Cyclohexane Substituted Phenothiazine Organic Dyes for Dye Sensitized Solar Cells

M.Sc. Thesis

By

Nitin Gumber

DISCIPLINE OF CHEMISTRY

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Cyclohexane Substituted Phenothiazine Organic Dyes for Dye Sensitized Solar Cells

A THESIS

Submitted in partial

fulfillment of the requirements for the award of the degree

of

Master of Science

by

Nitin Gumber

(1603131012)

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Cyclohexane Substituted Phenothiazine Organic Dyes for Dye Sensitized Solar Cells** in the partial fulfillment of the requirements for the award of the degree of **Master of Science** and submitted in the **Discipline of Chemistry**, **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2017 to June 2018 under the supervision of Dr. Rajneesh Misra, Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Nitin Gumber

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Dr. Rajneesh Misra

Nitin Gumber has successfully given his/her M.Sc. Oral Examination held on.....

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Date: ..../..../....

Signature of PSPC Member #1

Date: ..../..../....

Signature of PSPC Member #2

Date: ..../..../....

Dedicated to my Parents……..

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ABSTRACT

Over the last few years considerable attention was given to the field of dye sensitized solar cells (DSSC). DSSC are the type of solar cells which uses film of TiO_2 coated with a monolayer of dye that absorbs light in the visible region. The advantages over inorganic solar cells is the low-cost production and metal free dyes hence non-toxic. The main aim of the thesis is to synthesize two D-A type molecules having phenothiazine as donor moiety and cyanoacrylic acid as the acceptor by Pd-Catalyzed Sonogashira and Suzuki Coupling. The Photochemical, electrochemical and theoretical properties were investigated. The absorption was observed in the range of 395-405 nm. The DFT calculations reveal that HOMO is on phenothiazine and LUMO on cyanoacrylic acid.

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ACRONYMS

OLEDs	Organic light emitting diodes
D-π-A	π- bridged donor acceptor
DMSO	Dimethyl sulfoxide
D-A	Donor-Acceptor
DMF	*N*, *N*-Dimethyl formamide
TMS	Tetramethylsilane
NMR	Nuclear magnetic resonance
SCE	Saturated calomel electrode
$PdCl_2(PPh_3)_2$	Dichlorobis(triphenylphosphine) palladium(II)
PPh_3	Tri-phenylphosphine
DCM	Dichloromethane
NBS	*N*-Bromosuccinimide
DFT	Density functional theory
HRMS	High Resolution Mass Spectroscopy
$CDCl_3$	Chloroform-d
CuI	Copper Iodide
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular orbital
Et_3N	Triethyl Amine

NOMENCLATURE

π	pi
λ	Wavelength
δ	Chemical shift
nm	Nanometre
^{o}C	Degree Celsius
mmol	Millimole
mL	Millilitre
RT	Room temperature
eV	Electron Volt
V	Volt

CHAPTER ONE

1. INTRODUCTION

1.1. General Introduction

The growing demand of energy has led the scientists to look for a renewable source of energy and from the last few decades a lot of attention has been given in the field of solar energy. The commercially sold and in demand solar cells are based on inorganic silicon semiconductors and in the upcoming years the price will rise dramatically. In this context alternatives are being found out which includes ruthenium based polypyridyl complexes like N719, N3 and dye sensitized solar cells invented by Gratzel in 1988. Due to toxicity, low extinction coefficient in case of metal based solar cells the dye sensitized solar cells have received a great recognition *[1-3]*.

Typical DSSC consists of 4 components: A mesocrystalline oxide layer fabricated on conducting glass electrode, a sensitizer (dye), redox electrolyte and a cathode. The light is engrossed by the dye molecule, that is anchored to the surface of titanium oxide layer. Electrons get excited and transferred into conduction band of oxide layer. Holes are generated at the dye ground state, which is further rejuvenated through reduction by the redox electrolyte, which further is regenerated at the cathode by electrons via an external circuit *[4]*.

Donor–acceptor molecular frameworks with extended π-conjugation are of considerable interest due to their wide variety of day to day applications as

organic light-emitting diodes (OLEDs), dye sensitized solar cells (DSSC), organic photovoltaics (OPVs) *[5]*.

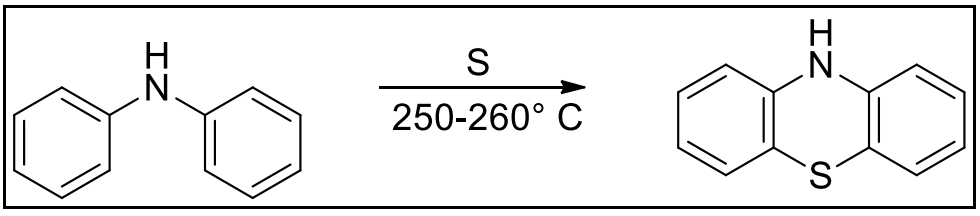
As donors triphenylamines *[6-8]*, indoline *[9-10]*, phenothiazine *[11-14]*, porphyrin have been successfully utilized. Main electron acceptor moieties include rhodanine acetic acid *[15]*, fullerenes *[16]*, nanotubes *[17]* but most of the research groups uses canoacrylic acid since it can act both as anchoring as well as electron withdrawing group.

D-π-A type molecules are necessary for the push pull charge transfer and plays an exceptional role in building up the HOMO and LUMO level of the dye. We can easily tune in the HOMO-LUMO by changing the donor, acceptor moieties or even with the π linker.

These types of molecules exhibit a broad absorption range and can be tuned to get low HOMO-LUMO gap thus making them suitable for organic photovoltaics *[18]*.

Phenothiazine is non-planar, rigid and widely known as a donor due to its strong electron-donating nature. Pure phenothiazine is a light yellow crystalline solid with melting point 180-181°C.

The foremost preparation of phenothiazine was done by Bernthsen *et al.* using diphenylamine and sulfur at 250-260 °C. The conditions were improved by adding little amount of iodine as catalyst and reduces the reaction time and temperature.



Scheme 1. Preparation of Phenothiazine (Bernthsen, *et al*. 1883) *[19]*

Although the compound was firstly prepared by Bernthsen in 1883 by the reaction of diphenylamine with sulfur, but alternatives have been used nowadays and recent syntheses includes cyclization of 2-substituted diphenyl sulfides.

Phenothiazine was discovered to have insecticidal properties in 1934 *[20]*. Later work showed its usefulness as an urinary antiseptic *[21]* and an anthelmintic *[22]*.

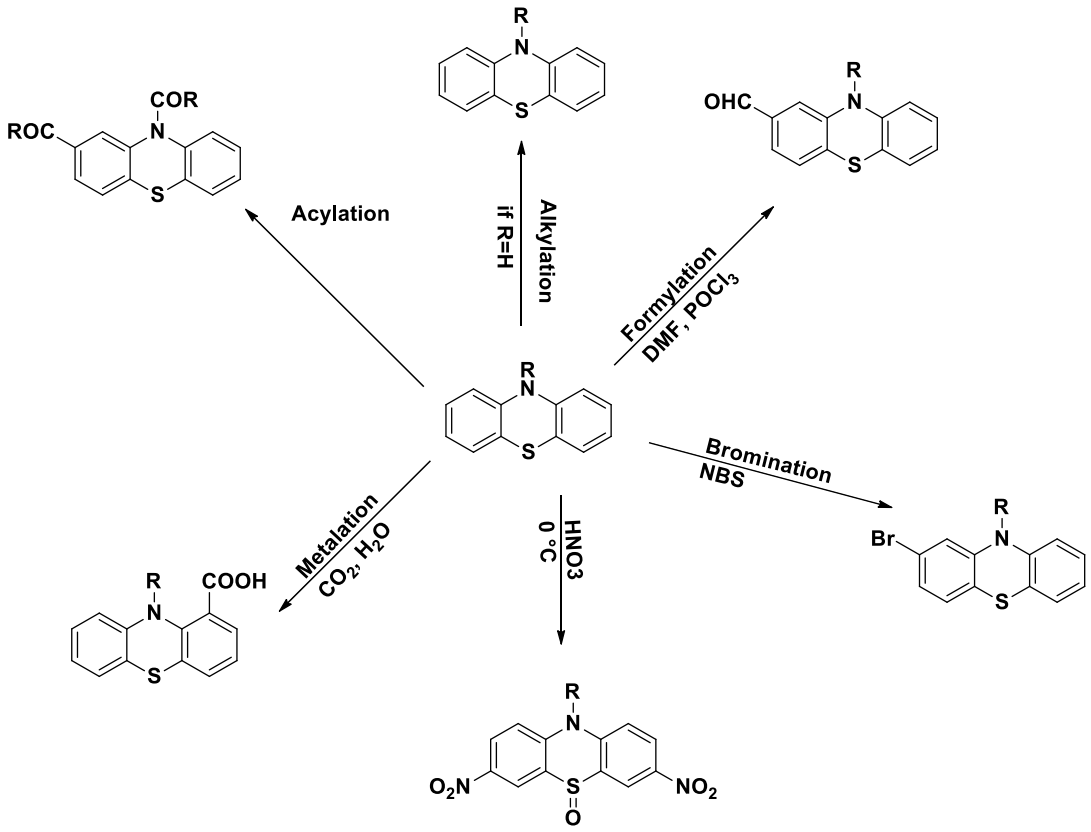
The photonic and electronic properties of the donor-acceptor systems can be tuned by changing or substituting the functional groups *[23]*. The electron donating phenothiazine plays an important role as building block in a variety of π-conjugated D-A molecular systems.

There are many reports found in literature on the applications of phenothiazine-based materials for DSSC's.

The presence of sulfur and nitrogen make it electron rich thus making phenothiazine stronger electron donor even better than porphyrin, carbazole, tetrahydroquinoline and many other and since the non-planar butterfly conformation of phenothiazine in the ground state can prevent the molecular aggregation which is in favor for achieving high photovoltage *[24]*. In addition, not to suppress only dye aggregation but also to reduce the amount of dark currents the alkyl bridges are often used which lessens the recombination of C.B electrons with redox electrolyte *[25]*.

1.2. Chemical Reactivity of Phenothiazine

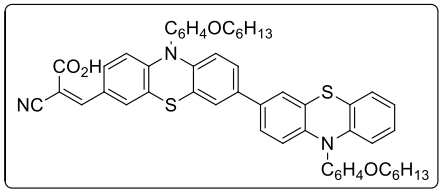
Some of the known reactions reported in literature for phenothiazine are *[19,26]*:



Scheme 2. Reactions of **Phenothiazine**.

1.3. Reported Phenothiazine Based Dyes

Some of the dyes having good power conversion efficiency(ŋ) are shown below *[27-30]*.



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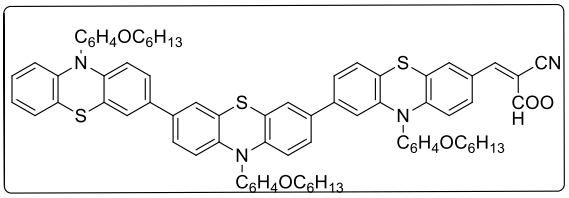

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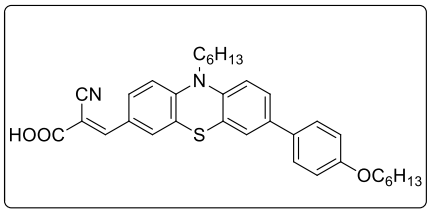

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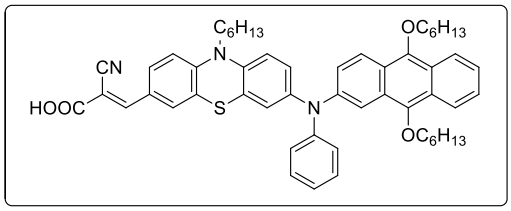

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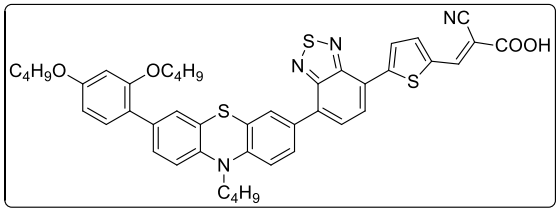

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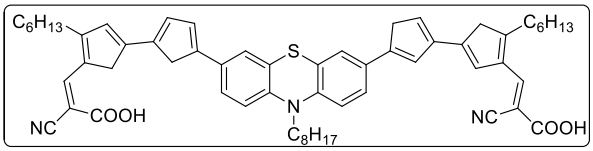
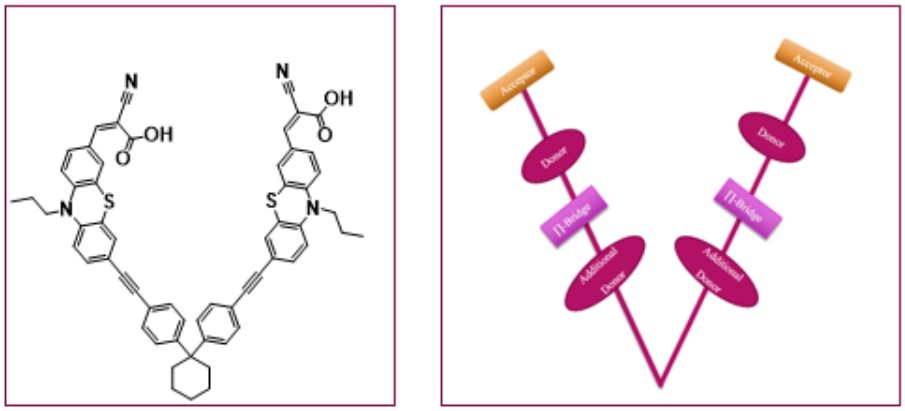


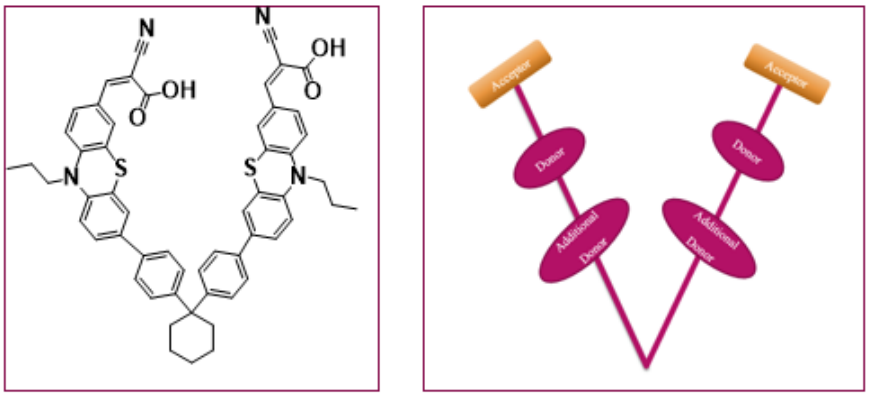
1.4. Aim of the Project

Herein, we have synthesized V-Shaped cyclohexane substituted phenothiazine derivatives with donor-acceptor type molecule with a slight change in the π spacer which have different molecular frameworks. Phenothiazine moiety acts as donor while cyanoacrylic acid as the acceptor part. We characterized the desired dyes with ^{1}H, ^{13}C NMR. Here, our aim is to study the photophysical, structural and electrochemical properties of the synthesized compounds.



CHBAPTA

Fig 1: Structure and Molecular Framework of **CHBAPTA**.



CHBPTA

Fig 2: Structure and Molecular Framework of **CHBPTA**.

CHAPTER TWO

2. EXPERIMENTAL SECTION

2.1. Materials and methods

Chemicals were used as received without further purificiation unless otherwise indicated. All the moisture or oxygen sensitive reactions were performed under inert atmosphere. Phenothiazine is commercially available and purchased. ^{1}H NMR spectra were recorded using a Brukar AV 400 MHz spectrometer. Chemical shifts are described in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard {$CDCl_3$ and DMSO-d_6}. ^{13}C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent as internal standard {DMSO-d_6}. The ^{1}H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet." UV-visible absorption spectra of all compounds were recorded on Parkin Almer UV/Vis spectrophotometer lambda 35 in DMF solution.Cyclic voltamograms were recorded on CH1620D electrochemical analyzer using Glassy carbon as working electrode, Saturated Calomel Electrode (SCE) and Pt wire as the counter electrode as the reference electrode. The scan rate was $100mVs^{-1}$ for cyclic voltammetry. A solution of tetrabutylammonium perchlorate ($TBAClO_4$) was used as supporting electrolyte.

2.2. General procedure for the preparation of the precursors:

The precursors 1a, 2a, 2b, 2c were synthesized as per reported procedure *[19,31]*.

2.2.1. Synthesis of 1a

This involves condensation between cyclohexanone and aniline in 100 mL round bottom flask. To a stirring solution of cyclohexanone (1 mL, 10.2 mmol) in 35% HCl (5 mL) excess aniline (3.34 mL, 36.7 mmol) was added and allowed to stir for 48 hours at 150 °C. After cooling the solution, it was made basic with aq. NaOH to pH=13, and the oily layer was separated and evaporated and extracted with DCM. The crude mixture was purified by silica gel column chromatography (DCM) to give light-yellow compound **1a.** Yield, 1.9g. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.03 (d, 4H), 6.59 (d, 4H), 3.38 (brs, 4H), 2.16 (m, 4H), 1.48(m, 6H).

2.2.2. Synthesis of 1b

An aqueous solution of 7 mL $NaNO_2$ $(1.27g, 18.4\ mmol)$ was added dropwise to a stirring mixture of **1a** (2.3g, 8.6 mmol) in 0.7ml of 25% H_2SO_4 at 0 °C for 1 hour. After stirring for another 2 hours at 0 °C, the reaction mixture was dropped slowly into stirring aqueous solution of 50 mL KI (3.71g, 22.36 mmol) at 50 °C and the reaction mixture was again kept to stir vigorously at 50 °C for 6 hours. The reaction mixture was extracted with DCM, washed with $Na_2S_2O_3$ solution and brine solution and solvent was removed under vacuo. Column chromatography using silica gel (Hexane) was done to yield white solid compound. Yield, 2.76g. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.57 (d, 4H), 6.98 (d, 4H), 2.18 (m, 4H), 1.52 (m, 6H).

2.2.3. Synthesis of 1c

In a dry flask compound **1b** (1 g, 2.04 mmol), $Pd(PPh_3)_4$ (24 mg, 0.0204 mmol), CuI (8 mg, 0.0408 mmol) and dry TEA (10 mL) were mixed followed by degassing for 20 minutes and then the addition of 2-methylbut-3-yn-2-ol (0.8 mL, 8.16 mmol) and stirred under argon atmosphere for 16 hours at 70°C. Then the reaction mixture was allowed to cool to room temperature and compound mixture was poured in H_2O and extracted with DCM. The solvent was evaporated under reduced pressure. The obtained compound 1g was then dissolved in isopropanol (15 ml) in 100 mL flask followed by addition of KOH (0.84g, 15 mmol). The mixture was allowed to stir for 3.5 hours at 60 °C. Then the reaction mixture was allowed to cool to room temperature and poured in H_2O and extracted with DCM. The solvent was removed under reduced pressure and finally purified using silica gel column chromatography (hexane/dichloromethane, 24:1) to yield the product **1c**. Yield, 0.4g. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.39 (d,4H), 7.21 (d, 4H), 3.01(s, 1H), 2.24 (m, 4H), 1.52 (m, 6H).

2.2.4. Synthesis of 2a

Phenothiazine (1.4 g, 7.02 mmol), NaOH (0.36 g, 9.12 mmol) and bromopropane (0.87 mL, 7.72 mmol) were dissolved in 50 mL DMSO and mixture was stirred at room temperature for overnight. The reaction mixture was quenched using H_2O and extracted with DCM and dried over anhydrous Na_2SO_4. The solvent was removed under vacuo and purified with silica gel column chromatography (Hexane) to yield the desired product **2a**. Yield, 1.57g. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.17 (m,4H), 6.90 (m, 4H), 3.84 (t, 2H), 1.85 (m, 2H), 1.03 (t, 3H).

2.2.5. Synthesis of 2b

2a (2.0 g, 8.2 mmol) and dry DMF (2.52 mL, 32.9 mmol) was dissolved in solvent DCE (60 mL) and then $POCl_3$ (3.07 mL, 32.9 mmol) is added slowly at 0 °C. Then the reaction mixture was allowed to reflux for overnight. After completion of reaction it was quenched with H_20 and extracted with DCM and dried over Na_2SO_4. Solvent was removed under reduced pressure and crude was purified by using silica gel column chromatography (hexane/dichloromethane, 3:2) to yield a yellow solid **2b.** Yield, 2.02g. ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.80 (s,1H), 7.64 (d, 1H), 7.58 (s, 1H), 7.13 (dd, 2H), 6.96 (s, 1H), 6.92 (m, 2H), 3.86 (t, 2H), 1.85 (m,2H), 1.03 (s, 3H).

2.2.6. Synthesis of 2c

2b (2.02g, 8.1 mmol) was dissolved in THF (200 mL) and NBS (1.67g, 9.4mmol) was added to the reaction mixture at 0 °C. After addition it was allowed to stir for 2 hours continuously. After completion of reaction NBS was quenched with water and the reaction mixture was extracted with DCM. Solvent was evaporated in vacuo and the crude mixture was purified by silica gel column chromatography (hexane/dichloromethane, 1:1) to yield a yellow solid **2c**. Yield, 2.4g. ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.80 (s,1H), 7.65 (d, 1H), 7.58 (s, 1H), 7.26-7.23 (m, 2H), 6.90 (d, 1H), 6.71 (d, 1H), 3.82 (t, 2H), 1.83 (m,2H), 1.01 (t, 3H).

2.2.7. Synthesis of 2d

In a dried oven flask equipped with magnetic stirring bar was charged with **2c** (1.8g, 5.17 mmol**,** bis(pinacolato)diboron (1.3 g, 5.17 mmol), Potassium acetate (1.36g, 13.9 mmol) in Dioxane (30 mL) and degassed for about 20 minutes. $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (126 mg, 0.11 mmol) was then added and refluxed overnight. The reaction mixture was treated with water at room

temperature, extracted with DCM, washed with brine, and dried over Na_2SO_4. The Solvent was removed under reduced pressure. A mixture of this 1g and 2**c** (1.78g, 5.10 mmol) and 2 M aqueous solution of K_2CO_3 (8 mL) in THF (25 mL). After degassing for 15 minutes $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) was added and heated to reflux under a N_2 atmosphere for about 12 h. Then, the solvent was evaporated under vacuum and the mixture was purified by column chromatography on silica gel using a 2:3 mixture of hexane and CH_2Cl_2 as eluent to afford the product. Yield, 1.4g.

2.2.8. Synthesis of 3a

In a dry flask compound **2c** (3.67 g, 10.5 mmol) in THF (25 mL) was dissolved and mixture was degassed for 15 minutes followed by addition of $Pd(PPh_3)_4$ (93 mg, 0.048 mmol), CuI (13.3 mg, 0.07 mmol), dry TEA (7 mL) and **1c** (1.0 g, 3.5 mmol) and stirred under argon atmosphere for 16 hours at 80 °C. After the completion of reaction, the solvent was evaporated under reduced pressure and extracted with DCM-H_2O mixture. The product was purified by silica gel column chromatography (DCM) to give a yellow solid. Yield, 1.7g. ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.80 (s,2H), 7.64 (d, 2H), 7.57 (s, 1H), 7.40 (d, 4H), 7.29-7.24 (m, 7H), 6.89 (d, 2H), 6.80 (d, 2H), 3.85 (t,2H), 2.26 (s, 3H), 1.85 (m,4H), 1.03 (t,6H).

2.2.9. Synthesis of CHBAPTA

3a (0.13g, 0.158 mmol) and cyanoacetic acid (0.08g, 0.95 mmol) were mixed and refluxed in the presence of piperidine (0.2 mL, 2.2 mmol) in $CHCl_3$ (15 ml) as a solvent under argon for 24 h. The reaction mixture was then acidified with 50 mL 2 M HCl. After completion of reaction the solvent was evaporated and extracted with chloroform and water. Chloroform was evaporated and the impure mixture was purified using silica gel column chromatography. The desired compounds were eluted by

DCM:MeOH (90:10 v/v) to yield the desired dye. Yield, 0.1g. ^{1}H NMR (400 MHz, DMSO-D_6): δ=8.15 (s,2H), 7.92 (d, 2H), 7.79 (s, 2H), 7.43 (d, 4H), 7.32 (d, 6H), 7.29 (s, 2H), 7.16 (d, 2H), 7.06 (d, 2H), 3.90 (t, 4H), 2.25 (s, 4H), 1.70 (m ,4H), 1.45 (s, 6H), 0.95 (t, 6H). ^{13}C NMR (100 MHz, , DMSO-D_6, δ in ppm): 163.47, 152.24, 148.23, 147.75, 142.80, 131.34, 131.06, 129.27, 128.92, 127.01, 125.71, 122.16, 119.28, 117.10, 116.46, 116.21, 115.72, 99.71, 89.43, 87.94, 48.50, 45.64, 35.53, 22.24, 19.07, 10.56

2.2.10. Synthesis of CHBPTA

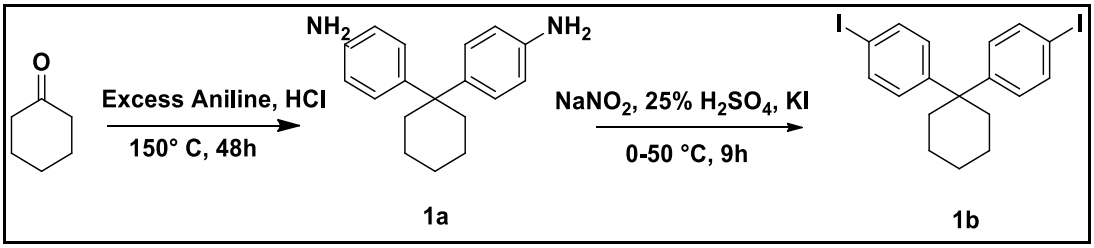
3c (70mg, 0.018 mmol)**,** cyanoacetic acid (45mg, 0.52 mmol) were mixed and refluxed in the presence of piperidine (0.12 mL, 1.2 mmol) in $CHCl_3$ (20 ml) as a solvent under argon for 24 h. The reaction mixture was then acidified with 50 mL 2 M HCl. After completion of reaction the solvent was evaporated and extracted with chloroform and water. Chloroform was evaporated and the impure mixture was purified using silica gel column chromatography. The desired compound was eluted by DCM:MeOH (80:20 v/v) to yield the desired dye. Yield 0.5g. ^{1}H NMR (400 MHz, DMSO-D_6): δ= 7.85 (s,2H), 7.74 (d, 2H), 7.68 (d, 2H), 7.52 (d, 2H), 7.44 (m, 5H), 7.36 (m, 4H), 7.07 (m, 5H), 3.87 (s, 4H), 2.29 (s, 4H), 1.70 (t ,4H), 1.48 (s, 6H), 0.94 (t, 6H). ^{13}C NMR (100 MHz, DMSO-D_6, δ in ppm): 164.03, 147.65, 146.97, 142.85, 136.20, 135.23, 134.07, 128.22, 127.80, 126.48, 123.30, 119.90, 116.82, 116.06, 79.15, 48.93, 45.66, 31.18, 29.51, 19.87, 11.39

CHAPTER THREE

3. Results and Discussion

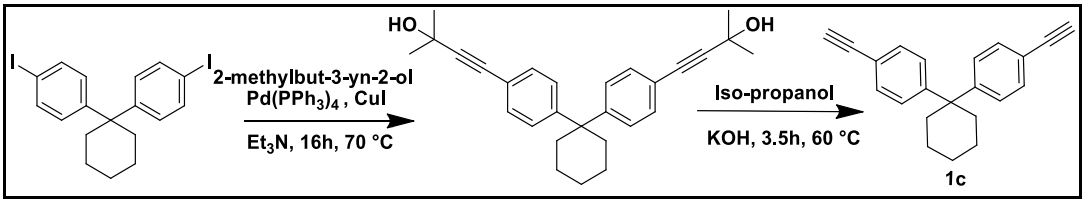
3.1. Synthesis and characterization

The precursor **1a** was synthesized using condensation between cyclohexanone and aniline in ratio of 1:2 in the presence of acid. The diamine compound was further diazotized using $NaNO_2/H_2SO_4$ and further reacted with KI to produce diiodo **1b** compound.



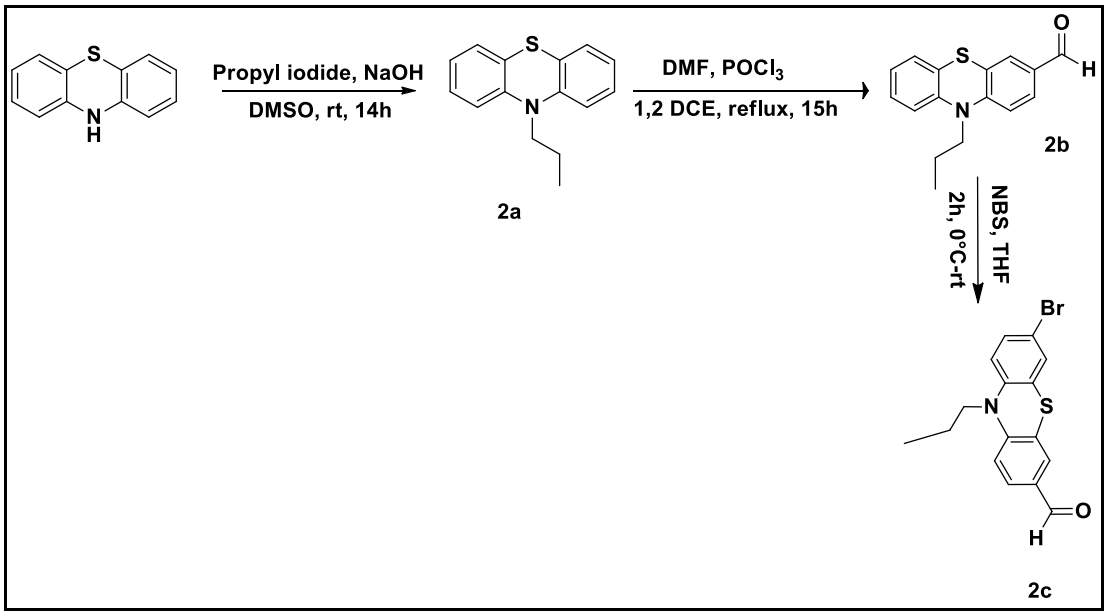
Scheme 3. Synthesis of **1a** and **1b**.

Further the precursor **1c** was synthesized using Pd-Cu catalyzed Sonogashira coupling reaction of precursor 1b followed by base catalyzed deprotection.



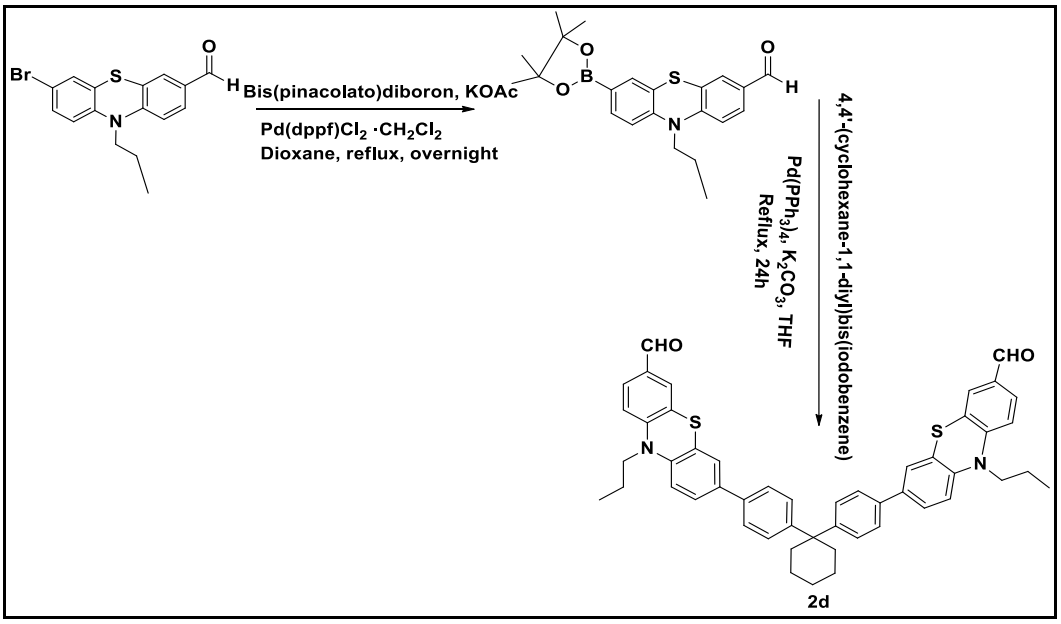
Scheme 4. Synthesis of **1c**.

2a, **2b**, **2c** were synthesized using the already reported procedures firstly converting phenothiazine to propyl derivative by followed by vilsmeier-haack reaction to yield mono formylated product and then reacting it with NBS to yield the bromo derivative.



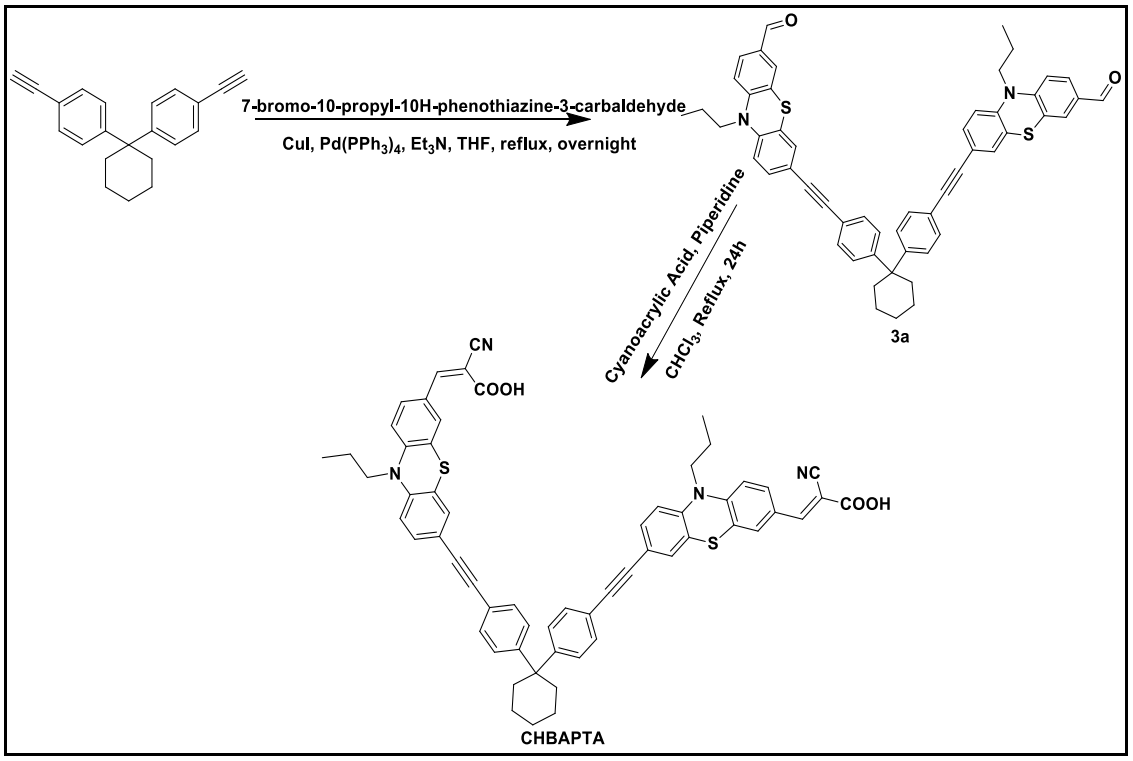
Scheme 5. Synthesis of **2a, 2b, 2c**.

2d was synthesized using Pd-Catalyzed Suzuki miyara coupling reaction giving the boronate ester of **2c** from bromo substituent which was further treated with **1c** in the ratio 2:1 to yield **2d**.



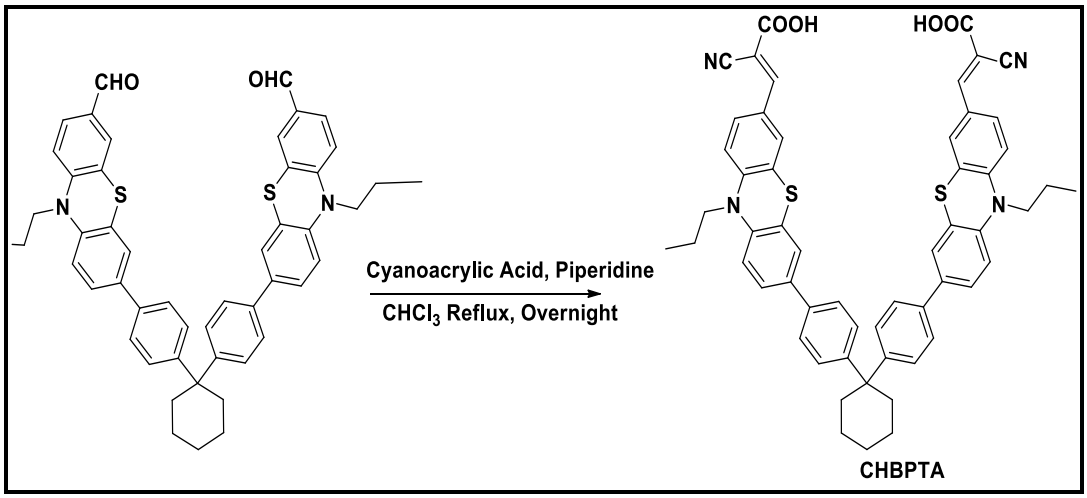
Scheme 6. Synthesis of **2d**.

The compound **CHABPTA** was synthesized using well known Pd-catalyzed Sonogashira coupling of **2c** (7-bromo-10-propyl-10H-phenothiazine-3-carbaldehyde) and **1c** in the ratio 2:1 which was further reacted with cyanoacryclic acid using knoevenagel's condensation conditions to afford the product.



Scheme 7. Synthesis of **3a** and **CHBAPTA**.

The compound **CHBPTA** was synthesized from **2d** using knoevenagel condensation with cyan acrylic acid to produce the desired product.



Scheme 8. Synthesis of **CHBPTA**.

3.2. Photophysical Properties

The UV-Visible spectra of dyes **CHBTA** and **CHBAPTA** were recorded in DMF at room temperature and the data is listed in table 1. Both the phenothiazine derivatives exhibit a strong absorption which may correspond to $\pi \rightarrow \pi^*$ and charge transfer transitions

The CHBAPTA exhibit a slightly red shift as compared to CHBPTA due to increase in conjugation by incorporating alkyne group. Conjugation increases the energy level of HOMO and hence less energy transition Is required in a more conjugated system however it is not so much pronounced here.

295,302 nm may correspond to $\pi \rightarrow \pi^*$ transition and 395,402 nm may correspond to charge transition for **CHBPTA** and **CHBAPTA** respectively.

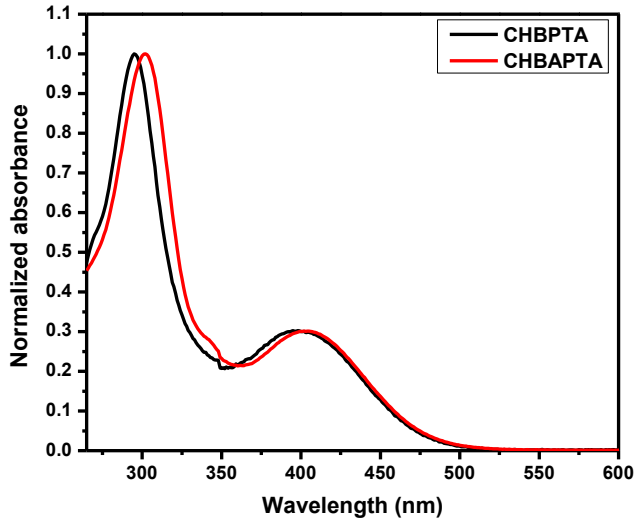


Fig 3. Absorption spectra of **CHBPTA** and **CHBAPTA** in DMF.

3.3. Electrochemical Properties

The electrochemical behavior of phenothiazine derivatives **CHBPTA** and **CHBAPTA** were studied by the cyclic voltammetric (CV) in DMF solution using tetrabutylammonium perchlorate ($TBAClO_4$) as a supporting electrolyte. The electrochemical data are listed in Table 1. and cyclic curve representations are shown in Figure 4 and the phenothiazine-derivatives exhibit one reversible oxidation wave corresponding to the oxidation of phenothiazine donor unit. The oxidation peak for **CHBPTA** and **CHBAPTA** observed at 0.75 and 0.84 eV respectively.

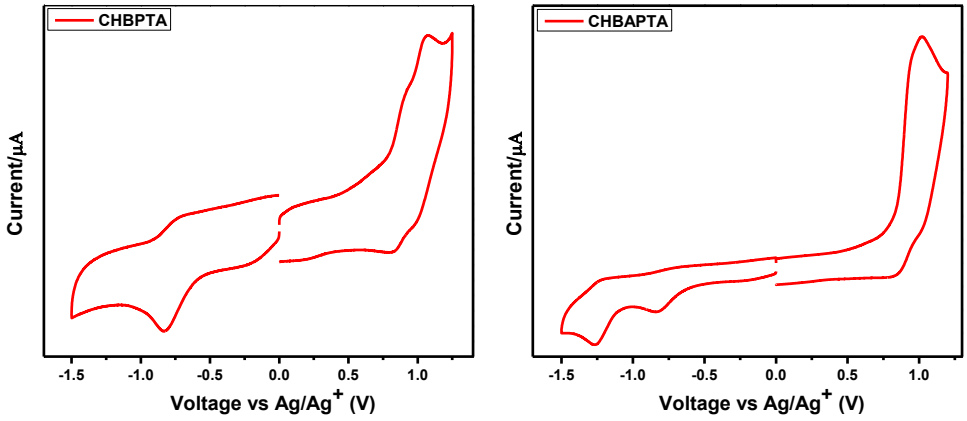


Fig 4. Cyclic voltammograms of **CHBPTA** and **CHBAPTA** (5×10^{-4} M) in DMF**.**

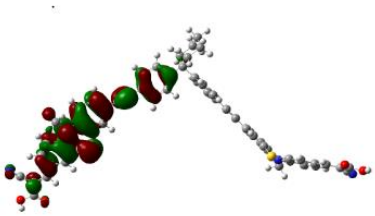
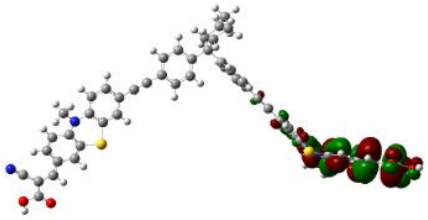
Comp	λ_{abs} [nm]	E_{oxd}^{onset} [volts][a]	E_{red}^{onset} [volts][a]
CHBPTA	295, 395	0.75	-0.61
CHBAPTA	302, 402	0.84	-0.61

[a] DMF, 0.1M $TBAClO_4$, glassy carbon working electrode, platinum wire counter electrode and Ag/Ag^+ reference electrode, calibrated against ferrocene

Table 1: Photophysical and electrochemical properties of **CHBPTA** and **CHBAPTA**.

3.4 Theoretical Calculations:

To explore the electronic structure of the phenothiazine-derivatives **CHBPTA** and **CHBAPTA**, density functional theory (DFT) calculation were performed at the B3LYP/6-31G**. The contours of the HOMO and LUMO of CHBPTA and CHBAPTA are shown in Table 2. The HOMO is delocalized mainly on the phenothiazine moiety of the molecule and partly localized on the adjacent phenyl group. The LUMO is mainly on the acceptor part, which is cyanoacrylic acid. The HOMO–LUMO energy gap for phenothiazine derivative **CHBPTA** and **CHBAPTA** are 1.36 and 1.45 eV respectively.

Compound	HOMO (eV)	LUMO (eV)
CHBPTA	 **-5.17**	 **-3.81**

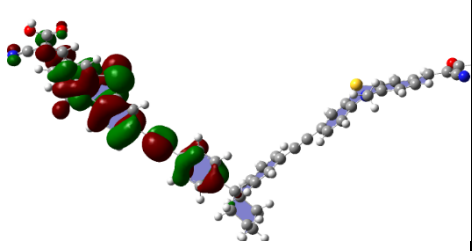
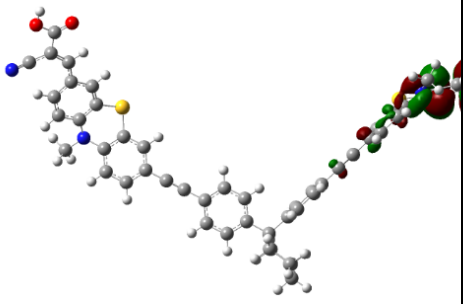
CHBAPTA	 **-5.26**	 **-3.81**

Table 2. HOMO and LUMO orbitals of **CHBPTA** and **CHBAPTA** at the B3LYP/6-31G** level**.**

CHAPTER FOUR

4. Conclusions

The donor-acceptor phenothiazine-based molecules are synthesized by Pd-catalyzed Sonogashira and Suzuki coupling followed by knoevenagel condensation to yield the desired V-shape Dyes. The products are characterized by ^{1}H and ^{13}C NMR spectroscopy. The optical, electrochemical and theoretical properties were studied. The UV-Vis spectrum shows 2 peaks which may be assigned as $\pi - \pi^*$ and charge transfer transitions. There is a slight redshift in the more conjugated system as compared to other which is as expected. The theoretical DFT calculations reveal the HOMO is mainly concentrated on phenothiazaine moiety in both the dyes and LUMO on the cyano and carboxylic acid group.

APPENDIX A

^{1}H NMR, ^{13}C NMR Spectra

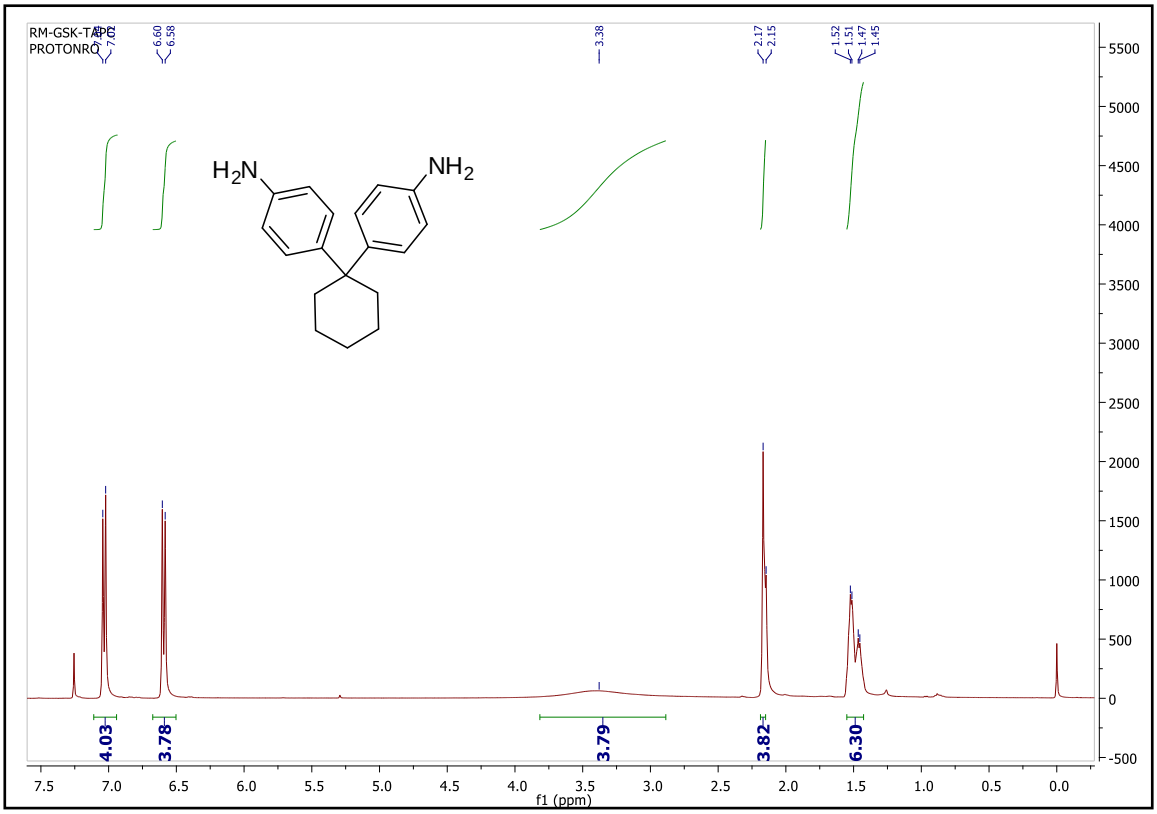


Figure 5. 400 MHz ^{1}H NMR spectrum of **1a** in $CDCl_3$.

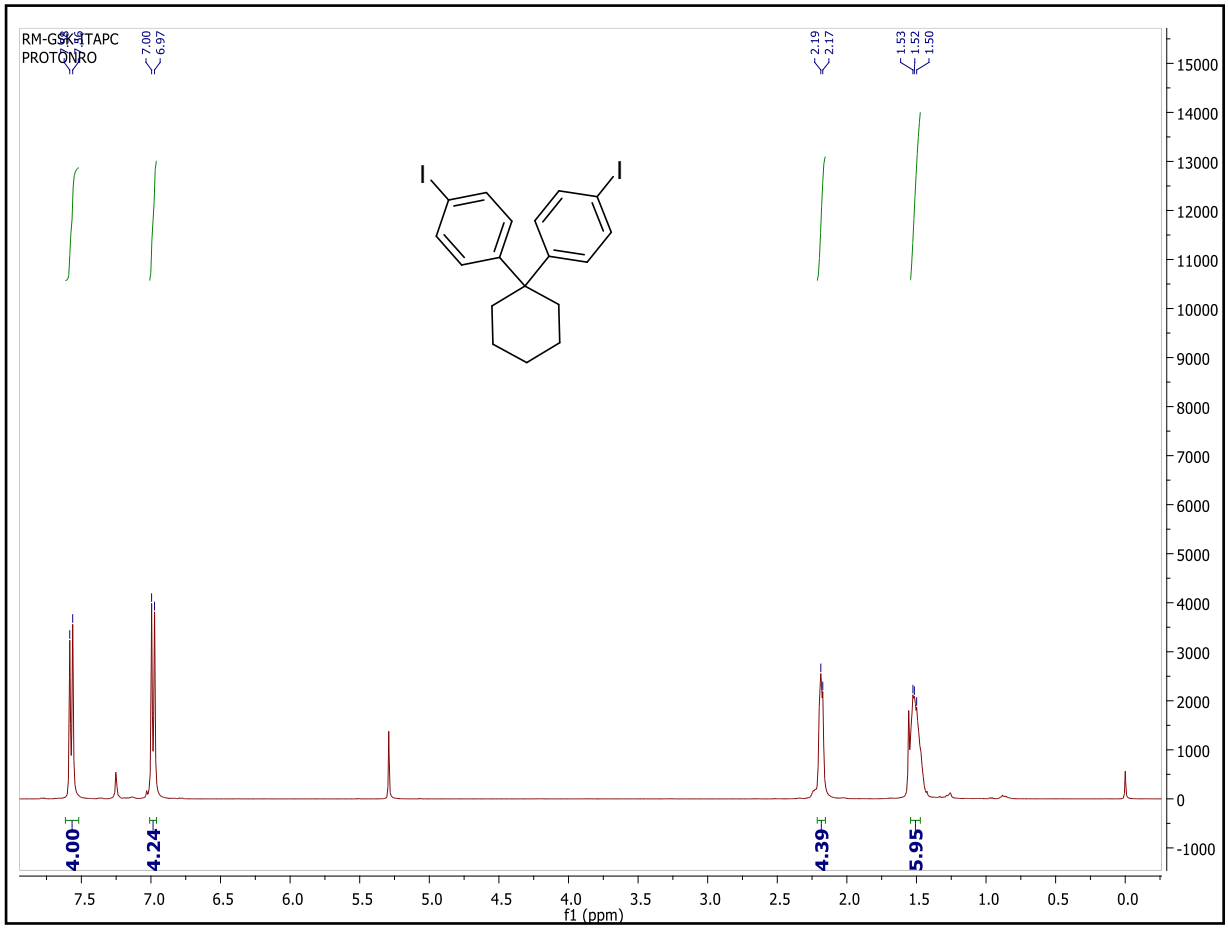


Figure 6. 400 MHz ^{1}H NMR spectrum of **1b** in $CDCl_3$.

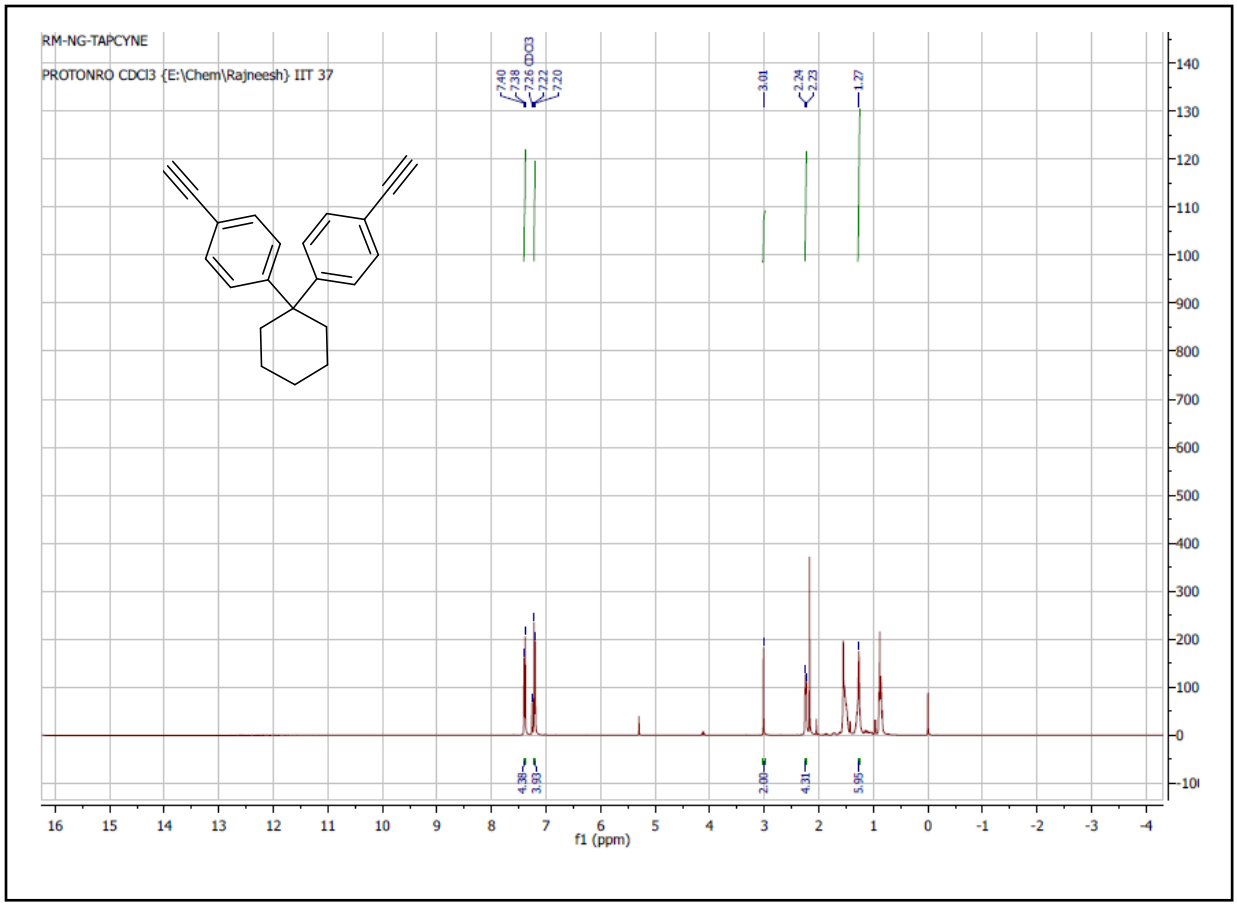


Figure 7. 400 MHz ^{1}H NMR spectrum of **1c** in $CDCl_3$.

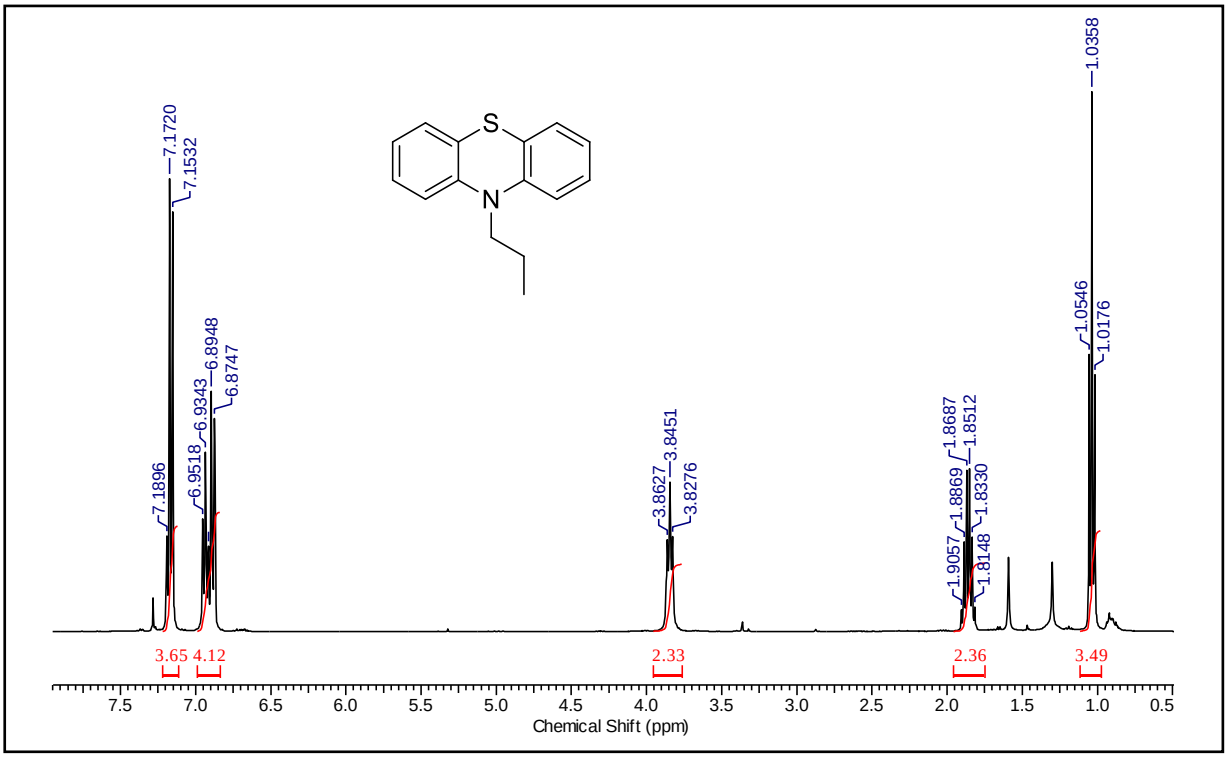


Figure 8. 400 MHz ^{1}H NMR spectrum of **2a** in $CDCl_3$

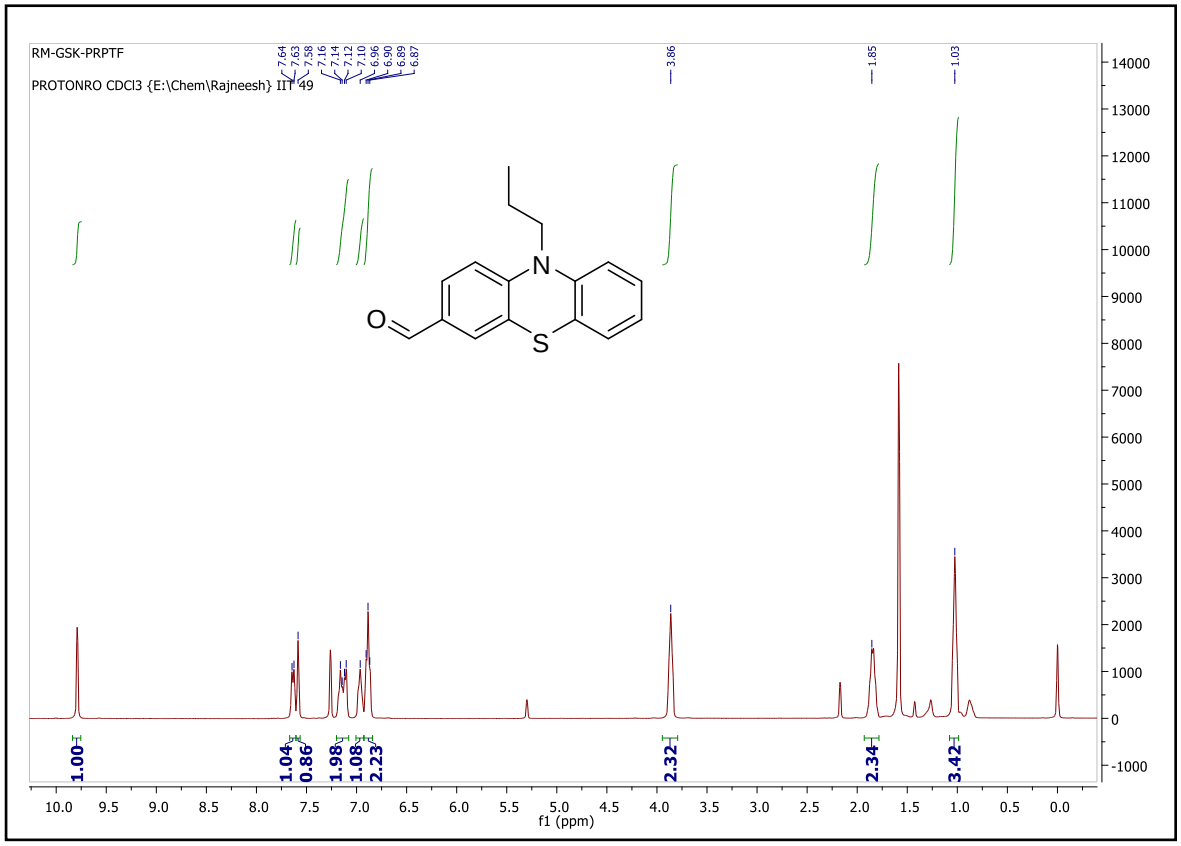


Figure 9. 400 MHz ^{1}H NMR spectrum of **2b** in $CDCl_3$.

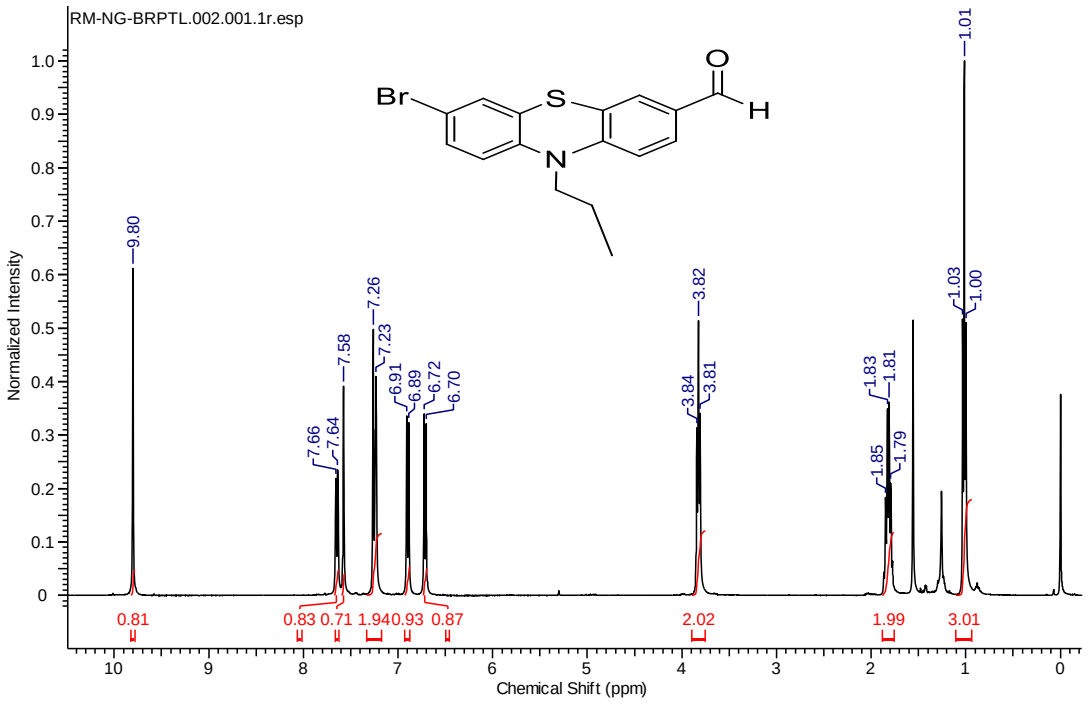


Figure 10. 400 MHz ^{1}H NMR spectrum of **2c** in $CDCl_3$.

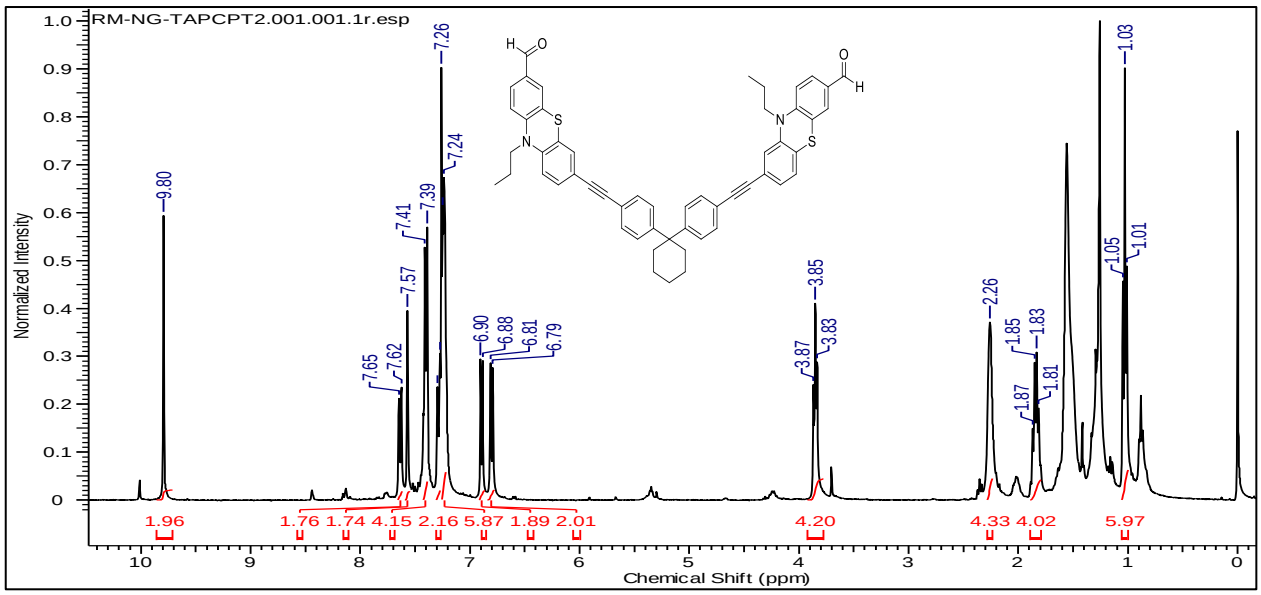


Figure 11. 400 MHz ^{1}H NMR spectrum of **3a** in $CDCl_3$.

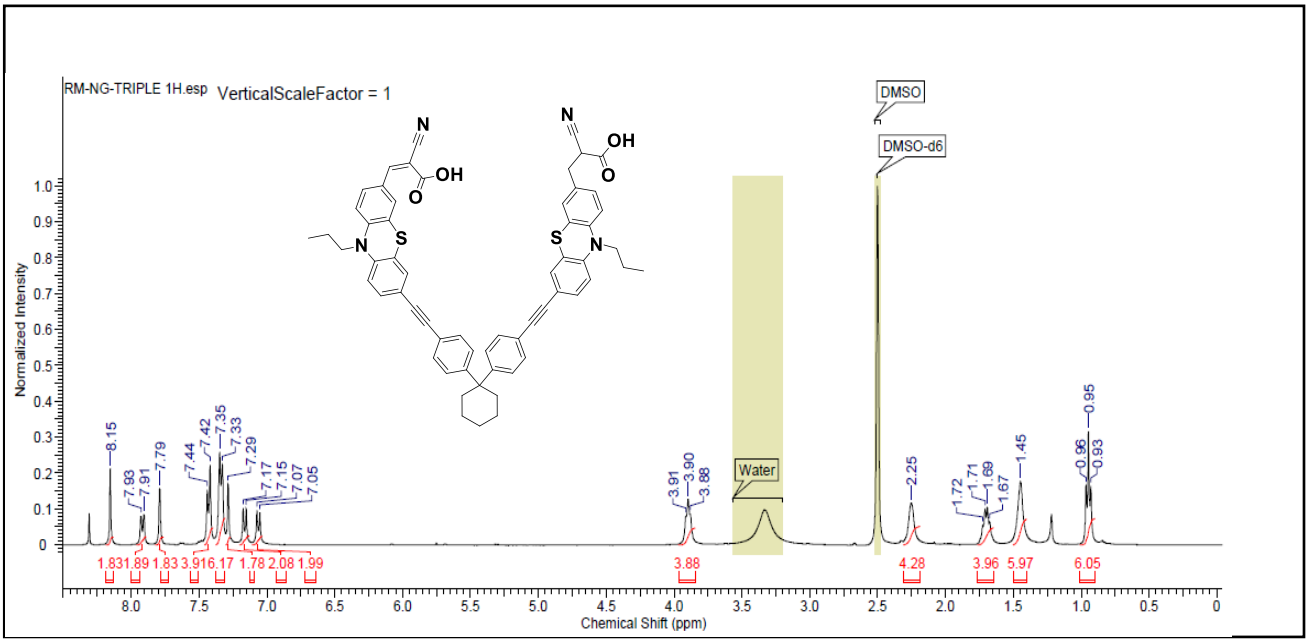


Figure 12. 400 MHz ^{1}H NMR spectrum of **CHBAPTA** in DMSO-D_6.

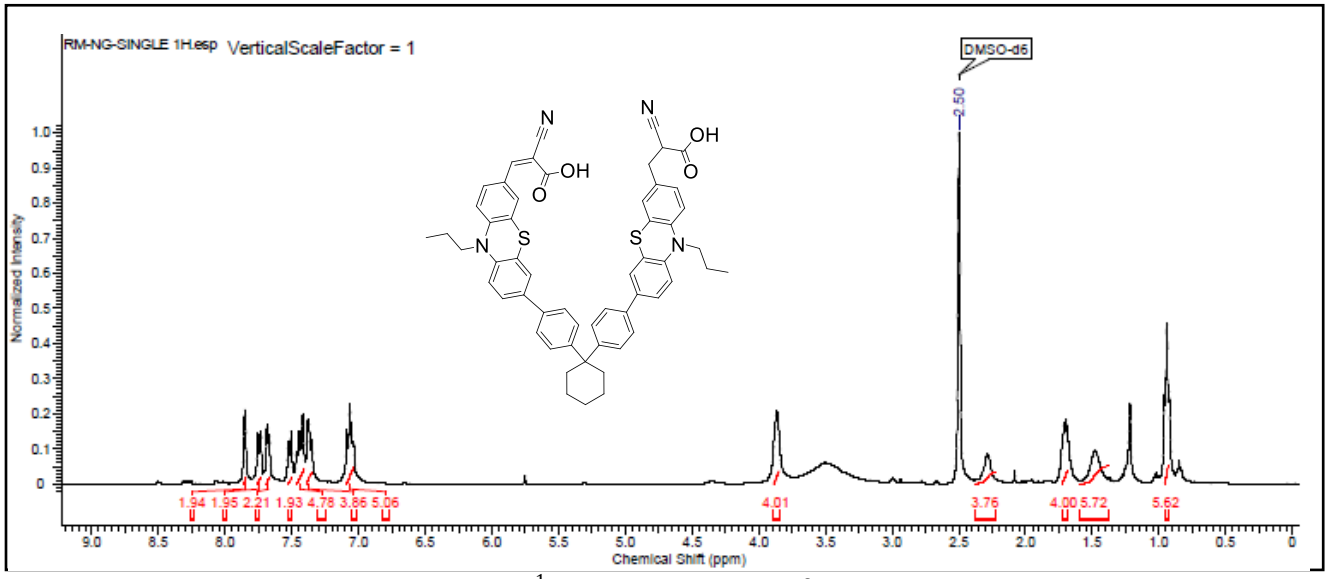


Figure 13. 400 MHz ^{1}H NMR spectrum of **CHBPTA** in DMSO-D_6.

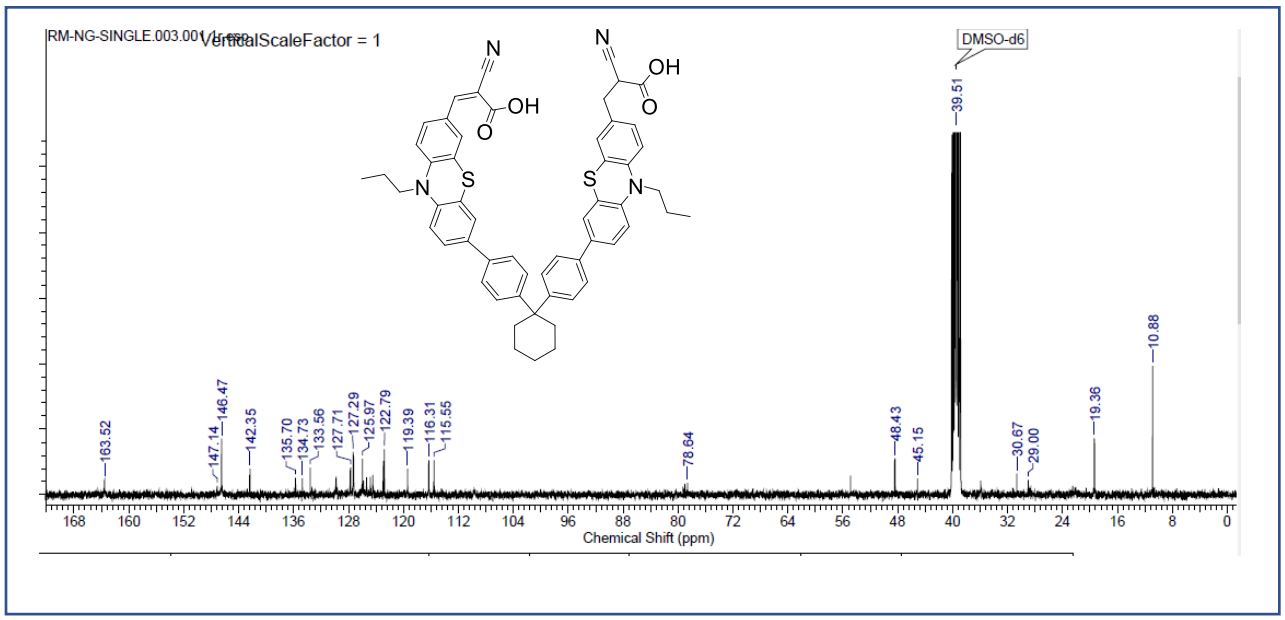


Figure 14. 100 MHz ^{13}C NMR spectrum of **CHBPTA** in DMSO-D$_6$.

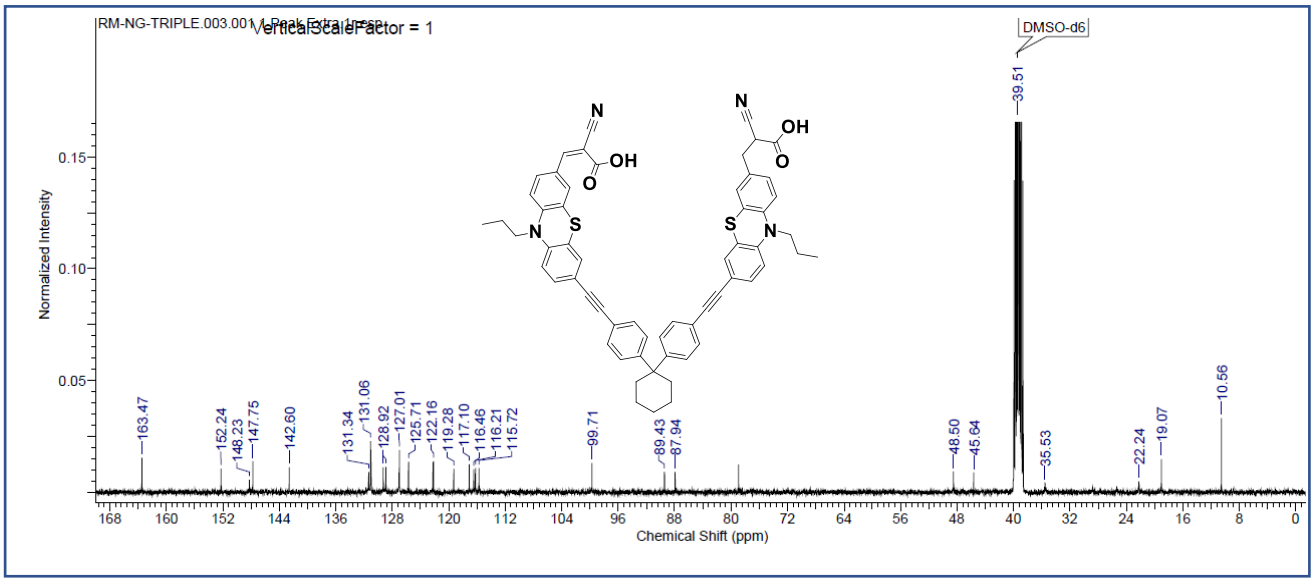


Figure 15. 100 MHz ^{13}C NMR spectrum of **CHBAPTA** in DMSO-D$_6$.

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