Synthesis and photoswitching studies of azobenzene based molecular transporter and photoswitchable ligands

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Certificate of Examination

This is to certify that the dissertation titled "***Synthesis and photoswitching studies of azobenzene based molecular transporter and photoswitchable ligands***" submitted by Ms. Rashmi Sinha (Reg. No. MS11084) 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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Date: 22/04/2016

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.

Rashmi Sinha

Candidate

Date: 22/04/2016

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)

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Abbreviations

2-D	-	2-Dimensional
3-D	-	3-Dimensional
K_2CO_3	-	Potassium carbonate
K_3PO_4	-	Tripotassium phosphate
Cs_2CO_3	-	Caesium carbonate
DMSO	-	Dimethyl sulfoxide
NaOH	-	Sodium hydroxide
Na_2SO_4	-	Sodium sulphate
$NaNO_2$	-	Sodium nitrite
$NaBH_4$	-	Sodium borohydride
H_2O	-	Water
HCl	-	Hydrochloric acid
PTSA	-	p-Toluenesulfonic acid
NMP	-	N-Methyl-2-pyrrolidone
EtOH	-	Ethanol
AcOH	-	Acetic acid
RT	-	Room Temperature
CuI	-	Copper iodide
$SOCl_2$	-	Thionyl chloride

PCl_5	-	Phosphorus pentachloride
TEA	-	Triethylamine
DCM	-	Dichloromethane
THF	-	Tetrahydrofuran
DMF	-	Dimethylformamide
PCC	-	Pyridinium chlorochromate
TLC	-	Thin Layer Chromatography
MS	-	Mass Spectrometry
ESI	-	Electrospray Ionisation
NMR	-	Nuclear Magnetic Resonance
^{1}H-NMR	-	Proton NMR
^{13}C-NMR	-	Carbon-13 NMR
FT-IR	-	Fourier Transform - Infrared Spectroscopy
RBF	-	Round bottom flask
Eq.	-	Equivalent(s)
LED	-	Light Emitting Diode
CFL	-	Compact Fluorescent Lamp

Abstract

Azobenzene is a photoswitchable molecule, which can switch between thermodynamically stable *trans* and kinetically stable *cis* geometrical isomers. *Trans* isomer is having a planar (2-D) structure, whereas the *cis* isomer is having a non-planar (3-D) structure, both of them can be interconverted between each other using UV light irradiation and visible light irradiation. Besides, the reverse reaction can happen under thermal condition with certain half-life. The switching rates as well as the half-life of reverse switching are influenced by substituents on the azobenzene molecules. In our current work, we are trying to make multiple azobenzene connected molecules (with different substitution on azobenzene), which can be used as a molecular transporter. In this regard, we are trying to connect multiple azobenzene molecules to a core moiety through various linkages in such a way that upon UV light irradiation, they all can switch together from *trans* to *cis* to form a three dimensional cage like structure, which can be utilized for holding and releasing of the guest molecule. Apart from that, we are also trying to synthesize some azobenzene based switchable ligands. The development of transition metal complexes with ligands containing different photochromic families has received great attention in recent years. The photochromic properties can be perturbed by external stimuli, i.e. light, which can lead to variation in the ligand strength, which in turn can cause spin crossover. In order to achieve the above two applications, few molecules with multiple azobenzene functionalization have been designed and targeted for synthesis. The current status and photoswitching studies on those resulting molecules are part of the thesis.

Chapter 1

Introduction

1.1 General

Photoresponsive materials are those, which can change their intrinsic properties with the light as an external stimulus, are of great importance. The light induced molecular change leads to a significant modification in some of the properties of concerned molecule such as, mechanical properties, electrical, magnetic, optical, pH change etc.[1] There are variety of photoresponsive compounds, which are very well known to show reversible chemical transformations, such as *cis–trans* isomerization, intramolecular group transfer reactions, ionization and pericyclic ring-opening and ring-closing reactions.[2,3] These types of compounds are capable of undergoing clean interconversions between two different notable states upon irradiation by light at appropriate wavelength. Each state has a particular absorption maximum, which can be observed by UV-Vis spectroscopy. Such changes have led to their applications in a wide variety of consumer products such as toys, sunglass lenses, optical filters, optoelectronic devices and optical memory, photochromic inks for security markings, cosmetic products etc.[4] Due to their wide applications, a number of classes of photochromic molecules have been reported during the past few decades.

Photochromic behaviour associated with the reversible *trans–cis* photoisomerization of N=N double bond is very well known. In literature, it is demonstrated that, these reversible isomerization reactions can occur on both the lowest excited singlet-state surface and the triplet-state surface.[5] Many approaches for the reversible photocontrol of switchable compounds have been explored with a wide variety of chromophores such as azobenzene, stilbene, hemithioindigos, spiropyrans, diarylethenes, and fulguides. Photochromic systems can be classified in to two categories (depending on the thermal stability of the photogenerated isomer)[6] :

- P-type; also called photochemically reversible type system, which do not revert back to the initial isomer even at high temperatures, e.g., fulgides and diarylethenes .

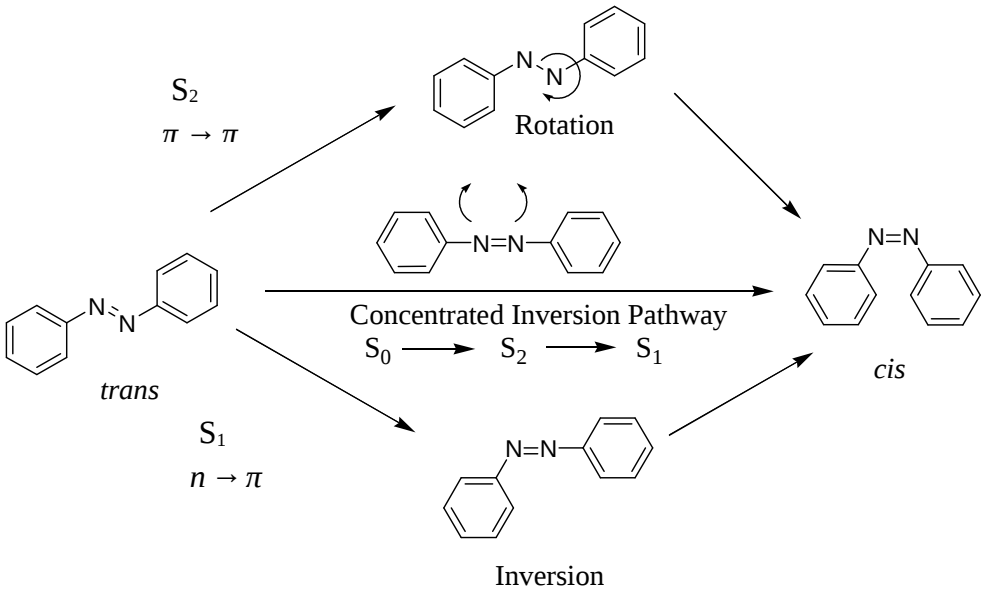
- T-type; also called thermally reversible type system, which can thermally revert back to the initial form (switch between *cis* to *trans*), e.g., azobenzenes, stilbenes, spiropyranes and hemithioindigos.

Apart from the geometrical changes associated with the photochromism, often it also changes the polarity and charge distribution of compounds.[7]

1.2 Azobenzene and its photoisomerization

One of the most widely used organic chromophore as an optical switch is azobenzene. It is having R-N=N-R′ functional group, where R and R′ can be aryl or alkyl. Due to π – delocalization on azobenzene compounds, they exhibit colours like red, yellow or orange. They have thus found wide applications as dyes, pigments, radical initiators, therapeutic agents, as well as functional materials.[8,9]

The photoisomerization of azobenzene from *trans*- to *cis*- form can occur within femtoseconds with a strong light source, but the isomerization rate mainly depends on the chemical structure of the system (substitution on azobenzene moiety).[6]



Scheme 1: Possible mechanisms of azobenzene isomerization[6]

The possible pathways of photoisomerization of azobenzene is proposed by three mechanism- the first one involving a simple rotation around the N–N bond (at its π–π* excited state), second one is having an inversion pathway (at its n-π* excited state), and the third implying mixed mechanisms, such as the concerted inversion or the inversion-assisted rotation (**Scheme 1**).[6] Through UV studies a strong UV band exhibiting

vibrational structure has been observed that was attributed to symmetry allowed π-π* transition. A weaker band appears in visible region (λ_{max} ~450 nm), which correspond to the symmetry forbidden n → π* transition. The n to π* and π to π* transitions excite azobeneze to S_1 (n, π*) and S_2 (π, π*) states, respectively.[10]

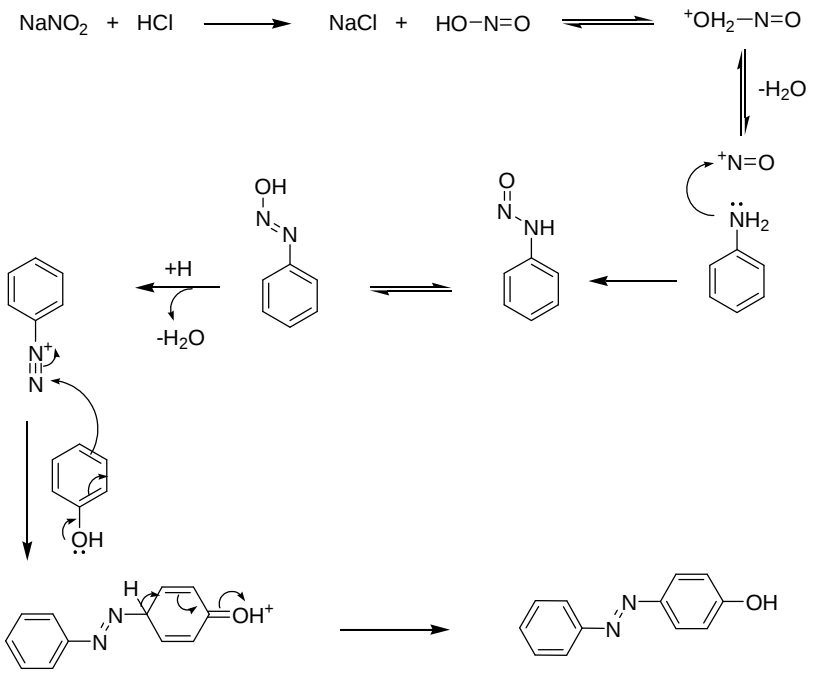
1.3 Synthesis of azo compounds

There are many methods available for the synthesis of azo compounds like oxidative coupling of anilines for preparing symmetrical azobenzene, but to prepare unsymmetrical azobenzene there are two important high yielding methods available:

1.) Azo coupling reaction and
2.) Mills reaction

1.3.1 Azo coupling reaction

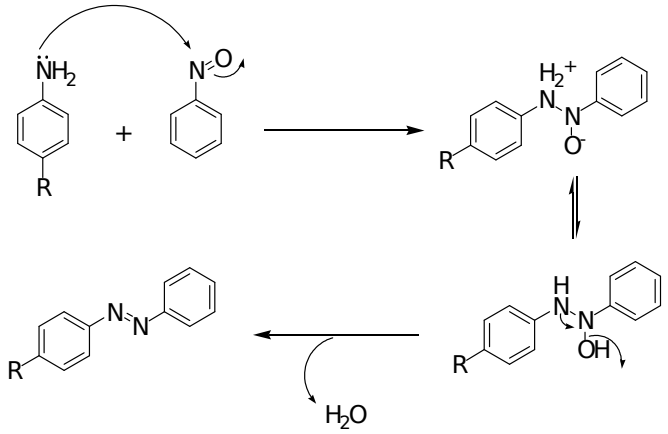
Peter Griess discovered it in 1858. The methodology is based upon the diazotization of an aromatic amine such as aniline with sodium nitrite in the presence of a mineral acid. Due to the exothermicity and unstable nature, the diazotization reactions are typically carried out at low temperature around 0-5 °C. After the formation of diazonium salt, it reacts with electron rich aromatic substrates such as substituted arenes having electron donor group like amine and hydroxyl to give desired azobenzene derivatives (**Scheme 2**).[11]



Scheme 2: Mechanism of azo coupling reaction and formation of 4-hydroxyazobenzene

Generally, such type of substitution takes place at the *para* position to the electron donating group on the aromatic ring that acts as a nucleophile. However, when the *para* position is already occupied, then substitution takes place at *ortho* position and not *meta*.

1.3.2 Mills reaction



Scheme 3: Mechanism of Mills reaction

Unsymmetrical azobenzene derivatives can also be synthesized by the treatment of aromatic nitroso compounds with primary arylamines using Mills reaction.[7] Oxone can be used as an oxidising agent to form nitroso arenes from their corresponding amines, which then condensed with substituted anilines to form unsymmetrical azobenzenes in good yield. This reaction is done under acidic condition at rt- 40 ºC. We can use acids like, acetic acid to protonate nitroso oxygen so that the amine nucleophile can attack the nitroso nitrogen followed by dehydration to give azobenzene. (**Scheme 3**)

1.4 Applications of azobenzene based molecular systems

There are many applications based on azobenzene systems. However, in the following section, we describe certain applications, closely related to our targets. The applications of our interest include host-guest systems, photoswitchable ligands for molecular spin crossover complexes.

1.4.1 Applications based on azobenzene host-guest interaction

1.) “The controllable uptake and release of pyridinium ions with a photoactive calixarene-capped azobenzene”.[12]

In this system, azobenzene has been used as a host molecule, where calixarene-capped azobenzene (CCA) was synthesized, follwed by screening with various

pyridinium, ammonium, and diimidazolium-derived guest compounds for their reversible encapsulation and release from CCA host (**Figure 1**). The function of this host container depends on the photoisomerization reaction of azobenzene, upon irradiation with lights of different wavelengths, two geometrically distinct forms are produced ("open" and "closed").

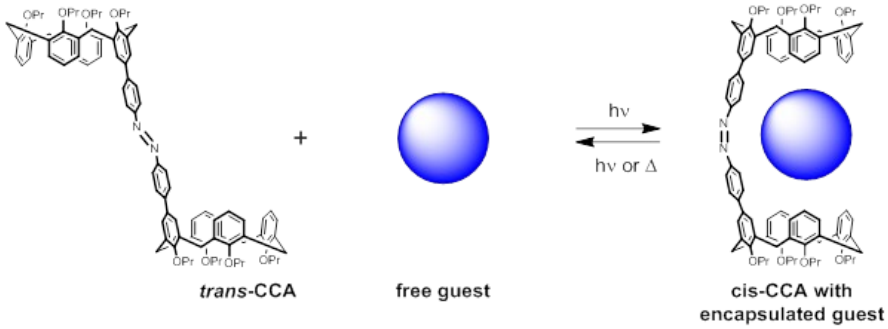


Figure 1: Uptake and and release of guest ions with a photoactive Calixarene-capped azobenzene.[12]

2.) "Strong binding of a divalent azobenzene guest to a complementary host".[13]

In the previous system, the azobenzene connected calixarene was used as a host, whereas here, it is used as a photochromic guest. In this report, they have considered azobenzene as a drosophila, and its significant structural changes upon E–Z photoisomerisation have been used to modulate microscopic property changes (**Figure 2**). Due to tuneable interaction between a secondary ammonium ion and a dibenzo-24-crown-8, they choose anthracene-spacered divalent crown ether as the complementary divalent host. It can either lock or unlock the E-isomer by making or breaking of the host–guest complex and there by functionalize its photoisomerisation ability.

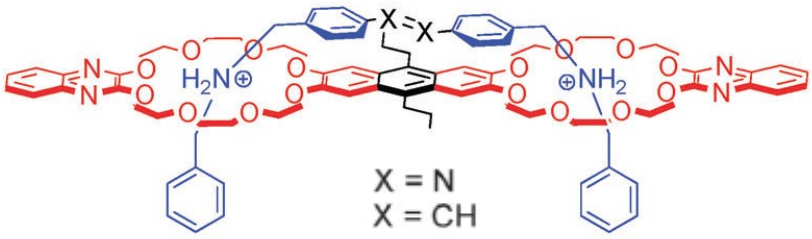


Figure 2: Isomerization of divalent azobenzene and stilbene axles and divalent host[13]

1.4.2 Applications based on switchable ligands

Switchable ligands are effectively used for spin-crossover in metal complexes, which are among the best-known classes of molecular bistable systems. By changing the temperature, or pressure, electric or magnetic field, irradiation with light, the magnetic property, optical, and other physicochemical properties can be reversibly switched.[14,15] Spin-crossover is known for d^4–d^8 first-row transition-metal ions. They switch between a diamagnetic low-spin (LS; S = 0) state and a paramagnetic high-spin (HS; S = 2) state or between two different paramagnetic states via external stimuli. Irradiation with light is mostly used to control a molecule's state, because of the high speed of switching, high selectivity, and easy and precise addressing. There are wide applications of spin-crossover molecules as photoswitchable building blocks for molecular electronics and spintronics, ultrahigh-density memories, displays, communication networks, and photosensors.

One such example is a photoisomerizable diarylethene-derived ligand, (phen*), which has been introduced into a spincrossover iron(II) complex, [Fe($H_2B(pz)_2)_2$phen*] (1; pz =1- pyrazolyl), shown in **Figure-3**. Complexes of iron(II) with d^6 configurations have been chosen to switch between a diamagnetic low-spin (LS; S = 0) state and a paramagnetic high-spin (HS; S = 2) state. Due to ligand-based photocyclization in the complex, it modifies the ligand field, and results in a highly efficient paramagnetic high-spin → diamagnetic low-spin transition at the coordinated Fe(II) ion.[15] These kind of molecules can be used for controlling the magnetic properties in the solid state at a single molecule level with light, because of the excellent photophysical properties of diarylethenes.

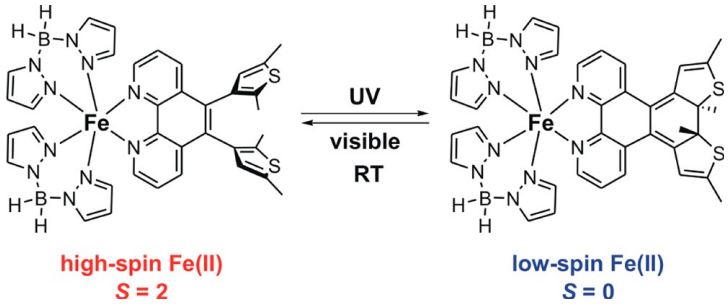
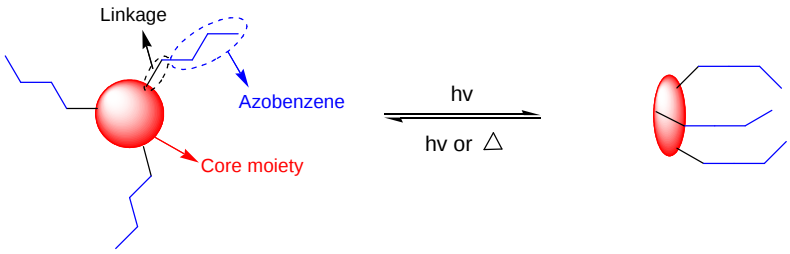


Figure 3: Diarylethene based ligands and typical photocyclization and photocycloreversion reaction[15]

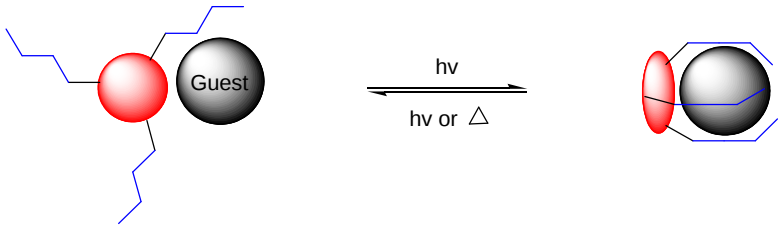
1.5 Proposed Research

Section 1. Photoswitchable molecular transporter

In section **1**, the synthetic targets are designed to use the basic photoswitching properties of azobenzene, and connecting multiple azobenzene moieties through different linkages to a core moiety. The target upon irradiation, all the azobenzenes are expected to undergo *trans* to *cis* isomerization in such a way that a 3-D space will be created (**Scheme 4**). Here, the idea is to use that 3-D space for holding (encapsulation) and releasing (transportation) of some guest molecules (**Scheme 5**).



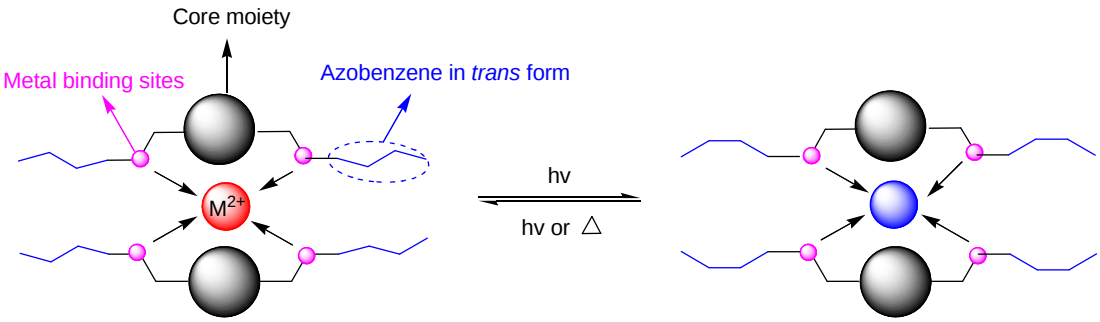
Scheme 4: Expected isomerization in target molecules.



Scheme 5: Target molecule as a photoswitchable molecular transporter

Section 2. Photoswitchable ligands

In the second part of the project, the major goal is to design and synthesize switchable ligands, which can coordinate to transition metals in such a way that it may change the magnetic properties of transition-metal ions, where it may switch between a “diamagnetic low-spin (LS; S = 0) state” and a “paramagnetic high-spin (HS; S = 2) state” via UV and visible light irradiation. We have chosen the target molecules by considering that azobenzenes are directly connected to metal binding sites (nitrogen), therefore when azobenzene will switch, it shall provide a maximum effect through variation in ligand strength (**Scheme 6**).

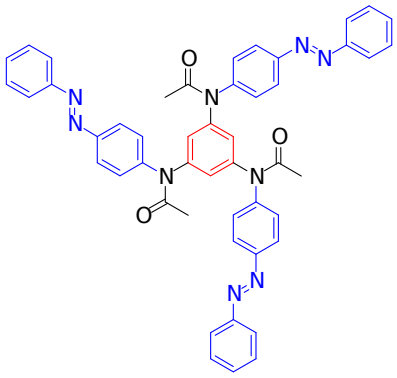


Scheme 6: Effects of switchable ligands on transition metal ion

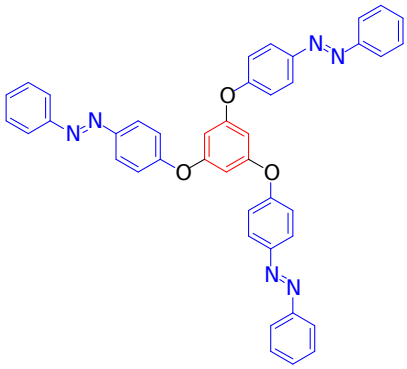
1.6 Target molecules

Section 1. Targets for photoswitchable molecular transporter

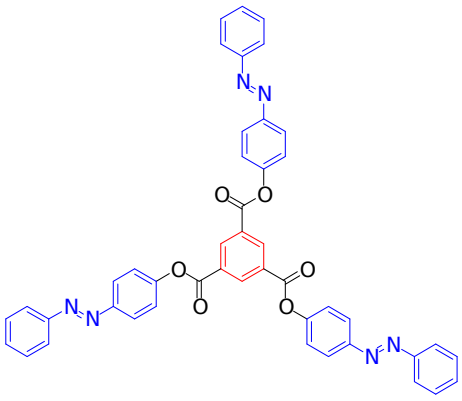
To understand the switching behavior in multiple azobenzene connected molecular systems, and to simplify our spectral characterizations, we designed target molecules in such a way that the core molecule (benzene) and azobenzenes are same in all the molecules. Basically, we designed our targets by varying the linkages for connecting the core and photoswitchable units. For symmetry reasons, benzene core funtionalized at 1, 3, 5-positions has been chosen. The linkages include ether, amine and ester. (**Scheme 7**) The choice of the targets is mainly based on the ease of synthesis and their higher symmetry, as all of them are expected to show a reasonably well-resolved spectral data, otherwise it may complicate in the analysis part.



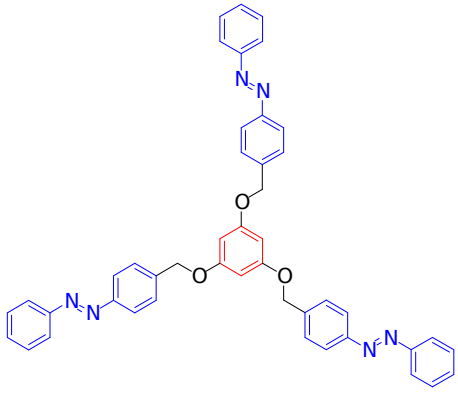
Target 1



Target 2



Target 3

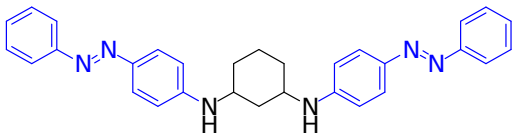


Target 4

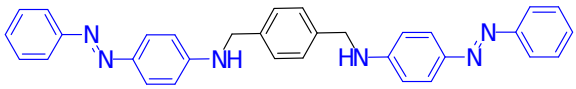
Scheme 7: Target molecule for photoswitchable molecular transporter

Section 2. Targets for photoswitchable ligands

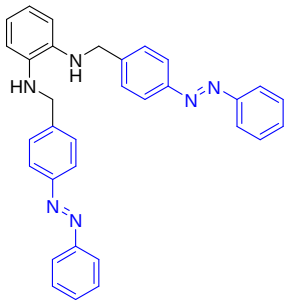
In this section **2**, targets have been designed in such a way that they can have both photoswitchable groups (azobenzene) and coordinating sites. In this regard, azamacrocycles and related azobenzene connected diamines have been chosen and targeted for synthesis (**Scheme 8**). In this regard, we designed multiple azobenzene connected symmetrical molecules e.g: Terephthalaldehyde, 1,3-Cyclohexanedione, 1,2-dibromoethane etc. The main reason for choosing these targets is, after coordinating with metal complexes, the magnetic, optical, and other physicochemical properties can be reversibly switched by electric and magnetic field, irradiation with light, changing the temperature, or pressure.



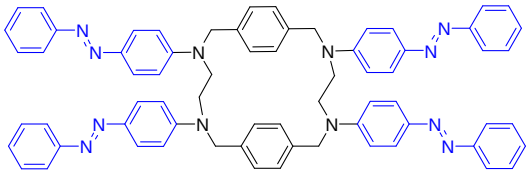
Target 5



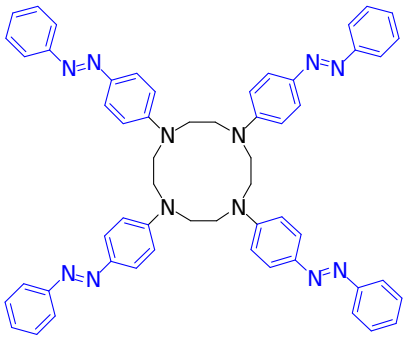
Target 6



Target 7



Target 8



Target 9

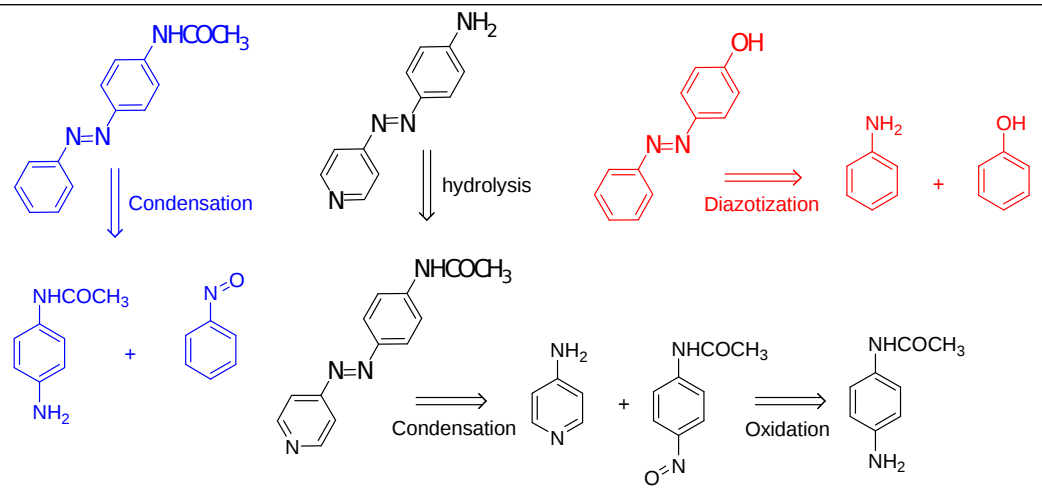
Scheme 8: Target molecules for switchable ligands and azamacrocycles

1.7 Retrosynthetic routes adopted

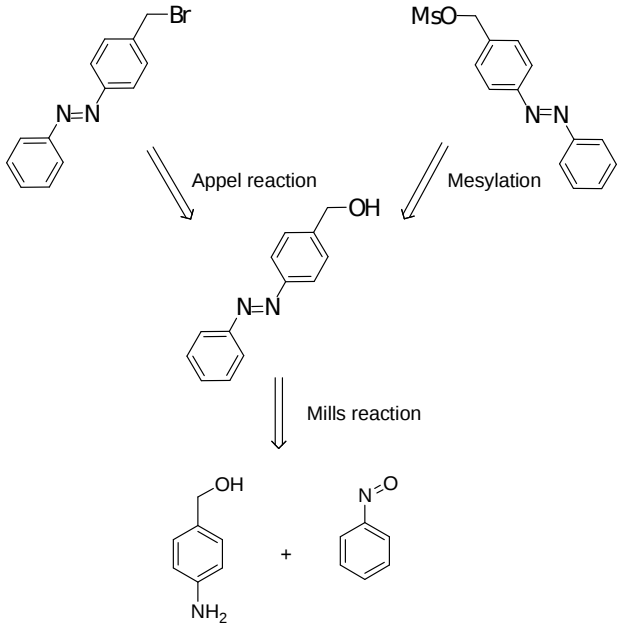
Section 1. Targets for molecular transporter

In order to achieve our targets, the following retrosynthetic routes were followed (Scheme **9**). Commercially available trimesic acid and phloroglucinol have been used as starting materials for obtaining the benzene core. For connecting azobenzenes and their analogues with the benzene core through different linkages, various azobenzene derivatives such as 4-amino phenylazopyridine, 4-acetylamino phenylazobenzene, 4-hydroxyazobenzene, 4-bromomethyl phenylazobenzene, and 4-methylsulfonyloxymethylphenylazobenzene have been considered to be part of the retro synthesis of the targets. In this regard, the synthesis of the above mentioned azobenzenes have been chosen as the preliminary targets. (**Scheme 9**, Route **1** and **2**). After the synthesis of azo compounds, the immediate task would be to connect them with the benzene core. Apparently, the connections through *N*-arylation, *O*-arylation, *O*-alkylation and esterification have been considered. (Scheme **9**, Route **3, 4, 5** and **6**)

Route 1

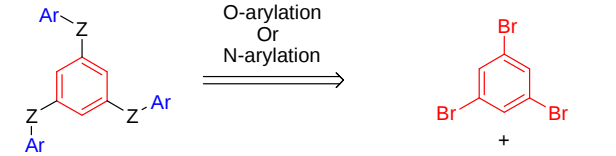


Route 2



Route 3

Target 1 & 2



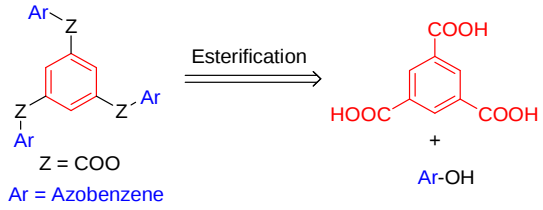
Z = 'O' Or 'NHCOCH$_3$'

Ar = Azobenzene

Ar-NHCOCH$_3$ Or Ar-OH

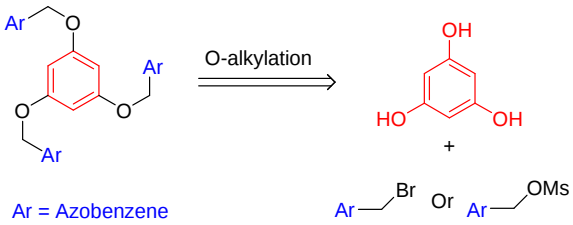
Route 4

Target 3



Route 5

Target 4

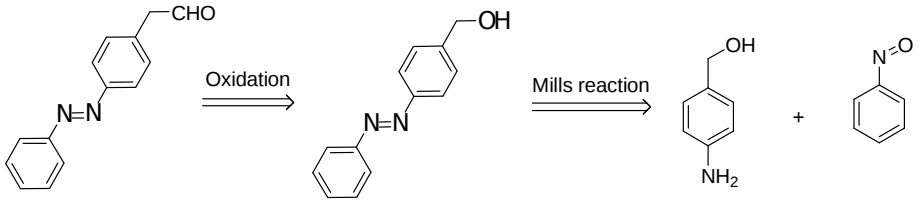


Scheme 9: Retrosynthetic routes adopted for the synthesis of targeted molecules as a molecular transporter

Section 2. Targets for photoswitchable ligands and azamacrocycles

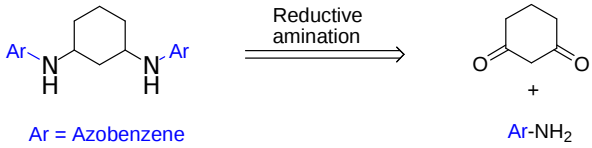
In order to achieve our second goal, with respect to the switchable ligands and azamacrocycles the following retrosynthetic routes have been considered (**Scheme 10**). Commercially available terephthalaldehyde, 1,3-cyclohexanedione, 1,2-dibromoethane, 1,2-diaminobenzene and 4-aminobenzene have been considered for the synthesis. Connecting the dicarbonyl compounds with 4-aminoazobenzene through reductive amination was considered to be one of the important strategies. (Scheme **10,** Route **2, 3**) On the other hand, 4-formylphenylazobenzene has been chosen as a coupling partner for reductive amination steps with phenylene diamine. The synthesis of 4-formylphenylazobenzene was targeted for synthesis as in the route 1, scheme 10. For the synthesis of aza macrocycle, we followed the retrosynthetic route **5** and **6**.

Route 1



Route 2

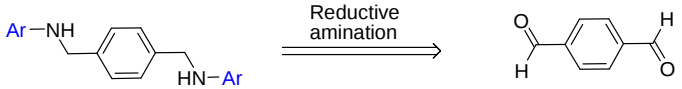
Target 5



Ar = Azobenzene

Route 3

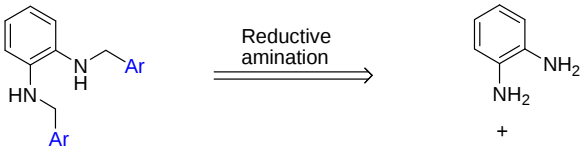
Target 6



Ar = Azobenzene

Route 4

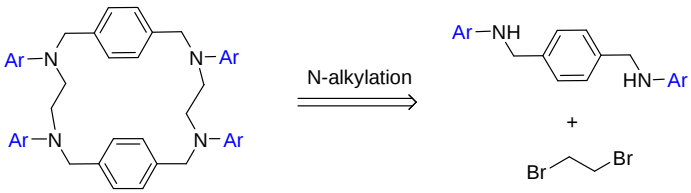
Target 7



Ar = Azobenzene

Route 5

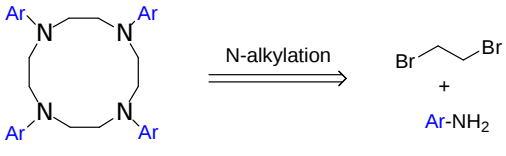
Target 8



Ar = Azobenzene

Route 6

Target 9



Ar = Azobenzene

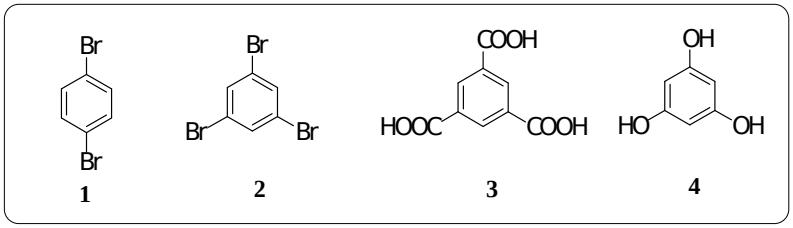
Scheme 10: Retrosynthetic routes adopted for the synthesis of switchable ligands and azamacrocycles

Chapter 2

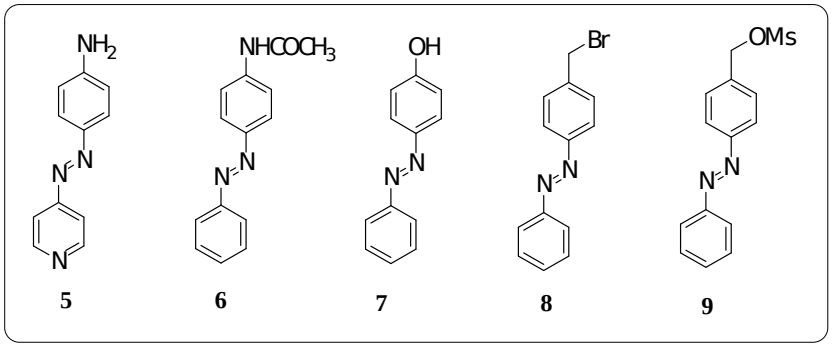
Results and Discussion

Section 1. Targets for molecular transporter

As indicated in the previous section, targets for the molecular transporter have been designed in such a way that multiple azobenzenes needed to be connected to a benzene core through different linkages. The preliminary aim in this photoswitchable molecular transporter project was to synthesize the derivatives of azobenzenes. Since the core molecules **1, 2, 3** and **4** have been purchased from Sigmaaldrich and Himedia (**Scheme 11**), the follow up step would be to couple those azobenzenes with the core molecules through various coupling. For the photoswitchable units, we tried to synthesize the following azobenzene derivatives, namely **5, 6, 7, 8,** and **9**, we followed our prososed retrosynthetic routes, which include the Mills method and azocoupling (**Scheme 12**). After that, we tried to connect multiple azobenzene to our core moiety, which include *N*-arylation, *O*-arylation, *O*-alkylation and esterification.



Scheme 11: Core Moieties



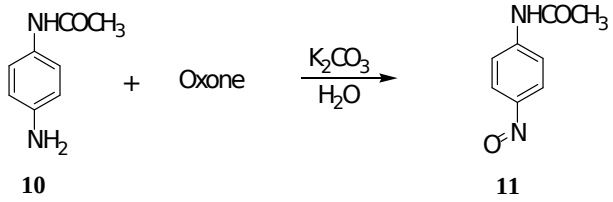
Scheme 12: Azobenzene Derivatives

2.1.1 Synthesis of photoswitchable units

2.1.1.1 Synthesis of 4-amninophenylazopyridine (5)

Compound **5** was planned to synthesize from its corresponding acetyl derivative **13** using Mills method. We followed a two-step method for the synthesis of **5**, viz, (1) Preparation of nitroso compound, and (2) Coupling reaction of nitroso compound **11** with 4-aminopyridine (**12**).

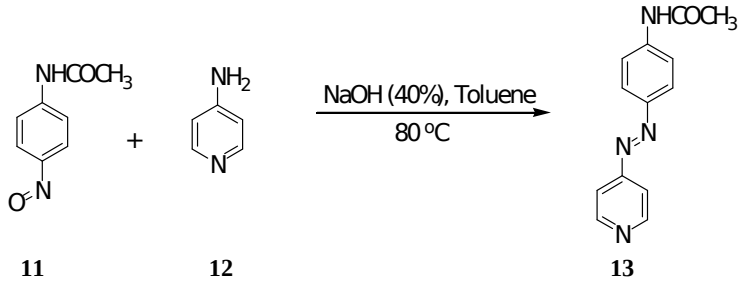
1. For the preparation of nitroso compound **11** (**Scheme 13**) literature[16] procedure using oxone was adopted and a pale greenish product was obtained, which was kept under vaccum after the filtration, and it was immediately used for the next reaction.



10 **11**

Scheme 13: Preparation of *N*-(4-nitrosophenyl)acetamide

2. In this step, the above mentioned nitroso compound **11** was treated with 4-aminopyridine (**12)** under basic condition and toluene was added as a solvent and kept the reaction mixture on heating at 80 ºC. However, the desired product did not form (**Scheme 14**).

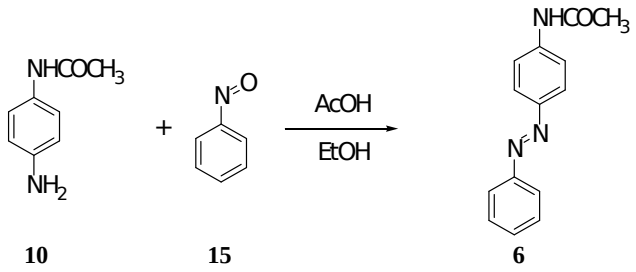


11 **12** **13**

Scheme 14: Preparation of 4-aminoacetanilideazopyridine

2.1.1.2 Preparation of 4-acetylaminophenylazobenzene (6)

Compound **6** was prepared using Mills method. The reaction between 4-aminoacetanilide (**13)** and nitrosobenzene (**15)** in the presence of acetic acid along with ethanol gave the desired orange color product with an isolated yield of 85%. (**Scheme** 15)

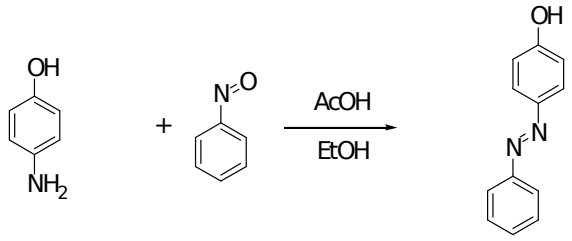


10 **15** **6**

Scheme 15: Preparation of 4-acetylaminophenylazobenzene (6)

2.1.1.3 Synthesis of 4-hydroxyazobenzene (7)

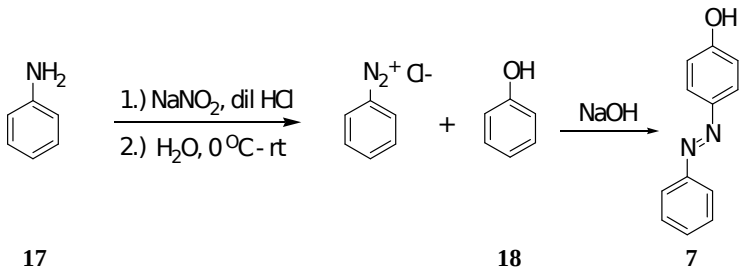
For the preparation of 4-hydroxyazobenzene, again we followed the Mills method. 4-aminophenol (**16)** was used instead of 4-aminoacetanilide (**10)** and the same procedure as in the previous reaction was followed. However, in this case the isolated yield was only 6% (Scheme **16**).



16 **15** **7**

Scheme 16: Preparation of 4-hydroxyazobenzene (7)

Because of poor yield, another procedure was followed. This time **7** was carried out through azo coupling reaction as reported in the literature involving the formation of diazonium salt by using sodium nitrite and HCl at low temperature below 5 ºC (**Scheme 17**). The resulting diazonium salt was then treated with phenol (**18)** to form the desired product with 75% yield.

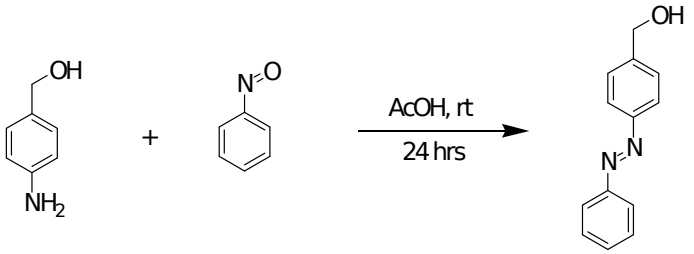


17 18 7

Scheme 17: Preparation of 4-hydroxyazobenzene

2.1.1.4 Synthesis of 4-bromomethylphenylazobenzene (8)

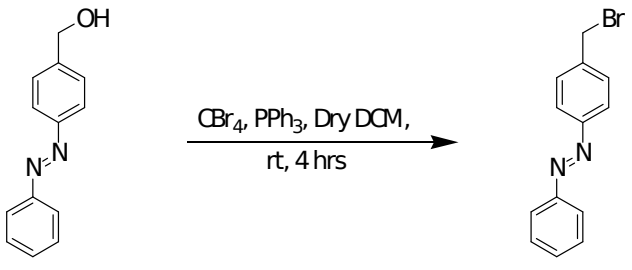
Compound **8** can be prepared through Appel reaction of 4-hydroxymethylazobenzene (**20**). Firstly, compound **20** was prepared through Mills method. A simple reaction between 4-aminobenzophenol (**19)** and nitrosobenzene (**15)** in the presence of acetic acid gave the desired product **20** with an isolated yield of 53% (**Scheme 18**).



19 15 20

Scheme 18: Preparation of 4-hydroxymethylazobenzene (**20**)

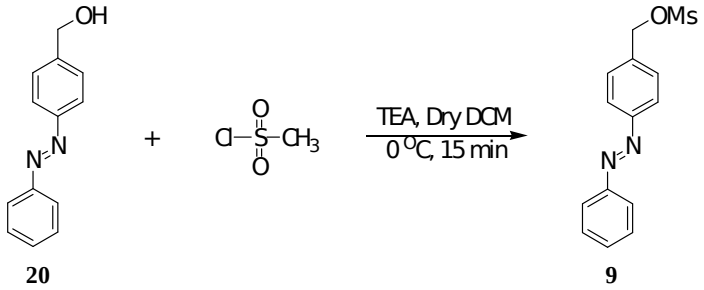
Compound **20** was then used for the preparation of **8** (**Scheme 19**). We wanted to convert the hydroxyl group into a good leaving group. So, we used tetrabromomethane and triphenylphosphene in dry DCM under Appel reaction conditions to convert it into bromide. Here, the yield was poor, we got only 45% of compound **8.**



20 8

Scheme 19: Preparation of 4-bromomethylphenylazobenzene (**8**)

Due to poor yield of bromo derivative, we decided to convert hydroxyl group into mesylate. For this purpose, we used methanesulfonylchloride under base condition (**Scheme 20**), here we got only one spot whose R_f value was found to be same as the starting material **20.** However, in $KMNO_4$ solution, we could easily distinguish between them. In this case, after work up and distillation of solvent under vacuum, we obtained a sticky and foamy orange colored compound, which was utilized for the next steps without further purification.



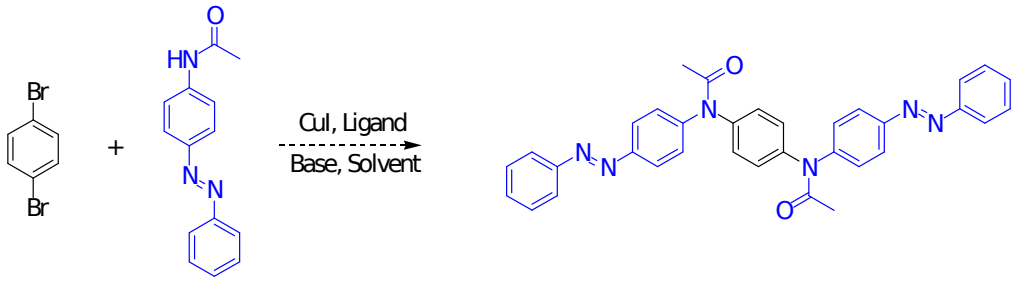
20 **9**

Scheme 20: Preparation of 4-methylsulfonoxymethylphenylazobenzene (**9**)

2.1.2 Coupling of core moiety and photoswitchable units

2.1.2.1 *N*-arylation of 1,4-dibromobenzene

Prior to the synthesis of target **1** (*tris*-coupling), in order to optimize the conditions for multiple coupling, we decided to synthesize *bis*-coupled product. In this regard, we tried to connect the 1,4-dibromobenzene (**21)** and **7** through *N*-arylation (**Scheme 21**). We have tried various conditions as shown in **Table 1**, which include the CuI based Ma coupling procedures. We have modified the conditions by changing solvent, ligand and base. During all the reactions, **21** was taken as a limiting substrate and the counterpart, **7** was taken in excess (3 equivalent). However, we were not able to obtain the desired product. Since, *N*-arylation of 1,4-dibromobenzene (**21)** was not working, we didn't try the *N*-arylation of 1,3,5-tribromobenzene (**22**).



21 **6**

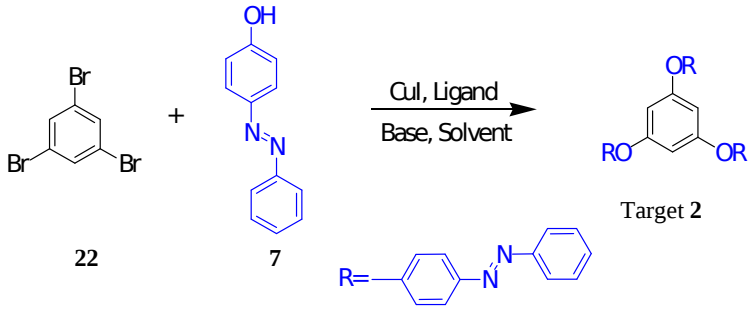
Scheme 21: Preparation of target **1**

Table 1. Optimization table for target molecule **1**

Entry	Catalyst (mol%)	Ligand (mol%)	Solvent	Base	Temp (°C) & Time (hrs)	Results
1	CuI (10)	2,2'-Bipyridyl (20)	1,4-Dioxane	Cs2CO3	110, 48	NR
2	CuI (10)	N,N'-Dimethylethylene-diamine (20)	1,4-Dioxane	K3PO4	110, 48	NR
3	CuI (10)	2,2'-Bipyridyl (20)	1,4-Dioxane	K3PO4	110, 48	NR
4	CuI (10)	1,10-Phenanthroline (20)	DMF	K3PO4	130,48	NR

2.1.2.2 *O*-Arylation of 1,3,5-tribromobenzene

After the unsuccessful attempts in making target **1**, we shifted our focus on *O*-arylation. We tried to couple 1,3,5-tribromobenzene (**22**) with **7** (**Scheme 22**). In this regard, we treated 1 equivalent of core molecule **22** with 4.5 equivalent of **7** under various conditions as shown in **Table 2**. In case of $Fe(acac)_3$ condition, we got 2 new spots, however, NMR data did not match with the target **2** or the expected by-products, namely mono and *bis*-*O*-arylated products. In other cases, we got new spots but they were very less intense w.r.t. starting material, and after celite filtration those spots got disappeared. So, we could not perform column chromatography.



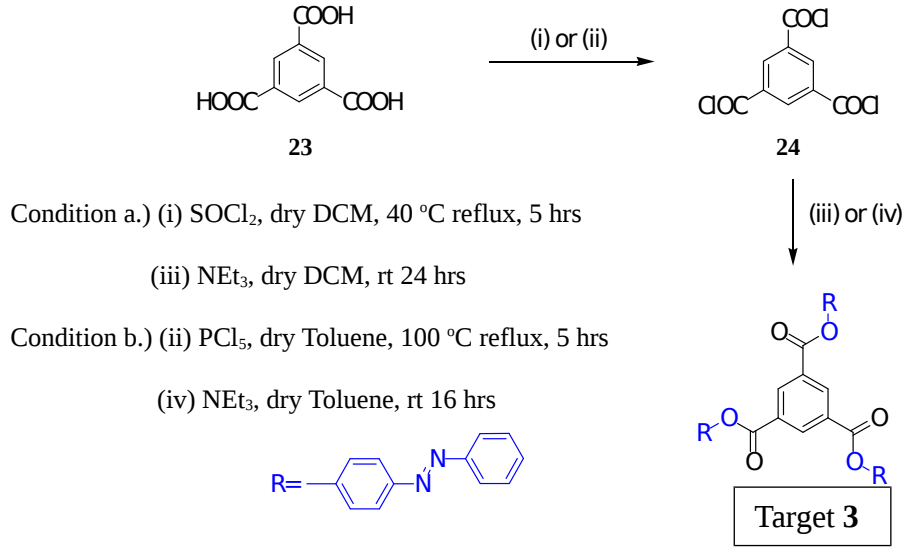
Scheme 22: Preparation of target **2**

Table 2: Optimization table for target molecule **2**

Entry	Catalyst (mol%)	Ligand/ Additive	Solvent	Base	Temperature (°C) & Time (hrs)	Results
1.	CuI (10)	$Fe(acac)_3$ (20 mol%)	dry DMF	K_2CO_3	110, 48	NR
2.	CuI (10)	Picolinic acid (20 mol%)	DMSO	K_3PO_4	110, 72	NR
3.	CuI (10)	NMP	NMP	K_3PO_4	110, 72	NR

2.1.2.3 Esterification of 1,3,5-trimesic acid

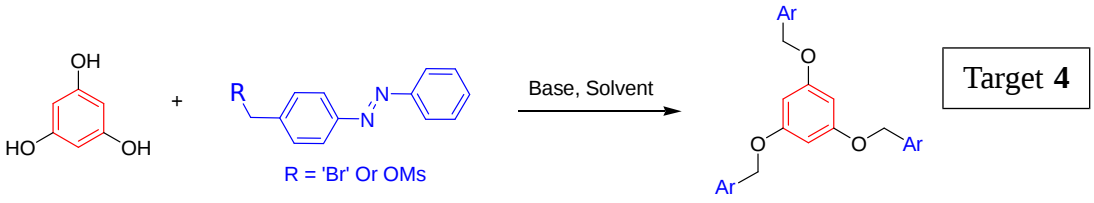
After trying *N*-arylation and *O*-arylation, we shifted our focus on esterification. Esterification was carried out in two steps, first we converted trimesic acid (**23**) into trimesoyl chloride (**24**), and then, **24** was treated with 4-hydroxyazobenzene (**7**) in the presence of base TEA. To convert **23** into **24**, we tried 2 alteranative conditions (**Scheme 23)**. In case of $SOCl_2$, we got 3 new yellow coloured spots and few UV-active spots. Whereas, PCl_5 reaction gave only 2 new spots, one was non-polar and another was highly polar. Since ester should be non-polar w.r.to alchohol, and we tried to purify the non-polar spot. However, in column, the top (non-polar spot) decomposed and we were not able to obtain the desired ester product, which presumably hydrolyzed under silica gel column condition. Therefore, we could not purify that compound.



Scheme 23: Preparation of target molecule **3**

2.1.2.4 *O*-alkylation of phloroglucinol

After the unsuccessful attempts in making *O*-arylated product, we tried to do *O*-alkylation. We tried to couple phloroglucinol (**4**) with **8** as well as **9** (**Scheme 24**). In case of 4-bromomethylphenylazobenzene (**8**), we got 5 spots, then column purification was carried out, however it was not purified properly. NMR is showing the product with some impurities.



Scheme 24: Preparation of target molecule **4**

Table 3: Optimization table for target molecule **4**

Entry		Base	Solvent	Temperature (°C) & Time (hrs)	Results
1.	R = Br	K_3PO_4	Acetonitrile	65, 48	NR
2.	R = OMs	K_3PO_4	dry DMF	65, 48	NR
3.	R = Br	K_3PO_4	dry DMF	65, 48	5 spots

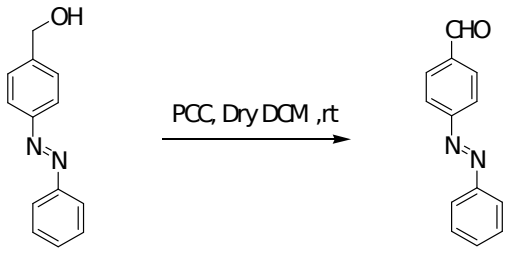
Section 2. Targets for photoswitchable ligands

This part of the chapter describes the status on the section **2** targets comprising synthesis of photoswitchable ligands and azobenzene based azamacrocycles. Here, we used 1,3-cyclohexadione (**25**), 1,4-terephthalaldehyde (**26)** and 1,2-diaminobenzene (**27**) as core or spacer moieties and 4-aminoazobenzene (**28**) and 4-formylphenylazobenzene (**29**) as photo switchable units. Except **29**, all the core molecules and **28** were purchased from Sigma Aldrich and TCI, India, respectively. In this context, most of the core molecules and azobenzenes were planned to connect using reductive amination and *N*-alkylation.

2.2.1 Preparation of photoswitchable units

2.2.1.1 Synthesis of 4-formylphenylazobenzene (29)

Compound **29** was synthesized in two steps; 1.) Preparation of compound **20**, and 2.) PCC oxidation of **20.** Reaction between 4-aminobenzylalcohol (**19**) and nitroso benzene (**15**) gave **20,** as in scheme **16**. After that PCC oxidation was done under dry condition at room temperature to get **29** in quantitative yield (**Scheme 25**).



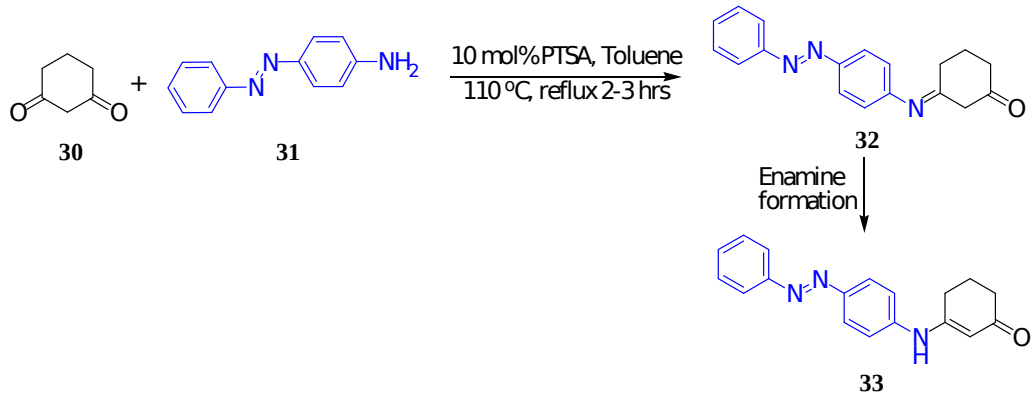
20 **29**

Scheme 25: Preparation of 4-formylphenylazobenzene

2.2.2 Coupling of core moiety/spacer and photoswitchable units.

2.2.2.1 Synthesis of Target 5

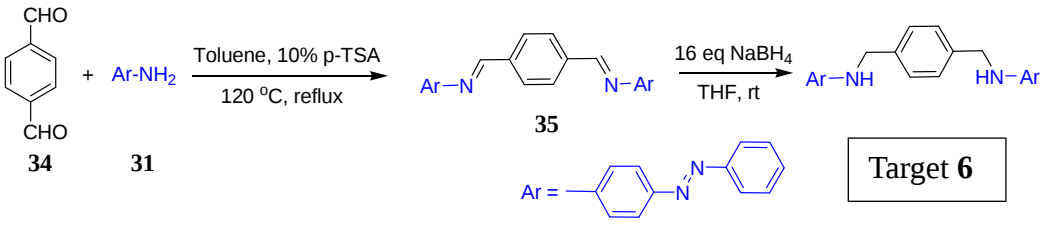
We planned to synthesize target **5** from 1,3-Cyclohexanedione (**30**) and 4-aminoazobenzene (**31**). First, we tried this reaction in single step through reductive-amination in methanol, but it didn't work. Then we went for two-step process, using toluene, however we ended-up getting enamine, instead of imine (**Scheme 26**) and half of the amount of 4-aminoazobenzene was left. Therefore, we stopped this reaction.



Scheme 26: Preparation of target molecule **5**

2.2.2.2 Synthesis of Target 6

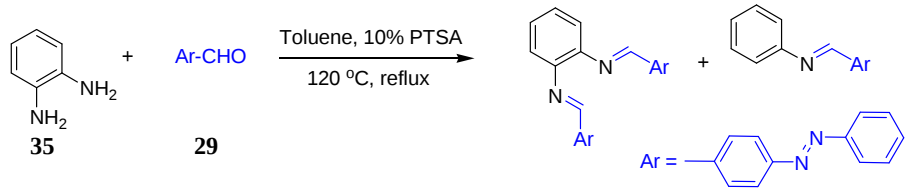
Target **6** was synthesized in two steps from terephthalaldehyde (**34**) and **31**, first imine was formed and then it was reduced though $NaBH_4$ in THF (**Scheme 27**). For reduction part, we followed the literature [17] and we got the product in good yield. In synthesizing this molecule we faced many difficulties, the imine that was formed was not at all soluble in any solvent at room temperature. It was soluble in DMSO only at higher temperature. Therefore, it was not soluble in THF even after adding $NaBH_4$. However, after 23-24 hours it got soluble, which was our final product.



Scheme 27: Preparation of target molecule **6**

2.2.2.3 Synthesis of Target 7

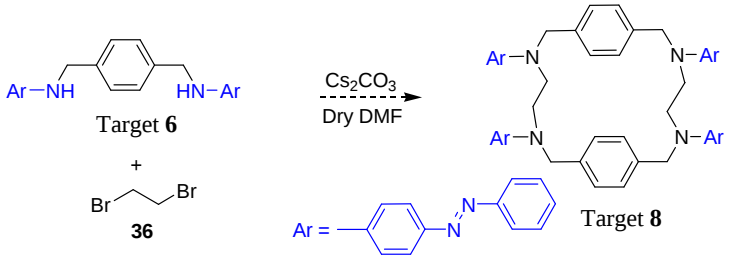
In order to synthesize Target **7**, we used, 1,2 -diaminobenzene (**35**) and **29** (**Scheme 28**), and we followed the same condition as Target **5** and **6,** in this case we got two spots (probably mono and di-imine) which were very close to each-other, therefore, we could purify that compound.



Scheme 28: Preparation of Target molecule **7**

2.2.2.4 Synthesis of Target 8

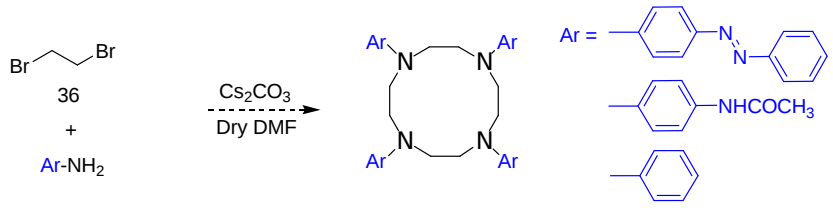
After getting target **6**, we planned to synthesize azamacrocycle. For that we tried to couple it with dibromoethane (**36**), using Cs_2CO_3 as a base in dry DMF (**Scheme 29**). We increased the reaction temperature from room temperature up to 100 °C. However, we got only the starting material. There was no any new spot even after 24 hrs.



Scheme 29: Preparation of Target molecule **8**

2.2.2.5 Synthesis of Target 9

In order to synthesize target **9**, we followed the same condition as in the previous experiment. In this regard, dibromoethane (**36**) was tried to couple with **31** using Cs_2CO_3 as a base in dry DMF (**Scheme 30**). In this case, we got only one spot which was having the same R_f as 4-aminoazobenzene, but in $KMNO_4$, the color was different for both and so we purified this and collected the NMR, IR and HRMS data. However, all the data confirmed that it was only the starting material. Therefore, we tried the same reaction with different anilines, however, in none of the case, we got our desired product.



Scheme 30: Preparation of Target molecule **9**

2.3 Photoswitching studies

2.3.1 Photoswitching studies of target 6

We performed the photoswitching experiments of *bis*-azobenzene coupled product (target **6**) by following the UV-Vis spectroscopy. The absorption spectra for target **6** showed two maxima at 258 and 415 nm. Upon irradiation at 365 nm for 5 minute, we observed a decrease in the 415 nm absorptions, however the band at 258 nm showed an increase (**Figure. 4**). On the other hand, 20 minutes irradiation led to the increase in both the absorption bands, and after 30 minutes, it reached a photostationary state (PSS).

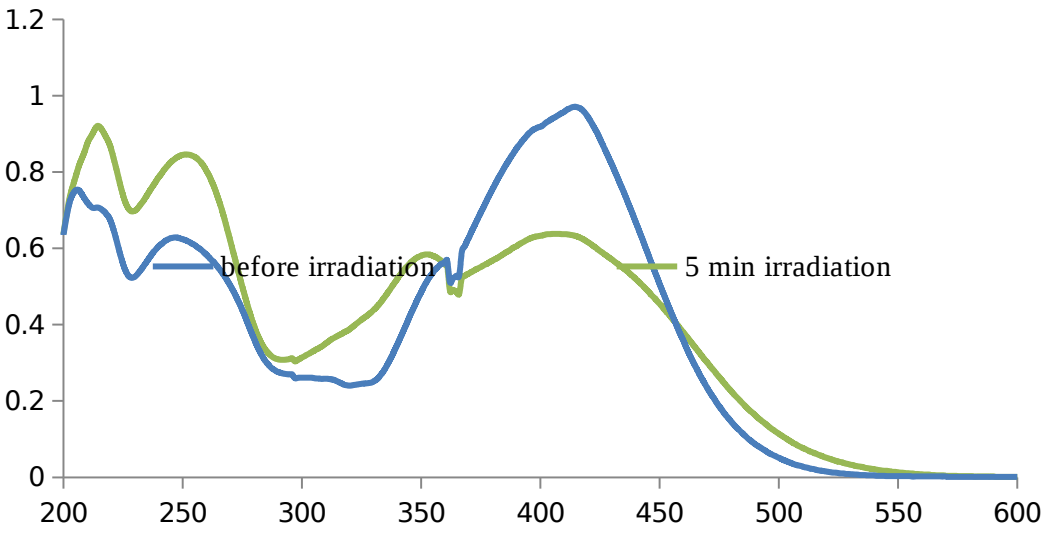
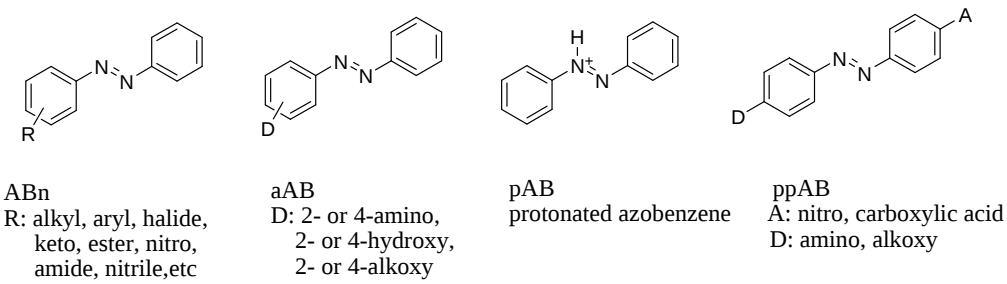


Figure 4: Photoswitching studies of target **6** in Acetonitrile

Normally there are there kind of azobenzene,[18] a.) When π-π* transition occurs in UV region and n-π* transition in visible region (π-π* and n-π* is well separated) that means it is normal azobenzene (ABn). b.) When π-π* transition shifted to higher wavelength, which lead to overlap between the two transitions that means it is electron rich azobenzene (aAB), e.g: aminoazobenzene. c.) When π-π* and n-π* is nearly

degenerate in energy e.g: psedostilbenes, psedostilbenes includes protonated azobenzene (pAB) and push-pull azobenzene (ppAB) (**Figure 5**).



ABn
R: alkyl, aryl, halide, keto, ester, nitro, amide, nitrile,etc

aAB
D: 2- or 4-amino, 2- or 4-hydroxy, 2- or 4-alkoxy

pAB
protonated azobenzene

ppAB
A: nitro, carboxylic acid
D: amino, alkoxy

Figure 5: Types of substituted azobenzenes

In the case of target **6**, π-π* and n-π* of the azobenzene is overlapping. Therefore, when we irradiated at 365 nm, *cis* also absorbed at this wavelength, because of that, we were not able to see the complete conversion of *trans* to *cis*. Although there was a change in absorption spectrum, there was no new feature that can be assigned to *cis* isomer. Therefore, we need to do the photoswitching using different wavelength of LED.

Apart from that, we tried to dissolve it in H_2O by converting them into their salt of HCl, which can protonate the 2° amine. The UV-Vis spectra of the salt as an aqueous solution were recorded (**Figure 6**). In this case, the λ_{max} got shifted from 415 nm to 498 nm. However, upon irradiation at 365 nm for 5-30 minutes, we observed no change in UV spectra. This might be due to its psedostilbenes character, which includes protonated azobenzene (pAB) and push-pull azobenzene (ppAB).

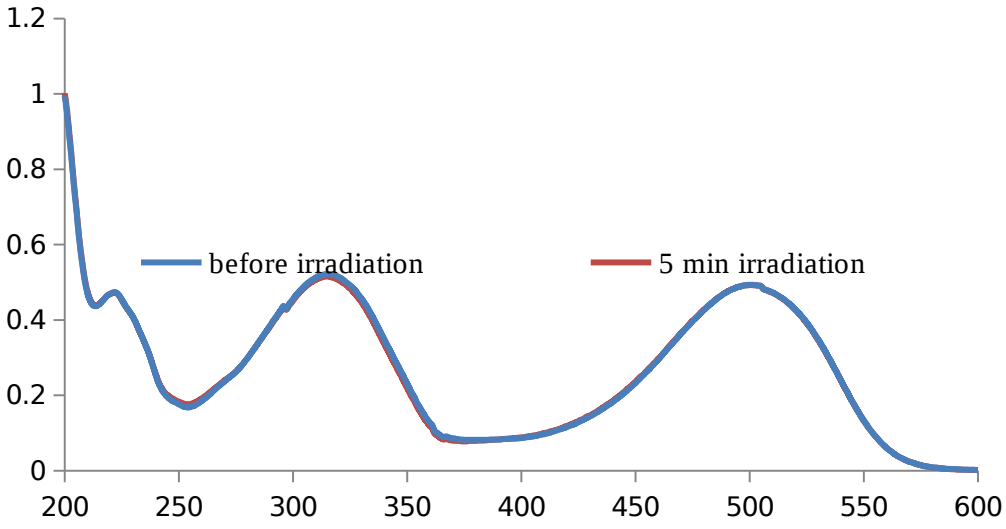


Figure 6: Photoswitching studies of target 6 in water

To compare this result, the UV spectrum was recorded for 4-aminoazobenzene as its salt (**Figure 8**). In this case also the λ_{max} got shifted from 388 nm (free amine) to 496 nm (HCl salt). Normally, aminoazobenzene forms two types of salt with acid (**Figure 7**). [19] When one equivalent of HCl is used, it will protonate at NH_2 funtional group (1) and UV spectrum will be same as azobenzene, however, when excess of HCl is used, the salt of the quinone-iminohydrazone (2) will form and the spectrum of this salt will be different from that of azobenzene.

(1) (2)

Figure 7: Types of 4-aminoazobenzene salt with acid

Probably in the case of 4-aminoazobenzene as well as target **6,** it is forming quinone-iminohydrazone like structure. Therefore, it is not switching or we are not able to see the switching due to fast switching behavior of molecule due to free rotation along N-N single bond.

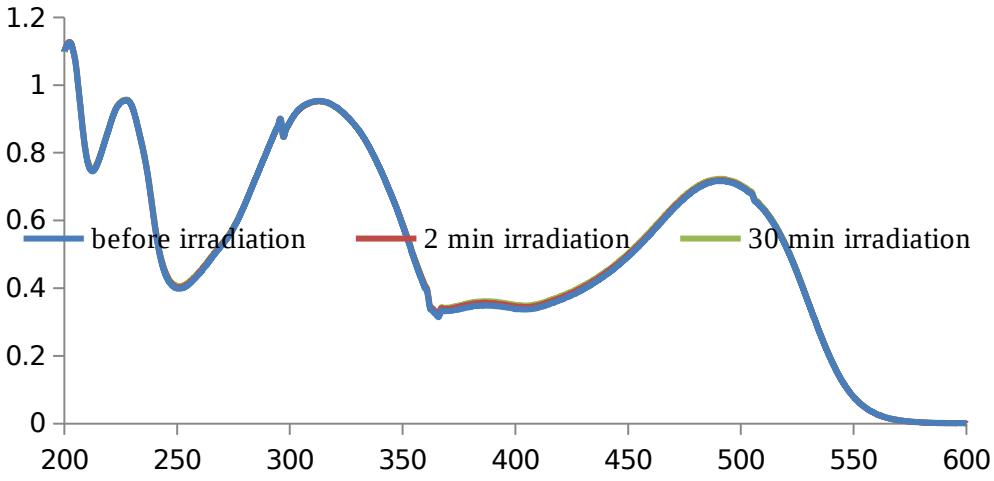


Figure 8: Photoswitching studies of 4-aminoazobenzene in water

Chapter 3

Conclusions and perspectives

Through this investigation on synthesis of multiple azobenzene connected molecular system towards the applications of molecular transporter and spin crossover etc., the following conclusions have been obtained:

- In section 1, some photoswitchable units such as 4-acetylaminoazobenzene, 4-hydroxyazobenzene, 4-hydroxymethylazobenzene, and 4-bromomethylazobenzene, were synthesized and characterized by NMR and MS.

- These azobenzene derivatives were tried to connect with core moieties through, *N*-arylation, *O*-arylation, *O*-alkylation and esterification. In the case of esterification of trimesic acid, a non-polar product was formed, however, during purification using silica gel column chromatography, it hydrolysed back to the alcohol. Hence, the reaction conditions and purification methods have to be optimized further. In case of O-alkylation of phloroglucinol, we got so many spots, therefore, after column we could not get the pure product.

- In section 2, one photoswitchable unit, 4-formylphenylazobenzene as well as one of the target molecules, 6 (1,4-Benzenedimethanamine,N^1,N^4-diphenylazobenzene), were synthesized and characterized by NMR and MS. Using this ligand molecule, we performed photoswitching studies in acetonitrile and water. Utilizing this ligand, metal ion binding studies and making spin cross-over complexes can be explored.

Chapter 4

Experimental Section

4.1 General Methods:

All the solvents and reagents were purchased from commercial suppliers (Sigma Aldrich, Merck, HiMedia and TCI). The reactions monitored by TLC was purchased from Merck and visualized in UV light and iodine chamber. Column chromatography was performed on silica gel (60-120 mesh and 100-200 mesh) purchased from HiMedia. The IR spectra were recorded on “Perkin elmer Lamda- 35” FT-IR spectrometer. UV spectra were recorded on “Labindia UV3000”. HRMS spectra were recorded in Bruker maxis spectrometer using ESI mode. The ^{1}H NMR and ^{13}C NMR were recorded on an “Avance-III, Bruker Biospin” 400 MHz and 100 MHz, respectively at room temperature. Chemical shifts are reported in parts per million (ppm,δ) relative to tetramethylsilane (δ 0.00). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were recorded as multiplet (m). Coupling constants are reported in Hertz (Hz).

4.2 Synthesis

N-(4-nitrosophenyl)acetamide (11)

After Oxone (4.70 g, 4.6 mmol, 4.6 eq) had dissolved completely in water (100 mL), Potassium carbonate (1.18 g, 8.65 mmol, 2.6 eq) was added immediately into a solution of 4-aminoacetanilide (.500 g, 3.329 mmol, 1 eq) in 50 mL of water. The reaction mixture turned into pale green. Green solid nitroso product was observed after the filtration, which was filtered using water and then dissolved in ethyl acetate and dried under vaccum. The product was directly used in next step for the preparation of 4-aminoazopyridine; HRMS (ESI+) *m/z* calculated for $C_8H_8N_2O_2$: $[M+H]^+$: 165.0664; found 165.0667;

4-Acetylaminophenylazobenzene (6)

4-aminoacetanilide (1.03 g, 6.66 mmol, 1 eq) was dissolved in EtOH (3.4 mL), nitrosobenzene (0.713 g, 6.66 mmol, 1 eq) was dissolved in AcOH (13.6 mL) under Ar atmosphere (green solution was formed). Then, 4-aminoacetanilide solution was added into nitrosobenzene solution and the reaction mixture was heated at 40 ^oC under Ar gas over 24 hrs with continuous monitoring through TLC. Upon completion, work up was done using aq. $NaHCO_3$ and ethyl acetate then subjected to column purification in hexane and ethyl acetate (4:1) to yield orange solid product in 85% yield; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.25 (s, 3H), 7.53-7.48 ppm (m, 4H), 7.95-7.92 (t, 4H), 7.71-7.69 (d, 2H); IR (KBr, cm^{-1}): 3313, 3195, 3036, 1907, 1671, 1596, 1540, 1372, 1315, 1259, 1155, 1142, 842 cm^{-1} ; HRMS (ESI+) *m/z* calculated for $C_{14}H_{13}N_3O$: $[M+H]^+$: 240.1137; found 240.1141; melting point : 140 ^oC

4-Hydroxyazobenzene (7)

Fresh aniline (.50 mL, 5.37 mmol, 1 eq) was dissolved in a mixture of concentrated HCl (.50 mL, 16.4 mmol) and water (5 mL). It was cooled (< 5 ^oC) before subsequent dropwise addition of a solution of $NaNO_2$ (0.401 g, 6.04 mmol 1.05 eq) in water (5 mL). It was stirred for 30 min, before addition of phenol in an aq. Solution of NaOH (1.0 M). The reaction mixture was kept for stirring for 30 min at RT. Filtration was done using cold water and drying under vaccum and crude product was purified using column chromatography in Hexane and ethyl acetate (99:1) to yield dark orange solid product in

78 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.92-7.89 (m, 4H), 7.54-7.46 (m, 3H), 6.98-6.95 (m, 2H), 5.54 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm): 115.80, 122.56, 124.99, 129.06, 130.47, 147.15, 152.65, 158.21; IR (KBr, cm^{-1}): 3439, 3131, 2924, 2359, 1586, 1505, 1453, 1415, 1276, 1238, 1219, 1141, 836; HRMS (ESI+) *m/z* calculated for $C_{12}H_{10}N_2O$: $[M+H]^+$: calculated 199.0871; found 199.0868; melting point : 118 ^{o}C.

4-Hydroxymethylazobenzene (20)

In an oven dried RBF, N_2 was produced and nitrosobenzene (1.01 g, 7.9 mmol, 1.09 eq) was dissolved in AcOH (10 mL), 4-aminobenzylalcohol (1.166 g, 8.12 mmol, 1 eq) was added and kept for stirring at RT. After 4-5 hours some golden coloured compound solidified. After completion of the reaction work up was done using aq. $NaHCO_3$, and organic layer was extracted in ethyl acetate. Column purification was done in hexane and ethyl acetate (50:4) to yield 53 % of pure light orange solid product. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 4.80 (s, 2H), 7.55 (d, *J* = 7.64 Hz, 5H), 7.95 (d, *J* = 7.92 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm): 64.88, 122.85, 123.09, 127.44, 129.11, 131.04, 143.83, 152.07, 152.60. IR (KBr, cm^{-1}): 3328, 2916, 2853, 1640, 1023, 684, 525; melting point : 136 ^{o}C.

4-Bromomethylphenylazobenzene (8)

4-hydroxymethylazobenzene (500 mg, 2.4 mmol, 1 eq) and CBr_4 (1.56 g, 4.7 mmol, 2 eq) was taken in an oven dried RBF and dry DCM was added in Ar atmosphere. Before the addition of PPh_3, the reaction mixture was cooled to 0 ^{o}C then PPh_3 was added portion wise for 20-25 minutes (color was changed from orange to dark brown), the reaction mixture was kept for stirring at room temperature for 2 hrs. Crude product was vaccum distilled and then extracted in ethyl acetate without the addition of water, column purification was done in hexane to yield 45 % of orange solid product. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 4.58 (s, 2H), 7.58-7.52 (m, 5H), 7.96-7.91 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm): 32.80, 122.93, 123.29, 129.13, 129.90, 131.25, 140.52, 152.31, 152.56; IR (KBr, cm^{-1}): 2924, 1411, 1150, 841, 683, 603, 465; melting point: 75 ^{o}C.

4-Methylsulfonoxymethylphenylazobenzene (9)

In an oven dried RBF, 4-hydroxymethylazobenzene (500 mg, 2.355 mmol, 1 eq) and TEA (657 µL, 4.523 mmol, 2 eq) were dissolved in dry DCM under Ar atmosphere. A solution of Methanesulfonyl chloride in dry DCM was added dropwise with external cooling of 4-hydroxymethylazobenzene and TEA reaction mixture. Reaction got completed within 10 min, the R_f value was exactly same as 4-hydroxymethylazobenzene. However, In $KMNO_4$ solution there both were showing the different character. In this case, after work up and distillation of solvent under vacuum, a sticky and foamy orange colored compound was obtained, which was utilized for the next steps without further purification.

4-Formylphenylazobenzene (29)

In an oven dried RBF, 4 A^o molecular sieves were taken and 4-hydroxymethylazobenzene (500 mg, 2.4 mmol, 1 eq) was dissolved in dry DCM and then PCC (609 mg, 2.8 mmol, 1.2) was added in inert condition. After the completion of reaction, work up was done using aq. $NaHCO_3$, and organic layer was extracted in DCM, then Purification was done in hexane and ethyl acetate (50:1) to yield dark orange solid product in 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.58-7.56 (m, 3H), 7.98 (d, *J* = 1.58 Hz, 2H), 8.07 (d, *J* = 8.2 Hz, 4H), 10.13 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm): 32.16, 122.36, 125.55, 128.73, 128.83, 129.69, 131.63, 144.27, 148.72; IR (KBr, cm^{-1}): 3440, 3054, 2841, 1697, 1596, 1196, 844, 681; melting point: 96 ^{o}C.

1,4-Benzenedimethanamine,N^1,N^4-diphenylazobenzene (target 6)

This reaction was carried out using Dean-stark apparatus. Terephthalaldehyde (100 mg, 0.745 mmol, 1 eq) and 4-aminoazobenzene (294 mg, 1.49 mmol, 2 eq) were dissolved in Dry toluene then catalytic amount of PTSA (5 mol%) was added. After the addition of PTSA some orange precipitate came out of the reaction, it was not dissolving in any other solvent. Therefore, it (imine) was filtered out and kept for drying under vaccum to yield 80%. For the reduction part, the imine (110 mg, 0.223 mmol, 1 eq) was dissolved in THF and after external cooling, $NaBH_4$ (135 mg, 3.56 mmol, 16 eq) was added pinch wise till 20 min. After 24 hrs it got dissolved and one spot at the same R_f of 4-aminoazobenzene was observed. In iodine chamber the colour was different for both. Therefore, product was separated in ethylacetate and $NaBH_4$ got dissolved in water. Product was dried out under vaccum distillation without column purification to yield 65%. ^{1}H NMR (400 MHz, DMSO): δ (ppm): 4.39 (d, *J* = 5.56 Hz, 2H), 6.73 (d, *J* = 8.12 Hz, 2H), 7.36 (s, 4H),

7.42-7.36 (t, 2 H), 7.52-7.49 (t, 4H), 7.75-7.69 (m, 8H); ^{13}C NMR (100MHz, DMSO): δ (ppm): 46.26, 112.44, 113.81, 122.19, 125.49, 125.64, 127.83, 129.64, 129.92, 138.43, 143.40, 152.42, 152.87; IR (KBr, cm^{-1}): 3413, 2882, 1600, 1517, 1425, 1332, 1267, 1136, 826, 768, 686, 546; HRMS (ESI+) *m/z* calculated for $C_{32}H_{28}N_6$ $[M+H]^+$: 497.2454; Found: 497.2437; melting point: 198 °C.

4.3 Photoswitching Studies:

Photoswitching studies have been carried out in micromolar concentrated solutions of various azobenzenes using a quartz cuvette. The irradiation was done either using LED light sources (365 nm and 405 nm wavelength sources) or by using a white light house hold CFL bulb. The photoswitching or *cis-trans* isomerization was followed by recording UV-Vis spectra at different intervals of time.

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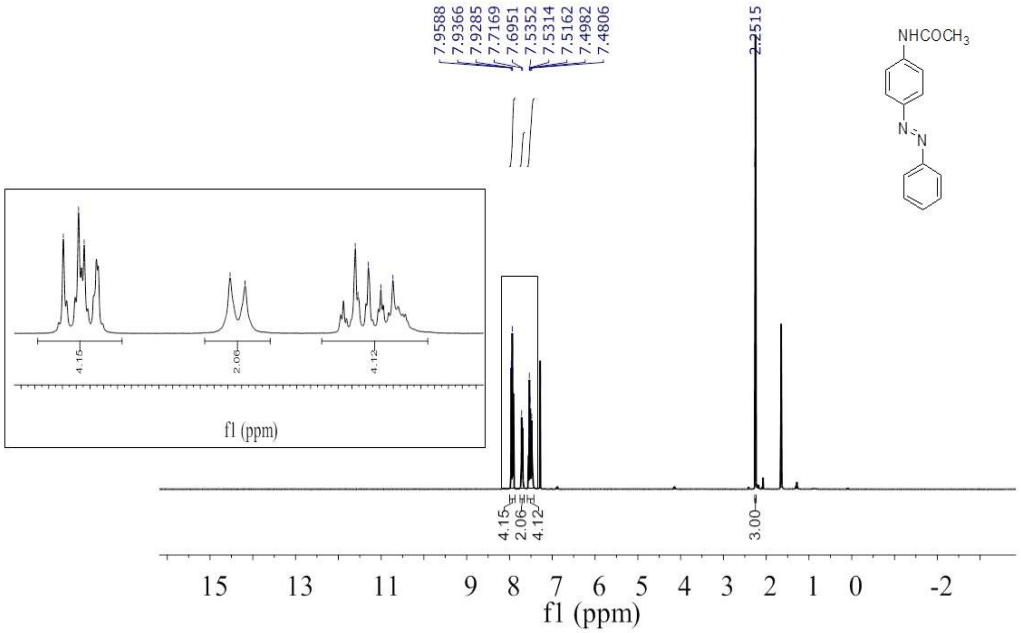
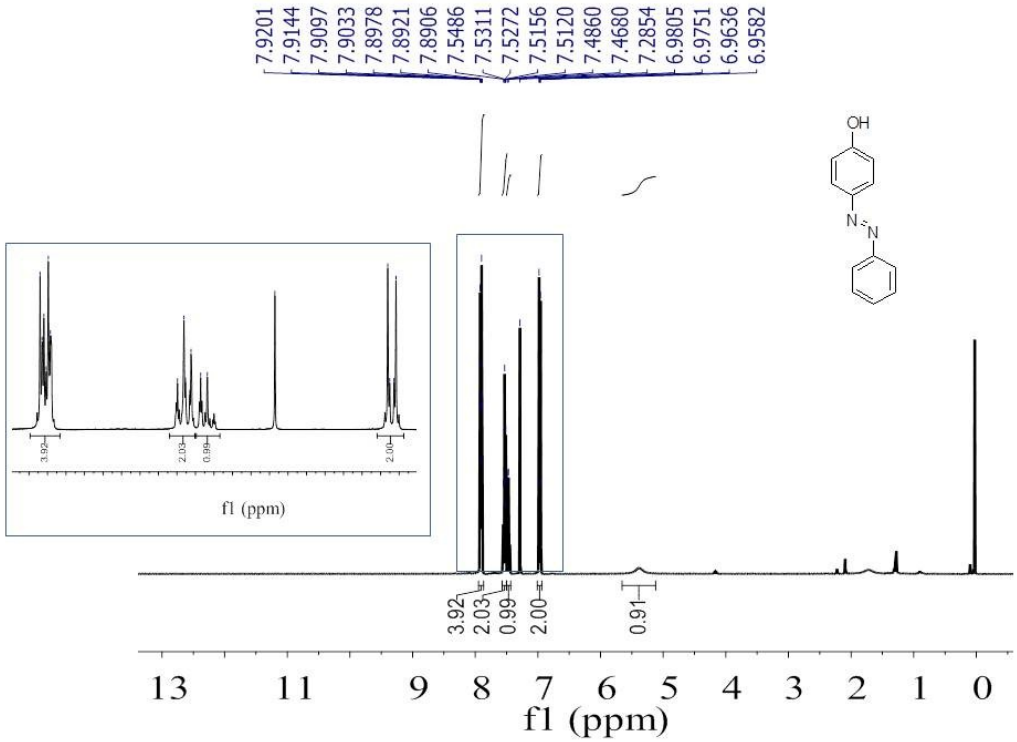
Appendix

^{1}H-NMR of 4-acetylaminophenylazobenzene (6) in $CDCl_3$



^{1}H-NMR of 4-hydroxyazobenzene (7) in $CDCl_3$



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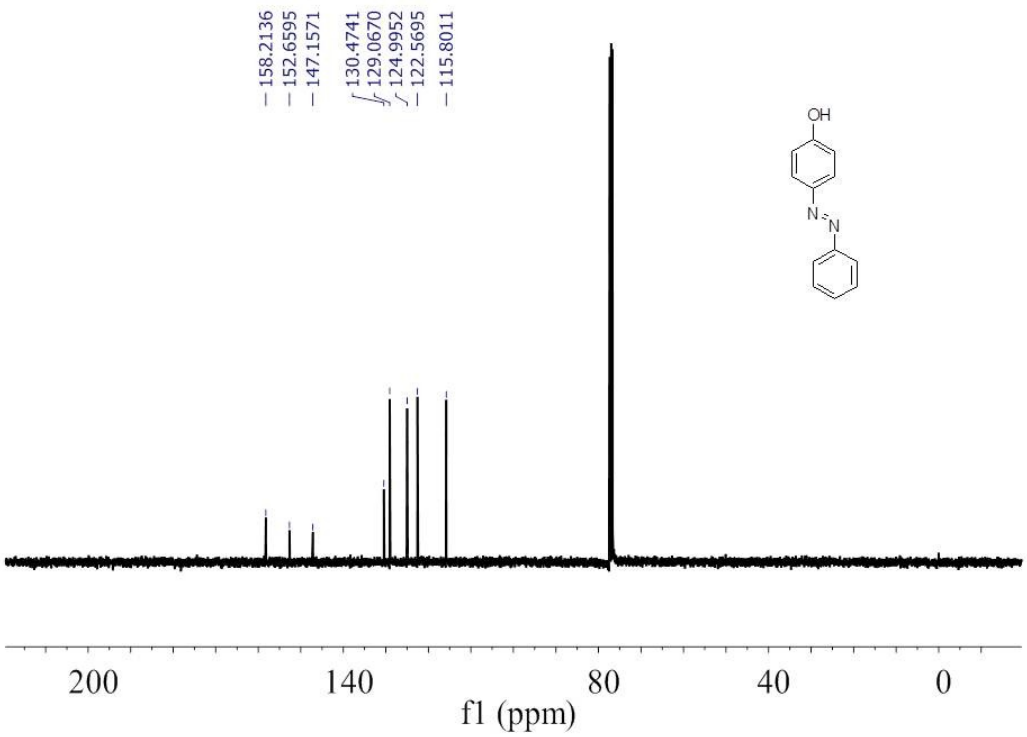
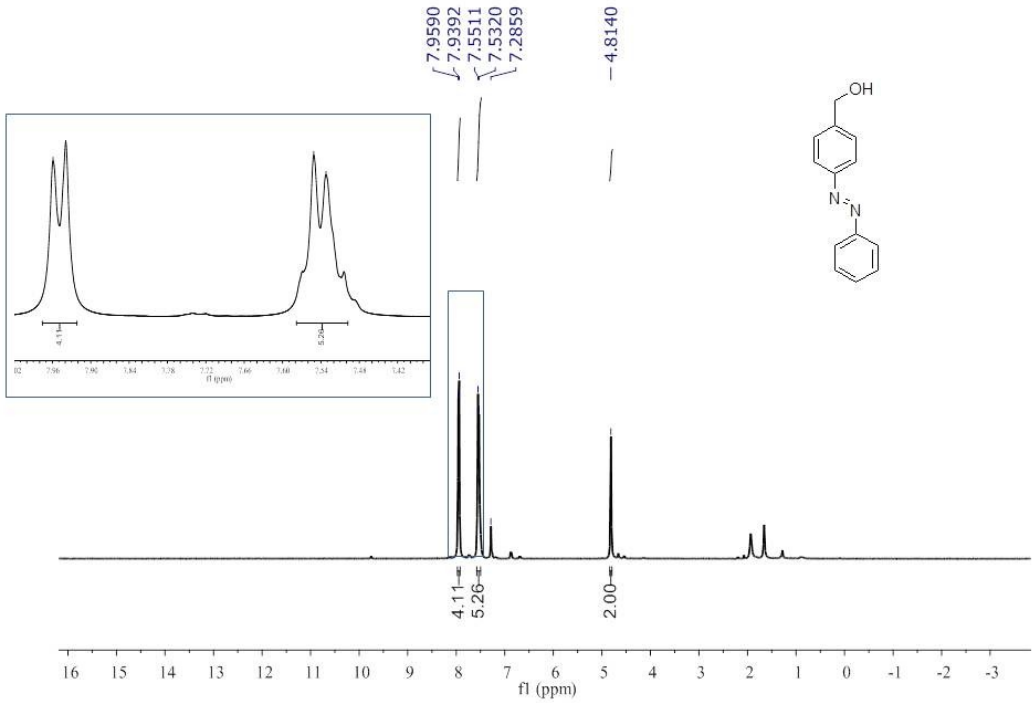


^{1}H-NMR of 4-hydroxymethylazobenzene (20) in $CDCl_3$



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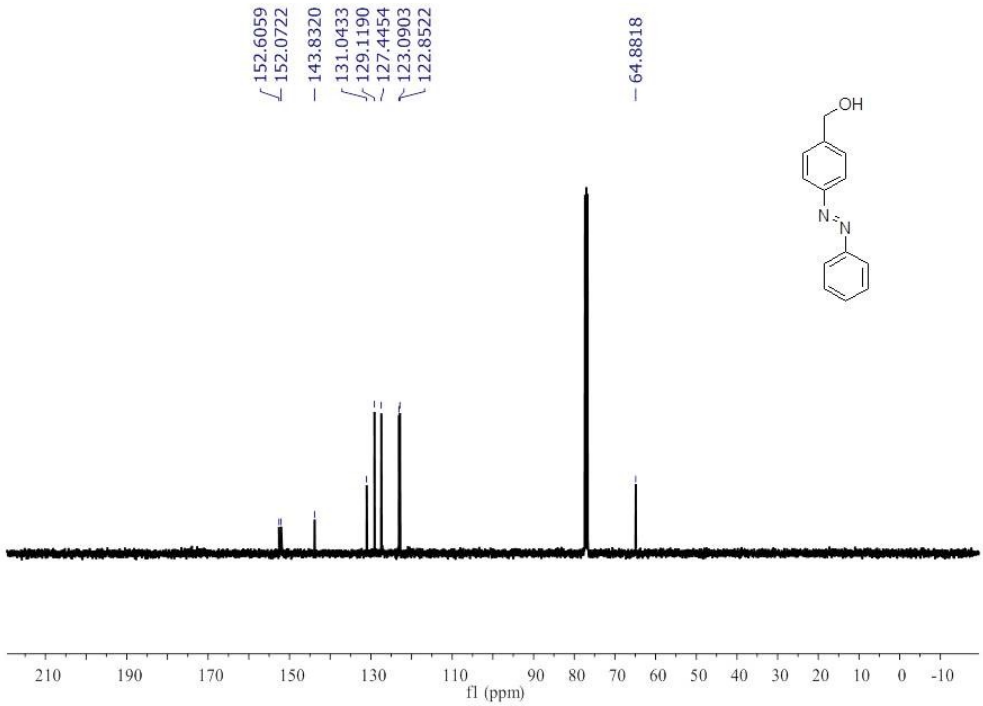
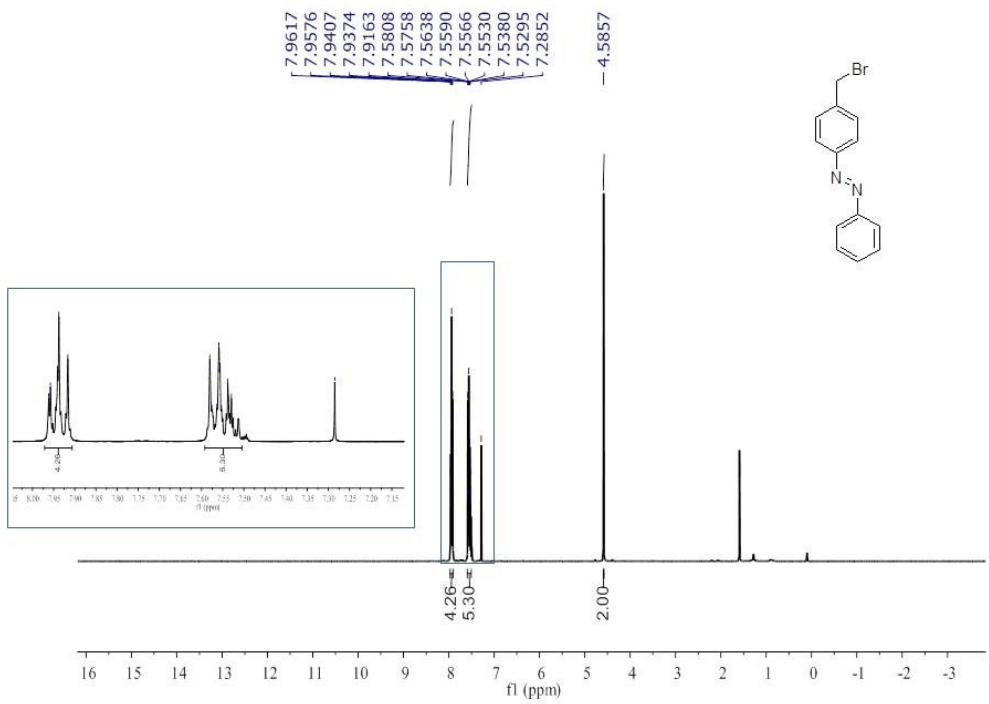


^{1}H-NMR of 4-bromomethylphenylazobenzene (8) in $CDCl_3$



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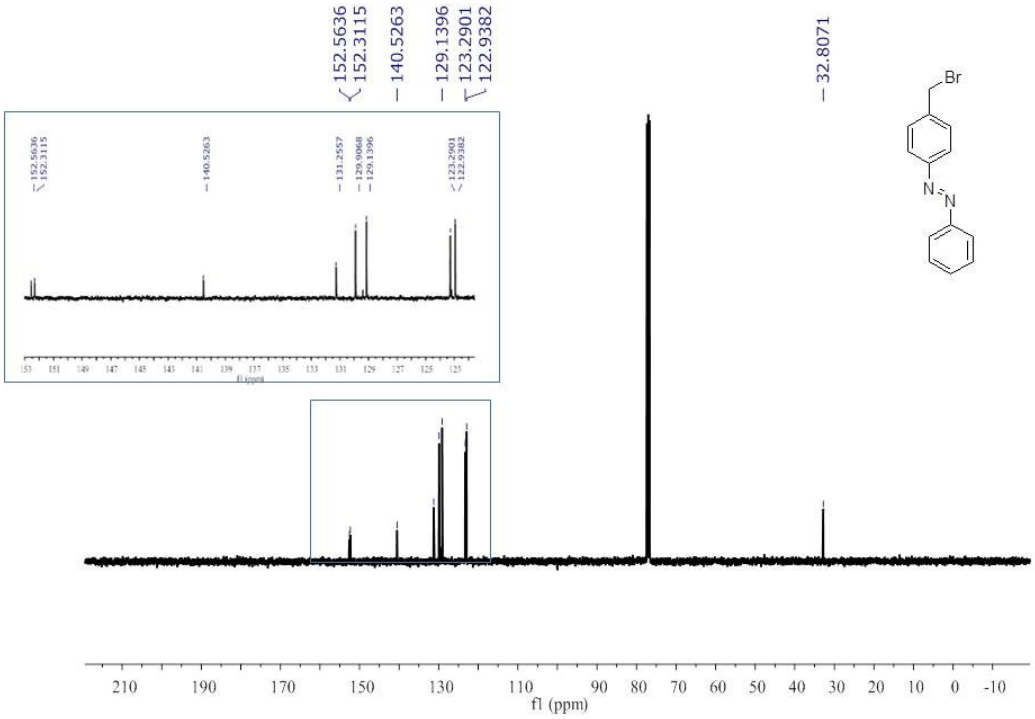
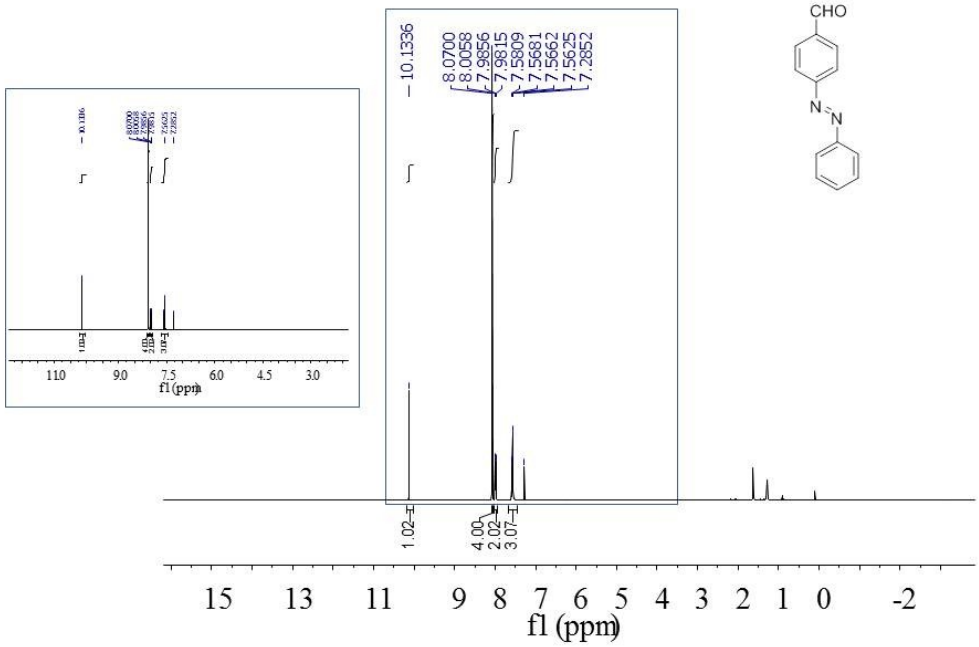
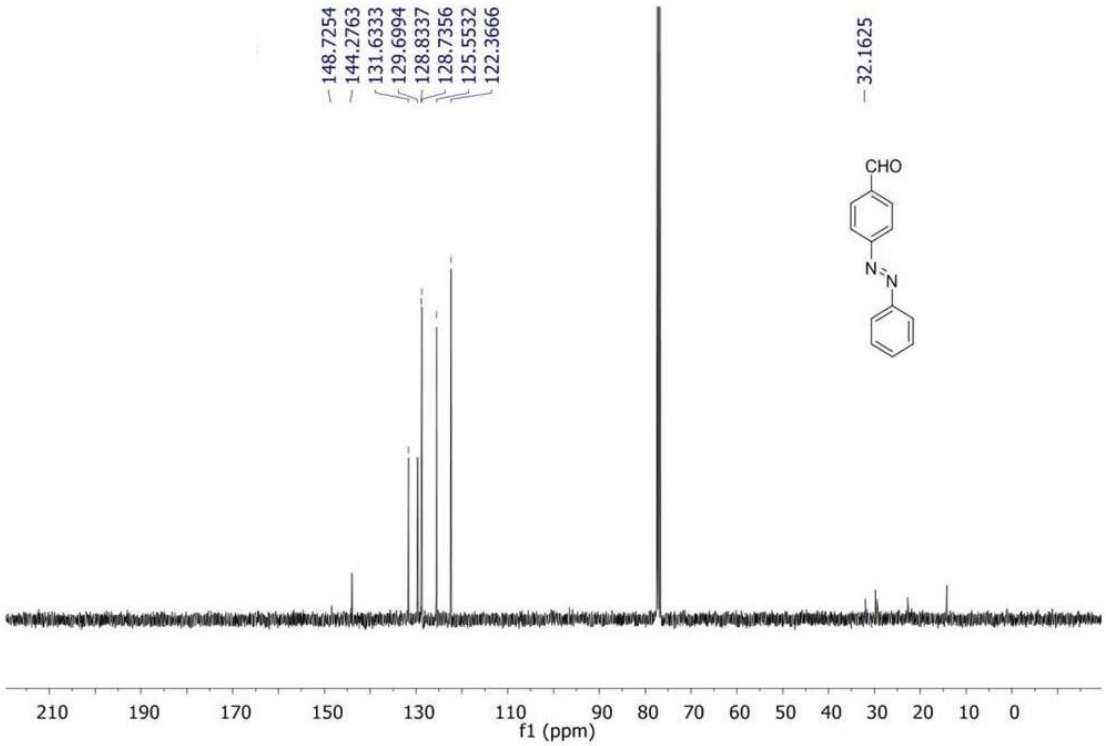


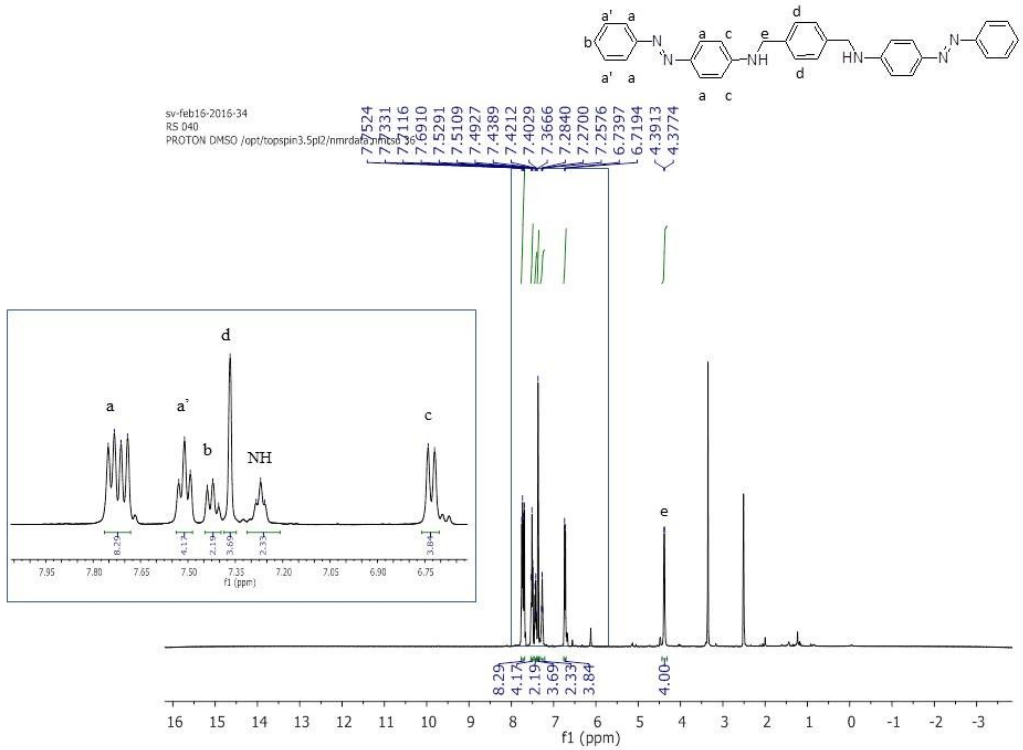
^{1}H-NMR of 4-formylphenylazobenzene (29) in $CDCl_3$



^{13}C-NMR of 4-formylphenylazobenzene (29) in $CDCl_3$



^{1}H-NMR of 1,4-Benzenedimethanamine,N^1,N^4-diphenylazobenzene (target 6) in DMSO-d_6



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