Synthesis and Studies of Azoarene and Azoheteroarene Connected Benzene Carboxamides as Potential Photoresponsive Liquid Crystals

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Certificate of Examination

This is to certify that the dissertation titled "Synthesis and Studies of Azoarene and Azoheteroarene Connected Benzene Carboxamides as Potential Photoresponsive Liquid Crystals" submitted by Mr. Amal Sam Sunny (Reg. No. MS14176) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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(Supervisor)	(Committee member)	(Committee member)

Dated:

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Sugumar Venkataramani at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Amal Sam Sunny

(Candidate)

Dated:

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Sugumar Venkataramani

(Supervisor)

Acknowledgement

I would like to thank my supervisor, Dr. Sugumar Venkataramani, for guiding me throughout the project and motivating me when I was feeling down. I would also like to thank Dr. Santanu Kumar Pal and Dr. Vijaya Anand for their inputs throughout the project.

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Amal Sam Sunny

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Abbreviations

DMSO	:	Dimethyl sulfoxide
NaOH	:	Sodium hydroxide
Na_2SO_4	:	Sodium sulfate
$NaNO_2$	:	Sodium nitrite
NaOAc	:	Sodium acetate
K_2CO_3	:	Potassium carbonate
KI	:	Potassium iodide
CuCN	:	Copper Cyanide
HBr	:	Hydrogen bromide
H_2O	:	Water
HCl	:	Hydrochloric acid
MeOH	:	Methanol
EtOH	:	Ethanol
RT	:	Room Temperature
DCM (CH_2Cl_2)	:	Dichloromethane
DMF	:	*N*, *N*-Dimethylformamide
DCE	:	1, 2-Dichloroethane
THF	:	Tetrahydrofuran
CH_3CN	:	Acetonitrile
$SOCl_2$	:	Thionyl Chloride
Et_3N	:	Triethylamine

Et_2O	:	Diethyl ether
TFA	:	Trifluoroacetic acid
TLC	:	Thin Layer Chromatography
MS	:	Mass Spectrometry
ESI	:	Electronspray Ionization
NMR	:	Nuclear Magnetic Resonance
^{1}H NMR	:	Proton NMR
^{13}C NMR	:	Carbon-13 NMR
RBF	:	Round Bottom Flask
Eq.	:	Equivalence
LED	:	Light Emitting Diode

Contents

Abstract

Azobenzenes show reversible photoisomerization between *E*- and *Z*-isomers. Such molecules exhibit reversible photochromic properties and show potential applications in the field of data storage, optical sensors, actuators, rewritable imaging applications etc. Such photoswitchable units have been incorporated in various classes of molecules and materials to impart light control in such applications. Liquid crystalline (LC) materials equipped with photoresponsive groups have received a lot of attention in recent years. The ability of photochromic liquid crystals (LC) to change their mesomorphic state upon irradiation renders them several potential applications. Through functionalization of liquid crystals with azobenzene systems as photochromic groups, the LC phases can be changed to the isotropic phase upon irradiation. This has been attributed to the destabilization of LC phases arising due to the geometrical constraints in *Z*-isomer of the azobenzene. In this regard, we designed and synthesized six molecules, having amide linkages, that can enhance liquid crystalline propensity through hydrogen bonding networks and arenes that can lead to π-π stacking. Their photoswitching behavior and photostationary states (PSS) were investigated through UV-Vis and ^{1}H NMR spectroscopic techniques. Their preliminary results on liquid crystalline properties, investigated using Polarized Optical Microscopy (POM) are described. Through this work, the design and synthesis of the target molecules, their spectral characterization, photoswitching studies and LC studies are reported.

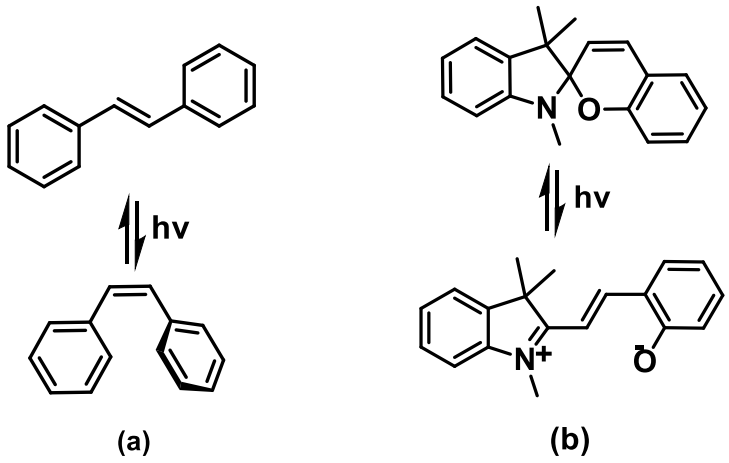
Chapter 1. Introduction

1.1 Introduction to Photoswitchable Systems

Photoswitchable molecules are a class of molecules that can undergo reversible photoisomerization between at least two distinct thermodynamically stable forms, by using light as stimuli. This process of reversible switching between the different forms, upon irradiation with light, is called photochromism. Compounds that show this property are called photochromic compounds. The interconvertible isomeric states differ in their physico-chemical properties like dipole moment, wavelength of absorption, spectrochemical properties etc. Some examples of photochromic materials include azobenzenes, stilbenes, spiropyrans, fulgides, diarylethenes and chromenes. [1]

Based on the thermal stability of the isomers produced upon irradiation, photochromic compounds can be categorized into two classes (**Scheme 1.1**).[2]

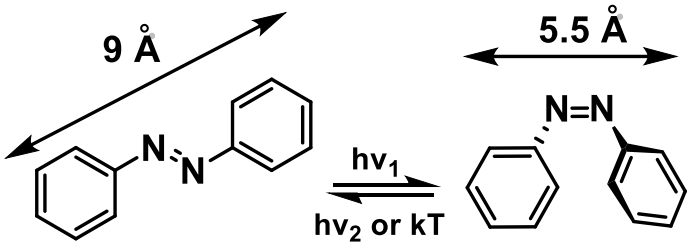
- **P-type:** They can be reversed only photochemically, and not thermally. E.g. fulgides and diarylethenes.
- **T-type:** They can be thermally reversed from *cis* to *trans* form. E.g. stilbenes, azobenzenes, spiropyrans etc.



Scheme 1.1: Examples of photochromic systems; (a) Stillbene, (b) Spiropyran to merocyanine.

1.1.1 Azobenzene as a Photoresponsive Material

Azo compounds are those having R-N=N-R′ functional group, where R and R′ can be aryl or alkyl. The N=N is called the azo group. When both R and R′ are phenyl groups, we get an azobenzene. Azobenzenes show reversible photoisomerization between a thermodynamically stable state (*E* isomer) and a kinetically stable state (*Z* isomer). The *E* to *Z* isomerization can be achieved by using appropriate wavelength of light, while *Z* to *E* isomerization can occur thermally or photochemically.



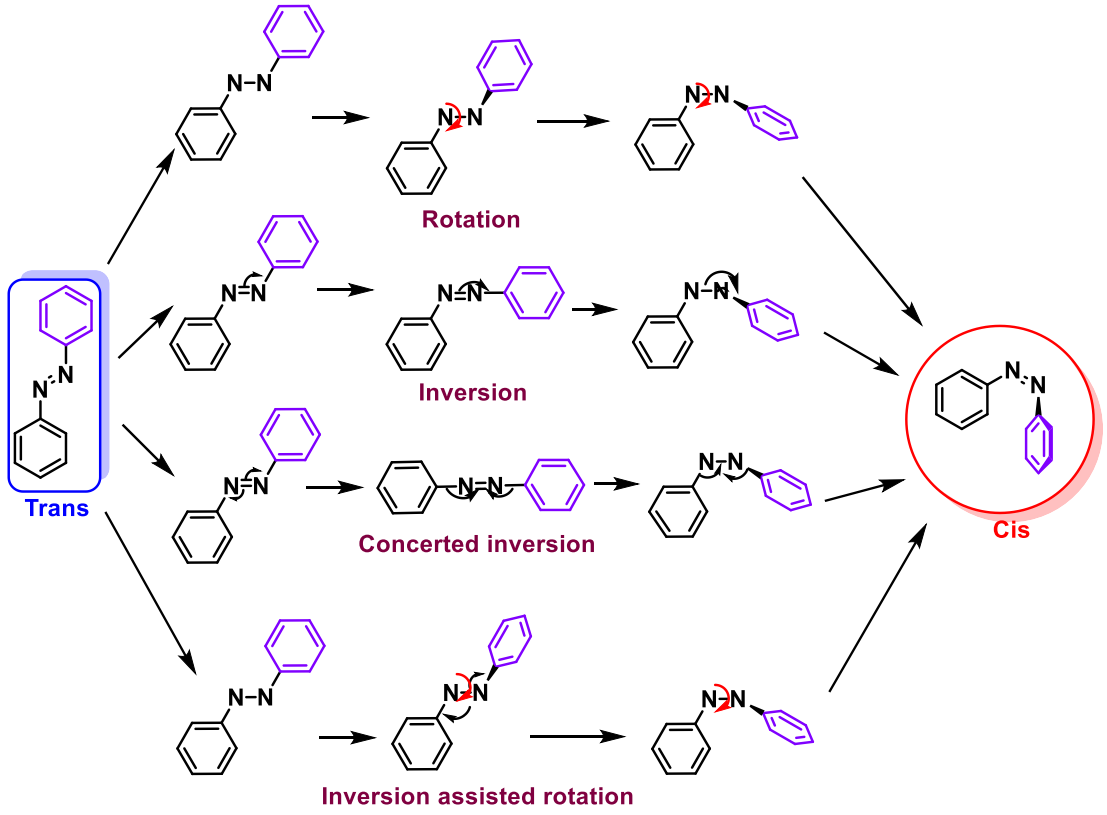
Scheme 1.2: Photoisomerization of Azobenzene.

Due to the extended conjugation in azobenzenes, they show bright colors like red, orange, yellow etc. depending on the substituents. The position (*ortho-*, *meta-*, *and para-*) of the substituents can influence the spectroscopic, photophysical and chemical properties of azobenzene derivatives (**Scheme 1.2**). The thermodynamically stable form (*E* isomer), has a planar structure with C_{2h} symmetry, while the kinetically stable form (*Z* isomer) has a non-planar structure with C_2 symmetry. In addition, azobenzenes can be synthesized easily with commonly available cheaper starting materials. This tunability of photoswitching behavior and ease of synthesis of azobenzenes make it an ideal component for numerous molecular devices and functional materials.

1.1.2 Azobenzene Photoisomerization and Thermal Reverse Isomerization Mechanism

The isomerization mechanism of azobenzene has been a debated topic since the isolation of *cis* azobenzene. Advances in spectroscopic techniques and computational methods have shed light on the problem. The two isomers can be switched with appropriate wavelengths of light: UV light, corresponding to the energy gap of π to π* (S_2 state) transition, induces *trans*-to-*cis* isomerization, and blue light, corresponding to the energy gap of n to π* (S_1 state) transition, induces *cis*-to-*trans* isomerization. Four mechanisms have been proposed for the

photoisomerization of azobenzenes - rotation, inversion, concerted inversion, inversion-assisted rotation (**Scheme 1.3**).[3]



Scheme 1.3: The four proposed mechanisms in photoisomerization of azobenzene[3].

All the proposed mechanisms predict the existence of photostationary states since a molecule relaxing from any one of the four transition states can afford either the *cis* or the *trans* isomer.

Factors affecting the thermal *cis* to *trans* reverse isomerization of azobenzenes:

1. **Solvent Effects**[4]**:** This factor only affects the rate of reverse thermal isomerization (*Z*- to *E*-isomer) and not the quantum yield of photoisomerization. As the solvent polarity increases, the rate of reverse thermal isomerization increases as the activation energy decreases. The isomerization mechanism of azobenzene is also affected by the solvent polarity and viscosity. Viscous nonpolar solvents favor the inversion mechanism, whereas non-viscous polar solvents favor rotation mechanism.

2. **Substituent Effects**[5]**:** Changing the substituents on the aryl rings of azobenzene causes significant changes in the spectroscopic properties like absorption, emission etc. This

is because the substituent groups alter the separation between π-π* and n-π* energy levels. For example, the substitution of all four *ortho* positions of the azobenzene with bulky electron rich groups causes the isomerization to occur by visible light.

3. **Effect of Acid[6]:** Acids increase the rate of thermal isomerization of azobenzene. The H^+ ion reacts with the azo group and forms its conjugate acid, which lowers the activation energy of *Z* to *E* isomerization.

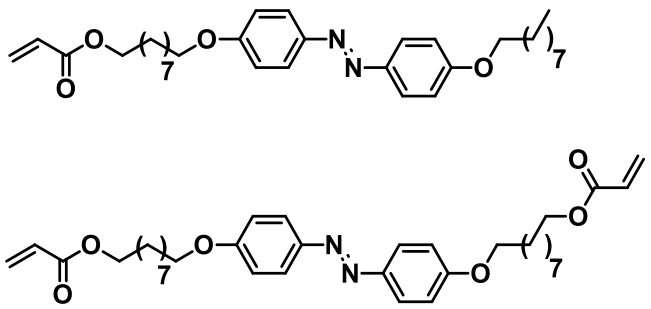
4. **Hydrogen-Bonding Effects[7]:** Hydrogen bonding influences both *E-Z* and *Z-E* isomerization. Intermolecular and intramolecular H-bonding can lead to a tautomeric equilibria, that results in a fast photoswitching. This effect is more pronounced in protic solvents.

1.1.3 Applications of Azobenzene Based Molecules

Azobenzenes have a wide range of applications from photo pharmacology to optochemical genetics to data storage. Azobenzenes generally have been used in dyes and pigments, food additives and indicators, drug delivery and are also applicable in nonlinear optics, electronics and liquid crystals, photochemical molecular switches etc. Here, we give a few representative examples of azobenzene derivatives being used in the development of functional devices.

1. Photoresponsive Liquid Crystals:

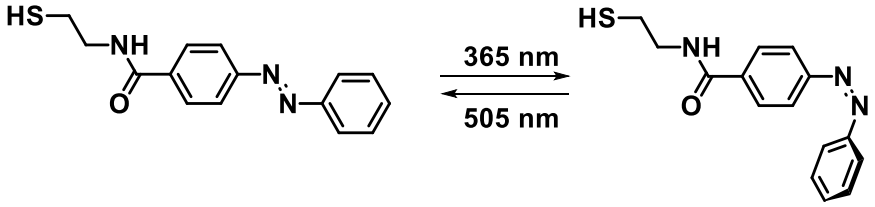
   Polymer materials doped with photoresponsive molecules can exhibit photo-contraction. This allows the conversion of light energy into mechanical energy. Several such materials have been described in literature. Ikeda et al., in a seminal paper published in 2003[8], showed that the bending motions of a film of liquid crystal polymer doped with azobenzene could be precisely controlled using polarized light (**Scheme 1.4**). Similar materials have been synthesized for the development of functional materials like light-fuelled motors, photoresponsive microvalves and micropumps.



Scheme 1.4: Monomer units used for preparing photoresponsive thin film[8].

2. Molecular Switches:

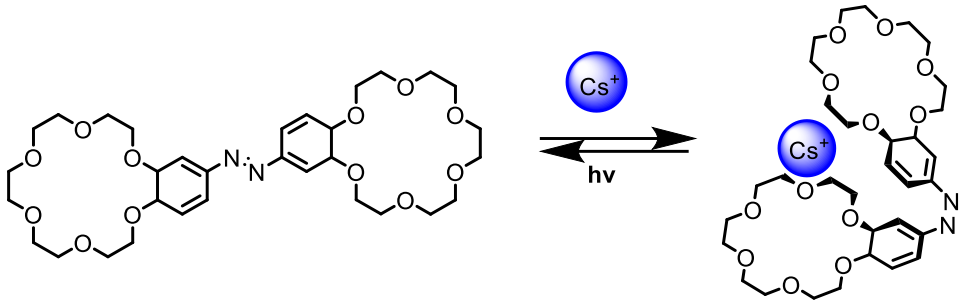
   Azobenzenes are extensively used for making molecular switches due to their reversible photoisomerization upon irradiation with suitable wavelengths. In 2003, Yesuda et al. described the phase switching of *N*-(2-mercaptoethyl)-4-phenylazobenzamide. This molecule showed a significant change in its conductive property upon photoswitching.[9] (**Scheme 1.5**).



Scheme 1.5: Schematic structures of *trans*-*cis* isomerization of *N*-(2-mercaptoethyl)-4-phenylazobenzamide used in the study of Yesuda et al.[9]

3. Metal Ion Binding:

   Azobenzenophane type crown ethers in which 4, 4′ position of azobenzene are linked to poly-oxyethylene chain can be used for reversible metal ion binding, as demonstrated by Osamuet et al. in 1983[10]. In *trans* form, the crown ethers are far apart and cannot capture the metal ion. However, after isomerization to *cis*, the two crown ethers come close and can trap the metal (**Scheme 1.6**). This trapping of metal ion is thus reversible.



Scheme 1.6: Reversible metal ion binding of azobenzene based crown ether[10].

1.2 Introduction to Liquid Crystals

Liquid crystals (LC) are characterized by a degree of molecular ordering that is intermediate between a crystal and a liquid.[11] Since liquid crystals have orientational order, they are anisotropic in nature. The first liquid crystalline molecule was discovered by Friedrich Reinitzer in 1888. The molecule he discovered now belongs to a class of liquid crystals known as cholesteric LCs[12].

1.2.1 Classification of Liquid Crystals

Classically, liquid crystals are divided into two types: thermotropic[13] and lyotropic[14] (**Figure 1.1**).

A. Thermotropic Liquid Crystals

According to Vertogen, "When the liquid crystalline phases are obtained by varying the temperature of the compounds, they are called thermotropic LCs"[13]. The LC phase can form by heating a solid or by cooling an isotropic liquid. The temperature at which the molecule changes from crystalline to liquid crystalline is called its melting point, and the temperature at which the molecule changes from liquid crystalline to an isotropic liquid is called its clearing point.

Thermotropic LCs are of three types based on the shape of the molecules[15]: (a) calamitic (rod-like), (b) bent-core (banana-like), and (c) discotic (disk-like) LCs.

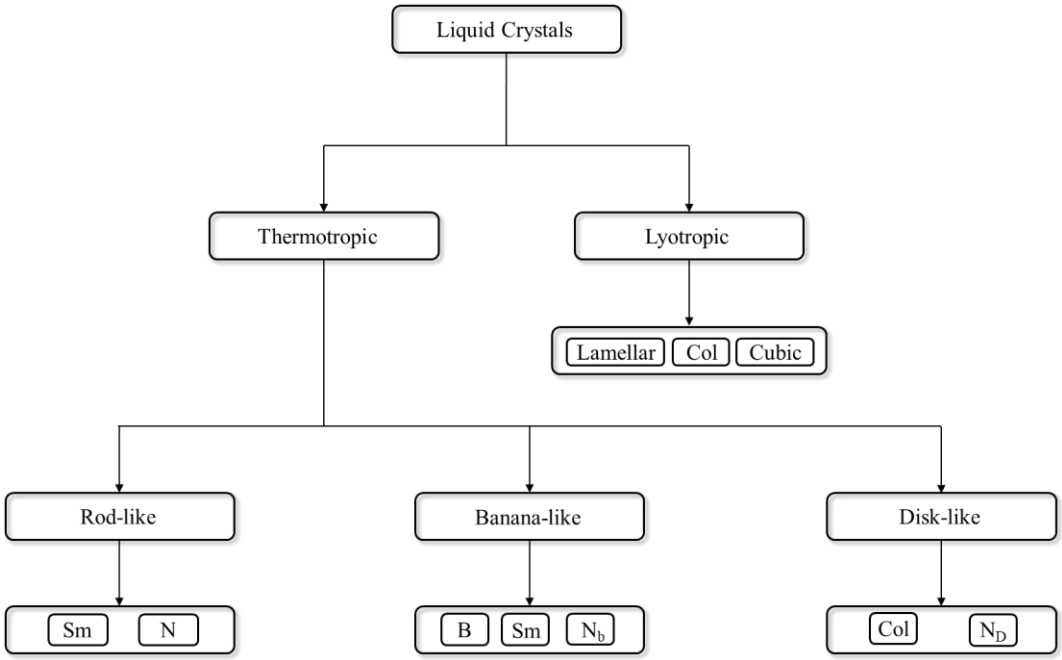


Figure 1.1: Classification of LCs.

A.1 Calamitic (rod-like) LC:

These are the most common type of thermotropic LCs. They have an elongated shape, where their molecular length is significantly greater than their molecular breadth (**Figure 1.2)**.

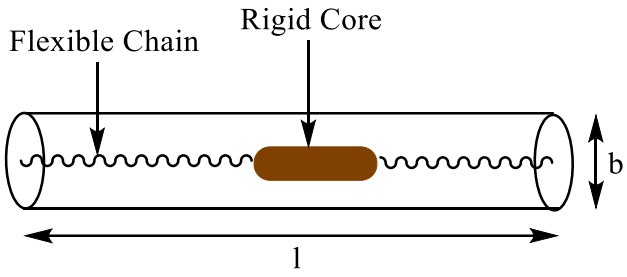


Figure 1.2: Representation of a calamitic LC molecule where l >> b[15].

Calamitic LCs exist in two mesophases: nematic and smectic.

A.1.1 Nematic Phase: In the nematic phase, molecules have orientational order but no positional order. The molecules align in such a way that their long axis remains parallel to each other. This preferred direction of orientation is called the director. Among all the LC phases, this is the least ordered mesophase. (**Figure 1.3**).

A.1.2 Smectic Phase: In the smectic phase, molecules have both orientational and positional order. Here, molecules are arranged in layers[15] (**Figure 1.3**). The layers are able to slide over each other since the attractive force between the layers is relatively weak. This imparts fluidity in the system. However, the smectic phase is more viscous than the nematic phase.

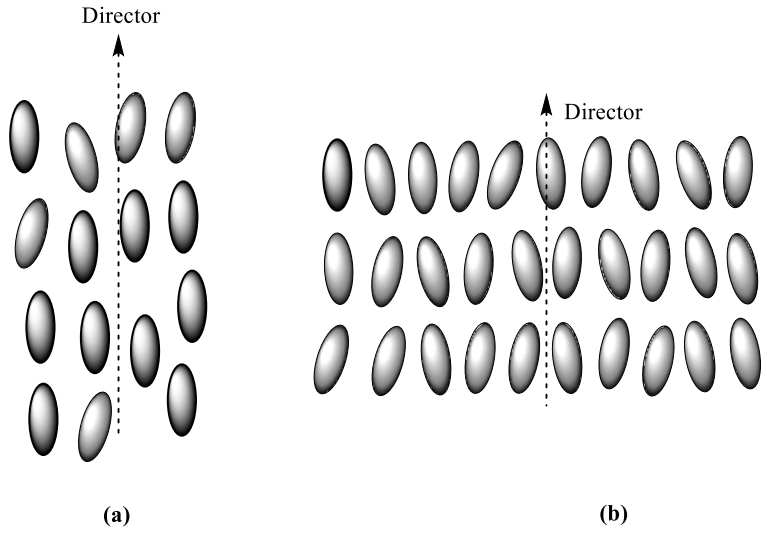
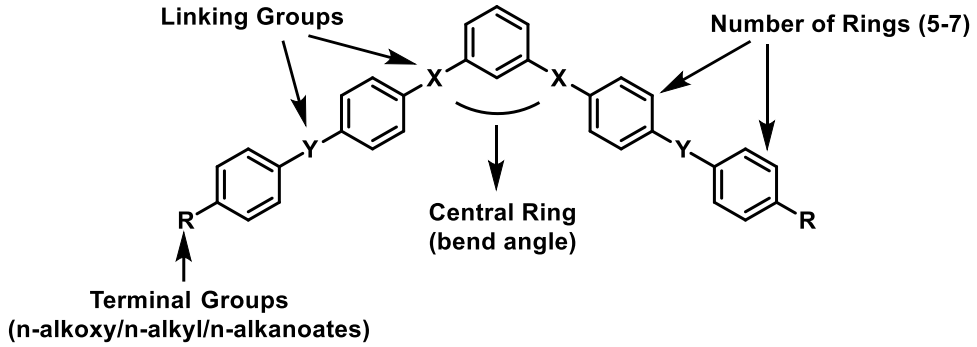


Figure 1.3: Representation of calamitic (a) nematic LC phase[15] (b) smectic LC phase[15].

A.2 Bent-Core (banana-like) LC:

Typically, their molecular structure is composed of three units: a bend central core, two linear rigid cores, and terminal chains[16] (**Scheme 1.7**). The bent structure of the banana LC molecules reduces the rotational disorder about the long axis of the molecule. This reduced disorder of the molecules allows them to pack in a directed manner within the mesophase[17].



Scheme 1.7: General template for banana LC molecules[17].

A.3 Discotic (disk-like) LC:

Discotic LCs are formed by the self-organization of disk-like molecules. These molecules self-assemble into 1-D stacks which in turn assemble into 2-D and 3-D lattices, giving rise to primary, secondary and tertiary structures respectively[15]. (**Figure 1.4**).

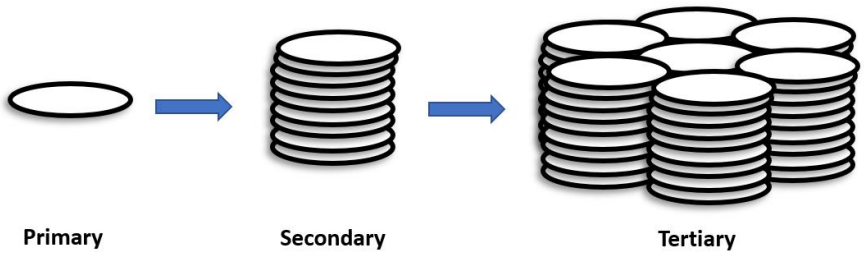


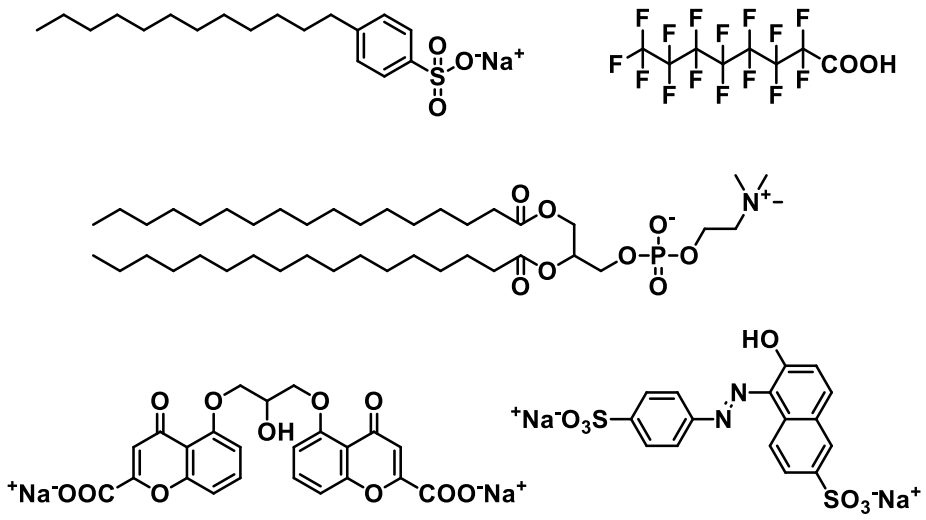
Figure 1.4: Self-assembly and self-organization of discotic liquid crystalline molecules into columnar phases[15].

Discotic liquid crystalline molecules usually have a planar central core substituted by saturated alkyl chains. The alkyl chains normally have three or more carbon atoms. The crystalline character of these molecules is promoted by the π-π stacking of the central cores, and the liquid character is promoted by the saturated alkyl chains[15].

B. Lyotropic Liquid Crystals

Amphiphilic compounds when dissolved in a suitable solvent at a certain concentration and temperature gives lyotropic LCs (**Scheme 1.8**).[19] Temperature, concentration of the solute and concentration the solvent (usually water) play important role in lyotropic LC systems.

Lyotropic LCs have potential applications in drug delivery and gene therapy[20].



Scheme 1.8: Different surfactant molecules that form lyotropic liquid crystalline phases[15].

1.3 Photoswitchable Liquid Crystals

Liquid-crystal materials can also be made photoresponsive. It will allow one to induce or modify anisotropic order by irradiating the sample at a particular wavelength of light[21]. This can be achieved by incorporating light-absorbing molecules in the LC material, which can switch between different states upon irradiation. These photoresponsive molecules can be either dispersed in a host LC matrix or they can be directly used as mesogens. In such materials, light absorption can affect the phase stability and the alignment of molecules in the mesophase. Irradiation at a particular wavelength may cause an isothermal transition from one LC phase to another[22], resulting in a reorientation of the director[23]. These changes at the microscopic level can manifest as changes in the physical macroscopic properties of the material.[29, 30]

The light-induced reorientation of molecules in LC phase is classified into three types[24], as sketched in figure 1.5.

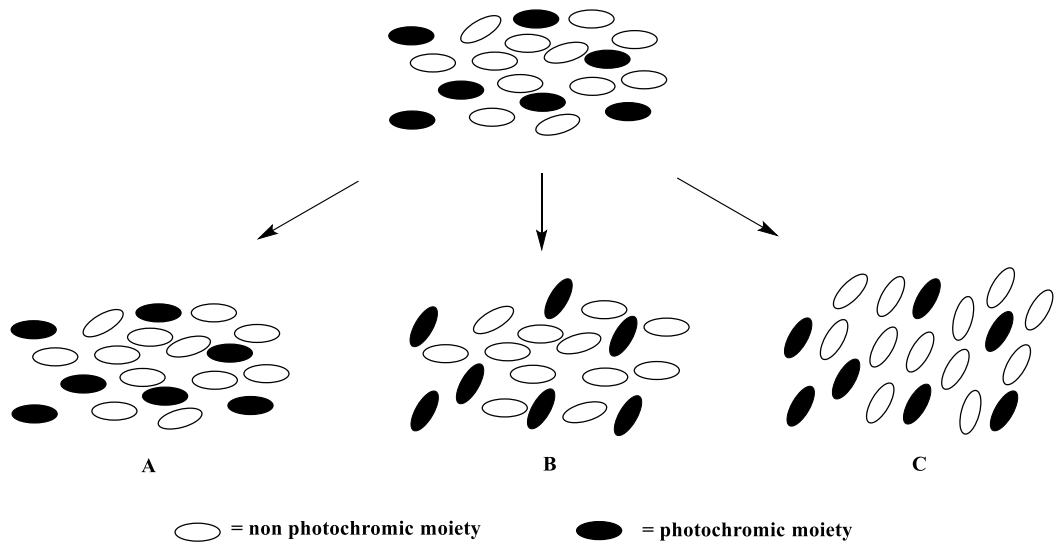
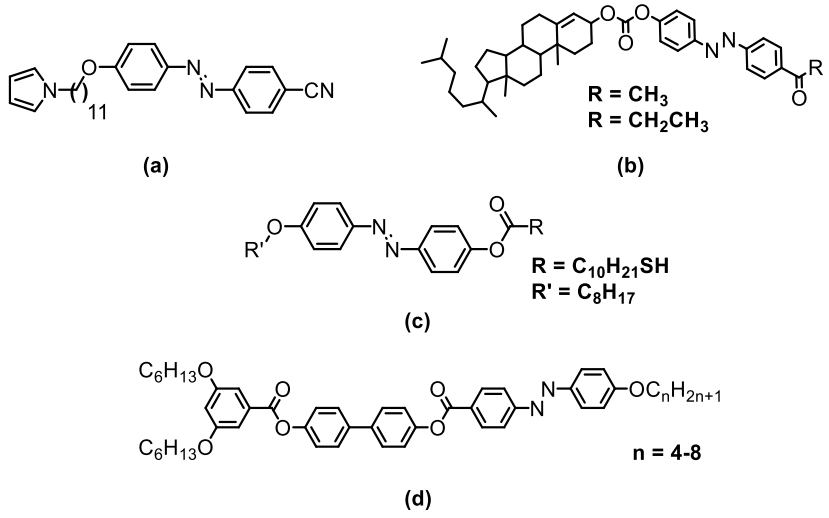


Figure 1.5: Types of molecular reorientation in photoresponsive LCs[24] upon irradiation: (A) No photoreorientation, (B) photoreorientation of only the photoresponsive molecules; (C) cooperative photoreorientation of both photochromic and non-photochromic molecules.

In case A, the reorientation is almost completely suppressed due to the high stability of arrangement in the mesomorphic state. In case B, the reorientation takes place only for the azobenzene residues and not for the nonphotochromic groups. In case C, the reorientation of the azobenzene residues causes a reorientation of non-photochromic mesogenic groups below the glass transition temperature (Tg).Over the years, several photoresponsive liquid crystals have been reported. Some of the examples are shown in Scheme 1.9.



Scheme 1.9: Some examples of photoresponsive LCs.

In 9a, Chen et al., described photoswitchable LCs with heterocycles[25]. They described the thermotropic and electrochemical properties of a series of *N*-substituted pyrrole monomers attached to an azobenzene by alkyl spacer. Based on the studies, they revealed the dependence of clearing temperature on chain length. They also found that the nematic phase got destabilized as a result of β-substitution in the pyrrole ring.

In 9b, Li et al., reported the synthesis and studies of liquid crystals containing mesogenic cholesteryl group connected to an azobenzene moiety via a carbonyldioxy spacer[26]. The molecules have a banana-shape in *trans* configuration and forms a nematic mesophase. However, upon irradiation with 365 nm light, the molecules underwent transition to the isotropic phase. The removal of UV light immediately leads to the reversal of the nematic mesophase. Hence, the photoisomerization from *trans* to *cis* form destabilizes the LC phase.

In 9c, Zep et al., discussed about phototunable liquidcrystalline structures made of metallic clusters (gold and silver nanoparticles) coated with photosensitive azo molecules[27]. They were able to manipulate the life time of azo-containing mesogen in the *cis* form by coating them on gold and silver nanoparticles. The *cis* form of the molecule was stable in solution and irradiation with visible light was required to achieve reverse isomerization. However, when the molecules were coated on the surface of nanoparticles, the *cis* form got highly destabilized, and the *trans* form was restored almost immediately once the UV irradiation stopped. The high instability of *cis* form of the azo ligands at the metal surface was attributed to the crowded environment on the metal surface.

In 9d, Alaasar et al., reported the synthesis and studies of a series of triple chain azobenzene based rod-like molecules that showed isothermal switching from an achiral LC phase to an isotropic liquid with non-polarized light[28].

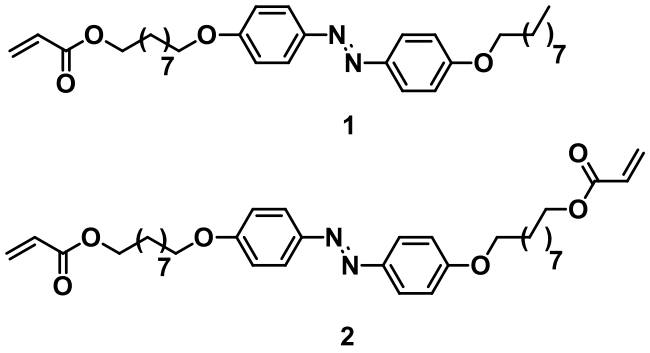
1.3.1 Applications of Photoresponsive Liquid Crystals

Photo-mechanical deformations produced in isotropic materials like monolayer, gel, and amorphous polymer films usually occur in a uniform way, i.e., there is no preferential direction for deformation. However, if anisotropic materials are used, they will have a preferred direction for deformation. Hence using such materials can improve the efficiency with which

light energy can be converted into mechanical energy. This is where liquid crystalline materials come in handy. One such promising class of materials is liquid-crystalline elastomers (LCEs).

LCEs are polymeric materials in which the motions of the polymeric matrix can be coupled with the changes in the orientational order of the mesogens[29]. By making the mesogens embedded in the polymer matrix photoresponsive, one can trigger a change in the LC orientational order with light. This change in orientation of the mesogens produces deformation in the polymer material[30]. These photo-induced deformations can be utilized for several real-life applications.

One such application was demonstrated by Ikeda and co-workers where they converted the deformations produced in an azo-CLCP film (**Scheme 1.10**) into rotational motion[31]. This was the first demonstration of a light-fueled plastic motor. Other important applications involve the use of azo-CLCP film for the design and fabrication of microvalves[33] and micropumps[34]. Photoresponsive LCEs are also being studied for their potential application in biotechnology, especially for the generation of artificial muscles.



Scheme 1.10: azo-CLCP is prepared by the photopolymerization of monomer 1 and 2 with a ratio of 20/80 mol/mol[31].

1.4 Characterization of Liquid Crystal Phases

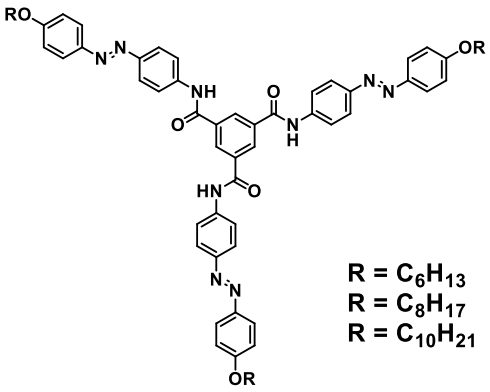
Three techniques are mainly employed for the characterization of liquid crystals: Polarized Optical Microscopy (POM), Differential Scanning Calorimetry (DSC) and X-ray scattering. If the molecule is liquid crystalline, it will produce a birefringence pattern. This can be observed using POM. DSC detects the LC phase by monitoring the enthalpy changes during the heating and the cooling cycles. If a molecule is liquid crystalline, it will show at least two transitions

in each cycle. One from solid to LC phase and one from LC phase to isotropic liquid. DSC is usually used as a complementary tool to POM. However, DSC cannot identify the type of LC phase. For that, X-ray diffraction studies are required, which gives information regarding the packing parameters in each phase.

Chapter 2. Results and Discussion

2.1 Thesis Background

From our group, Devi et al., have synthesized three derivatives of alkoxy azobenzene connected benzenetricarboxamides (**Scheme 2.1**). All the three derivatives were DLCs. UV spectroscopic studies revealed that the molecules showed significant photoswitching in both solid state and LC phase. However, there was no change in the arrangement of molecules in the mesomorphic state.



Scheme 2.1: Alkoxy azobenzene connected benzenetricarboxamide derivatives.

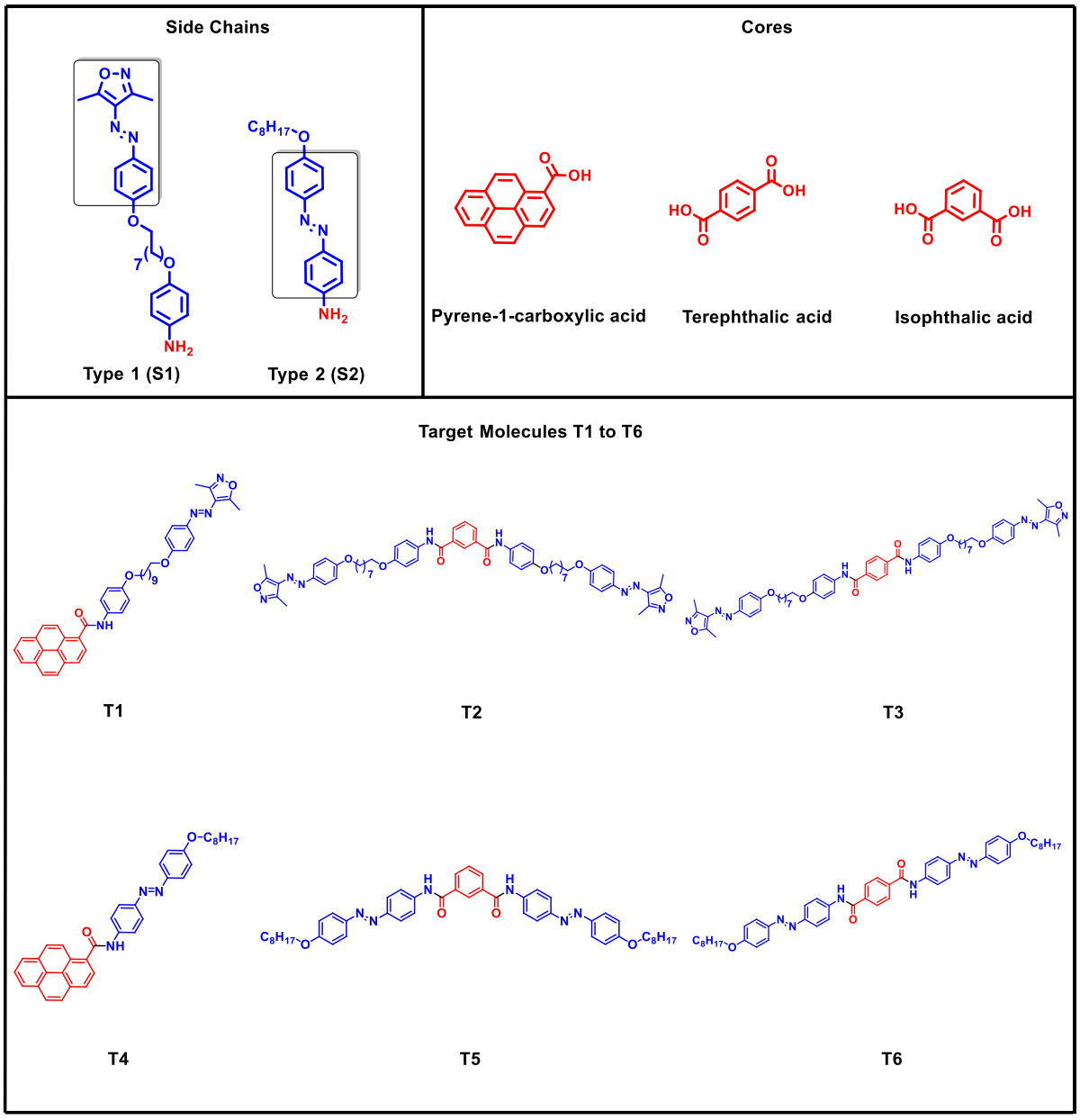
But, most practical applications require photoresponsive liquid crystals. This is what we wanted to improve upon in this project.

2.2 Our Approach

Towards the synthesis of photoswitchable liquid crystals, we focused on mono- and di-carboxamides. We designed two types of side chains by changing the position of the photoresponsive unit. In the side chain of type 1, the photoswitchable unit is at the terminal end and in type 2, the photoswitchable unit is near the core (**Scheme 2.2**).

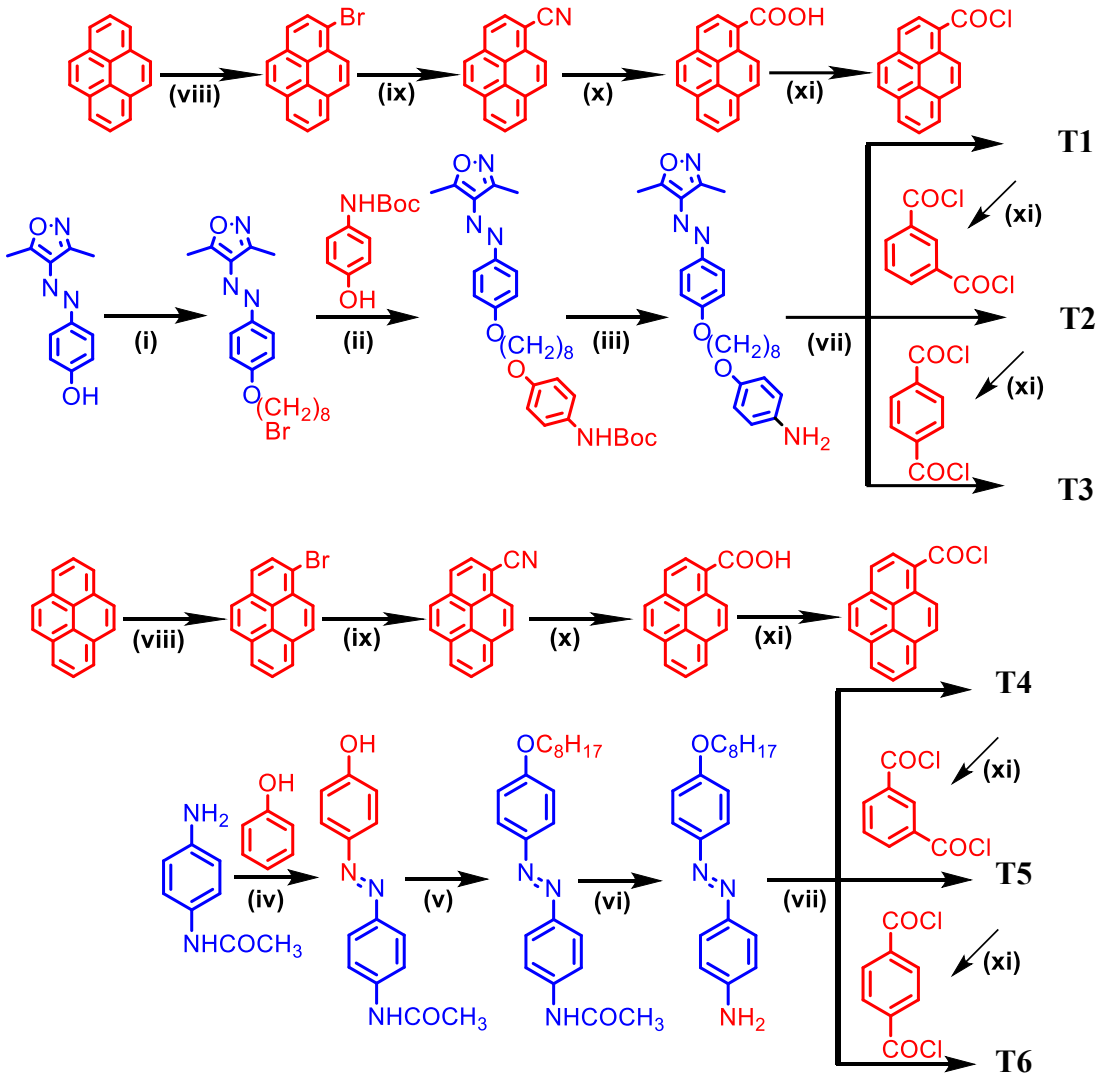
We have selected three different cores for attaching the side chains; pyrene-1-carboxylic acid, terephthalic acid and isophthalic acid (**Scheme 2.2**). Linear and bend core liquid crystals are extremely well studied and reported. Hence choosing terephthalic and isophthalic acids as cores make sense. As for pyrene-1-carboxylic acid, it promotes π-π stacking, increasing the propensity for the molecule to be liquid crystalline.

Now we have two different side chains with varying positions of photoresponsive unit and three different cores. Considering all the possibilities, we thus designed six target molecules (**Scheme 2.2**).



Scheme 2.2: Target design. Side chains (**S1** and **S2**), cores and target molecules (**T1** to **T6**).

2.3 Synthesis



Scheme 2.3: Synthesis scheme of **T1-T6**. (i) 1, 8-Dibromooctane, K_2CO_3, dry DMF, 50 ^oC, 3h, 77%; (ii) K_2CO_3, cat. KI, CH_3CN, reflux, 18h, 78%; (iii) CH_2Cl_2-TFA (6:1), 2h, stirring at RT, 90%; (iv) Conc. HCl, $NaNO_2$, Aq. NaOAc, 0 ^oC, 4h, 91%; (v) K_2CO_3, 1-Bromooctane, cat. KI, dry DMF, 100 ^oC, 8h; 80%; (vi) Conc. HCl, EtOH, reflux, 6h, 70%; (vii) Dry 1, 2-Dichloroethane, Et_3N, 0 ^oC to stirring at RT, 12h, Yield: Target 1: 40%; Target 2: 42%; Target 3: 52%; Target 4: 43%; Target 5: 42%; Target 6: 45%; (viii) H_2O_2, HBr, MeOH/Et_2O (1:1), 0 ^oC to stirring at RT, 12h, 70%; (ix) CuCN, dry DMF, 160 ^oC, 24h, 40%; (x) NaOH soln. (5M), EtOH, 50 ^oC, 24h, 60%; (xi) $SOCl_2$, 85 ^oC reflux, 5h.

For the synthesis of side chain S1, we first synthesized 4-hydroxyphenyl azo isoxazole. We then performed an *O*-alkylation of this compound with 1, 8-dibromooctane, the product of which was treated with a Boc-protected hydroxyl amine. Finally, Boc deprotection was performed to afford the desired side chain S1. Similarly, for the synthesis of side chain S2, we began with the diazotization of *p*-aminoacetanilide, followed by a reaction with phenol. The product obtained from this reaction was subjected to *O*-alkylation reaction with 1-bromooctane and the amide group was finally hydrolyzed to afford side chain S2.

For the synthesis of pyrene-1-carboxylic acid, first we performed the bromination of pyrene. The product of the reaction was treated with copper cyanide to afford pyrene-1-carbonitrile which was hydrolyzed under basic conditions to obtain the desired product. The other cores, terephthalic and isophthalic acids were brought from commercial sources.

Now the cores were activated by converting them to acid chloride and we joined the side chain to the core by performing an acid-amine coupling (**Scheme 2.3**).

2.4 Photoswitching Studies

1. Analysis of Photoswitching Studies Using ^{1}H NMR Spectroscopy.

We analyzed the photoswitching behavior of **T2** and **T3**. Both the studies were performed in DMSO-d_6 as a solvent at the compound concentrations 2.0 mM. The *trans* isomer was irradiated at 365 nm for 25 minutes in both the cases until a photostationary state was reached. By analyzing the spectra, we concluded that the target molecule **2** underwent 95% conversion to *ZZ*, whereas and the target **3** underwent 93% conversion. Further, both the molecules were irradiated at 505 nm for 20 minutes until the photostationary state was reached. Target molecule **2** underwent 79% reverse isomerization to *trans* and the target molecule **3** led to 69% conversion (**Figure 2.1** and **2.2**).

Interestingly, we observed, in the case of target molecule **T3**, that the solubility of compound increases as a result of *trans* to *cis* photoisomerization. This is evident from the noisy spectrum in *trans* form while the *cis* form gives relatively clean noise free spectrum (**Figure 2.2**).

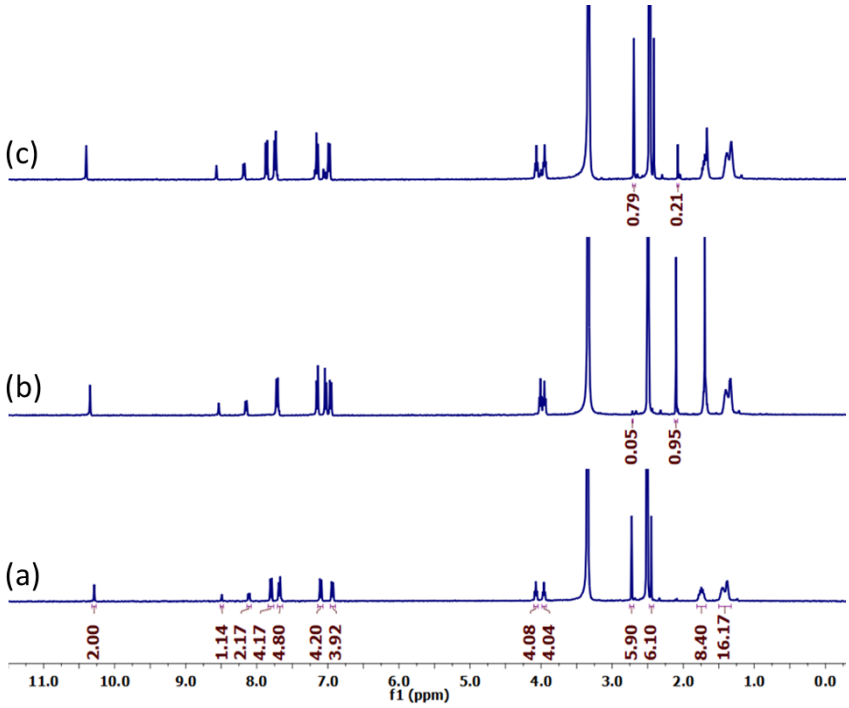


Figure 2.1: Analysis of photoswitching studies of **T2** using ^{1}H NMR. (a) Before irradiation (DMSO-d_6, 2.0 mM); (b) After 365 nm irradiation for 25 minutes; (c) After 505 nm irradiation for 20 minutes.

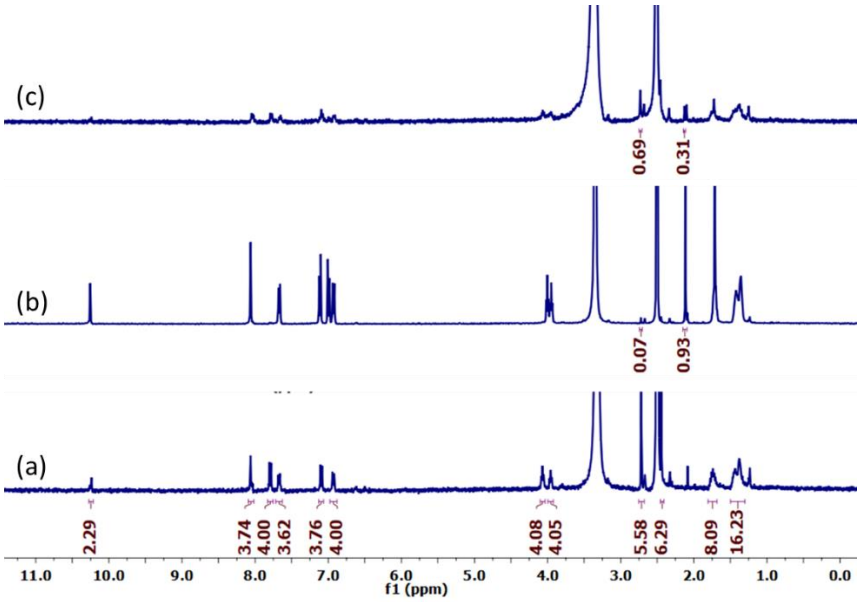


Figure 2.2: Analysis of photoswitching studies of **T3** using ^{1}H NMR. (a) Before irradiation (DMSO-d_6, 2.0 mM); (b) After 365 nm irradiation for 25 minutes; (c) After 505 nm irradiation for 20 minutes.

2. **Analysis of Photoswitching Studies Using UV-Vis Spectroscopy (in Solution Phase)**

We performed the photoswitching of all the compounds in solution phase. The studies for compounds **1** and **4** were done in $CHCl_3$ and the rest of the samples were done in DMSO due to solubility issues. Target molecules **T2**, **T3**, **T5** and **T6** showed almost quantitative forward and reverse switching. For all these molecules, there is a decrease in the intensity of π-π* transition with a blue shift, upon irradiating at 365 nm. Also, the n-π* band increases in intensity while forward switching. The presence of isosbestic point in the spectra of target molecules **T2**, **T3**, **T5** and **T6** indicated that both the azo groups in the compounds undergo switching simultaneously. However, molecules **T1** and **T4** do not show reverse switching in solution phase (**Figure 2.3**).

3. **UV-Vis Photoswitching Studies (in Solid State)**

We performed photoswitching of all compounds in solid state. The studies for all the compounds were done in KBr medium. Target molecules **T1**, **T2**, **T3**, **T5** and **T6** showed both forward and reverse switching. However, molecule **T4** does not show solid state switching (**Figure 2.4**).

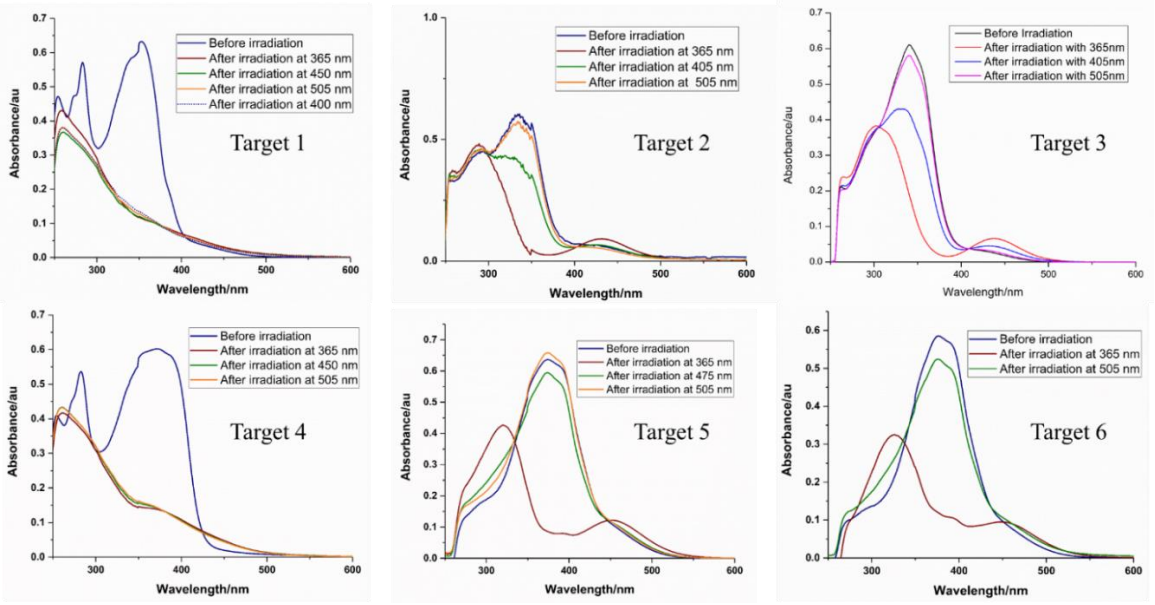


Figure 2.3: Comparison of photoswitching properties of the target molecules **1**-**6**. All the molecules except 1 and 4 undergo almost quantitative forward and reverse photoswitching. Molecules 1 and 4 do not show reverse photoswitching.

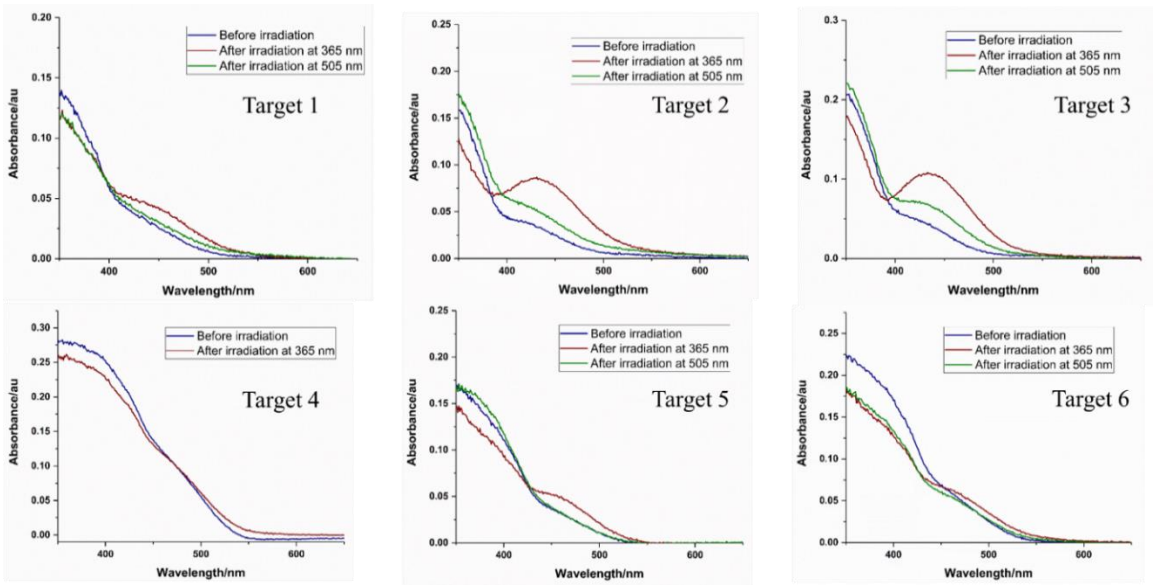


Figure 2.4: Comparison of solid state photoswitching properties of the target molecules **1-6** (in KBr medium).

2.5 Fluorescence Studies

While performing the solution phase photoswitching studies of target molecule **1**, we observed a green light emanating from the solution after irradiation at 365 nm light for about 20 minutes (**Figure 2.5b**). We concluded that the molecule must be showing fluorescence in the *cis* form. We wanted to confirm this by performing fluorescence studies for the molecule. Our observation was confirmed by the studies and the molecule indeed showed greater intensity of fluorescence emission in the *cis* form (**Figure 2.5a**).

The understanding of the exact reason for this behavior is currently underway. However, molecules showing similar behavior are reported in literature. In 2014, Nachtigall et al[35]. described the photochemistry of pyrene azobenzene dyad (**Scheme 2.4**).

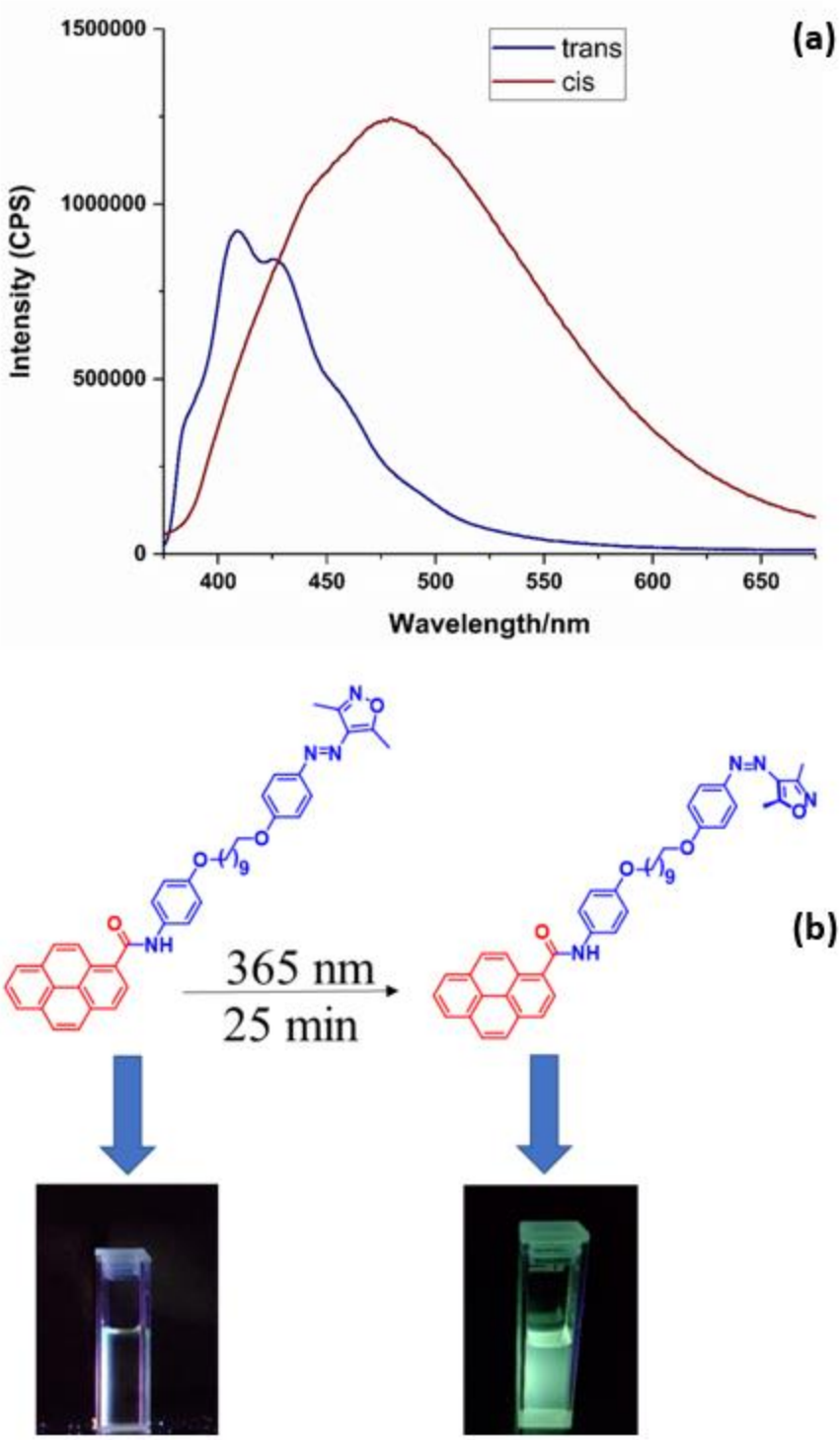
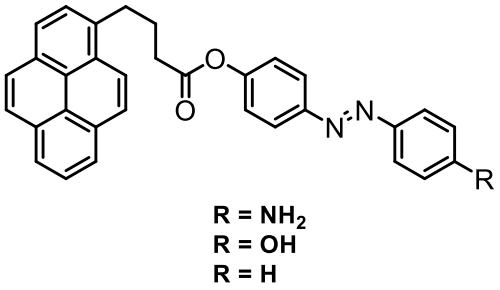


Figure 2.5: (a) Fluorescence spectra of target molecule **T1** (before and after photoswitching); (b) Photograph depicting the fluorescence emission of **T1** after photoisomerization.



Scheme 2.4: Pyrene–Azobenzene Dyads (Nachtigall et al., 2014)[35].

In this molecule, the authors observed the pyrene fluorescence quenching in the *trans* isomer. However, upon irradiation with 365 nm light, the molecule converted in to *cis* form and it shows greater intensity of fluorescence emission.

This behavior was attributed to the quenching of pyrene fluorescence, as a result of intra-excitation energy transfer from the pyrene chromophore to the azobenzene. This happens due to the stacking of the azo group on top of the pyrene. However, as the azobenzene is converted to its *cis* form, it cannot stack effectively owing to the steric repulsion arising from the non-planar *cis* azobenzene. Thus, the azo group moves away from the core and pyrene is exposed. This causes the fluorescence emission of the molecule to increase (**Figure 2.6**).

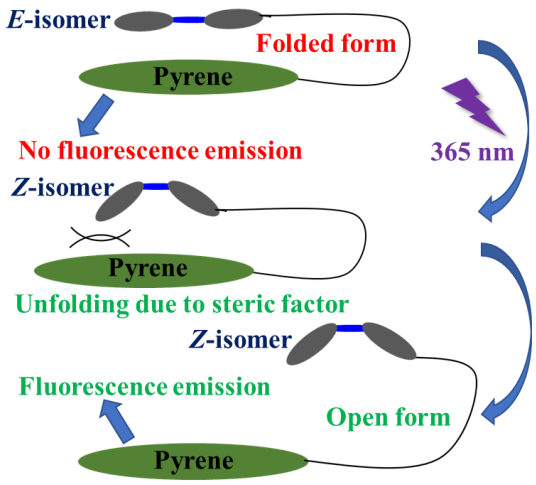


Figure 2.6: Schematic representation of the fluorescence quenching and enhancement in pyrene-azobenzene dyad[35].

2.6 Polarized Optical Microscopy (POM) Studies

POM studies were performed for all the target molecules in collaboration with Dr. Santanu Kumar Pal's group at IISER Mohali. A molecule will show birefringence when pressed if it is liquid crystalline. This is because LCs' orientation is disturbed by pressing. This disturbance in the molecular order leads to birefringence. For our molecules, only target **4** showed this property, and hence, it is liquid crystalline (**Figure 2.7**). Others are unlikely to form liquid crystals. For target molecule **3**, we did not observe any birefringence in POM.

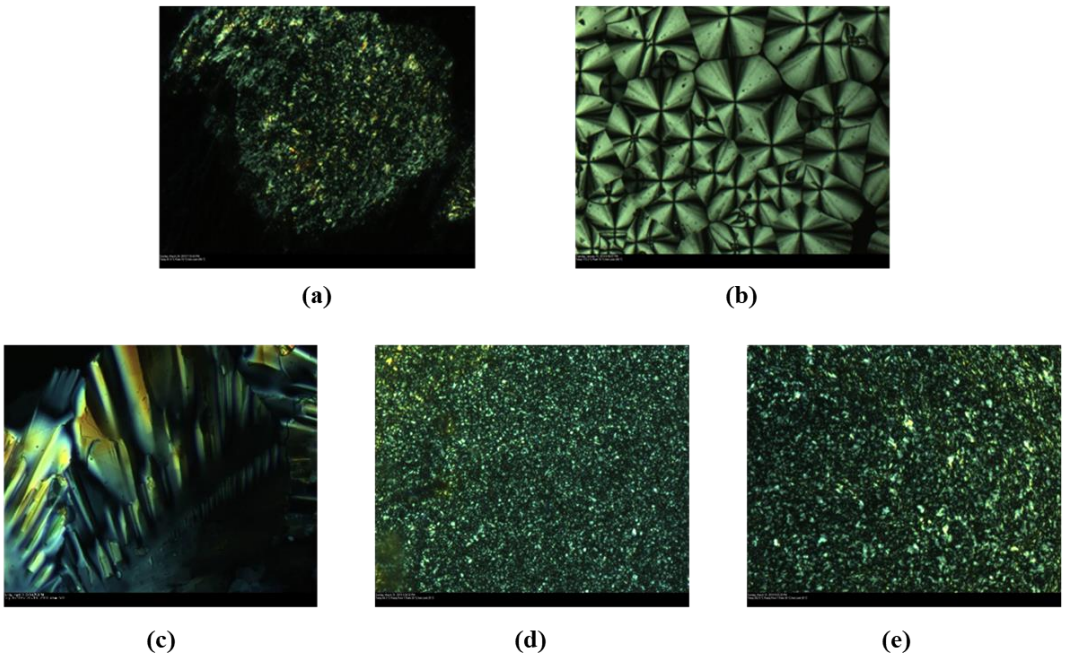


Figure 2.7: POM images of target molecules; (a) **T1** (20X, 41.9 ^{o}C); (b) **T2** (50X, 173.3 ^{o}C); (c)**T4** (50X, 215.2 ^{o}C); (d) **T5** (20X, 64.3 ^{o}C); (e) **T6** (20X, 262.5 ^{o}C).

Chapter 3: Conclusions and Perspectives

The goal of our project was to synthesize photoswitchable liquid crystals. Towards this goal, we designed six target molecules having three different cores and two different side chains. All the target molecules were successfully synthesized and fully characterized by NMR and HRMS. UV-Vis and NMR studies were performed for understanding their photoswitching behavior. Target molecules **2**, **3**, **5** and **6** showed almost quantitative photoswitching in both solution and solid state. Interestingly, target molecule **1** does not undergo reverse photoswitching in solution phase, but it does in solid state. Another interesting observation that we made in our studies was the fluorescence quenching in the *trans* state of target molecule **1**. Presumably folding of azoarene unit through π-stacking with the pyrene unit plays an important role in this regard. Further studies are required to understand this phenomenon. The preliminary results on liquid crystalline properties were investigated using Polarized Optical Microscopy (POM). Target molecule **4** is a potential candidate for liquid crystalline property. Further studies are underway.

To explain the fluorescence quenching observed in the *trans* state of target molecule **1**, fluorescence spectra at varying concentrations, and varying solvent polarity have to be recorded. Further, performing 2D NMR studies will reveal the configuration adopted by the molecule in the solution phase. XRD studies and POM studies of Target molecule **4** after photoswitching are also required to understand whether the molecule is a photoresponsive LC.

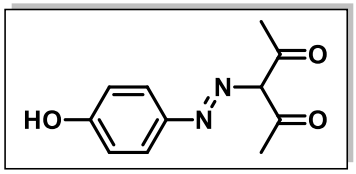
Chapter 4: Experimental Section

4.1 General Methods and Instrumentation.

Chemicals not synthesized in the lab were commercially purchased from Sigma Aldrich, Himedia and Merck. Progress of reactions was monitored using TLC plate (Merck) and detected using UV (254 nm and 365 nm) chamber. The completed reaction was quenched and the organic extracts were dried using anhydrous sodium sulphate and solvent was removed by rotary evaporation (Buchi). Separation and purification was done by column chromatography using silica gel (100-200 and 60-120 mesh size), purchased from Himedia. LED of different wavelength were purchased from Applied Photophysics. 'H and ^{13}C NMR spectra were recorded in Bruker Avance-III 400MHz and 100 MHz spectrometer using $CDCl_3$/DMSO-d_6 as solvent. Chemical shift values were recorded in ppm scale. HRMS was recorded in both ESI positive and negative modes using Waters SYNAPT G25 High definition mass spectrometer. UV-Vis spectroscopy for photoswitching was done using Agilent and Labindia spectrophotometers.

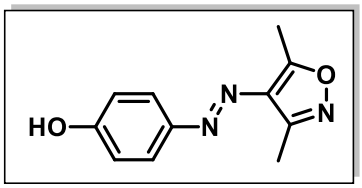
4.2 Synthesis

1. **3-(2-(4-hydroxyphenyl) hydrazono) pentane-2,4-dione:**



A mixture of aniline or substituted anilines (20.0 mmol) and deionized water in a two neck round bottom flask was cooled to 0 ^oC. To this 37% conc. HCl (6.5 mL) was added and stirred to get a clear solution. Then a cold aqueous solution of sodium nitrite (1.52 g, 22.0 mmol in 20 mL of water) was added dropwise into the reaction mixture slowly. After the addition, the diazonium salt started forming. The reaction mixture was allowed to stir for half an hour for completion. Afterwards, at 0 ^oC a cold aqueous solution of sodium acetate (5.90 g, 70.0 mmol) and acetyl acetone (2.00 g, 20.0 mmol in 100 mL of water and 10 ml of ethanol) was added. The reaction was continued at RT and was monitored by TLC. After completion of the reaction, the reaction mixture was filtered off to obtain a yellow-orange solid product, which was dried under vacuum to yield the desired product.

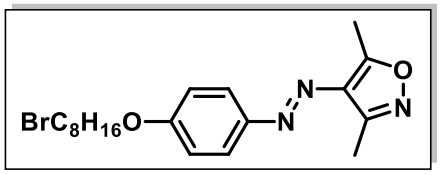
2. (*E*)-4-((3,5-dimethylisoxazol-4-yl) diazenyl) phenol:



A mixture of arylazoacetylacetone derivative (1.0 mmol), hydroxylamine hydrochloride (2.0 mmol) and Na_2CO_3 (4.0 mmol) in 10 mL absolute ethanol was refluxed. The reaction was followed using TLC up to the completion of the reaction. After completion of the reaction (12 hours), ethanol was evaporated and the product was extracted using EtOAc water. The extracted organic layer was washed with brine solution and dried using sodium sulfate. The organic layer was then evaporated to dryness was purified by column chromatography (Silica, Eluent: 1:10 ethylacetate/n-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.52 (s, 3H), 2.73 (s, 3H), 5.57 (br, 1H, -OH), 6.92-6.94 (d, *J* = 8.7 Hz, 2H), 7.75-7.77 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 11.67, 12.12, 115.76, 124.20, 147.36, 154.36, 158.11, 162.34, 168.33; HRMS TOF MS ES+ Theoretical m/z: 218.0930, Observed m/z: 218.0920.

3. (*E*)-4-((4-((8-bromooctyl)oxy)phenyl)diazenyl)-3,5-dimethylisoxazole

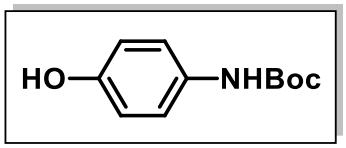


To a mixture of compound 2 (1.0 mmol) and K_2CO_3 (2.0 mmol) in dry DMF (15 mL), 1, 8 – Dibromooctane (2.0 mmol, 0.4 mL) was added and heated at 50 ^{o}C. The reaction was followed using TLC up to the completion of the reaction. After completion of the reaction (12 hours), product was extracted using EtOAc water. The extracted organic layer was washed with brine solution and dried using sodium sulfate. The organic layer was then evaporated to dryness was purified by column chromatography (Silica, Eluent: 1:3 ethylacetate/n-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37-1.52 (m, 8H), 1.78-1.90 (m, 4H), δ 2.52 (s, 3H), 2.72 (s, 3H), 3.40-3.43 (t, *J* = 6.8 Hz, 2H), 4.01-4.04 (t, *J* = 6.5 Hz, 2H), 6.96-6.98 (d, *J* = 9.0 Hz, 2H), 7.77-7.80 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 11.79, 12.25, 26.06, 28.21,

28.81, 29.27, 29.31, 29.84, 32.89, 34.16, 68.38, 114.76, 122.72, 124.07, 132.35, 147.22, 154.05, 161.50, 168.27, 180.03.

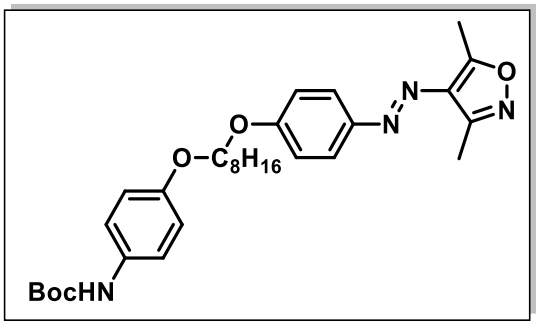
4. **tert-butyl (4-hydroxyphenyl) carbamate**



To a mixture of 4-Aminophenol (1.0 mmol) and Et_3N (2.0 mmol, 12.8 mL) in THF (15 mL), di-tert-butyl dicarbonate (1.2 mmol) was added and stirred at RT. The reaction was followed using TLC up to the completion of the reaction. After completion of the reaction, THF was evaporated and product was extracted using EtOAc water. The extracted organic layer was washed with brine solution and dried using sodium sulfate. The organic layer was then evaporated to dryness was purified by column chromatography. (Eluent: 1:10 ethylacetate/n-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (s, 9H), 6.33 (br, 1H, -NH), 6.74-6.77 (m, 2H), 7.19-7.21 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.51, 29.76, 115.62, 165.78, 178.67, 191.17, 195.39.

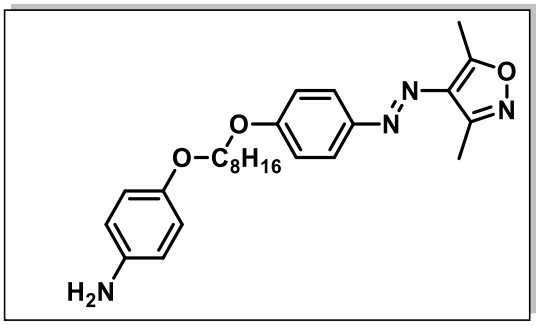
5. **tert-butyl (*E*)-(4-((8-(4-((3,5-dimethylisoxazol-4- yl) diazenyl) phenoxy) octyl) oxy) phenyl) carbamate**



To a mixture of compound 3 (1.0 mmol) and K_2CO_3 (1.5 mmol) in acetonitrile (10 mL), compound 4 (1.5 mmol) was added. A catalytic amount of KI was also added to the reaction mixture. This mixture was then refluxed at 85 ^{o}C. The reaction was followed using TLC up to the completion of the reaction. A yellow solid was obtained which was filtered, washed with acetonitrile and was dried in high vacuum to obtain the pure product.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25-1.29 (m, 8H), 1.50 (s, 9H), 1.73-1.85 (m, 4H), 2.52 (s, 3H), 2.72 (s, 3H), 3.90-3.93 (t, *J* = 6.5 Hz, 2H), 4.01-4.04 (t, *J* = 6.5 Hz, 2H), 6.34 (br, 1H, -NH), 6.81-6.84 (d, *J* = 8.9 Hz, 2H), 6.96-6.98 (d, *J* = 8.8 Hz, 2H), 7.23 (br, 2H), 7.78-7.80 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.80, 12.26, 26.09, 26.11, 28.51, 28.99, 29.30, 29.40, 29.43, 29.84, 68.36, 68.43, 114.77, 114.96, 122.98, 124.07, 131.19, 132.38, 147.21, 153.06, 154.06, 155.27, 161.44, 168.27, 187.31; HRMS TOF MS ES+ Theoretical m/z: 537.3077, Observed m/z: 537.3050.

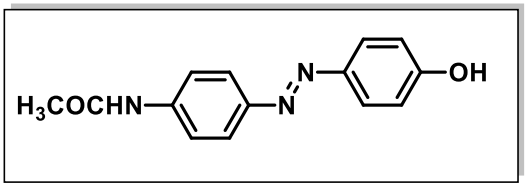
6. (*E*)-4-((8-(4-((3,5-dimethylisoxazol-4-yl) diazenyl) phenoxy) octyl) oxy) aniline



Compound 5 was dissolved in DCM-TFA mixture in 6:1 ratio and was stirred at RT for 2 hours. The reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was neutralized by 10 % NaOH. The product was extracted using DCM water work up. The extracted organic layer was washed with brine solution and dried using sodium sulfate. The organic layer was then evaporated to dryness was purified by column chromatography (Silica, Eluent: 1:4 ethylacetate/n-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40-1.48 (m, 8H), 1.73-1.84 (m, 4H), 2.52 (s, 3H), 2.72 (s, 3H), 3.41 (br, 2H, -NH), 3.86-3.90 (t, *J* = 6.5 Hz, 2H), 4.01-4.04 (t, *J* = 6.5 Hz, 2H), 6.62-6.65 (d, *J* = 8.8 Hz, 2H), 6.73-6.75 (d, *J* = 8.7 Hz, 2H), 6.96-6.98 (d, *J* = 8.9 Hz, 2H), 7.78-7.80 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.77, 12.23, 14.33, 21.19, 26.04, 26.13, 29.29, 29.42, 29.44, 29.52, 60.53, 68.42, 68.71, 114.76, 115.74, 116.51, 124.05, 132.34, 139.96, 147.20, 152.38, 154.04, 161.53, 168.23; HRMS TOF MS ES+ Theoretical m/z: 437.2553 Observed m/z: 437.2539

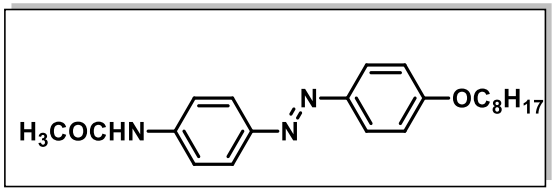
7. (*E*)-*N*-(4-((4-hydroxyphenyl) diazenyl) phenyl) acetamide



A mixture of p-aminoacetanilide (3.3 g, 22 mM) and deionized water in a two neck round bottom flask was cooled to 0 ^{o}C. To this 37% conc. HCl (6.5 mL) was added and stirred to get a clear solution. Then a cold aqueous solution of sodium nitrite (1.52 g, 22 mM in 20 mL of water) was added dropwise into the reaction mixture. After the addition, the diazonium salt started forming. The reaction mixture was allowed to stir for half an hour for completion. After half an hour, at 0 ^{o}C a cold aqueous solution of sodium acetate (5.9 g, 70 mM) and phenol (2.16g, 23 mM in 100 mL of water) was added. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered off to obtain orange solid product, which was dried under vacuum to yield the desired product.

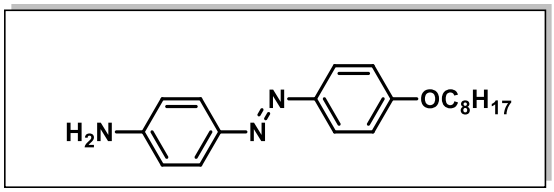
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.08 (s, 3H), 6.91 (br, 1H, -NH), 6.93 (br, 1H, -OH), 7.74-7.76 (m, 6H), 10.27-10.30 (d, J = 15.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 24.27, 116.04, 119.37, 123.11, 124.61, 141.67, 145.39, 147.69, 160.70, 168.95; HRMS TOF MS ES+ Theoretical m/z: 255.1008 Observed m/z: 256.1086.

8. (*E*)-*N*-(4-((4-(octyloxy) phenyl) diazenyl) phenyl) acetamide



To a dry DMF (35 mL) solution of compound 7 (3.7 g, 14.5 mM), potassium carbonate (20.04 g, 14.5 mM) and pinch of potassium iodide have been charged and stirred at RT. After ten minutes alkyl bromide (2.4 g, 14.5 mM) was added slowly and then the reaction mixture was heated to 100 ^{o}C. The reaction was monitored by TLC and after the completion, the DMF was evaporated under vacuum. The crude compound was used for the hydrolysis step without further purification.

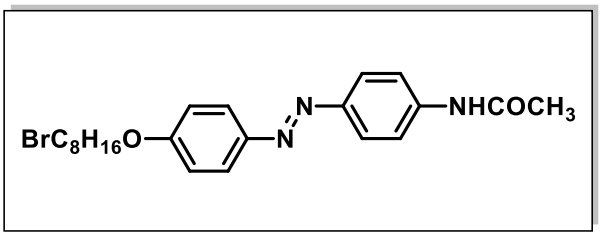
9. (*E*)-4-((4-(octyloxy) phenyl) diazenyl) aniline



To the crude compound 8 (1.75 g, 5.16 mM) in ethanol (150 mL), 37% con. HCl (4 mL) was added and let it refluxed. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was neutralized by adding aqueous sodium bicarbonate solution. The extraction of the reaction mixture was done in ethyl acetate. The extracted organic layer was washed with brine solution and evaporated to dryness and was purified by column chromatography (Eluent: 1:4 ethylacetate: n-hexane).

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.91-0.94 (t, *J* = 6.8 Hz, 3H), 1.32-1.37 (m, 8H), 1.46-1.54 (m, 2H), 1.81-1.85 (quin., 2H), 4.01 (br, 2H, -NH_2), 4.02-4.05 (t, *J* = 6.5 Hz, 2H), 6.74-6.76 (d, *J* = 8.6 Hz, 2H), 6.99-7.02 (d, *J* = 8.9 Hz 2H), 7.79-7.81 (d, *J* = 8.6 Hz, 2H), 7.86-7.88 (d, *J* = 8.8 Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.17, 22.71, 26.07, 29.27, 29.29, 29.41, 31.86, 68.32, 114.66, 114.74, 124.06, 124.66, 145.63, 147.06, 149.00, 160.82; HRMS TOF MS ES+ Theoretical m/z: 326.2232, Observed m/z: 326.2247.

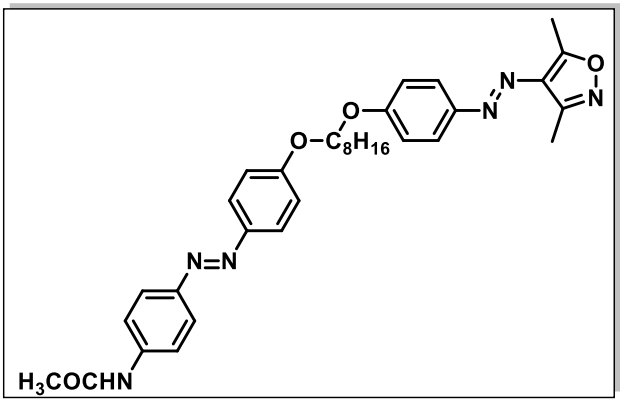
10. (*E*)-*N*-(4-((4-((8-bromooctyl) oxy) phenyl) diazenyl) phenyl) acetamide



To a dry DMF (35 mL) solution of compound 7 (3.7 g, 14.5 mM), potassium carbonate (20.04 g, 14.5 mM) and pinch of potassium iodide have been charged and stirred at RT. After ten minutes alkyl bromide (2.4 g, 14.5 mM) was added slowly and then the reaction mixture was heated to 100 ^{o}C. The reaction was monitored by TLC and after the completion, DMF was evaporated and product was extracted using EtOAc water. The extracted organic layer was washed with brine solution and dried using sodium sulfate. The organic layer was then evaporated to dryness and was purified by column chromatography (Silica, Eluent: 1:10 ethylacetate/n-hexane).

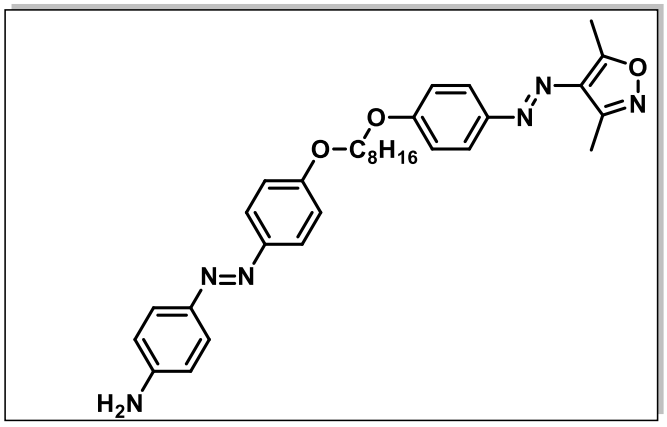
^{1}H NMR (400 MHz, DMSO-d_6): δ 1.31-1.41 (m, 8H), 1.71-1.80 (m, 4H), 2.09 (s, 3H), 3.49-3.53 (t, *J* = 6.7 Hz, 2H), 4.02-4.06 (t, *J* = 6.4 Hz, 2H), 7.07-7.10 (d, *J* = 8.9, 2H), 7.75-7.83 (m, 6H), 10.28 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 6.59, 24.29, 25.45, 27.60, 28.05, 28.57, 32.29, 35.40, 68.02, 115.12, 119.18, 122.73, 123.36, 124.40, 141.81, 146.12, 208.53; HRMS TOF MS ES+ Theoretical m/z: 446.1443, Observed m/z: 446.1423.

11. *N*-(4-((*E*)-(4-((8-(4-((*E*)-(3,5-dimethylisoxazol-4- yl) diazenyl) phenoxy) octyl) oxy) diazenyl) phenyl) acetamide



To ACN (35 mL) solution of compound 10 (2.4 g, 14.5 mM), potassium carbonate (20.04 g, 14.5 mM) and pinch of potassium iodide have been charged and stirred at RT. After ten minutes compound 2 (3.7 g, 14.5 mM) was added slowly and then the reaction mixture was heated to 85 ^{o}C. The reaction was monitored by TLC. After 10 hours, a yellow solid was obtained which was filtered, washed with acetonitrile and was dried in high vacuum to obtain the pure product.

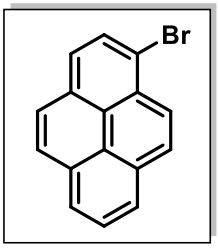
12. 4-((*E*)-(4-((8-(4-((*E*)-(3,5-dimethylisoxazol-4- yl) diazenyl) phenoxy) octyl)oxy) phenyl) diazenyl) aniline



To the crude compound 11 (1.75 g, 5.16 mM) in ethanol (150 mL), 37% con. HCl (4 mL) was added and let it refluxed. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was neutralized by adding aqueous sodium bicarbonate solution. The extraction of the reaction mixture was done in ethyl acetate. The extracted organic layer was washed with brine solution and evaporated to dryness and was purified by column chromatography (Eluent: 1:4 ethylacetate: n-hexane).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.29-1.43 (m, 8H), 1.73 (m, 4H), 2.43 (s, 3H), 2.71 (s, 3H), 4.00-4.05 (m, 4H), 5.97 (br, 2H, -NH_2), 6.64-6.66 (d, *J* = 8.7 Hz, 2H), 7.01-7.04 (d, *J* = 8.8 Hz, 2H), 7.06-7.08 (d, *J* = 8.9 Hz, 2H), 7.60-7.61 (d, *J* = 8.6 Hz, 2H), 7.70-7.72 (d, *J* = 8.8 Hz, 2H), 7.73-7.79 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 11.27, 11.66, 25.38, 25.41, 28.54, 28.60, 28.66, 67.77, 67.93, 113.40, 114.76, 114.91, 123.34, 123.85, 124.57, 131.52, 142.83, 146.36, 146.42, 152.07, 153.06, 159.81, 161.14, 168.53, 178.66; HRMS TOF MS ES+ Theoretical m/z: 541.2927, Observed m/z: 541.2901.

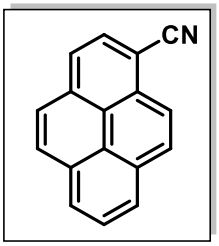
13. 1-Bromopyrene



To a stirred solution of pyrene (10.0 g, 49.5 mmol) in methanol and diethyl ether mixture (60 mL, 1:1), hydrobromic acid (9.2 mL of 48% aqueous solution, 54.4 mmol), and hydrogen peroxide (5.6 mL of 30% aqueous solution, 49.5 mmol) was added over a period of 15 min at 5−10 °C temperature. After complete addition, the reaction mixture was allowed to reach room temperature and stirred at room temperature for 12 h. The reaction progress was monitored by TLC. After the maximum conversion to mono bromopyrene, water (50 mL) was added to the reaction mixture, and the compound was extracted with DCM (3 × 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. Thus, the obtained residue was subjected to column chromatography (60− 120 mesh size silica) using hexane as eluent to obtain pure compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-8.06 (m, 4H), 8.09-8.20 (m, 4H), 8.36-8.39 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.94, 124.00, 125.02, 125.52, 125.57, 125.75, 125.82, 125.93, 126.52, 127.11, 127.46, 127.71, 128.98, 129.61, 130.03, 130.59, 130.95, 131.16.

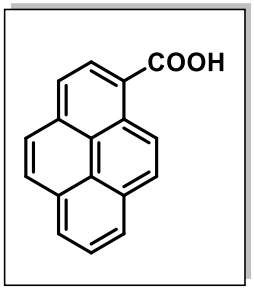
14. Pyrene-1-carbonitrile



A mixture of CuCN (3.16g, 35.37 mmol) and 1-bromopyrene (5 g, 17.685 mmol) in 30 mL of dry DMF was charged into a single-neck RB flask. The reaction mixture was refluxed for 24 h. The reaction mass was then cooled to room temperature, and 30% aq. ammonia solution (60 mL) was added. The precipitate obtained was filtered and washed with dilute aq. ammonia solution (10 mL) and then with water. This precipitate was then washed with dichloromethane thoroughly. The dichloromethane filtrate was dried over sodium sulfate, and the solvent was removed by rotary evaporator. The residue obtained was purified by column chromatography on silica gel 60−120 mesh, initially using 2% CHCl3/ hexane and cautiously increasing the polarity to 10% CHCl3/hexane.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.16 (m, 3H), 8.21-8.32 (m, 5H), 8.42-8.44 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 105.69, 119.00, 123.64, 124.07, 124.11, 124.55, 127.00, 127.09, 127.12, 127.20, 129.69, 130.64, 130.95, 133.10, 134.32.

15. Pyrene-1-carboxylic acid

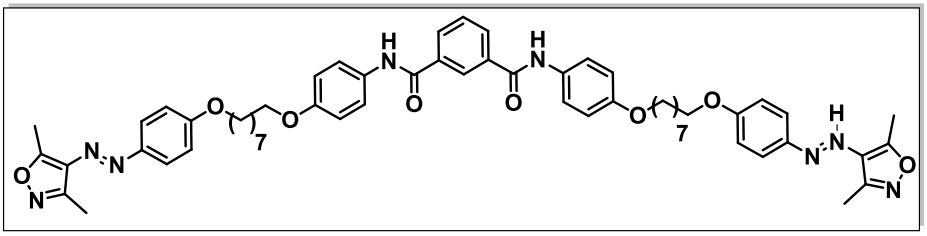


A mixture of compound 14 (2.2g, 7.5 mmol), aqueous solution of NaOH (4M, 60 mL) and absolute ethanol (90 mL) was heated at 100 ºC in a 250 mL RB flask for 1 day. After

cooling to RT, the mixture was acidified with 37% HCL until pH became 1. The product precipitated out and was collected by filtration. The compound was then washed with deionized water and absolute ethanol.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.78 (br, 1H, -COOH), 8.19-8.36 (m, 9H), 8.61-8.63 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 123.69, 123.87, 124.42, 124.89, 125.31, 125.62, 125.82, 126.61, 127.27, 127.78, 128.06, 128.30, 130.21, 130.75, 131.62, 131.85, 170.95; HRMS TOF MS ES+ Theoretical m/z: 245.0603, Observed m/z: 245.0610.

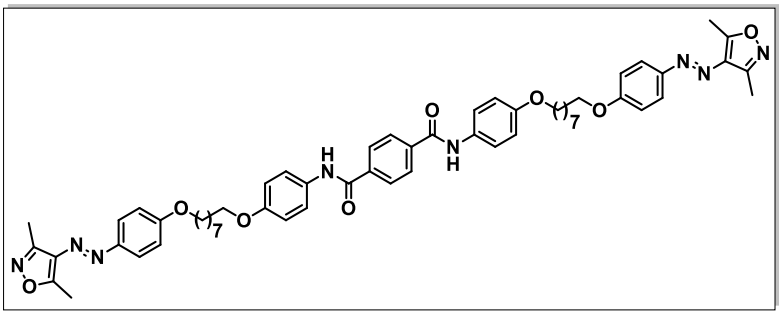
16. *N*1, *N*3-bis(4-((8-(4-((*E*)-(3,5-dimethylisoxazol-4-yl) diazenyl) phenoxy) octyl) oxy)phenyl) isophthalamide.



50 mg (1 Eq.) of isophthalic acid was added to 10 mL $SOCl_2$ in a 25 mL RB and was stirred at 60 ^{o}C for 5 hours. Once the clear solution formed, the excess $SOCl_2$ was removed by heating at 80 ^{o}C. When all $SOCl_2$ evaporated, we added 1, 2-DCE (5 mL) to the RB to dissolve the acid chloride. In a separate 50 mL RB, 165 mg (2.5 Eq.) of compound 6 was dissolved in 1, 2-DCE along with 0.1 mL (4 Eq.) Et_3N. To this mixture, the contents of the 25 mL RB was added dropwise under inert conditions at 0 ^{o}C. After the addition, the reaction mixture was stirred at RT for 12 hours. The precipitate obtained was filtered and was washed with $CHCl_3$ and EtOH. We thus obtained pure compound as light yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.38-1.43 (m, 16H), 1.70-1.75 (m, 8H), 2.44 (s, 6H), 2.72 (s, 6H), 3.93-3.96 (t, *J* = 5.2 Hz, 4H), 4.05-4.08 (t, *J* = 5.7 Hz, 3H), 6.92-6.94 (d, *J* = 8.6 Hz, 4H), 7.08-7.10 (t, *J* = 8.7 Hz, 4H), 7.66-7.68 (d, *J* = 8.5 Hz, 4H), 7.78-7.80 (d, *J* = 8.8 Hz, 4H), 8.09-8.11 (m, 2H), 8.49 (s, 1H), 10.28 (s, 2H); HRMS TOF MS ES+ Theoretical m/z: 1003.5082, Observed m/z: 1003.5049.

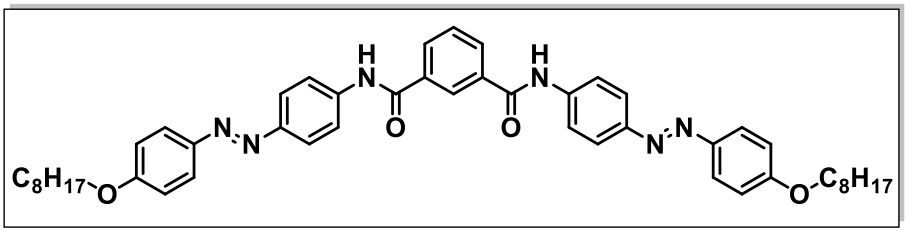
17. *N*1,*N*4-bis(4-((8-(4-((*E*)-(3,5-dimethylisoxazol-4-yl) diazenyl) phenoxy) octyl) oxy) phenyl) terephthalamide



50 mg (1 Eq.) of terephthalic acid was added to 10 mL $SOCl_2$ in a 25 mL RB and was stirred at 60 ^oC for 5 hours. Once the clear solution formed, the excess $SOCl_2$ was removed by heating at 80 ^oC. When all $SOCl_2$ evaporated, we added 1, 2-DCE (5 mL) to the RB to dissolve the acid chloride. In a separate 50 mL RB, 165 mg (2.5 Eq.) of compound 6 was dissolved in 1, 2-DCE along with 0.1 mL (4 Eq.) Et_3N. To this mixture, the contents of the 25 mL RB was added dropwise under inert conditions at 0 ^oC. After the addition, the reaction mixture was stirred at RT for 12 hours. The precipitate obtained was filtered and was washed with $CHCl_3$ and EtOH. We thus obtained pure compound as light yellow solid.

^1H NMR (400 MHz, DMSO-d_6): δ 1.33-1.44 (m, 16H), 1.70-1.77 (m, 8H), 2.45 (s, 6H), 2.72 (s, 6H), 3.94-3.97 (t, *J* = 5.9 Hz, 4H), 4.05-4.09 (t, *J* = 6.3 Hz, 4H), 6.92-6.94 (d, *J* = 9.0 Hz, 4H), 7.08-7.11 (d, *J* = 8.6 Hz, 4H), 7.66-7.68 (d, *J* = 8.7 Hz, 4H), 7.78-7.80 (d, *J* = 8.8 Hz, 4H), 8.06 (s, 4H), 10.24 (s, 2H); HRMS TOF MS ES+ Theoretical m/z: 1003.5082, Observed m/z: 1003.2133.

18. *N*1,*N*3-bis(4-((*E*)-(4-(octyloxy) phenyl) diazenyl) phenyl) isophthalamide

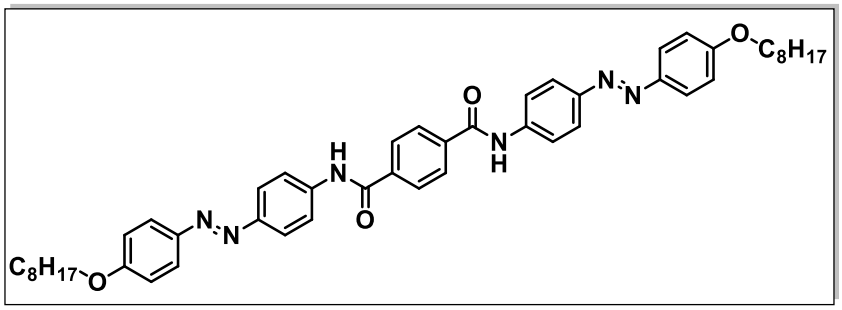


50 mg (1 Eq.) of isophthalic acid was added to 10 mL $SOCl_2$ in a 25 mL RB and was stirred at 60 ^oC for 5 hours. Once the clear solution formed, the excess $SOCl_2$ was removed by heating at 80 ^oC. When all $SOCl_2$ evaporated, we added 1, 2-DCE (5 mL) to the RB to dissolve the acid chloride. In a separate 50 mL RB, 160 mg (2.5 Eq.) of compound 9 was dissolved in

1, 2-DCE along with 0.1 mL (4 Eq.) Et_3N. To this mixture, the contents of the 25 mL RB was added dropwise under inert conditions at 0 ^oC. After the addition, the reaction mixture was stirred at RT for 12 hours. The precipitate obtained was filtered and was washed with $CHCl_3$ and EtOH. We thus obtained pure compound as light yellow solid.

^1H NMR (400 MHz, DMSO-d_6): δ 0.85-0.88 (t, *J* = 3.3 Hz, 6H), 1.23-1.45 (m, 24H), 1.72-1.77 (m, 4H), 4.06-4.09 (t, *J* = 6.3 Hz, 4H), 6.88 (s, 2H), 7.11-7.13 (d, *J* = 8.4 Hz, 4H), 7.86-7.90 (t, *J* = 9.5 Hz, 6H), 8.01-8.09 (m, 12H), 8.32 (s, 2H), 10.72 (s, 2H), 13.30 (br, 2H, -NH); HRMS TOF MS ES+ Theoretical m/z: 781.4441, Observed m/z: 781.4476.

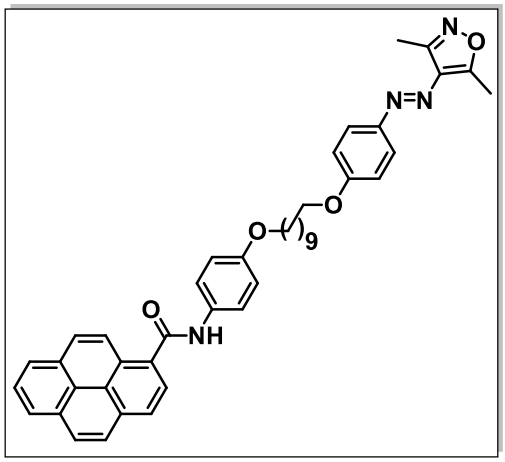
19. *N*1,*N*4-bis(4-((*E*)-(4-(octyloxy) phenyl) diazenyl) phenyl) terephthalamide



50 mg (1 Eq.) of terephthalic acid was added to 10 mL $SOCl_2$ in a 25 mL RB and was stirred at 60 ^oC for 5 hours. Once the clear solution formed, the excess $SOCl_2$ was removed by heating at 80 ^oC. When all $SOCl_2$ evaporated, we added 1, 2-DCE (5 mL) to the RB to dissolve the acid chloride. In a separate 50 mL RB, 160 mg (2.5 Eq.) of compound 9 was dissolved in 1, 2-DCE along with 0.1 mL (4 Eq.) Et_3N. To this mixture, the contents of the 25 mL RB was added dropwise under inert conditions at 0 ^oC. After the addition, the reaction mixture was stirred at RT for 12 hours. The precipitate obtained was filtered and was washed with $CHCl_3$ and EtOH. We thus obtained pure compound as light yellow solid.

^1H NMR 400 MHz, DMSO-d_6): δ 0.85-0.88 (t, *J* = 5.8 Hz, 6H), 1.27-1.45 (m, 24H), 1.71-1.77 (m, 4H), 4.06-4.09 (t, *J* = 6.6 Hz, 4H), 6.87 (s, 2H), 7.11-7.13 (d, *J* = 8.8 Hz, 4H), 7.85-8.00 (t, *J* = 9.3 Hz, 6H), 8.01-8.09 (m, 12H), 8.32 (s, 1H), 10.72 (s, 1H), 13.27 (br, 2H, -NH); HRMS TOF MS ES+ Theoretical m/z: 781.4441, Observed m/z: 781.4476.

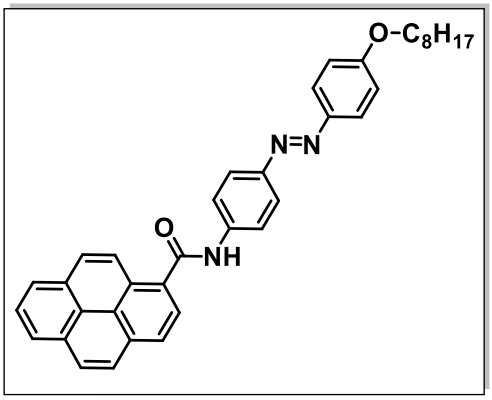
20. (*E*)-*N*-(4-((10-(4-((3,5-dimethylisoxazol-4-yl) diazenyl) phenoxy) decyl)oxy) phenyl) pyrene-1-carboxamide



50 mg (1 Eq.) of pyrene-1-carboxylic acid was added to 10 mL $SOCl_2$ in a 25 mL RB and was stirred at 60 ^oC for 5 hours. Once the clear solution formed, the excess $SOCl_2$ was removed by heating at 80 ^oC. When all $SOCl_2$ evaporated, we added 1, 2-DCE (5 mL) to the RB to dissolve the acid chloride. In a separate 50 mL RB, 186 mg (2.0 Eq.) of compound 6 was dissolved in 1, 2-DCE along with 0.1 mL (4 Eq.) Et_3N. To this mixture, the contents of the 25 mL RB was added dropwise under inert conditions at 0 ^oC. After the addition, the reaction mixture was stirred at RT for 12 hours. The precipitate obtained was filtered and was washed with $CHCl_3$ and EtOH. We thus obtained pure compound as light yellow solid.

^1H NMR (400 MHz, DMSO-d_6): δ 1.33-1.42 (m, 12H), 1.69-1.76 (m, 4H), 2.44 (s, 3H), 2.71 (s, 3H), 3.96-3.99 (t, *J* = 6.6 Hz, 2H), 4.05-4.08 (t, *J* = 6.3 Hz, 2H), 6.96-7.01 (m, 2H), 7.08-7.12 (m, 2H), 7.76-7.80 (t, *J* = 8.2 Hz, 4H), 8.12-8.16 (t, *J* = 7.5 Hz, 1H), 8.25-8.30 (m, 4H), 8.36-8.40 (m, 3H), 8.47-8.50 (d, J = 8.9 Hz, 1H); HRMS TOF MS ES+ Theoretical m/z: 693.3441, Observed m/z: 693.3530.

21. (*E*)-*N*-(4-((4-(octyloxy) phenyl) diazenyl) phenyl) pyrene-1-carboxamide



50 mg (1 Eq.) of pyrene-1-carboxylic acid was added to 10 mL $SOCl_2$ in a 25 mL RB and was stirred at 60 ^oC for 5 hours. Once the clear solution formed, the excess $SOCl_2$ was removed by heating at 80 ^oC. When all $SOCl_2$ evaporated, we added 1, 2-DCE (5 mL) to the RB to dissolve the acid chloride. In a separate 50 mL RB, 160 mg (2.0 Eq.) of compound 9 was dissolved in 1, 2-DCE along with 0.1 mL (4 Eq.) Et_3N. To this mixture, the contents of the 25 mL RB was added dropwise under inert conditions at 0 ^oC. After the addition, the reaction mixture was stirred at RT for 12 hours. The precipitate obtained was filtered and was washed with $CHCl_3$ and EtOH. We thus obtained pure compound as light yellow solid.

^1H NMR (400 MHz, DMSO-d_6): δ 0.85-0.88 (t, *J* = 5.9 Hz, 3H), 1.27-1.47 (m, 10H), 1.72-1.77 (m, 2H), 4.06-4.10 (t, *J* = 6.4 Hz, 2H), 6.91 (s, 1H), 7.12-7.14 (d, *J* = 8.6 Hz, 2H), 7.88-7.90 (d, *J* = 8.4 Hz, 2H), 7.93-7.95 (d, *J* = 8.4 Hz, 2H), 8.10-8.11 (d, *J* = 8.6 Hz, 2H), 8.14-8.18 (t, *J* = 7.4 Hz, 2H), 8.28-8.35 (m, 4H), 8.39-8.44 (m, 3H), 8.51-8.53 (d, *J* = 8.4 Hz, 1H), 11.10 (s, 1H); HRMS TOF MS ES+ Theoretical m/z: 554.2808, Observed m/z: 554.2825.

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Appendix

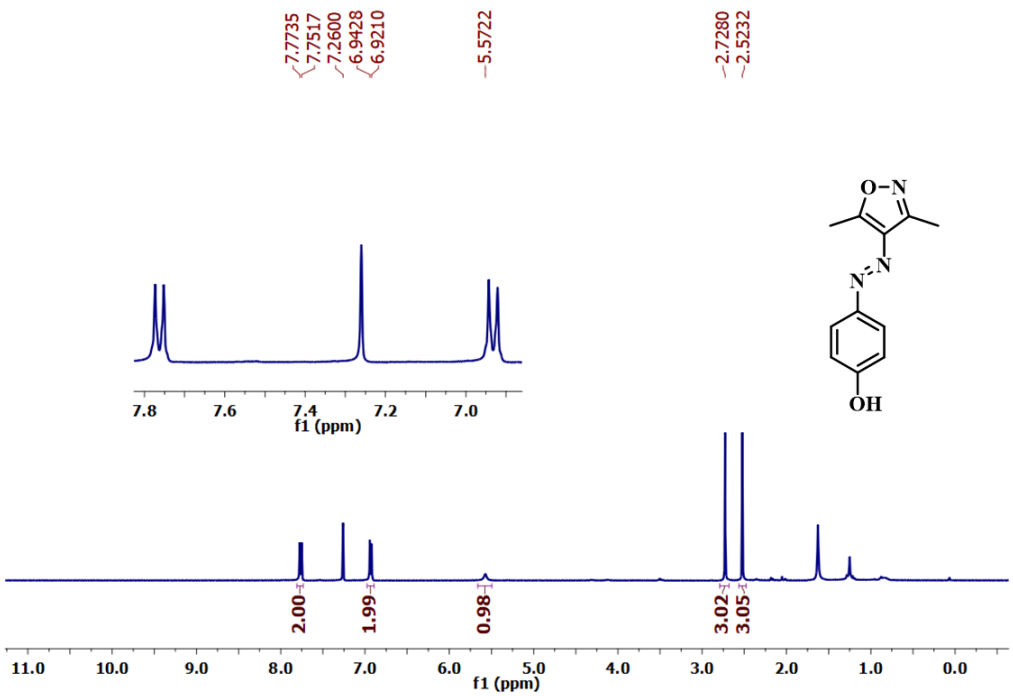

Figure A1: ^{1}H NMR spectrum of molecule **2** in $CDCl_3$.

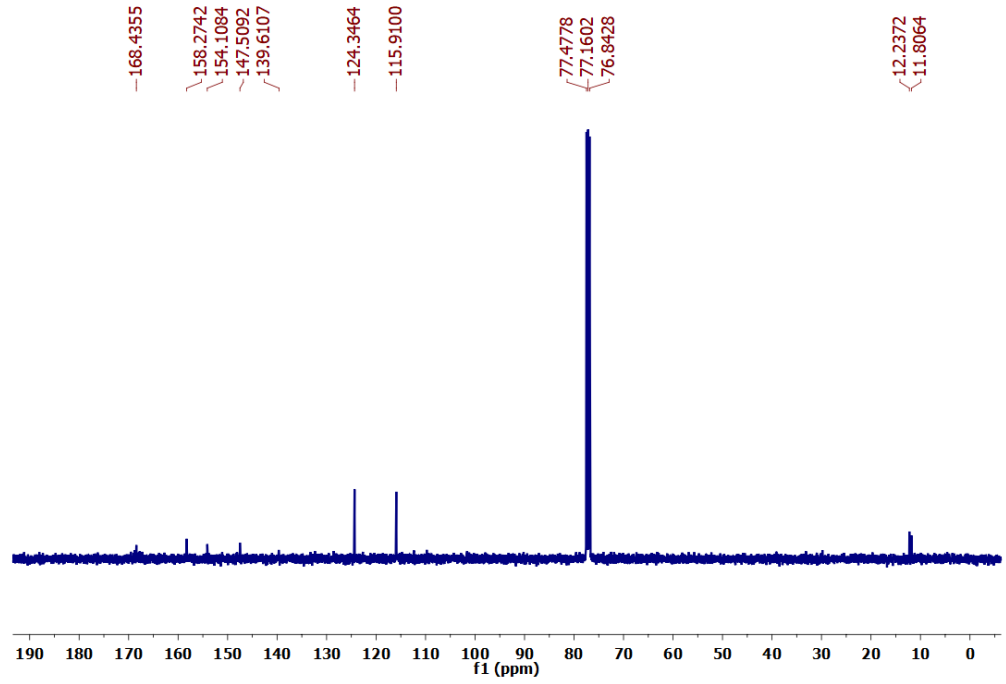

Figure A2: ^{13}C NMR spectrum of molecule **2** in $CDCl_3$.

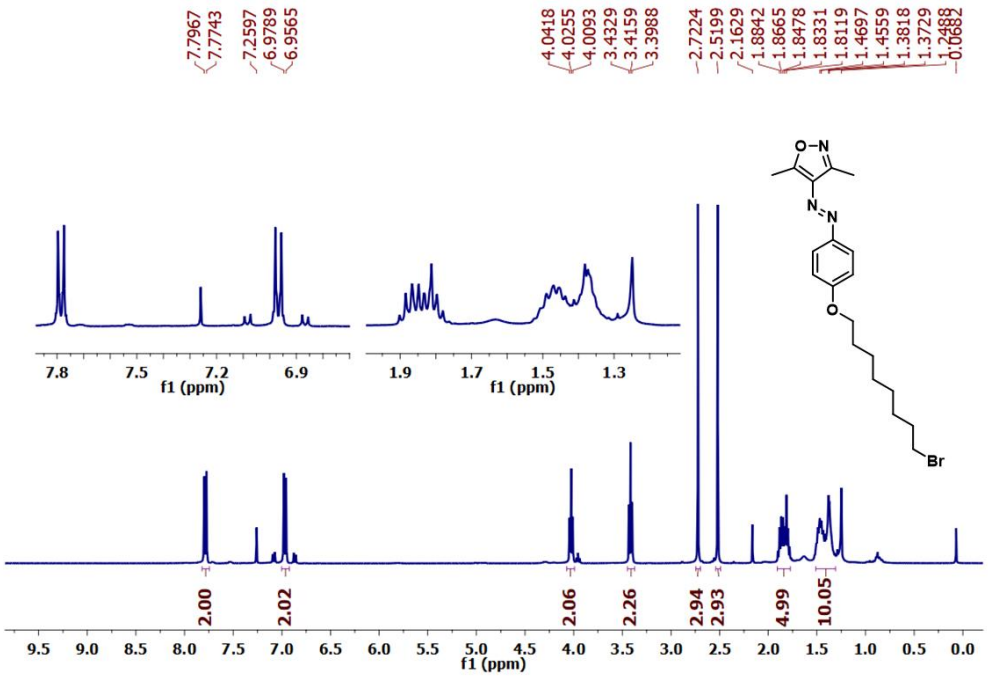

Figure A3: ^{1}H NMR spectrum of molecule **3** in $CDCl_3$.

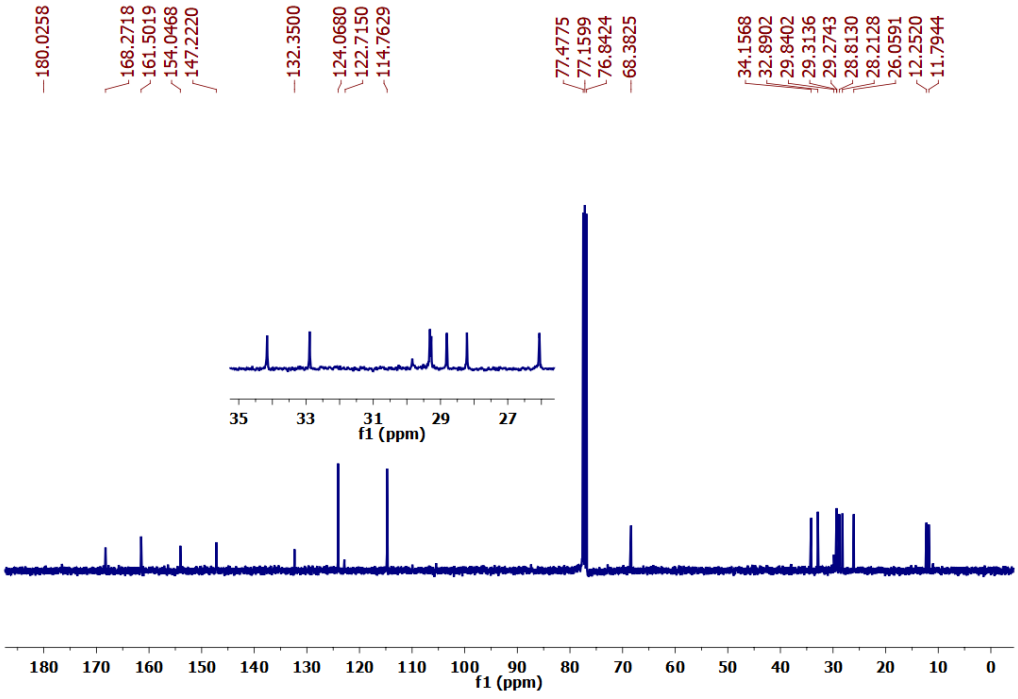

Figure A4: ^{13}C NMR spectrum of molecule **3** in $CDCl_3$.

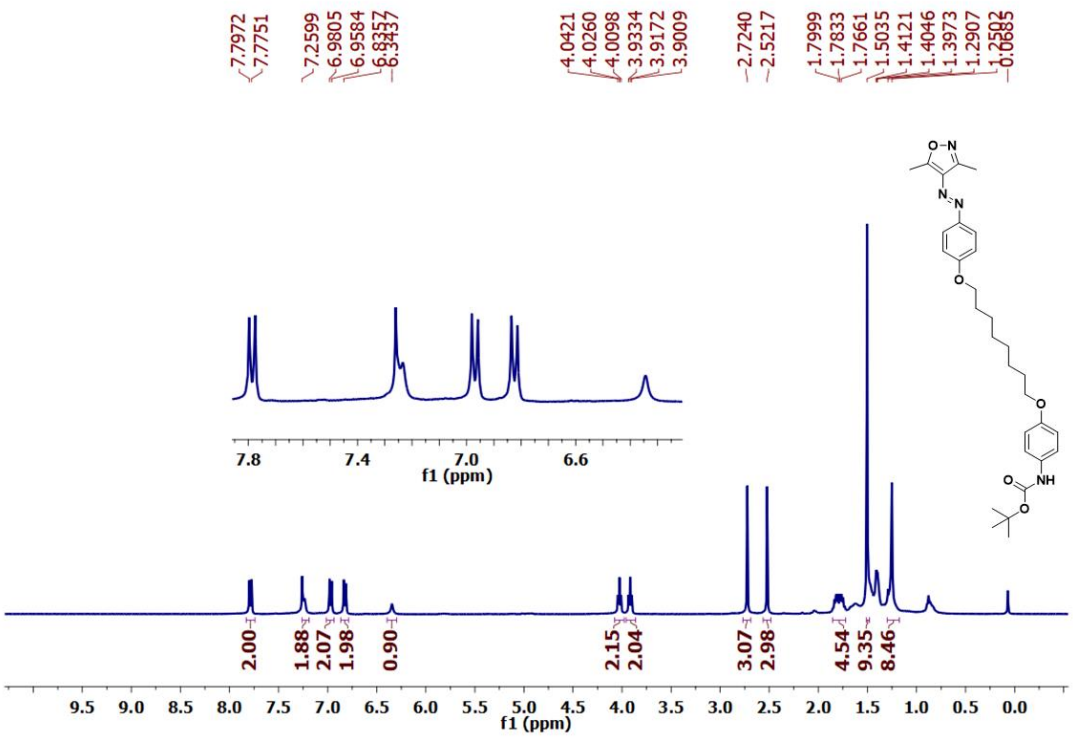

Figure A5: ^{1}H NMR spectrum of molecule **5** in $CDCl_3$.

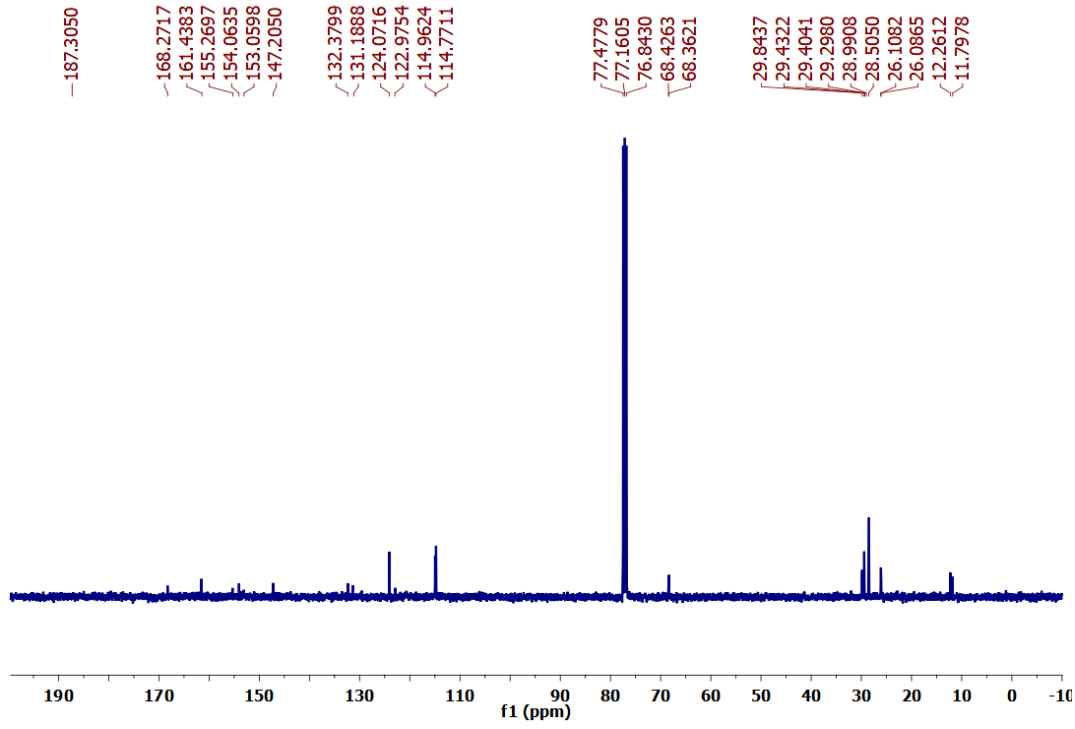

Figure A6: ^{13}C NMR spectrum of molecule **5** in $CDCl_3$.

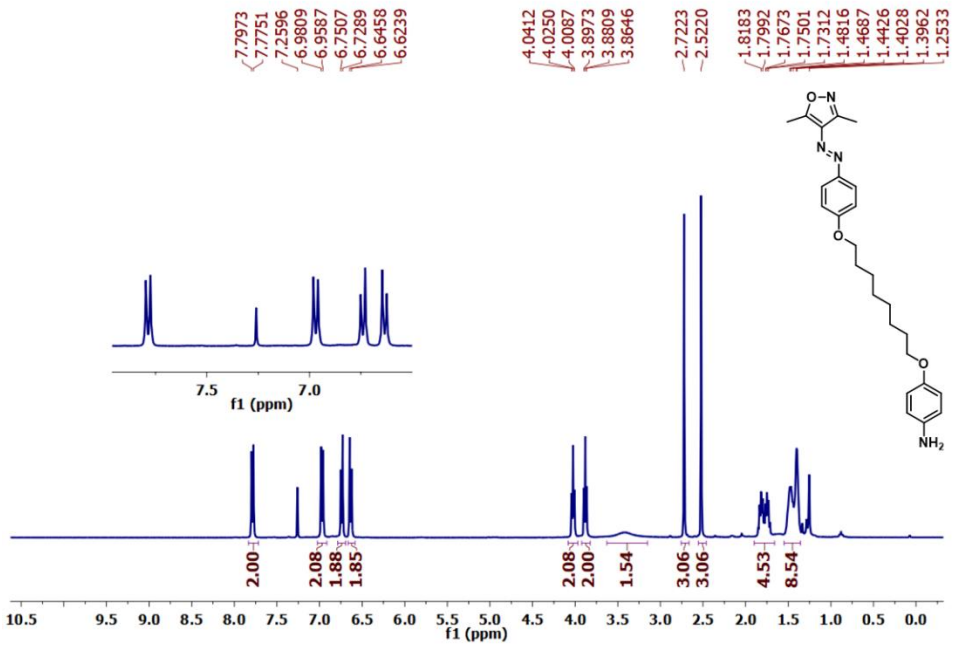

Figure A7: ^{1}H NMR spectrum of molecule **6** in $CDCl_3$.

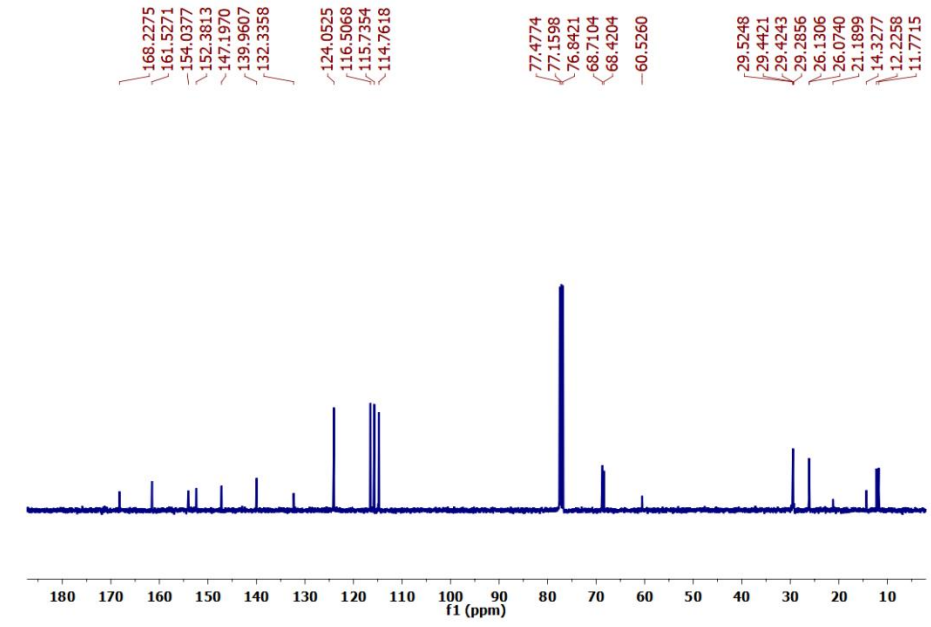

Figure A8: ^{13}C NMR spectrum of molecule **6** in $CDCl_3$.

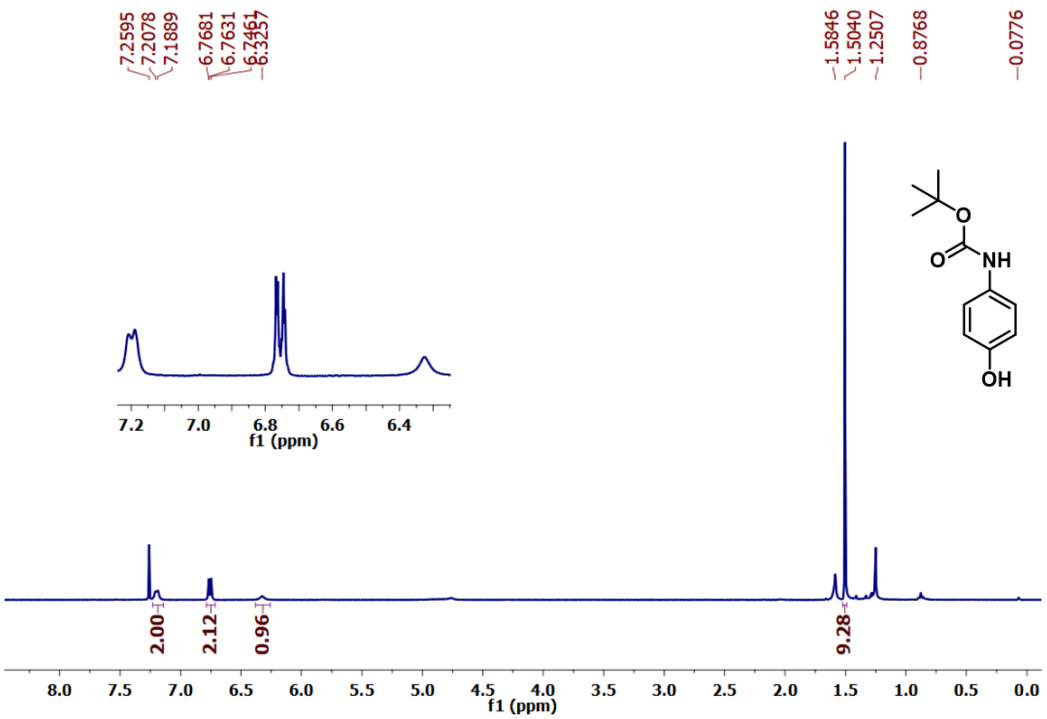

Figure A9: ^{1}H NMR spectrum of molecule **4** in $CDCl_3$.

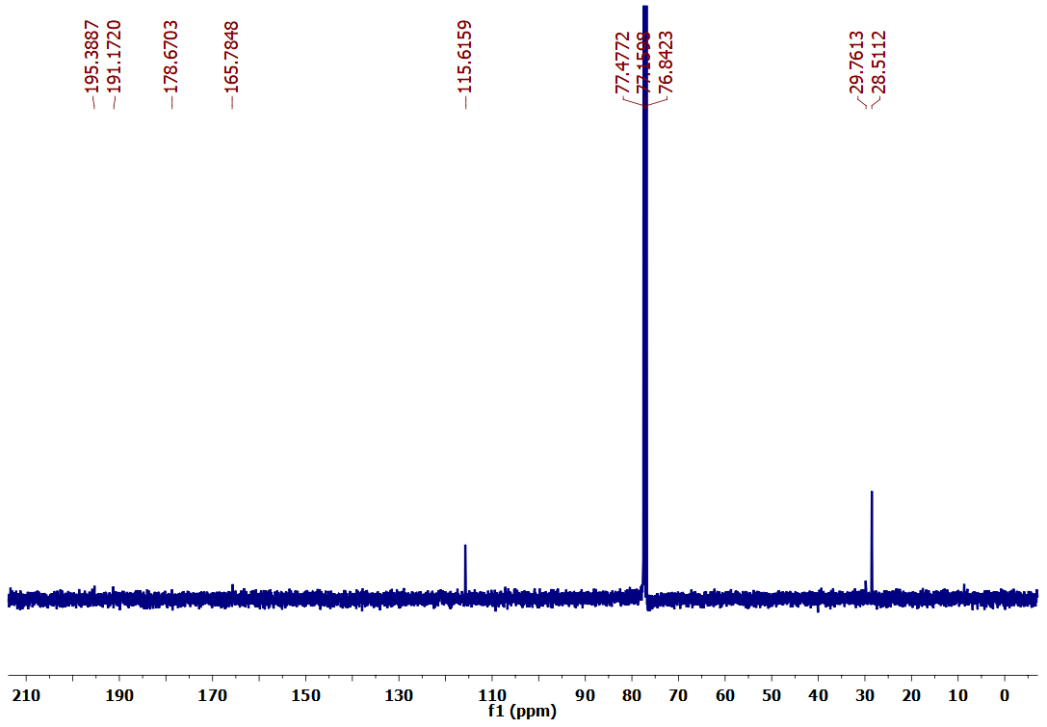

Figure A10: ^{13}C NMR spectrum of molecule **4** in $CDCl_3$.

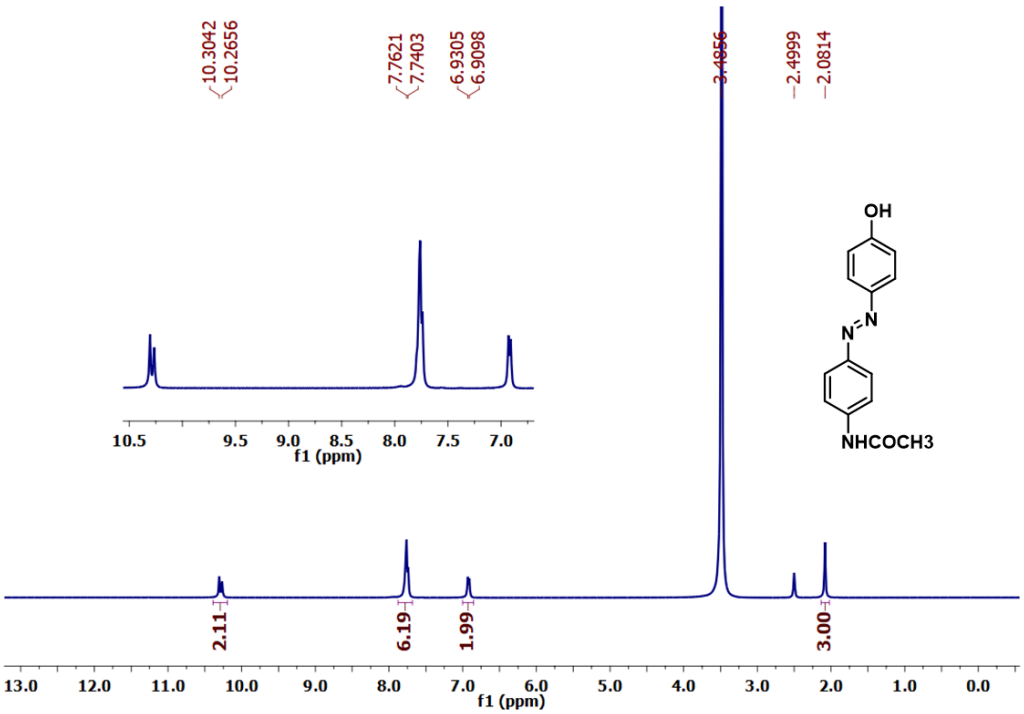

Figure A11: ^{1}H NMR spectrum of molecule **7** in DMSO-d_6.

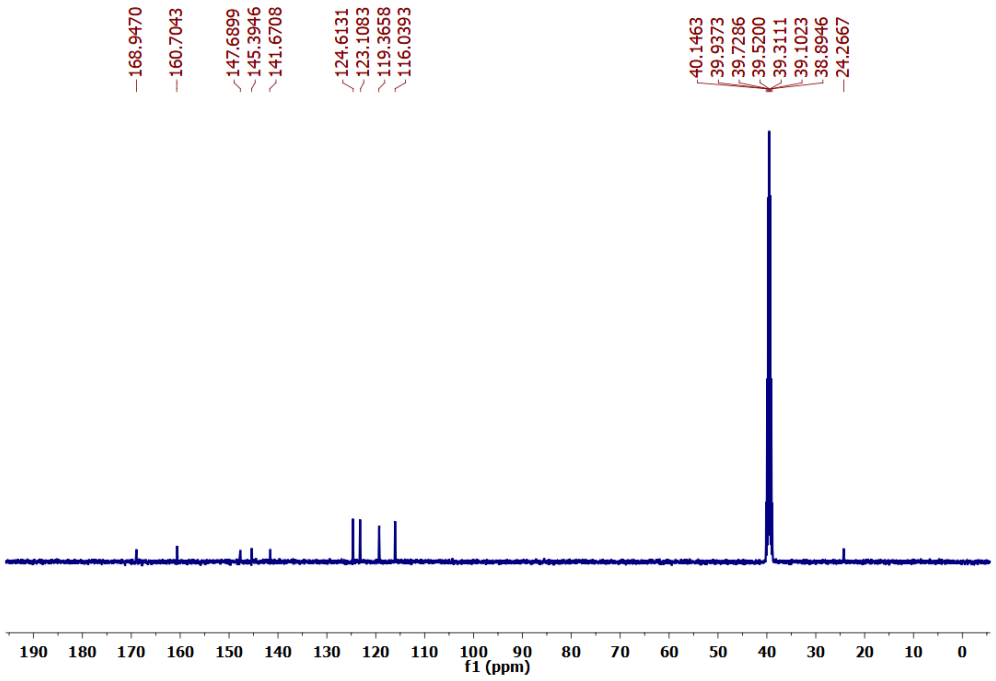

Figure A12: ^{13}C NMR spectrum of molecule **7** in DMSO-d_6.

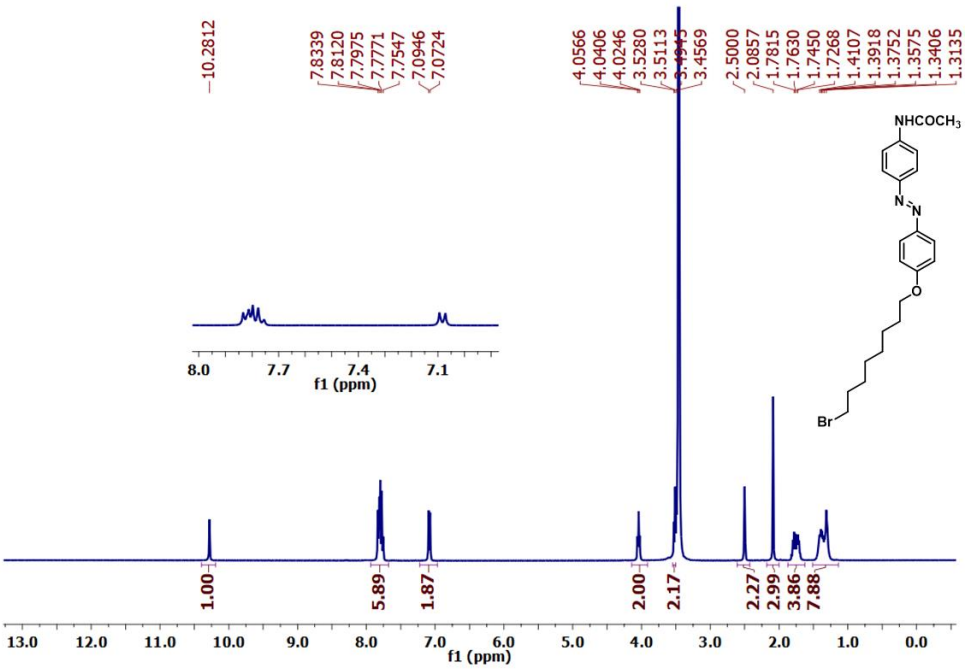

Figure A13: ^{1}H NMR spectrum of molecule **10** in $CDCl_3$.

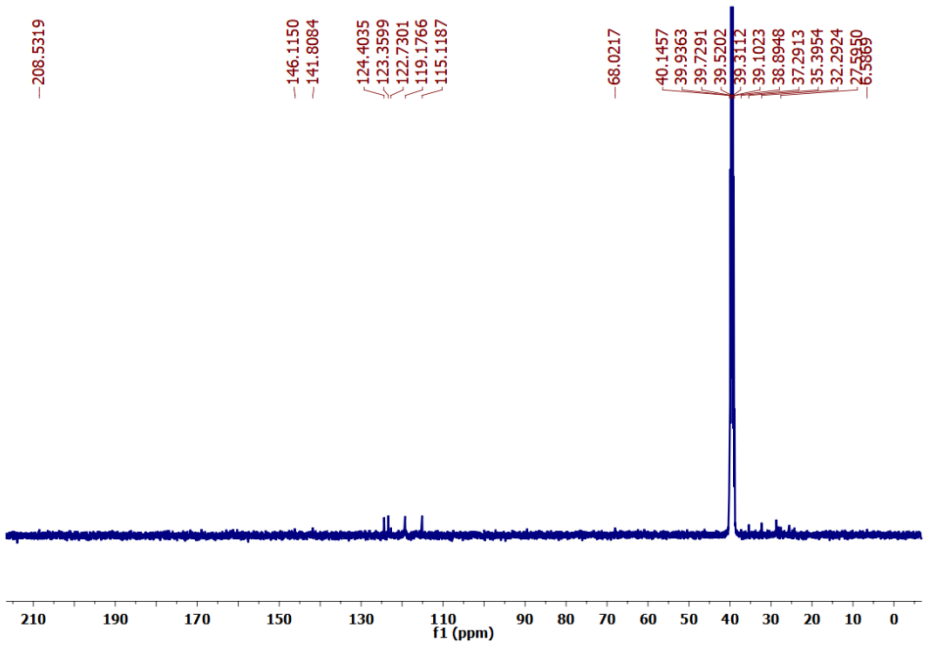

Figure A14: ^{13}C NMR spectrum of molecule **10** in $CDCl_3$.

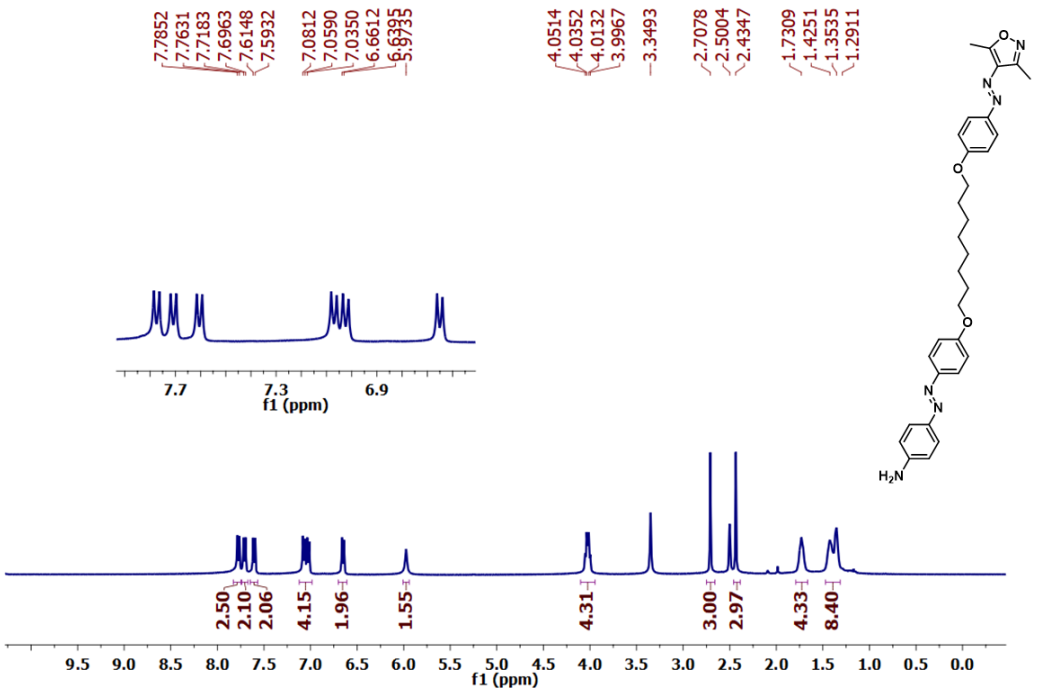

Figure A15: ^{1}H NMR spectrum of molecule **12** in DMSO-d_6.

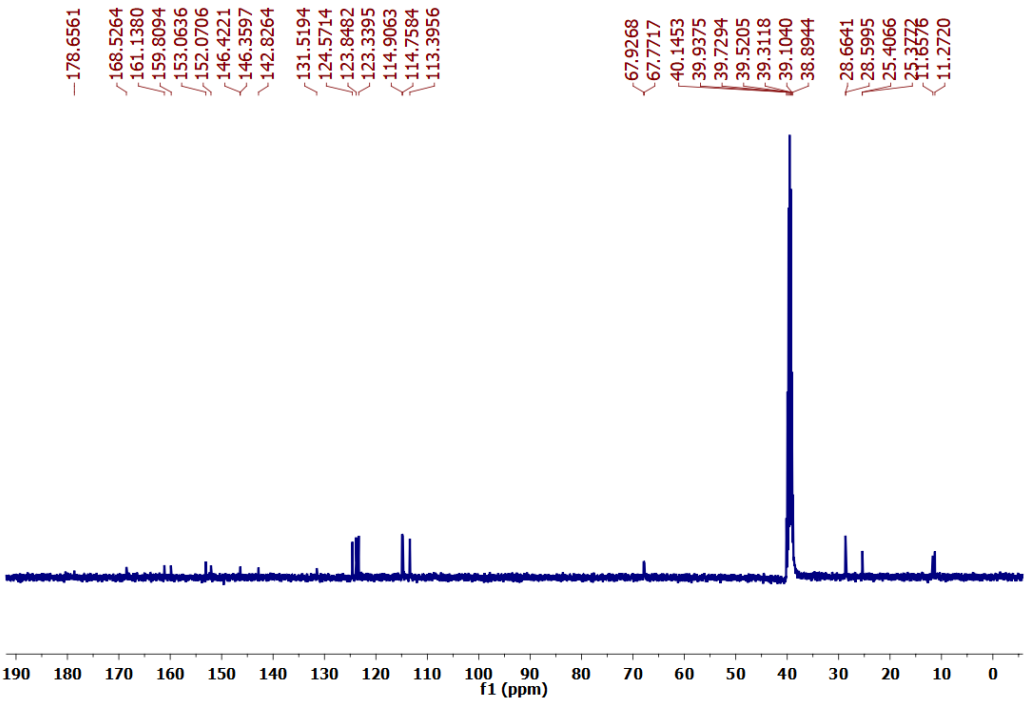

Figure A16: ^{13}C NMR spectrum of molecule **12** in DMSO-d_6.

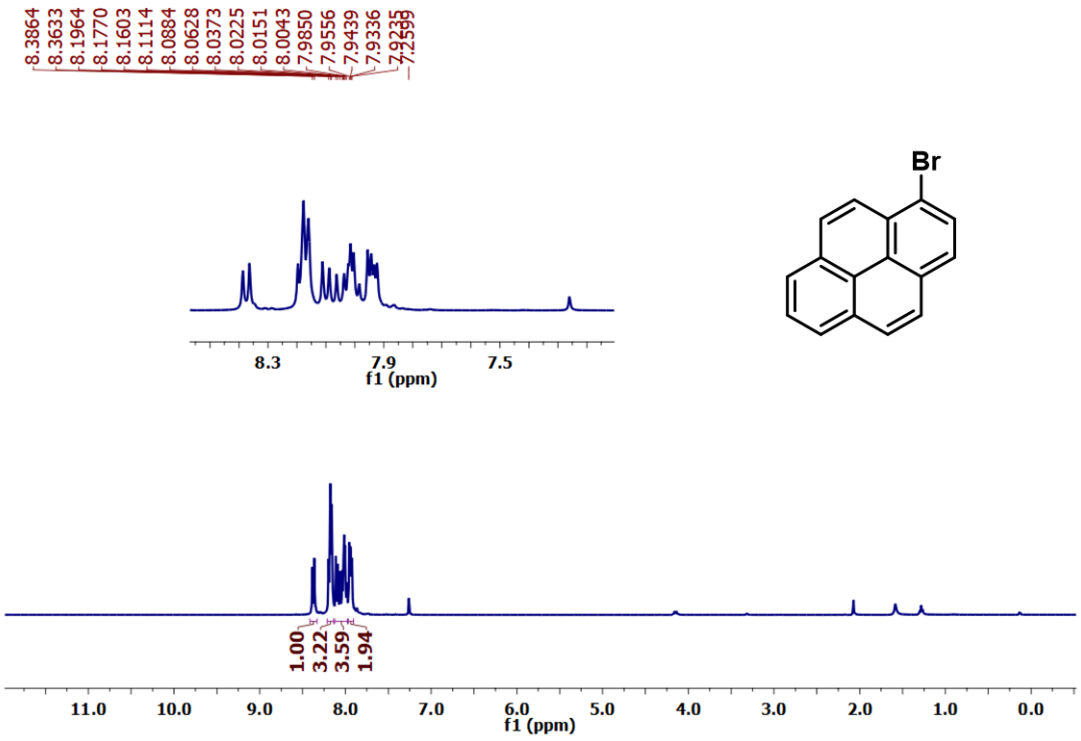

Figure A17: ^{1}H NMR spectrum of molecule **13** in $CDCl_3$.

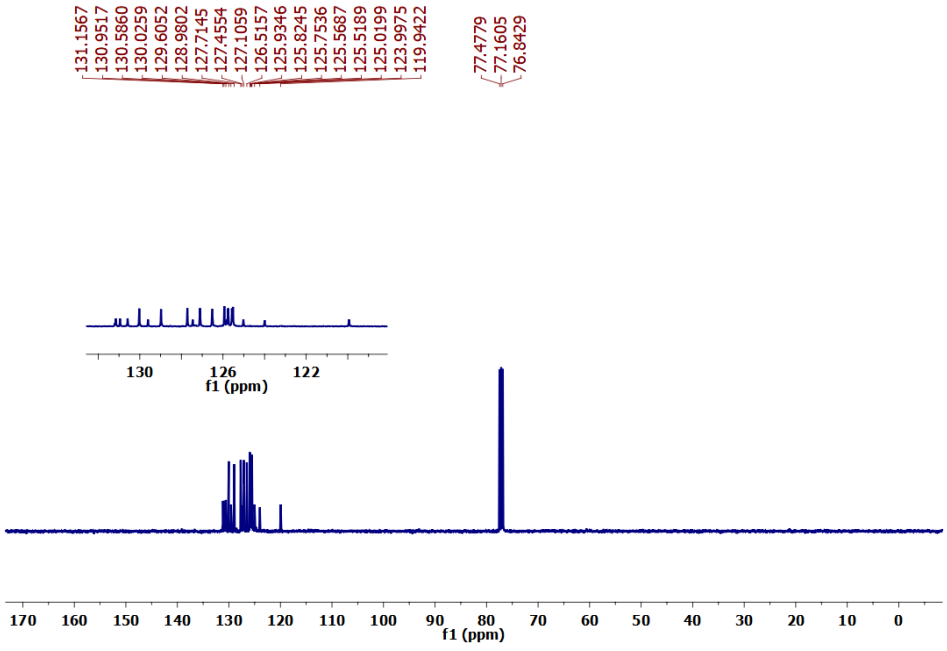

Figure A18: ^{13}C NMR spectrum of molecule **13** in $CDCl_3$.

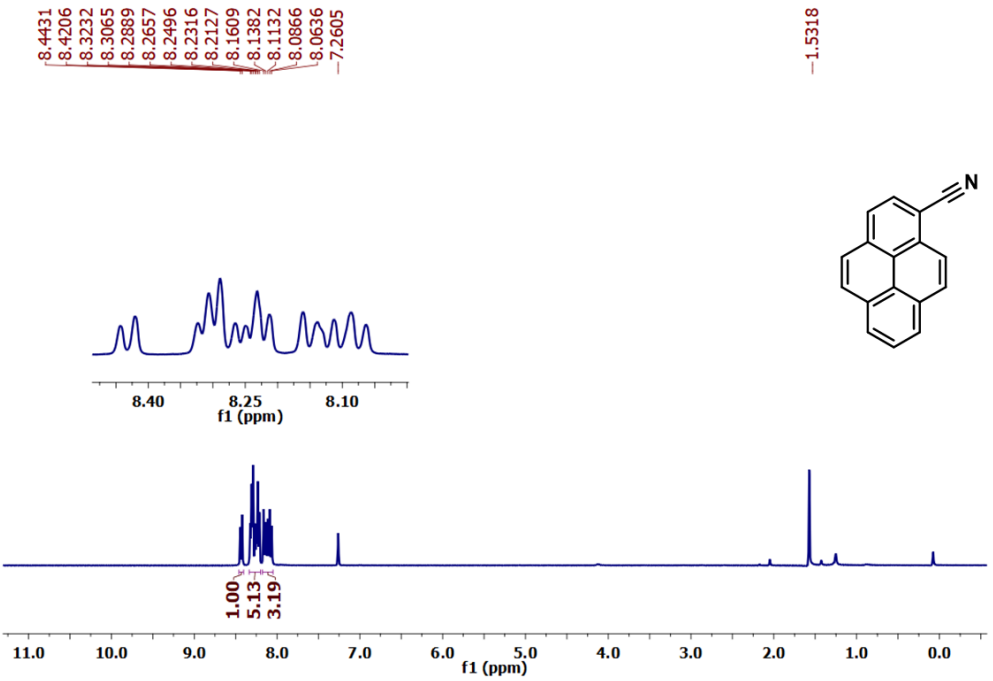

Figure A19: ^{1}H NMR spectrum of molecule **14** in $CDCl_3$.

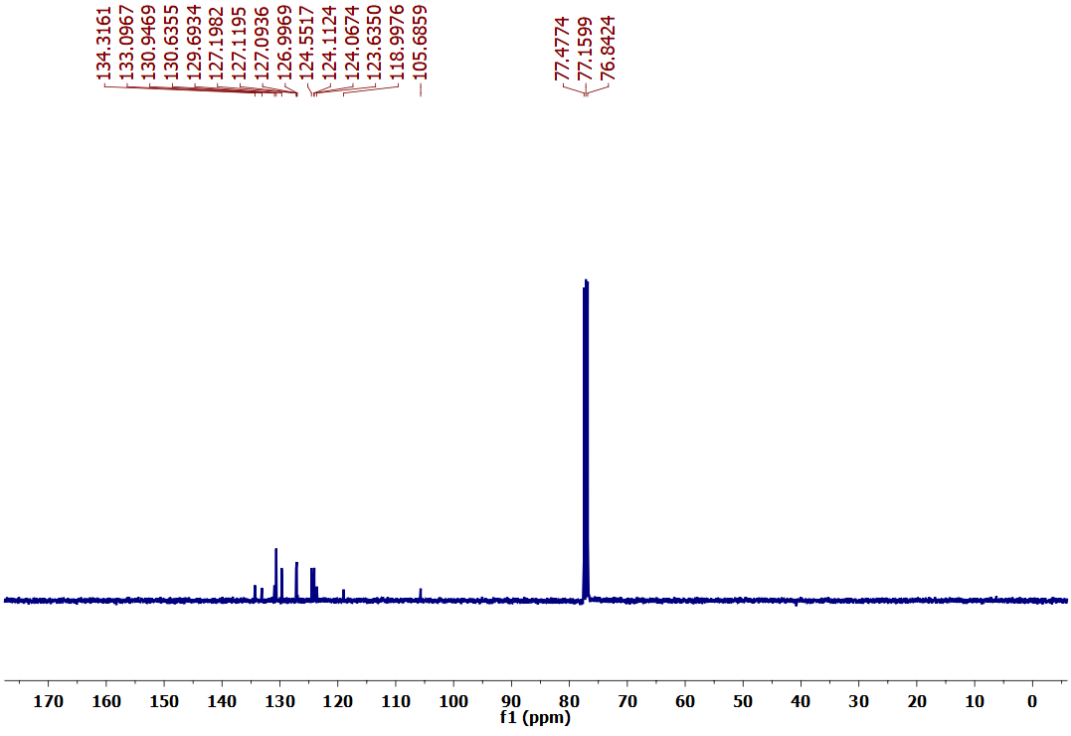

Figure A20: ^{13}C NMR spectrum of molecule **14** in $CDCl_3$.

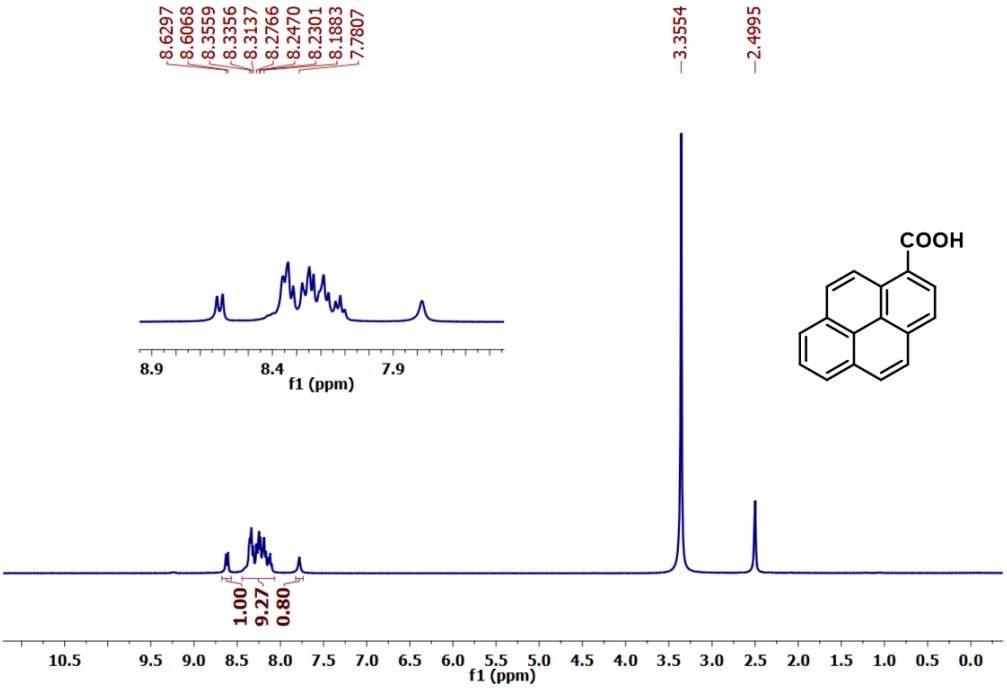

Figure A21: ^{1}H NMR spectrum of molecule **15** in DMSO-d$_6$.

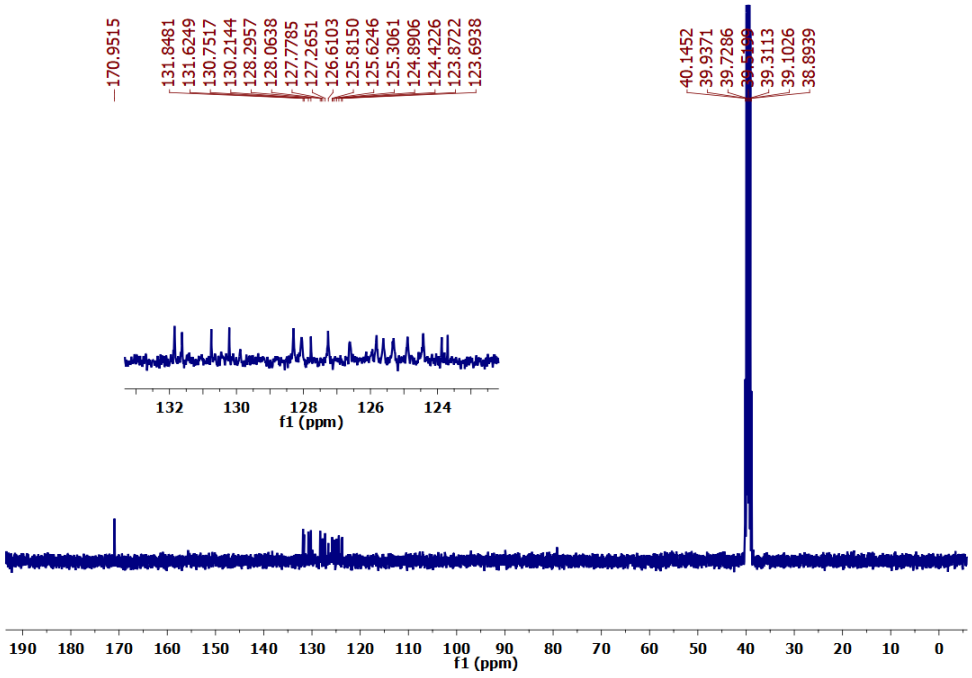

Figure A22: ^{13}C NMR spectrum of molecule **15** in DMSO-d$_6$.

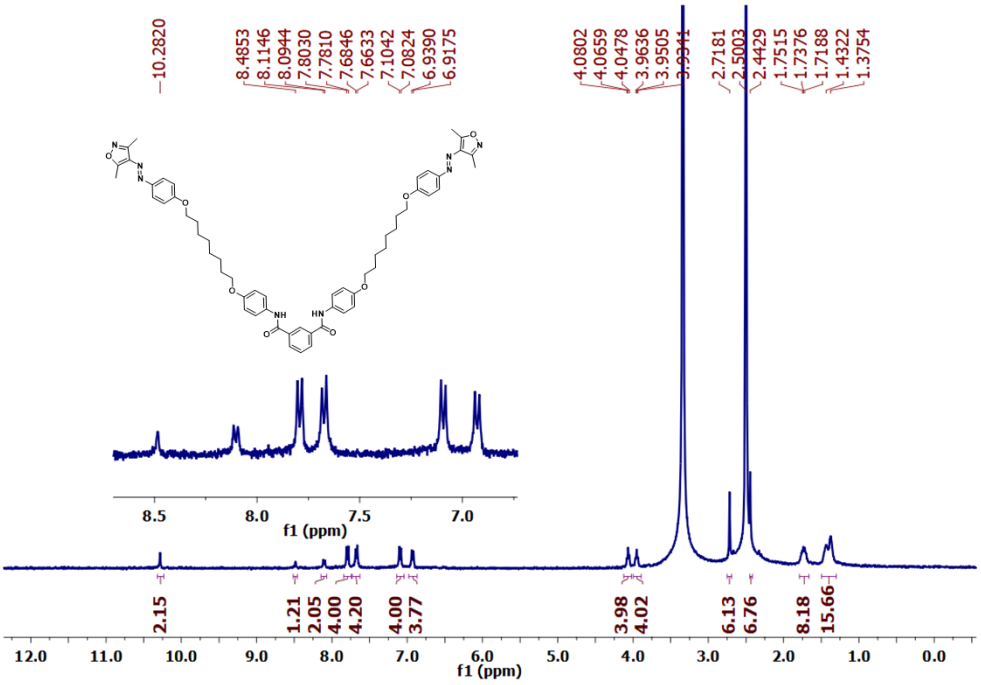

Figure A23: ^{1}H NMR spectrum of molecule **16** in DMSO-d_6.

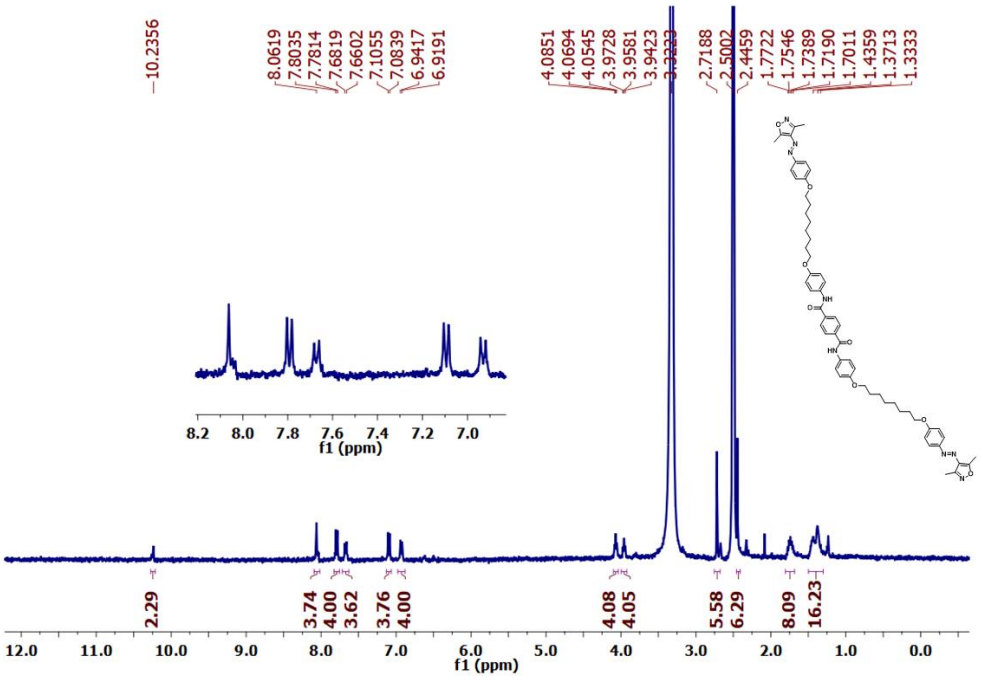

Figure A24: ^{1}H NMR spectrum of molecule **17** in DMSO-d_6.

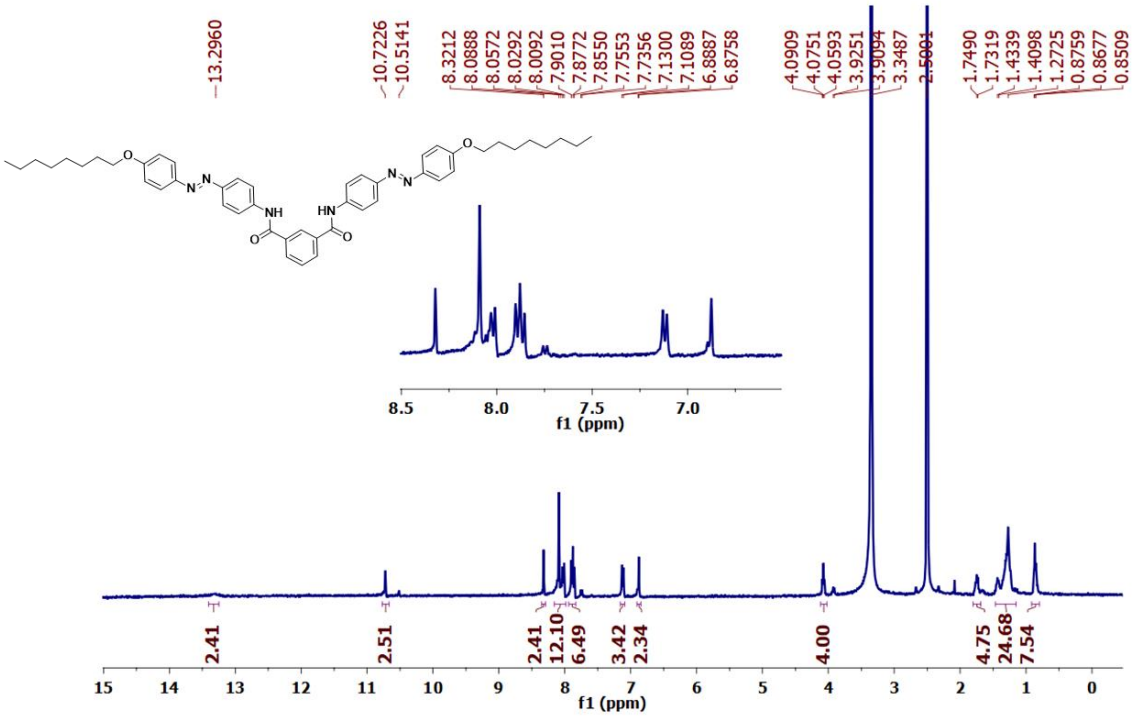

Figure A25: ^{1}H NMR spectrum of molecule **18** in DMSO-d_6

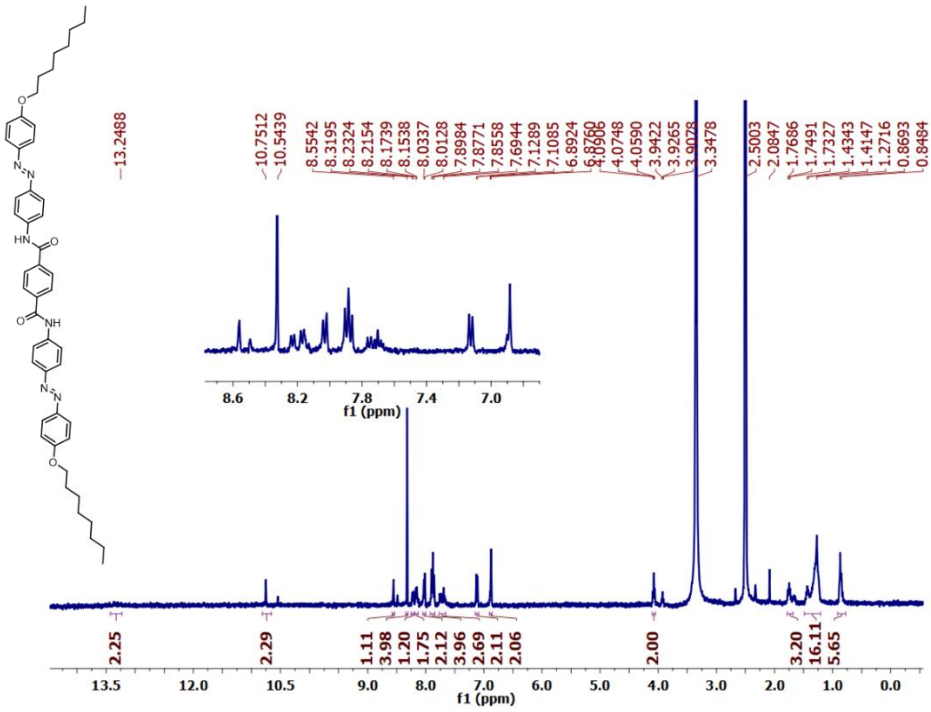

Figure A26: ^{1}H NMR spectrum of molecule **19** in DMSO-d_6.

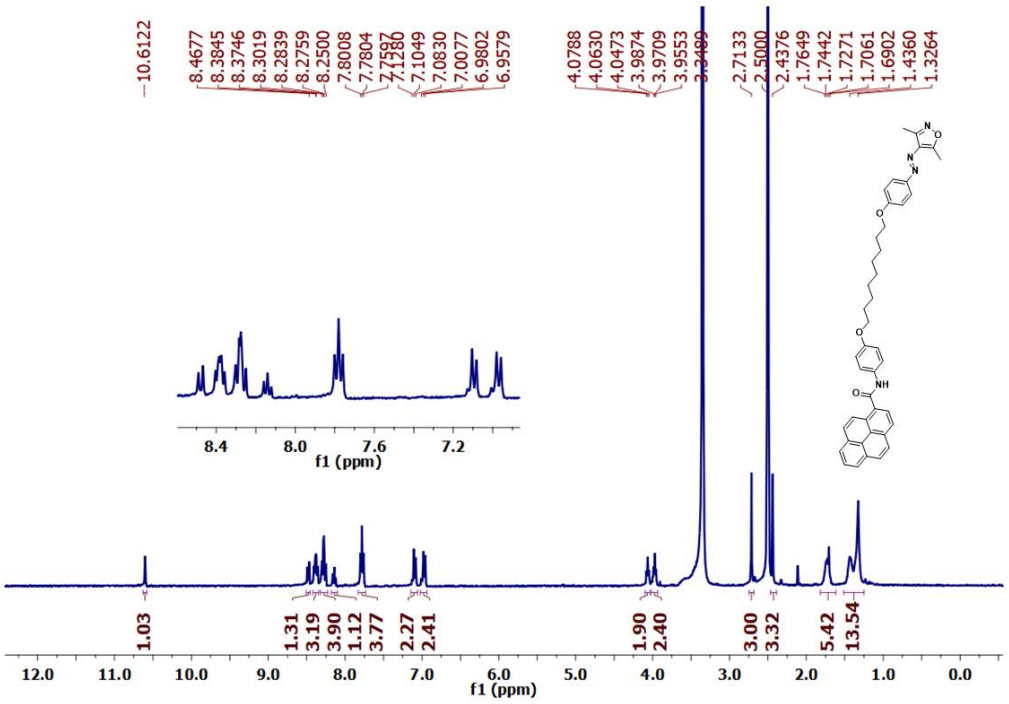

Figure A27: ^{1}H NMR spectrum of molecule **20** in DMSO-d_6.

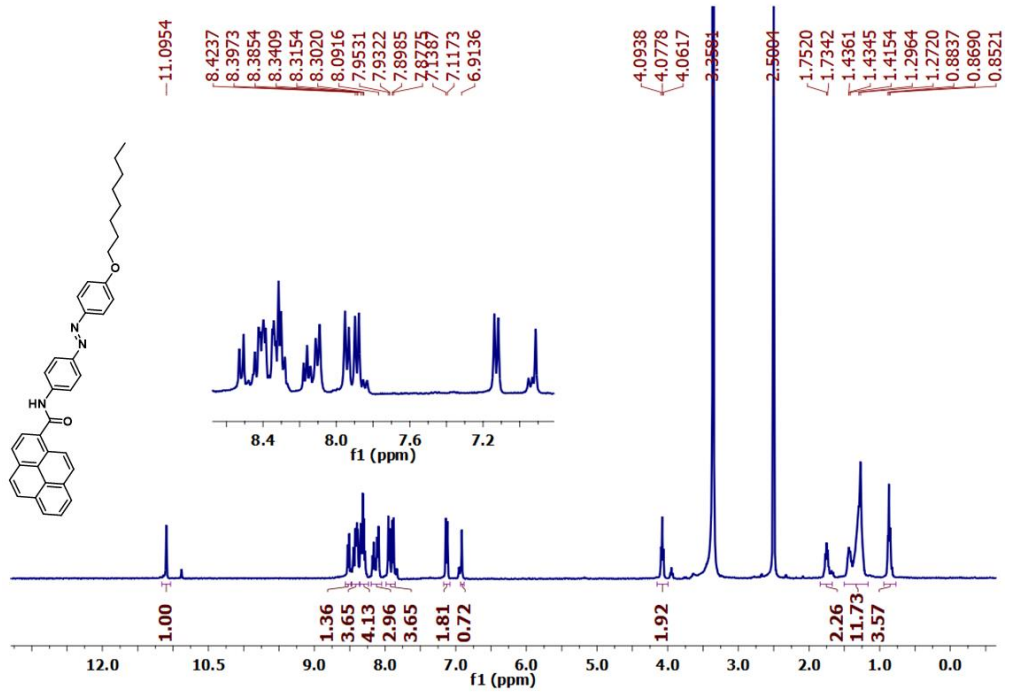

Figure A28: ^{1}H NMR spectrum of molecule **21** in DMSO-d_6.

Amal Sam Sunny

PERSONAL INFORMATION

Date of Birth	10th June 1995
Address	Peace Cottage Alencherry, Yeroor PO, Kollam, Kerala, 691312.
Email	amalssunny@gmail.com
Contact Number	+919400671647

EDUCATION

2014 – 2019	BS-MS Dual Degree Program in Chemical Sciences**,** Indian Institute of Science Education and Research, Mohali. **Current CPI: 8.9** Currently in 10th Semester.
2012 - 2014	Class XII**,** St. John's Central School, Kollam. *(CBSE)* **Marks aggregate: 96%**
2010 - 2012	Class X**,** St. John's Central School, Kollam. *(CBSE)* **Marks aggregate: 95%**

PROFESSIONAL EXPERIENCE

(1) Project Experience

August 2018 - April 2019	**Master Thesis**. Synthesis and Studies of Azoarene and Azoheteroarene Connected Benzene Carboxamides as Potential Photoresponsive Liquid Crystals. Supervisor: Dr. Sugumar Venkataramani, IISER Mohali.
May–July 2018	Synthesis and Characterization of Phtoswitchable Discotic Liquid Crystals. Supervisor: Dr. Sugumar Venkataramani, IISER Mohali.
May–July 2017	Synthesis and Characterization of Tricarboxamide derivatives. Supervisor: Dr. Sugumar Venkataramani, IISER Mohali.
May–July 2016	Evaluation of Substituent Effect in *Z*-Isomer Stability of Arylazopyrazoles. Supervisor: Dr. Sugumar Venkataramani, IISER Mohali.
May–July 2015	A Computational Study of Hydrogen Bond Strength While Varying the Substituents at the Opposite End of a Long Chain Hydrocarbon. Supervisor: Dr. CV Suresh, NIIST Trivandrum.

(2) Teaching Experience

- Worked as a *teaching assistant* for the lab courses CHM 211 and CHM 212.
- Volunteered for organizing demonstrations of chemical reactions in *Inspire Science Camp conducted by DST, Government of India*, on 2015.

RESEARCH SKILLS

(1) Analytical Skills

- Synthesis and characterization of organic molecules.
- Separation techniques in organic chemistry: TLC, Column Chromatography. Ample expertise on FTIR, UV-Vis, ATR, Fluorescence spectroscopy, Titrations using Potentiometer and Conductometer, Table Top NMR, Polarized Optical Microscope (POM) and Differential Scanning Calorimetry (DSC)
- Experience in spectral analysis such as NMR.

(2) Programming Sills

- Python
- C and C++
- SageMath

FELLOWSHIPS AND CREDENTIALS

(1) DST INSPIRE fellowship at the undergraduate level from Aug 2014 to May 2019.
(2) Among the top 1% in Higher Secondary Examinations conducted by Central Board of Secondary Education (CBSE).

EXTRA CURRICULAR ACTIVITIES

- Chess (Fide rating: 1304, Online Rating: 1789)
- Cricket, badminton