PHENYLETHYNYL-BODIPY OLIGOMERS: BRIGHT DYES AND FLUORESCENT BUILDING BLOCKS

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PHENYLETHYNYL-BODIPY OLIGOMERS: BRIGHT DYES AND FLUORESCENT BUILDING BLOCKS

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ABSTRACT

PHENYLETHYNYL-BODIPY OLIGOMERS: BRIGHT DYES AND FLUORESCENT BUILDING BLOCKS

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Supramolecular chemistry is an emerging field of chemistry which has attracted much attention in recent years as a result of its broad applicability in many areas. Thus, the design of functional supramolecular systems is strongly in demand in this field. For this purpose, we have developed novel phenylethynyl-BODIPY oligomer series which have absorption and emission maxima at the red part of the visible region of electromagnetic spectrum. Careful design to assemble the decyl groups to the system allowed us to dissolve the molecules in organic solvents easily. That`s why, not only we could characterize the molecules, but also spectroscopic and photopysical properties of them were investigated. As expected, as the number of repeating units "n" increase, peak absorption and emission wavelengths are shifted to the red end of the visible spectrum, with smaller increments as "n" increases. Consequently, these rigid rod like overall arrangement of oligomers could lead to applications as functional building blocks.

Keywords: Supramolecular chemistry, boradiazaindacene, oligomer, building block, fluorescent

ÖZ

FENİLETİNİL-BODIPY OLIGOMERLERİ: PARLAK BOYAR MADDELER VE FLORESAN YAPI BLOKLARI

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Supramoleküler kimya, kimyanın hızla gelişmekte olan dallarından birisidir ve bir çok alanda geniş uygulanabilirliği nedeniyle son yıllarda çok fazla ilgi çekmektedir. Sonuçta, bu konudaki işlevsel supramoleküler sistemlerin tasarımı çok güçlü bir şekilde talep edilmektedir. Bu amaçla elektromanyetik tayfın görünür bölgesinin kırmızı kısmında soğurum ve emisyon tepe noktaları olan yeni feniletinil-BODIPY oligomer dizileri geliştirdik. Sisteme desil gruplarini dikkatli bir şekilde yerleştirmek, molekülleri organik çözücüler içinde rahatça çözebilmemizi sağladı. Bu şekilde, sadece moleküllerin yapısını aydınlatmakla kalmadık, aynı zamanda onların spektroskopik ve fotofiziksel özelliklerini de inceledik. Beklendiği üzere, tekrarlayan "n" birimlerinin sayısı arttıkça, soğurum ve emisyon dalgaboyu tepe noktaları, "n"in artmasıyla daha küçük ölçekler halinde, tayfın görünür bölgesinin kırmızı tarafına kaydı. Sonuç olarak, genel görünümü çubuk şeklinde olan bu oligomerler işlevsel yapı blokları olarak uygulamalara öncülük edebilirler.

Anahtar kelimeler: Supramoleküler kimya, boradiazaindasen, oligomer, yapı bloğu, floresan

Dedicated to my family and close friends…

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TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF SCHEMES

SCHEMES

LIST OF FIGURES

FIGURES

LIST OF ABBREVIATIONS

BODIPY, BDP: Boradiazaindacene

THF: Tetrahydrofuran

TLC: Thin Layer Chromotography

PDT: Photodynamic Therapy

NIR: Near Infrared

NMP: N-methylpyrrolidone

OPE: Oligo(1,4-phenyleneethynylene)

OPV: Oligo(1,4-phenylenevinylene)

CHAPTER 1

INTRODUCTION

1.1. BODIPY® Chemistry

1.1.1. General properties of BODIPY Dyes

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (hereafter abbreviated to BODIPY) dyes were first discovered in 1968 by Treibs and Kreuzer.[1] These dyes have been used much and became popular in recent three decades because it has many good properties. Hence, now many research groups design new projects based on this small molecule and synthesize different types of it by changing its core. One of their most important characteristics is that they are strongly UV (ultra violet) absorbing molecules and they emit radiation with high quantum yields, in addition they have sharp fluorescence peaks.

Another property of this molecule is that it is relatively insensitive to polarity and pH of their environment which means that its absorption and emission characteristics do not change much by changing the solvent. Also they are stable to physiological conditions. Furthermore, their fluorescence characteristics can be tuned by small modifications. These properties make it available to label proteins[2] and DNA[3]. However, there are some undesirable properties of these compounds for many applications in biotechnology. Some of these properties are; most of them emit at less than 600 nm and a small number of them are soluble in water. Thus, there are different ways to modify the BODIPY framework which will lead to use them more effectively for imaging in living cells and whole organisms.

The IUPAC numbering system of BODIPY and dipyrromethene are different which sometimes lead to confusion. But α, β and meso terms are used to indicate the same positions (Figure 1).

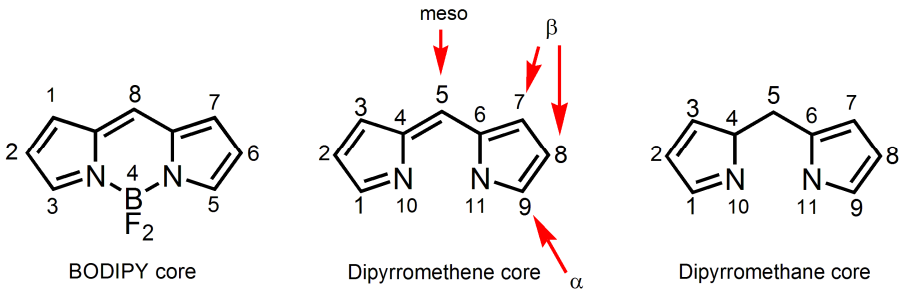


Figure 1. Numbering System of BODIPY, dipyrromethene and dipyrromethane

The BODIPY **1** molecule which has no substituents has not been synthesized because of synthetic difficulties. None of the pyrrole-based carbons are blocked from electrophilic attack. One step before the BODIPY **1** molecule has been done but it is too unstable and decomposes above -30 °C.[4] The symmetrical dimethyl substituted BODIPY **2**[5] and unsymmetrical dimethyl substituted BODIPYs **3** and **4** molecules have been synthesized (Figure 2). However, the most common BODIPY types which are used and synthesized including our group are the tetra and hexa substituted BODIPY molecules **5** and **6**. After investigating these molecules it is seen that there are relatively minor differences according to their UV absorption maxima, fluorescence emission maxima and quantum yields of these compounds. Although, it is a fact that some small calibration errors could be done while measuring these spectroscopic properties, it is observed that as the substitution around the BODIPY molecule increases, UV absorption maxima and fluorescence emission maxima shift to the longer wavelengths.

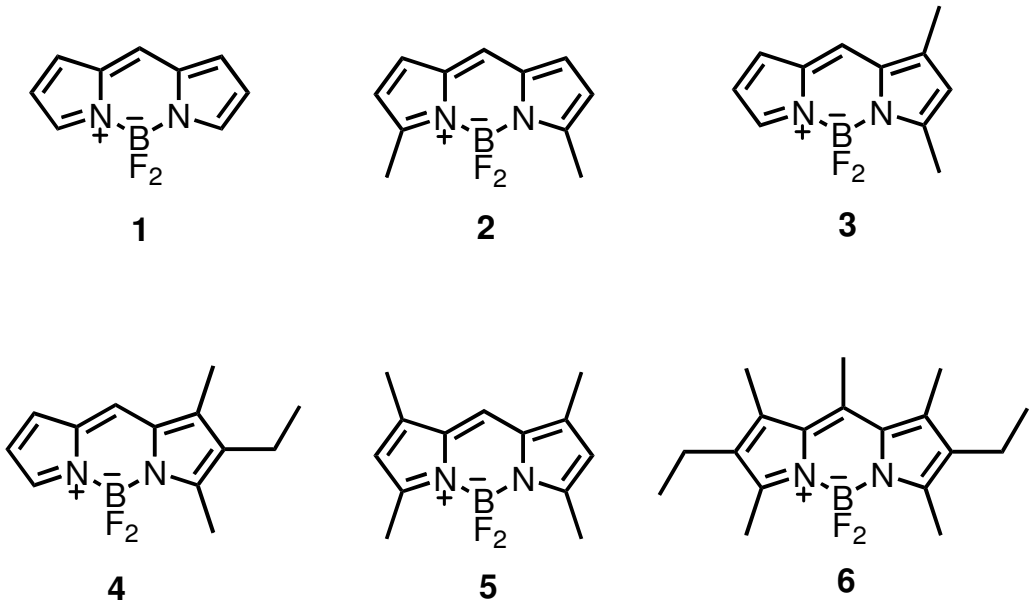


Figure 2. Different BODIPY core derivatives

From the view of absorption and emission wavelengths there are no differences between alkylation and arylation of *meso* position of the BODIPY (**7** with **8**, and **9** with **10**) (Figure 3). However, when comparing the molecules **8** and **10** it is seen that their quantum yields are quite different. This is due to the free rotation of **8**`s phenyl which causes to loss of energy from excited state via non-irradiative process, while the free rotation of phenyl in molecule **10** was prevented by the methyl groups in 1, 7 positions.

Consistent with this, introduction of *ortho*-substituents on the phenyl ring has been observed to increase quantum yields, and similar explanations have been invoked.

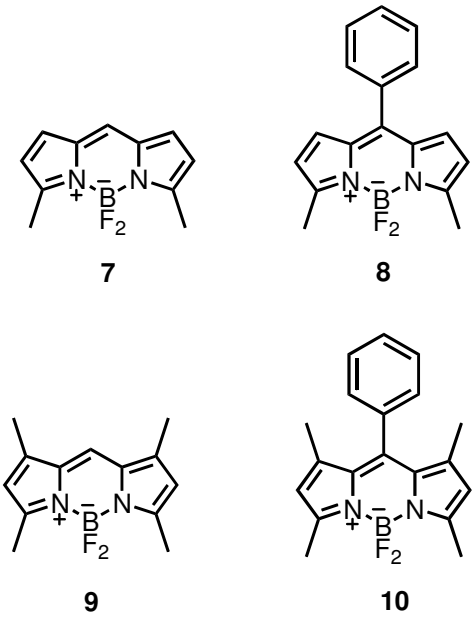


Figure 3. Comparison of 1,7-dimethyl substituted and unsubstituted BODIPYs

1.1.2. Halogenation of BODIPY

When considering the mesomeric structure of BODIPY molecule it is seen that the 2- and 6- positions bear the least positive charge, so they are open to electrophilic attacks (Figure 4).

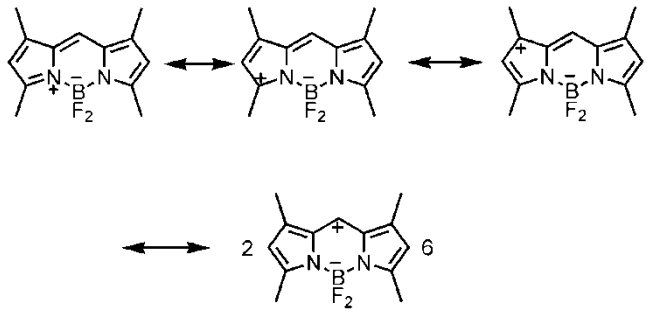
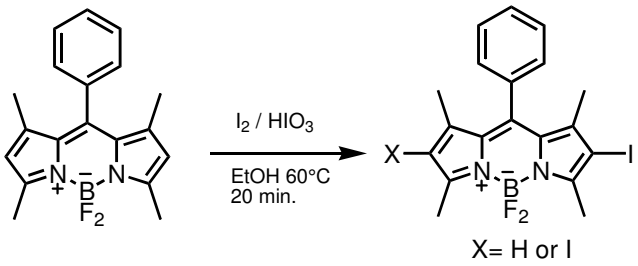


Figure 4. Available sites in a simple BODIPY core for electrophilic attacks

One of the electrophilic reactions applied to these positions are the addition of halogens. The examples of fluorine, chlorine, bromine and iodine exist in the literature. The important thing is that when a halogen atom is substituted, then that compound is available for metal catalyzed reactions like Sonogashira, Suzuki, Stille and so on.

Bromination of these 2- and 6- positions are made with both NBS in DMF and Br_2 in CH_2Cl_2 at room temperature.[6, 7] In these reactions the mono- product and di- product can be resulted by using appropriate equivalents of bromine source. When substituted with the bromine atoms a significant red shift occurs on the UV absorption and emission spectra, and the quantum yield is quenched because of the heavy atom effect.

Like bromination, iodination of the BODIPY core is also very easy. Also, mono and diiodinated products can be obtained. The iodinated products have red shifted absorption and fluorescence maxima and quenched quantum yields. There are two procedures of iodination from this position. The first way is iodination by using ICl in DMF[8] and the second route is iodination by I_2/HIO_3 in EtOH[9] (Scheme 1). Diiodinated BODIPY molecule was synthesized first by Nagano, and it was seen that it is more resistant to photobleaching than Rose Bengal; this is because the BODIPY molecule has a more positive oxidation potential than the xanthone unit of Rose Bengal. This molecule is an efficient photosensitizer which can be useful in photodynamic therapy.



Scheme 1. Mono- and di-iodination of BODIPY

The halogenation of the BODIPY is important for us because after that the molecule is available for metal catalyzed cross coupling reactions.

1.2. Red Visible and Near Infrared Dyes

1.2.1. General Properties

There is much current interest in the development of new infrared absorbing dyes for use as key materials in optoelectronics systems.[11] The development of the gallium-arsenic semiconductor laser, which emits laser light at 780-830 nm, enabled the development of new optoelectronic systems such as laser optical recording systems, thermal writing displays, and laser printing systems. Medical application systems in photodynamic therapy for the treatment of cancer were also recently developed with the use of lasers as light sources. In such systems, the infrared absorbing dyes are used as effective photo receivers for laser light.

Some cyanine infrared absorbing dyes have been known for some time to be useful in photochemistry, but their use was very restricted. Therefore, the developments of new types of infrared absorbing dyes have been anticipated as a source of functional materials for high technology applications. Hence, the chemistry and applications of infrared absorbing dyes will become one of the most interesting and important fields in the study of new dye chemistry. Infrared absorbing dyes are very new classes of dyes developed in the past decades.

In recent years, the focus of research on dye chemistry has largely changed from involvement in the traditional chemistry of dyes and pigments to investigation of special dyes for electro-optical applications. Perkin obtained the first commercial synthetic dye mauveine in 1856. After this time to knowledge regarding the development of new dyes has accumulated and many dyes have been synthesized.

Traditionally dyes have been used as coloring matters for polymer substrates such as textiles and plastics, whereas in high-technology applications, dyes are used as key materials which absorb light efficiently. Light sources used most of the time normally emit single wavelength light, like laser light or narrow wavelength light, like light produced by a halogen lamp. Laser lights have good properties such as their being highly monochromatic, very well collimated, and coherent, and in some cases, laser sources are extremely powerful. These properties make the laser lights a very useful light source for a variety of applications in science and industry. Special characteristics are required for high technology applications. Therefore, in order to develop these dyes it is important to know the relationship between the chemical structures of the dyes and characteristics such as their absorption spectra and absorptivity.[11]

In principle, dyes are highly versatile materials and can be used in many ways. Griffiths have summarized the exploitable properties of dye chromophores.[12] These properties are light absorption, light emission, light induced polarization, photoelectrical properties, and chemical and photochemical reactivities. He emphasized that most of these properties are related to the ability of the dyes to interact strongly with visible electromagnetic radiation, leading to such phenomena as color, fluorescence, and a variety of photochemical and photoelectrical processes.

Infrared absorbing dyes can be applied in the following areas: laser optical recording systems, laser printing systems, laser thermal writing displays, infrared photography, and medical or biological applications.[13]

In order to new infrared absorbing dyes, the structures of the dyes should be correlated to the characteristics of them. A new methodology was reported for the development of new special dyes.[14] This methodology consists of two parts: the route for the development of new special dyes and the four software schemes applied at each stage. There are many demands in the development of new dyes as the key materials for electro-optical applications, for example. Some basic chromophores which have suitable physical properties are selected, and properties such as λ_{max}, ε, melting point, and so on

are determined by the dye database.[15] The database contains information on some 6,000 dyes, and each entry gives the chemical name, dye number, λ_{max}, and ε values in several solvents, melting point, some other properties such as fluorescence, isomerisation, sublimation, and toxicology and also end uses in some cases together with original literature references.

After the selection of dye chromophores by using the database, the molecular design is looked for the molecular orbital (MO) calculation method.

The search for new fluorophores that absorb and emit in the red visible and/or near infrared (NIR) region of the spectrum is of continuing interest in many different fields of chemistry, ranging from optical spectroscopy-based sensing through imaging applications to materials chemistry related issues, such as molecular switches and devices, lasing media, or electrooptical applications.[16]

The spectral range between 650–900 nm, which is often called "optical window", has many advantages: significant reduction of the background signal due to the lowest autoabsorption and autofluorescence of biomolecules in the NIR region, low light scattering and deep penetration of the NIR light, and the possibility to use low-cost excitation light sources.Therefore, NIR fluorescent dyes with high performance enable the development of noninvasive and simple diagnosis techniques such as *in vivo* imaging and photodynamic therapy (PDT).[17]

Furthermore, Sunlight possesses around 50% of its intensity in the near-infrared (NIR) region that covers wavelengths from 700 to 2000 nm. Broadband infrared absorbers acting over this invisible spectral range are required for efficient heat-ray blocking. Another field of interest is energy conversion: NIR-absorbing dyes convert infrared radiation into heat to initiate thermally driven processes, such as laserwelding of polymers, flash fusion of toners and optical data storage. These processes are initiated by low power semiconductor lasers (emission at 780 and 830 nm) and high-power Nd:YAGlasers (1064 nm). Commercially available NIR dyes, such as polymethyne

dyes, possess low thermal and photostabilities that restrict their application in this field. A significant bathochromic shift can be obtained using strong donor–acceptor interactions in the molecule, or by the extending the p-system of the chromophores.[18]

In addition to the wavelength range of operation, the key requirements for fluorescent dyes to be suitably employable in such fields are efficiency, in terms of a high extinction coefficient, a high rate of conversion of absorbed photons into emitted photons, and versatility with respect to the dye`s synthesis as well as to its functionalization.[16]

A promising starting point for the construction of dyes showing intense and well-defined absorption bands in the red and/or NIR spectral range is the cyanine chromophore (Cy; Figure 5).[19] Cyanine dyes are also called polymethine dyes. Cyanine dyes are charged or neutral, usually heterosubstituted, p-conjugated compounds in which the chromophore extends over an odd number of unsaturated centers. As a consequence of this topological peculiarity, which restricts the perturbation of the p-electrons over the σ skeleton, the electronic absorption bands of polymethines are narrow and intense and can be shifted by proper choice of the chromophore and substituents from the UV/Vis into the infrared (IR) region, which makes them by far the most important class of organic dyes.[20]

However, whereas a vast number of cyanine dyes have been synthesized so far and absorption maxima up to 1500 nm have been realized,[21] the fluorescence quantum yield of cyanines does not generally exceed 0.50 (for certain di- or trimethines) and drops rapidly with a further decrease towards monomethines or with an increase in the chain length. This effect can be caused by various factors that are predominantly connected to the (multiple) flexible bonds of the molecules. For instance, twisting of single and/or double bonds can readily dissipate the excitation energy.[22] Other researchers identified the many vibrational degrees of freedom as a major nonradiative pathway for flexible and semiflexible cyanines.[23] Even for largely rigid or bridged cyanines, the remaining flexible bonds can still be an effective funnel for nonemissive deactivation. In analogy to rhodamine (Rh) chemistry (for the chemical structure, see Figure 5), only the complete fixation of the chromophoric system seems to guarantee an intrinsically high conversion

of the absorbed light into fluorescence emission.[24] However, the disadvantages here are the time consuming and often complex synthesis of fully rigid cyanines and, in the case of the rhodamines, that the remaining positions for functionalization at the chromophoric core are limited. Moreover, as positively charged ions, the solubility of rhodamines is generally restricted to highly polar solvents and, for any application, the presence of the dye`s counterion has to be taken into account.

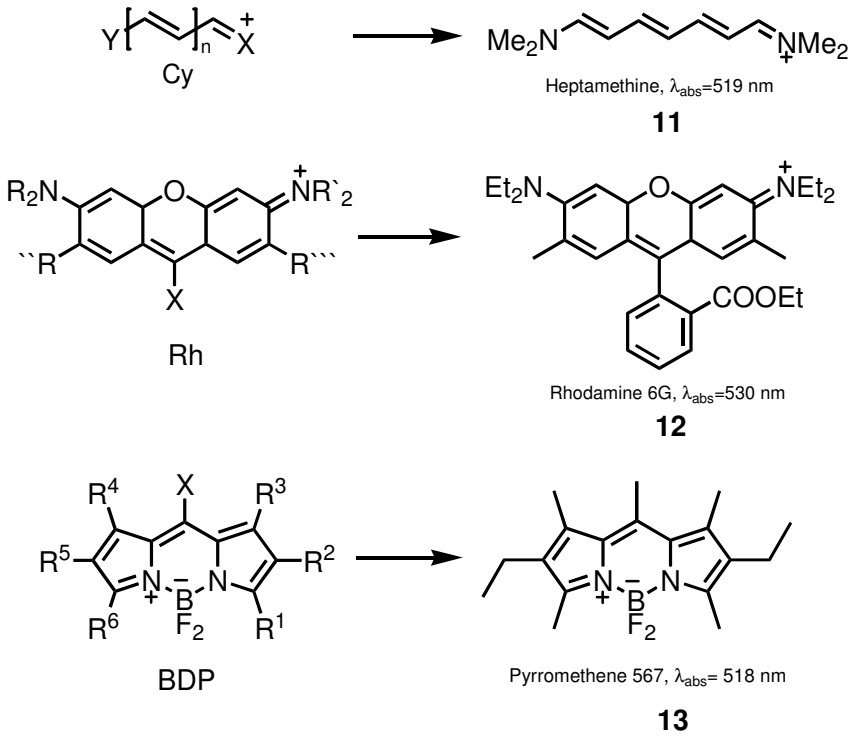
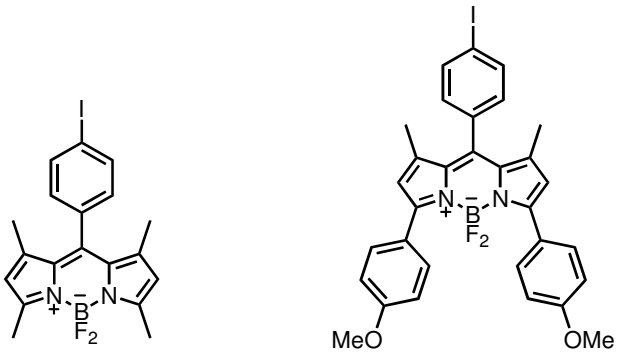


Figure 5. General structure of the cyanine (Cy), rhodamine (Rh), BODIPY (BDP) and representative examples in the right of the arrow. In the majority of actual examples, X and Y are heterocyclic or aromatic substitutents. For Rh, R to R''' are mostly short alkyl substituents or hydrogens. For BDP, the substituents R^n can vary from H to alkyl and other small functional groups, or to larger aryl moieties

1.2.2. BODIPY Based Red Visible and NIR Dyes

1.2.2.1. Substitution with Electron Donating Groups

An example to modulate the BODIPY core in order to absorb and fluoresce at longer wavelengths is a study conducted by the Burgess group.[30] Synthetic schemes that allowed for incorporation of variable substitution on the 3,5-diaryl units could afford a series of dyes with tunable fluorescent characteristics, and the added conjugation should shift their absorption maxima to longer wavelengths than the corresponding alkyl-substituted materials. In this study they synthesized five novel molecules. And all of these molecules have absorption maxima above 540 nm. In normal cases unsubstituted BODIPY molecules can absorb maximum at 528 nm. In addition, they have seen that if an electron donating group is substituted an extra shift to the red part of the absorbance spectrum. For example the molecule **15** has the absorption maxima peak at 585 nm because it has the 4-$MeOC_6H_4$ group directly attached to the BODIPY where methoxy group is an effective electron donating unit (Figure 6). However, in compound **14** that peak is at 504 nm since there are no substitution and no electron donating group (Figure 6).



λ_{abs}= 504 nm
λ_{ems}= 514 nm

14

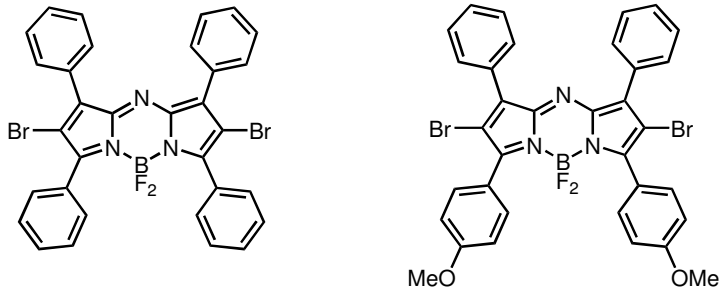
λ_{abs}= 585 nm
λ_{ems}= 629 nm

15

Figure 6. Electron donating group effect to the BODIPY

1.2.2.2. Replacement of Carbon Atom by a Nitrogen Atom

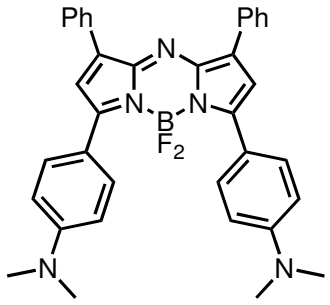
By exchanging the carbon atom at the meso position of BODIPY with a nitrogen atom has a significant effect by means of absorption, emission wavelengths and extinction coefficients. These molecules earned special attention in last years and it is the O`Shea group which first evaluated the important properties of these molecules. They named these molecules as BF_2 chelates of tetraarylazadipyrromethenes (after that named as Aza-BODIPY) and the aim of them is to use as a photodynamic therapy (PDT) reagent.[26] Although this group used this molecule, it was first synthesized in the 1940`s, but the important characteristics were not been studied.[27] The reason of using Aza-BODIPY in this area is because of the limited wavelength range of in vivo usage (650-800 nm). Otherwise other molecules in the body which absorb at lower wavelengths interfere with the light which is used in PDT applications. This can be understood more easily by considering the working principle of PDT, which is as follows: a photosensitiser (in this case Aza-BODIPY) is introduced to the body within tumour. Then the tumour is irradiated with a low energy light. The photosensitiser absorbs the light and energy absorbed is transferred to surrounding biological tissue through singlet oxygen, which results in oxidative cellular damage.[25] The spectroscopic properties of **16** in chloroform indicate that it has a sharp absorption peak at 650 nm and an extinction coefficient of 79000 (Figure 7). By introducing electron donating methoxy groups they have reached an absorption maxima at 688 nm.



16 **17**

Figure 7. Specific examples of the Aza-BODIPYs

By exploring the awesome characteristics of Aza-BODIPY, the same research group used the molecule in another study by small modification. They have showed that it can be modified in order to be used as a near IR colorimetric molecular sensor.[25] In the area of biological sensors, the 300-600 nm range is used at most which results in some problems. In this range strong interference due to background absorbance and auto-fluorescence from endogenous chromophores in sample media causes undesired results.[28] So the O`Shea group substituted two basic amine donors in order to create a push-pull effect. And it became a successful internal charge transfer (ICT) sensor. The amine groups are sensitive to the pH of the medium, when protonated it causes a spectral change. When analyzing the structure of the Aza-BDP in Figure 8 from X-ray crystal structure, it is seen that the aniline-substituted rings are coplanar with the pyrrole rings, which indicates a strong electronic interaction within the chromophore unit. When investigating the photophysical properties of the synthesized molecules, the authors have seen that its absorption maxima of 799 nm, is very different from the other Aza-BODIPY`s. This striking bathochromic shift is explained by the molecule`s including electron donor-acceptor moieties.

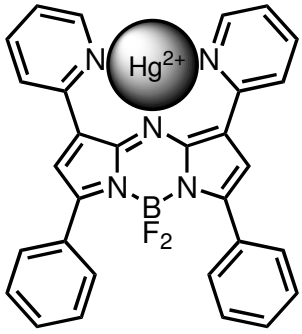


Aza-BDP

Figure 8. Another representative Aza-BDP used for pH sensing

After it is shown that a molecular sensor is possible based on this structure, a different interpretation done by the Akkaya group in order to synthesize near-IR mercury ion sensing Aza-BODIPY`s (Figure 9).[29] This is the first application of Aza-BODIPY`s as

molecular sensors which is a respected study since it is in the list of highly cited letters of the publisher.



Hg^{2+} sensor Aza-BDP

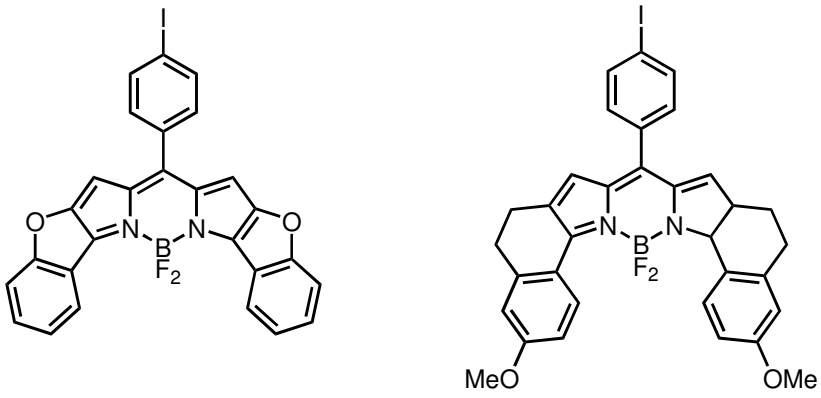
Figure 9. Aza-BDP used for sensing metal cations

1.2.2.3. Rigidification of Rotatable Moieties

With the aim of restricting the bond rotations of the BODIPY chromophore, different approaches were conducted by the Burgess and Carreira groups. They have started with different pyrrole analogues for synthesis. Both groups compared newly synthesized molecules to the already synthesized unconstrained molecules and they have seen that there are significant differences on account of photophysical properties. So they have concluded that more rigid, constrained systems are more likely to take part in designing near IR chromophores.

Burgess group synthesized five new molecules which are constrained, so as to see if they have more favorable fluorescence characteristics than the unconstrained ones that were prepared before.[30] Their molecules **18** and **19** have relatively rigid conformations caused by the heteroatom or ethylene bridge linkers that preclude free rotation of the substituted benzene molecular fragments. These molecules absorb ($\lambda_{max\ abs}$= 620-660

nm) and emit ($\lambda_{max\ fluor}$= 630-680 nm) in the longer wavelengths, they have higher extinction coefficients (< 100 000 M^{-1} cm^{-1}), and their fluorescence quantum yields are higher (up to 0.72).



18 **19**

Figure 10. Examples to the rigid BODIPY molecules

On the other hand Carreira group synthesized a conformationally restricted Aza-Bodipy and compared it to another Aza-BODIPY dye which is unrestricted.[31] In the article the newly synthesized molecule is described as a highly fluorescent, photostable aza-dipyrromethene dye with very sharp and intense absorption in the NIR region. In addition, the quantum yield is not sensitive to solvent polarity, and the absorption band remains sharp throughout a range of concentrations. With these properties it is told that the molecule is well-situated for the future experiments in biological probes. It is also told that investigations are continuing to make the water soluble derivatives since it is an essential property to be used in biosensing experiments.

The special characteristics of the dye **20** which was newly synthesized by the Carreira group[31] was compared to the known dye **21**. The most notable property of **20** is its absorbance peak which is intense and sharp at $\lambda_{max\ abs}$=740 nm with an extinction coefficient of ε= 159 000 M^{-1} cm^{-1} and a full width at half maximum height of 30.4 nm.

Conversely, the molecule **21** which was synthesized before has $\lambda_{max\ abs}$= 688 nm with ε= 78 500 M^{-1} cm^{-1} and a fwhm of 57 nm. Thus, the effect of restricting the methoxyphenyl substituent is remarkable, resulting in 52 nm bathochromic shift and halving of the fwhm. Also, the emission maxima of **20** occurs at $\lambda_{max\ fluo}$= 751 nm with Φ= 0.28. Moreover, the quantum yield of the **20** is insensitive to solvent polarity: $\Phi_{toluene}$= 0.28, Φ_{EtOAc}= 0.27, Φ_{MeCN}= 0.26, and Φ_{EtOH}= 0.26.

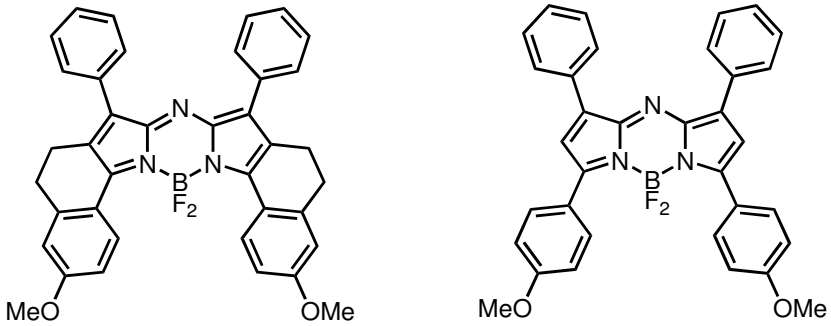


Figure 11. Comparison of rigidified and unrigidified Aza-BODIPYs

Also, the compound **20** has superb stability, and a solution of it in chloroform can stay unchanged for months. The photostability was also compared to the compound **21** and a well-known FDA approved indocyanine green dye (ICG), (Φ = 0.11 in DMSO). As a result, **20** preserves 97.7 % of its fluorescence intensity after 1 hour of strong excitation, molecule **21** is similar to **20** (98.0 %); on the other hand, ICG loses 75 % of its initial intensity after 1 hour.[31]

Consequently, the dye which was synthesized by the Carreira group meets the necessary requirements of a NIR chromophore which are peak fluorescence of 700-900 nm, high quantum yield, narrow excitation/emission spectrum and high chemical stability and photostability and finally convenient commercially viable synthesis in order to produce in large amounts.

1.2.2.4. Extension of the π Conjugation of the Structure

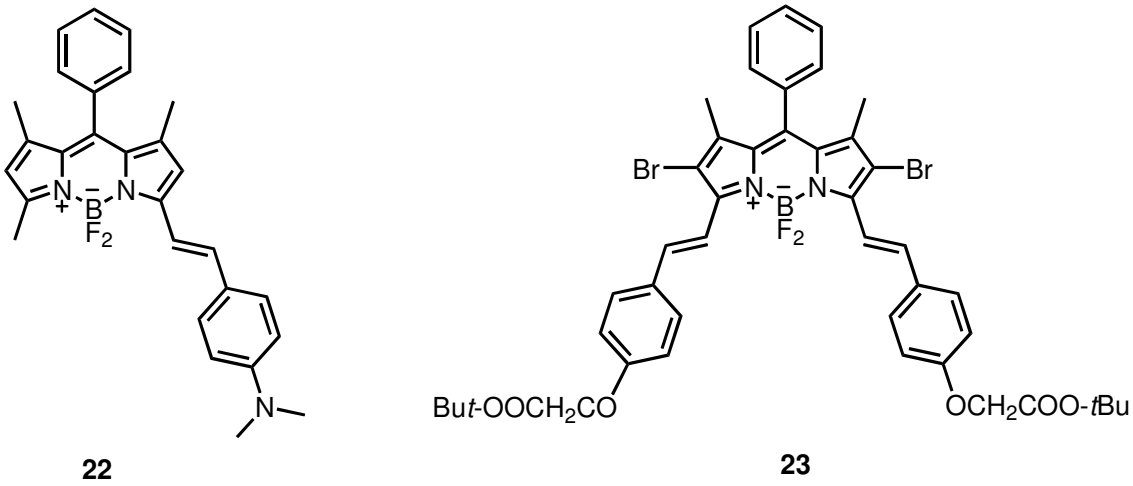
Another common effort in order to produce near IR BODIPY derivative is extending the conjugation of π electrons in the molecule. This way of synthesis largely studied in recent years by the Akkaya and Rurack groups.

In 2001, Rurack group first reported the synthesis, spectroscopic and electrochemical properties of the 3-dimethylaminostyryl-substituted dye **22** (Figure 12).[32] This dye is the first example of an unsymmetrically substituted BODIPY dye carrying an analyte-sensitive group conjugated to the core. This compound was synthesized by condensation of the tetramethyl BODIPY derivative with the p-dimethylaminobenzaldehyde using piperidinium acetate as a catalyst.

Due to the introduction of a donor-stryl-spacer group at the 3- position the spectroscopic behavior of **22** is more reminiscent of donor-acceptor stilbenes or styryl bases. However, this molecule should not be evaluated together with the meso-donor substituted BODIPY dyes, where no direct electronic conjugation exists between two groups. The absorption band of the synthesized molecule is centered at 585±5 nm and shows no solvent dependent shifts which is interpreted by the author as the ground state dipole moment is rather small.

Another work has been done by the Akkaya group in the year of 2006.[33] They have synthesized the molecule **23** in Figure 12. This research is important because the double condensation product **23** was not known before. The unsymmetrical product was known for years but no one did not isolated the symmetrical doubly condensated product. The reaction has a simple procedure; the known Knoevenagel condensation reaction. In the paper three new fluorophores has been synthesized, and their spectroscopic properties have been investigated. These new fluorophores have absorption maxima in the range of 650-660 nm. This means that these molecules have 60-70 nm bathochromic shift compared with the mono condensated product which was synthesized by the Rurack group. Moreover, these dyes have large quantum yields with

20 nm Stokes` shifted emission peaks. After this paper different studies were conducted in the same group with the same strategy. A water soluble molecule was synthesized which was designed to be used in photodynamic therapy. After investigation it was seen that that molecule can act as an efficient photosensitizer.[34] In addition, as a recent published studies, molecules were synthesized in order to use as a photosensitizer in a dye sensitized solar cell (DSSC)[35] and a pH sensor[36].



22 **23**

Figure 12. Examples to the π-conjugation extended BODIPYs

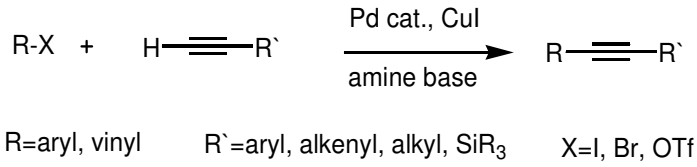
1.2.3. Cross-Coupling Reactions to sp Carbon Atoms

Alkyne cross coupling reactions proved their worth as an important tool in organic synthesis over the past quarter century since they have seen incredible growth.[37] Examples of these different applications include the preparation of pharmaceuticals, complex natural products, and advanced materials such as molecular wires and sensors. Attractive properties of alkynes are its rigidity, electron-rich and unsaturated nature which makes it available for further derivatization and/or transformation. The cross couplings of alkynes were started four decades ago by Stephens and Castro. They used an alkynylcopper and a haloarene for coupling. After that many developments took

place but the most important one is using palladium as a catalyst. The Pd-catalyzed reaction of a terminal alkyne with a haloarene in the presence of a copper as a co-catalyst and an amine as a base is the most widely used cross–coupling technique, and it is known as Sonogashira reaction.

1.2.3.1. Sonogashira Reaction

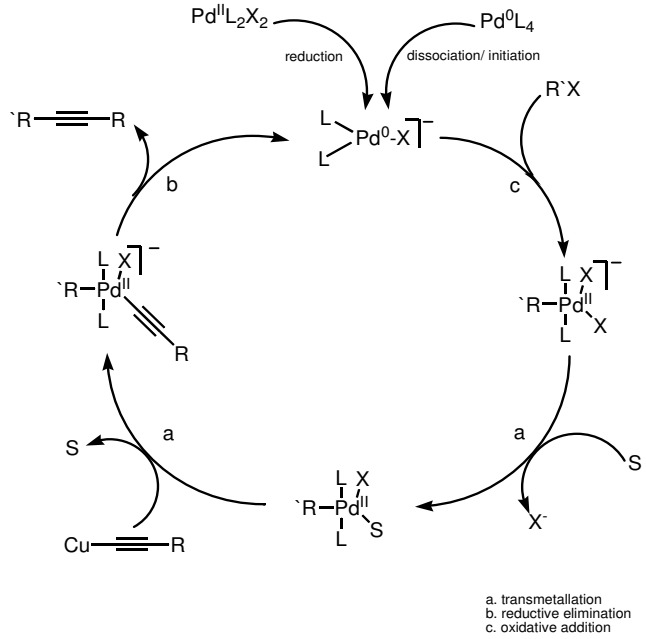
As told before, the most significant contribution to the field of cross-coupling was the innovation of palladium as a catalyst.[37] In 1975 three different groups made separate progress in this reaction. The groups of Cassar and Heck independently showed that aryl and vinyl halides cross-couple with with terminal acetylenes by using a Pd-complex and a base. These procedures resemble the known `Heck reaction`. After that year, Sonogashira and Hagihara found that this reaction can be done more smoothly and under milder conditions by using CuI as a co-catalyst and an amine base as a solvent/reactant (Scheme 2). This development is similar to a Pd catalyzed Stephens-Castro cross-coupling, and is now called as Sonogashira reaction. This procedure is currently the most commonly used method for alkyne cross-coupling due to the simplicity of starting material preparation, mild coupling conditions and the ability to tolerate a large variety of functional groups. A tremendous number of modifications have been made in order to improve yields, to create even milder reaction conditions for unactivated organic electrophiles and to overcome by-products like homo-coupled products and difficulties with the cross-coupling reactions by using electron-deficient alkynes.



Scheme 2. Reaction conditions of Sonogashira coupling

1.2.3.2. Mechanism of Sonogashira Reaction

Widely accepted mechanism of Sonogashira reaction is similar to the mechanism proposed by Sonogashira and Hagihara. However, there is evidence from recent studies that a more complex mechanism involving a pentacoordinated anionic Pd species (Scheme 3).[37]



Scheme 3. Mechanism of Sonogashira coupling

Typically, 2-5 mol % Pd is used with generally twice this amount of CuI as a co-catalyst. In some cases a smaller amount if Pd can also be used, and the reaction proceeds also without CuI. The classical and the most widely used Pd catalysts are $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$. Diacetylene by-product, formed by reduction of the Pd(II) complex, plagues the Sonogashira reactions which sometimes is the major acetylene-containing product. Although this dimer is seen in reactions where Pd(0) catalyst used, can be minimized by careful purging of oxygen from the reaction solvent by running the reaction in an inert atmosphere.

Aryl iodides are the most commonly used organohalides under Sonogashira conditions, and usually react at room temperature. Until recently, cross couplings with unactivated aryl bromides need a temperature of 80°C. However, in recent years many research are conducted in design of highly active catalysts, allowing milder reaction conditions and the ability to react with aryl bromides even at room temperature. Moreover, some typically inert aryl chlorides also can be cross coupled at room temperature.[37]

The majority of cross-couplings proceed smoothly using the standard two Pd catalysts: $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$. There is usually a small difference between two catalysts. But it is seen that $Pd(PPh_3)_4$ shows better reactivity and smaller reaction times when reacting with bromoarenes than the other catalyst, when it is freshly prepared. $Pd(PPh_3)_4$ is a bright yellow crystalline solid when it is freshly prepared, however this is a easily decomposing reagent. It decomposes when exposed to air, with time and temperature above 0°C. Another advantage of $Pd(PPh_3)_4$ is that the reductive elimination step is required for $Pd(PPh_3)_2Cl_2$ is avoided, so very little or none of dimer acetylene is formed. On the other hand, $Pd(PPh_3)_2Cl_2$ has the benefit of air and temperature stability and is less expensive than $Pd(PPh_3)_4$, yet will always produce at least an equivalent amount of dimer acetylene by-product.

The other crucial element for Sonogashira reaction is the amine base. Et_3N, Et_2NH, iPr_2NH are the most widely bases used, show good results in most reactions, although it is mostly substrate depended. Stronger bases such as piperidine and pyrrolidine are also commonly used, and frequently increase reaction rate.

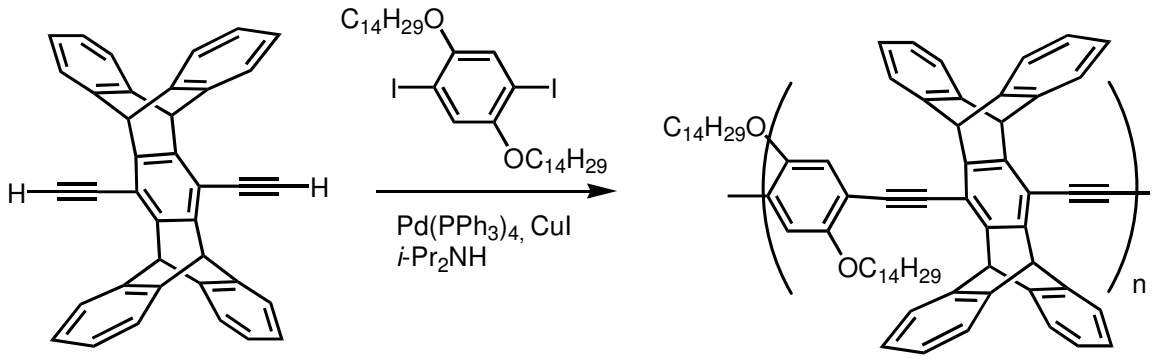
In the Sonogashira protocol in most cases amine does not only act as a base but it also acts as a solvent. Later, it is reported that the yield and reaction rate can be increased when using base with a solvent. THF is the most commonly used solvent. A detailed report by Krause gives important information about this. He studied Sonogashira reaction with and without THF. And he resulted that when THF used as a co-solvent the yields are higher and the reaction conditions are milder. Another interesting result

also declared by authors that it is unnecessary to degas the reaction if a careful slow addition of alkyne is performed. Other co-solvents used are DMF, NMP, benzene, and toluene. There is not much study on reaction improvements due to solvent effects, although it is seen that increase in the solubility of catalysts, reactants, and products assess the reaction success.

1.2.3.3. Applications of the Sonogashira Reaction

There are a large number of applications to the Sonogashira reaction, ranging from the synthesis of natural products to the design of non-natural, technologically advanced materials. An arylalkyne gives the molecule a rigid molecular framework for unique structural shape and geometry and it also provides an unsaturation to the molecule which can be utilized for further synthetic transformations.

Alkyne cross-coupling is a widely used method for construction of conjugated materials with potential utilization in electronic and photonic devices as well as many other technologically applicable materials.[38] Due to the extensive conjugation in phenylacetylene and polyyne oligomers and polymers, these are often act as semiconductors. Applications of such materials include non-linear optics, polarizers for liquid crystals displays, light emitting diodes, and detection of explosives. A very unique poly(phenyleneethynylene) (PPE) sensor was prepared by polymerization with Sonogashira coupling of diethynylpentiptycene with diiodoarene (Scheme 4).[39] A thin film of the highly porous, shape-persistent polymer could detect trace amounts of 2,4,6-trinitrotoluene (TNT) by fluorescence quenching.



Scheme 4. A successful TNT sensor prepared by Sonogashira coupling

Alkyne cross coupling is also an important tool in the assembly of unique nanoarchitectures used as molecular devices. The Moore group synthesized a macrocycle which acts as a "molecular turnstile" based on the rigid outer framework and the rotation of the central spindle (Figure 11).[40] Actually, synthesis of this molecule requires consecutive Sonogashira reactions which do not block each other. When looked to the procedure of this molecule it can be seen that, this reaction exemplifies the strategic control of alkyne cross-coupling by means of bromoarene reactivity, selective protodesilylation, and use of the triazene functionality as a masked iodoarene. For instance, if one wants to cross-couple one of the two haloarene centers; bromoarene and iodoarene, then he should first consider the iodine positioned center since it is more reactive. In most cases, at room temperature iodoarene cross-couples easily. On the other hand bromoarene needs a temperature of at least 60°C to react.

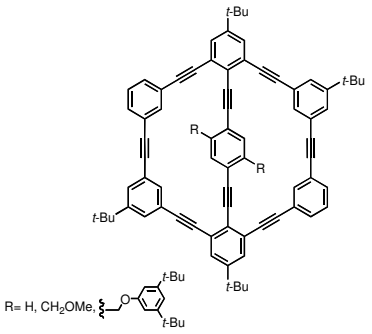


Figure 13. "Molecular turnstile" prepared by Sonogashira coupling

Another research area related with Sonogashira coupling is linking the porphyrin units in order to create different types of molecular rods, stacks, or other large assemblies functioning as “light harvesters”. An example to this type of unit is the ”tripodaphyrin” molecule, which is composed of four porphyrin molecules connected to the central methane unit(Figure 12).[41]

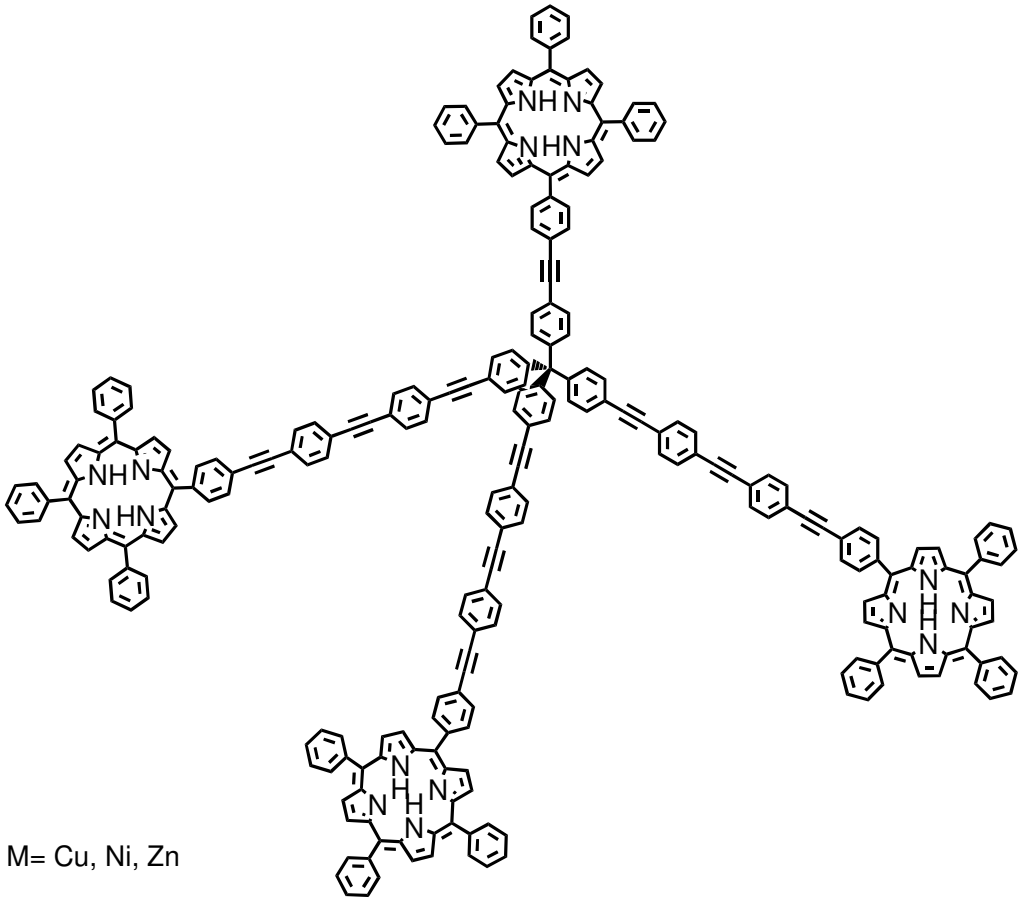
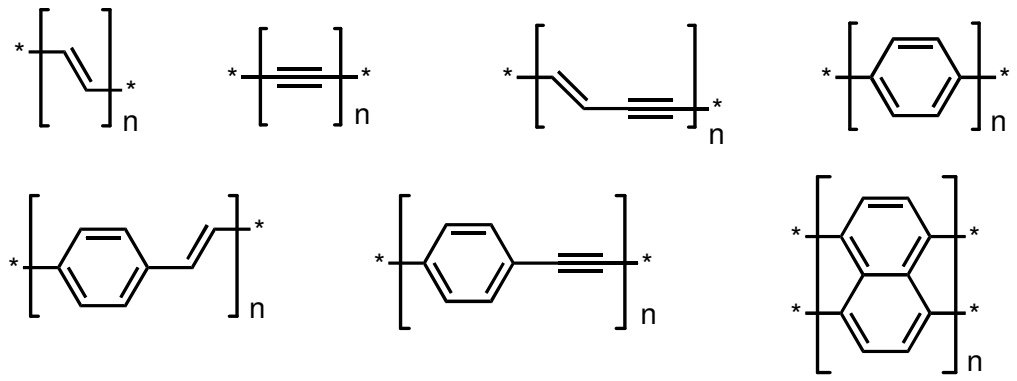


Figure 14. Light harvesting assembly synthesized with Sonogashira coupling

1.3. Conjugated Oligomers

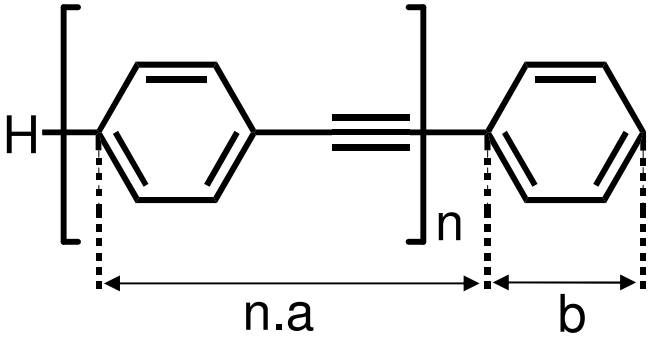
1.3.1. General Properties

Because of their interesting optical, electrical and optoelectronic properties, conjugated oligomers represent target compounds for many applications in materials science. Moreover, they are the model compounds for the corresponding polymers.[42] Carbon rich extended π electron systems can consist of building blocks such as olefinic double bonds, triple bonds, benzene rings or higher condensed aromatic ring systems. Therefore, the repeat units of conjugated oligomers are single or composite units of such building blocks. The scheme summarizes a few typical examples of them.[43]



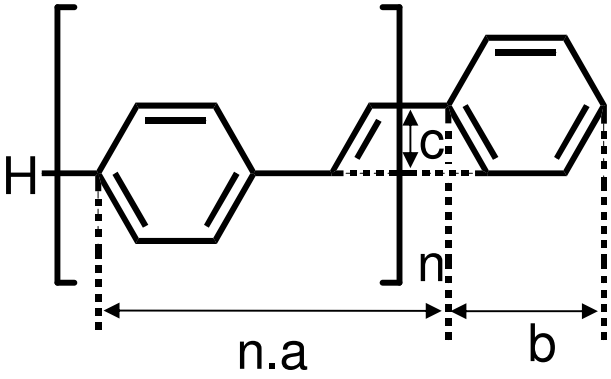
Scheme 5. Some examples of the conjugated oligomers[43]

The exactly defined length of such oligomers is due to the monodisperse character of the compounds having an precisely defined number of repeat units n. On condition that, the conformational effects do not considerably affect the extent of the oligomeric molecules, L between the terminal positions of the conjugated system can be described as a linear function of n. The Scheme 6 shows the L(n) for the oligo(1,4-phenyleneethynylene)s (OPE) and oligo(1,4-phenylenevinylene)s (OPV).[42]



24

L= n.a+b a=0.68, b=0.28



25

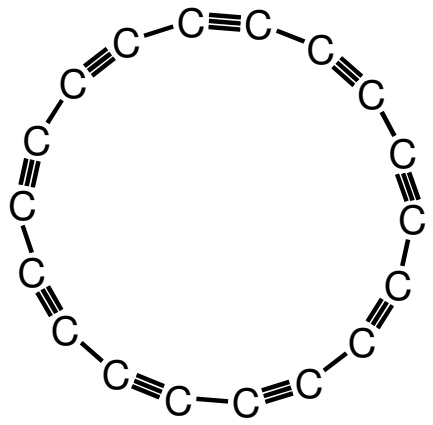
$n.a + b \leq L \leq [n^2(a^2+c^2)+ b^2 + 2nab]^{1/2}$

$L \approx n.a + b$ a=0.66, b=0.28, c=0.11

Scheme 6. Length L (in nm) of OPE series 1 and OPV series 2 with number of repeating units n. a, b and c values are the average values which were obtained from the crystal structure data[42]

There are torsions along the chain of the benzene rings **24** and **25**; however, it does not affect the L, length of the molecule. For the second molecule, there is the probability of cisoid and transoid conformers for the two neighboring molecules. Hence, to some extent the L is different than the calculated case. So, the number of conformers (N) increases with the repeated units.

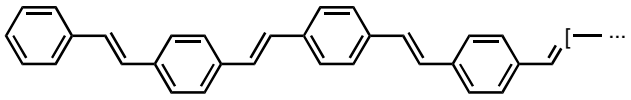
Since the energy of deformation of bond angles s relatively low, one can expect in higher oligomers some deviation from the ideal geometry obtained for the repeat unit in small molecules.[42] A very interesting example illustrates this situation (Scheme 7). The cyclooctadecanonayne **26** molecule is known to be a cyclic molecule despite the expected 180° angle of acetylenes.[43, 44] The bond angle is reduced to about 160°; this decrease causes strain energy of 18*4= 72 kcal mol^{-1}. According to the authors, the structure which has alternating bond lengths is more favorable than the corresponding cumulune structures with equal bond lengths.[43, 44]



26

Scheme 7. In cyclooctadecanonayne molecule bond angles of between acetylenes are 160°, not expected 180°

Aside from the linear arrangements of repeat units, cyclic, star shaped and dendritic arrangements can also be realized. The Scheme 8 illustrates some of these examples.



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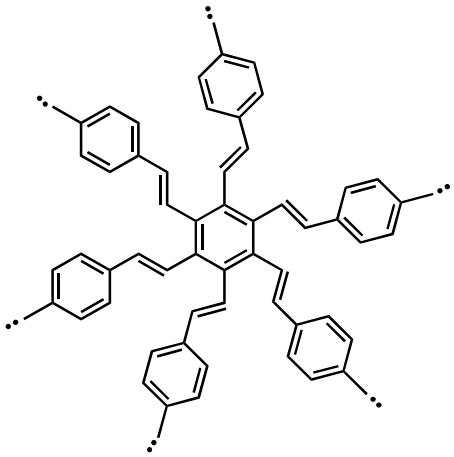


28

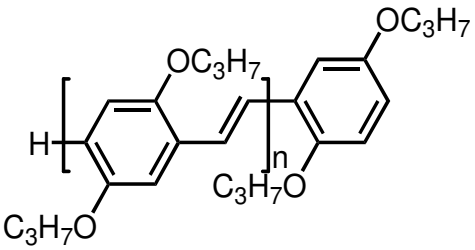
Scheme 8. Oligomers consisting of (*E*)- stilbene units; rigid rod 3 and star 4

1.3.2. Common Examples of Conjugated Oligomers

1.3.2.1. Oligo (1,4-phenylenevinylene)s OPV

In these molecules when the number of repeating units increase there appears a problem; solubility. The unsubstituted OPVs become insoluble in most organic solvents when the repeating unit is bigger than 3. In order to synthesize the long chain oligomers, solubilizing groups like alkoxy or alkyl groups are substituted.

In the literature, the 2,5-dipropoxy substituted OPVs were synthesized and studied in detail (Scheme 9).[45, 46]

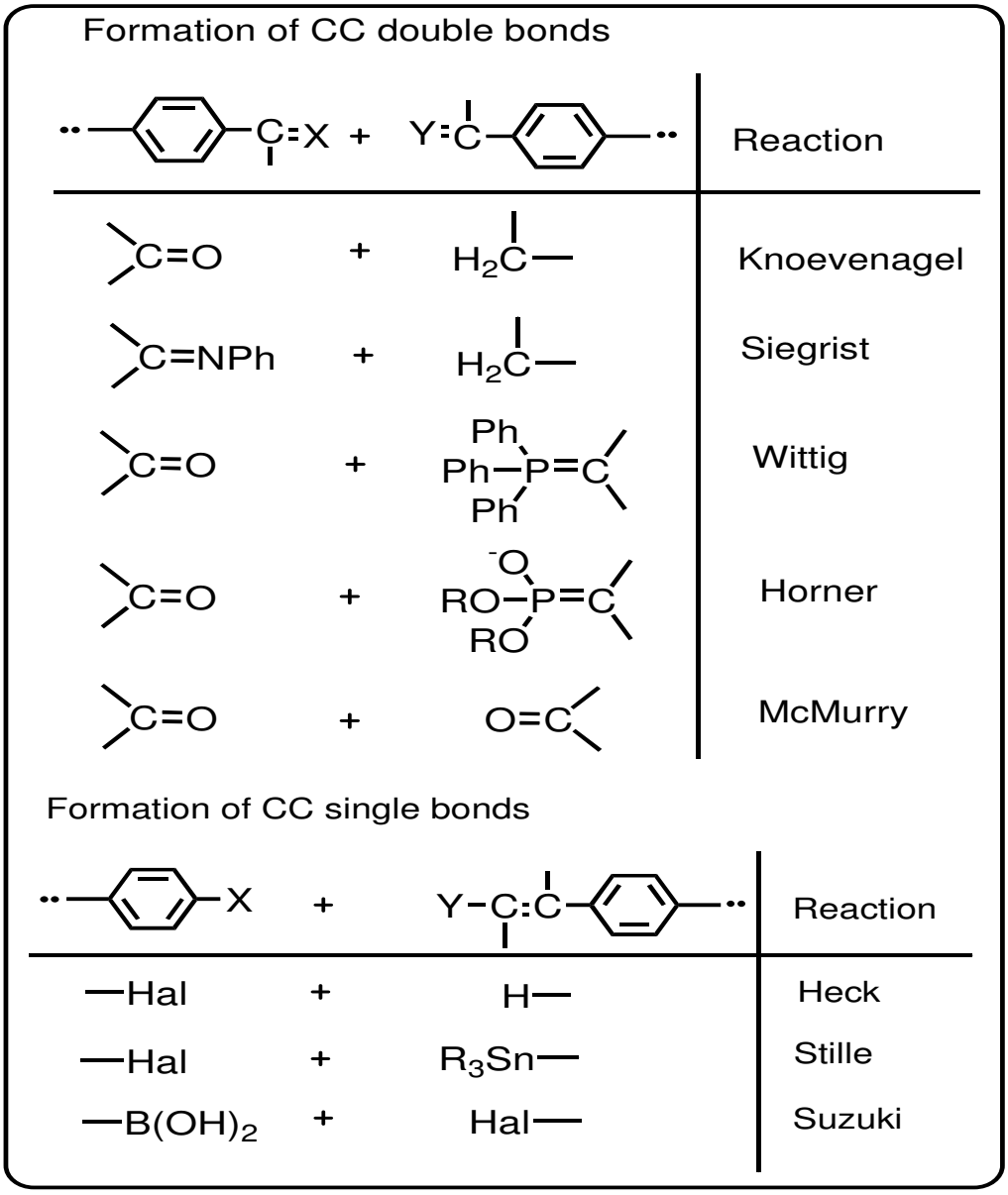


n= 1,2,3,4,5,6,7,8,11,15

Scheme 9. Oligo (2,5-dipropoxyphenylenevinylene)s (OPEs)

The synthesis of OPVs includes the repetitive formation of C-C double or single bonds. Table 1 gives the reactions which are used most for this purpose.

Table 1. Commonly used CC coupling reactions for the generation of OPVs.



For the Knoevenagel condensation reaction with elimination of water requires activated methylene groups like CH_2CN. However, for the Siegrist reaction where aniline is eliminated such an activation is not needed. According to Meier, the stereoselectivity of the Siegrist reaction is very high (trans/cis ration is 1000/1). This is due to the antiperiplanar mechanism where the leaving group is large.[47] The thermodynamic

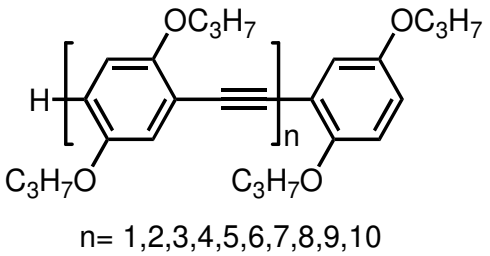
trans/cis equilibrium of stilbenoid compounds is in the range of 95:5. For the Wittig-Horner and McMurry reactions; the yields are high, but the stereoselectivities are low. The palladium catalyzed Heck, Stille and Suzuki reactions can sometimes results in structural defects, so careful purification is needed for most of the case. Generally, combinations of these reactions are needed.

OPVs find application areas in materials science. These areas are: organic light emitting diodes (OLED), field effect transistors (FET), semiconductors (doped), photoconductors, solar cells, photovoltaic devices, optical brighteners, laser dyes, non linear optics (NLO), optical switching, imaging techniques, photoresists and liquid crystals.[48, 49, 50]

Small-molecule based OLEDs have been on the market for several years. For a LED to be good it has to be some properties. These include some physical properties and the emission should produce a bright color at the desired wavelength and the materials of the device should be stable towards oxygen, water, light, etc. It is known that OPVs fulfill some of these desired characteristics but not all of them.

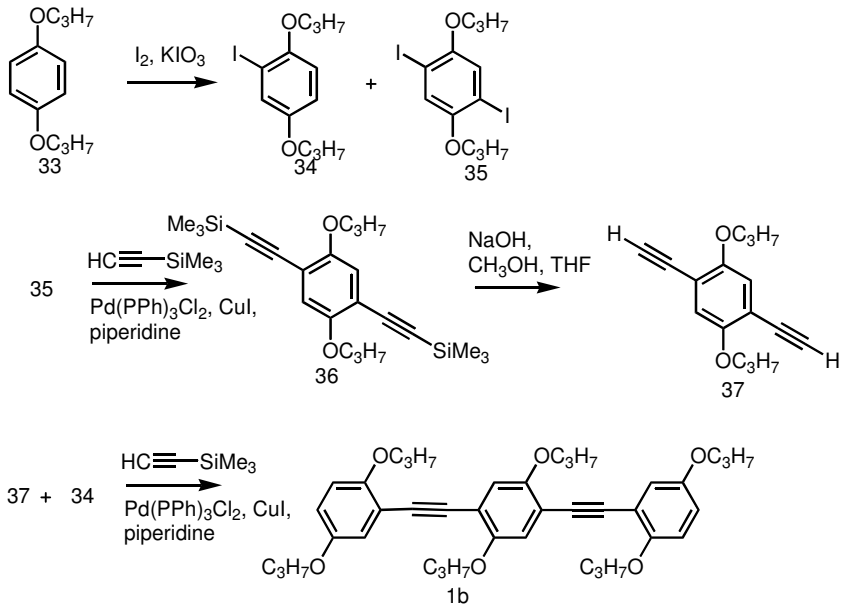
1.3.2.2. Oligo (1,4-phenyleneethynylene)s OPE

Oligo (1,4-phenyleneethynylene)s become hardly soluble in organic solvents when the repeating chain is three. Hence, the Meier and co-workers substituted the molecule with propoxy groups and studied the molecule until n=10 (Scheme 5).[51, 52] This is the longest known OPE series.



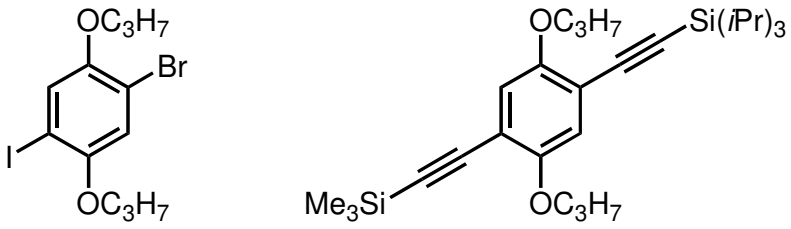
Scheme 10. Oligo(2,5-dipropoxy-1,4-phenyleneethynylene)s (OPEs)

For the OPVs a variety of synthesis methods were developed. And these reactions all should be considered when synthesizing long chain OPVs. However, for the synthesis of OPEs, Sonogashira-Hagihara coupling dominates the synthesis methods. A simple example for the synthesis is shown in the Scheme 11. The synthesis first starts with mono- and diiodination of 1,4-dipropoxybenzene. Then the diiodinated molecule **35** its reacted with the ethynyltrimethylsilane according to the Sonogashira protocol. The silyl groups were deprotected with NaOH. Finally, synthesized molecule **37** and **34** were reacted to yield the final product. Longer series of OPEs were synthesized with this synthesis route.



Scheme 11. Preparation of OPE 1b (n=2)

For higher series of OPEs, different selective reaction routes should be used for chemoselective reactions. Meier and co-workers benefited and used these methods while synthesizing molecules. For instance, iodine is more reactive than bromine in molecule **38** in Sonogashira coupling. Yet, in some cases iodine is reacting without CuI cocatalyst. Hence, bromine is protected when reacting **38**, only iodine is reacting in mild conditions. In later steps bromine is forced to react in more harsh conditions. The other trick used is the trimethylsilyl and triisopropylsilyl deprotecting groups. The trimethylsilyl group is cleaved in different conditions with triisopropyl group. Former is deprotected with NaOH or K_2CO_3, however, latter is deprotected with F^- ion in Bu_4NF.



Scheme 12. Building blocks for selective Sonogashira couplings

The absorption and fluorescence properties of the OPE series shows that there is a convergence. As the number of n increase there is not much change in the absorption and emission wavelengths. Actually, the results are nearly the same with the OPV series. The graph shows the approach of λ_{max} to λ_{∞} for increasing n.

The application areas of OPE series in Materials Science is also nearly the same with OPV series.

CHAPTER 2

EXPERIMENTAL

2.1 Instrumentation

All chemicals and solvents purchased from Aldrich were used without further purification. ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Bruker DPX-400 in $CDCl_3$ or DMSO-d_6 with TMS as internal reference. Column chromatography of all products was performed using Merck Silica Gel 60 (particle size: 0.040–0.063 mm, 230–400 mesh ASTM). Reactions were monitored by thin layer chromatography using fluorescent coated aluminum sheets. Absorption spectrometry was performed using a Varian spectrophotometer. Steady state fluorescence measurements were conducted using a Varian Eclipse spectrofluorometer. Solvents used for spectroscopy experiments were spectrophotometric grade. Fluorescence quantum yields of all target compounds were measured in $CHCl_3$ and refractive index corrections were made. The quantum yield of **44** was measured with Fluorescein (Φ = 0.79 in EtOH); **48** with Rhodamine 6G (Φ=0.95 in ethanol); 53, 54 and 57 with Sulforhodamine 101 hydrate (0.9 in EtOH). Mass spectrometry measurements were done at the Ohio State University Mass Spectrometry and Proteomics Facility, Ohio, USA.

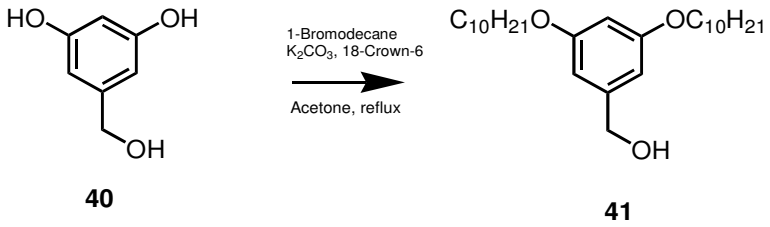
2.2 Syntheses

2.2.1 3,5-Bis(decyloxy)benzyl alcohol (41)

A mixture of 3,5-dihydroxybenzyl alcohol **40** (42.81 mmol, 6.00 g), 1-bromodecane (107.03 mmol, 23.7 g), K_2CO_3 (171.24 mmol, 23.7 g), and 18-crown-6 (4.281 mmol, 1.13 g) in dry acetone were refluxed under nitrogen atmosphere for 24 h. Solvent was evaporated under reduced pressure and water was added to the residue. Reaction product extracted into chloroform (3x100 mL) and after organic phase dried over anhydrous Na_2SO_4. After the evaporation of the solvent, silica gel column chromatography using 2:1 $CHCl_3$: Hexanes as the eluant afforded desired product (17.1 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.38 (s, 2H), 6.25(s, 1H), 4.45(s, 2H), 3.30(t, *J* = 6.6 Hz, 4H), 2.36 (s, 1H), 1.65 (m, 4H), 1.1-1.4 (m, 28H), 0.8 (t, *J* = 6.5 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5, 143.2, 105.0, 100.5, 68.1, 65.3, 34.0, 32.9, 31.91, 31.89, 29.60, 29.58, 29.52, 29.46, 29.41, 29.34, 29.30, 29.27, 28.8, 28.2, 26.1, 24.8, 22.7, 14.1



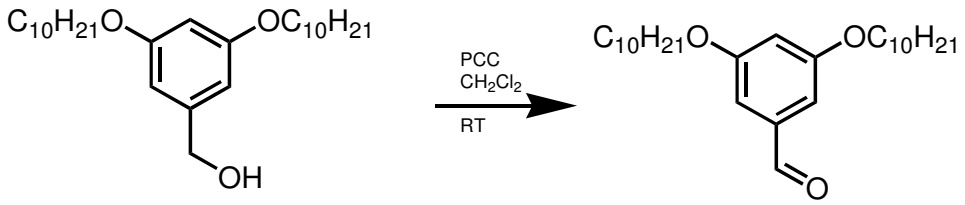
Scheme 13. Alkylation of compound **40**

2.2.2 3,5-Bis(decyloxy)benzaldehyde (42)

In a 500 mL round-bottomed flask containing 250 mL CH_2Cl_2 were added **41** (21.40 mmol, 9.00 g) and PCC (53.49 mmol, 11.53 g), and the reaction mixture was stirred for 3 h at room temperature. Reaction mixture was then washed with water and organic phase was evaporated at reduced pressure. Silica gel column chromatography using $CHCl_3$ as the eluant afforded a white solid (8.1g, 90%).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 9.80 (s, 1H), 6.93 (s, 2H, ArH), 6.60 (s, 1H, ArH), 3.92 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 1.70 (m, 4H, C*H*$_2$), 1.38 (m, 4H, C*H*$_2$), 1.20 (s, 24H, C*H*$_2$), 0.80 (t, 6H, *J* = 6.6 Hz, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, 300K): δ = 192.0, 160.8, 138.4, 108.1, 107.1, 68.5, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.7, 14.1.



41 **42**

Scheme 14. Oxidation of compound **41**

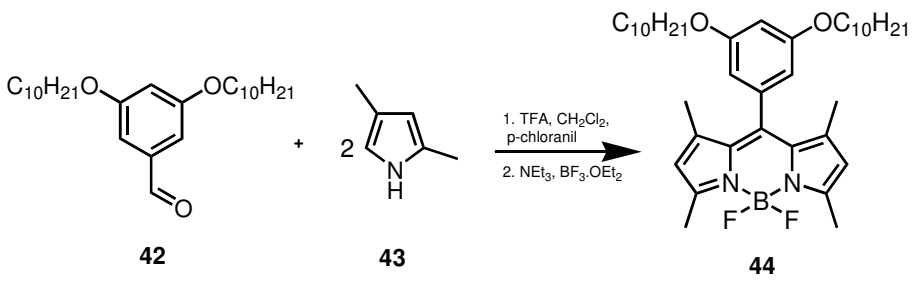
2.2.3 4,4-Difluoro-8-(3′,5′-bis(decyloxy)phenyl)-1,3,5,7-tetramethyl -4-bora-3a,4adiaza -s-indacene (44)

To a 1 L round-bottomed flask containing 400 mL argon-degassed CH_2Cl_2 were added 2,4-dimethyl pyrrole **43** (15.8 mmol, 1.50 g) and **42** (7.17 mmol, 3 g. One drop of TFA was added and the solution was stirred under N_2 at room temperature for 1d. After addition of a solution of DDQ (7.17 mmol, 1.628 g) in 100 mL of CH_2Cl_2 to the reaction mixture, stirring was continued for 30 min. 6 mL of Et_3N and 3 mL of $BF_3.OEt_2$ were successively added and after 30 min, the reaction mixture was washed three times with water and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography using 2:1 $CHCl_3$: Hexanes as the eluant. Red solid (1.381 g, 30%).

^{1}H NMR (400 MHz, $CDCl_3$, 300K) : δ = 6.45 (s, 1H, ArH), 6.35 (s, 2H, ArH), 5.90 (s, 2H, H2, H6), 3.85 (t, 4H, *J* = 6.56 Hz, OC*H*$_2$), 2.47 (s, 6H, C*H*$_3$), 1.70 (m, 4H, C*H*$_2$), 1.49 (s, 6H, C*H*$_3$), 1.35 (m, 4H, C*H*$_2$), 1.20 (s, 24H, C*H*$_2$), 0.80 (t, 6H, *J* = 6.5 Hz, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 155.4, 143.2, 136.4, 131.2, 121.0, 106.4, 102.3, 68.4, 31.9, 29.6, 29.5, 29.3, 29.2, 26.0, 22.7, 14.6, 14.2, 14.0.

HRMS (ESI) calcd for $C_{39}H_{59}BF_2N_2O_2Na$ (M+Na) 658.4572, found 658.4542. Δ=4.6ppm.



Scheme 15. General BODIPY reaction

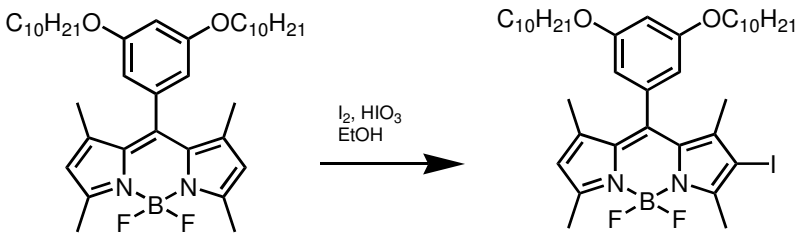
2.2.4 4,4-Difluoro-8-(3′,5′-bis(decyloxy)phenyl)-2-iodo-1,3,5,7-tetramethyl-4-bora-3a,4adiaza-s-indacene (45)

44 (1.91 mmol, 1.21 g) and Iodine (1.52 mmol, 387 g) were added to a 500 mL round-bottomed flask and to this solution was added Iodic acid (1.52 mmol, 268 g) dissolved in 2 mL of water. The reaction mixture was stirred at 60°C and was monitered by TLC 1:1 $CHCl_3$: Hexanes. When TLC indicated that all the starting material had been consumed, saturated $Na_2S_2O_3$ solution in water was added and the product was extracted into $CHCl_3$. The solvent was evaporated and the residue was purified by silica gel column chromatography using 1:1 $CHCl_3$: Hexanes as the eluant. Red solid (0.98 g, 67%).

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ = 6.48 (s, 1H ArH), 6.32 (d, 2H, *J* = 1.9 Hz, ArH), 5.97 (s, 1H, H2), 3.85 (t, 4H, *J* = 6.6 Hz, OCH_2), 2.55 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 1.68 (m, 4H, CH_2), 1.49 (s, 6H, CH_3), 1.35 (m, 4H, CH_2), 1.20 (s, 24H, CH_2), 0.8 (t, 6H, *J* = 6.6 Hz, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, 300K): δ = 161.3, 157.7, 154.4, 145.1, 143.2, 141.5, 136.2, 131.6, 130.7, 122.1, 106.2, 102.5, 84.1, 68.4, 38.2, 33.8, 32.9, 31.9, 31.3, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.8, 28.2, 26.1, 26.0, 25.8, 22.7, 16.5, 15.7, 14.7, 14.5, 14.1.

HRMS (ESI) calcd for $C_{39}H_{58}BF_2IN_2O_2Na$ (M+Na) 784.3538, found 784.3513. Δ=3.2 ppm.



44 **45**

Scheme 16. Mono iodination of BODIPY

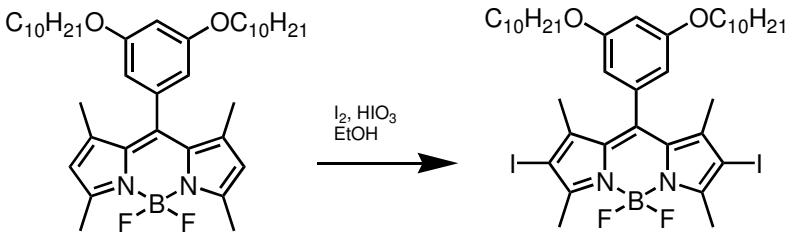
2.2.5 4,4-Difluoro-8-(3,5-bisdecyloxy)phenyl-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a,4adiaza-s-indacene (46)

44 (2.47 mmol, 1.57 g) and Iodine (6.18 mmol, 1.57 g) were added to a 500 mL round-bottomed flask and to this solution was added Iodic acid (4.93 mmol, 0.87 g) dissolved in 2 mL of water. The reaction mixture was stirred at 60°C and was monitored by TLC 1:1 $CHCl_3$: Hexanes. When all the starting material had been consumed, saturated $Na_2S_2O_3$ solution in water was added and the product was extracted into $CHCl_3$. The solvent was evaporated and the residue was purified by silica gel column chromatography using 1:1 $CHCl_3$: Hexanes as the eluant. Red solid (2.09 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ = 6.49 (s, 1H, ArH), 6.28 (s, 2H, ArH), 3.85 (t, 4H, *J* = 6.5 Hz, OC*H*$_2$), 2.55 (s, 6H, C*H*$_3$), 1.69 (m, 4H, C*H*$_2$), 1.49 (s, 6H, C*H*$_3$), 1.35 (m, 4H, C*H*$_2$), 1.20 (s, 24H, C*H*$_2$), 0.80 (t, 6H, *J* = 6.3 Hz, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, 300K): δ = 161.4, 156.7, 145.4, 141.4, 136.1, 131.0, 106.1, 102.7, 85.5, 68.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 26.0, 22.7, 16.9, 16.0, 14.1.

HRMS (ESI) calcd for $C_{39}H_{57}BF_2I_2N_2O_2Na$ (M+Na) 910.2505, found 910.2495. Δ=1.1 ppm.



44 **46**

Scheme 17. Diiodination of BODIPY

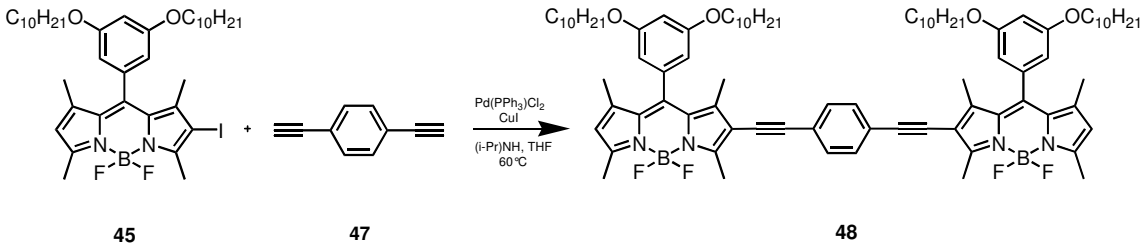
2.2.6 Dimer BODIPY (48)

Mono-iodo-bodipy **45** (102 mg, 0.134 mmol) was dissolved in 10 mL freshly distilled THF and 5 mL $(i\text{-}Pr)_2NH$. Then the reaction was purged with argon until all the chemicals were added. After 15 minutes $Pd(PPh_3)_2Cl_2$ (4.71 mg, 0.0067 mmol) and CuI (2.13 mg, 0.0112 mmol) were added to the reaction mixture. Then diethynyl benzene (7.04 mg, 0.056 mmol) was added after 10 minutes. The reaction was proceeded for 12 hours at 60°C. The reaction mixture was evaporated under reduced pressure and the compound was purified over silica gel using chloroform/hexane 3/1 as a red solid in 70% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.3 (s, 4H), 6.5 (s, 2H), 6.35 (d, *J* = 1.6 Hz, 4H), 6.0 (s, 2H), 3.85 (m, 8H), 2.62 (s, 6H), 2.5 (s, 6H), 1.7 (m, 8H), 1.61 (s, 6H), 1.52 (s, 6H), 1.1-1.4 (m, 56H), 0.81 (m, 12H).

^{13}C-NMR (100 MHz, $CDCl_3$, 300 K): δ = 160.2, 156.7, 155.4, 143.9, 141.6, 141.0, 135.0, 131.2, 130.1, 128.9, 122.0, 121.0, 113.7, 105.0, 101.3, 94.7, 83.0, 67.4, 30.9, 28.7, 28.5, 28.31, 28.34, 28.1, 25.0, 21.7, 13.8, 13.5, 13.1, 12.5, 12.1 ppm.

MS (MALDI) calcd for $C_{88}H_{120}B_2F_4N_4O_4$ 1394.94, found 1394.131.



Scheme 18. Synthesis of Dimer BODIPY

2.2.7 Mono 4-trimethylsilylacetylenebenzene ethynyl BODIPY (50)

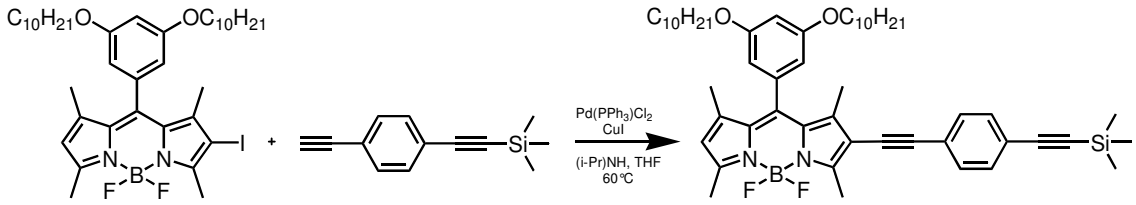
Mono iodo BODIPY **45** (240 mg, 0.316 mmol) and (2-(4-ethynylphenyl)ethynyl)trimethylsilane **49** (190 mg, 0.947 mmol) was reacted with the same Sonogashira protocol as above and the product was purified over silica gel using chloroform/hexane 1/1 as a red solid in 70% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.3 (m, 4H), 6.5 (d, *J* = 2.1 Hz, 1H), 6.32 (dd, *J* = 2.0 Hz, 2H), 5.98 (s, 1H), 3.85 (t, *J* = 3.9 Hz, 4H), 2.61 (s, 3H), 2.5 (s, 3H), 1.69 (m, 4H), 1,6 (s, 3H), 1.51 (s, 3H), 1.1-1.4 (m, 28H), 0.8 (t, *J* = 6.6 Hz, 6H), 0.18 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$, 300 K): δ = 161.3, 158.0, 156.5, 145.0, 142.8, 142.2, 136.1, 132.3, 132.0, 131.0, 130.1, 123.9, 122.6, 122.1, 114.8, 106.3, 104.8, 102.6, 96.2,

95.7, 84.3, 68.6, 32.0, 29.6, 29.4, 29.3, 29.2, 26.0, 22.8, 14.8, 14.5, 14.2, 13.6, 13.2, 1.1 ppm.

HRMS (ESI) calcd for $C_{52}H_{71}BF_2N_2O_2SiNa$ (M+Na) 854.5280, found 854.5209. Δ=8.3 ppm.



Scheme 19. Synthesis of compound **50**

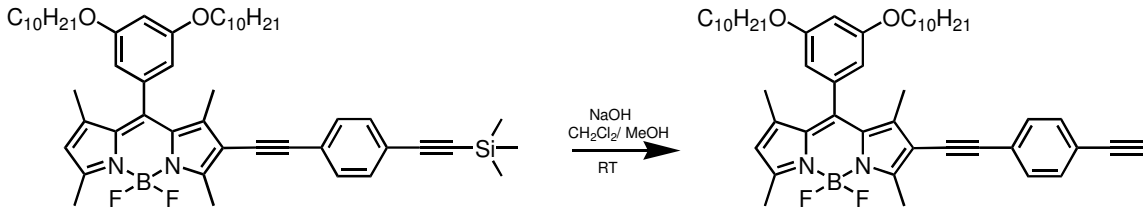
2.2.8 4-Ethynylbenzene ethynyl BODIPY (51)

Compound **50** (362 mg, 0.436 mmol) was dissolved in 10 mL CH_2Cl_2 and 10 mL MeOH. Then NaOH (174 mg, 4.36 mmol) was added and the reaction was stirred for 30 min at R.T. Then the reaction was finished by extracting with H_2O and CH_2Cl_2 3 times. The organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product is taken as a red solid without further purification in 95% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.32(dd, *J* = 8.4 Hz, 4H), 6.49 (s, 1H), 6.33 (d, *J* = 2.0 Hz, 2H), 5.96 (s, 1H), 3.85 (t, *J* = 6.5 Hz, 4H), 3.07 (s, 1H), 2.61 (s, 3H), 2.50 (s, 1H), 1.63 (m, 4H), 1.6 (s, 3H), 1.52 (s, 3H), 1.1-1.4 (m, 28H), 0.80 (t, *J* = 6.6 Hz, 6H)

^{13}C-NMR (100 MHz, $CDCl_3$, 300 K): δ = 161.2, 157.9, 156.3, 144.9, 142.6, 142.1, 136.0, 132.3, 132.0, 131.0, 129.9, 124.2, 122.0, 121.4, 114.6, 106.2, 102.5, 95.4, 84.3, 83.3, 78.7, 68.4, 31.8, 29.5, 29.36, 29.30, 29.1, 25.9, 22.6, 14.7, 14.4, 14.0, 13.5, 13.1 ppm.

HRMS (ESI) calcd for $C_{49}H_{63}BF_2N_2O_2Na$ (M+Na) 782.4885, found 782.4845. Δ=5.1 ppm.



50 **51**

Scheme 20. Deprotection of the silyl group

2.2.9 Mono iodo dimer BODIPY (52)

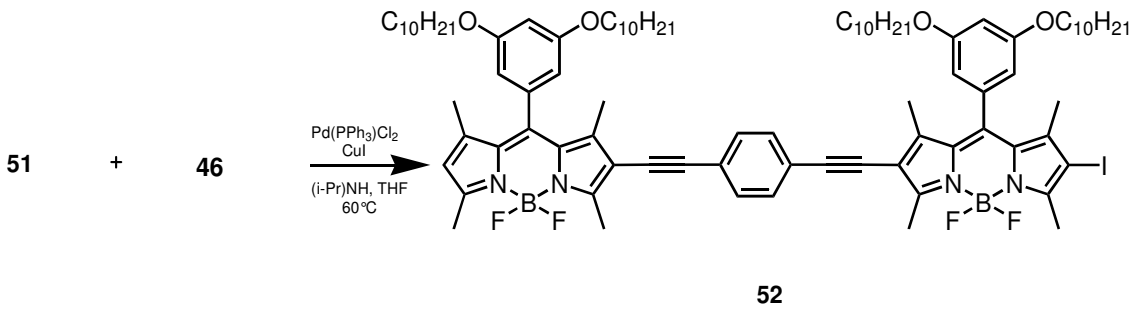
4-Ethynyl benzene ethynyl BODIPY **51** (78 mg, 0.103 mmol) and diiodo BODIPY **46** (91.1 mg, 0.103 mmol) were reacted according to the same Sonogashira protocol given above. Mono iodo dimer BODIPY was purified over silica gel using Chloroform/Hexane 1/1 as a red solid in 20% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.30 (s, 4H), 6.49 (m, 2H), 6.33 (dd, *J* = 6.9 Hz, 4H), 5.98 (s, 1H), 3.88 (t, *J* = 6.5 Hz, 8H), 2.62 (s, 6H), 2.58 (s, 3H), 2.50 (s, 3H), 1.68 (m, 8H), 1.60 (m, 6H), 1.52 (s, 6H), 1.1-1.4 (m, 56 H), 0.80 (t, *J* = 6.6 Hz, 12H)

^{13}C-NMR (100 MHz, $CDCl_3$, 300 K): δ = 160.3, 160.2, 157.4, 155.3, 141.6, 141.1, 135.0, 134.9, 131.2, 130.6, 130.13, 130.10, 129.0, 122.3, 121.7, 121.1, 115.0, 113.7,

111.2, 105.2, 105.1, 101.6, 101.5, 95.4, 94.6, 83.2, 82.4, 67.7, 30.8, 28.69, 28.65, 28.5, 28.3, 28.2, 28.1, 24.9, 21.6, 15.8, 13.7, 13.4, 13.0, 12.7, 12.5, 12.3.

MS (MALDI) calcd for $C_{88}H_{119}B_2F_4IN_4O_4$ 1520.8398, found 1519.995.



52

Scheme 21. Coupling reaction of **51** and **46**

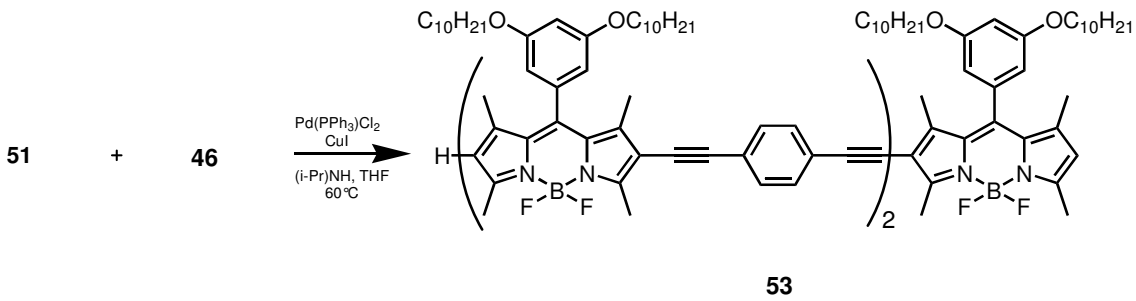
2.2.10 Trimer BODIPY (53)

Trimer BODIPY was also synthesized with this reaction and purified as a purple solid in 40% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.30 (s, 8H), 6.49 (m, 3H), 6.35 (d, *J* = 1.9 Hz, 6H), 5.96 (s, 2H), 3.38 (t, *J* = 6.2 Hz, 12H), 2.63 (s, 6H), 2.61 (s, 6H), 2.50 (s, 6H), 1.70 (m,12H), 1.62 (s, 6H), 1.58 (s, 6H), 1.52 (s, 6H), 1.1-1.4 (m, 84H), 0.80 (t, *J* = 5.1 Hz, 18H)

^{13}C-NMR (100 MHz, $CDCl_3$, 300 K): δ = 160.3, 160.2, 157.3, 156.7, 155.3, 143.8, 141.6, 141.0, 135.0, 131.2, 130.6, 130.0, 129.0, 122.2, 121.7, 121.0, 114.9, 113.8, 105.2, 101.4, 95.4, 94.7, 83.2, 82.5, 30.8, 28.6, 28.5, 28.3, 28.2, 28.1, 24.9, 21.6, 13.7, 13.4, 13.0, 12.6, 12.5, 12.3, 12.0 ppm.

MS (MALDI) calcd for $C_{137}H_{181}B_3F_6N_6O_6$ 2153.42, found 2152.685.



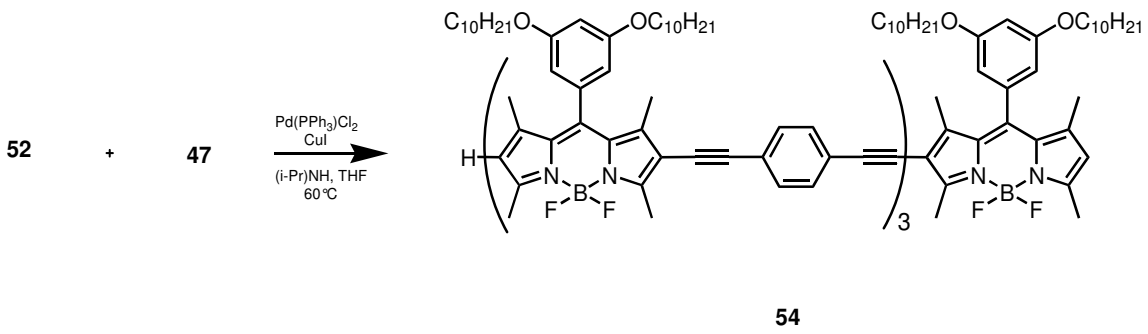
Scheme 22. Synthesis of Trimer BODIPY

2.2.11 Tetramer BODIPY (54)

52 (30 mg, 0.0197 mmol) and diethynyl benzene **47** (1.13 mg, 0.090 mmol) were reacted according to the above Sonogashira reaction. The product was purified over silica gel using Chloroform/Hexane 3/1 as a purple solid in 25% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.25 (s, 12H), 6.49 (m, 4H), 6.38 (m, 8H), 5.92 (s, 2H), 3.88 (m, 16H), 2.45-2.65 (m, 24H), 1.7 (m, 16H), 1.42-1.6 (m, 24H), 1.1-1.4 (m, 112H), 0.81 (m, 24H) ppm.

MS (MALDI) calcd for $C_{186}H_{242}B_4F_8N_8O_8$ 2911.9, found 2911.900.



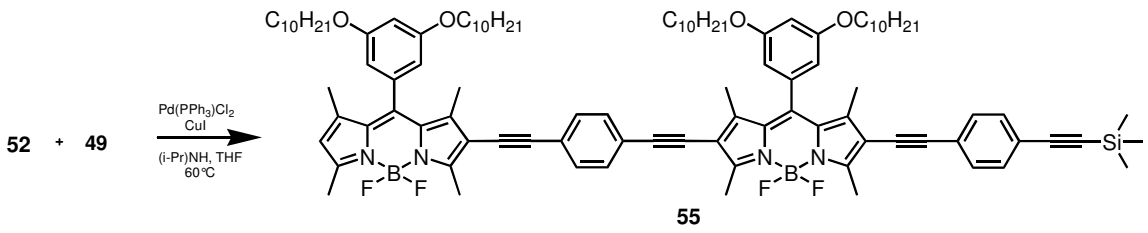
Scheme 23. Synthesis of Tetramer BODIPY

2.2.12 Mono 4-TMS protected Ethynyl Benzene Dimer Bodipy (55)

Mono iodo dimer BODIPY **52** (90 mg, 0.06 mmol), 4-trimethylsilylacetylene ethynyl benzene **49** (17.85 mg, 0.09 mmol) were reacted according to the above Sonogashira reaction. The product was purified over silica gel using Chloroform/Hexane 3/1 as a purple solid in 70% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.3 (m, 8H), 6.5 (m, 2H), 6.35 (m, 4H), 5.98 (s, 1H), 3.88 (m, 8H), 2.63 (s, 6H), 2.61 (s, 3H), 2.5 (s, 3H), 1.7 (m, 8H), 1.62 (s, 6H), 1.60 (s. 3H), 1.51 (s, 3H), 1.1-1.4 (m, 56H), 0.8 (m, 12H), 0.29 (s, 9H)

^{13}C-NMR (100 MHz, $CDCl_3$, 300 K): δ = 161.3, 161.2, 158.5, 158.3, 158.0, 157.7, 156.3, 144.9, 144.3, 142.7, 142.6, 142.1, 136.0, 135.7, 131.8, 131.1, 131.0, 130.9, 123.4, 123.3, 122.7, 122.6, 106.1, 106.0, 104.6, 102.6, 96.4, 96.2, 95.6, 84.2, 83.7, 83.5, 68.49, 68.45, 31.8, 29.54, 29.53, 29.35, 29.30, 29.1, 25.9, 22.6, 14.4, 14.0, 13.7, 13.3, 13.1, 1.0.



Scheme 24. Coupling reaction of **52** and **49**

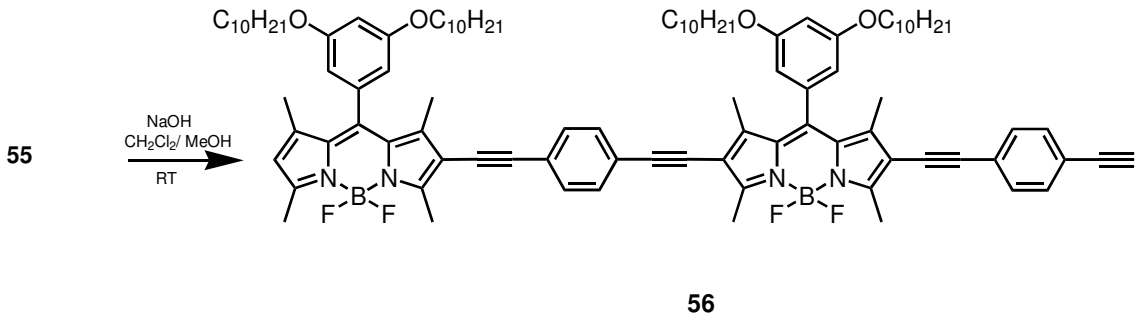
2.2.13 Mono ethynyl benzene dimer bodipy(56)

55 (40 mg, 0.025 mmol) was dissolved in 10 mL CH_2Cl_2 and 10 mL MeOH. Then NaOH (10 mg, 0.25 mmol) was added and the reaction was stirred for 30 min at R.T. Then the reaction was finished by extracting with H_2O and CH_2Cl_2 3 times. The organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product is taken as a red waxy solid without further purification in 95% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.28-7.39 (m, 8H), 6.45-6.50 (m, 2H), 6.34 (m, 4H), 5.93 (s, 1H), 3.85 (m, 8H), 2.62 (s, 6H), 2.60 (s, 3H), 2.49 (s, 3H), 1.68 (m, 8H), 1.60 (s, 6H), 1.58 (s, 3H), 1.49 (s, 3H), 1.1-1.4 (m, 56H), 0.78 (m, 12H)

^{13}C-NMR (100 MHz, $CDCl_3$, 300 K): δ = 161.3, 161.2, 158.7, 158.3, 157.7, 156.3, 145.0, 144.2, 144.0, 142.7, 142.5, 142.2, 136.0, 135.5, 132.0, 131.07, 131.05, 123.9, 123.3, 122.7, 122.4, 121.6, 106.19, 106.10, 102.6, 102.4, 96.5, 96.0, 95.7, 84.3, 83.8, 83.5, 83.3, 78.9, 68.48, 68.44, 31.8, 29.55, 29.54, 29.36, 29.30, 29.1, 25.9, 22.6, 14.7, 14.4, 14.1, 13.7, 13.4, 13.3, 13.1.

MS (MALDI) calcd for $C_{98}H_{124}B_2F_4N_4O_4$ 1518.9745, found 1518.158.



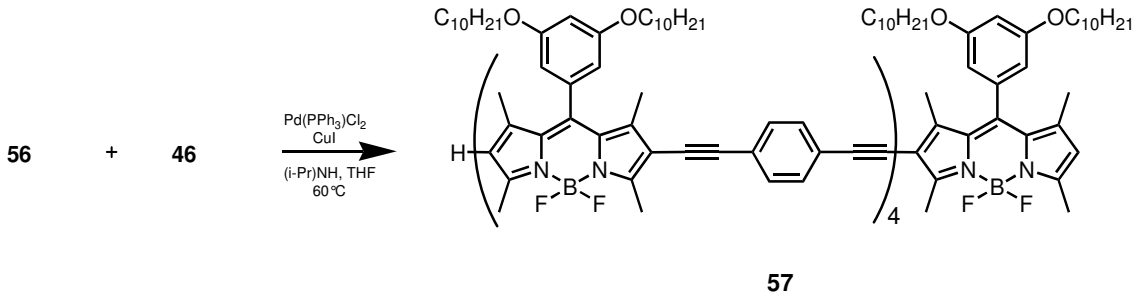
Scheme 25. Deprotection of silyl groups in **55**

2.2.14 Pentamer BODIPY(57)

56 (44 mg, 0.029 mmol), diiodo-BODIPY **46** (12.9 mg, 0.0145 mmol) were reacted according to the above Sonogashira reaction. The product was purified over silica gel using 3/1 Chloroform/Hexane as a purple solid in 30 % yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.35-7.1 (m, 16H), 6.25-6.50 (m, 15H), 5.85 (s, broad, 2H), 3.85 (m, 20H), 2.40-2.68 (m, 30H), 1.50 (m, 20H), 1.10-1.53 (m, 170H), 0.81 (m, 30H).

MS (MALDI) calcd for $C_{235}H_{303}B_5F_{10}N_{10}O_{10}$ 3670.38, found 3672.484.



Scheme 26. Synthesis of pentamer BODIPY

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Perspective of the Project

In the study we have synthesized a series of BODIPY dyes which show different spectroscopic properties. The molecules have oligomeric structures. The structures contain two building blocks; the BODIPY unit and the benzene moiety (Figure 1). By using these oligomers with different lengths have been synthesized. The longest oligomeric serie contains five BODIPY units and four benzene units. The units are arranged alternately and they have been connected each other with acetylenes.

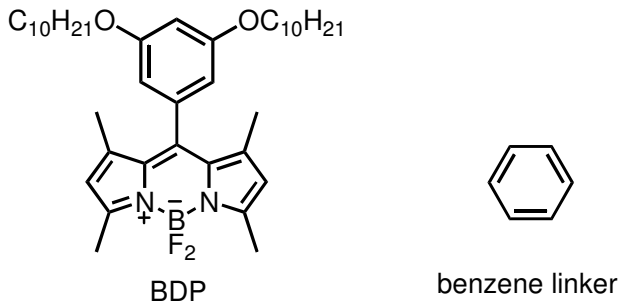
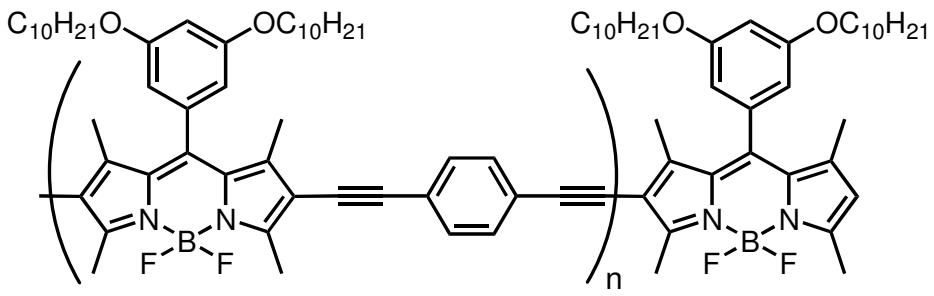


Figure 15. Building blocks used for constructing target oligomers

The synthesized molecules are shown in the Figure 2. The molecules are desired to be connected each other electronically. Hence, in the synthesis acetylenes were used in order to set up the conjugated system.



n	0	1	2	3	4
molecule	**44**	**48**	**53**	**54**	**57**

Figure 16. The target oligomers synthesized

As seen in the scheme the synthesized molecules are from n=0 to n=4. The aim of the project is to synthesize molecular series having long absorption and emission wavelength maxima. These properties were examined and the results were compared with each other and the molecules in the literature.

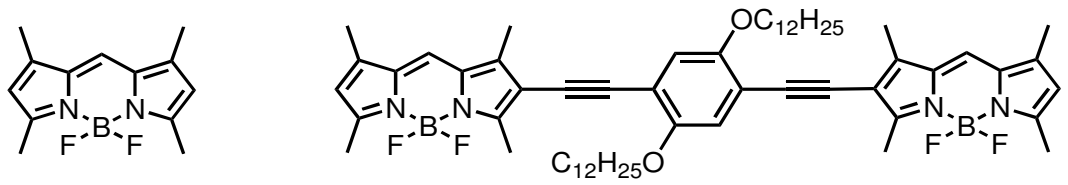
It is seen in the research that as the length of molecule increases there occur some problems. One problem is the synthetic design. A careful plan should be done prior to start the synthesis. As will be told in the synthesis part, mainly Sonogashira coupling was used along the synthesis to connect the building blocks. The other problem is the solubility problem which is surpassed by attaching long alkyl chain groups.

3.2 Synthesis of the Novel Oligomeric Series

1.1.1 Design of BODIPY core

For the aim of the project we tried to extend the π- electrons` conjugating in the molecule. For this purpose we thought to use acetylene bridges. However, direct connecting of the BODIPYs without using benzene linkers is not possible. Because, the acetylenes directly linked to the pyrrole is not stable and easily decomposes when treated with a base during deprotecting the silyl group. Hence, we used benzene linkers between BODIPYs.

The other important task which we ignored in the earlier times of the project was the solubility. As the chain length increases it causes us to hardly dissolve the molecule in common organic solvents. Because of this previously considered BODIPY molecule **58** was improper. Due to this fact, we are obliged to redesign the molecule. As seen in the molecular structures, long alkoxy chains were substituted to the system in order enhance the solubilities in organic solvents. Though, in the earlier stages of the project, we have positioned the alkoxy chains on the benzene moieties. Accordingly, we have seen that is not the correct way since the molecule has a solubility problem even the chain is short. The dimer molecule **59** has been synthesized barely by this route. Moreover, in order to dissolve a 5 mg of sample we needed to use at least 2-3 ml chloroform illustrating that the solubility is quiet low. Subsequently, we tried to attach the long alkyl chains on the BODIPY core, not on benzene. As a result, we have seen that this is the correct design since the solubility is not a problem to any further extent.



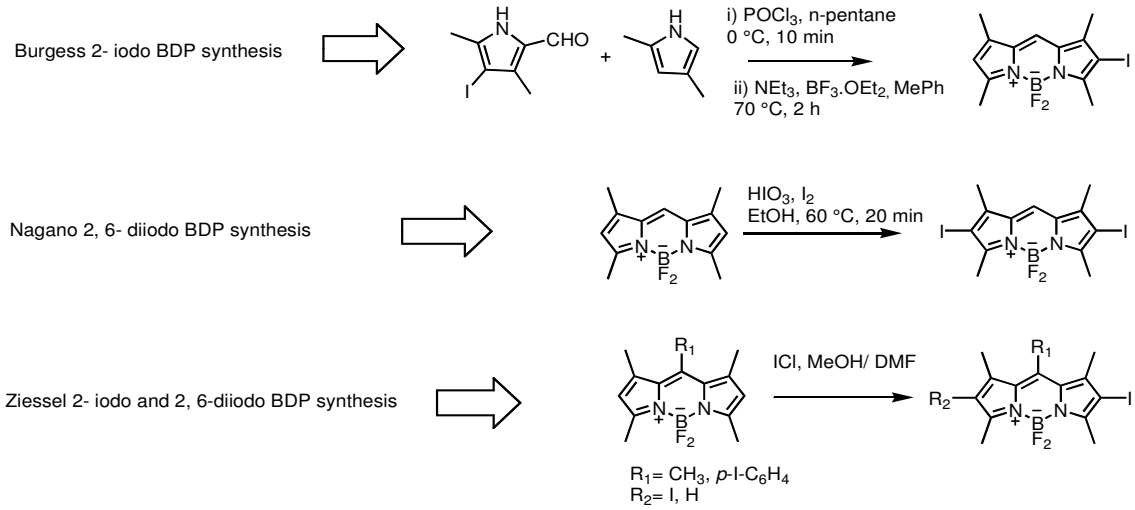
58 **59**

Figure 17. The 8-H tetramethyl BDP **58** and previously synthesized dimer BDP **59**

1.1.2 Halogenation of BODIPY molecule

The first thing after synthesizing BODIPY is substituting it with a halogen in order for it to be ready for metal catalyzed coupling reactions. The iodine is used throughout the project for halogenations. There are two reasons for this. The first reason is, iodination has a high yield, almost quantitative. The second reason is that the coupling reaction with iodine is easier than bromine or chlorine, can be completed in high yields at ambient temperatures.

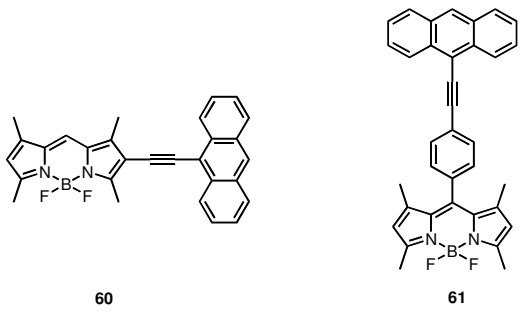
In literature, there are three known procedures for iodination of BODIPY from 2- and 6- positions. First, Burgess and co-workers has synthesized the 2- iodo BODIPY by starting with the 4-iodopyrrolecarbaldehyde.[55] Later, Nagano and co-workers synthesized 2,6-diiodo BODIPY by using HIO_3 and I_2.[53] Recently, another iodination procedure was revealed by the Ziessel group.[54] They have iodinated the BODIPY by ICl . Throughout the project all of them were tried by us, and we have decided to use the procedure of Nagano. Because the yield is quantitative in 2,6- diiodo BODIPY synthesis and 70% in 2- iodo BODIPY synthesis. Moreover, the reaction time is quite shorter than other procedures.



Scheme 27. Reaction methods reported in order get iodo BDPs

1.1.3 Sonogashira Couplings

As told before, the main reaction used for synthesis is the Sonogashira coupling. This type of reaction was first studied in connection with the BODIPY by the Burgess and co-workers.[55] In this study they have synthesized the coupling reaction to the 2- and 6-positions of the BODIPY and to the phenyl ring in the meso position of the BODIPY (Figure 4). In our project the positions we have studied are the 2- and 6-.



60 61

Figure 18. Previously synthesized Sonogashira coupling BDP products

The reaction yield is very important in our project. Thus, we tried so many reaction conditions. As a palladium source we have tried $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$. The last one is the one which is used mostly in the literature, but it has the drawback of decomposing easily. Since, the oxidation number of palladium is zero in that reagent it readily oxidizes in the presence of air. Due to this reason, we had some problems. Hence, we decided to use the $Pd(PPh_3)_2Cl_2$, which is stable in air. However, this reagent also has a disadvantage; it causes to yield acetylene-acetylene coupling by-product which decreases the yield. But, by optimizing the conditions we could reach 70-80 % yields in Sonogashira coupling reactions.

The other thing we have optimized is the molarity of the reaction. By using easily soluble compounds we could increased the density of the reaction by using minimum amount of THF as a solvent, so the both the reaction time and yield have increased.

3.3 Spectroscopic Properties

After synthesizing target compounds **44**, **48**, **53**, **54**, and **57** the photophysical properties were investigated. First, we measured the absorption and emission characteristics. The results indicate that as the conjugation of the π electrons in the system increase the absorption and the emission maxima shifts to the longer wavelength part of the electromagnetic spectrum (bathochromic shift, Figure 5). However, this trend does not follow in all the molecules we have synthesized. After a certain length the system is saturated and there will be no change in the spectroscopic characteristics of the molecules.

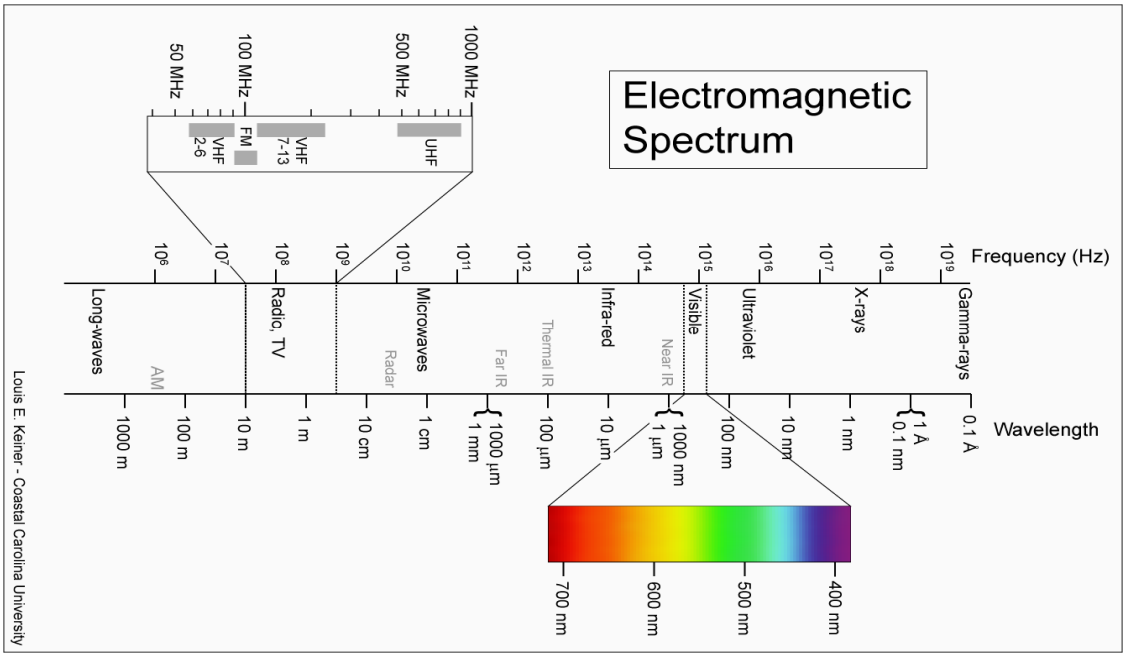


Figure 19. Electromagnetic Spectrum

The spectroscopic properties of the synthesized molecules have been shown in the table below. When we look at the table it is seen that the absorbance λ_{max} is increases up to tetramer **54**. After that the absorbance value does not increase, the tetramer **54** and the pentamer **57** have nearly the same absorbance λ_{max}.

Table 2. Spectroscopic and Photopysical Properties of the Novel Oligomeric Series

Compounds	**Absorbance λ_{max}**	**Emission λ_{max}**	**Quantum Yield Φ**	**Extinc. Coeff. (ε)**
Monomer 44	503 nm	512 nm	0.60	95359
Dimer 48	551 nm	586 nm	0.39	68998
Trimer 53	579 nm	621 nm	0.45	103774
Tetramer 54	597 nm	624 nm	0.60	117953
Pentamer 57	592 nm	620 nm	0.58	251256

The emission λ_{max}`s are showing nearly the same properties with the absorbance $\lambda_{max}$`s. However, the saturation point is earlier. The emission wavelength maxima increase up to trimer **53**. In the table it is seen clearly that; trimer **53**, tetramer **54** and the pentamer **57** have nearly the same emission λ_{max}.

Actually, these results are usual. The OPV and OPE series which were told in the introduction chapter show the same saturation characteristic. For instance the absorbance λ_{max} values (in nm) of consecutive series are: 338, 378, 399, 412, 419. These data show also that as the conjugation increases there is a drop in the increase of λ_{max} values.

The graphs of absorbance and emission of the compounds are given below. The graphs show that the peaks are narrow and sharp.

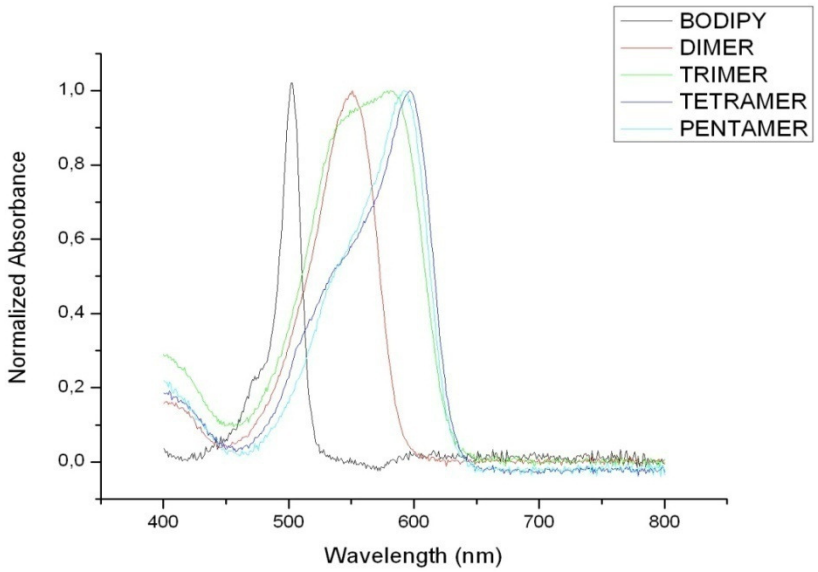


Figure 20. Normalized absorption λ_{max} of the novel oligomers

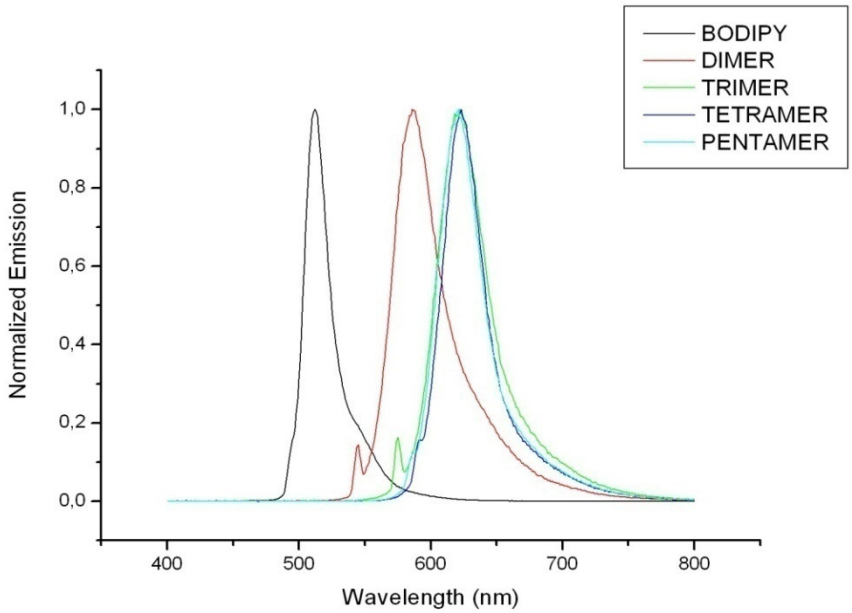


Figure 21. Normalized emission λ_{max} of the novel oligomers

The quantum yields were also calculated for the synthesized compounds. Fluorescein dye was used in order to measure the quantum yield of monomer **44**, Rhodamine 6G was used for dimer **48**, and Sulforhodamine 101 hydrate was for trimer **53**, tetramer **54** and pentamer **57**. The results show that the quantum yields are quiet high. By comparison monomer, tetramer and pentamer have the higher quantum yields than the dimer and trimer.

The extinction coefficients were also investigated by using the Beer-Lambert`s equation; A=ε.b.c. The results show that newly synthesized molecules have high extinction coefficients. When looking to the table for discussing the structure-extinction coefficient relationship, we see that there are three types of molecules in the serie. The monomer BODIPY **44** has a unique structure with ε= 95000. The dimer **48** and tetramer **54** are structurally similar. When taking into account these two we see that tetramer has nearly doubles the ε of dimer; 69000 for dimer, 118000 for tetramer. This trend is also true for the other similar compounds trimer **53** and pentamer **57**. The trimer molecule has ε value of 104000, while pentamer has 251000.

CHAPTER 4

CONCLUSION

Novel phenylethynyl-BODIPY oligomers have been designed and synthesized successively. The oligomers contain up to five BODIPY and four phenylethynyl units. The series contain totally 5 molecules. The spectroscopic and photophysical properties of these have also been investigated by comparing each other. As a result, it is seen that as the π- conjugation of the molecules increase, the molecules` absorption and emission wavelength maxima shifts to the red end of the visible region in electromagnetic spectrum. However, it is observed that as the length of the molecule increase, this shift becomes smaller. In absorption wavelength maxima the system reaches to saturation in tetramer **54**, and in emission wavelength maxima the saturation point is in trimer **53**. These results are in parallel with the literature values investigated for the long chain OPEs and OPVs.

In the design of the monomers we noted some important things. One of them is the solubility problem. Long alkyl chains permit us to dissolve the molecules in most organic solvents easy even the molecule is pentamer **57**. Substituting these chains on the phenyl ring in the meso position of the BODIPY was the correct turn, since substitution on the phenylethynynlenes is problematic. Moreover, the Sonogashira coupling to the BODIPY core was applied in high yields and it is standardized. In addition, different strategies of Sonogashira coupling in order acquire long chains have been applied effectively.

In conclusion novel bright dyes with high extinction coefficients and quantum yields have been synthesized. These dyes can function as useful building blocks in supramolecular chemistry and materials science.

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APPENDIX A

NMR SPECTRA

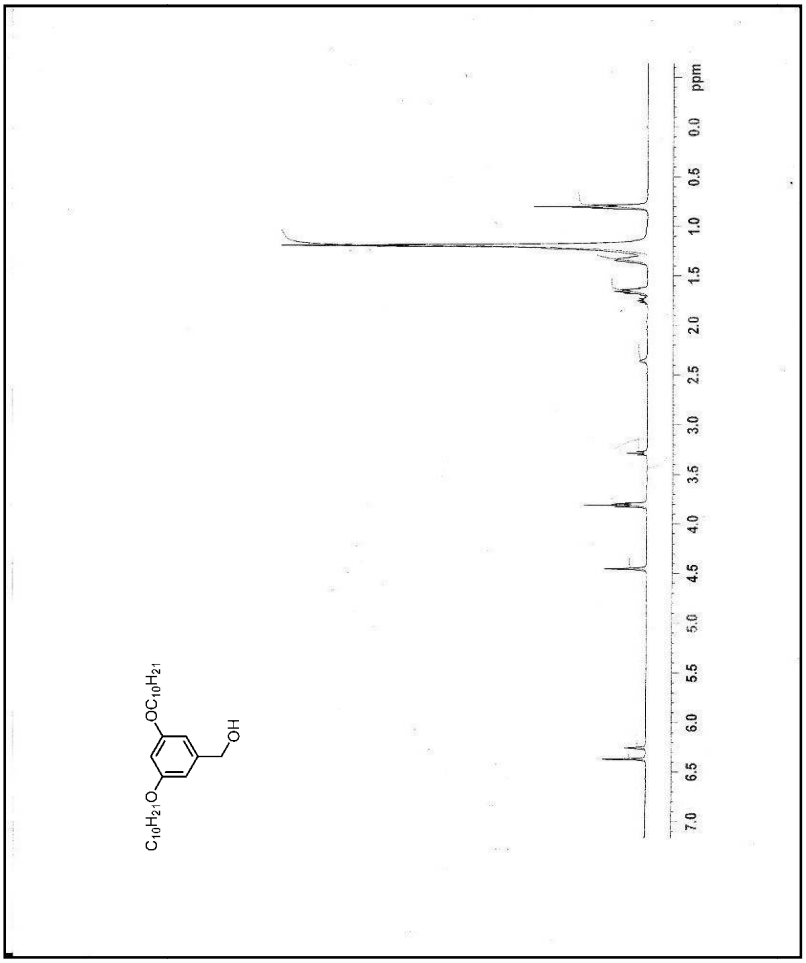

Figure 22. ^{1}H NMR spectrum of compound **41**

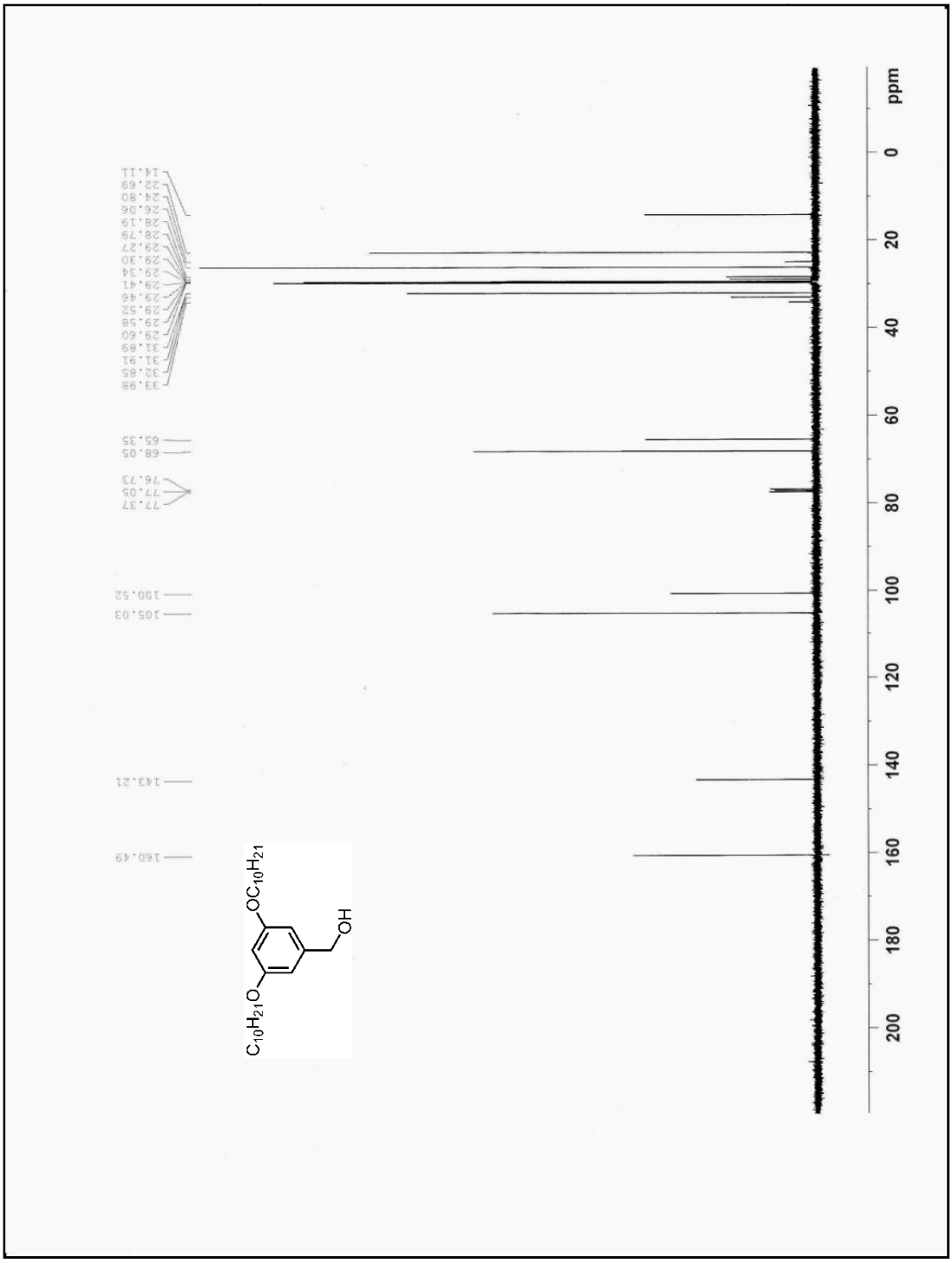

Figure 23. ^{13}C NMR spectrum of compound **41**

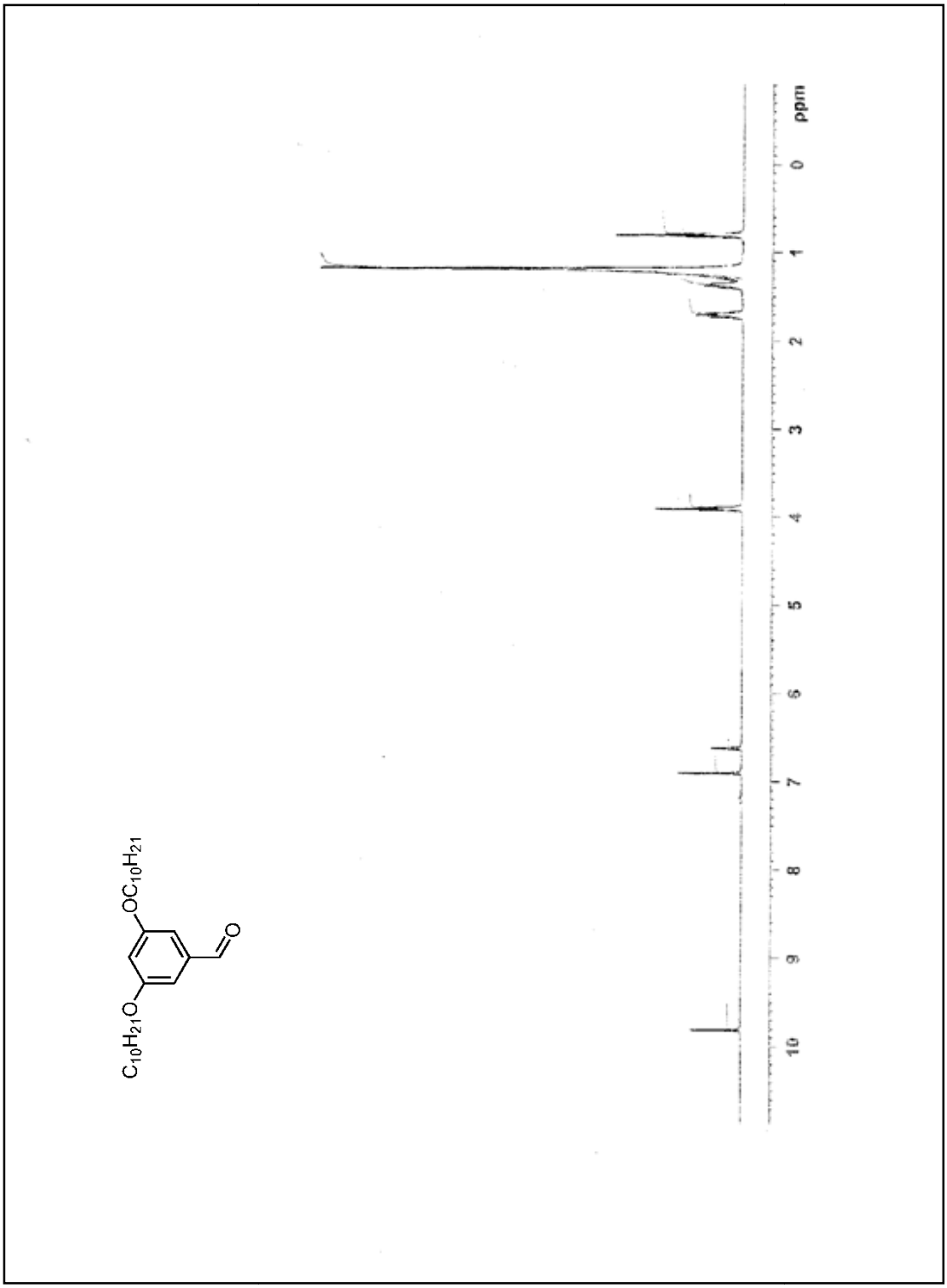

Figure 24. ^{1}H NMR spectrum of compound **42**

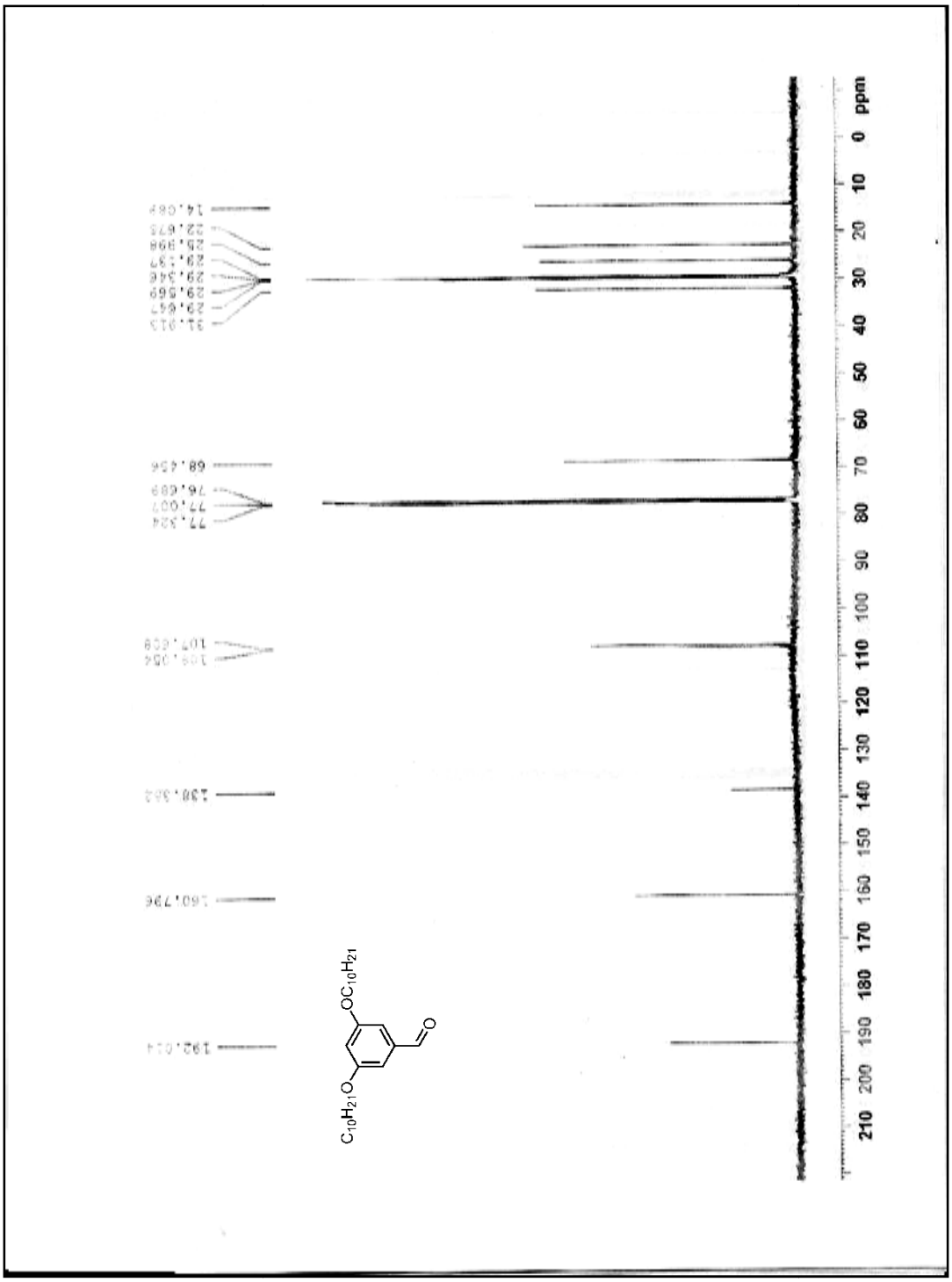

Figure 25. ^{13}C NMR spectrum of compound **42**

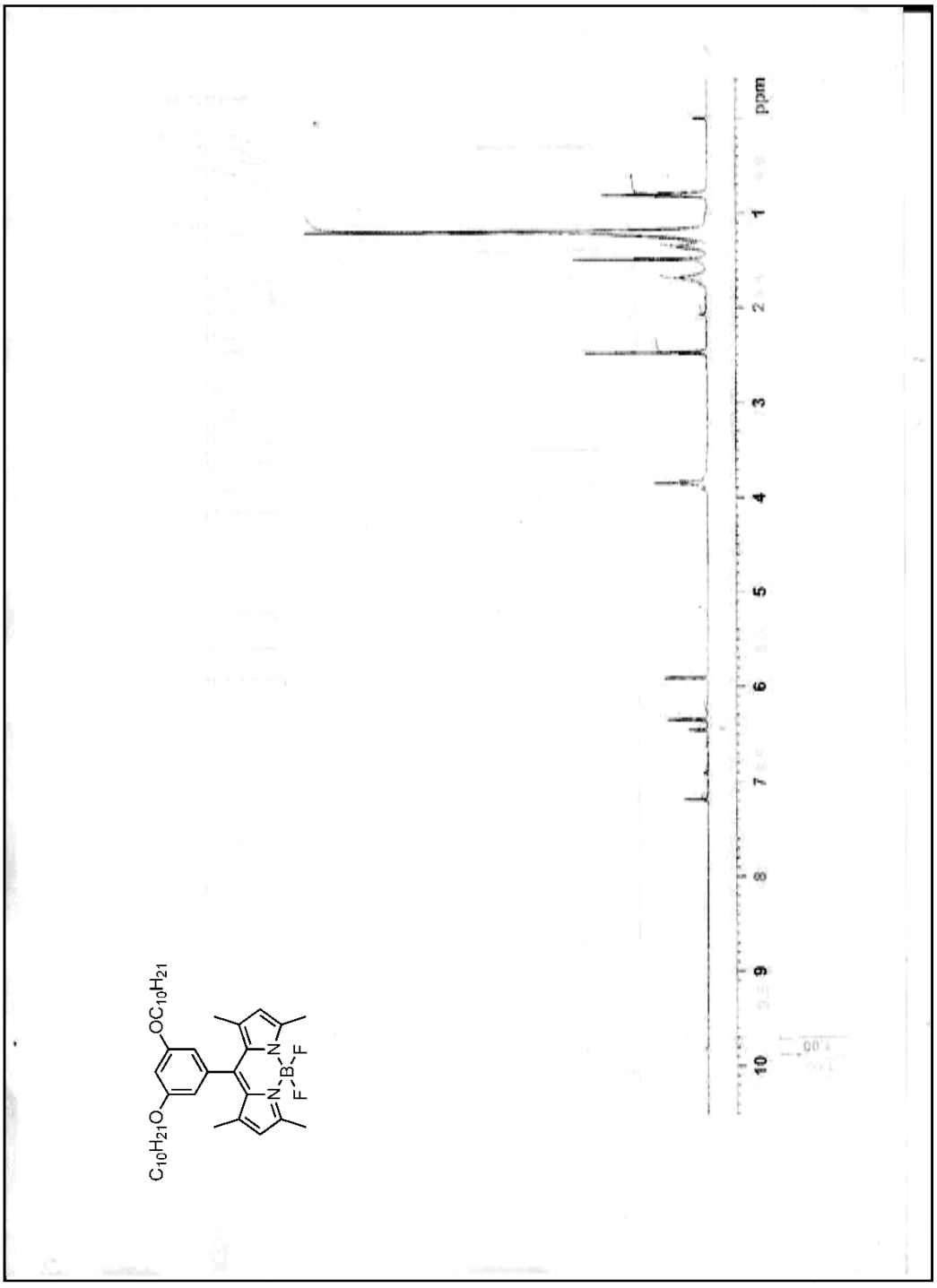

Figure 26. ^{1}H NMR spectrum of compound **44**

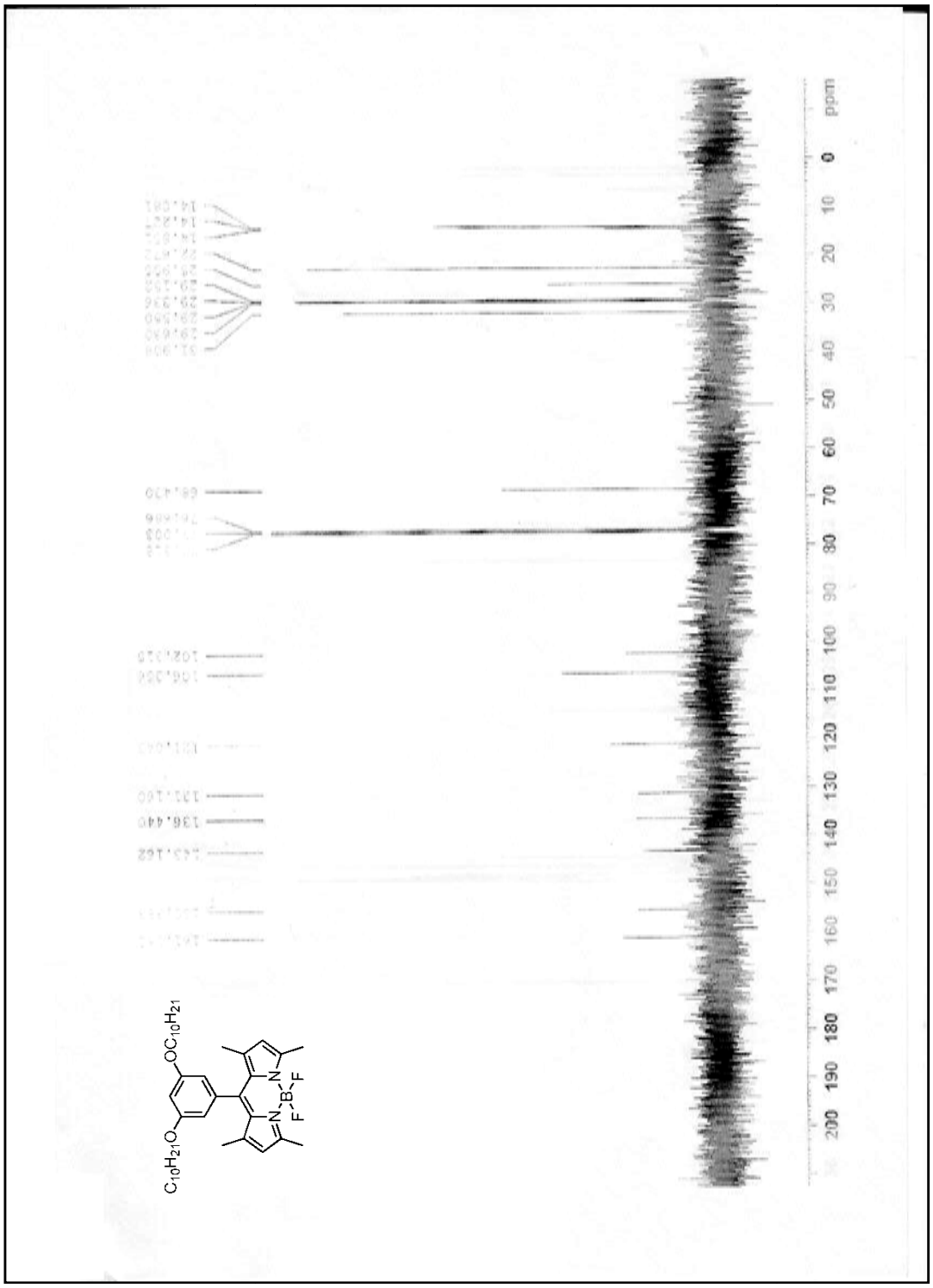

Figure 27. ^{13}C NMR spectrum of compound **44**

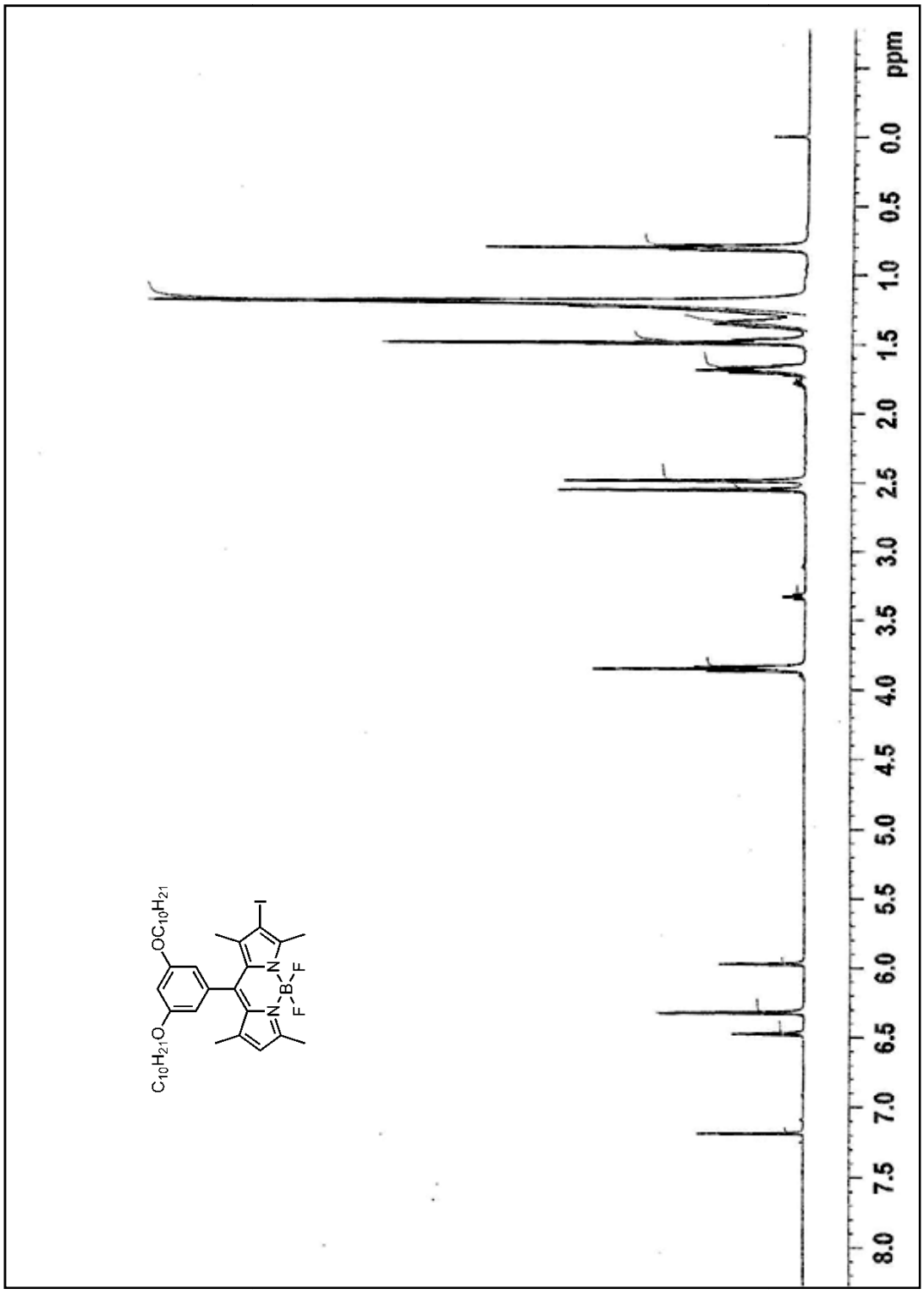

Figure 28. ^{1}H NMR spectrum of compound **45**

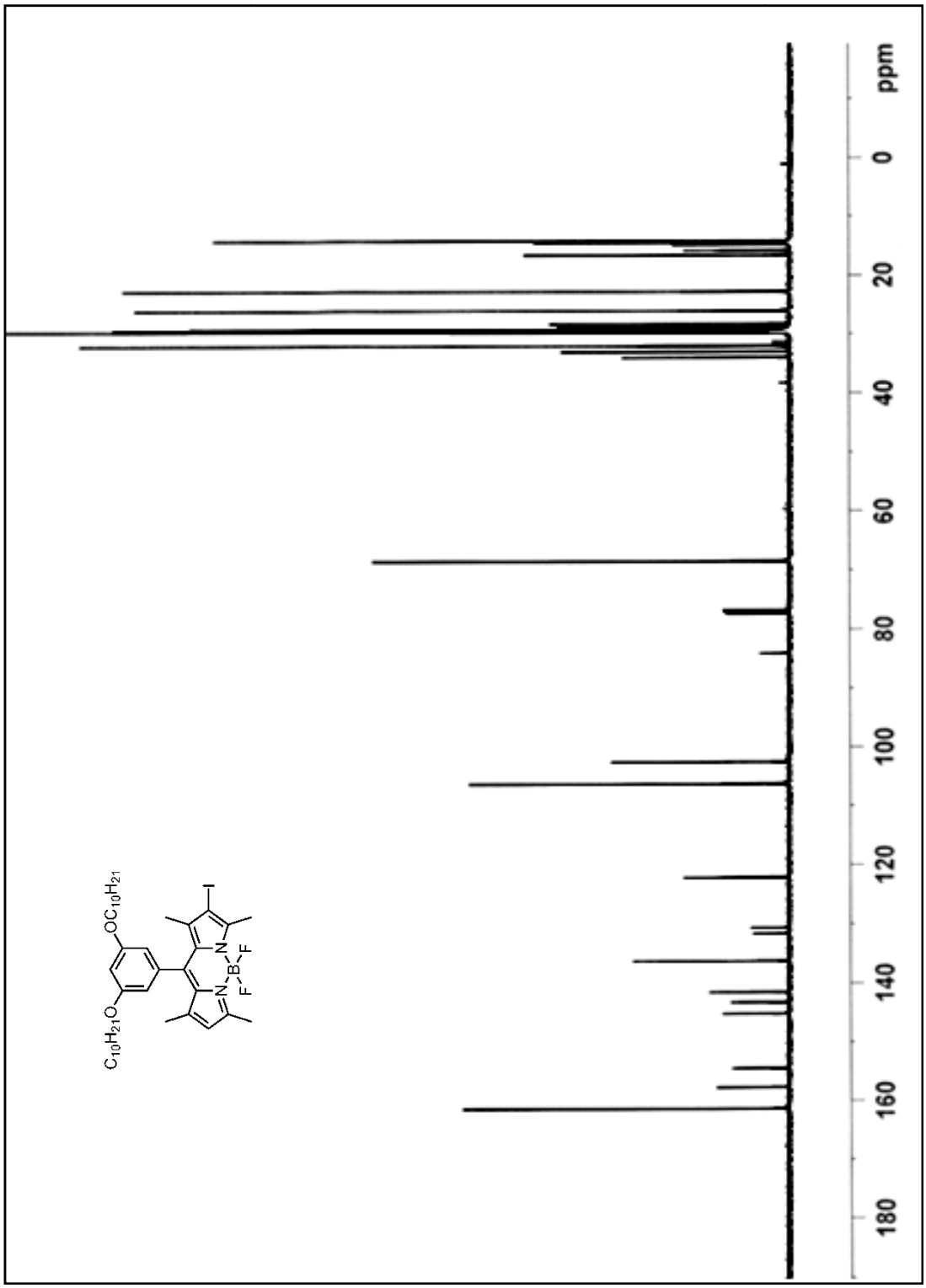

Figure 29. ^{13}C NMR spectrum of compound **45**

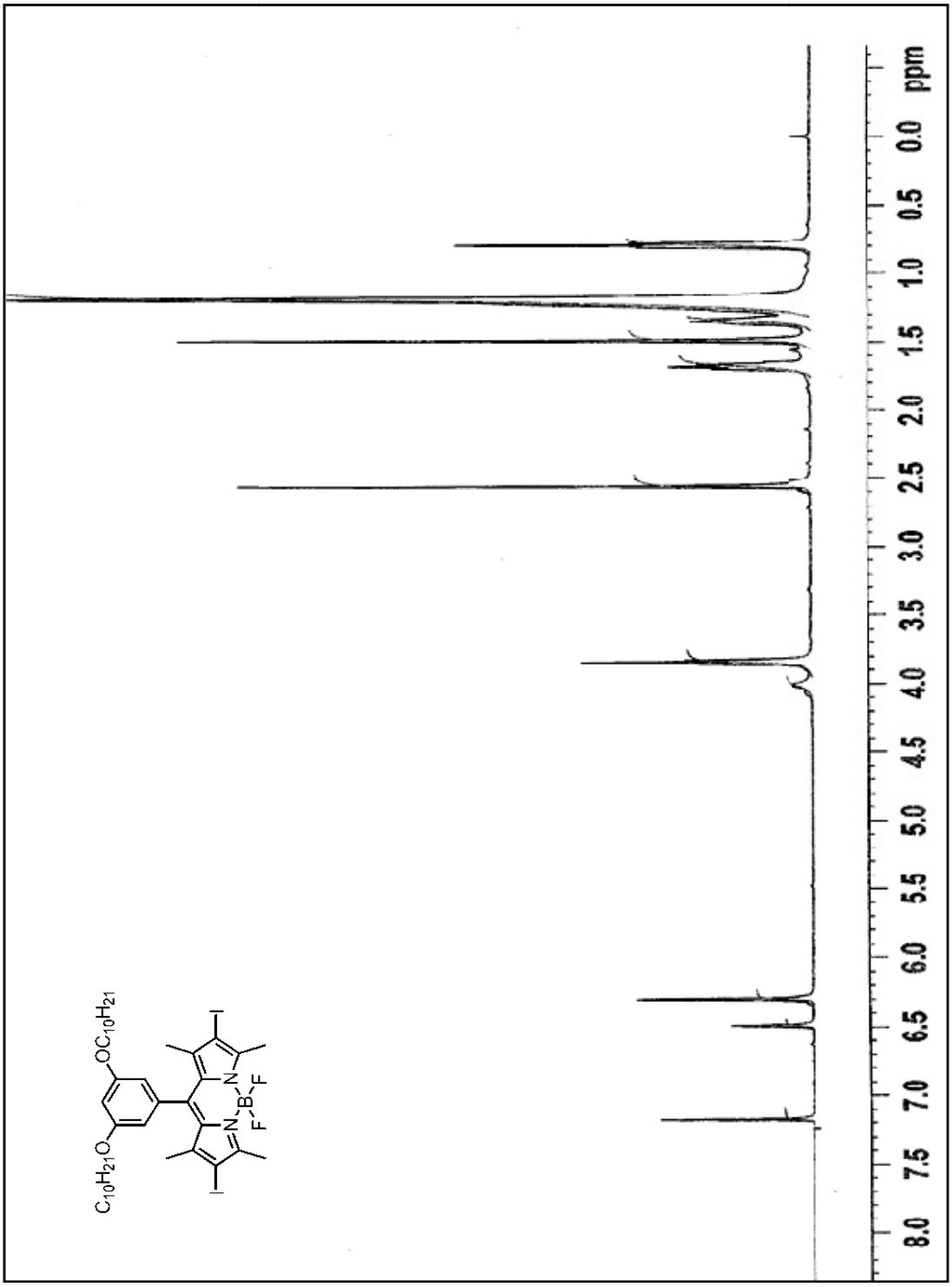

Figure 30. ^{1}H NMR spectrum of compound **46**

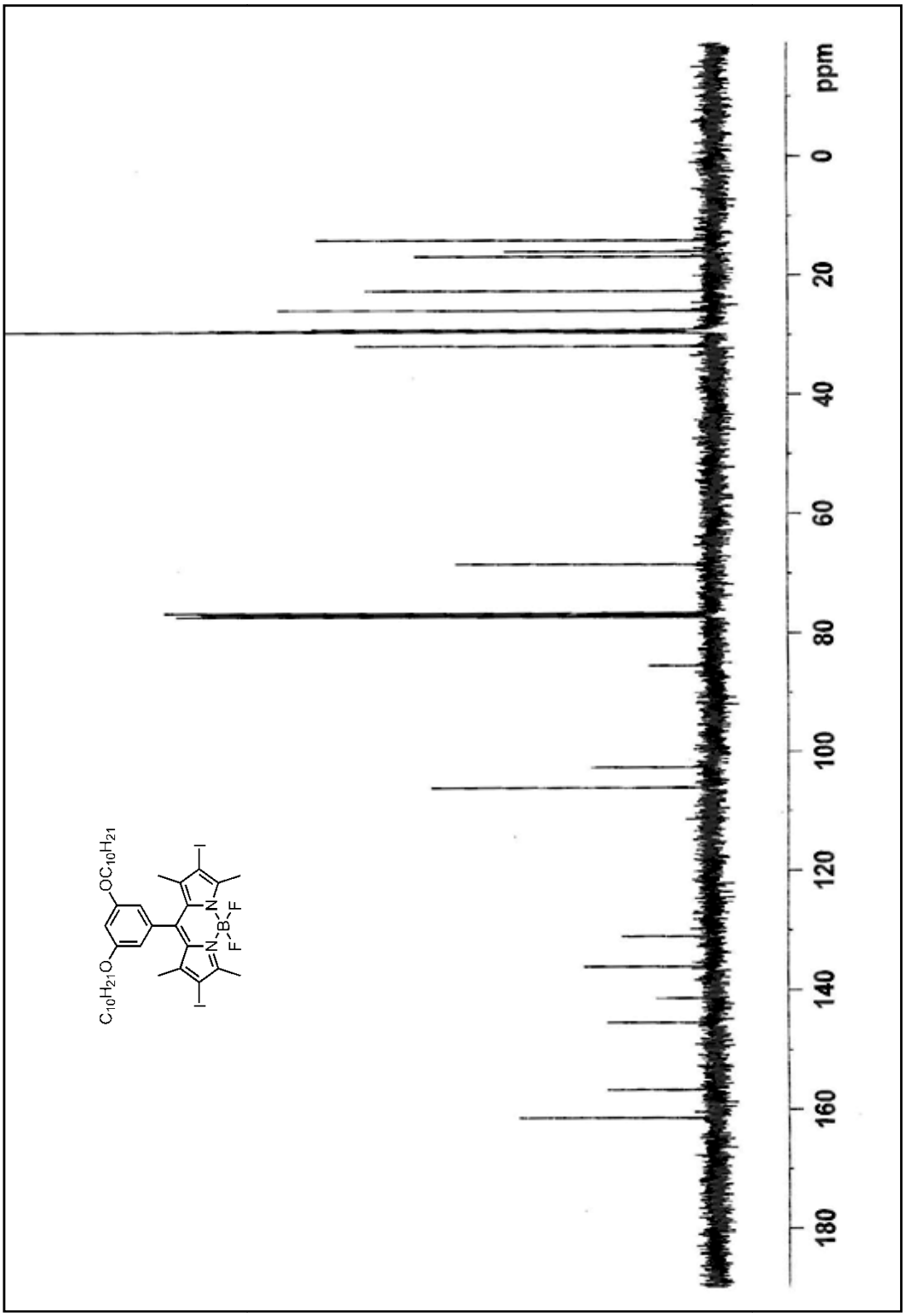

Figure 31. ^{13}C NMR spectrum of compound **46**

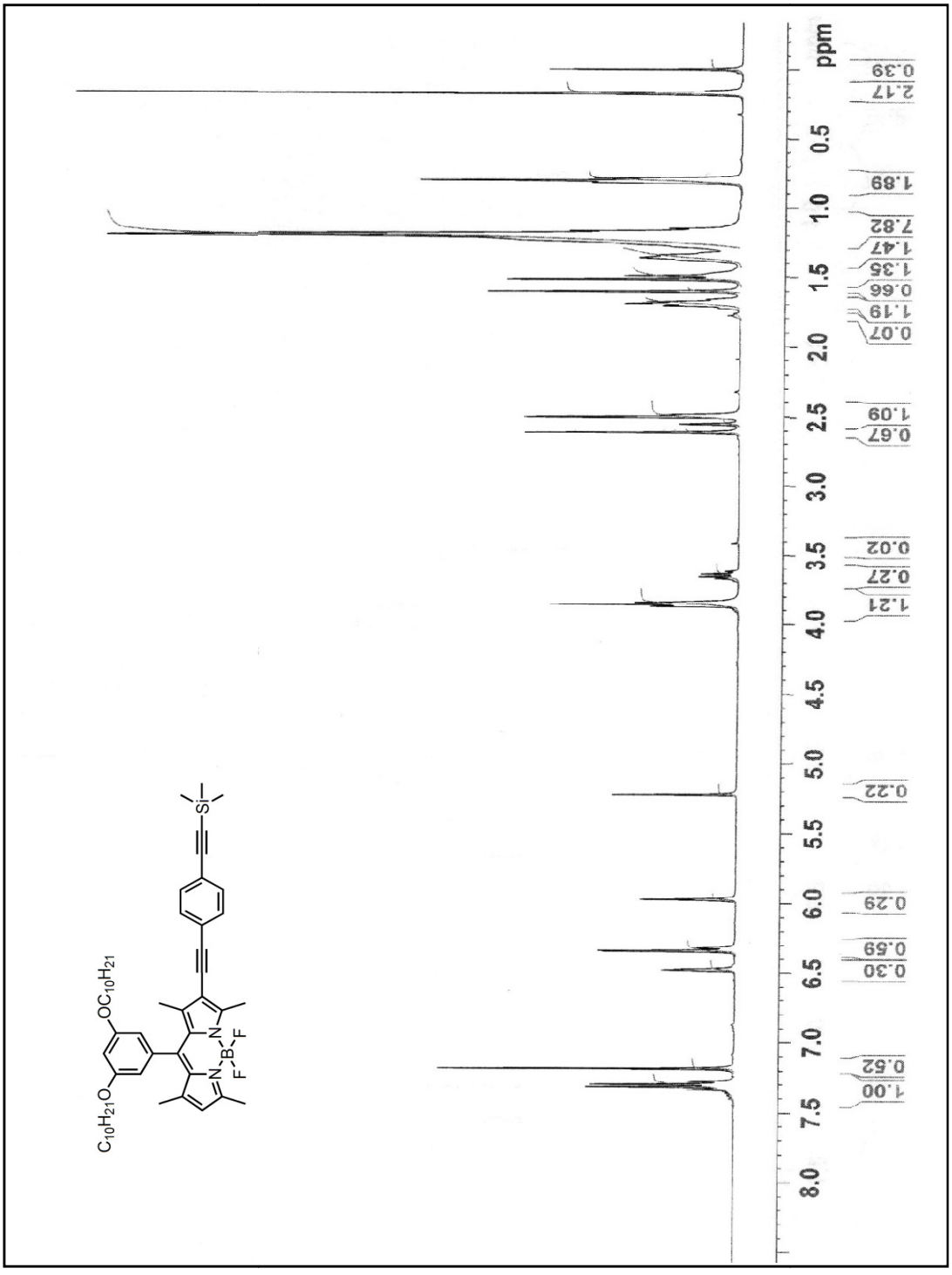

Figure 32. ^{1}H NMR spectrum of compound **50**

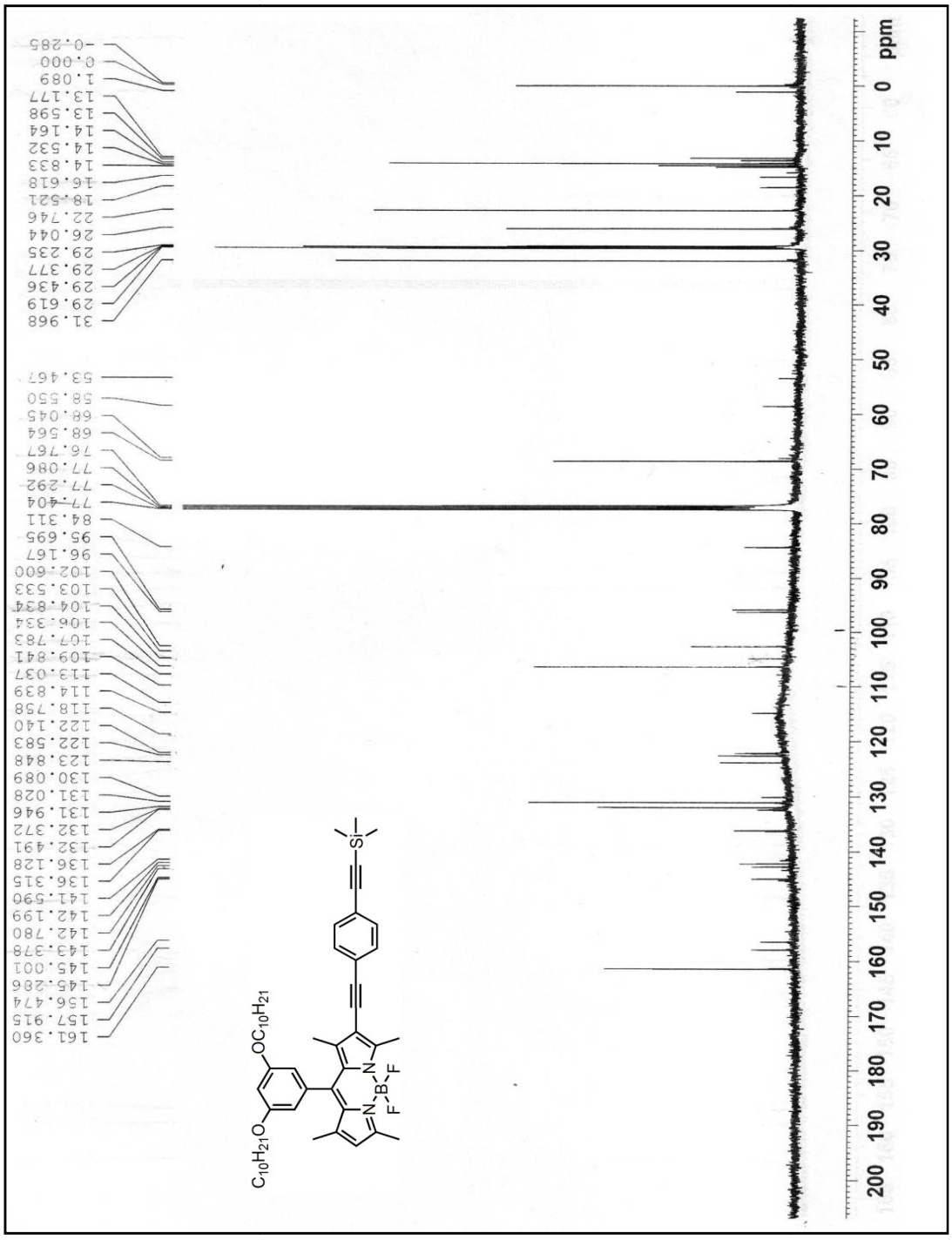

Figure 33. ^{13}C NMR spectrum of compound **50**

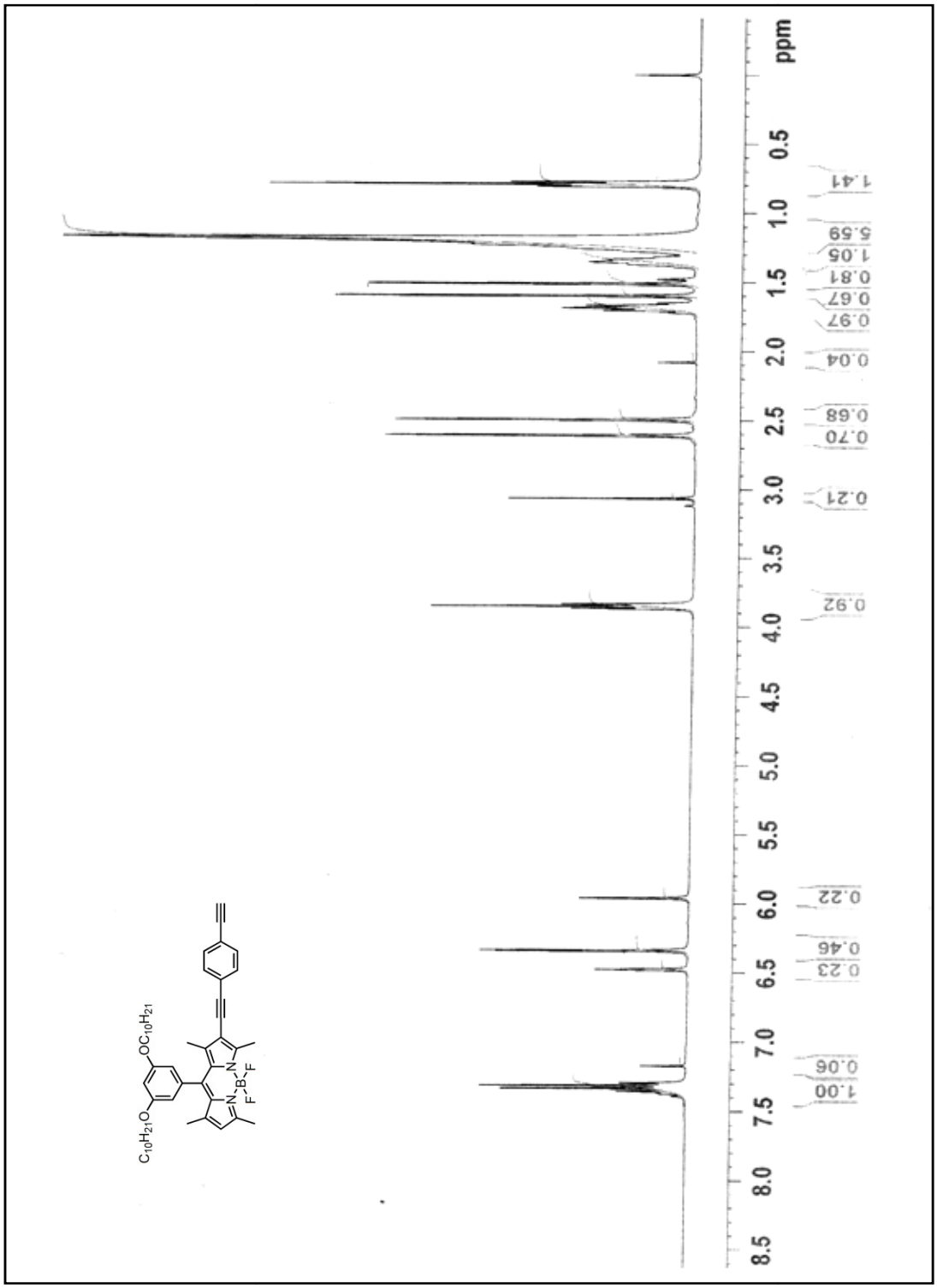

Figure 34. [1]H NMR spectrum of compound **51**

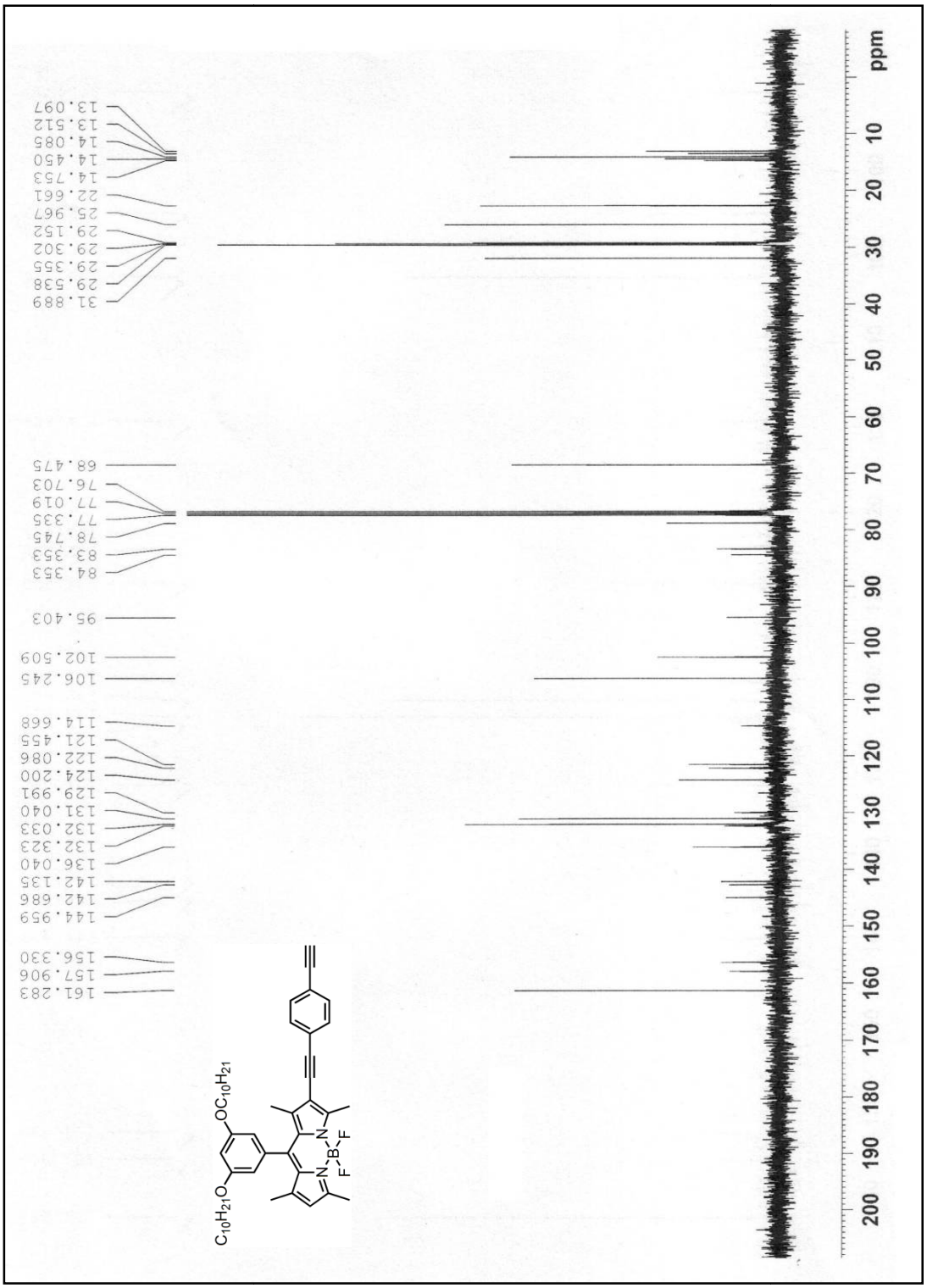

Figure 35. ^{13}C NMR spectrum of compound **51**

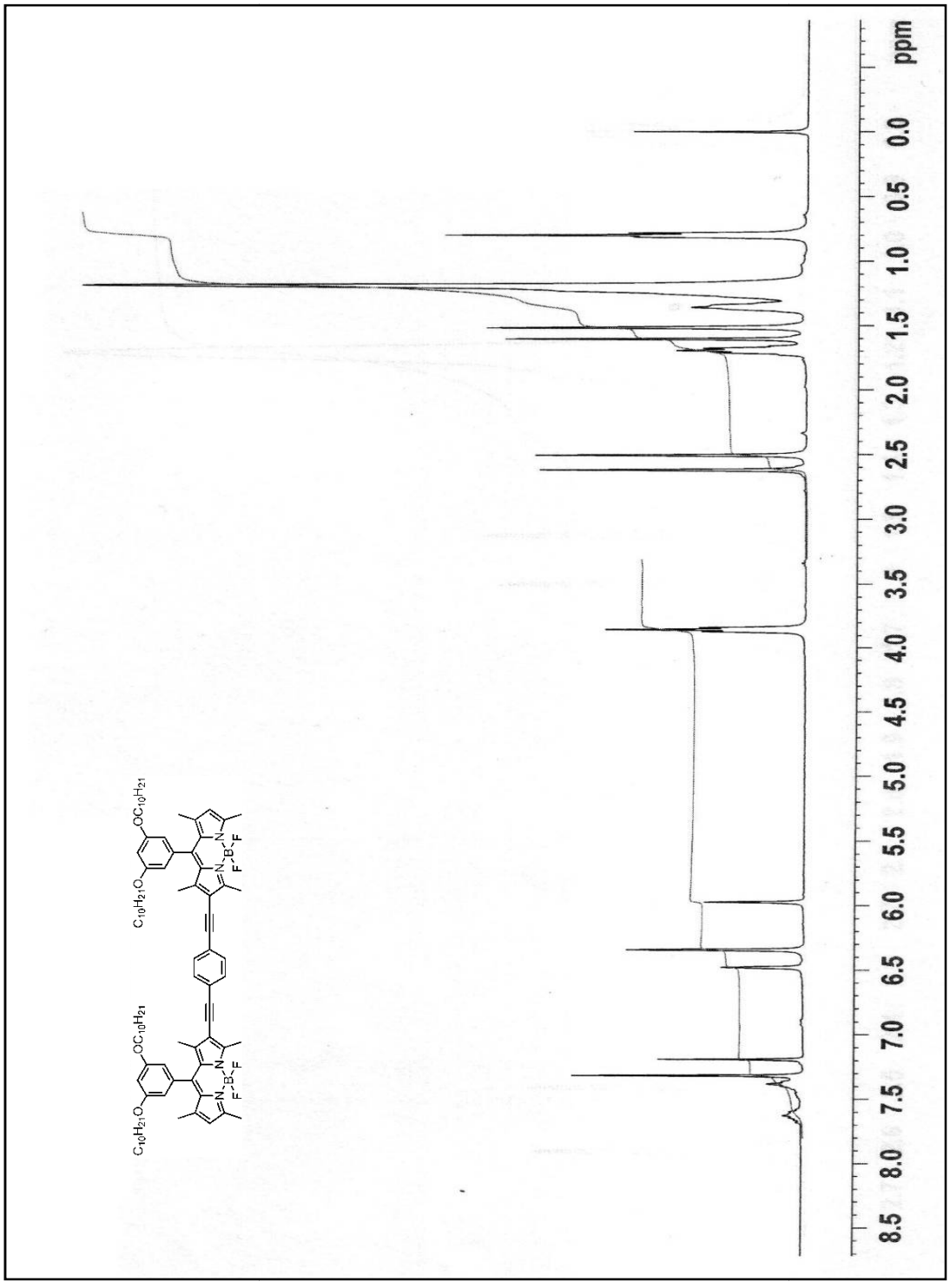

Figure 36. ^{1}H NMR spectrum of compound **48**

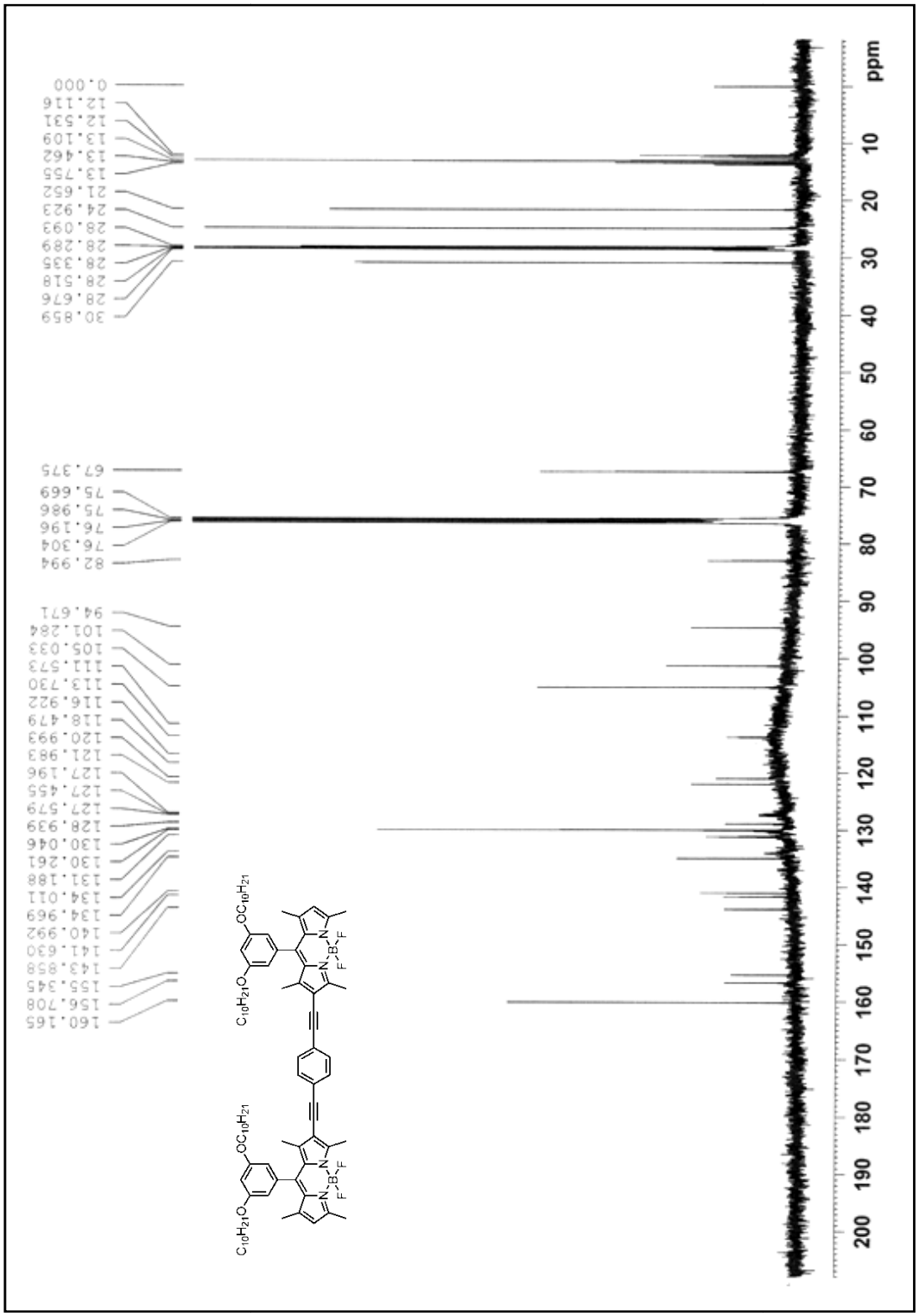

Figure 37. ^{13}C NMR spectrum of compound **48**

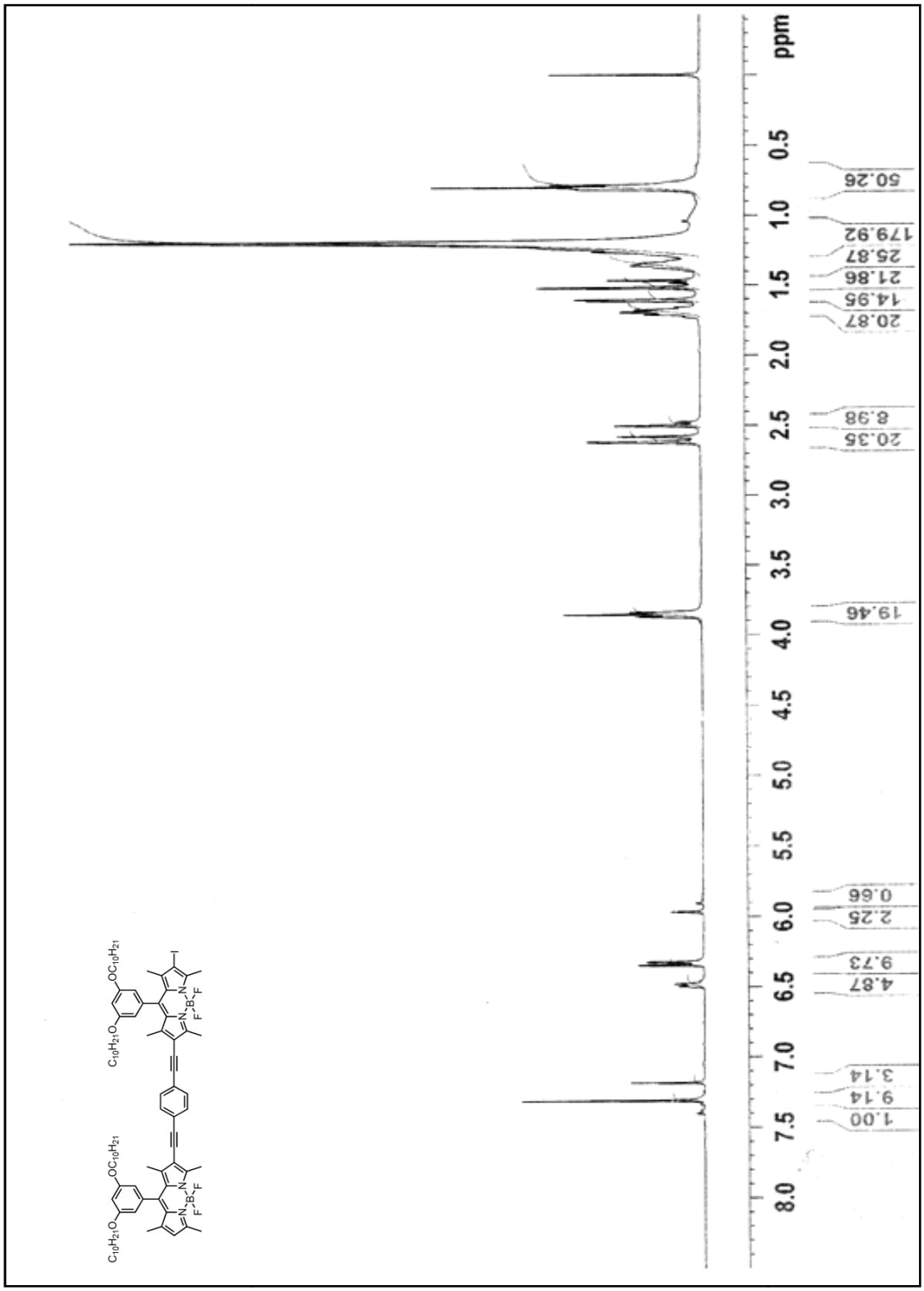

Figure 38. ^{1}H NMR spectrum of compound **52**

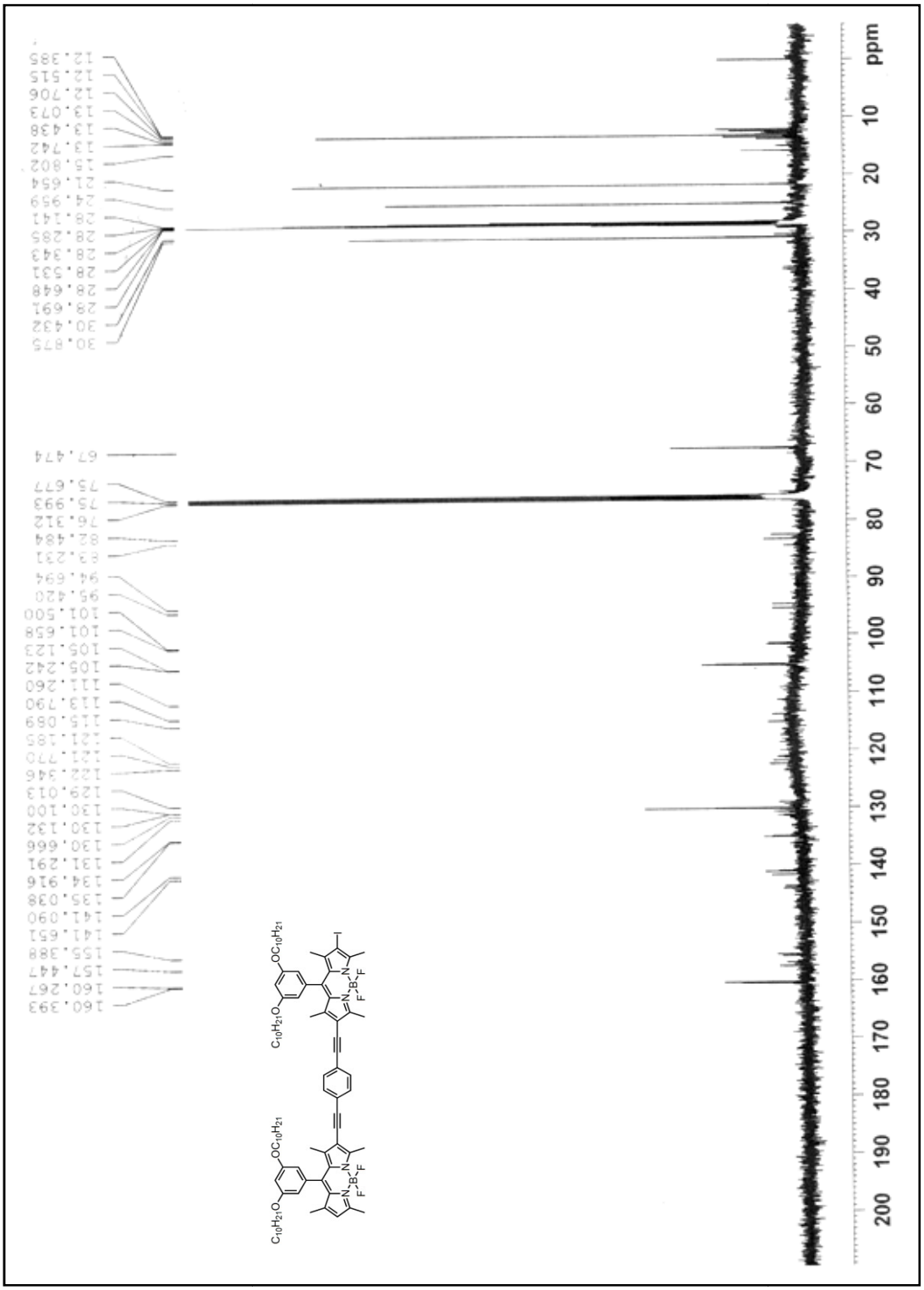

Figure 39. ^{13}C NMR spectrum of compound **52**

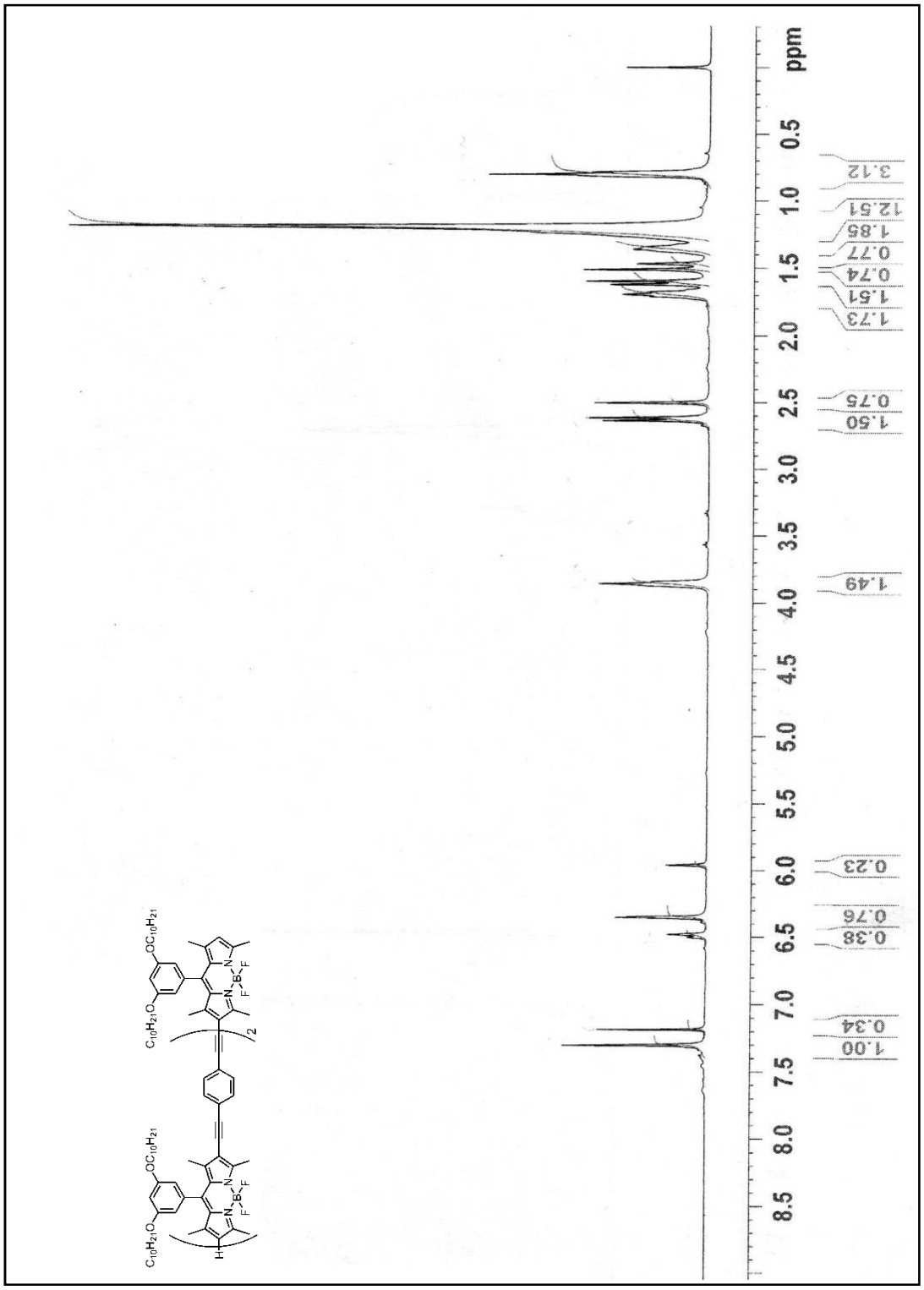

Figure 40. ^{1}H NMR spectrum of compound **53**

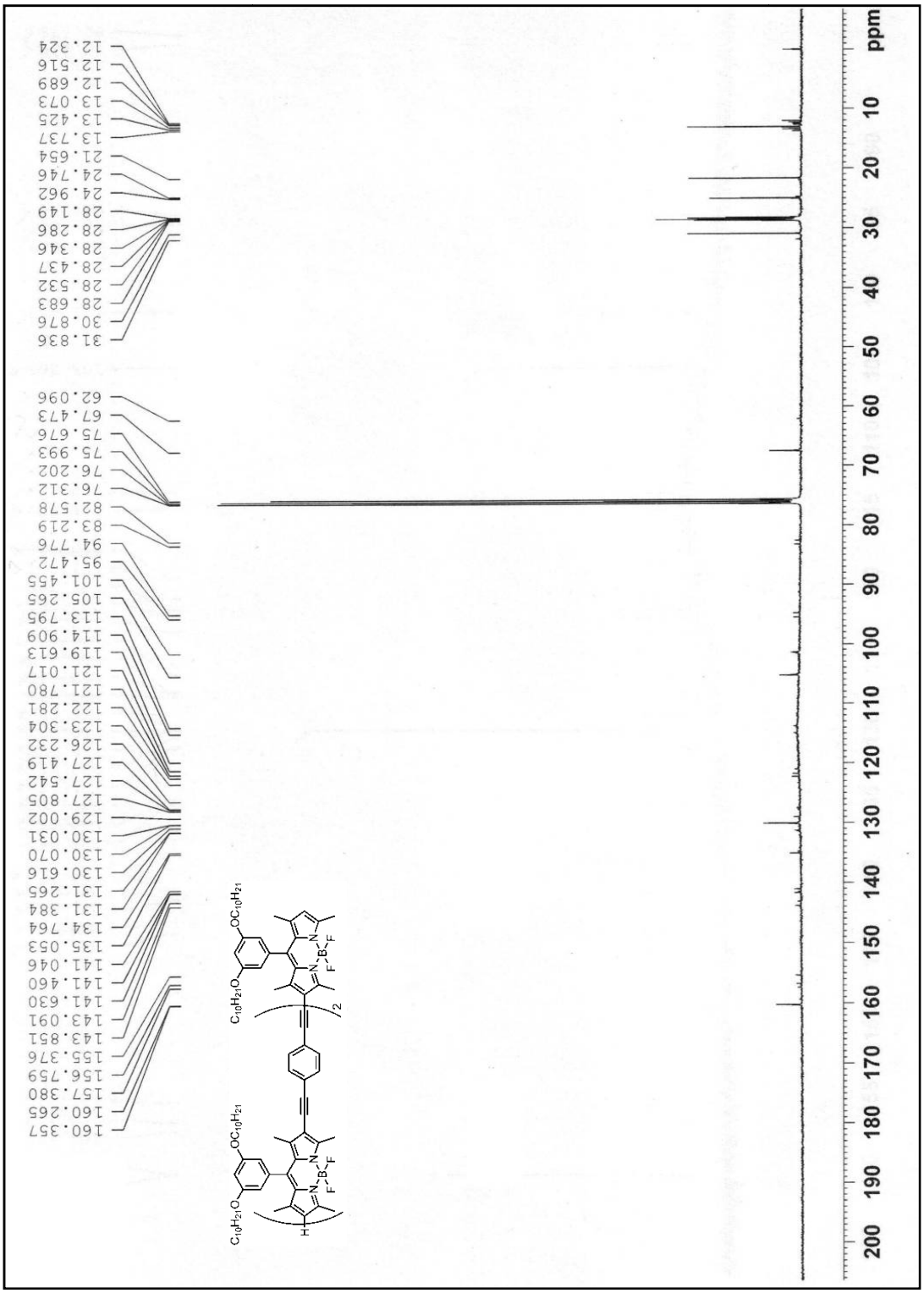

Figure 41. ^{13}C NMR spectrum of compound **53**

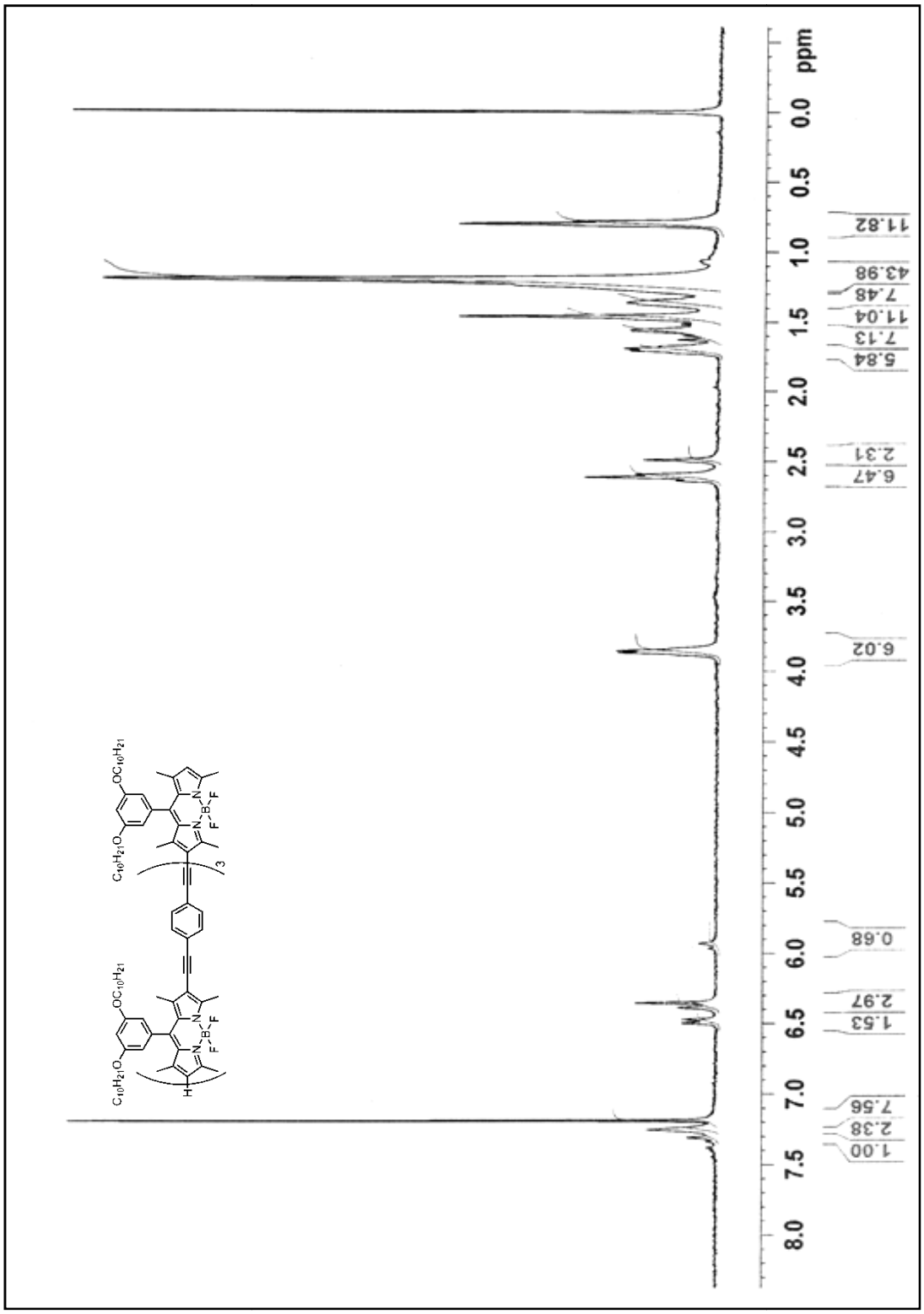

Figure 42. [1]H NMR spectrum of compound **54**

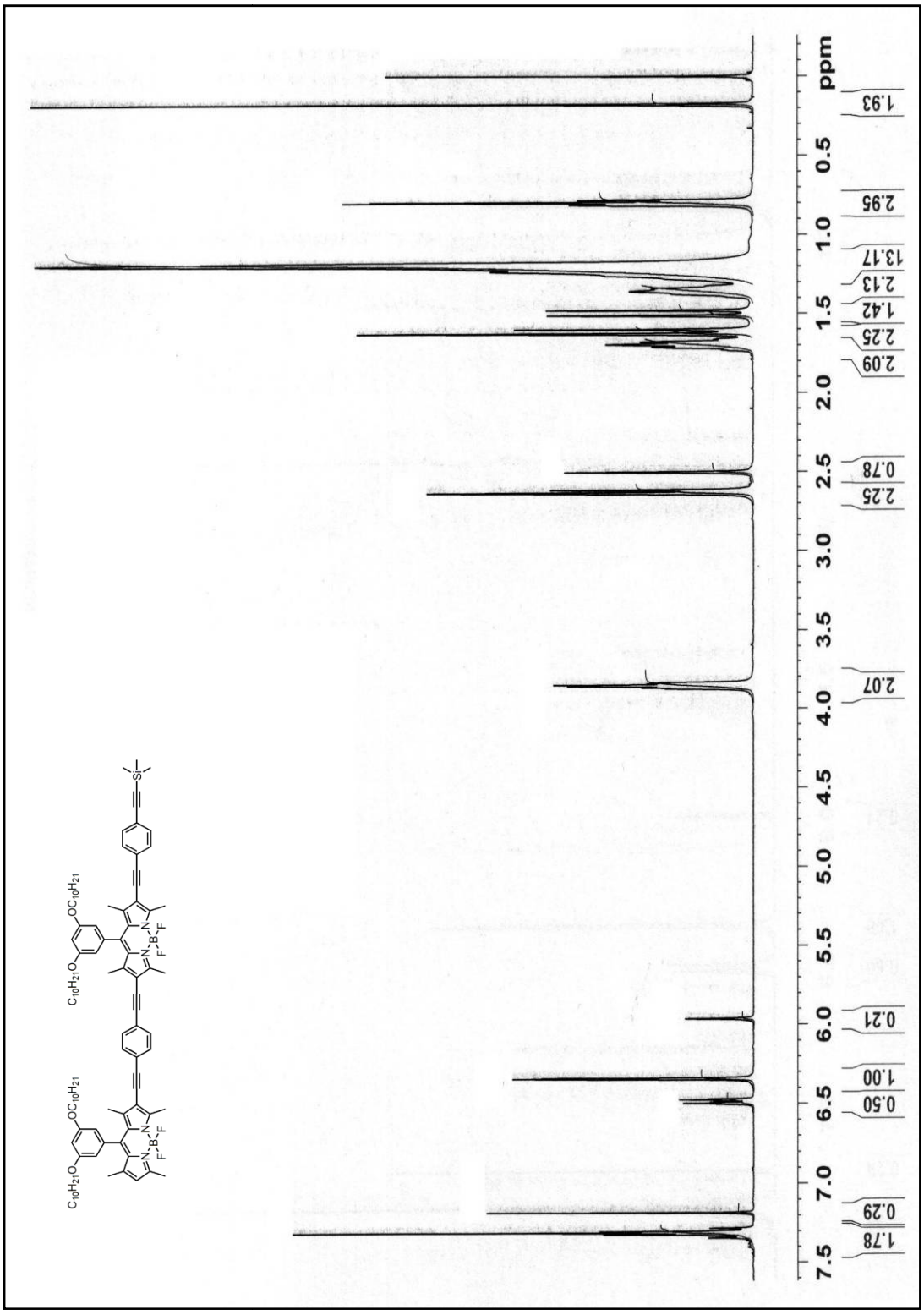

Figure 43. ^{1}H NMR spectrum of compound **55**

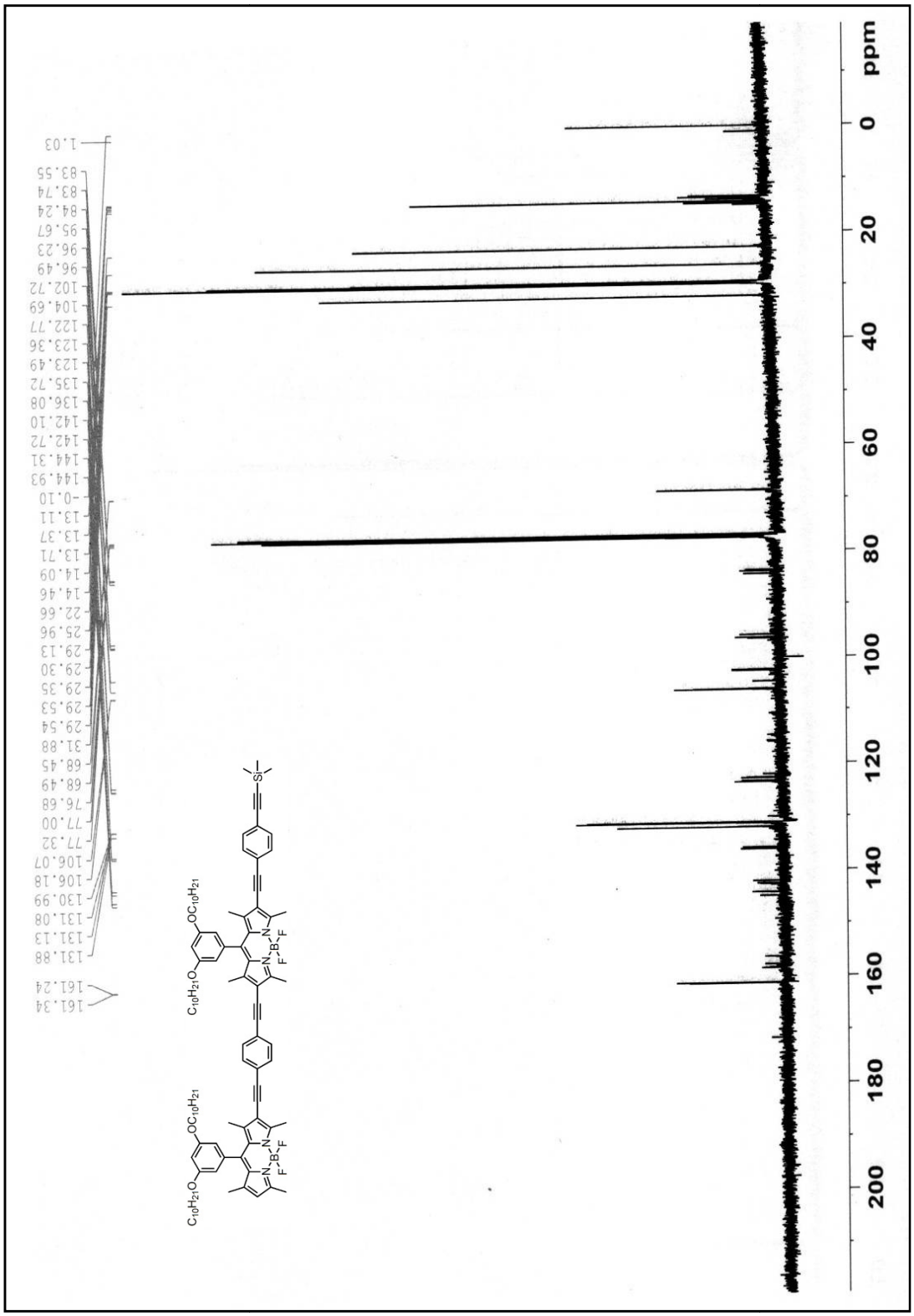

Figure 44. ^{13}C NMR spectrum of compound **55**

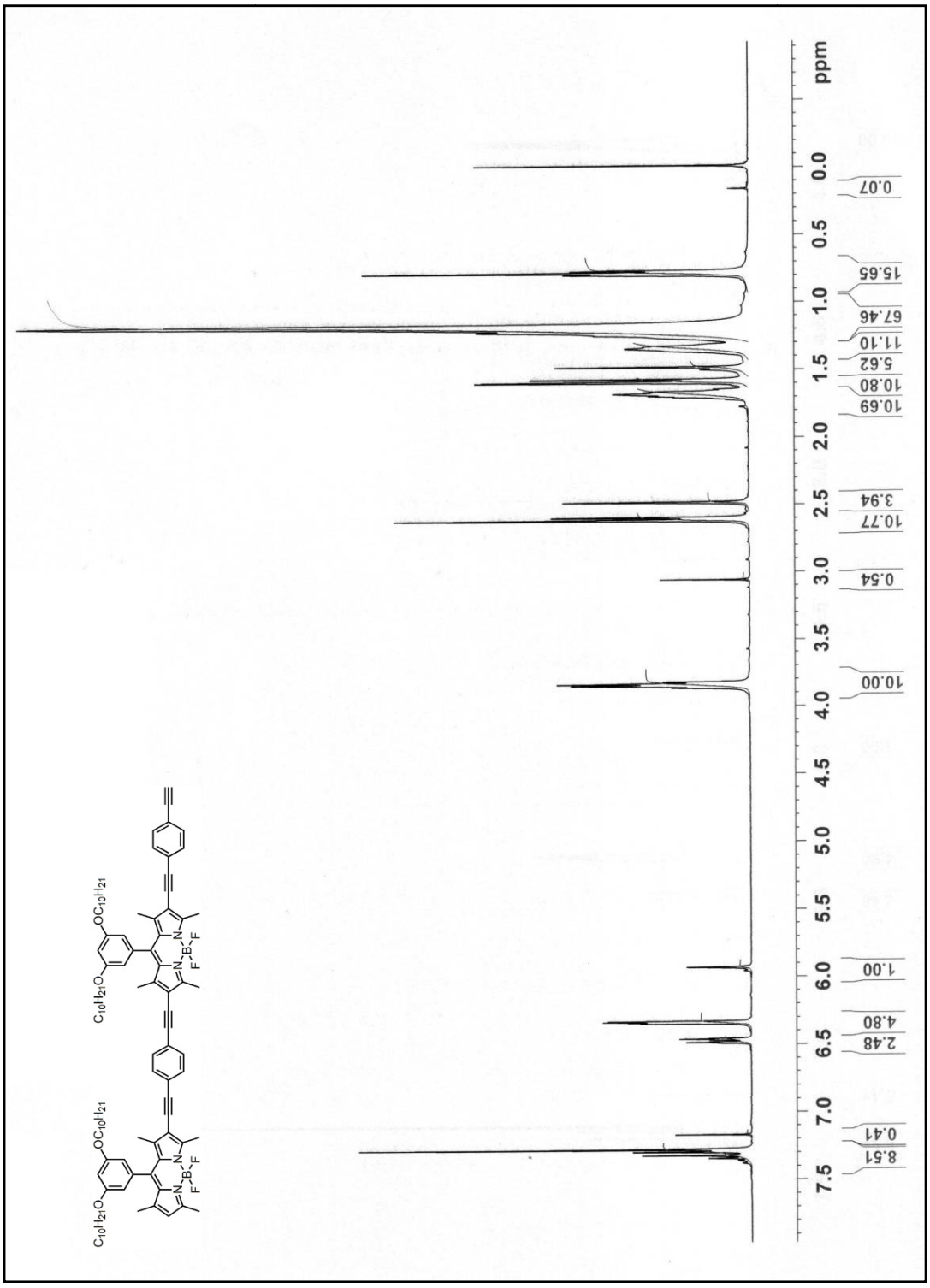

Figure 45. ^{1}H NMR spectrum of compound **56**

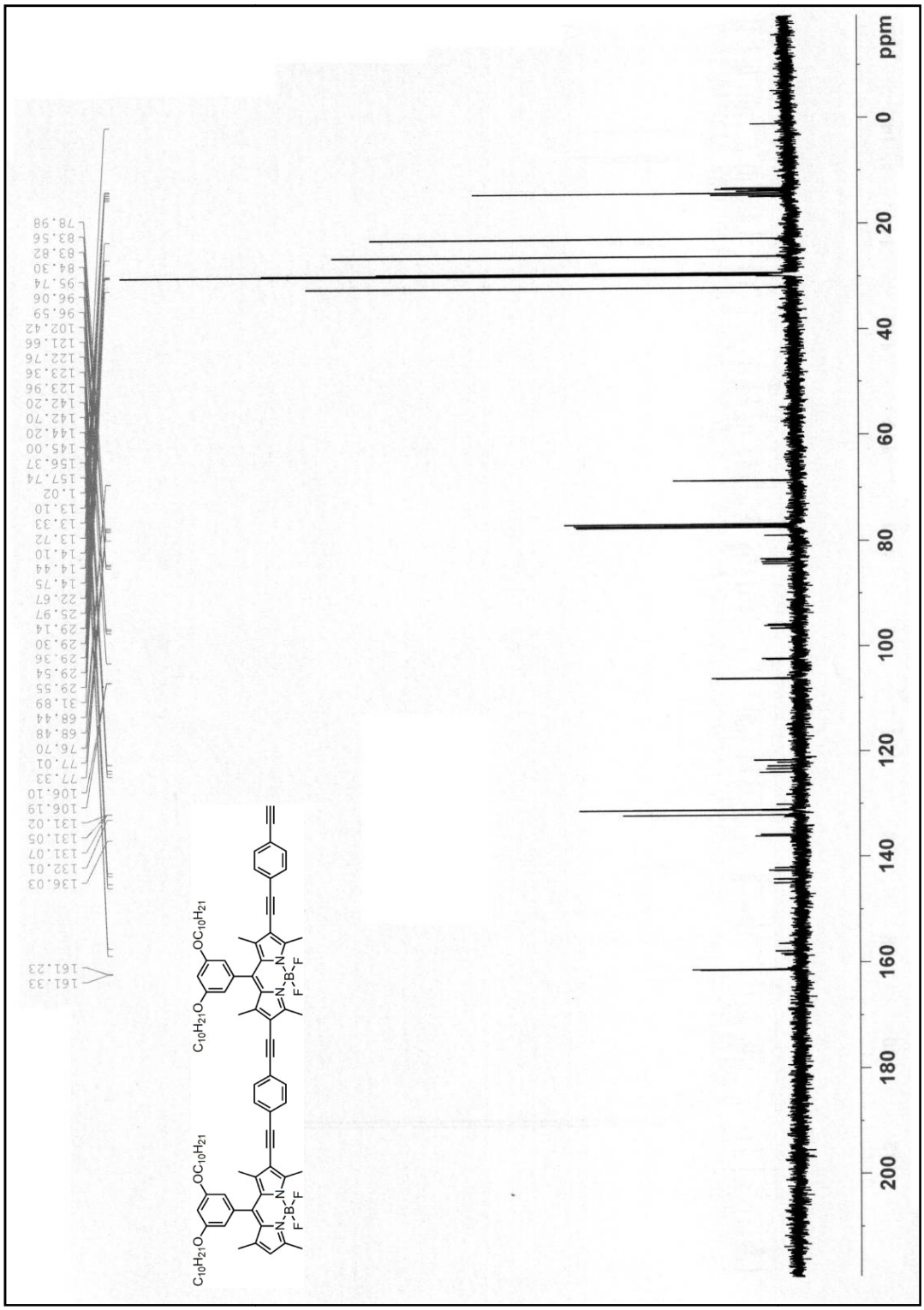

Figure 46. ^{13}C NMR spectrum of compound **56**

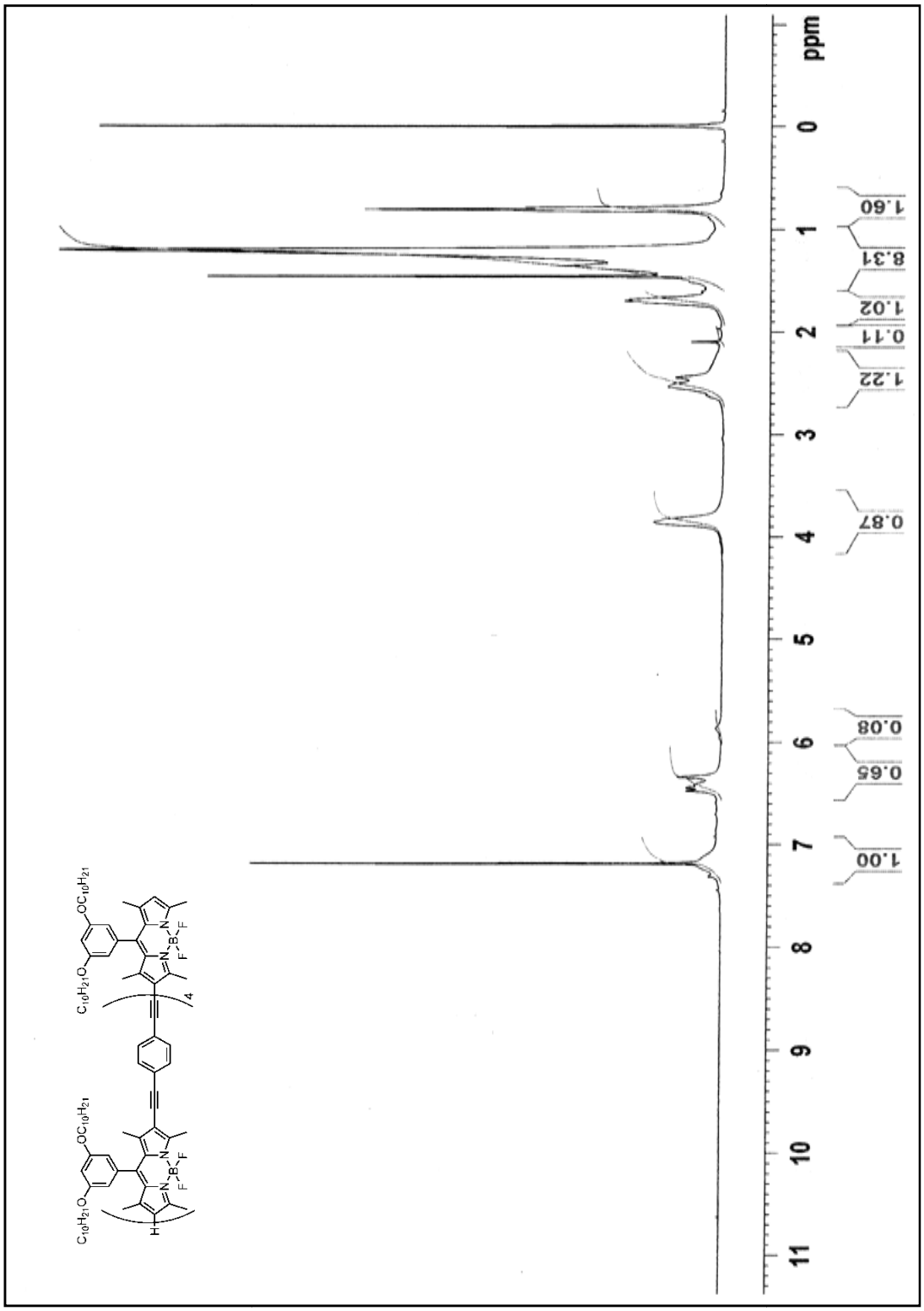

Figure 47. ^{1}H NMR spectrum of compound **57**

APPENDIX B

MASS SPECTRA

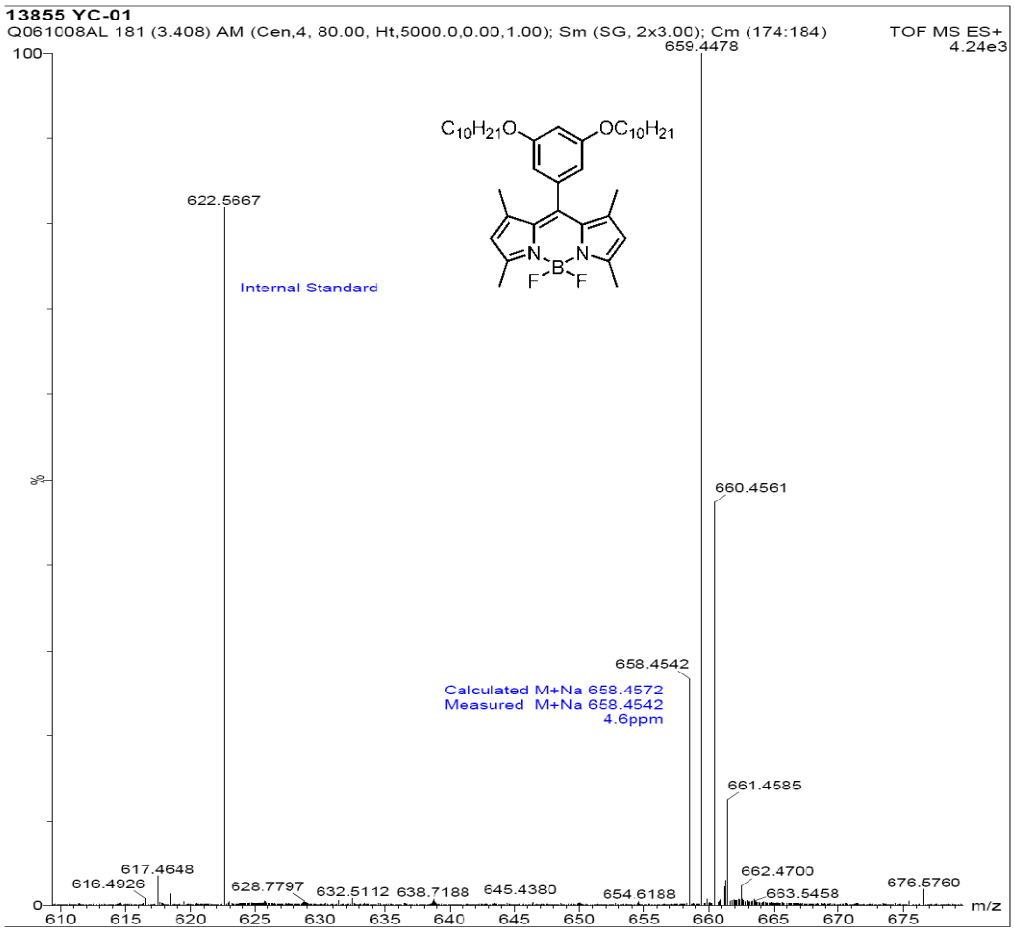

Figure 48. ESI-HRMS of compound **44**

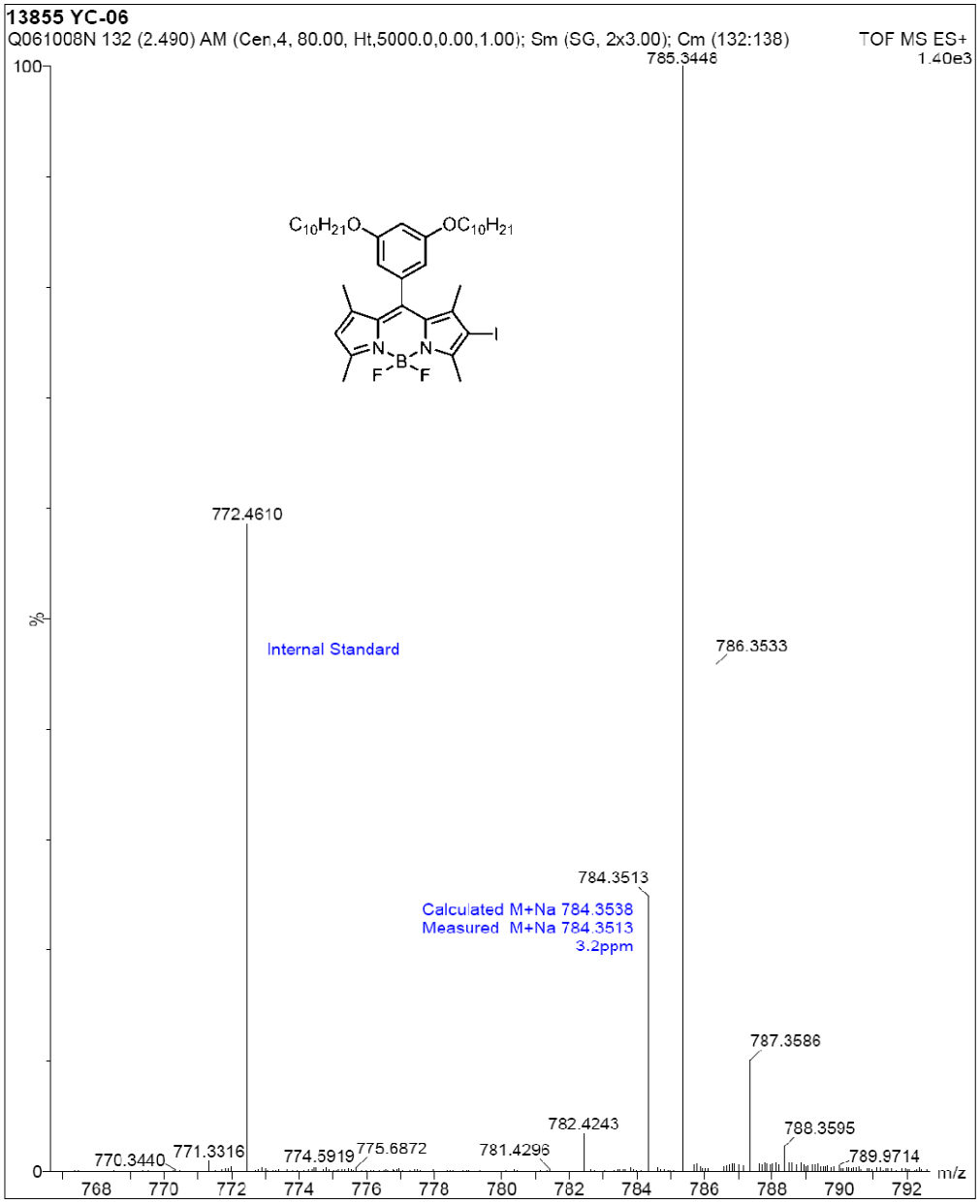

Figure 49. ESI-HRMS of compound **45**

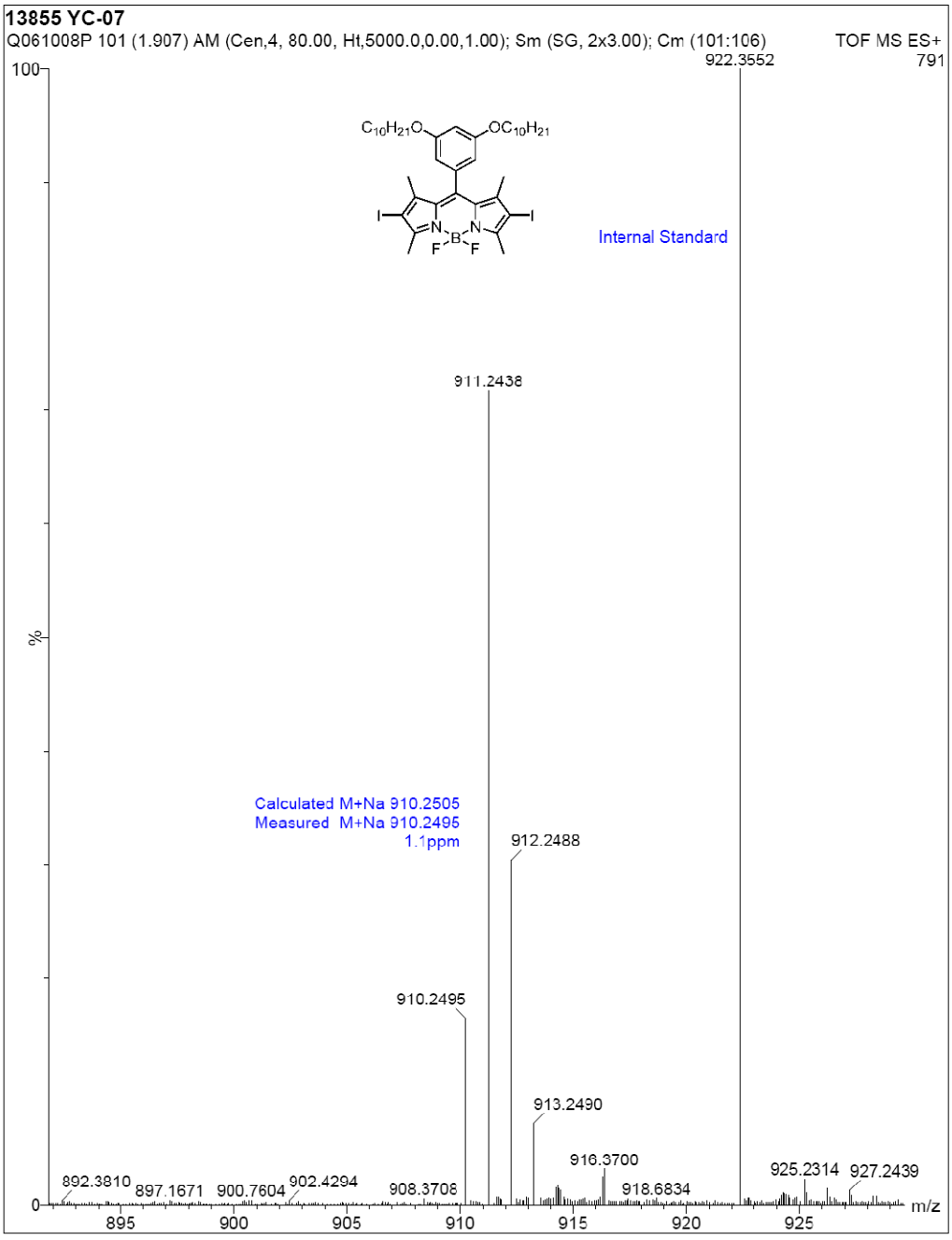

Figure 50. ESI-HRMS of compound **46**

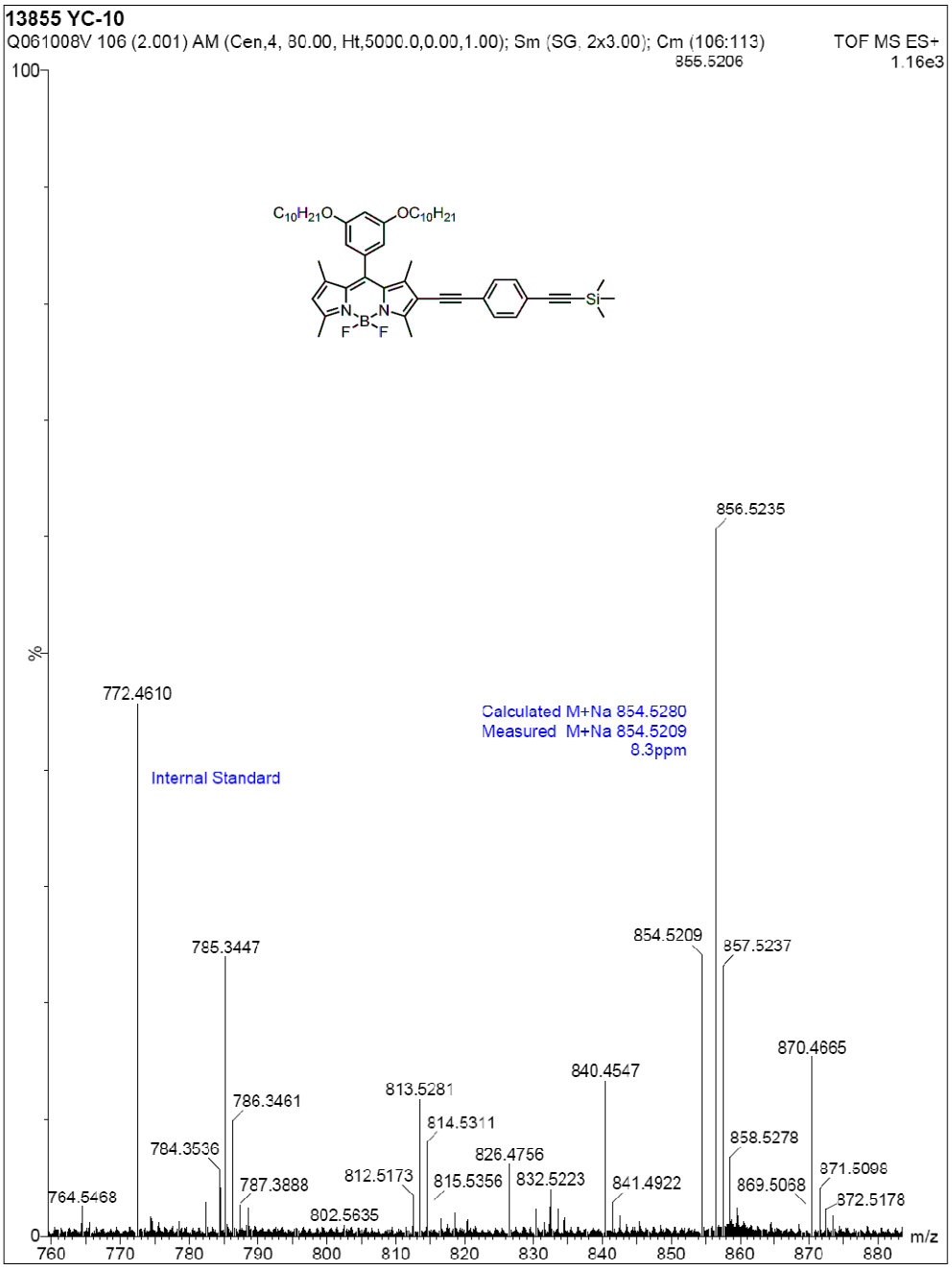

Figure 51. ESI-HRMS of compound **50**

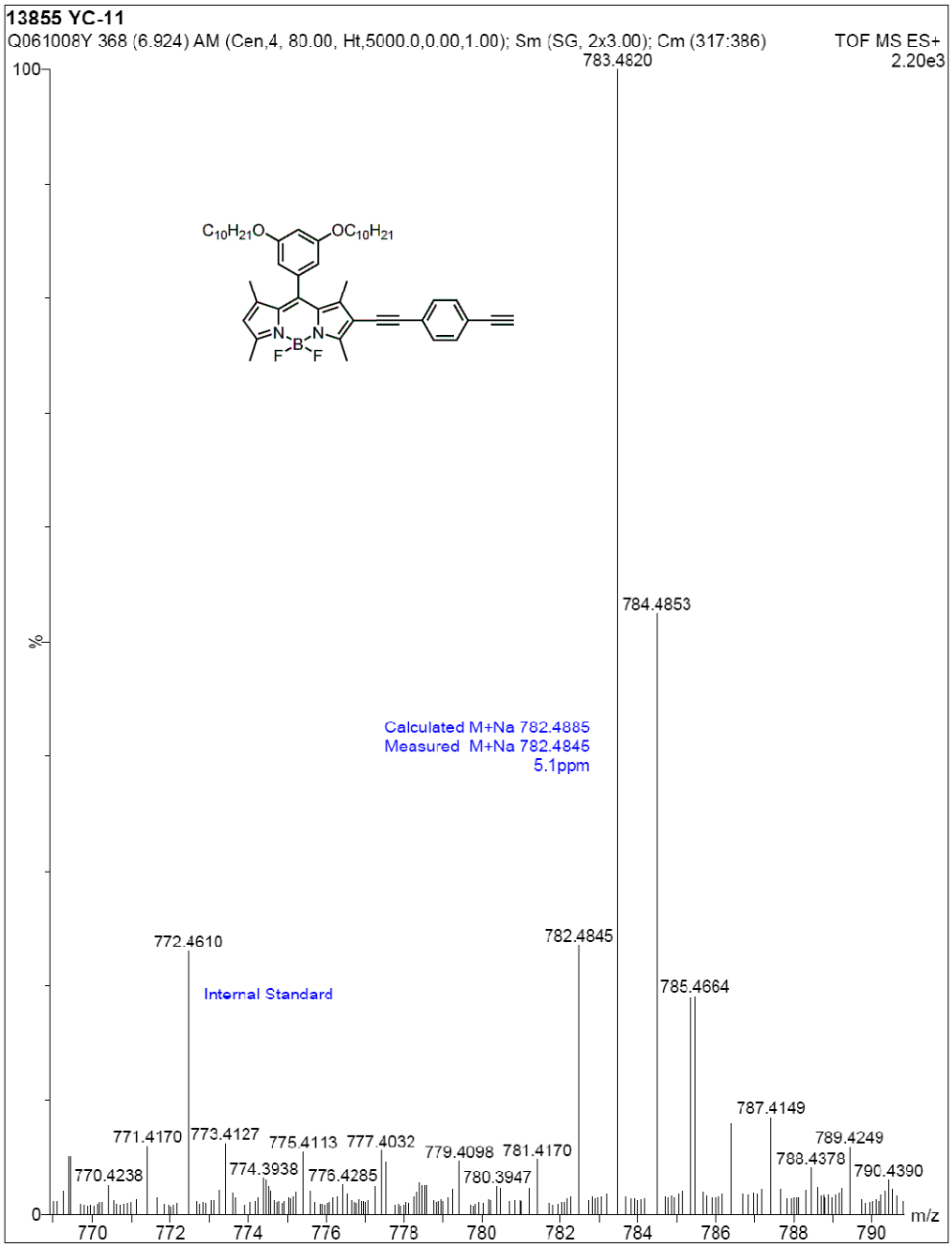

Figure 52. ESI-HRMS of compound **51**

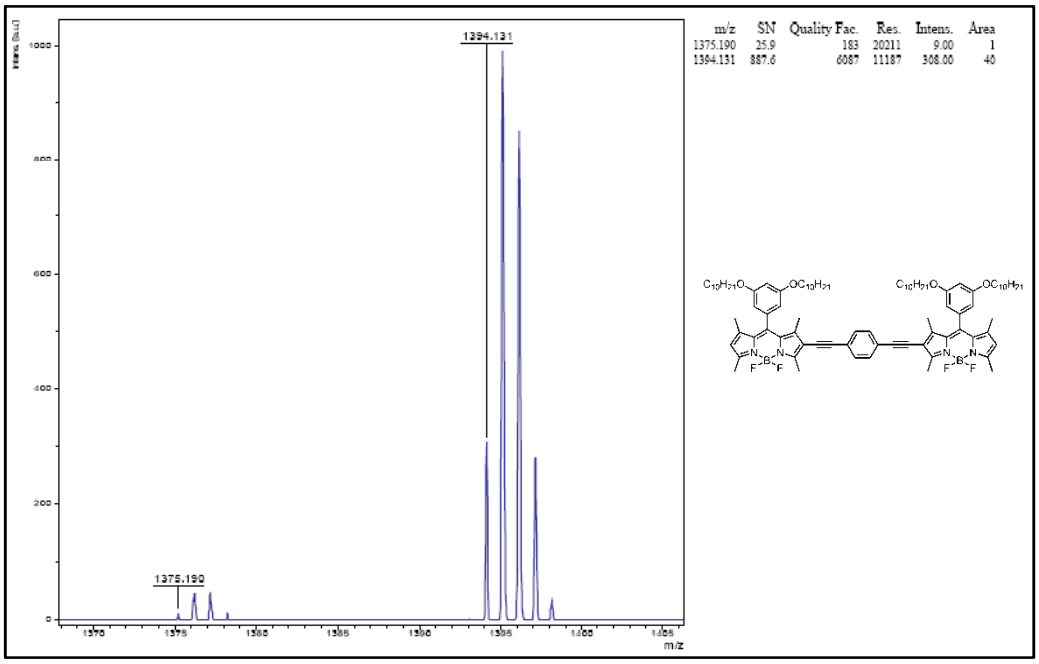

Figure 53. MALDI-MS of compound **48**

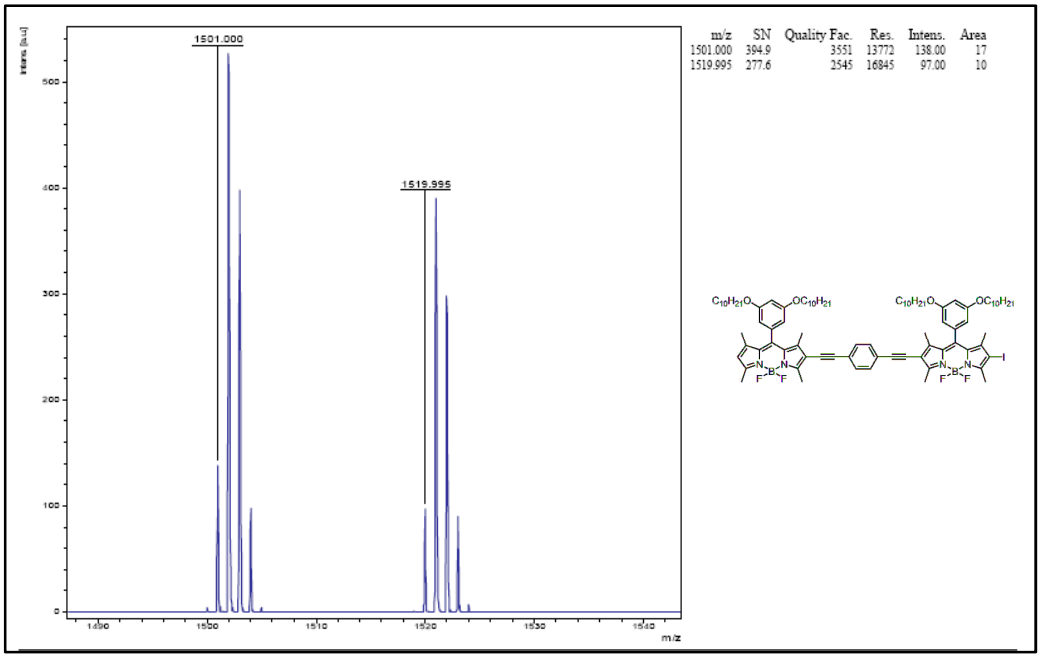

Figure 54. MALDI-MS of compound **52**

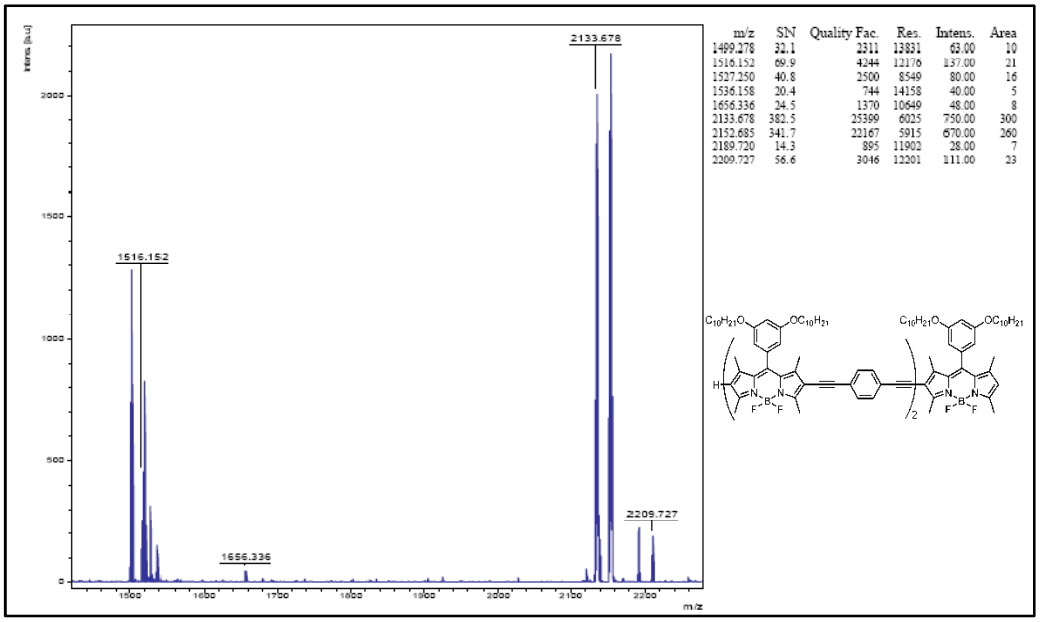

Figure 55. MALDI-MS of compound **53**

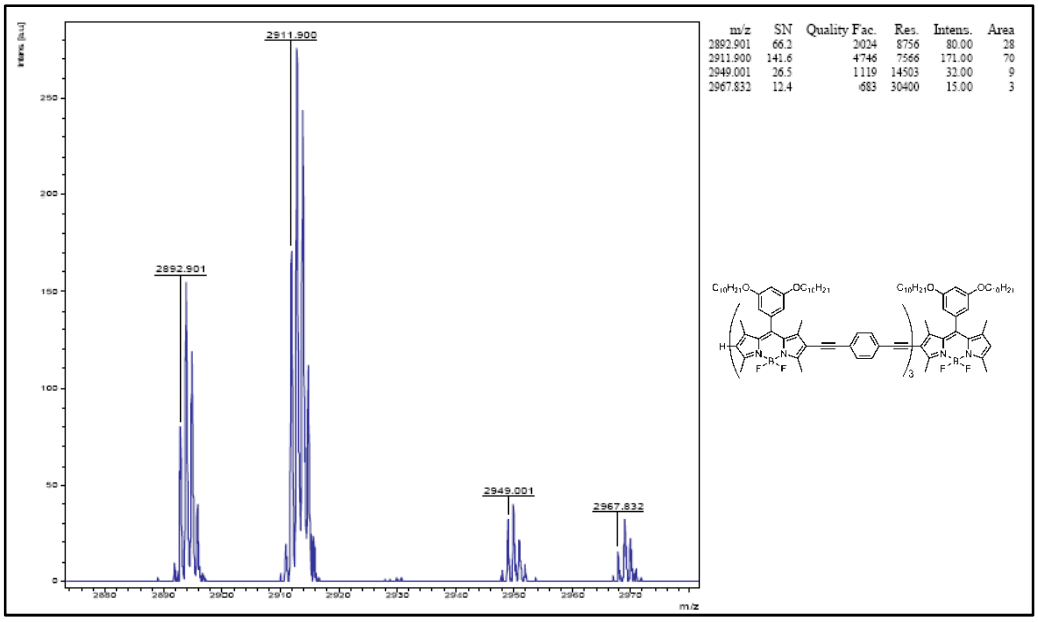

Figure 56. MALDI-MS of compound **54**

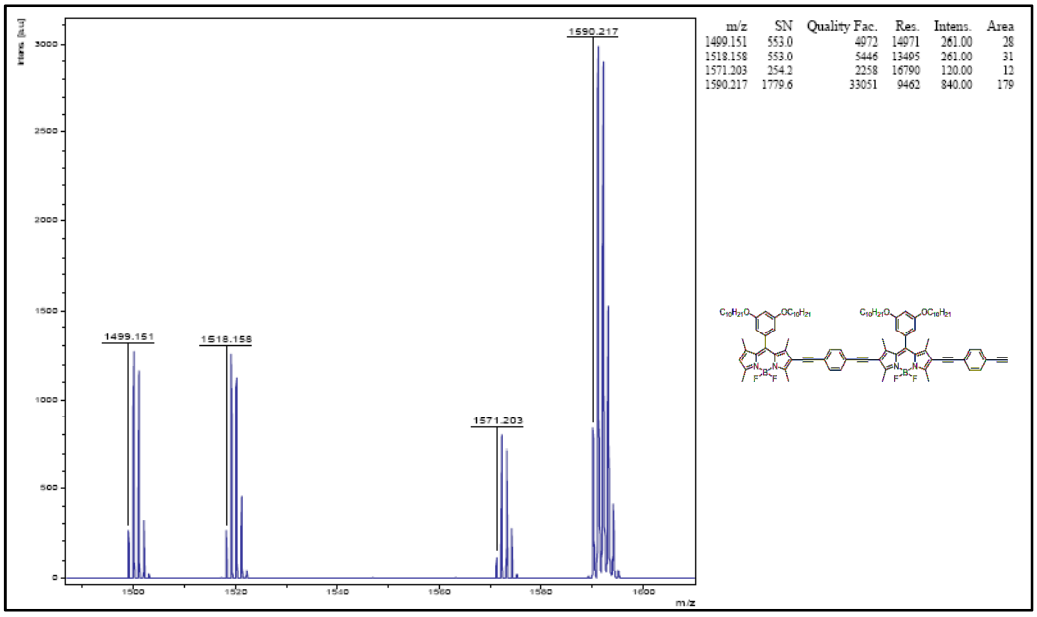

Figure 57. MALDI-MS of compound **56**

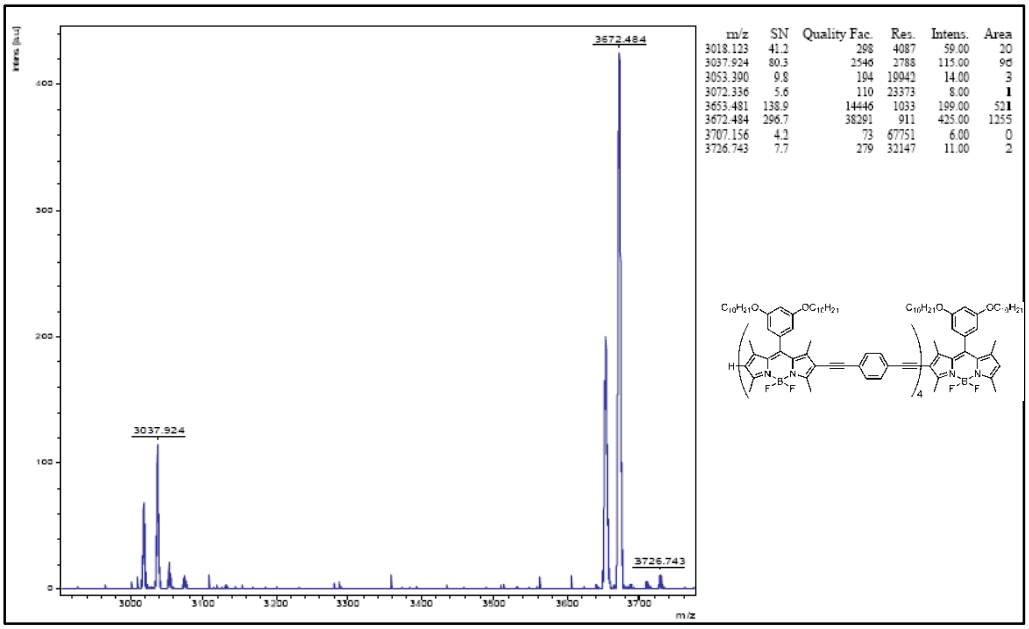

Figure 58. MALDI-MS of compound **57**