Synthesis and Photoswitching Studies of Water Soluble Azobenzene Based Molecules

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Certificate of Examination

This is to certify that dissertation titled "***Synthesis and Photoswitching Studies of Water Soluble Azobenzene Based Molecules***" submitted by Ms. Athira T John (Reg. No. MS11029) for the partial fulfillment of BS MS dual degree programme of Indian Institute of Science Education and Research Mohali, 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 university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussion. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Athira T John
(candidate)
Dated : 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)

Acknowledgement

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Contents

List of Abbreviations

$NaNO_2$	–	Sodium nitrite
H_2SO_5	–	Peroxymonosulfuric acid
DEAD	–	Diethyl azodicarboxylate
DDQ	–	Dicyanobenzoquinone
NMR	–	Nuclear Magnetic Resonance
HCl	–	Hydrochloric acid
DCM	–	Dichloromethane
HRMS	–	High Resolution Mass Spectrometry
AcOH	–	Acetic acid
PCC	–	Pyridiniumchlorochromate
RT	–	Room Temperature
DMSO	–	Dimethyl sulfoxide
KOH	–	Potassium hydroxide
K_2CO_3	–	Potassium carbonate
DMF	–	Dimethylformamide
ACN	–	Acetonitrile
TLC	–	Thin Layer Chromatography
TPP	–	Triphenylphosphine
KOAc	–	Potassium acetate
Dppf	–	*Bis*(diphenylphosphino)ferrocene
PCl_5	–	Phosphorus pentachloride
$SOCl_2$	–	Thionyl chloride
Eq	–	Equivalent

^{1}H NMR	–	Proton Nuclear Magnetic Resonance
^{13}C NMR	–	Carbon Nuclear Magnetic Resonance
RBF	–	Round Bottom Flask
FT-IR	–	Fourier Transform- Infrared Spectroscopy
TEA	–	Triethylamine
NaOH	–	Sodium Hydroxide
UV-Vis	–	Ultraviolet -Visible spectroscopy
nm	–	Nanometer
CFL	–	Compact flouresent light

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Abstract

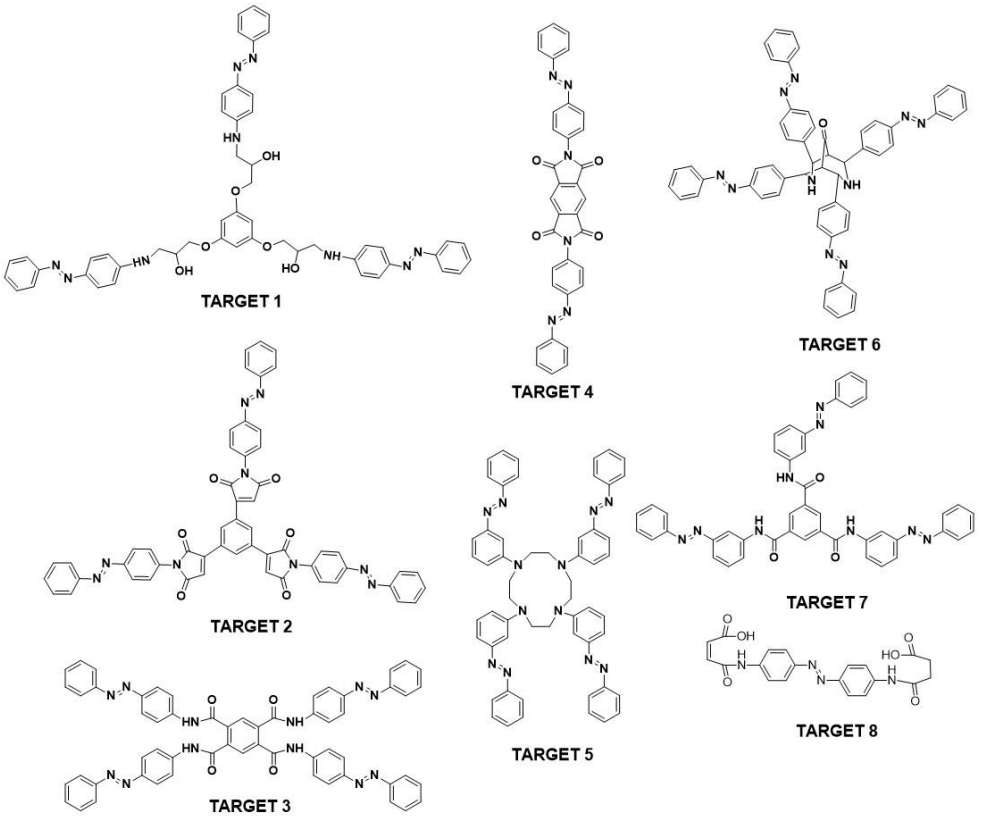
Azobenzene is a photoswitchable molecular machine that can be switched between its two differentisomers by the application of external stimuli, i.e. light. The *trans* to *cis*isomerization occurs following irradiation with UV light. The reverse isomerization (*cis* to *trans*) occurs either photochemically (under irradiation condition) or thermally (under the influence of temperature), due to the thermodynamic stability of the trans isomer. Since this isomerization process is reversible, azobenzenes can be used as photoswitches. The photochromic properties make them an integral part of many functional materials with multiple uses. Theapplications include molecular transporter- where it can be used for drug delivery, metal ion chelators- photoswicthable ligands for binding to metals, energy trap devices- mainly for storage of solar energy, and as an industrial dyes etc.

Our current interest lies in creating photoswitchable reversible molecular transporters. In this regard, our goal is to connect multiple azobenzene moieties to a common linker moiety in such a way that a light controlled void or space can be created. This space can be used to encapsulate the guest and can be used as a small molecular transporter. A long-term goal would be to utilize such systems in drug delivery applications.

Another research interest is to synthesize photoswitchable ligands that can be used as chelating agents for reversible metal ion binding. Besides, their photoswitching behavior can be exploited to study spin crossover through variation in ligand strength. In particular, the synthesis of macrocycles with photoswitchable groups to impart light-induced change in ligand strength can provide such application.

Attempts have been made to synthesize and to study different azobenzene based molecular transporters, metal ion binding ligands and azomacrocycles. In this regard, the following targets as shown in scheme 1 have been chosen and synthetic attempts have been made:

1. Target 1: Epichlorohydrin was tried to couple with phloroglucinol under basic conditions. (Status: Reaction did not yield the desired product)
2. Target 2: Maleimide connected azobenzene was prepared; however, Heck coupling has been tried. (Status: Target has not been achieved)



Scheme 1. Targets

3. Target 3: Acid amine coupling between 1,2,4,5-benzene tetracarboxylic acid and 4-aminoazobenzene.(Status: Product was not obtained)
4. Target 4: Pyromelliticdiimide product. (Status: Product was insoluble in most of the solvents and so it was not characterized)
5. Target 5: Azamacrocyles for spin crossover was targeted by reacting 3-aminoazobenzene and 1,2-dibromoethane (Status: The target product was not obtained)
6. Target 6: Mannich reaction has been attempted (Status: Multiple products, which have not been able to be separated)
7. Target 7: Triamide synthesis (Status: The target product was obtained, however due to delay in purification, the photoswitching part was not able to be performed)
8. Target 8: The diacid product has been synthesized (Status: Photoswitching studies have been done)

Chapter 1

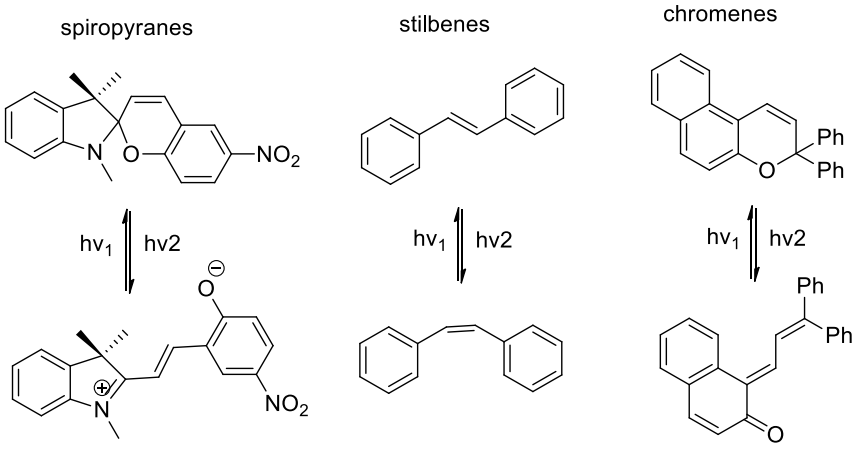
Introduction

1.1 General

Interaction of light with molecules has been always a fascinating area of research. Photoswitchable molecules are photochemically active compounds that can be switched between (at least) two states by irradiation with light. The consequence of molecules absorbing light is the formation of transient excited states, whose chemical and physical properties differ greatly from the original molecule.[1] As a result of irradiation, significant modification occurs in properties like - mechanical, magnetic, electrical, optical, pH etc. Photochromism is a special case of photochemical reaction, where the reversible transformation of a chemical species between two forms is favoured by the absorbtion of electromagnetic radiation.

1.2 Organic photoswitchable molecules

Organic photochromic molecular switches are based on molecules that can be reversibly interconverted, by any external stimuli. The most common chromic molecules are azobenzenes, stilbenes, spiropyranes, fulgides, diarylethenes and chromenes.[2] Depending on the thermal stability of the photogenerated isomer, photochromic systems can be classified as 1) P type (photochemically reversible type) and 2) T type (thermally reversible type). Azobenzenes and stilbenes belong to T type, whereas fulgides and diarylethenes belong to P type photochromic systems.



Scheme 2. Important photochromic compounds [2]

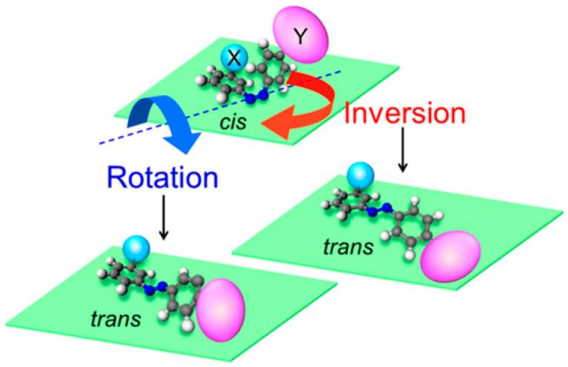
1.3 Azobenzene

Azobenzene is an aryl azo compound with two phenyl rings separated by (-N=N-). It is a diazine (HN=NH) derivative with phenyl groups in place of hydrogen. These are chemically stable molecules, which absorb light strongly and so their major application lies in dyes and pigments. The photochromic properties of azobenzenes can be used in different applications like surface modified materials, molecular transporters, metal ion chelators, energy storage etc. The light driven reversible isomerization of azobenzene between *cis* and *trans* forms makes them selective candidates as molecular switches. "Molecular switches" denote systems, either small molecules or supramolecular species, that can be reversibly shifted between at least two different states.[3] The two isomers can be switched with particular wavelengths of light. The *trans-cis*isomerization can occur when irradiated with UV light. The reverse *cis-trans*isomerization can be light driven or occurs thermally in the dark. The isomerization mechanism and quantum yield is dependent on many factors like isomeric form, excitation mode, irradiation wavelength, solvent properties, substituent's on the phenyl rings, temperature and pressure etc.[4]

1.4 Photoisomerization of azobenzene

Based on the energy ordering of the (n, π*) and (π, π*) electronic states, azoarene chromophores can be classified into three spectral types, namely, azobenzene type, aminoazobenzene type and pseudo-stilbene type.[5] Azobenzene type molecules show low intensity (n,π^*) absorbtion band in the visible region and high intensity ($\pi\rightarrow\pi^*$) band in the UV. For aminoazobenzene type molecules the ($n\rightarrow\pi^*$) and ($\pi\rightarrow\pi^*$) are very close and overlap in the near visible UV region. For pseudo-stilbene molecules the 4 and 4'position substitution with electron donor and acceptor substituents shift the ($\pi\rightarrow\pi^*$) transition past that of the ($n\rightarrow\pi^*$). From X-ray and computational studies it was observed that *trans*-azobenzene adopts a planar structure with C_{2h} symmetry, whereas *cis*-azobenzene adopts non-planar conformation with C_2 symmetry.[6] Electron diffraction data indicates the two phenyl rings of *trans* azobenzene twisted approx. 30^oCin the gas phase. The absorbtion spectra of *trans*- azobenzene have two well-separated bands in the UV region corresponding to ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transitions. The ($\pi\rightarrow\pi^*$) transition in *cis*-azobenzene is weaker, however,($n\rightarrow\pi^*$) transition absorbs more strongly than *trans*-azobenzene. The

two transitions excite azobenzene to S_1 (n,π^*) and S_2 (π,π^*) states. From the absorbtion spectra of azobenzene two different isomerizationpathways have been proposed; 1) in-plane inversion by the bending of an N=N-C bond and 2) out-of-plane rotation by the torsion of two phenyl rings. From time resolved spectroscopic studies, it has been found that the isomerization proceeds in the S_1 state via the inversion pathway. While in the gas phase rotation pathway is energetically more favourable.[7]



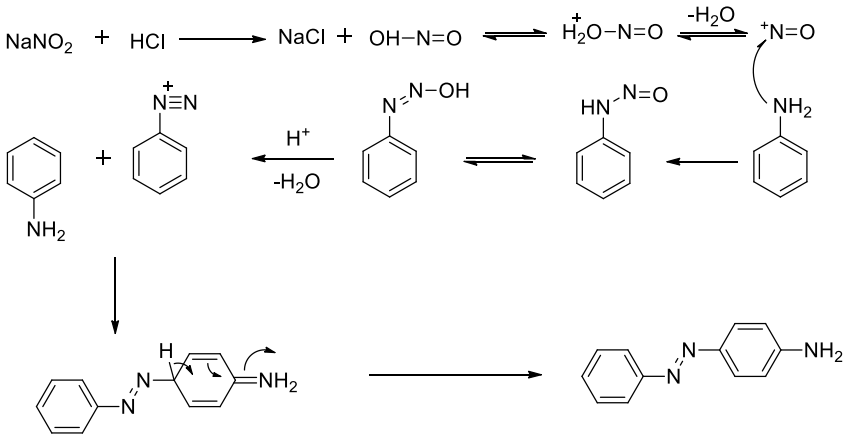
Scheme 3. Isomerization pathways of azobenzene(adopted from ref [8])

1.5 Synthesis of azo compounds

The classical methods to prepare azo compounds are the azo coupling reactions (coupling of diazonium salts with activated aromatic compounds), oxidative coupling of anilines, mills reaction (reaction between aromatic nitroso derivative and aniline) and Wallach reaction. We have adopted azo coupling and Mills reaction in our lab.

1.5.1 Azo coupling reaction

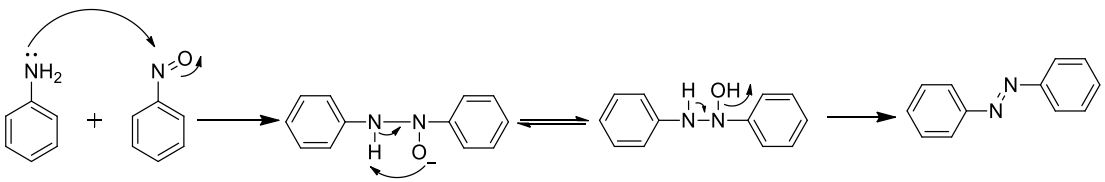
This is the main reaction used for synthesis of azo compounds. In azo coupling primary amine is converted to a diazonium salt, and then reacts with an electron rich nucleophile having electron donor groups like amine and hydroxyl to obtain the desired azobenzene derivatives. In accordance with the mechanism shown in **scheme 4** for the formation of diazonium salt, acid is necessary for the *insitu*generation of nitrous acid from $NaNO_2$. Then protonation and water elimination gives the nitrosating agent, which then reacts with amine to give *N*-nitroso derivative. A second protonation followed bywater elimination gives the diazonium salt, which is stabilized by resonance. Further electrophilic aromatic substitution with the electrophilic nitrogen of the diazonium salt occurs.[9]



Scheme 4. Mechanism of azo coupling reaction

1.5.2 Mills reaction

In Mills reaction condensation of aromatic nitroso derivatives with aniline in glacial acidic acid gives corresponding azobenzenes. The aromatic nitroso derivatives can be prepared by oxidation of aromatic methyl hydroxylamine and with *tert*-butyl hypochlorite. Instead of *tert*-butyl hypochlorite, many other oxidising agents like ferric chloride, Caro's acid (H_2SO_5), sodium or potassium dichromate and sulphuric acid, acetic acid/H_2O_2, *m*-chloroperbenzoic acid, potassium permanganate, ferric chloride, diethyl azodicarboxylate (DEAD), iodine/NaI/NaOAc, silver carbonate, (diacetoxyiodo) benzene, 2,3-dichloro-5,6- dicyanobenzoquinone (DDQ) and peroxyformic acid can be used. Two phase heterogeneous systems like oxone in water is an efficient way to synthesize azobenzenes (**Scheme5**). The mechanism of Mills reaction involves the attachment of aniline on the nitroso derivative in acid media that leads to Azobenzene.[10]

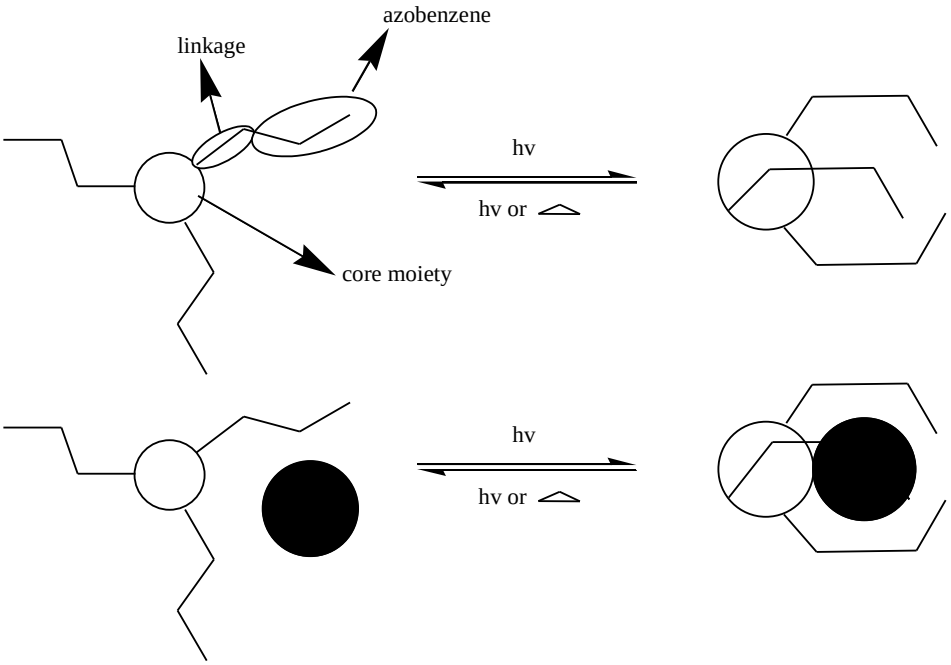


Scheme 5. Mechanism of Mills reaction

1.6 Motivation of our project

Our project mainly focuses on designing photoswitchable functional molecules for different applications, by utilizing the basic photochromic properties of azobenzene. Almost all the target molecules have been designed in such a way that multiple azobenzene molecules are connected to a core moiety through different linkages.

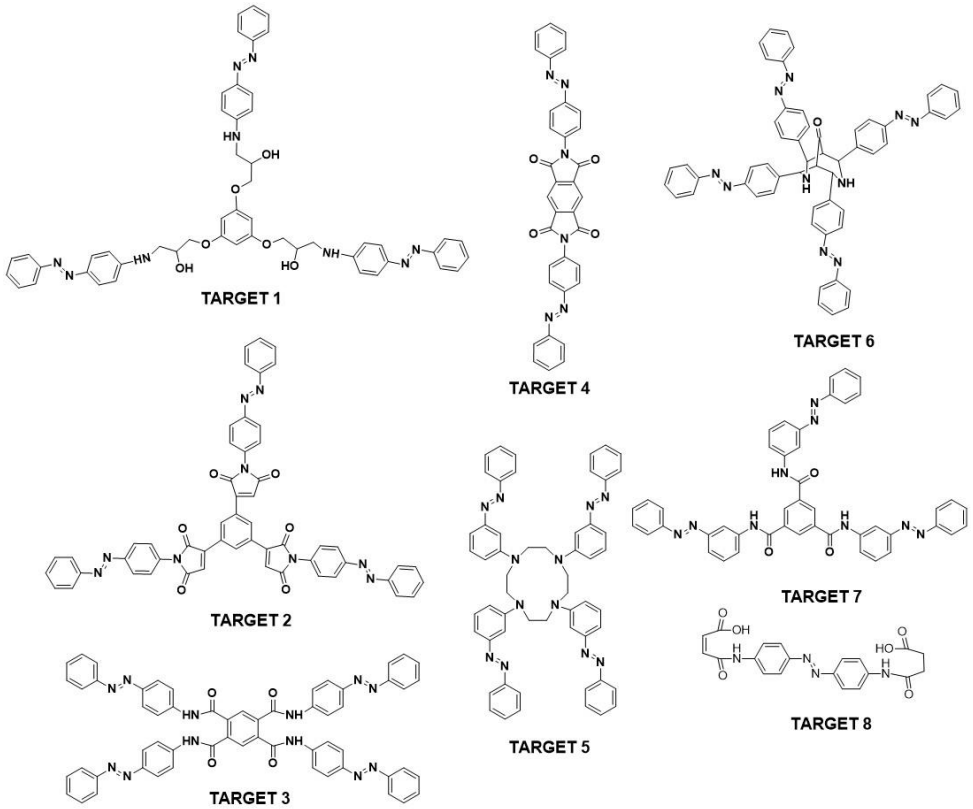
Preferably, all those azobenzene units are expected to undergo switching from *trans* to *cis* in the same direction, leading to a three-dimensional void that can be used for encapsulation and release of the guest molecule. For the choice of core moiety, we considered symmetry and the possibility of tri- and tetra- functionalization. In this regard, we utilized benzene, bispidone and azamacrocycle etc., as our preliminary core moieties, whereas we have chosen different linkages.



Scheme 6. Expected isomerization in the target molecules and photoswitchable molecular transporter

1.7 Target molecules

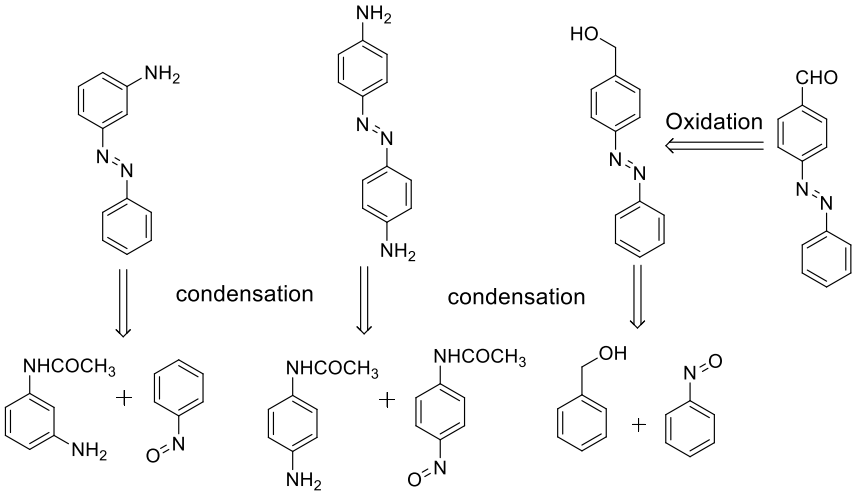
In order to achieve our research goal, we tried to connect the switchable unit to the core moiety by using different linkages. The benzene type core moieties have been functionalized using phluroglucinol, trimesic acid, 1,3,5-triiodobenzene, 1,2,4,5- benzene tetracarboxylic acid and pyromelliticdianhydride. Mannich reaction was exploited in obtaining the bispidone core. Base catalyzed azomacrocyclization has been attempted as well.



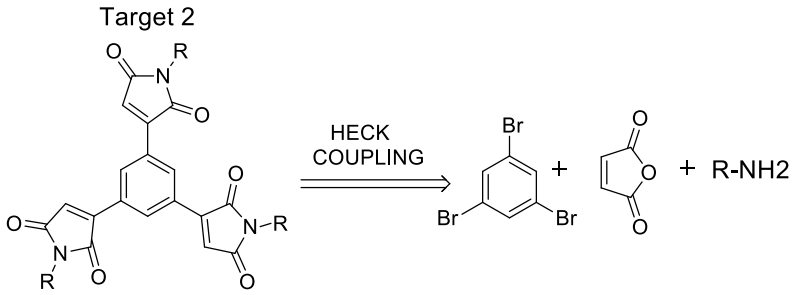
Scheme 7. Target molecules

1.8 Retrosynthetic routes:

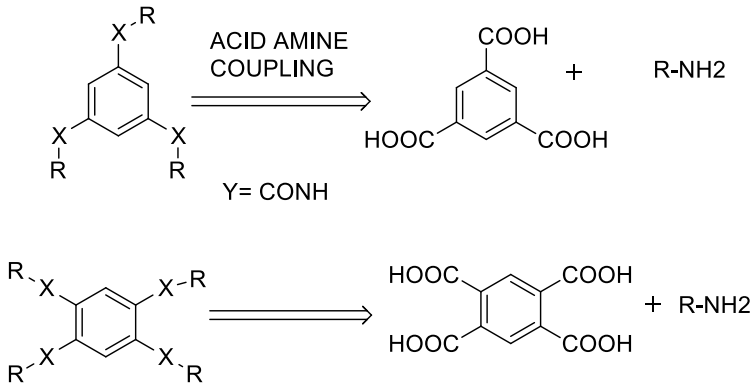
We tried to synthesize the target molecules by the following retrosynthetic routes (**Schemes 8- 14**). The commercially available trimesic acid, 1,3,5-tribromobenzene and phloroglucinol have been considered as the starting materials.1,2,4,5-Benzenetatracarboxylic acid has been prepared from pyromelliticdianhydride by heating it in water at 70^{o}C. With respect to the photoswitchable units, except4-amino azobenzene, which was commercially available, 3-aminoazobenzene, 2-aminoazobenzene, 4,4'-diaminoazobenzene, 4-hydroxymethylazobenzeneand 4-formylazobenzenehave been synthesized (**Scheme 8**). The targets molecules have been tried to synthesize by appropriate strategies.



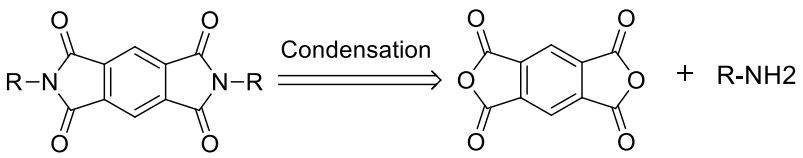
Scheme 8. Retrosynthetic strategies for the photoswitchable untis



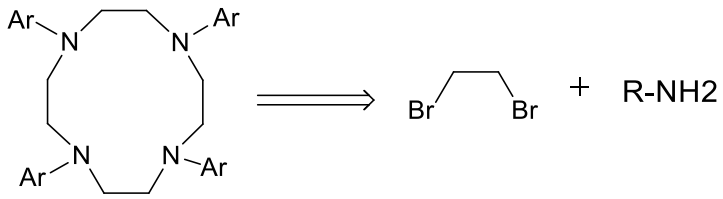
Scheme 9. Heck coupling strategy for target 2



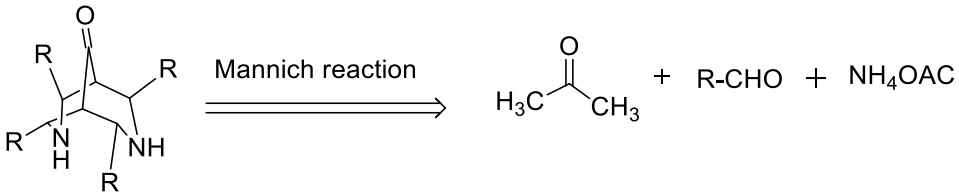
Scheme 10. Retrosynthesis of targets 7 and 3



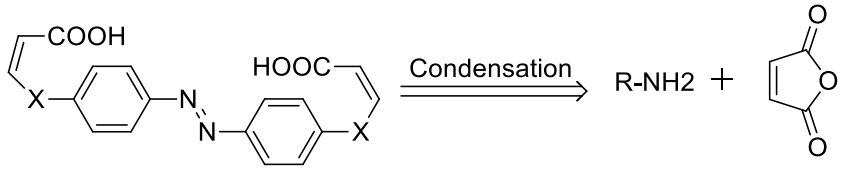
Scheme 11. Retrosynthesis of target 4



Scheme 12. Retrosynthetic route for target 5



Scheme 13. Mannich reaction based retrosynthetic route for target 6



Scheme 14. Retrosynthesis of target 8

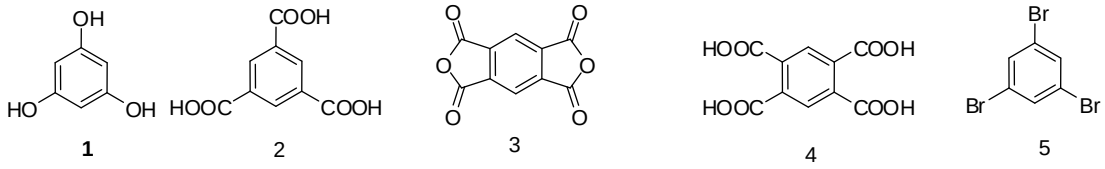
Chapter 2

2. Results and Discussion

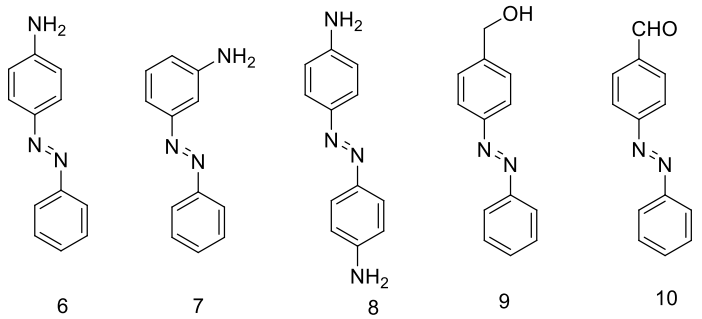
2.1 Design:

The ultimate goal of our present work is to synthesize multiple azobenzene connected molecular systems for various applications such as molecular transporter, reversible metal ion binding and spin cross-over. In this regard, we considered the targets indicated in scheme 1. The important challenges in designing those targets are the choice of core moieties, connection of photoswitchable units to the core and also the ease of synthesis. In order to choose the core moieties, symmetrically substituted molecules have been chosen, so that spectral characterization will be less complicated. For connections, few different strategies such as acid-amine coupling, Heck coupling, Mannich reaction and nucleophilic substitution strategies have been considered.

The molecules 1, 2, 3, 4 and 5 have been used for getting the core moieties with symmetrical functionalization of azobenzenes.(**Scheme9**) The azobenzene derivatives such as 6, 7, 8, 9 and 10 have been synthesized. (**Scheme 10**) To achieve this azocoupling, Mill's method and oxidative coupling have been used.



Scheme 15. Core molecules

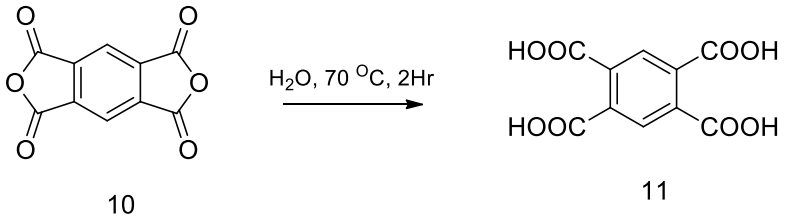


Scheme 16. Azobenzene derivatives

2.2 Synthesis of core moieties

2.2.1 Synthesis of benzene-1,2,4,5-tetracarboxylic acid(4)

For the preparation of benzene-1,2,4,5-tetracarboxylic acid, the following reaction has been performed as reported in the literature.[11]The product was isolated by filtration and confirmed by mass and proton NMR. It gave benzene-1,2,4,5-tetracarboxylic acid in 77% yield.



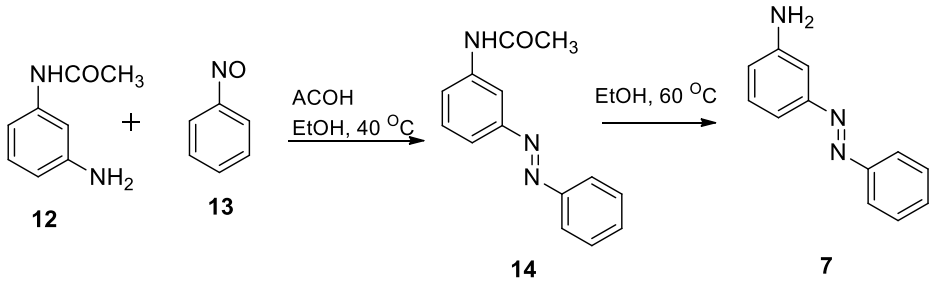
10 11

Scheme 17. Preparation of benzene-1,2,4,5-tetracarboxylic acid

2.3 Synthesis of photoswitchable units

2.3.1 Synthesis of 3-aminoazobenzene (7)

The synthesis of 3-aminoazobenzene was carried out by Mills reaction as reported in the literature involving condensation of nitrosobenzene with 3-aminoacetanilide in acetic acid and ethanol at 40^{o}C (**Scheme18**) to form the 3-acetamidoazobenzene.[12]It gave 66% yield. Conversion of 3-acetamideazobenzene to 3-aminoazobenzene has been performed in ethanol and 3N HCl at reflux condition around 60^{o}C.[13] After purification by column chromatography, the product was confirmed by mass and proton NMR. The conversion gave 98% yield of 3-aminoazobenzene.



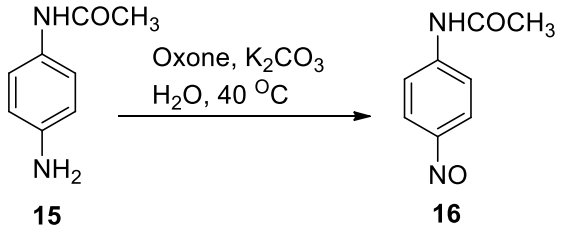
12 13 14 7

Scheme 18. Synthesis of 3-aminoazobenzene

2.3.3 Synthesis of 4,4'-diaminoazobenzene (8)

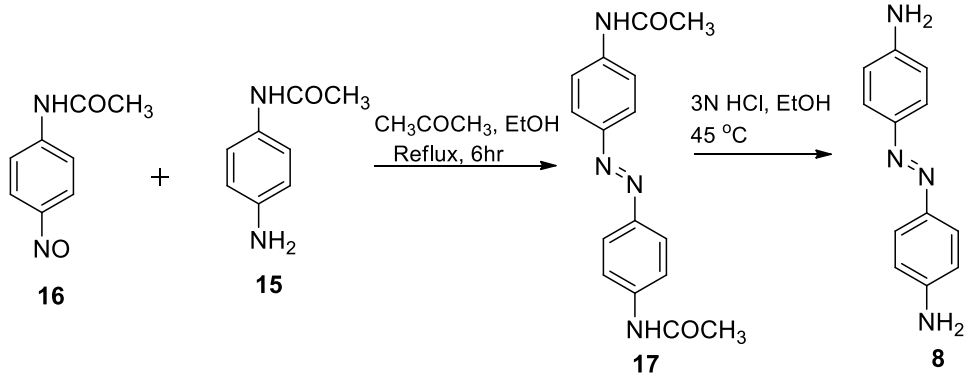
Compound **8** was synthesized from its corresponding acetyl derivative by Mill's method. The reaction scheme involves two stages (1) preparation of nitroso compound (2) coupling reaction of nitroso with 4-aminoacetanilide.

(1) Nitroso compound was obtained by oxidation of 4-aminoacetanilide using oxone as in the literature.[14] (**Scheme 19**) The pale greenish product formed gave 77% yield and was filtered and then used for further reaction.



Scheme 19. Synthesis of 4-nitrosoacetanilide

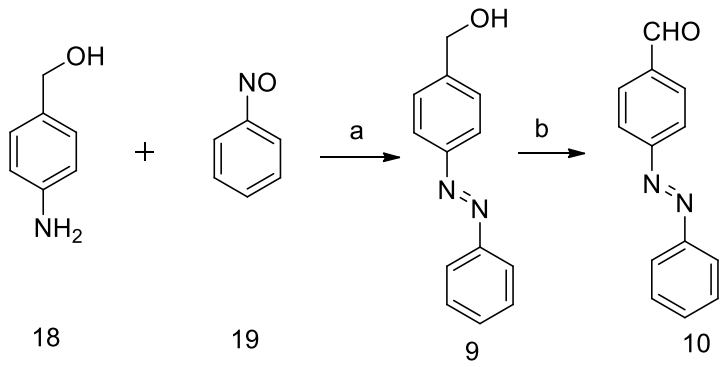
(2) The nitroso compound formed in the previous reaction was reacted with 4-aminoacetanilide in acetic acid and ethanol at 40°C to form the acetyl derivative of 9. [12] with an yield of 58%. Compound **8** was obtained in 96% yield by treating the 22 with 3N-HCl in ethanol at 60°C.[13]



Scheme 20. Synthesis of 4,4'-diaminoazobenzene

2.3.4 Synthesis of 4-formylazobenzene (10)

4-Formylazobenzenewas prepared by oxidation of 4-hydroxymethylazobenzene using pyridiniumchlorochromate (PCC) in dry DCM at room temperature with an yield of 96%.[15]4-Hydroxymethylazobenzene was prepared following the general protocol in the literature and purified by column chromatograpy to obtain53% yield.[16]The resulting products have been characterized through NMR and MS.

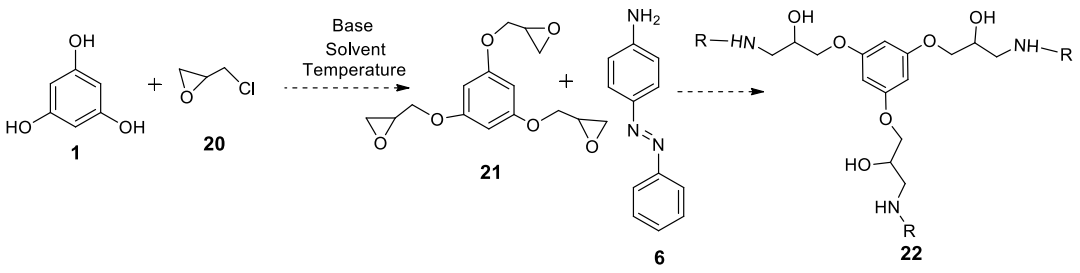


Scheme 21. Synthesis of 4-formylazobenzene. Conditions: (a) AcOH, RT, 54%; (b) PCC, Dry DCM, RT 98 %

2.4 Coupling of core moiety and photoswitchable units (Target synthesis)

2.4.1 Target 1-Triglycidyl product (22)

The target **1** has been planned to synthesize from *tris*(4-hydroxyphenyl)methane triglycidyl ether(**21**) and 4-aminoazobenzene(**6**). The key step in this reaction is to synthesize (**21**). We tried to synthesize *tris*(4-hydroxyphenyl)methane triglycidyl ether using phlouroglucinol (**1**) and epichlorohydrin (**20**) as reported in the literature.[17](**Table 1, entry a**). However, the desired product was not formed.We tried using different conditions, particularly by changing the solvent, base and number of equivalents of epichlorohydrin. (**Table 1, entries b–j**) In none of the conditions, we obtained the desired product. Presumably, epichlorohydrin underwent polymerization under the experimental conditions.



Scheme 22. Synthesis of Target 1

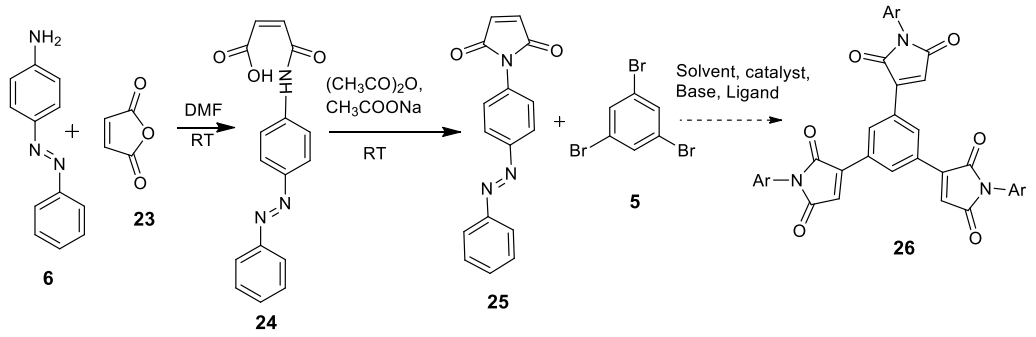
Table 1: Optimization of reaction conditions

Entry	1 (eq)	Base (eq)	20 (eq)	Solvent (ml)	Temperature (^oC)	Result
a	1	KOH(2)	6	DMSO(2)	20	NR
b	1	K_2CO_3 (6)	6	Neat	RT, 30, 45	NR
c	1	KOH (6)	6	DMSO (3)	RT, 50	NR
d	1	K_2CO_3 (6)	6	DMSO (3)	RT, 45, 60	NR
e	1	K_2CO_3 (6)	6	Dry DMF(2)	RT, 50	NR
f	1	K_2CO_3 (6)	6	Neat	RT, 70	NR
g	1	KOH (6)	6	DMSO (2)	RT, 70	NR
h	1	KOH (6)*	6	ACN (2)	RT, 40	NR
i	1	KOH (3)	10	DMSO (1)	RT	NR
j	1	K_2CO_3	10	DMSO (1)	RT	NR

NR = No result; * NaI (6.05 eq) added as an additive

In all these conditions, we observed the same TLC pattern with two different spots. They were separated and isolated, but the obtained yellow sticky compound was not the desired product.

2.4.2 Target 2: Heck reaction of 4-(*N*-maleimido)azobenzene and 1,3,5-tribromobenzene



Scheme 23. Heck reaction of 4-(*N*-maleimido)azobenzene

After the unsuccessful attempts to make target 1, we focused on the Heck reaction between 4-(*N*-maleimido)azobenzene (**25**) and 1,3,5-tribromobenzene (**5**)**.** Table 2 comprises of different conditions we have adopted for the optimization of the heck product. We started off with the literature reports[18]using maleic anhydride (**23**) and 4-aminoazobenzene (**6)** giving an intermediate 4-(maleimicacid)azobenzene (**24**) in 95% yield, which on condensation yields 4-(*N*-maleimido)azobenzene (**25**) in73% yield. For the heck reaction we followed the conventional procedure (**Table 2, entry 1**)[19] but the desired product was not formed. The reason for not observing the product may be due to the hydrolysis of maleimides in basic medium. So we tried to use milder basic condition by following the literature.[20](**Table 2, entry 3**), still the desired product was not formed.

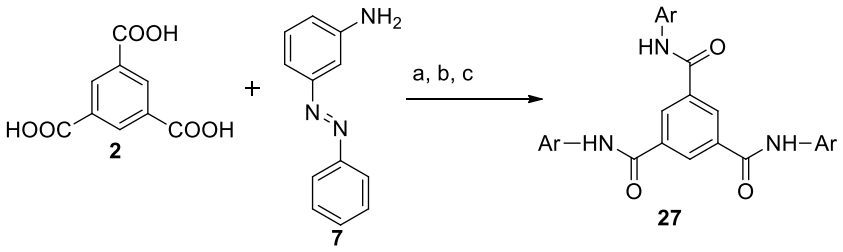
Table2: optimization of reaction conditions for target 2

Entry	Solvent (ml)	Catalyst (mol%)	Base (eq)	Ligand (mol%)	Result
a	Dioxane (2)	$Pd(OAc)_2$ (10)	CH_3COONa (3)	TPP (20)	NR
b	DMF (2)	$Pd(OAc)_2$ (10)	CH_3COONa (3)	TPP (20)	NR
c	Ethylene carbonate(1)	$Pd(OAc)_2$ (10)	KOAc (9)	Dppf (6)	NR

2.4.3 Acid amine coupling

2.4.3.1 Target 6-triamide

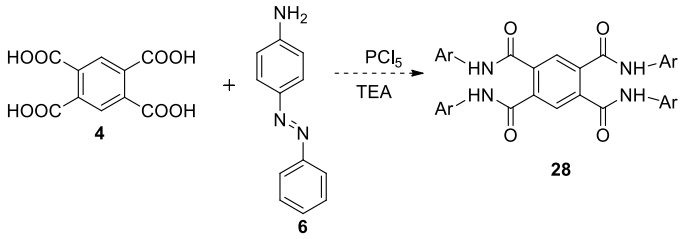
The synthesis of triamide was carried out by first converting trimesicacid (**2**) to trimesyl chloride and then coupling with 3- aminoazobenzene (**7**). The convertion to trimesyl chloride was performed using thionyl chloride and phosphorous pentachloride (**Table 3**). Then the formed acid chloride was coupled with amine to get the desired triamide. From the TLC pattern there were two close lying spots which could not be completely separated by column chromatography. In both the cases the obtained triamide was not of high purity with mixture of triamide and either the corresponding monoacid or diacid product.



Scheme 24. Synthesis of triamide, a – PCl_5/ $SOCl_2$, b – solvent, c - base

2.4.3.2 Target 3- Tetraamide (28)

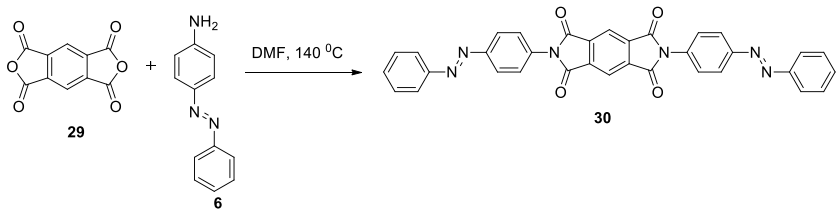
The reaction was performed by converting benzene-1,2,4,5-tetracarboxylic acid (**4**) to corresponding acid chloride using PCl_5 and followed by coupling with 4-aminoazobenzene (**6**) in presence of triethylamine as base. However we were not able to synthesize the desired product. The reason for not obtaining the desired product may be due to the absence of formation of the acid chloride.



Scheme 25. Synthesis of tetraamide

2.4.4 Target 4- pyromelliticimide product (30)

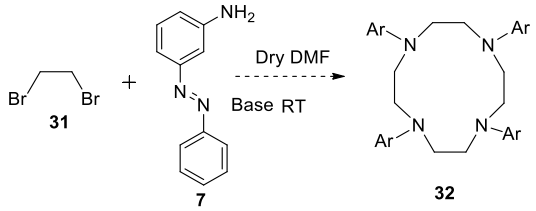
In order to synthesize target 4, pyromelliticdianhydride (**29**) was reacted with 4-aminoazobenzene (**6**) in DMF at 140 ^{0}C. The obtained solid was not able to get characterized due to solubility issues.



Scheme 26. Synthesis of pyromellitic imide product

2.4.5 Target 5- Azamacrocycle (32)

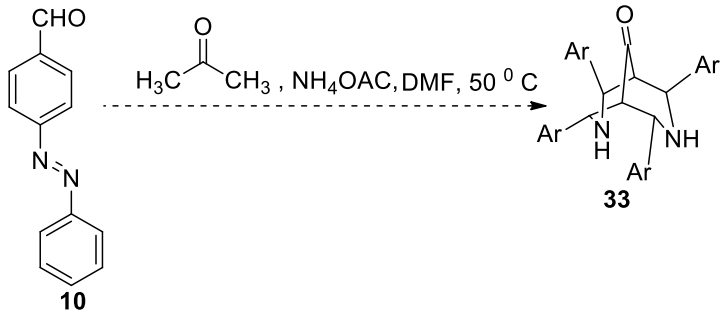
To synthesis of azamacrocycle was mainly to study the spincrossover of different metal ions. The reaction was performed by reacting dibromoethane (**31**) with 3-aminoazobenzene (**7**) in presence of Base - cesium carbonate and solvent as dry DMF. The reaction did not yield the desired product and starting material remained as such. One possible reason for not obtaining the product may be due to poor reactivity of the starting materials.



Scheme 27. Synthesis of macrocycle

2.4.6 Target 6-Mannich product (33)

The synthesis of Mannich product was initiated by formation of imine by the condensation of4-Formyl azobenzene (**10**) and ammoniumacetate followed by the attack of the tautomerized enol form of ketone on the imine. During TLC monitoring three close lying spots have been observed. However column purification did not lead to purification of those products.

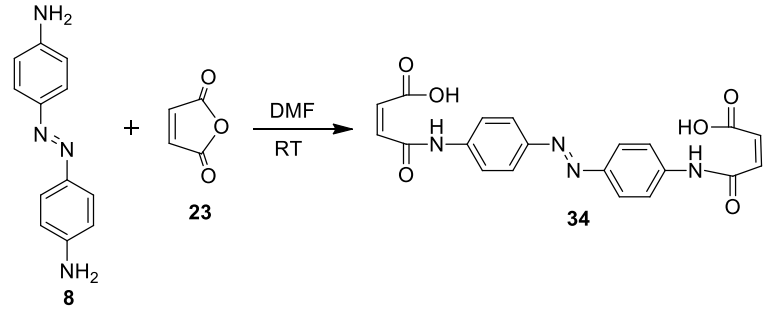


Scheme 28. Synthesis of Mannich product

2.4.7 Synthesis of 4,4'-*bis*(maleamicacid)azobenzene (34)

Compound **34** was prepared in order to bind to different metal ions. Synthesis of 4,4'-*bis*(maleamicacid)azobenzene was carried out by following the literature reports [21] using 4,4'-diaminoazobenzene (**8**) and maleic anhydride (**23**) in DMF yielding 93% of

the product. The di-acid was used for binding of metal ions when it underwent switching. In a different report maleic anhydride based molecules binding to metal ions without the azobenzene moiety has been synthesized[22].



Scheme 29. Synthesis of 4,4'-*bis*(maleamicacid)azobenzene

2.5 Photoswitching experiments

2.5.1 Photoswitching studies of 4,4'-*bis*(maleamicacid)azobenzene (34) in DMSO

The photoswitching experiments of the diacid (**Target 8** or **34**) have been performed using UV-Vis and NMR spectroscopies. In UV-Vis spectroscopy, the absorption spectra of 34 in DMSO showed a maximum at 396 nm, which can be attributed to π–π* absorption band of azo group. (**Figure 1**) Upon irradiation at a wavelength 405 nm, (using a LED) which falls in this absorption band leading to changes in the absorption spectrum. In 10 minutes, the spectral features due to *trans completely* bleached and two new absorption maxima at 326and 422 nm appeared. Interestingly, two isosbestic points at (350 and 468 nm) have also been observed, suggesting that the two species have one-to-one correspondence. This suggests that the newly observed maxima can be due to the π–π* and n-π* absorption bands of the *cis* isomer. After an hour irradiation with white light using household CFL bulb, the band corresponding to the *trans* isomer increased. However, the conversion was incomplete as it attained a photostationary state (PSS) with unknown amounts of *cis* and *trans* isomers.

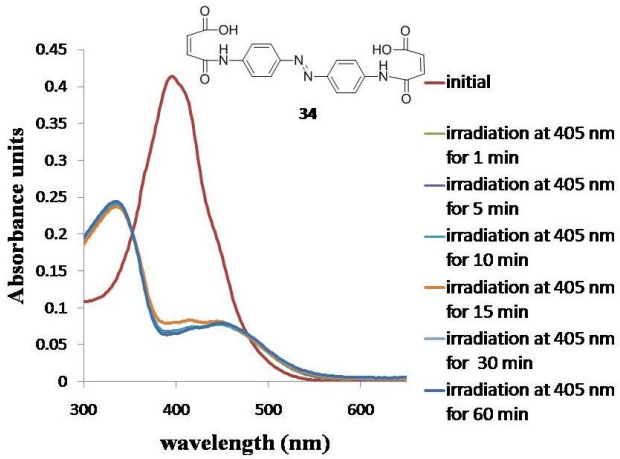


Figure 1. Photoswitching in 4,4'-*bis*(maleamicacid)azobenzene (**34**)

The photoswitching behavior of 34 was also performed using NMR spectroscopy in DMSO-d_6. Upon irradiation, the *trans* isomer underwent isomerization, which can be clearly understood from the upfield shifts of the amide N-H, aromatic and olefinic protons. (**Figure 1**) The carboxylic acid protons showed no change. This clearly indicated that the isomerization led to the breaking of conjugation and lowering of electron withdrawing power of the azo group. Since the carboxylic group is far away from the azo group, it did not feel the effect of geometrical change. Unlike UV-Vis spectroscopy, NMR studies showed that the photoswitching was incomplete. However, concentration studies indicated that the photoswitching at identical conditions led to different PSS. (**Table 3**) Lower concentration increased the amount of *cis* formation.

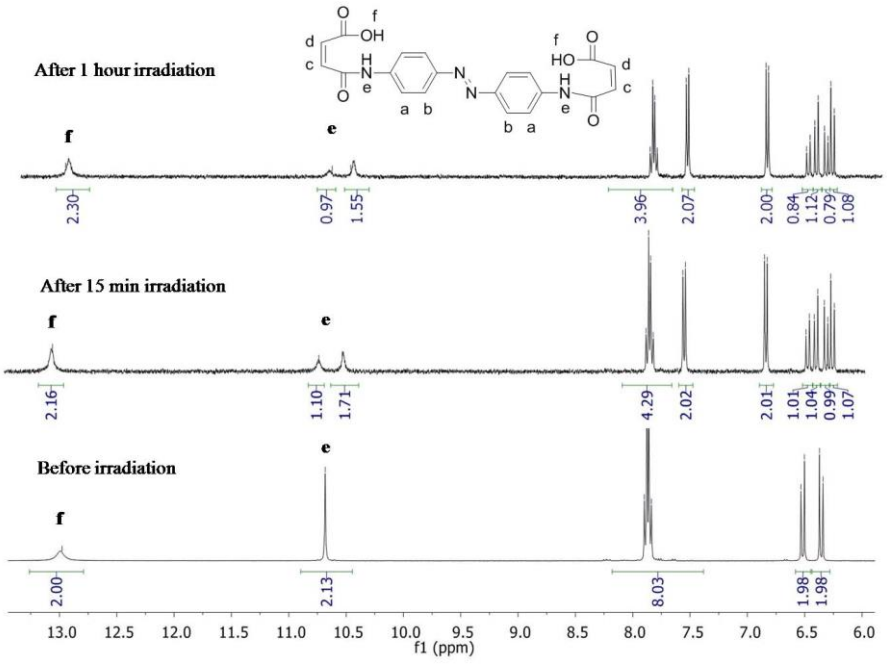


Figure 2. Photoswitching studies by NMR in DMSO-d_6

Table 3. Concentration dependency in *cis* conversion

Concentration (M)	Irradiation time	%*cis* conversion
0.006	1 hour	62
0.02	1 hour	54

2.5.2 Photoswitching studies of 4,4'-*bis*(maleamicacid)azobenzene in water

Similar to the photoswitching experiments in DMSO, the studies have also been performed in water. However, $NaHCO_3$ was added to make this molecule soluble in water. Here, the *trans* isomer showed a hypsochromic shift at an absorption maximum of 366 nm. During irradiation at 405 nm, we observed the isomerization. Interestingly, we observed two isosbestic points at 328 and 456 nm.

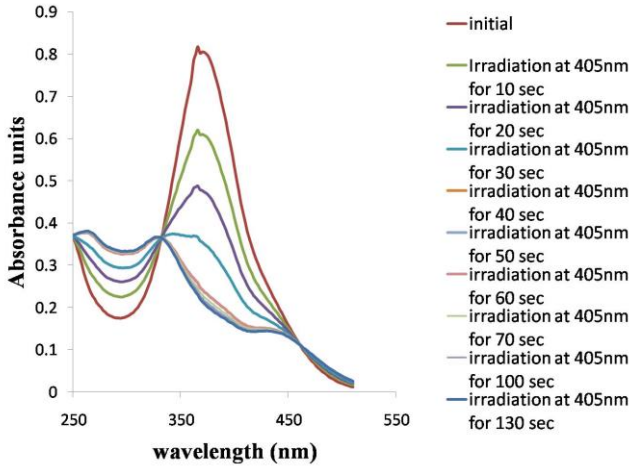


Figure 3. Photoswitching in 4,4'-*bis*(maleamicacid)azobenzene in water (**34**)

As in the earlier case, the switching studies have been carried out using NMR spectroscopy as well. However, the NMR showed a simple spectrumfor 34, because of non-appearance of amide and carboxylic protons. It showed almost 52% isomerization upon irradiation with 405 nm. In D_2O, only one olefinic proton showed upfield shift, whereas the other one was unperturbed.

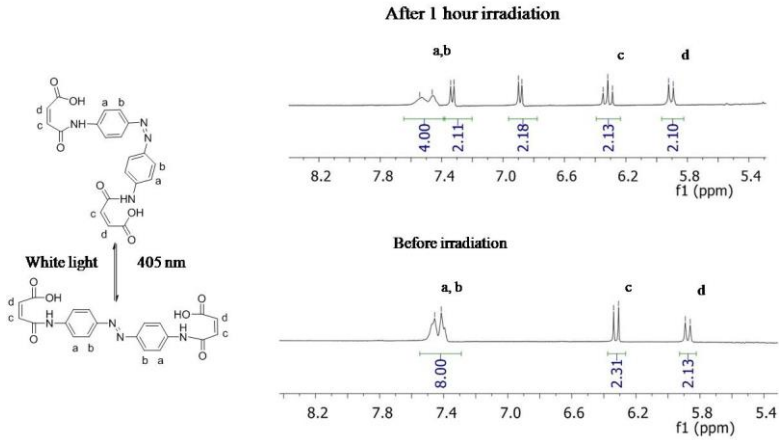


Figure 4. Photoswitching studies by NMR in D_2O

2.5.3 Investigation of metal ion binding with 4,4'*bis*(maleamicacid)azobenzene (34)

Since the diacid molecule contains carboxylic acid and amide, it can act as a ligand in binding with metal ions. Our aim in this regard is to understand, whether metal ions can be chelated by the diacid depending on the affinity of these two functional groups with the metal ions. If the chelation happens, the next and foremost important question will be whether we can reversibly transport the metal ions. To understand these, we tried the metal ion binding experiments using UV-Vis spectroscopy for selected metal ions.In this regard, both *trans* and *cis* isomers have been chosen for binding. Screening has been done using transition metals and lanthanides like Fe^{3+}, Zn^{2+}, Cs^{+}, and Eu^{2+}. Apart from that, we also tried the photoswitching behavior of the diacid before and after metal ion binding. Initially, we tried the metal ion binding studies using mixture of different stoichiometric ratios of metal ion and ligand concentrations. (**Figure 5a**) After that, the photoswitching was performed using 405 nm. (**Figure 5b**) However, we did not observe any appreciable change in the absorption spectra. Based on the above-mentioned experiments, we could not reach a conclusionon metal ion binding with the diacid. Indeed, the same observations were seen in the cases of other metal ions except Eu^{2+}.

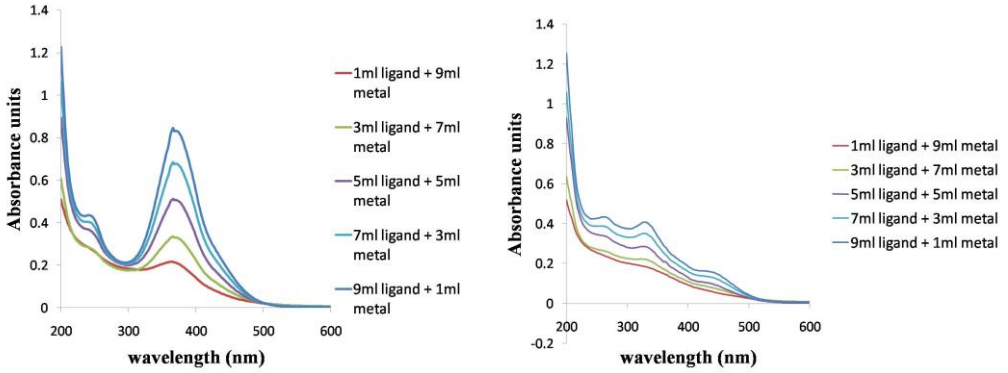


Figure 5.(a)Photoswitching in solutions of diacid and metal(Fe^{3+}) before irradiation (b) Photoswitching in diacid and metal (Fe^{3+}) after irradiation at 405 nm

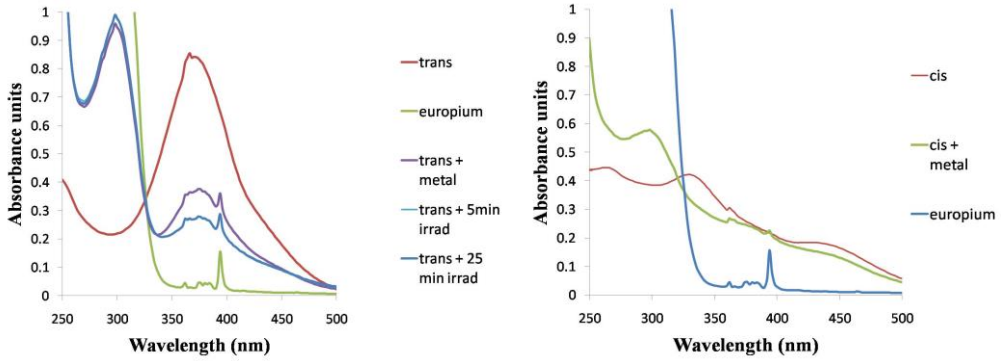
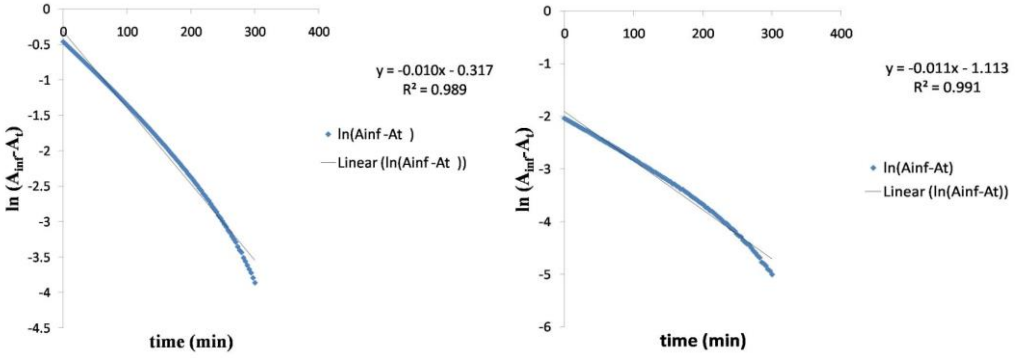


Figure 6. (a)Photoswitching in the solutions of diacidwith Eu^{2+} before irradiation (b)Photoswitching in the solutions of diacid with Eu^{2+}after irradiation at 405 nm

In case of europium, the spectra showed an interesting pattern, with isosbestic points, which was not observed in the cases of other metal ions. Despite the observations of slight variation in the observation pattern of both *trans* and *cis* spectra, it is not very clear, whether the metal ion has bound the ligand. In fact Eu^{2+} can easily form complex with carboxylic acid groups. So, we needed to rely on other experiments such as thermal reverse switching kinetics (*cis*-to-*trans* isomerization).



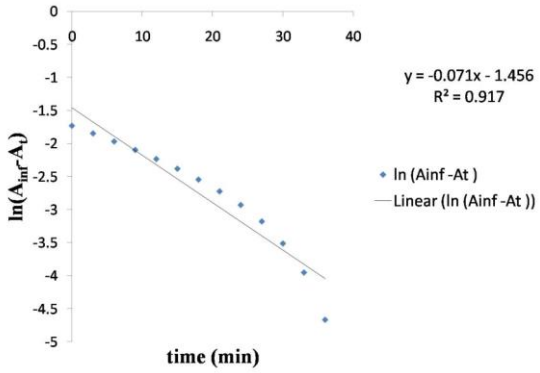


Figure 7. *Cis* to *trans* isomerization kinetics of diacid (a) Without metal (b) With metal (Fe^{3+}) (c) With metal (Eu^{2+})

The chemical kinetics datacan providecertain details on metal ion binding with the diacid. If the diacid binds to the metal there might be a change in the half-life compared to that of one without metal ion. So, we carried out the kinetics experiments at RT for diacid ligand with and without the metal ions. (**Figure 7 a, b and c** &**Table 4**) Kinetic studies have been done for two different metal Fe^{3+} and Eu^{2+} by following change in absorbance at 372 nm.In the absence of metal ion, it showed a first order kinetics with a rate constant, which is similar to that in the presence of Fe^{3+}. From the kinetics data we can see that there is a slight change in half life in the case of Fe^{3+} in diacid solution. But the change is not that significant to confirm the binding of Fe^{3+} with diacid. However, in case of $Eu^{2+}$the half-life is only 9.7 min, which indicates that the molecule is undergoing a fast switching in the presence of Eu^{2+}. This is contrary to the expectation that metal up on binding with *cis* can stabilize and increase the half-life. From this, we can infer that instead of metal acting as strong binding to the diacid, it is aiding in the conversion of the diacid from *cis* to *trans* form as a catalyst.

Table 4. Kinetics data in the thermal reverse isomerization of diacid with and without metal ions

Sample	k (Rate constant) (min^{-1})	$\tau_{1/2}$ (half-life)
Diacid	0.010	69.3 min
Diacid with Metal Fe^{3+}	0.011	63 min
Diacid with Metal Eu^{2+}	0.071	9.7 min

2.5.4 Effect of pH in photoswitching of 4,4'*bis*(maleamicacid)azobenzene

4,4'-*bis*(maleamicacid)azobenzene is water soluble under basic condition of pH 9 and shows a maximum switching under this condition. In order to understand the effect of pH in switching, solutions of different pH ranging from pH 2 to pH 10 was made and photoswitching was performed for all these solutions.

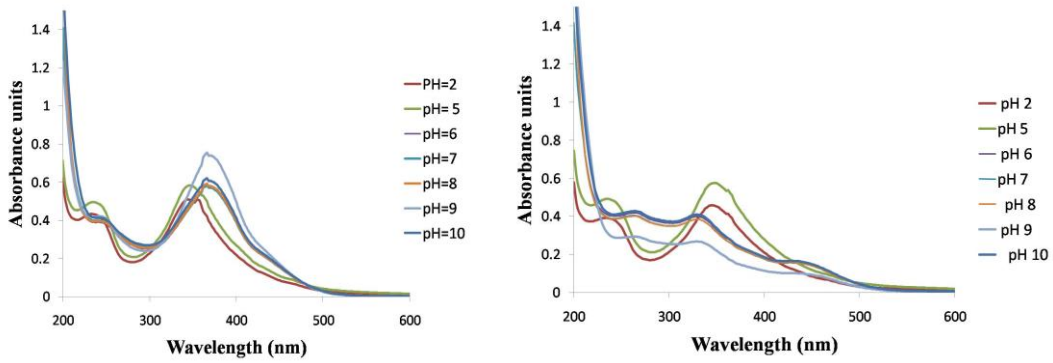


Figure 8. Photoswitching in diacid at different pH (a) Before irradiation (b) After irradiation at 405 nm

From the analysis of the above two spectra, we concluded that at acidic pH the diacid molecule cannot undergo switching. Probably the formation of pseudostilbene like structure in which one of the nitrogen in the azo group gets protonated and induces a rapid switching and reverse switching which is beyond the measurement timescales of normal UV-Vis spectroscopy.[23] On the neutral and very high pH, it showed only a partial switching. Only at a pH of 9, the switching was happened to a greater extent. This influence of variable pH in switching extend can be useful for pH sensors. Currently, experiments are underway in this regard.

Chapter 3

Conclusions and Perspectives

Through this investigation, we have tried to synthesize multiple azobenzene connected molecular systems and water soluble azobenzenes for molecular transporter and light controlled spin crossover applications. Based on these studies, we have the following conclusions:

- The photoswitchable units 3-Aminoazobenzene, 4,4'-diaminoazobenzene, 4-hydroxymethylazobenzene, 4-formylazobenzne and a core moiety 1,2,4,5-benzenetetracarboxylic acid were synthesized and characterized by NMR and MS.
- Various methods such as acid-amine coupling, Heck coupling, and Mannich reactions have been adapted to synthesize the target molecules. Due to unavoidable reasons such as polymerization of starting materials, no reactivity and inseparable close-lying spots etc., we were not able to isolate few of the desired target molecules.
- Target 7 was synthesized; however, purification column chromatography was unsuccessful due to high polarity of the product, which got stuck in the column.
- We have successfully synthesized the diacid (target-8) and its photoswitching studies have been investigated by NMR and UV spectroscopy.
- The effect of pH in photoswitching was investigated for the diacid, which showed an interesting behavior. At different pH, the photoswitching happened to different extend. In acidic conditions, the molecule showed no change in absorption pattern, which can be attributed either to fast switching or to no switching, whereas at higher pH (>9), the switching was partial. Maximum switching was observed at pH 9. This behavior can potentially be useful as a pH sensor.
- The metal ion chelating ability of the diacid has been investigated with metal ions like Fe^{3+}, Zn^{2+},$Cs^{+}$and Eu^{2+}. The observations were same in the cases of other metal ions except Eu^{2+} however, the results are inconclusive.
- From the kinetics data, we understood that there is a slight change in half-life in the case of Fe^{3+} in diacid solution. But the change is not that significant to confirm the binding of Fe^{3+} with diacid. However, in case of $Eu^{2+}$the half-life is only 9.7 min, which indicates that the molecule is undergoing a fast switching in the

presence of Eu^{2+}. From this, we can infer that instead of metal acting as strong binding to the diacid, it is aiding in the conversion of the diacid from *cis* to *trans* isomer as a catalyst.

Chapter 4

Experimental section

4.1 General methods:

The 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), $KMNO_4$ and iodine. The completed reaction was quenched and the organic extracts were dried using anhydrous sodium sulphate and solvent was removed by rotary evaporation. Separation and purification was done by column chromatography using silica gel (100-200 and 60-120 mesh) purchased from HiMedia. ^{1}H and ^{13}C NMR spectra were recorded in Bruker Avance-III 400MHz and 100 MHz spectrometers with trimethylsilane as standard using $CDCl_3/D_2O$/DMSO-d_6 as solvent. IR spectra were recorded in KBr plate or thin film on Perkin-Elmer FT IR spectrometer and Bruker Alpha IR spectrophotometer. HRMS was recorded in Both ESI positive and negative modes using Waters SYNAPT G25 High definition mass spectrometer

4.2 Synthesis

Benzene-1,2,4,5- tetracarboxylic acid (4)

Pyromelliticdianhydride (500mg, 2.3mmol) was dissolved in water (4ml) and reaction mixture was refluxed at 70 ^{0}C for 2hrs. Reaction was monitored through TLC. Upon completion of reaction white crystalline product formed was filtered using Buchner funnel. To remove the trace amount of water the product was dissolved in acetone and the solvent was evaporated under reduced pressure giving 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.99(s, 2H);^{13}C NMR(100MHz, $CDCl_3$): δ (ppm):167.764, 135.0501, 128.6879, TOF MS ES- of molecular formula $C_{10}H_5O_8$: calculated 252.9983; found 252.9979.

3-Aminoazobenzene (7) (Mills method)

3-Aminoacetanilide (150 mg, 1 mmol, 1 eq) taken in RBF was dissolved in ethanol (1 ml). A solution of nitroso benzene (107 mg, 1 mmol, 1 eq) in acetic acid (2 ml) was

added slowly to the reaction mixture and continued stirring for 23 hrs at 40 ^{0}C. After the completion of the reaction, monitored by TLC the product 3-acetamidoazobenzene was extracted using ethyl acetate and dried with anhydrous sodium sulphate. The crude product purified by column chromatography after evaporating the solvent gave 66% yield. 3-Aminoazobenzene was made from 3-acetamidoazobenzene by treating 3-acetamidoazobenzene (152 mg, 0.66 mmol, 1 eq) with 3N HCl (1 ml) in ethanol (2 ml) under reflux condition around 60 ^{0}C for 4 hrs. After extraction the organic layer was dried with anhydrous sodium sulphate and solvent was evaporated and desired product was purified by column chromatography yielding 97.6 % conversion. The desired product was orange solid.

^{1}H NMR(400 MHz, $CDCl_3$): δ (ppm): 7.95-7.93 (m, 4H, J=8Hz), 7.55-7.52 (m, 5H, J=12Hz), 4.81 (s, 2H); ^{13}C NMR(100MHz, $CDCl_3$): δ (ppm): 152.777, 152.557, 142.092, 133.3961, 131.1413, 129.3985, 129.3028, 129.1466, 122.8940, 122.6005, 120.6056, 64.9193.TOF MS ES+ of molecular formula $C_{12}H_{11}N_3$: calculated 198.1033; found 198.1026

4,4'-diaminoazobenzene (8) (Mills method)

Aqueous solution of Oxone (4.7 g, 15.31 mmol, 4.6 eq) in water (75 ml) with K_2CO_3 (1.2 g, 8.6 mmol, 2.6 eq) was taken in an RBF to which 4-aminoacetanilide (500 mg, 3.32 mmol, 1 eq) dissolved in water (50ml) was added quickly. Green solid product, (4-nitrosophenyl) acetamide was obtained after filtration. The wet solid product was directly used for next step to couple with 4-aminoacetanilide (347 mg, 2.31 mmol, 1 eq) in Acetic acid (2 ml) and ethanol (4 ml) giving 58% yield of 4,4'-diaminoacetanilideazobenzene, which was then converted to 4,4'-diaminoazobenzene using 3N HCl (1.5 ml) and ethanol (3 ml) under reflux condition around 60 ^{0}C for 4 hrs. After extraction the solvent was evaporated and compound was purified by column chromatography to yield 96% conversion.

^{1}H NMR (400 MHz, DMSO): δ (ppm): 7.53-7.51 (d, 4H, J=8Hz), 6.63-6.61(d, 4H, J=8Hz), 5.74 (s, 4H); ^{13}C NMR (100MHz, DMSO): δ (ppm): 151.5645, 143.9213, and 124.2362, 114.1166.TOF MS ES+ of molecular formula $C_{12}H_{12}N_4$: calculated 213.1142; found 213.1134.

4-Hydroxymethylazobenzene (9)

To a solution of 4-aminobenzylalcohol(1 g, 8.1 mmol, 1 eq) in acetic acid (3 ml) was added nitrosobenzene (956 mg, 8.9 mmol, 1.09 eq) in acetic acid (3 ml) and reaction was continued at room temperature for 2 hrs by TLC monitoring. After the completion of the reaction, extraction was done using ethyl acetate and the organic layer was dried, solvent was evaporated and compound was purified by column chromatography to yield 54 % of the desired product.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.95-7.93 (m, 4H, J=8Hz), 7.55-7.52 (m, 5H, J=12Hz), 4.81 (s, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm): 152.6547, 152.0389, 143.9333, 130.9700, 129.3026, 127.4954, and 123.0267, 122.9471.TOF MS ES+ of molecular formula $C_{13}H_{12}N_2O$: calculated 213.103; found 213.1022.

4-Formylazobenzene (10)

To a RBF containing molecular sieves 4-aminobenzylalcohol(500 mg, 2.35 mmol, 1 eq) was added followed by dry DCM (7 ml) and the reaction mixture was purged for 5 min, then PCC(607.8 mg, 2.82 mmol, 1.2 eq) was added and the reaction was continued for 90 minutes. After the completion of the reaction organic layer was extracted using ethyl acetate and organic layer was dried and solvent was evaporated. Purification was done by column chromatography yielding 98 % oxidation of alcohol to aldehyde.

^{1}H NMR(400 MHz, $CDCl_3$): δ (ppm): 10.13 (s, 1H), 8.07-8.00 (m, 4H, J=28Hz), 7.98-7.96 (m, 2H, J=8Hz), 7.58-7.56(m,3H, J=8Hz); ^{13}C NMR(100MHz, $CDCl_3$): δ (ppm): 148.7254, 144.2763, 131.6333, 129.6994, 128.8337, 128.7356, 125.5532, 122.3666.TOF MS ES+ of molecular formula $C_{13}H_{10}N_2O$: calculated 211.0873; found 211.0865.

4-(*N*-maleimido)azobenzene (25)

Solution of maleicanhydride (596 mg, 6.08 mmol, 1.2 eq) in DMF (2 ml) was added to of 4-aminoazobenzene (1 g, 5.07 mmol, 1eq) in DMF (2 ml) and continued to stir for 1 hr at room temperature. The solid intermediate formed was filtered and washed with 20 ml of DCM. After complete evaporation of the solvent the intermediate formed, 4-(maleimic acid)azobenzene was directly used in the next step. 4-(maleimic acid)azobenzene(1.05 g) was taken in an RBF and sodium acetate(1.06g, 1.29 mmol, 1.2 eq) was added followed by the addition of acetic anhydride (2 ml) and reaction was continued at 145 ^{0}C fot 1hr by

TLC monitoring. After the completion of the reaction the mixture was neutralized using 10% K_2CO_3 and extracted with ethyl acetate and purified by column chromatography yielding 76 % of desired product.

^{1}H NMR(400 MHz, $CDCl_3$): δ (ppm): 10.13 (s, 1H), 8.07-8.00 (m, 4H, J=28Hz), 7.98-7.96 (m, 2H, J=8Hz), 7.58-7.56(m,3H, J=8Hz); ^{13}C NMR(100MHz, $CDCl_3$): δ (ppm): 152.5341, 151.3516, 134.4084, 133.3008, 131.4289, 129.1583, 126.2347, 123.5401, 123.0046. TOF MS ES+ of molecular formula $C_{16}H_{11}N_3O_2$: calculated 278.0931; found 278.0934.

4,4'-*bis*(maleamicacid)azobenzene (34)

Maleicanhydride (133.15 mg, 1.35 mmol, 2.4 eq) was dissolved in DMF and was added to 4,4'-diaminoazobenzene dissolved in DMF and reaction was continued for 1 hr at room temperature. The solid formed was filtered using Buchner funnel and washed with 20 ml DCM and was dried under vacuum which gave 81 % yield.

^{1}H NMR(400 MHz, DMSO): δ (ppm): 12.97 (s, 2H), 10.68(S, 2H), 7.89-7.83 (d, 8H, J=24Hz), 6.53-6.50(d,2H, J=12Hz), 6.37-6.34 (d, 2H, J=12Hz); ^{13}C NMR(100MHz, DMSO): δ (ppm): 167.7775, 163.8919, 148.4062, 141.9598, 132.0194, 130.8849, 123.9422, 120.1162. TOF MS ES+ of molecular formula $C_{20}H_{16}N_4O_6$: calculated 409.115; found 409.1150.

4.3 Photoswitching studies:

Photoswitching studies have been carried out in micromolar concentrated solutions of the diacid ligand and metal solution using a quartz cuvette. The irradiation was done either using LED light source (365 nm and 405 nm wavelength source) or by using a white light household CFL bulb. The photoswitching or *cis* - *trans* isomerization was followed by recording UV-vis spectra at different intervals of time. Photoswitching studies have also been carried out by NMR using different concentrations of the diacid ligand in Quartz NMR tube and irradiation was done using 405 nm LED light source.

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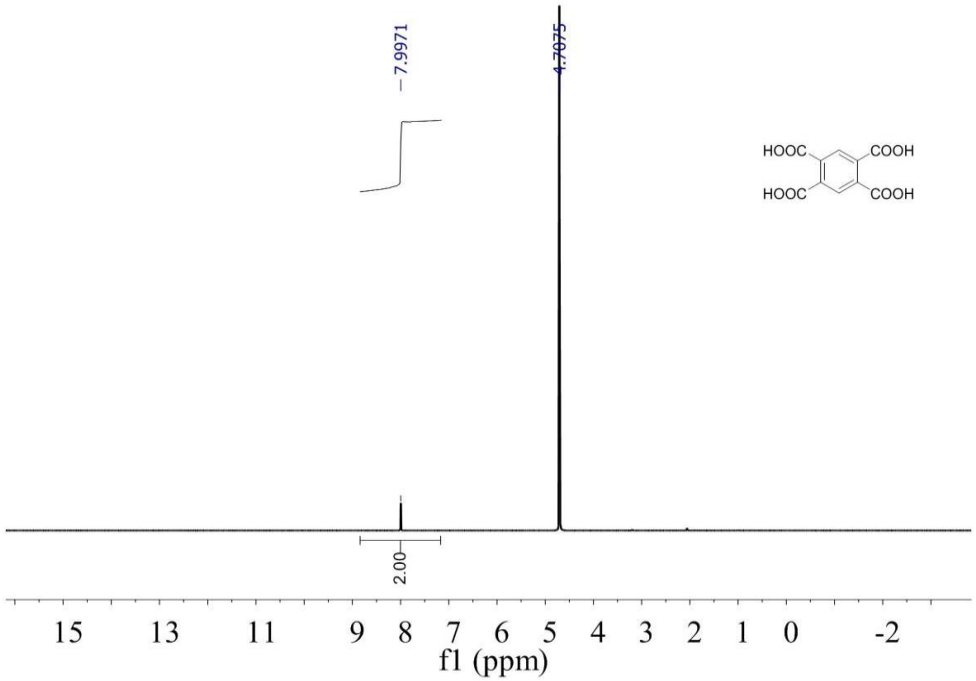
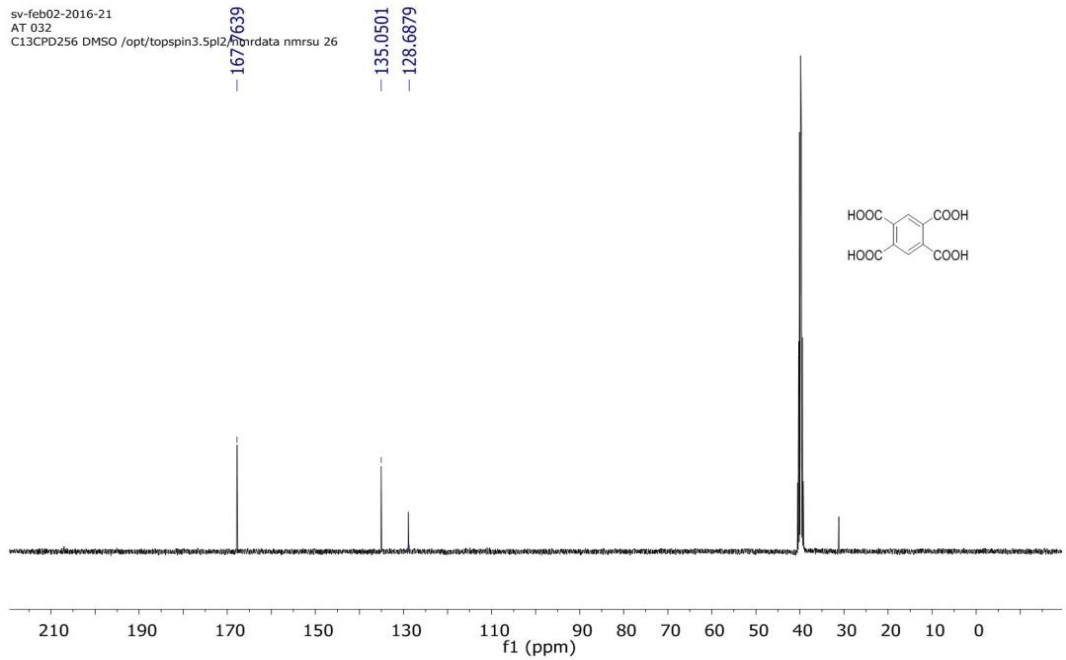
Appendix

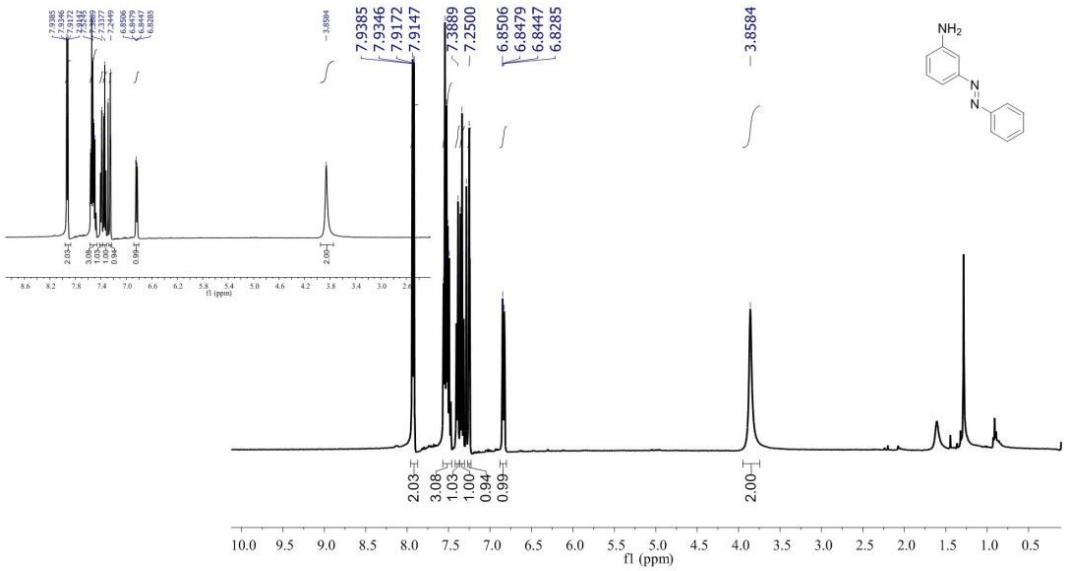
1,2,4,5- benzenetetracarboxylic acid: ^{1}H NMR, DMSO-d_6



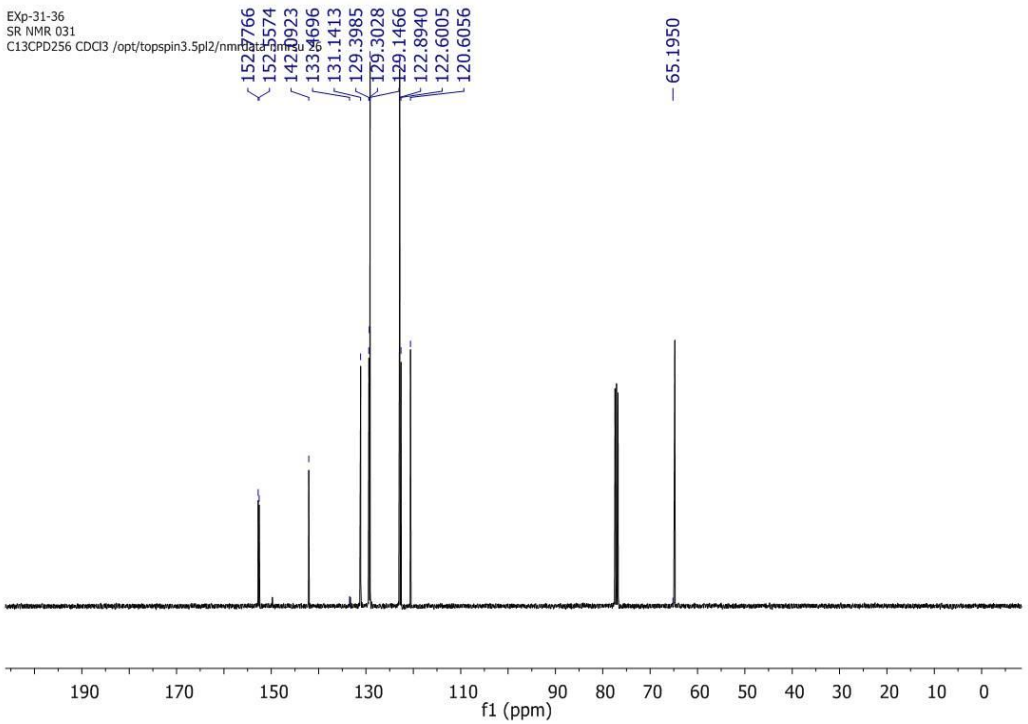
1,2,4,5- benzenetetracarboxylic acid: ^{13}C NMR, DMSO-d_6



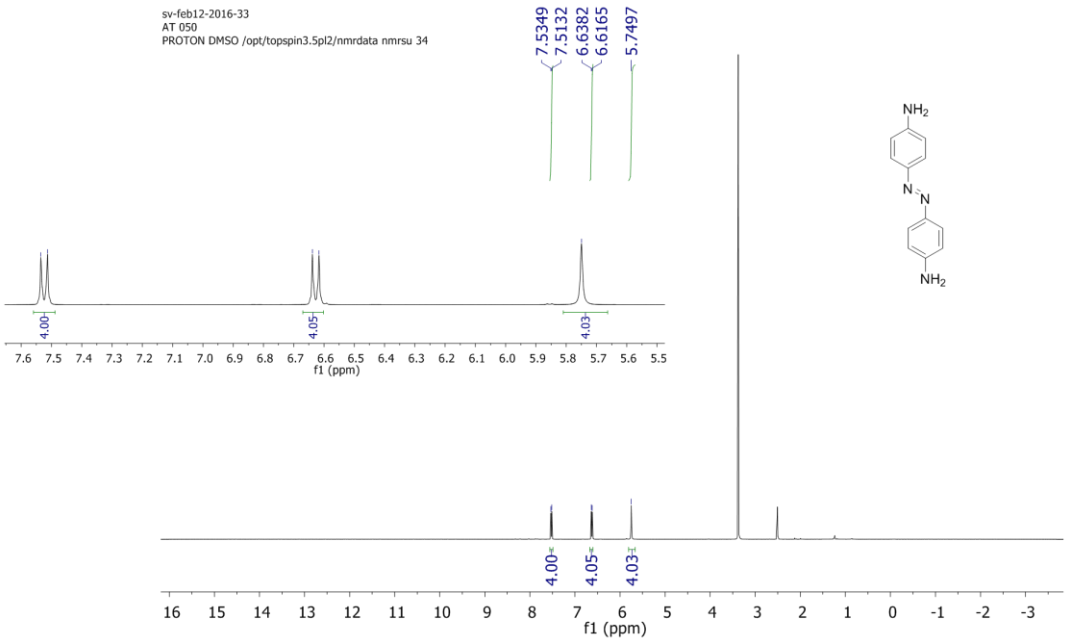
3-Aminoazobenzene: ^{1}H NMR, $CDCl_3$



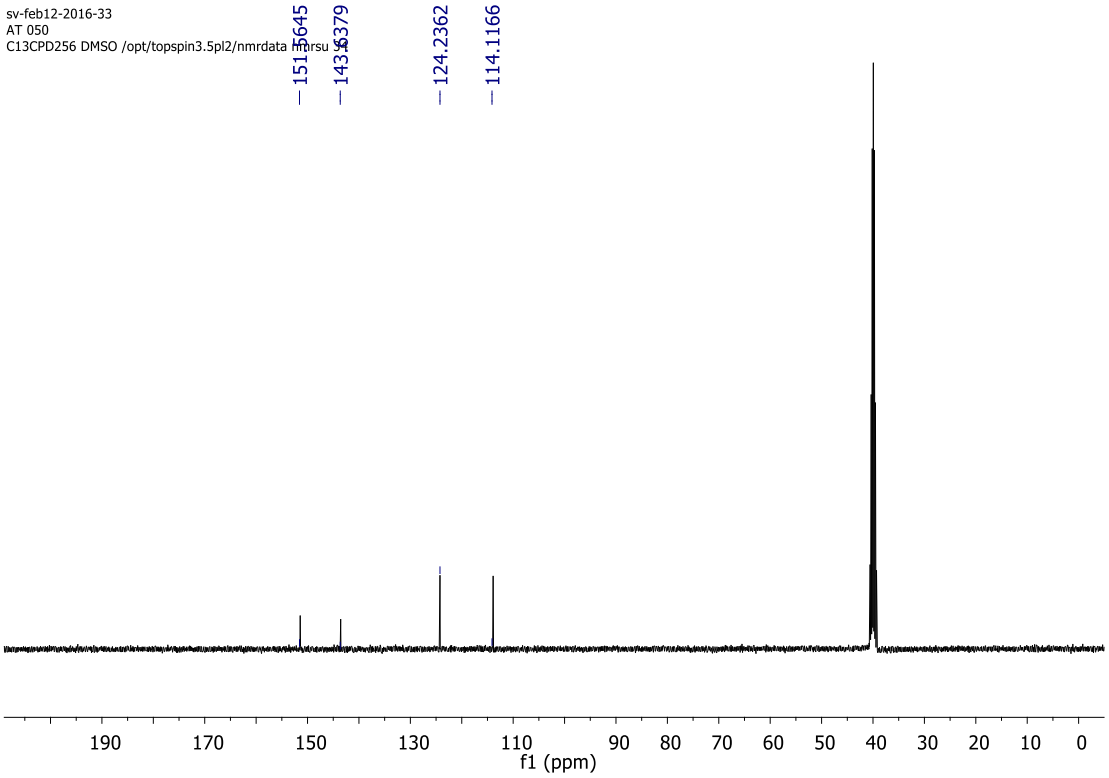
3-Aminoazobenzene: ^{13}C NMR, $CDCl_3$



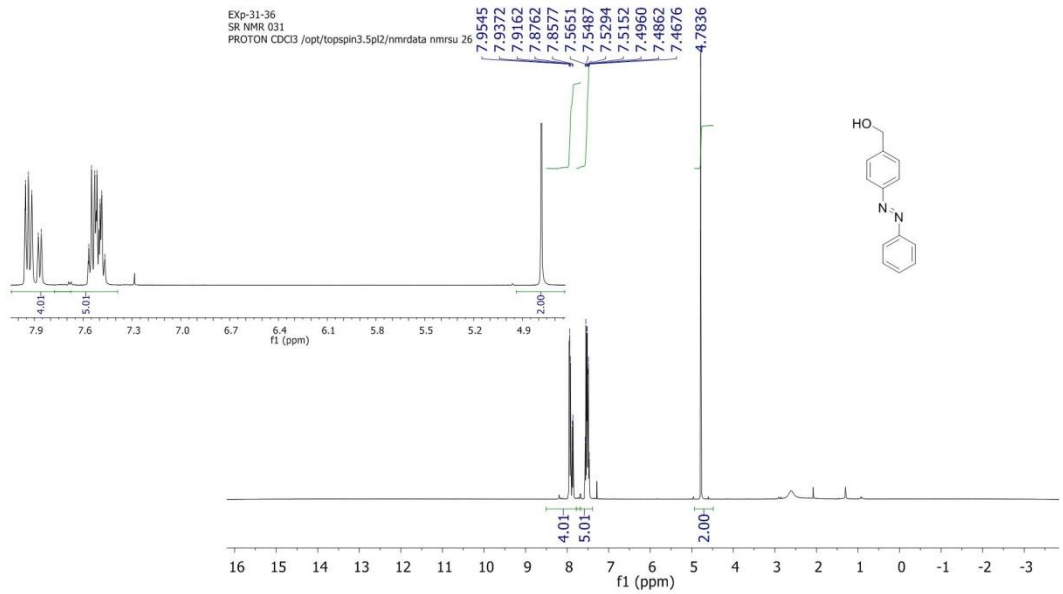
4,4’-diaminoazobenzene:^{1}H NMR, DMSO-d_6



4,4’-diaminoazobenzene:^{1}H NMR, DMSO-d_6



4-Hydroxymethylazobenzene: ^{1}H NMR, $CDCl_3$



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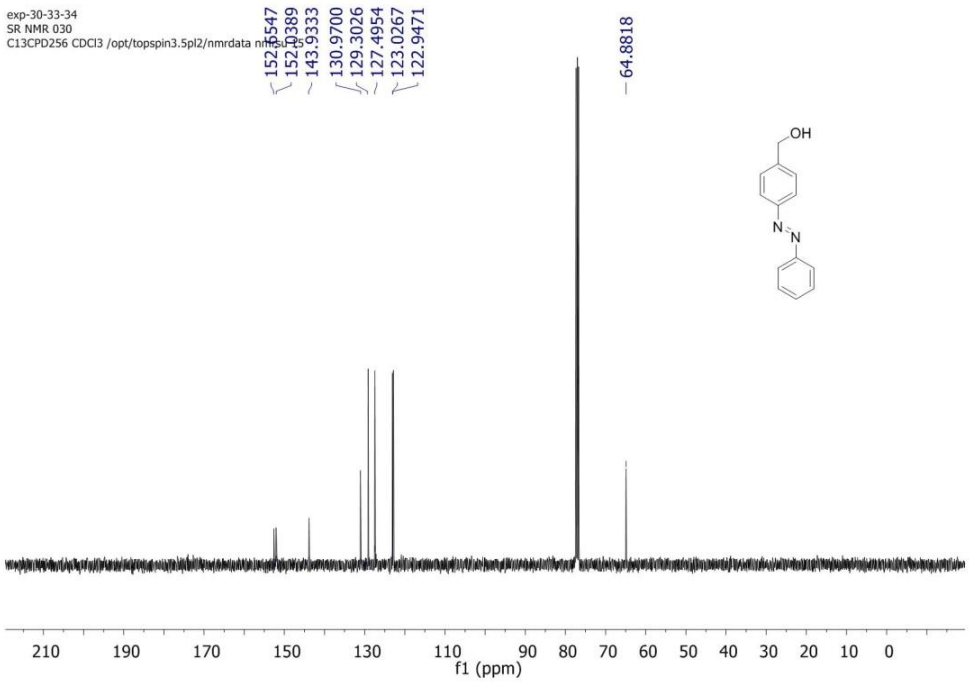
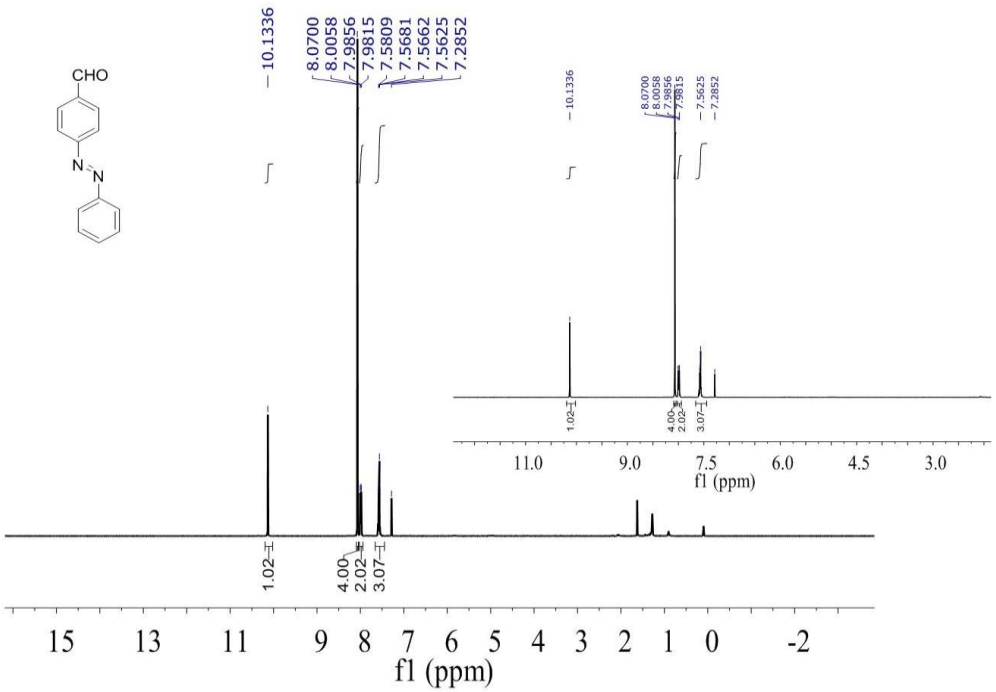
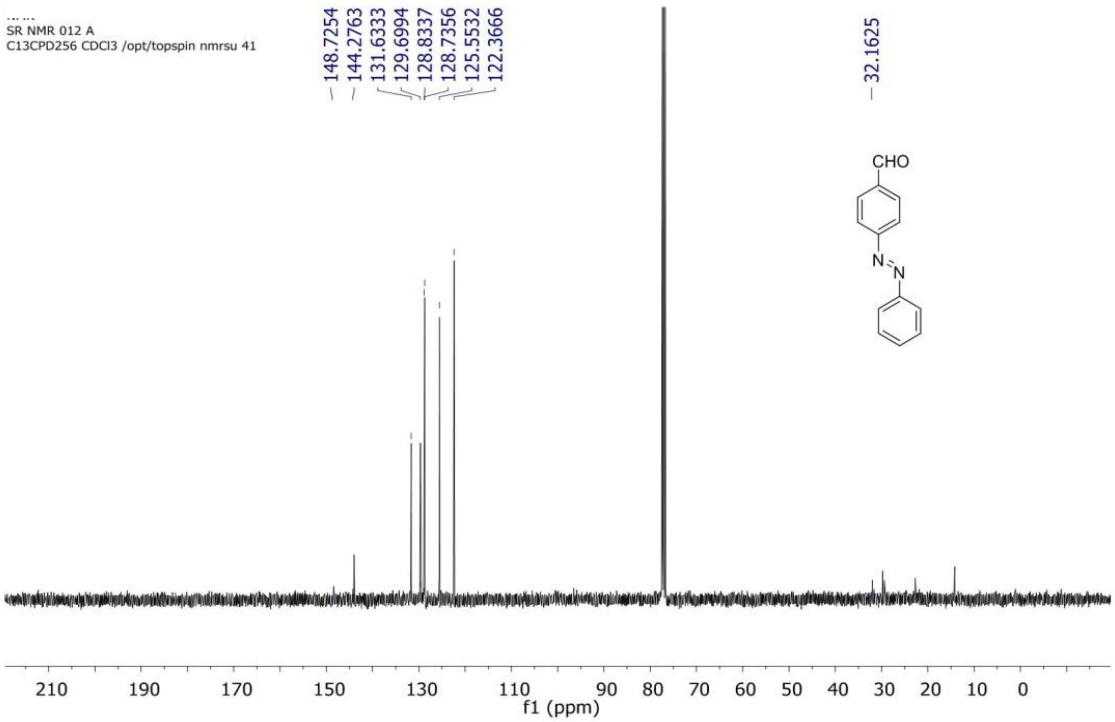


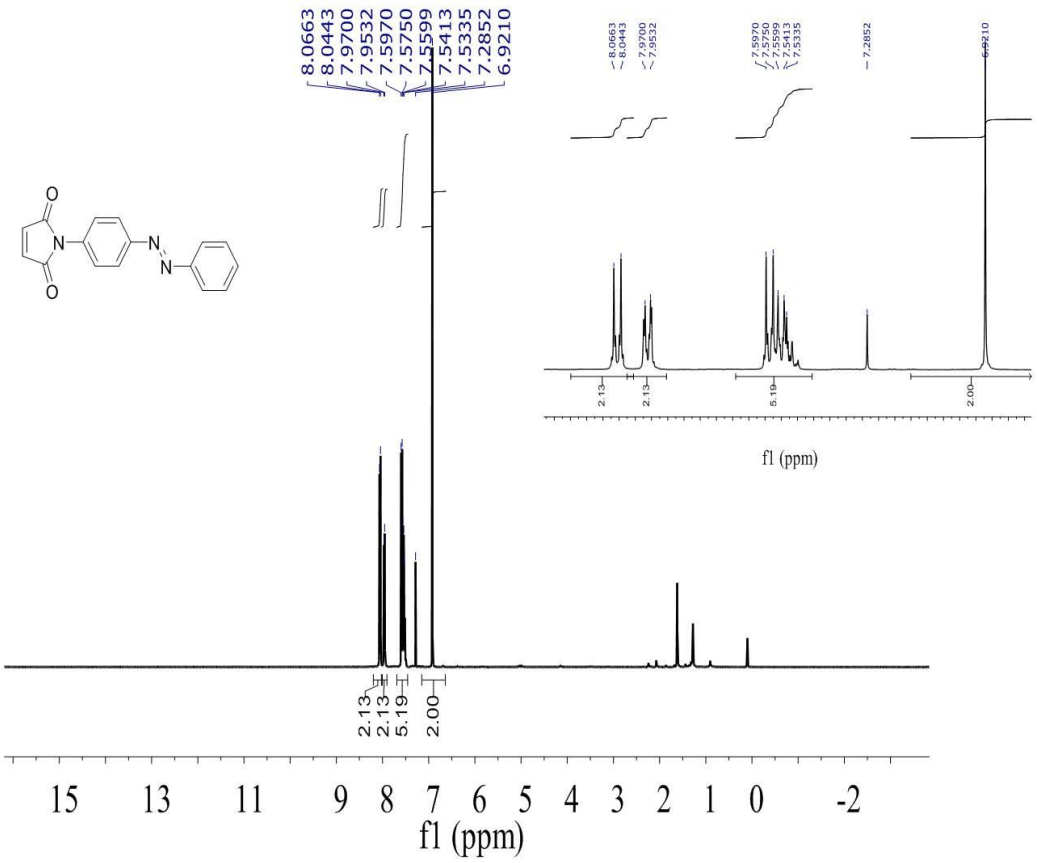
4-Formylazobenzene: ^{1}H NMR, $CDCl_3$



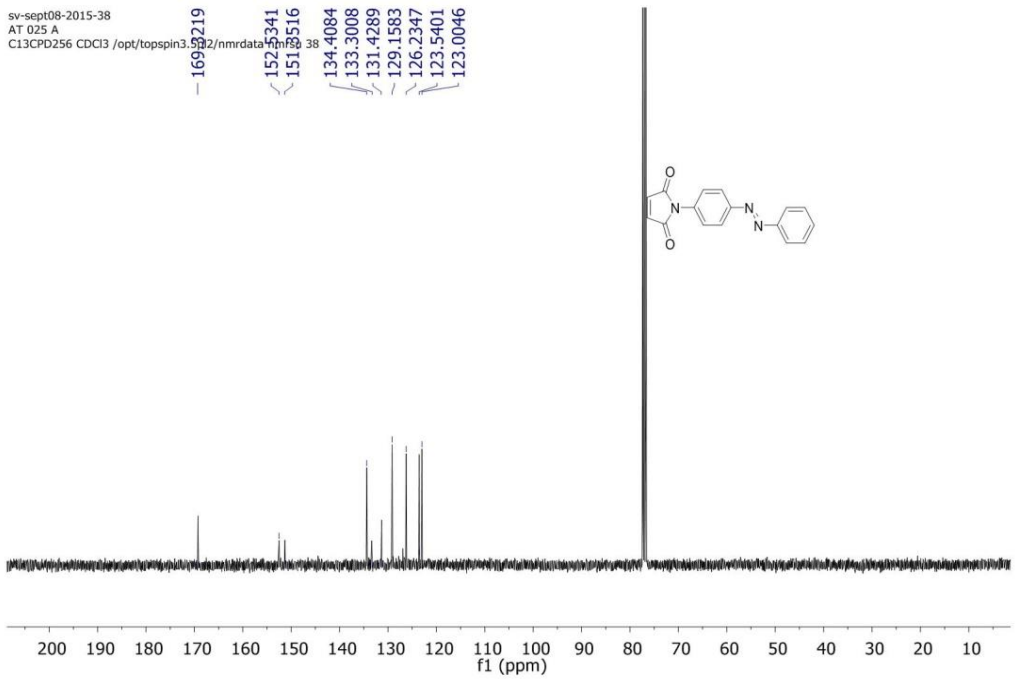
4-Formylazobenzene: ^{13}C NMR, $CDCl_3$



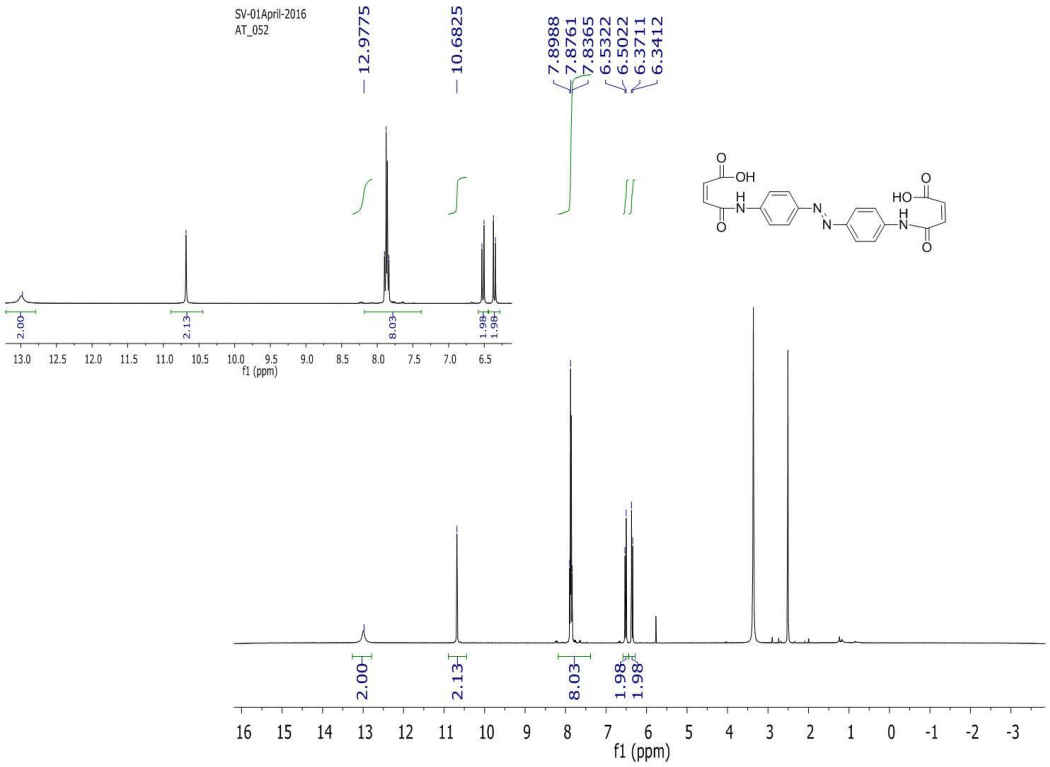
4-(*N*-maleimido)azobenzene:^{1}H NMR, $CDCl_3$



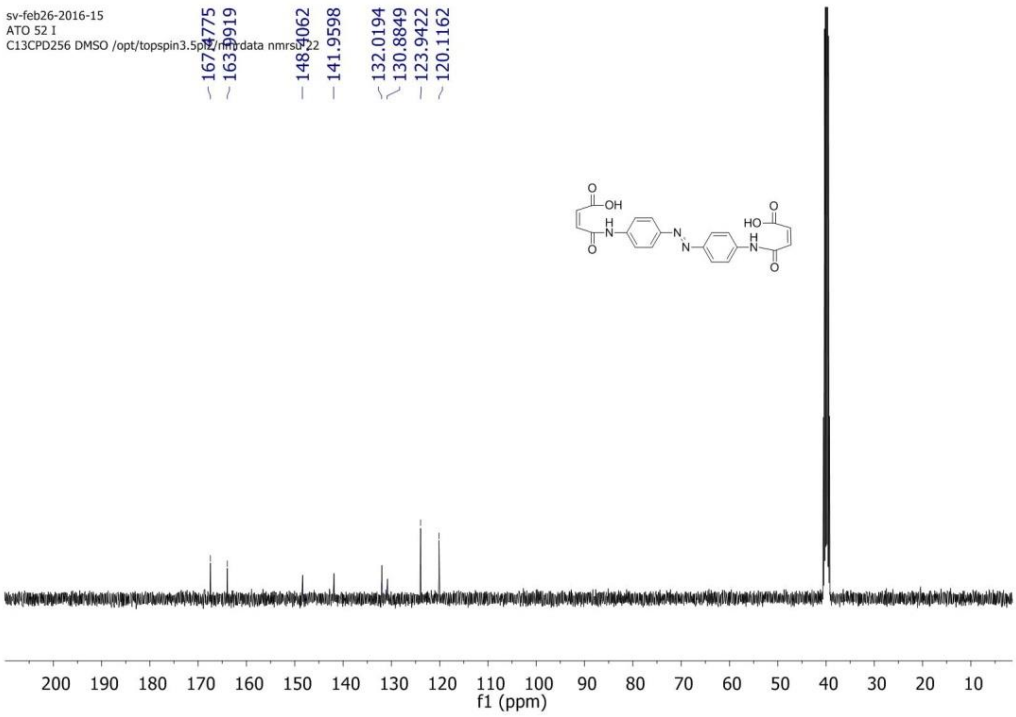
4-(*N*-maleimido)azobenzene: ^{13}C NMR, $CDCl_3$



4,4'-*bis*(maleamicacid)azobenzene: ^{1}H NMR, DMSO-d_6



4,4'-*bis*(maleamicacid)azobenzene: ^{13}C NMR, DMSO-d_6



CURRICULUM VITAE

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- Physical organic chemistry
- Biochemistry

EXPERIENCE WITH TECHNIQUES, SCIENTIFIC EQUIPMENT AND EXPERIMENTS:

CHEMISTRY

(i) Synthesis and characterization of organic molecules, Metal ligand complexes.
(ii) Ample expertise on IR, UV-Vis, ATR, AAS, Polarimeter, Gel Filtration Chromatography, Titrations using Potentiometer and Conductometer.
(iii) Experience in the spectral analysis such as NMR. Also experienced in analysing X-ray pattern using Powdered X-ray Diffractometer.

BIOLOGY:

(i) Protein crystallisation, Gel electrophoresis, PCR, SDS page, Restriction Digestion and Cloning, Plasmid isolation, Protein expression, primer Designing, Competent cell preparation, Protein purification by Ni-NTA Column.