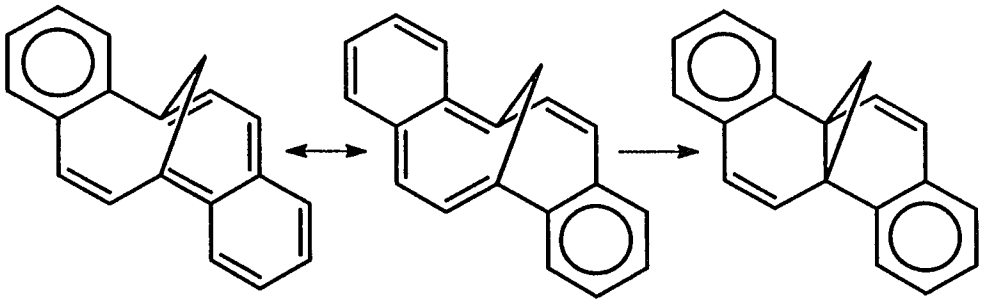


Figure 18. Benzannelated 1,6-methano[10]annulene [21]

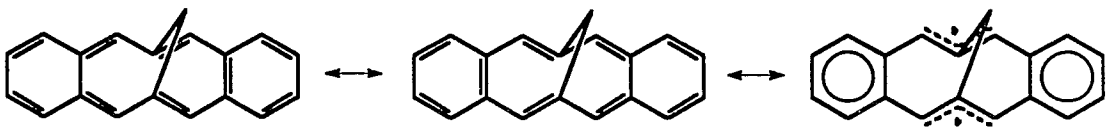
The ring system of the *anti*-dibenzannelated compound of 1,6-methano-[10]-annulene [23] has been shown to not only have a reduced ring current, but to forfeit its aromaticity entirely. Kekulé structures show that when this bridged annulene is fused with two benzene rings in an *anti*-configuration, one and only one may be benzenoid. This is analogous to the Anthracene model. One additional resonance structure, the norcaradiene structure having two benzenoid rings, a central cyclopropane bridge and no [10]-annulene ring system, has been synthesized by Hill.[58] This was the first example in which an aromatic annulene has been forced to give up its aromaticity after benzannelation.



[23] [24]

Figure 19. Dibenzannelated 1,6-methano[10]annulene [23]

An interesting system to be investigated would be the as yet unknown *anthra*-dibenz-1,6-methano-[10]-annulene [25]. The positioning of the two benzenoid rings in this fashion would not allow a single resonance structure in which both benzenoid rings would have a closed sextet of π-electrons, without the formation of two allyl radicals. In contrast to the above system, this would likely lead to either a very small reduction or even an enhancement of the aromatic character of this system.



[25] [25a]

Figure 20. *anthra*-Dibenz-1,6-methano[10]annulene [25]

Rees has investigated the effects of benzannelation on his 7b-methyl-7b-cyclopent-[c,d]-indene [13].[59] The central methyl group of the benzannelated [10]-annulene [26] resonates at ppm -0.79, which is shifted downfield almost 0.9 ppm from the resonance of the parent compound, at -1.67. A 67% reduction in the diamagnetic ring current from the parent compound [13] has thus been estimated, based on the comparison of the difference of the upfield shifts of the central methyl groups relative to that of a model compound, δ = +1.01, according to the following equation:

$$\text{Residual ring current} = \frac{1.01-(-0.79)}{1.01-(-1.67)} = 0.67 \qquad \textbf{Equation 4}$$

The observed coupling constants of the benzenoid ring give a Günther alternance parameter (Q) value of 1.166. For comparison, benzo-[10]-annulene has a Q-value of 1.21 and benzo-[14]-annulene has a Q-value of 1.15.[60] All three compounds are therefore classified by their Q-values as delocalized [4n +2] π-systems (Q > 1.10.) X-ray analysis shows increased bond length alternation between single and double bonds of the π-system relative to the parent compound [13]. The benzannelated [10]-annulene [26] also undergoes [1,5] methyl shift upon heating at a lower temperature than the parent compound [13]. No analogous dibenzannelated compounds are as yet known.

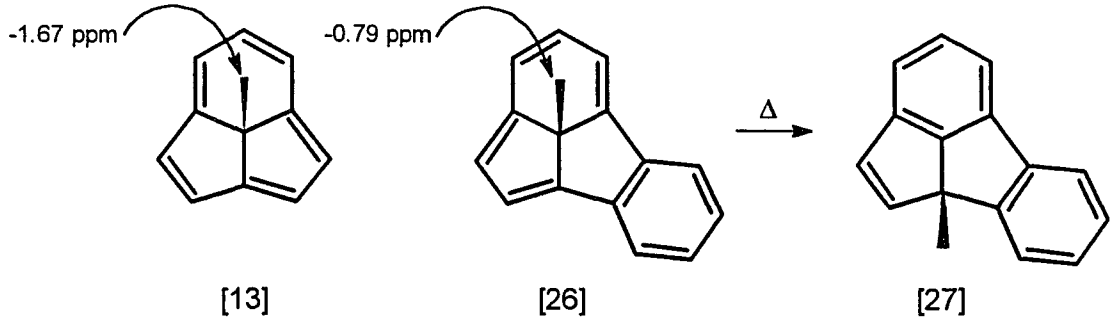
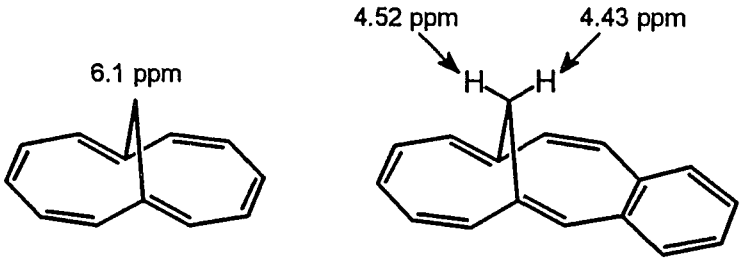


Figure 21. Benzannelated 7b-methyl-7b-cyclopent-[c,d]-indene [26]

1.10.2 Benzo-[12]-annulenes

Scott has synthesized the benzannelated derivative of 1,6-methano-[12]-annulene [16].[61] The bridge protons within the π-system are shifted upfield relative to the parent compound while the ring protons are shifted slightly downfield. Based on a value of 2.2 ppm for the methylene protons of an atropic system, it is predicted that 3,4-benzo-1,7-methano-[12]-annulene [28] sustains 50-60% of the ring current of the parent compound, which is roughly equal to the reduction caused by benzannelation in the ring current of Rees' bridged [10]-annulene [13].

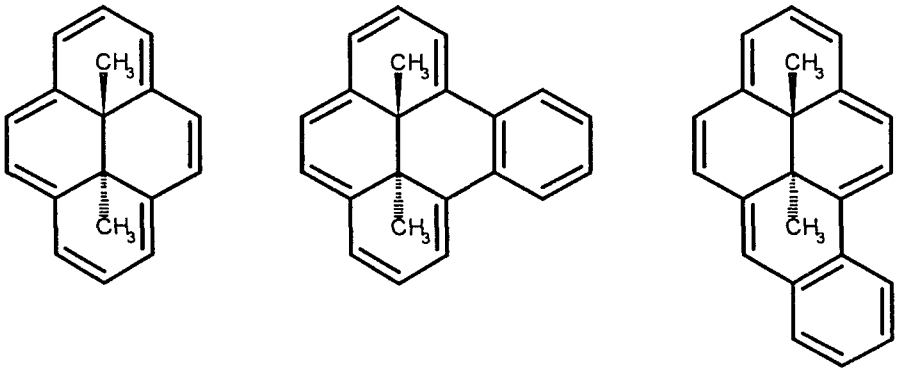


[16] [28]

Figure 22. Benzannelated 1,6-methano[12]annulene [28]

1.10.3 Benzo-[14]-annulenes

A very extensive and thorough analysis on the effect of benzannelation on the diamagnetic ring current of bridged [14]-annulenes has been carried out by R. H. Mitchell and his colleagues.[62] The great advantage of these systems is that they are all very rigid, regular hexagonal annulenes without the angle and bridging strain associated with the previous examples. Two monobenzannelated 15,16-dimethyldihydropyrenes [18] are possible. The symmetrical compound [29] has shielded internal methyl resonances at -1.85 ppm and the asymmetrical monobenzannelated compound [30] at -1.6 ppm. Both indicate a decrease in ring current of about 50% from the parent bridged [14]-annulene. The upfield shift of the methyl group and the decrease in the ring current are relatively independent of the point of fusion with the benzene ring.



[18] [29] [30]

Figure 23. Monobenzannelated 15,16-dimethyldihydropyrenes [29] and [30]

Unlike the monobenzannelated dimethyldihydropyrenes, the dibenzoannelated systems can affect the ring current in two different ways. Consider two compounds synthesized by Mitchell, the so-called *cisoid*- [31] and *transoid*-dibenzo [32] derivatives. The *cisoid* compound [31] has an internal methyl proton NMR resonance at 0.02 ppm and is calculated to have 18% of the ring current of the parent compound. The *transoid* compound [32] has an internal methyl proton NMR resonance at -3.58 ppm, or 87% of the ring current of the parent compound.

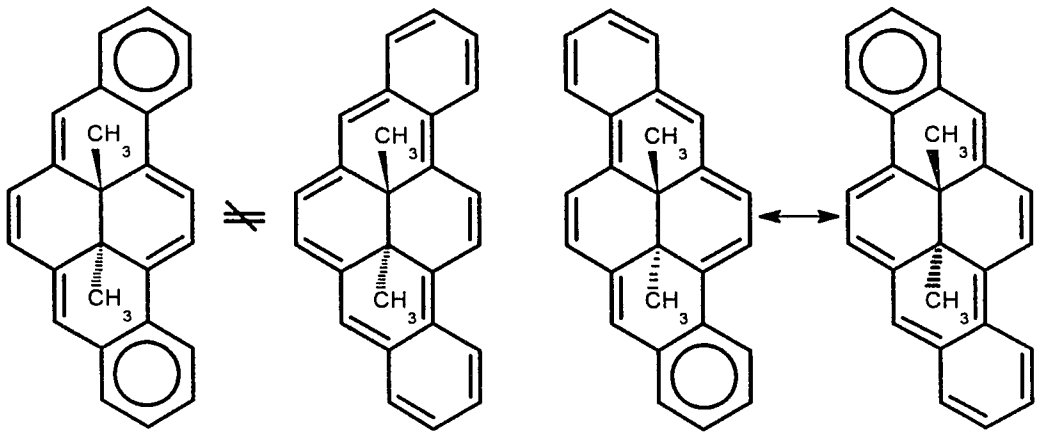


Figure 24. Dibenzannelated 15,16-dimethyldihydropyrenes [31] and [32]

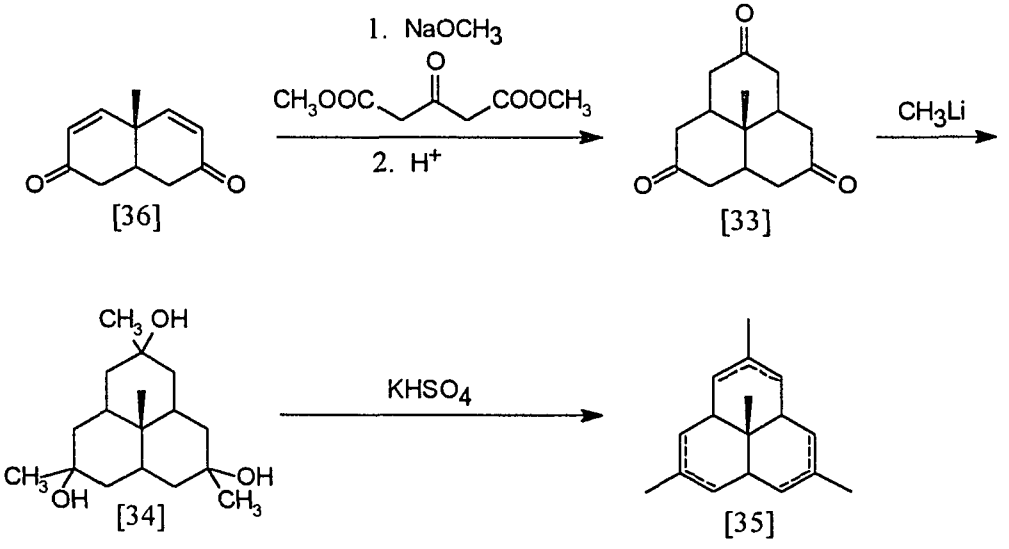
This difference can be understood in terms of the Kekulé structures. There are two distinct, non-equivalent resonance structures associated with the *cisoid* compound, [31] and [31b]. This compound can be drawn with two benzenoid rings, each containing a full sextet of electrons, while with the *transoid* compound [32] this configuration is

impossible. Both resonance structures of the *transoid* compound [32] are equivalent. Thus, the two benzenoid rings in the *cisoid* compound compete with and effectively localize the π-system of the macroring, while no such interruption is possible with the *transoid* compound. The bond localization and decrease in diatropicity of the annulene is translated into a subsequent downfield shift of the internal methyl group protons of the *cisoid* compound, while the *transoid* compound shows little of this effect. Mitchell has correlated the increase in bond localization with the decrease in diatropicity and strength of the ring current, as measured by the chemical shift shielding of the internal methyl group, for many additional di-, tri-, tetra-, and other benzannelated dihydropyrenes.[63]

2. Synthetic and Investigative Approach

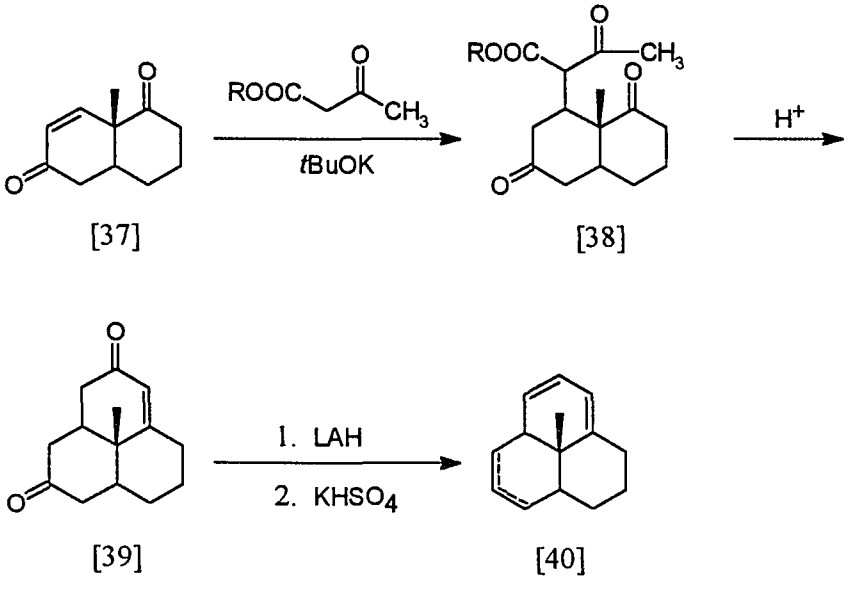
2.1 Prior Investigations of 13-Methylphenalene

Previous work in the Grohmann group on the synthesis of 13-methylphenalene and related compounds is as follows. One route of Grohmann, M. Moore, and P. Noire[64] in which they have attempted to synthesize 13-methylphenalene [1], starts with the tricyclic trione compound [33][65], which is treated with excess methyllithium, the product then purified by continuous extraction to obtain the triol [34]. Compound [34] is then dehydrated with potassium bislfate giving a compound whose mass spectrum is consistant with the triene structure [35]. Due to the difficulty in obtaining at that time sufficient quantities of the bis-enone [36] for the synthesis of the trione [33], this route was temporarily halted.



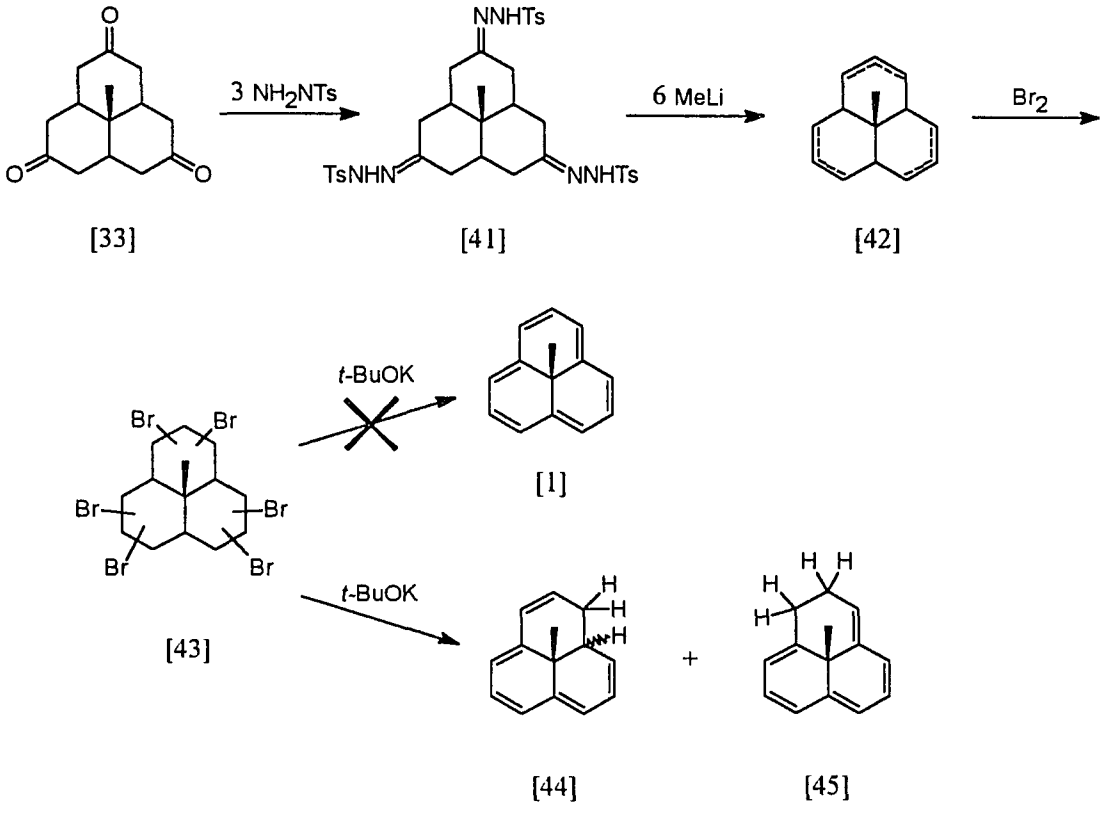
Scheme 1. The *bis*-Enone Approach towards 13-Methylphenalene[66]

A second route by Grohmann and Noire focused on obtaining the triene derivative [40] of 13-methylphenalene via a Michael reaction, ester cleavage and aldol condensation. Starting from *cis*-Δ'-3,8-octalindione [37], which is first reacted with alkyl acetoacetate and base to produce the Michael adduct [38] and then treated with acid to effect ester cleavage and aldol condensation to give the enedione [39], the triene [40] is obtained as a mixture of isomers by subsequent reduction and dehydration.



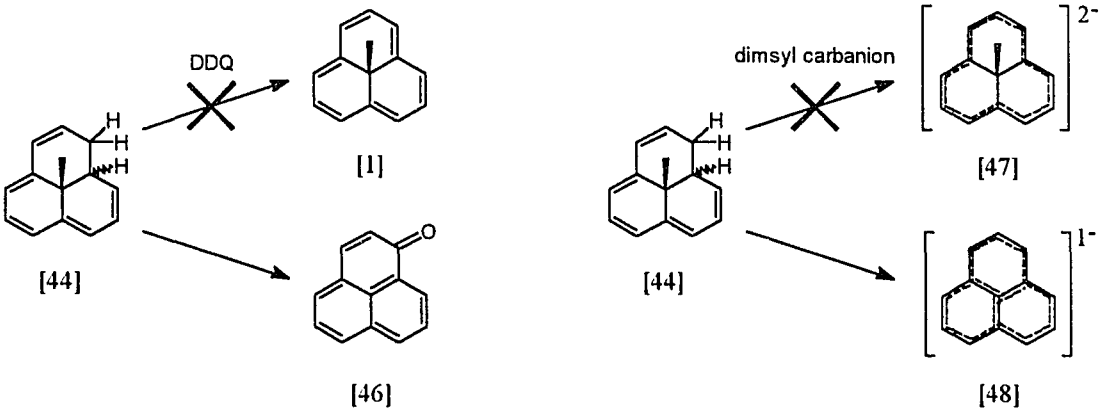
Scheme 2. The *cis*-Δ'-3,8-octalindione Approach towards 13-Methylphenalene [67]

Yet a third route starts from the trione [33] which is converted into the *tris*-tosylhydrazone [41], followed by elimination using methyllithium to form the isomeric mixture of trienes [42]. Bromination of this mixture to form hexabromides [43], followed by dehydrobromination gave a mixture which was at first not conclusively characterized. Grohmann and Huang[68] later repeated this synthesis and isolated the two highly air-sensitive isomeric dihydro-13-methylphenalenes [44] and [45], as well as two bromopentaenes, the structures of which have not yet been characterized.



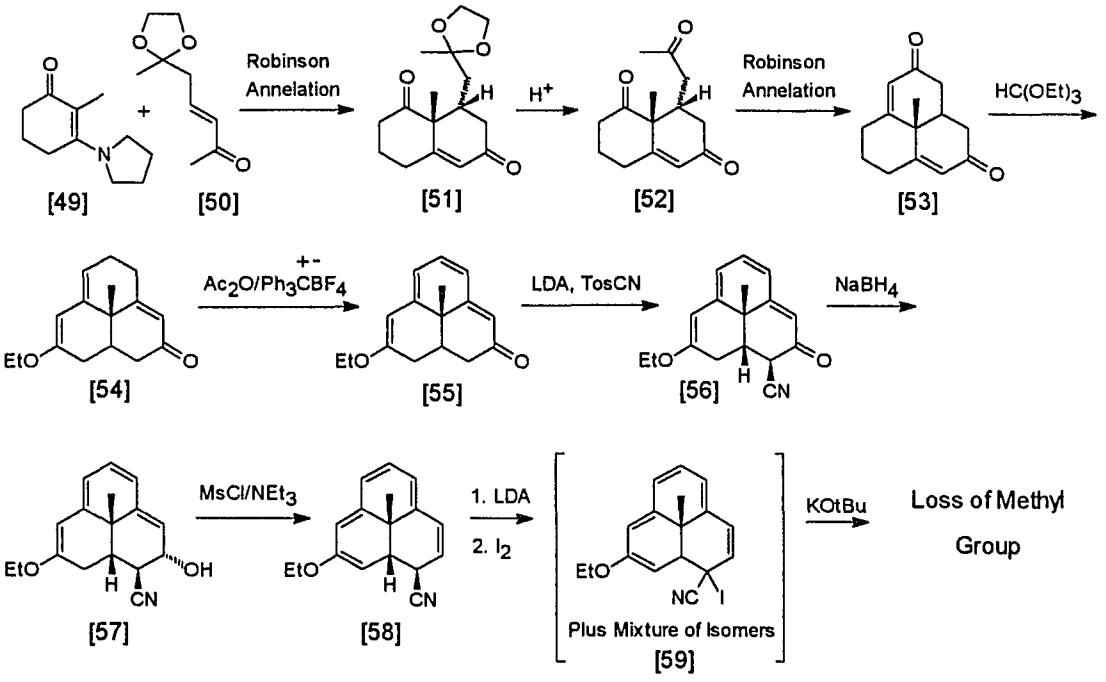
Scheme 3. The *tris*-Tosylhydrazone Route toward Dihydro-13-methylphenalene[69]

Treatment of [44] with DDQ at room temperature afforded the known perinaphthenone [46], with loss of the central methyl group. Likewise, treatment of the pentaenes or bromopentaenes with dimsyl carbanion[70] did not afford the expected dianion [47] but rather the phenalene anion [48], again with the loss of the central methyl group.



Scheme 4. Treatment of the Dihydro-13-methylphenalenes [44] with DDQ[71]

Another approach, by Dickgreber, Altenbach and Vogel,[72] attempted the synthesis of a derivative of 13-methylphenalene by a double enamine variation of the Robinson annelation to the *bis*-enone compound [53], followed by the successive introduction of unsaturation until the pentaene [58] was formed. Iodide substitution, using LDA and molecular iodine, led to a mixture of isomers which, upon addition of potassium butoxide in dioxane at -78°C, led to an oxygen-sensitive mixture with no ^{1}H NMR observable methyl group.

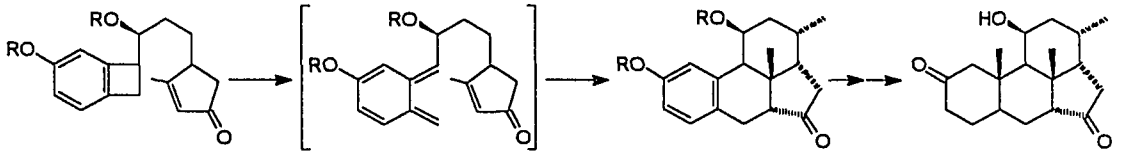


Scheme 5. The Dickgreber Approach Towards 13-Methylphenalene [1]

These separate studies have concluded with similar results. All attempts so far to introduce the sixth and last double-bond into the ring have ended with the observation of the disappearance of the central methyl group. These observations suggest that with this particular [12]-annulene, the central sp^3 carbon/methyl bond is extremely weak.

2.2 *Prior Investigations of the Monobenz-13-methylphenalene*

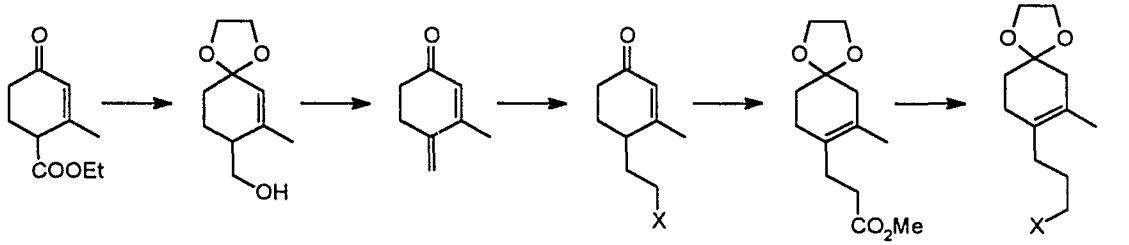
Grohmann and Alva have investigated the synthesis of benzannelated 13-methylphenalene. The key synthetic step was the thermolysis of a benzocyclobutene derivative, for example [60] below, to an *o*-quinodimethane[73] [61], followed by the immediate intramolecular Diels-Alder cycloaddition[74] to give the carbon skeleton, which could then be subsequently modified to give the desired benzannelated 13-methylphenalene. This elegant strategy was based on the stereoselective synthesis of *d*-deoxyquassinoid [63] by Kametani.[75]



[60] [61] [62] [63]

Scheme 6. Synthesis of *d*-Deoxyquassinoid [63][76]

One route toward Alva's benzocyclobutene derivative began with Hagemann's ester [64], which was protected and reduced to [65], converted to dienone [66] by mild acid hydrolysis, and to the diester [67] by a (1,6) Michael addition with sodium ethoxide and excess malonic ester. [67] was hydrolyzed and decarboxylated to the acid [68], esterified to [69], ketalized to [70], reduced to the alcohol [71], mesylated to [72], and finally converted to the iodide [73] by sodium iodide in acetone.

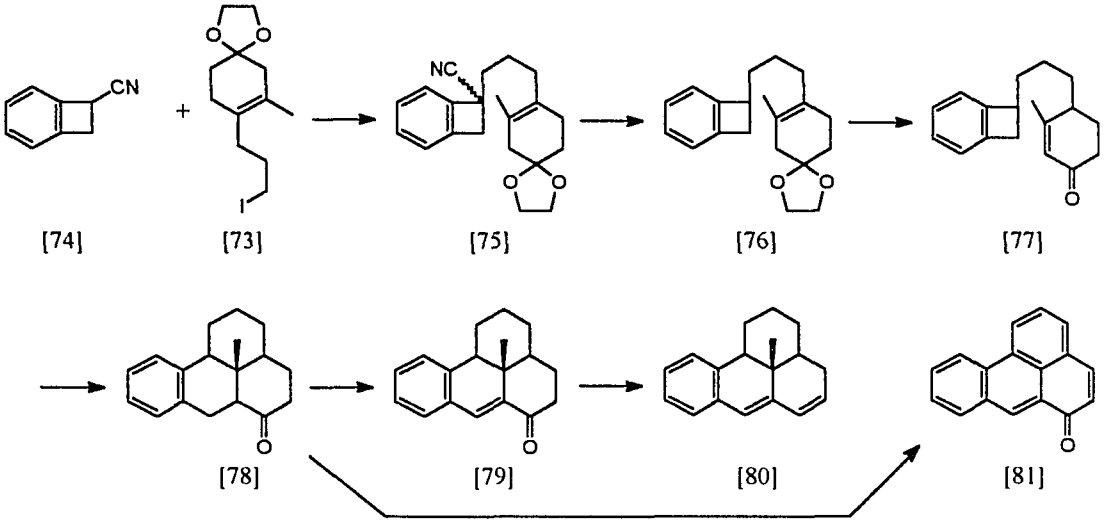


[64] [65] [66] [67] X = $(CO_2Et)_2$ [70] [71] X = OH
[68] = CO_2H [72] = OMs
[69] = CO_2Me [73] = I

Scheme 7. Part One of the Hagemann's Ester\1-Cyano-benzocyclobutene Approach Towards Benzannelated 13-methylphenalene [2] [77]

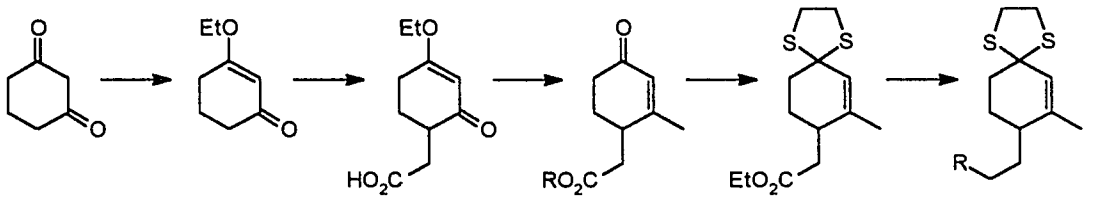
The known 1-cyano-benzocyclobutene[78] [74] was coupled to the iodide [73] using LDA to [75]. After deprotection of [75], several attempts of thermolytic IMDA reaction failed, probably due to the interference of the nitrile group, which favored sigmatropic rearrangement. Adduct [75] was decyanated by treatment with sodium in liquid ammonia and ethanol to give [76], which was deprotected to [77], and refluxed in *o*-dichlorobenzene to give the cyclized product [78]. Bromination/dehydrobromination with

NBS and DBU gave the ketone [79], which was subsequently reduced to the alcohol, mesylated, and finally demesylated on alumina to the triene [80]. No further unsaturation could be introduced into [80] due to the lack of additional functionalization in the other rings. Oxidation of [78] with DDQ resulted in the loss of the central methyl group, similar to the result observed previously by Huang, and the formation of the known aromatic ketone [81].



Scheme 8. Part Two of the Hagemann's Ester\1-Cyano-benzocyclobutene Approach Towards Benzannelated 13-methylphenalene [79]

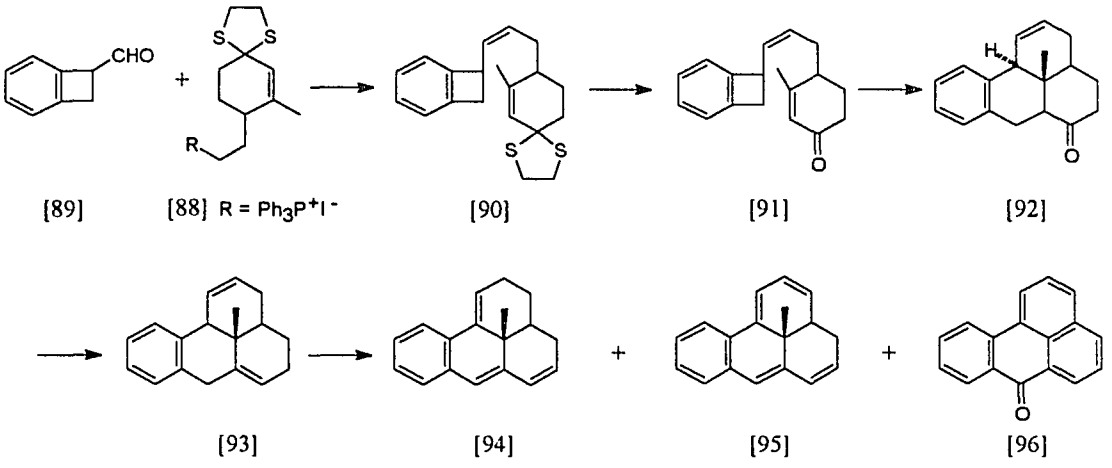
A second route by Grohmann and Alva toward a more functionalized version of [78] used a slightly different approach. Starting from dihydroresorcinol [82], which was converted by acid-catalyzed distillation over ethanol to [83], alkylated with t-butylbromoacetate to form the acid [84] (de-esterified upon distillation), methylated to form [85], trans-esterified to [86] by reflux in absolute ethanol, protected to the thioketal [87], and in a similar conversion to that of compounds [70]-[73], the triphenylphosphonium salt [88] was finally obtained.



[82] [83] [84] [85] R = H [86] = Et [87] [88] R = Ph_3P^+I

Scheme 9. Part One of the Dihydroresorcinol\1-Formylbenzocyclobutene Approach Approach Towards Benzannelated 13-methylphenalene[80]

In a Wittig reaction with 1-formylbenzocyclobutene [89], the phosphonium salt [88] was coupled to give [90] and then deprotected to give [91]. Thermolysis of [91] in refluxing toluene gave [92] in 42% yield. Reduction, mesylation, and demesylation over alumina resulted in the triene [93], which when treated with DDQ produced three products, the tetraene [94], pentaene [95], and the known aromatic ketone [96].



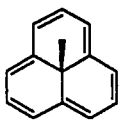
Scheme 10. Part Two of the Dihydroresorcinol\1-Formylbenzocyclobutene Approach Approach Towards Benzannelated 13-methylphenalene [81]

Again, as observed with the investigations of 13-methylphenalene[1], the introduction of the sixth double bond seems to lead invariably to loss of the central methyl group. This observation continues with the monobenzannelated-13-methylphenalene [2], and suggests that perhaps the stabilization of one additional benzenoid moiety is not enough to strengthen this bond. In order to explore quantify this idea further, an investigative study of the bond dissociation energies of 13-methylphenalene and its monobenzannelated derivative was initially launched by Huang and Alva, and is further extended to the di- and tri-benzannelated derivatives in this investigation.

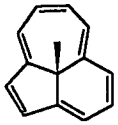
2.3 Calculation of the Bond-Dissociation Energy of the Central Methyl Group

2.3.1 Introduction

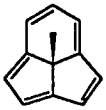
The consistent loss of the central methyl group prompted the calculation by Huang and Alva of the bond dissociation energy and bond length of the central sp^3 carbon-methyl bond in 13-methylphenalene and related compounds, using AM1.



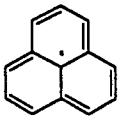
[1]



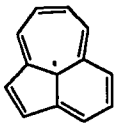
[97]



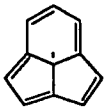
[13]



[1r]



[97r]



[13r]

	(kcal/mole)			(angstroms)
	Hf	Hf_{rad}	BDE	Bond Length
[1]	92.56	70.02	8.71	1.575
[97]	102.37	100.69	29.57	1.531
[13]	116.25	137.02	52.02	1.513
	Ethane		88	1.534

Table 1. AM1 Calculation and Comparison of the Bond Dissociation Energies and Bond Lengths of the Central sp^3 Carbon-Methyl Bond of Selected Compounds[82]

The results of the calculations showed sizable reduction in the bond dissociation energy of [1], along with a lengthening of the central methyl bond, relative to the non-symmetric [12]-annulene [97] and Rees' aromatic [10]-annulene system [13]. A representative average C-C single bond has a BDE of 81 kcal/mole, while ethane has a BDE of 88 kcal/mole and a bond length of 1.534 Å.[83] Based on this experimental and theoretical work it was first predicted that 13-methylphenalene would exhibit an usually weak carbon-carbon single bond.

Based partly on the continuing observation of the loss of the central methyl group in these two separate studies and in order to determine any correlation between the aromaticity or the antiaromaticity of a π-system and the bond-strength of its central methyl group, it was decided that it would be interesting to calculate the bond-dissociation energies using the computational method AM1[84] for a variety of similar compounds.

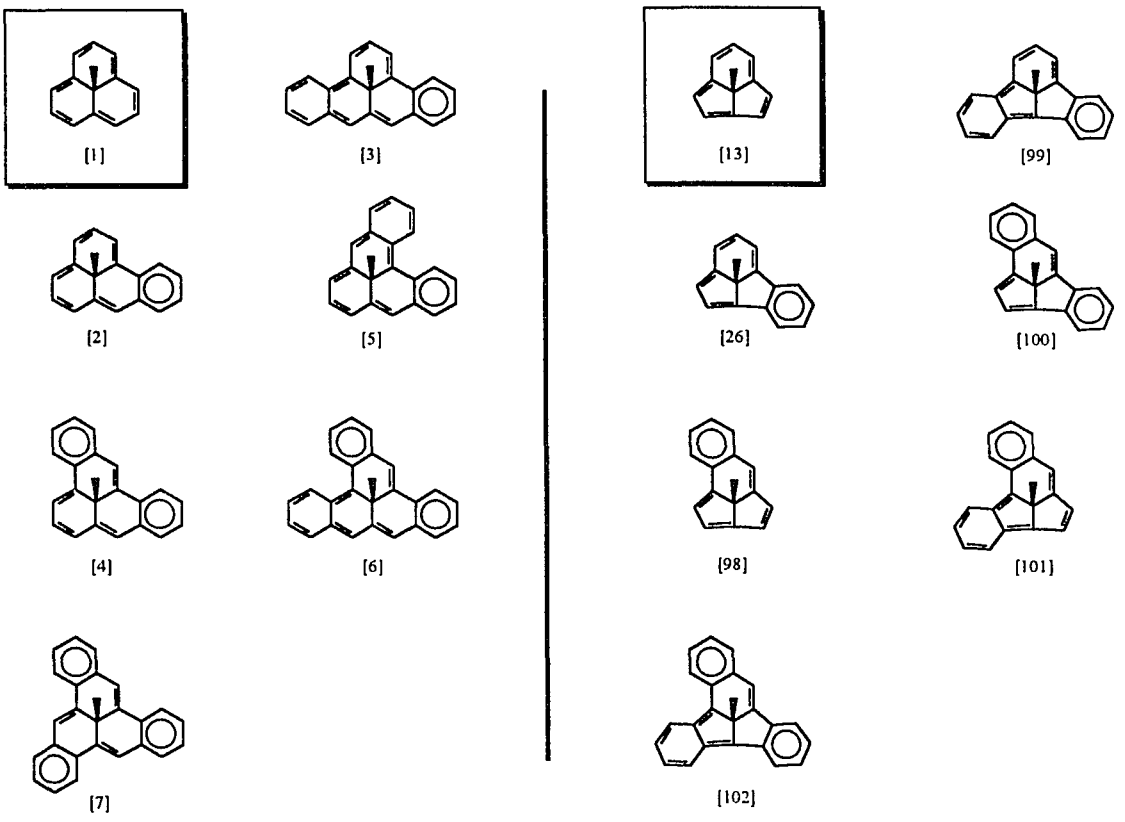


Figure 25. Compounds Investigated using AM1 Calculations

As discussed earlier, the bridge introduces into the conjugated π-perimeter conformational immobility, forcing the system into near planarity. This limits any pseudo Jahn-Teller distortion, allowing conjugation in the ring to exhibit a strong paramagnetic ring current for the [4*n*]-annulenes and a strong diamagnetic ring current for the [4*n* + 2]-annulenes. The presence of one or more benzene rings on the conjugated π-perimeter of an annulene reduces the ring current of the annulene by involving one (or more) π-bonds in the ring current of the benzene ring(s), rather than that of the annulene. This has a destabilizing

effect on [4*n* + 2]-annulenes by reducing the aromatic character of its ring current. A reduction in aromaticity in turn raises the energy of the π-system and lowers the energy difference between the molecule and the radical formed by homolysis of the central carbon-carbon bond. Upon increasing benzannelation there is further decrease in the BDE, but only when the second ring is fused in a manner in which there is maximum disruption of the π-system of the macroring.

In contrast, benzannelation has a stabilizing effect on [4*n*]-annulenes by reducing the antiaromatic character of its ring current. This lowers the energy of the π-system and increases the energy difference between the molecule and the radical formed by homolysis of the central carbon-carbon bond. It is predicted and shown that the antiaromatic systems exhibit rather small BDEs for the central methyl group, since bond breakage results in rearrangement and interruption of the very unstable paramagnetic [4n] π-system. As the paratropicity of the macroring is reduced by benzannelation, the BDE increases. However, it must also be noted that all carbon-carbon bond dissociation energies of the central methyl groups for both the [10]- and [12]-annulenes will already be somewhat reduced relative to a 'normal' carbon bond, due to the inherent strain in the bridge. Overall, it is hoped that the knowledge of the bond dissociation energy of the central carbon-carbon bond would provide an excellent indication of the aromatic/antiaromatic character of the system.

2.3.2 Methods and Procedures

Fourteen bridged benzannelated annulenes and the corresponding radicals formed by homolysis of the central carbon-carbon bond, a total of twenty eight compounds, were investigated. They are divided into two groups. The first is an antiaromatic series consisting of 13-methylphenalene [1], its monobenzannelated derivative [2], three dibenzannelated derivatives [3], [4] and [5], two tribenzannnelated derivatives [6] and [7], and all corresponding radicals. The second group is an aromatic series consisting of Rees' 7b-methyl-7bH-cyclopent-[c,d]-indene [13], two monobenzannelated derivatives [26] and [98], three dibenzannelated derivatives [99], [100] and [101], one tribenzannelated derivative [102], and all corresponding radicals.

Each of the twenty-eight compounds were first drawn using the PCMODEL[85] program, which also minimized the geometries by Molecular Mechanics (MM2.) These geometries were then translated by PCMODEL into the AMPAC[86] format, and used directly in the AM1 calculations. All calculations used RHF constraints. The enthalpies of formation were calculated with the keywords PRECISE, GEO-OK and in the case of symmetrical geometries, SYMMETRY. TRIPLET, or OPEN (2,2) were also used to investigate the geometries of open-shell systems, but gave usually higher enthalpy results. PRECISE increases the criteria for the termination of the electronic and geometric optimization by one-hundred fold. GEO-OK prevents a premature halt to the program when there is a difficulty in optimizing the geometry (or, more commonly, when two atoms are within 0.8

Angstroms apart.) SYMMETRY allows the equating of certain bond lengths, angles, and dihedrals, as specified by the user and the geometry of the molecule. TRIPLET specifies that a triple state exists, with one electon each in the two highest occupied molecular orbitals. OPEN(2,2) denotes two unpaired electrons in two open shells. The geometries of all compounds were completely optimized in all internal degrees of freedom. All radical geometries were calculated using the same half-electron method.[87] Computations were carried out by using the AMPAC program on IBM RS/6000 and Ulysses Systems I386 workstations.

The completed AM1 calculations were reported with a summary which included heat of formation (kcal/mole), electronic energy (eV), core-core repulsion (eV), number of filled levels, ionization potential (eV), molecular weight, number of SCF calculations required to complete the calculation, computation time, and the gradient norm. The gradient norm, the derivative of the energy with respect to all atomic coordinates, represents the change in energy of the system as infinitesimal changes are made in the geometry and should be quite near zero. All minimized structures, from which heats of formation are reported, had gradient norms of 1.0 or lower.

The bond-dissociation energy was calculated using the equation:

$$\Delta H_{f\,rad} + \Delta H_{CH_3\bullet} - \Delta H_f = BDE \qquad \textbf{Equation 5}$$

where $\Delta H_{f\ rad}$ is the calculated enthalpy of formation of the radical compound, $\Delta H_{CH_3\bullet}$ is the enthalpy of formation of methyl radical (defined as 31.62 kcal/mole,) ΔH_f is the calculated enthalpy of formation of the parent compound, and BDE is the bond dissociation energy.

The energy barrier for each dissociation was also determined by calculation of the bond-dissociation curve (path calculation.) The path calculation was performed by calculating the enthalpy of formation of a series of geometries as the central carbon/methyl group bond was lengthened in incremental 0.1 Angstrom steps. All homolytic bond dissociation computations were carried out using the BIRADICAL keyword. Each ΔH_f was compared, and the structure with the largest value was selected as nearest the transition state of the transformation. The gradient of the chosen structure was then minimized using the keywords POWELL and PRECISE, and finally checked with a FORCE calculation. POWELL instructs the AMPAC program to minimize the gradient norm using a certain combination of methods determined to be the "best choice" for the refining of the geometry of a transition state. FORCE requires the calculation of the second derivative of the energy of all pairs of atoms. Ground states and transition states are characterized by five eigenvalues at or near zero, while transition states must also have one, and only one, negative force constant. All transition state values reported showed one, and only one, negative force constant.

2.3.3 B. Results and Discussion

2.3.3.a The [12]-annulene series

The enthalpies of formation of the parent and radical compounds, their calculated bond-dissociation energies, and some activation energies of selected compounds, are listed in Tables 2 through 4. Table 2 shows the first group of [12]-annulene derivatives.

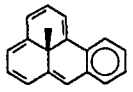
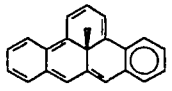
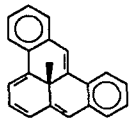
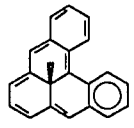
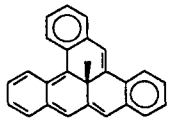
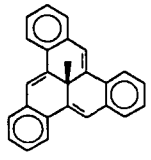
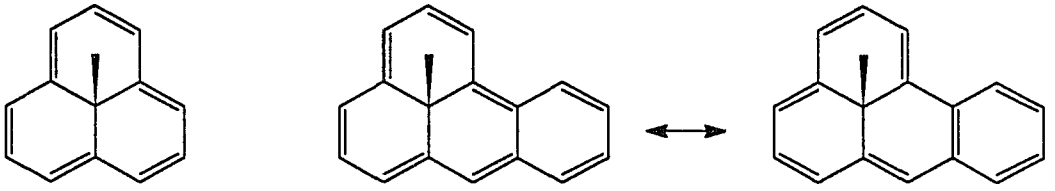
		ΔH_f(kcal/mol)	ΔH_f rad	B.D.E.	Trans. State	E_{act} forward	E_{act} reverse
(1)		89.77	69.97	11.82	123.82	34.05	22.23
(2)		100.96	89.26	19.92	138.22	37.26	17.34
(3)		137.46	106.87	1.03	161.82	24.36	23.33
(4)		112.48	107.29	26.43	152.78	40.30	13.78
(5)		132.93	114.99	13.68	170.11	37.18	23.50
(6)		144.90	132.23	18.95	184.05	39.15	20.20
(7)		125.20	126.95	33.37			

Table 2. AM1 Results for the [12]-annulenes.

Compound [1], 13-methylphenalene, has a BDE of 11.82 kcal/mole and is predicted to dissociate at very low temperature. Upon the annelation of one benzene ring, compound [2], this increases to 19.92, a net stabilization of 8.1.



[1] [2]

Figure 26. 13-Methylphenalene [1] and its Monobenzannelated Derivative [2]

Compound [3] is twice benzannelated in an anthracene-like conjugation, such that they are "resonance antagonistic." No resonance structure can be written in which each benzene ring is satisfied with an isolated three pi-bond system. Compound 3 is calculated to have a BDE of only 1.03 kcal/mole (a slightly higher value of around 8 kcal/mole is obtained if the symmetry is removed.)

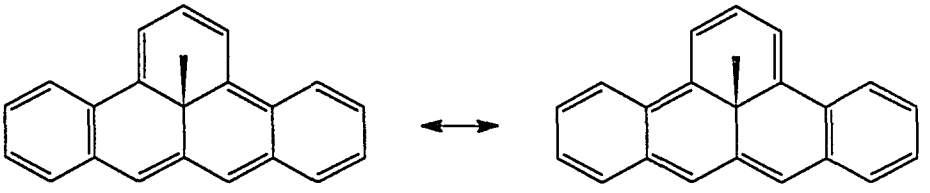


Figure 27. Resonance structures for Compound 3

In contrast to [3], compound [4] has two benzene rings located such that each is satisfied with a three π-bond system, which in turn isolates the remaining double bonds in the [12]-annulene ring, concurrently reducing the antiaromaticity and increasing the BDE to 26.43 kcal/mole, a 6.51 increase over compound [2].

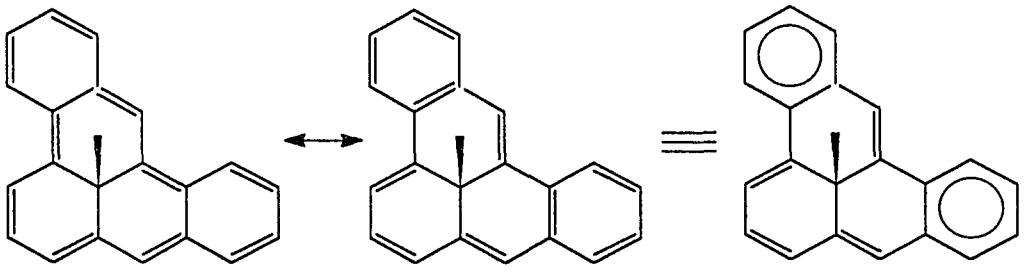
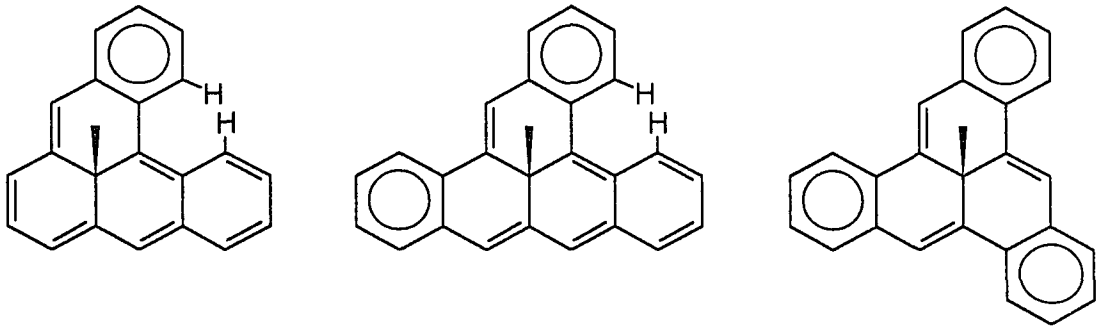


Figure 28. Selected Resonance structures for Compound 4

Compound [5] has similar resonance structures to compound [3], but has a somewhat higher BDE of 13.68 kcal/mole. This increase could be due to the fact that the molecule must deviate from planarity due to the internal H-H repulsion shown, resulting in increased bond alternation, reduced [12]-annulene conjugation and increased stability. Compound [6] is similar, with the additional stabilization provided by an extra benzene ring, and is calculated to have a BDE of 18.95 kcal/mole. Lastly, compound [7] is shown to have the largest central sp^3 carbon/methyl group BDE of 33.37 kcal/mole, with three benzene rings on the perimeter of the [12]-annulene system. All three rings are

simultaneously capable of supporting a closed-shell sextet of electrons, resulting in the largest stabilization of this series. It is predicted to be able to be isolated at room temperature.



[5] [6] [7]

Figure 29. Compounds 5, 6, and 7

Finally, the transition state energies were calculated for compounds 1-6. The energy of activation for the dissociation (forward reaction) was calculated by subtracting the ΔH_f from the calculated transition state energy. The energy of activation for the recombination (reverse reaction) was calculated by subtracting the ΔH_f from the sum of the ΔH_f radical and the methyl radical. The forward energies of activation were then fitted to a linear equation, developed by Huang and Dannenburg[88] following Leffler and Grunwald:

$$\Delta H_{act} = 24.51 - 0.520\ BDE \qquad \textbf{Equation 6}$$

Table 3 lists the calculated activation energies for the homolytic dissociation of the central carbon-methyl bond for compounds [1], [2], [4] and [3], respectively. A clear trend of an increasing barrier to this dissociation as benannelation in increased is suggested, as long as the benannelation is located at a position of maximum resonance interference with the central anti-aromatic ring.

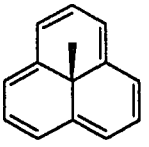
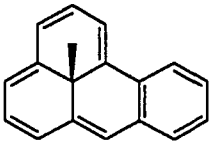
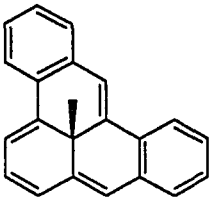
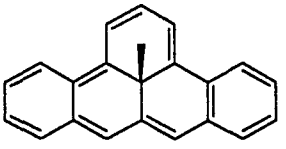
	Activation Energy (kcal/mol
	34.05
	37.26
	40.30
	24.36

Table 3. Calculated Activation Energies for selected benzo-derivatives of 13-methylphenalene

This result supports the assertion of the existence of an intrinsic barrier for the coupling of two carbon-centered radicals, the barrier being reported as possibly high as 24.5 kcal/mol for a carbon-carbon bond having a BDE of zero. Using this equation, compounds 1-6 give a barrier 3 to 5 kcal/mole higher (or radical recombination barrier slightly lower) than reported, except for compound 3 (marked) which agrees with equation 6. This makes the synthesis of compound 3 particularly interesting in that it is suggested by the results of Huang and Dannenberg that compounds with carbon-carbon BDEs of zero or negative value may be isolated.

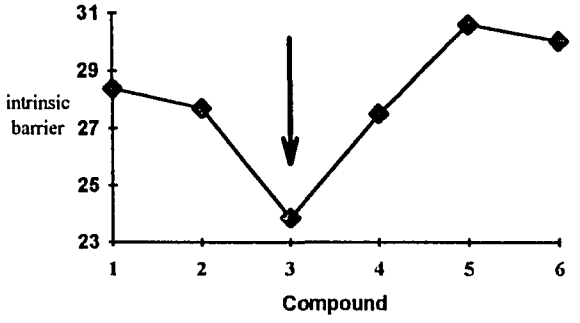


Figure 30. Intrinsic Barriers to Homolytic Bond Dissociation for Compounds [1]-[6]

2.3.3.b The [10]-annulene Series

In Table 4, the opposite trend than that of the [12]-annulenes is observed in the comparison of the BDEs in the [10]-annulene series with increased benzannelation. The parent compound [13] is calculated to have a bond dissociation of 72.40 kcal/mole. This is considerably higher than 13-methylphenalene. Unlike 13-methylphenalene, there are two different monobenzannelated derivatives of 7b-methyl-7bH-cyclopent-[c,d]-indene.

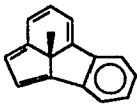
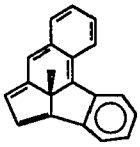
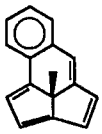
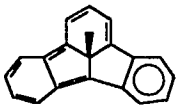
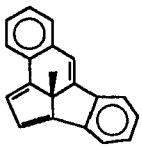
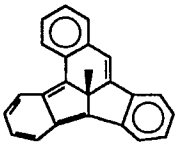
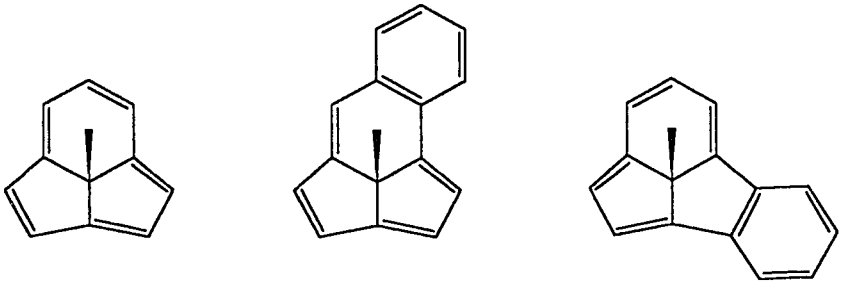
		ΔH_f (kcal/mole)	ΔH_f radical	B.D.E
(13)		118.86	159.64	72.40
(26)		125.11	145.06	51.57
(101)		152.62	163.42	42.42
(98)		126.98	154.99	59.63
(99)		149.90	152.91	34.63
(100)		135.10	162.81	59.33
(102)		160.82	170.98	41.78

Table 4. AM1 Results for the [10]-annulenes.

Compounds [26] and [98] have bond disassociation energies of 51.57 and 59.63 kcal/mole, a change of 20.83 and 12.77 kcal/mole from compound [13], respectively. It appears as if the point of Benzannelation affects the decrease in bond strength in different

ways, with benzannelation at the six-membered ring causing less reduction in the bond dissociation energy of the central carbon-methyl group bond than the five-membered ring benzannelation. This may be due to less bond alternation introduced by benzannelation at the six-membered ring, as it may cause less perturbation of the geometry of the macroring than benzannelation at the five-membered ring.



[13] [98] [26]

Figure 31. Compounds 13, 98, and 26.

This trend continues to be observed with the di- and tri-benzannelated compounds. First, consider the two dibenzannelated [10]-annulenes in which both benzenoid rings can not simultaneously sustain a closed-shell sextet of π-electrons, compounds [101] and [99.] Compound [99], with both five-membered rings benzannelated, has a bond dissociation energy of only 34.63 kcal/mole, a decrease of 16.94 kcal/mole from the less stable mono-benzannelated derivative compound [26]. However, compound [101], with one benzannelation at the six-membered ring, further weakens the BDE only 9.15 kcal/mole from compound [26], to 42.42 kcal/mole. It must also be noted that upon undergoing a

[1,5] methyl shift, both compounds would achieve aromaticity for their individual benzenoid rings. Compound [101] would then contain a naphthalene and benzenoid moieties, while compound [99] would contain three benzenoid rings.

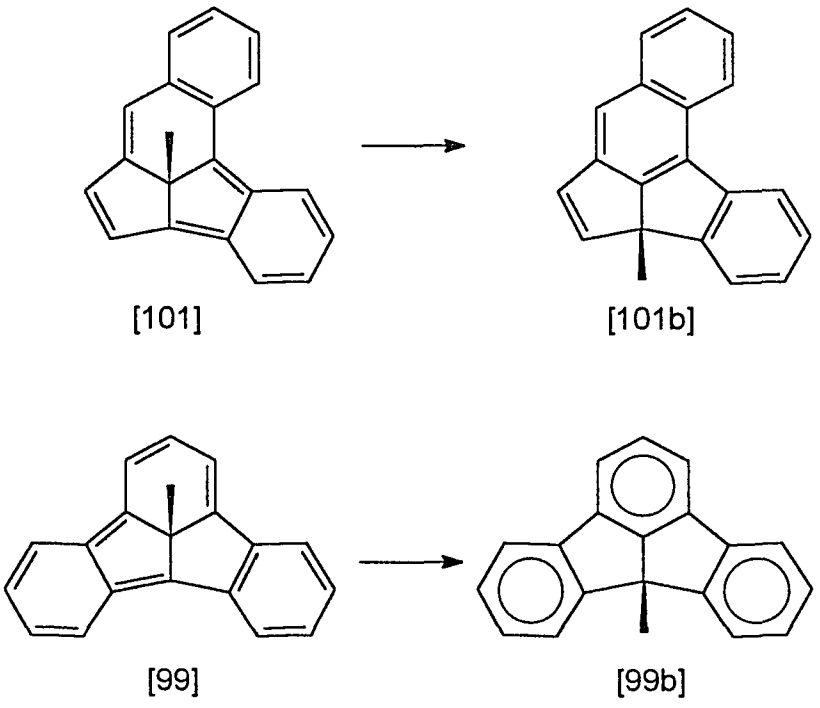


Figure 32. Compounds 101 and 99 and their postulated [1,5] methyl-shift rearrangements

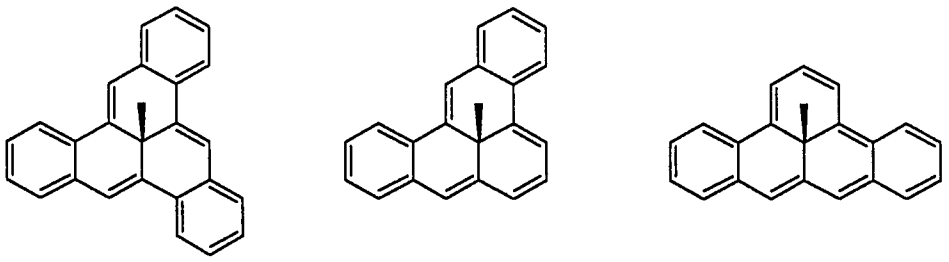
Compound 100 is observed to have a bond dissociation energy of 59.33, virtually identical to the BDE of the monobenzannelated compound [98]. Compound [102], having attributes of all three dibenzannelated compounds, shows an intermediate bond dissociation energy of 41.78 kcal/mole. Overall, the effect of Benzannelation on this bridged [10]-annulene series is not completely clear, perhaps due to angle strain or

symmetry considerations not found in the corresponding bridged [12]-annulene series.

3. Experimental Outline

Introduction

Three target compounds, shown in Figure 33, have been chosen for synthetic investigation. These compounds were carefully selected for study based on the conclusions and assumptions resulting from the prior AM1 investigation of the bond dissociation energy of the central sp^3 carbon/methyl bond.



[7] [4] [3]

Figure 33. Synthetic Targets of this Investigation

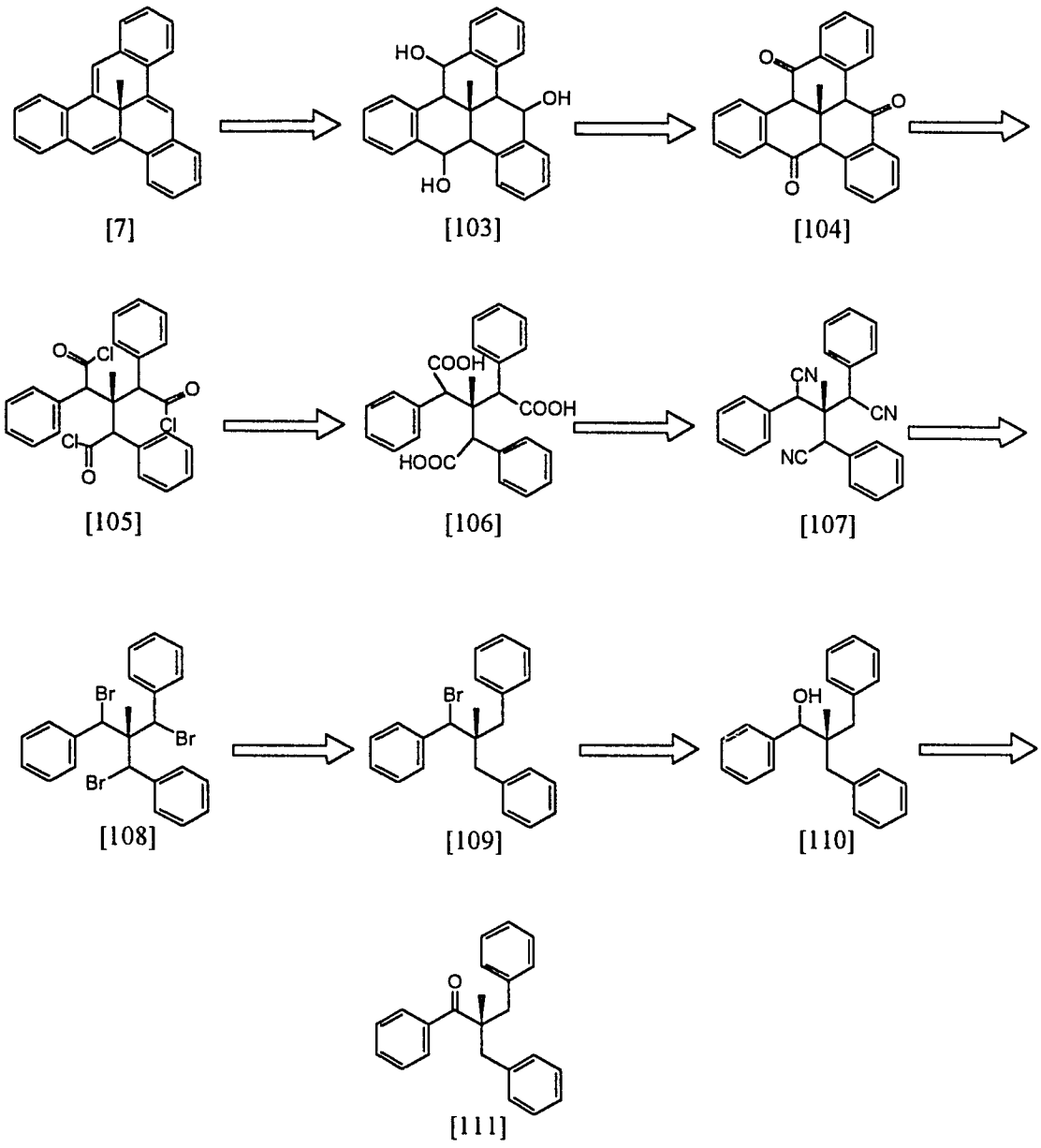
The first of the three target compounds, the symmetric tribenz-13-methylphenalene [7], represents that structure predicted to be the most stabilized by benzannelation. The BDE of its central sp^3 carbon\methyl bond has been calculated to be 33.37 kcal/mole. This may be partly understood in terms of simple resonance structures. A resonance structure exists in which all three benzenoid rings are simultaneously able to contain a full complement of six π-electrons, competing with and thus reducing the antiaromaticity of the ring current

of the parent [12]-annulene. The second target is Compound [4], and with a BDE of 26.43 kcal/mole, it is predicted to be the second-most stabilized by benzannelation, having at least one resonance structure in which both benzenoid rings are simultaneously able to contain a full complement of six π-electrons. The third and last synthetic target of this investigation, and the one least stabilized by benzannelation, is compound [3]. In complete contrast to [4], and in an extremely interesting example of the dependence of the BDE upon the location of the second point of benzannelation on the ring, compound [3] is predicted to have a BDE of only 1.03 kcal/mole. The synthesis and investigation of all three compounds should bring additional insight into the concepts of anti-aromaticity, as well as further the understanding of the effect of the benzannelation of annulenes, particularly that of the parent compound, 13-methylphenalene.

The synthetic approaches towards the three target compounds are divided into three sections. Section 3.1 is devoted to the synthesis of the symmetric tribenz-13-methylphenalene [7]; Section 3.2 is devoted to the synthesis of the unsymmetric dibenz-13-methylphenalene [4]; and Section 3.3 is devoted to the synthesis of the symmetric dibenz-13-methylphenalene [3].

3.1 The Intramolecular Friedel-Crafts Approach Toward Tribenz-13-Methylphenalene

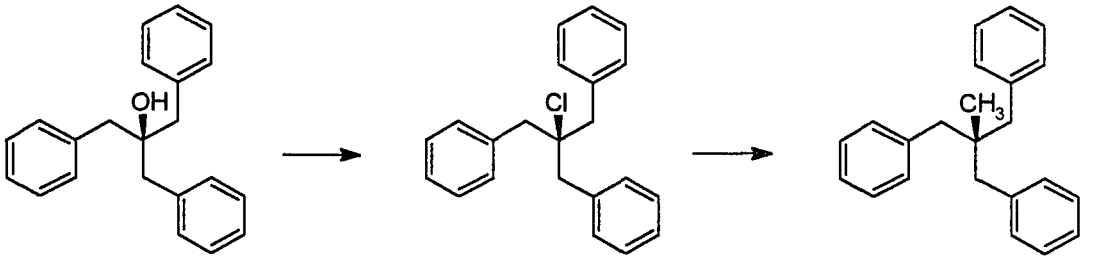
The first synthetic target was the symmetrical tribenz-13-methylphenalene [7.] It was based on a straight-forward synthetic sequence, shown in Scheme [11], involving bromination of 1,1,1-tribenzyl ethane, followed by nucleophilic substitution to the tri-nitrile compound [107], hydrolysis to the tri-acid [106], chlorination to the tri-acid chloride[105], and finally triple intramolecular Friedel-Crafts acylation to obtain the hexacyclic tri-ketone[104]. The ketone would then be subsequently reduced to the alcohol [103] followed by mild dehydration, at low temperature if possible, to afford the product tri-benzannelated-13-methylphenalene [7].



Scheme 11. Proposed Retrosynthetic Sequence for Tribenzannulated-13-methylphenalene

3.1.1 The 1,1,1-Tribenzylethane strategy

Our first approach focused on the synthesis of 1,1,1-tribenzylethane [114]. The first strategy was to obtain tribenzylcarbinol [112], then to form 1,1,1-tribenzylchloroethane [113] by substitution, and to conclude with methylation to form 1,1,1-tribenzylchloroethane using trimethylaluminum.[89]



[112] [113] [114]

Scheme 12. An Approach Towards 1,1,1-Tribenzylethane [114]

Tribenzylcarbinol [112] was synthesized by addition of one equivalent of dimethyl carbonate to 3 equivalents of benzylmagnesium chloride in diethyl ether, with an isolated yield of 50%. However, conversion of tribenzylcarbinol by acetyl chloride into 1,1,1-tribenzylchloroethane [113] resulted in only small yields at best. The presence of the tribenzylcarbinol acetate [115] was also detected by proton NMR.

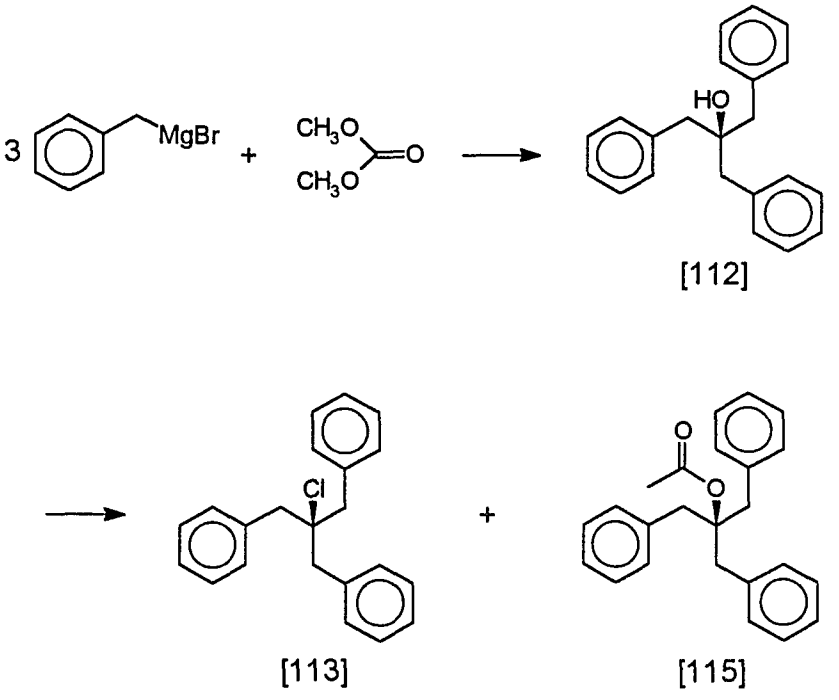
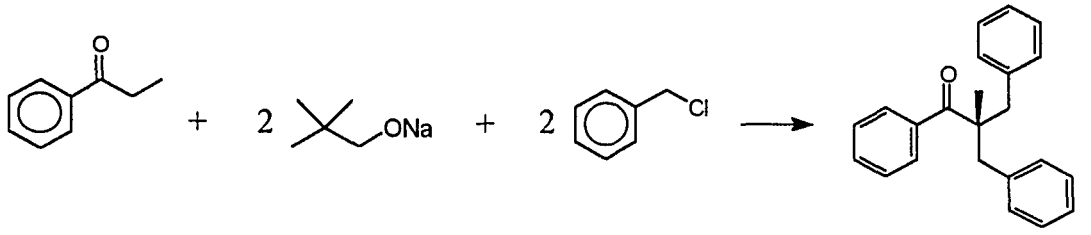


Figure 34. Synthesis of 1,1,1-Tribenzylcarbinol [112] and its Reaction with Acetyl Chloride

3.1.2 The 2,2-Dibenzylpropiopheone Approach

In view of both the difficulty in obtaining a usable amount of the tribenzylchloroethane and the difficult conditions necessary for its subsequent methylation by trimethyl aluminum, the previous route was abandoned in favor of the following procedure. Propriophenone was reacted with two equivalents each of base (sodium *tert*-amylate) and benzyl chloride, in refluxing benzene or toluene, to provide 2,2-dibenzylpropiophenone [111], with a maximum yield of 56%. In contrast to the previous route, this sequence provided a

compound in which both the internal methyl group and a ketone functionality were already present in the product.

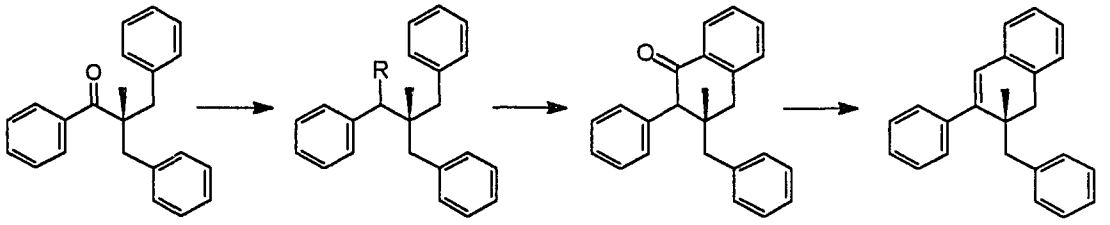


[111]

Figure 35. Synthesis of 2,2-Dibenzylpropiophenone [111]

3.1.2.a Functionalization of model compound [111]

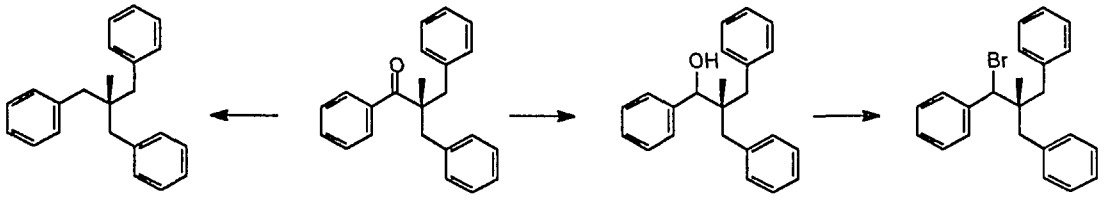
At this point, it was decided for simplicity that only the ketone [111] should be further modified, rather than proceeding with the functionalization of all three benzylic positions. Therefore, as shown in Scheme 13, the synthesis of the model compound [120] would allow the determination of the synthetic feasibility and conditions for each transformation up to and including ring closure. Upon successful completion of this synthetic exercise, the syntheses would be repeated with the tri-bromo compound [108] to obtain the fully cyclized system.



[111] [110] R = OH [119] [120]
[109] Br
[116] CN
[117] COOH
[118] COOCl

Scheme 13. Proposed Route Towards Model Compound [120]

The first modification of [111] was the full reduction of the carbonyl, accomplished by the Huang-Minlon modification of the Wolf-Kishner[90] reduction, to provide the 1,1,1-tribenzylmethane [121] in 45% yield as a control. Next, the ketone [111] was reduced in high yield (85%) via sodium borohydride in ethanol to the alcohol, 2,2-dibenzyl-1-phenyl-1-propanol [110]. Heating [110] in neat 48% HBr successfully led to conversion of the alcohol to afford 2,2-dibenzyl-1-phenyl-1-bromopropane [109] (95% yield.)

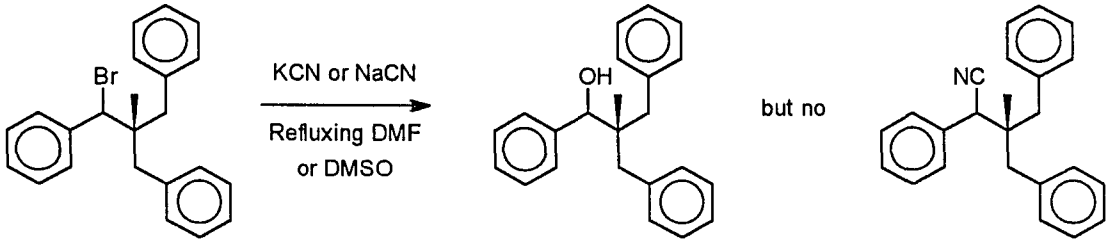


[121] [111] [110] [109]

Figure 36. Reactions of 2,2-Dibenzylpropiophenone [111]

3.1.2.b Attempts at Nitrile formation

A series of attempts at producing either the nitrile [116] or the carboxylic acid [117] however have unfortunately not been as successful. Our first strategy was the nucleophilic substitution of the bromide [109] using, alternatively, KCN, NaCN, and finally CuCN. All three experiments were carried out in vigorously dry conditions, using either DMF or DMSO as solvents. Unfortunately, the starting material in each case was invariably converted to the alcohol [110].

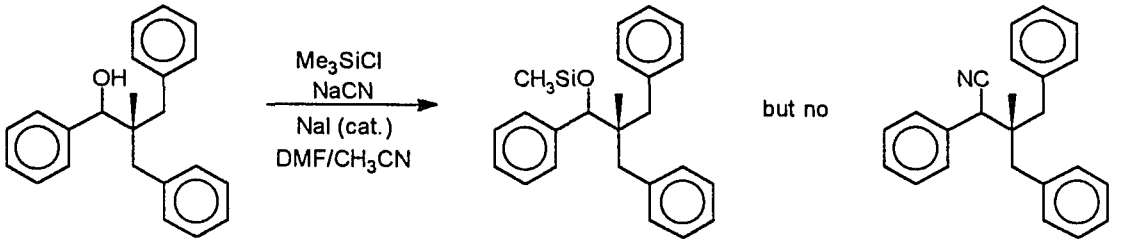


[109] [110] [116]

Figure 37. Attempted Formation of the Nitrile [116] from the Bromide [109]

An interesting observation was that upon refluxing the bromide compound [109] in dry, distilled (CaH_2) DMSO alone, the alcohol [110] was invariably recovered in almost quantitative yields. No apparent reason can be seen for this behaviour.

Following the method of Davis and Untch,[91] the alcohol [110] was heated with Me_3SiCl and NaCN, and a catalytic amount of NaI, in DMF/CH_3CN in an attempt to directly convert the alcohol [110] to the nitrile [116]. This reaction involves the formation of a acetonitrile/trimethylsilyl complex, which upon reaction with the silated alcohol would form a di-trimethylsilyl-ether and the nitrile compound. However, the results obtained suggested that the main product obtained from this reaction was from silylation of the alcohol [110], without further substitution.

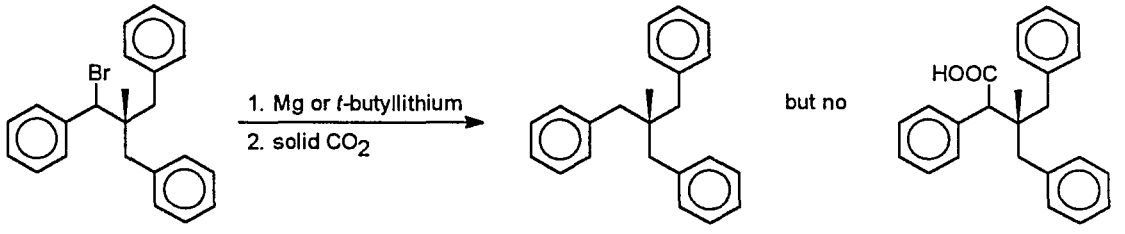


[110] [122] [116]

Figure 38. Attempted Formation of the Nitrile [116] from the Alcohol [110]

3.1.2.c Attempts at formation of the Acid

Conversion of the bromide compound [109] directly to a carboxylic acid functionality [117], by means of either a Grignard reagent or by metal-halogen exchange using butyllithium, and followed by the introduction of solid CO_2, failed. In the case of the Grignard reaction, the main product obtained was the tribenzylethane [121], while the butyllithium reaction gave a mixture of products, none identified as the carboxylic acid [117].



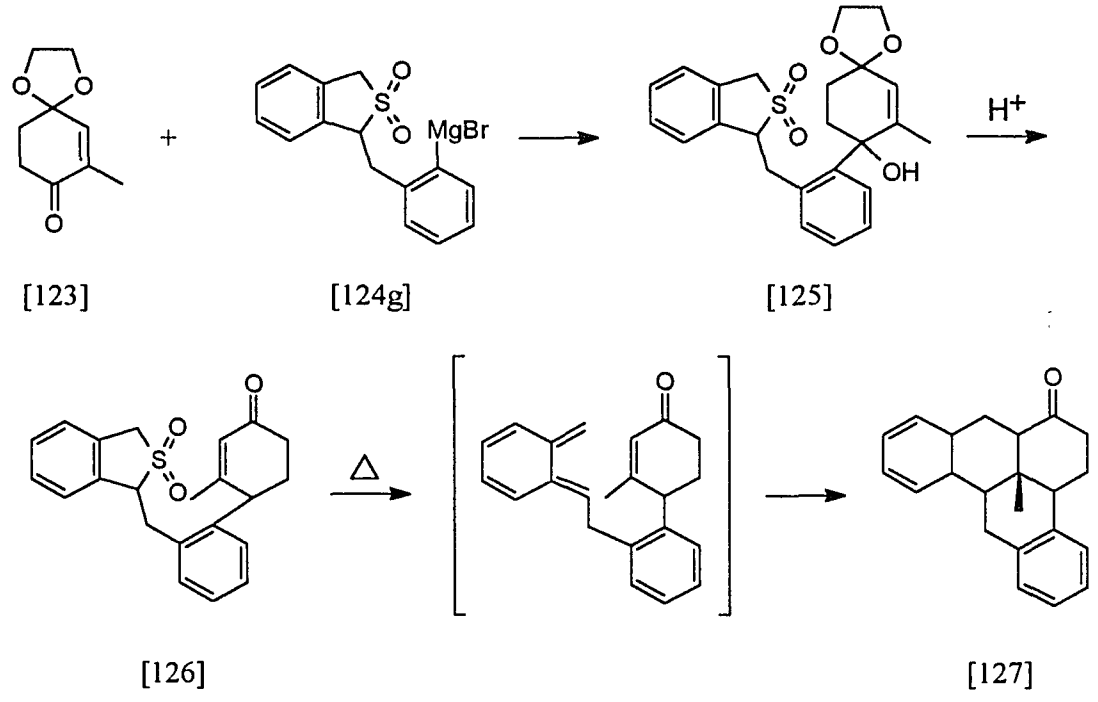
[109] [121] [117]

Figure 39. Attempted Formation of the Acid [117] from the Bromide [109]

Both regular magnesium turnings and activated magnesium (Rieke Mg[92]) were utilized in these trials. In each case, only reduction of the bromide to 1,1,1-tribenzylethane was observed. Extra careful and rigorously dry conditions did not seem to affect the results. In the last trial, both the Rieke method and the use of dry, solid carbon dioxide, formed by the passing of CO_2 gas through drierite and $CaCl_2$ and collected in a liquid nitrogen trap, failed to give the desired carboxylic acid.

3.2 The Intramolecular Diels-Alder Approach toward Dibenz-13-Methylphenalene [4]

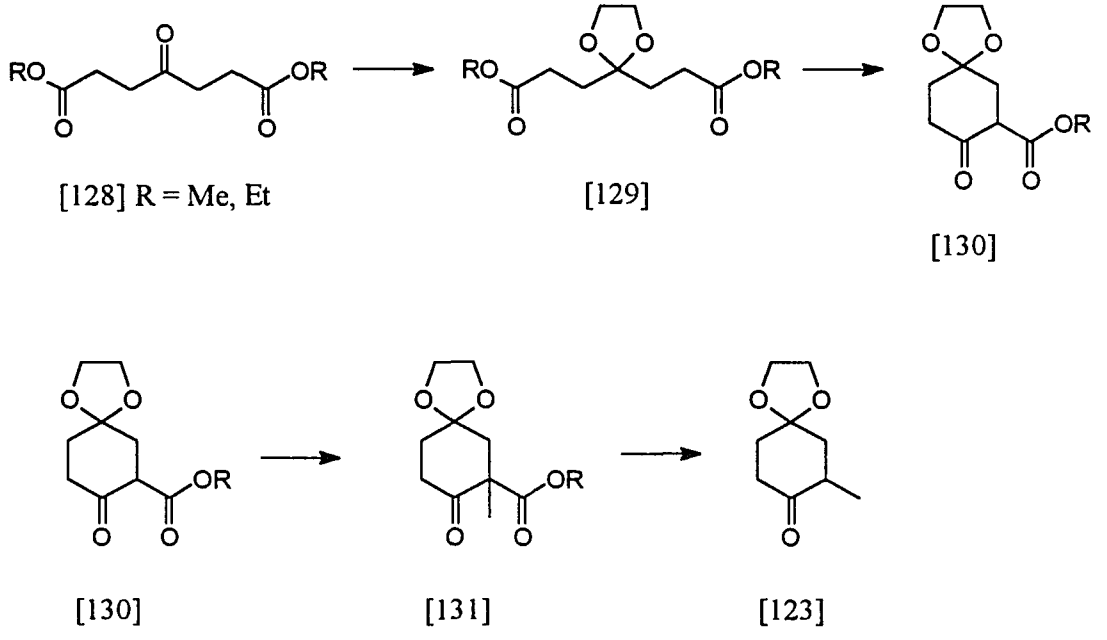
At this point, this synthetic approach was put aside, and the synthesis of the unsymmetric dibenz-13-methylphenalene [4] was begun. This route is based on the prior and successful work of Alva,[93] involving formation of an *o*-quinodimethane and its subsequent intramolecular Diels-Alder cycloaddition to give the carbon skeleton [127] of the target compound [4]. The key step here is the thermolysis of a benzthiophene to *o*-quinodimethane and sulfur dioxide, rather than thermolysis of benzcyclobutene, as in the work of Alva. Both methods have wide precedence in the literature.[94] The key sequences of this approach are shown in Scheme 14, with the initial goal being the synthesis of [123] and [124g].



Scheme 14. Proposed Outline for the Synthesis of the Carbon Skeleton [127] of the unsymmetric Dibenz-13-methylphenalene

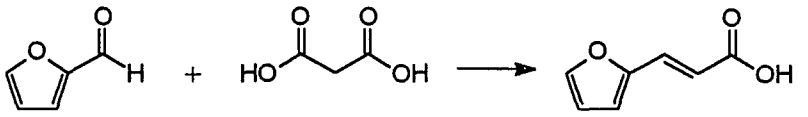
3.2.1 The Synthesis of [123]

The synthesis of the first of the two components required for the intramolecular Diels-Alder reaction is based on the known[95] cyclization of diethylketopimelate [128], leading ultimately to the formation of [123], 2-methyl-4-ethylenedioxycyclohexanone, as outlined in Scheme 15.



Scheme 15. The Synthesis of 2-Methyl-4-ethylenedioxycyclohexanone [123]

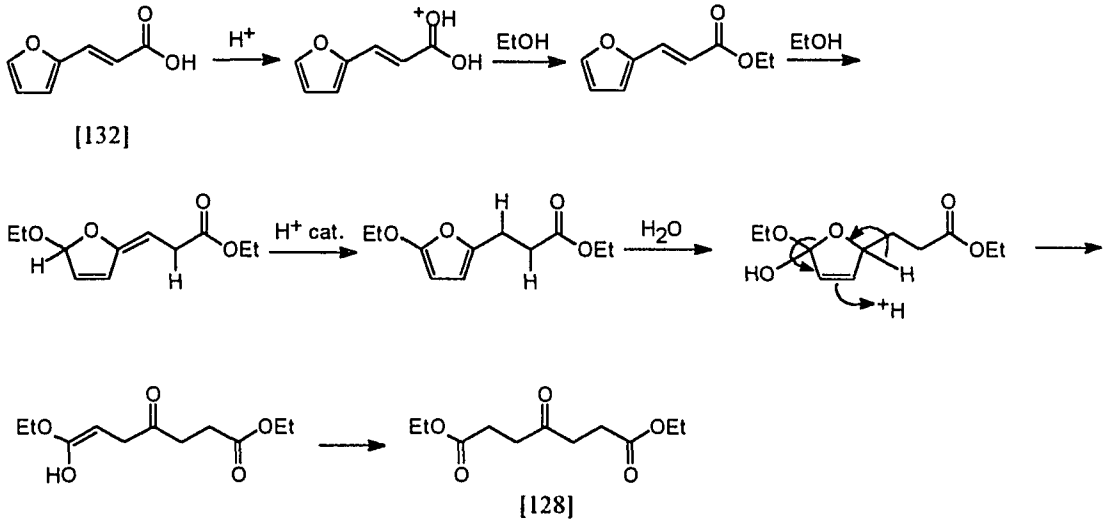
Dimethyl-γ-ketopimelate [17] itself is synthesized in two steps. The first is the known reaction[96] of furfural with malonic acid to form furylacrylic acid [132], as shown in Figure 40.



[132]

Figure 40. Synthesis of Furylacrylic Acid [132]

Furylacrylic acid [132] was subsequently converted to diethyl-γ-oxopimelate [128], undergoing rearrangement in the presence of HCl gas and 95% ethanol or methanol.[97] A proposed mechanism is shown in Scheme 16. Both dimethyl and diethyl esters have been synthesized in separate experiments.



[132]

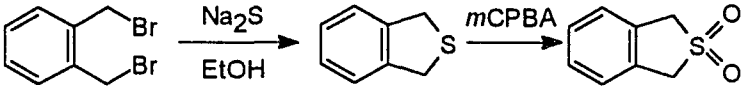
[128]

Scheme 16. The Mechanism of the Formation of Diethyl-γ-ketopimelate from Furylacrylic Acid

Next, dimethyl-γ-ketopimelate [128] was protected with ethylene glycol to form the ketal [129], and then cyclized with NaH to give 2-carbomethoxy-2-methyl-4-ethylene-dioxycyclohexanone [130]. This was methylated with MeI to give [131] and alkaline hydrolysis finally gave [123].[98] Alternatively, [129] could be both cyclized and methylated in a one pot conversion to [131] by quenching the cyclization reaction with methyl iodide instead of aqueous work-up. Alkaline hydrolysis again gave the desired 2-methyl-4-ethylene-dioxycyclohexanone [123].

3.2.2 The Synthesis of [124]

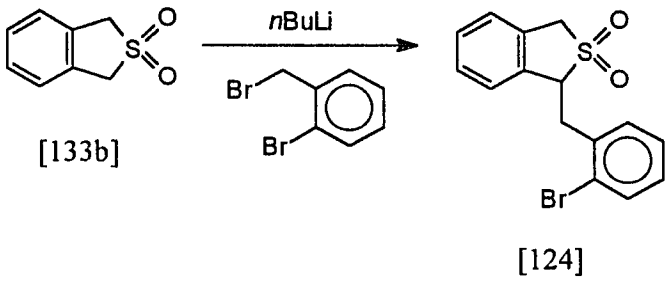
The use of *o*-quinodimethanes, generated from the extrusion of sulfur dioxide at high temperature, has had wide use and application in organic synthesis.[99] The route toward [124] was begun according to the outline shown in Figure 41. Benzthiophene [132] was prepared from anhydrous Na_2S and α,α'-dibromo-*o*-xylene, using high-dilution conditions.



[133a] [133b]

Figure 41. The Synthesis of 1,3-Dihydroisothianaphthene [133a] and 1,3 Dihydroisothianaphthene-2,2-dioxide [133b]

Next, [133a] was oxidized to the sulfone [133b] by *m*CPBA, and finally alkylated, using *n*-BuLi, to generate the anion. This was followed by addition of *o*-bromobenzyl-bromide to form [124] in 32% yield.

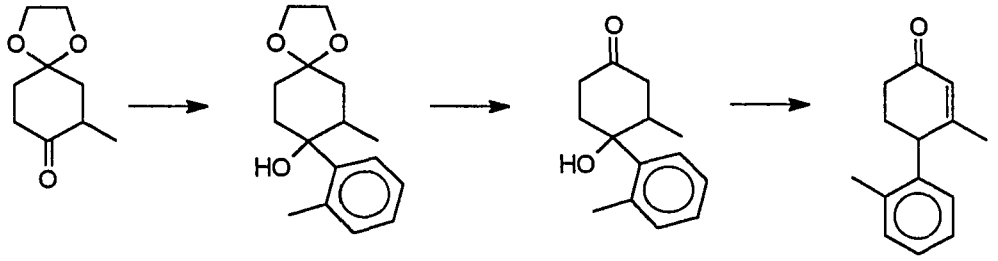


[133b] [124]

Figure 42. The Synthesis of [124]

3.2.3 The Coupling of [123] and [124]

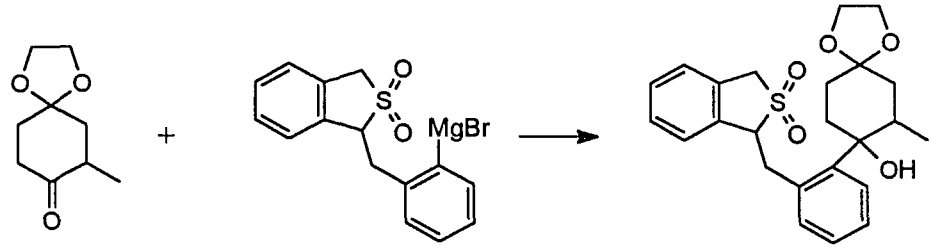
In order to study the feasibility of the coupling of [123] and [124], an initial model experiment was undertaken, reacting [123] with (2-methyl)-phenylmagnesiumbromide, which resulted in a 71% crude yield of 3-methyl-4-hydroxy-4-(2-methylbenzene)-1-ethylenedioxy-cyclohexane [134]. Mild acid hydrolysis gave 3-methyl-4-hydroxy-4-(2-methylbenzene)-cyclohexanone [135] and hydrolysis using concentrated H_3PO_4 gave 4-(2-methylbenzene)-cyclohex-2-enone [136].



[123] [134] [135] [136]

Figure 43. Model Reactions of [123]

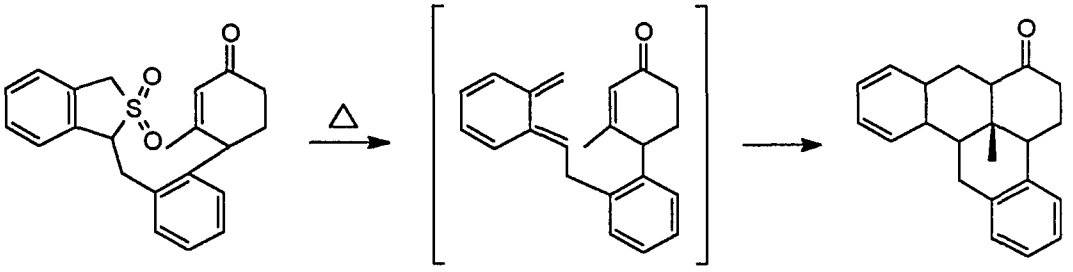
The coupling of [123] and [124] requires the formation of the corresponding grignard reagent [124g] prior to the addition of [123]. However, the condition for forming [124g] was incompatible with the presence of the acidic α-hydrogens present on the sulfone, and neither the desired product [125] nor starting material were observed.



[123] [124g] [125]

Figure 44. Attempted Coupling of [123] and the Grignard Reagent [124g]

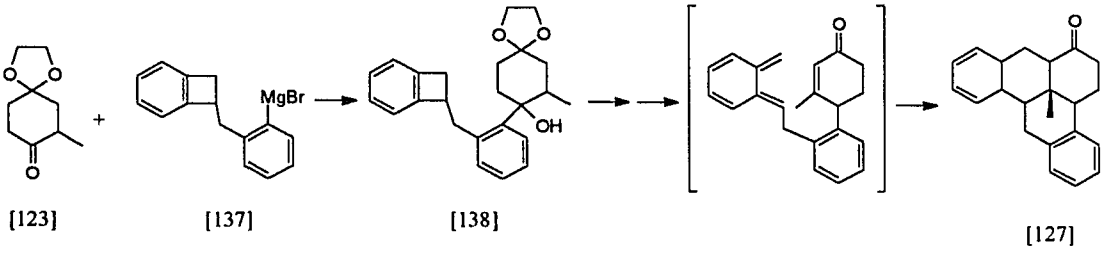
As shown in Figure 45, if coupled, [125] would be deprotected by mild acid hydrolysis to give the ketone [126]. Heated to around 300°C, [126] should extrude sulfur dioxide gas to form benzcyclobutene, which would then subsequently open to *o*-quinodimethane and undergo intramolecular Diels-Alder addition, leading finally to the methylphenalene derivative [127].



[126] [127]

Figure 45. Extrusion of SO_2, Formation of *o*-quinodimethane, and Subsequent IMDA of [126] to form [127]

One possible route around the problem of forming [124g] would be to reduce the sulfone back to the sulfide, carry out the grignard coupling, and then re-oxidize the sulfide back to the sulfone. Most likely, the best route would employ the use of a benzcyclobutene derivative [137], rather than the benzthiophene. This closely follows the previous use by Alva of 1-cyano-benzcyclobutene in his synthesis of the monobenz-13-methylphenalene [2].[100]



[123] [137] [138] [127]

Figure 46. Proposed Route Towards the Carbon Skeleton [127] of Dibenz-13-methylphenalene

3.3 The meta-*cyclophane/Cope rearrangement Approach toward the Symmetric Dibenz-13-Methylphenalene*

The third and last synthetic target of this investigation, the symmetric dibenzannulated-13-methylphenalene [3], is the least stable of the entire series of [12]-annulenes, as predicted by AM1 calculations. In contrast to the previous two synthetic targets, which have been predicted to be *stabilized* by benzannelation, compound [3] is an extremely inteesting example of the dependence of the BDE upon the location of the second point of benzannelation on the ring, and is predicted to be *destabilized* by benzannelation. Calculations suggest it should have a central sp^3 carbon/methyl BDE of only 1.03 kcal/mole, as opposed to 33.37 and 26.43 for the symmetric tri] and unsymmetric di-benz-13-methylphenalenes, respectively.

Although this target may ultimately prove elusive, there are some encouraging points which suggest this compound may be isolated under the right conditions. The first is that the AM1 heat of formation calculations for both the allene and the parent compound above are within 1 kcal/mole energy difference. The second is that the energy barrier between the parent compound and the radicals formed by homolysis of the central sp^3 carbon/methyl bond is resonably high enough (24.3 kcal/mole) to suggest that it may be isolated at low temperature. The last reason is that the existance of a compound containing a bond with a near-zero BDE is very exciting, and that the synthetic routes toward its isolation also provide an opportunity for the investigation of novel *meta*-cyclophanes.

This route has been constructed around the formation of a *meta*-cyclophane allene, which is expected to undergo Cope rearrangement to the desired annulene, similar to that which is observed for Boekelheide's dihydropyrenes.

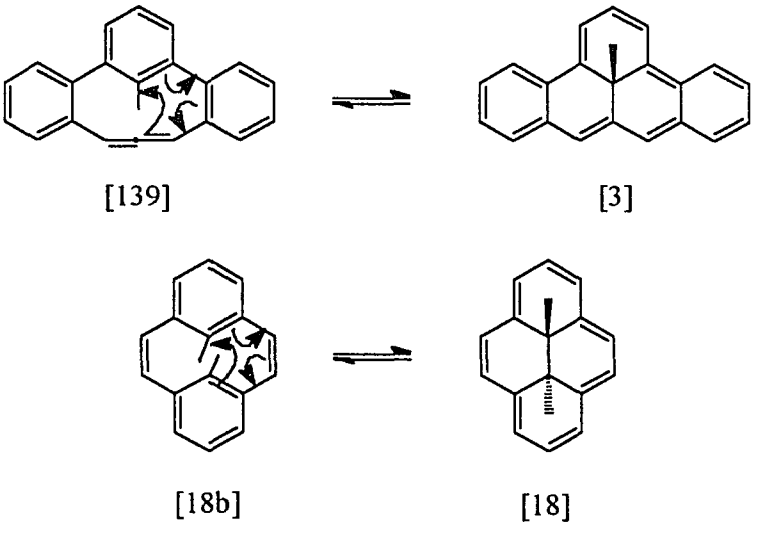
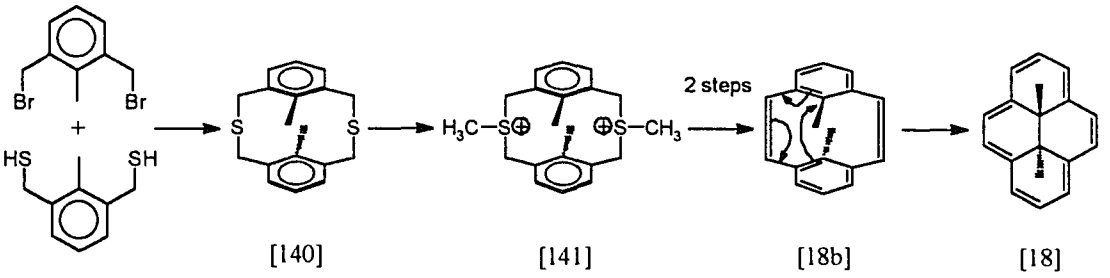


Figure 47. Comparison of the Cope rearrangement of [3] with Boekelheide's [18]

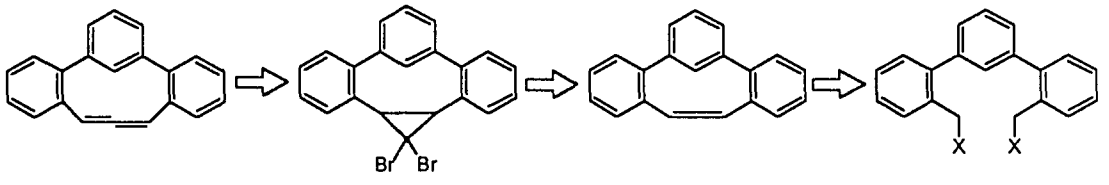
The precedence for this strategy is outlined in Scheme 17. Boekelheide[101] has synthesized *trans*-15,16-dimethyldihydropyrene [18] by first forming the *meta*-cyclophane disulfide [140] from the reaction of the appropriate dibromide and disulfide under high dilution conditions. By employing the Stevens rearrangement of the *bis*-sulfonium salt [141], followed by Hofmann elimination and irradiative or heat-induced valence tautomerism, the bridge [14]-annulene [18] was formed. It is this last step that has led to the idea that perhaps the same or similar sequence could lead to 13-methylphenalene and its benzoderivatives.



[140] [141] [18b] [18]

Scheme 17. Outline of the Synthetic Route Towards [18]

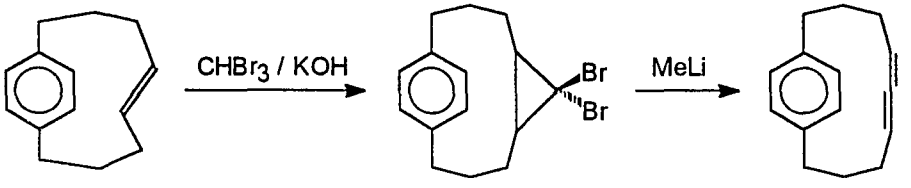
The route to the cyclophane-allene [139] has been broken into two sections for clarity. The retrosynthetic pathway for the second half is shown in Scheme 18 below. The allene [139] is formed by reaction of methyllithium and subsequent rearrangement of the dibromo cyclopropane [142]. The cyclopropane is produced by the reaction of the cyclophan-3-ene [143] with dibromocarbene. Compound [143], a [6]-metacyclophane-3-ene, can itself obtained by several strategies which are discussed later. Dreiding model considerations suggest that there is little strain present I the allene [139], and AM1 calculations give a heat of formation within one kcal/mole of the target dibenz-13-methylphenalene [3].



[139] [142] [143]

Scheme 18. Retrosynthetic Sequence for the Formation of the Allene [139] from a *meta*-terphenyl

The steps leading to [142] and [139] are based on the synthesis of [8]-paracyclophane and several novel derivatives by Noble and Hopf[102], including *trans*-[8]-paracyclophan-4-ene [144] and its reaction with dichloro- and dibromocarbene to form the cyclopropane adduct [145], which was then subsequently converted to the paracyclophane-allene [146] ([9]-paracyclophane-4,5-diene) by reaction with methyllithium. Therefore, it is known that cyclophane-enes and cyclophane-allenes similar to [139] and [142] do exist and are obtainable in reasonable yields. The methodology used to produce [146] can be applied toward the synthesis of [139] and ultimately towards the symmetric dibenz-13-methylphenalene [3].



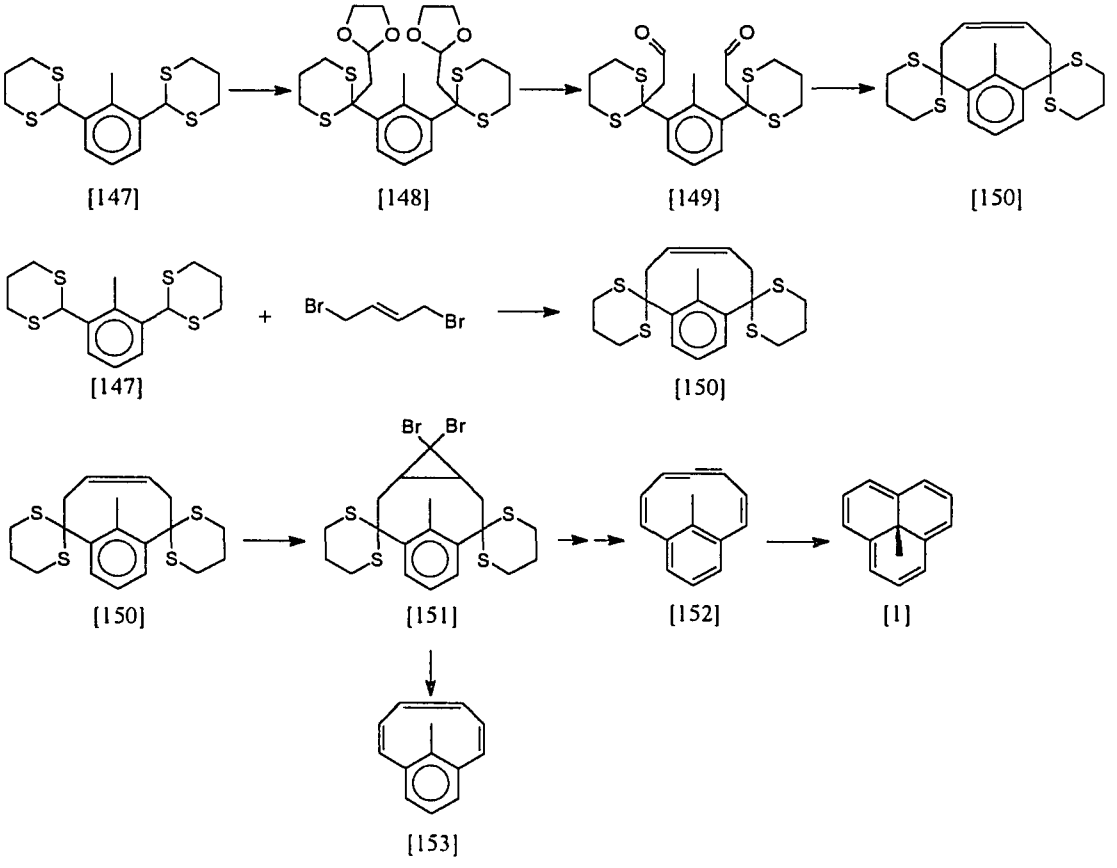
[144] [145] [146]

Scheme 19. Synthesis of Noble and Hopf's [9]-Paracyclophane-4,5-diene [146]

Therefore, the first goal and key intermediate in this strategy is the synthesis of a *meta*-terphenyl which is able to undergo cyclization to form either the cyclophane-3-ene [143] itself, or a compound which can be later transformed into the cyclophane-3-ene. Several routes have been explored and are discussed.

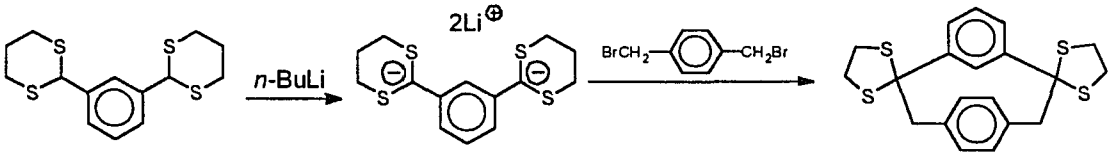
3.3.1 The Dithiane Approach towards *meta*-6-cyclophane-3-ene and 13-methylphenalene

Related to the meta-terphenyl approach and included here is a route toward 13-methylphenalene through the formation of *meta*-6-cyclophane-1,3,4,6-tetraene [152]. This involves the synthesis and use of a *meta*-dithiane [147], formed from the protection of 2-methylisophthalaldehyde with 1,3-propanedithiol, and closed either via double nucleophilic substitution or McMurry coupling with $TiCl_3$/DME/Zn-Cu,[103] as outlined in Scheme 20.

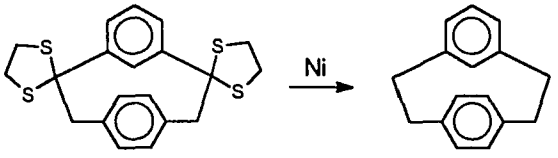


Scheme 20. Proposed Synthetic Outline for [153] and [1]

This synthetic sequence has precedence with Boekelheide's work with [2.2]-metaparacyclophane, which was produced in 36% yield from the dithiane derivative and α,α'-dibromoparaxylene.[104]



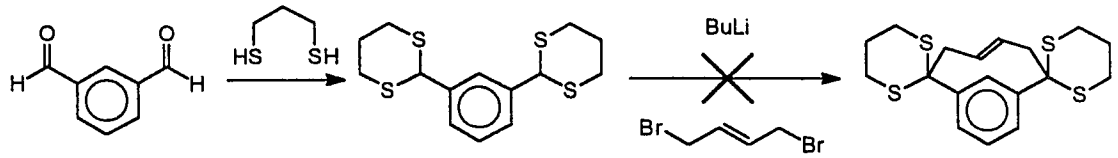
[147] [147b] [154]



[154] [155]

Scheme 21. Synthesis of [2.2]-metaparacyclophane [155]

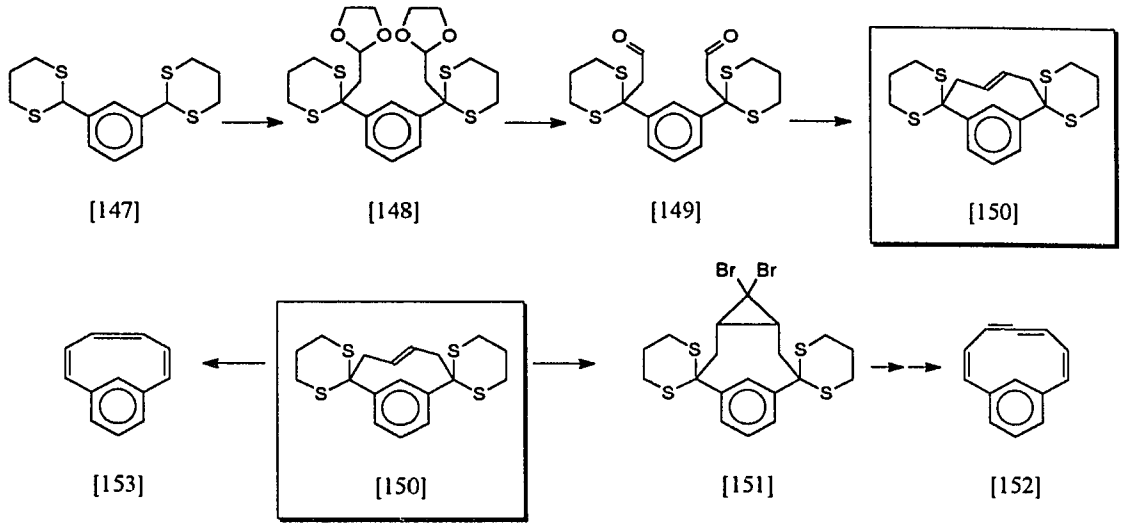
The model dithiane initially used isophthalaldehyde [156] and two moles of 1,3-propanedithiol to form the *meta*-dithiane [147]. There is no methyl group in this reaction series. Isophthalaldeyde was chosen to be used in the first model system due to its availability and the simplicity of the model system. The first attempt at ring closure used two moles of butyllithium to initially form the dianion, followed by addition of one mole of *trans*-1,4-dibromo-2-butene, which failed to give the [6]-metacyclophane-3-ene derivative [150].



[156] [147] [150]

Figure 48. Attempted Synthesis of [150]

In the next attempt at ring closure, the dianion [147] was reacted with two moles of 2-bromoacetaldehyde-ethylenedioxyacetal to give [149]. Selective deprotection to the dialdehyde would have been followed by McMurry coupling and ring closure to form the [6]-metacyclophane-3-ene derivative [150], but this step is predicted to be at best difficult to carry out, as the $TiCl_3$/Zn-Cu catalyst could be poisoned by the presence of the sulfur, and this route was abandoned. Further deprotection, reduction and elimination of [150] would have lead to [153], an unusual [6]-metacyclophane-1,3,5-triene. Alternatively, the dibromocarbene adduct [151] could be formed from [150], followed by subsequent steps leading to the allene [152].



Scheme 22. Proposed Synthetic Outline for the Synthesis of 6-Cyclophane-1,3,5-triene [153] and 7-Cyclophane-1,3,4,6-tetraene [152]

3.3.2 The *meta*-Terphenyl Approach To *meta*-6-Cyclophane-3-ene [143]

Several routes toward a *meta*-terphenyl containing a methyl group situated between the external phenyl groups which are suitable for ring closure have been investigated. These include copper(I)bromide/copper(I)cyanide catalyzed reaction of bromotoluene with 2,6-dibromotoluene; palladium-catalyzed coupling of aryl bromides with aryl trialkyl tin reagents; and finally twofold addition of arylmagnesium bromide to benzyne. The synthesis of an appropriate *meta*-terphenyl, followed by closure of the ring to ultimately lead to the allene [139] is the key goal towards the symmetric dibenz-13-methylphenalene.

3.3.2.a The Copper (I) Bromide catalyzed Approach

The first trial employed the use of copper [I] cyanide or copper [I] bromide in the coupling of arylbromides with 2,6-dibromotoluene [156.] 2-bromotoluene [154] was added to lithium metal in ether, and the aryllithium was then added to a solution of cooled (-30°C) CuCN or $CuBr/Me_2S$ complex in ether. The desired terphenyl [157] was observed however in only trace amount, the major products being dimethyl biphenyl [158] and bromodimethyl biphenyl [159.]

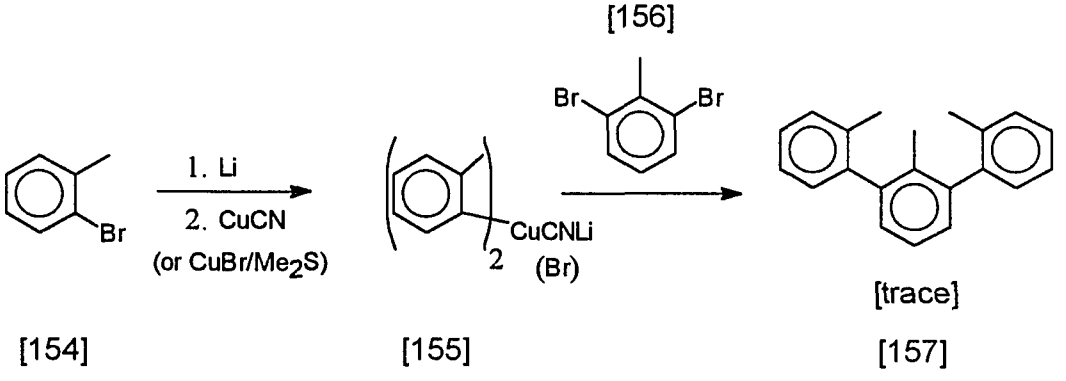
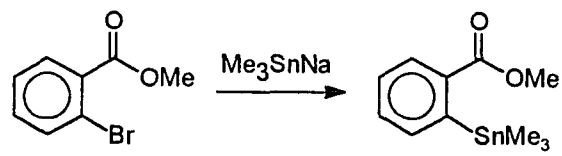


Figure 49. Attempted Cu(I) Catalyzed Synthesis of *meta*-Terphenyl [157]

3.3.2.b The Stille Approach: Pd Catalyzed Coupling of Aryl Bromide and Aryltrialkyltin

The second trial is based on Palladium-catalyzed coupling of aryltrialkyl tins and aryl bromides as pioneered and reviewed by Stille.[105] Aryltins were produced from the reaction of aryl bromide and trialkyltin sodium in tetraglyme. The trialkyltin sodium was produced *in situ* from the reaction of either hexabutyl- or hexamethylditin with sodium metal. The hexaalkylditins were either purchased or prepared from the reaction of trialkyltin chloride and magnesium.[106]

Two routes were employed using Stille chemistry. In the first, methyl-2-bromobenzoate [160] was reacted with two moles of sodium trimethyltin, to produce *o*-carbomethoxy-phenyltrimethylstannane [161.]



[160] [161]

Figure 50. Synthesis of *o*-Carbomethoxyphenyltrialkylstannane [161]

Next, 2,6-dibromotoluene [156] was reacted with two moles of *o*-carbomethoxy-phenyltrialkylstannane [161] in the presence of palladium [II] or [0] catalyst, but the reaction failed to couple beyond one mole of the tin compound to 2,6-dibromotoluene.

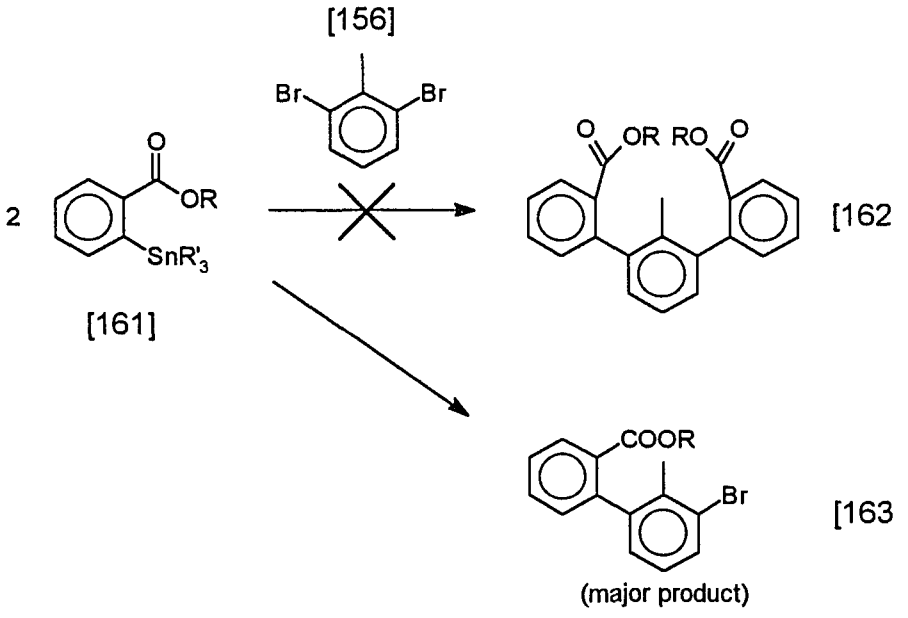


Figure 51. Attempted Pd Catalyzed coupling of [161] and 2,6-Dibromotoluene [156]

The alternate strategy, coupling two moles of sodium trialkyltin to 2,6-dibromotoluene to form the *bis*-2,6-(trialkylstannyl)-toluene [164], followed by palladium-catalyzed coupling to two moles of methyl-2-bromobenzoate to form [162], did not succeed owing to the inability to couple two moles of trialkyltin to 2,6-dibromotoluene in useful yields [Figure 52.]

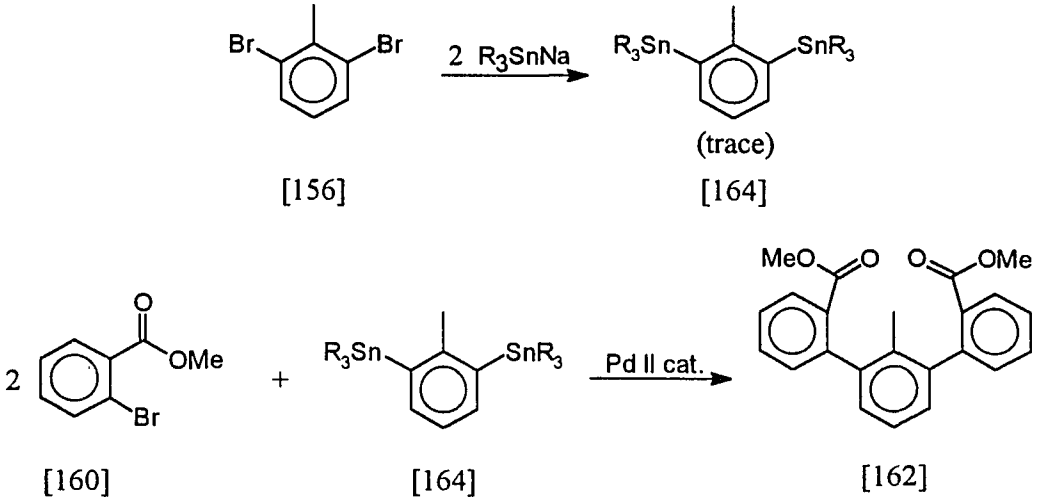
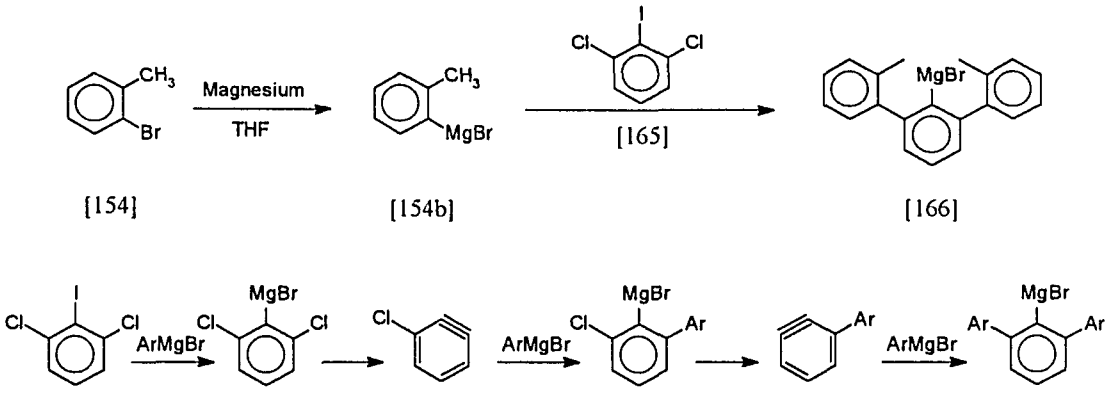


Figure 52. Attempted Synthesis of *bis*-2,6-(Trimethylstannyl)-toluene [164] and its Pd Catalyzed coupling with 2-Bromomethylbenzoate [160]

The failure of the Stille method for these purposes is most likely due solely to steric crowding. A review of the literature[107] supported the observation that *ortho*-substituted aryl trialkyl tin is less favored than *meta*- or *para*- substitution and that this favorability decreases with increasing size of the alkyl group. For example, the coupling of trimethyl tin sodium with methyl-2-bromobenzoate to form *o*-carbomethoxyphenyl-trimethylstannane proceeds in 42% yield (lit. 78%[108]) while that of tributyl tin sodium gave only a trace of product. The only literature reference to *o*-carbomethoxy phenyltri*butyl*stannane shows it being synthesized by [4 + 2] cycloaddition of methyl(tributylstannio)propiolate and butadiene, followed by oxidation with DDQ[109] and not by substitution. Lastly, there is not one example in Stille's work of an aryl bromide or aryl triflate coupling with an aryltrialkyltin in any other but the *para* position.

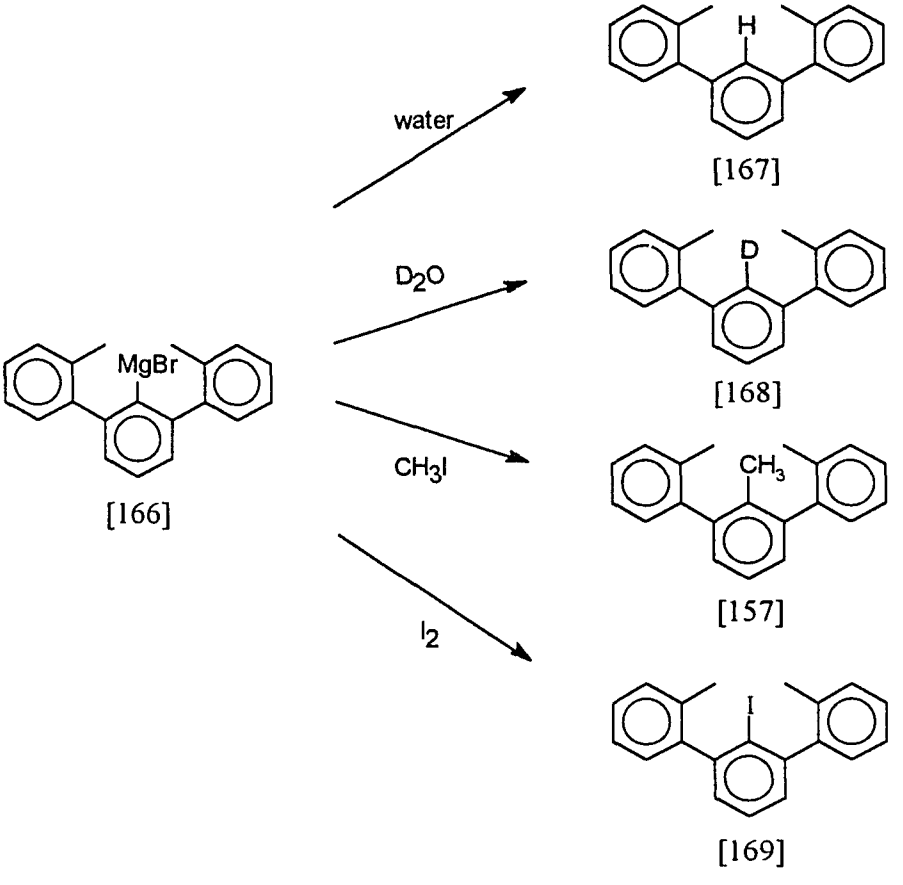
3.3.2.c The Hart Approach: Twofold addition of Aryl Magnesiumbromide to Benzyne

In 1986, Hart[110] published his work on the one-pot synthesis of *meta*-terphenyls via a twofold benzyne sequence. The *meta*-terphenyls are elegently synthesized by the reaction of two equivalents of arylmagnesiumbromide [154b] with 2,6-dichloroiodotoluene [165] in THF to afford relatively high yields of 80-90%. The mechanism is believed to begin by the exchange of $MgBr^-$ with iodide, followed immediately by elimination of MgCl to form benzyne. One equivalent of the arylmagnesiumbromide then adds to benzyne, subsequently followed by a second elimination of MgCl to again give benzyne, and a second addition of arylmagnesiumbromide.



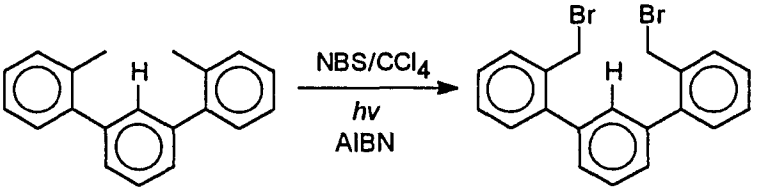
Scheme 23. The Mechanism of the Twofold addition of Aryl Magnesiumbromide to Benzyne

In our initial investigation, it was observed that the reaction does not proceed at all in diethyl ether. The required amount of three equivalents of arylmagnesium bromide (or one equivalent of vinylmagnesium bromide followed by two equivalents of arylmagnesium bromide) was reduced to 2.1 to give satisfactory yields of 88-90%. Several different derivatives can be obtained by the use of different arylmagnesiumbromides and/or quenching the reaction with methyl iodide, dimethylsulfate, iodine, or deuterium oxide, rather than water, at the completion of the reaction.



Scheme 24. Reactions of [166]

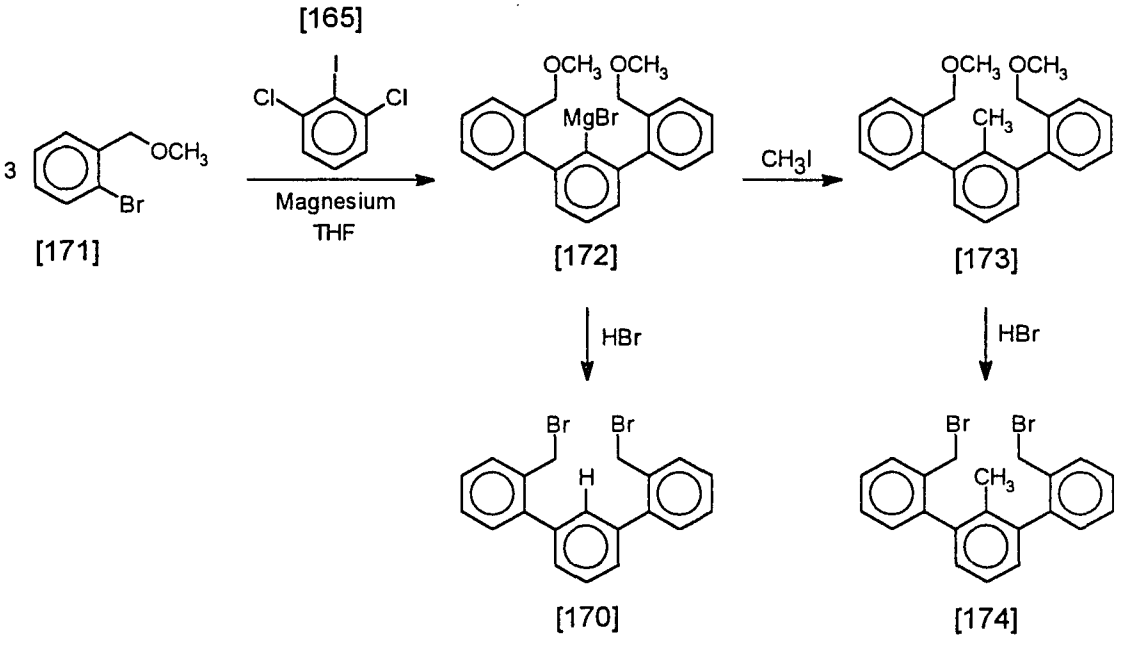
Overall, this method provides an easy route to a variety of terphenyls which can be tailor-made for further modification and investigation. Due to its easy availability and simplicity, the first model system used in this investigation was Hart's known terphenyl [169]. [169] was brominated with NBS in CCl_4 to afford the dibromide [170] in 55% yield.[111]



[167] [170]

Figure 53. Synthesis of 2,2'-*bis*-(bromomethyl)-*meta*-terphenyl [170] from 2,2'-dimethyl-*meta*-terphenyl [167]

An extremely important alternate route toward the dibromide [170] is the preparation of terphenyl [172], available by substituting 2-bromomethoxybenzylether [171] for 2-bromotoluene [154.] [172] is quenched with water, isolated and converted to the bromide [170] by heating in concentrated HBr. Alternatively, [172] can be quenched with methyl iodide to form the methylated terphenyl [173]. The ethoxy ethers can then be cleaved by HBr to the desired [174]. This route avoids the direct bromination of [157] by NBS, which would most likely lead to unwanted dibrominated and tribrominated isomers.



Scheme 25. Alternate Route Towards 2,2'-*bis*-(bromomethyl)-*meta*-terphenyl [170] and [174]

An alternate "back-up" route toward *meta*-terphenyls which has also been considered is Woods' three-step synthesis via the enol ether of dihydroresorcinol.[112] Most yields reported were equal or lower than those reported by Hart.

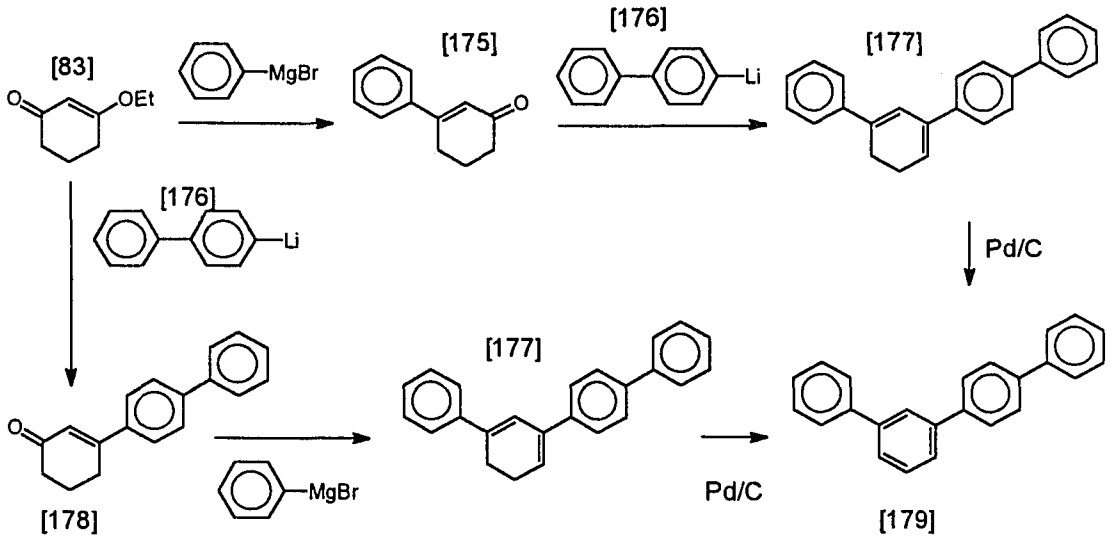
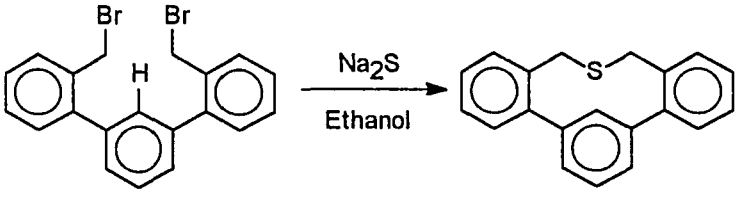


Figure 54. The Woods Synthesis of *meta*-Terphenyls.

One distinct advantage of Woods' method is that different aryl rings may be added, since they are incorporated stepwise onto the center ring. One distinct disadvantage is that addition substituents, such as a methyl group, are not as easily incorporated onto the center ring as they are using Hart's one-step method.

3.3.2.c.i Ring Closure and Formation of the sulfide

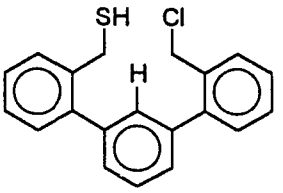
Bromination of [167] was followed by ring closure to 4-thia-1,2:6,7-dibenz-[7]-metacyclophane-1,6-diene [180] by reflux in a solution of sodium sulfide in ethanol, using high dilution techniques. This method has paralleled the earlier sucessful work of Vögtle and Schunder.[113] The order of addition is important. Addition of a solution of Na_2S to a refluxing solution of the dibromide, both in ethanol, resulted in quantitative solvolysis back to the 2,2'-*bis*-(ethoxymethyl)-*meta*-terphenyl [172.]



[170] [180]

Figure 55. Synthesis of 4-thia-1,2:6,7-dibenz-[7]-*meta*-cyclophane-1,6-diene [180]

The sulfide is sensitive to the presence of HCl, and easily undergoes ring opening to 2-thiomethyl-2'-chloromethyl-*meta*-terphenyl [181]



[181]

Figure 56. 2-Thiomethyl-2'-chloromethyl-*meta*-terphenyl [181]

Variable temperature (dynamic) ^{1}H NMR of [180] from 18°C to 137°C shows coalescence at about 80°C and the appearance of a singlet at δ 3.65, sharpest at 137°C.[114] Estimated free energy of activation for the twisting of the cyclophane is based on the equation:[115]

$$\Delta G_{act.} = RT_c\,[23 + \ln(\frac{T_c}{\Delta \nu})] \qquad \textbf{Equation 7}$$

where T_c is the coalescence temperature (353K), $\Delta\nu$ is the frequency separation of the two doublets (435 Hz), and R is the gas constant. $\Delta G_{act.}$ is calculated here to be 66.8 kJ mol^{-1}. This is in agreement with the previously calculated 16 kcal/mol of Vögtle and Schunder.[116] Single-crystal X-ray analysis is in agreement with the structure for 4-thia-1,2:6,7-dibenz[7]metacyclophane-1,6-diene. [180][117]

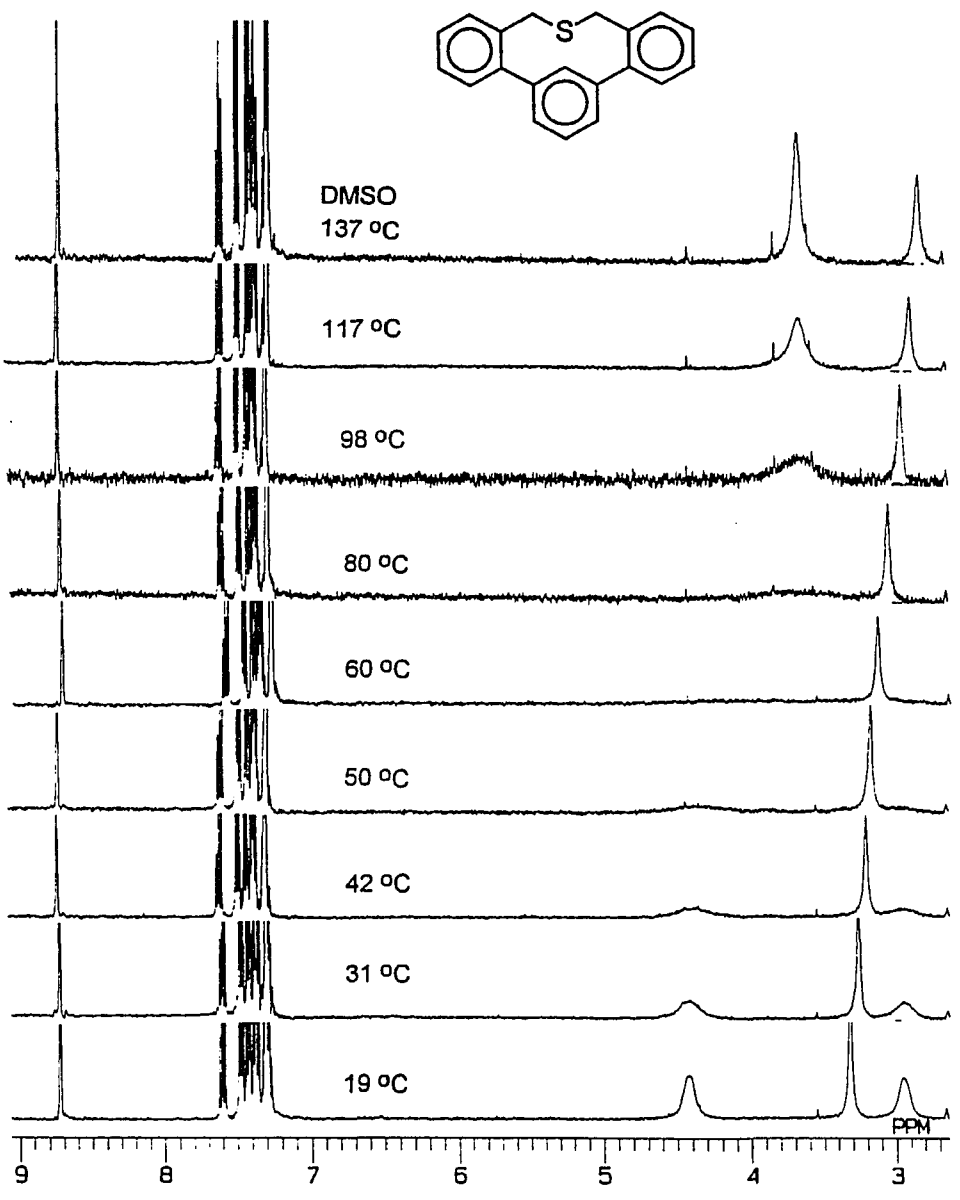
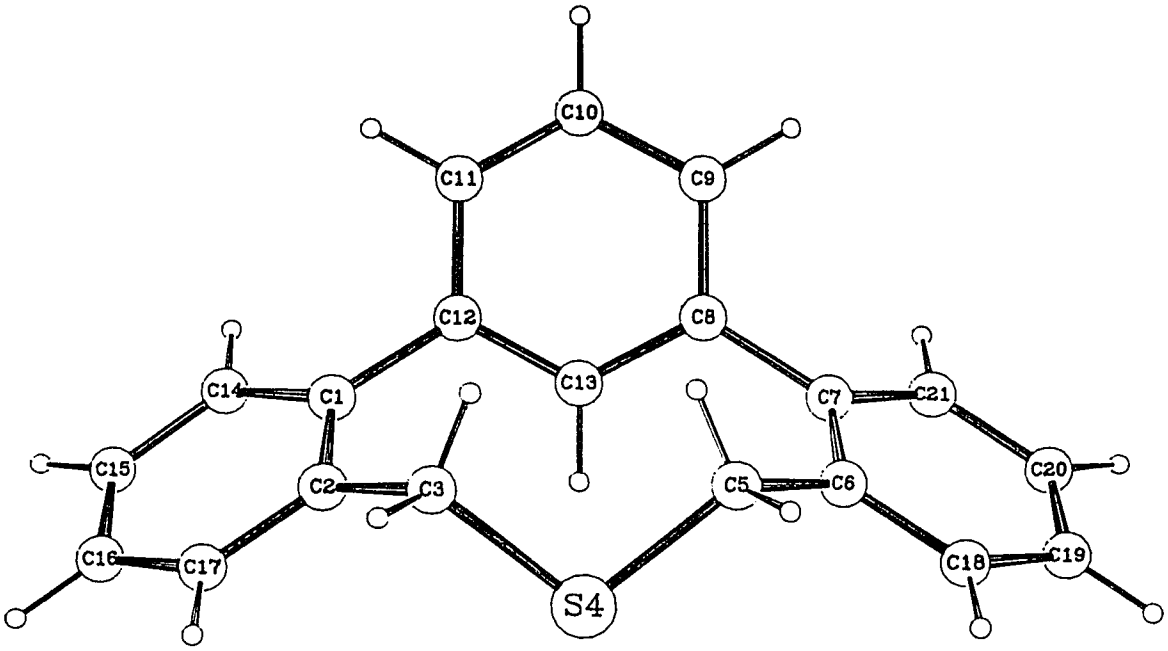


Figure 57. Dynamic ^{1}H NMR of 4-thia-1,2:6,7-dibenz-[7]-metacyclophane-1,6-diene [180] ($CDCl_3$)

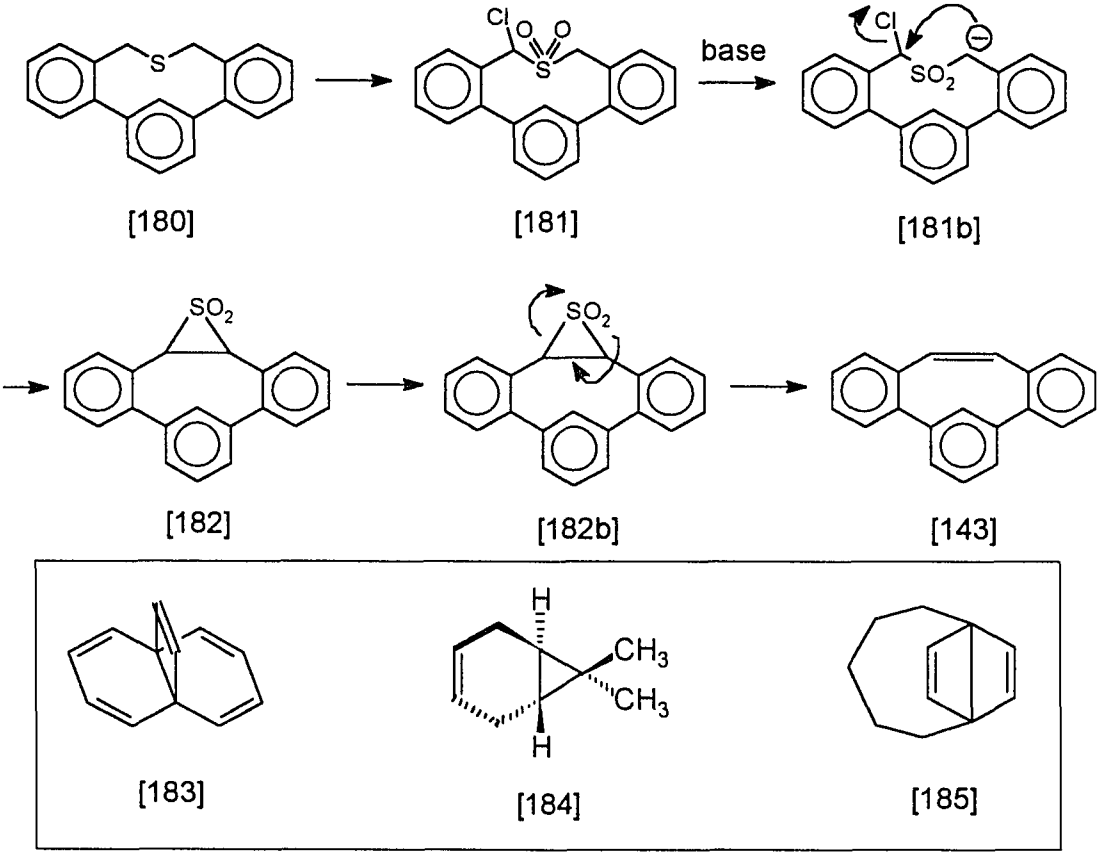


DL−1
(T150R)

Figure 58. X-ray Crystal Structure of 4-thia-1,2:6,7-dibenz-[7]-metacyclophane-1,6-diene [180]

3.3.2.c.ii The Ramberg-Bäcklund Rearrangement

The next step towards 6-cyclophane-3-ene [143] is the synthesis of the α-chlorosulfone [181], which will undergo base-induced Ramberg-Bäcklund[118] rearrangement to afford the [6]-cyclophane-3-ene compound [143]. The proposed mechanism is shown below. Base abstraction of an α-hydrogen results in formation of the episulfone [182], which subsequently extrudes sulfur dioxide to form the alkene [143.] This method has been successfully utilized in the synthesis of a wide variety of strained alkenes, including [183][119], [184][120] and [185].[121]



Scheme 26. Mechanism of the Ramburg-Bäcklund Rearrangement and Selected Examples of Resulting Strained Alkenes

3.3.2.c.iii Attempts at α-Chlorosulfone Formation

The first attempt, based on the work of Tuleen,[122] is one-pot chlorination of the sulfide [180] in CCl_4 solution at 20°C using NCS, followed immediately by oxidation by *m*CPBA to the α-chlorosulfone [181]. However, only the sulfone [187] (8*H*,10*H*-tribenzo-[*c,ef,h*]-[*1*]-thiecine-9,9-dioxide)[123] has been observed, despite several repeated efforts and a successful model chlorination/oxidation of dibenzyl sulfide using these conditions (on one occasion the sulfoxide [187b] was isolated when the number of equivalents of mCPBA was inadvertently halved.)

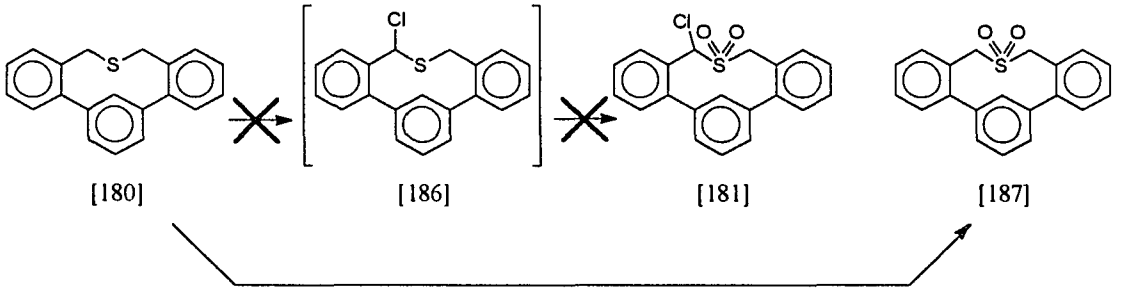


Figure 59. Attempted Synthesis of 8-Chloro-8*H*,10*H*-tribenzo-[*c,ef,h*]-[*1*]-thiecine-9,9-dioxide [187]

α-Chloro-dibenzylsulfone [188] was successfully synthesized from dibenzylsulfide [189] in a separate experiment under identical conditions as a control. In this model study, dibenzyl sulfide was stirred with NCS in CCl_4 for four hours, followed by oxidation with *m*CPBA. A proton NMR comparison of dibenzylsulfide/NBS/CCl_4 and 4-thia-1,2:6,7-dibenz-[7]-metacyclophane-1,6-diene[180]/NBS/CCl_4 shows that while the dibenzylsulfide has for the most part completely reacted with NCS to form the α-chlorodibenzylsulfide, no discernable reaction can be observed with the 4-thia-1,2:6,7-dibenz-[7]-metacyclophane-1,6-diene [180.]

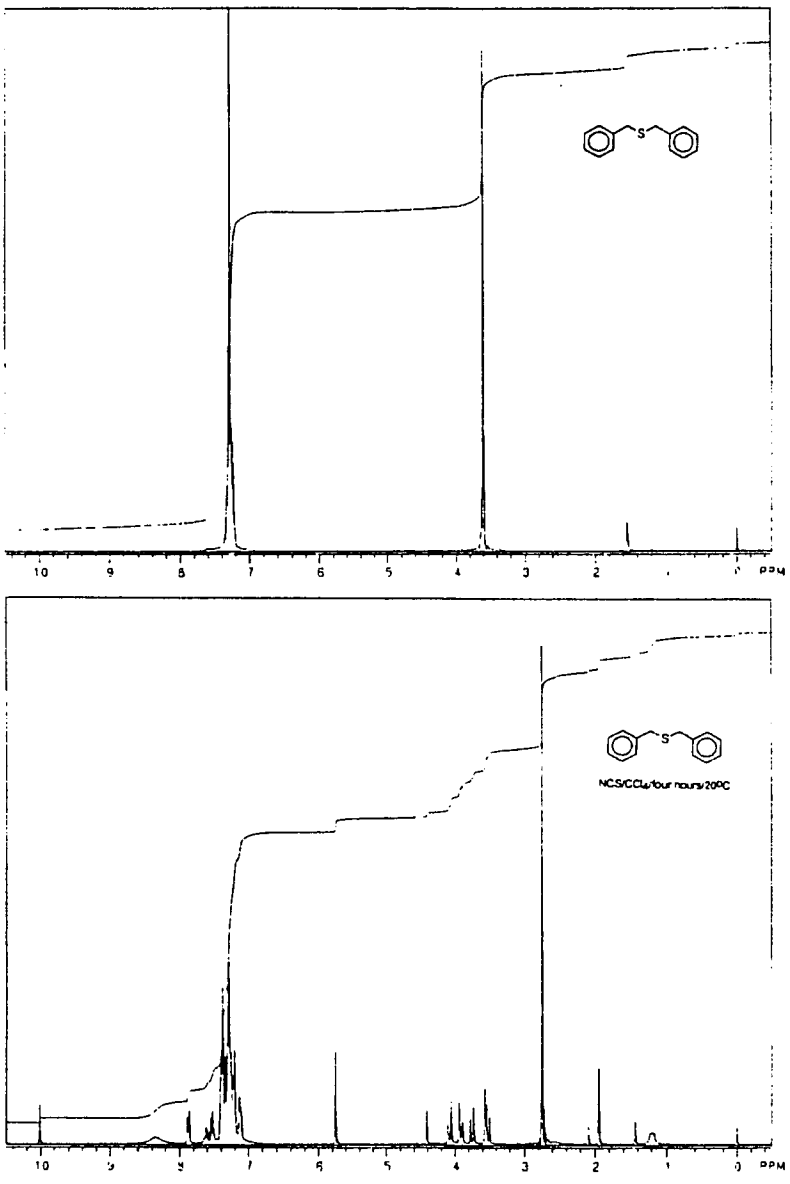


Figure 60. ^{1}H NMR Comparative Study of Dibenzylsulfide (top) and Dibenzylsulfide/NBS/CCl_4 (bottom)

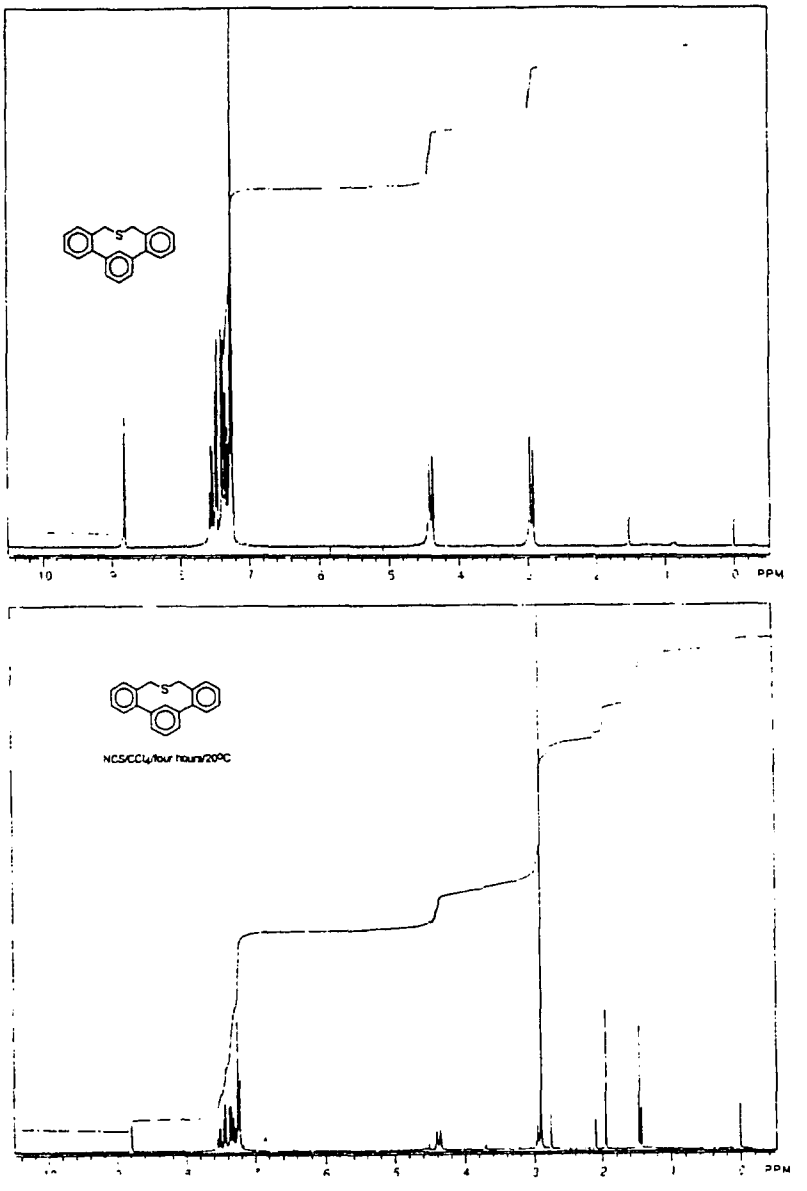


Figure 61. ^{1}H NMR Comparative Study of 4-Thia-1,2:6,7-dibenz-[7]-metacyclophane-1,6-diene[180] (top) and 4-Thia-1,2:6,7-dibenz-[7]-metacyclophane-1,6-diene[180]/NBS/CCl_4 (bottom)

Myers[124] has reported a one-pot procedure in which sulfones bearing α-hydrogens are chlorinated and subsequently induced to undergo the Ramberg-Bäcklund rearrangement to form alkenes. This method has been shown to be useful toward the synthesis of various alkenes from benzyl sulfones and in particular of tetrabenzocyclododecenes[125] which share some structural similarities to to the terphenyl sulfone [Figure 62.]

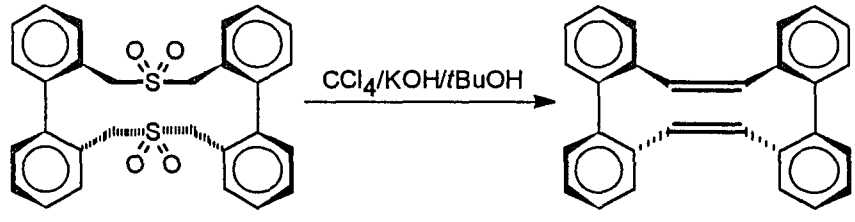


Figure 62. Successful Use of Myers' Reaction to form Tetrabenzocyclododecene

The sulfone [187] was dissolved in CCl_4, and added to a 1:1 mixture of CCl_4/*t*-BuOH and 10% w/v powdered KOH. Two separate studies, at reflux (78°C) for four hours and at 0° C overnight, were performed. In both cases the alkene was not observed. After reflux for four hours, only benz[*e*]acephenathrylene (benzo[*b*]fluoranthene) [189] was observed, identical by proton NMR and mixed mp with an authentic sample, with no sulfone remaining. At 0°C overnight, some sulfone did remained in the reaction mixture, estimated by proton NMR to be about 66% converted to benz[*e*]acephenathrylene. This observation suggests that once the alkene is formed, it immediately rearranges and is oxidized.

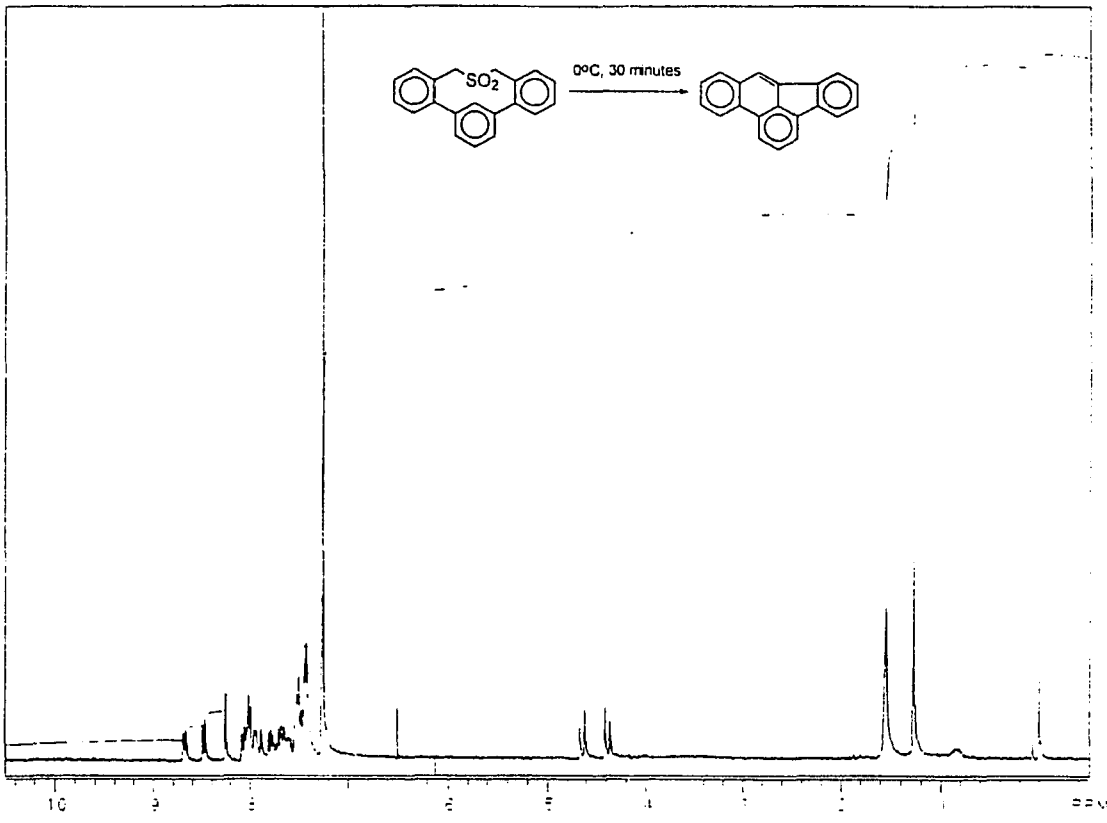


Figure 63. ^{1}H NMR of the Conversion of 8*H*,10*H*-Tribenzo-[*c,ef,h*]-[*1*]-thiecine-9,9-dioxide to Benz[e]acephenathrylene

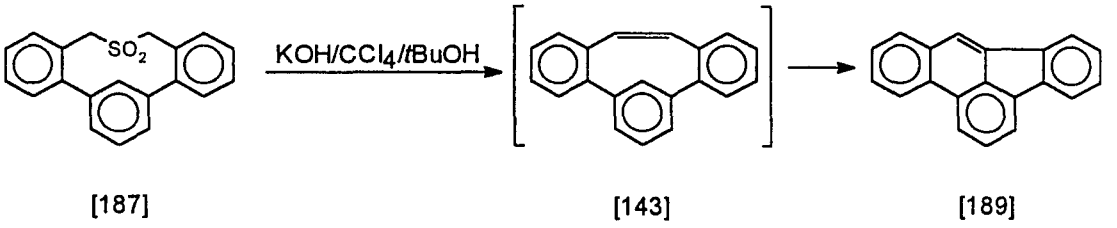
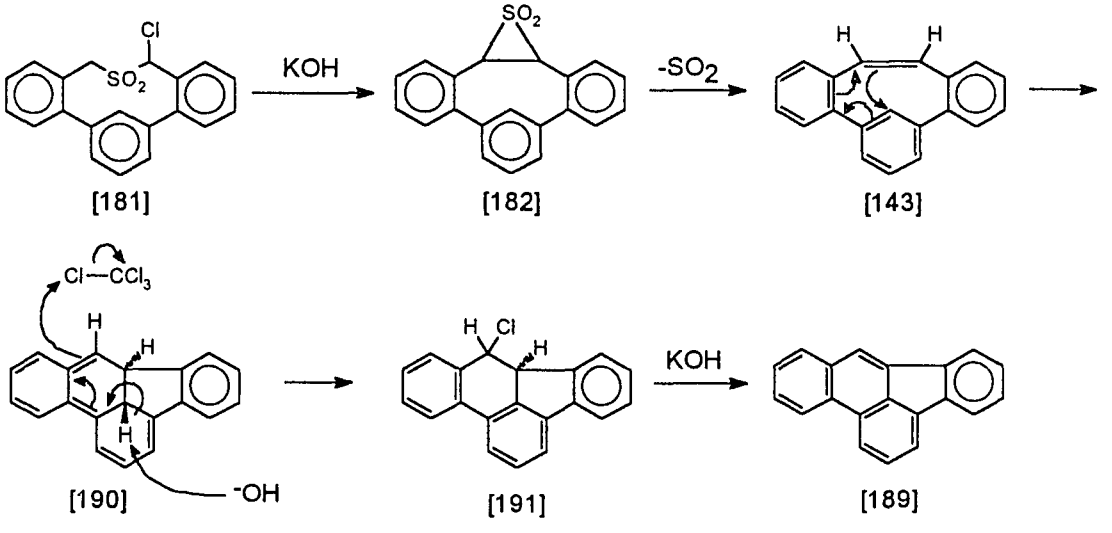


Figure 64. Reaction of [187] with KOH/CCl_4 (Myer's Reaction)

A proposed mechanism for this reaction is as follows. The sulfone is chlorinated by removal of an α-hydrogen by base, followed by attack on CCl_4. Ramberg-Bäcklund rearrangement induced by the presence of KOH forms the episulfone, followed by extrusion of sulfur dioxide to the alkene. Due to the likely proximity of the double bond to the central benzenoid ring, a Cope rearrangement, followed by base-catalyzed chlorination and elimination, results in re-aromatization and the formation of the product benzo[*b*]fluoranthene [189.]

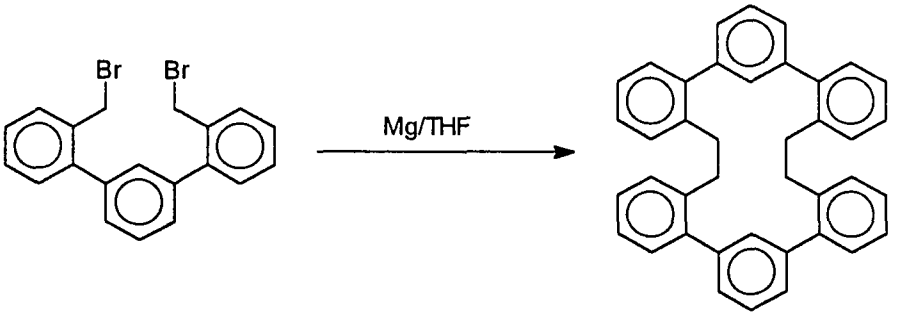


Scheme 27. Proposed Mechanism of the Reaction of [181] with KOH/CCl_4

This result is altogether not surprising. Dreiding model considerations suggest the alkene is extremely strained, and preliminary AM1 calculations suggest that the heat of fomation of the alkene is around 20 kcal/mole greater than that of th allene [139.] Although the desired alkene had not been isolated, this result indicates that the hoped-for Cope rearrangement of these systems does indeed occur, and that this strategy towards the allene [139] will likely yield the dibenz-13-methylphenalene under the right conditions.

3.3.2.c.iv Other Methods for Ring Closure

Two other methods at ring closure have been investigated. In the first method, the dibromide [170] was dissolved in THF and added to magnesium turnings to form the Grignard, followed by addition of solid carbon dioxide or by a solution of dimethylcarbonate. In one experiment, the dimer [192] was isolated in 16% yield.



[170] [192]

Figure 65. Synthesis of the Dimer [192]

Variable temperature (dynamic) proton NMR spectra were run separately in deuterated chloroform and deuterated dichloromethane. In both runs, coalescence of the eight benzyl hydrogens at δ 2.8 was reached at around 0°C. As the temperature was lowered, two doublets emerged at δ 2.45 and 3.00 (10 Hz) as well as the original broadened, lower intensity peak at 2.8. The two doublets were observed to be their sharpest at -60°C in both solvents. Using a value of 273 K for the coalescence temperature T_c, 220 Hz as the frequency separation, $\Delta\nu$, of the two doublets, $\Delta G_{act.}$ is calculated to be 52.6 kJ mol^{-1}. Single crystal X-ray analysis has determined the structure of the dimer[192.][126]

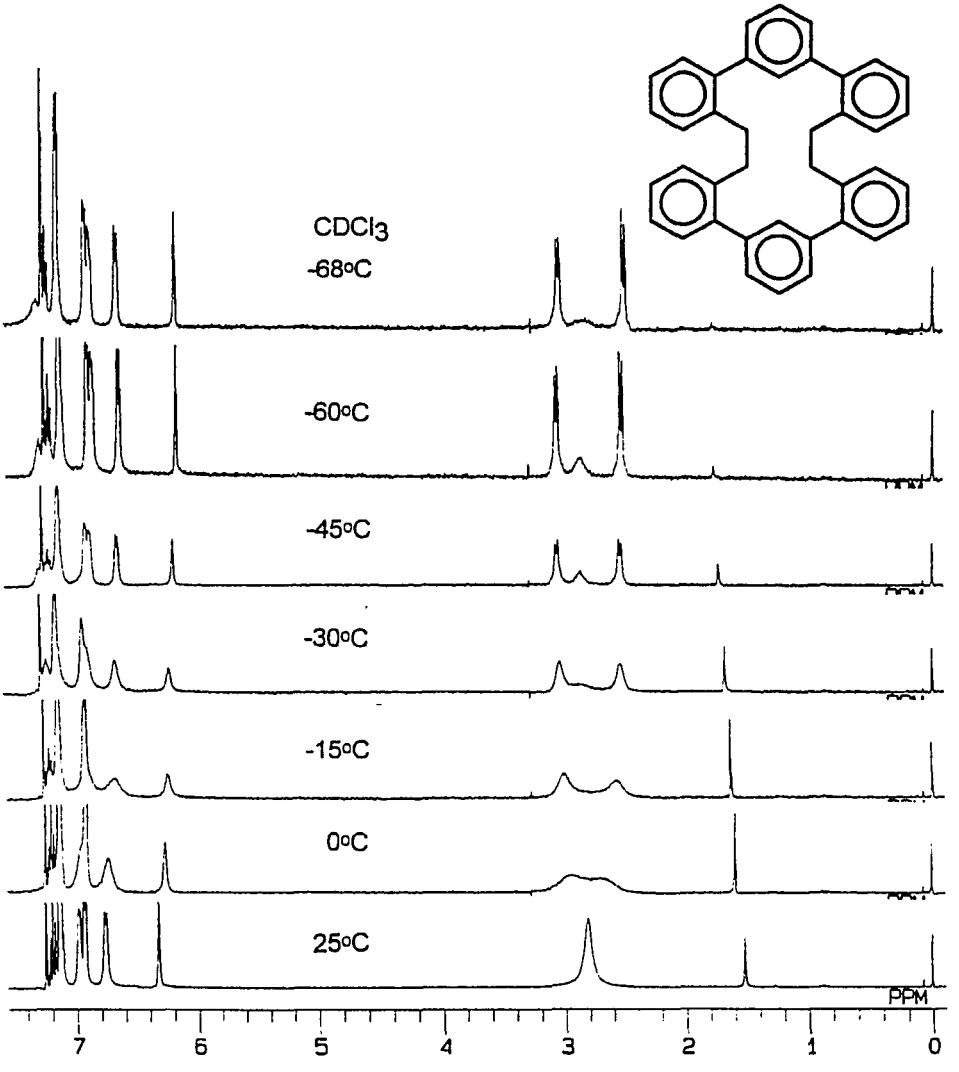


Figure 66. Dynamic ^{1}H NMR of Dimer [192] ($CDCl_3$)

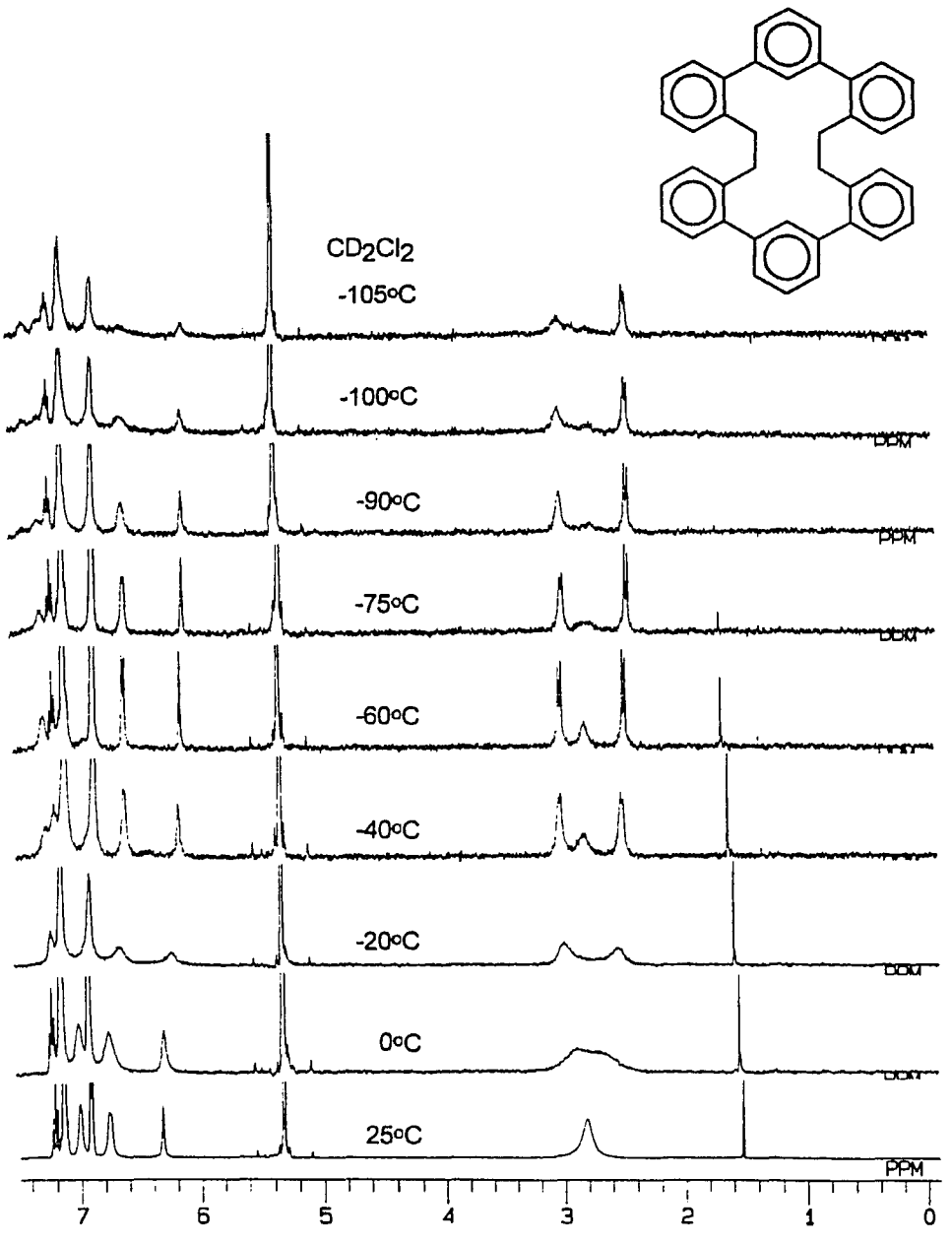
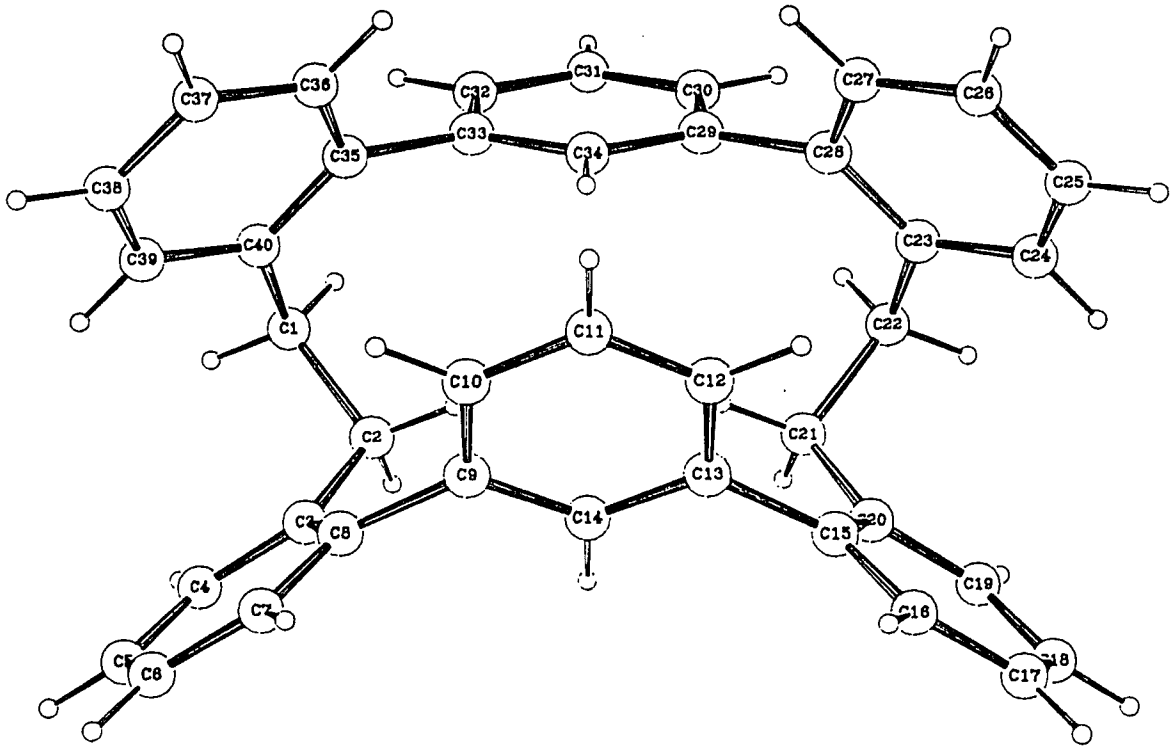


Figure 67. Dynamic ^{1}H NMR of Dimer [192] (CD_2Cl_2)



DL-2

Figure 68. X-ray Crystal Structure for the Dimer [192]

Mass spectra[127] of the Grignard reaction of 2,2'-(bromomethyl)-*meta*-terphenyl [170] and magnesium, followed by the addition of solid carbon dioxide has detected a trace presence of the ketone [193.]

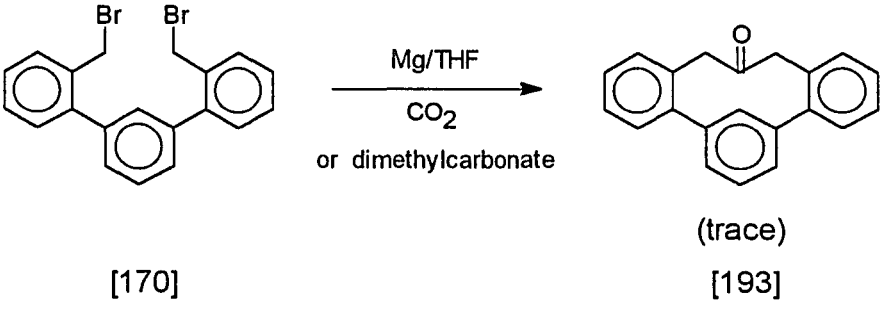
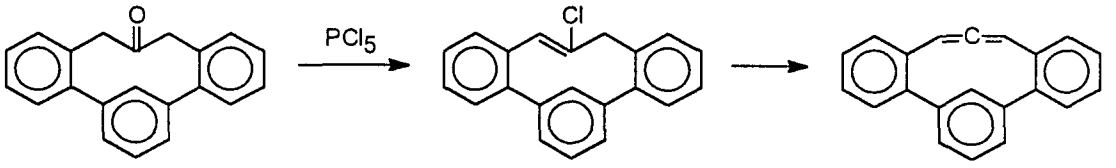


Figure 69. Preliminary Synthesis of Ketone [193]

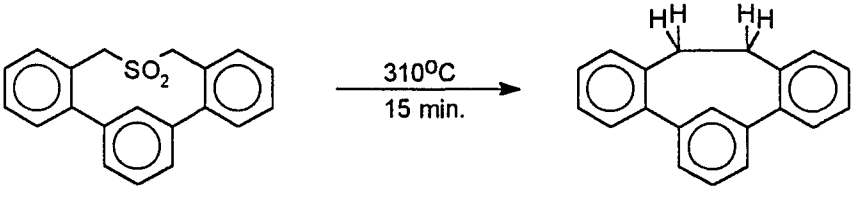
The existence of the ketone [193] is important as it can provide an access to the allene [139] which bypasses altogether the formation of the alkene [143.] This additional route is necessary if the alkene proves too labile and can not be isolated. Dreiding model studies suggest that the ketone, as well as the allene, are not nearly as strained as the alkene. A proposed route toward the allene [139] from the ketone involves chlorination with PCl_5 to form [194], followed by elimination of HCl. Since it is believed that the *meta*-cyclophane-alkyne would be more strained, the allene [139] should be favored as the major elimination product.



[193] [194] [139]

Figure 70. Proposed Route Towards the Allene [139] via Ketone [193]

Pyrolysis of the sulfone [187], neat at 310°C for 15 minutes, lead to the known 2,2'-ethano-*meta*-terphenyl [195], in a recovered yield of 85%.[128]



[187] [195]

Figure 71. Pyrolysis of [187]

X-ray analysis on [195] revealed two conformers existing in about a 70:30 per cent ratio. Variable temperature (dynamic) proton NMR studies were performed on [195] in order to determine the chemical shift of the four bridge hydrogens at low temperatures. At -40°C, four separate peaks (3.7, d, 1H; 3.5, t, 1H; 2.7, t, 1H; 1.3, d, 1H) were observed. The unusual upfield shift of one of the protons can be related to the positioning of this proton above the plane of the center benzene ring. Because this peak is a doublet, the proton is most likely about 90° out of plane from one of the vicinal protons and too far from the other for coupling to occur. Two vicinal protons appear as triplets but are most likely AB quartets.

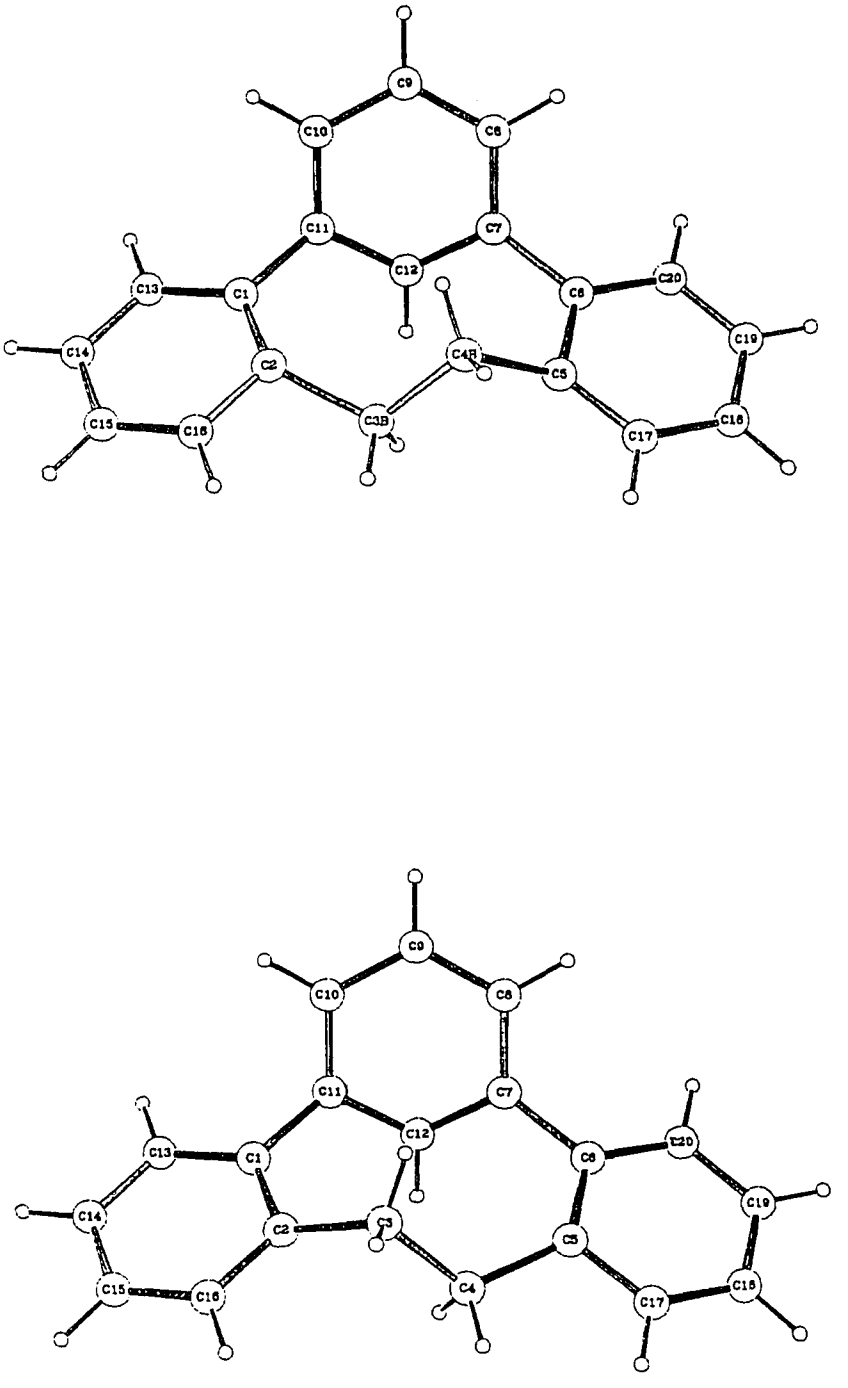


Figure 72. X-ray Crystal Structure of 8,9-Dihydro-tribenzo[*acdf*]cyclononene [195]
Major Conformer (top) and Minor Conformer (bottom)

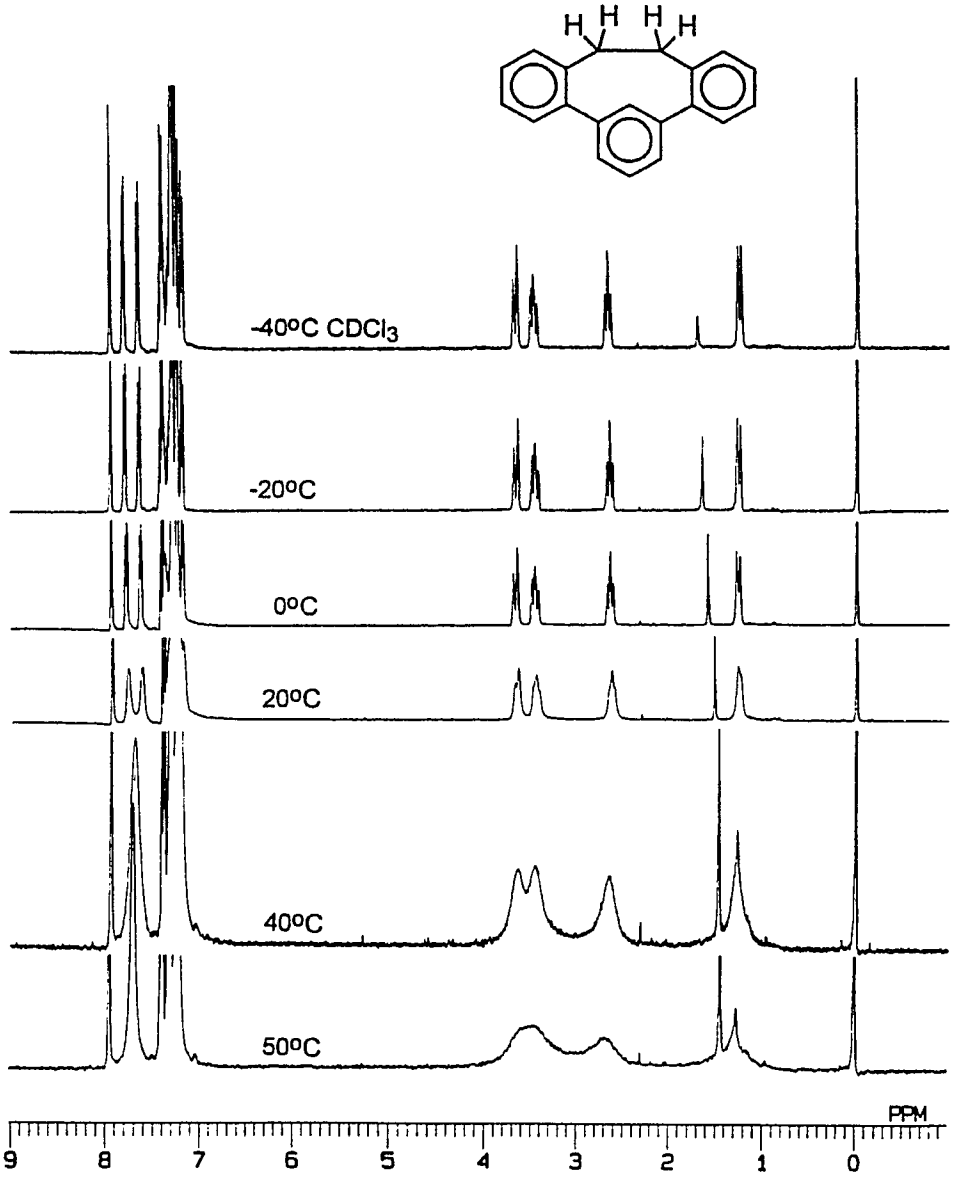


Figure 73. Dynamic ^{1}H NMR of 8,9-Dihydro-tribenzo[*acdf*]cyclononene [195]

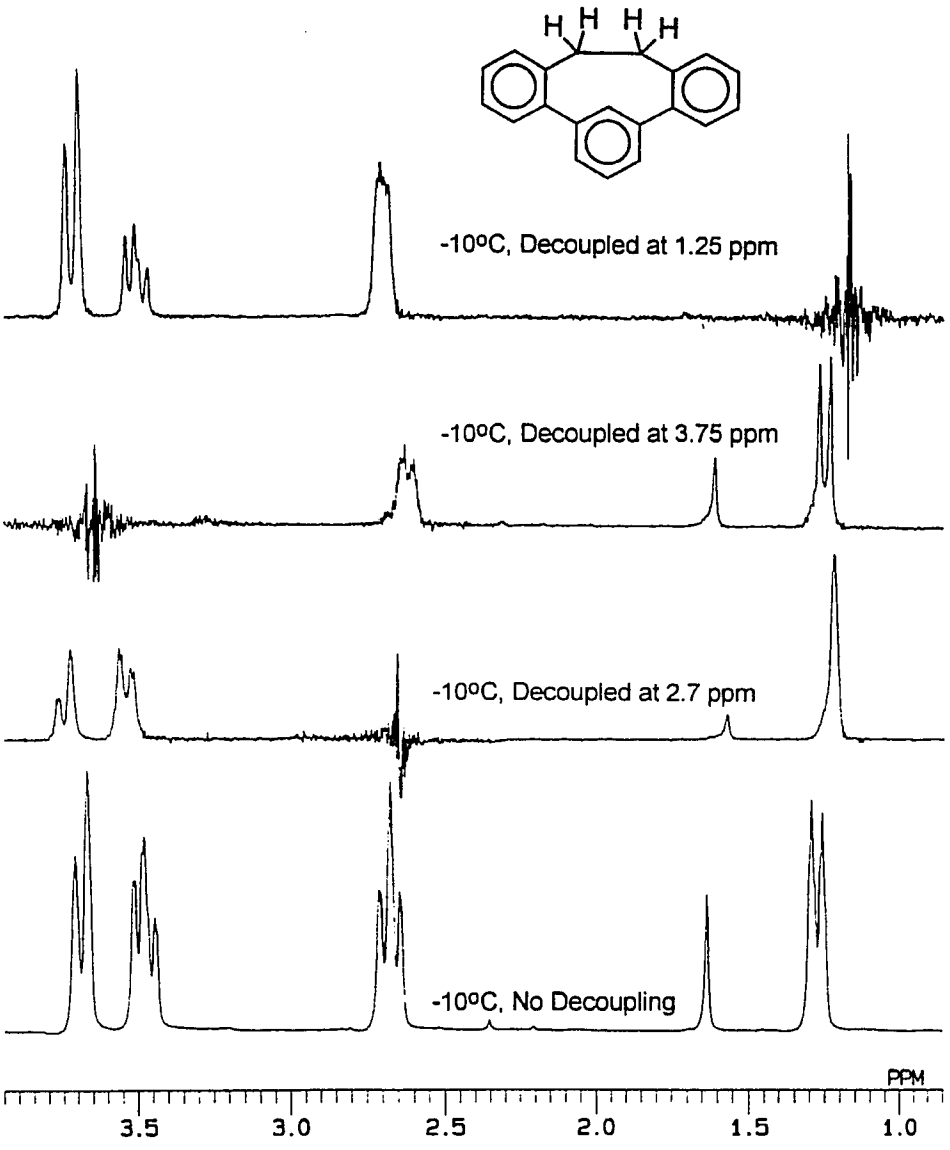


Figure 74. Decoupling Investigation of 8,9-Dihydro-tribenzo[*acdf*]cyclononene [195]

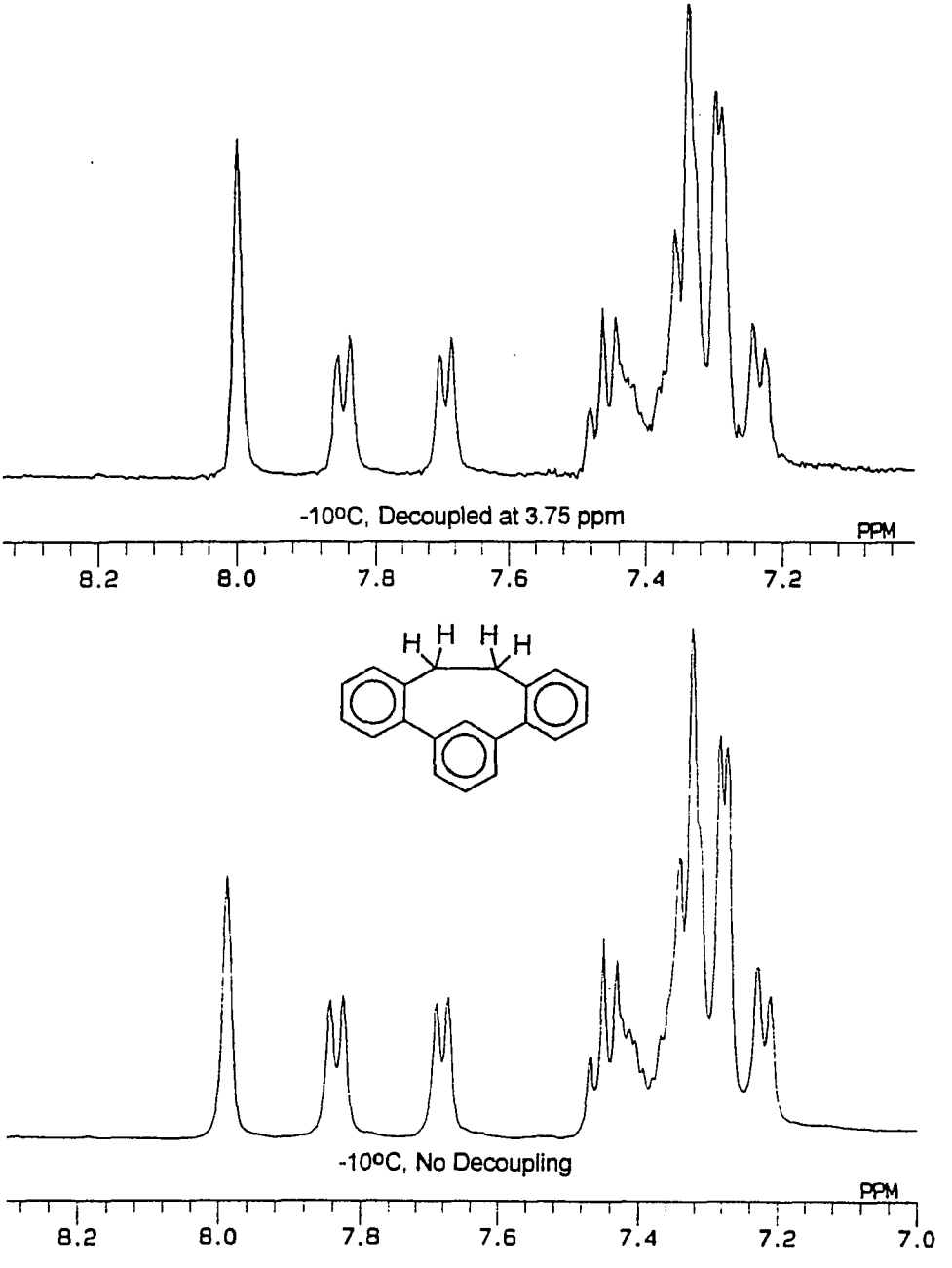


Figure 75. Decoupling Investigation of 8,9-Dihydro-tribenzo[*acdf*]cyclononene Focusing on the Aromatic Proton Region [195]

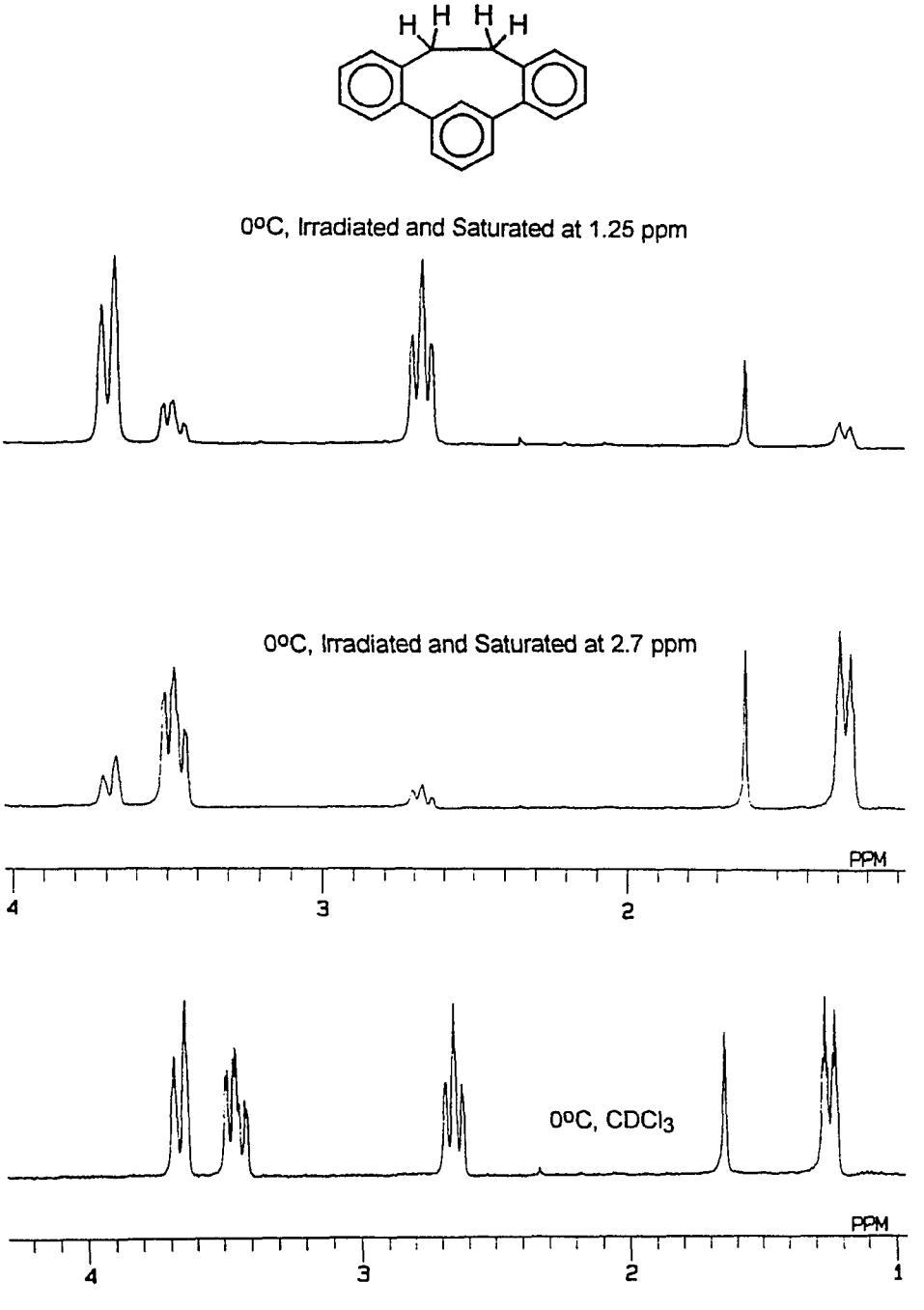
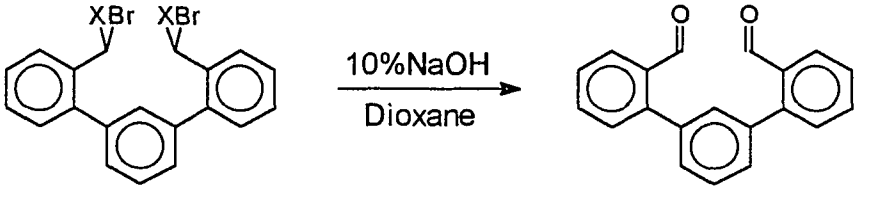


Figure 76. Irradiation Investigation of 8,9-Dihydro-tribenzo[*acdf*]cyclononene [195]

3.3.2.c.v Future Methods for Ring Closure

One earlier bromination of *meta*-terphenyl had erroneously led to a mixture of di, tri-, and tetra-bromides [196.] This mixture was refluxed in 10% NaOH/Dioxane, followed by oxidation with chromium trioxide/pyridine complex[129] to afford the dialdehyde [197] in relatively good yield (88%.)

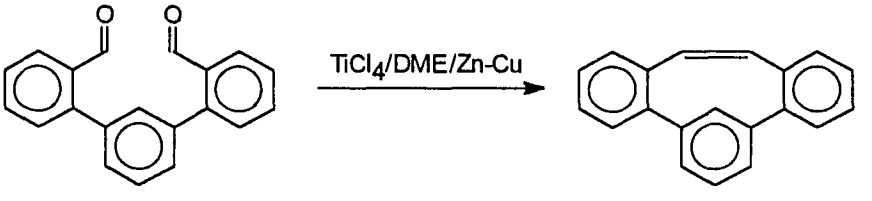


X = Br, H

[196] [197]

Figure 77. Synthesis of Dialdehyde [197]

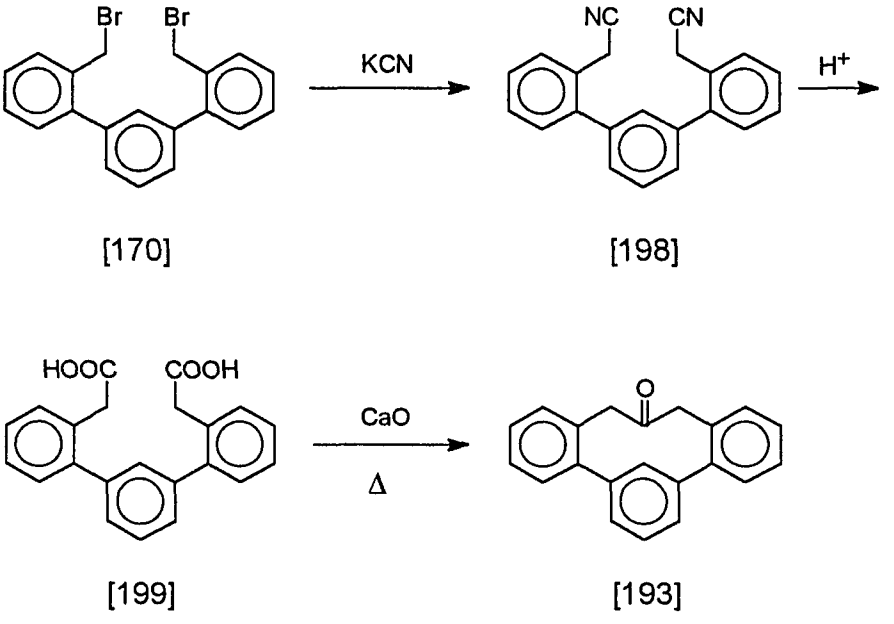
The dialdehyde could then be cyclized to the alkene by the use of McMurry's reagent, $TiCl_3$/DME/Zn-Cu, as previously described.



[197] [143]

Figure 78. Proposed McMurry Route Towards Alkene [143]

However, in view of the problems associated with the formation and stability of the alkene, a likely better and potentially more successful route would be to again bypass the formation of the alkene altogether. Substitution of the dibromide [xx] using KCN would lead to the dinitrile. This could then be hydrolyzed with sulfuric acid to the diacid. Using the Thorpe[130] method for the coupling of carboxylic acids, by heating in the presence of CaO, an additional route to the ketone could be provided.



Scheme 28. Proposed Dinitrile Route Towards Ketone [193]

A recent method by Vögtle, et. al.,[131] has provided an extremely promising route toward the Ketone [193]. A highly strained and distorted 1,2,3,-trihydrocyclohepta-[3,4,5,6,-*def*] biphenylene-2-one [201] was prepared in a modest yield of 17% by the cyclization of the *bis*-bromomethyl biphenylene [200] with *para*-tosylmethylisocyanide. (The dimer [202] was also recovered in 17% yield.) The corresponding alcohol [203] was obtained by reduction with sodium borohydride in 95% yield.

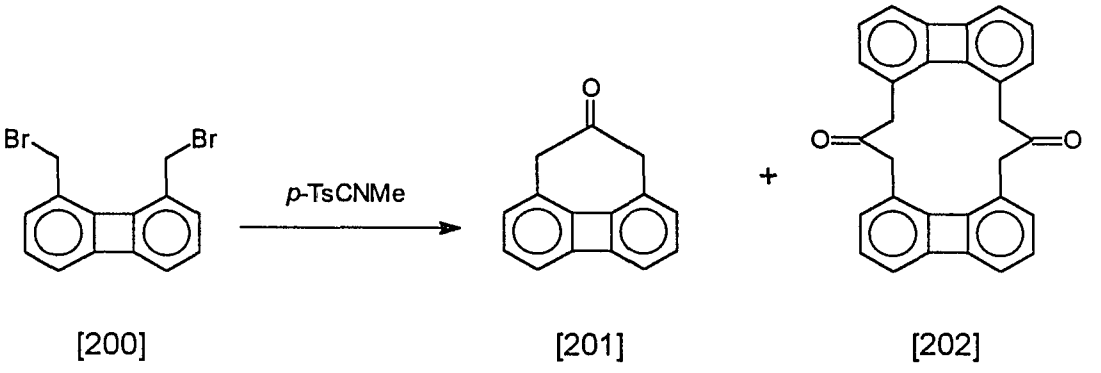


Figure 79. Vögtle's Route Toward a Clamped Biphenylene [201]

This route should provide access to the ketone [193] in resonable yield, allowing further investigation toward the synthesis of the allene [139] and eventually the symmetric dibenz-13-methylphenalene.

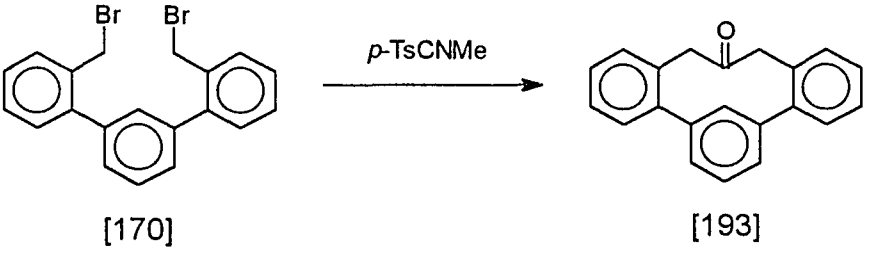


Figure 80. Proposed Route Towards Ketone [193] using *para*-Tosylmethylisocyanide

4. Experimental Section

General Procedure

All glassware used in moisture or air sensitive reactions was either oven-dried at over 100 °C overnight or flame-dried immediately prior to use, then assembled and flushed with nitrogen or argon. All glassware apparatus were assembled as described in each individual experiment. A common set-up included a three-necked round bottom flask (rbf) fitted wtih a pressure equalizing dropping funnel and or a condensor attached to a three-way connecting tube for dry and inert atmosphere inlet and $CaCl_2$ or KOH drying tube. Agitation of reaction mixtures was accomplished by the use of either a magnetic stirrer or mechanical stirrer equipped with a ground glass oil-sealed shaft. All water-miscible solvents used in reactions were removed prior to extraction by distillation or rotary evaporation in vacuo, and the residue dissolved in methylene chloride or diethyl ether. Acid or basic neutralization was achieved by the addition of a suitable aqueous solution, usually saturated sodium bicarbonate for acid neutralization and dilute HCl or NH_4Cl for basic neutralization. Standard work-up consisted of quenching with a suitable cold aqueous solution, extraction with a suitable organic solvent, drying the organic solvent over magnesium sulfate or calcium chloride, and removal of organic solvent by rotary evaporation in vacuo at a water aspiration pressure of roughly 11 torr, followed by evaporation in vacuo at an oil-pump pressure of roughly 0.1 torr.

Spectroscopy

Proton and carbon magnetic resonance spectra (^{1}H and ^{13}C NMR) were collected by a 300 MHz General Electric QE-300 nuclear magnetic resonance spectrophotometer. Dynamic proton NMR were collected by a Jeol 400MHz nuclear magnetic resonance spectrophotometer. All samples were prepared by dissolving 10-100 mg in a suitable deuterated solvent, usually $CDCl_3$ (99.8% D, 0.03% V/V tetramethylsilane, Aldrich.) Chemical shifts are reported in parts per million (ppm) downfield from the TMS internal standard, $\delta = 0$, and are expressed in the following order: Assignment; Chemical Shift; Coupling Constant (J in Hz.) Multiplicities are defined as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. We are grateful to Dr. Mike Blumenstein at Hunter College, City University of New York for providing us with the dynamic proton NMR studies.

Infrared spectra were recorded on a Perkin-Elmer 1310 IR spectrophotometer and are reported in wave numbers ($\nu = cm^{-1}$.) Liquid samples were observed neat by placing them between sodium chloride plates (23 x 4 mm.) Solid samples with low melting points were run as a melt on sodium chloride plates, all others were dissolved in carbon tetrachloride and run in solution cells. All spectra were recorded during 12 minute scans with a calibration band at 1601 cm^{-1} (polystyrene film.)

Gas Chromatography/Mass spectra were determined by either electron impact (EI) ionization or chemical ionization (CI) using methane as the carrier gas on a Hewlett-

Packard 5989A mass spectrometer. Some compounds, having molecular weights in the range of >400-600 amu were analyzed by direct probe inlet. The data presented shows the parent ion when present, followed by selected significant fragments or adducts. We are grateful to Dr. Cliff Sol at Hunter College, City University of New York, for providing us with the mass spectrometer analysis of the compounds listed.

X-ray crystal structure intensity data were measured on an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Cu K α radiation, ω-2θ scans.) The structures were solved by a multiple-solution procedure[132] and were refined by full-matrix least squares. In the final refinement, the nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure-factor calculations but their parameters are not refined. We are grateful to Dr. Louis Todaro at Hoffmann-La Roche for providing us with the X-ray analysis of compounds listed.

Melting points were determined using a Büchi Schmelzpunkbestimmungs instrument in soft-glass capillaries and are uncorrected.

Thin-layer Chromatography was perfomed using pre-coated plastic sheets of silica gel, with a thickness of 0.25 mm, supplied by Macherey-Nagel. UV-active compounds were observed by 254 nm UV lamp. Non UV-active compounds were either developed in iodine chambers or sprayed with phosphomolybdic acid in ethanol (230 g/4 L.)

Radial chromatography was carried out on a Chromatotron, model 792T, Harrison Research. The plates were coated following the procedure of Harrison,[133] with silica gel 60 PF-254, containing calcium sulfate as a binder (VWR Scientific.) The plate was first eluted with a non-polar solvent (hexane), followed by introduction of the sample, previously filtered through a short column. Solvent polarity was later increased by the introduction of the proper eluant, and the separation of compounds was followed by UV irradiation. Plates were occasionally washed by a solution of 30% methanol in dichloromethane.

Flash Chromatography was performed according to published procedure[134] using silica gel 60, available from Aldrich Chemical Co.

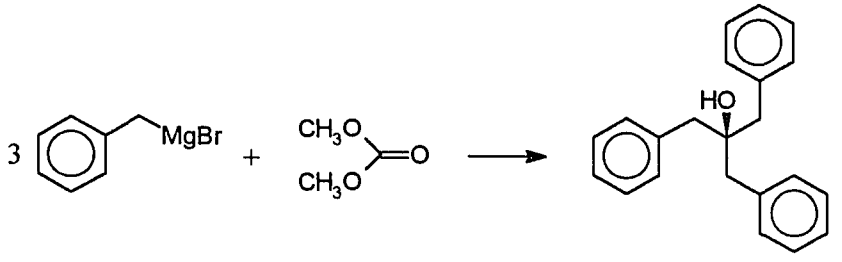
Solvents were ACS reagent grade and generally used as supplied. When required, they were purified as follows:

Tetrahydrofuran:	distilled under nitrogen over potassium metal
Benzene:	distilled under nitrogen over calcium hydride
Dimethyl sulfoxide:	distilled under nitrogen over calcium hydride
Diisopropylamine:	distilled under nitrogen over sodium metal
Triethylamine:	distilled under nitrogen over sodium metal
Methanol:	distilled over magnesium metal
Acetonitrile:	distilled over phosphorus pentoxide
Dichloromethane:	distilled over calcium hydride
Ethyl Acetate:	distilled over calcium hydride
Hexane:	distilled over calcium hydride

Potassium *t*-butoxide was sublimed at 180-200°C / 0.02 torr. *n*-Butyllithium was titrated using either 1,3-diphenylacetone *p*-tosylhydrazone[135] or 2,5-dimethoxybenzyl alcohol[136] as indicator.

4.1 Approaches Toward Tribenz-13-Methylphenalene

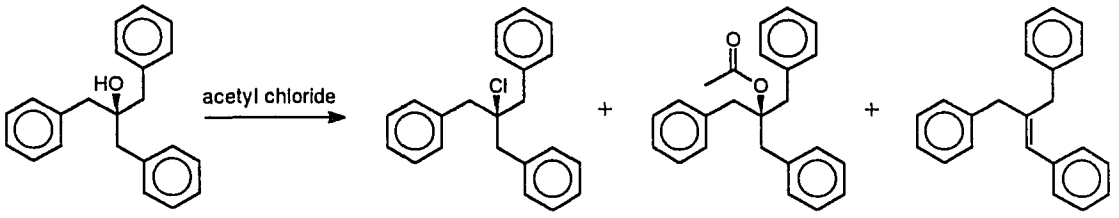
4.1.1 Synthesis of Tribenzylcarbinol [112][137]



A 2 L, three-necked rbf was fitted with a $CaCl_2$ drying tube, condenser, and dropping funnel. 18.23 g (0.75 mole) magnesium metal was added to 80.5 mL (0.70 mole) benzyl chloride in 1.2 L dry diethyl ether. The magnesium was allowed to dissolve, then 15.24 mL (0.22 mole) dimethyl carbonate, dissolved in 20 ml dry diethyl ether, was added drowise. The reaction was allowed to stir overnight. The reaction mixture was then cooled and washed with several 200 mL aliquots of saturated NH_4Cl, and a 500 mL aliquot of water. The ether was dried over $MgSO_4$, filtered, and removed by rotary evaporation. The residue was subsequently recrystallized from hexane. Mp 115-116°C, (lit. 115.-115.5°C), first fraction 32.44 g, 50% yield, MW 302.4, TLC showed single spot, 5:1 Hex/EtOAc.

Tribenzylcarbinol [112]. **^{1}H NMR:** δ 1.5 (s, 1H); 2.8 (s, 6H); 7.3 (m, 15H). Upon addition of D_2O, both the singlet at 1.5 and water impurity at 1.6 disappeared and a singlet at 4.8 appeared.

4.1.2 Synthesis of Tribenzylmethylchloride (1,3-diphenyl-2-benzyl-2-chloropropane) [113][138]



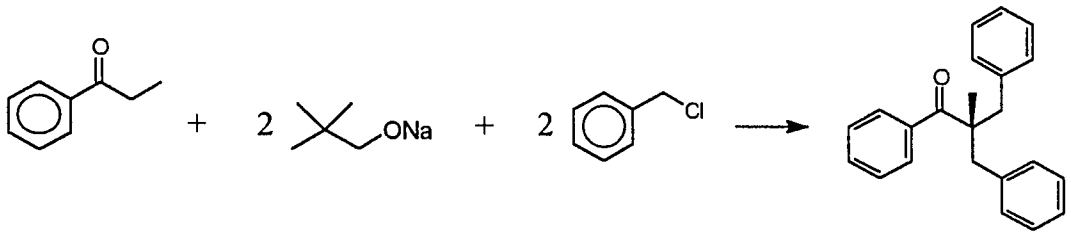
A 10 mL rbf was fitted with a condenser and 3.0 g tribenzylcarbinol were refluxed in 5 mL acetyl choride for one hour. After cooling overnight, fluffy whited crystals formed. These were vacuum filtered, washed with dry ether and weighed (0.26 g, 6% yield, mp 175-177°C, lit. 173°C.) TLC showed 2 major components, which may correspond to the chlorination and elimination products. The mixture was separated via chromatotron with 9:1 hexane/ethyl acetate eluent. A repeat experiment yielded a small amount of crystals, mp 75°C, and ^{1}H NMR suggested that the acetyl ester of tribenzyl carbinol had been recovered.

Tribenzylmethylchlorid **[113]** (Fraction 1.) **^{1}H NMR**: δ 3.0 (s, 6H); 7.3 (m, 15H).

1,3-Diphenyl-2-benzyl-propene-1 **[115b]** (Fraction 2.) **^{1}H NMR**: δ 3.4 (s, 4H); 3.6 (s, 4H); 6.6 (s, 1H); 7.4 (m, 15H.)

Tribenzylcarbinol, acetyl ester **[115a] ^{1}H NMR**: δ 2.1 (s, 3H); 3.2 (s, 6H); 7.2 (m, 15H.) **IR**: (neat, melt); 3100, 3070, 3035, 2950, 1955 (w); 1890 (w); 1820 (w); 1730 (s); 1600, 1580, 1460, 1375, 1250 (b, s); 1090, 1025, 750, and 700 cm^{-1}.

4.1.3 Synthesis of 2,2-dibenzylpropiophenone [111] [139]



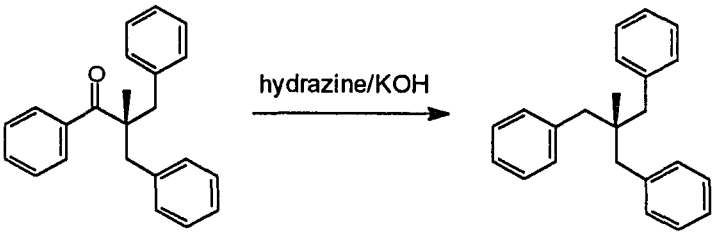
i. Preparation of sodium t-amyloxide. 55 mL (0.5 mole, 0.808g/mole) t-amyl alcohol were added to 250 mL distilled benzene in a clean, dry three-neck one L rbf fitted with a reflux condenser and a KOH drying tube. 13.8 g sodium metal were added in small thin pieces while stirring. The mixture was refluxed overnight. the unreacted sodium was removed and weighed (2.6 g) which showed about 0.5 mole had reacted.

ii. Formation of 2,2-dibenzylpropiophenone. The three-neck one liter rbf from the previous reaction was fitted with a 200 mL dropping funnel, a thermometer, and a

condenser, itself fitted with an argon inlet and KOH drying tube. The dropping funnel was charged with 26.6 mL (0.2 mole) freshly distilled propiophenone, 51.5 mL (0.45 mole) freshly distilled benzyl chloride, and 50 mL freshly distilled toluene. This thoroughly mixed solution was then added dropwise to the sodium amyloxide solution (turned yellow) and then refluxed over 3.5 hours. The reaction was worked up by cooling to 0°C, and then slowly adding 500 mL cold 1 M HCl solution and 100 mL brine. The organic layer was removed, and the aqueous layer extracted twice with 100 mL aliquots of diethyl ether. All non-aqueous layers were combined, dried with Na_2SO_4, and rotary-evaporated. The residue was subsequently fractionally distilled under high vacuum and temperature (ca. 1 torr, 135°C.) Two major components were collected, corresponding to mono- and di-benzylated propiophenone. The 2,2-dibenzylpropiophenone was recrystallized from absolute ethanol (33.4 g, 56% yield, mp 59.5-60.5°C.) The mono-benzylated product remained a liquid.

2,2-dibenzylpropiophenone. **[111]** **^{1}H NMR**: δ 7.1-7.7 (m, 13H); 6.8 (d, 2H, 8 Hz); 3.5 (d, 2H, 13 Hz), 2.8 (d, 2H, 13 Hz); 1.2 (s, 3H.)

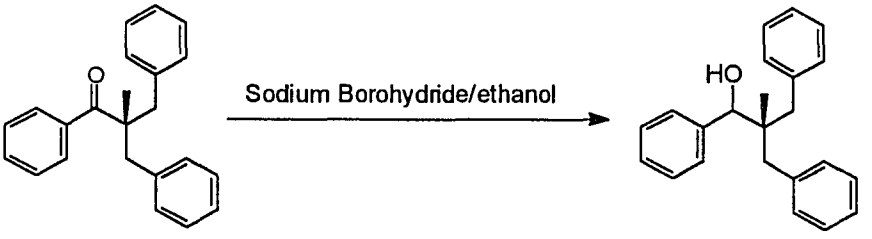
4.1.4 Wolf-Kishner Reduction of 2,2-dibenzylpropiophenone [111] to 2-benzyl-1,3-diphenyl-2-methylpropane [114][140]



A 50 mL rbf was fitted with a condenser and 1.0 g of 2,2-dibenzylpropiophenone (3 mmol,) 0.2 mL hydrazine (95%, 6 mmol) and 0.50 g KOH (85%, 7 mmol) were refluxed in 25 mL triethylene glycol for 4.5 hrs. The dark brown mixture was cooled, and ether and methylene chloride were added to aid solvation. The organic layer was washed three times with brine, then water, dried over $CaCl_2$ and finally rotary evaporated. TLC (5:1 Hex/EtOAc) and ^1H NMR detected the presence of both the desired product, 1,1,1-tribenzyl ethane, and the alcohol, 2,2-dibenzyl-1-phenyl-1-propanol. The crystalline residue was recrystallized from 95% ethanol (0.4 g, 45% yield, mp 113.5-114.5°C.)

2-benzyl-1,3-diphenyl-2-methylpropane. **[114] ^1H NMR**: δ 7.3 (m, 9H); 7.1 (m, 6H); 2.6 (s, 6H); 0.8 (s, 3H.)

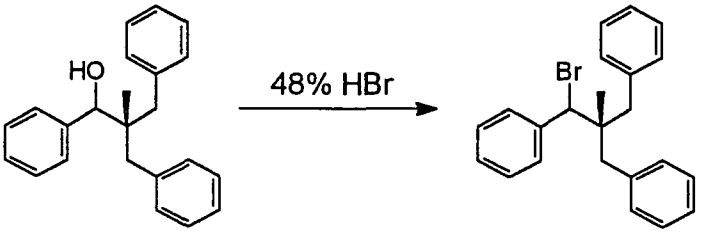
4.1.5 Reduction of 2,2-dibenzylpropiophenone [111] with $NaBH_4$ to 2,2-dibenzyl-1-phenyl-1-propanol [110]



10 g of 2,2-dibenzylpropiophenone (31.8 mmol) were dissolved in 60 mL of absolute ethanol and cooled to 0°C. 1.6 g (42 mmol) fo $NaBH_4$ were added to the ethanolic solution, followed by an eight hour reflux. The reaction mixture was cooled, 10 mL of 10% KOH was added extracted with methylene chloride. The organic layer was washed with water, brine, dryed and evaporated. The residue was recrystallized from hexane/ethyl acetate. 8.5 g (26.9 mmol) recovered, 85% yield, mp 127-8°C.

2,2-dibenzyl-1-phenyl-1-propanol.**[110]** **^{1}H NMR**: δ 7.2 (m, 15H); 4.4 (s, 1H); 3.1 (d, 2H, 15.0 Hz) 2.5 (d, 1H, 15 Hz); 2.4 (d, 1H, 15 Hz); 1.9 (s, 1H); 0.7 (s, 3H.) **IR**: (CCl_4); 3610 (s); 3100, 3080, 3040 (s); 2990, 2950, 2890, (s); 1960 (b, w); 1890 (b, w); 1820 (b, w); 1760 (b, w); 1610 (s); 1500 (s); 1460 (s); 1040 (s); and 710 cm^{-1}.

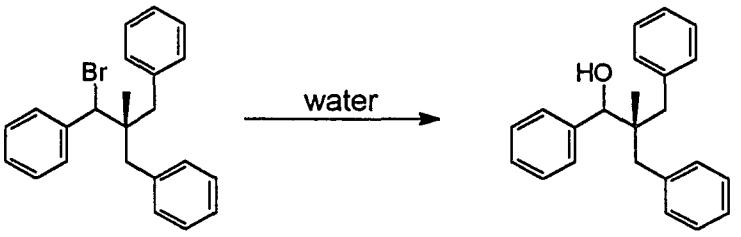
4.1.6 Conversion of 2,2-dibenzyl-1-phenyl-1-propanol [110] to 2,2-dibenzyl-1-phenyl-1-bromo-propane [109]



5.6 g (18 mmol) of 2,2-dibenzyl-1-phenyl-1-propanol were added to 25 mL 48% HBr (1.49 g/mL) and refluxed for one hour. The brominated product appears as a white solid in the flask during reflux. After cooling, the reaction mixture was neutralized with bicarbonate, extracted with methylene chloride, dryed over magnesium sulphate, filtered and the solvent evaporated. Recrystallized from hexane/ethyl acetate. 6.5 g, 95% yield, mp 158-9°C.

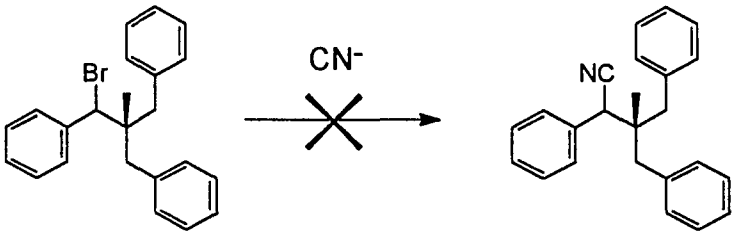
2,2-dibenzyl-1-phenyl-1-bromopropane. **[109] ^{1}H NMR**: δ 7.1-7.3 (m, 15H); 4.9 (s, 1H); 3.3 (d, 1H, 15 Hz); 3.2 (d, 1H, 15 Hz); 2.9 (d, 1H, 15 Hz); 2.5 (d, 1H, 15 Hz); 0.7 (s, 3H.) **^{13}C NMR**: δ 139.2 (w), 137.3 (w), 137.4 (w), 132.0, 130.9, 130.0, 128.5, 128.4, 128.0, 126.8, 126.7, 65.6, 43.5 (w), 43.2, 41.5, and 22.3.

4.1.7 Reaction of 2,2-dibenzyl-1-phenyl-1-bromopropane [109] with water



0.3 g of the bromo compound were refluxed in water for one hour. After diethyl ether work-up, ^1H NMR and mp determined the main product to be identical to a known sample of the alcohol, 2,2-dibenzyl-1-phenyl-1-propanol.

4.1.8 Attempted cyanide substitution of 2,2-dibenzyl-1-phenyl-1-bromopropane [109][141]



4.1.8.a In DMSO solvent.

A 50 ml rbf was fitted with a condenser and drying tube and 2 g (5.27 mmol) of 2,2-dibenzyl-1-phenyl-1-bromopropane were dissolved, with some necessary heating, in 20

mL dry, distilled DMSO. Next, 0.64 g (~9 mmol) KCN were added and the resulting mixture was heated at 110°C for 1.5 hours. The reaction was cooled, water was added, and the mixture was extracted three times with diethyl ether. The organic layers were combined and washed with 6 N HCl to remove the excess KCN. After drying over magnesium sulphate, filtering, and rotary evaporation of the solvent, it was determined by TLC and proton NMR that only 2,2-dibenzylpropiophenone and 2,2-dibenzyl-1-phenyl-1-propanol were present.

4.1.8.b In DMF solvent.

The above was repeated in DMF solvent. The mixture was heated overnight at ~75°C, then at 135°C for four hours. The dark brown reaction was worked-up as above. Single product was determined to be quantitative 2,2-dibenzyl-1-phenyl-1-propanol.

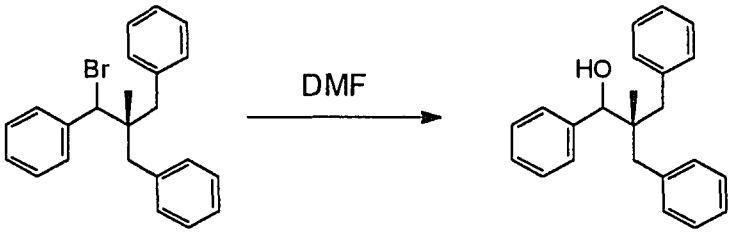
4.1.8.c Carefully Dry Conditions in DMF solvent.

50 mL dry, freshly distilled over CaH_2 DMF were added to a 100 mL flame-dried rbf, charged with dry argon and fitted with a condenser and $CaCl_2$ drying tube. 2,2-dibenzyl-1-phenyl-1-bromopropane and NaCN were dried under high vacuum at 60°C for five hours. All reagents were refluxed overnight, then worked-up as above. Two fractions were separated by chromatotron chromatography (6:1 Hex/EtOAc.) The higher Rf fraction was shown by proton NMR to be complicated and was not investigated further. The lower Rf fraction was determined to be 2,2-dibenzyl-1-phenyl-1-propanol.

4.1.8.d CuCN and DMF.

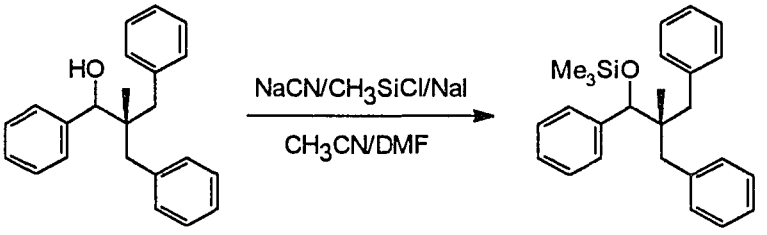
0.5 g of 2,2-dibenzyl-1-phenyl-1-bromopropane and 0.4 g (4.2 mmol) CuCN were dried under high vacuum and at 60°C for three hours. The mixture was then refluxed in 25 mL, freshly distilled DMF, under argon overnight. Mixture was worked-up by the extraction with diethyl ether/methylene chloride (1:1), drying over $MgSO_4$, filtering, and removal of solvent by rotary evaporation. Results were similar to that of the previous reactions of 2,2-dibenzyl-1-phenyl-1-bromopropane with NaCN and KCN.

4.1.9 Observation of 2,2-dibenzyl-1-phenyl-1-bromopropane [109] in refluxing DMF



An investigation into whether or not the bromide-compound can be formylated in dry DMF. A 100 mL rbf was fitted with a condenser, drying tube, and argon inlet, and 0.5 g of 2,2-dibenzyl-1-phenyl-1-bromopropane were refluxed in dry, distilled DMF overnight (140°C.) After routine work-up, it was observed that all starting material had been converted 2,2-dibenzyl-1-phenyl-1-propanol.

4.1.10 Attempted preparation of nitrile compound [116] from 2,2-dibenzyl-1-phenyl-1-propanol [110], using NaCN, Me_3SiCl and NaI in DMF/CH_3CN.[142]

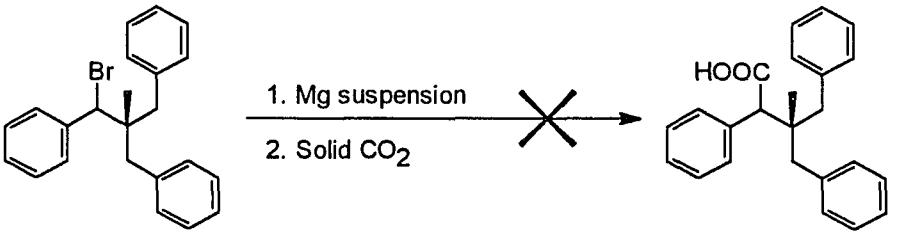


All reagents were previously dried under high vacuum and/or freshly distilled under dry conditions. 2 g (6.32 mmol) of 2,2-dibenzyl-1-phenyl-1-propanol, 0.7 g (14 mmol) of NaCN, 2 mg NaI, 15 mL DMF and 15 mL CH_3CN were mixed in a 100 mL rbf under argon atmosphere. Next, 1.8 mL (14 mmol) of Me_3SiCl were added, and the mixture was placed in a preheated oil bath at 65°C for 14 hours. TLC was taken and the mixture was heated at 80°C for an additional 10 hours, after which it was worked-up by dilution with water and extracted with hexane. A product was isolated by recrystallization from hexane/EtOAc (1.2 g, mp 110-111°C.) NMR suggested the reaction stopped at hydroxyl group being silylated.

2,2-dibenzyl-1-phenyl-1-propanol, trimethylsilylether. **[122] ^{1}H NMR**: δ 7.1-7.3 (m, 15H); 4.4 (s, 1H); 3.1 (d, 1H, 15 Hz); 3.0 (d, 1H, 15 Hz); 2.6 (d, 1H, 15 Hz); 2.3 (d, 1H, 15 Hz); 0.8 (s, 3H); 0.0 (s, 9H.) **IR**: (CCl_4); 3120, 3090, 3060 (s); 2990 (s); 1950 (b, w);

1880 (b, w); 1820 (b, w); 1610 (w); 1500 (s); 1460 (s); 1260 (s); 1110, 1080 (s); 900, 850, and 710 cm^{-1}.

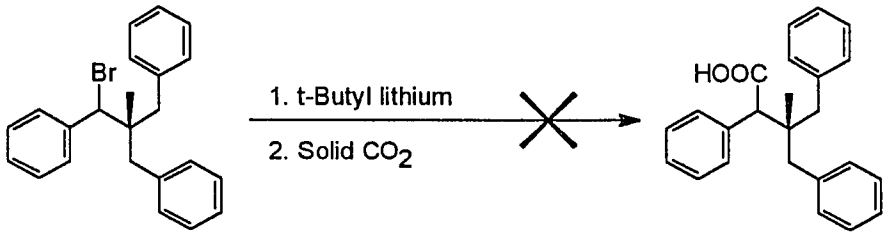
4.1.11 Attempted formation of 1-Phenyl-2,2-dibenzylbutanoic acid [117] from 2,2-dibenzyl-1-phenyl-1-bromopropane [109] and CO_2 using the Rieke modification of the Grignard reaction[143]



0.10 g (3.7mmol) crushed magnesium metal were placed into a 2-necked 100 mL rbf fitted with a condenser, $CaCl_2$ drying tube, and argon inlet. To this was added 15 mL dry distilled THF and 0.2 mL (2.3 mmol) freshly distilled 1,2-dibromoethane via a dropping funnel. After refluxing for one hour, the mixture became cloudy as most of the magnesium dissolved. Next, 0.15 g of potassium metal was carefully added and the mixture heated, melting the potassium and causing the formation of a fine black suspension of magnesium metal over a period of 45 minutes. Finally, 0.5 g (1.3 mmol) of dry 2,2-dibenzyl-1-phenyl-1-bromopropane (dissolved in 20 mL dry, distilled THF) was introduced via dropping funnel. No noticeable change occurred. After refluxing for one hour, small pieces of solid CO_2 (prepared from dry CO_2 gas passed through drierite and a liquid nitrogen trap) were dropped into the mixture. A total of 30 g of CO_2 were added

over 20 minutes. The mixture was brought back to reflux for 0.5 hour, cooled, and quenched with ice. Enough $NaHCO_3$ was added to bring the pH to 6, and the mixture was extracted with diethyl ether. The aqueous layer was acidified with HCl and again extracted with diethyl ether. Each organic fraction was separately worked-up, however ^1H NMR showed only 1,1,1-tribenzylethane [114], which was recovered in 47% yield.

4.1.12 Reaction of t-Butyl lithium with 2,2-dibenzyl-1-phenyl-1-bromopropane [109] and subsequent addition of CO_2

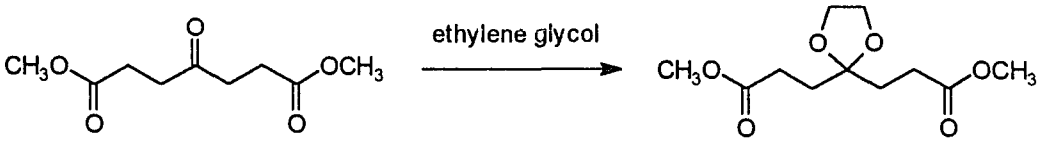


To a dry and clean 250 mL Schenck tube was added 2.0 g (5.3 mmol) of 2,2-dibenzyl-1-phenyl-1-bromopropane. This was heated under high vacuum at 60°C for one hour to remove any traces of water. The mixture was blanketed with argon and an argon inlet with a drying tube was attached. 50 mL of dry distilled THF was added and the mixture stirred until the dissolution of the bromide compound was complete. The reaction mixture was then immersed into a dry ice/isopropanol bath and cooled to -70°C. 8 mL (~14 mmol, 1.7 M in pentane) of t-butyl lithium was added via syringe to the reaction vessel, turning the bromide solution deep red. After stirring for five minutes, small chunks of solid CO_2 were added, turning the solution clear again. The reaction mixture was allowed

to warm, then quenched with ice water/Na_2CO_3, extracted with ether, acidified with 10% HCl to ~pH 3 , and extracted again with ether. The base and acid extractions were dried, filtered and evaporated separately. The acidified extraction showed only 2,2-dimethylpropanoic acid, while the basic extraction gave a complicated mixture of compounds, none of which were starting material nor product as determined by proton NMR.

4.2 Approaches toward the Unsymmetrical Dibenz-13-Methylphenalene

4.2.1 Synthesis of Dimethyl-γ-ethylenedioxypimelate [129m][144]



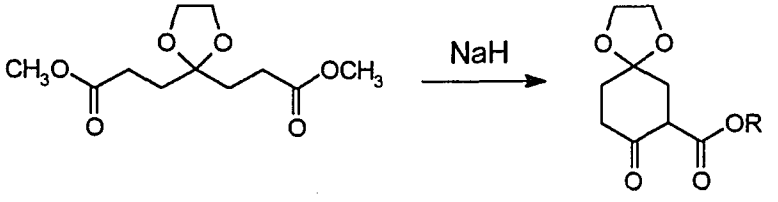
A mixture of 102.87 g (0.51 mol) of dimethyl-γ-ketopimelate [128m], 43 g (0.69 mol) ethylene glycol, and 200 mg TsOH in 250 mL benzene were heated in a 1 L rbf fitted with a Dean-Stark trap and refluxed overnight. After 18 hours, 14 mL of water had been collected and refluxing was discontinued. 150 mL additional benzene was added and the reaction was quenched with 50 mL sat. $NaHCO_3$, followed by 100 mL water. The benzene was dried, and then rotary evaporated. The remaining residue was distilled under vacuum. ^1H NMR showed the reaction to be incomplete, so the residue was again refluxed with 20 mL ethylene glycol, 0.2 g TsOH and 200 mL benzene. After an additional 48 hours, the mixture was worked-up and the residue distilled to give 57.5 g of product. 3 fractions, 43.5% yield (slight dimethyl-γ-ketopimelate impurity.) Bp 120-125°C at 1 torr.

Dimethyl-γ-ethylenedioxypimelate. **[129m] ^{1}H NMR**: δ 3.9 (s, 4H); 3.7 (s, 6H); 2.4 (t, 4H, 9 Hz); 2.0 (t, 4H, 9Hz.)

Experiment was repeated using 201.8 g (0.88 mole) diethyl-γ-oxopimelate [128e], 55 g (0.89 mole) ethylene glycol, and 0.4 g TsOH in 500 mL benzene. This time, a total of 23 mL water were collected and removed continuously throughout the refluxing period. 189.2 g collected, 0.69 mole, 79% yield.

Diethyl-γ-ethylenedioxypimelate. **[129e] ^{1}H NMR**: δ 4.1 (q, 4H, 6 Hz); 3.9 (s, 4H); 2.4 (t, 4H, 8 Hz); 2.0 (t, 4H, 8 Hz); 1.3 (t, 6H, 6 Hz.) **IR**: (neat) 3000, 2900 (b, s); 1720-1750 (s); 1450, 1370, 1160-1320 (s); 1040, 960, 910, and 870 cm^{-1}.

4.2.2 Synthesis of 2-Carbomethoxy-4-ethylenedioxycyclohexanone [130m]. Dieckmann condensation [145]



A mixture of 52 g (0.211 mol) dimethyl-γ-ethylenedioxypimelate [129m] and 6.5 g 80% NaH (0.217 mole) in 300 mL diethyl ether was refluxed under nitrogen for five days (after the first day, the mixture had solidified, so a mechanical stirrer was attached, more ether

was added and the reflux continued for four more days.) Next, the reaction was quenched with 40 mL cold acetic acid and 40 mL cold water. The ether layer was separated and neutralized with sat. $NaHCO_3$, dried, and filtered. Crystallization was induced by freezing overnight. 20.5 g collected, 0.096 mole, 45% yield.

2-Carbomethoxy-4-ethylenedioxycyclohexanone. **[130m] ^{1}H NMR**: δ 12.1 (s, 1H); 4.0 (s, 4H); 3.7 (s, 3H); 2.5 (t, 2H, 9 Hz); 2.4 (s, 2H); 1.8 (t, 2H, 9Hz.)

Experiment was repeated exactly as above, save for using 1.37 g **diethyl-γ-**ethylenedioxypimelate and toluene as the solvent. 1.1 g recovered, 90% yield.

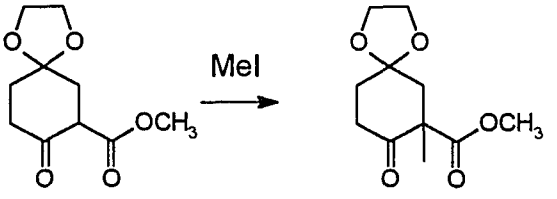
2-Carboethoxy-4-ethylenedioxycyclohexanone. **[130e] ^{1}H NMR**: δ 12.2 (s, 1H); 4.2 (q, 2H, 6 Hz); 4.0 (m, 4H); 2.5 (m, 4H); 1.8 (t, 2H, 4 Hz); 1.3 (t, 3H, 6Hz.)

4.2.3 Preparation of Methyl Iodide[146]

A one L three-necked flask is fitted with a dropping funnel, mechanical stirrer and a samll fractionating column and condenser for downward distillation. A solution of 267 g (1.6 mole) KI in 150 mL water is placed in the flask along with 20 g $CaCO_3$ and heated to 65° C with stirring. With the temperature constant, 157 mL (1.67 mole) of methyl sulfate is slowly added dropwise via a dropping funnel. The rate of addtion was adjusted to cause

quick and constant distillation of methyl iodide. The distillate was collected over an ice bath to retard evaporation. After the addition of methyl sulfate was complete, the reaction mixture temperature was brought to 70°C and heated for 15 minutes to finish the reaction. The distillate was thoroughly dried over $CaCl_2$, redistilled and stored cold over copper pellets in a dark bottle. 195 g recovered after distillation, 86% yield.

4.2.4 Synthesis of 2-Carbomethoxy-2-methyl-4-ethylenedioxycyclohexanone [131m][147]



0.18 g (7.8 mmol) of sodium metal were dissolved in 15 mL methanol, giving theoretically 0.42 g (7.8 mmole) NaOMe. This was added dropwise to a cold (-40°C ice/acetone bath) and vigorously stirred mixture of 1.5 g (7 mmol) of the the ketoester, 2-carbomethoxy-4-ethylenedioxycyclohexanone [130m]. After addition was completed, the temperature was allowed to rise to -15°C and was maintained there for one hour. Next, 1.4 g (0.614 mL, 10 mmol) of methyl iodide was added dropwise, and the mixture was allowed to reach room temperature with stirring. After two days, litmus showed the solution to be neutral. Ther methanol was mostly removed by rotary evaporation, the semi-solid residue extractedd with diethyl ether, and the inorganic salts removed by gravity filtration. Then,

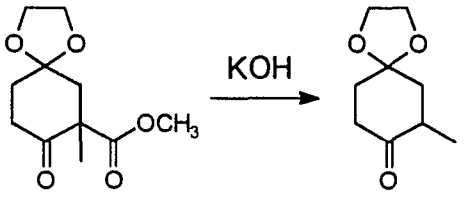
the ether extracts were washed with cold 1 M KOH and water, dried over $MgSO_4$, filtered and rotary evaporated. The oily residue was distilled (1.5 torr, 150°C) and 1.1 g (4.82 mmol) of oil were recovered. (69% yield.)

2-Carbomethoxy-2-methyl-4-ethylenedioxycyclohexanone. **[131m] ^{1}H NMR**: δ 4.0 (m, 4H); 3.7 (s, 3H); 3.1 (m, 1H); 2.7 (d, 1H, 15 Hz); 2.5 (m, 1H); 2.1 (m, 2H); 1.7 (d, 1H, 15 Hz) 1.3 (s, 3H.)

4.2.4.a Repeated Experiment.

2.2 g (95 mmol) sodium metal were carefully dissolved into 100 mL methanol. This was then added dropwise to a -40°C solution of 18.41 g (86 mmol) of the ketoester in 150 mL methanol. The temperature was allowed to rise to -15)C and was stirred for one hour. Next, 6 mL methyl iodide were added dropwise to the solution, resulting in an immediated yellow color. The mixture was allowed to warm to room temperature and stir for three days. The methanol was removed by rotary evaporation under water-aspirator vacuum at room temperature. 100 mL of distilled water was added to the remaining residue, which was then extracted with diethyl ether. The ether fractions were pooled, washed with cold 1 M NaOH, washed with cold water, dired, filtered and evoporated. An oil remained, which would not crystallize even after fractional distillation under high vacuum (1.5 torr, 150°C.) 15 g were collected, 66 mmol, 77% yield.)

4.2.5 Synthesis of 2-methyl-4-ethylenedioxycyclohexanone [123][147]

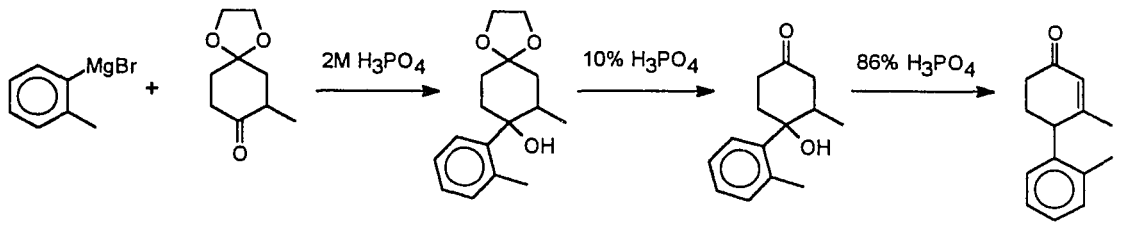


5 g (22 mmol) of 2-carbomethoxy-2-methyl-4-ethylenedioxycyclohexanone [131m] were refluxed in 50 mL 10% KOH for two days. Afterwards, 50 mL sat. NaCl solution was added and the mixture extracted three times with diethyl ether, then dried, filtered, and rotary evaporated. Viscous oil, bp 69-74°C, 0.5 torr (lit. 98-100°C, 4 torr.) 2.74 g collected, 73% yield.

Experiment was repeated using 10 g (41.3 mmol) 2-carbo**ethoxy**-2-methyl-4-ethylenedioxycyclohexanone [131e]. Crude weight 5.64 g, 80% crude yield (undistilled.) Distilled at 0.1 torr, Bp 54°C, 4.7 g recovered, 67% yield. ^{1}H NMR identical to that of previous synthesis from 2-carbomethoxy-4-ethylenedioxycylohexanone

2-Methyl-4-ethylenedioxycyclohexanone. **[123] ^{1}H NMR**: δ 4.0 (m, 4H); 2.6-2.8 (m, 2H); 2.4 (m, 1H); 1.9-2.1 (m, 3H); 1.7 (m, 1H); 1.1 (d, 3H, 9 Hz.)

4.2.6 Synthesis of 3-Methyl-4-hydroxy-4-(2-methylbenzene)-cyclohexanone [135] and 3-Methyl-4-(2-methylbenzene)-cyclohex-2-enone [136]



A two-necked, 200 mL rbf was fitted with a condenser, $CaCl_2$ drying tube, argon inlet, and a dropping funel. To 1.2 g crushed Mg turnings in 25 mL ether was added dropwise 6 mL of 2-bromotoluene in 10 mL dry diethyl ether. After the Mg had dissolved, a solution of 6.3 g of 4-ethylendioxy-2-methylcyclohexanone in 40 mL dry diethyl ether was slowly added dropwise. Upon completion of the reaction, the reaction was quenched with 100 mL cold 2 M H_3PO_4 and then extracted three times with ether. The ether layers were washed with water until neutral to litmus, dried, filtered and evaporated, leaving 6.9 g of oil, 71% crude yield. ^1H NMR of the mixture showed the continued presence of the ethylene dioxy protecting group, suggesting that the major product was 2-methyl-4-ethylenedioxy-1-(2-methylbenzene)-cyclohexan-1-ol. Therefore, all the product was refluxed overnight in a solution of 100 mL dioxane and 100 mL 10% H_3PO_4. This was worked up as above. The dioxane was removed by repeated rotary-evaporation with CCl_4. The ^1H NMR comparison of the product and the product in the presence of D_2O suggested that the compound had been deprotected without dehydration of the hydroxy group, to form 3-methyl-4-hydroxy-4-(2-methylbenzene)-cyclohexanone. Crystallized

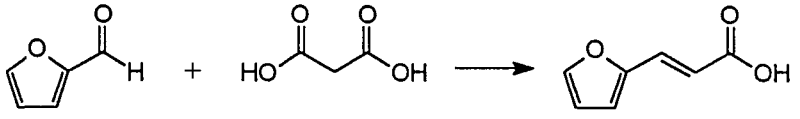
from ether. Next, 200 mg of 3-methyl-4-hydroxy-4-(2-methylbenzene)-cyclohexanone was heated in 15 mL 86% H_3PO_4 for 1 hour, cooled to 0°C, and neutralized. After workup, a small amount of 4-(2-methylbenzene)-cyclohex-2-enone was isolated.

2-methyl-4-ethylenedioxy-1-(2-methylbenzene)-cyclohexan-1-ol. **[134] ^{1}H NMR**: (mixture) δ 7.2 (m, 4H); 4.0 (m, 4H); 2.6 (s, 3H); 1.6-2.1 (m, 8H); 0.8 (d, 3H.)

3-methyl-4-hydroxy-4-(2-methylbenzene)-cyclohexanone. **[135] ^{1}H NMR**: δ 7.2-7.5 (m, 4H), 2.6-3.0 (m, 3H); 2.5 (s, 3H); 2.2-2.4 (m, 4H); 1.9 (s, 1H); 0.8 (d, 3H, 8 Hz.) Upon addition of D_2O, the peak at 1.9 disappeared and a new peak at 4.8 appeared.

3-methyl-4-(2-methylbenzene)-cyclohex-2-enone. **[136] ^{1}H NMR**: δ 7.0-7.3 (m, 4H); 6.2 (s, 1H); 3.8 (b, d, 1H); 2.4 (s, 3H); 2.3 (m, 4H); 1.8 (s, 3H.)

4.2.7 Synthesis of Furylacrylic Acid [132][148]

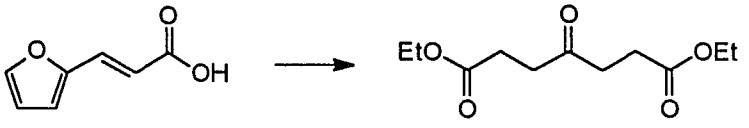


230 g (2.4 mole) of furfural, 248 g (2.4 mol) dry malonic acid and 100 mL anhydrous distilled pyridine were refluxed for three hours. The reaction was then poured over 500

mL ice water and precipitated by acidification with diluted HCl. The product was filtered and washed with diluted HCl and let dry. Product was recrystallized from ether/hexane. 185 g (1.34 mole) recovered. 56% yield, mp 142-3°C. Experiment was repeated using 185 g (1.78 mole) malonic acid, 145 mL (1.75 mole) furfural and 100 mL pyridine. Refluxed for 5 hours. 186.6 g recovered, 1.34 mole 77% yield, mp 136-8°C.

Furylacrylic Acid. **[132] ^{1}H NMR**: δ 7.5 (d, 1H 17 Hz); 7.5 (d, 1H, 2 Hz); 6.7 (d, 1H, 4 Hz); 6.5 (dd, 1H 4 and 2 Hz); 6.3 (d, 1H, 17 Hz.)

4.2.8 Synthesis of Diethyl-γ-oxopimelate (diethyl-4-ketopimelate) [128e][149]

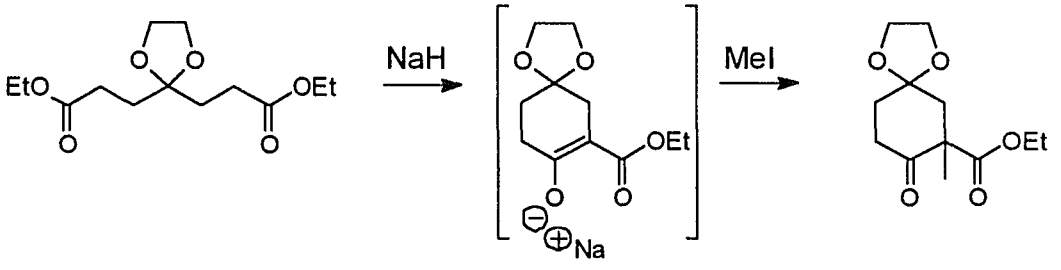


A two-necked 500 mL rbf was fitted with a condenser and gas inlet tube. 69 g (0.5 mole) of furylacrylic acid were dissolved into 200 mL of 95% ethanol (some water is required for the reaction to proceed.) Into the boiling solution a steady and slow stream of anhydrous HBr gas was introduced. After 90 minutes, the solution was saturated (and double in volume.) This was refluxed for about 3 hours. Next, a distillation head was attached and the ethanol removed under vacuum. The remaining residue was poured over 500 g of ice and neutralized with Na_2CO_3. This was extracted with ether, which was

then dried over $MgSO_4$, filtered and evaporated. The oily residue was twice distilled under high vacuum (0.03 torr, bp 98°C, oil bath 140°C.) 44.06 g recovered, 38% yield (some undistilled solid, 22 g, remained in flask.) Experiment was repeated using 110.78 g (0.8 mole) furylacrylic acid, 300 mL 95% ethanol, and anhydrous HCl gas. 68.94 g of product were recovered, 37.5% yield. Experiment was repeated using 186.64 g furylacrylic cid, 1 L 95% ethanol, and HCl gas. 201.83 g collected, 65% yield.

Diethyl-γ-oxopimelate. **[128e] ^{1}H NMR**: δ 4.1 (q, 4H, 6 Hz); 2.8 (t, 4H, 5 Hz); 2.6 (t, 4H, 5 Hz); 1.3 (t, 6H, 6 Hz.) **IR**: (neat) 3000, 2950 (b, s); 1710-1750 (s); 1420, 1380, 1360 (b, s); 1200 (b, s); 1110 (s); 1040; and 860 cm^{-1}.

4.2.9 One pot synthesis of 2-Carboethoxy-2-methyl-4-ethylenedioxycyclohexanone from diethyl-γ-ethylenedioxypimelate [131e]

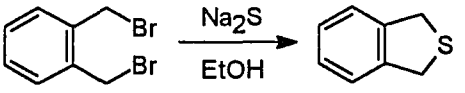


A three-necked 500 mL rbf ws fitted with mechanical stirrer, condenser, a drying tube, argon inlet and dropping funnel. 8 g 80% NaH was introduced into the apparatus and was washed twice with 10 mL aliquots of dry toluene. This was accomplished by applying by pasteur pipet the solvent on top of the NaH while in the rbf, swirling, letting the NaH

settle, then pipetting off the supernatent. 200 mL of dry distilled toluene was added and 25 mL dry absolute ethanol was carefully added dropwise with stirring. This mixture was then brought to a reflux and 55 g (0.2 mole) of diethyl-γ-ethylenedioxypimelate dissolved in 80 mL toluene was added via dropping funnel. After refluxing the reaction overnight, the mixture was cooled to room temperature and 25 mL (0.4 mole) distilled methyl iodide in 50 mL toluene was added via dropping funnel. This was allowed to stir overnight at room temperature. The reaction was washed with sat. $NaHCO_3$, brine, and water, then dried over $MgSO_4$, filtered, and rotary evaporated. Crude product was distilled under high vacuum (1.0 torr, bp 110°C, bath 160°C.) 35 g recovered, 0.144 mole, 72% yield. Experiment was repeated under same conditions except 1 L rbf was used, NaH was left unwashed, and exactly one equivalent of ethanol to NaH/toluene was added via dropping funnel. Undistilled crude 41.7 g, 0.17 mole, 86% yield.

2-Carboethoxy-2-methyl-4-ethylenedioxycyclohexanone. **[131e]** **^{1}H NMR**: δ 3.9-4.3 (m, 6H); 3.1 (m, 1H); 2.7 (d, 1H, 14 Hz); 2.5 (dt, 1H, 13 and 2 Hz); 2.0 (m, 2H) 1.7 (d, 1H, 14 Hz) 1.3 (m, 6H);

4.2.10 Preparation of Benzthiophene (1,3-dihydroisothianaphthene) [133a]



4.2.10.a Synthesis of anhydrous Na_2S.[150]

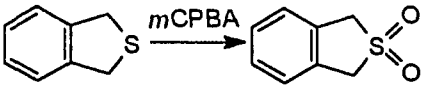
To a one L three-necked rbf (fitted with a dry ice condenser, KOH drying tube, argon inlet, and mechanical stirrer, and cooled with a dry ice/isopropanol bath to temperature of -60°C) was introduced a stream of anhydrous ammonia gas. After collecting roughly 500 mL of liquid ammonia, 20.26 g (1.26 mol) of elemental sulfur was added, forming a yellow suspension. To this cooled stirring solution was carefully added 29.1 g (1.26 mol) of sodium metal in small pieces. At this point, the solution turned from yellow to blue. After all the sodium was added, the mixture was allowed with stirring to warm to room temperature overnight while the ammonia evaporated. The Na_2S formed a white solid. In order to remove traces of ammonia and/or $NaNH_2$, 300 mL of anhydrous ethanol and 5 g NH_4Cl were added and the mixture partially distilled. The anhydrous Na_2S was then used for the following reaction without delay.

4.2.10.b Synthesis of Benzthiophene.[151]

The amount of Na_2S formed was a 60% molar excess than required to react with 100 g (0.38 mol) α,α'-dibromo-o-xylene. A water condenser replaced the dry ice condenser, and absolute ethanol added to bring the volume back to around 400 mL, and then 100 g of the α,α'-dibromo-o-xylene in 250 mL of absolute ethanol was added dropwise via a special, slow dropping funnel, which had to be periodically heated to prevent the crystallization of the α,α'-dibromo-o-xylene. A slow steady reflux was maintained throughout the addition, and was continued overnight. Workup consisted of removal of most of the ethanol by distillation, extration wtih hexane, drying over $MgSO_4$, filtering, removal of hexane by distillation, and vacuum distillation of the remaining residue (0.03 torr, bp 60°C.) 27.3 g were collected, 53.6% yield, about 20 g undistillable residue remained in the flask. Proton NMR suggests this may be dimer, as it is identical to the isolated product.

1,3-Dihydroisothianaphthene. **[133a] ^{1}H NMR**: δ 7.2 (m, 4H); 4.2 (s, 4H.)

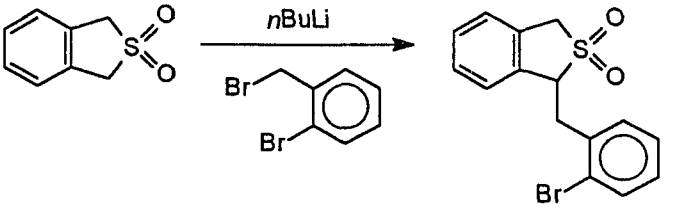
4.2.11 Synthesis of 1,3-dihydroisothianaphthene-2,2-dioxide [133b][152]



Into a three-necked 500 mL rbf fitted with a dropping funnel was placed a suspension of 50 g (0.22 mmol), 75% by weight) mCPBA in 250 mL methylene chloride. This was cooled to 0°C and then 9 g (66 mmol) of benzthiaphene dissolved in 100 mL methylene chloride was added dropwise over 30 minutes. The reaction was allowed to stir overnight. The reaction was worked up with several extractions with cold sat. $NaHCO_3$ to remove all traces of *m*CPBA. The organic fraction was dried over $MgSO_4$, filtered and rotary evaporated. The crystalline product was recrysallized from methylene chloride/hexane. Mp 152-3°C, 7.8 g recovered, 70% yield.

1,3-Dihydroisothianaphthene-2,2-dioxide. **[133b] ^{1}H NMR**: δ 7.3 (m, 4H); 4.4 (s, 4H.)

4.2.12 Coupling of 1,3-dihydroisothianaphthen-2,2-dioxide [133b] and 2-bromobenzylbromide to form [124][153]



A 100 mL three-necked rbf was fitted with a 10 mL dropping funnel, argon inlet, $CaCl_2$ drying tube, and a rubber septum. 0.50 g (3 mmol) 1,3-dihydroisothianaphthen-2,2-dioxide was dissolved in 20 mL dry, distilled THF. The temperature was lowered to -60° C, and 1.2 mL 2.5 M (3 mmol) n-butyllithium was added via syringe, turning the solution slightly pink. After 15 minutes, 0.75 g (3 mmol) of 2-bromobenzyl bromide dissolved in 10 ml dry distilled THF was added dropwise over 25 minutes via the dropping funnel. This turned the solution from pink to green. The reaction was allowed to stir for one hour, then worked up using ether and washing with brine, water, drying with $MgSO_4$, filtering, and evaporating. Recrystallized product from methylene chloride/hexane. Gave a positive Beilstein test. 0.3 g, 32 %, mp 146-147°C.

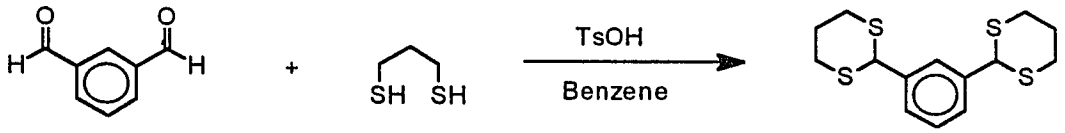
Larger Scale Repetition. 20 mmol (3.36 g) 1,3-dihydroisothianaphthen-2,2-dioxide, 20 mmol (5 g) 2-bromobenzylbromide, and 20 mmol (8 mL, 2.5 M) n-butyl lithium were used. Reaction turned dark red instead of pink upon addition of n-butyl lithium and dark green upon addition of 2-bromobenzylbromide. ^1H NMR of crude showed a mixture of

several products. Column chromatography (4:1 hexane/EtOAc) was used to separate the major components. The major product (2.7 g, 40%) was the desired monoalkylation product (recrystallized from 4:1 hexane/EtOAc.) The presence of di- and tri-alkylated products, as well as 1,3-dihydroisothia-naphthen-2,2-dioxide, were also detected.

1-(2-bromobenzene)-1,3-dihydroisothianaphthen-2,2-dioxide. **[124] ^{1}H NMR**: δ 7.6 (d, 1H, 9 Hz); 7.3 (m, 5H); 7.2 (m, 1H); 7.0 (d, 1H, 9 Hz); 4.6 (t, 1H, 8 Hz); 4.4 (AB q, 2H, 8 Hz); 3.6 (dd, 1H, both 8 Hz); 3.3 (dd, 1H, both 8 Hz.)

4.3 Approaches toward the Symmetrical Dibenz-13-Methylphenalene

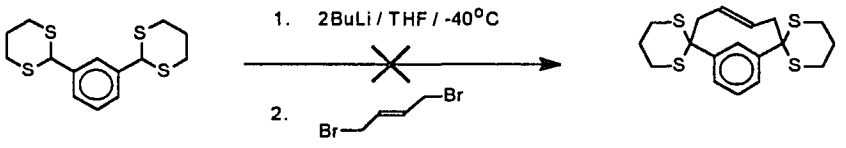
4.3.1 Synthesis of Dithiane [147].



10.80.g (80.52 mmol) of isophthalaldehyde [156], 18 ml (179.28 mmol) 1,3-propanedithiol, 10 mg TsOH, and 250 ml benzene solvent were fitted with a Dean-Stark trap, condenser and 500 ml rbf. The mixture was refluxed overnight, the water drawn off, and the mixture refluxed for another two hours. The reaction was allowed to cool, and poured over ice cold 10% Na_2CO_3. The aqueous layer was extracted three times with 50 ml aliquots of benzene, the organic layers were then pooled, dried over $MgSO_4$, filtered, rotary-evaporated, and recrystallized from benzene/hexane. Mp 130-131°C, 18.97g (two fractions,) 60.31 mmol, 75% yield.

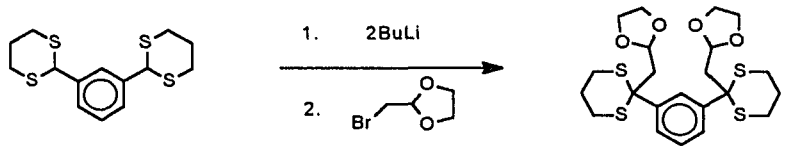
Dithiane **[147]. ^{1}H NMR**: δ 7.6 (s, 1H); 7.3 (m, 3H); 5.2 (s, 2H); 3.0 (m, 8H); 2.2 (m, 2H); 1.9 (m, 2H.) **^{13}C NMR**: (decoupled) δ 140.2, 129.8, 128.9, 128.4, 128.1, 51.8, 32.6, 25.7.

4.3.2 Attempted Nucleophilic Addition of Dithiane [147] to 1,4-dibromo-2-butene.



Into a 500 ml rbf fitted with a septum, a low (-100°C) temperature thermometer, and an Argon inlet and $CaCO_3$ drying tube was dissolved 2.9 g (9.2 mmol) dithiane in 250 ml dry distilled THF (0.04 M). The temperature was lowered to -40°C (2-propanol/dry ice.) 9.6 ml butyllithium solution in hexane (22.1 mmol, from a titrated 2.3 M solution) was injected over a five minute period. The solution turned yellow, then orange-red. After 3 hours at -40°C, 2.12 g (10 mmol) of *trans*-1,4-dibromo-2-butene in 150 ml dry distilled THF was added over four hours via dropping funnel. The solution remained at low temperature for an additional hour, then allowed to warm to room temperature overnight. The mixture was poured over ice cold brine and extracted with methylene chloride. After workup, 3.38 g of crude solid/polymer was recovered (uncharacterized.)

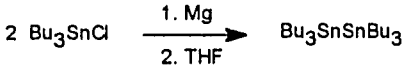
4.3.3 Synthesis of [148].



3.15 g (10 mmol) of the dithiane [147] was dissolved into 200 ml dry distilled THF and introduced into a flame-dryed, 3-necked 500 ml rbf fitted with a septum, a 25 ml dropping funnel, low temperature thermometer, and Argon inlet with a $CaCO_3$ drying tube. The temperature was lowered to -25°C (2-propanol/dry ice; at approx. -35°C the dithiane precipitates.) Next, 6 ml of titrated 2.5 M butyllithium in hexane was injected over a period of 10 minutes, turning the solution first yellow, then orange-red. After 45 minutes, 5.5 g (33 mmol) of 2-bromoacetaldehyde-ethylenedioxyacetal dissolved in 10 ml THF was added dropwise over 1 hour. The solution was stirred and allowed to warm to room temperature overnight. The reaction was worked up by pouring over ice cold brine, extracting with 3x 50 ml aliquots methylene chloride, pooling the organic layers, drying over $MgSO_4$, filtering, evaporating, and separating the product components by column chromatography (2:1 hexane/ethyl acetate.) Recrystallized from diethylether/hexane. Mp 111-113°C. 1.2 g, 26 % yield.

Compound [148]. **^{1}H NMR**: δ 8.6 (s, 1H); 7.9 (d, 2H, 7 Hz); 7.2 (t, 1H, 7 Hz); 4.9 (t, 2H, 2 Hz); 3.9 (m, 8H); 2.7 (m, 8H); 2.4 (d, 4H, 2 Hz); 2.0 (m, 4H.) **GC-MS**: M^+ at 486.

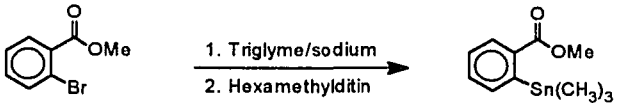
4.3.4 Synthesis of Hexabutylditin. [154]



1.4 g (58 mmol) of dryed, crushed Magnesium metal and 26g (80 mmol) tributyltinchloride were heated together at 100°C for four hours in a 100 ml rbf. The reaction was cooled to 50°C and then a few drops of dibromoethane were added, followed by 50 ml dry distilled THF. The solution turned black after a few minutes. The mixture was refluxed overnight, then worked up by the addition of water, followed by extraction with diethylether, drying with $MgSO_4$, filtering, rotary evaporation, and distillation (140-6°C @ 0.1 torr, lit. value 190°C @ 10 torr.) Clear colorless liquid. 16.89 g hexabutylditin distilled yield, 73% overall.

Hexabutylditin. **^{1}H NMR**: δ 1.5 (m, 12H); 1.3 (m, 12H); 0.9 (m, 20H.)

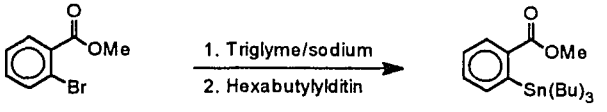
4.3.5 Synthesis of Methyl-2-(trimethylstannyl)-benzoate [161m]. [155]



Into a 3-necked 500 ml rbf fitted with an Argon gas inlet, mechanical stirrer, and condenser was added 130 ml dry, distilled triglyme and 2.2 g (96 mmol) sodium metal. The mixture was heated with vigorous stirring until the sodium had melted and formed into numerous tiny spheres. The solution was then allowed to cool, leaving the sodium with increased surface area. Next, 5 g (15.3 mmol) of hexamethylditin (Johnson-Mathey, ampoule) were added with vigorous stirring. The mixture was heated to 60°C and let stir at this temperature overnight. Afterwards, the dark green solution was allowed to cool, and then was filtered (through glass wool under Argon to remove the unreacted sodium) directly into a 3-necked 500 ml rbf fitted with an addition funnel, condenser, and Argon inlet/$CaCO_3$ drying tube. The mixture was cooled to 0°C and 6.56 g (4.35 ml, 30.5 mmol) of distilled methyl-2-bromobenzoate in 50 ml triglyme was added dropwise over one hour. 15 minutes into this addition, the solution turned from green to yellow to dark red. The reaction was allow to warm to room temperature and stirred overnight. Reaction was worked up by 3x 100 ml petroleum ether extractions, pooling, 3x 100 ml water extraction, drying over $MgSO_4$, filtering, evaporating, and distilling, 63°C-87°C @ 0.05 torr. 3 fractions, 1.23 g, 2.53g and 0.6 g respectively. 42% yield (lit. 78%.)

Methyl-2-(trimethylstannyl)-benzoate. **[161m] ^{1}H NMR**: δ 8.2 (d, 1H, 6 Hz); 7.7 (d, 1H, 6 Hz); 7.5 (t, 1H, 6 Hz) 7.4 (t, 1H, 6Hz); 3.9 (s, 3H); 0.3 (s, 9H.)

4.3.6 Synthesis of Methyl-2-(tributylstannyl)-benzoate [161b]

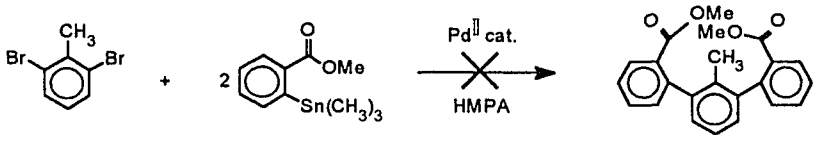


In a 3-neck 500 ml rbf fitted with an Argon inlet/$CaCO_3$ drying tube, dropping funnel and mechanical stirrer were melted 4. 1 g (178 mmol) of sodium metal in 150 ml triglyme and agitated vigorously into tiny spheres. Without cooling, 16.5 g (29.4 mmol) Bu_6Sn_2 were added dropwise to the solution. Bu_6Sn_2, unlike Me_6Sn_2, is not miscible in triglyme. The solution was stirred two hours at 120°C and overnight at 85°C. The yellow-green solution was cooled, and filtered through glass wool under Argon into a 3-necked 500 ml rbf fitted with dropping funnel, magnetic stirrer, and Argon inlet/$CaCO_3$ drying tube. The solution was cooled to 0C, and then 13 g (60.5 mmol) methyl-2-bromobenzoate in 35 ml triglyme was added dropwise. Solution turned from yellow-green to a reddish color, and some salt or precipitate was formed. Solution was worked up after stirring for a few hours by extraction with petroleum ether and water. Crude was distilled into four main fractions @ 0.05 torr. Fraction 1: 37-42°C, 8.15 g; fraction 2: 42-59°C, 2.3 g; fraction 3: 59-60°C,

3.99 g; fraction 4: >120°C, 2.14 g. 16.58 g total fractions. Fraction 1 and 2 were unreacted aryl bromide. Fraction 3 was a mixture of aryl bromide and aryl tin. Fraction 4 was pure aryltin. 9% yield, recovered.

Methyl-2-(tributylstannyl)-benzoate. **[161b] ^{1}H NMR**: δ 8.1 (d, 1H, 6 Hz); 7.6 (d, 1H, 6 Hz); 7.5 (t, 1H, 6 Hz); 7.4 (t, 1H, 6 Hz); 3.9 (s, 3H); 1.5 (m, 6H); 1.3 (m, 6H); 1.1 (m, 6H); 0.9 (t, 9H, 5 Hz.)

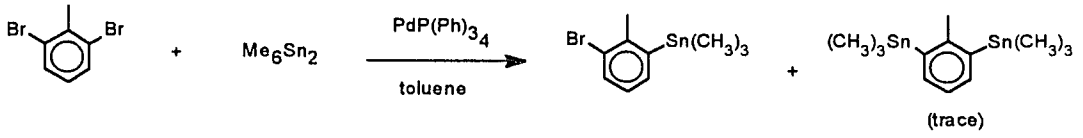
4.3.7 Attempted Synthesis of 2,2'-dicarbomethoxy-methyl-*meta*-terphenyl [162] [156]



Reaction was run under dry air. Into a 50 ml rbf fitted with a $CaCO_3$ drying tube and 25 ml dropping funnel was placed 0.25 g (1 mmol) distilled 2,6-dibromotoluene, 10 ml dry distilled HMPA, and 20 mg Pd^{II} catalyst (transbenzyl[chloro]bis[triphenylphospine] palladium II, MW 757.58, mp 166-170.) The solution was stirred and heated to 65°C as 0.6 g (2 mmol) of *o*-carbomethoxyphenyltrimethylstannane in 10 ml HMPA was added dropwise over 30 minutes. The reaction was stirred at 65°C for 24 hours. Blackening of the glass rbf walls was expected, but not observed. Mixture was quenched by the addition of cold water, followed by diethylether extraction, drying with $MgSO_4$, filtering,

evaporating and column chromatography (5:1 hexane/EtOAc.) GC-MS analysis showed a mixture, one minor product detected was the mono-adduct, M^+ at 306 [163].

4.3.8 Attempted Synthesis of 2,6-*bis*-(trimethylstannyl)-toluene [164d]



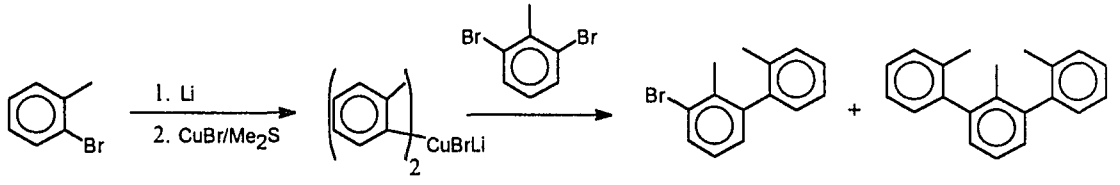
5 g 15.3 mmol) Me_6Sn_2, 0.24 g $Pd(P\varnothing_3)_4$, and 1.8 g (7.2 mmol) of 2,6-dibromotoluene [156] were refluxed in 25 ml dry distilled mesitylene for 15 hours, the reaction blackening after one hour. Next, the mesitylene was removed by vacuum evaporation, hexane was added, and the solution filtered through celite to remove colloidal Pd. The recovered residue after evaporation was distilled under high vacuum into four fractions. ^1H NMR and GC-MS analysis showed the major components to be unreacted 2,6-dibromotoluene (39%) and 2-bromo-6-(trimethyl)stannyltoluene, the mono adduct (49%.) GC-MS also detected a trace amount of the desired bis adduct.

2,6-Dibromotoluene. **[156] ^1H NMR**: δ 7.5 (d, 2H, 8 Hz); 6.9 (t, 1H, 8 Hz); 2.6 (s, 3H.) M^+ 250.

2-Bromo-6-(trimethylstannyl)-toluene. **[164m] ^{1}H NMR**: δ 7.5 (d, 1H, 8 Hz); 7.3 (d, 1H, 8Hz); 7.0 (dd, 1H, both 8 Hz); 2.5 (s, 3H); 0.3 (s, 9H.) **GC-MS**: M^+ detected at 334, with minor Sn isotopes from 327-340.

2,6-bis-(Trimethylstannyl)-toluene. **[164d] GC-MS**: M^+ detected at 420, with minor Sn isotopes from 410-423.

4.3.9 Attempted Synthesis of trimethyl-*meta*-terphenyl [157] [157]

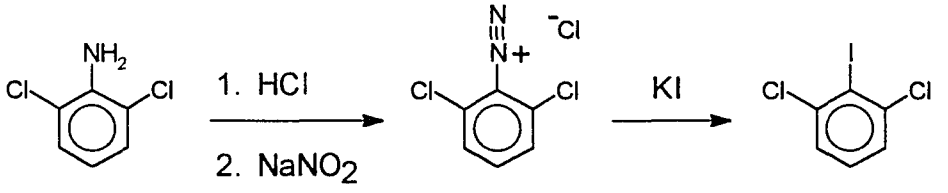


2.5 g (0.35 mol) of Li metal were cleaned of oil and pressed into this foil sheets. These were then weighed and stored in hexane before use. The sheets were cut into small pieces and added to 50 mL dry diethyl ether. 0.15 moles (25.65 g) of 2-bromotoluene in 50 mL diethyl ether were added slowly via dropping funnel over one hour until the solution turned yellow and most of the lithium metal was dissolved. An ice bath was used occasionally to control the reaction. After stirring one addtional hour, the contents were filtered (glass wool) under nitrogen into a dropping funnel attached to a three-necked round-bottomed flask fitted with a reflux condenser and an inert atmosphere inlet. Into the flask was placed as suspension of 15 g (73 mmol) CuBr, dimethylsulfide complex (205.6 MW) in 100 mL diethyl ether. This was then cooled to -45°C, whereby the

aryllithium solution was added dropwise over one hour. The reaction was warmed to 0°C and 20 mmol (5 g) of 2,6-dibromotoluene in 50 diethyl ether was added over 30 minutes. Lastly, the reaction mixture was purged with oxygen gas for 90 minutes, then worked-up by acidifying and washing with dilute HCl, water, drying with $MgSO_4$, filtering and rotary-evaporating. Thin-layer chromatography (hexane) revealed two major products.

However, GC-MS detected the presence of 2,2'-dimethyldiphenyl isomers [158] (58%, M^+ 182), 2,6-bromotoluene [156] (32%, M^+ 250), 6-bromo-2,2'-dimethyldiphenyl [159] (8%, M^+ 260), and only a trace of the desired 2,2'-dimethyl-*meta*-terphenyl [157] (<1%, M^+ 272).

4.3.10 Synthesis of 2,6-dichloroiodobenzene [165] [158]

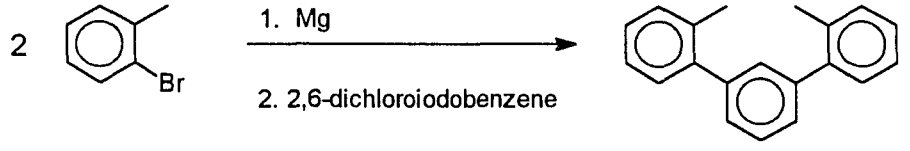


15 g (0.93 mmol) 2,6-dichloroaniline was dissolved in 60 ml concentrated HCl and 150 ml water. Heating to 85°C was neccessary to complete dissolution. Next, the aniline solution was cooled to 5°C, causing precipitation into small crystals with stirring. Next, 6.8 g (~0.11 mole) $NaNO_2$ in 30 ml ice cold water was added dropwise, turning the color

of the solution from white to orange. The solution was stirred for 30 minutes at 0-5°C. Next, 50 mg of Urea were added, stirred, and the entire solution poured into a 1 liter beaker containing 99 g (0.6 mole) KI in 150 ml water. After vigorous foaming and stirring for 30 minutes, the reaction was worked up with 2000 ml methylene chloride and 200 ml sat. Na_2SO_3. The organic layers were washed with 10% NaOH, brine, dryed over $MgSO_4$, filtered, and recrystallized from Hexane. Mp 64.5-65°C. The crude 2,6-dichloroiodobenzene was found to be easily distilled or sublimed (dist. @ 77°C, 0.025 torr, sublimed at lower temperature to prevent bumping.) Yield 75%.

2,6-Dichloroiodobenzene. **[165] ^{1}H NMR**: δ 7.35 (m, 2H); 7.2 (m, 1H.) **GC-MS**: M^+ peak at 272 (55%), minor isotopes at 273 (3%), 274 (34%), 275 (2%), and 276 (5%.)

4.3.11 Synthesis of 2,2'-Dimethyl-*meta*-terphenyl [167] [159]



17 mmol (2.91 g) 2-bromotoluene was dissolved in 20 ml dry THF and added slowly via an addition funnel to 20 mmol (0.5 g) magnesium metal in a 50 ml 3-necked rbf fitted with a reflux condenser, argon inlet, drying tube and an additional dropping funnel. The solution turned brown and cloudy and was refluxed overnight. Next, 5 mmol (1.36 g) of

distilled 2,6-dichloroiodobenzene in 20 ml THF was added slowly over one hour at room temperature, then refluxed three hours. Solution was quenched with saturated ammonium chloride, extracted with diethyl ether, and washed with water and brine. After drying over $MgSO_4$ and filtering, the crude was distilled with flame (140°C @ 0.02 torr.) 88% yield, distilled.

2,2'-Dimethyl-meta-*terphenyl*. **[167] ^{1}H NMR**: δ 7.5 (m, 2H); 7.5 (m, 10H); 2.3 (s, 6H.) **GC-MS**: M^+ at 258.

In a separate experiment, the reaction mixture was quenched with methyliodide and analyzed by GC-MS, showing both the methyl group and iodine adducts.

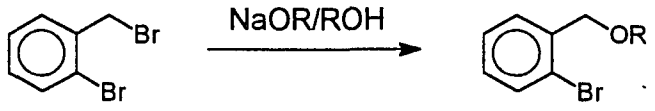
2-iodotoluene. **GC-MS**: M^+ at 218 (12%.)

2,6-bis-*[(2-methyl)-phenyl]-toluene*. **[157] GC-MS**: M^+ at 272 (13%.)

2,6-bis-*[(2-methyl)-phenyl]-iodobenzene*. **[169] GC-MS**: M^+ at 384 (70%.)

2,2'-dimethyl-meta-*terphenyl*. **[167] GC-MS**: M^+ at 258 (5%.)

4.3.12 Synthesis of 2-Bromo-methybenzyl ether and 2-Bromo-ethylbenzyl ether.



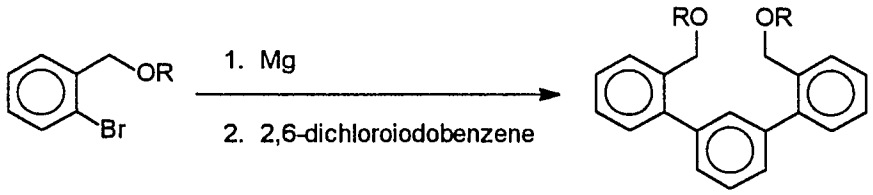
50 g (0.2 mole) bromobenzyl-2-bromide was dissolved in methanol and added dropwise to a solution of 5 g sodium metal in 200 ml methanol. After 12 hours, the methanol was removed by distillation and the residue worked up with cold saturated ammonium chloride solution and diethyl ether. After drying and filtering, the ether was removed and the crude distilled (42°C, 0.5 torr) to afford 33.5 g 2-bromomethylbenzylether. 83% yield.

Alternatively, running this reaction in anhydrous ethanol led to the isolation of 2-bromoethylbenzylether in 92% yield.

2-Bromo-methylbenzylether. **^{1}H NMR**: δ 7.6 (d, 1H, 8 Hz); 7.5 (d, 1H, 8 Hz); 7.3 (t, 1H, 8 Hz); 7.1 (t, 1H, 8 Hz); 4.5 (s, 2H); 3.5 (s, 3H.)

2-Bromo-ethylbenzylether. **^{1}H NMR**: δ 7.5 (m, 2H); 7.3 (t, 1H, 7 Hz); 7.1 (t, 1H, 7 Hz); 4.6 (s, 2H); 3.6 (q, 2H, 9 Hz); 1.3 (t, 3H, 9 Hz.)

4.3.13 Synthesis of 2,2'-*bis*-(Methoxymethyl)-*meta*-terphenyl [172m] and 2,2'-*bis*-(Ethoxymethyl)-*meta*-terphenyl [172e]



3.06 g (15.2 mmol) of 2-bromo-methylbenzylether were dissolved in 20 ml dry THF and added to 0.50 g (20 mmol) magnesium metal as described previously for the synthesis of 2,2'-dimethylterphenyl. The solution turned brown after 5 minutes, and was refluxed overnight. All magnesium did not immediately dissolve. 1.36 g (5 mmol) 2,6-dichloro-iodobenzene dissolved in 20 ml THF was then added over one hour and the resulting solution was refluxed overnight. Upon cooling, a salt formed. Reaction was worked up as previously described, leaving 1.86 g crude product, a yellow oil. This was heated under vacuum, (0.25 torr) to remove any reduced 2-bromomethylbenzylether, and the resulting oil was chromatographed using 9:1 Hexane/ethylacetate as eluent. Total recovered 2,2'-*bis*-(methoxymethyl)-*meta*-terphenyl, 1.08 g, yellow oil. 68% yield.

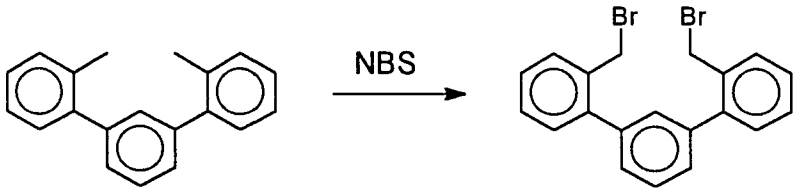
Alternatively, 12 g (56 mmol) of 2-bromo-ethylbenzylether was dissolved in 100 mL dry THF, and added slowly over 60 minutes to 2.5 g (102 mmol) magnesium turnings. Reaction turned from clear to brown within 2 minutes. The mixure was refluxed for 2 hours, then a solution of 7.4 g (27 mmol) of 2,6-dichloroiodobenzene in 100 mL THF was added dropwise over one hour to the refluxing solution. The reaction was stirred

overnight, then cooled to 0°C, poured over ice-cold saturated NH_3Cl. This was extracted with diethylether, washed with brine, dried over $MgSO_4$, filtered, and the solvent removed. 9.9 g of crude oily residue was purified by column chromatography, hexane/ethyl acetate, 9:1. 8.9 g (26 mmol) pure 2,2'-*bis*-(ethoxymethyl)-*meta*-terphenyl was isolated. 95% yield.

2,2'-bis-*(methoxymethyl)*-meta-*terphenyl*. **[172m] ^{1}H NMR**: δ 7.6 (m, 2H); 7.4 (m, 10H); 4.4 (s, 4H); 3.2 (s, 6H.) **GC-MS**: M^+ at 318.

2,2'-(ethoxymethyl)-*meta*-terphenyl. **[172e] ^{1}H NMR**: δ 7.6 (m, 2H); 7.4 (m, 1H); 7.3 (m, 9H); 4.4 (s, 4H); 3.5 (q, 4H, 7 Hz); 1.2 (t, 6H, 7 Hz.) **GC-MS**: M^+ at 346.

4.3.14 Synthesis of 2,2'-*bis*-(bromomethyl)-*meta*-terphenyl [170] from 2,2'-dimethyl-*meta*-terphenyl [167]

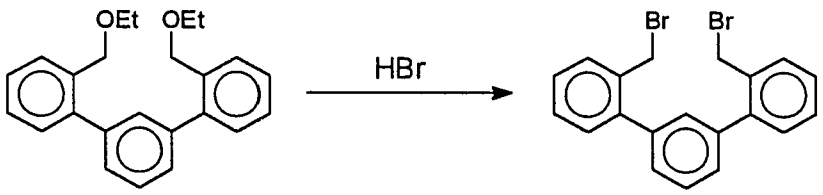


3 g (11.6 mmol) of 2,2'-dimethyl-*meta*-terphenyl were dissolved in 80 ml distilled CCl_4, along with 0.5 g AIBN, and 4.8 g NBS (27 mmol.) The mixture was brought to reflux under argon atmosphere, and then irradiated with a Hanovia mercury arc lamp for three

hours. The organic layer was evaporated, and the crude chromatographed using 5:1 hexane/methylene chloride. 2.38 g crystallized 2,2'-*bis*-(bromomethyl)-*meta*-terphenyl were recovered, mp 93-95°C (lit. 89-90°C.) 60% yield.

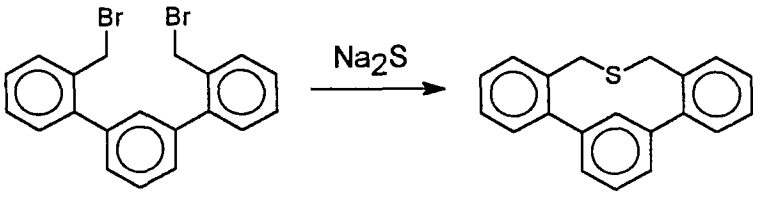
2,2'-bis-*(bromomethyl)*-meta-*terphenyl* **[170] ^{1}H NMR**: δ 7.5 (m, 6H); 7.4 (m, 6H); 4.5 (s, 4H.) **GC-MS**: M^+ at 416.

4.3.15 Conversion to 2,2'-*bis*-(bromomethyl)-*meta*-terphenyl [172e] from 2,2'-*bis*-(Ethoxymethyl)-*meta*-terphenyl [170]



2.0 g (6 mmol) of 2,2'-*bis*-(ethoxymethyl)-*meta*-terphenyl was heated to reflux for one hour in 25 mL 48% HBr. Mixture was cooled, neutralized with saturated Na_2CO_3, extracted with methylene chloride, washed with brine, dried with $MgSO_4$, filtered and the solvent was removed by vacuum evaporation. The residue was chromatographed (hexane/methylene chloride, 5:1.) 1.7 g of 2,2'-(bromomethyl)-*meta*-terphenyl were isolated. 70% yield.

4.3.16 Synthesis of 4-thia-1,2:6,7-dibenz-[7]-*meta*-cyclophane-1,6-diene [180][160]

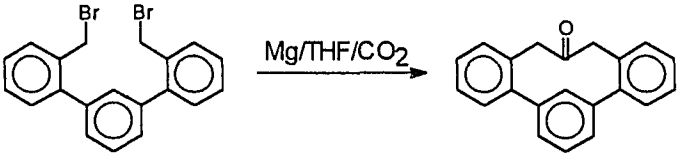


Into a dry-ice/2-propanol cooled 3-neck 500 ml rbf fitted with a dry ice/isopropanol condensor, argon inlet and stirrer was added a steady stream of ammonia gas until approximately 200 ml had condensed. Next, 0.22 g (6 mmol) elemental sulfur was added, allowed to stir, then 0.45 g (excess) of sodium metal was added. The mixture turned yellow and then blue. After stirring 45 minutes, the reaction was warmed with a warm water bath as the argon stream was increased to encourage ammonia evaporation. After all ammonia had evaporated, 150 ml of absolute ethanol and some ammonium chloride were added, and a dropping funnel, containing 1.22 g of 2,2'-(bromomethyl)-*meta*-terphenyl dissolved in 220 ml absolute ethanol, was attached. The dibromide was added slowly over four hours to the refluxing ethanol solution. Next, the ethanol was removed by distillation, ether was added, and washed with water, brine, dryed and filtered. No starting material remained. Chromatography 4:1 hexane/ethylacetate. TLC showed several products, including the likely presence of polymers. Mp of pure sulfide, 234-236°C (lit. 234-5.)[160] 1.2 g, 18% yield (lit. 11%.) The product is sensitive to the presence of HCl, and undergoes ring opening to 2-thiomethyl-2'-chloromethyl-*meta*-terphenyl.

Alternatively, $Na_2S{\bullet}9H_2O$ can be substituted for the anhydrous Na_2S. The same procedure above, repeated using 10 g (24 mmol) of the dibromide, led to the isolation of 3.26 g of sulfide (recrystallized from dry acetone.) Yield 47%.

4-thia-1,2:6,7-dibenz[7]metacyclophane-1,6-diene **[180]** (8*H*,10*H*-tribenzo-[*c,ef,h*][*1*] thiecine.) **^{1}H NMR**: δ 8.8 (s, 1H); 7.2-7.6 (m, 11H); 4.39 (d, 2H, 14 Hz); 2.94 (d, 2H, 14 Hz.) **^{13}C NMR**: (decoupled) δ 143.9, 139.8, 138.8, 138.7, 132.1, 128.2, 127.5, 127.0, 120.9 and 45.0. **GC-MS**: M^+ at 288.

4.3.17 Synthesis of Ketone [193].

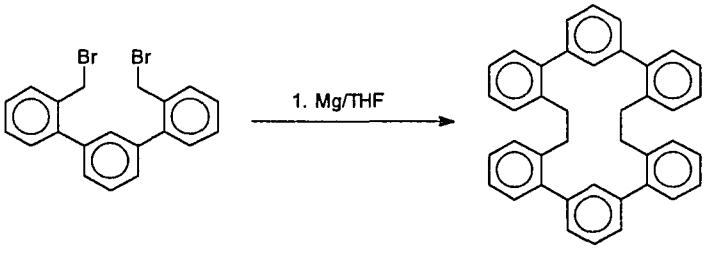


(trace)

0.12 g (0.29 mmol) of 2,2'-(bromomethyl)-*meta*-terphenyl was dissolved in 10 mL of dry, distilled tetrahydrofuran, then added to 0.11 g (4.5 mmol) crushed and dried magnesium turnings and refluxed overnight under an argon atmosphere. The reaction was cooled, and several pieces of solid carbon dioxide were added over a period of 15, followed by stirring for 10 minutes. Diethyl ether was added, and the reaction was quenched with aqueous

$NaHCO_3$, which was separated, neutralized to pH of around 4, and extracted with diethyl ether. Both the orginal $NaHCO_3$-washed ether layer and the extract from the $NaHCO_3$ washings were separately dried, filtered, and evaporated. GC-MS was performed on the residue recovered, the major product being 2,2'-dimethyl-*meta*-terphenyl. A trace of what is believed to be the cyclized ketone, M^+ at 284, was also detected.

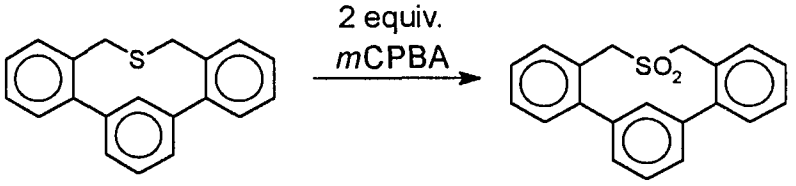
4.3.18 Attempted synthesis of 8,9-Dihydro-tribenzo[*acdf*]cyclononene/Synthesis of the dimer of 2,2'-dimethyl-*meta*-terphenyl [192].



1.0 g (2.4 mmol) of 2,2'-(bromomethyl)-*meta*-terphenyl was dissolved in 10 mL of dry, distilled tetrahydrofuran, then added to 0.2 g (8.2 mmol) crushed and dried magnesium turnings. The mixture was refluxed under argon for 1 hour. Next, a solution of 0.2 g (2.5 mmol) distilled dimethyl carbonate dissolved in 20 mL THF was added dropwise to the refluxing solution over a period of 30 minutes. The reaction was quenched with ice-cold saturated NH_4Cl and extracted with methylene chloride. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed. The residue was chromatographed (hexane/dichloromethane, 3:1) and one fraction produced 0.1 g (16% yield) hexagonal crystals, mp 217-218°C, of the cyclophane dimer of 2,2'-dimethyl-*meta*-terphenyl.

Dimer of 2,2'-dimethyl-meta-terphenyl. **[192] ^{1}H NMR**: (CD_2Cl_2) δ 7.1-7.3 (m, 12H); 6.9-7.0 (m, 8H); 6.8 (two singlets, 2H each); 6.3 (s, 2H); 2.8 (s, broad, 8H.) **^{13}C NMR**: (decoupled, CD_2Cl_2) δ 138.8, 131.1, 130.5, 130.3, 128.0, 127.7, 127.3, 126.0 and 34.1. **GC-MS**: M^+ at 258 (2,2'-dimethyl-*meta*-terphenyl) and 256 (possibly 2,2'-ethano-*meta*-terphenyl.) **MS** (direct inlet): M^+ at 512.

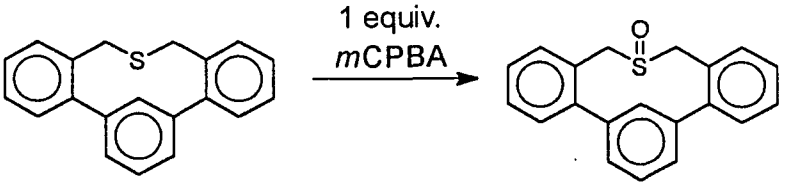
4.3.19 Synthesis of 8*H*,10*H*-tribenzo-[*c,ef,h*][*1*]thiecine-9,9-dioxide [187]



1.1 g (3.7 mmol) of 4-thia-1,2:6,7-dibenz[*7*]metacyclophane-1,6-diene [180] were dissolved in 25 mL dichloromethane, followed by the addition of 2.0 g, 85% (9.8 mmol, est.) *meta*-chloroperbenzoic acid. The mixture was kept under argon atmosphere and stirred at room temperature overnight. Reaction was quenched with saturated $NaHCO_3$, washed with brine, dried over $MgSO_4$, and the solvent evaporated. Residue was recrystallized from dichloromethane/hexane. 1.0 g (82% yield) recovered. Mp 283-285°C, with decomposition to a brown color (lit. 286-288.)

8H,10H-tribenzo-[c,ef,h]-[1]-thiecine-9,9-dioxide. **[180] ^{1}H NMR**: δ 7.9 (s, 1H); 7.4-7.6 (m, 11H); 4.65 (d, 2H, 15 Hz); 4.39 (d, 2H, 15 Hz); **^{13}C NMR**: (decoupled) δ 143.2, 140.5, 137.4, 137.3, 134.4, 130.4, 129.6, 129.1, 128.3, 128.1, 127.9, 125.4, and 69.6.

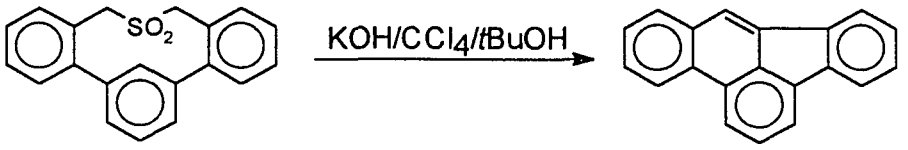
4.3.20 Synthesis of 8*H*,10*H*-tribenzo-[*c,ef,h*][*1*]thiecine-9-oxide [187b]



1.6 g (5.6 mmol) of 4-thia-1,2:6,7-dibenz[7]metacyclophane-1,6-diene [180] were dissolved in 50 mL dry distilled chloroform, followed by the addition of 1.2 g, 85% (6.0 mmol, est.) *meta*-chloroperbenzoic acid. The mixture was kept under argon atmosphere and stirred at room temperature overnight. Reaction was quenched with saturated $NaHCO_3$, washed with brine, dried over $MgSO_4$, and the solvent evaporated. Residue was recrystallized from dichloromethane/hexane. 1.5 g (91% yield) recovered. Mp 220.5-221°C.

8H,10H-tribenzo-[c,ef,h]-[1]-thiecine-9-oxide. **[187b] ^{1}H NMR**: δ 7.4-7.6 (m, 11H); 6.7 (s, 1H); 4.57 (d, 2H, 13.5 Hz); 3.96 (d, 2H, 13.5 Hz); **^{13}C NMR**: (decoupled) δ 142.7, 140.4, 137.6, 134.0, 132.2, 129.7, 128.6, 128.5, 127.9, 126.0 and 72.7.

4.3.21 Synthesis of Benzo[*b*]fluoranthene (Benz[*e*]acephenanthrylene) [189][161]



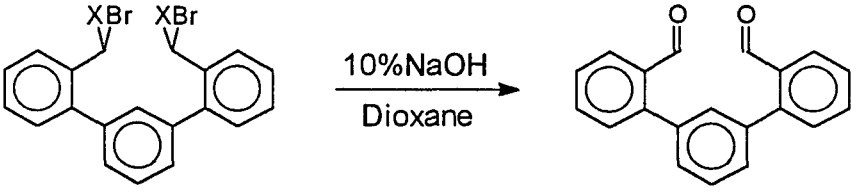
0.25 g of 8*H*,10*H*-tribenzo-[*c,ef,h*]-[*1*]-thiecine-9,9-dioxide [187] was added to a mixture of 25 mL carbon tetrachloride and a solution of 0.5 g KOH in 10 mL *t*-butanol. The mixture was refluxed for 4 hours. The reaction was followed by Thin-layer chromatography (5:1, hexane/ dichloromethane) and the appearance of a fluorescent and bright purple spot was noted. The reaction was worked up by the addition of water, extraction with dichloromethane, drying over $MgSO_4$, filtering and vacuum removal of solvent. 0.1 g recovered, 51% yield. Mp 167-168°C (lit. 168°C, [162] Aldrich 163-165°C, mixed 163-165°C.) TLC: identical R_f to known Aldrich sample. Proton NMR was also identical to known sample. A sample removed 30 minutes after the addition of the sulfone to the KOH/CCl_4 revealed only the presence of starting sulfone and product, as detected by proton NMR.

The reaction was run exactly as above at 0°C. 0.25 g of 8*H*,10*H*-tribenzo-[*c,ef,h*]-[*1*]-thiecine-9,9-dioxide was added to an ice-cold mixture of 25 mL carbon tetrachloride and a solution of 0.5 g KOH in 10 mL *t*-butanol. The mixture was placed into a refrigerator

containing a magnetic stirrer and was stirrer overnight (12 hours.) The reaction was worked up as above. Sulfone and product were separated by column chromatograph (9:1, hexane/dichloromethane.) 0.03 g recovered (15% yield.) Mp 167-168°C, mixed 163-165°C.) TLC: identical R_f to known Aldrich sample. Proton NMR was also identical to known sample.

Benzo[b]fluoranthene **[189]** (Benz[*e*]acephenanthrylene.) **^{1}H NMR**: δ 8.7 (d, 1H, 8 Hz); 8.4 (d, 1H, 8 Hz); 8.2 (s, 1H); 7.9-8.1 (m, 4H); 7.8 (t, 1H, 8 Hz); 7.6-7.7 (m, 2H); 7.4 (t, 2H, 4 Hz.) **GC-MS**: M^+ at 252.

4.3.22 Synthesis of Dialdehyde [197].[163]



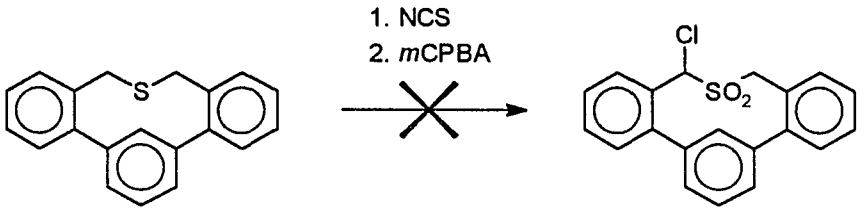
X = Br, H

14 g of a mixture of di-, tri-, and tetra-brominated 2,2'-dimethyl-*meta*-terphenyl [196] was refluxed overnight in a solution of 10 mL 1:1 10%NaOH/Dioxane. Diethyl ether was added, and the mixture was washed several times with water, brine, and then dried over $MgSO_4$. The residue of about 11 g was analyzed by GC-MS and the dialdehyde (M^+ at

286,) mono-aldehyde/mono-alcohol (M^+ 288) and the di-alcohol (no M^+ present, largest peak was 273, [-OH] from M^+ of 290.) were detected in a 2:5:3 ratio as determined by GC peak area. The entire residue (estimate of 38 mmol of alcohol equivalents) was dissolved in 50 mL dichloromethane, and added in one quick portion at 0°C to a solution of 12 g (120 mmol) chromium trioxide and 19 g (120 mmol) freshly distilled pyridine in 300 mL freshly distilled dichloromethane. From the burgundy mixture separated slightly a black tar. The organic layer was decanted and rotary-evaporated, worked up with diethyl ether, 3 x 200 mL 5% NaOH, 3 x 200 mL 5% HCl, 1 x 100 mL of 5% sodium bicarbonate and 2 x 100 mL brine. The organic layer was dried over $MgSO_4$, filtered, and rotary evaporated. The residue was chromatographed (hexane/ethyl acetate, 4:1) and 7.2 g of the aldehyde were recovered. Orange oil. 88% yield, estimated using an average value of 493 g/mol (tribromo-dimethyl-*meta*-terphenyl) for the mixture of the di-, tri-, and tetra-bromides.

Dialdehyde [197]. **^{1}H NMR**: δ 10.1 (s, 2H); 8.1 (d, 2H, 8 Hz); 7.7 (t, 2H, 6 Hz); 7.4-7.6 (m, 8H.) **GC-MS**: M^+ at 286.

4.3.23 Attempted Synthesis of the 8-chloro-8*H*,10*H*-tribenzo-[*c,ef,h*][*1*]thiecine-9,9-dioxide [180] using *N*-chlorosuccinimide



1.7 g (5.6 mmol) of crushed 4-thia-1,2:6,7-dibenz[*7*]metacyclophane-1,6-diene were dissolved/suspended in 25 mL carbon tetrachloride and cooled to 0°C, followed by the addition of 0.8 g (6.0 mmol) crushed and recrystallized *N*-chlorosuccinimide. Reaction was run under an atmosphere of argon and stirred for 5 hours. Next, 3.0g, 85% (14.7 mmol, est.) *meta*-chloroperbenzoic acid were added, and the mixture was kept under argon atmosphere and stirred at room temperature overnight. Reaction was quenched with saturated $NaHCO_3$, washed with brine, dried over $MgSO_4$, and the solvent evaporated. Residue was recrystallized from dichloromethane/hexane. 1.3 g of pure sulfone (73% yield) recovered. No chlorination was detected in this and five repeated experiments.

NCS and 4-thia-1,2:6,7-dibenz[7]metacyclophane-1,6-diene. **^{1}H NMR**: (4 hours, CCl_4, 25°C, crude-no workup, $CDCl_3$ added.) δ 8.8 (s); 7.2-7.5 (m); 4.2 (d, 14 Hz); 2.9 (d from sulfide, with large singlet superimposed); 1.9 (s); 1.45 (s.)

4.3.23.a α-Chloro-dibenzylsulfone [188c]

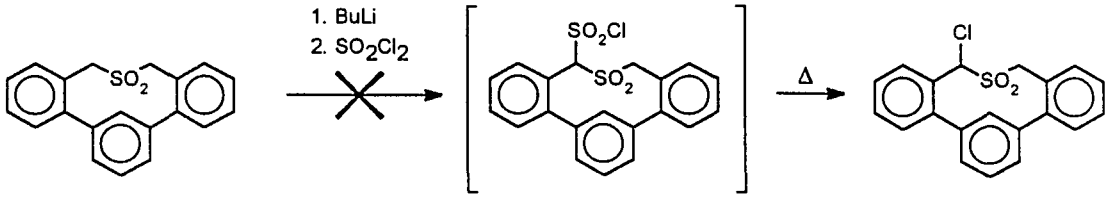
α-Chloro-dibenzylsulfone was successfully synthesized from dibenzylsulfide in a separate experiment under identical conditions as a control. 1.1 g (5 mmol) dibenzylsulfide and 0.7 g *N*-chlorosuccinimide in 50 mL CCl_4, stirred for five hours, filtered, 1.7 g (10 mmol) m-CPBA added, stirred overnight. Worked-up identically as above, residue (1.3 g) was analyzed by proton NMR only and not purified.

Dibenzylsulfide (Aldrich.) **[188a] ^{1}H NMR**: δ 7.3 (m, 10H); 3.6 (s, 4H.)

α-Chloro-dibenzylsulfide. **[188b] ^{1}H NMR**: (4 hours after the addition of NCS, crude-no workup, $CDCl_3$ added) δ 10.10 (s); 8.2 (broad singlet); 7.9 (d, 8 Hz); 7.5 (t, 8 Hz); 7.1-7.4 (m); 5.8 (s); 4.4 (s); 4.1 (d, 13 Hz); 4.9 (d, 13 Hz); 3.7 (d, 13 Hz); 3.6 (s); 3.5 (d, 13 Hz); 2.7 (s); 1.9 (s.)

α-Chloro-dibenzylsulfone. **[188c] ^{1}H NMR**: δ 7.4 -7.6 (m, 10H); 5.4 (s, 1H); 4.7 (d, 1H, 14 Hz); 4.3 (d, 1H, 14 Hz.)

4.3.24 Attempted Synthesis of the 8-chloro-8*H*,10*H*-tribenzo-[*c,ef,h*][*1*]thiecine-9,9-dioxide [181] using *n*-butyllithium and SO_2Cl_2.



A 25 mL three-necked rbf was fitted with a 10 mL dropping funnel, argon inlet, $CaCl_2$ drying tube, and a rubber septum. 0.10 g (0.3 mmol) 8*H*,10*H*-tribenzo-[*c,ef,h*][*1*]thiecine-9,9-dioxide [187] was dissolved in 10 mL dry, distilled THF. The temperature was lowered to -60°C, and 0.2 mL 2.0 M (0.3 mmol) n-butyllithium (previously titrated using 2,5-dimethoxybenzyl alcohol as an indicatory standard.[164]) was added via syringe, turning the solution a deep blue. The reaction was stirred for 30 minutes, followed by the dropwise addition of a solution of 0.1 mL (1.2 mmol) sulfuryl chloride dissolved in 5 mL THF. The reaction turned immediatedly from blue to yellow. The reaction was allowed to stir for one hour, then worked up using ether and washing with brine, water, drying with $MgSO_4$, filtering, and evaporating. 0.9 g residue was chromatographed (hexane/ethylacetate, 9:1), but no single product could be isolated. GC-MS detected the presence of several products, mostly unidentified, but including:

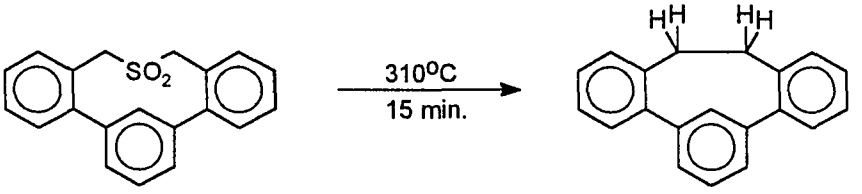
8,9-Dihydro-tribenzo[acdf]*cyclononene* **[195]** (the cyclophane alkane, M^+ at 256, 9% by GC peak area)

8H,10H-tribenzo-[c,ef,h]-[1]-thiecine-9,9-dioxide **[187]** (sulfone, M^+ at 320, 13% by GC peak area)

and what may be

8-chloro-8H,10H-tribenzo-[c,ef,h]-[1]-thiecine-9,9-dioxide **[181]** (desired α-chloro sulfone, M^+ at 354, 8% by GC peak area.)

4.3.25 Synthesis of 8,9-Dihydro-tribenzo[*acdf*]cyclononene [195]



0.03 g of 8*H*,10*H*-tribenzo-[*c,ef,h*]-[*1*]-thiecine-9,9-dioxide were placed into a clean NMR tube, which was then immersed in a high-temperature oil bath. The temperature was raised at a moderate rate to 310°C and the sample heated for 15 minutes. The clear crystals of the sulfone decomposed to a brown color with the evolution of gas. Moistened blue litmus became red at the open end of the tube. After cooling, $CDCl_3$ was added and proton and carbon NMR analysis was performed (small sulfone impurity.) The solution

was then allowed to slowly evaporate, and 0.02 g of crystals (mp 149-151°C, lit. 153°C [165]) were recovered and analyzed by X-ray crystallography, which confirmed the structure as 8,9-Dihydro-tribenzo[*acdf*]cyclononene, 84% yield. Variable temperature NMR was run with the purified crystals.

8,9-Dihydro-tribenzo[acdf]cyclononene. **^{1}H NMR**: δ 8.0 (s, 1H); 7.8 (broad s, 1H); 7.6 (broad s, 1H); 7.1-7.4 (m, 9H); 3.6 (broad s, 1H); 3.4 (broad s, 1H); 2.6 (broad s, 1H); 1.3 (broad s, 1H.) **^{13}C NMR**: (decoupled) δ 140.5, 133.3 (w), 131.5 (w), 128.3, 127.7, 126.3 (w), 126.1 (w), 125.4 (w), 124.2 (w), 124.0 (w), 41.6 and 33.6.

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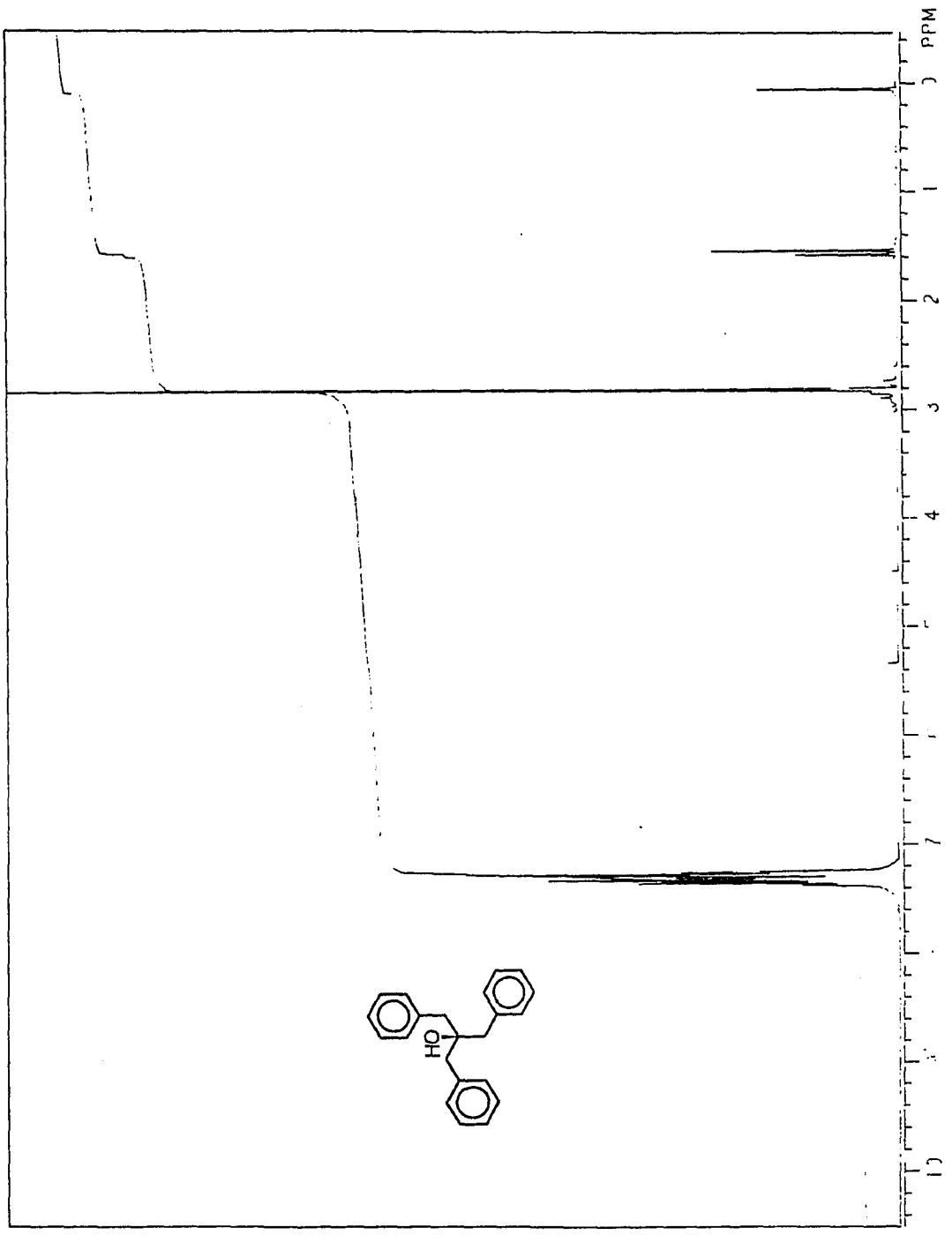
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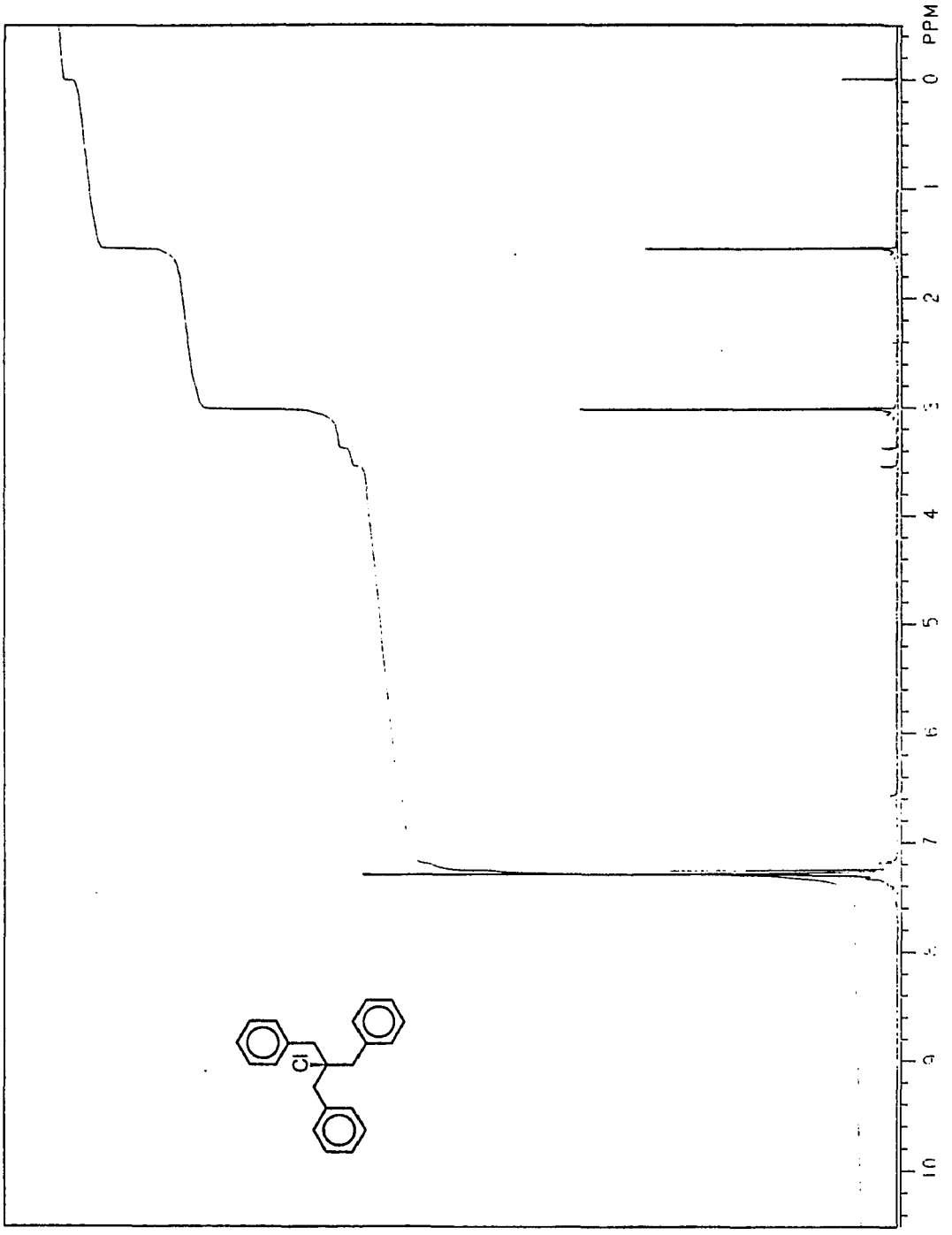
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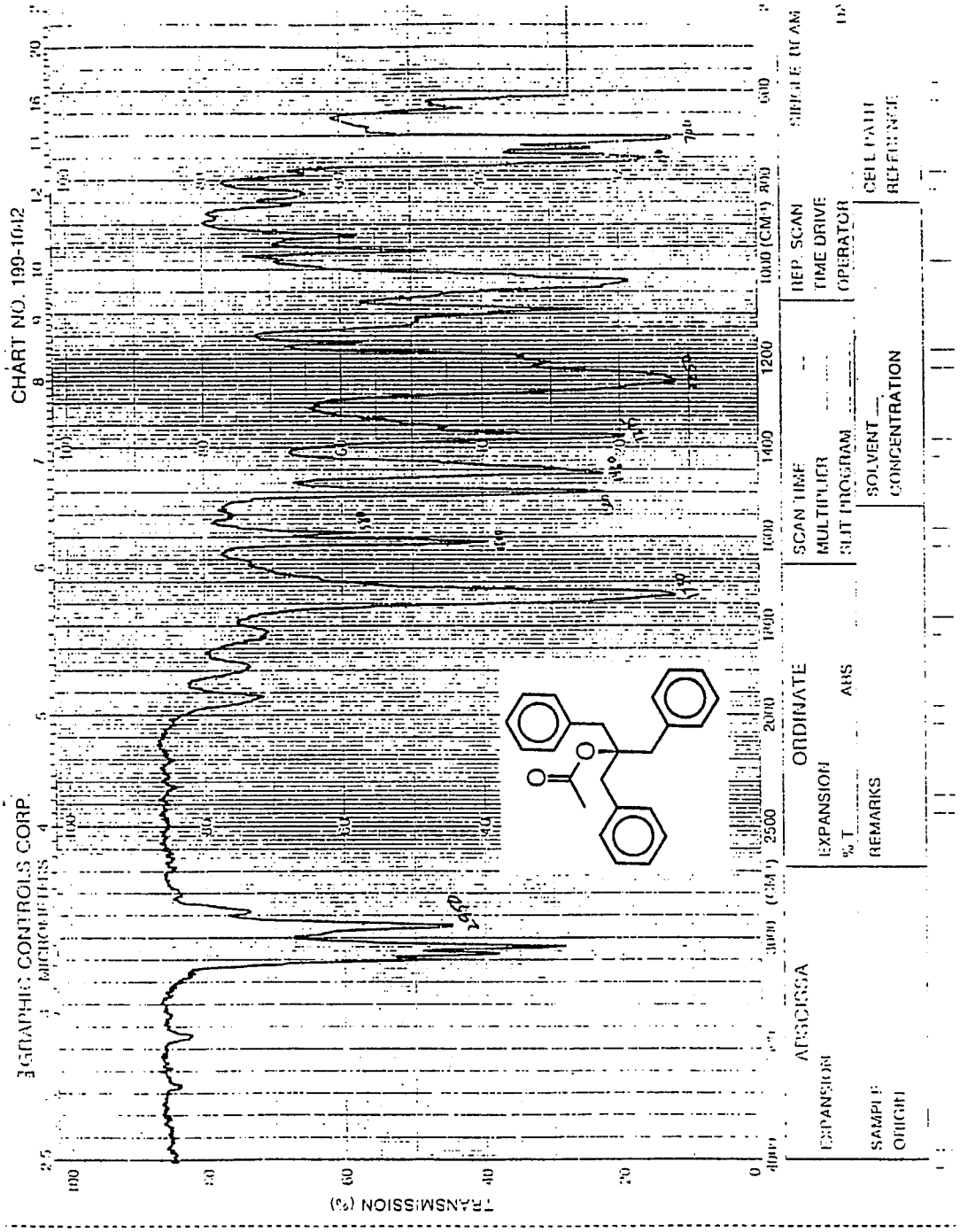
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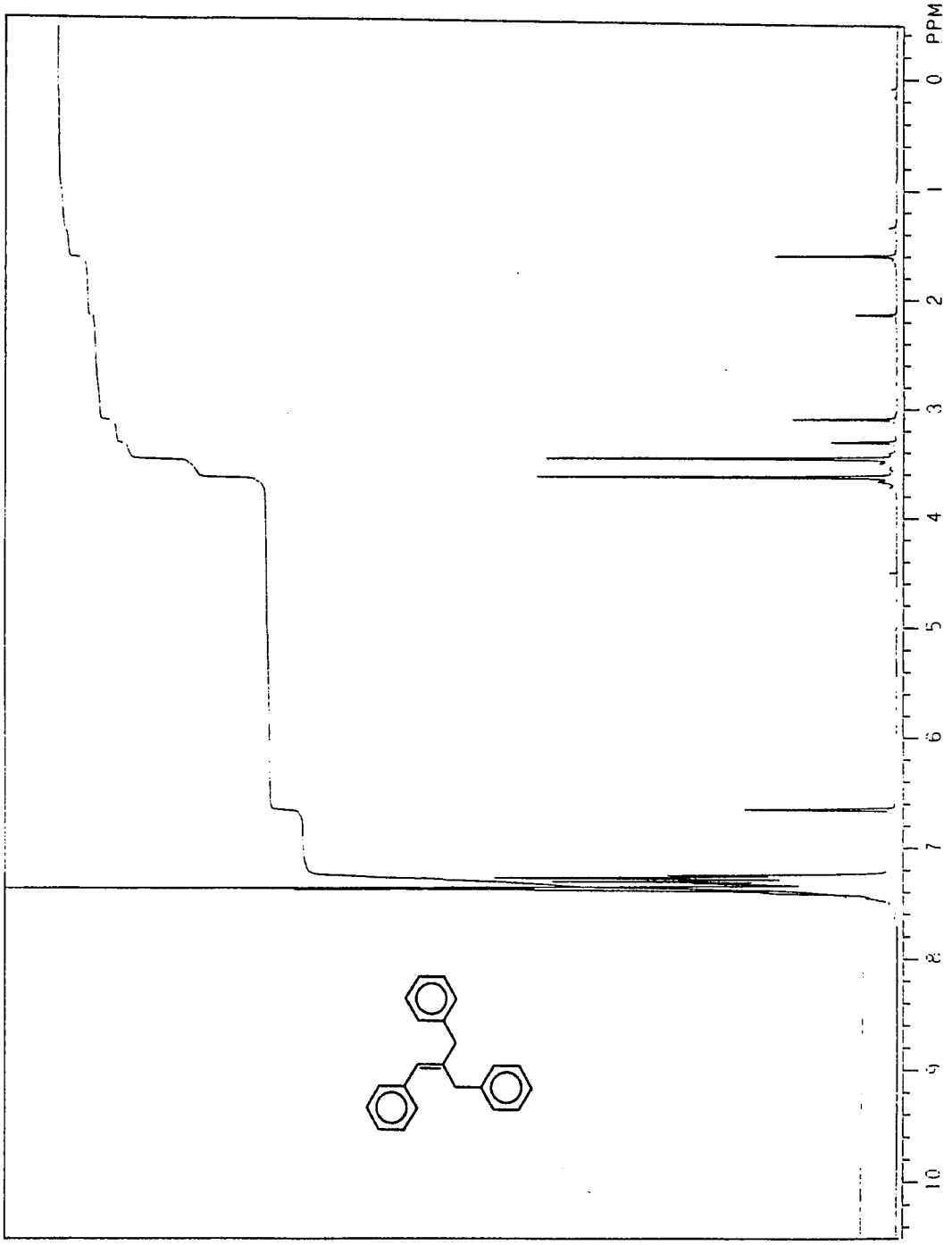
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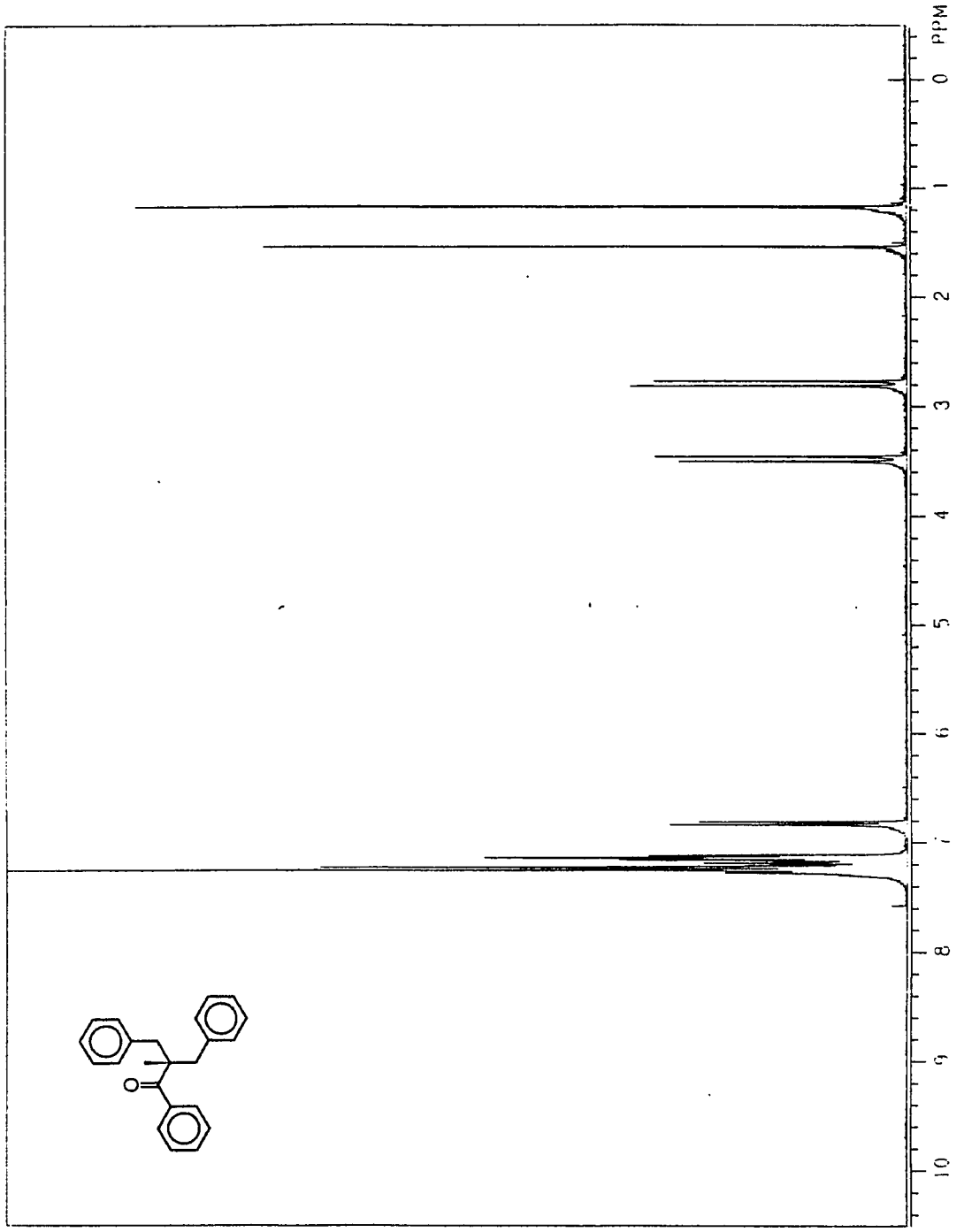
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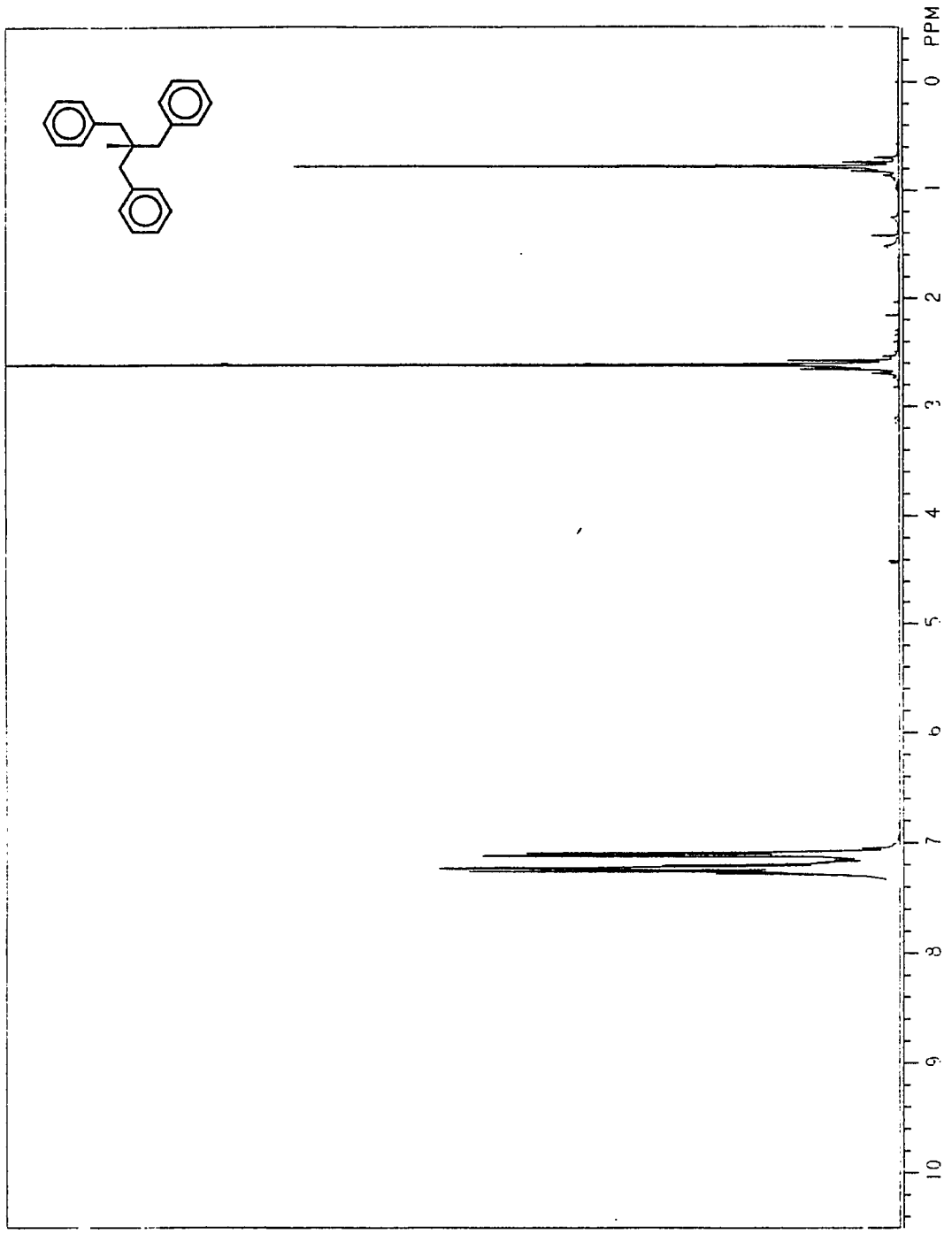
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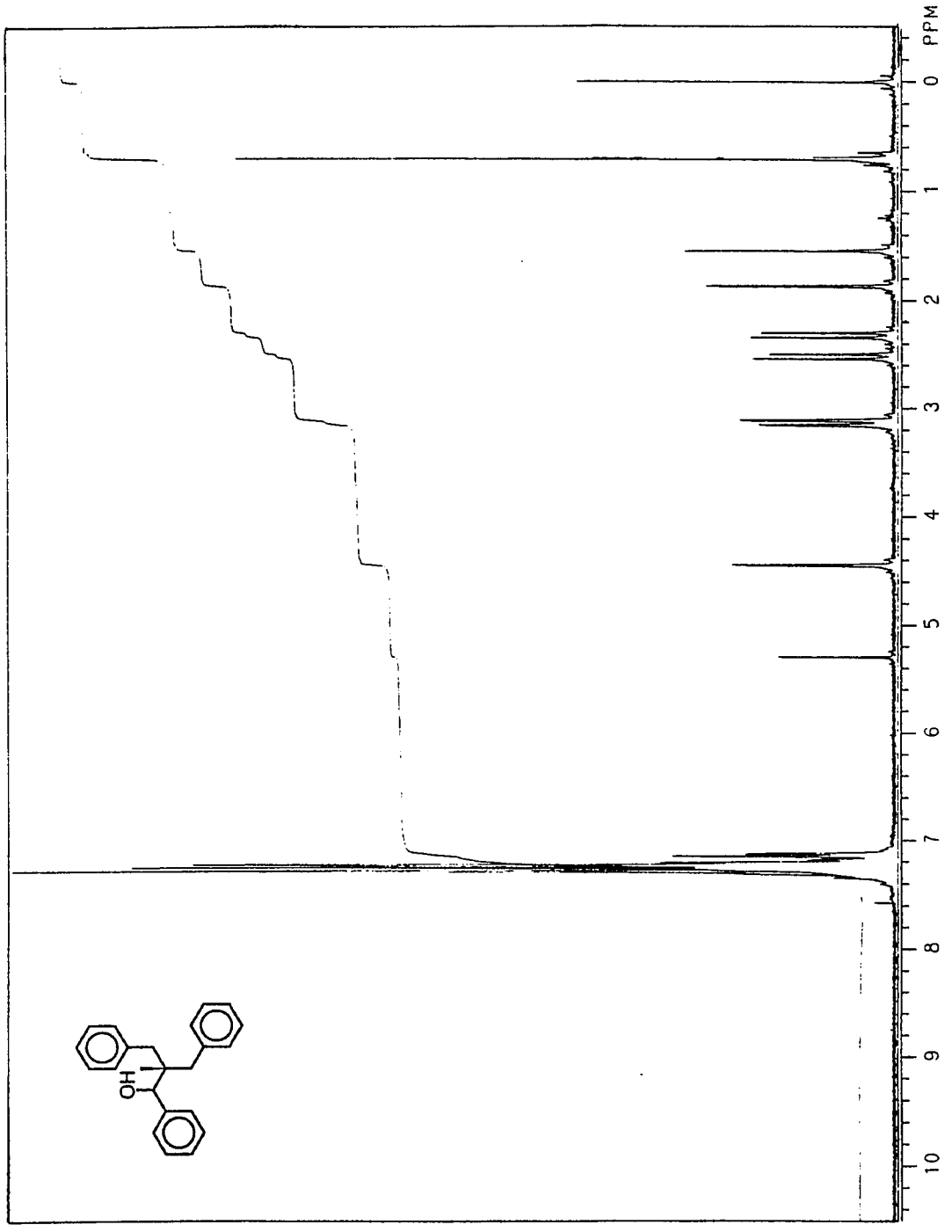
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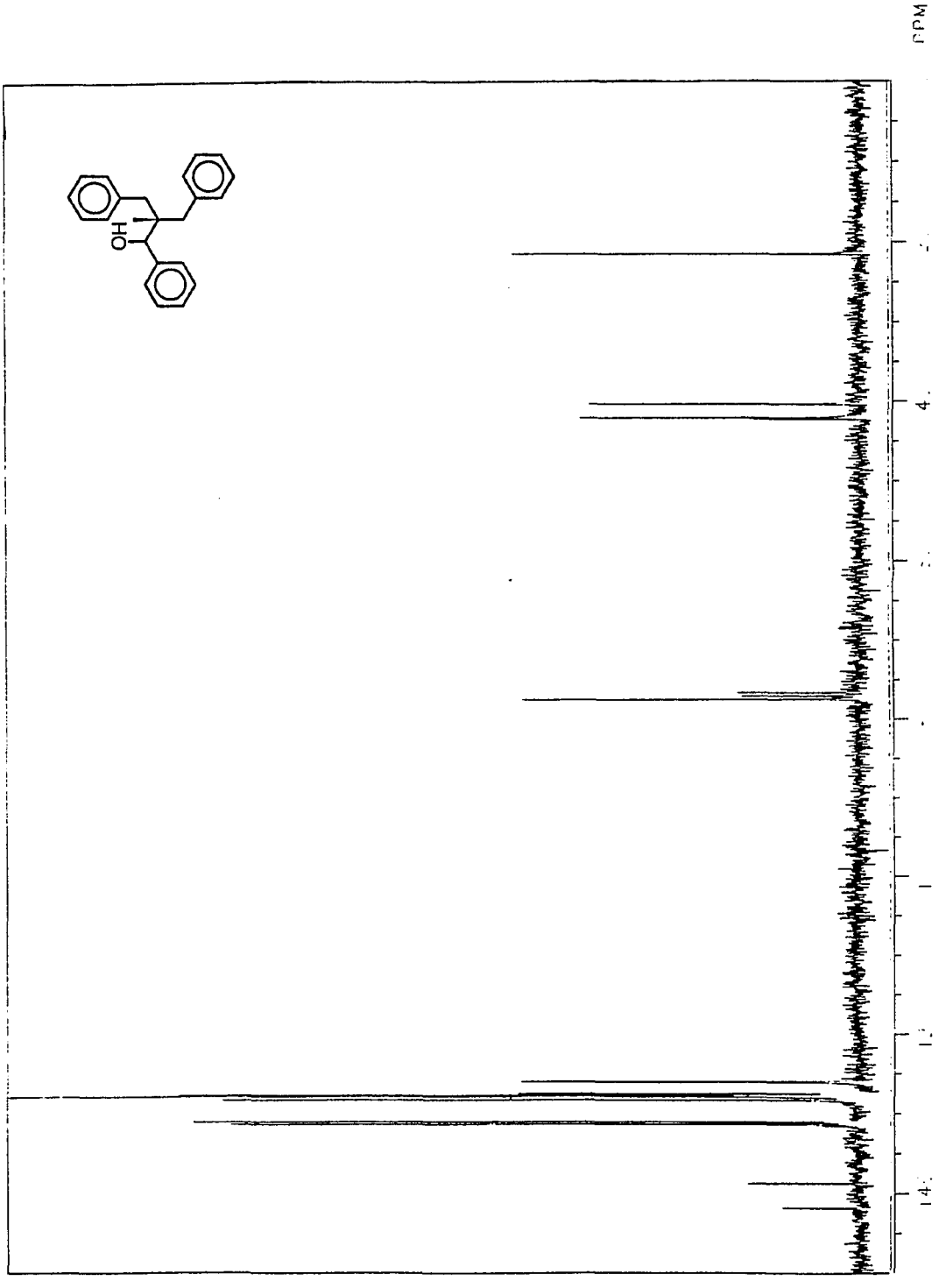
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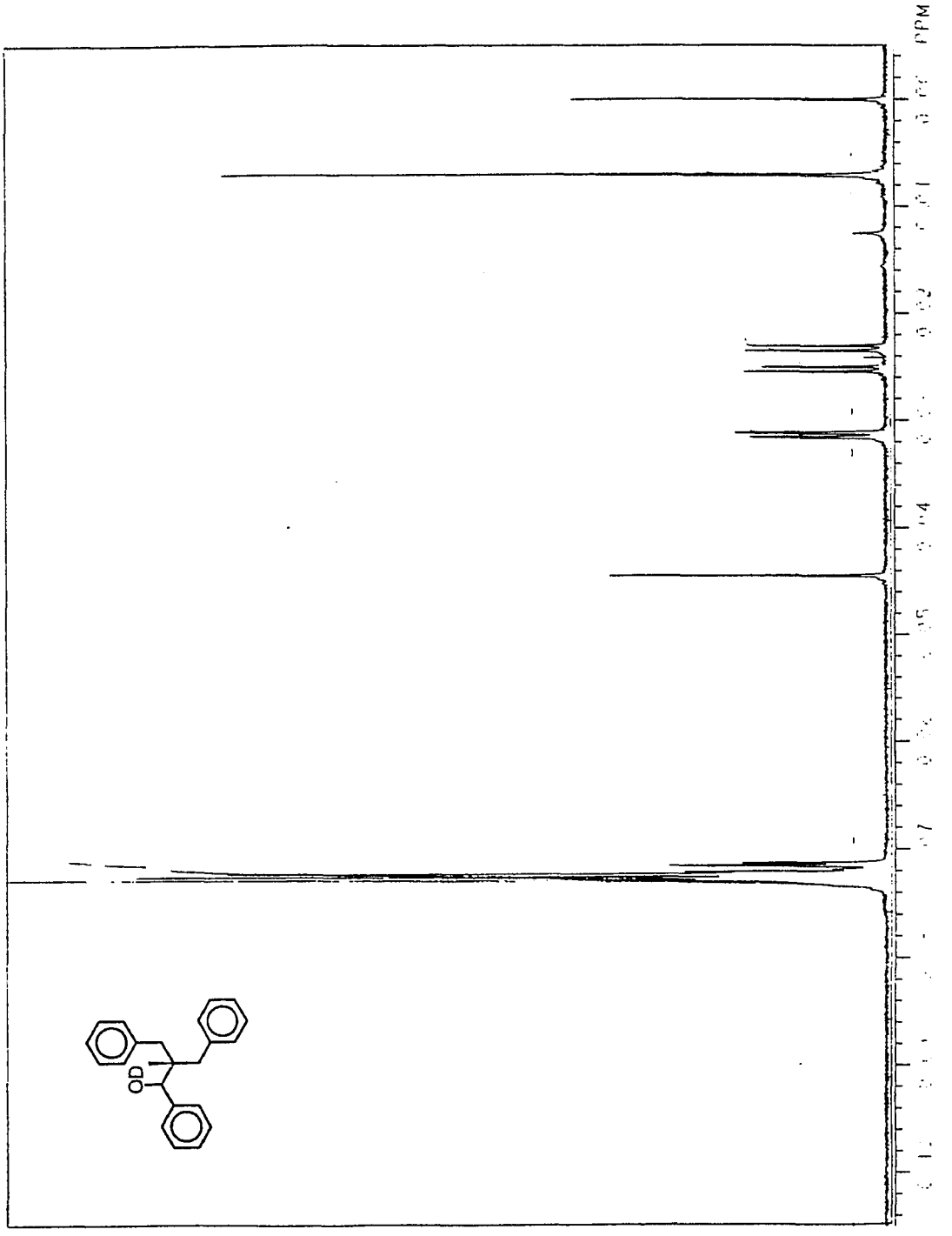
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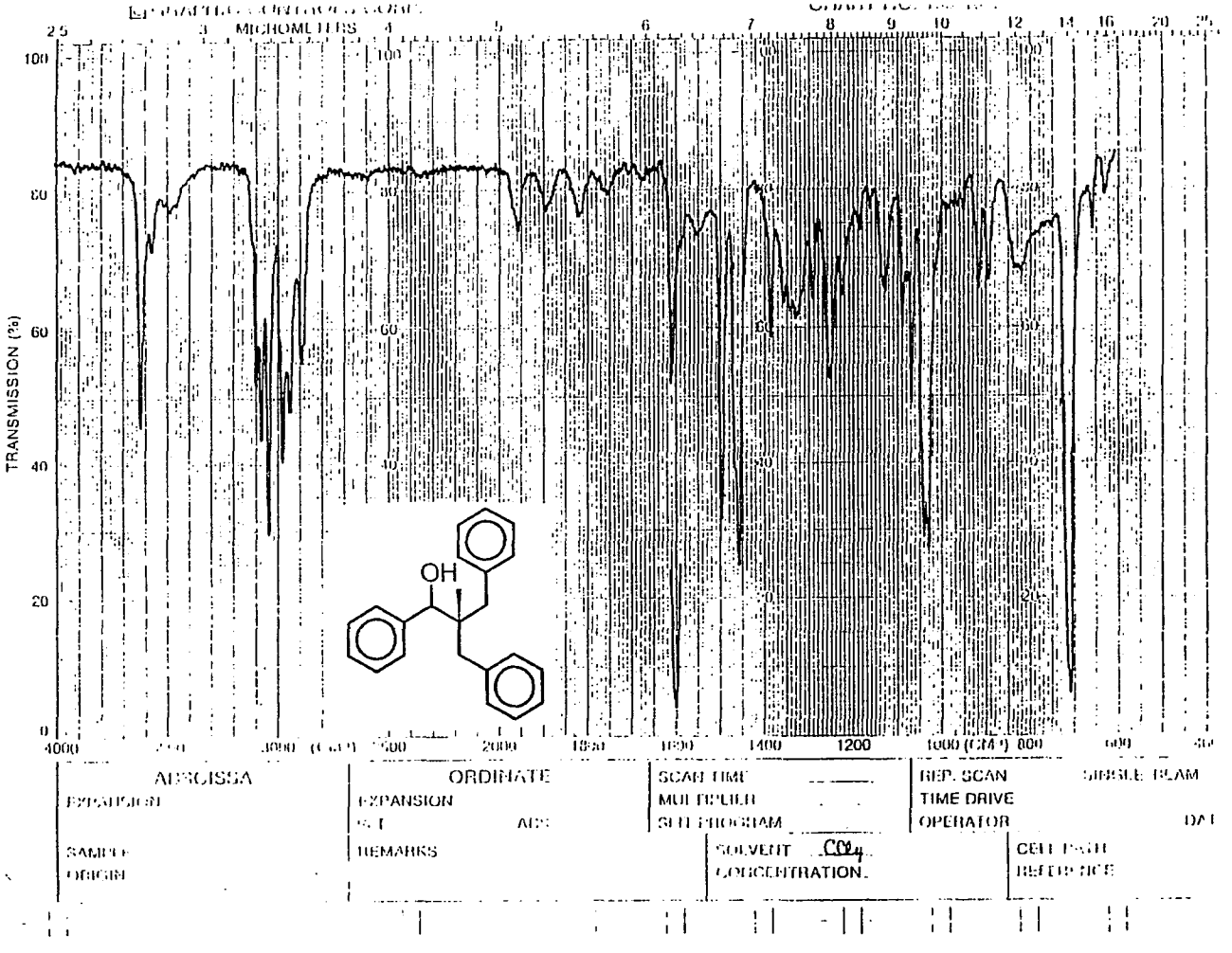
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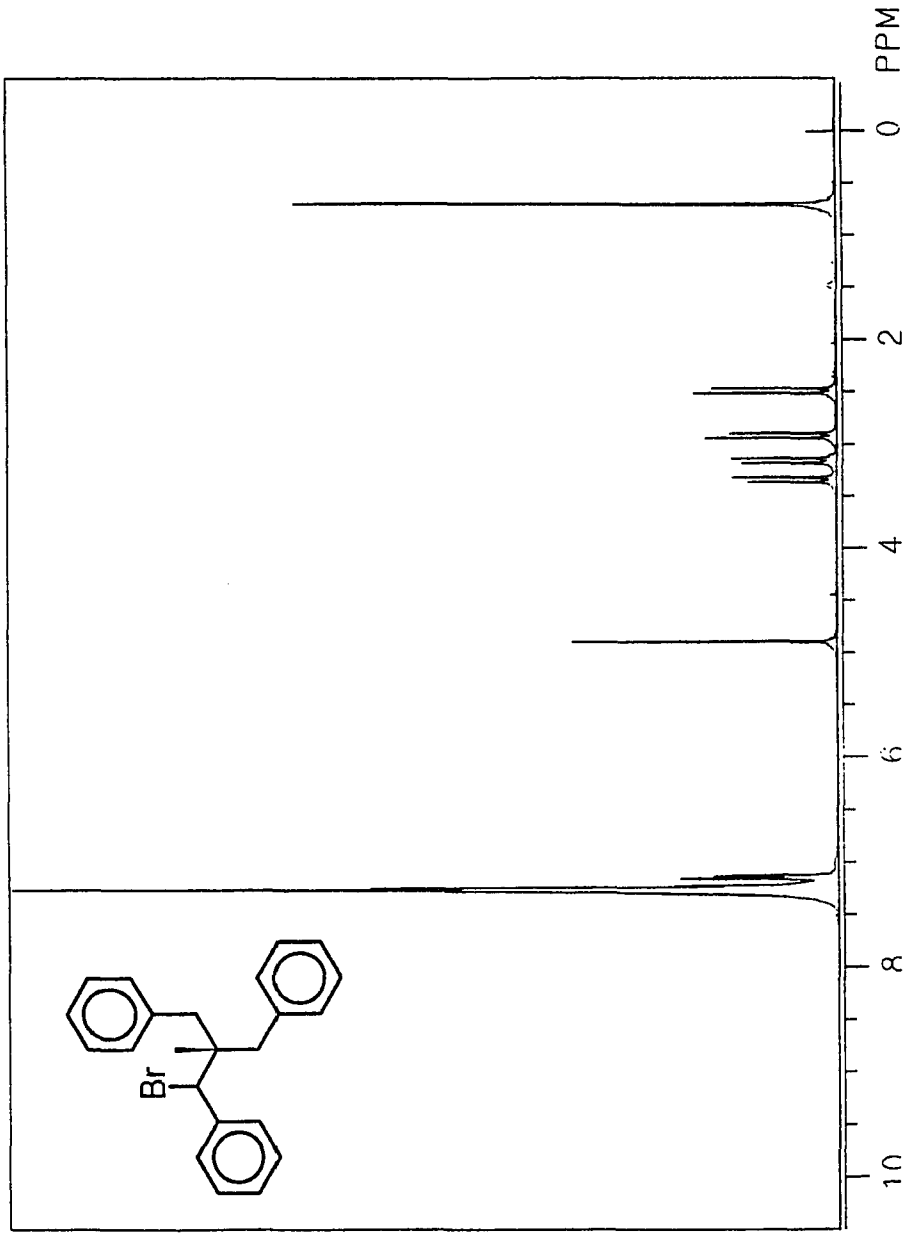
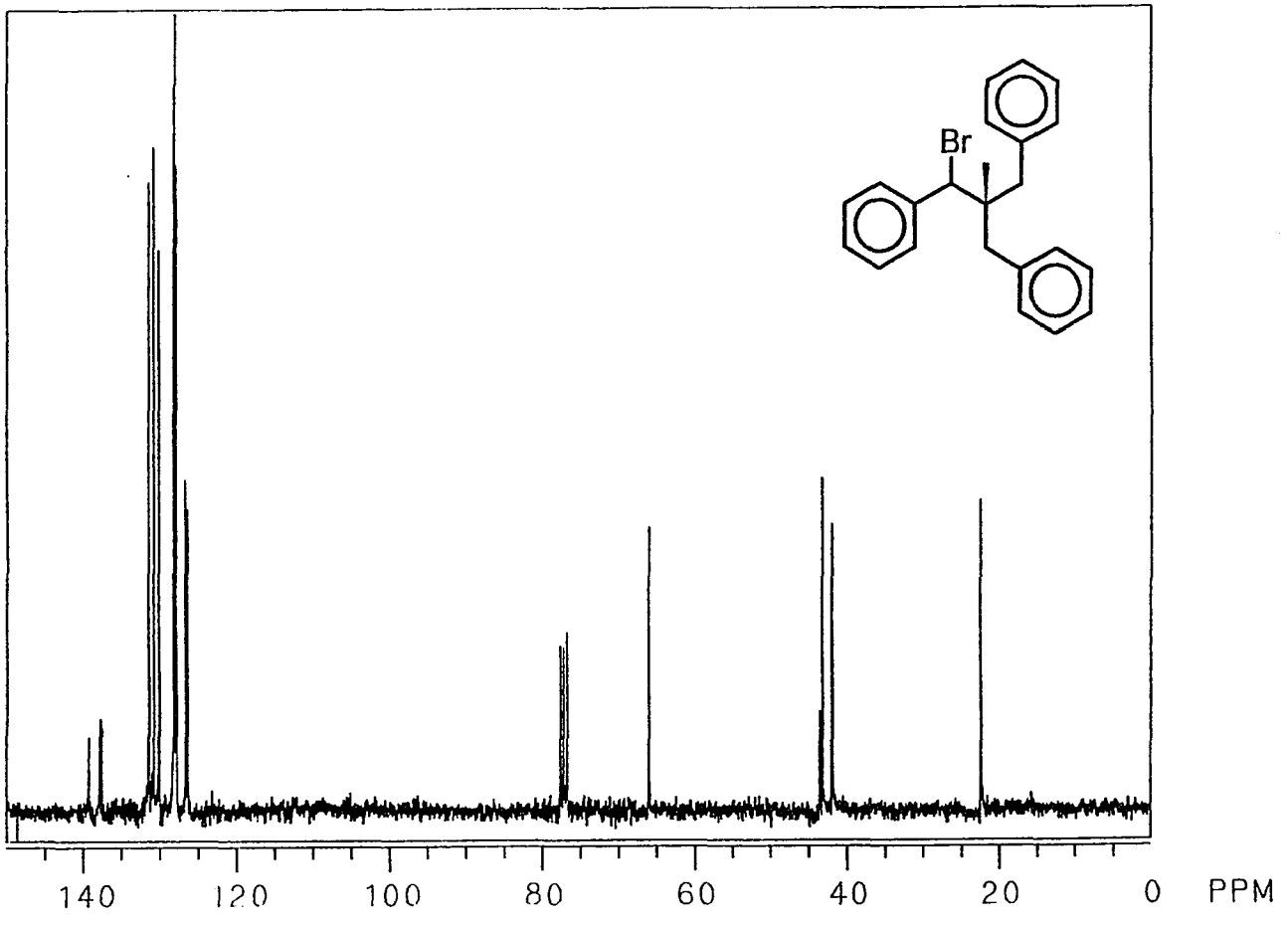
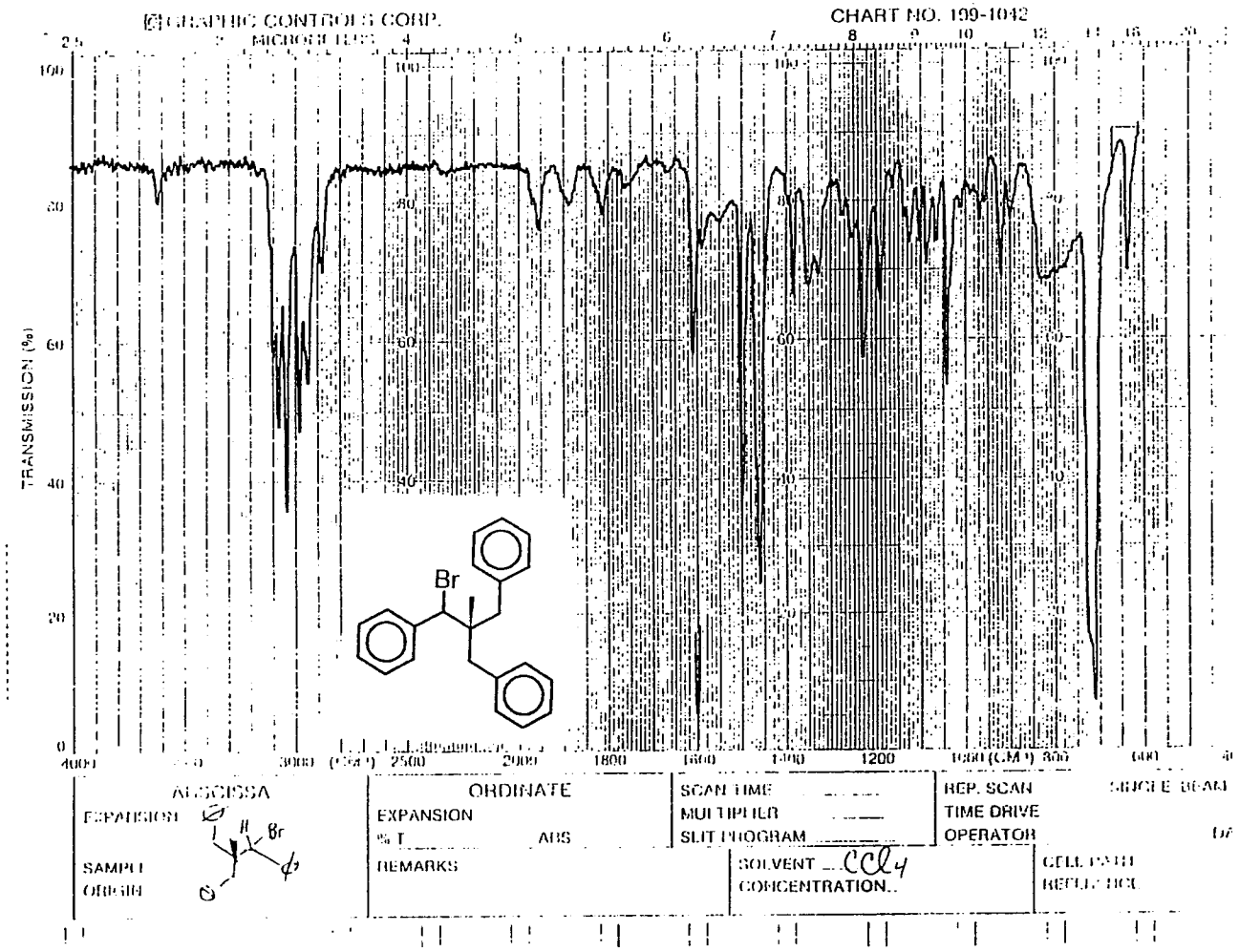
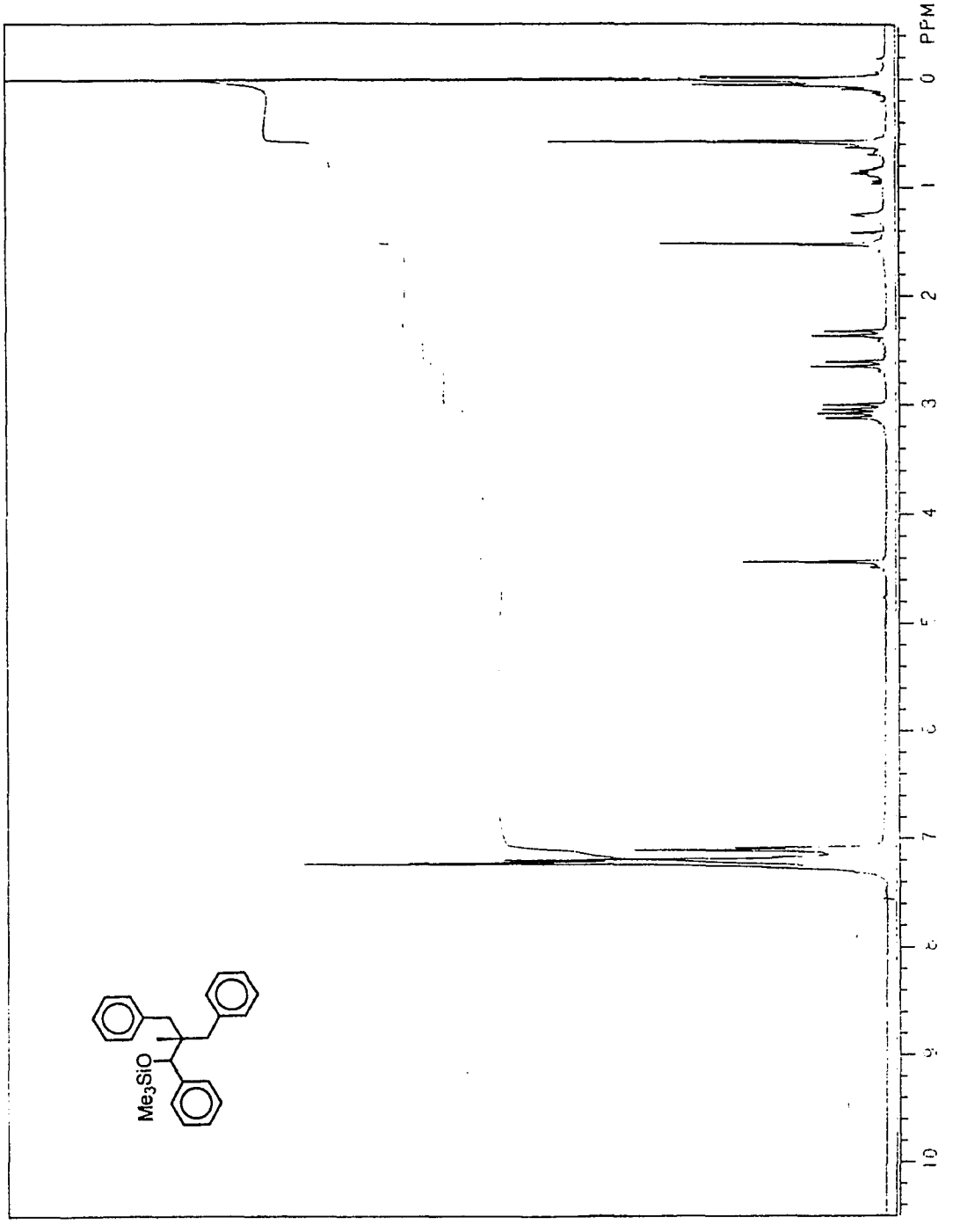
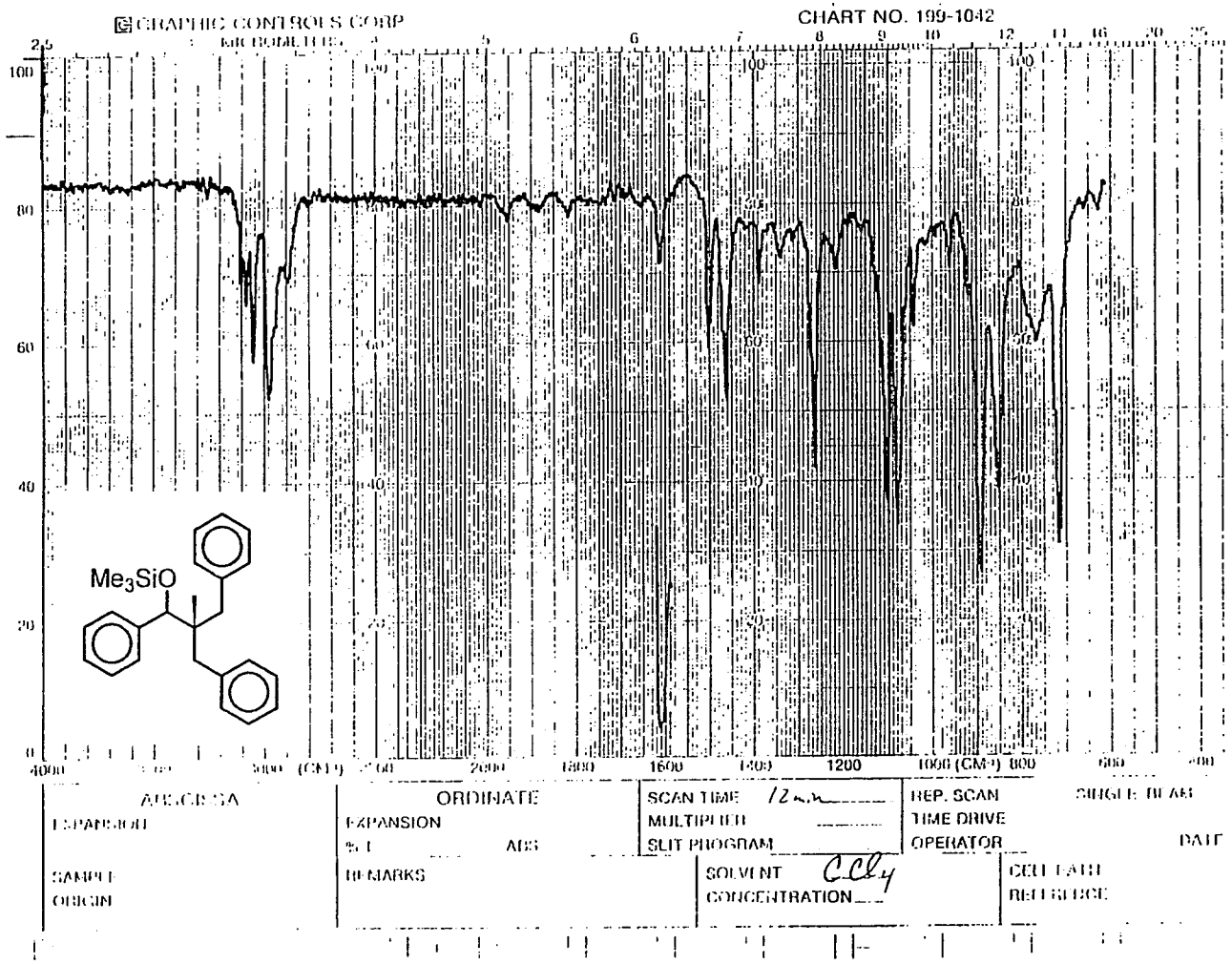
SOLVENT CCl4
CONCENTRATION

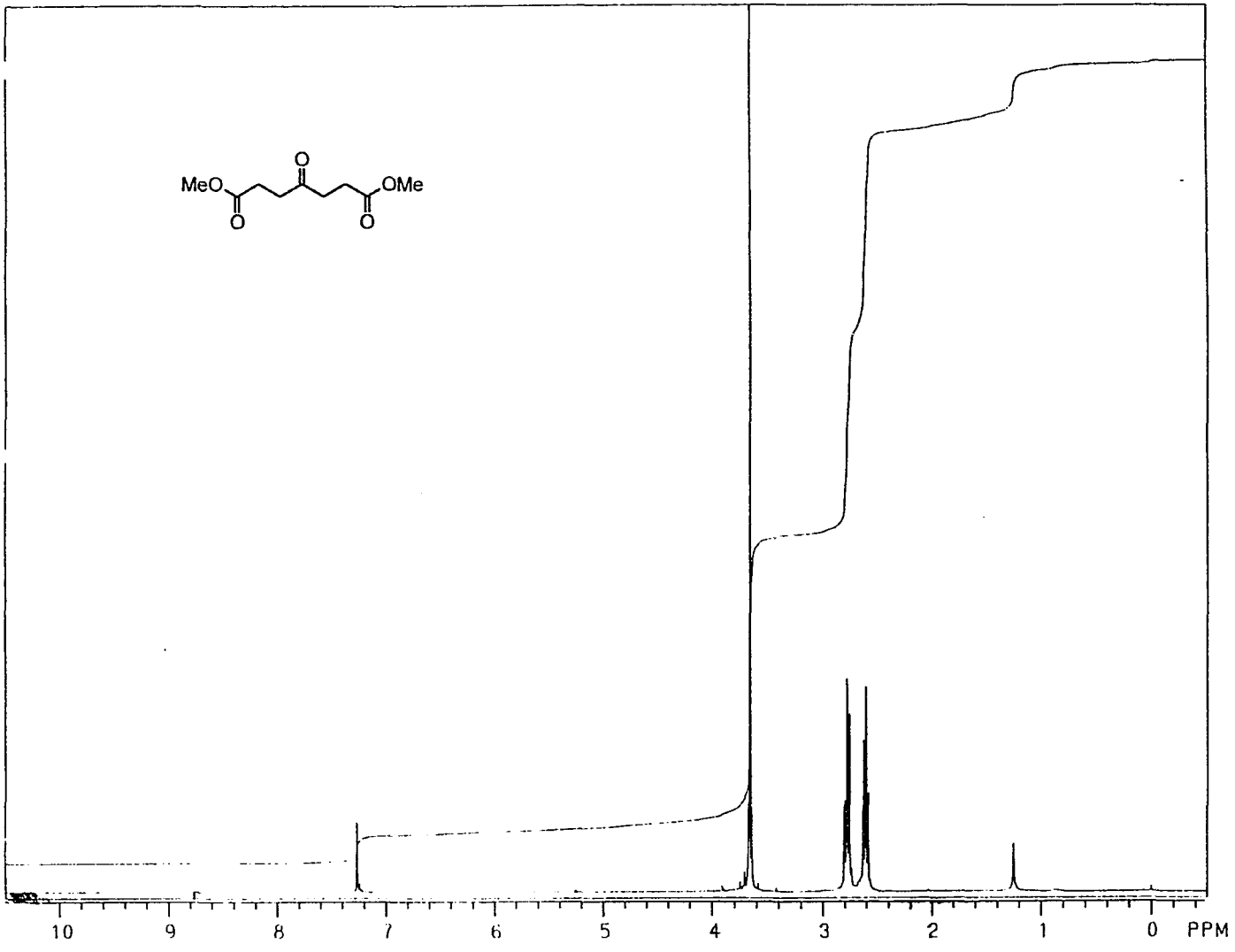

Br
10
8
6
4
2
0
PPM

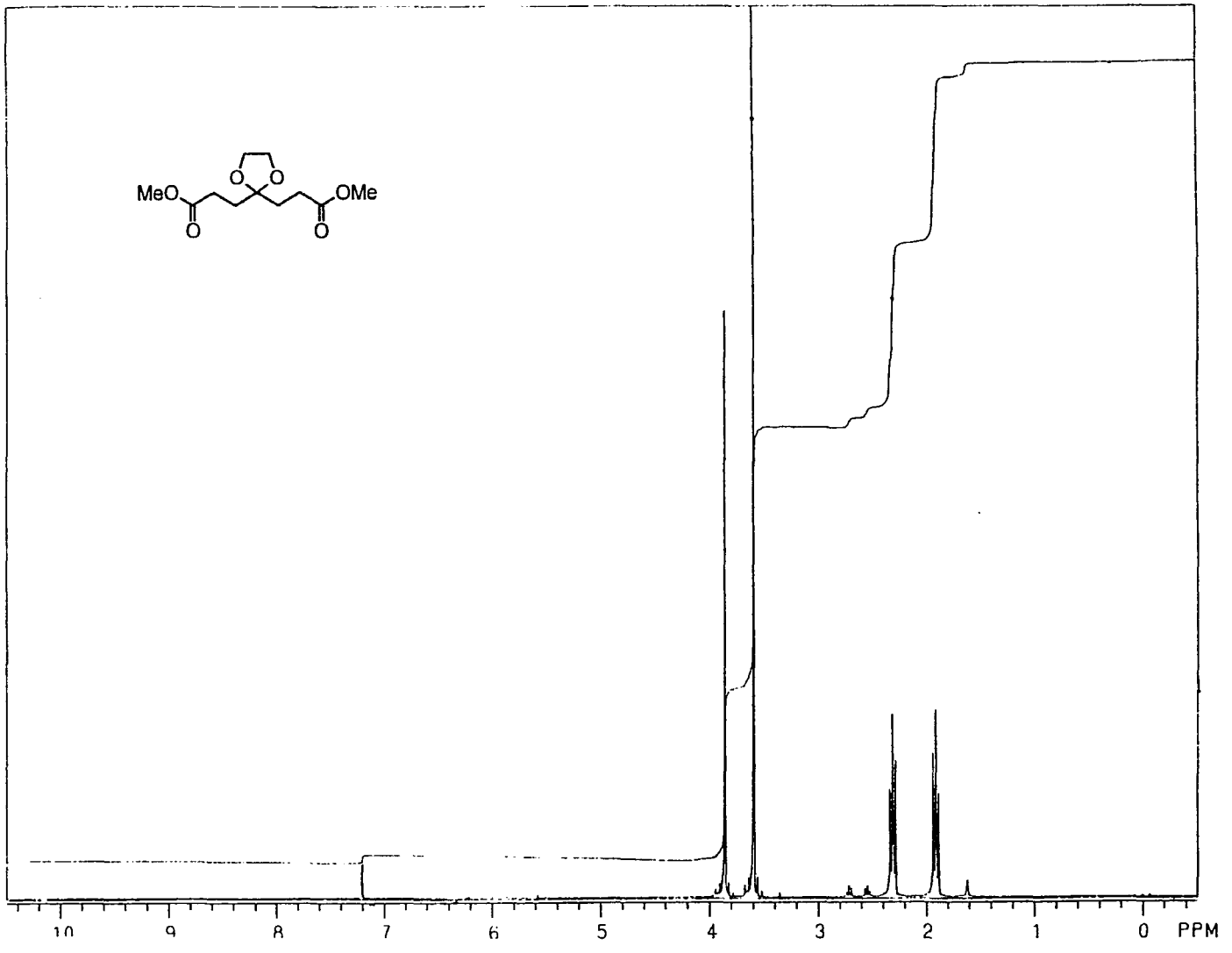

Br
140
120
100
80
60
40
20
0
PPM

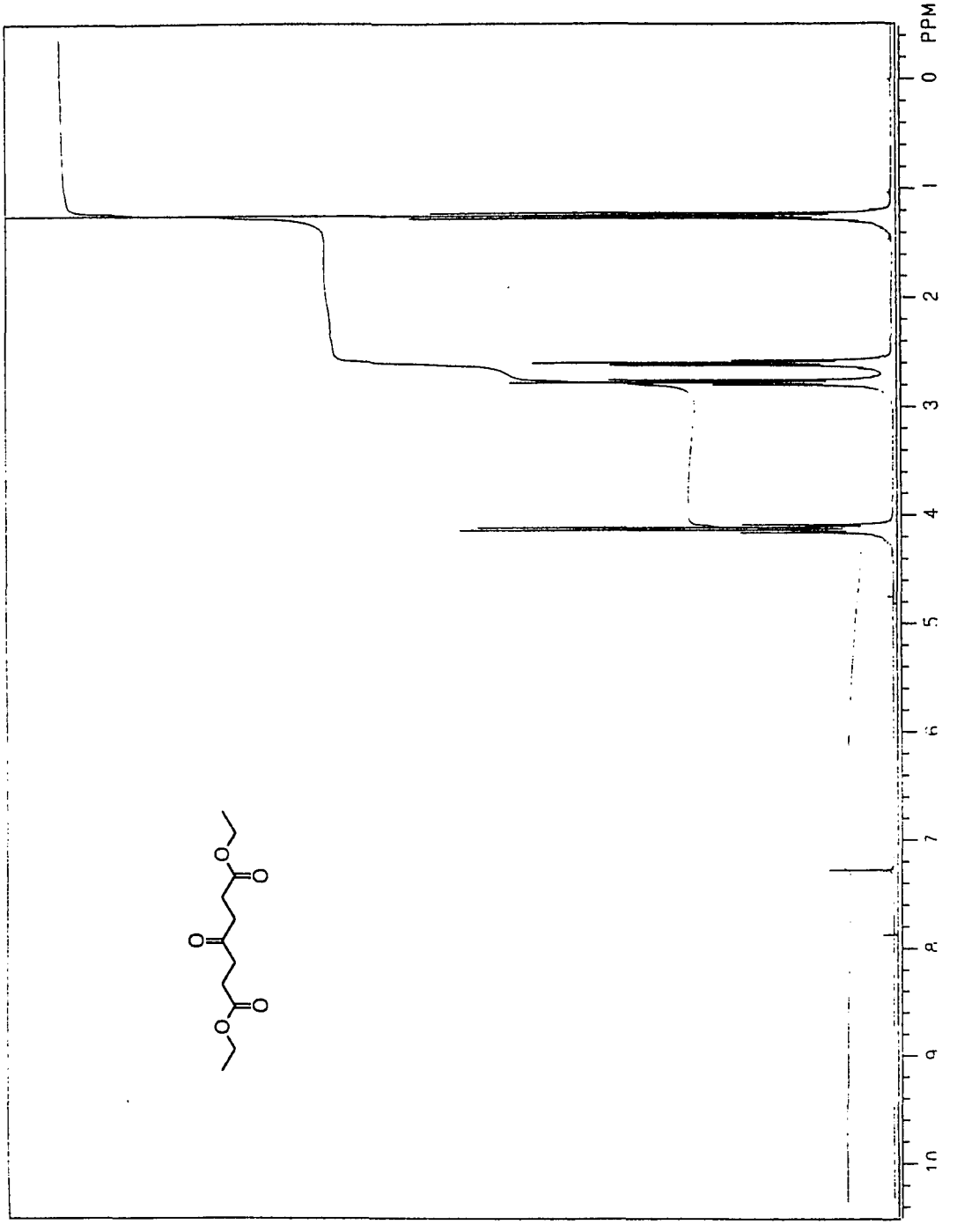

GRAPHIC CONTROLS CORP.
CHART NO. 199-1042
MICRONS
TRANSMISSION (%)
100
80
60
40
20
0
4000
3000
2500
2000
1800
1600
1400
1200
1000
800
600
Br
ABSCISSA
EXPANSION
SAMPLE
ORIGIN
ORDINATE
EXPANSION
% T
ABS
REMARKS
SCAN TIME
MULTIPLIER
SLIT PROGRAM
REP. SCAN
TIME DRIVE
OPERATOR
SOLVENT CCl4
CONCENTRATION
SINGLE BEAM

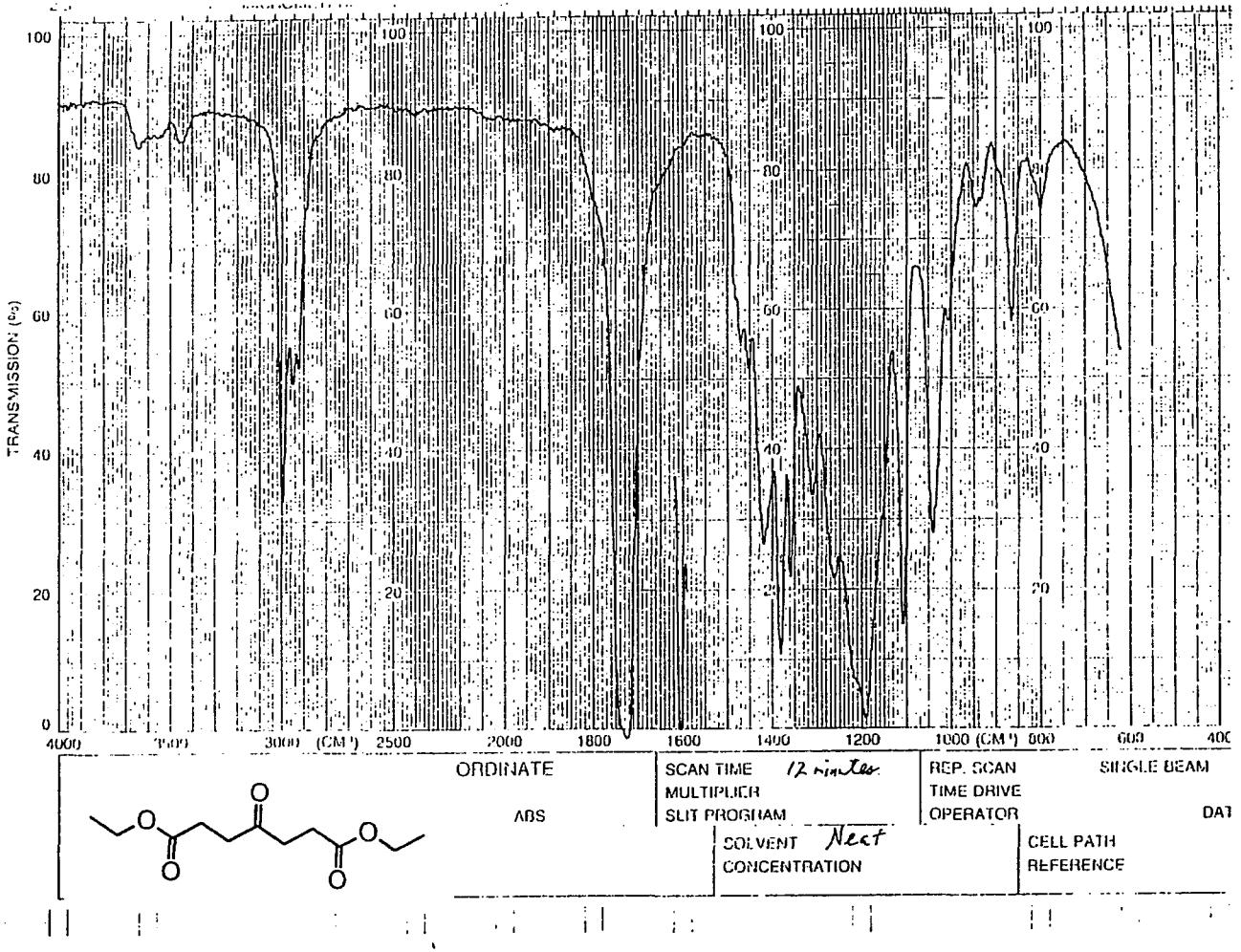

Me3SiO
PPM

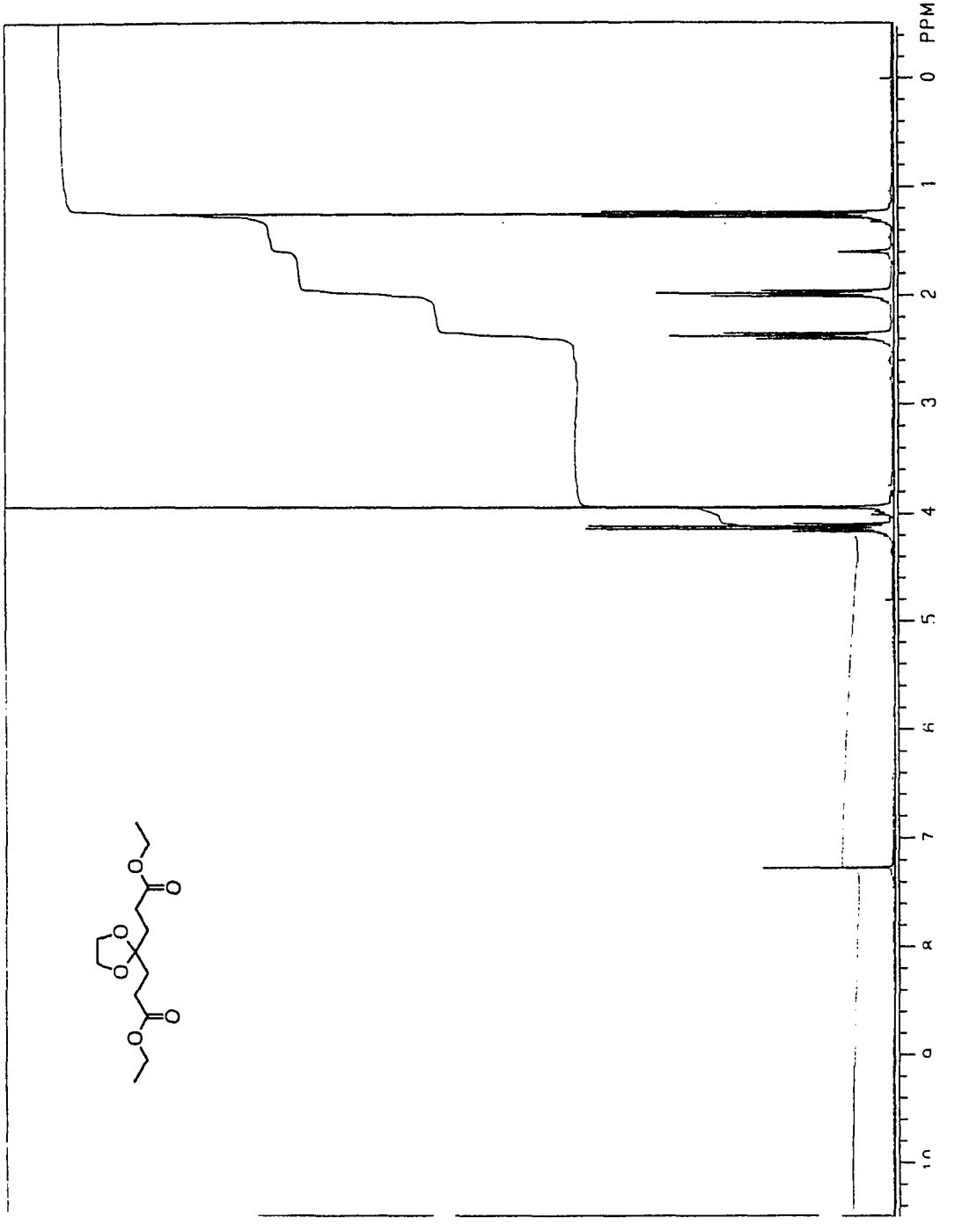

GRAPHIC CONTROLS CORP
CHART NO. 199-1042
MICROMETERS
100
80
60
40
20
0
4000
3000 (CM-1)
2400
2000
1800
1600
1400
1200
1000 (CM-1)
800
600
400
Me3SiO
ABSCISSA
EXPANSION
SAMPLE
ORIGIN
ORDINATE
EXPANSION
% T
ABS
REMARKS
SCAN TIME 12 min
MULTIPLIER
SLIT PROGRAM
SOLVENT CCl4
CONCENTRATION
REP. SCAN
TIME DRIVE
OPERATOR
CELL PATH
REFERENCE
SINGLE BEAM
DATE

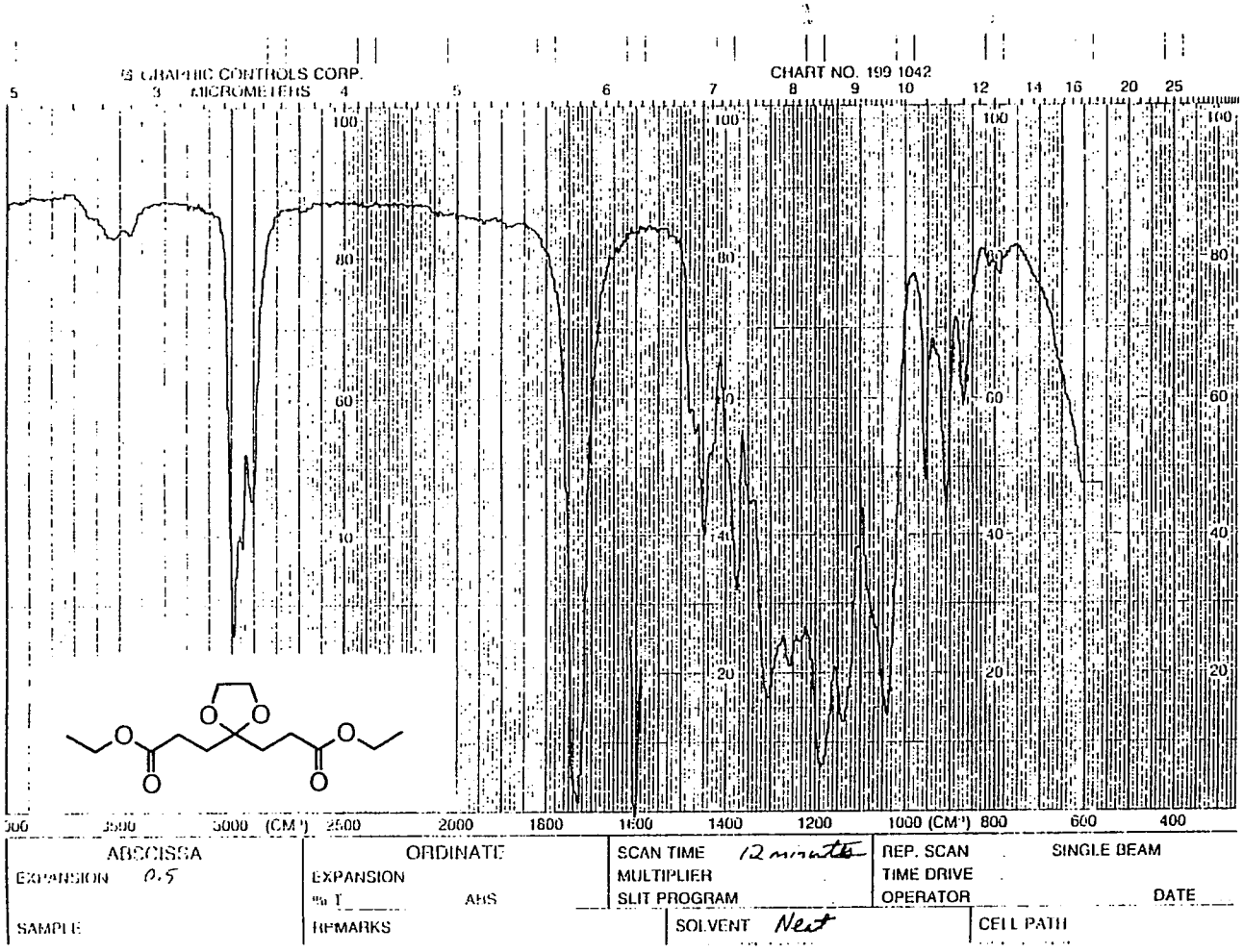

MeO
O
O
O
OMe
O
10
9
8
7
6
5
4
3
2
1
0
PPM

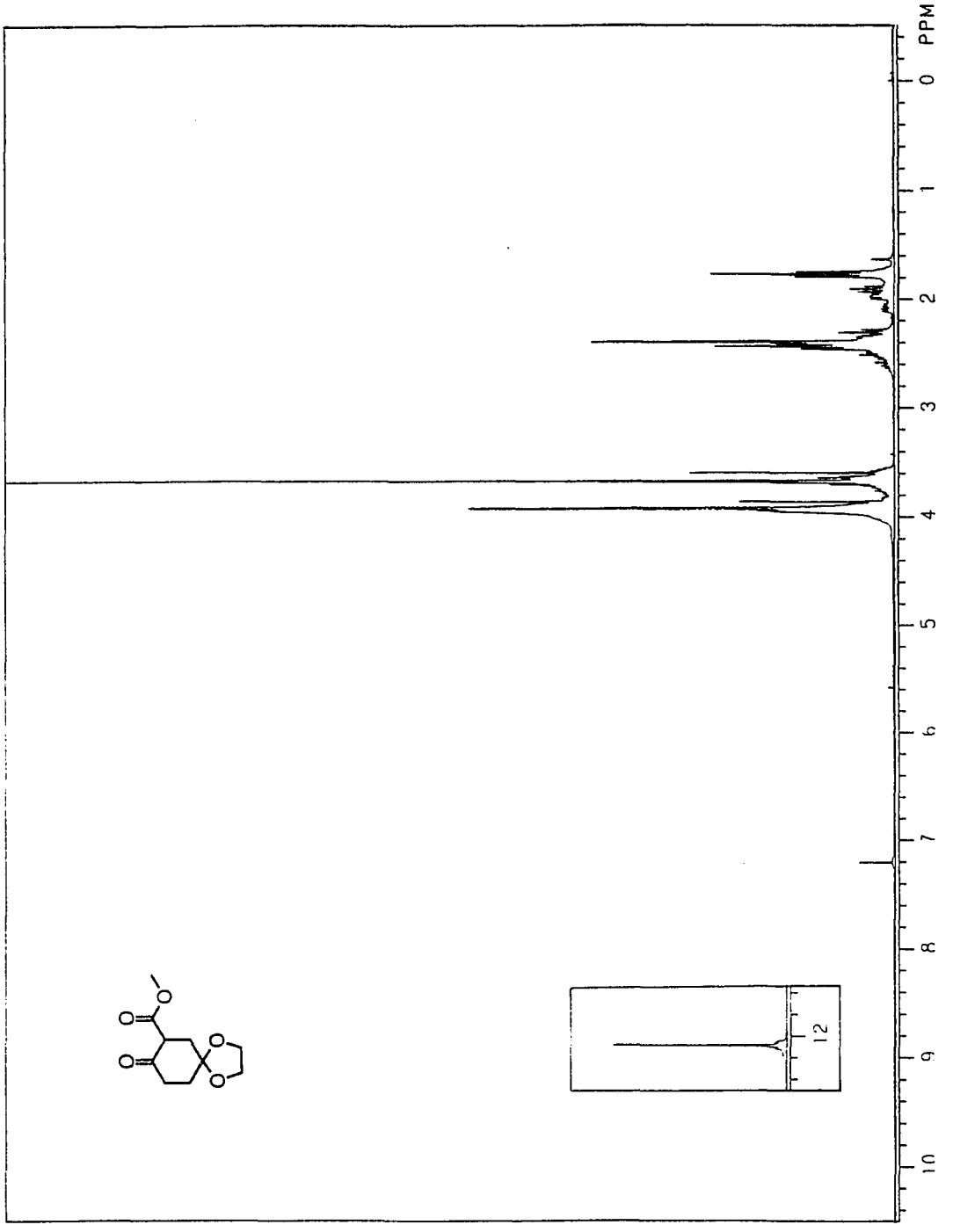

MeO
OMe
O
O
O
O
10
9
8
7
6
5
4
3
2
1
0
PPM

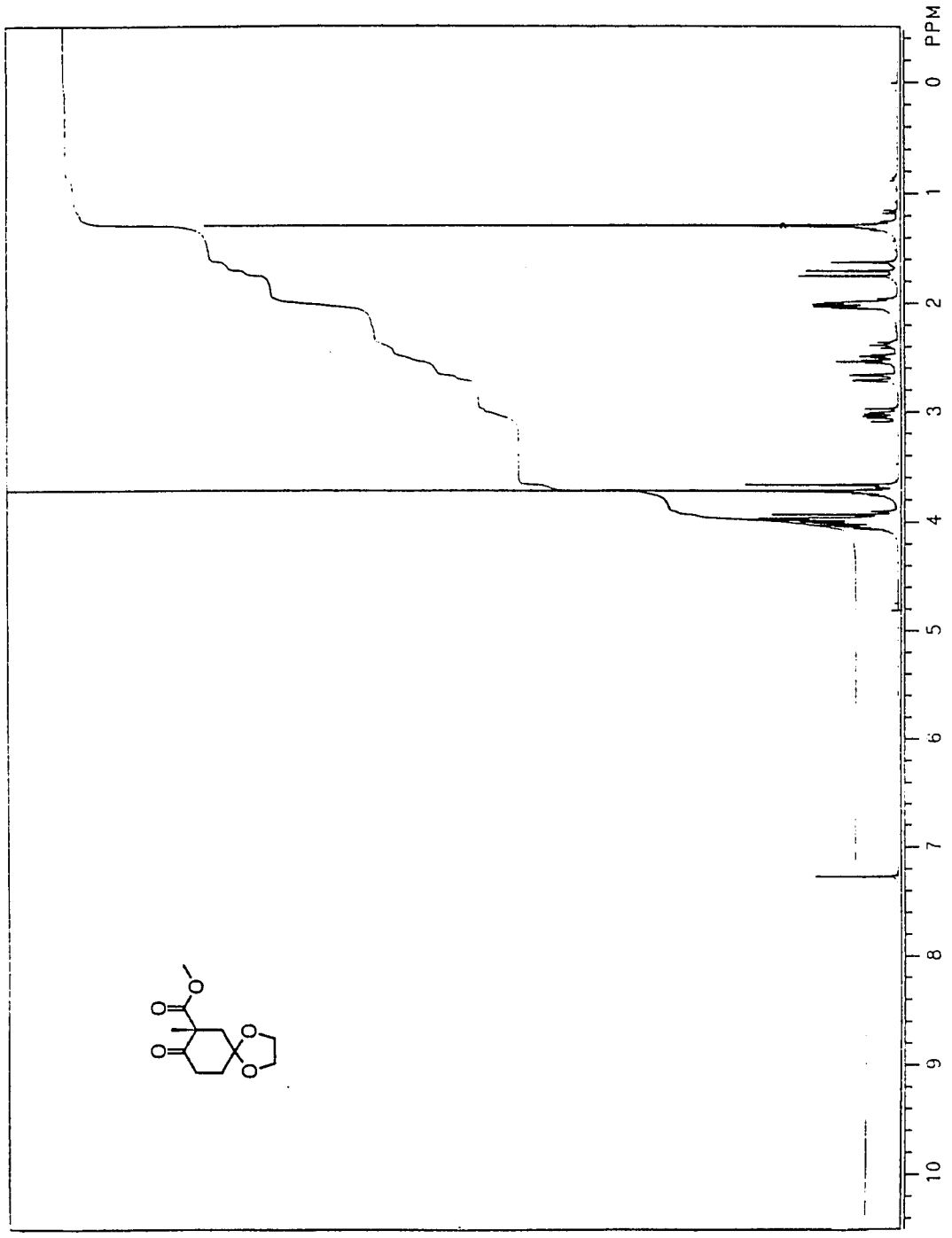

PPM
0
1
2
3
4
5
6
7
8
9
10

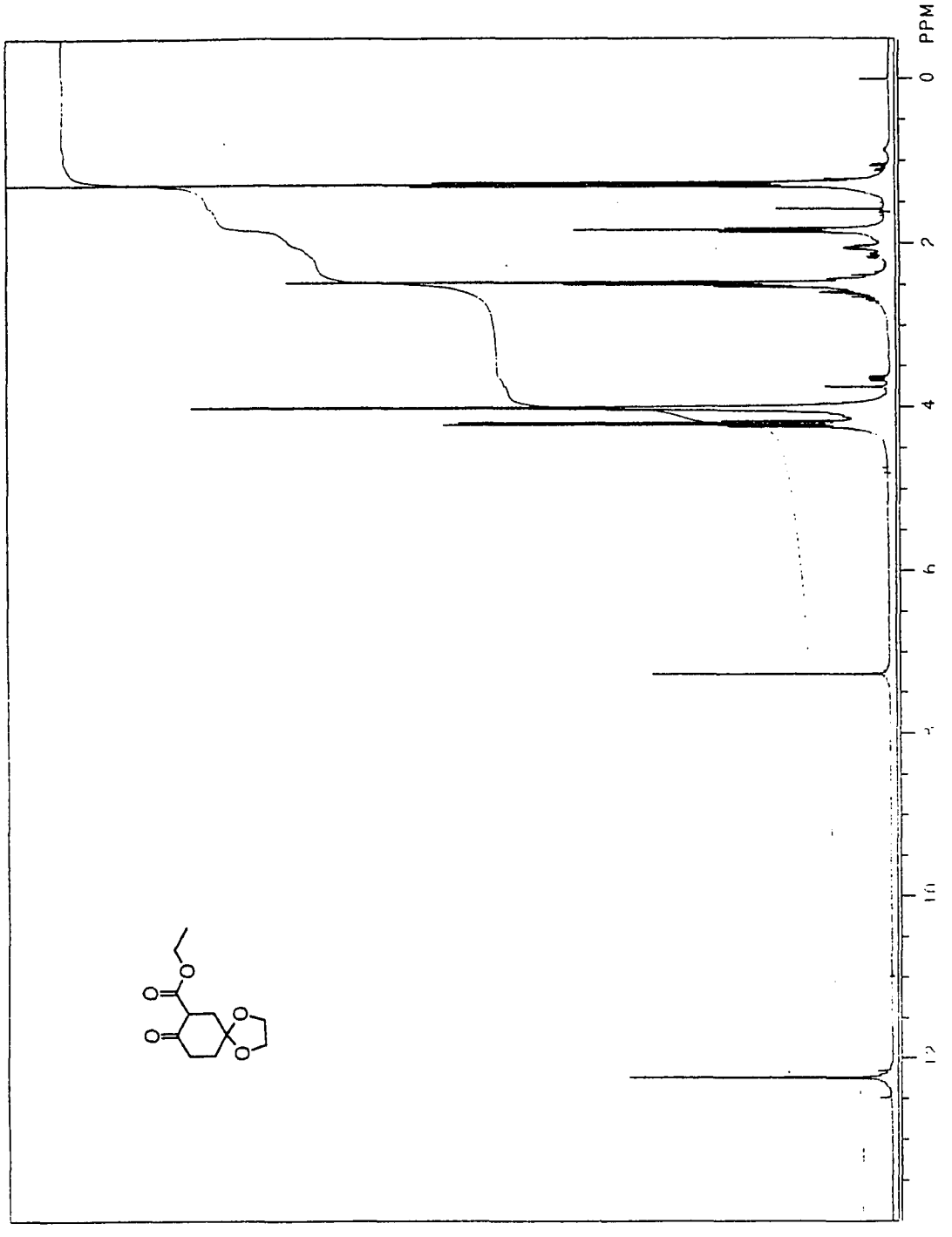

TRANSMISSION (%)
100
80
60
40
20
0
4000
3000 (CM⁻¹)
2500
2000
1800
1600
1400
1200
1000 (CM⁻¹)
800
600
ORDINATE
ABS
SCAN TIME 12 minutes
MULTIPLIER
SLIT PROGRAM
REP. SCAN
TIME DRIVE
OPERATOR
SINGLE BEAM
SOLVENT Neat
CONCENTRATION
CELL PATH
REFERENCE

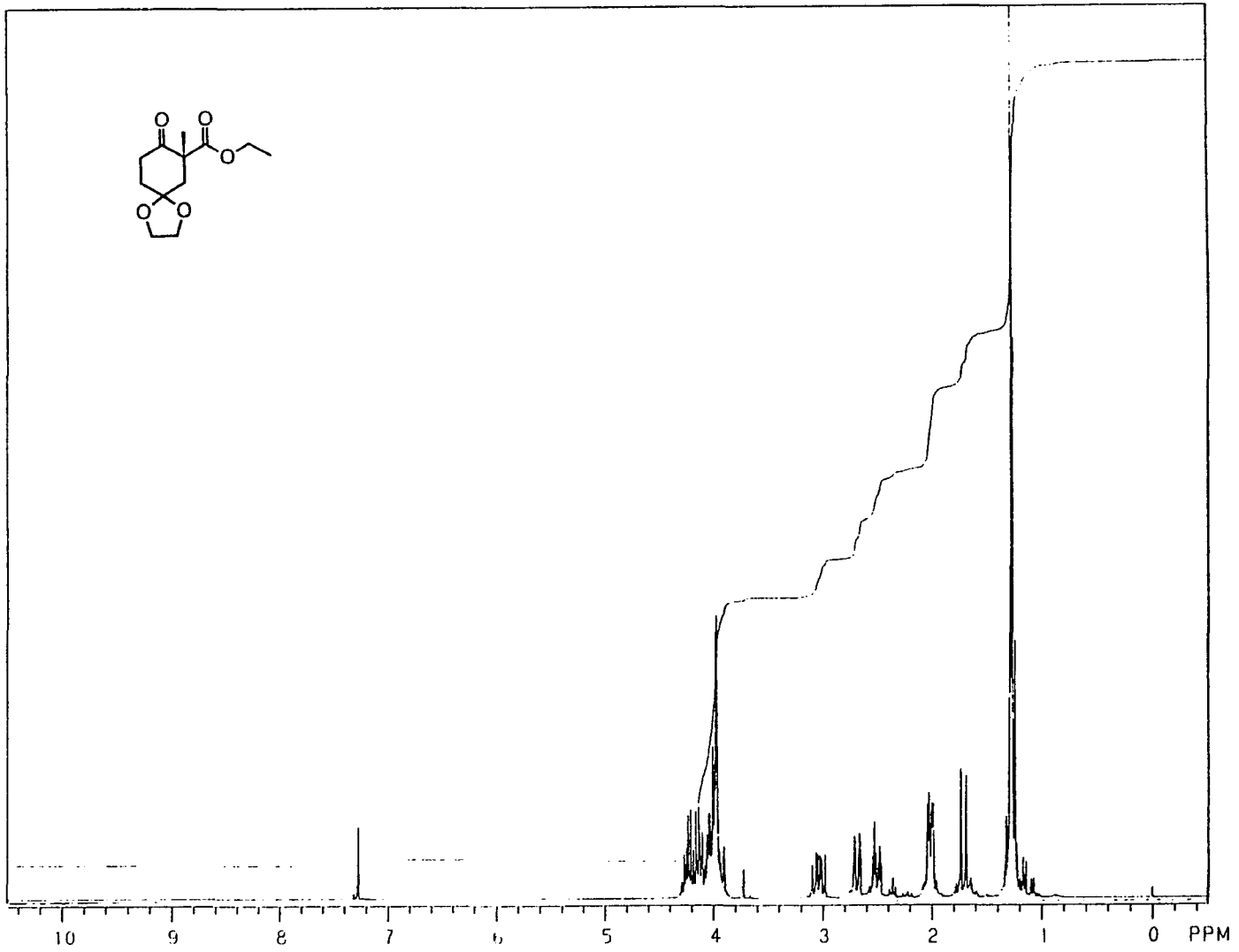

PPM
0
1
2
3
4
5
6
7
8
9
10

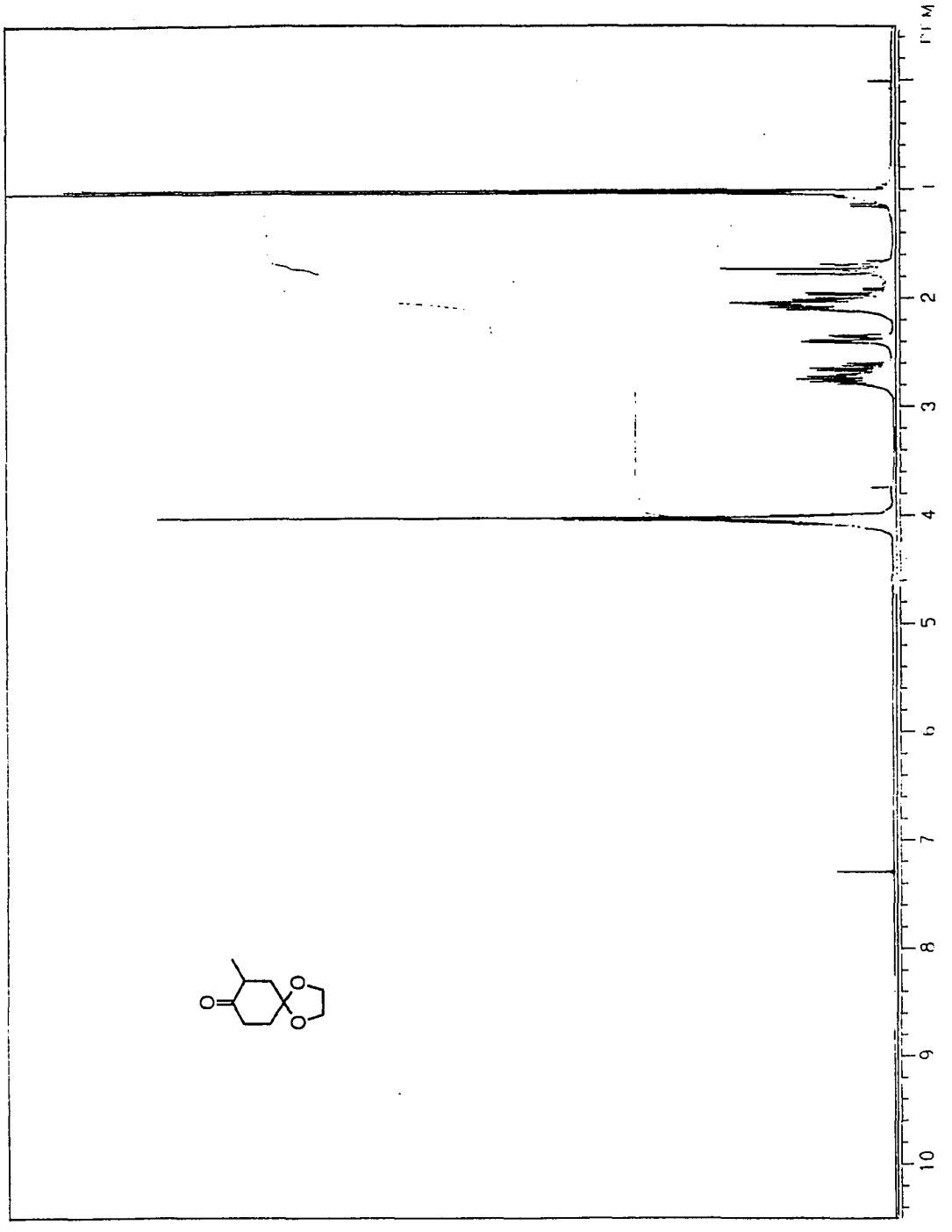

GRAPHIC CONTROLS CORP.
CHART NO. 199 1042
MICROMETERS
(CM⁻¹)
ABSCISSA
EXPANSION 0.5
SAMPLE
ORDINATE
EXPANSION
%T ABS
REMARKS
SCAN TIME 12 minutes
MULTIPLIER
SLIT PROGRAM
SOLVENT Neat
REP. SCAN
TIME DRIVE
OPERATOR
SINGLE BEAM
DATE
CELL PATH

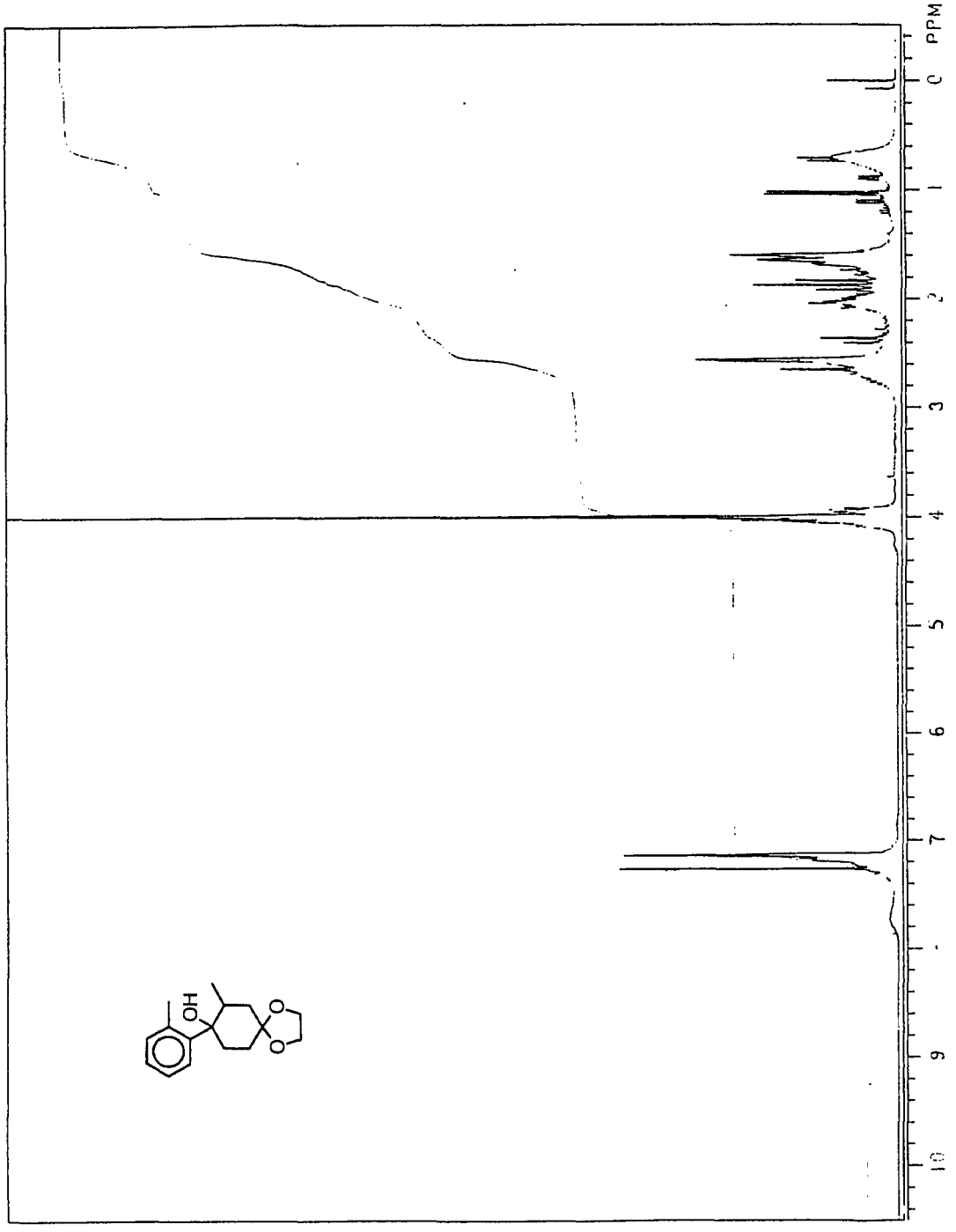

0 PPM
1
2
3
4
5
6
7
8
9
10
12

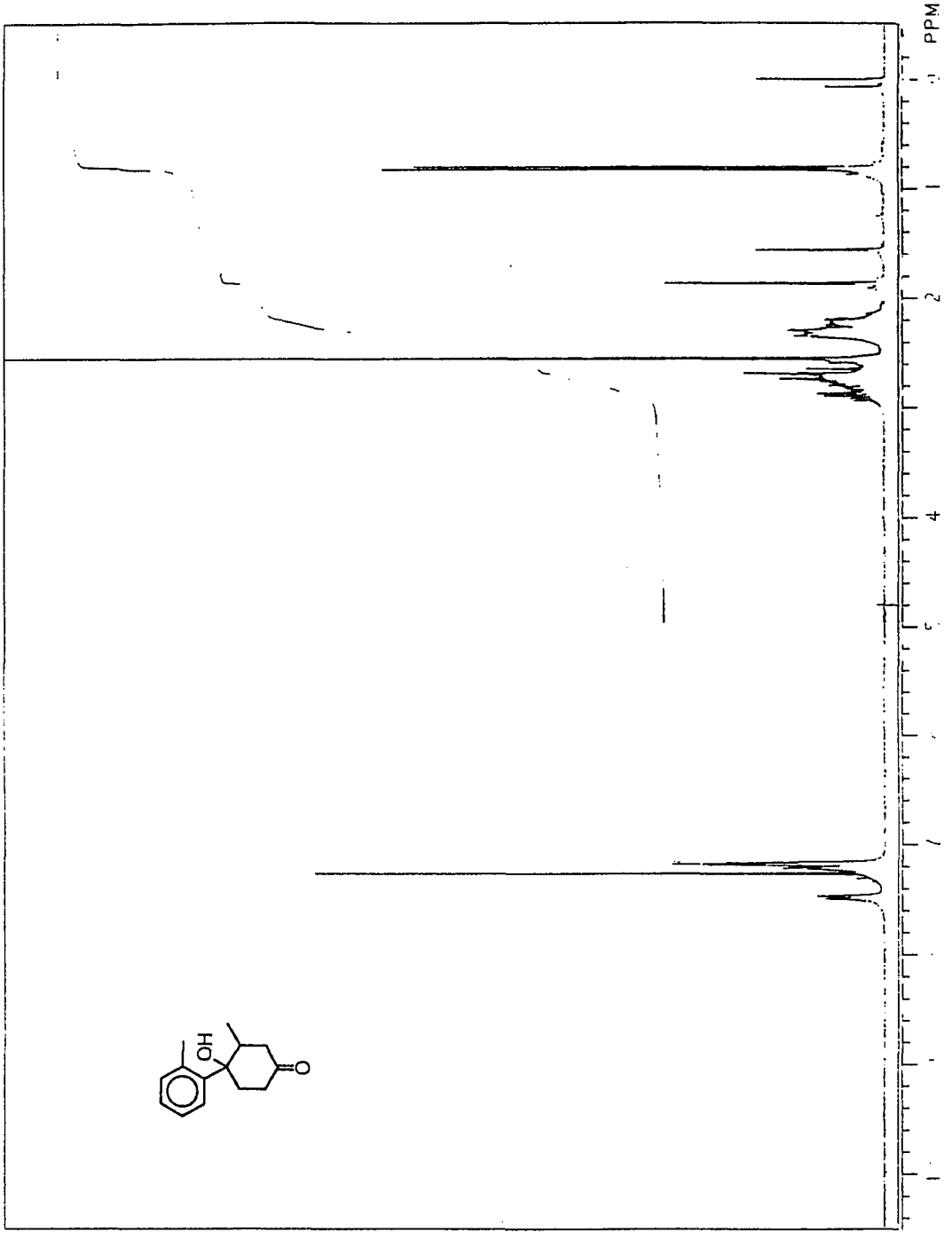

PPM
0
1
2
3
4
5
6
7
8
9
10

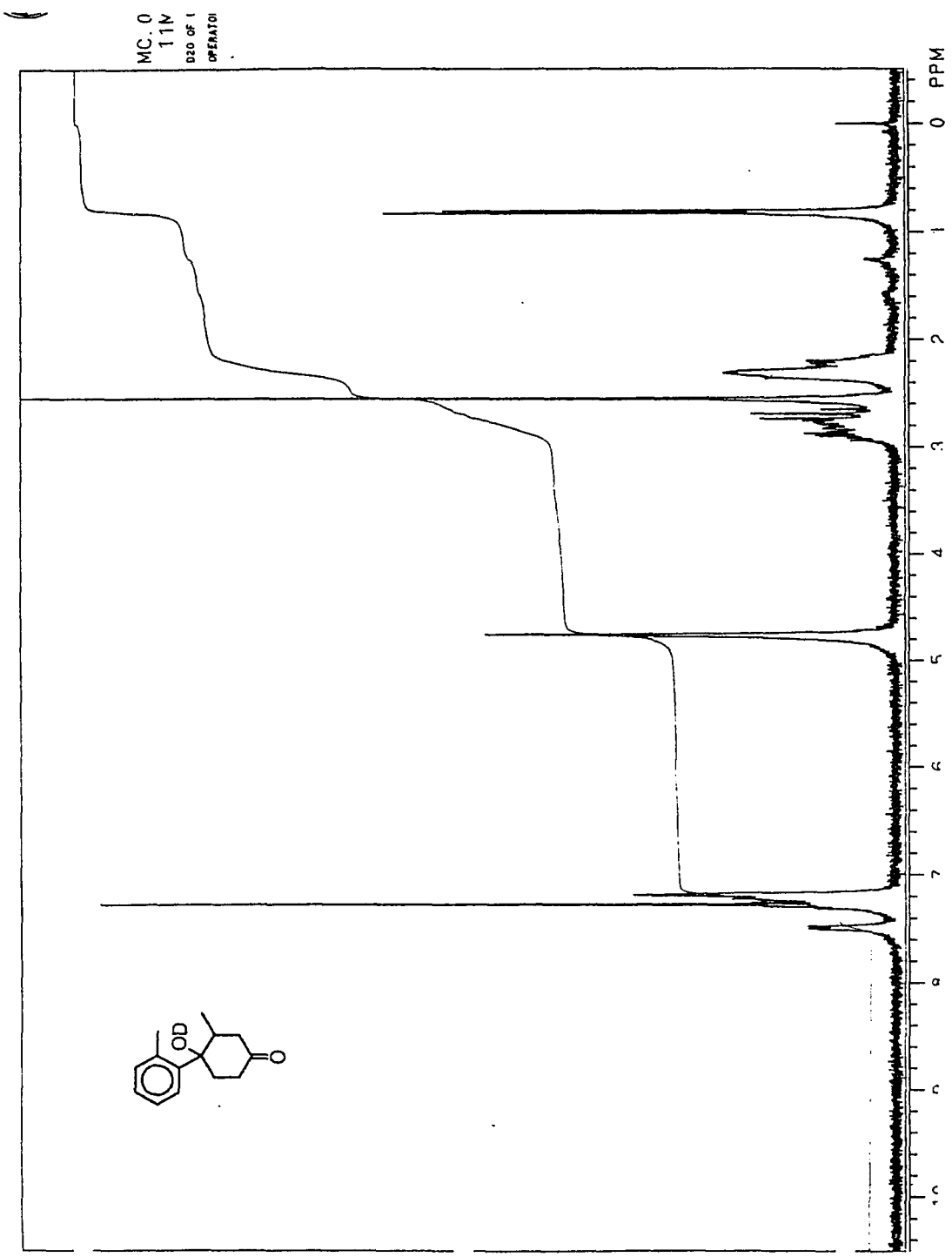

PPM
0
2
4
6
10
12

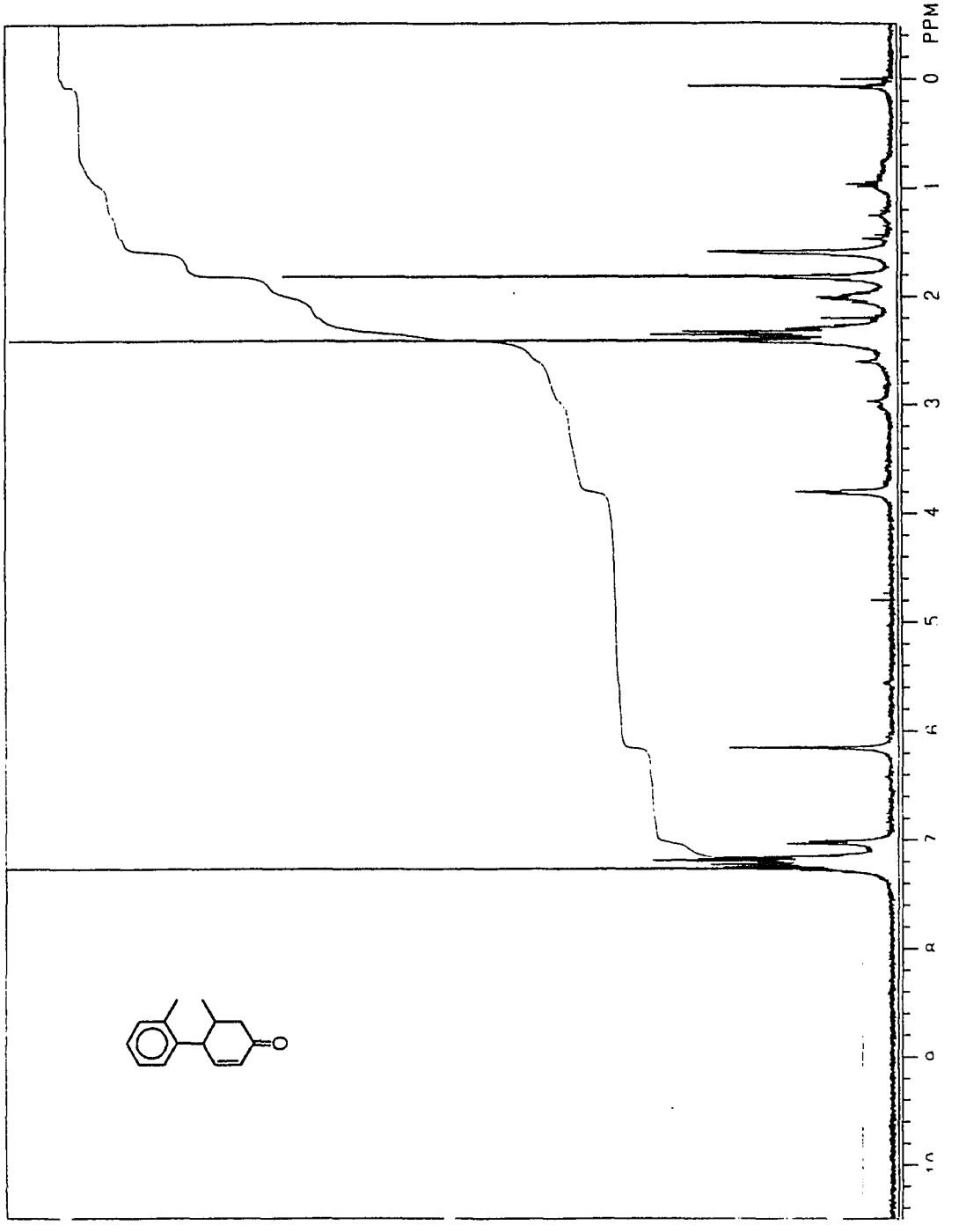

10
9
8
7
6
5
4
3
2
1
0
PPM

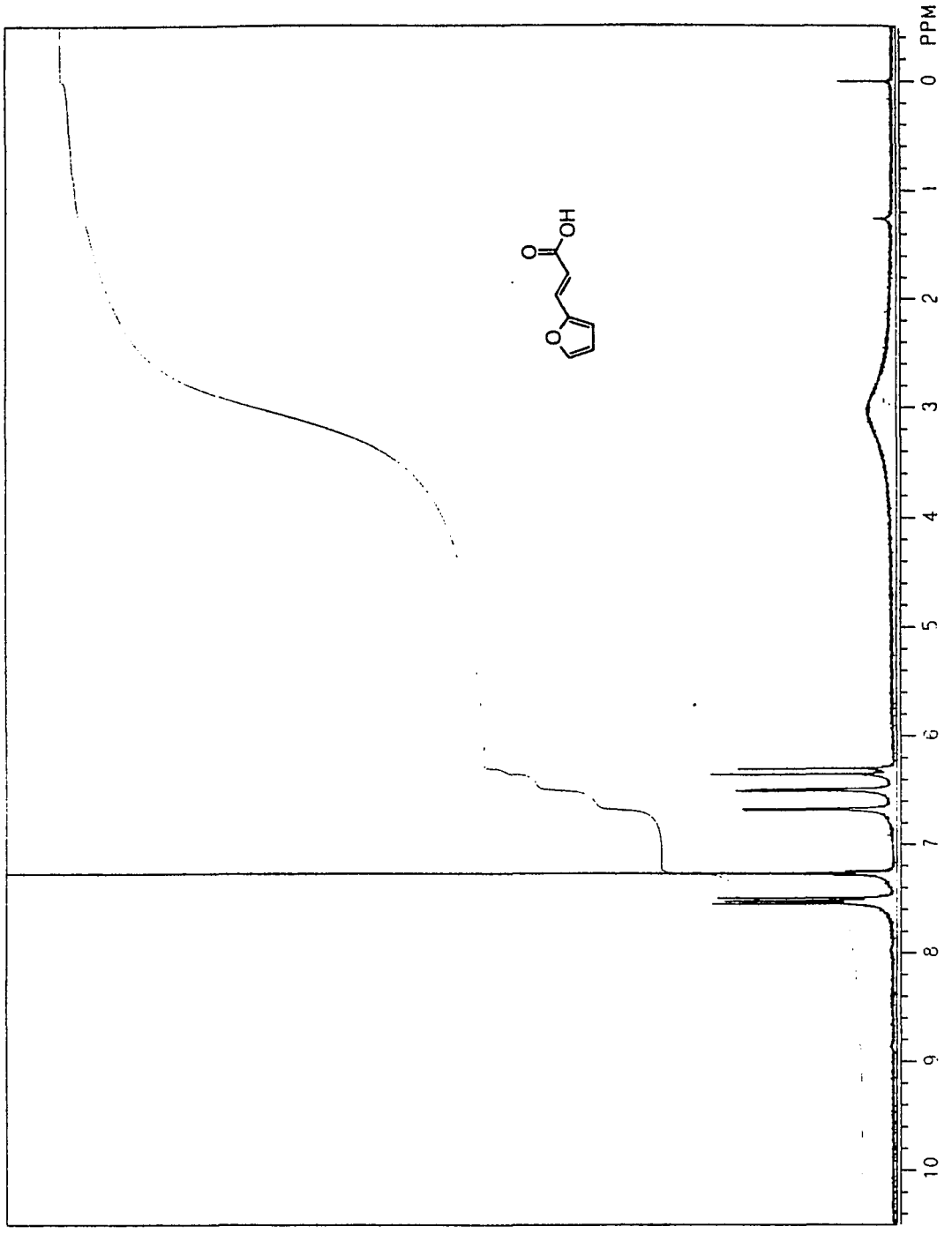

PPM
1
2
3
4
5
6
7
8
9
10
O
O
O

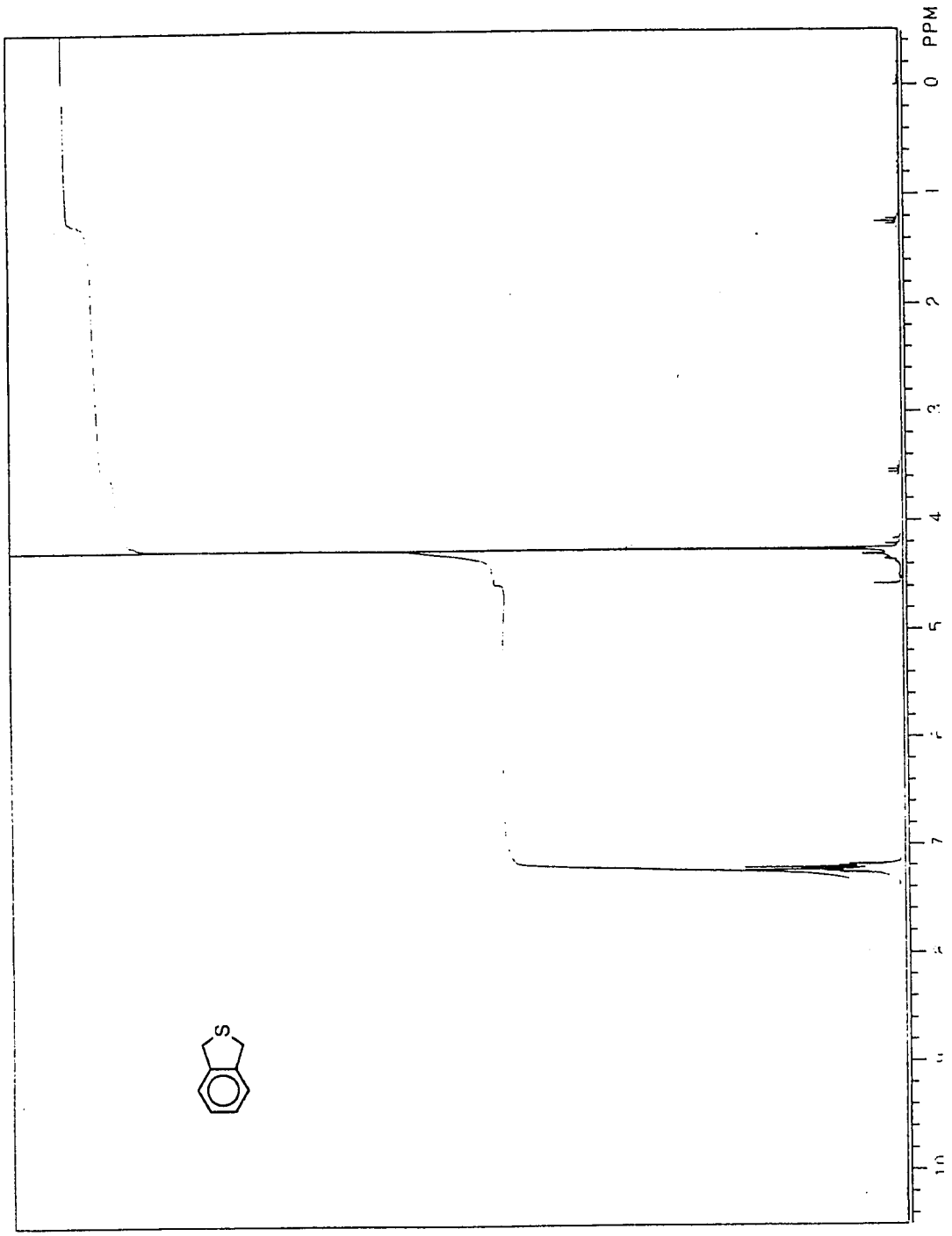

PPM
0
1
2
3
4
5
6
7
8
9
10
OH
O
O

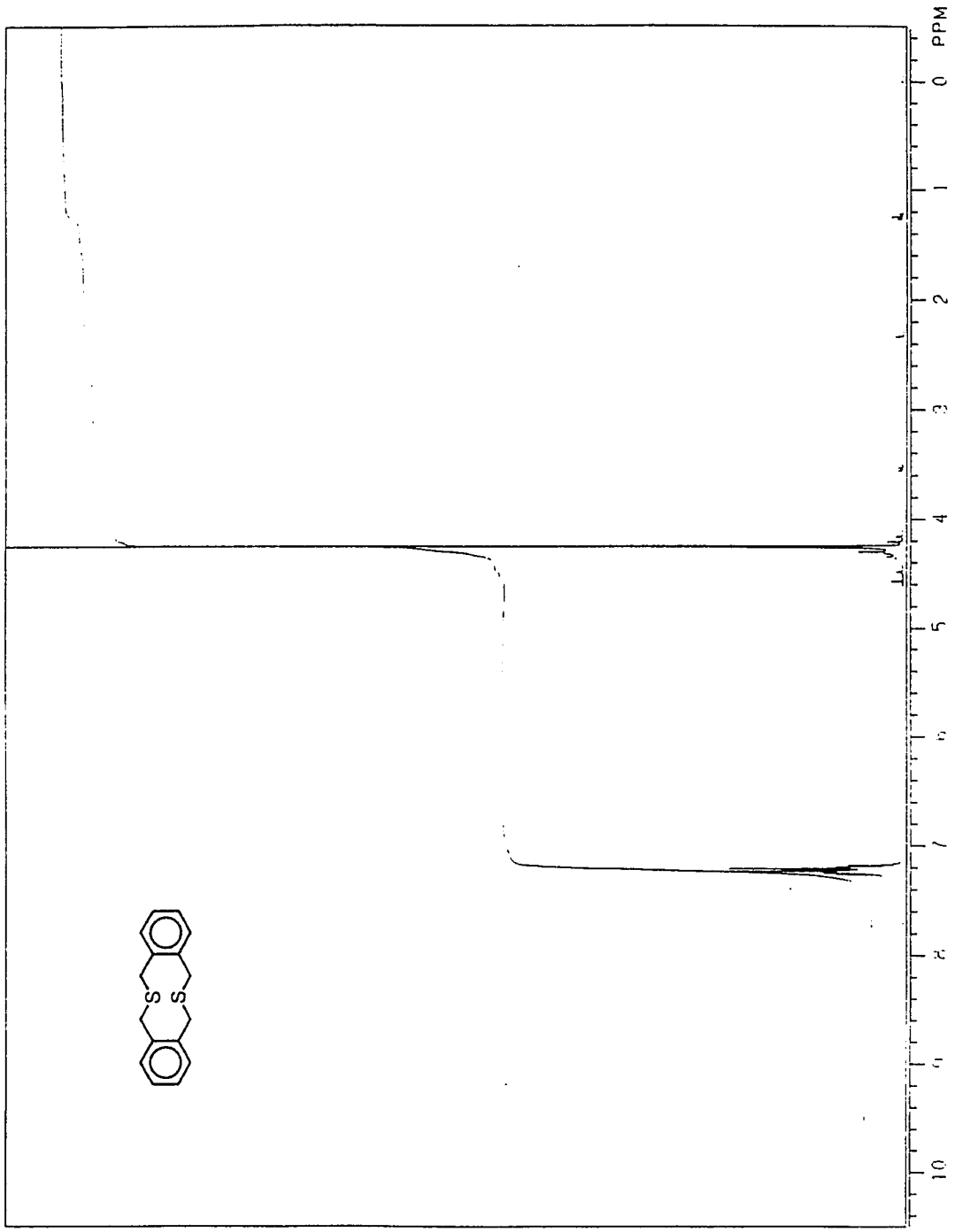

PPM
OH
O

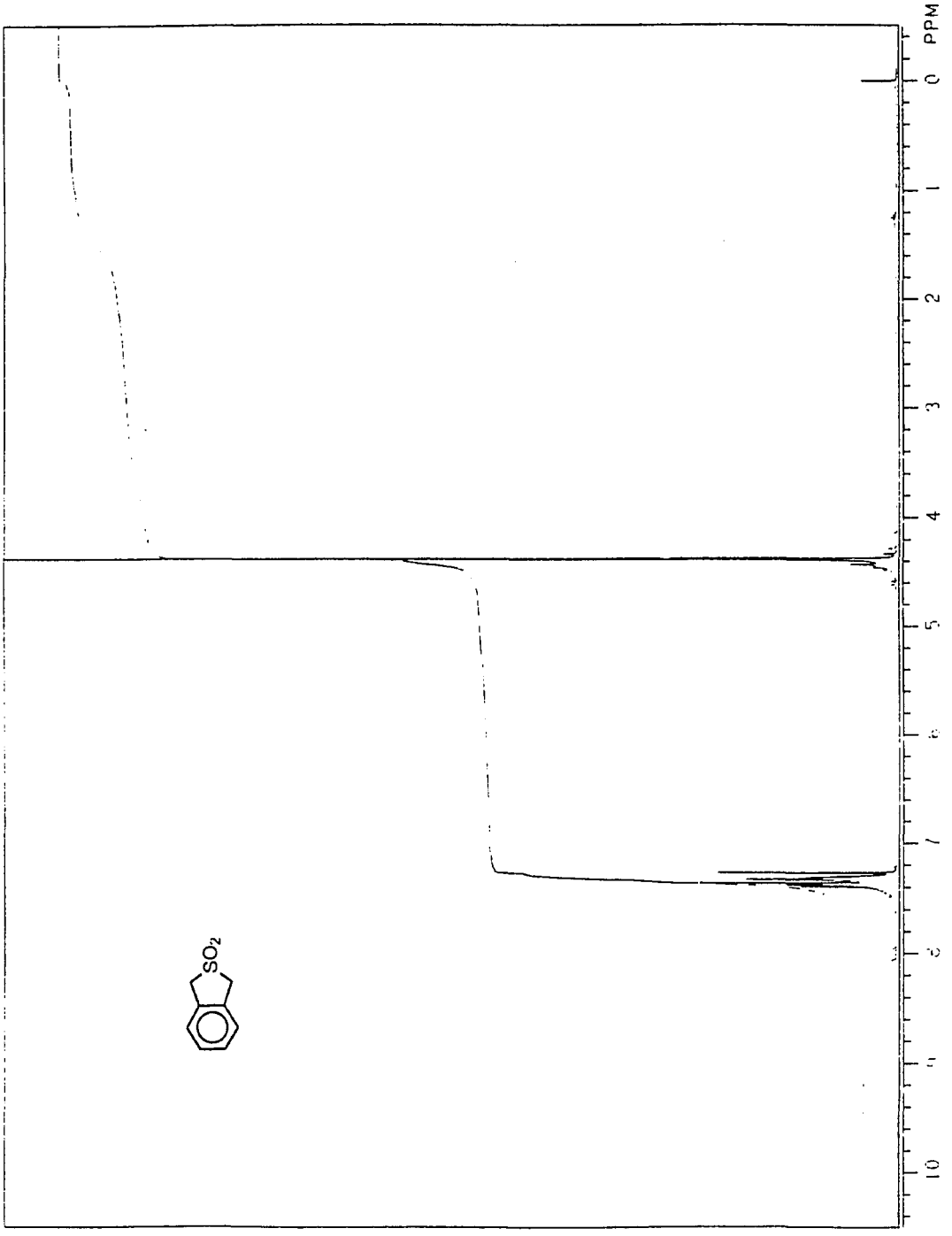

MC_0
11N
D2O OF 1
OPERATOR
PPM
0
1
2
3
4
5
6
7
8
9
10
OD
O

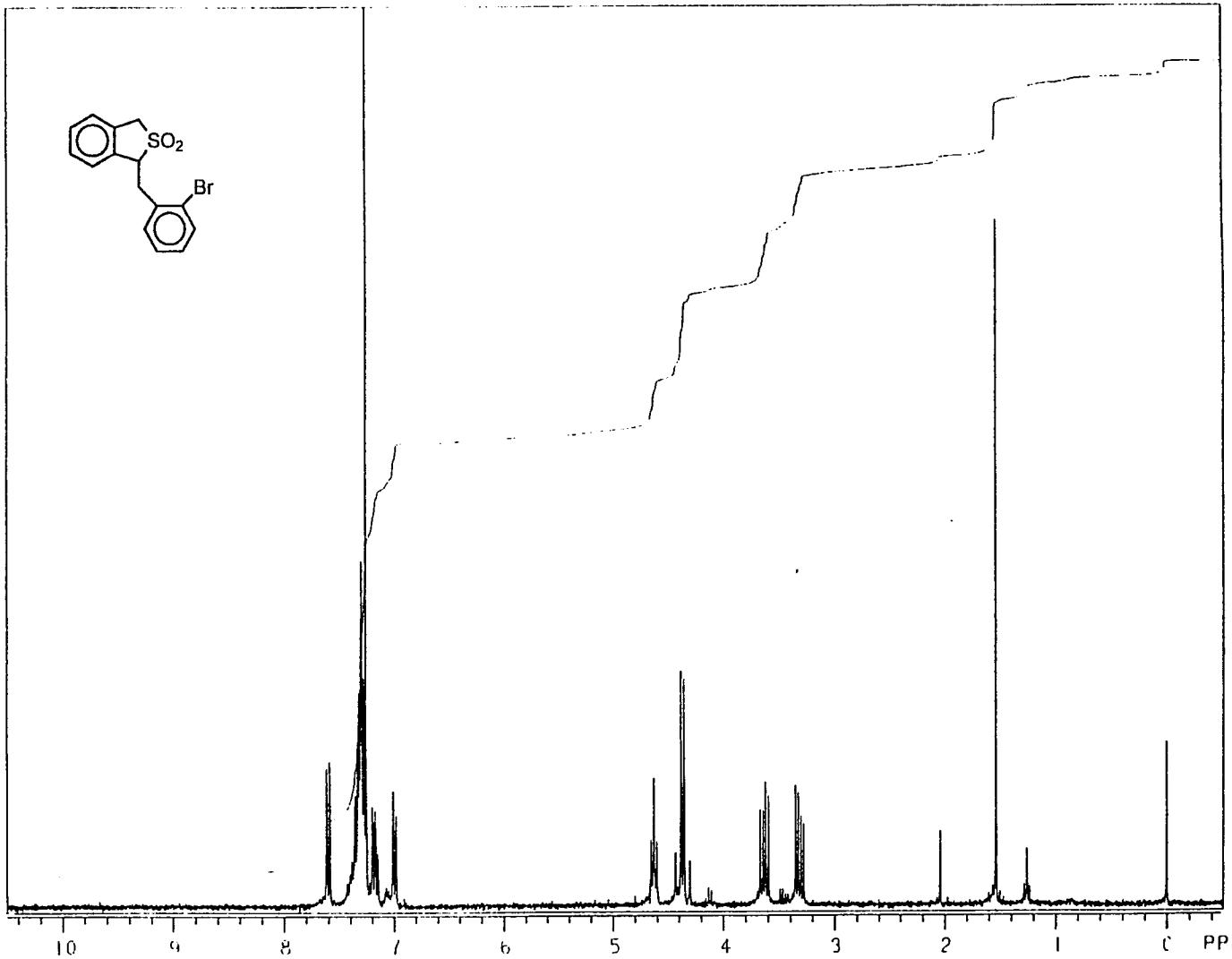

PPM
0
1
2
3
4
5
6
7
8
9
10
O

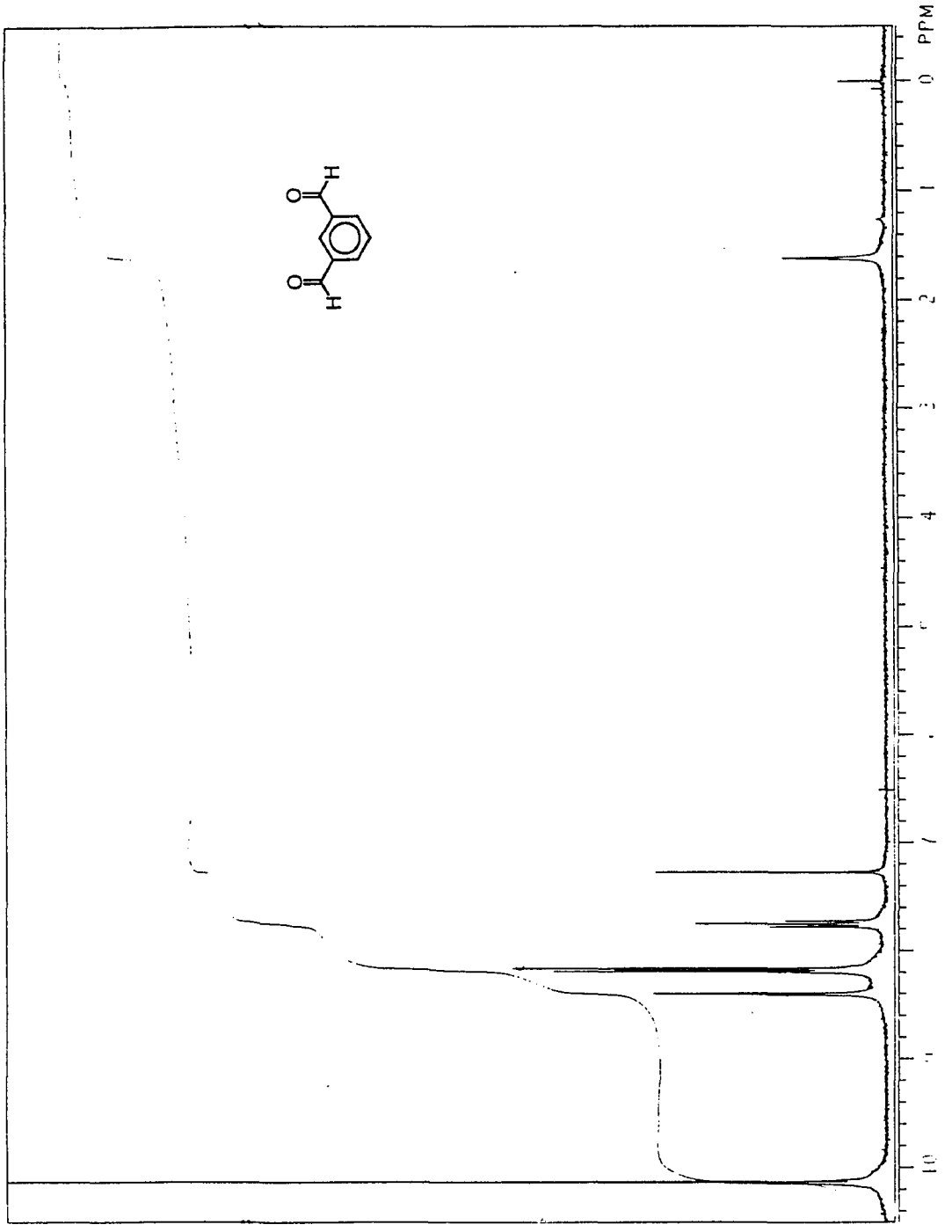

OH
O
O
10
9
8
7
6
5
4
3
2
1
0 PPM

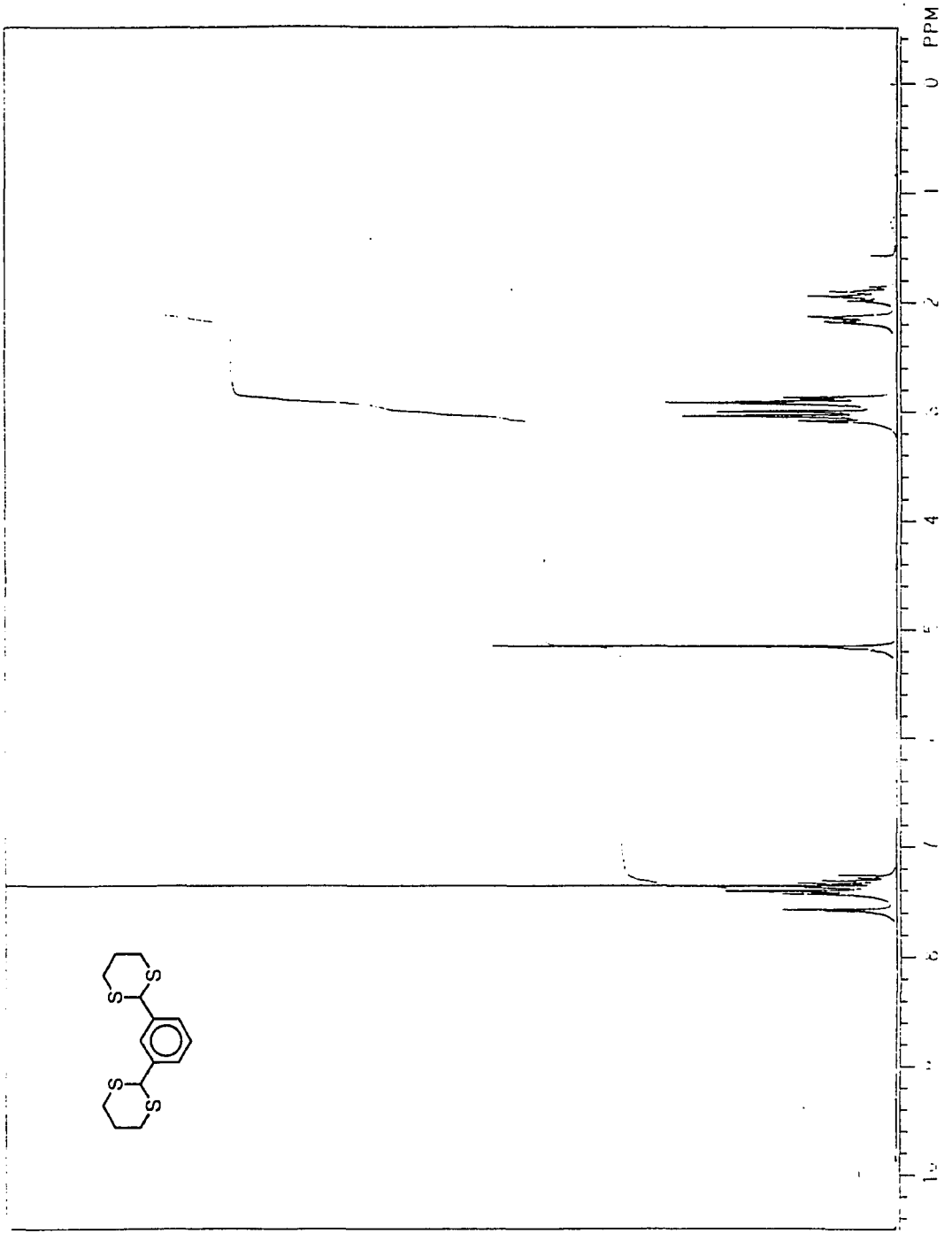

S
0 PPM

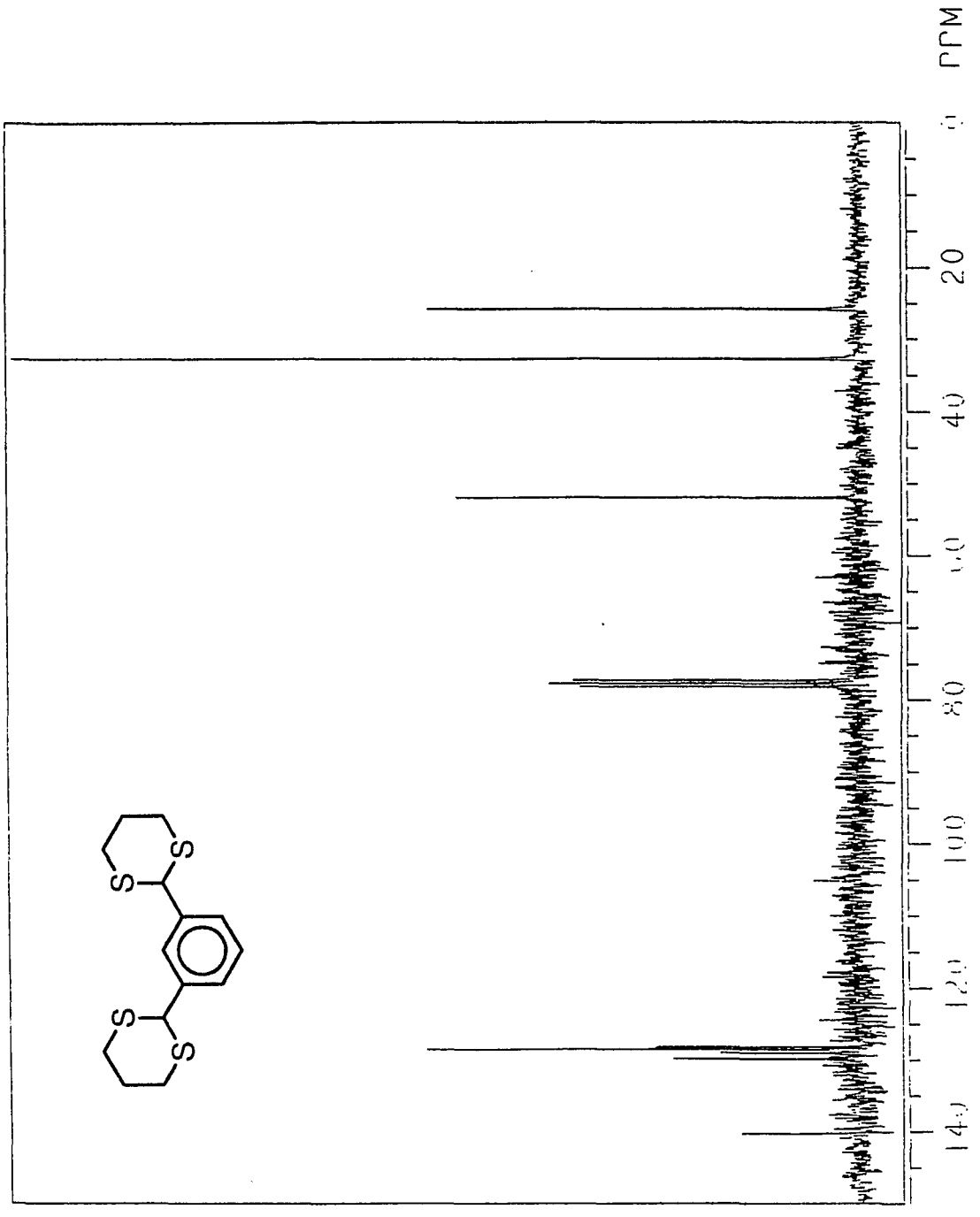

S
S
PPM
0
1
2
3
4
5
6
7
8
9
10

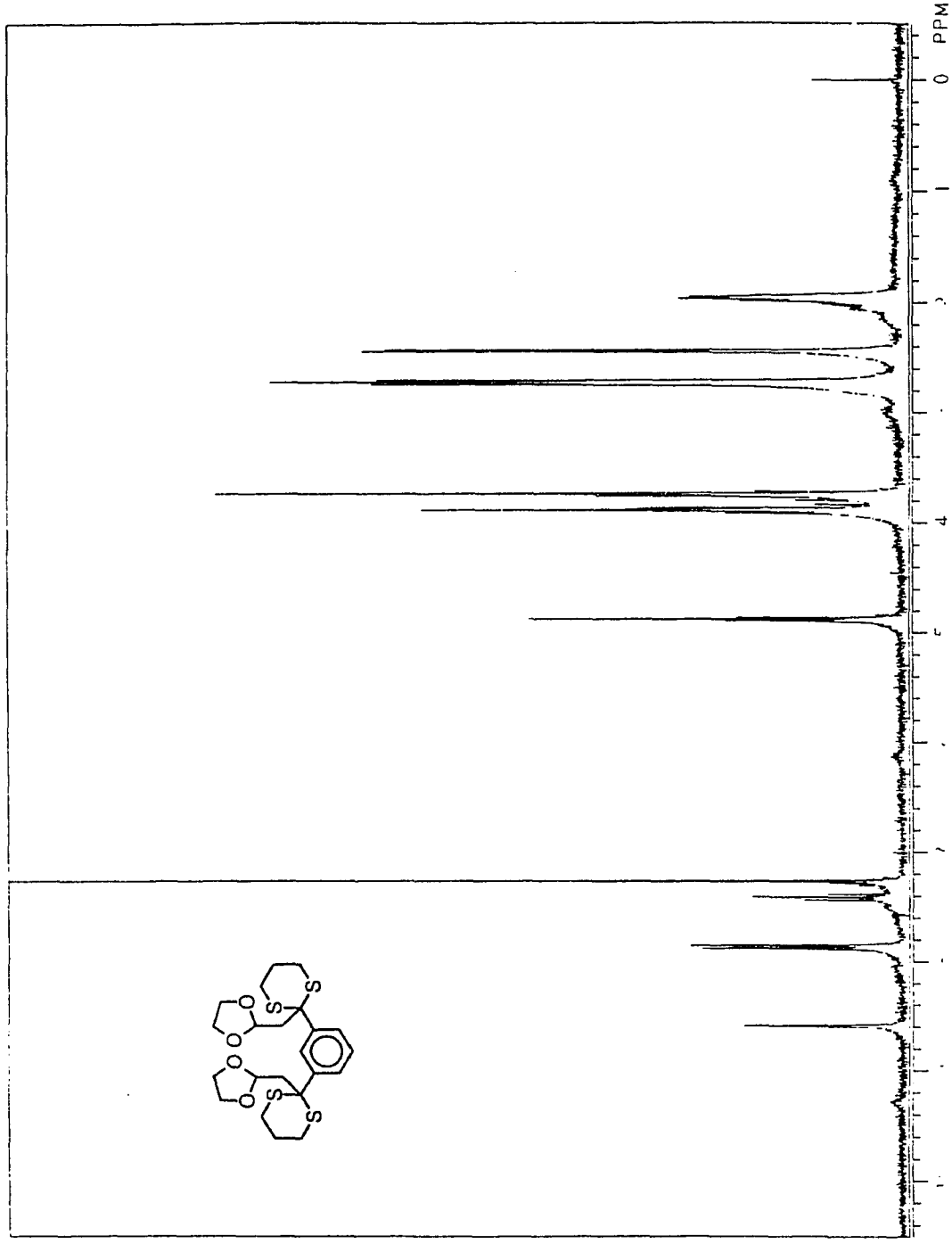

PPM
0
1
2
3
4
5
6
7
8
9
10
SO2

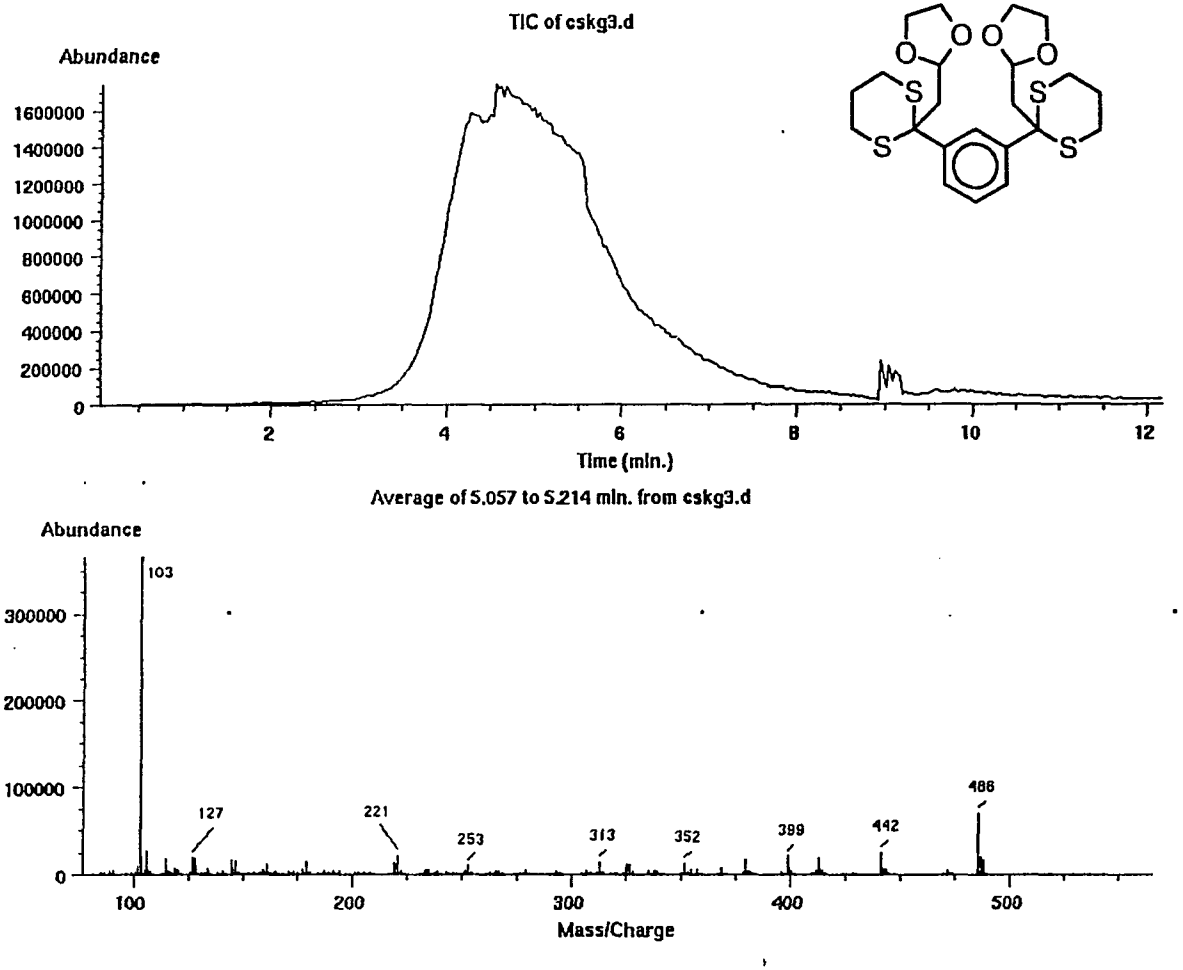

SO2
Br
10
9
8
7
6
5
4
3
2
1
0
PPM

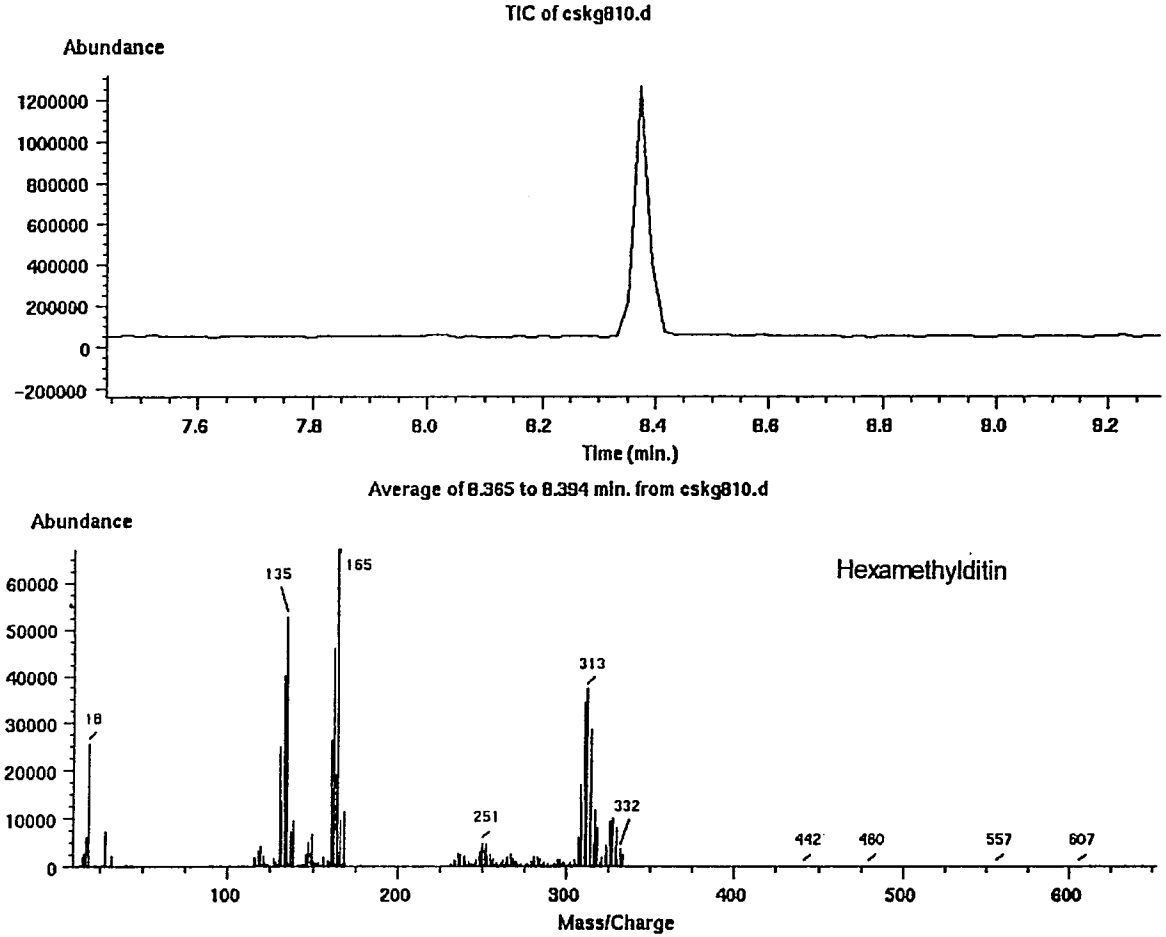

O
H
O
H
PPM
0
1
2
3
4
10

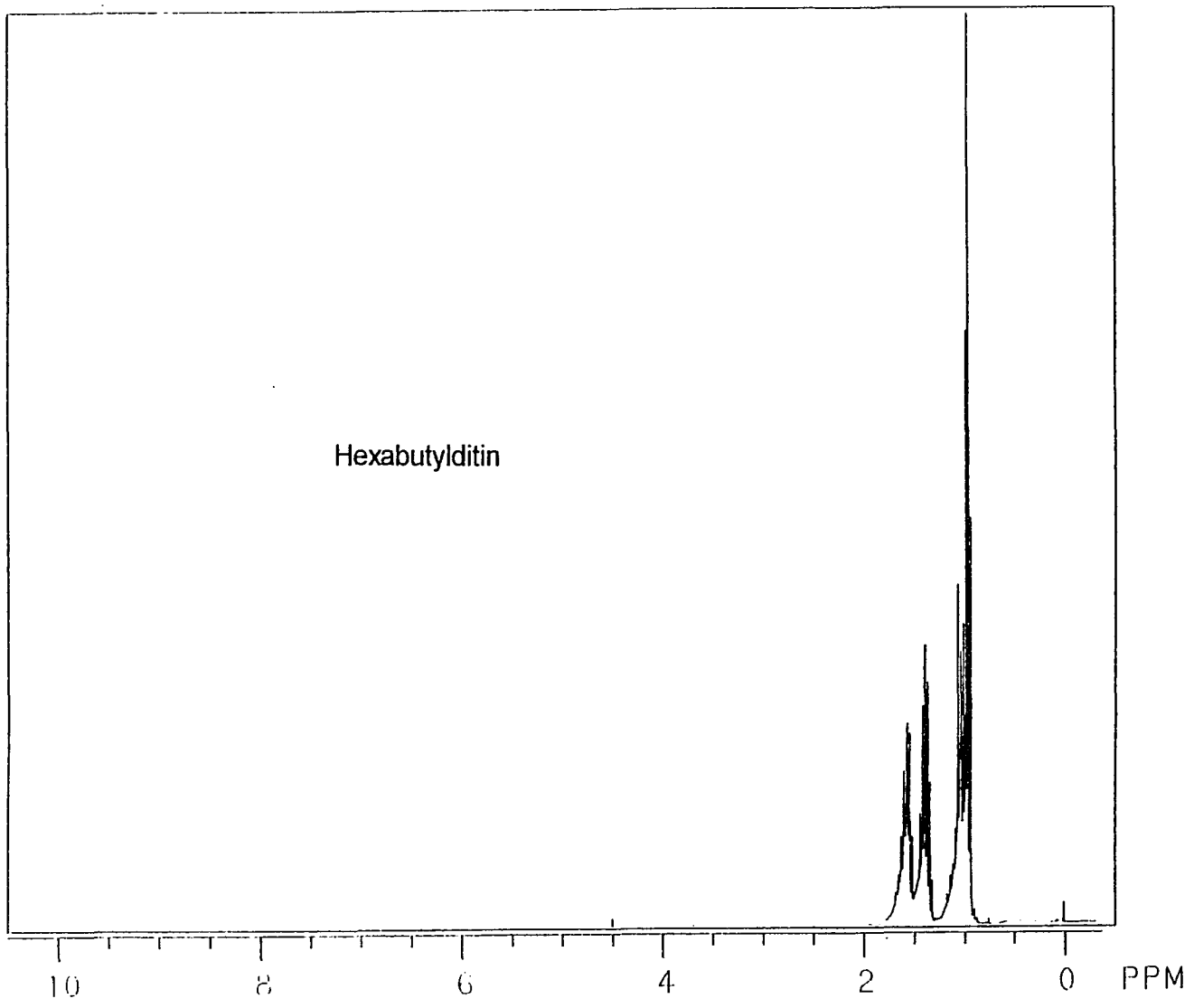

S
S
S
S
0 PPM

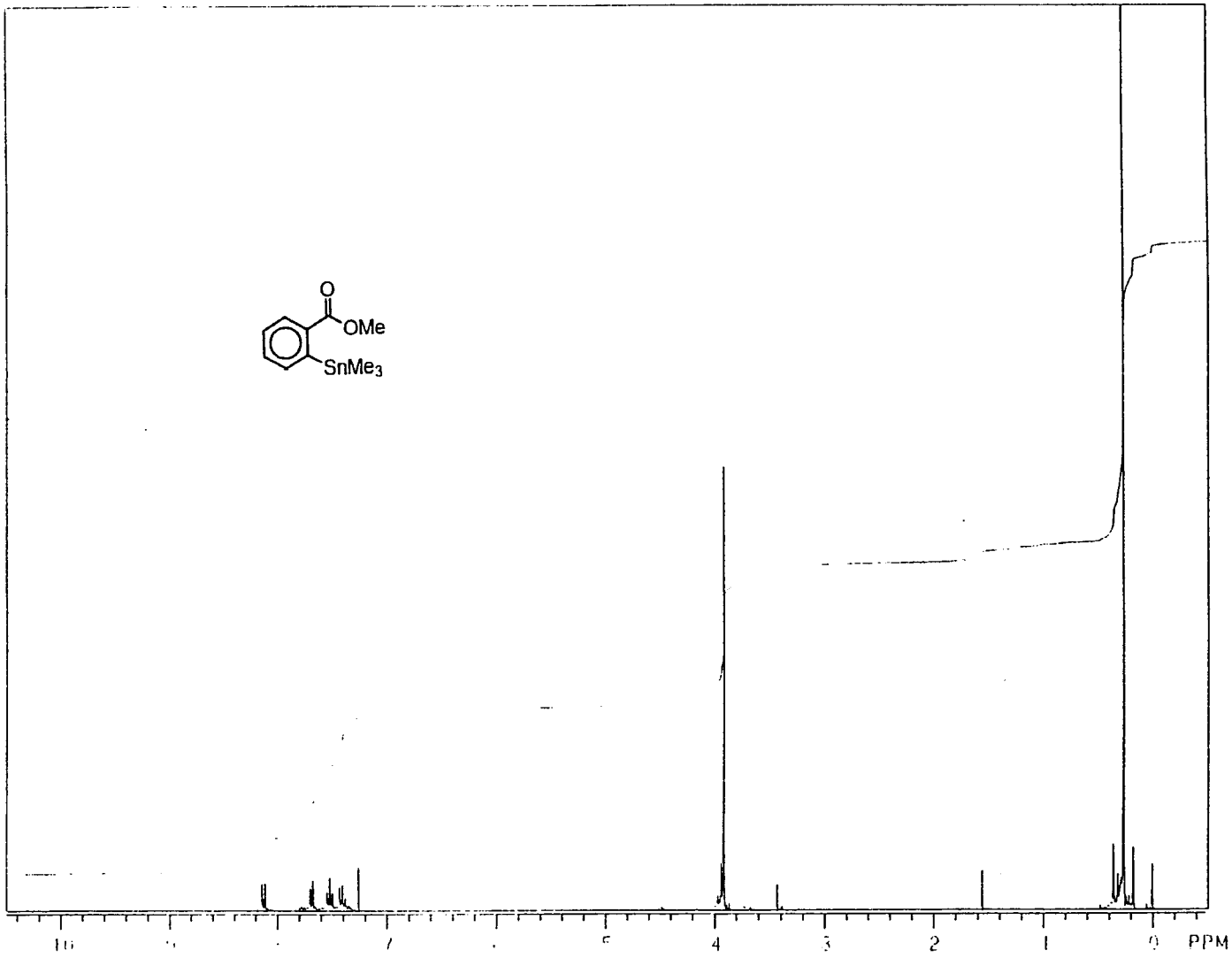

S
S
S
S
PPM
20
40
80
100
120
140

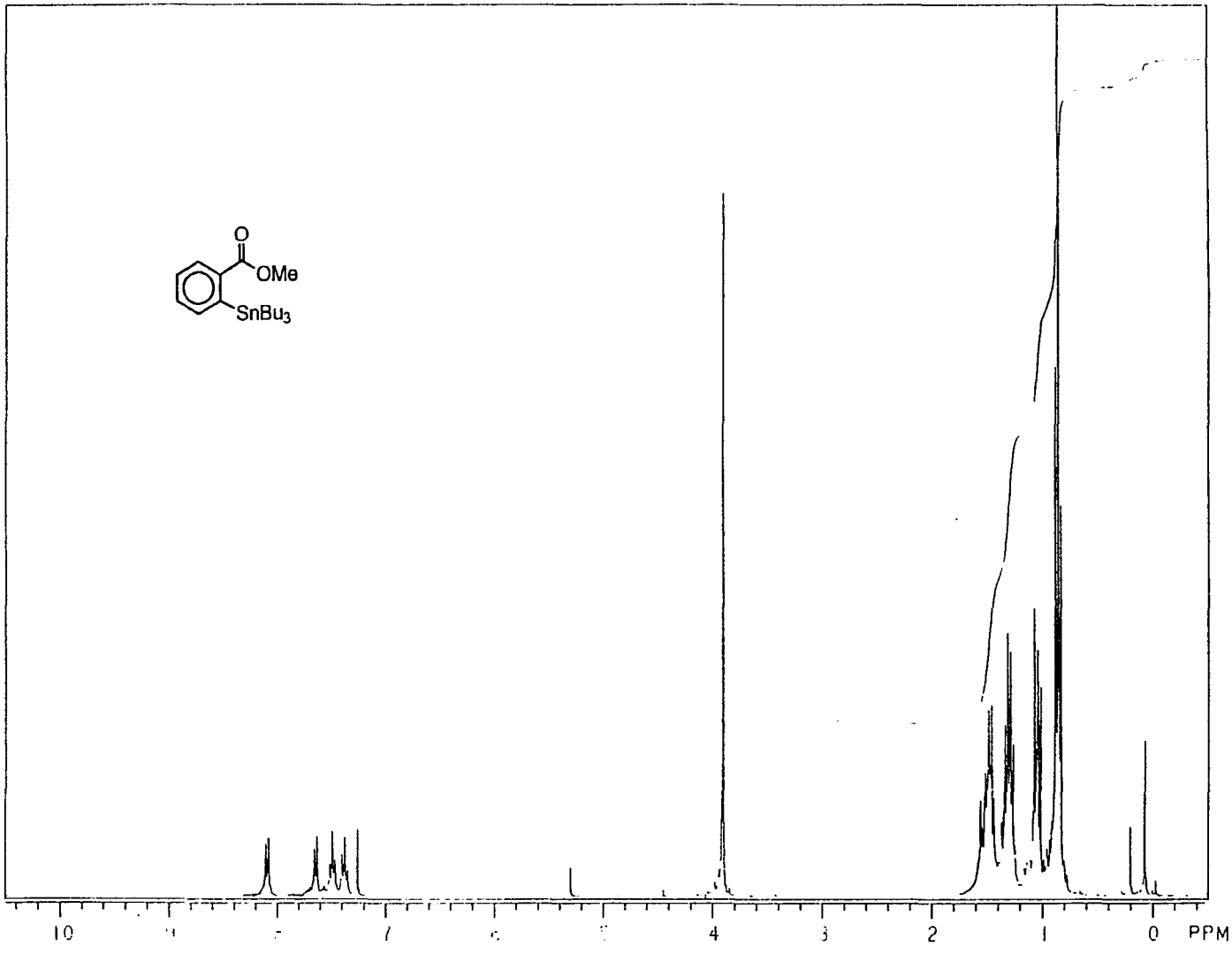

0 PPM

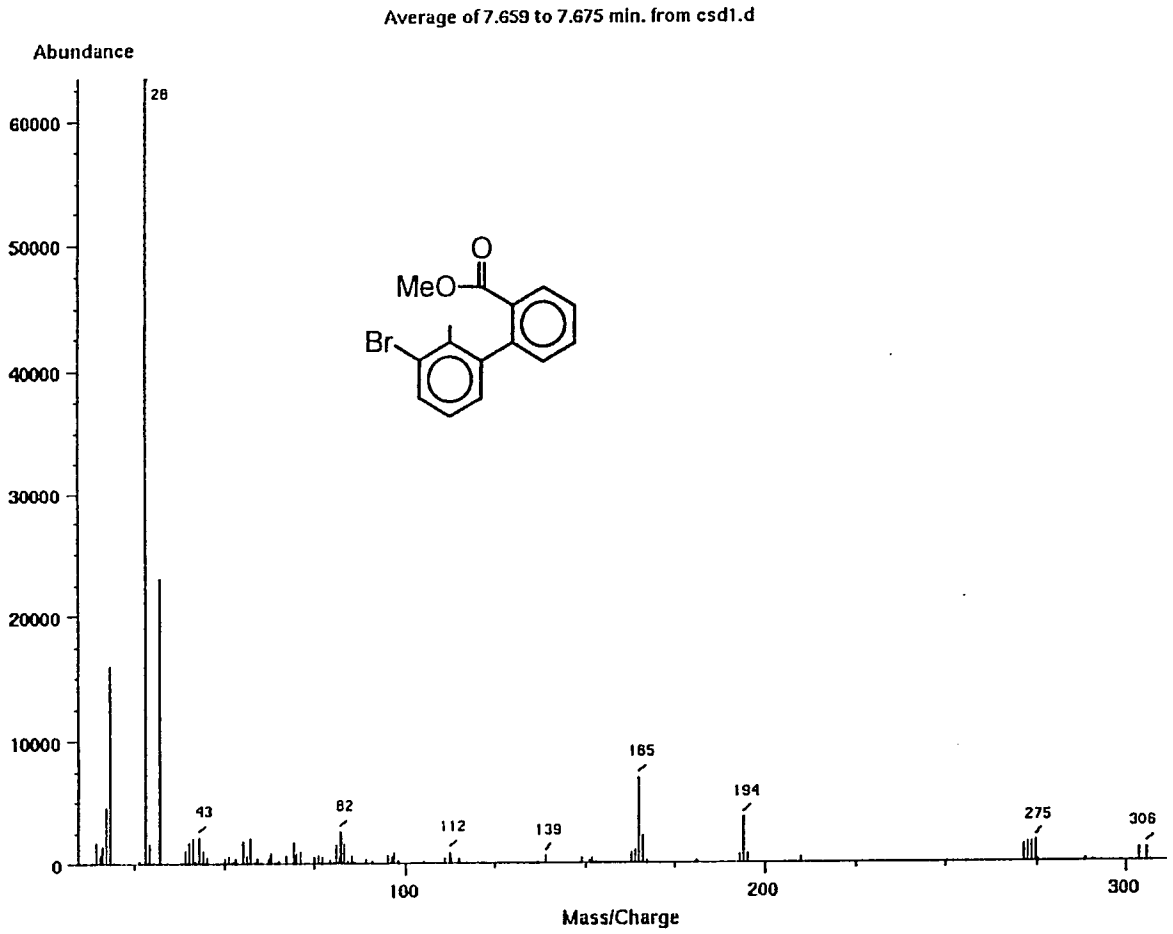

TIC of cskg3.d
Abundance
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
2
4
6
8
10
12
Time (min.)
O
O
O
O
S
S
S
S
Average of 5.057 to 5.214 min. from cskg3.d
Abundance
300000
200000
100000
0
103
127
221
253
313
352
399
442
486
100
200
300
400
500
Mass/Charge

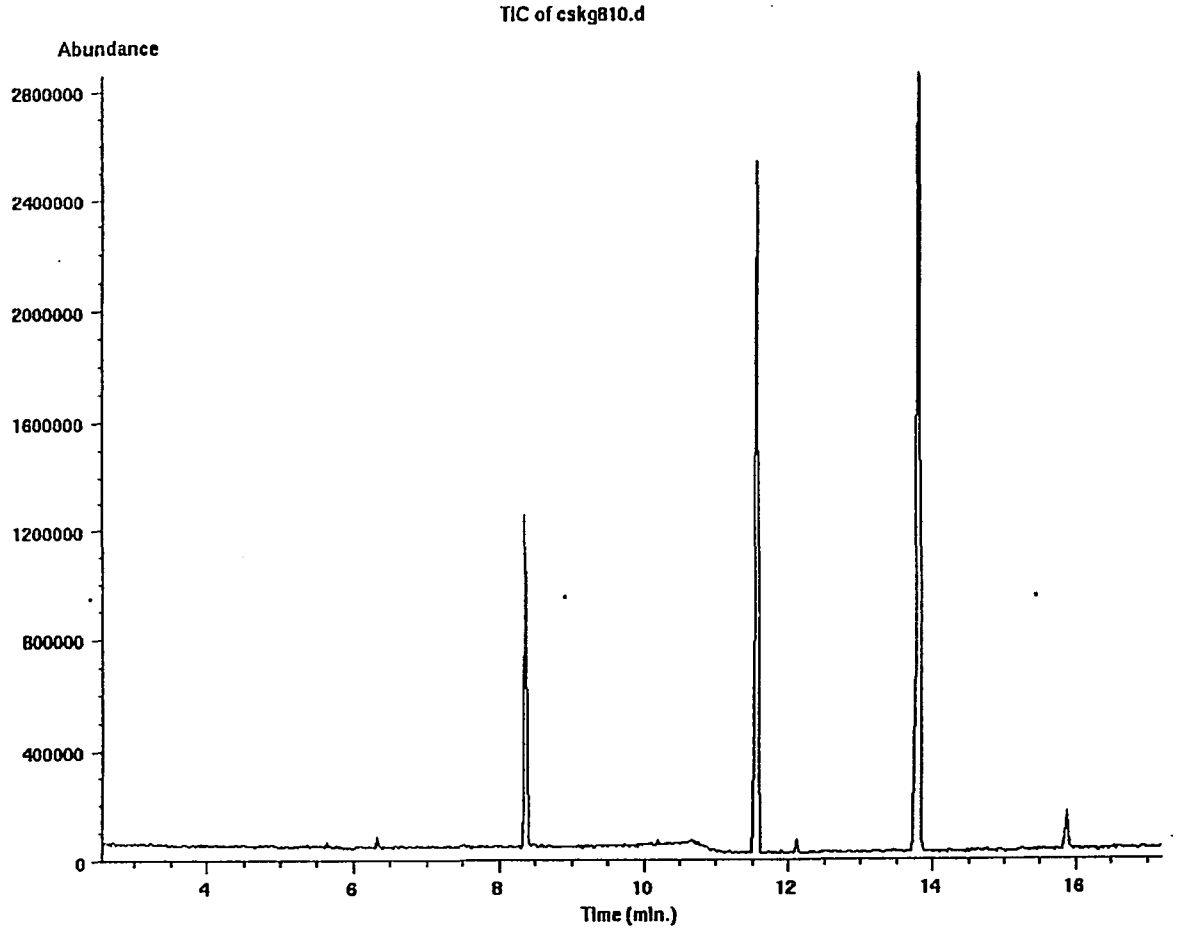

TIC of cskg810.d
Abundance
1200000
1000000
800000
600000
400000
200000
0
-200000
7.6
7.8
8.0
8.2
8.4
8.6
8.8
9.0
9.2
Time (min.)
Average of 8.365 to 8.394 min. from cskg810.d
Abundance
Hexamethylditin
60000
50000
40000
30000
20000
10000
0
18
135
165
251
313
332
442
480
557
607
100
200
300
400
500
600
Mass/Charge

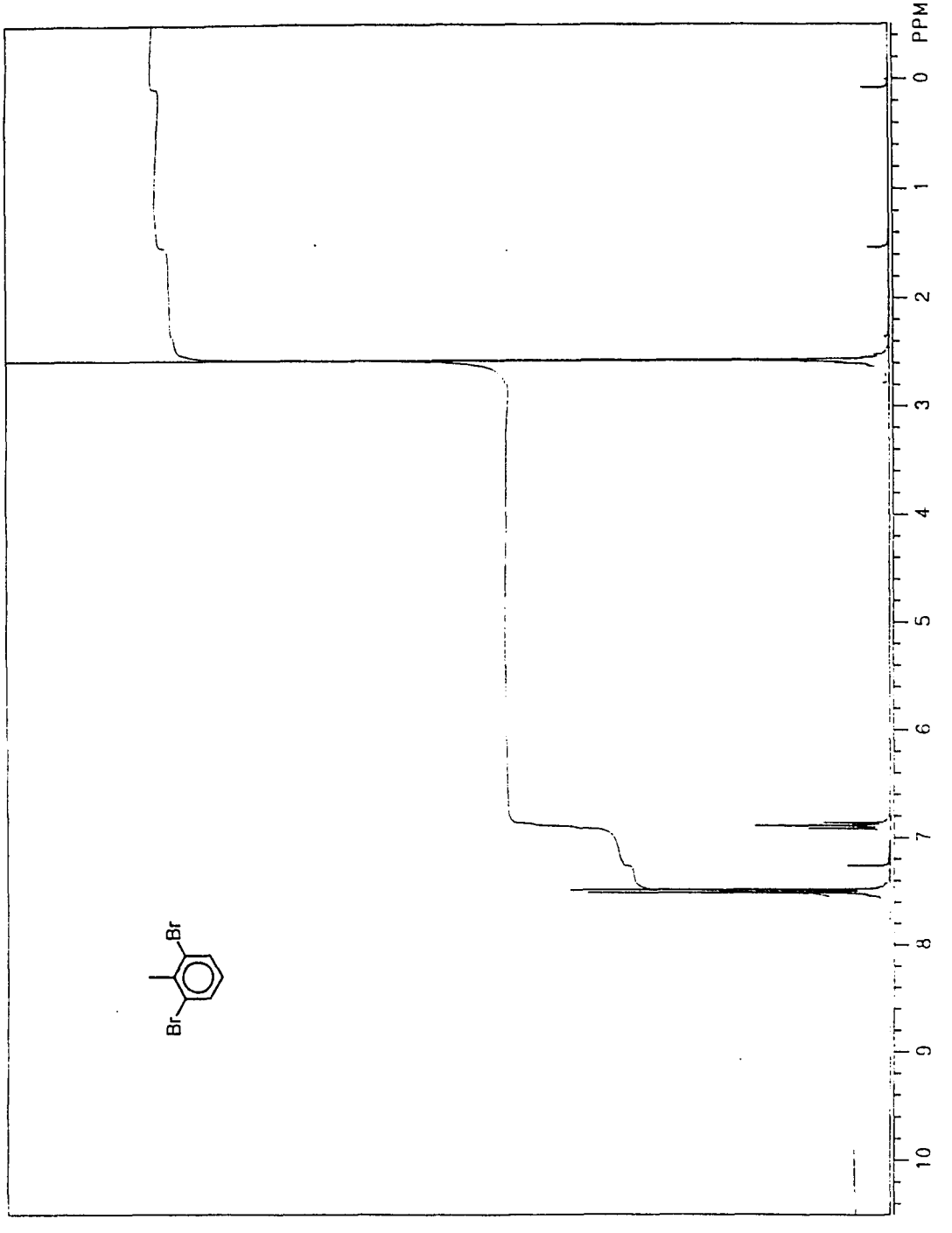

Hexabutylditin
10
8
6
4
2
0
PPM

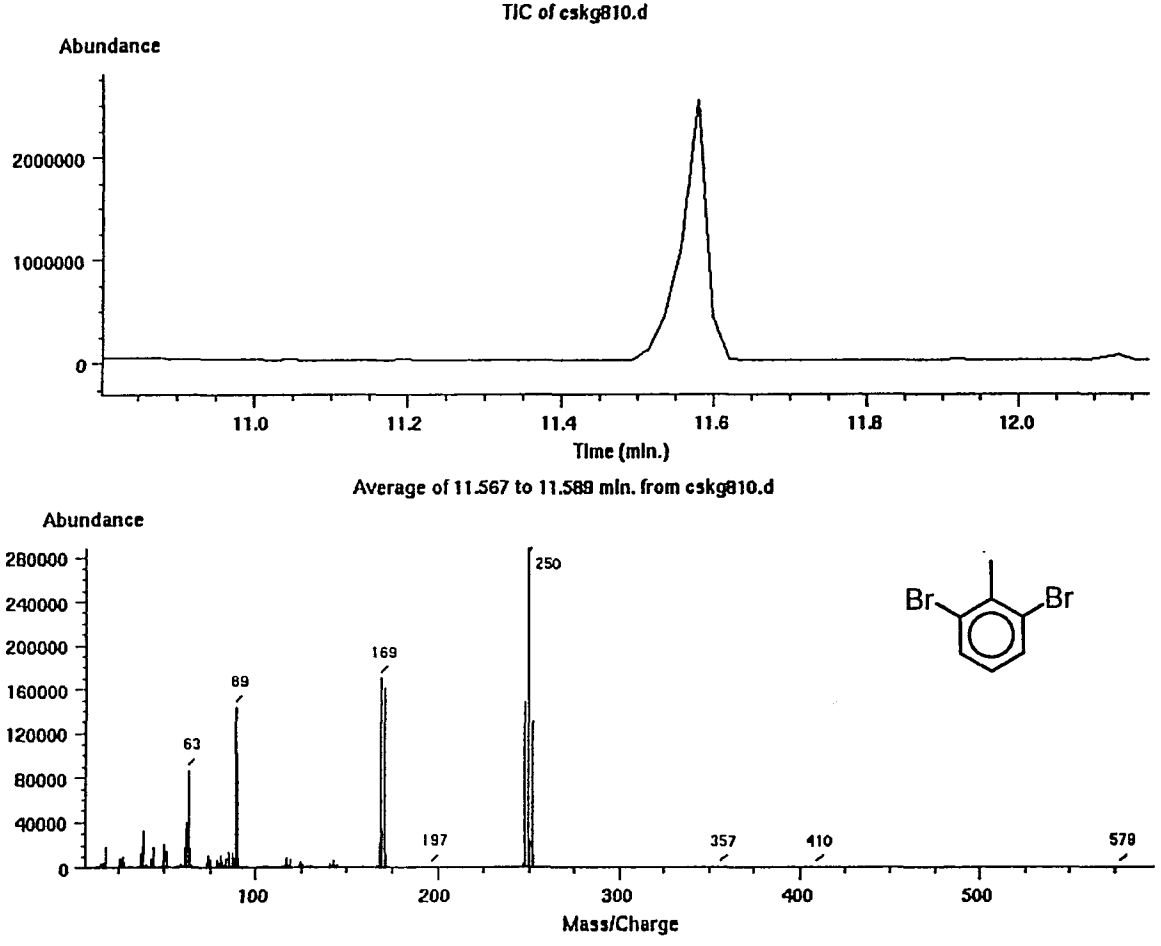

O
OMe
SnMe3
4
3
2
1
0
PPM

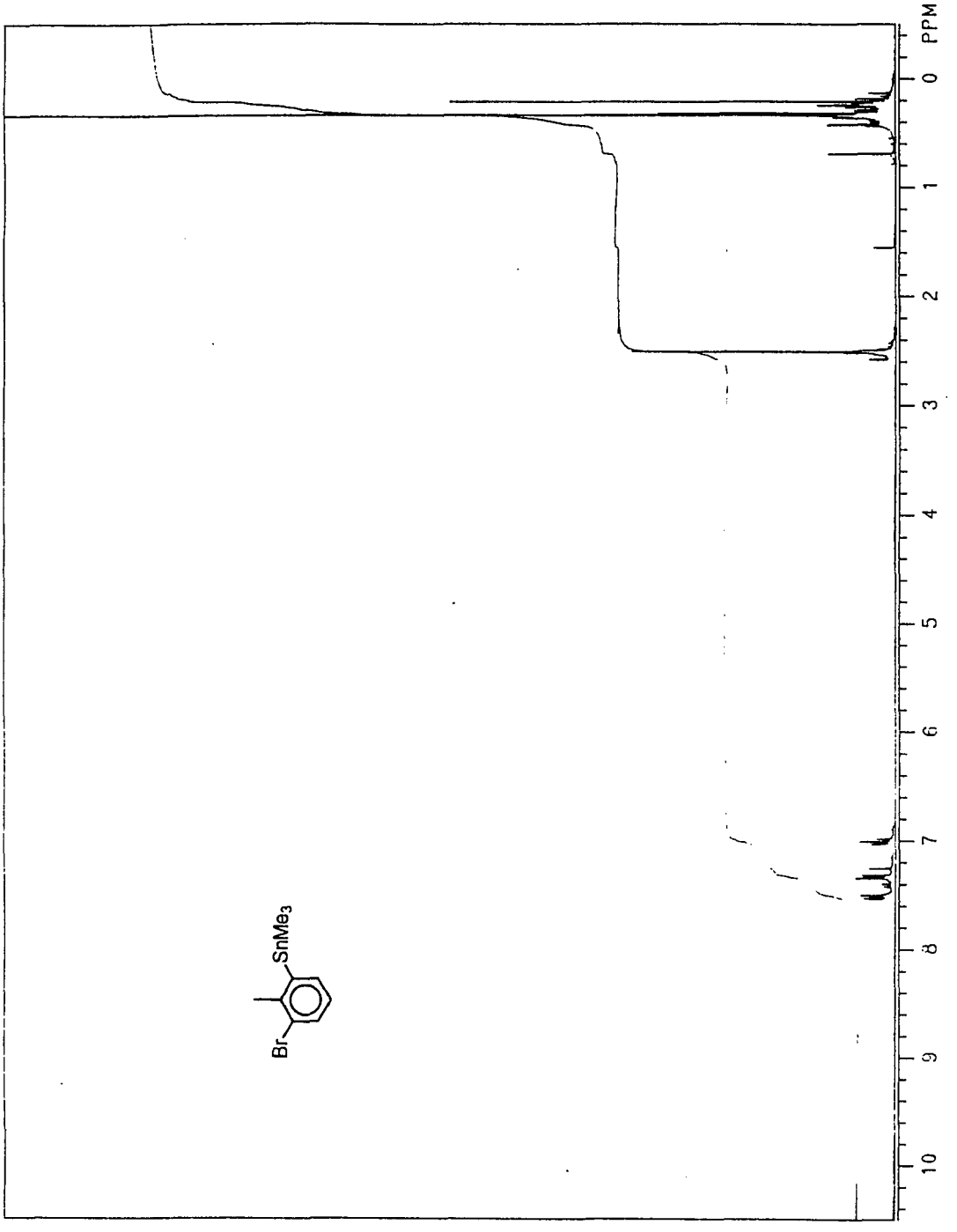

O
OMe
SnBu3
10
4
3
2
1
0
PPM

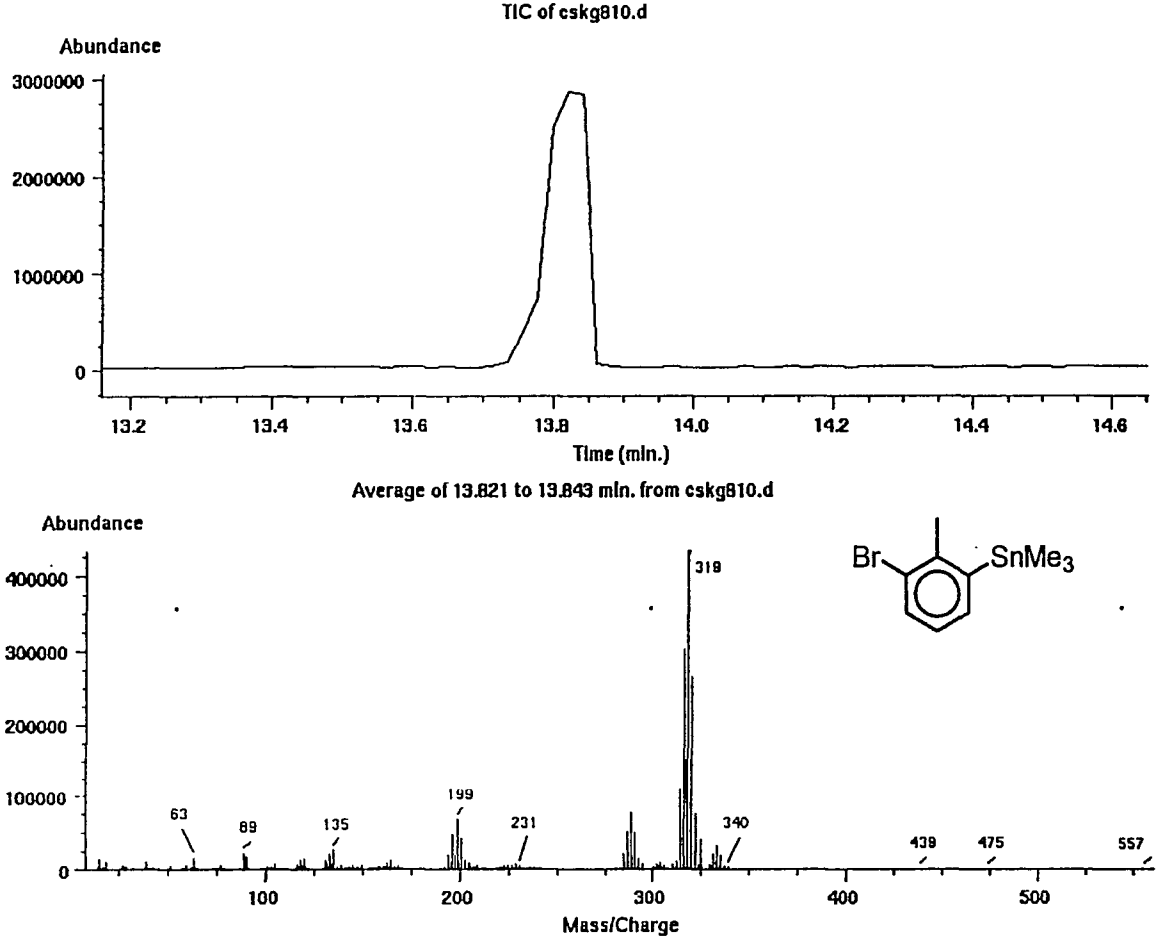

Average of 7.659 to 7.675 min. from csd1.d
Abundance
60000
50000
40000
30000
20000
10000
0
28
43
82
112
139
165
194
275
306
100
200
300
Mass/Charge
O
MeO
Br

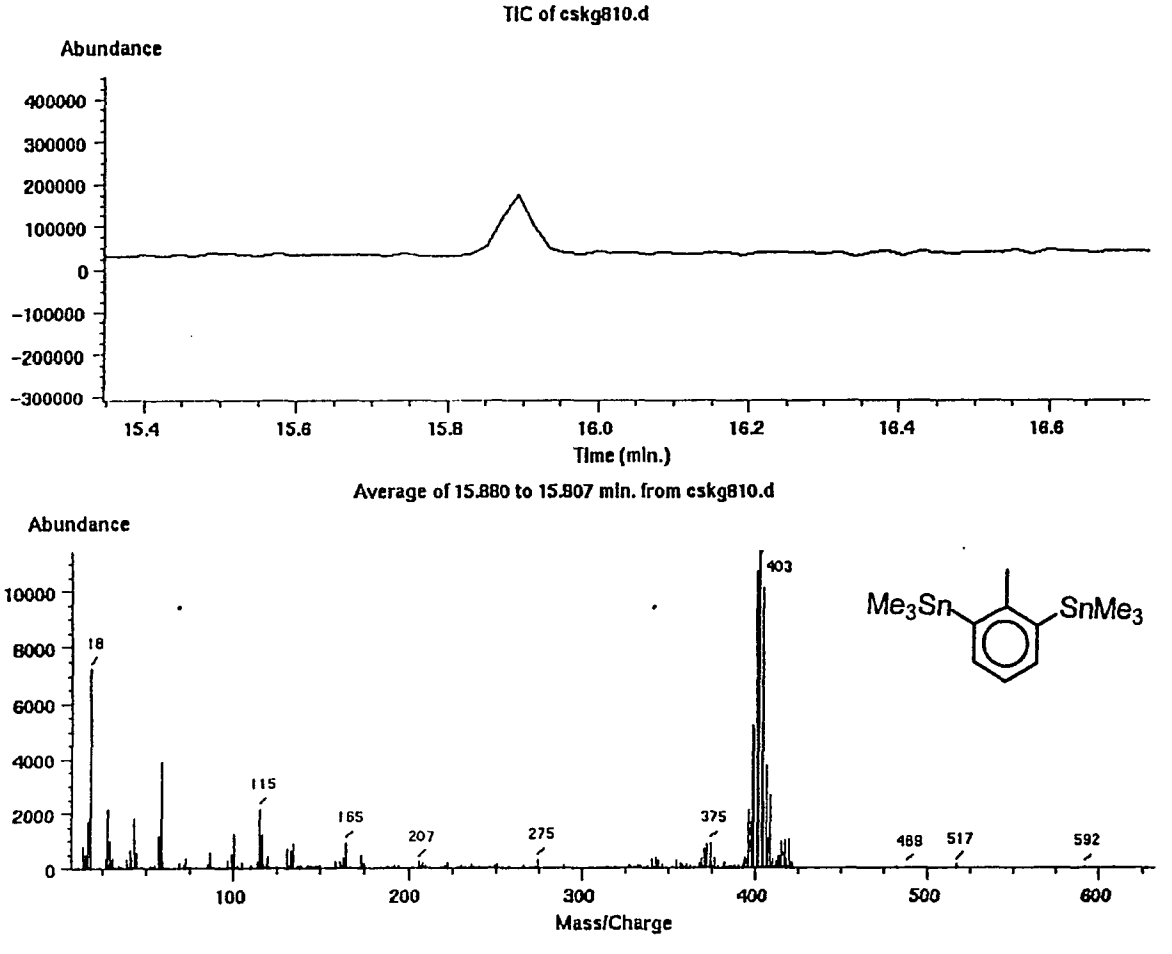

TIC of cskgB10.d
Abundance
2800000
2400000
2000000
1600000
1200000
800000
400000
0
4
6
8
10
12
14
16
Time (min.)

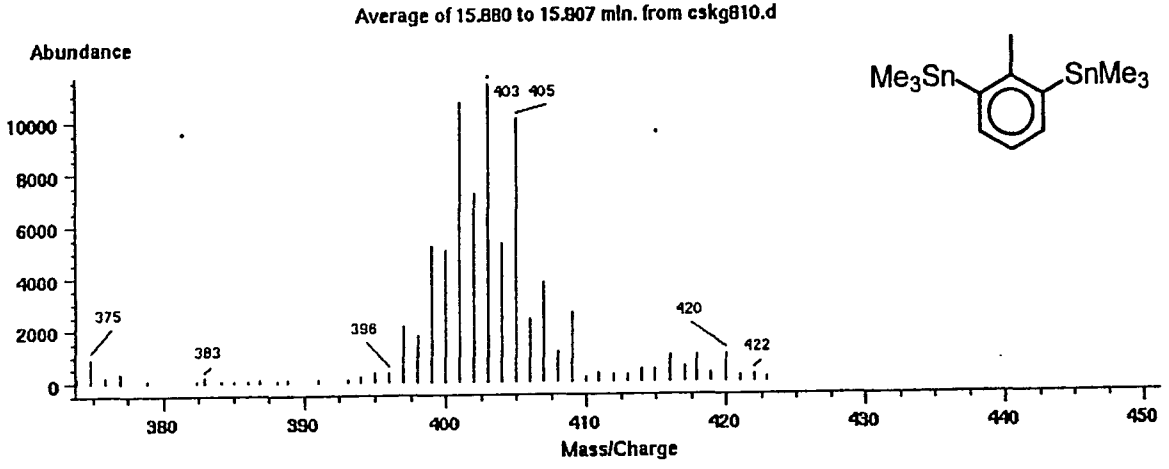

Br
Br
PPM
0
1
2
3
4
5
6
7
8
9
10

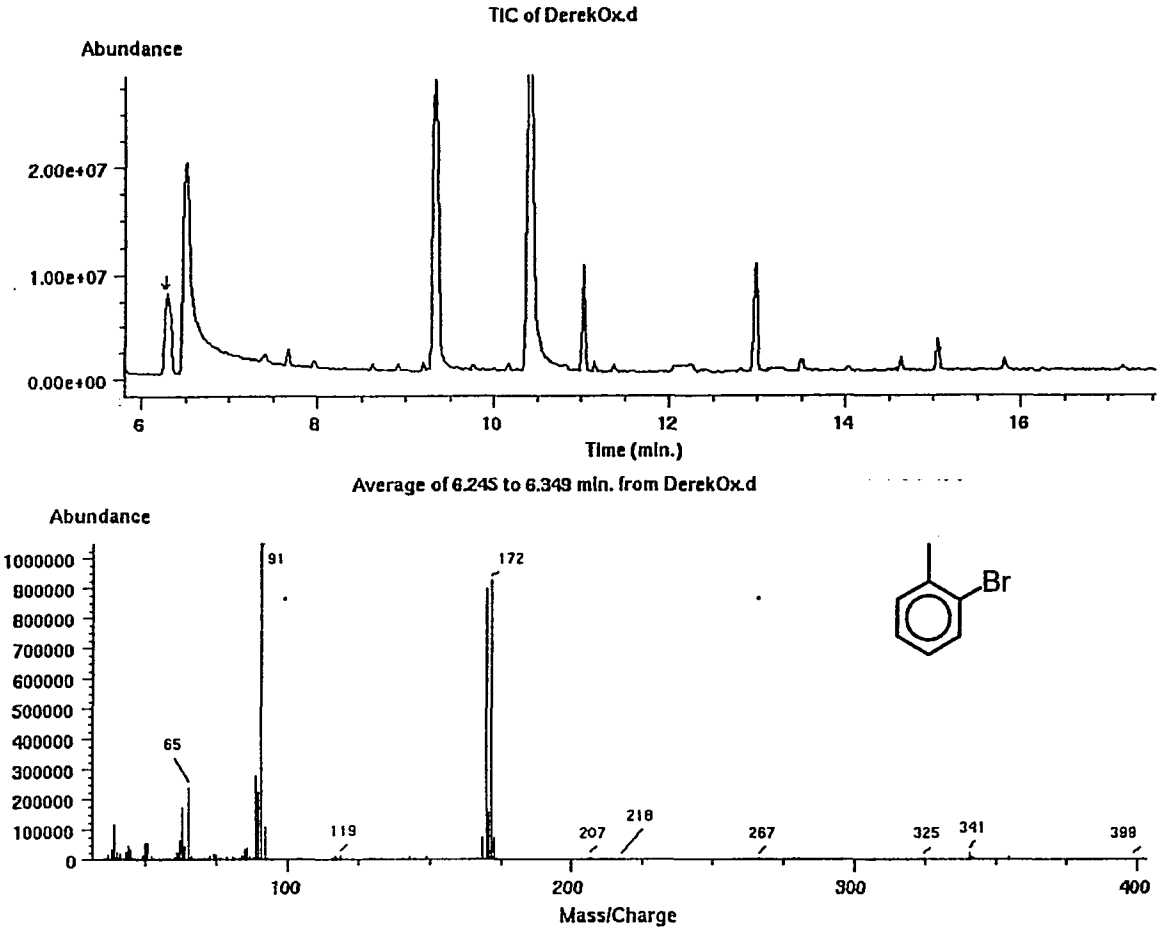

TIC of cskg810.d
Abundance
2000000
1000000
0
11.0
11.2
11.4
11.6
11.8
12.0
Time (min.)
Average of 11.567 to 11.589 min. from cskg810.d
Abundance
280000
240000
200000
160000
120000
80000
40000
0
63
89
169
197
250
357
410
579
100
200
300
400
500
Mass/Charge
Br
Br

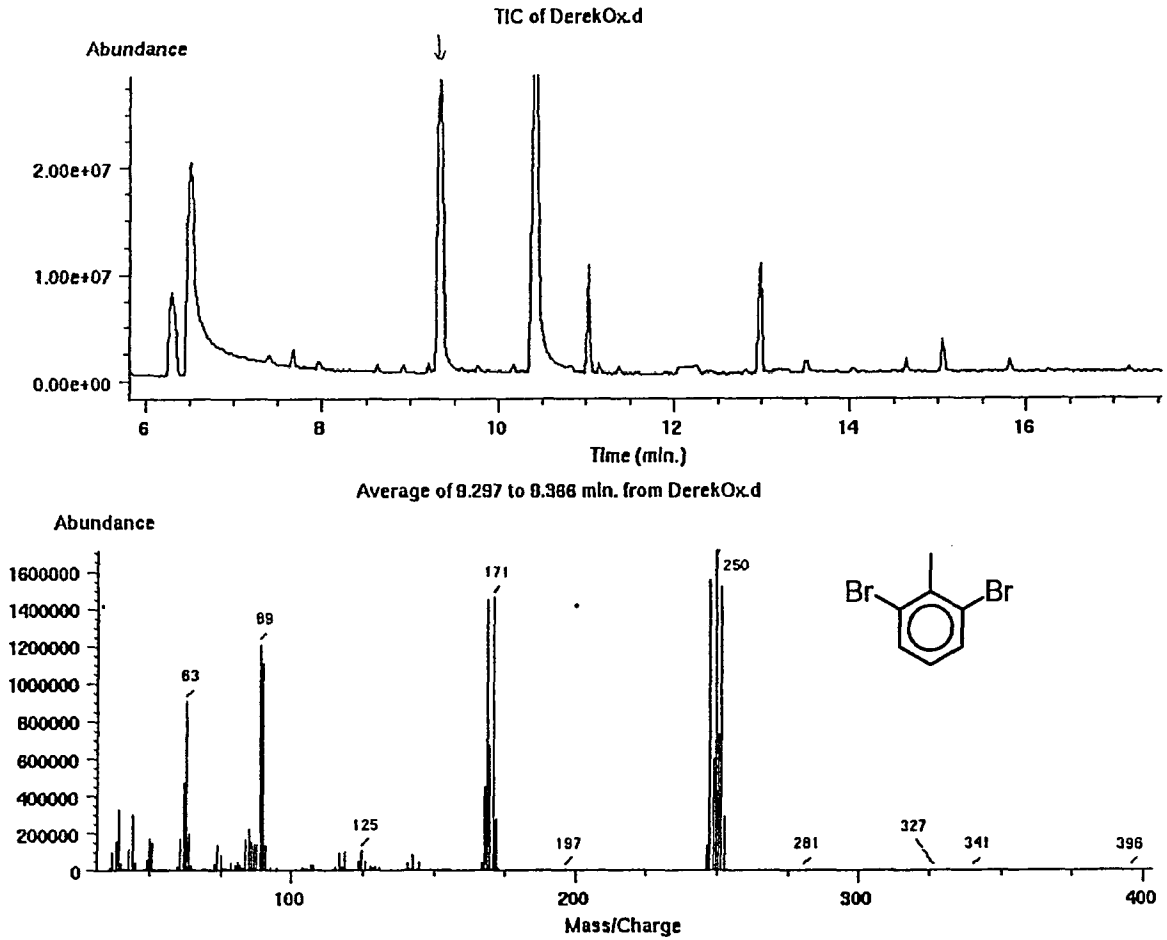

PPM
0
1
2
3
4
5
6
7
8
9
10
SnMe3
Br

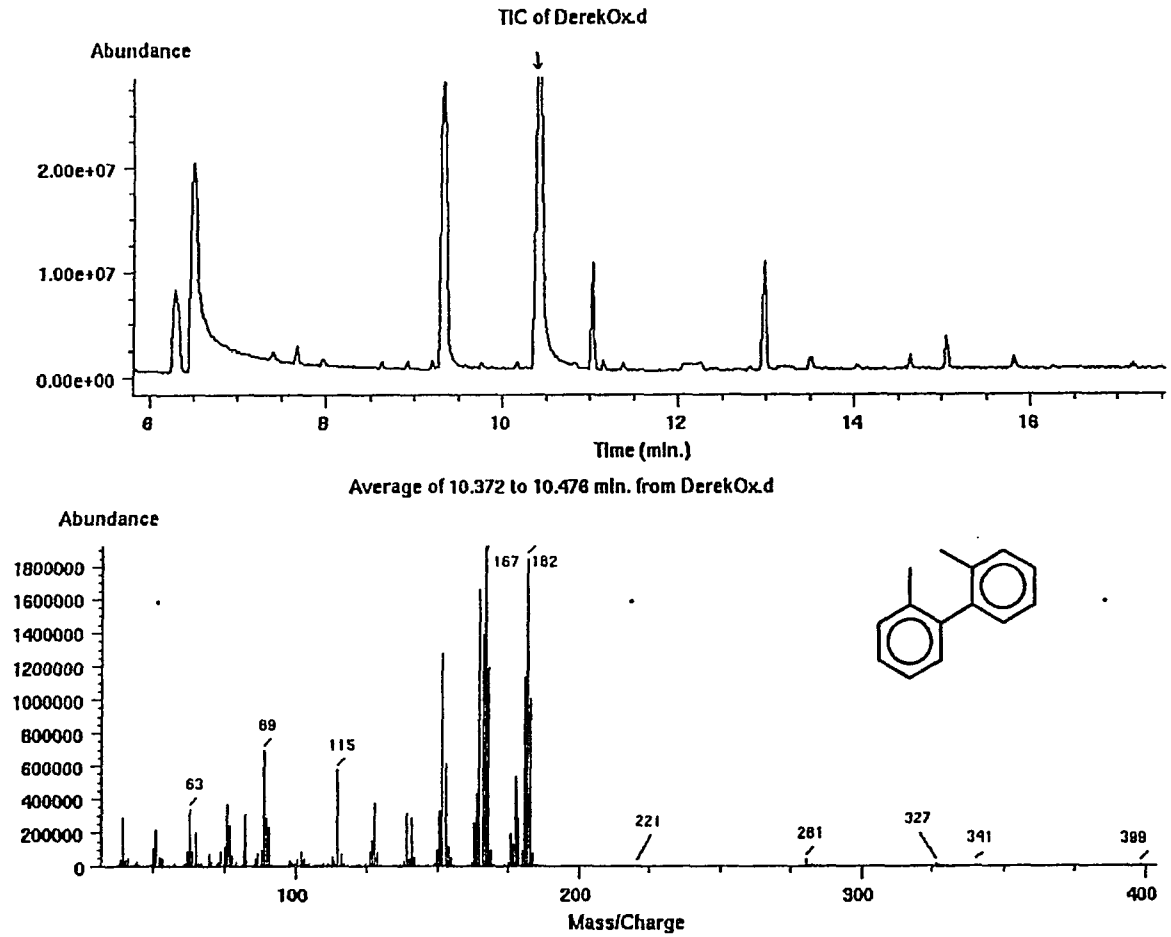

TIC of cskg810.d
Abundance
3000000
2000000
1000000
0
13.2
13.4
13.6
13.8
14.0
14.2
14.4
14.6
Time (min.)
Average of 13.821 to 13.843 min. from cskg810.d
Abundance
400000
300000
200000
100000
0
63
89
135
199
231
318
340
439
475
557
100
200
300
400
500
Mass/Charge
Br
SnMe3

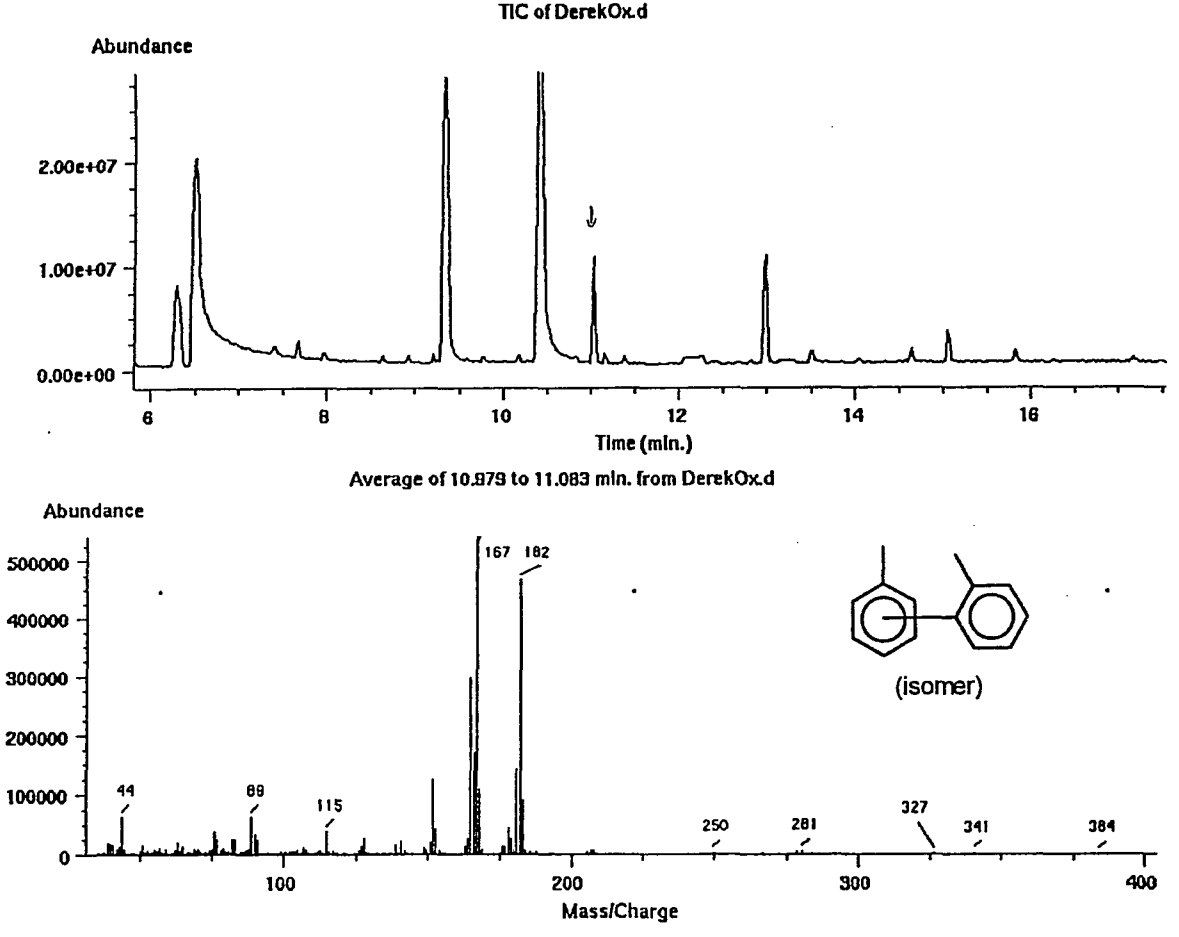

TIC of cskg810.d
Abundance
400000
300000
200000
100000
0
-100000
-200000
-300000
15.4
15.6
15.8
16.0
16.2
16.4
16.6
Time (min.)
Average of 15.880 to 15.907 min. from cskg810.d
Abundance
10000
8000
6000
4000
2000
0
18
115
165
207
275
375
403
488
517
592
100
200
300
400
500
600
Mass/Charge
Me3Sn
SnMe3

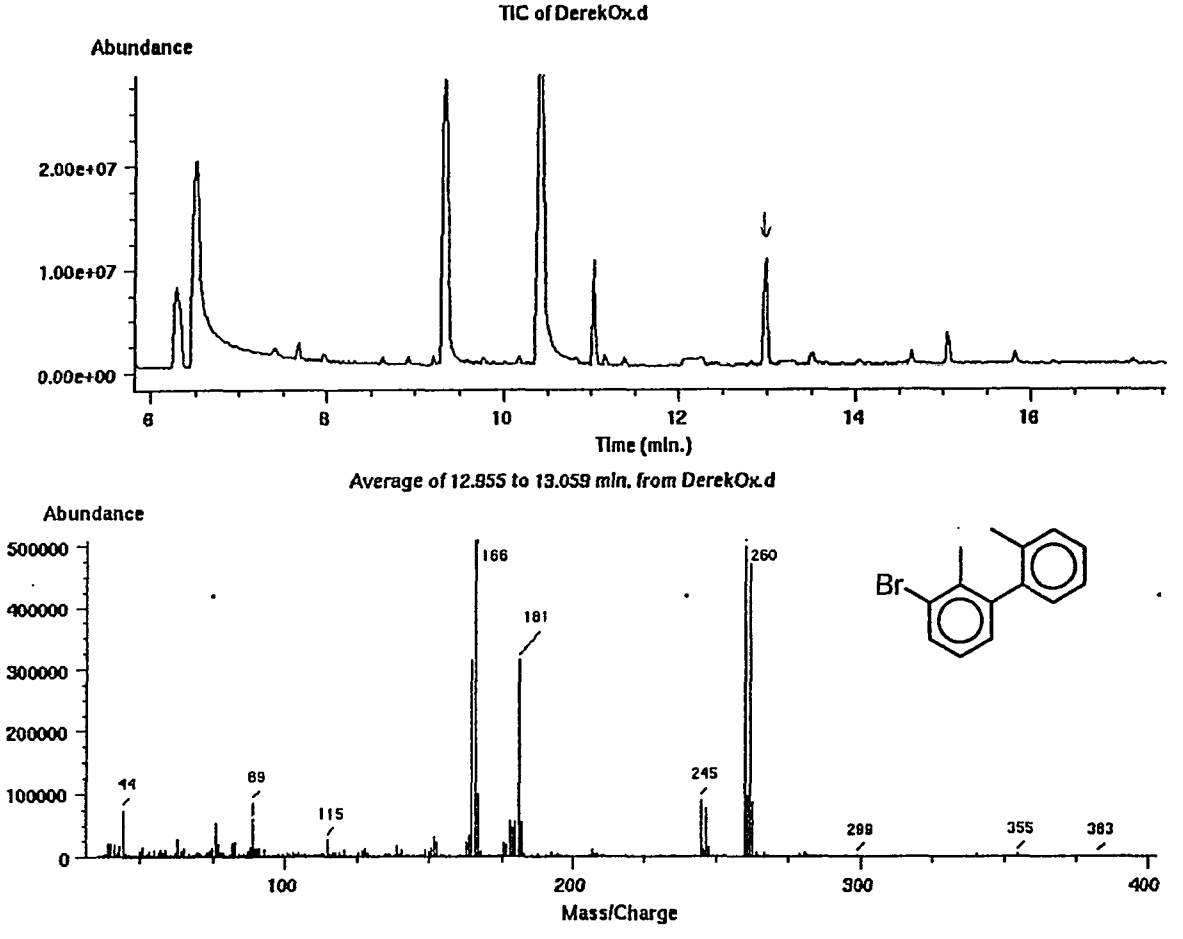

Average of 15.880 to 15.907 min. from cskg810.d
Abundance
10000
8000
6000
4000
2000
0
375
383
396
403 405
420
422
380
390
400
410
420
430
440
450
Mass/Charge
Me3Sn
SnMe3

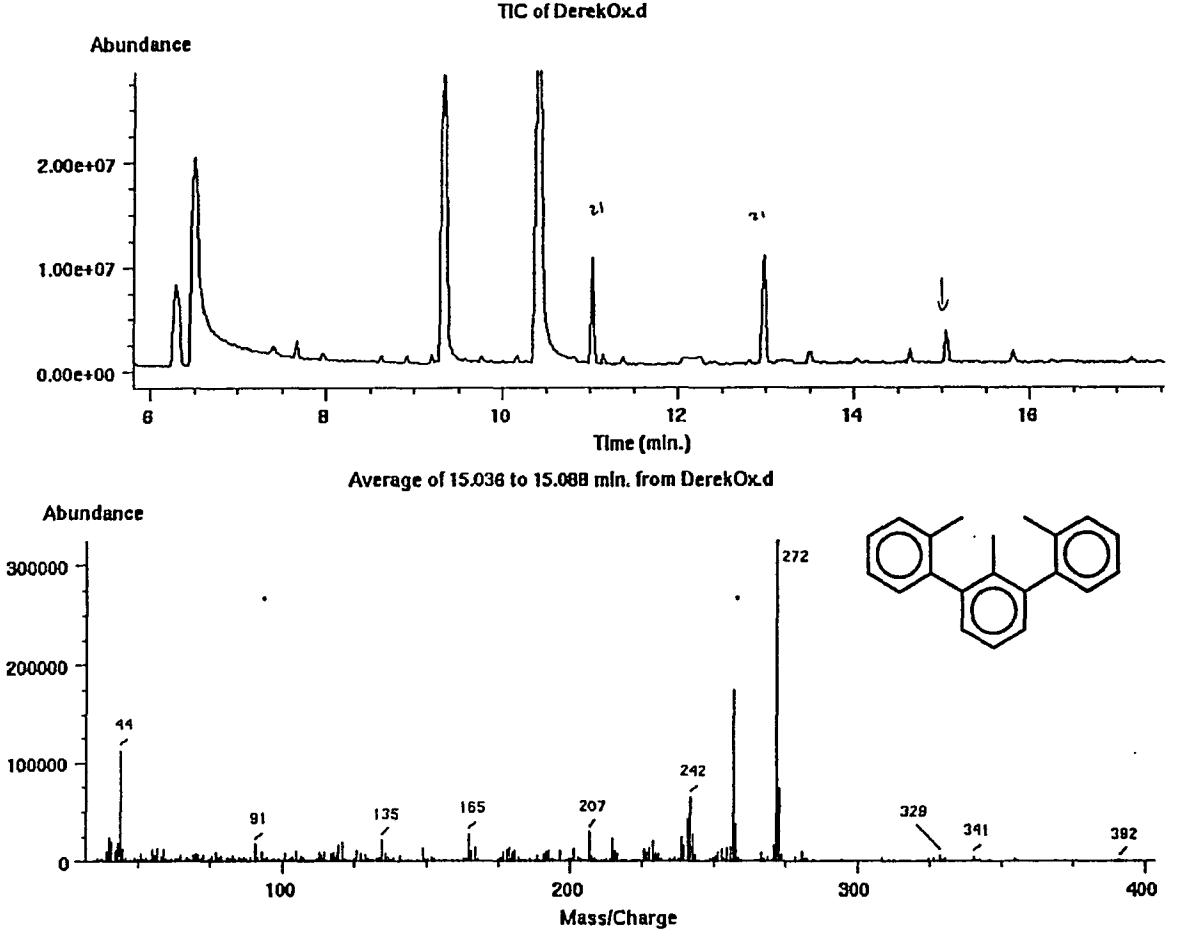

TIC of DerekOx.d
Abundance
2.00e+07
1.00e+07
0.00e+00
6
8
10
12
14
16
Time (min.)
Average of 6.245 to 6.349 min. from DerekOx.d
Abundance
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
91
172
65
119
207
218
267
325
341
388
100
200
300
400
Mass/Charge
Br

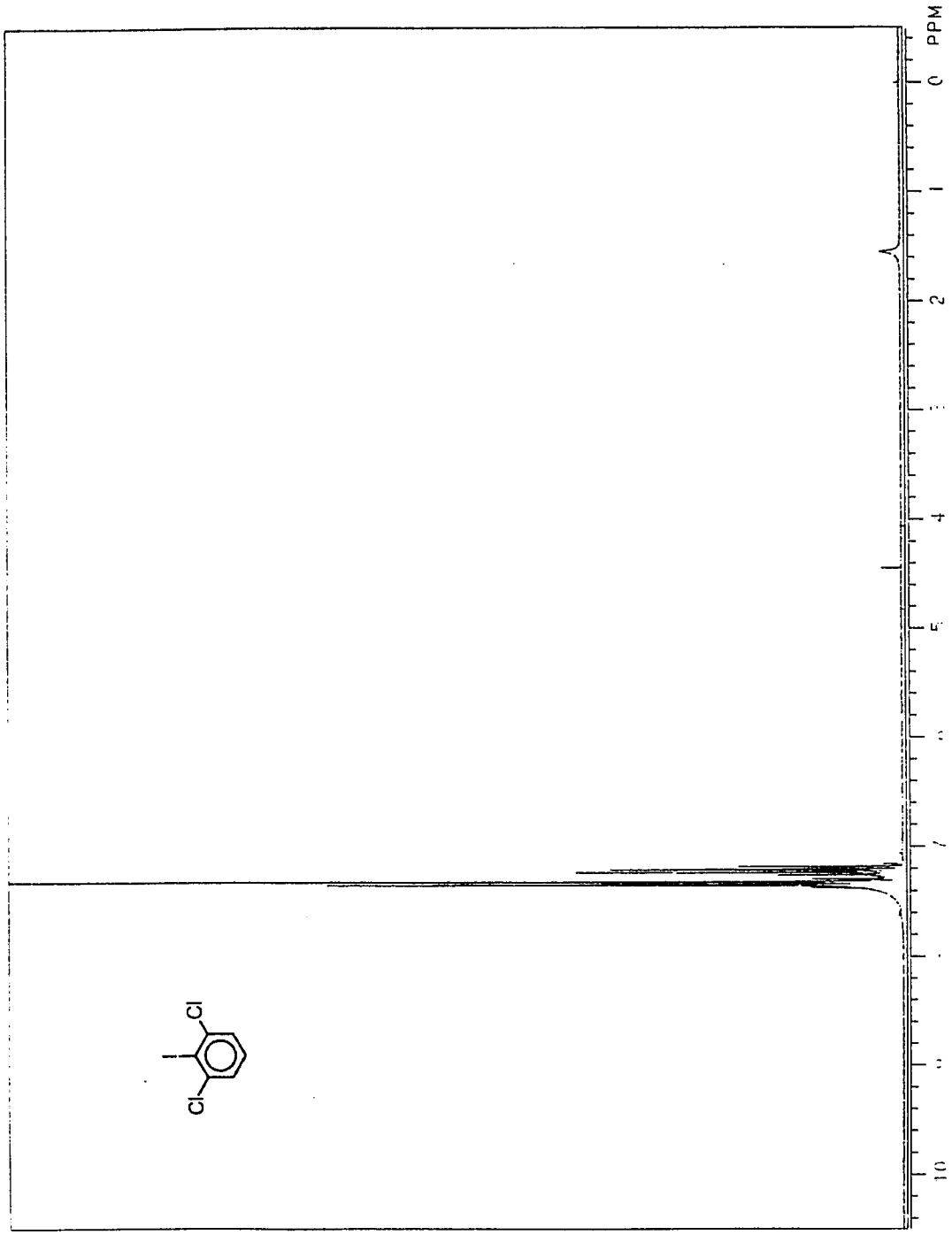

TIC of DerekOx.d
Abundance
2.00e+07
1.00e+07
0.00e+00
6
8
10
12
14
16
Time (min.)
Average of 9.297 to 9.366 min. from DerekOx.d
Abundance
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
63
89
125
171
197
250
281
327
341
396
100
200
300
400
Mass/Charge
Br
Br

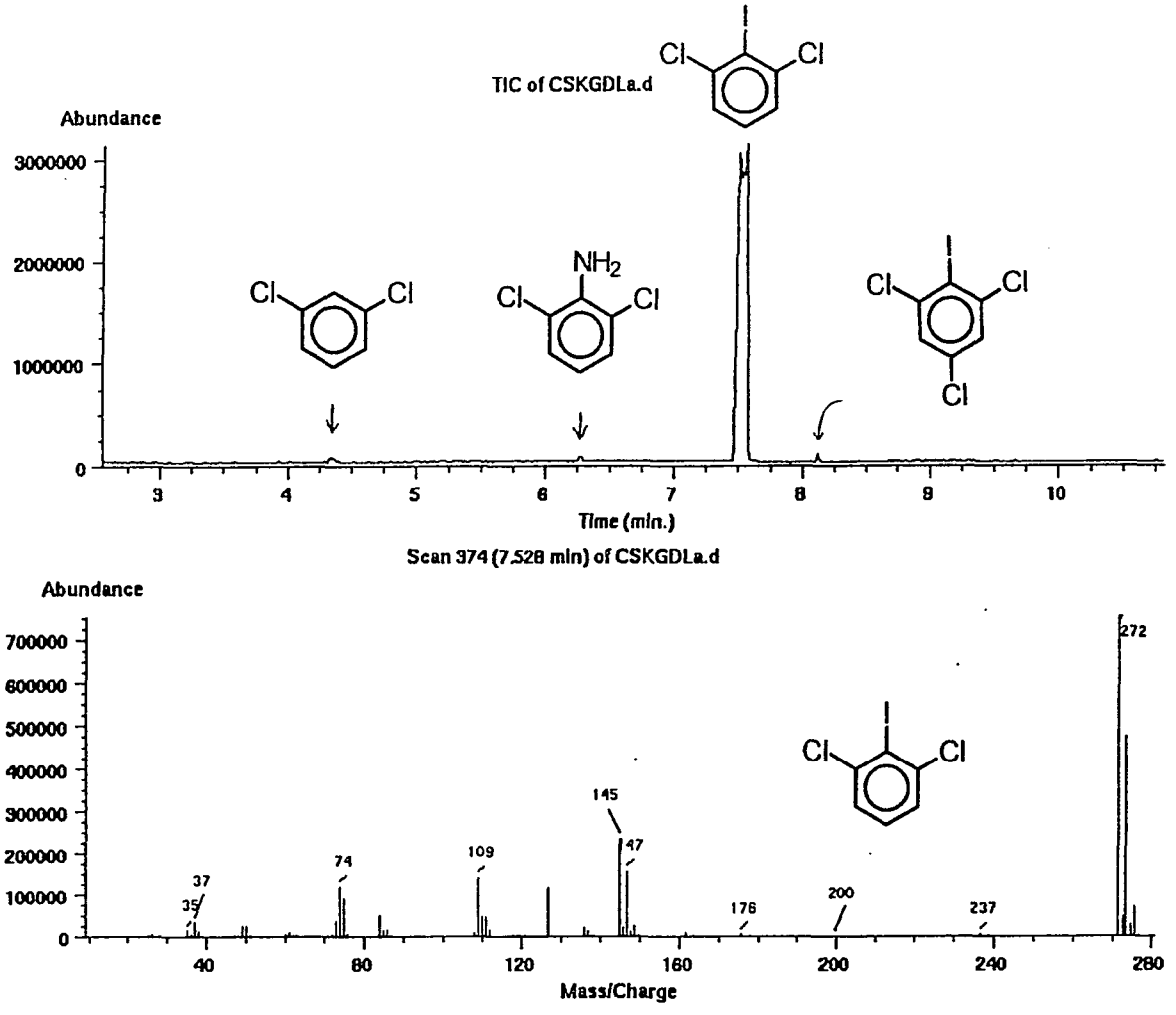

TIC of DerekOx.d
Abundance
2.00e+07
1.00e+07
0.00e+00
6
8
10
12
14
16
Time (min.)
Average of 10.372 to 10.476 min. from DerekOx.d
Abundance
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
63
69
115
167
182
221
281
327
341
389
100
200
300
400
Mass/Charge

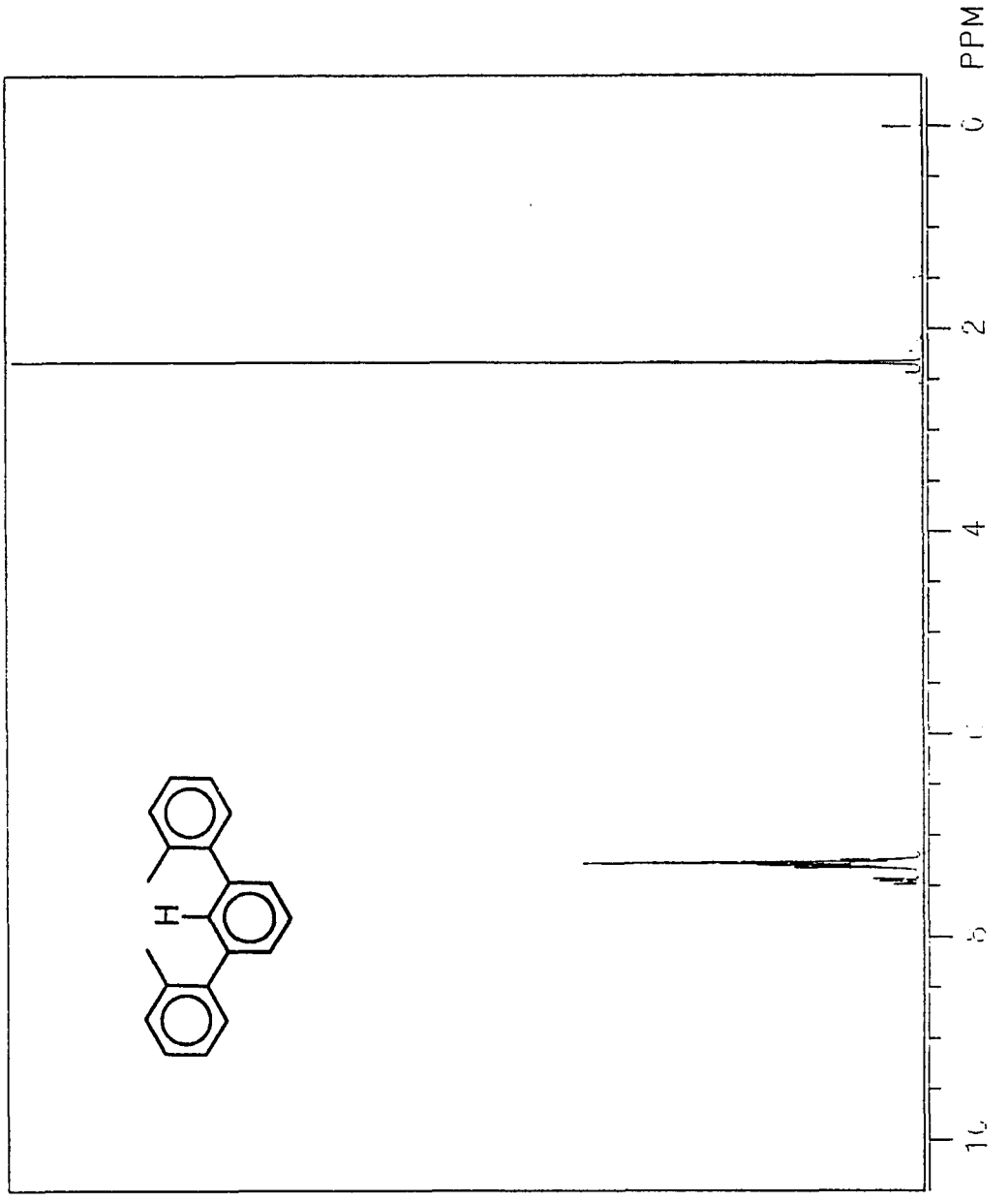

TIC of DerekOx.d
Abundance
2.00e+07
1.00e+07
0.00e+00
6
8
10
12
14
16
Time (min.)
Average of 10.979 to 11.083 min. from DerekOx.d
Abundance
500000
400000
300000
200000
100000
0
167
182
44
69
115
250
281
327
341
384
100
200
300
400
Mass/Charge
(isomer)

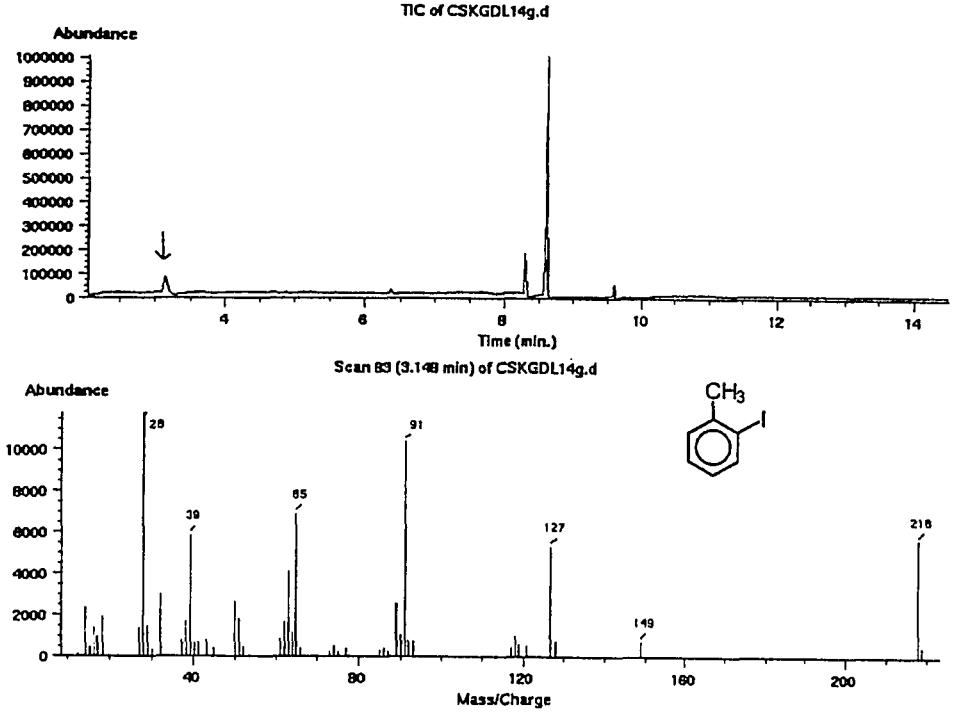

TIC of DerekOx.d
Abundance
2.00e+07
1.00e+07
0.00e+00
6
8
10
12
14
16
Time (min.)
Average of 12.955 to 13.059 min. from DerekOx.d
Abundance
500000
400000
300000
200000
100000
0
166
181
260
44
89
115
245
289
355
383
Br
100
200
300
400
Mass/Charge

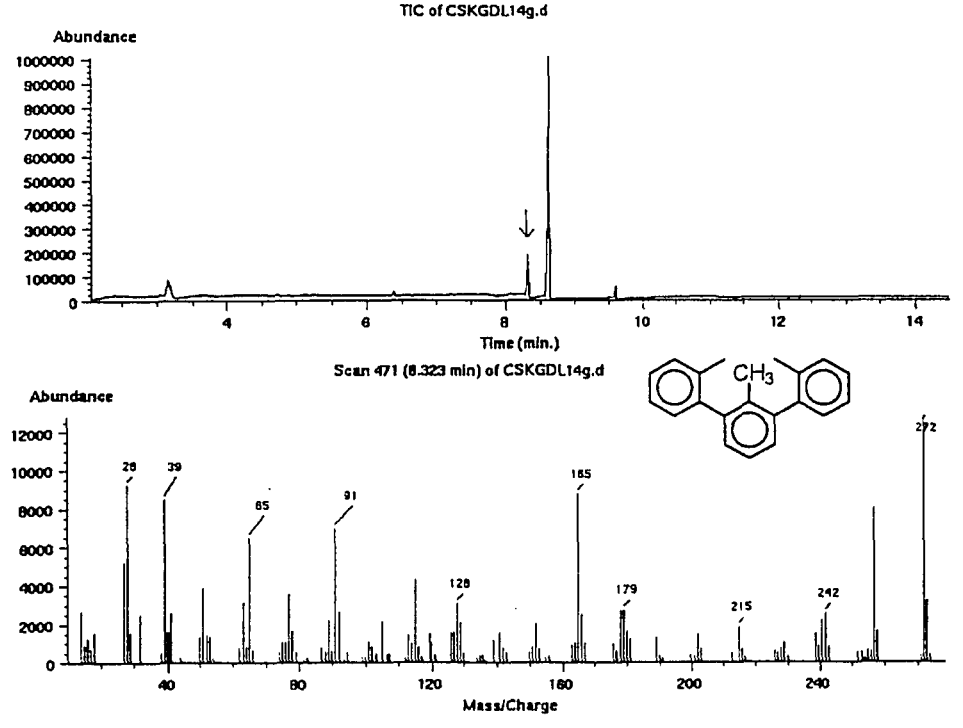

TIC of DerekOx.d
Abundance
2.00e+07
1.00e+07
0.00e+00
6
8
10
12
14
16
Time (min.)
Average of 15.036 to 15.088 min. from DerekOx.d
Abundance
300000
200000
100000
0
44
91
135
165
207
242
272
328
341
382
100
200
300
400
Mass/Charge

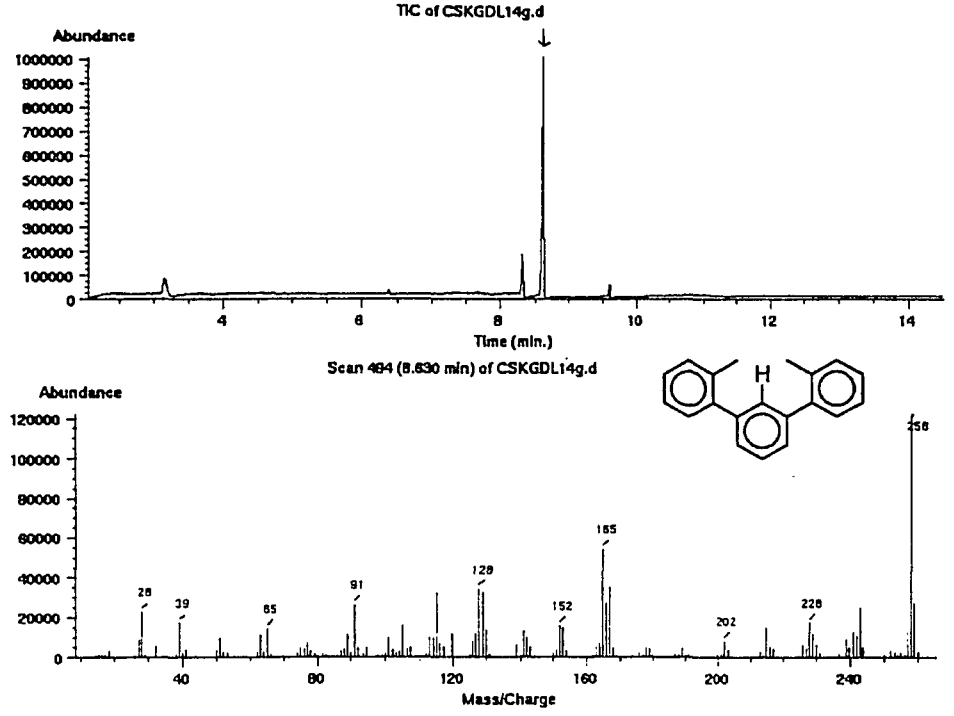

PPM
0
1
2
4
10
Cl
I
Cl

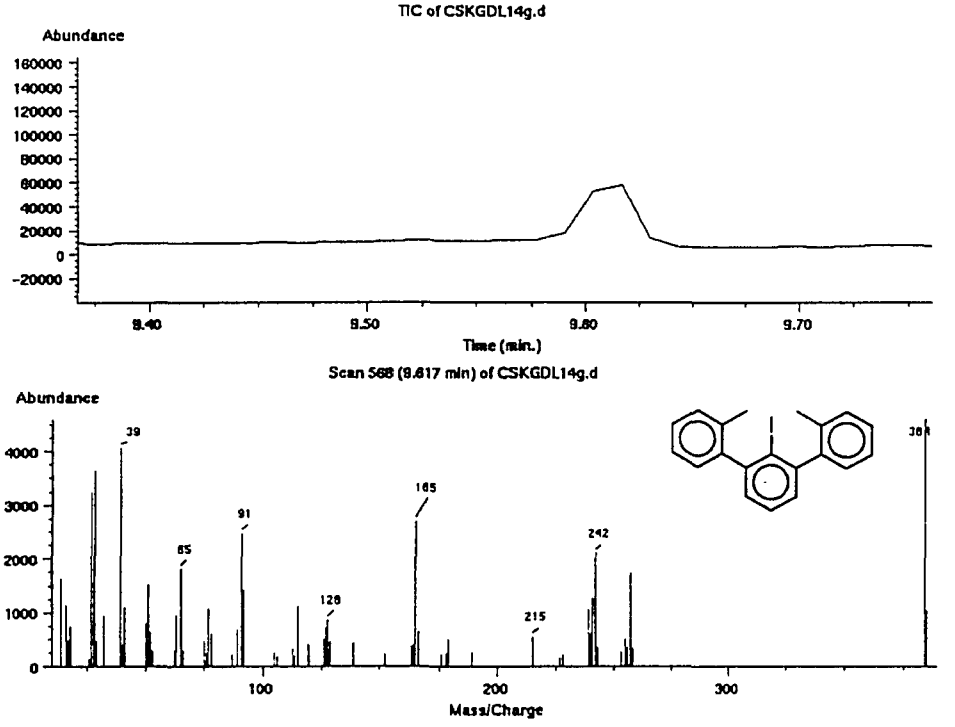

TIC of CSKGDLa.d
Abundance
3000000
2000000
1000000
0
3
4
5
6
7
8
9
10
Time (min.)
Cl
Cl
NH2
Cl
Cl
Cl
Cl
Cl
Scan 374 (7.528 min) of CSKGDLa.d
Abundance
700000
600000
500000
400000
300000
200000
100000
0
37
35
74
109
145
147
176
200
237
272
40
80
120
160
200
240
280
Mass/Charge
Cl
Cl

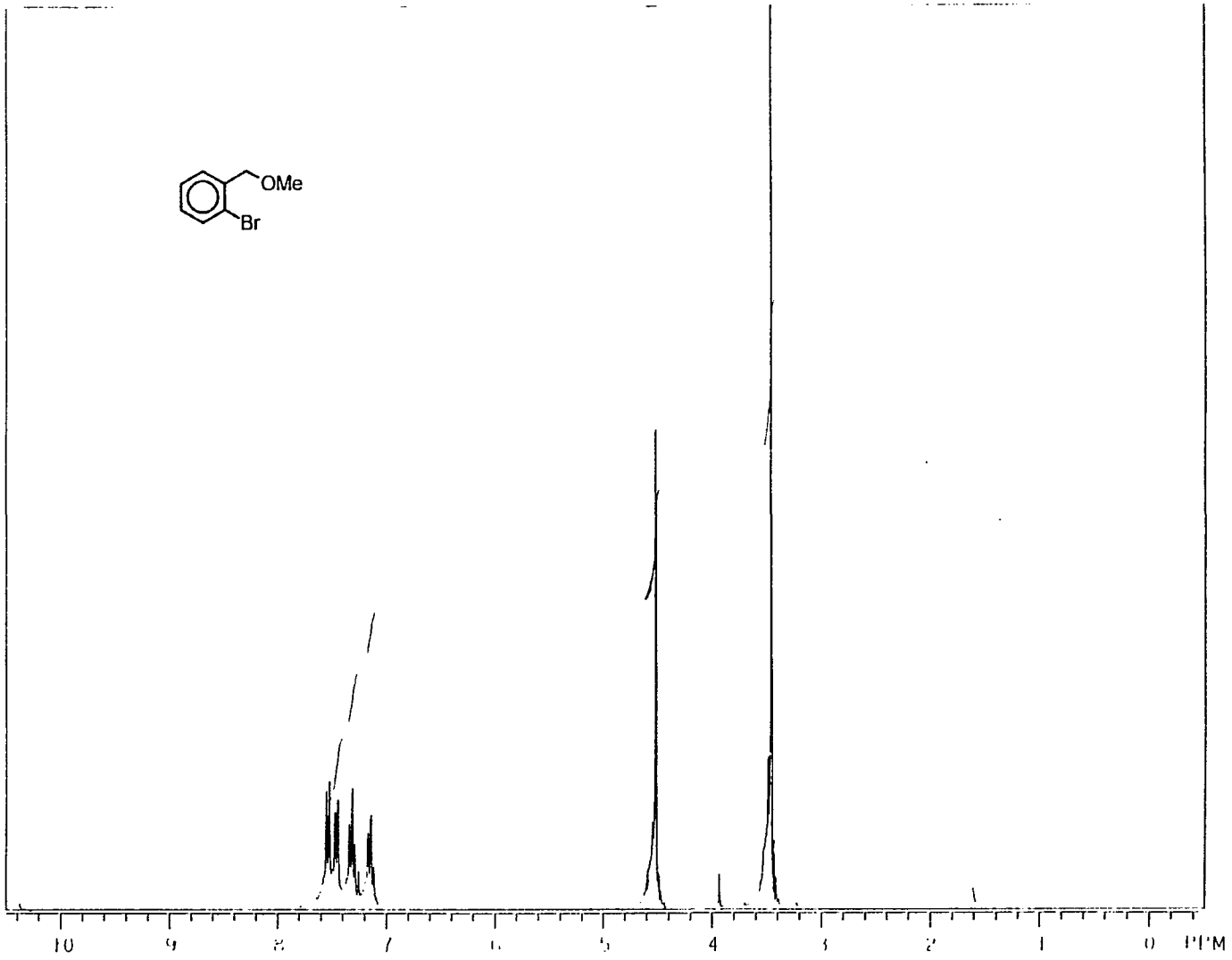

PPM
6
2
4
H

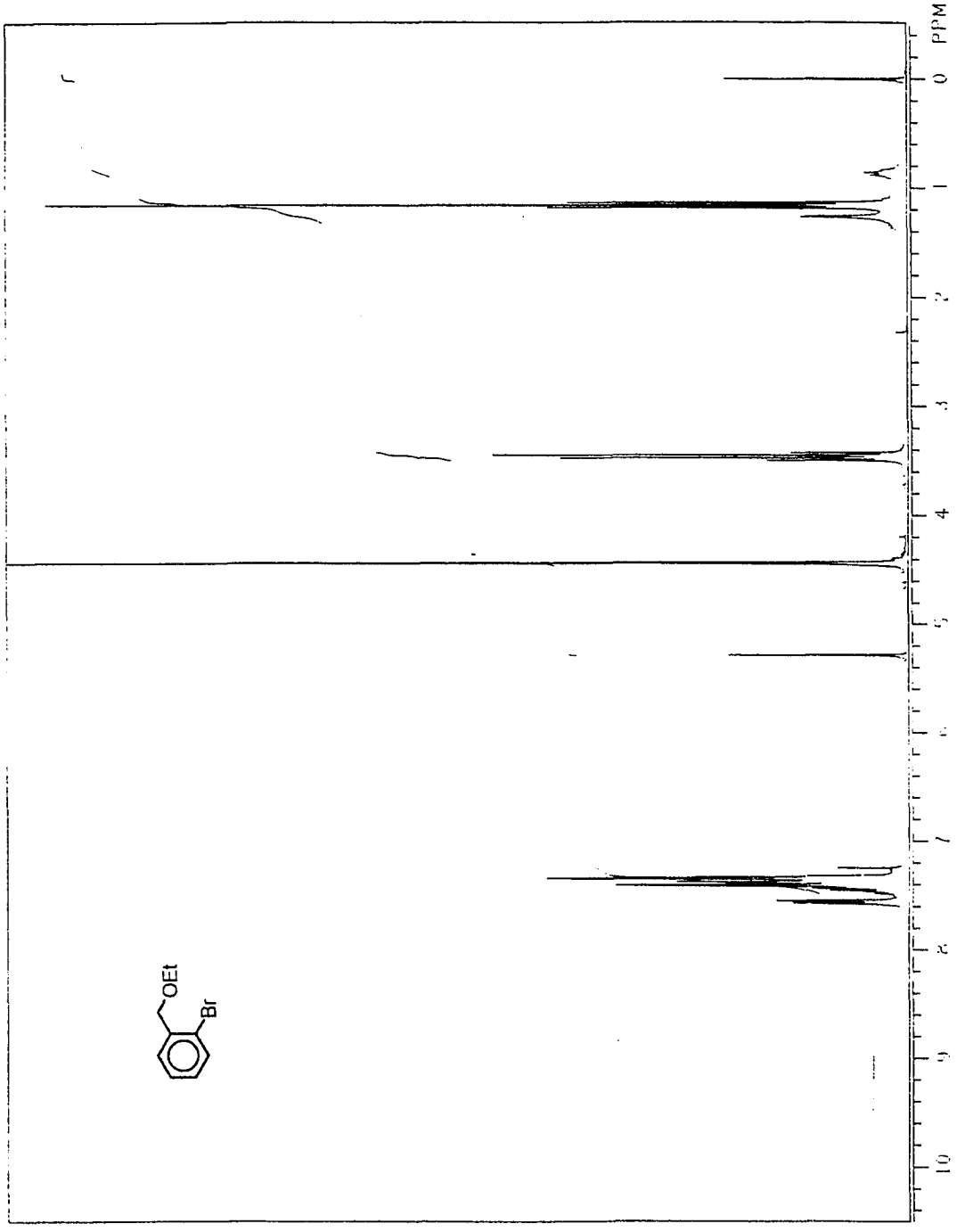

TIC of CSKGDL14g.d
Abundance
Time (min.)
Scan 83 (3.148 min) of CSKGDL14g.d
Abundance
Mass/Charge
CH3
I
28
39
65
91
127
149
216

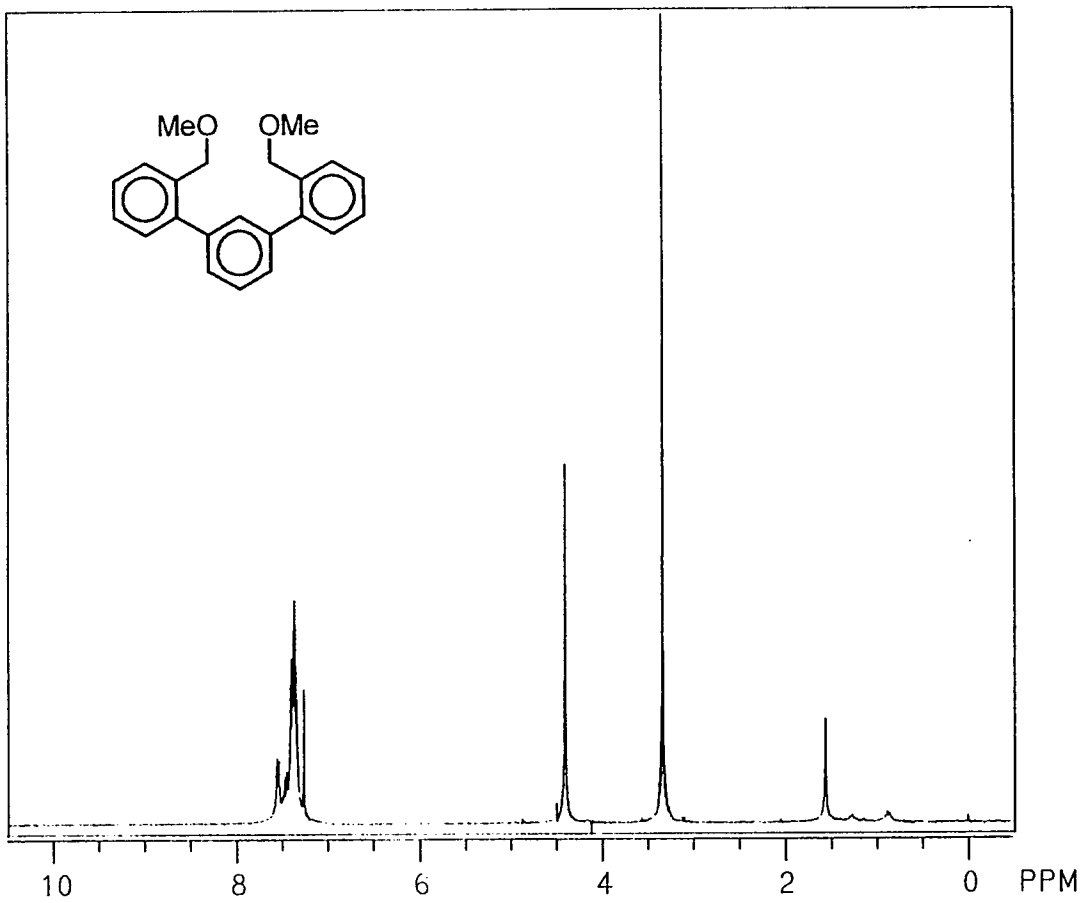

TIC of CSKGDL14g.d
Abundance
Time (min.)
Scan 471 (8.323 min) of CSKGDL14g.d
Abundance
Mass/Charge
CH3
28
39
65
91
128
165
179
215
242
272

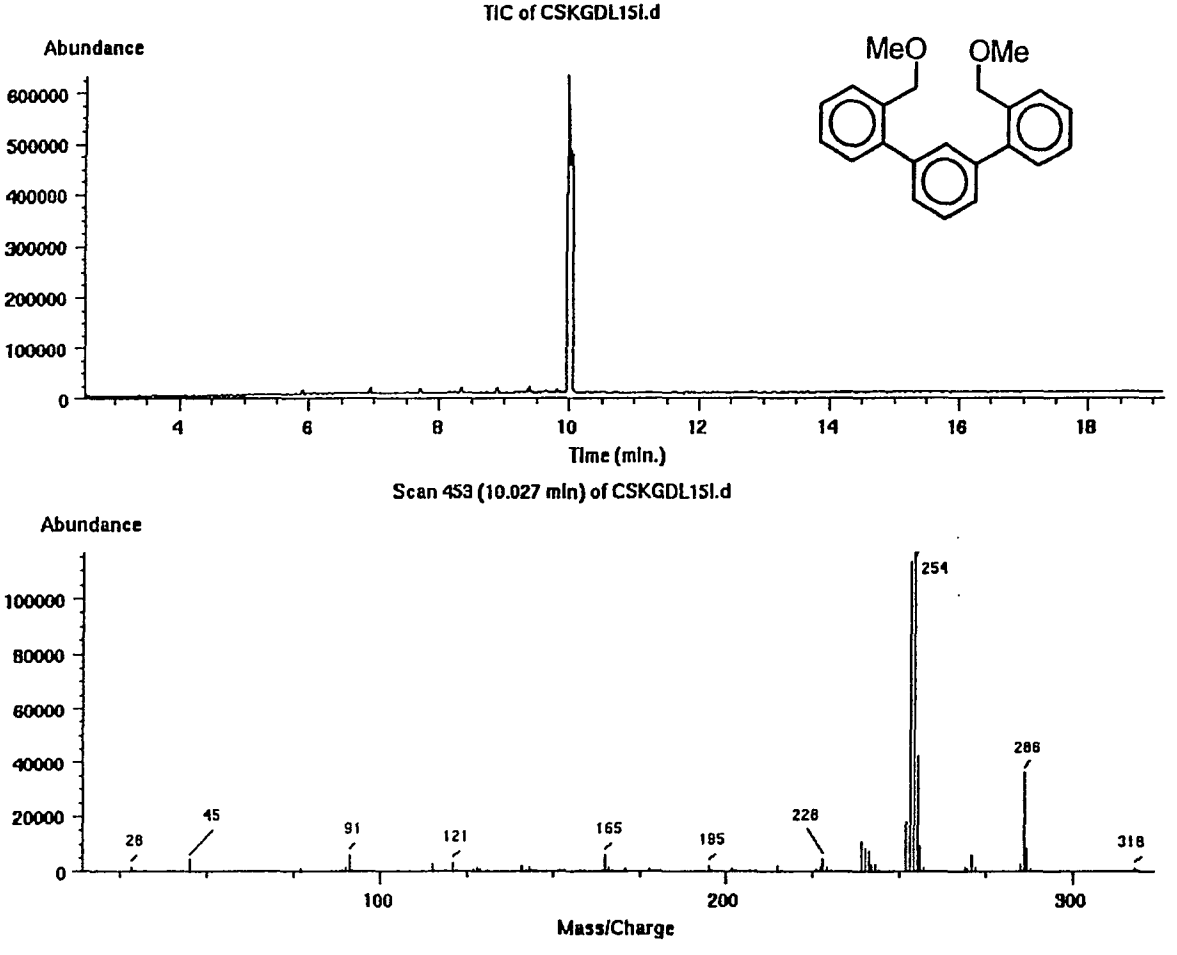

TIC of CSKGDL14g.d
Abundance
Time (min.)
Scan 484 (8.630 min) of CSKGDL14g.d
Abundance
Mass/Charge
28
39
65
91
128
152
165
202
228
256

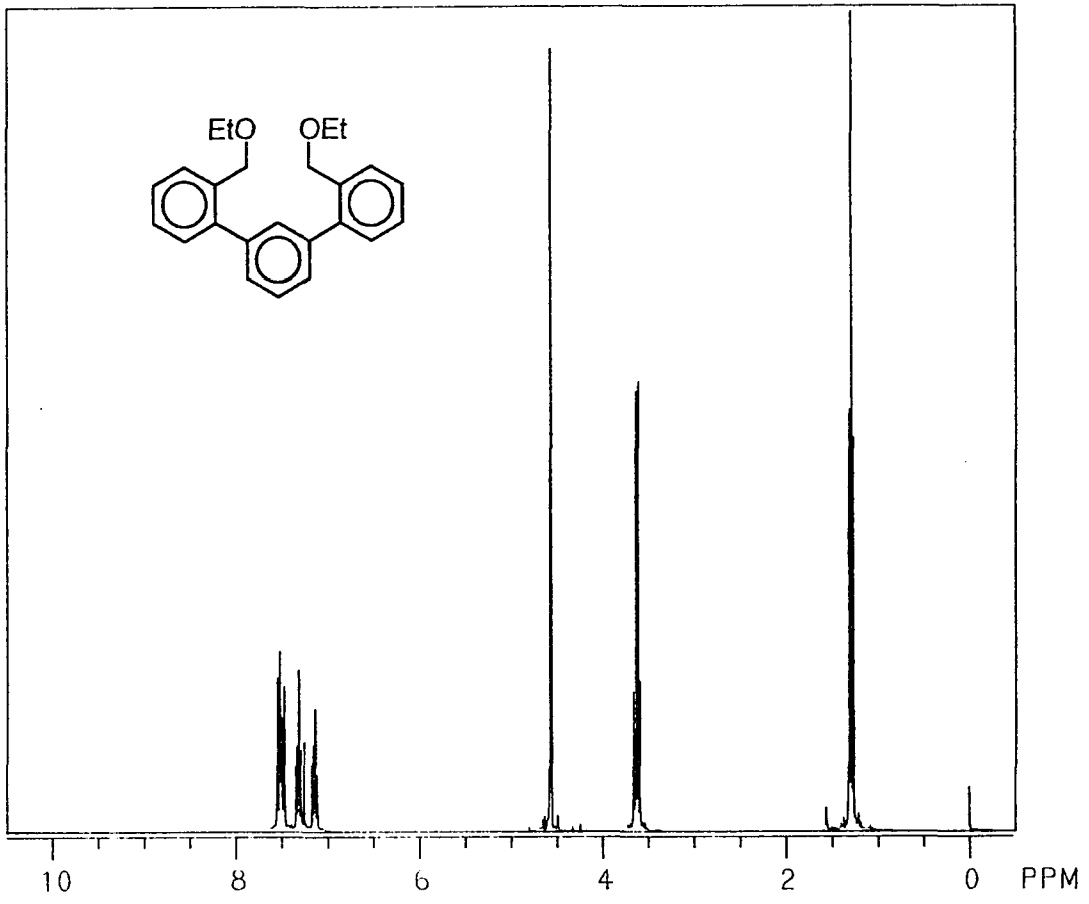

TIC of CSKGDL14g.d
Abundance
Time (min.)
Scan 568 (9.617 min) of CSKGDL14g.d
Abundance
Mass/Charge
39
65
91
126
165
215
242

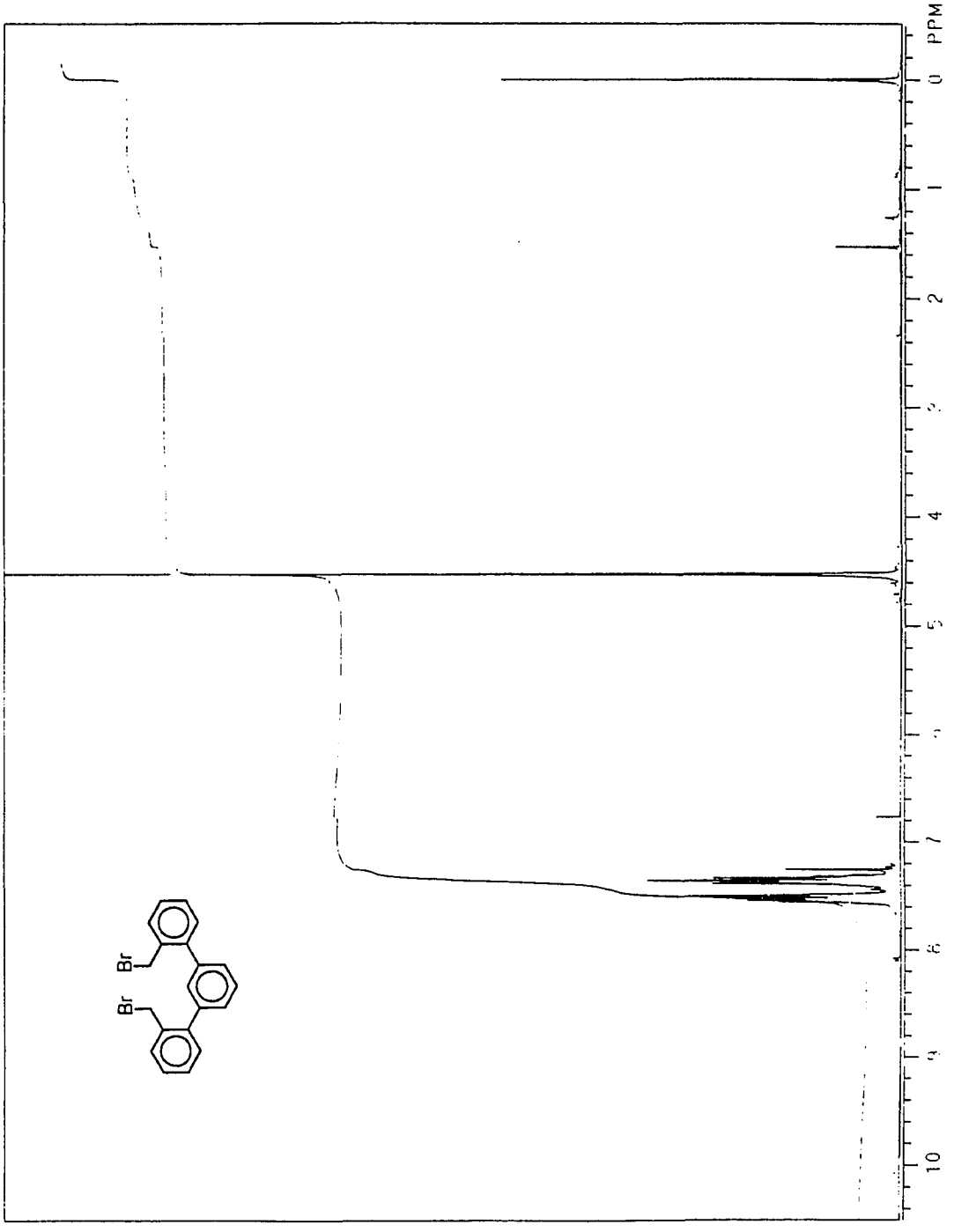

OMe
Br
10
9
8
7
6
5
4
3
2
1
0
PPM

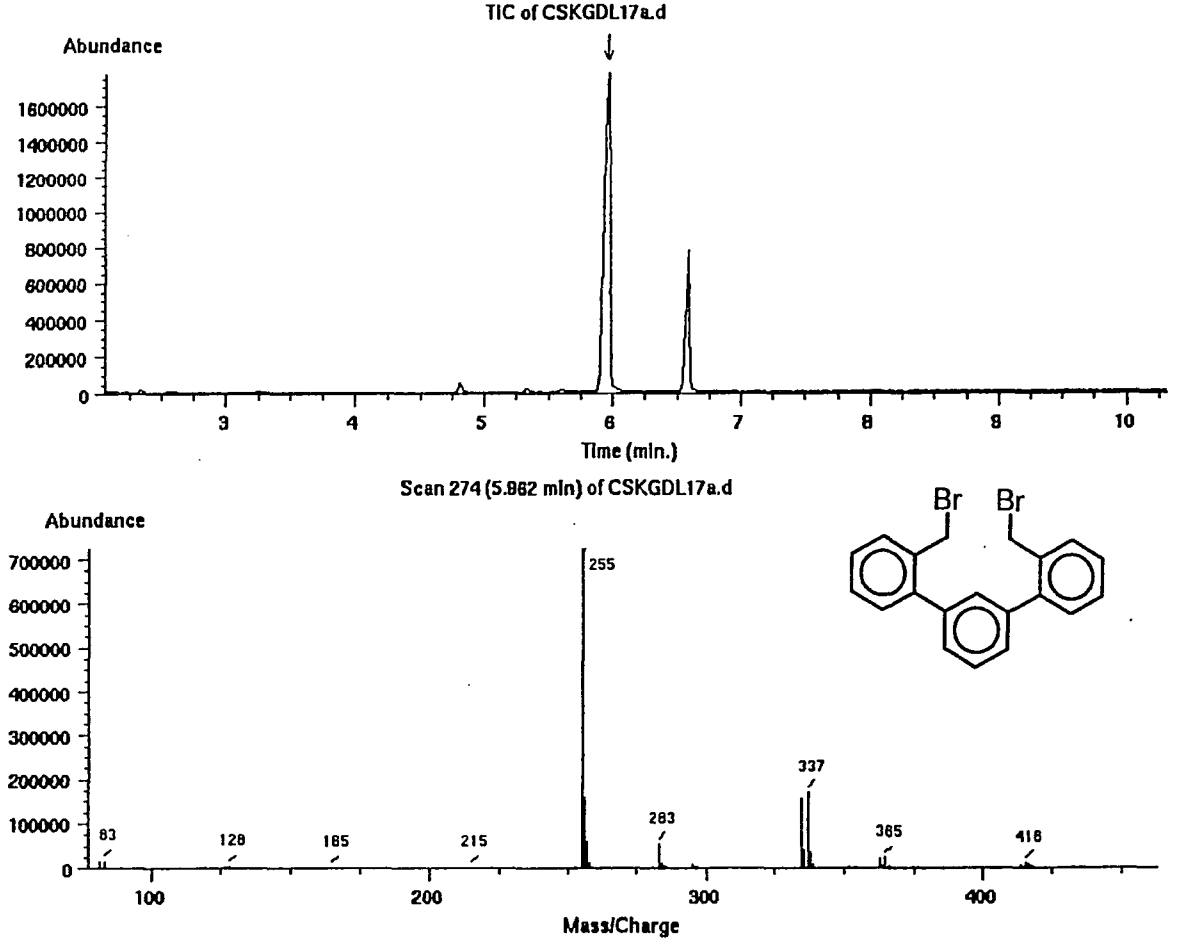

OEt
Br
PPM
0
1
2
3
4
5
6
7
8
9
10

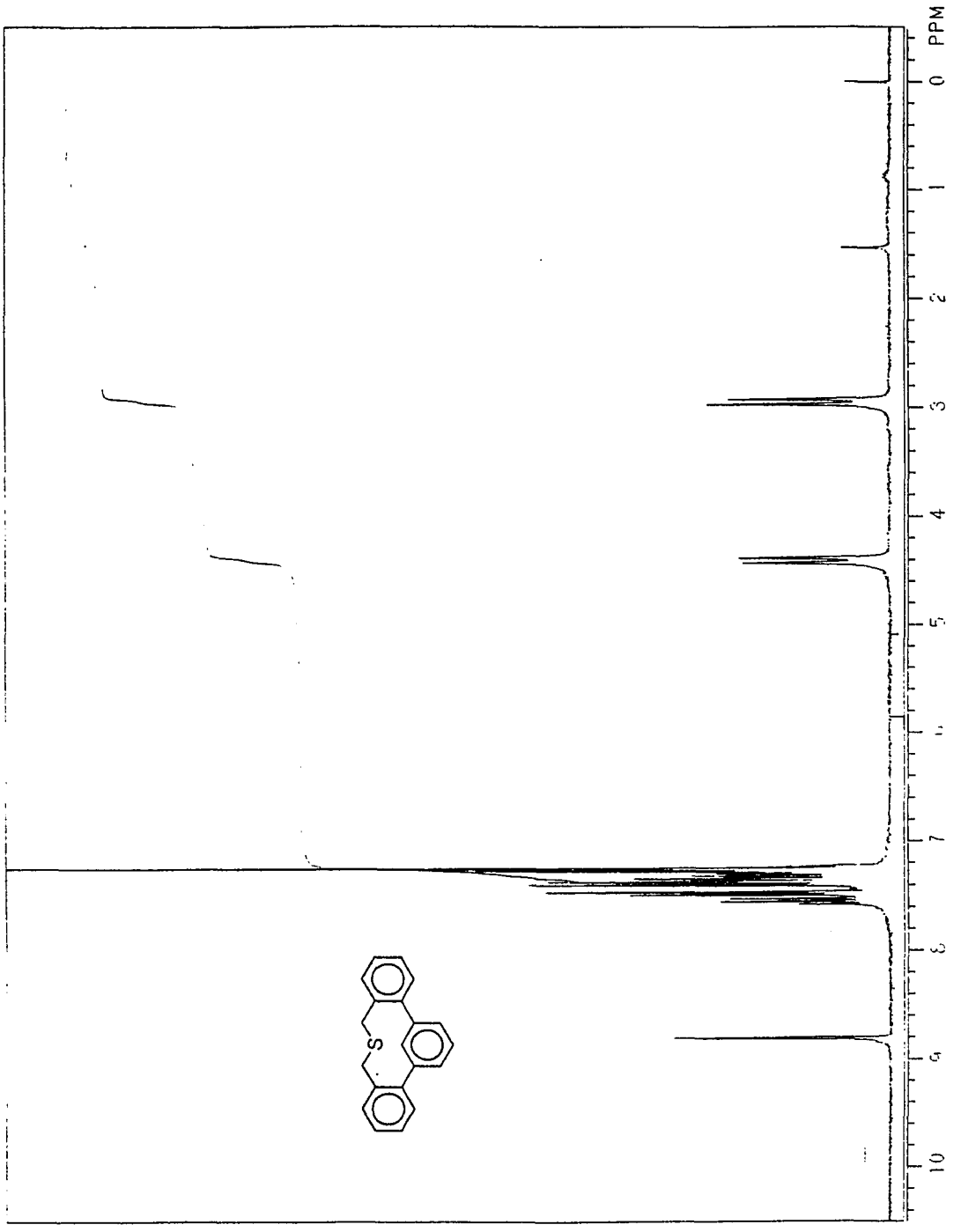

MeO
OMe
10
8
6
4
2
0
PPM

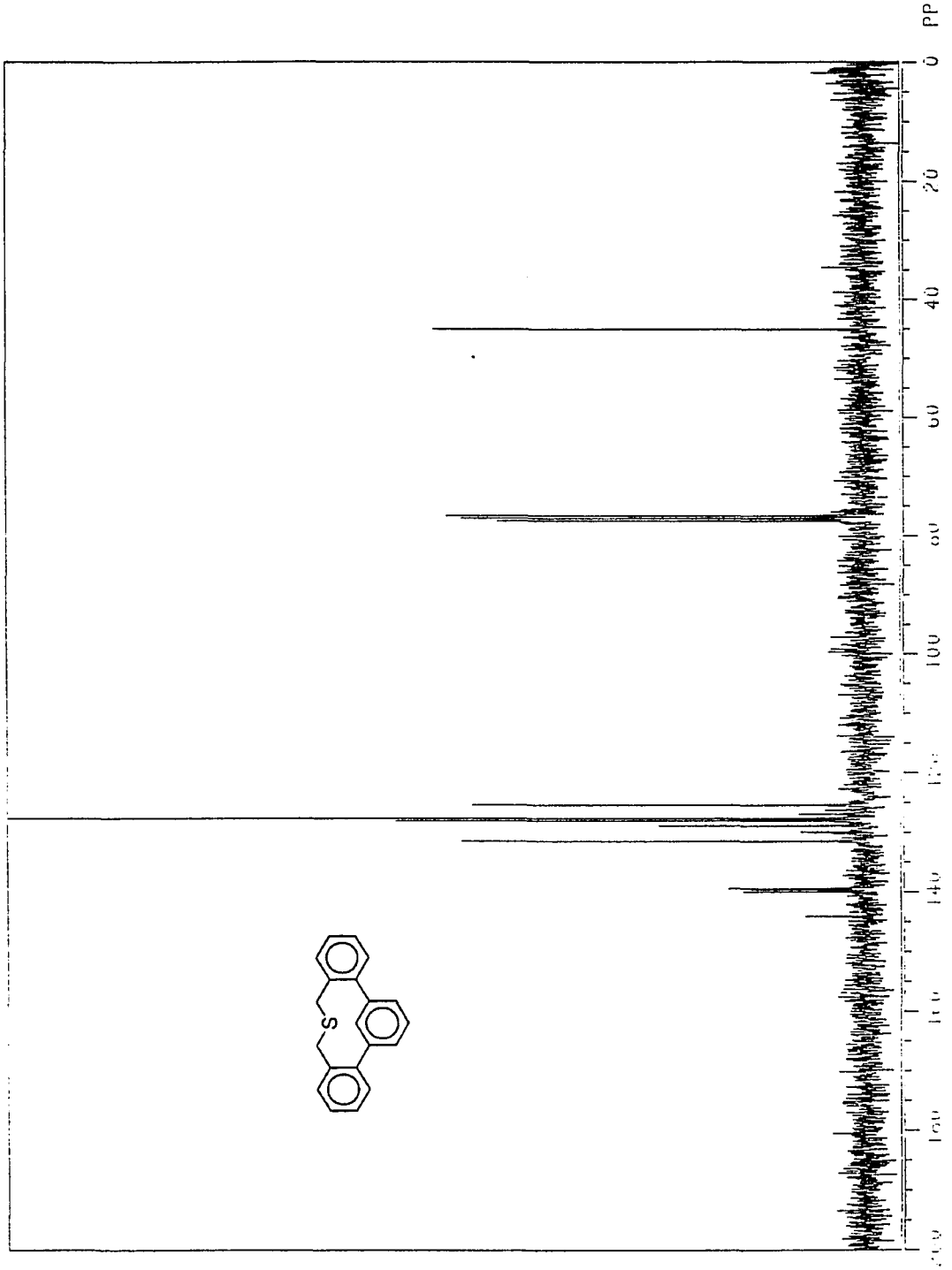

TIC of CSKGDL15I.d
Abundance
600000
500000
400000
300000
200000
100000
0
4
6
8
10
12
14
16
18
Time (min.)
MeO
OMe
Scan 453 (10.027 min) of CSKGDL15I.d
Abundance
100000
80000
60000
40000
20000
0
28
45
91
121
165
195
228
254
288
318
100
200
300
Mass/Charge

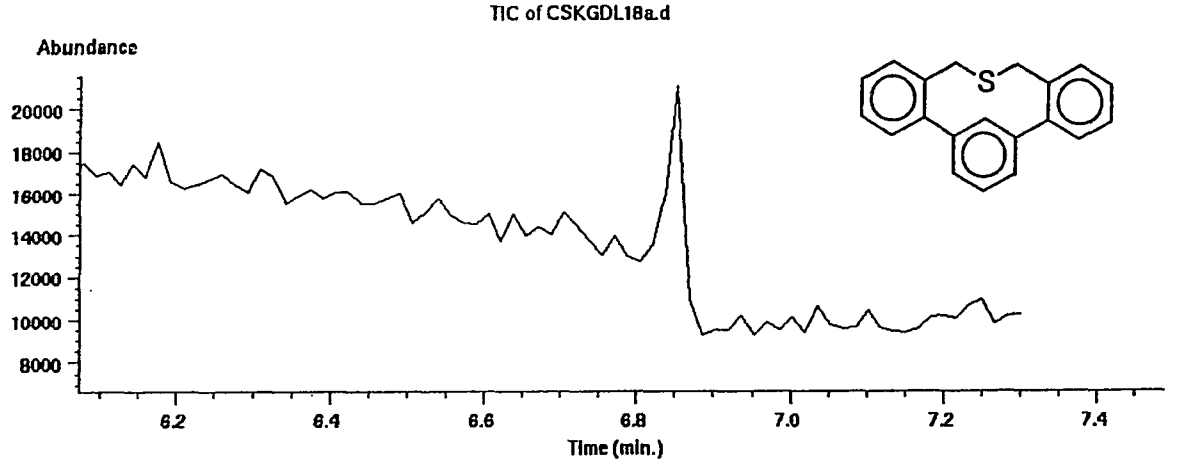

EtO
OEt
10
8
6
4
2
0
PPM

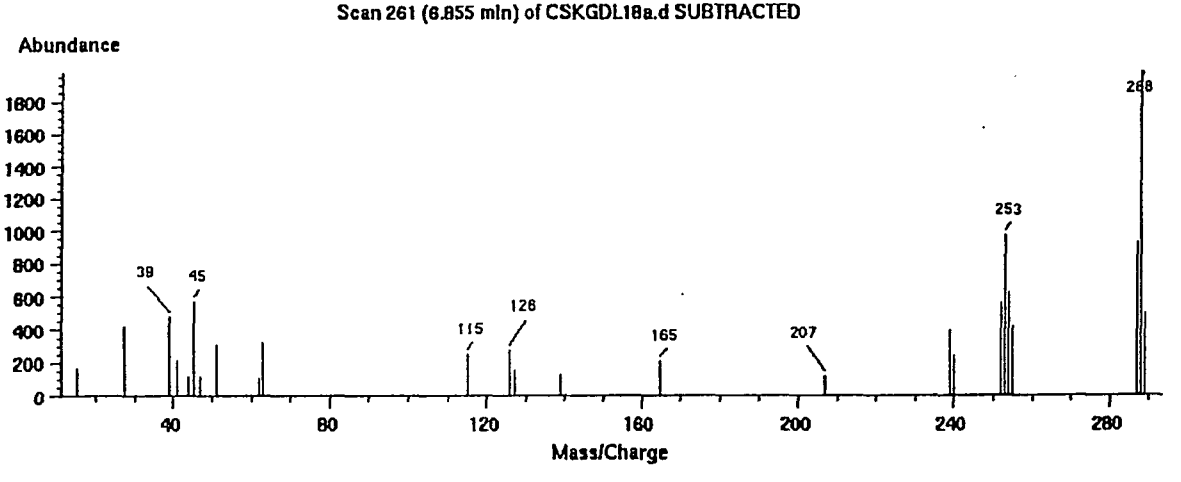

Br
Br
PPM
0
1
2
4
5
7
10

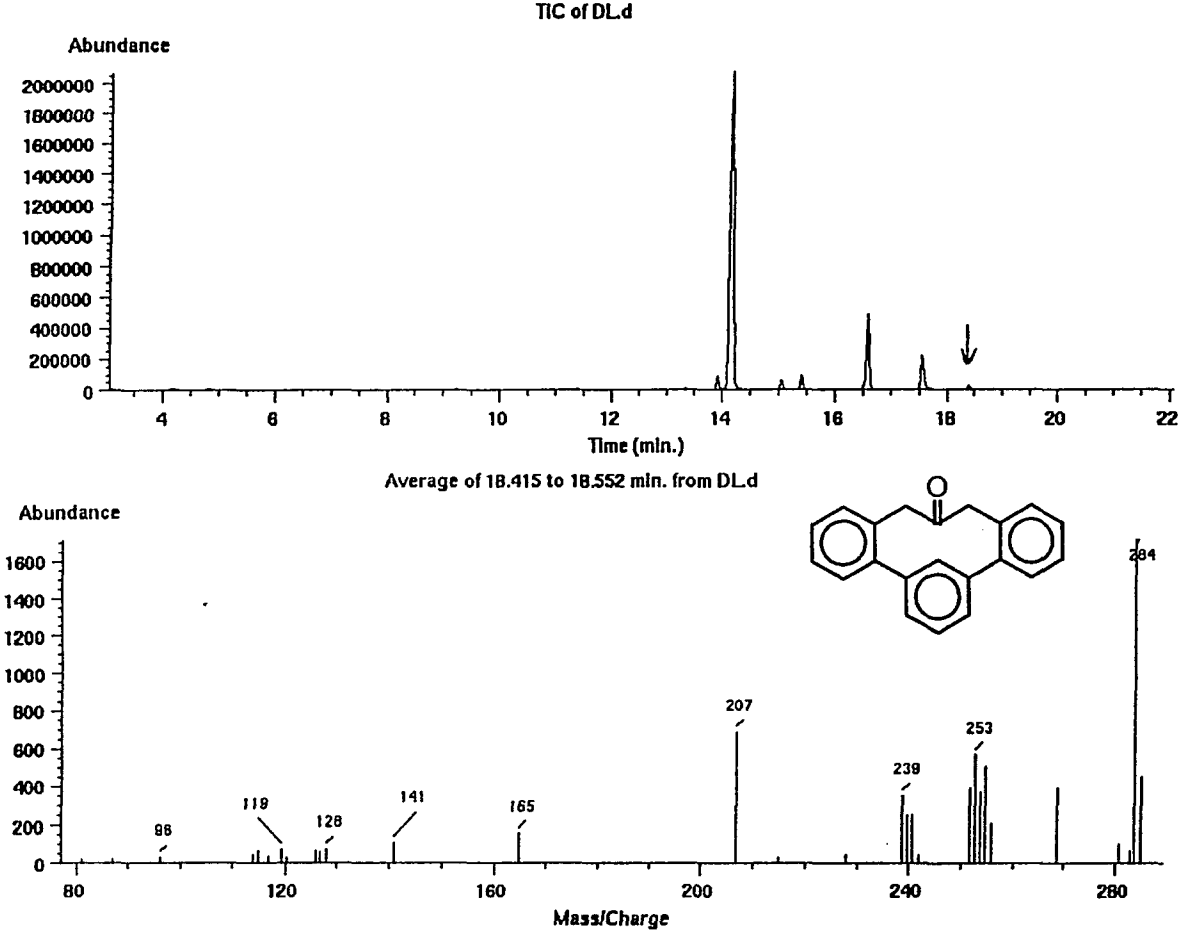

TIC of CSKGDL17a.d
Abundance
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
3
4
5
6
7
8
9
10
Time (min.)
Scan 274 (5.862 min) of CSKGDL17a.d
Abundance
700000
600000
500000
400000
300000
200000
100000
0
83
128
185
215
255
283
337
385
418
100
200
300
400
Mass/Charge
Br
Br

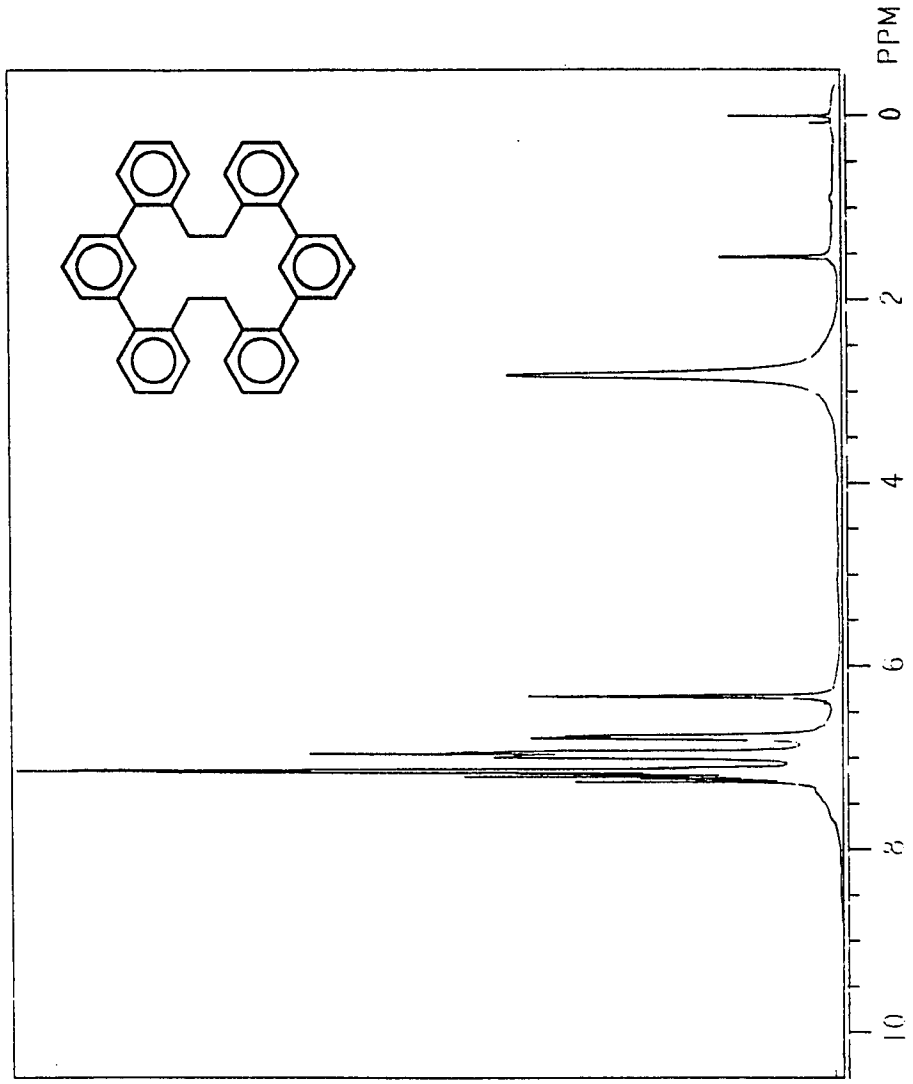

PPM
0
1
2
3
4
5
6
7
8
9
10
S

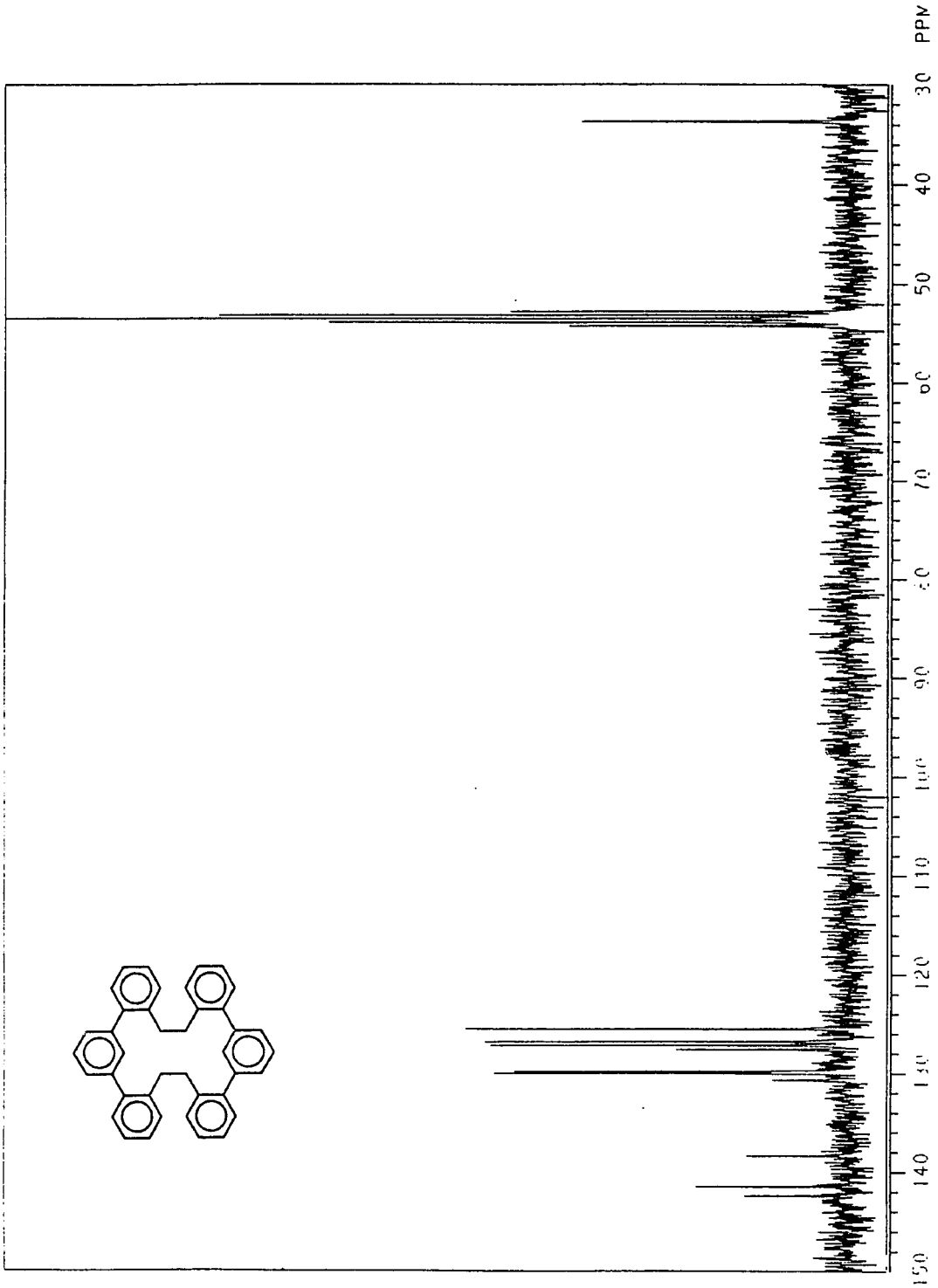

S
PP
0
20
40
60
80
100

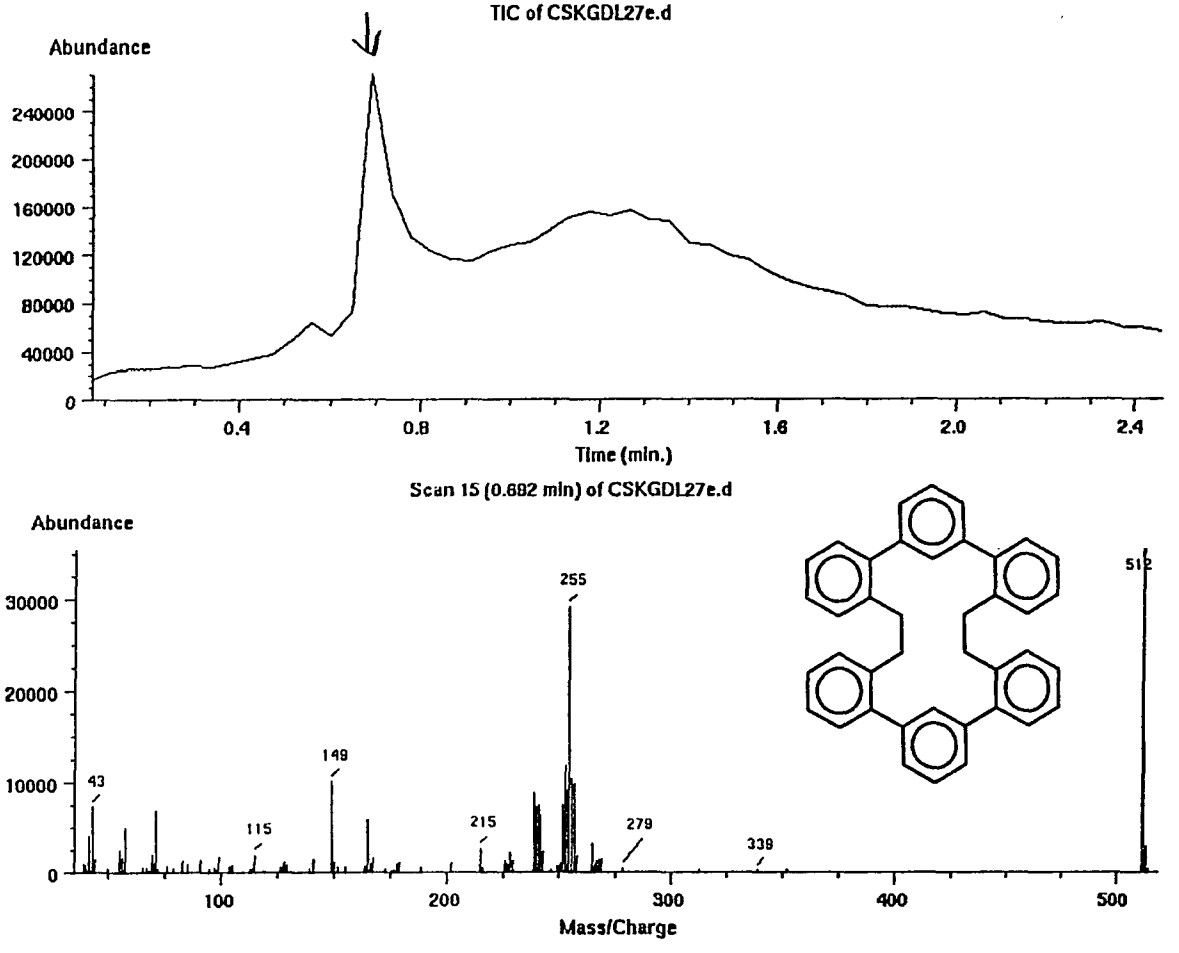

TIC of CSKGDL18a.d
Abundance
20000
18000
16000
14000
12000
10000
8000
6.2
6.4
6.6
6.8
7.0
7.2
7.4
Time (min.)
S

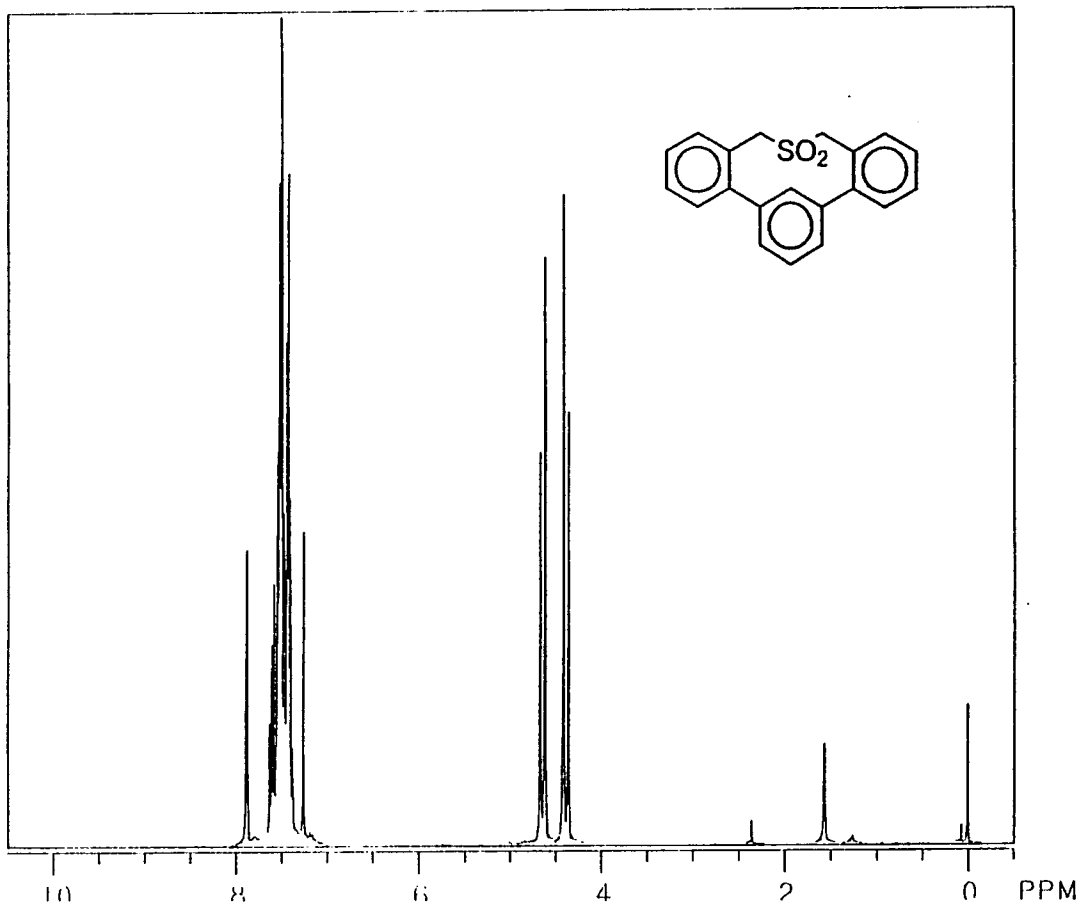

Scan 261 (6.855 min) of CSKGDL18a.d SUBTRACTED
Abundance
1800
1600
1400
1200
1000
800
600
400
200
0
39
45
115
128
165
207
253
268
40
80
120
160
200
240
280
Mass/Charge

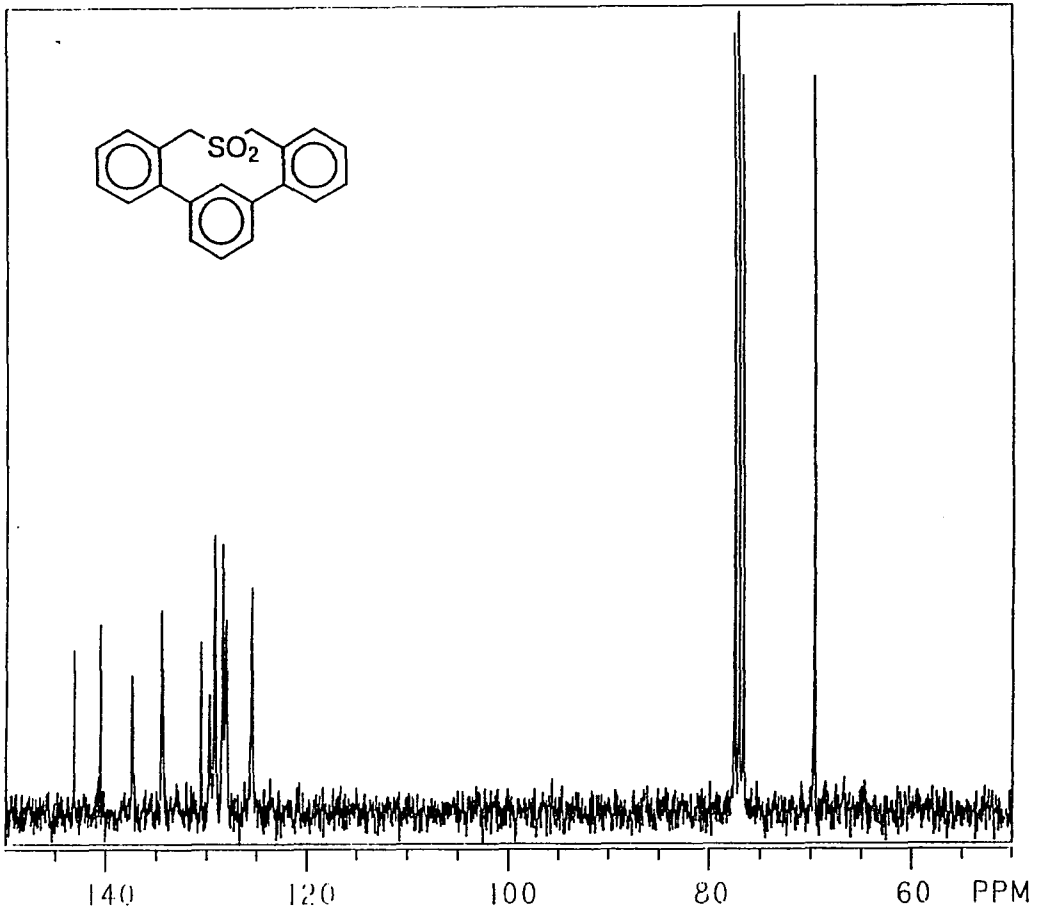

TIC of DL.d
Abundance
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
4
6
8
10
12
14
16
18
20
22
Time (min.)
Average of 18.415 to 18.552 min. from DL.d
Abundance
1600
1400
1200
1000
800
600
400
200
0
98
119
128
141
165
207
239
253
284
80
120
160
200
240
280
Mass/Charge

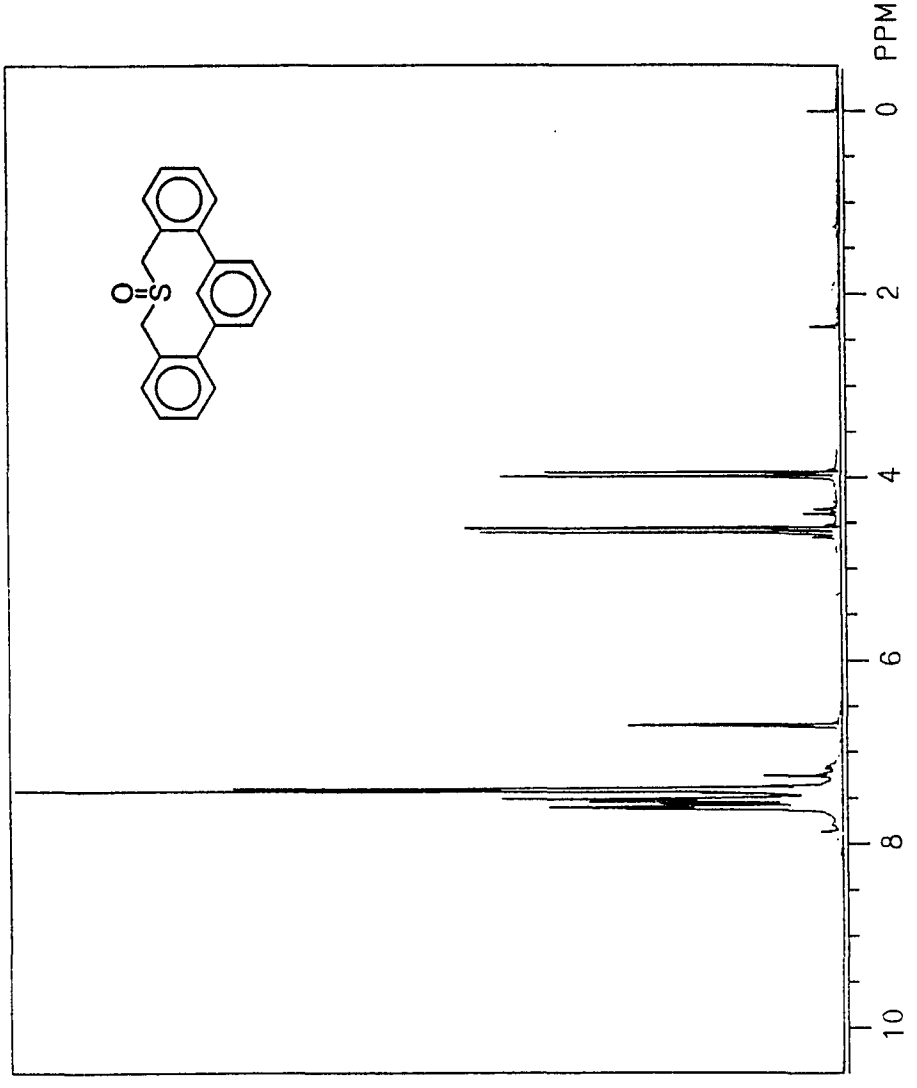

PPM
0
2
4
6
8
10

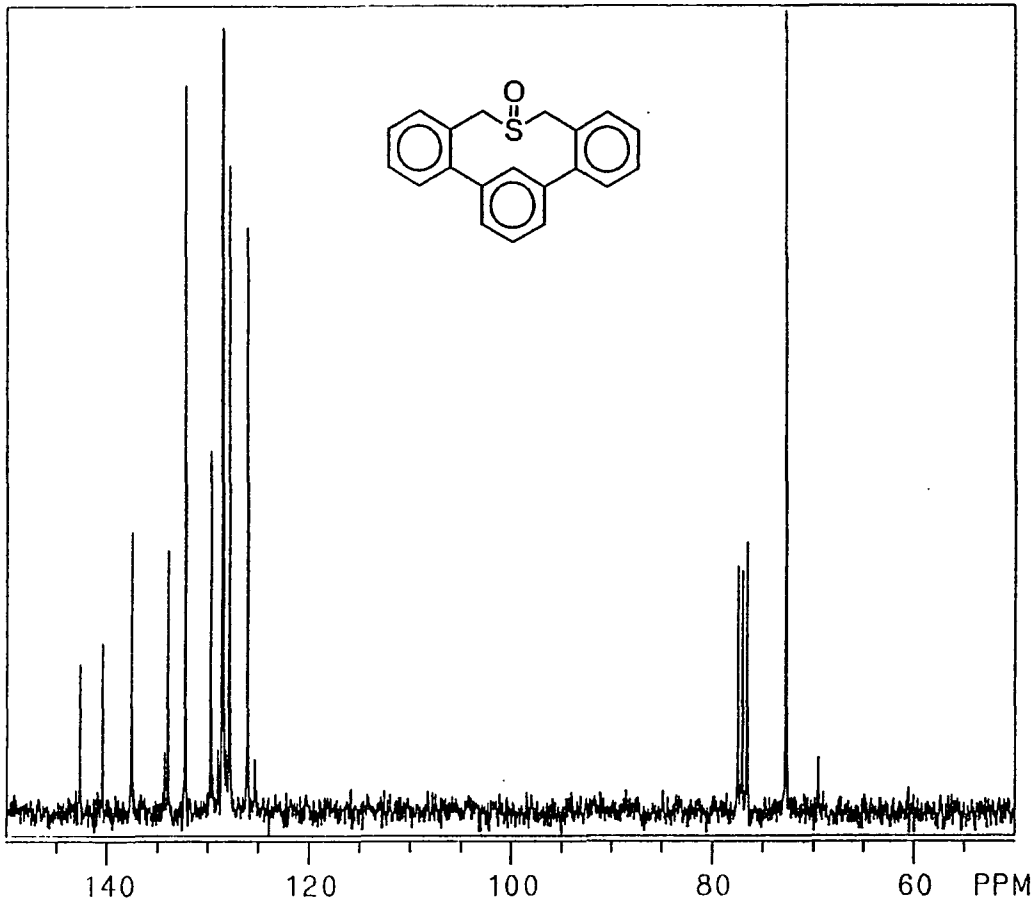

PPM
30
40
50
60
70
90
110
120
140
150

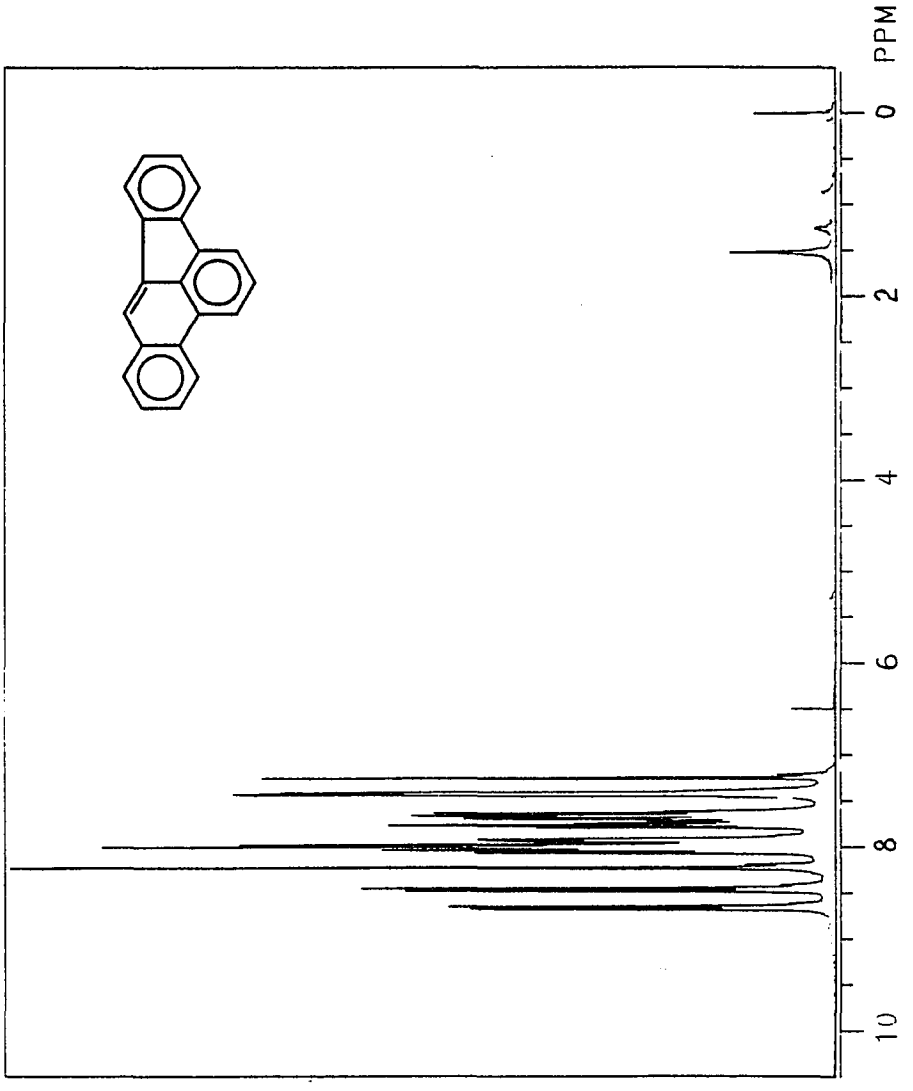

TIC of CSKGDL27e.d
Abundance
240000
200000
160000
120000
80000
40000
0
0.4
0.8
1.2
1.6
2.0
2.4
Time (min.)
Scan 15 (0.682 min) of CSKGDL27e.d
Abundance
30000
20000
10000
0
43
115
149
215
255
279
339
512
100
200
300
400
500
Mass/Charge

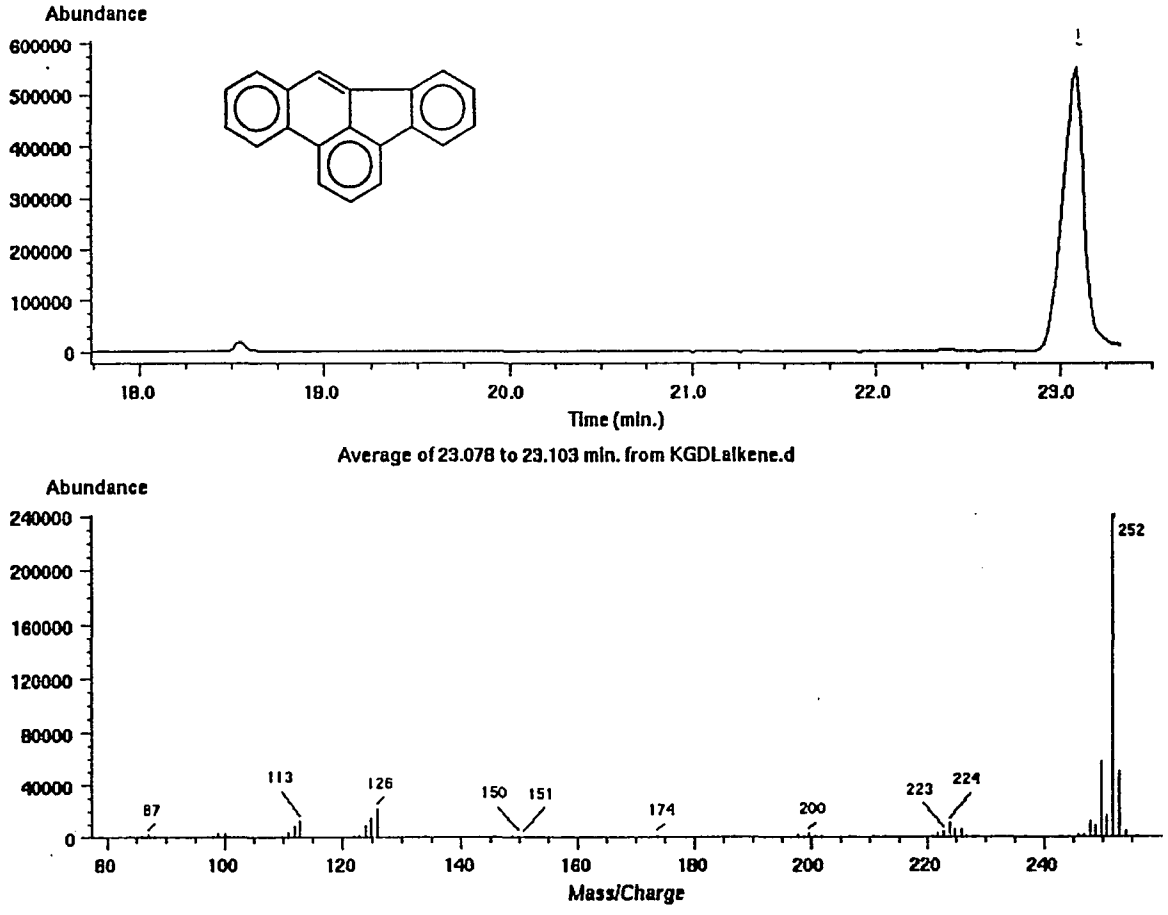

SO2
10
8
6
4
2
0
PPM

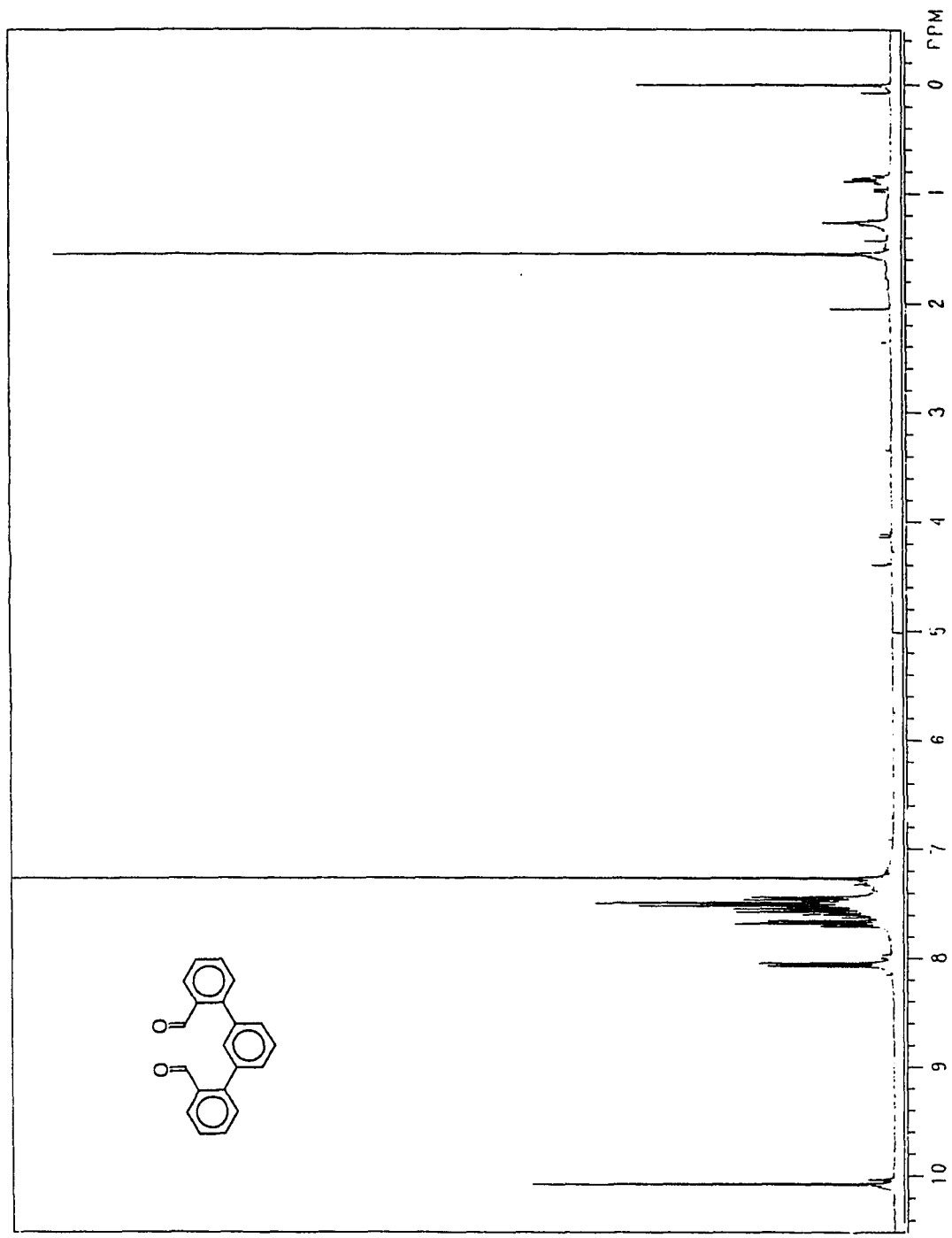

SO2
140
120
100
80
60
PPM


O=S
0
2
4
6
8
10
PPM


O
S
140
120
100
80
60
PPM


PPM
0
2
4
6
8
10


Abundance
600000
500000
400000
300000
200000
100000
0
18.0
19.0
20.0
21.0
22.0
23.0
Time (min.)
Average of 23.078 to 23.103 min. from KGDLalkene.d
Abundance
240000
200000
160000
120000
80000
40000
0
87
113
126
150
151
174
200
223
224
252
80
100
120
140
160
180
200
220
240
Mass/Charge


PPM
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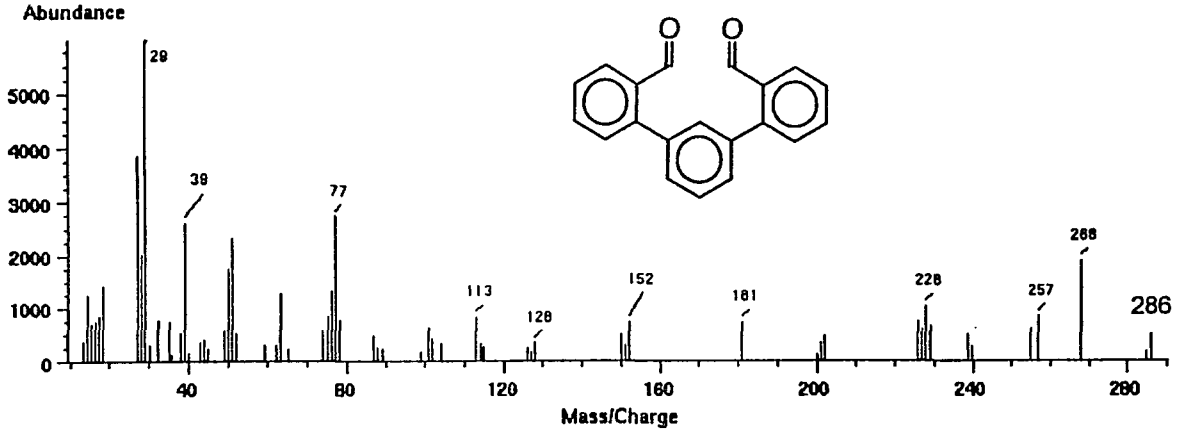
1
2
3
4
5
6
7
8
9
10
O
O


Abundance
5000
4000
3000
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1000
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39
77
113
128
152
181
228
257
268
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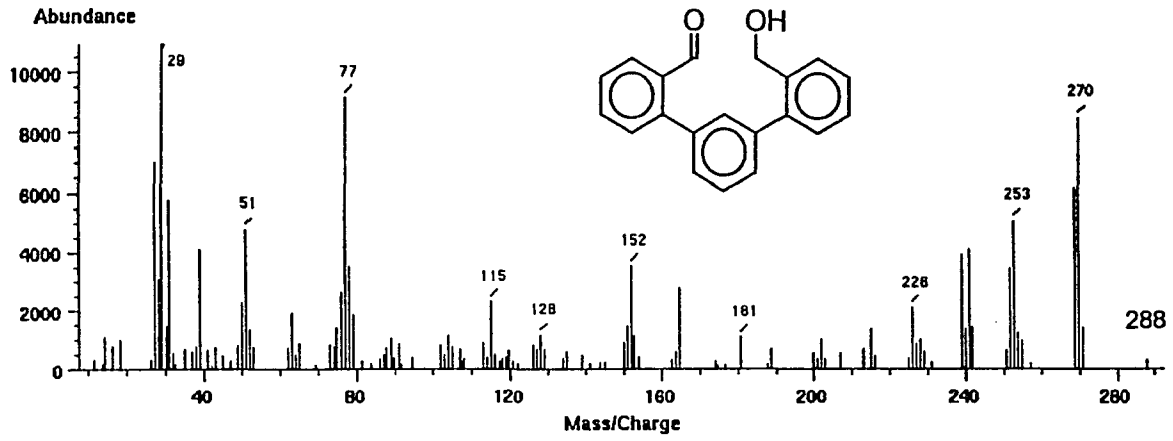
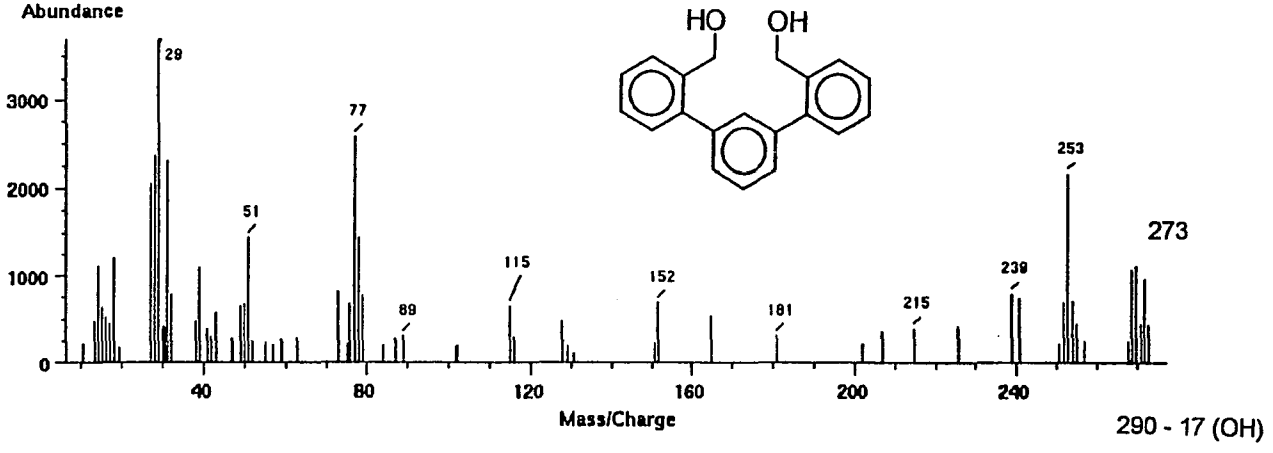
40
80
120
160
200
240
280
Mass/Charge


Abundance
10000
8000
6000
4000
2000
0
29
51
77
115
128
152
181
228
253
270
288
40
80
120
160
200
240
280
Mass/Charge
O
OH


Abundance
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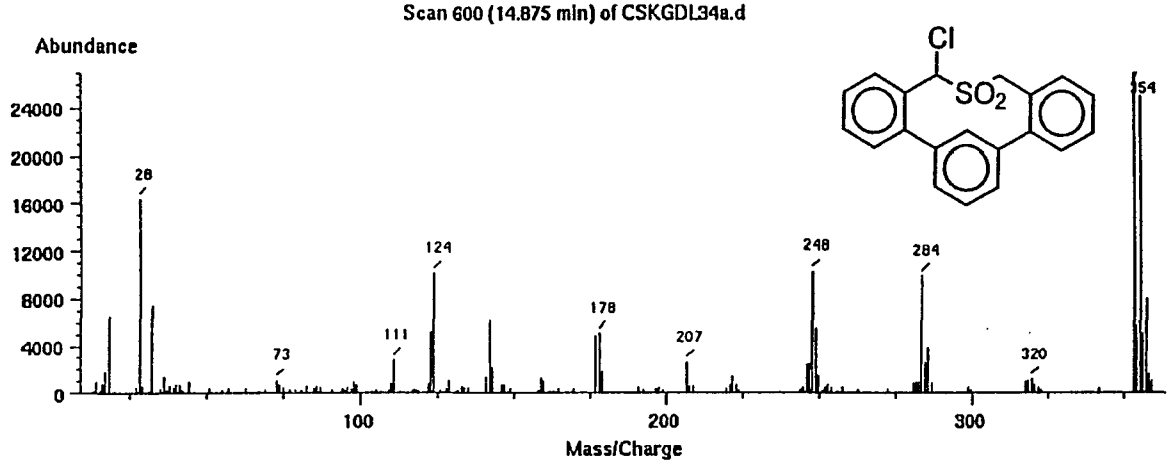
2000
1000
0
29
51
77
89
115
152
181
215
239
253
273
40
80
120
160
200
240
Mass/Charge
HO
OH
290 - 17 (OH)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Abundance
24000
20000
16000
12000
8000
4000
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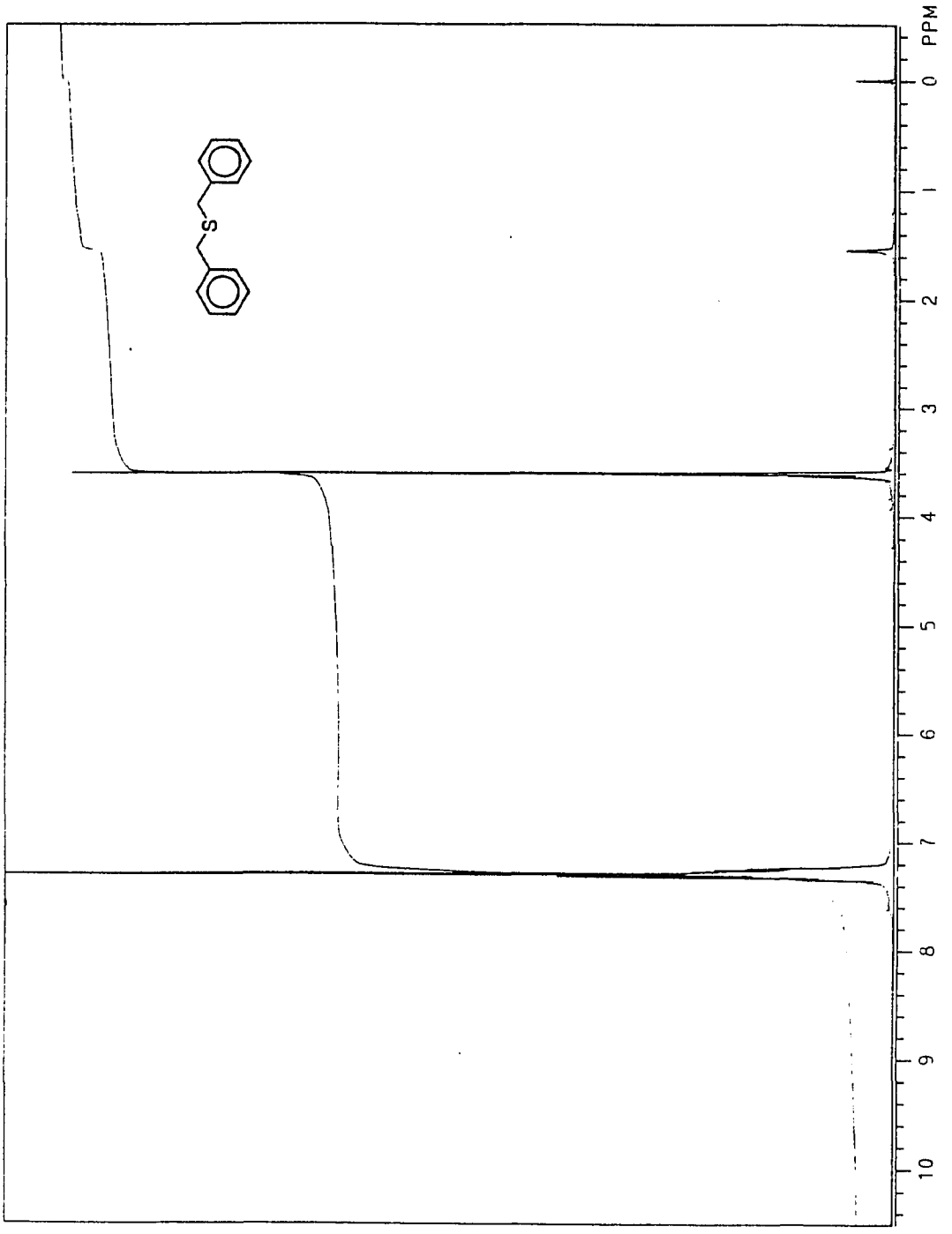
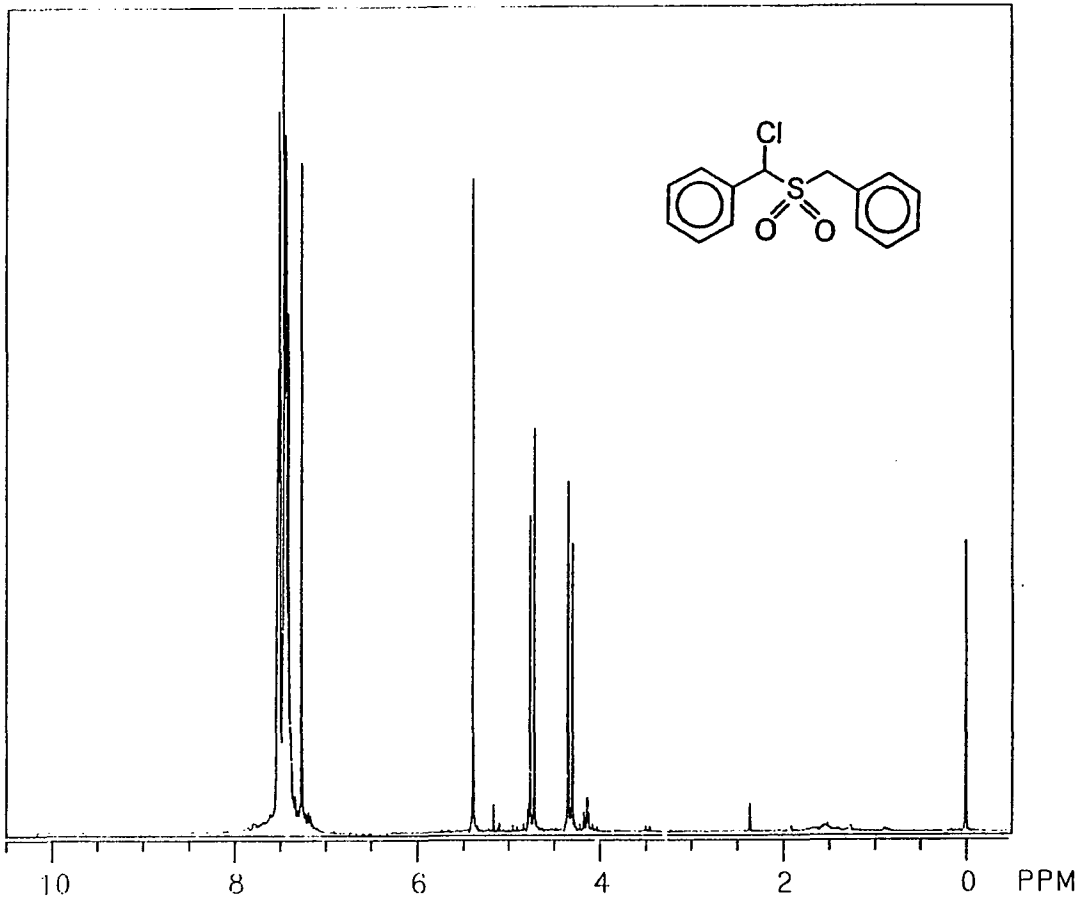
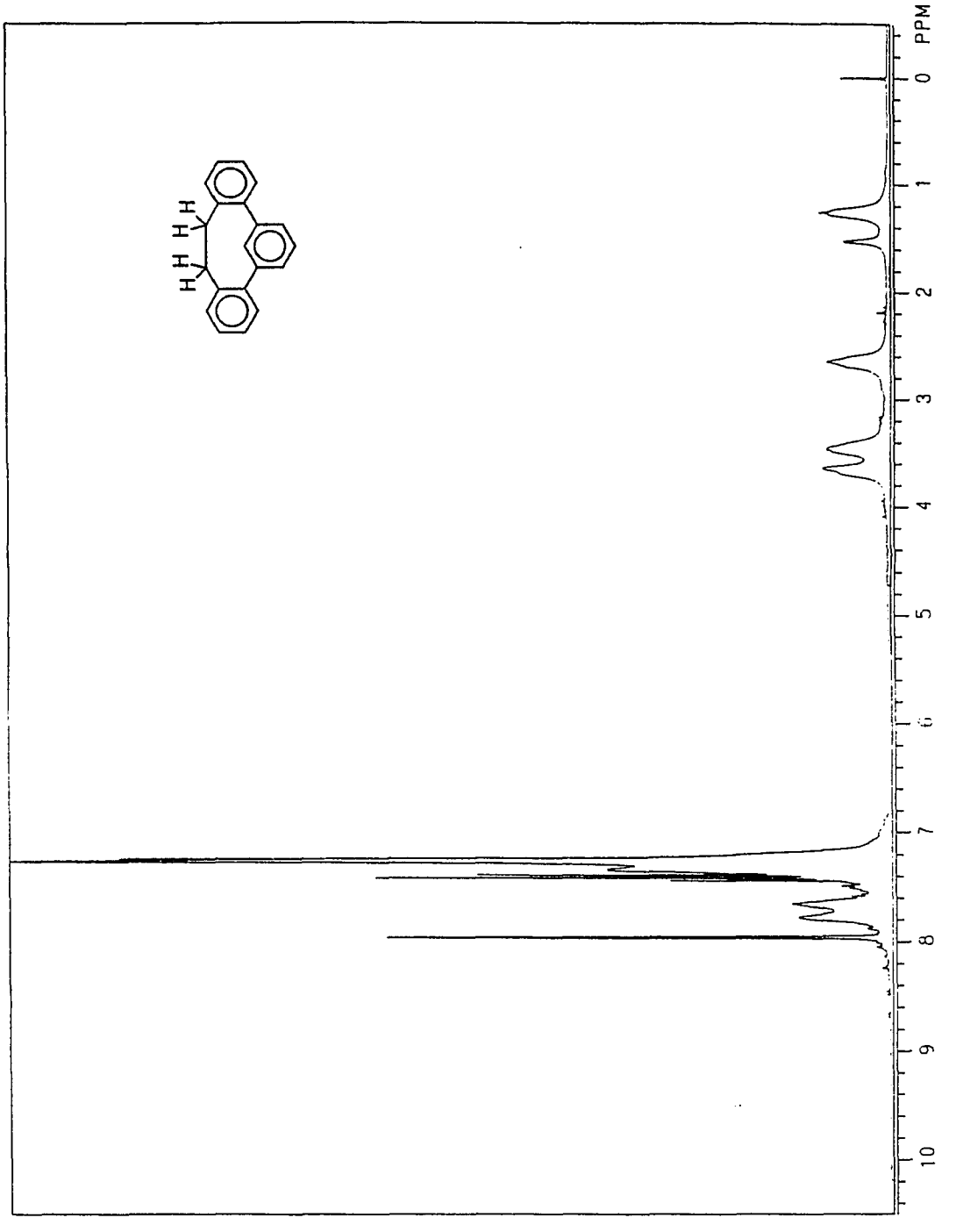
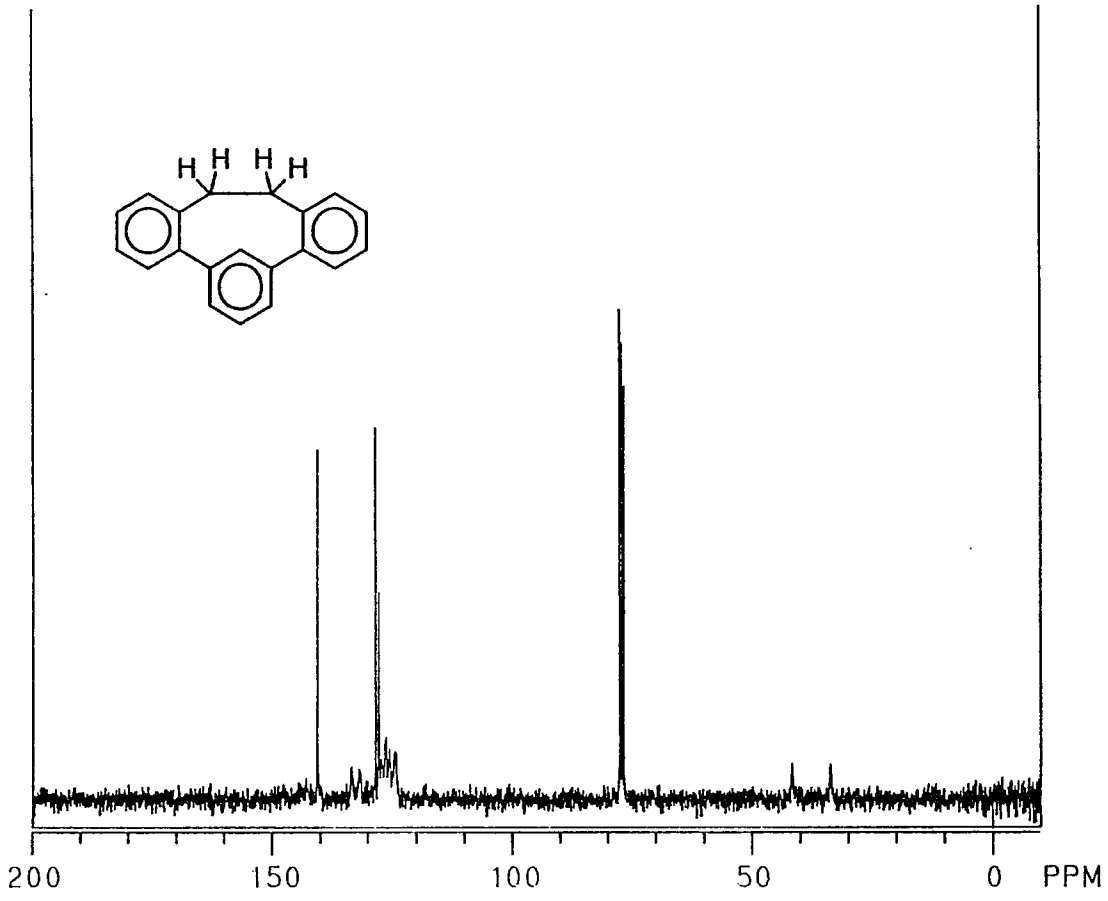
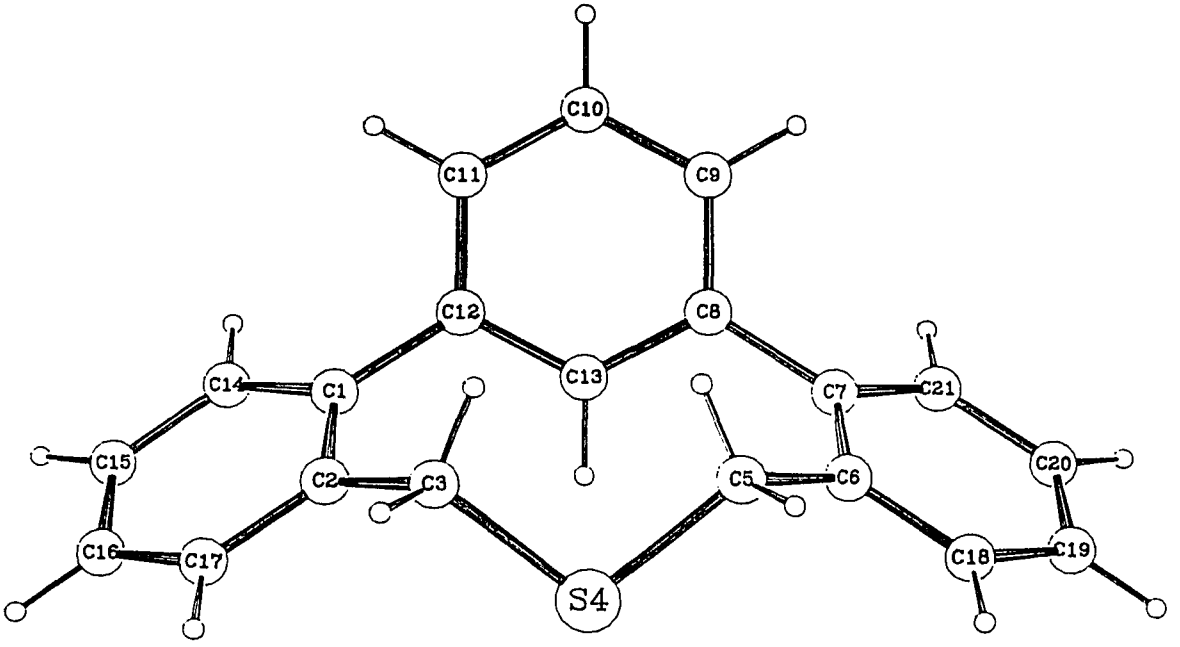
28
73
111
124
178
207
248
284
320
354
100
200
300
Mass/Charge
Cl
SO2


S
PPM
0
1
2
3
4
5
6
7
8
9
10


Cl
S
O
O
10
8
6
4
2
0
PPM


H
H
H
H
H
PPM
0
1
2
3
4
5
6
7
8
9
10


H H H H
200
150
100
50
0
PPM


C10
C11
C9
C12
C8
C14
C1
C13
C7
C21
C15
C2
C3
C5
C6
C20
C16
C17
S4
C18
C19

DL−1

(T150R)

X-ray sample T150 was submitted on February 22, 1994.

Table I. X-ray Data for DL-1 at 295 K

Formula	$C_{20}H_{16}S$
Formula weight	288.42
Crystal size (mm)	0.16 x 0.19 x 0.57
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	13.949(1)
b (Å)	12.597(1)
c (Å)	8.563(2)
β (°)	100.86(1)
V (Å^3)	1477.7(33)
Z	4
d_{calc} (g cm^{-3})	1.296
μ(Cu $K\alpha$) (cm^{-1})	17.9
Absorption correction	numerical
min transmission (%)	63.54
max transmission (%)	77.62
Maximum θ (°)	60
Unique reflections	2189
Observed reflections [$I > 3.0\sigma(I)$]	1522
Number of variables	190
R	0.043
R_w	0.053
$(\Delta\rho)_{max}$ (e Å^{-3})	0.28
$(\Delta\rho)_{min}$ (e Å^{-3})	–0.23

Table II. Final Atomic Parameters for DL-1 at **295 K**

Atom	x	y	z	B(Å^2)
S4	0.07805(6)	0.61825(7)	0.1673(1)	4.07(2)
C1	0.2927(2)	0.4446(2)	0.3337(4)	3.82(7)
C2	0.1931(2)	0.4301(3)	0.2644(4)	3.70(7)
C3	0.1416(2)	0.4959(3)	0.1260(4)	4.13(8)
C5	0.1316(3)	0.7172(3)	0.0500(4)	4.30(8)
C6	0.1746(2)	0.8161(3)	0.1372(4)	3.51(7)
C7	0.2732(2)	0.8227(3)	0.2133(4)	3.46(7)
C8	0.3357(2)	0.7265(3)	0.2270(4)	3.63(7)
C9	0.4228(2)	0.7197(3)	0.1698(4)	4.64(8)
C10	0.4710(2)	0.6233(3)	0.1756(5)	5.43(9)
C11	0.4322(2)	0.5321(3)	0.2293(5)	5.02(9)
C12	0.3456(2)	0.5380(3)	0.2886(4)	3.71(7)
C13	0.3028(2)	0.6366(2)	0.2935(3)	3.43(7)
C14	0.3378(3)	0.3715(3)	0.4462(4)	5.15(9)
C15	0.2862(3)	0.2869(3)	0.4928(5)	5.9(1)
C16	0.1892(3)	0.2741(3)	0.4278(5)	6.0(1)
C17	0.1438(3)	0.3442(3)	0.3135(4)	4.91(9)
C18	0.1172(2)	0.9071(3)	0.1295(4)	4.42(8)
C19	0.1547(3)	1.0020(3)	0.1949(4)	4.94(8)
C20	0.2516(3)	1.0088(3)	0.2676(4)	5.05(9)
C21	0.3097(2)	0.9194(3)	0.2760(4)	4.41(8)
H3A	0.192	0.517	0.063	5.0
H3B	0.092	0.449	0.060	5.0
H5A	0.079	0.741	-0.040	5.2
H5B	0.185	0.681	0.007	5.2
H9	0.450	0.784	0.125	5.6
H10	0.535	0.620	0.141	6.6
H11	0.466	0.462	0.226	6.0
H13	0.246	0.643	0.348	4.2
H14	0.409	0.380	0.494	6.2
H15	0.320	0.235	0.574	7.1
H16	0.152	0.214	0.463	7.3
H17	0.074	0.333	0.265	5.9
H18	0.047	0.904	0.075	5.4
H19	0.112	1.066	0.189	6.0
H20	0.279	1.078	0.314	6.1
H21	0.380	0.924	0.329	5.3

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(cosγ)*B(1,2) + ac(cosβ)*B(1,3) + bc(cosα)*B(2,3)]

Table III. Final Anisotropic Thermal Parameters (U's) for DL-1 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
S4	0.0540(4)	0.0540(4)	0.0481(4)	-0.0045(5)	0.0139(3)	-0.0033(4)
C1	0.063(2)	0.044(2)	0.040(2)	0.005(2)	0.013(1)	-0.005(2)
C2	0.060(2)	0.043(2)	0.040(2)	-0.002(2)	0.016(1)	-0.010(1)
C3	0.055(2)	0.054(2)	0.045(2)	-0.004(2)	0.005(2)	-0.012(2)
C5	0.063(2)	0.063(2)	0.036(2)	-0.008(2)	0.006(2)	0.007(2)
C6	0.052(2)	0.051(2)	0.032(1)	-0.003(2)	0.014(1)	0.007(1)
C7	0.051(2)	0.046(2)	0.039(2)	-0.006(2)	0.020(1)	-0.000(1)
C8	0.043(2)	0.056(2)	0.040(2)	-0.007(2)	0.007(1)	-0.007(2)
C9	0.043(2)	0.073(2)	0.062(2)	-0.004(2)	0.013(2)	0.002(2)
C10	0.040(2)	0.087(3)	0.083(2)	0.004(2)	0.020(2)	0.006(2)
C11	0.043(2)	0.071(2)	0.076(2)	0.010(2)	0.011(2)	0.004(2)
C12	0.043(2)	0.055(2)	0.041(2)	0.003(2)	0.003(1)	-0.006(2)
C13	0.045(2)	0.048(2)	0.038(2)	-0.004(2)	0.008(1)	-0.004(1)
C14	0.086(2)	0.054(2)	0.054(2)	0.017(2)	0.010(2)	-0.004(2)
C15	0.125(3)	0.044(2)	0.057(2)	0.013(2)	0.024(2)	0.004(2)
C16	0.113(3)	0.055(2)	0.070(2)	-0.004(2)	0.038(2)	-0.001(2)
C17	0.081(2)	0.049(2)	0.062(2)	-0.010(2)	0.026(2)	-0.012(2)
C18	0.061(2)	0.062(2)	0.049(2)	0.006(2)	0.021(1)	0.013(2)
C19	0.085(2)	0.052(2)	0.059(2)	0.006(2)	0.033(2)	0.010(2)
C20	0.083(2)	0.050(2)	0.065(2)	-0.009(2)	0.031(2)	-0.003(2)
C21	0.061(2)	0.051(2)	0.060(2)	-0.014(2)	0.023(2)	-0.001(2)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

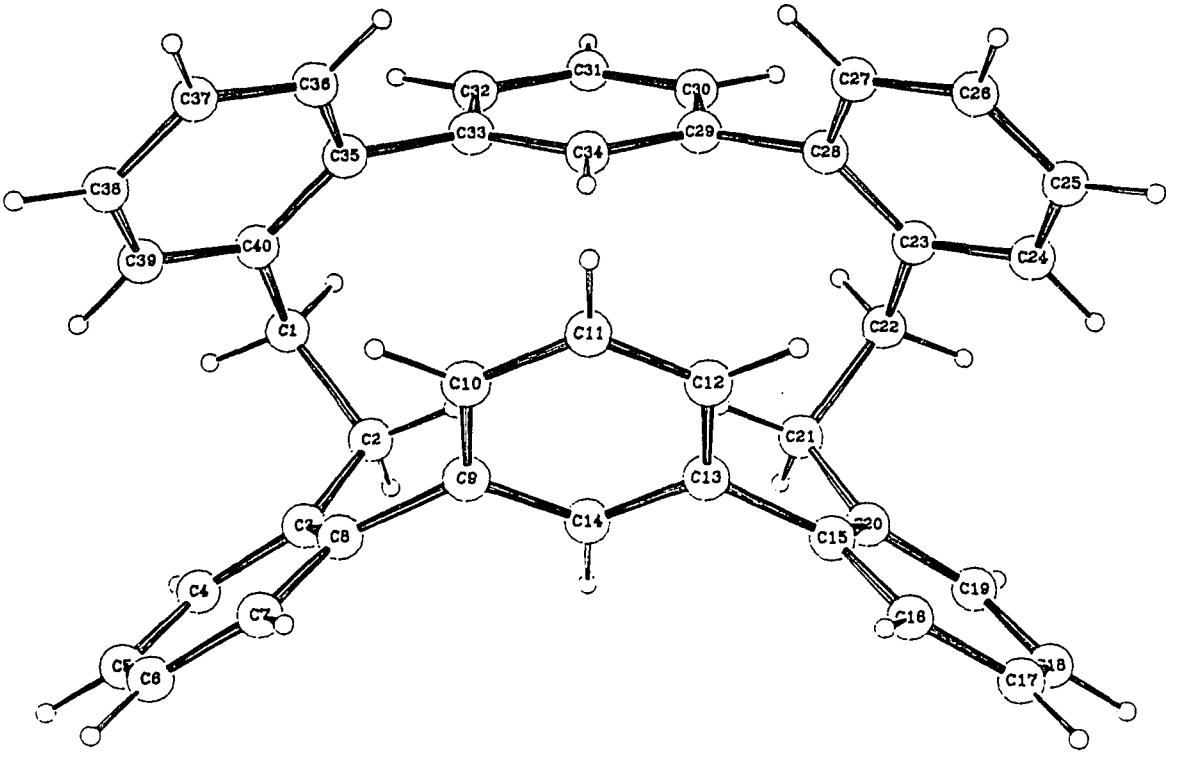
Table IV. Bond Distances (Å) for DL-1 at **295 K**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S4	C3	1.845(4)	C8	C9	1.396(5)
S4	C5	1.844(4)	C8	C13	1.384(5)
C1	C2	1.416(4)	C9	C10	1.384(5)
C1	C12	1.478(5)	C10	C11	1.385(6)
C1	C14	1.394(5)	C11	C12	1.398(5)
C2	C3	1.513(4)	C12	C13	1.382(4)
C2	C17	1.388(5)	C14	C15	1.387(6)
C5	C6	1.517(5)	C15	C16	1.372(6)
C6	C7	1.410(4)	C16	C17	1.381(5)
C6	C18	1.392(5)	C18	C19	1.380(5)
C7	C8	1.484(4)	C19	C20	1.380(5)
C7	C21	1.389(5)	C20	C21	1.382(5)

Table V. Bond Angles (°) for DL-1 at **295 K**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C3	S4	C5	101.6(2)	C9	C8	C13	118.1(3)
C2	C1	C12	119.5(3)	C8	C9	C10	119.4(3)
C2	C1	C14	119.0(3)	C9	C10	C11	121.5(3)
C12	C1	C14	121.5(3)	C10	C11	C12	119.7(3)
C1	C2	C3	122.7(3)	C1	C12	C11	124.1(3)
C1	C2	C17	118.5(3)	C1	C12	C13	117.9(3)
C3	C2	C17	118.4(3)	C11	C12	C13	117.8(3)
S4	C3	C2	118.8(2)	C8	C13	C12	123.0(3)
S4	C5	C6	116.8(2)	C1	C14	C15	121.0(3)
C5	C6	C7	122.5(3)	C14	C15	C16	120.0(3)
C5	C6	C18	118.9(3)	C15	C16	C17	119.9(4)
C7	C6	C18	118.4(3)	C2	C17	C16	121.7(3)
C6	C7	C8	119.8(3)	C6	C18	C19	121.6(3)
C6	C7	C21	119.0(3)	C18	C19	C20	120.1(3)
C8	C7	C21	121.2(3)	C19	C20	C21	119.2(3)
C7	C8	C9	124.0(3)	C7	C21	C20	121.7(3)
C7	C8	C13	117.7(3)				

Standard deviations are in parentheses.


C31
C32
C30
C27
C26
C37
C36
C33
C29
C28
C35
C34
C25
C38
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C24
C39
C22
C1
C11
C10
C12
C2
C21
C9
C13
C14
C15
C20
C8
C4
C19
C7
C18
C6
C17

DL-2

X-ray sample T156 was submitted on April 27, 1994.

Table I. X-ray Data for DL-2 at **295 K**

Formula	$C_{40}H_{32}$
Formula weight	512.70
Crystal size (mm)	0.31 x 0.48 x 0.48
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	13.879(1)
b (Å)	8.824(1)
c (Å)	24.550(2)
β (°)	106.32(1)
V (Å^3)	2885.4(50)
Z	4
d_{calc} (g cm^{-3})	1.180
μ(Cu $K\alpha$) (cm^{-1})	4.69
Absorption correction	none
Maximum θ (°)	60
Unique reflections	4280
Observed reflections [$I > 3.0\sigma(I)$]	2837
Number of variables	361
R	0.048
R_w	0.064
$(\Delta\rho)_{max}$ (e Å^{-3})	0.16
$(\Delta\rho)_{min}$ (e Å^{-3})	–0.15

Table II. Final Atomic Parameters for DL-2 at **295 K**

Atom	x	y	z	B(Å^2)
C1	0.4466(2)	0.3703(4)	0.3846(1)	5.05(7)
C2	0.4309(2)	0.5113(4)	0.3466(1)	4.91(7)
C3	0.3944(2)	0.6449(3)	0.3737(1)	4.46(6)
C4	0.4604(2)	0.7081(3)	0.4221(1)	5.51(8)
C5	0.4306(3)	0.8215(4)	0.4524(1)	6.71(9)
C6	0.3324(3)	0.8745(4)	0.4349(1)	6.79(9)
C7	0.2669(2)	0.8152(3)	0.3865(1)	5.61(8)
C8	0.2969(2)	0.7005(3)	0.35513(9)	4.35(6)
C9	0.2238(2)	0.6513(3)	0.3010(1)	4.14(6)
C10	0.1335(2)	0.5824(3)	0.3000(1)	4.77(7)
C11	0.0640(2)	0.5465(4)	0.2488(1)	5.32(7)
C12	0.0835(2)	0.5815(4)	0.1978(1)	4.83(7)
C13	0.1729(2)	0.6503(3)	0.1977(1)	4.17(6)
C14	0.2424(2)	0.6828(3)	0.2493(1)	4.52(6)
C15	0.1936(2)	0.7006(3)	0.1435(1)	4.31(6)
C16	0.1348(2)	0.8160(3)	0.1124(1)	5.36(8)
C17	0.1524(2)	0.8752(4)	0.0643(1)	5.96(8)
C18	0.2322(2)	0.8193(4)	0.0466(1)	6.09(8)
C19	0.2911(2)	0.7036(3)	0.0767(1)	5.25(7)
C20	0.2728(2)	0.6420(3)	0.1252(1)	4.29(6)
C21	0.3349(2)	0.5070(3)	0.1528(1)	4.75(7)
C22	0.3117(2)	0.3659(4)	0.1147(1)	4.84(7)
C23	0.2045(2)	0.3137(3)	0.10436(9)	3.90(6)
C24	0.1327(2)	0.3600(3)	0.0549(1)	4.79(7)
C25	0.0326(2)	0.3222(4)	0.0451(1)	5.51(8)
C26	0.0017(2)	0.2408(4)	0.0851(1)	5.48(8)
C27	0.0718(2)	0.1949(3)	0.1345(1)	4.65(7)
C28	0.1733(2)	0.2282(3)	0.14443(9)	3.80(6)
C29	0.2445(2)	0.1744(3)	0.19840(9)	3.76(6)
C30	0.3203(2)	0.0710(3)	0.1991(1)	4.28(6)
C31	0.3833(2)	0.0206(3)	0.2503(1)	4.45(6)
C32	0.3716(2)	0.0719(3)	0.3013(1)	4.21(6)
C33	0.2961(2)	0.1755(3)	0.30157(9)	3.76(6)
C34	0.2331(2)	0.2252(3)	0.2498(1)	3.88(6)
C35	0.2789(2)	0.2319(3)	0.35549(9)	3.90(6)
C36	0.1874(2)	0.1995(4)	0.3656(1)	4.70(7)
C37	0.1662(2)	0.2462(4)	0.4149(1)	5.52(7)
C38	0.2367(2)	0.3277(4)	0.4546(1)	5.65(8)
C39	0.3270(2)	0.3629(3)	0.4443(1)	5.22(7)
C40	0.3503(2)	0.3175(3)	0.3953(1)	4.15(6)
H1A	0.496	0.395	0.422	6.1
H1B	0.474	0.287	0.366	6.1
H2A	0.380	0.487	0.310	5.9
H2B	0.496	0.539	0.339	5.9
H4	0.531	0.670	0.435	6.6
H5	0.479	0.865	0.487	8.0

Table II (cont.). Final Atomic Parameters for DL-2 at **295 K**

Atom	x	y	z	B(Å^2)
H6	0.309	0.955	0.457	8.1
H7	0.197	0.855	0.374	6.7
H10	0.118	0.558	0.337	5.7
H11	0.000	0.495	0.249	6.4
H12	0.033	0.557	0.161	5.8
H14	0.308	0.730	0.249	5.4
H16	0.078	0.857	0.125	6.4
H17	0.108	0.957	0.042	7.1
H18	0.247	0.862	0.012	7.3
H19	0.348	0.663	0.063	6.3
H21A	0.320	0.484	0.189	5.7
H21B	0.408	0.533	0.160	5.7
H22A	0.358	0.282	0.133	5.8
H22B	0.324	0.390	0.077	5.8
H24	0.154	0.421	0.026	5.7
H25	-0.017	0.354	0.009	6.6
H26	-0.071	0.215	0.079	6.6
H27	0.049	0.137	0.164	5.6
H30	0.329	0.033	0.163	5.1
H31	0.438	-0.054	0.250	5.3
H32	0.417	0.035	0.338	5.1
H34	0.178	0.299	0.250	4.7
H36	0.136	0.141	0.337	5.6
H37	0.100	0.221	0.422	6.6
H38	0.223	0.361	0.491	6.8
H39	0.377	0.423	0.473	6.3

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$

Table III. Final Anisotropic Thermal Parameters (U's) for DL-2 at **295 K**

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C1	0.048(1)	0.077(2)	0.058(2)	0.004(1)	-0.001(1)	-0.009(2)
C2	0.053(1)	0.083(2)	0.052(1)	-0.008(1)	0.018(1)	-0.004(1)
C3	0.066(1)	0.062(2)	0.042(1)	-0.017(1)	0.016(1)	-0.000(1)
C4	0.085(2)	0.070(2)	0.048(1)	-0.021(2)	0.008(1)	-0.002(2)
C5	0.127(2)	0.069(2)	0.049(2)	-0.028(2)	0.008(2)	-0.003(2)
C6	0.139(3)	0.069(2)	0.049(1)	-0.006(2)	0.025(2)	-0.002(2)
C7	0.103(2)	0.062(2)	0.050(1)	0.002(2)	0.025(1)	0.002(1)
C8	0.070(1)	0.058(2)	0.039(1)	-0.009(1)	0.019(1)	0.001(1)
C9	0.057(1)	0.053(2)	0.049(1)	0.001(1)	0.018(1)	0.001(1)
C10	0.057(1)	0.068(2)	0.060(1)	0.008(1)	0.023(1)	0.002(1)
C11	0.050(1)	0.081(2)	0.072(2)	0.002(2)	0.019(1)	0.001(2)
C12	0.048(1)	0.070(2)	0.062(1)	0.004(1)	0.011(1)	0.000(2)
C13	0.052(1)	0.057(2)	0.046(1)	0.003(1)	0.009(1)	0.000(1)
C14	0.064(1)	0.061(2)	0.046(1)	-0.006(1)	0.013(1)	0.001(1)
C15	0.059(1)	0.058(2)	0.040(1)	-0.010(1)	0.004(1)	0.001(1)
C16	0.079(2)	0.062(2)	0.053(2)	-0.001(2)	0.003(1)	0.000(2)
C17	0.104(2)	0.063(2)	0.047(2)	-0.006(2)	0.001(1)	0.007(2)
C18	0.107(2)	0.072(2)	0.046(1)	-0.025(2)	0.012(1)	0.002(2)
C19	0.080(2)	0.067(2)	0.049(1)	-0.017(2)	0.012(1)	0.003(1)
C20	0.054(1)	0.061(2)	0.043(1)	-0.014(1)	0.006(1)	0.001(1)
C21	0.043(1)	0.083(2)	0.053(1)	-0.003(1)	0.010(1)	0.007(1)
C22	0.059(1)	0.078(2)	0.054(1)	0.012(1)	0.027(1)	0.008(1)
C23	0.053(1)	0.056(2)	0.040(1)	0.007(1)	0.0148(9)	-0.005(1)
C24	0.072(2)	0.064(2)	0.042(1)	0.005(2)	0.010(1)	-0.006(1)
C25	0.075(2)	0.073(2)	0.050(2)	0.003(2)	-0.002(1)	-0.006(2)
C26	0.057(2)	0.085(2)	0.059(2)	-0.002(2)	0.004(1)	-0.004(2)
C27	0.050(1)	0.075(2)	0.048(1)	-0.002(1)	0.008(1)	-0.003(1)
C28	0.052(1)	0.054(2)	0.038(1)	0.003(1)	0.013(1)	-0.006(1)
C29	0.046(1)	0.057(2)	0.039(1)	-0.001(1)	0.0128(9)	-0.001(1)
C30	0.048(1)	0.066(2)	0.049(1)	0.002(1)	0.015(1)	-0.003(1)
C31	0.050(1)	0.064(2)	0.054(1)	0.008(1)	0.013(1)	0.001(1)
C32	0.044(1)	0.066(2)	0.049(1)	0.004(1)	0.012(1)	0.002(1)
C33	0.045(1)	0.057(2)	0.040(1)	-0.000(1)	0.0109(9)	0.001(1)
C34	0.045(1)	0.058(2)	0.043(1)	0.002(1)	0.010(1)	0.002(1)
C35	0.048(1)	0.059(2)	0.038(1)	0.007(1)	0.007(1)	0.006(1)
C36	0.056(1)	0.077(2)	0.047(1)	-0.000(1)	0.017(1)	0.003(1)
C37	0.079(2)	0.081(2)	0.059(1)	0.003(2)	0.035(1)	0.007(2)
C38	0.104(2)	0.067(2)	0.051(1)	0.000(2)	0.034(1)	0.002(1)
C39	0.089(2)	0.062(2)	0.042(1)	0.003(2)	0.010(1)	0.003(1)
C40	0.054(1)	0.061(2)	0.038(1)	0.008(1)	0.005(1)	0.005(1)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table IV. Bond Distances (Å) for DL-2 at **295 K**

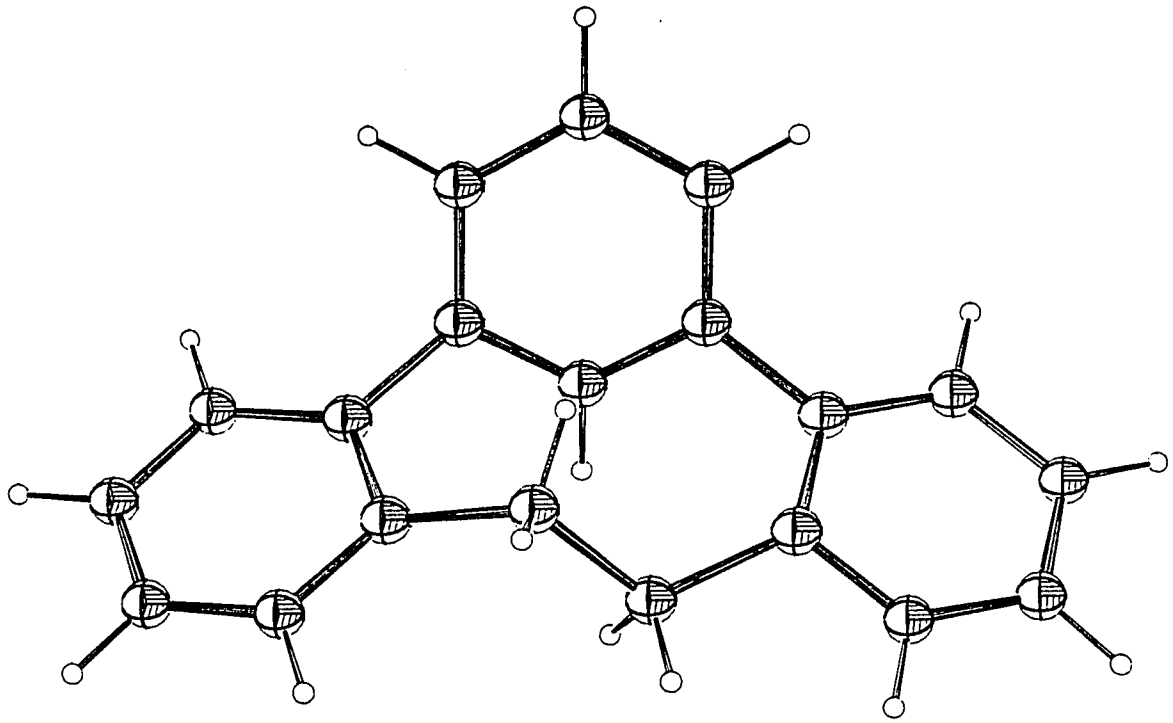
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C1	C2	1.533(4)	C20	C21	1.514(4)
C1	C40	1.507(4)	C21	C22	1.537(4)
C2	C3	1.509(4)	C22	C23	1.510(3)
C3	C4	1.398(3)	C23	C24	1.397(3)
C3	C8	1.390(4)	C23	C28	1.402(4)
C4	C5	1.378(5)	C24	C25	1.383(4)
C5	C6	1.390(5)	C25	C26	1.378(4)
C6	C7	1.380(4)	C26	C27	1.385(3)
C7	C8	1.404(4)	C27	C28	1.391(3)
C8	C9	1.493(3)	C28	C29	1.491(3)
C9	C10	1.388(4)	C29	C30	1.389(4)
C9	C14	1.391(4)	C29	C34	1.391(3)
C10	C11	1.389(3)	C30	C31	1.387(3)
C11	C12	1.390(4)	C31	C32	1.384(4)
C12	C13	1.382(4)	C32	C33	1.392(4)
C13	C14	1.390(3)	C33	C34	1.395(3)
C13	C15	1.504(4)	C33	C35	1.495(3)
C15	C16	1.392(4)	C35	C36	1.390(4)
C15	C20	1.399(4)	C35	C40	1.401(3)
C16	C17	1.375(4)	C36	C37	1.385(4)
C17	C18	1.390(5)	C37	C38	1.374(4)
C18	C19	1.385(4)	C38	C39	1.381(4)
C19	C20	1.395(4)	C39	C40	1.391(4)

Standard deviations are in parentheses.

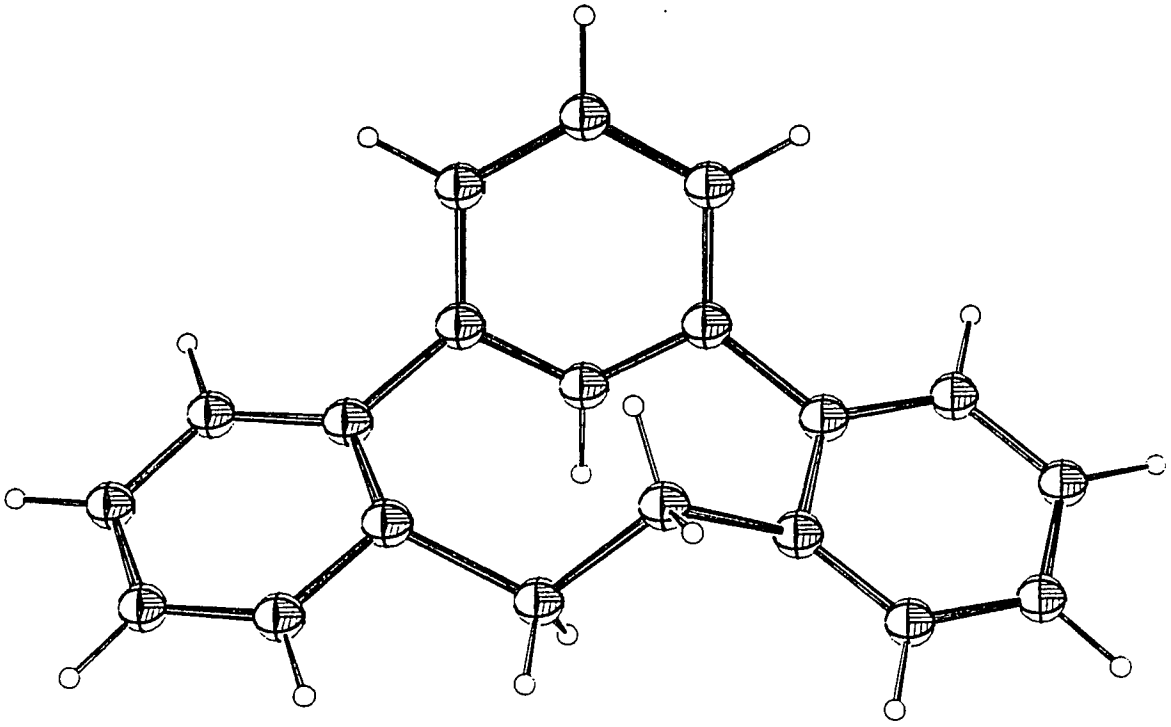
Table V. Bond Angles (°) for DL-2 at **295 K**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C1	C40	112.1(2)	C20	C21	C22	111.7(2)
C1	C2	C3	112.0(2)	C21	C22	C23	112.1(2)
C2	C3	C4	117.8(2)	C22	C23	C24	119.0(2)
C2	C3	C8	123.2(2)	C22	C23	C28	122.1(2)
C4	C3	C8	118.9(3)	C24	C23	C28	118.8(2)
C3	C4	C5	121.7(3)	C23	C24	C25	121.1(3)
C4	C5	C6	119.6(3)	C24	C25	C26	120.0(2)
C5	C6	C7	119.4(3)	C25	C26	C27	119.5(3)
C6	C7	C8	121.3(3)	C26	C27	C28	121.3(3)
C3	C8	C7	119.1(2)	C23	C28	C27	119.2(2)
C3	C8	C9	123.0(2)	C23	C28	C29	122.4(2)
C7	C8	C9	117.7(2)	C27	C28	C29	118.4(2)
C8	C9	C10	121.8(2)	C28	C29	C30	122.1(2)
C8	C9	C14	120.0(2)	C28	C29	C34	119.2(2)
C10	C9	C14	118.1(2)	C30	C29	C34	118.7(2)
C9	C10	C11	120.6(3)	C29	C30	C31	120.2(2)
C10	C11	C12	120.3(3)	C30	C31	C32	120.8(2)
C11	C12	C13	120.1(2)	C31	C32	C33	120.0(2)
C12	C13	C14	118.9(2)	C32	C33	C34	118.8(2)
C12	C13	C15	121.7(2)	C32	C33	C35	122.1(2)
C14	C13	C15	119.3(2)	C34	C33	C35	119.1(2)
C9	C14	C13	122.0(2)	C29	C34	C33	121.5(2)
C13	C15	C16	118.2(3)	C33	C35	C36	118.1(2)
C13	C15	C20	122.6(2)	C33	C35	C40	122.6(2)
C16	C15	C20	119.1(3)	C36	C35	C40	119.2(2)
C15	C16	C17	122.1(3)	C35	C36	C37	121.6(2)
C16	C17	C18	118.9(3)	C36	C37	C38	119.4(3)
C17	C18	C19	119.8(3)	C37	C38	C39	119.4(3)
C18	C19	C20	121.4(3)	C38	C39	C40	122.4(2)
C15	C20	C19	118.6(2)	C1	C40	C35	122.3(2)
C15	C20	C21	123.1(2)	C1	C40	C39	119.7(2)
C19	C20	C21	118.1(2)	C35	C40	C39	117.9(2)

Standard deviations are in parentheses.



DL-3 (major conformer)



DL–3 (minor conformer)

X-ray sample T158 was submitted on December 20, 1994.

Table I. X-ray Data for DL-3 at 295 K

Formula	$C_{20}H_{16}$
Formula weight	256,35
Crystal size (mm)	0.13 x 0.26 x 0.40
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	6.869(1)
b (Å)	9.697(1)
c (Å)	21.055(2)
β (°)	98.67(1)
V (Å^3)	1386.4(4)
Z	4
d_{calc} (g cm^{-3})	1.228
μ(Cu $K\alpha$) (cm^{-1})	4.89
Absorption correction	none
Maximum θ (°)	75
Collected reflections	2851
Observed reflections [$I > 3.0\sigma(I)$]	1817
Number of variables	199
R	0.053
R_w	0.064
$(\Delta\rho)_{max}$ (e Å^{-3})	0.21
$(\Delta\rho)_{min}$ (e Å^{-3})	–0.14

Table II. Final Atomic Parameters for DL-3

Atom	x	y	z	B(Å^2)
C1	0.4851(3)	0.2714(2)	0.5350(1)	4.38(4)
C2	0.2885(3)	0.3022(3)	0.5091(1)	4.97(5)
C3	0.2120(4)	0.2671(3)	0.4377(1)	4.43(6)
C4	0.2070(4)	0.3936(4)	0.3917(1)	4.80(7)
C5	0.3026(3)	0.3788(3)	0.3286(1)	5.70(6)
C6	0.4944(3)	0.3364(2)	0.3205(1)	4.44(4)
C7	0.6166(3)	0.2656(2)	0.3750(1)	4.38(4)
C8	0.7027(3)	0.1357(2)	0.3710(1)	5.27(5)
C9	0.7568(3)	0.0605(3)	0.4267(1)	5.82(6)
C10	0.7043(3)	0.1034(2)	0.4847(1)	5.28(5)
C11	0.6172(3)	0.2328(2)	0.4883(1)	4.37(4)
C12	0.6017(3)	0.3175(2)	0.4348(1)	4.16(4)
C13	0.5412(4)	0.2719(3)	0.6009(1)	5.56(6)
C14	0.4098(4)	0.3057(3)	0.6424(1)	6.30(7)
C15	0.2181(4)	0.3379(3)	0.6171(1)	5.92(6)
C16	0.1587(3)	0.3355(3)	0.5518(1)	5.25(5)
C17	0.1897(4)	0.4435(3)	0.2771(1)	6.52(7)
C18	0.2567(4)	0.4683(3)	0.2203(1)	6.51(7)
C19	0.4425(4)	0.4248(3)	0.2121(1)	6.69(7)
C20	0.5579(4)	0.3594(3)	0.2621(1)	5.76(6)
C3B	0.1981(9)	0.3724(7)	0.4414(3)	4.1(1)
C4B	0.2120(9)	0.2769(7)	0.3807(3)	4.0(1)
H3A	0.075	0.230	0.435	5.3
H3B	0.300	0.195	0.423	5.3
H4A	0.276	0.471	0.417	5.8
H4B	0.066	0.419	0.378	5.8
H8	0.725	0.098	0.328	6.3
H9	0.835	-0.026	0.425	7.0
H10	0.729	0.043	0.523	6.3
H12	0.579	0.419	0.440	5.0
H13	0.680	0.247	0.619	6.7
H14	0.453	0.307	0.690	7.6
H15	0.122	0.363	0.646	7.1
H16	0.019	0.358	0.534	6.3
H17	0.053	0.473	0.282	7.8
H18	0.171	0.518	0.185	7.8
H19	0.492	0.441	0.170	8.0
H20	0.692	0.327	0.256	6.9
H3BA	0.272	0.460	0.436	5.0
H3BB	0.056	0.394	0.442	5.0
H4BA	0.079	0.242	0.362	4.8
H4BB	0.302	0.197	0.393	4.8

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$

Table III. Final Anisotropic Thermal Parameters (U's) for DL-3

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C1	0.052(1)	0.046(1)	0.067(1)	-0.0070(9)	0.007(1)	0.001(1)
C2	0.050(1)	0.076(1)	0.064(1)	-0.005(1)	0.012(1)	0.002(1)
C3	0.042(1)	0.059(2)	0.067(2)	-0.008(1)	0.007(1)	-0.000(2)
C4	0.046(1)	0.071(2)	0.065(2)	0.009(1)	0.008(1)	0.002(2)
C5	0.048(1)	0.108(2)	0.062(1)	0.002(1)	0.011(1)	0.008(1)
C6	0.048(1)	0.055(1)	0.068(1)	-0.0072(9)	0.0129(9)	-0.006(1)
C7	0.0381(9)	0.053(1)	0.077(1)	-0.0054(9)	0.0129(9)	-0.002(1)
C8	0.045(1)	0.060(1)	0.098(2)	0.000(1)	0.022(1)	-0.008(1)
C9	0.049(1)	0.056(1)	0.120(2)	0.007(1)	0.024(1)	0.003(1)
C10	0.047(1)	0.054(1)	0.099(2)	0.002(1)	0.010(1)	0.010(1)
C11	0.0392(9)	0.050(1)	0.076(1)	-0.0060(9)	0.0055(9)	0.001(1)
C12	0.0376(8)	0.045(1)	0.075(1)	-0.0057(9)	0.0080(9)	-0.002(1)
C13	0.072(1)	0.063(1)	0.073(1)	-0.006(1)	0.002(1)	0.012(1)
C14	0.103(2)	0.073(2)	0.063(1)	-0.010(1)	0.012(1)	0.003(1)
C15	0.095(2)	0.058(1)	0.078(1)	0.003(1)	0.031(1)	0.002(1)
C16	0.062(1)	0.066(1)	0.075(1)	0.005(1)	0.022(1)	0.009(1)
C17	0.066(1)	0.117(2)	0.063(1)	0.019(1)	0.002(1)	-0.004(1)
C18	0.086(2)	0.091(2)	0.068(1)	-0.000(2)	0.002(1)	0.002(1)
C19	0.083(2)	0.110(2)	0.062(1)	-0.022(2)	0.014(1)	0.002(1)
C20	0.063(1)	0.086(2)	0.074(1)	-0.013(1)	0.023(1)	-0.017(1)
C3B	0.041(3)	0.055(4)	0.062(4)	0.004(3)	0.013(3)	0.000(3)
C4B	0.038(3)	0.056(4)	0.058(3)	-0.011(3)	0.011(3)	-0.015(3)

The form of the anisotropic displacement parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$, where a^*, b^*, and c^* are reciprocal lattice constants.

Table IV. Bond Distances (Å) for DL-3

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C1	C2	1.410(3)	C7	C8	1.400(3)
C1	C11	1.483(3)	C7	C12	1.375(3)
C1	C13	1.381(3)	C8	C9	1.384(3)
C2	C3	1.553(4)	C9	C10	1.388(4)
C2	C16	1.397(3)	C10	C11	1.397(3)
C2	C3B	1.616(7)	C11	C12	1.385(3)
C3	C4	1.560(5)	C13	C14	1.388(4)
C4	C5	1.575(4)	C14	C15	1.380(4)
C5	C6	1.415(3)	C15	C16	1.373(3)
C5	C17	1.384(3)	C17	C18	1.366(4)
C5	C4B	1.665(7)	C18	C19	1.380(4)
C6	C7	1.484(3)	C19	C20	1.373(3)
C6	C20	1.385(3)	C3B	C4B	1.59(1)

Table V. Bond Angles (°) for DL-3

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C1	C11	116.3(2)	C6	C7	C12	115.3(2)
C2	C1	C13	119.6(2)	C8	C7	C12	118.4(2)
C11	C1	C13	124.1(2)	C7	C8	C9	119.0(2)
C1	C2	C3	119.5(2)	C8	C9	C10	121.0(2)
C1	C2	C16	117.8(2)	C9	C10	C11	119.1(2)
C1	C2	C3B	130.5(3)	C1	C11	C10	124.9(2)
C3	C2	C16	121.2(2)	C1	C11	C12	114.2(2)
C16	C2	C3B	105.8(3)	C10	C11	C12	118.0(2)
C2	C3	C4	113.7(2)	C7	C12	C11	121.4(2)
C3	C4	C5	118.6(3)	C1	C13	C14	121.6(2)
C4	C5	C6	129.9(2)	C13	C14	C15	118.9(2)
C4	C5	C17	111.4(2)	C14	C15	C16	120.3(2)
C6	C5	C17	117.3(2)	C2	C16	C15	121.7(2)
C6	C5	C4B	110.7(3)	C5	C17	C18	122.9(2)
C17	C5	C4B	124.3(3)	C17	C18	C19	119.7(2)
C5	C6	C7	118.1(2)	C18	C19	C20	118.9(2)
C5	C6	C20	118.9(2)	C6	C20	C19	122.2(2)
C7	C6	C20	123.0(2)	C2	C3B	C4B	113.6(5)
C6	C7	C8	124.4(2)	C5	C4B	C3B	104.9(5)

Standard deviations are in parentheses.