EFFICIENT ENERGY TRANSFER IN COFACIAL BORADIAZAINDACENE (BODIPY) DYES BUILT ON A XANTHANE SCAFFOLD AS A MODEL FOR EARLY STEPS IN PHOTOSYNTHESIS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

TARIK DİNÇ

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCES
IN
BIOCHEMISTRY

SEPTEMBER 2006

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all requirements as a thesis for the degree of Master of Science.

Assoc. Prof. Dr. Nursen Çoruh
Chairman of the Department

This is to certify that we have read this thesis and in our opinion, it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Engin U. Akkaya
Supervisor

Examining Committee Members

Prof. Dr. İdris M. Akhmedov (METU, CHEM) _____

Prof. Dr. Engin U. Akkaya (METU, BIOCHEM) _____

Prof. Dr. Dönüş Tuncel (BILKENT Univ., CHEM) _____

Prof. Dr. Ahmet Önal (METU, CHEM) _____

Asst. Prof. Neslihan Şaki (Kocaeli Univ., BIOCHEM) _____

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : TARIK DINC

Signature :

ABSTRACT

EFFICIENT ENERGY TRANSFER IN COFACIAL BORADIAZAINDACENE (BODIPY) DYES BUILT ON A XANTHANE SCAFFOLD AS A MODEL FOR EARLY STEPS IN PHOTOSYNTHESIS

DINC, TARIK

M.S., Department of Biochemistry

Supervisor: Prof. Dr. Engin U. AKKAYA

September 2006, 62 pages

Energy transfer is a natural phenomena that bases of the photosynthesis. In photosynthesis, chlorophyls and auxlary absorbing dyes units absorb solar energy and transfer the energy to the reaction center where other chemical reactions occur.

Studies showed that energy transfer depends strongly on distance and rigidy of the structure. Rigid structures that close in space transfer energy nearly %100 efficiency.

Supramolecular chemistry tries to mimic nature and miniurize natural phenomence on to molecular scale. Thus, articifial photosynthesis has been very popular in supramolecular chemistry. A lot of studies have been dedicated to diffent parts of photosynthesis.

BODIPY dyes have very well defined photophysical properties that can be used in multichromic systems and designing molecular switching potential tool on in supramolecular chemistry.

In this study extended BODIPY dyes constructed on a rigid xanthane scaffold have been deviced for energy transfer.

Keywords; BODIPY, energy transfer, Multichromic systems, molecular switching

ÖZ

FOTOSENTEZİN İLK AŞAMALARINA MODEL OLARAK KSANTEN İSKELETİNE YERLEŞTİRİLMİŞ BORADİAZAİNDASEN BOYALARINDA ENERJİ TRANSFERİ

TARIK, DİNÇ
Yüksek Lisans, Biyoimya Bölümü
Tez Yöneticisi: Prof. Dr. Engin U. AKKAYA

Eylül 2006, 62 sayfa

Enerji transferi fotosentez olayında yer alan bir olgudur. Fotosentezde klorofil molekülleri ve yardımcı absorblayan boyalar güneş enerjisini emerler ve diğer kimyasal reaksiyonların gerçekleştiği reaksiyon merkezine iletirler.

Yapılan calışmalar enerji transferinin genel olarak uzaklığa ve yapının sağlamlığına bağlı olduğunu göstermiştir. Parçaları birbirine yakın olanan esnemez yapılarda enerji transferinin yaklaşık %100 olduğunu göstermiştir.

Supramoleküler kimya doğadaki olayları taklit ederek daha küçük düzeyde yapmaya çalışır. Bu yüzden yapay fotosentez supramoleküler kimyada çok popüler bir dal haline gelmiştir.

BODIPY boyaları oldukça iyi fotofiziksel özelliklere sahip moleküllerdir. Bu özelliklerinden dolayı çoklu boya sistemlerinde ve moleküler dönüştürücülerde kullanibilirler ve potensiyel araç olarak supramoleküler kimyada kullanılabilirler.

Bu çalışmada sağlam ksanten iskeletine iliştirilmiş olan uzatılmış BODIPY türevleri enerji transferinde kullanılmıştır.

Anahtar kelimeler: BODIPY, enerji transferi, Çoklu boya sistemleri, moleküler dönüştürücüler.

To my family and my grandfather

ACKNOWLEDGEMENT

I would like to express my sincere thanks to my supervisor Prof. Dr. Engin U. Akkaya for his guidance, support and patience during the course of this research as well as his unlimited knowledge and experience that I have benefited from greatly.

I wish to thank to my family for their love, support, understanding, encouragement and everything they did for me.

Finally, I would like to thank all past and current U.S.O. (underground supramolecular organization) group members. I will never forget the beautiful friendship in our lab.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

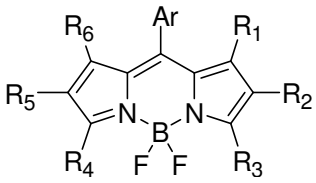
LIST OF ABBREVIATIONS

TFA: Trifluoroacetic acid

DMSO: Dimethylsulfoxide

BODIPY: Boradiazaindacene

NMR: Nuclear Magnetic Resonance



R= H or any group

CHAPTERS

CHAPTER 1

INTRODUCTION

1.1. Supramolecular Chemistry

Science is knowledge that we use to understand nature. Mankind is always inspired by nature, and has tried to understand and utilize the laws of nature through scientific approaches. [**1**]

The area of supramolecular chemistry is still young one [**2**]. It has moved into spotlight just after Cram D. J., Lehn J.M. and Pedersen C.J shared the Nobel Prize in Chemistry in 1987 *for their development and use of molecules with structure-specific interactions of high selectivity*. [**3]** Supramolecular chemistry has first defined by Jean-Marie Lehn who is the founder of the field as "Just as there is a field of molecular chemistry based on the covalent bond, there is a field of supramolecular chemistry, the chemistry of molecular assemblies and of the intermolecular bond". (Figure 1) [**4**]Moreover he states that "Chemists working in this area can be thought of as architects combining individual covalently bonded molecular building blocks, designed to be held together by intermolecular forces, in order to create functional architectures." [**4**]

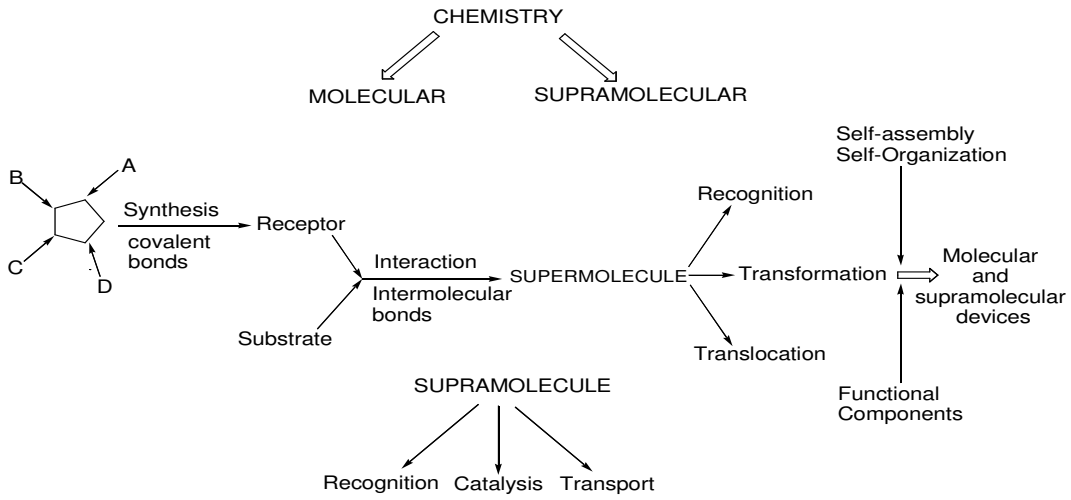


Figure 1: Molecular chemistry and supramolecular chemistry according to J. M. Lehn.

Despite the fact that supramolecular chemistry has been a new breath in chemistry, its applications in self-organization (e.g. membranes and micelles) organic semiconductors, molecular sensors, nanotechnology, recognition of biologically important molecules, biochemistry, artificial enzymes and medicine has appeared very quickly. Supramolecular chemistry owes this fascinating development to its highly multidisciplinary nature. Both inorganic and organic chemistry supply us molecules for constructing supramolecular systems and physical chemistry helps us for investigating the properties and dynamics of the systems. Lastly, biological systems are inspired for construction different systems.

The current literature clearly shows that chemical research is rapidly moving molecular to supramolecular species due to at least of four reasons:

1- The high degree of knowledge of gainedon molecular species
2- The extraordinary progress made by synthetic methods
3- The continuous research for new chemical functions
4- The need to fill the gap which separates chemistry from biology [**5**]

1.2. Supramolecular Chemistry of Life

In the view point of supramolecular chemistry, biological systems are magnificent and target systems. All the parts of the living systems communicate each other and perform their work according to information coming from other communicating systems. All the information flow and work done are performed in a supramolecular fashion. As a result of these supramolecular processes, life is maintained.

In biological chemistry, the supramolecular hosts are the receptor sites of enzymes, genes, antibodies of immune system and ionophores. The guests are substrates, inhibitors, cofactors drugs or antigens. All of these components exhibit supramolecular properties such as molecular recognition, self-assembly, self-organization and kinetic and thermodynamic complementarity. [**6**]

1.3. Non-covalent interactions

The basis of supramolecular chemistry is the use of intermolecular forces in a designed fashion. The quantification of non-covalent forces is of paramount importance for the design of synthetic host-guest complexes, of new drugs and of new materials, of enzyme analogue catalysts, for active –site directed mutagenesis and for many other applications. These forces include electrostatic interactions (*ion-ion interaction, ion-dipole interaction, dipole-dipole interaction, hydrogen bonding*) and dispersive forces (*Wan der Vaals interactions, cation-π interactions, π- π interactions, Hydrophobic interactions*). Table 1 summarizes non-covalent interactions and their binding energies.

Table 1: Non-covalent interactions and their binding energies.

Type of Bond	Binding Energy (kJ/mol)
Ion-ion interactions	100-350
Ion-dipole interactions	50-200
Dipole-Dipole interactions	5-50
Hydrogen binding	4-120
Cation-π interactions	4-80
π – π stacking	0-50
Van der Waals forces	<5

1.3.1. ION-ION INTERACTIONS:

A type of chemical bonding in which one or more electrons are transferred completely from one atom or molecule to another, thus converting the neutral atoms or molecules into electrically charged ions. [**6**] A supramoelcular example can be given between *tris*(diazabicyclooctane) derivative of benzene (**1**) and $Fe(CN)_6^{3-}$ (**2**).(Figure 2)

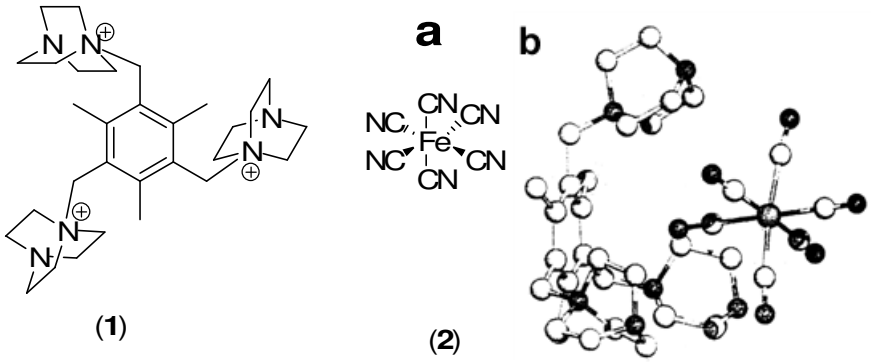


Figure 2: : a-) Structures of *tris*(diazabicyclooctane) derivative of benzene and $Fe(CN)_6^{3-}$ b-) The X-ray data of the complexation.

Ion-ion interactions play important roles in folding of natural and bio-molecules. Monovalent and divalent ions stabilize negative charges of phosphate groups on DNA, hence DNA can maintain its helical structure. (Figure 3)

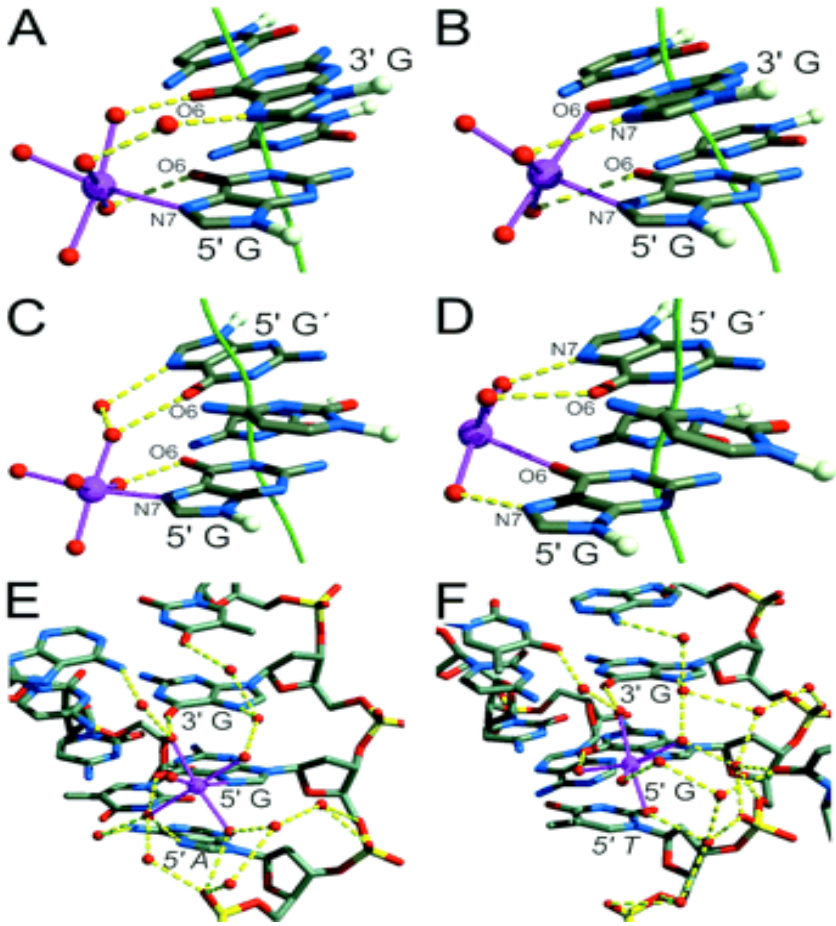
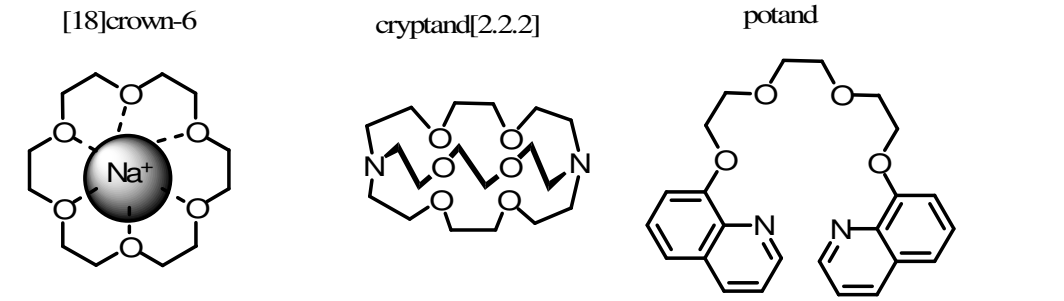


Figure 3:Three-bond and four-bond modes of Mn^{2+} binding in the DNA major groove. (*A* and *C*) The three-bond mode is shown for sites 1-GG and 5-GC, respectively. (*B* and *D*) The four-bond mode is shown for sites 4-GG and 6-GC, respectively. The guanine N7 and O6 atoms defining the metal binding mode and the contributing bases are labeled (G' indicates the complementary base to C in the GC step). A nonzero shift parameter for a base pair step is visualized as a deviation of the double helix axis (green). Coordination bonds (magenta) between metal ion (magenta) and water molecules (red), and hydrogen bonds (yellow) between bases and first and second shell, coordinated water molecules are shown. (*E*) The site 1-GG (*A*) is shown with its full hydrogen bonding network. A hydrogen bond occurs between the N7 atom of the adenine base (5' A) adjacent to the GG base step and a metal-coordinated water molecule, contributing to the orientation of the metal ion-hydrate. (*F*) Site 3-GG binds Mn^{2+} in the same three-bond mode as site 1-GG, but lacks the additional coordination shell bond from the adjacent thymine base (5' T). **[7]**

1.3.2. ION-DIPOLE INTERACTIONS:

Ion dipole interactions are resulted in between charged species (ions) and lone pairs of another specie. Classic supramolecular examples crown ethers [**8**], cryptands[**9**], podands[**10**] (Figure 4). These type of molecules has been used to as hosts to bind metal ions, charged organic molecules as guests. Various sized crown ethers, cryptands, potands are synthesized to various sized ions.[**11**-**15**]



(3) (4) (5)

1,4,7,10,13,16-hexaoxacyclooctadecane

4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8.8.8]hexacosane

1,2-bis(2-(quinolin-8-yloxy)ethoxy)ethane

Figure 4: Ion-dipole interactions

This type of interaction can be seen in biological systems where the bio-molecules interacts with metal ions. The very well known is porphyrin derivatives which bind Fe^{2+} , Mg^{2+}, Zn^{2+} in hemoglobin and chlorophyll (Figure 5)

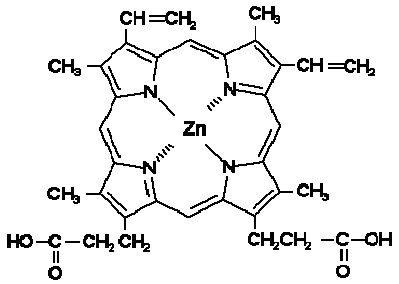


Figure 5: A porphyrin derivative **(6)**complex with Zn^{2+}

1.3.3. DIPOLE-DIPOLE INTERACTION:

A kind of interaction in which one dipole moment of a molecule effects the other molecule's dipole moment. This interaction is seen in polar molecules. Hence one part of molecules are partially positive charged and the other part of the molecules are partially negatively charged. This interaction is seen in organic solute in organic solvent, water and between solvent molecules. [**16**] (Figure 6)

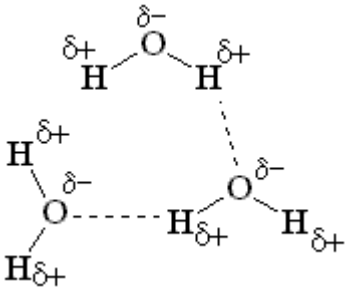


Figure 6 : Dipole-dipole interaction between polar water molecules.

1.3.4. HYDROGEN BOND

Hydrogen bond is a relatively weak chemical bond arising when a hydrogen atom covalently linked to an atom X forms an additional bond with another Y either in the same or in another molecule; strong hydrogen bonds are formed when X and Y are electronegative atoms like N, O, F. [**6**] Because of its relatively strong and highly directional nature, hydrogen bonding has been described as the 'masterkey' interaction in biochemistry and supramolecular chemistry. Figure 7 shows bond length of hydrogen bond and some biologically important hydrogen bonds. Hydrogen bonding is starring very important roles in living systems. Hydrogen bonds responsible for the overall shape of many proteins, recognition of substrates by numerous enzymes and for the double helix structure of DNA. (Figure 8)

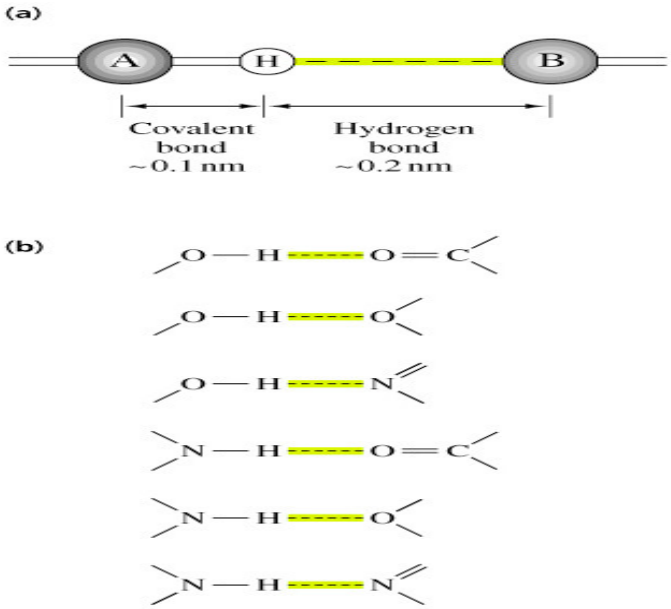


Figure 7:a- Hydrogen bond length b- important hydrogen bonds.[**15**]

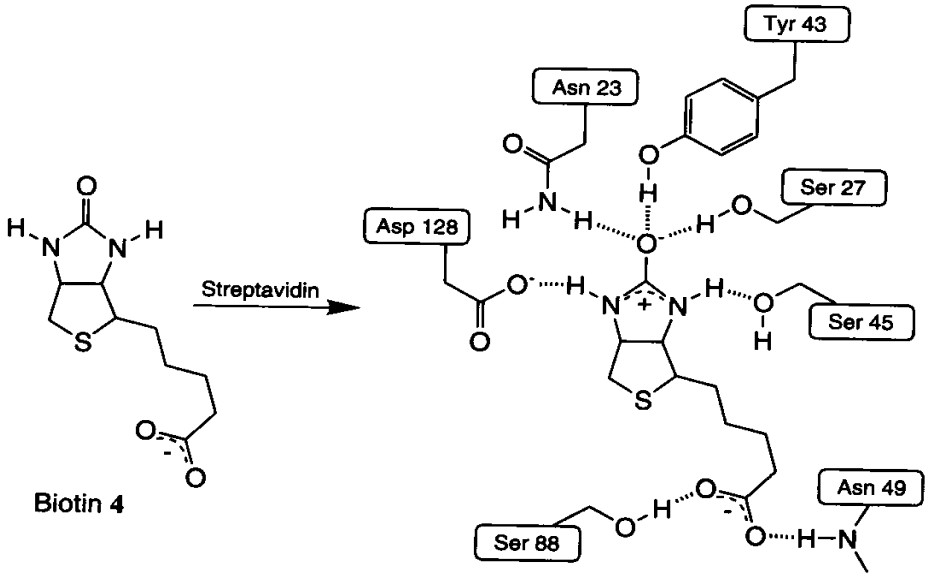


Figure 8: Binding of Biotin 4 molecule in the active site of Streptavidin enzyme through hydrogen bonds. [**1**]

1.3.5. CATION- π INTERACTIONS:

This type of interaction is seen in protein structures. The cationic site amino acids (Arg, Lys, or protonated His) interact with aromatic sited amino acids (Phe, Trp) in the protein structure. (Figure 9)[**6**]

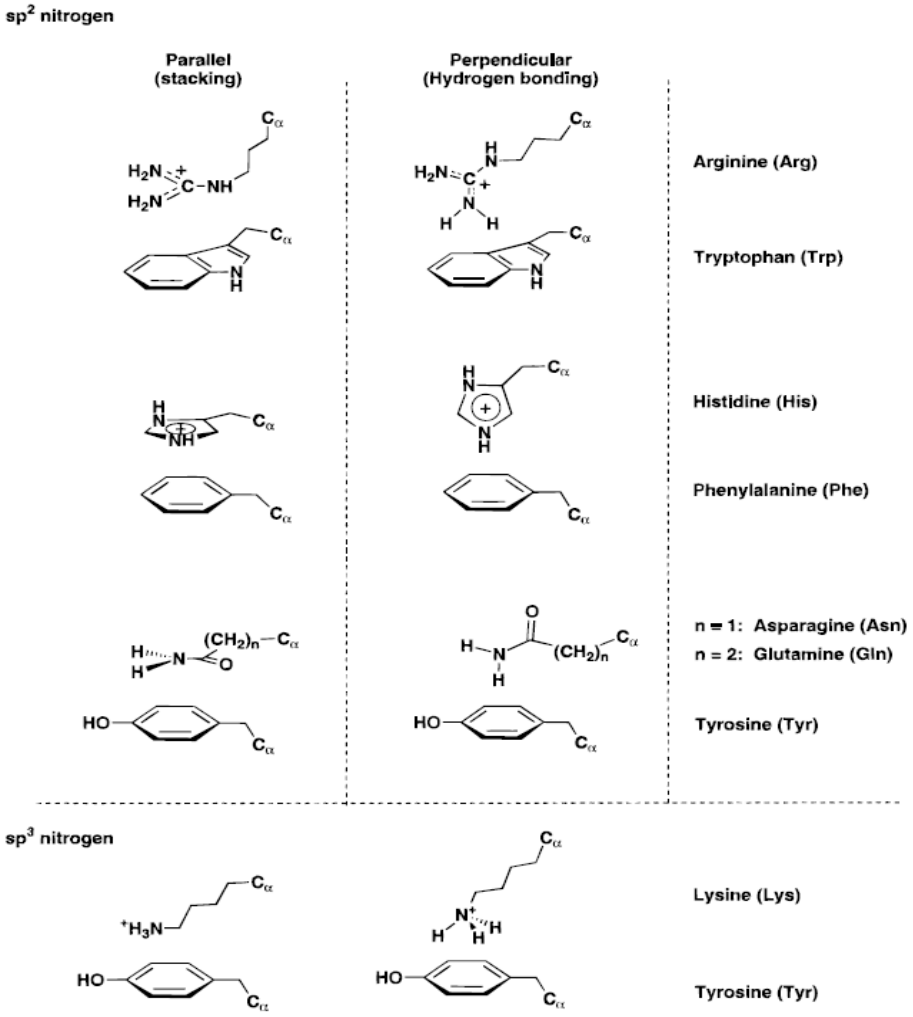


Figure 9: Cation—π interactions in protein structures.

1.3.6. π – π STACKING:

This weak electrostatic interaction occurs between aromatic rings, often in situations where on is relatively electron poor and one is electron rich. There are two general types of π stacking face-to-face and edge-to-face. π – π interactions

between aryl rings of nucleobase pairs also help to stabilize the DNA double helix. [**6**] Figure 10 shows orientation of aromatic groups due to π – π interaction.

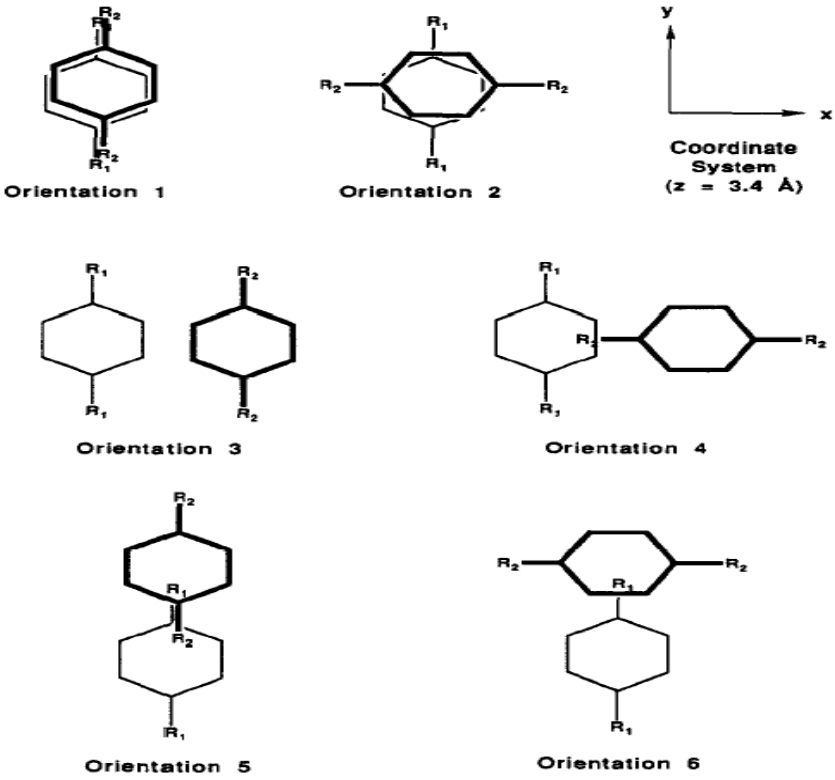


Figure 10: π – π stacking interactions.

1.3.7. VAN DER WAALS FORCES:

They are electrostatic attractions between fluctuating weak dipoles like C-H bonds, which at some time period can assume local charge distributions which differ from the permanent time-averaged moments and can assume an energetically favorable mutual orientation.[**16**] They are common in 3D protein structures.

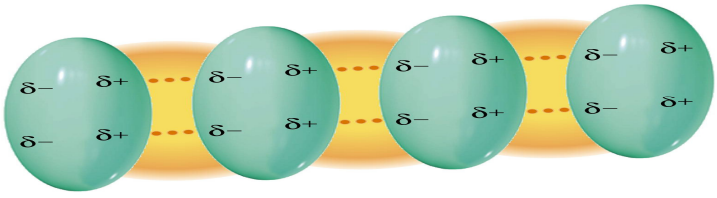


Figure 11:Polarization of non-polar molecular due to presence of other molecules.

1.3.8. HYDROPHOBIC INTERACTIONS

These forces are one of the main factors of the self-organization of biomolecules. For example, hydrophobic interactions are the major determining factors for the folding of proteins and the construction of the biomembranes. [**1]**

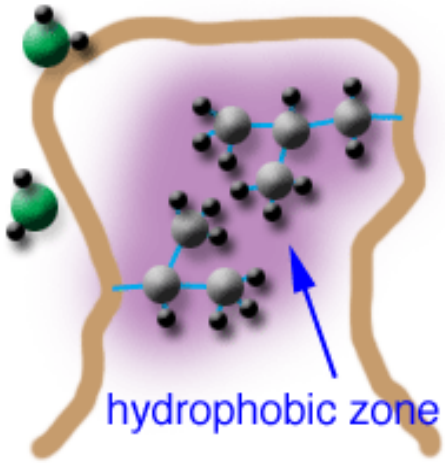


Figure 12: Hydrophobic interations in interior of an enzyme

1.4. Photochemistry

We call an organic molecule is a dye or pigment if it absorbs the light when it interacts. This process is called absorption of photon which usually occur 10^{-15} second. After the absorption deactivation process occur to dissipate the absorbed energy which is called relaxation process. Relaxation processes occur in several ways which are *fluorescence*, *phosphorescence*, *internal conversion intersystem crossing*, *radiationless*, *deactivation*, *energy transfer*. (Figure 13)

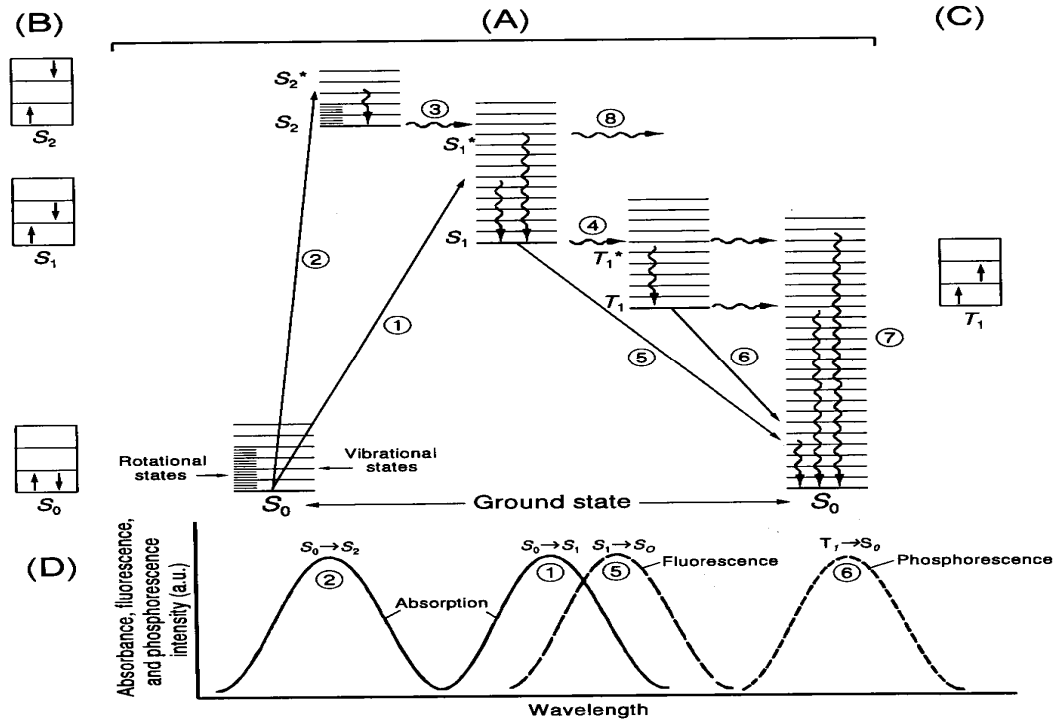


Figure 13: All possible events when a photon interacts with a organic dye molecule. (A) Straight arrows represent absorption and emission of light, wavy arrows represent non-radiative transitions. (B) and (C) show the electron spin states in the singlet ground state and in the singlet and triplet excited states. (D) shows simplified absorption and emission spectra numbered to correspond to steps in (A) [**17**]

Steps 1 and 2 are *absorption* to excited singlet states S_1 and S_2 respectively. Step 3 is *internal conversion* which occurs in 10^{-14} -10^{-13} second. In this step portion of the excited state is released as heat to surroundings by a sequence of small transitions through the vibrational sublevels of the electronically excited state. Step 5 is *fluorescence* in which excited molecule emits a photon from the first excited state. Step 4 is identified as *intersystem crossing*. It refers to conversion of an excited singlet state to an excited triplet state followed by a radiative (step 6 - *phosphorescence*) or nonradiative (step 7 –*radiationless deactivation*) of the excited triplet state to ground singlet state. Step 8 is the preferred step called *energy transfer* which occurs one of two ways. [**17**]

1.5. Energy transfer

Energy transfer can be taught as radiationless transition between two localized electronically states. Energy transfer is the most useful process in the deactivation steps because it can give us chance to manipulate the other processes of deactivation. If there is no energy transfer, dye molecule absorbs the light and give out as fluorescence or other deactivation ways. (Figure 14)

Figure 14: Simple Absorption and emission as fluorescence process

However, if there is a another dye 2 which absorbs at dye 1 fluorescence wavelength in the vicinity dye 1 then energy transfer from dye 1 to dye 2 occurs and dye 2 make emission as fluorescence. If the conditions are set well the energy transfer %100 and there will no emission from DYE 1

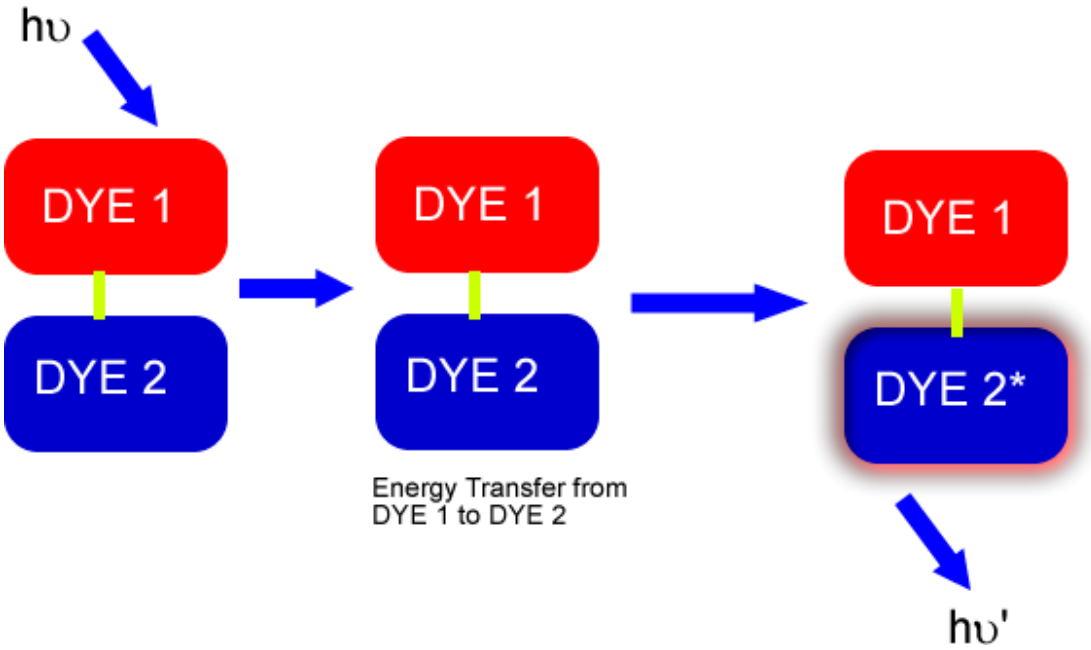


Figure 15: Energy transfer from DYE 1 to DYE 2 when DYE 1 is excited.

1.5.1. RESONANCE ENERGY TRANSFER

This mechanism (a.k.a Coulombic, Förster-type) by which energy transfer takes place in plant pigment systems is called resonance energy transfer has been firstly formulated by Thedor Förster.[**18-19**] In this type there is a direct coupling via the mutual radiation fields of two oscillator, corresponding, respectively to fluorescence in the donor molecule and absorption in the acceptor. The oscillation associated with de-excitation of one molecule is coupled at close range to a sympathetic oscillation in a neighboring molecule, causing transfer of excitation energy to the latter. Thus the first molecule donates its high energy directly to the second one without the intervation of fluorescence or absorption in the usual sense. [**20**] (Figure 16) This type of mechanism follows through-space and does not require physical contact between donor and acceptor. The rate of energy transfer is inversely depends on sixth power distance of between the donor and acceptor. The important conditions for efficient resonance energy transfer are a good overlap between fluorescence spectrum of donor with absorption spectrum of acceptor and distance between donor and acceptor. A typical example of an efficient Coloumbic mechanism is that of singlet-singlet energy transfer between large aromatic molecules, a process used by Nature in the antenna systems of the photosynthetic apparatus. [**21**]

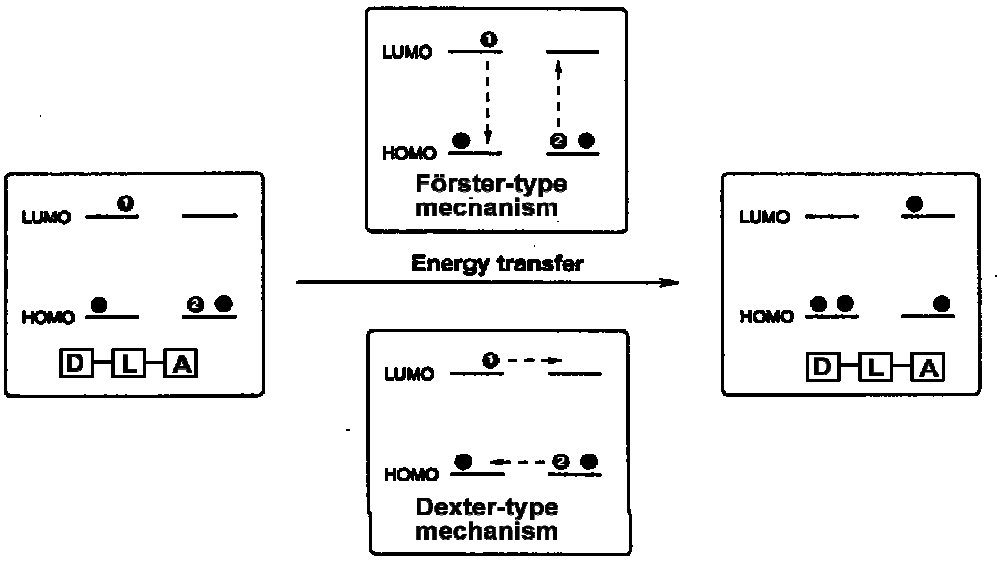


Figure 16:Förster type and Dexter type energy transfer mechanisms. D indicates energy donor molecule L indicates bridge A is energy acceptor molecule.

1.5.2. DEXTER TYPE ENERGY MECHANISM

Dexter type (a.ka. exchange mechanism) requires orbital overlap between donor and acceptor by a bridge and the decay is exponentially depend on the distance. The exchange mechanism can be regarded as a double electron-transfer process, one electron from the LUMO of the excited donor to the LUMO of the acceptor, and the other from the acceptor HOMO to the donor HOMO.

1.6. Supramolecular Photochemistry

Although supramolecular chemistry has initiated from investigation of complexation organic molecules(crown ethers, cryptands,calixarenes) with metal ions one of its branch has evolved to *supramolecular photochemistry* from molecular photochemistry to reveal the nature's photo-secrets.

Supramolecular photochemistry deals with the interaction of light with the supramolecular systems. It has grown up very rapidly after the exploration of reaction centre of bacterial photosynthesis which lead to Nobel Prize in Chemistry to J. Deisenhofer, R. Huber, and H.Michael in 1988. [21]

1.7. Supramolecular Photochemistry of life

1.7.1. PHOTOSYNTHETIC UNITS

Electromagnetic energy lying mainly in the visible or near IR region is capable of initiating photochemistry in the photosynthetic apparatus for the purpose of converting solar energy into chemical energy by a series of processes known as photosynthesis. Photosynthesis takes place in green plants, algae, cyanobacteria and photosynthetic bacteria. The sunlight absorbing units are chlorophyll a as major chlorophyll b. carotenoids and phycobilins as accessory pigments. Chlorophylls.

contain a Mg^{2+} ion centered on macrocycle of tetrapyrrole ring called porphyrin. Depending on whether it is bacteriochlorophyll, chlorophyll a or chlorophyll b porphyrin units vary in structure so their absorbance values differ. Figure 17 shows structures of porphyrin derivatives which present in chlorophylls.

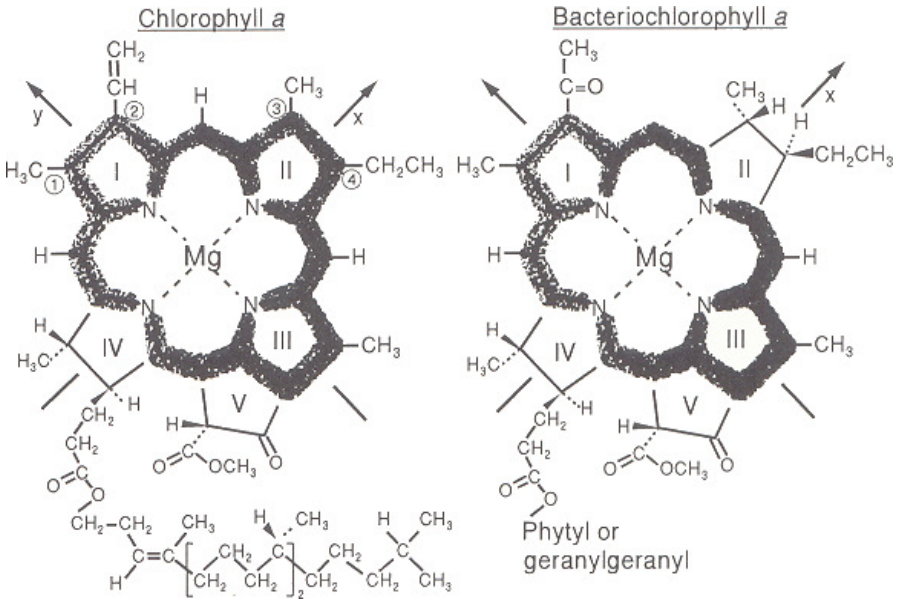


Figure 17: Porphyrin derivatives in chlorophyll a and bacteriochlorophyll a .

Figure 18 shows absorption spectra of chlorophyll a, chlorophyll b and bacteriochlorophyll in solution. The is significant diffence between bacteriochlorophyll a and chlorophyll b chlorophyll a due to their substituents. (Figure 19)

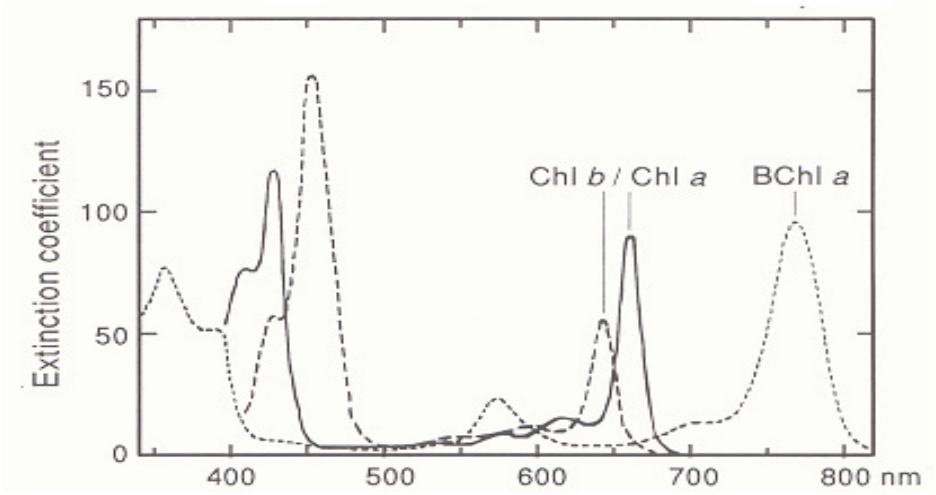
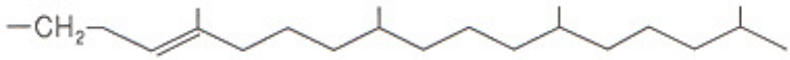
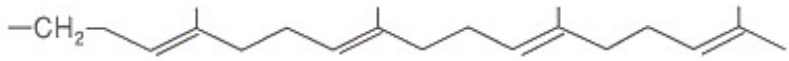


Figure 18: Absorbance spectra of chlorophyll b, chlorophyll a and bacteriochloropyll a in solution.

	R_1 / C-2	R_2 / C-3	R_3 / C-4	R_4
Chlorophyll *a*	$-CH=CH_2$	$-CH_3$	$-CH_2CH_3$	P
Chlorophyll *b*	$-CH=CH_2$	$-(C=O)-H$	$-CH_2CH_3$	P
Bacteriochlorophyll *a*	$-(C=O)-CH_3$	$-CH_3$	$-CH_2CH_3$	P or GG
Bacteriochlorophyll *b*	$-(C=O)-CH_3$	$-CH_3$	$=CH-CH_3$	P



phytyl side chain (P)



geranyl-geranyl side chain (GG)

Figure 19: Substituents on porphyrin derivatives.

Figure 20 shows absorbance and fluorescence of chlorofophylls in a correlated maner.

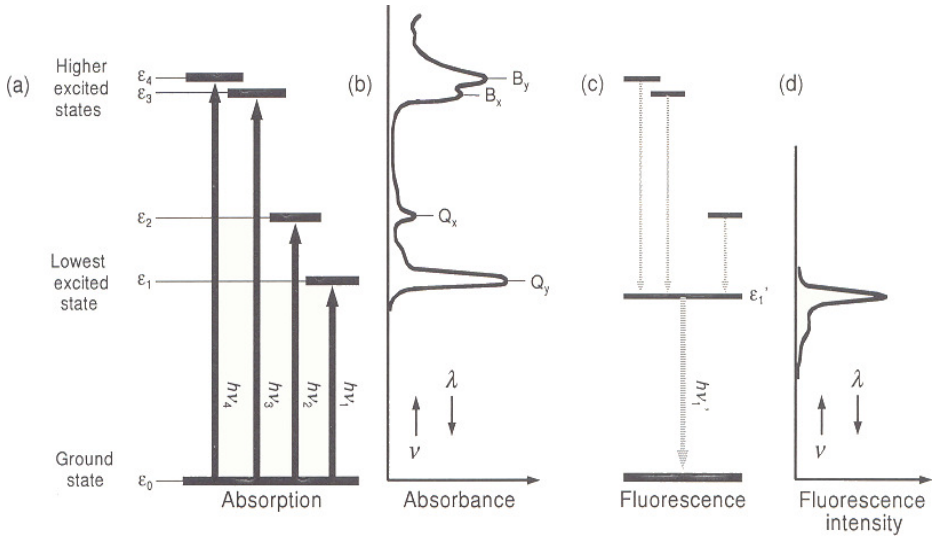


Figure 20: a- b- Absorption to of light and excitation to different states. c- d- emission of light as fluorescence**.**

There are accessory pigments which absorb light where chlorophyll do not absorb called carotenoids and phycobilins. They can be found in higher plants, algae and photosynthetic bacteria. Caroteinoids are long-chain, conjugated hydrocarbons containing a string of isoprene residus and distinguished from one another by their and groups. Figure 21 shows common 5 carotenoids with their absorption maximas.

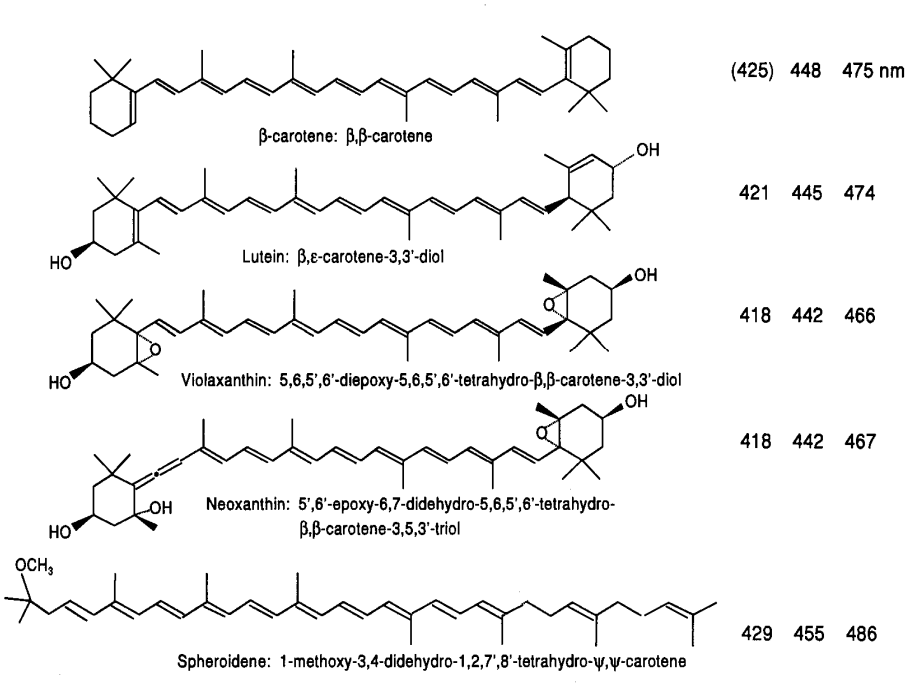


Figure 21: Common carotenoids with their visible maxima **[20]**

The efficiency of singlet-singlet energy transfer from certain carotenoids to chlorophyll range from %70 to %100. Carotenoids can also act as a quencher of triplet chlorophyll to provide protection against photo-oxitative damage.

The other group non-chlorophyll, light-harvesting pigments are the phycobilins.(Figure 22) They are abundant in red algae and cynobacteria. Phycobilins are non-cyclic tetra pyrroles and they are bound to polypeptide through thioether linkage.

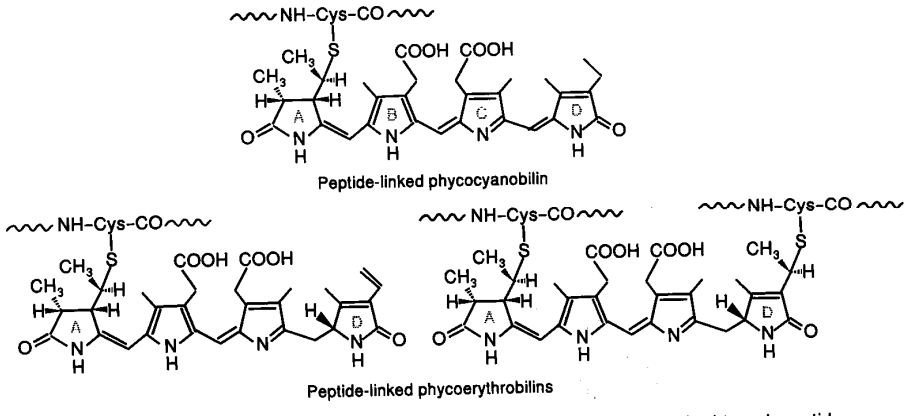


Figure 22: Phycobilins pigments bond to protein backbone

1.7.2 Energy Transfer in Photosynthetic Units

The best studied photosynthetic unit is purple bacteria due to achieving of high resolution X-ray of crystal structure determination of the photosynthetic unit of Rhodopseudomanas acidophilla. (Figure23)[27]

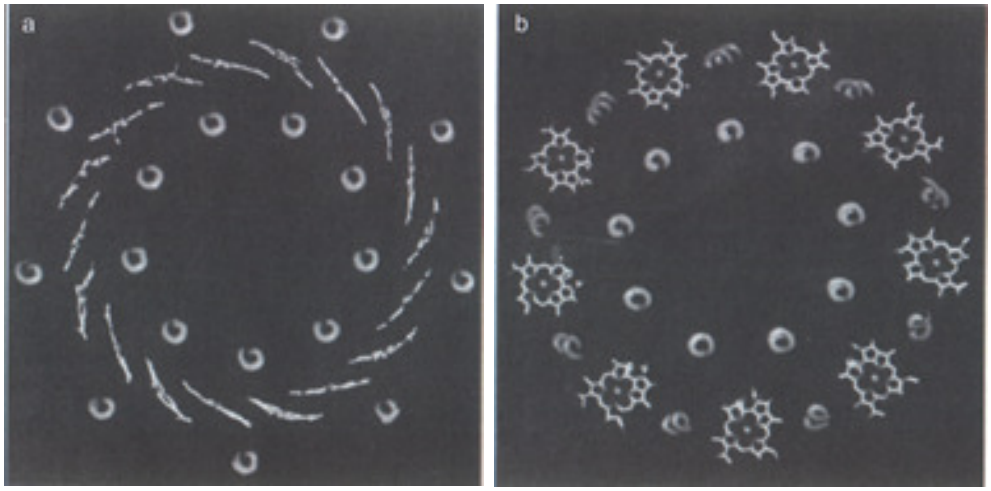


Figure 23: Structure of the LH2 molecule of Rhodopseudomonas acidophilla which contains rings of 18 (a) and 9 (b) bacteriochlorophyll molecules.

This complex is composed of two rings of bacteriochlorophyll (BChl) molecules a set of 18 molecules close to membrane surface in an almost face-to-face arrangement like a turbine wheel, and another set of nine molecules lying in a plane perpendicular to the rings of the BChl of the first type, in the middle of the bilayer.[28] These structures are contained within the walls of two protein cylinders with radii of 1.8 and 3.4 nm. (Figure 24) Because of different chemical environments, there are two sets absorption and photophysical properties. The 18 BChl belonging to the larger wheel have the lowest energy absorption maximum at 850 nm, thus it called B850, and the nine BChl in the middle of bilayer have lowest absorption maximum at 800 nm. There are other differences between the set of pigments. The B800 species are largely monomeric whereas the B850 species are strongly exciton-coupled with the exciton state delocalized over several BChl molecules. All BChl are maintained in a fixed spatial relationship by the surrounding polypeptides. Carotenoids are also associated within the LH2 structure with the dual function of contributing to light absorption and protecting the system against the system against photoxidation, by quenching the singlet oxygen molecules produced by photosentization.[29] The light absorbed by the B800 array is transferred to the line B850 wheel within 1ps. Energy migration among different exciton states of B850 then occurs on the 300 fs time scale.[30]

The absorbed energy collected by the LH2 unit is then transferred to LH1 complex via Förster type energy transfer then reaction center of (RC) where charge separation reactions take place. (Figure 25).

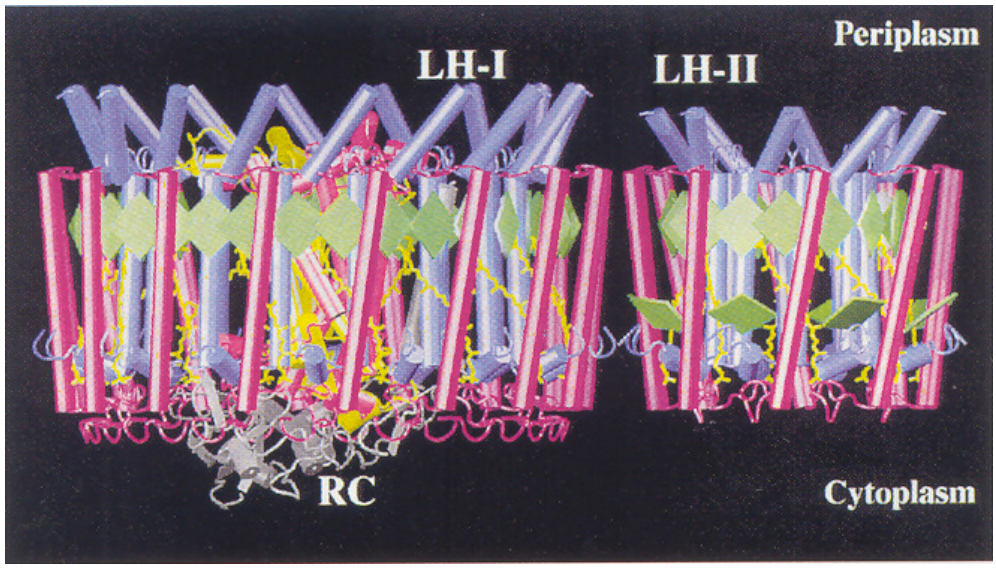


Figure 24: LH1 and LH2 in protein structure.

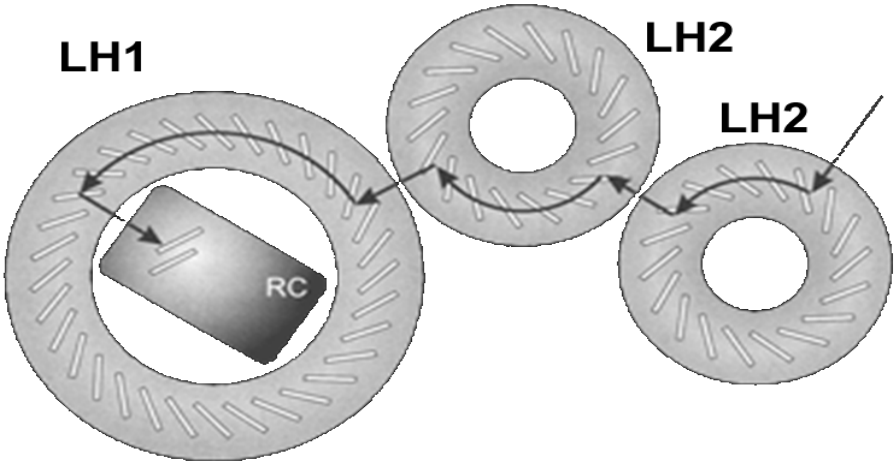


Figure 25: Energy transfer from LH2 to LH1 than reaction center.

Structure of LH2 is better known than LH1 complex. Two-dimensinal crystals of the LH1 complex of Rhdosdospirillum rubrum has provided evidence of clear similarity of LH1 and LH2 –LH1 is formed from 32 BChl molecules arranged as the B850 molecules of LH2, so that the LH1 wheel is larger. [31] LH1 and LH2 are in close contact (estimated to be closer than 30 A^0) so LH2-→ LH1 energy is

quite fast (3ps) The rate of successive energy transfer from LH1 to reaction center is 35 ps. [28]

In conclusion, in natural photosynthetic unit energy migration within almost isoenergetic subunits of a single complex is followed by fast energy transfer to a complex of lower energy with minimal cost. All process are belived to to occur by a Förster mechanism. [32].

1.8. Energy Transfer in Artificial Systems

There have been many energy transfer cassettes were synthesized to mimic this process. Mutual parallel branched porphyrin derivatives (**7 8**) and their zinc copper derivatives were investigated. (Figure 26) [**33**]

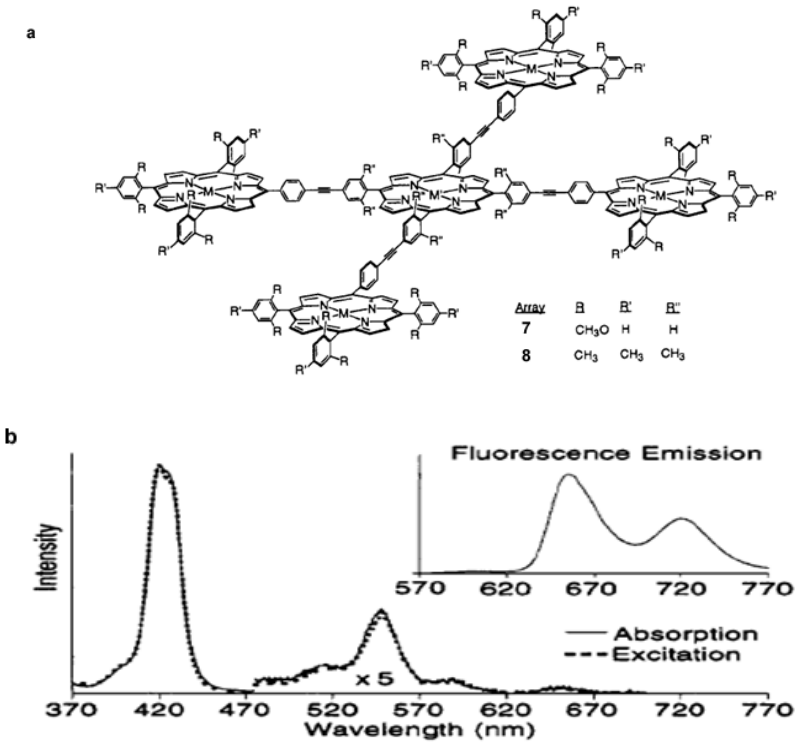


Figure 26: a- Porphyrin derivative 7 and 8. b- Absorption, fluorescence excitation (λ_{em}=721 nm) and fluorescence emission (λ_{ex}=421 or 547) spectra of 9 in CH_2Cl_2 at 303 K

Four leads conclude that:

- Singlet excited-energy transfer from the Zn porphyrin to the free base porphyrin is between %95 to %99
- Energy is transferred via through bond mechanism

Side to face porphyrin derivatives **9**, **10** and **11** Figure 27 were synthesized to investigate mutual orientation of of porphyrin rings. [**34**]

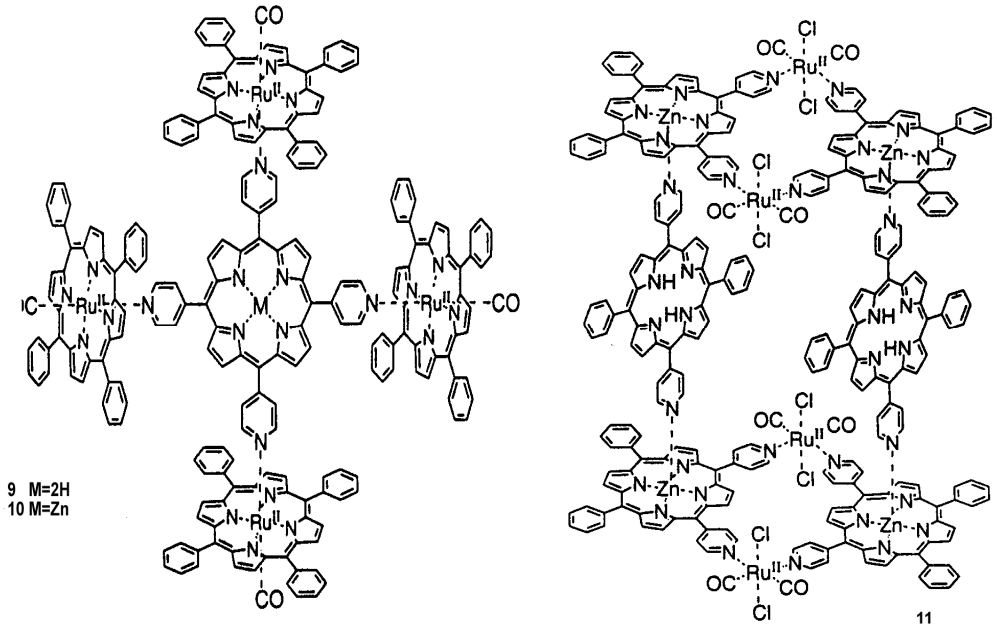


Figure 27: Side to side porphyrin derivatives.

There are other systems besides porphyrins are investigated. These include cyclodextrins [**35**-**41]** , dendrimers, [**42**-**50**], rotaxanes,[**51-60**] to obtain divergent systems which can make energy transfer like chlorophylls.

1.9. BODIPY

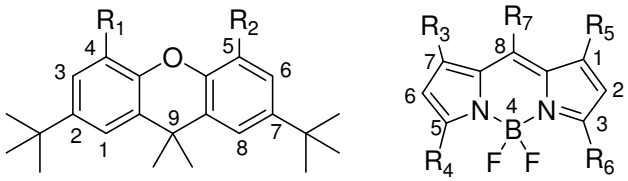
BODIPY dyes (a.k.a Boradiazaindacenes, BDPs, difluorobora-dipyrromethenes, etc.) are amazing fluorescent dyes that have high quantum yields, large extinction coefficients and narrow emission bands. [**61**] Because of these remarkable spectral properties and easy modification of BODIPY dyes make them useful in labeling of biomolecules, [**62-63**] ion-sensing and signaling [**64**-**71**] energy transfer cassettes, [**72**-**75**]

1.10. Aim of the Study

In this study we aim to perform energy transfer like LH2 to LH1. Our state points were :

- The dye should have very well defined properties like large extinction coefficient, high quantum yield, narrow emission bands, and red shifted absorption and emission bands.
- The dyes should be easily chemically and physically altered so that we can change emission wavelength.
- The dyes should be very well oriented that energy transfer should overcome the other relaxation processes.
- The system should be very rigid to enhance fluorescence emission from the dyes.

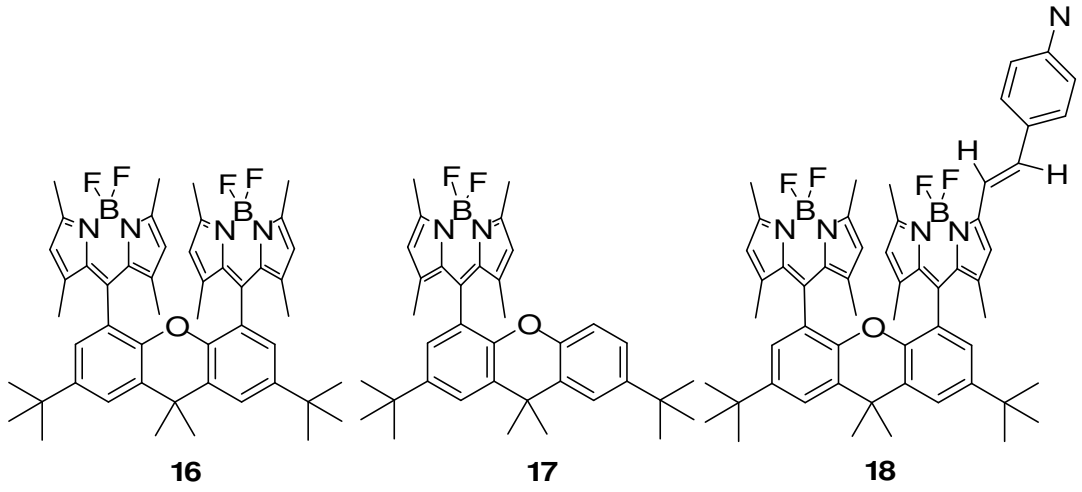
Keep this considerations in mind we have chosen BODIPY as our fluorophore **II** (Figure 28) which is easily modifiable on positions R_6, R_4, R_7 and fluorine atoms. To support fluorophores we chosed xanthene derivative **I** (Figure 28) as a scaffold. This scaffold provide us with a good solubility due to two tert-butyl groups and two methyl group which connected to tertiary carbon atom. These groups and substituents on the BODIPY helps the structure's rigidity.



I **II**

Figure 28: Structures of xanthene derivate I as scaffold and BODIPY derivative II as flourophore.

We synthesized BODIPY based fluophores **16**-**20**, investigate their spectral data and observed the energy transfer process in fluorophore **18**. The other fluorophores were synthesized for comparison.



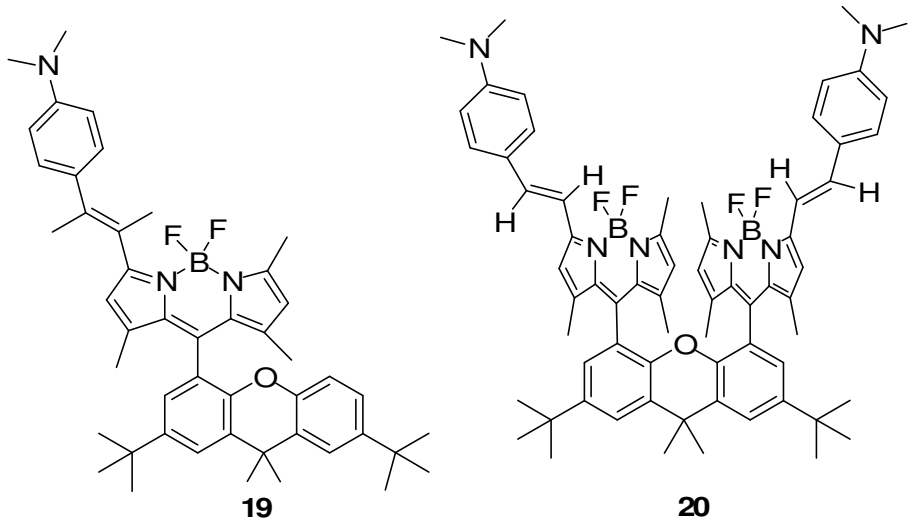


Figure 29: Novel fluorophores (16-20) that were synthesized, and investigated in this study

CHAPTER 2

EXPERIMENTAL

2.1. INSTRUMENTATION

In this study, the compounds were characterized and analyzed by Nuclear Magnetic Resonance Spectroscopy (NMR), Ultra-Violet/Visible Absorbance Spectroscopy, Fluorescence Emission Spectroscopy. ^{1}H and ^{13}C- Nuclear Magnetic Resonance spectra of the synthesized compounds were recorded by using Bruker Gmbh DPX-400, 400 MHz High Performance Digital FT-NMR Spectrometer at METU NMR Laboratory. The NMR solvent was the $CDCl_3$ in which tetramethylsilane was an internal reference and chemical shifts **δ** were calculated in ppm scale. Spin multiplicities are shown by the following symbols s (singlet), d (doublet), t (triplet).

Ultra-Violet/Visible Absorbance spectrums were recorded by Varian Bio 100 UV/VIS Spectrophotometer. Before measurements background correction was obtained by applying blank sample. Fluorescence Emission were obtained by Varian Cary Eclipse Fluorescence Spectrophotometer. All absorbance and emission measurements were taken in Sigma Spectrophotometer Silica (Quartz) cuvets with 10 mm light path, and tetrahydrofurane (THF) was used as solvent.

All solvents were distilled over $CaCl_2$ before using. 2.7 Di-*tert*-butyl-9,9-dimethyl-xanthane and 2,4 Dimethylpyrrole were obtained from Sigma&Aldrich in 97% purity. Trifuoroacetic acid was obtained from Acros Organics in 99 % purity. Hexamethylenetetramine was obtained from MERCK-Schuchardt in >99% purity. NMR solvent ($CDCl_3$) was obtained from Merck KGaA in 98.9 % purity. Merck

Silica Gel 60 (particle size 0.040-0.0963 mm, 230-400 mesh ASTM) was used as stationary phase in column chromatography during purification steps. Merck Silica Gel 60 F_{254} TLC Aluminum Sheets 20x20 cm were used in monitoring reactions by thin layer chromatography.

2.2. Synthesis 2, 7-di-tert-butyl-4,5-bis(chloromethyl)-9,9-dimethyl-9H-xanthene (13):

The synthesis was carried out according to procedure given by Grummit and Buck [**76**]. 2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene **12** (1 g, 3.10 mmol), of *p*-formaldehyde (0.4g), orthophosphoric acid (0.28 ml), HCl (1.2 ml) and acetic acid (8.2 ml) were heated in a pressure tube at 85 ^{0}C for overnight. The reaction mixture was dissolved in $CHCl_3$ and solution was washed with saturated $NaHCO_3$ solution until all no more CO_2 gas evolution was observed meaning that all the acid content was neutralized. Then, organic solution was dried over Na_2SO_3 and all solvent was evaporated under reduced pressure to give white powder. The overall yield was %90 (1.170 g) (Figure 30)

^{1}H NMR (400 MHz, $CDCl_3$,) δ(ppm) 1.27 (18 H, s, $C(CH_3)_3$), 1.57 (6H, s, $C(CH_3)_2$), 4.75 (4H, s, CH_2), 7.17 (2H, s, Ar-H), 7.28 (2H, s, Ar-H). (Figure 46)
^{13} C NMR (100 MHz, $CDCl_3$) δ(ppm) 31.9, 32.0, 32.8, 34.9, 42.5, 123.9, 124.4, 125.9, 130.0, 146.1, 146.4. (Figure: 47)

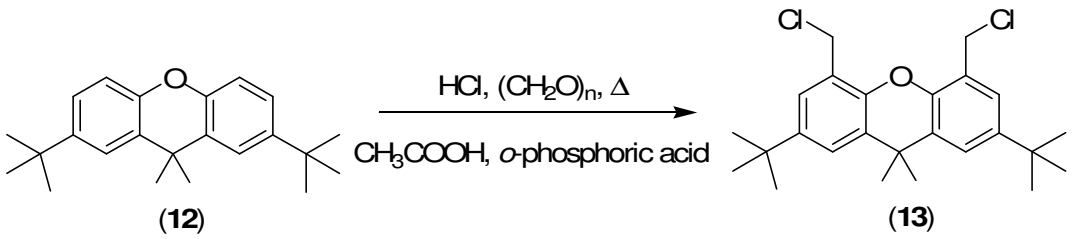


Figure 30: Synthesis of 2,7-di-tert-butyl-4,5-bis(chloromethyl)- 9,9-dimethyl-9H-xanthene (13):

2.3. Synthesis of 2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-dicarbaldehyde (14):

2,7-di-tert-butyl-4,5-bis(chloromethyl)- 9,9-dimethyl-9H-xanthene **13** (1.2 g, 2.86 mmol) and $NaHCO_3$ (600 mg, 7.14 mmol) were heated in 200 ml DMSO for 3 days. The reaction mixture was dissolved in $CHCl_3$ and solution was washed with water until all the DMSO removed. Then mixture was dried over Na_2SO_3 and $CHCl_3$ removed under reduced pressure. The product was purified by using column chromatography (Solid phase is silica gel, mobile phase is $CH_3OH/CHCl_3$ 1:99). In total 324.75 mg, 0.858 mmol product was obtained with 30% yield. The reaction schema is shown in Figure 31.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 18H, $C(CH_3)_3$)), 1.62 (s, 6H, $C(CH_3)_2$), 7.64(d, 2H, Ar-H, J_{meta}=2.38 Hz), 7.74 (d, 2H, Ar-H, J_{meta}=2.39 Hz), 10.6 (s, 2H, CHO) (Figure 48)

^{13} C NMR (100 MHz, $CDCl_3$) δ(ppm) 31.7, 32.6, 32.8, 35.1, 62.4, 123.8, 124.4, 129.8, 130.9, 147.0, 149.9, 189.2. Figure 49)

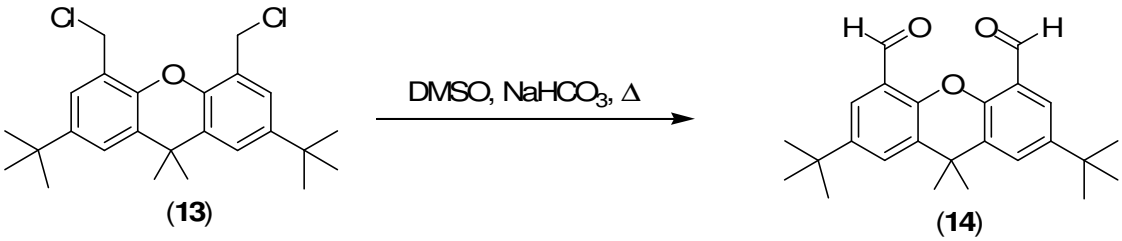


Figure 31: Synthesis of 2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-dicarbaldehyde (14):

2.4. Synthesis of 2,7-di-tert-butyl-9,9-dimethyl -9H-xanthene-4-carbaldehyde (15)

2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene **12** (967 mg 3 mmol) Hexamethylenetetramine (840 mg-6 mmol) and CF_3COOH (6 ml) were refluxed for 24 hours. (Figure 32). The acid was removed under reduced pressure and the residue was then subjected to silica gel column chromatography. (CH3OH/CHCl3 1:99) to yield compound **15** (540 mg, 51%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 18H, $C(CH_3)_3$)), 1.62 (s, 6H, $C(CH_3)_2$), 6.8 (d, 1H, Ar-H, J_{ortho}=8.5 Hz), 7.06 (dd, 1H, Ar-H, J_{ortho}=8.5, J_{meta}=2.3Hz), 7.3 (d, 1H, Ar-H, J_{meta}=2.3 Hz) 7.52 (d, 1H, Ar-H, J_{meta}=2.2 Hz), 7.62 (d, 1H, Ar-H, J_{meta}=2.3 Hz), 10.5 (s, 1H, CHO) (Figure 50)

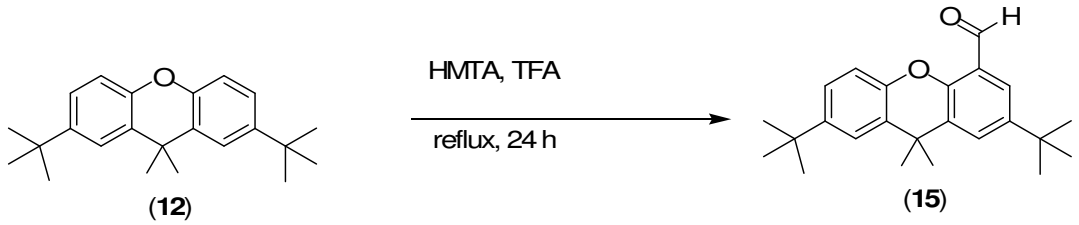


Figure 32: Synthesis of of 2,7-di-tert-butyl-9,9-dimethyl -9H-xanthene-4-carbaldehyde (15)

2.5. Synthesis of Bis-(boradiazaindacenyl)-derivatized xanthene (16):

2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-dicarbaldehyde **14** (400 mg, 1.05 mmol) was dissolved in 750 ml CH_2Cl_2. Then Argon gas was bubbled through solution for 30 minutes. 2-4 dimethyl pyrole (456 mg, 4.8 mmol) and a drop of CF_3COOH (TFA) were added the solution. After 4 hours mixing at the room temperature, tetrachloro-1,4-benzoquinone (258.3 mg, 1.05 mmol) in 50 ml absolute CH_2Cl_2 was added. After 30 minutes, Et_3N (4 ml) and $BF_3.OEt_2$(4 ml) were added and the solution was mixed at the room temperature for overnight. (Figure 33)

Then, the solution was concentrated under the reduced pressure and washed with water 3 times and dried over Na_2SO_3. Next all the solvent was evoprated and the product was purifed by column chromatography (Solid phase is silica gel, mobile

phase is $CH_3OH/CHCl_3$ 1:99). In total 162.9 mg product was obtained (yield is 20%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.25-1.29 (overlapping singlets, 18H+ 12H, $C(CH_3)_3$+ pyr-CH_3), 1.57 (s, 6H, $C(CH_3)_2$), 2.03 (s, 12H, pyr-CH_3), 5.21 (s 4H, pyr-H), 7.17 (d, 2H, Ar-H, J_{meta}=1.96 Hz), 7.33 (d, 2H, Ar-H, J_{meta}=2.0 Hz) (Figure 51)

^{13} C NMR (100 MHz, $CDCl_3$) δ(ppm) 21.4, 31.7, 32.8, 62.4, 123.8, 124.4, 129.8, 130.9, 147.0, 149.9, 189.2. Figure 52)

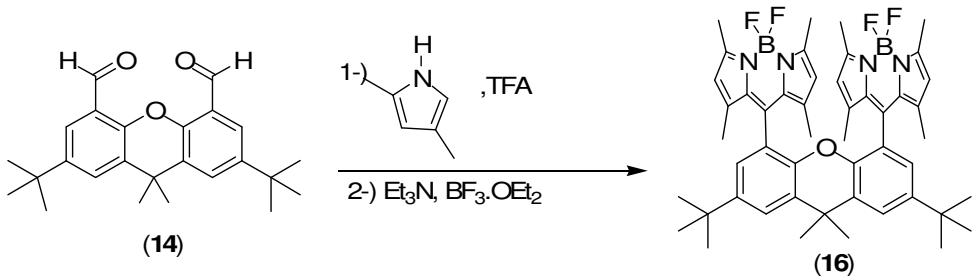


Figure 33: Synthesis of Bis-(boradiazaindacenyl)-derivatized xanthene (16)

2.6. Synthesis of Boradiazaindacenyl-xanthane derivative 17

2,4-Dimethylpyrrole (540 mg, 5.14 mmol) was added to a solution of 2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4-carbaldehyde **15** (540 mg, 2.57 mmol) in argon bubbled CH_2Cl_2 (750 mL). Then a drop of CF_3COOH was added and the solution was allowed to stir for 4 h at room temperature. Then, tetrachloro-1,4-benzoquinone (258 mg, 2.57 mmol) in dry CH_2Cl_2 (50 mL), Et_3N (4 mL) and BF_3:OEt_2 (4 mL) were added in that order to the solution, and stirred at room temperature overnight. The solution was concentrated under reduced pressure and washed with water several times, then dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography ($CH_3OH/CHCl_3$ 1:99) to obtain reddish product **17** (350.4 mg, 24%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 18,H, $C(CH_3)_3$)), 1.34 (s, 6H, $C(CH_3)_2$), 1.59(s, 6H, pyr-CH_3), 2.50(s, 6H pyr-CH_3) 5.87 (s 2H, pyr-H), 6.77 (d, 1H, Ar-H,

J_{ortho}=8.6 Hz), 7.01 (d, 1H, Ar-H, J_{meta}=2.6 Hz), 7.06 (dd, 1H, Ar-H, J_{ortho}=8.5, J_{meta}=2.3Hz), 7.3 (d, 1H, Ar-H, J_{meta}=2.3 Hz), 7.4 (d, 1H, Ar-H, J_{meta}=2.3 Hz), (Figure 53)

^{13} C NMR (100 MHz, $CDCl_3$) δ(ppm) 21.4, 31.7, 32.8, 62.4, 123.8, 124.4, 129.8, 130.9, 147.0, 149.9, 189.2. Figure 54)

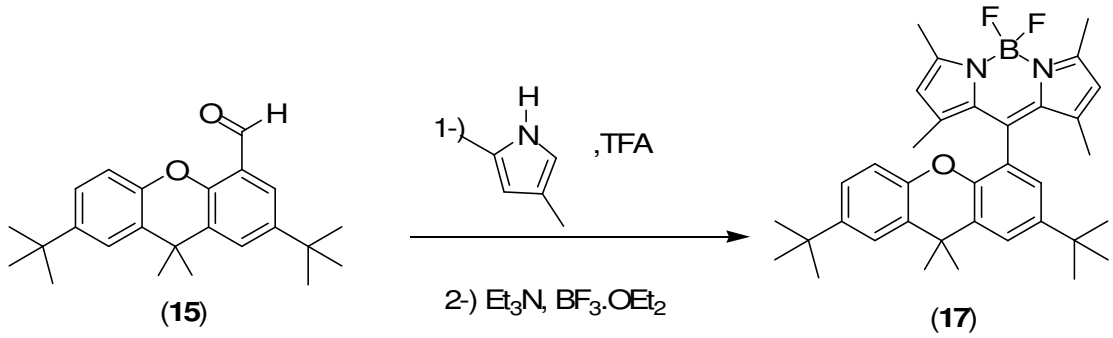


Figure 34: Synthesis of Boradiazaindacenyl-xanthane derivative (**17**)

2.7. Synthesis of Bischromohoric xanthane derivative 18:

Compound **16** (110 mg, 1.35 mmol) and N,N-dimethyl-4-aminobenzaldehyde (143.1 mg, 1.35 mmol) in a mixture of benzene (18 mL), acetic acid (510 mL) and piperidine (560 mL). Water formed during the reaction was removed azeotropically by heating in a Dean–Stark apparatus for 3 h. The solution containing the crude product was concentrated under reduced pressure and purified by silica gel column chromatography (1:4 ethylacetate/hexane) in 75% yield.

^{1}H NMR (400 MHz, CDCl3) d 1.20 (unresolved singlets, 18H+ 12H, $C(CH_3)_3$ pyr-CH_3), 1.57 (s, 6H, $C(CH_3)_2$), 2.34 (s, 3H, pyr-CH_3), 2.39 (s, 3H, pyr-CH_3), 2.41 (s, 3H, pyr-CH_3), 3.0 (s, 6H, $N(CH_3)_2$), 5.20 (s, 1H, pyr-H), 5.51 (s, 1H, pyr-H), 5.55 (s, 1H, pyr-H), 5.65 (s, 1H, pyr-H), 6.63–6.65 (m, 2H), 6.88–7.05 (m, 4H), 7.4–7.45 (m, 4H (Figure 57);

^{13}C NMR (100 MHz, CDCl3) d 31.4, 33.3, 33.7, 34.7, 119.8, 120.7, 112.4, 123.2, 123.3, 125.2, 125.5, 128.7, 130.9, 131.5, 136.7, 140.5, 141.8, 143.9, 144.1, 153.6, 156.9. (Figure 58)

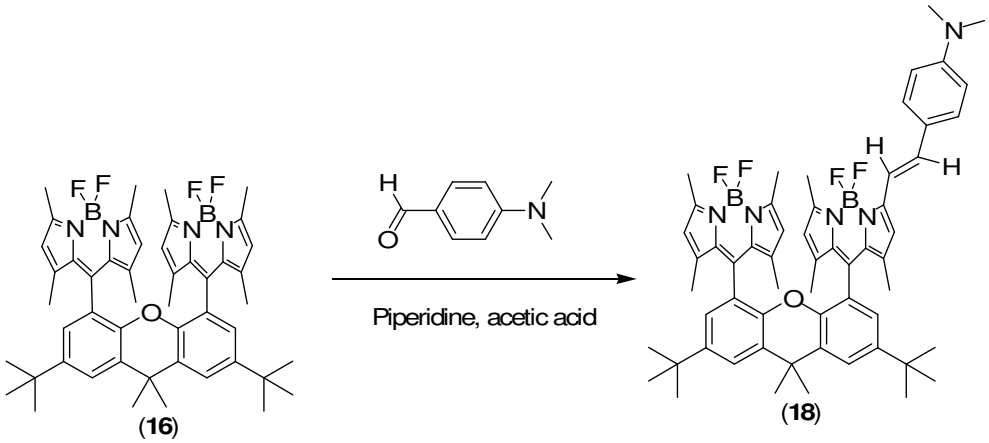


Figure 35: Synthesis of Bischromohoric xanthane derivative (**18**)

2.8. Synthesis of Extended conjugation boradiazadacenyl xanthane derivative 19

Compound **17** (100 mg, 0.176 mmol) and N,N-dimethyl-4-aminobenzaldehyde (25.6 mg, 0.176 mmol) in a mixture of benzene (18 mL), acetic acid (506 mL) and piperidine (557 mL). Any water formed during the reaction was removed azeotropically by heating in a Dean–Stark apparatus for 3 h. The reaction mixture was concentrated under reduced pressure and then subjected to silica gel column chromatography (1:4 ethylacetate/hexane) to yield the desired product 19 in 50% yield (61 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 18H, $C(CH_3)_3$), 1.35 (s, 3H, pyr-CH_3), 1.39 (s, 3H, pyr-CH_3), 1.59 (s, 6H, $C(CH_3)_2$), 2.5 (s, 3H, pyr-CH_3), 3.01 (s, 6H, $N(CH_3)_2$), 5.87 (s, 1H, pyr-H), 6.49 (s, 1H, pyr-H), 6.66 (d, 2H, J=8.7 Hz), 7.04–7.10 (m, 4H), 7.31 (d, J=2.3 Hz, 1H), 7.43–7.46, (m, 4H); (Figure 56)

^{13}C NMR (100 MHz, CDCl3) d 31.5, 32.2, 32.4, 34.5, 34.7, 116.3, 122.1, 122.2, 123.0, 124.4, 125.2, 128.7, 129.1, 130.4, 145.8, 146.5, 148.1. (Figure 57)

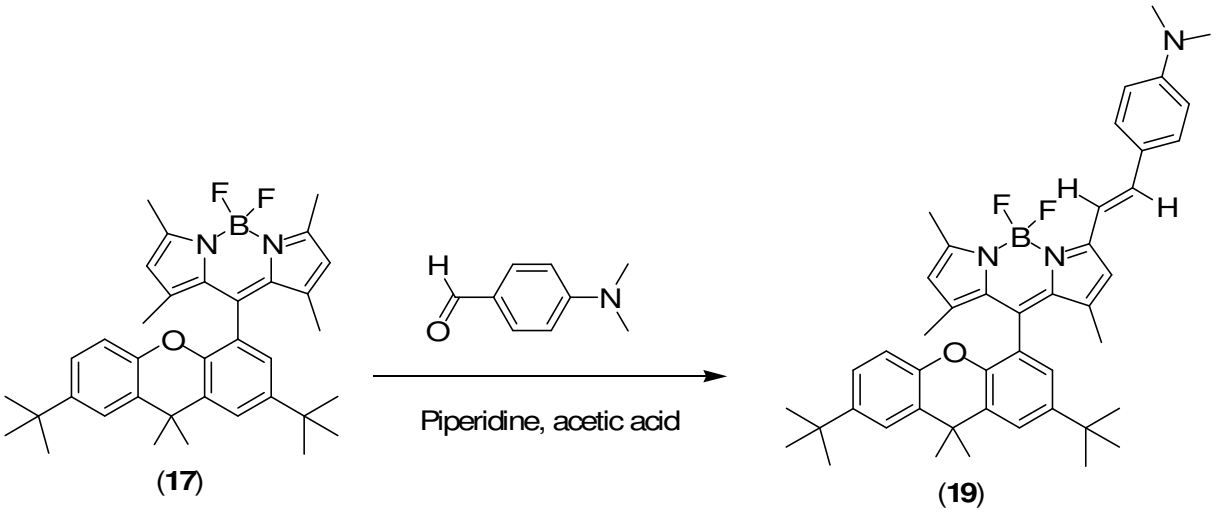


Figure 36: Synthesis of Extended conjugation boradiazadacenyl xanthane derivative (**19**)

2.9. Extended conjugation bis-(boradiazaindacenyl) xanthene derivative 20

Compound **16** (110 mg, 0.176 mmol) and N,N-dimethyl-4-aminobenzaldehyde (52.6 mg, 0.352 mmol) in a mixture of benzene (18 mL), acetic acid (506 mL) and piperidine (557 mL). Any water formed during the reaction was removed azeotropically by heating in a Dean–Stark apparatus for 3 h. The reaction mixture was concentrated under reduced pressure and then subjected to silica gel column chromatography (1:4 ethylacetate/hexane) to yield the desired product **20** in 40% yield (65 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24–1.30 (two unresolved singlets, 18H+12H), 1.59 (s, 6H), 2.55 (s, 6H), 3.01 (s, 12H, $N(CH_3)_2$) 5.85 (s, 2H), 6.50 (s, 2H), 6.64 (d, 4H, J=8.7 Hz), 6.78–6.82 (m, 2H), 7.02–7.25 (m, 8H), 7.35 (d, 2H). (Figure 59)

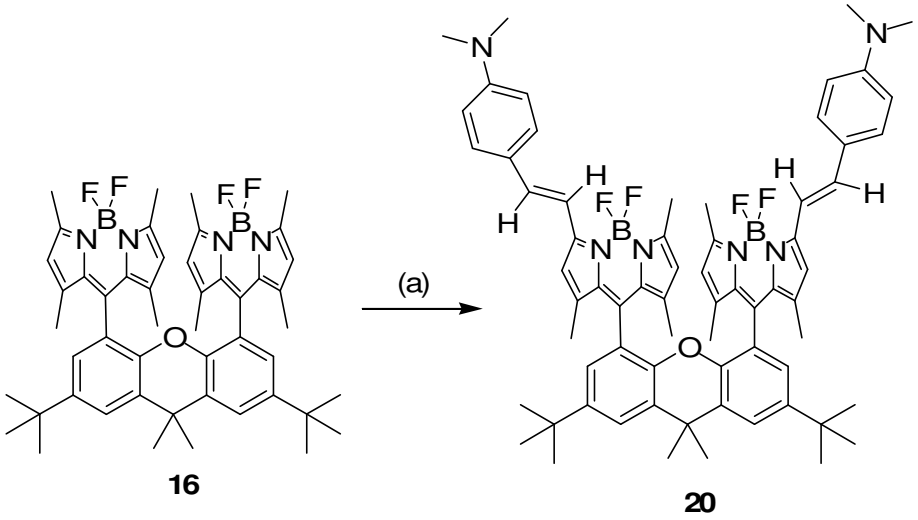


Figure 37: Extended conjugation bis-(boradiazaindacenyl)xanthene derivative **(20)**

CHAPTER 3

RESULT AND DISCUSSION

3.1. Synthesis

As a synthetic strategy we chose an approach that would allow us to synthesize both monomer BODIPY's, dimer BODIPY's and their derivatives.

BODIPY dyes are usually synthesized from aldehydes. Although, there are some methods that use corresponding acetyl chlorides, unfortunatelly we were not be able to get satisfactory results in our case. Therefore, we focused on the synthesizing aldehyde derivatives of xanthane.

In inserting aldehyde functional group to xanthane, to obtain compound **15** we tired two methods. Firstly, we refluxed compound **12** with CF_3COOH and hexamethyltetraamine for 24 hours in 1 to 1 equivalents. After chromatographic separation we obtained mainly monoaldehyde derivative of xanthane which is compound **15**. However, when we used 1 to 2 equivalents, we could not obtain dialdehyde derivative in significant amount. It was again mainly mono aldehyde derivative (compound **15**).

Then, we used chloromethyl intermediate for synthesizing dialdehyde **14**. Compound **12** was reacted with formaldehyde in very acidic media (acetic acid, hydrochloric acid, phosphoric acid) in a pressure tube for overnight. This reaction gives very satisfactory yields of chloromethyl derivative of xathane. After removal of the components by extraction and drying the organic phase this chloromethyl intermediate (compound **13**) could be used in aldehyde reaction. Compound **13** turned to compound dialdehyde **14** in the presence of $NaHCO_3$ in DMSO within 3 days.

Synthesizing BODIPY's from different aldeydes is common, when equivalent amounts of 2,4-dimethylpyrole and oxidizing agent used in the reaction. Aldeyde derivatives, 2,4-dimethylpyrole and a drop of CF_3COOH (TFA) are reacted in absolute CH_2Cl_2 at room temperature for four hours. Then the intermediate product is oxidized with tetrachloro-1,4-benzequinone. After half an hour Et_3N and $BF_3.OEt_2$

were added. Then the reactions were let to be stirred for overnight at room temperature. After, eligible chromatographic separations methods application, BODIPY dyes were obtained nearly %20 in yield.

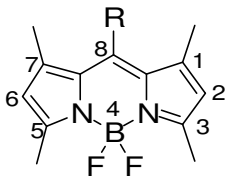


Figure 38: BODIPY core structure

BODIPY dyes which are synthesized from 2,4-dimethylpyrole derivatives have interesting properties. Methyl groups on 3 and 5 positions have acidic hydrogens due to electron withdrawing property of heterocyclic boradiazaindace ring. This acidic property can be taken advantage of, in the synthesis of other BODIPY fluorophores for example with aromatic aldehydes. In our case N,N-dimethyl-4-aminobenzaldehyde would react with BODIPY, resulting extension of conjugation. This extension of conjugation gives us an opportunity to shift the absorption and emmission spectra to longer wavelengths.[**77**]

The reaction is performed in solution containing acetic acid and piperidine. The solvent is usually benzene or toluene, because any water forming in the reaction should be removed. Dean-Stark apparatus is a good choice, because water can be removed azeotropically during reflux.

3.2 Photophysical Part

Efficient energy transfer mostly depends on spectral overlap between donor and acceptor, distance between donor and acceptor, and orientation factors, effectiveness of alternate deactivation modes (intersystem crossing, vibrational relatations).

Due to ease of modification of BODIPY dyes, one can construct remarkable BODIPY dyes that have high extinction coefficients, well defined spectral properties and high solubility.

Previously, side to side BODIPY dimer **21** and later concurrently with this study **22** were synthesized and spectral properties were investigated in our group. [**64**, **68**, **70**, **71**]. As a part of synthesizing novel BODIPY bases dyes, we synthesized face to face BODIPY fluorophors **16**, **18** and **20** in this study.

Xanthane derivative scaffold **12** gave us a good opportunity for solubility and very strict construction. It is known and our previous studies also showed that planar aromatic compounds may have low solubilities. They tend to form aggregates in the solution. This unwanted situation affects both yields and spectral properties. As it can be observed from three dimensional energy minimized structure of compound **18,** the two face to face BODIPY fluorophores are held orthogonal to xanthane scaffold. (Figure **39**)

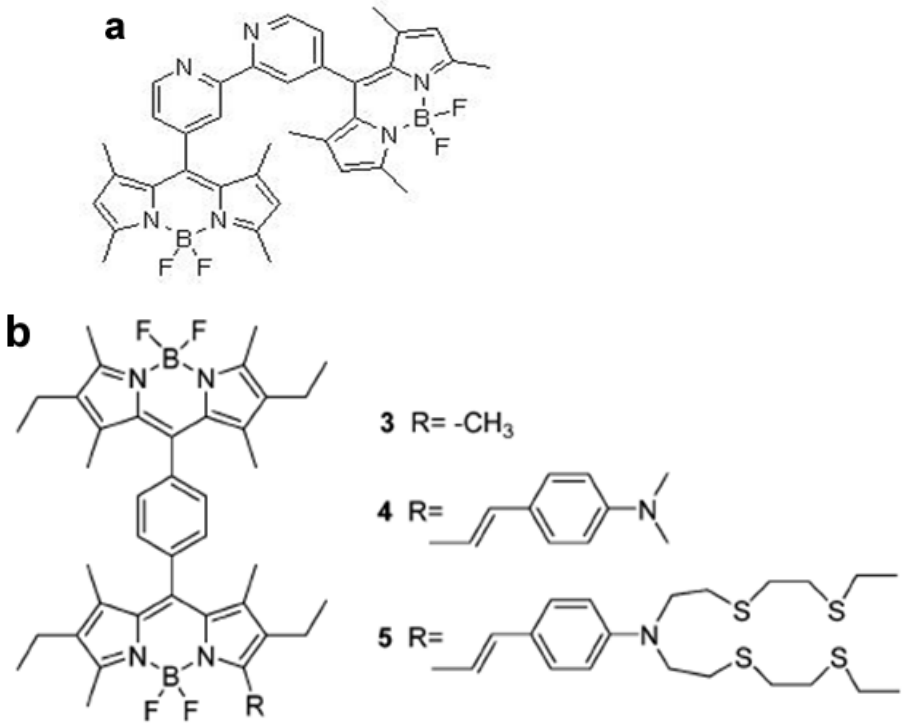


Figure 39: a- b- Side to side BODIPY derivatives that were synthesized in our group.

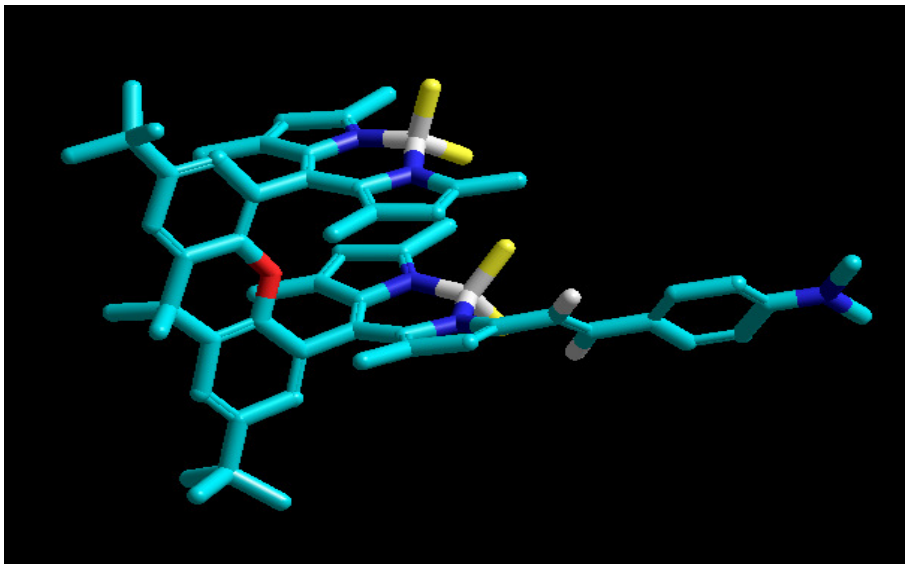


Figure 40: 3D energy minimized structure of compound **18**

Tert-Butyl groups on xantahene and position of BODIPY units prevents the aggregation. The four methyl groups on 1, 1' 2, 2' prevent rotation of BODIPY dyes in relation to the xanthane scaffold

As it can see from the ^{1}H NMR spectra of BODIPY compounds methyl groups that are present at 3 and 5 positions have chemical shift at 2.5 ppm. Methyl groups which are at 1 and 7 positons have changing chemical shifts. In the mono BODIPY compounds **17** and **19** these methyl groups have chemical shift 1.59 ppm. These groups shift to δ 1.25-1.29 in dimers which indicates these methyl groups are oriented below and above the benzene ring of xanthane. Energy minization by Hyperchem software also clarify this conformation. (Figure 39) From this two facts we conclude that BODIPY dimers **16**, **18** and **20** are very strict in structure. This strict structure enhance spectral properties of BODIPY dimers like LH1 and LH2 in which porphyrin units are well oriented by proteins.

When two identical flourophore units present very close to each other excimer formation develops. This excimer have different spectral properties from the original monomer. In Figure 40 absorbance of monomer BODIPY dye **17** and dimer **16** are depicted.

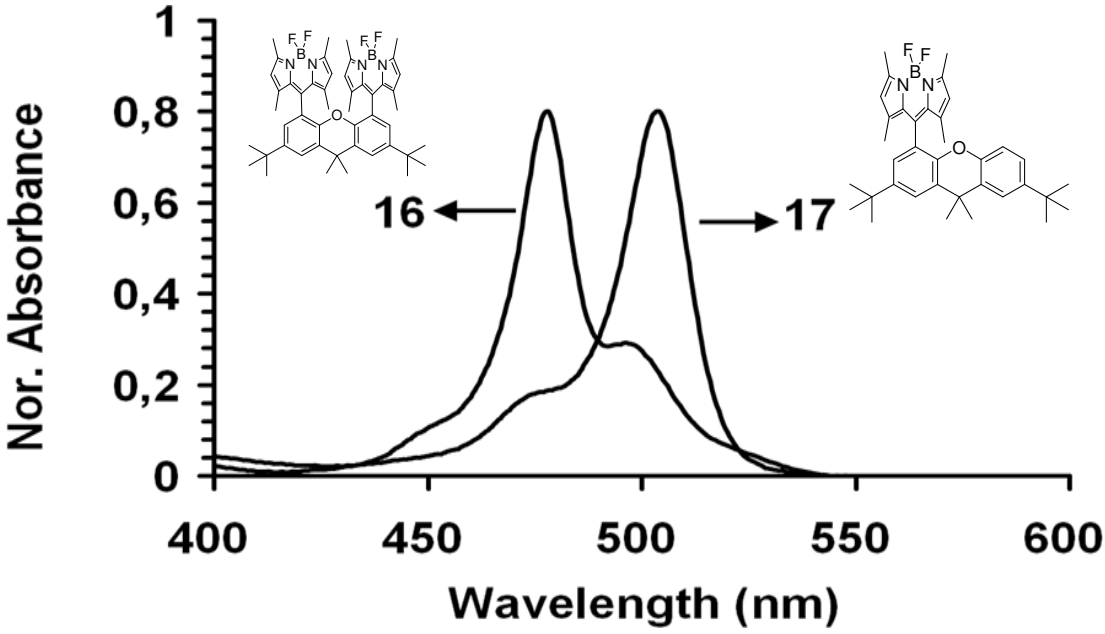


Figure 41: Absorbance spectra of compounds **16** and **17** in acetonitrile

Absorbance of monomer BODIPY **17** with a major absorbance peak at 504 nm in acetonitrile resemble the simple phenyl based BODIPY defined in the literature. However dimer **16** have peak at 478 nm with a shoulder at 504 nm. Moverover, emission spectra of **16** and **17** are very different from each other. (Figure 41) Monomer 17 has a well defined narrow emission, whereas dimer **16** emission broadens and sharp peaks disappears. This observation is in accordance with another study in which BODIPY dimers are in sugar moiety [**78**].

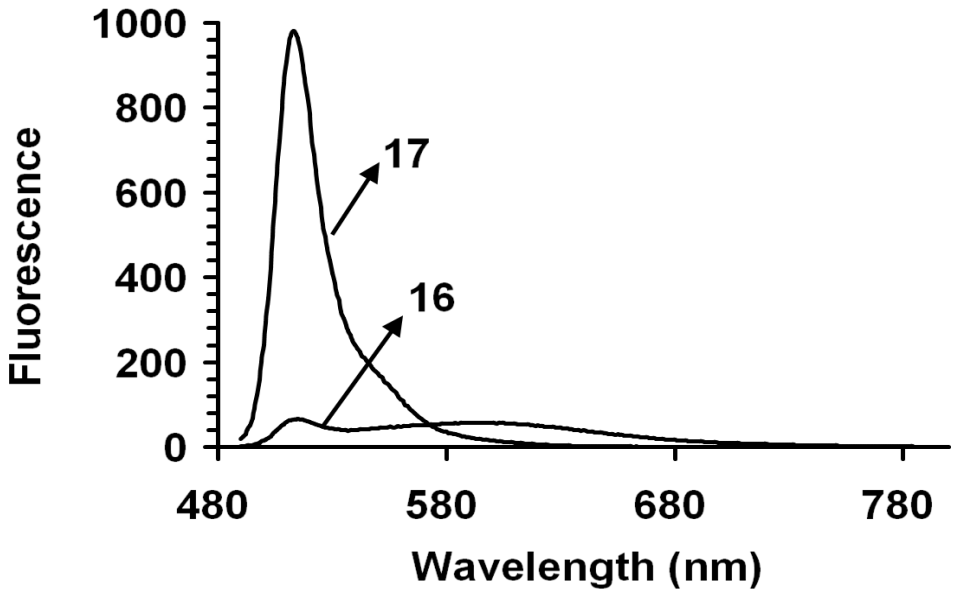


Figure 42: Emission spectra of **16** and **17** at fixed absorbance.

This changes in absorbance and fluorescence spectra are resulted from mutual reorientation of electronic and vibrational energy levels due presence of same fluorophore. This process is called Davydov splitting which is usually observed in crystals.

Figure 42 shows absorbance data of monomers **17**, **19** , dimers **18** and **20** and acidified **20**, **19**, **18**. The absorbance spectrum of **18** is composed of monomers **17** and **19** as it can be predicted. Dimer **18** has two well separated absorption maxima at 455 and 575 nm where monomer **17** has maximum at 455 nm and **19** has maximum 575 nm.

Extending conjugation of BODIPY dyes by means of condensation them with aromatic aldehydes shifts absorbance and fluorescence maxima to longer wavelengths and broader the peaks due to increasing vibrational and rotational levels.

Extended BODIPY dyes **18**, **19**, and **20** have changes in absorption spectra by addition of acid. Due to fact that they contain diaklyamino group they can be protonated, resulting changes in electron donor capacity of the amino group. Maxima which belong the extended dyes conjugation and shift to shorter wavelengths. The acid addition on BODIPY dimer **18** decrease both long wavelength absorption and short wavelength absortion. This means that as conjugation decreases, molecule **18** gains spectral properties of molecule **16 .** This phenomena gives opportunity to modify the signal that we obtain.

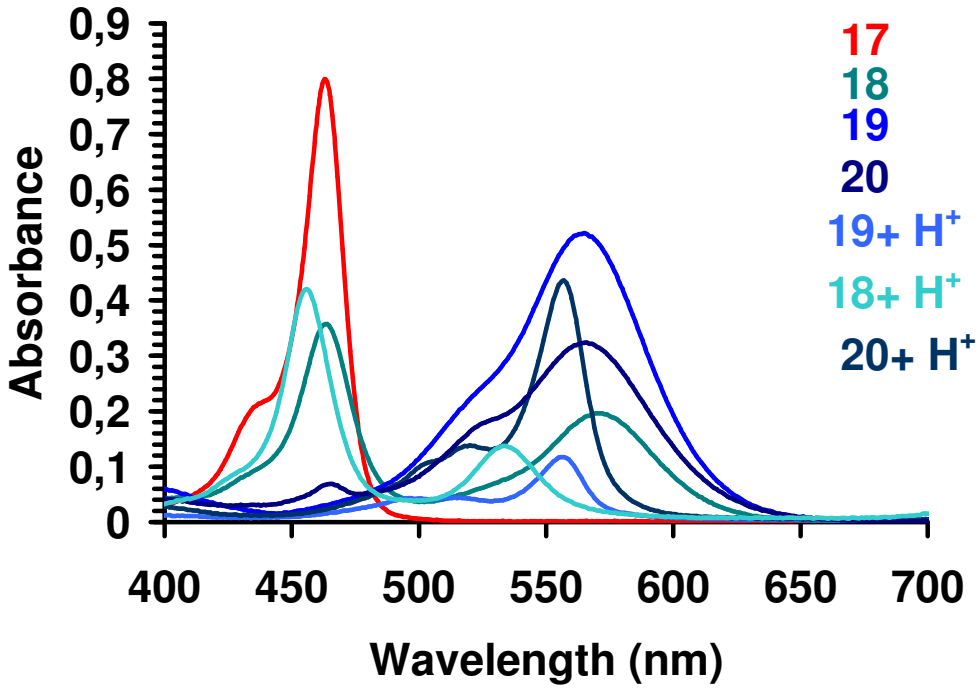


Figure 43: Emission spectra of compounds **17**, **18**, **19**, and **20**, and acidified of **18**, **19** and **20**

Figure 43 show emission spectra of monomer BODIPY **17** extended BODIPY monomer **19** and dimer **18**. In this measurement all of the BODIPY's absorbance is fixed to 0.1 and they are excited at 480 nm. This wavelength is where the compound **17** can be efficiently excited as it can be seen in the figure. However in this wavelength compound **19** does not absorb. (small figure in Figure 44). Dimer **18** can absorb at 478 nm with no emission (i.e. no fluorescence) it transfers its energy to the extended conjugation dye and that dye emits. So we observe it its emission near 650 nm. This shows that the energy transfer is very efficient. This efficiency is further enhanced by addition of acid. (Figure 44)

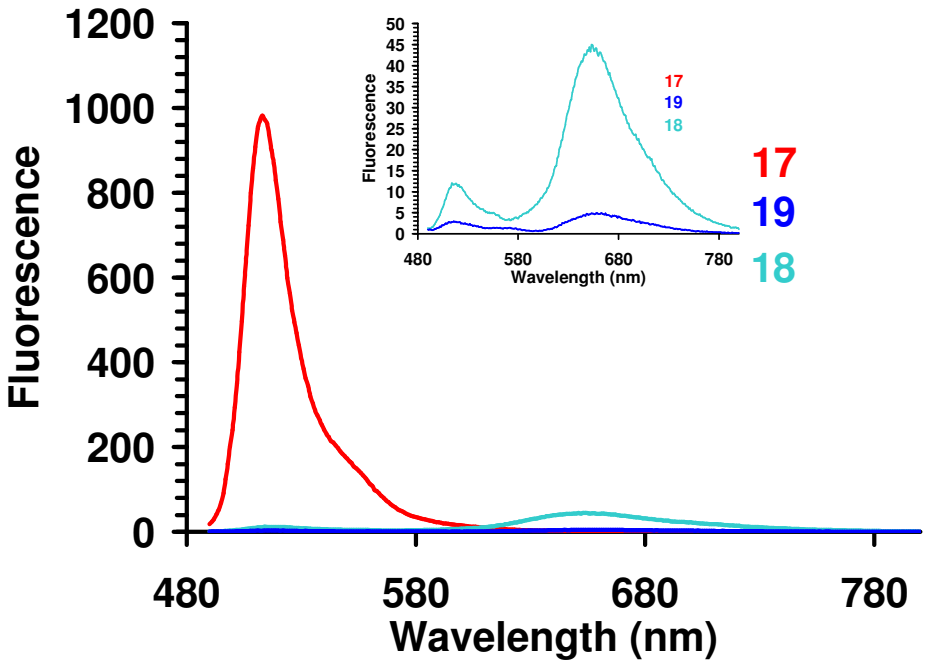


Figure 44: Energy transfer process in **19**. Compounds **17** and **18** are also showed for energy transfer.

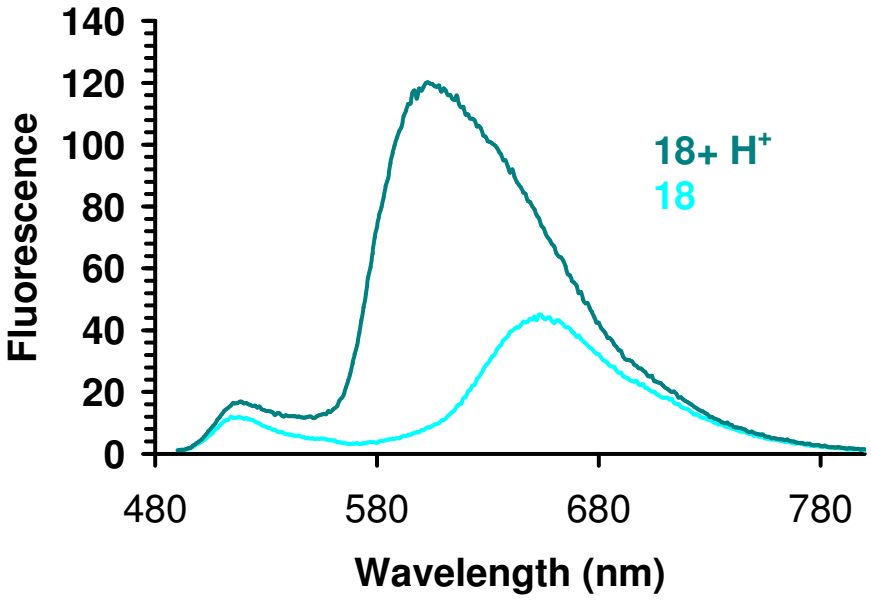


Figure 45: Emmision spectra of compound **18** and acidified compound **18**

CHAPTER 4

CONCLUSION

In this study we synthesized BODIPY dyes which were attached to a xanthane scaffold. Two BODIPY dyes were tethered to the xanthane molecule. Due to the rigidity of xanthene structures, these two BODIPY dyes were aligned themselves in a cofacial arrangement. This arrangement was proven by the NMR spectroscopy. These BODIPY dimers display an excimer formation, which can be observed from emission and absorption spectra.

When this BODIPY dimer has been condenstate the appropriate aldehydes its conjugation is extended. Two absorption peaks develop. One of them belongs to unmodified BODIPY and the other belongs to extended conjugation BODIPY. However there is one emmision band that belongs to extentend conjugation BODIPY. This shows the energy transfer in a very clear manner. However, in extended conjugation dimers due to increased vibrational modes and due to proximity of parts, the extended conjugation dimer, behave like extendended conjugation monomer.

Thus, efficient energy transfer, which is an early step in the photosynthesis process has been satisfactorily mimicked in a simple organic system. Next goal, is to be able to produce stable charge separated states to harvest the transferred energy in an useful device. Work to those ends, is in progress in our studies.

REFERENCES

[1] Yui, N., Kishida, A., and Yamaoka, T., *Supramolecular Design for Biological Applications (edited by Yui, N.)*, CRC Press LLC, New York, **2002**,

[2] Vögtle, F., *Supramolecular Chemistry*, Wiley, New York, **1991**,

[3] http://nobelprize.org/chemistry/laureates/1987/press.html. accessed on Agust 10 2006

[4] Lehn, J.M., *Supramolecular Chemistry*, VCH, Germany, **1995**,

[5] Balzani, V. and Scandola F., *Supramolecular Photochemistry*, Ellis Horwood, **1991**,

[6] Steed, J. W., Atwood, J. L., *Supramolecular Chemistry*, Wiley. **2000,**

[7] Davey, C. A. and Richmond, T.J., *PNAS,* **2002**, 11169

[8] Petersen, C. J., *J. Am. Chem. Soc.*, **1967**, 89, 2495

[9] Lehn, J. M., *Acc. Chem. Res.*, **1978**, 11, 49

[10] Weber, E., Vögtle, F., *Tetrahedron Lett*. **1975**, 2415

[11] Rudkevitch, D.M., *et. al*, *Angew. Chem. Int, Ed*., Engl., **1994**, 33, 467

[12] Chambron, J.C., Sauvage J.P., *Tetrahedron Lett*., **1986**, 27, 865

[13] Vögtle, F., *et al., Angew. Chem,* **1986***,* 98, 1119

[14] Grammenundi, S., *et al., J.Inclus.Phenon,* **1987**, 5, 695

[15] Stoddart *et al., Tetrahedron Lett.,* **1988**, 27, 1095

[16] Parker, Sybil P.(Editor), *Dictionary of Chemistry,* USA, McGraw-Hill Companies, **2003**,

[17] Ke, Bacon, *Photosynthesis Photobiochemistry and Photobiophysiscs*, Netherlands, Kluwer Academic Publishers, **2001**

[18] Förster, T., *Ann. Physik. (Leipzig)*, **1948**, *2,* 55–75

[19] Förster, T., *Mechanism of energy transfer in: Comprehensive Biochemistry Vol. 22*, New York Elsevier, **1967**, pp. 61–77

[20] Collings, F., Critchley C., *Artifical Photosynthesis From Basic Biology to Industrial Application*, GmbH, Wiley-CH, 2005

[21] Weber, K., Hockett, L., Creager, S. E., *J. Phys. Chem. B*, **1997,** 101, 8286

[26] http://nobelprize.org/nobel_prizes/chemistry/laureates/1988/index.html accesed on Agust 10 2006

[27] Mcdermott, *et. al*., *Nature*, **1995**, 374, 517

[28] Balzani V., Venturi M., Credi A., *Molecular Devices and Machines A journey into the Nanoworld*, Wiley- VCH, Mörlenbach, 2003, pp 97-98

[29] Haper, D., P., Tevini, M., *General Photobiology*, Pergamon, Oxford, **1987**

[30] Pullerits, T., Sundström V., *Acc. Chem. Resc*., **1996**, 29, 381

[31] Karrash, S., Bullough, P.A., *EMBO J*., **1995**, 14, 631

[32] Kühlbrandt , W., Wang, D.N., Fujıyoshi, Y., *Nature*, **1994**, 367, 517

[33] Prathapan, S., Johnson, T.E., Lindsey, J.S., *J. Am. Chem.Soc.*, **1993**, 115, 7519

[34] (a) Prodi, A., Indelli, M. C., Kleverlaan, C.J., Scandola, F., Alessio, E., *Chem. Eur. J.,* **1999**, 5, 2668. (b)Alessio, E., Geremia, S., Mestroni, S., Giangerrara, T., Slouf, M., Prodi, A*., Inorg. Chem*., **1999**, 38, 2557. (c) Prodi, A., Indelli, M.T., Kleverlaanö C.J., Alessio, E., Scandola, F., *Coord. Chem. Rev.*, **2002**, 229, 48.

[35] Berberan-Santos, M.N., Canceill, J., Brochan, J.C., Jullien, L., Lehn, J.M., Pouget, J., Tauc, P., *J. Am. Chem. Soc*., **1992**, 114, 6427

[36] Berberan-Santos, M.N., Pouget, J., Valeur, B., Canceill, J., Jullien, L., Lehn, J.M., *J.Phys.Chem*., **1993**, 97, 11376

[37] Berberan-Santos, M.N, Canceill, J., Gratton, E., Julien. L., Lehn, J.M, So, J., Sutin, J., Valeur, B., *J.Phys. Chem*., **1996**, 100, 15.

[38] Berberan-Santos, M.N, Choppinnet, P., Fedorov, A., Jullien, L., Valeur, B., *J. Am. Chem. Soc.*, **1999**, 121, 2526

[39] Jullien, L., Canceill, J., Valeur, B., Bardez, E., Lefevre, P., Lehn, J. M., Marchi-Artzner, V., Pansu, R., *J.Am. Chem. Soc.*, **1996**, 118, 5432

[40] Konishi, T. Ikeda, A., Asai, M., Hatano, T., Shinkai, S., Fujitsuka, M., Ito, O., Tsuchiya, Y., Kikuchi, J.-i. *J. Phys. Chem. B.,* **2003**, 107, 11261

[41] Faiz, J. A., Williams, R. M., Silva, M. J. J. P., De Cola, L., Pikramenou, Z. *J. Am. Chem. Soc.,* **2006**, 128, 4520

[42] Ghaddar, T.H., Wishart, J.F., Thompson, D.W., Whitesell, J.K., Fox, M.A., *J. Am. Chem. Soc.*, **2002**, 124, 8285.

[43] Campagna, S., Serroni, S., Puntoriero, F., Loiseau, F., De Cola, L., Kleverlaan, C.J., Becher, J., *Chem. Eur. J.*, **2002**, 8, 4461

[44] Ceroni, P., Vicinelli, V., Maestri, M., Balzani V., Müller, W.M., Müller, U., Hahn, U., Osswald F., Vögtle, F., *New J. Chem*, **2001**, 25, 989

[45] Steward, G.M., Fox, M.A., *J. Am. Chem. Soc.,* **1996**, 118, 4354

[46] Köhn, F., Hofkens, J., Wiesler, U.M., Cotlet, M, Van Der Auweraer, M, Mullen, K., De Schryver, F.C., *Chem, Eur. J*., **2001**, 7, 4126

[47] Rodlert, M., Vestberg, R., Malmström, E., Perrson, M., Lindgren, M., *Synthetic Metals*., **2002**, 127, 37

[48] Yilmaz, M. D., Bozdemir, O. A., Akkaya, E. U. *Org. Lett*., 2006, 8, 2871

[49] Vicinelli, V., Ceroni, P., Maestri, M., Balzani, V., Gorka, M., Vögtle, F., *J. Am. Chem., Soc.,* **2002**, 124, 6461

[50] Schenning, A.P.H.J., Peeters, E., Mejier, E.W., *J.Am. Chem. Soc*., **2000**, 122

[51] Calzaferri, G., Pauchard, M., Maas, H., Huber, S., Khatyr, A., Schaafsma, T., *J. Mater., Chem.*, **2002**, 12

[52] Iijima, T., Vignon, S.A., Tseng, H. R., Balzani, V., Stoddart, J.F., *Chem. Eur. J.*, **2004**, 10, 6375

[53] Tamura, M., Gao, D., Ueno, A., *Chem, Eur., J.*, **2001**, 7,1390

[54] Haque, S.A., Park, J.S., Srinivasarao, M, Durrant, J.R. *Adv. Mater*, **2004**, 16, 1177

[55] Li, K., Schuster, D. I., Guldi, D. M., Herranz, M. A., Echegoyen, L. *J. Am. Chem. Soc.*, **2004**, 126, 3388

[56] Hiratani, K., Kaneyama, M., Nagawa, Y. Koyama, E., Kanesato, M. *J. Am. Chem. Soc.*, **2004**, 126, 13568

[57] Schuster, D. I., Li, K., Guldi, D. M., Ramey, J., *Org. Lett.*, **2004**, 6, 1919

[58] Sandanayaka, A. S. D., Watanabe, N., Ikeshita, K-I., Araki, Y., Kihara, N., Furusho, Y., Ito, O., Takata, T. J. *Phys. Chem. B.,***2005**, 109, 2516

[59] Li, Y., Li, H., Li, Y., Liu, H., Wang, S., He, X., Wang, N.,Zhu, D., *Org. Lett*., **2005**, 7, 4835

[60] Kwan, P. H., Swager, T. M., *J. Am. Chem. Soc*., **2005**, 127, 5902

[61] Haugland, R.P., *Handbook of Flourescent Probes and Research Products*, Molecular Probes, 9th ed., Eugene OR, **2003**.

[62] Yee, M., Fas, S.C., Stohlmeyer, M.M., Wandless, T.J., Cimphrich, K.A., *J. Biol. Chem.*, **2005**, 280, 29053

[63] Tan, K., Jaquinod, L., Paolesse, R., Nardis, S., Di Natale, C., Di Carlo, A., Prodi, L., Montalti, M., Zaccheroni, N., Smith, K. M., *Tetrahedron*, **2004**, 60, 1099.

[64] Turfan, B., Akkaya, E. U., *Org. Lett*., **2002**, 4, 2857.

[65] Ulrich, G., Ziessel, R. J., *Org. Chem.,* **2004**, 69, 2070.

[66] Gabe, Y.; Urano, Y.; Kikuchi, K.; Kojima, H.; Nagano, T. J. Am. Chem. Soc. 2004, 126, 3357–3367.

[67] Rurack, K., Kollmannsberger, M., Resch-Genger, U., Daub, J., *J. Am. Chem. Soc.,* **2000**, 122, 968–969.

[68] Coskun, A., Baytekin, B. T., Akkaya, E. U., *Tetrahedron Lett*., **2003**, 44,5649

[70] Coskun, A., Akkaya, E. U., *Tetrahedron Lett*., **2004**, 45, 4947

[71] Coskun, A., Akkaya, E. U.*, J. Am. Chem. Soc*., **2005**, 127, 10464

[72] Burghart, A., Thoresen, L. H., Chen, J., Burgess, K., Bergström, F., Johansson, L.B.-A° , *Chem. Commun.*, **2000**, 2203

[73] Wan, C.-W., Burghart, A., Chen, J., Bergström, F., Johansson, L.B.-A° ., Wolford, M. F., Kim, T. G.; Topp, M. R., Hochstrasser, R. M., Burgess, K. *Chem. Eur. J*., **2003**, 9, 4430

[74] Ulrich, G., Goze, C., Guardigli, M., Roda, A., Ziessel, R., *Angew. Chem., Int. Ed.*, **2005**, 44, 3694

[75] Maas, H., Calzaferri, G., *Angew. Chem.*, *Int. Ed.*, **2002**, 41,2284

[76] Grummit, O., Buck, A. *Organic Syntheses*, CV 3, 195.

[77] Haugland, R.P., Kang, H.C., (Molecular Probes, Inc.).

[78] Bergström, F., Mikhalyovö M., Hagglöf, P., Wortmann, R., Ny, T., Johansson, L. B.A., *J. Am. Chem. Soc.*, **2002**, 124, 196

APPENDIX

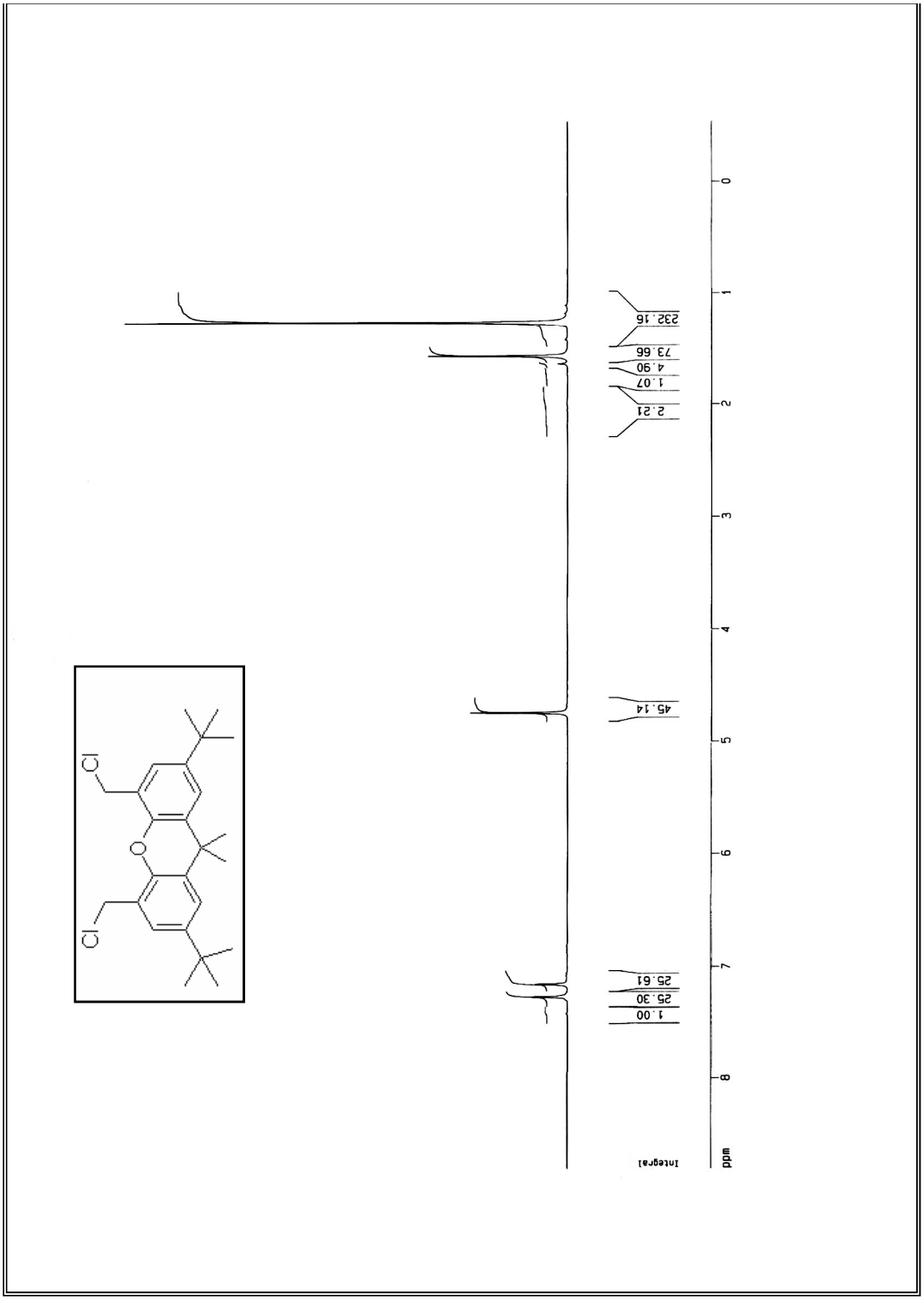


Figure 46: ^{1}H spectrum of compound **13**

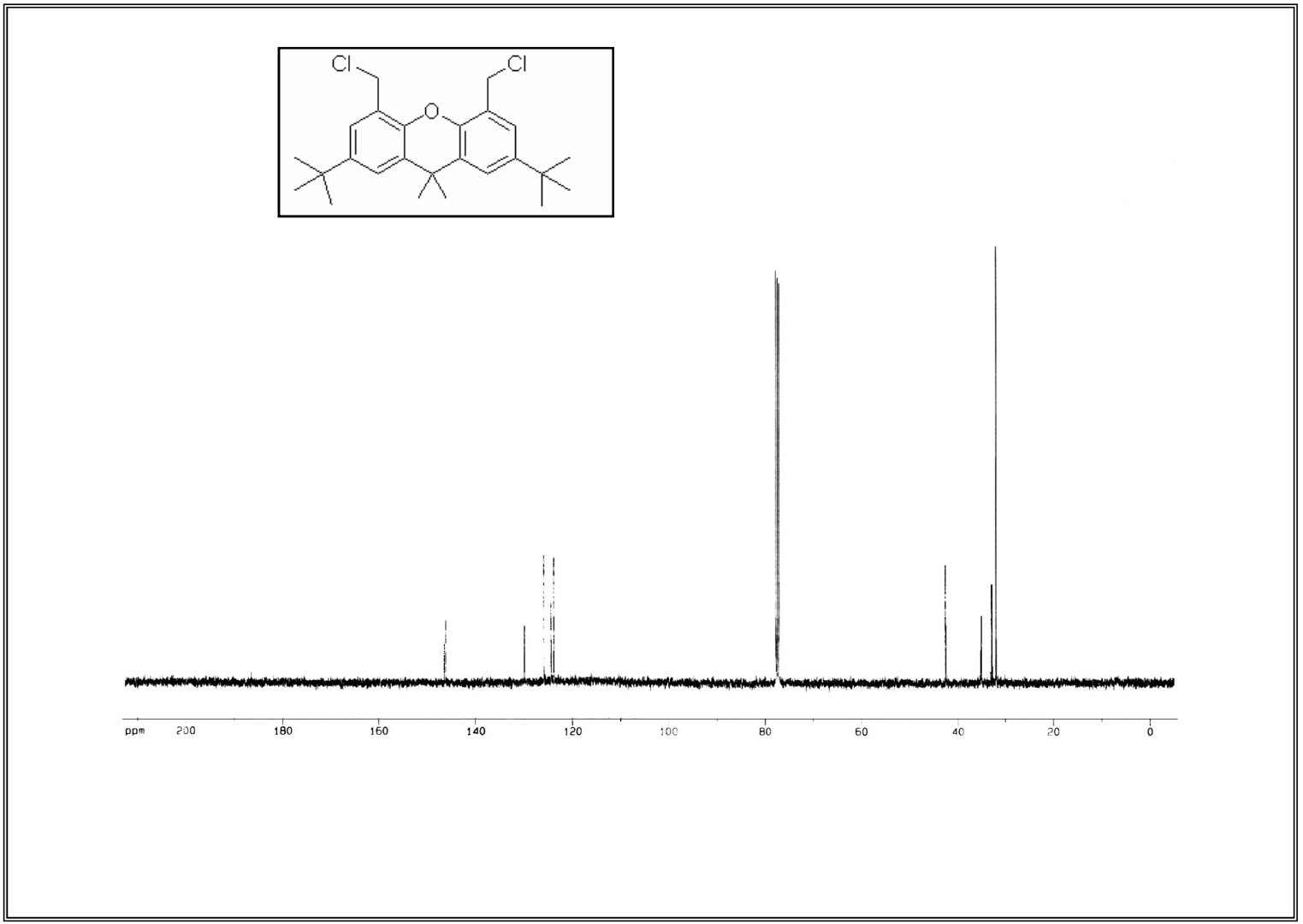


Figure 47: ^{13}C spectrum of compound **13**

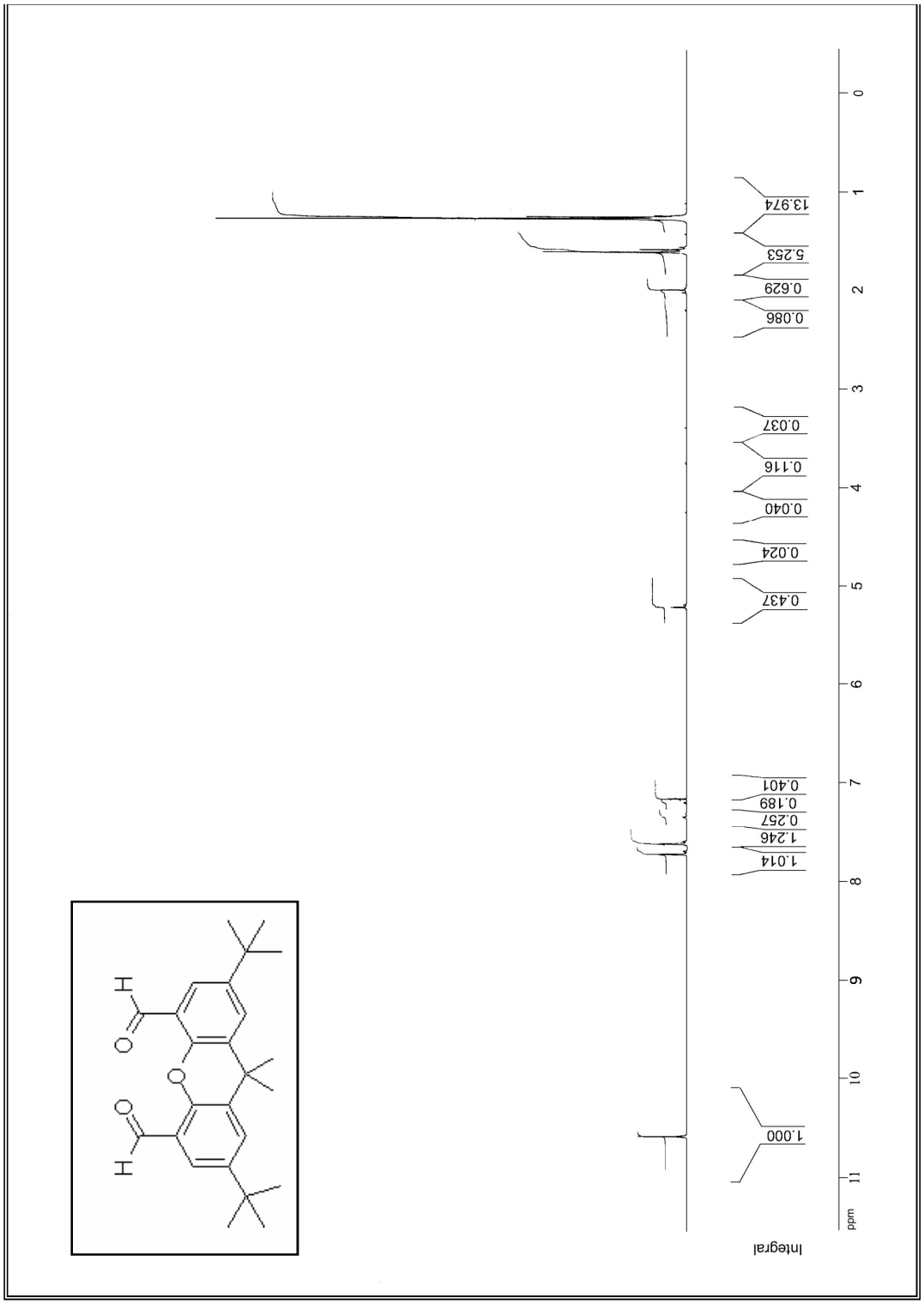


Figure 48: ^{1}H spectrum of compound **14**

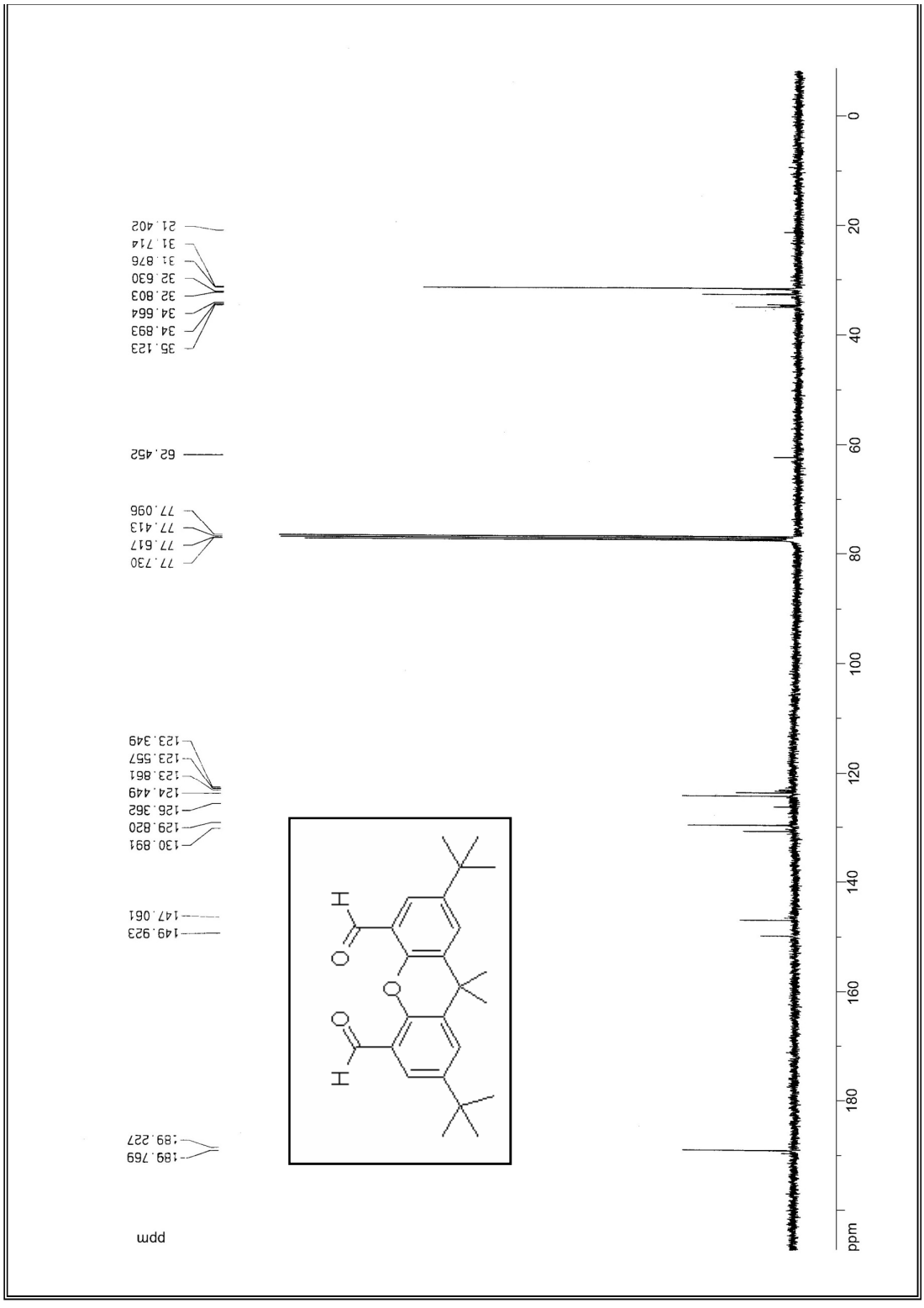


Figure 49: ^{13}C spectrum of compound **14**

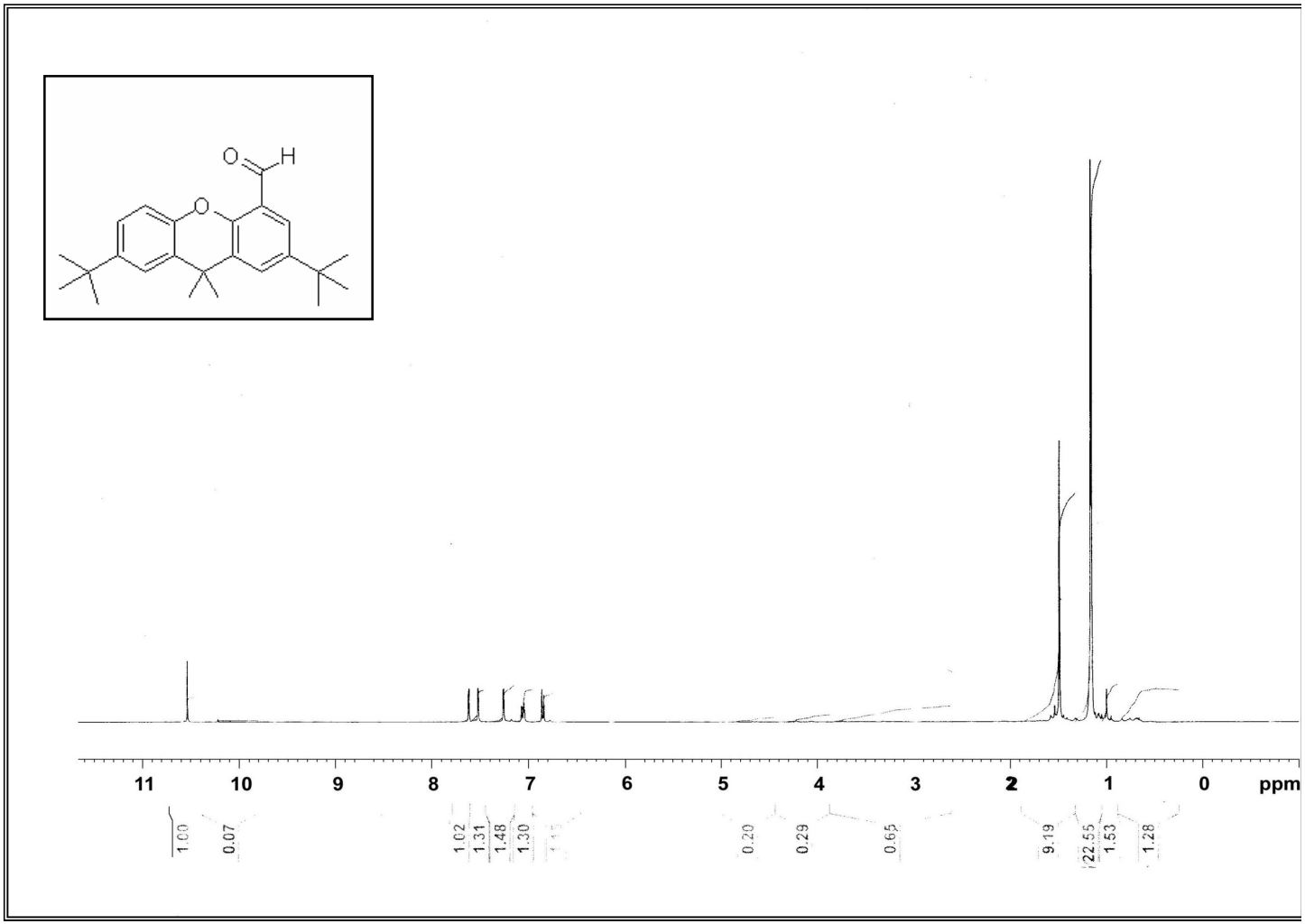


Figure 50: ^{1}H spectrum of compound **15**

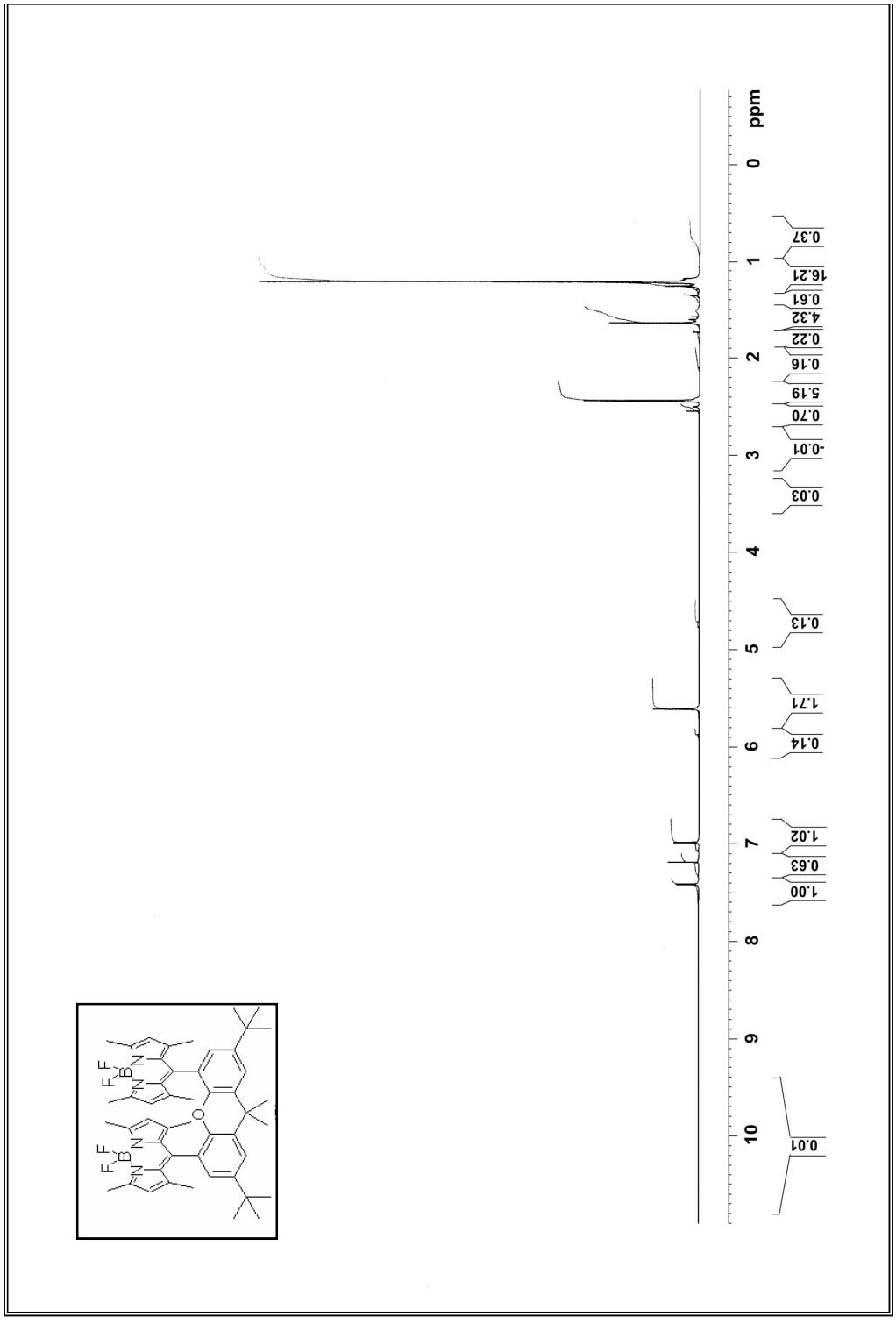


Figure 51: ^{1}H spectrum of compound **16**

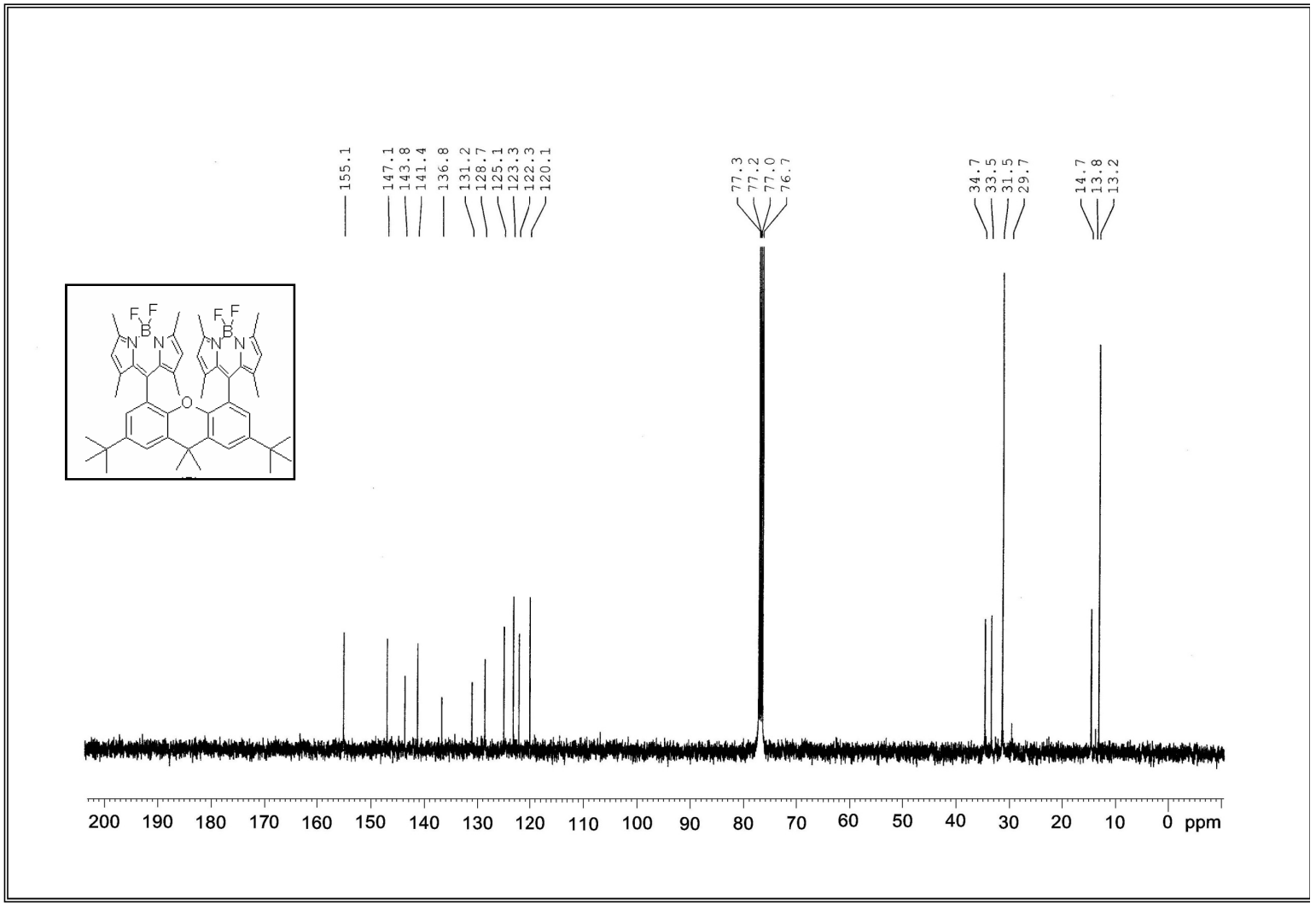


Figure 52: ^{13}C spectrum of compound **16**

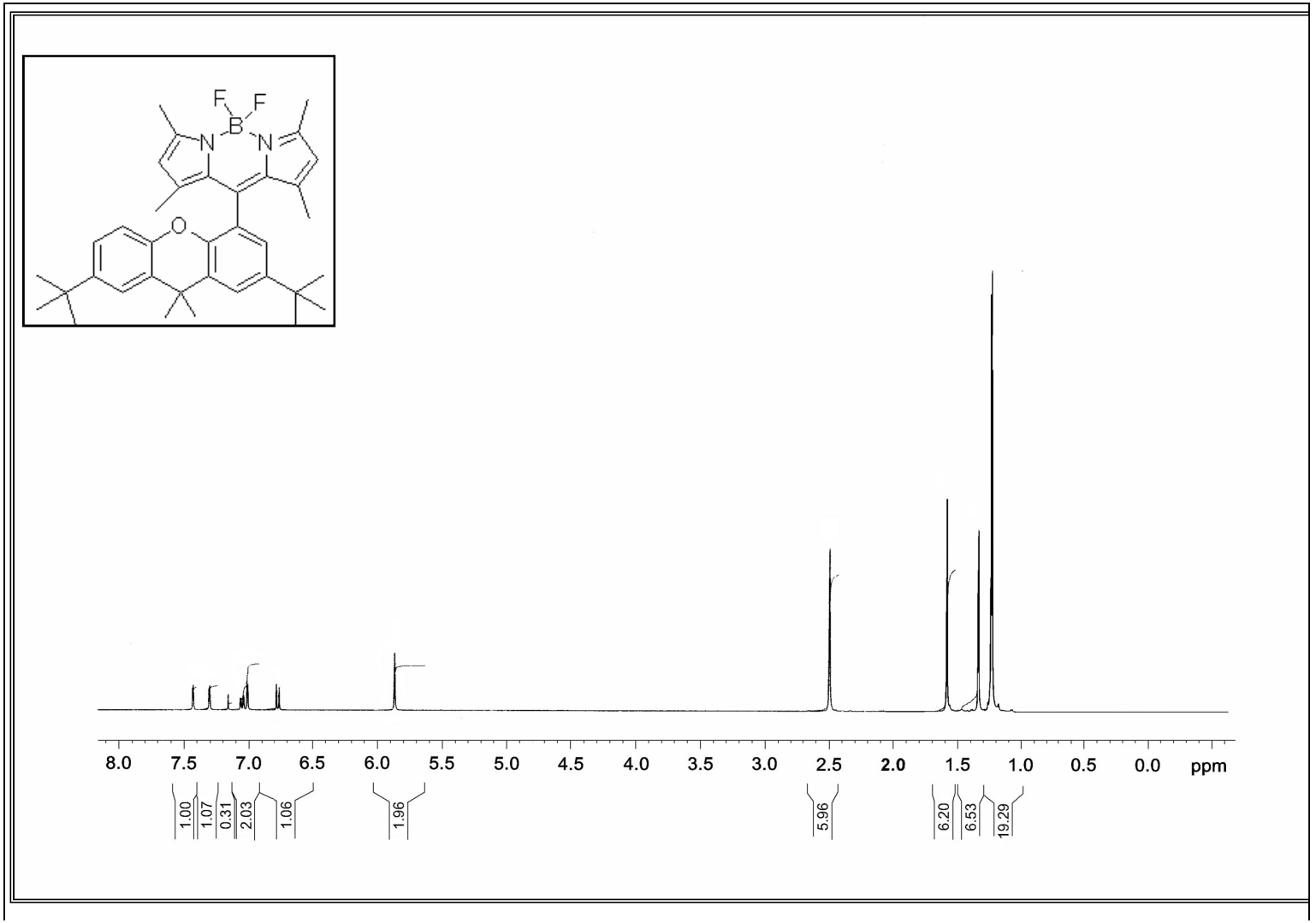


Figure 53: ^{1}H spectrum of compound **17**

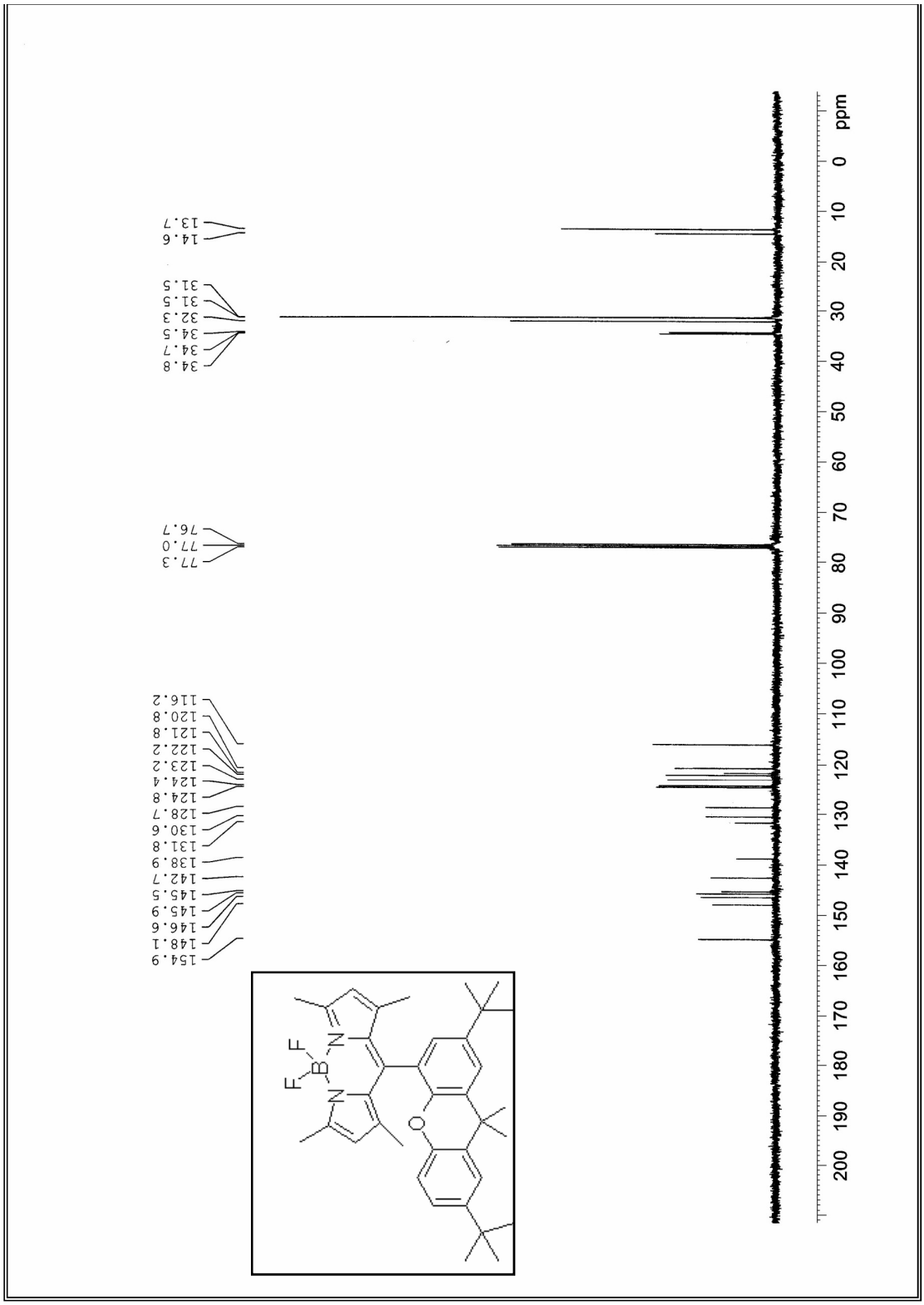


Figure 54: ^{13}C spectrum of compound **17**

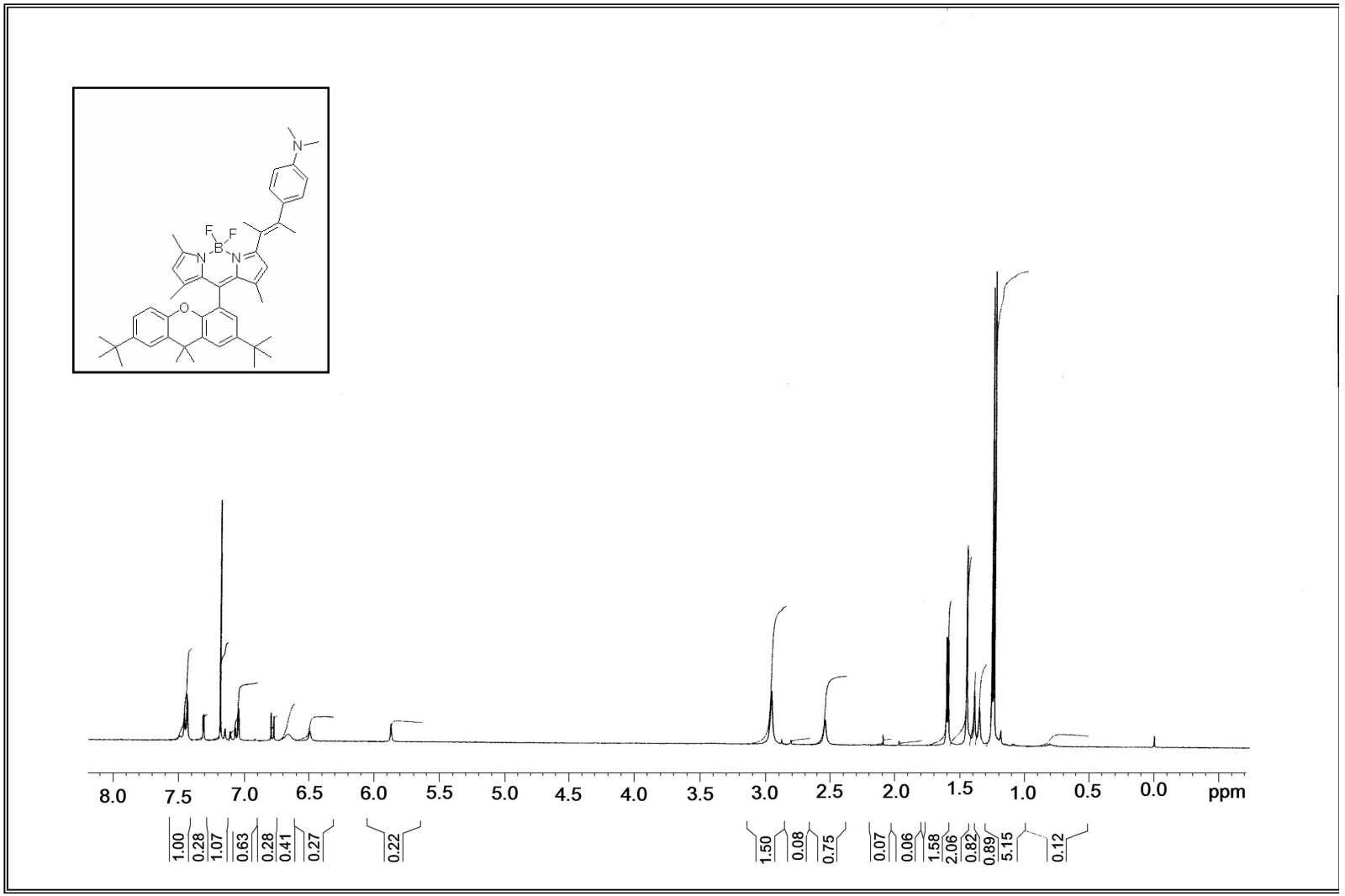


Figure 55: ^{1}H spectrum of compound **19**

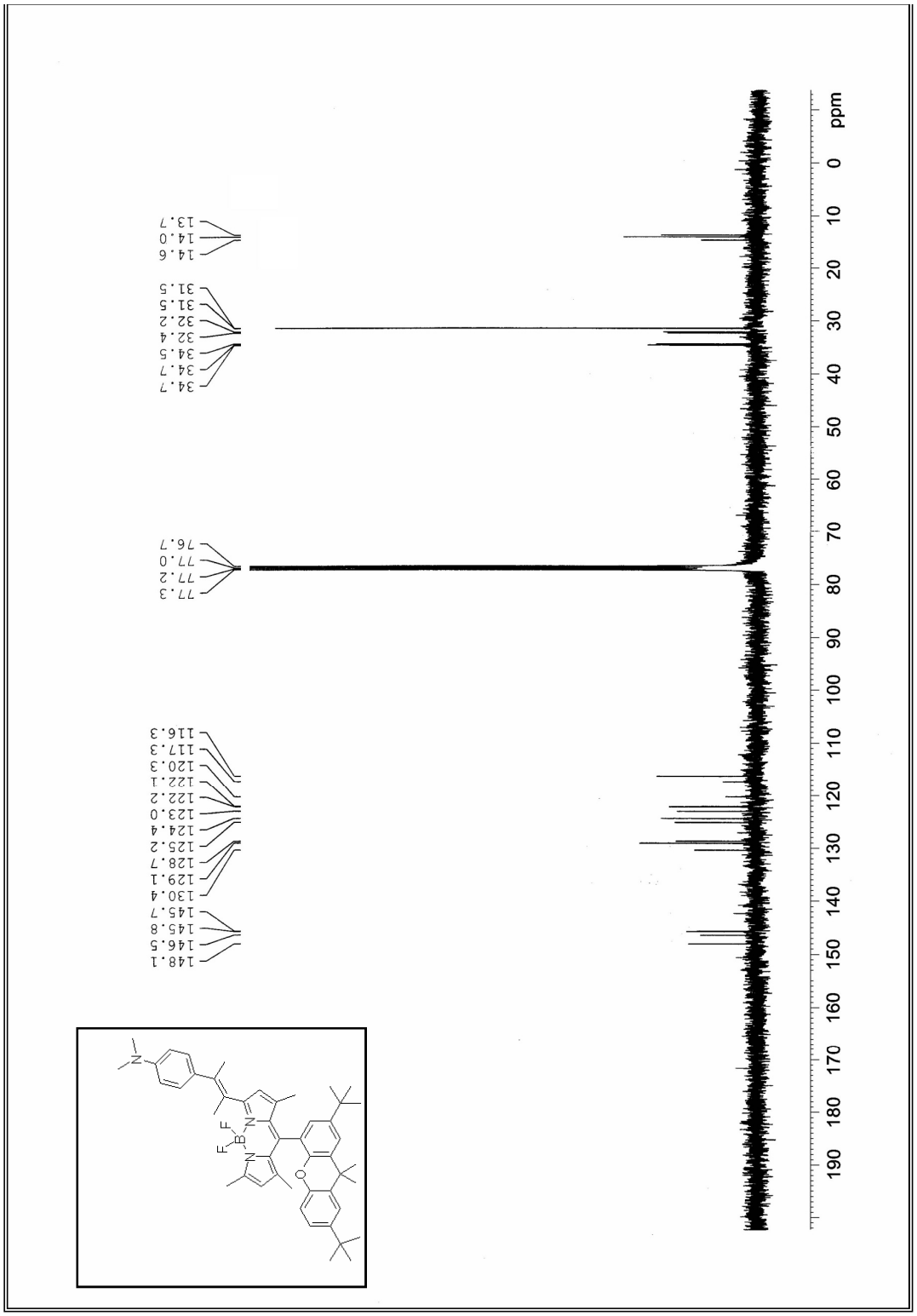


Figure 56: ^{13}C spectrum of compound **19**

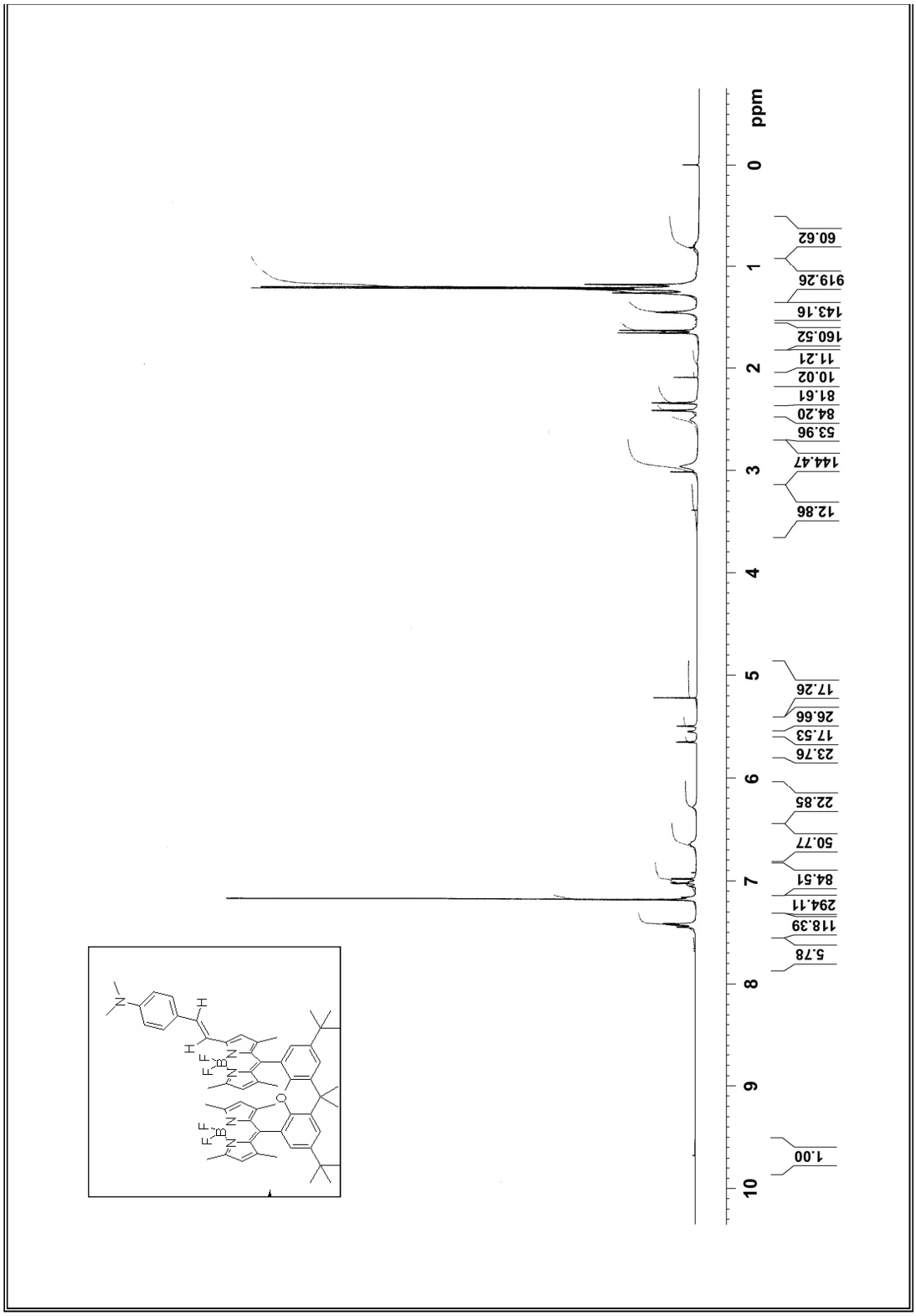


Figure 57: ^{1}H spectrum of compound **18**

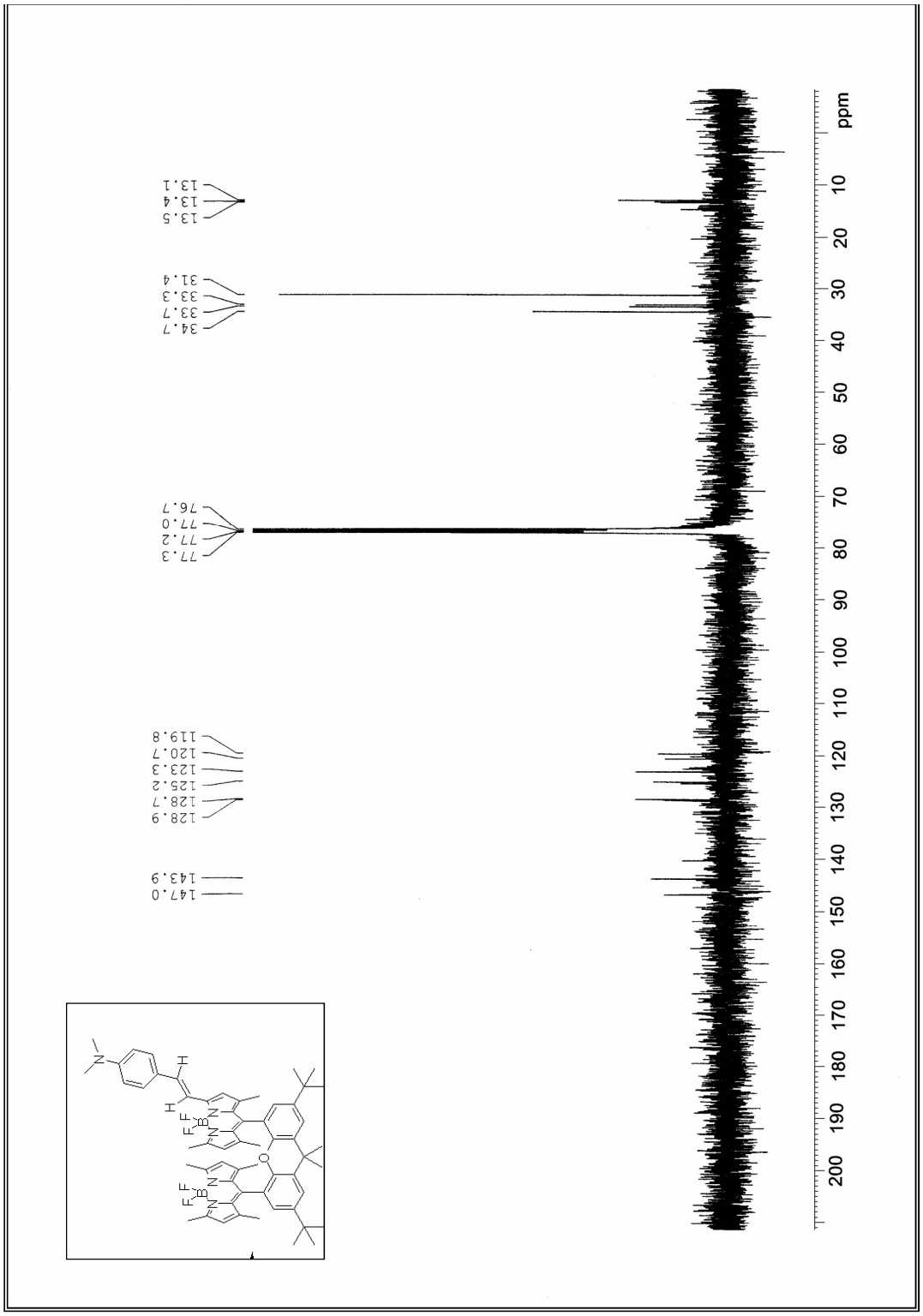


Figure 58: ^{13}C spectrum of compound **18**

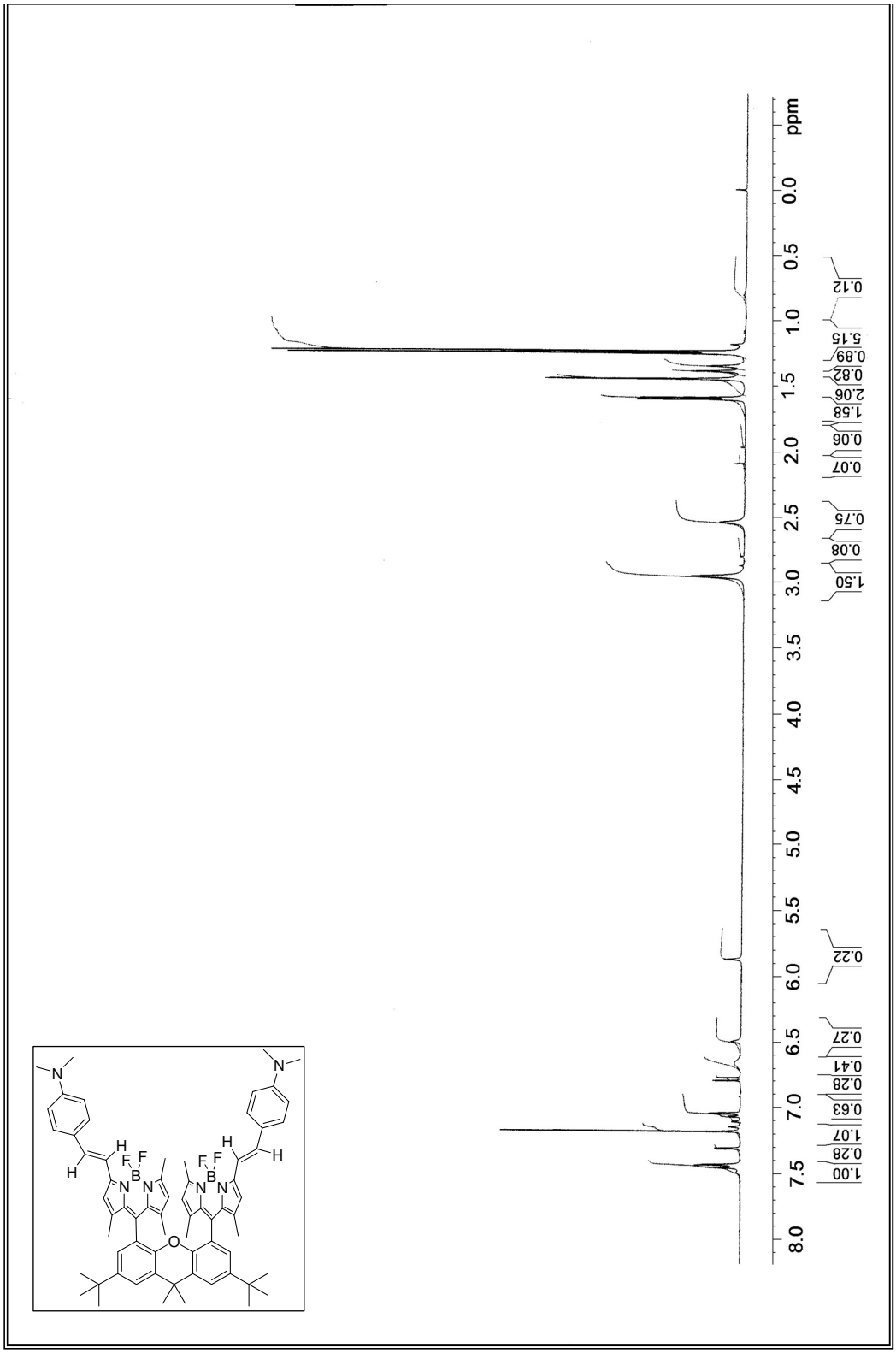


Figure 59: ^{1}H spectrum of compound **20**

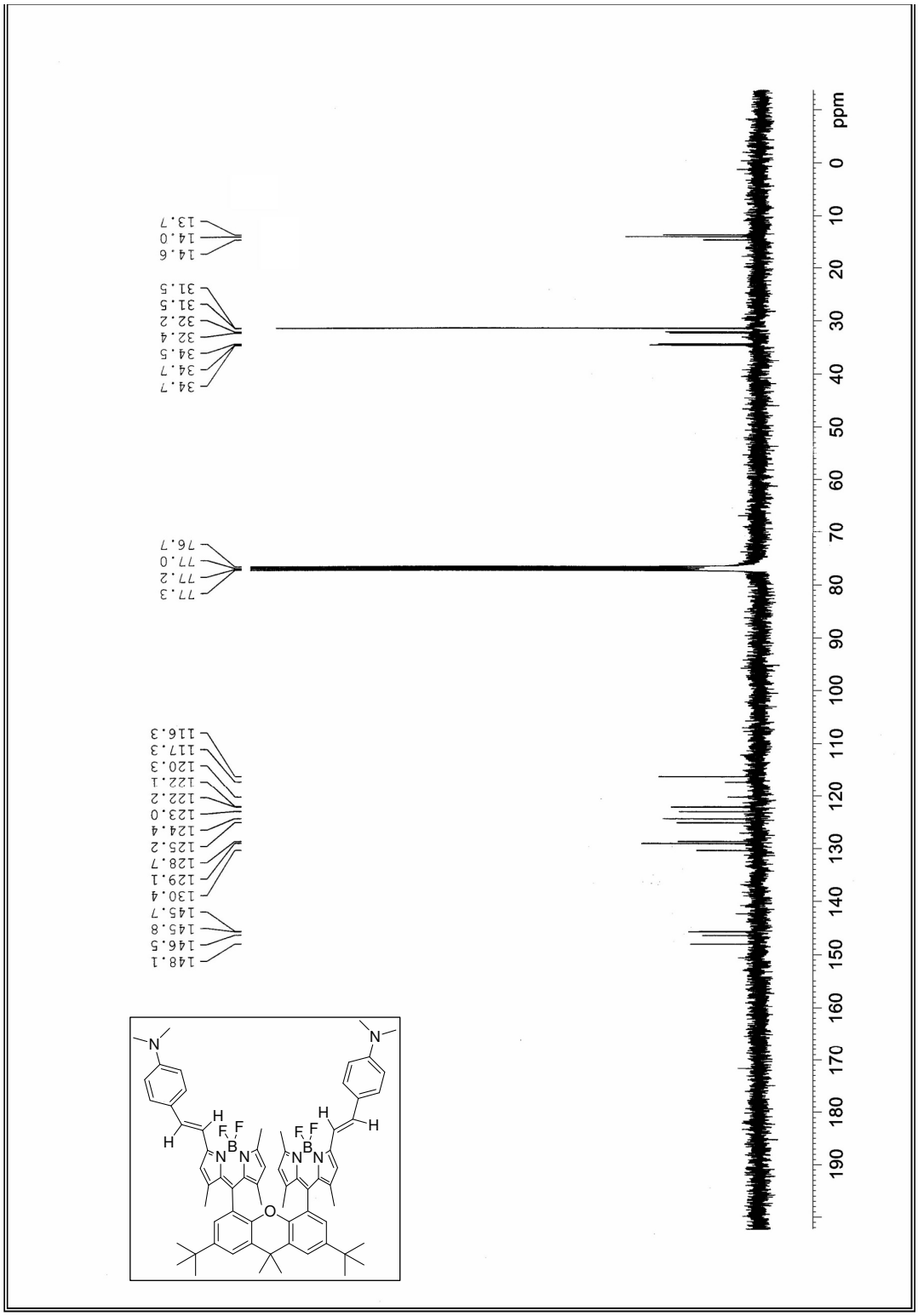


Figure 60: ^{13}C spectrum of compound **20**