New Directions in the Chemistry of Azo-compounds

A Thesis submitted to The University Manchester for the degree of Master of Philosophy in the Faculty of Engineering and Physical Sciences

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Omer Khayyam Rasheed

School of Chemistry

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6 SYNTHESIS OF CLAISEN REARRANGED COMPOUNDS

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ABSTRACT

The synthesis and chemical reactivity of azo-dyes is reviewed and their application to the field of molecular sensors is outlined. The main body of the thesis is concerned with the development of synthetic strategies for the construction of sensing agents which are of potential value in the diagnosis of metal-dependent neurodegenerative diseases. The functionalisation of readily available azo-dyes is described including the use of Heck, Stille reactions and the application of a novel benzannulation reaction to the synthesis of benzo-fused azo-dyes. During these investigations an unprecedented redox-cyclisation reaction of naphthol-derived azo dyes was discovered, leading to the synthesis of the previously unknown 2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine ring system. These novel heterocycles were fully characterised by spectroscopic and X-ray diffraction techniques. The development of an Ullmann-type displacement reaction of halo substituted azo-dyes is also reported. This process will enable the conjugation of azo-dyes to macrocyclic systems and provides a modular approach to the synthesis of macrocycles capable of sensing heavy metals in biological systems.

DECLARATION

No portion of the work referred to in this thesis has been submitted in the support of an application for another degree or qualification of this or any other university or other institute of learning.

COPYRIGHT STATEMENT

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Abbreviations

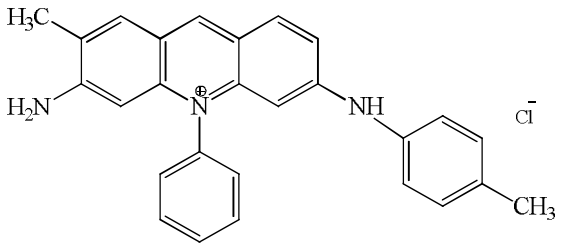
ATRC	Atom Transfer Radical Cyclisation
ATRP	Atom Transfer Radical Polymerization
ATR	Atom Transfer Reaction
ATRA	Atom Transfer Radical Addition
AIBN	2-2'-azobis(2-propionitrile)
Ar	Aromatic
Bu	Butyl
t-Bu	*tert*-Butyl
^{o}C	Degree Celsius
^{13}C NMR	Carbon nuclear magnetic resonance
D	debye
DBU	1,8-Diazobicylco[5.4.0]undec-7-ene
Diglyme	Bis(2-methoxyethyl) ether
DMF	*N*,*N*'-Dimethylformamide
d	Doublet
D	Deuterium
DMSO	Dimethylsulfoxide
EI	Electron impact ionisation
ES+/-	Electrospray (positive *or* negative mode)
Et	Ethyl
equiv.	Equivalents
g	Grams

^{1}H NMR	Proton nuclear magnetic resonance
Hz	Hertz
IR	Infrared
m	Multiplet
M	Molarity
M+	Molecular ion
mg	Milligrams
mol	Mole(s)
m/z	mass-to-charge ratio
Nu	Nucleophile
NLO	Nonlinear-optic
o-	*ortho*-
ppm	Parts per million
s	Singlet
t	Triplet
TBTH	tributyltinhydride
μ	Dipole moment
σ	sigma
μW	microwave
δ	Chemical shift

PART 1: INTRODUCTION AND RESULTS AND DISCUSSIONS

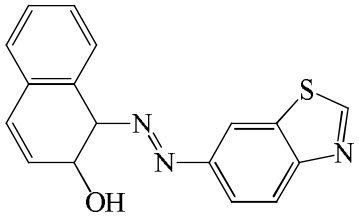
CHAPTER 1: INTRODUCTION

In 1856 W. H. Perkin discovered Mauveine[1a] **1**, the first synthetic organic dye. Since then literally thousands of synthetic dyes have been prepared; for example azobenzothiazolyl dyes[1b] and acridine dyes[1c]. In 1987 Zollinger reported that over 7 x 10^5 tonnes of synthetic dyes are produced annually.[2] These days, dyes are widely used in environmental[3a], biological[3b]and analytical sciences.[3c] Most dyes are classified according to their chemical structure or application method, however, chemical classification is more important as it depends upon the functional groups present in a molecule.[4a]



1

Figure 1.1: Structural formula of Mauveine A.



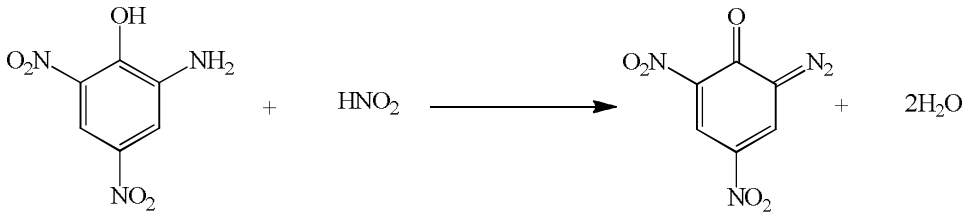
2

Figure 1.2: 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole.

To date the largest single group of dyes which have been developed are the azo dyes, all of which incorporate the -N=N- functional group attached directly to aromatic rings.[4b,21](figure 1.2).

1.1 Diazo compounds:

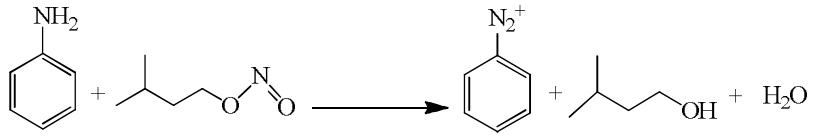
The first preparation of aromatic diazo compounds was reported by Peter Griess in 1858.[5] In this work Griess reported that diazotisation of *ortho*-aminophenol **3** with nitrous acid (which itself was generated *in situ* by the reduction of nitric acid with arsenous acid) afforded the diazo-compound **4**. After considerable investigation the correct structure of **4** was finally deduced in which the $-NH_2$ group had been replaced by $-N_2$.[5a,6]



3 **4**

Scheme 1: Preparation of diazonitrophenol 4 according to Griess.[6]

Griess's original method for diazotisation was modified by Knoevenagel who found that nitrite esters were equally effective in this transformation[7,8] as illustrated in the preparation of **7** from **5** in acidic media.



5 **6** **7**

Scheme 1.1: Preparation of diazonium compound using Knoevenagel's method.

1.2 Methods for preparation of Diazo compounds:

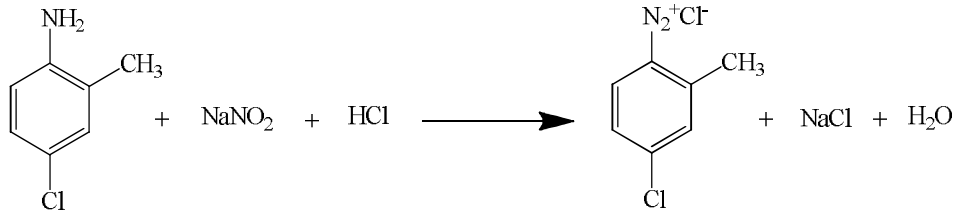
Subsequent to these early investigations a number of modified procedures have been developed for syntheses of diazo-compounds, as outlined below.

1.2.1 Direct method:[9a]

Metallic nitrite is added in the solution of strongly basic amines in aqueous mineral acids.[9a]

$$ArNH_2 + NaNO_2 + 2HX \longrightarrow ArN_2X + NaX + 2H_2O$$

The direct method is explained when 4-chloro toluidine **8** treated with nitric acid in acid at 0 °C.[9a]

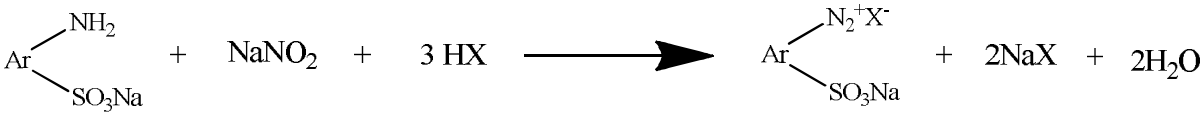


8 **9**

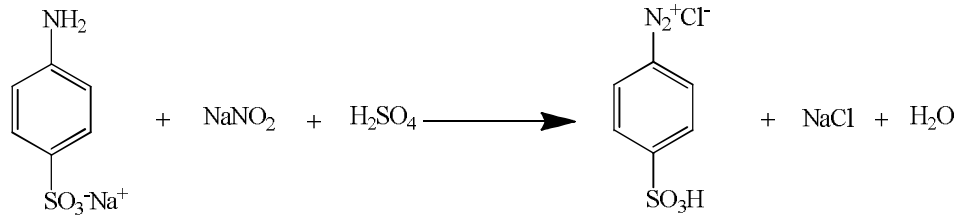
Scheme 1.2: Diazotisation of 4:-Chloro-o-toluidine (8)**.**

1.2.2 Inverted method:[9b]

Alkaline solutions of metallic nitrite and salt of sulphonated or carboxylated aryl amines when treated with excess of cold mineral acid.[9b]



The solutions of sodium sulphanalate and sodium nitrite in water are added into dilute solution of sulphuric acid with stirring, diazocompound was precipitated out.



10 **11**

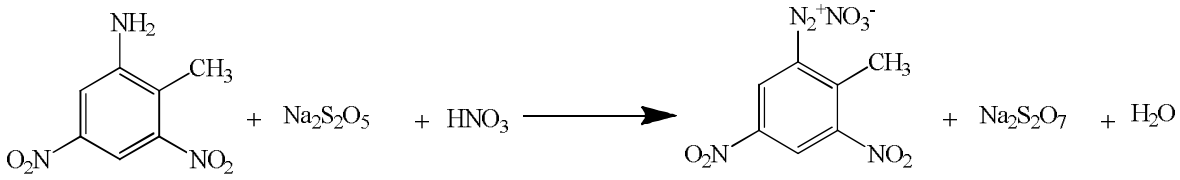
Scheme 1.3*:* Diazotisation of sulphanilic acid.

1.2.3 Witt method:[10]

Metabisulphite is added in the solution of aryl amine in nitric acid.[9c]

$$2ArNH_2 + Na_2S_2O_5 + 4HNO_3 \longrightarrow 2ArN_2^+NO_3^- + Na_2S_2O_7 + 4H_2O$$

The dinitrotoluidine **12** was treated with sodium metabisulphite and then nitric acid was added in the mixture at 0 ˚C to obtain the diazonium compound in quantitative yield (Scheme 1.4).

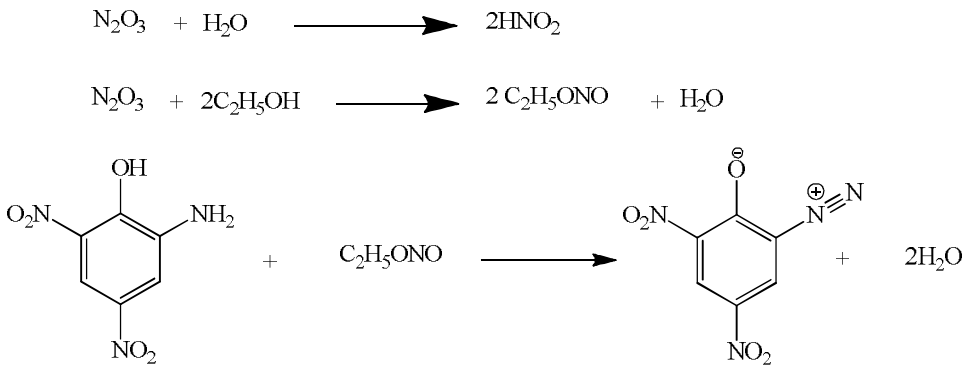


12 **13**

Scheme 1.4: Diazotisation of 3,5-dinitro-o- toluidine.

1.2.4 Griess method:[6]

Gaseous Dinitrogen trioxide is passed through the solution containing aryl amine in water or alcohol (Scheme 1 5).[9d]



14 **15**

Scheme 1.5: Diazotisation of picramic acid.

1.2.5 Knoevenagel method:[8]

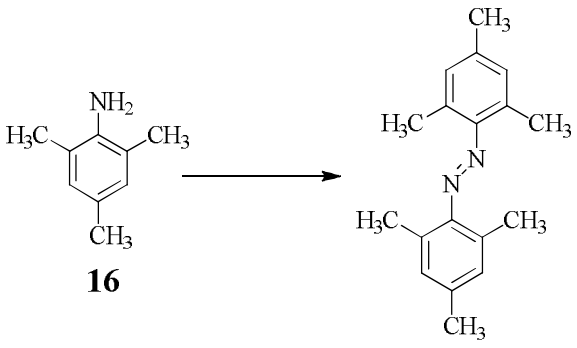
Alkyl nitrite or ester of nitrous acid is added to a solution of salts of aryl amine in water or alcohol or any other inert solvent (Scheme 1.2).[9e]

1.2.6: General Method:

Diazo compounds can be prepared by other methods as well which include

1- Oxidation reactions for synthesis of Diazo compound[9f] (these reactions are carried out in presence of oxidizing agents like mercuric oxide,[11] mercuric acetate,[12] bromine,[13] nitrous acid,[14] nitrogen trioxide).[15]
2- Reduction reaction for synthesis of Diazo compound[9f] [9f] (nitrous acid,[16] hydroxylamine,[17] acetyl chloride[18] are reducing agents used to prepare diazo-compounds).

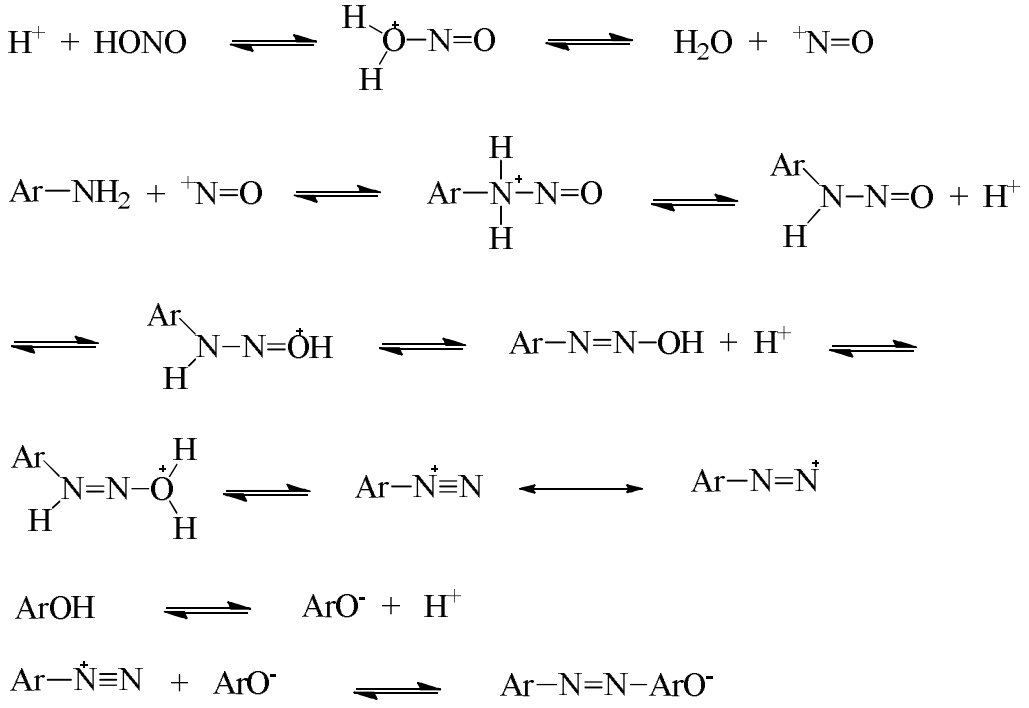
An example of oxidative diazo-compound formation is the work of Naureldin and Bellegrade who prepared azo compounds **17** by oxidation method using $KMnO_4$ and $CuSO_4.5H_2O$ (Scheme 1.6).[19]



Scheme 1.6: Preparation of 1,2-bis(2,4,6-trimethylphenyl)diazene: Reaction conditions $KMnO_4$, $CuSO_4.5H_2O$, DCM, 24 hrs, reflux.

1.3 Azo dye Formation:

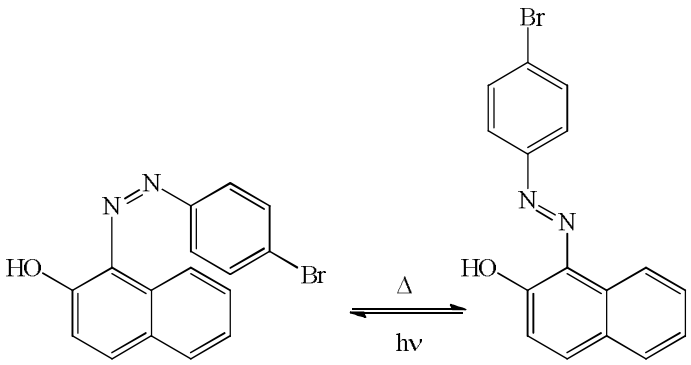
Azo dyes are synthesised in two steps: diazotisation and then coupling.[20] Conventional acid/ base catalysed reactions are effective in the synthesis of azo dyes. Diazotisation is carried out by protonating the compound under acidic conditions at a low temperature and the diazo compound is then coupled with the nucleophile under basic conditions.[21]The mechanism for diazotisation and coupling is shown in Scheme 1.7.[22,23]



Scheme 1.7: Diazotisation and Coupling.

1.4 Isomerisation of diazo compounds:

In 1937 Hartley reported that azobenzenes could exist as either the *cis* **18** or *trans* **19a** geometrical isomers.[9g] Conversion of the thermodynamically more stable *trans*-isomer **19a** into the *cis*-isomer **18** could be achieved by irradiation with light while the unstable *cis*-isomer **18** is isothermally unstable with respect to the *trans*-isomer **19a.**

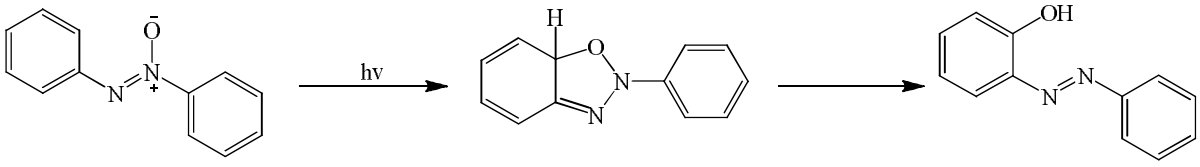


18 **19a**

The stereochemical course of these reactions was deduced from measurements of the dipole moments of the compounds concerned; the unstable *cis*-isomer of azobenzene has a dipole moment of 3.0 D whereas the *trans*-isomer has no dipole moment (μ = 0 D). In aqueous conditions the equilibrium ratio between the *cis*- and *trans*-isomers of azobenzene is 7 to 93.[24,25] The *cis* form of azobenzene derivatives are even more unstable then azobenzene itself.[26,27]

1.5 Photochemistry of diazo compounds:

In 1976 N. J. Bunce *et al* studied the intermolecular reaction and photo arrangement between azoxybenzene and 2-hydroxy azobenzene.[28,5a]

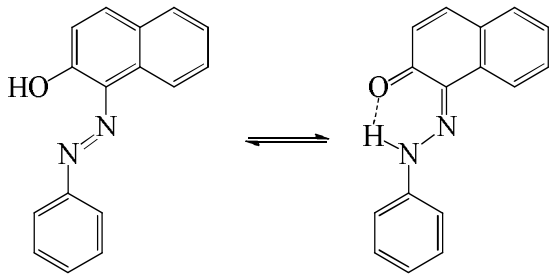


20 **21** **22**

1.6 Alkylation reactions of azo-phenols:

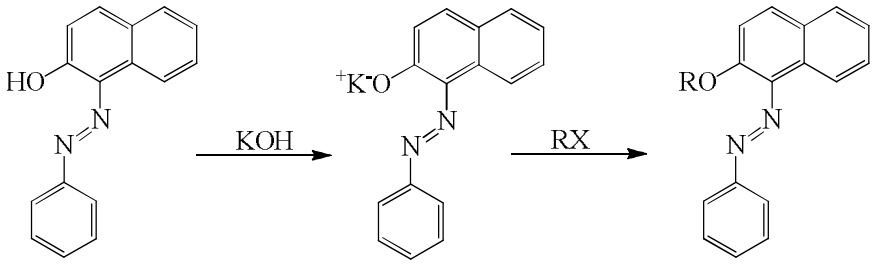
A number of studies have shown that, in aqueous media, many azo-dyes, and especially those derived from β-naphthol, exist as in equilibrium between the tautomeric "azo" forms **23** and "hydrazone" forms **24**. Stabilization of the hydrazone tautomer **24** can be achieved *via*

hydrogen bonding between the N-H group of the hydrazine and the neighbouring carbonyl oxygen.[29] The presence of a strong hydrogen bond is manifested in the appearance of a low field –OH proton in the ^{1}H NMR spectrum (*ca.* 15 ppm in $CDCl_3$).



23 **24**

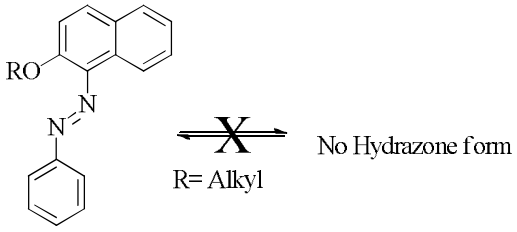
Under suitable conditions these dyes can still be deprotonated affording alkoxides **25** which upon reaction with alkyl halides afford the corresponding ethers **26** (Scheme 1.9).[9h,30]



23 **25** **26**

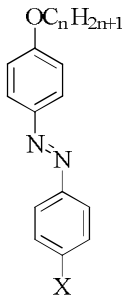
Scheme 1.8: Alkylation reaction of Sudan Dye 1.

By definition the resultant *ortho*-azo ethers **26** can exist only in the azo-form as they cannot tautomerise into the hydrazone form except *via* a 1,5-alkyl shift.[31]



26

There are relatively few reports concerning the synthesis of ethers such as **26**, the reports by Steinstrasser and Pohl,[32] 4′-alkylazobenzenes, Sharma *et al.*[33] describing long alkyl chain azo compounds being representative examples where these investigations are limited to the synthesis of the novel liquid crystalline dyes.[34]



27

In 1928, J. Burns *et al.* studied the substituted products of azobenzene along with other substituted diazo compounds and were the first to prepare (*E*)-1-(3-bromo-methoxyphenyl)-2-phenyldiazene.The substituted azobenzene **27** were obtained by oxidation and complete reduction.[35]The difficulties observed during the alkylation of azo-dyes such as **28** led Yoshioda[36] to adopt the Yamauchi procedure (Figure 1.3) for the methylation of phenolic azo-dyes; this processes utilises *tri*- methyl sulphonium salts as the alkylating agent (Scheme 1.10).

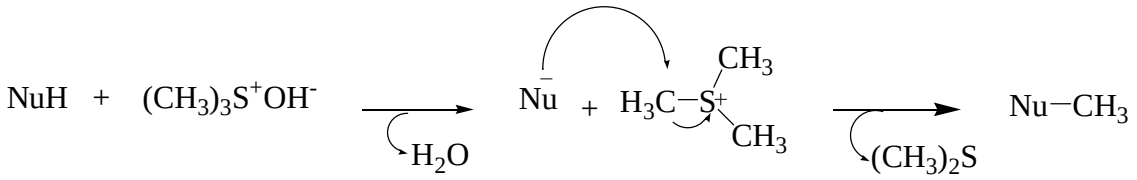
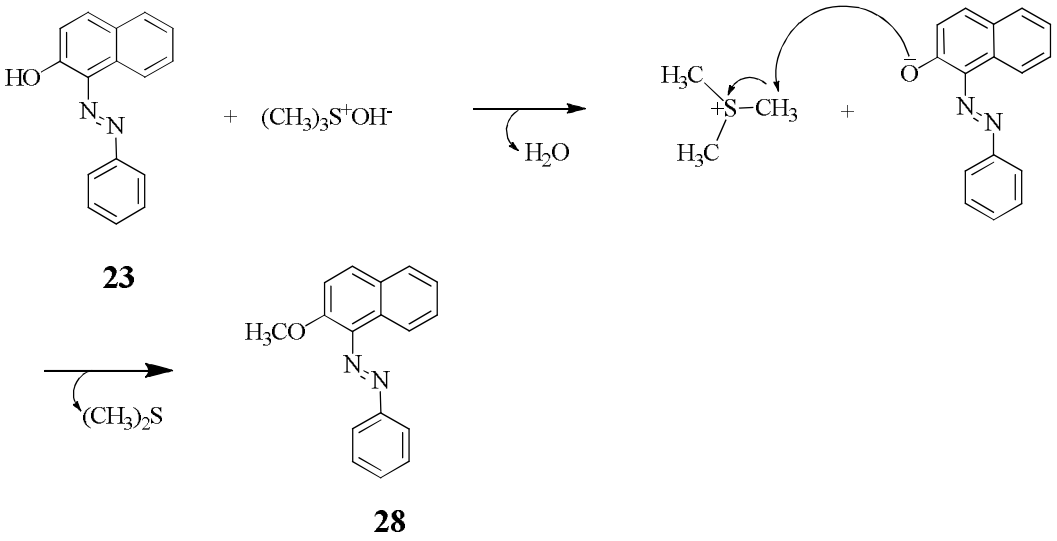
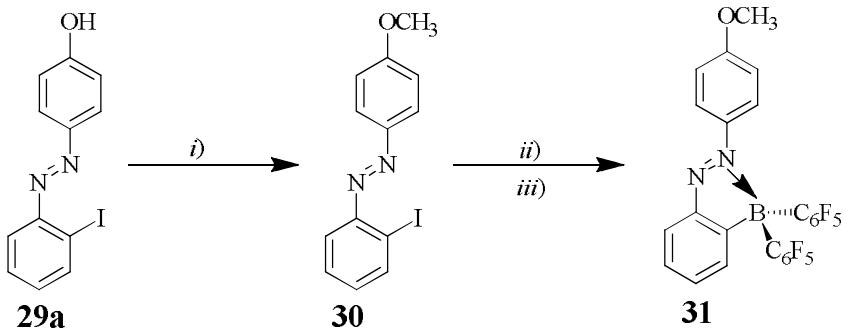


Figure 1.3: The Yamauchi methylation protocol.



Scheme 1.9: Methylation of Sudan dye 1 with trimethyl sulphonium hydroxide.

More Yoshino *et al.* have synthesised fluorescent azobenzenes which incorporate both boron residues and alkoxy groups *ortho-* to the azo moiety.[30]



Scheme 1.10: Synthesis of the intensely fluorescent azobenzene: Reaction conditions: *i*) CH_3I, KOH, DMSO *ii*) *n*-BuLi, -112 ˚C *iii*) $(C_6F_5)_2BF.OEt_2$, Et_2O.

The synthesis and elecrtrochemical behaviour of 2 halogenated derivatives of 4-methoxy(azobenzene) derivatives have also recently been the subject of investigation by Ucar's group where the desired intermediates **29a-29c** were prepared according to Yildirir's route.[37]

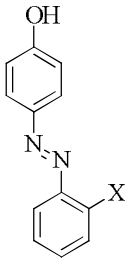
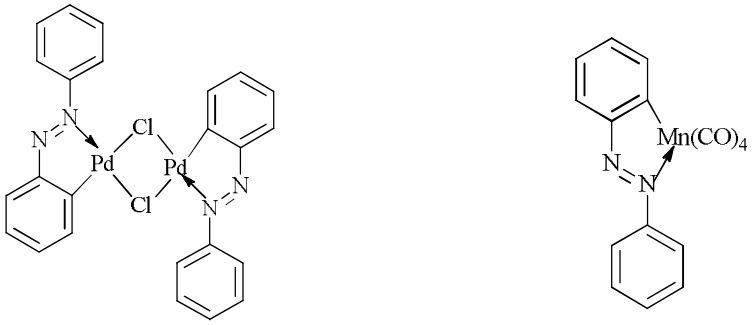


Figure 1.4: X= I (**29a**), Br(**29b**), Cl(**29c**).

1.7 Metal complexes of Azo dyes:

Azo-dyes are also capable as serving as N-donor ligands and there is an extensive body of literature in this area.[38] Azoderivatives of transition metal complexes have attracted much attention in recent years due to their potential application in catalytic processes which may have an industrial dimension.[39] The synthesis of novel metal chelating systems, based upon azo scaffolds, has also been extensively investigated.[40] For example, systems based upon dye metal complexes, which possess *ortho*-metallated aromatics such as **32** and **33,** are relatively common.[41]

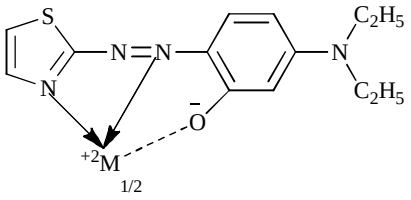


32 **33**

Figure 1.5: Representative cyclometallated azo-complexes

Transition metal chelate complexes such as **34** are widely used in optical recording devices,[42a] toner, ink-jet printing and oil-soluble light fast dyes,[42b] high density memory storage,[42c] and in non-linear optical elements.[43,44] Transition metal complexes which incorporate the azo-moiety have also found application in textile dyeing and the colouring of

polyamide fibres primarily because of the high intensity of colour which is afforded from such systems.[44]



34

Figure 1.6: Representative metal-azo dyes (M = Ni, Co, Cu).

1.7.1 Metal-Halogen Exchange Chemistry:

In 1927, C.S. Marvel reported the exchange of lithium with halogen by using *n*-butyl lithium.[45]

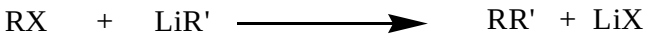
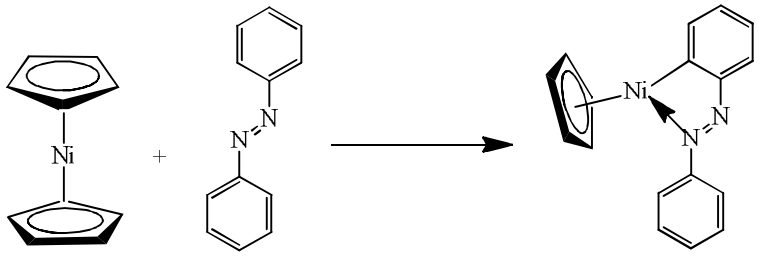


Figure 1.7: R, R' = Alkyl, X = halide.

The first example of the preparation of a cyclometallated azo compound **37** was reported by Kleimann and Debeck in 1963 (Scheme 1.11).[46]

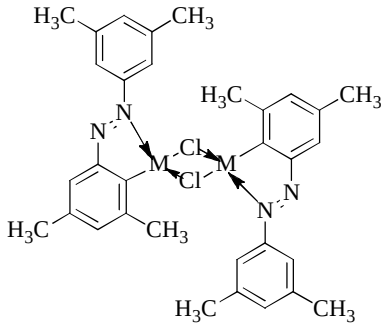


35 **36** **37**

Scheme 1.11: Synthesis of cyclopentadienyl[o-(phenylazo)phenyl]nickel: dicyclopentadienylnickel; azobenzene (excess), 135 °C, 4 hrs.

This initial observation was further exemplified by Cope and Siekman who were able to isolate dimeric palladium and platinum complexes such as **38** from the reaction between azo-

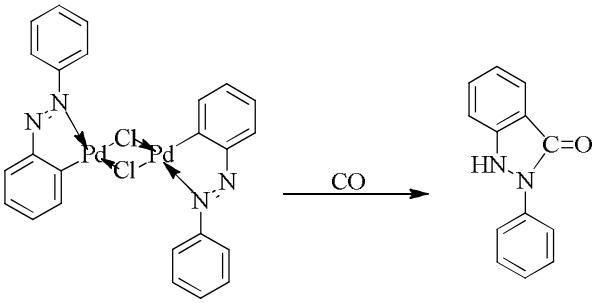
compounds and potassium tetrachloroplatinate(II) or palladium(II) dichloride, reactions which are believed to proceed *via* an electrophilic aromatic substitution mechanism.[47]



38

Figure 1.8: Chelated metal-azo complexes: **M = Pd(II), Pt(II**).

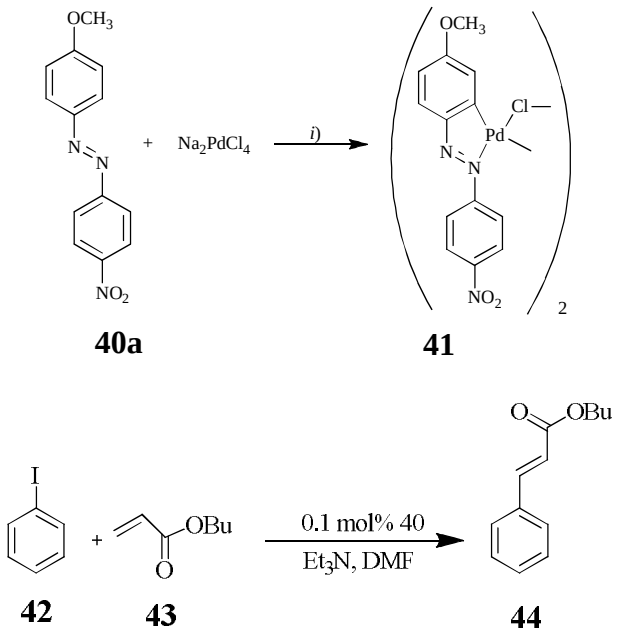
In 1967, H. Takahashi and J. Tsuji attempted to determine the orientation of σ-bond formation between the carbon and metal by carbonylation[48] (Schemes 1.12).



32 **39**

Scheme 1.12: Carbonylation reaction of a metal azo complex: Reaction conditions: EtOH, 100˚C, 5 hrs.

Latterly Bergbreiter *et al.* demonstrated that the azo-moiety could serve as a ligand for palladium(II) in polymer-bound dyes, and that these complexes served as highly efficient catalysts (requiring a 0.1% loading for quantitative conversion) in Heck reactions **40a**.[49](Scheme 1.13)



Scheme 1.13: Catalytic activity of azo-metalic complex: Reaction conditions: *i*) EtOH, 80 ˚C, 3 hrs, 80% yield *ii*) 0.1 mol% **40**, Et_3N, DMF, 1 hour, 110 ˚C, > 99% (yield).

The synthesis of multiply metallated azo-compounds (e.g. **47**) also appears to be a relatively facile reaction as demonstrated by Curic *et al.* Here the metallation was shown to proceed at ambient temperature when using an excess of $PdCl_2(CH_3CN)_2$ **46** in polar solvents such as DMF.[50] These are considered the basic building blocks for organometallic polymers and metallomesogens.

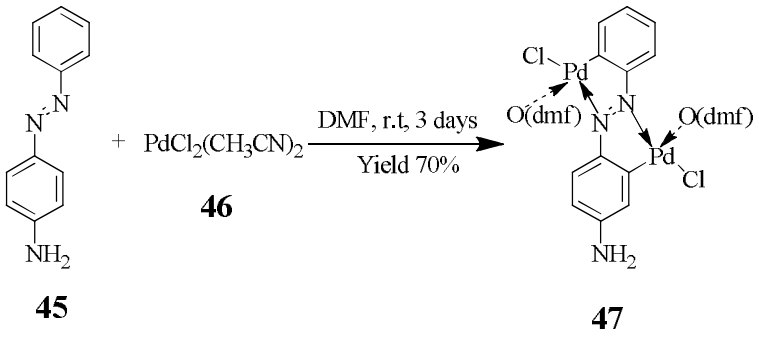
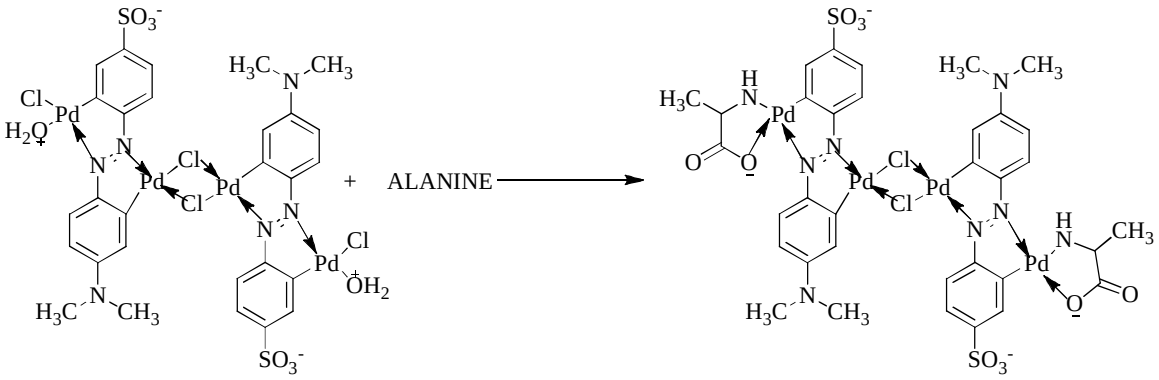


Figure 1.9: Preparation of {PdCl(dmf)}2(μ-aazb) complexes.

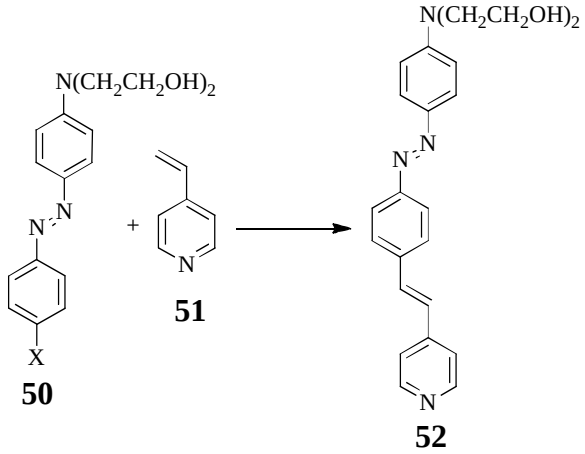
Ortho-palladated (and platinated)azo complexes have applications in other areas besides catalysis – as exemplified for example by the work of Li[51] who has developed sensors for amino acid detection based upon these systems. In this work a palladated complex derived from methyl orange provided the central core of the recognition device.[47]



48 **49**

Scheme 1.14: Reaction of palladium azo complex with amino acid.

The synthesis of conjugated aromatics for use in NLO devices has been the subject of innumerable investigations. In the context of the present discussion a common strategy for the synthesis of such compounds relies upon the introduction conjugated bridging moieties which are attached to a central azo-aromatic core, a strategy which is illustrated by the work of Guang (Scheme 1.13).[52]



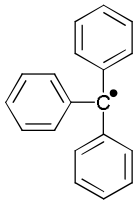
50 **51** **52**

Scheme 1.15: Reaction conditions: $Pd(OAc)_2$, PPh_3, Et_3N, DMF, 140 ˚C, (X= Br, I).[52]

1.8 Atom Transfer Radical Cyclisation (ATRC) Reactions:

The chemistry of organic free radicals can be traced back more then a century to Gomberg's seminal discovery in 1900 where it was discovered that reaction of triphenylchloromethane

with zinc metal afforded the free radical **53** which is reactive enough to dimerize itself (Figure 1.12).[53]



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$$(C_6H_5)_3CCl + Zn \longrightarrow (C_6H_5)_3C^{\bullet}$$

Figure 1.12

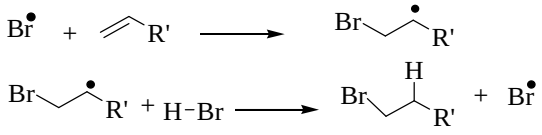
Subsequent to these observations the chemistry of free radicals has been extensively investigated, from both a theoretical and synthetic perspective.[54,55] Radical-based reactions are now routinely used in synthesis, and they are especially useful for the construction of ring systems which contain sensitive polar functionality. Latterly, the development of efficient Atom Transfer Radical Polymerisation (ATRP) reactions in the field of polymer chemistry[56] has re-ignited interest in the area of radical-based Atom Transfer Reactions (ATR) from synthetic chemists' perspective. The concept of Atom transfer radical reactions (ATR) and Atom Transfer Radical Addition (ATRA) originates from Kharasch's work in the 1940's who noted that in certain cases HBr adds to unsymmetrical alkenes in an *anti*–Markovnikoff sense. These reactions are now thought to proceed *via* a radical chain mechanism, Scheme 1.13, requiring the presence of a reagent such as a peroxide in order to initiate the chain reaction.[57]

Initiation

$$R\text{-}O\text{-}O\text{-}R \xrightarrow{\triangle} 2\ R\text{-}O^{\bullet}$$

$$R\text{-}O^{\bullet} + H\text{-}Br \longrightarrow R\text{-}OH + Br^{\bullet}$$

Propagation



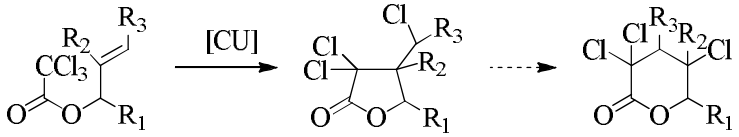
Termination

Radical-radical coupling disproportionation

Scheme 1.16

During these investigations Kharasch also noted, quite by chance, that *poly*-halogenated alkanes such as CCl_4 and $CHCl_3$ also undergo addition reactions to alkenes in presence of radical initiators, again a process which is believed to proceed *via* a free radical chain mechanism.[54]

These reactions remained, by and large, a mechanistic curiosity until Nagashima developed a general cyclisation strategy for the synthesis of γ-lactones and γ-lactams which utilised an atom transfer reaction of unsaturated *tri*-haloesters in the key bond forming steps.[58]



54 **55** **56**

Scheme 1.16: Nagashima's ATRC route to γ-lactones.[57,58]

The Nagashima protocol should be compared to the related, and more common tin hydride – promoted cyclisation process (Scheme 1.15) which results in overall reductive cyclisation of the substrate. It could be argued that the ATRC variant of this reaction is potentially of greater synthetic value given the fact that useful functionality (*i.e.* a carbon-halogen bond) is incorporated into the product after the cyclisation event and that toxic reagents such as TBTH (tributyl tin hydride) are not required in stoichiometric quantities.

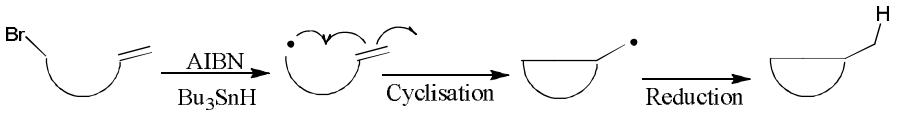
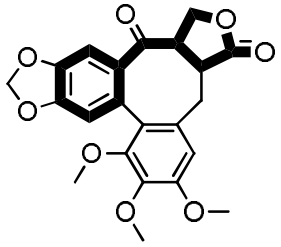


Figure 1.10

It is now known that a variety of transition metal catalysts are effective in promoting ATRC reactions although the copper-based systems are often those of choice because of their ready availability.[66]The potential benefits of ATRC reactions prompted the Quayle group to investigate their synthetic utility in natural product synthesis. This investigation has led to the development of approaches to the synthesis of steganone **(57)** and related lignans including polycyclic arenes such as lactonamycin **(59)**. These studies have also resulted in the development of a new approach to the synthesis of the aromatic core of Gilvocarcin **(60)** and the realisation of "bifurcate ATRC" reactions for the construction of the 2-oxabicyclo [4.3.0]nonane nucleus of eunicellin (**58)**.[59]



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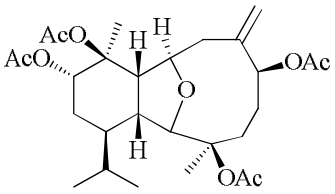

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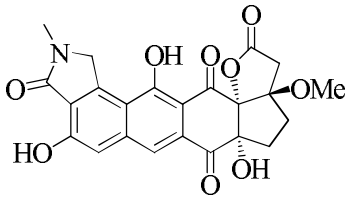

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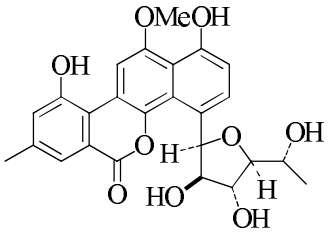

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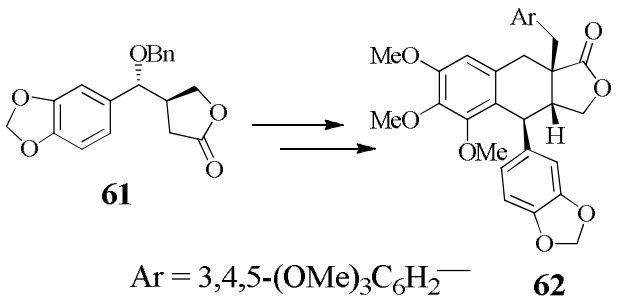


Figure 1.11: Synthetic targets currently under investigation within the Quayle Group.[59,60,73]

During these investigations Quayle *et al*. developed a new ATRC-Benzannulation sequence (the "BHQ Reaction" Figure 1.13) for the synthesis of naphthalene derivatives **(66)** starting from readily available *ortho*-allyl phenols. In this process tricholoro-acetates **(64)** are reacted with Cu(I) complexes (e.g. **63**) and a series of cyclisation and extrusion reactions which ultimately result in the isolation of naphthalene derivatives. Lactones such as **(65)** are believed to be intermediates in this reaction.[61]

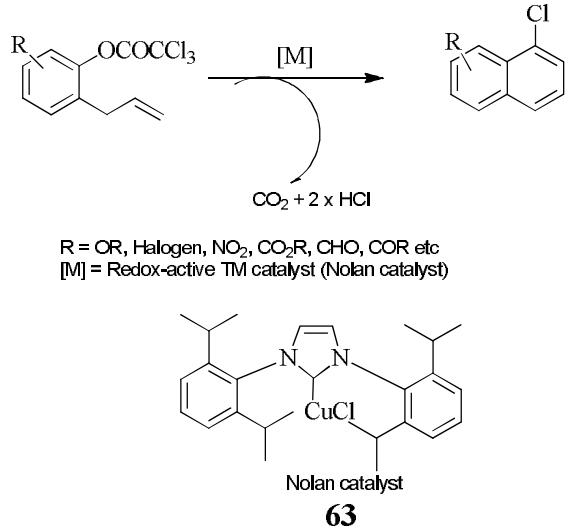


Figure 1.12: The 'BHQ reaction'.

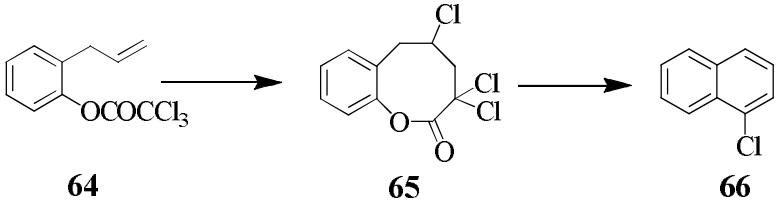


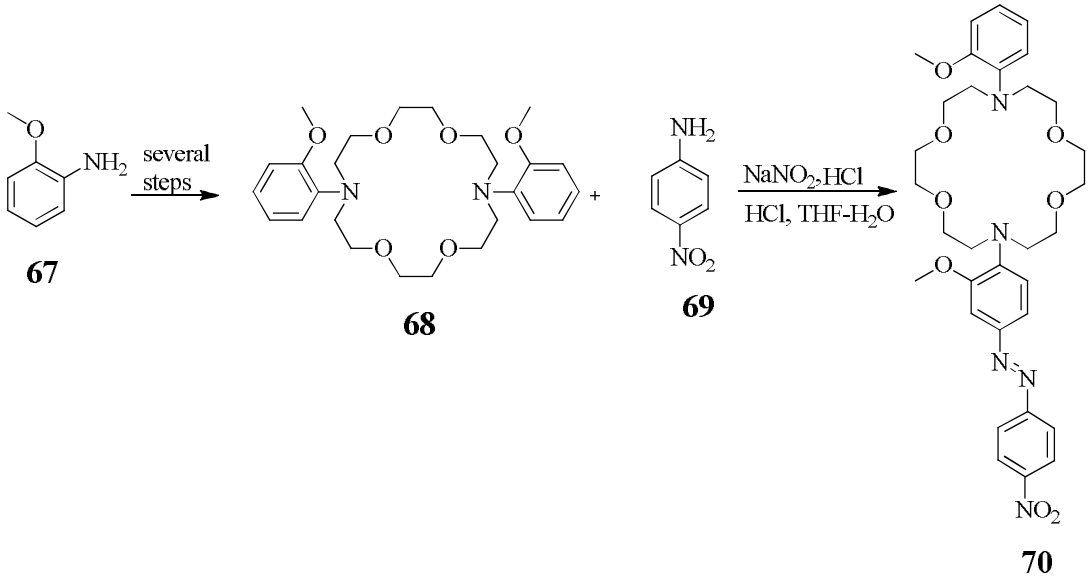
Figure 1.13: ATRC and Benzannulation sequence: Reaction conditions: 5 mol% Nolan catalyst, 200˚C, μW.[73]

CHAPTER II: RESULT AND DISCUSSIONS

2.1 Supramolecular Chemistry:

In the past few decades investigations into the general area of supramolecular chemistry has grown exponentially. A substantial number of these studies have been concerned with determining the mechanisms by which small molecules (*e.g.* drugs) are recognised by much larger systems (*e.g.* enzymes) and how this recognition results in a observable response. The factors which affect formation of self-assembled systems depend upon a subtle interplay of many different interactions including hydrogen bonding, electrostatic and hydrophobic interactions.[62]

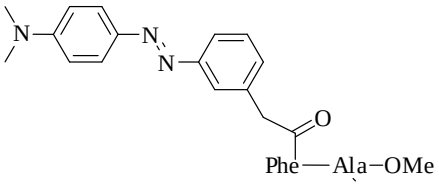
The development of chemosensors which are able to interrogate the processes involved in supramolecular chemistry is an area which has many potential everyday applications. There are now a number of chemosensors which are able to detect specific anions, cations and small organic molecules. The binding characteristics of these synthetic receptors are largely based upon the ability of crown ethers (and related substances) to bind selectively to metal ions or charged species. The synthesis of crown ethers by Pedersen resulted in a flurry of activity in the general area of "recognition chemistry".[63] The ability to link a binding event with an observable response has taxed the ingenuity of synthetic and analytical chemists however relatively general solutions to this technical problem are available. For example Gunnlaugsson and Leonard have shown that azo-dyes linked to crown ethers can be utilised in a colourimetric-based chemesonsor for the detection of Na^+ and K^+ level in blood serum (Scheme 2.1).[64] Binding of the metal ion to the crown ether moiety results in a change in the absorption characteristics of the azo-dye which can then be used to quantify the concentration of metal ion in solution.



Scheme 2.1: Synthesis of azo-crowns for Na^+/K^+ detection.[64]

2.2 Applications:

Azo-dyes have found extensive applications ranging from the textile industry and paper industries, printing processes, colour photography, as components in photo-electronic devices and optical storage technology, additives in petroleum products, polymer additives, to historically as food additives and colourants. Azo-compounds are also used in medicine for the treatment of thrombocytopenia and anemia[65] and have also been shown to be exert anti-fungal, anti-microbial anti-tumour, anti-viral and herbicidal properties.[66] Their photophysical properties have been utilised in the construction of molecular switches for the regulation of enzyme reactions and as markers for peptides (*e.g.* **71**) for a variety of biological applications.

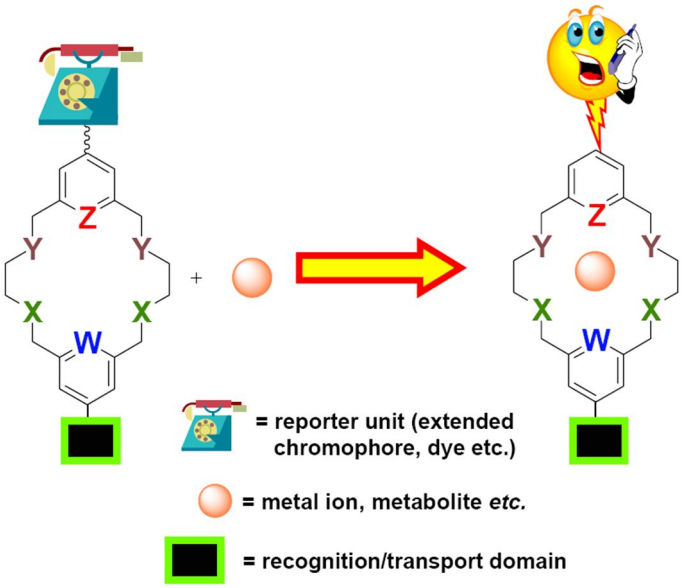


71

Figure 2.1: Peptide marker.

2.3 Outline of Project:

Recently Quayle *et al*. have developed a modular approach to the synthesis of pyridine-containing crown ethers which also possess a range of additional hard/soft ligating centres embedded within the macrocyclic core. These crown ethers were prepared with a view to optimizing their binding capabilities to biologically relevant "soft" metal ions such as Cu^{2+}, Hg^{2+} and Zn^{2+}. These macrocycles were prepared as part of a much broader programme of research concerned with the development of probes which would be able to map the distribution of heavy metals within various tissue types. As an initial model study it was conceived that attachment of a complexant to a scaffold which also possessed a reporting unit (*e.g.* a dye which could respond to a given metal) and a carrier unit (which would aid active transport of dye/complexant to a specific organ or tissue) would generate a sensor which could be used to map the distribution of Cu^{2+} within animal tisues.[67] This programme necessitated the development of robust synthetic techniques for the



Scheme: Modular approach to ligand synthesis

conjugation of the reporting unit (*e.g.* a dye), complexant (*e.g.* a crown ether) and a transport device (*e.g.* a carbohydrate derivative) to a central scaffold, and that this methodology should be general enough to be able to generate families of sensors which could be evaluated/optimized in biological systems (Figure 2.2).

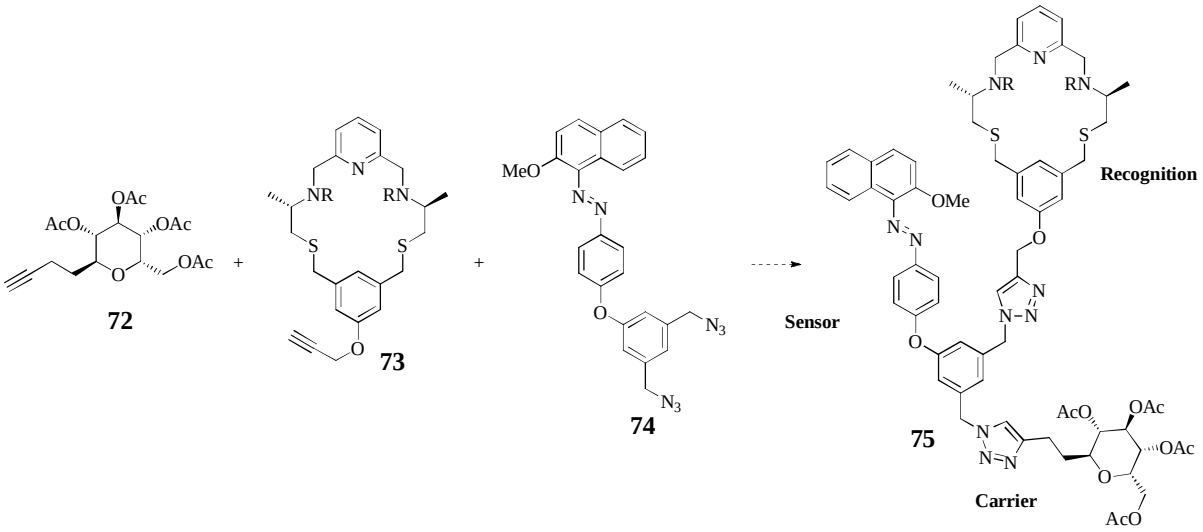


Figure 2.2: Design concept for the assembly of a sensing device for heavy metals.

The initial aim of this project therefore was to provide proof of principle in terms of defining a robust synthetic strategy for the synthesis of functionalised dyes such as **74** which could then be attached to a series of carbohydrates and crown ethers in order to optimise the complexing and transport properties of the sensing system. This necessitated an investigation into the basic chemistry of azo-dyes, which would enable functionalisation of readily available dyes as defined in Figure 2.3, below.

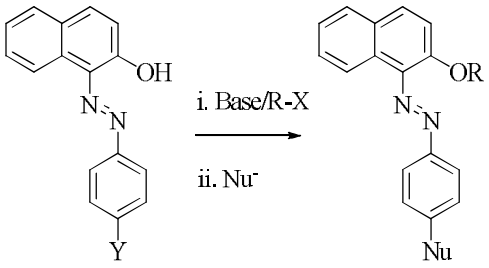
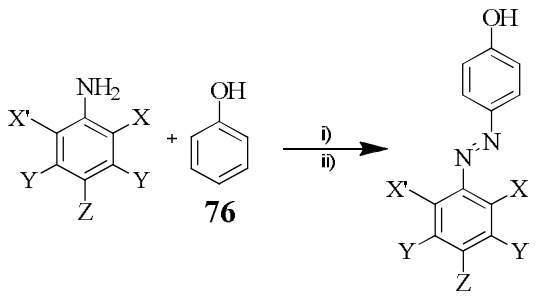


Figure 2.3: Basic reactivity patterns under investigation.

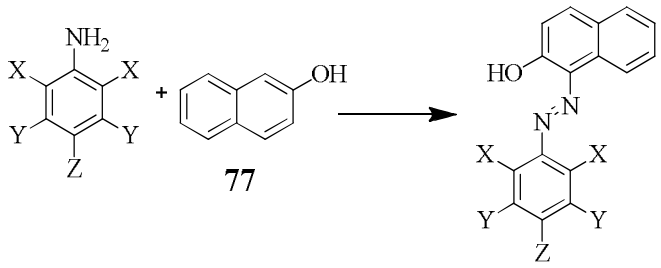
2.4 Preparation of azo-dye substrates:

Despite the fact that the first azo dye was first prepared in 1856, their derivatisation is still largely unexplored, and hence at the outset of the work the alkylation of readily available azo-dyes was to be explored.

The preparation of the desired azo-compounds followed conventional and well established routes,[68] namely from the coupling reaction between a diazonium salt and a phenol under carefully controlled conditions of temperature and pH. Using this standard set of procedures we were able to prepare many azo-dyes form either phenols (Scheme 2.2) or naphthols (Scheme 2.3) in good yield (Table 2.1, 2.2). Although some of these products had been reported in the literature previously, analytical data for many of them was scant and incomplete. All of the products from these coupling reactions were therefore fully characterised by IR, ^{1}H NMR, ^{13}C NMR and microanalysis/high resolution mass spectrometry.



Scheme 2.2: Diazotization and Coupling System A: Reaction conditions and reagents: i) HCl, $NaNO_2$, 0 ˚C ii) NaOH, Na_2CO_3, 0 ˚C.



Scheme 2.3: Diazotization and Coupling System B: Reaction conditions and reagents: i) HCl, $NaNO_2$, 0˚C ii) NaOH, Na_2CO_3, 0 ˚C.

Table 2.1: System A

Comp.	X	X'	Y	Z	Yield %
104a	H	H	H	I	92
104b	H	H	H	Br	87
104c	H	H	H	NO_2	92
104d	H	H	H	OH	91
104e	H	H	H	Cl	87
104f	H	H	H	F	93
105a	I	H	H	H	89
105b	Br	H	H	H	85
107	H	H	$-CH_3$	H	92
108	*iso*-propyl	*iso*-propyl	H	H	96

Table 2.2: System B

Comp.	X	Y	Z	Yield %
91a	I	H	H	89
91b	Br	H	H	97
92a	H	H	I	88
92b	H	H	Br	98
92c	H	H	NO_2	98
92d	H	H	Cl	97
92e	H	H	F	94
97	H	CH_3	H	98

It should be noted that the azo-dyes in the naphthalene series which also possess an *ortho*-hydroxyl group with respect to the N=N linkage can exist in equilibrium with their tautomeric "hydrazone" forms.[29] This results in the formation of an α-ketohydrazone tautomer in which the carbonyl group can form an intramolecular H-bond with the NH of the hydrazone and in many cases this is the predominant tautomer, at least in the solid state. We were able to verify this analysis in the case of **19a** whose X-ray structure clearly shows that it exists in the hydrazone form in the solid state (Figure 2.4). Comparison of the spectral data for **19a** with its methyl ether **28b** clearly indicates that in solution **19a** also exists predominantly as its α-ketohydrazone tautomer. This observation may have implications upon the reactivity of these azo dyes in solution, a point which will be addressed in section 2.5.

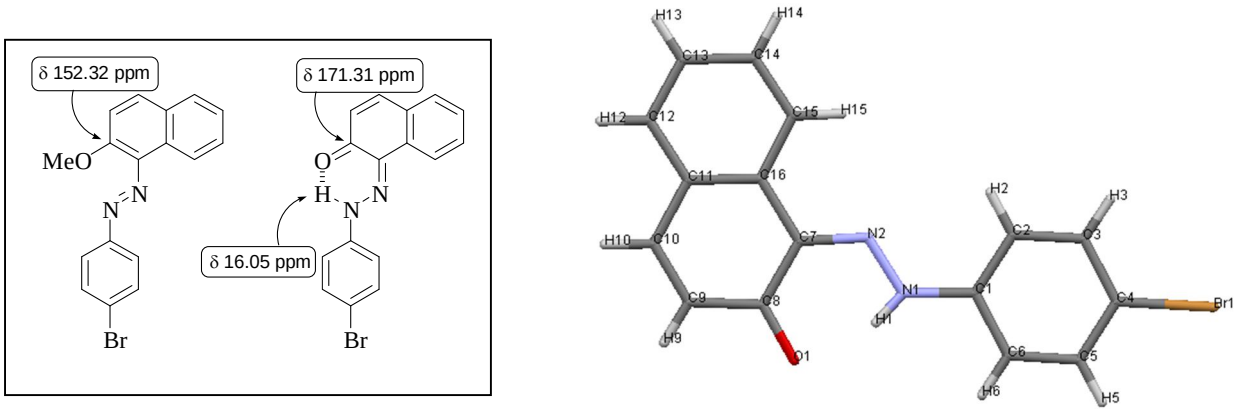
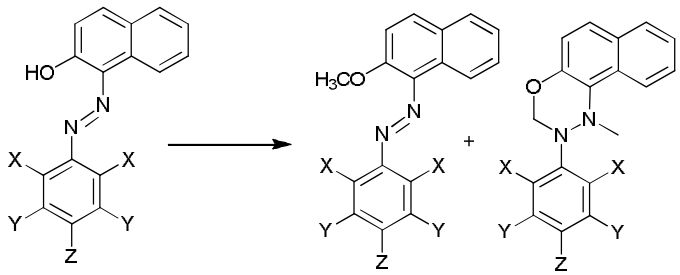


Figure 2.4: X-ray Crystallography Structure 1: 1-[(*E*)-(4-bromophenyl)diazenyl]-2-naphthol **19** and a comparison of NMR spectral data in solution with methyl ether **28b**.

2.5 Methylation of azo-dyes:

Having prepared a variety of dyes the alkylation of their phenolic-OH groups was next attempted. The preparation of related systems has literature precedent, however a number of groups had noted previously, but without explanation, that this may not be a trivial reaction. Initially we elected to alkylate the free "phenols" with methyl iodide in the presence of a base. Unexpectedly we observed that this seemingly simple operation was hampered, in the

naphthol series of compounds, by the intervention of a competing redox-cyclisation reaction which afforded variable quantities of the hitherto unknown 2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazines **(80)**



Scheme 2.4: Methylation of substituted naphthol azo-dyes: Reagents and Reaction conditions: CH_3I, KOH, DMSO, r.t, 5 hrs.

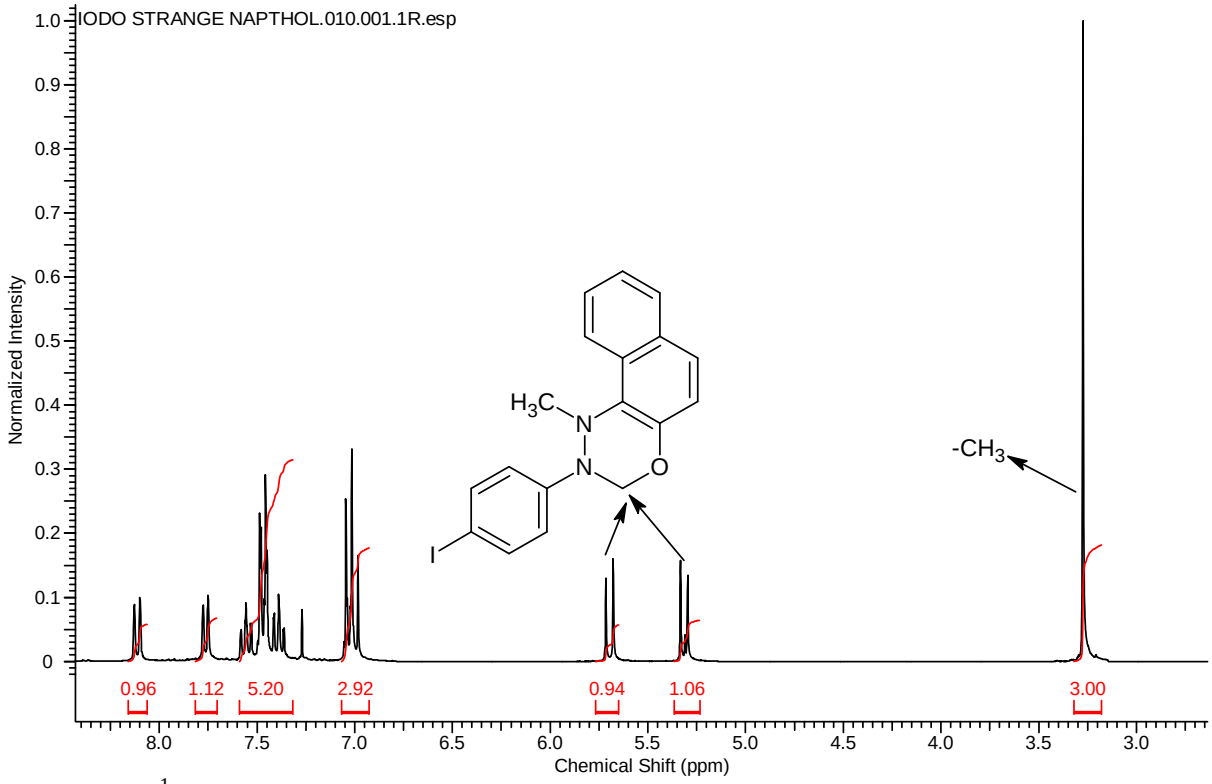


Figure 2.5: ^{1}HNMR spectrum of 2-(4-iodophenyl)-1-methyl-2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine **(80a)**

Initially we chose to investigate the methylation of **92a** using KOH in DMSO as base and iodo methane as alkylating agent. Chromatography of the products from this reaction led to the isolation of the anticipated product, ether **28a** (in 62 % yield) together and a by-product **80a** (in 32 % yield) in which the starting material had clearly suffered major changes. The ^{1}H

NMR of the by-product **80a** indicated that methylation had indeed taken place, but that the chemical shift of the incorporated methyl group (δ 3.27 ppm) was more in keeping with an *N*-methyl rather then an O-methyl residue. Interestingly **80a** also exhibited an AB system at δ 5.32 and δ 5.69 ppm which was associated with the CH_2 of a methylene group (correlates with a methylene group at δ 70.33 ppm in the ^{13}C NMR spectrum). Examination of the aromatic region of the ^{1}H NMR spectrum of **80a** also suggested that the azo-moiety was no longer present, and that reduction of this group had most likely taken place. From the spectroscopic evidence we assigned the structure of this by-product as **80a**. Fortunately we were also able to obtain crystals of **28b, 80a** and **80b** which were of good enough quality to enable single crystal X-ray structures to be determined. These crystal structure determinations (Figure 2.6) clearly confirmed that the structures assigned to **28b** and **80b** on the basis of the spectroscopic data were indeed correct and also proved beyond doubt the structure of the O-methyl ether **80a** (Figure 2.7).

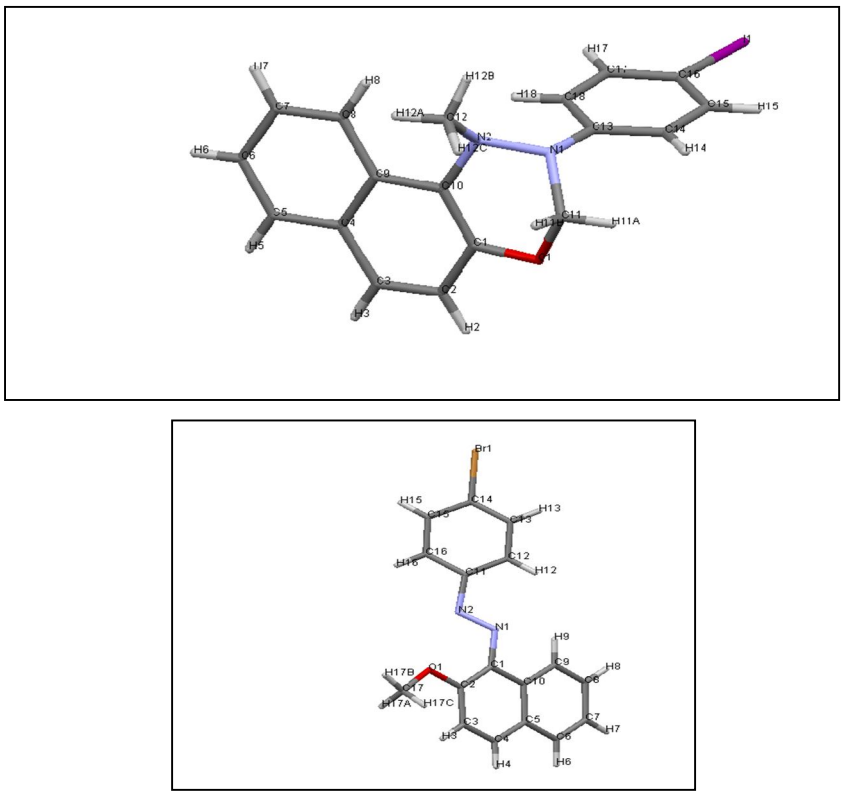


Figure 2.6: X-ray crystallography Structure of (*E*)-1-(4-bromophenyl)-2-(2-methoxy-1-naphthyl) diazene **(80b)** and2-(4-iodophenyl)-1-methyl-2,3-dihydro-1H-naphtho[1, 2-e][1, 3, 4] oxadiazine **(28a)**

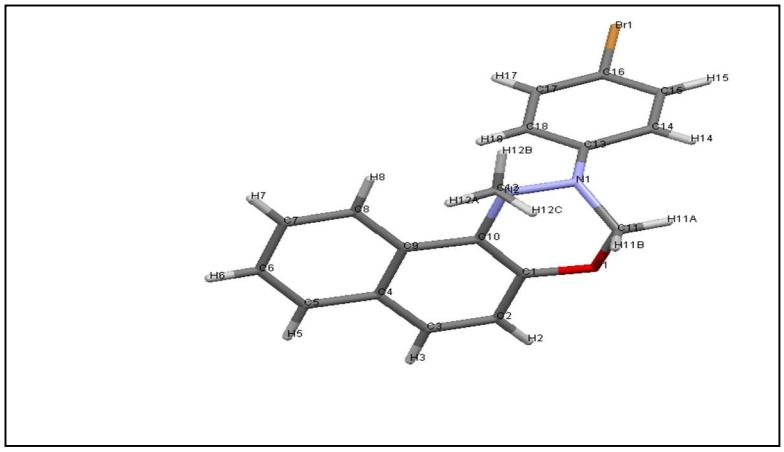


Figure 2.7: X-ray crystal structure of 2-(4-Bromophenyl)-1-methyl-2,3-dihydro-1H-naphtho [1, 2-e][1, 3, 4] oxadiazine **(28b).**

At this juncture an extensive number of blank experiments were conducted (Table 2.3) in order to elucidate the mechanism by which the by-products were formed during the alkylation sequence. In general, reaction of the azo-dye with methyl iodide usually resulted in the isolation of up to four major products (Scheme 2.4, 2.5) the exact ratio being dependent upon the substrate and exact reaction conditions which were employed (Table 2.3).

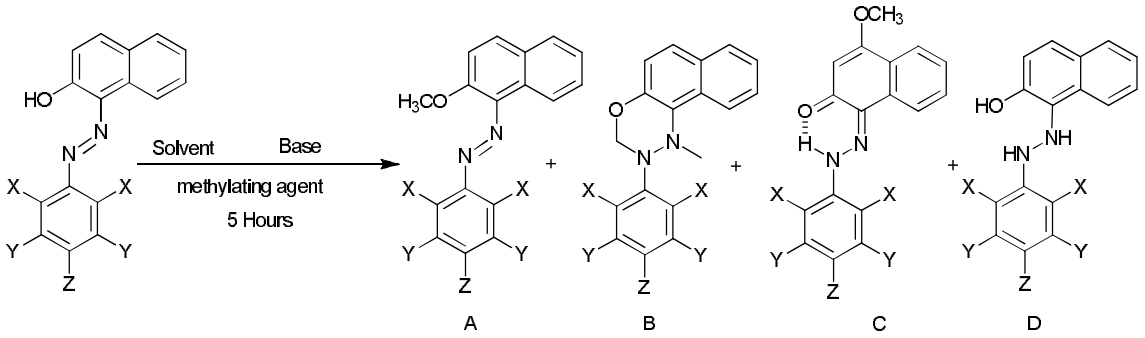


Figure 2.8: Alkylation Reactions of azo dyes (see Table 2.3).

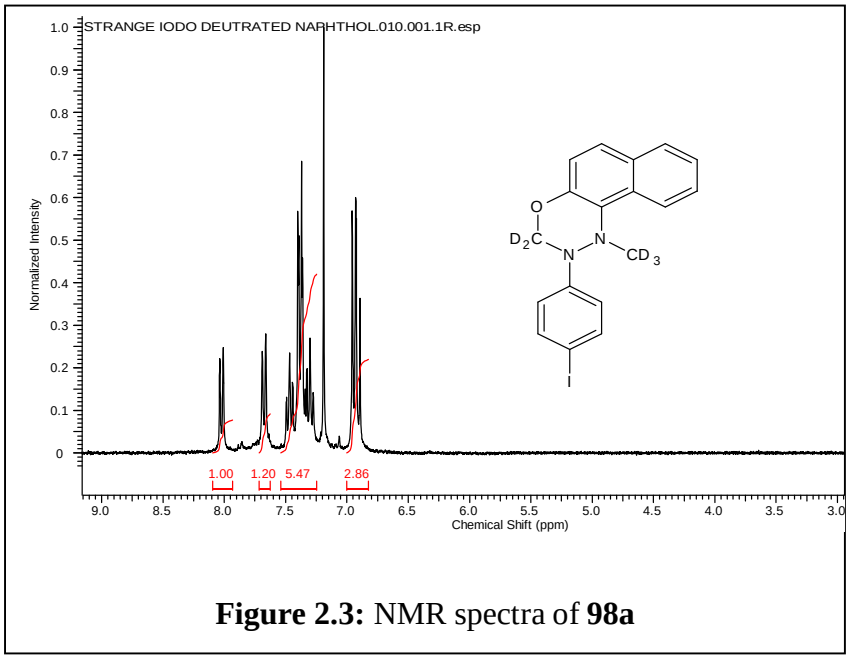
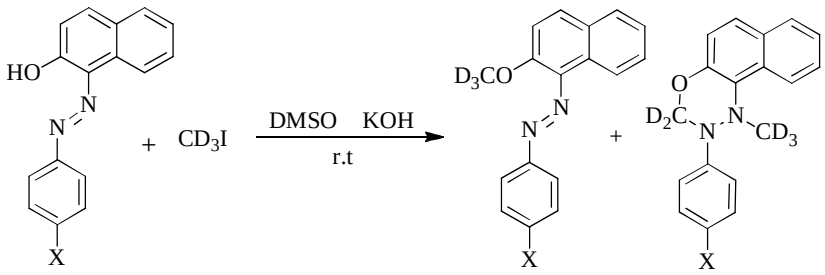


Figure 2.3: NMR spectra of **98a**

For example conducting the alkylation reaction of **92a** with methyl iodide-d3 in DMSO using KOH as base afforded the by-product **98a** whose ^{1}H NMR clearly indicated that the methylene and methyl groups of the rearranged product were both derived from the alkylating agent. Specifically the ^{1}H NMR spectrum of the by-product revealed that the AB system associated with the methylene group at δ 5.32 ppm and δ 5.69 ppm and the methyl group at δ 3.27 were no longer apparent. In keeping with the deuterium incorporation studies (*vide supra*) formaldehyde was also shown not to be the source of the methylene group.



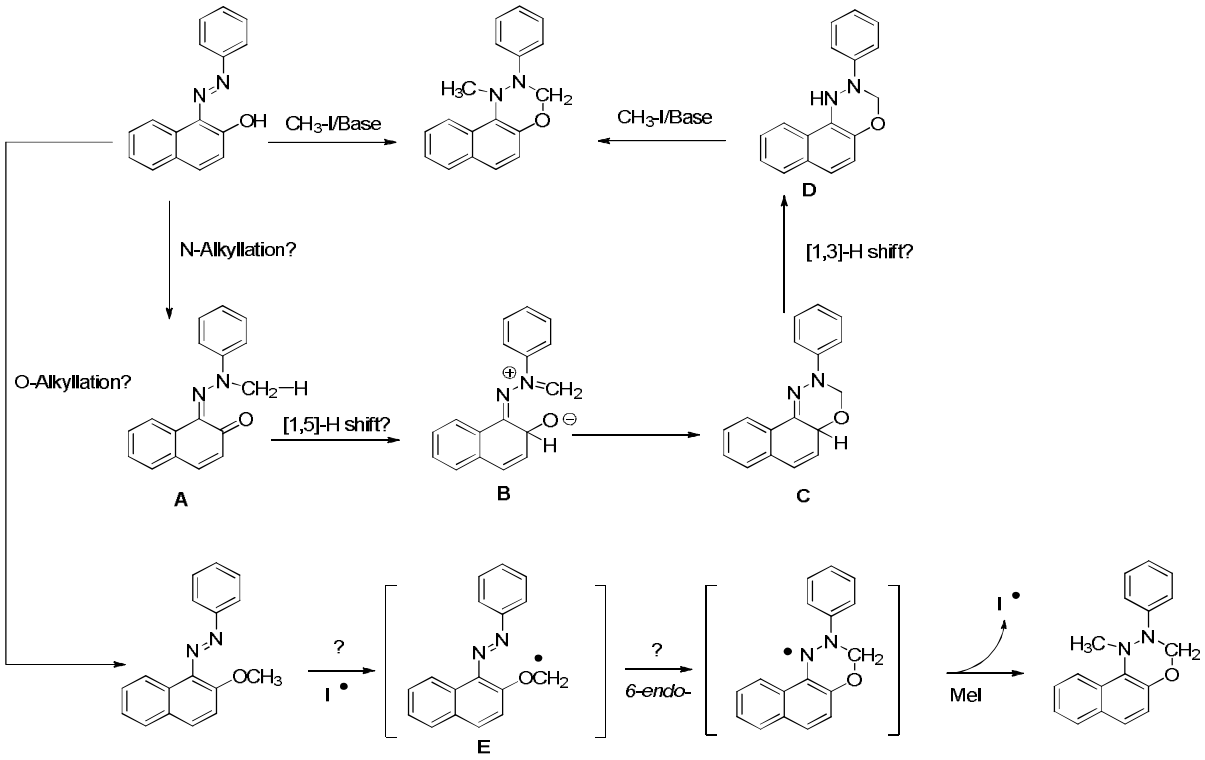
Scheme 2.5: Deuterated Methylation of substituted naphthol azo-dyes: Reagents and Reaction conditions: CD_3I, KOH, DMSO, r.t, 5 hrs.**(see Table 2.3).**

Table 2.3: Methylation reactions carried out of azo-dyes

Reactant	Solvent	Base	Temp	R-I	X	Y	Z	YIELD A %	YIELD B %	YIELD C %	YIELD D %
23	DMSO	KOH	r.t	CH_3I	H	H	H	70	27	-	-
23	Dry DMSO	KOH	r.t	CH_3I	H	H	H	69	27	-	-
23	Degassed DMSO	KOH	r.t	CH_3I	H	H	H	69	27	-	-
91a	DMSO	KOH	r.t	CH_3I	I	H	H	85	-	-	-
92a	DMSO	KOH	r.t	CH_3I	H	H	I	62	32	-	-
92a	Dry DMSO	KOH	r.t	CH_3I	H	H	I	63	31	-	-
92a	Degassed DMSO	KOH	r.t	CH_3I	H	H	I	62	32	-	-
92c	DMSO	KOH	r.t	CH_3I	H	H	NO_2	30	26	38	
92c	Dry DMSO	KOH	r.t	CH_3I	H	H	NO_2	32	27	34	
92c	Degassed DMSO	KOH	r.t	CH_3I	H	H	NO_2	32	26	34	
92b	DMSO	KOH	r.t	CH_3I	H	H	Br	64	33	-	-
92d	DMSO	KOH	r.t	CH_3I	H	CH_3	H	67	32	-	-
92e	DMSO	KOH	r.t	CH_3I	H	H	F	28	69	-	-
92d	DMSO	KOH	r.t	CH_3I	H	H	Cl	69	26	-	-
91b	DMSO	KOH	r.t	CH_3I	Br	H	H	-	-	-	-
92b	DMF	KOH	r.t	CH_3I	H	H	Br	62	31	-	-

92b	Dry DMF	KOH	r.t	CH_3I	H	H	Br	61	32	-	-
92b	Degassed DMF	KOH	r.t	CH_3I	H	H	Br	61	30	-	-
92c	DMF	KOH	r.t	CH_3I	H	H	NO_2	49	27	-	-
92c	Dry DMF	KOH	r.t	CH_3I	H	H	NO_2	50	27	-	-
92c	Degassed DMF	KOH	r.t	CH_3I	H	H	NO_2	50	26	-	-
92c	DMSO	^{t}BuOK	r.t	CH_3I	H	H	NO_2	31	24	-	-
92c	Dry DMSO	NaH	r.t	CH_3I	H	H	NO_2	-	21	-	39
92c	DMSO	KOH	r.t	$(CH_3)_2SO_4$	H	H	NO_2	30	11	-	-
92c	Dry DMSO	KOH	r.t	$(CH_3)_2SO_4$	H	H	NO_2	28	10	-	-
92a	DMSO	KOH	r.t Dark	CH_3I	H	H	I	601	30	-	-
91a	Acetone	K_2CO_3	Reflux	CH_3I	I	H	H	22	-	-	-
92c	Ethanol	KOH	r.t	Formalin	H	H	NO_2	-	-	-	-
92c	DMSO	KOH	r.t	Formalin	H	H	NO_2	-	-	-	-
92a	Dry DMF	NaH	Reflux	CH_3I	H	H	I	-	-	-	-
92a	DMSO	KOH	r.t	CD_3I	H	H	I	62	31	-	-
19a	DMSO	KOH	r.t	CD_3I	H	H	Br	60	30	-	-

In an effort to gain additional insights into the mechanism of this redox-cyclization reaction we have also conducted the alkylation reactions in the probe of an ESR spectrometer. While these experiments are still at an exploratory stage it would appear that there are long-lived radical species formed during the course of these reactions. Whether these species are implicated in the conversion of the azo-dyes into the cyclised products such as **179** has yet to be established, as has a mechanistic rational for the formation of these unusual by-products.

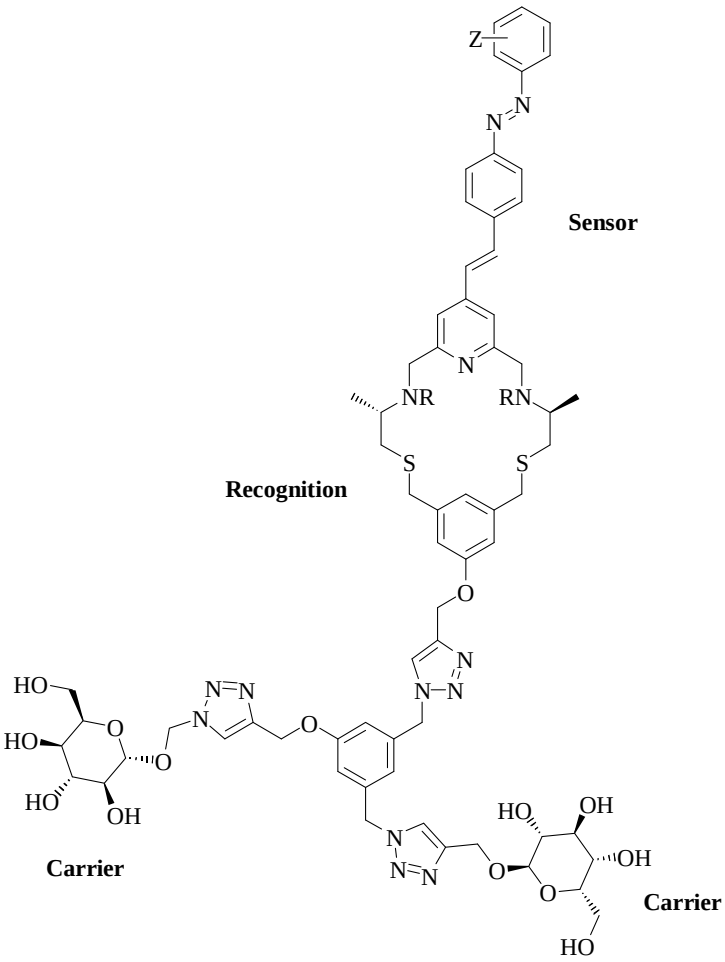


Scheme 2.6: Possible Mechanism for the cyclization of azo-dyes during methylation

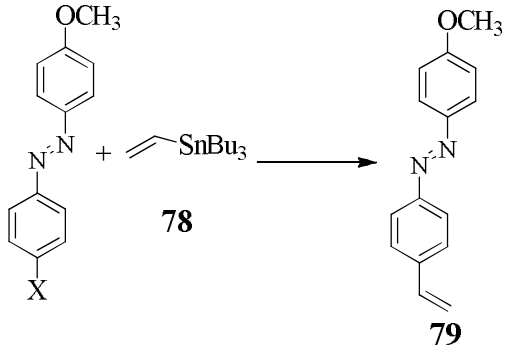
A mechanism for this novel transformation is depicted in Scheme 2.6. In this working hypothesis it is recognised that the initial alkylation could proceed at either nitrogen or oxygen. *N*-Alkylation to the keto-hydrazone **A** and symmetry-allowed 1,5-H shift would generate the zwitterion **B**. Cyclization of **B** to **C** and tautomerism to **D** followed by re-alkylation would ultimately generate the observed product. Alternatively O-alkylation and subsequent –radical generation (to E) and 6-*endo*-cyclization could lead to the same observed product. These reaction pathways are currently the subject of further investigation from a theoretical standpoint.[95]

2.6 Modification of the pyridine nucleus:

When considering how the reporting dye unit could be attached to the recognition unit in our sensor we also wished to examine the possibility of coupling the dye unit directly onto the pyridine ring of the macrocycle. We envisaged that this could be accomplished in a number of ways, the most direct of which would be to utilise one of the plethora of palladium-catalysed coupling reactions (*e.g.* Heck or Stille reaction) now available for such purposes. The application of palladium catalysed reactions for the conjugation of azo-dyes has however only received scant attention[52] and we therefore wished to determine whether such reactions were feasible in the systems we wished to develop.



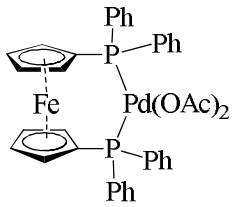
Using **40a** and **40b** as a model substrates we have shown that coupling with vinyl(tri-*n*- butyl)stannane proceeds efficiently when using a catalyst system comprising of $Pd(OAc)_2/PPh_3$ or $Pd(dppf)(OAc)_2$ at 100 °C in DMF (Scheme 2.6, Table 2.4). Unfortunately conducting similar Stille reactions on azo-dyes derived from naphthol have, as yet, proved to be ineffective.



Scheme 2.6: Reagents and Reaction Conditions: a) $Pd(OAc)_2$, PPh_3, DMF, 100˚C, 18 hrs b) Ferrocene catalyst, DMF, 100 ˚C.

Table 2.4:

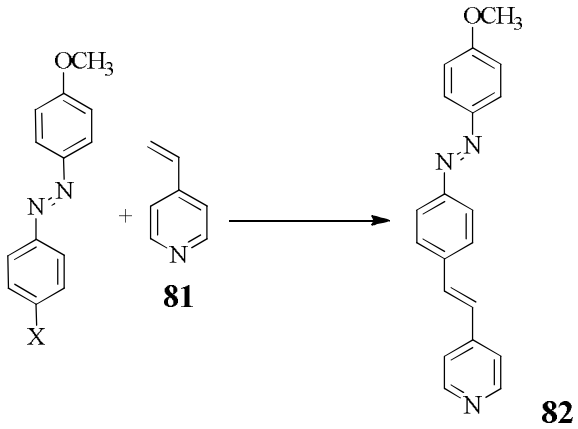
Reactant	X	Yield %
40a	I	74
40b	Br	76



80

Figure 2.6:[1,1′-Bis(diphenylphosphino)ferrocene]palladium(II)acetate.

We have also shown that 4-vinylpyridine **81** undergoes Heck reactions with the azo-dyes **40a** and **40b** in excellent isolated yield at the slightly more elevated temperature of 140 °C in DMF (Scheme 2.7, Table 2.5).

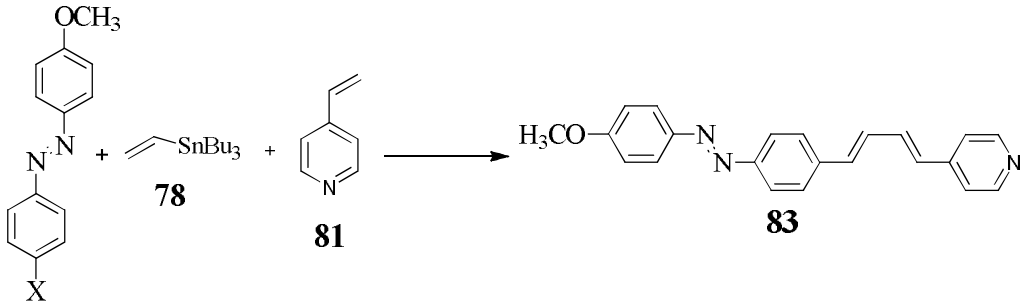


Scheme 2.7: Reagents and Reaction Conditions: $Pd(OAc)_2$, PPh_3, Et_3N, DMF, 140˚C.

Table 2.5: Heck Reaction for diazo compound

Reactant	X	Yield %
40a	I	74
40b	Br	76

Unfortunately initial attempts at developing a one-pot tandem Heck-Stille reaction have as yet been unsuccessful. (Scheme 2.8)

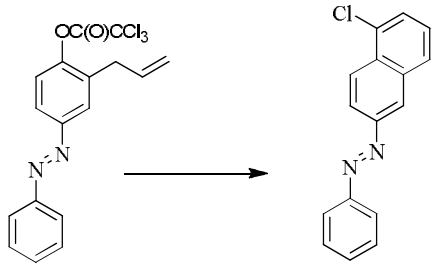


Scheme 2.8: Reagents and Reaction Conditions: $Pd(OAc)_2$, PPh_3, DMF, Et_3N, 140˚C, 18 hrs.

Similarly attempted Sonogashira coupling of diazo compound with representative alkynes also proved to be unsuccessful.

2.7 Atom Transfer Free Radical Reactions (ATRC):

Current interest of azo-compounds in diverse areas ranging from nano-technology to their development as antifungal agents, The Quayle group wondered whether the BHQ reaction could be applied in the elaboration of this ubiquitous class of compounds (Scheme 2.9).



84 **85**

Scheme 2.9: ATRC reactions: 5 mol% Nolan catalyst, diglyme, 162 ˚C, 3 hrs.

During the course of these investigations Quayle group wondered whether the BHQ reaction could be applied in the elaboration of the synthesis of novel azo-containing aromatics. In this sequence they demonstrated that allylation of phenolic azo-dyes with allyl bromide in the presence KOH using DMSO as solvent afforded high yields of the desired allyl ethers. Lewis-Acid promoted Claisen-rearrangement of the allyl ethers **112, 112a-112e, 113 - 116** were best achieved using Et_2AlCl in CH_2Cl_2 at room temperature and generally proceeded in near quantitative yields. Tricholoroacetylation (Cl_3CCOCl, Et_3N, Et_2O) of the rearranged azo-dyes followed by BHQ reaction (Nolan catalyst, 5 mol%; diglyme, 162 ˚C for 3 hours)

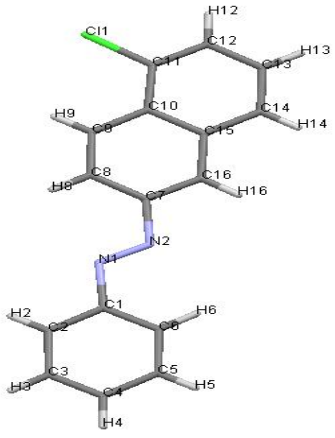
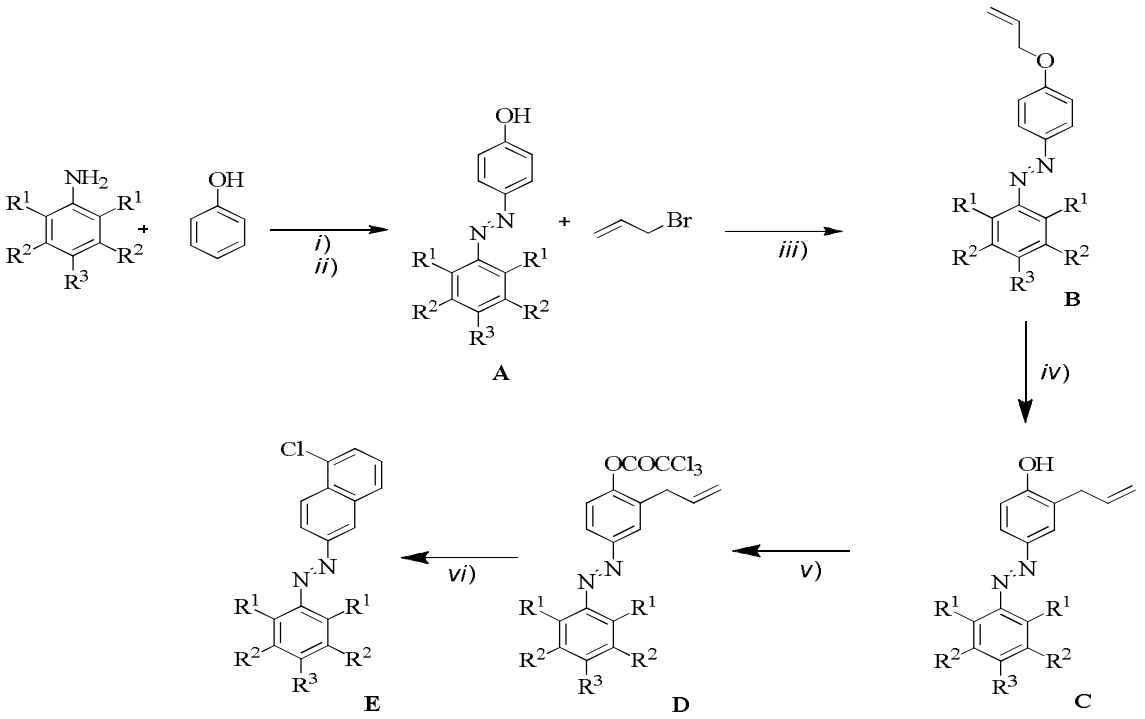


Figure 2.7.: X-ray crystal structure of (*E*)-1-(5-chloronaphthalen-2-yl)-2-phenyldiazene, **85**

also proceeded smoothly affording the benzannulated products **85, 85a-85d, 125** in good isolated yields (Scheme 2.10). Remarkably we were also able to affect a double Claisen-BHQ sequence using **124** as substrate, in which the BHQ reaction afforded the azo-dye **126** in good overall yield (Table 2.5). Proof of structure for the product of the Claisen-benzannulation sequence in the case of **85** was also established upon the basis of a single crystal X-ray determination (Figure 2.7).

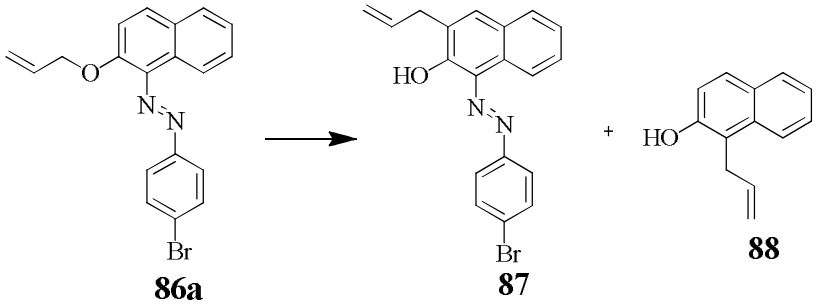


Scheme 2.10: Synthesis of functionalized azo dyes:*i*) $NaNO_2$, 2 M HCl, 0˚C *ii*) NaOH, Na_2CO_3 , 0˚C *iii*) KOH, DMSO, r.t *iv*) Et_2AlCl, DCM, r.t, 15 hrs *v*) Et_2O, Trichloroacetylchloride, 0˚C, 3 hrs *vi*) Nolan catalyst, 170˚C, 3 hrs

Table 2.6:

R_1	R_2	R_3	Isolated Yield **A%**	Isolated Yield **B%**	Isolated Yield **C%**	Isolated Yield **D%**	Isolated Yield **E%**
H	**H**	**H**	-	94	83	81	78
H	**Me**	**H**	94	93	84	81	77
H	**H**	**Cl**	96	92	87	83	80
H	**H**	**F**	97.	94	91	89	87
H	**H**	**Br**	94	88	81	80	80
H	**H**	**I**	93	88	83	81	77
H	**H**	**OH**	91	88	79	80	72
iso-prop	**H**	**H**	96	92	87	82	-
H	**H**	**NO_2**	94	81	-	-	-

Extension of this methodology to the synthesis of benzannulated dyes derived the naphthol system was hampered by problems associated with the Claisen rearrangement which only proceeded in poor yields **87** (23% in yield) and **88** (17% in yield) even after extensive attempts to optimise this reaction (Scheme 2.11).



86a **87** **88**

Scheme 2.11: Synthesis of Claisen rearranged azo-dye: Reagents and reaction conditions: Et_2AlCl, CH_2Cl_2, 0˚C → r.t, 15 hrs.; :23% in yield

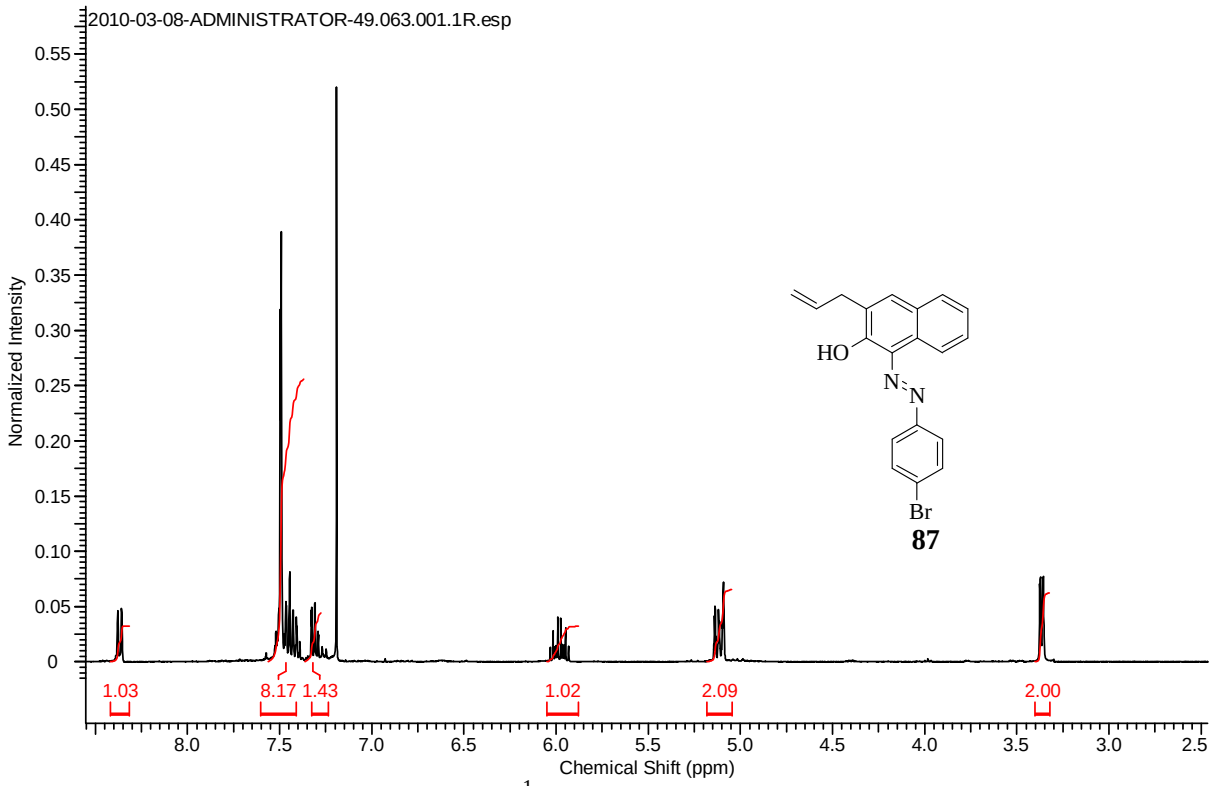
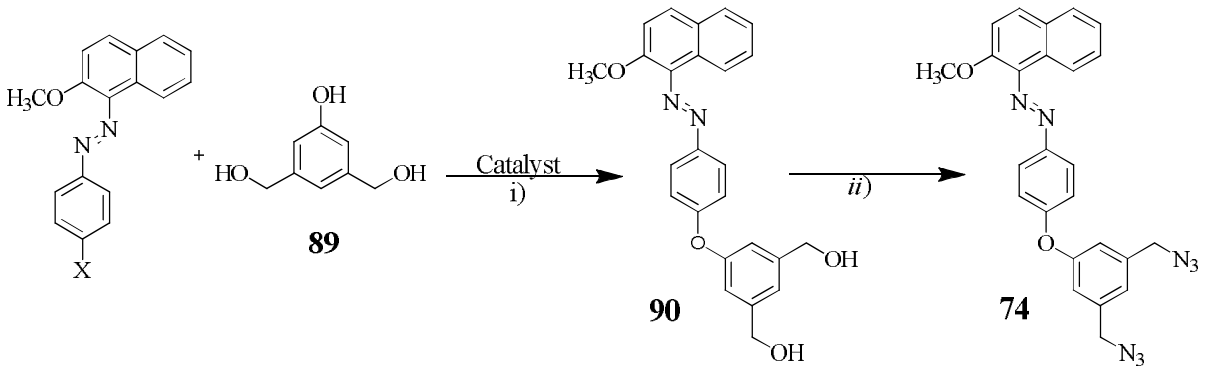


Figure 2.8: ^{1}H NMR Spectrum of **87**

2.8 Synthesis of "click" precursors:

A prime objective of this project was to determine whether an azo-dye such as **28, 28a-28e** could be linked to a suitably functionalised "spacer unit" thereby enabling assembly of the sensing agent using "click" chemistry. In our "first generation", proof of concept stage, this approach necessitated the development of a synthetic route to the bis-azide **74**. Naively Quayle group presumed that **74** could be obtained from the azo-dye **28, 28a-28e** by way of an Ullmann reaction with the phenol **89**. Although the application of the Ullmann reaction to the synthesis of aromatic ethers possessing azo-functionality has little literature precedent we were able to prepare, after some optimisation (Table 2.7) the key intermediate **90** from **28** and **89** using a catalyst system comprising of the Nolan copper carbene complex in the presence of picolinic acid. Finally transformation of the diol **90** into the desired bis-azide **74** was accomplished using a standard coupling reaction with diphenylphosphorylazide in presence of DBU, Scheme 2.12.



Scheme 2.12: Ullmann-type ether synthesis: i) CuI (10 mol %), K_3PO_4, picolinic acid (15 mol %), Dry DMSO, 130˚C, 24 hours ii) DPPA, dry DCM, 1,8-diazabicyclo[5.5.0]undec-7-ene, r.t, 12 hours.

Substrate (X)	Conditions			Isolated Yield (%)
	Reagents	Temp (°C)	Time (hrs)	
Br	CuI (10 mol%); Picolinic Acid (10 mol%); K_3PO_4	110	24	15
	CuI (15 mol%); Picolinic Acid (15 mol%); K_3PO_4	120	24	33
	Nolan Cat. (5 mol%); Picolinic Acid (15 mol%); K_3PO_4	120	24	50
F	CuI (15 mol%); Picolinic Acid (15 mol%); K_3PO_4	110	24	7
	CuI (15 mol%); Picolinic Acid (15 mol%); K_3PO_4	120	24	29
	Nolan Cat. (5 mol%); Picolinic Acid (15 mol%); K_3PO_4	120	24	47
I	CuI (15 mol%); Picolinic Acid (15 mol%); K_3PO_4	120	24	28
	Nolan Cat. (5 mol%); Picolinic Acid (15 mol%); K_3PO_4	120	24	52
	Nolan Cat. (5 mol%); K_3PO_4	120	24	23
	K_3PO_4	120	24	none

Table 2.7: Optimisation of the Ullmann reaction for the synthesis of ether **90**

2.9 Future Work

The work embodied within this thesis demonstrates that azo-dyes can be incorporated into a functionalised linker unit which will ultimately be used in the assembly of a sensing device for metal ions in biological systems. This has particular relevance to conditions such as Alzheimer's disease where it has been suggested that high local concentrations of heavy metals within the brain may be responsible for plaque formation. It is with this hypothesis in mind that the synthesis of sensors which respond to heavy metals may be useful in determining whether there is a causal link between heavy metals within brain tissue and the onset of neurodegenerative diseases.

It is envisaged that the route which has been developed for the synthesis of the bis-azide **74** will enable conjugation of crown-carbohydrate hybrids to reporter dye units. It is envisaged that fully assembled macromolecules will be able to pass across lipid membranes and sense metal ions in specific tissues within the body. It has yet to be ascertained whether the attachment of carbohydrates to dye-crown conjugates will facilitate transport across the blood-brain barrier. The synthesis of crown ethers possessing mixed donor sites capable of selective complexation to "soft" metal ions such as Cu(II) will also be the focus of further studies in this area.

PART II: EXPERIMENTAL SECTION

EXPERIMENTAL

Introduction

All reactions were carried out in dry glassware under an atmosphere of dry nitrogen unless mentioned otherwise.

A Sanyo Gallenkamp melting point apparatus was used for melting points. Infrared spectra were measured by Bruker Alpha FT-IR machine and absorption peaks (_max) are quoted in wave numbers (cm^{-1}).

Deuterated chloroform ($CDCl_3$) was used as solvent unless otherwise stated to record the Nuclear magnetic resonance (NMR) spectra. ^1H NMR spectra were recorded on Bruker Advance Ultra shield 300 (300 MHz), Bruker Advance Ultrashield 500 (500 MHz). Signal splitting patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m).

Low resolution mass spectra were measured on Micromass Trio 200 spectrometer. High resolution mass spectra were measured on Kratos Concept IS spectrometer.

A Carlo Erba EA 1108 Elemental Analyzer was used for determination of % levels of carbon, hydrogen and nitrogen. A Metrohm 686 Titroprocessor +665 Dosimat Autotitor was used to measure chlorine. Reagents and solvents used during experimentation were purchased from Sigma Aldrich and Across organics.

General Procedures:

Procedure A:

To a stirred solution of aniline (1 eq) in 2 M HCl (13 mL) at 0 °C, was added sodium nitrite solution in water (1 M, 10 mL) slowly so that no gas formation or colouring occurred. Sodium hydroxide (1 eq) and sodium carbonate (2 eq) were added to β-naphthol (1 eq) in water (20 mL/mmol of naphthol), stirred, cooled to 0 °C. The diazo compound (1 eq) was added slowly at 0 °C. After 30 min the mixture was acidified by adding 2 M HCl or acetic acid. The precipitate formed was filtered and washed with water. The crude product was purified by crystallisation.[69]

Procedure B1:

To a stirred solution of aniline (1 eq) in 2 M HCl (13 mL) at 0 °C, was added sodium nitrite sodium nitrite solution in water (1 M, 10 mL) slowly so that no gas formation and colouring occurred. Sodium hydroxide (1 eq) and sodium carbonate (2 eq) were added to phenol (1 eq) in water (20 mL/mmol of phenol), stirred and cooled to 0 °C. The diazo compound (1 eq) was added slowly at 0 °C. After 30 min the mixture was acidified by adding 2 M HCl or acetic acid. The precipitate formed was filtered and washed with water. The crude product was purified by crystallisation.[69]

Procedure B2:

To a stirred solution of hydroxy aniline (1 eq) in 3.5 M HCl (40 mL) at 0 °C, was added aqueous solution of sodium nitrite (0.05 M, 18 mL) slowly so that no gas formation and colouring occurred. The obtained diazonium salt was diluted with pre-cooled ethanol (200 mL/ eq of aniline). Sodium hydroxide (10 %) was added to phenol (1 eq) in water (42 mL/ eq of phenol) and ethanol (50 ml/ eq of phenol), stirred and cooled to 0 °C. The phenolate

solution was added slowly at 0 °C. After 2 hours at 0 °C the solution was neutralised the solution by adding 2 M HCl or acetic acid. The precipitate formed was filtered and washed with water. The filtrate was extracted into ethyl acetate; the organic layer was washed with brine, dried over $MgSO_4$, and then reduced *in vacuo*. The crude product was purified by crystallisation with dichloromethane.[70]

Procedure C1:

To a stirred mixture of powdered potassium hydroxide (5 eq), diazo compound (1 eq), in DMSO (10 mL) and methyl iodide (2 eq) were added to the mixture. The reaction mixture was stirred for 5 hours at room temperature, and then poured it into water. The organic layer was extracted into diethyl ether or dichloromethane and then washed with brine, dried over $MgSO_4$, and reduced *in vacuo*. The crude product was purified by flash chromatography. The residue was crystallised from ethanol and petroleum ether.[30]

Procedure C2:

To a stirred mixture of powdered potassium hydroxide (5 eq) in DMSO (10 mL), was added the diazo compound (1 eq). Dimethyl sulphate (2 eq) was then added to the mixture, which was stirred for 5 hours at room temperature and then poured it into water .The organic material was extracted into dichloromethane, washed with brine, dried over $MgSO_4$, and then reduced *in vacuo*. The crude product was purified by flash chromatography, followed by crystallisation from ethanol and petroleum ether.[30]

Procedure C3:

To a stirred mixture of potassium-*tert*-butoxide (2 eq) in DMSO (10 mL), was added the diazo compound (1 eq) followed by methyl iodide (2 eq). The reaction mixture was stirred overnight at room temperature, then poured into water. The organic layer was extracted into

DCM, washed with brine, dried over $MgSO_4$, and then reduced *in vacuo*. The crude was purified by flash chromatography. The residue was crystallised from ethanol and petroleum ether.[30]

Procedure C4:

A stirred mixture of dry DMSO (7 mL) and sodium hydride (12 mmol) was heated at 90 °C for 15 min (sodium hydride had previously been washed with petroleum spirit to remove the mineral oil). The reaction mixture was cooled and then the diazo naphthol dye (0.5 mmol) was added, followed by methyl iodide (2 eq). The reaction mixture was stirred for 5 hrs at room temperature. It was then poured into water and the organic layer was extracted with dichloromethane and washed with water and brine, dried over $MgSO_4$, and reduced *in vacuo*. The crude product was purified by column chromatography.[71]

Procedure D:

To a stirred mixture of powdered potassium hydroxide (5 eq) in DMSO, was added the diazo compound (1 eq). Allyl bromide (2 eq) was then added to the mixture. The reaction mixture was stirred for 5 hours at room temperature, then poured into water. The organic material was extracted into DCM and then washed with brine and water, dried over $MgSO_4$, and reduced *in vacuo*. The crude product was purified by flash chromatography.

Procedure E1:

To a stirred mixture of methylated diazo phenols (5 mmol), $Pd(OAc)_2$ (0.05 mmol) and PPh_3 (0.10 mmol) in DMF, was added vinyl pyridine (7.5 mmol) under nitrogen. The resultant mixture was heated under reflux for 24 hours. After cooling to room temperature, the reaction mixture was added to water to precipitate the product. The precipitate was washed with ethanol three times and purified by flash chromatography.[72]

Procedure E2:

To a stirred mixture of methylated diazo phenols (5 mmol), $Pd(OAc)_2$ (0.05 mmol) and PPh_3 (0.10 mmol) in DMF, was added vinyl pyridine (7.5 mmol) under nitrogen. The resultant mixture was heated under reflux for 24 hours. After cooling to room temperature, the solvent was reduced *in vacuo* by using rotary evaporator and residue was extracted it with ethyl acetate; the organic layer was washed with brine, dried over $MgSO_4$, and then reduced *in vacuo*. The crude product was purified by flash chromatography.

Procedure F:

To a stirred solution of allylated diazo compound (1 eq) in dry DCM (10 mL), diethylaluminium chloride (2 eq) was added at 0 °C and then the mixture was stirred at room temperature for 15 hours. The reaction mixture was quenched by the addition of saturated solution of Na/K tartrate tetrahydrate and the organic layer was extracted with ethyl acetate. The organic layer was washed it with brine (3 times) and then water (3 times) and dried over $MgSO_4$. The crude mixture was purified by column chromatography.[73]

Procedure G:

To the stirred solution of Claisen rearranged phenol dye (1 eq) and triethylamine (1.2 eq) in dry ether, trichloroacetylchloride (1.2 eq) was added dropwise at 0 °C for 3 hours and then the reaction mixture was quenched by the addition of water (20 mL). The quenched reaction mixture was diluted with ether. The organic layer was separated and then washed with sodium bicarbonate (saturated solution) 3 times, brine 3 times and then water 3 times. The organic layer was dried over $MgSO_4$. The crude mixture was purified by column chromatography.[73]

Procedure H:

The trichloroacetate diazo species (1 eq) was heated with the Nolan catalyst (5 mol %) and diglyme (625 µL/mmol trichloroacetate) at 170 °C for 3 hours. The reaction was allowed to cool, and purified directly by flash column chromatography (100 % Pet. Ether).

Procedure I:

To a stirred mixture of phenolic substrate (1 eq.) in acetone (10 ml /1 g of substrate) with potassium carbonate (1.2 eq), allyl bromide (1.2 eq) was added and the reaction mixture was heated under reflux for 5 hours, and then allowed to cool and the inorganic components were separated by filtration, and solvent was reduced *in vacuo.*[74]

Procedure J:

The allyl phenol ether and N,N-diethyl aniline (2 ml/ eq of substrate) was heated at reflux for 8 hours in a Schlenk tube and allowed to cool. The reaction mixture was diluted with petroleum ether to obtain the product.[74]

Procedure K:

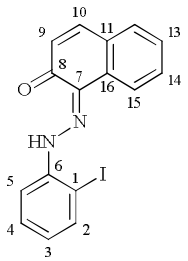
Diazo naphthol (1 eq), Copper (I) iodide (20 mol%; 38 mg) or Nolan catalyst (5 mol%; 24 mg), picolinic acid (40 mol%; 50 mg), potassium phosphate tribasic(20 mmol; 424 mg) and 3,5-bis(hydroxy methyl)phenol (1.2 eq; 185 mg) were placed in an oven dried Schlenk tube under nitrogen followed by the addition of dry dimethylsulphoxide (2 mL/ eq of substrate). The reaction mixture was stirred and heated for 48 hours at 130 °C. The reaction mixture was allowed to cool and ethyl acetate was added in it. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over $MgSO_4$ and reduced *in vacuo.* The product was purified by column chromatography (hexane and ethyl acetate 1:3).[75]

Procedure L:

To the stirred mixture of methylated diazo phenol (1 mmol), $Pd(OAc)_2$ (0.2 mmol), PPh_3 (0.2 mmol) in DMF (10 mL) was added vinyltributylstananne (1.2 mmol) under nitrogen. The reaction mixture was heated for 24 hours at 100 °C and then allowed to cool to room temperature. The solvent was reduced *in vacuo*, and DCM (15 mL) was added to the residue and washed with brine (3 times) and water (3 times). The organic layer was dried over $MgSO_4$ and reduced *in vacuo*. The product was purified by column chromatography (hexane and DCM 1:1).[76]

1 SYNTHESIS OF DIAZO NAPHTHOL COMPOUNDS

1.1 Synthesis of 1-[(*E*)-[(2-iodophenyl)diazenyl]-2-naphthol (91a):[69,77]



Was prepared using general procedure A [2-iodoaniline (2.19 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), β-naphthol (1.5 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound, (3.31 g, 89%) as a red solid (**mp** 176-178ºC; lit.[69] 180 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 6.85 (1H, d, *J* = 9 Hz, Ar-**H**$_9$) 6.97 (1H, td, *J* = 7, 1.5 Hz, Ar-**H**$_3$) 7.36 (1H, td, *J* = 8, 1, Ar-H) 7.44 (1H, td, J = 8, 1, Ar-H) 7.48-7.56 (2H, m, Ar-**H**) 7.67 (1H, d, *J* = 9 Hz, Ar-**H**$_5$) 7.86 (1H, dd, *J* = 8, 1 Hz, Ar-**H**$_{10}$) 7.96 (1H, dd, *J* = 8, 1 Hz, Ar-**H**$_2$) 8.47 (1H, d, *J* = 8 Hz, Ar-**H**$_{15}$) 15.78 (1H, s, NH).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 117.4 (CH, Ar-H, **C**$_2$), 121.8 (CH, Ar-H, **C**$_{15}$), 124.4 (CH, Ar-H, **C**$_9$), 126 (CH, Ar-H, **C**$_{12}$), 128.3 (CH, Ar-H, **C**$_3$), 128.6 (CH, Ar-H, **C**$_{13}$), 128.8 (CH, Ar-H, **C**$_{14}$), 129.2 (CH, Ar-H, **C**$_4$), 139.6 (CH, Ar-H, **C**$_{10}$), 140.4 (CH, Ar-H, **C**$_5$), 130.4, 133.2, 145.5, 170.9.

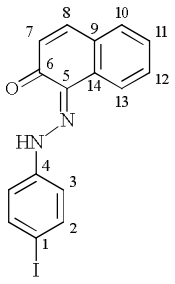
MS (ES+): m/z $[M + H]^+$ 375; $[M + Na]^+$ 397.

Accurate Mass: $C_{16}H_{12}ON_2I$ requires 374.9989 found 374.999.

Microanalysis: $C_{16}H_{12}N_2I$ requires C 51.36; H 2.96; N 7.49; I 33.92%. Found: C 51.66; H 2.28; N 7.04; I 32.60%.

IR ν_{max} (film): 1370, 1488, 1551, 1596, 1600, 1616, 3059, 3067 cm^{-1}.

1.2 Synthesis of 1-[(*E*)-[(4-iodophenyl)diazenyl]-2-naphthol (92a):[69,77]



Was prepared using general procedure A [4-iodoaniline (2.19 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), β-naphthol (1.5 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound, (3.31 g, 88%) as a red solid (**mp** 168-169 ºC; lit.[69] 165-167 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 6.84 (1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.37-7.43 (1H, m, Ar-**H**$_{11}$) 7.46 (2H, d, *J* = 9 Hz, Ar-**H**$_3$) 7.52-7.63 (2H, m, Ar-**H**$_{10, 12}$), 7.72 (1H, d, *J* = 10 Hz, Ar-**H**$_8$) 7.78 (2H, d, *J* = 9 Hz, Ar-**H**$_2$) 8.51 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$), 16.11(1 H, br. s, NH).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 120.1 (CH, Ar-H, **C**$_2$), 121.7 (CH, Ar-H, **C**$_{13}$), 124.7 (CH, Ar-H, **C**$_7$), 126.1 (CH, Ar-H, **C**$_{11}$), 128.7 (CH, Ar-H, **C**$_{12}$), 129.1 (CH, Ar-H, **C**$_{10}$), 138.5 (CH, Ar-H, **C**$_3$), 140.5 (CH, Ar-H, **C**$_8$), 91.6, 128.2, 130.3, 133.3, 144.4, 172.4.

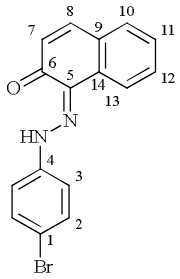
MS (ES+): m/z $[M + H]^+$ 375; $[M + Na]^+$ 397.1.

Accurate Mass: $C_{16}H_{12}N_2IO$ requires 374.9989 found 374.9991.

Microanalysis: $C_{16}H_{12}N_2$ requires C 51.36; H 2.96; N 7.49%. Found **C** 51.48; H 2.90; N 7.17%.

IR ν_{max} (film): 742, 816, 1206, 1370, 1490, 1551, 1596, 1600, 1616, 3069, 3343 cm^{-1}.

1.3 Synthesis of 1-[(*E*)-[(4-bromophenyl)diazenyl]-2-naphthol (92b):[69,77]



Was prepared using general procedure A [4-Bromoaniline (1.72 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), β-naphthol (1.5 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound, (3.28 g, 98%) as dark brick red solid (**mp** 166.5-168ºC; lit.[69] 170 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 6.85 (1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.40 (1H, td, *J* = 8 Ar-**H**$_{12}$) 7.50-7.62 (6H, m, Ar-**H**$_{2,3,10,11}$) 7.71 (1H, d, *J* = 9 Hz, Ar-**H**$_8$) 8.51 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$) 16.05 (1H, s, NH).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 120.1 (CH, Ar-H, **C**$_3$), 121.7 (CH, Ar-H, **C**$_{13}$), 124.4 (CH, Ar-H, **C**$_7$), 125.9 (CH, Ar-H, **C**$_{11}$), 128.6 (CH, Ar-H, **C**$_{10}$), 128.9 (CH, Ar-H, **C**$_{12}$), 132.6 (CH, Ar-H, **C**$_2$), 140.2 (CH, Ar-H, **C**$_8$), 120.7, 128.1, 130.2, 133.3, 144, 171.3.

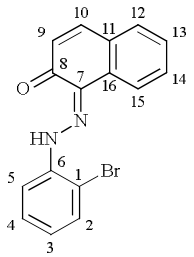
MS (ES+): m/z $[M + Na]^+$ 349.21.

Accurate Mass: $C_{16}H_{12}N_2{}^{79}BrO$ requires 327.0128 found 327.0136.

Microanalysis: $C_{16}H_{12}N_2{}^{79}Br$ requires C 58.74; H 3.39; N 8.56; Br 24.42%. Found C 58.59; H 3.31; N 8.15; Br 24.38%.

IR ν_{max} (film): 758, 817, 1136, 1207, 1364, 1492, 1601, 1618, 3037 cm^{-1}.

1.4 Synthesis of 1-[(*E*)-[(2-bromophenyl)diazenyl]-2-naphthol (91b):[69,77]



Was prepared using general procedure A [2-bromoaniline (1.72 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), β-naphthol (1.5 g, 10 mmol), HCl (13 mL, 2M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound (3.28 g, 98%) as dark brick red solid (**mp** 171-172ºC; lit.[69] 174 ºC).

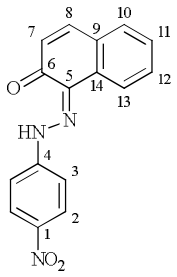
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.81 (br. s., 1H, OH), 6.84 (1H, d, *J* = 10 Hz, Ar-**H**$_9$), 7.13 (1H, t, *J* = 7 Hz, Ar-**H**$_3$), 7.34-7.49 (2H, m, Ar-**H**$_{4,13}$), 7.49-7.60 (2H, m, Ar-**H**$_{12,14}$), 7.65 (1H, d, *J* = 9 Hz, Ar-**H**$_5$), 7.71 (1H, d, *J* = 9 Hz, Ar-**H**$_{10}$), 8.10 (1H, d, *J* = 8 Hz, Ar-**H**$_2$), 8.55 (1H, d, *J* = 7, Ar-**H**$_{15}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 118.1 (CH, Ar-H, **C**$_2$), 121.9 (CH, Ar-H, **C**$_{15}$), 124.4 (CH, Ar-H, **C**$_9$), 125.9 (CH, Ar-H, **C**$_{12}$),128.1 (CH, Ar-H, **C**$_{3,5}$), 128.8 (CH, Ar-H, **C**$_{13}$), 128.93 (CH, Ar-H, **C**$_{14}$), 131.9 (CH, Ar-H, **C**$_4$), 140.3 (CH, Ar-H, **C**$_{10}$), 121.7, 128.4, 130.9, 134.3, 144.1, 171.1.

Accurate Mass: $C_{16}H_{12}N_2{}^{79}BrO$ requires 327.0128 found 327.0142.

IR ν_{max}(film): 738, 815, 1204, 1487, 1584, 1700, 2096, 3009 cm^{-1}.

1.5 Synthesis of 1-[(*E*)-[(4-nitrophenyl)diazenyl]-2-naphthol (92c):[69,78]



Was prepared using general procedure A2 [4-nitroaniline (1.38 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), β-naphthol (1.5 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound (2.88 g, 98%) as dark brick red solid (**mp** 217.5-218 ºC; lit.[69] 257 ºC).

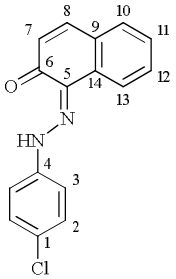
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.69 (1H, s, OH) 6.70 (1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.34-7.50 (1H, m, Ar-**H**$_{11}$) 7.50-7.61 (2H, m, Ar-**H**$_{10,12}$) 7.64-7.78 (3H, m, Ar-**H**$_{3,8}$) 8.33 (2H, d, *J* = 9 Hz, Ar-**H**$_2$) 8.42 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$), 16.13 (1H, NH)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 116.6 (CH, Ar-H, **C**$_7$), 122.5 (CH, Ar-H, **C**$_{13}$), 125.7 (CH, Ar-H, **C**$_3$), 126.3 (CH, Ar-H, **C**$_{11}$), 127.6 (CH, Ar-H, **C**$_{10}$), 128.6 (CH, Ar-H, **C**$_{12}$), 129.1 (CH, Ar-H, **C**$_2$), 129.8 (CH, Ar-H, **C**$_8$), 132.1, 133.3, 143.5, 147.9, 180.

Accurate Mass: $C_{16}H_{12}N_3O_3$ requires 292.0719 found 292.0727.

IR ν_{max} (film): 745, 1103, 1204, 1323, 1452, 1518, 1590, 2423 cm^{-1}.

1.6 Synthesis of 1-[(*E*)-[4-chlorophenyl)diazenyl]-2-naphthol (92d):[69,77]



Was prepared using general procedure A2 [4-chloroaniline (1.27 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), β- naphthol (1.5 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound (2.71 g, 97%) as dark red solid (mp 161-162 ºC; lit.[69] 162 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 6.89 (1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.30-7.36 (1H, m, Ar-**H**$_{12}$) 7.45 (2H, dd, *J* = 9, 2 Hz, Ar-**H**$_3$) 7.56 (1H, td, *J* = 8, 1 Hz, Ar-**H**$_{11}$) 7.62 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 7.69 (2H, dd, *J* = 9, 2 Hz, Ar-**H**$_2$) 7.74 (1H, d, *J* = 9 Hz, Ar-**H**$_8$) 8.55 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$).

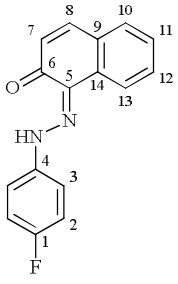
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 119.8 (CH, Ar-H, **C**$_2$), 121.7 (CH, Ar-H, **C**$_{13}$), 124.33 (CH, Ar-H, **C**$_{10}$), 125.8 (CH, Ar-H, **C**$_7$), 128.6 (CH, Ar-H, **C**$_{12}$), 128.9 (CH, Ar-H, **C**$_{11}$), 129.7 (CH, Ar-H, **C**$_3$), 132.9 (CH, Ar-H, **C**$_8$), 119.6, 129.3, 130.9, 134.3, 145.4, 171.

MS (ES+): m/z $[M+H]^+$ 283; $[M-H]^-$ 281; $[M + Na]^+$ 305.

Accurate Mass: $C_{17}H_{14}N_2{}^{35}ClO$ requires 305.046 found 305.0453.

IR ν_{max} (film): 1210, 1467, 1561, 1619, 3051 cm^{-1}.

1.7 Synthesis of 1-[(*E*)-[4-flourophenyl)diazenyl]-2-naphthol (92e):[77]



Was prepared using general procedure A2 [4-flouroaniline (1.11 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g,2 M, 40 mmol), β- naphthol (1.5 g, 10 mmol), HCl (13 mL, 2 M, 26

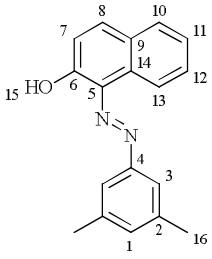
mmol),Na_2CO_3(2.5 g)] affording the title compound, (2.51 g, 97 %) as dark red colour compound (**mp** 176-178 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 6.95 (1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.08 (1H, t, *J* = 8 Hz, Ar-**H**$_{11}$) 7.14-7.23 (2H, m, Ar-**H**$_2$) 7.41 (1H, td, *J* = 7, 1 Hz, Ar-**H**$_{12}$) 7.57 (1H, d, *J* = 8 Hz, Ar-**H**$_8$) 7.64 (1H, d, *J* = 7 Hz, Ar-**H**$_{10}$) 7.76 (2H, dt, *J* = 9, 4 Hz, Ar-**H**$_3$) 8.6 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 116.6 (CH, Ar-H, **C**$_2$), 121 (CH, Ar-H, **C**$_3$), 121.5 (CH, Ar-H, **C**$_{13}$), 123.5 (CH, Ar-H, **C**$_{10}$), 125.4 (CH, Ar-H, **C**$_7$), 128.5 (CH, Ar-H, **C**$_{12}$), 128.6 (CH, Ar-H, **C**$_{11}$), 138.7 (CH, Ar-H, **C**$_8$), 121.1, 128.3, 129.2, 133.2,164.2, 166.3.

IR ν_{max} (film): 779, 849, 1016, 1190, 1457, 1560, 1819, 3051 cm^{-1}.

1.8 Synthesis of 1-[(*E*)-[(3,5-dimethylphenyl)diazenyl]-2-naphthol (93):[79]



Was prepared using general procedure A2 [3,5-dimethylaniline (1.22 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), β- naphthol (1.5 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound, (2.88 g, 98%) as dark red solid (**mp** 183-184 ºC; lit.[79] 170 ºC).

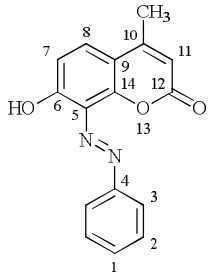
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.41 (6H, s, CH_3) 6.87 (1H, d, *J* = 10 Hz, Ar-**H**$_7$) 6.95 (1H, s, Ar-**H**$_1$) 7.31-7.45 (2H, m, Ar-**H**$_{11,12}$) 7.49-7.63 (3H, m, Ar-**H**$_{3,8}$) 7.71 (1H, d, *J* = 9 Hz, Ar-**H**$_{10}$) 8.57 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$) 16.34 (1H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.3 (CH_3), 116.3 (CH, Ar-H, $\mathbf{C}_7$), 121.6 (CH, Ar-H, $\mathbf{C}_3$), 124.9 (CH, Ar-H, $\mathbf{C}_{13}$), 125.5 (CH, Ar-H, $\mathbf{C}_{11}$), 127.9 (CH, Ar-H, $\mathbf{C}_{12}$), 128.5 (CH, Ar-H, $\mathbf{C}_{10}$), 129.9 (CH, Ar-H, $\mathbf{C}_8$), 133.63 (CH, Ar-H, $\mathbf{C}_1$), 128.7, 129.3, 139.3, 139.7, 144.6, 171.9.

Accurate Mass: $C_{18}H_{17}N_2O$ requires 277.1335 found 277.1347.

IR ν_{max} (film): 1252, 1273, 1468, 1508, 3036, 3190 cm^{-1}.

1.9 Synthesis of (*E*)-7-hydroxy-4-methyl-8-(phenyldiazenyl)naphthalene-2(1H)-one (94):[80]



Was prepared using general procedure A2 [aniline (0.9 mL, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), 4-methylumbelliferone (1.76 g, 10 mmol), HCl (13 mL, 2M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound, (2.60 g, 93%) as dark red colour compound.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.42 (3H, d, *J* = 1 Hz, CH_3) 6.21 (1H, s, Ar-$\mathbf{H}_{11}$), 6.91 (1H, d, *J* = 9 Hz, Ar-$\mathbf{H}_7$) 7.52 (2H, d, *J* = 2 Hz, Ar-$\mathbf{H}_3$) 7.52-7.58 (2H, m, Ar-$\mathbf{H}_{3,8}$) 7.93-7.98 (2H, m, Ar-$\mathbf{H}_{1,2}$) 14.26 (1 H, s).

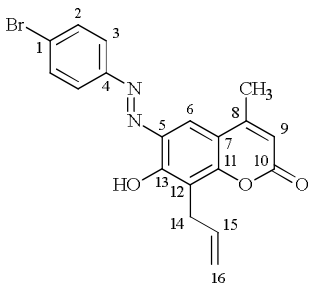
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 19 (CH_3), 112 (CH, Ar-H, $\mathbf{C}_{11}$), 114.7 (CH, Ar-H, $\mathbf{C}_7$), 122.7 (CH, Ar-H, $\mathbf{C}_2$), 125.8 (CH, Ar-H, $\mathbf{C}_8$), 129.4 (CH, Ar-H, $\mathbf{C}_3$), 131.8 (CH, Ar-H, $\mathbf{C}_1$), 112.7, 150.3, 152.7, 156.5, 160.4.

MS (ES+): $[M + Na]^+$ 303.

Accurate Mass: $C_{16}H_{13}N_2O_3$ requires 281.0921 found 281.0924.

IR ν_{max} (film): 1438, 1495, 1596, 1629, 1731, 3054, 3850 cm^{-1}.

1.10 Synthesis of (*E*)-8-allyl-6-(bromophenyl)diazenyl)-7-hydroxy-4-methyl-2H-chromen-2-one (95):



Was prepared using general procedure A2 [4-Bromoaniline (1.76 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 80 mmol), 8-allyl-7-hydroxy-4-methyl-2H-chromen-2-one[99] (1.84 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (5 g)] affording the title compound, (3.74 g, 92%) as dark red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.50 (3H, d, *J* = 1 Hz,CH_3) 3.68 (2H, d, *J* = 6 Hz, CH_2, $\mathbf{H}_{14}$) 5.05 (1H, dd, *J* = 9, 1 Hz,CH_2, $\mathbf{H}_{16}$) 5.14 (1H, dd, *J* = 17, 1 Hz, CH_2, $\mathbf{H}_{16}$) 5.91-6.10 (1H, m, CH, $\mathbf{H}_{15}$) 6.22 (1H, s, CH, Ar-$\mathbf{H}_9$) 7.66-7.70 (2H, m, CH, Ar-$\mathbf{H}_3$) 7.74-7.78 (2H, m, CH, Ar-$\mathbf{H}_2$) 8.10 (1H, s, CH, Ar-$\mathbf{H}_6$), 13.6 (1H, s).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 18.8 (CH_3), 26.5 (CH_2, $\mathbf{C}_{14}$), 115.7 (CH_2, $\mathbf{C}_{16}$), 123.6 (CH, Ar-H, $\mathbf{C}_3$), 128.2 (CH, Ar-H, $\mathbf{C}_6$), 132.7 (CH, Ar-H, $\mathbf{C}_2$), 112.5, 113.7, 116.3, 134.4, 148.8, 152.3, 154.6, 160.3.

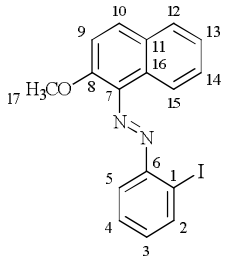
MS (ES+): $[M+H]^+$ 399.

Accurate Mass: $C_{19}H_{16}N_2BrO_3$ requires 399.0339 found 399.0346.

IR ν_{max} (film): 1388, 1559, 1600, 1730, 3201 cm^{-1}.

2 SYNTHESIS OF METHYLATED DIAZO NAPHTHOL COMPOUNDS

2.1 Synthesis of (*E*)-1-(2-iodophenyl)-2-(2-methoxy-1-naphthyl)diazene (96):



Was prepared using general procedure C [1-[(*E*)-[(2-iodophenyl)diazenyl]-2-naphthol (1.55 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol) affording the *title compound* (3.29 g, 85%)] as dark red solid (**mp** 76.5-78ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.11 (3H, s,OCH_3) 7.18 (1H, td, *J* = 8,1 Hz, Ar-**H**$_{13}$) 7.42 (1H, d, *J* = 9, Ar-**H**$_9$)7.45-7.52 (1H, m, Ar-**H**$_3$) 7.63 (1H, td, *J* = 9,1, Ar-**H**$_{14}$) 7.77 (1H, dd, *J* = 8,1.5 Hz, Ar-**H**$_2$) 7.83 (1H, d, *J* = 8 Hz, Ar-**H**$_{12}$) 7.95 (1H, d, *J* = 9 Hz, Ar-**H**$_5$) 8.08 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 8.98 (1H, d, *J* = 9, Ar-**H**$_{15}$ Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 57.5 (CH_3, **C**$_{17}$), 114.4 (CH, Ar-H, **C**$_9$), 117.3 (CH, Ar-H, **C**$_5$), 124.3 (CH, Ar-H, **C**$_{13}$), 126.6 (CH, Ar-H, **C**$_{15}$), 127.9 (CH, Ar-H, **C**$_{14}$), 128.7 (CH, Ar-H, **C**$_4$), 128.8 (CH, Ar-H, **C**$_{13}$), 131.6 (CH, Ar-H, **C**$_{10}$), 133.1 (CH, Ar-H, **C**$_3$), 139.8 (CH, Ar-H, **C**$_2$), 101.8, 127.8, 134.7, 151.8, 153.3.

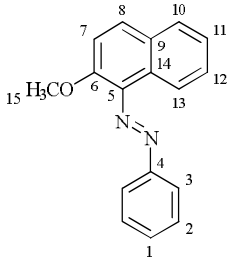
MS (ES+): m/z $[M+H]^+$ 375; $[M + Na]^+$ 397.

Accurate Mass:$C_{17}H_{14}N_2IO$ requires 389.0145 found 389.0151.

Microanalysis:$C_{17}H_{14}N_2I$ requires C 52.60; H 3.38; N 7.22; I 32.61 %. Found: C 52.73; H 3.20; N 7.05; I 32.53%.

IR ν_{max} (film): 1461, 1592, 1620, 2936, 3061, 3482 cm^{-1}.

2.2 Synthesis of (*E*)-1-(2-methoxy-1-naphthyl)-2-phenyldiazene (28):[81]



Was prepared using general procedure C [Sudan Dye 1 (1.02 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol)] affording the *title compound* (0.75 g, 70%; **mp** 80 °C, lit[81b] 80-81 °C) as dark red colour compound. The crude product was purified by column chromatography (SiO_2 gel; eluent hexane/DCM 60%)

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.01 (3H, s,OCH_3) 7.37-7.64 (6H, m, Ar-$\mathbf{H}_{1,2,7,11,12}$) 7.84 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{10}$) 7.89 (1H, d, *J* = 9 Hz, Ar-$\mathbf{H}_8$) 8.04 (2H, d, *J* = 6 Hz, Ar-$\mathbf{H}_3$) 8.38 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{13}$).

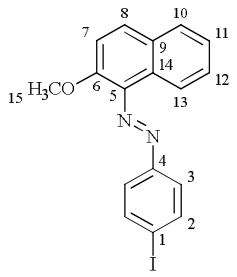
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 57.4 (CH_3, $\mathbf{C}_{15}$), 114.7 (CH, Ar-H, $\mathbf{C}_7$),122.6 (CH, Ar-H, $\mathbf{C}_3$), 123.1 (CH, Ar-H, $\mathbf{C}_{13}$), 124.4 (CH, Ar-H, $\mathbf{C}_{11}$), 127.6 (CH, Ar-H, $\mathbf{C}_{12}$), 127.8 (CH, Ar-H, $\mathbf{C}_{10}$), 129.1 (CH, Ar-H, $\mathbf{C}_2$), 130.9 (CH, Ar-H, $\mathbf{C}_8$), 131.9 (CH, Ar-H, $\mathbf{C}_1$), 128.4, 129.2, 136.5, 148.3, 153.5.

MS (ES+): m/z $[M+H]^+$ 263 $[M + Na]^+$ 285.

Accurate Mass: $C_{17}H_{15}N_2O$ requires 263.1179 found 263.1192.

IR ν_{max} (film): 1365, 1427, 1460, 1618, 1738, 3100 cm^{-1}.

2.3 Synthesis of (*E*)-1-(4-iodophenyl)-2-(2-methoxy-1-naphthyl)diazene (28a):



Was prepared using general procedure C [1-[(*E*)-[(4-iodophenyl)diazenyl]-2-naphthol (1.55 g, 4.14 mmol, 10 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol)] affording the *title compound* (2.4 g, 62%, **mp** 71-73.2 °C).as dark red colour compound. The crude product was purified by column chromatography (SiO_2; eluent hexane/DCM 30%)

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.01 (3H, s, CH_3) 7.35-7.47 (2H, m, Ar-**H**$_{7,11}$) 7.55 (1H, ddd, *J* = 8,7,1 Hz, Ar-**H**$_{12}$) 7.76 (2H, d, *J* = 8 Hz, Ar-**H**$_2$) 7.84 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 7.88-7.94 (3H, m, Ar-**H**$_{3,8}$) 8.44 (1H, d, *J* = 9 Hz, Ar-**H**$_{13}$).

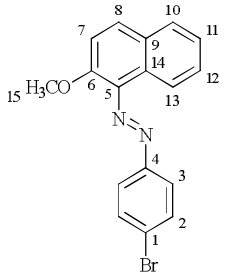
^{13}CNMR (75 MHz, $CDCl_3$) δppm 57.3 (CH_3), 114.5 (CH, Ar-H, **C**$_7$), 123.1 (CH, Ar-H, **C**$_{13}$), 124.2 (CH, Ar-H, **C**$_3$), 124.5 (CH, Ar-H, **C**$_{11}$), 127.9 (CH, Ar-H, **C**$_{12}$), 131.6 (CH, Ar-H, **C**$_8$), 138.3 (CH, Ar-H, **C**$_2$), 97.3, 128.5, 129.1, 135.9, 148.8, 152.9.

MS (ES+): m/z $[M+H]^+$ 389; $[M + Na]^+$ 411.1.

Accurate Mass: $C_{17}H_{14}N_2IO$ requires 389.0145 found 389.0147.

IR ν_{max} (film): 1453, 1593, 2838, 2972, 3008 cm^{-1}.

2.4 Synthesis of (*E*)-1-(4-bromophenyl)-2-(2-methoxy-1-naphthyl)diazene (28b):



Was prepared using general procedure C [1-[(*E*)-[(4-bromophenyl)diazenyl]-2-naphthol (1.35 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol)] affording the *title compound* (2.18 g, 64%, **mp** 78-80.2 °C) as dark red solid. The crude product was purified with column chromatography (SiO_2 gel; eluent hexane/DCM 30%).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.01 (3H, s, CH_3) 7.39-7.47 (2H, m, Ar-**H**$_{7, 11}$) 7.55 (1H, td, *J* = 8, 1 Hz, Ar-**H**$_{12}$) 7.70 (2H, d, *J* = 8 Hz, Ar-**H**$_2$) 7.84 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 7.87-7.94 (3H, m, Ar-**H**$_{3,8}$) 8.44 (1H, d, *J* = 9 Hz, Ar-**H**$_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 57.3(CH_3), 114.5(CH, Ar-H, **C**$_7$), 123.1(CH, Ar-H, **C**$_{13}$), 124.1(CH, Ar-H, **C**$_3$),124.5(CH, Ar-H, **C**$_{11}$), 127.9(CH, Ar-H, **C**$_{10}$), 128.5(CH, Ar-H, **C**$_{12}$), 132.3(CH, Ar-H, **C**$_2$), 135.9(CH, Ar-H, **C**$_8$), 125.1, 129.1, 131.6,148.8, 152.3.

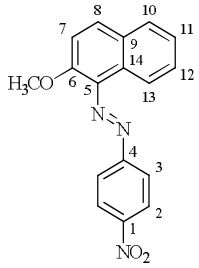
MS (ES+): $[M + Na]^+$ 363.1.

Accurate Mass: $C_{17}H_{14}N_2{}^{79}BrO$ requires 341.0284 found 341.0294.

Microanalysis:$C_{17}H_{14}N_2{}^{79}Br$ requires C 59.84; H 3.84; N 8.21; Br 23.42%. Found **C** 59.71; H 3.83; N 8.14; Br 24.01 %.

IR υ_{max} (film): 1430, 1472, 2876, 2932, 3007 cm^{-1}.

2.5 Synthesis of (*E*)-1-(4-nitrophenyl)-2-(2-methoxy-1-naphthyl)diazene (28c):



Was prepared using general procedure C [1-[(*E*)-[(4-nitrophenyl)diazenyl] -2-naphthol (1.21 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol)] affording the *title compound* (0.90 g, 30%) as a dark red solid. The crude was purified by column chromatography (SiO_2; eluent hexane/DCM 90%; **mp** 135-137 °C).

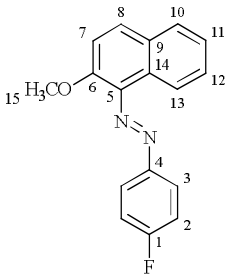
^{1}H NMR (300 MHz, $CDCl_3$) δppm 4.07 (3H, s,OCH_3) 7.41-7.51 (2H, m, Ar-**H**$_{7,11}$) 7.61 (1H, ddd, *J* = 8,7,1 Hz, Ar-**H**$_{12}$) 7.86 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 7.99 (1H, d, *J* = 9 Hz, Ar-**H**$_8$) 8.10 (2H, dd, *J* = 9,2 Hz, Ar-**H**$_3$) 8.43 (2H, dd, *J* = 9,2 Hz, Ar-**H**$_2$) 8.66 (1H, d, *J* = 9 Hz, Ar-**H**$_{13}$).

^{13}CNMR (75 MHz, $CDCl_3$) δ ppm 57.2 (CH_3), 114.2 (CH, Ar-H, **C**$_7$), 123.4 (CH, Ar-H, **C**$_{13}$), 123.1 (CH, Ar-H, **C**$_3$), 124.9 (CH, Ar-H, **C**$_{11}$), 128.7 (CH, Ar-H, **C**$_{10}$), 128.1 (CH, Ar-H, **C**$_{12}$), 124.7 (CH, Ar-H, **C**$_2$), 133.7 (CH, Ar-H, **C**$_8$), 129.2, 135.4, 148.4, 150.5, 156.9.

MS (ES+): m/z $[M+H]^+$ 308; $[M + Na]^+$ 330.

Accurate Mass: $C_{17}H_{14}N_3O_3$ requires 308.1030 found 308.1033.

2.6 Synthesis of (*E*)-1-(4-fluorophenyl)-2-(2-methoxy-1-naphthyl)diazene (28d):



Was prepared using general procedure C [1-[(*E*)-[(4-fluorophenyl)diazenyl]-2-naphthol (1.10 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol)] affording the *title compound* (0.70 g, 69%, **mp** 75-77 ˚C) as a dark red solid The crude was purified by column chromatography (SiO_2; eluent hexane/DCM 90%).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.05 (3H, s, CH_3) 7.28-7.34 (2H, m, Ar-**H**$_2$) 7.42-7.52 (2H, m, Ar-**H**$_{7,11}$) 7.58 (1H, ddd, *J*=8, 7, 1 Hz, Ar-**H**$_{12}$) 7.89 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 7.94 (1H, d, *J* = 9 Hz, Ar-**H**$_8$) 8.04-8.13 (2H, m, Ar-**H**$_3$) 8.41 (1H, d, *J* = 8 Hz).

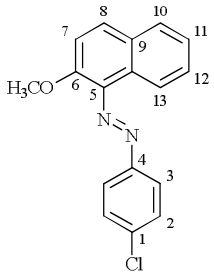
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 57.4 (CH_3, **C**$_{15}$), 114.6 (CH, Ar-H, **C**$_7$), 115.8 (CH, Ar-H, **C**$_2$), 123.1 (CH, Ar-H, **C**$_{13}$), 124.6 (CH, Ar-H, **C**$_3$), 127.7 (CH, Ar-H, **C**$_{12}$), 127.9 (CH, Ar-H, **C**$_{10}$), 124.9 (CH, Ar-H, **C**$_{11}$), 131.1 (CH, Ar-H, **C**$_8$), 116.1, 124.5, 124.5, 129.2, 136.2, 148.8.

MS (ES+): m/z $[M+H]^+$ 281; $[M + Na]^+$ 303.

Accurate Mass: $C_{17}H_{14}N_2FO$ requires 281.1085 found 281.1084.

IR ν_{max} (film): 1236, 1463, 1485.5, 1590, 1598, 2885, 3501 cm^{-1}.

2.7 Synthesis of (*E*)-1-(4-chlorophenyl)-2-(2-methoxy-1-naphthyl)diazene (28e):[27]



Was prepared using general procedure C [1-[(*E*)-[(4-chlorophenyl)diazenyl]-2-naphthol (1.16 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL,10 mmol)] affording the title compound (0.70 g, 69%; **mp** 66 °C, lit[27] 63.5-66 °C) as dark red solid. The crude product was purified by column chromatography (SiO_2; eluent hexane/DCM 90).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.01 (3H, s, CH_3) 7.41 (1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.46 (1H, t, *J* = 8 Hz, Ar-**H**$_{11}$) 7.53-7.58 (3H, m, Ar-**H**$_{2,12}$) 7.84 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 7.90 (1H, d, *J* = 9 Hz, Ar-**H**$_8$) 7.99 (2H, d, *J* = 8 Hz, Ar-**H**$_3$) 8.45 (1H, d, *J* = 9 Hz, Ar-**H**$_{13}$).

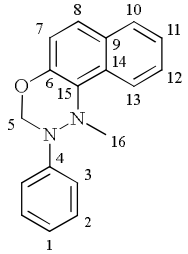
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 114.5 (CH_3), 123.1 (CH, Ar-H, **C**$_7$), 123.8 (CH, Ar-H, **C**$_{13}$), 123.8 (CH, Ar-H, **C**$_3$), 124.5 (CH, Ar-H, **C**$_{11}$), 127.8 (CH, Ar-H, **C**$_{10}$), 127.8 (CH, Ar-H, **C**$_{12}$), 129.2 (CH, Ar-H, **C**$_2$), 131.5 (CH, Ar-H, **C**$_8$).

MS (ES+): $C_{17}{}^{1}H_{14}N_2{}^{35}ClO$ m/z $[M+H]^+$ 297; $[M + Na]^+$ 319.

Accurate Mass: $C_{17}{}^{1}H_{14}N_2{}^{35}ClO$ requires 297.0789 found 297.079.

IR ν_{max} (film): 1244, 1465, 1581, 1595, 3067 cm^{-1}.

2.8 Synthesis of 1-methyl-2-phenyl-2,3-hydro-1H-napthol[1,2-e][1,3,4]oxadiazine (80):



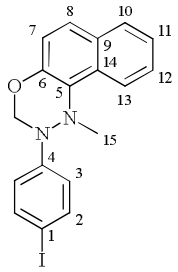
The *title compound* (0.307 mg, 27%, **mp** 69-70 °C) was obtained by using general procedure C, after column chromatography (SiO_2 gel; eluent hexane/DCM 60%) as light redish colour solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.30 (3H, s, CH_3) 5.35 (1H, d, *J* = 10 Hz, $OC\underline{H}_{5a}\underline{H}_{5b}$), CH_2 5.76 (1H, d, *J* = 10 Hz, $OCH_{5a}\underline{H}_{5b}$) 6.84-6.93 (1H, m, Ar-**H**$_1$) 7 (1H, d, *J* = 8 Hz, Ar-**H**$_7$) 7.15-7.26 (4H, m, Ar-**H**$_{2,3}$) 7.35-7.41 (1H, m, Ar-**H**$_{11}$) 7.45 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 7.51-7.60 (1H, m, Ar-**H**$_{12}$) 7.76 (1H, d, *J* = 8 Hz, Ar-**H**$_8$) 8.16 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 45.8 (CH_3, **C**$_{16}$), 71.6 (CH_2, **C**$_5$), 118.5 (CH, Ar-H, **C**$_3$), 118.7 (CH, Ar-H, **C**$_7$), 121.1 (CH, Ar-H, **C**$_{13}$), 123.2 (CH, Ar-H, **C**$_{11}$), 125.1 (CH, Ar-H, **C**$_{10}$), 126.2 (CH, Ar-H, **C**$_{12}$), 129.1 (CH, Ar-H, **C**$_8$), 129.9 (CH, Ar-H, **C**$_2$), 131.9 (CH, Ar-H, **C**$_1$), 122.6, 127.4, 129.4, 130.1, 142.9, 146.1.

IR ν_{max} (film): 1375, 1464, 1490, 1624, 3053 cm^{-1}.

2.9 Synthesis of 2-(4-iodophenyl)-1-methyl-2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine (80a):



Was prepared using general procedure C. Purification of the crude product by flash chromatography (SiO_2; eluent hexane: DCM 7:3) afforded the *title compound* (0.63 g, 32 % in yield) as light coloured crystalline solid (**mp** 146-148 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.27 (3H, s, CH_3) 5.31 (1H, d, *J* = 11 Hz, $OC\underline{H_a}H_b$) 5.70 (1H, d, *J* = 11Hz, $OCH_a\underline{H_b}$) 6.96-7.06 (3H, m, Ar-**H**$_{3,7}$) 7.39 (1H, td, *J* = 7, 1 Hz, Ar-**H**$_{12}$) 7.43-7.50 (3H, m, Ar-**H**$_{2,8}$) 7.56 (1H, td, *J* = 8 , 1 Hz, Ar-**H**$_{11}$) 7.76 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 8.11 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$).

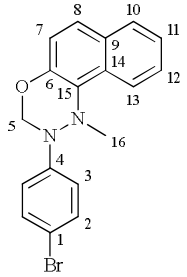
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 45.7 (CH_3), 70.3 (CH_2), 118.2 (CH, Ar-H, **C**$_7$), 118.9 (CH, Ar-H, **C**$_3$), 121.4 (CH, Ar-H, **C**$_{13}$), 123.8 (CH, Ar-H, **C**$_{11}$), 124.7 (CH, Ar-H, **C**$_8$), 126.2 (CH, Ar-H, **C**$_{12}$), 128.5 (CH, Ar-H, **C**$_{10}$), 137.8 (CH, Ar-H, **C**$_2$), 127.4, 128.1, 129.7, 142.9, 147.2.

Accurate Mass: $C_{18}H_{15}N_2IO$ requires 402.0224 found 402.0228.

Microanalysis: $C_{18}H_{15}N_2I$ requires C 53.75; H 3.76; N 6.96; I 31.55%. Found C 53.67; H 3.50; N 6.76; I 31.76%.

IR ν_{max} (film): 1475, 1576, 1588, 1599, 1622, 2956, 3000 cm^{-1}.

2.10 Synthesis of 2-(4-bromophenyl)-1-methyl-2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine (80b):



Was prepared using general procedure C. Purification of the crude product by flash chromatography (SiO_2; eluent hexane/DCM 7:3) afforded the *title compound* (481 mg, 33%) as light orange coloured crystalline solid (**mp** 137.4-139.4 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.18 (3H, s, CH_3) 5.23 (1H, d, *J* = 11 Hz, $\underline{CH_a}H_b$) 5.55 (1H, d, *J* = 11Hz, $CH_a\underline{H_b}$) 6.86 (1H, d, *J* = 9 Hz, Ar-$\mathbf{H}_7$) 7.04 (2H, dd, *J* = 9, 2 Hz, Ar-$\mathbf{H}_3$) 7.20 (2H, dd, *J* = 9,2 Ar-$\mathbf{H}_2$) 7.30 (1H, td, *J* = 7,1 Hz, Ar-$\mathbf{H}_{11}$) 7.37 (1H, d, *J* = 9.Hz, Ar-$\mathbf{H}_{10}$) 7.47 (1H, td, *J* = 8,1 Hz, Ar-$\mathbf{H}_{12}$) 7.67 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_3$) 8.02 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{13}$).

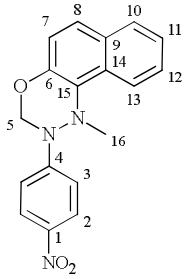
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 45.8 (CH_3), 70.5(CH_2), 118.2(CH, Ar-H, $\mathbf{C}_7$),118.5(CH, Ar-H, $\mathbf{C}_3$), 121.4(CH, Ar-H, $\mathbf{C}_{13}$),123.8(CH, Ar-H, $\mathbf{C}_{11}$), 124.7(CH, Ar-H, $\mathbf{C}_{10}$), 126.2(CH, Ar-H, $\mathbf{C}_{12}$), 128.6(CH, Ar-H, $\mathbf{C}_8$),131.9 (CH, Ar-H, $\mathbf{C}_2$), 114.1, 127.4, 128.2, 129.7, 143, 146.5.

Accurate Mass: $C_{18}H_{15}N_2{}^{79}BrO$ requires 354.0369 found 354.0369.

Microanalysis: $C_{18}H_{15}N_2{}^{79}Br$ requires C 60.86; H 4.26; N 7.89; Br 22.49%. Found C 60.91; H 4.10; N 7.67; Br 22.99%.

IR ν_{max} (film): 1473, 1483, 1578, 1595, 2884, 3637 cm^{-1}.

2.11 Synthesis of 2-(4-nitrophenyl)-1-methyl-2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine (80c):



Was prepared using general procedure C. Purification of the crude product by flash chromatography (SiO_2; eluent Hexane/DCM 2:8) afforded the *title compound* (0.343 g, 26%) as light orange coloured crystalline solid (**mp** 188.6-189.1 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.31 (3H, s, CH_3) 5.39 (1H, d, *J* = 11 Hz, $OC\underline{H_{5a}}H_{5b}$) 5.85 (1H, d, *J* = 11 Hz, $OCH_{5a}\underline{H_{5b}}$) 7.01 (1H, d, *J* = 9 Hz, Ar-$\mathbf{H}_7$) 7.35 (2H, dd, *J* = 9,2 Hz, Ar-$\mathbf{H}_3$) 7.41 (1H, td, *J* = 8,1 Hz, Ar-$\mathbf{H}_{11}$) 7.49 (1H, d, *J* = 9 Hz, Ar-$\mathbf{H}_8$) 7.58 (1H, td, *J* = 8,1 Hz, Ar-$\mathbf{H}_{12}$) 7.77 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{10}$) 8.06-8.16 (3H, d, Ar-$\mathbf{H}_{2,13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 45.61 (CH_3, $\mathbf{C}_{16}$), 69.3 (CH_2, $\mathbf{C}_5$), 115.5 (CH, Ar-H, $\mathbf{C}_3$), 118.1 (CH, Ar-H, $\mathbf{C}_8$), 125.4 (CH, Ar-H, $\mathbf{C}_2$), 121.2 (CH, Ar-H, $\mathbf{C}_{13}$), 128.7 (CH, Ar-H, $\mathbf{C}_{12}$), 126.5 (CH, Ar-H, $\mathbf{C}_{11}$), 127.3, 128.3, 128.7, 129.8, 142.8, 152.9.

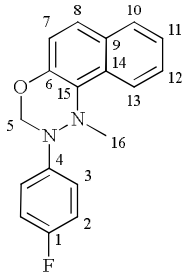
MS (ES+): m/z $[M + Na]^+$ 344.

Accurate Mass: $C_{18}H_{16}N_3O_3$ requires 322.1186 found 322.1189.

Microanalysis: $C_{18}H_{16}N_3$ requires C 67.1; H 4.7; N 13.0%. Found **C** 66.8; H 4.6; N 12.63%.

IR ν_{max} (film): 1316, 1465, 1495, 1591, 3052 cm^{-1}.

2.12 Synthesis of 2-(4-fluorophenyl)-1-methyl-2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine (80d):



Was prepared using general procedure C. Purification of the crude product by flash chromatography (SiO_2; eluent hexane/DCM 3:7) afforded the *title compound* (0.317 g, 26%) as light orange coloured crystalline solid (**mp** 144.5 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.28 (3H, s, CH_3) 5.33 (1H, d, *J* = 11 Hz, $OC\underline{H_{5a}}H_{5b}$) 5.66 (1H, d, *J* = 11 Hz, $OCH_{5a}\underline{H_{5b}}$) 6.75-6.93 (2H, m) 7.01 (1H, d, *J* = 9 Hz, Ar-$\mathbf{H}_7$) 7.09-7.21 (2H, m) 7.38 (1H, ddd, *J*=8, 7, 1 Hz, Ar-$\mathbf{H}_{11}$) 7.46 (1H, d, *J* = 9 Hz, Ar-$\mathbf{H}_8$) 7.55 (1H, ddd, *J*=8, 7, 1 Hz, Ar-$\mathbf{H}_{12}$) 7.76 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{10}$) 8.11 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{13}$).

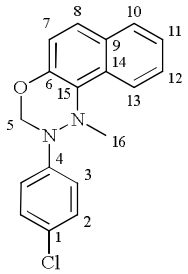
^{13}CNMR (300 MHz, $CDCl_3$) δ ppm 45.9 (CH_3, $\mathbf{C}_{16}$), 71.2 (CH_2, $\mathbf{C}_5$), 115.3 (CH, Ar-H, $\mathbf{C}_2$), 118.2 (CH, Ar-H, $\mathbf{C}_7$), 118.4 (CH, Ar-H, $\mathbf{C}_3$), 121.5 (CH, Ar-H, $\mathbf{C}_{13}$), 123.7 (CH, Ar-H, $\mathbf{C}_{11}$), 124.6 (CH, Ar-H, $\mathbf{C}_{10}$), 126.1 (CH, Ar-H, $\mathbf{C}_{12}$), 128.5 (CH, Ar-H, $\mathbf{C}_8$), 115.6, 118.3, 127.5, 128.2, 129.8, 143.1.

Accurate Mass: $C_{18}H_{15}N_2FO$ requires 294.1163 found 294.1162.

Microanalysis: $C_{18}H_{15}N_2$ requires C 73.45; H 5.14; N 9.52%. Found C 73.98; H 4.95; N 9.49%.

IR ν_{max} (film): 1237, 1477, 1574, 1619 cm^{-1}.

2.13 Synthesis of 2-(4-chlorophenyl)-1-methyl-2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine (80e):



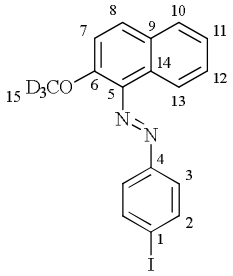
Was prepared using general procedure C. Purification of the crude product by flash chromatography (SiO_2; gradient elution hexane : DCM 6:4 to 5:5) afforded the *title compound* (0.89 g, 29%) as light yellow coloured crystalline solid **(mp** 125-126 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.29 (3H, s, CH_3) 5.33 (1H, d, *J* = 11 Hz, $OC\underline{H_{5a}}H_{5b}$) 5.70 (1H, d, *J* = 11 Hz, $OCH_{5a}\underline{H_{5b}}$) 7.03 (1H, d, *J* = 9 Hz, Ar-$\mathbf{H}_7$) 7.11-7.24 (4H, m, Ar-$\mathbf{H}_{2,3}$) 7.41 (1H, t, *J*=8 Hz, Ar-$\mathbf{H}_{11}$) 7.48 (1H, d, *J* = 9 Hz, Ar-$\mathbf{H}_8$) 7.58 (1H, t, *J* = 8 Hz, Ar-$\mathbf{H}_{12}$) 7.78 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{10}$) 8.14 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 45.8 (CH_3, $\mathbf{C}_{16}$), 70.6(CH_2, $\mathbf{C}_5$), 118 (CH, Ar-H, $\mathbf{C}_3$), 118.2(CH, Ar-H, $\mathbf{C}_7$), 121.4(CH, Ar-H, $\mathbf{C}_{13}$), 123.1(CH, Ar-H, $\mathbf{C}_{11}$), 124.7(CH, Ar-H, $\mathbf{C}_8$), 126.1(CH, Ar-H, $\mathbf{C}_{11}$), 128.5(CH, Ar-H, $\mathbf{C}_{10}$), 128.9(CH, Ar-H, $\mathbf{C}_2$), 126.7, 127.4, 128.1, 129.7, 142.9, 146.

IR ν_{max} (film): 1372, 1464, 1487, 1594, 1737, 3051 cm^{-1}.

2.14 Synthesis of (*E*)-1-(4-iodophenyl)-2-(2-methoxynaphthalen-1-yl)diazene (97a):



Was prepared using general procedure C [1-[(*E*)-[(4-iodophenyl)diazenyl]-2-naphthol (0.387 g), KOH (0.29 g, 5.17mmol), deuterated methyl iodide (0.15 mL, 10 mmol)] affording the *title compound* (0.251 g, 62%) as dark red solid. The crude was purified by column chromatography (SiO_2; eluent hexane/DCM 30%, **mp** 77-79 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.35-7.47 (2H, m, Ar-**H**$_{7,11}$) 7.50-7.60 (1H, m, Ar-**H**$_{12}$) 7.75 (2H, d, *J* = 8 Hz, Ar-**H**$_2$) 7.83 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 7.88-7.96 (3H, m, Ar-**H**$_{3,8}$) 8.43 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$).

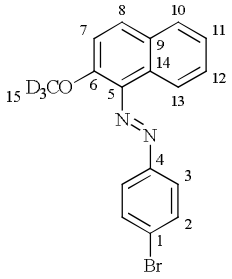
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 114.5 (CH, Ar-H, **C**$_7$), 123.2 (CH, Ar-H, **C**$_{13}$), 124.2 (CH, Ar-H, **C**$_3$), 124.5 (CH, Ar-H, **C**$_{11}$), 127.9 (CH, Ar-H, **C**$_{12}$), 131.7 (CH, Ar-H, **C**$_8$), 138.3 (CH, Ar-H, **C**$_2$), CD_3(not visible), 97.3, 129.5, 128.5, 135.8, 148.8, 152.9.

MS (ES+): m/z $[M+H]^+$ 392; $[M + Na]^+$ 414.

Accurate Mass: $C_{17}H_{11}{}^2H_3N_2IO$ requires 407.0546 found 407.0538.

IR υ_{max} (film): 1465, 1483, 1562, 1578, 1738, 2068, 3006 cm^{-1}.

2.15 Synthesis of (*E*)-1-(4-bromophenyl)-2-(2-methoxynaphthalen-1-yl)diazene (97b):



Was prepared using general procedure C [1-[(*E*)-[(4-bromophenyl)diazenyl]-2-naphthol (0.3 g, 10 mmol), KOH (0.29 g, 5.17 mmol), deuterated methyl iodide (0.15 mL, 10 mmol)] affording the *title compound* (0.213 g, 60%; **mp** 77 ˚C) as dark red solid. The crude was purified by column chromatography (SiO_2; eluent hexane/DCM 30%).

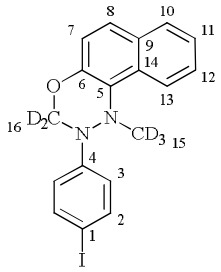
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.13 (1H, dd, *J* = 9,1 Hz, Ar-**H**$_7$) 7.27 (1H, d, *J* = 9 Hz Ar-**H**$_8$) 7.34 (1H, td, *J* = 8,1 Hz, Ar-**H**$_{11}$) 7.41-7.58 (3H, m, Ar-**H**$_{2,13}$) 7.68-7.78 (3H, m, Ar-**H**$_{3,10}$), 8.30(1H,d,J = 8 Hz, Ar-**H**$_{13}$).

^{13}C NMR(75 MHz, $CDCl_3$) δ ppm 114.5 (CH, Ar-H, **C**$_7$), 123.2 (CH, Ar-H, **C**$_{13}$), 124.1 (CH, Ar-H, **C**$_3$), 124.5 (CH, Ar-H, **C**$_{11}$), 127.9 (CH, Ar-H, **C**$_{10}$), 128.58(CH, Ar-H, **C**$_{12}$), 132.3 (CH, Ar-H, **C**$_2$), 135.9 (CH, Ar-H, **C**$_8$), CD_3 (not visible), 125.2, 129.1, 131.6, 131.2, 146.5, 148.8.

Accurate Mass: $C_{17}H_{11}{}^{2}H_3N_2BrO$ requires 344.0472 found 344.0475.

IR ν_{max}(film): 1435, 1481, 1562, 1610, 3035 cm^{-1}.

2.16 Synthesis of 2-(4-iodophenyl)-1-methyl-2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine-2 (98a):



Was prepared using general procedure C. Purification of the crude product by flash chromatography (SiO_2; eluent hexane/DCM 7:3) afforded the *title compound* (0.131 g, 31%) as light orange coloured crystalline solid (**mp** 145-146 ˚C).

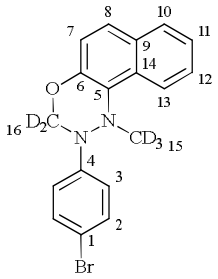
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 6.94-7.05 (3H, m, Ar-**H**$_{3,7}$) 7.33-7.41 (1H, m, Ar-**H**$_{11}$) 7.46 (3H, m, Ar-**H**$_{2,8}$) 7.55 (1H, t, *J* = 7 Hz, Ar-**H**$_{12}$) 7.76 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 8.10 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 118.2 (CH, Ar-H, **C**$_7$), 118.9 (CH, Ar-H, **C**$_3$), 121.4 (CH, Ar-H, **C**$_{13}$), 123.8 (CH, Ar-H, **C**$_{11}$), 124.7 (CH, Ar-H, **C**$_8$), 126.2 (CH, Ar-H, **C**$_{12}$), 128.6 (CH, Ar-H, **C**$_{10}$), (CD_2, CD_3; not visible), 137.8 (CH, Ar-H, **C**$_2$), 120.6, 127.3, 142.2, 145.9, 147.3, 147.6.

Accurate Mass: $C_{18}H_{10}{}^2H_5N_2IO$ requires 407.0546 found 407.0538.

IR ν_{max}(film): 1253, 1370, 1459, 1487, 1569, 3002cm^{-1}.

2.17 Synthesis of 2-(4-iodophenyl)-1-methyl-2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine-2 (98b):



Was prepared using general procedure C. Purification of the crude product by flash chromatography (SiO_2; eluent hexane/DCM 7:3) afforded the *title compound* (0.100 mg, 30%) as light coloured crystalline solid (**mp** 135-137 °C).

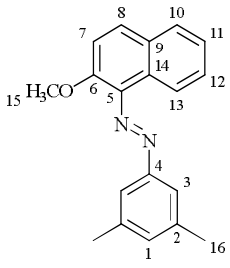
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 6.9(1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.03 (2H, dd, *J* = 9,2 Hz, Ar-**H**$_3$) 7.19 (2H, dd, *J* = 9,2 Hz, Ar-**H**$_2$) 7.29 (1H, td, *J* = 8,1 Hz, Ar-**H**$_{11}$) 7.36 (1H, d, *J* = 9 Hz, Ar-**H**$_{10}$) 7.46 (1H, td, *J* = 8,1 Hz, Ar-**H**$_{12}$) 7.66 (1H, d, *J* = 8 Hz, Ar-**H**$_8$) 8.01 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 118.2 (CH, Ar-H, **C**$_7$), 118.4 (CH, Ar-H, **C**$_3$), 121.4 (CH, Ar-H, **C**$_{13}$), 123.8 (CH, Ar-H, **C**$_{11}$), 124.7 (CH, Ar-H, **C**$_{10}$), 126.1 (CH, Ar-H, **C**$_{12}$), 128.5 (CH, Ar-H, **C**$_8$), 131.8 (CH, Ar-H, **C**$_2$), CD_2 and CD_3 (not visible), 114.1, 127.3, 128.1, 129.7, 142.9, 146.5.

Accurate Mass: $C_{18}H_{10}{}^2H_5N_2{}^{81}BrO$ requires 361.0644 found 361.0656.

IR ν_{max}(film): 1438, 1462, 1481, 1577, 3026 cm^{-1}.

2.18 Synthesis of (*E*)-1-(3,5-dimethylphenyl)-2-(2-methoxynaphthalen-1-yl)diazene (99):



Was prepared using general procedure C [1-[(*E*)-[(2-bromophenyl)diazenyl]-2-naphthol (1.15 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol)] affording the *title compound* (1.94 g, 67%, **mp** 68 °C) as a dark red solid. The crude was purified by column chromatography (SiO_2; eluent hexane/DCM 40%).

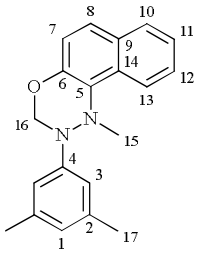
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.49 (6 H, s, CH_3) 4.01 (3H, s, OCH_3) 7.20 (1H, s, Ar-**H**$_1$) 7.41 (1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.45 (1H, d, *J* = 7 Hz, Ar-**H**$_{10}$) 7.54 (1H, t, *J* = 7 Hz, Ar-**H**$_{11}$) 7.70 (2H, s, Ar-**H**$_3$) 7.87 (2H, m, Ar-**H**$_{8,12}$) 8.38 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.2 (CH_3), 57.3 (OCH_3), 114.6 (CH, Ar-H, **C**$_7$), 120.4 (CH, Ar-H, **C**$_3$), 123.1 (CH, Ar-H, **C**$_{13}$), 124.3 (CH, Ar-H, **C**$_{11}$), 127.5 (CH, Ar-H, **C**$_{12}$), 127.7 (CH, Ar-H, **C**$_{10}$), 130.5 (CH, Ar-H, **C**$_8$), 132.5 (CH, Ar-H, **C**$_1$), 128.1, 129.1, 136.6, 137.4, 148.3, 153.6.

Accurate Mass: $C_{19}H_{18}N_2ONa$ requires 313.1311 found 313.1313.

IR υ_{max} (film): 1468, 1508, 2030, 2913, 3036 cm^{-1}.

2.19 Synthesis of 2-(3,5-dimethylphenyl)-1-methyl-2,3-dihydro-1H-naphtho[1,2-e][1,3,4]oxadiazine (100):



Was prepared using general procedure C. Purification of the crude product by flash chromatography (SiO_2; eluent hexane/DCM 6:4) afforded the *title compound* (0.400 mg, 32%) as light coloured crystalline solid (**mp** 154-155 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.22 (6H, s, CH_3,**H**$_{17}$) 3.28 (3H, s, CH_3,**H**$_{15}$) 5.31 (1H, d, *J* = 11 Hz, C$\underline{H}_a$H$_b$, **H**$_{16}$) 5.76 (1H, d, *J* = 11 Hz, CH$_a\underline{H}_b$,,**H**$_{16}$) 6.55 (1H, s, Ar-**H**$_1$) 6.89 (2H, s, Ar-**H**$_3$) 7.02 (1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.38 (1H, t, *J* = 8 Hz, Ar-**H**$_{11}$) 7.45 (1H, d, *J* = 9 Hz, Ar-**H**$_8$) 7.50 - 7.61 (1H, m, Ar-**H**$_{12}$) 7.76 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 8.16 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$).

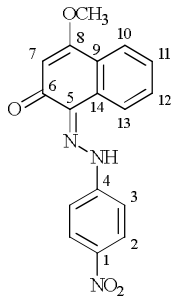
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 21.6 (**C**$_{17}$), 45.9 (CH, Ar-H, **C**$_{15}$), 70.6 (CH, Ar-H, **C**$_{16}$), 114.2 (CH, Ar-H, **C**$_7$), 118.4 (CH, Ar-H, **C**$_3$), 121.7 (CH, Ar-H, **C**$_{13}$), 123.5 (CH, Ar-H, **C**$_{11}$), 124.3 (CH, Ar-H, **C**$_{10}$), 125.9 (CH, Ar-H, **C**$_{12}$), 128.4 (CH, Ar-H, **C**$_8$), 138.6 (CH, Ar-H, **C**$_1$), 123, 128, 128.2, 129.7, 143.1, 147.7.

Accurate Mass: $C_{19}H_{18}N_2ONa$ requires 313.1311 found 313.1313.

Microanalysis: $C_{19}H_{18}N_2$ requires C 78.92; H 6.62; N 9.2%. Found **C** 78.67; H 6.71; N 8.82%.

IR ν_{max} (film): 1376, 1393, 1461, 1579, 1595, 2851,3009 cm^{-1}.

2.20 Synthesis of 4-methoxynaphthalene-1,2-one-1-[4-nitrophenyl)hydrazone] (101):[80]



The *title compound* (0.501, 38%) was obtained using general procedure C and purified by using column chromatography (SiO_2; gradient elution hexane: DCM 9:1 to 8:2) as red solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.04 (3H, s,OCH_3) 6.06 (1H, s, Ar-**H**$_7$) 7.46 (1H, td, *J* = 8,1 Hz, Ar-**H**$_{12}$) 7.53-7.67 (3H, m, Ar-**H**$_{3,11}$) 7.96 (1H, d, *J* = 7 Hz, Ar-**H**$_{10}$) 8.30 (2H, d, *J* = 9 Hz, Ar-**H**$_2$) 8.37 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$), 15.96 (1H, br. s., NH).

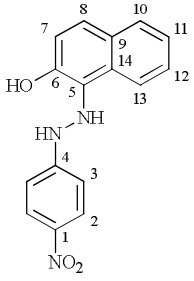
^{13}C NMR(300MHz, CDCl3) δ ppm 56.4 (OCH_3), 102.4 (CH, Ar-H, **C**$_7$), 130.5 (CH, Ar-H, **C**$_{13}$), 115.4 (CH, Ar-H, **C**$_3$), 125.7 (CH, Ar-H, **C**$_2$), 123.6 (CH, Ar-H, **C**$_{10}$), 122.6 (CH, Ar-H, **C**$_{12}$), 127.5 (CH, Ar-H, **C**$_{11}$), 125.06, 125.18, 130.74, 132.98, 143.59, 147.97, 167.02, 182.4.

MS (ES+): m/z $[M + Na]^+$ 346.

Accurate Mass: $C_{17}H_{13}N_3O_4Na$ requires 346.0840 found 346.0799.

IR ν_{max} (film): 1209, 1436, 1589, 3855 cm^{-1}.

2.21 Synthesis of 1-(2-methoxynaphthalen-1-yl)-2-(4-nitrophenyl)hydrazine (102):



The *title compound* (0.065 g, 39%).was prepared using general procedure C6 [DMSO (7 mL), sodium hydride (0.5 g), diazo compound (0.147 g), methyl iodide (0.06 mL)]. After column chromatography the *title compound* could be purified (SiO_2 gel; gradient elution hexane : DCM 8:2 to 6:4; **mp** 165 °C).

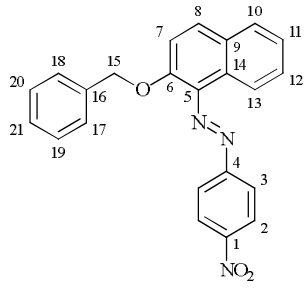
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.05 (2H, br. s., NH) 6.79 (2H, d, *J* = 8 Hz, Ar-**H**$_3$) 7.11 (1H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.41 (1H, t, *J* = 7 Hz, Ar-**H**$_{11}$) 7.58 (1H, t, *J* = 7 Hz, Ar-**H**$_{12}$) 7.68-7.87 (4H, m, Ar-**H**$_{2,8,10}$) 8.78 (1H, d, *J* = 8 Hz, Ar-**H**$_{13}$) 15.56 (1H, s, OH).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 115.1 (CH, Ar-H, **C**$_3$), 121.3 (CH, Ar-H, **C**$_7$), 121.6 (CH, Ar-H, **C**$_{13}$), 123.1 (CH, Ar-H, **C**$_2$), 124.4 (CH, Ar-H, **C**$_{11}$), 127.7 (CH, Ar-H, **C**$_{12}$), 128.1 (CH, Ar-H, **C**$_{10}$), 135.08 (CH, Ar-H, **C**$_8$), 128.3, 129.2, 133.1, 141, 148.4, 157.8.

MS (ES+): m/z $[M + Na]^+$ 318.

IR ν_{max} (film): 1327, 1497, 1578, 2158, 3061 cm^{-1}.

2.22 Synthesis of (*E*)-1-(2-(benzyloxy)naphthalene-1-yl)-2-(4-nitrophenyl)diazene: (103)



To a stirred mixture of powdered potassium hydroxide (1.16 g, 20.7 mmol), diazo compound (1.21 g, 4.14 mmol) in DMSO (10 mL), benzyl bromide (0.8 mL) was added to the mixture. The reaction mixture was stirred for 5 hours at room temperature, and then poured it into water. The organic layer was extracted with diethyl ether or dichloromethane and then

washed it with brine, dried over $MgSO_4$, and reduced *in vacuo*. The residue was crystallised with ethanol and petroleum ether (1.41 g, 93%).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 5.36 (2H, s, CH_2, **H**$_{15}$) 7.31-7.41 (3H, m, CH, Ar-**H**$_{12,17,18}$) 7.43-7.53 (4H, m, CH, Ar-**H**$_{7,19,20,21}$) 7.62 (1H, ddd, *J*= 8, 7, 1 Hz, CH, Ar-**H**$_{11}$) 7.86 (1H, d, *J*= 8 Hz, CH, Ar-**H**$_{10}$) 7.95 (1 H, d, *J*= 9 Hz, CH, Ar-**H**$_8$) 8.08 (2H, dd, *J*=9, 2 Hz, CH, Ar-**H**$_3$) 8.42 (2H, dd, *J*=9, 2 Hz, CH, Ar-**H**$_2$) 8.66 (1H, d, *J*= 9 Hz, CH, Ar-**H**$_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 72.4 (CH_2, **C**$_{15}$), 116.3 (CH, Ar-H, **C**$_7$), 123 (CH, Ar-H, **C**$_{13}$), 123.5 (CH, Ar-H, **C**$_3$), 124.8 (CH, Ar-H, **C**$_2$), 125 (CH, Ar-H, **C**$_{12}$), 127 (CH, Ar-H, **C**$_{19,20,21}$), 128 (CH, Ar-H, **C**$_{11}$), 128.1 (CH, Ar-H, **C**$_{10}$), 128.5 (CH, Ar-H, **C**$_{17,18}$), 133.4 (CH, Ar-H, **C**$_8$), 129.4, 129.8, 136.6, 148.8.

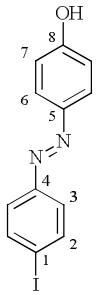
MS (ES+): m/z $[M+H]^+$ 384 $[M + Na]^+$ 406.

Accurate Mass: $C_{23}H_{17}N_3O_3Na$ requires 406.1153 found 406.1163.

Microanalysis: $C_{23}H_{17}N_3$ requires C 72; H 4.47; N 10.96%. Found C 71.81; H 4.33; N 10.78%.

3 SYNTHESIS OF DIAZO PHENOL COMPOUNDS

3.1 Synthesis of 4-[(*E*)-(iodophenyl)diazenyl]phenol (104a):[82]



Was prepared using general procedure B [4-iodoaniline (2.19 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), phenol (0.94 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound, (3.0 g, 92%; **mp** 164.5-166ºC, lit[82b] 167 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 5.45 (1H, br. s., OH) 6.95 (2H, d, *J* = 9 Hz, CH, Ar-**H**$_7$) 7.62 (2H, d, *J* = 8 Hz, CH, Ar-**H**$_3$) 7.79-7.92 (4H, m, CH, Ar-**H**$_{2,6}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 115.8 (CH, Ar-H, **C**$_7$), 124.2(CH, Ar-H, **C**$_3$), 125.1(CH, Ar-H, **C**$_6$), 138.26 (CH, Ar-H, **C**$_2$), 96.7, 147, 152, 158.5

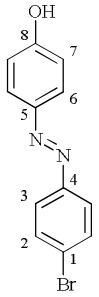
MS (ES+): m/z $[M+H]^+$ 325 $[M + Na]^+$ 346.9.

Accurate Mass: $C_{12}H_{10}N_2IO$ requires 324.9832 found 324.982.

Microanalysis:$C_{12}H_{10}N_2$ requires C 44.1; H 2.8; N 8.64; I 38.91%. Found C 43.1; H 2.7; N 8.2%.

IR ν_{max} (film): 783, 824, 1246, 1440, 1466, 1563, 1590.5, 2045, 3008 cm^{-1}.

3.2 Synthesis of 4-[(*E*)-(bromophenyl)diazenyl]phenol (104b):[83]



Was prepared using general procedure B [4-bromoaniline (1.72 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), phenol (0.94 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the *title compound*, (2.4 g, 87.2%; **mp** 168.4-170.1ºC, lit[83b] 155 ºC) as red solid.

^{1}H NMR (300 MHz, *$CDCl_3$*) δ ppm 5.39 (1H, s, OH) 6.96 (2H, dd, *J*=9,2 Hz, Ar-**H_7**) 7.64 (2H, dd, *J* = 9,2 Hz, Ar-**H_2**) 7.76 (2H, dd, *J* = 9,2 Hz, Ar-**H_6**) 7.88 (2H, dd, *J* = 9,2 Hz, Ar-**H_3**).

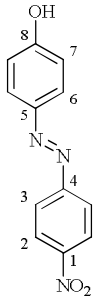
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 115.8 (CH, Ar-H, C_7), 124.1 (CH, Ar-H, C_6), 125.1 (CH, Ar-H, C_3), 132.2 (CH, Ar-H, C_2), 98.2, 146.9, 151.4, 158.6.

MS (ES+): $C_{12}H_8N_2{}^{79}BrO$ m/z $[M+H]^+$ 301; $[M + Na]^+$ 323.9.

Accurate Mass: $C_{12}H_8N_2{}^{79}BrO$ requires 274.9816 found 274.9825; $C_{12}H_8N_2{}^{81}BrO$ requires 276.9796 found 276.9805.

IR ν_{max} (film): 1476, 1587, 1592, 2060, 3168 cm^{-1}.

3.3 Synthesis of (*E*)-2-(4-nitrophenyl)diazenyl)phenol (104c):[86]



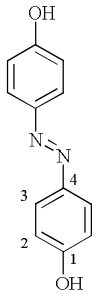
Was prepared using general procedure B [4-nitrophenol (1.39 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), phenol (0.94 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound, dark brown in colour (2.23 g, 92%; **mp** 195 °C, lit[83b] 210 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 5.39 (1H, s, OH) 6.94 (2H, dd, *J* = 9,2 Hz, Ar-**H_7**) 7.76 (2H, dd, *J* = 9,2 Hz, Ar-**H_6**) 7.89 (2H, dd, *J* = 9,2 Hz, Ar-**H_3**) 8.31 (2H, dd, *J* = 9,2 Hz, Ar-**H_2**).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 116.2 (CH, Ar-H, C_7), 124.4 (CH, Ar-H, C_6), 124.9 (CH, Ar-H, C_3), 131.1(CH, Ar-H, C_2), 146.2, 148.9, 152.3, 160.6.

IR ν_{max} (film): 1335, 1440, 1476, 1548, 1579, 3101 cm^{-1}.

3.4 Synthesis of (*E*)-4,4'-(diazene-1,2-yl)diphenol (104d):[87]



Was prepared using general procedure B2 [4-Hydroxyaniline (10 mmol), $NaNO_2$ (18 mL, 0.05 M), NaOH (0.45 g, 2 M, 80 mmol), phenol (0.94 g, 10mmol), HCl (40 mL, 3.5 M, 26 mmol), ethanol (200 mL)] affording the title compound (1.94 g, 91%), dark brown in colour (**mp** 205-207 ˚C, lit[85] 218 ˚C).

^{1}H NMR (300 MHz, CD_3OD) δ ppm 6.89 (4H, d, *J* = 8 Hz, Ar-**H_2**) 7.74 (4H, d, *J* = 8 Hz, Ar-**H_3**).

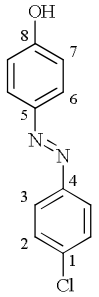
^{13}C NMR (75 MHz, CD_3OD) δ ppm 116.7 (CH, Ar-H, **C_2**), 125.4 (CH, Ar-H, **C_3**), 147.71, 161.35.

MS (ES+): m/z $[M+H]^+$ 215; **(ES-):** m/z $[M-H]^+$ 214.

Accurate Mass: $C_{12}H_9N_2O_2$ requires 213.0669 found 213.0670.

IR ν_{max} (film): 1356, 1499, 1585, 3078, 3501 cm^{-1}.

3.5 Synthesis of 4-[(*E*)-(chlorophenyl)diazenyl]phenol (104e):[88]



Was prepared using general procedure B [4-chloroaniline (1.72 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), phenol (0.94 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound as dark red solid (2.4 g, 87%; **mp** 159-161ºC, lit[83b] 160 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 5.91 (1H, br. s., OH) 6.95 (2H, d, *J* = 8 Hz, Ar-**H**$_7$) 7.47 (2H, d, *J* = 8 Hz, Ar-**H**$_2$) 7.85 (4H, dd, *J* = 12, 8 Hz, Ar-**H**$_{3,6}$).

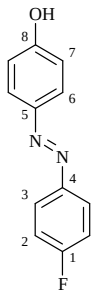
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 115.8 (CH, Ar-H, C_7),123.8 (CH, Ar-H, C_6), 125.1 (CH, Ar-H, C_3),129.2 (CH, Ar-H, C_2), 158.86, 151.05, 146.92, 136.20.

MS (ES+): $C_{12}H_{10}N_2{}^{35}ClO$ m/z $[M+H]^+$ 233 $[M + Na]^+$ 255 **(ES-):** [M - H] 231.

Accurate Mass: $C_{12}H_{10}N_2{}^{35}ClO$ requires 233.0477 found 233.0469.

IR ν_{max} (film): 1474, 1575, 1587, 3179 cm^{-1}.

3.6 Synthesis of 4-[(*E*)-(flourophenyl)diazenyl]phenol (104f):[89]



Was prepared using general procedure B [4-flouroaniline (1.10 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), phenol (0.94 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound as red solid (2.01 g, 93%, **mp** 158.2-159.4 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 5.47 (1 H, br. s., OH) 6.95 (2H, d, *J* = 8 Hz, Ar-**H**$_7$) 7.19 (2H, t, *J* = 8 Hz, Ar-**H**$_2$) 7.82-7.94 (4H, m, Ar-**H**$_{3,6}$).

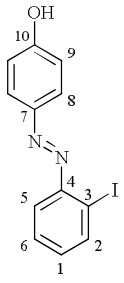
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 115.8 (CH, Ar-H, **C**$_2$), 116.1 (CH, Ar-H, **C**$_7$), 124.4 (CH, Ar-H, **C**$_6$), 124.9 (CH, Ar-H, **C**$_3$), 165.6, 162.3, 146.9, 149.1.

MS (ES+): m/z [M + H] 217;**(ES-):** m/z [M - H] 215.

Accurate Mass: $C_{12}H_8N_2FO$ requires 215.0628 found 215.0626.

IR ν_{max} (film): 1463, 1497, 1582, 1603, 3158 cm^{-1}.

3.7 Synthesis of 2-[(*E*)-(iodophenyl)diazenyl]phenol (105a):[30]



Was prepared using general procedure B [2-iodoaniline (2.19 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), phenol (0.94 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound (2.9 g, 89 %, **mp** 65.0-66.4 ºC) as red solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 6.96 (2H, d, *J* = 9 Hz, Ar-**H**$_9$) 7.13 (1H, t, *J* = 7 Hz, Ar-**H**$_1$) 7.41 (1H, t, *J* = 7 Hz, Ar-**H**$_6$) 7.60 (1H, d, *J* = 9 Hz, Ar-**H**$_5$) 7.95 (2H, d, *J* = 9 Hz, Ar-**H**$_8$) 8.01 (1H, d, *J* = 7 Hz, Ar-**H**$_2$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 115.9 (CH, Ar-H, **C**$_9$), 117.2 (CH, Ar-H, **C**$_5$), 125.7 (CH, Ar-H, **C**$_6$), 128.8 (CH, Ar-H, **C**$_6$), 131.5 (CH, Ar-H, **C**$_1$), 139.6 (CH, Ar-H, **C**$_2$), 158.8, 101.8, 146.8, 151.2, 164.3.

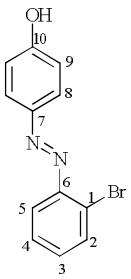
MS (ES+): m/z $[M+H]^+$ 325.1 $[M + Na]^+$ 347.

Accurate Mass: $C_{12}H_{10}N_2IO$ requires 324.9832 found 324.9847.

Microanalysis: $C_{12}H_{10}N_2$ requires C 43.1; H 2.8; N 8.64%. Found **C** 42, H 2.9; N 8.1; I 35.79%.

IR ν_{max} (film): 1452, 1503, 1586, 3052, 3519 cm^{-1}.

3.8 Synthesis of 2-[(*E*)-(bromophenyl)diazenyl]phenol (105b):[90]



Was prepared using general procedure B [2-bromoaniline (1.72 g, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), phenol (0.94 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] as red solid affording the title compound, (2.2 g, 85.2%).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.61 (1H, br. s., OH) 6.95 (2H, d, *J* = 9 Hz, Ar-**H**$_9$) 7.28 (1H, td, *J* = 8,1 Hz, Ar-**H**$_4$) 7.38 (1H, td, *J* = 8, 1 Hz, Ar-**H**$_3$) 7.64 (1H, dd, *J* = 8, 2 Hz, Ar-**H**$_2$) 7.74 (1H, dd, *J*= 8, 1 Hz, Ar-**H**$_5$) 7.94 (2H, d, *J* = 9 Hz, Ar-**H**$_8$).

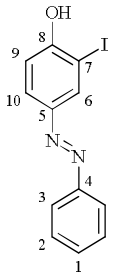
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 115.9 (CH, Ar-H, C_9), 117.7 (CH, Ar-H, C_5), 125.6 (CH, Ar-H, C_8), 127.9 (CH, Ar-H, C_3), 131.2 (CH, Ar-H, C_4), 133.6 (CH, Ar-H, C_5), 149.6, 147.2, 158.9, 125.

MS (ES+): $_{12}H_8N_2{}^{79}BrO$ m/z $[M+H]^+$ 277.

Accurate Mass: $C_{12}H_8N_2{}^{79}BrONa$ requires 298.9791 found 298.9796.

IR ν_{max} (film): 750, 837, 1143, 1250, 1457, 1588, 3058 cm^{-1}.

3.9 Synthesis of 2-iodo-4-[(*E*)-phenyldiazenyl]phenol (106):[84]



Was prepared using general procedure B [aniline (0.94 g, 10 mmol), $NaNO_2$ (10 mL), NaOH (0.45 g, 2 M), $NaNO_2$ (10 mL), 2-iodophenol (2.19 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the *title compound* as dark brown crystals (3.1 g, 93%, **mp** 76.9-78.2 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 5.74 (1H, br. s., OH) 7.13 (1H, d, *J* = 8 Hz, Ar-**H**$_9$) 7.41-7.59 (3H, m, Ar-**H**$_{1,2}$) 7.80-7.98 (3H, m, Ar-**H**$_{3,10}$) 8.30 (1H, s, Ar-**H**$_6$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 114.9 (CH, Ar-H, **C**$_9$), 122.7 (CH, Ar-H, **C**$_3$), 126.2 (CH, Ar-H, **C**$_{10}$), 129.1 (CH, Ar-H, **C**$_2$), 130.8 (CH, Ar-H, **C**$_1$), 132.1 (CH, Ar-H, **C**$_6$), 86.2, 147.6, 152.4, 157.1.

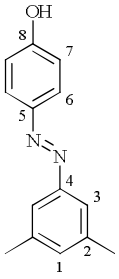
MS (ES+): m/z $[M + H]^+$ 325.1 $[M + Na]^+$ 346.9.

Accurate Mass: $C_{12}H_{10}N_2IO$ requires 324.9832 found 324.9829.

Microanalysis: $C_{12}H_{10}N_2$ requires C 44.4; H 2.8; N 8.64; I 39.15%. Found C 43.63; H 3.49; N 8.9%.

IR υ_{max} (film): 1408, 1564, 2169, 3054, 3262 cm^{-1}.

3.10 Synthesis of (*E*)-2-((3,5-dimethylphenyl)diazenyl)phenol (107):[85]



Was prepared using general procedure B [3,5-dimethylaniline (10 mmol, 1.3 mL), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), phenol (0.94 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound (3.03 g, 93%; oil, yellow in colour).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.42 (6H, s, CH_3) 5.23 (1H, br. s., OH) 6.94 (2H, d, *J* = 8 Hz, CH, Ar-**H**$_7$) 7.10 (1H, s, CH, Ar-**H**$_1$) 7.51 (2H, s, CH, Ar-**H**$_3$) 7.87 (2H, d, *J* = 8 Hz, CH, Ar-**H**$_6$).

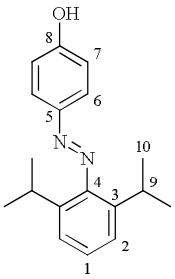
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 22.3 (CH_3), 116.4 (CH, Ar-H, **C**$_7$), 120.9 (CH, Ar-H, **C**$_3$), 123.9 (CH, Ar-H, **C**$_6$), 132.1 (CH, Ar-H, **C**$_1$), 138.9, 147.2, 152, 161.

MS (ES+): m/z $[M+H]^+$ 227; **(ES-):** m/z [M-H] 225.

Accurate Mass: $C_{14}H_{13}N_2O$ requires 225.1033 found 225.1031.

IR ν_{max}(film): 1423, 1587, 1599, 3046 cm^{-1}.

3.11 Synthesis of (*E*)-4-(2,6-*iso*-propylphenyl)diazenyl)phenol (108):



Was prepared using general procedure B [3,6-di*iso*-propylaniline (1.8 mL, 10 mmol), $NaNO_2$ (10 mL, 1 M), NaOH (0.45 g, 2 M, 40 mmol), phenol (0.94 g, 10 mmol), HCl (13 mL, 2 M, 26 mmol), Na_2CO_3 (2.5 g)] affording the title compound (2.7 g, 96%, **mp** 160-161 ˚C) dark brown in colour.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.19 (12H, d, *J*=6 Hz, CH_3, **H**$_{10}$) 3.03 (2H, quin, *J* = 6 Hz, CH, **H**$_9$) 6.98 (2H, d, *J* = 8 Hz, Ar-**H**$_7$) 7.17-7.32 (3H, m, Ar-**H**$_{1,2}$) 7.87 (2 H, d, *J* = 8 Hz, Ar-**H**$_6$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 23.4 (CH_3, C_{10}), 27.7 (CH, C_9), 115.7 (CH, Ar-H, C_7), 123.4 (CH, Ar-H, C_1), 124.7 (CH, Ar-H, C_2), 127.3 (CH, Ar-H, C_6), 139.3, 147.1, 151.2, 158.5.

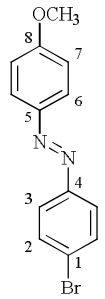
MS (ES+): m/z $[M+H]^+$ 283; **(ES-):** m/z [M-H] 281.

Accurate Mass: $C_{18}H_{21}N_2O$ requires 281.1659 found 281.1652.

IR ν_{max} (film): 1437, 1458, 1591, 2927, 3132 cm^{-1}.

4 SYNTHESIS OF METHYLATED DIAZO PHENOL COMPOUNDS

4.1 Synthesis of (*E*)-1-(4-bromophenyl)-2-(4-methoxyphenyl)diazene(40a):[92]



Was prepared using general procedure C [4-[(*E*)-(bromophenyl)diazenyl]phenol (1.15 g, 4.14mmol), KOH (1.16 g, 20.7mmol), methyl iodide (0.6mL,10 mmol) affording the title compound (2.7 g, 93%) as a dark orange red coloured compound. The compound was purified by recrystallisation in ethanol (**mp** 151.2-153 ºC, lit[94b] 146.0-146.5 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.90 (3H, s, CH_3) 7.02 (2H, dd, *J* = 9,2 Hz, Ar-**H**$_7$) 7.63 (2H, dd, *J*=9,2 Hz, Ar-**H**$_2$) 7.77 (2H, dd, *J* = 9,2 Hz, Ar-**H**$_6$) 7.92 (2H, dd, *J* = 9,2 Hz, Ar-**H**$_3$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 55.5 (CH_3), 114.2 (CH, Ar-H, C_7), 124.1 (CH, Ar-H, C_2), 124.8 (CH, Ar-H, C_6), 132.2 (CH, Ar-H, C_3), 162.3, 151.4.

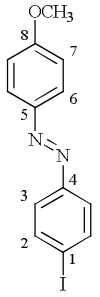
MS (ES+): $C_{13}H_{12}N_2{}^{79}BrO$ m/z $[M + H]^+$ 290.9 $[M + Na]^+$ 313.

Accurate Mass: $C_{13}H_{12}N_2{}^{79}BrO$ requires 291.0128 found 291.0138.

Microanalysis: $C_{13}H_{12}N_2Br$ requires C 53.63; H 3.81; N 9.12; Br 27.41%. Found C 53.32; H 3.72; N 9.52; Br 27.30%.

IR ν_{max} (film): 727, 829, 842, 1140, 1296, 1474, 1579, 1599, 2047 cm^{-1}.

4.2 Synthesis of (*E*)-1-(4-iodophenyl)-2-(4-methoxyphenyl)diazene (40b):[91]



Was prepared using general procedure C [4-[(*E*)-(iodophenyl)diazenyl]phenol (1.34 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol)] affording the *title compound* (3.1 g, 91%) as a dark brownish red coloured compound. Crude product was purified by crystallisation from ethanol (**mp** 176.6-178ºC, lit 179-181 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.91 (3H, s, CH_3) 7.02 (2H, d, *J* = 9 Hz, Ar-**H**$_7$) 7.62 (2H, d, *J* = 8 Hz, Ar-**H**$_2$) 7.85 (2H, d, *J* = 8 Hz, Ar-**H**$_3$) 7.93 (2H, d, *J* = 9 Hz, Ar-**H**$_6$).

^{13}C NMR (75 MHz, CDCl3)δ ppm 55.6 (CH_3), 114.2 (CH, Ar-H, C_7), 124.2 (CH, Ar-H, C_2), 124.9 (CH, Ar-H, C_6), 138.2 (CH, Ar-H, C_3), 152.4, 162.3.

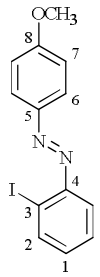
MS (ES+): m/z $[M+H]^+$ 339; $[M + Na]^+$ 361.

Accurate Mass: $C_{13}H_{12}N_2IO$ requires 338.9989 found 338.9999.

Microanalysis:$C_{13}H_{12}N_2I$ requires C 46.10; H 3.28; N 8.28%. Found **C** 45.66; H 3.23; N 8.20%.

IR ν_{max} (film): 1471, 1580,1600, 2049 cm^{-1}.

4.3 Synthesis of (*E*)-1-(2-iodophenyl)-2-(4-methoxyphenyl)diazene(109):[30]



Was prepared using general procedure C [2-(*E*)-(iodo phenyl)diazenyl]phenol (1.34 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol) affording the *title compound* (3 g, 90%) as a dark coloured solid. The compound was purified by recrystallisation with ethanol (**mp** 89.5-91 ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.91 (3H, s, CH_3) 7.04 (2H, d, *J* = 1 Hz, Ar-**H**$_7$) 7.14 (1H, td, *J* = 7, 1 Hz, Ar-**H**$_1$) 7.42 (1H, t, *J* = 7 Hz, Ar-**H**$_9$) 7.63 (1H, dd, *J* = 8, 1 Hz, Ar-**H**$_{10}$) 7.97-8.06 (3H, m, Ar-**H**$_{2,6}$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 55.6 (CH_3),114.3 (CH, Ar-H, **C**$_7$), 117.2 (CH, Ar-H, **C**$_{10}$), 125.5 (CH, Ar-H, **C**$_6$), 128.8 (CH, Ar-H, **C**$_9$), 131.5 (CH, Ar-H, **C**$_1$) 139.6 (CH, Ar-H, **C**$_2$), 102.1, 146.8, 151.4, 162.5.

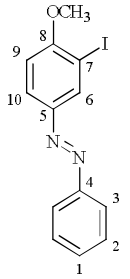
MS (ES+): m/z $[M+H]^+$ 339 $[M + Na]^+$ 361.13.

Accurate Mass: $C_{13}H_{12}N_2IO$ requires 338.9989 found 338.9992.

Microanalysis:$C_{13}H_{12}N_2$ requires C 46.1; H 3.2; N 8.3%. Found C 45.4;H 3.2; N 8.3%.

IRν_{max} (film): 1452, 1498, 1594, 3071 cm^{-1}.

4.4 Synthesis of (*E*)-1-(3-iodo-methoxyphenyl)-2-phenyldiazene (110):



Was prepared using general procedure C [2-iodo-4-[(*E*)-phenyldiazenyl] phenol (1.34 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), methyl iodide (0.6 mL, 10 mmol) affording the *title compound* (2.9 g, 88%) as a dark brownish red coloured compound. The compound was purified by recrystallisation in ethanol (**mp** 84-85 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.97 (3H, s, CH_3) 6.95 (1H, d, *J* = 8 Hz, Ar-**H**$_9$) 7.44-7.58 (3H, m, Ar-**H**$_{1,2}$) 7.90 (2H, d, *J* = 9 Hz, Ar-**H**$_3$) 7.98 (1H, d, *J* = 8 Hz, Ar-**H**$_{10}$) 8.43 (1H, s, Ar-**H**$_6$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 56.6 (CH_3), 110.2 (CH, Ar-H, **C**$_9$), 122.6 (CH, Ar-H, **C**$_3$), 126.5 (CH, Ar-H, **C**$_{10}$), 129.1 (CH, Ar-H, **C**$_2$), 130.7 (CH, Ar-H, **C**$_1$), 132.5 (CH, Ar-H, **C**$_6$), 86.5, 147.5, 152.4, 160.

MS (ES+): m/z [M + H] 339.

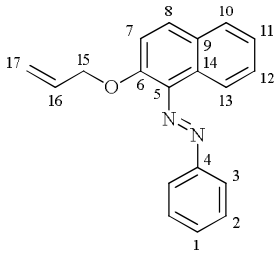
Accurate Mass: $C_{13}H_{12}N_2IO$ requires 338.9981 found 338.9989.

Microanalysis:$C_{13}H_{12}N_2$requires C 46.11; H 3.28; N 8.20%. Found C 46.6; H 3.31; N 8.11%.

IRν_{max} (film): 1429, 1454, 1269, 1560, 3051 cm^{-1}.

5 SYNTHESIS OF ALLYL DIAZO NAPHTHOL COMPOUNDS

5.1 Synthesis of (*E*)-1-(2-(allyloxy)naphthalen-1-yl)-2-phenyl)diazene (86):



Was prepared using general procedure D1 [Sudan-1 Dye (1.02 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), Allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (1.12 g, 94%, **mp** 114.2-115.5 ºC)] as a dark red coloured compound. Compound could be purified by recrystallization from petrol in DCM

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.74 (2H, d, *J* = 5 Hz, CH_2, **H**$_{15}$) 5.26 (1H, dd, *J* = 10, 2 Hz, CH_2, **H**$_{17}$) 5.47 (1H, dd, *J* = 17, 2 Hz, CH_2, **H**$_{17}$) 5.97 - 6.14 (1H, m, CH, **H**$_{16}$) 7.35-7.64 (6H, m, CH, Ar-**H**$_{1,2,7,10,11}$) 7.79-7.90 (2H, m, CH, Ar-**H**$_{8,\ 12}$) 8.05 (2H, dd, *J* = 8, 2 Hz, CH, Ar-**H**$_3$) 8.40 (1H, d, *J* = 8 Hz, CH_2, Ar-**H**$_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 71.4 (CH, **C**$_{15}$), 116.8 (CH, Ar-H, **C**$_7$), 117.29 (CH, **C**$_{17}$), 122.6 (CH, Ar-H, **C**$_3$), 123.2 (CH, Ar-H, **C**$_{13}$), 124.6 (CH, Ar-H, **C**$_{11}$), 127.4 (CH, Ar-H, **C**$_{10}$), 127.8 (CH, Ar-H, **C**$_{12}$), 129.1 (CH, Ar-H, **C**$_2$), 130.6 (CH, Ar-H, **C**$_8$), 130.9 (CH, Ar-H, **C**$_1$), 133.1 (CH, Ar-H, **C**$_{16}$), 119.4, 137.2, 147, 153.5, 206.8.

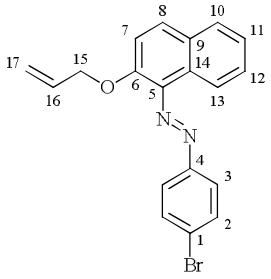
MS (ES+): m/z $[M+H]^+$ 289; $[M + Na]^+$ 311.

Accurate Mass: $C_{19}H_{17}N_2O$ requires 289.1335 found 289.1343.

Microanalysis: $C_{19}H_{17}N_2$ requires C 68.46; H 4.54; N 12.61%. Found C 68.31; H 4.21; N 12.42%.

IR ν_{max} (film): 1366, 1401, 1484, 1528, 1560, 1579, 3037 cm^{-1}.

5.2 Synthesis of (*E*)-1-(2-(allyloxy)naphthalen-1-yl)-2-(4-bromophenyl)diazene (86a):



Was prepared using general procedure D [1-[(E)-[(4-bromophenyl)diazenyl]-2-naphthol (1.35 g, 4.14mmol), KOH (1.16 g, 20.7mmol) and allyl bromide (0.9 mL, 10 mmol)] affording the *title compound* (1.42 g, 94%) as a dark red coloured compound. The compound could be purified by recrystallisation from DCM and hexane (**mp** 84-85 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.61 (2H, d, *J* = 4 Hz, CH_2, $\mathbf{H}_{15}$) 5.10-5.15 (1H, m, CH_2, $\mathbf{H}_{17}$) 5.34 (1H, dd, *J* = 17, 2 Hz, CH_2, $\mathbf{H}_{17}$) 5.85-6.01 (1H, m, CH_2, $\mathbf{H}_{16}$) 7.25 (1H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_7$) 7.32 (1H, ddd, *J*=8, 7, 1 Hz, CH, Ar-$\mathbf{H}_{11}$) 7.42 (1H, ddd, *J*=8, 7, 1 Hz, CH, Ar-$\mathbf{H}_{12}$) 7.58 (2H, dd, *J* = 9,2 Hz, CH, Ar-$\mathbf{H}_2$) 7.67-7.75 (2H, m, CH, Ar-$\mathbf{H}_{8,10}$) 7.79(2H, dd, *J*=9, 2 Hz, Ar-$\mathbf{H}_3$) 8.32 (1H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 53.3 (CH_2, $\mathbf{C}_{17}$), 71.2 (CH_2, $\mathbf{C}_{15}$), 117.2 (CH, Ar-H, $\mathbf{C}_7$), 123.2 (CH, Ar-H, $\mathbf{C}_{13}$), 124.1 (CH, Ar-H, $\mathbf{C}_3$), 124.6 (CH, Ar-H, $\mathbf{C}_{11}$), 127.7 (CH, Ar-H, $\mathbf{C}_{12}$), 127.8 (CH, Ar-H, $\mathbf{C}_8$), 131.3 (CH, Ar-H, $\mathbf{C}_{10}$), 132.2 (CH, Ar-H, $\mathbf{C}_2$), 132.9 (CH, Ar-H, $\mathbf{C}_{16}$), 116.5, 128.8, 129.3, 136.6, 147.2, 152.2.

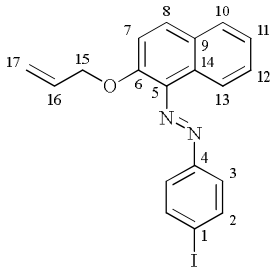
MS (ES+): m/z $[M + Na]^+$ 389.

Accurate Mass: $C_{19}H_{15}N_2{}^{79}BrONa$ requires 389.0260 found 389.0261.

Microanalysis: $C_{19}H_{15}N_2$ requires C 62.1; H 4.1; N 7.6%. Found C 61.6; H 4.0; N 6.9%.

IR ν_{max} (film): 1477, 1589, 2851, 3025 cm^{-1}.

5.3 Synthesis of (*E*)-1-(2-(allyloxy)naphthalen-1-yl)-2-(4-iodophenyl)diazene (86b):



Was prepared using general procedure D [1-[(*E*)-[(4-iodophenyl)diazenyl]-2-naphthol (1.55 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), and allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (1.62 g, 94.7%) as a dark red colour compound. The compound could be purified by recrystallization from hexane and DCM (**mp** 89.9-91.2ºC).

^{1}H NMR (300 MHz, *$CDCl_3$*) δ ppm 4.74 (2H, d, *J* = 4 Hz,CH_2, **H_{15}**) 5.27 (1H, dd, *J* = 10, 1 Hz, CH_2, **H_{17}**) 5.46 (1H, dd, *J* = 17, 2 Hz, CH_2, **H_{17}**) 5.97-6.12 (1H, m, CH_2, **H_{17}**) 7.39 (1H, d, *J* = 9 Hz, CH, Ar-**H_7**) 7.41-7.48 (1H, m, CH, Ar-**H_{11}**) 7.50-7.58 (1H, m, CH, Ar-**H_{12}**) 7.75 (2H, d, *J* = 8 Hz, CH, Ar-**H_3**) 7.85 (2H, m, CH, Ar-**$H_{8,10}$**) 7.92 (2H, d, *J* = 8 Hz, CH, Ar-**H_2**) 8.42 (1H, d, *J* = 8 Hz, CH, Ar-**H_{13}**).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 53.3 (CH_2, **C_{17}**), 71.3 (CH_2, **C_{15}**), 117.3 (CH, Ar-H, **C_7**), 123.3 (CH, Ar-H, **C_{13}**), 124.2 (CH, Ar-H, **C_3**), 124.7 (CH, Ar-H, **C_{11}**), 127.7 (CH, Ar-H, **C_8**), 127.8 (CH, Ar-H, **C_8**), 132.8 (CH, Ar-H, **C_{16}**), 133.1 (CH, Ar-H, **C_{10}**), 138.3 (CH, Ar-H, **C_2**), 116.62, 129.4, 131.3, 137.3, 147.4, 152.9.

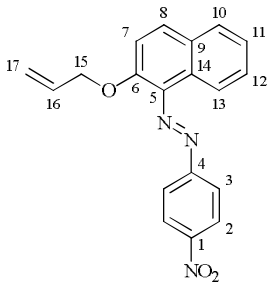
MS (ES+): m/z $[M+H]^+$ 415; $[M + Na]^+$ 437.

Accurate Mass: $C_{19}H_{16}N_2IO$ require 415.0302 found 415.0300.

Microanalysis: $C_{19}H_{16}N_2$ requires C 55.00; H 3.65; N 6.76%. Found **C** 54.52; H 3.71; N 6.11%.

IR ν_{max} (film): 1269, 1339, 1474, 1577, 1737, 3061 cm^{-1}.

5.4 Synthesis of (*E*)-1-(2-(allyloxy)naphthalen-1-yl)-2-(4-nitrophenyl)diazene (86c):



Was prepared using general procedure D [1-[(*E*)-[(4-nitrophenyl)diazenyl]-2-naphthol (1.21 g, 4.14mmol), KOH (1.16 g, 20.7mmol) and a allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (1.12 g, 82%) as dark red colour compound. Compound can be purified by column chromatography (SiO2 gel; eluent hexane/DCM 40%).Compound could be purified by recrystallisation frpom etrol in DCM (**mp** 124.2-125.5ºC).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.80 (2H, dt, *J* = 5, 1 Hz,$\mathbf{H}_{15}$) 5.32 (1H, dd, *J* = 10, 1Hz,$\mathbf{H}_{17}$) 5.51 (1H, dd, *J* = 1 Hz,$\mathbf{H}_{17}$) 5.92-6.25 (1H, m, CH, Ar-$\mathbf{H}_{16}$) 7.41 (1H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_7$) 7.44-7.52 (1H, m, CH, Ar-$\mathbf{H}_{11}$) 7.56-7.66 (1H, m, CH, Ar-$\mathbf{H}_{12}$) 7.85 (1H, d, *J* = 7 Hz, CH, Ar-$\mathbf{H}_{10}$) 7.95 (1H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_8$) 8.10 (2H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_3$) 8.42 (2H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_2$) 8.65 (1H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 71.1 (CH_2, C_{15}), 116.1 (CH, Ar-H, $\mathbf{C}_7$), 117.6 (CH_2, Ar-H, $\mathbf{C}_{17}$), 123.1 (CH, Ar-H, $\mathbf{C}_3$), 124.7 (CH, Ar-H, $\mathbf{C}_2$), 123.4 (CH, Ar-H, $\mathbf{C}_{13}$), 125.1 (CH, Ar-H, $\mathbf{C}_{11}$), 128.1 (CH, Ar-H, $\mathbf{C}_{10}$), 128.5 (CH, Ar-H, $\mathbf{C}_{12}$), 132.7 (CH, Ar-H, $\mathbf{C}_{16}$), 133.4 (CH, Ar-H, $\mathbf{C}_8$), 129.1, 129.3, 135.9, 148.4, 149, 156.8.

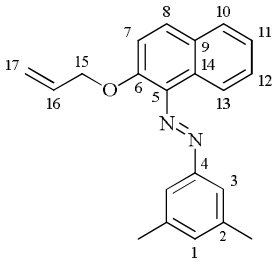
MS (ES+): m/z $[M+H]^+$ 334; $[M + Na]^+$ 356.

Accurate Mass: $C_{19}H_{16}N_3O_3$ requires 334.1186 found 334.1190.

Microanalysis: $C_{19}H_{16}N_3$ requires C 68.46; H 4.54; N 12.61%. Found **C** 68.31; H 4.21; N 12.42%.

IR ν_{max} (film): 1326, 1396, 1518, 1561, 1587, 3019 cm^{-1}.

5.5 Synthesis of (*E*)-1-(2-(allyloxy)naphthalen-1-yl)-2-(3,5-dimethylphenyl)diazene (111):



Was prepared using general procedure D1 [1-[(*E*)-[(3,5-dimethylphenyl)diazenyl]-2-naphthol (1.14 g, 4.14mmol), KOH (1.16 g, 20.7mmol) and allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (1.24 g, 95%, **mp** 105 ˚C) as a dark red coloured compound. The compound can be purified by recrystallization from hexane in DCM

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.47 (6H, s, CH_3) 4.69-4.77 (2H, m, CH_2, $\mathbf{H}_{15}$) 5.25 (1H, dd, *J* = 11, 2 Hz, CH_2, $\mathbf{H}_{17}$) 5.44 (1H, dd, *J* = 1 Hz, CH_2, H_{17}) 5.97-6.13 (1H, m, CH, $\mathbf{H}_{16}$) 7.18 (1H, s, CH, Ar-$\mathbf{H}_1$) 7.39 (1H, d, *J* = 9Hz, CH, Ar-$\mathbf{H}_7$) 7.42-7.48 (1H, m, CH, Ar-$\mathbf{H}_{11}$) 7.48-7.55 (1H, m, CH, Ar-$\mathbf{H}_{12}$) 7.66 (2H, s, CH, Ar-$\mathbf{H}_3$) 7.77-7.88 (2H, m, CH, Ar-$\mathbf{H}_{8,10}$) 8.33 (1H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.3 (CH_3), 71.4 (CH_2, $\mathbf{C}_{15}$), 116.8 (CH, Ar-H, $\mathbf{C}_7$), 117.3 (CH_2, $\mathbf{C}_{17}$), 120.4 (CH, Ar-H, $\mathbf{C}_3$), 123.2 (CH, Ar-H, $\mathbf{C}_{13}$), 124.5 (CH, Ar-H, $\mathbf{C}_{11}$), 127.3 (CH,

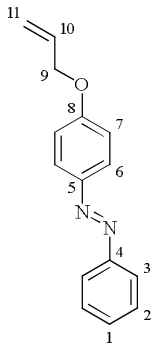
Ar-H, $\mathbf{C}_{12}$), 127.7 (CH, Ar-H, $\mathbf{C}_{10}$), 130.3 (CH, Ar-H, $\mathbf{C}_{8}$), 132.6 (CH, Ar-H, $\mathbf{C}_{1}$), 133.2 (CH, Ar-H, $\mathbf{C}_{16}$), 153.6 (CH, Ar-H, $\mathbf{C}_{2}$), 128.5, 129.4, 137.6, 138.7, 146.9.

MS (ES+): $[M + Na]^+$ 339.

Accurate Mass: $C_{21}H_{20}N_2NaO$ requires 339.1483 found 339.1468.

IR ν_{max} (film): 1273, 1431, 1503, 1588, 3045 cm^{-1}.

5.6 Synthesis of (*E*)-1-(2-(allyloxy)phenyl)-2-phenyldiazene (112):



Was prepared using general procedure D [2-phenyldiazenylphenol (0.81 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol), and allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (0.94 g, 94%) as dark yellow coloured compound. The compound could be purified by recrystallisation from petrol in DCM (**mp** 70-72 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.64 (2H, dt, *J* = 5, 1 Hz, CH_2, $\mathbf{H}_9$) 5.34 (1H, dq, *J* = 10, 1 Hz, CH_2, $\mathbf{H}_{11}$) 5.47 (1H, dq, *J* = 17, 2 Hz, CH_2, $\mathbf{H}_{11}$) 5.95-6.23 (1H, m, CH_2, $\mathbf{H}_{10}$) 6.97-7.14 (2H, m, CH, Ar-$\mathbf{H}_7$) 7.40-7.58 (3H, m, CH, Ar-$\mathbf{H}_{1,2}$) 7.81-8.01 (4H, m, CH, Ar-$\mathbf{H}_{3,6}$).

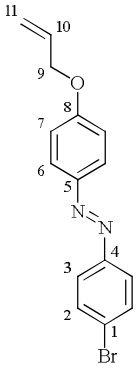
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 69.1 (CH_2, $\mathbf{C}_9$), 114.9 (CH, Ar-H, $\mathbf{C}_7$), 118.1 (CH_2, $\mathbf{C}_{11}$), 122.5 (CH, Ar-H, $\mathbf{C}_3$), 124.6 (CH, Ar-H, $\mathbf{C}_6$), 128.9 (CH, Ar-H, $\mathbf{C}_2$), 130.3 (CH, Ar-H, $\mathbf{C}_1$), 132.7 (CH, $\mathbf{C}_{10}$), 147.1, 152.7, 161.1.

MS (ES+): $[M + Na]^+$ 239.

Accurate Mass: $C_{15}H_{15}N_2O$ requires 239.1179 found 239.1182.

IR ν_{max} (film): 1496, 1579, 1598, 3023 cm^{-1}.

5.7 Synthesis of (*E*)-1-(2-(allyloxy)phenyl)-2-(4-bromophenyl)diazene (112a):



Was prepared using general procedure D [4-(*E*)-(bromo phenyl)diazenyl]phenol (1.15 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol) and allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (1.14 g, 88%) as a dark yellow coloured compound. The compound can be purified by recrystallisation from petrol in DCM (**mp** 114-116 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.64 (2H, d, *J* = 5 Hz, CH_2, $\mathbf{H}_9$) 5.34 (1H, dd, *J* = 10, 1 Hz, CH_2, $\mathbf{H}_{11}$) 5.46 (1H, dd, *J* = 1 Hz, CH_2, $\mathbf{H}_{11}$) 5.92-6.20 (1H, m, CH_2, $\mathbf{H}_{10}$) 7.04 (2H, dd, *J* = 9,2 Hz, CH_2, Ar-$\mathbf{H}_7$) 7.63 (2H, dd, *J* = 9,2 Hz, CH_2, Ar-$\mathbf{H}_2$) 7.77 (2H, dd, *J* = 9,2 Hz, CH_2, Ar-$\mathbf{H}_6$) 7.91 (2H, dd, *J* = 9,2 Hz, CH_2, Ar-$\mathbf{H}_3$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 69.1 (CH_2, $\mathbf{C}_9$), 115.1 (CH, Ar-H, $\mathbf{C}_7$), 118.1 (CH_2, $\mathbf{C}_{11}$), 124.1 (CH, Ar-H, $\mathbf{C}_6$), 124.8 (CH, Ar-H, $\mathbf{C}_3$), 132.2 (CH, Ar-H, $\mathbf{C}_2$), 132.7 (CH, $\mathbf{C}_{10}$), 124.5, 146.9, 151.5, 161.3.

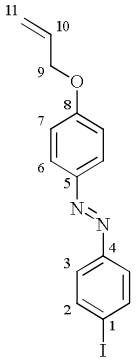
MS (ES+): $C_{15}H_{14}N_2O^{79}Br$ m/z $[M+H]^+$ 317.

Accurate Mass: $C_{15}H_{14}N_2O^{79}Br$ requires 317.0271 found 317.0271; $C_{15}H_{14}N_2O^{81}Br$ requires 319.0264 found 319.0248.

Microanalysis: $C_{15}H_{14}N_2$ requires C 56.8; H 4.13; N 8.3%. Found C 56.1; H 4.02; N 8.30%.

IR ν_{max} (film): 831, 840, 937, 990, 1240, 1567, 1578, 1598, 2985 cm^{-1}.

5.8 Synthesis of (*E*)-1-(2-(allyloxy)phenyl)-2-(4-Iodophenyl)diazene (112b):



Was prepared using general procedure D [4-[(*E*)-(iodophenyl)diazenyl]phenol (1.34 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol) and allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (1.32 g, 88%) as a dark brown coloured compound. The compound can be purified by recrystallisation from petrol in DCM (**mp** 132 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.64 (2H, dt, *J* = 5, 1 Hz, CH_2, $\mathbf{H}_9$) 5.34 (1H, dq, *J*= 10, 1 Hz, CH_2, $\mathbf{H}_{11}$) 5.46 (1H, dq, *J* = 17, 1 Hz, CH_2, $\mathbf{H}_{11}$) 6.02-6.16 (1H, m, CH, $\mathbf{H}_{10}$) 7.03 (2H, d, *J* = 9. Hz, CH, Ar-$\mathbf{H}_7$) 7.62 (2H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_3$) 7.85 (2H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_2$) 7.91 (2H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_6$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 69.1 (CH_2, $\mathbf{C}_9$), 115.1 (CH, Ar-H $\mathbf{C}_7$), 118.1 (CH_2, $\mathbf{C}_{11}$), 124.2 (CH, Ar-H, $\mathbf{C}_3$), 124.8 (CH, Ar-H, $\mathbf{C}_6$), 132.6 (CH, $\mathbf{C}_{10}$), 138.2 (CH_2, Ar-H, $\mathbf{C}_2$), 96.6, 146.9, 152.1, 161.3.

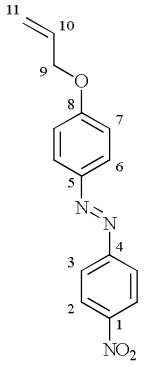
MS (ES+): m/z $[M+H]^+$ 365.

Accurate Mass: $C_{15}H_{14}N_2IO$ requires 364.0145 found 364.0141.

Microanalysis: $C_{15}H_{14}N_2I$ requires C 49.41; H 3.60; N 7.69; I 34.8%. Found C 49.11; H 3.63; N 7.27; I 33.73%.

IR ν_{max} (film): 1362, 1389, 1473, 1491, 1562, 1578, 1600, 1738 cm^{-1}.

5.9 Synthesis of (*E*)-1-(2-(allyloxy)phenyl)-2-(4-nitrophenyl)diazene (112c):



Was prepared using general procedure D [4-[(*E*)-(nitrophenyl)diazenyl]phenol (1.34 g, 4.14mmol), KOH (1.16 g, 20.7mmol) and allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (1.38, 81%, **mp** 145-146 ˚C) as dark brown colour compound. Compound can be purified by recrystallisation.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.66 (2H, d, *J* = 5 Hz, CH_2, $\mathbf{H}_9$) 5.36 (1H, dd, *J*= 10, 1 Hz, CH_2,$\mathbf{H}_{11}$) 5.47 (1H, dd, *J* = 17, 1 Hz, CH_2,$\mathbf{H}_{11}$) 5.98-6.17 (1H, m, CH,$\mathbf{H}_{10}$) 7.06 (2H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_7$) 7.98 (4H, dd, *J* = 8, 4 Hz, CH, Ar-$\mathbf{H}_{3,6}$) 8.37 (2H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_2$).

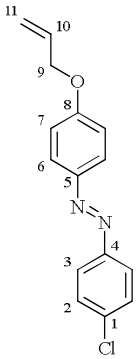
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 69.1 (CH_2, $\mathbf{C}_9$), 115.2 (CH, Ar-H, $\mathbf{C}_7$), 118.2 (CH_2, $\mathbf{C}_{11}$), 123.1 (CH, Ar-H, $\mathbf{C}_3$), 124.6 (CH, Ar-H, $\mathbf{C}_2$), 125.5 (CH, Ar-H, $\mathbf{C}_6$), 132.5 (CH, $\mathbf{C}_{10}$), 147.1, 148.3, 156.1, 162.2.

MS (ES+): m/z $[M+H]^+$ 284.

Accurate Mass: $C_{15}H_{13}N_3O_3$ requires 283.0962 found 283.0958.

IR ν_{max} (film): 1331, 1495, 1510, 1578, 1588, 1599, 1737, 3011 cm^{-1}.

5.10 Synthesis of (*E*)-1-(2-(allyloxy)phenyl)-2-(4-chlorophenyl)diazene (112d):



Was prepared using general procedure D [4-[(*E*)-(chlorophenyl)diazenyl]phenol (0.97 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol) and allyl bromide (0.6 mL, 7 mmol)] affording the *title compound* (0.98 g, 91%, **mp** 94.5 ˚C) as a dark yellow coloured compound. The compound could be purified by recrystallisation.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.64 (2H, d, *J* = 5 Hz, CH_2,**H**$_9$) 5.35 (1H, dd, *J* = 10, 1 Hz, CH_2,**H**$_{11}$) 5.47 (1H, dd, *J* = 17, 1.5 Hz, CH_2,**H**$_{11}$) 5.94-6.18 (1H, m, CH,**H**$_{10}$) 6.94 (2H, dd, CH, *J*=9, 2 Hz, Ar-**H**$_7$) 7.44 (2H, dd, *J*=9, 2 Hz, CH, Ar-**H**$_2$) 7.82 (2H, dd, CH, *J*=9, 2 Hz, Ar-**H**$_6$) 7.95 (2H, dd, *J*=9, 2 Hz, CH, Ar-**H**$_3$).

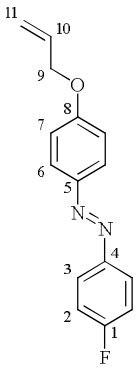
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 69.1 (CH_2, C_9), 115.1 (CH, Ar-H, C_7), 118.1 (CH_2, C_{11}), 123.8 (CH, Ar-H, C_6), 124.8 (CH, Ar-H, C_3), 129.2 (CH, Ar-H, C_2), 132.6 (CH, C_{10}), 136.1, 146.9, 151.1, 161.2.

MS (ES+): m/z $[M+H]^+$ 273; **(ES-):** m/z [M-] 271.

Accurate Mass: $C_{15}H_{12}N_2{}^{35}ClO$ requires 271.0643 found 271.0062.

IR ν_{max} (film): 1364, 1450, 1477, 1493, 1573, 1598, 1738 cm^{-1}.

5.11 Synthesis of (*E*)-1-(2-(allyloxy)phenyl)-2-(4-flourophenyl)diazene (112e):



Was prepared using general procedure D [4-[(*E*)-(flourophenyl)diazenyl]phenol (0.9 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol) and allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (0.9 g, 85%, **mp** 112 ˚C) as a dark yellow coloured compound. The compound can be purified by recrystallization from petrol in DCM.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.63 (2H, dt, *J* = 5, 1 Hz, CH_2,**H**$_9$) 5.34 (1H, dd, *J* = 10, 1 Hz, CH,**H**$_{11}$) 5.46 (1H, dd, *J* = 17, 1.5 Hz, CH,**H**$_{11}$) 6.02-6.17 (1H, m, CH,**H**$_{10}$) 7.01-7.07 (2H, m, Ar-**H**$_7$) 7.19 (2H, t, *J* = 8 Hz, Ar-**H**$_2$) 7.90 (4H, dt, *J* = 9, 2 Hz, Ar-**H**$_{3,6}$).

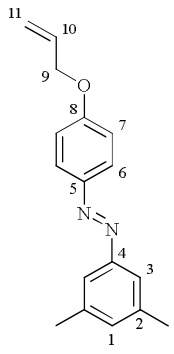
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 69.1 (CH_2, **C**$_9$), 114.9 (CH, Ar-H, C_7), 115.7 (CH_2, C_{11}), 116.1 (CH, Ar-H, C_2), 124.6 (CH, Ar-H, $C_{3,6}$), 132.7 (CH, C_{10}), 146.8, 149.2,161.1,165.6.

MS (ES+): m/z $[M+H]^+$ 257.

Accurate Mass: $C_{15}H_{14}N_2FO$ requires 257.1085 found 257.1079.

IR ν_{max} (film): 1228, 1248, 1491, 1579, 1592, 3016 cm^{-1}.

5.12 Synthesis of (*E*)-1-(2-(allyloxy)phenyl)-2-(3,5-dimethylphenyl)diazene (113):



Was prepared using general procedure D [(*E*)-(3,5-dimethylphenyl)diazenyl]phenol (0.94 g, 4.14mmol), KOH (1.16 g, 20.7mmol) and allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (1.02, 93%) as a dark brown oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.42 (6H, s, CH_3) 4.63 (2H, d, *J* = 5 Hz, CH_2, **H**$_9$) 5.34 (1H, dd, *J* = 10, 1 Hz, CH_2,**H**$_{11}$) 5.46 (1H, dd, *J* = 17, 1 Hz, CH_2, **H**$_{11}$) 6.10 (1H, ddt, *J* = 17, 10, 5, CH_2, **H**$_{10}$) 7.04 (2H, d, *J* = 9 Hz, CH, Ar-**H**$_7$) 7.10 (1H, s, CH, Ar-**H**$_1$) 7.51 (2H, s, CH, Ar-**H**$_3$) 7.91 (2H, d, *J* = 9 Hz, CH, Ar-**H**$_6$).

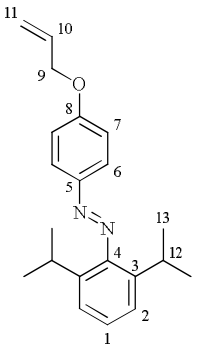
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 21.2 (CH_3), 69.1 (CH_2, **C**$_9$), 114.9 (CH, Ar-H, **C**$_7$), 117.9 (CH_2, **C**$_{11}$), 120.3 (CH, Ar-H, **C**$_3$), 124.5 (CH, Ar-H, **C**$_6$), 132.1 (CH, Ar-H, **C**$_1$), 132.1 (CH, **C**$_{10}$), 138.6, 147.1, 153.1, 160.9.

MS (ES+): m/z $[M + Na]^+$ 289.

Accurate Mass: $C_{17}H_{19}N_2O$ requires 267.1492 found 267.1486.

IR ν_{max} (film): 1453, 1498, 1581, 1597, 1738, 3019 cm^{-1}.

5.13 Synthesis of (*E*)-1-(4-(allyloxy)phenyl)-2-(2,6-*iso*-propylphenyl)diazene (114):

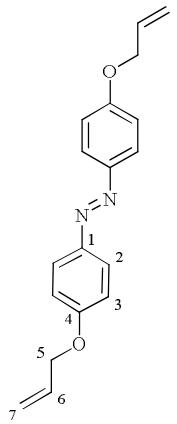


Was prepared using general procedure D [(*E*)-(2,6-di-*iso*-propylphenyl)diazenyl]phenol (1.18 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol) and allyl bromide (0.9 mL, 10 mmol)] affording the *title compound* (1.22, 92%) as dark brown colour oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.22 (12H, d, *J*=6 Hz, CH_3, $\mathbf{H}_{13}$) 3.09 (2H, quin, *J* = 7 Hz, CH, $\mathbf{H}_{12}$) 4.63 (2H, d, *J* = 5 Hz, CH_2,$\mathbf{H}_9$) 5.36 (1H, dd, *J* = 10, 1 Hz, CH_2,$\mathbf{H}_{11}$)5.47 (1H, dd, *J* = 17, 1.5 Hz, CH_2,$\mathbf{H}_{11}$) 5.98-6.23 (1H, m, CH,$\mathbf{H}_{10}$) 7.01 (2H, d, *J* = 8 Hz, Ar-$\mathbf{H}_7$) 7.27-7.40 (3H, m, Ar-$\mathbf{H}_{1,2}$) 7.82 (2H, d, *J* = 8 Hz, Ar-$\mathbf{H}_6$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 23.4 (CH_3, C_{13}), 27.6 (CH, C_{12}), 69.3 (CH_2, $\mathbf{C}_9$), 115.9 (CH, Ar-H, C_7), 117.8 (CH_2, $\mathbf{C}_{11}$), 124.1 (CH, Ar-H, C_1), 124.7 (CH, Ar-H, C_2), 127.4 (CH, Ar-H, C_6), 132.1 (CH, $\mathbf{C}_{10}$), 139.3, 147.1, 152.2, 159.5.

5.14 Synthesis of (*E*)-1,2-bis(4-allyloxy)phenyl)diazene (115):[92]



Was prepared using general procedure D [(*E*)-4,4'-(diazene-1,2-yl)diphenol (0.88 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol) and allyl bromide (0.9 mL, 10 mmol)] affording the *title compound* (1.15 g, 95.1%) as a bright orange coloured compound. The compound can be purified by recrystallization from petrol in DCM

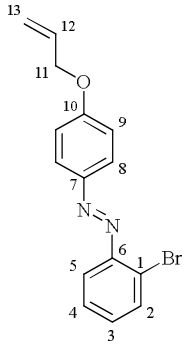
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.63 (4H, d, *J* = 5 Hz, CH_2, $\mathbf{H}_5$) 5.34 (2H, dd, *J*=10, 1 Hz, CH_2, $\mathbf{H}_7$) 5.46 (2H, dd, *J*=17, 1 Hz, CH_2, $\mathbf{H}_7$) 6.09 (2H, ddt, *J* = 17, 10, 5 Hz, CH, $\mathbf{H}_6$) 7.03 (4H, dd, *J*=9,2 Hz, CH, Ar-$\mathbf{H}_3$) 7.89 (4H, dd, *J*=9,2 Hz, CH, Ar-$\mathbf{H}_2$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 69 (CH_2, $\mathbf{C}_5$),114.9 (CH, Ar-H, $\mathbf{C}_3$),117.9 (CH_2, $\mathbf{C}_7$),124.2 (CH, Ar-H, $\mathbf{C}_2$),132.8 (CH, $\mathbf{C}_6$), 147.1, 160.5.

MS (ES+): m/z $[M+H]^+$ 295.

Accurate Mass: $C_{18}H_{19}N_2O_2$ requires 295.1441 found 295.1448.

5.15 Synthesis of (*E*)-1-(2-(allyloxy)phenyl)-2-(2-bromophenyl)diazene (116):



Was prepared using general procedure D [2-[(*E*)-(bromophenyl)diazenyl]phenol (1.15 g, 4.14 mmol), KOH (1.16 g, 20.7 mmol) and allyl bromide (0.9 mL, 10 mmol) affording the *title compound* (0.90 g, 92.1%) as dark reddish oil.

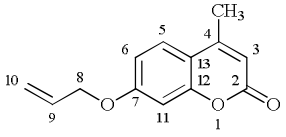
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.64 (2H, d, *J* = 5 Hz, CH_2,**H**$_{11}$) 5.35 (1H, dd, *J* = 10, 1 Hz, CH_2,**H**$_{13}$) 5.47 (1H, dd, *J* = 17, 2 Hz, CH_2,**H**$_{13}$) 5.99-6.18 (1H, m, CH_2,**H**$_{12}$) 7.05 (2H, d, *J* = 9 Hz, CH, Ar-**H**$_9$) 7.23-7.32 (1H, m, Ar-**H**$_3$) 7.34-7.43 (1H, m, Ar-**H**$_4$) 7.67 (1H, dd, *J* = 8, 2 Hz, Ar-**H**$_2$) 7.74 (1H, d, *J* = 9 Hz, Ar-**H**$_5$) 7.99 (2H, d, *J* = 9 Hz, Ar-**H**$_8$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 69.1 (CH_2, **C**$_{11}$), 115.1 (CH, Ar-H, **C**$_9$), 117.7 (CH, Ar-H, **C**$_5$), 118.1 (CH_2, **C**$_{13}$), 125.3 (CH, Ar-H, **C**$_8$), 127.9 (CH, Ar-H, **C**$_4$), 131.1 (CH, Ar-H, **C**$_3$), 132.6 (CH, **C**$_{12}$), 133.6 (CH, Ar-H, **C**$_2$), 125.1, 149.7, 147.2, 161.5.

MS (ES+): $C_{15}H_{14}N_2{}^{79}BrO$ m/z $[M+H]^+$ 317 $[M + Na]^+$ 339.

Accurate Mass: $C_{15}H_{14}N_2{}^{79}BrO$ requires 317.0284 found 317.0295; $C_{15}H_{14}N_2{}^{81}BrO$ requires 317.0264 found 317.0287.

5.16 Synthesis of 7-(allyloxy)-4-methyl-2h-chromen-2-one (117):[74]



Was prepared using general procedure 4-methylumbelliferone (1.76 g, 10 mmol), K_2CO_3 (1.65 g, 12 mmol) and allyl bromide (1.1 mL, 12 mmol) affording the *title compound* (2.10 g, 97%) as white colour powder.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.40 (3H, s, CH_3) 4.60 (2H, dt, *J* = 5, 2 Hz, CH_2,**H**$_{10}$) 5.34 (1H, dq, *J* = 11, 1 Hz, CH_2,**H**$_8$) 5.44 (1H, dq, *J* = 17, 1 Hz, CH_2,**H**$_8$) 6.05 (1H, ddt, *J* = 17, 11, 5 Hz, CH,**H**$_9$) 6.13 (1H, s, CH, Ar-**H**$_3$) 6.82 (1H, d, *J* = 3 Hz, CH, Ar-**H**$_6$) 6.88 (1H, dd, *J* = 9, 3 Hz, CH, Ar-**H**$_{11}$) 7.50 (1H, d, *J* = 9 Hz, CH, Ar-**H**$_5$).

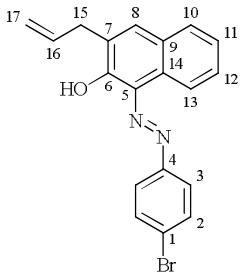
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 18.6 (CH_3), 69.2 (CH_2, **C**$_{10}$), 101.7 (CH, Ar-H **C**$_6$), 111.9 (CH, Ar-H, **C**$_3$), 112.7 (CH, Ar-H, **C**$_{11}$), 118.4 (CH_2, **C**$_8$), 125.4 (CH, Ar-H, **C**$_5$), 132.1 (CH, **C**$_9$), 113.6, 152.4, 155.1, 161.2, 161.5.

MS (ES+): m/z $[M + H]^+$ 184.

Accurate Mass: $C_{13}H_{12}O_3$ requires 184.0883 found 184.0880.

6 SYNTHESIS OF CLAISEN REARRANGED COMPOUNDS

6.1 Synthesis of (*E*)-1-azenyl-3-allyl-((4-bromophenyl)diazenyl)naphthalene-2-ol (87):



Was prepared using general procedure F; (*E*)-1-(2-(allyloxy)naphthalen-1-yl)-2-(4-bromophenyl)diazene (0.365 g,1.08 mmol) and Et_2AlCl (2.2 mL,1 M soln. in hexane) in dry DCM (10 mL). The *title compound* (26%, crystalline) was obtained by column

chromatography (0.146 g, 40% DCM in hexane). The compound can further be purified by recrystallisation (pet ether and DCM).

^{1}H NMR (400 MHz, CDCl3) δ ppm 3.46 (2H, d, *J* = 7 Hz, CH_2, **H**$_{15}$) 5.18-5.20 (1H, m, CH_2, **H**$_{17}$) 5.23 (1H, dd, *J* = 9, 2 Hz, CH_2, **H**$_{17}$) 6.08 (1H, ddt, *J* = 2, 10, 6 Hz, CH_2, **H**$_{16}$) 7.37-7.44 (1H, m, CH, Ar-**H**$_{12}$) 7.52 (1H, d, *J* = 7 Hz, CH,Ar-**H**$_{10}$) 7.54-7.57 (1H, m, CH, Ar-**H**$_{11}$) 7.59 (5H, m, CH, **H**$_{2,3,8}$) 8.47 (1H, d, *J* = 8 Hz, CH, Ar-**H**$_{13}$).

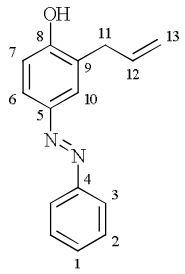
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 33.4 (CH_2, **C**$_{15}$), 116.7 (CH_2, **C**$_{17}$), 126.2 (CH, Ar-H, **C**$_{12}$), 128.3 (CH, Ar-H, **C**$_{11}$), 128.4 (CH, Ar-H, **C**$_{10}$), 119.2 (CH, Ar-H, **C**$_{2}$), 121.5 (CH, Ar-H, **C**$_{13}$), 132.6 (CH, Ar-H, **C**$_{3}$), 139 (CH, Ar-H, **C**$_{10}$), 119.7, 128.1, 130.1, 135.5, 135.6, 174.6.

MS (ES-): m/z $[M-H]^-$ 365, 367.

Accurate Mass: $C_{19}H_{14}N_2O^{79}Br$ + e require 365.0290 found 365.0294.

Microanalysis: $C_{19}H_{14}N_2$ requires C 62.10; H 4.10,7.63. Found C 62.06; H 4.06; N 7.47%.

6.2 Synthesis of (*E*)-2-allyl-4-(phenyldiazenyl)phenol (118):[93]



Was prepared using general procedure F; (E)-1-(2-(allyloxy)phenyl)-2-(phenyldiazene (0.257 g, 1.08 mmol) and Et_2AlCl (2.2 mL, 1 M soln. in hexane) in dry DCM (10 mL).The *title compound* (0.213 g, 83%, crystalline; **mp** 91.7 ˚C, lit 89-90 ˚C) was obtained by column chromatography (40% DCM in hexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.52 (2H, d, *J* = 6 Hz, CH_2, $\mathbf{H}_{11}$) 5.21 (1H, t, *J* = 1 Hz, CH_2, $\mathbf{H}_{13}$) 5.26 (1H, dd, *J* = 8, 1 Hz, CH_2, $\mathbf{H}_{13}$) 6.09 (1H, ddt, *J* =16, 10, 6 Hz, CH_2, $\mathbf{H}_{12}$) 6.94 (1H, dd, *J*=9,3 Hz, CH, Ar-$\mathbf{H}_7$) 7.44-7.56 (3H, m, CH, Ar-$H_{1,2}$) 7.76-7.82 (2H, m, CH, Ar-$\mathbf{H}_{6,10}$) 7.89 (2H, dd, *J* = 8,2 Hz, CH, Ar-$\mathbf{H}_3$).

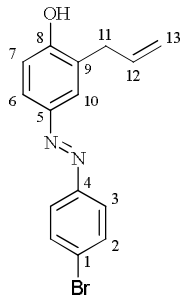
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 35.1 (CH_2, $\mathbf{C}_{11}$), 116.2 (CH, Ar-H, $\mathbf{C}_7$), 117.1 (CH_2, $\mathbf{C}_{13}$), 122.5 (CH, Ar-H, $\mathbf{C}_3$), 123.5 (CH, Ar-H, $\mathbf{C}_6$), 125.1 (CH, Ar-H, $\mathbf{C}_{10}$), 129.1 (CH, Ar-H, $\mathbf{C}_2$), 130.3 (CH, Ar-H, $\mathbf{C}_1$), 135.7 (CH, $\mathbf{C}_{12}$), 126.1, 147.1, 152.7, 156.9.

MS (ES+): m/z $[M+H]^+$ 239; **(ES-):** m/z $[M-H]^+$ 237.

Accurate Mass: $C_{15}H_{13}N_2O$ requires 237.1025 found 237.1033.

IR ν_{max} (film): 1444, 1465, 1502, 1592, 1737, 3068 cm^{-1}.

6.3 Synthesis of (*E*)-2-allyl-4-((4-bromophenyl)diazenyl)phenol (118a):[93]



Was prepared using general procedure F; (*E*)-1-(2-(allyloxy)phenyl)-2-(4-bromophenyl)diazene(0.341 g, 1.08 mmol) and Et_2AlCl (2.2 mL, 1 M soln. in hexane) in dry DCM (10 mL).The *title compound* (81%, crystalline; **mp** 98 ˚C, lit 105-107 ˚C) was obtained by column chromatography (0.277 g, 40% DCM in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.51 (2H, d, *J* = 6 Hz, CH_2, $\mathbf{H}_{11}$) 5.20 (1H, t, *J* = 1 Hz, CH_2, $\mathbf{H}_{13}$) 5.23-5.27 (1H, m, CH_2, $\mathbf{H}_{13}$) 5.99-6.15 (1H, m, CH, $\mathbf{H}_{12}$) 6.93 (1H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_7$) 7.63 (2H, dd, *J* = 1 Hz, CH, Ar-$\mathbf{H}_2$) 7.72-7.80 (4H, m, CH, Ar-$\mathbf{H}_{3,6,10}$).

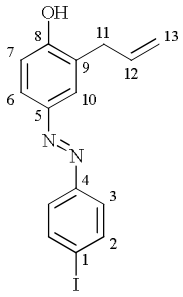
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 34.9 (CH_2, **C_{11}**), 116.2 (CH, Ar-H, **C_7**), 117.1 (CH_2, **C_{13}**), 123.6 (CH, Ar-H, **C_6**), 124.1 (CH, Ar-H, **C_3**), 125.2 (CH, Ar-H, **C_{10}**), 132.2 (CH, Ar-H, **C_2**), 137.7 (CH, **C_{12}**), 126.2, 146.9, 151.4, 157.2.

MS (ES-): $C_{15}H_{12}N_2{}^{79}BrO$ m/z $[M-H]^-$ 315, 317.

Accurate Mass: $C_{15}H_{12}N_2{}^{79}BrO$ requires 315.0138 found 315.0134; $C_{15}H_{12}N_2{}^{81}BrO$ requires 317.0118 found 317.0095.

IR ν_{max} (film): 1269, 1479, 1568, 1580, 2914 cm^{-1}.

6.4 Synthesis of (*E*)-2-allyl-4-((4-iodophenyl)diazenyl)phenol (118b):[93]



Was prepared using general procedure F; (*E*)-1-(2-(allyloxy)phenyl)-2-(4-Iodophenyl)diazene(0.393 g, 1.08 mmol) and Et_2AlCl (2.2 mL, 1.0 M soln. in hexane) in dry DCM (10 mL). The *title compound* (0.302 g, 83%, crystalline; **mp** 130 ˚C, lit[93] 134-136 ˚C) was obtained by column chromatography (40% DCM in hexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.51 (2H, d, *J* = 6 Hz, CH_2,**H_{11}**) 5.21 (1H, t, *J* = 1 Hz, CH_2,**H_{13}**) 5.27 (1H, d, *J* = 1 Hz, CH_2,**H_{13}**) 5.51 (1H, br. s., OH) 5.86-6.16 (1H, m, CH,**H_{12}**) 6.93 (1H, d, *J* = 9 Hz, Ar-**H_7**) 7.61 (2H, d, *J* = 8 Hz, Ar-**H_3**) 7.73-7.80 (2 H, m, Ar-**$H_{6,10}$**) 7.85 (2H, d, *J* = 8 Hz, Ar-**H_2**).

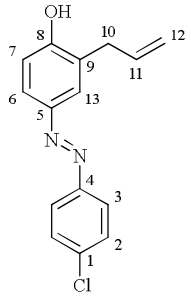
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 35.1 (CH_2, **C**$_{11}$), 116.2 (CH, Ar-H, **C**$_7$), 117.1 (CH_2, **C**$_{13}$), 123.7 (CH, Ar-H, **C**$_6$), 124.2 (CH, Ar-H, **C**$_3$), 125.3 (CH, Ar-H, **C**$_{10}$), 135.6 (CH, **C**$_{12}$), 138.2 (CH, Ar-H, **C**$_2$), 96.6, 126.1, 147.1, 152.1, 157.2.

MS (ES+): m/z $[M+H]^+$ 365; (ES-): m/z $[M-H]^-$ 363.

Accurate Mass: $C_{15}H_{12}N_2IO$ requires 326.9999 found 362.9996.

IR ν_{max} (film):1271, 1422, 1447, 1500, 1588, 2968 cm^{-1}.

6.5 Synthesis of (*E*)-2-allyl-4-((4-chlorophenyl)diazenyl)phenol (118c):[93]



Was prepared using general procedure F; [(*E*)-1-(2-(allyloxy)phenyl)-2-(4-chlorophenyl)diazene (0.293 g, 1.08 mmol) and Et_2AlCl (2.2 mL, 1 M soln. in hexane) in dry DCM (10 mL).The *title compound* (0.237 g, 87%, crystalline; **mp** 97 ˚C, lit[93] 98-99 ˚C) was obtained by column chromatography (40% DCM in Hexane).

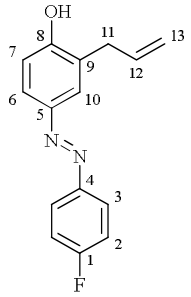
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.51 (2H, d, *J* = 6 Hz, CH_2,**H**$_{10}$) 5.20 (1H, t, *J* = 1 Hz, CH_2,**H**$_{12}$) 5.24 (1H, dd, *J* = 7, 1 Hz, CH_2, **H**$_{12}$) 5.99-6.16 (1H, m, CH, **H**$_{11}$) 6.91 (1H, d, *J* = 8 Hz, Ar-**H**$_7$) 7.37-7.54 (2H, m, Ar-**H**$_2$) 7.72-7.78 (2H, m, Ar-**H**$_{6,13}$) 7.80-7.86 (2H, m, Ar-**H**$_3$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 34.9 (CH_2, C_{10}), 116.2 (CH, Ar-H, C_7), 117.1 (CH_2, C_{12}), 123.6 (CH, Ar-H, C_6),123.7 (CH, Ar-H, C_3),125.1 (CH, Ar-H, C_{13}),129.2 (CH, Ar-H, C_2),135.7 (CH, C_{11}), 157.2, 151, 146.8, 136.1, 126.3.

MS (ES-): $[M-H]^-$ 271.

Accurate Mass: $C_{15}H_{12}N_2{}^{35}ClO$ requires 271.0643 found 271.0651.

6.6 Synthesis of (*E*)-2-allyl-4-((4-flourophenyl)diazenyl)phenol (118d):



Was prepared using general procedure F; (E)-1-(2-(allyloxy)phenyl)-2-(4-flourophenyl)diazene(0.276 g, 1.08 mmol) and Et_2AlCl (2.2 mL, 1 M soln. in hexane) in dry DCM (10 mL).The *title compound* (0.223 g, 87%, crystalline; **mp** 97-98 ˚C) was obtained by column chromatography (40% DCM in hexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.52 (2H, d, *J* = 6 Hz, CH_2,**H_{11}**) 5.19 (1 H, t, *J*=1 Hz, CH_2, **H_{13}**) 5.24 (1 H, dd, *J*=7, 1 Hz, CH_2, **H_{13}**) 5.87 (1 H, br. s., OH) 6.10 (1H, m, CH, **H_{12}**) 6.87 (1H, d, *J* = 8 Hz, CH, Ar-**H_7**) 7.20 (2H, t, *J*=8.67 Hz, CH, Ar-**H_2**) 7.75 (1 H, dd, *J* = 8, 2.45 Hz, CH, Ar-**H_6**) 7.81 (1 H, d, *J* = 2 Hz, CH, Ar-**H_{10}**) 7.89-7.96 (2H, m, CH, Ar-**H_3**).

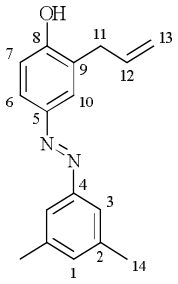
^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 34.6 (CH_2, **C_{11}**),115.9 (CH, Ar-H, **C_7**),116.1 (CH, Ar-H, **C_2**),116.7 (CH_2, **C_{13}**),123.3 (CH, Ar-H, **C_6**),124.4 (CH, Ar-H, **C_3**),126.6 (CH, Ar-H, **C_{10}**),135.7 (CH, C_{12}),124.3,146.6,149.1,157.1,165.5.

MS (ES-): $[M-H]^-$ 255.

Accurate Mass: $C_{15}H_{12}N_2FO$ requires 255.0939 found 255.0924.

IR ν_{max} (film): 1271, 1363, 1405, 1496, 1587, 3001 cm^{-1}.

6.7 Synthesis of (*E*)-2-allyl-4-((3,5-dimethylphenyl)diazenyl)phenol (119):



Was prepared using general procedure F; (*E*)-1-(2-(allyloxy)phenyl)-2-(3,5-dimethylphenyl)diazene (0.288 g, 1.08mmol) and Et_2AlCl (2.2 mL, 1 M soln. in hexane) in dry DCM (10 mL).The *title compound* (0.259 g, 87%, yellow oil) was obtained by column chromatography (40% DCM in hexane).

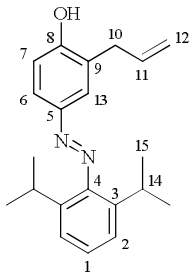
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.42 (6H, s, CH_3,**H**$_{14}$) 3.51 (2H, d, *J* = 6 Hz, CH_2,**H**$_{11}$) 5.16-5.20 (1H, m, CH_2,**H**$_{13}$) 5.20-5.28 (1H, m, CH_2,**H**$_{13}$) 5.92-6.17 (1H, m, CH,**H**$_{12}$) 6.91 (1H, d, *J* = 8 Hz, Ar-**H**$_7$) 7.10 (1H, s, Ar-**H**$_1$) 7.52 (2 H, s, Ar-**H**$_3$) 7.70-7.81 (1H, m, Ar-**H**$_{6,10}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.2 (CH_3, **C**$_{14}$), 34.9 (CH_2, **C**$_{11}$), 116.01 (CH, Ar-H, **C**$_7$), 116.8 (CH, Ar-H, **C**$_{13}$), 120.3 (CH, Ar-H, **C**$_3$),123.3 (CH, Ar-H, **C**$_6$), 125.1 (CH, Ar-H, **C**$_{10}$), 132.1 (CH, Ar-H, **C**$_1$), 135.8, 138.6, 147.1, 152.9, 156.9.

MS (ES-): $[M-H]^+$ 265.

Accurate Mass: $C_{17}H_{17}N_2O$ requires 265.1346 found 265.1339.

6.8 Synthesis of (*E*)-2-allyl-4-(2,6-*iso*-propylphenyl)diazenyl)phenol (120):



Was prepared using general procedure F; (*E*)-1-(2-(allyloxy)phenyl)-2-(2,6-di-*iso*propylphenyl)diazene (0.257 g, 1.08 mmol) and Et_2AlCl (2.2 mL, 1.0 M soln. in hexane) in dry DCM (10 mL). The *title compound* (0.221 g, 86%, crystalline) was obtained by column chromatography (50 % DCM in hexane).

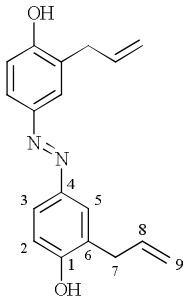
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.16 (12H, d, *J* = 6 Hz, CH_3,**H**$_{15}$) 2.89-3.08 (2H, m, CH,**H**$_{14}$) 3.52 (2H, d, *J* = 6 Hz, CH_2,**H**$_{10}$) 5.16-5.31 (2H, m, CH_2,**H**$_{12}$) 5.63 (1H, br. s., OH) 6.08 (1H, ddt, *J* = 16, 10, 6 Hz, CH, **H**$_{11}$) 6.93 (1H, d, *J*=9 Hz, Ar-**H**$_7$) 7.17-7.28 (3H, m, Ar-**H**$_{1,2}$) 7.68-7.78 (2H, m, Ar-**H**$_{6,13}$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 23.4 (CH_3, **C**$_{15}$), 27.7 (CH, **C**$_{14}$), 35.2 (CH_2, **C**$_{10}$), 116.2 (CH, Ar-H, C_7), 117.2 (CH_2, C_{12}), 122.8 (CH, Ar-H, C_2), 123.4 (CH, Ar-H, C_6), 125.1 (CH, Ar-H, **C**$_1$), 127.2 (CH, Ar-H, **C**$_{13}$), 139.3 (CH, **C**$_{11}$), 126.1, 135.7, 147.1, 151.2, 157.1.

MS (ES+): m/z $[M+H]^+$ 323; **(ES-):** m/z $[M-H]^-$ 321.

Accurate Mass: $C_{21}H_{27}N_2O$ requires 323.2118 found 323.2126.

6.9 Synthesis of (*E*)-2-allyl-4-(3-allyl-4-hydroxyphenyl)diazenyl)phenol (121):



Was prepared using general procedure F; (*E*)-1,2-bis(4-allyloxy)phenyl)diazene

(0.317 g, 1.08 mmol) and Et_2AlCl (3.5 mL, 1.0 M soln. in hexane) in dry DCM (10 mL) The *title compound* (0.272 g, 86%, crystalline; **mp** 159-160 ˚C) was obtained by recrystallisation.

^{1}H NMR (300 MHz, CD_3OD) δ ppm 3.42 (4H, d, *J* = 6 Hz, CH_2, **H_7**) 4.99-5.17 (4H, m, CH_2, **H_9**) 5.87-6.13 (2H, m, CH, **H_8**) 6.87 (2 H, d, *J* = 8 Hz, CH, Ar-**H_2**) 7.46-7.66 (4H, m, CH, Ar-**$H_{3,5}$**).

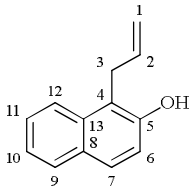
^{13}C NMR (75 MHz, CD_3OD)δ ppm 35.1 (CH_2, **C_7**), 115.7 (CH_2, **C_9**), 115.8 (CH, Ar-H, **C_2**), 123.3 (CH, Ar-H, **C_3**), 124.9 (CH, Ar-H, **C_5**), 137.7 (CH, **C_8**), 128.4, 147.4, 158.8.

MS (ES+): m/z $[M+H]^+$ 295.

Accurate Mass: $C_{18}H_{19}N_2O_2$ requires 295.1441 found 295.1438.

IR ν_{max} (film): 1272, 1355, 1432, 1498, 1584, 3027 cm^{-1}.

6.10 Synthesis of 1-allylnaphthalen-2-ol:[74](88)



(E)-1-(2-(allyloxy)naphthalen-1-yl)-2-(4-bromophenyl)diazene (0.672 g, 2.07 mmol) in N,N-Diethylaniline (2 mL) was heated at 180 ˚C for 15 hours. The reaction mixture was allowed to cool and then extracted with ethylacetate. Washed the organic layer with 2 M HCl (3 x 30 mL) and then with water.The combined organic layers were dried over $MgSO_4$ and reduced *in vacuo.* Compound was purified by column chromatography (88% in yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.85 (2H, d, *J* = 5 Hz, CH_2, **H**$_3$) 5.04-5.15 (3H, m, CH_2, **H**$_1$, Ar-**H**$_6$) 6.03-6.14 (1H, m, CH, **H**$_2$) 7.12 (1H, d, *J*= 8 Hz, CH, Ar-**H**$_7$) 7.37 (1H, ddd, J = 8, 7, 1, CH_2, Ar-**H**$_{10}$) 7.48 (1H, d, *J*= 9 Hz, CH_2, Ar-**H**$_{11}$) 7.69 (1H, d, *J*= 8 Hz, CH_2, Ar-**H**$_9$) 7.79 (1H, d, *J*= 8 Hz, CH_2, Ar-**H**$_{12}$).

IR max(film): 1261 1354, 1390, 1437, 1514, 1597 ,1626, 3412cm-1.

MS (ES-): m/z $[M-H]^+$ 183.

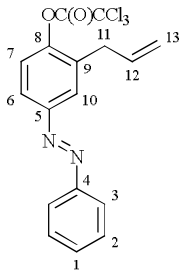
Accurate Mass: $C_{13}H_{11}O$ + e require 183.0812 found 183.0815.

Method B:

Was prepared using general procedure F; (*E*)-1-(2-(allyloxy)naphthalen-1-yl)-2-(4-bromophenyl)diazene (0.365 g,1.08mmol) and Et_2AlCl (2.2 mL,1 M soln. in hexane) in dry DCM (10 mL). The *title compound* (17% in yield) was obtained by column chromatography (40% DCM in hexane) as pinl coloured crystals.

7 ACYLATION

7.1 Synthesis of 4-[(*E*)-phenyldiazenyl]-2-(prop-2-en-1-yl)phenyltrichloroacetate (84):

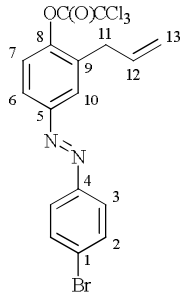


Was prepared by using general procedure J; (*E*)-2-allyl-4-(phenyldiazenyl)phenol (1 eq.,0.234 g), trichloroacetylchloride (0.2 mL) and triethylamine (0.25 mL) in 3 mL dry ether at 0 °C for 3 hours. The *title compound* (0.299 g, 81%) was obtained as brownish oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.50 (2H, dd, *J* = 6, 1 Hz, CH_2, $\mathbf{H}_{11}$) 5.15 (1H, dq, *J* = 8, 1 Hz, CH_2, $\mathbf{H}_{13}$) 5.19 (1H, m, CH_2, $\mathbf{H}_{13}$) 5.92-6.07 (1H, m, CH, $\mathbf{H}_{12}$) 7.35 (1H, dd, *J* = 7,2 Hz, CH, Ar-$\mathbf{H}_7$) 7.51-7.55 (3H, m, CH, Ar-$\mathbf{H}_{1,2}$) 7.87-7.97 (4H, m, CH, Ar-$\mathbf{H}_{3,6,10}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 34.1 (CH_2, $\mathbf{C}_{11}$), 117.3 (CH_2, $\mathbf{C}_{13}$), 121.8 (CH, Ar-H, $\mathbf{C}_7$), 122 (CH, Ar-H, $\mathbf{C}_6$), 122.9 (CH, Ar-H, $\mathbf{C}_3$), 125.4 (CH, Ar-H, $\mathbf{C}_{10}$), 129.1 (CH, Ar-H, $\mathbf{C}_2$), 131.3 (CH, Ar-H, $\mathbf{C}_1$), 134.7 (CH, Ar-H, $\mathbf{C}_{12}$), 132.9, 151.2, 150.2, 152.5,160.2.

7.2 Synthesis of4-[(*E*)-(4-bromophenyl)diazenyl]-2-(prop-2-en-1-yl)phenyltrichloroacetate (84a):

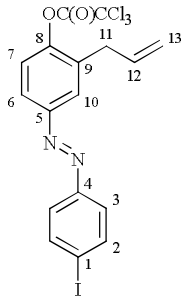


Was prepared by using general procedure J; (*E*)-2-allyl-4-(4-bromophenyldiazenyl)phenol (1 eq., 0.316 g), trichloroacetylchloride (0.2 mL) and triethylamine (0.25 mL) in 3 mL dry ether at 0 °C for 3 hours. The *title compound* (0.252 g, 80 %) was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.50 (2H, d, *J* = 7 Hz, CH_2, **H**$_{11}$) 5.14 (1H, dd, *J* = 9, 1 Hz, CH_2, **H**$_{13}$) 5.17-5.22 (1H, m, CH_2, **H**$_{13}$) 5.89-6.05 (1H, m, CH_2, **H**$_{12}$) 7.35 (1H, d, *J* = 9 Hz, CH, Ar-**H**$_7$) 7.67 (2H, dd, *J* = 9,2 Hz, CH, Ar-**H**$_2$) 7.81 (2H, dd, *J* = 9,2 Hz, Ar-**H**$_3$) 7.85-7.91 (2H, m, CH, Ar-**H**$_{6,10}$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 34.1 (CH_2, **C**$_{11}$), 117.4 (CH_2, **C**$_{13}$), 121.9 (CH, Ar-H, **C**$_7$), 122.1 (CH, Ar-H, **C**$_7$), 124.4 (CH_2, Ar-H, **C**$_3$), 125.4 (CH, Ar-H, **C**$_{10}$), 132.4 (CH, Ar-H, **C**$_2$), 65.8, 125.8, 134.6, 150.4, 151.1, 155.6, 160.1.

7.3 Synthesis of 4-[(*E*)-(4-iodophenyl)diazenyl]-2-(prop-2-en-1-yl)phenyltrichloroacetate (84b):

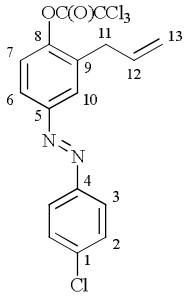


Was prepared by using general procedure J; (*E*)-2-allyl-4-(4-iodophenyldiazenyl)phenol (1 eq., 0.364 g), trichloroacetylchloride (0.2 mL), and triethylamine (0.25 mL) in 3 mL dry ether at 0 °C for 3 hours. The *title compound* (0.412 g, 81%) was obtained as dark brown oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.49 (2H, d, *J* = 6 Hz, CH_2, **H**$_{11}$) 5.14 (1H, dd, *J* = 10, 1 Hz, CH_2, **H**$_{13}$) 5.17-5.20 (1H, m, CH_2, **H**$_{13}$) 5.99 (1H, m, CH, **H**$_{10}$) 7.35 (1H, dd, *J* = 9,2 Hz, CH, Ar-**H**$_7$) 7.66 (2H, dd, *J* = 9,2 Hz, CH, Ar-**H**$_3$) 7.85-7.91 (4H, m, CH, Ar-**H**$_{2,6,10}$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 34.1 (CH_2, C_{11}), 117.4 (CH_2, C_{13}), 121.9 (CH, Ar-H, C_7), 122.2 (CH, Ar-H, C_6), 124.5 (CH, Ar-H, C_3), 125.4 (CH, Ar-H, C_{10}), 133.1 (CH, C_{10}), 138.4 (CH, Ar-H, C_2), 98.1, 150.4, 150.9, 151.7, 160.1.

7.4 Synthesis of4-[(*E*)-(4-chlorophenyl)diazenyl]-2-(prop-2-en-1-yl)phenyltrichloroacetate (84c):

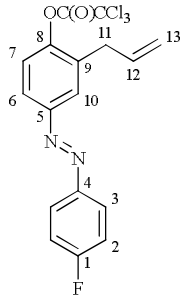


Was prepared by using general procedure J; (*E*)-2-allyl-4-(4-chlorophenyldiazenyl)phenol (1 eq., 0.272 g), trichloro acetyl chloride (0.2 mL), and triethylamine (0.25 mL) in 3 mL dry ether at 0 °C for 3 hours. The *title compound* (0.346 g, 83 %) was obtained as dark brown oil

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.49 (2H, dd, *J* = 6, 2 Hz, CH_2,**H_{11}**) 5.14 (1H, dd, *J* = 9, 1 Hz, CH_2, **H_{13}**) 5.17-5.20 (1H, m, CH_2, **H_{13}**) 5.99 (1H, m, CH, **H_{12}**) 7.35 (1H, d, *J* = 9 Hz, CH, Ar-**H_7**) 7.51 (2H, d, *J* = 8 Hz, CH, Ar-**H_2**) 7.86-7.91 (4H, m, CH, Ar-**$H_{3,6,10}$**).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 34.1 (CH_2, **C_{11}**), 117.4 (CH_2, **C_{13}**), 121.9 (CH, Ar-H, **C_7**), 122.1 (CH, Ar-H, **C_6**), 124.2 (CH, Ar-H, **C_3**), 125.4 (CH, Ar-H, **C_3**), 129.4 (CH, Ar-H, **C_2**), 134.6 (CH, Ar-H, **C_{12}**), 89.4, 133, 137.3, 150.4, 150.8, 150.9,160.1.

7.5 Synthesis of 4-[(*E*)-(4-flourophenyl)diazenyl]-2-(prop-2-en-1-yl)phenyltrichloroacetate (84d):

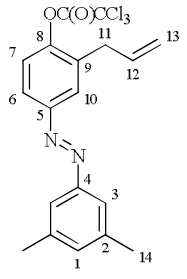


Was prepared by using general procedure J (*E*)-2-allyl-4-(4-flourophenyldiazenyl)phenol (1 eq., 0.256 g), trichloroacetylcholride (0.2 mL) and triethylamine (0.25 mL) in 3mL dry ether at 0 °C for 3 hours. The *title compound* (0.356 g, 89%) was obtained.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.50 (2H, d, *J* = 6 Hz, CH_2,**H**$_{11}$) 5.14 (1H, d, *J* = 1 Hz, CH_2,**H**$_{13}$) 5.16-5.19 (1H, m, CH_2,**H**$_{13}$) 5.99 (1H, m, CH,**H**$_{12}$) 7.22 (2H, t, *J* = 9 Hz, CH, Ar-**H**$_2$) 7.35 (1H, d, *J* = 8.20 Hz, CH, Ar-**H**$_7$) 7.84-7.91 (2H, m, CH, Ar-**H**$_{6,10}$) 7.96 (2H, dd, *J* = 9, 5 Hz, CH, Ar-**H**$_3$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 34.1 (CH_2, **C**$_{11}$), 116.2 (CH, Ar-H, **C**$_2$), 117.3 (CH, Ar-H, **C**$_{13}$), 121.8 (CH, Ar-H, **C**$_7$), 122.1 (CH, Ar-H, **C**$_6$), 124.9 (CH, Ar-H, **C**$_3$), 125.1 (CH, Ar-H, **C**$_{10}$), 132.9 (CH, **C**$_{12}$), 89.4, 148.9, 150.2, 150.9, 160.1, 165.5.

7.6 Synthesis of 4-[(*E*)-(3,5-dimethylphenyl)diazenyl]-2-(prop-2-en-1-yl)phenyltrichloroacetate (122):

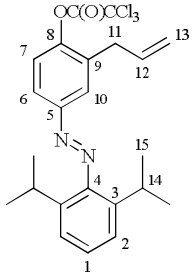


Was prepared by using general procedure J (*E*)-2-allyl-4-(3,5-dimethyl phenyldiazenyl)phenol (1 eq.,0.266 g), trichloroacetylchloride (0.2 mL) and triethylamine (0.25 mL) in 3 mL dry ether at 0 °C for 3 hours. The *title compound* (0.332 g, 81%) was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.43 (6H, s, CH_3,**H_{14}**) 3.49 (2H, d, *J* = 7 Hz, CH_2, **H_{11}**) 5.11-5.16 (1H, m, CH_2, **H_{13}**) 5.19 (1H, t, *J* = 1 Hz, CH_2, **H_{13}**) 5.91-6.07 (1H, m, CH_2, **H_{12}**) 7.16 (1H, s, CH, Ar-**H_1**) 7.35 (1H, dd, *J* = 9,1 Hz, CH, Ar-**H_7**) 7.56 (2H, s, CH, Ar-**H_3**) 7.84-7.89 (1H, m, Ar-**$H_{6.10}$**).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.2 (CH_3, **C_{14}**), 34.1 (CH_2, **C_{11}**), 117.3 (CH_2, **C_{13}**), 120.7 (CH, Ar-H, **C_3**), 121.8 (CH, Ar-H, **C_7**), 121.9 (CH, Ar-H,**C_6**), 125.2 (CH, Ar-H, **C_{10}**), 133.1 (CH, Ar-H, **C_1**), 134.7 (CH, **C_{12}**), 65.8, 117.8, 150.1, 151.2, 152, 160.

7.7 Synthesis of 4-[(*E*)-(2,6-diisopropylphenyl)diazenyl]-2-(prop-2-en-1-yl)phenyltrichloroacetate (123):



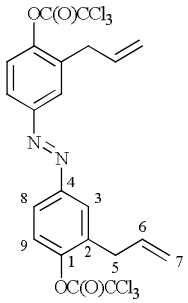
Was prepared by using general procedure J (E)-2-allyl-4-(2,6-*iso*-propylphenyldiazenyl)phenol (1 eq., 0.322 g), trichloroacetylchloride (0.2 mL), triethylamine (0.25 mL) in 3 mL dry ether at 0 °C for 3 hours. The *title compound* (0.378 g, 81%) was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.17 (12H, d, *J* = 6 Hz, CH_3) 3.02 (2H, quin, *J* = 6 Hz, CH, **H_{14}**) 3.49 (2H, d, *J* = 6 Hz, CH, **H_{11}**) 5.12 (1H, d, *J* = 3.01 Hz, CH, **H_{13}**) 5.17 (1H, d, *J* =

2 Hz, CH_2, $\mathbf{H}_{13}$) 5.87-6.05 (1H, m, CH, $\mathbf{H}_{12}$) 7.19-7.26 (3H, m, CH, Ar-$\mathbf{H}_{2,7}$) 7.34 (1H, m, CH, Ar-$\mathbf{H}_1$) 7.82 (1H, d, *J* = 3 Hz, Ar-$\mathbf{H}_6$) 7.85 (1 H, s, Ar-$\mathbf{H}_{10}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 23.5 (CH_3, $\mathbf{C}H_3$), 34.1 (CH_2, $\mathbf{C}_{11}$), 27.8 (CH, $\mathbf{C}_{14}$), 117.4 (CH_2, $\mathbf{C}_{13}$), 121.5 (CH, Ar-H, $\mathbf{C}_6$), 121.9 (CH, Ar-H, $\mathbf{C}_1$), 123.5 (CH_2, Ar-H, $\mathbf{C}_2$), 125.4 (CH, Ar-H, $\mathbf{C}_{10}$), 128.1 (CH, Ar-H, $\mathbf{C}_7$), 84.8, 139.5,151.1, 155.5, 160.2.

7.8 Synthesis of (*E*)-diazene-1,2-diylbis-2-(prop-2-en-1-yl)benzene-4,1-diyl bis(trichloroacetate) (124):



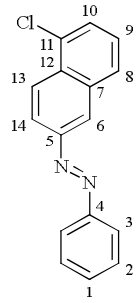
Was prepared by using general procedure J; (*E*)-2-allyl-4-(3-allyl-4-hydroxyphenyl)diazenyl)phenol(1 eq., 0.294 g), trichloroacetylchloride (0.2 mL) and triethylamine (0.25 mL) in 3mL dry ether at 0 °C for 3 hours. The *title compound* (0.473 g, 81%) was obtained as brown oil

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.49 (4H, d, *J* = 6 Hz, CH_2, H_5) 5.12-5.17 (2H, m, CH_2, H_7) 5.18-5.21 (2H, m, CH_2, H_7) 6 (2H, m, CH, H_6) 7.3 (2H, d, *J* = 9.04 Hz, CH, Ar-H_8) 7.87-7.93 (4H, m, CH, Ar-$H_{3,9}$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 34.1 (CH_2, $\mathbf{C}_5$), 117.4 (CH_2, $\mathbf{C}_7$), 121.9 (CH, Ar-H, $\mathbf{C}_8$), 122.1 (CH, Ar-H, $\mathbf{C}_9$), 125.5 (CH, Ar-H, $\mathbf{C}_3$), 133.1 (CH, $\mathbf{C}_6$), 84.8, 134.6, 150.4, 150.9, 160.1.

8 BENZANNULATION

8.1 Synthesis of (*E*)-1-(5-chloronaphthalen-2-yl)-2-phenyldiazene (85):



The trichloroacetate species (0.5 mmol, 192 mg, 1 eq.) was heated with the Nolan catalyst (16 mg, 5 mol %) and diglyme (0.5 mL) at 170 °C for 3 hrs. The reaction was allowed to cool, and then purified directly by flash column chromatography (100% pet. ether). The desired product (0.103 g) was obtained in 78% yield (**mp** 113-114 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.41-7.59 (4H, m, CH, Ar-$\mathbf{H}_{1,2,9}$) 7.66 (1H, dd, *J* = 7, 1 Hz, CH, Ar-$\mathbf{H}_{10}$) 7.89-8.04 (3H, m, CH, Ar-$\mathbf{H}_{3,8}$) 8.18 (1H, dd, *J* = 9, 2 Hz, CH, Ar-$\mathbf{H}_{14}$) 8.38 (1H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_{13}$) 8.48 (1H, d, *J* = 2 Hz, CH, Ar-$\mathbf{H}_{6}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 118.6 (CH, Ar-H, $\mathbf{C}_{14}$), 122.9 (CH, Ar-H, $\mathbf{C}_{3}$), 125.7 (CH, Ar-H, $\mathbf{C}_{13}$), 126.7 (CH, Ar-H, $\mathbf{C}_{9}$), 127.2 (CH, Ar-H, $\mathbf{C}_{6}$), 127.6 (CH, Ar-H, $\mathbf{C}_{10}$), 128.5 (CH, Ar-H, $\mathbf{C}_{8}$), 129.2 (CH, Ar-H, $\mathbf{C}_{2}$), 131.2 (CH, Ar-H, $\mathbf{C}_{1}$), 131.9, 132.1, 134.8, 150.6, 152.6.

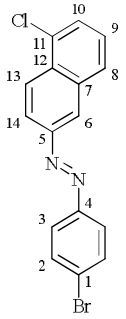
MS (ES+): m/z $[M+H]^+$ 267.

Accurate Mass: $C_{16}H_{12}N_2Cl$ requires 267.0684 found 267.0674.

Microanalysis: $C_{16}H_{12}N_2$ requires C 72.01; H 4.10; N 10.51%. Found C 71.76; H 3.96; N 10.32%.

IR ν_{max} (film): 1286, 1334, 1415, 1457, 1570, 3011 cm^{-1}.

8.2 Synthesis of (*E*)-1-(5-chloronaphthalen-2-yl)-2-(4-bromophenyl)diazene (85a):



The trichloroacetate species (0.5 mmol, 230 mg) was heated with the Nolan catalyst (16 mg, 5 mol %) and diglyme (0.5 mL) at 170 °C for 3 hrs. The reaction was allowed to cool, and then purified directly by flash column chromatography (100% pet. ether). The desired product (0.138 g) was obtained in 80% yield (**mp** 162-163 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.48 (1H, t, *J* = 7 Hz, CH, Ar-**H**$_9$) 7.57-7.63 (3H, t, *J* = 6 Hz, CH, Ar-**H**$_{2,10}$) 7.88 (2H, dd, *J* = 9,2 Hz, CH, Ar-**H**$_3$) 7.95 (1H, d, *J* = 8 Hz, CH, Ar-**H**$_8$) 8.15 (1H, dd, *J* = 9, 2 Hz, CH, Ar-**H**$_{14}$) 8.36 (1H, d, *J* = 9 Hz, CH, Ar-**H**$_{13}$) 8.46 (1H, s, CH, Ar-**H**$_6$).

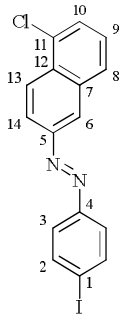
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 118.2 (CH, Ar-H, **C**$_{14}$), 124.4 (CH, Ar-H, **C**$_3$), 125.8 (CH, Ar-H, **C**$_{13}$), 126.8 (CH, Ar-H, **C**$_9$), 127.8 (CH, Ar-H, **C**$_6$), 127.8 (CH, Ar-H, **C**$_{10}$), 128.5 (CH, Ar-H, **C**$_8$), 132.4 (CH, Ar-H, **C**$_2$), 125.7, 132.1, 132.2, 134.7, 150.4, 151.3.

MS (ES+): m/z $[M+H]^+$ 344.

Accurate Mass: $C_{16}H_{10}N_2{}^{79}Br^{35}Cl$ requires 343.9710 found 343.9718.

IR ν_{max} (film): 1334, 1449, 1474, 1566, 3012 cm^{-1}.

8.3 Synthesis of (*E*)-1-(5-chloronaphthalen-2-yl)-2-(4-iodophenyl)diazene (85b):



The trichloroacetate species (0.5 mmol, 253 mg) was heated with the Nolan catalyst (16 mg, 5 mol %) and diglyme (0.5 mL) at 170 °C for 3 hrs. The reaction was allowed to cool, and then purified directly by flash column chromatography (100% pet. ether). The desired product(0.301 g) was obtained in 77% yield (**mp** 153 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.45 (1H, t, *J* = 8 Hz, CH, Ar-**H**$_9$) 7.67 (1H, dd, *J* = 8 Hz, CH, Ar-**H**$_{10}$) 7.73 (2H, dd, *J* = 9,2 Hz, CH, Ar-**H**$_3$) 7.91 (2H, dd, *J* = 9,2 Hz, CH, Ar-**H**$_2$) 7.95 (1H, d, *J* = 8 Hz, CH, Ar-**H**$_8$) 8.14 (1H, dd, *J* = 9, 2 Hz, CH, Ar-**H**$_{14}$) 8.36 (1H, d, *J* = 9 Hz, CH, Ar-**H**$_{13}$) 8.47 (1H, d, *J* = 2 Hz, CH, Ar-**H**$_6$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 118.2 (CH, Ar-H, **C**$_{14}$), 124.5 (CH, Ar-H, **C**$_3$), 125.8 (CH, Ar-H, **C**$_{13}$), 126.8 (CH, Ar-H, **C**$_9$), 127.8 (CH, Ar-H, **C**$_{10}$), 127.8 (CH, Ar-H, **C**$_6$), 128.5 (CH, Ar-H, **C**$_8$), 138.4 (CH, Ar-H, **C**$_2$), 98.1, 132.1, 132.2, 134.7, 150.4,151.9.

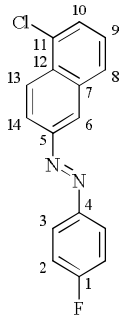
MS (ES+): m/z $[M+H]^+$ 392.

Accurate Mass: $C_{16}H_{10}N_2ICl$ requires 391.9572 found 391.9574.

Microanalysis: $C_{16}H_{10}N_2$ requires C 48.95; H 2.50; N 7.13%. Found C 49.5; H 2.29; N 7.05%.

IR ν_{max} (film): 1334, 1391, 1471, 1566, 1577, 3030 cm^{-1}.

8.4 Synthesis of (*E*)-1-(5-chloronaphthalen-2-yl)-2-(4-flourophenyl)diazene (85c):



The trichloroacetate species (0.5 mmol, 200 mg) was heated with the Nolan catalyst (16 mg, 5 mol %) and diglyme (0.5 mL) at 170 °C for 3 hrs. The reaction was allowed to cool, and then purified directly by flash column chromatography (100% pet. ether). The desired product (0.123 g) was obtained in 87% yield (**mp** 134-135 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.07-7.17 (2H, m, CH, Ar-**H**$_2$) 7.33-7.40 (1H, m, CH, Ar-**H**$_9$) 7.54 (1H, d, *J* = 8 Hz, CH, Ar-**H**$_{10}$) 7.84 (1H, d, *J* = 8 Hz, CH, Ar-**H**$_8$) 7.91 (2H, dd, *J* = 9, 5 Hz, CH, Ar-**H**$_3$) 8.03 (1H, dd, *J* = 9, 2 Hz, CH, Ar-**H**$_{14}$) 8.25 (1H, d, *J* = 9 Hz, CH, Ar-**H**$_{13}$) 8.33 (1H, d, *J* = 2 Hz, CH, Ar-**H**$_6$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 115.9 (CH, Ar-H, **C**$_2$), 118.4 (CH, Ar-H, **C**$_{14}$), 124.9 (CH, Ar-H, **C**$_3$), 125.8 (CH, Ar-H, **C**$_{13}$), 126.7 (CH, Ar-H, **C**$_9$), 127.3 (CH, Ar-H, **C**$_6$), 127.6 (CH, Ar-H, **C**$_{10}$), 128.5 (CH, Ar-H, **C**$_8$), 131.9, 132.1, 134.7, 149.1, 150.4, 166.2.

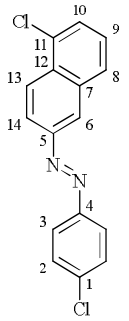
MS (ES+): m/z $[M+H]^+$ 285.

Accurate Mass: $C_{16}H_{11}N_2{}^{35}ClF$ requires 285.0590 found 285.0586.

Microanalysis: $C_{16}H_{11}N_2Cl$ requires C 67.50; H 3.54; N 9.84; Cl 12.45%. Found C 67.26; H 3.13; N 9.83; Cl 12.48%.

IR ν_{max} (film): 1453, 1492, 1590, 3021 cm^{-1}.

8.5 Synthesis of (*E*)-1-(5-chloronaphthalen-2-yl)-2-(4-chlorophenyl)diazene (85d):



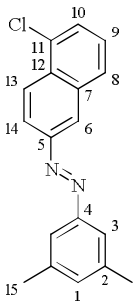
The trichloroacetate species (0.5 mmol, 207 mg) was heated with the Nolan catalyst (16 mg, 5 mol %) and diglyme (0.5 mL) at 170 °C for 3 hrs. The reaction was allowed to cool, and then purified directly by flash column chromatography (100% pet. ether). The desired product(0.120 g) was obtained in 80% yield (**mp** 143 ˚C).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.49 (1H, t, *J* = 8 Hz, CH, Ar-**H**$_9$) 7.53 (2H, dd, *J* = 9,2 Hz, CH, Ar-**H**$_2$) 7.67 (1H, dd, *J* = 7,1 Hz, CH, Ar-**H**$_{10}$) 7.95 (3H, dd, *J* = 9,2 Hz, CH, Ar-**H**$_{3,8}$) 8.15 (1H, dd, *J* = 9, 2 Hz, CH, Ar-**H**$_{14}$) 8.37 (1H, d, *J* = 9 Hz, CH, Ar-**H**$_{13}$) 8.47 (1 H, s, CH, Ar-**H**$_6$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 118.1 (CH, Ar-H, **C**$_{14}$), 124.2 (CH, Ar-H, **C**$_3$), 125.8 (CH, Ar-H, **C**$_{13}$), 126.8 (CH, Ar-H, **C**$_9$), 127.8 (CH, Ar-H, **C**$_{10}$), 127.8 (CH, Ar-H, **C**$_6$), 128.5 (CH, Ar-H, **C**$_8$), 129.4 (CH, Ar-H, **C**$_2$), 132.1, 136.4, 137.7, 137.2, 150.4, 156.8.

IR ν_{max} (film): 1459, 1481, 1590, 3076 cm^{-1}.

8.6 Synthesis of (*E*)-1-(5-chloronaphthalen-2-yl)-2-(3, 5-dimethylphenyl)diazene (125):



The trichloroacetate species (0.5 mmol, 205 mg) was heated with the Nolan catalyst (16 mg, 5 mol %) and diglyme (0.5 mL) at 170 °C for 3 hrs. The reaction was allowed to cool, and then purified directly by flash column chromatography (100% pet. ether). The desired product (0.147 g) was obtained in 77% yield (mp 123-124 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.45 (6H, s, CH_3) 7.17 (1H, s, CH, Ar-**H**$_1$) 7.43-7.51 (1H, m, CH, Ar-**H**$_9$) 7.62 (2H, s, CH, Ar-**H**$_3$) 7.65 (1H, dd, *J* = 7, 1 Hz, CH, Ar-**H**$_8$) 7.95 (1H, d, *J* = 8 Hz, CH, Ar-**H**$_{10}$) 8.16 (1H, dd, *J* = 9, 2 Hz, CH, Ar-**H**$_{14}$) 8.36 (1H, d, *J* = 9 Hz, CH, Ar-**H**$_{13}$) 8.45 (1H, d, *J* = 2 Hz, CH, Ar-**H**$_6$)

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.2 (CH, Ar-H, **C**H_3), 118.6 (CH, Ar-H, **C**$_{14}$), 120.7 (CH, Ar-H, **C**$_3$), 125.7 (CH, Ar-H, **C**$_{13}$), 126.6 (CH, Ar-H, **C**$_9$), 126.9 (CH, Ar-H, **C**$_{10}$), 127.5 (CH, Ar-H, **C**$_9$), 128.5 (CH, Ar-H, **C**$_8$), 132.1 (CH, Ar-H, **C**$_6$), 133.0 (CH, Ar-H, **C**$_1$), 145.8, 150.6, 152.9, 134.8,131.8, 138.8

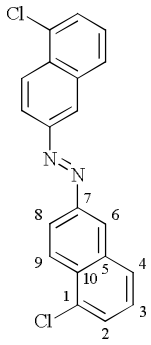
MS (ES+): m/z $[M+H]^+$ 295

Accurate Mass: $C_{18}H_{16}N_2{}^{35}Cl$ requires 295.0997 found 295.1002.

Microanalysis: $C_{18}H_{16}N_2Cl$ requires C 73.0; H 5.1; N 9.5%. Found C 72.7; H 5.0; N 9.1%.

IR ν_{max} (film): 1335, 1445, 1460, 1567, 3071 cm^{-1}.

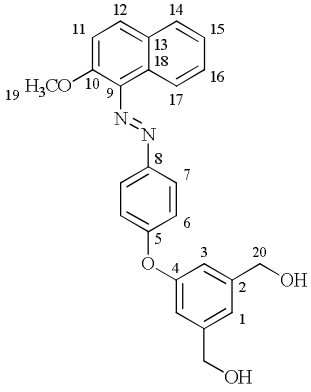
8.7 Synthesis of (*E*)-1, 2-bis (5-chloronaphthalen-2-yl) diazene (126):



The trichloroacetate species (0.5 mmol, 291 mg) was heated with the Nolan catalyst (16 mg, 5 mol %) and diglyme (0.5 mL) at 170 °C for 3 hours. The reaction was allowed to cool, and then purified directly by flash column chromatography (100% pet. ether). The desired product (0.124 g) was obtained in 72% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.50 (2H, t, *J*=8 Hz, CH, Ar-**H**$_3$) 7.68 (2H, dd, *J* = 8,1 Hz, CH, Ar-**H**$_2$) 7.99 (2H, d, *J* = 8 Hz, CH, Ar-**H**$_4$) 8.24 (2H, dd, *J*=10,2 Hz, CH, Ar-**H**$_9$) 8.40 (2H, d, *J* = 10 Hz, CH, Ar-**H**$_8$) 8.55 (2H, s, CH, Ar-**H**$_6$).

9 Synthesis of (*E*)-1-((4-(3,5-bis(hydroxymethyl)phenoxy)-2-(2-methoxy-1-diazene(94):



Was prepared by using general procedure K; (*E*)-1-(4-bromophenyl)-2-(2-methoxy-1-naphthyl)diazene (0. 340 g, 1 mmol), Copper (I) iodide (20 mol%; 38 mg) or Nolan catalyst (5 mol %,24 mg), picolinic acid (40 mol%, 50 mg), potassium phosphate tribasic (20 mmol,

424mg), 3,5-bis(hydroxymethyl)phenol (1.2 eq, 185 mg) were taken in oven dried schlenck tube under nitrogen followed by dry dimethylsulfoxide (2 mL). The product was purified by column chromatography (hexane and ethylacetate 1:3) as red coloured glass solid. The purified yield of the product was 50% (0.207 g).

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.01 (3H, s, CH_3) 4.72 (4H, d, *J* = 5 Hz, CH_2, $\mathbf{H}_{20}$) 7.05 (2H, s, CH, Ar-$\mathbf{H}_3$) 7.14-7.21 (3H, m, CH, Ar-$\mathbf{H}_{1,6}$) 7.38-7.45 (2H, m, CH, Ar-$\mathbf{H}_{11,15}$) 7.51 (1H, t, *J* = 8 Hz, CH, Ar-$\mathbf{H}_{16}$) 7.83 (1H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_{14}$) 7.88 (1H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_{12}$) 8.03 (2H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_7$) 8.33 (1H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_{17}$).

$^{1.3}$C NMR (75 MHz, $CDCl_3$) δ ppm 54.1 (CH_2, $\mathbf{H}_{20}$), 57.4 (CH_3), 114.7 (CH, Ar-H, $\mathbf{C}_{11}$), 118.3 (CH, Ar-H, $\mathbf{C}_3$), 119.1 (CH, Ar-H, $\mathbf{C}_6$), 120.1 (CH, Ar-H, $\mathbf{C}_1$), 122.7 (CH, Ar-H, $\mathbf{C}_{17}$), 124.4 (CH, Ar-H, $\mathbf{C}_7$), 124.6 (CH, Ar-H, $\mathbf{C}_{11}$), 127.6 (CH, Ar-H, $\mathbf{C}_{15}$), 127.8 (CH, Ar-H, $\mathbf{C}_{14}$), 130.1 (CH, Ar-H, $\mathbf{C}_{16}$), 138.3 (CH, Ar-H, $\mathbf{C}_{12}$), 129.2, 129.8, 130.8, 138.1, 148.4, 149.7, 157.5, 159.

Accurate Mass: $C_{25}H_{21}N_2O_4$ $[M+H]^+$ requires 413.1506 found 413.151.

Microanalysis: $C_{25}H_{20}N_2$ requires C 72.40; H 5.35; N 6.76%. Found C 70.71; H 5.07; N 6.55%.

IR ν_{max} (film): 1447, 1582, 1618, 3300 cm^{-1}.

Substrate B:

Was prepared by using general procedure K; (*E*)-1-(4-iodophenyl)-2-(2-methoxy-1-naphthyl)diazene (0. 388 g, 1 mmol), Copper(1)iodide (20 mol%, 38 mg) or Nolan catalyst (5 mol %,24 mg), picolinic acid (40 mol%, 50 mg), potassium phosphate tribasic (20 mmol, 424mg), 3,5-bis(hydroxymethyl)phenol (1.2 eq, 185 mg) were taken in oven dried schlenck tube under nitrogen followed by dry dimethylsulfoxide (2 mL/eq of substrate). The product

was purified by column chromatography (hexane and ethylacetate1:3). The purified yield of the product was 52%.

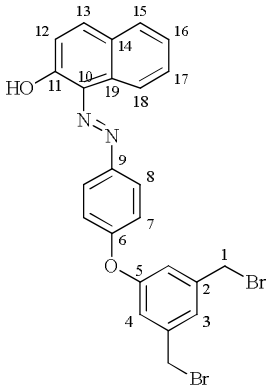
Substrate C:

Was prepared by using general procedure K; (*E*)-1-(4-chlorophenyl)-2-(2-methoxy-1-naphthyl)diazene (1 mmol, 0.296 g), Copper (1) iodide (20 mol%, 38 mg) or Nolan catalyst (5 mol %,24 mg), picolinic acid (40 mol%, 50 mg), potassium phosphate tribasic (20 mmol, 424mg), 3,5-bis(hydroxymethyl)phenol (1.2 eq, 185 mg) were taken in oven dried schlenck tube under nitrogen followed by dry dimethylsulphoxide (2 mL). The product was purified by column chromatography (hexane and ethylacetate1:3). The purified yield of the product was 50%.

Substrate D:

Was prepared by using general procedure K; (*E*)-1-(4-fluorophenyl)-2-(2-methoxy-1-naphthyl)diazene (1 mmol, 0. 280 g), Copper (1) iodide (20 mol%, 38 mg) or Nolan catalyst (5 mol %,24 mg), picolinic acid (40 mol%, 50 mg), potassium phosphate tribasic (20 mmol, 424 mg), 3,5-bis(hydroxymethyl)phenol(1.2 eq, 185 mg) were taken in oven dried schlenck tube under nitrogen followed by dry dimethylsulphoxide (2 mL). The product was purified by column chromatography (hexane and ethyl acetate 1:3). The purified yield of the product was 47%.

10 Synthesis of (*E*)-1-((4-(3,5-bis(bromomethyl)phenoxy)diazenyl)naphthalene-2-ol (127):



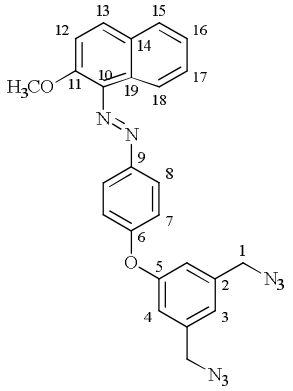
To the stirred mixture of (*E*)-1-((4-(3, 5-bis (hydroxymethyl)phenoxy)-2-(2-methoxy-1-diazene (0.347g, 0.84 mmol), in acetic acid (2 mL), HBr 30% in acetic acid (1 mL, 3.5 mmol) was added for 48 hours. After that the reaction mixture was diluted with water and extract with ether, the organic layer was washed with saturated solution of sodium bicarbonate and then with brine. The organic layer was dried and reduced *in vacuo*. The crude product was purified with column chromatography (hexane and DCM 6:4). The purified yield of the product is 0.302g, 68%

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.41-4.48 (4H, m, CH_2, **H**$_1$) 6.95-7.05 (3H, m, CH, Ar-H$_{4,12}$) 7.11-7.24 (3H, m, CH, Ar-**H**$_{3,7}$) 7.34-7.47 (1 H, m, CH, Ar-**H**$_{16}$) 7.59 (1H, t, *J* = 8 Hz, CH, Ar-**H**$_{17}$) 7.68 (1H, d, *J* = 7 Hz, CH, Ar-**H**$_{15}$) 7.78 (1H, d, *J* = 9 Hz, CH, Ar-H$_{13}$) 7.84 (2H, d, *J* = 9 Hz, CH, Ar-**H**$_8$) 8.65 (1H, d, *J* = 8 Hz, CH, Ar-**H**$_{18}$) 15.94 (1H, s, OH).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 32.1 (CH_2, **C**$_1$), 119.2 (CH, Ar-H, **C**$_4$), 120.1 (CH, Ar-H, **C**$_7$), 121.3 (CH, Ar-H, **C**$_8$), 121.6 (CH, Ar-H, **C**$_{18}$), 123.2 (CH, Ar-H, **C**$_{12}$), 124.6 (CH, Ar-H, **C**$_3$), 125.3 (CH, Ar-H, **C**$_{17}$), 128.5 (CH, Ar-H, **C**$_{16}$), 129.9 (CH, Ar-H, **C**$_{15}$), 133.3 (CH, Ar-H, **C**$_{13}$), 128.1, 128.5, 138.5, 140.3, 142.8, 156.5, 157.3, 165.8.

Accurate Mass: $C_{24}H_{18}N_2{}^{79}Br_2O_2$ requires 522.9662 found 522.9667.

11 Synthesis of (*E*)-1-((4-(3,5-bis(azidomethyl)phenoxy)phenyl)-2-(2-methoxynaphthalene-1-yl)diazene (74):



To the stirred mixture of 1-((4-(3,5-bis(hydroxymethyl)phenoxy)diazenyl)naphthalene -2-ol (0.414g, 1 mmol) and diphenylphosphorylazide (0.3 mL, 1.2 mmol) in dry DCM (3 mL) was added 1,8-diazabicyclo [5.5.0]undec-7-ene (0.2 mL, 1.2 mmol) at 0 °C for 2 hours and then at room temperature overnight. The reaction mixture was diluted with water and then extracted it with DCM. The crude product (0.371 g, 80 %) was purified by column chromatography (ethyl acetate: hexane 6:4)

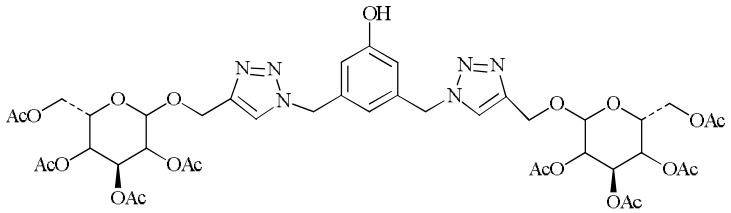
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.01 (3H, s, CH_3) 4.39 (4H, s, CH_2, **H**$_1$) 7.04 (2H, s, CH, Ar-**H**$_4$) 7.09 (1 H, s, CH, Ar-**H**$_3$) 7.19 (2H, d, *J* = 8 Hz, CH, Ar-**H**$_7$) 7.42 (2 H, m, CH, Ar-**H**$_{12,16}$) 7.53 (1H, t, *J* = 6 Hz, CH, Ar-**H**$_{17}$) 7.84 (1H, d, J = 9, CH, Ar-**H**$_{13}$) 7.89 (1H, d, *J* = 9 Hz, CH, Ar-**H**$_{15}$) 8.06 (2H, d, *J* = 9 Hz, CH, Ar-**H**$_8$) 8.37 (1H, d, *J* = 8 Hz, CH, Ar-**H**$_{18}$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 54.1 (CH_2, **C**$_1$), 57.4 (CH_3), 114.7 (CH, Ar-H, **C**$_{12}$), 118.3 (CH, Ar-H, **C**$_4$), 119.2 (CH, Ar-H, **C**$_7$), 122.7 (CH, Ar-H, **C**$_3$), 123.1 (CH, Ar-H, **C**$_{18}$), 124.6 (CH, Ar-H, **C**$_8$), 124.4 (CH, Ar-H, **C**$_{16}$), 127.6 (CH, Ar-H, **C**$_{17}$), 127.8 (CH, Ar-H, **C**$_{13}$), 130.8 (CH, Ar-H, **C**$_{15}$), 128.4, 129.2, 136.4, 138.3, 148.4, 149.7, 157.5, 159.1.

Accurate Mass: $C_{25}H_{21}N_8O_2$-1 requires 465.1782 found 465.1784.

IR ν_{max}(film): 1271, 1290, 1489, 1584, 2092, 2168, 3046 cm^{-1}.

12 Synthesis of Clicked Product (128):



The reaction mixture containing 3,5-bis(azidomethyl)phenol (1 mmol, 0.204 g), propargyl sugar (2 mmol, 0.744 g), $CuSO_4.5H_2O$ (10 mol%) and sodium ascorbate (20 mol%) in THF(15 mL)/H_2O(3 mL) was stirred at room temperature for 24 hours, then extracted with DCM. After that the organic layer was washed with 1 M HCl (3 x 30 mL), then with 1 M NH_4OH (3 x 30 mL) and with water. The organic layer was dried over $MgSO_4$ and reduced *in vacuo.* The product (0.557 g, 57 %) obtained was white coloured foamy solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.85-2.15 (24H, m, OAc) 3.93 (2H, t, *J* = 6 Hz) 4.07-4.13 (3H, m) 4.28 (1H, s) 4.63 (2H, d, *J* = 7 Hz) 4.71-4.79 (2H, m) 4.87-4.95 (2H, m) 4.99 (2H, dd, *J* = 10, 3 Hz) 5.11-5.19 (2H, m) 5.28 (1H, s) 5.33-5.48 (5H, m) 6.74 (3H, t, *J* = 7 Hz) 7.52-7.59 (2H, m).

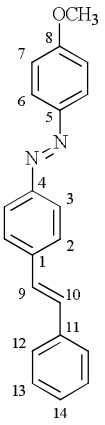
^{13}C NMR (75 MHz, $CDCl_3$) δppm 20, 20.1, 20.2, 52.9, 53.1, 60.1, 62.2, 66.5, 68.3, 70.2, 70.3, 99.9, 100, 114, 114.8, 117.7, 118.2, 122.7, 136.5, 137.5, 144.1, 157.6, 158, 169.2, 169.5, 169.7, 170.

MS (ES+): m/z $[M + Na]^+$ 999

Accurate Mass: $C_{42}H_{52}N_6O_{21}Na$ requires 999.3040 found 999.3078

13 Palladium Chemistry:

13.1 Synthesis of (*E*)-1-(4-methoxyphenyl)-2-(4-(*E*)-styrylphenyl)diazene(129):[94]



Was prepared by using general procedure E1; (*E*)-1-(4-iodophenyl)-2-(4-methoxyphenyl)diazene (0.676 g, 2 mmol), $Pd(OAc)_2$ (11.4 mg), PPh_3 (13 mg), DMF (10 mL), Et_3N (1 mL) and styrene(520 mg). The precipitate was washed with ethanol to remove impurities. The yield of the product was (0.508 g, 81%) (**mp** 205 ˚C; lit 204-205 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.91 (3H, s, CH_3) 7.03 (2H, dd, *J* = 9,2 Hz, CH, Ar-$\mathbf{H}_7$) 7.20 (2H, d, *J* =4 Hz, CH, Ar-$\mathbf{H}_{9,10}$) 7.31 (1 H, t, *J* = 7 Hz, CH, Ar-$\mathbf{H}_{14}$) 7.35-7.44 (2H, m, CH, Ar-$\mathbf{H}_{13}$) 7.56 (2H, d, *J* = 7 Hz, CH, Ar-$\mathbf{H}_{12}$) 7.66 (2H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_2$) 7.88-7.97 (4H, m, CH, Ar-$\mathbf{H}_{3,6}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 55.5 (CH_3), 114.2 (CH, Ar-H, $\mathbf{C}_7$), 123.1 (CH, Ar-H, $\mathbf{C}_3$), 124.7 (CH, Ar-H, $\mathbf{C}_6$), 126.6 (CH, Ar-H, $\mathbf{C}_{12}$), 127.1 (CH, Ar-H, $\mathbf{C}_2$), 127.9 (CH, Ar-H, $\mathbf{C}_{14}$), 128.7 (CH, Ar-H, $\mathbf{C}_{13}$), 130 (CH, Ar-H, $\mathbf{C}_{9,10}$), 137, 139.4, 147.1, 152, 162.

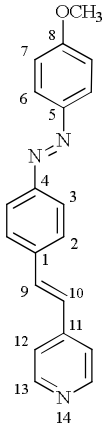
Accurate Mass: $C_{21}H_{19}N_2O$ requires 315.1492 found 315.1486.

IR ν_{max} (film): 1405, 1413, 1586, 3011 cm^{-1}.

Substrate B:

Was also prepared by using (*E*)-1-(4-bromophenyl)-2-(4-methoxyphenyl)diazene (0.582 g, 2 mmol), $Pd(OAc)_2$ (11.4 mg), PPh_3 (13 mg), DMF (10 mL), Et_3N (1 mL) and styrene (520 mg). The precipitate was washed with ethanol to remove impurities. The yield of the product was 82%.

13.2 Synthesis of (*E*)-1-(4-methoxyphenyl)-2-(pyridine-4-yl)vinyl)diazene (82):



Was prepared by using general procedure K (*E*)-1-(4-bromophenyl)-2-(4-methoxyphenyl)diazene (0.582 g, 2 mmol), $Pd(OAc)_2$ (11.4 mg), PPh_3 (13 mg), DMF (10 mL), Et_3N (1 mL) and 4-vinylpyridine (0.4mL, 3 mmol). The precipitate was washed with ethanol to remove impurities. The yield of the product was 76% (0.478 g, **mp** 224-226 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.91 (3 H, s, CH_3) 7.03 (2H, d, *J* = 9 Hz, CH, Ar-**H**$_7$) 7.11 (1H, d, *J* = 16 Hz, **H**$_{10}$) 7.32-7.42 (3H, m, CH, Ar-**H**$_2$, **H**$_9$) 7.68 (2H, d, *J* = 8 Hz, Ar-**H**$_{12}$) 7.93 (4H, t, *J* = 8 Hz, Ar-**H**$_{3,6}$) 8.61 (2H, d, *J* = 6 Hz, Ar-**H**$_{13}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 55.5 (CH_3), 114.2 (CH, Ar-H, **C**$_7$), 120.9 (CH, Ar-H, **C**$_2$), 123.2 (CH, Ar-H, **C**$_3$), 124.8 (CH, Ar-H, **C**$_6$), 127.2 (CH, **C**$_{10}$), 127.7 (CH, Ar-H, **C**$_{12}$), 132.3 (CH, **C**$_9$), 150.2 (CH, Ar-H, **C**$_{13}$), 138.0, 144.3, 147.1, 152.6, 162.2.

MS (ES+): m/z $[M + H]^+$ 316.

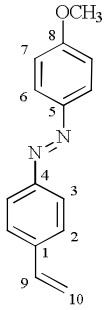
Accurate Mass: $C_{20}H_{18}N_3O$ requires 316.1436 found 316.1486.

IR ν_{max} (film): 1247, 1494, 1577, 1591, 3091 cm^{-1}.

Substrate B:

Was also prepared by using (*E*)-1-(4-iodophenyl)-2-(4-methoxyphenyl)diazene (0.676 g, 2 mmol), $Pd(OAc)_2$ (11.4 mg), PPh_3 (13 mg), DMF (10 mL), Et_3N (1 mL) and 4-vinylpyridine (0.4mL, 3 mmol). The precipitate was washed with ethanol to remove impurities. The yield of the product was 74%.

13.3 Synthesis of (*E*)-1-(4-methoxyphenyl)-2-(4-vinylphenyl)diazene (79):



Was prepared by using general procedure L; (*E*)-1-(4-bromophenyl)-2-(4-methoxyphenyl)diazene (0.145 g, 0.5 mmol), $Pd(OAc)_2$ (11 mg), PPh_3 (13 mg) and tributylvinylstannane (0.2 mL), DMF (10 mL). The product (0.904 g) yield was 76.1% (**mp** 116 ˚C).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 3.91 (3H, s, CH_3) 5.35 (1H, dd, *J* = 11,1 Hz, $\mathbf{H}_{10}$) 5.86 (1H, d, *J* = 17 Hz, $\mathbf{H}_{10}$) 6.68-6.86 (1H, m, $\mathbf{H}_9$) 7.03 (2H, d, *J* = 9 Hz, CH, Ar-$\mathbf{H}_7$) 7.55 (2H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_2$) 7.87 (2H, d, *J* = 8 Hz, CH, Ar-$\mathbf{H}_6$) 7.93 (2H, d, *J* = 9,2 Hz, CH, Ar-$\mathbf{H}_3$).

^{13}C NMR (75 MHz, $CDCl_3$)δ ppm 55.5 (CH_3), 114.2 (CH, Ar-H, **C**$_7$), 115.2 (CH, Ar-H, **C**$_{10}$), 122.8 (CH, Ar-H, **C**$_6$), 124.3 (CH, Ar-H, **C**$_3$), 126.8 (CH, Ar-H, **C**$_2$), 136.2 (CH, Ar-H, **C**$_9$), 139.5, 147.1, 152.2, 162.1.

MS (ES+): m/z $[M+H]^+$ 239.

Accurate Mass: $C_{15}H_{15}N_2O$ requires 239.1179 found 239.1182

IR ν_{max}(film): 1493, 1577, 1596, 1626, 2920, 2956 cm^{-1}.

Substrate B:

Was prepared by using general procedure L; (*E*)-1-(4-iodophenyl)-2-(4-methoxyphenyl)diazene (0.168 g, 0.5 mmol), $Pd(OAc)_2$ (11 mg), PPh_3 (13 mg), DMF (10 mL) and tributylvinylstannane (0.2 mL). The product yield was 74%.

PART III: BIBLIOGRAPHY AND APPENDIX

CHAPTER 1:

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CHAPTER II

APPENDIX

COUMPOUND 19

Table 1. Crystal data and structure refinement for s3389ma.

Identification code	s3389ma
Empirical formula	C16 H11 Br N2 O
Formula weight	327.18
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 12.8532(12) A alpha = 90 deg. b = 3.8810(4) A beta = 92.898(2) deg. c = 25.926(2) A gamma = 90 deg.
Volume	1291.6(2) A^3 Z,
Calculated density	4, 1.682 Mg/m^3
Absorption coefficient	3.178 mm^-1
F(000)	656
Crystal size	0.30 x 0.15 x 0.05 mm
Theta range for data collection	1.57 to 28.26 deg.
Limiting indices	-16<=h<=16, -5<=k<=5, -33<=l<=33
Reflections collected / unique	9877 / 3011 [R(int) = 0.0351]
Completeness to theta =	25.00 98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8573 and 0.59342
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	3011 / 0 / 185
Goodness-of-fit on F^2	1.179
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0960
R indices (all data)	R1 = 0.0478, wR2 = 0.1222
Largest diff. peak and hole	0.752 and -0.766 e.A^-3

Table 2.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3389ma. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

x	y	z	U(eq)		
Br(1)	4014(1)		7077(1)	-636(1)	22(1)
C(1)	1619(2)		4420(8)	591(1)	16(1)
C(2)	2538(2)		6097(8)	745(1)	16(1)
C(3)	3257(3)		6868(8)	382(1)	17(1)
C(4)	3042(2)		5949(8)	-136(1)	16(1)
C(5)	2136(3)		4262(8)	-293(1)	18(1)
C(6)	1418(3)		3498(8)	74(1)	18(1)
C(7)	240(2)		3237(8)	1735(1)	16(1)
C(8)	-700(3)		1421(8)	1548(1)	18(1)
C(9)	-1451(2)		522(8)	1918(1)	19(1)
C(10)	-1282(2)		1234(8)	2425(1)	18(1)
C(11)	-361(3)		3005(8)	2624(1)	17(1)
C(12)	-220(3)		3720(8)	3159(1)	18(1)
C(13)	660(3)		5416(8)	3345(1)	19(1)
C(14)	1421(3)		6417(8)	3006(1)	18(1)
C(15)	1286(2)		5779(8)	2487(1)	16(1)
C(16)	399(2)		4038(8)	2282(1)	15(1)
N(1)	860(2)		3501(7)	936(1)	17(1)
N(2)	992(2)		4205(7)	1426(1)	15(1)
O(1)	-852(2)		595(6)	1077(1)	22(1)

Table 3. Bond lengths [A] and angles [deg] for **s3389ma**.

Br(1)-C(4)	1.897(3)
C(1)-C(2)	1.389(4)
C(1)-C(6)	1.398(4)
C(1)-N(1)	1.402(4)
C(2)-C(3)	1.384(4)
C(2)-H(2)	0.9500

C(3)-C(4)	1.404(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.380(5)
C(5)-C(6)	1.389(5)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-N(2)	1.340(4)
C(7)-C(16)	1.455(4)
C(7)-C(8)	1.460(4)
C(8)-O(1)	1.270(4)
C(8)-C(9)	1.438(5)
C(9)-C(10)	1.349(5)
C(9)-H(9)	0.9500
C(10)-C(11)	1.442(5)
C(10)-H(10)	0.9500
C(11)-C(16)	1.410(4)
C(11)-C(12)	1.415(5)
C(12)-C(13)	1.375(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.402(5)
C(13)-H(13)	0.9500
C(14)-C(15)	1.371(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.406(4)
C(15)-H(15)	0.9500
N(1)-N(2)	1.304(4)
N(1)-H(1)	0.79(5)

C(2)-C(1)-C(6)	120.5(3)
C(2)-C(1)-N(1)	123.0(3)
C(6)-C(1)-N(1)	116.5(3)
C(3)-C(2)-C(1)	119.6(3)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	119.3(3)
C(2)-C(3)-H(3)	120.3
C(4)-C(3)-H(3)	120.3
C(5)-C(4)-C(3)	121.6(3)
C(5)-C(4)-Br(1)	119.0(2)
C(3)-C(4)-Br(1)	119.4(2)
C(4)-C(5)-C(6)	118.7(3)
C(4)-C(5)-H(5)	120.7
C(6)-C(5)-H(5)	120.7
C(5)-C(6)-C(1)	120.3(3)
C(5)-C(6)-H(6)	119.8
C(1)-C(6)-H(6)	119.8
N(2)-C(7)-C(16)	116.9(3)
N(2)-C(7)-C(8)	123.1(3)
C(16)-C(7)-C(8)	120.0(3)
O(1)-C(8)-C(9)	120.4(3)

O(1)-C(8)-C(7)	121.8(3)
C(9)-C(8)-C(7)	117.8(3)
C(10)-C(9)-C(8)	121.4(3)
C(10)-C(9)-H(9)	119.3
C(8)-C(9)-H(9)	119.3
C(9)-C(10)-C(11)	122.3(3)
C(9)-C(10)-H(10)	118.9
C(11)-C(10)-H(10)	118.9
C(16)-C(11)-C(12)	120.1(3)
C(16)-C(11)-C(10)	119.5(3)
C(12)-C(11)-C(10)	120.4(3)
C(13)-C(12)-C(11)	120.0(3)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	120.0(3)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
C(15)-C(14)-C(13)	120.5(3)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(14)-C(15)-C(16)	121.1(3)
C(14)-C(15)-H(15)	119.4
C(16)-C(15)-H(15)	119.4
C(15)-C(16)-C(11)	118.3(3)
C(15)-C(16)-C(7)	122.8(3)
C(11)-C(16)-C(7)	119.0(3)
N(2)-N(1)-C(1)	120.5(3)
N(2)-N(1)-H(1)	107(4)
C(1)-N(1)-H(1)	133(4)
N(1)-N(2)-C(7)	117.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 4.

Anisotropic displacement parameters (A^2 x 10^3) for s3389ma.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	28(1)	18(1)	22(1)	0(1)	11(1)	-4(1)
C(1)	18(2)	12(1)	18(2)	0(1)	3(1)	3(1)
C(2)	21(2)	14(1)	14(2)	0(1)	2(1)	-1(1)
C(3)	19(2)	15(2)	17(2)	1(1)	2(1)	-2(1)
C(4)	20(2)	13(1)	17(2)	4(1)	8(1)	1(1)
C(5)	24(2)	16(2)	14(2)	0(1)	2(1)	3(1)
C(6)	20(2)	15(2)	19(2)	0(1)	-3(1)	-1(1)
C(7)	16(2)	11(1)	19(2)	2(1)	-1(1)	-1(1)
C(8)	19(2)	15(2)	20(2)	2(1)	2(1)	0(1)

C(9)	14(2)	18(2)	25(2)	2(1)	0(1)	-2(1)
C(10)	17(2)	14(1)	24(2)	3(1)	7(1)	2(1)
C(11)	19(2)	12(1)	20(2)	2(1)	0(1)	4(1)
C(12)	22(2)	14(2)	17(2)	2(1)	8(1)	4(1)
C(13)	23(2)	17(2)	16(2)	-1(1)	2(1)	6(1)
C(14)	18(2)	16(2)	20(2)	-1(1)	0(1)	3(1)
C(15)	17(2)	14(1)	19(2)	1(1)	7(1)	2(1)
C(16)	17(2)	10(1)	18(2)	1(1)	2(1)	4(1)
N(1)	19(1)	17(1)	16(1)	0(1)	0(1)	-3(1)
N(2)	18(1)	13(1)	15(1)	0(1)	3(1)	2(1)
O(1)	23(1)	26(1)	19(1)	-2(1)	-1(1)	-6(1)

Table 5.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s3389ma.

	x	y	z	U(eq)	
H(2)	2672	6710	1096	19	
H(3)	3889	8008	483	21	
H(5)	2004	3635	-644	21	
H(6)	789	2344	-27	22	
H(9)	-2078	-596	1804	23	
H(10)	-1789	544	2659	22	
H(12)	-733	3027	3388	21	
H(13)	753	5911	3703	23	
H(14)	2035	7545	3137	21	
H(15)	1801	6526	2261	19	
H(1)	330(40)	2470	900(20)	42(15)	

Table 6: Torsion angles [deg] for s3389ma

C(6)-C(1)-C(2)-C(3)			0.3(5)
N(1)-C(1)-C(2)-C(3)	179.0(3)		
C(1)-C(2)-C(3)-C(4)		0.2(5)	
C(2)-C(3)-C(4)-C(5)	-0.6(5)		
C(2)-C(3)-C(4)-Br(1)	178.8(2)		
C(3)-C(4)-C(5)-C(6)		0.6(5)	
Br(1)-C(4)-C(5)-C(6)			-178.9(2)
C(4)-C(5)-C(6)-C(1)	-0.2(5)		
C(2)-C(1)-C(6)-C(5)	-0.3(5)		
N(1)-C(1)-C(6)-C(5)	-179.0(3)		
N(2)-C(7)-C(8)-O(1)		1.1(5)	
C(16)-C(7)-C(8)-O(1)			-178.0(3)
N(2)-C(7)-C(8)-C(9)			-180.0(3)
C(16)-C(7)-C(8)-C(9)		0.9(4)	

O(1)-C(8)-C(9)-C(10)	176.9(3)	
C(7)-C(8)-C(9)-C(10)	-2.0(5)	
C(8)-C(9)-C(10)-C(11)	1.7(5)	
C(9)-C(10)-C(11)-C(16)		-0.1(5)
C(9)-C(10)-C(11)-C(12)		179.6(3)
C(16)-C(11)-C(12)-C(13)		-0.2(5)
C(10)-C(11)-C(12)-C(13)		-179.8(3)
C(11)-C(12)-C(13)-C(14)		-0.4(5)
C(12)-C(13)-C(14)-C(15)		1.3(5)
C(13)-C(14)-C(15)-C(16)		-1.6(5)
C(14)-C(15)-C(16)-C(11)		1.0(4)
C(14)-C(15)-C(16)-C(7)		-178.4(3)
C(12)-C(11)-C(16)-C(15)		-0.1(4)
C(10)-C(11)-C(16)-C(15)		179.6(3)
C(12)-C(11)-C(16)-C(7)		179.3(3)
C(10)-C(11)-C(16)-C(7)		-1.0(4)
N(2)-C(7)-C(16)-C(15)	0.8(4)	
C(8)-C(7)-C(16)-C(15)		180.0(3)
N(2)-C(7)-C(16)-C(11)		-178.6(3)
C(8)-C(7)-C(16)-C(11)	0.6(4)	
C(2)-C(1)-N(1)-N(2)	0.0(5)	
C(6)-C(1)-N(1)-N(2)	178.7(3)	
C(1)-N(1)-N(2)-C(7)	-179.6(3)	
C(16)-C(7)-N(2)-N(1)	180.0(3)	
C(8)-C(7)-N(2)-N(1)	0.8(4)	

Symmetry transformations used to generate equivalent atoms:

Table 7: Hydrogen bonds for s3389ma [A and deg.]

D-H.	A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...	O(1)	0.79(5)	1.76(6)	2.515(4)	158(6)

Symmetry transformations used to generate equivalent atoms:

COUMPOUND 28b

Table 1: Crystal data and structure refinement for s3421y

Identification code	s3421ya
Empirical formula	C17 H13 Br N2 O
Formula weight	341.20
Temperature	100(2) K

Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 12.476(8) A alpha = 90 deg.
	b = 4.246(3) A beta = 94.980(9) deg.
	c = 26.524(17) A gamma = 90 deg.
Volume	1399.8(15) A^3 Z, Calculated density 4, 1.619 Mg/m^3
Absorption coefficient	2.936 mm^-1
F(000)	688
Crystal size	0.40 x 0.20 x 0.05 mm
Theta range for data collection	1.54 to 25.03 deg.
Limiting indices	-14<=h<=14, -5<=k<=5, -31<=l<=31
Reflections collected / unique	11804 / 2451 [R(int) = 0.1012]
Completeness to theta =	25.03 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8671 and 0.3863
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2451 / 0 / 191
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0766, wR2 = 0.1940
R indices (all data)	R1 = 0.0970, wR2 = 0.2228
Largest diff. peak and hole	3.009 and -2.290 e.A^-3

Table 2:
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3421ya. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

x	y	z	U(eq)	
Br(1)	3795(1)	8509(2)	10524(1)	26(1)
O(1)	-974(4)	-709(12)	8666(2)	24(1)
N(1)	911(5)	2812(14)	8460(2)	21(1)

N(2)	549(5)	3659(12)	8869(2)	19(1)
C(1)	156(5)	1571(15)	8086(3)	18(1)
C(2)	-734(5)	-259(16)	8176(2)	18(1)
C(3)	-1367(6)	-1604(16)	7766(3)	24(2)
C(4)	-1125(6)	-1120(17)	7284(3)	23(2)
C(5)	-256(6)	797(17)	7170(3)	20(2)
C(6)	-35(6)	1468(17)	6666(3)	25(2)
C(7)	824(6)	3310(17)	6570(3)	26(2)
C(8)	1497(6)	4570(19)	6975(3)	26(2)
C(9)	1287(6)	4025(16)	7466(3)	21(2)
C(10)	406(6)	2143(17)	7579(3)	21(2)
C(11)	1365(5)	4751(16)	9237(3)	18(1)
C(12)	2452(6)	4159(18)	9226(3)	25(2)
C(13)	3166(6)	5250(20)	9611(3)	26(2)
C(14)	2796(6)	6959(15)	9996(2)	18(1)
C(15)	1706(6)	7610(19)	10019(3)	26(2)
C(16)	1001(6)	6489(17)	9631(3)	25(2)
C(17)	-1790(6)	-2944(18)	8753(3)	24(2)

Table 3: Bond lengths [A] and angles [deg] for s3421ya

Br(1)-C(14)	1.910(7)
O(1)-C(2)	1.372(8)
O(1)-C(17)	1.424(9)
N(1)-N(2)	1.263(8)
N(1)-C(1)	1.410(9)
N(2)-C(11)	1.426(9)
C(1)-C(2)	1.394(10)
C(1)-C(10)	1.425(10)
C(2)-C(3)	1.409(11)
C(3)-C(4)	1.355(11)
C(3)-H(3)	0.9500
C(4)-C(5)	1.409(10)
C(4)-H(4)	0.9500
C(5)-C(6)	1.416(10)
C(5)-C(10)	1.426(10)
C(6)-C(7)	1.369(11)
C(6)-H(6)	0.9500
C(7)-C(8)	1.411(11)
C(7)-H(7)	0.9500
C(8)-C(9)	1.370(10)
C(8)-H(8)	0.9500
C(9)-C(10)	1.413(10)
C(9)-H(9)	0.9500
C(11)-C(12)	1.383(10)
C(11)-C(16)	1.387(10)
C(12)-C(13)	1.376(11)
C(12)-H(12)	0.9500
C(13)-C(14)	1.366(10)

C(13)-H(13)	0.9500
C(14)-C(15)	1.393(10)
C(15)-C(16)	1.380(11)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(2)-O(1)-C(17)	117.6(6)
N(2)-N(1)-C(1)	116.4(6)
N(1)-N(2)-C(11)	113.2(5)
C(2)-C(1)-N(1)	125.5(6)
C(2)-C(1)-C(10)	120.0(6)
N(1)-C(1)-C(10)	114.4(6)
O(1)-C(2)-C(1)	118.9(6)
O(1)-C(2)-C(3)	121.4(6)
C(1)-C(2)-C(3)	119.6(6)
C(4)-C(3)-C(2)	120.8(7)
C(4)-C(3)-H(3)	119.6
C(2)-C(3)-H(3)	119.6
C(3)-C(4)-C(5)	121.9(7)
C(3)-C(4)-H(4)	119.1
C(5)-C(4)-H(4)	119.1
C(4)-C(5)-C(6)	122.3(7)
C(4)-C(5)-C(10)	118.3(6)
C(6)-C(5)-C(10)	119.4(7)
C(7)-C(6)-C(5)	120.8(7)
C(7)-C(6)-H(6)	119.6
C(5)-C(6)-H(6)	119.6
C(6)-C(7)-C(8)	119.8(7)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1
C(9)-C(8)-C(7)	120.7(7)
C(9)-C(8)-H(8)	119.7
C(7)-C(8)-H(8)	119.7
C(8)-C(9)-C(10)	121.0(7)
C(8)-C(9)-H(9)	119.5
C(10)-C(9)-H(9)	119.5
C(9)-C(10)-C(1)	122.4(7)
C(9)-C(10)-C(5)	118.3(6)
C(1)-C(10)-C(5)	119.3(6)
C(12)-C(11)-C(16)	120.0(7)
C(12)-C(11)-N(2)	124.7(6)
C(16)-C(11)-N(2)	115.4(6)
C(13)-C(12)-C(11)	119.7(7)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(14)-C(13)-C(12)	119.6(7)
C(14)-C(13)-H(13)	120.2
C(12)-C(13)-H(13)	120.2

C(13)-C(14)-C(15)	122.3(7)
C(13)-C(14)-Br(1)	119.3(5)
C(15)-C(14)-Br(1)	118.4(5)
C(16)-C(15)-C(14)	117.3(6)
C(16)-C(15)-H(15)	121.3
C(14)-C(15)-H(15)	121.3
C(15)-C(16)-C(11)	121.1(7)
C(15)-C(16)-H(16)	119.5
C(11)-C(16)-H(16)	119.5
O(1)-C(17)-H(17A)	109.5
O(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
O(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

COUMPOUND 80a

Table 1: Crystal data and structure refinement for s3295n

Identification code	s3295n
Empirical formula	C18 H15 I N2 O
Formula weight	402.22
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.0517(8) A alpha = 90 deg. b = 18.6702(16) A beta = 102.9460(10)deg. c = 8.4319(7) A gamma = 90 deg.
Volume	1542.2(2) A^3 Z,
Calculated density	4, 1.732 Mg/m^3
Absorption coefficient	2.080 mm^-1
F(000)	792
Crystal size	0.16 x 0.16 x 0.05 mm
Theta range for data collection	2.08 to 28.25 deg.
Limiting indices	-12<=h<=13, -23<=k<=24, -11<=l<=11
Reflections collected / unique	13235 / 3664 [R(int) = 0.0519]

Completeness to theta	=	25.00 100.0 %
Absorption correction		None
Max. and min. transmission		0.9032 and 0.7320
Refinement method		Full-matrix least-squares on F^2
Data / restraints / parameters		3664 / 0 / 200
Goodness-of-fit on F^2		0.933
Final R indices [I>2sigma(I)]		R1 = 0.0335, wR2 = 0.0562
R indices (all data)		R1 = 0.0488, wR2 = 0.0595
Largest diff. peak and hole		1.102 and -0.646 e.A^-3

Table 2:
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3295n. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	7741(3)	9900(2)	4910(4)	17(1)
C(2)	8389(3)	9317(2)	5812(4)	19(1)
C(3)	7913(3)	8646(2)	5488(4)	19(1)
C(4)	6773(3)	8510(2)	4168(4)	17(1)
C(5)	6254(3)	7814(2)	3788(4)	20(1)
C(6)	5208(4)	7689(2)	2475(4)	24(1)
C(7)	4657(3)	8259(2)	1452(4)	23(1)
C(8)	5128(3)	8945(2)	1789(4)	17(1)
C(9)	6161(3)	9097(2)	3180(4)	14(1)
C(10)	6641(3)	9808(2)	3627(4)	14(1)
C(11)	7384(3)	11136(2)	4686(4)	20(1)
C(12)	4609(3)	10580(2)	2664(4)	19(1)
C(13)	7801(3)	11100(2)	1946(4)	14(1)
C(14)	8555(3)	11735(2)	1994(4)	17(1)
C(15)	9436(3)	11830(2)	965(4)	19(1)
C(16)	9558(3)	11298(2)	-146(4)	15(1)
C(17)	8801(3)	10677(2)	-232(4)	17(1)
C(18)	7938(3)	10577(2)	821(4)	14(1)
I(1)	10953(1)	11423(1)	-1644(1)	19(1)
N(1)	6856(3)	11033(1)	2961(3)	17(1)
N(2)	6038(3)	10398(1)	2642(3)	14(1)
O(1)	8266(2)	10565(1)	5398(3)	20(1)

Table 3: Bond lengths [A] and angles [deg] for s3295n

C(1)-C(10)	1.374(4)
C(1)-O(1)	1.375(4)
C(1)-C(2)	1.402(4)
C(2)-C(3)	1.347(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.430(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.409(4)
C(4)-C(9)	1.430(4)
C(5)-C(6)	1.366(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.404(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.373(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.410(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.433(4)
C(10)-N(2)	1.430(4)
C(11)-O(1)	1.431(4)
C(11)-N(1)	1.445(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-N(2)	1.480(4)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(18)	1.390(4)
C(13)-C(14)	1.403(4)
C(13)-N(1)	1.420(4)
C(14)-C(15)	1.383(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.390(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.380(4)
C(16)-I(1)	2.099(3)
C(17)-C(18)	1.385(4)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
N(1)-N(2)	1.433(3)
C(10)-C(1)-O(1)	122.4(3)
C(10)-C(1)-C(2)	121.6(3)
O(1)-C(1)-C(2)	115.9(3)
C(3)-C(2)-C(1)	120.7(3)
C(3)-C(2)-H(2)	119.6
C(1)-C(2)-H(2)	119.6
C(2)-C(3)-C(4)	120.7(3)
C(2)-C(3)-H(3)	119.7

C(4)-C(3)-H(3)	119.7
C(5)-C(4)-C(3)	122.1(3)
C(5)-C(4)-C(9)	119.0(3)
C(3)-C(4)-C(9)	118.8(3)
C(6)-C(5)-C(4)	121.4(3)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(5)-C(6)-C(7)	119.6(3)
C(5)-C(6)-H(6)	120.2
C(7)-C(6)-H(6)	120.2
C(8)-C(7)-C(6)	120.7(3)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(7)-C(8)-C(9)	121.0(3)
C(7)-C(8)-H(8)	119.5
C(9)-C(8)-H(8)	119.5
C(8)-C(9)-C(4)	118.1(3)
C(8)-C(9)-C(10)	123.1(3)
C(4)-C(9)-C(10)	118.8(3)
C(1)-C(10)-N(2)	121.5(3)
C(1)-C(10)-C(9)	119.1(3)
N(2)-C(10)-C(9)	119.1(3)
O(1)-C(11)-N(1)	112.1(3)
O(1)-C(11)-H(11A)	109.2
N(1)-C(11)-H(11A)	109.2
O(1)-C(11)-H(11B)	109.2
N(1)-C(11)-H(11B)	109.2
H(11A)-C(11)-H(11B)	107.9
N(2)-C(12)-H(12A)	109.5
N(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
N(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(18)-C(13)-C(14)	118.6(3)
C(18)-C(13)-N(1)	122.1(3)
C(14)-C(13)-N(1)	119.2(3)
C(15)-C(14)-C(13)	120.5(3)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(14)-C(15)-C(16)	119.9(3)
C(14)-C(15)-H(15)	120.1
C(16)-C(15)-H(15)	120.1
C(17)-C(16)-C(15)	120.3(3)
C(17)-C(16)-I(1)	119.8(2)
C(15)-C(16)-I(1)	119.9(2)
C(16)-C(17)-C(18)	119.8(3)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1
C(17)-C(18)-C(13)	121.0(3)

C(17)-C(18)-H(18)	119.5
C(13)-C(18)-H(18)	119.5
C(13)-N(1)-N(2)	113.2(2)
C(13)-N(1)-C(11)	116.8(3)
N(2)-N(1)-C(11)	111.4(2)
C(10)-N(2)-N(1)	112.2(2)
C(10)-N(2)-C(12)	117.1(2)
N(1)-N(2)-C(12)	108.9(2)
C(1)-O(1)-C(11)	112.8(2)

Symmetry transformations used to generate equivalent atoms:

Table 4:

Anisotropic displacement parameters (A^2 x 10^3) for s3295n, the anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	15(2)	24(2)	15(2)	-1(2)	7(1)	-2(2)
C(2)	13(2)	30(2)	13(2)	0(2)	2(1)	1(2)
C(3)	19(2)	22(2)	17(2)	6(2)	6(1)	7(2)
C(4)	14(2)	22(2)	14(2)	1(2)	5(1)	3(2)
C(5)	21(2)	18(2)	22(2)	6(2)	6(2)	5(2)
C(6)	24(2)	19(2)	27(2)	-1(2)	2(2)	-3(2)
C(7)	18(2)	28(2)	19(2)	-1(2)	-3(2)	0(2)
C(8)	16(2)	17(2)	17(2)	3(1)	3(1)	2(1)
C(9)	13(2)	19(2)	12(2)	-1(1)	8(1)	1(1)
C(10)	12(2)	19(2)	14(2)	1(1)	4(1)	-1(1)
C(11)	26(2)	17(2)	19(2)	-5(2)	9(2)	0(2)
C(12)	17(2)	21(2)	22(2)	1(2)	7(2)	3(2)
C(13)	13(2)	18(2)	11(2)	2(1)	0(1)	0(1)
C(14)	19(2)	16(2)	14(2)	-3(1)	2(2)	1(2)
C(15)	18(2)	16(2)	19(2)	3(2)	1(2)	-3(2)
C(16)	12(2)	19(2)	13(2)	3(1)	2(1)	3(1)
C(17)	16(2)	16(2)	16(2)	-2(1)	1(1)	4(1)
C(18)	12(2)	14(2)	14(2)	2(1)	-2(1)	-3(1)
I(1)	19(1)	20(1)	21(1)	0(1)	8(1)	-3(1)
N(1)	19(2)	17(2)	17(2)	-4(1)	6(1)	-5(1)
N(2)	11(1)	14(1)	18(2)	-1(1)	3(1)	-1(1)
O(1)	22(1)	19(1)	17(1)	-3(1)	-1(1)	-4(1)

Table 5:

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s3295n.

x	y	z	U(eq)
H(2)	9173	9396	6661	23
H(3)	8339	8260	6142	23

H(5)	6641	7424	4460	24
H(6)	4856	7218	2255	29
H(7)	3951	8170	517	27
H(8)	4752	9324	1074	20
H(11A)	7894	11594	4864	24
H(11B)	6612	11170	5234	24
H(12A)	4067	10140	2587	29
H(12B)	4229	10892	1739	29
H(12C)	4586	10829	3681	29
H(14)	8459	12103	2739	20
H(15)	9956	12257	1018	22
H(17)	8871	10319	-1010	20
H(18)	7433	10144	772	17

Table 6: Torsion angles [deg] for s3295n

C(10)-C(1)-C(2)-C(3)	-2.9(5)
O(1)-C(1)-C(2)-C(3)	176.6(3)
C(1)-C(2)-C(3)-C(4)	2.8(5)
C(2)-C(3)-C(4)-C(5)	179.6(3)
C(2)-C(3)-C(4)-C(9)	1.1(5)
C(3)-C(4)-C(5)-C(6)	-176.7(3)
C(9)-C(4)-C(5)-C(6)	1.8(5)
C(4)-C(5)-C(6)-C(7)	1.7(5)
C(5)-C(6)-C(7)-C(8)	-2.2(5)
C(6)-C(7)-C(8)-C(9)	-0.9(5)
C(7)-C(8)-C(9)-C(4)	4.3(5)
C(7)-C(8)-C(9)-C(10)	-176.9(3)
C(5)-C(4)-C(9)-C(8)	-4.7(4)
C(3)-C(4)-C(9)-C(8)	173.8(3)
C(5)-C(4)-C(9)-C(10)	176.5(3)
C(3)-C(4)-C(9)-C(10)	-5.0(4)
O(1)-C(1)-C(10)-N(2)	4.7(5)
C(2)-C(1)-C(10)-N(2)	-175.8(3)
O(1)-C(1)-C(10)-C(9)	179.4(3)
C(2)-C(1)-C(10)-C(9)	-1.2(5)
C(8)-C(9)-C(10)-C(1)	-173.7(3)
C(4)-C(9)-C(10)-C(1)	5.0(4)
C(8)-C(9)-C(10)-N(2)	1.1(4)
C(4)-C(9)-C(10)-N(2)	179.8(3)
C(18)-C(13)-C(14)-C(15)	-1.3(5)
N(1)-C(13)-C(14)-C(15)	-177.0(3)
C(13)-C(14)-C(15)-C(16)	1.2(5)
C(14)-C(15)-C(16)-C(17)	0.2(5)
C(14)-C(15)-C(16)-I(1)	-177.6(2)
C(15)-C(16)-C(17)-C(18)	-1.5(5)
I(1)-C(16)-C(17)-C(18)	176.3(2)
C(16)-C(17)-C(18)-C(13)	1.3(5)

C(14)-C(13)-C(18)-C(17)	0.1(5)
N(1)-C(13)-C(18)-C(17)	175.6(3)
C(18)-C(13)-N(1)-N(2)	-2.8(4)
C(14)-C(13)-N(1)-N(2)	172.6(3)
C(18)-C(13)-N(1)-C(11)	128.5(3)
C(14)-C(13)-N(1)-C(11)	-56.0(4)
O(1)-C(11)-N(1)-C(13)	-69.8(4)
O(1)-C(11)-N(1)-N(2)	62.4(3)
C(1)-C(10)-N(2)-N(1)	10.9(4)
C(9)-C(10)-N(2)-N(1)	-163.7(3)
C(1)-C(10)-N(2)-C(12)	-116.2(3)
C(9)-C(10)-N(2)-C(12)	69.2(4)
C(13)-N(1)-N(2)-C(10)	91.1(3)
C(11)-N(1)-N(2)-C(10)	-42.9(3)
C(13)-N(1)-N(2)-C(12)	-137.6(3)
C(11)-N(1)-N(2)-C(12)	88.5(3)
C(10)-C(1)-O(1)-C(11)	12.9(4)
C(2)-C(1)-O(1)-C(11)	-166.6(3)
N(1)-C(11)-O(1)-C(1)	-45.6(4)

Symmetry transformations used to generate equivalent atoms:

Table 7: Hydrogen bonds for s3295n [A and deg.].

D-H...	A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

COUMPOUND 80b

Table 1: Crystal data and structure refinement for s3296abs.

Identification code	z:\s3296\work\s3296abs
Empirical formula	C18 H15 Br N2 O
Formula weight	355.23
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.8330(19) A alpha = 90 deg. b = 18.444(4) A beta = 102.020(3) deg. c = 8.3921(16) A gamma = 90 deg.
Volume	1488.6(5) A^3 Z,
Calculated density	4, 1.585 Mg/m^3

Absorption coefficient	2.765 mm^-1
F(000)	720
Crystal size	0.30 x 0.20 x 0.10 mm
Theta range for data collection	2.12 to 26.46 deg.
Limiting indices	-12<=h<=12, -17<=k<=23, -10<=l<=10
Reflections collected / unique	8510 / 3059 [R(int) = 0.0352]
Completeness to theta =	26.46 99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.593
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3059 / 0 / 200
Goodness-of-fit on F^2	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0811
R indices (all data)	R1 = 0.0498, wR2 = 0.0846
Largest diff. peak and hole	0.658 and -0.485 e.A^-3

Table 2.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3296abs. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	7800(3)	-115(2)	4872(3)	16(1)
C(2)	8462(3)	-707(2)	5779(3)	17(1)
C(3)	7967(3)	-1387(2)	5442(3)	17(1)
C(4)	6816(3)	-1522(2)	4135(3)	15(1)
C(5)	6290(3)	-2228(2)	3751(4)	19(1)
C(6)	5222(3)	-2349(2)	2452(4)	22(1)
C(7)	4661(3)	-1770(2)	1445(4)	22(1)
C(8)	5145(3)	-1080(2)	1777(3)	16(1)
C(9)	6198(3)	-926(2)	3158(3)	14(1)
C(10)	6687(3)	-207(2)	3597(3)	13(1)
C(11)	7437(3)	1134(2)	4662(3)	18(1)
C(12)	4626(3)	574(2)	2685(4)	17(1)

C(13)	7857(3)	1111(2)	1883(3)	14(1)
C(14)	8612(3)	1756(2)	1932(3)	15(1)
C(15)	9505(3)	1866(2)	879(3)	16(1)
C(16)	9632(3)	1334(2)	-247(3)	15(1)
C(17)	8872(3)	699(2)	-339(3)	15(1)
C(18)	8008(3)	583(2)	747(3)	14(1)
Br(1)	10903(1)	1462(1)	-1654(1)	19(1)
N(1)	6904(2)	1032(1)	2936(3)	15(1)
N(2)	6069(2)	390(1)	2625(3)	14(1)
O(1)	8341(2)	558(1)	5351(2)	20(1)

Table 3: Bond lengths [A] and angles [deg] for s3296abs

C(1)-C(10)	1.372(4)
C(1)-O(1)	1.377(3)
C(1)-C(2)	1.410(4)
C(2)-C(3)	1.354(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.425(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.414(4)
C(4)-C(9)	1.429(4)
C(5)-C(6)	1.365(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.401(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.368(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.413(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.433(4)
C(10)-N(2)	1.429(3)
C(11)-O(1)	1.429(3)
C(11)-N(1)	1.447(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-N(2)	1.469(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(18)	1.392(4)
C(13)-C(14)	1.399(4)
C(13)-N(1)	1.424(3)
C(14)-C(15)	1.385(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.385(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.382(4)

C(16)-Br(1)	1.905(3)
C(17)-C(18)	1.386(4)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
N(1)-N(2)	1.433(3)
C(10)-C(1)-O(1)	122.4(3)
C(10)-C(1)-C(2)	122.0(3)
O(1)-C(1)-C(2)	115.6(3)
C(3)-C(2)-C(1)	119.9(3)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(2)-C(3)-C(4)	121.1(3)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	122.0(3)
C(5)-C(4)-C(9)	119.1(3)
C(3)-C(4)-C(9)	118.8(3)
C(6)-C(5)-C(4)	121.1(3)
C(6)-C(5)-H(5)	119.5
C(4)-C(5)-H(5)	119.5
C(5)-C(6)-C(7)	119.9(3)
C(5)-C(6)-H(6)	120.1
C(7)-C(6)-H(6)	120.1
C(8)-C(7)-C(6)	120.7(3)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(7)-C(8)-C(9)	121.2(3)
C(7)-C(8)-H(8)	119.4
C(9)-C(8)-H(8)	119.4
C(8)-C(9)-C(4)	117.9(3)
C(8)-C(9)-C(10)	123.2(3)
C(4)-C(9)-C(10)	119.0(3)
C(1)-C(10)-N(2)	121.7(2)
C(1)-C(10)-C(9)	119.0(2)
N(2)-C(10)-C(9)	119.1(2)
O(1)-C(11)-N(1)	111.9(2)
O(1)-C(11)-H(11A)	109.2
N(1)-C(11)-H(11A)	109.2
O(1)-C(11)-H(11B)	109.2
N(1)-C(11)-H(11B)	109.2
H(11A)-C(11)-H(11B)	107.9
N(2)-C(12)-H(12A)	109.5
N(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
N(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(18)-C(13)-C(14)	119.0(2)
C(18)-C(13)-N(1)	122.1(2)
C(14)-C(13)-N(1)	118.8(2)

C(15)-C(14)-C(13)	120.5(3)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(14)-C(15)-C(16)	119.4(3)
C(14)-C(15)-H(15)	120.3
C(16)-C(15)-H(15)	120.3
C(17)-C(16)-C(15)	120.9(3)
C(17)-C(16)-Br(1)	119.1(2)
C(15)-C(16)-Br(1)	119.9(2)
C(16)-C(17)-C(18)	119.5(3)
C(16)-C(17)-H(17)	120.3
C(18)-C(17)-H(17)	120.3
C(17)-C(18)-C(13)	120.6(3)
C(17)-C(18)-H(18)	119.7
C(13)-C(18)-H(18)	119.7
C(13)-N(1)-N(2)	113.4(2)
C(13)-N(1)-C(11)	117.4(2)
N(2)-N(1)-C(11)	111.4(2)
C(10)-N(2)-N(1)	111.9(2)
C(10)-N(2)-C(12)	117.2(2)
N(1)-N(2)-C(12)	108.9(2)
C(1)-O(1)-C(11)	112.5(2)

Symmetry transformations used to generate equivalent atoms:

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Table 1: Crystal data and structure refinement for s3396m

Identification code	s3396m
Empirical formula	C16 H11 Cl N2
Formula weight	266.72
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.0347(14) A alpha = 90 deg. b = 4.6307(5) A beta = 101.800(2) deg. c = 21.089(2) A gamma = 90 deg.
Volume	1246.0(2) A^3 Z,
Calculated density	4, 1.422 Mg/m^3
Absorption coefficient	0.292 mm^-1
F(000)	552

Crystal size	0.22 x 0.19 x 0.10 mm
Theta range for data collection	1.60 to 28.30 deg.
Limiting indices	-16<=h<=17, -6<=k<=6, -27<=l<=27
Reflections collected / unique	10114 / 2937 [R(int) = 0.0456]
Completeness to theta =	25.00 99.9 %
Absorption correction	None
Max. and min. transmission	0.9714 and 0.9386
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2937 / 0 / 172
Goodness-of-fit on F^2	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1119
R indices (all data)	R1 = 0.0682, wR2 = 0.1321
Largest diff. peak and hole	0.443 and -0.247 e.A^-3

Table 2.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3396m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	1301(2)	9667(4)	-888(1)	16(1)
C(2)	359(2)	11150(5)	-937(1)	19(1)
C(3)	55(2)	13128(5)	-1435(1)	20(1)
C(4)	686(2)	13640(5)	-1876(1)	20(1)
C(5)	1623(2)	12139(5)	-1828(1)	20(1)
C(6)	1931(2)	10149(4)	-1340(1)	18(1)
C(7)	2682(2)	4495(4)	207(1)	16(1)
C(8)	1990(2)	3628(5)	607(1)	18(1)
C(9)	2308(2)	1694(5)	1091(1)	18(1)
C(10)	3330(2)	474(4)	1205(1)	16(1)
C(11)	3710(2)	-1558(5)	1698(1)	17(1)
C(12)	4687(2)	-2767(5)	1776(1)	20(1)
C(13)	5360(2)	-1963(4)	1366(1)	20(1)
C(14)	5044(2)	71(5)	891(1)	19(1)
C(15)	4026(2)	1305(4)	793(1)	15(1)
C(16)	3672(2)	3343(4)	298(1)	16(1)

Cl(1)	2921(1)	-2542(1)	2239(1)	23(1)
N(1)	1544(1)	7646(4)	-364(1)	18(1)
N(2)	2438(1)	6552(4)	-307(1)	17(1)

Table 3. Bond lengths [A] and angles [deg] for s3396m

C(1)-C(2)	1.392(3)
C(1)-C(6)	1.397(3)
C(1)-N(1)	1.433(3)
C(2)-C(3)	1.389(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.381(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.391(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.378(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(16)	1.373(3)
C(7)-C(8)	1.412(3)
C(7)-N(2)	1.430(3)
C(8)-C(9)	1.357(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.421(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.414(3)
C(10)-C(15)	1.432(3)
C(11)-C(12)	1.370(3)
C(11)-Cl(1)	1.746(2)
C(12)-C(13)	1.401(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.376(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.420(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.413(3)
C(16)-H(16)	0.9500
N(1)-N(2)	1.254(2)
C(2)-C(1)-C(6)	120.2(2)
C(2)-C(1)-N(1)	115.61(19)
C(6)-C(1)-N(1)	124.20(18)
C(3)-C(2)-C(1)	119.5(2)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(4)-C(3)-C(2)	120.3(2)
C(4)-C(3)-H(3)	119.8
C(2)-C(3)-H(3)	119.8
C(3)-C(4)-C(5)	120.0(2)

C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(6)-C(5)-C(4)	120.4(2)
C(6)-C(5)-H(5)	119.8
C(4)-C(5)-H(5)	119.8
C(5)-C(6)-C(1)	119.61(19)
C(5)-C(6)-H(6)	120.2
C(1)-C(6)-H(6)	120.2
C(16)-C(7)-C(8)	120.20(19)
C(16)-C(7)-N(2)	114.90(18)
C(8)-C(7)-N(2)	124.90(18)
C(9)-C(8)-C(7)	120.16(19)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(8)-C(9)-C(10)	121.39(19)
C(8)-C(9)-H(9)	119.3
C(10)-C(9)-H(9)	119.3
C(11)-C(10)-C(9)	124.40(19)
C(11)-C(10)-C(15)	117.00(18)
C(9)-C(10)-C(15)	118.60(19)
C(12)-C(11)-C(10)	122.56(19)
C(12)-C(11)-Cl(1)	118.17(17)
C(10)-C(11)-Cl(1)	119.26(16)
C(11)-C(12)-C(13)	120.0(2)
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-H(12)	120.0
C(14)-C(13)-C(12)	120.0(2)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(13)-C(14)-C(15)	120.8(2)
C(13)-C(14)-H(14)	119.6
C(15)-C(14)-H(14)	119.6
C(16)-C(15)-C(14)	122.08(19)
C(16)-C(15)-C(10)	118.40(18)
C(14)-C(15)-C(10)	119.52(19)
C(7)-C(16)-C(15)	121.23(19)
C(7)-C(16)-H(16)	119.4
C(15)-C(16)-H(16)	119.4
N(2)-N(1)-C(1)	113.13(17)
N(1)-N(2)-C(7)	113.59(17)

Symmetry transformations used to generate equivalent atoms:

Table 4:

Anisotropic displacement parameters (A^2 x 10^3) for s3396m. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12

C(1)	17(1)	13(1)	16(1)	-2(1)	-1(1)	-3(1)
C(2)	17(1)	21(1)	20(1)	-2(1)	4(1)	-3(1)
C(3)	16(1)	20(1)	23(1)	-3(1)	-2(1)	4(1)
C(4)	24(1)	16(1)	17(1)	0(1)	-4(1)	-1(1)
C(5)	21(1)	21(1)	18(1)	0(1)	4(1)	-3(1)
C(6)	14(1)	17(1)	24(1)	0(1)	3(1)	0(1)
C(7)	17(1)	13(1)	15(1)	-2(1)	1(1)	-1(1)
C(8)	16(1)	18(1)	20(1)	-3(1)	5(1)	0(1)
C(9)	20(1)	18(1)	18(1)	-2(1)	7(1)	-3(1)
C(10)	20(1)	13(1)	13(1)	-2(1)	2(1)	-2(1)
C(11)	21(1)	17(1)	14(1)	-2(1)	4(1)	-3(1)
C(12)	25(1)	16(1)	16(1)	1(1)	-1(1)	0(1)
C(13)	15(1)	21(1)	23(1)	-4(1)	1(1)	-2(1)
C(14)	17(1)	19(1)	21(1)	-2(1)	4(1)	-2(1)
C(15)	16(1)	13(1)	17(1)	-4(1)	1(1)	-2(1)
C(16)	17(1)	15(1)	16(1)	-3(1)	5(1)	-4(1)
Cl(1)	28(1)	25(1)	19(1)	4(1)	8(1)	0(1)
N(1)	19(1)	15(1)	18(1)	-1(1)	2(1)	0(1)
N(2)	17(1)	15(1)	18(1)	-1(1)	1(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s3396m.

x	y	z	U(eq)	
H(2)	-73.	10811	-632	23
H(3)	-590	14133	-1473	25
H(4)	479	15017	-2211	24
H(5)	2054	12489	-2132	24
H(6)	2567	9110	-1311	22
H(8)	1301	4401	537	21
H(9)	1837	1143	1358	22
H(12)	4909	-4151	2108	24
H(13)	6033	-2822	1417	24
H(14)	5513	659	625	23
H(16)	4127	3928	23	19

Table 6: Torsion angles [deg] for s3396m.

C(6)-C(1)-C(2)-C(3)	-0.6(3)
N(1)-C(1)-C(2)-C(3)	-179.26(18)
C(1)-C(2)-C(3)-C(4)	-0.5(3)
C(2)-C(3)-C(4)-C(5)	1.0(3)
C(3)-C(4)-C(5)-C(6)	-0.3(3)
C(4)-C(5)-C(6)-C(1)	-0.8(3)
C(2)-C(1)-C(6)-C(5)	1.2(3)

N(1)-C(1)-C(6)-C(5)	179.79(18)
C(16)-C(7)-C(8)-C(9)	1.3(3)
N(2)-C(7)-C(8)-C(9)	-178.78(19)
C(7)-C(8)-C(9)-C(10)	-0.6(3)
C(8)-C(9)-C(10)-C(11)	-179.7(2)
C(8)-C(9)-C(10)-C(15)	-0.6(3)
C(9)-C(10)-C(11)-C(12)	177.4(2)
C(15)-C(10)-C(11)-C(12)	-1.7(3)
C(9)-C(10)-C(11)-Cl(1)	-3.7(3)
C(15)-C(10)-C(11)-Cl(1)	177.22(14)
C(10)-C(11)-C(12)-C(13)	1.2(3)
Cl(1)-C(11)-C(12)-C(13)	-177.80(16)
C(11)-C(12)-C(13)-C(14)	0.9(3)
C(12)-C(13)-C(14)-C(15)	-2.3(3)
C(13)-C(14)-C(15)-C(16)	-178.38(19)
C(13)-C(14)-C(15)-C(10)	1.6(3)
C(11)-C(10)-C(15)-C(16)	-179.66(18)
C(9)-C(10)-C(15)-C(16)	1.2(3)
C(11)-C(10)-C(15)-C(14)	0.3(3)
C(9)-C(10)-C(15)-C(14)	-178.84(18)
C(8)-C(7)-C(16)-C(15)	-0.7(3)
N(2)-C(7)-C(16)-C(15)	179.35(17)
C(14)-C(15)-C(16)-C(7)	179.51(19)
C(10)-C(15)-C(16)-C(7)	-0.5(3)
C(2)-C(1)-N(1)-N(2)	-174.20(18)
C(6)-C(1)-N(1)-N(2)	7.2(3)
C(1)-N(1)-N(2)-C(7)	-179.00(16)
C(16)-C(7)-N(2)-N(1)	-177.63(17)
C(8)-C(7)-N(2)-N(1)	2.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for s3396m [A and deg.]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)