Synthetic attempts in connecting multiple azobenzenes through amide and alkyne linkers

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Certificate of Examination

This is to certify that the dissertation titled"***Synthetic attempts in connecting multiple azobenzenes through amide and alkyne linkers***"submitted by Mr. Aman Kumar Bhonsle (Reg. No. MS11071) for the partial fulfillment 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.

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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

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Abbreviation

RBF	-	Round bottom flask
DCM	-	Dichloromethane
THF	-	Tetrahydrofuran
NEt_3	-	Triethylamine
EtOAc	-	Ethyl acetate
TMS-acetylene-		Trimethylsilyl acetylene
K_2CO_3	-	Potassium carbonate
$NaHCO_3$	-	Sodium Bicarbonate
Na_2CO_3	-	Sodium Carbonate
Na_2SO_4	-	Sodium sulfate
^{1}H-NMR	-	Proton NMR
^{13}C-NMR	-	Carbon NMR
FT-IR	-	Fourier transform infra-red
$SOCl_2$	-	Thionyl Chloride
PCl_5	-	Phosphorous pentachloride
nm	-	nanometer
UV-Vis	-	Ultraviolet – visible spectroscopy

Contents

Abstract

Azobenzene are robust molecule which can undergo reversible photo switching between the thermodynamically stable *trans* to less stable *cis* form via external stimuli, Light. Due to this behavior it can be used as molecular transporter. Underlying this concept, we are trying to connect multiple azobenzene to core moiety via various kind of linkage. In this work we deal with two kinds of linkage viz. amide linkage and alkyne linkage to make the azobenzene based molecules.

Chapter 1: Introduction

1.1 General

Azobenzene are photo switchable molecules that make them to show applications in diverse fields of science. Azobenzene and its derivatives have been studied for over a long period of time owing to their colorant properties that led to use them as vital dyes for textiles. Later it was found out that azobenzene molecule can undergo photoswitching. Photoswitching is a light driven reversible transformation between two isomers. The change in geometry and shape in some photo-reversible molecules using light can effect powerful changes to a variety of properties that opened up more applications. Also, the photoswitching leads to dramatic photo responsive change in absorption spectra.

Azobenzene switching depends upon the irradiation wavelength. It switches from thermodynamically stable *trans* isomer to less stable *cis* isomer by irradiating with UV light corresponding to either π–π* absorption mode or n-π* mode.

Photoreversible molecules are divided into three categories as follows:-

1. Photodimerization

In this type, a dimer is formed, which is connected by carbon-carbon bond. Anthracene photodimerize under UV light (below 300 nm) and revert back under visible light.[1]

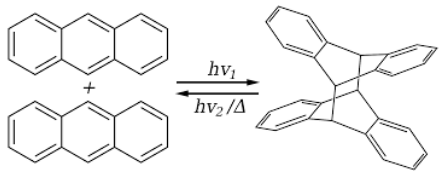


Figure 1. Photodimerization shown by anthracene molecule under UV-Vis light

2. Intramolecular photoinduced bond formation

In this type, spiropyran undergo change in confirmation under UV-Vis light and transfer the electron to other Donor-Acceptor system and facilitate the reaction.[2]

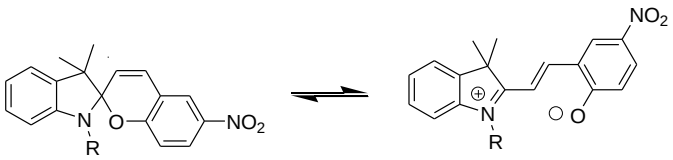
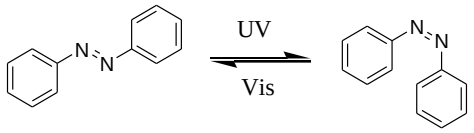


Figure 2. Intramolecular photoinduced ring opening in spiropyrans

3. Photoisomerization

In photoisomerization, molecule show photochromic behavior i.e. switching from one form to another form under UV-Vis light. For example, azobenzene.



Trans-azobenzene *Cis*-azobenzene

Figure 3. *cis-trans* isomerization shown in azobenzene

1.2 Photochemistry of azobenzene

While explaining the photochemistry of azobenzene two type of question arise

1. How the photoisomerization occurs.

2. How to follow photoswitching.

1.2.1 Photoisomerization in azobenzene

Azo compounds have two important type of electronic states, viz (π^*, n) and (π^*, π). Based on the ordering of energy states, they are classified into three types, namely azobenzene type, aminoazobenzene type and pseudo-stilbene type. Azobenzene type molecules show low intensity n-π^* absorption band in the visible region and high intensity π-π^* band in the UV region. For aminoazobenzene type molecules, the n-π^* and π-π^* states are very close and overlap in the near visible UV region.[3] For pseudo-stilbene molecules, the 4 and 4' position substitution with electron donor and acceptor substituents shifts the π-π^* transition past that of the n-π^*. From X-ray and computational studies, it was observed that *trans*-azobenzene adopts a planar structure with C_{2h} symmetry, whereas *cis*-azobenzene adopts a non-planar structure with C_2 symmetry. Gas phase electron diffraction data indicates that the two-phenyl rings of *trans* azobenzene are twisted approximately 30 ^oC. The absorbtion spectra of *trans*-azobenzene has two

well-separated bands in the UV region corresponding to π-π^* and n-π^* transitions. The π-π^* transition in *cis*-azobenzene is weaker than the n-π^* transition. The two transitions excite azobenzene to S_1 (n, π^*) and S_2 (π, π^*) states. From the absorbtion spectra of azobenzene two different isomerization pathways have been proposed:

1) In-plane inversion by the bending of an N=N-C bond

2) Out-of-plane rotation by the torsion of two phenyl rings.

From time resolved spectroscopy, it has been found out that the isomerization proceeds in the S_1 state via the inversion pathway, whereas in the gas phase rotation pathway is energetically more favorable. [4]

1.2.2 Spectroscopic techniques to detect photo switching

The photo switching in azobenzene can be followed by various spectroscopic techniques like UV-Vis spectroscopy, Raman spectroscopy and Nuclear Magnetic Resonance spectroscopy etc. As azobenzene has got two excited energy states, namely (π*, n) and (π*, π), upon switching the corresponding transitions will have varied intensities. This is due to the fact that the conjugation is breaking during the isomerization. Since appreciable changes in the UV-Vis spectrum is expected, the electronic spectroscopy is a simplest method for following the photoswitching.

1.3 General application of azobenzene based molecules

Azobenzene has vast applications in a variety of photosensitive devices, such as smart polymer

liquid crystals, intelligent enzymes etc. Various switches and molecular machines have been developed by using the photochromic properties of azobenzene and benefiting from its easy synthesis. Azobenzenes have many applications in biology also like one example shown by Woolley et al. They introduced azobenzene moiety in a polypeptide chain to control the α-helical conformations of DNA and to have a synthetic tool that allows photomodulation of the very important conformation–interaction relationship in biological recognition. Peptides with pairs of cysteine residues were intramolecularly cross-linked with thiol reactive azobenzene-based photoswitches. The photoswitching of the azobenzene changes the conformation of the peptide depending on the location of the cysteine. When azo group of polypeptide **2** is in its *trans* form, it retains its affinity for DNA and

its α-helical conformation. Through photoisomerization of *trans* to the *cis* isomer, the helicity of the peptide disrupts that inhibits the association with DNA. The photoreversion to the *trans* form recovers again to the final conformation of the α-helix of DNA. [5]

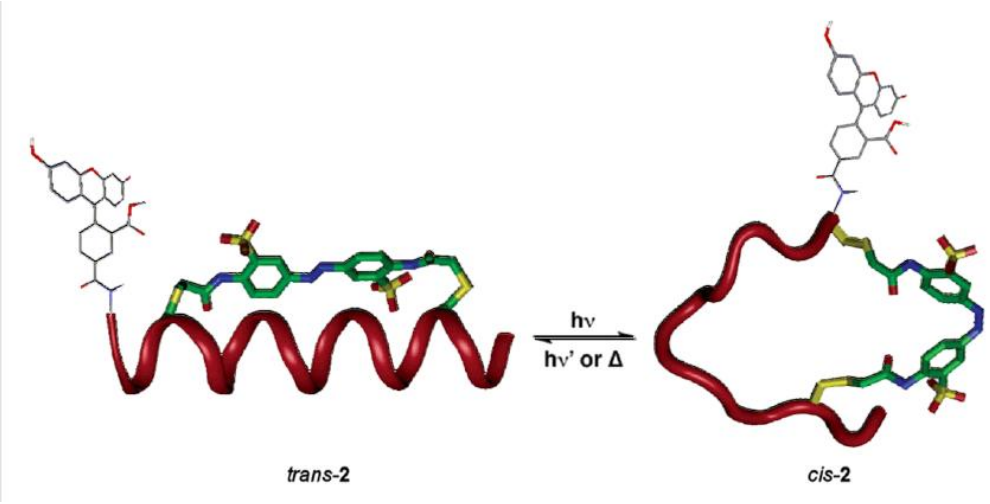


Figure 4. Photo-controlled structural dynamics in α-helix polypeptide connected azoderivative **2**

The photochromic behavior of azobenzenes also finds applications in "host–guest" recognition. For example, the *bis* azo compound **3** behaves as an excellent receptor of guanidinium ions through hydrogen-bonding interactions. The recognition is very effective when the azobenzene adopts the *cis* configuration (Figure 5). [6]

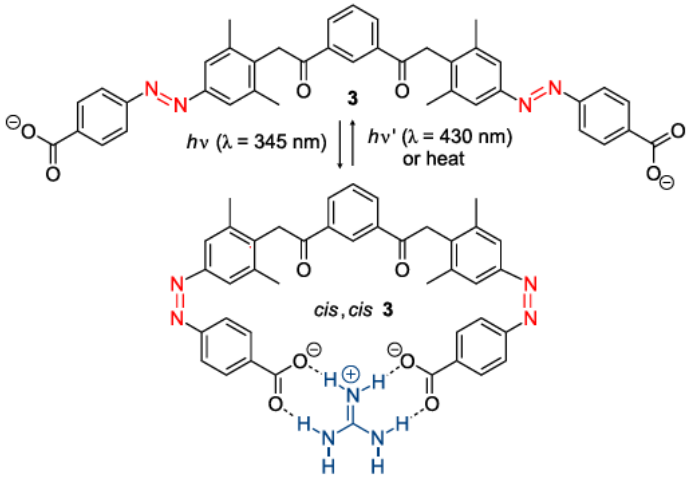


Figure 5. Recognition of a guanidinium ion by a *cis,cis*-bis-azo derivative **3**

Azobenzene derivatives have shown significant impact in supramolecular chemistry. Among these, many azobenzenes connected supramolecular systems such as azophane,

azocryptand, and azacrowns etc are well-known. Azobenzene based molecular device has been described in many literature.

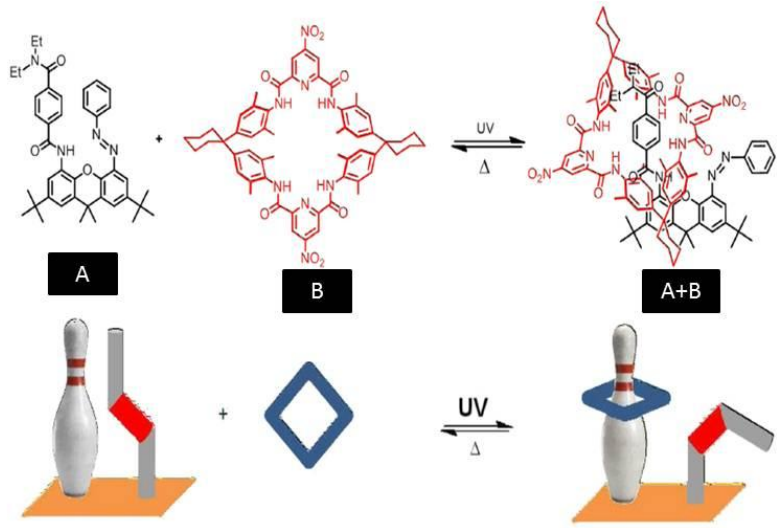


Figure 6. Pseudorotaxane-based molecular machine.(adopted from reference [7])

In 2003, a psuedorotaxane based moleculer machine has been described by Kyu-Sung Jeong et al.[7] Assembly between **A** and **B** occurs only when the azobenzene moiety in **A** adopts the *cis* configuration. The pseudorotaxane **A+B** can disassemble into its two components when the isomerization to *trans*-azobenzene occurs by an external stimulus (**Figure 6**). In 2004**,** Tamaoki et al. designed a molecular device capable of photo-emulating a hinge motion. This switch consists in two azobenzene units that share a fragment with two coplanar xanthenes (**Figure 7**). The photoisomerization of the system forces a molecular motion similar to a hinge, in which the two aromatic rings are at an angle of 90°. The photoisomerization process involves three isomeric forms: (*trans*,*trans*), (*cis*,*cis*) and (*trans*,*cis*) . The heats of formation of these three isomers were determined by *ab initio* quantum chemical calculations. The isomers (*trans*,*trans*) and (*cis*,*cis*) are 28.0 and 2.6 kcals·mol^{-1} more stable than the intermediate isomer, respectively. [8]

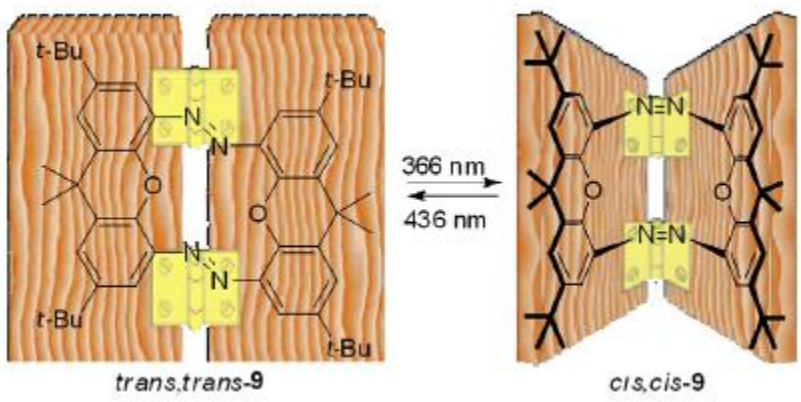


Figure 7. Molecular hinge.

The large energy difference between (*trans*,*trans*) and (*trans*,*cis*) isomers indicates the ring strain that exists in the (*trans*,*cis*) isomer, and the thermal isomerization from (*cis*,*cis*) to (*trans*,*cis*) is forbidden. The half-life of (*trans*,*cis*)-isomer is only 28 s at 23 °C. In these systems, in which the photochemical reaction intermediate has a short half-life and the final (*cis*,*cis*)-product is more stable than the intermediate, the photochemical yield is highly dependent on the used light intensity.[9]

1.4 Objective of Project

Our main objective in this project is to make a photoswitchable compound, which can be used as a potential molecular transporter. In this regard, we are trying to connect multiple azobenzene to a core moiety through various linkages so that it can undergo switching in the same direction and work as a host-guest system to encapsulate small organic compounds, drug molecules and ions. (**Fig 8** and **9**)

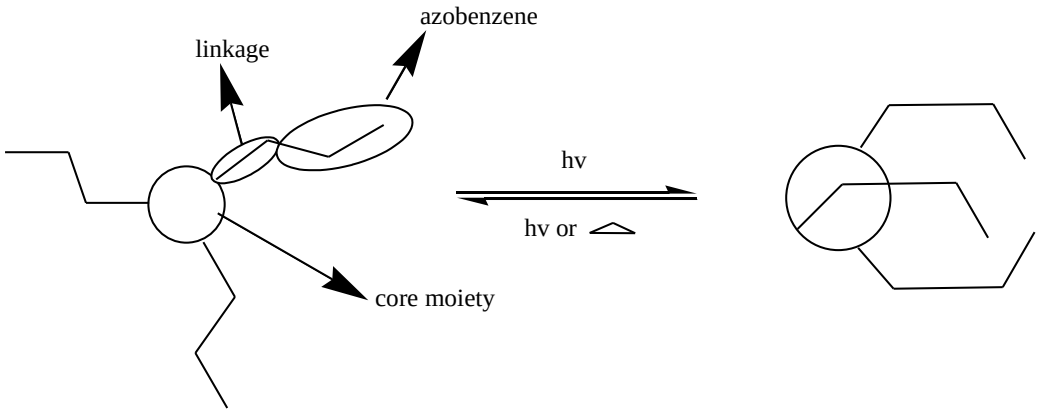


Figure 8. *Trans-cis* isomerization in target molecule

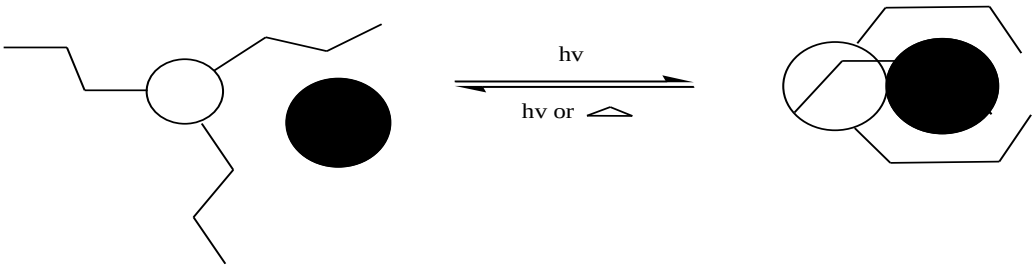


Figure 9. Expected Host-Guest interaction in the target system

1.5 Challenges:

With respect to the design part of the target system, where multiple azobenzenes are needed to be connected to a core moiety, we have the following three modifications that we need to consider:-

1. Choice of azobenzene.

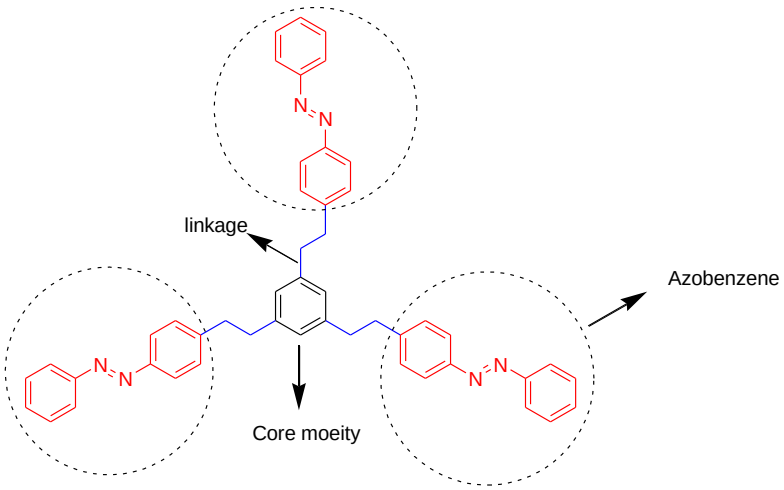
2. Core moiety modification

3. Linkage modification

Our current approaches is to play around with the linkage Modification .We are focusing on two kind of linkage

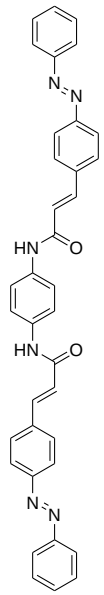
1.Amide linkage

2.Alkyne linkage

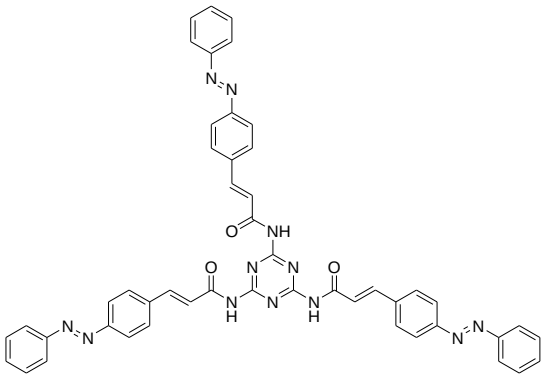


Scheme1. Designing the photoswitchable molecular transporter.

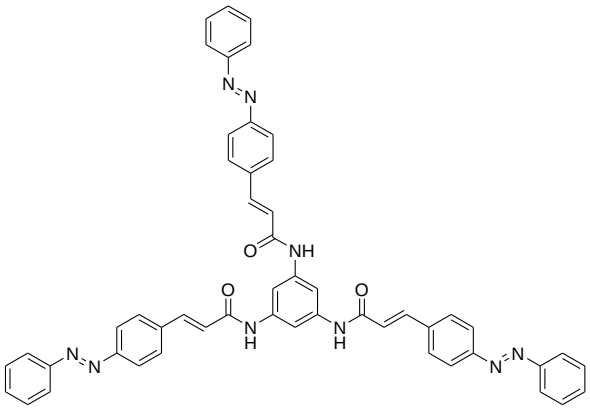
1.6 Target Molecules



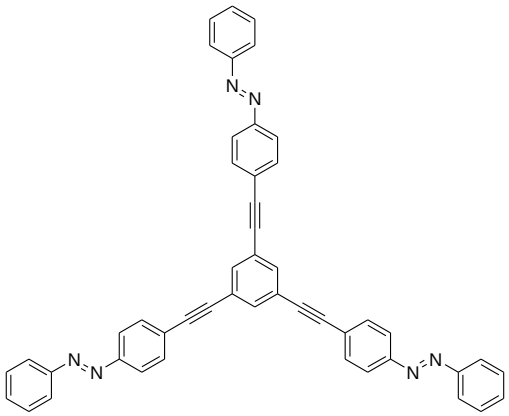
Target 1



Target 2



Target 3

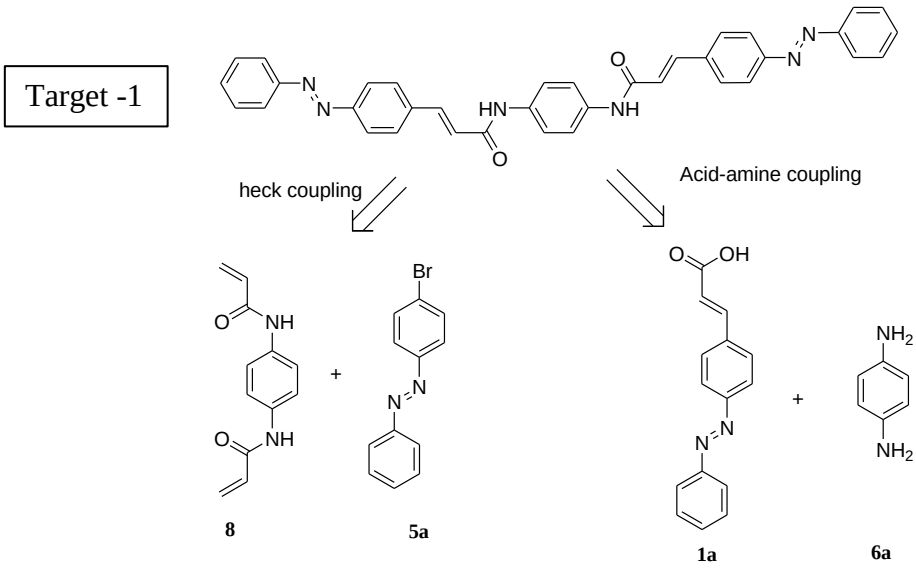


Target 4

1.7 Synthesis of azobenzene based molecules

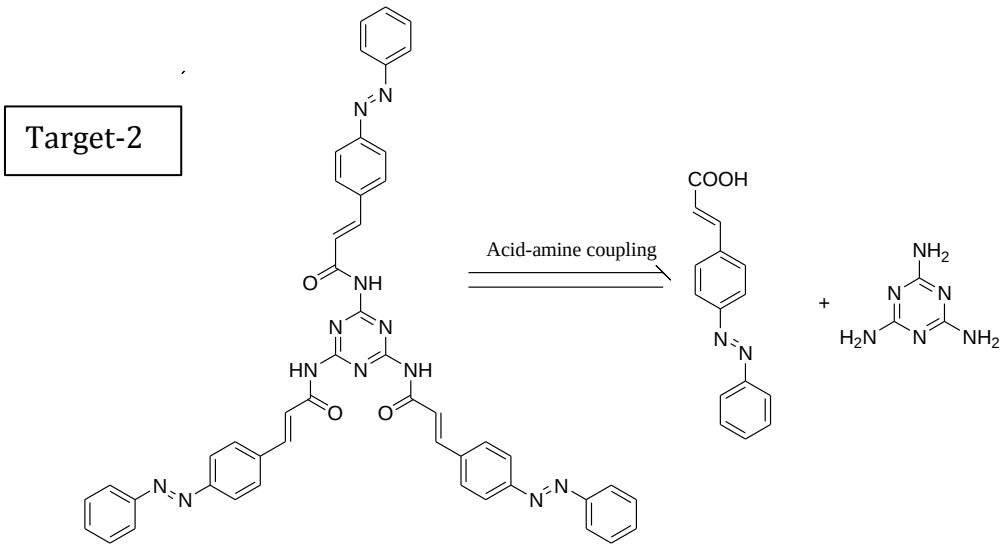
1.7.1 Retrosynthesis

For Target**1**,two route were designed viz. Acid-amine coupling using **1a** and **6a** or Heck coupling between compound **8** and **5a**. [10][11]



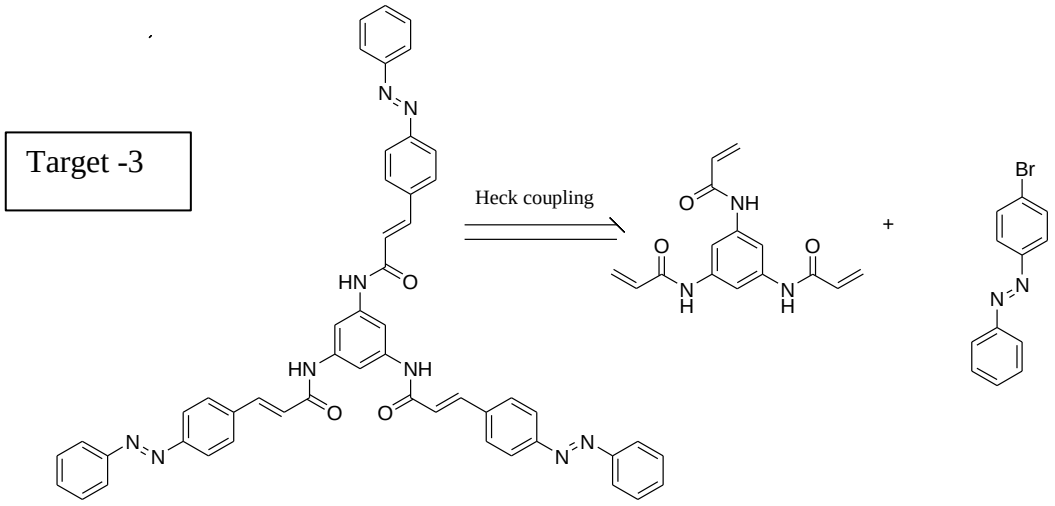
Scheme 2. Synthesis of target **1** via two pathways viz. Heck coupling and acid-amine coupling

For target **2**, precursor**1a** and compound **7** was taken and acid amine coupling was tried.[12]



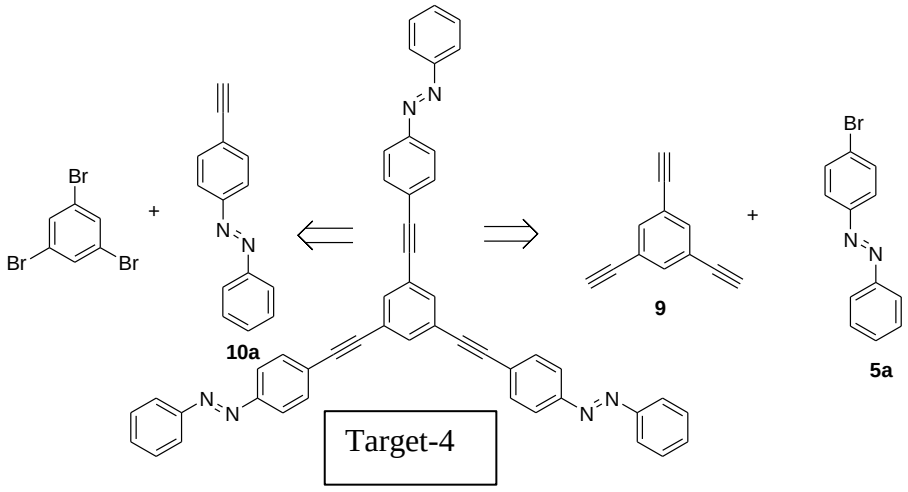
Scheme 3.Synthesis of target **2** via acid- amine coupling

Target **3** was *tris* amide coupled azobenzene which was tried using the Heck coupling strategy given below :



Scheme 4. Synthesis of target **3** using Heck coupling

For target 4 synthesis, two strategies were followed. In first strategy compound **9** was Sonogashira coupled with compound **5a.** In second strategy 1,3,5-tribromobenzene was Sonogashira coupled with **10a**



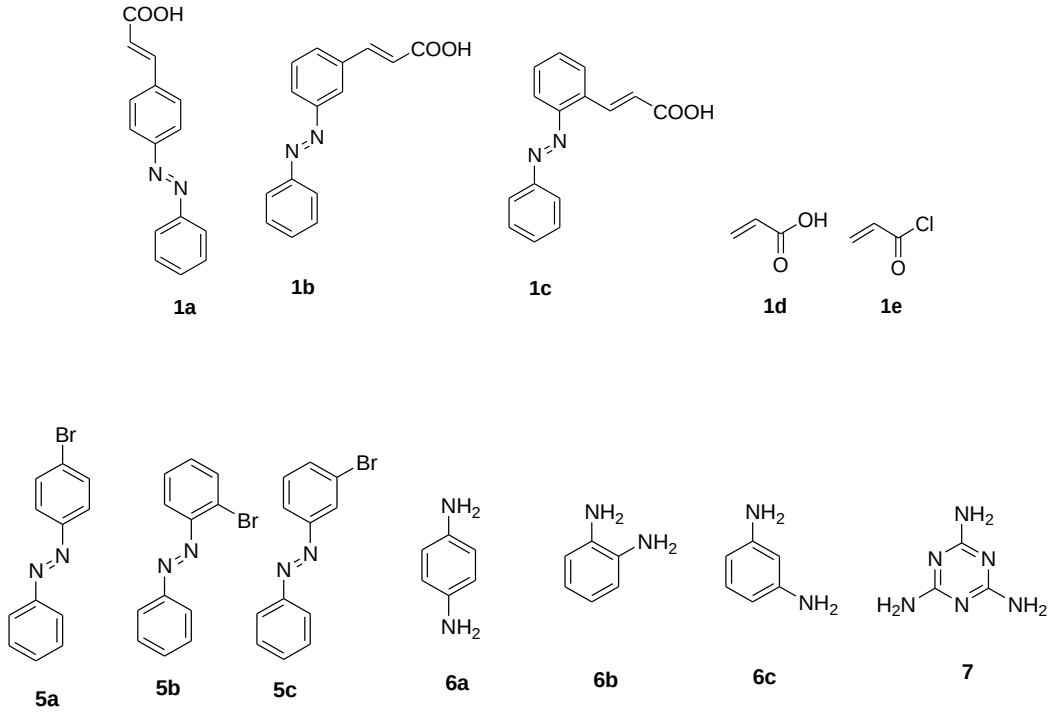
Scheme 5. Synthesis of target **4** using Sonogashira coupling.

Chapter 2. Results and Discussion

In this section, the status on attempts towards synthesizing multiple azobenzenes connected target molecules through amide and alkyne linkages will be described.

2.1 Amide linkage:

For synthesizing our target molecules, the precursor has to be synthesized in multiple steps that include Mills method and Heck coupling. During the synthesis of the target molecules, we also considered their analogous molecules. (**Scheme 6**)

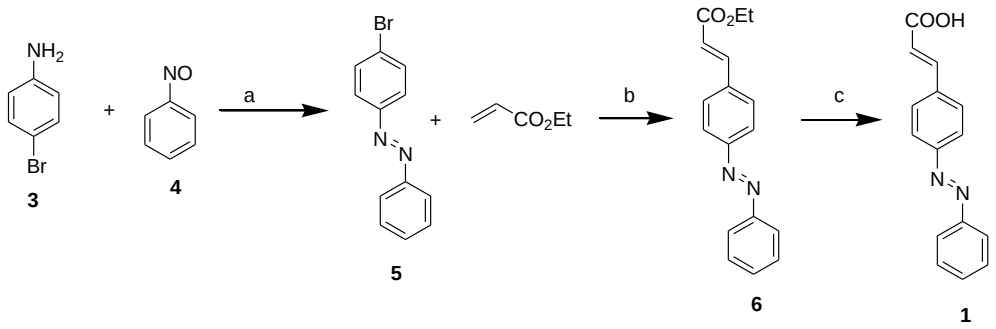


Scheme 6. Precursors considered for the synthesis of the target molecules

2.1.1 Synthesis of precursor for target molecule

2.1.1.1 Synthesis of 3-[4-[(1*E*)-2-phenyldiazenyl]phenyl]-2-Propenoic acid (**1**)

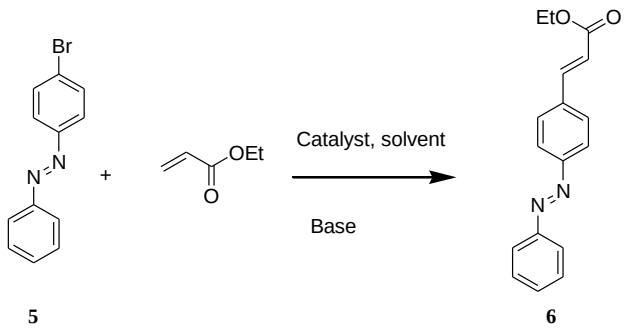
From the commercially available 4-bromoaniline and nitrosobenzene, Mills method[13]was employed to get the 4-bromoazobenzene (5), followed by Heck coupling to get compound (6), which upon hydrolysis to get our precursor (1).



Scheme 7. Synthesis of (**1**). a) Ethanol, Acetic acid ,40 ºC ; 83% , b) $Pd(OAc)_2$, PPh_3, K_2CO_3, DMF, 110 ºC; 84% , c) LiOH, Ethanol, 40 ºC; 98%

2.1.2 Optimization studies

We have performed some optimization studies in the Heck coupling stage (**Scheme 8**) for improving the yield. For getting precursor **6** we tried different base like K_2CO_3, DIPEA. For initial cases yield was low. After increasing the catalytic loading we got the product with improved yield.



Scheme 8. Synthesis of Heck coupled product **6**

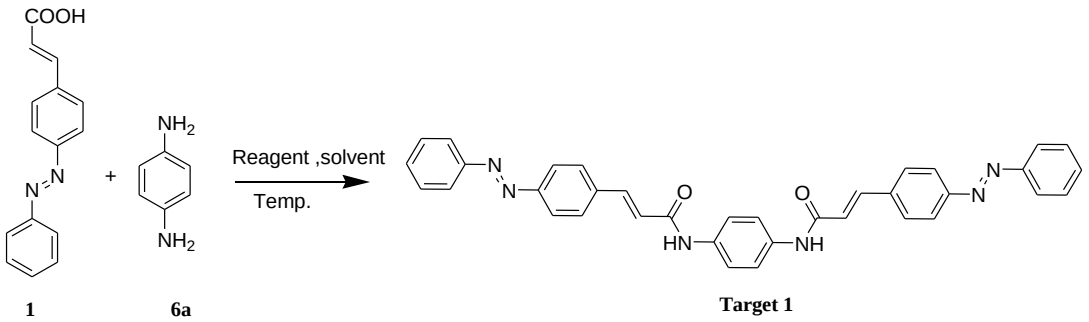
Table 1. Optimization table for Heck coupled product **6**

Entry	Catalyst(mol%)	Ligand(mol%)	Base	Solvent	Time	Yield
1.	$Pd(OAc)_2$(5)	PPh_3(10)	K_2CO_3	DMF	24 hr	60%
2.	$Pd(OAc)_2$(5)	PPh_3(10)	DIPEA	DMF	24 hr	64%
3.	$Pd(OAc)_2$(20)	PPh_3(10)	K_2CO_3	DMF	24 hr	84%

Optimization studies for Target-1

After getting the precursor **1** we tried the acid amine coupling with commercially available phenylenediammine. We screened variety of reagent and solvent. For the first two case starting material was not soluble in Dry DCM, after adding $SOCl_2$ (PCl_5) it got dis-

solved but product could not be obtained for final stage. Then solvent was changed to Dry Toluene. In this case starting material was not dissolved even after addition of $SOCl_2$ (PCl_5). Then solvent was changed to Dry THF and in this case for first step color changes orange to black but product could not be obtained.



1 **6a** **Target 1**

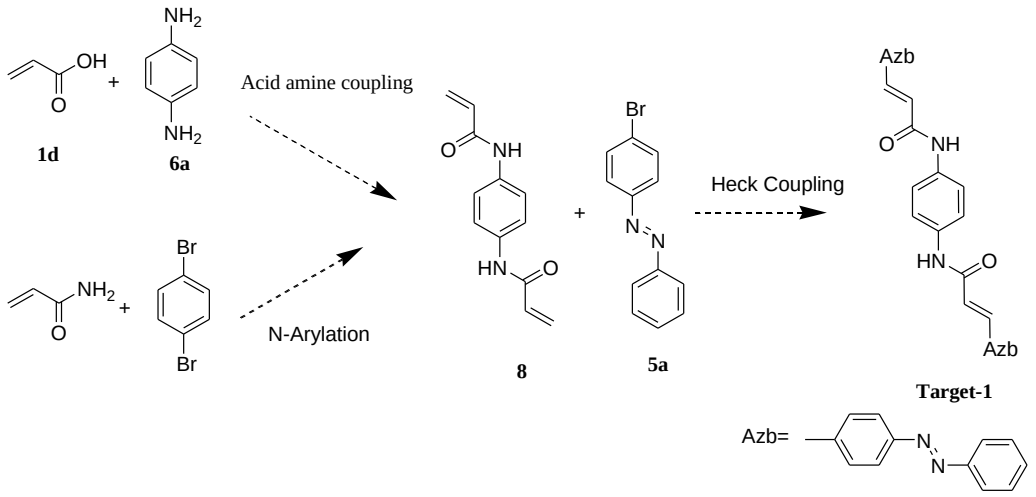
Scheme 9. Synthesis of target **1** using acid amine coupling.

Table 2. Optimization table for Synthesis of target **1**

Entry	Reagent	Base	Solvent	Temperature(^oC)	Time	Result
1	$SOCl_2$	NEt_3	Dry DCM	40	24 hr	NR
2	PCl_5	NEt_3	Dry DCM	40	24 hr	NR
3	$SOCl_2$	NEt_3	Dry Toluene	80	24 hr	NR
4	PCl_5	NEt_3	Dry Toluene	80	24 hr	NR
5	$SOCl_2$	NEt_3	Dry THF	Reflux	24 hr	NR

2.1.3 Alternative strategy

In the alternate way we tried to synthesize the compound **8** which could give desired product after Heck coupling. For the synthesis of compound **8** we adopted two strategy viz. acid amine coupling and N-arylation [14]. pathways.



Scheme 10. Alternative strategy for synthesis of Target **1**

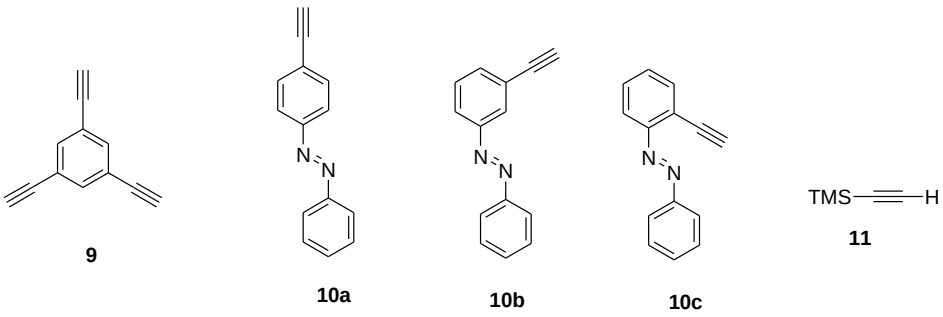
Table 3. Optimization table for synthesis of target **1** (alternative strategy)

Entry	Reactant/reagent	Base	Solvent	Time	Temp (^{o}C)	Result
1	Acrylic acid+$SOCl_2$	NEt_3	DCM	24	40	NR
2	Acrylic acid+PCl_5	NEt_3	DCM	24	40	NR
3	Acrylic acid+EDC.HCl	DMAP	DCM	24	RT	NR
4	Acryloyl chloride	NEt_3	DCM	24	RT	Insoluble solid, not product
5	Na-Ascorbate, $CuSO_4$. $5H_20$	t-BuONa	DMSO	7	100	Mixed spots

NR = No result (No desired product)

2.2 Alkyne linkage

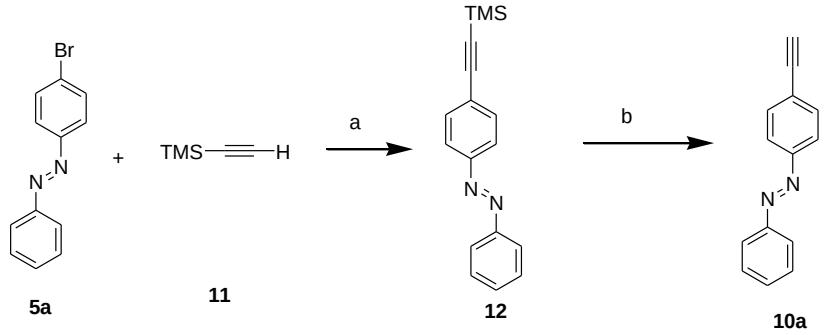
We tried to synthesize our target molecule (Target **4)** which has alkyne linkage. In this course Sonogashira coupling and some deprotection strategy were followed. For synthesizing main unit, other substrates were also synthesized (**Scheme 11**).



Scheme 11. Precursor for synthesizing target molecule

2.2.1 Synthesis of precursor (10a)

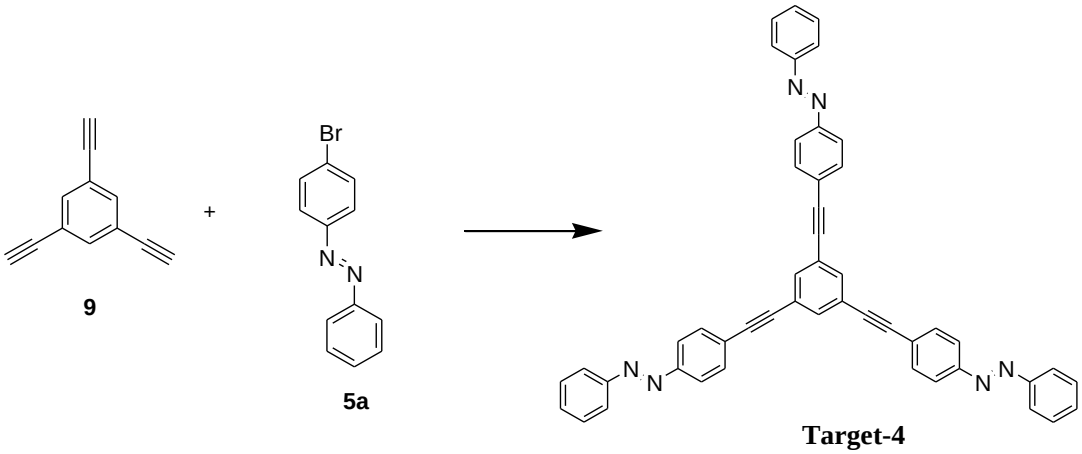
Compound **5a** underwent Sonogashira transformation with TMS-acetylene to get compound **12** and followed by deprotection of TMS group we got product **10a**.Using the same procedure **10b**, **10c** were also synthesized in 92% yield.



Scheme 12. Synthesis of **10a** .a) $Pd(PPh_3)_2$,CuI, NEt_3, 16 h, 65 ^{0}C; 87% b) K_2CO_3, Methanol 6h, RT; 92%.

2.2.2 Optimization studies for Target 4

For the synthesis of **target 4**, firstly compound **9** was synthesized following standard procedure. [15] After having **9,** Sonogashira coupling was performed with compound **5a** under various condition to get desired product. In all the case we were getting the starting material (**5a**).Even we tried to perform monocoupling by taking phenylacetylene and compound 5a but that also didn't work.

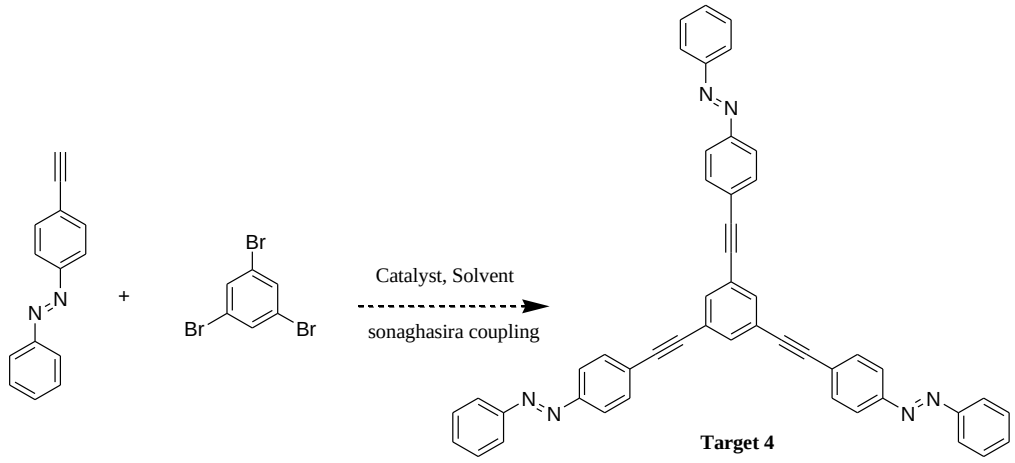


Scheme 13. Synthesis of target **4** using Sonogashira coupling.

Table 4. Optimization table for synthesis of target **4**

Entry	Catalyst (mol%)	Solvent	Base	Temp (^{o}C)	Time	Result
1	$Pd(PPh_3)_2Cl_2$ (20), CuI (20)	Neat	NEt_3	65	24 hr	NR
2	$Pd(PPh_3)_2Cl_2$ (20), CuI (20)	THF	NEt_3	90	24 hr	NR
3	$Pd(PPh_3)_2Cl_2$ (20), CuI (20), PPh_3 (5)	Neat	NEt_3	65	24 hr	NR
4	$Pd(PPh_3)_4$ (20), CuI (20)	Neat	NEt_3	90	24 hr	NR

Alternative strategy As earlier strategy didn't work, we moved to other strategy to synthesize our target molecule. Here we tried same Sonogashira coupling but with different linkage. We screened the reaction for different catalysts.



Scheme 14. Synthesis of target **4** via Sonogashira coupling

Table 5. Optimization table for target **4** (alternative strategy)

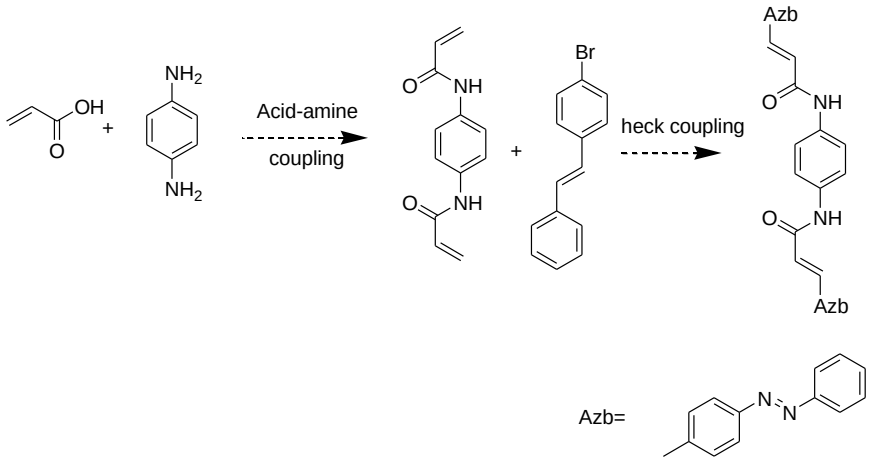
Entry	Catalyst (mol%)	Base	Time	Temp (^{o}C)	Result
1	$Pd(PPh_3)_2Cl_2$ (20), CuI (20)	NEt_3	16 hr	65	NR
2	$Pd(PPh3)_4$ (20), CuI (20)	NEt_3	16 hr	65	NR

Chapter 3. Conclusions and Perspectives

In our current investigation, we tried to connect multiple azobenzenes to a core moiety in order to understand the photoswitching behavior. In this regard, we considered benzene as our core moiety and unsubstituted azobenzenes as our photoswitchable units. Amides and alkyne likages have been chosen as our linking units. To synthesize such targets, we have considered various synthetic strategies and procedures. The summary and outlook of the project are the following:

3.1 Amide linkage target

We have considered *bis* and *tris*- amide coupled azobenzene systems as our initial targets. Here, we have utilized two generalized strategies, where Heck coupling and acid-amine couplings as a part of it. (**Scheme 16**)



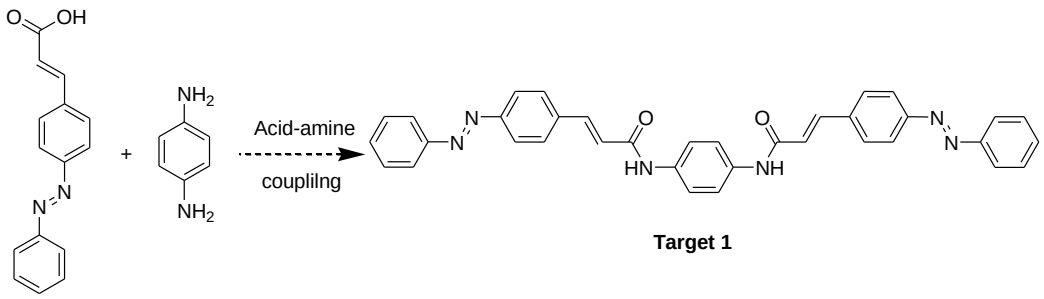
Scheme 15. Synthesis of target **1** using acid amine coupling and Heck coupling

In the first strategy, acrylic acid has been used to make amide with 1,4-phenylenediamine using $SOCl_2$ and PCl_5 as the reagents for preparing acid chloride. We have tried few different conditions by varying the solvents, and temperature. However, we haven't generated the desired product. On the other hand, when acryloyl chloride was used as a reagent, an insoluble product was isolated, which could not be characterized. In all the above-mentioned conditions, any one or more of following reaction might have happened, which may be the reason for not isolating the desired product.

1. Polymerization of olefin
2. Aza-Michael type addition

3. Phosphoramide formation (reaction of amine with $POCl_3$, a by-product in the PCl_5 reaction)

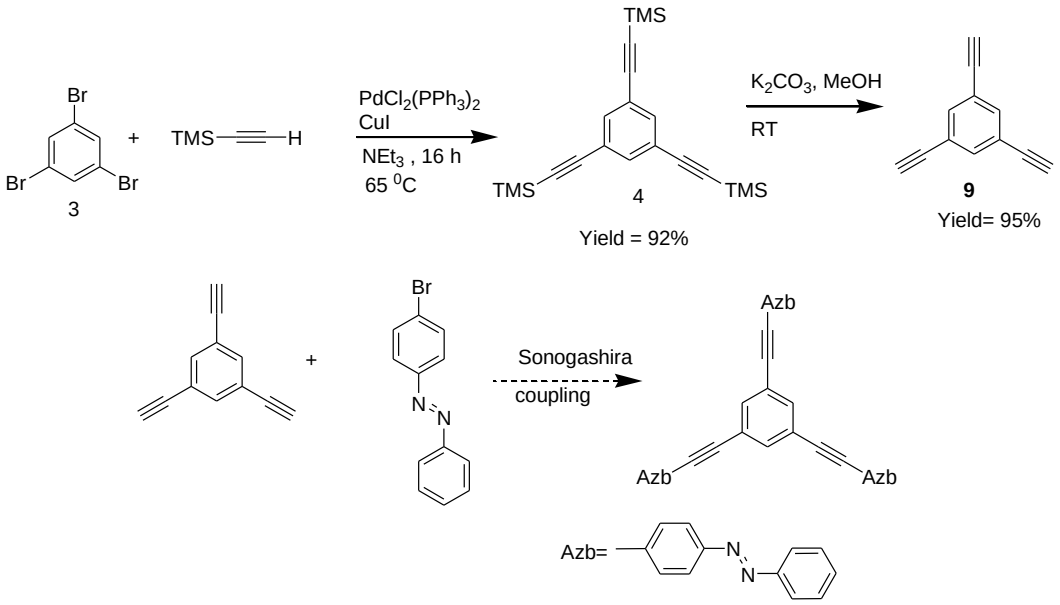
In another strategy, 4-bromoazobenzene was coupled with ethyl acrylate using Heck coupling, followed by base hydrolysis that led to the formation of azobenzene-coupled acrylic acid. This was tried to react with 1,4-diaminobenzene to get the same product. However, we ended up with the same kind of situation, where amide coupling could not be achieved even under different conditions. Acid-amine coupling needs to be tried using mixed anhydride procedure or by using activation strategies with the respect to the acids in order to get the desired products.



Scheme 16. Target **1** synthesis via acid amine coupling.

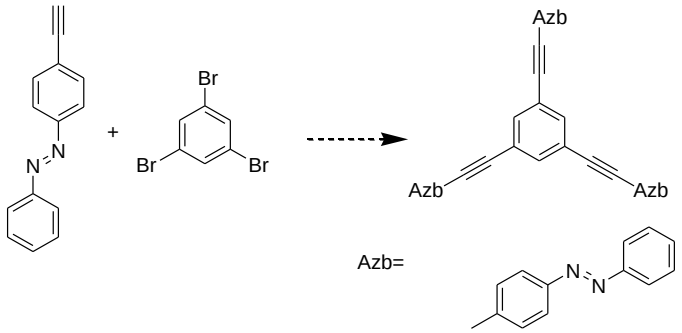
3.1 Alkyne linkage target.

In the second target, alkyne was used as a connector between the core and the pho-toswitchable unit. For symmetry reasons, 1,3,5- substitution has been chosen. The target molecule was planned to synthesize using two different approaches. In the first one, the core 1,3,5-tribrombenzene was functionalized with alkyne using Sonogashira coupling using TMS acetylene, followed by base hydrolysis to remove TMS group[15]. Then this 1,3,5-triethynylbenzene was treated with bromoazobenzene under Sonogashira coupling. Even after utilizing harsh cotions, we were not able to get the product.



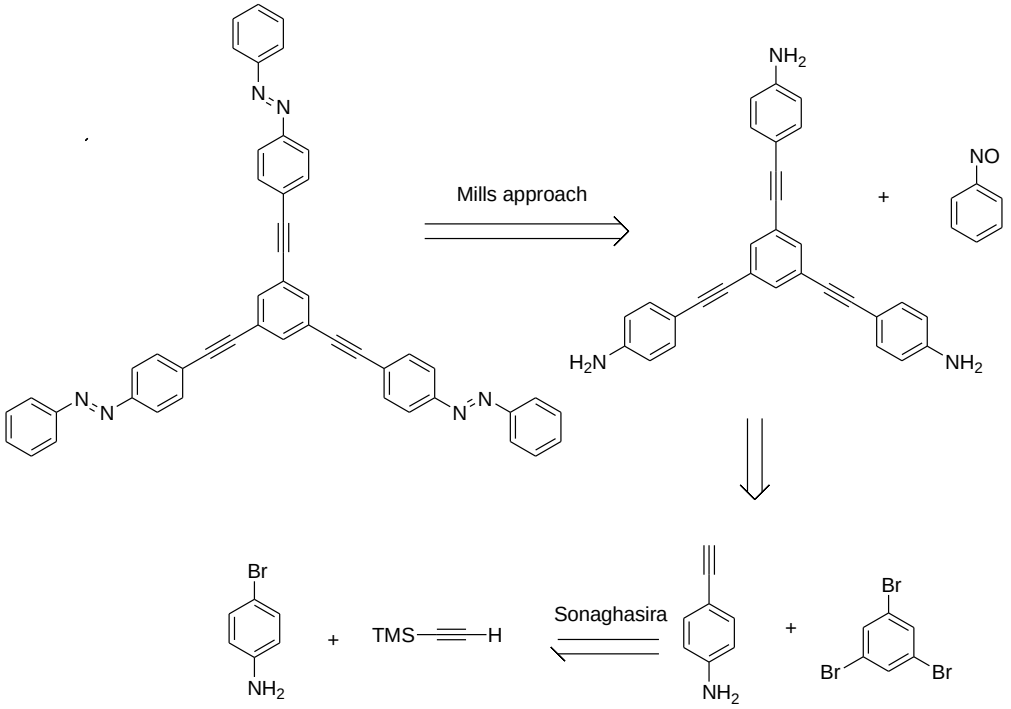
Scheme 17. Synthesis of alkyne connected target **4**

So, we changed to another approach where, the 4-bromoazobenzene was converted into 4-ethynylazobenzene under Sonogashira condition using TMS acetylene, followed by removal of TMS group. When this molecule was coupled with 1,3,5-tribromobenzene, again the same problem persisted. Despite the use of harsh condition or microwave reaction conditions, the reaction did not work.



Scheme 18. Synthesis of target 4 with alternate strategy

Presumably, the reason might be the electron withdrawing nature of the azobenzene that hindered the reactivity under Sonogashira coupling. To achieve the target, Sonogashira coupling with 4-ethynylaniline with 1,3,5-tribromobenzene followed by Mill's method might be a viable strategy.[16] This strategy is currently underway.



Scheme 19. Alternative strategy for target **4**

Chapter 4. Experimental Section

General:

All the chemicals were purchased from commercial suppliers (Sigma Aldrich, Himedia, and Merck). All the solvents were dried according to the standard procedure or by using MBraun MB-SPS solvent drying unit. Column chromatography was done with silica gel (100-200 mesh size).The reaction was monitored with silica gel TLC plate (Merck). IR spectra were recorded on Bruker Alpha IR spectrophotometer. NMR data were recorded using a Bruker Avance III 400MHz NMR spectrometer. For ^{1}H-NMR, the 400 MHz was the frequency, whereas for ^{13}C, 100 MHz was the frequency used. All the NMR values were taken in ppm with TMS as standard. All the coupling constants were reported in Hz. Mass spectra were recorded in both ESI positive and negative modes using Waters SYNAPT G2S High Definition HRMS mass spectrometer.

Synthesis:

(*E*)-1-(4-bromophenyl)-2-phenyldiazene (5){ Mills Method}

In two necks RBF flushed with argon, 4-bromoaniline (1gm, 5.8mmol) was added to a solution of Nitrosobenzene(0.931 gm,8.7mmol) and Acetic acid followed by ethanol .The reaction mixture was heated to 40 ºC for 4hrs. Colors changed from greenish to brown. Upon the completion of reaction, work up was done with Aq.Na_2CO_3 and DCM. Crude product was then purified with column chromatography to get bright orange crystal with desired product (1.25gm, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.58 - 7.51 (m, 2H), 7.69 - 7.66 (m, 2H), 7.84 - 7.82 (m, 2H), 7.95 - 7.92 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 122.95, 124.36, 125.38, 129.16, 131.34, 132.33, 151.32, 152.44 ; IR(KBr): 3058, 1655, 1570, 1477, 1280, 837 (cm^{-1}) ESI-TOF: $(M+H)^+$ of molecular formula $C_{12}H_9BrN_2$ calculated 261.0007,found 261.0027 M.P: 86 ºC

3-[4-(2-phenyldiazenyl)phenyl]-ethyl ester (6) {Heck coupling}

In a two neck RBF with inert atmosphere ,compound **5**(100mg,0.382mmol) was dissolved in DMF and $Pd(OAc)_2$(10mol%),PPh_3(20 mol%) and K_2CO_3 (2eq)was added. Degassing was done 2-3 times and finally ethyl acrylate was added via syringe. The reaction mixture was heated to reflux at 120 ºC for 24 hrs. Upon completion, reaction

mixture was filtered through Celite Pad and solvent was removed under rotary evaporator to get crude product which was subjected to purification in column to get orange crystal with 86% yield.^{1}H NMR($CDCl_3$): δ 4.32 (q,2H) ,6.5(d,1H),7.95(m,4H),7.52-7.85(m,6H); ^{13}C NMR($CDCl_3$): δ 119.6, 123.5, 123.0, 129.2,128.9, 131.4, 136.8 ,143.5, 153.3, 152.6 IR (KBr): 3082, 2995, 1696, 1309, 1180, 843 (cm^{-1}).ESI-TOF: $(M+H)^+$ for the molecular formula $C_{17}H_{17}N_2O_2$: calculated 281.1245; found 281.1282

3-[4-[(1*E*)-2-phenyldiazenyl]phenyl]-2-Propenoic acid (1){hydrolysis of ester}

Compound **6** (136 mg, 0.485 mmol) was taken in one neck RBF and LiOH(163 mg,3.88 mmol)was added into it. Reaction mixture was heated to 40 ºC for 2-3 hrs. After completion, few drop of HCl was added to get precipitate which was washed with water and then ethyl acetate to get 98% yield.^{1}H NMR(DMSO): δ 6.60(d,1H) ,7.87-7.95 (m ,6H),7.59-7.71(m,4H),12.5(s,1H);

^{13}CNMR(DMSO):δ 123.5,123.2,121.4,129.8,137.6,143.2,152.9,167.9; IR (KBr): 3437, 2826, 2605, 1690,1680, 983, 836, 680 (cm^{-1}).ESI-TOF : $(M+H)^+$ for molecular formula $C_{15}H_{12}N_2O_2$: calculated 253.0977; found 253.0971.

Tris-1, 3, 5-triethynylbenzene (9)

To a solution of *1,3,5*-tribromobenzene (200.1 mg, 0.64 mmole) in triethylamine(7.0 mL) were added $Pd(PPh_3)_2Cl_2$ (13.0 mg, 0.02 mmole) and CuI (3.8 mg, 0.02 mmole) and the mixture was stirred for 15 minutes under argon atmosphere. Commercial trimethylsilylacetylene(0.36 mL, 2.55 mmole) was added and the reaction was heated to 65°C and stirred for 16 hours.

Hexane (10 mL) was added to the reaction mixture, and subjected to shot path column chromatography on silica gel. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with hexane to give 283.9 mg (0.64 mmole, 100%) of *1,3,5-tris*(trimethylsilylethynyl)benzene as pale yellow solid. This product was dissolved in methanol (5.0 mL) and a solution of anhydrous potassium carbonate(13.0 mg) was added and the mixture was stirred at room temperature for 6 h.Then, water (5 mL) was added and the organic solvents were evaporated. The residue was extracted with dichloromethane, washed with water and brine, and dried over anhydrous sodium sulfate to give 89.8 mg (0.60 mmole, 94% in two steps) as off white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 3H), 3.13(s, 3H); ^{13}C (100MHz, $CDCl_3$): δ 78.7, 81.6, 122.9, 135.6; IR (KBr): 3289, 3062, 2108, 1787, 1580, 884,678,612 (cm^{-1}); M.P: 86 ^{o}C

(*E*)-1-(4-(2-(trimethylsilyl)ethynyl)phenyl)-2-phenyldiazene (12)

4-Bromoazobenzene (**5**) (500mg, 1.91mmole) was taken in two neck RBF and $Pd(PPh_3)_2Cl_2$ (20 mole% ,268 mg), CuI (20 mole% , 72.8mg), Triethylamine was added .The reaction mixture was stirred for 15 minute and degassing was done. TMS acetylene (2eq, 3.82 mmol) was added and reaction was stirred for 16 hrs. at 65 ºC. After completion of reaction mixture was subjected to filtration through Celite pad and after that crude product was purified through column chromatography to get 92 % yield. ^{1}H NMR (400 MHz, CDCl3): δ 7.48-7.5 (m, 3H). 7.62-7.66 (m, 2H), 7.87-7.92 (m, 2H), 7.93-7.96 (m, 2H); ^{13}C NMR (100 MHz, CDCl3): δ 0.3, 97.0, 104.6, 122.7, 122.9, 125.8, 129.1, 131.3, 132.9, 151.8, and 152.6 (cm^{-1}); IR (KBr): 3048, 2147, 1940, 1693, 1591, 1491, 1247, 851 (cm^{-1}). M.P: 84 ^{o}C

(*E*)-1-(4-ethynylphenyl)-2-phenyldiazene (10a)

Compound **12** was dissolved in methanol and anhy.K_2CO_3 was added .reaction was monitored till deprotection of silyl group finished .Work up was done using DCM and water to get the desired product (95%).

^{1}H NMR(DMSO): δ 4.48 (s,1H) ,7.5-7.65 (t,3H) ,7.6-7.75 (d,2H) ,7.89-7.93 (d, 4H); ^{13}C NMR(DMSO): δ 123.2, 123.3, 130.0, 133.4, 151.8, and 152.3; IR (KBr): 2957, 2898, 2162, 1580, 1410, 1251, 1160; M.P: 80 ^{o}C

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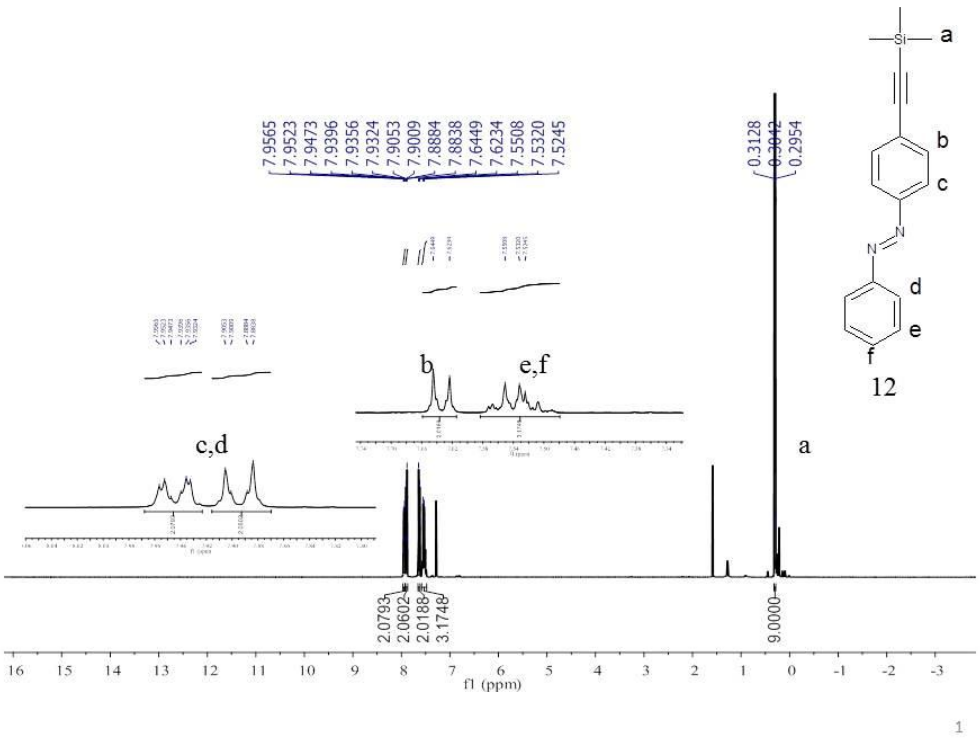
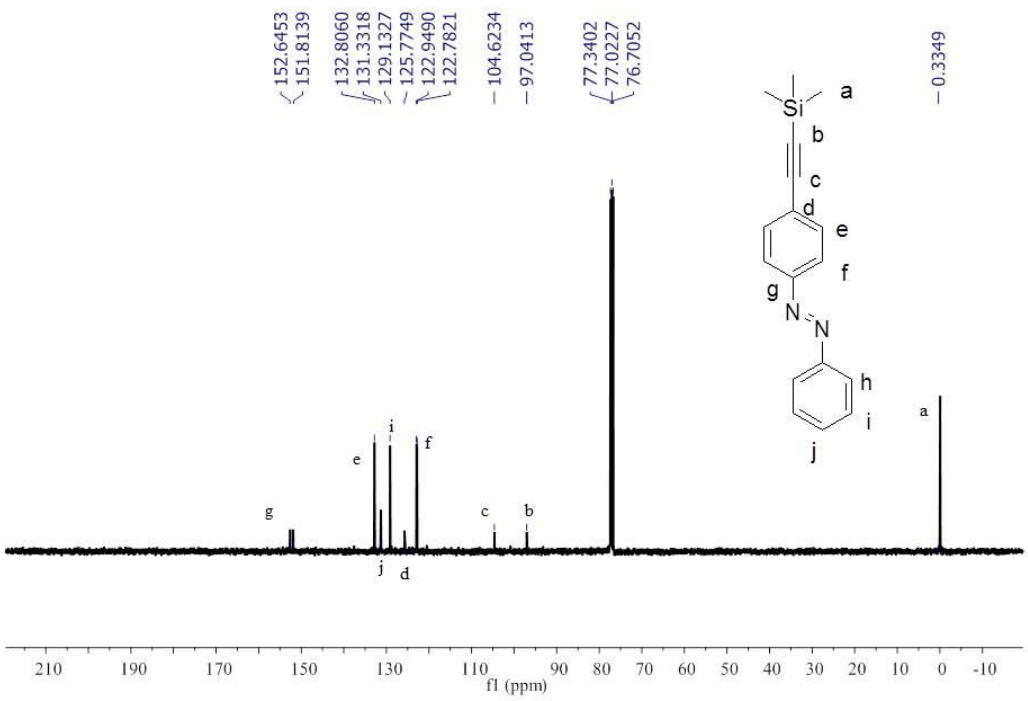
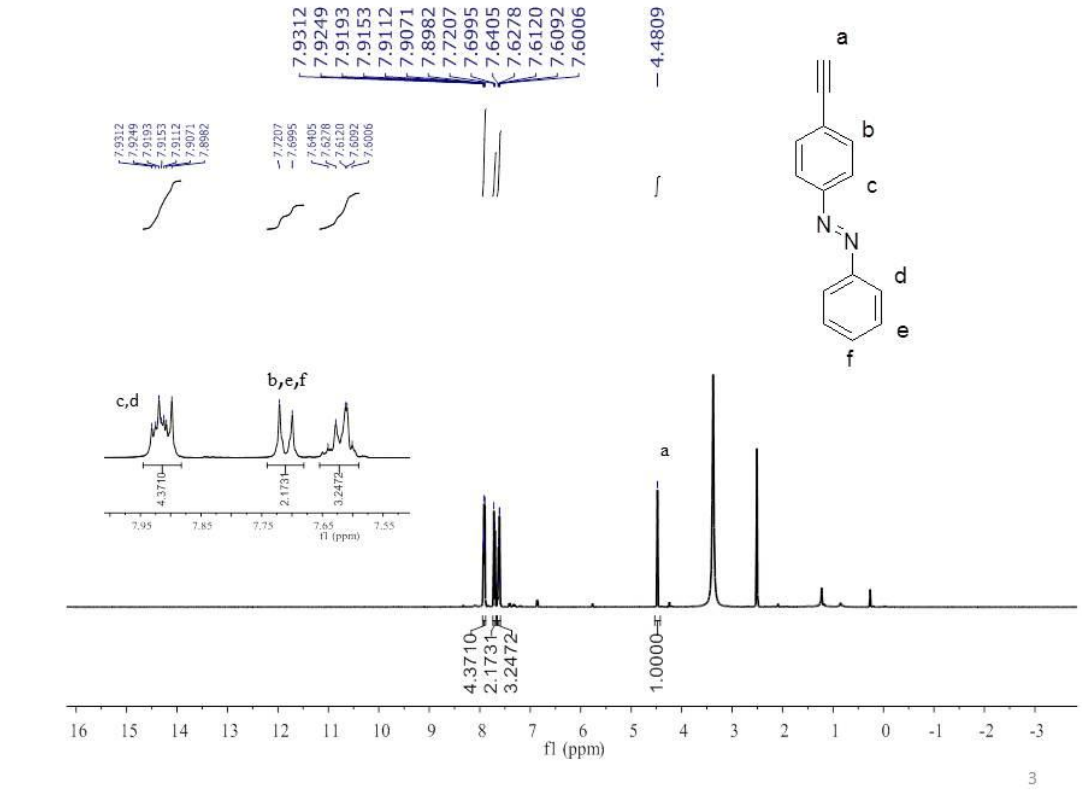
Appendix

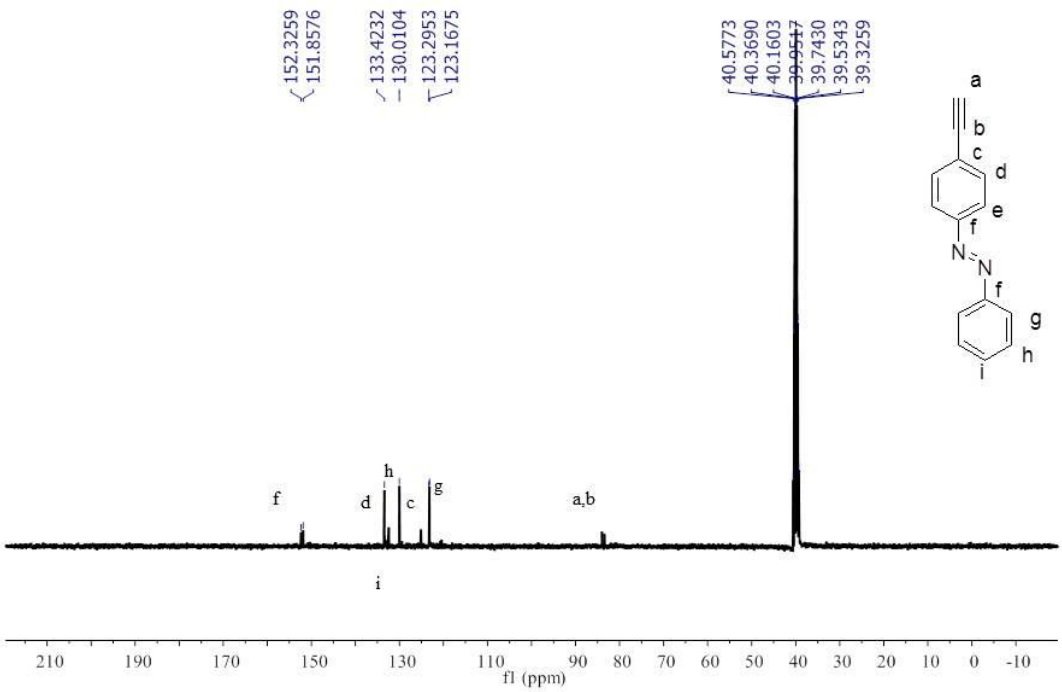
^{1}H & ^{13}C-NMR spectra of Diazene, 1-phenyl-2-[4-[2-(trimethylsilyl)ethynyl]phenyl] (12a)



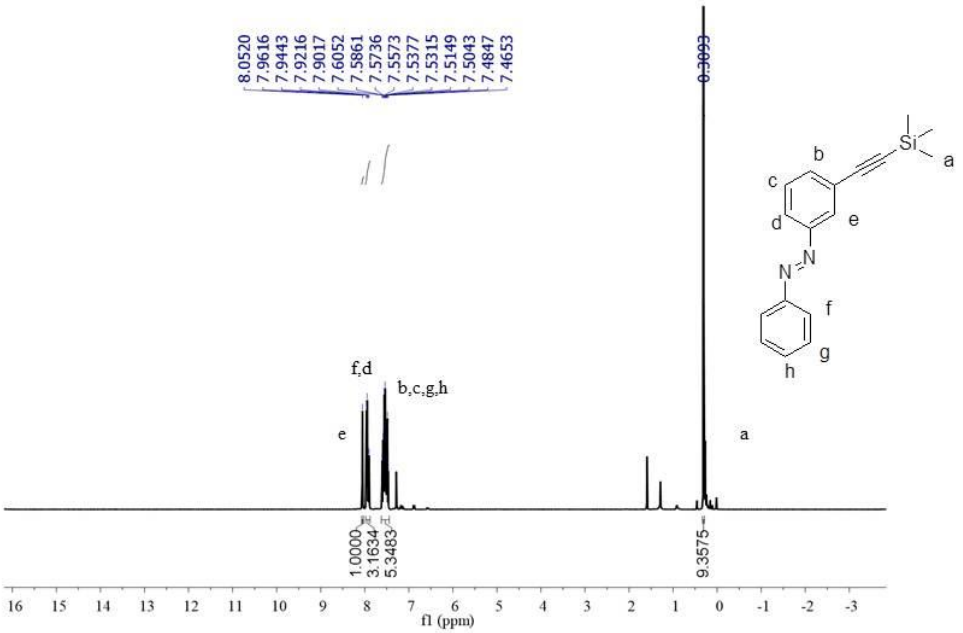


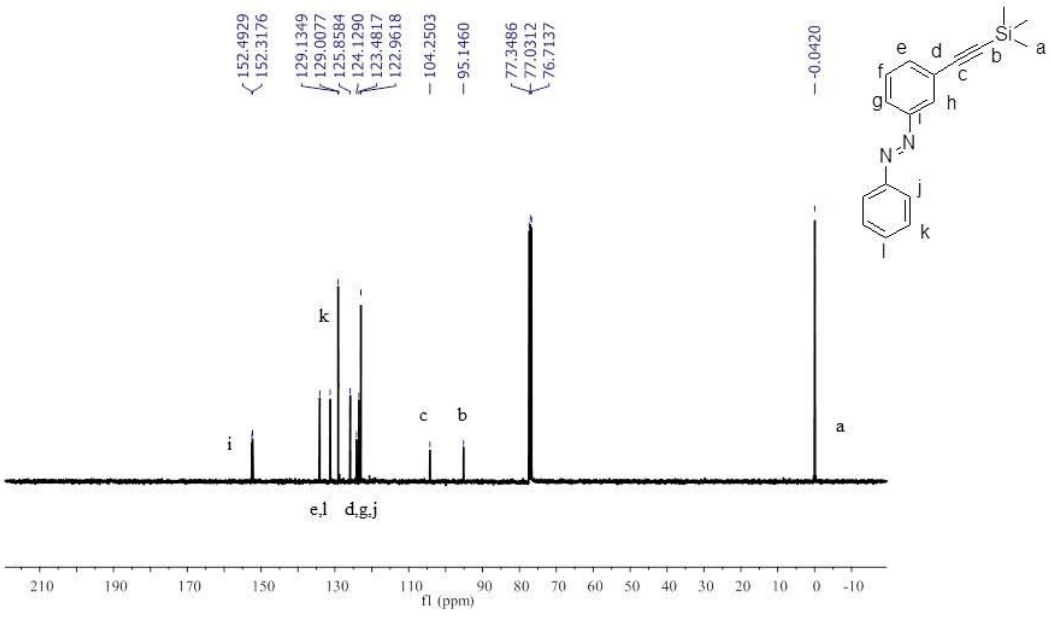
^{1}H & ^{13}C NMR of (E)-1-(4-ethynylphenyl)-2-phenyldiazene (10a)



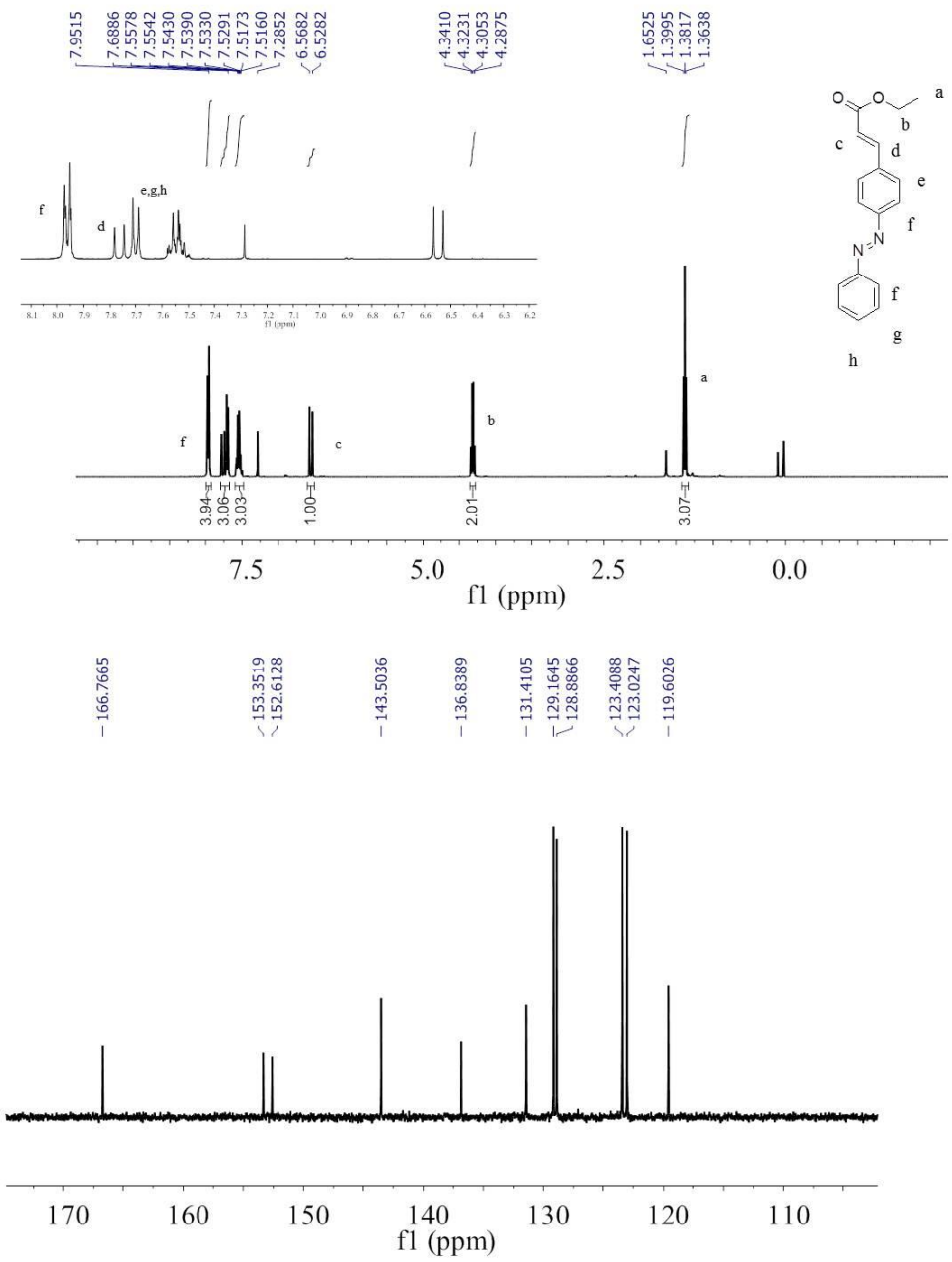


^{1}H &^{13}C NMR Of (E)-1-(3-(2-(trimethylsilyl)ethynyl)phenyl)-2-phenyldiazene(12b)

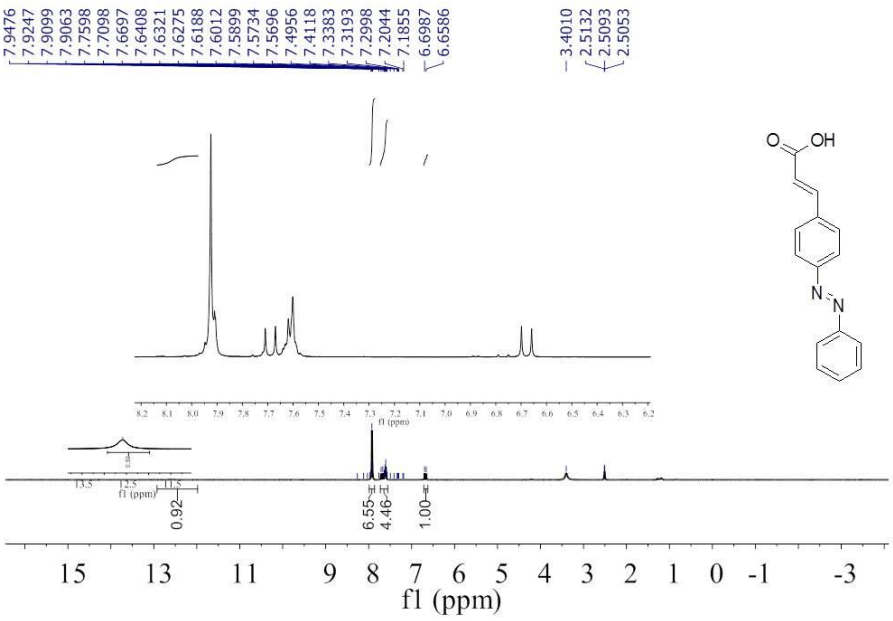


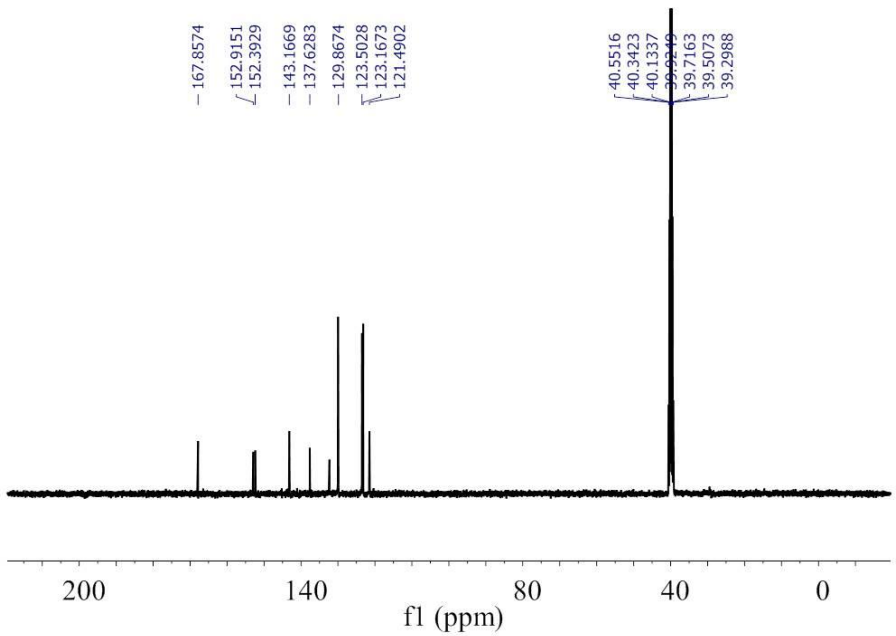


^{1}H & ^{13}C-NMR spectra of 3-[4-(2-phenyldiazenyl)phenyl]-ethyl ester (6)

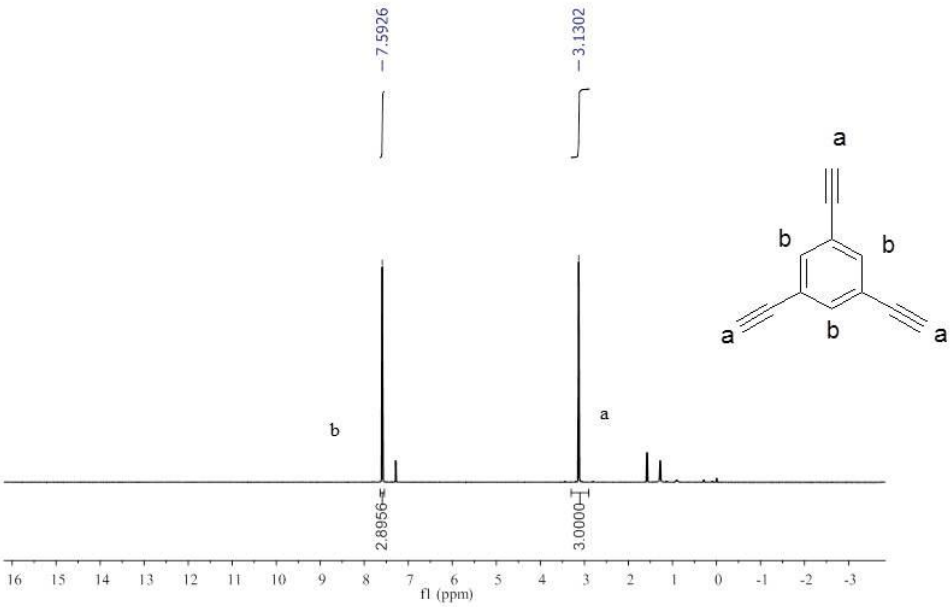


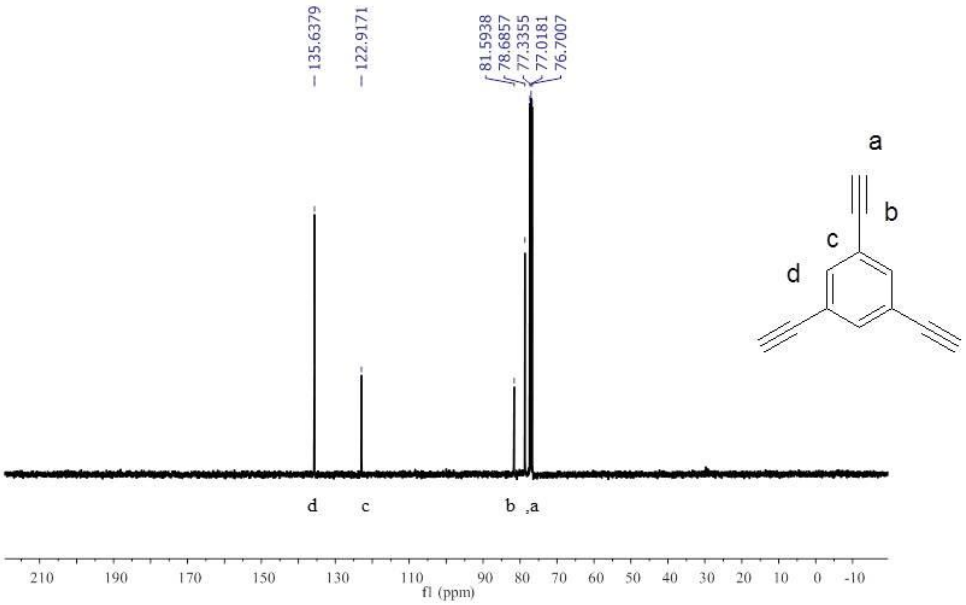
^{1}H & ^{13}C-NMR spectra of 3-[4-[(1*E*)-2-phenyldiazenyl]phenyl]-2-Propenoic acid (1)



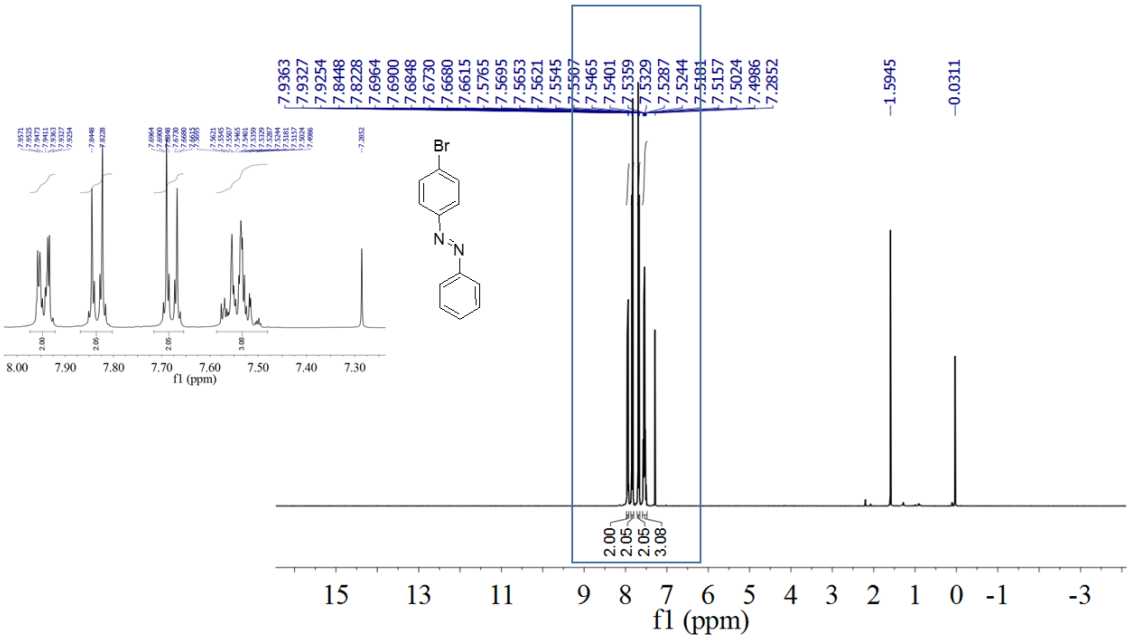


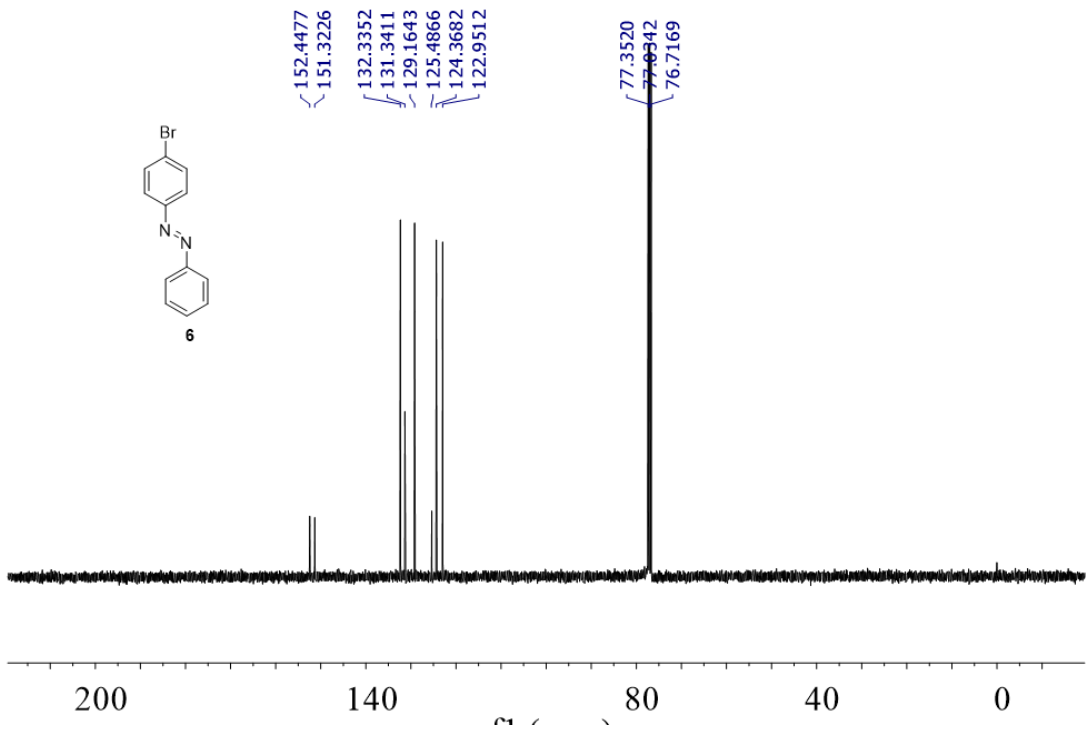
^{1}H & ^{13}C-NMR spectra of 1, 3, 5-triethynylbenzene (9)





^{1}H&^{13}C-NMR spectra of (E)-1-(4-bromophenyl)-2-phenyldiazene (5)





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2011-16 **Integrated BS-MS.** *Indian institute of Science Education and Research. (Mohali)* CPI-7.0 (on scale of 10)

2009-10 **Intermediate.** *S.D.Sen.Sec.School, Narwana, Haryana* (Haryana Board) Aggregate- 85.20%

2007-08 **Xth Board**. *S.D.Sen.Sec.School, Narwana, Haryana* (Haryana Board) Aggregate- 88.00%

Master Thesis

Title *Synthetic attempts in connecting multiple azobenzenes through amide and alkyne linkers*

Supervisor Dr.Sugumar Venkataramani. Assistant Professor (IISER Mohali).

Area of Interests

- Physical Organic Chemistry
- Synthetic Organic Chemistry

- Basic inorganic Chemistry

Experience

- Research experience:

Hand on experience with characterization techniques like IR, NMR spectroscopy, Mass spectrometry and UV-VIS spectroscopy , Separation techniques like column chromatography, acid base extraction and thin layer chromatography,

- Teaching Experience :

  Aug-Nov, 2015: Teaching Assistant for the lab course CHM211 "Chemistry Lab III". Instrumentation techniques like UV-VIS, FTIR, ATR, Fluorescence and NMR were taught.

Recognition

2011 INSPIRE fellowship for a period of five years.
2010 Awarded with Dr. Bheem Rao Ambedkar chatrvarti Yojna by Govt. of Haryana.
2008 Awarded with Dr. Bheem Rao Ambedkar chatrvarti Yojna by Govt. of Haryana.

Personal skills

- Group leading capability
- Honesty and integrity

Computer Skills

- MestReNova, ChemDraw used in organic chemistry
- Basic Knowledge of operating system Windows 7/8 , Linux

Language

English Fluent
Hindi Native