Synthesis and Electronic Properties of Oligo[2,7-biphenylenylene-(*E*)-vinylene]s

by

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Abbreviations

Ac	acetyl
Anal.	analytical
*n*Bu	*n*-butyl
*t*Bu	*tert*-butyl
Calcd.	calculated
d	day(s)
DBU	1,8-diazabicyclo[5.4.0]-undec-7-ene
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
EI	electron impact
equiv.	equivalence
ESR	electron spin resonace
Et	ethyl
FAB	fast atom bombardment
Ph	phenyl
h	hour(s)
Hz	hertz
IR	infrared
J	coupling constant
LAH	lithium aluminum hydride
λ	wavelength
M^+	molecular ion
*m*CPBA	*m*-chloroperoxybenzoic acid
Me	methyl
m/e	mass to charge ratio
min	minute(s)
mp	melting point
MS	mass spectrometry
NMR	nuclear magnetic resonance
PDC	pyridinium dichromate
ppm	part per million
r.t.	room temperature
THF	tetrahydrofuran
TLC	thin layer chromatography
TFA	trifluoroacetic acid
TFAn	trifluoroacetic anhydride
UV-VIS	ultraviolet-visible

Abstract

A convenient method for the synthesis of dialkyl 2,7-biphenylenedicarboxylates has been developed. An iterative approach of S-alkylation, sulfone formation and Ramberg-Bäcklund reaction for oligo- and stereodefined oligo[2,7-biphenylenylene-(*E*)-vinylene]s (**OBV**) has been etablished as a general synthetic strategy from which the number of biphenylenes in the conjugated chain could be incorporated conveniently. Fully conjugated oligomers containing one, two and three biphenylene units have been synthesized with high (*E*)-stereoselectivity. Significant electron delocalization in these oligomers through extensive conjugation of the biphenylene chromophores linked by carbon-carbon double bonds has been demonstrated by UV-VIS spectroscopy and cyclic voltammetry experiments. An empirical mathemathical approach has estimated a value of 2.35 eV as the bandgap (E_g) of poly[2,7-biphenylenylene-(*E*)-vinylene] with infinite chain length. Temperature-dependent redox activities of **OBV**'s has also been revealed by cyclic voltammetry experiments performed at different temperatures.

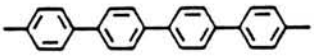
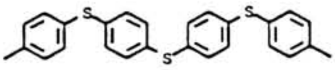
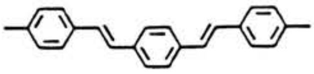
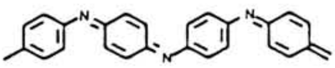
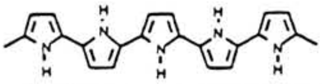
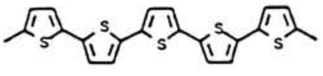
1. INTRODUCTION

1. 1 General Background of Extended π-Systems[1]

Polyconjugated systems have been a center of scientific interest for the last decade. Research on conjugated polymers is multidisciplinary. It spans from theory, which uses one-dimensional chains as a first model for the description of the physical properties of solids, to chemistry, which provides numerous novel structures and materials, and finally to engineering research, which focuses on the their application on real devices. These materials, thus, have attracted academic and industrial research groups not only because of their theoretically fascinating properties but also because of their technological potentials.[2]

Interest in conducting polymers began in the mid-1960s. Originally, the research concentrated on metallically conducting donor-acceptor complexes.[1b, 1d] By electron transfer from the neutral donor to the acceptor, radical-ion salts of tetracyano-*p*-quinodimethane (TCNQ) were described for the first time. The free motion of charge carriers along the stacks of TCNQ units in the crystal is responsible for the electrical conductivity. In the 70s, investigations of charge-transfer salts of TCNQ as acceptor and tetrathiafulvalene (TTF) as donor followed. Whereas alkali metal complexes of TCNQ show relatively low conductivities ($\sigma = 10^{-3}$ S/cm), donor-acceptor complexes TCNQ-TTF reach conductivities up to $\sigma = 10^4$ S/cm, while radical-ion salts of dicyanoquinodimethane (DCNQI) reach conductivities of $\sigma = 5 \times 10^5$ S/cm, which lie in the range of copper ($\sigma = 6.4 \times 10^5$ S/cm).

While charge-transfer complexes formed the first group of organic conductors, the boost in the second group which comprises of covalent organic polymer as the conductors did not take place until 1977 when MacDiarmid and Heeger discovered that partial oxidation of polyacetylene (PA, prepared by the Shirakawa method) led to an increase in conductivity by many orders of magnitude.[3] The conductivity of PA prepared by the Shirakawa method reaches values ($\sigma = 1.7 \times 10^5$ S/cm) comparable to those of the highly conducting DCNQI salts and even of metals. Since then, this material has served as a prototype for the synthesis and study of other conjugated systems. Today, it is known that PA is not unique. Many other organic compounds with a conjugated π-system become highly conducting under the influence of oxidants or reductants (Fig. 1).[1a, 1d]

Polymer	Chemical Structure	Conductivibes (undoped) (S/cm)	Conductivities (doped) (S/cm)	Dopant
PA		10^{-4}	10^{3}-1.7×10^{5}	I_2, AsF_5, Li, Na
PPP		10^{-11}- 10^{-8}	10^{2}-10^{3}	AsF_5, Li, K
PPS		10^{-8}	100-500	AsF_5
PPV		10^{-8}	3-5×10^{3}	AsF_5
PAni		10^{-10}	30-200	HCl
PPy		10^{-7}	10^{2}-7.5×10^{3}	$BF4^-$, $ClO4^-$, Tosylat$^-$, $FeCl4^-$
PT		10^{-8}	10-10^{3}	$BF4^-$, $ClO4^-$, Tosylat$^-$, $FeCl4^-$

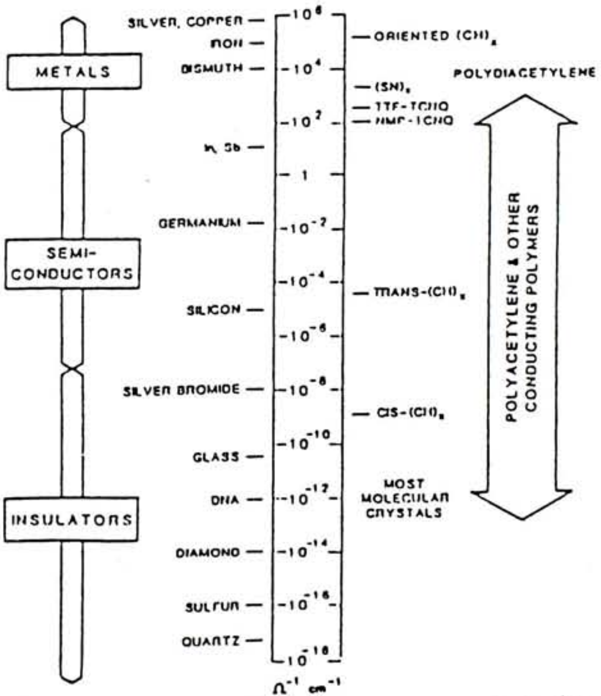


Fig. 1. Conductivities of different materials.[1a, 1d]

Presently, the research on conjugated polymers no longer focuses only on the search for materials with high electrical conductivities, but also on the study of other interesting physical properties polymers offered by conjugated systems such as non-linear optical activities and piezoelectricity.[4, 5] As the field is maturing, chemists, equipped with the advances in organic chemistry, now confront challenges of modulating and tuning these properties by varying the monomeric chromophore, conjugation linker, alignment of polymer chains, influence of dopants, etc. Their targets are compounds with tailored physical properties for specific application.

1. 2. Design and Synthesis of Conjugated Systems[6]

The search for novel electrophores and chromophores is fundamentally and practically important. Particularly essential features of electro- or photoactive materials are:

1. a small HOMO/LUMO energy difference which brings about attractive optical, electrical, and photoelectrical effect,
2. high hyperpolarizabilities leading to non-linear optical effects, and
3. fast chemical processes which allow for the rapid change of these properties.

There are generally two ways of synthesizing extended conjugated systems. The first one is the direct polymerization (chemical or electrochemical) of monomers. This method is generally convenient and time-saving, but unfortunately, it always gives rise to polydispersed mixtures of products. Separation of the mixture into monodispersed components is virtually impossible for high molecular weight systems. Moreover, the polymerization reaction must be highly selective because any side reactions will produce a structural defect in the macromolecules which cannot be removed even if it can ever be detected at all. Another frequently encountered drawback is the difficulties in the characterization and processing of the resulting high molecular weight products since they commonly have low solubilities. The polydispersity and the low solubility result in signal broadening and overlapping in spectroscopic measurements. Therefore, correlation between structure and physical behavior of these intractable macromolecules is rarely achievable.

The above issues, however, can be addressed by the studies of their oligomeric analogues. Soluble, structurally defined and monodispersed oligomers offer enhanced solubilities, and thus superior characterizabilities and processibilities over their polymeric counterparts. This approach allows chemists to precisely follow the change of physical behavior as a function of the number of repeating unit and extrapolate the resulting properties to the polymer. It is particularly valuable to extract information from oligomeric systems which is not available from a study of the polymer itself. Typical example are the UV-VIS absorption study of oligo(phenyleneacetylene)s[7] (Fig. 2); and the voltammetric study on oligo(phenylenevinylene)s[8] (Fig. 3).

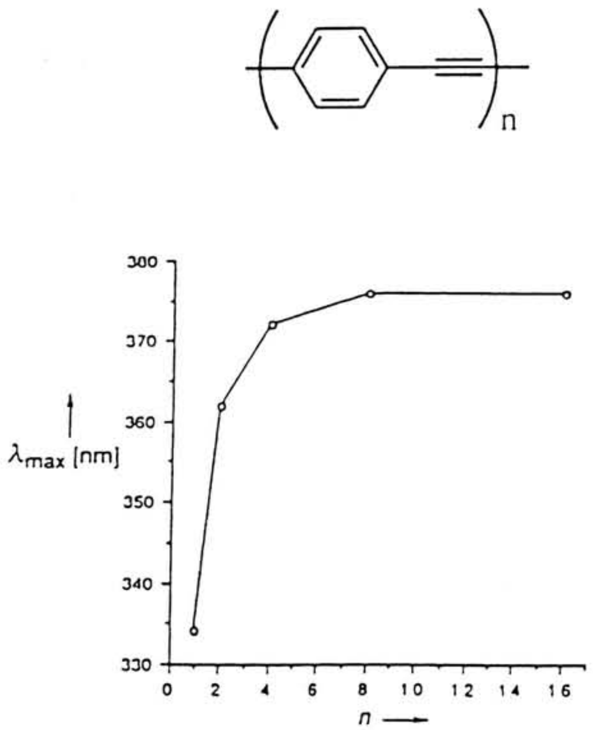


Fig. 2. UV-VIS absorption maxima
vs n in oligo-defined
oligo(phenyleneacetylene)s.

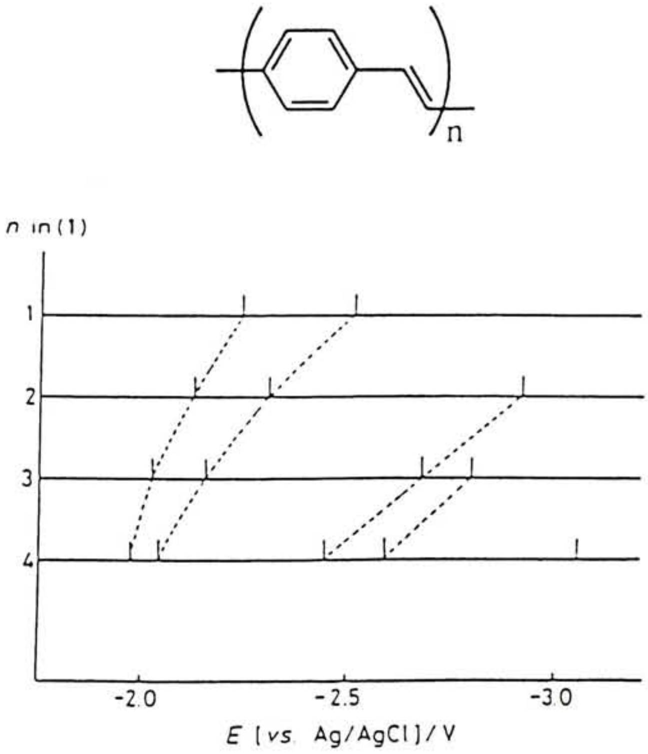
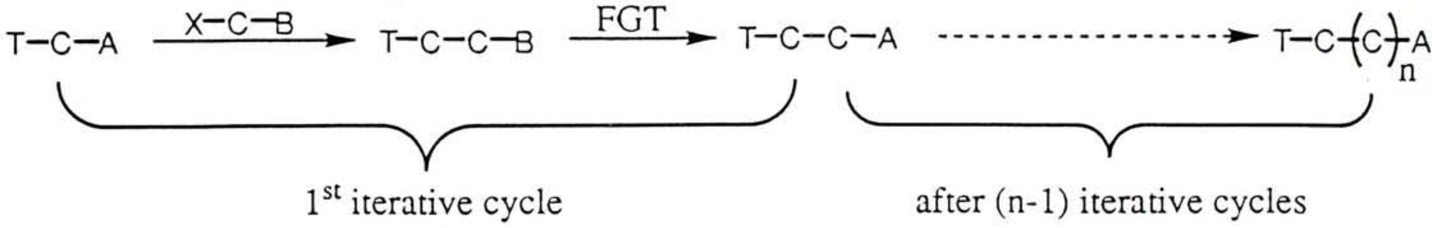


Fig. 3. Correlation diagram for the redox
states in oligo-defined
oligo(pheneylenevinylene)s.

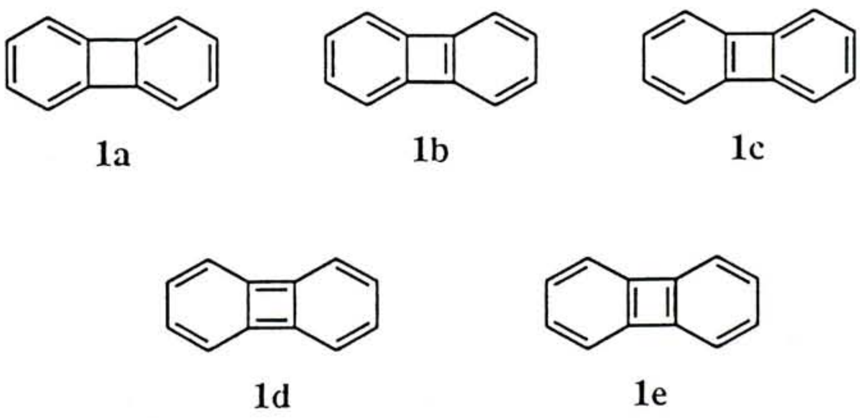
Stepwise chain growth of oligomer is the most commonly used method for generating structurally defined systems[7, 9, 10]. Although this methodology involves much effort in syntheses and purifications of intermediates, the redundancy and complication of preparation can be logically and systematically relieved by iterative approaches in which the same reaction squence is repeatedly carried out:



As the simplest type, the idea is examplified by an iterative cycle consisting of a coupling reaction between the two functionalities A and X followed by an functional group transformation from B to A. The degree of polymerization can, therefore, be controlled conveniently in every step of the way.

1. 3. Review on Biphenylene[11]

There are five canonical uncharged structures for biphenylene, two of which contain a cyclobutadiene ring and three which do not. X-ray crystallography shows that biphenylene is best represented by the structure **1a** shown in Fig. 4.[12, 13] The bonds between the 6-membered rings approximate to single bonds in length and there is some bond alternation in the 6-membered rings, indicating that the canonical structure **1a** containing the tetrakis(methylene)cyclobutane moiety is the major contributor.



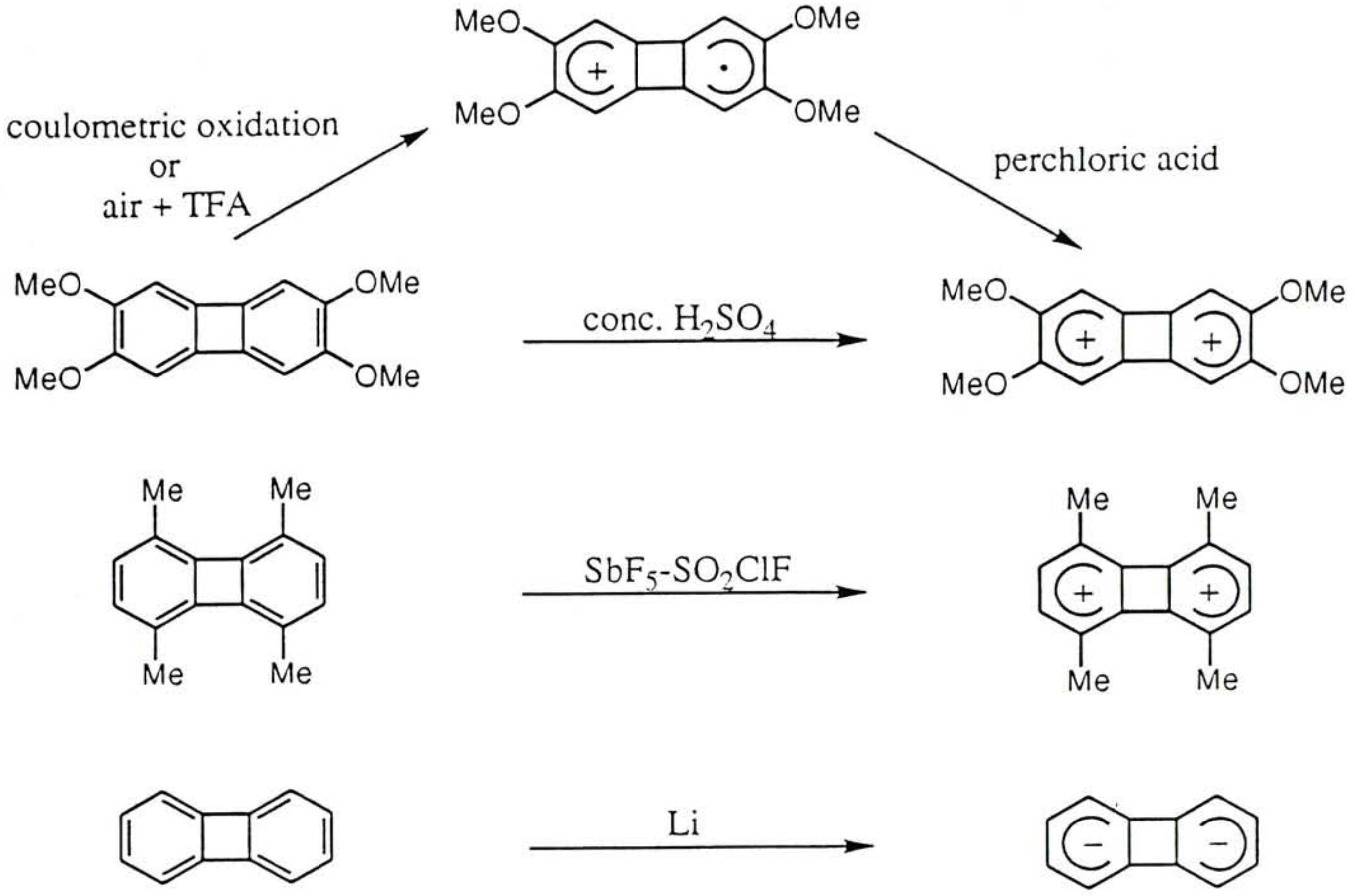
1a **1b** **1c**

1d **1e**

Fig. 4. The five canonical structures of biphenylene.

Biphenylene is a cyclic conjugated compound. It consists of 12 π-electrons. It (or its derivatives) has been demonstrated that the 4n π-system could be transformed to the fully delocalized 10 or 14 (4n + 2) π-system either by oxidation or reduction. Rolán and Parker[14] first reported the electrochemical oxidation of tetramethoxybiphenylene. The two one-electron transfers occurred at +0.53 and +1.06 V in the mixed solvent system of CH_2Cl_2/TFAn/TFA (45:5:1) whereas for tetramethoxybiphenyl, the oxidations occurred at +1.24 and +1.62 V in the same solvent system. Coulometric oxidation of tetramethoxybiphenylene (1.0 mM) in dry acetonitrile resulted in the consumption of 1.0 Faraday per mole and the precipitation of a dark blue solid. In a degassed solvent system of CH_2Cl_2/TFAn/TFA (45:5:1), tetramethoxybiphenylene underwent two consecutive one-electron oxidations giving first a deep blue (λ_{max} 414, 680; ε 28000, 19300) and then a yellow (λ_{max} 459; ε 55500) solution. Chemical oxidations also demonstrated the formation of the corresponding cation radical and dication by UV-VIS spectroscopy and ESR spectroscopy. The one-electron oxidation product was obtained by air oxidation of tetramethoxybiphenylene in TFA and further oxidation to the dication could be achieved by adding small amount of perchloric acid to the TFA solution. On the other hand, the dication was formed immediately by treating tetramethoxybiphenylene with concentrated sulfuric acid as shown by the UV-VIS spectrum (λ_{max} 459). The radical cation gave an ESR signal in TFA of about 23 resolved lines whereas the dication gave only a weak, broad ESR signal probably due to the residue presence of the radical cation. Later, Olah and Liang[15] studied the chemical oxidation of biphenylene and tetramethylbiphenylene (with SbF_5-SO_2ClF) by the deshielding of ^1H and ^{13}C NMR signals in going from the neutral species to the dications. More recently, Günther and Edlund[16] conducted a quantitative conversion of biphenylene to its dianion by lithium metal.

These results (summarized in Scheme 1) unequivocally expressed the redox activity of the biphenylene system and the stability of the charged species which are the basic criteria for the design of electro-active conjugated systems.



Scheme 1. Redox reactions of biphenylenes.

Cyclic voltammetry of biphenylene systems has also been reported.[17] Biphenylene underwent reversible one-electron oxidations and quasi-reversible one-electron reductions while methyl-substituted biphenylenes underwent reversible one-electron oxidations only (Fig. 5).

The HOMO-LUMO energy difference of biphenylene is calculated, by HMO theory, to be 0.89 β which is significantly lower than that of benzene (2 β).[10] The UV-VIS spectrum of biphenylene shows two main band systems, at 235-260 nm and 330-370 nm, which is typical of a polycyclic aromatic hydrocarbon, as opposed to that of a bridged biphenyl which shows only one band at 240-250 nm. Construction of conjugated polymers based on this interesting chromophore has also been studied theoretically[18]. *Ab initio* valence effective Hamiltonian (VEH) technique was employed to estimate the ionization potentials, bandgaps and bandwidths of certain types of biphenylene polymers (Table 1). The small bandgaps (especially in [*N*]phenylene) suggest that suitably linked conjugated biphenylene systems might enter the class of highly conducting polymers.

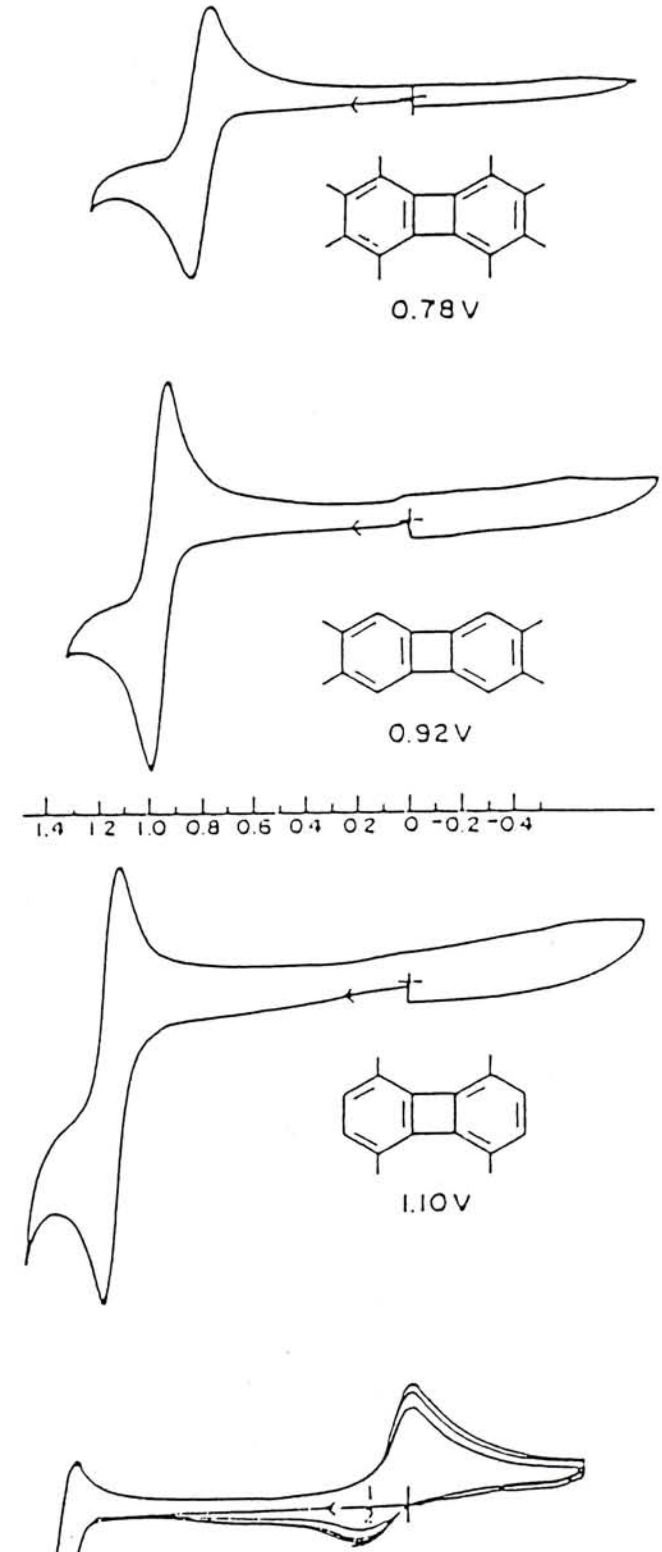


Fig. 5. Cylic voltammograms of biphenylenes.

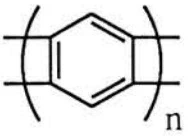
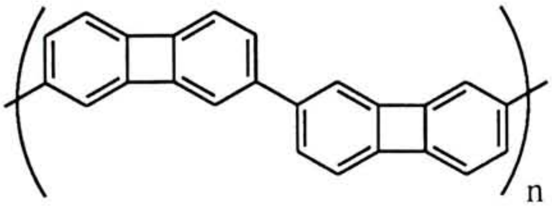
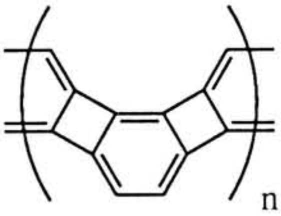
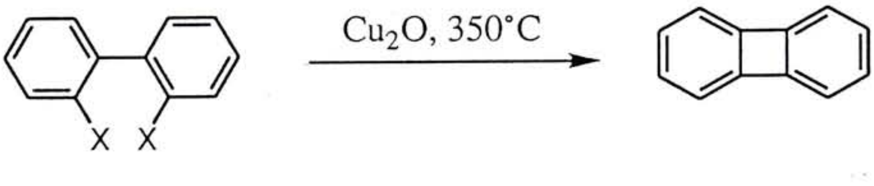
Polymer	Ionization potential (eV)	Bandgap (eV)	Bandwidth (eV)
	3.4	0.1	5.9
	5.5	3.0	1.8
	5.1	2.8	1.1

Table 1. VEH results on biphenylene polymers.

1. 4. Synthetic routes to Biphenylenes

Biphenylene was first prepared by Lothrop[19] in 1941 by an Ullman reaction of 2,2'-dibromo- or 2,2'-diiodobiphenyl with cuprous oxide (Scheme 2).

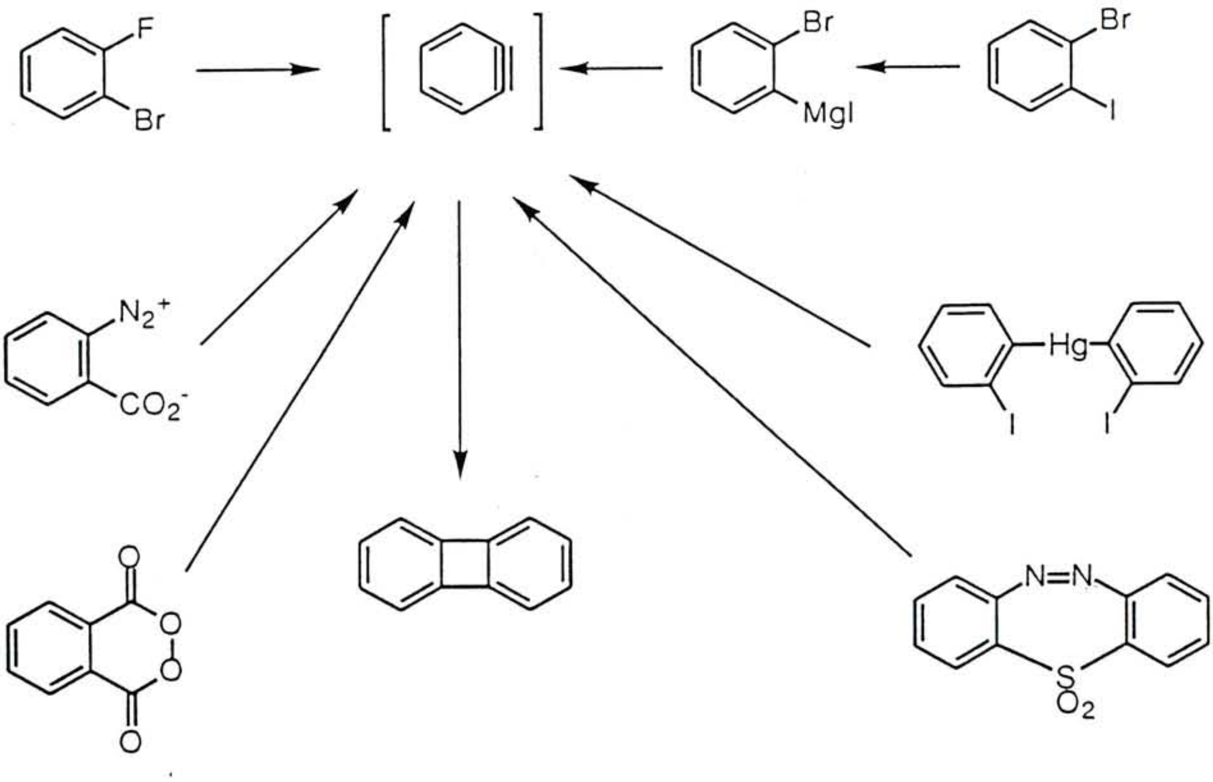


X = Br or I

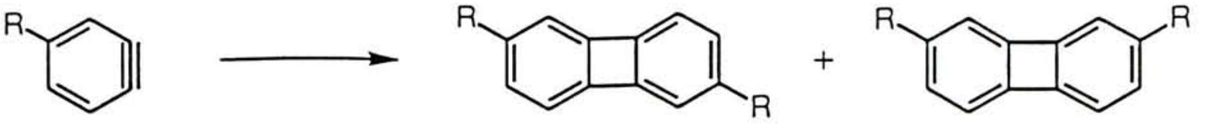
Scheme 2. Ullman reaction for the synthesis of biphenylene.

Presently, there are four general methods which allow the assemblage of the biphenylene unit.[10, 11, 13] The first one is the intramolecular coupling of a biphenyl at the ortho positions of the two rings as in Lothrop's method. The reaction is effected by heating the precursor with copper or cuprous oxide at elevated temperatures (> 300°C). If the biphenyls are suitably substituted, this method provides a convenient access to a variety of substituted biphenlyenes notwithstanding the generally low yields encountered.[11]

Dimerization of substituted benzyne constitutes a second route to biphenylenes. A number of benzyne precursors are summarized in Scheme 3, the most popular one being benzenediazonium-2-carboxylate generated from the aprotic diazotization of anthranilic acid.[11, 20, 21] Again, low yield is a common feature in these dimerizations. A serious limitation of this method for constructing substituted biphenylenes is that there is little if any orientation of the arynes before dimerization takes place and a mixture of products is obtained which makes separation of the isomers very difficult. For example, 3-methyl- or 3-methoxy benzyne dimerizes to give a mixture of 2,6-methyl- and 2,7-methylbiphenylene or 2,6-methoxy- and 2,7-methoxybiphenylene with little regioselectivity (Scheme 4).[11]



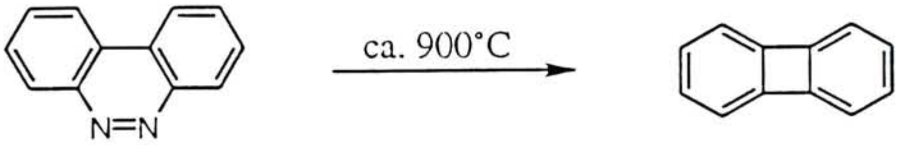
Scheme 3. Synthesis of biphenylene *via* benzyne dimerization.



R = Me 55 : 45
R = OMe 45 : 55

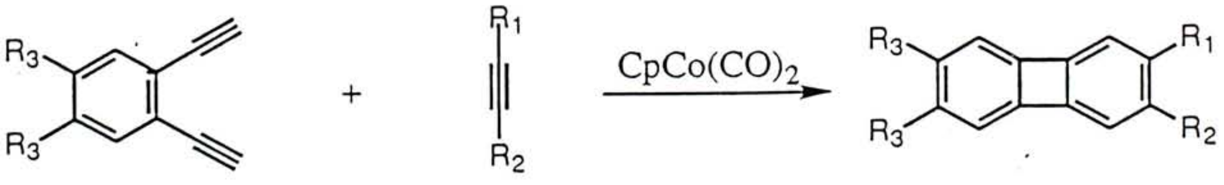
Scheme 4. Isomeric biphenylenes obtained from dimerization of substituted benzyne

The third method utilizes flash vacuum pyrolysis which requires specially constructed apparatus for large scale preparations. However, relatively few readily accessible precursors for this purpose are available. Perhaps benzo[*c*]cinnoline[13] (Scheme 5) is the best known example.



Scheme 5. Formation of biphenylene *via* denitrogenation.

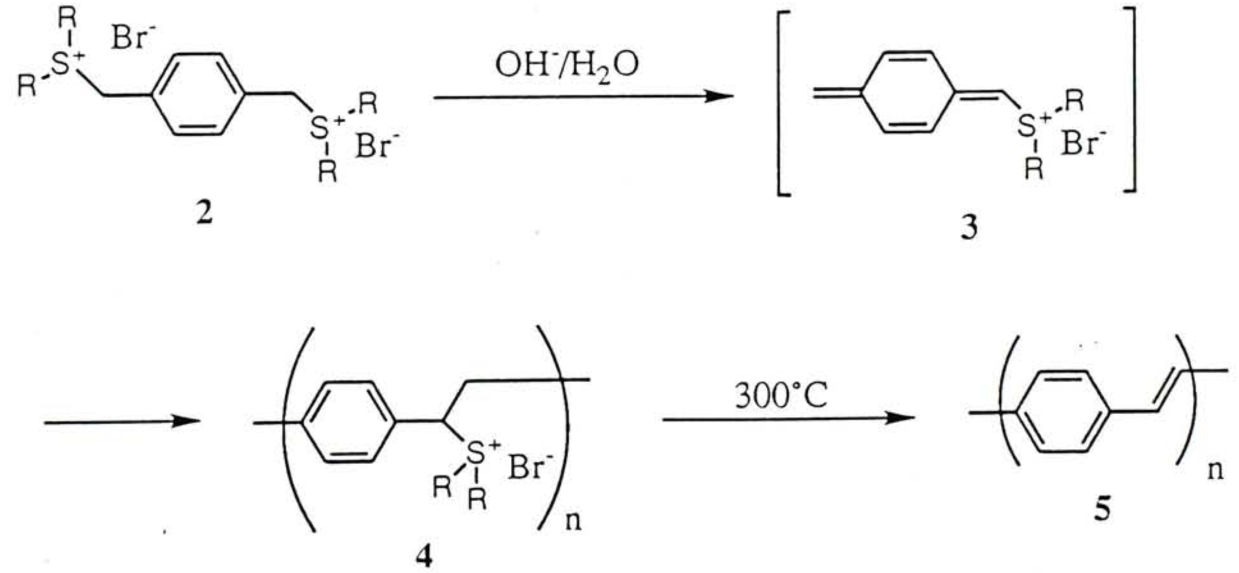
The fourth method has been more recently developed by Vollhardt and his co-workers[10, 13, 22] in which a biphenylene unit is constructed by cobalt-catalyzed co-cyclization of an *o*-di-ethynylbenzene with an acetylene (Scheme 6). This method is usually more high-yielding than the traditional ones (almost quantitative in some cases), and a number of biphenylenes and oligo(biphenylene)s have been prepared although only 1,2-, 2,3- and 2,3,6,7-substitution patterns have so far been reported. Obviously, the limitation of this method lies in the restriction of using symmetrically substituted diethynylbenzenes since a mixture of substituted biphenylenes are formed from two unsymmetrical reacting partners.



Scheme 6. Cobalt catalyzed biphenylene synthesis.

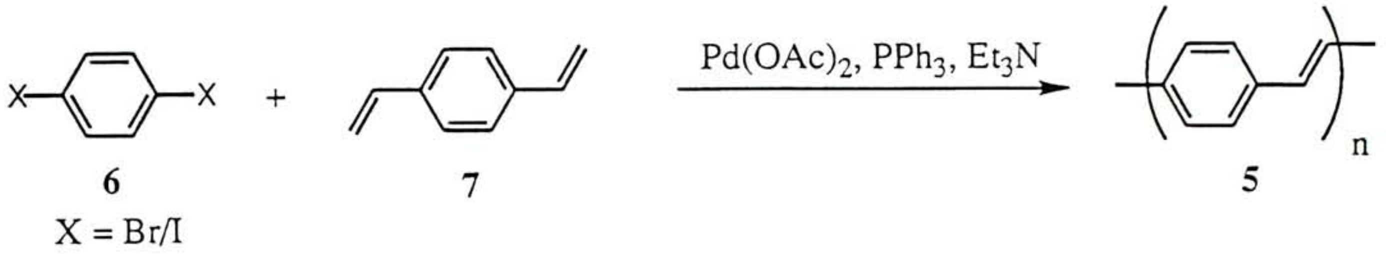
2. Synthetic Methodology for Conjugated Arylenevinylenes

Arylenevinylenes form a group of important conjugated systems. Poly(arylenevinylene)s, especially poly(1,4-phenylenevinylene) (**5**, **PPV**), have been extensively investigated over the past few years.[6] From the standpoint of polymer and oligomer synthesis, there are a number of routes for chemical constructions of vinylene groups which link conjugatively to the chromophores. The most common method for the synthesis of poly(arylenevinylene)s was first described by Wessling and Zimmermann[6, 23] in which the bissulfonium salts **2** derived from α,α'-dibromo-*p*-xylene were polymerized *via* the quinodimethane-like intermediate **3** under the action of a base such as sodium hydroxide to give the corresponding polyelectrolyte **4**. Conjugation was finally completed by thermal elimination of the sulfonium moiety (Scheme 7). This method remains useful today for preparing and processing high molecular weight polymers since the water-soluble polyelectrolyte **4** can be handled and precasted conveniently.[24-27] Organic soluble polymers can also be obtained by introducing lipophilic side chains on the chromophores although the incorporation of substituents may sterically inhibit the conjugative interaction between the subunits.[6]



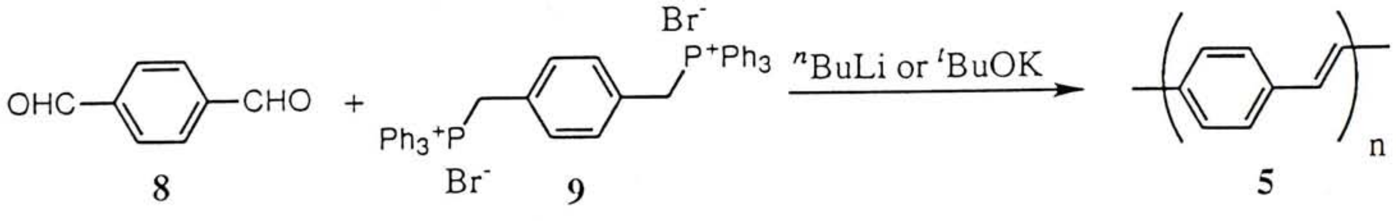
Scheme 7. The Wessling-Zimmermann route to poly(arylenevinylene)s.

Heck reaction is another popular route for constructing poly(arylenevinylene)s (Scheme 8).[6] The palladium-catalyzed coupling reaction between aryl halides **6** and *p*-divinylbezene **7** usually results in very high (*E*)-stereoselectivity which renders it a good method of stereodefined polymer synthesis.



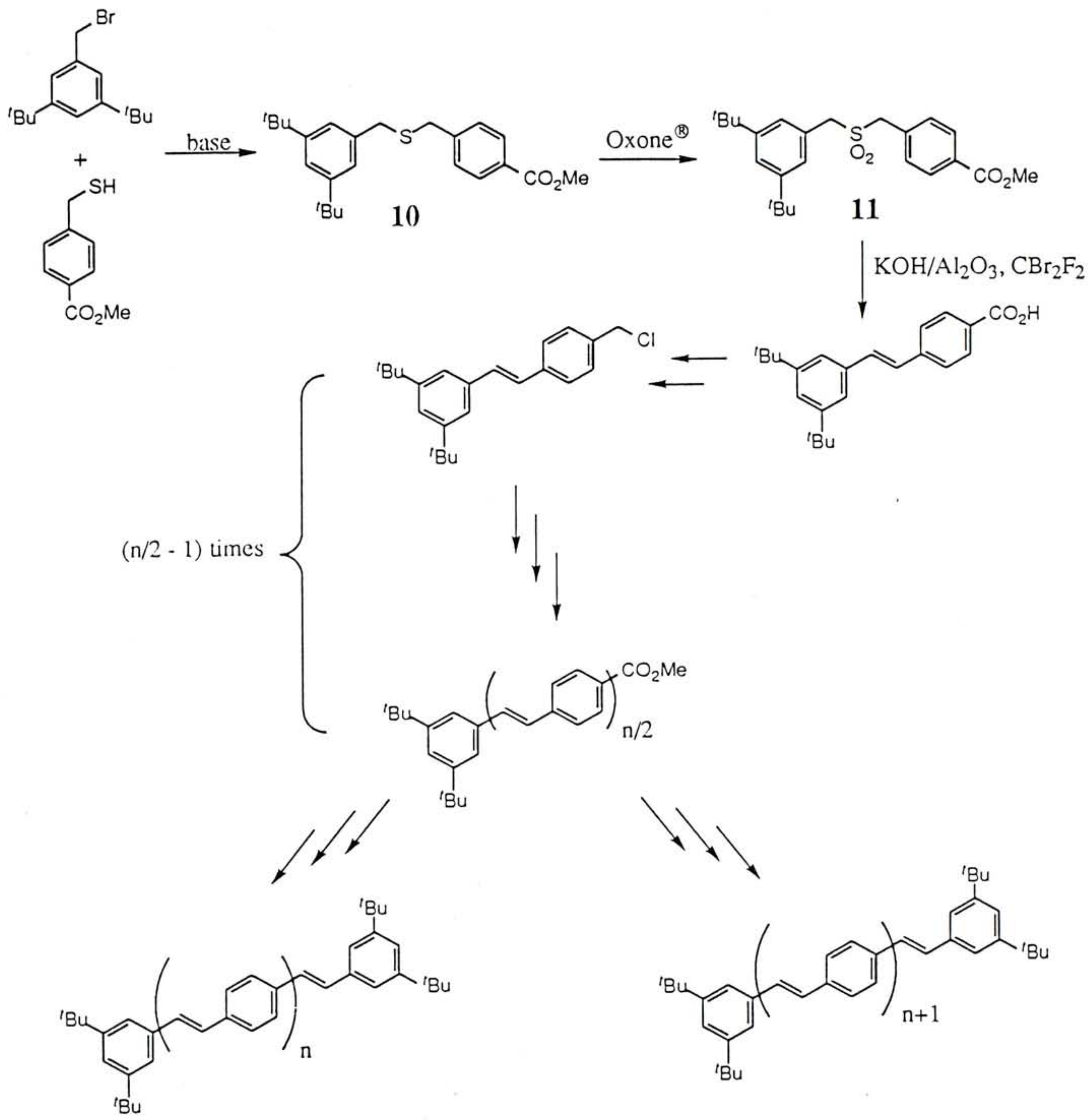
Scheme 8. Synthesis of poly(arylenevinylene)s *via* Heck reaction

Another common way to generate stereo- and structurally defined oligomers is the Wittig reaction of aryl aldedydes **8** and arylmethylphosphonium salts **9** (Scheme 9).[6, 8, 28, 29] The extent of (*E*)-stereoselectivity, however, depends on the electronic and steric environment of the system.[30] Ylides which are strongly stabilized give excellent (*E*)-stereoselectivity[28] while in those cases where electronic effect is insignificant, poor stereoselectivity is observed and (*E*)-(*Z*) isomerization is necessary for enrichment of the thermodynamically more stable (*E*)-isomer.[31]



Scheme 9. Synthesis of poly(arylenevinylene)s *via* Wittig reaction.

The final method worthwhile mentioning here was developed in our laboratory. The vinylene linker is generated through the modified Ramberg-Bäcklund reaction[32] of the sulfone **11** which is obtained from oxidation of the precursor sulfide **10** (Scheme 10). The sulfide is generally synthesized through the coupling reaction between arylmethyl halides and arylmethyl thiols in the presence of a suitable base. This method has been proved to be efficient in the synthesis of oligo(phenylenevinylene)s with excellent (*E*)-stereoselectivity.[9]

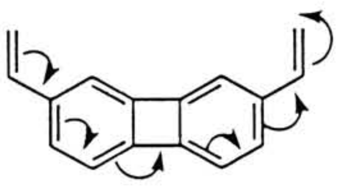


Scheme 10. Synthesis of oligo(arylenevinylene)s *via* the iterative cycle of S-alkylation, oxidation and Ramberg-Bäcklund raction.

3. Result and Discussion

3. 1. Design of Biphenylene Chromophore and Its Conjugated System

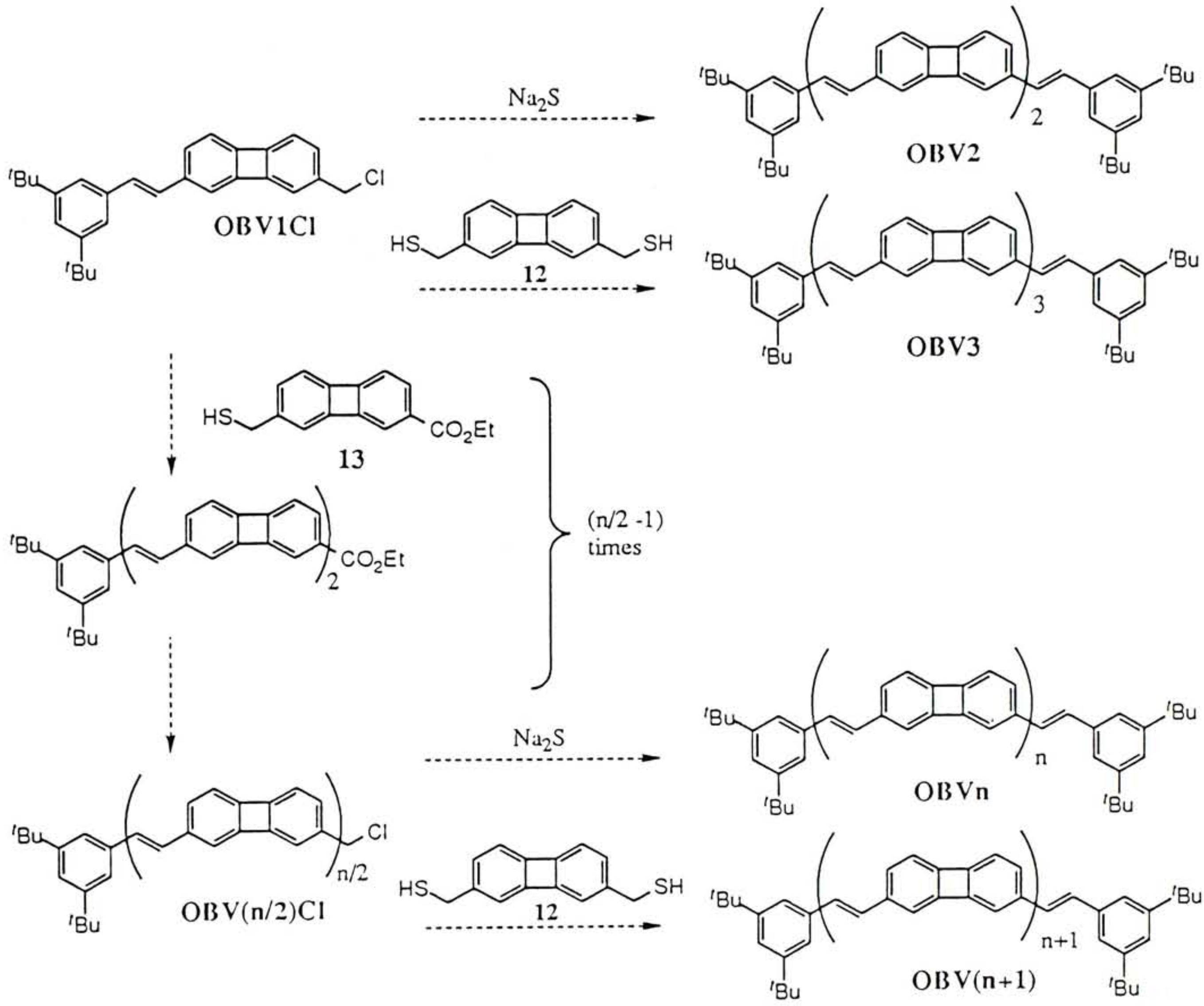
As described in **Section 1**, biphenylene is a fascinating chromophore for novel conjugated system. In order to fully utilize the electron delocalization in the biphenylene system in its entirety, 2,7-substituted biphenylene is designed as the basic chromophore unit. Electron delocalization through the two fused benzene rings is pictorially described below.



Since the iterative sequence of S-alkylation, sulfone formation and Ramberg-Bäcklund reaction was demonstrated to be an effective route to oligo- and stereodefined oligo(phenylenevinylene)s,[9] it has been an interest in our group to apply this approach to systems with chromophores other than benzene. Therefore, with the consideration of the favourable conjugation of 2,7-biphenylenylene systems, the iterative synthetic strategy for oligo[2,7-biphenylenylene-(*E*)-vinylene]s (**OBV**'s) was designed as depicted in Scheme 11. Starting with the chloride **OBV1Cl** , **OBV2** and **OBV3** were expected to be obtainable respectively from the coupling of OBV1Cl with sodium sulfide and with the dithiol **12**. The next interative cycle was to function through the coupling of **OBV1Cl** with the building block **13**. With the addition of each building block **13**, the number of biphenylene unit increases by one. Mathematically, couplings of

(a) **OBV(n/2)Cl** with the dithiol **12** will generate **OBV(n+1)**; and coupling of

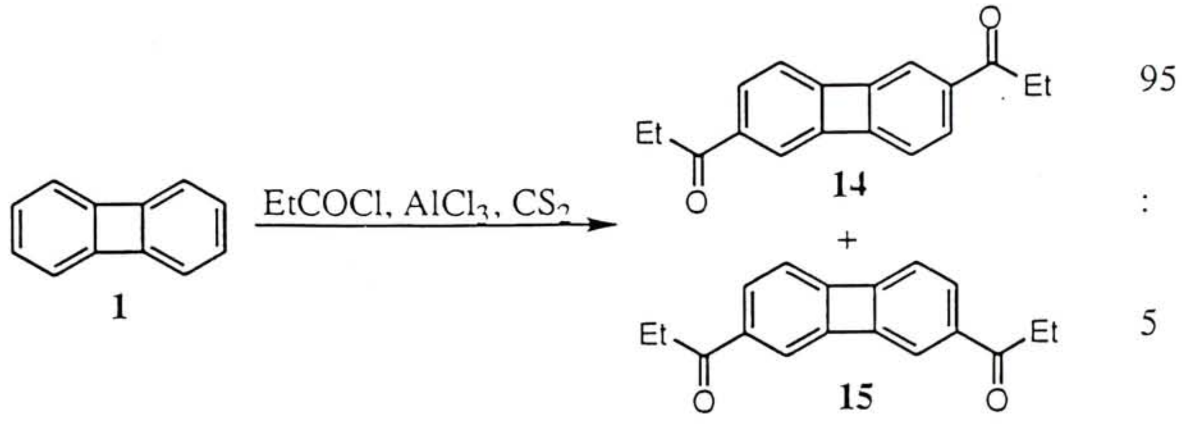
(b) **OBV(n/2)Cl** with sodium sulfide will generate **OBVn**.



Scheme 11. Synthetic strategy of oligo[2,7-biphenylenylene-(*E*)-vinylene)s (**OBV**'s)

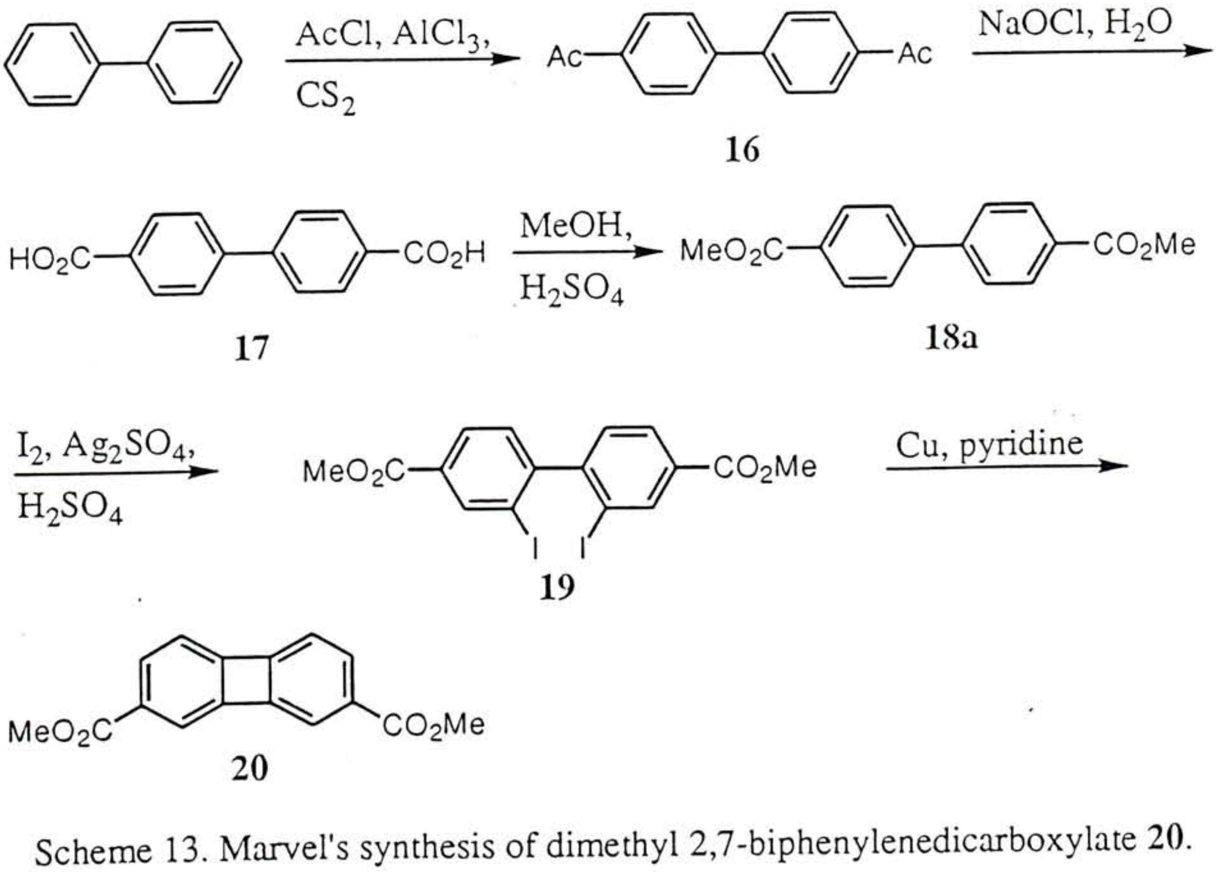
3. 2. Preparation of Dialkyl 2,7-biphenylenedicarboxylate

At the outset of our work, there were only a few reports on the synthetic aspects of 2,7-substituted biphenylenes. The first known 2,7-disubstituted biphenylene was 2,7-diethylcarbonylbiphenylene (**15**) which was isolated as a minor product in the preparation of 2,6-diethylcarbonylbiphenylene (**14**) reported by McOmie in 1965[33, 34] (Scheme 12). The preference in the 2,6-selectivity can be understood by comparing the stabilities of the group of canonical-resonance-stabilized carbonium ions that would be formed through 2,6-attack on the one hand with the group formed through 2,7-attack on the other with an electron-withdrawing substituent at the 2-position, i.e., an ethylcarbonyl group in this case.[11]



Scheme 12. Friedel-Crafts acylation of biphenylene.

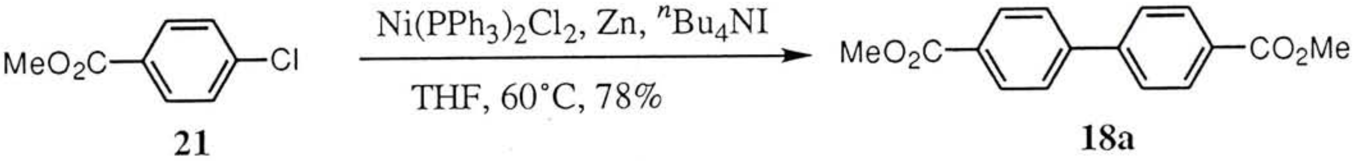
The next 2,7-disubstituted biphenylene did not appear until 1978 when Marvel and his coworkers reported the synthesis of dimethyl 2,7-biphenylenedicarboxylate (**20a**) which was used as a cross-linking agent in preparing polyesters.[35] We therefore set out to repeat their work (Scheme 13) with the hope to secure sizable quantities of **20a** as the source of the biphenylene unit for our project. As expected, Friedel-Crafts acylation of biphenyl in carbon disulfide gave 80% yield of 4,4'-diacetylbiphenyl (**16**). However, in our hands, haloform reaction of **16** using sodium hypochlorite solution as the oxidant failed to give the desired 4,4'-biphenyldicarboxylic acid (**17**).



Scheme 13. Marvel's synthesis of dimethyl 2,7-biphenylenedicarboxylate **20**.

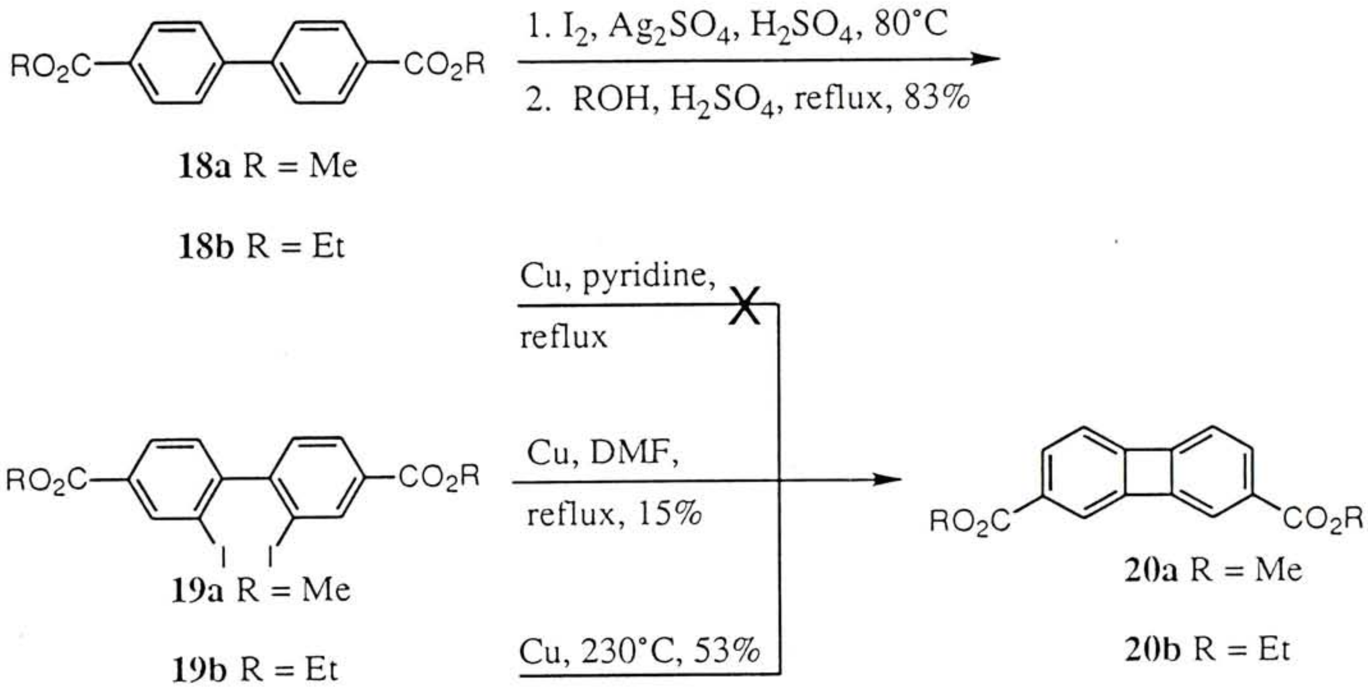
A precipitate was obtained which was insoluble in most orgainc solvents. Attempted esterification of this solid in methanol with added conc. sulfuric acid led to a mixture of compounds which could not be separated. The same result was obtained by treatment of the presumably carboxylic acid with thionyl choride followed by methanol. After a couple of trials, Marvel's synthetic pathway for preparing **20a** was abandoned.

In the search of a better method of preparing a dialkyl 4,4-biphenyldicarboxylate, nickel(0)-catalyzed homocoupling of aryl halide was employed (Scheme 14).[36, 37] In the course of this work, we found that not only the *in situ* generation of nickel(0) complex through reduction of nickel(II) by zinc powder (as indicated by its characteristic blood red color) required a dry reaction medium, but also the catalytic coupling reaction had to proceed in absolute dryness since in the presence of any proton source, nickel(0)-catalyzed dehalogenation of aryl halide to the corresponding arene would compete with the desired pathway, resulting in a much lower yield of the product and a tedious separation procedure. Since this type of metal catalyzed reaction demands an absolutely dry reaction medium which, in turn, complicates the prior treatments of solvents, reactants and reagents, it usually works best in medium scales. Nevertheless, we successfully carried out the reaction using up to 100 g of the starting methyl *p*-chlorobenzoate (**21**) to give the desired **18a** with good yields (~80%).



Scheme 14. Nickel(0)-catalyzed coupling of aryl halide.

After having solved our problem in preparing dimethyl 4,4'-biphenyldicarboxylate (**18a**), we returned to Marvel's route for iodinating this material. Iodination at the 2,2'-positions was facilitated by silver sulfate with iodine in conc. sulfuric acid (Scheme 15). The literature method worked well in this case except that the reaction actually gave the hydrolyzed product , i.e. the diacid, rather than the diesters **19**. Since the diacid was too polar to be monitored by TLC, reaction time, reaction temperature and concentration had to be optimized in order to minimize the extent of incomplete or over iodination. The optimized reaction time, reaction temperature and concentration are reported in **Section 5**. The diacid obtained was transformed back to the diesters **19** by esterification in methanol or ethanol containing catalytic amount of conc. sulfuric acid. The overall yeilds were generally higher than 80%.

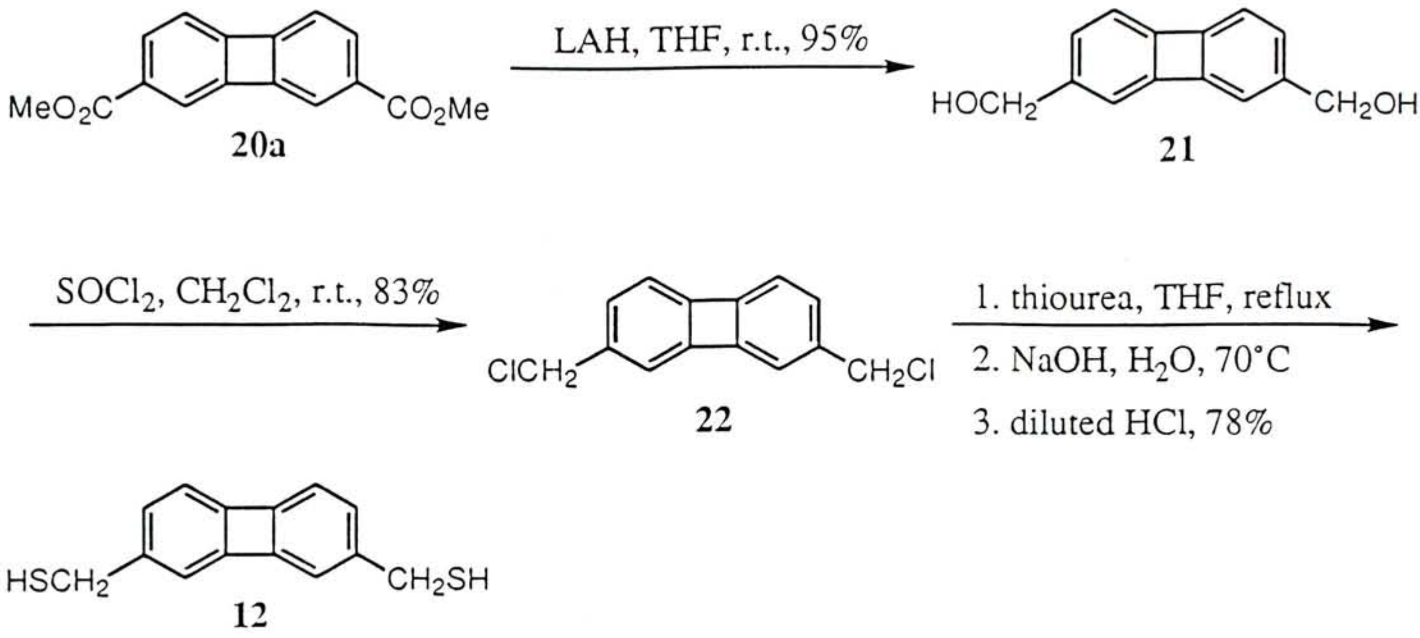


Scheme 15. Sythetic scheme of dialkyl 2,7-biphenylenedicarboxylate.

The key-step in synthesizing dialkyl 2,7-biphenylenedicarboxylates **20** was the Ullman reaction (Scheme 14). In Marvel's route, this intramolecular cyclization was effected by refluxing dimethyl 2,2'-diiodobiphenyl-4,4'-dicarboxylate **20a** with copper powder in dry pyridine. Again, in our experiments, this procedure failed to give any of the desired product. However, in refluxing DMF (dried by distillation over P_2O_5) as the reaction medium, the Ullman reaction succeeded in generating the desired biphenylene though the yields were poor (< 15%) and the long reaction times were long (7 days). Attempts to increase the yield by using higher-boiling solvents such as DMSO or N,N-dimethylacetamide (both freshly distilled over P_2O_5) failed. Disappointingly, the reaction neither responded to the assistance of ultrasound irradiation[38] nor the use of purified copper powder (diluted HCl-stirred, acetone-washed and vacuum-dried) as the reagent. Finally, this Ullman reaction was found to proceed somewhat better at high temperature in the solid phase, i.e. without the use of any solvent. Heating of copper powder and dialkyl 2,2'-diiodo-4,4'-biphenyldicarboxylates **19a** or **19b** at 230°C for 10 hours led to the desired product with satisfactory yields (~50%). Commercially available or purified copper powder (diluted HCl-stirred, acetone-washed and vacuum-dried) gave the same yields. The reaction required a dry medium since protio-dehalogenation occurred in the presence of a proton source, giving back the deiodinated ester **18a** or **18b**. However, protio-dehalogenation still occurred to a certain extent in every trial and the colum chromatographed dimethyl or diethyl 2,7-biphenylenedicarboxylate (**20a** or **20b**) had to be purified by recrystallization from toluene or hexane, respectively, in order to remove the residual dimethyl or diethyl 4,4'-biphenyldicarboxylate (**18a** or **18b**) which was carried over unseparable from the preceding chromotographic purification procedures.

3. 3. Synthesis of 2,7-Bis(mercaptomethyl)biphenylene

The dithiol building block 2,7-bis(mercaptomethyl)biphenylene (**12**) for S-alkylating the **OBVnCl** 's was prepared through the reaction of the dichloride **22** with thiourea in refluxing THF followed by subsequent hydrolysis with aqueous sodium hydroxide (Scheme 16). The dichloride **22** was obtained by chlorinating the diol **21** with thionyl choride in refluxing dichloromethane whereas the diol **21** was formed by the reduction of the diester **20a** in dry THF at r.t. Although the diester **20a** had low solubility in THF, the LAH reduction was manageable in dilute solutions (~0.5 g in 100 mL THF).



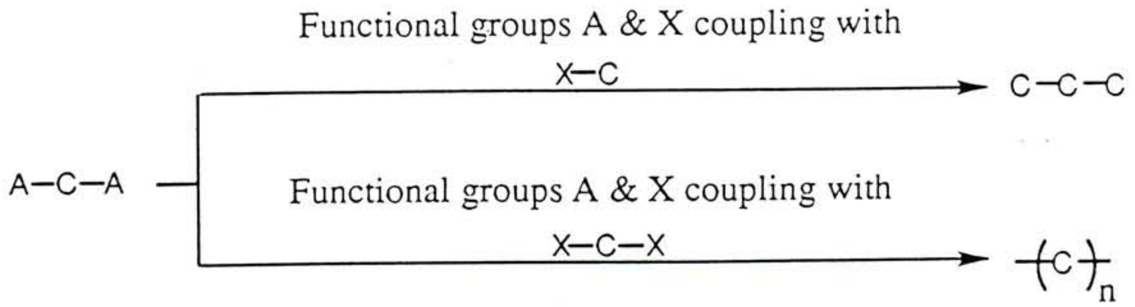
Scheme 16. Synthetic scheme of 2,7-bis(mercaptomethyl)biphenylene **12**.

3. 4. Synthesis of 30 (OBV1Cl)

In order to utilize our proposed stepwise chain growth technique in constructing the conjugated biphenylene system, unsymmetrically disubstituted biphenylene must be generated since a symmetrically difunctional compound would undergo non-selective reactions with the coupling partner, leading to

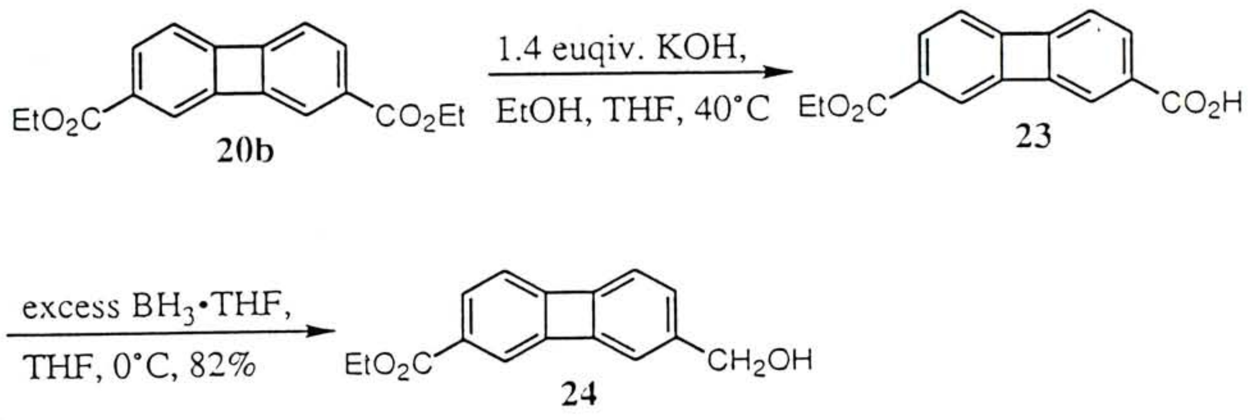
(a) the termination of chain growth if the coupling partner is monofunctional; or

(b) the polymerization between the two reactants if the coupling partner is also symmetrically difunctional (Scheme 17).



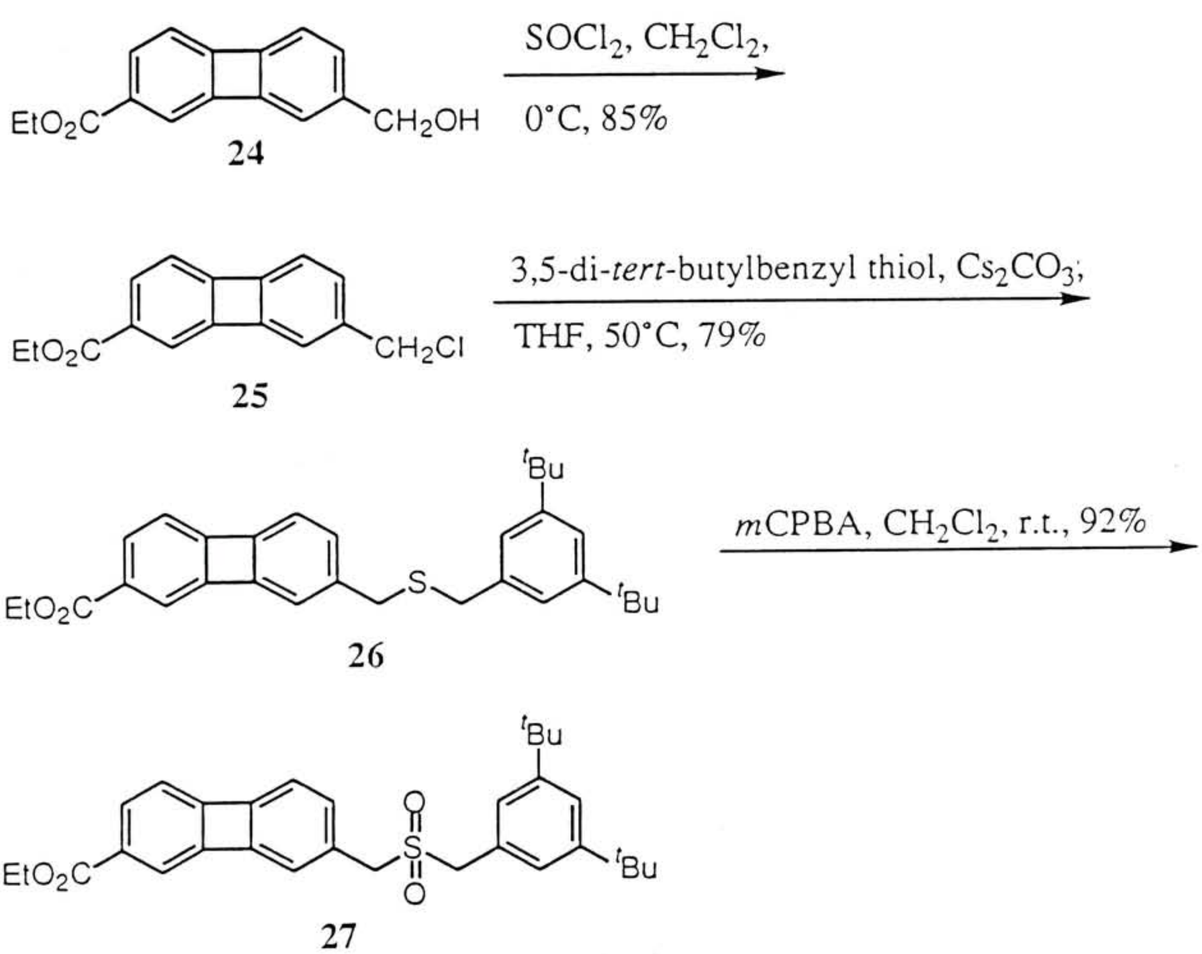
Scheme 17. Coupling reactions of symmetrically difunctional compounds.

With the diester **20** in hand, a selective hydrolysis was performed. Using 1.4 equiv. of potassium hyroxide, basic hydrolysis of the ester group occurred in a mixed solvent system of ethanol and THF at 40°C. The diethyl ester **20b** was used instead of the dimethyl ester **20a** because of the superior solubility of the former in ethanol and THF. Chemoselective reduction of the carboxylic funtionality in the acid-ester **23** was effected by borane•THF complex at 0°C. A large excess of borane•THF complex was used because in our trials, we found that the use of excess borane•THF complex greatly accelerated the reaction (completed within 30 min) with the ester group untouched while the reaction did not complete over 1 day if only one equiv. of borane•THF complex had been used (Scheme 18).



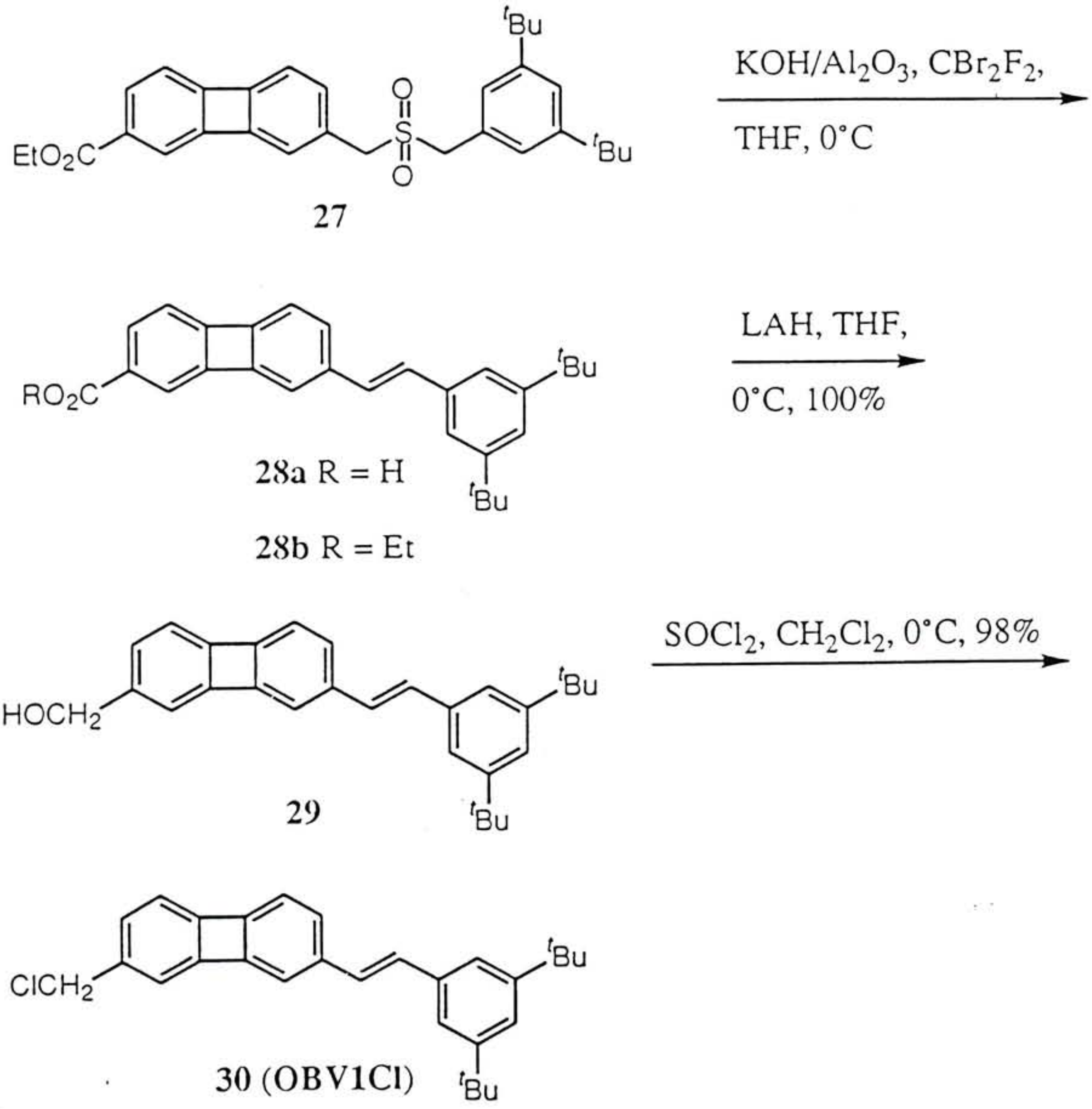
Scheme 18. Selective hydrolysis-reduction of the diester **20b**.

After having secured the bifunctional biphenylene derivative **24**, the hydroxymethyl functionality was subjected to a series of reactions for contructing the required sulfone **27** for the Ramberg-Bäcklund reaction while the ester functionality was deliberately retained for future synthetic use (Scheme 19). Thionyl chloride chlorination of the alcohol **24** in dry dichloromethane at 0°C was clean and high-yielding. Unlike most other benzyl chlorides, the resulting arylmethyl chloride **25** was kinetically inert enough to be purified by column chromatography. The introduction of a di-*tert*-butylphenyl group to the side chain of the biphenylene was accomplished by S-alkylation at the benzylic position of the chloride **25** under the action of cesium carbonate as base. The 3,5-di-*tert*-butylphenyl group served as the solubilization appendage for the system since the desired conjugated biphenylene oligomers were anticipated to have low solubilities in most organic solvents. It also acted as a stable terminal group of the system which was adequately inert to most reaction involved. The resulting thioether **26** was oxidized by *m*CPBA to the corresponding sulfone in dichloromethane. Although Oxone® was extensively used in our laboratory as the oxidant for thioethers,[9, 32] the oxidation by *m*CPBA in this case was superior for a shorter reaction time and higher yield as compared to the use of Oxone®.



Scheme 19. Synthesis of the sulfone **27**.

Our modified Ramberg-Bäcklund procedure employing alumina-supported potassium hydroxide-dibromodifluoromethane has been extensively employed in generating stilbenoid type compounds with excellent (*E*)-stereoselectivity.[9, 32] This reaction was equally effective in generating an (E)-double bond between the biphenylene and the benzene ring (Scheme 20). Ramberg-Bäcklund reaction of the sulfone ethyl ester **27** yielded the olefin **28**. The reaction mixture turned from yellow to fluorescent yellow once dibromodifluoromethane was added, indicating the formation of conjugation between the di-*tert*-butylphenyl group and the biphenylene chromophore by a carbon-carbon double bond. The reaction was complete within 5 min. at 0°C and was accompanied by a small extent of hydrolysis of the ethyl ester group caused by the basic catalyst. Taking the advantage of the reliable reductions of both carboxylic acid and ester functionalities by lithium aluminum hyhride, the resulting mixture **28a** and **28b** were subjected to LAH reduction in THF at 0°C without prior separation. The reduced product, i.e., the alcohol **29** was then isolated and purified by column chromatography with an essentially quantitative yield from the sulfone **27** in two steps.



Scheme 20. Ramberg-Bäcklund reaction of the sulfone **27** and synthesis of **30 (OBV1Cl)**

The presence of only an (*E*)-carbon-carbon double bond (J = 16.2 Hz) was confirmed by the ^{1}H NMR spectrum of the alcohol **29** and the signals for the three aromatic protons of the 3,5-di-*tert*-butylphenyl group form a multiplet at 7.32-7.34 ppm (Fig. 7).

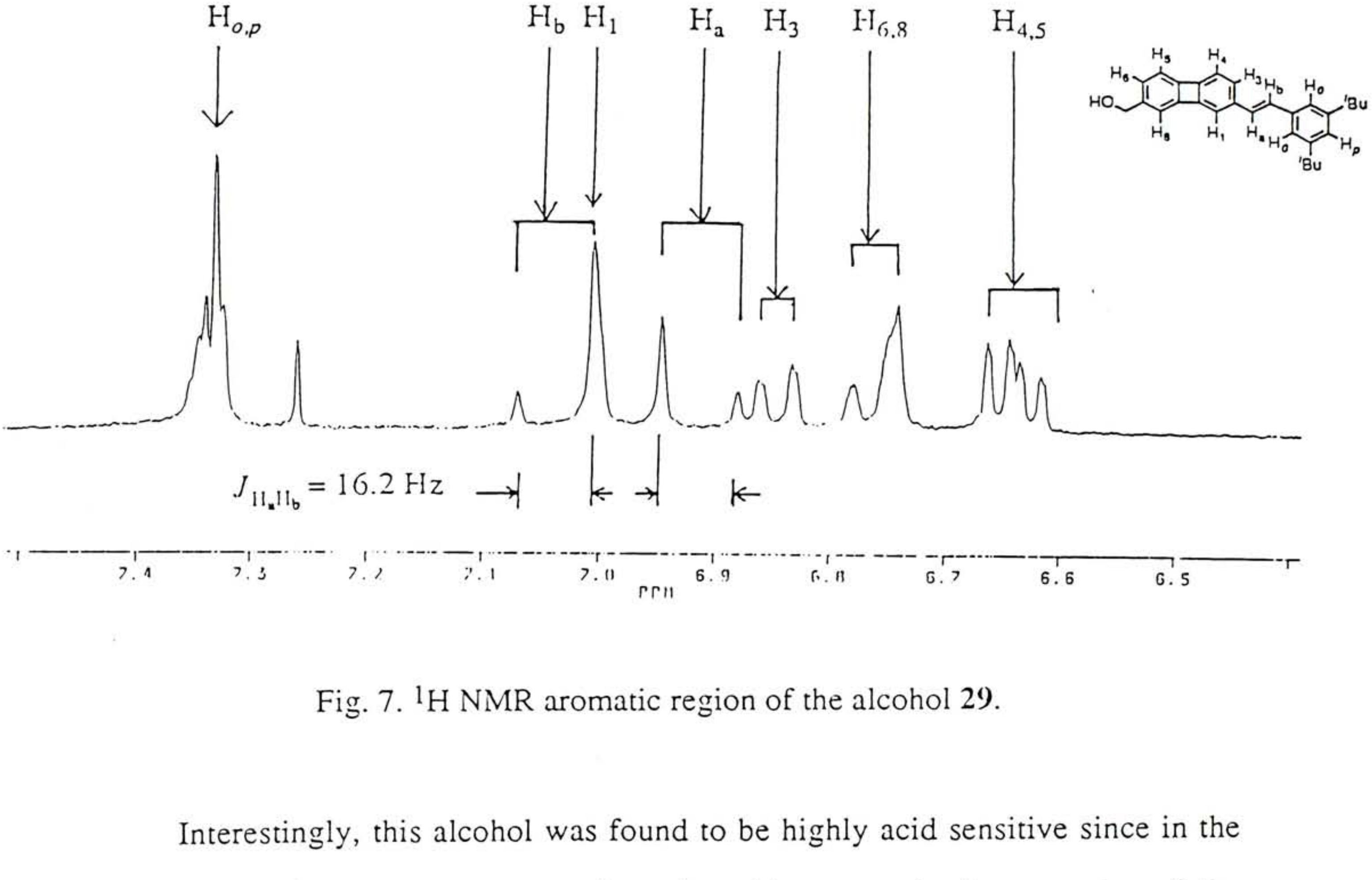
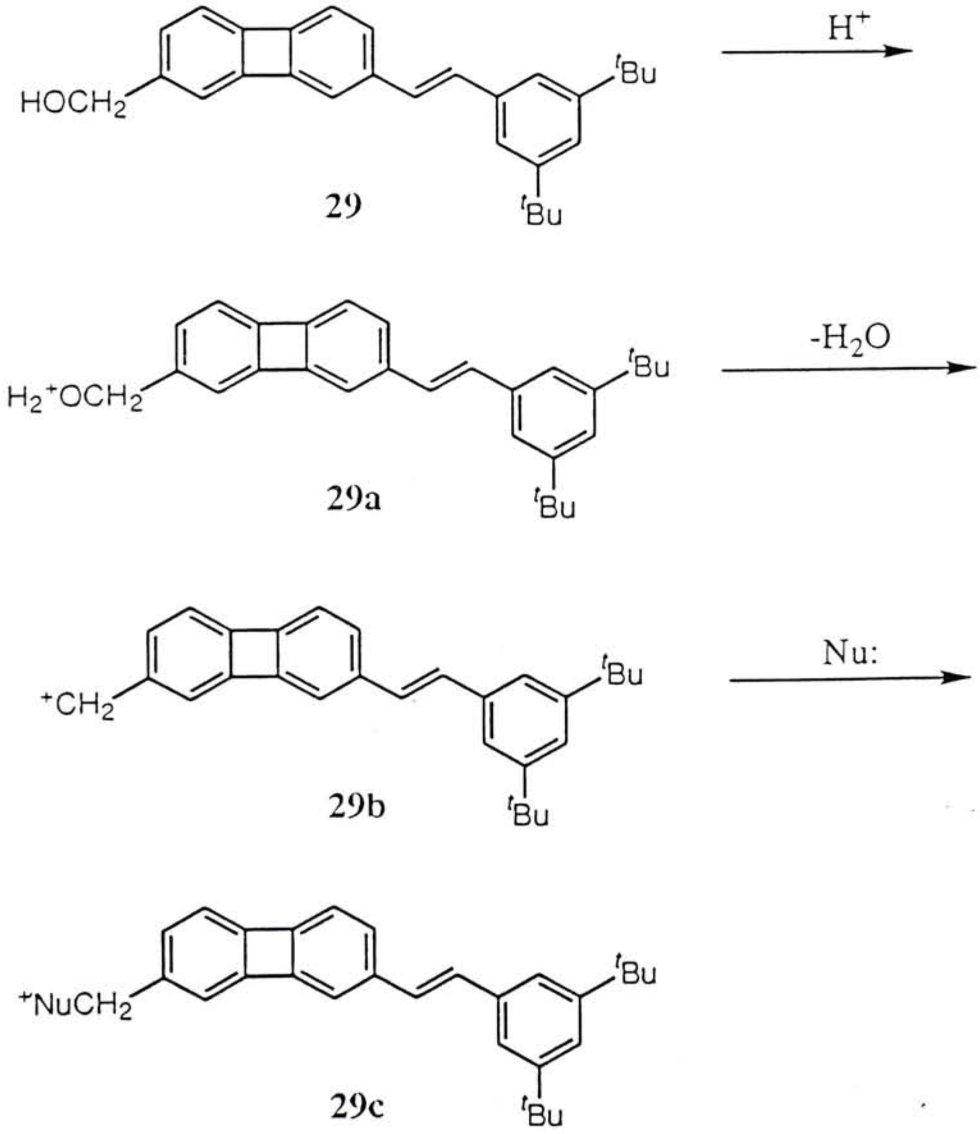


Fig. 7. ^{1}H NMR aromatic region of the alcohol **29**.

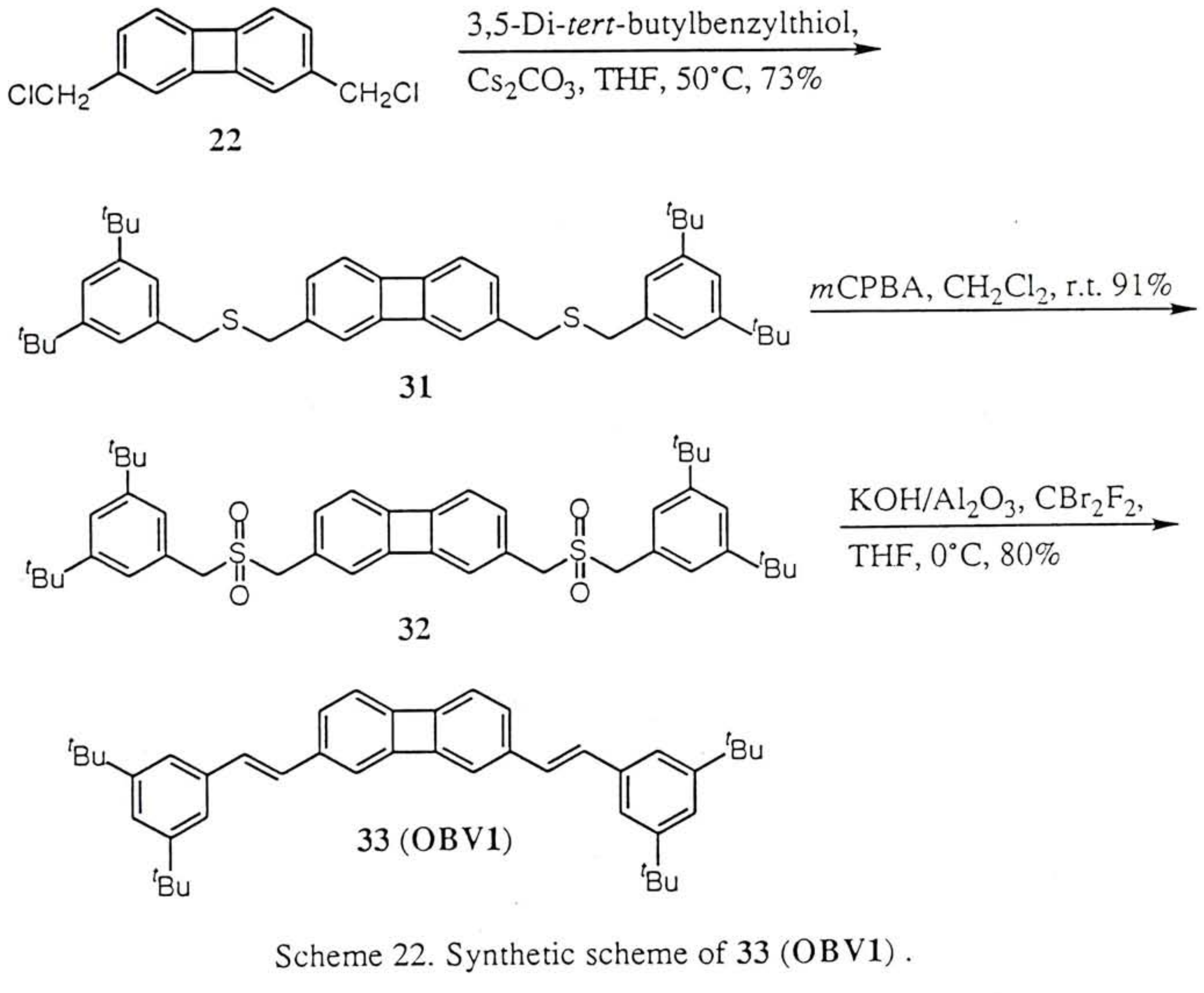
Interestingly, this alcohol was found to be highly acid sensitive since in the work-up procedure, trace amount of acetic acid present in the reservior of the rotavaporator led to extensive reactions on the alcohol **29**, giving a very complicated mixture of compounds. Attempts to separate this mixture into each characterizable component failed. The extensive decomposition of this alcohol in acids probably arised from the fast protonation at the biphenylenemethylhydroxyl group, and the easy formation of the stabilized biphenylenemethyl cation **29b**. The net result was the subsequent extensive attacks by any agent bearing a nucleophilic funtionality, leading to the formation of a number of products (Scheme 21). As this type of decomposition was not observed in the non-conjugated alcohol **24**, the increased conjugation in this alcohol is suspected to be the reason for the facile formation of the biphenylenemethyl cation **29b**. Thus, in the work-up procedure, care had to be taken for avoiding contact with any acidic solution. Chlorination of the alcohol **29** was effected by thionyl chloride in dichloromethane at 0°C, giving **30** (**OBV1Cl**) as one of the building blocks in our system. Owing to similar electronic factor at the biphenylenemethyl position, the chloride **30** decomposed rapidly in basic medium and in silica gel. Thus it was only partially purified by rapidly passing the crude product through a short column of silica gel. The chemical stabilities of the alcohol **29** and the chloride **30** were so low that they underwent decomposition even during storage at -20°C. As a consequence, both materials were not stored and were used immediately after preparation from their precusor, i.e., the ester/acid mixture **28** which was stable for storage at -20°C.



Scheme 21. Postulated decomposition pathway of the alcohol **29** in acid media

3. 5. Synthesis of OBV1

The monomer **33** (**OBV1**) served as the prototype of fully conjugated biphenylene. It is an important basis for establishing structure-properties relationship with its higher homologues by comparision. Starting from the dichloride **22**, it was obtained in three steps *via* the reaction sequence of S-alkylation, sulfone formation and Ramberg-Bäcklund reaction (Scheme 22).



Scheme 22. Synthetic scheme of **33** (**OBV1**) .

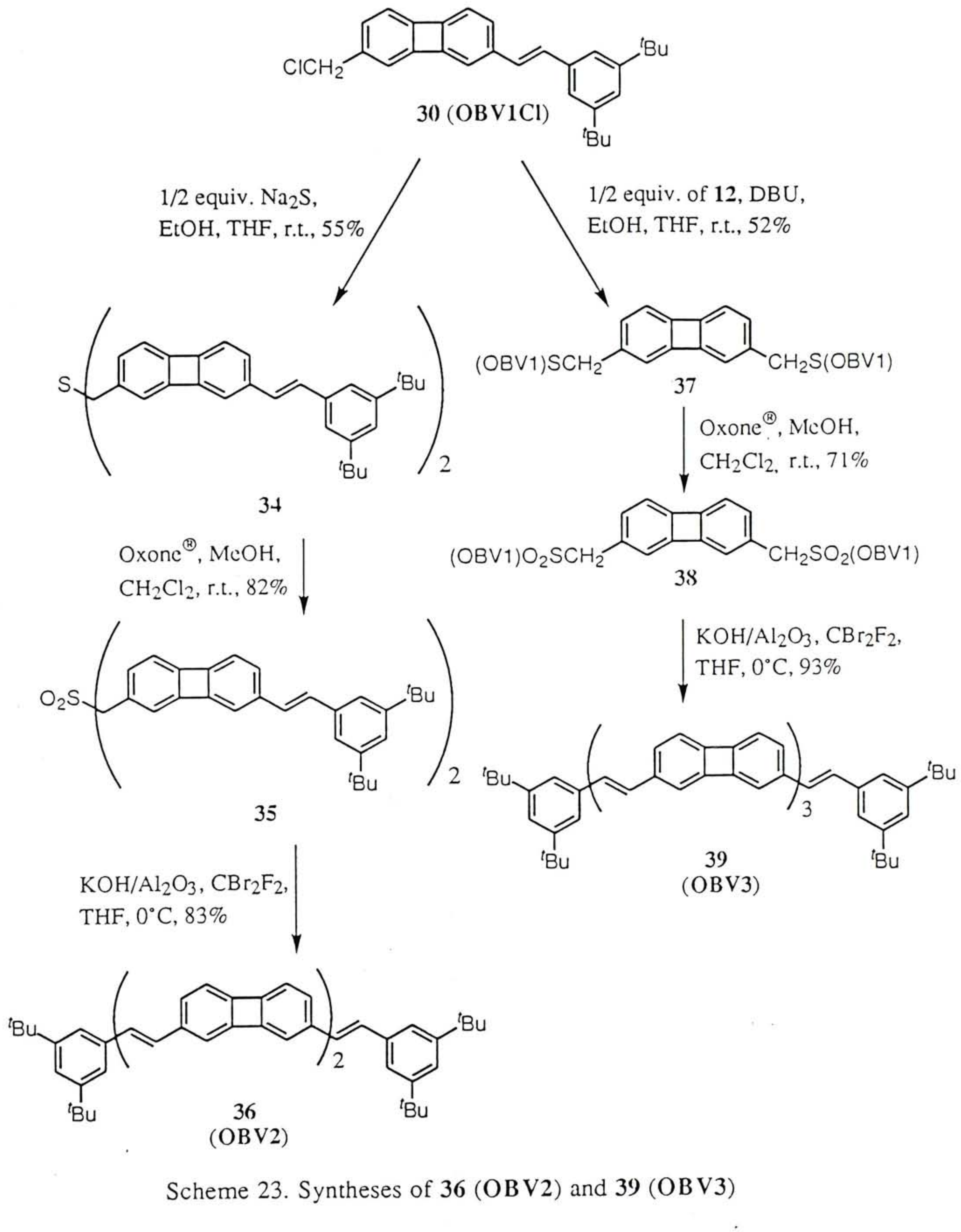
The formation of the bissulfide **31** was effected by heating the dichloride **22** and 3,5-di-*tert*-butylbenzylthiol with cesium carbonate as the base. Oxidation of the bisssulfide **31** was again performed by *m*CPBA in dichloromethane. The corresponding bissulfone **32** was obtained in 90% yield. Conjugation throughout the phenyl rings and the biphenylene chromophore was indicated by the strongly fluorescent yellow color of **33** (**OBV1**) which was generated by Ramberg-Bäcklund reaction of the precursor bissulfone **32** in 80% yield.

3. 6. Syntheses of OBV2 and OBV3

Making use of the building block chloride **30**, **36** (**OBV2**) and **39** (**OBV3**) were synthesized following the reaction sequence of S-alkylation, sulfone formation and Ramberg-Bäcklund reaction (Scheme 23). In the synthesis of **36** (**OBV2**), the precursor monosulfide **34** was obtained through the coupling of the chloride **30** (**OBV1Cl**) with sodium sulfide in a mixed solvent system of THF and ethanol which dissolved both the chloride **30** and sodium sulfide. In the synthesis of **39** (**OBV3**), the bissulfide **37** was obtained through the coupling of the chloride **30** with the dithiol **12** in the presence of DBU as base in anhydrous benzene. Chemoselective oxidations of the sulfides **34** and **37** to the corresponding sulfones **35** and **38** were performed by Oxone® in a mixed solvent system of dichloromethane and methanol. In our cases, this solvent system was found to be superior than the traditional ones using methanol or dichloromethane/water/cat. $^{n}Bu_4SO_4$. Although these sulfones were much less soluble than the precursor sulfides, they were still soluble enough for column chromotographic purifications. Finally, Ramberg-Bäcklund reactions of these sulfones gave the corresponding **36** (**OBV2**) and **39** (**OBV3**) as the fully conjugated olefins.

^1H NMR spectra (Fig. 8) of **OBVn**'s (n = 1-3) show the AB pattern of the vinyl protons (H_a and H_b) at the terminal sites with large coupling constants ($J \sim 16$ Hz). This pattern is observable since chemical environments between the biphenylenyl and the phenyl regions are distinguishable. However, the inner vinyl protons ($H_{a'}$ and $H_{a''}$) in **OBV3** between the biphenylenyl regions form a extreme AB pattern whose coupling cannot be discerned in the seriously overlapped region of the biphenylenyl proton signals. In **OBV2**, the two inner vinyl protons ($H_{a'}$) are chemical shift equivalent by symmetry, and the relative stereochemistry cannot be revealed by NMR technique. Nevertheless, we assume these carbon-carbon double bonds to have (*E*)-

stereochemistry since no (Z)-stereochemistry has ever been observed in the formation of stilbenoid compounds by our Ramberg-Bäcklund reaction.[9, 32]



Scheme 23. Syntheses of **36** (**OBV2**) and **39** (**OBV3**)

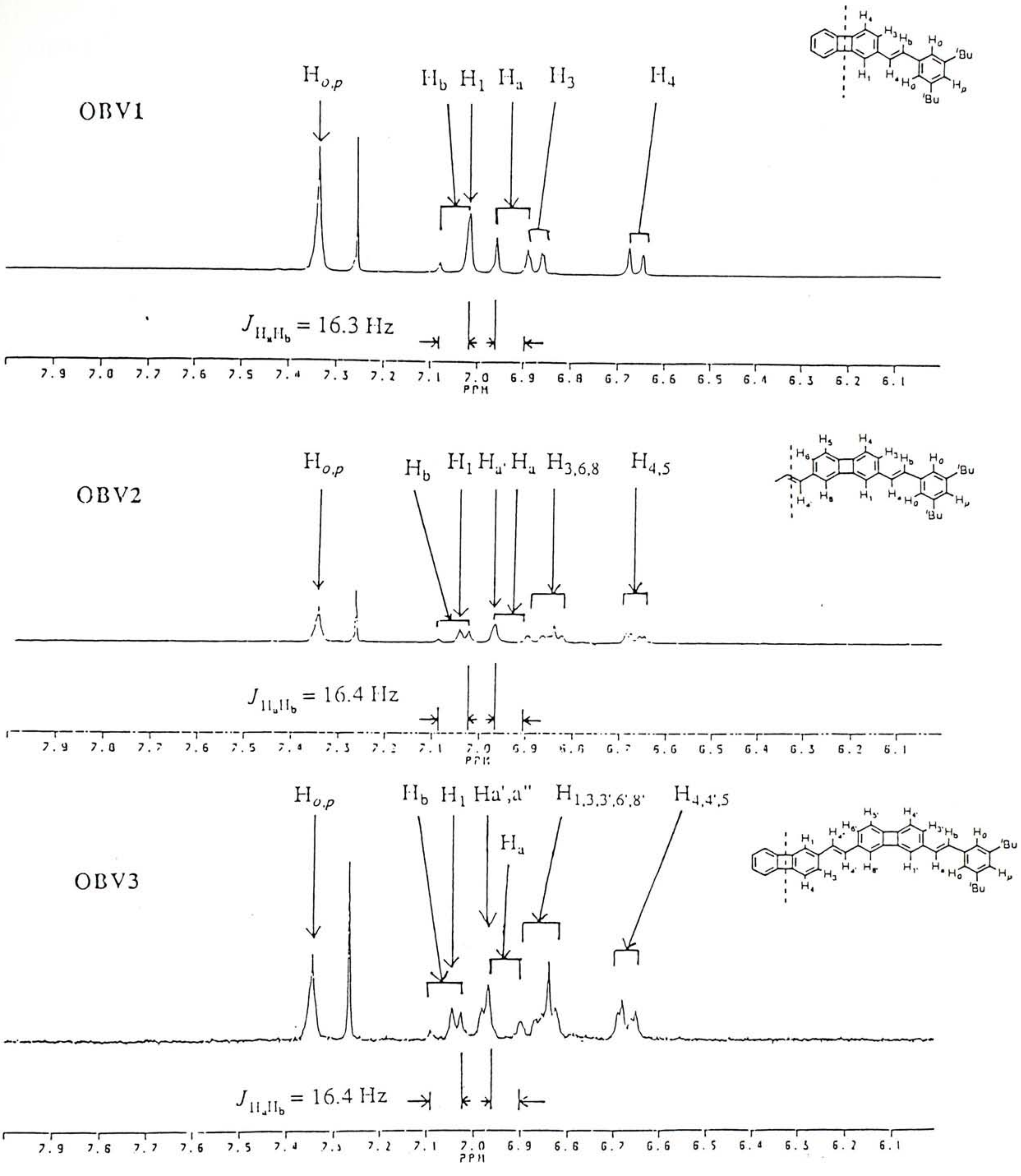


Fig. 8. ^{1}H NMR spectra of **OBV1-3** at the aromatic region.

In their ^{13}C NMR spectra, it is interesting that the biphenylene carbon peaks change from singlet to doublet to triplet in **OBV1**, **OBV2**, and **OBV3**, respectively, while the pattern of the terminal phenyl carbons are not much affected in the trend due to the already confined chemcial environment in that region (Fig. 9).

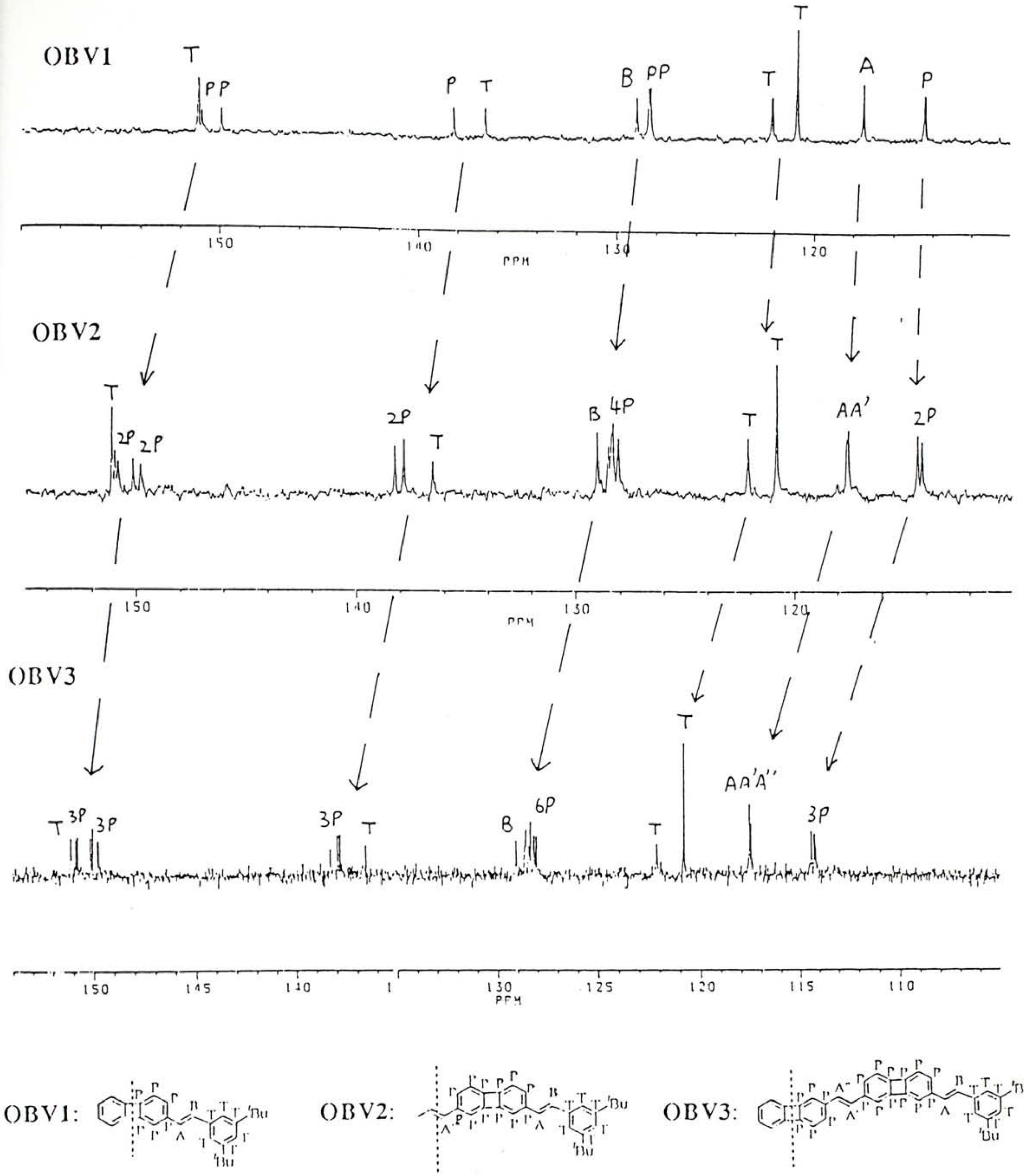
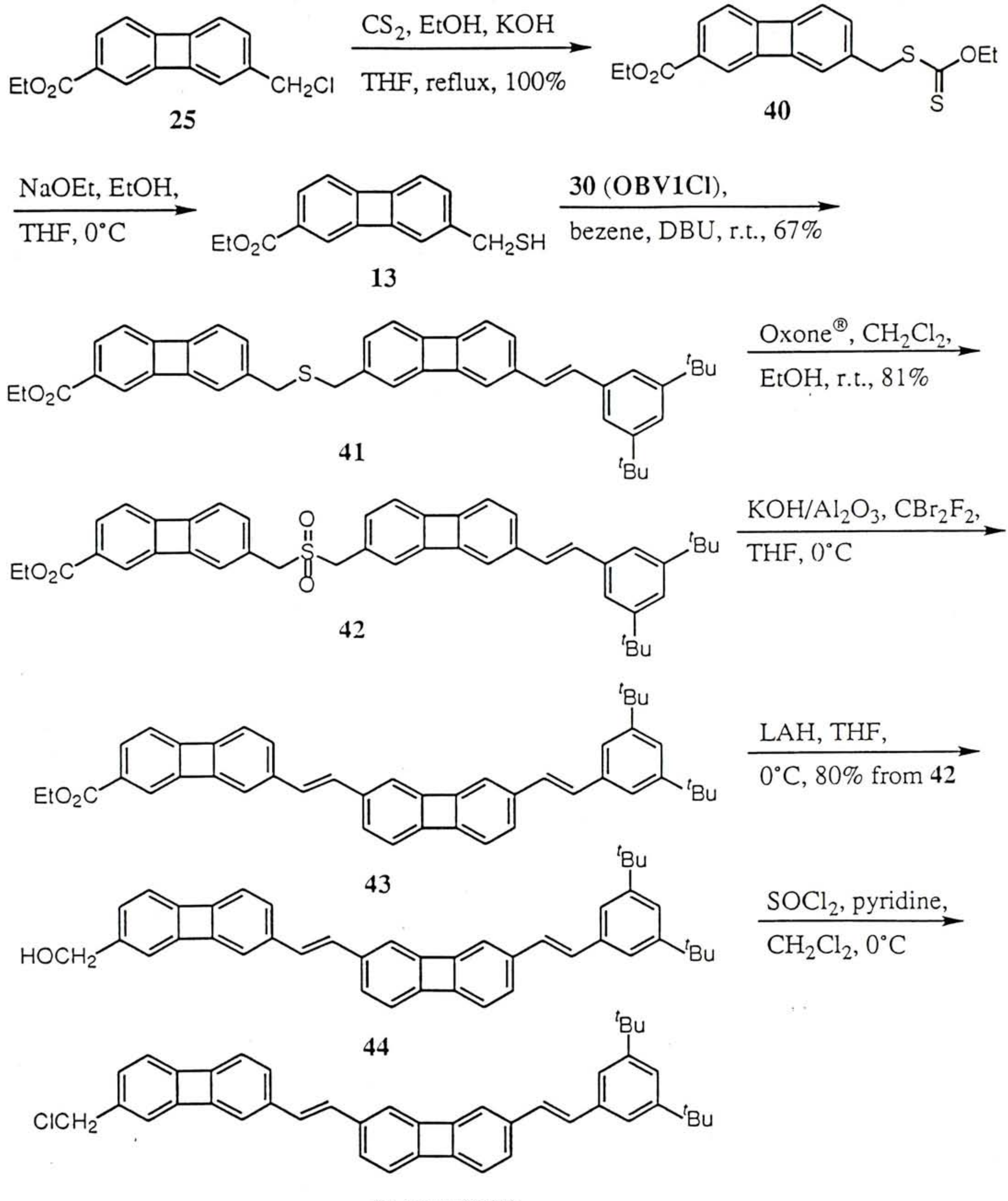


Fig. 9. ^{13}C NMR spectra of **OBV1-3** at the aromatic carbon region.

3. 7. Synthesis of the buliding block 13 and 45 (OBV2Cl)

To increase the number of biphenylene units in our system, the building block **13** bearing a mercapto functionality for S-alkylation and a ester group for LAH reduction-SOCl$_2$ chlorination sequence was syntheiszed. The next iterative cycle was then performed in order to generate the chloride **45** (**OBV2Cl**) (Scheme 24) as the precursor for **48** (**OBV4**) and **51** (**OBV5**) . Potassium ethyldithiocarbonate was *in situ* generated by refluxing carbon disulfide, ethanol and potassium hydroxide in THF.

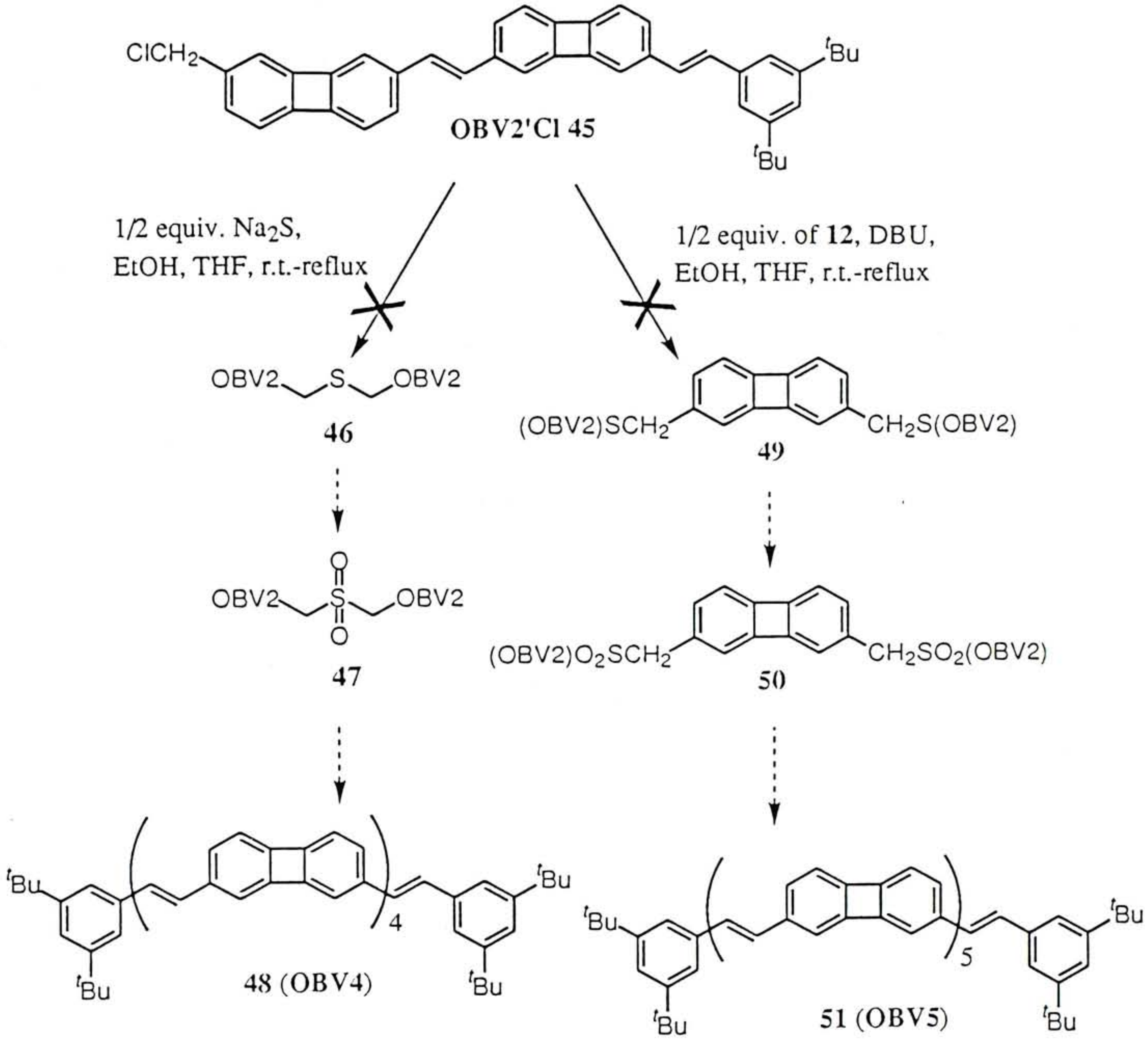


Scheme 24. Synthetic scheme for the building block **13** and **45** (**OBV2Cl**).

Its nucleophilic attack on the chloride **25** yielded the xanthate ester **40**. The building block **13** was obtained through the hydrolysis of the xanthate ester **40** by sodium ethoxide, and was used immediately after preparation without further purification because of its high susceptibility to air oxidation. The five-step iterative procedure of S-alkylation, oxidation, Ramberg-Bäcklund, LAH reduction and $SOCl_2$ chlorination was then preformed to give the crude chloride **45** (**OBV2Cl**) in 43% yield. Similar to their **OBV1** analogues preparation, the alcohol **44** was acid sensitive and the chloride **45** underwent extensive decomposition in silica gel. They were both used immediately in the next step after preparations due to their chemical instabilities.

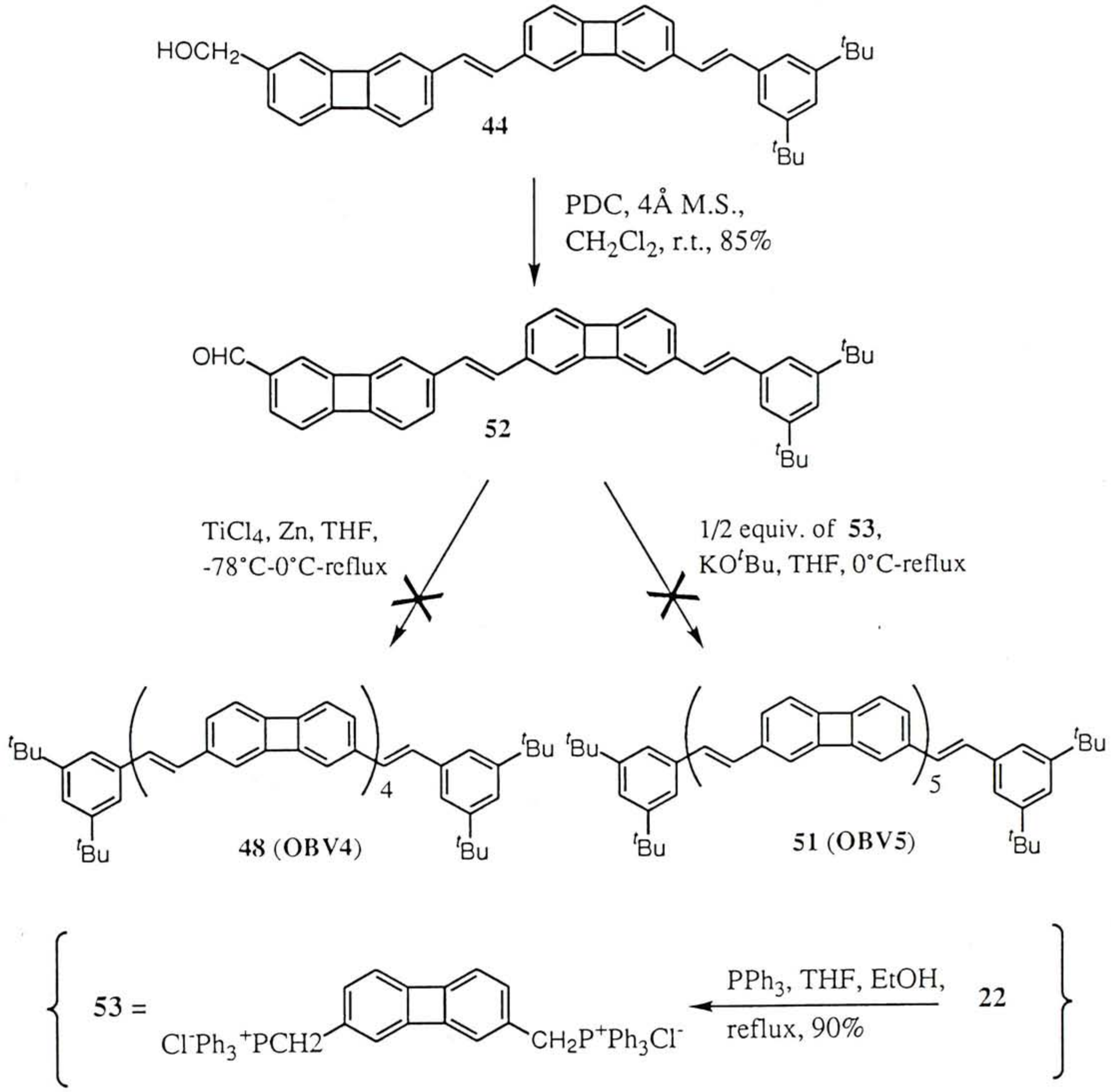
3. 8. Attempted synthesis of OBV4 and OBV5

Following the previous routes under similar conditions, syntheses of **48** (**OBV4**) and **51** (**OBV5**) were attempted (Scheme 25). Unexpectedly, S-alkylations of **45** (**OBV2Cl**) by sodium sulfide and the dithiol **12** were unsuccessful owing to the apparent inertness of **45** to the thiolates. TLC showed extremely slow conversion of **45** to a large number of new spots under usual S-alkylation conditions. Attempts to isolate a pure substance by column chromatography failed due to the complexity of the product mixture. Similar results were noted in its reaction with stronger nucleophiles such as thiourea. After a number of unsuccessful trials, the route of S-alkylation was abandoned and other methods for generating **OBV4** and **OBV5** were sought. Attracted by the clean oxidation of the alcohol **44** to the corresponding aldehyde **52** by PDC, two methods utilizing carbonyl compounds for generating olefins were attempted. They were, respectively, the reductive coupling of **52** by the McMurry procedure[39, 40] and the Wittig reaction of **52** with the bisphosphonium salt **53**[6, 8, 28, 29, 41] (Scheme 26). Unfortunately, both reactions failed to give the desired products. In the case of the reductive coupling using $TiCl_4$ with Zn as the reducing agent, the reaction proceeded very slowly to give a very complicated mixture whereas in the Wittig reaction, the aldehyde **52** remained unreacted even at refluxing temperature for 2 days and was re-isolated without decomposition.



Scheme 25. Attempted syntheses of **48** (**OBV4**) and **51** (**OBV5**).

The inertness of the aldehyde functionality in **52** is perplexing. Whatever electronic effects conferred on it by the extended conjugation of two biphenylene and one benzene units are not clear to us. Further investigation is necessary for unveiling this mystery.

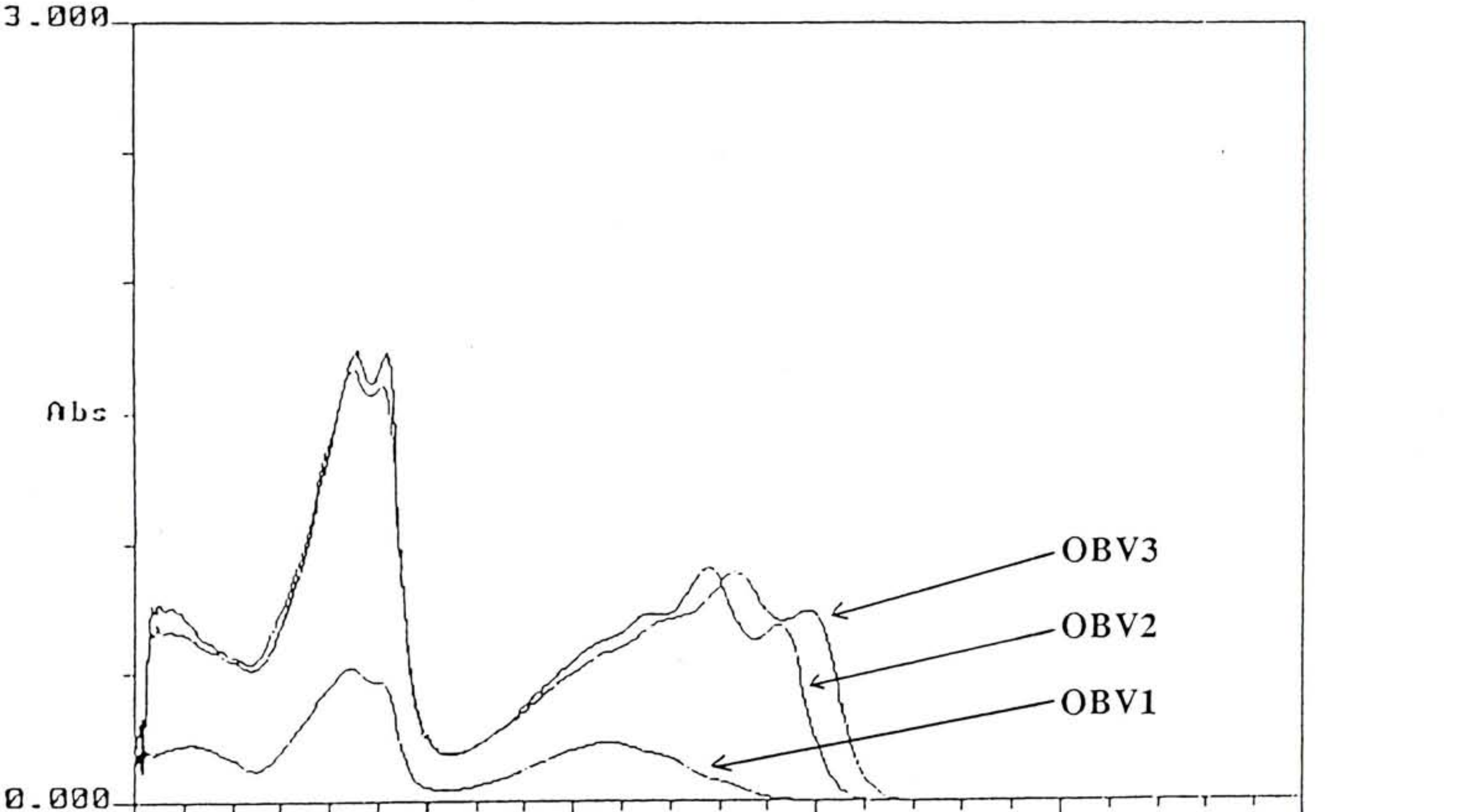


Scheme 26. Attempted syntheses of **48** (**OBV4**) and **51** (**OBV5**) from **52** *via* McMurry and Wittig reactions.

3. 10. Electronic properties of OBV

OBVn's (n = 1- 3) show two major bands of absorption in the UV-VIS spectra (Fig. 10). The first band (310-330 nm) arises from the phenyl rings whereas the second band (450-500 nm) is assigned to the biphenylene chromophore absorption. Significant bathochromic shift ($\Delta\lambda_{max1}$ = 41 nm) and hyperchromic shift ($\Delta\varepsilon_1$ =

13400) is observed in the second band from **OBV1** to **OBV2**. It is an evidence of the effective electron delocalization between the biphenylene chromophores. On the other hand, no bathochromic shift is observed in the first band, indicating conjugations at the phenyl regions are very similar in different **OBV**'s. This suggests electron delocalization between phenyl ring and biphenylene chromophore is not enhanced by the higher conjugation derived from the conjugated oligomer chain. However, bathochromic shift in the second absorption band from **OBV2** to **OBV3** is not as significant as from **OBV1** to **OBV2**.



Compound	λ_{max1} (nm)	λ_{max2} (nm)	ε_1 ($M^{-1}cm^{-1}$)	ε_2 ($M^{-1}cm^{-1}$)
OBV1	414	none	46000	none
OBV2	455	485	180000	140000
OBV3	466	497	180000	150000

Fig. 10. UV-VIS spectrum of **OBV**'s in CH_2Cl_2 and spectroscopic data of the biphenylene absorption band.

Empirically, this UV-VIS absortption trend suggests the conjugation between the biphenylene chromophores are becoming saturated. This fact can also be supported by the very close extinctions coefficients of the absorption maxima. Since the value of an extinction coefficient of absoroption is proportional to effective chromophore density in the molecule, the close values of the extinction coefficients between **OBV2** and **OBV3** means the effective chromophore densities in the two molecules are similar. We also predict the effective chromophore density, and hence the absorption wavelength and the value of extinction coefficient, will reach the saturated values rapidly in higher **OBV**'s (Fig. 11)

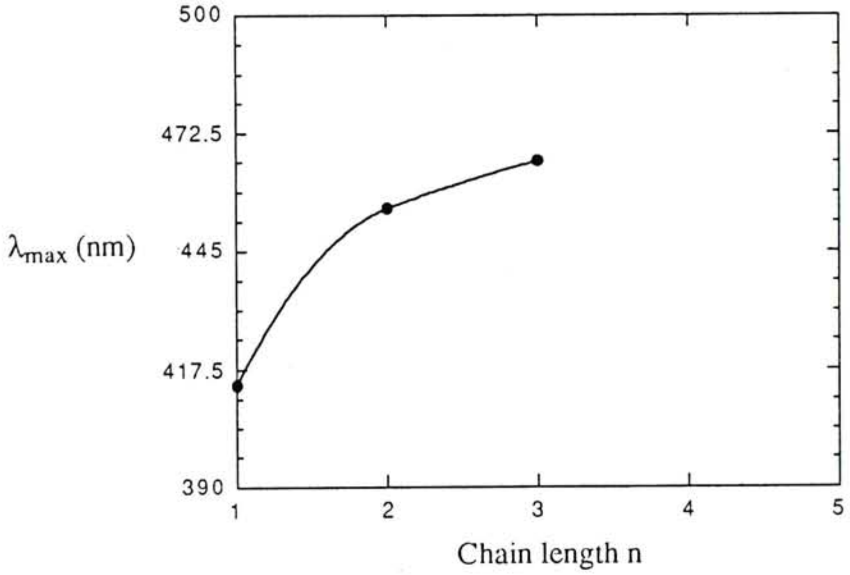


Fig. 11. Plot of λ_{max} *vs* chain legnth n (no. of biphenylene in **OBV**'s).

In order to testify the rapid convergence of absorption maxima in our system, an empirical mathematical approach is the only alternative since syntheses of higher **OBV**'s are so far unsuccessful. The study of the optical absorption trend in the **OBV**-series is based on the asuumption of a linear correlation $E_n = E_\infty + E/n$ between $E_n = h/\lambda_{max}$ (optical absorption energy) and 1/n of the oligomeric **OBV** series. This empirical dependence of the absorption energies on the conjugation length has been applied to systems such as polyacetylene, polyphenylene, polythiophene and polypyrrole in which more or less linear correlations were demonstrated.[42-45] The method is firmly established in the literature[42-44] although there is not a sound physical and theoretical basis for it. In our case, the linearity of the plot of the absorption energies (E_g) *vs* the reciprocal chain lengths (1/n) is demonstrated by a regression coefficient of 0.9992 (Fig. 12).

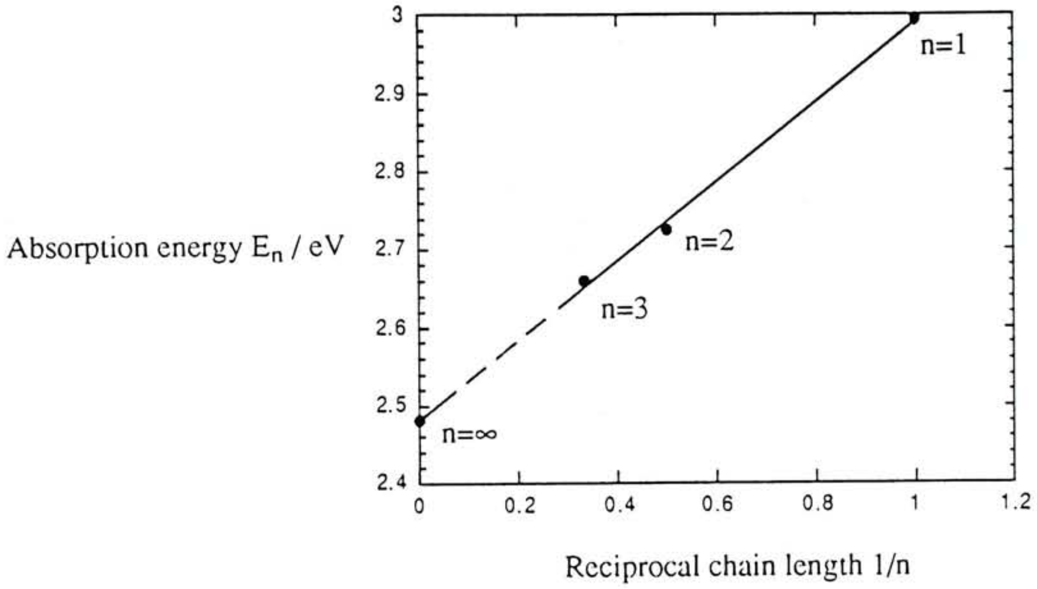


Fig. 12. Plot of absorption maxima *vs* reciprocal chain length 1/n of **OBVn**.

Extrapolation of the assumed linear plot towards the y-intercept yields the value of an absorption energy of 2.48 eV when the chain length approaches infinitely large. This estimated absorption energy of poly[2,7-biphenylenylene-(*E*)-vinylene] (2.35 eV) is lower than the theoretically estimated (by VEH method) bandgaps (E_g) of polypyrrole (2.99 eV)[42], poly(*para*-phenylene) (3.23 eV)[42] and poly(2,7-biphenylene) (2.80 eV)[17] with infinitely long chain lengths.

Red shifts are also observed in the colors of the **OBV**'s (Table 2). The red shifts from solution samples to solid samples is a result of the more restricted rotational and vibrational movements of the molecular framework in the solid state, creating a more effective π-overlapping between the chromophores in the chains which enhances the conjugation in the system.[45]

Compound	Colors of CH_2Cl_2 solutions	Colors of solids
OBV1	yellow	yellow
OBV2	yellow	orange
OBV3	orange	red

Table 2. Colors of solution samples and solid **OBV**'s

Redox activities of **OBV**'s are demonstrated by cyclic voltammetry and the redox data obtained are presented in Table 3. In order to study the temperature influence on the redox activities, cyclic voltammetry experiments of the compounds were performed, respectively, at 20°C, 0°C, and -78°C. Interestingly, temperature-dependent redox selectivities of **OBV**'s are observed. At 20°C and 0°C, oxidations were observed. Fig. 13 shows the voltammograms for the oxidations of **OBVn** (n = 1-3). From **OBV1** to **OBV2**, the number of accessible reversible redox states increases from one to two. However, only one irreversible peak was observed for **OBV3** although the number of accessible redox states were expected to increase with increasing chain length as in the CV study of oligo(phenylenevinylene) (**OPV**).[8, 46] There was no significant difference between the redox activities at 20°C and 0°C except that the potentials ($E°_{oxid}$) dropped to lower values at 0°C. At -78°C, reductions of **OBV**'s were the dominant electrochemical reactions. Fig. 13 also shows the cyclic voltammograms for their reductions. Again, there was an inconsistency in the number of redox states with the chain lengths since **OBV1** had two reverible reductions, **OBV2** had only one reversible reduction, and **OBV3** had one reversible reduction accompanied by two small irreversible peaks. The ill-defined reduction peaks of **OBV3** was probably due to the increasing background currents developed in the electrochemical cell during the measurements. However, several observed characteristic electrochemical behavior such as:

(a) the inconsistency in the number of accessible redox states with chain lengths in oxidations (20°C and 0°C)/reductions (-78°C);

(b) the temperature-depending redox selectivities of **OBV**'s; and

(c) the low reversibilities in the redox reactions of **OBV3**

can neither be explained nor further elaborated before a more detailed and sophisticated study is carried out. Nevertheless, the redox behavior all **OBV**'s still followed the postulated rules as in the case of **OPV**[8, 47] that with increasing chain length of **OBV**'s, redox states of identical charge (e.g., mono- or dianion/dication) shift to smaller potentials, i.e. towards lower energies, which is in agreement with the higher conjugatons in higher oligomers. In the CV study of **OPV**'s, the potential difference between subsequent redox states (e.g., $\Delta E_{1,\,2,\,\mathrm{red}} = E^\circ_{2,\,\mathrm{red}} - E^\circ_{1,\,\mathrm{red}}$) decreases with increasing chain length.[46] This is attributable to the higher conjugations in higher oligomers, which enhance the delocalizations of the excess electrons so as to reduce the Coulombic repulsions between them. Owing to the unsuccessful syntheses of higher **OBV**'s and the inconsistent number of redox peaks observed in **OBVn** (n =1-3), such redox characteristics in our system cannot be justified. For a more concrete and quantitative relationship between the electronic properties and the geometric structures to be established, both additional experimental and theoretical studies are needed.

	20°C		0°C		-78°C		
Cpd.	$E^\circ_{1,\,\mathrm{oxid}}$	$E^\circ_{2,\,\mathrm{oxid}}$	$E^\circ_{1,\,\mathrm{oxid}}$	$E^\circ_{2,\,\mathrm{oxid}}$	$E^\circ_{1,\,\mathrm{red}}$	$E^\circ_{2,\,\mathrm{red}}$	$E^\circ_{3,\,\mathrm{red}}$
OBV1	0.86		0.81		-1.98	-2.18	
OBV2	0.74	1.01	0.73	0.97	-1.91		
OBV3	0.73*		0.72*		-1.82	-2.15*	-2.33*

Table 3. Redox data of **OBV**'s in $CH_2Cl_2/{}^{n}Bn_4NBF_4$, scan rate = 100 mV/s, conc ~ 0.1 mM, calibrated *vs* $FeCp_2^+/FeCp_2$. *: irreversible peak

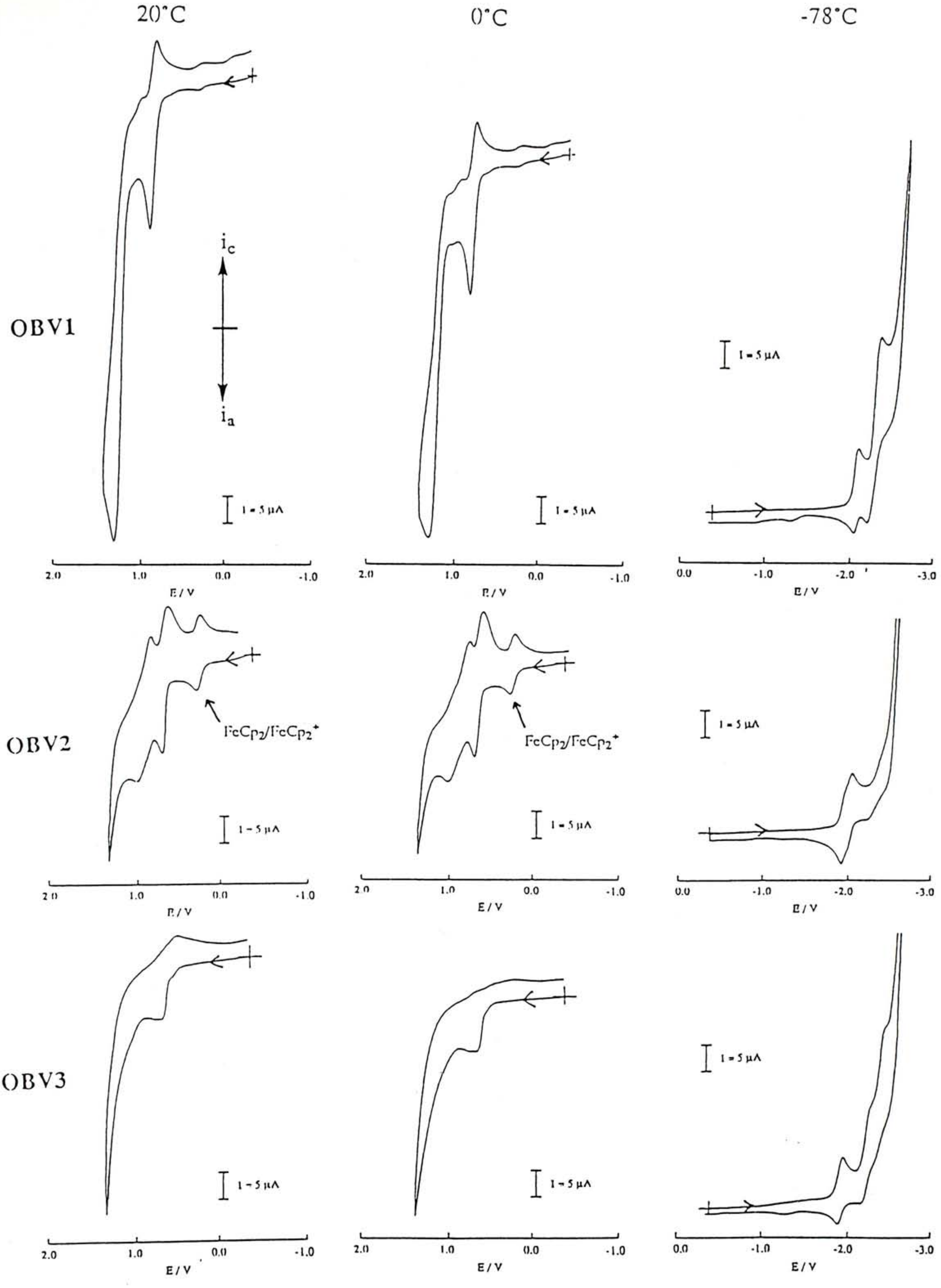


Fig. 13. Cyclic voltammograms of **OBVn** (n = 1-3) at different tempertures. Electrolytic medium: $CH_2Cl_2/^nBn_4NBF_4$; scan rate = 100 mV/s; conc ~ 0.1 mM; calibrated*vs* $FeCp_2^+/FeCp_2$.

4. Conclusion

We have developed a convenient method for the syntheses of dialkyl 2,7-biphenylenedicarboxylates (**20a** and **20b**) from methyl *p*-chlorobenzoate (**21**). The Ullman reactions of dialkyl 2,2'-diiodobiphenyl-4,4'-dicarboxylates (**19a** and **19b**) with copper powder was effected at 230°C in solid phase to afford respectively **20a** and **20b** with satisfactory yields. An iterative synthetic approach of S-alkylation, sulfone formation and Ramberg-Bäcklund reaction to oligo[2,7-biphenylenylene-(*E*)-vinylene]s (**OBV**) has been established from which fully conjugated systems containing one, two and three biphenylene units have been synthesized with high (*E*)-stereoselectivities. Solubilities of these rigid systems have been achieved by the introduction of di-*tert*-butylphenyl groups at the terminal sites of the **OBV**'s. Strong bathochromic and hyperchromic shifts in the UV-VIS absorption measurements as well as the result of the cyclic voltammetry experiments of the **OBV** series have unequivocally evidenced the extensive electron delocalization through the biphenylene chromophores linked by carbon-carbon double bonds. An empirical mathematical approach has estimated a value of 2.35 eV as the bandgap (E_g) of poly[2,7-biphenylenylene-(*E*)-vinylene] with infinite chain length. Variation-temperature cyclic voltammetry experiments have demonstrated the temperature-dependent redox activities of the **OBV** series as one of its characteristic electronic properties.

5. Experimental

Melting points were measured on a Reichert Microscope apparatus and are uncorrected. UV-VIS spectra were recorded on a Hitachi U-3300 spectrophotometer using dichloromethane as the solvent. IR spectra were recorded on a Nicolet (205) FT-IR spectrophotometer as neat film or KBr plate. ^{1}H NMR spectra were recorded on a Bruker WM 250 (250 MHz) spectrometer. Chemical shifts (δ) are reported in ppm downfield from internal standard tetramethylsilane and coupling constants (J) are reported in hertz (Hz). ^{13}C spectra were either obtained on a Bruker WM 250 (62.9 MHz) or a Bruker ARX 500 (125 MHz) spectrometer. Cyclic voltammetry was performed on a EG&G PAR Model 173 Potentiostat, Model 175 Universal Programmer, and Model RE0089 X-Y Recorder. Mass spectra (EI, FAB or High-Resolution EI) were obtained from Shanghai Institute of Organic Chemistry, Academic Sinica, China. Elemental analyses were carried out at MEDAC Ltd., Department of Chemistry, Brunel University, United Kingdom.

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Bis(triphenylphosphine)nickel(II) chloride,[36] dimethyl 4,4'-biphenyldicarboxylate,[37] 3,5-di-*tert*-butylbenzylthiol[9] and KOH/Al_2O_3 (1:2, w/w) catalyst[32] for Ramberg Bäcklund reactions were prepared according to literature methods. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Dichloromethane and benzene were distilled over phosphorous pentaoxide and stored over 4Å molecular sieves. ^{n}Bu$_4$NBF$_4$ (supporting electrolyte) used in cyclic voltammetry was dried at r.t. under vacuum for 1 day prior to use. Reactions were monitored by thin layer chromatography (TLC) performed on Merck precoated silica gel 60F$_{254}$ plates. Flash column chromatography was carried out on Merck Keisel gel 60 (70-230 mesh).

Dimethyl 2,2'-diiodobiphenyl-4,4'-dicarboxylate (19a).[35d] To a vigorously stirred solution of dimethyl biphenyl-4,4'-dicarboxylate (**18a**) (46.9 g, 0.17 mol) and silver sulfate (159.5 g, 0.51 mol) in conc. sulfuric acid (570mL) in a 1 L round-bottom flask was added iodine (103.2 g, 0.41 mol) in one lot. With the flask stoppered, the mixture was heated at 80°C for 36 h. The resulting purple suspension was poured into diluted sodium sulfite solution (2 L) at 0°C and the yellow suspension was extracted with ethyl acetate. The combined organic extract was washed with water, dried (Na_2SO_4) and concentrated to give a white solid which was re-esterified in refluxing methanol/conc. sulfuric acid (600 mL/20 mL) for 24 h. After removal of methanol (400 mL) and subsequent cooling at 0°C, essentially pure product (80.0 g, 86%) was obtained as white solids: mp 155-156°C (methanol) [lit.[35d] 152-153°C (methanol)]; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.99 (s, 6H), 7.29 (s, 2H), 8.13 (dd, 2H, J = 1.6, 8.0 Hz), 8.64 (d, 2H, J = 1.6 Hz); ^{13}C NMR (CDCl3, 62.9 MHz) δ 52.4, 98.3, 129.3, 129.5, 131.5, 140.2.

Diethyl 2,2'-Diiodobiphenyl-4,4'-dicarboxylate (19b). To a vigorouly stirred solution of dimethyl biphenyl-4,4'-dicarboxylate (**18b**) (46.9 g, 0.17 mol) and silver sulfate (159.5 g, 0.51 mol) in conc. sulfuric acid (570 mL) in a 1 L round-bottom flask was added iodine (103.2 g, 0.41 mol) in one lot. With the flask stoppered, the mixture was heated at 80°C for 36 h. The resulting purple suspension was poured into diluted sodium sulfite solution (2L) at 0°C and the yellow suspension was extracted with ethyl acetate. The combined organic extract was washed with water, dried (Na_2SO_4) and concentrated to give a white solid which was re-esterified in refluxing ethanol/conc. sulfuric acid (600 mL/20 mL) for 24 h. After removal of ethanol (400 mL) and subsequent cooling at 0°C, essentially pure product (80.0 g, 86%) was obtained as white solids: mp 72-75°C (ethanol); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.35 (t, 6H, J = 7.2 Hz), 4.34 (q, 4H, J = 7.2 Hz), 7.17 (d, 2H, J = 7.9 Hz), 8.03 (dd, 2H, J = 1.6, 7.9 Hz), 8.53 (d, 2H, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 61.5, 98.3, 129.2, 129.5, 131.9, 140.1, 152.3, 164.7; MS (EI) 550 (M^+, 6), 423 (100), 395 (26), 367 (25); IR (film) 2981, 1722, 1379, 1368, 1260, 1247, 1110, 1000, 765 cm^{-1}. Calcd. for $C_{18}H_{16}O_4I_2$: C, 39.03; H, 2.93. Found: C, 38.83; 2.82.

Dimethyl 2,7-biphenylenedicarboxylate (20a). A mixture of the diester **19a** (10.0 g 18.0 mmol) and copper powder (40.0 g, 630 mmol) was heated at 230°C under nitrogen for 12 h. Upon cooling, the resulting mixture was extracted with dichloromethane. The organic extract was dried (Na_2SO_4) and concentrated to give a residue which was flash column chromatographed using hexane/dichloromethane (3:1) as eluent to a yellow solid. Further recrystallisation of this material from toluene gave the pure product (3.2 g, 58%) as bright yellow crystals: mp 200-202°C (toluene) [lit.* 190-193°C (acetone)]; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.87 (s, 6H), 6.76 (dd, 2H, J = 0.75, 7.3 Hz), 7.25-7.27 (m, 2H), 7.61 (dd, 2H, J = 1.2, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 52.0, 117.8, 118.0, 131.2, 132.3, 150.4, 154.6, 166.3; MS *m/e* (% relative intensity) (EI) 268 (M$^+$, 100), 237 (69), 209 (40), 178 (14), 150 (24).

Diethyl 2,7-biphenylenedicarboxylate (20b). A mixture of the diester **19b** (10.0 g 18.0 mmol) and copper powder (40.0 g, 630 mmol) was heated at 230°C under nitrogen for 16 h. Upon cooling, the resulting mixture was extracted with dichloromethane. The combined organic extract was dried (Na_2SO_4) and concentrated to give a residue which was flash column chromatographed using hexane/dichloromethane (3:1) as eluent to afford a yellow solid. Further recrystallization of this material from hexane gave the pure product (3.2 g, 56%) as bright yellow crystals: mp 105-107°C (hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.37 (t, 6H, J = 7.1 Hz), 4.33 (q, 4H, J = 7.1 Hz), 6.79 (dd, 2H, J = 0.9, 7.3 Hz), 7.31-7.32 (m, 2H), 7.64 (dd, 2H, J = 1.3, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 15.0, 61.8, 118.6, 118.7, 151.0, 155.2, 166.6; MS *m/e* (% relative intensity) (EI) 296 (M$^+$, 100), 268 (25), 251 (42), 240 (29), 223 (49), 195 (18); IR (film) 1721, 1712, 1276, 1244, 1230, 770 cm^{-1}. Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.81; H, 5.44.

2,7-Bis(hydroxymethyl)biphenylene (21). To a solution of the diester **20a** (500 mg, 1.9 mmol) in dry THF (100 mL) at 0°C was added $LiAlH_4$ (300 mg, 7.9 mmol). After stirring for 5 h at r.t., the reaction mixture was quenched with water and the aqueous mixture was extracted with ethyl acetate. The combined organic extract was dried (Na_2SO_4) and concentrated to give a white solid which was purified by flash column chromatography using hexane/ethyl acetate (1:2) as eluent to afford the product (380 mg, 95%) as white crystals: mp 174-175°C; ^1H NMR (acetone-d_6, 250 MHz) δ 4.30 (t, 2H, J = 5.8 Hz), 4.55 (d, 4H, J = 5.8 Hz), 6.77 (d, 2H, J = 7.7 Hz), 6.89-6.91 (m, 4H); ^{13}C NMR (acetone-d_6, 125 MHz) δ 64.8, 117.4, 117.5, 126.7, 143.8, 150.3, 151.7; MS *m/e* (% relative intensity) (EI) 212 (M^+, 100), 195 (22), 181 (39), 165 (43), 152 (50); IR (KBr) 3600-3200, 2900, 1180, 1032, 1008, 832 cm^{-1}. Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 78.94; H, 5.73.

2,7-Bis(chloromethyl)biphenylene (22). With the content protected against atmospheric moisture by a $CaCl_2$ drying-tube, thionyl chloride (0.2 mL, 2.7 mmol) was added to a solution of the diol **21** (100 mg, 0.48 mmol) in dry dichloromethane (20 mL) at 0°C was added. After refluxing for 3 h, the reaction mixture was quenched with water and the aqueous mixture was extracted with dichloromethane. The combined organic extract was dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/dichloromethane (4:1) as eluent to afford the pure product (100 mg, 83%) as white crystals: mp 104-107°C; ^1H NMR ($CDCl_3$, 250 MHz) δ 4.31 (s, 4H), 6.54 (d, 2H, J = 7.0 Hz), 6.65 (s, 2H), 6.70 (d, 2H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 46.9, 117.3, 118.1, 128.8, 137.93, 150.6, 151.1; MS *m/e* (% relative intensity) (EI) 248 (M^+, 31), 213 (100), 178 (70); IR (film) 1280, 1260, 840, 721, 679 cm^{-1}. Anal. Calcd. for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05. Found: C, 66.97; H, 4.22.

2,7-Bis(mercaptomethyl)biphenylene (12). A mixture of the dichloride **22** (50 mg, 0.2 mmol) and thiourea (30 mg, 0.4 mmol) in dry THF (2 mL) was refluxed for 5 h under nitrogen. Water (1 mL) was added to the hot reaction mixture to dissolve all the solids which had formed. Sodium hydroxide (160 mg, 40 mmol) in water (2 mL) was then added and the solution was kept at 70°C (bath temperature) for 15 min under nitrogen. Upon cooling, the solution was acidified with 10% hydrochloric acid (20 mL) and the aqueous was extracted with dichloromethane. The combined organic extract was dried (Na_2SO_4) and concentrated to give a yellowish wax which was purified by flash column chromatography using hexane/dichloromethane (2:1) as eluent to afford the product (39 mg, 79%) as pale yellow crystals: mp 84-87°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.71 (t, 2H, *J* = 7.6 Hz), 3.54 (d, 4H, *J* = 7.6 Hz), 6.55 (d, 2H, *J* = 7.5 Hz), 6.56-6.68 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 29.6, 117.1, 117.8, 127.4, 141.4, 149.4, 151.1; MS *m/e* (% relative intensity) (EI) 244 (M^+, 40), 211 (91), 178 (100), 165 (25); IR (KBr) 3700-3200, 3000-2800, 1650, 1480, 1280, 826, 714 cm^{-1}. Anal. Calcd. for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95. Found: C, 68.30; H, 5.26.

Ethyl 7-hydroxymethyl-2-biphenylenecarboxylate (24). A mixture of the diester **20b** (4.0 g, 13.5 mmol) and potassium hydroxide pellets (85%, 1.2 g, 18.9 mmol) in ethanol (80 mL) and dry THF (40 mL) was heated at 40°C for 24 h under nitrogen. The solution was acidified with 10% hydrochloric acid (50 mL) and the aqueous mixture was extracted with ethyl acetate. The combined organic extract was dried (Na_2SO_4) and concentrated to give the crude monoacid which was redissolved in dry THF (50 mL). To this solution at 0°C was added borane in THF (1.0 M, 80.0 mL, 80.0 mmol). After stirring for 30 min under nitrogen, the reaction mixture was quenched with water and the aqueous mixture was extracted with ethyl acetate. The combined organic extract was dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/ethyl acetate (3:1) as eluent to afford the product (2.8 g, 82%) as yellow crystals: mp 93-94°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.29 (t, 3H, *J* = 7.1 Hz), 1.78 (bs, 1H), 4.24 (q, 2H, *J* = 7.1 Hz), 4.40 (s, 2H), 6.60-6.73 (m, 4H), 7.15 (s, 1H), 7.52 (dd, 1H, *J* = 1.1, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 60.9, 65.5, 116.6, 117.2, 117.4, 118.3, 126.9, 130.3, 132.2, 142.6, 149.1, 150.7, 150.9, 155.8, 166.2; MS *m/e* (% relative intensity) (EI) 254 (M^+, 100), 225 (12), 209 (33), 181 (37), 152 (33); IR (film) 3600-3200, 3200-2850, 1710, 1476, 1403, 1281, 1232, 760 cm^{-1}. Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.71; H, 5.62.

Ethyl 7-chloromethyl-2-biphenylenecarboxylate (**25**). With the content protected against atmospheric moisture by a $CaCl_2$ drying-tube, thionyl chloride (0.4 mL, 5.3 mmol) was added to a solution of the alcohol **24** (900 mg, 3.5 mmol) in dry dichloromethane (20 mL) at 0°C. After stirring for 2 h, the reaction mixture was quenched with water and the aqueous mixture was extracted with dichloromethane. The combined organic extract was dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/dichloromethane (4:1) as eluent to afford the product (830 mg, 86%) as yellow crystals: mp 129°C; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.37 (t, 3H, J = 7.2 Hz), 4.31 (q, 2H, J = 7.2 Hz), 4.39 (s, 2H), 6.65-6.81 (m, 4H), 7.24 (s, 1H), 7.61 (dd, 1H, J = 1.3, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.0, 47.5, 61.7, 117.8, 118.3, 119.0, 119.2, 129.7, 131.3, 133.0, 139.5, 150.6, 151.1, 151.7, 156.0, 166.8; MS *m/e* (% relative intensity) (EI) 272 (M^+, 84), 237 (100), 209 (70), 163 (40); IR (film) 1706, 1280, 1239, 750 cm^{-1}. Anal. Calcd. for $C_{16}H_{13}O_2$: C, 70.46; H, 4.80. Found: C, 70.43; H, 4.89.

Ethyl 7-(3',5'-di-*tert*-butylbenzylthiomethyl)-2-biphenylenecarboxylate (**26**). To a suspension of 3,5-di-*tert*-butylbenzylthiol (500 mg, 2.1 mmol) and cesium carbonate (1.0 g, 3.17 mmol) in dry THF (10 mL) at 45°C (bath temperature) was added the chloride **25** (550 mg, 2.0 mmol) in dry THF (15 mL) dropwise over 3 min. After stirring for 20 h at 50°C (bath temperature) under nitrogen, the reaction mixture was quenched with water and the aqueous mixture was extracted with dichloromethane. The combined organic extract was dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/ether (10:1) as eluent to afford the product (750 mg, 79%) as yellow crystals: mp 85-88°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.32 (s, 18H), 1.37 (t, 3H, J = 7.2 Hz), 3.42 (s, 2H), 3.63 (s, 2H), 4.32 (q, 2H, J = 7.2 Hz), 6.64-6.71 (m, 4H), 7.12 (s, 2H), 7.21 (s, 1H), 7.30 (d, 1H, J = 1.5 Hz), 7.60 (d, 1H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.2, 31.3, 34.6, 34.7, 36.0, 60.6, 116.3, 117.0, 117.9, 119.1, 120.8, 123.1, 128.8, 129.9, 132.0, 136.7, 148.0, 150.6, 150.7, 155.6, 165.9; MS *m/e* (% relative intensity) (EI) 472 (M^+, 13), 269 (13), 237 (100), 209 (37); IR (film) 2963, 2905, 2868, 1714, 1598, 1471, 1446, 1363, 1279, 1231, 1115, 1085, 758, 711 cm^{-1}. Anal. Calcd. for $C_{31}H_{36}O_2S$: C, 78.77; H, 7.68. Found: C, 78.51; H, 7.81.

Ethyl 7-(3',5'-di-*tert*-butylbenzylsulfonylmethyl)-2-biphenylenecarboxylate (27). To a solution of the sulfide **26** (7.5 g, 15.9 mmol) in dichloromethane (120 mL) was added *m*CPBA (12.4 g, 71.9 mmol) in three portions. After stirring for 9 h at r.t. under nitrogen, the reaction mixture was washed with 1 M sodium hydroxide soultion (50 mL x 2) and water. The organic solution was dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/ethyl acetate (3:1) as eluent to afford the product (7.4 g, 92%) as yellow crystals: mp 188-189°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.33 (s, 18H), 1.37 (t, 3H, J = 7.0 Hz), 3.91 (s, 2H), 4.20 (s, 2H), 4.33 (q, 2H, J = 7.0 Hz), 6.72-6.79 (m, 4H), 7.24 (m, 3H), 7.45 (t, 1H, J = 1.8 Hz), 7.60 (dd, 1H, J = 1.1, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 31.4, 34.9, 58.1, 58.9, 60.9, 117.2, 117.8, 118.4, 120.3, 123.0, 125.0, 126.7, 128.9, 130.8, 131.7, 132.3, 150.4, 151.0, 151.5, 155.1, 165.9; MS *m/e* (% relative intensity) (EI) 504 (M^+, 2), 440 (11), 237 (100), 209 (25), 203 (26); IR (film) 2965, 2906, 2870, 1713, 1477, 1316, 1283, 1232, 1116, 759 cm^{-1}. Anal. Calcd. for $C_{31}H_{36}O_4S$: C, 73.78; H, 7.19. Found: C, 73.63; H, 7.28.

2-[(*E*)-3',5'-di-*tert*-butylstyryl]-7-hydroxymethylbiphenylene (29). To a vigorously stirred solution of the sulfone **27** (7.4 g, 15.0 mmol) in dry THF (300 mL) at 0°C under nitrogen was added KOH/Al_2O_3[32] (1/2 w/w, 130 g). CBr_2F_2 (6.4 mL, 70.0 mmol) was then added in one portion. After stirring for 3 min, the reaction mixture was filtered and the catalyst was washed thoroughly with ethyl acetate. The combined organic solution was washed with water, dried (Na_2SO_4) and evaporated to give 9.0 g of a mixture of the crude acid **28a** and ester **28b** which was reduced without further purification in the next step. To a solution of the crude mixture **28a** and **28b** (100 mg, 0.17 mmol) in dry THF (5 mL) at 0°C was added $LiAlH_4$ (16 mg, 0.42 mmol). After stirring for 2 h under nitrogen, the reaction mixture was quenched with water and the aqueous mixture was extracted with ethyl acetate. The combined organic extract was dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/ethyl acetate (6:1) as eluent to afford the product (70 mg, 100% from the sulfone **27**) as yellow crystals: mp 126-127°C; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.35 (s, 18H), 4.49 (s, 2H), 6.62 (d, 1H, *J* = 4.7 Hz), 6.65 (d, 1H, *J* = 4.7 Hz), 6.74-6.78 (m, 2H), 6.85 (d, 1H, *J* = 7.2 Hz), 6.92 (d, 1H, *J* = 16.2 Hz), 7.00 (s, 1H), 7.05 (d, 1H, *J* = 16.2 Hz), 7.32-7.34 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.4, 34.8, 65.5, 114.2, 116.8, 117.0, 117.4, 120.7, 122.0, 126.8, 128.1, 128.2, 128.8, 136.5, 138.0, 141.2, 149.7, 150.2, 150.9, 151.0; MS *m/e* (% relative intensity) (EI) 397 (M^++1, 31), 396 (M^+, 100); IR (film) 3500-3200, 2900-2850, 1590 cm^{-1}. Anal. Calcd. for $C_{29}H_{32}O$: C, 87.83; H, 8.13. Found: C, 87.67; H, 8.14.

2-[(E)-3',5'-di-*tert*-butylstyryl]-7-chloromethylbiphenylene (30, OBV1Cl). With the content protected against atmospheric moisture by a $CaCl_2$ drying-tube, thionyl chloride (88 μL, 0.11 mmol)was added to a solution of the alcohol **29** (40 mg, 0.09 mmol) in dry dichloromethane (5 mL) at 0°C. After stirring for 2 h, the reaction mixture was quenched with water and the aqueous mixture was extracted with dichloromethane. The organic extract was washed with water, dried (Na_2SO_4) and concentrated to give a residue which was passed through a short silica gel column using hexane/ethyl acetate (6:1) as eluent to afford the crude chloride **30** (**OBV1Cl**) (37 mg,

≤ 100%). Since this material underwent extensive decomposition on standing at r.t., it had to be used immediately after preparration.

2,7-Bis(3',5'-di-*tert*-butylbenzylthiomethyl)biphenylene (31). To a suspension of 3,5-di-*tert*-butylbenzylthiol (1.2 g, 5.0 mmol) and cesium carbonate (1.7 g, 5.1 mmol) in dry THF (10 mL) at 45°C was added the dichloride **22** (500 mg, 2.0 mmol) in dry THF (15 mL). After stirring for 20 h at 50°C under nitrogen, the reaction mixture was quenched with water and the aqueous mixture was extracted with dichloromethane. The combined organic extract was dried (Na_2SO_4) and concentrated to give a thick oil which was purified by flash column chromatography using hexane/ether (50:1) as teluent to afford the bissulfide **31** (950 mg, 73%) as colorless oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.31 (s, 36H), 3.41 (s, 4H), 3.63 (s, 4H), 6.56-6.66 (m, 6H), 7.13 (m, 4H), 7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.8, 36.2, 36.5, 116.7, 118.6, 120.9, 123.3, 128.6, 137.0, 138.6, 149.4, 150.9, 151.2; HRMS *m/e* (EI) Calcd. for $C_{44}H_{56}S_2$: 648.3824. Found: 648.3880; IR (film) 3000-2800, 1598, 1480-1430, 1362, 1249 cm^{-1}.

2,7-Bis(3',5'-di-*tert*-butylbenzylsulfonylmethyl)biphenylene (32). To a solution of the bissulfide **31** (850 g, 1.3 mmol) in dichloromethane (20 mL) was added *m*CPBA (2.0 g, 5.8 mmol) at 0°C. After stirring for 20 h at r.t. under nitrogen, the resulting solution was washed with 1 M sodium hydroxide solution (25mL x 2) and water. The organic solution was dried (Na_2SO_4) and concentrated to give an off-white solid which was purified by flash column chromatography using hexane/ethyl acetate/dichloromethane (6:1:1) as eluent to afford the bissulfone **32** (850 mg, 91%) as white crystals: mp > 245°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.34 (s, 36H), 3.91 (s, 4H), 4.88 (s, 4H), 6.70-6.73 (m, 6H), 7.23-7.24 (m, 4H), 7.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.4, 34.9, 58.2, 58.9, 117.8, 120.1, 123.0, 125.1, 126.8, 128.3, 131.7, 151.0, 151.2, 151.6; MS *m/e* (% relative intensity) (EI) 712 (M^+, 1), 585 (6), 446 (18), 445 (54), 382 (31), 381 (95), 204 (17), 203 (100), 179 (22), 178

(85); IR (film) 3000-2800, 1600, 1474, 1363, 1314, 1248, 1115, 757 cm^{-1}. Anal. Calcd. for $C_{44}H_{56}O_4S_2$: C, 74.12; H, 7.92. Found: C, 74.25; H, 8.09.

2,7-Bis[(*E*)-3',5'-di-*tert*-butylstyryl]biphenylene (33, OBV1). To a vigorously stirred solution of the bissulfone **32** (300 mg, 0.4 mmol) in dry THF (10 mL) at 0°C under nitrogen was added KOH/Al_2O_3[32] (1/2 w/w, 4.2 g). CBr_2F_2 (0.3 mL, 3.3 mmol) was then added in one portion. After stirring for 10 min, the reaction mixture was filtered and the catalyst was washed thoroughly with dichloromethane. The combined filtrate was washed with water, dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/dichloromethane (10:1) as eluent to afford the titled compound **33** (**OBV1**) (195 mg, 80%) as yellow crystals: mp 227-229°C; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 36H), 6.66 (d, 2H, *J* = 7.4 Hz), 6.87 (d, 2H, *J* = 7.5 Hz), 6.94 (d, 2H, *J* = 16.3 Hz), 7.01 (s, 2H), 7.03 (d, 2H, *J* = 16.3 Hz), 7.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.9, 114.4, 117.5, 120.9, 122.1, 128.3, 128.4, 129.0, 136.6, 138.2, 149.9, 150.9, 151.1; MS *m/e* (% relative intensity) (EI) 581 (M^++1, 54), 580 (M^+, 100), 283 (11); IR (film) 3000-2800, 1592, 1450, 1362, 1248, 1209, 955, 706 cm^{-1}; UV-VIS [λ_{max}, nm (ε, $Lmol^{-1}cm^{-1}$)] 309 ($10.3x10^4$), 414 ($4.56x10^4$). Anal. Calcd. for $C_{44}H_{52}$: C, 90.98; H, 9.02. Found: C, 91.15; H, 9.03.

Bis{7-[(*E*)-3',5'-di-*tert*-butylstyryl]biphenylen-2-ylmethyl} sulfide (34). To a solution of the crude chloride **30** (106 mg, 0.26 mmol) in dry THF (10 mL) under nitrogen was added a solution of sodium sulfide (60%, 17 mg, 0.13 mmol) in ethanol (1 mL). After stirring for 12 h, water was added and the mixture was extracted with dichloromethane. The combined organic extract was washed with water, dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/dichloromethane (4:1) as eluent to afford the monosulfide **34** (68 mg, 67%) as yellow crystals: mp 136-138°C; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.35 (s, 36H), 3.46 (s, 4H), 6.57-6.65 (m, 6H), 6.72 (s, 2H), 6.84 (d, 2H, J = 7.2 Hz), 6.92 (d, 2H, J = 16.8 Hz), 6.99 (s, 2H), 7.01 (d, 2H, J = 16.8 Hz), 7.33 (bs, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.9, 36.3, 114.3, 116.9, 117.4, 118.6, 120.8, 122.1, 128.2, 128.3, 128.8, 128.9, 136.6, 138.4, 149.6, 149.8, 151.1; MS *m/e* (% relative intensity) (FAB) 791 (M^++1, 11), 379 (100); HRMS *m/e* (EI) Calcd. for $C_{58}H_{62}S$: 790.4572. Found: 790.4537; IR (film) 3000-2800, 1730, 1470, 1280 cm^{-1}.

Bis{7-[(*E*)-3',5'-di-*tert*-butylstyryl]biphenylen-2-ylmethyl} sulfone (35). A mixture of the sulfide **34** (44 mg, 0.06 mmol) and Oxone® (100 mg, 0.16 mmol) in dichloromethane (4 mL) and methanol (2 mL) was stirred under nitrogen for 24 h. The reaction mixture was then filtered through a short bed of silica gel with thorough washing with dichloromethane. The combined filtrate was washed with water, dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/ethyl acetate (4:1) as eluent to afford the monosulfone **35** (37 mg, 82%) as yellow crystals: mp 186-188°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 36H), 4.03 (s, 4H), 6.65-6.69 (m, 4H), 6.75-6.76 (m, 4H), 6.87 (d, 2H, J = 7.3 Hz), 6.93 (d, 2H, J = 16.8 Hz), 7.01 (s, 2H), 7.03 (d, 2H, J = 16.8 Hz), 7.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.9, 59.0, 115.0, 117.2, 118.2, 119.5, 120.9, 122.2, 127.4, 128.1, 128.3, 129.5, 130.9, 131.6, 138.8, 149.1, 151.1, 151.6, 151.8; MS *m/e* (% relative intensity) (FAB) 823 (M^+, 4), 759 (7), 379 (100); IR (film) 3000-2800, 1728, 1465, 1451, 1286, 1277, 1121 cm^{-1}. Anal. Calcd. for $C_{58}H_{62}O_2S$: C, 84.63; H, 7.59. Found: C, 83.88; H, 8.01.

(*E*)-1,2-Bis{7'-[(E)-3",5"-di-*tert*-butylstyryl]biphenylen-2'-yl}ethene (36, OBV2). To a vigorously stirred solution of the sulfone **35** (20 mg, 0.02 mmol) in dry THF (5 mL) at 0°C under nitrogen was added KOH/Al_2O_3[32] (1/2 w/w, 20 mg). CBr_2F_2 (0.3 mL, 3.28 mmol) was then added in one portion. After stirring for 10 min, the reaction mixture was filtered and the catalyst was washed thoroughly with dichloromethane. The combined filtrate was washed with water, dried (Na_2SO_4) and concentrated to give an orange solid which was purified by flash column chromatography using hexane/dichloromethane (6:1) as eluent to afford the titled compound **36** (**OBV2**) (15 mg, 83%) as orange crystals: mp > 245°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 36H), 6.66 (d, 2H, *J* = 7.2 Hz), 6.67 (d, 2H, *J* = 7.2 Hz), 6.82-6.89 (m, 6H), 6.95 (d, 2H, *J* = 16.4 Hz), 6.96 (s, 2H), 7.04 (s,2H), 7.05 (d, 2H, *J* = 16.4 Hz), 7.34 (bs, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.9, 114.2, 114.4, 117.5, 120.8, 122.1, 128.1, 128.4, 128.6, 129.1, 136.6, 137.9, 138.3, 149.8, 150.2, 150.8, 151.0, 151.1; MS *m/e* (% relative intensity) (FAB) 756 (M^+, 34), 307 (22), 154 (100), 136 (70); HRMS *m/e* (EI) Calcd. for $C_{58}H_{60}$: 756.4695. Found: 756.4736; IR (film) 3000-2800, 1500-1400 cm^{-1}; UV-VIS [λ_{max}, nm (ε, Lmol^{-1}cm^{-1})] 310 (34.8×10^4), 323 (34.6×10^4), 455 (18.1×10^4), 485 (14.0×10^4).

2,7-Bis{7'-[(*E*)-3",5"-di-*tert*-butylstyryl]biphenylen-2'-ylmethylthiomethyl}biphenylene (37). To a solution of the dithiol **12** (50 mg, 0.20mmol) and the crude chloride **30** (160 mg, ≤ 0.39 mmol) in dry benzene (2 mL) was added DBU (72 μL, 0.48 mmol). After stirring for 2 h under nitrogen, 10% hydrochloric acid (*ca.* 10 mL) was added and the aqueous mixture was extracted with dichloromethane. The combined organic extract was dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/dichloromethane (5:1) as eluent to afford the bissulfide **37** (104 mg, 52%) as yellow crystals: mp 155-157°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 36H), 3.43 (s, 4H), 3.44 (s, 4H), 6.53-6.70 (m, 14H), 6.83 (d, 2H, *J* = 7.3 Hz), 6.92 (d, 2H, *J* = 16.3 Hz), 6.97 (s, 2H), 7.01 (d, 2H, *J* = 16.3 Hz), 7.33-7.34 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.8, 36.3, 114.3, 116.8, 117.4, 118.6, 120.8, 122.1, 128.2, 128.3, 128.6, 128.7, 128.9, 136.7, 138.1, 138.3, 138.4, 149.5, 149.8, 151.0, 151.2; MS *m/e* (% relative intensity) (FAB) 1001 (M^+, 22), 589 (14), 379 (100); IR (film) 3000-2800, 1500, 1400 cm^{-1}. Anal. Calcd. for $C_{72}H_{72}S_2$: C, 86.35; H, 7.25. Found: C, 85.26; H, 7.33.

2,7-Bis{7'-[(*E*)-3",5"-di-*tert*-butylstyryl]biphenylen-2'-ylmethylsulfonylmethyl}biphenylene (**38**). A mixture of the bissulfide **37** (43 mg, 0.04 mmol) and Oxone® (160mg, 0.26 mmol) in dichloromethane (4 mL) and methanol (2 mL) was stirred under nitrogen at r.t. 24 h. The reaction mixture was then filtered through a short bed of silica gel with thorough washing with dichloromethane. The combined filtrate was washed with water, dried (Na_2SO_4) and concentrated to give a yellowish soild which was purified by flash column chromatography using hexane/ethyl acetate/dichloromethane (6:1:1) as eluent to afford the bissulfone **38** (37 mg, 81%) as yellow crystals: mp > 245°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 36H), 4.00 (s, 4H), 4.02 (s, 4H), 6.64-6.74 (m, 14H), 6.87 (d, 2H, *J* = 6.7 Hz), 6.92 (d, 2H, *J* = 16.9 Hz), 7.00 (s, 2H), 7.02 (d, 2H, *J* = 16.9 Hz), 7.33-7.34 (m, 6H); MS *m/e* (% relative intensity) (FAB) 1065 (M+, 20), 936 (17), 379 (100); IR (film) 3000-2800, 1600, 1480, 1100 cm^{-1}.

(*E*,*E*)-2,7-Bis{2-[7'-[(E)-3",5"-di-*tert*-butylstyryl]biphenylen-2'-yl]ethenyl}biphenylene (**39**, **OBV3**). To a vigorously stirred solution of the bissulfone **38** (35 mg, 0.03mmol) in dry THF (5 mL) at 0°C under nitrogen was added KOH/Al_2O_3[32] (1/2 w/w, 650 mg). CBr_2F_2 (0.3 mL, 3.28 mmol) was then added in one portion. After stirring for 10 min, the reaction mixture was filtered and the catalyst was washed thoroughly with dichloromethane. The combined organic filtrate was washed with water, dried (Na_2SO_4) and concentrated to give a reddish solid which was purified by flash column chromatography using hexane/dichloromethane (6:1) as eluent to afford the tetraene **39** (**OBV3**) (29 mg, 93%) as red crystals: mp > 245°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 36H), 6.66 (d, 4H, *J* = 7.2 Hz), 6.68 (d, 2H, *J* = 7.2 Hz), 6.82-6.85 (m, 8H), 6.88 (d, 2H, *J* = 7.2 Hz), 6.96-6.98 (m, 6H), 7.04 (d, 2H, *J* = 16.4 Hz), 7.04 (s, 2H), 7.34 (bs, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.9, 114.3, 114.4, 117.5, 117.6, 120.8, 122.1, 128.1, 128.2, 128.3, 128.6, 129.1, 136.6, 137.8, 138.0, 138.3, 149.8, 150.1, 150.2, 150.8, 150.9, 151.1; MS *m/e* (%

relative intensity) (EI) 933 (M^+, 2), 467 (2), 380 (2), 207 (10), 71 (10), 83 (11), 91 (12), 69 (12), 55 (20), 57 (21), 43 (24), 44 (100); IR (film) 3000-2800, 1600, 1430, 950 cm^{-1}; UV-VIS [λ_{max}, nm (ε, $Lmol^{-1}cm^{-1}$)] 310 ($33.3x10^4$), 321 ($32.0x10^4$), 466 ($17.7x10^4$), 497 ($15.0x10^4$).

Xanthate ester (**40**). A mixture of potassium hydroxide pellets (85%, 620 mg, 11.0 mol) and ethanol (0.65 mL, 11.0 mmol) in dry THF (10 mL) was refluxed for 1 h under nitrogen. The mixture was cooled to 0°C and carbon disulfide (0.66 mL, 11.0 mmol) was added. The resulting suspension was further refluxed for 2 h and upon cooling, was added to a precooled (0°C) solution of the chloride **25** (1.5 g, 5.5 mmol) in dry THF (5 mL). After stirring for 12 h at r.t. under nitrogen, the reaction mixture was quenched with water and the aqueous mixture was extracted with dichloromethane. The organic extract was dried (Na_2SO_4) and concentrated to give a yellowish wax which was purified by flash column chromatography using hexane/dichloromethane (4:1) as eluent to afford the product (2.0 g, 100%) as yellow crystals: mp 89-90°C; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.36 (t, 3H, J = 7.1 Hz), 1.42 (t, 3H, J = 7.1 Hz), 4.18 (s, 2H), 4.31 (q, 2H, J = 7.1 Hz), 4.65 (q, 2H, J = 7.1 Hz), 6.62-6.79 (m, 4H), 7.22 (s, 1H), 7.59 (d, 1H, J = 1.1, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 13.7, 14.3, 41.0, 60.8, 70.1, 116.7, 117.3, 118.3, 119.0, 129.2, 130.5, 132.2, 137.4, 149.0, 150.6, 150.9, 155.5, 166.0, 193.9; MS *m/e* (% relative intensity) (EI) 358 (M^+, 6), 237 (100), 209 (31), IR (film) 3000-2830, 1710, 1279, 1231, 1114, 1086, 1048, 758 cm^{-1}. Calcd. for $C_{19}H_{18}O_3S_2$: C, 63.66; H, 5.06. Found: C, 63.68; 5.11.

7'-Ethoxycarbonylbiphenylen-2'-ylmethyl 7-[(*E*)-3",5"-di-*tert*-butylstyryl] biphenylen-2-ylmethyl sulfide (**41**). Sodium metal (400 mg, 18.0 mmol) was added to ethanol (20 mL) under nitrogen. After all the sodium had reacted, a solution of the xanthate ester **40** (550 mg, 1.5 mmol) in dry THF (10 mL) was added to the sodium ethoxide solution. After stirring for 7 h, the reaction mixture was acidified with 10% hydrochloric acid until red with litmus. The acidic aqueous solution was extracted with dichloromethane and the combined organic extract was dried (Na_2SO_4). Rotavaporation left the crude thiol **13** (405 mg, ≤ 100%) as a yellowish solid. To a solution of this crude dithiol **13** (220 mg, 0.81 mmol) and the crude chloride **30** (310 mg, 0.74 mmol) in dry benzene (10 mL) was added DBU (0.13 mL, 0.89 mmol). After stirring for 5 h under nitrogen, the reaction mixture was quenched with water and the aqueous mixture was extracted with dichloromethane. The combined organic extract was dried (Na_2SO_4) and concentrated to give a yellow solid which was purified by flash column chromatography using hexane/dichloromethane (3:1) as eluent to afford the product (320 mg, 67%) as yellow crystals : mp 157-159°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (t, 3H, J = 7.1 Hz), 1.36 (s, 18H), 3.46 (s, 4H), 4.31 (q, 2H, J = 7.1 Hz), 6.56-6.75 (m, 8H), 6.84 (d, 1H, J = 7.4 Hz), 6.92 (d, 1H, J = 16.3 Hz), 6.98 (s, 1H), 7.01 (d, 1H, J = 16.3 Hz), 7.23 (s, 1H), 7.33-7.34 (m, 3H), 7.66 (dd, 1H, J = 1.1, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 15.1, 31.5, 34.9, 36.3, 36.4, 60.8, 114.3, 116.5, 116.8, 117.3, 117.4, 118.1, 118.5, 119.2, 120.8, 122.1, 128.2, 128.3, 128.8, 129.0, 130.3, 132.2, 136.6, 138.1, 138.3, 139.9, 148.5, 149.6, 149.8, 150.8, 151.1, 155.8, 166.1; MS *m/e* (% relative intensity) (EI) 648 (M^+, 16), 380 (53), 379 (100); IR (film) 3000-2800, 1750, 1470 cm^{-1}. Anal. Calcd. for $C_{45}H_{44}O_2S$: C, 83.29; H, 6.83. Found: C, 83.04; 6.93.

7'-Ethoxycarbonylbiphenylen-2'-ylmethyl 7-[(*E*)-3",5"-di-*tert*-butylstyryl] biphenylen-2-ylmethyl sulfone (**42**). A mixture of the sulfide **41** (300 mg, 0.46 mmol) and Oxone® (850 mg, 1.39 mmol) in dichloromethane (10 mL) and ethanol (5 mL) was stirred for 24 h under nitrogen. The resulting solution was filtered through a short bed of silica gel with thorough washing with dicholromethane. The combined filtrate was washed with water, dried (Na_2SO_4) and concentrated to give a yellowish solid which was purified by flash column chromatography using hexane/ethyl acetate/dichloromethane (4:1:1) as eluent to afford the product (250 mg, 81%) as yellow crystals: mp 232°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.35 (t, 3H, J = 7.0 Hz), 1.36 (s, 18H), 4.02 (s, 2H), 4.03 (s, 2H), 4.31 (q, 2H, J = 7.0 Hz), 6.62-

6.87 (m, 9H), 6.92 (d, 1H, J = 16.3 Hz), 6.98 (s, 1H), 7.01 (d, 1H, J = 16.3 Hz), 7.24 (s, 1H), 7.33-7.35, (m, 3H), 7.61 (d, 1H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.2, 29.6, 31.4, 34.8, 58.6, 59.2, 60.8, 114.8, 117.1, 117.7, 118.1, 118.4, 119.4, 120.1, 120.8, 122.1, 127.2, 128.0, 128.3, 128.5, 129.3, 130.8, 131.5, 131.7, 132.2, 136.3, 138.6, 149.0, 150.3, 150.5, 151.0, 151.3, 151.7, 155.0, 165.8; MS *m/e* (% relative intensity) (EI) 680 (M^+, 3), 616 (4), 380 (45), 379 (100); IR (film) 3000-2800, 1713, 1277, 1231,1116 cm^{-1}. Anal. Calcd. for $C_{45}H_{44}O_4S$: C, 79.38; H, 6.51. Found: C, 79.38; 6.58.

Alcohol (44). To a vigorously stirred solution of the sulfone **42** (220 mg, 0.32 mmol) in dry THF (10mL) at 0°C under nitrogen was added KOH/Al_2O_3[32] (1/2 w/w, 3.3 g). CBr_2F_2 (0.3 mL, 3.28 mmol) was then added in one portion. After stirring for 10 min, the reaction mixture was filtered and the catalyst was washed thoroughly with dichloromethane followed by ethyl acetate. The combined organic fitrate was washed with water, dried (Na_2SO_4) and concentrated to give the crude ester **43** (197 mg, ≤ 100%) which was redissloved in dry THF (10 mL) and cooled to 0°C. $LiAlH_4$ (200 mg, 5.25 mmol) was then added to this solution. After stirring for 2 h under nitrogen, the reaction mixture was quenched with water and the aqueous was extracted with dichloromethane. The organic extract was dried (Na_2SO_4) and concentrated to give a yellowish product which was purified by flash column chromatography using hexane/ethyl acetate (8:1) as eluent to afford the alcohol **44** (195 mg, 80%) as yellow crystals: mp > 245°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 18H), 4.49 (s, 2H), 6.63-6.68 (m, 4H), 6.75-6.89 (m, 6H), 6.94-6.96 (m, 3H), 7.03 (d, 1H, J = 16.2 Hz), 7.03 (s, 2H), 7.34 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.9, 65.8, 114.2, 114.4, 116.9, 117.1, 117.6, 120.8, 122.1, 126.9, 128.0, 128.1, 128.4, 129.1, 136.5, 137.8, 138.3, 141.3, 151.1; MS *m/e* (% relative intensity) (EI) 573 (M^+ + 1), 51), 572 (M^+, 100); IR (film) 3700-3200, 3000-2800, 1483 cm^{-1}.

Aldehyde (52). A mixture of the alcohol **44** (37 mg, 0.07 mmol), PDC (37mg, 0.10 mmol) and powdered 4Å molecular sieve (50 mg) in dichloromethane (5 mL) was stirred under nitrogen for 1 h. The reaction mixture was filtered through a short bed of silica gel with thorough washing with dichloromethane. The combined filtrate was concentrated to give an orange solid which was purified by flash column chromatography using hexane/dichloromethane (4:1) as eluent to afford the aldehyde **52** (32 mg, 85%) as orange crystals: mp > 245°C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.36 (s, 18H), 6.65-6.69 (m, 2H), 6.78-6.96 (m, 8H), 7.02-7.08 (m, 3H), 7.15 (s, 1H), 7.26 (s, 1H), 7.32-7.34 (m, 3H), 9.72 (s, 1H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 31.5, 34.9, 114.2, 114.5, 115.5, 116.7, 117.5, 117.7, 119.4, 120.9, 122.2, 127.1, 127.5, 128.3, 128.9, 129.2, 129.4, 136.6, 136.8, 137.4, 137.5, 138.5, 139.9, 149.7, 150.3, 150.6, 150.8, 151.2, 151.4, 157.8, 190.8; MS *m/e* (% relative intensity) (EI) 573 (M+ + 1, 49), 570 (M+, 100); IR (film) 3000-2800, 1730, 1692, 1464, 1286, 1123, 1074 cm^{-1}.

2,7-Bis(triphenylphosphoniomethyl)biphenylene dichloride (53). A solution of the dichoride **22** (100 mg, 0.40 mmol) and triphenylphosphine (1.0 g, 4.0 mmol) was refluxed in THF (5 mL) and ethanol (1 mL) under nitrogen for 7 days. The reaction mixture was concentrated to give a residue which was purified by flash column chromatography using hexane/chloroform/ethanol (2:1:1) as the eluent to afford the product (280 mg, 90%) as pale yellow crystals: mp 230-235°C (dec.); ^{1}H NMR (CDCl$_3$, 250 MHz) δ 5.31 (d, 4H, J = 14.9 Hz), 6.17-6.21 (m, 4H), 6.41 (dd, 2H, J = 3.2, 6.9 Hz), 7.58-7.82 (m, 30H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 31.8 (d, J_{cp} = 45.9 Hz), 117.6 (d, J_{cp} = 18.9 Hz), 119.1, 120.8, 127.8 (d, J_{cp} = 10.1 Hz), 129.9, 130.1, 132.7, 134.6, 134.7, 150.5 (d, J_{cp} = 40.9 Hz); MS *m/e* (% relative intensity) (FAB) 702 (M+ - 2Cl- + 1, 4) 440 (M+ - 2Cl- -PPh$_3$ + 1, 29) 439 (M+ - 2Cl- -PPh$_3$, 50), 178 (M+ - 2Cl- -2PPh$_3$ + 1) 149 (M+ - 2Cl- -2PPh$_3$ - 2CH$_2$, 100); IR (film) 2950, 2860, 1438, 1112, 747, 719, 690, 509 cm^{-1}.

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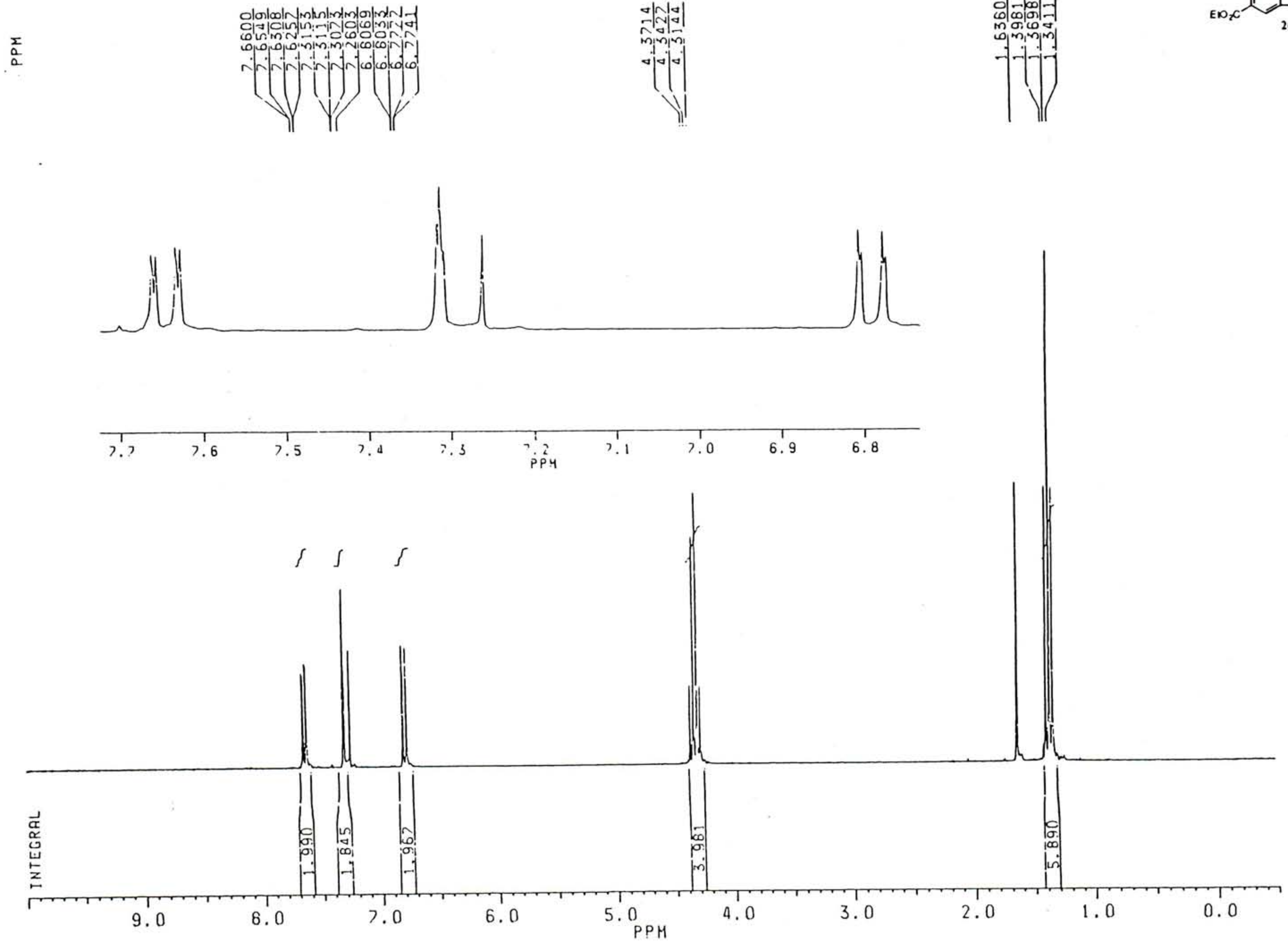
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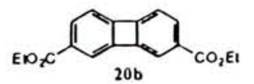
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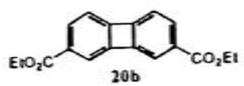
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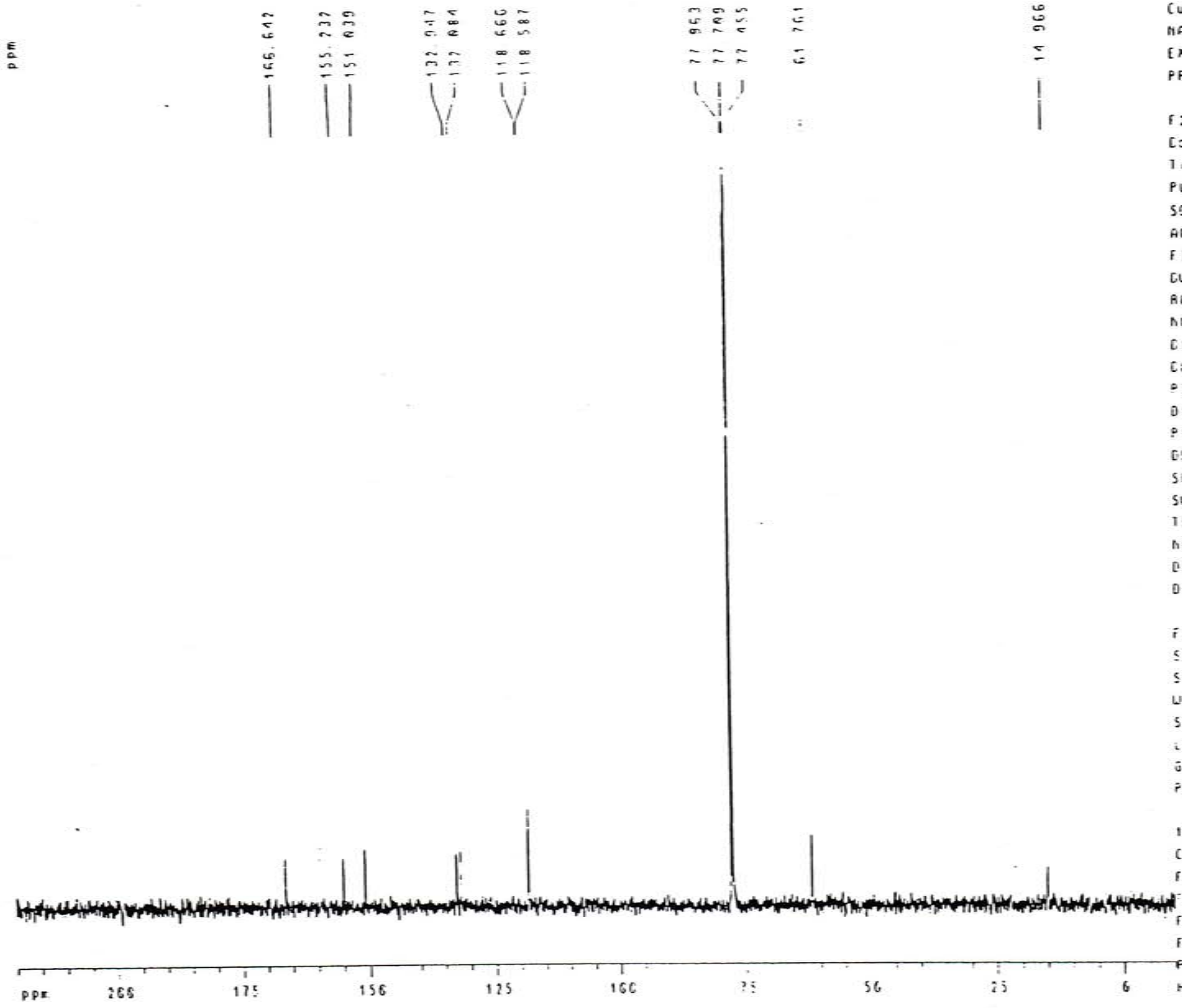

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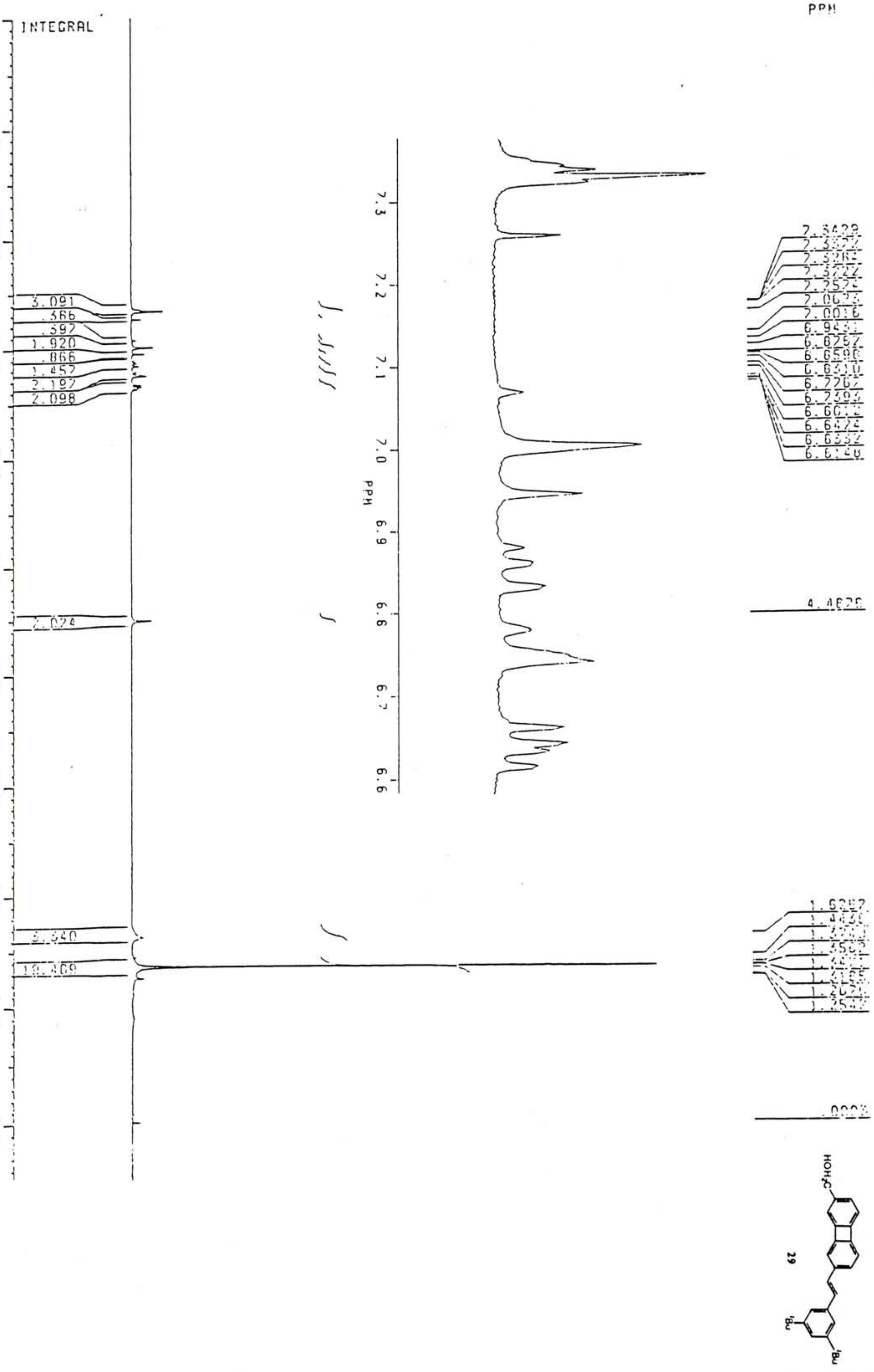
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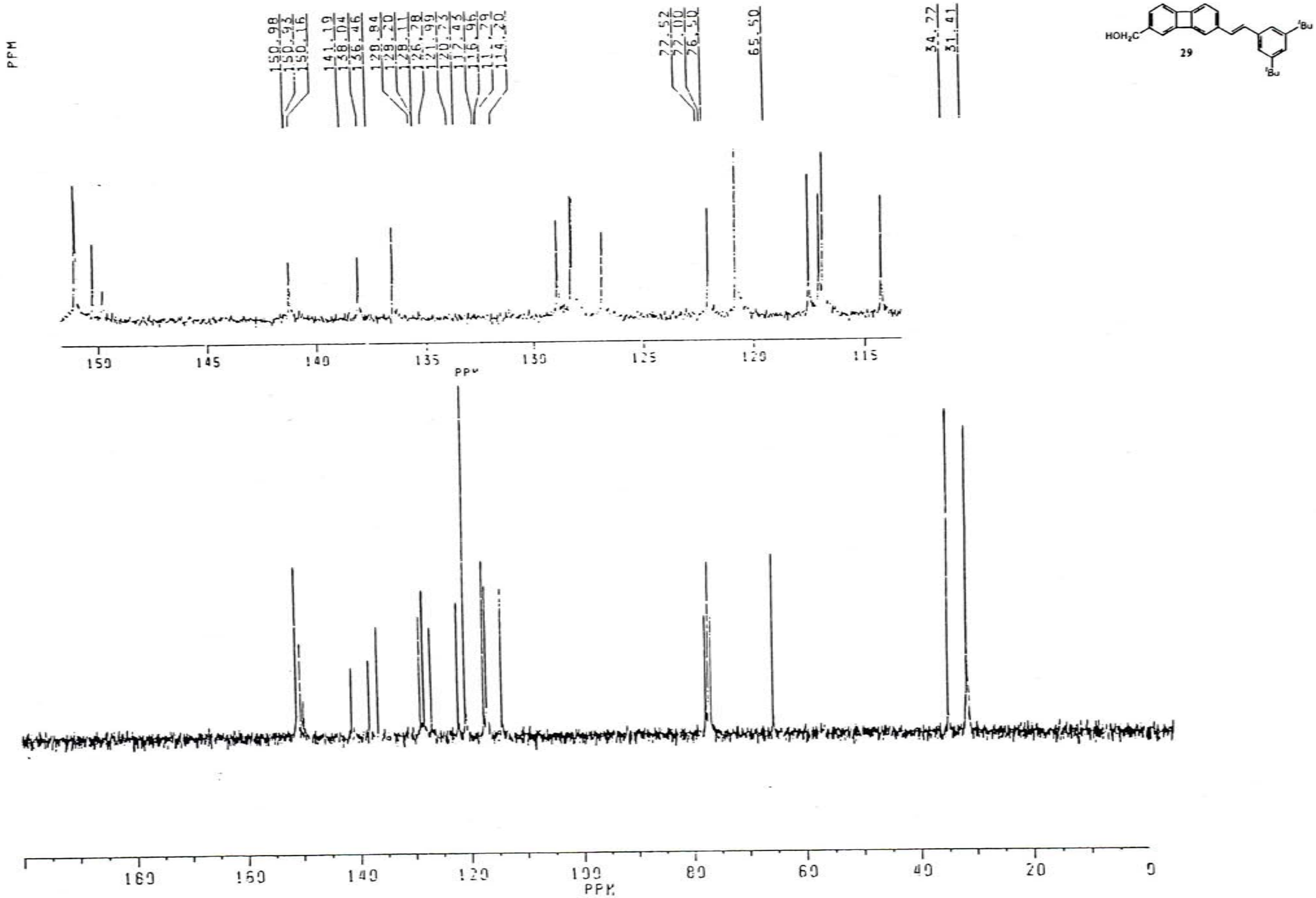
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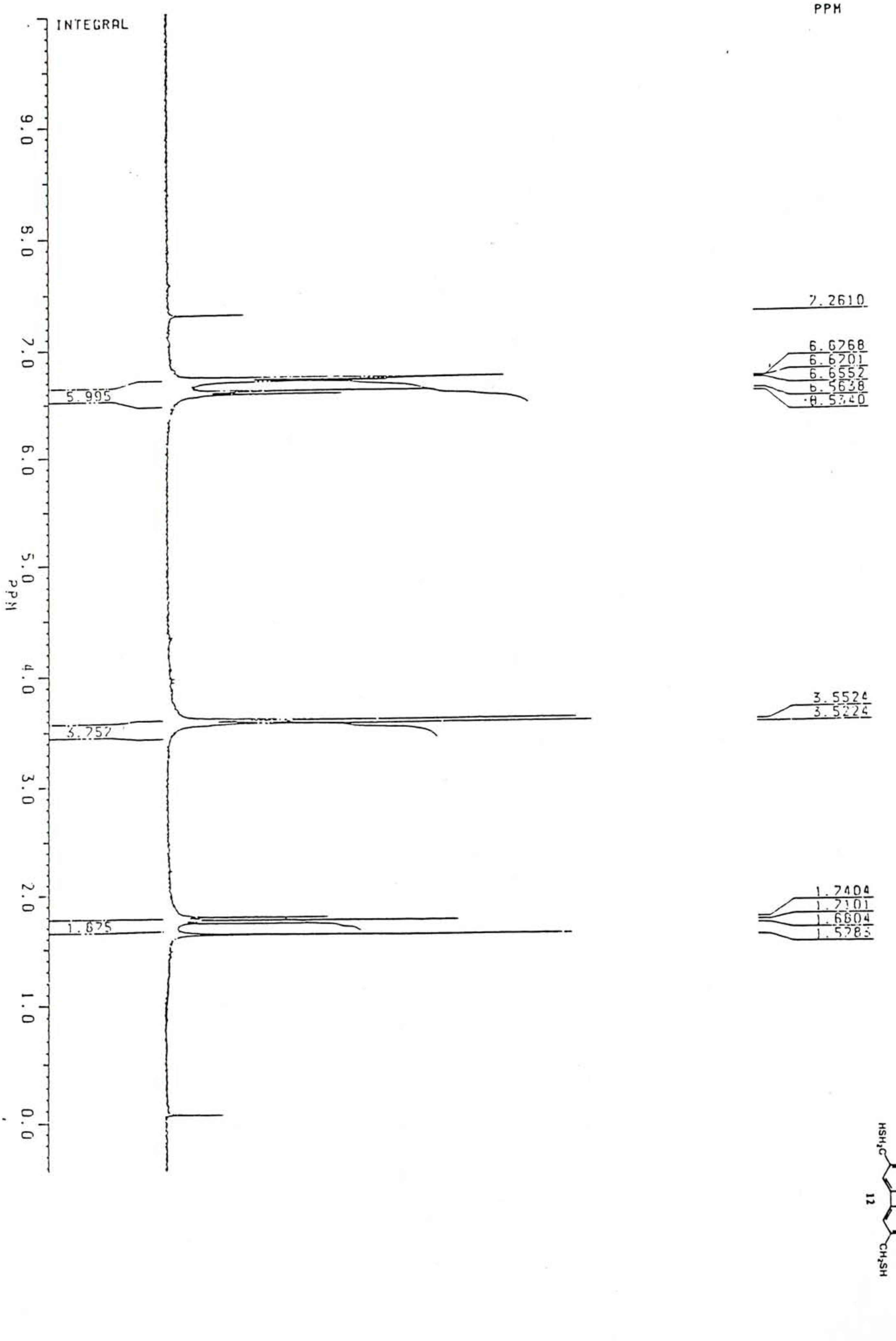
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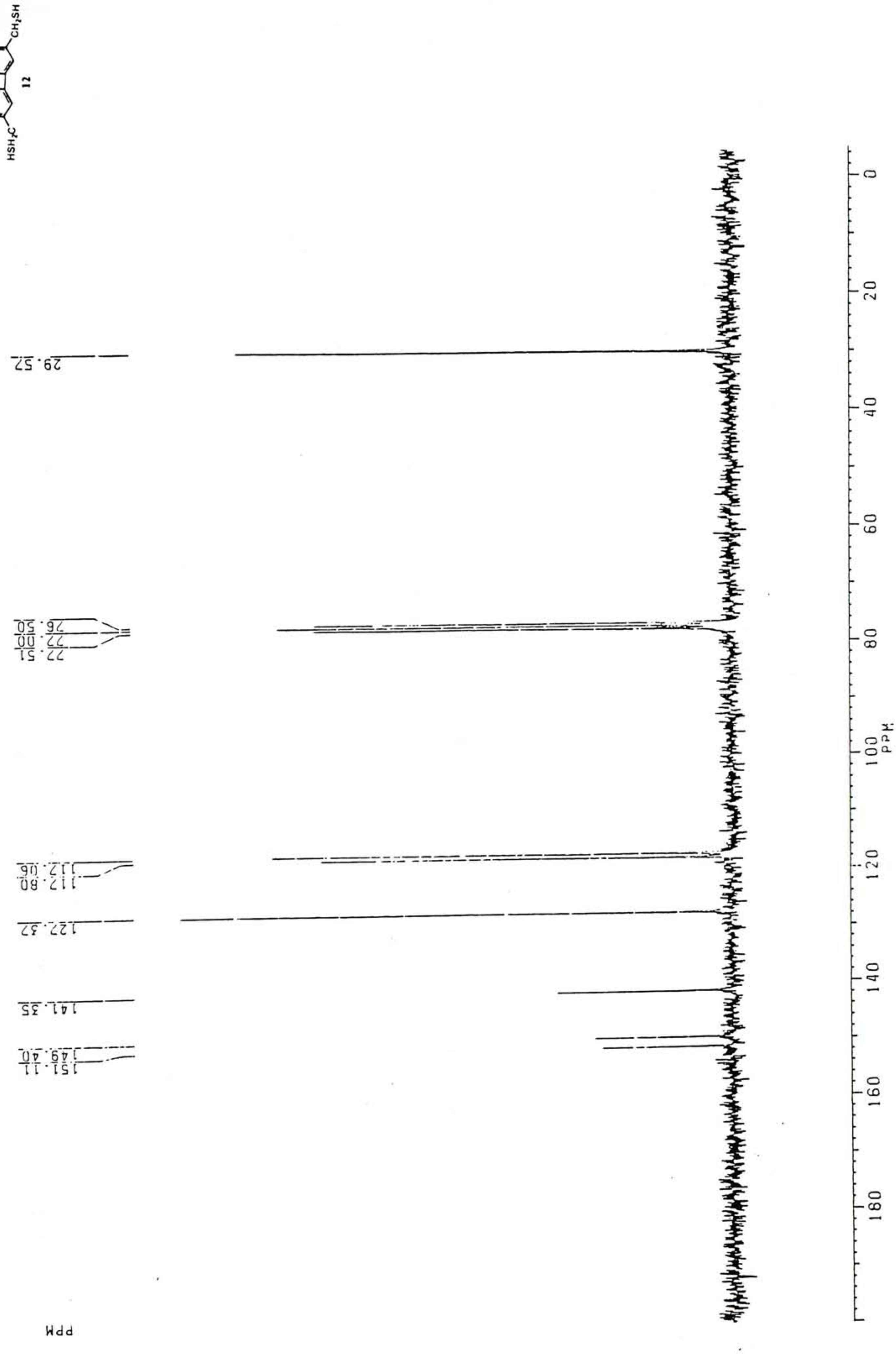

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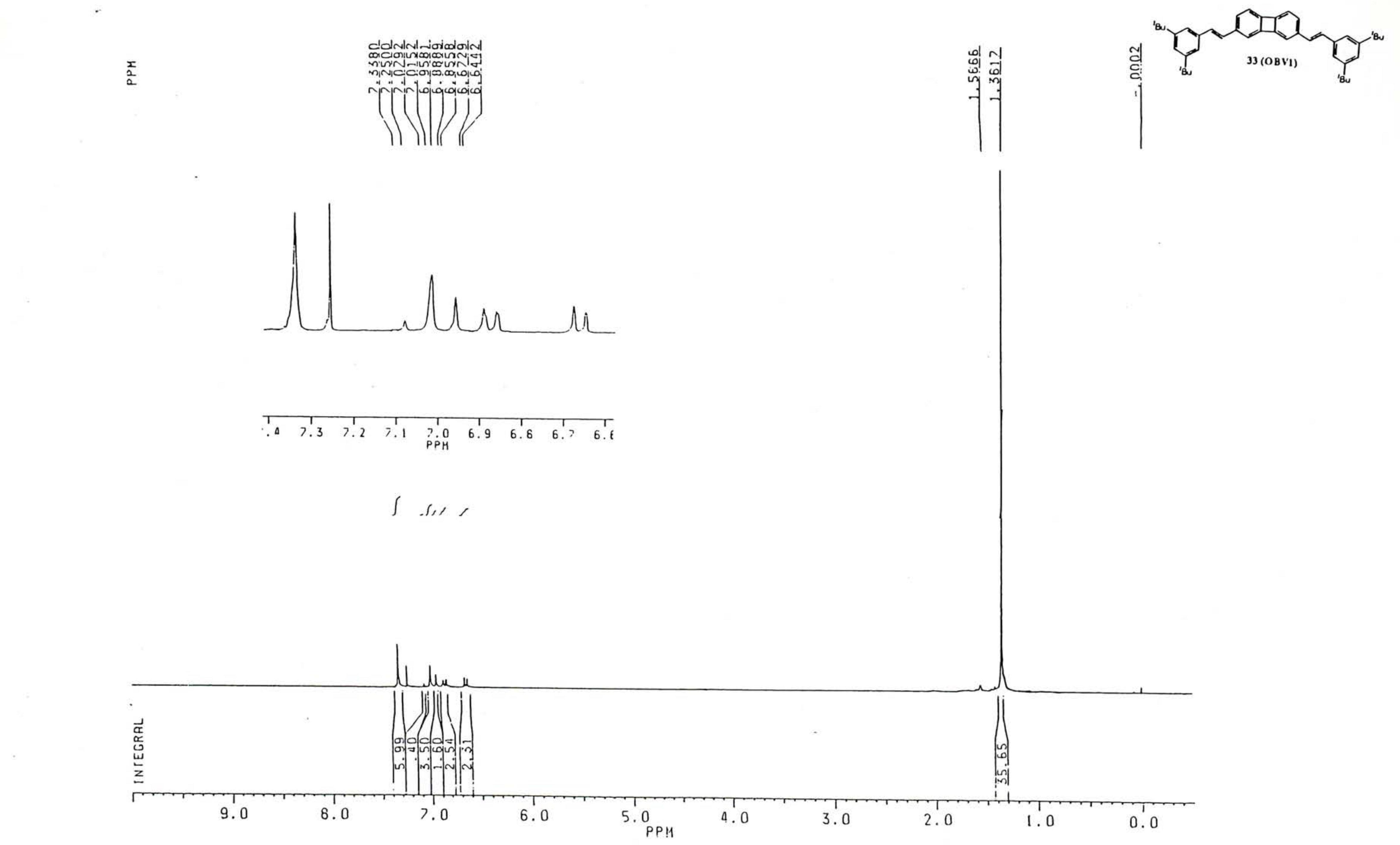
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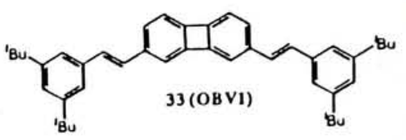
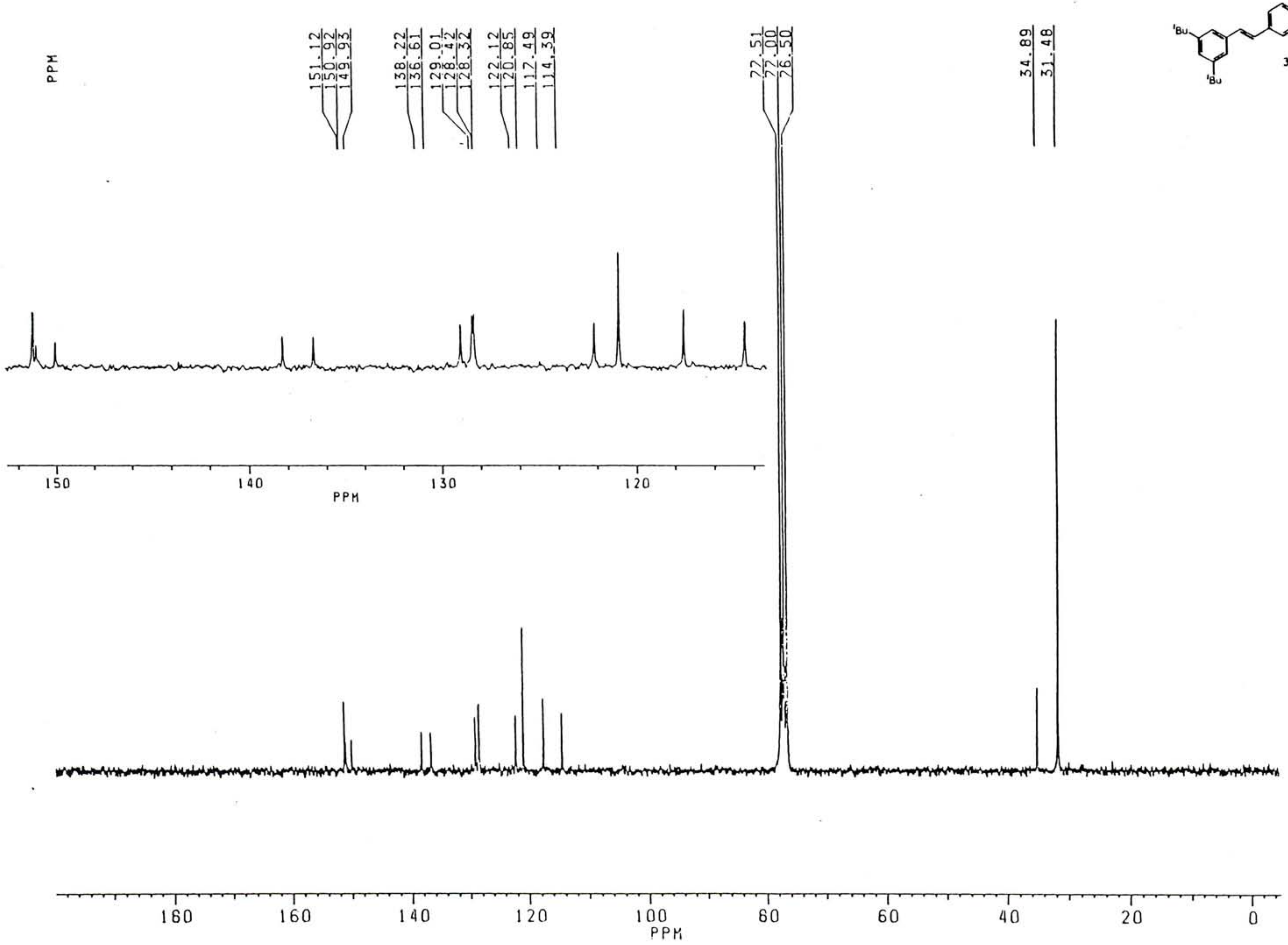
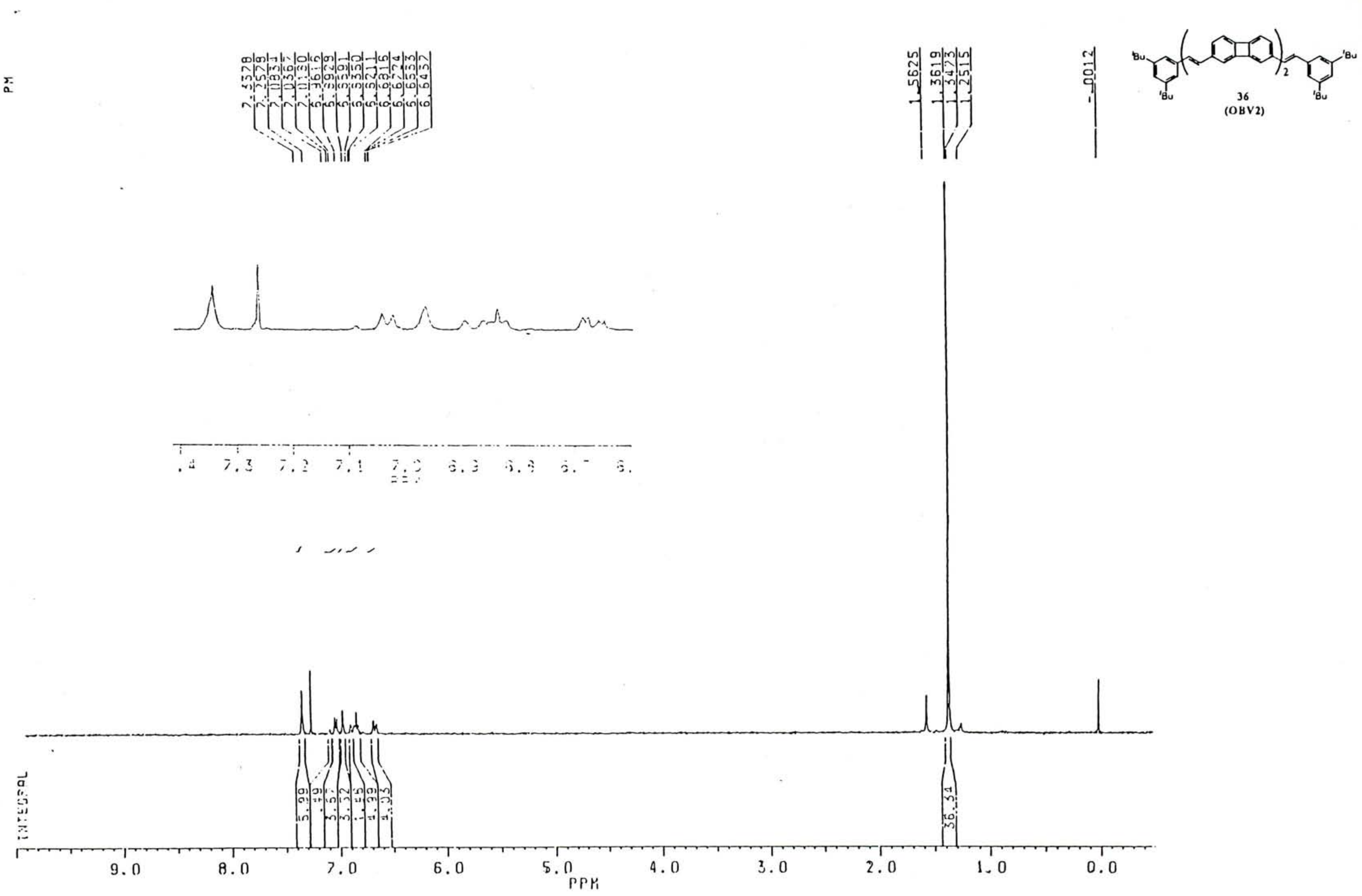


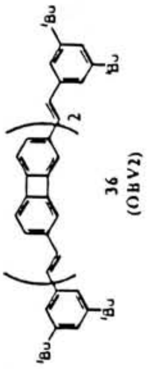
33 (OBVI)

ᵗBu
ᵗBu
ᵗBu
ᵗBu



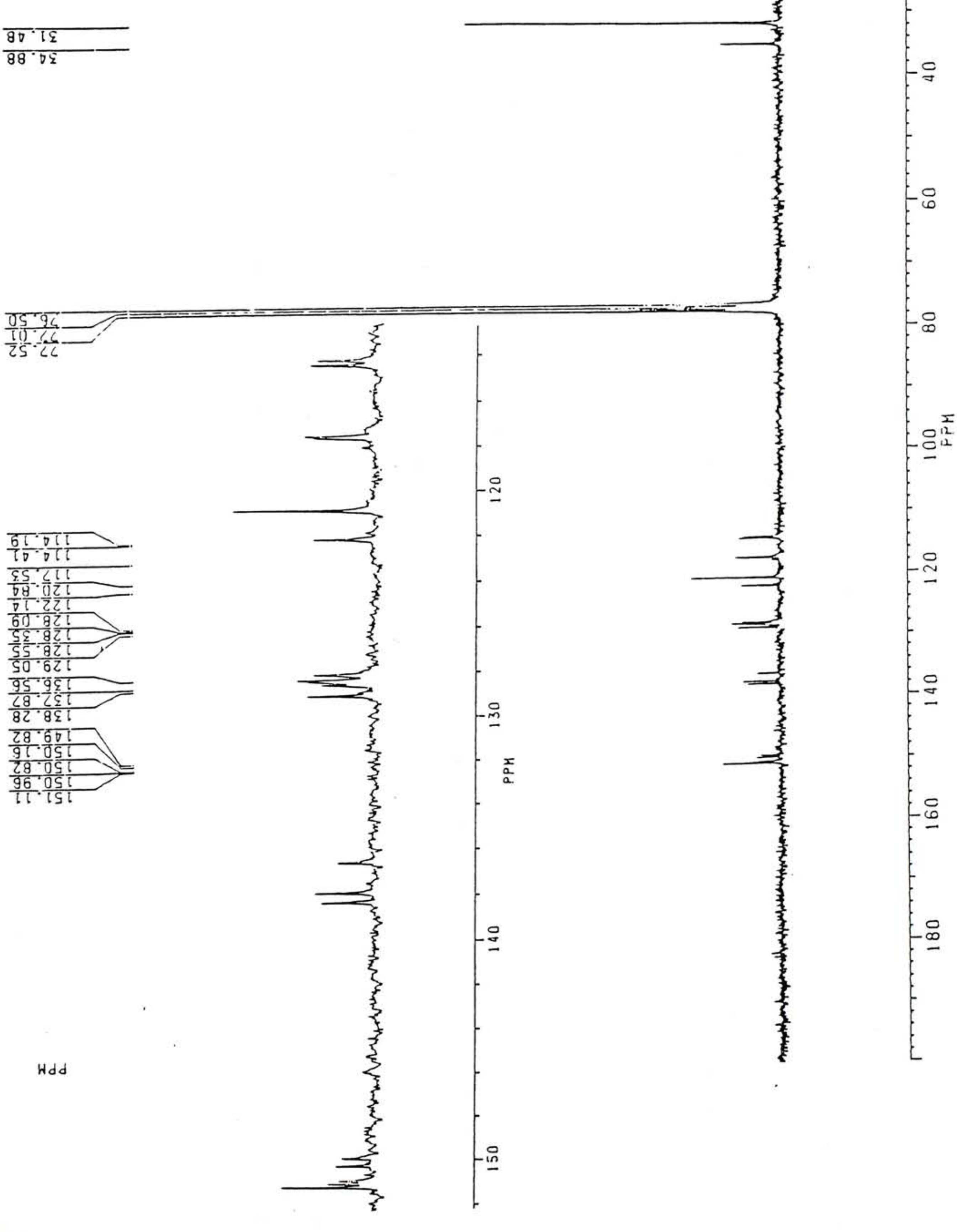
PPM
151.12
150.92
149.93
138.22
136.61
129.01
128.42
128.32
122.12
120.85
117.49
114.39
77.51
77.00
76.50
34.89
31.48
150
140
130
120
PPM
180
160
140
120
100
80
60
40
20
0
PPM


36
(OBV2)
PM
7.3578
7.2579
7.0834
7.0367
7.0130
6.9616
6.8929
6.8591
6.8350
6.8211
6.6815
6.6724
6.6533
6.6437
1.5625
1.3619
1.3473
1.2515
-.0012
ᵗBu
ᵗBu
ᵗBu
ᵗBu
2
.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.
INTEGRAL
5.99
.49
3.57
3.32
1.45
4.39
4.03
36.34
9.0
8.0
7.0
6.0
5.0
PPM
4.0
3.0
2.0
1.0
0.0

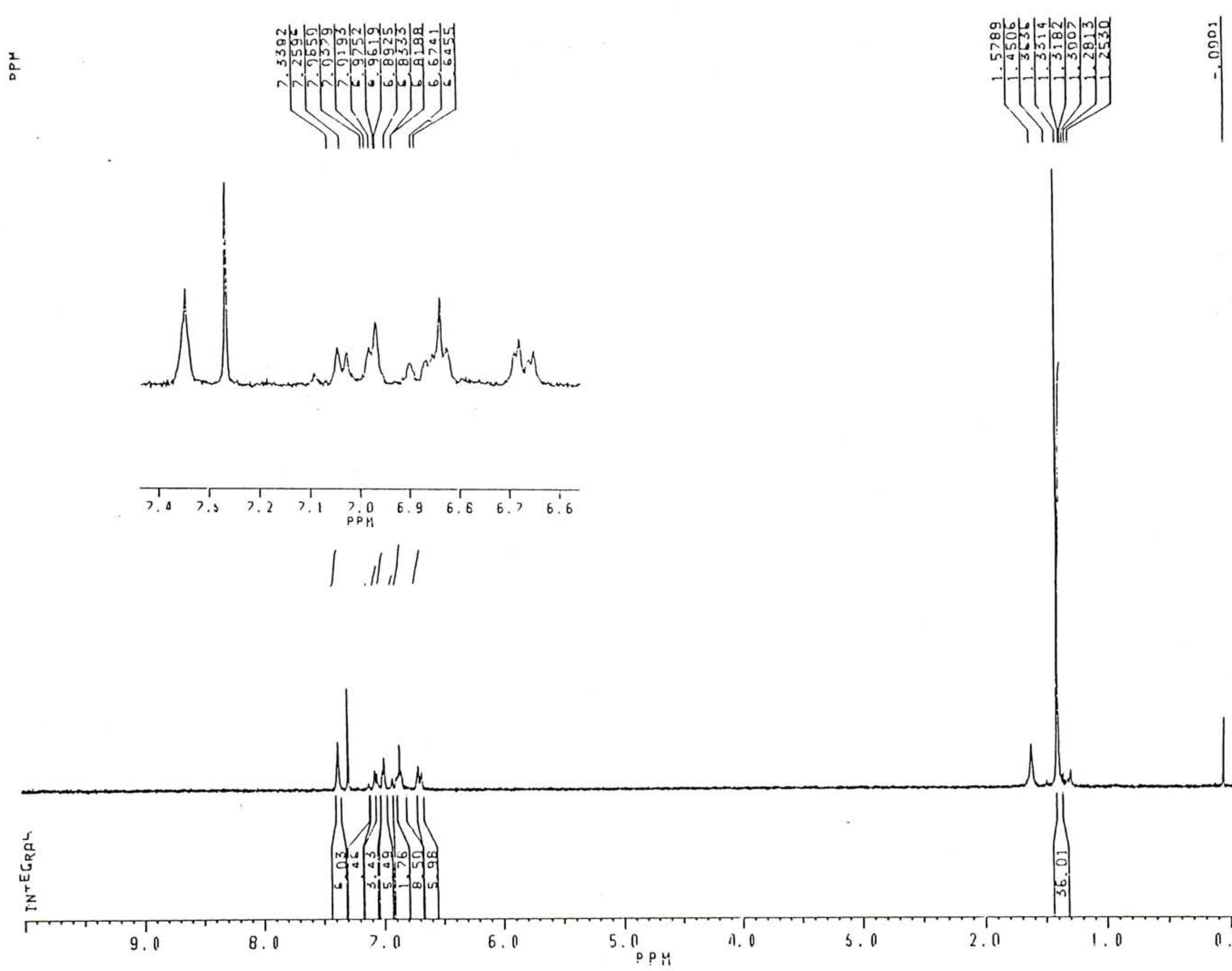


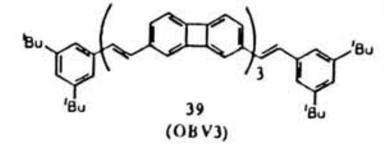
ᵗBu
ᵗBu
ᵗBu
ᵗBu
2

36
(OBV2)

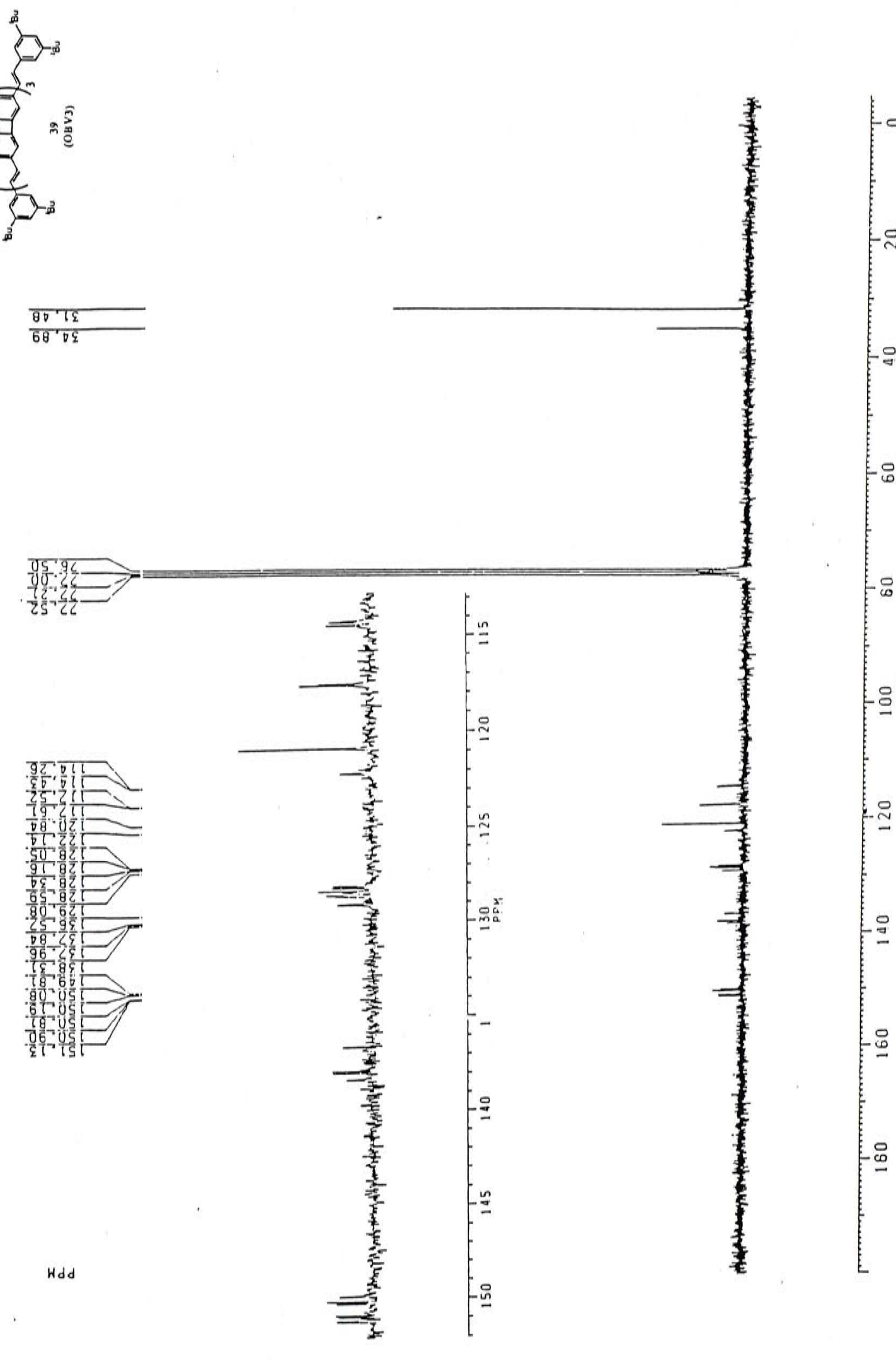


31.48
34.88
76.50
77.01
77.52
114.19
114.41
117.53
120.84
122.14
128.09
128.35
128.55
129.05
136.56
137.87
138.28
149.82
150.16
150.82
150.96
151.11
PPM
120
130
140
150
PPM
0
20
40
60
80
100
120
140
160
180
PPM


PPM
7.3392
7.2596
7.0659
7.0379
7.0193
6.9752
6.9619
6.8925
6.8333
6.8188
6.6741
6.6455
1.5789
1.4506
1.3636
1.3314
1.3182
1.3007
1.2813
1.2530
-.0001
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
PPM
INTEGRAL
6.03
.46
3.43
5.49
1.76
8.50
5.98
36.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


^{t}Bu
^{t}Bu
3
^{t}Bu
^{t}Bu

39
(OBV3)



tBu
tBu
tBu
tBu
3
39
(OBV3)
31.48
34.89
PPM
115
120
125
130
PPM
140
145
150
0
20
40
60
80
100
PPM
120
140
160
180