Radical Cation Cyclization of Cyclopropyl Silyl Ethers Induced by PET

Synthetic Applications for the Construction of Polycyclic Compounds

and

Photoacylation of 1,4-Naphthoquinones

A Concise Access to the Biologically Active Quinonoid Compounds

Dissertation

Submitted to the Department of Chemistry

University of Bielefeld

In partial fulfillment of requirements for the degree of a

Doctor rerum naturalium

(Doctor of Philosophy)

by

Prashant Ankushrao Waske, M. Sc.,

Bielefeld 2006

Radical Cation Cyclization of Cyclopropyl Silyl Ethers Induced by PET

Synthetic Applications for the Construction of Polycyclic Compounds

and

Photoacylation of 1,4-Naphthoquinones

A Concise Access to the Biologically Active Quinonoid Compounds

Dissertation

Submitted to the Department of Chemistry

University of Bielefeld

In partial fulfillment of requirements for the degree of a

Doctor rerum naturalium

(Doctor of Philosophy)

by

Prashant Ankushrao Waske, M. Sc.,

Bielefeld 2006

Dissertation advisor: Prof. Dr. Jochen Mattay

Dissertation co-referee: Prof. Dr. Dietmar Kuck

Date of oral examination: 03.05.2006

Dedicated to my Beloved Parents

The research work presented here is accomplished under the guidance of

Professor Dr. Jochen Mattay

at the Department of Chemistry, Organic Chemistry-I, University of Bielefeld, Germany,

during May 2001 until December 2005.

Aknowledgement

I would like to take this opportunity to express my gratitude to those peoples who made my stay at Bielefeld pleasant and memorable.

First of all I would like to thank my research advisor Prof. Jochen Mattay for giving me opportunity to work in his group on a very interesting research topic, “synthetic aspects of photochemistry”. I am very grateful to him for his valuable support, continuous enthusiasm and encouragement for this work. He has provided many opportunities to increase my abilities as a researcher and responsibilities as a group member.

My most sincere thanks to Prof. Dr. Dietmar Kuck, for his outstanding cooperation, numerous scientific discussions, helpful suggestions and his valuable reference.

I would like to thank Mrs. Arja Gaestel for her continuous help in official matters as well as friendly discussions.

I am very grateful to Prof. Dr. Norbert Sewald for giving his valuable reference.

I would like to thank all the AK Mattay past and present group members for helping me to carry out research and the pleasant working environment. In particular, Dr. Jens Bunte and Dr. Heiko Rinderhagen for making me familiar with the photochemistry. I also thank to Dr. Michael Oelgemoeller (Lecturer, Dublin City University) and Dr. Christian Schiel for helpful discussions and suggestions about the quinone photochemistry.

I also thank our Photochemistry team, especially to Dr. Juliane Grota for helpful discussions about the mechanistic photochemistry and giving the responsibility to maintain our GC instruments and to Dr. Nikolay Tzvetkov for his kind help as a translator during my beginning days and also I am thankful to him for his friendship.

My special thanks to senior colleagues Dr. Ceno Agena, Dr. Philip Schmold, Dr. Lars Christmann, Dr. Lars Ulmer and Dr. Marco Hering for support and help in the begining.

Also my special thanks to Dr. Björn Decker, Dr. Michael Schiendorfer, Mr. Christian Schäfer, Mr. Björn Schnatwinkel, Mr. Ion Stoll (for nice calendars), Mr. Jörg Srübe and Dr. Michael Klaes, my wonderful colleagues for their fun-filled working environment, interesting discussions and speaking with me in ‘german’.

I would like to thank Mr. Olaf Barton my colleague as well as caption our basket ball team, for encouraging me to join the basket ball team and many chemistry related discussions. I also thank Mr. Mirco Beining for discussing spiro-chemistry related problems as well as many general discussions.

My special thanks to Mr. Dieter Barth and Mr. Thomas Geisler for their technical help on the daily basis and for maintaining the solvent distillation up to date.

I would like to express my deep gratitude to Mr. Peter Mester for carrying out countless 1D and 2D NMR measurements. Without his help it would have not been possible to identify the chemical structures of new substances.

Dr. Matthias Letzel, I thank him for measuring crucial MS and exact mass analysis of organic compounds in a very short time, which was very helpful for the identification of new photoproducts. I am thankful to Mr. Eckard Westermayer for several MS measurements.

I would also like to thank Mrs. Beate Neumann and Dr. Hans-Georg Stammler for single crystal X-ray analysis.

My special thanks to Dr. Ulrich Neuert for his assistance in Computer, Server, Software and Printer (especially Kyocera FS-1750 duplex) related problems.

I am also grateful to all the OC-II *Praktikants* who worked really hard to finish the given synthetic projects.

I am very thankful to all my Indian friends in Germany, especially Dr. Santosh Bhor, Dr. Vivek Khedkar, Dr. Anup Jawalekar and Dr. Khalil Shaikh for their friendship, moral support, constant encouragement, chemistry and non-chemistry related discussions.

I am thankful to Dr. Gokulakannan, (Dr.) Gomathi Gandhi, Mr. Dhananjaya, Mr. Parmeshwaranji, Mrs. Lakshmiji and their children for making my stay at Bielefeld pleasant. I am also thankful to our other Indian students in Universität Bielefeld for making memorable round table discussions in Uni. Mensa during lunch time.

Once again I thank Mr. Mirco Beining, Mr. Björn Schnatwinkel and Dr. Nikolay Tzvetkov for their patience in reading this thesis and helpful suggestions.

I would also like to express by deepest gratitude to my brother Mr. Shashikant (Research Scientist, Ranbaxy Ltd.) for his constant support encouragement, giving tips and tricks for using analytical and preparative HPLC. His important suggestions made the purification of structurally novel compounds possible via HPLC. I am also thankful to Pramodini Vahini for promoting me as a 'Bhau' to 'Kaka' by giving birth to Shreya (Siddhi). I also thank to Shubhangee (Akka) my sister for the constant encouragement and support.

I wish to thank my beloved parents, father (Papa) and my mother (Aie) for their blessings, constant support, love, and encouragements.

Last but not least, I would like to thank Universität Bielefeld, the Volkswagen-stiftung and Landes Nordrhein-Westfalen for the financial support.

Table of Contents

List of Tables

List of Figures

List of Schemes

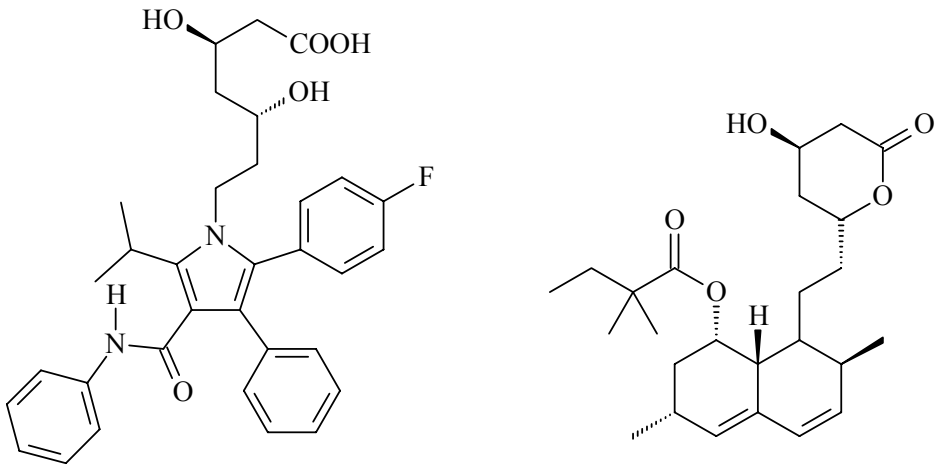
List of Abbreviations

1D-/2D-NMR	One / two dimensional Nuclear Magnetic Resonance
A	Acceptor
CH	Cyclohexane
CI	Chemical Ionization
CIP	Contact Ion Pairs
COSY	Correlation Spectroscopy
C_q	Quaternary Carbon
D	Donor
DCA	9,10-Dicyanoanthracene
DCB	9,10-Dicyanobenzene
DCN	9,10-Dicyanonaphthalene
DEPT	Distorsionless Enhancement by Polarization Transfer
DMSO	Dimethyl Sulfoxide
EA	Ethyl Acetate
EI	Electronic Ionization
EI-MS	Electronic Ionization Mass Spectroscopy
eq.	Molar Equivalents
ET	Electron Transfer
FTIR	Fourier Transfer Infrared spectroscopy
GC	Gas Chromatography
GC/MS	Coupling of Gas Chromatography and Mass Spectroscopy
h	reaction time in hour (s)
HMBC	Heteronuclear Multiple Bond Correlation
HPLC	High Pressure (Performance) Liquid Chromatography
HRMS	High Resolution Mass Spectroscopy
HSQC	Heteronuclear Multiple Quantum Correlation
Hz	Hertz
IR	Infrared spectroscopy
m/z	Mass to charge ratio
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
NOESY	Nuclear Overhauser Enhancement Spectroscopy
Nu	Nucleophile

OAc	Acetate
PET	Photoinduced Electron Transfer
Ph	Phenyl
ppm	parts per million
Pr	Propyl
PTSA	*p*-Toluene Sulphonic Acid
R	Organic moiety rest
rt	room temperature
SET	Single Electron Transfer
SSIP	Solvent Separated Ion Pairs
TBAF	Tetrabutyl ammonium fluoride
TBDMS	*tert*-Butyldimethylsilyl
TBDPS	*tert*-Butyldiphenylsilyl
THF	Tetrahydrofuran
TIPS	Tri-*iso*-propylsilyl
TLC	Thin Layer Chromatography
TMS	Trimethyl silyl
TMS-Cl	Trimethyl silyl chloride
UV/Vis	Ultraviolet/Visible light
δ	Chemical shift in ppm

1 Introduction

Chemical synthesis has made enormous contributions to the development of mankind in the last century. In our daily life we are using so many synthetic materials; one of most commonly used synthetic material is plastic. Another very important aspect of synthetic chemistry is medicine. The pharmaceutical industry worldwide is growing tremendously. The main task of the pharmaceutical industry is the cost effective chemical synthesis of naturally occurring as well as modified biologically active compounds. For example, atorvastatin and simvastatin is a member of the drug class of statins, used for lowering cholesterol level and thereby preventing cardiovascular diseases. Atorvastatin is currently marketed by the pharmaceutical company Pfizer as Lipitor® and is the best selling drug (for year 2005) in the world.



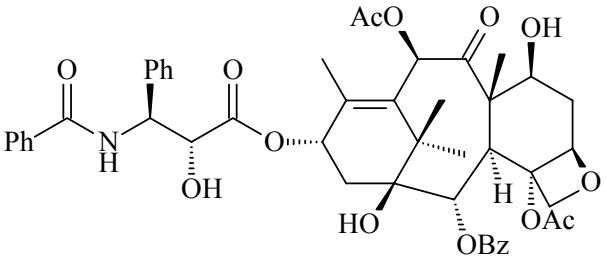
Atorvastatin Simvastatin

Figure 1: Examples of biologically active compounds.

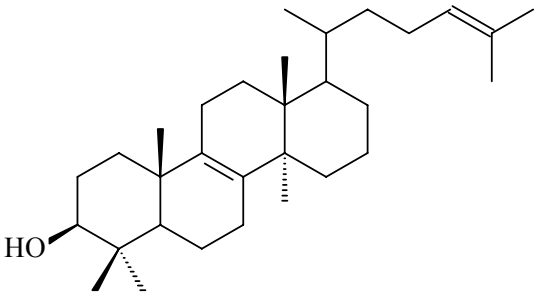
In order to shorten the chemical steps for the synthesis of biologically active compounds, development of new methodologies in organic synthesis are obvious. These new methodologies are also very important for the synthesis of target molecules for the biological testing. In 21 century, world is concerned about the environmental pollutions. Unfortunately chemical industry is the one of the leading pollutant to the environment due to its toxic waste and use of environmentally hazardous chemical reagents. Uses of environmentally benign methods for the chemical synthesis are the central issues, which leads to the new branch of chemistry as "Green Chemistry."[1]

Use of solar energy for the chemical synthesis has invented a new tool for organic chemist.[2,3] Use of artificial light (using UV lamps) increased the usefulness of this new branch of chemistry. Photochemical reactions are favorite reactions for formation of medium to large sized rings. The most commonly used one is (2+2) cycloaddition beside higher order cycloadditions including the photochemical variant of the DIELS ALDER reaction.[4] Photochemical radical cyclization reactions are very important in organic chemistry[5,6] due to the selectivity of the reactions and easy setup procedures.[6,7] In photochemistry most of the research has been carried out only in the restricted area of singlet and triplet initiated reactions. In addition so many advances has been made in the Di-π-methane rearrangement,[8,9] PATERNÓ-BÜCHI reaction[10,11] and NORRISH-YANG photocyclization.[12] Lots of modifications can be carried out for the development of new methodologies using photochemistry.

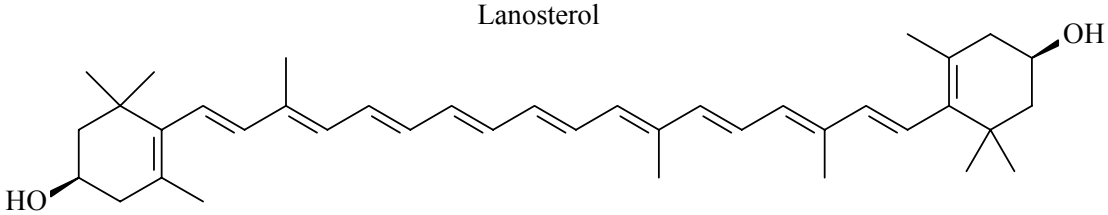
Nature is synthesizing so many complex molecules inside plants, animals and human beings. To synthesize these molecules chemically, we require high synthetic skills and new methodologies. Inside plants, complex compounds are synthesized mostly using terpene units as a starting material. The complete mechanism for the formation of these products inside the plants is still unclear. Biochemists are suggesting the mechanism of their formation via complex cascade reactions.[13,14] Mother nature is carried out these transformation very easily using different reagents which are only available in plants. Taxol™ is also well known naturally occurring product which is showing very good anti-cancer property.[15] The ‘texaoids’ have became known for their novel core and unusual tricyclo[9.3.1.0.]pentadecane framework,[16] which has proven to be a significant challenge to the synthetic chemists.[17,18] Following are some interesting natural products.



Taxol



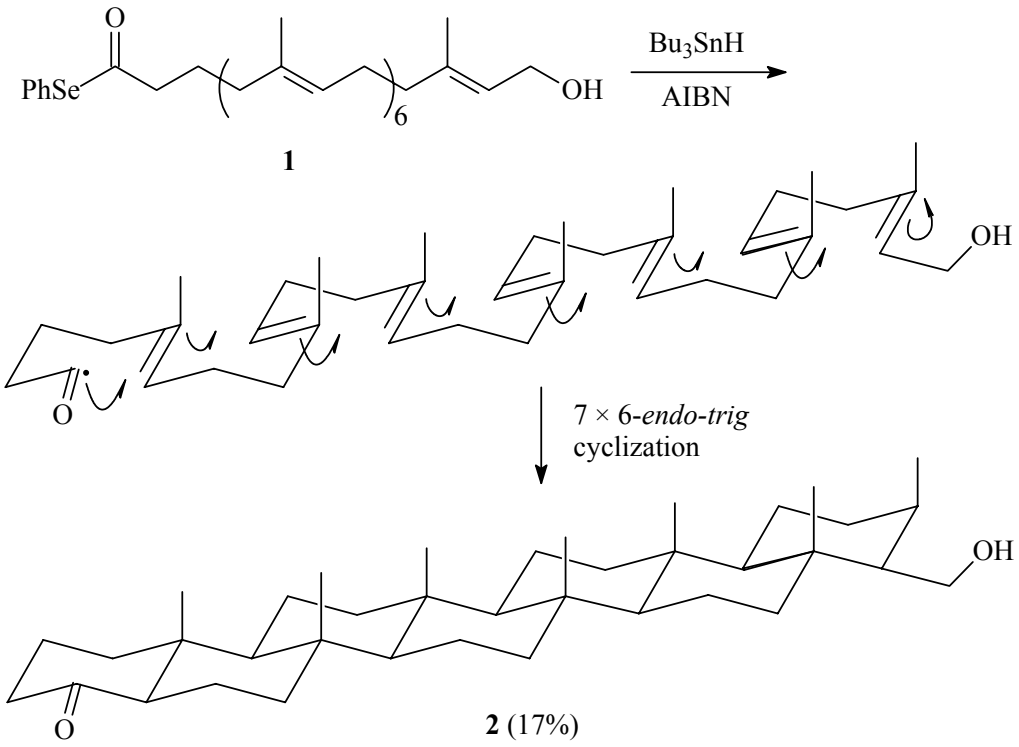
Lanosterol



Xanthophyll

Figure 2: Structures of natural products.

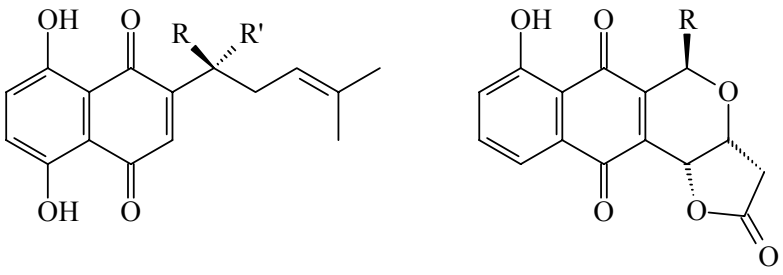
It was a great achievement for the organic chemistry, in which cascade cyclization reaction was carried out chemically. These cascade reactions are also called "Domino reactions." Domino reaction is a process involving two or more bond forming transformations (usually C-C bonds), which takes place under the same reaction conditions without adding additional reagents and catalysts, and in which the subsequent reactions result as a consequence of the functionality formed in the previous step.[19,20] This type of reaction would allow the minimization of waste, since the amount of solvents, reagents, adsorbents and energy would be dramatically decreased, compared to stepwise reactions. Often, these domino reactions are accompanied by dramatic increases in molecular complexity and impressive selectivity. Thus, these reactions would allow an ecologically and economically favorable chemical production. Bu_3SnH-AIBN reagent can be used for such kind of reactions. PATTENDEN et al. examined the scope for and extensive range of complementary radical-mediated cascade processes from polyene precursors in the synthesis of variety of polycyclic ring systems, including taxiods and steroids (Scheme 1).[21] This is really an interesting cyclization reaction in which 3-6 consecutive rings were generated in one step.



Scheme 1: Novel cascade of seven radical-mediated 6-*endo-trig* cyclizations.

The Sn(IV) mediated intramolecular cascade cyclizations are commonly used in organic synthesis. The use of environmentally toxic tin metal makes the reaction less attractive to the chemist. There are also some other reagents reported in literature like metal salts which can be used for such kind of cyclization, their uses are limited due to the lack of selectivity, nature and further reaction with different functional groups. The search of mild alternative method for cascade cyclization is obvious. Photoinduced Electron Transfer reactions commonly called "PET" reactions can be the best alternatives. MATTAY et al. studied PET reactions in detail and published several reports which are really very important for basic understanding.[22] First time it was proved by DEMUTH et al. that cascade reactions could be carried out under PET conditions.[23,24] Such a PET triggered cascade cyclizations were found to mimic the parent nonoxidative enzymatic processes which in turn have originally been proposed to proceed via cationic intermediates, generated upon enzymatic protonation and anti-MARKONIKOV addition of water. These transformations are ultimately giving access to the hitherto shortest biomimetic synthesis of steroidal skeleton in enantiomeric pure form. In PET conditions the combination of sensitizers and co-sensitizers were used. In first step the solution of starting material (reactant) and sensitizer is excited using particular wavelength, the excited molecules donates electron to the sensitizer and forms radical cation. The so formed radical cation could be used for intra- and intermolecular cyclization. The detailed mechanism will be discussed in results and discussion section.

There are varieties of biologically active naturally occurring molecules, which are having quinone functionality.[25] Some of these compounds are having high biological activity and were used as medicines in the form of plant extract for centuries. Alkanin, Shikonin and their derivatives, found in most of the many traditional medical plants of the *Boraginaceae* family (mainly in the genusof *Alkanna, Lithospermum*), have been used as natural purple dyes as a medicine since ancient times in China, Japan, and Europe. [26] Structures of some medicinally important compounds are shown as follows (Figure 3).

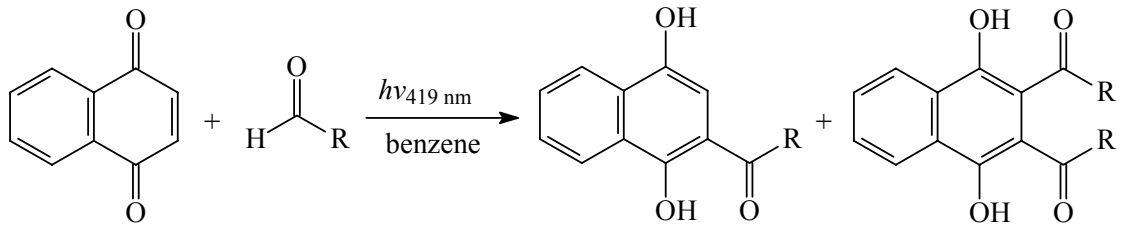


Alkanin R = H, R' = OH
Shikonin R = OH, R' = H

Kalafungin R= Me
Frenolicin B R = Pr

Figure 3: Structures of Alkanin, Shikonin, Kalafugin and Frenolicin.

Due to their high chemical reactivity and polyoxygenated nature, most of the biologically active acylated quinones or hydroquinones are challenging synthetic targets. The synthesis of acylated quinone is the key step in synthesis of such a biologically active quinonoid molecules. Generally, the common method used for acylation is 'FRIEDEL-CRAFTS' acylation method using $AlCl_3$ reagent and acid chloride.[27] This method can not be used directly due to the fact that we could not control the regioselectivity of the reaction. In addition, many compounds do not tolerate the high reactivity of strong acids such as $AlCl_3$. Due to these facts the search for an alternative method is a real challenge. The selective photoacylation of quinone could be the mildest method for the synthesis of such kind of intermediates. The first photo-acylation of quinone has been carried out by KLINGER in 1888, who exposed solutions of the starting materials to natural sunlight over long periods of time.[28] During last few decades lots of progress has been made in this area, most of the reports concern the photoacylation of *ortho* quinones but reports about the photoacylation of 1,4-naphthoquinones remain rare. MATTAY et al. first time introduced a concept of "Photo FRIEDEL-CRAFTS" acylation reaction of 1,4-naphthoquinones (Scheme 2).[29]

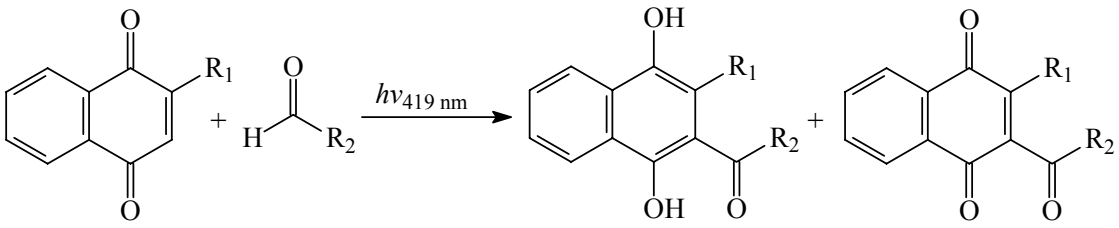


Scheme 2: Photo FRIEDEL-CRAFTS acylation of 1,4-naphthoquinones.

In a typical reaction, the argon flushed solution of 1,4-naphthoquinone and aldehyde in benzene was irradiated using 419 nm until starting material is completely converted. After completion of the reaction the solvent was removed under reduced pressure and crude reaction material was purified with column chromatography. KRAUS et al. reported the photochemical acylation reactions of 1,4-naphthoquinones using medium pressured mercury lamp.[30] They observed only formation of acylated hydroquinone as a sole product in good yields. MATTAY et al. were carried out photoacylation of 1,4-naphthoquinones with aldehyde using specific wavelength of 419 nm. The selection of particular wavelength for such a reaction was just to reduce the further decomposition of products formed and to minimize side reactions. With this modified procedures, in some cases they observed formation of a bis-acylated product along with a mono-acylated product. Furthermore, when 5-methoxy-1,4-naphthoquinone (methyl juglone) was used for photoacylation reaction, in some cases the reaction proceeded with formation of a regioselective mixture. The varieties of combination of photoacylation reaction of substituted naphthoquinones with aliphatic as well as aromatic aldehydes, reveal us to conclude that indeed these reactions preceded with the formation of acylated hydroquinones along with in some cases bis-acylated products. Surprisingly, we did not observe the formation of bis-acylated products when aliphatic aldehydes were used. For the first time we observed formation of an ester as a side product in a photoacylation reaction, in addition esters were not formed when aliphatic aldehydes were used, the only exception was acrolein.

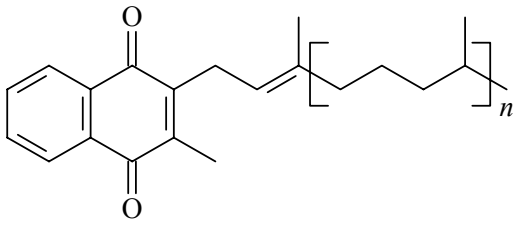
The photoreaction of 2-substituted-1,4-naphthoquinone and aromatic as well as aliphatic aldehydes proceeded with formation of acylated quinone as a sole product. This is a novel reaction which affords only formation mono-acylated quinone as a product in good yields.

These reactions proceeds with high regioselectivity and proved to be extremely useful method for the synthesis of 2-substituted quinone molecules (Scheme 3).[31] The detailed mechanism for the formation these products will be discussed in results and discussion section.



Scheme 3: Photoacylation of 2-substituted quinones with aldehydes.

There are some interesting naturally occurring biologically active compounds (Figure 4) which are bearing same structural framework which can be synthesized directly by photoacylation reaction of 2-substituted quinone with respective aldehyde or the important key intermediate for their synthesis can be synthesized by phoacylation reactions.



n = 3: **Vitamin K1**
n = *n*: **Vitamin K2**

Figure 4: Structure of Vitamin K.

2 Objectives

To develop an entirely new synthetic methodology in organic chemistry is a real challenge. In order to carry out organic transformations in environmentally friendly manner, the selection of reagent is very important issue. The photochemistry is an environmentally benign tool for the carrying out organic transformation in facile way. The usefulness of this method is due to its easy reaction setup and high selectivity. We studied photochemical reactions for the synthesis of key intermediate for total synthesis of biologically active compounds. Our present work is emphasized on following points:

1. **Photoinduced Electron Transfer (PET) Initiated Intramolecular Cyclization of Cyclopropyl Silyl Ethers:**
   a) Synthesis of different substituted cyclopropyl silyl ethers.
   b) PET induced cyclization of synthesized cyclopropyl silyl ethers.

2. **Photoacylation of Substituted 1,4-Naphthoquinones with Aldehydes:**
   a) Photoacylation of 1,4-naphthoquinones with aromatic and aliphatic aldehydes.
   b) Photoacylation of 5-methoxy-1,4-naphthoquinones with aromatic and aliphatic aldehydes.
   c) Photoacylation of 2-methoxy-1,4-naphthoquinones with aliphatic aldehydes.
   d) Photochemical one pot synthesis of 2-acylated 2-methyl-1,4-naphthoquiones.

3 Introduction to the Electron Transfer (ET)

3.1 General Introduction

In organic chemistry, reaction mechanism are largely described as two-electron centered. Electron movements are pictured as taking place two by two in familiar curved arrow mechanisms, notions of one-electron organic chemistry did not enjoy much acceptance in the past. Free radicals have certainly part of the organic chemist's mechanistic arsenal for long time. The most fundamental definition of a redox process involves transfer of electrons: the removal of one or several electrons from the species is called oxidation, whereas any gain of one or several electrons is called reduction. These definitions are best adaptable to the transformations involving metal-containing species where it is easy to keep the track of the valency change at metal center. Metal ion mediated oxidation and reduction of organic compounds were used for electron transfer mechanism.[32] A classical example is SANDMEYER reaction where Cu(I) plays an important role (Equation 1).

$$ArN_2^+ + Cu^I \rightarrow Ar^\cdot + N_2 + Cu^{II}$$

Equation 1: General expression for SANDMEYER reaction.

The research work by KOCHI et al. pioneered reaction between metal ion oxidants and alkylmetals or hydrocarbons settled many problems in the organic chemistry.[33]

In synthetic organic chemistry, reactive species such as radical cations, radical anions and radicals are generated by the process of electron transfer. This process can be simply described by using terms Donor (D) and Acceptor (A). The species which donates (transfers) an electron is donor (D) and which accept an electron is acceptor (A) (Equation 2).

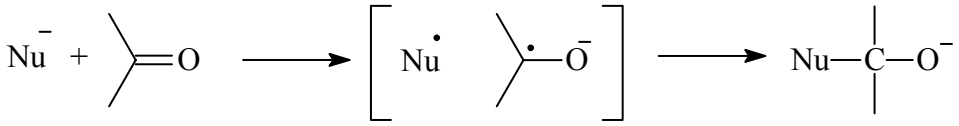
$$D + A \rightleftharpoons D^{+\cdot} + A^{-\cdot}$$

$$D + A^+ \rightleftharpoons D^{+\cdot} + A^\cdot$$

$$D^- + A^+ \rightleftharpoons D^\cdot + A^\cdot$$

Equation 2: General equation for formation of radical cation, radical anion and free radicals.

Mechanistically, electron transfer takes places when the energies of (D A) reaches to the same as energy as activated ($D^{+\cdot}$ $A^{-\cdot}$). The energy diagram shows the DA and $D^{+\cdot}$ $A^{-\cdot}$ for the competing electron transfer and polar pathways (Figure 5). Because of the strong electronic interaction between D and A in the transition state of the polar process, this is generally favored over the ET process.[34] The electronic interaction take the form of either group transfer, as in the SN2 transition state or group coupling, as in the nucleophilic addition process (Equation 3). Thus the difference between electron shift promoted ET and polar process is: the ET process resulted in little change in bonding (D and A simply gives $D^{+\cdot}$ $A^{-\cdot}$), whereas polar process give a product that is fundamentally different from $D^{+\cdot}$ $A^{-\cdot}$.



Equation 3: The nucleophilic addition process.

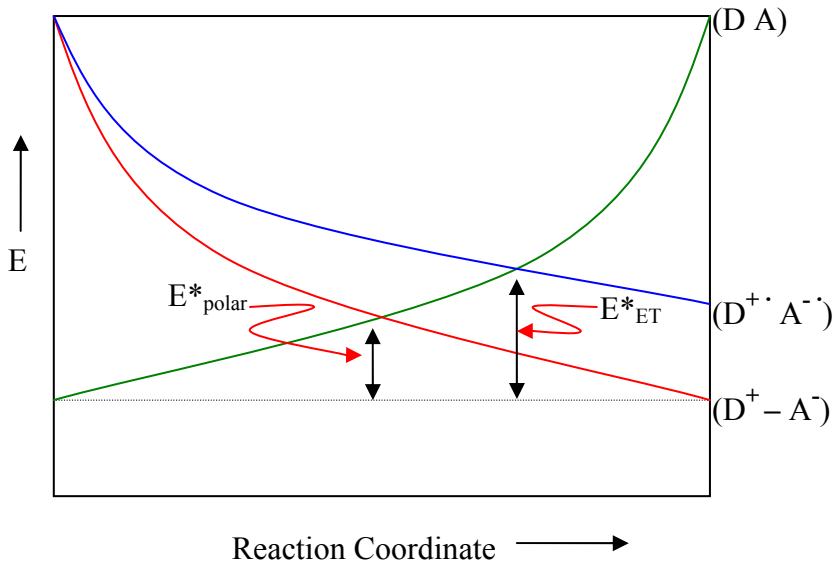


Figure 5: Schematic diagram showing ET and polar pathways.

Thus in general a polar pathway would be favored over ET, unless factors reversing this preference are at hand. PROSS has analyzed this problem in detail and concluded that the following factors should work in favor of ET process[35] :

1. Strong donor-acceptor pairing which will move the avoided crossing toward the initial step.
2. Steric interactions between D and A which will decrease the probability of group coupling between $D^{+\cdot}$ $A^{-\cdot}$.

3. Low bond strength between D^{+} —A^{-} which will decrease the likelihood of groups coupling between $D^{+\cdot}$ and $A^{-\cdot}$.
4. Strong delocalization of the radical centers of $D^{+\cdot}$ and $A^{-\cdot}$.

In case of electron transfer between neutral organic reactants, the initial ion pair consists of oxidized donor and reduced acceptor. Very often we use the generic term *charge transfer intermediate* to describe these ion pairs. Radical ions are charged intermediates having an odd number of electrons.

According to the MARCUS Theory[36] of electron transfer (R. A. MARCUS received Noble prize in Chemistry, 1992), in the excited state, the solvent provides the GIBBS free energy necessary to make the energies of electron on donor and acceptor equal. The point when these energies are equal is transition state, after this only electron transfer takes place. In order to reach the transition state, the FRANK-CONDON principle requires the energy level between which the electron is to be transferred. This requirement is satisfied by increasing the energy of the system, until the energy levels match each other, by bond and the solvent reorganization, associated with the bond and solvent reorganization energy λ. Bond reorganization involves bond stretching and/or compression, angle deformation and torsional movements, whereas solvent reorganization involves solvent-induced changes in electrostatic environment around the reactant. MARCUS derived a parabolic express for the free energy of activation ΔG*.[36]

$$\Delta G^{*} = \frac{\lambda}{4} * \left(1 + \frac{\Delta G}{\lambda} \right)^{2}$$

ΔG* = Free energy of activation
ΔG = Standard free energy; ΔG = -R∗T∗ *ln*K
λ = Reorganization energy

Equation 4: Expression for the free energy of activation ΔG*.

Electron transfer (ET) is reversible reaction, in which back electron transfer (BET) can take place. The rate constant of electron transfer can be calculated by using following equation:

$$A + D \underset{k_{BET}}{\overset{k_{ET}}{\rightleftharpoons}} \dot{A}^{-} + D^{+\cdot}$$

$$K = \frac{k_{ET}}{k_{BET}}$$

$$k = A * \exp\left(- \frac{\Delta G^{*}}{k_{B} T} \right)$$

Equation 5: Rate constants of electron transfer.

By introducing values of ΔG* in the above equation, the equation for rate constants of electron transfer in solution can be written as:

$$k_{ET} = A * \exp\left(- \frac{(\Delta G + \lambda)^2}{4\, k_B\, T} \right)$$

Equation 6: Rate of electron transfer in solutions.

The MARCUS theory predicted that the rate constants of electron transfer should pass through maximum when standard energy is changed in a series of reactions. The plot of $ln\ K_{ET}$ Vs -ΔG predicted to be shaped like a downward parabola, the rate constant increases as ΔG decreases. The $-\Delta G < \lambda$ defines the *normal region* of electron transfer and when $\Delta G < -\lambda$ called *inverted region* of electron transfer. At $\Delta G = -\lambda$, the electron transfer reaction has zero activation barrier.

3.2 Photoinduced Electron Transfer (PET)

Electron transfer initiated by the absorption of light plays an important role in many chemical processes. When an organic molecule is irradiated using an appropriate wavelength of light, it undergoes excitation leading to the ejection of an electron (oxidation), which is accepted by a suitable acceptor molecule. This process is termed Photoinduced Electron Transfer (PET).
The biological photosynthesis is one of the simple examples of this kind in which sunlight is harnessed for the growth and nourishment of plants. PET involves formation of positively and negatively charged ion species separated within the reaction centre and is also called *charge separation*.

PET plays a key role in several emerging technologies, such as semiconductor photocatalysis, artificial photosynthesis, silver halide photography, spectral sensitization and xerography.[34] Photoinduced electron transfer is of great interest to organic chemists concerned with synthesis of novel organic compounds that may be difficult to synthesize by other routes. We are very much interested to explore this field of research in detail.
When ground state molecules absorb visible or ultraviolet light, the electron in the highest occupied orbital undergoes transition to the unoccupied orbital lying at higher energies. In case of organic molecules photochemical excitation of electron donor (D) and electron acceptor (A) molecules lead to well defined changes in their redox properties e. g. A (D) becomes even

stronger acceptor (donor). After photochemical excitation in solutions, donor goes to the excited state and encounters complex with acceptor in a solvent cage. As a result of electron transfer, ionic pairs formed via a solvent separated ion pairs (SSIP) and exciplex (Figure 6).[37] Both the mechanism involves initial formation of encounter complex. Photoinduced electron transfer between two spherical organic molecules takes place via several collisions. One of these collisions will have thermodynamically allowed electron transfer, which lead to the formation of charged ionic pairs such as radical cation and radical anion. If these ions are initially formed inside solvent cage they are termed *geminate ions* (the Latin *geminus* means "twin-born"). The coulombic forces draw these ions in a close proximity; these ions are called contact ions. Since the close proximity of ions, the electron may return to the donor yielding no net change. At the same time the polar solvent can rearrange and subsequently stabilize the ion pairs and may prevent the back electron transfer to the donor. The solvent molecules can penetrate the ions and form *solvent separated ion pairs*. In some cases these ions separate from each other in such a way that is no more correlation with each other. In this case these separated ions are free to enter the cage of other ions or free to participate in chemical transformations, this process is called ion dissociation or charge separation.[37]

Electron trasnfer via a solvent seperated ion pair (SSIP)

$$D^* + A \rightleftharpoons D^* \text{ ---- } A \rightleftharpoons [D^+ \text{-----} A^-] \rightleftharpoons D^+ + A^-$$

encounter complex SSIP free ions

Electron trasnfer via an exciplex (EX)

$$D^* + A \rightleftharpoons D^* \text{ ---- } A \rightleftharpoons [D^+ A^-]^* \rightleftharpoons D^+ + A^-$$

encounter complex EX free ions

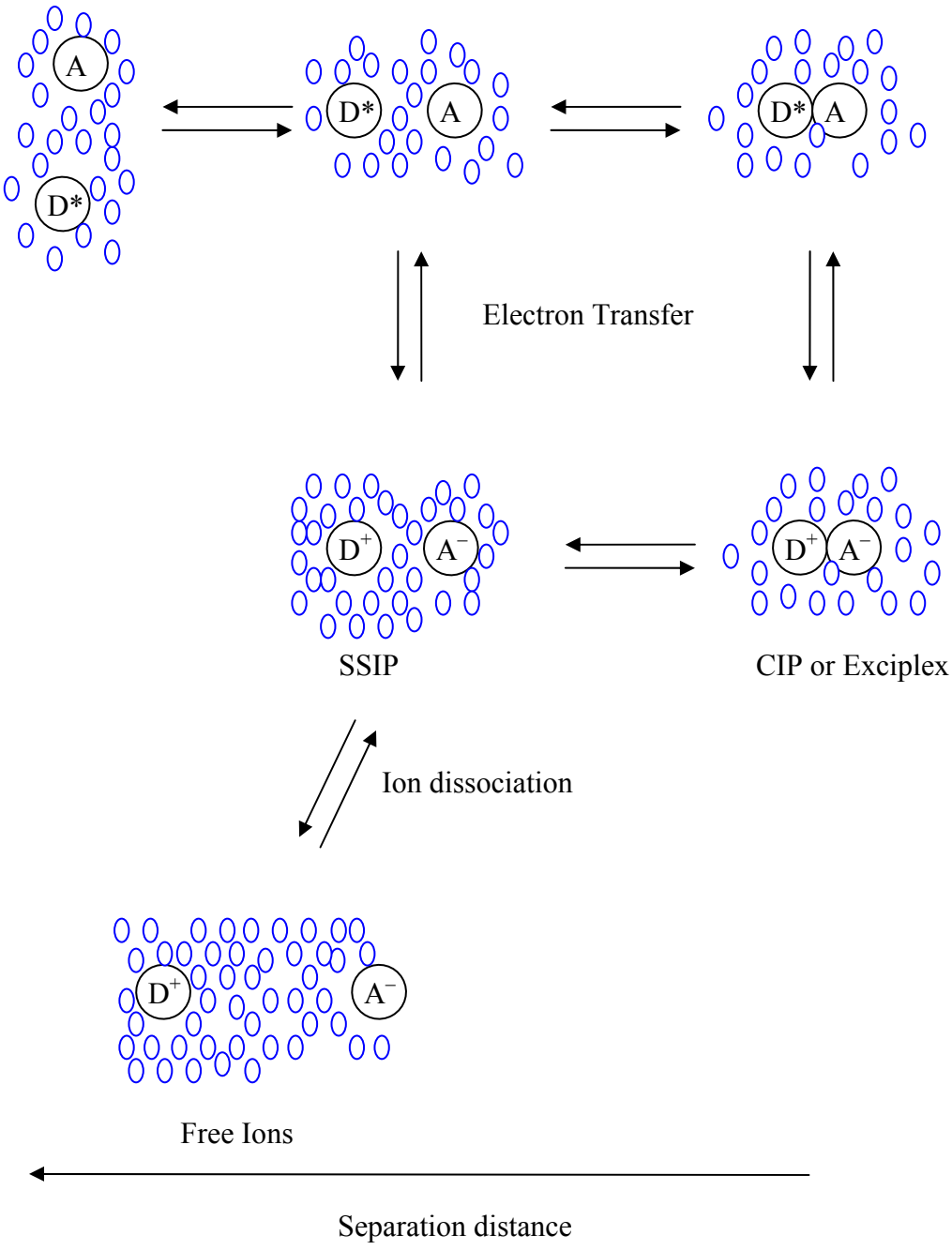


Figure 6: Classification of photoinduced electron transfer in solution.

The solvent plays a very important role for the charge separation. It has been proved that using polar solvent we can achieve the expected solvent separated radical ionic pairs and favor the photoinduced electron transfer. The polar solvents surround the ions and penetrate the space between the ions, which blocks the Coulombic field and allow the ions to move further, in this way it blocks the back electron transfer.

The feasibility of producing radical ions via photoinduced electron transfer can be predicted by using the well known WELLER equation.[22,38] A simplified version is given below (Equation 7).

$$\Delta G = E^{ox}_{1/2}\ (D) - E^{red}_{1/2}\ (A) - \Delta E_{excit} + \Delta E_{coul}$$

$E^{ox}_{1/2}$ (D) = Half oxidation potential of donor; $E^{red}_{1/2}$ (A) = Half reduction potential of acceptor
ΔE_{excit} = Excitation energy of the electronically excited species (either A or D)
ΔE_{coul} = Coulombic interaction in the given solvent

Equation 7: Simplified version of WELLER equation.

The equation can be used to calculate the degree and the direction of charge transfer, even in system of incomplete electron transfer, since only parameters that are experimentally accessible were employed.

3.2.1 Rates of electron transfer and quantum efficiency of photoinduced electron transfer process

The calculation of yields of the generation of ion pairs during photoinduced electron transfer will give more information and is necessary for the photochemist. There are several approaches in which we can just compare the rate of electron transfer k_{el}. From rates of electron transfer we can get information about the velocity of the reaction. In photochemical processes there are different competing processes to the electron transfer. The other competing processes are emission and radiationless deactivation (k_d), energy transfer (k_{en}), other photochemical pathways (k_{other}) (Equation 8). The quantum efficiency for the generation of ions is defined as ϕ_{IP}.[37]

$$\phi_{IP} = \frac{k_{el}}{k_{el} + k_{en} + k_d + k_{other}}$$

Equation 8: Quantum efficiency for generation ion pairs.

The quantum yield, Φ, is the amount of species formed (n_s) divided by number of moles of photons (quanta) absorbed (n_q) by the reaction system (Equation 9).

$$\Phi = \frac{n_s}{n_q}$$

Equation 9: Quantum yield.

The another useful expression is the τ_{IP}, the life time of the ion pair formed by electron transfer (Equation 10)

$$\tau_{IP} = \frac{1}{k_{ret}}$$

Equation 10: Life time of the ion pair.

Where k_{ret} is the rate of electron return, in which an electron returns to its origin generating the original ground state reactants, which is different than back electron transfer (B_{ET}). In back electron transfer acceptors returns its electron to the donor and goes to the excited state. Electron return process is known as non productive, because it destroys the ion pairs. The photochemists are carrying out further research for maximizing the quantum yields and life time for ions pairs. The Figure 7 shows the rates of electron transfer and electron return.

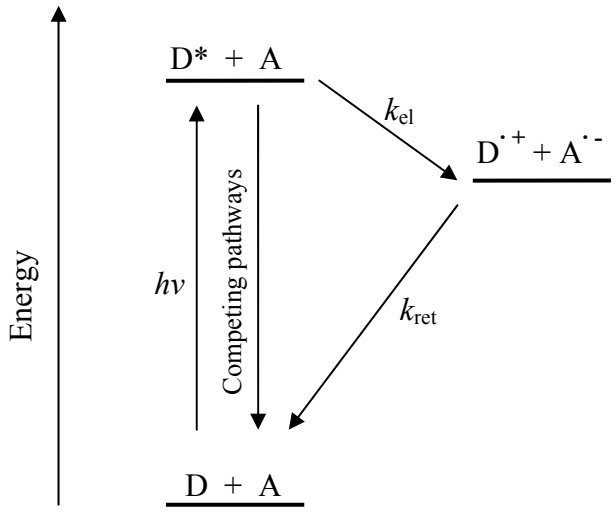


Figure 7: An energy diagram showing rates of electron transfer and electron return.

3.2.2 Sensitizers and co-sensitizers

Most often sensitizers were employed to speed up the photoinduced electron transfer reaction. These sensitizers get excited at an appropriate ultraviolet light, some electronic changes take place during excitation and lead to change in their redox property, which increases their activity. The sensitizer can be good electron donor as well good electron acceptor. Sensitizers are used in catalytic amounts and at the end are regenerates after each cycle. The schematic

representation of sensitizer catalyzed photoinduced electron transfer is shown as follows (Figure 8).

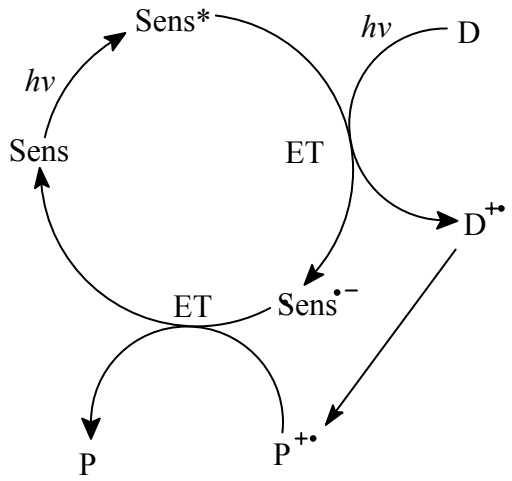


Figure 8: Simple sensitized process.

In this process, Sensitizer (Sens) gets electronically excited and accepts an electron from the donor molecule (D) which is a reactant. After gain of an electron, sensitizer forms radical anion ($Sens^{\bullet-}$) and donor forms radical cation ($D^{\bullet+}$). The so formed radical cation can be cyclized via intra- or intermolecular pathway leading to the formation of product radical cation ($P^{\bullet+}$), which after electron transfer (ET) from sensitizer and hydrogen transfer from solvent molecules forms neutral product. In some cases use of combination of sensitizer and co-sensitizer can afford good reaction transformation. The commonly used sensitizers are shown in (Figure 9).

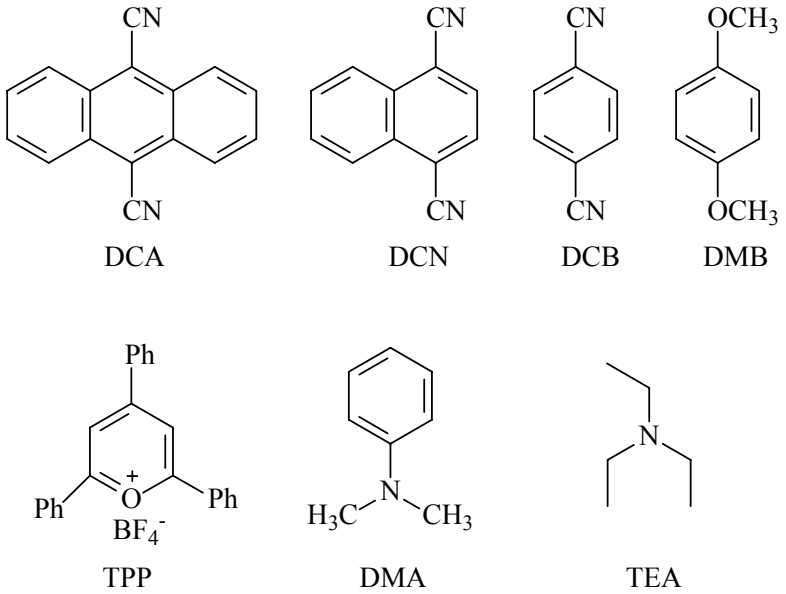


Figure 9: Structures of commonly used sensitizers.

In some cases, use of co-sensitizer along with sensitizer favors the photoinduced electron transfer reaction. In this case first electron transfer takes place from co-sensitizer to sensitizer leading to the formation of sensitizer radical anion and co-sensitizer radical cation. Subsequent electron transfer from substrate regenerates the co-sensitizer and forms radical cation of substrate which cyclizes further to afford product. The acceleration of the reaction is presumably due to the better charge separation, however back electron transfer plays a minor role. The schematic representation of co-sensitizer process is as shown in (Figure 10).

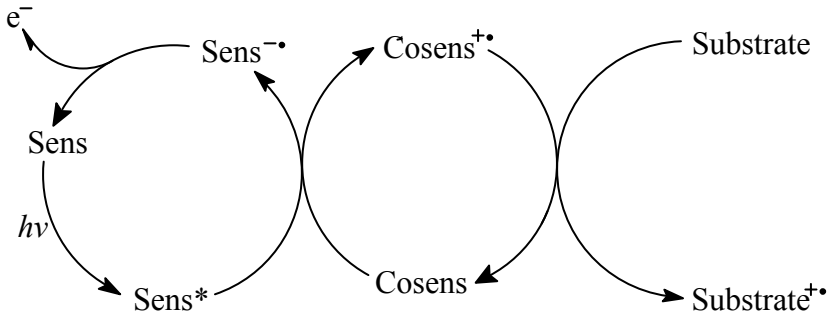
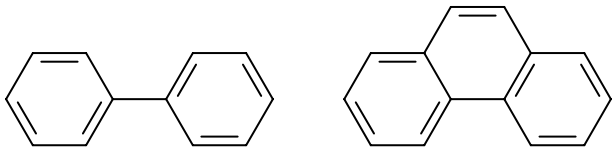


Figure 10: Co-sensitization process. [39]

Generally, selection of co-sensitizer is also an important issue, the normally used sensitizers are biphenyl, phenanthrene as shown in Figure 11.



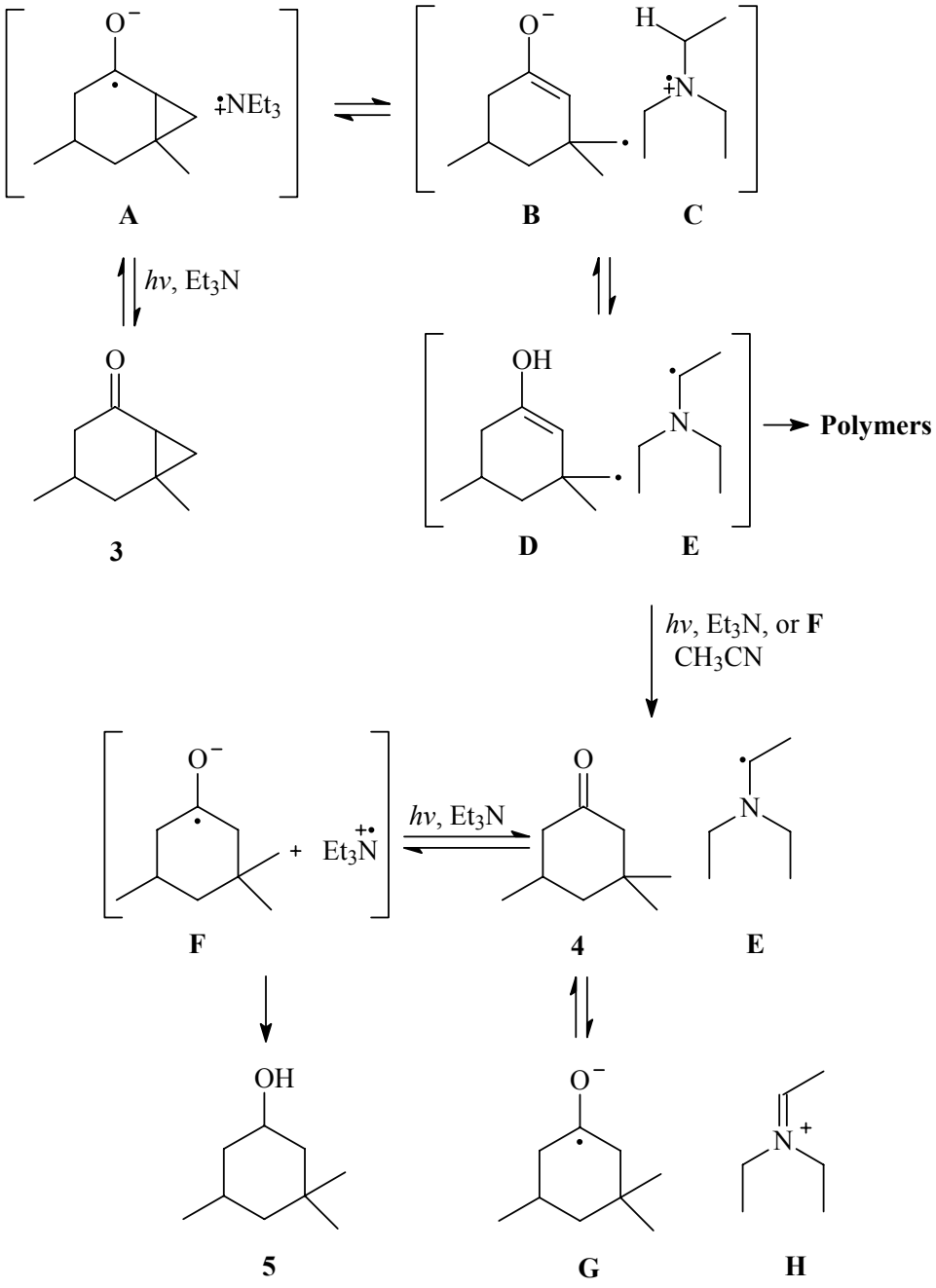
Biphenyl Phenanthrene

Figure 11: Structures of commonly used co-sensitizers.

3.2.3 Generation of radical anions via photoinduced electron transfer

Photoinduced electron transfer chemistry has successfully established in Organic Chemistry for the generation of radical anions by photoinduced reduction of organic molecules. This is an interesting example of 'Umpolung', in which one can reverse the polarity the reactants.[40] In recent years, photochemically induced radical anionic cyclization has been consequently applied for the construction of various polycyclic compounds. By activating only one reactant (acceptor molecule) under mild conditions, starting from neutral compounds, e. g. suitable substituted α-cyclopropyl ketones, the reductive PET reaction leads to the formation of

ketyl radical anion and the corresponding donor radical cation. [41] For reductive PET reaction, triethyl amine (TEA) is used as electron donor sensitizer. By using 254 nm source in acetonitrile, the TEA gets electronically excited and donates an electron to the acceptor substrate, which leads to the formation of radical cation at TEA and radical anion at substrate molecule. For reductive PET reactions, in most cases ketone is used as a starting material. COSSY et al. reported detailed mechanism of PET initiated electron transfer to the cyclopropylketones.[42] On irradiation of ketone **3** in presence of TEA in acetonitrile, fast electron transfer takes place leading to the formation of contact ion pair (Scheme 4). The radical anion **B** most probably has a pK_a in the range of ~10 and the triethylamine amine radical cation **C** has a pK_a of ~8 in water.[43] Therefore the radical anion **B** is basic enough to deprotonate the amine radical cation. The proton transfer can take place if ion pair is previously formed.[44] The radical **F** can then abstracts a hydrogen atom from solvent or TEA to produce ketone **4** and radical **E**. The ketone can be further reduced to alcohol **5** by a second electron transfer either by amino radical or from second molecule of TEA.

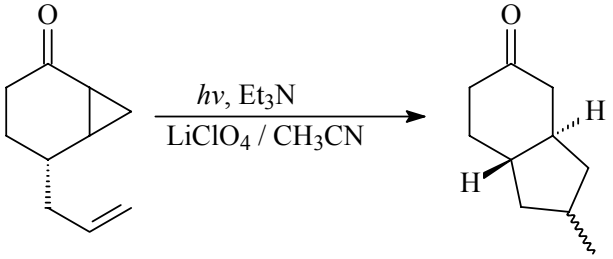


Scheme 4: Reductive PET of cyclopropyl ketone using TEA as donor.

The addition of $LiClO_4$ salt was found to be quite beneficial.[45] By using one equivalent of $LiClO_4$ and ten equivalents of TEA, the yields of ketone can be optimized and formation of alcohol **5** can be terminated.[46] The radical anion so formed via PET initiated electron transfer reaction can be used for several intra- and intermolecular reactions.

COSSY et al. have reported that bicyclic tertiary cycloalkanols can be synthesized from *δ,ε*-unsaturated ketones in good yields, initiated by photoreductive electron transfer (PET) from triethylamine (TEA) in acetonitrile or by photoionization in pure hexamethylphosphoric triamide (HMPA).[47] This methodology has also been successfully used for the synthesis of

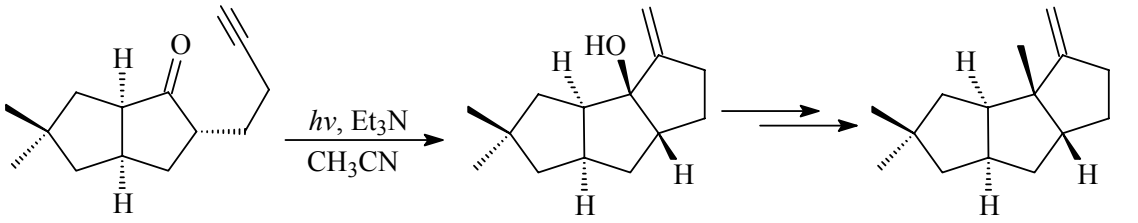
natural products[48] and biologically active *N*-heterocyclic molecules such as (±)-isooxyskyanthine.[47b,49] In all these cases, intramolecular cyclization of *δ,ε*-unsaturated radicals have been proven to be synthetically useful method for the construction of five-membered fused carbocyclic and heterocyclic structures. One of the interesting cyclizations is shown below (Scheme 5).



6 **7** (70%)
ds ratio 5.5:1

Scheme 5: PET initiated ring opening followed by cyclization.

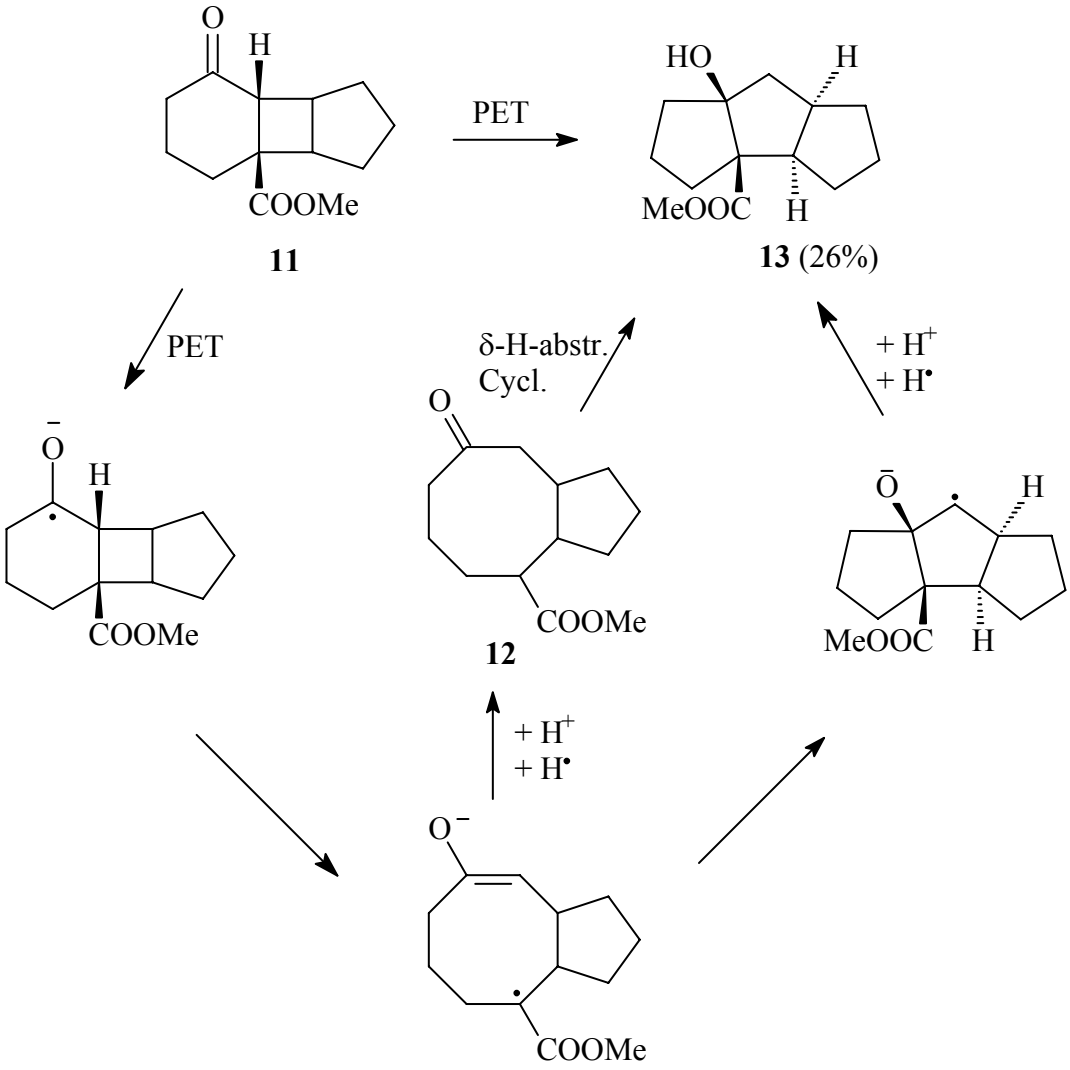
COSSY and co-workers used PET initiated reductive cyclization method for the synthesis of natural product (±)-hirsutene.[a,50]



8 **9** (58%) **10**
(±)-Hirsutene

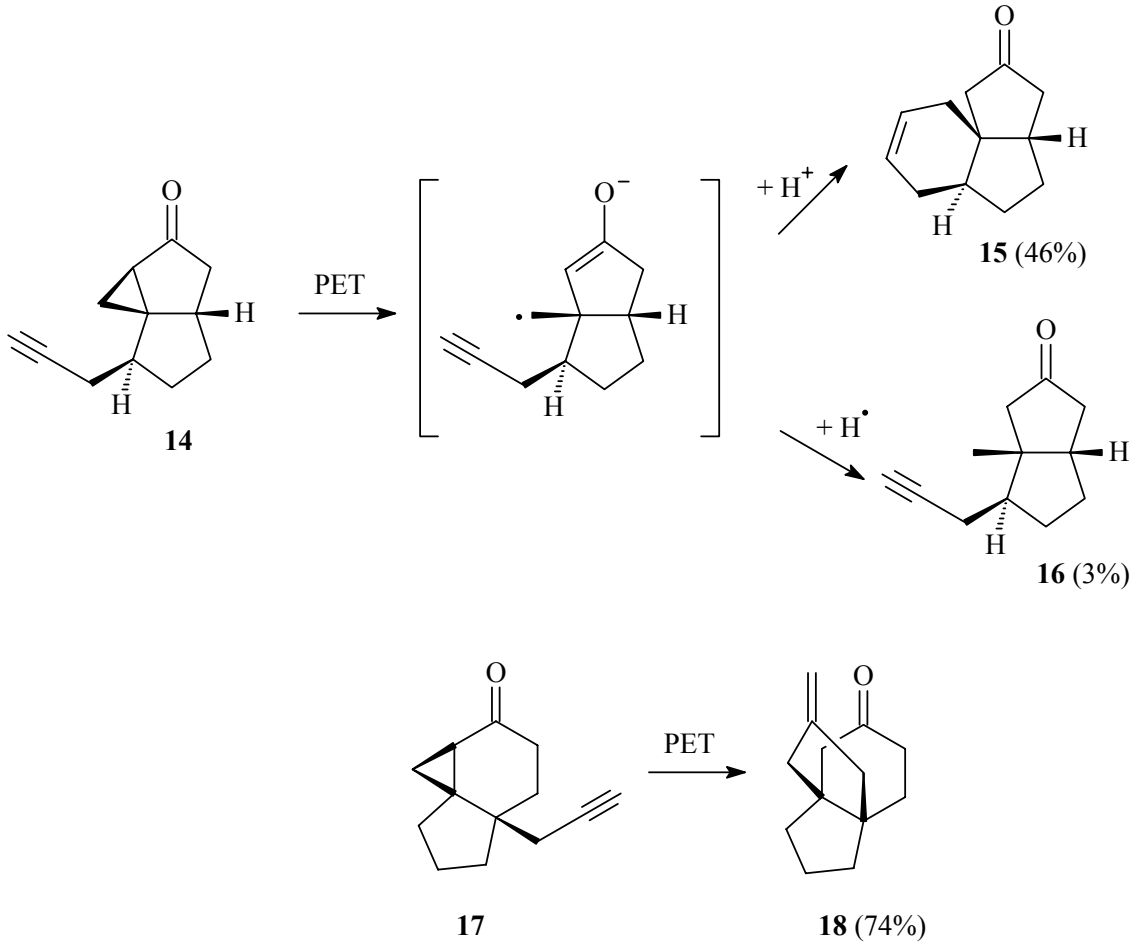
Scheme 6: Synthesis of (±)-hirsutene using PET reaction.[a,]

The synthesis of novel linearly fused triquinane system **13** (Scheme 7) was first time reported by BISCHOF and MATTAY.[51] This novel method includes the PET initiated ring opening of cyclobutane ring in **11**, which leads to the formation radical anion. The presence of ester group plays an important role in the stabilization of the radical. The formation of keto-ester compound **12** has not been observed, but the possibility of formation linear triquinane product **13** via *δ*-hydrogen abstraction of keto-ester **12** can not be ruled out completely.



Scheme 7: Synthesis of novel linear triquinane via PET.

Specifically fused five membered ring triquinanes and propellanes represent an important class of natural products and belong to the polyquinane family.[52] Recently, TZVETKOV and MATTAY carried out reductive PET initiated cyclopropyl ring opened tandem intramolecular cyclization reactions of different substituted *α*-cyclopropyl indenones and hexahydropentalenones, which leads to the formation of propallane and angular triquinane systems.[41] Several preconditions are required for carrying out such a kind of reactions: (i) both the cyclopropyl group and the unsaturated substituent have to be *cis* to each other and (ii) the side chain with suitable length has to be in the *α*-position to the cyclopropane unit. Following are the interesting examples of such a cyclization (Scheme 8).

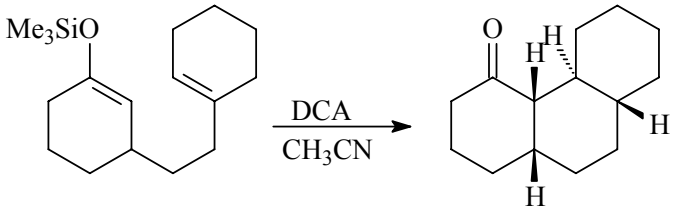


Scheme 8: PET induced cyclization of cyclopropyl ketones.
Reagents and PET conditions: *hv* 254 or 300 nm, Et_3N (5 eq.), $LiClO_4$ (1 eq.), CH_3CN.

When a cyclopropyl ketone **14** was irradiated under reductive PET fully cyclized product **15** in 46% yield and non cyclized product **16** in 3% yield were isolated. The cyclopropyl ketone **17** under reductive PET afforded fully cyclized ketone **18** in 74% as an only one *exo*-isomer.

3.2.4 Generation of radical cations via photoinduced electron transfer reactions of silyl enol ethers.

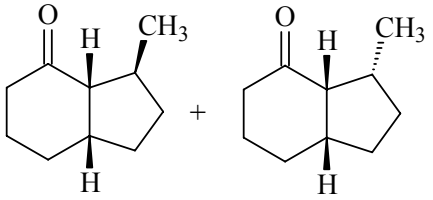
When a solution of silyl enol ether was irradiated using sensitzers such as DCA, DCN and chloroanil[53], the electron rich double bond is easily oxidized to afford the radical cation.[54] The primary product (radical cation) formed after photoinduced electron transfer in the presence of nucleophile leads to the mesolytic cleavage of Si-O bond affording the α-keto radical, which undergoes intramolecular cyclization depending upon the type of tether present. MATTAY et al. described the PET initiated oxidation of silyl enol ether leading to the radical cation which undergoes intramolecular reactions.[55] The silyl enol ether **19** was irradiated in presence of DCA as a sensitizer, the reaction afforded novel tricyclic ketone **20** in 26% yield.



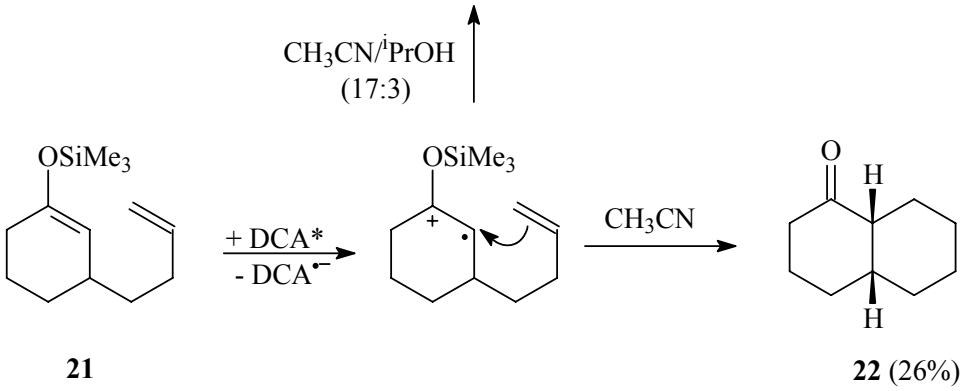
19 **20** (26%)

Scheme 9: PET initiated cyclization of silyl enol ether.

In above case (Scheme 9) reaction follows the 6-*endo-trig* cyclization way. Later they discovered that the reaction mode (5-*exo* or 6-*endo*) can be controlled just by addition some amount of alcohol, which makes the mesolytic cleavage of Si-O facile. In addition, using alcoholic solvents yields of the reaction are improved (Scheme 10).[39] When a PET reaction of silyl ether **21** was carried out in pure acetonitrile, the reaction afforded 6-*endo-trig* cyclized bicyclic ketone product **22**. The same reaction in presence of isopropanol afforded 5-*exo-trig* cyclized products **23** and **24** as a stereoisomeric mixture in 20% yield.



23 (11%) **24** (9%)

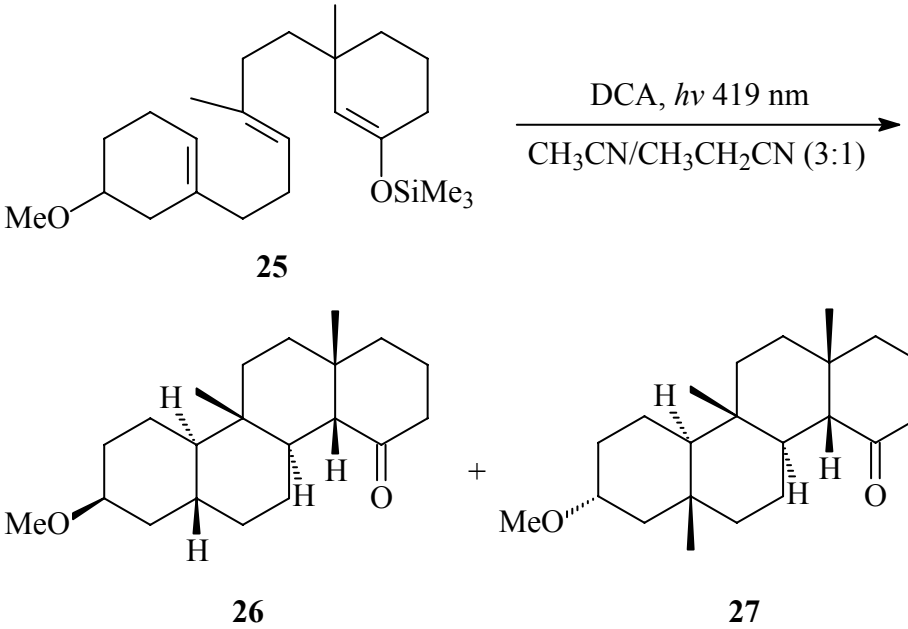


21 **22** (26%)

Scheme 10: PET initiated reaction in $CH_3CN/^{i}PrOH$.

In most of the cases they observed only formation of *cis* isomers of the products. That's why the method represents an important tool for stereoselective synthesis of polycyclic compounds. BUNTE, MATTAY et al. studied these reactions carefully and carried out quantum chemical calculations. These investigations revealed that the reactions follow radical cation pathway.[56]

The PET initiated reaction can be used for the construction of polycyclic compounds with high stereoselectivity. For the first time, by using this method consecutive four rings were prepared which leads to the formation of steroidal framework.[57]

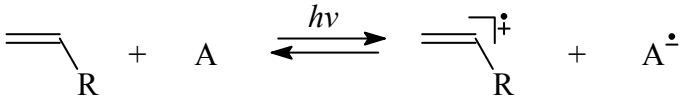


Scheme 11: PET initiated stereoselective cyclization of silyl enol ether.

The silyl enol ether **25** under PET condition using DCA sensitizer afforded the formation of only 1:1 ratio of epimeric pair **26** and **27** in 27% yield (Scheme 11). In this case only two diastereomeric products were formed from the diastereomeric starting material although five stereogenic centers are generated in one step.

3.2.5 Generation of radical cations via oxidative PET of olefins

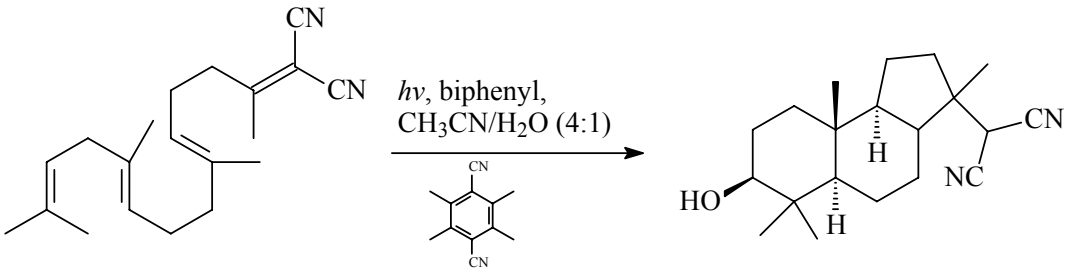
Radical cations can also be generated via oxidative photoinduced electron transfer of olefins. The so formed radicals can be used intra- or intermolecular reactions.



Equation 11: Radical cations via PET of olefins.

When a solution of olefin in presence of sensitizer is irradiated in acetonitrile solvent, electron transfer takes place, which affords the radical cation of the olefin and radical anion of the acceptor (Equation 11). In some cases back electron takes place from acceptor, which leads to triplet excited state of olefins which undergoes cycloaddition reactions.[58] The detailed study about the photoinduced reactions of olefins has been recently reported by GROTA.[59,60]

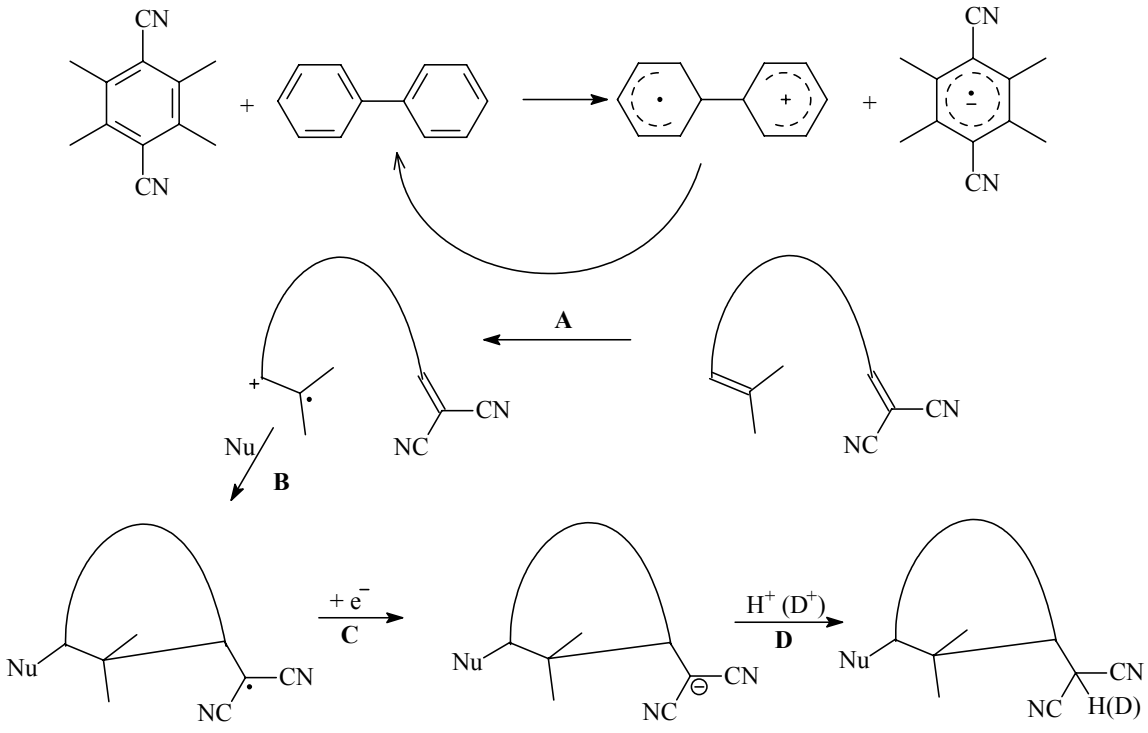
DEMUTH et al. have studied photoinduced electron transfer initiated intramolecular cyclizations of substituted polyalkenes (Scheme 12).[23] The polyalkene **28** under PET condition afforded only fully cyclized product **29** in 25% yield.



28 **29** (25%)

Scheme 12: PET induced intramolecular cyclization of polyalkenes.

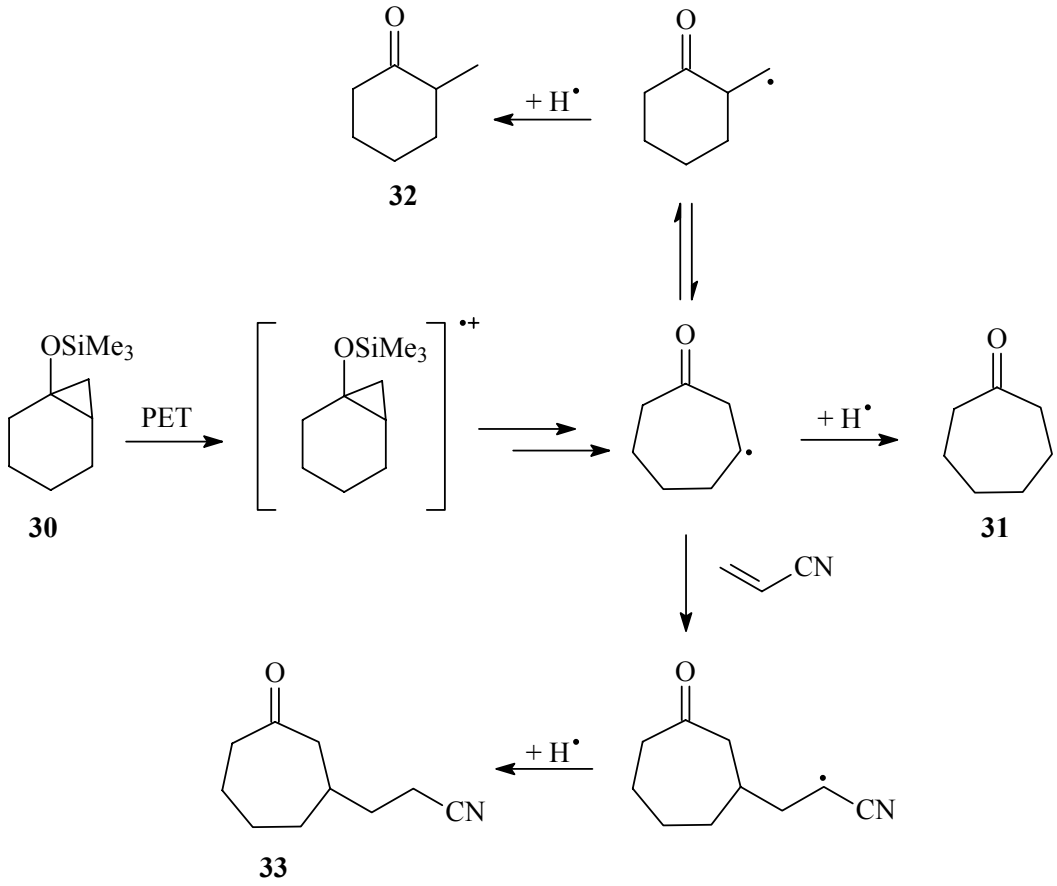
Mechanistically, DEMUTH et al. proved that the addition of protic solvents favors the radical cyclization, which ends up with the 5-*exo*-*trig* mode of cyclization.[61] The mechanistic illustrations of his experiments are shown in Scheme 13.



Scheme 13: Mechanistic investigation by DEMUTH et al.

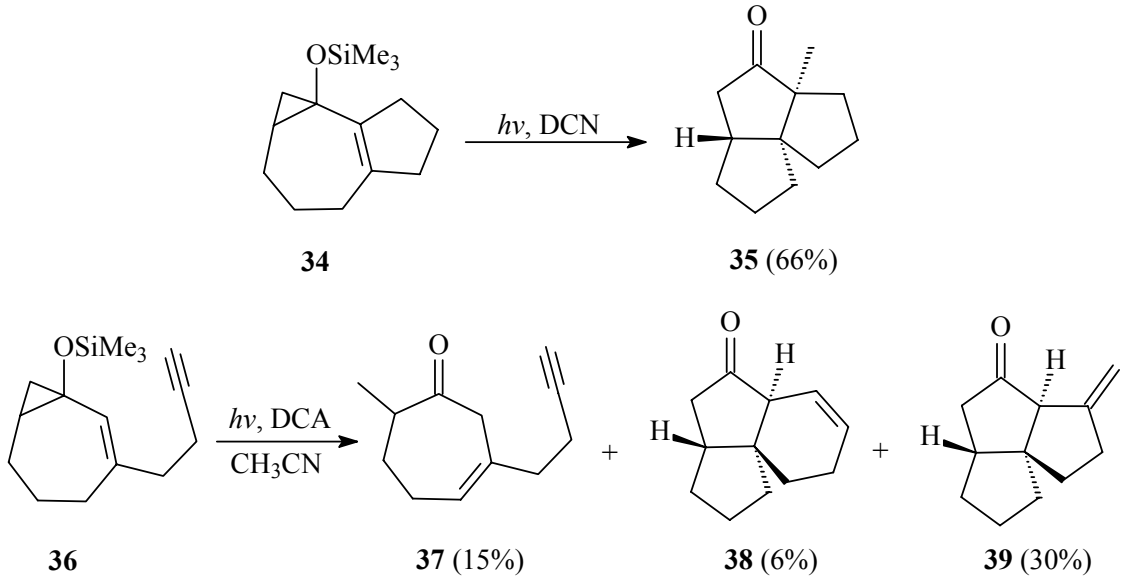
3.2.6 Generation of radical cation from cyclopropyl silyl ether via photoinduced electron transfer

When a solution of cyclopropyl silyl ether was irradiated under PET conditions, the cyclopropyl silyl ether was easily oxidized. The electron transfer takes place leading to the formation of radical cations. RINDERHAGEN and MATTAY used a simple system to study this novel type oxidation reaction initiated by PET.[62] The so formed radical can be used for intra- and intermolecular reactions. The primary results of their research are shown below. Irradiation of cyclopropyl silyl ether **30** in presence of sensitizer forms radical cation which leads to the ring opening of cyclopropane ring. There are two possibilities of ring opening, via *endo* cleavage or *exo*cyclic cleavage. The newly invented method is useful for ring expansion reactions followed by trapping of the radical by using electron deficient olefins such as acrylonitrile. Surprisingly when trapping acrylonitrile was used only formation of *endo*cyclic radical was observed, which leads to the formation **33**. In absence of trapping agent two products **31** and **32** were isolated, which are derived from *endo*cyclic as well as *exo*cyclic ring opening. The study regarding generation of *β*-keto radical and their intra- and intermolecular addition reaction has been already published by RINDERHAGEN and MATTAY (Scheme 14).[63]



Scheme 14: PET initiated ring opening of cyclopropyl silyl ethers.

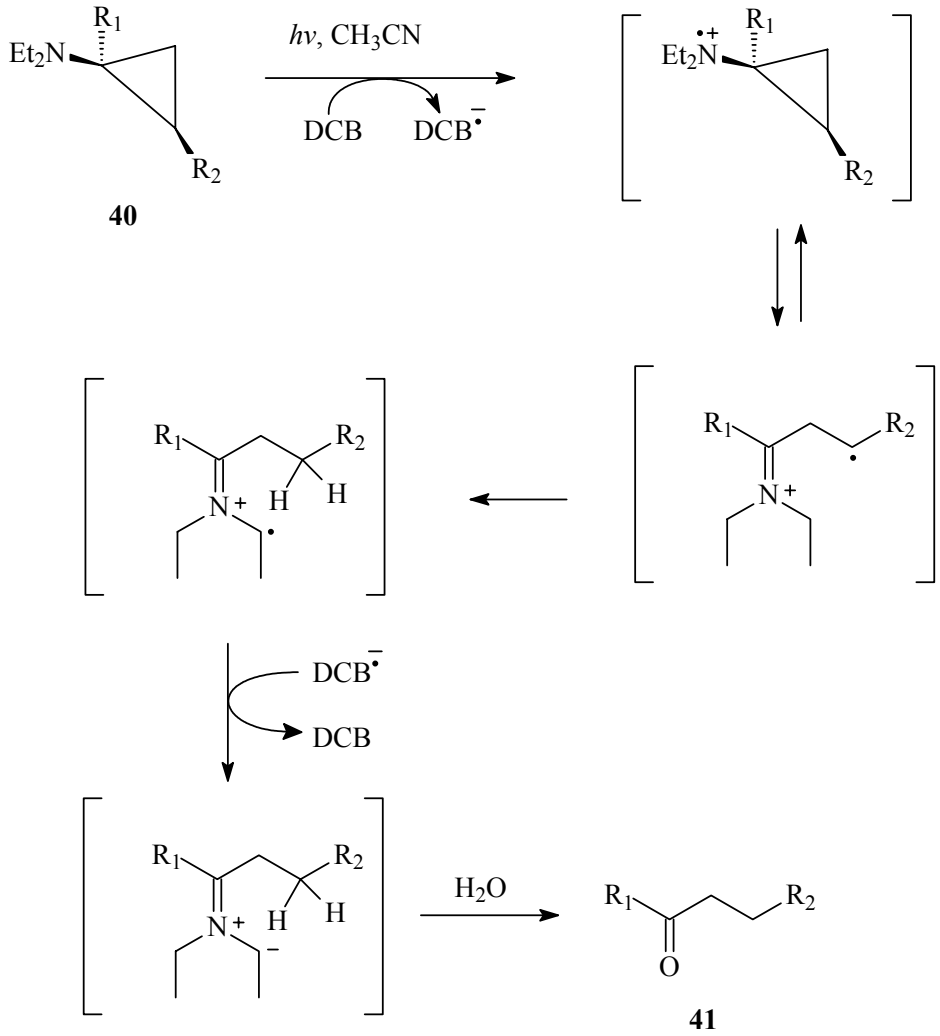
It was proven for the first time that these kinds of reactions can be used for construction of polycyclic compounds. When the solution of cyclopropyl silyl enol ether was irradiated at $\lambda = 419$ nm, in presence of DCA as a sensitizer in acetonitrile. The cyclopropyl ring opening takes place leading to the formation of *endo*cyclic radical, which undergoes intramolecular cyclization depending upon presence of tether. Finally polycyclic compounds are formed. Some interesting examples of this kind of reactions are shown below (Scheme 15).[64,65] The cyclopropane **34** afforded entirely angular triquinane compound **35** in 66% yield. The irradiation of compound **36** leads to the formation of ring opened non-cyclized ketone **37**, *endo*cyclized ketone **38** and *exo*cyclized ketone **30**. This reaction affords the non-cyclized product **37**, but still the complete cyclization process is dominant.



Scheme 15: PET initiated synthesis of polycyclic compounds.'

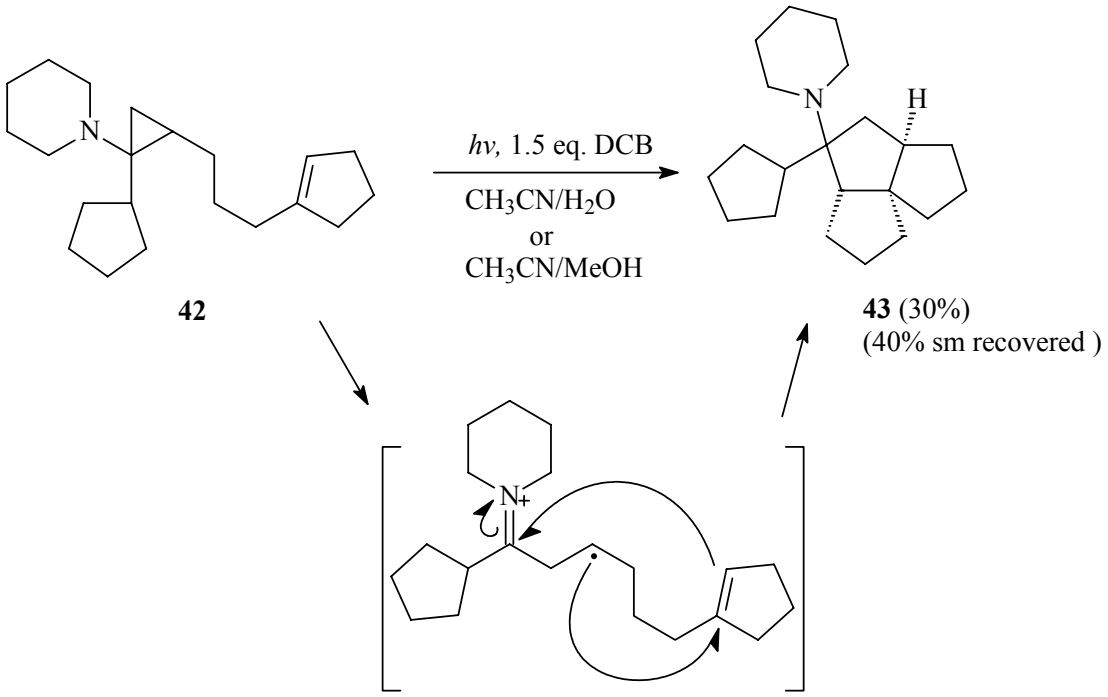
3.2.7 Generation of radical cations using cyclopropyl amines via PET

Cyclopropyl amines after PET initiated electron transfer lead to the formation of radical cations. The cyclopropyl ring opening affords the *β-imino* radical, after hydrolysis, ring enlarged product is formed. CHA et al. reported the facile ring opening of cyclopropyl amine initiated via photoinduced electron transfer using DCB as a sensitizer.[66] The simple ring opening reaction is summarized in Scheme 16.



Scheme 16: Ring opening of amino cyclopropanes.

CHA et al. were unable to trap the radical using electron deficient olefins, but they successfully carried out the intramolecular radical cyclization reaction using different alkene tethers. In general, when amino cyclopropane **40** was irradiated under PET conditions using DCB as a sensitizer the *β*-imino radical is generated, this radical can be used for intra-molecular reactions or just directly after hydrolysis the *β*-keto ester **41** is formed. The reaction affords the formation of polycyclic compounds with *5-exo-trig* cyclization. This selectivity is completely depending on the presence of protic solvents. They reported reactions in CH_3CN/H_2O or CH_3CN/MeOH. An interesting example of such a kind is shown in Scheme 17.



Scheme 17: PET initiated intramolecular cylizations of aminocyclopropanes.

In case of cyclopropyl amine **42** under PET conditions, the fully cyclized product **43** is isolated in 30% yield, whereas the 40% of unreacted starting material (sm) is recovered back from the reaction mixture.

4 Results and Discussion

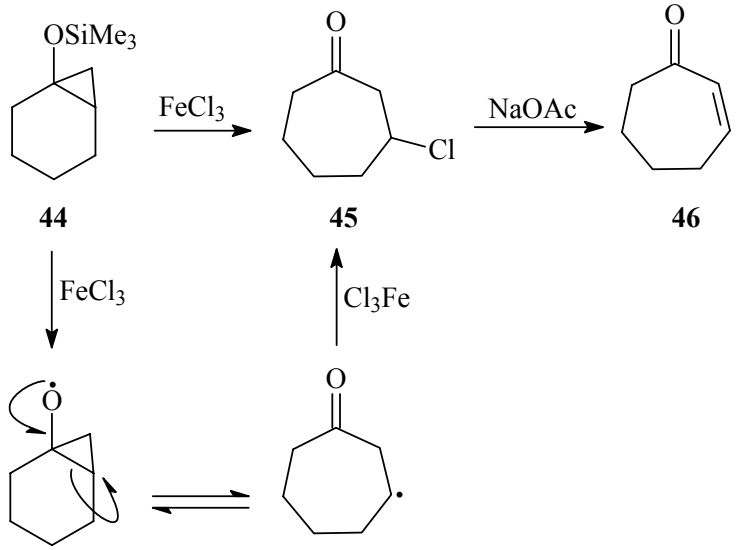
4.1 Photoinduced Electron Transfer Reactions of Cyclopropyl Silyl Ethers

4.1.1 Introduction

Since almost three decades radical cascade reactions (also called domino reactions) have often been used for synthesizing polycyclic compounds.[67,68,69,70,71] Still the tin hydride method introduced by GIESE et al. is one of the mostly applied method to perform radical chain processes despite some disadvantages. In order to circumvent toxic tin reagents and to facilitate the working-up procedures, for example, electron transfer activation has been introduced to generate radical or radical ions.[71b,72] In these reactions metal salts are generally used as oxidizing and reducing agents, respectively.

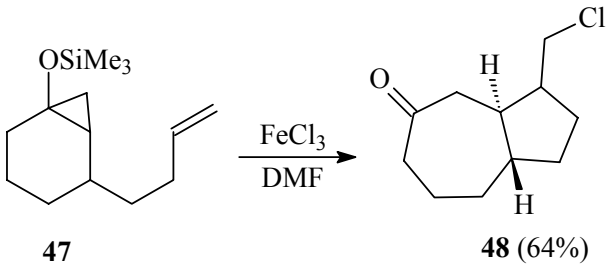
4.1.2 Facile ring opening reaction with $FeCl_3$

The cyclopropyl silyl enol ethers can be easily oxidized by metallic salts as Fe(III), Mn or Ag(I) via single electron transfer reactions (SET). The advantages of such reagents are availability and their high reactivity. The main disadvantages for using these reagents are: these metal ions are not good electron acceptors in the reaction mixture and in addition to this they act as LEWIS acid as well. This limit makes the compatibility with some functional groups and makes the elucidation of the mechanism more difficult. The ring of cyclopropyl silyl ethers can be achieved with $FeCl_3$ salt.[73] This method is useful for ring enlargement and follow up cyclization reactions. The schematic explanation of this reaction is as follows. The mechanism of this kind of reaction is not fully understood but thought to proceed via β scission of the cyclopropyl alkoxy radical followed by intermolecular chlorine abstraction by the β-keto radical (Scheme 18). e. g. when **44** was treated with $FeCl_3$ solution, reaction proceeds with the formation of chloro-ketone **45**. The cycloheptenone **46** can be prepared by treating **45** with NaOAc.



Scheme 18: Ring opening of cyclopropyl silyl enol ether using $FeCl_3$.

BOOKER-MILBURN et al. have studied cyclopropyl silyl enol ethers for intramolecular radical cyclization.[74] The treatment of cyclopropyl silyl ether **47** with DMF solution of ferric chloride (2.2 eq.) yielded the *trans* fused chloro ketone **48** in 64% yield as a single diastereomer (Scheme 19).



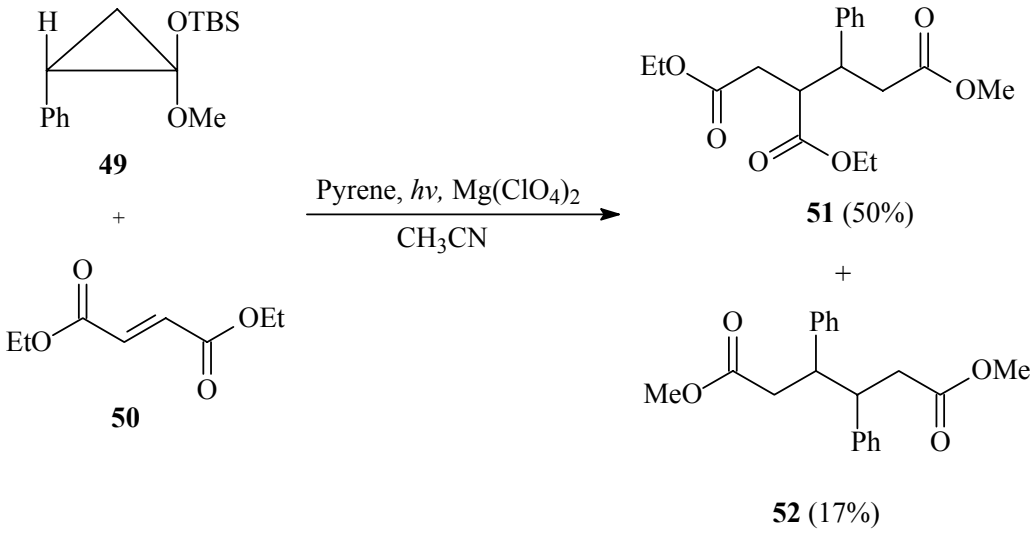
Scheme 19: Intramolecular radical cyclization initiated by $FeCl_3$.[b]

Another way to generate radical ions is possible by the photoinduced electron transfer (PET).[75] This procedure has several advantages: metal reagents and other toxic compounds are avoided, the working-up procedures are often very easy, and in general, photochemistry certainly provides powerful methods for a new and sustainable chemistry.[76,77]

4.1.3 Photoinduced electron transfer reactions of cyclopropanone acetals

Upon oxidative photoinduced electron transfer (PET) the cyclopropane ring opens and forms a reactive *β*-keto radical which undergoes intramolecular cyclization. The oxidative ring-opening reactions of cyclopropanone acetals with carbonyl compounds via PET have been

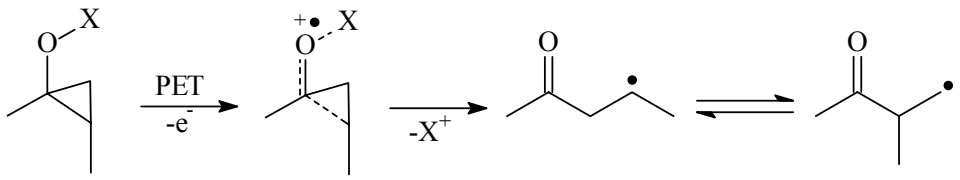
already studied by OKU and co-workers (Scheme 20).[77] They carried out reaction of 2-phenylcyclopropane acetal **49** with symmetrically substituted unsaturated diester (e.g. diethyl formulate **50)** in the presence of phenanthrene or pyrene and $Mg(ClO_4)_2$ in oxygen free acetonitrile, the solution was irradiated at λ = 280 nm (Scheme 20).[77c] The cyclopropane ring opening takes place affording *β-carbonyl* radical, which reacts in an intermolecular fashion affording dimer **52** and coupled product **51**. In absence of additive $Mg(ClO_4)_2$ no reaction was observed. The role of $Mg(ClO_4)_2$ can be explained in terms of its stabilization effect on the radical anion derived from diester suppressing the back electron transfer.[78]



Scheme 20: PET reactions of cyclopropyl ether by OKU et al.[c]

4.1.4 Photoinduced electron transfer reactions of cyclopropyl silyl ethers[79]

When a solution of cyclopropyl silyl enol ether and DCA was irradiated at 419 nm, the facile ring opening of cyclopropane ring takes place leading to the *β*-keto radical. The *endo*cyclic radical can isomerize to *exo*cyclic radical and vice versa. The so formed radical can be further cyclized in 1,5-*exo* or 1,6-*endo* manner depending on the type of tether used.

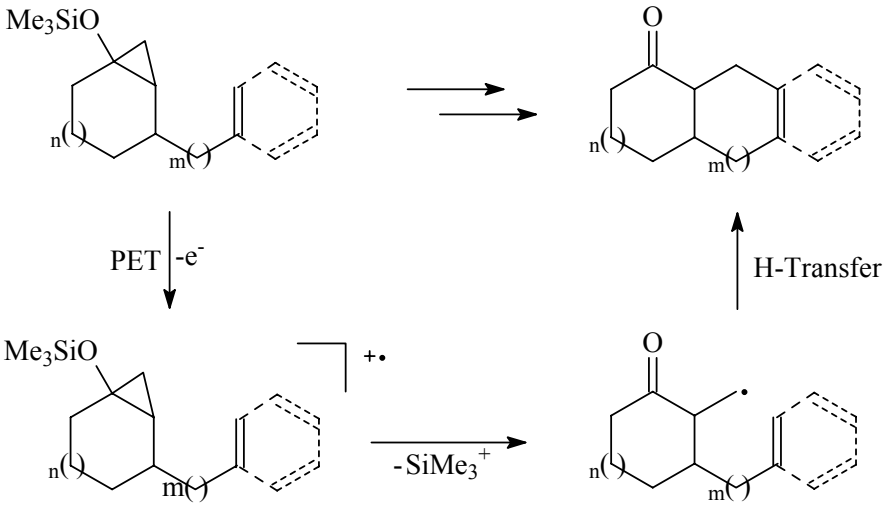


X = SiR_3; R = alkyl group

Scheme 21: PET initiated ring opening of cyclopropyl silyl enol ether.

All these reactions have in common that the redox properties of molecules are changed upon excitation, i.e. both the electron donating as well as electron accepting behavior of the excited species are drastically enhanced. This leads either to oxidative PET or to reductive PET processes. The reaction works very well in presence of sensitizers and co-sensitizers.

Here we will present some further examples of PET initiated radical/radical cationic cascade reactions of bicyclic cyclopropyl silyl ethers functionalized by unsaturated side chains leading to polycyclic compounds. We were especially interested in checking the suitability of alkyne and arene groups in comparison of simple alkenes (Scheme 22).

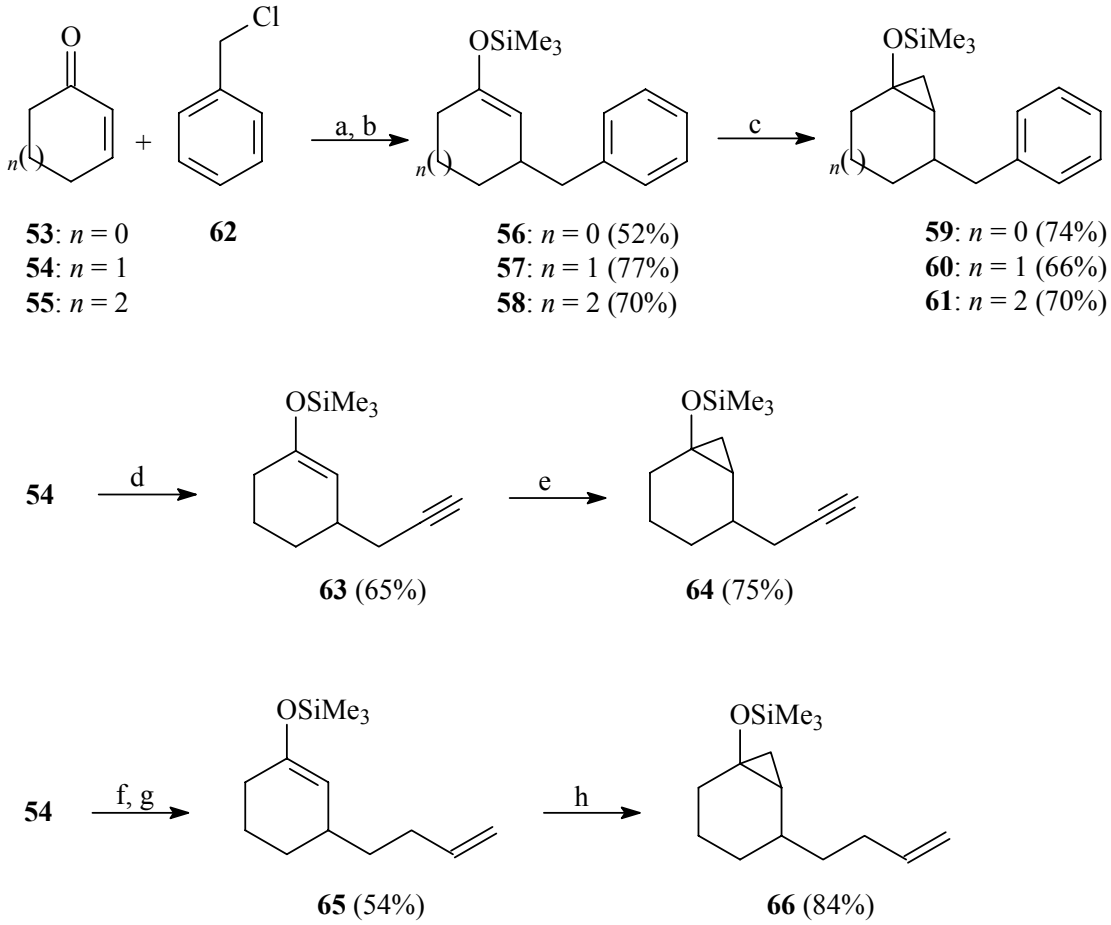


Scheme 22: Photoinduced cyclopropane ring opening: a general scheme.

4.2 Synthesis of Cyclopropyl Silyl Ethers

The silyl enol ethers were prepared by the copper catalyzed conjugate addition of various GRIGNARD'S Reagent (GR) to the enones followed by trapping of the enolates with trimethylsilyl chloride (Scheme 23). The stereochemistry at the newly formed tertiory carbon is not analysed due to the unstable nature of the product. The addition of propargyl magnesium bromide catalyzed by CuI to 2-cyclohexenone did not afford the expected product, however, use of the procedure developed by LEE afforded the propargylated silyl enol ether in good yield.[80] In general, the corresponding bromides were used for the preparation of GR. In case of benzyl bromide we observed only the formation of 1,2-diphenyl ethane. This problem was circumvented by using benzyl chloride. The 1:1 mixture of diethyl ether/THF proved to be the best solvent for the preparation of GR and conjugate addition reactions. The selective cyclopropanation of respective silyl enol ethers in presence of alkenes or alkyne were successfully carried out using diethylzinc, methylene iodide and methylene chloride as the

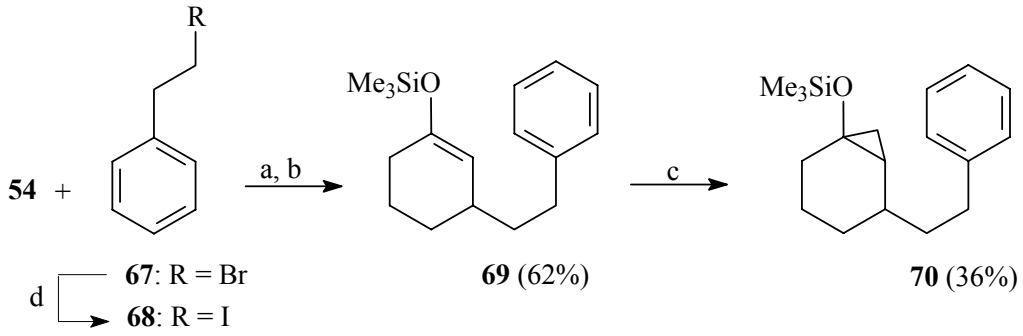
solvent of choice. The stereochemistry of cyclopropanated product was not checked due to the higly air sensitive nature of product. The cyclopropyl silyl ether reacts with moisture leads to the formation of cyclopropanol product, so they were always kept cold and stored under argon/nitrogen atmosphere. Unfortunately, our cyclopropanation conditions were not suitable for related cyclopropanation of *tert*-butyl dimethyl silyl enol ethers, but we found that the corresponding trimethyl silyl enol ether **63** could be cyclopropanated in 75% yield (Scheme 23).



Scheme 23: Synthesis of cyclopropyl silyl ethers.
Reagents and conditions: a) Mg turnings, dry THF/diethyl ether 0 °C; b) CuI, TMS-Cl, –78 °C, Et_3N, RT; c) Et_2Zn, CH_2I_2, CH_2Cl_2, RT, 12 h; d) In metal, propargyl bromide, dry THF, RT 1 h, Me_2S, TMSOTf, 3h; e) Et_2Zn, CH_2I_2, CH_2Cl_2, 2 days; f) Mg turnings, 4-bromobut-1-ene, dry THF/diethyl ether, 0 °C; g) CuI, TMS-Cl, –78 °C, 3 h, Et_3N, RT; h) Et_2Zn, CH_2I_2, CH_2Cl_2, 2 h.

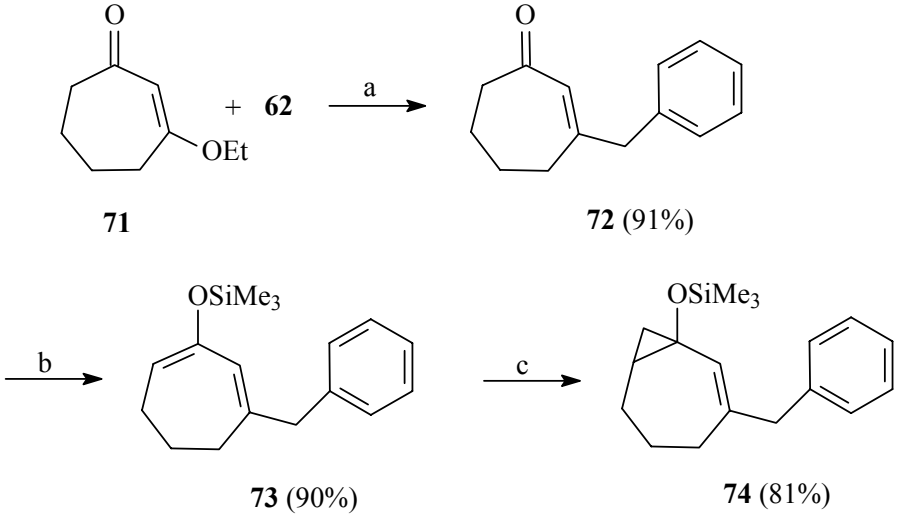
In case of 2-phenyl-1-bromo ethane **67**, we did not observe any formation of GR. To overcome this problem we converted the less reactive bromide to the iodide **68** by refluxing it with NaI in acetone (Scheme 24). The primary alkyllithium was readily prepared at –78 °C (dry ice-acetone bath) under an atmosphere of dry argon by addition of 2.2 molar equivalents of commercial *tert*-butyllithium (*t*-BuLi) in pentane to an approximately 0.1 M solution of **68** in dry *n*-pentane/diethyl ether (3:2 by volume).[81] The CuI catalyzed conjugate addition of this

organolithium compound to 2-cyclohexenone in presence of TMS-Cl afforded silyl enol ether **69** **(**Scheme 24**)**.



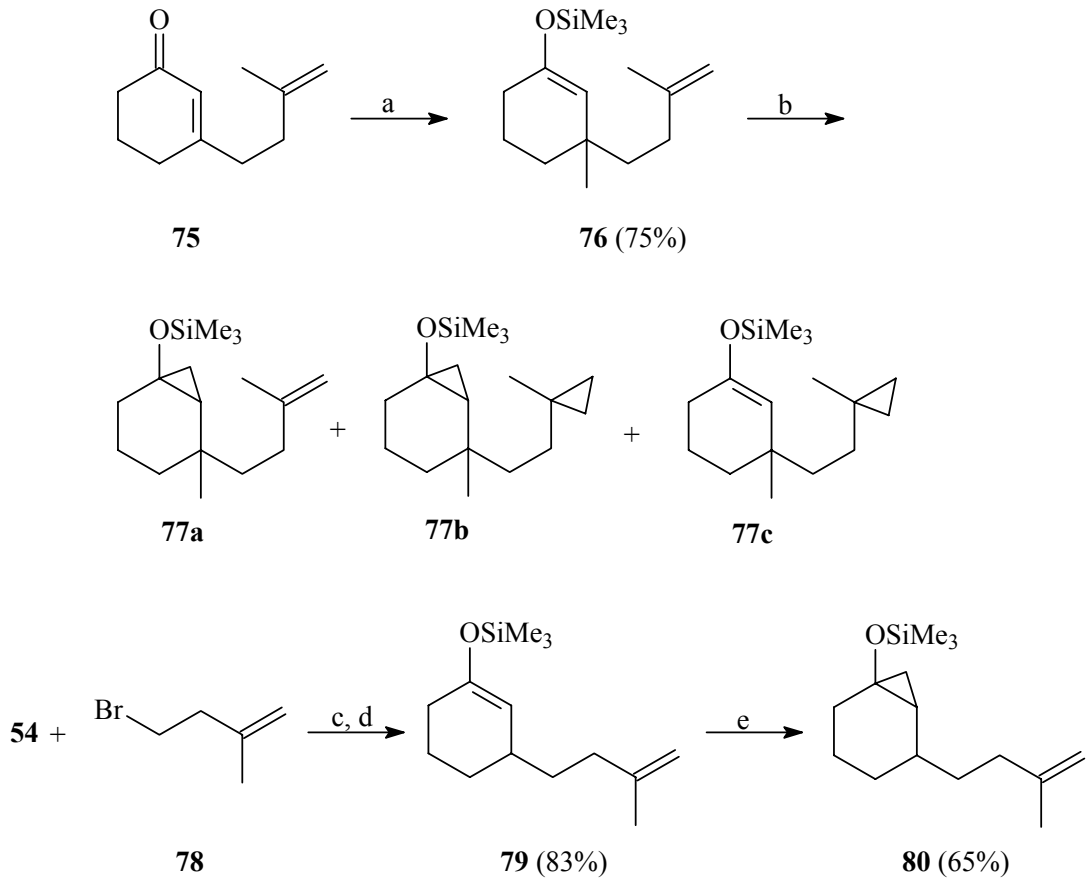
Scheme 24: Synthesis of cyclopropyl silyl ether **70**.
Reagents and conditions: (a) *t*-BuLi, THF, –78 °C to RT; b) CuI, TMS-Cl, –78 °C, Et_3N, RT; c) Et_2Zn, CH_2I_2, CH_2Cl_2, 12 h; d) NaI, acetone, reflux 2 h, (72%).

The 3-substituted enones were prepared from the reaction of vinylogous ester **71** with GR prepared from corresponding bromides or chlorides (Scheme 25). The enone **72** is a very important intermediate in pharmaceutical industry, besides of several filed patents and to the best of our knowledge no one has reported its actual synthesis. We prepared enone **72** by the reaction of 3-ethoxy-2-cycloheptenone **71**[64,65] and benzyl magnesium chloride in 91% yield. Treatment of enone **72** with lithium diisopropyl amide (LDA) in presence of TMS-Cl afforded its silyl enol ether **73**, which was cyclopropanated to **74** in 81% yield, using Et_2Zn, CH_2I_2 in CH_2Cl_2.



Scheme 25: Synthesis of cylclopropyl silyl ether **74**.
Reagents and conditions: a) Mg turnings, dry THF/diethyl ether, 0 °C, 3 h; b) LDA, TMS-Cl, dry THF, –78 °C to RT, 2 h; c) Et_2Zn, CH_2I_2, CH_2Cl_2, 12 h.
The cyclohexenone **75** was synthesized by treatment of 3-ethoxy-2-cyclohexenone and GR prepared from 4-bromo-2-methyl-1-butene and subsequent acid hydrolysis (Scheme 26).[82] Treatment of **75** with methyllithium under our previously developed conditions gave enol ether

76 in 75% yield. The cyclopropanation of **76** with Et_2Zn, CH_2I_2 in various solvents resulted in the mixture of products **77a-c** in poor yields (Scheme 26).

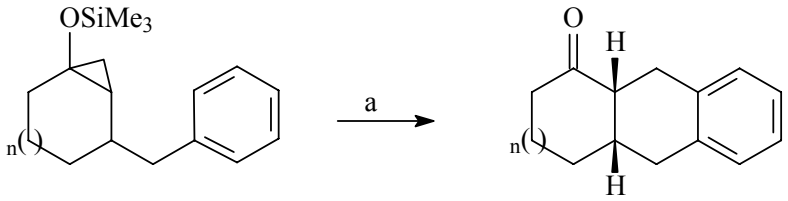


Scheme 26: Synthesis of cyclopropyl silyl ethers **77a-c** and **80**.
Reagents and conditions: a) CuI, MeLi, 0 °C, 10 min, –78 °C, TMS-Cl, 3 h, Et_3N, RT; b) Et_2Zn, CH_2I_2, CH_2Cl_2; c) Mg turnings, THF/diethyl ether, 0 °C; d) CuI, TMS-Cl, –78 °C, Et_3N, RT; e) Et_2Zn, CH_2I_2, CH_2Cl_2, 12 h.

However, the enol ether **79** was prepared in good yield by copper catalysed conjugate addition of GR as shown in Scheme 26. The silyl enol ether **79** could be cyclopropanated to **80** in 65% yield by using our standard conditions.

4.3 Photoinduced Electron Transfer Initiated Cyclizations of Cyclopropyl Silyl Ethers

The deoxygenated solutions of respective cyclopropyl silyl ethers in dry acetonitrile containing the PET sensitizer dicyanoanthracene (DCA) were irradiated in a Rayonet photochemical reactor using 419 nm lamps. All the reactions were monitored by GC or GC-MS.

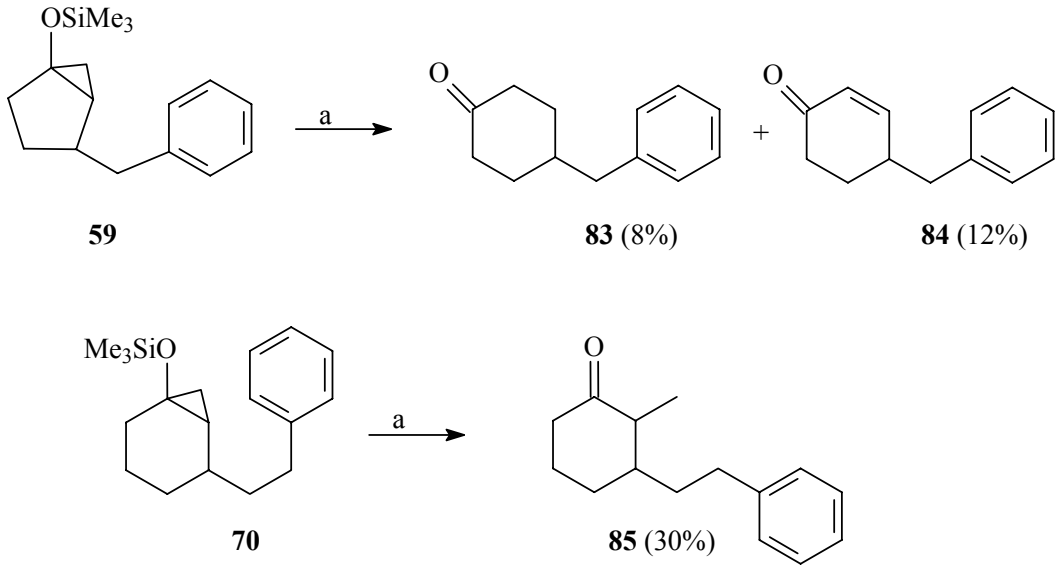


60: $n = 1$
61: $n = 2$

81: $n = 1$ (20%)
82: $n = 2$ (11%)

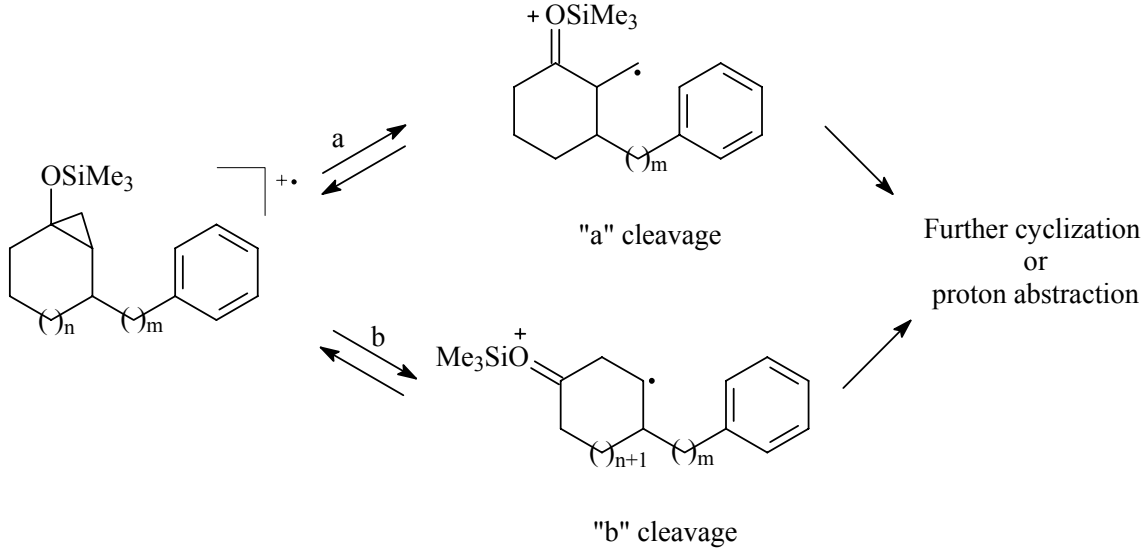
Scheme 27: Photoinduced electron transfer reaction of **60** and **61**.
Reagents and conditions: a) DCA, acetonitrile, irradiated for 12 h at 419 nm.

The irradiation of **60** and **61** in dry acetonitrile resulted in the formation of tricyclic products **81** and **82** with high stereoselectivity (Scheme 27). The cyclopropane ring opening (cf. Scheme 22) and their cyclization can be explained as follows: the sensitizer DCA gets electronically excited at 419 nm and thus is enabled to oxidize the substrate to its radical cation. *Exo*cyclic cyclopropane ring opening leads to the formation of a *β*–keto radical which further cyclizes to the tricyclic products. The last step is the elimination of a hydrogen atom to retain the aromatic ring. Surprisingly we observed only formation of *cis* isomers. The structure and stereochemistry were assigned using modern NMR techniques such as ^{1}H COSY, HMBC, HMQC and NOESY. The cyclopropane **59** under PET condition leads to the formation of non-cyclized ring enlarged products **83** and **84** (Scheme 28). In this case cyclopropyl ring opening takes place via *endo*cyclic cleavage, indicating the formation of the thermodynamically favored more stable secondary radical. Obviously the formation of a new strained polycyclic product is energetically disfavored.



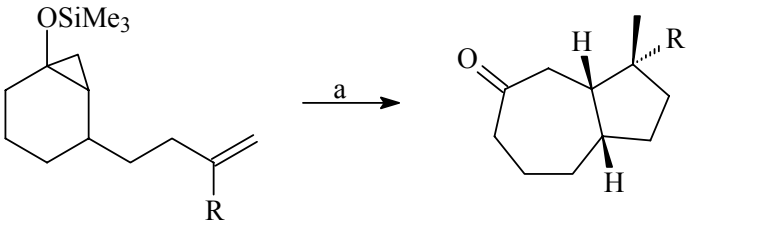
Scheme 28: PET reaction of cyclopropane **51** and **70**.
Reagents and conditions: a) DCA, acetonitrile, irradiated for 12 h at 419 nm.

Irradiation of **70** leads to the *exo*cyclic ring opened noncyclized product **85** as well. In this case intra-molecular cyclization was not observed due to the large distance between *exo*cyclic radical and phenyl ring (Scheme 28). To explain the two contrasting ring opening results from very similar structures, we propose that both processes involve the *endo*cyclic ring opening (cleavage of bond "b", see Scheme 29) as first step followed by a reversible ring-closure process. If n = 1 or 2 and m = 1 or 2 (as in case of **60, 61** and **70**), reclosure could became more facile leading to a cyclohexylmethyl radical which attack the phenyl ring depending on the chain lengths of its tether. If n = 0 (as in case of **59**) the formation of ring enlarged product is favored leading to **83** and the α-β unsaturated ketone **84** respectively. The structure of cyclopropane radical cations and their reactivity has been already discussed by ROTH and co-workers.[83] Further mechanistic investigations are underway using flash laser photolysis and quantum chemical calculations and will be published separately.[84]



Scheme 29: Cleavage of *exo*cyclic (a) and *endo*cyclic (b) C-C bond.

In accordance with this rationalization treatment of **66** and **80** under PET conditions leads to the cleavage of bond "b", the formed cyclic radical undergoes *5-exo-trig* cyclization affording products **86** and **87** (Scheme 30). In these cases the final step is saturation of the radical, which takes places either by direct abstraction of hydrogen from solvent molecule or by reduction to the corresponding anion by the sensitizer radical anion followed up by protonation (e.g. by traces of water in the highly hygroscopic acetonitrile). The stereochemistry at ring junction is *cis*, and was confirmed by NOESY analysis.



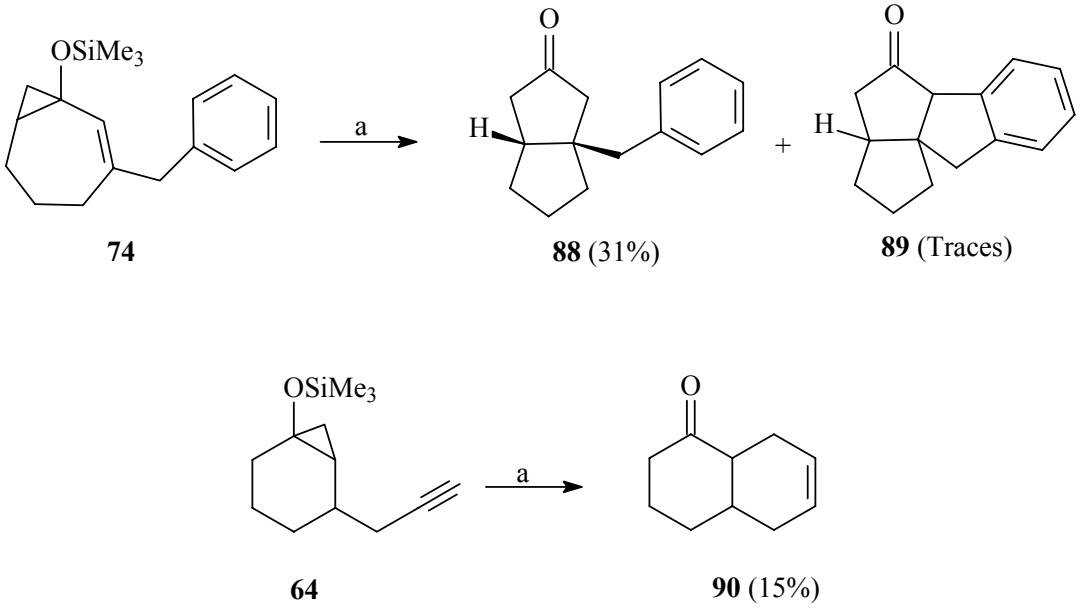
66: R = H
80: R = Me

86: R = H (10%)
87: R = Me (14%)

Scheme 30: Synthesis of *cis* fused bicyclic ketones **86** and **87**.
a) DCA, acetonitrile, irradiated for 12 h at 419 nm

In case of **74** we observed formation of the bicyclic product **88** as only one isomer (31%) in which both substituents are *cis* to each other (Scheme 31). This is not surprising for products which contain a bicyclooctenone substructure because of the high ring strain of the corresponding *trans* products. In addition we observed some traces of product **89**, which indicates that the second cyclization step is energetically disfavored. The propargyl substituted compound **64** was irradiated under PET conditions affording the bicyclic product **90** via *6-endo*

cyclization. If the cyclopropane ring would have opened in a *endo*cyclic way, the formed secondary radical must cyclize in a *5-endo* mode which is known to be "disfavored" according to the BALDWIN-BECKWITH rules.[85,86]



Scheme 31: Cylization of cyclopropane **74** and **64**.
Reagents and conditions: a) DCA, acetonitrile, irradiated for 12 h at 419 nm.

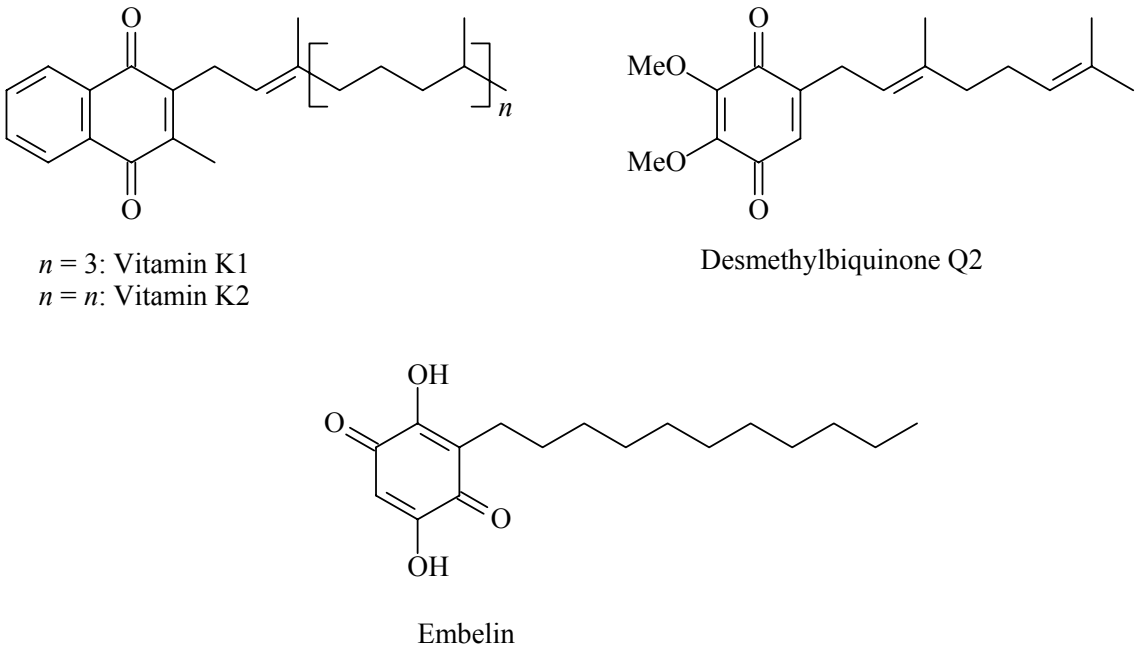
4.4 Conclusion

Various new ring-fused cyclopropyl silyl ethers with benzylic, olefinic or acetylenic side chain have been synthesized in good yields. We have also been able to demonstrate that the PET induced ring opening of cyclopropyl silyl ethers is quite suitable for the production of polycylic compounds with high stereoselectivity. PET oxidative initiated reactions of these cyclopropyl silyl ethers lead to β-carbonyl radical cationic species and β-keto radicals, respectively, which can be used for the construction of polycyclic compounds.[64] The termination step is supposed to be either a hydrogen radical transfer from the solvent (acetonitrile) or a stepwise electron transfer/protonation by traces of water in the solvent.

5 Photoacylation of Quinones

5.1 Introduction

Quinonoid compounds are very important molecules in medicinal chemistry. There are several biological active compounds having quinonoid structural framework. Quinonoid compounds have been used for centuries as medicines and coloring pigments. The most commonly used coloring pigment for drawing designs on hand and coloring hairs is *mehandi*, it is used in India as well as Arabian countries for centuries. Chemically it is nothing but 2-hydroxy naphthoquinone. The structures of important quinonoid compounds are as follows (Figure 12).



n = 3: Vitamin K1
n = *n*: Vitamin K2

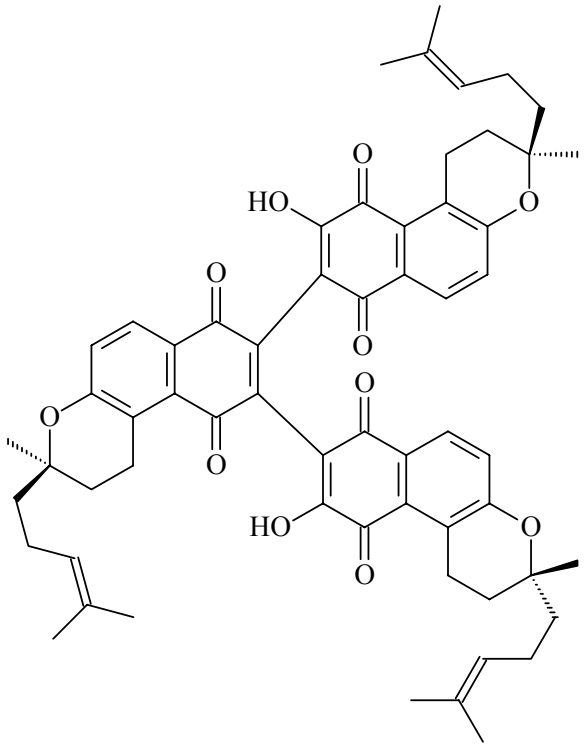
Desmethylbiquinone Q2

Embelin

Figure 12: Naturally occurring quinonoid compounds: Vitamin K, Desmethylbiquinone Q2[87] and Embelin.[88]

Vitamin K is also one of the important compound for human beings as well as for animals which denotes a group of 2-methyl-naphthoquinone derivatives. They are needed for the posttranslational modification of certain proteins, mostly required for blood coagulation. H. DAM and E. A. DOISY shared the 1943 Noble Prize for medicine for their work on vitamin K. They found that vitamin K plays very important role in blood coagulation. They experimentally proved that the lack of vitamin K leads to the severe blood hemorrhage in chicken.[89]

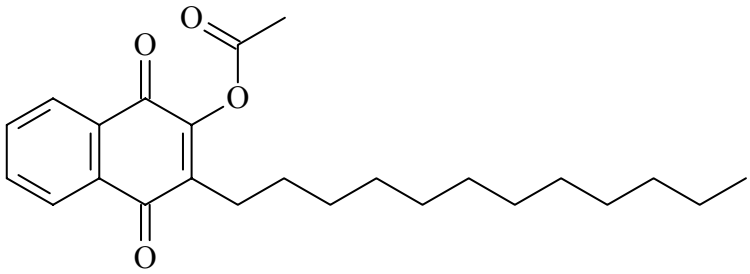
There are some other biologically active quinonid compounds such as Trisquinones (Conocurvone). Conocurvone is having three quinone molecules attached with each other with some specific order. This compound shows exceptionally high and selective anti-HIV activity in a variety of cellular in vitro tests as reported. (Figure 13).[90]



Trimeric naphthoquinone Conocurvone

Figure 13: Structure of Conocurvone.

Synthesis of natural derivatives of quinone as well as its new analogues could lead to a new source for biologically active compounds.



Acequinocyl

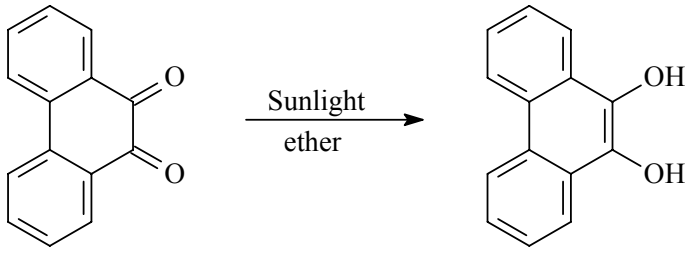
Figure 14: Structure of Acequinocyl.

Acequinocyl[91] was used as an insecticide in early 1940s and has a naphthoquinone structural framework (Figure 14). In conclusion the quinonoid compounds are very important biologically

active molecules and general method development for their chemical synthesis is necessary. Due to the polyoxygenated nature of these compounds its synthesis is a great challenge. We explored a new route for synthesis of key intermediates which leads to important precursors for synthesis of biologically active quinoniod compounds. By using photochemistry, we studied extensively the photoacylation of substituted 1,4-naphthoquinones with a variety of aldehydes. This novel method leads to an easy access for mono-acylated hydroquinone as well quinone products and is called Photo-FRIEDEL-CRAFTS acylation reaction. This method is regarded as an environmentally benign method as we use only a solution of starting materials for irradiation and we can reuse the solvent. In this way we can avoid the use of hazardous and environmentally polluting reagents which is the main aim of 'Green and Sustainable Chemistry.'

5.2 History of Photoreactions of Quinones[92]

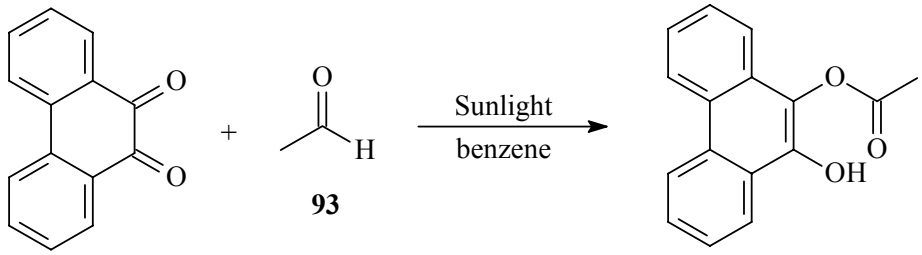
Photoreactions of quinones were first comprehensively studied by KLINGER in 1886. He irradiated a solution of 9,10-phenanthrenquinone **91** in ether using a natural sunlight (Scheme 32). The reaction yielded photoreduced dihydroquinone **92**.[93]



91 **92**

Scheme 32: Photoreaction by KLINGER.

This photoreduction reaction increased his interest in this area and he tried to optimize this reaction by changing solvents. He substituted the ether solvent with acetaldehyde. He was astonished to see the results of this reaction. The reaction proceeded with the formation of monoester of phenanthrenhydroquinone in **94** in good yields.[94]

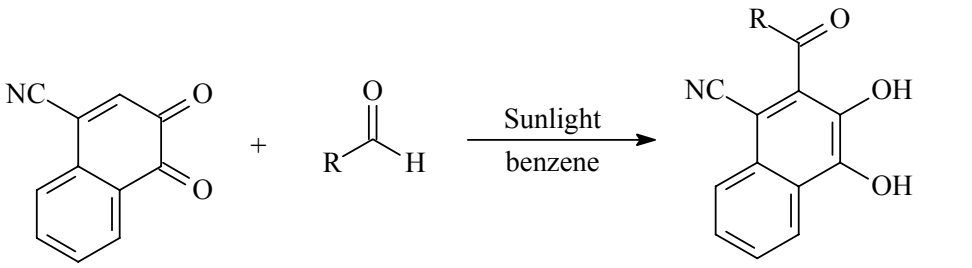


91 **93** **94** (58%)

Scheme 33: Reaction of aldehyde and with phenanthrenone by KLINGER.

He observed formation of monoester with both aliphatic as well as aromatic aldehydes. In some cases he observed formation of acylated hydroquinone as a side product.

SCHÖNBERG et al. reported on similar photoreactions. He used cyano substituted *orho*-naphthoquinones **95**. His result shows that the formation of monoester product depends on the type of aldehyde used.[95] In case of aromatic aldehydes as well as cinnamaldehyde, monoester products were isolated, whereas with aliphatic aldehyde such as acetaldehyde **93** and propanaldehyde **96** the formation of acylated hydroquinones **97** and **98** as major products was observed. So he concluded that the by changing substituent on the quinone moiety, partly the chemoselectivity can be controlled.



95

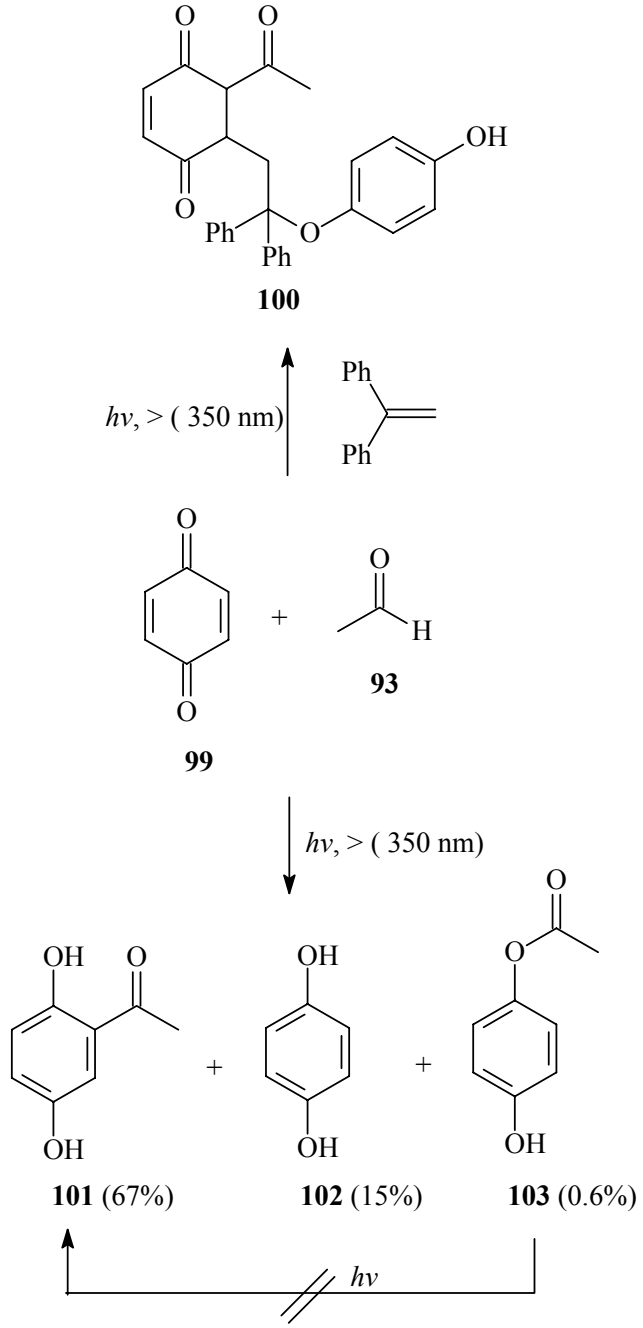
93: R = Me
96: R = Et

97: R = Me (40%)
98: R = Et (17%)

Scheme 34: Photoacylation of cyano-*ortho*-naphthoquinone by SCHÖNBERG.

5.3 Mechanism for the Formation of Monoesters and Acylated Quinones

The mechanistic study carried out by BRUCE et al. is very important for the understanding of the products formed in the course of irradiation. They carefully studied the photoinduced acylation of *para*-benzoquinone **99** with aldehyde **93**.[96] This reaction afforded two major products: mono-acylated product **101** and hydroquinone **102**. The minor product monoester **103** (0.6%) was also additionally formed in the reaction (Scheme 35). In their further experiments, they demonstrated that the acylated hydroquinone was unambiguously not formed from monoester via Photo-Fries rearrangement.[97]



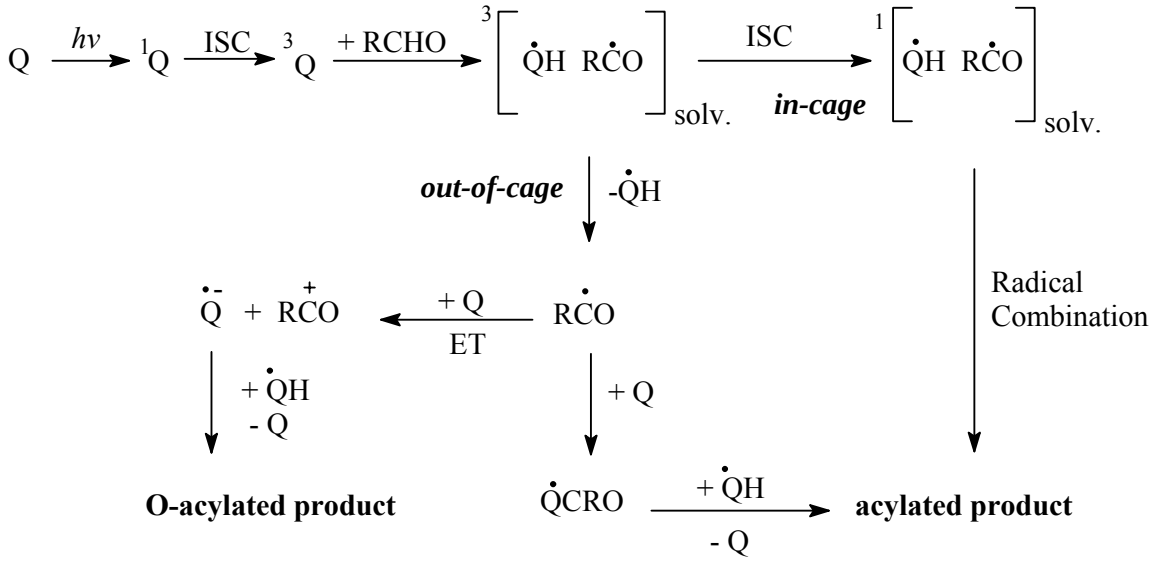
Scheme 35: Mechanistic study by BRUCE and CUTTS.

When parallel reactions of benzoquinone were irradiated at -78°C and 15°C, both results gave the formation of acylated compound **101** in 72 and 76% yield. With this experiment BRUCE concluded that an *in-cage* controlled radical combination might play a minor role. To verify this assumption he carried out irradiation reaction of **99** and **93** in presence of scavengers 1,1-diphenylethylene, the reaction afforded the thermally unstable trapping product **100** in 39% along with small amounts of **101**.

After extensively studying further reactions, BRUCE concluded that the chemoselectivity of the acylation of *para*-quinones is influenced by three main factors.[98]

1. The nucleophilicity of the acyl radical[99] : with decreasing nucleophilicity of the derived acyl radical, the formation of the monoesters becomes favorable.
2. The redox properties of quinone[100] : quinones with high reductive potential gave their esters.
3. When the balance between redox properties of quinone and acyl radical are in favor, the thermal electron transfer (ET) can occur affording corresponding acyl cation and quinone radical anion which leads to the formation of monoester product.

The general mechanism for the formation of monoester as well acylated hydroquinone in case of *para*quinone is schematically represented as follows (Scheme 36): When a solution of quinone is irradiated in presence of aldehyde, the quinone gets excited into singlet which after inter system crossing (ISC), forms its triplet state, subsequent abstraction of hydrogen from the aldehyde leads to the formation of QH radical and acyl radical. At this stage if the radicals are surrounded by solvent molecules (in solvent cage), just the combination of radicals leads to the formation of acylated product. In another case if the radicals are not in close contact (out of solvent cage), the free acyl radical may attack a quinone molecule in its electronic ground state or undergoes electron transfer followed by recombination to the monoester.



Scheme 36: In-cage and *out-of-cage* mechanism for acylated and O-acylated product.

The possibility of nucleophilic addition of acyl radical to the ground quinone yielding acylated quinone also can not be ruled out completely.

6 Results and Discussion

6.1 Background: Photoacylation of Quinones

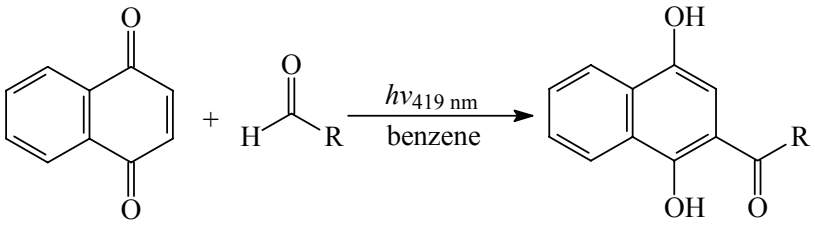
Acylated naphthoquinone derivatives based on 5-hydroxy-1,4-naphthoquinone (Juglone) or Naphthazarine represent an important class of natural products.[25,30,101,102] Due to their high chemical reactivity and polyoxygenated nature, most of the biologically active acylated quinones or hydroquinones are challenging synthetic targets. A versatile pathway for the synthesis of these molecules is the photochemical acylation of quinones with aldehydes. The reaction was also developed as an example of environmentally friendly and benign 'Green Photochemistry'.[29]

This extremely useful photoreaction was discovered by KLINGER in 1886, who exposed solutions of the starting materials to natural sunlight over long periods of time.[93,94] During the last few decades, a number of additional reports appeared in the literature,[92,98,103] but most of the studies focused on unsubstituted 1,2- or 1,4-quinones.[104,105,106,107] In contrast, however, reports based on 2- or 5-substituted 1,4-naphthoquinones remained rare.[92,108,109] In order to fill this gap, we have studied photochemical acylation reactions of 2-methyl-, 2-methoxy- and 5-methoxy-1,4-naphthoquinone with different aliphatic as well as aromatic aldehydes.

In earlier work reported by OELGEMOELLER and MATTAY,[109] they were especially interested in the isolation of the main products, acylated hydroquinones, which often simply precipitated during the reaction and were isolated by filtration.[109] They did not check for any further products which may have remained in the reaction mixture. Therefore, main goal of the present study was the identification and isolation of all the products formed during the course of the photoacylation. For comparison, we furthermore reinvestigated some of our previously reported experiments.[29,108,109] In order to avoid prolonged irradiation times of up to 5 days, which were often required for our early multigram runs, we have used more dilute solutions of the reactants. We have furthermore replaced the high-pressure Hg-lamp (λ_{max} > 200 nm / 300 nm using quartz / Pyrex glass) with RPR 4190 Å lamps (λ_{max} = 419 ± 15 nm) fitted in a Rayonet photochemical chamber reactor. 1,4-Naphthoquinone and 2-methyl-1,4-naphthoquinone were commercially available and were used after recrystallization. 5-Methoxy-1,4-naphthoquinone and 2-methoxy-1,4-naphthoquinone were synthesized from the corresponding hydroxynaphthoquinones Juglone and Lawsone according to the method of GARDEN and THOMSON.[110]

6.2 Photoacylations Involving 1,4-Naphthoquinone

By using the modified procedure described above the 1,4-naphthoquinone **104** was irradiated in the presence of several aliphatic and aromatic aldehydes until GC analysis showed complete conversion of the quinone (Scheme 37). The reaction mixtures obtained were carefully separated using flash chromatography and, whenever necessary, the products were further purified by HPLC. In line with our earlier findings, aliphatic aldehydes only gave the acylated hydroquinones **106a-c** in fair to good yields.



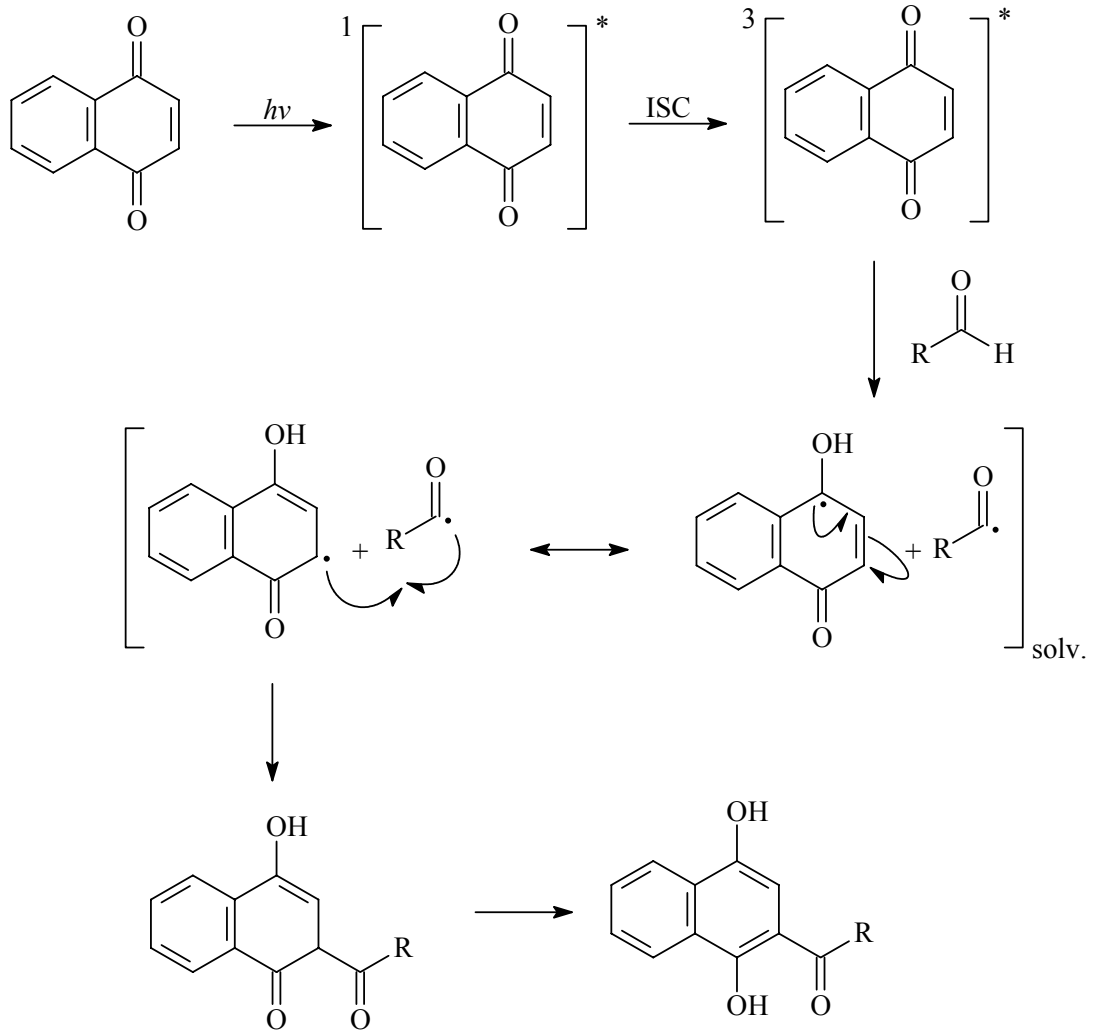
104 **105** **106**

Scheme 37: Photoacylation reaction of 1,4-naphthoquinones with aliphatic aldehydes.

Table 1: Results showing photoacylation reactions of **104a-c** with **105a-c** yielding products **106a-c**.

Entry	R-group	Time (h)	**106** (%)
a	$(CH_2)_2$-CH_3	15	60
b	$(CH_2)_{10}$-CH_3	12	35
c	CH-$(CH_3)_2$	12	21

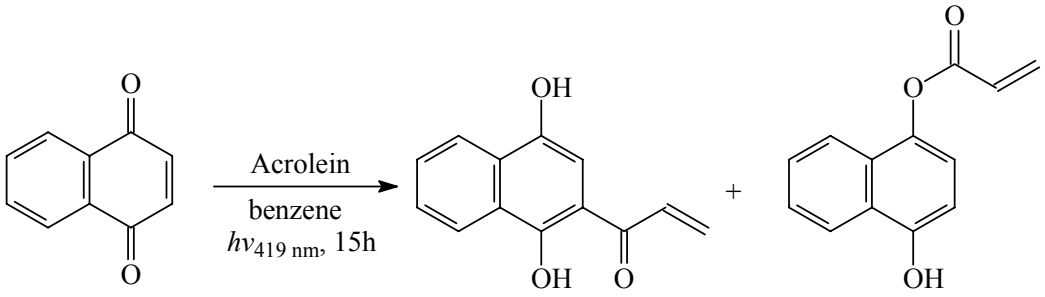
When a solution of **104** and aliphatic aldehyde **105a-c** in benzene was irradiated at $\lambda = 419$ nm, the reaction yielded solely formation of acylated hydroquinone. Any other formation of products like monoester was not observed. In this way reaction of butyraldehyde **105a** with **104** afforded acylated hydroquinone **106a** in 60% yield. Mechanistically the formation of this product can be explained as follows (Scheme 38).



Scheme 38: *In-cage* mechanism for the formation of acylated hydroquinone.

As discussed in the mechanism part, two different mechanisms may be considered for the mono-acylated product formation, *in-cage* mechanism and *out-of-cage* mechanism. Certainly it is difficult to clearly differentiate between the mechanisms involved in the reaction. But we believe that in case of aliphatic aldehydes, as we observed only formation of single acylated product, reaction may have proceeded through *in-cage* way. In addition the possibility of formation of product via *out-of-cage* can not be completely ruled out.

In contrast with aliphatic aldehydes, when acrolein was used as an aldehyde, the reaction proceeded with the formation monoester product **108** along with acylated product **107**.

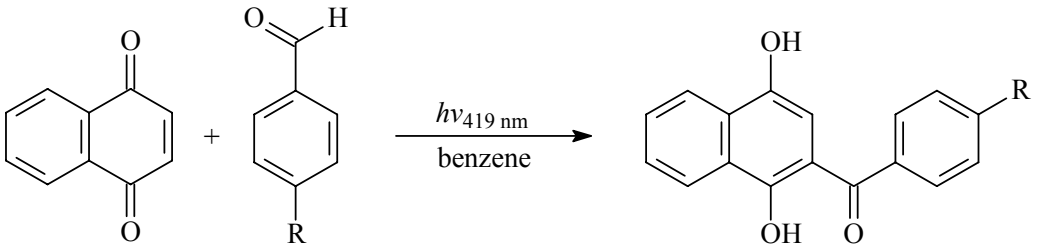


104 **107** (18%) **108** (7%)

Scheme 39: Photoreaction of **104** with acrolein, yielding ester **107** and acylated compound **108**.

Following BRUCE'S suggestions (cf. Scheme 36) most probably in this case, the formed of acyl radical could transfer its electron to the quinone affording acyl cation and quinone radical anion, nucleophilic attack of quinone radical to the acyl cation takes place yielding O-acylated compound (monoester). In this case, *out-of-cage* as well as *in-cage* mechanisms would be simultaneously involved.

In case of aromatic aldehydes such as p-CN- and p-MeO- benzaldehyde **109a** and **109b**, the acylation reaction is proceeding with high selectivity. The reaction afforded solely formation of acylated product **110** (Scheme 40; Table 2).



104 **109** **110**

Scheme 40: Photoacylation of quinone **104** with aromatic aldehydes.

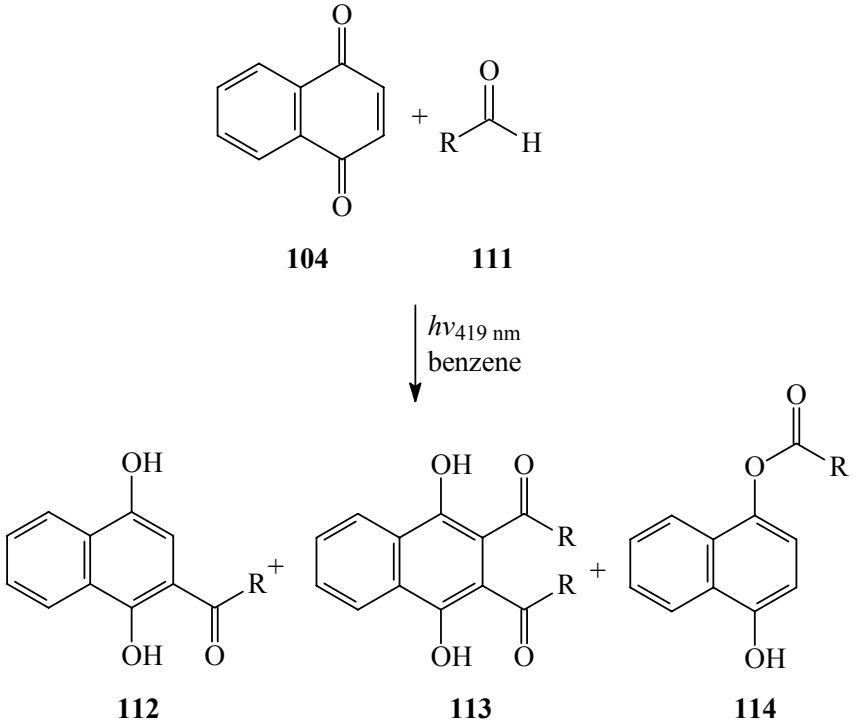
Table 2: Photoreactions with aromatic aldehydes.

Entry	R-group	Time (h)	**110** (%)
a	CN	96	20
b	MeO	63[a]	25

[a] Traces of ester was observed as an impurity in NMR

In case of aromatic aldehydes it was observed that the formation of photoproducts was slightly dependent on the *para*-substituents at the aromatic ring. It was observed that the reaction of *p*-methyl benzaldehyde afforded the formation of ester **114a** as a side product (5%) along with acylated product **112a** in 61% (Scheme 41; Table 3).

In addition, when *p*-chloro-benzaldehyde **111b** was used as reactant, the reaction afforded a new product which is the bis-acylated product **113b** along with formation of mono-acylated **112b** and monoester product **114b**. Surprisingly in this reaction, we observed formation of all theoretically possible products, which indicates that in one reaction medium the respective products can be formed in different pathways.



Scheme 41: Photoacylation of **104** yielding mono-, diacylated and ester products.

Table 3: Isolated yields of the acylated products.

Entry	R-group	Time (h)	**112** (%)	**113** (%)	**114** (%)
a	*p*-Me-C_6H_4	12	61	–	5
b	*p*-Cl-C_6H_4	12	17	11	9
c	Ph	18	34	12	–

In other words, in the same reaction medium different pathways are involved affording products. In this particular reaction *in-cage* and *out-of-cage* reaction pathways are involved. BRUCE and co-workers had already reported formation of diacylated product via thermal oxidation/reduction equilibrium between the monoacylated product and initial quinone, followed by rapid, secondary acylation of the intermediately generated acylated quinone.[98b] MATTAY and co-workers also observed formation of diacylated products and they studied the photoacylation of 1,4-naphthoquinone with benzaldehyde carefully and concluded that bis (acylation)

proceeded (at least partly) by secondary photoacylation of the monoadduct and the corresponding aldehyde. Furthermore, it can be speculated that whether the stability or polarity of the intermediately formed acyl radical might play an additional role in the formation of bisacylated product. [29a]

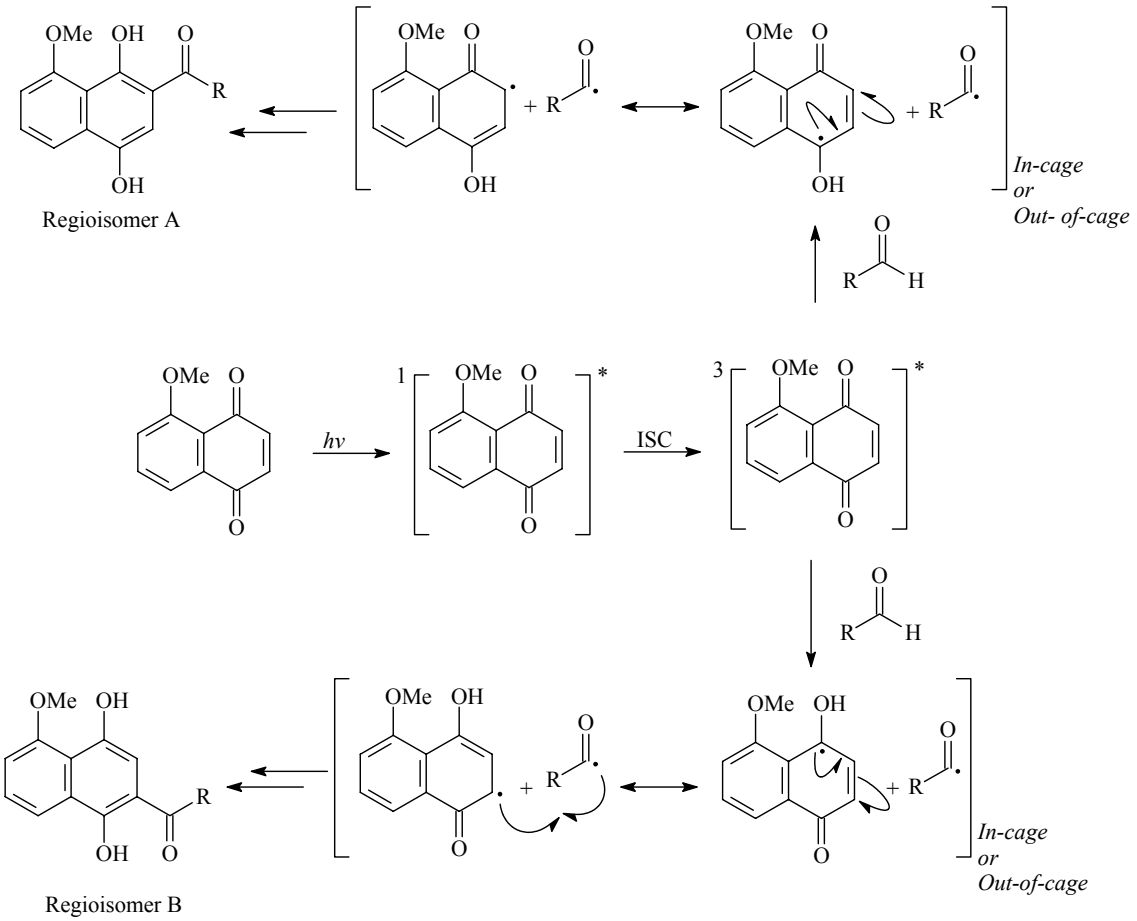
With acrolein and aromatic aldehydes, the formation of the monoacylated hydroquinones **107, 110** and **112** was still the dominant process. In case of acrolein, 4-methyl- and 4-chlorobenzaldehyde, however, the corresponding monoesters **108**, **114a**, **114b** were obtained in 5-9% yield. The bisacylation products **113b** and **113c** were furthermore formed in significant yields of 11-12% during photolysis of **104** with either benzaldehyde or 4-chlorobenzaldehyde, respectively. The isolation of the monoesters was surprising, since 1,4-naphthoquinone was known to undergo *C*-acylation exclusively.[106b] In contrast, 1,4-benzoquinone often yields mixtures of analogue *C*- and *O*-acylation products[105] and this differing behavior was explained on the basis of the nucleophilicity of the acyl radicals and the redox properties of the quinone and the acyl radicals.[99,100] BRUCE and coworkers postulated that the formation of esters (*O*-acylation) proceeds *via* an *inter-molecular* electron transfer (ET) from the acyl radical to the ground state quinone, followed by combination of the resulting ionic species and hydrogen scavenging.[105b] In contrast, TAKUWA assigned the chemoselectivity of the photoacylation of 1,2-naphthoquinones to the nucleophilic character of the acyl radical intermediates, which decreases in the order of $CH_3\dot{C}=O > CH_2=CH\dot{C}=O > Ph\dot{C}=O$.[107f] Our findings are in general agreement with both explanations since we observed *O*-acylation only for the more electrophilic acrolein and aromatic aldehydes. The redox potentials of aromatic acyl radicals furthermore differ by about 500 mV from those of their aliphatic counterparts.[99]

6.3 Photoacylations Involving 5-Methoxy-1,4-Naphthoquinone

We have furthermore studied photoreactions of 5-methoxy-1,4-naphthoquinone (methyl juglone) **115** with different aliphatic and aromatic aldehydes (Scheme 43; Table 4). Main aim of this project was the identification and isolation of possible *O*-acylation products. The formation of esters was indeed observed for *p*-chlorobenzaldehyde. In comparison with the results obtained for 1,4-naphthoquinone **104** itself, aromatic aldehydes bearing an electron withdrawing group at the 4-position obviously ease the *O*-acylation pathway thus supporting BRUCE'S postulated ET mechanism.[105b]

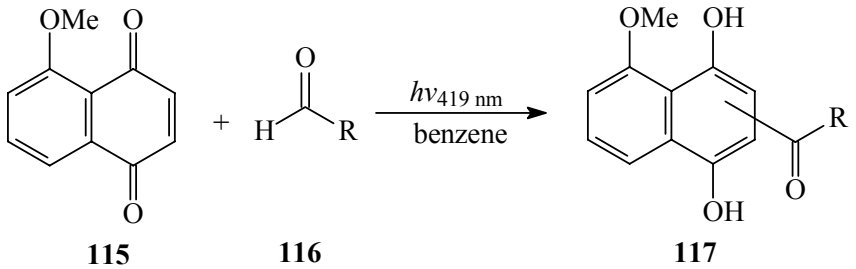
When a solution of methyl juglone was irradiated in presence of isobutyraldehyde, *p*-MeO and *p*-Me substituted benzaldehyde the regioselective mixture of acylated products were formed (Scheme 42). Due to the unsymmetrical quinone molecule two possible regioisomers are

expected to be formed. At this stage it is difficult to speculate the factors affecting the regioselectivity. It can be possible to control the regioselectivity of the photoacylation reaction, by using different additives and / or carrying out the reaction in confined spaces. The formation of two different regioisomers by photoacylation process is as follows.



Scheme 42: Formation of regioisomers via photoacylation.

Surprisingly we did not observe formation of an ester when acrolein was used as aldehdyde (Scheme 43; Table 4). It shows that formation of esters is depending on the nucleophilicity of quinone radical anion and also redox potential of quinone and aldehyde in which the thermal ET can take place. The photoacylation reactions of **115** with aliphatic and aromatic aldehydes **116** are summarized in Scheme 43 and Table 4.



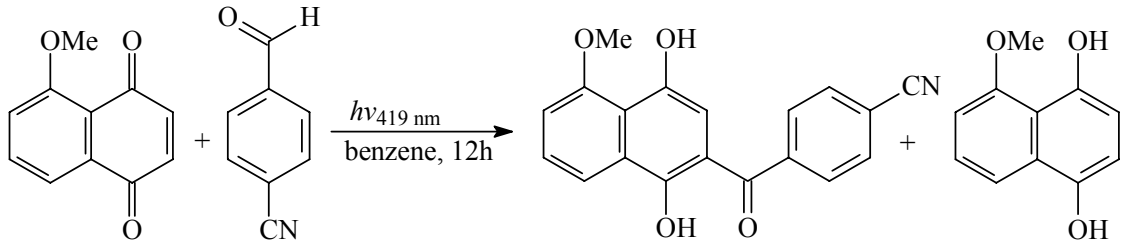
Scheme 43: Photoreaction of methyl juglone with aldehydes **116a-e**.

Table 4: Isolated product yields for photoacylation of methyl juglone with aldehydes.

Entry	R-group	Time (h)[a]	**117** (%)[b, c]
a	$CH(CH_3)_2$	15	37
b	$CH{=}CH_2$	12	15
c	Ph	53	30
d	*p*-$MeOC_6H_4$	18	34
e	*p*-MeC_6H_4	15	66

[a] Until starting material is consumed. [b] Regioselectivity is not determined.[c] Regioisomeric mixture.

When a solution of methyl juglone **115** was irradiated in presence of *p*-CN-benzaldehyde **118**, surprisingly only one regioisomer **119** was isolated in 12% yield along with reduced methyl juglone **120** in 13% (Scheme 44). It was difficult to assign the chemical structure only by using NMR techniques due to fact that only the position of -OMe group was altered in both regioisomers. After careful analysis of 2D NMR techniques the structure of hydroquinone **119** was assigned to 3-benzoylated hydroquinone.



115 **118** **119** (12%) **120** (13%)

Scheme 44: Formation of only one regioisomer **119**.

In addition the structure of **119** was confirmed unambiguously by single crystal X-ray analysis (Figure 15). The phenyl ring of the benzoyl group is non–coplanar with hydroquinone moiety (dihedral angle 52.3°) and the methoxy group is pointing to the opposite side to the hydroxyl group.

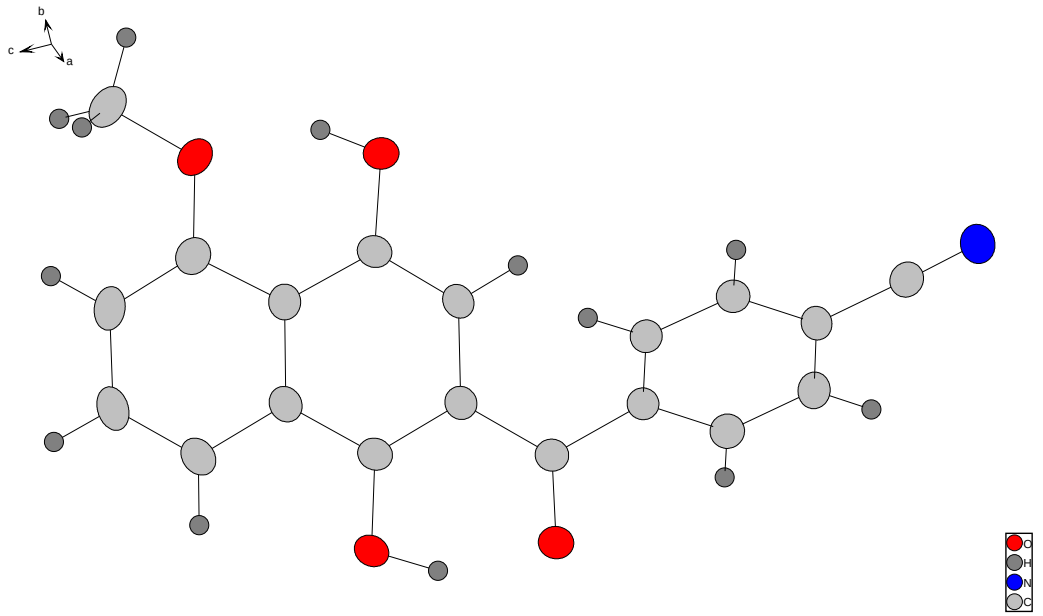


Figure 15: X-ray structure of **119**.

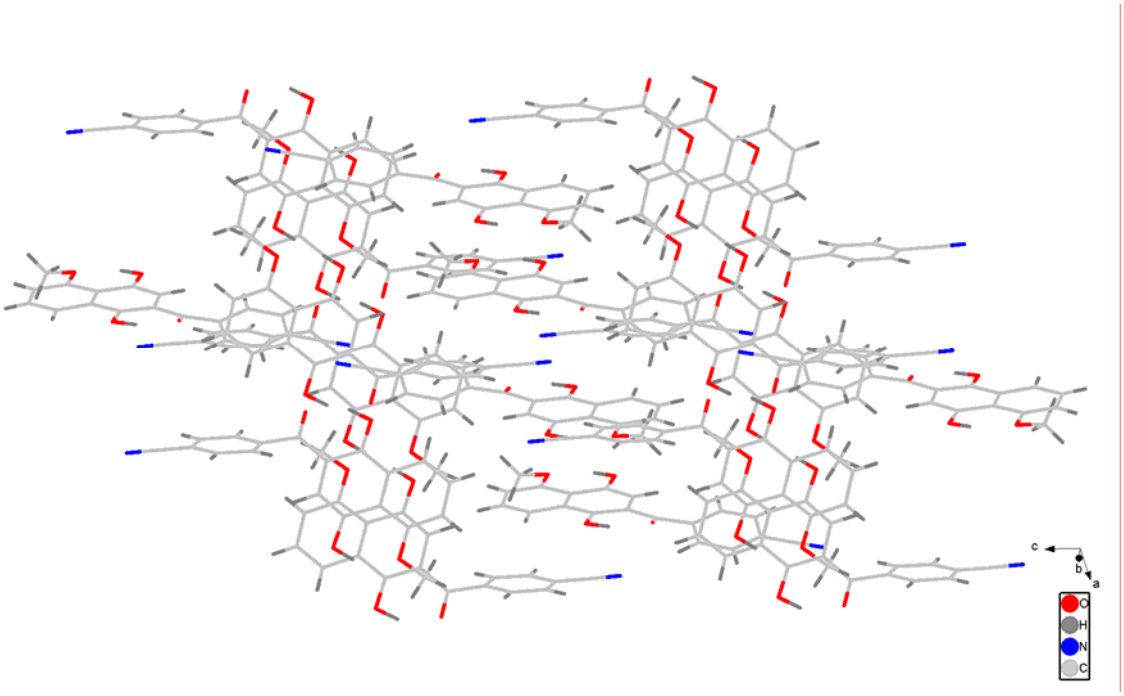
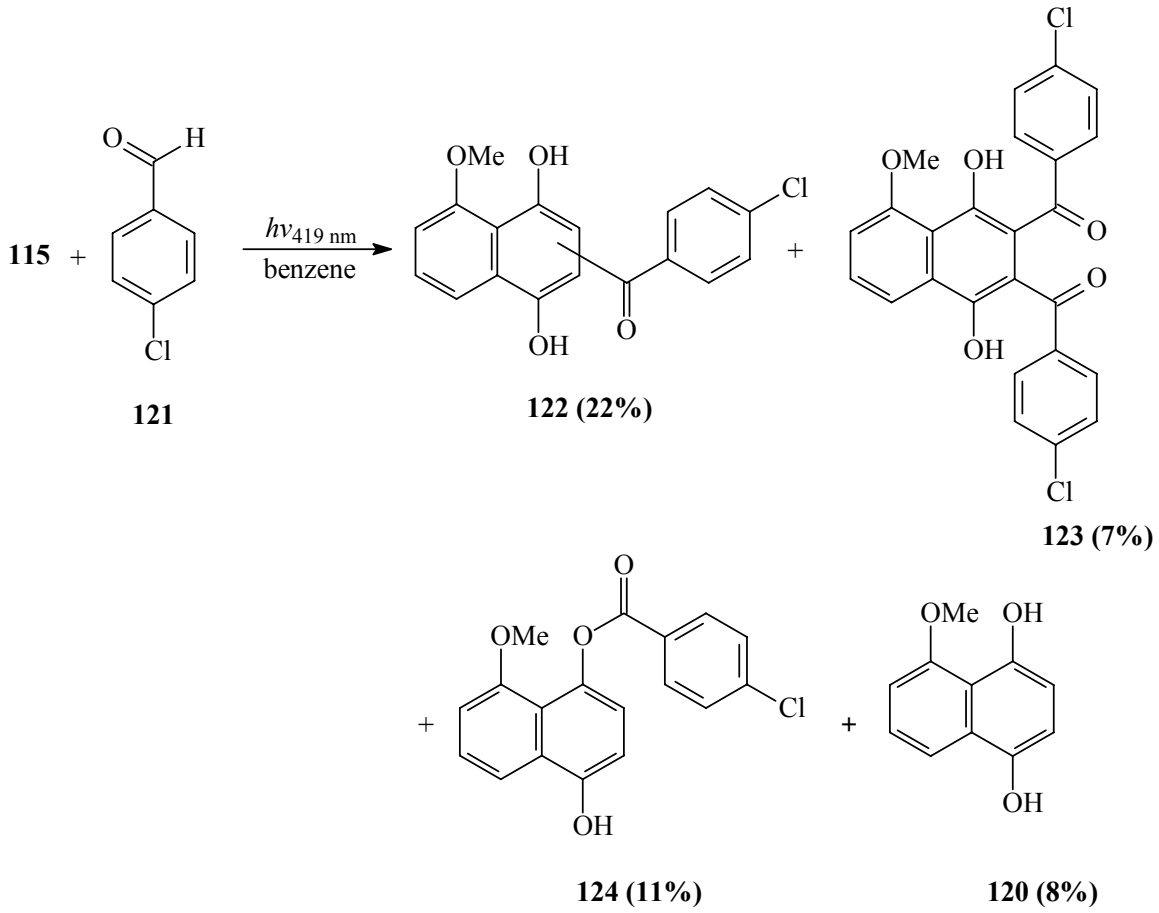


Figure 16: Unit cell of compound **119.**

When a solution of methyl juglone **115** and *p*-chloro-benzaldehyde **121** in benzene was irradiated using λ = 419 nm, the reaction afforded formation of nearly all theoretically possible products such as mono-acylated hydroquinone **122** in 22%, diacylated hydroquinone **123** in 7%, monoester **124** in 11% and reduced methyl juglone **120** in 8% (Scheme 45). The mechanism involved might be rationalized as follows: The monoacylated product is formed via *in-cage* or *out-of-cage*. As we discussed earlier the diacylated product is formed via secondary photoacylation in which first monoacylated product is getting oxidized and methyl juglone is

getting reduced. The formation of monoester proceeds via attack of methyl juglone radical anion to the acyl cation.



Scheme 45: Photoreaction of **115** with *p*-chloro-benzaldehyde.

Surprisingly we observed only formation of only one regioisomer. For the structure determination we used 1D and 2D NMR techniques. The structures of the diacylated product **123** and the ester **124** were confirmed by single crystal X-ray analysis (Figure 17). Unfortunately, the attempts to crystallize monoacylated product **122** failed, and therefore the exact position of the acyl substituent remained unsolved.

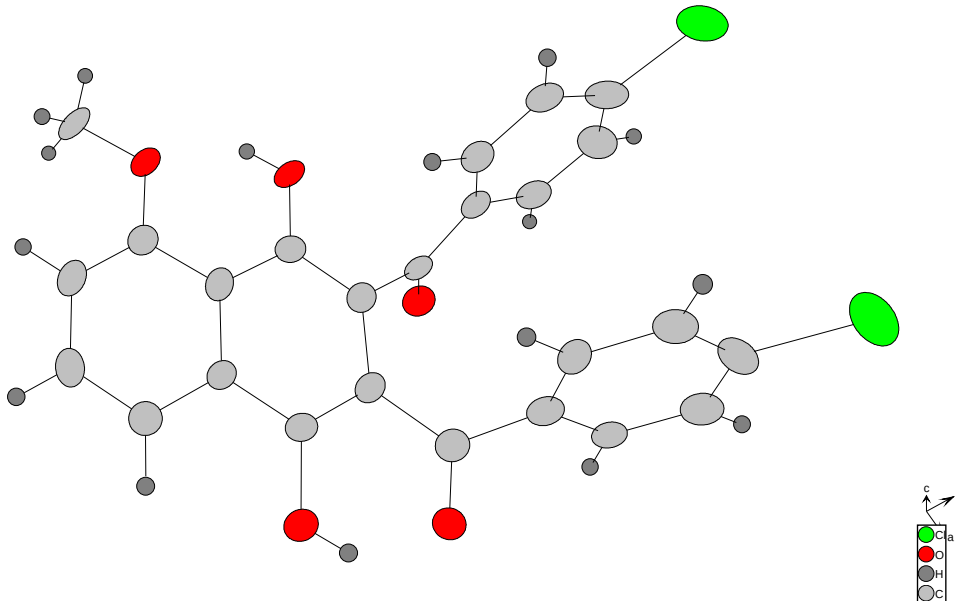


Figure 17: X-ray structure of diacylated compound **123**.

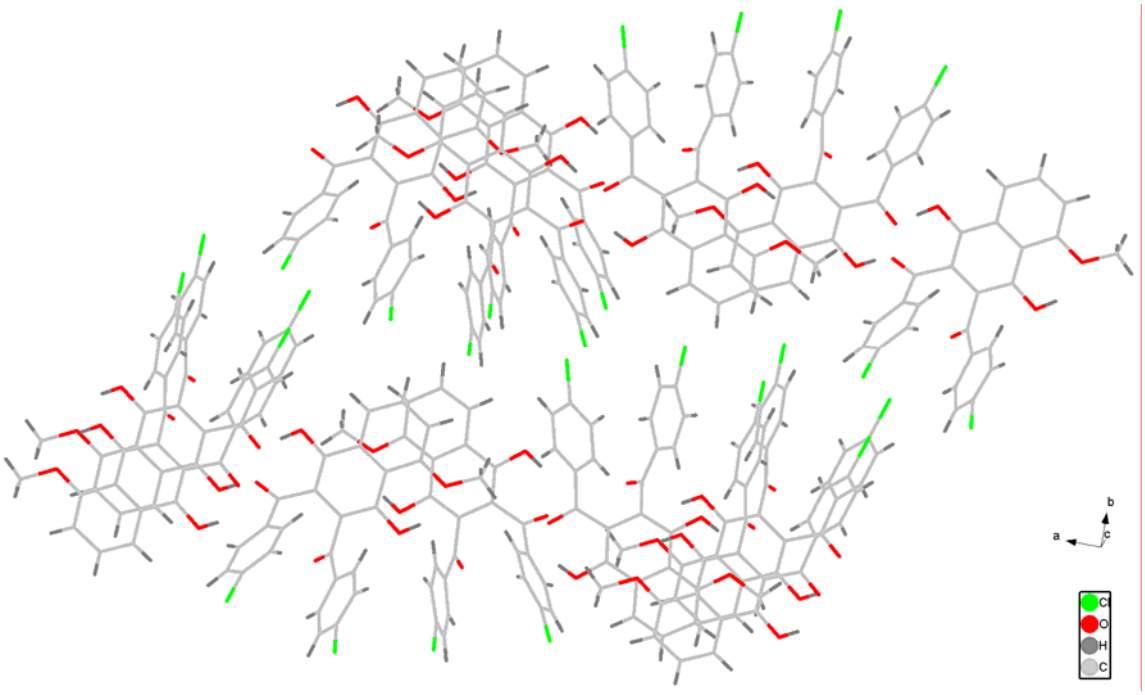


Figure 18: Unit cell of compound **123.**

The ester **124** was allowed to crystallize in solution of 1:3 acetone/n-hexane for one week at +7° C. The X-ray structure shows that benzoate and methoxy groups are on same side. In addition an acetone molecule is located in vicinity to the chloro group of aromatic ring.

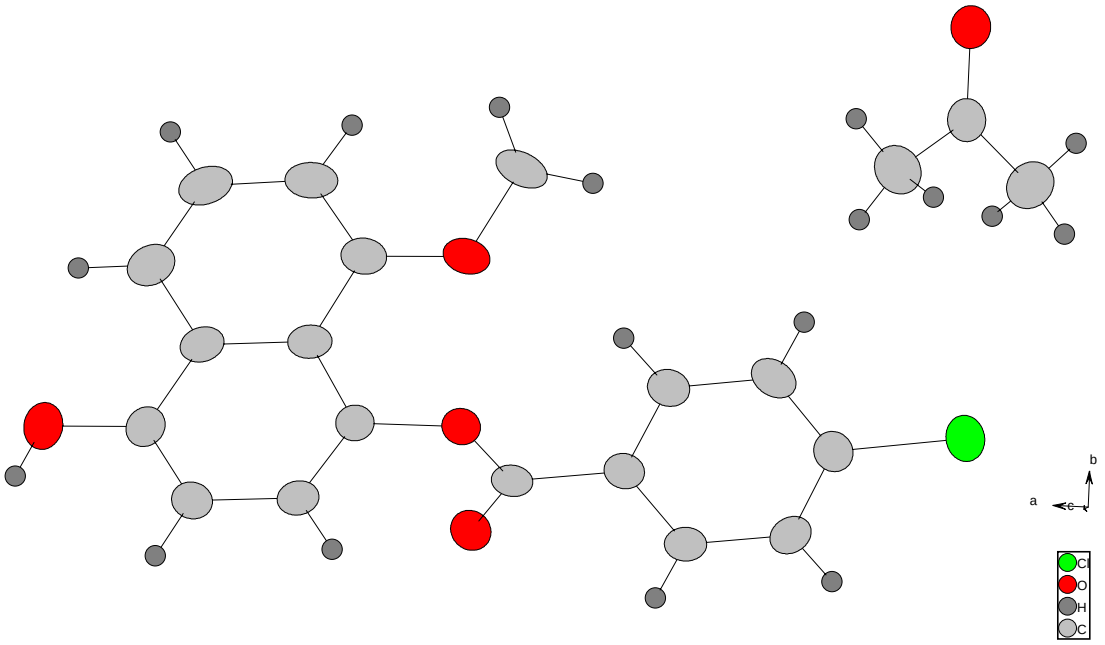


Figure 19: Systematic view of X-ray structure of **124.**

The unit cell of the ester compound **124** shows the arrangement of molecules in crystal lattice. The molecules are arranged in head to head arrangement in accordance with chloro group. The acetone molecules can be seen in the centre of two ester molecules, most probably it is having hydrogen bonding ‘O’ of the methoxy group.

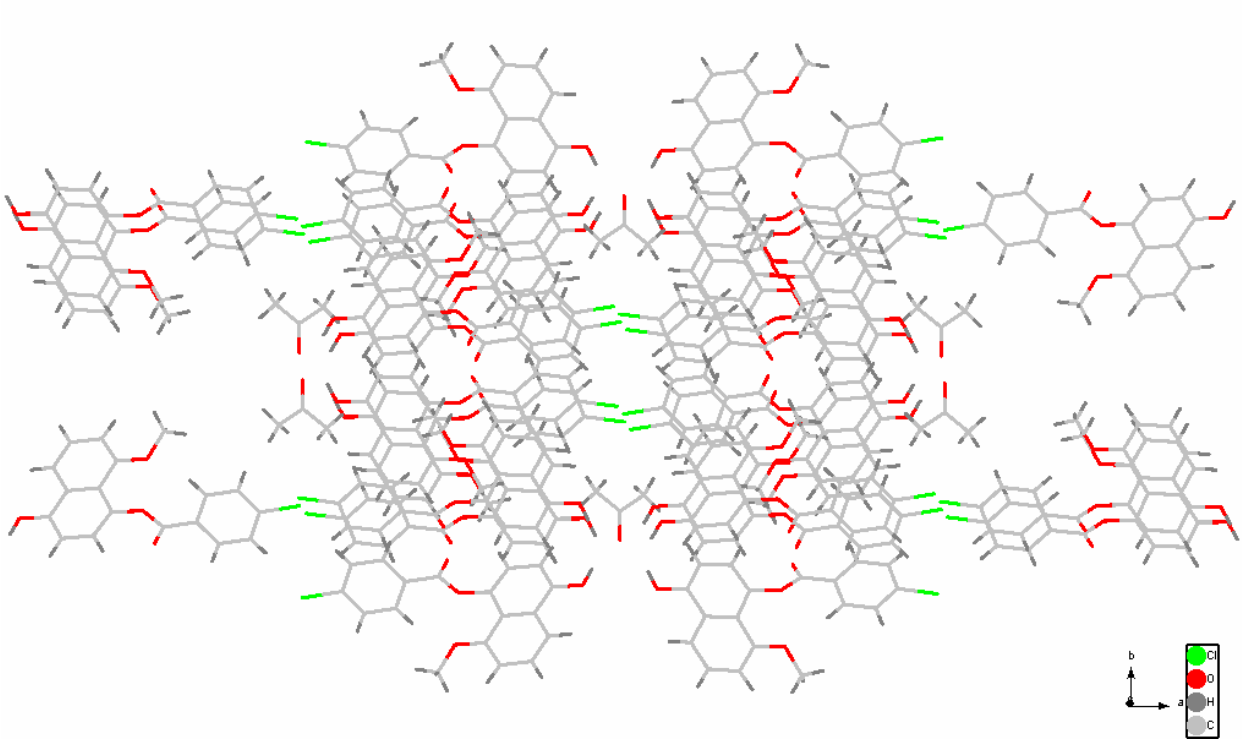
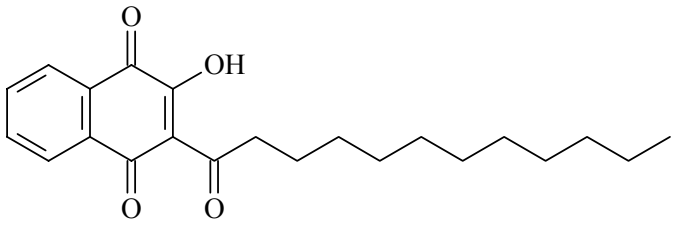


Figure 20: Unit cell packing of compound **124.**

6.4 Photoacylations Involving 2-Methoxy-1,4-Naphthoquinone

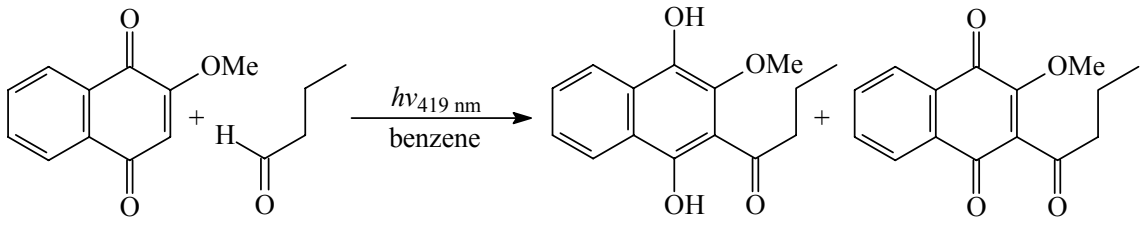
To avoid the formation of bisacylation products, we have selected 2-methoxy-1,4-naphthoquinone **125** as model substrates. This compound additionally provides a convenient access to quinonoid antibiotics based on compound **125**[111] such as 2-dodecanoyl-3-hydroxy-1,4-naphthoquinone[112] (Figure 21) or pesticides such as the important acaricide Acequinocyl (Figure 14),[91] respectively. Best to our knowledge, only one brief example of a photoacylation involving **129** has been reported so far by SCHENCK and KOLTZENBURGH.[113] To fill this gap we studied photoacylation reactions of 2-substituted 1,4-naphthoquinones **125** and **129**.



DHN

Figure 21: Structure of 2-dodecanoyl-3-hydroxy-1,4-naphthoquinone (DHN).

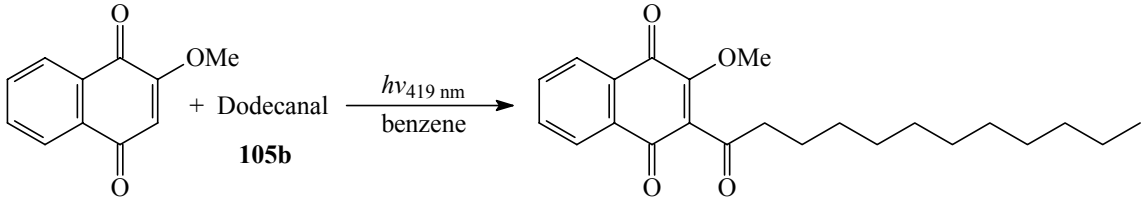
For our first test reaction we selected 2-methoxy-1,4-naphthoquinone **125**. We irradiated a solution of **125** and butyraldehyde **105a** in benzene. The reaction was continued until starting material was totally consumed. After purification of the crude product via column chromatography we isolated two products in approximately 2:1 ratio. The NMR analysis of the pure products revealed the isolated products are the monoacylated hydroquinone **126** in 24% yield and its oxidized derivative monoacylated quinone **127** in 11% yield (Scheme 46). We were astonished to see the acylated quinone as product pointing to the main questions: is this product being formed in the reaction or it is just oxidized from the primary photoproduct hydroquinone? If is formed via oxidation of primary photoproduct then second question is: where it got oxidized? The possibility of oxidation of primary photoproduct in the reaction medium is completely ruled out, otherwise we would have observed formation of diacylated tetra-keto product. We postulated that the oxidation of acylated hydroquinone is taking place during the work up. To confirm it, we checked the stability of acylated hydroquinone **126** in solid state as well as in solution. These experiments show that in solution the hydroquinone **126** remains stable but get easily oxidized to the corresponding quinone **127** in solid state.



125 **105a** **126** (24%) **127** (11%)

Scheme 46: Photoacylation of 2-methoxy-1,4-naphthoquinone with butyraldehyde.

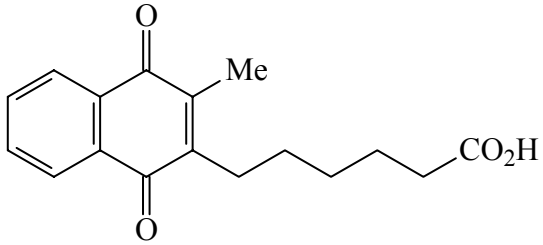
When dodecanal **105b** was used as an aldehyde, only one product was isolated in 23% yield. The NMR analysis shows that this compound is an acylated quinonone **128** (Scheme 47). Surprisingly in this reaction only the acylated quinone is formed instead of a mixture of the primary acylated hydroquinone and its quinone derivative. As discussed previously the quinone is formed by oxidation during the work up procedure. Obviously electron donating groups at the 2-position of 1,4-naphthoquinone facilitates the aerial oxidation process.[114]



125 **128** (23%)

Scheme 47: Synthesis of quinone **128** via photoacylation.

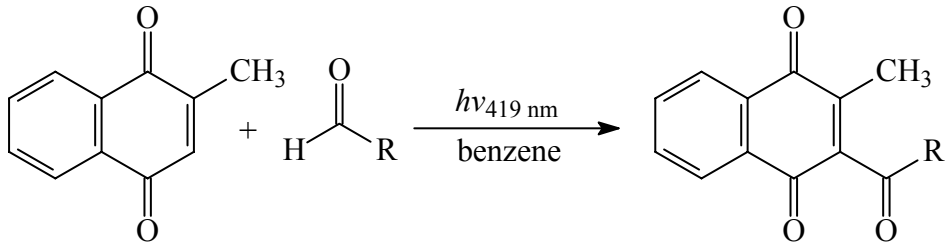
To confirm the additional effect of electron donating group at the 2-position of naphthoquinone, we tested some other reactions using 2-methyl-1,4-naphthoquinone **129**. It will be really interesting to check some other reactions using different aliphatic as well as aromatic aldehydes. Additionally, the acylation of **129** will provide a convenient access for the synthesis of intermediates for biologically active compounds such as potent antimalarials '**M5**' (Figure 22).[115]



M5

Figure 22: Structure of potent antimalarial **M5**.[a]

Irradiation of 2-methyl-1,4-naphthoquinone **129** with various aliphatic as well as aromatic aldehydes **130** gave the corresponding acylated quinones **131** in moderate yields of 23-49% (Scheme 48; Table 5). The 'hydroquinones' formed initially are obviously oxidized during work-up. In contrast to the parent 1,4-naphthoquinone **104**, no ester formation was observed. Thus, this method represents a highly selective pathway to 2-acyl-3-methyl-1,4-naphthoquinones. As an exception small amounts of ester were detected as an impurity in the NMR when the reaction was carried out using *p*-MeO-benzaldehyde **130d**.



129 **130** **131**

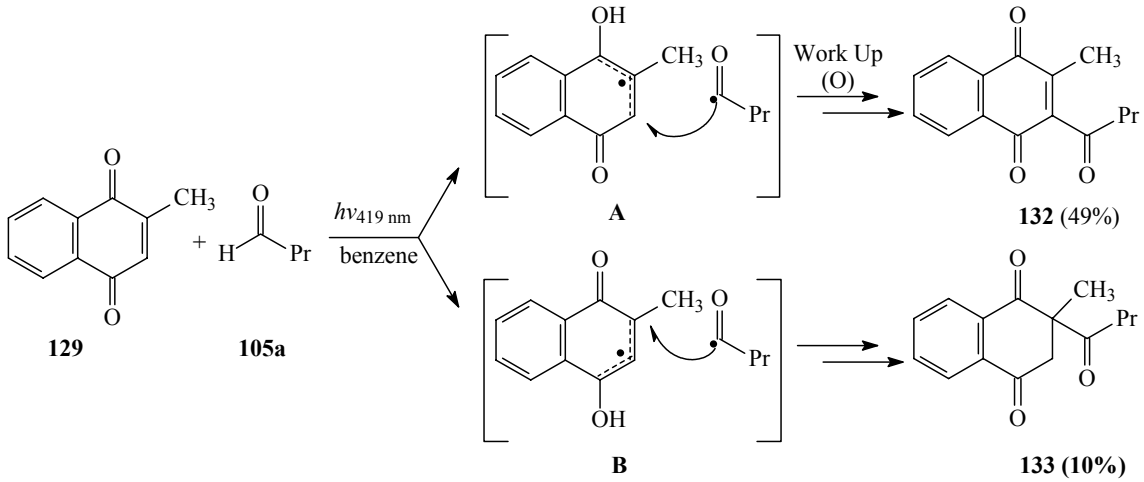
Scheme 48: Photoacylation of 2-methyl-1,4-naphthoquinone.

Table 5: Isolated yields for the photoreaction of 2-methyl-1,4-naphthoquinone

Entry	R-group	Time (h)[a]	**131** (%)
a	$CH(CH_3)_2$	18	36
b	$C_{11}H_{23}$	12	39
c	Ph	18	23
d	*p*-$MeOC_6H_4$	12	42
e	*p*-MeC_6H_4	12	35

[a] Until starting material is consumed.

An exceptional case was the reaction of **129** with butyraldehyde leading to the unusual tri-keto compound **133** in 10% yield in addition to 49% of the acylated quinone **132** (Scheme 49).



Scheme 49: Photoacylation of 2-methyl-1,4-naphthoquinone **129** with butyraldehyde **105a**.

The formation of **133** may be best explained by the following *in-cage* scenario: hydrogen transfer from the aldehyde to the excited quinone **129*** leads to the corresponding semiquinone radical pair A and B. Radical combination with the acyl radical followed by tautomerization and oxidation (in case of **132**) affords the observed products **132** and **133**.[116] An alternative *out-of-cage* attack of the acyl radical to a ground state quinone **129** would lead preferentially to the acylated quinone **132** *via* the most stable radical intermediate. The structure of **133** was unambiguously confirmed by 2D-NMR techniques such as ^{1}H–^{1}H COSY, ^{1}H–^{13}C HMBC and HSQC analysis respectively. In Figure 23, we can clearly differentiate between the signals of aliphatic CH_2 and signal for CH_2 cyclic. Two separate doublets were observed for cyclic CH_2 and respective correlation was seen in HMBC spectra.

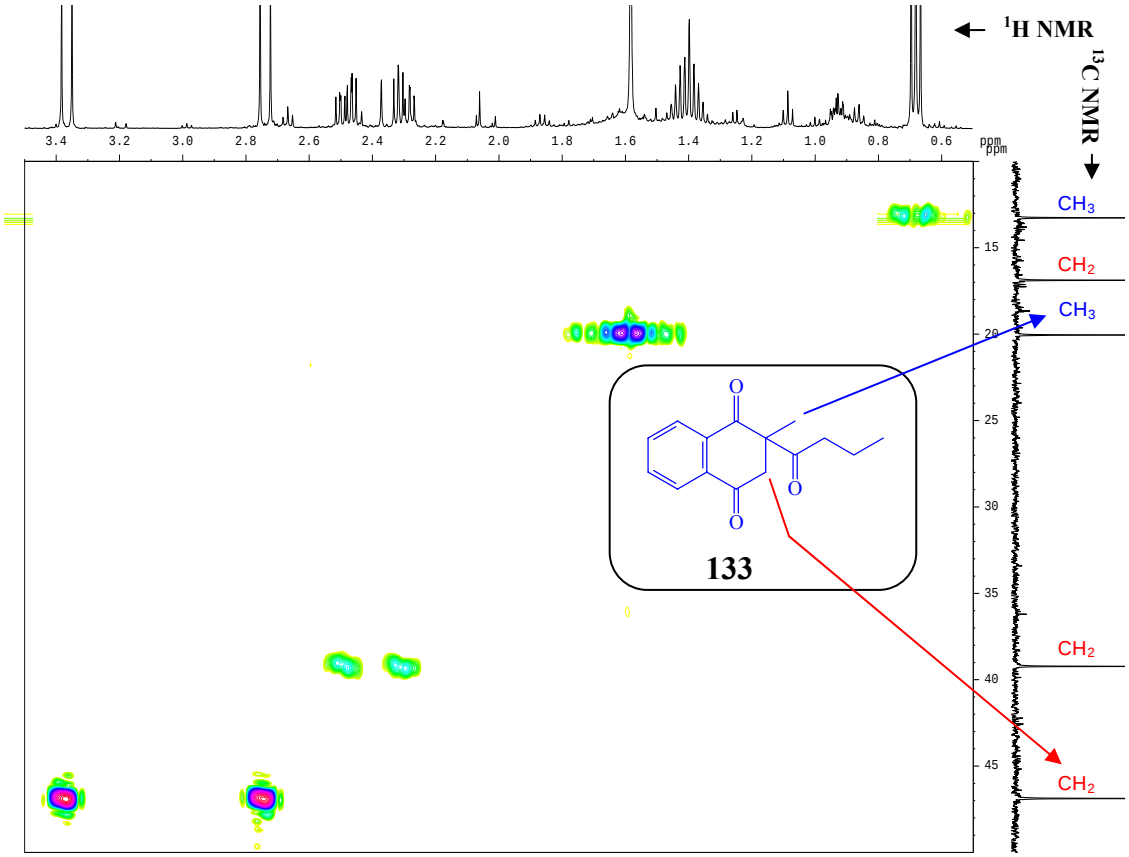


Figure 23: HMBC spectra of tri-keto compound **133**.

Steric hindrance by the methyl group in position 2 of quinone **129** would furthermore prevent such an addition. Thus, the isolation of **133** suggests that an *in-cage* mechanism is indeed operating, at least in part. Further mechanistic investigations will be carried out using either thermally or chemically generated acyl radicals.

6.5 Conclusion

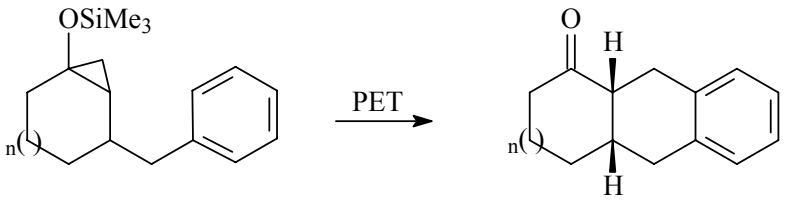
In conclusion, the photochemical acylation of 1,4-naphthoquinones proceeds with the formation of acylated hydroquinones or quinones as major products in moderate to good yields. In contradiction to the literature, monoesters are additionally isolated in some cases and their formation seems to depend on the nucleophilicity and the redox behavior of the acyl radical intermediates and the redox properties of the quinone. The photoacylation protocol could be used for the straight-forward preparation of synthetically important precursors to the quinonoid pharmaceuticals and agrochemicals.

7 Summary

The central theme of the research presented in this thesis is dealing with the use of photochemical irradiation methods for the synthesis of cyclic organic compounds as well as synthesis of acylated quinones.

Photochemical methods are environmentally benign methods, by making use of these methods we can carry out synthesis of organic compounds in an environmentally friendly manner.

The photochemical irradiation of cylcopropyl silyl ether offered an anthracenoid compound **81** in one step in a stereoselective manner.



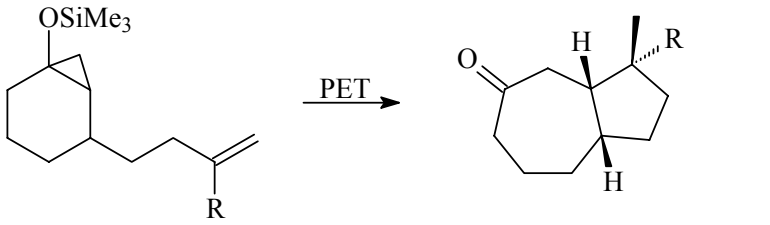
60: *n* = 1
61: *n* = 2

81: *n* = 1 (20%)
82: *n* = 2 (11%)

cf. **Scheme 27:** Photoinduced electron transfer reaction of **60** and **61.**

The formation of *cis* products is the specialty of the photoinduced reaction. In most of the cases it is observed that the cyclization proceeds always with the formation of *cis* cyclized products. The reaction also proceeds smoothly when seven membered cyclopropyl ether **61** was used. In above cases, the ring opening of cyclopropane takes place affording an *exo*cyclic radical which cyclizes with aryl moiety affording fully cyclized thermally favorable product.

In case of an alkene tether, the reaction followed through the formation of an *endo*cyclic radical, which undergoes 1,5-*exo*-trig mode of cyclization, yielding *cis* fused bicyclic [5.3.0] compounds **86** and **87**.



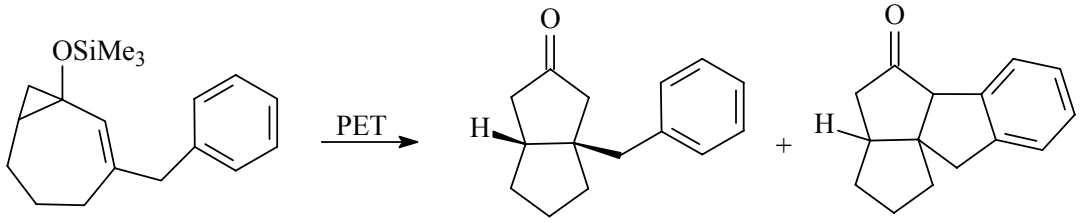
66: R = H
80: R = Me

86: R = H (10%)
87: R = Me (14%)

cf. **Scheme 30:** Synthesis of *cis* fused bicyclic ketones **86** and **87.**

In order to check the possibility of an *endo* cyclization we substituted the side chain with a methyl group, which should increase the steric hindrance of the corresponding 6-*exo* attack. However, even in this case (**80**) we did not observe formation of an *endo*-cyclized product.

The PET reaction of cyclopropane **74** yields entirely bicyclooctanone derivative **88** along with minor traces of compound **89**. The *endo*cyclic cyclopropane ring opening followed by 1,5-*exo* cyclization forms the bicyclic compound with α-keto radical, instead of getting cyclized to **89** the radical intermediate after proton transfer forms the compound **88** in 31%.



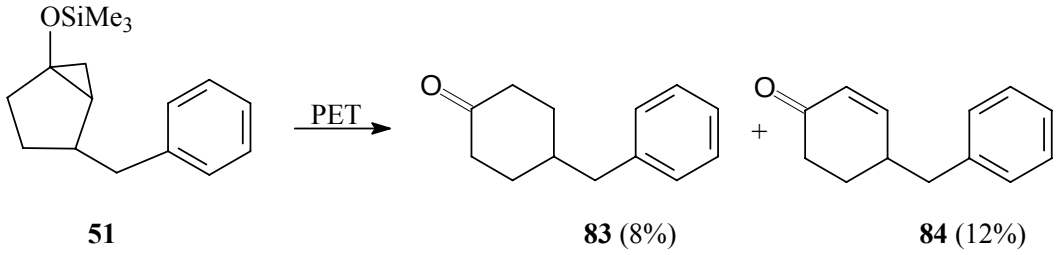
74

88 (31%)

89 (Traces)

cf. **Scheme 31:** Cylization of cyclopropane **74**.

Compound **89** can be detected only as an impurity in the NMR. About stereochemistry: as observed previously only *cis* ring fused product was isolated.
In contrast, the PET reaction of substituted cyclopentane derivative afforded solely non-cyclized product. The reaction proceeds with the *endo*cyclic cyclopropane ring opening yielding β-keto radical, which after H-transfer forms mono-substituted cyclohexanone **83**.



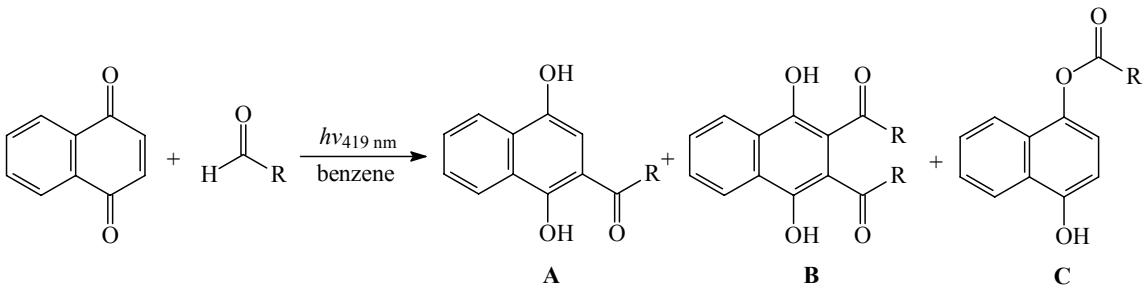
51 **83** (8%) **84** (12%)

cf. **Scheme 28:** PET reaction of cyclopropane **51**.

In addition to this the radical intermediate after loss of hydrogen afforded substituted the cyclohexenone **84**. Eventually the formation of a fully cyclized more strained compound is thermodynamically unfavored.

In conclusion, various new ring-fused cyclopropyl silyl ethers with benzylic, olefinic or acetylenic side chains have been synthesized in good yields. We have also been able to demonstrate that the PET induced ring opening of cyclopropyl silyl ethers is quite suitable for the production of polycylic compounds with high stereoselectivity. This method can be used as an alternative for the synthesis of fused cyclic compounds. In some cases ring enlarged products were isolated indicating that this method is suitable for the production of 4-substituted cyclohexanone and cyclohexenone derivatives.

Photoacylation of quinones with aldehydes leads to a new alternative method for 'FRIEDEL-CRAFTS' acylation reaction. In order to generalize this reaction variety of aldehyde quinone pairs were studied in great detail. Aromatic as well as aliphatic aldehydes were used for such reactions. The reaction of 1,4-naphthoquinone with aliphatic aldehydes afforded entirely mono-acylated products. In case of acrolein we observed formation of an ester product. This was first surprise to us. In literature it is known that the 1,4-naphoquinones never afford esters.



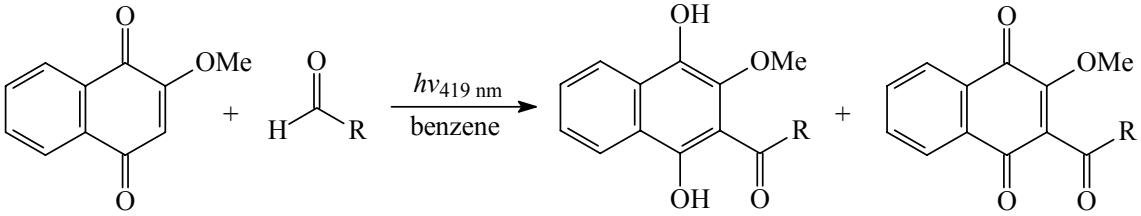
Scheme 50: Summary of photoacylation reaction of 1,4-naphthoquinone.

Table 6: Summary of photoacylation reaction of 1,4-naphthoquinone.

Aldehydes (R)	**A (**Yield)	**B (**Yield)	**C (**Yield)
$CH(CH_3)_2$	21%	–	–
$(CH_2)_{10}$-CH_3	35%	–	–
$(CH_2)_2$-CH_3	60%	–	–
$CH{=}CH_2$	18%	–	7%
Ph	34%	12%	–
p-MeO-C_6H_4	25%	–	–
p-CN-C_6H_4	20%	–	–
p-Cl-C_6H_4	17%	11%	9%
p-Me-C_6H_4	61%	–	5%

In case of aromatic aldehydes the formation of acylated products were observed as well. In case of *p*-Cl-benzaldehyde, a diacylated product was isolated along with ester formation. With of *p*-Me-benzaldehyde the formation of a mono-acylated product is still the dominant process over ester formation.

In case of 2-methoxy-1,4-naphthoquinone, formation of acylated quinone was observed in addition to the acylated hydroquionone. This method provides an easy access to the synthesis of acylated quinonoid compounds.



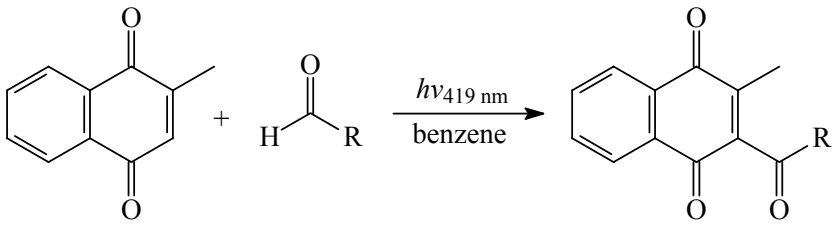
D **E**

Scheme 51: Summary of photoacylation reaction of 2-methoxy-1,4-naphthoquinone

Table 7: Summary of photoacylation reaction of 2-methoxy-1,4-naphthoquinone.

Aldehyde (R)	**D (**Yield)	**E (**Yield)
$(CH_2)_2$-CH_3	24%	11%
$(CH_2)_{10}$-CH_3	–	23%

In the above case we neither isolated a diacylated product nor an ester. Probably, the presence of the methoxy group prevents the bisacylation reaction and, in addition, it facilitates the formation of the acylated quinone.



F

Scheme 52: Summary of photoacylation reaction of 2-methyl-1,4-naphthoquinone.

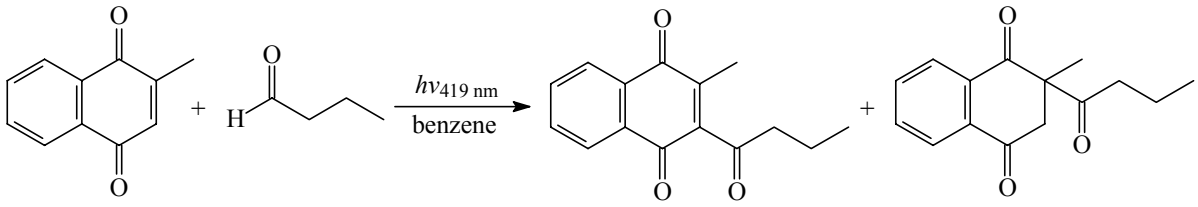
Table 8: Summary of photoacylation reaction of 2-methyl-1,4-naphthoquinone.

Aldehyde (R)	**F** (Yield)
Ph	23%
p-Me-C_6H_4	35%
p-MeO-C_6H_4	42%
$CH(CH_3)_2$	36%

In case of 2-methyl-1,4-naphthoquinone, it was expected that there will be no formation of diacylated products and esters. In addition the reaction was expected to yield only acylated quinones instead of acylated hydroquinones, due to the presence of methyl group. The reaction went well as expected and only acylated quinone products were isolated.

The reaction entirely afforded the formation of acylated quinone as a sole product when aliphatic and aromatic aldehydes were used. This method gives an easy access to the synthesis of acylated quinones.

Surprisingly, the reaction with butyraldehyde afforded the unusual tri-keto compound **133** along with the acylated quinone. This gives some information about mechanisms involved in the reaction.



129 **105a** **132** (49%) **133** (10%)

cf. **Scheme 49:** Photoacylation of 2-methyl-1,4-naphthoquinone **129** with butyraldehyde **105a.**

In summary, photochemical reactions can be a good alternative for the synthesis of acylated quinononones and acylated hydroquinones. Certainly, by using this method the synthesis of key intermediates for total synthesis of biologically active quinonoid compounds can be carried out.

8 Experimental

8.1 General Methods and Instruments

- **Thin Layer Chromatography (TLC)**

  Silica gel coated on aluminum plate with florescent indicator form Merck silica gel size 60, F_{254}, layer thickness 0.25 mm and Macherey & Nagel SIL G/UV254.

  Aluminiumoxide coated on aluminum plate (0.20 mm with fluorescent indicator) from Macherey & Nagel ALOX N/UV254.

  Detection: UV-Lampe, Desaga 360/254 nm, Heidelberg; Iodide chamber and ethanolic solution of molybdatephosphoric acid (20%) and after heating with hot gun.

- **Column Chromatography**

  Silica gel MN-60 (Mesh size 40-63 µm and 63-200 µm) from Macherey & Nagel, Nagel & Co., Düren, Germany.

  Aluminiumoxide (AlxOy)-neutral (Mesh Size 50-200 µm, Activity 1) from Macherey & Nagel, Nagel & Co., Düren, Germany.

- **Analytical Gas Chromatography (GC)**

  Shimadzu GC-17A: Application software Version 3.2 with software Class VP 4.2, Shimadzu AOC-20i Auto injector and Shimadzu GC-2010 with application software GC-solution 2.10.00 (2001), Shimadzu AOC-20i Auto injector.

  Capillary Column:

  GC-17A: Hewlett-Packard 2 (Length: 25 m, Inner diameter 0.2 mm, Thickness 0.33 µm)

  GC-2010: Hewlett-Packard 5 MS (Length: 25 m, Inner diameter 0.2 mm and thickness 0.33 µm).

  Flow gas: Nitrogen with pressure 1.0 bar.

  Constant Temperatures: Detector Temperature: 300°C and Injector Temperature: 280°C.

  Variable Column Temperature Program Methods

  Method 1: Temperature program: from 50°C with 5°C/min to 80°C and then 10°C/min to 280°C and wait at 280°C for 4 minutes. Total rum time 30 minutes.

  Method 2: Temperature program: At 75°C wait for 5 minutes, then with 10°C/min to 280°C and wait for 4.5 minutes at 280°C. Total run time 30 minutes.

Method 3: Temperature program: Start at 150°C with 10°C/min to 280°C and wait at 280°C for 17 minutes. Total run time 30 minutes.

- **Preparative Gas Chromatography (prep GC)**

  Instrument: Hewlett-Packard Gas chromatography 5890 Series-II with automatic fraction collector and automatic sample injector Hewlett- Packard 7673.

  Capillary Column: Hewlett-Packard HP5 (Length: 30 m, Inner diameter: 0.53 mm, thickness: 50 µm). Flow gas: hydrogen with pressure 0.4-0.5 bar.

  Coolant for fraction collector: Liquid nitrogen.

- **Analytical GC/MS**

  Instrument: Shimadzu GC-17A/MS QP 5050A with software Class 5000 V 2.0 and LabSolutions GCMSsolution V 1.02 from Shimadzu. The measurement with chemical ionization (CI-mode) was carried out by using Isobutane as a CI-Gas, and for electronic ionization (EI-mode) was carried out using Ionic charge of 70 eV.

  Capilary column: Hewlett-Packard 5MS (Length: 25 m, Inner diameter: 0.2 mm, Thickness: 0.33µm). Flow gas: Helium with pressure: 0.95 bar.

  Temperature programme:

  Constant Temperatures: Detector Temperature: 300°C and Injector Temperature: 280°C.

  Variable Column Temperature Program Methods:

  Method 1: Temperature from 50°C with 5°C/min to 80°C, then with 10 °C/min to 280°C and wait for 4 minutes at 280°C. Total rum time: 30 minutes.

  Method 2: Temperature program: At 75°C wait for 5 minutes, then 10°C/min to 280°C and wait for 4.5 minutes at 280°C. Total run time 30 minutes.

  Method 3: Temperature program: From 150°C with 10°C/min to 280 °C and then wait at 280°C for 17 minutes. Total run time: 30 minutes.

- **HPLC**

  Pump: Merk Hitachi, L-6250

  Detector: Merk Hitachi, UV-Vis, LaChrom L-7420

  Normal Column: Merck LiChrospher Si 60 with precolumn Merck LiChrospher Si 60.

- **IR Spectroscopy**

  Perkin-Elmer Gitter-IR-Spekrometer 841 oder FT-IR ATI Matson Genesis Series.

Sample measurements: The liquid samples are used as it is for the IR measurements and a thin film was obtained by dropping liquid sample on a NaCl plate. The IR spectra for solid sample were reported using its KBr window. The IR absorption bands were measured in wave numbers ($\tilde{\nu}$) in cm^{-1}.

- **Nuclear Magnetic Resonance Spectroscopy (NMR)**

^{1}H NMR

Instruments: Bruker AM 250 (250.133 MHz), DRX 500 (500.132 MHz), with internal standard: $CDCl_3$ (7.24 ppm), DMSO-d_6 (2.49 ppm), CD_2Cl_2 (5.32ppm) and acetone-d_6 (2.05 ppm).

Measurement temperature: 300 K.

The chemical shifts (δ) are given in ppm and are uncorrected. The coupling constants (*J*) are given in Hz. The multiplicity of signals are given in are as follows: s = Singlet, d = doublet, t = triplet, q = quartet and m = multiplate.

^{13}C NMR

Instrument: Bruker AM 250 (62.896 MHz) and DRX 500 (125.772 MHz), internal standard: $CDCl_3$ (77.0 ppm), DMSO-d_6 (39.50 ppm), CD_2Cl_2 (53.5 ppm) and acetone-d_6 (29.8 ppm)

Measurement temperature: 300 K.

Sample preparation for 1D and 2D NMR spectroscopy

Organic compounds (7-21 mg) were dissolved in deutorated solvents in a NMR tube and submitted for analysis. For 2D NMR analysis such as ^{1}H-^{1}H COSY, HMBC, HSQC, NOE, NOESY, the NMR tube containing dissolved product was flushed with argon gas for removal of oxygen and immediately sample was submitted for analysis. For evaluation of 1D NMR spectrum, Bruker 1D NMR software program was used. 2D NMR spectra were further evaluated using software program Bruker X-Win NMR version 2.6 and 3.1 and print out were made using Bruker X-Win NMR plot 2.6.

- **Kugelrohr Distillation**

Kugelrohr distillation was carried out using instruments Büchi GKR 5. The rotating round flasks were cooled using dry ice.

- **Solvents**

  Acetone, Benzene, Chloroform, Dichloromethane, Ethanol, Methanol and *i-Propanol* were purchased as an Analytical Grade reagent form Baker chemicals and was used for reactions without further purification.

  Acetonitrile (Analytical Grade) was stored over the 4 Å molecular sieves under argon atmosphere and used for the photochemical reactions.

  Ethyl acetate, cyclohexane, diethyl ether n-pentane, dichloromethane were received as technical grade and used for the extraction of reaction mixture after distillation.

  Ethyl acetate used for column chromatography was filtered through column of aluminum oxide after distillation.

  Dry *THF* prepared by first distillation over KOH, and then again distilled over $LiAlH_4$ under argon atmosphere using triphenyl methane as an indicator.

  Dry *diethyl ether* was prepared by first distilling over KOH and then again distilled over $LiAlH_4$, under argon atmosphere.

- **Mass Spectrometry**

  Instrument: Micromass VG Autospec X oder Bruker FT-ICR APEX III (7.0 T).

  Mass spectroscopic measurements were carried out using EI and CI standard sources. In EI mode using 8 kV and CI mode 6kV ions were accelerated. The software program used was OPUS software Version 3.6 from Micromass (1998).

- **Photochemical Reaction**

  Photoreactor: Rayonet Chamber RPR-100, by Southern New England Ultraviolet Company, Brandford, USA with in build "Merry-Go-Round". In this photoreactor, we can irradiate all the reaction tubes at the same conditions. This reactor is ventilated in such a way that the internal temperature of the reactions remains constant between 35-37°C.

  Light Sources: 16 tube lamps RPR-4190Å (E_{max} ~ 419 nm, Pyrex irradiation tubes used).

- **Melting point**

  Instruement: Büchi B-540 (< 100 °C ± 0.3°C, < 250°C ± 0.5°C, < 400°C ± 0.8°C)

  All given melting points are uncorrected.

- **Ultrasonic bath**

  Ultraschallbad (ultrasonic bath) Bandelin Sonorex Super RK 255 H, from. Bandelin, Berlin, Germany.

- **UV/VIS-Spectroscopy**

  Instrument: Perkin-Elmer UV/VIS-Spektrometer Lambda 40 with software program WinLab Version 2.70.01 and WinLab Version 1.1 (1997) from. Perkin-Elmer Co.

8.2 General Procedures

8.2.1 General Procedure A: Synthesis of silyl enol ethers with CuI mediated 1,4-addition on enones.

To a stirred suspension of magnesium metal (Mg), catalytic amount of iodine crystals and dry THF/diethyl ether (1:1 by volume) were added corresponding bromide or chloride (1.2 eq.) in such that the solution was slightly boiling, after addition the solution was heated under reflux for 1h. This GR was added to the previously cooled suspension of CuI (1eq.) in THF. The reaction temperature was maintained 0 °C for 10 min and then cooled to –78 °C by using dry ice-acetone bath. The solution of corresponding enones and TMS-Cl in dry THF were added dropwise and stirred for 3 h. Triethyl amine was added and reaction mixture was brought to room temperature (RT), reaction was monitored by GC-MS. Solvents were removed under high vacuum; *n*-pentane was added and the mixture was quickly filtered. The solvent was evaporated under reduced pressure and the crude product was used immediately for the next reaction.

8.2.2 General procedure B: Synthesis of silyl enol ether by LDA

The solution of diisopropyl amine in dry THF was placed in an oven dried apparatus under argon atmosphere and cooled to 0 °C. *n*-BuLi (1.6 M in hexane) were added dropwise, the stirring was continued for next 25 min and the reaction mixture was cooled to –78 °C using dry ice-acetone bath, followed by addition of respective enones in dry THF. The solution was stirred for 1 h and neat TMS-Cl was added. The solution was brought to RT and stirred for an additional hour at this temperature (monitored by GC-MS). After removal of solvent under reduced pressure, the residue was diluted with *n*-pentane. The precipitate of lithium chloride was removed by filtration; the solvent was removed under vacuum. The product was used immediately for next reaction.

8.2.3 General procedure C: Cyclopropanation of silyl enol ethers

The respective silyl enol ether was placed in dry apparatus under argon atmosphere, dry dichloromethane was added. The solution was cooled to 0° C using ice bath, diethyl zinc (1.0 M in hexane) was added. After stirring for 10 min, the solution of diiodomethane in dry THF was added dropwise, the reaction mixture was warmed to RT and stirred for 2–24 h. The conversion was monitored by Gas Chromatography (GC), after complete consumption of starting material;

the solution was carefully washed with saturated aqueous ice-cold solution of ammonium chloride until complete dissolution of zinc salt. The aqueous phase was separated and extracted two times with diethyl ether; collective organic layers were washed with water and dried over sodium sulphate. The solvent was evaporated and the residue was purified with kugelrohr distillation.

8.2.4 General procedure D: PET oxidative reaction

The solution of cyclopropyl silyl ether and PET sensitizer DCA in dry acetonitrile was placed into a dry Pyrex tubes (diameter 12 mm, length 20 cm, capacity 12 mL). Flushed with argon for 25 min and irradiated for 12–24 h using 419 nm lamps. After complete consumption of starting material (monitored by GC and GC-MS), solvent removed under vacuum and the residue was purified by silica gel column chromatography (EtOAc/Cyclohexane).

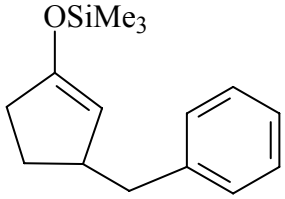
8.2.5 General Procedure E: Synthesis of 3-substituted enones by reaction of vinylogous ester with GR

The GR was prepared analogously to the general procedure A, under argon atmosphere, the vinylogous ester in dry THF was added dropwise to the solution of GR at 0 °C. After addition, the reaction mixture was brought to RT and stirred for additional hour. Water was added and reaction mixture was acidified with dilute HCl, solution was stirred for next 1 h. The ether phase was separated and aqueous phase was extracted with ether. The collective ether phases were washed with aq. $NaHCO_{3,}$, brine and dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/cyclohexane).

8.3 Synthesis of Silyl Enol Ethers

8.3.1 Synthesis of 3-benzyl-1-trimethylsilyloxylcyclopent-1-ene (56)[d]

Molecular Formula: $C_{15}H_{22}OSi$
Molecular Weight: 246.42
Exact Mass: 246.1439

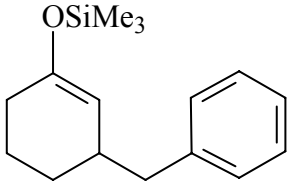


Following general procedure A, Cyclopentenone **53** (820 mg, 10 mmol) was treated with GR prepared from benzyl chloride (2.9 mL, 25 mmol) and Mg turnings (610 mg, 25 mmol) in presence of CuI (1.90 g, 10 mmol) and TMS-Cl (1.5 mL, 12 mmol), gave silyl enol ether **56** (1.254 g, 70%).

GC-MS (EI, 70 eV): m/z (%) = 246 (1), 155 (100), 139 (4.5), 115 (1), 91 (6) 75 (10).

8.3.2 Synthesis of 3-benzyl-1-trimethylsilyloxylcyclohex-1-ene (57)

Molecular Formula: $C_{16}H_{24}OSi$
Molecular Weight: 260.45
Exact Mass: 260.1596

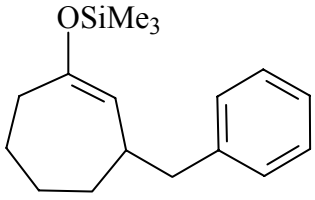


Following General procedure A, Cyclohexenone **54** (1.705 g, 17.77 mmol) was treated with GR prepared from benzyl chloride (5.1 mL, 44.7 mmol) and Mg turnings (911 mg, 37.3 mmol) in presence of CuI (3.376 g, 17.7 mmol) and TMS-Cl (2.2 mL, 17.7 mmol), gave **57** (3.755 g, 77%).

GC-MS (EI, 70 eV): m/z (%) = 260 (1), 245 (6), 169 (100), 153 (4), 139 (1), 128 (2), 115 (4), 91 (31), 75 (32), 65 (14).

8.3.3 Synthesis of 3-benzyl-1-trimethylsilyloxylcyclohept-1-ene (58)

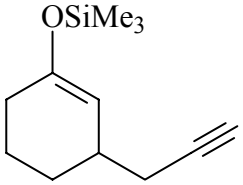
Molecular Formula: $C_{17}H_{26}OSi$
Molecular Weight: 274.48
Exact Mass: 274.1752



Following General procedure A, Cycloheptenone **55** (550 mg, 5 mmol) was treated with GR prepared form benzyl chloride (1.4 mL, 12.5 mmol) and Mg turnings (305 mg, 12.5 mmol) in presence of CuI (950 mg, 5 mmol) and TMS-Cl (0.8 mL, 6 mmol), gave **58** (150 mg, 70%).

GC-MS (EI, 70 eV): m/z (%) = 274 (1), 184 (100), 167 (2), 141 (1), 115 (1.4), 103 (1), 91 (9), 73 (56).

8.3.4 Synthesis of 3-propargyl-1-trimethylsililoxylcyclohex-1-ene (63)

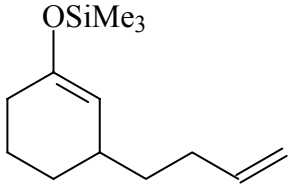


Molecular Formula: $C_{12}H_{20}OSi$
Molecular Weight: 208.38
Exact Mass: 208.1283

To a stirred solution of **54** (145 mg, 1.5 mmol) in dry THF (3 mL) were added successfully dimethyl sulfide (0.1 mL, 1.95 mmol) and TMSOTf (366 mg, 1.65 mmol) at –78 °C under a argon atmosphere. After 10 min, organoindium reagent generated in situ from indium metal (344 mg, 1.65 mmol) and propargyl bromide (0.55 mL, 4.7 mmol) in THF at room temp was added and mixture was stirred at –78 °C for 30 min. The reaction mixture was quenched with saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with ether (3 × 25 mL) and combined organic layers were washed with water, brine and dried with sodium sulphate, filtered and concentrated under reduced pressure, gave **63** (204 mg, 65%).

GC-MS (EI, 70 eV)): m/z (%) = 208 (M^+, 1), 168 (41), 150 (2), 110 (1), 96 (1), 78 (3), 72 (100), 61 (3), 44 (22).

8.3.5 Synthesis of 3-(but-3-enyl)-1-trimethylsilyloxylcyclohex-1-ene (65)[b]

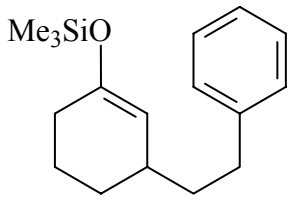


Molecular Formula: $C_{13}H_{24}OSi$
Molecular Weight: 224.42
Exact Mass: 224.1596

Following general procedure A, **54** (960 mg, 10 mmol) was treated with GR prepared from 1-bromo-3-butene (2.970 g, 22 mmol) and Mg turnings (536 mg, 22 mmol) in presence of CuI (1.90 g, 10 mmol) and TMS-Cl (2.8 mL, 22 mmol), gave silyl enol ether **65** (1.20 g, 54%).

GC-MS (EI, 70 eV): m/z (%) = 224 (M^+, 2), 170 (26), 152 (12), 136 (2), 114 (4), 100 (19).

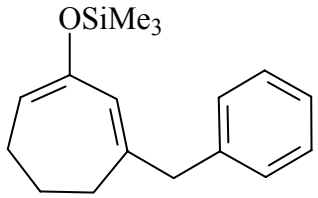
8.3.6 Synthesis of 3-(2-phenylethyl)-1-trimethylsilyloxylcyclohex-1-ene (69)



Molecular Formula: $C_{17}H_{26}OSi$
Molecular Weight: 274.48
Exact Mass: 274.1752

Solution of 2-phenyl-1-iodo ethane **68** (1.919 g, 8.27 mmol) was placed in a dry apparatus equipped with argon balloon, magnetic needle and septum 15 mL dry
n- pentane/diethyl ether (3:2 by volume) was added. The solution was cooled to –78 °C by using dry ice-acetone bath, the stirrer was started and solution of *t*-BuLi (1.160 g, 18.2 mmol) in *n*-pentane was then added dropwise via argon flushed syringe. Stirring was then continued at –78 °C for additional 5 min, the cooling bath was then removed and mixture was allowed to warm and stand at RT for 1h to consume the unreacted *t*-BuLi. The mixture was then added dropwise to a solution of CuI (826 mg, 4.35 mmol) in dry diethyl ether at 0 °C, stirring was continued for 10 min and then solution was cooled to
– 78 °C. The solution of cyclohexenone **54** (391 mg, 4.35 mmol) and TMS-Cl (0.8 mL, 6.525 mmol) were added via syringe. Reaction was monitored by GC and workedup as reported in *general procedure A*, gave silyl enol ether **69** (692 mg, 62%).
GC-MS (EI, 70 eV): m/z (%) = 274 (M^+, 1), 183 (100), 156 (2), 144 (5), 129 (6), 117 (2), 105 (3), 91 (13), 85 (2), 73 (59).

8.3.7 Synthesis of 6-benzyl-1-trimethylsilyloxyl-1,6-cycloheptadiene (73)

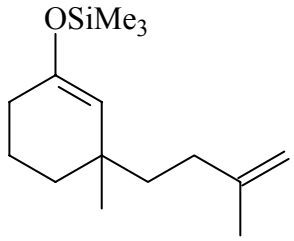


Molecular Formula: $C_{17}H_{24}OSi$
Molecular Weight: 272.46
Exact Mass: 272.1596

Following general procedure B, Enone **72** (70 mg, 0.35mmol) was treated with LDA prepared from diisopropyl amine and (42 mg, 0.42 mmol) and *n*-Butyllithium (0.3 mL, 0.38 mmol) in presence of TMS-Cl (0.06 mL, 0.52 mmol). Gave enol ether **73** (85 mg, 90%).

GC-MS (EI, 70 eV): m/z (%) = 272 (M^+, 52), 257 (17), 181 (9), 165 (13), 153 (9), 141 (3), 128 (3), 115 (4), 91 (35), 73 (100).

8.3.8 Synthesis of 3-methyl-3-(3-methylbut-3-enyl)-1-trimethylsilyloxylcyclohex-1-ene (76)

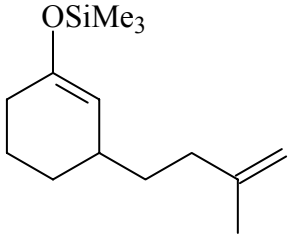


Molecular Formula: $C_{15}H_{28}OSi$
Molecular Weight: 252.47
Exact Mass: 252.1909

CuI (695 mg, 3.698 mmol) was taken in a dry 25 mL round bottom flask; 10 mL of dry diethyl ether was added and solution was cooled to 0 °C using ice bath and MeLi (168 mg, 7.681 mol) was added. The stirring was continued for additional 10 min and then solution was cooled to –78 °C using dry ice acetone bath. The solution of **54** (500 mg, 3.048 mmol) and TMS-Cl (0.6 mL, 6.096 mmol) in 5 mL dry diethyl ether was added via syringe. The reaction was monitored by GC and reaction mixture was worked up using general procedure A, gave silyl enol ether **76** (570 mg, 75%).

GC-MS (EI, 70 eV): m/z (%) = 252 (M^+, 1), 237 (4), 183 (100), 170 (6), 162 (2), 118 (2), 105 (3), 91 (5), 73 (80).

8.3.9 Synthesis of 3-(3-methylbut-3-enyl)-1-trimethylsilyloxylcyclohex-1-ene (79)



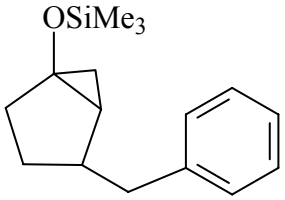
Molecular Formula: $C_{14}H_{26}OSi$
Molecular Weight: 238.45
Exact Mass: 238.1752

Following general procedure A: **54** was treated with GR prepared form 4-bromo-2-methyl-1-butene (5.02 g, 33.7 mmol) and Mg turnings (720 mg, 30 mmol) in presence of CuI (2.850 g, 15 mmol) and TMS-Cl (2.3 mL, 18 mmol), gave enol ether **79** (2.80 g, 83%).

GC-MS (EI, 70 eV): m/z (%) = 238 (1), 182 (52), 170 (8), 147 (8), 105 (4), 73 (100), 52 (2)

8.4 Synthesis of Cyclopropyl Silyl Ethers

8.4.1 Synthesis of 4-benzyl-1-trimethylsilyloxylbicyclo[3.1.0]hexane (59)[d]

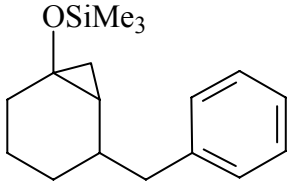


Molecular Formula: $C_{16}H_{24}OSi$
Molecular Weight: 260.45
Exact Mass: 260.159644

Following gerneral procedure C; To a stirred solution of silyl enol ether **56** (2.429 g, 9.87 mmol) in 10 mL dichloromethane, was added diethyl zinc (30.2 mL, 23.6 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (3.277 g, 12.2 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to RT and stirred for 12 h. Reaction was monitored by GC and usual workup gave **59** (1.90 g, 74%) as colorless oil.

GC-MS (EI, 70 eV)): m/z (%) = 260 (M^+, 2), 245 (4), 231 (6), 169 (98), 142 (10), 127 (11), 103 (91), 79 (17), 73 (100).

8.4.2 Synthesis of 4-benzyl-1-trimethylsilyloxylbicyclo[4.1.0]heptane (60)



Molecular Formula: $C_{17}H_{26}OSi$
Molecular Weight: 274.48
Exact Mass: 274.1752

Following general procedure C, To a stirred solution of silyl enol ether **57** (1.49 g, 5.38 mmol) in 5 mL dichloromethane, was added diethyl zinc (14.4 mL, 11.3 mmol). Solution was cooled to 0° C using ice bath and neat CH_2I_2 (2.821 g, 10.56 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to RT and stirred for 12 h and usual workup gave **60** (980 mg, 66%) as colorless oil.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

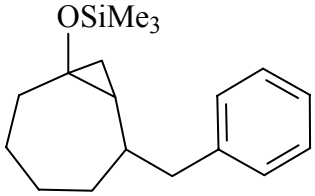
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.15 (9H, s), 0.30 (1H, dd, *J* = 5.6, 5.6 Hz), 0.83 – 0.89 (1H, m), 0.90 – 0.99 (3H, m), 1.55 – 1.64 (1H, m), 1.65 – 1.75 (2H, m), 1.84 (1H, ddd, *J* = 5.0, 13.8, 5.6 Hz), 2.18 (1H, dd, *J* = 3.7, 13.2 Hz), 2.70 (1H, dd, *J* = 7.8, 8.0 Hz), 2.81 (1H, dd, *J* = 7.5, 7.5 Hz), 7.19 (3H, dd, *J* = 7.5, 7.5 Hz), 7.27 (2H, dd, *J* = 8.1, 6.9 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.40 (CH_3), 19.00 (CH_2), 21.00 (CH_2), 24.29 (CH), 26.88 (CH_2), 31.98 (CH_2), 39.64 (CH), 44.35 (CH_2), 57.41 (C_q), 125.72 (CH), 128.14 (C_q), 128.96 (CH), 140.00 (CH) ppm.

GC-MS (EI, 70 eV): m/z (%) = 274 (M^+, 1), 259 (3), 246 (5), 245 (2), 231 (9), 185 (10), 184 (60), 183 (100), 169 (11), 156 (15), 155 (26), 142 (13), 130 (17), 129 (9), 93 (13), 91 (25).

IR (neat): $\tilde{\nu}$ = 2928, 2862, 1704, 1453 cm^{-1}.

8.4.3 Synthesis of 4-benzyl-1-trimethylsilyloxylbicyclo[5.1.0]octane (61)



Molecular Formula: $C_{18}H_{28}OSi$
Molecular Weight: 288.51
Exact Mass: 288.1909

Following general procedure C, To a stirred solution of silyl enol ether **58** (1.37 g, 5 mmol) in 5 mL dichloromethane, was added diethyl zinc (14.4 mL, 11.3 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (1.53 g, 5.629 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to RT and stirred for 12 h, usual workup gave **61** (1.0 g, 70%) as a colorless oil.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.05 (9H, s), 0.25 (1H, m), 0.50 – 0.70 (1H, m), 0.94 (2H, dd, *J* = 4.3, 2.5 Hz), 1.03 (2H, dd, *J* = 10.6, 10.6 Hz), 1.49 – 1.60 (2H, m), 1.63 – 1.77 (1H, m), 1.88 (1H, d, *J* = 13.8 Hz), 2.10 – 2.25 (2H, dm, *J* = 14.4 Hz), 2.40 (1H, dd, *J* = 8.1, 8.1 Hz), 2.56 (1H, dd, *J* = 6.9, 6.9 Hz), 7.15 (3H, ddd, *J* = 1.2, 4.3, 6.2 Hz), 7.25 (2H, dd, *J* = 7.5, 8.7 Hz) ppm.

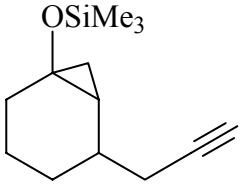
^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.20 (CH_3), 24.97 (CH), 28.09 (CH_2), 31.78 (CH_2), 38.34 (CH), 38.86 (CH_2), 43.12 (CH_2), 44.48 (CH_2), 69.65 (C_q), 125.64 (CH), 128.14 (CH), 129.32 (CH), 141.32 (C_q) ppm.

GC-MS (EI, 70 eV): m/z (%) = 288 (M^+, 3), 273 (3), 259 (6), 231 (5), 197 (71), 184 (12), 170 (39), 157 (26), 144 (29), 130 (11), 114 (5), 91 (23), 73 (100).

IR (neat): $\tilde{\nu}$ = 2932, 2368, 2344, 1702, 1456 cm^{-1}.

HRMS (EI^+): found m/z 288.19093, calcd for $C_{18}H_{28}OSi$ M^+ 288.19094.

8.4.4 Synthesis of 4-(prop-2-ynyl)-1-trimethylsilyloxylbicyclo[4.1.0]heptane (64)



Molecular Formula: $C_{13}H_{22}OSi$
Molecular Weight: 222.40
Exact Mass: 222.1439

Following general procedure C, To a stirred solution of silyl enol ether **63** (150 mg, 0.433 mmol) in 2 mL dichloromethane, was added diethyl zinc (2.2 mL, 1.03 mmol). Solution was cooled to 0°C using ice bath and neat CH_2I_2 (211 mg, 0.793 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to RT and stirred for 2 days, usual workup gave **64** (120 mg, 75%) as colourless oil.

1D NMR analysis (^1H, ^{13}C, ^{13}C-DEPT);

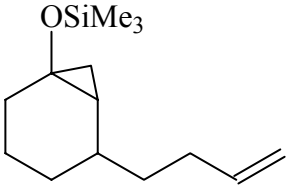
^1H NMR (500 MHz, $CDCl_3$): δ = 0.13 (3H, s), 0.18 (6H, s), 0.82 – 0.93 (1H, m), 1.15 – 1.35 (2H, m), 1.68 – 1.78 (3H, m), 1.90 – 1.99 (3H, m), 2.12 (2H, tt), 2.20 – 2.30 (2H, m) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.90 (Si-$(CH_3)_3$), 22.08 (CH_2), 22.58 (CH_2), 25.00 (CH_2), 35.18 (CH_2), 33.41 (CH), 33.99 (CH), 38.04 (CH), 69.21 (C_q), 84.10 (C_q) ppm.

GC-MS (EI, 70 eV): m/z (%) = 222 (M^+, 1), 206 (7), 154 (2), 131 (3), 116 (2), 93 (5), 77 (2), 72 (100).

IR (neat): $\tilde{\nu}$ = 2929, 2866, 1715, 1686 cm^{-1}.

8.4.5 Synthesis of 4-(but-3-enyl)-1-trimethylsilyloxylbicyclo[4.1.0]heptane (66)[b]

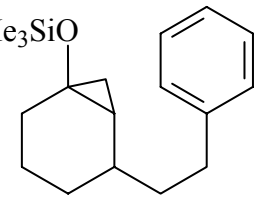


Molecular Formula: $C_{14}H_{26}OSi$
Molecular Weight: 238.45
Exact Mass: 238.1752

Following general procedure C; To a stirred solution of silyl enol ether **65** (223 mg, 1 mmol) in 2 mL dichloromethane, was added diethyl zinc (2.9 mL, 2.32 mmol). Solution was cooled to 0° C using ice bath and neat CH_2I_2 (264 mg, 0.9 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to RT and stirred for 2 days, usual workup gave **66** (200 mg, 84%) as a colorless oil.

GC-MS (EI, 70 eV): m/z (%) = 238 (M^+, 2), 194 (8), 183(9), 166 (3), 155 (3), 142 (3), 132 (2), 126 (4), 114 (3), 104 (2), 90 (5), 74 (30), 72 (100), 67 (6), 59 (5), 44 (14).

8.4.6 Synthesis of 4-(2-phenylethyl)-1-trimethylsilyloxylcyclohex-1-ene (70)



Molecular Formula: $C_{18}H_{28}OSi$
Molecular Weight: 288.51
Exact Mass: 288.1909

Following general procedure C, To a stirred solution of silyl enol ether **69** (652 mg, 2.525 mmol) in 2.5 mL dichloromethane, was added diethyl zinc (7.6 mL, 6.04 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (1.362 g, 5.10 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to RT and stirred for 2 days, usual workup gave **70** (545 mg, 36%) as a colorless oil.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

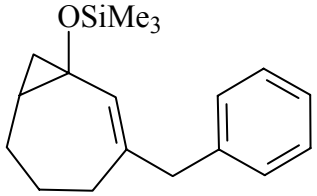
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (9H, s), 0.85 – 0.86 (1H, m), 1.10 – 1.40 (2H, m), 1.50 – 1.65 (6H, m), 1.80 – 1.90 (1H, m), 1.96 – 2.10 (2H, m), 2.40 – 2.55 (1H, m), 2.60 – 2.70 (1H, m), 7.16 (2H, dd, *J* = 6.2, 7.0 Hz), 7.27 (2H, dd, *J* = 7.0, 8.0 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.48 (CH_2), 27.14 (CH_2), 29.13 (CH_2), 30.48 (CH_2), 33.55 (CH_2), 34.55 (CH), 34.97 (CH_2), 51.00 (C_q), 125.57 (CH), 125.63 (C_q), 128.27 (CH), 128.32 (CH) ppm.

GC-MS (EI, 70 eV): m/z (%) = 288 (M^+, 6), 184 (17), 183 (100), 144 (4), 127 (3), 91 (14), 75 (18).

IR (neat): $\tilde{\nu}$ = 2920, 28235, 1704, 1453 cm^{-1}.

8.4.7 Synthesis of 3-benzyl-1-trimethylsilyloxylbicyclo[5.1.0]oct-2-ene (74)



Molecular Formula: $C_{18}H_{26}OSi$
MolecularWeight: 286.49
Exact Mass: 286.1752

Following general procedure C, To a stirred solution of silyl enol ether **73** (118 mg, 0.433 mmol) in 2 mL dichloromethane, was added diethyl zinc (1.3 mL, 1.03 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (117mg, 0.438 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to RT and stirred for 12 h, usual workup gave **74** (100 mg, 81%) as a colorless oil.

1D NMR analysis (^1H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.19 (1H, dd, *J* = 1.8, 5.0 Hz), 0.70 – 0.77 (1H, m), 0.78 – 0.83 (1H, m), 0.85 – 0.97 (2H, m), 1.50 – 1.68 (1H, m), 1.74 – 1.86 (2H, m), 2.18 – 2.28 (1H, m), 3.15 (2H, d, *J* = 3.8 Hz), 5.55 (1H, s), 7.03 (2H, dd, *J* = 2.0, 7.0 Hz), 7.13 (2H, dd, *J* = 5.0, 7.0 Hz), 7.18 (1H, dd, *J* = 7.5, 6.9) ppm.

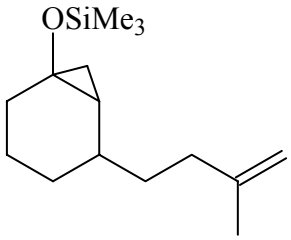
^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.32 (CH_3), 21.24 (CH_2), 22.55 (CH_2), 25.42 (CH), 28.33 (CH_2), 31.07 (CH_2), 45.76 (CH_2), 57.60 (C_q), 126.04 (CH), 127.37 (CH), 128.19 (CH), 128.98 (C_q), 129.11 (CH), 139.59(C_q) ppm.

GC-MS (EI, 70 eV): m/z (%) = 286 (20), 271 (14), 257 (15), 244 (8), 196 (20), 195 (100), 179 (7), 167 (12), 91 (35), 73 (83).

IR (neat): $\tilde{\nu}$ = 2929, 2863, 1706, 1662, 1455, 1376 cm^{-1}.

HRMS (EI^+): found m/z 286.17528, calcd for $C_{18}H_{26}OSi$ M^+ 286.17529.

8.4.8 Synthesis of 4-(3-methylbut-3-enyl)-1-trimethylsilyloxylbicyclo[4.1.0]heptane (80)



Molecular Formula: $C_{15}H_{28}OSi$
Molecular Weight: 252.47
Exact Mass: 252.1909

Following general procedure C, To a stirred solution of silyl enol ether **79** (133 mg, 0.561 mmol) in 2 mL dichloromethane, was added diethyl zinc (0.6 mL, 0.49 mmol). Solution was cooled to 0°C using ice bath and neat CH_2I_2 (135 mg, 0.505 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to RT and stirred for 12 h, usual workup gave **80** (91 mg, 65%) as a colourless oil.

1D NMR analysis (^1H, ^{13}C, ^{13}C-DEPT);

^1H NMR (500 MHz, $CDCl_3$): δ = 0.12 (9H, s), 0.30 (1H, t, *J* = 3.5 Hz), 0.80 – 0.98 (3H, m), 1.30 (2H, td, *J* = 7.3, 7.0 Hz), 1.41 – 1.68 (4H, m), 1.70 (4H, ddd, *J* = 6.2, 5.4, 4.2 Hz), 2.00 (3H, ddd, *J* = 6.8, 7.2, 7.7 Hz), 4.68 (2H, s) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.43 (CH_3), 18.95 (CH_2), 21.20 (CH_2), 22.50 (CH_2), 24.80 (CH), 31.20 (CH_2), 35.60 (CH_2), 36.30 (CH_2), 37.80 (CH), 57.23 (C_q), 109.00 (CH_2), 146.00 (C_q) ppm.

GC-MS (EI, 70 eV): m/z (%) = 252 (M^+, 2), 195 (17), 183 (14), 196 (4), 162 (4), 155 (2), 143 (5), 107 (26), 93 (7), 79 (7), 75 (26), 73 (100), 55 (10).

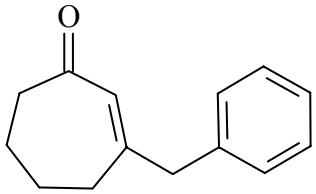
IR (neat): $\tilde{\nu}$ = 2917, 2873, 1558 cm^{-1}.

HRMS (EI^+): found m/z 252.18994, calcd for $C_{15}H_{28}OSi$ M^+ 252.19094.

8.5 Synthesis of Enones

8.5.1 Synthesis of 3-benzyl-2-cycloheptene-1-one (72)

Molecular Formula: $C_{14}H_{16}O$
Molecular Weight: 200.28
Exact Mass: 200.1201



Follwing general pocedure E, Under argon atmosphere 3-ethoxy-2-cycloheptene-1-one **71** (500 mg, 3.246 mmol) was treated with GR prepared from benzyl chloride **62** (449 mg, 3.57 mmol) and Mg turnings (85 mg, 3.5 mmol) in THF/ether (1:1 by volume). The crude product was purified using silica gel column chromatography (25% EtOAc in cyclohexane) afforded enone **72** (590 mg, 91%).

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.64 – 1.70 (2H, m), 1.71 – 1.78 (2H, m), 2.34 (2H, t, *J* = 6.2 Hz), 2.56 (2H, t, *J* = 6.4 Hz), 3.46 (2H, s,), 5.94 (1H, s), 7.15 (2H, d, *J* = 7.0 Hz), 7.28 (1H, ddd, *J* = 4.0, 7.0, 8.0 Hz), 7.29 (2H, dd, *J* = 2.0, 8.0 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.28 (CH_2), 25.17 (CH_2), 32.31 (CH_2), 42.25 (CH_2), 47.09 (CH_2), 126.77 (CH), 128.58 (CH), 129.09 (CH), 130.61 (CH), 137.58 (C_q), 160.09 (C_q), 204.07 (C=O) ppm.

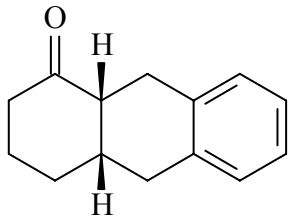
GC-MS (EI, 70 eV): m/z (%) = 200 (M^+, 7), 129 (13), 115 (11), 109 (100), 92 (1), 91 (21), 81 (46), 79 (22), 81 (46), 79 (22), 67 (14), 65 (36).

IR (neat): $\tilde{\nu}$ = 2939, 2865, 1658, 1492, 1454, 1265 cm^{-1}.

8.6 Photoinduced Electron Transfer Initiated Intramolecular Cyclization of Cyclopropyl Silyl Ethers

8.6.1 *Cis*-3,4,4a,9,9a,10-Hexahydro-1(2H)-anthracenone (81)[117]

Molecular Formula: $C_{14}H_{16}O$
Molecular Weight: 200.28
Exact Mass: 200.1201



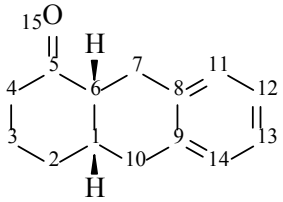
Following general procedure D, The solution of cyclopropane **60** (200 mg, 0.72 mmol) and DCA (55 mg, 0.24 mmol) in 120 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 419 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **81** (29 mg, 20%).

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.54 (1H, dddd, *J* = 3.7, 3.7, 3.7, 3.1 Hz), 1.74 (1H, tttt, *J* = 4.0, 3.7, 4.0, 4.0 Hz), 1.82 – 1.93 (1H m), 2.04 (1H, dq, *J* = 1.2, 1.2 Hz), 2.11 (1H, qq, *J* = 2.8, 2.9 Hz), 2.40 (2H, dddd, *J* = 5.6, 6.9, 6.2, 6.2 Hz), 2.46 – 2.53 (1H, m), 2.69 (1H, dd, *J* = 11.9, 11.9 Hz), 2.92 (1H, d, *J* = 10.0 Hz), 2.96 (2H, t, *J* = 2.8 Hz), 7.04 (1H, dd, *J* = 2.5, 6.2 Hz), 7.10 (2H, ddd, *J* = 7.2, 5.4, 1.8 Hz), 7.16 (1H, dd, *J* = 2.5, 3.1 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.05 (CH_2), 28.63 (CH_2), 32.69 (CH_2), 37.79 (CH_2), 40.74 (CH_2), 41.91 (CH_2), 50.82 (CH), 125.72 (CH), 125.91 (CH), 128.42 (CH), 129.30 (CH), 135.04 (CH), 135.04 (C_q), 135.36 (C_q), 211.80 (C=O) ppm.

2D NMR analysis (^{1}H-COSY, HMBC, HMQC and NOESY);



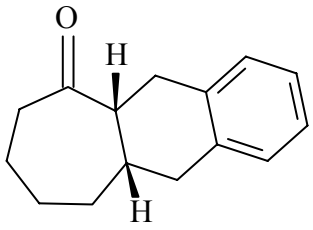
HMBC correlations of C-6 (50.82) to H-6 (δ 2.40), C-4 (41.91) to H-4 (2.50), C-1 (40.74) to H-1 (1.82–1.93), C-10 (37.79) to H-7 & H-10 (2.69 & 2.96), C-2 (32.69), to H- 2 (1.54 & 2.04), C-7 (28.63) H-7 (2.96), C- 3 (26.05), H- 3 (1.54; 1.74; 2.04; 2.11). NOESY correlation of H-6 and H-1 leads to the assignment of *cis* ring fusion.

GC-MS (EI, 70 eV): m/z (%) = 200 (M^+, 100), 185 (27), 167 (24), 154 (47), 142 (21), 129 (59), 115 (17), 91 (13), 77 (18).

IR (KBr): $\tilde{\nu}$ = 2377, 2320, 1718, 1689, 1519 cm^{-1}.

8.6.2 (5a*R*,10a*S*)-5,5a,7,8,9,10,10a,11-Octahydro-6H-cyclohepta[b]naphthalene-6-one (82)

Molecular Formula: $C_{15}H_{18}O$
Molecular Weight: 214.31
Exact Mass: 214.1357



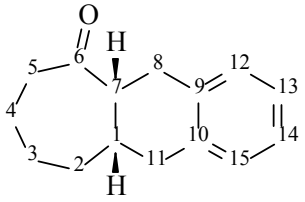
Following general procedure D, The solution of cyclopropane **61** (200 mg, 0.69 mmol) and DCA (30 mg, 0.131 mmol) in 120 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 419 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **82** (23 mg, 16%).

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (2H, ddd, *J* = 12.5, 10.0, 9.8 Hz), 1.46 – 1.70 (3H, m), 1.71 – 1.80 (2H, m), 1.81 – 2.10 (1H, m), 2.41 (2H, ddt, *J* = 6.3, 6.3, 2.0 Hz), 2.51 – 2.60 (2H, m), 2.65 (2H, dt, *J* = 11.0, 8.0 Hz), 2.84 (2H, ddd, *J* = 16.0, 16.2, 11.5 Hz), 7.09 (3H, ddd, *J* = 8.0, 3.0, 4.0 Hz), 7.26 (1H, dd, *J* = 6.9, 3.7 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.79 (CH_2), 32.74 (CH_2), 35.79 (CH_2), 35.52 (CH), 37.75 (CH_2), 41.19 (CH_2), 44.22 (CH_2), 54.92 (CH), 125.92 (CH), 128.25 (CH), 128.47 (CH), 128.58 (CH), 135.16 (C_q), 136.31 (C_q), 215.64 (C=O) ppm.

2D NMR analysis (^{1}H-COSY, HMBC, HMQC and NOESY)



HSQC correlation of C-7 (54.92) to H-7 (2.51-2.60), C-5 (41.19) to H-5 (2.54), C-2 (41.19) to H-2 (2.50-2.65), C-11 (35.75) to (1.81-2.10 & 2.40-2.70 & 2.84), C-8 (32.74) to H-8 (2.84), C-3 (25.79) to H-3 (1.54 & 2.10).

NOESY correlation between H-1 and H-7 lead to the assignment of *cis* ring fusion.

GC-MS (EI, 70 eV): m/z (%) = 214 (M^+, 90), 210 (6), 199 (20), 181 (26), 172 (11), 167 (3), 157 (15), 155 (17), 142 (28), 129 (100), 115 (35), 91 (15), 80 (10), 77 (16).

IR (KBr): $\tilde{\nu}$ = 2925, 2857, 1690, 1454 cm^{-1}.

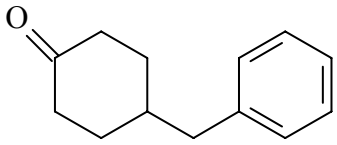
HRMS (EI^+): found m/z 214.1347, calcd for $C_{15}H_{18}O$ M^+ 214.1359.

8.6.3 4-Benzylcyclohexanone (83)[118] and 4-benzyl-2-cyclohexen-1-one (84)[119]

Following general procedure D, The solution of cyclopropane **59** (100 mg, 0.384 mmol) and DCA (25 mg, 0.109 mmol) in 60 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 419 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford products **83** (6 mg, 8%) and **84** (9 mg, 12%).

Ketone (83)

Molecular Formula: $C_{13}H_{16}O$
Molecular Weight: 188.27
Exact Mass: 188.1201

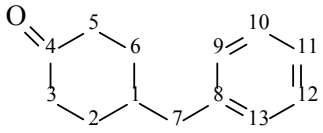


1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 – 1.37 (1H, m), 1.42 (2H, dq, *J* = 4.3, 3.7 Hz), 1.99 (3H, td, *J* = 3.1, 4.3 Hz), 2.20 – 2.40 (4H, m), 2.60 (2H, d, *J* = 6.9 Hz), 7.15 (2H, d, *J* = 6.9 Hz), 7.20 (1H, t, *J* = 7.2 Hz), 7.28 (2H, t, *J* = 7.2 Hz) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.91 (CH_2), 38.14 (CH), 40.76 (CH_2), 42.19 (CH_2), 126.11 (CH), 128.35 (CH), 129.01 (CH), 140.36 (C_q), 211.20 (C=O) ppm.

2D NMR analysis (^{1}H-COSY, HMBC, HMQC).

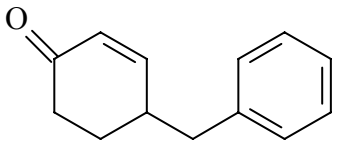


HMBC correlation of C-8 (140.36) to H-7 (2.60), C-7 (42.19) to H-1 (1.99), C-1 (38.14) to H-6 & H-2 (1.42) & H-5; H-2 (2.20-2.40) & H-7 (2.60), C-4 (211.20), to H-5; H-3; (2.20-2.40) & H-7 (2.60); H-6. COSEY correlation of H-2 to H-1; H-13; H-9 and H-1 to H-6; H-7 and H-2.

GC-MS (EI, 70 eV): m/z (%) = 188 (M^+, 1), 187 (7), 186 (50), 168 (60), 129 (8), 127 (2), 115 (4), 91 (100), 77 (6), 74 (1.2), 65 (54), 63 (13).

IR (KBr): $\tilde{\nu}$ = 1718, 1654 cm^{-1}.

Enone (84):



Molecular Formula: $C_{13}H_{14}O$
Molecular Weight: 186.25
Exact Mass: 186.1044

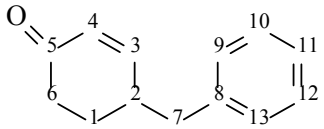
1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.66 (1H, tdd, *J* = 4.7, 4.3, 5.0 Hz), 1.99 (1H, dtd, *J* = 4.3, 5.0, 4.7 Hz), 2.27 (1H, dtd, *J* = 5.0, 4.5, 5.0 Hz), 2.42 (1H, tt, *J* = 4.8, 4.8 Hz), 2.65 (2H, dd, *J* = 8.5, 5.4 Hz), 2.72 (1H, ddd, *J* = 10.3, 5.3, 1.5 Hz), 5.92 (1H, dd, *J* = 1.8, 10.2 Hz), 6.77 (1H, dt, *J* = 2.0, 10.0 Hz), 7.13 (2H, d, *J* = 6.9 Hz), 7.18 (1H, dd, *J* = 1.8, 7.4 Hz), 7.26 (2H, dd, *J* = 1.8, 7.3 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.62 (CH_2), 36.79 (CH_2), 37.95 (CH), 40.90 (CH_2), 128.60 (CH), 128.56 (CH), 129.05 (CH), 129.31 (CH), 138.80 (C_q), 153.80 (CH), 199.70 (C=O) ppm.

IR (KBr): $\tilde{\nu}$ = 1716, 1673 cm^{-1}.

2D NMR analysis (^{1}H-COSY, HMBC, HMQC):

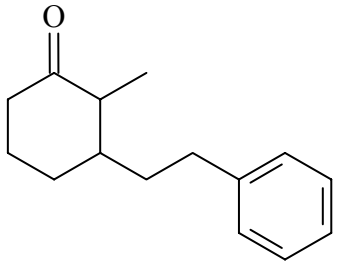


HMBC correlation of C-8 (138.80), to H-7 (2.65), H-9; H-13 (7.13), C-2 to (37.95) H-1a (1.66); H-1b (1.99), H-6a & H-6b (2.42); H-7 (2.65); H-3 (5.92) & H-4 (6.77), C-5 (199.70) to H-1; H-6; H-4.

GC-MS (EI, 70 eV): m/z (%) = 186 (M^+, 33), 168 (4), 158 (1), 129 (5), 127 (2), 115 (3), 91 (100), 79 (2), 77 (4), 65 (37), 51 (11).

8.6.4 2-Methyl-3-(2-phenylethyl)-cyclohexanone (85)

Molecular Formula: $C_{15}H_{20}O$
Molecular Weight: 216.32
Exact Mass: 216.1514



Following general procedure D, The solution of cyclopropane **70** (100 mg, 0.347 mmol) and DCA (45 mg, 0.19 mmol) in 50 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 419 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **85** (23 mg, 30%).

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

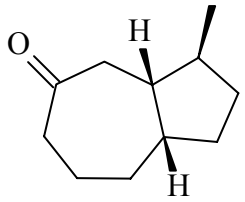
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 (3H, d, *J* = 6.2 Hz), 1.31 (1H, dd, *J* = 12.8, 3.4 Hz), 1.36 (1H, dd, *J* = 12.5, 3.1 Hz), 1.40 (1H, dd, *J* = 5.0, 1.8 Hz), 1.43 (1H, dd, *J* = 13.1, 3.1 Hz), 1.58 – 1.72 (2H, m), 1.94 (1H, dt, *J* = 13.0, 3.0 Hz), 2.05 – 2.15 (1H, m), 2.33 (1H, sep, *J* = 6.2 Hz), 2.46 (1H, dddd, *J* = 1.8, 1.8, 1.8, 2.5 Hz), 2.60 (2H, t, *J* = 7.8 Hz), 7.15 (3H, dd, *J* = 6.0, 6.9 Hz), 7.26 (2H, ddd, *J* = 4.0, 7.0, 5.0 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.35 (CH_3), 31.98 (CH_2), 32.98 (CH_2), 34.87 (CH_2), 39.86 (CH), 44.87 (CH_2), 48.23 (CH_2), 125.83 (CH), 128.25 (CH), 128.38 (CH), 142 (C_q), 212.80 (C=O) ppm.

GC-MS (EI, 70 eV): m/z (%) = 216 (M^+, 20), 131 (10), 115 (11), 111 (65), 104 (14), 92 (23), 91 (100), 79 (7), 77 (10), 65 (13), 56 (8), 55 (30).

IR: (KBr): $\tilde{\nu}$ = 3391, 2961, 2932, 2866, 1710, 1452, 1070, 1452, 1070, 1070 cm^{-1}.

8.6.5 (3*S*,3a*R*,8a*S*)-3-Methyloctahydroazulen-5(1H)-one (86)[120]



Molecular Formula: $C_{11}H_{18}O$
Molecular Weight: 166.26
Exact Mass: 166.1357

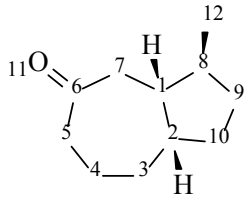
Following general procedure D, The solution of cyclopropyl silyl ether **66** (150 mg, 0.63 mmol) and DCA (48 mg, 0.21 mmol) in 60 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min. and irradiated for 12 h using 419 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **86** (10 mg, 10%).

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (3H, d), 1.15 – 1.35 (4H, m), 1.50 – 1.55 & 1.85 – 1.95 (2H, m), 1.60 – 1.70 & 2.45 – 2.58 (2H, m), 1.75 – 1.88 (2H, m), 1.09 – 1.95 (1H, m), 2.02 – 2.10 (1H, m), 2.10 – 2.20 (1H, m), 2.35 – 2.45 (2H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.07 (CH_3), 24.86 (CH_2), 32.12 (CH_2), 32.53 (CH_2), 36.14 (CH_2), 37.64 (CH), 44.04 (CH_2), 44.28 (CH), 45.26 (CH_2), 45.88 (CH), 215.20 (C=O) ppm.

2D NMR analysis (^{1}H-COSY, HMBC, HMQC and NOESY):



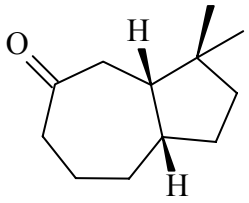
HMBC correlation of C-6 (215.20) to H-4 (1.50-1.55) & H-5; H-7 (1.75-1.95), & H-7 (2.30-2.50), C-12 (16.07) to H-9 & H-10 (1.15-1.35), H-1 & H-2 (1.75-1.85), H-8 (2.10-2.20).

NOESY correlation between H-12 to H-1 & H-2 lead to the assignment of *cis* ring fusion.

GC-MS (EI, 70 eV): m/z (%) = 166 (M^+,1), 165 (14), 123 (15), 121 (46), 110 (11), 107 (24), 94 (60), 80 (55), 78 (40), 67 (82), 55 (94), 41 (100).

IR (KBr): $\tilde{\nu}$ = 1653, 1507 cm^{-1}.

8.6.6 (3a*S*,8a*S*)-3,3-Dimethyloctahydroazulen-5(1H)-one (87)



Molecular Formula: $C_{12}H_{20}O$
MolecularWeight: 180.29
Exact Mass: 180.1514

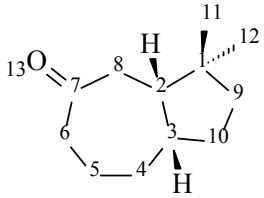
Following general procedure D, The solution of cyclopropyl silyl ether **80** (120 mg, 0.476 mmol) and DCA (48 mg, 0.21 mmol) in 60 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 419 nm lamps. The residue was purified by silica column chromatography (9% EtOAc in cyclohexane) to afford **87** (12 mg, 14%).

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.75 (3H, s), 0.96 (3H, s), 1.26 – 1.32 (2H, m), 1.38 – 1.46 (1H, m), 1.45 – 1.50 (2H, m), 1.57 & 2.50 (2H, m), 1.60 & 2.40 (1H, m), 1.68 – 1.78 (2H, m), 1.87 – 1.95 (2H, m), 1.98 – 2.10 (1H, m), 2.24 (1H, dd, *J* = 16.4, 12.0 Hz), 2.48 – 2.52 (1H, m) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.31 (CH_3), 27.84 (CH_2), 27.93 (CH_3), 30.5 (CH_2), 37.02 (CH_2), 40.30 (CH_2), 43.65 (CH_2), 44.70 (C_q), 44.17 (CH_2), 46.69 (CH), 51.28 (CH), 215.18 (C=O) ppm.

NMR analysis (^{1}H-COSY, HMBC, HMQC and NOESY)



HMBC correlation of C-1 (217.18) to H-8 & H-6 (2.20-2.52), C-2 (51.28) to H-11 & H-12 (0.75, 0.96), H-3a (2.49); H-8 (2.20-2.48), C-3 (46.69) to H-11 & H-12; H-4 (1.42-1.50), H-10 (2.00), H-8.

NOESY correlation between H-3 and H-2 and H-11 lead to the assignment of *cis* stereochemistry of the molecule.

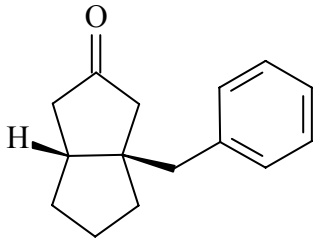
GC-MS (EI, 70 eV): m/z (%) = 180 (M^+, 10), 165 (8), 152 (3), 147 (11), 136 (13), 124 (20), 120 (11), 109 (23), 94 (24), 90 (8), 79 (20), 70 (30), 66 (60), 40 (100), 38 (32).

IR (KBr): $\tilde{\nu}$ = 1690, 1540 cm^{-1}.

HRMS (EI^+): found m/z 180.15086, calcd for $C_{12}H_{20}O$ M^+ 180.15142.

8.6.7 3a-Benzyl-hexahydropentalen-2-one (88)[121]

Molecular Formula: $C_{15}H_{18}O$
Molecular Weight: 214.31
Exact Mass: 214.1357

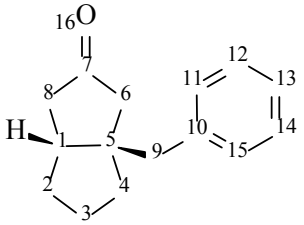


Following general procedure D, The solution of cyclopropyl silyl ether **74** (160 mg, 0.56 mmol) and DCA (52 mg, 0.228 mmol) in 96 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 17 h using 419 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **88** (36 mg, 31%).

1D NMR (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (1H, ddd, *J* = 5.0, 11.7, 6.4 Hz), 1.50 (1H, ddd, *J* = 7.5, 12.5, 6.5 Hz), 1.65 – 1.80 (4H, m), 1.90 – 2.10 (2H, m), 2.25 – 2.45 (3H, m), 2.65 (1H, d, *J* = 13.1 Hz), 2.69 (1H, d, *J* = 13.1 Hz), 6.79 (2H, dd, *J* = 1.5, 6.9 Hz), 7.16 (1H, dd, *J* = 7.2, 4.7 Hz), 7.22 (2H, dd, *J* = 1.9, 6.5 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.86 (CH_2), 32.52 (CH_2), 37.82 (CH_2), 44.44 (CH_2), 45.46 (CH_2), 48.95 (CH_2), 51.79 (C_q), 126.37 (CH), 128.20 (CH), 130.02 (CH), 138.62 (C_q), 219.87 (C=O) ppm.



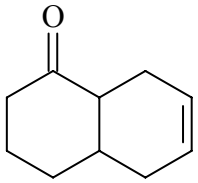
2D NMR analysis (^{1}H-COSY, HMBC, HMQC and NOESY)

HMBC correlation of C-7 (219.87) to H-6 & H-8 (1.90-2.10; 2.25; 2.45), C-10 (138.62) to H-9 (2.65), C-1 (44.44) to H-3 & H-2 (1.70) & H-8 (1.90-2.09) and to H-9. NOESY correlation between H-9 & H-1a leads to the assignment of *cis* ring fusion.

GC-MS (EI, 70eV): m/z (%) = 214 (M^+, 16), 149 (11), 123 (34), 117 (5), 95 (100), 81 (81), 67 (23), 65 (30).

IR (KBr): $\tilde{\nu}$ = 2947, 2868, 1737, 1660, 1450, 1405, 1166 cm^{-1}.

8.6.8 3,4,4a,5,8,8a-Hexahydro-1-(2H)-naphthalenone (90)[122]



Molecular Formula: $C_{10}H_{14}O$
Molecular Mass: 150.22
Exact Mass: 150.1044

Following general procedure D, The solution of cyclopropyl silyl ether **64** (100 mg, 0.45 mmol) and DCA (25 mg, 0.109 mmol) in 60 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 17 h using 419 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **90** (10 mg, 15%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 – 2.45 (10H, m), 2.55 (1H, dd, *J* = 6.9, 7.5 Hz), 2.75 (1H, dd, *J* = 4.3, 7.5 Hz), 4.87 (2H, t, *J* = 1.2 Hz) ppm.

GC-MS (EI, 70 eV): m/z (%) = 150 (M^+, 13), 134 (11.4), 121 (19.5), 106 (24), 91(35), 79 (100), 77 (76), 52 (43), 40 (32).

IR (KBr): $\tilde{\nu}$ = 1720, 1666 cm^{-1}.

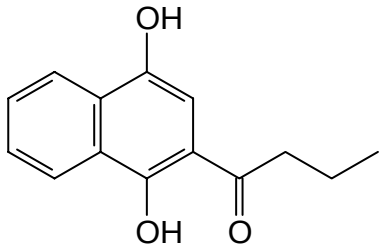
8.7 General Procedure F: Irradiation of Quinones with Aldehydes

Standard photochemical experiment: A solution of 1 mmol of the naphthoquinone and 9 mmol of aldehydes in 60 ml of dry benzene was split over 5 Pyrex tubes (capacity 12 ml). The tubes were degassed with argon and irradiated using a Rayonet photochemical reactor. The reaction was continued until GC analysis indicated complete consumption of the quinone starting material. The combined solutions were evaporated under vacuum and the crude residue was purified by flash column chromatography, followed, if require, by preparative HPLC.

8.8 Photoacylation of 1,4-Naphthoquinones with Aliphatic Aldehydes

8.8.1 1-(1,4-Dihydroxy-naphthalen-2-yl)-butan-1-one (106a)[a]

Molecular Formula: $C_{14}H_{14}O_3$
Molecular Weight: 230.26
Exact Mass: 230.0942



Following the general procedure F, irradiation of 316 mg (2 mmol) of 1,4-naphthoquinone **104** and 1.30 g (18 mmol) of butyraldehyde **105a** in 100 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 273 mg (60%) of 1-(1,4-dihydroxy-naphthalen-2-yl)-butan-1-one **106a** as brown solid, mp 144-145 °C.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR 500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 0.94 (3H, t, *J* = 7.2 Hz, -$CH_2C\underline{H_3}$), 1.70 (2H, q, *J* = 7.5 Hz, $C\underline{H_2}CH_3$), 2.86 (2H, t, *J* = 7.2 Hz, -$COC\underline{H_2}$), , 7.30 (1H, s, OH), 7.44 (1H, dd, *J* = 8.1, 6.9 Hz), 7.54 (1H, dd, *J* = 7.5, 7.5 Hz), 8.08 (1H, d, *J* = 8.7 Hz), 8.33 (1H, d, *J* = 8.1 Hz), 13.62 (1H, s, OH) ppm.

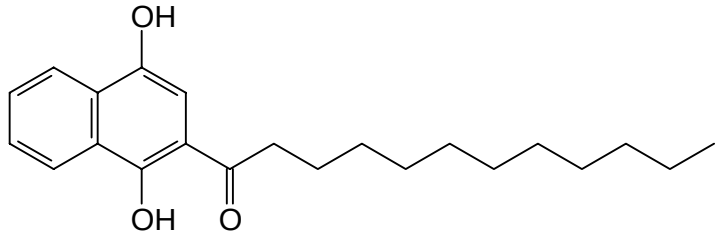
^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 13.5 (CH_3), 17.7 (CH_2), 40.2 (CH_2), 104.6 (CH), 121.6 (CH), 125.7 (CH), 125.9 (C_q), 128.9 (CH), 129.0 (C_q), 143.6 (C_q), 156.3 (C_q), 205.7 (C=O) ppm.

MS (EI): m/z (%) = 230 (M^+, 85%), 215 (3), 212 (13), 202 (3), 197 (35), 187 (100), 131 (15), 105 (13), 87 (1), 69 (1), 43 (14).

IR (KBr): $\tilde{\nu}$ = 3410, 2967, 1662, 1630, 1596, 1463, 1384, 1292, 1202, 1138, 1073, 768, 731 cm^{-1}.

8.8.2 1-(1,4-Dihydroxy-naphthalen-2-yl)-dodecan-1-one (106b)

Molecular Formula: $C_{22}H_{30}O_3$
Molecular Weight: 342.48
Exact Mass: 342.2194



Following the general procedure F, irradiation of 316 mg (2 mmol) of 1,4-naphthoquinone **104** and 3.32 g (18 mmol) of dodecanal **105b** in 100 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 240 mg (35%) of 1-(1,4-dihydroxy-naphthalen-2-yl)-dodecan-1-one **106b** as a yellow solid mp 128–129 °C.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 0.81 (3H, t, *J* = 6.9 Hz, C<u>H</u>$_3$-CH$_2$), 1.10–1.30 (16H, m), 2.93 (2H, t, *J* = 7.5 Hz, C<u>H</u>$_2$-CH$_2$), 7.10 (s, 1H, Ar-H), 7.48 (1H, dd, *J* = 8.1, 1.2 Hz), 7.57 (1H, dd, *J* = 8.1, 1.2 Hz), 8.13 (1H, d, *J* = 8.1 Hz), 8.33 (1H, d, *J* = 8.7 Hz), (2H, s, for 2×OH not observed) ppm.

^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 13.0 (CH_3), 23.6 (CH_2), 23.7 (CH_2), 28.4 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 30.3 (CH_2), 31.0 (CH_2), 37.8 (CH_2), 103.7 (CH), 111.2 (C_q), 121.3 (CH), 123.2 (CH), 125.0 (C_q), 125.3 (CH), 128.2 (CH), 128.8 (C_q), 143.5 (C_q), 154.8 (C_q), 205.4 (C=O) ppm.

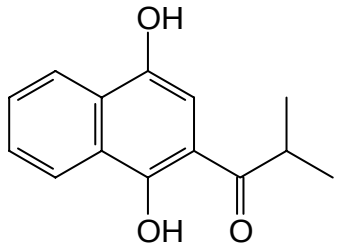
MS (EI): m/z (%) = 342 (M^+, 100%), 325 (5), 324 (12), 239 (5), 225 (3), 215 (14), 202 (31), 199 (5), 197 (12), 187 (54), 173 (10), 160 (5), 131 (10), 115 (2), 105 (8), 77 (6), 55 (11), 43 (11).

IR (KBr): $\tilde{\nu}$ = 3358, 2956, 2920, 2850, 1635, 1580, 1468, 1401, 1378, 1293, 1240, 1137, 1076, 879, 767 cm^{-1}.

HRMS (EI^+): found m/z 342.21883, calcd for $C_{22}H_{30}O_3$ M^+ 342.21949.

8.8.3 1-(1,4-Dihydroxy-naphthalen-2-yl)-2-methyl-propan-1-one (106c)

Molecular Formula: $C_{14}H_{14}O_3$
Molecular Weight: 230.26
Exact Mass: 230.0942



Following the general procedure F, irradiation of 316 mg (2 mmol) of 1,4-naphthoquinone **104** and 1.30 g (18 mmol) of isobutyraldehyde **105c** in 100 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 96 mg (21%) of 1-(1,4-dihydroxy-naphthalen-2-yl)-2-methyl-propan-1-one **106c** as a brown thick oil.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 1.21 (6H, d, *J* = 6.9 Hz, $CH(C\underline{H}_3)_2$), 3.45 (1H, sep, *J* = 6.7 Hz), 5.49 (1H, s, OH), 7.55 (1H, dd, *J* = 1.2, 6.9 Hz, Ar-H), 7.64 (1H, dd, *J* = 1.2, 7.5 Hz), 8.09 (1H, d, *J* = 8.1 Hz), 8.43 (1H, d, *J* = 8.1 Hz), 13.92 (1H, s, OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ = 19.1 ($2\times CH_3$), 35.1 (CH), 105.3 (CH), 110.5 (CH), 121.5 (CH), 124.5 (CH), 126.2 (C_q), 126.4 (CH), 129.3 (C_q), 129.7 (CH), 142.9 (C_q), 158.0 (C_q), 209.9 (C=O) ppm.

MS (EI): m/z (%) = 230 (M^+, 14%), 229 (7), 228 (39), 227 (5), 213 (8), 211 (13), 210 (53), 200 (6), 188 (5), 186 (45), 172 (4), 159 (13), 158 (82), 130 (35), 104 (11), 102 (42), 76 (25), 43 (49).

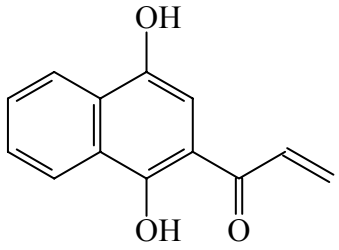
IR (KBr): $\tilde{\nu}$ = 3430, 2974, 1630, 1598, 1476, 1396, 1303, 1214, 1041, 822, 768 cm^{-1}.

8.8.4 1-(1,4-Dihydroxy-naphthalen-2-yl)-propenone (107) and acrylic acid 4-hydroxy-1-naphthalen-1-yl ester (108)

Following the general procedure F, irradiation of 316 mg (2 mmol) of 1,4-naphthoquinone **104** and 1.01 g (18 mmol) of acrolein in 100 ml of benzene for 15h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) and HPLC gave 76 mg (18%) of 1-(1,4-dihydroxy-naphthalen-2-yl)-propenone **107** as brown solid, mp 162–163 °C and 30 mg (7%) of acrylic acid 4-hydroxy-1-naphthalen-1-yl ester **108** as thick brown oil.

107:

Molecular Formula: $C_{13}H_{10}O_3$
Molecular Weight: 214.22
Exact Mass: 214.0629



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 5.90 (1H, dd, *J* = 1.8, 8.7 Hz), 6.50 (1H, dd, *J* = 1.8, 15.0 Hz, C$\underline{H_2}$=CH), 7.12 (1H, s, Ar-H), 7.28 (1H, dd, *J* = 10.6, 6.2 Hz, C$\underline{H_2}$=CH), 7.49 (dd, 1H, *J* = 1.2, 8.4 Hz), 7.60 (dd, 1H, *J* = 1.2, 7.2 Hz), 8.13 (d, 1H, *J* = 8.1 Hz), 8.37 (1H, dd, *J* =12.5, 8.1 Hz, C$\underline{H}$=CH_2), 14.04 (2H, s, 2×OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ = 103.4 (CH), 121.5 (CH), 123.4 (CH), 125.0 (C_q), 125.5 (CH), 128.8 (CH), 129.2 (CH_2), 129.7 (C_q), 130.3 (CH), 143.8 (C_q), 157.6 (C_q), 192.6 (C=O) ppm.

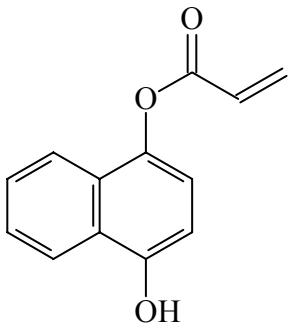
MS (EI): m/z (%) = 214 (M^+, 100%), 212 (36), 191 (1), 188 (2), 187 (15), 186 (17), 184 (23), 171 (4), 157 (16), 149 (7), 139 (4), 130 (13), 155 (6), 105 (12), 95 (5), 85 (6), 77 (20), 55 (45).

IR (KBr): $\tilde{\nu}$ = 3416, 1735, 1663, 1631, 1593, 1390, 1297, 1253, 1150, 1073, 767, 720 cm^{-1}.

HRMS (EI^+): found m/z 214.06234, calcd for $C_{13}H_{10}O_3$ M^+ 214.06299.

108:

Molecular Formula: $C_{13}H_{10}O_3$
Molecular Weight: 214.22
Exact Mass: 214.0629



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 5.93 (1H, s, OH), 6.10 (1H, d, *J* = 10.6 Hz, C<u>H</u>=CH_2), 6.45 (1H, dd, *J* = 10.6, 6.9 Hz, CH=CH_2), 6.54 (1H, d, *J* = 8.1 Hz, Ar-H), 6.72 (1H, d, *J* = 17.5 Hz, CH=CH_2), 6.99 (1H, d, *J* = 8.1 Hz), 7.44 (2H, dd, *J* = 6.9, 7.2 Hz), 7.74 (1H, d, *J* = 8.1 Hz), 8.07 (1H, d, *J* = 8.1 Hz) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ = 107.7 (CH), 117.8 (CH), 120.8 (CH), 122.2 (CH), 125.14 (C_q), 125.5 (CH), 126.9 (CH), 127.3 (C_q), 127.6 (CH_2), 133.1 (CH), 139.6 (C_q), 149.8 (C_q), 165.6 (C=O) ppm.

MS (EI): m/z (%) = 214 (M^+, 10%), 161 (10), 160 (93), 159 (19), 149 (1), 131 (14), 123 (1), 111 (1), 109 (2), 97 (2), 79 (1), 69 (2), 57 (4), 55 (47), 51 (6), 43 (20).

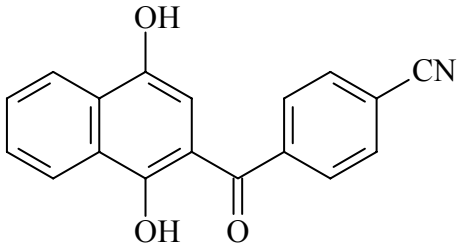
IR (KBr): $\tilde{\nu}$ = 3415, 1723, 1633, 1589, 1400, 1257, 1176, 1147, 1065, 981, 805, 767, 748 cm^{-1}.

HRMS (EI^+): found m/z 214.06277, calcd for $C_{13}H_{10}O_3$ M^+ 214.06299.

8.9 Photoacylation of 1,4-Naphthoquinones with Aromatic Aldehydes

8.9.1 4-[(1,4-Dihydroxy-2-naphthyl)carbonyl]benzonitrile (110a)

Molecular Formula: $C_{18}H_{11}NO_3$
Molecular Weight: 289.29
Exact Mass: 289.0738



Following the general procedure F, irradiation of 316 mg (2 mmol) of 1,4-naphthoquinone **104** and 2.36 g (18 mmol) of *p*-cyanobenz aldehyde in 100 ml of benzene for 96h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 116 mg (20%) of 4-[(1,4-dihydroxy-2-naphthyl)carbonyl]benzonitrile **110a** as yellow solid, mp 146–149 °C

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; acetone-d_6/DMSO-d_6) δ = 6.84 (1H, s, Ar-H), 7.65 (1H, dd, *J* = 7.8, 2.1 Hz), 7.75 (1H, dd, *J* = 2.1, 8.1 Hz), 7.93 (2H, d, *J* = 8.1 Hz), 8.04 (2H, dd, *J* = 2.1, 8.1 Hz), 8.20 (1H, d, *J* = 8.1 Hz), 8.44 (1H, d, *J* = 8.7 Hz), 9.10 (1H, s, OH), 13.29 (1H, s, OH) ppm.

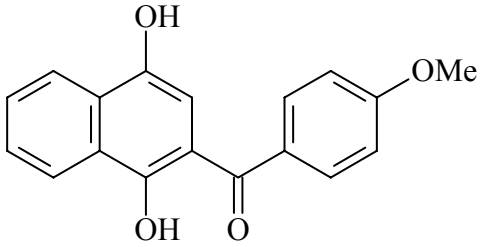
^{13}C NMR (125 MHz; acetone-d_6/DMSO-d_6) δ = 106.9 (CH), 112.5 (C_q), 118.6 (C_q), 123.2 (CH), 124.8 (CH), 126.5 (C_q), 127.4 (CH), 130.2 (2×CH), 130.7 (CH), 130.8 (C_q), 133.10 (2×CH), 143.0 (C_q), 145.7 (C_q), 158.17 (C_q), 200.3 (C=O) ppm.

MS (EI): m/z (%) = 289 (M^+, 100%), 288 (24), 273 (1), 263 (1), 243 (1), 231 (2), 215 (1), 204 (2), 187 (20), 186 (35), 177 (2), 160 (1), 151 (1), 144 (3), 132 (2), 131 (15), 115 (1), 102 (40), 88.0 (2), 77 (16).

IR (KBr): $\tilde{\nu}$ = 3450, 2230, 1682, 1635, 1598, 1403, 1250, 1034, 998 cm^{-1}.

8.9.2 (1,4-Dihydroxy-naphthalen-2-yl)-(4-methoxyphenyl)-methanone (110b)

Molecular Formula: $C_{18}H_{14}O_4$
Molecular Weight: 294.31
Exact Mass: 294.0892



Following the general procedure F, irradiation of 316 mg (2 mmol) of 1,4-naphthoquinone **104** and 2.49 g (18 mmol) of *p*-methoxybenzaldehyde in 100 ml of benzene for 63h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 146 mg (25%) of (1,4-dihydroxy-naphthalen-2-yl)-(4-methoxyphenyl)-methanone **110b** as brown solid, mp 93–96 °C

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 3.80 (3H, s, OMe), 6.91 (2H, d, *J* = 7.5 Hz, Ar-H), 6.93 (1H, s, Ar-H), 7.38 (1H, d, *J* = 4.3 Hz), 7.48 (1H, d, *J* = 7.2 Hz), 7.57 (1H, d, 2H, *J* = 1.8, 8.1 Hz), 7.66 (2H, d, *J* = 6.9 Hz), 8.13 (1H, d, *J* = 8.1 Hz), 8.38 (1H, d, *J* = 8.1 Hz), 13.39 (s, 2H, OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 54.9 (OMe), 107.0 (CH), 111.4 (C_q), 113.0 (2×CH), 117.8 (C_q), 125.7 (CH), 128.9 (CH), 131.0 (2×CH), 143.3 (CH), 156.8 (C_q), 162.0 (C_q), 199.0 (C=O) ppm.

MS (EI): m/z (%) = 294 (M^+, 12%), 186 (3), 158 (2), 152 (3), 136 (8), 135 (100), 107 (6), 104 (3), 92 (8), 77 (13), 76 (4), 63 (3).

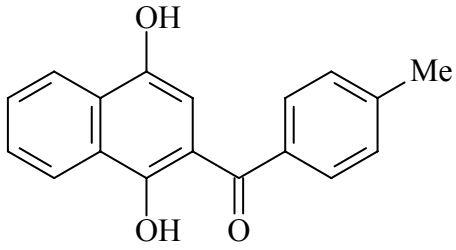
IR (KBr): $\tilde{\nu}$ = 3410, 2929, 1731, 1668, 1601, 1514, 1255, 1169, 1027, 844, 766 cm^{-1}.

8.9.3 (1,4-Dihydroxy-naphthalen-2-yl)-*p*-tolyl-methanone (112a) and 4-methyl-benzoic acid 4-hydroxy-naphthalen-1-yl ester (114a)

Following the general procedure F, irradiation of 316 mg (2 mmol) of 1,4-naphthoquinone **104** and 2.16 g (18 mmol) of *p*-methylbenzaldehyde **111a** in 90 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 340 mg (61%) of (1,4-dihydroxy-naphthalen-2-yl)-*p*-tolyl-methanone **112a** as brown solid, mp 128–129 °C and 30 mg (5%) of 4-methyl-benzoic acid 4-hydroxy-naphthalen-1-yl ester **114a** as brown solid, mp 166–167 °C.

112a:

Molecular Formula: $C_{18}H_{14}O_3$
Molecular Weight: 278.31
Exact Mass: 278.0942



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

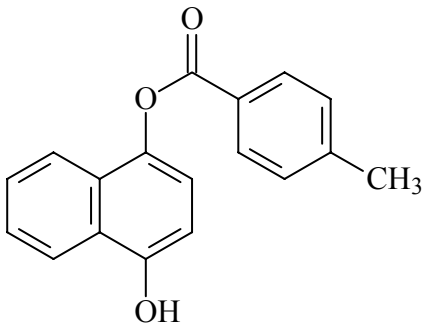
^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 2.38 (3H, s, Ar-Me), 6.93 (1H, s, Ar-H), 7.26 (2H, d, *J* = 8.1 Hz), 7.52 (1H, t, *J* = 7.5 Hz), 7.57 (2H, d, *J* = 7.5 Hz), 7.62 (1H, t, *J* = 7.8 Hz), 8.16 (1H, d, *J* = 8.1 Hz), 8.39 (1H, d, *J* = 8.1 Hz), (2H, s, 2×OH, not observed) ppm.

^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 20.4 (CH_3), 106.5 (CH), 111.1 (C_q), 121.4 (CH), 123.3 (CH), 125.0 (C_q), 125.4 (CH), 128.0 (2×CH), 128.4 (2×CH), 128.6 (CH), 134.9 (C_q), 141.2 (C_q), 143.2 (C_q), 156.0 (C_q), 199.8 (C=O) ppm.

MS (EI): m/z (%) = 278 (M^+, 81%), 263 (3), 187 (15), 186 (100), 158 (8), 139 (2), 131 (6), 130 (28), 119 (16), 105 (4), 102 (18), 91 (29), 76 (97).

IR (KBr): $\tilde{\nu}$ = 3342, 1437, 1729, 1686, 1604, 1512, 1426, 1300, 1260, 1168, 1026, 845, 772, 615 cm^{-1}.

114a:



Molecular Formula: $C_{18}H_{14}O_3$
Molecular Weight: 278.31
Exact Mass: 278.0942

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 2.47 (3H, s, Ar-Me), 6.55 (1H, d, *J* = 7.9 Hz, Ar-H), 7.03 (1H, d, *J* = 7.9 Hz), 7.35 (2H, d, *J* = 7.9 Hz), 7.45 (2H, ddd, *J* = 6.7, 6.7, 6.7 Hz), 7.78 (1H, d, *J* = 7.5 Hz), 8.01 (1H, s, OH), 8.07 (1H, d, *J* = 7.5 Hz), 8.21 (2H, d, *J* = 7.9) ppm.

^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 21.7 (CH_3), 107.9 (CH), 118.0 (CH), 120.9 (CH), 122.3 (CH), 124.8 (C_q), 125.2 (CH), 126.5 (C_q), 126.81 (CH), 127.5 (C_q), 129.4 (2×CH), 130.1 (C_q), 130.3 (2×CH), 139.8 (C_q), 144.7 (C_q), 149.9 (C_q), 166.4 (C=O) ppm.

MS (EI): m/z (%) = 278 (M^+, 15%), 159 (3), 131 (2), 120 (11), 119 (100), 105 (3), 91 (32), 89 (3), 77 (7), 65 (9).

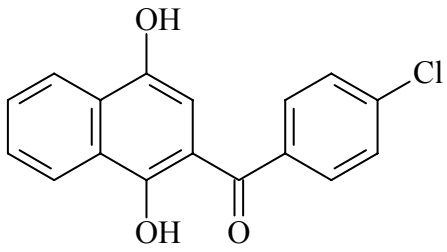
IR (KBr): $\tilde{\nu}$ = 3443, 2924, 2858, 1734, 1708, 1608, 1386, 1257, 1178, 1081, 1017, 756 cm^{-1}.

HRMS (EI^+): found m/z 278.09434, calcd for $C_{18}H_{14}O_3$ M^+ 278.09429.

8.9.4 (4-Chloro-phenyl)-(1,4-dihydroxy-naphthanlen-2-yl)-methanone (112b), [3-(4-chloro-benzoyl)-1,4-dihydroxy-naphthalen-2-yl]-(4-chloro-phenyl)-methanone (113b) and 4-chloro-benzoic acid 4-hydroxy-naphthalen-1-yl ester (114b).

Following the general procedure F, irradiation of 316 mg (2 mmol) of 1,4-naphthoquinone **104** and 2.52 g (18 mmol) of *p*-chlorobenzaldehyde **111b** in 100 ml of benzene for 12 h Brown solid, mp 200–201 °C;. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 100 mg (17%) of (4-chloro-phenyl)-(1,4-dihydroxy-naphthanlen-2-yl)-methanone **112b** as brown solid, mp 200–201 °C, 100 mg (11%) of [3-(4-chloro-benzoyl)-1,4-dihydroxy-naphthalen-2-yl]-(4-chloro-phenyl)-methanone **113b** as yellow solid, mp 178-180 °C and 53 mg (9%) of 4-chloro-benzoic acid 4-hydroxy-naphthalen-1-yl ester **114b** as brown solid, mp 189–190 °C. **112b:**

Molecular Formula: $C_{17}H_{11}ClO_3$
Molecular Weight: 298.73
Exact Mass: 298.0396



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 6.92 (1H, s, Ar-H), 7.46 (3H, m, Ar-H), 7.63 (1H, dd, *J* = 8.1, 3.1 Hz), 7.79 (4H, m, Ar-H), 9.93 (2H, s, 2×OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 106.0 (CH), 122.3 (CH), 124.2 (CH), 126.4 (CH), 128.4 (CH), 129.4 (2×CH), 129.7 (C_q), 130.5 (CH), 130.9 (2×CH), 134.9 (C_q), 136.9 (C_q), 137.4 (C_q), 140.5 (C_q), 144.2 (C_q), 199.1 (C=O) ppm.

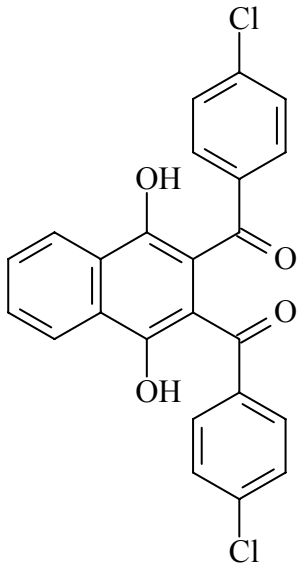
MS (EI): m/z (%) = 298 (M^+, 84%), 297 (10), 296 (8), 281 (3), 263 (3), 261 (19), 234 (3), 207 (6), 189 (2), 186 (100), 178 (3), 159 (3), 158 (11), 141 (14), 139 (41), 112 (3), 111 (25), 105 (6), 102 (18), 77 (12), 74 (4).

IR (KBr): $\tilde{\nu}$ = 3386, 2859, 1919, 1693, 1675, 1588, 1575, 1387, 1208, 1093, 840, 816 cm^{-1}.

HRMS (EI^+): found m/z 298.03797, calcd for $C_{17}H_{11}ClO_3$ M^+ 298.03967.

113b:

Molecular Formula: $C_{24}H_{14}Cl_2O_4$
Molecular Weight: 437.28
Exact Mass: 436.0269



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; acetone-d_6/DMSO-d_6) δ = 6.96 (4H, dd, *J* = 1.2, 8.1 Hz, Ar-H), 7.11 (4H, d, *J* = 8.1 Hz), 7.74 (2H, dd, *J* = 3.1, 3.1 Hz), 8.40 (2H, m, Ar-H), 12.12 (2H, s, 2×OH) ppm.

^{13}C NMR (125 MHz; acetone-d_6/DMSO-d_6) δ = 110.0 (C_q), 124.1 (2×CH), 128.0 (2×CH), 128.5 (C_q), 129.3 (4×CH), 130.0 (4×CH), 137.3 (C_q), 138.0 (C_q), 153.8 (C_q), 195.6 (C=O) ppm.

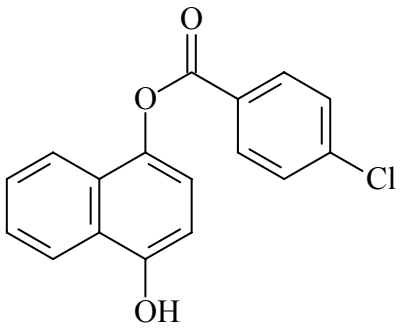
MS (EI): m/z (%) = 437 (M^+, 6%), 436 (22), 423 (3), 418 (100), 383 (3), 325 (2), 290 (4), 263 (3), 233 (3), 205 (2), 192 (2), 187 (4), 178 (2), 174 (11), 140 (18), 112 (10), 104 (2), 77 (4), 75 (10).

IR (KBr): $\tilde{\nu}$ = 3401, 1685, 1622, 1589, 1401, 1285, 1025, 1007, 842 cm^{-1}.

HRMS (EI^+): found m/z 436.02499, calcd for $C_{24}H_{14}Cl_2O_4$ M^+ 436.02691.

114b:

Molecular Formula: $C_{17}H_{11}ClO_3$
Molecular Weight: 298.73
Exact Mass: 298.0396



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 6.86 (1H, d, *J* = 8.1 Hz, Ar-H), 7.11 (1H, d, *J* = 8.1 Hz), 7.42 (2H, ddd, *J* = 3.5, 3.5, 3.5 Hz), 7.52 (2H, dddd, *J* = 1.8, 2.5, 1.8, 2.5 Hz), 7.72 (1H, dddd, *J* = 3.7, 3.1, 1.2, 3.1 Hz), 8.20 (2H, ddd, *J* = 1.8, 1.8, 2.5 Hz), 8.24 (1H, ddd, *J* = 2.5, 1.2, 3.1 Hz), 8.93 (1H, s, OH) ppm.

^{13}C NMR (125 MHz; acetone-d_6/DMSO-d_6) δ = 106.3 (CH), 117.5 (CH), 120.0 (CH), 121.9 (CH), 124.4 (CH), 124.7 (C_q), 125.9 (CH), 126.8 (C_q), 127.4 (C_q), 128.2 (2×CH), 130.8 (2×CH), 138.42 (C_q), 139.10 (C_q), 150.5 (C_q), 163.7 (C=O) ppm.

MS (EI): m/z (%) = 298 (M^+, 16%), 159 (3), 158 (2), 141 (2), 140 (32), 138 (100), 131 (3), 113 (6), 111 (19), 105 (3), 103 (4), 77 (7), 74 (2).

IR (KBr): $\tilde{\nu}$ = 3419, 1737, 1660, 1593, 1399, 1258, 1090, 1014, 755 cm^{-1}.

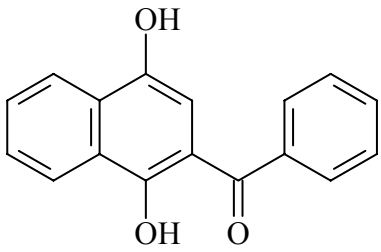
HRMS (EI^+): found m/z 298.03797, calcd for $C_{17}H_{11}ClO_3$ M^+ 298.03967.

8.9.5 (1,4-Dihydroxy-naphthalen-2-yl)-phenyl-methanone (112c) and (3-benzoyl-1,4-dihydroxy-naphthalen-2-yl)-phenyl-methanone (113c)[a]

Following the general procedure F, irradiation of 320 mg (2.1 mmol) of 1,4-naphthoquinone **104** and 2.0 g (18.9 mmol) of benzaldehyde **111c** in 44 ml of benzene for 24h. The crude product was purified with flash column chromatography (silica gel, 15% EA in CH) gave 246 mg (34%) of (1,4-dihydroxy-naphthalen-2-yl)-phenyl-methanone **112c** as yellow solid; mp 125°C and 90 mg (12%) of (3-benzoyl-1,4-dihydroxy-naphthalen-2-yl)-phenyl-methanone **113c** as yellow solid, mp 144-145°C.

112c:

Molecular Formula: $C_{17}H_{12}O_3$
Molecular Weight: 264.28
Exact Mass: 264.0786



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 6.85 (1H, s, Ar-H), 7.43 (2H, dd, *J* = 6.9, 7.5 Hz), 7.50 (2H, dd, *J* = 7.5, 7.5 Hz), 7.65 (2H, dd, *J* = 6.9, 1.2 Hz), 7.85 (1H, dd, *J* = 6.9, 1.8 Hz), 8.11 (1H, d, *J* = 8.1 Hz), 8.48 (1H, d, *J* = 8.1 Hz), 9.98 (1 H, s, OH), 13.53 (1H, s, OH) ppm.

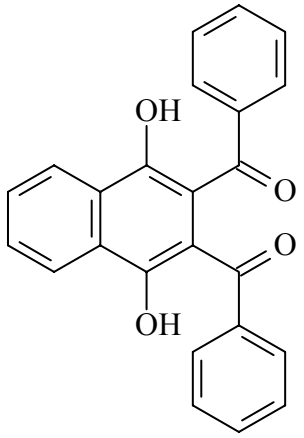
^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 107.9 (CH), 121.7 (CH), 124.5 (CH), 126.5 (CH), 128.2 (CH), 128.8 (2×CH), 128.9 (CH), 129.7 (CH), 130.0 (CH), 133.9 (C_q), 138.1 (C_q), 138.6 (C_q), 142.7 (C_q), 158.6 (C_q), 192.0 (C=O) ppm.

MS (EI): m/z (%) = 264 (M^+, 100%), 247 (3), 234 (3), 207 (3), 189 (4), 186 (70), 179 (2), 159 (4), 158 (11), 131 (13), 105 (49), 77 (87).

IR (KBr): $\tilde{\nu}$ = 3431, 3075, 1677, 1596, 1451, 1391, 1331, 1299, 1254, 1172, 1015, 769 cm^{-1}.

113c:

Molecular Formula: $C_{24}H_{16}O_4$
Molecular Weight: 368.39
Exact Mass: 368.1048



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 7.35–7.70 (10H, m, Ar-H), 7.83 (2H, m, Ar-H), 8.21 (2H, m, Ar-H), 9.60 (2H, s, 2×OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ = 118.7 (2×CH), 119.9 (2×C), 125.2 (2×CH), 128.1 (2×CH), 129.3 (2×CH), 131.1 (2×C), 136.5 (2×CH), 141.4 (2×C), 159.2 (2×C), 200.9 (2×C=O) ppm.

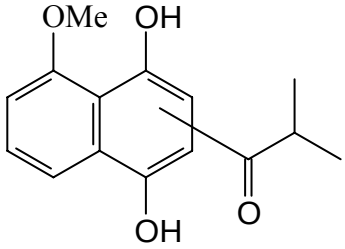
MS (EI): m/z (%) = 368 (M^+, 95), 350 (100), 289 (7), 263 (2), 233 (2), 205 (3), 178 (5), 152 (2), 105 (27), 77 (51), 51 (18), 39 (2).

IR (KBr): $\tilde{\nu}$ = 3300, 3060, 1730, 1620, 1590, 1490, 1440, 1240, 1170, 1030, 1010, 990, 830, 750, 690 cm^{-1}.

8.10 Photoacylation of Methyl Juglone with Aliphatic Aldehydes

8.10.1 1-(1,4-Dihydroxy-5-methoxy-naphthalen-2-yl)-2-methyl-propan-1-one and 1-(1,4-dihydroxy-8-methoxy-naphthalen-2-yl)-2-methyl-propan-1-one (117a)

Molecular Formula: $C_{15}H_{16}O_4$
Molecular Weight: 260.29
Exact Mass: 260.1048



Following the general procedure F, irradiation of 188 mg (1 mmol) of 5-methoxy-1,4-naphthoquinone **115** and 652 mg (9 mmol) of **116a** in 60 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave regioisomer A 35 mg (14%) and regioisomer B 59 mg (23%). **117a** as brown oil.

Regioisomer A:

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 1.29 (6H, d, *J* = 6.9 Hz, CH(C<u>H</u>$_3$)$_2$), 3.60 (1H, sep, *J* = 6.7 Hz, C<u>H</u>(CH$_3$)$_2$), 4.09 (3H; s, OMe) 7.02 (1H, d, *J* = 7.5 Hz, Ar-H), 7.10 (1H, s), 7.43 (1H, dd, *J* = 8.1, 8.1 Hz), 8.11 (1H, d, *J* = 8.1 Hz), 8.82 (1H, s, OH), 13.58 (1H, s, OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$)19.1 (CH(<u>C</u>H$_3$)$_2$), 35.2 (<u>C</u>H(CH$_3$)$_2$), 56.3 (OMe), 106.2 (CH), 108.0 (CH), 112.2 (C_q), 118.1 (CH), 119.5 (C_q), 125.9 (CH), 127.9 (C_q), 145.4 (C_q), 155.2 (C_q), 155.5 (C_q), 210.4 (C=O) ppm.

MS (EI): m/z (%) = 260 (M^+, 100%), 242 (27), 232 (4), 228 (7), 227 (40), 218 (13), 217 (99), 199 (9), 189 (31), 174 (25), 159 (3), 135 (3), 129 (5), 118 (10), 102 (6), 90 (3), 87 (2), 75 (4), 63 (46).

IR (KBr): $\tilde{\nu}$ = 3401, 2969, 1645, 1612, 1473, 1401, 1279, 1217, 911, 825, 750, 553 cm^{-1}.

HRMS (EI$^+$) found m/z 260.10344, calcd for $C_{20}H_{30}O_3$ M^+ 260.10486.

Regioisomer B:

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 1.10 (6H, d, *J* = 6.9 Hz, CH(<u>C</u>H$_3$)$_2$), 3.37 (1H, sep, *J* = 6.7 Hz, <u>C</u>H(CH$_3$)$_2$), 3.99 (3H, s, OMe), 6.88 (1H, d, *J* = 8.1 Hz, Ar-H), 7.09 (1H, s), 7.48 (1H, t, *J* = 8.1 Hz), 13.90 (2H, s, 2×OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ = 19.0 (CH_3), 36.05 (CH), 56.2 (OMe), 106.8 (CH), 106.9 (CH), 112.4 (C_q), 114.7 (CH), 116.7 (C_q), 129.8 (CH), 131.7 (C_q), 143.1 (C_q), 157.8 (C_q), 159.0 (C_q), 209.8 (C=O) ppm.

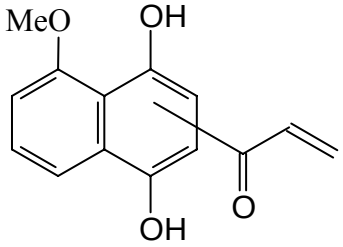
MS (EI): m/z (%) = 260 (M^+, 32%), 218 (13), 217 (100), 202 (10), 190 (2), 174 (4), 161 (3), 146 (4), 131 (5), 129 (3), 118 (9), 103 (3), 102 (5), 77 (3), 63 (31).

IR (KBr): $\tilde{\nu}$ = 3401, 2965, 1656, 1627, 1586, 146, 1382, 1047, 912, 811, 755 cm^{-1}.

HRMS (EI^+) found m/z 260.10344, calcd for $C_{20}H_{30}O_3$ M^+ 260.10486.

8.10.2 1-(1,4-Dihydroxy-5-methoxy-naphthalen-2-yl)-propenone or 1-(1,4-dihydroxy-8-methoxy-naphthalen-2-yl)-propenone (117b)

Molecular Formula: $C_{14}H_{12}O_4$
Molecular Weight: 244.25
Exact Mass: 244.0735



Following the general procedure F, irradiation of 188 mg (1 mmol) of 5-methoxy-1,4-naphthoquinone **115** and 504 mg (9 mmol) of acrolein in 60 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 36 mg (15%) of either 1-(1,4-dihydroxy-5-methoxy-naphthalen-2-yl)-propenone or 1-(1,4-dihydroxy-8-methoxy-naphthalen-2-yl)-propenone **117b** as brown oil.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 3.94 (3H, s, OMe), 6.73 (1H, d, *J* = 8.0 Hz), 6.80 (1H, d, *J* = 8.0 Hz), 7.18 (1H, t, *J* = 8.0 Hz), 7.39 (1H, s, Ar-H), 7.75 (3H, dd, *J* = 8.0, 7.6 Hz), 9.52 (1H, s, OH), 10.96 (1H, s, OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) 55.0 (OMe), 107.6 (CH), 108.3 (CH), 115.5 (CH), 125.1 (2 × CH), 126.1 (C_q), 126.7 (C_q), 129.4 (CH), 134.9 (C_q), 136.3 (C_q), 140.6 (C_q), 156.2 (C_q), 158.0 (C_q), 194.1 (C=O) ppm.

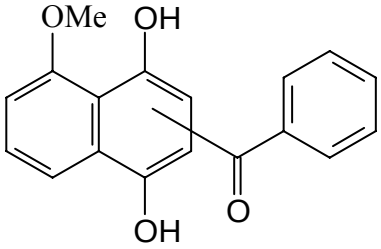
MS (EI): m/z (%) = 244 (M^+, 4%), 228 (5), 203 (14), 190 (18), 185 (24), 183 (2), 173 (10), 159 (11), 145 (4), 131 (31), 115 (24), 102 (12), 91 (3), 77 (13), 58 (12), 55 (22).

IR (KBr): $\tilde{\nu}$ = 3451, 2925, 2846, 1716, 1653, 1594, 1441, 1285, 1249, 1171, 1079, 1038, 722 cm^{-1}.

8.11 Photoacylation of Methyl Juglone with Aromatic Aldehydes

8.11.1 (1,4-Dihydroxy-5-methoxy-naphthalen-2-yl)-phenyl-methanone and (1,4-dihydroxy-8-methoxy-naphthalen-2-yl)-phenyl-methanone (117c)

Molecular Formula: $C_{18}H_{14}O_4$
Molecular Weight: 294.31
Exact Mass: 294.0892



Following the general procedure F, irradiation of 188 mg (1 mmol) of 5-methoxy-1,4-naphthoquinone **115** and 954 mg (9 mmol) of benzaldehyde **116c** in 60 ml of benzene for 53h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave regioisomer A 48 mg (16%) and regioisomer B 40 mg, (14%) **117c**.

Regioisomer A:

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) 4.05 (3H, s, OMe), 6.93 (1H s, Ar-H) 7.02 (1H, d, *J* = 7.5 Hz), 7.42 (1H, dd, *J* = 8.1, 8.1 Hz), 7.49 (2H, dd, *J* = 7.5, 7.5 Hz), 7.53 (2H, ddd, *J* = 7.5, 1.2, 8.1 Hz), 7.70 (2H, dd, *J* = 6.9, 1.2 Hz), 8.14 (1H, d, *J* = 7.5 Hz), 8.78 (1H, s, OH), 13.23 (1H, s, OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 56.3 (OMe), 109.2 (CH), 118.2 (CH), 126.0 (CH), 127.8 (C_q), 128.0 (C_q), 128.3 (2×CH), 128.9 (2×CH), 130.2 (CH), 131.6 (CH), 133.2 (C_q), 133.6 (C_q), 138.0 (C_q), 145.1 (C_q), 155.8 (C_q), 201.2 (C=O) ppm.

MS (EI): m/z (%) = 294 (M^+, 21%), 263 (6), 246 (6), 216 (3), 189 (6), 116 (4), 105 (100), 78 (3), 77 (40), 51 (8).

IR (KBr): $\tilde{\nu}$ = 3405, 1710, 1595, 1488, 1393, 1260, 1241, 1220, 1044, 889, 822 cm^{-1}.

Regioisomer B:

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

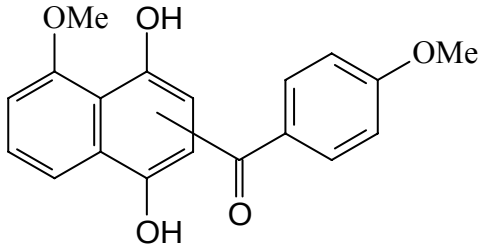
^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 3.99 (3H, s, OMe), 6.57 (1H, d, *J* = 7.8 Hz, Ar-H), 6.91 (1H, s), 7.39 (2H, dd, *J* = 7.5, 1.2 Hz), 7.46 (2H, dd, *J* = 7.8, 1.2 Hz), 7.70 (2H, ddd, *J* = 6.9, 1.2, 6.9 Hz), 7.76 (1H, d, *J* = 8.1 Hz), 8.80 (1H, s, OH), 11.91 (1H, s, OH) ppm. **^{13}C NMR** (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 56.2 (OMe), 106.5 (CH), 109.6 (CH), 115.2 (CH), 116.1 (C_q), 118.2 (C_q), 128.1 (2×CH), 129.3 (2×CH), 130.5 (C_q), 131.9 (CH), 138.4 (C_q), 143.1 (C_q), 158.2 (C_q), 199.1 (C=O) ppm.

MS (EI): m/z (%) = 294 (M^+, 21%), 293 (10), 292 (45), 291 (14), 278 (5), 276 (6), 275 (30), 264 (5), 263 (5), 247 (3), 246 (3), 217 (3), 201 (4), 189 (4), 159 (4), 116 (5), 106 (8), 105 (100), 104 (4), 101 (4), 88 (3), 77 (52).

IR (KBr): $\tilde{\nu}$ = 3407, 2940, 1735, 1600, 1449, 1395, 1261, 1070, 1047, 888, 704 cm^{-1}.

8.11.2 (1,4-Dihydroxy-5-methoxy-naphthalen-2-yl)-(4-methoxy-phenyl)-methanone and (1,4-dihydroxy-8-methoxy-naphthalen-2-yl)-(4-methoxy-phenyl)-methanone (117d)

Molecular Formula: $C_{19}H_{16}O_5$
Molecular Weight: 324.33
Exact Mass: 324.0997



Following the general procedure F, irradiation of 188 mg (1 mmol) of 5-methoxy-1,4-naphthoquinone **115** and 1.22 g (9 mmol) of *p*-methoxybenzaldehyde **116d** in 60 ml of benzene for 18h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave regioisomer A 60 mg, (19%) as light orange solid, mp 132–134 °C and regioisomer B 50 mg, (15%) as brown solid**,** mp 172–175 °C **117d**.

Regioisomer A:;

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 3.88 (3H, s, OMe), 4.05 (3H, s, OMe), 6.56–7.03 (4H, m, Ar-H), 7.44 (1H, dd, *J* = 8.1, 8.1 Hz, Ar-H), 7.74 (2H, dd, *J* = 1.8, 8.7 Hz), 8.12 (1H, d, *J* = 8.7 Hz), 8.77 (1H, s, OH), 13.14 (1H, s, OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 55.4 (OMe), 56.3 (OMe), 108.6 (CH), 109.4 (CH), 113.6 (2×CH), 118.1 (CH), 118.9 (C_q), 120.2 (C_q), 125.9 (CH), 131.6 (2×CH), 132.3 (C_q), 145.0 (C_q), 152.4 (C_q), 155.3 (C_q), 162.6 (C_q), 199.6 (C=O) ppm.

MS (EI): m/z (%) = 324 (M^+, 25%), 323 (3.2), 321 (3.4), 293 (2.5), 217 (6.2), 216 (45.8), 201 (2.0), 189 (3.8), 188 (9.0), 174 (3.1), 161 (2.7), 160 (17.8), 152 (17.8), 145 (3.8), 136 (8.9), 135 (8.9), 131 (2.9), 118 (2.9), 107 (7.0), 92 (11.3), 77 (14.9).

IR (KBr): $\tilde{\nu}$ = 3359, 2937, 2835, 2366, 1728, 1605, 1463, 1395, 1258, 1171, 1073, 1028, 888, 780, 752 cm^{-1}.

HRMS (EI^+): found m/z 324.09930, calcd for $C_{19}H_{16}O_5$ M^+ 324.09977.

Regioisomer B:

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 3.75 (3H, s, OMe), 3.92 (3H, s, OMe), 6.81 (4H, dddd, *J* = 2.5, 10.6, 8.7, 7.5 Hz, Ar-H), 7.34 (1H, ddd, *J* = 8.1, 5.6, 2.5 Hz), 7.72 (3H, dd, *J* = 8.7, 1.8 Hz), 7.69 (1H, s, OH), 11.18 (1H, s, OH) ppm.

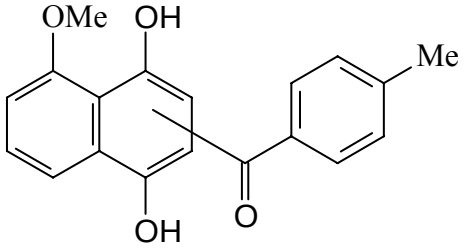
^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 55.1 (OMe), 55.9 (OMe), 105.8 (CH), 109.6 (CH), 113.2 (2×CH), 115.5 (CH), 127.5 (CH), 130.0 (C_q), 131.0 (C_q), 131.7 (2×CH), 132.6 (C_q), 135.6 (C_q), 144.2 (C_q), 151.0 (C_q), 157.6 (C_q), 162.6 (C_q), 196.9 (C=O) ppm. **MS (EI)**: m/z (%) = 324 (M^+, 7%), 323 (13), 322 (60), 321 (3), 307 (4), 294 (7), 291 (3), 251 (2), 188 (5), 187 (3), 152 (2), 147 (3), 136 (9), 135 (100), 116 (3), 107 (9), 104 (3), 101 (2).

IR (KBr): $\tilde{\nu}$ = 3414, 1664, 1599, 1510, 1406, 1259, 1169, 1050, 988, 824, 761 cm^{-1}.

HRMS (EI^+): found m/z 324.09930, calcd for $C_{19}H_{16}O_5$ M^+ 324.09977.

8.11.3 (1,4-Dihydroxy-5-methoxy-naphthalen-2-yl)-*p*-tolyl-methanone and (1,4-dihydroxy-8-methoxy-naphthalen-2-yl)-*p*-tolyl-methanone (117e)

Molecular Formula: $C_{19}H_{16}O_4$
Molecular Weight: 308.33
Exact Mass: 308.1048



Following the general procedure F, irradiation of 188 mg (1 mmol) of 5-methoxy-1,4-naphthoquinone **115** and 1.08 g (9 mmol) of *p*-methyl-benzaldehyde **116e** in 60 ml of benzene for 15h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave regioisomer A 140 mg (46%) as brown solid, mp 166–169 °C and regioisomer B 60 mg (20%) as brown solid**,** mp 205–206°C **117e**.

Regioisomer A:

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 2.43 (3H, s, Me), 4.05 (3H, s, OMe), 6.96 (1H, s, Ar-H), 7.02 (1H, d, *J* = 7.5 Hz), 7.29 (2H, d, *J* = 8.1 Hz), 7.42 (1H, t, *J* = 8.1 Hz), 7.63 (2H, d, *J* = 7.5 Hz), 8.12 (d, 1H, *J* = 8.1 Hz), 8.76 (1H, s, OH), 13.20 (1H, s, OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ =21.6 (CH_3), 56.3 (OMe), 104.5 (C_q), 108.8 (CH), 109.4 (CH), 118.2 (CH), 125.9 (CH), 126.4 (C_q), 127.7 (C_q), 128.8 (2×CH), 129.3 (2×CH), 130.2 (C_q), 135.3 (C_q), 142.3 (C_q), 145.11 (C_q), 155.6 (C_q), 200.9 (C=O) ppm.

MS (EI): m/z (%) = 308 (M^+, 100%), 293 (5.0), 247 (3), 247 (9), 216 (63), 201 (7), 189 (8), 188 (14), 174 (6), 173 (14), 160 (27), 145 (8), 130 (2), 120 (8), 118 (6), 102 (6), 91 (38), 65 (12).

IR (KBr): $\tilde{\nu}$ = 3427, 1737, 1608, 1465, 1395, 1236, 1213, 1073, 888, 776, 749 cm^{-1}.

HRMS (EI^+): found m/z 308.10440, calcd for $C_{19}H_{16}O_4$ M^+ 308.10486.

Regioisomer B:

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; acetone-d_6/DMSO-d_6) δ =2.37 (3H, s, Me), 4.01 (3H, s, OMe), 6.90 (2H, s, 2×OH), 6.94 (2H, dd, *J* = 3.1, 8.1 Hz, Ar-H), 7.24 (2H, d, *J* = 8.1 Hz), 7.47 (1H, t, *J* = 8.1 Hz), 7.65 (2H, d, *J* = 8.1 Hz), 7.79 (1H, t, *J* = 8.4 Hz) ppm.

^{13}C NMR (125 MHz; acetone-d_6/DMSO-d_6) δ = 20.1 (Me), 55.0 (OMe), 105.3 (CH), 107.6 (CH), 114.5 (CH), 114.9 (CH), 116.0 (CH), 127.0 (CH), 127.7 (CH), 128.4 (CH), 135.12 (C_q), 141.4 (C_q), 143.6 (C_q), 150.7 (C_q), 157.1 (C_q), 196.8 (C=O) ppm.

MS (EI): m/z (%) = 308 (M^+, 100%), 307 (8), 293 (7), 289 (4), 275 (3), 265 (3), 261 (3), 250 (3), 237 (3), 221 (2), 217 (12), 188 (39), 171 (8), 160 (3), 146 (3), 130 (5), 119 (38), 102 (5), 91 (37), 65 (12).

IR (KBr): $\tilde{\nu}$ = 3424, 1671, 1604, 1585, 1471, 1297, 1274, 1199, 1051, 1006, 821, 766 cm^{-1}.

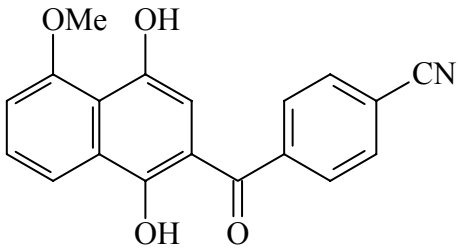
HRMS (EI^+): found m/z 308.10440, calcd for $C_{19}H_{16}O_4$ M^+ 308.10486.

8.11.4 4-[(1,4-Dihydroxy-8-methoxy-2-naphthyl)carbonyl]benzonitrile (119) and 5-methoxy-naphthalene-1,4-diol (120)

Following the general procedure, irradiation of 188 mg (1 mmol) of 5-methoxy-1,4-naphthoquinone **155** and 1.18 g (9 mmol) of *p*-cyanobenzaldehyde **118** in 90 ml of benzene for 12 h, followed by flash column chromatography (silica gel, 30% EA in CH) gave 39 mg (12%) of 4-[(1,4-dihydroxy-8-methoxy-2-naphthyl)carbonyl]benzonitrile **119** as brown solid, 186–188 °C and 27 mg (13%) of 5-methoxy-naphthalene-1,4-diol **120**.

119:

Molecular Formula: $C_{19}H_{13}NO_4$
Molecular Weight: 319.32
Exact Mass: 319.0844



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; acetone-d_6) δ = 4.17 (3H, s, OMe), 6.68 (1H, s, Ar-H), 7.33 (1H, d, *J* = 7.5 Hz), 7.58 (1H, t, *J* = 8.1 Hz), 7.94 (2H, d, *J* = 8.1 Hz), 8.04 (2H, d, *J* = 8.1 Hz), 8.09 (1H, d, *J* = 8.1 Hz), 8.91 (1H, s, OH), (1H, s, OH, not observed) ppm.

^{13}C NMR (125 MHz; acetone-d_6) δ = 57.0 (OMe), 108.7 (CH), 110.8 (CH), 113.6 (C_q), 115.7 (C_q), 118.1 (CH), 118.7 (C_q), 127.8 (CH), 128.2 (C_q), 130.2 (2×CH), 131.2 (C_q), 133.2 (2×CH), 142.7 (C_q), 146.8 (C_q), 156.4 (C_q), 156.9 (C_q), 200.6 (C=O) ppm.

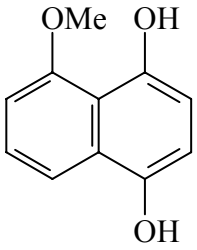
MS (EI): m/z (%) = 319 (M^+, 74%), 189 (45), 161 (14), 130 (100), 103 (16), 76 (10).

IR (KBr): $\tilde{\nu}$ = 3412, 2365, 1718, 1599, 1386, 1348, 1286, 1260, 1105, 1077, 1051, 1015 cm^{-1}.

HRMS (EI^+): found m/z 319.08504, calcd for $C_{19}H_{13}NO_4$ M^+ 319.08446.

120:[123]

Molecular Formula: $C_{11}H_{10}O_3$
Molecular Weight: 190.20
Exact Mass: 190.062994



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 3.48 (3H, s, OMe), 4.00 (1H, s, OH), 4.06 (1H, s, OH), 6.78 (1H, d, *J* = 7.5 Hz, Ar-H), 6.85 (1H, d, *J* = 8.1 Hz), 6.93 (1H, dd, *J* = 8.1, 1.2 Hz), 7.30 (1H, dd, *J* = 8.1, 8.1 Hz), 8.30 (1H, dd, *J* = 1.8, 8.1 Hz) ppm.

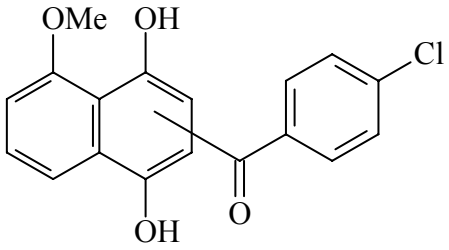
^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 55.5 (OMe), 106.5 (CH), 107.8 (CH), 115 (CH), 119.0 (CH), 125.4 (CH), 129.4 (C_q), 129.6 (C_q), 130.6 (C_q), 132.3 (C_q), 152.1 (C_q) ppm.

8.11.5 (4-Chloro-phenyl)-(1,4-dihydroxy-5-methoxy-naphthanlen-2-yl)-methanone or (4-chloro-phenyl)-(1,4-dihydroxy-8-methoxy-2-naphthanlen-2-yl)-methanone (122), [3-(4-chloro-benzoyl)-1,4-dihydroxy-8-methoxy-naphthalen-2-yl]-(4-chloro-phenyl)-methanone (123), 4-chloro-benzoic acid 4-hydroxy-8-methoxy-naphthalen-1-yl ester (124) and 5-methoxy-naphthalene-1,4-diol (120)

Following the general procedure F, irradiation of 188 mg (1 mmol) of 5-methoxy-1,4-naphthoquinone **115** and 1.26 g (9 mmol) of *p*-chlorobenzaldehyde **121** in 60 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 76 mg (22%) of either (4-chloro-phenyl)-(1,4-dihydroxy-5-methoxy-2-naphthanlen-2-yl)-methanone or (4-chloro-phenyl)-(1,4-dihydroxy-8-methoxy-2-naphthanlen-2-yl)-methanone **122** brown solid, mp 173–176 °C**,** 34 mg (7%) of [3-(4-chloro-benzoyl)-1,4-dihydroxy-8-methoxy-naphthalen-2-yl]-(4-chloro-phenyl)-methanone **123** as brown solid, mp 144–146 °C, 38 mg (11%) of 4-chloro-benzoic acid 4-hydroxy-8-methoxy-naphthalen-1-yl ester **124** as brown solid mp 177–179 °C and 15 mg (8%) of 5-methoxy-naphthalene-1,4-diol **120**.

122:

Molecular Formula: $C_{18}H_{13}ClO_4$
Molecular Weight: 328.75
Exact Mass: 328.0502



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; CD_2Cl_2) δ = 4.07 (3H, s, OMe), 6.85 (1H, s, Ar-H), 7.10 (1H, d, *J* = 8.1 Hz), 7.48 (1H, d, *J* = 8.1 Hz), 7.52 (2H, dd, *J* = 1.8, 8.1 Hz), 7.69 (2H, dd, *J* = 8.7, 1.8 Hz), 8.12 (1H, d, *J* = 7.5 Hz), 8.80 (1H, s, OH), 13.05 (1H, s, OH) ppm.

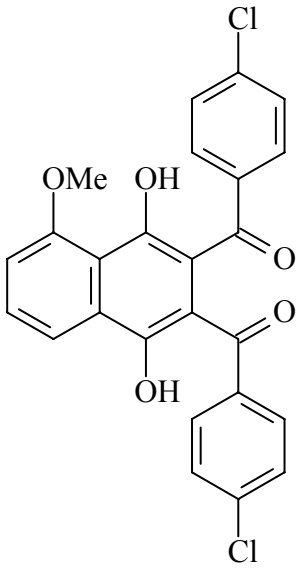
^{13}C NMR (125 MHz; CD_2Cl_2) δ = 56.8 (OMe), 108.9 (CH), 109.5 (CH), 113.3 (C_q), 118.2 (CH), 126.7 (CH), 128.9 (2×CH), 130.9 (2×CH), 131.9 (C_q), 136.8 (C_q), 138.2 (C_q), 145.9 (C_q), 156.0 (C_q), 156.2 (C_q), 200.2 (C=O) ppm.

MS (EI): m/z (%) = 328 (M^+, 41%), 326 (13), 216 (12), 189 (19), 160 (6), 139 (100), 111 (27),, 75 (14).

IR (KBr): $\tilde{\nu}$ = 3380, 2865, 1912, 1689, 1670, 1590, 1386, 1209, 1090, 850 cm^{-1}.

HRMS (EI$^+$): found m/z 328.05053, calcd for $C_{18}H_{13}ClO_4$ M^+ 328.05024.

123:



Molecular Formula: $C_{25}H_{16}Cl_2O_5$
Molecular Weight: 467.31
Exact Mass: 466.0374

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; acetone-d_6) δ = 4.19 (3H, s, OMe), 7.32 (3H, dd, *J* = 8.1, 5.0 Hz, Ar-H), 7.46 (2H, d, *J* = 8.1 Hz), 7.66 (3H, ddd, *J* = 8.1, 8.7, 1.8 Hz), 7.80 (2H, d, *J* = 8.7 Hz), 8.00 (1H, d, *J* = 8.7 Hz), 9.54 (1H, s, OH), (1H, s, OH, not observed) ppm.

^{13}C NMR (125 MHz; acetone-d_6) δ = 57.1 (OMe), 109.4 (CH), 117.3 (CH), 119.5 (C_q), 120.2 (C_q), 129.1 (4×CH), 129.3 (CH), 130.0 (C_q), 131.6 (2×CH), 132.0 (2×CH), 138.2 (C_q), 138.5 (C_q), 138.8. (C_q), 139.0 (C_q), 147.6 (C_q), 157.9 (C_q), 194.9 (C=O), 197.6 (C=O) ppm.

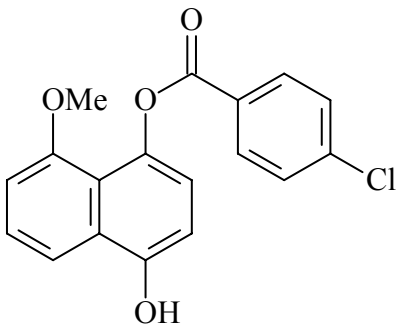
MS (EI): m/z (%) = 466 (M^+, 10%), 450 (3), 433 (2), 396 (1), 206 (4), 189 (5), 139 (17), 111(9) 75 (2), 43 (100).

IR (KBr): $\tilde{\nu}$ = 3426, 1737, 1641, 1599, 1463, 1439, 1397, 1257, 1225, 1170, 1072, 1011 cm^{-1}.

HRMS (EI^+): found m/z 466.0377, calcd for $C_{25}H_{16}Cl_2O_5$ M^+ 466.03747.

124:

Molecular Formula: $C_{18}H_{13}ClO_4$
Molecular Weight: 328.75
Exact Mass: 328.0502



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 3.59 (3H, s, OMe), 6.94 (1H, d, *J* = 4.4 Hz), 6.96 (1H, d, *J* = 4.4 Hz) 7.04 (1H, d, *J* = 8.1 Hz), 7.40 (1H, t, *J* = 8.1 Hz), 7.66 (2H, d, *J* = 8.7 Hz), 7.88 (1H, d, *J* = 8.7 Hz), 8.21 (2H, d, *J* = 8.7 Hz), 9.18 (1H, s, OH) ppm.

^{13}C NMR (125 MHz; $CDCl_3$/acetone-d_6 1:1) δ = 56.0 (OMe), 107.4 (CH), 108.6 (CH), 115.8 (CH), 120.1 (CH), 120.6 (C_q), 126.2 (CH), 128.3 (C_q), 129.7 (2×CH), 130.3 (C_q), 132.4 (2×CH), 139.6 (C_q), 140.0 (C_q), 151.9 (C_q), 156.0 (C_q), 165.6 (C=O) ppm.

MS (EI): m/z (%) = 328 (M^+, 18%), 216 (8), 189 (7), 138 (19), 110 (5), 83 (2), 58 (46), 43 (100).

HRMS (EI^+): found m/z 328.048390, calcd for $C_{18}H_{13}ClO_4$ M^+ 328.05023.

IR (KBr): $\tilde{\nu}$ = 3627, 2324, 2296, 1778, 1652, 1583, 1485, 1246, 1091 cm^{-1}.

120:[123] See previously described analytical data for compound **120**.

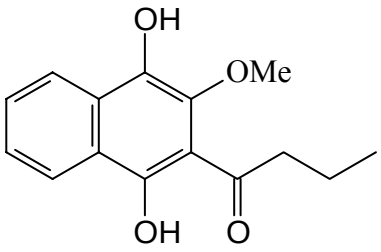
8.12 Photoacylation Reactions of 2-Methoxy-1,4-Naphthoquinone

8.12.1 1-(1,4-Dihydroxy-3-methoxy-naphthalen-2-yl)-butan-1-one (126) and 2-butyryl-3-methoxy-1,4-naphthoquinone (127)

Following the general procedure F, irradiation of 188 mg (1 mmol) of 2-methoxy-1,4-naphthoquinone **125** and 576 mg (8 mmol) of butyraldehyde **105**a in 60 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) and HPLC gave 63 mg (24%) of 1-(1,4-dihydroxy-3-methoxy-naphthalen-2-yl)-butan-1-one **126** brown solid, mp 109–110 °C and 29 mg (11%) of 2-butyryl-3-methoxy-1,4-naphthoquinone **127** as brown solid, mp 144-146 °C.

126:

Molecular Formula: $C_{15}H_{16}O_4$
Molecular Weight: 260.29
Exact Mass: 260.1048



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 0.93 (3H, t, *J* = 7.2 Hz, *CH*$_3$-CH_2), 1.75 (2H, m), 3.80 (3H, s, OMe), 5.59 (1H, s, OH), 7.46 (1H, dd, *J* = 7.2, 1.2 Hz, Ar-H), 7.63 (1H, dd, *J* = 1.2, 7.2 Hz), 8.08 (1H, d, *J* = 8.1 Hz), 8.37 (1H, d, *J* = 8.1 Hz), 13.8 (1H, s, OH) ppm.

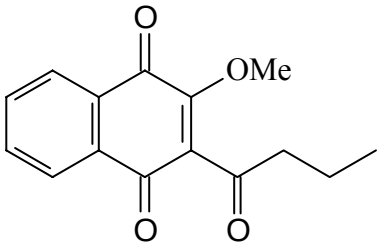
^{13}C NMR (125 MHz; $CDCl_3$) δ = 13.9 (CH_3), 18.3 (CH_2), 44.2 (CH_2), 62.3 (OMe), 108.8 (CH), 121.4 (CH), 123.1 (C_q), 124.5 (CH), 125.5 (CH), 128.4 (C_q), 129.9 (C_q), 135.9 (C_q), 138.4 (C_q), 157.3 (C_q), 206.3 (C=O) ppm.

MS (EI): m/z (%) = 260 (M^+, 94%), 258 (52), 257 (6), 246 (36), 231 (34), 230 (57), 227 (57), 217 (27), 209 (14), 199 (19), 190 (66), 181 (11), 174 (16), 163 (22), 159 (13), 128 (12), 115 (21), 105 (37), 89 (22), 79 (4), 71 (77).

IR (KBr): $\tilde{\nu}$ = 3427, 2964, 2937, 2365, 1708, 1679, 1626, 1600, 1570, 1454, 1399, 1332, 1772, 1216, 1124, 1046, 911, 729 cm^{-1}.

127:

Molecular Formula: $C_{15}H_{14}O_4$
Molecular Weight: 258.27
Exact Mass: 258.0892



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 0.97 (3H, t, *J* = 7.2 Hz, *CH*$_3$-CH_2), 1.71 (2H, m), 2.72 (2H, t, *J* = 7.5 Hz), 4.10 (3H, s, OMe), 7.73 (2H, m, Ar-H), 8.04 (2H, m) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) 13.6 (CH_3), 16.6 (CH_2), 46.8 (CH_2), 61.4 (OMe), 126.1 (CH), 126.5 (CH), 130.0 (C_q), 130.9 (C_q), 131.1 (C_q), 133.7 (CH), 134.5 (CH), 155.3 (C_q), 181.4 (C=O), 183.7 (C=O), 202.0 (C=O) ppm.

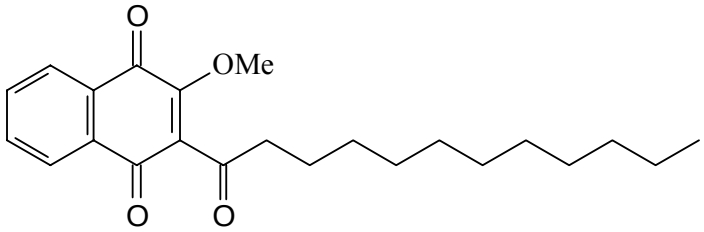
MS (EI): m/z (%) = 258 (M^+, 4%), 257 (1), 243 (8), 230 (6), 228 (9), 215 (100), 209 (1), 187 (71), 173 (10), 167 (5), 149 (4), 129 (4), 104 (23), 89 (7), 87 (2), 76 (21), 71 (13).

IR (KBr): $\tilde{\nu}$ = 3441, 2699, 2877, 2359, 1709, 1662, 1581, 1440, 1274, 1071, 902, 735 cm^{-1}.

HRMS (EI^+) found m/z 258.08939, calcd for $C_{15}H_{14}O_4$ M^+ 258.08921.

8.12.2 2-Dodecanoyl-3-methoxy-1,4-naphthoquinone (128)

Molecular Formula: $C_{23}H_{30}O_4$
Molecular Weight: 370.49
Exact Mass: 370.2144



Following the general procedure F, irradiation of 188 mg (1 mmol) of 2-methoxy-1,4-naphthoquinone **125** and 1.69 g (9 mmol) of dodecanal **105b** in 60 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 85 mg (23%) of 2-dodecanoyl-3-methoxy-1,4-naphthoquinone **128** as thick brown oil.

1D NMR analysis (^1H, ^{13}C, ^{13}C-DEPT);

^1H NMR (500 MHz; $CDCl_3$) δ = 0.85 (3H, *J* = 7.2 Hz, *CH_3*-CH_2), 1.23 (m, 16H), 2.70–2.75 (3H, t, *J* = 7.2 Hz), 4.09 (3H, s, OMe), 7.71 (ddd, 2H, *J* = 1.2, 7.5, 6.9 Hz), 8.03 (2H, ddd, *J* = 1.2, 6.9, 8.7 Hz) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ = 14.1 (CH_3), 22.6 (CH_2), 23.12 (CH_2), 29.0 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 45.0 (CH_2), 61.4 (OCH_3), 126.1 (CH), 126.5 (CH), 130.9 (CH), 131.1 (CH), 133.7 (CH), 134.5 (CH), 155.2 (C_q), 157.2 (C_q), 181.4 (C=O), 183.8 (C=O), 202.2 (C=O) ppm.

MS (EI): m/z (%) = 370 (M^+, 51%), 358 (1), 355 (4), 342 (22), 328 (3), 281 (11), 267 (3), 245 (5), 230 (70), 215 (100), 202 (13), 190 (10), 188 (14), 187 (58), 174 (5), 173 (13), 163 (6), 157 (4), 147 (2), 130 (2), 155 (4), 105 (11), 101 (5), 91 (5), 77 (8), 69 (9), 57 (16).

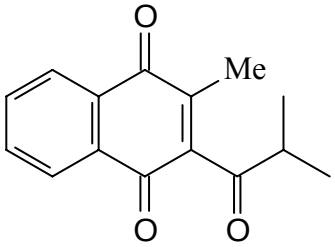
IR (KBr): $\tilde{\nu}$ = 2925, 2854, 2365, 1710, 1679, 1647, 1599, 1460, 1369, 1332, 1300, 1270, 1217 cm^{-1}.

HRMS (EI^+): found m/z 370.21447, cald for: $C_{23}H_{30}O_4$ M^+ 370.21441.

8.13 Photoacylation Reactions of 2-Methyl-1,4-Naphthoquinone

8.13.1 2-Isobutyryl-3-methyl-1,4-naphthoquinone (131a)

Molecular Formula: $C_{15}H_{14}O_3$
Molecular Weight: 242.27
Exact Mass: 242.0942



Following the general procedure F, irradiation of 344 mg (2 mmol) of 2-methyl-1,4-naphthoquinone **129** and 1.30 g (18 mmol) of isobutyraldehyde **130a** in 90 ml of benzene for 18h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 170 mg (36%) of 2-isobutyryl-3-methyl-1,4-naphthoquinone **131a** as brown oil.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 1.18 (6H, d, *J* = 7.5 Hz, CH*(CH$_3$)$_2$*), 2.05 (3H, s, Me), 2.96 (pentate, 1H, *J* = 6.9 Hz, *CH*$(CH_3)_2$), 7.79 (1H, dd, *J* = 3.7, 8.7 Hz, Ar-H), 8.02 (2H, dd, *J* = 8.7, 3.1 Hz), 8.08 (1H, ddd, *J* = 8.7, 1.2, 5.6 Hz) ppm.

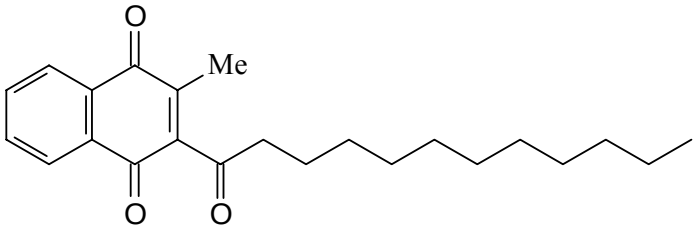
^{13}C NMR (125 MHz; $CDCl_3$) δ = 17.3 (2×CH_3), 20.9 (CH_3), 41.6 (CH), 126.1 (CH), 126.5 (CH), 131.2 (C_q), 131.7 (C_q), 134.0 (2×CH), 143.2 (C_q), 145.4 (C_q), 183.6 (C=O), 184.9 (C=O), 207.7 (C=O) ppm.

MS (EI): m/z (%) = 242 (M^+, 76%), 241 (5), 227 (12), 216 (4), 214 (8), 199 (74), 188 (21), 174 (75), 159 (13), 143 (16), 115 (100), 104 (35), 89 (22), 76 (51)

IR (KBr): $\tilde{\nu}$ = 2971, 1699, 1662, 1595, 1465, 1382, 1328, 1290, 1260, 998, 780, 705 cm^{-1}.

8.13.2 2-Dodecanoyl-3-methyl-1,4-naphthoquinone (131b)

Molecular Formula: $C_{23}H_{30}O_3$
Molecular Weight: 354.49
Exact Mass: 354.2194



Following the general procedure F, irradiation of 344 mg (2 mmol) of 2-methyl-1,4-naphthoquinone **129** and 3.32 g (18 mmol) of dodecanal **130b** in 100 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 280 mg (39%) of 2-dodecanoyl-3-methyl-1,4-naphthoquinone **131b** as yellow solid, mp 91–92 °C.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 0.84 (3H, t, *J* = 6.9 Hz, $CH_2\mathit{CH_3}$), 1.10–1.30 (16H, m; -$\mathit{(CH_2)_8}$-), 2.05 (3H, s, Me), 2.70 (2H, t, *J* = 7.5 Hz), 7.71 (2H, dd, *J* = 3.1, 9.4 Hz, Ar-H), 8.01 (2H, dd, *J* = 3.1, 9.3 Hz) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ = 13.1 ($CH_2\mathit{CH_3}$), 14.0 (CH_2), 22.6 (Me), 22.9 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.8 (CH_2), 44.2 (CH_2), 126.1 (CH), 126.5 (CH), 131.5 (CH), 131.6 (C_q), 134.0 (CH), 134.1 (C_q), 142.4 (C_q), 145.0 (C_q), 183.4 (C=O), 185.0 (C=O), 204.0 (C=O) ppm.

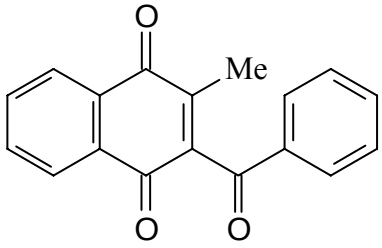
MS (EI): m/z (%) = 354 (M^+, 57%), 339 (12), 255 (16), 241 (13), 227 (20), 214 (100), 201 (28), 186 (16), 174 (89), 143 (13), 115 (47), 105 (14), 91 (5), 76 (17), 71 (17), 43 (61).

IR (KBr): $\tilde{\nu}$ = 2917, 2851, 1704, 1666, 1595, 1464, 1377, 1326, 1292, 1145, 1117, 720 cm^{-1}.

HRMS (EI^+): found m/z 354.21890, calcd for $C_{23}H_{30}O_3$ M^+ 354.21949.

8.13.3 2-Benzoyl-3-methyl-1,4-naphthoquinone (131c)

Molecular Formula: $C_{18}H_{12}O_3$
Molecular Weight: 276.29
Exact Mass: 276.0786



Following the general procedure, irradiation of 344 mg (2 mmol) of 2-methyl-1,4-naphthoquinone **129** and 1.91 g (18 mmol) of benzaldehyde **130c** in 100 ml of benzene for 18h, followed by flash column chromatography (silica gel, 30% EA in CH) gave 126 mg (23%) of 2-benzoyl-3-methyl-1,4-naphthoquinone **131c**.

Pale yellow solid, 146–147 °C;

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 2.04 (3H, s, Me), 7.47 (dd, 2H, *J* = 7.8 Hz, Ar-H), 7.61 (1H, dd, *J* = 7.5, 1.2 Hz), 7.73 (2H, m,), 7.88 (2H, dd, *J* = 7.5, 1.2 Hz), 8.05 (1H, ddd, *J* = 1.2, 2.5, 7.8 Hz), 8.15 (1H, ddd, *J* = 1.8, 1.2, 7.5 Hz) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ = 13.5 (Me), 126.3 (CH), 129.0 (2×CH), 129.1 (2×CH), 131.5 (C_q), 131.8 (C_q), 134.0 (CH), 134.1 (CH), 134.5 (CH), 135.6 (C_q), 143.9 (C_q), 144.3 (C_q), 183.3 (C=O), 184.7 (C=O), 193.6 (C=O) ppm.

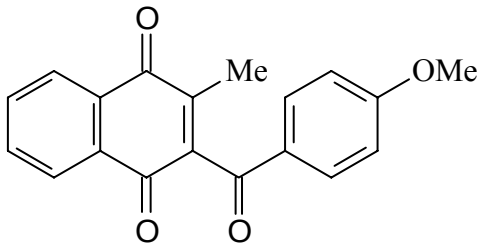
MS (EI): m/z (%) = 276 (M^+, 73%), 275 (24), 248 (3), 247 (11), 233 (3), 219 (3), 202 (2), 191 (2), 189 (2), 171 (4), 143 (2), 116 (2), 115 (15), 106 (7), 105 (100), 89 (5), 78 (4), 67 (5).

IR (KBr): $\tilde{\nu}$ = 1676, 1657, 1629, 1596, 1450, 1378, 1291, 1274, 1238, 1179, 976, 777, 712, 688, 674 cm^{-1}.

HRMS (EI^+): found m/z 276.07792, calcd for $C_{18}H_{12}O_3$ M^+ 276.07864.

8.13.4 2-(4-Methoxy-benzoyl)-3-methyl-1,4-naphthoquinone (131d)

Molecular Formula: $C_{19}H_{14}O_4$
Molecular Weight: 306.32
Exact Mass: 306.0892



Following the general procedure F, irradiation of 344 mg (2 mmol) of 2-methoxy-1,4-naphthoquinone **129** and 2.45 g (18 mmol) of *p*-methoxybenzaldehyde **130d** in 100 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 254 mg (42%) of 2-(4-methoxy-benzoyl)-3-methyl-1,4-naphthoquinone **131d** pale yellow solid, mp 140–142 °C.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; acetone-d_6) 1.98 (3H, s, Me), 3.89 (3H, s, OMe), 7.05 (2H, dd, *J* = 1.8, 8.7 Hz, Ar-H), 7.80 (1H, dd, *J* = 8.7, 1.8 Hz), 7.87 (2H, m), 8.02 (2H, dd, *J* = 1.8, 8.7 Hz), 8.12 (1H, dd, *J* = 1.8, 6.9 Hz) ppm.

^{13}C NMR (125 MHz; acetone-d_6) δ = 13.5 (CH_3), 56.0 (OMe), 115.1 (2×CH), 126.8 (2×CH), 127.0 (CH), 129 (C_q), 130.0 (C_q), 132.4 (CH), 133.07 (C_q), 134.8 (CH), 134.9 (CH), 145.2 (C_q), 165.5 (C_q), 184.2 (C=O), 185.3 (C=O), 192.4 (C=O) ppm.

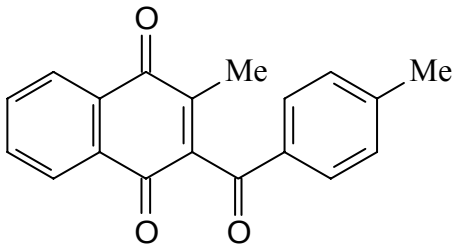
MS (EI): m/z (%) = 306 (M^+, 37%), 305 (4), 291 (3), 289 (2), 277 (3), 275 (6), 263 (2), 200 (7), 135 (100), 116 (2), 115 (7), 110 (2), 104 (3), 92 (11), 78 (2), 65 (2).

IR (KBr): $\tilde{\nu}$ = 1731, 1668, 1596, 1570, 1509, 1457, 1422, 1330, 1291, 1260, 1247, 1175, 1018, 832, 763, 706, 511 cm^{-1}.

HRMS (EI^+): found m/z 306.08924, calcd for $C_{19}H_{14}O_4$ M^+ 306.08921.

8.13.5 2-(4-Methyl-benzoyl)-3-methyl-1,4-naphthoquinone (131e)

Molecular Formula: $C_{19}H_{14}O_3$
Molecular Weight: 290.32
Exact Mass: 290.0942



Following the general procedure F, irradiation of 344 mg (2 mmol) of 2-methyl-1,4-naphthoquinone **129** and 2.16 g (18 mmol) of *p*-methylbenzaldehyde **130e** in 100 ml of benzene for 12 h, followed by flash column chromatography (silica gel, 30% EA in CH) gave 203 mg (23%) of 2-(4-methyl-benzoyl)-3-methyl-1,4-naphthoquinone **131e** as pale yellow solid, mp 193–194 °C.

1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; CD_2Cl_2) δ = 2.02 (3H, s, Me), 2.42 (3H, s, Me), 7.31 (2H, d, *J* = 7.5 Hz, Ar-H), 7.79 (4H, ddd, *J* = 1.8, 2.5, 7.5 Hz), 8.04 (1H, dd, *J* = 1.8, 6.9 Hz), 8.14 (1H, ddd, *J* = 1.8, 1.2, 7.5 Hz) ppm.

^{13}C NMR (125 MHz; CD_2Cl_2) δ = 13.6 (CH_3), 21.9 (CH_3), 126.5 (CH), 126.8 (CH), 129.4 (2×CH), 130.1 (2×CH), 131.9 (C_q), 132.2 (C_q), 133.2 (C_q), 134.9 (CH), 134.5 (CH), 144.1 (C_q), 144.7 (C_q), 146.2 (C_q), 183.8 (C=O), 185.1 (C=O), 193.4 (C=O) ppm.

MS (EI): m/z (%) = 290 (M^+, 61%), 289 (9), 276 (4), 261 (5), 247 (4), 200 (2), 120 (9), 119 (100), 115 (11), 104 (3), 91 (43), 65 (16).

IR (KBr): $\tilde{\nu}$ = 1669, 1654, 1601, 1410, 1331, 1292, 1273, 1239, 1181, 1121, 975, 861, 762, 742, 708, 620, 534 cm^{-1}.

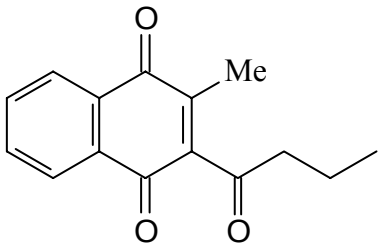
HRMS (EI^+): found m/z 290.09361, calcd for $C_{19}H_{14}O_3$ M^+ 290.09429.

8.13.6 2-Butyryl-3-methyl-1,4-naphthoquinone (132) and 2-butyryl-2-methyl-2,3-dihydro-1,4-naphthoquinone (133)

Following the general procedure F, irradiation of 344 mg (2 mmol) of 2-methyl-1,4-naphthoquinone **129** and 1.30 g (18 mmol) of butyraldehyde **105a** in 100 ml of benzene for 12 h. The crude product was purified with flash column chromatography (silica gel, 30% EA in CH) gave 233 mg (49%) of 2-butyryl-3-methyl-1,4-naphthoquinone **132** light yellow solid, mp 76–79 °C and 48 mg (10%) of 2-butyryl-3-methyl-2,3-dihydro-1,4-naphthoquinone **133** as colorless oil.

132:

Molecular Formula: $C_{15}H_{14}O_3$
Molecular Weight: 242.27
Exact Mass: 242.0942



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 0.98 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 1.72 (2H, q, *J* = 7.3 Hz, CH_2CH_3), 2.06 (3H, s, Me), 2.69 (2H, t, *J* = 7.5 Hz, -COCH_2-), 7.72 (2H, dd, *J* = 3.1, 8.7 Hz, Ar-H), 8.03 (1H, ddd, *J* = 3.1, 2.5, 8.7 Hz), 8.08 (1H, ddd, *J* = 2.5, 8.7, 5.6 Hz) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) δ = 13.1 (CH_3), 13.6 (CH_2), 16.4 (Me), 46.1 (CH_2), 126.1 (CH), 126.5 (CH), 133.5 (C_q), 134.0 (CH), 134.1 (CH), 135.6 (C_q), 142.4 (C_q), 145.6 (C_q), 183.4 (C=O), 185.0 (C=O), 203.9 (C=O) ppm.

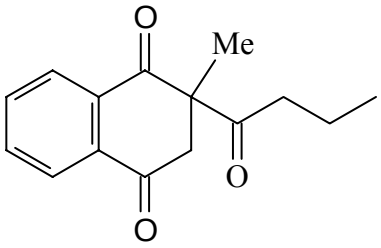
MS (EI): m/z (%) = 242 (M^+, 80%), 228 (4), 227 (23), 200 (20), 199 (95), 196 (2), 174 (12), 171 (100), 143 (21), 116 (12), 115 (69), 89 (17), 89 (16), 76 (18), 67 (16), 58 (14), 43 (36).

IR (KBr): $\tilde{\nu}$ = 2961, 2935, 2875, 2362, 1702, 1663, 1594, 1458, 1375, 1326, 1289, 1151, 1006, 958, 793, 703 cm^{-1}.

HRMS (EI^+): found m/z 242.09425, calcd for $C_{15}H_{14}O_3$ M^+ 242.09429.

133:

Molecular Formula: $C_{15}H_{16}O_3$
Molecular Weight: 244.29
Exact Mass: 244.1099



1D NMR analysis (^{1}H, ^{13}C, ^{13}C-DEPT) and 2D NMR analysis (^{1}H-COSY, HMBC, HMQC and HSQC);

^{1}H NMR (500 MHz; $CDCl_3$) δ = 0.68 (3H, t, *J* = 7.2 Hz, CH_2CH_3), 1.36–1.46 (2H, m), 1.58 (3H, s, CCH_3), 2.30 (1H, ddd, *J* = 17.9, 7.8, 6.2 Hz), 2.46 (1H, ddd, *J* = 17.9, 7.7, 6.6 Hz), 2.73 (1H, d, *J* = 16.9 Hz, CCH_2), 3.36 (1H, d, *J* = 16.3 Hz, CCH_2), 7.69 (2H, dddd, *J* = 1.2, 5.6, 8.1, 5.6 Hz, Ar-H), 7.98 (1H, dd, *J* = 6.9, 1.8 Hz), 8.06 (1H, dd, *J* = 1.8, 6.9 Hz) ppm.

^{13}C NMR (125 MHz; $CDCl_3$) 13.2 (CH_3), 16.8 (CH_2), 20.0 (CH_3), 39.2 (CH_2), 46.8 (CH_2), 65.0 (C_q), 126.6 (CH), 127.1 (CH), 133.8 (C_q), 134.1 (CH), 134.6 (CH), 135.2 (C_q), 193.4 (C=O), 195.3 (C=O), 206.8 (C=O) ppm.

MS (EI): m/z (%) = 244 (M^+, 16%), 228 (3), 201 (5), 185 (12), 175 (14), 174 (100), 159 (91), 159 (9), 149 (11), 131 (6), 128 (5), 117 (4), 105 (10), 91 (5), 76 (14), 71 (45), 55 (2), 43 (66).

IR (KBr): $\tilde{\nu}$ = 2963, 2934, 2874, 1687, 1665, 1594, 1458, 1379, 1286, 1265, 1216, 978 cm^{-1}.

HRMS (EI^+): found m/z 244.10967, calcd for $C_{15}H_{16}O_3$ M^+ 244.10994.

9 X-Ray Analysis

9.1 4-(1,4-Dihydroxy-8-methoxy-naphthalene-2-carbonyl)-benzonitrile (119)

The compound **119** was crystallized from 1/1 mixture of acetone/n–hexane at 280 K. The red crystals appeared after one week with mono–clinic crystal system.

Measurement device	Nonius KappaCCD
Empirical formula	C19 H13 N O4
Formula weight	319.30
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic P 21/c
Unit cell dimensions	a = 9.2250(2) A alpha = 90 deg.
	b = 10.5760(3) A beta = 104.2370(15) deg.
	c = 15.4410(4) A gamma = 90 deg.
Volume	1460.21(6) A^3
Calculated density (Z)	4, 1.452 Mg/m^3
Absorption coefficient	0.103 mm^{-1}
F(000)	664
Crystal size, colour and habit	0.29 × 0.28 × 0.07 mm^3, red fragment
Theta range for data collection	2.98 to 27.49 deg.
Index ranges	-11<=h<=11, -13<=k<=13, -20<=l<=19
Reflections collected / unique	22523 / 3332 [R(int) = 0.034]
Completeness to theta	= 27.49 99.6%
Absorption correction	multi-scan
Max. and min. transmission	0.9928 and 0.9707
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3332 / 0 / 269
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.1027 [2817]
R indices (all data)	R1 = 0.0472, wR2 = 0.1096
Largest diff. peak and hole	0.295 and -0.207 $e.A^{-3}$
Remarks	Hydrogens were refined isotropically.

Table 9: Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **(119)**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	**y**	**z**	**U**(eq)
O(1)	4013(1)	3346(1)	3967(1)	31(1)
O(2)	3767(1)	3797(1)	5568(1)	26(1)
O(3)	-627(1)	7981(1)	5618(1)	34(1)
O(4)	-249(1)	7539(1)	4032(1)	31(1)
N(1)	3869(1)	6440(1)	-407(1)	31(1)
C(1)	3792(1)	6092(1)	285(1)	25(1)
C(2)	3661(1)	5654(1)	1152(1)	23(1)
C(3)	3395(1)	4374(1)	1280(1)	25(1)
C(4)	3267(1)	3969(1)	2112(1)	25(1)
C(5)	3374(1)	4840(1)	2808(1)	22(1)
C(6)	3634(1)	6117(1)	2671(1)	22(1)
C(7)	3792(1)	6528(1)	1844(1)	23(1)
C(8)	3339(1)	4344(1)	3713(1)	23(1)
C(9)	2553(1)	5035(1)	4284(1)	21(1)
C(10)	2824(1)	4730(1)	5188(1)	22(1)
C(11)	2117(1)	5432(1)	5761(1)	22(1)
C(12)	2477(1)	5175(1)	6694(1)	25(1)
C(13)	1796(1)	5846(1)	7239(1)	27(1)
C(14)	720(1)	6769(1)	6893(1)	27(1)
C(15)	380(1)	7053(1)	5996(1)	25(1)
C(16)	1067(1)	6396(1)	5394(1)	22(1)
C(17)	762(1)	6648(1)	4451(1)	23(1)
C(18)	1492(1)	5988(1)	3931(1)	22(1)
C(19)	-1072(2)	8862(2)	6210(1)	40(1)

Table 10: Bond lengths (Å).

Bond	Bond length (Å)	Bond	Bond lengths (Å)
O(1)-C(8)	1.2383(15)	C(7)-H(7)	0.979(14)
O(2)-C(10)	1.3503(14)	C(8)-C(9)	1.4668(16)
O(2)-H(2)	0.97(2)	C(9)-C(10)	1.3940(16)
O(3)-C(15)	1.3779(15)	C(9)-C(18)	1.4174(16)
O(3)-C(19)	1.4346(16)	C(10)-C(11)	1.4300(16)
O(4)-C(17)	1.3715(14)	C(11)-C(12)	1.4224(16)
O(4)-H(4)	0.91(2)	C(11)-C(16)	1.4241(16)
N(1)-C(1)	1.1484(16)	C(12)-C(13)	1.3667(18)
C(1)-C(2)	1.4490(16)	C(12)-H(12)	0.964(15)
C(2)-C(7)	1.3962(17)	C(13)-C(14)	1.4008(19)
C(2)-C(3)	1.3990(18)	C(13)-H(13)	0.951(16)
C(3)-C(4)	1.3858(17)	C(14)-C(15)	1.3750(17)
C(3)-H(3)	0.960(16)	C(14)-H(14)	0.935(17)
C(4)-C(5)	1.4001(17)	C(15)-C(16)	1.4289(16)
C(4)-H(4A)	0.976(15)	C(16)-C(17)	1.4383(16)
C(5)-C(6)	1.3973(17)	C(17)-C(18)	1.3602(17)
C(5)-C(8)	1.5009(16)	C(18)-H(18)	0.973(14)
C(6)-C(7)	1.3896(16)	C(19)-H(19A)	1.019(19)
C(6)-H(6)	0.981(15)	C(19)-H(19B)	1.029(19)
		C(19)-H(19C)	0.999(19)

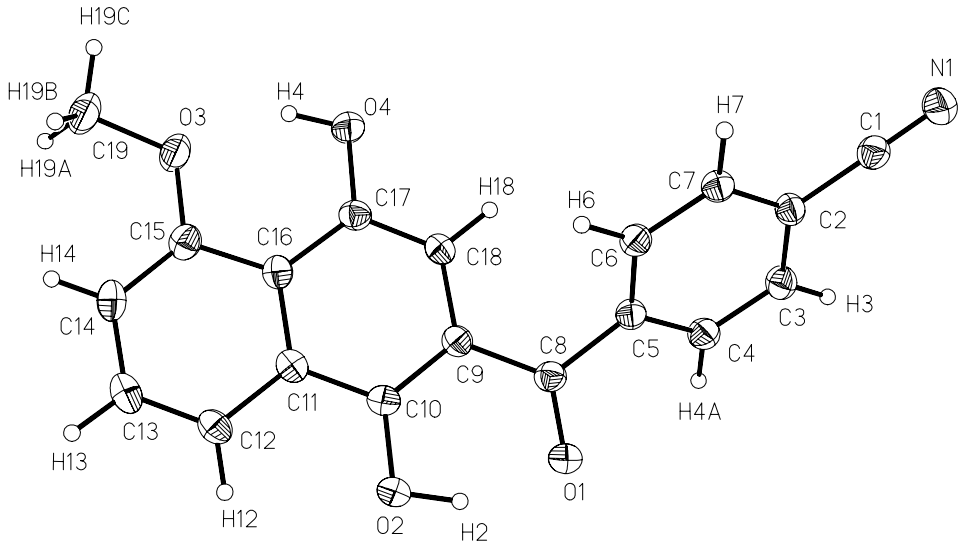


Table 11: Bond angles (deg).

Bond	Bond angle (deg)	Bond	Bond angle (deg)
C(10)-O(2)-H(2)	104.5(12)	C(9)-C(10)-C(11)	120.16(11)
C(15)-O(3)-C(19)	117.39(10)	C(12)-C(11)-C(16)	120.44(11)
C(17)-O(4)-H(4)	107.2(13)	C(12)-C(11)-C(10)	119.92(11)
N(1)-C(1)-C(2)	178.81(13)	C(16)-C(11)-C(10)	119.63(10)
C(7)-C(2)-C(3)	121.12(11)	C(13)-C(12)-C(11)	119.78(12)
C(7)-C(2)-C(1)	119.01(11)	C(13)-C(12)-H(12)	120.1(8)
C(3)-C(2)-C(1)	119.87(11)	C(11)-C(12)-H(12)	120.1(8)
C(4)-C(3)-C(2)	119.25(11)	C(12)-C(13)-C(14)	121.05(11)
C(4)-C(3)-H(3)	119.4(9)	C(12)-C(13)-H(13)	120.9(10)
C(2)-C(3)-H(3)	121.3(9)	C(14)-C(13)-H(13)	118.0(10)
C(3)-C(4)-C(5)	120.14(12)	C(15)-C(14)-C(13)	120.15(11)
C(3)-C(4)-H(4A)	119.9(9)	C(15)-C(14)-H(14)	119.1(10)
C(5)-C(4)-H(4A)	119.9(9)	C(13)-C(14)-H(14)	120.7(10)
C(6)-C(5)-C(4)	120.15(11)	C(14)-C(15)-O(3)	123.11(11)
C(6)-C(5)-C(8)	121.50(10)	C(14)-C(15)-C(16)	121.38(12)
C(4)-C(5)-C(8)	118.12(11)	O(3)-C(15)-C(16)	115.51(11)
C(7)-C(6)-C(5)	120.11(11)	C(11)-C(16)-C(15)	117.14(10)
C(7)-C(6)-H(6)	119.2(9)	C(11)-C(16)-C(17)	118.70(10)
C(5)-C(6)-H(6)	120.7(9)	C(15)-C(16)-C(17)	124.16(11)
C(6)-C(7)-C(2)	119.23(11)	C(18)-C(17)-O(4)	116.88(10)
C(6)-C(7)-H(7)	120.6(8)	C(18)-C(17)-C(16)	120.04(11)
C(2)-C(7)-H(7)	120.2(8)	O(4)-C(17)-C(16)	123.08(10)
O(1)-C(8)-C(9)	121.25(11)	C(17)-C(18)-C(9)	122.19(11)
O(1)-C(8)-C(5)	117.89(10)	C(17)-C(18)-H(18)	118.2(8)
C(9)-C(8)-C(5)	120.85(10)	C(9)-C(18)-H(18)	119.6(8)
C(10)-C(9)-C(18)	119.14(11)	O(3)-C(19)-H(19A)	110.1(11)
C(10)-C(9)-C(8)	119.52(10)	O(3)-C(19)-H(19B)	109.5(10)
C(18)-C(9)-C(8)	121.31(10)	H(19A)-C(19)-H(19B)	112.0(15)
O(2)-C(10)-C(9)	122.82(11)	O(3)-C(19)-H(19C)	104.9(10)
O(2)-C(10)-C(11)	117.01(10)	H(19A)-C(19)-H(19C)	111.8(15)
		H(19B)-C(19)-H(19C)	108.4(15)

Symmetry transformations used to generate equivalent atoms.

Table 12: Anisotropic displacement parameters ($Å^2 \times 10^3$) for (119). The anisotropic displacement factor exponent takes the form $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	38(1)	28(1)	26(1)	5(1)	9(1)	10(1)
O(2)	29(1)	26(1)	22(1)	4(1)	5(1)	6(1)
O(3)	36(1)	39(1)	26(1)	-8(1)	4(1)	14(1)
O(4)	34(1)	35(1)	25(1)	3(1)	6(1)	14(1)
N(1)	38(1)	31(1)	25(1)	1(1)	10(1)	2(1)
C(1)	27(1)	24(1)	24(1)	-2(1)	7(1)	1(1)
C(2)	22(1)	27(1)	20(1)	1(1)	6(1)	2(1)
C(3)	29(1)	25(1)	22(1)	-3(1)	7(1)	0(1)
C(4)	27(1)	22(1)	24(1)	-1(1)	6(1)	0(1)
C(5)	20(1)	25(1)	20(1)	1(1)	4(1)	3(1)
C(6)	21(1)	24(1)	20(1)	-2(1)	4(1)	1(1)
C(7)	22(1)	23(1)	23(1)	0(1)	5(1)	1(1)
C(8)	23(1)	22(1)	22(1)	0(1)	4(1)	1(1)
C(9)	21(1)	22(1)	20(1)	-1(1)	4(1)	-1(1)
C(10)	20(1)	21(1)	23(1)	1(1)	3(1)	-2(1)
C(11)	21(1)	23(1)	21(1)	0(1)	4(1)	-5(1)
C(12)	26(1)	26(1)	22(1)	2(1)	4(1)	-5(1)
C(13)	32(1)	31(1)	20(1)	-2(1)	7(1)	-10(1)
C(14)	29(1)	31(1)	24(1)	-8(1)	10(1)	-7(1)
C(15)	22(1)	27(1)	26(1)	-5(1)	4(1)	-1(1)
C(16)	21(1)	23(1)	21(1)	-3(1)	5(1)	-4(1)
C(17)	22(1)	23(1)	22(1)	1(1)	3(1)	1(1)
C(18)	24(1)	24(1)	19(1)	1(1)	4(1)	0(1)
C(19)	47(1)	41(1)	33(1)	-11(1)	9(1)	15(1)

Table 13: Hydrogen coordinates ($\mathbf{Å} \times 10^4$) and isotropic displacement parameters ($\mathbf{Å}^2 \times 10^3$) for **(119)**.

	x	y	z	U(eq)
H(2)	4100(2)	3430(2)	5076(14)	63(6)
H(4)	-610(2)	7920(2)	4459(14)	63(6)
H(3)	3315(17)	3769(15)	807(10)	33(4)
H(4A)	3066(16)	3081(15)	2207(10)	29(4)
H(6)	3736(16)	6730(14)	3159(10)	29(4)
H(7)	3996(14)	7418(14)	1747(9)	22(3)
H(12)	3209(16)	4539(14)	6942(9)	25(3)
H(13)	2067(17)	5723(16)	7869(11)	37(4)
H(14)	224(18)	7198(16)	7264(11)	40(4)
H(18)	1247(15)	6167(13)	3293(10)	26(4)
H(19A)	-1710(2)	8418(18)	6568(12)	54(5)
H(19B)	-140(2)	9270(18)	6616(12)	51(5)
H(19C)	-1640(2)	9530(18)	5811(12)	50(5)

9.2 [3-(4-Chloro-phenyl)-1,4-dihydroxy-8-methoxy-naphthalen-2-yl]-(4-chloro-phenyl)-methanone (123)

Measurement device	Nonius KappaCCD
Empirical formula	C25 H16 Cl2 O5
Formula weight	467.28
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic P c a 21
Unit cell dimensions	a = 23.137(10) A alpha = 90 deg. b = 13.597(5) A beta = 90 deg. c = 6.740(3) A gamma = 90 deg.
Volume	2120.4(14) A^3
Z, Calculated density	4, 1.464 Mg/m^3
Absorption coefficient	0.343 mm^{-1}
F(000)	960
Crystal size, colour and habit	0.24 × 0.20 × 0.01 mm^3, colourless plate
Theta range for data collection	3.04 to 25.00 deg.
Index ranges	-27<=h<=25, -16<=k<=15, -8<=l<=7
Reflections collected / unique	16606 / 3581 [R(int) = 0.0566]
Completeness to theta	= 25.00 99.2%
Absorption correction	None
Max. and min. transmission	1.000000 and 0.654534
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3581 / 1 / 292
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1111 [2880]
R indices (all data)	R1 = 0.0749, wR2 = 0.1255
Absolute structure parameter	0.17(10)
Largest diff. peak and hole	0.423 and -0.352 $e.A^{-3}$
Remarks	

Table 14: Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **(123)**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	5194(1)	4429(1)	6821(2)	52(1)
Cl(2)	3263(1)	5399(1)	7430(2)	48(1)
O(1)	4911(1)	211(2)	1839(5)	32(1)
O(2)	4340(1)	-1398(2)	3121(4)	30(1)
O(3)	1788(1)	-508(2)	3532(4)	29(1)
O(4)	2416(1)	1054(2)	3084(4)	29(1)
O(5)	3673(1)	1980(2)	330(4)	32(1)
C(1)	4981(2)	3356(3)	5568(7)	36(1)
C(2)	5204(2)	3163(3)	3680(8)	37(1)
C(3)	5044(2)	2300(3)	2728(7)	28(1)
C(4)	4658(2)	1641(3)	3643(6)	25(1)
C(5)	4438(2)	1862(3)	5538(7)	27(1)
C(6)	4599(2)	2716(3)	6542(7)	30(1)
C(7)	4523(2)	673(3)	2666(6)	27(1)
C(8)	3934(2)	243(3)	2874(6)	25(1)
C(9)	3878(2)	-761(3)	3143(6)	23(1)
C(10)	3323(2)	-1226(3)	3400(6)	23(1)
C(11)	3278(2)	-2260(3)	3564(6)	26(1)
C(12)	2743(2)	-2698(3)	3712(6)	29(1)
C(13)	2238(2)	-2122(3)	3682(6)	29(1)
C(14)	2272(2)	-1117(3)	3551(6)	25(1)
C(15)	2818(2)	-619(3)	3412(6)	24(1)
C(16)	2880(2)	432(3)	3161(6)	24(1)
C(17)	3425(2)	854(3)	2850(6)	25(1)
C(18)	3479(2)	1891(3)	2041(6)	22(1)
C(19)	3353(2)	2773(3)	3295(6)	23(1)
C(20)	3119(2)	2678(3)	5205(7)	28(1)
C(21)	3071(2)	3485(3)	6475(7)	30(1)
C(22)	3274(2)	4388(3)	5806(7)	35(1)
C(23)	3484(2)	4519(3)	3885(8)	38(1)
C(24)	3526(2)	3708(3)	2611(7)	33(1)
C(25)	1222(2)	-975(3)	3347(7)	35(1)

Table 15: Bond lengths (Å).

Bond	Bond length (Å)	Bond	Bond lengths (Å)
Cl(1)-C(1)	1.756(4)	C(8)-C(17)	1.442(5)
Cl(2)-C(22)	1.757(5)	C(9)-C(10)	1.442(5)
O(1)-C(7)	1.230(5)	C(10)-C(11)	1.415(6)
O(2)-C(9)	1.376(4)	C(10)-C(15)	1.430(5)
O(3)-C(14)	1.392(5)	C(11)-C(12)	1.376(6)
O(3)-C(25)	1.460(4)	C(12)-C(13)	1.407(6)
O(4)-C(16)	1.367(4)	C(13)-C(14)	1.372(5)
O(5)-C(18)	1.244(5)	C(14)-C(15)	1.437(5)
C(1)-C(2)	1.397(7)	C(15)-C(16)	1.446(5)
C(1)-C(6)	1.404(6)	C(16)-C(17)	1.401(5)
C(2)-C(3)	1.387(6)	C(17)-C(18)	1.516(5)
C(3)-C(4)	1.408(6)	C(18)-C(19)	1.496(6)
C(4)-C(5)	1.408(6)	C(19)-C(20)	1.402(6)
C(4)-C(7)	1.505(6)	C(19)-C(24)	1.410(5)
C(5)-C(6)	1.394(6)	C(20)-C(21)	1.396(6)
C(7)-C(8)	1.489(5)	C(21)-C(22)	1.390(6)
C(8)-C(9)	1.383(5)	C(22)-C(23)	1.394(7)
		C(23)-C(24)	1.401(6)

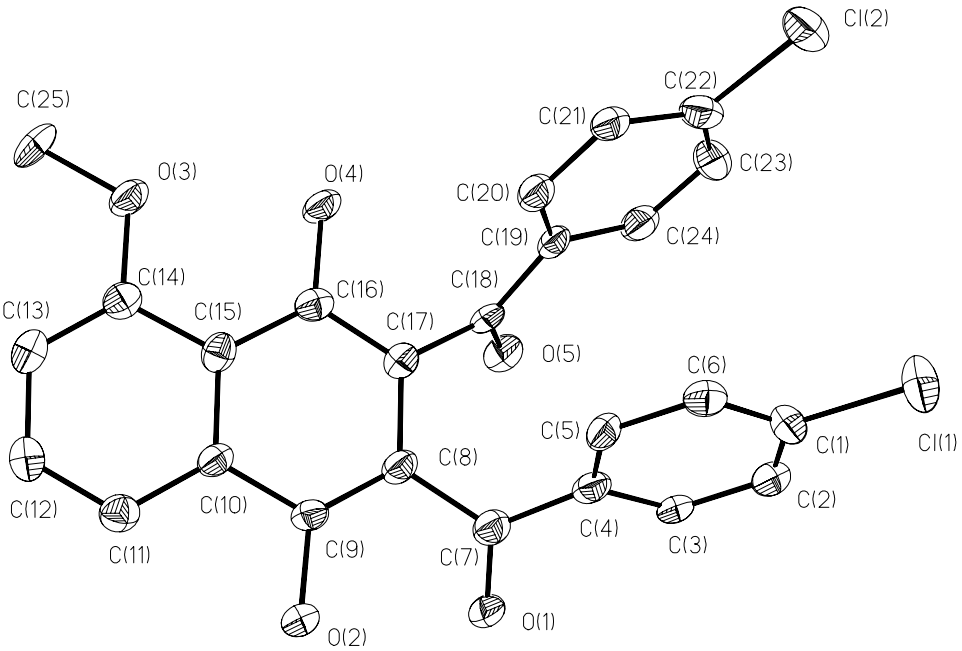


Table 16: Bond angles (deg).

Bond	Bond angle (deg)	Bond	Bond angle (deg)
C(14)-O(3)-C(25)	117.5(3)	C(14)-C(13)-C(12)	120.5(4)
C(2)-C(1)-C(6)	122.7(4)	C(13)-C(14)-O(3)	123.2(3)
C(2)-C(1)-Cl(1)	119.4(4)	C(13)-C(14)-C(15)	121.6(4)
C(6)-C(1)-Cl(1)	117.8(4)	O(3)-C(14)-C(15)	115.2(3)
C(3)-C(2)-C(1)	118.9(4)	C(10)-C(15)-C(14)	116.6(3)
C(2)-C(3)-C(4)	120.3(4)	C(10)-C(15)-C(16)	119.3(3)
C(5)-C(4)-C(3)	119.4(4)	C(14)-C(15)-C(16)	124.0(3)
C(5)-C(4)-C(7)	120.5(4)	O(4)-C(16)-C(17)	116.5(3)
C(3)-C(4)-C(7)	119.8(4)	O(4)-C(16)-C(15)	122.6(3)
C(6)-C(5)-C(4)	121.4(4)	C(17)-C(16)-C(15)	120.8(3)
C(5)-C(6)-C(1)	117.3(4)	C(16)-C(17)-C(8)	119.8(3)
O(1)-C(7)-C(8)	120.7(3)	C(16)-C(17)-C(18)	120.6(3)
O(1)-C(7)-C(4)	119.5(3)	C(8)-C(17)-C(18)	118.2(3)
C(8)-C(7)-C(4)	119.5(3)	O(5)-C(18)-C(19)	121.0(3)
C(9)-C(8)-C(17)	119.6(3)	O(5)-C(18)-C(17)	117.0(3)
C(9)-C(8)-C(7)	119.0(3)	C(19)-C(18)-C(17)	121.7(3)
C(17)-C(8)-C(7)	121.4(3)	C(20)-C(19)-C(24)	119.5(4)
O(2)-C(9)-C(8)	123.2(3)	C(20)-C(19)-C(18)	121.3(3)
O(2)-C(9)-C(10)	114.6(3)	C(24)-C(19)-C(18)	118.9(4)
C(8)-C(9)-C(10)	122.1(3)	C(21)-C(20)-C(19)	121.4(4)
C(11)-C(10)-C(15)	120.9(3)	C(22)-C(21)-C(20)	117.9(4)
C(11)-C(10)-C(9)	120.7(3)	C(21)-C(22)-C(23)	122.1(4)
C(15)-C(10)-C(9)	118.4(3)	C(21)-C(22)-Cl(2)	119.0(4)
C(12)-C(11)-C(10)	120.1(4)	C(23)-C(22)-Cl(2)	118.9(3)
C(11)-C(12)-C(13)	120.4(4)	C(22)-C(23)-C(24)	119.5(4)
		C(23)-C(24)-C(19)	119.4(4)

Symmetry transformations used to generate equivalent atoms.

Table 17: Anisotropic displacement parameters ($Å^2 \times 10^3$) for (123). The anisotropic displacement factor exponent takes the form $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	51(1)	34(1)	71(1)	-18(1)	-11(1)	-9(1)
Cl(2)	45(1)	26(1)	73(1)	-11(1)	12(1)	2(1)
O(1)	18(1)	31(2)	48(2)	-9(2)	5(1)	0(1)
O(2)	18(1)	28(2)	45(2)	1(1)	-2(1)	2(1)
O(3)	16(1)	36(2)	36(2)	-1(1)	-2(1)	-2(1)
O(4)	14(1)	33(2)	39(2)	5(1)	-2(1)	1(1)
O(5)	26(2)	38(2)	32(2)	4(1)	2(1)	-1(1)
C(1)	31(2)	23(2)	53(3)	-12(2)	-7(2)	3(2)
C(2)	20(2)	29(2)	61(3)	0(2)	-1(2)	1(2)
C(3)	15(2)	28(2)	43(3)	-1(2)	-4(2)	4(2)
C(4)	16(2)	28(2)	31(2)	7(2)	-1(2)	3(2)
C(5)	17(2)	26(2)	38(2)	2(2)	-6(2)	-3(2)
C(6)	24(2)	28(2)	39(3)	2(2)	-4(2)	5(2)
C(7)	22(2)	28(2)	32(2)	4(2)	-3(2)	0(2)
C(8)	17(2)	29(2)	28(2)	1(2)	-3(2)	-1(2)
C(9)	18(2)	26(2)	26(2)	1(2)	-2(2)	3(2)
C(10)	17(2)	27(2)	24(2)	-4(2)	0(2)	0(2)
C(11)	25(2)	29(2)	26(2)	-2(2)	-3(2)	1(2)
C(12)	32(2)	24(2)	30(2)	0(2)	0(2)	-5(2)
C(13)	25(2)	33(2)	29(2)	1(2)	2(2)	-8(2)
C(14)	22(2)	30(2)	22(2)	-1(2)	-2(2)	0(2)
C(15)	23(2)	28(2)	22(2)	2(2)	-4(2)	-4(2)
C(16)	21(2)	29(2)	22(2)	-3(2)	-1(2)	3(2)
C(17)	21(2)	27(2)	28(2)	0(2)	-1(2)	-1(2)
C(18)	11(2)	29(2)	26(2)	2(2)	-2(2)	1(2)
C(19)	14(2)	23(2)	32(2)	9(2)	-3(2)	-1(1)
C(20)	19(2)	26(2)	38(2)	5(2)	-2(2)	-1(2)
C(21)	18(2)	25(2)	47(3)	2(2)	2(2)	2(2)
C(22)	27(2)	25(2)	52(3)	0(2)	7(2)	7(2)
C(23)	36(3)	18(2)	60(3)	4(2)	4(2)	0(2)
C(24)	20(2)	32(2)	45(3)	4(2)	5(2)	-1(2)
C(25)	14(2)	53(3)	37(2)	-1(2)	0(2)	-10(2)

Table 18: Hydrogen coordinates (Å × 10^4) and isotropic displacement parameters (Å^2 × 10^3) for **(123)**.

	x	y	z	U(eq)
H(2)	4640	-1092	2792	46
H(4)	2111	735	3294	43
H(2)	5460	3614	3060	44
H(3)	5197	2153	1453	34
H(5)	4173	1420	6146	32
H(6)	4456	2858	7831	36
H(11)	3617	-2654	3572	32
H(12)	2715	-3392	3835	34
H(13)	1870	-2432	3753	35
H(20)	2991	2051	5643	33
H(21)	2905	3418	7757	36
H(23)	3598	5154	3444	45
H(24)	3669	3787	1300	39
H(25A)	1208	-1359	2117	52
H(25B)	921	-469	3319	52
H(25C)	1158	-1412	4482	52

9.3 4-Chloro-benzoic acid 4-hydroxy-8-methoxy-naphthalen-1-yl ester (124)

Measurement device	Nonius KappaCCD
Empirical formula	C18 H13 Cl O4 + 0.5 C3 H6 O
Formula weight	357.77
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic C 2/c
Unit cell dimensions	a = 27.3490(9) A alpha = 90 deg. b = 15.8590(3) A beta = 95.3230(15) deg. c = 7.7140(3) A gamma = 90 deg.
Volume	3331.35(18) A^3
Z, Calculated density	8, 1.427 Mg/m^3
Absorption coefficient	0.254 mm^{-1}
F(000)	1488
Crystal size, colour and habit	0.30 × 0.30 × 0.06 mm^3, Colourless plate
Theta range for data collection	2.97 to 27.48 deg.
Index ranges	-35<=h<=35, -18<=k<=20, -10<=l<=9
Reflections collected / unique	26091 / 3812 [R(int) = 0.044]
Completeness to theta	= 27.48 99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.9849 and 0.9276
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3812 / 0 / 291
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0882 [2860]
R indices (all data)	R1 = 0.0572, wR2 = 0.0967
Largest diff. peak and hole	0.223 and -0.298 $e.A^{-3}$
Remark	Hydrogens were refined isotropically.

Table 19: Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **(124)**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	25(1)	1240(1)	31(1)	38(1)
O(1)	2315(1)	343(1)	3343(1)	30(1)
O(2)	2470(1)	1120(1)	1004(1)	25(1)
O(3)	4431(1)	1003(1)	3566(2)	39(1)
O(4)	2429(1)	2581(1)	2468(1)	31(1)
C(1)	652(1)	1083(1)	567(2)	29(1)
C(2)	983(1)	1640(1)	-58(2)	30(1)
C(3)	1482(1)	1522(1)	385(2)	27(1)
C(4)	1643(1)	847(1)	1451(2)	24(1)
C(5)	1304(1)	292(1)	2065(2)	26(1)
C(6)	806(1)	405(1)	1623(2)	29(1)
C(7)	2170(1)	731(1)	2053(2)	24(1)
C(8)	2971(1)	1117(1)	1614(2)	24(1)
C(9)	3249(1)	454(1)	1166(2)	26(1)
C(10)	3748(1)	400(1)	1775(2)	29(1)
C(11)	3954(1)	1023(1)	2841(2)	29(1)
C(12)	3680(1)	1746(1)	3262(2)	27(1)
C(13)	3912(1)	2411(1)	4268(2)	34(1)
C(14)	3649(1)	3107(1)	4621(2)	36(1)
C(15)	3151(1)	3185(1)	4032(2)	32(1)
C(16)	2912(1)	2551(1)	3069(2)	28(1)
C(17)	3173(1)	1802(1)	2637(2)	25(1)
C(18)	2166(1)	3341(1)	2801(2)	35(1)
O(5)	0	4729(1)	2500	38(1)
C(19)	0	3957(1)	2500	34(1)
C(20)	362(1)	3481(1)	1555(3)	43(1)

Table 20: Bond lengths (Å)

Bond	Bond length (Å)	Bond	Bond length (Å)
Cl(1)-C(1)	1.7434(15)	C(9)-H(9)	0.936(16)
O(1)-C(7)	1.2061(17)	C(10)-C(11)	1.373(2)
O(2)-C(7)	1.3527(17)	C(10)-H(10)	0.959(16)
O(2)-C(8)	1.4067(17)	C(11)-C(12)	1.424(2)
O(3)-C(11)	1.3695(18)	C(12)-C(13)	1.423(2)
O(3)-H(3)	0.85(2)	C(12)-C(17)	1.426(2)
O(4)-C(16)	1.3591(17)	C(13)-C(14)	1.359(2)
O(4)-C(18)	1.4396(18)	C(13)-H(13)	0.961(17)
C(1)-C(2)	1.384(2)	C(14)-C(15)	1.399(2)
C(1)-C(6)	1.391(2)	C(14)-H(14)	0.945(19)
C(2)-C(3)	1.386(2)	C(15)-C(16)	1.380(2)
C(2)-H(2)	0.948(18)	C(15)-H(15)	0.967(17)
C(3)-C(4)	1.397(2)	C(16)-C(17)	1.4419(19)
C(3)-H(3A)	0.968(17)	C(18)-H(18A)	0.987(16)
C(4)-C(5)	1.392(2)	C(18)-H(18B)	0.963(18)
C(4)-C(7)	1.485(2)	C(18)-H(18C)	1.025(18)
C(5)-C(6)	1.385(2)	O(5)-C(19)	1.225(3)
C(5)-H(5)	0.926(17)	C(19)-C(20)#1	1.488(2)
C(6)-H(6)	0.923(18)	C(19)-C(20)	1.488(2)
C(8)-C(9)	1.363(2)	C(20)-H(20A)	0.98(2)
C(8)-C(17)	1.4238(19)	C(20)-H(20B)	0.92(2)
C(9)-C(10)	1.403(2)	C(20)-H(20C)	0.91(3)

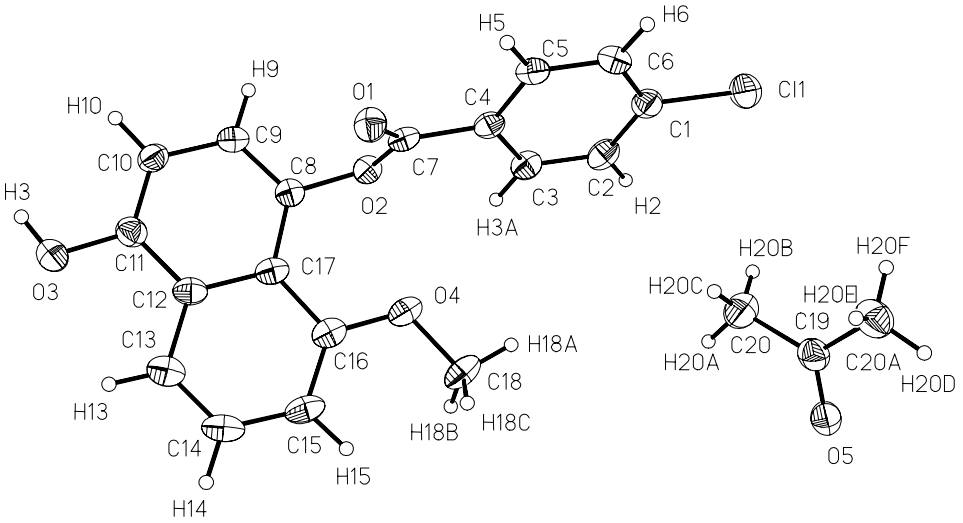


Table 21: Bond angles (deg).

Bond	Bond angle (deg)	Bond	Bond angle (deg)
C(7)-O(2)-C(8)	115.07(10)	O(3)-C(11)-C(12)	115.36(12)
C(11)-O(3)-H(3)	109.2(15)	C(10)-C(11)-C(12)	121.27(14)
C(16)-O(4)-C(18)	117.05(12)	C(13)-C(12)-C(11)	120.16(14)
C(2)-C(1)-C(6)	121.66(14)	C(13)-C(12)-C(17)	120.53(14)
C(2)-C(1)-Cl(1)	119.23(11)	C(11)-C(12)-C(17)	119.30(12)
C(6)-C(1)-Cl(1)	119.11(12)	C(14)-C(13)-C(12)	119.60(16)
C(1)-C(2)-C(3)	119.31(14)	C(14)-C(13)-H(13)	121.3(10)
C(1)-C(2)-H(2)	120.6(10)	C(12)-C(13)-H(13)	119.1(10)
C(3)-C(2)-H(2)	120.1(10)	C(13)-C(14)-C(15)	121.57(15)
C(2)-C(3)-C(4)	119.81(14)	C(13)-C(14)-H(14)	118.5(12)
C(2)-C(3)-H(3A)	122.4(9)	C(15)-C(14)-H(14)	119.9(11)
C(4)-C(3)-H(3A)	117.8(10)	C(16)-C(15)-C(14)	120.64(14)
C(5)-C(4)-C(3)	120.06(14)	C(16)-C(15)-H(15)	116.2(10)
C(5)-C(4)-C(7)	118.29(12)	C(14)-C(15)-H(15)	123.2(10)
C(3)-C(4)-C(7)	121.52(13)	O(4)-C(16)-C(15)	123.79(13)
C(6)-C(5)-C(4)	120.41(14)	O(4)-C(16)-C(17)	115.98(12)
C(6)-C(5)-H(5)	120.1(10)	C(15)-C(16)-C(17)	120.23(14)
C(4)-C(5)-H(5)	119.5(10)	C(8)-C(17)-C(12)	117.13(13)
C(5)-C(6)-C(1)	118.75(14)	C(8)-C(17)-C(16)	125.42(14)
C(5)-C(6)-H(6)	121.4(11)	C(12)-C(17)-C(16)	117.43(12)
C(1)-C(6)-H(6)	119.8(11)	O(4)-C(18)-H(18A)	103.9(9)
O(1)-C(7)-O(2)	123.73(13)	O(4)-C(18)-H(18B)	111.2(10)
O(1)-C(7)-C(4)	123.86(13)	H(18A)-C(18)-H(18B)	109.4(14)
O(2)-C(7)-C(4)	112.41(11)	O(4)-C(18)-H(18C)	111.3(10)
C(9)-C(8)-O(2)	117.90(12)	H(18A)-C(18)-H(18C)	110.8(13)
C(9)-C(8)-C(17)	122.07(13)	H(18B)-C(18)-H(18C)	110.1(14)
O(2)-C(8)-C(17)	120.02(12)	O(5)-C(19)-C(20)#1	120.48(11)
C(8)-C(9)-C(10)	120.71(13)	O(5)-C(19)-C(20)	120.48(11)
C(8)-C(9)-H(9)	118.2(10)	C(20)#1-C(19)-C(20)	119.0(2)
C(10)-C(9)-H(9)	121.0(10)	C(19)-C(20)-H(20A)	110.8(12)
C(11)-C(10)-C(9)	119.35(14)	C(19)-C(20)-H(20B)	111.7(14)
C(11)-C(10)-H(10)	122.8(9)	H(20A)-C(20)-H(20B)	101.0(18)
C(9)-C(10)-H(10)	117.8(9)	C(19)-C(20)-H(20C)	111.8(16)
O(3)-C(11)-C(10)	123.38(13)	H(20A)-C(20)-H(20C)	112.3(18)
		H(20B)-C(20)-H(20C)	109(2)

Symmetry transformations used to generate equivalent atoms.

Table 22: Anisotropic displacement parameters ($Å^2 \times 10^3$) for (124). The anisotropic displacement factor exponent takes the form $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	30(1)	38(1)	44(1)	-2(1)	-7(1)	2(1)
O(1)	30(1)	30(1)	30(1)	8(1)	3(1)	2(1)
O(2)	27(1)	24(1)	24(1)	2(1)	5(1)	1(1)
O(3)	28(1)	39(1)	50(1)	-11(1)	-2(1)	-1(1)
O(4)	39(1)	23(1)	34(1)	-1(1)	10(1)	5(1)
C(1)	30(1)	29(1)	27(1)	-5(1)	-3(1)	2(1)
C(2)	37(1)	27(1)	26(1)	2(1)	3(1)	8(1)
C(3)	32(1)	25(1)	26(1)	2(1)	6(1)	2(1)
C(4)	30(1)	22(1)	20(1)	-3(1)	3(1)	2(1)
C(5)	34(1)	21(1)	25(1)	-1(1)	-1(1)	-1(1)
C(6)	31(1)	26(1)	28(1)	-2(1)	1(1)	-5(1)
C(7)	31(1)	17(1)	24(1)	-3(1)	5(1)	2(1)
C(8)	26(1)	24(1)	21(1)	3(1)	4(1)	-1(1)
C(9)	31(1)	21(1)	26(1)	-2(1)	4(1)	-2(1)
C(10)	30(1)	24(1)	32(1)	-2(1)	6(1)	2(1)
C(11)	27(1)	29(1)	31(1)	-1(1)	4(1)	-3(1)
C(12)	34(1)	23(1)	24(1)	0(1)	7(1)	-5(1)
C(13)	40(1)	32(1)	29(1)	-2(1)	5(1)	-7(1)
C(14)	52(1)	28(1)	30(1)	-6(1)	5(1)	-10(1)
C(15)	49(1)	23(1)	27(1)	-2(1)	13(1)	0(1)
C(16)	37(1)	24(1)	23(1)	3(1)	10(1)	1(1)
C(17)	35(1)	21(1)	21(1)	2(1)	8(1)	-2(1)
C(18)	48(1)	25(1)	35(1)	4(1)	12(1)	13(1)
O(5)	29(1)	33(1)	52(1)	0	4(1)	0
C(19)	28(1)	34(1)	37(1)	0	-5(1)	0
C(20)	40(1)	41(1)	48(1)	-5(1)	3(1)	6(1)

Table 23: Hydrogen coordinates (Å x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **(124)**.

	x	y	z	U(eq)
H(3)	4570(8)	562(14)	3220(3)	68(7)
H(2)	873(6)	2096(11)	-790(2)	41(5)
H(3A)	1727(6)	1900(10)	0(2)	34(4)
H(5)	1413(6)	-145(10)	2800(2)	33(4)
H(6)	576(6)	55(10)	2050(2)	39(5)
H(9)	3096(6)	24(10)	480(2)	31(4)
H(10)	3928(6)	-86(9)	1450(2)	25(4)
H(13)	4254(6)	2364(11)	4660(2)	41(5)
H(14)	3812(7)	3555(12)	5240(3)	48(5)
H(15)	2955(6)	3670(10)	4280(2)	36(4)
H(18A)	1832(6)	3239(10)	2230(2)	32(4)
H(18B)	2307(6)	3823(11)	2270(2)	40(5)
H(18C)	2156(6)	3441(11)	4110(2)	39(5)
H(20A)	595(7)	3866(12)	1070(3)	53(6)
H(20B)	217(8)	3238(14)	560(3)	70(7)
H(20C)	516(9)	3071(15)	2230(3)	85(8)

10 References and notes

1 (a) R. A. Sheldon, *Green Chemistry* **2005**, *7*, 267–278.

(b) P. T. Anastas, J. C. Warner, In *Green Chemistry*, *Theory and Practice,* Oxford University Press, Oxford **1998**.

(c) M. Eissen, J. O. Metzger, E. Schmidt, U. Schneidewind, *Angew. Chem. Int. Ed.* **2002**, *41*, 414.

2 (a) M. Iqbal, An Introduction to Solar Radiation, Academic Press, New York,**1983**.

(b) H. D. Roth, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1193.

(c) E. Talukdar, E. H. S. Wang, V. K. Mathur, *Solar Energy* **1991**, *47*, 165–171.

(d) E. Paterno, G. Chieffi, *Gazz. Chim. Ital.* **1909**, *39*, 341.

(e) L. Fields, J. R. Pitts, M. J. Hale, C. Bingham, A. Lewandowski, D. E. King, *J. Phys. Chem.* **1993**, *97*, 8701.

(f) L. P. F. Chibante, A. Thess, J. M. Alford, J. M. Diener, R. E. Smalley, *J. Phys. Chem.* **1993**, *97*, 8696.

3 (a) P. Esser, B. Pohlmann, H. –D. Scharf, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2009.

(b) B. Pohlmann, H. –D. Scharf, U. Jarolimek, P. Mauermann, *Solar Energy* **1997**, *61*, 159–168.

4 (a) O. Diels and K. Alder, *Ann.* **1928**, *98*, 460.

(b) J. A. Norton, *Chem. Revs.* **1942**, *31*, 319.

(c) S. Sankararaman, *Pericyclic Reactions - A Textbook*, Wiley-VCH, Weinheim, **2005**.

5 S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, Inc., New York, **1973**

6 (a) H. Togo, Advanced Free Radical Reactions for Organic Synthesis, *Elsevier Science*, **2004**.

(b) B. Giese, *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, Pergamon Press, Oxford, **1986**.

(c) D. P. Curran, N. A. Porter, B. Giese, *Stereochemistry of Radical Reactions*, VCH, Weinheim, **1996**.

(d) J. Fossey, D. Lefort, J. Sorba, *Free Radicals in Organic Chemistry*, Wiley, Chichester, **1995**.

7 (a) S. Bertrand, N. Hoffmann, J. –P. Pete, *Eur. J. Org. Chem.* **2000**, 2227–2238.

(b) P. Renaud, L. Giraud, *Synthesis* **1996**, 913–926.

(c) S. Bertrand, N. Hoffmann, S. Humbel, J. P. Pete, *J. Org. Chem.* **2000**, *65*, 8690–8703.

8 (a) H. E. Zimmerman, R. W. Binkley, R. S. Givens, M. A. Sherwin, *J. Am. Chem. Soc.*

1967, *89*, 3932–3933.

(b) H. E. Zimmerman, P. S. Mariano, *J. Am. Chem. Soc*. **1969**, *91*, 1718–1727.

(c) H. E. Zimmerman, G. E. Samuelson, *J. Am. Chem. Soc*. **1967**, *89*, 5971–5973.

(d) H. E. Zimmerman, M. G. Steinmetz, C. L. Kreil, *J. Am. Chem. Soc*. **1978**, *100*, 4146–4162.

9 (a) H. E. Zimmerman, *In Rearrangements in Ground and Excited States*, DeMayo, P., Ed.; Academic Press: New York, **1980**, Vol. *3*.

(b) H. E. Zimmerman, D. Armesto, *Chem. Rev.* **1996**, *96*, 3065–3112.

10 E. Paterno, G. Chieffi, *Gazz. Chim. Ital.* **1909**, *39*, 341.

(b) G. Büchi, C. G. Inman, E. S. Lipinsky, *J. Am. Chem. Soc*. **1954**, *76*, 4327.

11 (a) H. A. J. Carless, In *Synthetic Organic Photochemistry*, W. M. Horspool, Ed.; Plenum Press: New York, **1984**, 425.

(b) J. Mattay, R. Conrads, R. Hoffmann, In *Methoden der Organischen Chemie, Houben–Weyl*, E21c; G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann, Eds.; Thieme Verlag: Stuttgart, **1995**, 3133.

12 (a) P. J. Wagner, B.-S. Park, *Organic Photochemistry,* 11, A. Padwa, Ed.; Dekker: New York, Basel, **1991**, 227.

(b) P. J. Wagner, P. J. In *Handbook of Photochemistry and Photobiology*; W. M. Horspool, P.-S. Song, Eds.; CRC Press: Boca Raton, **1995**, 449.

13 (a) E. J. Corey, W. E. Russey, P. R. Ortiz de Montellano, *J. Am. Chem. Soc*. **1966**, *88*, 4750–4751.

(b) T. W. Goodwin, In *Biosynthesis of Isoprenoid Compounds*, J. W. Porter, S. L. Spurgeon, Eds.; Wiley: New York, **1980**, Vol. *1*, pp 443–480.

14 (a) G. Ourisson, M. Rohmer, K. Poralla, *Annu. Rev. Microbiol.* **1987**, *41*, 301–333.

(b) G. Ourisson, M. Rohmer, R. Anton, *Recent Adv. Phytochem.* **1979**, *13*, 131–162.

(c) M. Rohmer, P. Bouvier, G. Ourisson, *Proc. Natl. Acad. Sci. U.S.A*. **1979,** *76*, 847–851.

15 (a) E. F. Rowinsky, L. A. Cazenave, R. C. Donehower, *J. Natl. Cancer Inst.* **1990**, *82*, 1247.

(b) E. K. Rowinsky, R. C. Donehower, *Pharmacol. Ther.* **1991**, *52*, 35.

(c) P. B. Schiff, J. Fant, S. B. Horwitz, *Nature* **1979**, *22*, 665.

(d) J. J. Manfredi, S. B. Horwitz, *Pharmacol. Ther.* **1984**, *25*, 83.

16 (a) C. S. Swindell, *Org. Prep. Proced. Int.* **1992**, *23*, 465.

(b) K. C. Nicolaou, W.-M. Dai, R. K. Guy, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 15.

(c) A. N. Boa, P. R. Jenkins, N. J. Lawrence, *Contemp. Org. Synth.* **1994**, *1*, 47.

17 For reviews see:

(a) C. S. Swindell, *Org. Prep. Proced. Int.* **1992**, *23*, 465.

(b) K. C. Nicolaou, W.-M. Dai, R. K. Guy, *Angew. Chem.*, *Int. Ed. Engl.* **1994**, *33*, 15.

(c) A. N. Boa, P. R. Jenkins and N. J. Lawrence, *Contemp. Org. Synth.* **1994**, *1*, 47.

18 For recent developments see, for example:

(a) Y.-F. Lu and A. G. Fallis, *Can. J. Chem.* **1995**, *73*, 2239.

(b) R. Hara, T. Furukawa, Y. Horiguchi, I. Kuwajima, *J. Am. Chem. Soc.* **1996**, *118*, 9186.

(c) P. Magnus, L. Diorazio, T. J. Donohoe, M. Giles, P. Pye, J. Tarrant, S. Thom, *Tetrahedron* **1996**, *52*, 14147.

19 R. Robinson, *J. Chem. Soc.* **1917**, 762.

20 (a) W. S. Johnson, M. B. Gravestock, R. J. Parry, R. F. Myers, T. A. Bryson, D. H. Miles, *J. Am. Chem. Soc.* **1971**, *93*, 4330.

(b) W. S. Johnson, M. B. Gravestock and B. E. McCarry, *J. Am. Chem. Soc.* **1971**, *93*, 4332.

(c) M. B. Gravestock, W. S. Johnson, B. E. McCarry, R. J. Parry and B. E. Ratcliffe, *J. Am. Chem. Soc.* **1978**, *100*, 4274.

21 (a) L. Chen, G. B. Gill, G. Pattenden, H. Simonian, *J. Chem. Soc. Perkin Trans. 1*, **1996**, 31.

(b) S. A. Hitchcock, S. J. Houldsworth, G. Pattenden, D. C. Pryde, N. M. Thomson, A. J. Blake, *J. Chem. Soc. Perkin Trans. 1*, **1998**, 3181.

(c) G. J. Hollingworth, G. Pattenden, D. J. Schulz, *Aust. J. Chem.* **1995**, *48*, 381.

(d) S. Handa and G. Pattenden, *Chem. Commun.* **1998**, 311.

(e) S. Handa and G. Pattenden, *Contemp. Org. Synth.* **1997**, *4*, 196.

(f) S. Handa, G. Pattenden, *J. Chem. Soc.*, *Perkin Trans. 1*, **1999**, 843–845.

22 For a review on PET see:

(a) J. Mattay, *Angew. Chem.* **1987**, *99*, 849–869, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 825–845.

(b) J. Mattay, *Synthesis* **1989**, 233–252.

23 (a) C. Heinemann, M. Demuth, *J. Am. Chem. Soc.* **1997**, *119*, 1129–1130.

(b) C. Heinemann, M. Demuth, *J. Am. Chem. Soc.* **1999**, *121*, 4894–4895.

(c) M. E. Ozser, H. Icil, Y. Makhynya, M. Demuth, *Eur. J. Org. Chem.* **2004**, 3686–3692.

24 For other recent references to cascade cyclizations *via* radical intermediates, see:

(a) B. B. Snider, *Chem. Rev.* **1996**, *96*, 339–363.

(b) A. Batsanov, L. Chen, G. B. Gill, G. Pattenden, *J. Chem. Soc. Perkin Trans. 1* **1996**, 45–55.

(c) P. A. Zoretic, Y. Zhang, A. A. Ribeiro, *Tetrahedron Lett.* **1996**, *37*, 1751–1754.

25 (a) S. Patai, Ed., *The chemistry of the Quinonoid Compounds*, John Wiley & Sons, New York, **1974**.

(b) R. H. Thompson, *Naturally Occurring Quinones*, 2nd ed., Academic Press, New York, **1971**.

(c) R. A. Morton, ed., *Biochemistry of Quinones*, Academic press, New York, **1965**.

26 Thomas, R. H. In *Naturally Occurring Quinones, III, Recent Advances*; Chapman and Hall: New York, **1987**, p 219.

27 (a) C. Friedel and J. M. Crafts, *Compt. Rend.* **1877**, *84*, 1392 and 1450.

(b) C. A. Thomas, In *Anhydrous Aluminum Chloride in Organic Chemistry*, New York, **1941**, p 77.

28 H. Klinger, *Justus Liebigs Ann. Chem.* **1888**, *249*, 137.

29 (a) M. Oelgemöller, C. Schiel, R. Fröhlich, J. Mattay, *Eur. J. Org. Chem*. **2002**, 2465.

(b) C. Schiel, M. Oelgemöller, J. Mattay, *Synthesis,* **2001**, 1275.

30 H. Maeda and G. A. Kraus, *J. Org. Chem.* **1996**, *61*, 2986.

31 (a) P. A. Waske, J. Mattay, M. Oelgemöller, *Tetrahedron Lett.* **2006**, *47*, 1329–1332.

(b) P. A. Waske, C. Schiel, M. Oelgemöller, J. Mattay, *Org. Bio. Chem.* (in press.).

32 J. S. Littler, In *'The mechanism of oxidation of organic compounds with one-equivalent metal-ion oxidants: Bonded and non bonded electron transfer, in Essays on free radical chemistry'. London Chem. Soc.* **1970**,. Special publication No. *24*, p 383.

33 C. J. Schesener, C. Amatore, J. K. Kochi, *J. Am. Chem. Soc.* **1984**, *106*, 3567.

34 L. Eberson, In *Electron Transfer reactions in Organic Chemistry,* Vol. *25*, Springer-Verlag, Berlin, **1987**, p 24.

35 A. Pross, Acc. *Chem. Res.* **1985**, *18*, 212.

36 (a) R. A. Marcus, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1111–1121.

(b) R. A. Marcus, *Pure and Appl. Chem.* **1997**, *69*, 13–29.

(c) R. A. Marcus, *N. J. Chem.* **1987**, *11*, 79–82.

37 G. J. Kavarnos, *Fundamentals of Photoinduced Electron Transfer*, VCH: Weinheim, **1993**, 21–57.

38 A. Z. Weller, *Phys. Chem. Neue Folge*, **1982**, *133*, 93.

39 S. Hintz, J. Mattay, R. V. Eldik, W.-F. Fu, *Eur. J. Org. Chem.* **1998**, 1583–1596.

40 (a) T. Kirschberg, J. Mattay, *Tetrahedron Lett.* **1994**, *35*, 7217–7220.

(b) T. Kirschberg, J. Mattay, *J. Org. Chem.* **1996**, *61*, 8885–8896.

41 (a) N. Tzvetkov, M. Schmidtmann, A. Müller and J. Mattay, *Tetrahedron Lett.*

2003, *42*, 5979–5982.

(b) N. T. Tzvetkov, B. Neumann, H.-G. Stammler, J. Mattay, *Eur. J. Org. Chem.* **2006**, 351–370.

42 J. Cossy, N. Furet, S. BouzBouz, *Tetrahedron* **1995**, *51*, 11751–11764.

43 U. C. Yoon, P. S. Mariano, *Acc. Chem. Res.* **1992**, *25*, 233–240.

44 J. D. Simon, K. S. Peters, *J. Am. Chem. Soc*. **1982**, *104*, 6542–6547.

45 J. Santamaria, In *'Photoinduced electron transfer'* Ed. M. A. Fox, M. Chanon; *Elsevier* **1988**, 433–540.

46 J. Cosy, N. Furet, *Tetrahedron Lett.* **1993**, *34*, 8107–8110.

47 (a) D. Belotti, J. Cossy, J.-P. Pete, C. Portella, *Tetrahedron Lett.* **1985**, *26*, 4591.

(b) J. Cossy, D. Belotti, J.-P. Pete, *Tetrahedron Lett.* **1987**, *28*, 4547.

(c) J. Cossy, J.-P. Pete, C. Portella, *Tetrahedron Lett.* **1989**, *30*, 7361.

(d) J. Cossy, *Bull. Soc. Chim. Fr.* **1994**, *131*, 344.

48 J. Cossy, D. Belotti, J. –P. Pete, *Tetrahedron* **1990**, *46*, 1859.

49 (a) J. Cossy, D. Belotti, *Tetrahedron Lett.* **1988**, *29*, 6113.

(b) J. Cossy, C. Leblanc, *Tetrahedron Lett.* **1991**, *32*, 3051.

(c) J. Cossy, D. Belotti, C. Leblanc, *J. Org. Chem.* **1993**, *58*, 2351.

(d) J. Cossy, D. Belotti,N. K. Cuong, C. Chassagnard, *Tetrahedron* **1993**, *49*, 7691.

(e) J. Cossy, A. Madaci, J.-P. Pete, *Tetrahedron Lett.* **1994**, *35*, 1541.

50 J. Cossy, J.-P. Pete, *Adv. Electron transfer Chem.* **1992**, *2*, 215–272.

51 (a) E. W. Bischof, J. Mattay, *J. Photochem. Photobiol. A: Chem.* **1992**, *63*, 249–251.

(b) Th. Kirschberg, J. Mattay, *J. Inf. Rec. Mats.* **1994**, *21*, 593–594.

52 (a) E. Breitmaier, In *Terpene*; Ed. B. G. Teubner; Stuttgart- Leipzig, **1999**.

(b) P. Nuhn, In *Naturstoffe*, 2nd ed., Ed. S. Hirzel, Press: Stuttgart, **1990,** Chapter 8.

53 (a) T. M. Bockman, D. Shukla, J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2* **1996**, 1623–1632.

(b) T. M. Bockman, J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2* **1996**, 1633–1643.

54 J. O. Bunte, J. Mattay in *CRC Handbook of Organic Photochemistry and Photobiology* Eds.: W. M. Horspool, F. Lenci, CRC Press, Boca Raton, 2nd ed., CRC Press, Boca Raton, USA, **2004**, chapters 10, 10.1–10.16.

55 (a) S. Hintz, R. Fröhlich, J. Mattay, *Tetrahedron Lett.* **1996**, *37*, 7349–7352.

(b) S. Hintz, J. Mattay, *J. Inf. Rec.* **1996**, *23*, 35–38.

(c) A. Heidbreder, J. Mattay, *J. Inf. Rec.* **1994**, *21*, 575–577.

(d) A. Heidbreder, J. Mattay, *Tetrahedron Lett.* **1992**, *33*, 1973–1976.

56 J. O. Bunte, E. K. Heilmann, B. Hein, J. Mattay, *Eur. J. Org. Chem.* **2004**,

3535–3550.

57 J. O. Bunte, S. Rinne, J. Mattay, *Synthesis* **2004,** 619.

58 K. Mizuno, Y. Otsuji, *"Addition and Cycloaddition Reactions via Photoinduced Electron transfer" in Top. Curr. Chem, 169*, J. Mattay (Ed.), Springer, Berlin **1994**, 301–346.

59 J. Grota, *Ph. D. Thesis*, University of Bielefeld, **2004**.

60 J. Grota, I. Domke, I. Stoll, T. Schröder, J. Mattay, M. Schmidtmann, H. Bögge, A. Müller, *Synthesis* **2005**, *14*, 2321

61 K. -D. Warzecha, X. Xing and M. Demuth, *Pure & App/ Chem.* **1997**, *69*, 109–112.

62 H. Rinderhagen, J. Mattay, *J. Inf. Rec. Mats*. **1998**, *24*, 261–264.

63 H. Rinderhagen, J. Mattay, *J. Inf. Rec. Mats*. **2000**, *25*, 229–233.

64 H. Rinderhagen, J. Mattay, *Chem. Eur. J.* **2004**, *10*, 851

65 H. Rinderhagen, *Ph. D. Thesis,* University of Bielefeld*,* **2002**.

66 J. D. Ha, J. Lee, S. C. Blackstock, J. K. Cha, *J. Org. Chem.* **1998,** *63,* 8510–8514.

67 Giese, B. *Angew. Chem.* **1983**, *95*, 771**–**782; *Angew. Chem. Int. Ed. Engl*. **1983**, *22*, 753.

68 Giese, B. *Angew. Chem.* **1985**, *97*, 555**–**567; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 553.

69 Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, Pergamon Press: Oxford, **1986**.

70 Curran, D. P. *Synthesis* **1988**, 417**–**439.

71 (a) *Radicals in Organic Synthesis*, Eds.: P. Renaud, and M. Sibi), Wiley-VCH: Weinheim, **2001**.

(b) Linker, T.; Schmittel, M. *Radikale und Radikalionen in der Organischen Synthese*, Wiley-VCH: Weinheim, **1998**.

72 (a) *Electron transfer in chemistry, Vol. 1-5* (Ed.: V. Balzani), Wiley-VCH: Weinheim, **2001**.

(b) *Top. Curr. Chem, Vol. 169* (Ed.: Mattay, J.), Springer: Berlin, **1994–1996**.

(c) L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer: Heidelberg, **1987.**

73 Y. Ito, S. Fujii, M. Nakatsuka, F. Kawamoto, T. Saegusa, *Org. Synth. Coll.* Vol. *6*, **1988**, 327

74 (a) K. I. Booker-Millburn, *Synlett* **1992**, 809.

(b) K. I. Booker-Millburn, D. F. Thomson, *J. Chem. Soc. Perkin Trans. 1*, **1995**, 2315.

(c) K. I. Booker-Millburn, D. F. Thompson, *Synlet,* **1993**, 592.

(d) K. I. Booker-Millburn, D. F. Thomson, *Tetrahedron* **1995**, *51*, 12955.

(e) K. I. Booker-Millburn, R. F. Dainty, *Tetrahedron Lett.* **1998**, *39*, 5097.

(f) K. I. Booker-Millburn, H. Jenkins, J. P. H. Charmant, P. Mohr, *Org Lett.* **2003**, *5*, 3309.

75 (a) *Top. Curr. Chem*. (Ed.: J. Mattay), *Vol. 156, 158, 159, 163, 168*, Springer: Berlin **1990**–**1993**.

(b) M. Fox, A. M. Chanon, *Photoinduced Electron Transfer*, Elsevier: Amsterdam, **1988**, Part A–D.

(c) J. Mattay, *Angew. Chem.* **1987**, *99*, 849–870; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 825.

(d) J. Mattay, *Synthesis* **1989**, 233–252.

(e) G. J. Kavarnos, *Fundamentals of Photoinduced Electron Transfer*, VCH: Weinheim, **1993**.

76 (a) A. Albini, M. Fagnoni, *Green Chem.* **2004**, *6*, 1–6.

(b) M. Oelgemöller, J. Mattay, *CRC Handbook of Organic Photochemistry and Photobiology*, (Eds.: W.Horspool, F. Lenci), CRC Press: Boca Raton **2004**, p 88-1–88-45.

(c) J. Mattay, *Chem. Uns. Zeit* **2002**, *36*, 98–106.

77 (a) M. Abe, A. Oku, *J. Org. Chem.* **1995**, *60*, 3065–3073.

(b) A. Oku, H. Takahashi, S. M. Asmus, *J. Am. Chem. Soc.* **2000**, *122*, 7388–7389**.**

(c) M. Abe, M. Nojima, A. Oku, *Tetrahedron. Lett*. **1996**, *37*, 1833–1836.

(d) A. Oku, M. Abe, M. Iwamoto *J. Org. Chem.* **1994**, *59*, 7445–7452.

78 For the stabilization of radical ions by metal salts see: K. Mizunu, Z. Hiromoto, K. Ohnishi, Y. Otsuji, *Chem. Lett.* **1983**, 1059.

79 P. A. Waske, J. Mattay, *Tetrahedron* **2005**, *66*, 10321–10330.

80 (a) P. H. Lee, K. Lee, S. Kim, *Org. Lett.* **2001**, *3*, 3205–3207.

(b) N. Iwasawa, T. Miura, K. Kiyota, H. Kusama, K. Lee, P. H. Lee, Org. Lett. **2002**, *4*, 4463–4466.

81 W. F. Bailey,. E. R. Punzaklan, *J. Org. Chem.* **1990**, *55*, 5404–5406.

82 S. Wolf, W. C. Agosta, *J. Am. Chem. Soc.* **1983**, *105*, 1292–1299.

83 (a) H. D. Roth, M. L. M. Schilling, F. C. Schilling, *J. Am. Chem. Soc.* **1985**, *107*, 4152–4158.

(b) J. Delgado, A. Espinós, M. C. Jiménez, M. A. Miranda, H. D. Roth, R. Tormos, *J. Org. Chem.* **1999**, *64*, 6541–6546.

84 A full paper covering both theoretical and spectroscopic details of siloxy cyclopropane radical cations will be published separately, H. Rinderhagen, P. A. Waske, T. Bally, J. Mattay, in preparation.

85 Baldwin, J. E. *J. Chem. Soc. Chem. Commun.* **1976**, 734–736.

86 A. L. J. Beckwith, C. J. Easton, A. K. Serelis, *J. Chem. Soc., Perkin Trans.* 2, **1985**, 443–450.

87 L. K. Shubina, S. N. Fedorov, O. S. Radchenko, N. N. Balaneva, S. A. Kolesnikova, P. S. Dmitrenok, A. Bode, Z. Dong, V. A. Stonik, *Tetrahedron Lett.* **2005**, *46*, 559–562.

88 Z. Nikolovska-Coleska, L. Xu, Z. Hu, Y. Tomita, P. Li, P. P. Roller, R. Wang, X. Fang, R. Guo, M. Zhang, M. E. Lippman, D. Yang, S. Wang, *J. Med. Chem.* **2004**, *47*, 2430–2440.

89 H. Dam, *Nature* **1935**, *135*, 652.

90 L. A. Decosterd, I. C. Parsons, K. R. Gustafson, J. H. II. Cardellina, J. B. McMahon, G. M. Cragg, Y. Murata, L. K. Pannell, J. R. Steiner, J. Clardy, M. R. Boyd, *J. Am. Chem. Soc.* **1993**, *115*, 6673.

91 (a) H. Suganuma, *J. Synth. Org. Chem. Jpn.* **2001**, *59*, 23.

(b) Y. Koura, S. Kinoshita, K. Takasuka, S. Koura, N. Osaki, S. Matsumoto and H. Miyoshi, *J. Pesticide Sci.*, **1998**, *23*, 18.

92 M. Oelgemöller and J. Mattay, in *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed., eds. W. M. Horspool and F. Lenci, CRC Press, Boca Raton, **2004**, Ch. 88, p. 1–35.

93 H. Klinger, *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 1862.

94 (a) H. Klinger, *Justus Liebigs Ann. Chem.* **1888**, *249*, 137.

(b) H. Klinger and O. Standke, *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 1340.

(c) H. Klinger and W. Kolvenbach, *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 1214.

95 A. Schönberg, W. I. Awad, G. A. Mousa, *J. Am. Chem. Soc.* **1955**; *77*, 3850–3852.

96 J. M. Bruce, E. Cutts, *J. Chem. Soc., Chem. Commun.* **1965**, 2–3.

97 R. Martin, *Org. Prep. Proc. Int.,* **1992**, *24*, 373–435.

98 (a) J. M. Bruce, Photochemistry of quinones, in The Chemistry of the quinonoid compounds, Eds. S. Patai, John Willy & Sons, New York, **1974**, Vol. *1*, chap. 9, 465–538.

(b) J. M. Bruce, *Quart. Rev.* **1967**, *21*, 405–428.

99 C. Chatgiliaoglu, D. Crich, M. Kamatsu, I. Ryu, *Chem. Rev.* **1999**, *99*, 1991–2069.

100 (a) M. E. Peover, *J. Chem. Soc.* **1962**, 4540–4559.

(b) Polarography (Oxidationspotential), in Methoden der organischen Chemie (*Houben-Weyl*), Ed. E. Müller and C. Grundmann, Thieme Stuttgart, **1976**, Vol VII/3a: Choninone, Part-I, 730–732.

101 P. Contant, M. Haess, J. Riegl, M Scalone and M. Visnick, *Synthesis* **1999**, 821.

102 W. M. Owton, *J. Chem. Soc., Perkin Trans. 1* **1999**, 2409.

103 (a) M. B. Rubin, *Fortschr. Chem. Forsch.* **1969**, *13*, 251.

(b) T. Mukherjee, *Proc. Indian Natl. Sci. Acdd., Part A* **2000**, 239.

104 1,4-Quinones:

(a) G. A. Kraus, M. Kirihara, *J. Org. Chem.* **1992**, *57*, 3256.

(b) G. A. Kraus, H. Maeda, *Tetrahedron Lett.* **1994**, *35*, 7723.

(c) G. A. Kraus, A. Melekhov, *Tetrahedron Lett.* **1998**, *39*, 3957.

(d) R. Pacut, M. L. Grimm, G. A. Kraus and J. M. Tanko, *Tetrahedron Lett.* **2001**, *42*, 1415.

105 1,4-Quinones:

(a) J. M. Bruce and E. Cutts, *J. Chem. Soc. C.* **1966**, 449.

(b) J. M. Bruce, D. Creed and J. N. Ellis, *J. Chem. Soc. C*, **1967**, 1486.

(d) J. M. Bruce and K. Dames, *J. Chem. Soc. C*, **1970**, 645.

106 1,4-Quinones:

(a) K. Maruyama and Y. Miyagi, *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1303.

(b) K. Maruyama, A. Takuwa and O. Soga, *Chem. Lett.* **1979**, 1097.

107 1,2-Quinones:

(a) K. Maruyama, H. Sakurai and T. Otsuki, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2777.

(b) K. Maruyama, T. Otsuki and Y. Naruta, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 791.

(c) K. Maruyama, A. Takuwa and O. Soga, *Chem. Lett.* **1979**, 1097.

(d) K. Maruyama and Y. Naruta, *Chem. Lett.* **1977**, 847.

(e) K. Maruyama and A. Takuwa, *Chem, Lett.* **1974**, 471.

(f) A. Takuwa, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2973.

108 C. Schiel, *Ph. D Thesis*, University of Bielefeld, **2002**.

109 M. Oelgemöller, *Diplom thesis*, University of Münster, **1995**.

110 J. F. Garden and R. H. Thomson, *J. Chem. Soc.* **1957**, 2483.

111 For Antimalarials based on **125**, see:

(a) L. F. Fieser and H. Heymann, *J. Biol. Chem.* **1948**, *176*, 1363.

(b) L. F. Fieser, E. Berliner, F. J. Bondhus, F. C. Chang, W. G. Dauben, M. G. Ettlinger,

G. Fawaz, M. Fields, M. Fieser, C. Heidelberger, H. Heymann, A. M. Seligman, W. R. Vaughan, A. G. Wilson, E. Wilson, M.-I Wu, M. T. Leffler, K. E. Hamlin, R. J. Hathaway, E. J. Matson, E. E. Moore, M. B. Moore, R. T. Rapala and H. E. Zaugg, *J. Am. Chem. Soc.,* **1948**, *70*, 3151.

112 (a) J. Hase and T. Nishimura, *Yakugaku Zasshi - J. Pharm. Soc. Jpn.* **1955**, *75*, 203.
(b) J. Hase and T. Nishimura, *Yakugaku Zasshi - J. Pharm. Soc. Jpn.* **1955**, *75*, 207.

113 The reaction of **129** and acetaldehyde gave exclusively 2-methyl-3-acetyl-naphthohydroquinone, although no yield was reported: G. O. Schenck and G. Koltzenburg, *Naturwiss.* **1954**, *41*, 452.

114 (a) E. A. Couladouros, Z. F. Plyta and P. Papageorgiou, *J. Org. Chem.* **1996**, *61*, 3031.
(b) M. S. Pearson, B. J. Jensky, F. X. Greer, J. P. Hangstrom and N. M. Well, *J. Org. Chem.* **1978**, *43*, 4617.

115 For Antimalarials based on **129**, see:
(a) C. Biot, H. Bauer, R. H. Schirmer, E. Davioud-Charvet, *J. Med. Chem.* **2004**, *47*, 5972.
(b) E. Davioud-Charvet, S. Delarue, C. Biot, B. Schwöbel, C. C. Boehme, A. Müssigbrodt, L. Maes, C. Sergheraert, P. Grellier, R. H. Schirmer and K. Becker, *J. Med. Chem.* **2001**, *44*, 4268.

116 Both, *in-cage* and *out-of-cage* mechanisms have been described in the literature and both mechanism operate more-or-less simultaneously depending on the specific reaction conditions of the irradiation experiment (*i.e.* temperature, solvent, quinone/aldehyde applied).[92]

117 H. W. Thompson, D. J. Long, *J. Org. Chem.* **1988**, *53*, 4201.

118 M. MacDonald, D. Vander Velde, J. Aubé, *J. Org. Chem.* **2001,** *66,* 2636.

119 W. A. Kinney, G. D. Crouse, L. A. Paquette, *J. Org. Chem.* **1983**, *48*, 4986.

120 N. Iwasawa, M. Funahashi, S. Hayakawa, T. Ikeno, K. Narasaka, *Bull. Chem. Soc. Japan*, **1999**, *72*, 85.

121 D. P. Curran, U. Diederichsen, M. Palovich, *J. Am. Chem. Soc.* **1997**, *119*, 4797.

122 Fringuelli, F.; Pizzo, F.; Taticch, T. D. J. Halls, A.; Wenkert, E. *J. Org. Chem.* **1982**, *47*, 5056.

123 G. Qabaja, G. B. Jones, *J. Org. Chem.* **2000**, *65*, 7187.

Curriculum Vitae

Name:	Prashant Ankushrao Waske
Date of Birth:	19th June 1977
Place of Birth:	Chitali, India
Parents:	Ankushrao Sitaram Waske
	Sanjeewani Ankushrao Waske
Marital Status:	Unmarried
Nationality:	Indian

Education:

1982–1989:	1st – 7th standard; Zila Parishad Shala, Anapatwadi, India.
1989–1992:	8th – 10th Standard, Bharat Vidya Mandir Wagholi, Baghshala Anapatwadi, India.
1992–1994:	11th – 12th Standard; Maharaja Sayajirao Junior College, Satara, India.
1994–1997:	Bachelor of Science (Chemistry); Yashwantrao Chavan Institute of Science, Satara, Shivaji University, India.
1997–2000:	Master of Science (Organic Chemistry); Poona College of Arts, Science & Commerce, Camp, Pune, University of Pune, India.
August 1999–March 2001:	Project Assistant at Division of Organic Chemistry: Technology, National Chemical Laboratory, Pune, India.
May 2001-May 2006:	Doctor rerum naturalium (Doctor of Philosophy) Department of Chemistry Organic Chemistry-I, University of Bielefeld, Germany.

Research advisor: Professor Dr. Jochen Mattay