A HOMOGENEOUS SYSTEM FOR PHOTOGENERATION OF HYDROGEN INITIATED BY BODIPY BASED PHOTOINDUCED ELECTRON TRANSFER

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IN

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By

HALE ATILGAN

August, 2015

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

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ABSTRACT

A HOMOGENEOUS SYSTEM FOR PHOTOGENERATION OF HYDROGEN INITIATED BY BODIPY BASED PHOTOINDUCED ELECTRON TRANSFER

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M.S. in Department of Chemistry

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August, 2015

The key technology to fulfill the energy needs in the future is the generation of fuels by harvesting solar energy. Due to high abundance and low prices of cobalt, water-splitting (based on cobalt) method has received a lot of attention compared to noble metals. Several times cobaltoxime based catalysts were studied for proton reduction.

In this project, our aim was to produce a homogeneous photocatalytic system for photogeneration of hydrogen with high efficiency. To do so, we synthesized ten integrated molecules in which we are making use of the highly quantum efficient and photostable BODIPY chromophore. After the synthesis and characterization of target molecules, we achieved to demonstrate hydrogen evolution with five of our molecules.

Keywords: Photocatalysis, water splitting, hydrogen generation, BODIPY, photoinduced electron transfer

ÖZET

BODIPY TABANLI FOTOİNDÜKLEMELİ ELEKTRON TRANSFERİ SİSTEMLERİ ARACILIĞIYLA HOMOJEN HİDROJEN FOTOJENERASYONU

Hale Atılgan

Kimya Bölümü, Yüksek Lisans

Tez Yöneticisi: Prof. Dr. Engin Umut Akkaya

Ağustos, 2015

Güneş enerjisinin toplanmasıyla yakıtların üretilmesi, geleceğin enerji ihtiyacını karşılayacak bir teknolojidir. Kobalt, soy metallere gore, yerkürede daha çok miktarda bulunduğundan ve daha ucuz olduğundan dolayı suyun parçalanması metodunda sıkça kullanılmaktadır. Proton indirgenmesinde bir çok kez kobaltoksim katalistleri kullanılmıştır.

Bu projede, homojen bir fotokatalitik system oluşturularak hidrojen fotojenerasyonunun yüksek verlimlilikle sağlanması amaçlanmaktadır. Bunu yapmak için, yüksek kuantum verimliliğine ve fotostabiliteye sahip BODIPY boyaları kullanılarak on molekül sentezlenmiştir. Hedeflenen moleküllerin sentezi ve karakterizasyonundan sonra, moleküllerin beş tanesi hidrojen üretmiştir.

Anahtar Kelimeler: Fotokataliz, suyun parçalanması, hidrojen üretimi, BODIPY, fotoindüklemeli elektron transferi

Dedicated to my family

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I would like to thank my mother Şehirli Atılgan and father Ahmet Atılgan. I am always proud of being their daughter. Your consultant love, support and guidance made me who I am today. My amazing brother, Halil Atılgan, thank you very much for supporting all my crazy ideas for all the time. I cannot imagine being the person I am today without such a great brother through the years. Thanks for everything that helped me get to this day.

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Finally I would like to thank TUBITAK for financial support (project no: 113T080).

LIST OF ABBREVIATIONS

AcOH	**:**	Acetic Acid
BODIPY	**:**	Boradiazaindacene
$CHCl_3$	**:**	Chloroform
ER	**:**	Electron Relay
Et_3N	**:**	Triethylamine
HOMO	**:**	Highest Occupied Molecular Orbital
LUMO	**:**	Lowest Unoccupied Molecular Orbital
MS	**:**	Mass Spectroscopy
NMR	**:**	Nuclear Magnetic Resonance
PS	**:**	Photosensitizer
SC	**:**	Sacrificial Reagent
TEOA	**:**	Triethanolamine
TFA	**:**	Trifluoroacetic Acid
THF	**:**	Tetrahydrofuran
TLC	**:**	Thin Layer Chromotography
TON	**:**	Turn Over Number
WOC	**:**	Water Oxidation Catalyst
WRC	**:**	Water Reduction Catalyst

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CHAPTER 1

1.INTRODUCTION

In the beginning of 19th century, the need for fossil fuel consumption sharply increased following the industrial revolution in UK and only recently it was realized that the earth's atmosphere is not an infinite sink for CO_2 and other pollutants. In near future, serious global catastrophic problems such as ozone hole and global warming will be faced. An additional 50% increase is expected in the global energy need for the year 2030.[1] Due to the steep rise in energy demand as the global population increases, the decrease in fossil energy resources and environmental concerns of nuclear energy, there has been rapidly growing interest to search for renewable and clean energy resources.[2] The most important energy source that has the potential to satisfy this demand is solar energy which emerges as a front-running clean, abundant and secure source. The conversion of solar energy into storable and easily transportable energy in the form of molecular hydrogen via the light induced water splitting is one of the most promising approaches toward the generation of green and renewable energy.[3]

The photochemical hydrogen generation through direct water splitting is a key transformation toward the conversion of solar energy into stored more sustainable fuels which does not emit greenhouse gases upon combustion.[4] The photocatalytic hydrogen generation system has been designed to perform reductive side of water splitting-i.e., light induced conversion of aqueous protons into H_2. For this, the system has been established based on the effective coupling of light harvesting system with a sacrificial electron donor and a catalyst.[5] Novel catalysts are still being developed to overcome thermodynamic and kinetic problems related to the water splitting reaction. These studies on catalyst development specifically focus on stopping the back oxidation reaction, separation of H_2 and O_2, production of

sacrificial water reductants for the removal of oxygen and the use of earth abundant elements. Although there is a great success, there is still need for the development of high quantum efficiency photo-absorbers that operate in the usable wavelength range, and two-photon efficient systems that have potential to enlarge this wavelength range.

In this work, our aim is to produce a new homogeneous photocatalytic system for the photogeneration of hydrogen with high efficiency using a highly absorbing photosensitizer and a cobalt complex as catalyst. To implement this goal, we are developing an integrated catalyst in which BODIPY has been employed as a chromophore due to its unique photophysical properties like high molar absoption coefficients, high quantum yields, narrow emission bandwidth with high peak intensities, great photostability and ease of functionalization.[6,7] The photosensitizer has been functionalized accordingly with a cobalt complex which will serve as a reduction center, dimethylamino and pyridine functionalities which will act as oxidation center. Additionally, pH dependent regulation of hydrogen generation can be achieved via the modulation of the photoinduced electron transfer.

CHAPTER 2

2.BACKGROUND INFORMATION

2.1. Energy Resources

Many nations' energy needs lean on coal, oil, and natural gas; however assurance of fossil fuels presents an important big problem. Fossil fuels are one of the finite resources. Sooner or later the world will run out of the fossil fuels, or their access will be very hard and expensive. Furthermore, fossil fuels are not environmentally friendly, they cause air, water, and soil pollution and also they evolve some greenhouse gases which contribute to global warming.[8]

There are many forms of renewable energy such as wind, solar and hydropower. These renewable resources offer alternatives to fossil fuels.[9] In addition, they produce almost no pollution or greenhouse gases and they will have no end.

2.1.1. Solar Energy

The sun is our most powerful source of energy. Sunlight is free and infinitely renewable. Since it is not likely fossil fuels and nuclear power, this solar power gives no polluting emissions to the environment and it does not cause global warming.[10] It has many more advantages. Solar panels work silently and they are easy to operate. What is more, their cost is also affordable. Because of the growing global demand, solar power has transposed to manufacturing. Utilities can also benefit from solar panels especially when the demand of electricity is high.

2.1.2. Wind Energy

Wind is the movement of air and the wind energy has been used for many years for sailing ships and drive windmills. In today's world, this clean energy is used by wind

turbines and to generate electricity. The power of wind should be kept in mind as a long-term energy strategy because natural power sources are used for the generation of wind power. Its generation is clean and it does not cause any pollution.[11]

2.1.3. Hydropower

Hydropower is the energy produced by movement of water. Water is a renewable resource renewed by cyclization of evaporation and precipitation. Water evaporates from lakes and oceans by the help of the heat of sun and they form clouds. After, the water falls back to Earth as rain or snow, and goes to lakes and rivers. When the wind is caught by turbines and generators, that energy can be used to generate electricity.[12]

2.1.4. Biomass Energy

Biomass energy comes from plants such as crops, forest residues etc. and it is used to make biofuels and to generate heat and electricity. Biomass does not give any harmful sulfur or mercury emissions like coals. By the help of biofuels in cars or airplanes, one can contribute more against global warming pollution. However, it should be taken into account that biomass energy should not only reduce global warming pollution, but it should also protect the environment and should not cause the foods' prices to increase.[9]

2.1.5. Geothermal Energy

Geothermal energy is the energy which comes from the reservoirs of hot water underneath of Earth's surface. That hot water can be used to power generators and to generate electricity. It is also can be used for home heating systems. It is a clean, green and renewable resource and it produces almost no global warming pollution.[13]

2.1.6. Hydrogen

Hydrogen is an important, alternative clean energy carrier and it has a significant role in the reduction of emissions of greenhouse gases.[14] Researches are based on to develop friendly, enviromentally and economical hydrogen generation technologies

which are essential for hydrogen economy.[15] Hydrogen also does not exist but it should be generated from fuels or water and it is the most abundant element in the universe.[16]

2.2. Energy Related Global Problems and Hydrogen as an Energy Carrier

During the recent years, most of the world's energy requirements for transportation, heating, energy generation etc. are supplied from fossil fuels like petroleum, coal and natural gas.[17] However; due to the increasing concerns over the depletion of fossil fuel supplies, global warming caused by greenhouse gases such as carbon dioxide, and enviromental pollution, there has been a much attention to the development of renewable resources which should be only long-term solution to this crucial problem of the world's increasing population.[18,19] In the recent years, many scientists and economists have seen hydrogen as a mean to solve all these problems caused by the usages of fossil fuels. To all appearances, it sounds simple such that: (i) hydrogen is one of the most plentiful elements on Earth, (ii) combustion of molecular hydrogen, H_2, with oxygen produces heat and that molecular hydrogen and oxygen is used in fuels to generate electricity, (iii) the only byproduct of the reaction of molecular hydrogen and oxygen is water, while the product of combustion of fossil fuels is carbon dioxide and some other pollutants, (iv) it is showed that hydrogen can be used in vehicles as an internal combustion engine. In consequence, if hydrogen could be used instead of fossil fuels, all the problems related to enviroment and global warming would be solved.[20,21]

Hydrogen is the most abundant element in the universe and is the third most abundant element on Earth's surface.[22,23] Hydrogen is very reactive; therefore, it is easily combined with any elements. Since it is present in water (H_2O), it exists in every living organism.[24] In addition, it is present in hydrocarbons (e.g. methane), in organic compounds. Hydrogen is colorless, oderless and it can undergo combustion

reaction with oxygen forming only water as a byproduct.[8] Hydrogen gas is very light and it can diffuse easily and if it is not combined, it can escape from the atmosphere.

In recent years, 95 % of hydrogen is generated from fossil fuels generating carbon dioxide. Hydrogen is also generated from electrolysis; however, it is not that used. Hydrogen is mainly used in the synthesis of ammonia and refining processes.[25]

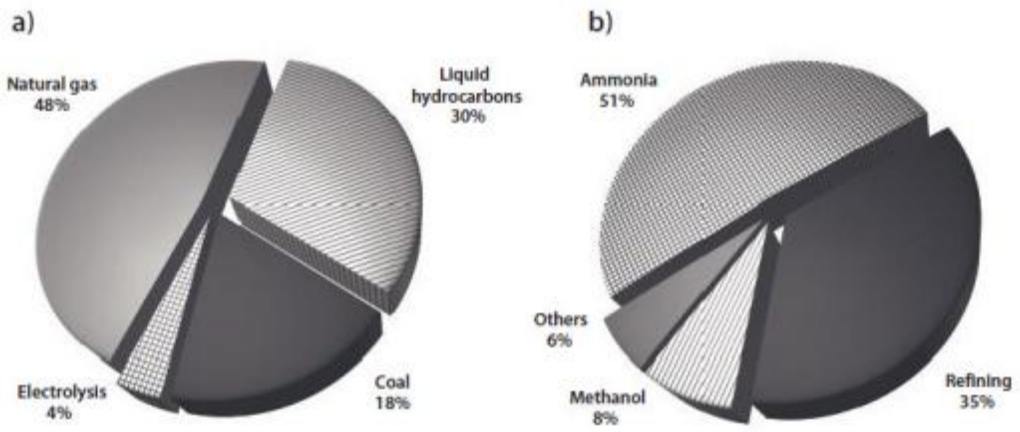


Figure 1. (a) Hydrogen production sources currently used in the world. (b) The main hydrogen-consuming sectors in the world. Copyright © 2011 Wiley-VCH Verlag GmbH & Co. KgaA. Reprinted with permission from ref (25).

However, since there is no molecular hydrogen on Earth, molecular hydrogen should be produced by using energy. In consequence, hydrogen can be seen as an energy carrier, not an alternative fuel.[26] There are many ways to produce hydrogen either from renewable resources or nonrenewable resources, which is schematically summarized in Figure 2.[27] As it is seen in Figure 2, hydrogen can be generated renewable resources such as wind, solar-thermal, biomass etc, from fossil fuels, natural gas, coal, and hydrogen also can be used to transfer energy to where it is used such as fuels cells, turbines etc.

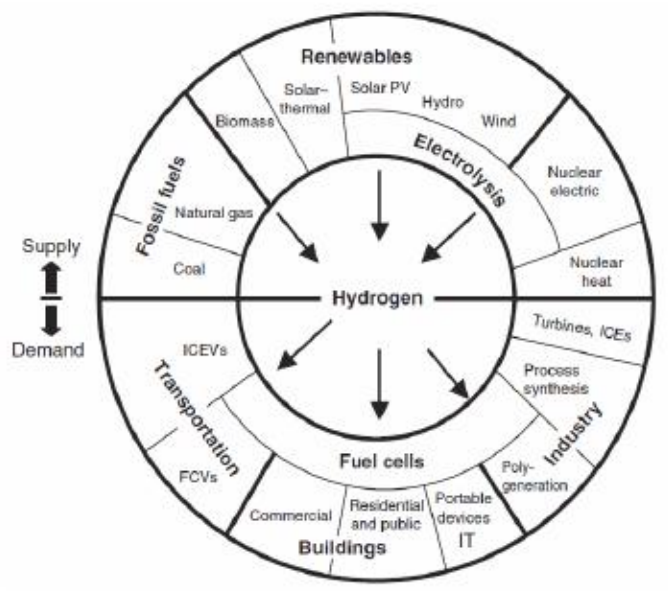


Figure 2. Hydrogen supply options and usages [ ]. PV, photovoltaic cells; ICEs, internal combustion engines; IT, information technology; FCVs, fuel cell vehicles; ICEVs, internal-combustion-engined vehicles. Copyright ©2008, Royal Society of Chemistry, Reprinted with permission from ref (27).

2.3. Hydrogen as the Solution to the Present Problems

Even though the element hydrogen is not found in its elemental pure form, it is considered the lightest most abundant element in the universe making up to 75% of the universe's elemental mass.[28] Most of the times it is found in the form of other compounds such as hydrocarbons and water which means that an extraction is required. In an experiment conducted by T. Von Honenhein in 1493 hydrogen gas was produced by mixing strong acids with metals. However, Henry Cavendish in 1766 was able to isolate hydrogen and consider it a gas for the first time. As for the name Hydrogen, it was given from greek hydro which meant water and genes or in other words, "creator".[8]

The reason hydrogen is considered the future solution of the nowadays energy problems is that is an energy carrier, nontoxic and its combustion does not cause pollution or even greenhouse gases.[29] In addition to these factors, hydrogen has high

energy content and there is no need for combustion. Useful energy from hydrogen can be provided by simple electrochemical conversion method and also from fossil fuels, nuclear power plants and renewable energy sources. This means that, as a fuel, it could be used in various fields as long as there are fossil fuels available and it could offer direct benefits in terms of reduced pollution and cleaner environment. Although hydrogen is a good energy carrier, various challenges about its production and storage and even transportation are present.[30]

Various methods have been implemented during the years such as: production through water electrolysis, thermochemical cycles, direct thermal decomposition of water, photolysis and biomass.[31] Another issue raised in when it comes to hydrogen is the transportation problems. Because it has to be delivered to the end user is through pipelines and tanks making it difficult for the economy.[32] One final issue with hydrogen is the storage. Hydrogen is the lightest element on earth with density 0.03, 0.06 and 0.07 kg/L at 350 atm, 700 atm and liquefied at 20 K respectively.[33] Therefore, it is a big problem to store hydrogen in its liquid form. Several techniques can be used for storage with a high volumetric and gravimetric density: high pressure gas cylinders, liquid hydrogen in cryogenic tanks, absorbed on interstital sites in a host metal, complex compounds, metals and complexes together with water. [34]

2.4. Hydrogen Production Technologies

Presently, hydrogen is used in chemical industry; however, in the following years it will become an important fuel for us. There are many hydrogen production technologies from both fossil and renewable resources, pyrolysis, and water.[35]

The U.S. light vehicle fleet is over 225 million, travelling over 7 billion miles a day, and it is consuming 8 million barrels of oil in a day.[36,37] Although US is the 3rd largest oil producer in the world, imported petroleum is expected to rise 60 % by 2025.[38] However, there has become an interest to improve new alternative fuels to supply people's need after oil embargo in US.[39] But there is something clear that uncertainty of the countries in the world nowadays is the result of the cost of the oil

to increase substantially in the past few years. Not only prices, but also the environmental problems is the another problems that we should deal with. According to the analysis done in the recent years show that pollutants are very high to damage people's health.[35] In addition, the vehicles are the reason for the increase in the amount of carbon dioxide, volatile organic compounds, and other greenhouse gases. To cope with all these problems, there should be done to alter the world's energy supply and find cleaner and alternative fuels. There is much alternative energy such as methane, gasoline, biodiesel; however, different technologies are needed to use these energies. However, hydrogen can be generated from all of these feedstocks and recently there have been many technologies to produce hydrogen.

2.5. Solar Water Splitting to Hydrogen and Oxygen

Hydrogen should be generated from water using natural sources such as sunlight (visible light) considering the enviromental issues. Hence, solar hydrogen production from water has been studied. There are some ways for solar hydrogen generation: (i) electrolysis of water using solar cell, (ii) reforming of biomass, (iii) water splitting photochemically or photoelectrochemically (artificial photosynthesis).[40] As it is seen in Figure 3, in the photosynthesis reaction by green plants which is an uphill reaction, the photon energy is converted to chemical energy with a largely positive change in Gibbs free energy through water splitting.[40] Hence, photocatalytic water splitting can be considered as an artificial photosynthesis and it is a very hot topic in chemistry.

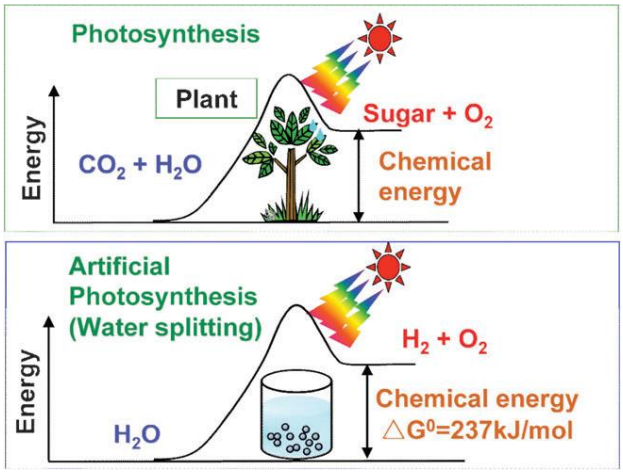


Figure 3. Photosynthesis by green plants and photocatalytic water splitting (artificial photosynthesis). Copyright © 2008, Royal Society of Chemistry. Reprinted with permission from ref (40).

Water splitting is the light driven of liquid water to gaseous hydrogen and oxygen as it is in the following:

$$H_2O_{(l)} \xrightarrow{\text{sunlight}} H_{2\,(g)} + \tfrac{1}{2}\, O_{2\,(g)}$$ [41]

At sea level, solar spectrum broadens from near infrared through the visible to near ultraviolet which is not absorbed by water itself. Therefore, some recyclable absorbing sensitizers are needed for photochemical reactions in order to absorb the light. These absorbing species have to be used to transduce the radiant energy to chemical energy in the form of electron holes pairs to drive the reaction.[38] Secondly, sacrifical donors which are reduced materials are needed for water splitting. These donors should be oxidized more easily than water such as triethanolamine (TEOA), ethylenediamine tetraacetic acid (EDTA). Using of these kind of compounds develops the efficiency of the splitting process; however, sacrifical donors have better not be more expensive than the H_2 produced for the practical systems. It is better to use reduced waste materials for that purpose; however, it is more useful for large-scale fuel production.[42]

There are 2 electrons involve in the splitting reaction of water to hydrogen and oxygen, which is corresponding to 1.23 eV/e which is the standard emf of that

reaction. The energy of photons in the solar spectrum is sufficient enough to drive this reaction; however, the efficiency of the reaction depends on how the reaction is performed. The reaction can be performed thermally with light by the help of concentrators and a solar furnace by heating water to 1500-2500 K .[43] However, at this point, the stability and cost of the capital equipment problems come out, and that decreases the reaction efficiency below 2 %. Therefore, this method is not a very good approach for solar water splitting.

There are some crucial properties for an efficient hydrogen evolution: (i) the sacrifical electron donor should be cheap and readily available; (ii) every intermediate charge relay has to be stable in the oxidized and the reduced states in order for the sensitizing dye to be multiple recycled; (iii) the oxidation of sensitizer should be faster than radiative and non-radiative relaxation of the excited state of sensitizer; (iv) durable catalyst must be effective in trapping the reduced relay for an efficient hydrogen evolution; (v) each component should be chemically and optically stable.[42]

2.5.1. Mechanism of Water Splitting Reaction

The mechanism of the water splitting reaction is as seen in Figure 4, when photosensitizer (PS) or chromophore absorbs a photon, the excited PS^* shows different properties than ground state PS. According to electron donor (ED), or electron acceptor (EA) groups, there occurs two electron transfer quenching pathways: reductive quenching and oxidative quenching respectively. In reductive quenching, the excited PS^* is reduced to PS^- by taking an electron from ED, then reducing PS^- gives its electron to electron acceptor group which is H_2 generating catalyst. In the oxidative queching pathway, the excited PS^* transfers its electron to electron acceptor group which can be either the catalyst in higher oxidation state or an electron transfer mediator such as methyl viologen. Then, oxidized PS^+ takes an electron from ED to go to its intial from PS.[44]

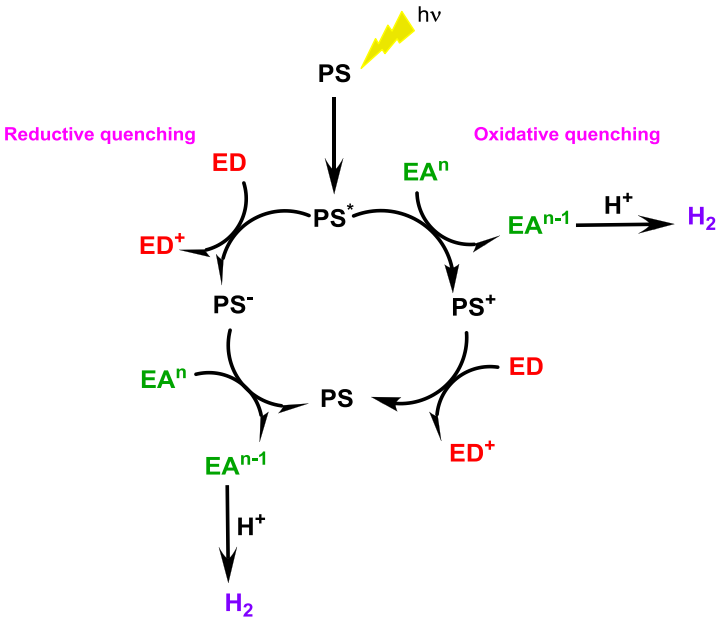


Figure 4. Water Splitting Mechanism.

2.5.2. Applications of Water Splitting Reaction

There are numerous examples of water splitting reaction for hydrogen generation such as an ion exchange acidic resin, and semiconductor photocatalysts. To begin with, water splitting reaction can be used to create a noble-metal-free Ni-based catalyst for the hydrogen generation from water. As shown in Figure 5, Yamashita *et al.* presented a new catalyst created by a simple ion exchange of trinuclear complex, $Ni(NiL_2)_2Cl_2$ (L= β-mercaptoethylamine) with a cation-exchange having strongly acidic $–SO_3^{2-}$ groups. To effort the hydrogen production of $Ni_{complex}$/ resins, H_2 production from water was carried under visible light irradiation in water solution containing triethanolamine (TEOA) as a sacrificial electron donor and Eosin Y as a photosensitizer. According to their experiments, Erythrosin B was found to be the best photosensitizer among rose Bengal and Eosin Y and pH = 7.5- 8.0 was the best pH value for H_2 production. Moreover, it was also shown that this recovered catalyst can be recyled without loss of activity.[45]

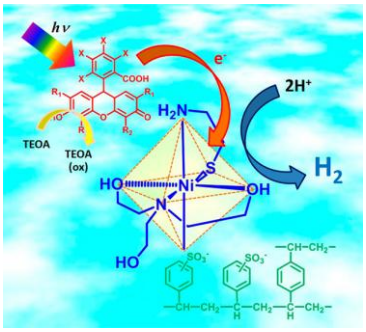


Figure 5. Example of application of water splitting reaction in ion exchange acidic resin reported by Yamashita *et al.* Copyright © 2014, American Chemical Society. Reprinted with permission from ref (45).

Water splitting is used in semiconductor photocatalysts for hydrogen generation. As Fujishima and Honda suggested, photoelectrochemical evolution of H_2 can be done on TiO_2 electrode by using water splitting reaction. When the electrons on valence band are excited, they jump to the conduction band when the photons of energy equals to or greater than its band gap energy, and water is reduced and oxidized to hydrogen and oxygen gas respectively.[46] Since TiO_2 is only able to convert high-energy UV light into chemical energy due to having high band gap energy, some thing should be done to shift the absorption edge of TiO_2 into the visible range in the spectrum. To do so, Brückner et al used surface coverage method by using gold nanoparticles (AU-NP) to shift its absorption edge to visible-light range. As it is seen in Figure 6, he observed the evolution of H_2 under irradiation of Au-TiO_2 catalyst with visible light.[47]

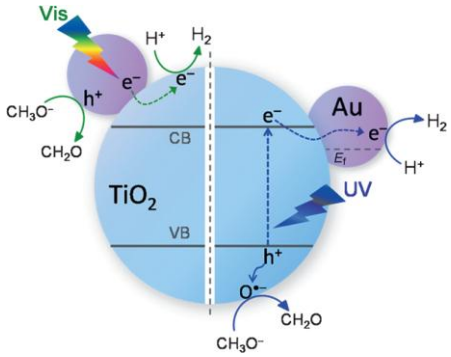


Figure 6. Example of application of water splitting in semiductor catalyst presented by Brückner *et al.* Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Reprinted with permission from ref (47).

2.6. Photocatalytic Systems for H_2 Generation

Photocatalytic systems for H_2 generation mostly include a photosensitizer (PS), an electron relay (ER), a sacrificial reagents (SR) or electron donor, and a water reduction catalyst (WRC).[48–50] The total reaction is taken into account to be a visible-light-driven photon reduction by using an electron donor reagent to generate hydrogen via an electron relay.

2.6.1. Photosensitizer

The photosensitizer (PS) can be considered as the most important part of the whole system. Its function in the visible-light-driven systems for hydrogen generation is the absorption of visible light.[51] Ruthenium complexes have a significant role in this field[49], although a plethora of compounds based on other noble metals such as iridium[52] and platinum.[53] Nevertheless, there are still rare noble-metal-free photosensitizers. As Lehn *et al.* Reported, $Ru(bpy)_3^{2+}$ is a very famous photosensitizer used in a photocatalytic hydrogen production systems as it is seen in Figure 7.[54]

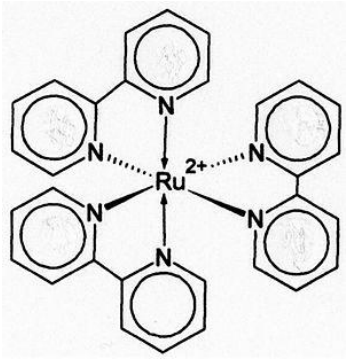
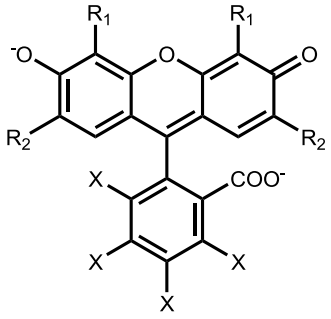


Figure 7. Lehn *et al.* Reported $Ru(bpy)_3^{2+}$ complex used as a photosensitizer in a photocatalytic system. Copyright © 1979, Verlag GmbH & Co. KGaA, Weinheim. Reprinted with permission from ref (54).

There are also more photosensitizer contaning no noble metals such as xanthene dyes Eosin Y (**1**), and Rose Bengal (**2**), which have been shown to catalyze visible-light-driven generation of H_2 gas from aqueous protons as it is seen in Figure 8. [4]



1, R_1=R_2=Br, X=H
2, R_1=H, R_2=I, X=Cl
3, R_1=H, R_2=Cl, X=H
4, R_1=R_2=H, X=H

Figure 8. Examples of photosensitizer which have no nobel metals in a photocatalytic systems for hydrogen generation reported by Eisenberg *et al.*[4]

Eisenberg *et al.* have showed that while the parent fluorescein dye **4** shows no photocatalytic activity under the same conditions, the iodinated analogue **2** shows initial catalytic activity; however, it degrades faster than **1** under the same conditions. In addition, when the chlorinated dye **3** is used, the initial rates are reduced by a factor of 10.[4]

2.6.2. Electron Relay

In a photocatalytic water splitting reaction, the function of an electron relay is transfering the electron to proton which will be reduced to hydrogen. When the photosensitizer is excited, it transfers its electron to a molecule which acts as a relay to a proton source.[55] In the literature, methyl viologen is one the best used electron relay in a photocatalytic system.[48]

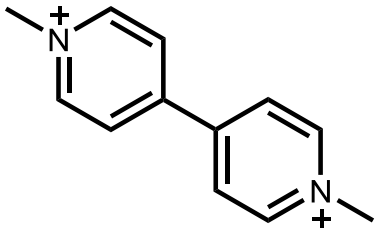


Figure 9. Methyl Viologen (MV^{2+}) as an electron relay.

Alberto *et al.* reported that ascorbate also acts as an electron relay in a photocatalytic system. They found that in the presence of [CoBr(aPPy)]Br catalyst, and electron donor tris-(2-carboxyethyl) phosphine (TCEP), production of hydrogen gas of the photosensitizer $Ru(bpy)_3^{2+}$ is depending on the AscOH concentration.[56]

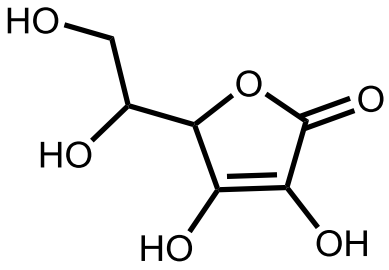


Figure 10. Example of an electron relay reported by Alberto *et al*.[56]

2.6.3. Sacrificial Reagent

Sacrificial reagents or donors are used as reducing agents that are oxidized easier than water, for instance, ethylenediamine tetraacetic acid (EDTA), triethylamine (TEA), or triethanolamine (TEOA).[42] These sacrifical donors provide electron refilling of the photosensitizer unit. Generally, when these donors are used in a solar process, the efficiency of the process is increased. According to Eisenberg *et al.*, TEOA is proven to be the most effective electron donor at hydrogen evolution under same conditions compared to TEA and EDTA, showing more than 20-fold increase in activity.[4]

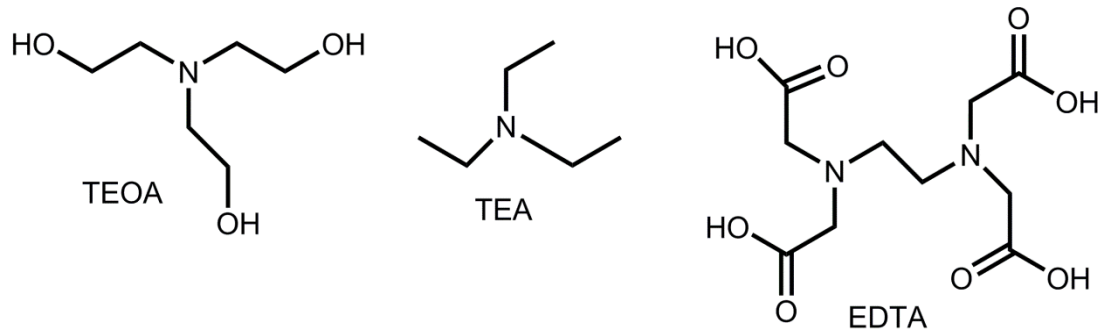


Figure 11. Some examples of electron donors in a photocatalytic system.[42]

2.6.4. Catalyst

The term "catalysis" was first used by Berzelius in 1836 to identify a new matter which has capability of popularizing the occurrence of a chemical reaction by a "catalytic contact".[57] According to him, a catalyst was a matter which acts as an accelerator for the speed of a chemical reaction when it is added to the reaction mixture. Catalysts had started to play a major role on chemical industry from the beginning of twentieth century, recently more than 95 % of chemicals are produced by a catalytic reaction.[58]

There are two types of catalysts; homogeneous catalysts and heterogeneous catalysts. In a heterogeneous reaction, the catalyst and the reactants are in different phase, whereas in a homogeneous reaction, the catalyst and the reactants are in the same phase. In literature, many homogeneous and heterogeneous catalysts made of noble metals such as ruthenium, iridium, and rhodium are developed. However, these noble metal made catalysts increase the cost. For water reduction, platinum has been used very often as a water reduction catalyst. Since platinum is very expensive and is low earth abundance, it should be replaced by a cheaper materials. Therefore, improvement of water oxidation catalysts (WOC) and water reduction catalysts (WRC) made of cheap and earth abundant elements is very crucial for solar energy conversion.[59]

In a photocatalytic system, function of a photocatalyst is to collect electrons for electrochemical potential and reduction of water and to serve as a gas evolution side,

meaning to produce H_2 gas.[60] The photocatalyst should have a suitable thermodynamic potential for water splitting and a sufficient narrow band gap to harvest photons. It is supposed to be also stable against photocorrosion.[58,61]

There are many macrocyclic cobalt complexes used as water reduction catalysts for hydrogen generation as it is listed in Figure 12.[44]

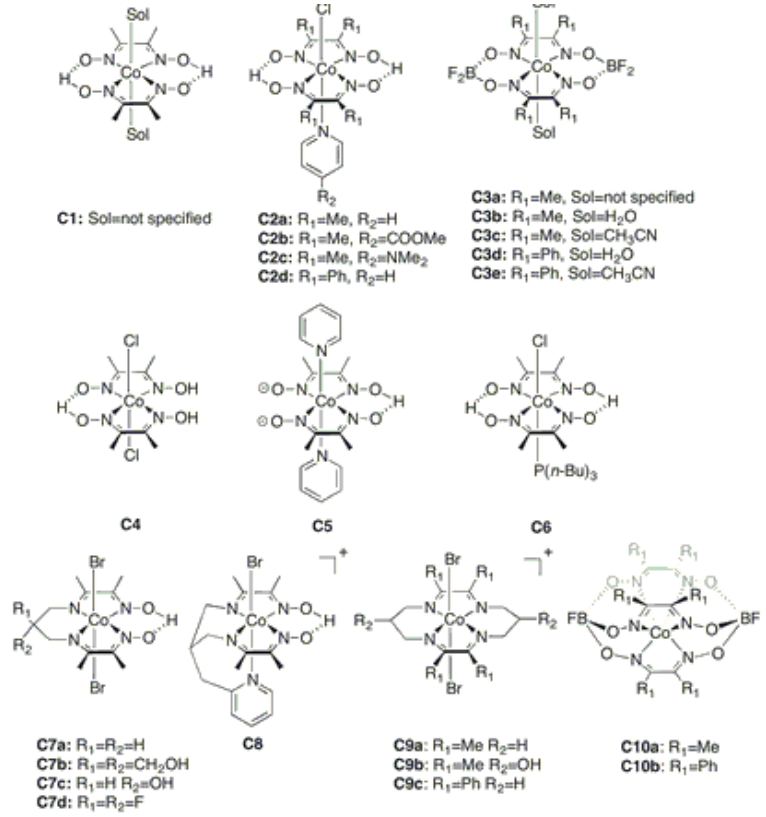


Figure 12. Examples of macrocyclic Co catalysts used as water reduction catalysts. Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from ref (44).

Eisenberg *et al.* showed that complex **5** has been found to produce H_2 gas with 100 turnovers, while related difluoroborylated species **6** produces H_2 gas in the presence of strong acid as it is seen in Figure 13. Moreover, it was also shown that complex **5** was used for the first time to produce H_2 from aqueous protons in a photocatalytic system in the presence of electron source.[44]

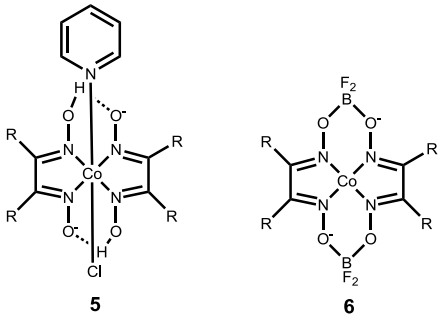


Figure 13. Photocatalysts reported by Eisenberg *et al.* which are used in a photocatalytic system. Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from ref (44).

2.7. BODIPY Dyes

BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) dye was synthesized for the first time unintentially in 1968 by Treibs and Kreuzer while they were trying to react 2,4-dimethylpyrrole with acetic anhydride in the presence of $BF_3.OEt_2$.[62] After a very long time Haugland and Kang reported the fluorescent properties of BODIPY dyes in 1985.[63,64] After the discovering of characteristics of BODIPY dyes, its bio-labelling applications are employed intensively.[65–67] In Figure 14, simple BODIPY core structure, and its IUPAC numbering are given.

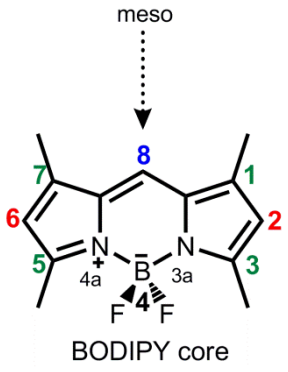


Figure 14. The structure and numbering system of BODIPY.

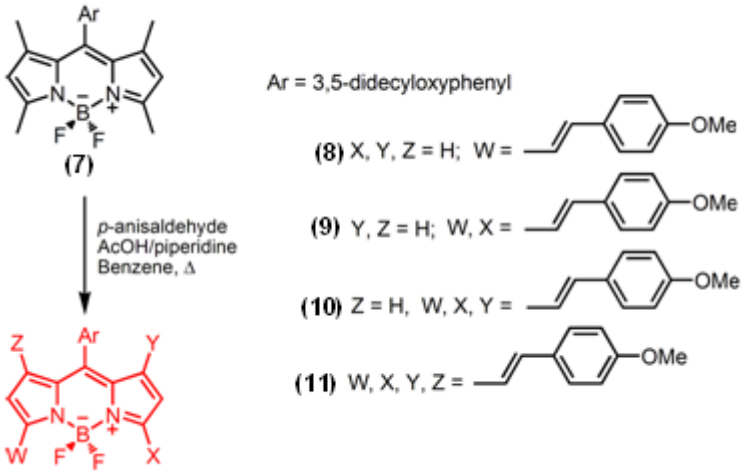
For the last three decades, BODIPY dye has been used widely and it still is very popular. This popularity comes from its admirable properties of BODIPY. To begin with, the BODIPY unit has a major absorption peak corresponding to S_0-S_1 transition near 500-520 nm with moderate and high absorption coefficients (40.000-100.000 M^-

^{1} cm^{-1}). It should be also taken into account that there is a weak peak at high-energy region around 370 ± 10 nm corresponding to S_0-S_2 transition.[68] Due to the relaxation of an excited electron from S_1 state, strong and sharp emission is observed between 530-550 nm. BODIPY dyes have high thermal, photostability, physiological medium compatibility.[69] They also have very high fluorescence quantum yield ($\phi_f > 0.50$) and long fluorescence lifetimes. In BODIPY dyes, phosphorescence does not occur very often because these dyes have very low triplet quantum yields.[69]

Although BODIPY dyes have many advantages mentioned above, they also have some disadvantages such as solubility in aqueous solution. Moreover, they are lack of functional groups and low absorbance and emission wavelength for biomedical applications. However, these problems can be addressed by appropriate functionalization of the BODIPY core at meso (8), 1-7, 2-6, 3-5 positions and boron center.[66,70] Functionalization of meso (8) position can be done with a suitable aldehyde or an acid chloride while performing the condensation reaction.[71] When there is phenyl group at the meso position, the methyl groups at 1 and 7 positions of the BODIPY unit force phenyl group to be almost perpendicular to BODIPY core. In addition, meso position can be derived by the replacement of carbon atom with nitrogen atom, corresponding to aza-BODIPYs[72] which shifts absorption and emission peaks to red end of the visible spectrum (650-850 nm).

Methyl groups at 1-7, and 3-5 positions have acidic character; hence, they are appropriate for Knoevenagel Condensation reaction.[73] With the help of this condensation reaction, one can shift the absorption and emission peaks to the red side of the spectrum due to the extension of π-conjugation as it is seen in Figure 15. As judged by Akkaya's research group tetra-, tri-, di-, and monostyryl modifications have greater versatility.[73] Several reasons have been attributed for this behavior such as the fact that Knoevenagel Condensation reaction has usually high yields in the case of 3-5 methyls; different aldehydes with different stereo-electronic characteristics can be used in different reaction conditions. Finally, in the case of strong charge donating groups, the molecules are likely to be used as switchable

molecules with internal charge transfer characteristics which can be used as chemosensors and molecular logic gates.[74,75] Together with Knoevenagel Condensation reaction, when there are good leaving groups at 3 and 5 positions of BODIPY core, they are willing to nucleophillic aromatic substitution. As Dehaen and Boens reported, 3,5-dichloro BODIPY dyes are open to nucleophillic substitutions.[76] In addition, in order to get photo-stable and redox active BODIPY derivatives, two fluorine atoms which are at the boron center can be replaced by alkoxides and aryl groups as it was reported by Ziessel *et al.*, which are used as sensitizers for organic photovoltaics and dye-sensitized solar cells.[77,78] 2 and 6 positions of BODIPY core are relatively electron rich; therefore, they are open to electrophillic aromatic substitution. At these positions, one can perform some types of reactions such as, sulfonation[79] which is important for water solubility, halogenation[80] ,formylation[81] , and nitration[82] reactions. In addition to these reactions, some outstanding reactions can be done at these positions (e.g., Sonogashira, Suzuki, Stille reactions) when it is introduced heavy atoms such as iodine and bromine which quenches the fluorescence due to effective inter-system crossing.[73]



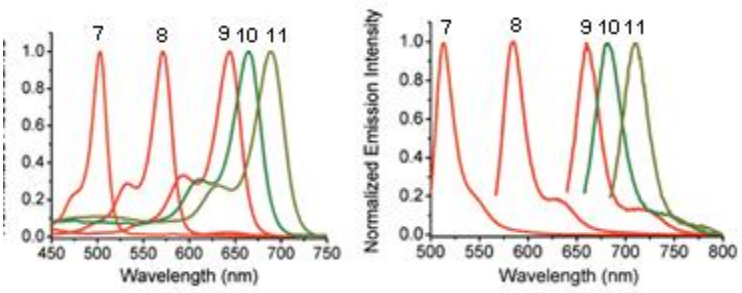


Figure 15.Functionalization of 3,5 and 1,7 positions by Knoevenagel condensation reaction. Copyright © 2009, American Chemical Society. Reprinted with permission from ref (73).

2.7.1. Synthesis of BODIPY Dyes

There are three different synthetic pathways to synthesize unsubstituted BODIPY dyes. First of all, according to Bruce *et al.*procedure[83,84], once the formation of dipyrromethane, it is oxidized by DDQ to obtain dipyrromethene followed by the addition of tertiary amine base and $BF_3.OEt_2$. Secondly, Pene-Cabrera and co-workers reported palladium-catalyzed reaction of 8-thiomethyl BODIPY and triethylsilane in the presence of copper(I) thienyl-2-carboxylate (CuTc) with very high yield[ ]. In the last synthetic pathway, in the presence of an acid, it occurs the condensation of unsubstituted pyrrole and pyrrole-2-carbaldehyde just before the addition of base and $BF_3.OEt_2$.[83,85]

Symmetric BODIPY dyes with meso derivatization are synthesized by acid-catalyzed condensation reaction of pyrroles with aldehydes, acid chlorides, or anhydrides in the presence of amine base and $BF_3.OEt_2$[70,86] as it is seen in Figure 16. When one use aldehydes in the condensation reactions, first of all dipyrromethane intermediate is formed, then it is oxidized to dipyrromethene by using quinone derivatives. Substituted BODIPY dyes at meso (8^{th} position) position are very common in usage compared to unsubstituted BODIPY dyes due to their properties. For instance, they bring high stability, high solubility in organic solvents. In addition, they can be further functionalized depending on the end use.

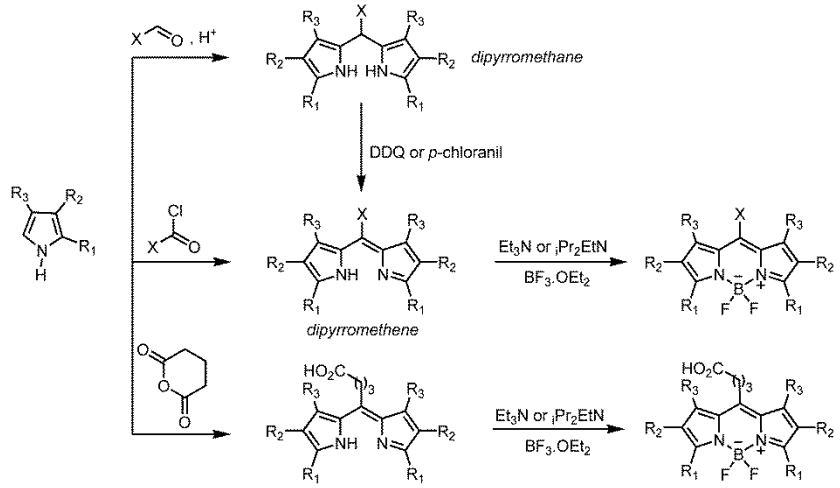


Figure 16. Synthetic pathways for meso-functionalized symmetric BODIPYs.

One can also synthesize meso-unsubstituted symmetric BODIPY dyes by the condensation of excess pyrrole derivatives (~2.2 eq.) with orthoesters.[83] In this kind of condensation reactions, first one obtain the dipyrromethene intermediate, then base and $BF_3.OEt_2$ complexation is added in order to obtain meso-unsubstituted symmetric BODIPY dyes. According to Burgess and co-workers, meso-unsubstituted symmetric BODIPY dyes can be obtained by pyrrole-2-carbaldehyde and $POCl_3$ without any excess pyrrole.[87–89] Both pathways are given in Figure 17.

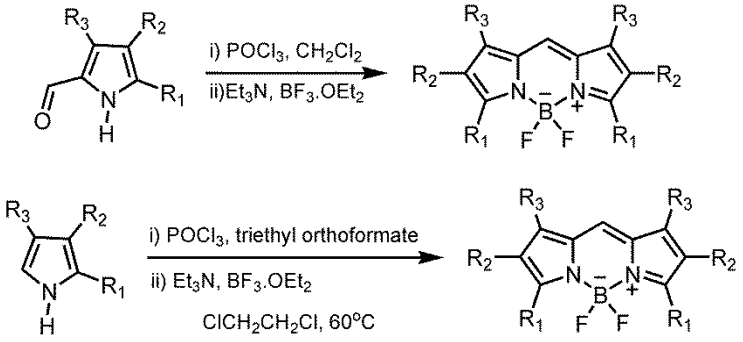


Figure 17. Synthetic pathways for meso-unsubstituted symmetric BODIPYs.

On the other hand, for synthesis of the asymmetric BODIPY dyes, condensation of pyrrole-2-carbaldehyde with other pyrrole derivatives can be used.[90,91]

2.7.2. Applications of BODIPY Dyes

There are many applications of BODIPY dyes due to the excellent properties of BODIPY dyes mentioned before. BODIPY derivatives can be used as fluorescent sensors, photosensitizers, photodynamic therapy agents. In addition, BODIPY dyes can be used in DNA labelling, light harvesting systems, molecular logic gates, ion sensing, liquid crystals, solar cells, energy transfer cassettes. Moreover, for the last years, BODIPY dyes have been used in photogeneration of hydrogen as photosensitizers.

There are some BODIPY based sensitizers which are used in photodynamic therapy as it is seen in Figure 18. Compound **12**[92] which was reported by Akkaya *et al* is one example of water soluble BODIPY based sensitizer which is used in photodynamic therapy. One can get longer wavelength by increasing conjugation, and it can be increased intersystem crossing with the help of heavy atom (Br), which increases the yield of singlet oxygen generation. Compound **13**[93] which was introduced by Nagano *et al* having a very low quantum yield (0,02) due to heavy atom. Finally, compound **14**[94] can be considered as another water soluble BODIPY based sensitizer.

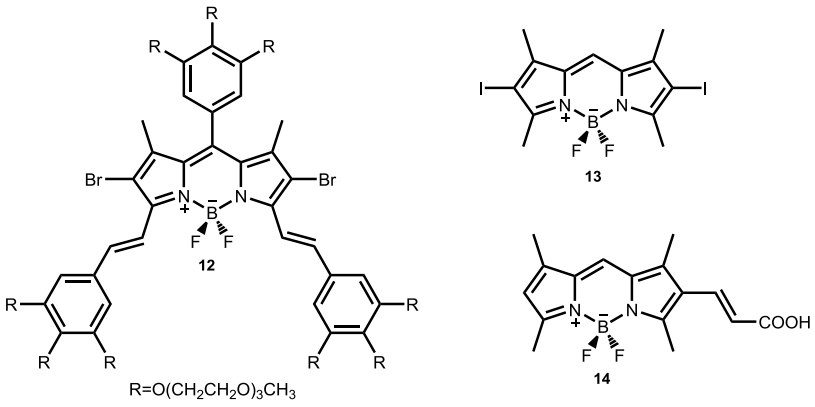


Figure 18. Some examples of BODIPY based photosensitizers used in photodynamic therapy.

Another applications of BODIPY dyes are PeT and ICT based sensors which can be seen in the Figure 19. Compound **15**[95] is a proton sensor. Strong electron donor dimethyl amino group promotes ICT. However; in the presence of a proton, dimethyl

amino group is protonated which blockes the ICT. Compound **16**[96] is used as a cadmium (II) sensor whose receptor part is anilino group. Compound **17**[97] has terpyridine group as recognition sites.

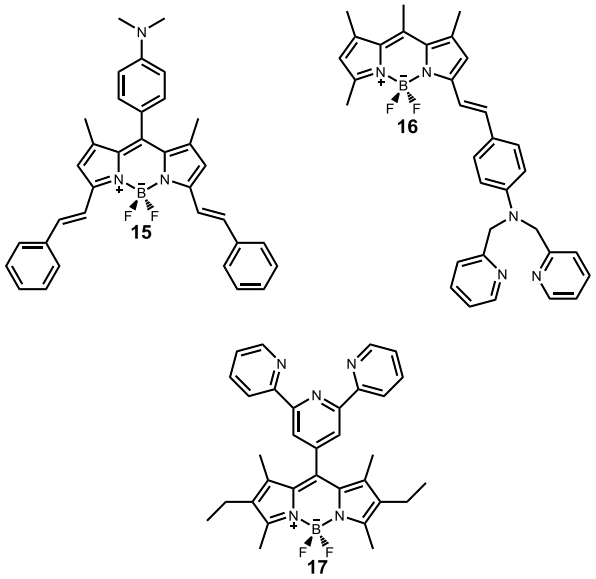


Figure 19. Some examples of BODIPY based chemosensors.

BODIPY dyes are also used in light harvesting systems and energy transfer cassettes. These systems consist of two parts which are donor and acceptor and there are two types of energy cassettes that are through space and through bond. In the Figure 20, compound **18** which was synthesized by Akkaya *et al* was designed for dendritic light harvesting systems.[98] In this molecule, the acceptor part is perylene bisimide and donor part is BODIPY core. Compound **19**[99] is an example of energy transfer cassette through bond type. Compound **20**[100] is the example of space energy transfer array. Compound **21** is the example of two BODIPY units which have been linked together for a terminal acceptor BODIPY unit via aromatic linkers having various lenghts.[101]

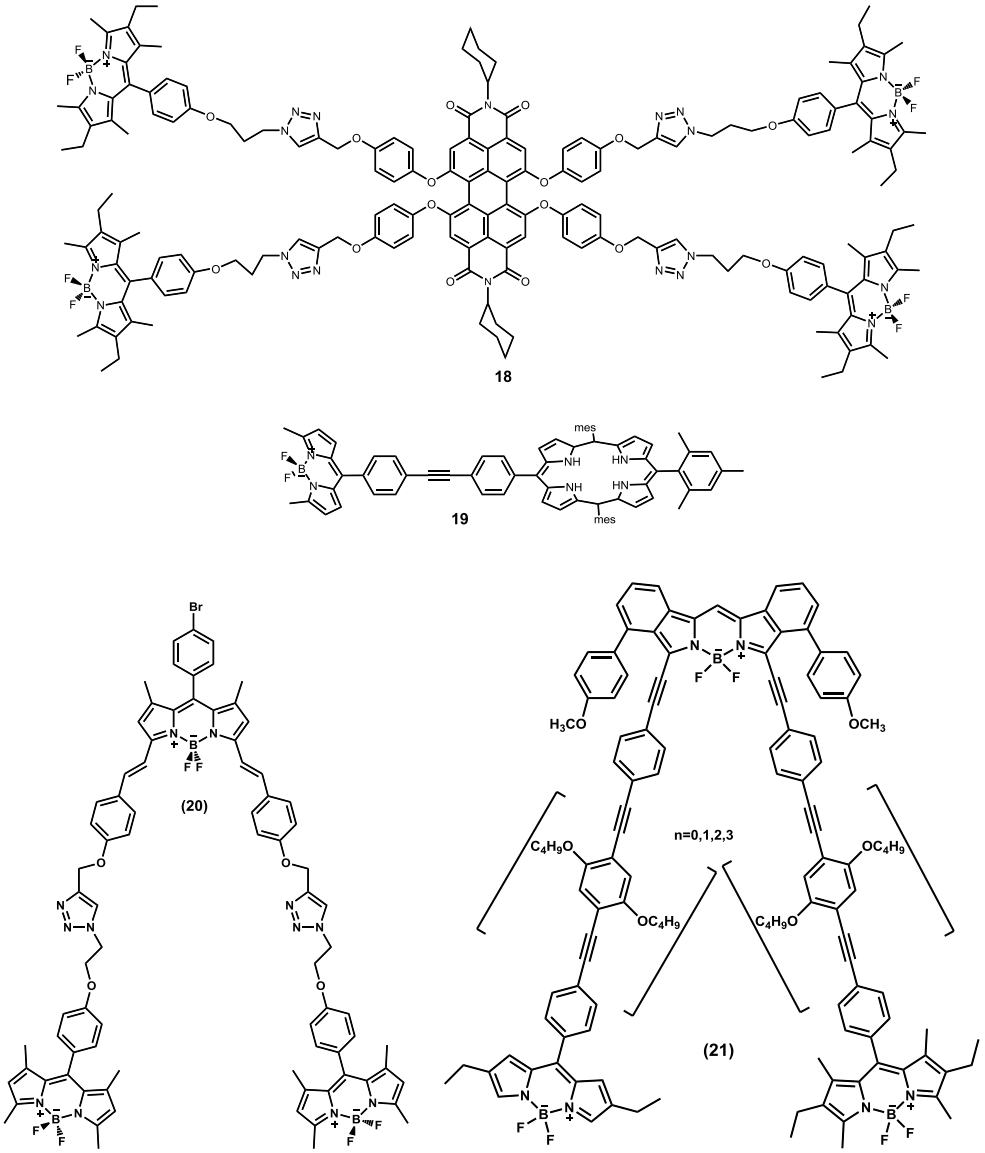


Figure 20. Examples of light harvesting systems and energy transfer cassettes.

CHAPTER 3

3. EXPERIMENTAL

3.1. General

All chemicals and solvents purchased from Aldrich were used without further purification. Column chromatography of all products was performed using Merck Silica Gel 60 (particle size: 0.040–0.063 mm, 230–400 mesh ASTM). Thin layer chromatography by Merck TLC Silica gel 60 F254 was used to monitor reactions. 1H NMR and 13C NMR spectra were recorded on Bruker DPX-400 (operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) in CDCl3 with tetramethylsilane as internal standard. All spectra were recorded at 25 oC and coupling constants (*J* values) are given in Hz. Chemical shifts are given in parts per million (ppm). Splittings in the spectra are shown as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Absorption spectrometry was performed using a Varian spectrophotometer. Fluorescence spectra were determined on a Varian Eclipse spectrofluorometer. All spectroscopy experiments were performed using spectrophotometric grade solvents. Mass spectroscopy measurements were conducted using MSBQTOF at Bilkent University, UNAM, Mass Spectrometry Facility.

3.1.1. Synthesis of Compound (23)

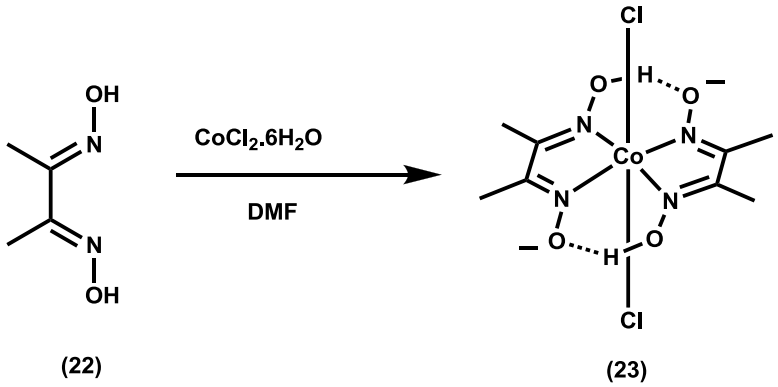


Figure 21.Synthesis of Compound **(23)**.

After all the starting material was consumed, DMF was removed under high vacuum and the product was purified by silica gel chromatography. Since the solubility of the product was not good, its characterization was performed with mass spectrometry. ESI-HRMS ($M-H^+$) calculated 358.97241, found 358.97682 Δ=-12.23ppm

3.1.2. Synthesis of Compound (24)

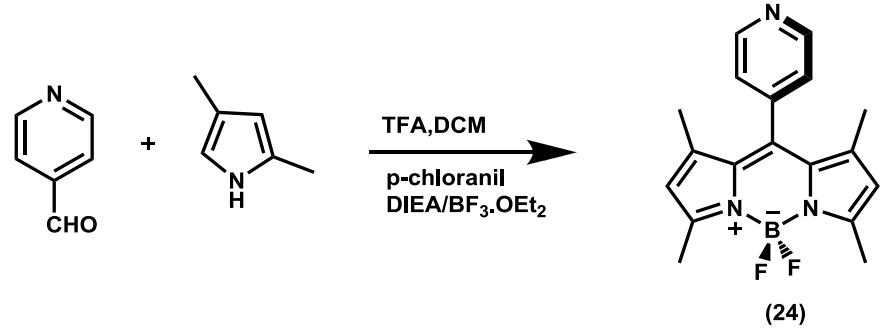


Figure 22. Synthesis of Compound **(24)**.

To a 500 mL round-bottomed flask containing 250 mL argon-degassed dichloromethane, 2,4-dimethylpyrrole (2.11 mL, 20.54 mmol), 4-pyridine carboxyaldehyde (0.88 mL, 9.34 mmol) were added. Then, to the reaction mixture trifluoroacetic acid (888 µL) was added at dark and it was mixed for 1 day. Then, p-chloranil (1 g, 4.1 mmol) was added and mixed for 1 additional hour. After that, TEA (8 mL) was added and mixed for 1 additional hour and $BF_3.OEt_2$ (8 mL) was added

and the reaction mixture was left to stir at room temperature overnight. When the starting material was consumed, water (100 mL) was added and the reaction mixture was extracted into DCM (3x100 mL), evaporated. The residue was purified by silica gel column chromatography using EtOAc:DCM (1:1) as the eluant and the compound was obtained as orange solid (0.85 g, 28 %). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.08 (d, 2H, *J*=8.88 Hz), 6.80 (d, 2H, *J*=8.76 Hz), 5.99 (s, 2H), 2.57(s, 6H), 1.51(s, 6H) . ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 156.5, 150.4, 143.7, 142.6 137.66, 123.3, 121.7, 14.7. ESI-HRMS ($M\text{-}H^+$) calculated 323.15254, found 323.14983, Δ= 8.39 ppm

3.1.3. Synthesis of Compound (25)

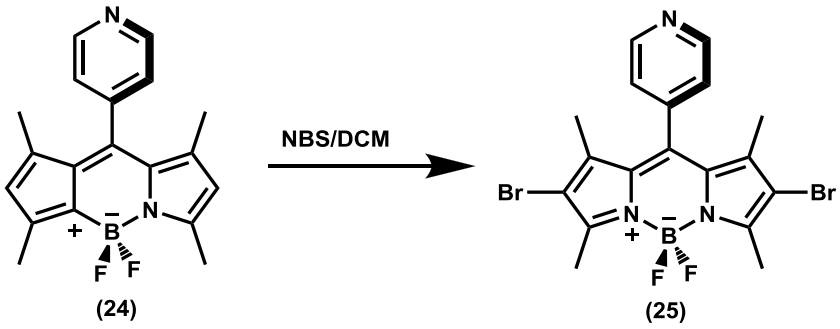


Figure 23. Synthesis of Compound **(25)**.

Compound **(24)** (100 mg, 0,307 mmol) was dissolved in 15 mL of DCM and 5 mL of DMF. Then, to the reaction mixture NBS (130 mg, 0.737 mmol) dissolved in 5 mL of DCM was added at room temperature. The progress of the reaction was monitored by TLC. After the starting material was consumed totally, water (100 mL) was added and the reaction mixture was extracted into DCM (3x100 mL), evaporated. The residue was purified by silica gel column chromatography using DCM as an eluant (0.142 g, 96 %). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.83 (d, 2H, *J*=5.92 Hz), 7.31 (d, 2H*J*=5.70 Hz), 2.61(s, 6H), 1.39(s, 6H) . ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 150.6, 150.3, 145.9, 123.0 118.4, 99.9, 9.2, 9.0. ESI-HRMS ($M+H^+$) calculated 480.98812, found 480.99430, Δ= -12.85 ppm

3.1.4. Synthesis of Compound (26)

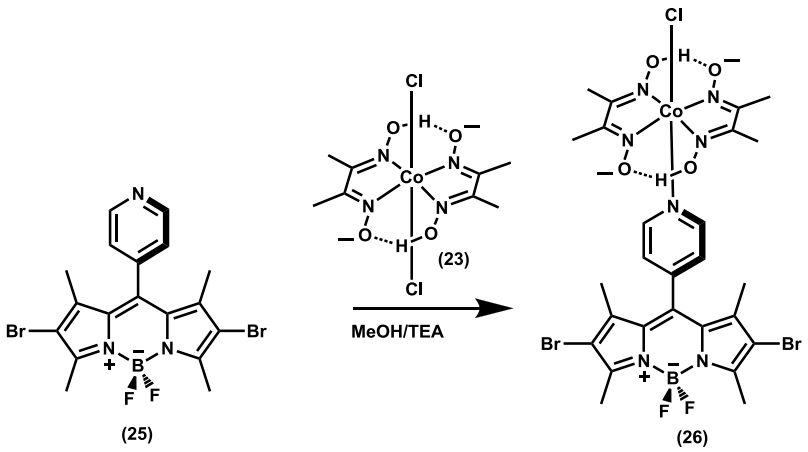


Figure 24. Synthesis of Compound **(26)**.

Compound **(23)** (76.2 mg, 0.211 mmol) was dissolved in 15 mL of MeOH and TEA (29 µL, 0.212 mmol). After the solution turns brownish and fully dissolves, compound **(25)** (50 mg, 0.106 mmol) which was dissolved in 1 mL of $CHCl_3$, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the orange-red solids were filtered off, washed with methanol, and dried under vacuum (81mg, 48%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.53 (d, 2H, *J*=5.63 Hz), 7.26 (d, 2H*J*=5.55 Hz), 2.61(s, 6H), 2.46 (s, 12H) 1.16(s, 6H). ESI-HRMS ($M-H^+$) calculated: 803.9844, found: 803.9823, Δ= 2.66 ppm

3.1.5. Synthesis of Compound (27)

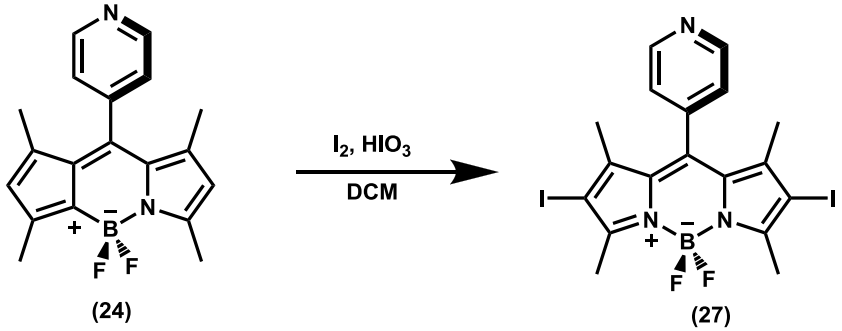


Figure 25. Synthesis of Compound **(27)**.

Compound **(24)** (100 mg, 0.308 mmol) was dissolved in 20 mL of DCM and 10 mL of EtOH. Then, I_2 (250 mg, 0.769 mmol) was added to the reaction mixture. HIO_3 (108 mg, 0.615 mmol) was dissolved in minimum amount of water and added dropwise to the solution and the reaction mixture was heated under reflux at 50°C. When the starting material was consumed totally, saturated solution of Na_2SO_3 was added and mixed for 20 min and the reaction mixture was extracted into DCM (3x100 mL), evaporated. The residue was purified by silica gel column chromatography using DCM as an eluant (130 mg, 75 %). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.85 (d, 2H, *J*=5.11 Hz), 7.31 (d, 2H *J*=5.81 Hz), 2.68 (s, 6H), 1.45(s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 157.8, 154.4, 150.8, 145.1 144.82, 124.3, 123.1, 17.2, 16.1. ESI-HRMS ($M-H^+$) calculated 574.94583, found 574.94706, Δ= -2.15ppm

3.1.6. Synthesis of Compound (28)

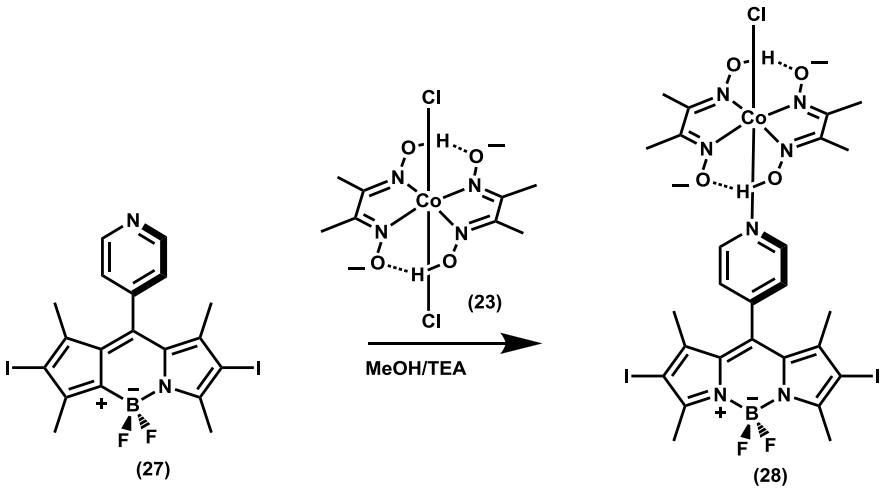


Figure 26. Synthesis of Compound **(28)**.

Compound **(23)** (62.5 mg, 0.173 mmol) was dissolved in 15 mL of MeOH and TEA (24 µL, 0.173 mmol). After the solution turns brownish and fully dissolves, compound **(27)** (50 mg, 0.087 mmol) which was dissolved in 1 mL of $CHCl_3$, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the reddish solids were filtered off, washed with methanol, and dried under vacuum. ^{1}H NMR ($CDCl_3$, 400

MHz, δ ppm) 8.52 (d, 2H, *J*=6.42 Hz), 7.25 (d, 2H *J*=6.50 Hz), 2.65 (s, 6H), 2.46 (s, 12H), 1.18 (s, 6H). ESI-HRMS ($M-H^+$) calculated 900.95, found 900.94763, Δ= -0.98 ppm

3.1.7. Synthesis of Compound (29)

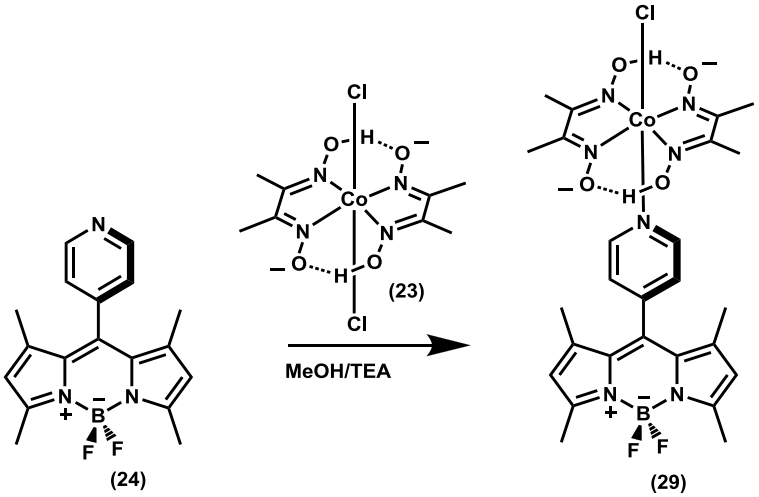


Figure 27. Synthesis of Compound **(29)**.

Compound **(23)** (113.7 mg, 0.315 mmol) was dissolved in 15 mL of MeOH and TEA (44 µL, 0.630 mmol). After the solution turns brownish and fully dissolves compound **(24)** (50 mg, 0.158 mmol) which was dissolved in 1 mL of $CHCl_3$, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the greenish solids were filtered off, washed with methanol, and dried under vacuum (0.098 g, 48 %). ^1H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.43 (d, 2H, *J*=6.07 Hz), 7.25 (d, 2H*J*=6.06 Hz), 6.0 (s, 2H), 2.53 (s, 6H), 2.43 (s, 12H), 1.15(s, 6H) . ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 157.6, 152.6, 151.8, 147.1, 141.3, 125.4, 122.4, 29.6, 14.1,13.0. ESI-HRMS ($M-H^+$) calculated 648.16337, found 648.15960, Δ= 5.82 ppm

3.1.8. Synthesis of Compound (30)

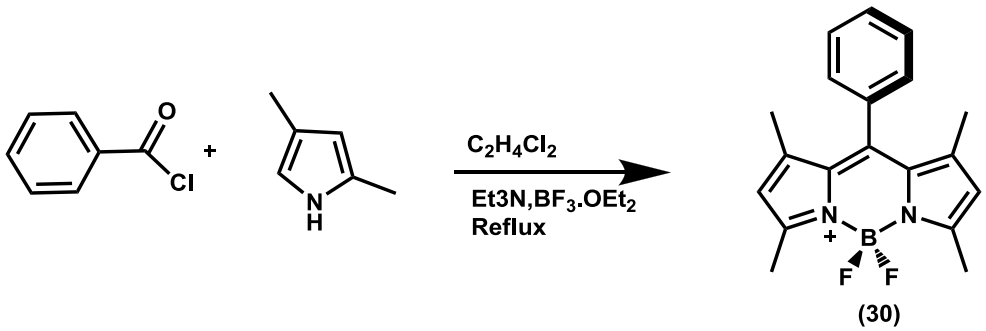


Figure 28. Synthesis of Compound **(30)**.

To a 500mL round-bottomed flask containing 500 mL argon-degassed dichloroethane, 2,4-dimethyl pyrrole (9.56 mmol, 0.924 g) and benzoyl chloride (4,34 mmol, 0.611 g) were added. The solution was refluxed for 1 day at 90^{o}C. After that, 5 mL of Et_3N and 5 mL of $BF_3.OEt_2$ were successively added and after 30 min, the reaction mixture was washed with water (3 x 100 mL), which was then extracted into the CH_2Cl_2 (3 x 100 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography using 1:5 (EtOAc/Hexane)as the eluent.Red solid (0.631 g, 21%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 3H), 7.29 (m, 2H), 6.00 (s, 2H), 2.58 (s, 6H), 1.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 129.4, 129.1, 128.9, 128.2, 127.9, 119.8, 115.6, 15.1, 11.7. ESI-HRMS ($M-H^-$) calculated 324.17184 found 324.17633, Δ= -13.64 ppm

3.1.9. Synthesis of Compound (31)

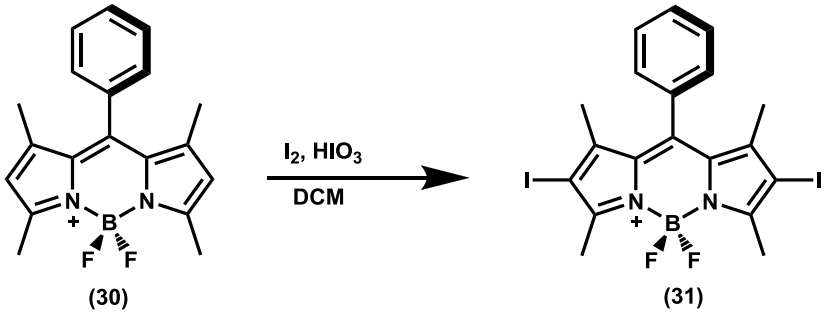


Figure 29. Synthesis of Compound **(31)**.

Compound **(30)** (100 mg, 0.308 mmol) was dissolved in 20 mL of DCM and 10 mL of EtOH. Then, I_2 (196 mg, 0.771mmol) was added to the reaction mixture. HIO_3 (109 mg, 0.617mmol) was dissolved in minimum amount of water and added dropwise to the solution and the reaction mixture was heated under reflux at 50^oC for an hour. When the starting material was consumed totally, saturated solution of Na_2SO_3 was added and mixed for 20 min at room temperature and the reaction mixture was extracted into DCM (3x100 mL), evaporated. The residue was purified by silica gel column chromatography using DCM as an eluant. HA 52 (100 mg, 0.308 mmol) was dissolved in 20 mL of DCM and 10 mL of EtOH. Then, I_2 (250 mg, 0.769 mmol) was added to the reaction mixture. HIO_3 (108 mg, 0.615 mmol) was dissolved in minimum amount of water and added dropwise to the solution and the reaction mixture was heated under reflux at 50^oC. When the starting material was consumed totally, saturated solution of Na_2SO_3 was added and mixed for 20 min and the reaction mixture was extracted into DCM (3x100 mL), evaporated. The residue was purified by silica gel column chromatography using DCM as an eluant. (130 mg, 73 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 3H), 7.26 (s, 2H), 2.65 (s, 6H), 1.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 145.3, 142.4, 134.7, 129.5, 129.4, 127.8, 29.6, 16.9, 15.9. ESI-HRMS ($M-H^-$) calculated 573.95058 found 573.94237, Δ= 14.3 ppm

3.1.10. Synthesis of Compound (32)

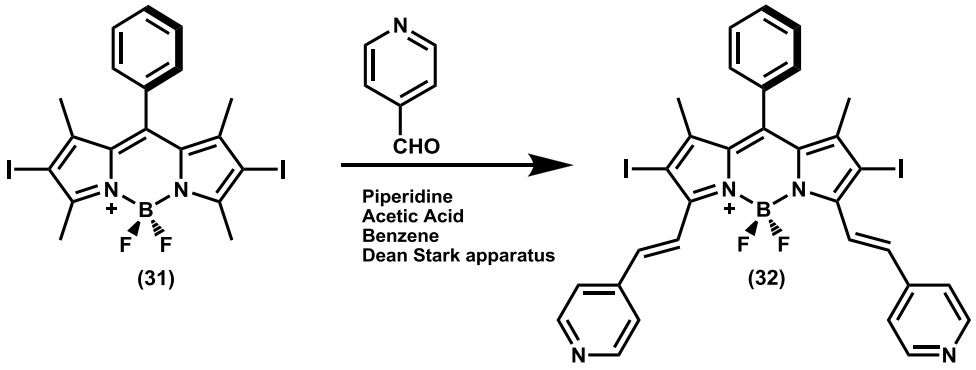


Figure 30. Synthesis of Compound **(32)**.

Compound **(31)** (177 mg, 0.307 mmol) and 4-pyridine carboxyaldehyde (72 µL, 0.710mmol) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution, piperidine (270 µL, 2.73 mmol) and acetic acid (220 µL, 3.84 mmol) were added. The mixture was heated under reflux at 100 oC overnight by using a Dean Stark trap and it is monitored by TLC. When all the starting material had been consumed, the mixture was cooled to room temperature and the solvent was evaporated. Water (100 mL) was added to the residue and the product was extracted with the DCM (3 x100 mL). The organic phace dried over Na_2SO_4, evaporated. The residue was purified by silica gel column chromatography using 92:8 (EtOAc: MeOH) solution as the eluant and the compound was obtained as blue solid (0.065 g, %28 yield). ^{1}H NMR (400 MHz, CDCl3) δ 8.70 (d, J= 5.8 Hz, 4H), 8.09 (d, J = 16.7 Hz, 2H), 7.86 (d, J = 16.7 Hz, 2H), 7.60-7.58 (m, 3H), 7.54 (d, J = 5.8 Hz, 4H), 7.34-7.32 (m, 2H), 1.50 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 149.9, 147.1, 144.1, 136.5, 129.9, 129.7, 127.9, 123.0, 121.6, 17.6. ESI-HRMS (M-H^-) calculated 752.00367 found 751.99281, Δ= 14.3 ppm

3.1.11. Synthesis of Compound (33)

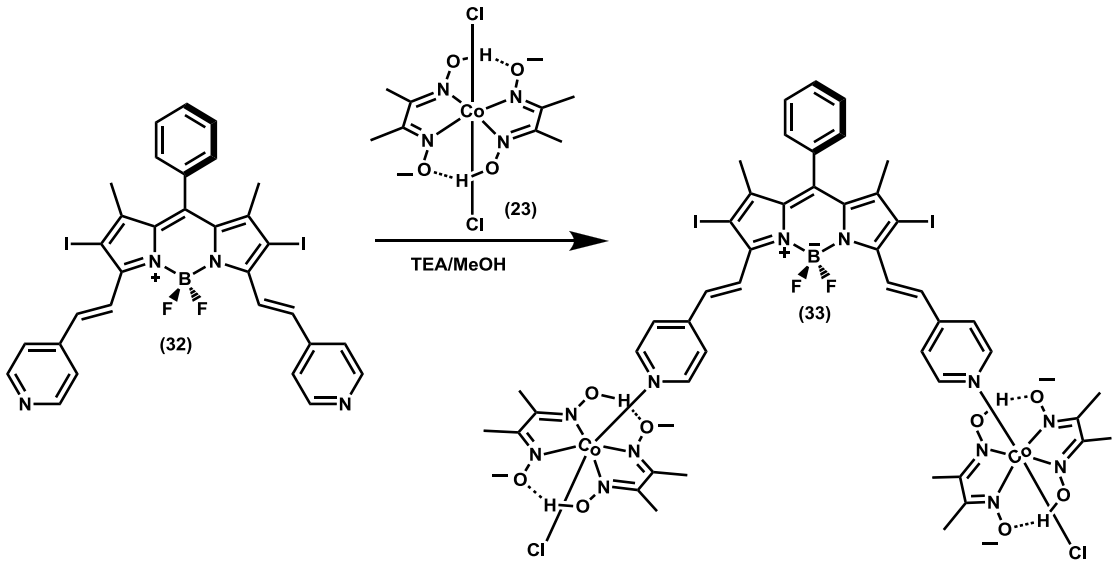


Figure 31. Synthesis of Compound **(33)**.

Compound **(23)** (43.2 mg, 0.121mmol) was dissolved in 15 mL of MeOH and TEA (16.65 µL, 0.121mmol). After the solution turns brownish and fully dissolves, compound (32) (55 mg, 0.083mmol) which was dissolved in 1 mL of CHCl3, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the greenish solids were filtered off, washed with methanol, and dried under vacuum (0.101 g, % 60 yield). ^{1}H NMR (400 MHz, CDCl3) δ 8.29 (d, J = 6.4 Hz, 4H), 7.88 (d, J = 16.7 Hz, 2H), 7.71 (d, J = 16.6 Hz, 2H), 7.60 (d, J = 7.3 Hz, 4H), 7.36 (d, J = 6.4 Hz, 3H), 2.48 (s, 24H), 1.48 (s, 6H), 1.28 (s, 6H). ESI-HRMS ($M-H^{+}$) calculated: 1424.00729 found: 1423.00695, Δ= 7.26 ppm

3.1.12. Synthesis of Compound (34)

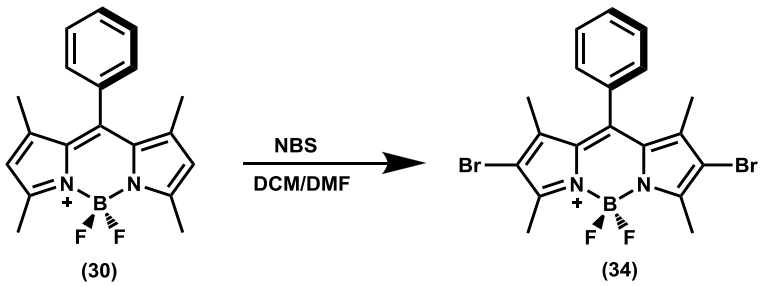


Figure 32. Synthesis of Compound **(34)**.

Compound **(30)** (100 mg, 0,308mmol) was dissolved in 15 mL of DCM and 5 mL of DMF. Then, to the reaction mixture NBS (132 mg, 0.740mmol) dissolved in 5 mL of DCM was added at room temperature. The progress of the reaction was monitored by TLC. After the starting material was consumed totally, water (100 mL) was added and the reaction mixture was extracted into DCM (3x100 mL), evaporated. The residue was purified by silica gel column chromatography using 1:1 DCM/Hexane as an eluant (0.09 g, %61 yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 3H), 7.31 – 7.26 (m, 2H), 2.63 (s, 6H), 1.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 142.1, 140.5, 134.4, 129.5, 129.4, 127.7, 13.7, 13.6. ESI-HRMS ($M-H^{-}$) calculated: 477.97832 found: 477.97505, Δ= 6.83 ppm

3.1.13. Synthesis of Compound (35)

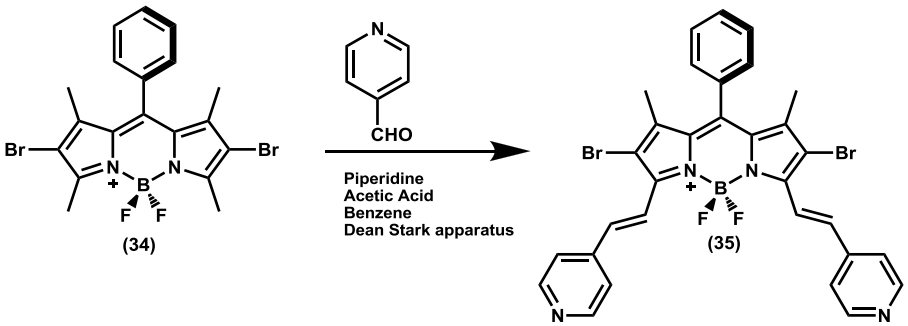


Figure 33. Synthesis of Compound **(35)**.

Compound **(34)** (148 mg, 0.307mmol) and 4-pyridine carboxyaldehyde (72 µL, 0.709mmol) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution, piperidine (270 µL, 2.73 mmol) and acetic acid (220 µL, 3.84 mmol) were added. The mixture was heated under reflux at 100 ^{o}C overnight by using a Dean Stark trap and it is monitored by TLC. When all the starting material had been consumed, the mixture was cooled to room temperature and the solvent was evaporated. Water (100 mL) was added to the residue and the product was extracted with the DCM (3 x100 mL). The organic phace dried over Na_2SO_4, evaporated. The residue was purified by silica gel column chromatography using 98:2 (EtOAc: MeOH) solution as the eluant and the compound was obtained as blue solid (0.063 g, %31 yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J*= 4.1 Hz, 4H), 8.07 (d, *J* = 16.6 Hz, 2H), 7.89 (d, *J* = 16.6 Hz, 2H), 7.62-7.60 m, 3H), 7.54 (d, *J* = 4.1 Hz, 4H), 7.35-7.33 (m, 2H), 1.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 150.8, 147.2, 142.2, 141.0, 135.5, 134.7, 130.1, 129.5, 127.8, 127.0, 122.8, 18.1.

3.1.14. Synthesis of Compound (36)

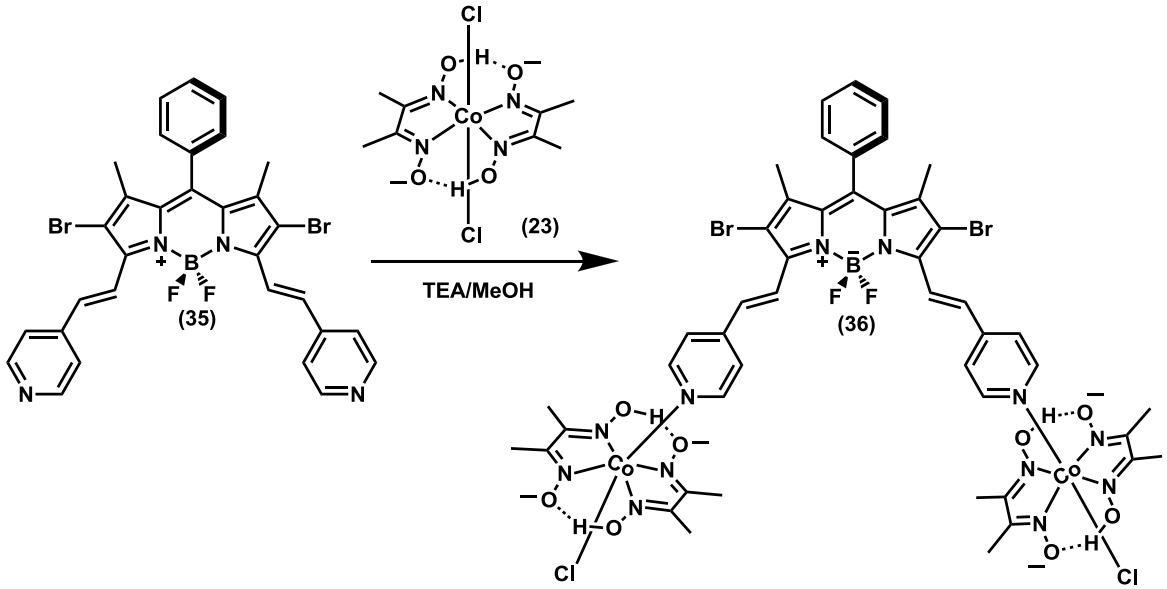


Figure 34. Synthesis of Compound **(36)**.

Compound **(23)** (120 mg, 0.333mmol) was dissolved in 15 mL of MeOH and TEA (47 µL, 0.333mmol). After the solution turns brownish and fully dissolves, compound **(35)** (55 mg, 0.083mmol) which was dissolved in 1 mL of $CHCl_3$, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the greenish solids were filtered off, washed with methanol, and dried under vacuum (0.081 g, %19 yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 4H), 8.05 (d, *J* = 16.7 Hz, 2H), 7.88 (d, *J* = 16.6 Hz,2H), 7.59 (dd, *J* = 9.8, 6.4 Hz, 4H), 7.53 (s, *J* = 4.9 Hz, 3H), 7.32 (dd, *J* = 5.5, 2.2 Hz, 2H), 2.17 – 2.03 (m, 6H), 1.27 (d, *J* = 6.1 Hz, 6H). ESI-HRMS ($M+Na^+$) calculated: 1328.03503, found: 1328.026226, Δ= 6.6 ppm.

3.1.15. Synthesis of Compound (37)

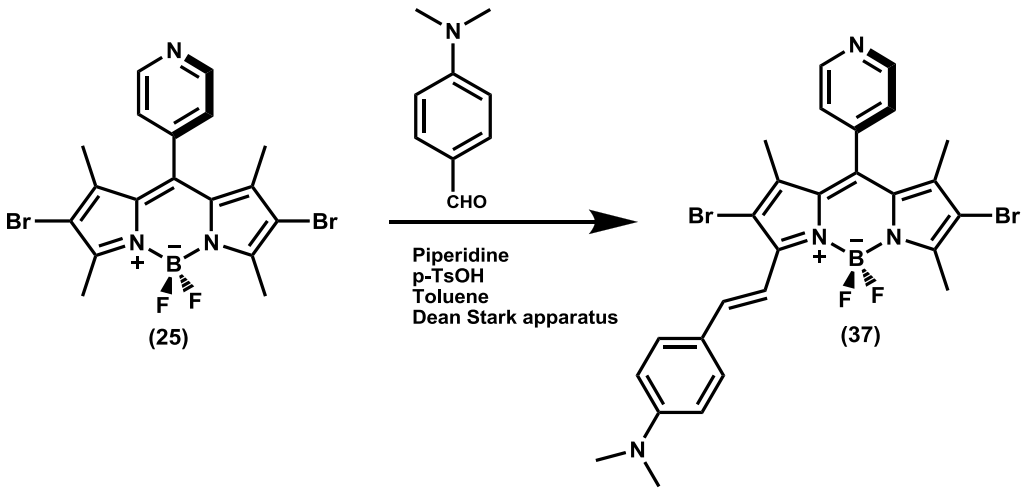


Figure 35. Synthesis of Compound **(37)**.

Compound **(25)** (257 mg, 0.534mmol) and 4-pyridine carboxyaldehyde (198 mg, 1.3mmol) were added to a 100 mL round-bottomed flask containing 50 mL toluene and to this solution, piperidine (275 µL) and p-TsOH (catalytic amount) were added. The mixture was heated under reflux at 120 ^{o}C overnight by using a Dean Stark trap and it is monitored by TLC. When all the starting material had been consumed, the mixture was cooled to room temperature and the solvent was evaporated. Water (100 mL) was added to the residue and the product was extracted with the DCM (3 x100 mL). The organic phase dried over Na_2SO_4, evaporated. The residue was purified by flash column chromatography using DCM as the eluant and the compound was obtained as blue solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 5.5 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 3.08 (s, 6H), 2.67 (s, 3H), 1.47 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 143.6, 143.5, 141.4, 129.7, 123.6, 114.0, 112.9, 112.0, 40.2, 33.8, 31.9, 29.3, 22.6, 14.1, 13.7. ESI-HRMS ($M\text{-}H^-$) calculated 610.04706, found 610.04559, Δ= 2.42 ppm

3.1.16. Synthesis of Compound (38)

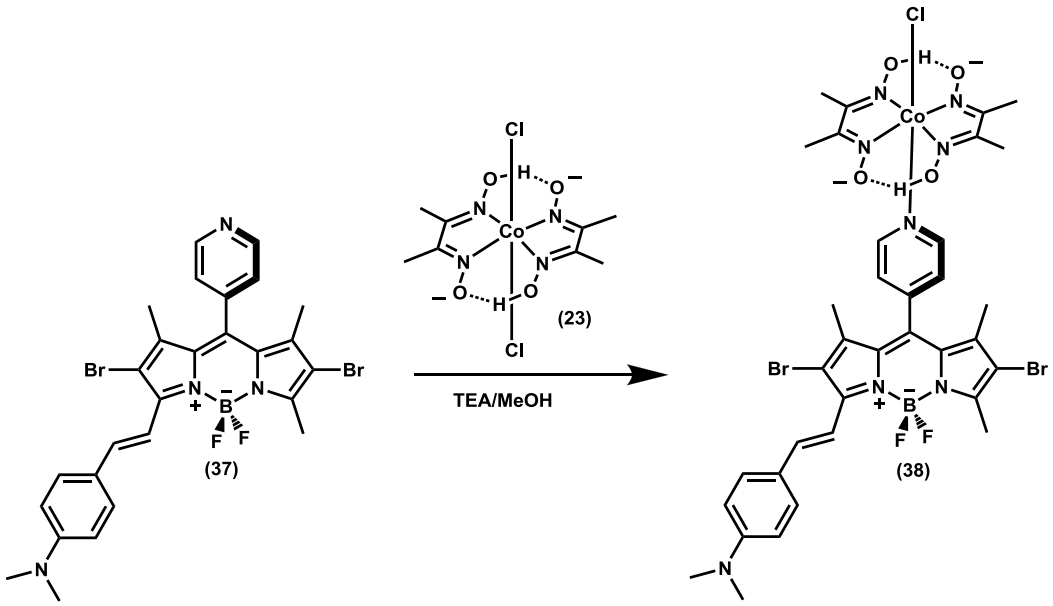


Figure 36. Synthesis of Compound **(38)**.

Compound (23) (59 mg, 0.163mmol) was dissolved in 15 mL of MeOH and TEA (23 µL, 0.163mmol). After the solution turns brownish and fully dissolves, compound (37) (50 mg, 0.081mmol) which was dissolved in 1 mL of $CHCl_3$, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the greenish solids were filtered off, washed with methanol, and dried under vacuum. ESI-HRMS ($M-H^-$) calculated 934.05062, found 934.0431, Δ= 8.11 ppm

3.1.17. Synthesis of Compound (39)

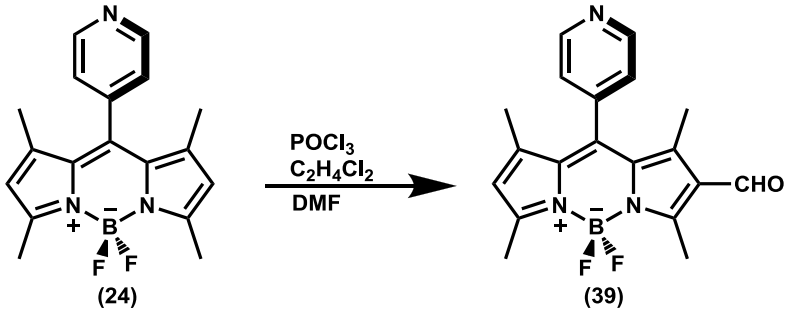


Figure 37. Synthesis of Compound **(39)**.

A mixture of DMF (1.5 mL) and $POCl_3$ (1.5 mL) was stirred under argon for 5 min in the ice bath. After warming solution up to room temperature, it was stirred for additional 30 min. Compound **(24)** (200 mg, 0.615 mmol) in 40 mL dichloroethane was added to the solution and temperature raised to 60^0C. After stirring for 3 hrs, the mixture was cooled to room temperature and then poured in to iced cooled saturated aqueous solution of $NaHCO_3$ (200 mL). Then reaction mixture was stirred for 30 min after warming solution to room temperature. After 30 min. the mixture was washed with H_2O (2x100 mL). The product was extracted into the dichloromethane. Organic phase dried over Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography using 95:5 (EtOAc/Acetone)as the eluent. Yellowish-red solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (d, *J* = 1.3 Hz, 1H), 8.87 (s, 2H), 7.35 (d, *J* = 4.5 Hz, 2H), 6.21 (s, 1H), 2.84 (s, 3H), 2.65 (s, 3H), 1.72 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 150.9, 150.68, 146.4, 142.8, 138.6, 124.6, 123.0, 113.9, 29.6, 15.0, 14.1, 13.0. ESI-HRMS ($M-H^-$) calculated 351.14745, found 351.14907, Δ= -4.6 ppm

3.1.18. Synthesis of Compound (40)

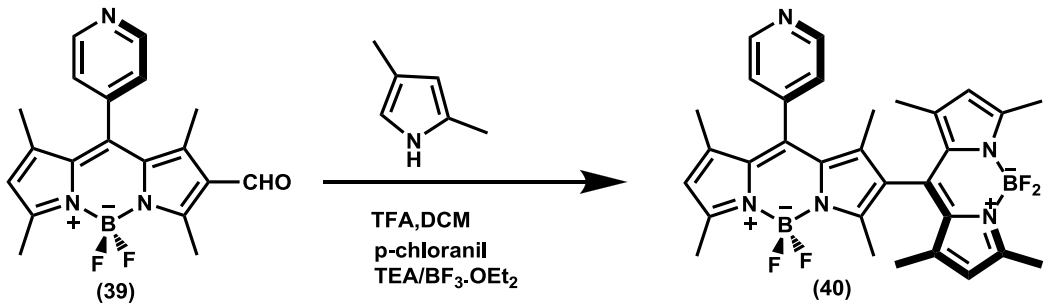


Figure 38. Synthesis of Compound **(40)**.

To a 500mL round-bottomed flask containing 250 mL argon-degassed CH_2Cl_2, were 2,4-Dimethyl pyrrole (35µL, 0.340 mmol)) and compound **(39)** (50 mg, 0.142 mmol)) were added. The solution was stirred under N_2 at room temperature for 1 day. After that, 13.5 µL of Et_3N, p-chloranil (35 mg) and 0.5 mL of $BF_3.OEt_2$ were successively added and after 30 min, the reaction mixture was washed three times with water (3 x 100 mL), which was then extracted into the CH_2Cl_2 (3 x 100 mL) and

dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography using 98:2 (DCM/MeOH) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.39 (s, 1H), 6.14 (s, 1H), 6.01 (s, 1H), 2.63 (s, 2H), 2.55 (s, 3H), 2.45 (s, 2H), 1.72 (s, 4H), 1.47 (s, 2H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 155.9, 151.9, 150.2, 144.9, 142.1, 138.0, 137.8, 133.5, 123.3, 121.3, 29.6, 14.8, 14.6, 13.9, 12.8, 12.3.

3.1.19. Synthesis of Compound (41)

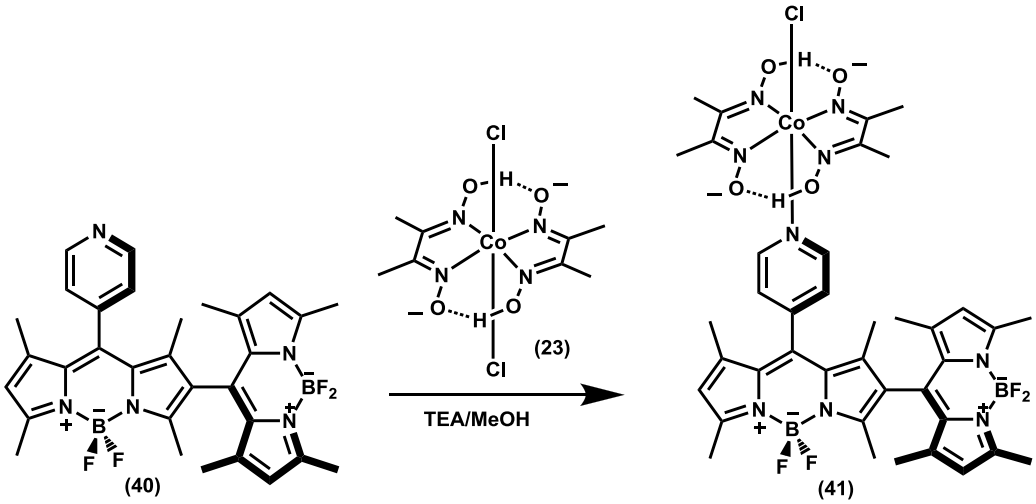


Figure 39. Synthesis of Compound **(41)**.

Compound **(23)** (63 mg, 0.175mmol) was dissolved in 15 mL of MeOH and TEA (25 µL, 0.175mmol). After the solution turns brownish and fully dissolves, compound **(40)** (50 mg, 0.088mmol) which was dissolved in 1 mL of $CHCl_3$, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the greenish solids were filtered off, washed with methanol, and dried under vacuum. ESI-HRMS ($M-H^-$) calculated: 895.27, found: 894.26763, Δ= -0.32s ppm.

3.1.20. Synthesis of Compound (42)

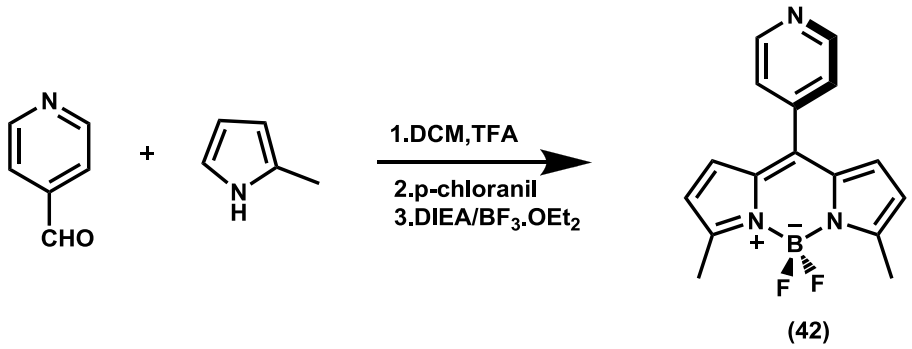


Figure 40. Synthesis of Compound **(42)**.

To a 500 mL round-bottomed flask containing 250 mL argon-degassed dichloromethane, 2-methylpyrrole (1.67 mg, 20.55 mmol), 4-pyridine carboxyaldehyde (0.891 mL, 9.34 mmol) were added. Then, to the reaction mixture trifluoroacetic acid (888 µL) was added at dark and it was mixed for 1 day. Then, p-chloranil (1 g, 4.1 mmol) was added and mixed for 1 additional hour. After that, DIEA (8 mL) was added and mixed for 1 additional hour and $BF_3.OEt_2$ (8 mL) was added and the reaction mixture was left to stir at room temperature overnight. When the starting material was consumed, water (100 mL) was added and the reaction mixture was extracted into DCM (3x100 mL), evaporated. The residue was purified by silica gel column chromatography using DCM:MeOH (98:2) as the eluant and the compound was obtained as orange solid (85 mg, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.9 Hz, 2H), 7.36 (d, *J* = 5.9 Hz, 2H), 6.62 (d, *J* = 4.1 Hz, 2H), 6.27 (d, *J* = 4.2 Hz, 2H), 2.64 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 149.7, 141.8, 138.6, 133.7, 129.9, 124.5, 120.1, 14.9. ESI-HRMS ($M+H^+$) calculated 297.13579, found 297.13799, Δ= -7.4 ppm

3.1.21. Synthesis of Compound (43)

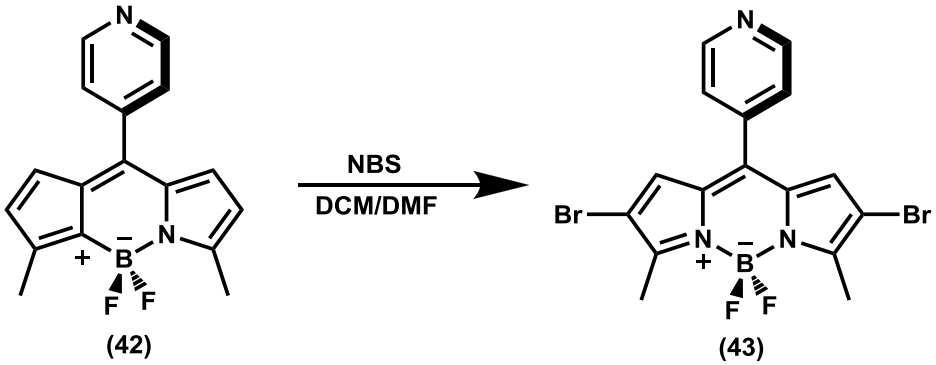


Figure 41. Synthesis of Compound **(43)**.

Compound **(42)** (100 mg, 0,337 mmol) was dissolved in 15 mL of DCM and 5 mL of DMF. Then, to the reaction mixture NBS (143.8 mg, 0.808 mmol) dissolved in 5 mL of DCM was added at room temperature. The progress of the reaction was monitored by TLC. After the starting material was consumed totally, water (100 mL) was added and the reaction mixture was extracted into DCM (3x100 mL), evaporated. The residue was purified by silica gel column chromatography using DCM as an eluant 147 mg, 96 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.5 Hz, 2H), 7.39 (d, *J* = 4.5 Hz, 2H), 6.76 (s, 2H), 2.66 (s, 6H).). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 150.1, 140.8, 138.2, 132.4, 129.9, 124.2, 109.7, 13.5. ESI-HRMS ($M+H^+$) calculated 452.95682, found 455.95926, Δ= -5.39 ppm

3.1.22. Synthesis of Compound (44)

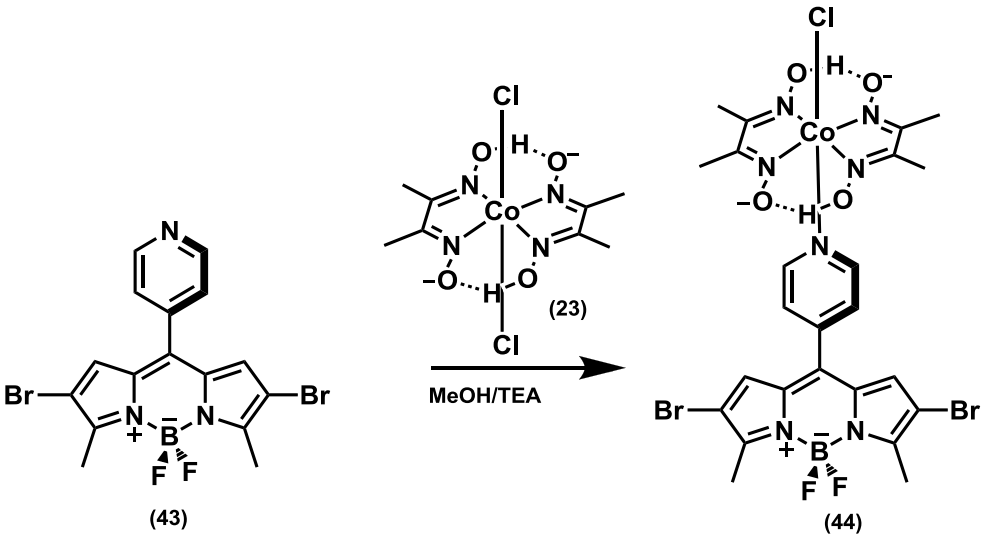


Figure 42. Synthesis of Compound **(44)**.

Compound **(23)** (159.27 mg, 0.442 mmol) was dissolved in 15 mL of MeOH and TEA (61.7 µL, 0.442 mmol). After the solution turns brownish and fully dissolves, compound (**43)** (100 mg, 0.221 mmol) which was dissolved in 1 mL of $CHCl_3$, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the greenish solids were filtered off, washed with methanol, and dried under vacuum. ESI-HRMS ($M-H^-$) calculated 775.95365, found 775.94379, Δ= 12.7 ppm

3.1.23. Synthesis of Compound (45)

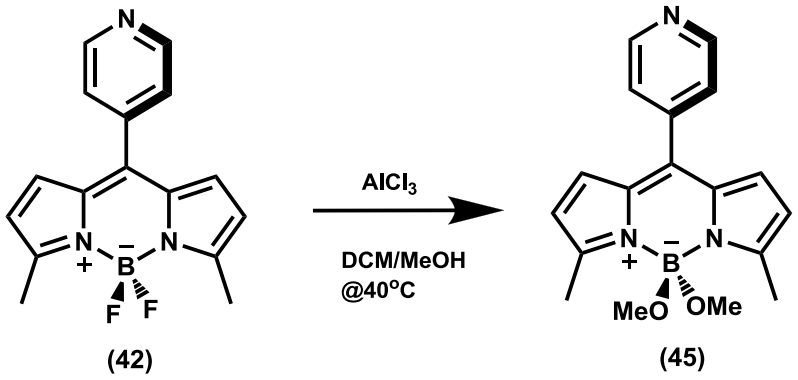


Figure 43. Synthesis of Compound **(45)**.

Compound **(42)** was dissolved in DCM in the presence of $AlCl_3$ under argon. The resulting mixture was refluxed for 5 min prior to addition of alcohol (MeOH). After 5 min at room temperature, the crude mixture was concentrated under reduced pressure and the residue was purified by alumina gel column chromatography using DCM:MeOH (98:2) as an eluant. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 5.9 Hz, 2H), 7.46 (d, *J* = 6.0 Hz, 2H), 6.63 (d, *J* = 4.1 Hz, 2H), 6.30 (d, *J* = 4.2 Hz, 2H), 2.97 (s, 6H), 2.65 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 149.6, 142.6, 138.3, 135.1, 128.4, 124.8, 119.7, 49.2, 14.9. ESI-HRMS ($M+Na^+$) calculated 343.15771, found 343.15995, Δ= -6.53 ppm

3.1.24. Synthesis of Compound (46)

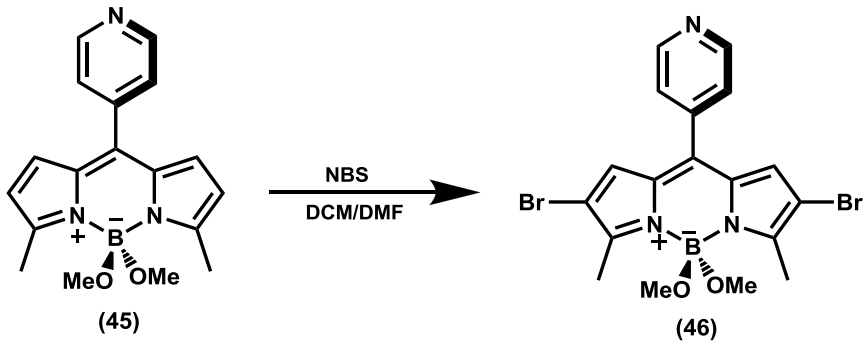


Figure 44. Synthesis of Compound **(46)**.

Compound **(45)** (50 mg, 0,156 mmol) was dissolved in 15 mL of DCM and 5 mL of DMF. Then, to the reaction mixture NBS (66.50 mg, 0.374 mmol) dissolved in 5 mL of DCM was added at room temperature. The progress of the reaction was monitored by TLC. After the starting material was consumed totally, water (100 mL) was added and the reaction mixture was extracted into DCM (3x100 mL), evaporated. The residue was purified by alumina gel column chromatography using DCM:MeOH (98:2) as an eluant (0.71 mg, 96 %). ^{1}H NMR (400 MHz, CDCl3) δ 8.83 (d, J = 13.1 Hz, 2H), 7.43 (d, J = 4.4 Hz, 2H), 6.76 (d, J = 19.2 Hz, 2H), 2.97 (s, 6H), 2.65 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 157.2, 141.7, 133.8, 128.7, 124.4, 109.4, 49.4, 13.2. ESI-HRMS ($M+Na^+$) calculated 498.97874, found 498.98075, Δ= -4.04 ppm

3.1.25. Synthesis of Compound (47)

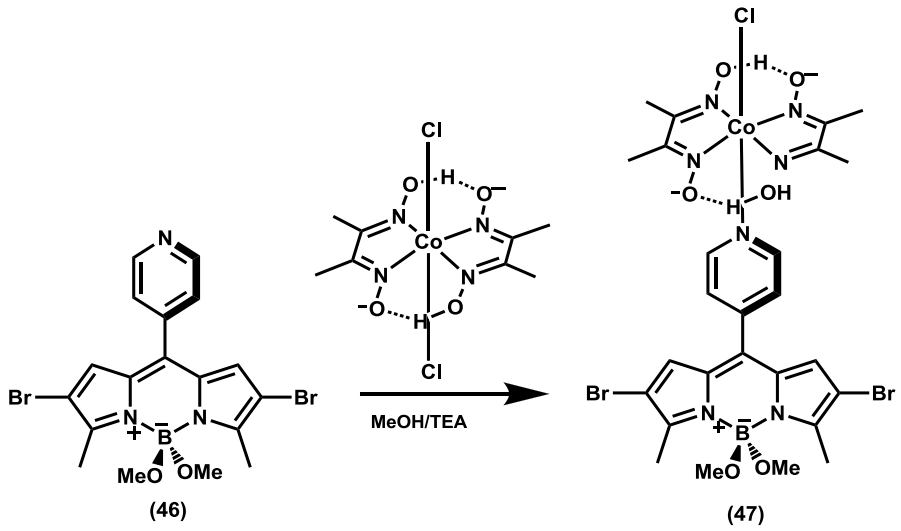


Figure 45. Synthesis of Compound **(47)**.

Compound **(23)** (75.3 mg, 0.208 mmol) was dissolved in 15 mL of MeOH and TEA (29.03 µL, 0.208 mmol). After the solution turns brownish and fully dissolves, compound (**46)** (50 mg, 0.104 mmol) which was dissolved in 1 mL of $CHCl_3$, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the purple solids were filtered off, washed with methanol, and dried under vacuum. ESI-HRMS ($M-H^-$) calculated 798.9858, found 798.9566, Δ= 36.59 ppm

3.1.26. Synthesis of Compound (48)

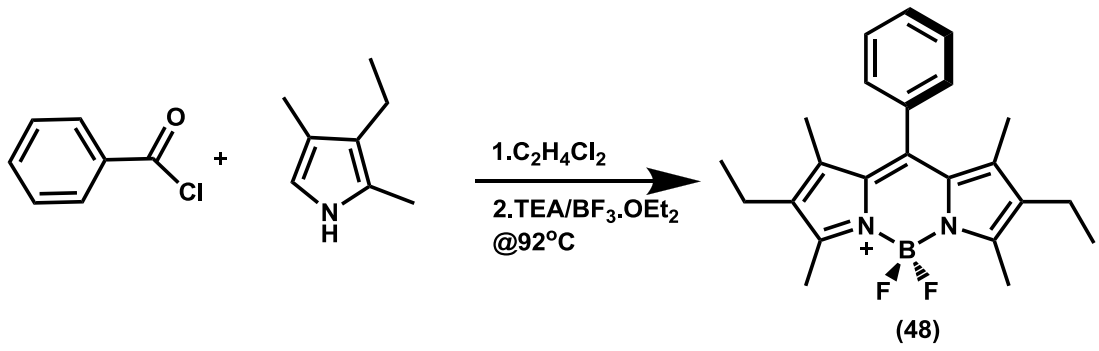


Figure 46. Synthesis of Compound **(48)**.

To a 500mL round-bottomed flask containing 500 mL argon-degassed dichloroethane, 3-ethyl,2,4-dimethyl pyrrole (10.4 mmol, 0.992 g) and benzoyl chloride (4,35 mmol, 0.611 g) were added. The solution was refluxed for 1 day at 90oC. After that, 5 mL of Et3N and 5 mL of $BF_3.OEt_2$ were successively added and after 30 min, the reaction mixture was washed with water (3 x 100 mL), which was then extracted into the CH2Cl2 (3 x 100 mL) and dried over anhydrous Na2SO4. The solvent was evaporated and the residue was purified by silica gel column chromatography using 1:2 (DCM/Hexane)as the eluent. Orange solid (0.45 g, 28%). ^{1}H NMR (400 MHz, CDCl3) δ 7.48-7.50 (m, 3H), 7.29-7.32 (m, 2H), 2.58 (s, 6H), 2.33 (q, J= 15.0 Hz, 4H),1.32 (s, 6H), 1.02 (t, J= 7.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 153.6, 140.2, 138.3, 135.8, 132.7, 131.6, 130.8, 129.3, 129.0, 128.7, 128.2, 17.0, 14.6, 12.4, 11.6 ppm. ESI-HRMS (M-Na+) calculated 402.21639 found 402.22312, Δ= 16.74 ppm

3.1.27. Synthesis of Compound (49)

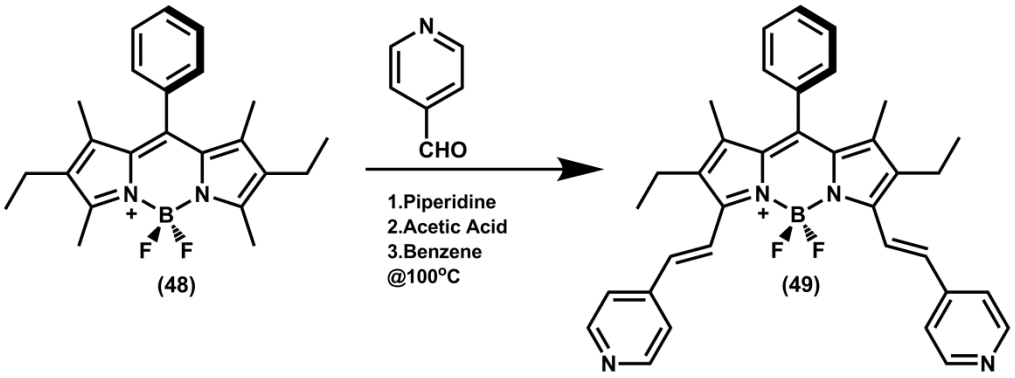


Figure 47. Synthesis of Compound **(49)**.

Compound **(48)** (100 mg, 0.260 mmol) and 4-pyridine carboxyaldehyde (70 µL, 0.650 mmol) were added to a 100 mL round-bottomed flask containing 20 mL benzene and to this solution, piperidine (200 µL, 2.73 mmol) and acetic acid (200 µL, 3.84 mmol) were added. The mixture was heated under reflux at 100 oC overnight by using a Dean Stark trap and it is monitored by TLC. When all the starting material had been consumed, the mixture was cooled to room temperature and the solvent was evaporated. Water (100 mL) was added to the residue and the

product was extracted with the DCM (3 x100 mL). The organic phace dried over Na_2SO_4, evaporated. The residue was purified by silica gel column chromatography using EtOAc as the eluant and the compound was obtained as blue solid (0.065 g, %45 yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J*= 5.9 Hz, 4H), 7.95 (d, *J*= 16.7 Hz, 2H), 7.54-7.56 (m, 3H), 7.49 (d, *J*= 5.9 Hz, 4H), 7.33-7.36 (m, 2H), 7.18 (d, *J*= 16.7 Hz, 2H), 2.63 (q, *J*= 15.0 Hz, 4H), 1.37 (s, 6H), 1.18 (t, *J*= 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.6, 144.5, 140.1, 135.4, 134.7, 134.7, 132.9, 129.3, 128.2, 124.0, 122.8, 121.3, 18.2, 13.9, 11.5 ppm. ESI-HRMS ($M+H^+$) calculated 558.28754 found 558.29298, Δ= -9.74 ppm

3.1.28. Synthesis of Compound (50)

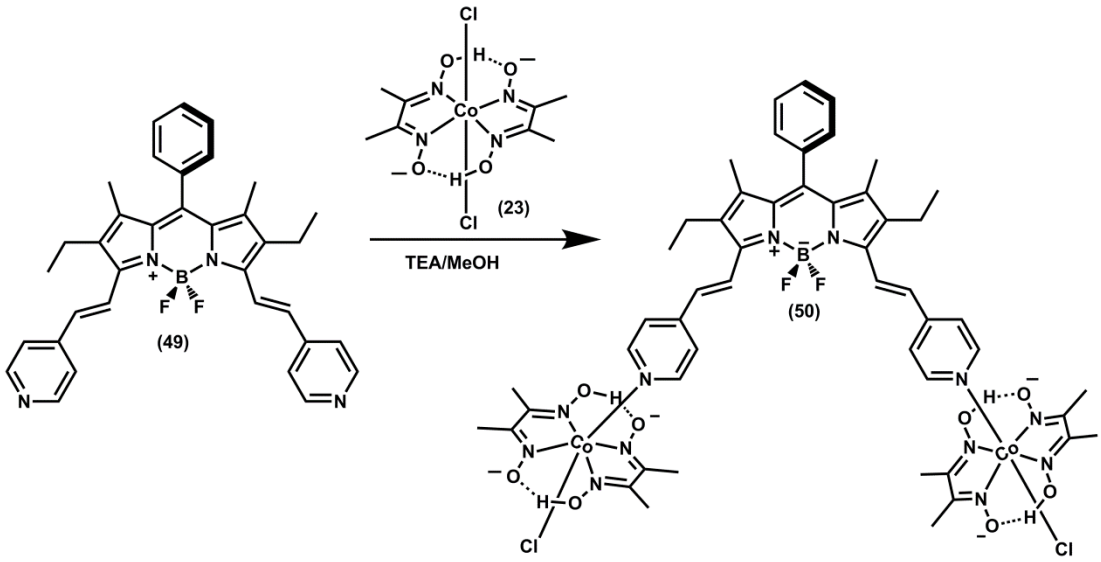


Figure 48. Synthesis of Compound **(50)**.

Compound **(23)** (72.3 mg, 0.201 mmol) was dissolved in 15 mL of MeOH and TEA (28.0 µL, 0.212 mmol). After the solution turns brownish and fully dissolves, compound (**49)** (28 mg, 0.005 mmol) which was dissolved in 1 mL of $CHCl_3$, and 40 mL of MeOH was added to the reaction mixture and the reaction was left to stir for 1 hour. When the starting material was consumed totally, the orange-red solids were filtered off, washed with methanol, and dried under vacuum (81 mg, %33 yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J*= 6.1 Hz, 4H), 7.82 (d, *J*= 16.6 Hz, 2H), 7.55 (s, 3H), 7.33 (d, *J*= 6.1 Hz, 2H), 7.28 (m, 2H), 7.01 (d, *J*= 16.6 Hz, 2H), 2.47-2.57 (m,

28H),1.34 (s, 6H), 1.09 (t, *J*= 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 150.9, 148.9, 147.3, 142.3, 141.0, 135.6, 134.7, 134.6, 130.1, 129.7, 129.6, 127.8, 127.1, 122.9, 18.1, 13.9, 13.2, 13.1 ppm. ESI-HRMS ($M\text{-}H^-$) calculated 1228.2766, found 1228.27364, Δ= 2.41 ppm.

CHAPTER 4

4. RESULTS AND DISCUSSIONS

There is an energy problem in the world. It is known that in the near future, there will be important catastrophic problems such as global warming and ozone hole problems. Therefore, due to increase in demand of energy and decrease in fossil fuels, there is a great interest of finding a solution to this problem.

Hydrogen is considered as the future solution of energy problems of today's world. It is an alternative and clean energy carrier. It does not cause any environmental pollution causing global warming. Hydrogen offers a cleaner environment. There are various methods for hydrogen generation such as electrolysis of water using a solar cell, reforming of biomass, photocatalytic of photoelectrochemical water splitting (artificial photosynthesis).[40]

The most important energy source is solar energy which can be converted to the storable and transportable energy in the form of molecular hydrogen, which can be done via the light-driven reduction of aqueous protons in water called water splitting. Water splitting method for hydrogen generation is one of the most promising approaches toward the generation of green and renewable energy.[2]

In the photocatalytic hydrogen generation system, reduction of water occurs to yield hydrogen, light induced conversion of aqueous protons into H_2. Water splitting system to generate hydrogen has two types of mechanisms as it is seen in Figure 50. There are two types of pathways in water splitting mechanism: oxidative quenching and reductive quenching. First of all, both two pathways start with the excitation of photosensitizer. When the photosensitizer is excited, it goes to excited state. After that, according to electron donor (ED) or electron accepting (EA) groups, there occurs two different pathways. In oxidative pathway, excited photosensitizer (PS*)

gives an electron to EA group and PS* is oxidized to PS^+ and oxidized PS^+ takes an electron from ED group to form its initial ground state form. After that, reduced EA^{n-1} gives its electron to aqueos proton, H^+ in the water to generate molecular hydrogen, H_2. On the other hand, in reductive quenching, excited PS* takes an electron from ED group and is reduced to PS^-. Then, reduced PS^- gives its electron to EA group to form EA^{n-1} giving its electron to aqueous proton to produce molecular hydrogen, H_2.[44]

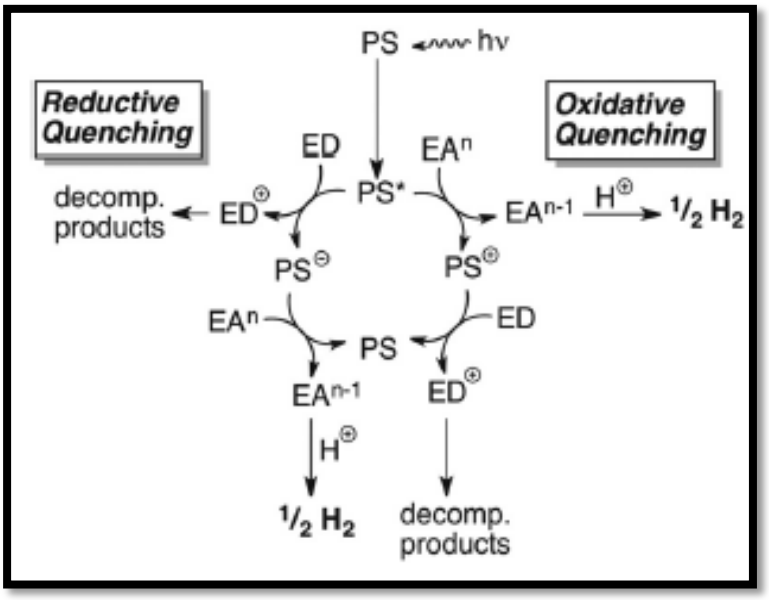


Figure 49. Water splitting mechanisms. Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from ref (44).

In light-driven water splitting mechanisms, there are three main parts of the whole system. Firstly, the most important part of the whole system is photosensitizer whose function is to absorb the visible light. There are many types of photosensitizers in the literature. In our study, BODIPY chromophore has been chosen for being the photosensitizer due to its excellent properties such as high quantum yields, high absorption coefficients, great stability. Moreover, BODIPY can be easily functionalized and it has simple synthesis method and diverse applications.[102] Second part of the system is sacrifical electron donor group. It is used as reducing agent

which is oxidized easier than water. In our study, triethanolamine (TEOA) is used for sacrifical electron group since it is known as the best electron group for water splitting mechanisms.[4] Last part of the water splitting mechanism is catalyst. Catalysts are used to reduce aqueous protons to yield molecular hydrogen by taking electrons. In our study cobalt-dimethylglyoxime complexes known as cobaltoximes are used for being catalysts because they are cheap and earth-abundant metals unlike noble metals such as platinium. Cobaltoxime complexes for water splitting have shown very good results for different types of photosensitizers such as Pt terpyridyl acetylide chromophores, xanthene dyes, tetrapyrrole-macrocycles, and perylene based dyes. Cobaltoxime complexes have also resulted productively in Ru-sensitized TiO_2 nanoparticles and carbon nanotubes for hydrogen generation.[103]

In this study, we designed and synthesized of 10 BODIPY sensitized cobaltoxime complexes as structural models of light-driven proton reduction catalysts. Cobaltoxime complexes are attached to meso (8^{th}), 3^{rd} and 5^{th} positions of BODIPY cores via covalent bonding by using pyridine molecule. Iodine and bromine are attached to 2^{nd} and 6^{th} positions of BODIPY cores in order to promote triplet state excitation.

Bodipy derivatives can be synthesized either via acid catalyzed condensation of aldehyde by using pyrrole or acylchloride derivatives of aldehyde with excess pyrrole. We have decided to form BODIPY cores by using aldehyde (4-pyridine carboxyaldehyde for Compound **24** and Compound **42**) in the presence of acid. We have preferred to form BODIPY skeletons by using acylchloride (benzoyl chloride) with excess pyrrole (2,4-dimethyl pyrrole) for Compound **30** and **50**. Formed air sensitive dipyrromethanes then have been oxidized by p-chloranil to form dipyrromethene. Abstraction of acidic proton through the use of excess base (triethylamine, or N,N-diisopropylethylamine) followed by borontrifluoride on the dipyrrin affords the target BODIPY cores.

After synthesis of BODIPY cores, we have went on with functionalization of BODIPYs with heavy atoms, Br and I. It is known that reductive and oxidative

electron transfer occur from photosensitizer via their lowest-lying triplet excited states. No quenching of singlet fluorescence of dyes occurs upon addition of sacrifical electron donor or catalyst. Therefore, the singlet excited state does not take part in electron transfer[104], meaning that the reduction of the cobaltoxime catalyst to generate molecular hydrogen occurs via the intermediacy of dye-based triplet excited states, $^{3*}PS^{2-}$ which is produced after intersystem crossing (ISC) of initially formed singlet excited states, $^{1*}PS^{2-}$. All mentioned here implies that there should be heavy atom modification on BODIPY cores. Also, it should be done before extension of conjugation in order to eliminate side products generated from reaction of halogens with olefinic hydrogens. We have both used bromine and iodine functionalization in order to see the effect of different heavy atoms for photogeneration of hydrogen. However, we have preferred bromine more than iodine due to the low stability of C-I bond. Compounds **25**, **34**, **43**, **46** were brominated by using NBS, and in the synthesis of compounds **27** and **31**, ionic acid and I_2 were used for iodination. Then, we extended the conjugation for compounds **32**, **35**, **37** and **49** via Knoevenagel condensation reaction which requires the removal of in situ generated water from the reaction medium via Dean-Stark Apparatus. For the compounds **32**, **35** and **49**, simple Knoevenagel condensation reaction was performed by using acetic acid, piperidine, and benzene as a solvent; however, the same procedure was failed for the compound **37**. Therefore, in the synthesis of compound **37** p-Toluenesulfonic acid, piperidine, and toluene as the solvent were used. Lastly, the complexation procedure was used with cobalt-dimethylglyoxime for the synthesis of compounds **26**, **28**, **29**, **33**, **36**, **38**, **41**, **44**, **47** and **50**. For the construction of BODIPYs **42**, **45**, 2-methylpyrrole was used in order to eliminate the orthogonality of pyridine molecule in the meso position of BODIPY to BODIPY core itself. Our aim was to promote electron transfer from BODIPY to cobaltoxime complex to generate hydrogen. In the synthesis of compound **45**, $AlCl_3$ and MeOH were used to substitute fluoride ions with methoxy ions by nucleophillic substitution reaction, which was done to provide more electron to the BODIPY core for the reduction of protons since methoxy ions are more electron donating than fluoride ions.

For the compounds **26**, **28** and **29** the synthetic pathway was followed as it is seen in Figure 50.

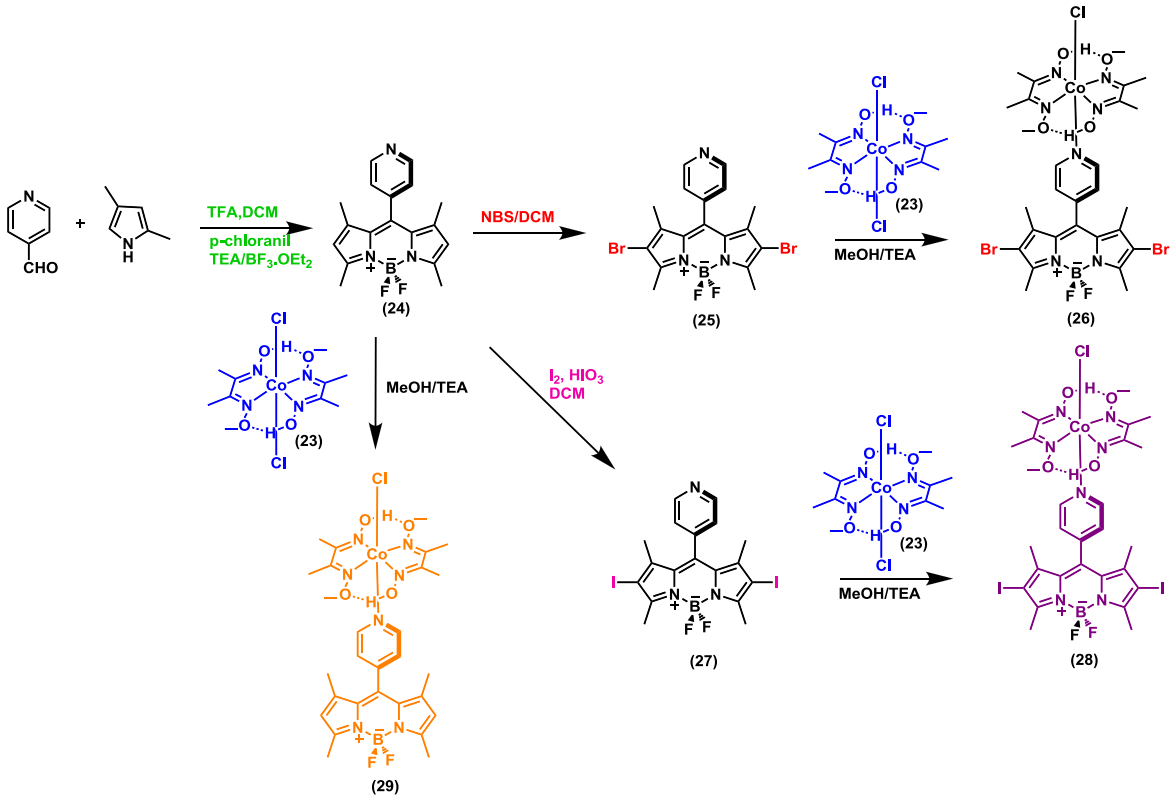


Figure 50. Synthetic pathway for compounds **26**, **28**, **29**.

For the compounds **33**, **36** the synthetic pathway was followed as it is seen in Figure 51.

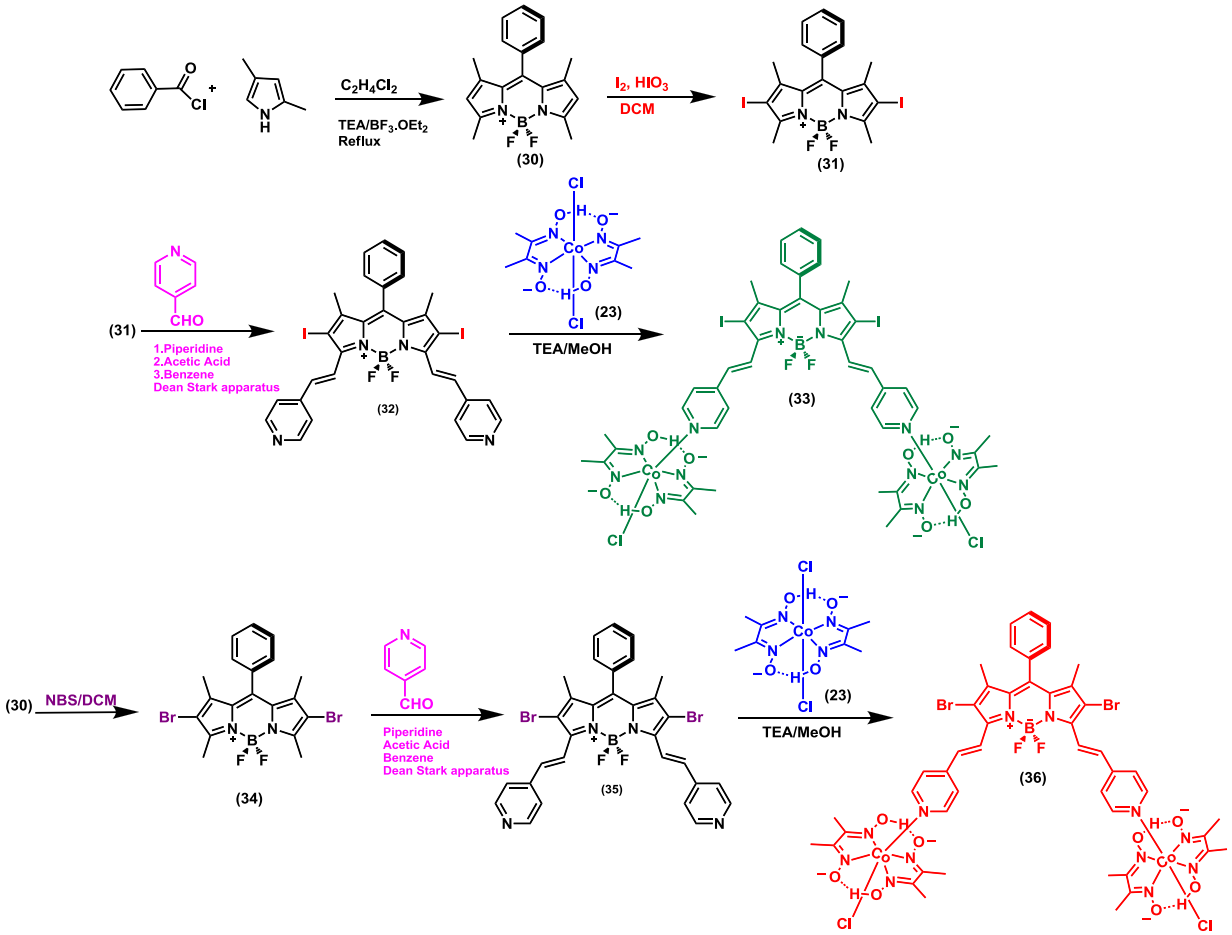


Figure 51. Synthetic pathway for compounds **33**, **36**.

For the compound **38** the synthetic pathway was followed as it is seen in Figure 52.

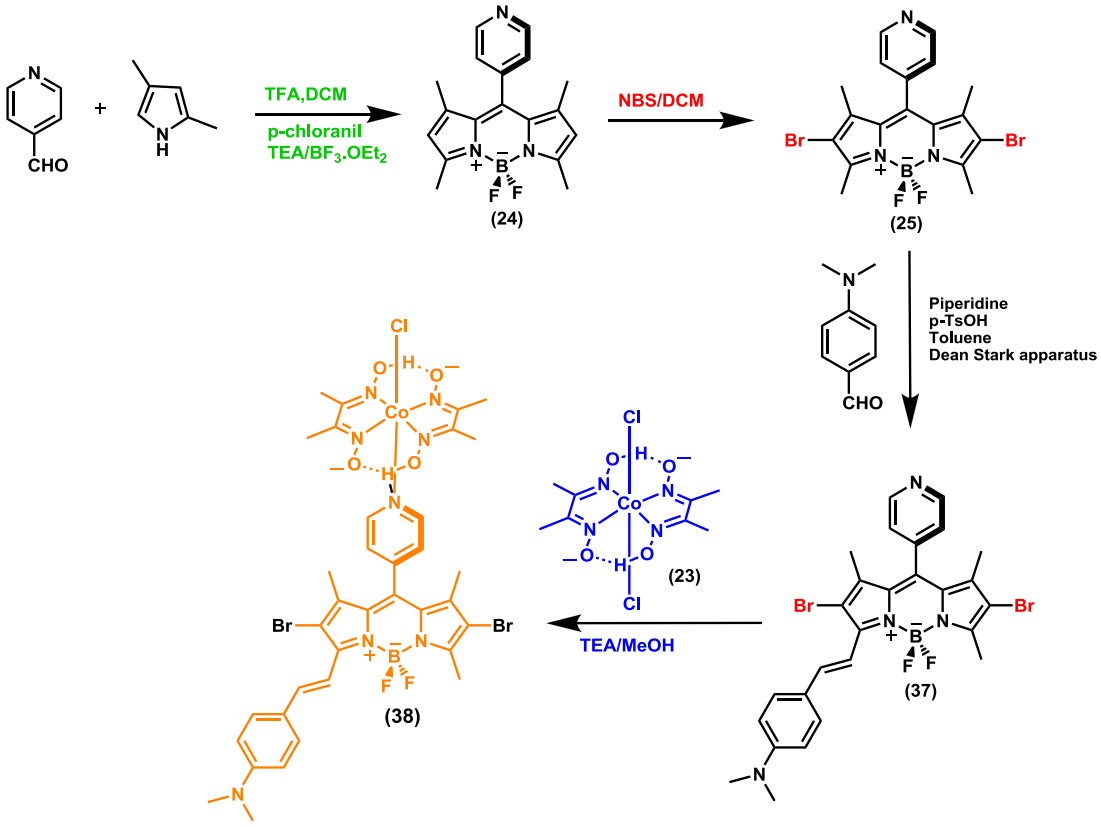


Figure 52. Synthetic pathway for compound **38**.

For the compounds **44** and **47** the synthetic pathway was followed as it is seen in Figure 53.

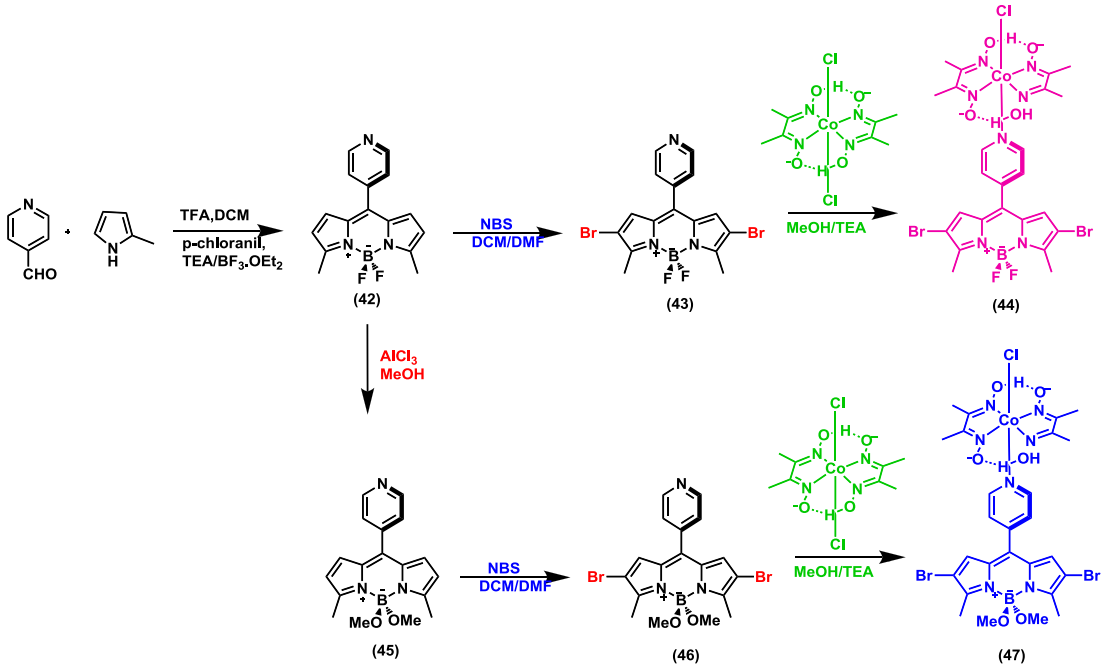


Figure 53. Synthetic pathway for compounds **44** and **47**.

For the compound **41** the synthetic pathway was followed as it is seen in Figure 54.

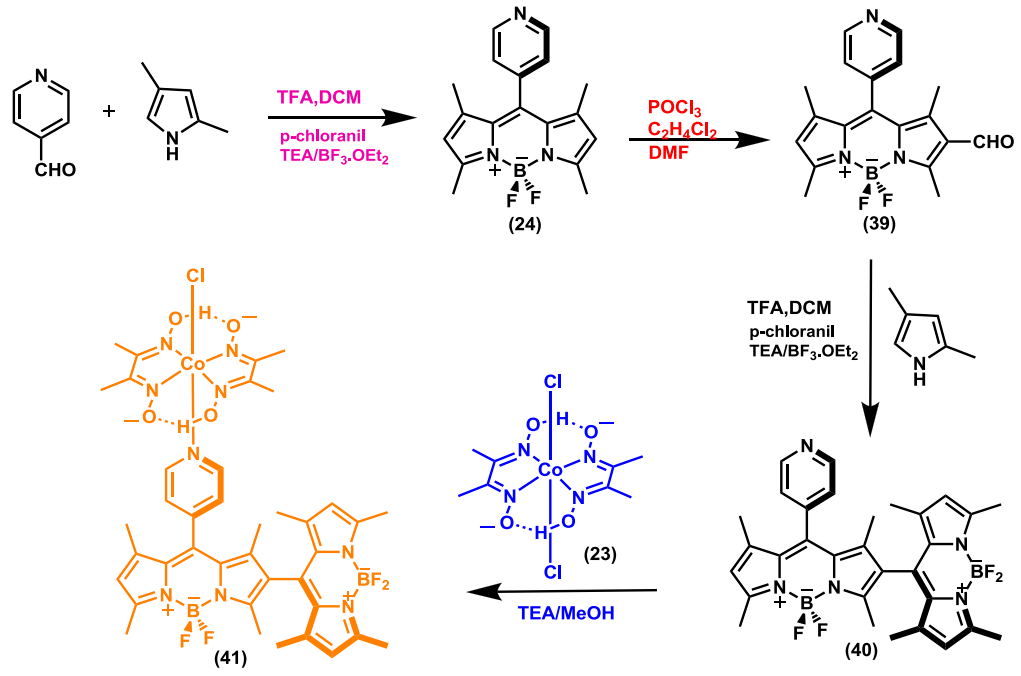


Figure 54. Synthetic pathway for compound **41**.

As it is mentioned before, there has to be halogenation on the BODIPY core in order to promote ISC. However, we wanted to see the effect of a halogen in the

photogeneration of hydrogen in an intramolecular system. To do so, we have synthesized compound **41** which is an orthogonal BODIPY derivative. According to previous results obtained in our research group, when two similar BODIPY molecules are assembled to each other orthogonally, they display one absorbance peak and as result, there is no need for heavy atom effect in order to heavily populate the triplet excited state.[105,106] Therefore, we have synthesized the compound **41**.

For the compound **50**, the synthetic pathway was followed as it is seen in Figure 55.

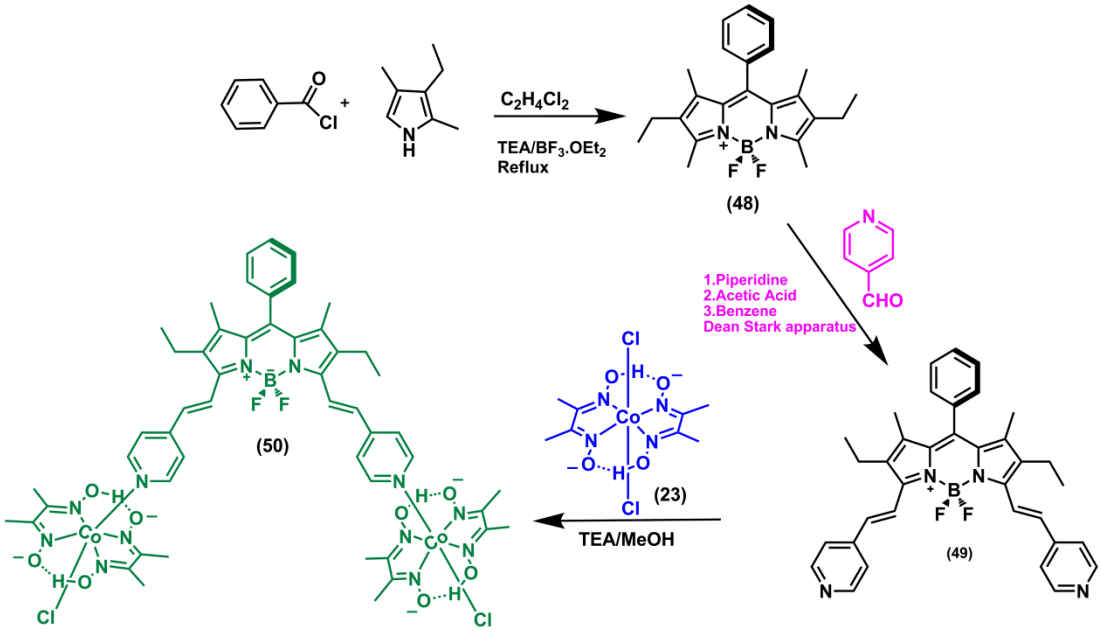


Figure 55. Synthetic pathway for compound **50**.

During the synthesis process, unfortunatelly 3 of our target molecules (compounds **26**, **28** and **29**) were published by Dr. Weare's research group. Since we do not have a set up for hydrogen generation experiments, we decided to collaborate with Dr. Weare's group for our last 7 target molecules.

For the mass spectroscopic measurements, all the samples were diluted in methanol and they were analyzed via a 5 µL/min flow injection at 300 µL/min in methanol. The mass spectrometer was operated in positive-ion mode with a capillary voltage of 3.5 kV.

The molecular structures of compounds **26** and **28** are shown in Figure 56. X-Ray crystals of these complexes were obtained by recrystallization from DCM/methanol (1:3, v/v) for compound **26** or DCM/ diethyl ether (1:3, v/v) for compound **28**.[107]

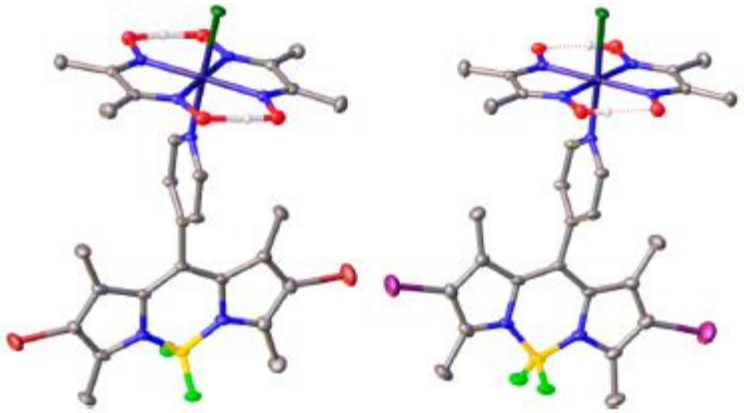


Figure 56. Molecular structures of compounds **26** and **28** respectively. Copyright © 2014 American Chemical Society. Reprinted with permission from ref (106).

The absorption features of the BODIPY-cobaltoxime complexes **26** and **28** show similar trends to their nonhalogenated analogues 28[107] as it is discussed in Prof. Weare's studies.[107] The compounds **33** and **36** are absorbed in higher wavelength than the others except compound **38** in which dimethyl amino group which is a better electron donating group which results in red shift is attached.

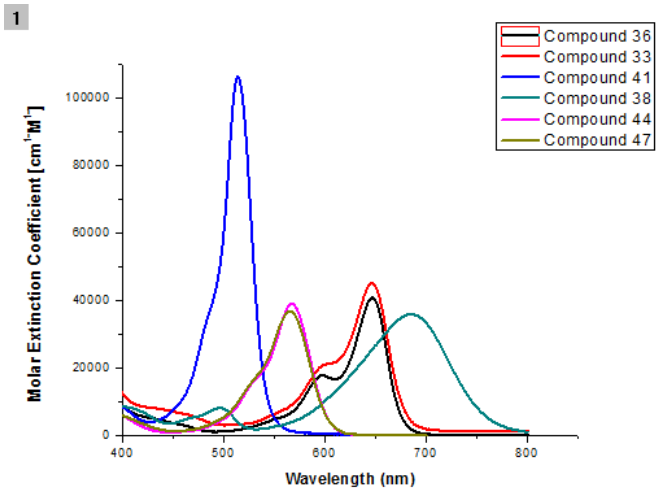


Figure 57. Molar extinction coefficients of compounds **33**,**36**,**38**,**41**,**44** and **47**.

The halogenation of the BODIPY cores by either bromine or iodine quenches the fluorescence due to the heavy atom effect, forming the photoexcited triplet states. As Dr. Walter's states while brominated BODIPY (compound **26**) has 0.24 fluorescence quantum yield, iodinated BODIPY (compound **28**) has 0.03 fluorescence quantum yield as it is expected due to the mass of iodine compared to bromine. After the complexation, the remaining BODIPY centered fluorescence emission is quenched for all samples. This could be explained by the electron transfer from excited BODIPY cores to the cobaltoxime.[107]

Hydrogen evolution measurements were determined using the method described by Castellano and co-workers.[107] A 70% v/v acetonitrile solution (HPLC grade) in water was prepared and to the solution distilled triethanolamine was added as a 5% v/v mixture of the total solution. Then the solution was acidified with 12 M HCl to a pH of 7.7 in order to prevent decomposition in highly alkaline (amine+water) solution. This solution was added to the appropriate cobaltoxime complex in an EPA vial which was immediately selaed and shielded from the light. After that, solutions were irradiated with 525±10 nm (compounds **26**, **28**, **29**, **41**, **44** and **47**) green LED and 650±10 nm (compounds **33**, **36**, **38** and **50**), (150 mW) red LED light for 20 hour. According to hydrogen evolution measurements that have been done by Dr. Weare's research group, compound **26** and **28** showed hydrogen evolution where compounds **33**, **38** and **41** showed some hydrogen evolution, exhibited 9.6 TONs (47.66309 µmol H_2), 11.8 TONs (52.45489 µmol H_2), 0.465 µmol H_2, 0.356 µmol H_2 and 1.8 µmol H_2 respectively. Compound **29** and **36** showed no hydrogen evolution. Previous studies showed the importance of heavy atom effect for intersystem crossing.[103] However, for these two compounds, the aim was to see whether the result would be same if it was an intramolecular system. The hydrogen evolution profiles for the compounds **26** and **28** are shown in Figure 58.

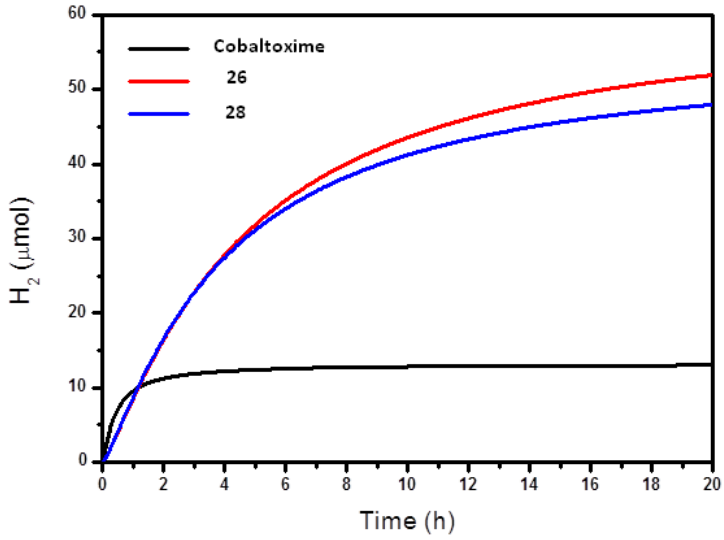


Figure 58. Hydrogen evolution profiles of compounds **26** (68) and **28** (65) irradiated at 525 nm at pH 7.7 in 7:3 acetonitrile/ water solution with 5% triethanolamine.

Hydrogen production profiles based on pressure measurements during catalysis and mass spectrometry of headspace afterwards. Compounds **26** and **28** were present in 4.4 and 5.0 µM respectively. The cobaloxime was present at 1.1 µM. It was observed that iodinated BODIPY has a higher rate for hydrogen evolution compared to brominated one, which could be explained with the iodized photosensitizers having a faster rate for single-triplet intersystem crossing since iodine has the larger heavy atom effect compared to bromine.[70,92]

According to the studies, it is suggested that only the triplet state of the BODIPY chromophores is able to transfer an electron to the cobaltoxime catalytic center.[103] And it was shown that formation of photoexcited triplet states can be achieved only by halogenation. However, Akkaya's research group showed that there is no need for a halogen to populate the triplet excited state when two similar BODIPY molecules are assembled to each other orthogonally.[106] Therefore, we have decided to synthesize compound **41** and the hydrogen evolution experiments showed that compound **41** generated hydrogen 1.8 µmol H_2. This is the first heavy atom free example of a homogeneous photocatalytic system for hydrogen generation in the

literature which is a remarkable result. Hydrogen evolution results for compound **33**, **36**, **38** and **41** can be seen in Table 1.

Compound #	**nH_2 µmol** *(after 22h irradiation)*
33	**0,465 µmol H_2**
38	**0,356 µmol H_2**
41 (3.3 µmol)	**1,8 µmol H_2.**

Table:1 Hydrogen Evolution Results

CHAPTER 5

5. CONCLUSION

In this study, ten novel photocatalytic complexes have been synthesized and characterized. We achieved to demonstrate catalytic light-driven hydrogen production for halogenated BODIPY based cobaltoxime complexes **26**, **28**, **33**, **38** and non-halogenated complex **41** which is the first example in the literature. We have concluded that the photoexcited triplet state is necessary for an efficient electron transfer from BODIPY core to the cobaltoxime to reduce molecular hydrogen. In addition, we have concluded that halogenation is not a must for an orthogonal BODIPY based cobaltoxime catalyst. Although turn over numbers are not considerably high, this study is the proof of principle and after this study, many types of BODIPY based complexes can be synthesized.

BODIPY based cobaltoxime molecular complexes are promising reduction photocatalysts and can be improved to get better results.

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APPENDIX A

NMR SPECTRA

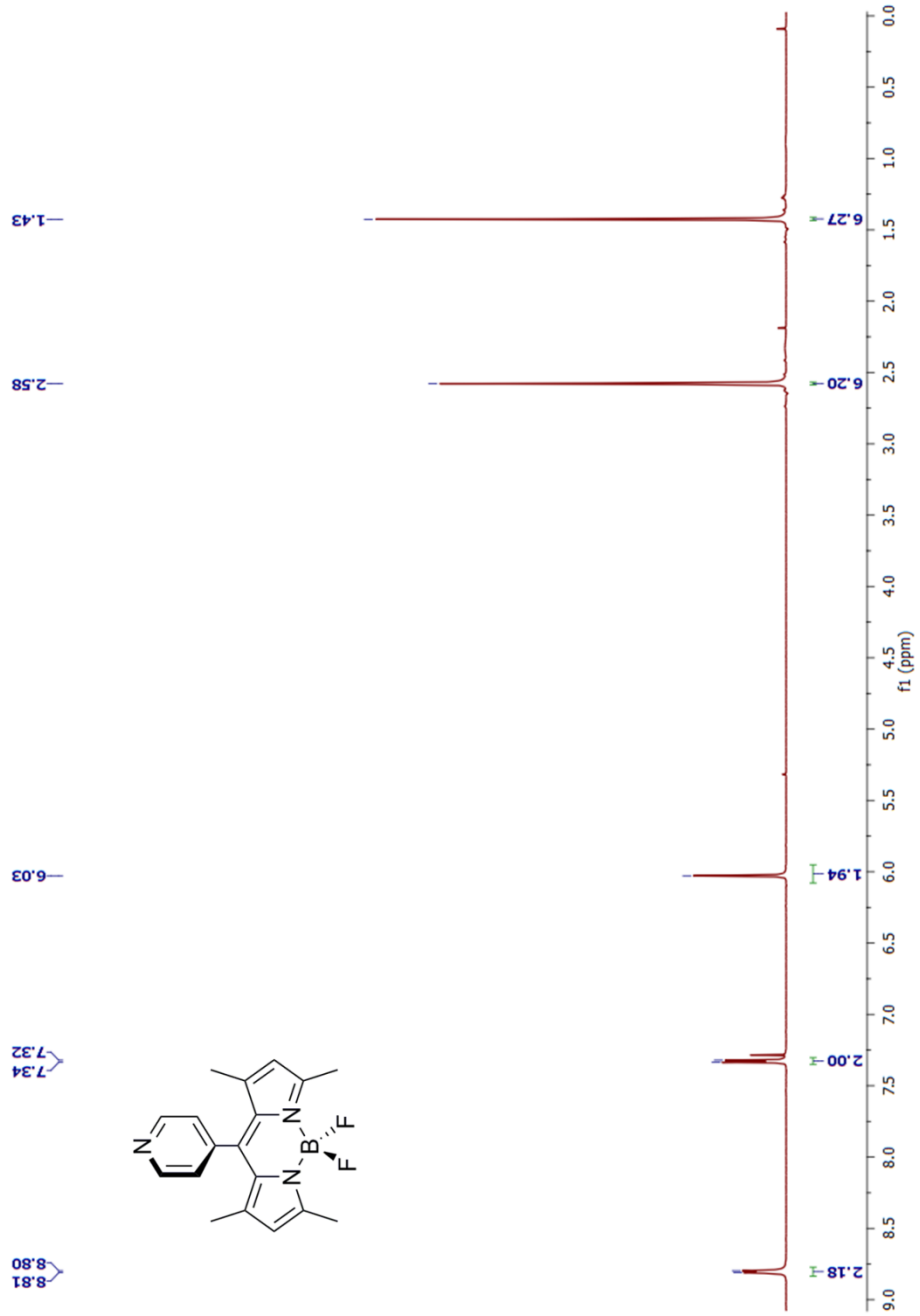

Figure 59. ^{1}H spectrum of compound **24**.

,

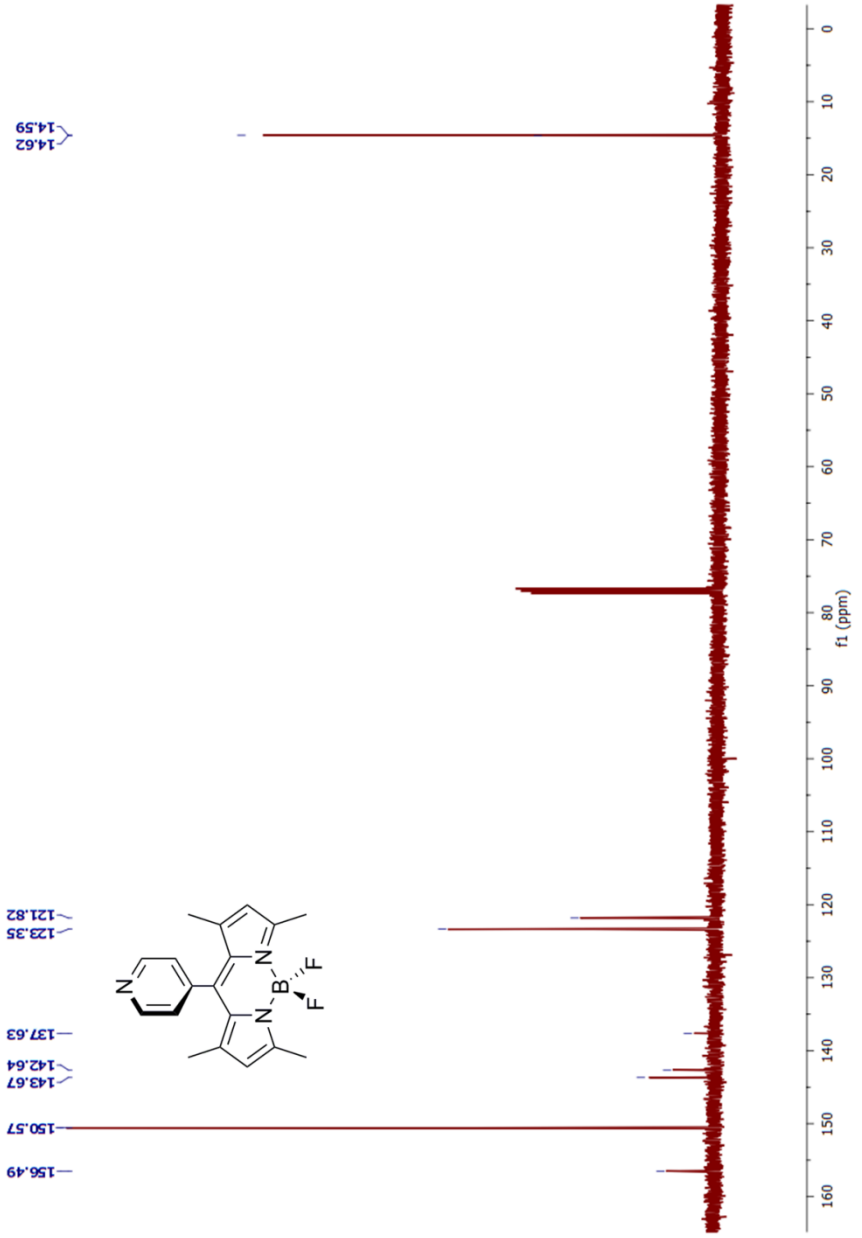

Figure 60. ^{13}C spectrum of compound **24**.

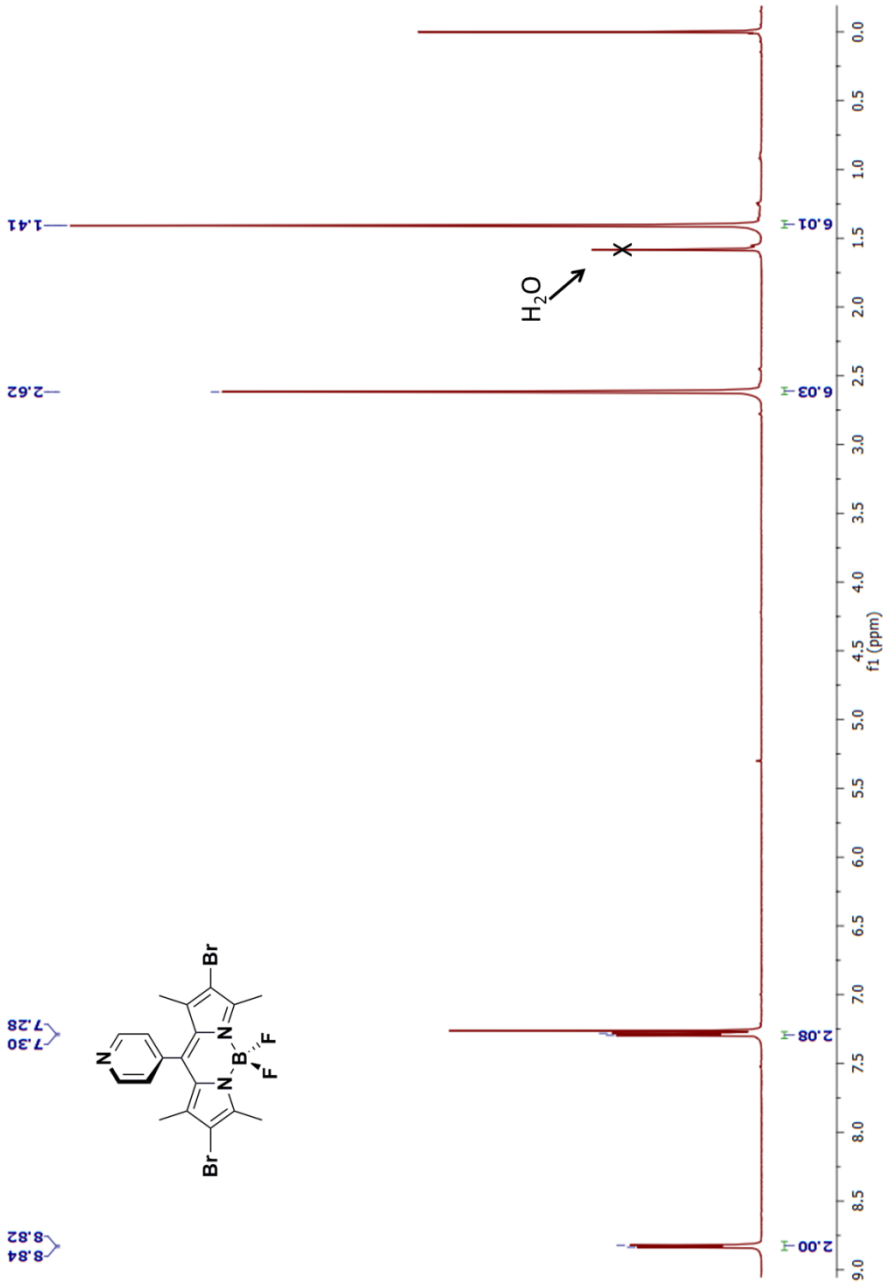

Figure 61.[1]H spectrum of compound **25**.

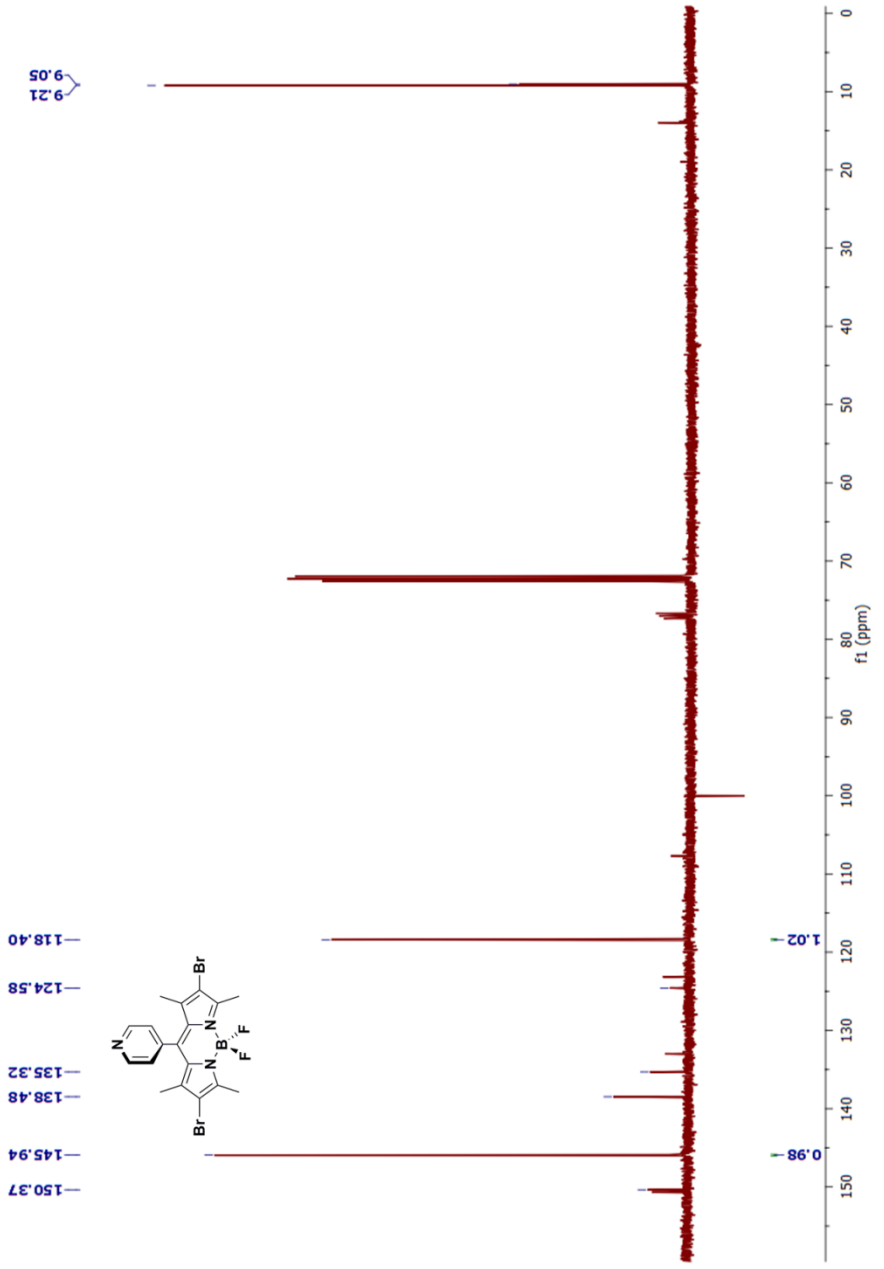

Figure 62. ^{13}C spectrum of compound **25**.

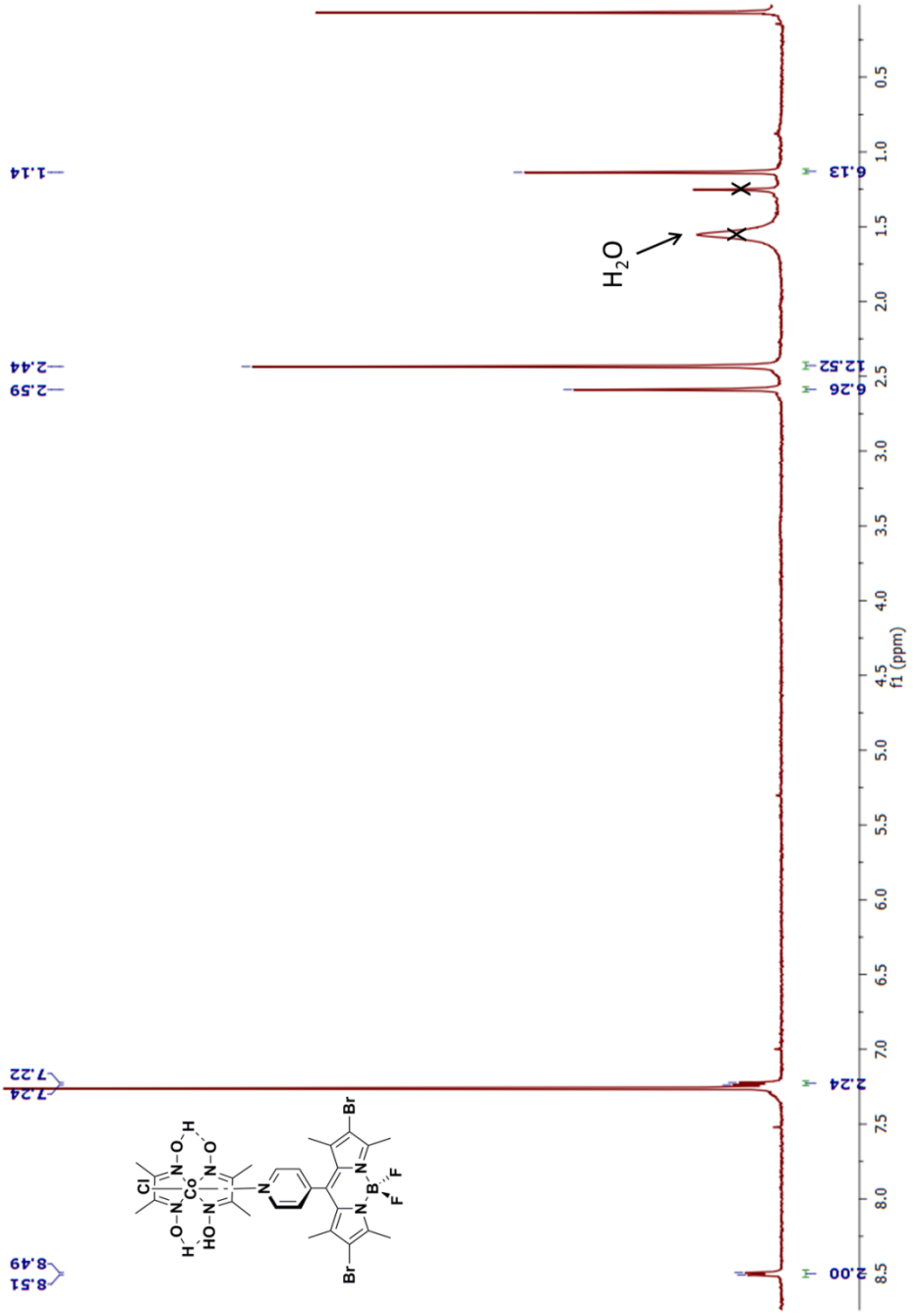

Figure 63.[1]H spectrum of compound **26**.

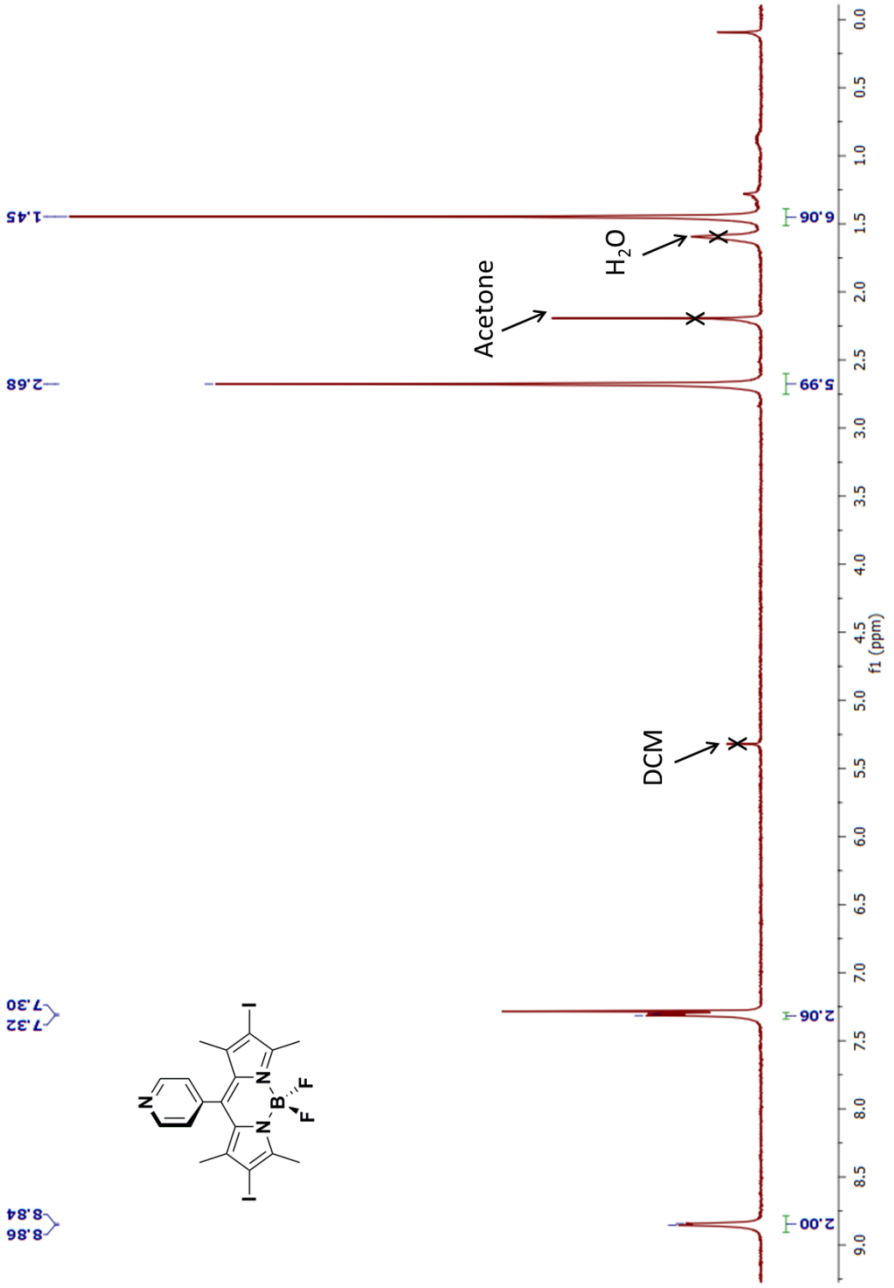

Figure 64. ^{1}H spectrum of compound **27**.

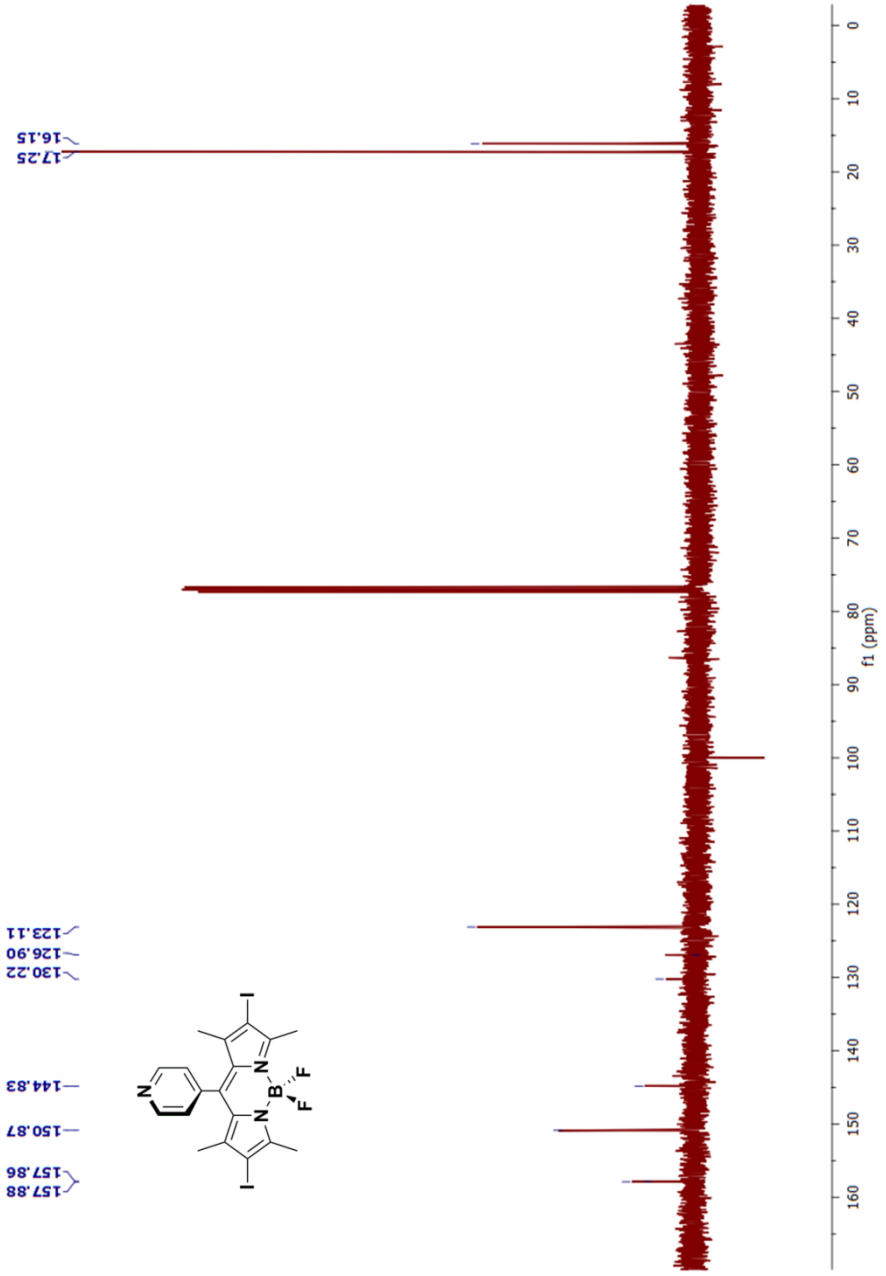

Figure 65. ^{13}C spectrum of compound **27**.

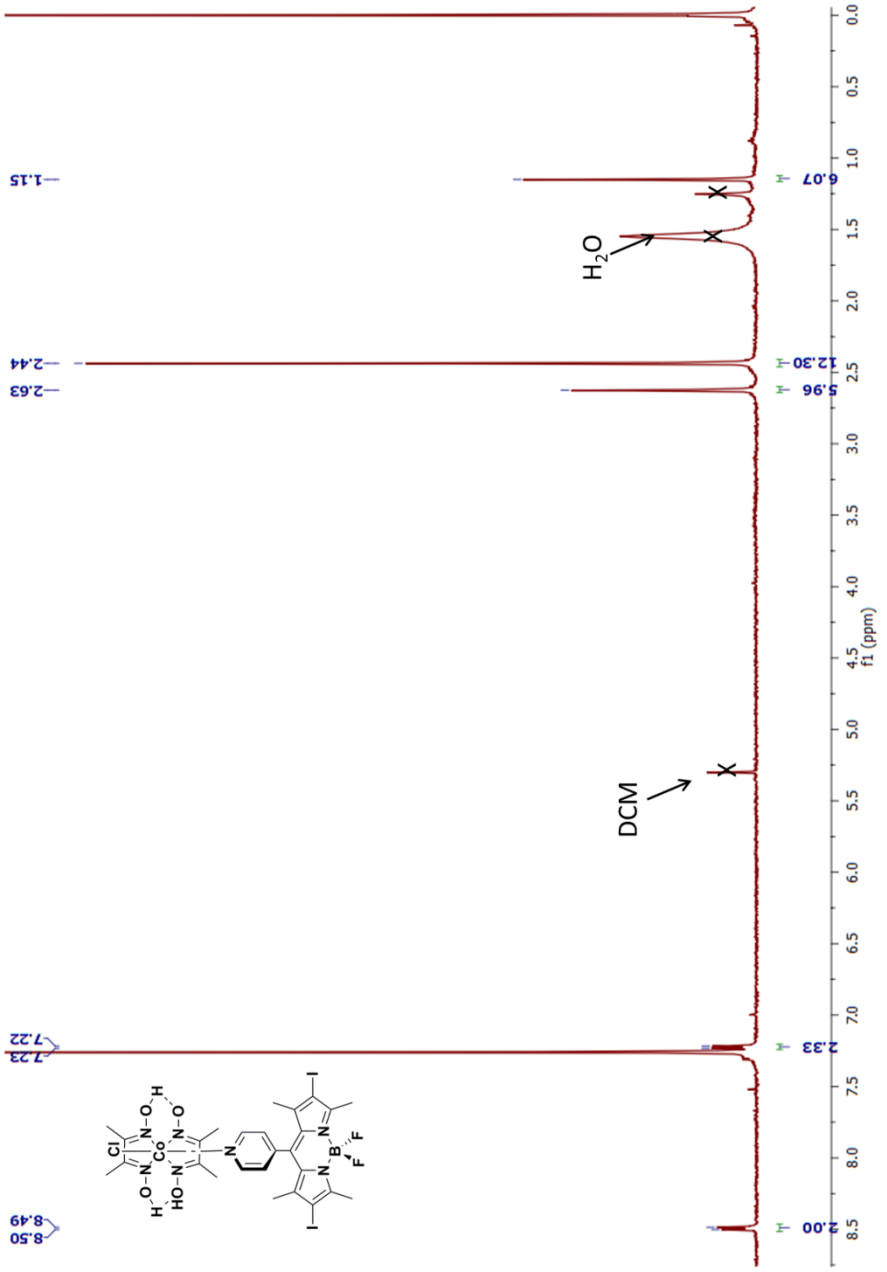

Figure 66. ^{1}H spectrum of compound **28**.

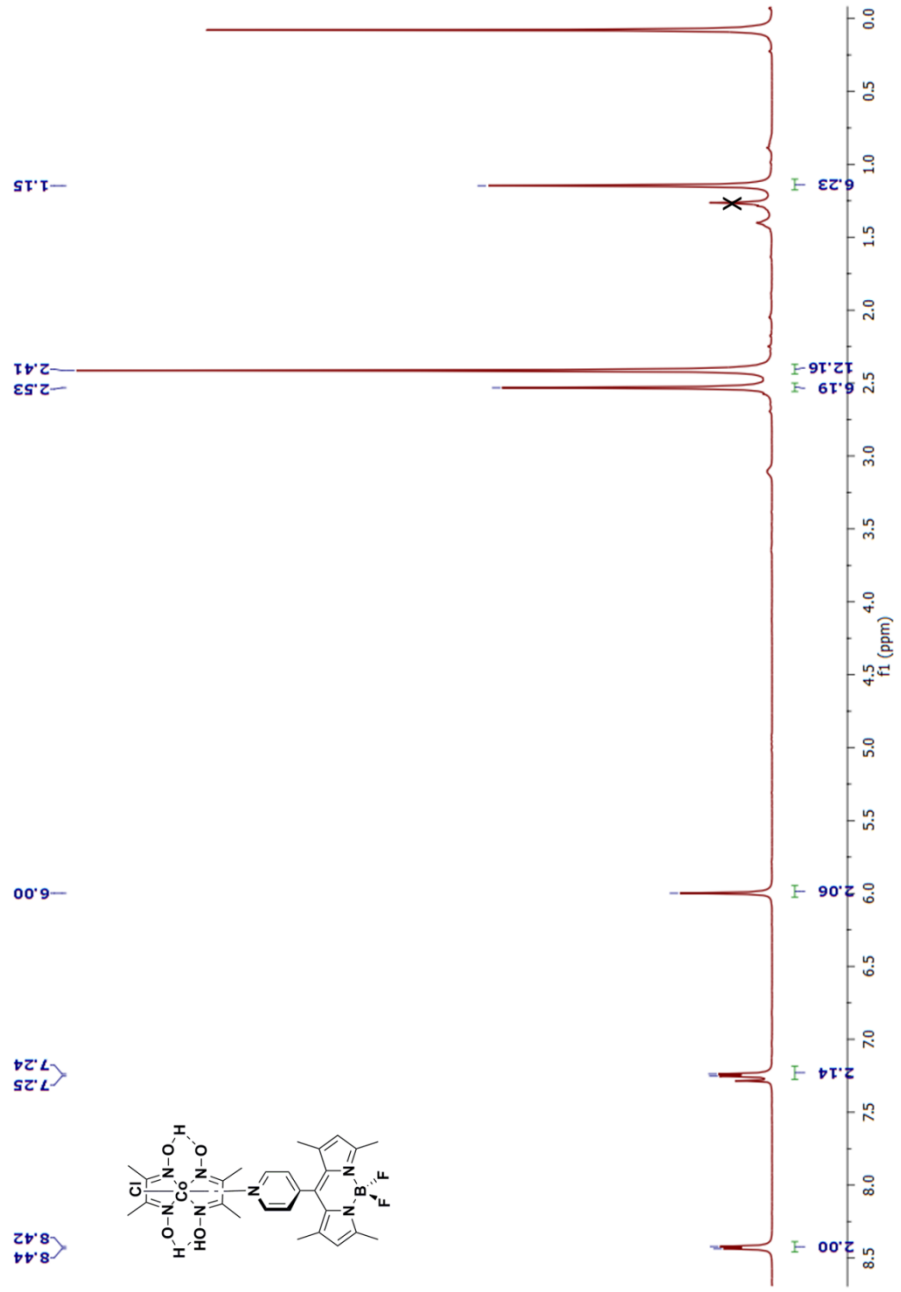

Figure 67. ^{1}H spectrum of compound **29**.

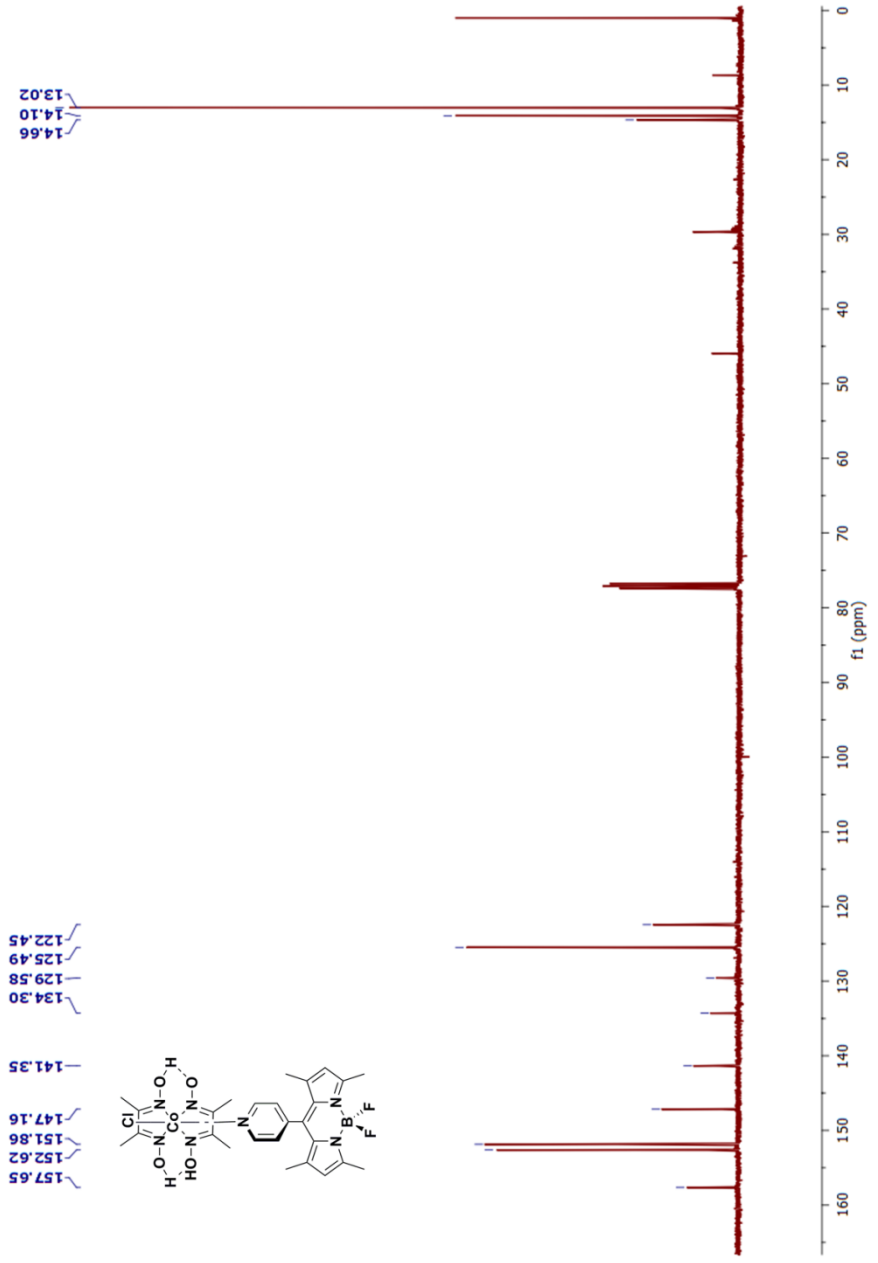

Figure 68. ^{13}C spectrum of compound **29**.

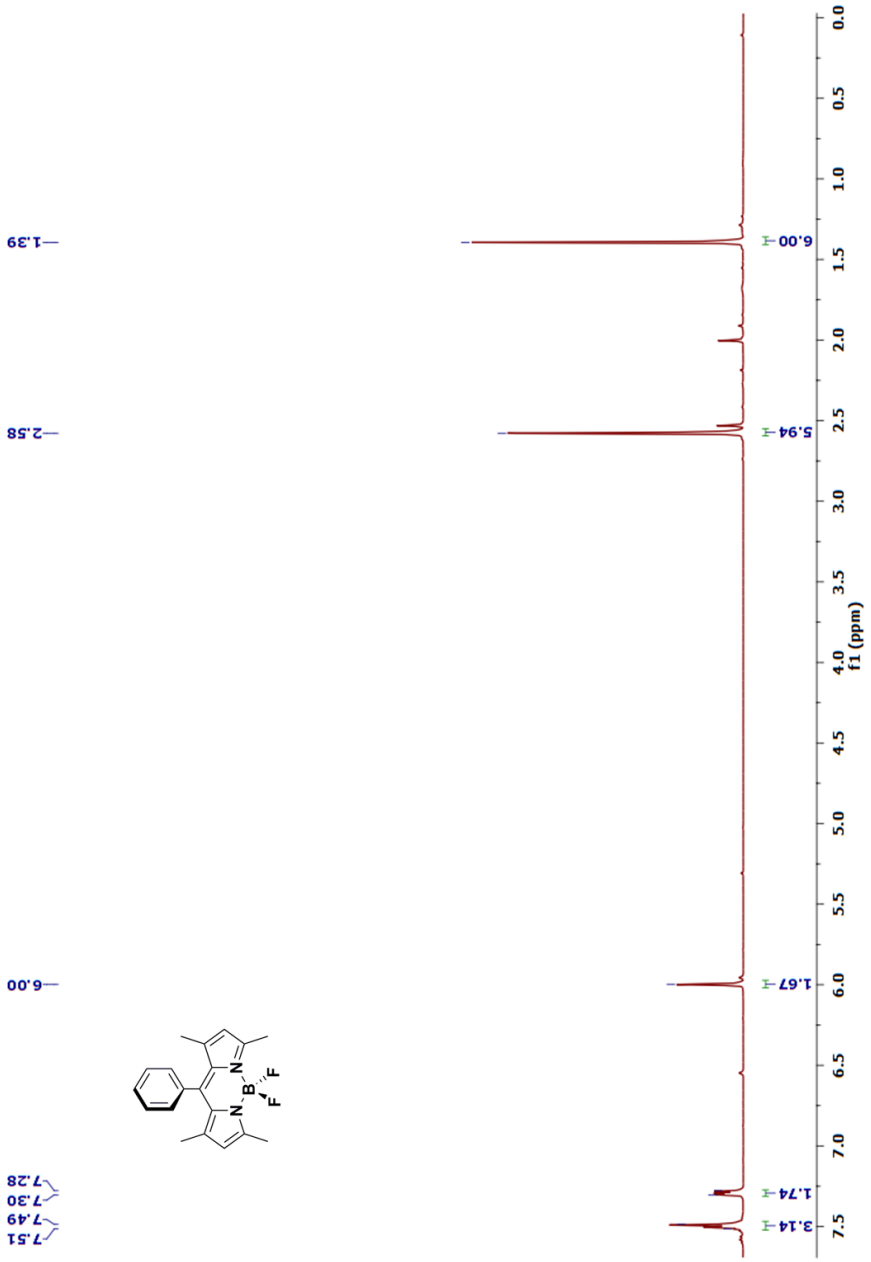

Figure 69. ^{1}H spectrum of compound **30**.

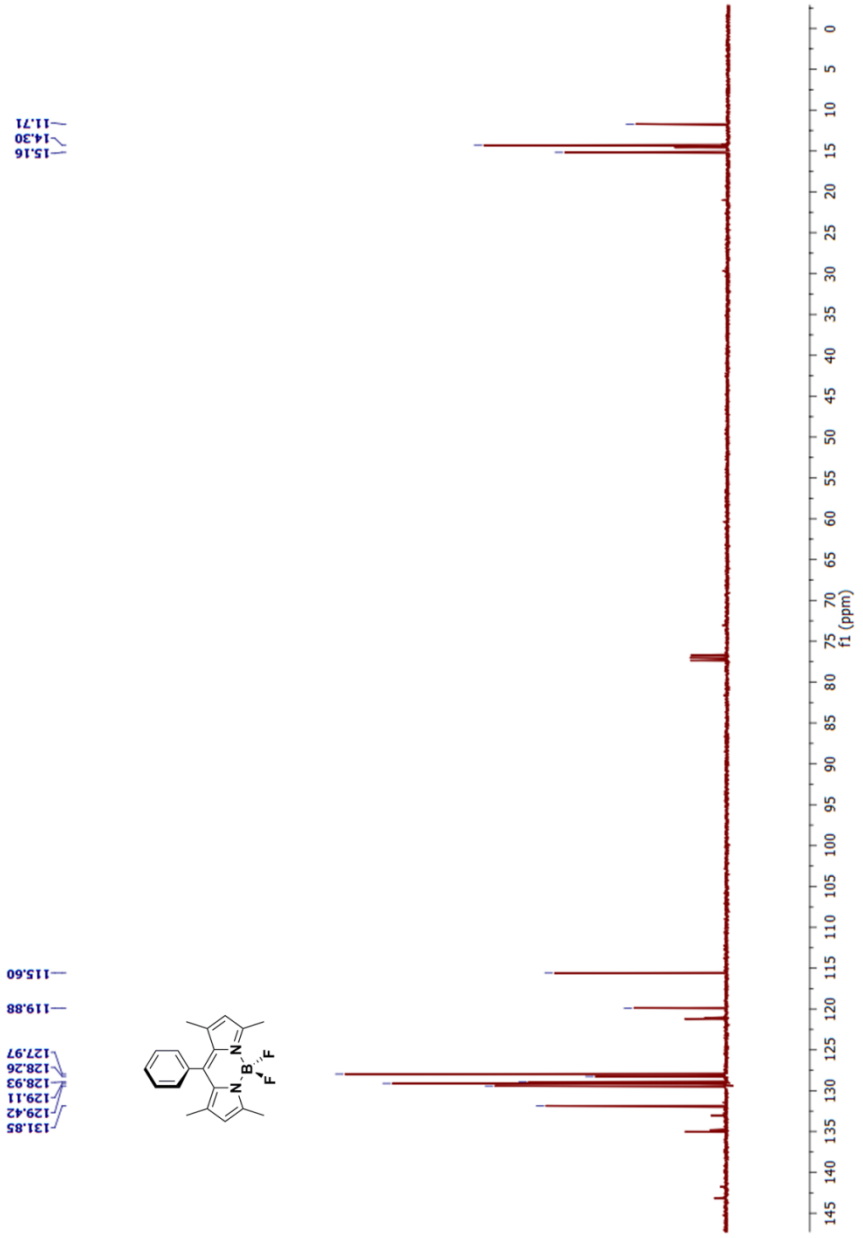

Figure 70. ^{13}C spectrum of compound **30**.

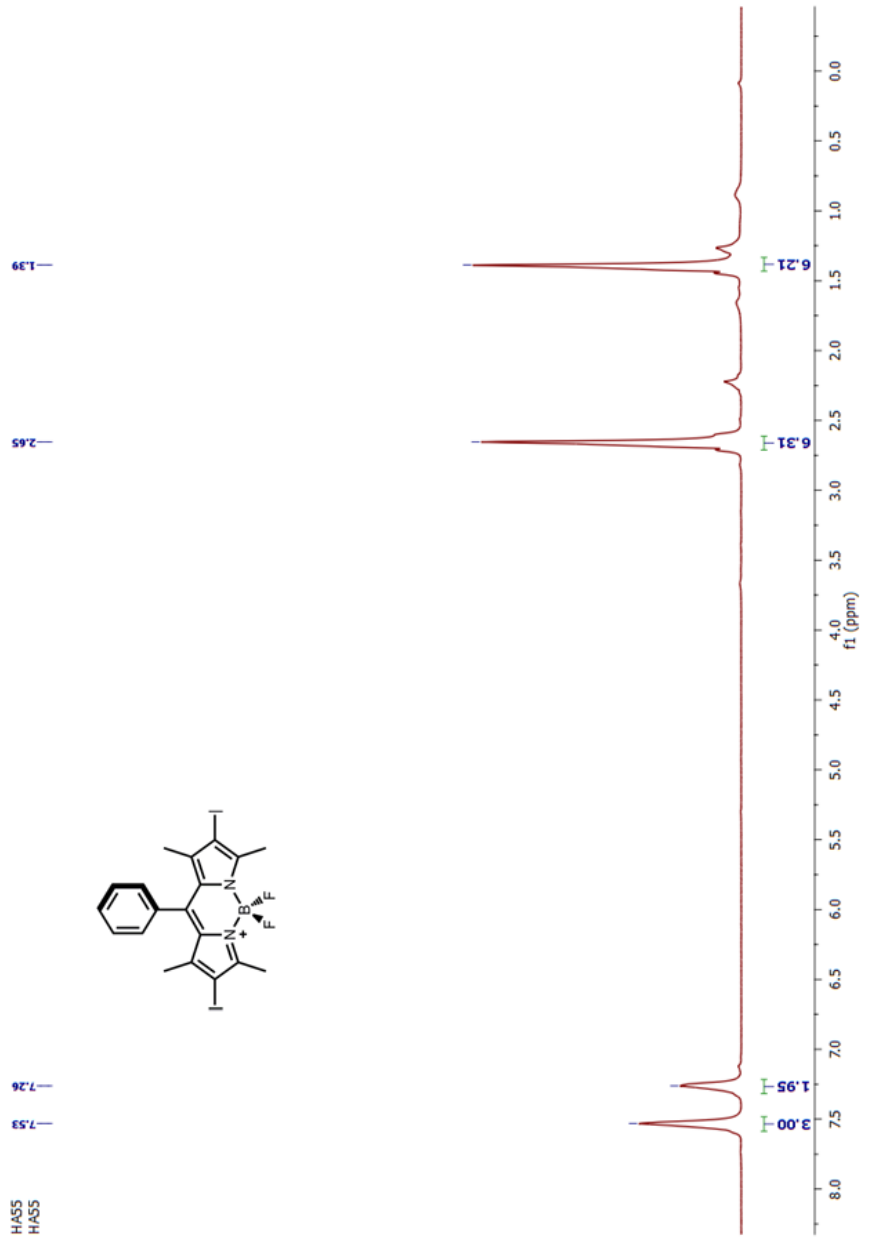

Figure 71. ^{1}H spectrum of compound **31**.

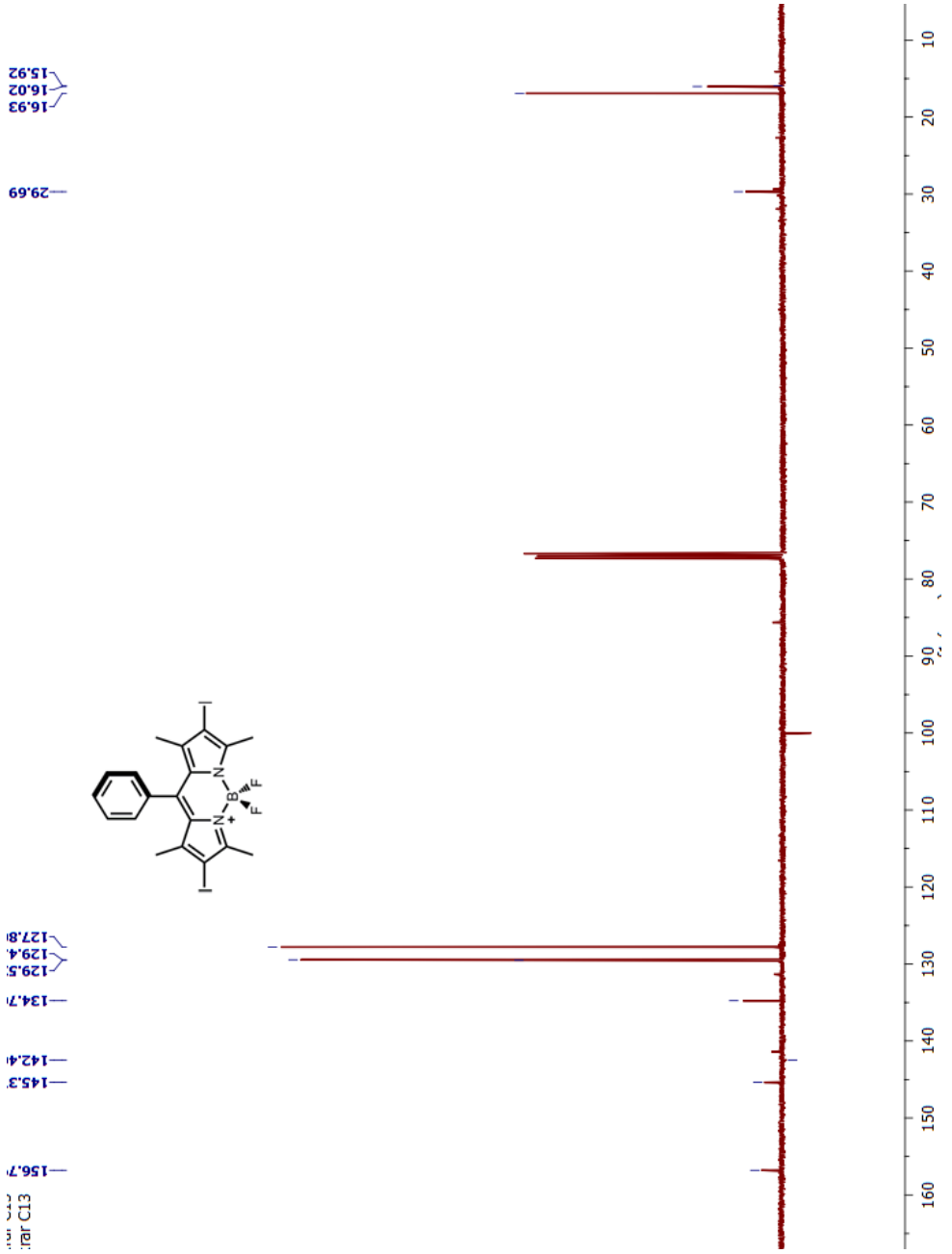

Figure 72. ^{13}C spectrum of compound **31**.

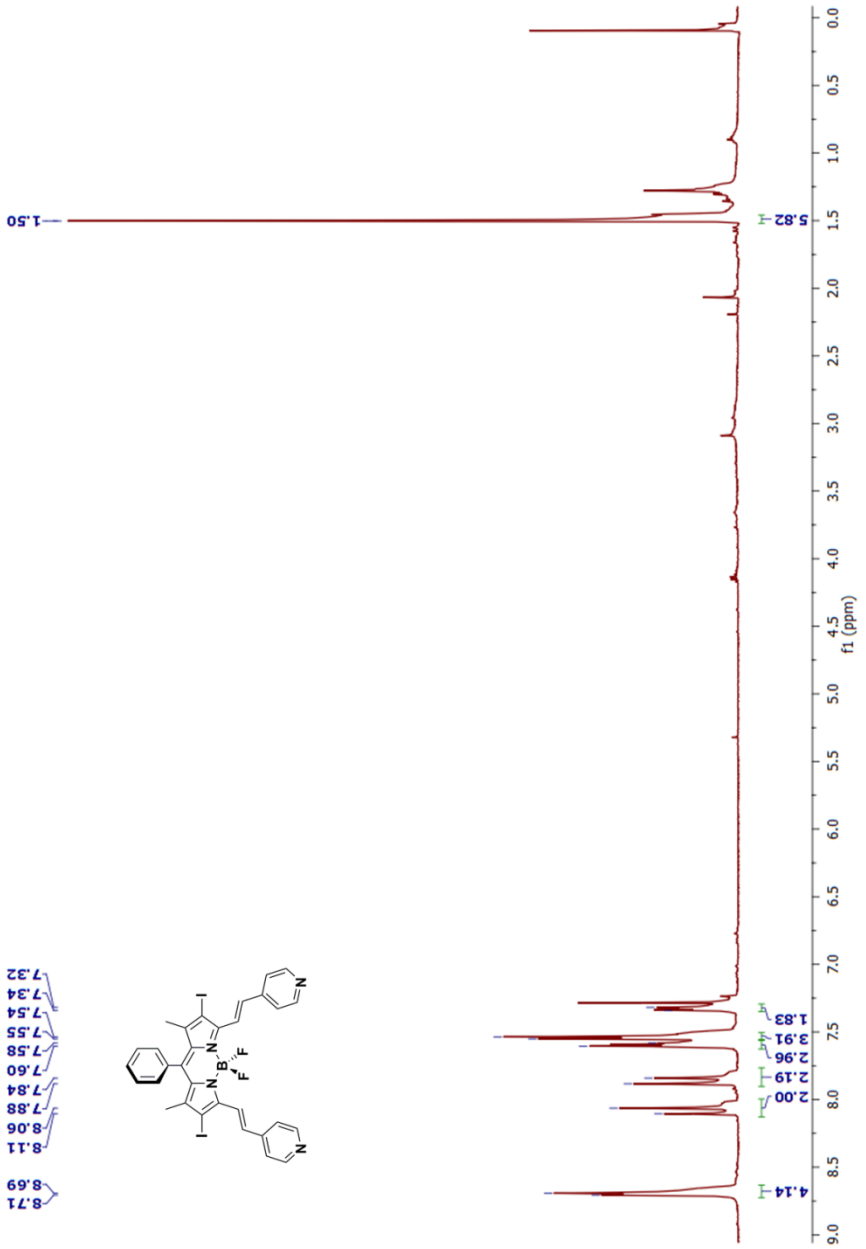

Figure 73. ^{1}H spectrum of compound **32**.

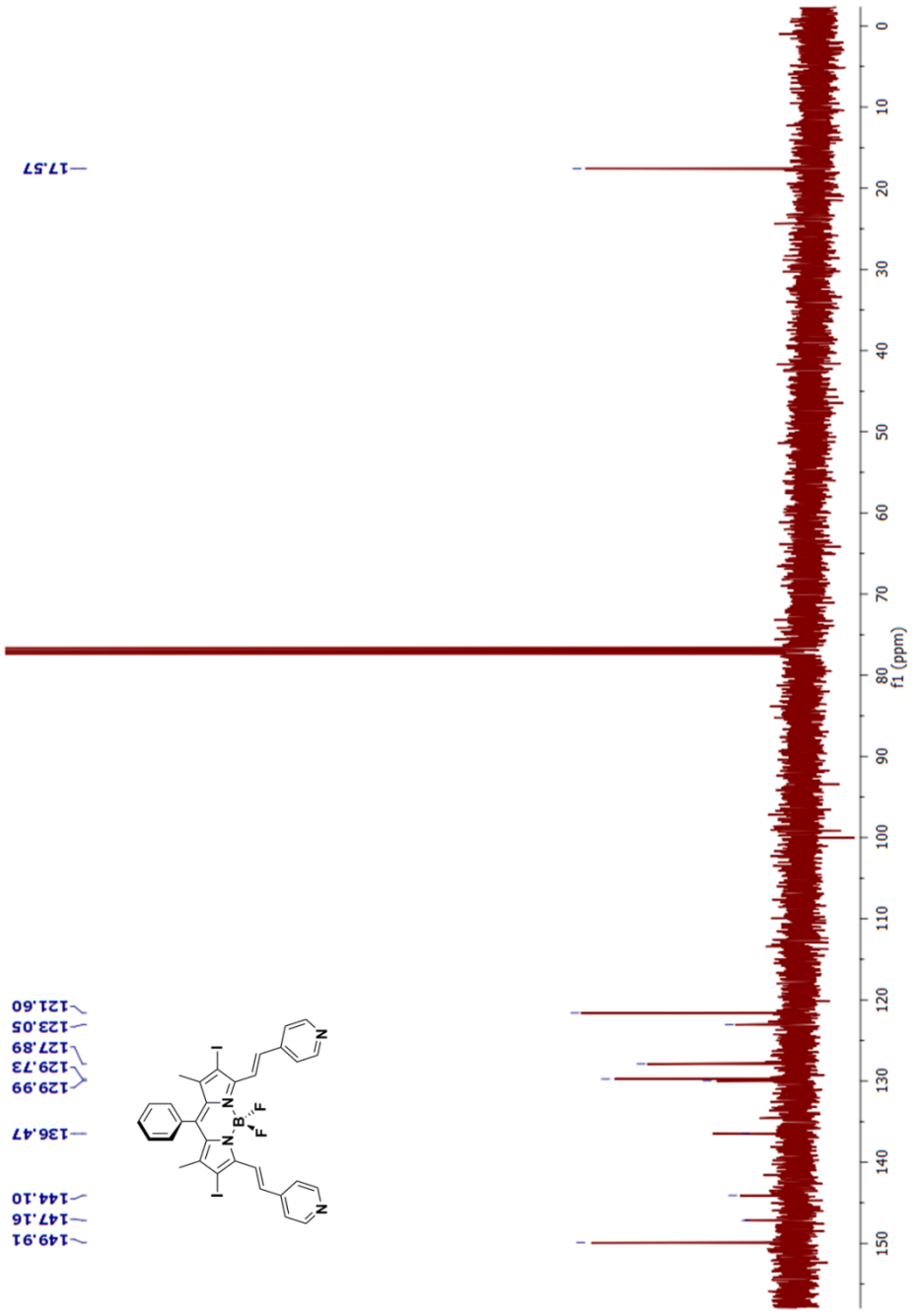

Figure 74. ^{13}C spectrum of compound **32**.

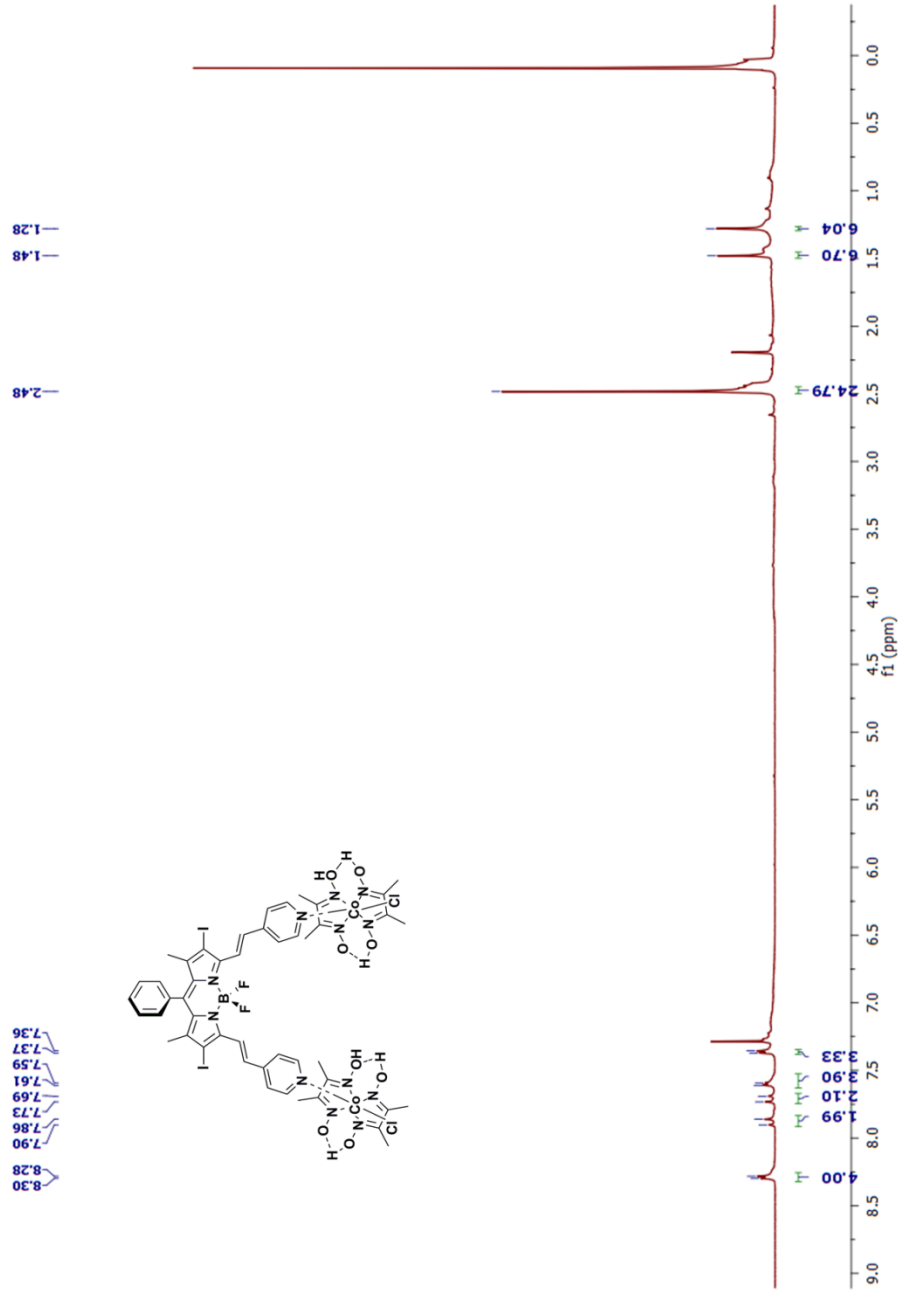

Figure 75. ^{1}H spectrum of compound **33**.

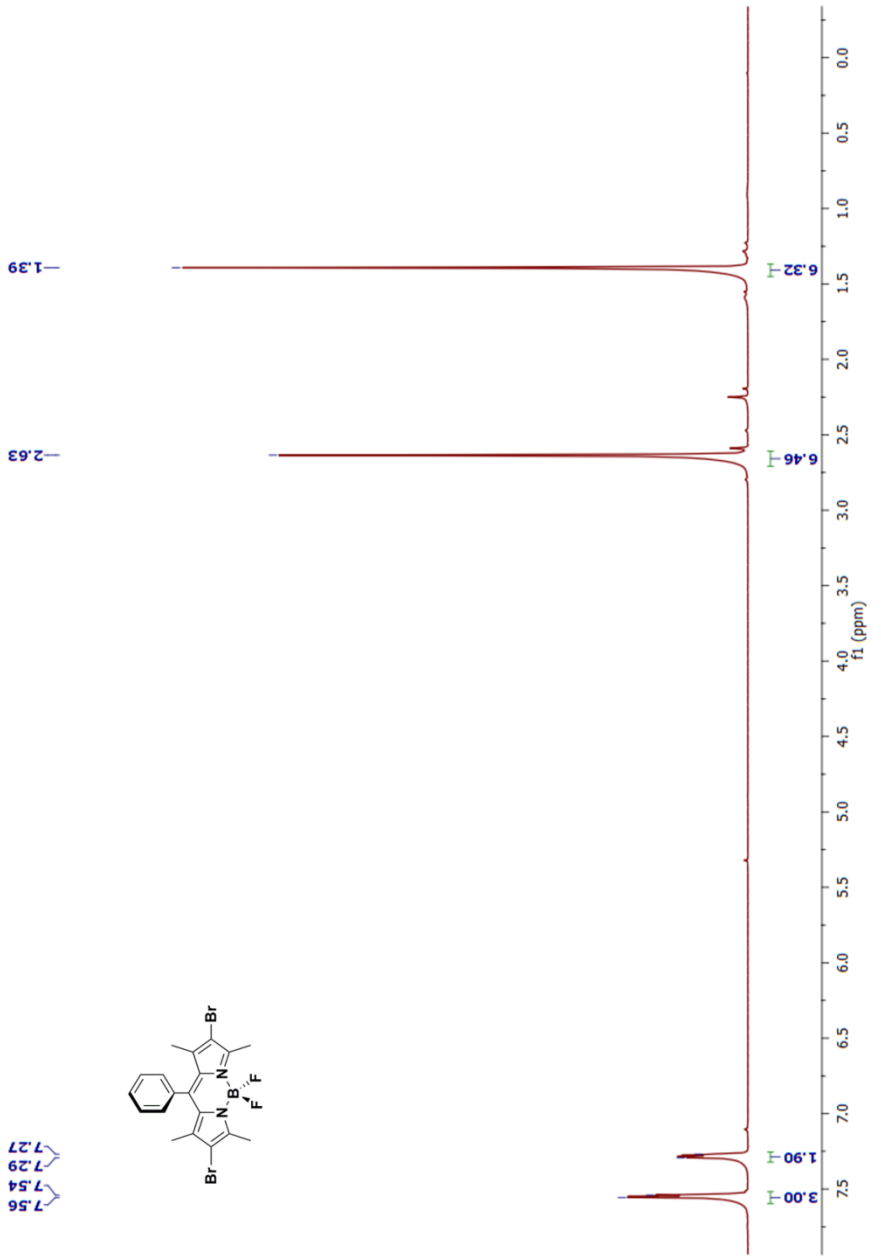

Figure 76. ^{1}H spectrum of compound **34**.

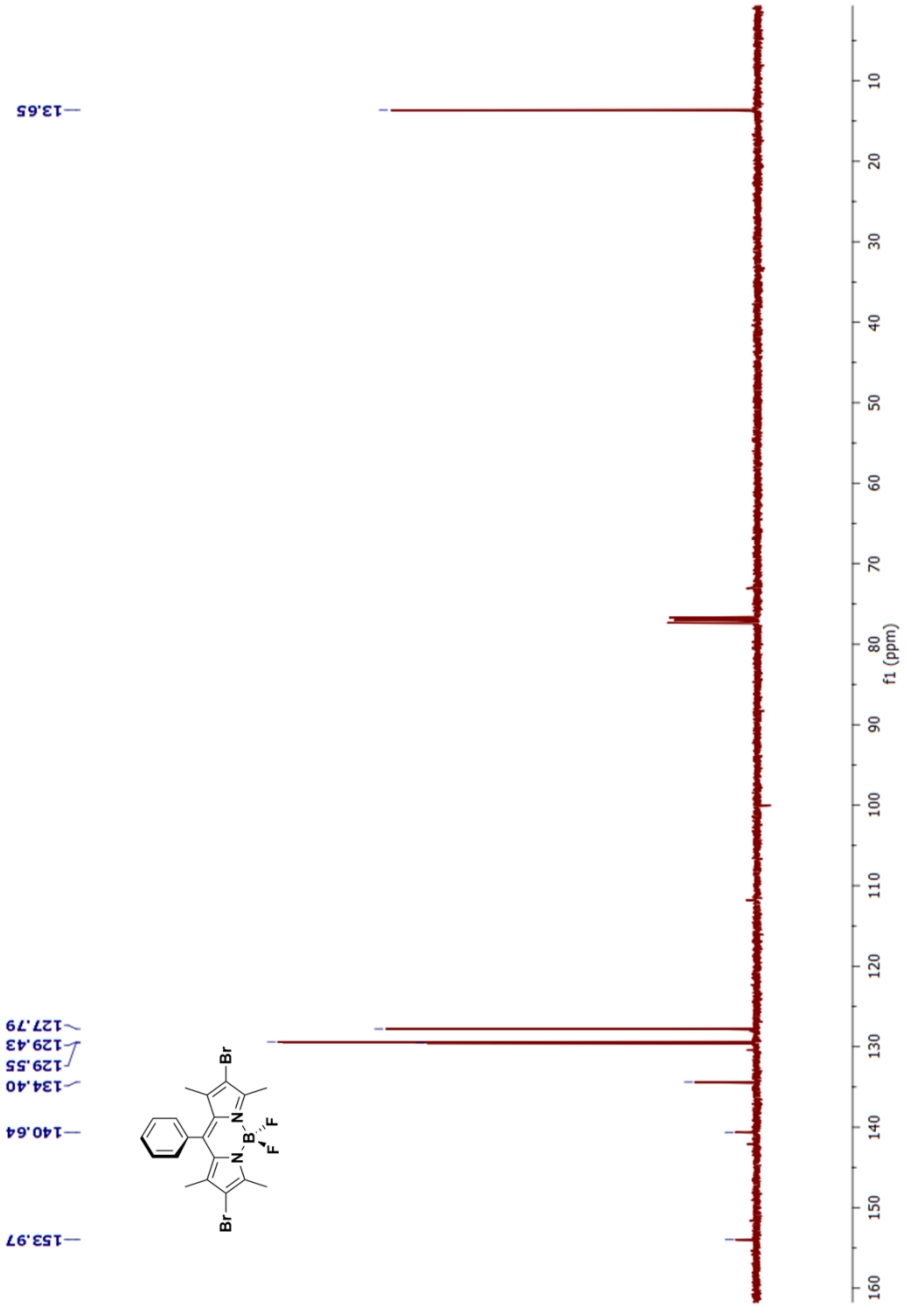

Figure 77. ^{13}C spectrum of compound **34**.

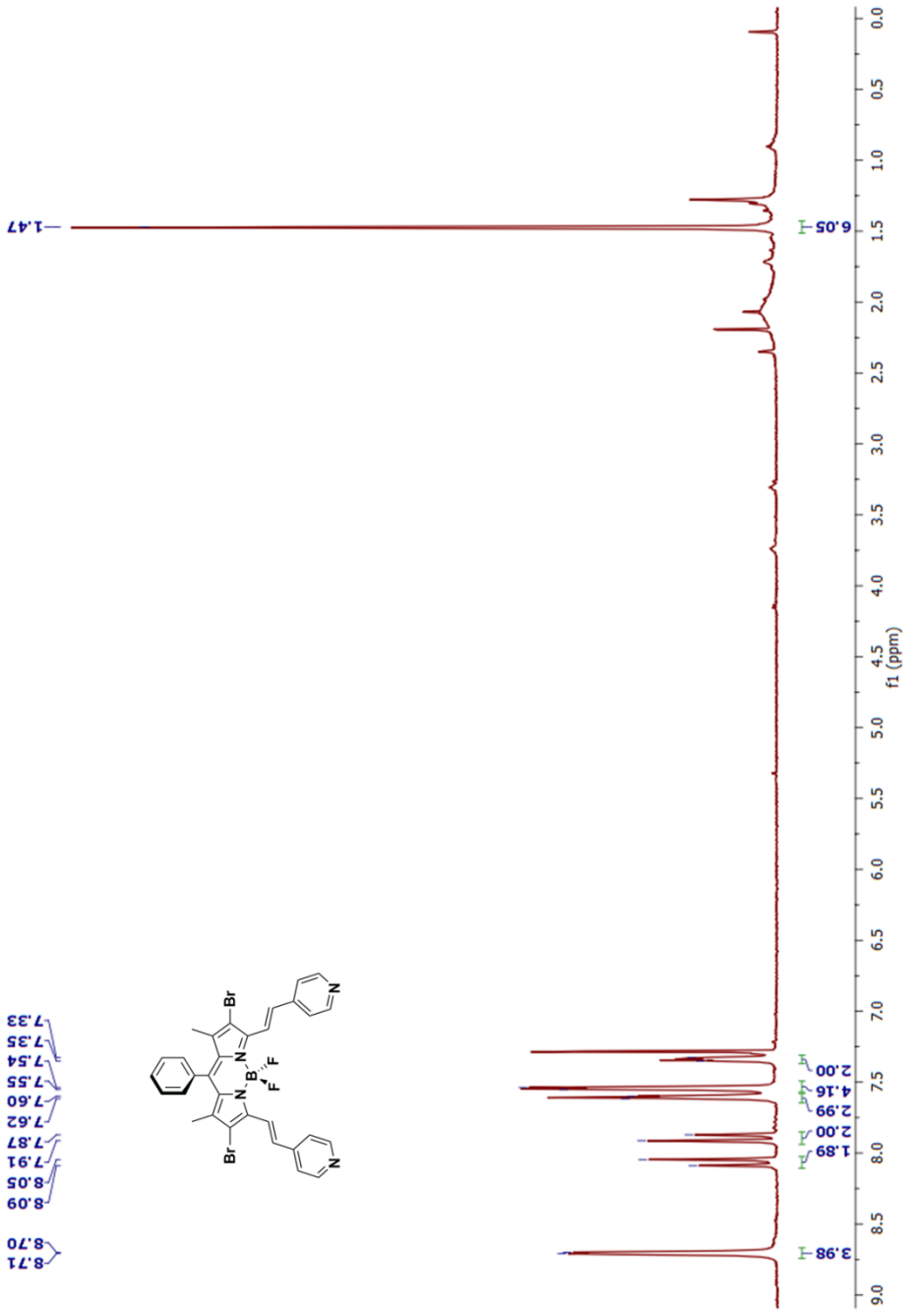

Figure 78. ^{1}H spectrum of compound **35**.

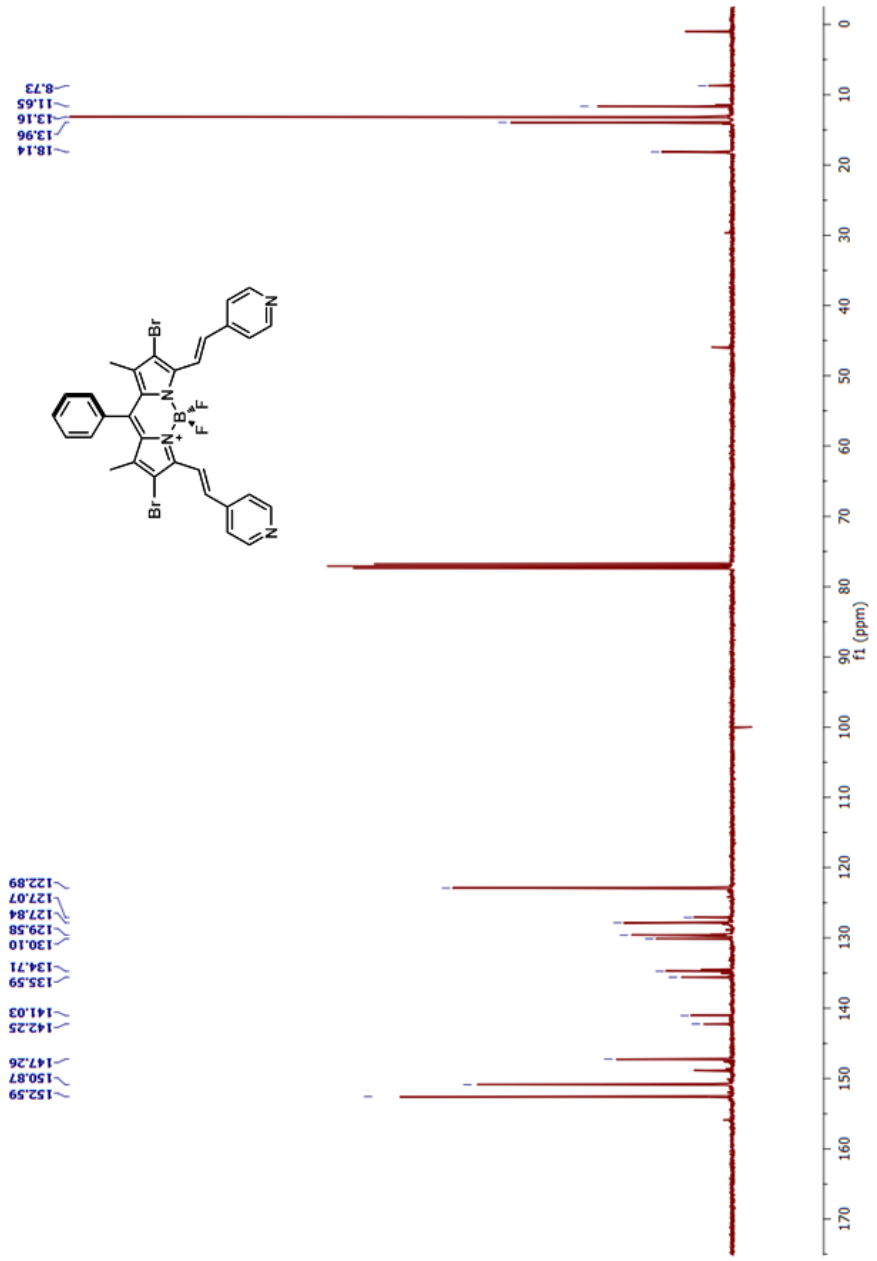

Figure 79. ^{13}C spectrum of compound **35**.

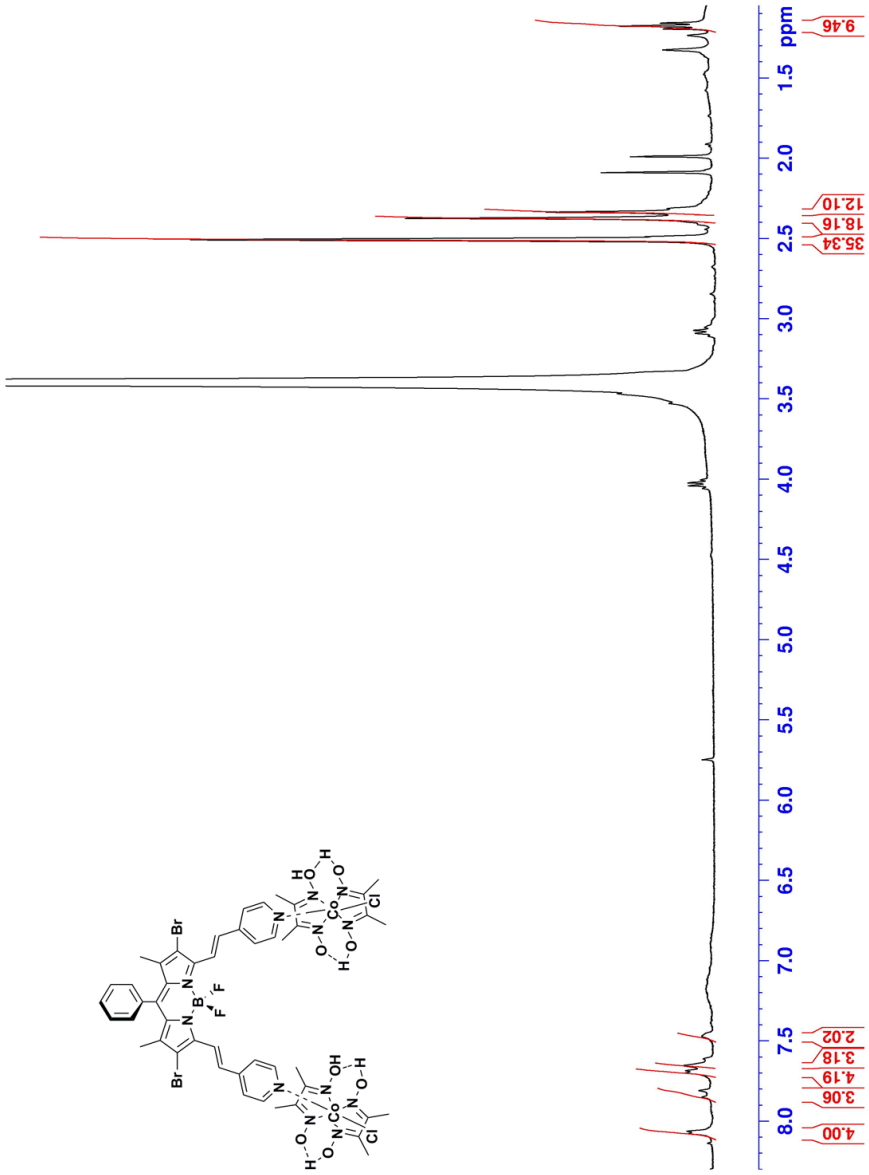

Figure 80. ^{1}H spectrum of compound **36**.

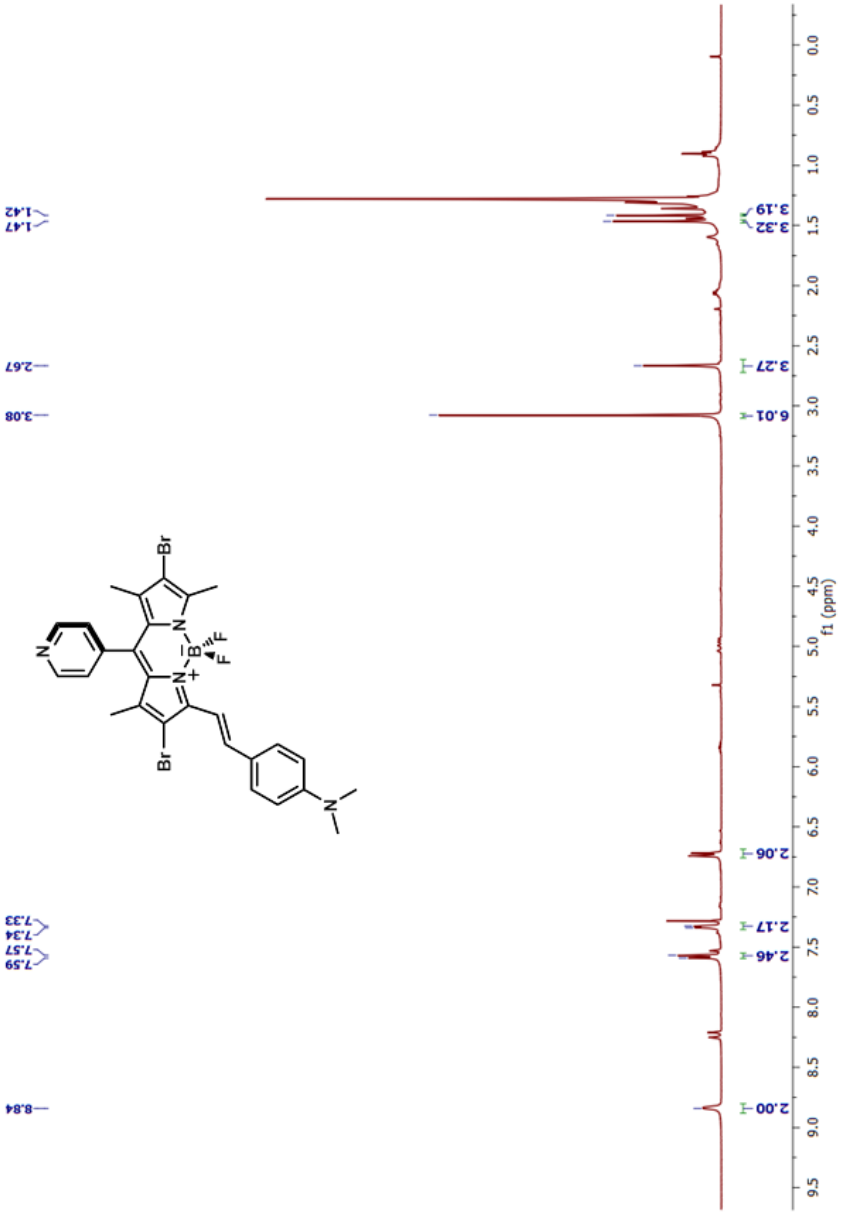

Figure 81. ^{1}H spectrum of compound **37**.

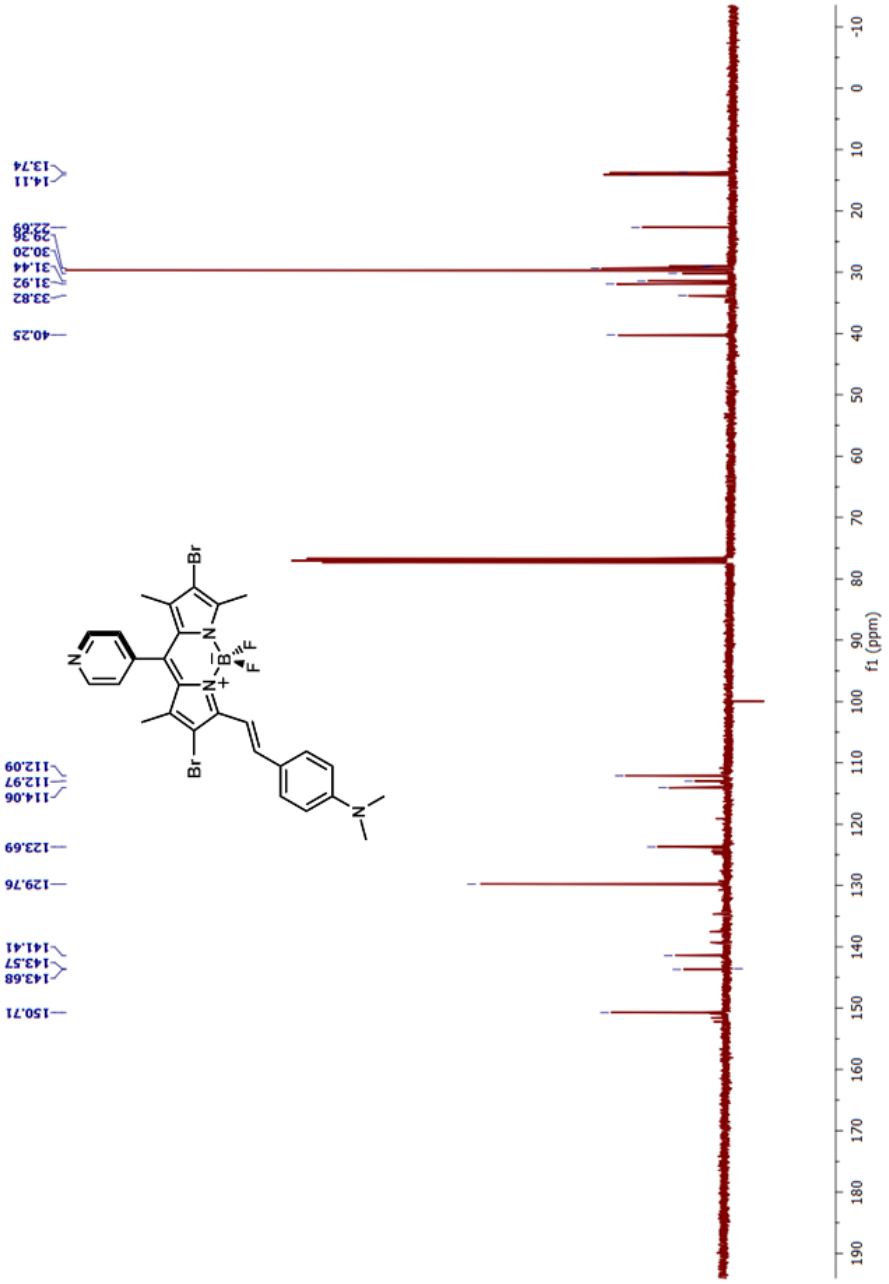

Figure 82. ^{13}C spectrum of compound **37**.

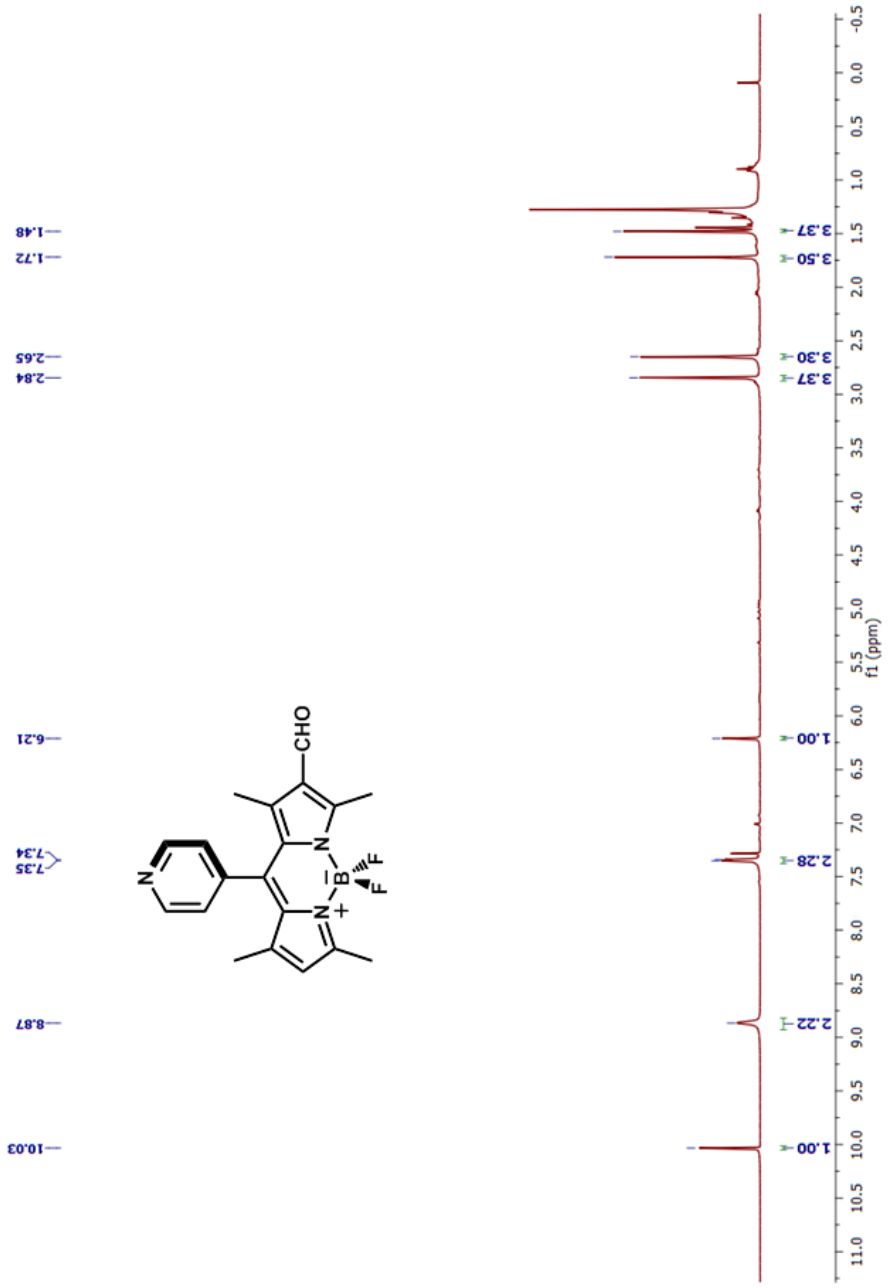

Figure 83. ^{1}H spectrum of compound **39**.

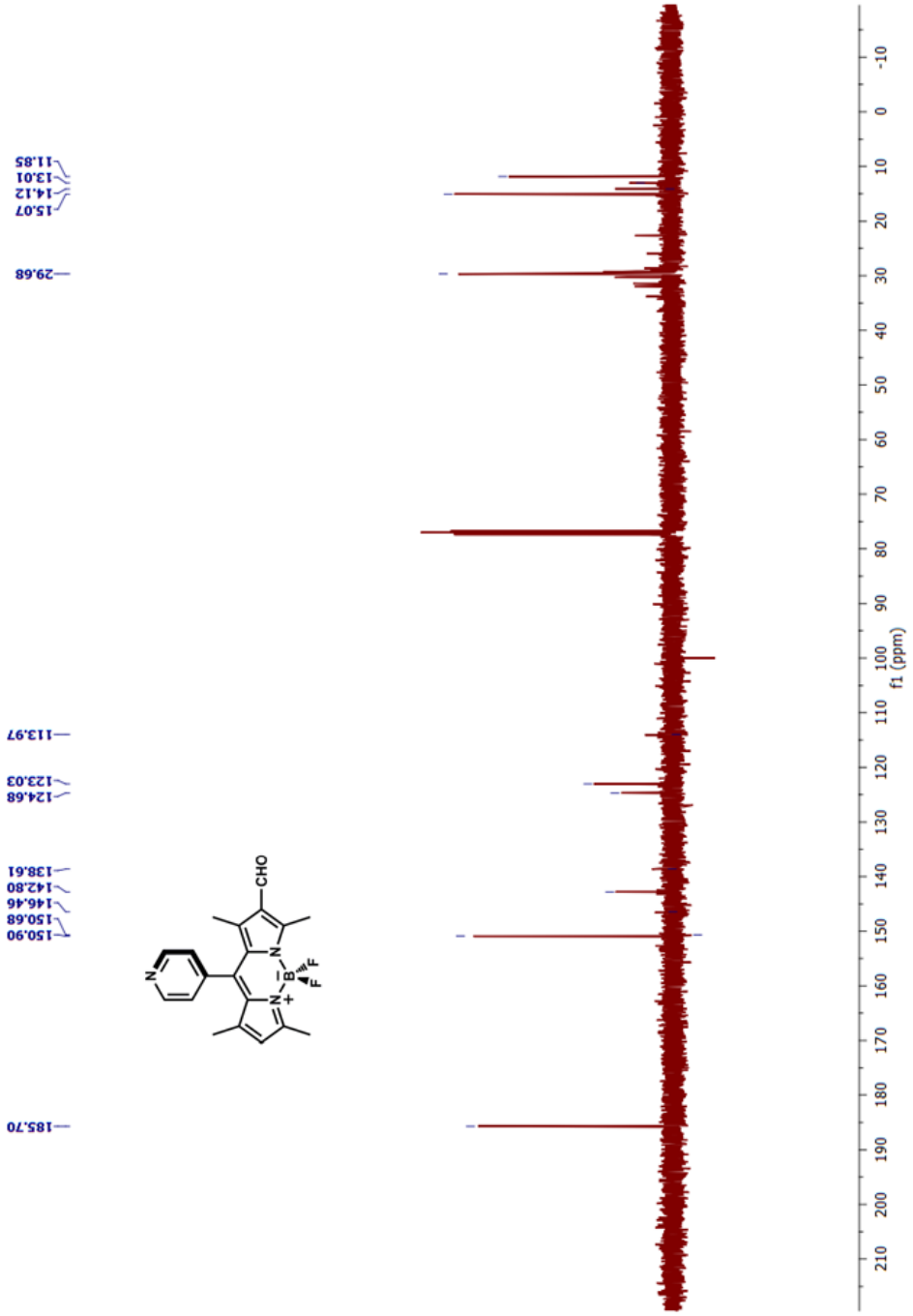

Figure 84. ^{13}C spectrum of compound **39**.

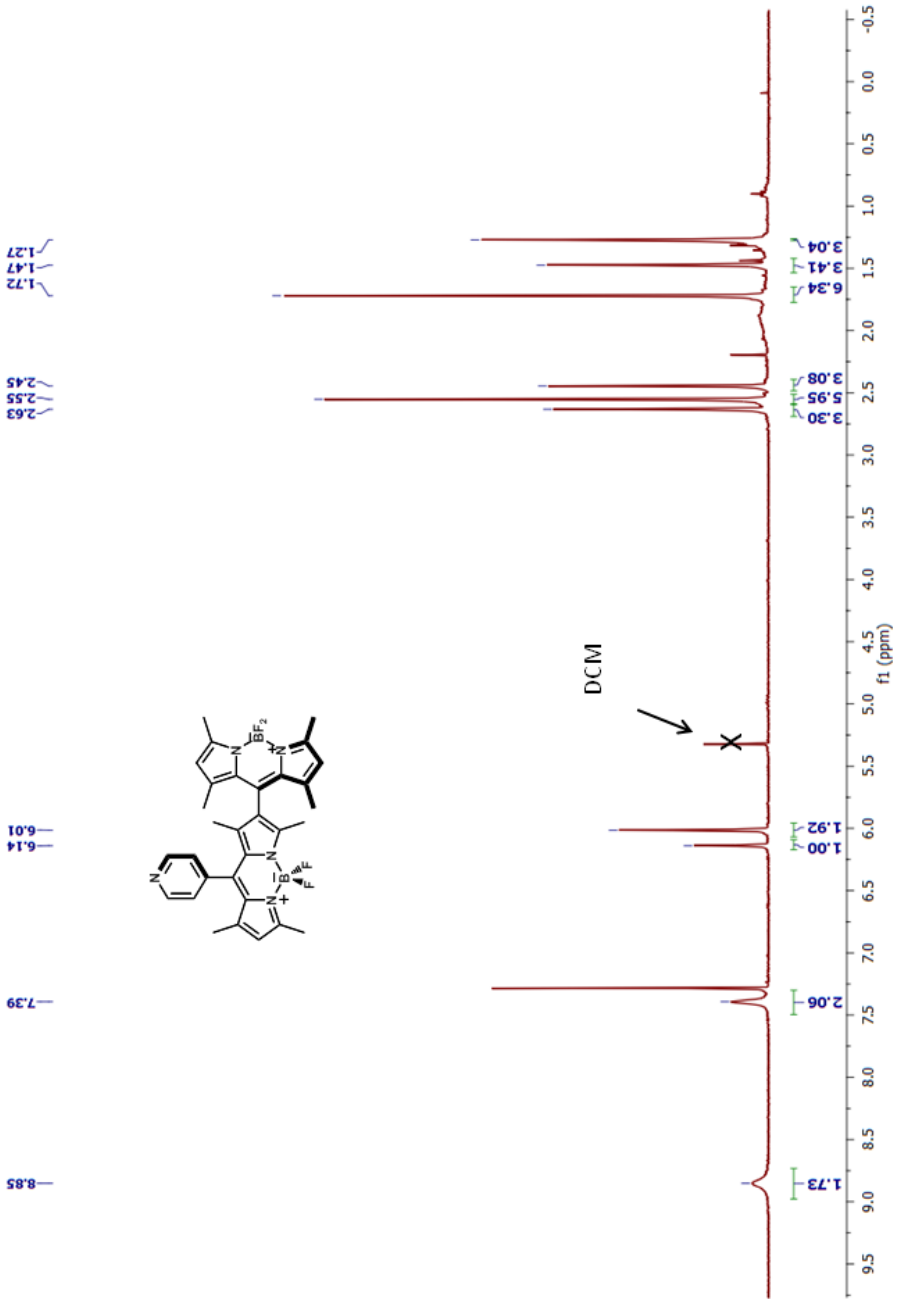

Figure 85. ^{1}H spectrum of compound **40**.

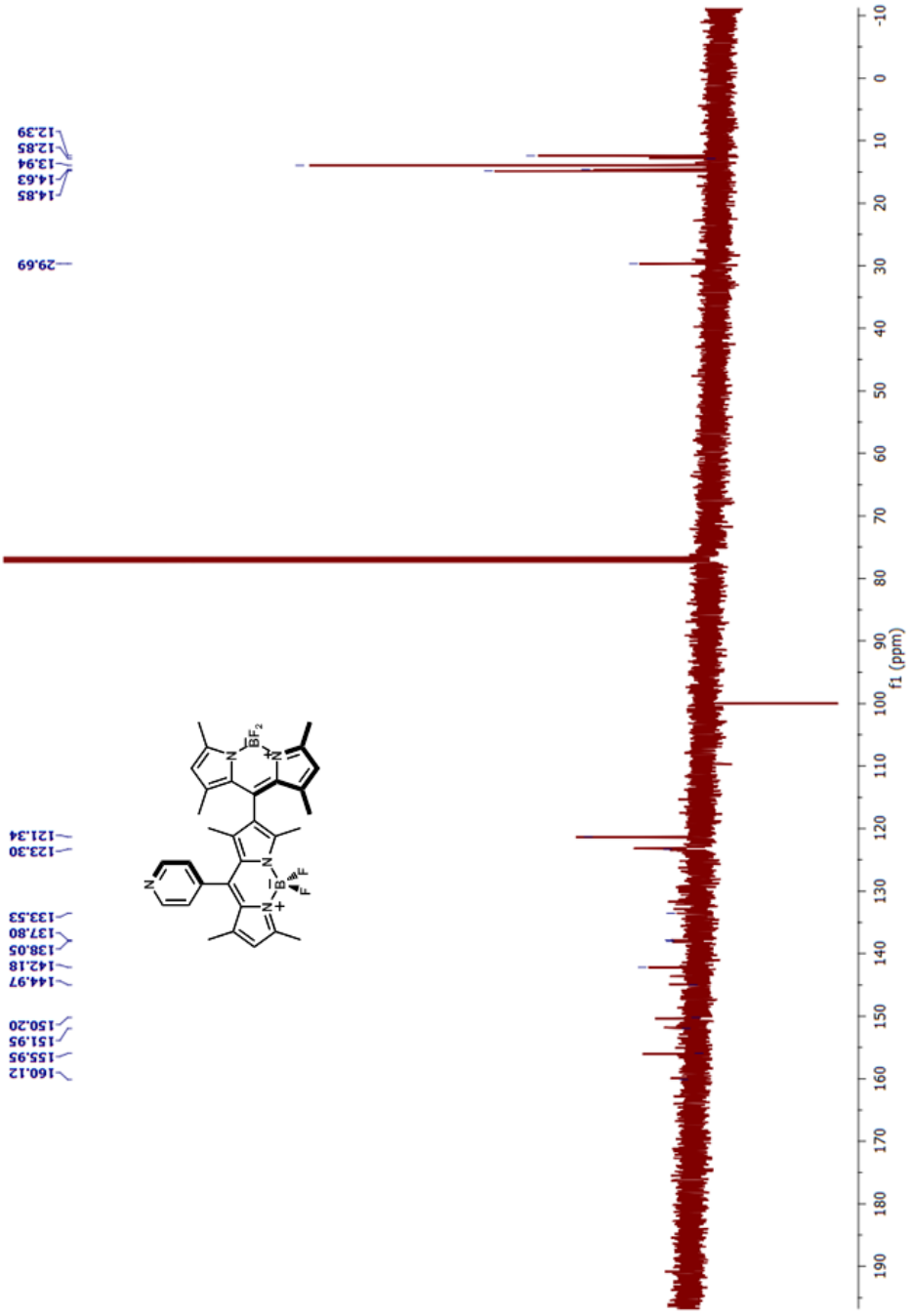

Figure 86. ^{13}C spectrum of compound **40**.

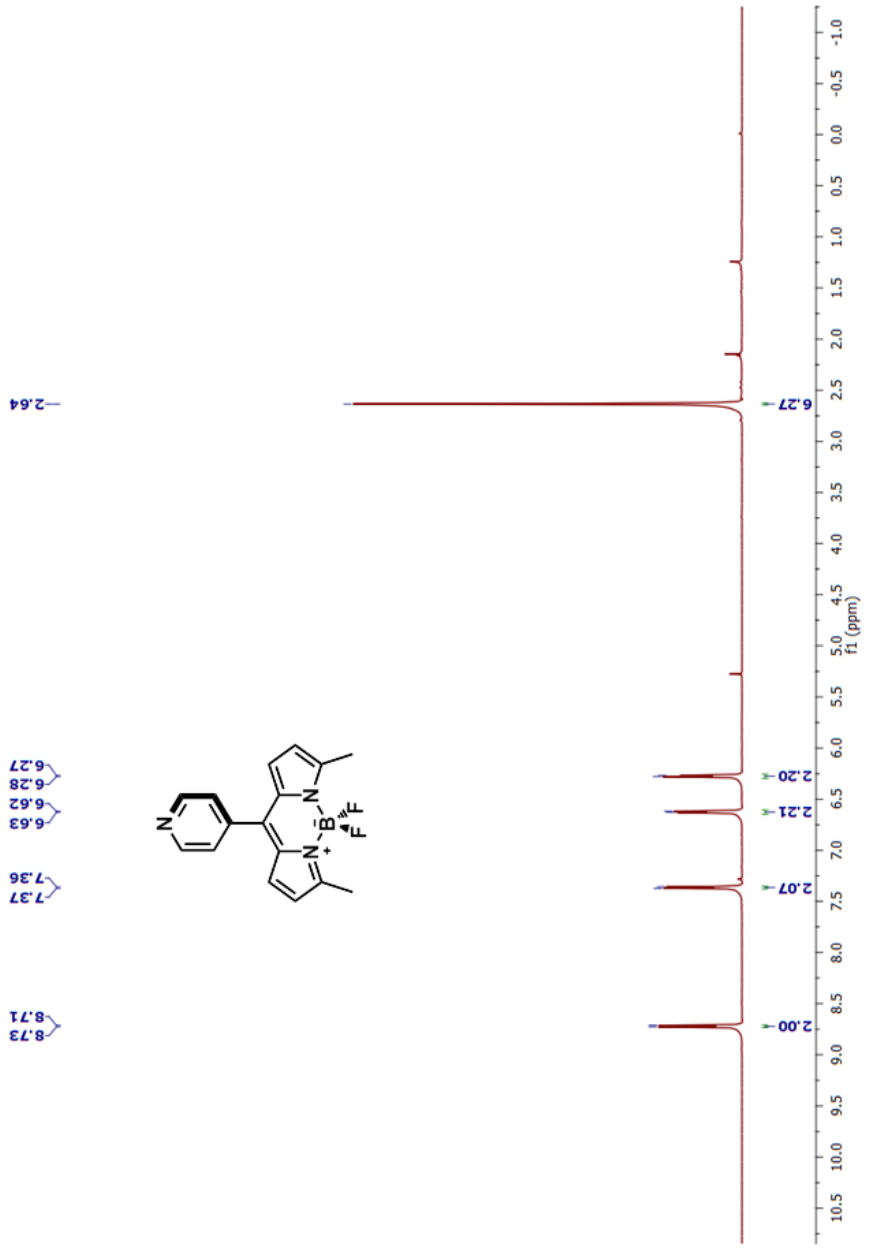

Figure 87. ^{1}H spectrum of compound **42**.

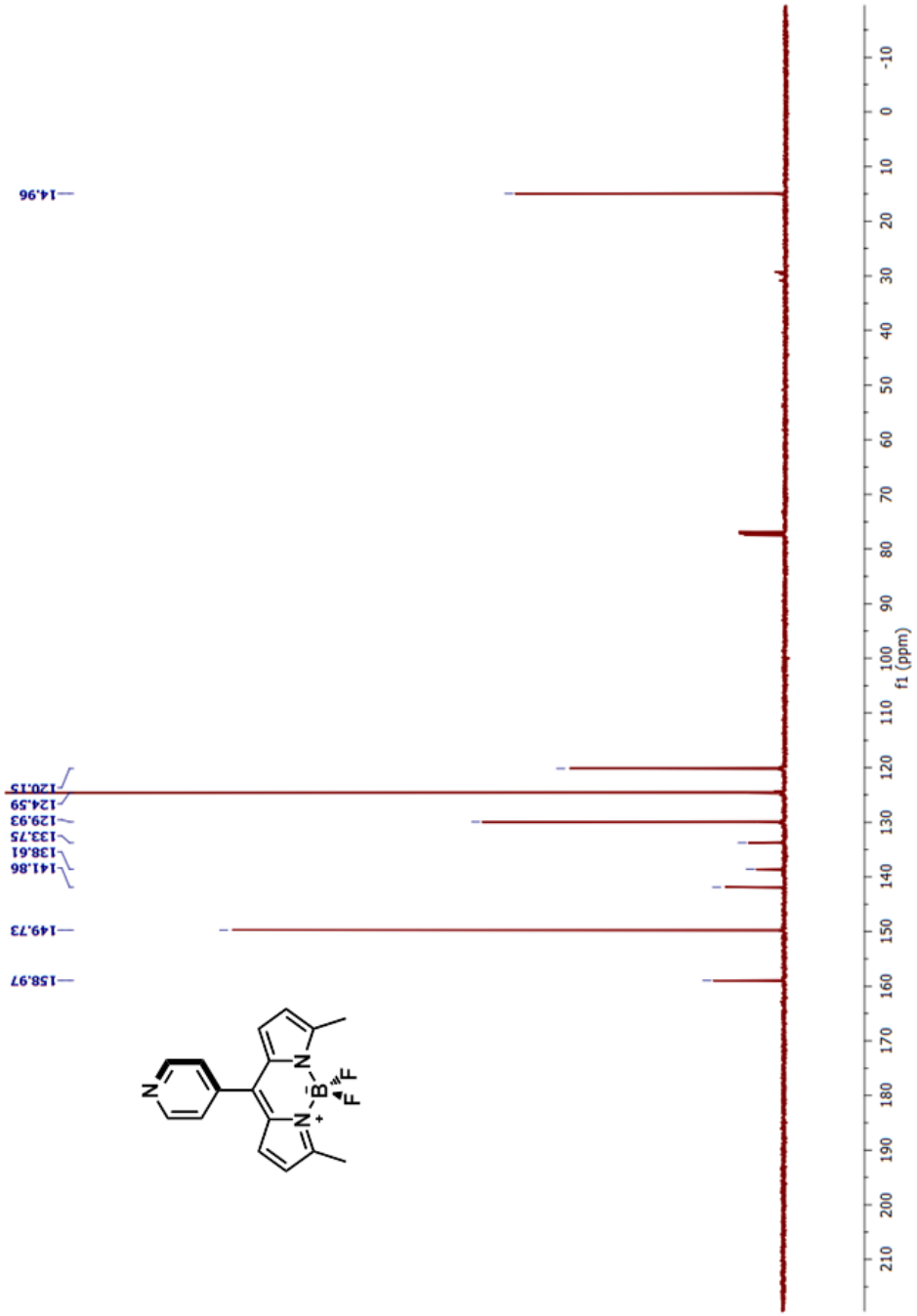

Figure 88. ^{13}C spectrum of compound **42**.

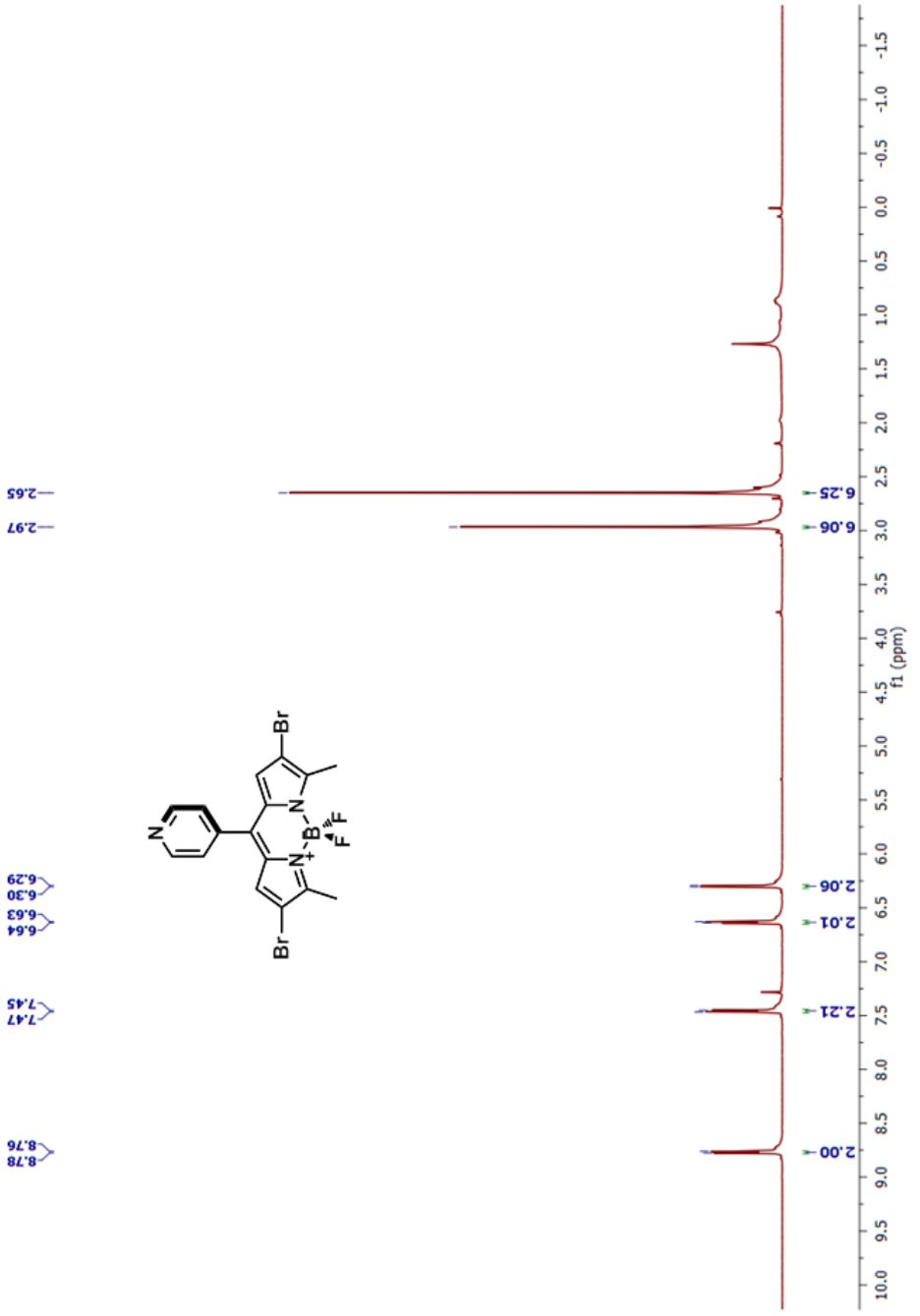

Figure 89. ^{1}H spectrum of compound **43**.

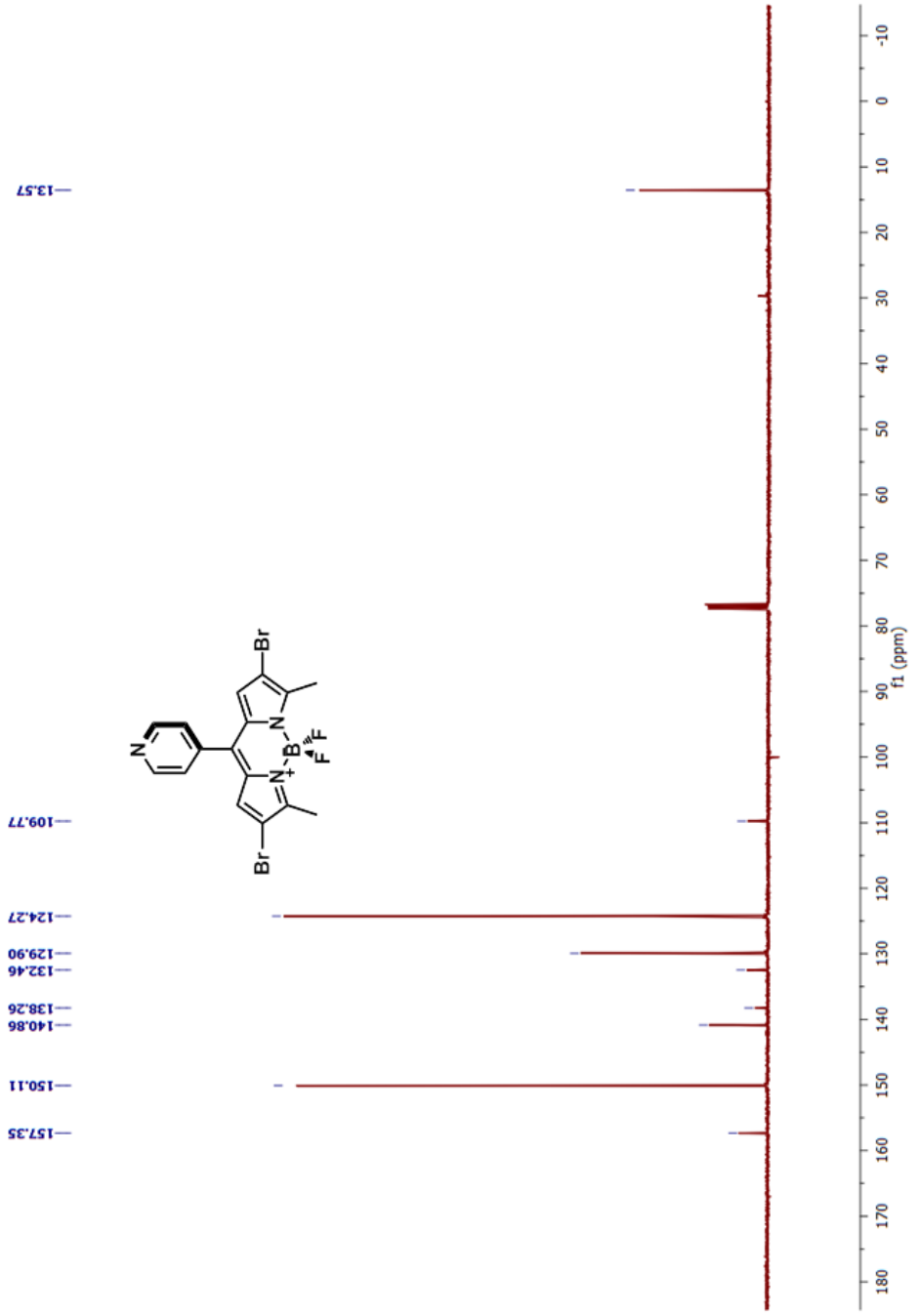

Figure 90. ^{13}C spectrum of compound **43**.

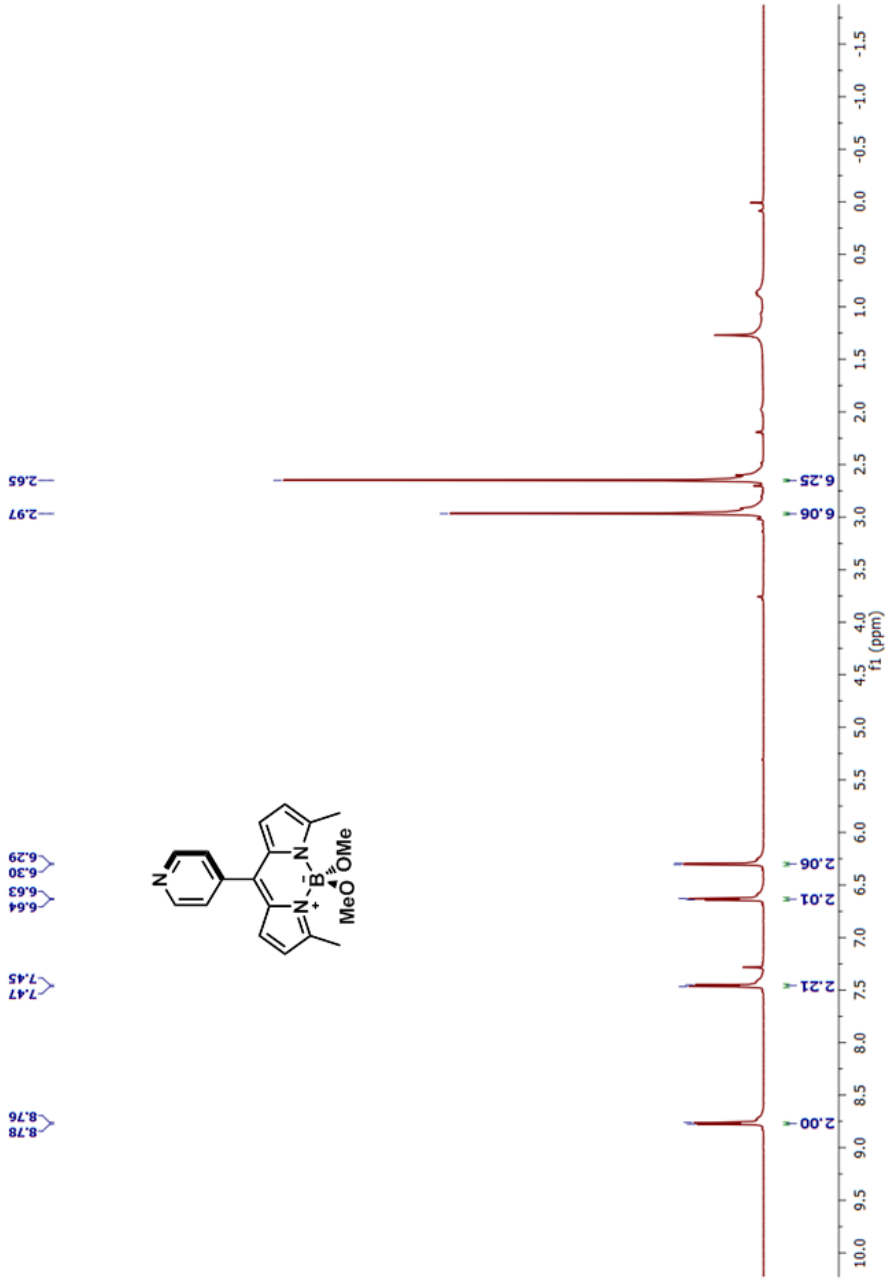

Figure 91. ^{1}H spectrum of compound **45**.

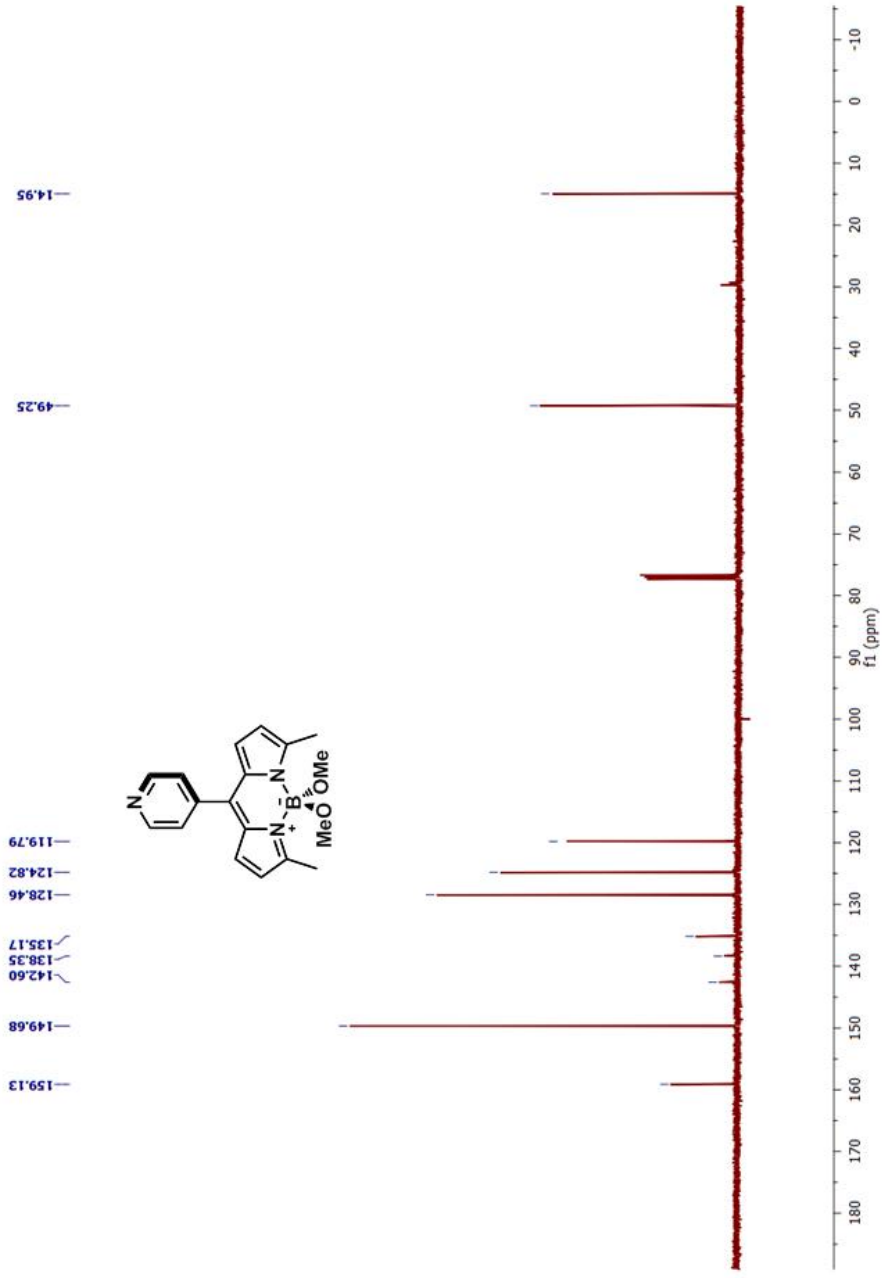

Figure 92. ^{13}C spectrum of compound **45**.

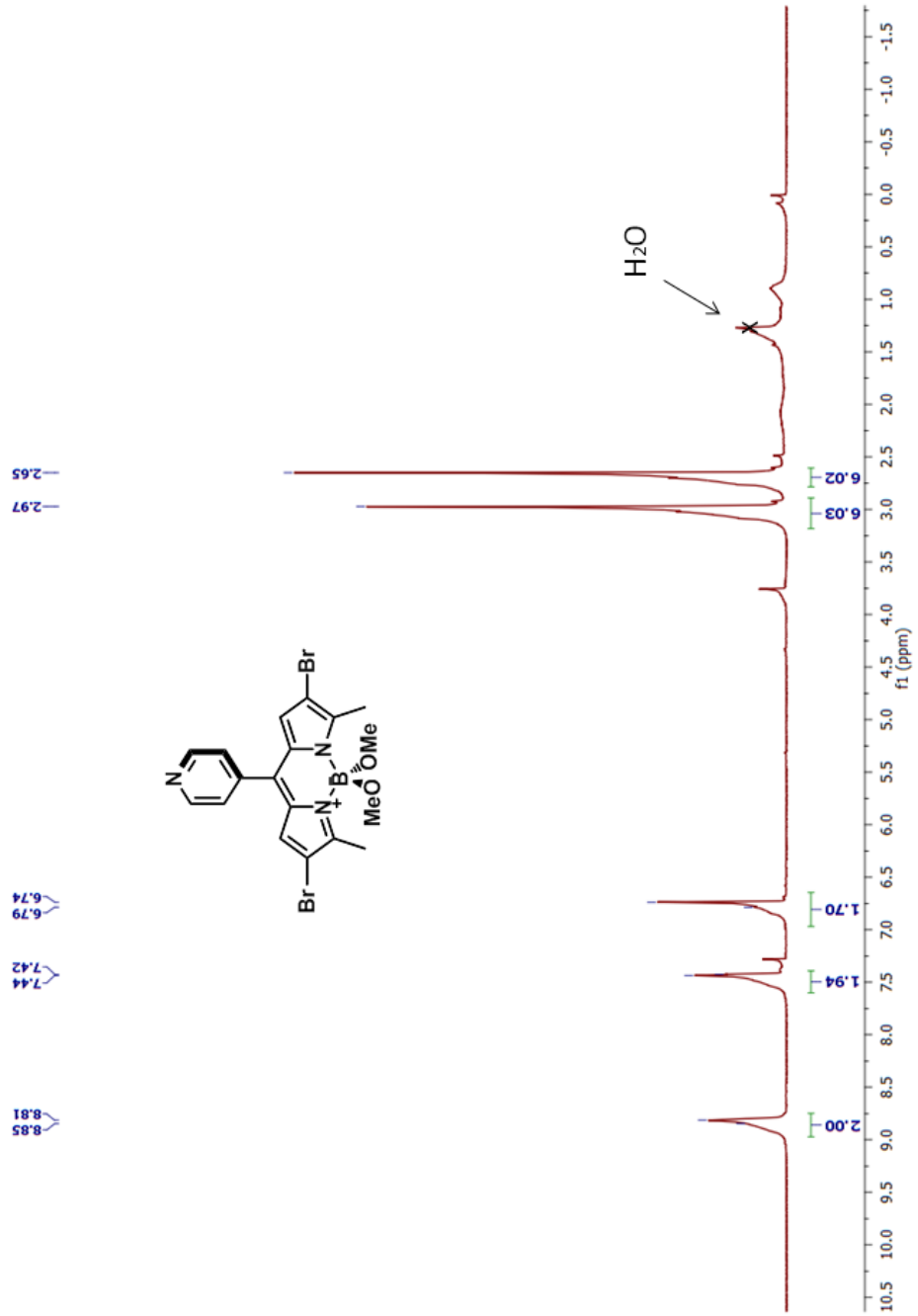

Figure 93. ^{1}H spectrum of compound **46**.

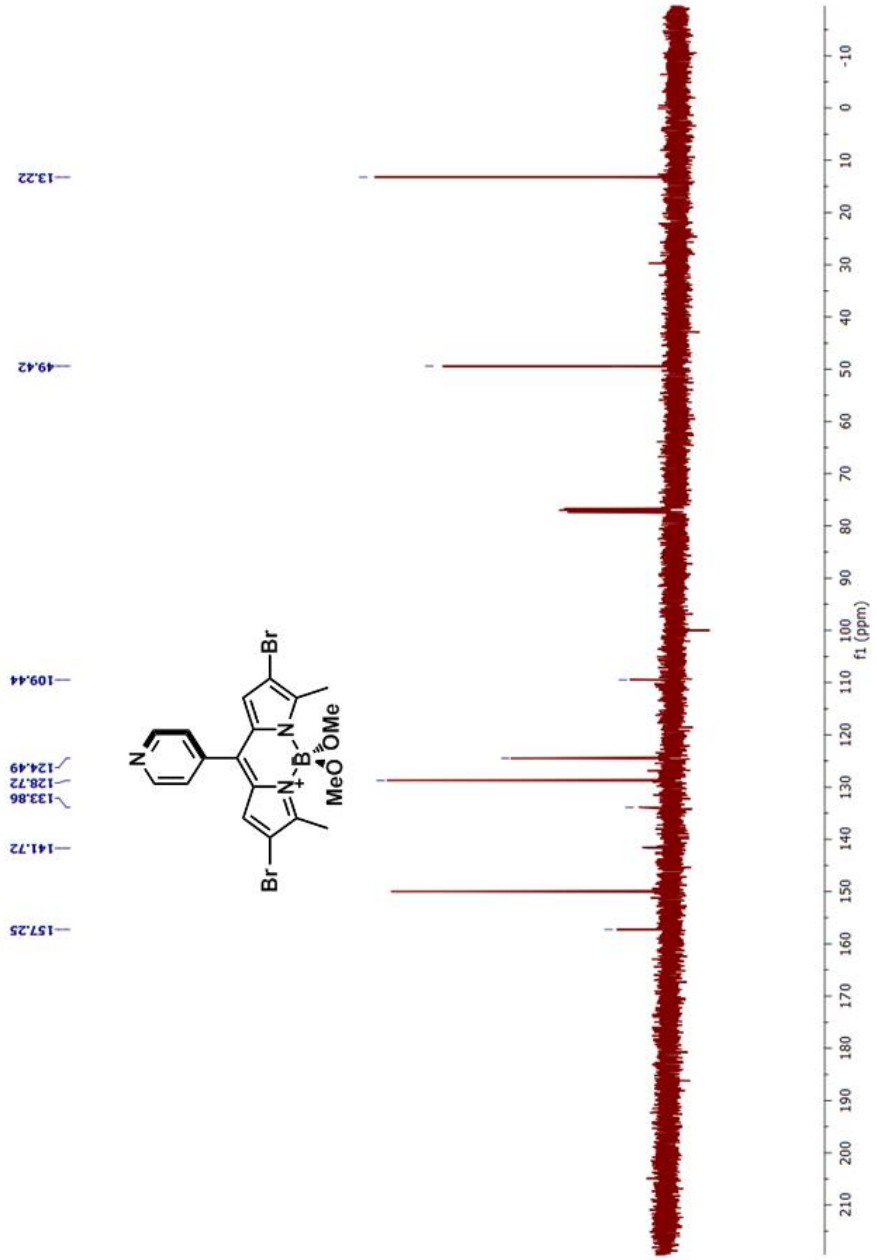

Figure 94. ^{13}C spectrum of compound **46**.

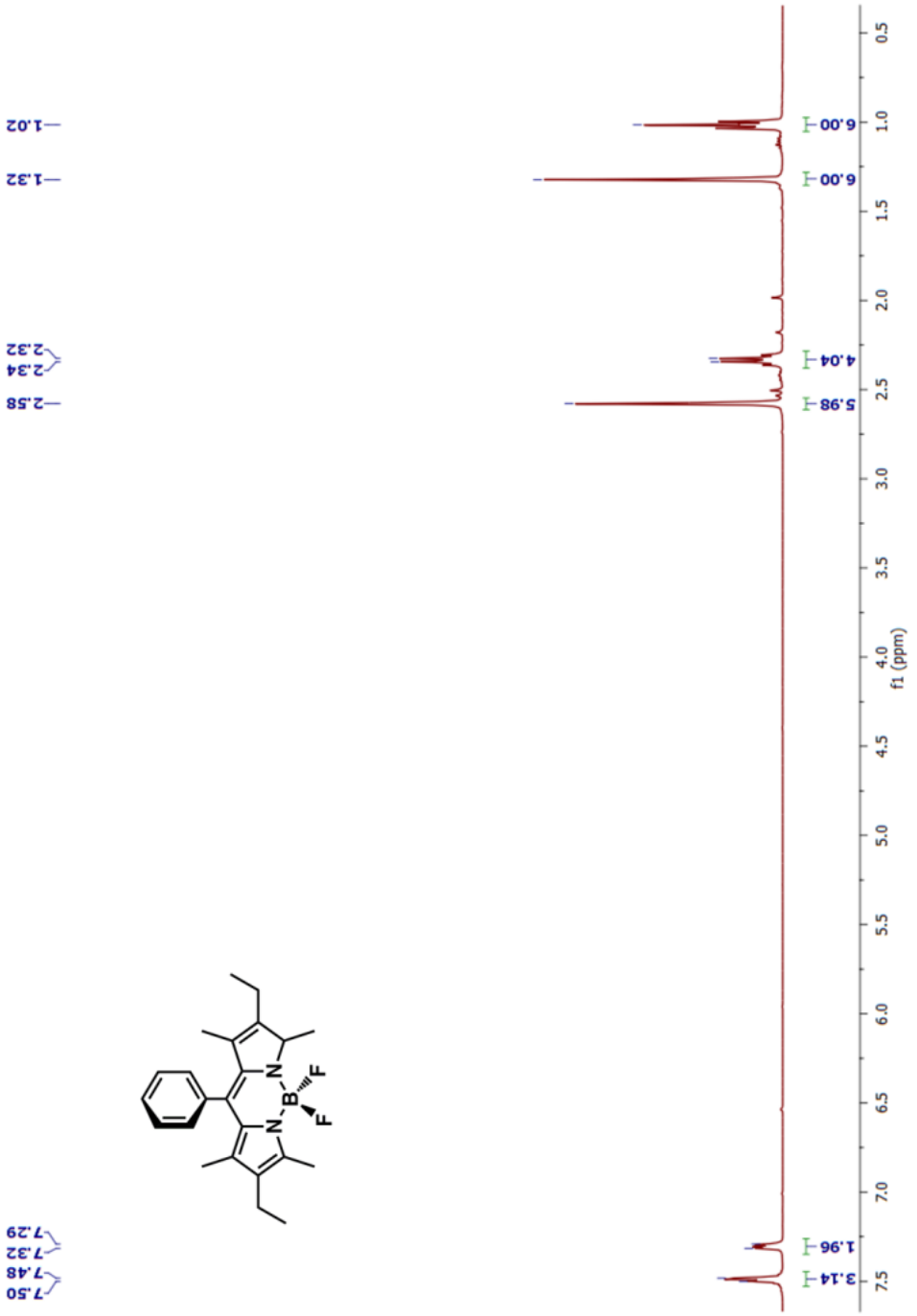

Figure 95. ^{1}H spectrum of compound **48**.

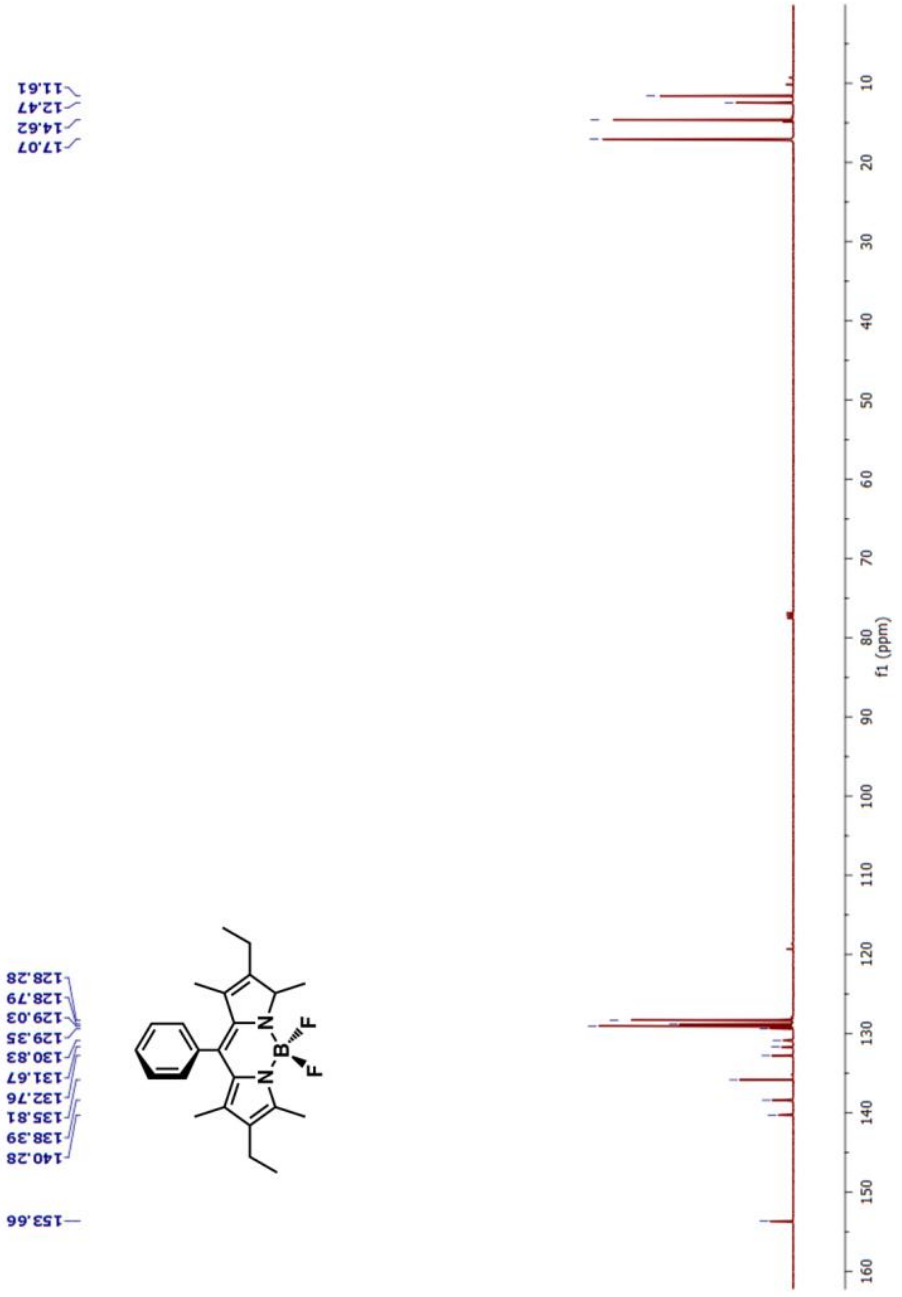

Figure 96. ^{13}C spectrum of compound **48**.

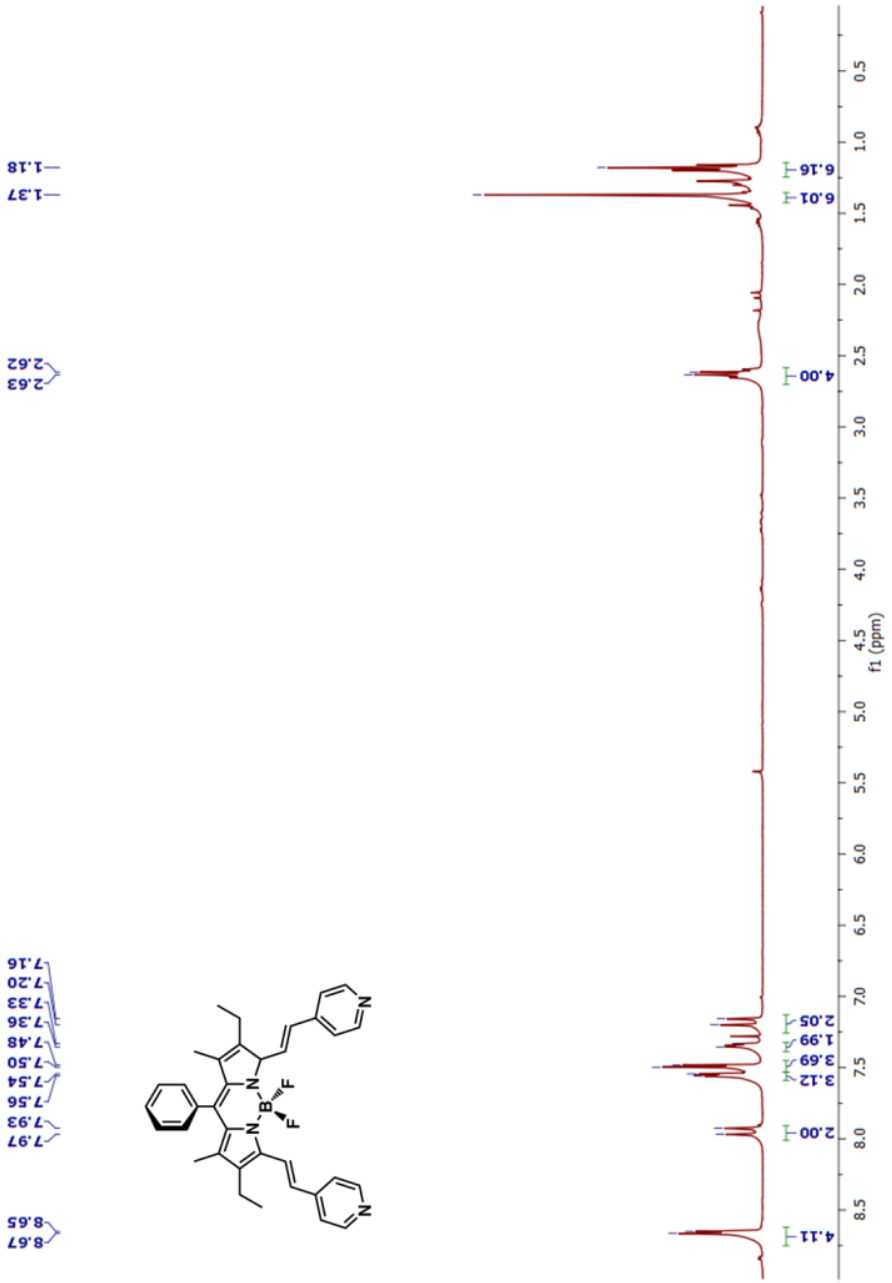

Figure 97. ^{1}H spectrum of compound **49**.

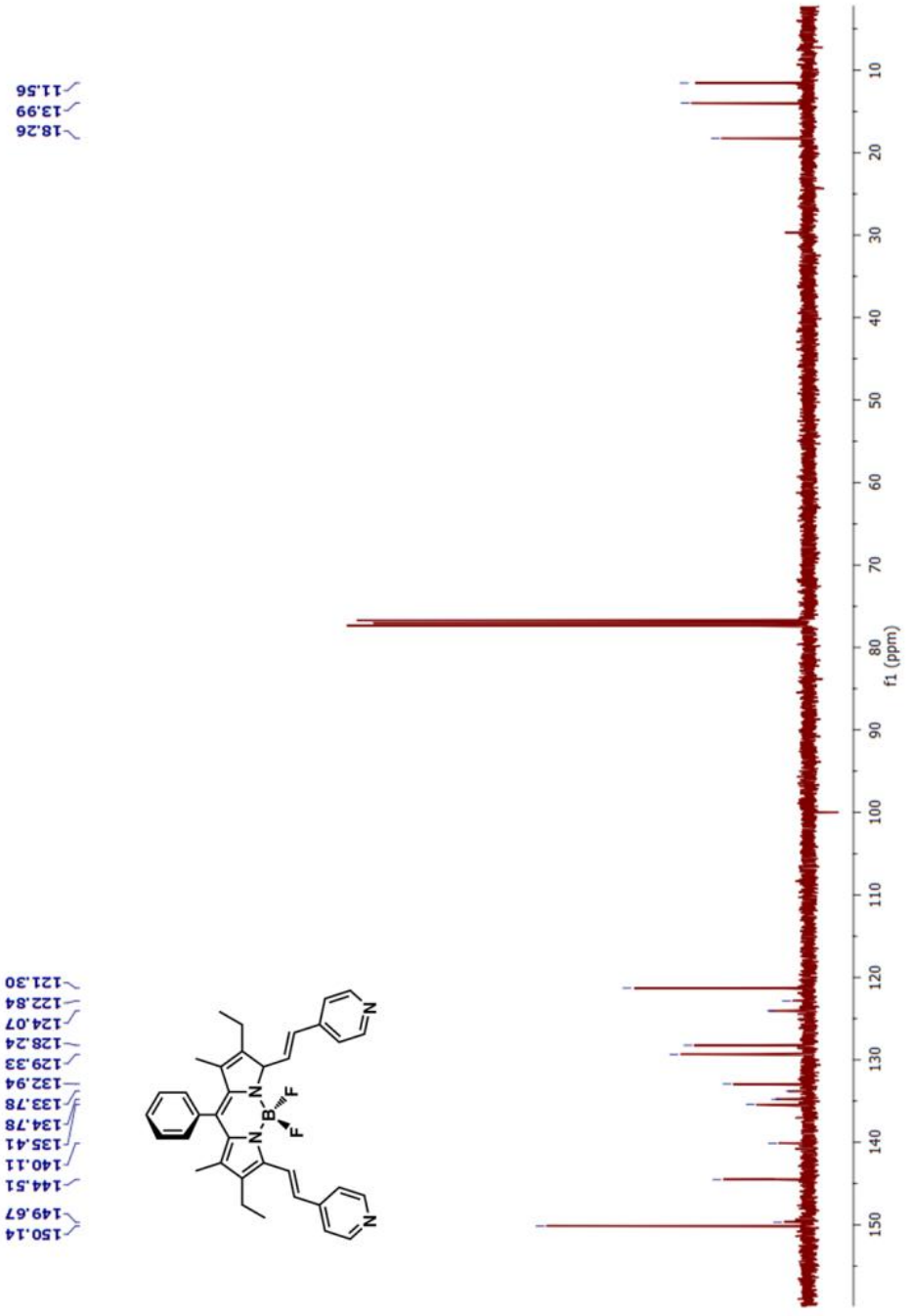

Figure 98. ^{13}C spectrum of compound **49**.

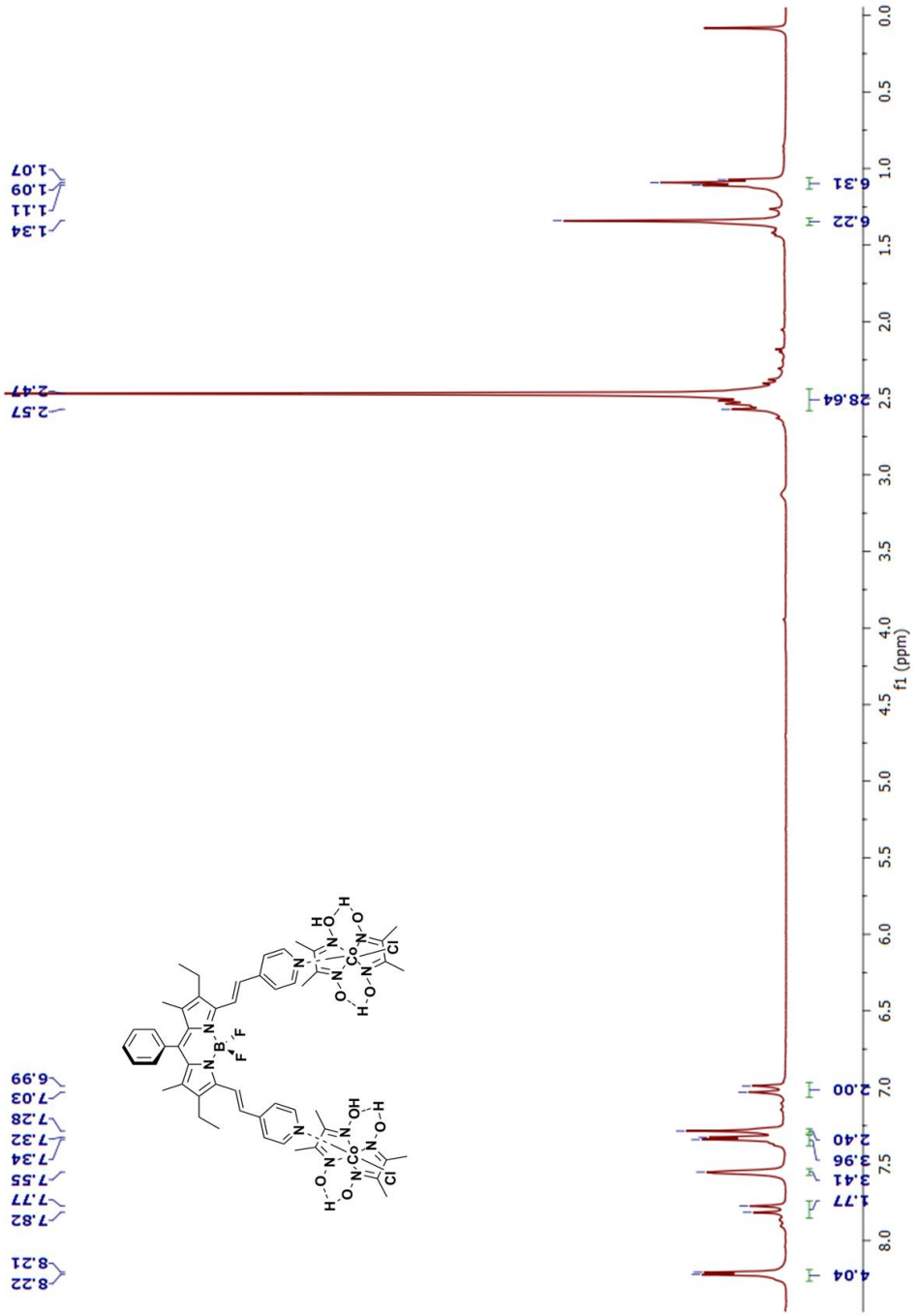

Figure 99. ^{1}H spectrum of compound **50**.

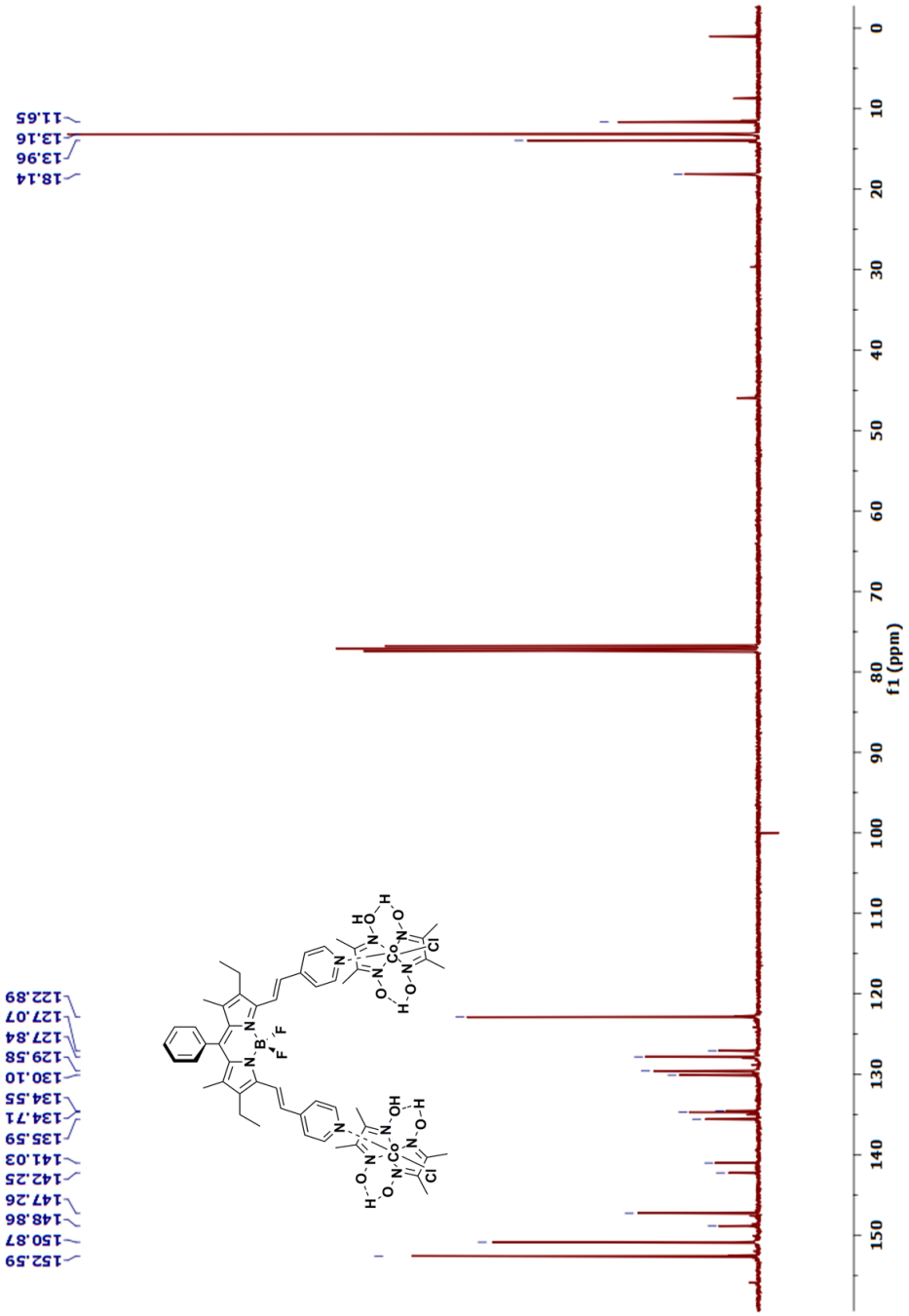

Figure 100. ^{13}C spectrum of compound **50**.

APPENDIX B

MASS SPECTRA

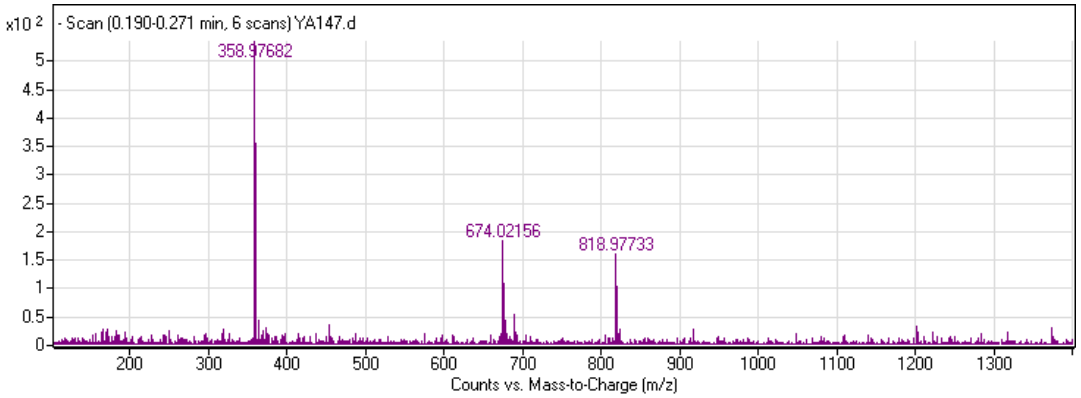

Figure 101. ESI-HRMS of compound **23**.

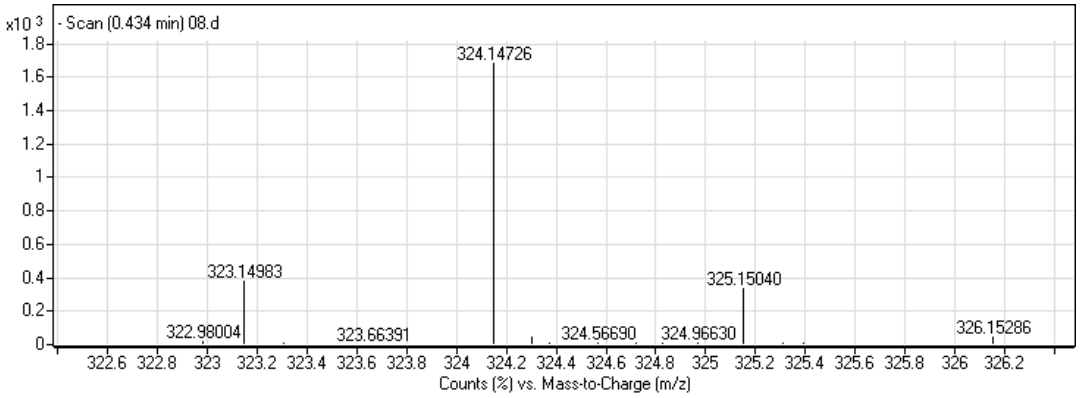

Figure 102. ESI-HRMS of compound **24**.

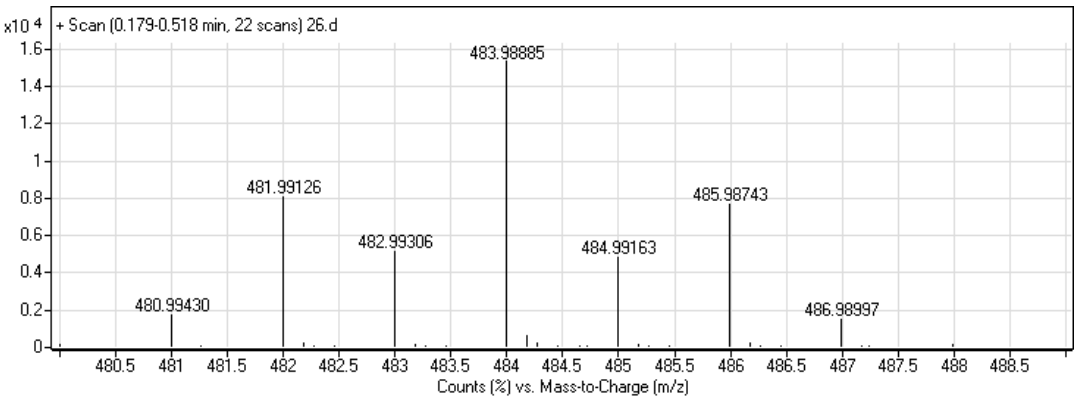

Figure 103. ESI-HRMS of compound **25**.

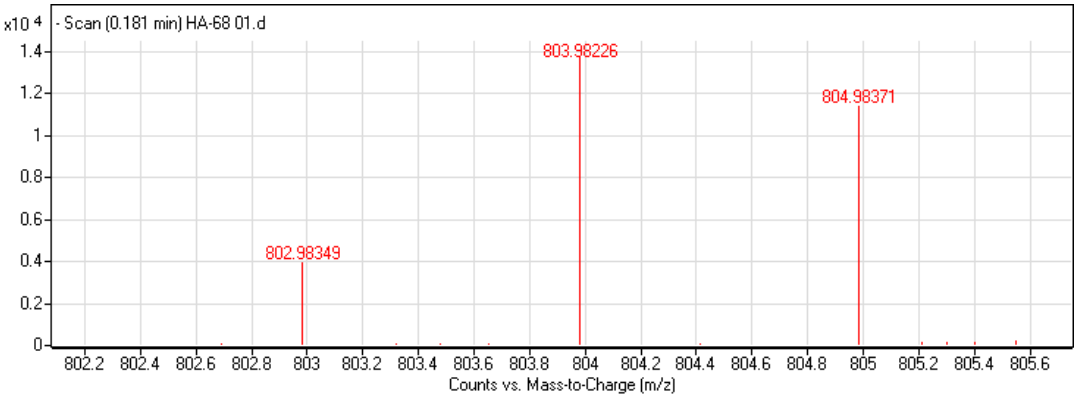

Figure 104. ESI-HRMS of compound **26**.

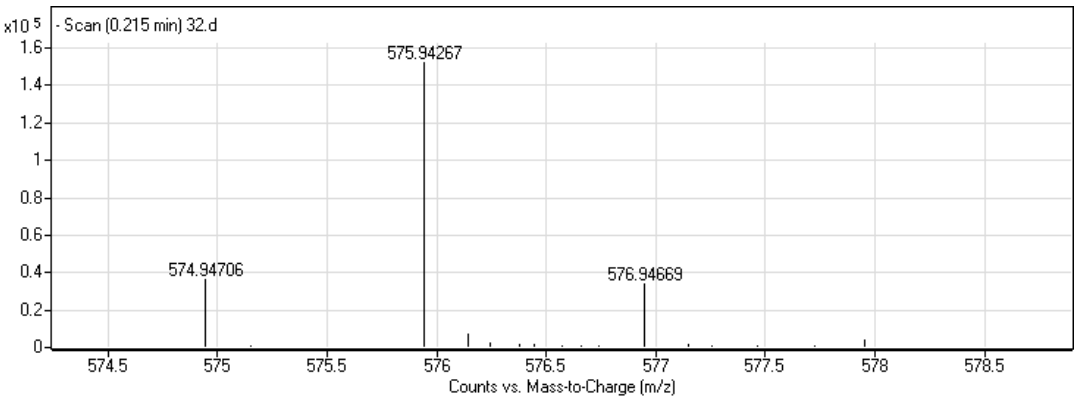

Figure 105. ESI-HRMS of compound **27**.

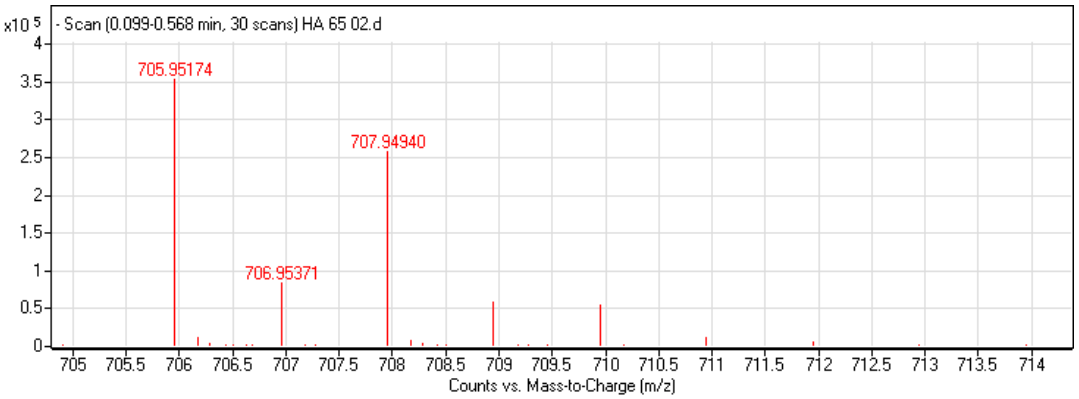

Figure 106. ESI-HRMS of compound **28**.

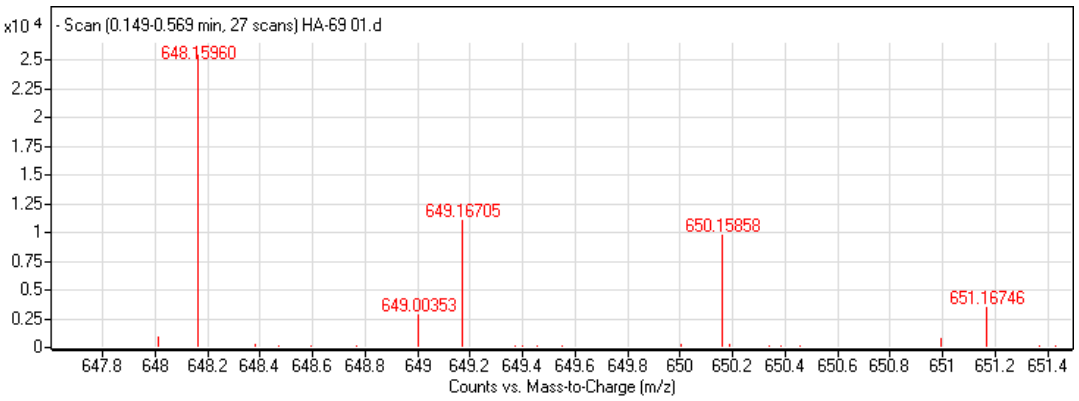

Figure 107. ESI-HRMS of compound **29**.

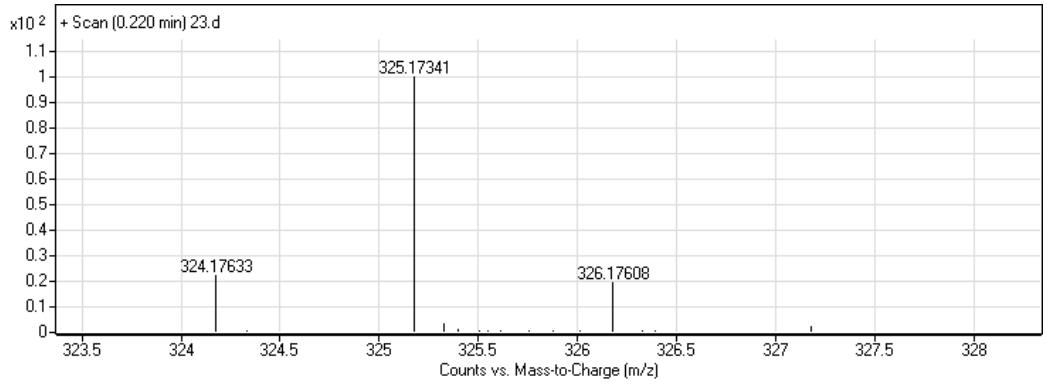

Figure 108. ESI-HRMS of compound **30**.

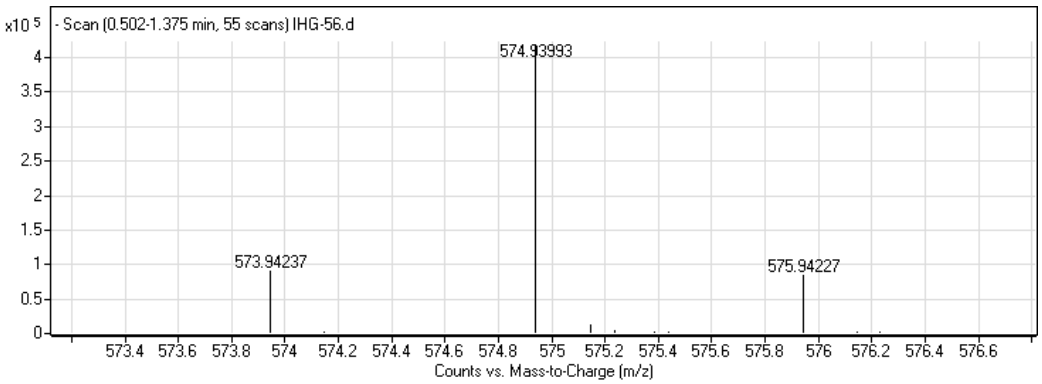

Figure 109. ESI-HRMS of compound **31**.

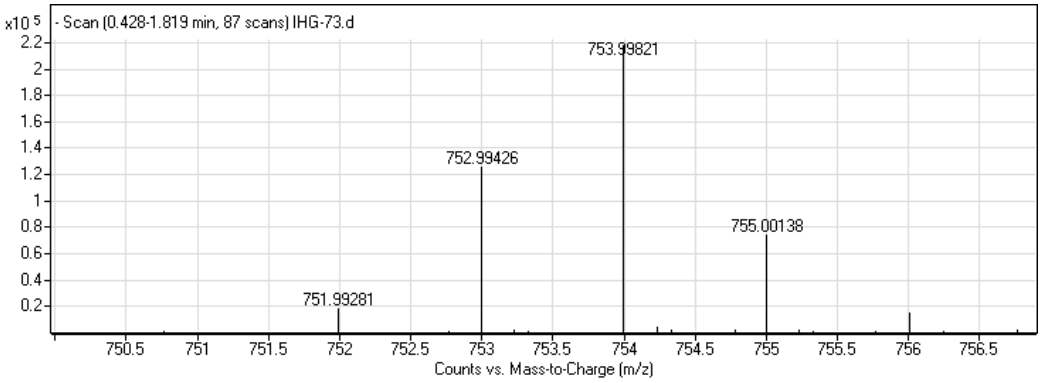

Figure 110. ESI-HRMS of compound **32**.

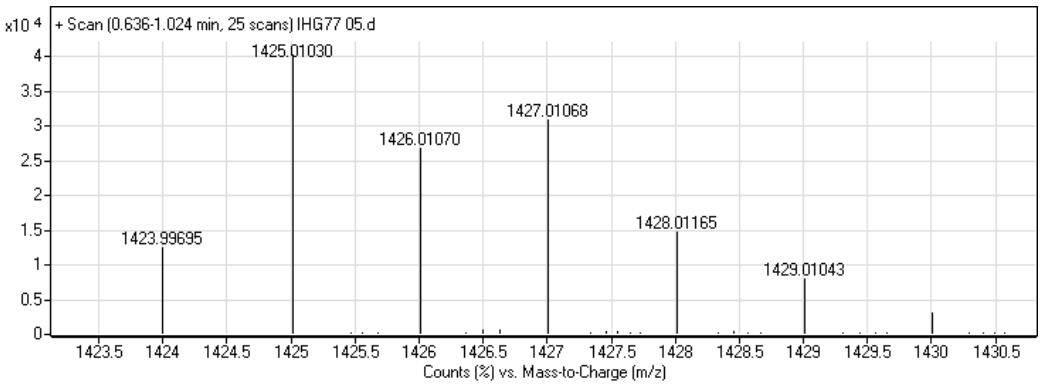

Figure 111. ESI-HRMS of compound **33**.

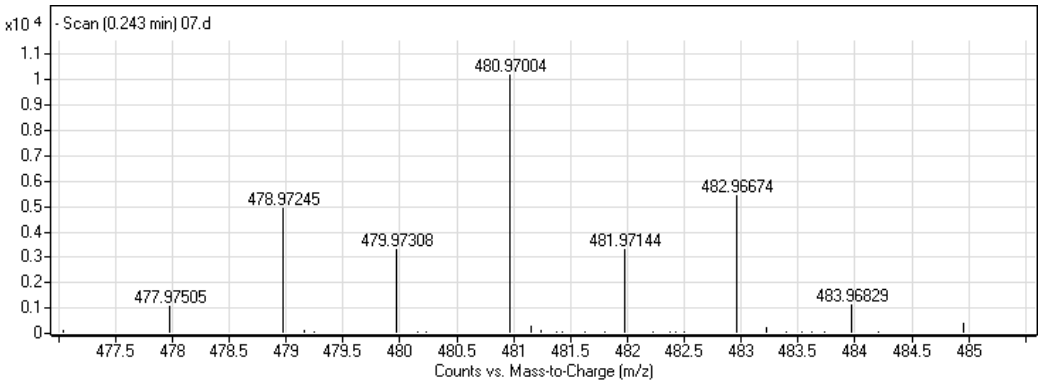

Figure 112. ESI-HRMS of compound **34**.

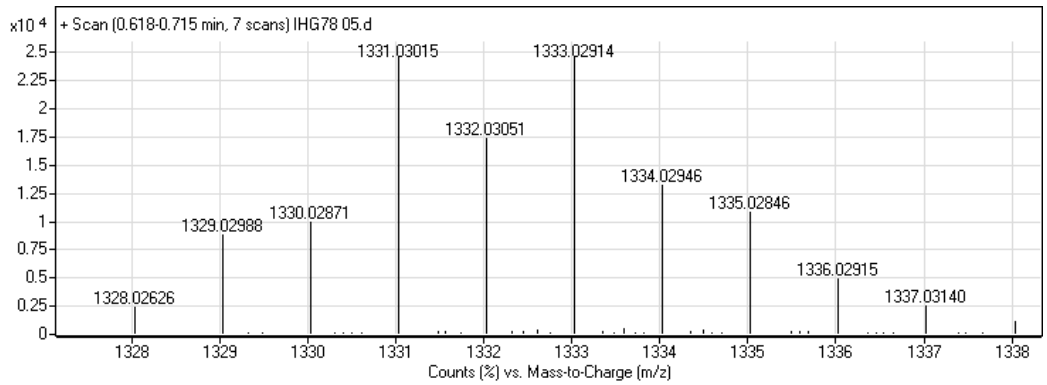

Figure 113. ESI-HRMS of compound **36**.

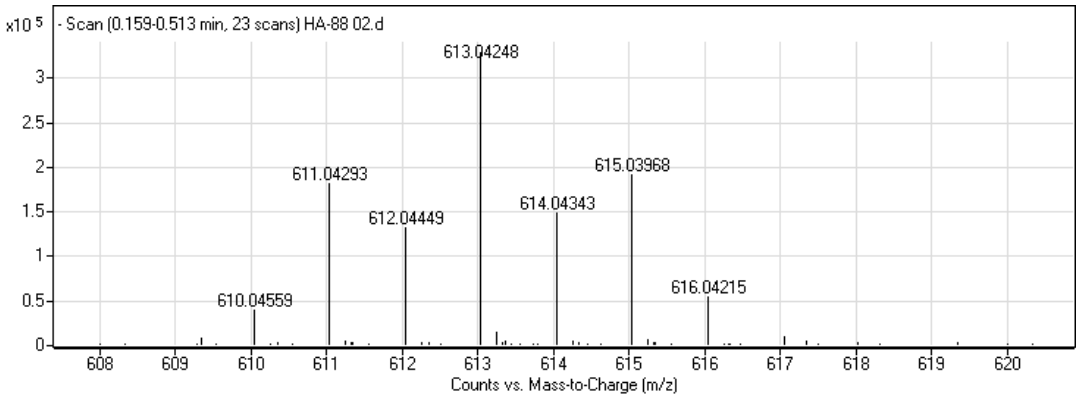

Figure 114. ESI-HRMS of compound **37**.

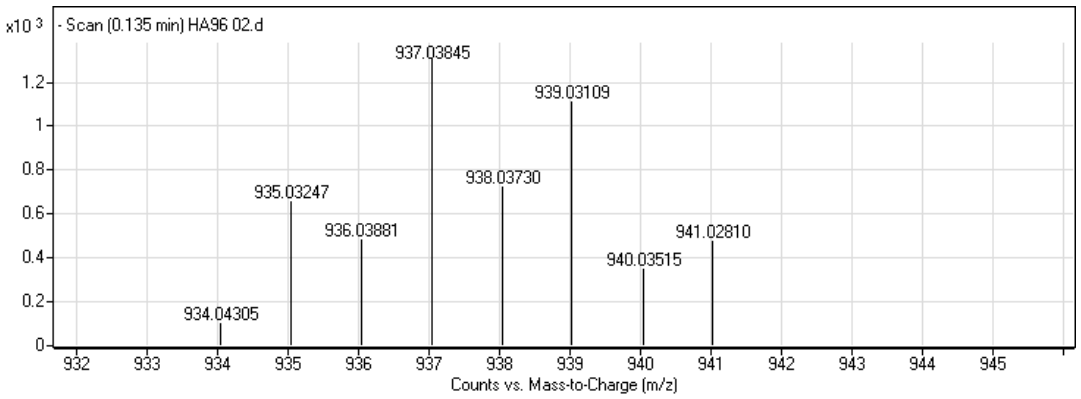

Figure 115. ESI-HRMS of compound **38**.

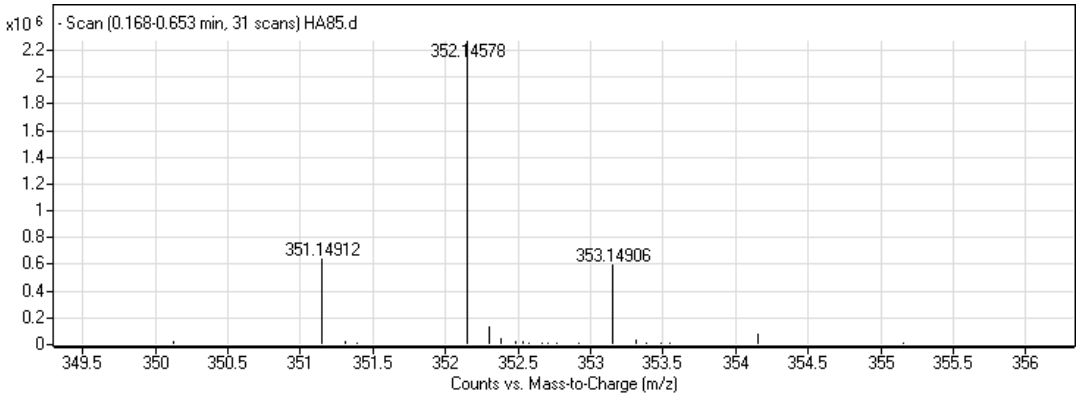

Figure 116. ESI-HRMS of compound **39**.

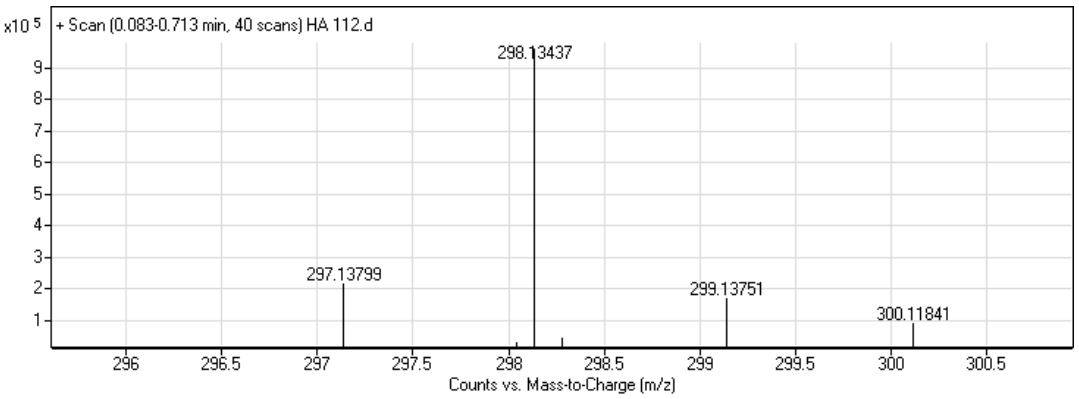

Figure 117. ESI-HRMS of compound **42**.

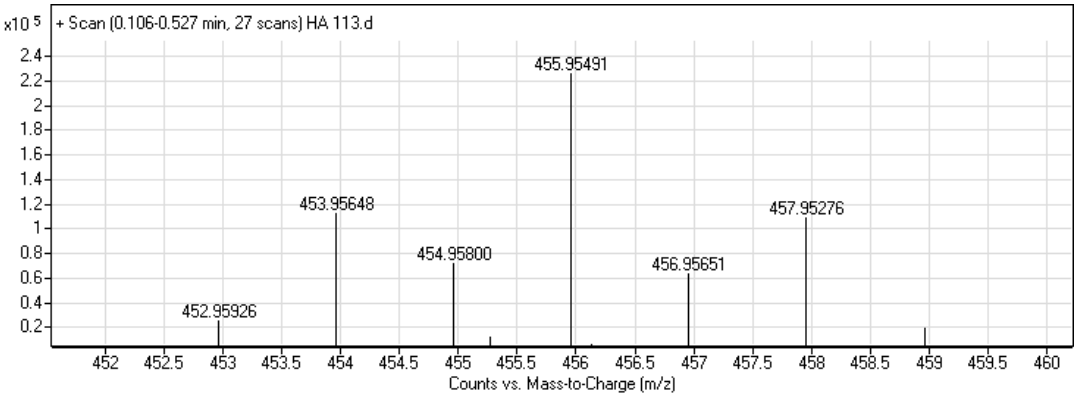

Figure 118. ESI-HRMS of compound **43**.

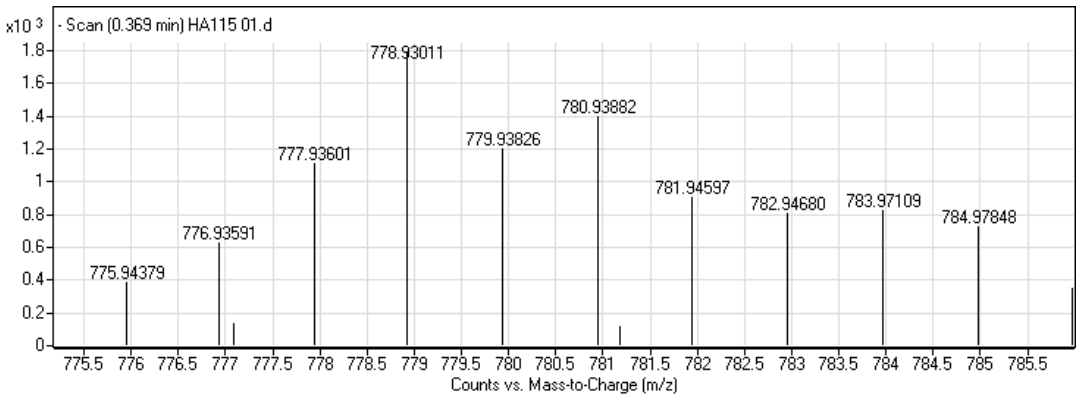

Figure 119. ESI-HRMS of compound **44**.

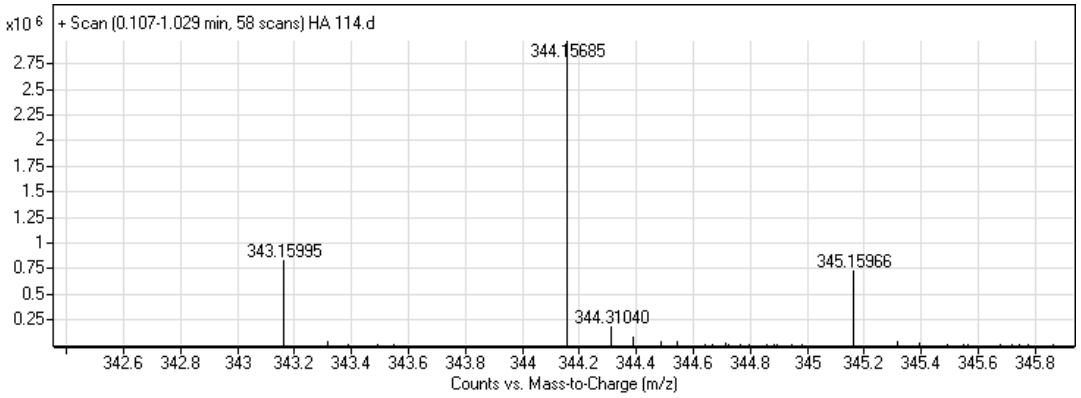

Figure 120. ESI-HRMS of compound **45**.

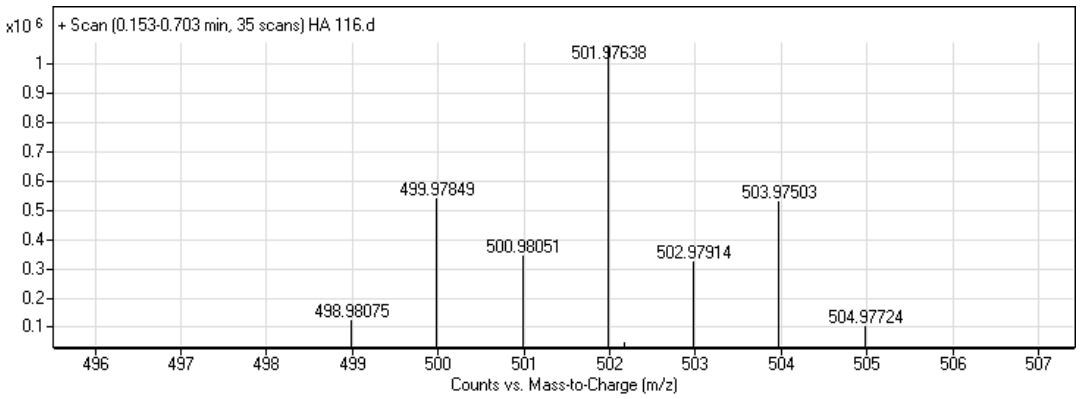

Figure 121. ESI-HRMS of compound **46**.

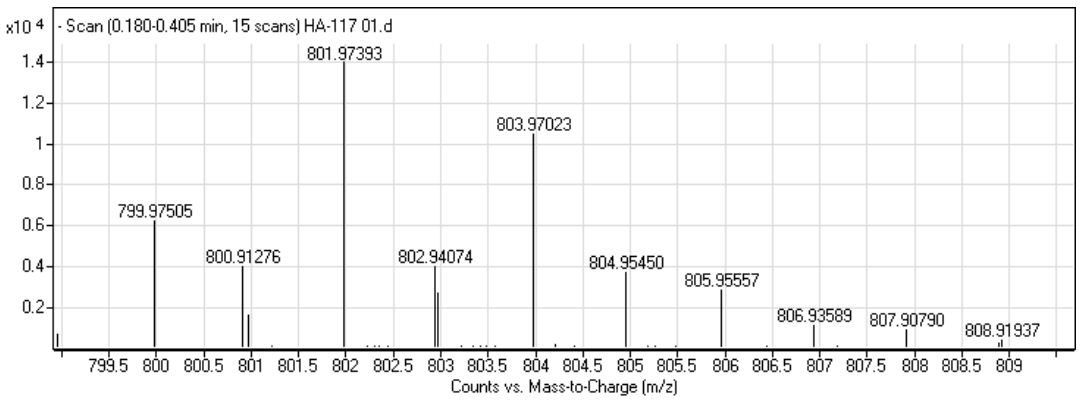

Figure 122. ESI-HRMS of compound **47**.

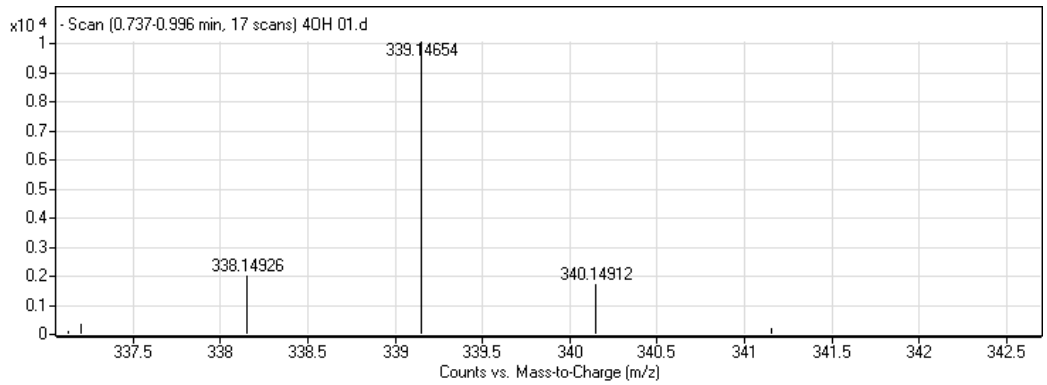

Figure 123. ESI-HRMS of compound **48**.

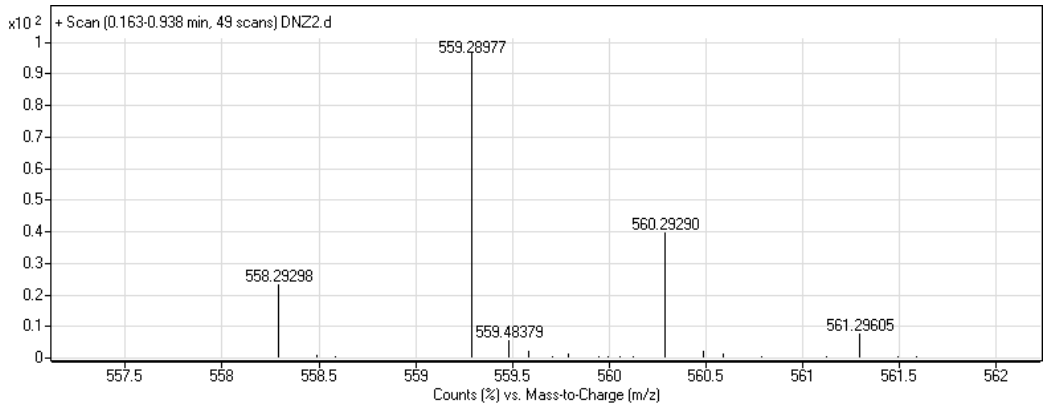

Figure 124. ESI-HRMS of compound **49**.

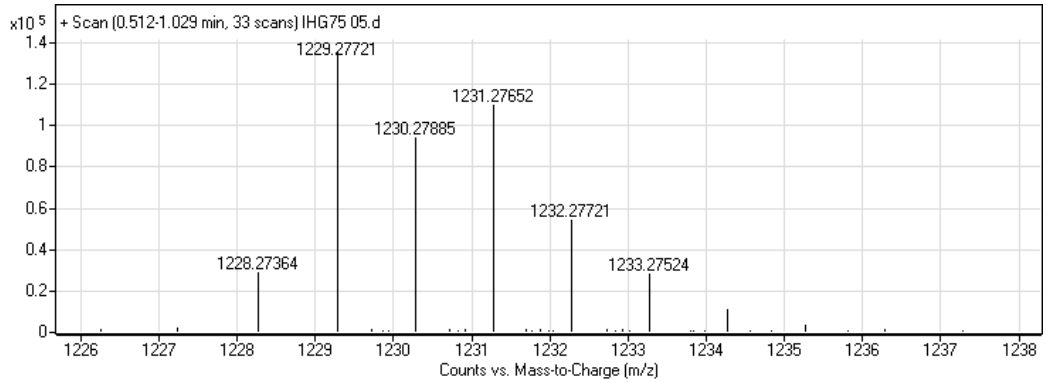

Figure 125. ESI-HRMS of compound **50**.