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STUDIES OF THE PREPARATION OF PI-EXTENDED ANTHRACENES AND THEIR REACTIVITY WITH AN EMPHASIS ON THEIR PHOTOREACTIVITY

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United Arab Emirates University

College of Science

Department of Chemistry

STUDIES OF THE PREPARATION OF PI-EXTENDED ANTHRACENES AND THEIR REACTIVITY WITH AN EMPHASIS ON THEIR PHOTOREACTIVITY

Hasnaa Abdelkareem Sadeq

This thesis is submitted in partial fulfilment of the requirements for the degree of
Master of Science in Chemistry

Under the Supervision of Professor Thies Thiemann

May 2015

Declaration of Original Work

I, Hasnaa Sadeq, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled "*Studies of the Preparation of PI-Extended Anthracenes and their Reactivity with an Emphasis on their Photoreactivity"*, hereby, solemnly declare that this thesis is an original research work that has been done and prepared by me under the supervision of Professor Thies Thiemann , in the College of Science at the UAEU. This work has not been previously formed as the basis for the award of any academic degree, diploma or a similar title at this or any other university. The materials borrowed from other sources and included in my thesis have been properly cited and acknowledged.

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Abstract

Both *9,10-diaryl* and *9,10-diarylethenyl* substituted *Anthracenes* have recently been forwarded as light-regulated semiconducting materials, as well as potential constituent molecules in light-harvesting devices for the organic solar cell applications. So, it is of importance to understand whether such *9,10-substituted Anthracenes* are stable under photo-irradiation for a long time, and what type of reactions they could undergo. In the present thesis, photochemistry of *9-anthranylacrylates* and *9-aroylethenylanthracenes* has been investigated. *Anthranylacrylates* and *9-aroylethenylanthracenes* have been prepared by Wittig-olefination reaction from *9-anthranylcarbaldehyde*. Bromination of these molecules was found to give an access to *10-aryl-9-aroylethenylanthracenes* after Suzuki-Miyaura coupling reactions. While *9-ethenyl-substituted Anthracenes* in principle could undergo a photochemical [2+2] cycloaddition through their ethenyl unit or a photochemical [4+4] dimerisation via their *anthranyl* core unit, our result showed a photochemical E-Z-isomerisation of the ethenyl substituent in the case of the 9-aroylethenylanthracenes, while the *anthranyl acrylates* showed a slow photochemically induced polymerization. In order to “protect” the *anthranyl* unit, the 9-ethenylanthracenes were submitted to Diels-Alder reactions. The cycloadducts were subjected to photo-irradiation, also. In all, 9-ethenylanthracenes were found to be photoreactive under UV-irradiation. This could lead to the degradation of *ethenylanthracene*-containing materials; it should be taken into account when using these conditions.

Keywords: Photoreactions, photoirradiation, Suzuki-Miyaura reaction, Wittig olefination reaction, organic molecules, *Anthracenes*.

Title and Abstract (in Arabic)

التفاعلات الضوئية للمركبات العضوية: دراسة تحضير مشتقات مركبات الأنثراسين ذات الامتداد غير المشبع للتعرف على نشاطها الضوئي

تم التعرف حديثاً على مشتقات مركبات الأنثراسين مثل 9 و10-داياريل و 9 و10- داي اثينيل بأن لها تطبيقات في تنظيم أشباه الموصلات وكذلك كمواد لها القدرة على إمتصاص الضوء و تطبيقاته في مجال المركبات العضوية التي تستعمل في صناعة الخلايا الضوئية ، و من هنا تأتي أهمية هذه المركبات و التعرف على قدرتها على الثبات و تحمل ظروف امتصاص الإشعاع و نواتج التفاعلات عند فترات طويلة المدى.

و تتناول هذه الأطروحة دراسة المركبات 9-أنثرانيل اكريلات و 9- أرايلايثينيل أنثراسين لتناول نفس الدراسات المشار لها ، هذا وقد تم تحضير هذه المركبات باستعمال تفاعل فيتج من مشتقاتها مثل 9- انثرانيل كاربالدهيد ، وعند هلجنة هذه المركبات بالبرومين تم تسهيل الحصول على مركبات 9-اريل و 9- ارويلايثيليناالانثراسين من خلال التفاعل الرابطي سازوكي – ميوارا .

ومع مشتقات أن 9-ايثينيل انثراسين يمكن ن يسير من خلال تفاعل الدمج الضوئي (2+2) الإضافة الحلقية من خلال الرابطة الثنائية أو الإضافة الضوئية (4+4) بدمج وحدتين من المركب من خلال المجموعة البنائية للأنثراسين و متشاكل أي-زد للمجموعة الإثيلينية في حالة المركب 9- اروايثينيل الأنثراسينو بينما مركب أنثرانيل أكريلات يحصل له تفاعل بلمرة ضوئية بطيء، و لذلك لا بد من حماية مجموعة الانثرانيل الوظيفية ، فمركب 9-ايثيلين انثراسين تم تطبيق تفاعل ديلز الدر عليها، و التفاعل الحلقي للناتج تم تعرضه للضوء و وجد أن جميع مركبات 9- ايثيلين أنثراسين نشطة ضوئياً عند تعريضها للأشعة فوق البنفسجية، و هذا يؤدي إلى تفكك هذه المركبات عند استعمالها في تحضير بعض المواد مما يتطلب أخذ الأمر بعين الاعتبار و استعمال المثبتات الضوئية المناسبة.

الكلمات المفتاحية: التفاعلات الضوئية، أنشطة الإشعاع الضوئي، تفاعل سازوكي-ميوارا، تفاعل فيتج، مشتقات مركبات الأنثراسين

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My thanks are due to chair and all members of the Department of Chemistry at the UAEU for assisting me during the course of graduate study. My special thanks are extended to Ahmed Taha (Research Specialist) at the Library Research Desk for providing me with the relevant reference material. I would like to thank Dr John Graham for the HOMO-LUMO calculations (Figure 3).

Especially I thank my mom, dad. My hard-working parents have sacrificed their lives for my sister and myself and provided unconditional love and care. I love them so much, and I would not have made it this far without them. I know I always have my family to count on when times are rough. Special thanks to my dear husband to support me special last year, He standing beside me on the most difficult moments and I thank him for helping me and support me, I will not forget this at all.

Dedication

To my beloved family and kind husband

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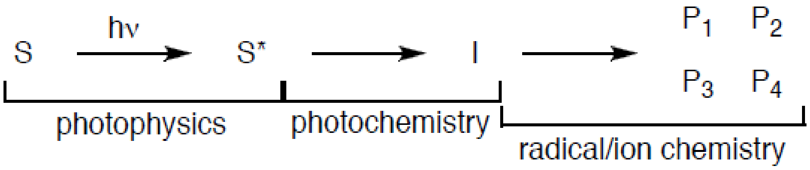
Chapter 1: Introduction

1.1. Photochemistry- A General View

Photochemistry is the study of chemical and physical changes, which result from the interaction of radiation from the visible and higher regions of the electromagnetic spectrum with materials. A primary photochemical reaction is the immediate consequence of the absorption of light. Subsequent chemical changes are called secondary processes (Scheme 1). For these to happen, firstly, a molecule must be able to absorb light, the radiation energy must match the energy difference of the ground and the excited state.

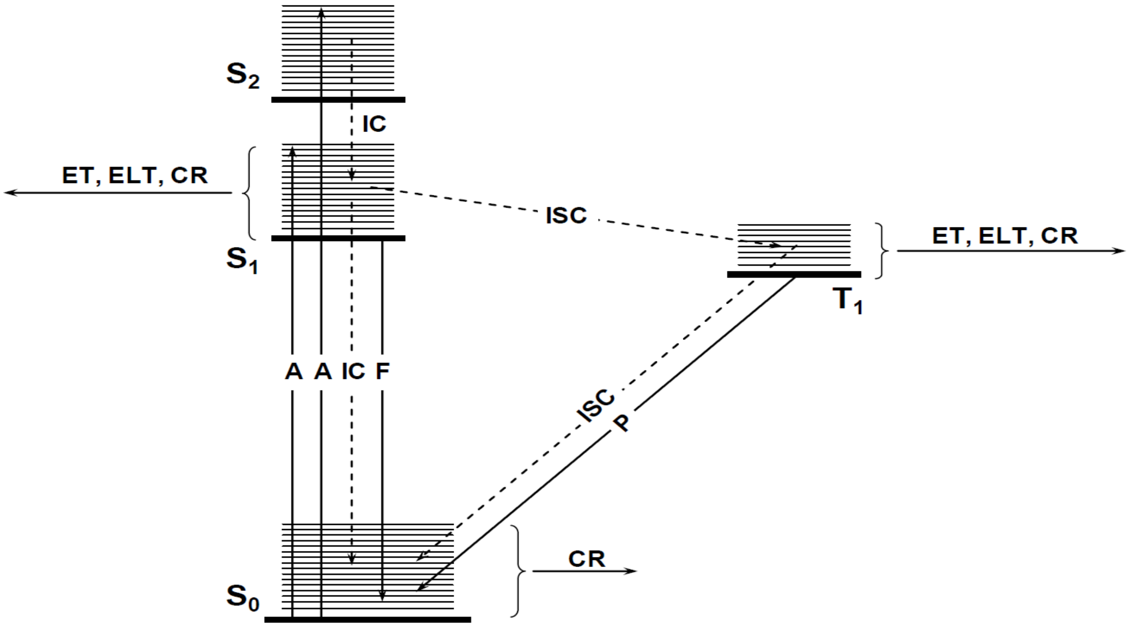


$$\boxed{\Phi = \text{quantum yield} = \frac{\#\ \text{molecules that undergo a process}}{\#\ \text{of photons absorbed by starting material}}}$$

Scheme 1: General schematic of a photochemical reaction

[*General schematic of a photochemical reaction, where S = substrate, S* = excited substrate, I = reaction intermediate, and P1 – P4 = reaction products of the photochemical reaction*]

When the molecule absorbs light, the electronic state of the molecule will change, but the ground state and excited electronic states have different vibrational and rotational states. The transfer of an electron from the ground state by absorption of light to the excited state takes place much more rapidly than any movement of the atom nuclei. This leads to the Franck-Condon principle. Overall, bonding in an excited state is usually lower than in the ground state, so that the bond X-X in the excited state is longer than the ground state. Therefore, the bond X-X in the excited state is longer than the ground state. The Jablonski diagram is usually used to illustrate the varying molecular electronic states, energy levels, possible of photochemical processes.



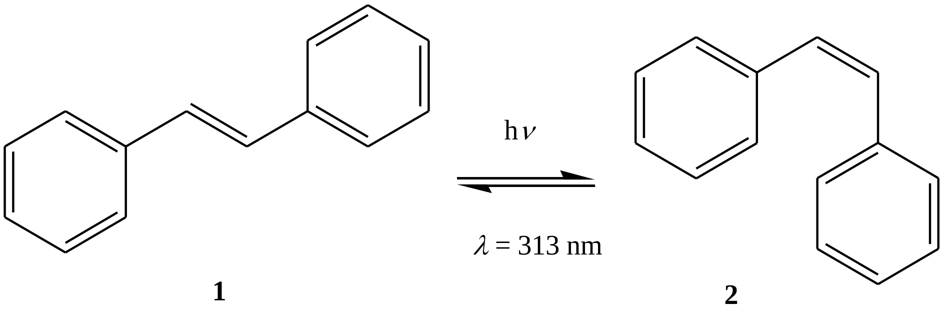
Scheme 2: Jablonski diagram

[*where S_0 is the singlet ground state, S1, S2 .. are the (1^{st}, 2^{nd}) excited singlet states, T1 is a triplet state, ISC stands for intersystem crossing, A for absorption of light, IC stands for internal conversion, CR for chemical reaction, ET for energy transfer, ELT for electron transfer, P for phosphorescence (with a lifetime of the excited state of 10^{-4}-10^{-2} s) and F for fluorescence* (Ali 2011)].

1.2. Important Types of Organic Photochemical Reactions

1.2.1. *Cis-trans*-isomerisation

Photo *cis-trans* isomerization is of interest as with careful selection of the irradiation wavelength. It is possible to induce a photo-stationary state in which the more thermodynamically instable isomer predominates. The classical mechanism ("one bond flip") for this reaction is via the first excited state of alkenes (ππ*), in which there is negligible bonding, and so a 180° rotation can occur, yielding the opposite isomer. When the wavelength of the light is chosen to irradiate selectively the more stable isomer, it is possible to force the formation of the more instable isomer in a 'photo-stationary state'. For example, this may be observed for the *trans-cis* isomerization of stilbene at λ = 313 nm as shown in Scheme 3.



Scheme 3: Cis-trans-isomerisation of stilbene (compound 1 and compound 2)

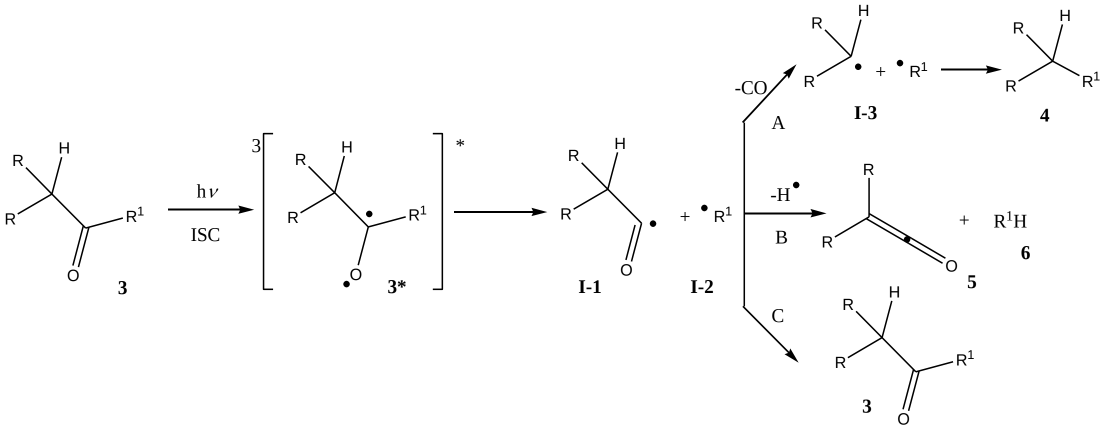
[*The cis-isomer* ***2*** *may convert back to the trans-isomer* ***1*** *over time via a thermal method when light irradiation is not sustained*]

1.2.2. Carbonyl compound photochemistry

Carbonyl compounds absorb in the UV region (= 230 - 340 nm), which corresponds to excitation of a non-bonding 2p orbital electron of the oxygen atom to the anti-bonding

π^*–orbital of the carbonyl. The chemical follow-up reactions include α-carbon and γ-hydrogen abstractions in so-called Norrish-type reactions.

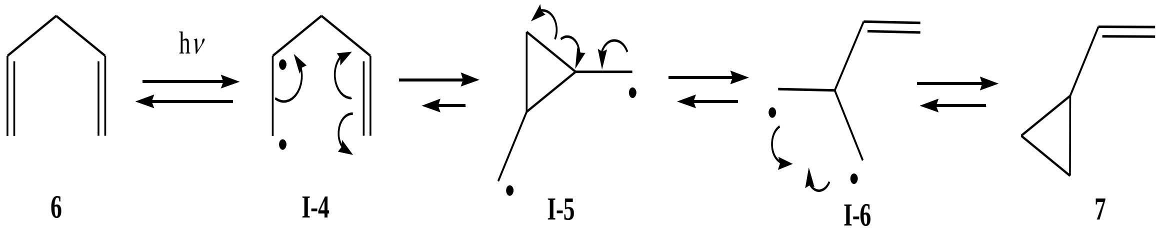
α-Cleavage (Norrish Type I) is observed for excited state carbonyl compounds, where an acyl radical **I-1** and an alkyl radical **I-2** are formed. These can undergo several follow-up reactions, namely decarbonylation (Pathway A) to yield alkanes **4**, disproportionation (Pathway B) to ketenes **5** and recombination (Pathway C) to re-form starting material **3** as shown in Scheme 4.



Scheme 4: Norrish type reactions of carbonyl compounds

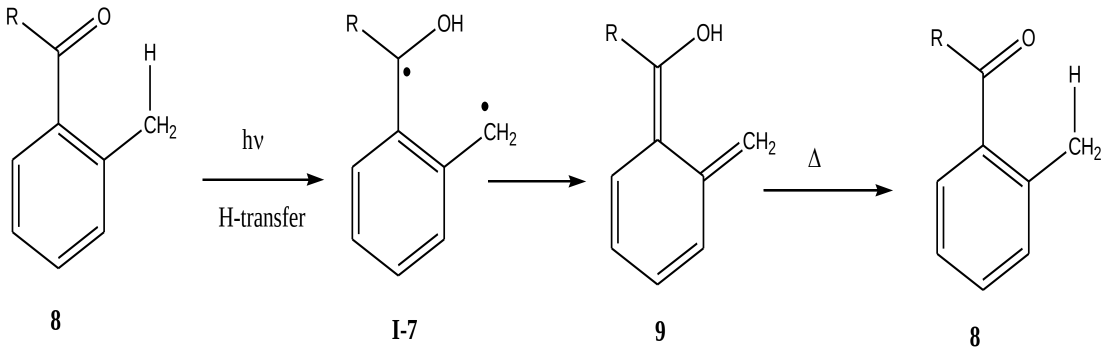
1.2.3 Rearrangements reactions

A common photo-rearrangement is the di-π-methane rearrangement, in which 1,4-dienes **6** undergo a photochemical transformation to yield vinylcyclopropanes **7** (Scheme 5). In general, photochemical rearrangements are difficult to identify beforehand, and it is necessary study the photoreaction products.



Scheme 5: Photochemical dimethane – vinylcyclopropane rearrangement

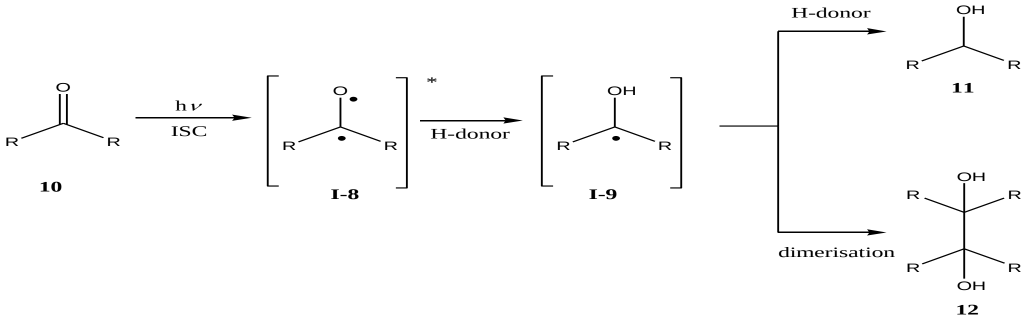
Another type of rearrangement reaction is used in sunscreen blockers, where UV light initiates the photo-tautomerisation of the active compound **8**, thus preventing light causing damage to skin (Scheme 6). Thermally, the ortho-quinodimethane 9 is converted back to the starting material **8**. This last reaction can proceed on the skin on a warm day.



Scheme 6:Phototautomerisation of 8 to 9 and thermal “recycling” of 9 to 8.

1.2.4 Photo Redox Reactions

A photo-reduction is defined as the addition of one or more electrons to a photo-excited species or the photochemical hydrogenation of a substance. In these reactions, a photo-excited species I-8 reacts with a suitable H-donor. The radical I-9 formed may undergo reaction with other hydrogen donors to form alcohols 11 or undergoes other reactions, such as a dimerization to 12 as shown in Scheme 7. In addition, photo-oxidations are known, where a photo-oxidation refers to the loss of one or more electrons from a species because of photo-excitation.

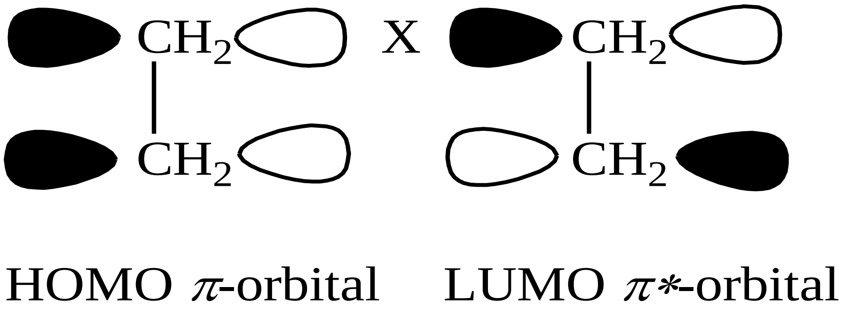


Scheme 7: Photoreduction of a ketone10

1.2.5 [2+2] photocycloaddition reactions

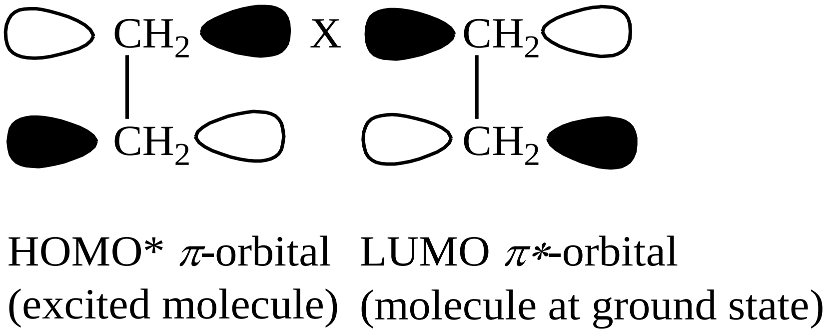
The [2+2] cycloaddition reaction obtains its significance in organic synthesis from its ability to create two carbon-carbon bonds with concomitant installation of up to four new stereogenic centres. This potentially highly useful synthetic reaction can be promoted photochemically, but can also be mediated by Lewis acids, or catalysed by transition metals.

According to the Woodward-Hoffman rules (Woodward 1969), a photochemical [2+2] cycloaddition is symmetry allowed, while the equivalent thermal reaction is symmetry forbidden. These statements can be expanded by examining the frontier molecular orbital (FMO) theory by Kenichi Fukui (Fukui 1982). This could be illustrated using the [2+2] cycloaddition of two ethene molecules. In a thermal reaction, the molecules react in their ground states; so, the π orbital (HOMO) of one ethene molecule is expected to interact with the π* orbital (LUMO) of other one as shown in Scheme 8.



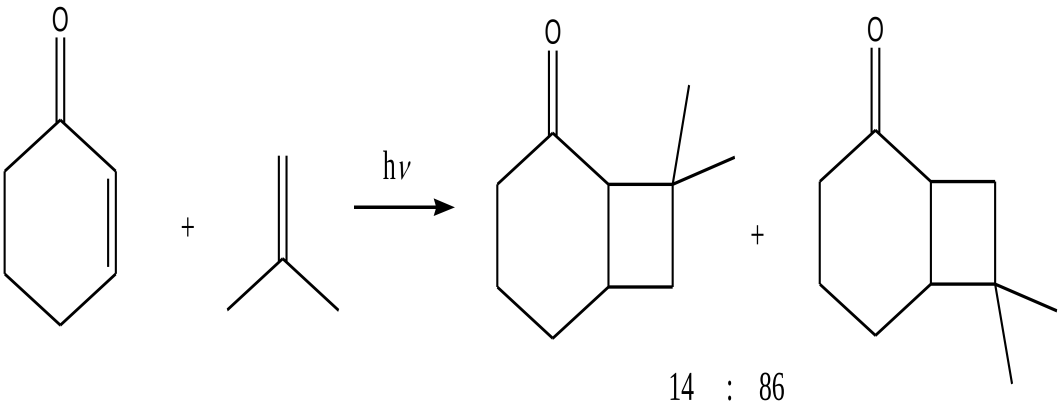
Scheme 8**:** Orbital interactions in the thermal [2+2] cycloaddition of ethene

On the other hand, since the orbitals on the top set of carbon atoms are of opposite signs, the overlap does not lead to a bonding interaction. Therefore, this reaction is unlikely to be occurred through a concerted process and is said to be symmetry forbidden. This is not the case for the photochemical reaction. During this process, a molecule of ethene absorbs a photon of light; this promotes one of its electrons from the π to the π*orbital. The HOMO of the excited state ethene is now the π* orbital and overlap between this new HOMO and the LUMO of a ground state ethene creates a bonding interaction as shown in Scheme 9. For this reason, the reaction is said to be symmetry allowed and can proceed through a concerted pathway.



Scheme 9: Orbital interactions in the photochemical [2+2] cycloaddition of ethene.

When the ethene molecules are replaced with unsymmetrical alkenes, the photochemical [2+2] cycloaddition can produce two region-isomers, the head-to-head and the head-to-tail products, which may also depend on the wavelength of photoirradiation (Klaus 1995). For instance, irradiation of cyclohexenone (**13**) and isobutene (14) yields a head-to-head isomer 15a in addition to the head-to-tail product 15b as shown in Scheme 10 (Weedon 1984).



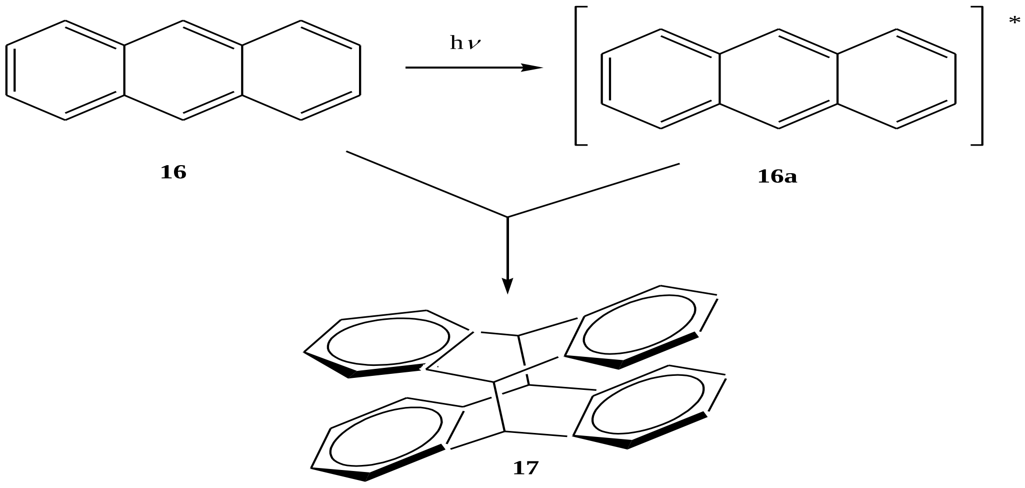
13 **14** **15a** **15b**

Scheme 10: HH- and HT-isomers in the photoreaction of cyclohexenone with isobutene

The region-selectivity in this reaction is generally explained through electrostatic interactions. During the cycloaddition, the head-to-tail orientation maximizes the electrostatic interactions between the excited state enone and the ground state alkene. This interpretation was verified when high region-selectivity was observed in reactions involving highly polarized enones and alkenes. Other factors affecting region-selectivity include the steric interactions between substituted enones and alkenes as well as solvent polarity and temperature.

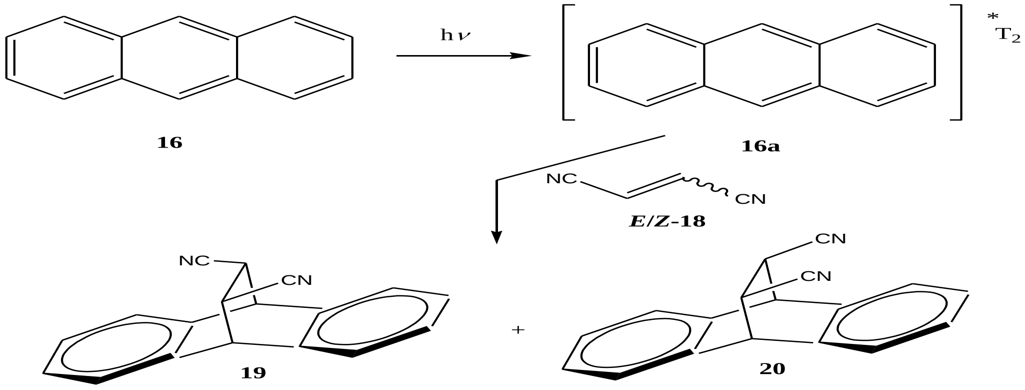
1.3. The Photochemistry of Anthracene

Anthracene is an interesting molecule, which was isolated in 1833 from coal tar. High purity anthracene is used as a scintillator for detectors of high-energy photons, electrons and □-particles. It is a precursor of anthraquinone dyes. Thermally allowed [4+2]-Diels-Alder type reactions proceed well with anthracenes as its resonance energy due to aromaticity is only 347 kJ/mol (in comparison: benzene 152 kJ/mol and phenanthrene 381 kJ/mol). The [4+4]-cycloaddition of anthracene is one of the well-known photochemical processes (Bouas-Laurent 2000, Becker 1993, Roth 1989) as already 1867 Fritsche noted that anthracene changes under sunlight as shown in Scheme 11. The product is the dimer of anthracene, **17**.



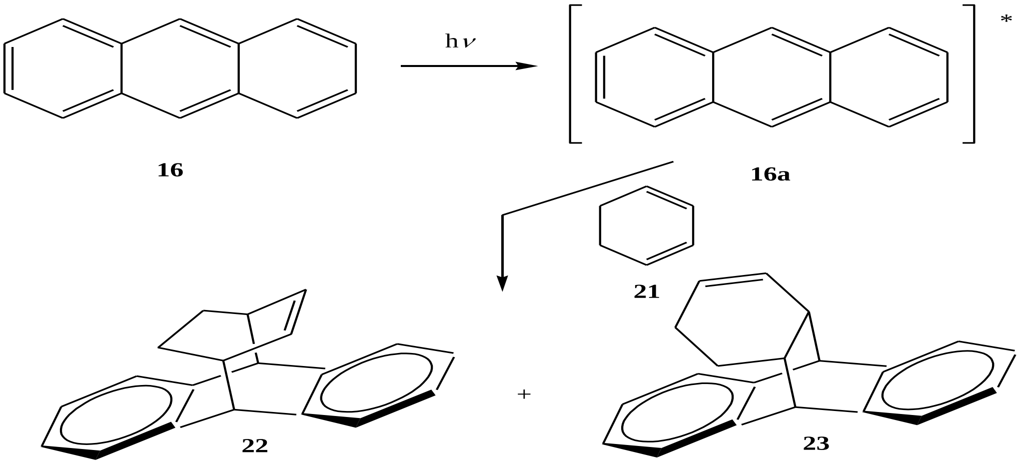
Scheme 11: Photochemical [4+4]-cycloaddition of anthracene.

[*When anthracene is photolyzed by a two-laser flash-photolysis, where the excited acquired triplet state was seen to react with fumaronitrile and maleonitrile to give the respective cycloadducts,* ***19*** *and* ***20*** (Wang et al. 1993)]



Scheme 12: Anthracene photochemical excitation to triplet state in reaction with dienophile

An interesting result, where anthracene was photochemically excited in the presence of 1,3,-cyclohexadiene, showed that a halogen containing solvent quenches the excited singlet state of anthracene rapidly, while the triplet state is not much affected. The excited singlet state gives the [4+4]-product with cyclohexa-1,3-diene (21), 22, but the excited triplet state of anthracene gives the [2+2]-type cycloadduct 23 with cyclohexa-1,3-diene (21) as shown in Scheme 13 (Il’ichev 2009).



Scheme 13: The excited singlet state in halogenated solvents is quenched

[*Compound* ***23*** *is obtained as the major product, while in non-heavy atom solvents 22 are obtained*]

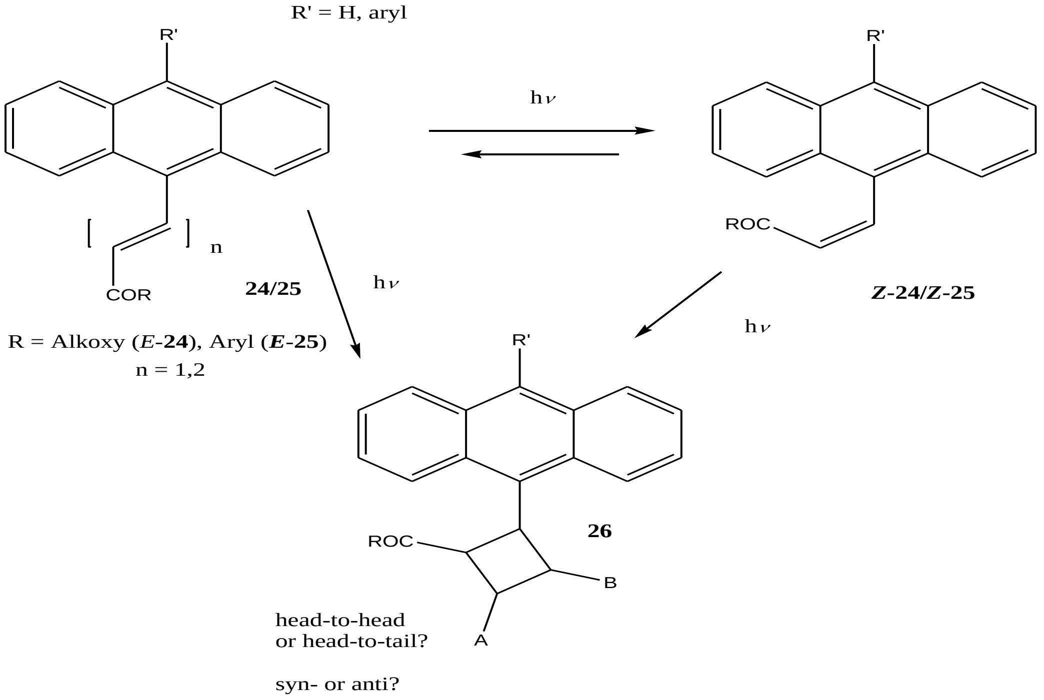
1.3.1 Photochemistry of anthracenes – photochemical [4+4]-cycloaddition

The realization that anthracene undergoes a photochemical [4+4]-cycloaddition was followed up with work on 9-substituted anthracenes, where similar [4+4]-cycloadducts were noted (Lalas 1960, Becker 1989, Becker 1993b, Becker 1993c, Lapouyade 1968). X-ray crystal structural analyses of the dimers (Hengstenberg 1932, Ehrenberg 1966, 1968) were carried out to show that the dimers were mostly HT-dimers.

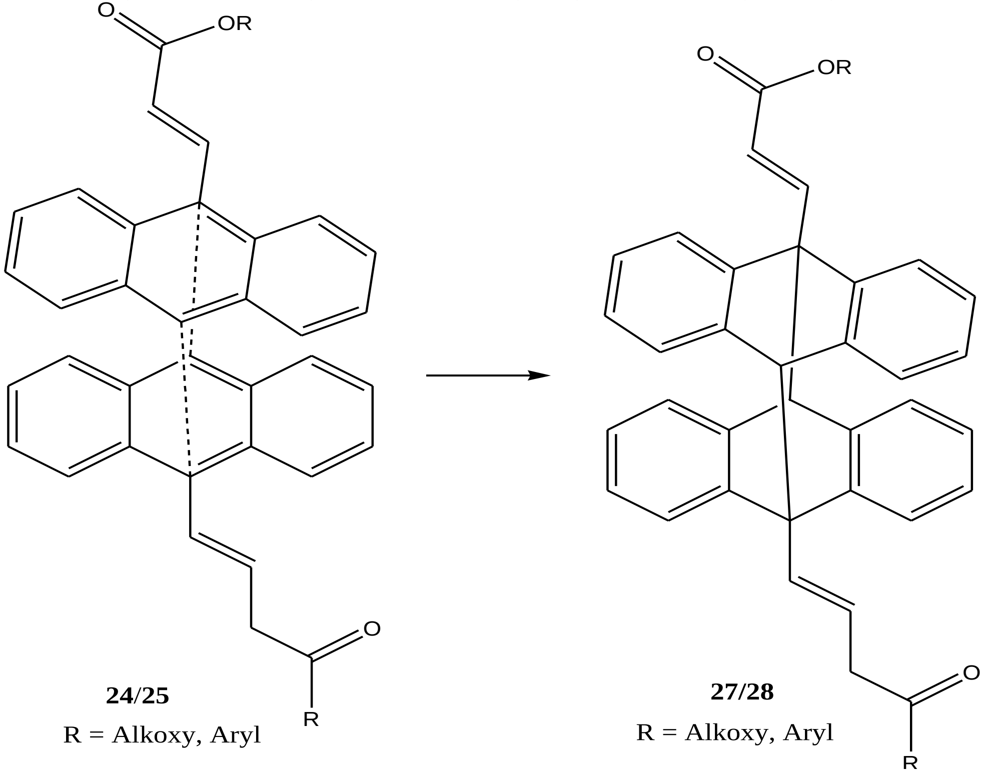
Xu et al. (2013) have used a photo-[4+4]-cycloaddition for the construction of polymeric structures, based on a 9-alkoxy substituted anthracene precursor. The alkoxy substituent was connected to a [5]-pillarene at the other terminus, where the polymeric assembly was held together by a 1,12-bis-imidazoyldodecane. Here, the compound was photoirradiated at > 360 nm. This dimerisation was found to be reversible by photoirradiation at< 300 nm or by heating the dimer. Other precedents of [4+4]-cycloaddition reactions with switching in the area of materials can be found (Bringmann 2011; Schäfer 2004, 2007, 2009; Zheng 2002; Ferri 2004; Molard 2005; Connal 2008; Kurchaski 2011; Wells 2011; Wang 2013).

To the best of our knowledge, little information has been obtained of the photochemical behavior of 9-ethenyl or 9-ethynyl substituted anthracenes (see above, Becker 1983, Becker 1985b), especially where the other terminus of the double bond or triple bond is substituted by an electron withdrawing substituent. There is one example of benzoylethenylanthracenes, which was shown to give *E*/*Z*-isomerisation upon photoirradiation, coupled with a novel rearrangement (Becker 1983, Becker 1985b). These together with aryl-substituted anthracenes (in Dougherty 1986) make for interesting anthranyl-based photoelectronic materials.

Some use of these has been found in molecular wires (Valkenier 2011), in light-regulated semiconducting materials and as potential constituent molecules in light-harvesting devices for organic solar cell applications (Marrocchi 2010; Belghiti 2014). Here, however, the photochemical stability of such compound is of importance. As dominant photochemical transformations one can see the *E*-*Z*-isomerisation of the double bond (Scheme 14), a possible [2+2]-cycloaddition of the double bond (Scheme 14) and a [4+4]-cycloaddition of the anthranyl unit as shown in Scheme 15.



Scheme 14: Pathways of the photolysis of anthran-9-ylacrylates & 9-aroylethenylanthracenes



Scheme 15: Pathways of the photolysis of anthran-9-ylacrylates & 9-aroylethenylanthracenes

1.4. Objectives of the work

a.) 9-Ethenylanthracenes will be prepared, where the ethenyl group has an electron-withdrawing substituent at its end such as an aroyl or ester function.

b.) The photochemistry of the molecules will be studied at < 300 nm

c.) The photochemistry of the molecules will be studied at > 300 nm

d.) Diels-Alder adducts of the molecules are to be prepared

e.) The photochemistry of the cycloadducts is to be studied.

Chapter 2: Methodology

2.1. General

Anthracenes with a substituent at C9 were prepared by Wittig olefination. For this, the synthesis of diverse phosphoranes is important. Materials were purified using column chromatographic separation techniques. The products were characterized by ^{1}H NMR (400 MHz), ^{13}C NMR (100.5 MHz), IR and melting point, where applicable. CHNS data was obtained for some of the compounds.

The anthranylacrylates and 9-aroylethenylanthracenes were subjected to Diels-Alder reaction with arylmaleimides and maleic anhydrides. Mostly, the reactions involved heating of the anthranylacrylates and the arylmaleimides without solvent or in xylene and filtration and washing the products with organic solvent. The products were characterized by ^{1}H NMR (400 MHz), ^{13}C NMR (100.5 MHz), IR and melting point, where applicable. CHNS data was obtained for some of the compounds.

The anthranylacrylates and 9-aroylethenylanthracenes were photoirradiated in a Luzchem LZC 4V photoreactor using USHIO G8T5 lamps (at □ = 253.7 nm) and with Hitachi FL8BL-B (at λ = 352 nm [peak output]). The photolysis reactions were monitored by ^{1}H NMR spectroscopy. If the reactions seemed promising, the reaction mixtures were separated by column chromatography on silica gel, and the products were characterized by ^{1}H NMR (400 MHz), ^{13}C NMR (100.5 MHz), IR and melting point, where applicable.

The *N*-aryl-9-substituted-9,10-dihydro-9,10(4,'5')-succinimido)anthracenes as the cycloadducts between the anthranylacrylates/aroylethenylanthracenes and N-arylmaleimides were submitted to photoirradiation with USHIO G8T5 lamps (at □ = 253.7 nm).). The photolysis reactions were monitored by ^{1}H NMR spectroscopy. If the reactions seemed promising, the reaction mixtures were separated by column chromatography on silica gel, and the products were characterized by ^{1}H NMR (400 MHz), ^{13}C NMR (100.5 MHz), IR and melting point, where applicable. For X-ray crystal structural analysis, 9-(4-chlorobenzoylethenyl) anthracene was sent to the Department of Inorganic Chemistry, University of Hamburg.

2.2. Experimental Part

Melting points were measured with a Stuart SMP10 melting point apparatus and uncorrected. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 100.5 MHz) spectra were taken on a Varian 400 MHz spectrometer. Infrared spectra were taken on a spectrometer (solid samples as KBr pellets, liquid samples using NaCl plates). Column chromatography was carried out on silica gel S (0.2-0.5 mm and 0.063-0.1 mm, Riedel de Haen) and with Sigma Aldrich 60 Å (230 – 400 mesh, Merck grade 9385). Analytical thin layer chromatography (TLC) was carried out on silica on TLC Alu foils from Fluka (with fluorescent indicator at= 254 nm).

For detection, a UVGL-58 lamp was used from UYP (Upland, CA, USA). UV-VIS spectra were obtained from a Varian Cary 50 conc UV-VIS spectrophotometer, with CH_2Cl_2 [Sigma Aldrich, purris. p.a., ≥ 99.9% (GC)] and acetonitrile [Panreac, HPLC grade and Romil Chemical, Far-UV grade 190, pur. 99.9%] as solvent. For the photoirradiation, a Luzchem LZC 4V photoreactor was used with 13 USHIO G8T5 lamps (7.2 W low-pressure mercury arc lamp with a radiation peak at $\lambda = 253.7$ nm) and with 14 Hitachi FL8BL-B (0.75 W, UV irradiance 8.0 $(cm)^2$, with a radiation peak at= 352 nm). CH_2Cl_2 [Sigma Aldrich, purris. p.a., ≥ 99.9% (GC)] and benzene were taken as solvents in the photoirradiation experiments.

2.3. Chemicals and Reagents

Triphenylphosphine (Aldrich), 9-formylanthracene (Aldrich), anthracene, and ethyl bromoacetate were acquired commercially. Diethyl maleate (**60**) was prepared by reaction of maleic anhydride (MSA, **46**) with ethanol in the presence of conc. HCl, where the product was purified by column chromatography on silica gel.

2.3.1. Procedure A

1) **Maleic acid mono 4-bromophenylamide (47a)**

To a stirred solution of maleic anhydride (**46**, 1.96 g, 20 mmol) in tetrahydrofuran (THF, 25 mL) is given 4-bromoaniline (**45a**, 3.44 g, 20 mmol). The reaction mixture is stirred at rt for 3h. Thereafter, the suspension is diluted with water (150 mL) and filtered. The filter cake is washed with water (2 X 100 mL) and air-dried at rt to give **47a** as a very pale green solid (4.37 g, 81%), mp. 204 ^{o}C (196 – 200 ^{o}C [Kumar 2011, Kirchner 1959, Krishnan 1976]); ν_{max} (KBr/cm^{-1}) 3466 (b), 3075, 1707, 1629, 1567, 1540, 1489, 1396, 1323, 855, 826, 681, 613, 506, 436; δ_H (400 MHz, DMSO-d^6) 6.28 (1H, d, ^3J = 12.0 Hz), 6.42 (1H, d, ^3J = 12.0 Hz), 7.47 (2H, d, ^3J = 8.8 Hz), 7.56 (2H, d, ^3J = 8.8 Hz), 10.5 (1H, s, NH); δ_C (400 MHz, DMSO-d^6) 115.9, 121.8 (2C), 130.7, 132.0, 132.1 (2C), 138.4, 163.8 (C$_{quat}$, CO), 167.4 (C$_{quat}$, CO).

2) Maleic acid mono phenylamide (47b)

Maleic anhydride (**46**, 1.96 g, 20 mmol) and aniline (**45b**, 1.86 g, 20 mmol) in THF (25 mL) were reacted according to procedure A to give **47b** as a solid (82%); ν_{max} (KBr/cm^{-1}) 3458 (bs), 3275, 3210, 3099, 2887, 1698, 1620, 1558, 1450, 1419, 1331, 1267, 1227, 1190, 1000, 972, 852, 758, 691, 609, 526; □$_H$ (400 MHz, DMSO-d^6) 6.28 (1H, d, ^3J = 11.6 Hz), 6.45 (1H, d, ^3J = 11.6 Hz), 7.06 (1H, ^3J = 7.6 Hz), 7.30 (2H, d, ^3J = 8.8 Hz, ^3J = 7.6 Hz), 7.59 (2H, d, ^3J = 8.8 Hz), 10.4 (1H, s, NH); □$_C$ (100.5 MHz, DMSO-d^6) 120.0 (2C, CH), 124.4, 129.3 (2C, CH), 130.9, 132.1, 138.9, 163.7 (C$_{quat}$, CO), 167.4 (C$_{quat}$, CO).

3) Maleic acid mono 2-methylphenylamide (47c)

Maleic anhydride (**46**, 1.96 g, 20 mmol) and 2-methylaniline (**45c**, 2.14 g, 20 mmol) in THF (25 mL) were reacted according to procedure A. In certain cases, the product did not crystallize directly from THF. Then, the reaction solution was poured into hexane, where the product precipitated. After filtration and drying, **47c** (3.83 g, 93.5%) was obtained as a colourless solid, mp. 129 ^{o}C; ν_{max} (KBr/cm^{-1}) 3329, 2988, 1713, 1620, 1582, 1548, 1460, 1313, 977, 851, 764, 708, 609; δ_H (400 MHz, DMSO-d^6) 2.19 (3H, s, CH$_3$), 6.27 (1H, d, ^3J = 12.4 Hz), 6.55 (1H, d, ^3J = 12.4 Hz), 7.07 – 7.21 (3H, m), 7.39 (1H, d, ^3J = 8.0 Hz), 9.92 (1H, s, NH); δ_C (400 MHz, DMSO-d^6) 18.2 (CH$_3$), 125.6, 126.2, 126.4, 130.7, 130.8, 132.5, 132.9, 135.7, 164.1 (C$_{quat}$, CO), 167.1 (C$_{quat}$, CO).

4) Maleic acid mono 4-methylphenylamide (47d)

Maleic anhydride (**46**, 1.96 g, 20 mmol) and 4-methylaniline (**45d**, 2.14 g, 20 mmol) in THF (25 mL) were reacted according to procedure A to give **47d** as a solid(3.85 g, 94%), mp. 212 ^{o}C; ν_{max} (KBr/cm^{-1}) 3438 (b), 3287, 3214, 3094, 1699, 1635, 1540, 1510, 1406, 1328, 850, 815; δ_H (400 MHz, DMSO-d^6) 2.23 (3H, s, CH$_3$), 6.27 (1H, d, ^3J = 12.0 Hz), 6.42 (1H, d, ^3J = 12.0 Hz), 7.10 (2H, d, ^3J = 8.0 Hz), 7.47 (2H, d, ^3J = 8.0 Hz), 10.4 (1H, bs); □$_C$ (100.5 MHz, DMSO-d^6) 20.9 (CH$_3$), 120.0 (2C, CH), 129.6 (2C, CH), 131.1, 131.9, 133.5, 136.3, 163.5 (C$_{quat}$, CO), 167.3 (C$_{quat}$, CO).

5) Maleic acid mono 4-methoxyphenylamide (47e)

Maleic anhydride (**46**, 3.03 g, 30.9 mmol) and 4-methoxyaniline (**45e**, 3.81 g, 30.9 mmol) in THF (38 mL) were reacted according to procedure A to give **47e** as a solid, mp. 204 ^{o}C; ν_{max} (KBr/cm^{-1}) 3350 (b), 3120 (b), 1699, 1326, 1308, 1281, 1247, 1178, 1035, 977, 858, 834, 623, 596, 524; □$_H$ (400 MHz, DMSO-d^6) 3.68 (3H, s, OCH$_3$), 6.28

(1H, d, ^3J = 12.4 Hz), 7.52 (1H, d, ^3J = 12.4 Hz), 6.87 (2H, d, ^3J = 9.2 Hz), 7.52 (2H, d, ^3J = 9.2 Hz); 10.4 (1H, s, NH); δ_{C} (100.5 MHz, DMSO-d^6) 55.6 (OCH$_3$), 114.4 (2C, CH), 121.7 (2C, CH), 131.4 (CH), 131.7 (C$_{\text{quat}}$), 132.1 (CH), 156.3 (C$_{\text{quat}}$), 163.3 (C$_{\text{quat}}$, CO), 167.2 (C$_{\text{quat}}$, CO).

6) Maleic acid mono 2,5-dimethoxyphenylamide (47f).

Maleic anhydride (**46**, 4.24 g, 43.3 mmol) and 2,5-dimethoxyaniline (**45f**, 6.6 g, 43.1 mmol) in THF (40 mL) were reacted according to procedure A to give **47f** as a olive-green solid, mp. 155 ^{o}C; ν_{max} (KBr/cm^{-1}) 3350, 3056, 3022, 3001, 2972, 2834, 1725, 1718, 1626, 1557, 1489, 1281, 1262, 1216, 1175, 1130, 1056, 1024, 977, 854, 798, 719, 611; δ_{H} (400 MHz, DMSO-d^6) 3.75 (3H, s, OCH$_3$), 3.65 (3H, s, OCH$_3$), 6.31 (1H, d, ^3J = Hz), 6.64 (1H, dd, ^3J = 8.8 Hz, ^4J = 2.8 Hz), 6.68 (1H, d, ^4J = 2.8 Hz), 6.94 (1H, d, ^3J = 8.8 Hz), 9.80 (1H, s); δ_{C} (100.5 MHz, DMSO-d^6) 55.8 (OCH$_3$), 56.6 (OCH$_3$), 108.8 (CH), 109.4 (CH), 112.4 (CH), 127.7 (C$_{\text{quat}}$), 131.1 (CH), 131.9 (CH), 144.2 (C$_{\text{quat}}$), 153.2 (C$_{\text{quat}}$), 163.5 (C$_{\text{quat}}$, CO), 167.8 (C$_{\text{quat}}$, CO).

7) Maleic acid mono 2,4-difluorophenylamide (47g).

Maleic anhydride (**46**, 4.32 g, 44.1 mmol) and 2,4-difluoroaniline (**45g**, 5.69 g, 44.1 mmol) in THF (40 mL) were reacted according to procedure A (90 min., rt) to give **47g** (2.59 g, 26%) as a grey solid, mp. 207 ^{o}C; ν_{max} (KBr/cm^{-1}) 3460, 3230, 3067, 1713, 1638, 1569, 1515, 1484, 1439, 1151, 969, 852, 60, 487; □$_{\text{H}}$ (400 MHz, DMSO-d^6) 6.54 1H, d, ^3J = 12.4 Hz), 6.73 (1H, d, ^3J = 12.4 Hz), 7.28 (1H, bs), 7.43 – 7.48 (1H, m), 8.04 – 8.08 (1H, m), 10.5 (1H, s, NH); δ_{C} (100.5 MHz, DMSO-d^6) 104.6 (CH, dd, ^2J = 26.8 Hz, ^2J = 23.8 Hz), 111.7 (CH, dd, ^2J = 8.9 Hz, ^4J = 3.0 Hz), 122.4 (C$_{\text{quat}}$, dd, ^2J =

9.7 Hz, ^4J = 2.9 Hz), 126.1 (CH, dd, ^3J = 9.7 Hz, ^3J = 3.0 Hz), 131.1 (CH), 131.4 (CH), 154.5 (C_{quat}, dd, ^1J = 247.8 Hz, ^3J = 11.9 Hz), 159.3 (C_{quat}, dd, ^1J = 243.3 Hz, ^3J = 12.0 Hz), 163.9 (C_{quat}, CO), 167.6 (C_{quat}, CO).

8) Maleic Acid mono 2,6-difluorophenylamide (47h)

Maleic anhydride (**46**, 4.92 g, 50.2 mmol) and 2,6-difluoroaniline (**45h**, 5.85 g, 45.3 mmol) in THF (43 mL) were reacted according to procedure A (24h, rt). Afterwards, the reaction mixture was filtered and the filter cake was washed with diethyl ether (2 X 25 mL) to give **47h** (6.57 g, 64.(5)%) as a colorless solid, mp. 184 ^{o}C; ν_{max} (KBr/cm^{-1}) 3420, 3120, 3003, 1708, 1633, 1552, 1496, 1472, 1412, 1304, 1245, 1021, 970, 860, 787, 703, 621, 593, 495; δ_H (400 MHz, DMSO-d^6) 6.36 (1H, d, ^3J = 12.0 Hz), 6.44 (1H, d, ^3J = 12.0 Hz), 7.11 – 7.16 (2H, m), 7.30 – 7.37 (1H, m), 10.2 (1H, s, NH); $\square_C$ (100.5 MHz, DMSO-d^6) 112.3 (2C, CH, dd, $^2J_{CF}$ = 17.8 Hz, $^4J_{CF}$ = -5.2 Hz), 114.1 (C_{quat}, dd, $^3J_{CF}$ = 16.4 Hz, $^2J_{CF}$ = 16.4 Hz), 128.7 (CH, dd, $^3J_{CF}$ = 9.6 Hz, ^3J = 9.6 Hz), 129.6 (CH), 132.1 (CH), 158.0 (2C, C_{quat}, dd, $^1J_{CF}$ = 247.8 Hz, $^3J_{CF}$ = 5.2 Hz), 163.5 (C_{quat}, CO), 167.6 (C_{quat}, CO).

2.3.2. Procedure B

9) 4-Bromophenylmaleimide (48a)

A mixture of **47a** (3.06 g, 10.8 mmol) and sodium acetate trihydrate ($NaOAc\cdot 3H_2O$, 4.37 g, 32.1 mmol) in acetic anhydride (30 mL) was held at 110 ^{o}C for 6h. Thereafter the cooled solution was given slowly to a sat. aq. solution of Na_2CO_3. The mixture was extracted with ether/ethyl acetate (1/1 v/v, 3 X 90 mL). The organic phase was separated, dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluent: $CHCl_3$) to give **48a** as a pale yellow solid (1.59 g, 6.3 mmol, 58%), mp. 147 ^oC (Lit. 128 – 130 ^oC [Matuszak 2009, Butler 2007]); ν_{max} (KBr/cm^{-1}) 3090, 1721, 1492, 1400, 1386, 1149, 1066, 831, 707, 686, 585, 501; δ_H (400 MHz, $CDCl_3$) 6.85 (2H, s), 7.24 (2H, d, ^3J = 8.8 Hz), 7.58 (2H, d, ^3J = 8.8 Hz); δ_C (100.5 MHz, $CDCl_3$) 121.6 (C_{quat}), 127.4 (2C, CH), 130.2 (C_{quat}), 132.3 (2C, CH), 134.3 (2C, CH), 169.1 (2C, C_{quat}, NCO).

10) *N*-Phenylmaleimide (48b)

A mixture of **47b** (2.05 g, 10.7 mmol) and sodium acetate trihydrate ($NaOAc^{\cdot}3H_2O$, 4.37 g, 32.1 mmol) in acetic anhydride (30 mL) were reacted at 105 ^oC according to procedure B. Column chromatography on silica gel ($CHCl_3$/hexane 2:1) gave **48b** (612 mg, 3.53 mmol, 33%) as a yellow, crystalline solid, mp. 88 – 89^oC (85 - 87 ^oC [Aldrich Catalogue 2005/2006]); ν_{max} (KBr/cm^{-1}) 3093, 1716, 1598, 1586, 1508, 1394, 1146, 1072, 1031, 1009, 832, 757, 695, 629, 586, 497, 466; δ_H (400 MHz, $CDCl_3$) 6.84 (2H, s), 7.31 – 7.39 (3H, m), 7.44 – 7.49 (2H, m); δ_C (100.5 MHz, $CDCl_3$) 126.1 (2C, CH), 128.0 (CH), 129.2 (2C, CH), 131.2 (C_{quat}), 134.2 (2C, CH), 169.5 (2C, C_{quat}, CO).

11) 2-Methylphenylmaleimide (48c)

A mixture of **47c** (2.2 g, 10.7 mmol) and sodium acetate trihydrate ($NaOAc^{\cdot}3H_2O$, 4.37 g, 32.1 mmol) in acetic anhydride (30 mL) were reacted at 105^oC (13h) according to procedure B. Column chromatography on silica gel (CH_2Cl_2) gave **48c** (2.04 g, quant) as a very pale yellow solid, mp. 76-78^oC (Lit. 76- 77^oC [Fujita 1989]); ν_{max} (KBr/cm^{-1}) 3093, 2929, 1716, 1496, 1458, 1391, 1150, 1116, 1065, 83, 823, 768, 688, 630, 588, 475; δ_H (400 MHz, $CDCl_3$) 2.16 (3H, s, CH_3), 6.87 (2H, s), 7.11 (1H, d, ^3J = 7.6 Hz), 7.27 – 7.37 (3H, m); δ_C (100.5 MHz, $CDCl_3$) 17.9 (CH_3), 126.9 (CH), 128.7 (CH), 129.5 (CH), 129.9 (C_{quat}), 131.2 (CH), 134.4 (2C, CH), 136.5 (C_{quat}), 169.6 (C, C_{quat}, CO).

12) **4-Methylphenylmaleimide** (**48d**)

A mixture of **47d** (2.2 g, 10.7 mmol) and sodium acetate trihydrate ($NaOAc{\cdot}3H_2O$, 4.37 g, 32.1 mmol) in acetic anhydride (30 mL) were reacted at 105°C according to procedure B to give **48d** (1.08 g, 5.8 mmol, 54%) as a yellow crystalline solid, mp. 159 – 160°C (Lit. mp. 158 – 160 °C [Matuszak 2009, Butler 2007]); ν_{max} (KBr/cm^{-1}) 3454 (w), 3093, 1708, 1518, 1408, 1391, 1153, 834, 710, 685, 503; δ_H (400 MHz, $CDCl_3$) 2.38 (3H, s, CH_3), 6.83 (2H, s), 7.19 (2H, d, ^3J = 8.8 Hz), 7.26 (2H, d, ^3J = 8.8 Hz); δ_C (100.5 MHz, $CDCl_3$) 21.2 (CH_3), 126.0 (2C, CH), 128.4 (C_{quat}), 129.8 (2C, CH), 134.2 (2C, CH), 138.1 (C_{quat}), 169.7 (2C, C_{quat}, CO); Found: C, 70.33; H, 4.95; N, 7.48%. Calcd. for $C_{11}H_9NO_2$ (187.19) C, 70.58; H, 4.85; N, 7.48%.

13) **4-Methoxyphenylmaleimide** (**48e**)

A mixture of **47e** (2.74 g, 12.4 mmol) and sodium acetate trihydrate ($NaOAc{\cdot}3H_2O$, 5.04 g, 37.0 mmol) in acetic anhydride (30 mL) were reacted at 105 °C according to procedure B to give **48e** (1.03 g, 5.1 mmol, 41%) as a yellow crystalline solid, mp. 157 – 158°C (Lit. 157°C [Deshpande 2010]); $_{max}$ (KBr/cm^{-1}) 3467, 3173, 3110, 3079, 3011, 2965, 2939, 2914, 2836, 1701, 1507, 1445, 1400, 1303, 1251, 1156, 1106, 1055, 828, 721, 687, 604, 582, 527, 431; $_H$ (400 MHz, $CDCl_3$) 3.81 (3H, s, OCH_3), 6.82 (2H, s), 6.97 (2H, d, ^3J = 8.4 Hz), 7.21 (2H, d, ^3J = 8.4 Hz); δ_C (100.5 MHz, $CDCl_3$) 55.5 (OCH_3), 114.5 (2C, CH), 123.7 (C_{quat}), 127.6 (2C, CH), 134.1 (2C, CH), 159.2 (C_{quat}), 169.8 (2C, C_{quat}, CO); Found: C, 65.02; H, 4.46; N, 6.89%. Calcd for $C_{11}H_9NO_3$ (203.19) C, 65.65; H, 4.45; N, 6.79%.

14) **2,5-Dimethoxyphenylmaleimide** (**48f**)

A mixture of **47f** (2.7g, 10.7(5) mmol) and sodium acetate trihydrate ($NaOAc^{\cdot}3H_2O$, 4.37g, 32.1 mmol) in acetic anhydride (30mL) were reacted at 105°C (6h) according to procedure B to give **48f** as a yellow crystalline solid: (935 mg, 37.(5)%), mp. 132 – 134 °C (Lit. 122 °C [Mustafa 1956]); $_{max}$ (KBr/cm^{-1}) 3117, 3007, 2964, 2942, 2832, 1708, 1515, 1455, 1388, 1284, 1232, 1193, 1155, 1043, 1014, 822, 724, 692; $_{H}$(400 MHz, $CDCl_3$) 3.73 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 6.73 (1H, bs), 6.82 (2H, bs), 6.93 (2H, s); $_{C}$ (100.5 MHz, $CDCl_3$) 55.8 (OCH_3), 56.3 (OCH_3), 113.1 (CH), 115.7(CH), 115.8(CH), 120.1(C_{quat}), 134.4(2C, CH), 149.6 (C_{quat}), 153.5(C_{quat}), 169.6(2C, C_{quat}, CO). Found C, 61.62; H, 4.84; N, 6.01%. Calcd for $C_{12}H_{11}NO_4$ (203.19) C, 61.80; H, 4.75; H, 6.01%.

15) **2,4-Difluorophenylmaleimide** (**48g**)

A mixture of **47g** (2.43g, 10.8mmol) and sodium acetate trihydrate ($NaOAc^{\cdot}3H_2O$, 4.37 g, 32.1mmol) in acetic anhydride (30mL) reacted at 105°C (20h) according to procedure B, column chromatography on silica gel (CH_2Cl_2/ether 2:1) gave **48g** (1.11 g, 5.31 mmol, 50%) as a colourless, crystalline solid: mp. 92°C; ν_{max}(KBr/cm^{-1}) 3097, 1719, 1519, 1414, 1397, 1275, 1146, 975, 865, 831, 719, 689, 600, 439; $_{H}$(400 MHz, $CDCl_3$)

6.91 (2H, s), 6.97 – 7.02 (2H, m), 7.23-7.29 (1H, m); δ_C (100.5 MHz, $CDCl_3$) 105.3 (CH, dd, $^2J_{CF}$ 26.9 Hz, $^2J_{CF}$ 23.9 Hz), 112.0 (CH, dd, $^2J_{CF}$ 22.4 Hz, $^4J_{CF}$ 3.7 Hz), 114.9 (C_{quat}, dd, $^2J_{CF}$ 13.5 Hz, $^4J_{CF}$ 3.7 Hz), 130.7 (CH, dd, $^3J_{CF}$ 9.6 Hz, $^3J_{CF}$ 1.6 Hz), 134.7 (2C, CH), 158.1(dd, $^1J_{CF}$ 255.0 Hz, $^3J_{CF}$ 12.8 Hz), 162.9 (C_{quat}, $^1J_{CF}$ 251.4 Hz, $^3J_{CF}$ 11.3 Hz), 168.6(C_{quat}, CO).

16) **2,6-Difluorophenylmaleimide** (**48h**)

A mixture of **47h** (2.43 g, 10.8 mmol) and sodium acetate trihydrate ($NaOAc{\cdot}3H_2O$, 4.37 g, 32.1 mmol) in acetic anhydride (30 mL) were reacted at 105 ^oC (20h) according to procedure B. Column chromatography on silica gel (CH_2Cl_2) gave **48h** (1.25 g, 6.0 mmol, 56%) as a colourless, crystalline solid: mp. 108 ^oC [91-93 ^oC (Schwarzer et al. 2008]; ν_{max} (KBr/cm^{-1}) 3492, 3123, 1724, 1596, 1514, 1475, 1387, 1243, 1220, 1161, 1136, 1048, 990, 825, 781, 691, 584; δ_H (400 MHz, $CDCl_3$) 6.92 (2H, s), 7.04 (2H, m), 7.40 (1H, m); δ_C (100.5 MHz, $CDCl_3$) 108.4 (dd, C_{quat}, $^2J_{CF} = 16.0$ Hz, $^2J_{CF} = 16.0$ Hz), 112.1 (2C, CH, md, $^2J_{CF} = 18.6$ Hz), 131.0 (2C, CH, dd, $^3J_{CF} = 9.7$ Hz, $^3J_{CF} = 9.7$ Hz), 135.0 (2C, CH), 158.9 (2C, C_{quat}, dd, $^1J_{CF} = 253.0$ Hz, $^4J_{CF} = 3.7$ Hz).

17) **Ethoxycarbonylmethylidenetriphenylphosphorane** (**35**)

To a solution of triphenylphosphine (PPh_3, 12.3 g, 46.8 mmol) in $CHCl_3$ (25 mL) was added ethyl bromoacetate (**33**, 7.77 g, 46.8 mmo, careful: lachrymator!). The solution heated up during the addition. The reaction mixture was stirred at room temperature for

14h. Then, it was poured into ether (300 mL). The precipitate formed was allowed to settle for 3h. Thereafter, the ethereal supernatant was decanted and aq. Na_2CO_3 (10 g Na_2CO_3 in 100 mL H_2O) was added, followed by CH_2Cl_2 (35 mL). The reaction mixture was stirred at room temperature for 45 min. Thereafter, the mixture was extracted with CH_2Cl_2 (3 X 35 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to leave an oily residue from which ethoxycarbonylmethylidenetriphenylphosphorane (**35**) crystallized upon seeding to give **35** as a colourless solid (14.1 g, 87%); - ν_{max} (KBr/cm^{-1}) 3055, 2975, 2900, 1605, 1483, 1437, 1371, 1330, 1121, 1062, 892, 755, 695, 545, 507.

18) **Benzoylmethyltriphenylphosphonium bromide** (**31-H**)

To a solution of triphenylphosphine (PPh_3, 5.9. g, 22.4 mmol) in $CHCl_3$ (25 mL) was added α–bromo-4-acetophenone (**30-H**, 4.46 g, 22.5 mmol), and the resulting reaction mixture was stirred for 14h at room temperature. Thereafter, the mixture was given to ether (300 mL). The precipitate formed was allowed to settle for 3h. Thereafter the solid was filtered to give benzoylmethyltriphenylphosphonium bromide (9.6 g, 93%) as a colourless solid: ν_{max}(KBr/cm^{-1}) 3059, 2941, 2637, 1660 (s), 1435, 1327, 1303, 1207, 1111, 993, 750, 718, 687, 517, 503; δ_H (400 MHz, $CDCl_3$) 6.36 (2H, d, $^2J_{PH}$ = 12.0 Hz), 7.46 – 7.78 (12H, m), 7.89 – 7.95 (6H, m), 8.35 (2H, dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz); δ_C (100.5 MHz, $CDCl_3$) 38.8 (CH_2, J_{CP} = 62.0 Hz), 128.6 (3C, C_{quat}, J_{CP} = 12.0 Hz), 129.0 (2C, CH), 130.0 (2C, CH), 130.1 (6C, CH, J_{CP} = 13.5 Hz), 132.2 (C_{quat}, J_{CP} = 10.5 Hz), 134.0 (6C, CH, J_{CP} = 10.5 Hz), 134.7 (3C, CH, J_{CP} = 2.9 Hz), 134.8 (CH), 192.2 (C_{quat}, CO, J_{CP} = 6.0 Hz).

19) 4-Methoxybenzoylmethyltriphenylphosphonium bromide (31-OMe)

To a solution of triphenylphosphine (PPh_3, 5.9. g, 22.4 mmol) in $CHCl_3$ (25 mL) was added α–bromo-4-methoxyacetophenone (**30-OMe**, 5.17 g, 22.5 mmol), and the resulting reaction mixture was stirred for 14h at rt. Thereafter, the mixture was given to ether (300 mL). The precipitate formed was allowed to settle for 3h. Thereafter the solid was filtered to give 4-methoxybenzoylmethyltriphenylphosphonium bromide (**31-OMe**, 9.9 g, 90%) as a colourless solid; as a colourless solid: ν_{max} (KBr/cm^{-1}) 2936, 2769, 2708, 1652, 1590, 1438, 1326, 1265, 1215, 1165, 1108, 992, 750, 718, 686, 540, 508; δ_H (400 MHz, $CDCl_3$) 3.78 (3H, s, OCH_3), 6.12 (2H, d, J_{CP} = 12.4 Hz), 6.90 (2H, d, ^3J = 8.8 Hz), 7.58 – 7.60 (6H, m), 7.63 – 7.69 (3H, m), 7.84 – 7.89 (6H, m), 8.31 (2H, d, ^3J = 8.8 Hz); δ_C (100.5 MHz, $CDCl_3$) 38.0 (CH_2, J_{CP} = 61.3 Hz), 55.7 (OCH_3), 114.2 (2C, CH), 119.0 (3C, C_{quat}, J_{CP} = 89.7 Hz), 130.1 (6C, CH, J_{CP} = 12.8 Hz), 132.6 (3C, CH), 134.0 (6C, CH, J_{CP} = 10.6 Hz), 134.6 (2C, CH), 164.9 (C_{quat}), 190.0 (C_{quat}, CO, J_{CP} = 4.6 Hz).

20) 4-Fluorobenzoylmethylidenetriphenylphosphorane (32-F)

To a solution of triphenylphosphine (PPh_3, 5.9. g, 22.4 mmol) in $CHCl_3$ (25 mL) was added α–bromo-4-fluoroacetophenone (**30-F**, 4.87 g, 22.5 mmol), and the resulting reaction mixture was stirred for 14h at rt. Thereafter, the mixture was given to ether (300 mL). The precipitate formed was allowed to settle for 3h. Thereafter the solid was filtered to give 4-fluorobenzoylmethyltriphenylphosphonium bromide (**31-F**, 9.04 g, 84%) as a colourless solid. To 4-fluorobenzoylmethyltriphenylphosphonium bromide (9.04 g, 18.9 mmol) was added aq. Na_2CO_3 (5 g Na_2CO_3 in 100 mL H_2O), followed by

CH_2Cl_2 (35 mL). The reaction mixture was stirred at rt for 45 min. Thereafter, the mixture was extracted with CH_2Cl_2 (3 X 35 mL).

The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to leave an oily residue, from which 4-fluorobenzoylmethylidenetriphenylphosphorane (**32-F**, 5.93 g, 79%) crystallized as a pale yellow solid: ν_{max} (KBr/cm^{-1}) 3049, 1600, 1516, 1502, 1480, 1438, 1410, 1390, 1226, 1190, 1163, 1107, 883, 754, 747, 719, 694, 542, 517, 506; δ_H (400 MHz, $CDCl_3$) 7.00 (2H, dd, ^3J = 8.8 Hz, ^3J = 8.8 Hz), 7.45 – 7.72 (15H, m), 7.95 (2H, bm); δ_C (100.5 MHz, $CDCl_3$) 50.6 (CH, d, $^1J_{CP}$ = 112.3 Hz), 114.4 (2C, CH, J_{CF} = 21.0 Hz), 126.9 (3C, C_{quat}, d, $^1J_{CP}$ = 93.6 Hz), 128.6 (2C, d, J_{CF} = 11.3 Hz), 128.8 (6C, CH, J_{CP} = 12.0 Hz), 132.0 (3C, CH), 133.1 (6C, CH, J_{CP} = 9.8 Hz), 134.8 (C_{quat}), 163.8 (C_{quat}, $^1J_{CF}$ = 248.3 Hz), 183.7 (C_{quat}, CO).

21) 4-Bromobenzoylmethyltriphenylphosphonium bromide (31-Br)

To a solution of triphenylphosphine (PPh_3, 6.6 g, 25.2 mmol) in $CHCl_3$ (50 mL) was added α–bromo-4-bromoacetophenone (**30-Br**, 7.0 g, 25.4 mmol), and the resulting reaction mixture was stirred for 14h at room temperature. Thereafter, the mixture was given to ether (300 mL). The precipitate formed was allowed to settle for 3h. Thereafter the solid was filtered to yield 4-bromobenzoylmethyltriphenylphosphonium bromide (**31-Br**, 8.5g, 63%) as colourless solid: ν_{max} (KBr/cm^{-1}) 3387, 3081, 3012, 2804, 1673, 1584, 1437, 1437, 1397, 1211, 1071, 998, 753, 721, 691, 509; δ_H (400 MHz, $CDCl_3$) 6.34 (2H, d, $^2J_{PH}$ = 12.0 Hz), 7.59 (2H, d, ^3J = 8.8 Hz), 7.61 – 7.66 (6H, m), 7.71 – 7.75 (3H, m), 7.87 – 7.93 (6H, m); $\square_C$ (100.5 MHz, $CDCl_3$) 38.6 (CH_2, $^1J_{CP}$ = 60.6 Hz), 118.7 (3C, C_{quat}, $^1J_{CP}$ = 89.7 Hz), 130.2 (6C, CH, J_{CP} = 13.5 Hz), 130.5 (C_{quat}), 131.5 (2C, CH), 132.2 (C_{quat}), 132.3 (2C, CH), 134.0 (6C, CH, J_{CP} = 10.5 Hz), 134.8 (3C, CH, J_{CP} = 3.0 Hz), 191.3 (C_{quat}, CO, J_{CP} = 6.7 Hz).

22) 4-Bromobenzoylmethylidenetriphenylphosphorane (32-Br)

4-Bromobenzoylmethyl-triphenylphosphonium bromide (**31-Br**, 8.47 g, 15.7 mmol) was added to a mixture of CH_2Cl_2 (30 mL) and aq. Na_2CO_3 (8.0 g in 80 mL H_2O) and was stirred at room temperature for 45 min. Thereafter, the mixture was extracted with CH_2Cl_2 (2 X 50 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give 4-bromobenzoylmethylidenetriphenylphosphorane (**32-Br**, 6.71 g, 93%) as a pale yellow solid; $_{max}$ (KBr/cm^{-1}) 3052, 1579, 1521, 1481, 1436, 1401, 1379, 1175, 1107, 1068, 1008, 882, 744, 718, 693, 542, 524, 511.

23) 4-Methylbenzoylmethyltriphenylphosphonium bromide (31-Me)

To a solution of triphenylphosphine (PPh_3, 6.6 g, 25.2 mmol) in $CHCl_3$ (50 mL) was added bromo-4-methylacetophenone (**30-Me**, 5.4 g, 25.4 mmol), and the resulting reaction mixture was stirred for 14h at room temperatures. Thereafter, the mixture was given to ether (300 mL). The precipitate formed was allowed to settle for 3h. Thereafter the solid was filtered to yield 4-methylbenzoylmethyltriphenylphosphonium bromide (10.1 g, 80%, **31-Me**) as a colourless solid; $_{max}$ (KBr/cm^{-1}) 2946, 2754, 2647, 1655, 1602, 1437, 1329, 1305, 1189, 1110, 805, 747, 690, 517, 502; δ_H (400 MHz, $CDCl_3$) 2.37 (3H, s, CH_3), 6.28 (2H, d, $^3J_{PH}$ = 12.0 Hz), 7.28 (2H, d, ^3J = 8.0 Hz), 7.60 – 7.65 (6H, m), 7.71 – 7.74 (3H, m), 7.89 – 7.94 (6H, m), 8.24 (2H, d, ^3J = 8.0 Hz); □$_C$ (100.5 MHz, $CDCl_3$) 26.8 (CH_3), 38.7 (d, CH_2, $^1J_{CP}$ = 61.3 Hz), 119.0 (3C, C_{quat}, d, $^1J_{CP}$ = 89.7 Hz), 129.7 (2C, CH), 130.1 (6C, CH, d, J_{CP} = 13.5 Hz), 130.2 (3C, CH), 134.0(5) (6C, CH, d, J_{CP} = 11.3 Hz), 134.2 (C_{quat}), 134.6 (2C, CH, d, J_{CP} = 3.0 Hz), 146.2 (C_{quat}), 191.5 (C_{quat}, CO, J_{CP} = 5.9 Hz).

24) 4-Methylbenzoylmethylidenetriphenylphosphorane(32-Me)

4-Methylbenzoylmethyl-triphenylphosphonium bromide (**31-M**e, 12.08 g, 25.4 mmol) was added to a mixture of CH_2Cl_2 (50 mL) and aq. Na_2CO_3 (13.0 g in 130 mL H_2O) and was stirred at room temperature for 2h30min. Thereafter, the mixture was extracted with CH_2Cl_2 (3 X 50 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give 4-methylbenzoylmethylidenetriphenylphosphorane (**32-Me**, 10.1 g, 99.[5]]%) as a beige-coloured solid: ν_{max} (KBr/cm^{-1}) 3051, 2915, 1606 (w), 1581, 1517, 1502, 1482, 1436, 1405, 1385, 1178, 1104, 1078, 886, 835, 743, 716, 694, 543, 525, 513; □$_{H}$ (400 MHz, $CDCl_3$) 2.35 (3H, s, CH_3), 4.39 (1H, d, $^2J_{PH}$ = 24.8 Hz), 7.14 (2H, d, ^3J = 8.0 Hz), 7.43 – 7.48 (6H, m), 7.52- 7.57 (3H, m), 7.68 – 7.73 (6H, m), 7.86 (2H, d, ^3J = 8.0 Hz); □$_{C}$ (100.5 MHz, $CDCl_3$) 21.4 (CH_3), 50.2 (d, $^1J_{CP}$ = 112.2 Hz), 126.9 (2C, CH), 127.2 (3C, C_{quat}, J_{CP} = 91.3 Hz), 128.4 (2C, CH), 128.8 (6C, CH, J_{CP} = 12.0 Hz), 132.0 (3C, CH, J_{CP} = 3.0 Hz), 133.1 (6C, CH J_{CP} = 10.5 Hz), 138.4 (C_{quat}, J_{CP} = 15.0 Hz), 139.3 (C_{quat}), 184.8 (C_{quat}, CO, J_{CP} = 3.7 Hz).

25) 4-Chlorobenzoylmethylidenetriphenylphosphorane (32-Cl)

4-Chlorobenzoylmethyl-triphenylphosphonium bromide (**31-Cl**, 4.36 g, 10.3 mmol) was added to a mixture of CH_2Cl_2 (30 mL) and aq. Na_2CO_3 (4.1 g in 45 mL H_2O) and was stirred at room temperature for 3h. Thereafter, the mixture was extracted with CH_2Cl_2 (3 X 50 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give 4-chlorobenzoylmethylidenetriphenylphosphorane (**32-Cl**, 3.29 g, 93%) as a colourless solid: mp. 144 – 146 ^{o}C; ν_{max} (KBr/cm^{-1}) 3056, 1579, 1523, 1481, 1437, 1405, 1384, 1189, 1121, 1110, 1086, 882, 747, 723, 695, 540, 519; δ_H (400 MHz, CDCl$_3$) 4.40 (1H, bs), 7.29 (2H, d, ^3J = 8.0 Hz), 7.46 – 7.72 (15H, m), 7.88 (2H, d, ^3J = 8.0 Hz); δ_C (100.5 MHz, CDCl$_3$) 51.1 (CH, d, $^1J_{CP}$ = 110.2 Hz), 126.8 (3C, C$_{quat}$, $^1J_{CP}$ = 91.3 Hz), 127.8 (2C, CH), 128.4 (2C, CH), 128.9 (6C, CH, J_{CP} = 12.8 Hz), 132.1 (3C, CH), 133.1 (6C, CH, J_{CP} = 10.5 Hz), 135.2 (C$_{quat}$), 139.6 (C$_{quat}$), 183.4 (C$_{quat}$, CO).

26) **Methyl 9-anthranylacrylate (39-Me)**

To a solution of triphenylphosphine (PPh$_3$, 1.82 g, 6.94 mmol) in CH$_2$Cl$_2$ (20 mL) is added dropwise chlorotribromomethane (CBrCl$_3$, 1.42 g, 7.17 mmol), and the resulting solution is stirred at room temperature for 40 min, whereupon it turns orange-brown. Then, 9-anthranylacrylic acid (**39-H**, 1.5 g, 6.05 mmol) is added, and the suspension is stirred under reflux for 90 min. Thereafter, methanol (3 mL) is added dropwise, and the reddish solution is stirred under reflux for 10h. The cooled solution is concentrated *in vacuo* and the residue is subjected to column chromatography on silica gel (eluent: CH$_2$Cl$_2$) to give **39-Me** (913 mg, 58%) as bright yellow needles (hexane), mp. 120 – 122 ^{o}C; ν_{max} (KBr/cm^{-1}) 1717, 1638, 1168, 1155, 735; δ_H (400 MHz, CDCl$_3$) 3.92 (3H, s, OCH$_3$), 6.44 (1H, d, ^3J = 16.4 Hz), 7.46 – 7.51 (4H, m), 8.00 (2H, d, ^3J = 8.4 Hz), 8.22 (2H, d, ^3J = 8.4 Hz), 8.45 (1H, s), 8.65 (1H, d, ^3J = 16.4 Hz); $\square_C$ (100.5 MHz, CDCl$_3$) 52.0 (OCH$_3$), 125.2 (2C, CH), 125.4 (2C, CH), 126.3 (2C, CH), 126.8 (CH), 128.3 (CH), 128.8 (2C, CH), 129.0 (C$_{quat}$), 129.3 (C$_{quat}$), 131.2 (C$_{quat}$), 142.3 (CH), 166.9 (C$_{quat}$, CO). Found C, 82.49; H, 5.47%. Calcd. for $C_{18}H_{14}O_2$ (262.30) C, 82.42; H, 5.38%.

27) 9-[2-*E*-(Benzoylcarbonylethenyl)]anthracene (40-H)

A solventless mixture of 9-anthranylcarbaldehyde (**37**, 1.69g, 8.2mmol) and benzoylmethylidenetriphenylphosphorane (**32-H**, 5 g, 13.2 mmol) is heated at 140^{o}C for 14h. The cooled reaction mixture is subjected directly to column chromatography on silica gel (eluent: benzene) and gives the **40-H** (1.82 g, 72%) as a yellow solid, mp. 126^{o}C; $_{\text{max}}$(KBr/cm^{-1}) 1663, 1605, 1353, 1288, 1268, 1209, 1010, 739, 690, 619; □$_{\text{H}}$(400 MHz, CDCl$_3$) 7.48 -7.61 (8H, m), 8.01 – 8.04 (2H, m), 8.08 – 8.10 (2H, m), 8.29-8.32 (2H, m), 8.46 (1H, s), 8.80 (1H, d, ^{3}J = 16.0 Hz); □$_{\text{C}}$ (100.5 MHz, CDCl$_3$) 125.3 (2C, CH), 125.4 (2C, CH), 126.4 (2C, CH), 128.4 (CH), 128.7 (2C, CH), 128.8 (2C, CH), 128.9 (2C, CH), 129.6 (CH), 130.1 (C$_{\text{quat}}$), 131.0 (2C, C$_{\text{quat}}$), 131.3 (CH), 133.1 (2C, C$_{\text{quat}}$), 137.9 (C$_{\text{quat}}$), 141.9 (CH), 189.7 (C$_{\text{quat}}$, CO).

28) 9-[2-*E*-(4-Fluorophenylcarbonylethenyl)]anthracene (40-F)

A solventless mixture of 9-anthranylcarbaldehyde (37, 100mg, 0.48mmol) and 4-fluorobenzoylmethylidenetriphenylphosphorane (32-F, 400mg, 1.0mmol) is heated at 140 ^{o}C for 18h. The cooled reaction mixture is subjected directly to column chromatography on silica gel (eluent: benzene) and gives **40-F** (111mg, 71%) as a yellow solid, mp. 145 - 148 ^{o}C; ν_{max} (KBr/cm^{-1}) 3046, 1659, 1597 (s), 1504, 1410, 1355, 1267, 1208, 1152, 1010, 979, 850, 733; δ_{H} (400 MHz, CDCl$_3$) 7.18 (2H, dd, ^{3}J = 8.4 Hz, ^{3}J = 8.4 Hz), 7.49 – 7.54 (5H, m), 8.01 – 8.04 (2H, m), 8.11 (2H, dd, ^{3}J = 9.2 Hz, ^{4}J = 5.6 Hz), 8.27- 8.30 (2H, m), 8.47 (1H, s), 8.79 (1H, d, ^{3}J = 15.6 Hz); $_{\text{C}}$ (100.5 MHz, CDCl$_3$) 115.9 (2C, CH, $^{2}J_{\text{CF}}$ = 22.5 Hz), 125.2 (2C, CH), 125.5 (2C, CH), 126.5 (2C, CH), 128.6 (CH), 129.0 (2C, CH), 129.6 (2C, C$_{quat}$), 130.5 (2C, C$_{quat}$), 131.3 (3C, CH, and 2CH, $^{3}J_{CF}$ = 11.1 Hz), 134.2 (C$_{quat}$, $^{4}J_{CF}$ = 3.0 Hz), 142.2 (CH), 165.8 (C$_{quat}$, $^{1}J_{CF}$ = 255.1 Hz), 188.0 (C$_{quat}$, CO).

29) **9-[2-*E*-(4-Methoxyphenylcarbonylethenyl)]-anthracene** (**40-OMe**)

Analogous to the procedure used for **40-F**, **40-OMe** was prepared in 79% yield as a yellow solid, mp. 125 °C. – ν_{max} (KBr/cm^{-1}) 2924, 1654, 1606, 1595, 1261, 1174, 887, 733; δ_H (400 MHz, CDCl$_3$) 3.88 (3H, s, OCH$_3$), 6.98 (2H, d, ^{3}J = 8.4 Hz), 7.47 – 7.53 (4H, m), 7.54 (1H, d, ^{3}J = 16.0 Hz), 8.01 – 8.04 (2H, m), 8.08 (2H, d, ^{3}J = 8.4 Hz), 8.29 – 8.32 (2H, m), 8.46 (1H, s), 8.76 (1H, d, ^{3}J = 16.0 Hz); δ_C (100.5 MHz, CDCl$_3$) 55.5 (OCH$_3$), 114.0 (2C, CH), 125.4 (4C, CH), 126.3 (2C, CH), 128.2 (CH), 128.9 (2C, CH), 129.6 (C$_{quat}$, 2C), 130.5 (C$_{quat}$), 130.8 (C$_{quat}$), 131.0 (CH), 131.0[5] (2C, CH), 131.3 (C$_{quat}$, 2C), 141.0 (CH), 163.6 (C$_{quat}$), 188.0 (C$_{quat}$, CO).

30) **9-[2-*E*-(4-Methylphenylcarbonylethenyl)]-anthracene (40-Me**)

A solventless mixture of 9-anthranylcarbaldehyde (37, 1.63g, 7.93mmol) and 4-methylbenzoylmethylidenetriphenylphosphorane (**32-5.0 g, 12.7mmol, and 40-Me**) is heated at 140 ^{o}C for 18h. The cooled reaction mixture was subjected directly to column chromatography on silica gel (benzene) to give **40-Me** (1.71 g, 67%) as a bright-yellow solid, 123 – 125 ^{o}C; ν_{max} (KBr/cm^{-1}) 1659, 1608, 1593, 1402, 1385, 1270, 734; δ_H (400 MHz, CDCl$_3$) 2.44 (3H, s, CH$_3$), 7.31 (2H, d, ^{3}J = 8.0 Hz), 7.50 – 7.53 (4H, m), 7.55 (1H, d, ^{3}J = 15.6 Hz), 7.99 (2H, d, ^{3}J = 8.0 Hz), 8.02 – 8.05 (2H, m), 8.29 – 8.32 (2H, m), 8.48 (1H, s), 8.78 (1H, d, ^{3}J = 15.6 Hz); δ_C (100.5 MHz, CDCl$_3$) 21.7 (CH$_3$), 125.3 (2C, CH), 125.4 (2C, CH), 126.4 (2C, CH), 128.3 (CH), 128.8 (2C, CH), 128.9 (2C, CH), 129.5 (2C, CH), 129.6 (2C, C_{quat}), 130.3 (C_{quat}), 131.1 (2C, C_{quat}), 131.3 (CH), 135.3 (C_{quat}), 141.5 (CH), 144.0 (C_{quat}), 189.2 (C_{quat}, CO).

31) 9-[2-*E*-(4-Bromophenylcarbonylethenyl)]anthracene (40-Br)

A solventless mixture of 9-anthranylcarbaldehyde (37, 570mg, 2.76mmol) and 4-bromobenzoylmethylidenetriphenylphosphorane (**32-Br**, 2.03g, 4.42 mmol) is heated at 145^{o}C for 18h. The cooled reaction mixture is subjected directly to column chromatography on silica gel (eluent: benzene) and gives **40-Br** (707 mg, 66%) as a yellow solid, mp. 160 ^{o}C; $_{max}$ (KBr/cm^{-1}) 1660, 1597, 1291, 1266, 1216, 1175, 1029, 1007, 883, 842, 816, 738; δ_H (400 MHz, $CDCl_3$) 7.47- 7.54 (5H, m), 7.63-7.66 (2H, m), 7.92 – 7.95 (2H, m), 8.02 (2H, d, ^{3}J = 8.0 Hz), 8.27 (2H, d, ^{3}J = 7.6 Hz), 8.47 (1H, s), 8.81 (1H, d, ^{3}J = 15.6 Hz); $_{C}$ (100.5 MHz, $CDCl_3$) 125.2 (2C, CH), 125.5 (2C, CH), 126.6 (2C, CH), 128.3 (C_{quat}), 128.7 (CH), 129.0 (2C, CH), 129.6 (C_{quat}), 129.9 (C_{quat}), 130.2 (2C, CH), 130.3 (CH), 131.3 (C_{quat}), 132.1 (2C, CH), 136.6 (C_{quat}), 142.5 (CH), 188.5 (C_{quat}, CO).

32) 9-[2-*E*-(4-Chlorophenylcarbonylethenyl)]anthracene (40-Cl)

A solventless mixture of 9-anthranylcarbaldehyde (37, 788 mg, 3.825 mmol) and 4-chlorobenzoylmethylidenetriphenylphosphorane (**32-Cl**, 2.54 mg, 6.13 mmol) is heated at 130 ^{o}C for 14h. Then additional 4-chlorobenzoylmethylidene-triphenylphosphorane (**32-Cl**, 650 mg, 1.56 mmol) is added, and the mixture is heated for another 5h. The cooled reaction mixture is subjected directly to column chromatography on silica gel (eluent: benzene) and gives **40-Cl** (804 mg, 61%) as a yellow solid, melting point. 140 -

142 ^{o}C; ν_{max} (KBr/cm^{-1}) 3047, 1660, 1598, 1586, 1291, 1267, 1213, 1010, 883, 842, 733, 674; δ_H (400 MHz, $CDCl_3$) 7.48 – 7.54 (7H, m), 8.01 – 8.05 (4H, m), 8.27 – 8.30 (2H, m), 8.49 (1H, s), 8.81 (1H, d, ^{3}J = 16.0 Hz); δ_C (100.5 MHz, $CDCl_3$) 125.2 (2C, CH), 125.5 (2C, CH), 126.6 (2C, CH), 128.7 (2C, C_{quat}), 129.0 (2C, CH), 129.1 (CH), 129.6 (CH), 129.9 (C_{quat}), 130.1 (2C, CH), 130.4 (2C, C_{quat}), 131.3 (2C, CH), 136.2 (C_{quat}), 139.6 (C_{quat}), 142.5 (CH), 188.4 (C_{quat}, CO).

33) **9-[2-*E*-(3-Nitrophenylcarbonylethenyl)]anthracene** (**40-NO_2**)

A solution of 9-9-anthranylcarbaldehyde (37, 1.55g, 7.53mmol) and 3-nitrobenzoylmethylidenetriphenylphosphorane (32-NO_2, 4.46 g, 10.5 mmol) in $CHCl_3$ (15 mL) is heated for 14h. The cooled reaction mixture is subjected directly to column chromatography on silica gel (eluent: benzene) and gives **40-NO_2** (1.30 g, 49%) as an orange solid, mp. 129-131 ^{o}C; $_{max}$ (KBr/cm^{-1}) 1655, 1592, 1531, 1346, 984, 726, 701; δ_H (400 MHz, $CDCl_3$) 7.48 – 7.56 (5H, m), 7.70 (1H, dd, ^{3}J = 8.0 Hz, ^{3}J = 8.0 Hz), 8.02 (2H, d, ^{3}J = 8.4 Hz), 8.27 (2H, d, ^{3}J = 8.4 Hz), 8.37-8.39 (1H, m), 8.41-8.44 (1H, m), 8.47 (1H, s), 8.86 (1H, s), 8.87 (1H, d, ^{3}J = 16.0 Hz); $_{C}$ (100.5 MHz, $CDCl_3$) 123.5 (CH), 125.0 (2C, CH), 125.5 (2C, CH), 126.8 (2C, CH), 127.3 (CH), 129.05 (2C, CH), 129.1 (CH), 129.3 (C_{quat}), 129.6 (C_{quat}), 129.7, (CH), 130.0 (C_{quat}), 131.2 (CH), 134.2 (CH), 139.1 (C_{quat}), 143.9 (CH), 148.5 (C_{quat}), 187.4 (C_{quat}, CO).

2.3.3. Procedure C

34) **Cycloadduct 49a**: of **9-anthranylcarbaldehyde** (**37**) & **4-bromophenylmaleimide** (**48a**)

A mixture of 9-anthranylcarbaldehyde (37, 206 mg, 1.0 mmol) and 4-bromophenylmaleimide (48a, 252 mg, 1.0 mmol) were held under magnetic stirring at

110^{o}C for 13h. After 10 min., the mixture formed a homogeneous melt that solidified within further 20 min. TLC of the cooled solid mixture (eluent $CHCl_3$) revealed slight impurities due to the starting materials. The reaction mixture was subjected to column chromatography on silica gel ($CHCl_3$) to give **49a** (430 mg, 94%) as a colourless solid, mp. 272 ^{o}C; ν_{max} (KBr/cm^{-1}) 3071, 2965, 2853, 2751, 1779 (w), 1716, 1489, 1386, 1196, 1178, 1070, 1014, 777, 553; δ_H (400 MHz, $CDCl_3$) 3.47 (1H, dd, ^3J = 8.8 Hz, ^3J = 3.2 Hz), 3.89 (1H, d, ^3J = 8.8 Hz), 4.87 (1H, d, ^3J = 3.2 Hz), 6.39 (2H, d, ^3J = 8.8 Hz), 7.20 – 7.38 (6H, m), 7.40 (2H, d, ^3J = 8.8 Hz), 7.46 – 7.48 (1H, m), 7.69 – 7.71 (1H, m), 10.9 (1H, s, CHO); δ_C (100.5 MHz, $CDCl_3$) 46.2 (CH), 47.4 (CH), 48.0 (CH), 57.9 (C_{quat}), 122.9 (C_{quat}), 123.0 (CH), 123.7 (CH), 124.8 (CH), 125.6 (CH), 127.0 (CH), 127.4 (CH), 127.6 (CH), 127.7 (CH), 127.8 (2C, CH), 129.9 (C_{quat}), 132.3 (2C, CH), 136.6 (C_{quat}), 138.3 (C_{quat}), 138.8 (C_{quat}), 140.9 (C_{quat}), 174.6 (C_{quat}, CON), 175.0 (C_{quat}, CON), 199.6 (CHO).

35) **Cycloadduct 49b** of **9-anthranylcarbaldehyde** (**37**) and ***N*-phenylmaleimide** (**48b**)

A mixture of 9-anthranylcarbaldehyde (37, 412 mg, 2.0 mmol) and 4-methoxyphenylmaleimide (48b, 346 mg, 2.0 mmol) was held under magnetic stirring at 115 ^{o}C for 13h, according to procedure C. Column chromatography of the reaction mixture on silica gel (eluent: chloroform) gave **49b** (653 mg, 86%), after crystallization from diethyl ether, as a pale yellow solid; $_{max}$ (KBr/cm^{-1}) 3070, 2963, 2853, 2759, 1776 (w), 1716, 1597 (w), 1498, 1388, 1195, 762, 751, 712, 693, 553; δ_H (400 MHz, $CDCl_3$) 3.46 (1H, dd, ^3J = 8.8 Hz, ^3J = 3.2 Hz), 3.89 (1H, d, ^3J = 8.8 Hz), 4.88 (1H, d, ^3J = 3.2 Hz), 6.49 (1H, m), 7.20 – 7.28 (9H, m), 7.38 – 7.40 (1H, m), 7.47 (1H, d, ^3J = 8.0 Hz), 7.70 – 7.73 (1H, m), 10.88 (1H, s, CHO); $_C$ (100.5 MHz, $CDCl_3$) 46.2 (CH), 47.4 (CH), 48.0 (CH), 57.9 (C_{quat}), 123.0 (CH), 123.7 (CH), 124.8 (CH), 125.6 (CH), 126.3 (2C, CH), 126.9 (CH), 127.4 (CH), 127.6 (CH), 128.9 (CH), 129.1 (3C, CH), 131.0 (C_{quat}), 136.6 (C_{quat}), 138.4 (C_{quat}), 138.9 (C_{quat}), 141.0 (C_{quat}), 174.9 (C_{quat}, CO), 175.4 (C_{quat}, CO), 199.9 (CHO). Found C, 79.09; H, 4.71; N, 3.61%. Calcd. for $C_{25}H_{17}NO_3$ (379.41) C, 79.14; H, 4.52; N, 3.69%.

36) **Cycloadduct 49c** of **9-anthranylcarbaldehyde** (**37**) and **2-methylphenylmaleimide** (**48c**).

A mixture of 9-anthranylcarbaldehyde (**37**, 412mg, 2.0mmol) and 2-methylphenylmaleimide (48c, 383mg, 2.0mmol) held under magnetic stirring at 115°C for 15h, according to procedure C. Crystallization from ether gave **49c** (as a mixture of rotamers, 779 mg, 98%) as a pale yellow solid, mp. 280 °C; $_{max}$ (KBr/cm^{-1}) 2852, 2759, 1727, 1709, 1495, 1463, 1455, 1389, 1218, 1201, 758, 701; δ_H (400 MHz, $CDCl_3$) 3.51 (1H, dd, A, ^3J = 9.2 Hz, ^3J = 3.2 Hz), 3.52 (1H, dd, B, ^3J = 8.8 Hz, ^3J = 3.6 Hz), 3.91 (1H, d, A, ^3J = 9.2 Hz), 3.94 (1H, d, B, ^3J = 8.8 Hz), 4.90 (1H, d, B, ^3J = 3.6 Hz), 4.91 (1H, d, A, ^3J = 3.2 Hz), 5.50 (1H, d, ^3J = 8.0 Hz), 6.89-7.78 (11H, m); $_C$ (100.5 MHz, $CDCl_3$) 16.4 (A, CH_3)/17.6 (B, CH_3), 45.7(A)/46.2(B) (CH), 47.5(A)/47.6(B) (CH), 48.1(B)/48.2(A) (CH),57.4(A)/57.9(B)(C_{quat}),122.9(s)/123.0(L) (CH), 123.8(L)/123.9(s) (CH), 124.7(s)/124.8(L) (CH), 125.7(L)/126.0(s) (CH), 126.6(s)/126.8(L) (CH), 126.85 (L)/126.9(s) (CH), 126.9(s)/127.1(L) (CH), 127.4 (L)/127.5(s) (CH), 127.5(L)/127.6(s) (C_{quat}), 127.6 (L)/127.6(s) (CH), 127.6 (L)/127.8(s) (CH), 130.3 (L)/130.4(s) (C_{quat}), 130.8 (L)/131.0(s) (CH), 135.3 (L)/135.9(s) (C_{quat}), 136.7 (L)/137.1(s) (C_{quat}), 138.5 (L)/

138.85(s) (C_{quat}), 138.9 (L)/139.5(s) (C_{quat}), 141.0 (L)/141.7(s) (C_{quat}), 174.7 (A)/174.8(B) (NCO), 175.2 (A)/175.3(B) (NCO), 199.8 (B)/199.9 (A) (CHO).

37) Cycloadduct 62c of anthracene (16) and 2-methylphenylmaleimide (48c)

A mixture of anthracene (16, 368 mg, 2.0 mmol) and 2-methylphenylmaleimide (48c, 374 mg, 2.0 mmol) were held under magnetic stirring at 115 °C for 13h, according to procedure C. The reaction melt crystallized during the reaction after ca. 30 min. Upon cooling, a grey solid was obtained that was filtered and crystallized from ether to give **62c** as a greyish solid (690 mg, 91%); mp. 252 °C; ν_{max} (KBr/cm^{-1}) 1776 (w), 1712 (s), 1493, 1466, 1381, 1193, 759, 747, 730, 621, 538; δ_H (400 MHz, $CDCl_3$) 1.05 (3H, s, A, CH_3), 2.06 (3H, s, B, CH_3), 3.41 (2H, m, A/B), 4.90 (2H, d, ^3J = 4.8 Hz), 5.51 (1H, d, ^3J = 8.0 Hz), 6.92 – 7.48 (12H, m); δ_C (100.5 MHz, $CDCl_3$, DEPT 90, DEPT 135) 16.4 (A, CH_3), 17.6 (B, CH_3), 45.3 (A, CH), 45.8 (B, CH), 47.2 (CH, A/B), 124.2 (A, CH), 124.4 (B, CH), 126.6 (CH, A or B), 126.8 (2C, CH, B), 126.8 (2C, CH, B), 126.8 (CH, A or B), 127.2 (2C, CH, B), 127.3 (CH, A or B), 127.4 (2C, CH, A), 127.7 (CH, A or B), 130.6 (C_{quat}, A), 130.7 (C_{quat}, B), 130.8 (CH, A), 140.0 (CH, B), 135.4 (B, C_{quat}), 136.1 (A, C_{quat}), 138.8 (2C, B, C_{quat}), 139.3 (2C, A, C_{quat}), 141.3 (2C, C_{quat}, B), 141.9 (2C, C_{quat}, A), 175.9 (2C, C_{quat}, A, NCO), 176.1 (2C, C_{quat}, B, NCO). Found C, 81.99; H, 5.13; N, 3.78%. Calcd. for $C_{25}H_{19}NO_2$ (365.42) C, 82.17; H, 5.24; H, 3.83%.

38) Cycloadduct 49d of 9-anthranylcarbaldehyde (37) and 4-methylphenylmaleimide (48d)

A mixture of 9-anthranylcarbaldehyde (37, 412 mg, 2.0 mmol) and 4-methylphenylmaleimide (48d, 374 mg, 2.0 mmol) were held under magnetic stirring at 115 °C for 13h, according to procedure C. Stirring proved to be difficult. TLC showed the presence of starting material after 13h. The cooled reaction mixture was diluted with diethyl ether (10 mL). Thereafter, the solid was filtered off and washed well with diethyl ether (3 X 15 mL) to give **49d** as a colorless solid, mp. 248 °C (620 mg, 79%); ν_{max} (KBr/cm^{-1}) 3035, 2963, 2851, 2751, 1778 (w), 1716, 1512, 1458, 1387, 1209, 1161, 774, 601, 543, 509; δ_H (400 MHz, CDCl$_3$) 2.28 (3H, s, CH$_3$), 3.47 (1H, dd, ^3J = 8.4 Hz, ^3J = 3.2 Hz), 3.88 (1H, d, ^3J = 8.4 Hz), 4.88 (1H, d, ^3J = 3.2 Hz), 6.36 (2H, d, ^3J = 8.4 Hz), 7.07 (2H, d, ^3J = 8.4 Hz), 7.18 – 7.28 (5H, m), 7.37 – 7.39 (1H, m), 7.47 (1H, d, ^3J = 6.8 Hz), 7.69 – 7.72 (1H, m), 10.87 (1H, s, CHO); δ_C (100.5 MHz, CDCl$_3$) 21.2 (CH$_3$), 46.2 (CH), 47.4 (CH), 48.0 (CH), 57.9 (C$_{quat}$), 123.0 (CH), 123.7 (CH), 124.8 (CH), 125.6 (CH), 126.0 (2C, CH), 126.9 (CH), 127.3 (CH), 127.5 (CH), 127.6 (CH), 128.3 (C$_{quat}$), 129.8 (2C, CH), 136.6 (C$_{quat}$), 138.4 (C$_{quat}$), 138.9 (C$_{quat}$), 139.1 (C$_{quat}$), 141.0 (C$_{quat}$), 175.1 (CON, C$_{quat}$), 175.6 (CON, C$_{quat}$), 199.9 (CHO). Found C, 79.50; H, 4.90; N, 3.62%. Calcd. for $C_{26}H_{19}NO_3$ (393.43) C, 79.37; H, 4.87; H, 3.56%.

39) Cycloadduct 49e of 9-anthranylcarbaldehyde (37) and 4-methoxyphenylmaleimide (48e)

A mixture of 9-anthranylcarbaldehyde (37, 206 mg, 1.0 mmol) and 4-methoxyphenylmaleimide (48e, 203 mg, 1.0 mmol) were held under magnetic stirring at 115 °C for 13h, according to procedure C. Column chromatography of the reaction mixture on silica gel (eluent: chloroform) gave **49d** as a colorless solid in nearly quant. yield (405 mg), mp. 241 – 243 °C; ν_{max} (KBr/cm^{-1}) 3068, 2962, 2841, 1776 (w), 1716, 1609 (w), 1513, 1466, 1391, 1302, 1251, 1196, 1171, 1030, 834, 779, 764, 548; δ_H (400 MHz, $CDCl_3$) 3.48 (1H, dd, ^3J = 8.8 Hz, ^3J = 3.6 Hz), 3.73 (3H, s, OCH_3), 3.87 (1H, d, ^3J = 8.8 Hz), 4.88 (1H, d, ^3J = 3.6 Hz), 6.39 (2H, d, ^3J = 9.2 Hz), 6.78 (2H, d, ^3J = 9.2 Hz), 7.19 – 7.39 (6H, m), 7.46 (1H, d, ^3J = 7.2 Hz), 7.70 – 7.72 (1H, m), 10.87 (1H, s, CHO); δ_C (100.5 MHz, $CDCl_3$) 46.2 (CH), 47.4 (CH), 48.0 (CH), 55.4 (OCH_3), 57.9 (C_{quat}), 114.4 (2C, CH), 123.0 (CH), 123.5 (C_{quat}), 123.8 (CH), 124.8 (CH), 125.6 (CH), 126.9 (CH), 127.3 (CH), 127.4 (2C, CH), 127.5 (CH), 127.6 (CH), 136.6 (C_{quat}), 138.4 (C_{quat}), 138.9 (C_{quat}), 141.0 (C_{quat}), 159.7 (C_{quat}), 175.2 (C_{quat}, NCO), 175.7 (C_{quat}, NCO), 199.9 (CHO). Found C, 76.43; H, 4.80; N, 3.44%. Calcd. for $C_{26}H_{19}NO_4$ (409.43) C, 76.27; H, 4.68; H, 3.42%.

40) Cycloadduct 49f of 9-anthranylcarbaldehyde (37) and 2,5-dimethoxyphenylmaleimide (48f)

A mixture of 9-anthranylcarbaldehyde (37, 206 mg, 1.0 mmol) and 2,5-dimethoxyphenylmaleimide (48f, 233 mg, 1.0 mmol) were held under magnetic stirring at 115 ^oC for 5h30min, according to procedure C. The cooled, solidified reaction mixture was taken up in diethyl ether (20 mL) and filtrated and the filter cake was washed with diethyl ether (2 X 15 mL) to give **49f** as a pale brown solid (410 mg, 93.[4]%); ν_{max} (KBr/cm^{-1}) 3069, 2937, 2834, 1782, 1713, 1513, 1456, 1383, 1280, 1230, 1200, 1162, 1047, 819. 761, 545; δ_H (400 MHz, $CDCl_3$) 3.52 (1H, dd, ^3J = 8.4 Hz, ^3J = 3.2 Hz), 3.58 (3H, s, OCH_3), 3.67 (3H, s, OCH_3), 3.92 (1H, d, ^3J = 8.4 Hz), 4.88 (1H, d, ^3J = 3.2 Hz), 5.14 (1H, bs), 6.81 (2H, bs), 7.19 – 7.74 (8H, m); δ_C (100.5 MHz, $CDCl_3$) 46.2 (A, CH) / 45.7 (B, CH), 47.6 (A, CH) / 47.7 (B, CH), 48.2 (A, CH) / 48.4 (B, CH), 55.7 (A, OCH_3) / 55.8 (B, OCH_3), 56.3 (A, OCH_3) / 56.0 (B, OCH_3), 57.4 (B, C_{quat}) /

58.0 (A, C_{quat}), 113.0 (CH, A) / 113.1 (CH, B), 113.4 (CH, A) / 114.1 (CH, B), 116.1 (CH, B) / 116.6 (CH, A), 119.9 (C_{quat}, A/B), 122.9 (CH, B) / 123.0 (CH, A), 123.5 (CH, B) / 124.0 (CH, A), 124.6 (CH, B) / 124.8 (CH, A), 125.7 (CH, A) / 125.8 (CH, B), 126.7 (CH, B) / 126.8 (CH, A), 127.0 (CH, B) / 127.1 (CH, A), 127.2 (CH, B) / 127.3 (CH, A), 127.4 (CH, B) / 127.6 (CH, A), 134.5 (C_{quat}, B) / 136.9 (C_{quat}, A), 138.6 (C_{quat}, B) / 138.7 (C_{quat}, A), 138.8 (C_{quat}, A) / 139.7 (C_{quat}, B), 141.0 (C_{quat}, A) / 141.9 (C_{quat}, B), 173.5 (C_{quat}, NCO), 174.3 (C_{quat}, B, NCO), 174.7 (C_{quat}, A, NCO), 175.2 (C_{quat}, B, NCO), 199.9 (CHO, A), 200.2 (CHO, B).

41) **Cycloadduct 49g of 9-anthranylcarbaldehyde** (**37**) and **2,4-difluorophenylmaleimide** (**48g**)

A mixture of 9-anthranylcarbaldehyde (37, 412 mg, 2.0 mmol) and 2,4-difluorophenylmaleimide (48g, 418 mg, 2 mmol) were held under magnetic stirring at 115 ^{o}C for 13h, according to procedure C. The cooled, solidified reaction mixture was taken up in diethyl ether (20 mL) and filtrated and the filter cake was washed with diethyl ether (2 X 15 mL) to give **49g** as a pale brown solid (809 mg, 97.[4]%), mp. 221 ^{o}C; ν_{max} (KBr/cm^{-1}) 3079, 2963, 1713, 1516, 1394, 1279, 1194, 1150, 1702, 764, 754, 540; δ_H (400 MHz, $CDCl_3$) 3.53 (1H, dd, ^3J = 8.4 Hz, ^3J = 3.2 Hz), 3.95 (1H, d, ^3J = 8.4 Hz), 4.88 (1H, d, ^3J = 3.2 Hz), 5.79 (1H, m), 6.74 – 7.73 (10H, m), 10.9 (1H, s, CHO); δ_C (100.5 MHz, $CDCl_3$) 46.2 (CH), 47.6 (CH), 48.1 (CH), 58.0 (C_{quat}), 105.0 (CH, dd, J_{CF} = 26.1 Hz, J_{CF} = 22.4 Hz), 112.0 (CH, bd, J_{CF} = 21.7 Hz), 115.0 (C_{quat}, dd, J_{CF} = 14.3 Hz, J_{CF} = 4.5 Hz), 123.0 (CH), 123.8 (CH), 124.9 (CH), 125.6 (CH), 127.0 (CH), 127.4 (CH), 127.6 (CH), 127.7 (CH), 129.6 (CH, bd, J_{CF} = 8.9 Hz), 136.7 (C_{quat}), 138.5

(C$_{quat}$), 138.7 (C$_{quat}$), 140.7 (C$_{quat}$), 163.0 (2C, C$_{quat}$, J_{CF} = 252.0 Hz, J_{CF} = 11.1 Hz), 174.1 (C$_{quat}$, NCO), 174.5 (C$_{quat}$, NCO), 199.5 (CHO).

42) **Cycloadduct 49h of 9-anthranylcarbaldehyde** (**37**) and **2,6-difluorophenyl-maleimide** (**48h**)

A mixture of 9-anthranylcarbaldehyde (37, 412mg, 2.0mmol) and 2,6-difluorophenyl-maleimide (48h, 418 mg, 2.0 mmol) were held under magnetic stirring at 115^{o}C for 13h, according to procedure C. The cooled crystallized adduct was washed with diethyl ether/hexane (1:1) to give **49h** (772 mg, 93%) as a pale beige solid, mp. 283 ^{o}C (dec.); ν_{max} (KBr/cm^{-1}) 3489 (w), 3083, 2965, 2869, 2764, 1786 (w), 1724 (s), 1624, 1599, 1506, 1476, 1379, 1192, 1008, 790, 771, 758, 740, 701, 534; δ_H (400 MHz, CDCl$_3$) 3.53 (1H, dd, ^3J = 8.4 Hz, ^3J = 4.0 Hz), 3.96 (1H, d, ^3J = 8.4 Hz), 4.86 (1H, bs), 6.74 – 7.66 (11H, m), 10.9 (1H, s, CHO); δ_C (100.5 MHz, CDCl$_3$) 45.9 (CH), 47.8 (CH), 48.2 (CH), 57.6 (C$_{quat}$), 108.0 (C$_{quat}$, m), 111.9 (2C, m), 122.9 (CH), 123.4 (CH), 124.7 (CH), 125.8 (CH), 126.8 (CH), 127.5 (CH), 127.6 (CH), 127.8 (CH), 131.2 (m), 136.2 (C$_{quat}$), 137.9 (C$_{quat}$), 139.1 (C$_{quat}$), 141.3 (C$_{quat}$), 157.8 (2C, C$_{quat}$, ddd, J = 257.5 Hz, J = 18.6 Hz, J = 3.0 Hz), 173.2 (C$_{quat}$, NCO), 173.6 (C$_{quat}$, NCO), 199.8 (CHO).

43) **Cycloadduct 56 of 9-anthranylcarbaldehyde** (**37**) **and naphthoquinone** (**54**)

After photoaromatisation, column chromatography on silica gel (CH$_2$Cl$_2$) gives cycloadduct **56** as an orange-yellow solid; mp. 280 - 281 ^{o}C; ν_{max} (KBr/cm^{-1}) 1730, 1660, 1611, 1591, 1456, 1292, 772, 712, 600; δ_H (400 MHz, CDCl$_3$) 5.98 (1H, s), 7.08 – 7.11 (4H, m), 7.48 – 7.50 (2H, m), 7.67 – 7.69 (2H, m), 7.98 – 8.00 (4H, m), 11.1 (1H, s, CHO); δ_C (100.5 MHz, CDCl$_3$) 47.8 (CH), 60.7 (C$_{quat}$), 124.2 (2C, CH), 124.7 (2C,

CH), 125.8 (2C, CH), 126.1 (2C, CH), 126.4 (CH), 126.8 (CH), 131.2 (C_{quat}), 131.5 (C_{quat}), 134.1 (2C, C_{quat}), 134.2 (2C, C_{quat}), 141.6 (CH), 143.9 (CH), 155.8 (C_{quat}), 156.5 (C_{quat}), 180.8 (C_{quat}, CO), 181.4 (C_{quat}, CO), 196.5 (CHO).

2.3.4. Procedure D

44) Cycloadduct 51a-Me of methyl 9-anthranylacrylate (39-Me) and 4-bromophenylmaleimide (48a)

A mixture of 4-bromophenylmaleimide (**48a**, 252mg, 1mmol) and methyl 9-anthranylacrylate (**39-262mg, 1mmol, and Me**) was heated at 120^{o}C for 3h45 min. The mixture initially produced a melt, which then solidified. The mixture was cooled and the solid was taken up in diethyl ether (15 mL) and filtered. The filter cake was washed with diethyl ether (2 X 10 mL) to give **51a-Me** (500 mg, 97.(3)%) as a colorless solid, mp. 270 – 279 ^{o}C; ν_{max} (KBr/cm^{-1}) 3413 (mult. w), 3037, 2962, 1776(w), 1710 (s), 1705 (s), 1646 (w), 1499, 1458, 1388, 1314, 1270, 1200, 1176, 777; δ_H (400 MHz, $CDCl_3$) 3.43 (1H, dd, ^3J = 8.4 Hz, ^3J = 3.2 Hz), 3.52 (1H, d, ^3J = 8.4 Hz), 3.89 (3H, s, $CO_2C\underline{H_3}$), 4.89 (1H, d, ^3J = 3.2 Hz), 6.38 (2H, d, ^3J = 8.8 Hz), 6.67 (1H, d, ^3J = 16.8 Hz), 7.17 – 7.45 (10H, m), 7.95 (1H, d, ^3J = 16.8 Hz); $\square_C$ (100.5 MHz, $CDCl_3$) 45.9 (CH), 48.0 (CH), 48.2 (CH), 52.0 (OCH_3), 52.1 (C_{quat}), 122.7 (C_{quat}), 123.5 (CH), 123.9 (CH), 124.2 (CH), 125.5 (CH), 126.8 (CH), 127.2 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 127.8 (2C, CH), 130.1 (C_{quat}), 132.2 (2C, CH), 138.0 (C_{quat}), 139.1 (C_{quat}), 140.6 (C_{quat}), 141.7 (C_{quat}), 142.7 (CH), 166.5 (C_{quat}, CO), 174.1 (C_{quat}, NCO), 175.0 (C_{quat}, NCO).

45) Cycloadduct 51d-Me of methyl 9-anthranylacrylate (39-Me) and 4-methylphenylmaleimide (48d)

A mixture of methyl 9-anthranylacrylate (9-Me, 262mg, 1.0mmol) and 4-methylphenylmaleimide (48d, 187mg, 1.0mmol) was reacted at 130 ^{o}C for 3h15 min according to procedure D to give **51d-Me** as pale yellow solid (400 mg, 89 %); ν_{max}(KBr/cm^{-1}) 3473 (mw), 2988, 2947, 1778 (w), 1713 (s), 1513, 1394, 1288, 1199, 769; δ_H (400 MHz, CDCl$_3$) 2.27 (3H, s, CH$_3$), 3.42 (1H, dd, ^3J = 8.4 Hz, ^3J = Hz), 3.51 (1H, d, ^3J = 8.4 Hz), 3.88 (3H, s, CO$_2$CH$_3$), 4.90 (1H, d, ^3J = 3.2 Hz), 6.35 (2H, d, ^3J = 8.0 Hz), 6.69 (1H, d, ^3J = 16.4 Hz), 7.06 (2H, d, ^3J = 8.0 Hz), 7.18 – 7.39 (7H, m), 7.44 (1H, d, ^3J = 7.6 Hz), 7.97 (1H, d, ^3J = 16.4 Hz); $_C$ (100.5 MHz, CDCl$_3$) 21.2 (CH$_3$), 45.9 (CH), 48.0 (CH), 48.2 (CH), 51.9 (OCH$_3$), 52.0 (C$_{quat}$), 123.5 (CH), 123.8 (CH), 124.2 (CH), 125.5 (CH), 126.1 (2C, CH), 126.7 (CH), 127.2 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 128.4 (C$_{quat}$), 129.7 (2C, CH), 138.1 (C$_{quat}$), 138.9 (C$_{quat}$), 139.2 (C$_{quat}$), 140.8 (C$_{quat}$), 141.9 (C$_{quat}$), 142.8 (CH), 166.6 (C$_{quat}$, $\underline{C}$O$_2$CH$_3$), 174.5 (C$_{quat}$, CNO), 175.5 (C$_{quat}$, CNO); Found: C, 77.52; H, 5.17; N, 3.12%. Calcd for C$_{29}$H$_{23}$NO$_4$ (449.50) C, 77.49; H, 5.16; H, 3.12%.

46) Cycloadduct 51e-Me of methyl 9-anthranylacrylate (39-Me) and 4-methoxyphenylmaleimide (48e)

A mixture of methyl 9-anthranylacrylate (39-Me, 186 mg, 0.71 mmol) and 4-methoxyphenylmaleimide (**48e**, 144 mg, 0.71 mmol) were reacted at 115 ^{o}C for 3h according to procedure D to give **51e-Me** as a pale yellow solid (294 mg, 89 %); ν_{max} (KBr/cm^{-1}) 2959, 2839, 1713, 1514, 1458, 1395, 1252, 1200, 1178, 1033, 775, 761; δ_H (400 MHz, CDCl$_3$) 3.42 (1H, dd, ^3J = 8.4 Hz, ^3J = 3.2 Hz), 3.51 (1H, d, ^3J = 8.4 Hz), 3.72 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 4.90 (1H, d, ^3J = 3.2 Hz), 6.37 (2H, d, ^3J = 8.8 Hz), 6.69 (1H, d, ^3J = 16.4 Hz), 6.77 (2H, d, ^3J = 8.8 Hz), 7.18 – 7.39 (7H, m), 7.44 (1H, d, ^3J = 6.8 Hz), 7.97 (1H, d, ^3J = 16.4 Hz); δ_C (100.5 MHz, $CDCl_3$) 45.9 (CH), 48.0 (CH), 48.2 (CH), 51.9 (OCH_3), 52.0 (C_{quat}), 55.4 (OCH_3), 114.3 (2C, CH), 123.5 (CH), 123.7 (C_{quat}), 123.8 (CH), 124.2 (CH), 125.5 (CH), 126.7 (CH), 127.2 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 127.6 (2C, CH), 129.7 (2C, CH), 138.2 (C_{quat}), 139.2 (C_{quat}), 140.8 (C_{quat}), 141.9 (C_{quat}), 142.8 (CH), 159.8 (C_{quat}), 166.6 (C_{quat}, $\underline{C}O_2CH_3$), 174.5 (C_{quat}, CNO), 175.5 (C_{quat}, CNO). Found C, 75.26; H, 4.97; N, 3.00%. Calcd. for $C_{29}H_{23}NO_5$ (465.50) C, 74.83; H, 4.98; N, 3.01%.

47) Cycloadduct 51e-Et of ethyl 9-anthranylacrylate (39-Et) and 4-methoxyphenylmaleimide (48e)

A mixture of ethyl 9-anthranylacrylate (**39-Et**, 177 mg, 0.64 mmol) and 4-methoxyphenylmaleimide (**48e**, 130 mg, 0.64 mmol) were reacted at 110 °C for 13h according to procedure D to give **51e-Et** as a colorless solid (234 mg, 76 %), mp. 149-150 °C; ν_{max} (KBr/cm^{-1}) 2979, 1779 (w), 1716 (s), 1513, 1458, 1392, 1300, 1252, 1198, 1030, 773, 553; δ_H (400 MHz, $CDCl_3$) 1.38 (3H, t, ^3J = 7.2 Hz), 3.42 (1H, dd, ^3J = 8.4 Hz, ^3J = 3.2 Hz), 3.52 (1H, d, ^3J = 8.4 Hz), 3.73 (3H, s, OCH_3), 4.34 (2H, q, ^3J = 7.2 Hz), 4.90 (1H, d, ^3J = 2.8 Hz), 6.38 (2H, d, ^3J = 7.6 Hz), 6.69 (1H, d, ^3J = 16.8 Hz), 6.77 (2H, d, ^3J = 7.6 Hz), 7.20 – 7.39 (6H, m), 7.31 (1H, d, ^3J = 7.6 Hz), 7.44 (1H, d, ^3J = 6.8 Hz), 7.96 (1H, d, ^3J = 16.8 Hz); δ_C (100.5 MHz, $CDCl_3$) 14.3 (CH_3), 45.9 (CH), 48.0 (CH), 48.2 (CH), 52.0 (C_{quat}), 55.4 (OCH_3), 60.8 (OCH_2), 114.3 (2C, CH), 123.6 (CH), 123.8 (C_{quat}), 123.9 (CH), 124.2 (CH), 125.5 (CH), 126.7 (CH), 127.3 (CH), 127.4 (CH), 127.5 (2C, CH), 127.6 (CH), 138.2 (C_{quat}), 139.3 (C_{quat}), 140.8 (C_{quat}), 142.0

(C$_{quat}$), 142.5 (CH), 159.6 (C$_{quat}$), 166.2 (C$_{quat}$, CO), 174.7 (C$_{quat}$, CNO), 175.7 (C$_{quat}$, CNO).

48) **Cycloadduct 51e-Et of ethyl 9-anthranylacrylate** (**39-Et**) and ***N*-phenylmaleimide** (**48b**)

A mixture of ethyl 9-anthranylacrylate (**39-Et**, 276 mg, 1.0 mmol) and ***N*-**phenylmaleimide (**48b**, 173 mg, 1.0 mmol) were reacted at 115 ^{o}C for 12h according to procedure D to give **51e-Et** (392 mg, 87.[3]%) as a colorless solid, mp. 225 – 227 ^{o}C. ν_{max} (KBr/cm^{-1}) 1716, 1495, 1387, 1209, 1191, 1159, 768, 756; δ_H (400 MHz, CDCl$_3$) 1.38 (3H, t, ^3J = 7.2 Hz, CH$_3$), 3.45 (1H, dd, ^3J = 8.8 Hz, ^3J = 3.2 Hz), 3.54 (1H, d, ^3J = 8.8 Hz), 4.34 (2H, q, ^3J = 7.2 Hz, OCH$_2$), 4.91 (1H, d, ^3J = 3.2 Hz), 6.46 – 6.48 (1H, m), 6.68 (1H, d, ^3J = 16.8 Hz), 7.18 – 7.32 (10H, m), 7.37 – 7.40 (1H, m), 7.45 (1H, d, ^3J = 8.0 Hz), 7.95 (1H, d, ^3J = 16.8 Hz); □$_C$ (100.5 MHz, CDCl$_3$) 14.3 (CH$_3$), 45.9 (CH), 48.0 (CH), 48.3 (CH), 52.0 (C$_{quat}$), 60.9 (OCH$_2$), 123.6 (CH), 123.9 (CH), 124.2 (CH), 125.5 (CH), 126.4 (2C, CH), 126.7 (CH), 127.3 (CH), 127.5 (CH), 127.6 (CH), 128.8 (CH), 129.0 (2C, CH), 131.2 (C$_{quat}$), 138.1 (C$_{quat}$), 139.3 (C$_{quat}$), 140.8 (C$_{quat}$), 142.0 (C$_{quat}$), 142.4 (CH), 166.1 (C$_{quat}$, CO), 174.4 (C$_{quat}$, NCO), 175.4 (C$_{quat}$, NCO). Found C, 77.52; H, 5.24; N, 3.20%. Calcd. for $C_{29}H_{23}NO_4$ (449.50) C, 77.49; H, 5.16; N, 3.12%.

49) **Cycloadduct 51g-Et of ethyl-9-anthranylacrylate** (**39-Et**) **and 2,4-difluorophenylmaleimide** (**48g**)

A mixture of ethyl 9-anthranylacrylate (**39-Et**, 552 mg, 2.0 mmol) and 2,4-fluorophenylmaleimide (**48g**, 418 mg, 2.0 mmol) were reacted at 115 ^{o}C for 13h. As there was a slight solubility of the product noted in diethyl ether, the product was recrystallized in ether/hexane 1:1 to give **51g-Et** (883 mg, 91%) as a pale yellow solid, mp. 147 ^{o}C; ν_{max} (KBr/cm^{-1}) 2961, 1720, 1515, 1393, 1217, 1194, 1145, 1101, 973, 852, 790, 539; δ_{C} (100.5 MHz, CDCl$_3$) 160.4 (C$_{quat}$, J_{CF} = 267.0 Hz), 163.0 (C$_{quat}$, J_{CF} = 263.0 Hz, J_{CF} = 11.5 Hz), 166.1 (CO), 173.5 (NCO), 174.5 (NCO).

50) **Cycloadduct 51h-Et** of **ethyl 9-anthranylacrylate** (**39-Et**) and **2,6-difluorophenylmaleimide** (**48h**)

A mixture of ethyl 9-anthranylacrylate (**39-Et**, 552 mg, 2.0 mmol) and 2,6-fluorophenylmaleimide (**48h**, 418 mg, 2.0 mmol) were reacted at 115 ^{o}C for 13h. As there was a slight solubility of the product noted in diethyl ether, the product was recrystallized in ether to give **51h-Et** (905 mg, 93%) as colourless solid; ν_{max} (KBr/cm^{-1}) 3484, 3075, 2981, 2935, 2873, 1717, 1599, 1507, 1477, 1458, 1375, 1309, 1273, 1182, 1161, 1115, 1011, 791, 779, 759; δ_{H} (400 MHz, CDCl$_3$) 1.39 (3H, t, ^{3}J = 7.8 Hz, CH$_3$), 3.53 (1H, dd, ^{3}J = 8.8 Hz, ^{3}J = 2.8 Hz), 3.65 (1H, d, ^{3}J = 8.8 Hz), 4.35 (2H, q, ^{3}J = 7.8 Hz, OCH$_2$), 4.91 (1H, d, ^{3}J = 2.8 Hz), 6.71 (1H, d, ^{3}J = 16.8 Hz), 6.75 – 7.46 (11H, m), 7.97 (1H, d, ^{3}J = 16.8 Hz); □$_{C}$ (100.5 MHz, CDCl$_3$) 14.3 (CH$_3$), 45.6 (CH), 48.2 (CH), 48.7 (CH), 51.8 (C$_{quat}$), 60.9 (OCH$_2$), 111.8 (ddd, J_{CF} = 20.0 Hz, J_{CF} = 20.0 Hz, J_{CF} = 4.0 Hz), 123.4, 123.8, 124.1, 125.5, 126.7, 127.3, 127.4, 127.6, 131.1 (dd, J_{CF} = 9.7 Hz, J_{CF} = 9.7 Hz), 137.6, 138.9, 141.1, 142.2, 142.4, 157.9 (ddd, J_{CF} = 254.3 Hz, J_{CF} = 22.6 Hz, J_{CF} = 3.5 Hz), 166.1 (C$_{quat}$, NCO), 172.7 (C$_{quat}$, NCO), 173.7 (C$_{quat}$, CO).

51) **Cycloadduct 53a of 9-anthranylacrylic acid / 4-methylphenylmaleimide (4d**)

A mixture of anthranylacrylic acid (**39-H**, 190 mg, 0.76 mmol) and *N*-(4-methylphenyl) maleimide (**48d**, 160 mg, 0.85 mmol) in xylene (0.5 mL) was heated under reflux for 14h. Thereafter, the cooled suspension was taken up with diethyl ether (5 mL), and the resulting precipitate was filtered and washed to give cycloadduct (**53a**, 230 mg, 69%) as an off-white solid, mp. 288 – 291 ^{o}C; ν_{max} (KBr/cm^{-1}) 3700 – 2850 (bs, OH), 3168, 1780 (w), 1701 (s), 1664 (w), 1515, 1457, 1398, 1282, 1215, 1185, 1170, 991 (w), 773; δ_H (400 MHz, $CDCl_3$) 2.28 (3H, s, CH_3), 3.45 (1H, dd, ^3J = 8.8 Hz, ^3J = 3.2 Hz), 3.56 (1H, d, ^3J = 8.8 Hz), 4.92 (1H, d, ^3J = 3.2 Hz), 6.36 (2H, d, ^3J = 8.0 Hz), 6.74 (1H, d, ^3J = 16.4 Hz), 7.07 (2H, d, ^3J = 8.0 Hz), 7.23 – 7.48 (8H, m), 8.11 (1H, d, ^3J = 16.4 Hz); δ_C (100.5 MHz, $CDCl_3$) 21.6 (CH_3), 45.9 (CH), 48.1 (CH), 48.2 (CH), 52.1 (C_{quat}), 123.5 (CH), 123.8 (CH), 124.3 (CH), 125.5 (CH), 126.1 (2C, CH), 126.8 (CH), 126.9 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 128.5 (C_{quat}), 129.7 (2C, CH), 138.1 (C_{quat}), 138.9 (C_{quat}), 139.1 (C_{quat}), 140.8 (C_{quat}), 141.7 (C_{quat}), 145.4 (CH), 170.7 (C_{quat}, CO), 174.4 (C_{quat}, NCO), 175.5 (C_{quat}, NCO).

52) Cycloadduct 53b of 9-anthranylacrylic acid (39-H) and *N-p*-bromophenylmaleimide (48a)

A mixture of 9-anthranylacrylic acid (**39-H**, 95mg, and 0.38mmol) and *N-p*-bromophenyl-maleimide (**48a**, 105 mg, 0.42 mmol) in xylene (1.3 mL) was stirred at 135 ^{o}C for 40h. Afterwards, the cooled suspension was filtered and washed well with ether (3 x 15 mL) to give **53b** (174 mg, 91.(6)%); mp. > 270 ^{o}C; ν_{max} (KBr/cm^{-1}) 3600 – 2800 (bs, OH), 1773 (w), 1704 (s), 1646 (w), 1491, 1459, 1389, 1289 (w), 1197, 753; δ_H (400 MHz, DMSO-d^6) 3.46 (1H, dd, ^3J = 8.0 Hz, ^3J = 2.4 Hz), 3.75 (1H, d, ^3J = 8.0 Hz), 4.88 (1H, d, ^3J = 2.4 Hz), 6.37 (2H, d, ^3J = 8.4 Hz), 6.50 (1H, d, ^3J = 16.4 Hz), 7.18 – 7.55 (10H, m), 7.7 5 (1H, d, ^3J = 16.4 Hz); δ_C (100.5 MHz, DMSO-d^6) 45.3, 48.3, 51.6, 122.0, 123.2, 123.7, 124.9, 125.7, 126.9, 127.3, 127.4, 127.5, 128.5, 128.9 (2C, CH), 131.3, 132.4 (2C, CH), 139.1, 139.9, 141.5, 142.4, 142.5, 167.4 (C_{quat}, $\underline{C}O_2H$), 174.9 (C_{quat}, NCO), 175.5 (C_{quat}, NCO).

53) **Cycloadduct 58c of 9-(3-nitrophenyl)anthranylacrylic acid** and **4-bromophenylmaleimide** (**48a**)

A mixture of 9-(3-nitrophenyl)-anthranylacrylic acid (291 mg, 0.79 mmol) and *N*-(4-bromophenyl)-maleimide (**48a**, 200 mg, 0.79 mmol) in xylene (1.5 mL) was heated under reflux for 68h. The cooled suspension was filtered and washed copiously with ether (4 X 15 mL) to give a beige solid (450 mg, 91.[5]%), mp. 260 ^{o}C; ν_{max} (KBr/cm^{-1}) 3600 – 2870 (bs, OH), 3389, 3130, 1716 (s), 1524, 1490, 1385, 1351, 1196.

54) **Cycloadduct 58b of 9-phenylanthranylacrylic acid and 4-bromophenyl-maleimide** (**4a**)

A mixture of 9-phenylanthranylacrylic acid (255mg, 0.79mmol) and *N*-(4-bromophenyl)-maleimide (**48a**, 200 mg, 0.79 mmol) in xylene (1.5 mL) was heated under reflux for 68h. The cooled suspension was filtered and washed copiously with ether (4 X 15 mL) to give a beige solid (400 mg, 88%), as a pale beige solid, mp. 265 – 266 ^{o}C; ν_{max} (KBr/cm^{-1}) 3680 – 2800 (bs, OH), 3426, 1779 (w), 1717 (s), 1650 (w), 1492, 1384, 1195, 1070 (w), 1013 (w), 777, 703, 652.

55) **Cycloadduct *E*-52d-F of 9-[2-(4-fluorophenylcarbonylethenyl)]anthracene** (***E*-40-F**) and ***N*-4-methylphenylmaleimide** (**48d**)

A solution of ***E*-40-F** (250 mg, 0.77 mmol) and *N*-(4-methylphenyl)-maleimide **(48d**, 160 mg, 0.86 mmol) in xylene (0.5 mL) was held at reflux for 14h. Thereafter the cooled solution was subjected to column chromatography on silica gel (hexane/ether/CH_2Cl_2 1:1:1) to give ***E*-52d-F** (384 mg, 97%), as pale-yellow solid, mp. 120-123 ^{o}C; ν_{max}(KBr/cm^{-1}) 3071, 2958, 2925, 1712 (s), 1675, 1514, 1387, 1223, 1156, 768; δ_H (400 MHz, $CDCl_3$) 2.28 (3H, s, CH_3), 3.47 (1H, dd, ^{3}J = 8.8 Hz, ^{3}J = 3.2 Hz), 3.65 (1H, d, ^{3}J

= 8.8 Hz), 4.86 (1H, d, ^3J = 3.2 Hz), 6.37 (2H, d, ^3J = 8.4 Hz), 7.09 (2H, d, ^3J = 8.4 Hz), 7.17 – 7.47 (10H, m), 7.84 (1H, d, ^3J = 16.4 Hz), 8.00 (1H, d, ^3J = 16.4 Hz), 8.19 – 8.22 (2H, m); δ_C (100.5 MHz, $CDCl_3$) 21.2 (CH_3), 45.9 (CH), 47.8 (CH), 48.5 (CH), 52.5 (C_{quat}), 115.9 (2C, CH, $^2J_{CF}$ = 21.5 Hz), 123.5 (CH), 124.0 (CH), 124.1 (CH), 125.5 (CH), 126.2 (2C, CH), 126.8 (CH), 127.4 (2C, bs, CH), 127.5 (CH), 128.5 (C_{quat}), 129.8 (2C, CH), 131.2 (CH), 131.7 (2C, CH, $^3J_{CF}$ = 9.7 Hz), 134.1 (C_{quat}, $^4J_{CF}$ = 9.7 Hz), 138.2 (C_{quat}), 139.1 (C_{quat}), 139.4 (C_{quat}), 140.8 (C_{quat}), 142.2 (C_{quat}), 142.4 (CH), 165.8 (C_{quat}, $^1J_{CF}$ = 253.8 Hz), 174.8 (C_{quat}, NCO), 175.5 (C_{quat}, NCO), 188.8 (C_{quat}, CO).

56) Cycloadduct *E*-52e-F of 9-[2-(4-fluorophenylcarbonylethenyl)]anthracene (*E*-40-F) and *N*-4-methoxyphenylmaleimide (48e)

A solution of ***E*-40-F** (250 mg, 0.77 mmol) and *N*-(4-methoxyphenyl)-maleimide (**48e**, 180 mg, 0.89 mmol) in xylene (0.5 mL) was held at reflux for 14h. Thereafter the cooled solution was subjected to column chromatography on silica gel (hexane/ether/CH_2Cl_2 1:1:1) to give ***E*-52e-F** (402mg, 99%) as a pale-yellow solid, mp. 189-194°C; ν_{max}(KBr/cm^{-1}) 1709 (s), 1513 (s), 1393, 1252, 1225, 1157, 1031, 831, 768, 751, 566; δ_H(400 MHz, $CDCl_3$) 3.47 (1H, dd, ^3J = 8.8 Hz, ^3J = 3.2 Hz), 3.65 (1H, d, ^3J = 8.8 Hz), 3.74 (3H, s, OCH_3), 4.86 (1H, d, ^3J = 3.2 Hz), 6.39 (2H, d, ^3J = 8.8 Hz), 6.79 (2H, d, ^3J = 8.8 Hz), 7.16 – 7.45 (10H, m), 7.84 (1H, d, ^3J = 16.4 Hz), 7.99 (1H, d, ^3J = 16.4 Hz), 8.19 – 8.21 (2H, m); δ_C (100.5 MHz, $CDCl_3$) 45.9 (CH), 48.0 (CH), 48.4 (CH), 52.5 (C_{quat}), 55.4 (OCH_3), 114.5 (2C, CH), 115.9 (2C, CH, $^2J_{CF}$ = 22.3 Hz), 123.5 (CH), 123.7 (C_{quat}), 124.0 (CH), 124.1 (CH), 125.5 (CH), 126.8 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 127.6 (2C, CH), 131.2 (CH), 131.6 (2C, CH, $^3J_{CF}$ = Hz), 134.1 (C_{quat}, $^4J_{CF}$ = 5.2 Hz), 138.2 (C_{quat}), 139.5 (C_{quat}), 140.8 (C_{quat}), 142.2 (C_{quat}), 142.4 (CH), 159.7

(C_{quat}), 165.8 (C_{quat}, $^1J_{CF}$ = 255.1 Hz), 175.0 (C_{quat}, NCO), 175.7 (C_{quat}, NCO), 188.8 (C_{quat}, CO).

57) Cycloadduct *E*-52a-F of 9-[2-(4-fluorophenylcarbonylethenyl)]-anthracene (*E*-40-F) and *N*-4-bromophenylmaleimide (48a)

A solution of ***E*-40-F** (250 mg, 0.77 mmol) and *N*-(4-bromophenyl)-maleimide (**48a**, 220 mg, 0.87 mmol) in xylene (0.5 mL) was held at reflux for 14h. Thereafter, diethyl ether (20 mL) was added to the cooled solution, and the flask was left to stand overnight at room temperature.

The precipitate was filtered and air-dried to give ***E*-52a-F** (422 mg, 95%) as a pale-yellow solid, mp. 266-270°C; ν_{max} (KBr/cm^{-1}) 2923, 1713 (s), 1490, 1388, 1221, 1190, 1154, 779; δ_H (400 MHz, $CDCl_3$) 3.49 (1H, dd, ^3J = 8.4 Hz, ^3J = 3.2 Hz), 3.66 (1H, d, ^3J = 8.4 Hz), 4.84 (1H, d, ^3J = 3.2 Hz), 6.39 – 6.41 (2H, m), 7.16 – 7.48 (12H, m), 7.82 (1H, d, ^3J = 16.4 Hz), 7.99 (1H, d, ^3J = 16.4 Hz), 8.18 – 8.21 (2H, m); δ_C (100.5 MHz, $CDCl_3$) 45.9 (CH), 47.9 (CH), 48.5 (CH), 52.5 (C_{quat}), 115.9 (2C, CH, $^2J_{CF}$ = 21.3 Hz), 122.9 (C_{quat}), 123.5 (CH), 124.0 (CH), 124.2 (CH), 125.5 (CH), 126.9 (CH), 127.4 (CH), 127.5 (CH), 127.6 (CH), 128.0 (2C, CH), 130.1 (C_{quat}), 131.3 (CH), 131.6 (2C, CH, $^3J_{CF}$ = 9.6 Hz), 132.3 (2C, CH), 134.0 (C_{quat}, $^4J_{CF}$ = 3.0 Hz), 138.1 (C_{quat}), 139.4 (C_{quat}), 140.6 (C_{quat}), 142.1 (C_{quat}), 142.2 (CH), 174.4 (C_{quat}, NCO), 175.1 (C_{quat}, NCO), 188.7 (C_{quat}, CO).

58) Cycloadduct *E*-52d-Br of 9-[2-(4-bromophenylcarbonylethenyl)]-anthracene (*E*-40-Br) and *N*-4-methylphenylmaleimide (48d)

A solution of ***E*-40-Br** (280mg, 0.77mmol) and *N*-(4-methylphenyl)-maleimide (**48d**, 160 mg, 0.86 mmol) in xylene (0.5 mL) was held at reflux for 14h. Afterwards, to the cooled solution was added a mixture of hexane and ether (1:1 v/v, 10 mL). The formed precipitate was filtered, washed with hexane/ether 1/1 (10 mL) and air dried to give ***E*-52d-Br** as a pale yellow solid (423 mg, quant.), mp. 128 – 130 ^{o}C; ν_{max} (KBr/cm^{-1}) 2923, 1777 (w), 1712, 1672, 1626, 1584, 1514, 1386, 1195, 1175, 1009, 767; δ_H (400 MHz, CDCl$_3$) 2.28 (3H, s, CH$_3$), δ_C (100.5 MHz, CDCl$_3$) 21.2 (CH$_3$), 45.9 (CH), 47.9 (CH), 48.4 (CH), 52.5 (C$_{quat}$), 123.5 (CH), 123.9 (CH), 124.2 (CH), 125.6 (CH), 126.2 (2C, CH), 126.8 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 128.4 (C$_{quat}$), 128.5 (C$_{quat}$), 129.8 (2C, CH), 130.5 (2C, CH), 131.1 (CH), 132.1 (2C, CH), 136.4 (C$_{quat}$), 138.2 (C$_{quat}$), 139.1 (C$_{quat}$), 139.4 (C$_{quat}$), 140.8 (C$_{quat}$), 142.2 (C$_{quat}$), 142.8 (CH), 174.8 (C$_{quat}$, NCO), 175.5 (C$_{quat}$, NCO), 189.4 (C$_{quat}$, CO).

59) Cycloadduct *E*-52f-Me of 9-[2-(4-methylphenylcarbonylethenyl)-anthracene (*E*-40-Me) and *N*-2,5-dimethoxyphenylmaleimide (48f)

A solution of ***E*-40-Me** (322 mg, 1.0 mmol) and *N*-(2,5-dimethoxyphenyl)-maleimide (**48f**, 233 mg, 1.0 mmol) in xylene (0.5 mL) was held at reflux for 14h. Afterwards, to the cooled solution was added ether (3 mL). The formed precipitate was filtered, washed with hexane/ether 1/1 (10 mL) and air dried to give ***E*-52f-Me** as a pale yellow solid (555 mg, quant.), mp. 251 ^{o}C; ν_{max} (KBr/cm^{-1}) 2965, 2839, 1781 (w), 1707 (s), 1672, 1633, 1603, 1509, 1458, 1384, 1281, 1225, 1205, 1182, 1044, 1023, 807, 770, 760, 570; δ_H (400 MHz, CDCl$_3$, major rotamer) 2.43 (3H, s, CH$_3$), 3.51 (1H, dd, ^3J = 8.4 Hz, ^3J =

3.4 Hz), 3.58 (3H, s, OCH_3), 3.67 (1H, d, ^3J = 8.4 Hz), 3.70 (3H, s, OCH_3), 4.93 (1H, d, ^3J = 3.4 Hz), 6.82 – 6.85 (2H, m), 7.19 – 7.47 (6H, m), 7.84 (1H, d, ^3J = 16.0 Hz), 7.99 (1H, d, ^3J = 16.0 Hz), 8.08 (2H, m); δ_C (100.5 MHz, $CDCl_3$, major rotamer) 21.8, 46.0, 48.2, 48.7, 52.5, 55.7, 56.4, 113.1, 113.4, 116.5, 120.3, 123.8, 124.0, 124.1, 125.6, 126.8, 127.1, 127.2, 127.3, 129.2 (2C), 129.5 (2C), 131.6, 135.2, 138.6, 139.9, 140.8, 141.8, 142.3, 144.0, 149.0, 153.4, 174.3, 175.2, 190.0.

60) Cycloadduct *E*-52d-Me of 9-[2-(4-methylphenylcarbonylethenyl)]-anthracene (*E*-40-Me) and *N*-4-methylphenylmaleimide (48d)

A solution of ***E*-40-Me** (322 mg, 1.0 mmol) and *N*-(4-methylphenyl)maleimide (**48d**, 187 mg, 1.0 mmol) in xylene (0.5 mL) was held at reflux for 14h. Afterwards, to the cooled solution was added ether (2.5 mL) and hexane (2.5 mL). The precipitate was filtered, washed with hexane/ether (1:1, *v*/*v*, 3 mL) and air-dried to give ***E*-52d-Me** (441 mg, 87%) as a pale yellow solid, mp. 188 °C; ν_{max} (KBr/cm^{-1}) 2923, 1712 (s), 1513, 1386, 1311, 1184, 768; δ_H (400 MHz, $CDCl_3$) 2.28 (3H, s, CH_3), 2.43 (3H, s, CH_3), 3.65 (1H, d, ^3J = 8.4 Hz), 3.48 (1H, d, ^3J = 8.4 Hz), 4.93 (1H, bs), 6.37 (2H, d, ^3J = 8.4 Hz), 7.08 – 7.47 (12H, m), 7.84 (1H, d, ^3J = 16.0 Hz), 7.99 (1H, d, ^3J = 16.0 Hz), 8.06 – 8.09 (2H, m); δ_C (100.5 MHz, $CDCl_3$, DEPT 90, DEPT 135) 21.2 (CH_3), 21.8 (CH_3), 45.9 (CH), 47.9 (CH), 48.5 (CH), 52.5 (C_{quat}), 123.6 (CH), 124.0 (CH), 124.1 (CH), 125.5 (CH), 126.2 (2C, CH), 126.8 (CH), 127.3 (CH), 127.3(5) (CH), 127.5 (CH), 128.6 (C_{quat}), 129.1 (2C, CH), 129.4 (2C, CH), 129.8 (2C, CH), 131.6 (CH), 135.2 (C_{quat}), 138.2 (C_{quat}), 139.0 (C_{quat}), 139.6 (C_{quat}), 140.8 (C_{quat}), 141.8 (CH), 142.3 (C_{quat}), 144.0 (C_{quat}), 174.7 (C_{quat}, NCO), 175.6 (C_{quat}, NCO), 189.9 (C_{quat}, CO).

61) **Cycloadduct *E*-52e-Me of 9-[2-(4-methylphenylcarbonylethenyl)]-anthracene** (***E*-40-Me**) and ***N*-4-methoxyphenylmaleimide** (**48e**)

A solution of ***E*-40-Me** (322 mg, 1.0 mmol) and *N*-(4-methoxyphenyl)maleimide (**48e**, 223 mg, 1.1 mmol) in xylene (0.5 mL) was held at reflux for 4h. Afterwards, to the cooled solution was added ether (2.5 mL) and hexane (2.5 mL). The precipitate was filtered, washed with hexane/ether (1:1, *v*/*v*, 3 mL) and air-dried to give ***E*-52e-Me** (505 mg, 95%) as a beige colored solid, mp. 196 ^{o}C; ν_{max} (KBr/cm^{-1}) 3061, 2962, 1776 (w), 1712 (s), 1674, 1626, 1406, 1513 (s), 1457, 1396, 1311, 1300, 1249, 1229, 1212, 1184, 1168, 1027, 767; δ_H (400 MHz, CDCl$_3$) 2.43 (3H,s, CH$_3$), 3.73 (3H, s, OCH$_3$), 3.47 (1H, dd, ^3J = 10 Hz, ^3J = 3.2 Hz), 3.64 (1H, d, ^3J = 10 Hz), 4.92 (1H, d, ^3J = 3.2 Hz), 6.40 (2H, d, ^3J = 8.8 Hz), 6.79 (2H, d, ^3J = 8.8 Hz), 7.19 – 7.46 (10H, m), 7.83 (1H, d, ^3J = 16.0 Hz), 7.99 (1H, d, ^3J = 16.0 Hz), 8.07 (2H, d, ^3J = 8.0 Hz); δ_C (100.5 MHz, CDCl$_3$) 21.8 (CH$_3$), 45.9, 47.9, 48.4, 52.5, 55.4, 114.5 (2C, CH), 123.6, 123.8, 124.1, 125.5, 126.8, 127.3, 127.4, 127.6, 129.1 (2C, CH), 129.4 (2C, CH), 127.4 (2C, CH), 131.6, 135.2, 138.2, 139.6, 140.8, 141.8, 142.4, 144.0, 159.6 (C$_{quat}$), 174.9 (NCO, C$_{quat}$), 175.7 (NCO, C$_{quat}$), 189.9 (C$_{quat}$, CO).

62) **Cycloadduct *E*-52d-Cl** of **9-[2-(4-chlorophenylcarbonylethenyl)]-anthracene** (***E*-40-Cl**) and ***N*-4-methylphenylmaleimide** (**48d**)

A solution of ***E*-40-Cl** (304 mg, 0.89 mmol) and *N*-(4-methylphenyl)maleimide (**48d**, 185 mg, 1.0 mmol) in xylene (0.5 mL) was held at reflux for 14h. Then, to the cooled solution was added ether (2.5 mL) and hexane (2.5 mL). The precipitate was filtered, washed with hexane/ether (1:1, *v*/*v*, 3 mL) and air-dried to give ***E*-52d-Cl** (381 mg, 81%) as a colourless solid: mp. 235^{o}C; $_{max}$ (KBr/cm^{-1}) 2922, 1711, 1629, 1588, 1512, 1386, 1186, 1089, 767; δ_H (400 MHz, $CDCl_3$) 2.29 (3H, s, CH_3), 3.48 (1H, dd, ^3J = 8.4 Hz, ^3J = 3.2 Hz), 3.65 (1H, d, ^3J = 8.4 Hz), 4.93 (1H, d, ^3J = 3.2 Hz), 6.37 (2H, d, ^3J = 8.4 Hz), 7.10 (2H , d, ^3J = 8.4 Hz), 7.19 – 7.49 (8H, m), 7.82 (d, 1H, ^3J = 16.0 Hz), 8.01 (1H, d, ^3J = 16.0 Hz), 7.48 (2H, d, ^3J = 7.6 Hz), 8.11 (2H, d, ^3J = 7.6 Hz); $_C$ (100.5 MHz, $CDCl_3$) 21.2 (CH_3), 45.9 (d), 47.8, 48.5, 52.4, 123.5, 123.9, 124.2, 125.6, 126.2, 126.8, 127.3, 127.4 (2C, CH), 127.5, 128.5, 129.1 (2C, CH), 129.8 (2C, CH), 130.4 (2C, CH), 131.2, 136.0, 138.1, 139.1, 139.4, 139.6, 140.8, 142.2, 142.8, 174.8 (C_{quat}, NCO, 175.5 (C_{quat}, NCO), 189.2 (C_{quat}, CO).

63) Cycloadduct *E*-52e-OMe of 9-[2-(4-methoxyphenylcarbonylethenyl)]-anthracene (*E*-40-OMe) and *N*-4-methoxyphenylmaleimide (48e)

A solution of ***E*-40-OMe** (127 mg, 0.375 mmol) and *N*-(4-methoxyphenyl)-maleimide (**48e**, 100 mg, 0.45 mmol) in xylene (0.3 mL) was held at reflux for 14h. Then, to the cooled solution was added ether (1.5 mL) and hexane (1.5 mL). The precipitate was filtered, washed with hexane/ether (1:1, *v*/*v*, 1.5 mL) and air-dried to give ***E*-52e-OMe** (197 mg, 93%) as a colorless solid, mp. 193°C; ν_{max} (KBr/cm^{-1}) 2937, 2834, 1774 (w), 1709 (s), 1629, 1598, 1512, 1457, 1392, 1250, 1169, 1019; δ_H (400 MHz, $CDCl_3$) 3.46 (1H, dd, ^3J = 8.4 Hz, ^3J = 3.2 Hz), 3.65 (1H, d, ^3J = 8.4 Hz), 3.73 (3H, s, OCH_3), 3.87 (3H, s, OCH_3), 4.92 (1H, d, ^3J = 3.2 Hz), 6.40 (2H, d, ^3J = 8.8 Hz), 6.79 (2H, d, ^3J = 8.8 Hz), 6.98 (2H, d, ^3J = 9.2 Hz), 7.18 – 7.46 (8H, m), 7.84 (1H, d, ^3J = 16.0 Hz), 7.97 (1H, d, ^3J = 16.0 Hz), 8.17 (2H, d, ^3J = 9.2 Hz); δ_C (100.5 MHz, $CDCl_3$) 45.9, 47.9, 48.5, 52.5, 55.4 (OCH_3), 55.5 (OCH_3), 113.7 (2C, CH), 114.4 (2C, CH), 123.6, 123.8, 124.0(5), 124.1, 125.5, 126.8, 127.2(5), 127.3, 127.4, 127.6, 130.7, 131.4 (4C, CH), 138.2, 139.7, 140.8, 141.2, 142.4, 159.7 (C$_{quat}$), 163.6 (C$_{quat}$), 174.9 (C$_{quat}$, N$\underline{C}$O), 175.7 (C$_{quat}$, N$\underline{C}$O), 188.7 (C$_{quat}$, CO).

64) Cycloadduct 59-OMe of 9-[2-(4-methylphenylcarbonylethenyl)]-anthracene (*E*-40-Me) and maleic anhydride 46

A solution of ***E*-40-Me** (248 mg, 0.77 mmol) and maleic anhydride (**46**, 94 mg, 1.0 mmol) in xylene (0.5 mL) was held at reflux for 14h. To the cooled solution was added ether (2 mL) and hexane (4 mL). The precipitate (125 mg) was collected to give the cycloadduct **59-OMe** as a beige coloured-solid: mp. 211-223^{o}C; $_{max}$(KBr/cm^{-1}) 1771, 1668, 1621, 1607, 1459, 1401, 1385, 1231, 1081, 943, 930, 765; δ_H(400 MHz, CDCl$_3$) 2.45 (3H, s, CH$_3$), 3.66 (1H, dd, ^3J = 9.2 Hz, ^3J = 3.2 Hz), 3.82 (1H, d, ^3J = 9.2 Hz), 4.87 (1H, d, ^3J = 3.2 Hz), 7.75 (1H, d, ^3J = 16.0 Hz), 7.17-7.44 (11H, m), 7.93 (1H, d, ^3J = 16.0 Hz), 8.07 (1H, d, ^3J = 8.4 Hz); δ_C (100.5 MHz, CDCl$_3$) 21.8 (CH$_3$), 45.4 (CH), 49.0 (CH), 49.3 (CH), 51.9 (C$_{quat}$), 123.6 (CH), 124.0 (CH), 124.2 (CH), 125.6 (CH), 127.1 (CH), 127.6 (CH), 128.0 (CH), 128.1 (CH), 129.1 (2C, CH), 129.6 (2C, CH), 131.4 (CH), 135.0 (C$_{quat}$), 137.4 (C$_{quat}$), 139.0 (C$_{quat}$), 140.3 (C$_{quat}$), 140.5 (CH), 141.7 (C$_{quat}$), 144.4 (C$_{quat}$), 168.8 (C$_{quat}$, CO), 170.0 (C$_{quat}$, CO), 189.5 (C$_{quat}$, CO).

65) Cycloadduct *E*-52e-H of 9-[2-(benzoylcarbonylethenyl)]-anthracene (*E*-40-H) and *N*-(4-methoxyphenyl)-maleimide (48e)

A solution of ***E*-40-H** (308 mg, 1.0 mmol) and *N*-(4-methoxyphenyl)-maleimide (**48e**, 223 mg, 1.0 mmol) in xylene (0.3 mL) was held at reflux for 14h. . Then, to the cooled solution was added ether (1.5 mL) and hexane (1.5 mL). The precipitate was filtered, washed with hexane/ether (1:1, *v*/*v*, 1.5 mL) and air-dried to give ***E*-52e-H** (490 mg, 92%) as a beige solid, mp. 169- 170^{o}C; ν_{max} (KBr/cm^{-1}) 3068, 2936, 1775 (w), 1709 (s), 1665, 1630, 1513, 1387, 1251, 1176, 1009, 829, 781, 703, 569, 527; δ_{H} (400 MHz, $CDCl_3$) 3.46 (1H, dd, ^{3}J = 8.4 Hz, ^{3}J = 3.2 Hz), 3.65 (1H, d, ^{3}J = 8.4 Hz), 3.73 (3H, s, OCH_3), 4.92 (1H, d, ^{3}J = 3.2 Hz), 6.40 (2H, d, ^{3}J = 8.8 Hz), 6.80 (2H, d, ^{3}J = 8.0 Hz), 7.25 – 7.61 (11H, m), 7.85 (1H, d, ^{3}J = 16.0 Hz), 8.01 (1H, d, ^{3}J = 16.0 Hz), 8.17 (2H, d, ^{3}J = 8.0 Hz); δ_{C} (100.5 MHz, $CDCl_3$) 45.9, 47.9, 48.4, 52.5, 55.4, 114.4 (2C, CH), 123.6, 123.8, 124.0, 124.1, 125.5, 126.8, 127.3 (2C, CH), 127.5, 127.6 (2C), 128.7 (2C, CH), 129.0 (2C, CH), 131.5, 133.2, 134.1, 137.7, 138.2, 139.5, 140.8, 142.3, 159.7 (C_{quat}), 174.9 (C_{quat}, NCO), 175.7 (C_{quat}, NCO), 190.3 (C_{quat}).

66) Cycloadduct 57 of ethyl 9-anthranylacrylate (39-Et) and maleic anhydride (46)

A solution of **39-Et** (1.21g, 4.38mmol) and maleic anhydride (**46**, 475mg, 4.85mmol) in xylene (0.5 mL) was heated under reflux for 5h. Thereafter, the solution was cooled, and ether/hexane (10 mL, 1:1 *v*/*v*) was added to it. The precipitate was mechanically was ground while suspended in hexane/ether, filtered and dried in air to give **57** (1.59 g, 88%) as a colourless solid; $_{max}$(KBr/cm^{-1}) 1777, 1711, 1458, 1310, 1271, 1185, 1084, 943, 928, 765, 536; $_{H}$(400 MHz, $CDCl_3$) 1.41 (3H, t, ^{3}J = 6.8 Hz, CH_3), 3.59 (1H, d, ^{3}J = 9.2 Hz), 3.69 (1H, d, ^{3}J = 9.2 Hz), 4.37 (2H, q, ^{3}J = 6.8 Hz, OCH_2), 4.83 (1H, bs), 6.62 (1H, d, ^{3}J = 16.4 Hz), 7.18-7.42 (8H, m), 7.88 (1H, d, ^{3}J = 16.4 Hz); $_{C}$ (100.5 MHz, $CDCl_3$) 14.3 (CH_3), 45.47/45.44, 49.0, 4.2, 51.4, 61.1 (OCH_2), 123.5 (CH), 123.9 (CH), 124.2 (CH), 125.6 (CH), 127.0 (CH), 127.5 (CH), 127.6 (CH), 127.8 (CH), 128.1 (CH), 137.4 (C_{quat}), 138.8 (C_{quat}), 140.3 (C_{quat}), 141.4 (C_{quat}), 141.5 (CH), 165.9 (C_{quat}, CO), 168.5 (C_{quat}, CO), 170.0 (C_{quat}, CO).

67) Cycloadduct *E*-59e-H of 9-[2-(4-bromophenylcarbonylethenyl)] anthracene (*E*-40-Br) and maleic anhydride (46)

A solution of ***E*-40-Br** (387 mg, 1.0 mmol) and maleic anhydride (**46**, 117 mg, 1.2 mmol) in xylene (0.3 mL) was heated under reflux for 14h. During the reaction, a colorless precipitate formed. Thereafter, the solution was cooled, and ether/hexane (5 mL, 1:1 *v*/*v*) was added to it. The precipitate was filtered, washed with hexane (7 mL) and dried in air to give ***E*-59e-H** (440 mg, 92%) as a colourless solid: $_{max}$ (KBr/cm^{-1}) 3101, 2962, 1780, 1676, 1632, 1584, 1458, 1224, 1212, 1071, 944, 763; □$_{H}$ (400 MHz, $CDCl_3$) 3.64 (1H, dd, ^3J = 9.2 Hz, ^3J = 3.2 Hz), 3.81 (1H, d, ^3J = 9.2 Hz), 4.87 (1H, d, ^3J = 3.2 Hz), 7.72 (1H, d, ^3J = 16.0 Hz), 7.68 (2H, d, ^3J = 8.4 Hz), 7.17-7.44 (8H, m), 7.95 (1H, d, ^3J = 16.0 Hz), 8.02 (2H, d, ^3J = 8.4 Hz); $_{C}$ (100.5 MHz, $CDCl_3$) 45.42/45.45, 49.0, 49.3, 51.9, 123.5 (CH), 123.9 (CH), 124.2 (CH), 125.6 (CH), 127.1 (CH), 127.6 (CH), 128.0 (CH), 128.2 (CH), 128.7 (C_{quat}), 130.4 (2C, CH), 130.9 (CH), 132.2 (2C, CH), 136.3 (C_{quat}), 137.4 (C_{quat}), 138.9 (C_{quat}), 140.2 (C_{quat}), 141.5 (C_{quat}), 141.6 (CH), 168.9 (C_{quat}, CO), 169.9 (C_{quat}, CO), 188.8 (C_{quat}, CO).

68) Cycloadduct *E*-61-Me of 9-[2-(4-methylphenylcarbonylethenyl)]-anthracene (*E*-40-Me) and diethyl maleate (60)

A mixture of ***E*-40-Me** (225mg, 0.70mmol) and diethyl maleate (**60**, 400 mg, 2.32mmol) was heated at 130°C. After 14h, the reaction was found to be incomplete (as monitored by TLC), and further diethyl maleate (**60**, 310mg, 1.80mmol) was added. After an additional 16h at 130°C, the reaction was still found to be incomplete. Nevertheless, the reaction mixture was cooled and subjected directly to column chromatography on silica gel to give ***E*-61-Me** (150 mg, 43%) as a pale yellow solid: mp. 130°C; ν_{max} (KBr/cm^{-1})

2982, 1740, 1673, 1631, 1604, 1459, 1328, 1307, 1213, 1199, 1178, 1151, 1031, 1009, 769, 755; δ_H (400 MHz, $CDCl_3$) 1.06 (3H, t, ^3J = 7.2 Hz, CH_3), 1.24 (3H, t, ^3J = 7.2 Hz, CH_3), 2.45 (3H, s, CH_3), 3.18 (1H, dd, ^3J = 4.8 Hz, ^3J = 2.4 Hz), 3.67 (1H, d, ^3J = 4.8 Hz), 3.97 (2H, bq, ^3J = 7.2 Hz), 4.06 – 4.17 (2H, m), 4.77 (1H, d, ^3J = 2.4 Hz), 7.08 – 7.45 (8H, m), 7.33 (2H, d, ^3J = 7.6 Hz), 7.57 (1H, d, ^3J = 16.0 Hz), 8.01 (2H, d, ^3J = 7.6 Hz), 8.06 (1H, d, ^3J = 16.0 Hz); δ_C (100.5 MHz, $CDCl_3$) 14.0 (CH_3), 14.3 (CH_3), 21.7 (CH_3), 46.8/46.85, 49.6, 51.0 (OCH_2), 51.6 (OCH_2), 61.0, 61.3, 123.0 (CH), 123.7 (CH), 124.1 (CH), 124.7 (CH), 126.3 (CH), 126.4 (CH), 126.5 (CH), 126.6 (CH), 128.9 (2C, CH), 129.3 (CH), 129.5 (2C, CH), 135.1 (C_{quat}), 139.7 (C_{quat}), 141.8 (C_{quat}), 143.1 (C_{quat}), 144.2 (CH), 171.6 (C_{quat}, CO), 172.3 (C_{quat}, CO), 189.2 (C_{quat}, CO).

69) **Cycloadduct *E*-61-Cl of 9-[2-(4-chlorophenylcarbonylethenyl)]-anthracene (*E*-40-Cl) and diethyl maleate (60)**

The cycloadduct was prepared according to the procedure given for ***E*-61-Me**. The residue was subjected to column chromatography on silica gel to give ***E*-61-Cl** (45% yield) as a colorless, slowly solidifying oil; mp. 61 ^oC; ν_{max} (KBr/cm^{-1}) 3069, 2979, 2926, 2853, 1743, 1725, 1673, 1587, 1458, 1400, 1367, 1310, 1289, 1245, 1224, 1175, 1092, 1030, 1011, 751; δ_H (400 MHz, $CDCl_3$) 0.93 (3H, t, ^3J = 7.2 Hz, CH_3), 1.17 (3H, t, ^3J = 7.2 Hz, CH_3), 3.28 (1H, dd, ^3J = 10.8 Hz, ^3J = 1.2 Hz), 3.64 (1H, d, ^3J = 10.8 Hz), 3.85 – 3.95 (1H, m), 3.80 – 3.85 (2H, m), 4.02 – 4.11 (1H, m), 4.73 (1H, d, ^3J = 1.2 Hz), 7.08 – 7.49 (8H, m), 7.51 (2H, d, ^3J = 8.4 Hz), 7.59 (1H, d, ^3J = 16.0 Hz), 8.02 (1H, d, ^3J = 16.0 Hz), 8.05 (2H, d, ^3J = 8.4 Hz); δ_C (100.5 MHz, $CDCl_3$) 13.7 (CH_3), 14.0 (CH_3), 45.5, 49.4, 50.0, 51.9, 60.7, 61.0, 123.2 (CH), 123.5 (CH), 123.6 (CH), 125.9 (CH), 126.0 (CH), 126.3 (2C, CH), 126.9 (CH), 128.8 (CH), 129.1 (2C, CH), 130.2 (2C, CH), 135.9 (C_{quat}), 139.8/140.1 (C_{quat}), 140.9 (C_{quat}), 142.8/142.9 (C_{quat}), 144.9 (CH), 170.7 (C_{quat}, CO), 171.0 (C_{quat}, CO), 188.3 (C_{quat}, CO).

70) A suspension of anhydride 59

236 mg, xx mmol and Na_2CO_3 (500 mg) in THF (10 ml) and H_2O (1 mL) was stirred at rt for 24h. Thereafter, the mixture was acidified with half conc. HCl and extracted with $CHCl_3$ (3 X 15 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (ethyl actate / ether 1:3 --- ethyl acetate / ether 1:1 ---- ethyl acetate) to give xx as colorless solid (100 mg, %), which may have changed during the process of the column chromatography. NMR data in DMSO-d^6 shows very broad peaks in the region 6.85 – 7.95 ppm, in addition to a peak at 4.43 ppm. Other peaks may have been hidden under the DMSO and water peaks. The peak at 2.48 ppm shows a clear singlet for the methyl-substituent on the aromatic group.

71) Photoreaction of 9-(*E*)-benzoylethenylanthracene (*E*-40-H)

9-(*E*)-Benzoylethenylanthacene (***E*-40-H**, 50 mg, 0.16 mmol) in CH_2Cl_2 (2.2 mL) was photoirradiated at λ = 254 nm (peak output) for 72 h. The photoreaction was monitored by ^1H NMR spectroscopy. Afterwards, the cooled reaction mixture was submitted directly to column chromatography on silica gel (benzene) to give starting material and 9-(*Z*)-benzoylethenylanthracene (***Z*-40-H**, 22 mg), eluting after the starting material, as a yellow-orange solid, mp. 143°C; ν_{max} (KBr/cm^{-1}) 3054, 2923, 2853, 1663, 1603, 1232, 1004, 734, 696; δ_C (100.5 MHz, $CDCl_3$) 125.1 (2C, CH), 125.4 (2C, CH), 125.8 (2C, CH), 127.2, 127.8 (2C, CH), 128.0, 128.1 (2C, CH), 128.7 (2C, CH), 128.8, 130.7 (C_{quat}), 131.0, 132.4, 137.5, 139.3 (CH), 192.6 (C_{quat}, CO).

72) Photoreaction of 9-(*E*)-4-methylbenzoylethenylanthracene (*E*-40-Me)

9-(*E*)-4-Methylbenzoylethenylanthacene (***E*-40-Me**, 50 mg, 0.16 mmol) in CH_2Cl_2 (2.2 mL) was photoirradiated at 254 nm (peak output) for 24h. The photoreaction was monitored by ^{1}H NMR spectroscopy. Afterwards, the cooled reaction mixture was submitted directly to column chromatography on silica gel (benzene) to give starting material and 9-(*Z*)-4-methylbenzoylethenylanthracene (***Z*-40-Me**, 18 mg), eluting after the starting material, as a yellow-orange solid, mp. 144 °C; ν_{max} (KBr/cm^{-1}) 3043, 1664, 1608, 1426, 1232, 885, 840, 778, 731; δ_H (400 MHz, $CDCl_3$) 2.24 (3H, s, CH_3), 6.94 (2H, d, ^3J = 7.2 Hz), 7.40 – 7.45 (5H, m), 7.57 (2H, d, ^3J = 7.2 Hz), 7.85 (1H, d, ^3J = 11.6 Hz), 7.92 – 7.95 (2H, m), 8.08 – 8.10 (2H, m), 8.32 (1H, s); δ_C (100.5 MHz, $CDCl_3$) 125.0 (2C, CH), 125.5 (2C, CH), 125.7 (2C, CH), 127.0 (CH), 128.3 (2C, CH), 128.6[8] (2C, CH), 128.7 (2C, CH), 128.7(5) (CH), 130.5 (C_{quat}, 2C), 130.9 (C_{quat}), 131.0 (C_{quat}, 2C), 134.9 (C_{quat}), 139.1 (CH), 143.3 (C_{quat}), 191.5 (C_{quat}, CO).

73) Photoreaction of 9-(*E*)-3-nitrobenzoylethenylanthracene (*E*-40-NO_2)

Two samples of 9-(*E*)-3-nitrobenzoylethenylanthacene (***E*-40-NO_2**, 50 mg each, 0.16 mmol) in CH_2Cl_2 (2.2 mL) were photoirradiated at λ = 254 nm (peak output) for 72 h, respectively. The photoreaction was monitored by ^{1}H NMR spectroscopy. Afterwards, the combined cooled reaction mixtures were submitted directly to column chromatography on silica gel (benzene-hexane 4:1) to give starting material and 9-(*Z*)-nitrobenzoylethenylanthracene (***Z*-40-NO_2**, 48 mg), eluting after the starting material, as a yellow-orange, slowly solidifying oil, $_{\mathrm{max}}$ (KBr/cm^{-1}) 3082, 2918, 1673, 1614, 1528 (s, NO_2-asym. stretching), 1349 (s, NO_2-sym. stretching), 1224, 1090, 1014, 888, 730; δ_H (400 MHz, $CDCl_3$) 6.81 (1H, dd, ^3J = 7.6 Hz, ^3J = 7.6 Hz), 7.12 (1H, d, ^3J = 12.0 Hz), 7.33 – 7.49 (4H, m), 7.71 – 7.74 (2H, m), 7.77 (2H, d, ^3J = 8.0 Hz), 7.92 (1H, m), 7.96 – 7.99 (2H, ^3J = 8.0 Hz), 8.07 (1H, d, ^3J = 12.0 Hz), 8.10 (1H, s); δ_C (100.5 MHz, $CDCl_3$) 122.4, 124.9(5) (2C, CH), 125.0, 125.3 (2C, CH), 125.9, 126.6 (2C, CH), 127.9, 128.2, 128.7 (2C, CH), 129.1, 130.7, 131.1, 132.7, 138.7, 140.6, 146.6, 192.8 (C_{quat}, CO).

74) Photoreaction of 9-(*E*)-4-bromobenzoylethenylanthracene (***E*-40-Br**)

A sample of 9-(*E*)-3-bromobenzoylethenylanthacene (***E*-40-Br**, 60 mg, 0.15(5) mmol) in CH_2Cl_2 (2.2 mL) was photoirradiated at= 254 nm (peak output) for 72h. The photoreaction was monitored by ^{1}H NMR spectroscopy. The cooled reaction mixture was submitted directly to column chromatography on silica gel (benzene-hexane 4:1) to give starting material and 9-(*Z*)-4-bromobenzoylethenylanthracene (***Z*-40-Br**, 25 mg), eluting after the starting material, as a yellow-orange, slowly solidifying oil, $_{\mathrm{max}}$(KBr/cm^{-1}) 2918, 1668, 1587, 1225, 1091, 998, 907, 781, 734; δ_H (400 MHz, $CDCl_3$) 6.87 (1H, d, ^3J = 8.8 Hz), 7.24 (1H, d, ^3J = 12.4 Hz), 7.33 – 7.45 (8H, m), 7.85 – 7.87 (2H, m), 7.97-8.00 (2H, m), 8.24 (1H, s); $_C$ (100.5 MHz, $CDCl_3$) 125.1 (2C, CH), 125.2 (2C, CH), 126.0 (2C, CH), 127.4 (CH), 127.9 (2C, CH), 128.1 (CH), 128.7 (2C, CH), 128.9 (C_{quat}), 129.3 (2C, CH), 130.2 (C_{quat}), 130.6 130.9, 138.6, 139.6 (CH), 191.9 (C_{quat}, CO).

75) Photoreaction of 9-(*E*)-4-fluorobenzoylethenylanthracene (***E*-40-F**)

A sample of 9-(*E*)-3-fluorobenzoylethenylanthacene (***E*-40-Br**, 60 mg, 0.18 mmol) in CH_2Cl_2 (2.2 mL) was photoirradiated at= 254 nm (peak output) for 72h. The photoreaction was monitored by ^{1}H NMR spectroscopy. The cooled reaction mixture was submitted directly to column chromatography on silica gel (benzene-hexane 4:1) to give starting material and 9-(*Z*)-4-fluorobenzoylethenylanthracene (***Z*-40-F**, 25 mg), eluting after the starting material, as a yellow solid; ν_{max} (KBr/cm^{-1}) 3051, 2921, 2851, 1671, 1596, 1231, 1155, 998, 783, 735; δ_H (400 MHz, $CDCl_3$) 6.63 (2H, dd, ^3J = 8.4 Hz, ^3J = 8.4 Hz), 7.29 (1H, d, ^3J = 12.0 Hz), 7.40 – 7.46 (4H, m), 7.51 – 7.53 (2H, m), 7.90 – 7.93 (3H, m), 8.05 (2H, dm, ^3J = 8.4 Hz), 8.29 (1H, s); δ_C (100.5 MHz, $CDCl_3$) 114.7 (CH, $^2J_{CF}$ = 21.7 Hz), 125.1 (2C, CH), 125.3 (2C, CH), 126.0 (2C, CH), 127.4 (CH), 128.8 (2C, CH), 128.9 (CH), 130.3 (C_{quat}), 130.5(5) (2C, CH, J_{CF} = 9.0 Hz), 130.8 (2C, C_{quat}), 130.9 (2C, C_{quat}), 134.0 (C_{quat}, $^4J_{CF}$ = 2.9 Hz), 139.2 (CH), 165.0 (C_{quat}, $^1J_{CF}$ = 253.5 Hz), 191.7 (C_{quat}, CO).

76) Photoreaction of 9-(*E*)-4-methoxybenzoylethenylanthracene (*E*-40-OMe)

E-40-OMe (65 mg, mmol) in CH_2Cl_2 (2.5 mL) was photoirradiated at λ = 254 nm (peak output) for 60h. After 60h, the TLC showed small amounts of anthracene. Column chromatography of the photolysis mixture on silica gel in CH_2Cl_2-hexane (4:1) gave anthraquinone (**65**, 15 mg) as a pale yellow solid, mp. 283 ^{o}C (Lit. 286 ^{o}C); ν_{max} (KBr/cm^{-1}) 2925, 1676, 1591, 1579, 1333, 1285, 1305, 938, 810, 695; δ_H (400 MHz, $CDCl_3$) 7.70 – 7.77 (4H, m), 8.22 – 8.27 (4H, m); δ_C (100.5 MHz, $CDCl_3$) 127.2 (4C, CH), 133.4 (4C, C_{quat}), 134.1 (4C, CH), 183.2 (2C, C_{quat}, CO) and a mixture of 9-(*E*)- and 9-(*Z*)-4-methoxybenzoylethenylanthracenes (***E*-*Z*-40-OMe**, 40 mg, 1:2.5) with 9-

(*Z*)-4-methoxybenzoylethenylanthracene (slightly impure): ν_{max}(KBr/cm^{-1}) 2927, 1660, 1597, 1259, 1242, 1168, 782, 736; δ_H (400 MHz, CDCl$_3$) 6.59 (2H, d, ^3J = 9.2 Hz), 7.38 – 7.53 (5H, m), 7.64 (2H, d, ^3J = 8.8 Hz), 7.82 (1H, d, ^3J = 12.0 Hz, ^4J = 0.8 Hz), 7.92 – 7.94 (2H, m), 8.07 – 8.11 (2H, m), 8.31 (1H, s); δ_C (100.5 MHz, CDCl$_3$) 55.3 (OCH$_3$), 113.7 (2C, CH), 125.0 (CH), 125.5 (4C, CH), 125.7 (2C, CH), 127.0 (CH), 128.7 (2C, CH), 128.7(5) (C$_{quat}$), 130.5 (2C, CH), 130.7 (2C, C$_{quat}$), 131.0 (2C, C$_{quat}$), 131.0(5) (C$_{quat}$), 138.5 (CH), 163.0 (C$_{quat}$), 190.7 (C$_{quat}$, CO). Small amounts of [4+4]-cycloadducts cannot be excluded. However, these could not be isolated.

77) *N*-(methylphenyl)-9-formyl-9,10-dihydro-9,10(4,’5’)-succinimido)-anthracene (49d) Photoreaction

49d (100 mg, 0.25 mmol) was photoirradiated at λ = 254 nm (peak output) in CH$_2$Cl$_2$ (3.5 mL) for 60h. The reaction was monitored after 24h, 48, and 60h by ^{1}H NMR spectroscopy. TLC (CH$_2$Cl$_2$ – hexane 4:1) showed traces of 9-formylanthracene (**37**). Additionally, *N*-(methylphenyl)-9,10-dihydro-9,10(4,’5’)-succinimido)anthracene (**62d**) was observed as the main photoproduct. For comparative purposes, the cycloadduct between anthracene (**16**) and *N*-(4-methylphenyl)maleimide (**48d**) was prepared: A mixture of anthracene (**16**, 56 mg, 0.31 mmol) and *N*-(4-methylphenyl)maleimide (**48d**, 59 mg, 0.31 mmol) was heated to 140 °C for 4h. Then to the cooled solution was given a mixture of hexane and ether (1:1, *v*/*v*, 2 mL). The precipitate formed was filtered, washed with hexane/ether (2 mL) and dried to give **62d** as a colorless solid, mp. 230 °C; ν_{max} (KBr/cm^{-1}) 3022, 2959, 1778 (m), 1704, 1512, 1386, 1182, 1161, 779, 764, 751, 546; δ_H (400 MHz, $CDCl_3$) 2.28 (3H, s, CH_3), 3.36 (2H, bs), 4.88 (2H, bs), 6.37 (2H, d, ^3J = 8.0 Hz), 7.09 (2H, d, ^3J = 7.6 Hz), 7.19 – 7.42 (8H, m); δ_C (100.5 MHz, $CDCl_3$) 21.2 (CH_3), 45.8 (2C, CH), 47.0 (2C, CH), 124.3 (2C, CH), 125.1 (2C, CH), 126.2 (2C, CH), 126.8 (2C, CH), 127.1 (2C, CH), 128.7 (C_{quat}), 129.8 (2C, CH), 138.7 (2C, C_{quat}), 138.9 (C_{quat}), 141.3 (2C, C_{quat}), 176.3 (C_{quat}, CO).

78) *N*-(4-methoxyphenyl)-9-formyl-9,10-dihydro-9,10(4,'5')-succinimido)-anthracene (49e) Photoreaction

49e (100 mg, 0.24 mmol) was photoirradiated at λ = 254 nm (peak output) in CH_2Cl_2 (3.5 mL) for 60h. After 44h, the ratio was 2.05, 9-anthranylcarbaldehyde (**37**) to 7.95 remaining cycloadduct **49e**, according to ^{1}H NMR spectrum of the photolysis mixture. Also, the ratio of 4-methoxyphenylmaleimide (**48e**) produced to cycloadduct was found to be 3 to 7. *N*-4-(Methoxyphenyl)-9-formyl-9,10-dihydro-9,10(4,'5')-succinimido)-anthracene was not found, neither in the ^{1}H NMR nor as determined by TLC. For comparative purposes, the cycloadduct between anthracene and *N*-(4-methoxyphenyl)-maleimide (**62e**) was prepared: A mixture of anthracene (**16**, 178mg, 1.0 mmol) and *N*-(4-methoxyphenyl)maleimide (**48e**, 203mg, 1.0mmol) was heated to 120°C for 14h. Then to the cooled solution was given a mixture of hexane and ether (1:1, *v*/*v*, 2 mL). The precipitate formed was filtered, washed with hexane/ether (2 mL) and dried to give **62e** (346 mg, 91%) as a colorless solid, mp. > 250°C; ν_{max} (KBr/cm^{-1}) 3017, 2955, 2837, 1778 (m), 1702, 1608, 1510, 1464, 1392, 1300, 1198, 1168, 1030, 832, 763, 551; δ_H (400 MHz, $CDCl_3$) 3.34 (2H, bs), 3.74 (3H, s, OCH_3), 4.89 (2H, s), 6.40 (2H, d, ^3J = 8.8 Hz), 6.80 (2H, d, ^3J = 9.2 Hz), 7.19 – 7.25 (4H, m), 7.34 (2H, d, ^3J = 8.8 Hz), 7.42 (2H, d, ^3J = 8.8 Hz) δ_C (100.5 MHz, $CDCl_3$) 45.8 (2C, CH), 47.0 (2C, CH), 55.4 (OCH_3), 114.4 (2C, CH), 123.9 (C_{quat}), 124.4 (2C, CH), 125.1 (2C, CH), 126.8 (2C, CH), 127.1 (2C, CH), 127.6 (2C, CH), 138.8 (2C, C_{quat}), 141.3 (2C, C_{quat}), 159.6 (C_{quat}), 176.4 (2C, C_{quat}, CO). After 60h, the photolysis reaction mixture was subjected to column chromatography on silica gel (CH_2Cl_2 – hexane 4:1) to give 9-formylanthracene (**37**) as a yellow solid; ν_{max} (KBr/cm^{-1}) 1668 (s), 1553, 1250, 1049, 730; δ_H (400 MHz, $CDCl_3$) 7.55 (2H, ddd, ^3J = 8.8 Hz, ^3J = 8.8 Hz, ^4J = 1.2 Hz), 7.68 (1H, dd, ^3J = 8.8 Hz, ^3J = 8.8 Hz, ^4J = 1.2 Hz), 8.71 (1H, s), 8.07 (2H, dd, ^3J = 8.8 Hz, ^4J = 1.2 Hz), 8.99 (2H, dd, ^3J = 8.8 Hz, ^4J = 1.2 Hz), 11.5 (1H, s, CHO); δ_C (100.5 MHz, $CDCl_3$) 123.5 (2C, CH), 124.7 (C_{quat}), 125.7 (2C, CH), 129.2 (2C, CH), 129.3 (2C, CH), 131.1 (2C, C_{quat}), 135.3 (2C, C_{quat}), 135.3 (CH), 193.0 (CH), *N*-(*p*-methoxyphenyl)-maleimide (**48e**, spectral identification, see above) and starting material **49e**.

79) *N*-(2,5-dimethoxyphenyl)-9-formyl-9,10-dihydro-9,10(4,’5’)-succinimido) anthracene (49f) Photoreaction

49f (100 mg, 0.24 mmol) was photoirradiated at λ = 254 nm (peak output) in CH_2Cl_2 (3.5 mL) for 60h. The reaction mixture was purified by column chromatography to give 9-formylanthracene (**37**) and anthraquinone. No *N*-(2,5-dimethoxyphenyl)-9,10-dihydro-9,10(4,’5’)-succinimido)anthracene (**62f**) as decarbonylation product could be discerned in the reaction. For comparative purposes, the cycloadduct between anthracene (**62**) and *N*-(2,5-dimethoxyphenyl)maleimide (**48f**), **62f**, was prepared: A mixture of anthracene (**16**, 205 mg, 1.08 mmol) and *N*-(2,5-dimethoxyphenyl)maleimide (**48f**, 253 mg, 1.08 mmol) was heated to 120 ^{o}C for 14h.

Then to the cooled solution was given a mixture of hexane and ether (1:1, *v*/*v*, 2 mL). The precipitate formed was filtered, washed with hexane/ether (2 mL) and dried to give **62f** (432 mg, 94%) (rotamers A/B) as a colourless solid; $_{max}$ (KBr/cm^{-1}) for A/B) 3046, 3008, 2962, 2842, 1777 (m), 1716 (s), 1510 (s), 1466, 1378, 1282, 1226, 1197, 1161, 1040, 1019, 973, 807, 757, 722, 616, 555, 534; δ_H (400 MHz, $CDCl_3$) 3.36 (2H, s, A), 3.40 (2H, s, B), 3.59 (3H, s, OCH_3, A/B), 3.67 (3H, s, OCH_3, B), 3,69 (3H, s, OCH_3, A), 4.88 (2H, s, A/B), 5.13 (2H, s, A, arom. H), 6.81 (2H, s, B, arom. H), 6.84 – 7.42 (9H, m, arom H, A/B); δ_C (100.5 MHz, $CDCl_3$) 45.3 (A), 45.9 (B), 47.2 (B), 47.3 (A), 55.7 (B, OCH_3), 55.8 (A, OCH_3), 56.1 (A, OCH_3), 56.4 (B, OCH_3), 113.1 (CH, B), 113.4 (CH, A/B), 114.4 (CH, A), 115.9 (CH, A), 116.6 (CH, B), 120.3 (C_{quat}, B), 120.4 (C_{quat}, A), 124.2 (2C, CH, A), 124.3 (2C, CH, B), 125.2 (2C, CH, A), 125.3 (2C, CH, B), 126.6 (2C, CH, A), 126.8 (2C, CH, B), 126.9 (2C, CH, A/B), 139.1 (2C, C_{quat}, B), 141.2 (2C, C_{quat}, B), 142.1 (2C, C_{quat}, A), 144.0 (2C, C_{quat}, A), 148.8 (C_{quat}, A), 149.0 (C_{quat}, B), 153.1 (C_{quat}, A), 153.4 (C_{quat}, B), 175.5 (2C, NCO, A), 175.9 (2C, NCO, B).

80) Photoreaction of *N*-(4-methylphenyl)-9-(*E*)-4-methylbenzoylethylene-9,10-dihydro-9,10(4,'5')-succinimido)anthracene (*E*-52d-Me)

E-52d-Me (100 mg, 0.2 mmol) was photoirradiated at λ= 254 nm (peak output) in CH_2Cl_2 (3.5 mL) for 60h. The reaction mixture was subjected directly to column chromatography on silica gel (ether/CH_2Cl_2/hexane 1:3:5) to give *N*-(4-methylphenyl)-9-(*Z*)-4-methylbenzoylethylene-9,10-dihydro-9,10(4,'5')-succinimido)anthracene (***Z*-52d-Me**, 45 mg) as colorless crystals; $_{max}$ (KBr/cm^{-1}) 3036, 2922, 2854, 1711, 1667, 1606, 1514, 1457, 1385, 1232, 1178, 1002, 776, 766; δ_H (400 MHz, $CDCl_3$) 2.25 (3H, s, CH_3), 2.40 (3H, s, CH_3), 3.40 (1H, bd, ^3J = 6.4 Hz), 4.87 (1H, d, ^3J = 2.8 Hz), 6.29 (2H, d, ^3J = 8.0 Hz), 7.02 (2H, d, ^3J = 8.0 Hz), 7.12 – 7.28 (5H, m), 7.32 – 7.38 (3H, m), 7.44 (1H, dd, ^3J = 8.4 Hz, ^4J = 1.2 Hz), 7.68 (1H, bs), 7.90 (2H, bd, ^3J = 7.6 Hz)*, and starting material.

(**some H and ^{13}C NMR absorptions may be so broad at rt that they could not be detected*).

81) *N*-(4-methoxyphenyl)-9-(*E*)-benzoylethylene-9,10-dihydro-9,10(4,'5')-succinimido)-anthracene (*E*-52e-H) Photoreaction

E-52e-H (100 mg, 0.19[5] mmol) was photoirradiated at λ = 254 nm (peak output) in CH_2Cl_2 (3.5 mL) for 60h. The reaction mixture was subjected directly to column chromatography on silica gel (CH_2Cl_2) to give *N*-(4-methoxyphenyl)-9-(*Z*)-benzoylethylene-9,10-dihydro-9,10(4,'5')-succinimido)anthracene (***Z*-52e-H**, 43 mg) as an oil; ν_{max} (neat/cm^{-1}) 3064, 2838, 1775 (w), 1721, 1669, 1597, 1457, 1389, 1300, 1177, 1029, 1003, 909, 830, 732, 695, 551; δ_H (400 MHz, $CDCl_3$) 3.41 (bd, *J* = 3.2 Hz), 3.71 (3H, s, OCH_3), 4.88 (1H, d, *J* = 3.2 Hz), 6.32 (2H, d, ^3J = 8.8 Hz), 6.74 (2H, d, ^3J = 8.8 Hz), 7.14 – 7.56 (12H, m), 7.70 (1H, bs), 8.00 (bd, 2H, ^3J = 8.8 Hz)*; δ_C (100.5 MHz, $CDCl_3$) 46.0, 48.3, 55.4, 114.3 (2C, CH), 123.9, 124.2 (CH), 124.4 (broad), 125.5 (CH), 126.7 (broad), 126.8, 127.0 (CH), 127.0(5) (CH), 127.6 (2C, CH), 128.6 (2C, CH), 128.7(5) (broad), 133.0 (CH), 137.9 (CH), 140.0 (broad), 159.5(C_{quat}), 175.7 (C_{quat}, NCO), 176.2 (C_{quat}, NCO), and starting material.

(**some H and ^{13}C NMR absorptions may be so broad at rt that they could not be detected*).

82) *N*-(4-methoxyphenyl)-9-(*E*)-4-methylbenzoylethylene-9,10-dihydro-9,10 (4,'5')-succinimido)-anthracene (*E*-52e-Me) Photoreaction

E-52e-Me (100 mg, 0.19 mmol) was photoirradiated at = 254 nm (peak output) in CH_2Cl_2 (3.5 mL) for 5h. The reaction mixture was subjected directly to column chromatography on silica gel (CH_2Cl_2) to give *N*-(4-methoxyphenyl)-9-(*Z*)-4-methylbenzoylmethylene-9,10-dihydro-9,10(4,'5')-succinimido)anthracene (***Z*-52e-Me**, 45 mg) as an oil; ν_{max} (neat/cm^{-1}) 2959, 2837, 1775(w), 1713, 1666, 1606, 1513, 1457, 1389, 1299, 1252, 1178, 1030, 1002, 907, 830, 767, 747, 728, 551; δ_H (400 MHz, $CDCl_3$) 2.41 (3H, s, CH_3), 3.41 (bd, J = 6.4 Hz), 3.71 (3H, s, OCH_3), 4.88 (1H, d, J = 3.2 Hz), 6.33 (2H, d, ^3J = 8.8 Hz), 6.74 (2H, d, ^3J = 8.8 Hz), 7.14 – 7.39 (10H, m), 7.45 (1H, dd, ^3J = 8.8 Hz, ^4J = 1.2 Hz), 7.69 (1H, bs), 7.91 (bd, 2H, ^3J = 7.2 Hz)*; δ_C (100.5 MHz, $CDCl_3$) 21.7 (CH_3), 46.0, 48.3, 55.4 (OCH_3), 114.3 (2C, CH), 123.9 (C_{quat}), 124.2 (CH), 124.5 (broad), 125.5 (CH), 126.3, 126.7 (broad), 126.9 (CH), 127.0 (CH), 127.6 (2C, CH), 128.9 (broad), 129.3 (2C, CH), 135.5, 140.1 (broad), 143.9, 159.4 (C_{quat}), 175.7 (C_{quat}, NCO), 176.2 (C_{quat}, NCO).

(**some H and ^{13}C NMR absorptions may be so broad at rt that they could not be detected*)

83) *N*-(4-methoxyphenyl)-9-(*Z*)-benzoylethylene-9,10-dihydro-9,10(4,'5')-succinimido)-anthracene Photoirradiation

Z-52e-H (35 mg, 0.069 mmol) was photoirradiated at λ= 254 nm (peak output) in CH_2Cl_2 (3.5 mL) for 14h. A sample was taken after that time. ^{1}H NMR spectroscopy revealed that ***Z*-52e-H** had reverted to a (1:1) mixture of *E*- and *Z*-*N*-(4-methoxyphenyl)-9-benzoylethylene-9,10-dihydro-9,10(4,'5')-succinimido)anthracene (***E*/*Z*-52e-H)**.

84) Photoirradiation of (*E*)-9-[4-methylbenzoylethenyl]-anthacene *E*-40-Me at= 352 nm (peak)

E-40-Me (100 mg, 0.32 mmol) was photoirradiated at λ = 352 nm (peak output, Hitachi FL8BL-B) in CH_2Cl_2 (3 mL) for 5.5h. A sample was taken to reveal a mixture of (*E*)- and (*Z*)-9-[4-methylbenzoylethenyl]anthacene (42:58 ***E*/*Z*-40-Me**) by ^{1}H NMR spectrum (at 400 MHz).

85) Photoirradiation of 9-formylanthracene (37)

37 (100 mg, 0/48[5]) in benzene (3 mL) was photoirradiated using Hitachi FL8BL-B lamps (peak output λ = 352 nm) for 24h. The cooled solution was subjected directly to column chromatography on silica gel (hexane – CH_2Cl_2: 1.5/1) to give **66** (49 mg, 50%) as colourless crystals; ν_{max} (neat/cm^{-1}) 3016, 2822, 2719, 1725, 1475, 1451, 1378, 1122, 1068, 782, 758, 711; δ_H (400 MHz, $CDCl_3$) 5.49 (2H, s, CH), 6.62 (4H, dd, ^3J = 7.2 Hz, ^4J = 1.2 Hz), 7.02 (4H, dd, ^3J = 7.2 Hz, ^4J = 1.6 Hz), 10.1 (2H, s, CHO); δ_C (100.5 MHz, $CDCl_3$) 49.9 (2C, CH), 66.8 (2C, CH), 128.6 (4C, CH), 125.8 (4C, CH), 126.9 (4C, CH), 128.6 (4C, CH), 140.3 (4C, C_{quat}), 143.4 (4C, C_{quat}), 200.1 (2C, CHO) and anthraquinone.

86) Preparation of ethyl 3-anthran-9-ylpropionate (67)

To ethyl-3-anthran-9-ylacrylate (**39-Et**, 276 mg, 1.0 mmol) in toluene (5 mL) is given Pd/C (5 wt%, 80 mg) and acetic acid (142 mg). Thereafter is added $NaBH_4$ (182 mg). After stirring the mixture for a day at room temperature, further acetic acid (71 mg) and $NaBH_4$ (91 mg) are added. The reaction takes time to complete, and the progress is monitored by TLC (toluene), where the starting material shows yellow fluorescence and the product light blue fluorescence. After the reaction is complete, half conc. aq. HCl (1 mL) and water (15 mL) are added to hydrolyse excess $NaBH_4$. The mixture is extracted with CH_2Cl_2 (3 X 25 mL) and the organic phase is dried over anhydrous $MgSO_4$ and concentrated *in vacuo*.

Column chromatography of the residue on silica gel (CH_2Cl_2) gives **67** (230 mg, 85%) as a pale yellow viscous oil*; ν_{max} (neat/cm^{-1}) 1729, 1623, 1446, 1372, 1182, 1158, 1045, 834, 733, 602; δ_H (400 MHz, $CDCl_3$) 1.29 (3H, t, ^3J = 7.6 Hz, CH_3), 2.80 (2H, t, ^3J = 8.4 Hz), 3.97 (2H, t, ^3J = 8.4 Hz), 4.22 (2H, q, OCH_2), 7.48 (2H, m), 7.55 (2H, m), 8.02 (2H, d, ^3J = 8.4 Hz), 8.30 (2H, d, ^3J = 9.2 Hz), 8.37 (1H, s); δ_C (100.5 MHz, $CDCl_3$) 14.3 (CH_3), 23.3 (CH_2), 35.4 (CH_2), 60.7 (OCH_2), 124.0 (2C, CH), 125.0 (2C, CH), 125.9 (2C, CH), 126.4 (CH), 129.3 (2C, CH), 129.5 (2C, C_{quat}), 131.6 (2C, C_{quat}), 132.5 (C_{quat}). *slightly impure with ethyl 3-(9,10-dihydroanthran-9-yl)propionate (**68**).

87) Photoirradiation of ethyl 3-anthran-9-ylpropionate (67)

Ethyl 3-anthran-9-ylpropionate (**67**, 200 mg, 0.72 mmol) in benzene (4 mL) was photoirradiated at λ = 352 nm for 22h. After 22h, colorless crystals had precipitated and were hanging on the reaction tube's walls. The overstanding solution was decanted and the crystals were washed with hexane to give dimer **69** (110 mg, 55%) as a colorless solid; ν_{max} (KBr/cm^{-1}) 3066, 2978, 2924, 1728, 1474, 1449, 1424, 1374, 1301, 1260, 1181, 1082, 1019, 860, 792, 768, 697, 676, 642; δ_H (400 MHz, $CDCl_3$) 1.27 (6H, t, ^3J = 7.2 Hz, 2 CH_3), 2.36 (4H, t, ^3J = 7.6 Hz), 3.05 (4H, t, ^3J = 7.6 Hz), 3.92 (2H, s, CH), 4.19 (4H, q, ^3J = 7.2 Hz, 2 OCH_2), 6.80 – 6.88 (8H, m), 6.90 (4H, d, ^3J = 7.2 Hz, ^4J = 1.6 Hz), 6.94 (4H, d, ^3J = 7.2 Hz, ^4J = 1.2 Hz); δ_C (100.5 MHz, $CDCl_3$) 14.3 (2C, CH_3), 30.6 (2C, CH_2), 31.4 (2C, CH_2), 55.9 (2C, CH), 60.6 (2C, OCH_2), 64.2 (2C, C_{quat}), 125.4(5) (4C, CH), 125.5 (4C, CH), 125.7 (4C, CH), 127.6 (4C, CH), 142.1 (4C, C_{quat}), 143.5 (4C, C_{quat}), 174.0 (2C, CO).

88) 9-[2-(4-Methylphenacyl)ethyl]-anthracene (70-Me)

To 9-[2-(4-methylphenacyl)ethenyl]anthracene (***E*-40-Me**, 322 mg, 1.0 mmol) in toluene (5 mL) is given Pd/C (5 wt%, 100 mg) and acetic acid (142 mg). Thereafter is added $NaBH_4$ (182 mg), and the resulting mixture is stirred at room tempreture for 16h. Thereafter, the reaction is filtrated, the filter cake washed with CH_2Cl_2, and the filtrate concentrated *in vacuo*. The residue is subjected to chromatography on silica gel (CH_2Cl_2 – hexane 4 : 1) to give **70-Me** () as a colourless solid; ν_{max} (neat/cm^{-1}) 3050, 1677, 1606, 1445, 1408, 1347, 1290, 1180, 970, 732; δ_H (400 MHz, $CDCl_3$) 7.23 (2H, d, ^3J = 8.8 Hz), 7.46 – 7.54 (4H, m), 7.86 (2H, d, ^3J = 8.0 Hz), 8.03 (2H, dd, ^3J = 7.6 Hz, ^4J = 1.2 Hz), 8.28 (2H, d, ^3J = 8.8 Hz), 8.38 (1H, s); δ_C (100.5 MHz, $CDCl_3$) 21.7 (CH_3), 22.1 (CH_2), 39.6 (CH_2), 124.0 (2C, CH), 125.0 (2C, CH), 125.9 (2C, CH), 126.1 (CH), 128.2 (2C, CH), 129.3 (2C, CH), 129.4 (2C, CH), 129.5 (2C, C_{quat}), 131.6 (2C, C_{quat}), 133.5 (C_{quat}), 134.2 (C_{quat}), 144.0 (C_{quat}), 199.0 (C_{quat}, CO).

89) 9-[2-(Phenacyl)-ethyl]anthracene (70-H)

To 9-[2-(Phenacyl)ethenyl]anthracene (***E*-40-H**, 333mg, 1.08 mmol) in toluene (5 mL) is given Pd/C (5 wt%, 104 mg) and acetic acid (150 mg). Thereafter is added $NaBH_4$ (200 mg), and the resulting mixture is stirred at room temperature for 16h. Thereafter, the reaction is filtrated, the filter cake washed with CH_2Cl_2, and the filtrate concentrated *in vacuo*. The residue is subjected to chromatography on silica gel (CH_2Cl_2 – hexane 4 :

1) to give **70-H** (174 mg, 52%) as a colourless solid: ν_{max} (neat/cm^{-1}) 3053, 2926, 1681, 1447, 1348, 1280, 1204, 971, 731, 688; δ_H (400 MHz, CDCl$_3$) 3.46 (2H, t, ^3J = 8.4 Hz), 4.09 (2H, t, ^3J = 8.4 Hz), 7.41 – 7.53 (7H, m), 7.96 (2H, d, ^3J = 7.2 Hz), 8.03 (2H, d, ^3J = 8.0 Hz), 8.27 (2H, d, ^3J = 8.8 Hz), 8.39 (1H, s); δ_C (100.5 MHz, CDCl$_3$) 22.0 (CH$_2$), 39.7 (CH$_2$), 124.0 (2C, CH), 125.0 (2C, CH), 125.9 (2C, CH), 126.2 (CH), 126.3 (CH), 128.1 (2C, CH), 128.6 (2C, CH), 129.4 (2C, CH), 131.6 (2C, C$_{quat}$), 133.2 (2C, C$_{quat}$), 133.4 (C$_{quat}$), 136.7 (C$_{quat}$), 199.4 (C$_{quat}$, CO).

90) 9-[2-(4-Methoxyphenacyl)-ethyl]-anthracene (70-OMe)

104mg as a colourless solid: ν_{max} (neat/cm^{-1}) 2924, 1671, 1599, 1254, 1207, 1179, 1031, 972, 732; δ_H (400 MHz, CDCl$_3$) 3.40 (2H, t, ^3J = 8.0 Hz), 3.85 (3H, s, OCH$_3$), 4.06 (2H, t, ^3J = 8.0 Hz), 6.90 (2H, d, ^3J = 8.8 Hz), 7.45 – 7.53 (4H, m), 7.93 (2H, d, ^3J = 8.8 Hz), 8.03 (2H, d, ^3J = 8.4 Hz), 8.27 (2H, d, ^3J = 8.8 Hz), 8.38 (1H, s); δ_C (100.5 MHz, CDCl$_3$) 21.1 (CH$_2$), 39.3 (CH$_2$), 55.5 (OCH$_3$), 113.7 (CH), 113.7 (2C, CH), 124.0 (2C, CH), 125.0 (2C, CH), 125.9 (2C, CH), 126.1 (CH), 129.3 (2C, CH), 129.5 (C$_{quat}$), 130.03 (2C, CH), 130.3 (2C, C$_{quat}$), 131.6 (2C, C$_{quat}$), 163.5 (C$_{quat}$), 198.0 (C$_{quat}$, CO).

91) Dimer 71-Me

A solution of 9-[2-(4-methylphenacyl)-ethyl]-anthracene (**70-Me**, 111 mg, 0.34 mmol) in benzene (4.5 mL) was photoirradiated at λ = 352 nm for 22h. The reaction mixture was subjected directly to column chromatography on silica gel (CH$_2$Cl$_2$ – hexane 4 : 1) to give dimer **71-Me** as a colorless solid; ν_{max} (KBr/cm^{-1}) 2911, 1680, 1605, 1473, 1451, 1407, 1357, 1182, 812, 775, 679, 643; δ_H (400 MHz, CDCl$_3$) 2.28 (6H, s, 2 CH$_3$), 2.98 (4H, t, ^3J = 7.6 Hz), 3.13 (4H, t, ^3J = 7.6 Hz), 4.00 (2H, s), 6.74 – 6.76 (8H, m), 6.77 –

6.85 (4H, m), 6.89 – 6.91 (4H, m), 7.09 (4H, d, ^3J = 8.4 Hz), 7.67 (4H, d, ^3J = 8.4 Hz); δ_C (100.5 MHz, $CDCl_3$) 21.6 (2C, CH_3), 29.8 (2C, CH_2), 34.9 (2C, CH_2), 56.0 (2C, CH), 64.3 (2C, C_{quat}), 125.5 (4C, CH), 125.6 (4C, CH), 125.7 (4C, CH), 127.7 (4C, CH), 128.1 (4C, CH), 129.2 (4C, CH), 134.4 (2C, C_{quat}), 142.5 (4C, C_{quat}), 143.7 (4C, C_{quat}), 143.9 (2C, C_{quat}), 199.7 (2C, C_{quat}, CO).

92) Dimer 71-H

A solution of 9-[2-(phenacyl)-ethyl]-anthracene (**70-H**, 174 mg, 0.56 mmol) in benzene (5 mL) was photoirradiated at λ = 352 nm for 22h. The reaction mixture was subjected directly to column chromatography on silica gel (CH_2Cl_2 – hexane 4 : 1) to give dimer **71-H** as a colourless solid: ν_{max} (KBr/cm^{-1}) 3065, 2920, 1683, 1474, 1448, 1296, 1203, 780, 738, 690, 640; δ_H (400 MHz, $CDCl_3$) 3.09 (4H, t, ^3J = 8.0 Hz), 3.21 (4H, t, ^3J = 8.0 Hz), 4.07 (2H, s), 6.82 – 6.84 (8H, m), 6.88 – 6.92 (4H, m), 6.96 – 6.98 (4H, m), 7.34 – 7.38 (4H, m), 7.49 (2H, dd, ^3J = 7.4 Hz, ^3J = 7.4 Hz), 7.83 – 7.85 (4H, m); δ_C (100.5 MHz, $CDCl_3$) 29.7 (2C, CH_2), 35.1 (2C, CH_2), 56.0 (2C, CH), 64.3 (2C, C_{quat}), 125.5[5] (4C, CH), 125.6 (4C, CH), 125.7 (4C, CH), 127.8 (4C, CH), 128.0 (4C, CH), 128.5 (4C, CH), 136.8 (2C, C_{quat}), 142.4 (4C, C_{quat}), 143.7 (4C, C_{quat}), 200 (2C, C_{quat}, CO).

93) Dimer 71-OMe

A solution of 9-[2-(4-methoxyphenacyl)-ethyl]-anthracene (**70-OMe**, 100 mg, 0.29[5] mmol) in benzene (5 mL) was photoirradiated at λ = 352 nm for 22h. Afterwards, the solvent was allowed to evaporate at room temperature. The partially solid product was taken up in CH_2Cl_2/hexane (1:1, 8 mL). The remaining solid was filtered to give **71-OMe** (60 mg) as a colourless solid. The supernatant was subjected to column chromatography on silica gel (hexane/CH_2Cl_2/ether 1:1:1) to give further **71-OMe** (18 mg) for a combined yield of 78%; δ_H (400 MHz, $CDCl_3$) 2.93 (4H, t, ^3J = 8.0 Hz), 3.11 (4H, t, ^3J = 8.0 Hz), 3.72 (6H, s, 2 OCH_3), 3.98 (2H, s), 6.71 – 6.75 (8H, m), 6.81 – 6.83(5) (4H, m), 6.86(5) – 6.89 (4H, m), 7.73 (4H, d, ^3J = 9.2 Hz); δ_C (100.5 MHz, $CDCl_3$) 29.9 (2C, CH_2), 34.6 (2C, CH_2), 55.4 (2, OCH_3), 56.0 (2C, CH), 64.3 (2C, C_{quat}), 113.6 (4C, CH), 125.5 (4C, CH), 125.8 (4C, CH), 127.7 (4C, CH), 128.3 (4C, CH), 129.9 (2C, C_{quat}), 130.3 (4C, CH), 142.5 (4C, C_{quat}), 143.7 (4C, C_{quat}), 163.4 (2C, C_{quat}), 198.5 (C_{quat}, CO).

94) UV measurement

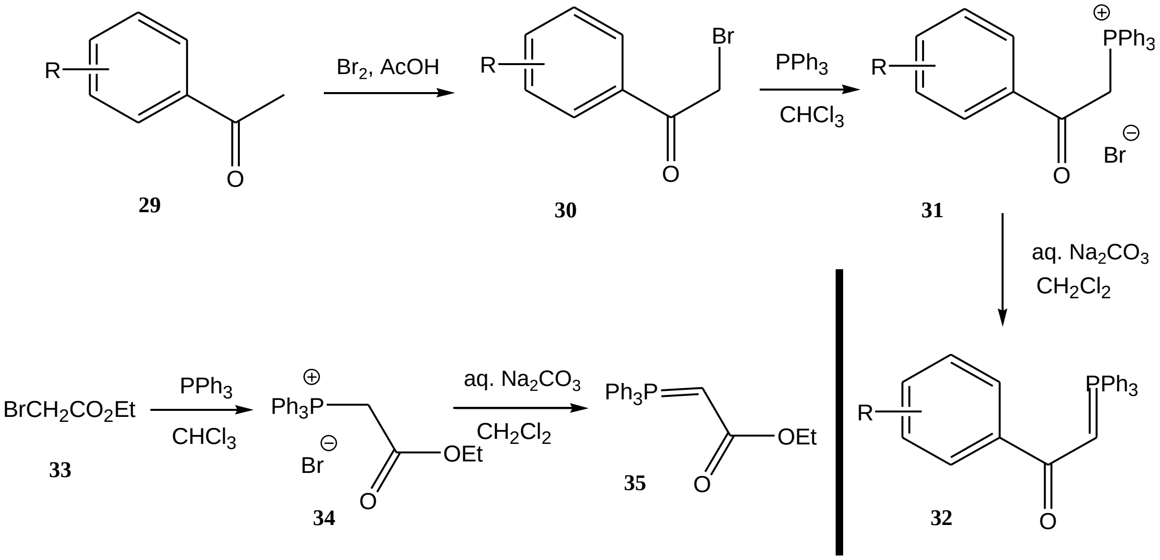
9-(Benzoylcarbonylethenyl)-anthracene (***E*-40-H**, 10.3 mg) was weighed into a 25 mL volumetric flask and acetonitrile was added to the gradation mark. Then, 2 mL of the ensuing solution was pipette into a second 25 mL volumetric flask and acetonitrile was added to the gradation mark. For the measurement, a standard quartz cuvette (1 cm) was used.

Chapter 3: Results and Discussion

3.1. Preparation of anthracenes with pi-substituents at C9

3.1.1 Preparation of the Phosphoranes

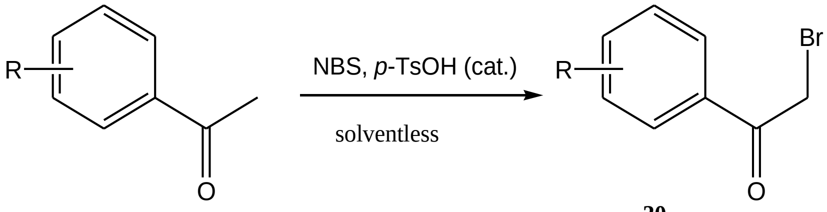
The phosphoranes for the subsequent Wittig-olefination reactions were prepared from α–bromoketones (e.g., substituted phenacyl bromides **30**) or from ethyl bromoacetate (**33**) by S_N-reaction with triphenylphosphine (PPh_3) in $CHCl_3$ as solvent, analogous to known procedures (Ramirez 1957) as shown in Scheme 16.



Scheme 16:Preparation of stabilized phosphoranes 32 and 35

Ethyl bromoacetate (**33**) was acquired commercially, but the phenacyl bromides **30** had to be prepared. Initially, they were made by reaction the corresponding acetophenones with bromine in acetic acid. The by-product of the reactions is hydrogen bromide (HBr). This and the fact that the phenacyl bromides are lachrymators make the work-up of the reactions very problematic. Additionally, often the phenacyl bromides are not pure enough for the next step of reaction to the phosphonium bromide, so that the phenacyl bromides have to be purified by column chromatography on silica gel.

Therefore, another synthetic procedure was adopted that is based on the bromination of the α–carbon to a carbonyl function by *N*-bromosuccinimide (NBS). Here, in recent times a lot of research has been carried out (Sreedhar 2007, Tanemura 2003, Meshram 2005). The best procedure, however, was found to be the one forwarded by Pravst et al. (Pravst et al. 2008), where a solventless melt of NBS and (substituted) acetophenone was heated in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH). The reaction mixtures were simply poured into water and extracted with CH_2Cl_2. After drying the organic extract and evaporating the solvent, the products were pure enough (as determined by ^{1}H NMR spectroscopy) to be used in the following step.



29

30

(adopted from Pravst et al. 2008)

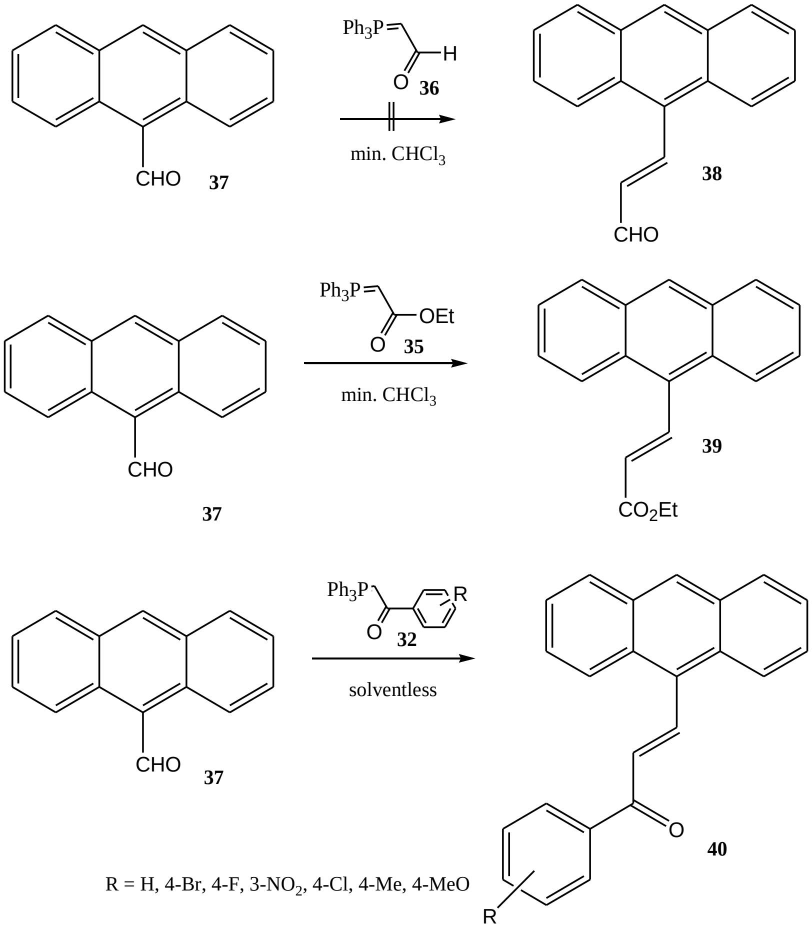
Scheme 17:Solventless halogenation of acetophenones 29 according to Pravst

The substituted acetophenones themselves were partly bought, partly prepared by acylation of the arenes such as of anisol (CH_3COCl, $AlCl_3$) (M. al Sulaibi 2011). For both the reaction of ethyl bromoacetate as well as of the phenacyl bromides with triphenylphosphine, the corresponding phosphonium bromides were isolated by precipitation from the reaction mixture by the addition of ether. The phosphonium bromides were converted to the phosphoranes by stirring the phosphonium bromides in a 10 wt% aq. Na_2CO_3 solution. The phosphoranes were crystallized.

3.1.2. Wittig reaction of 9-anthranylcarbaldehyde

9-Anthranylcarbaldehyde reacts with ethoxycarbonylmethylidenetriphenyl phosphorane in a minimum amount of $CHCl_3$ or even under solventless conditions. As the two benzo-units of the anthranyl system are thought to pose some steric hindrance in the transition state of the Wittig olefination it is good to maximize the concentration of both partners. Solventless Wittig reactions or Wittig reactions run with a minimum of $CHCl_3$ as solvent usually produce the olfination products in good yield, especially when run with stabilized phosphoranes (Thiemann, 2004; 2006; 2007). However, 9-anthranylcarbaldehyde could not be reacted with formylmethylidenetriphenyl-phosphorane in $CHCl_3$ or in higher-boiling solvents, where the temperature needed for any reaction to occur resulted in the decomposition of the phosphorane, even when the reaction was carried out under nitrogen.

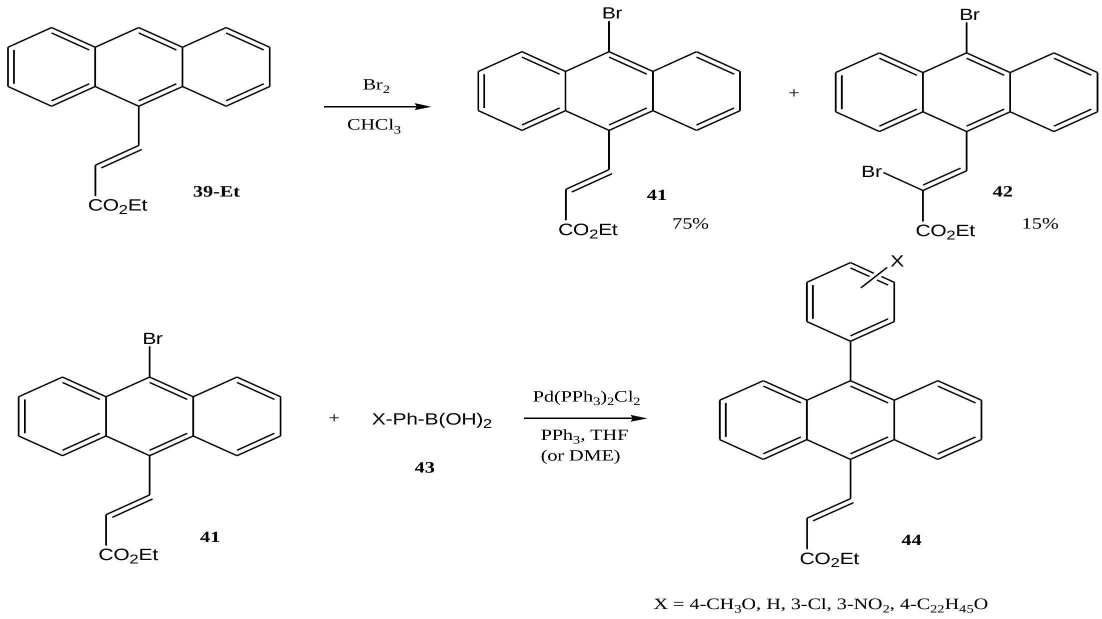
Phenacylmethylidenetriphenylphosphoranes **32** react also with **35** under solventless conditions at 140^{o}C, in reaction times of 3-4h. Again, these reactions are run in air. Initially, the Wittig reaction of 9-anthranylcarbaldehyde and 4-fluorophenylcarbonylmethylidenetriphenylphosphorane was run in refluxing xylene (about 125^{o}C). After 24h, the reaction seemed not to be complete. Thereafter, the reaction was run solventless. After 24h at 140^{o}C, the reaction was stopped. Monitoring the reaction by TLC proved difficult. Starting material and product behave differently on the TLC with benzene as eluent, with the product having a slightly larger R_f value. At λ= 365 nm, the starting material shows bright yellow fluorescence (under the UV lamp), the product does not. The Wittig olefination products can be purified by column chromatography on silica gel. However, it was also possible to add water to the reaction mixture, extract the mixture with benzene, and crystallize the product selectively from the extract, especially in the case of ethyl 9-anthranylacrylate (**39**) as shown in Scheme 18.



Scheme 18:Wittig olefination of 9-anthranylcarbaldehyde (37)

[*This reaction is stabilized phosphoranes with minimal $CHCl_3$ as solvent or under solventless conditions*]

9-anthranylcarbaldehyde when reacted with ethoxycarbonylmethylidenetripheny phosphorane in very small amounts of $CHCl_3$ at 110°C, the reaction to the Wittig-product is complete after 90 min. In later experiments, **37** and **35** were reacted solventless, where a magnetically stirred mixture of **37** and **35** was heated to 130°C. At 130°C, the mixture produces a melt, and this liquid undergoes Wittig olefination rapidly. No inert atmosphere is used when running the experiment. While such reaction conditions may be seen as a contribution to green chemistry, the easiest way of separating the product from phosphorane, used in slight excess, and triphenylphosphine oxide is by column chromatography with benzene as eluent. It was found that the bromination of ethyl anthranylacrylate (**39**) occurs mainly at C10 of the anthranyl unit, not at the double bond. The two-bromination products **41** and **42** can be separated easily. The ethyl 10-bromoanthranylacrylate **41** can be arylated at the C10 position by a Suzuki Miyaura reaction to give **44** as shown in Scheme 19 (Al Sulaibi 2011; Sadeq 2014).



Scheme 19: Bromination of 39-Et and Suzuki cross-coupling reaction of 41

3.1.3. Photochemistry of 9-Aroylethenylanthracenes at< 300 nm

Initially, crystals of ethyl 3-(9-anthranyl)-acrylate (**39-Et**) and ethyl 3-(9-bromoanthran-10-yl)-acrylate (**41**) were grown for X-ray crystallography (Figures 1 and 2). The X-ray crystal structure of both compounds showed that in the crystal the compounds are too far apart to photoreact (Bugenhagen 2013a, 2013b). A sample of a further compound, 9-(4-chlorobenzoylethenyl)-anthracene (***E*-40-Cl**) was sent to the Department of Inorganic

Chemistry, University of Hamburg for X-ray crystal structural analysis, the results being awaited. While solid state, bond-forming photoreactions of organic molecules are known (Ito 1999), it is unlikely that any of the aroylethenylanthracenes above will undergo photo-induced cycloadditions in the crystal.

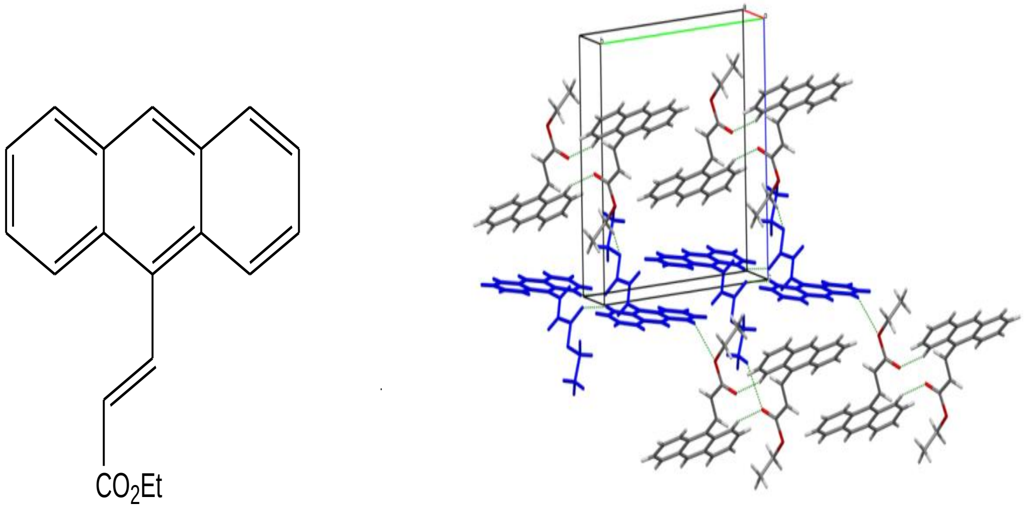


Figure 1: Crystal packing of ethyl 3-(anthran-9-yl)-acrylate (39-Et)

[*Showing intermolecular distances that are too large for photochemical dimerization reactions in the crystal* (Bugenhagen 2013a)]

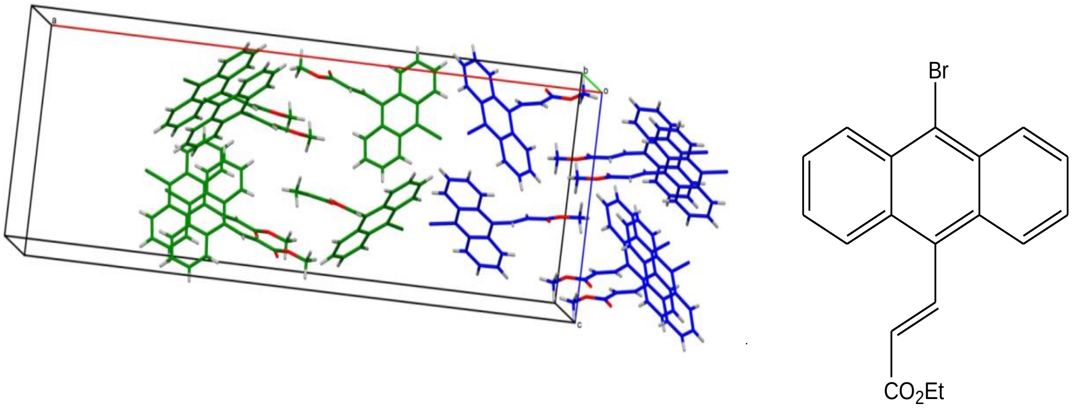
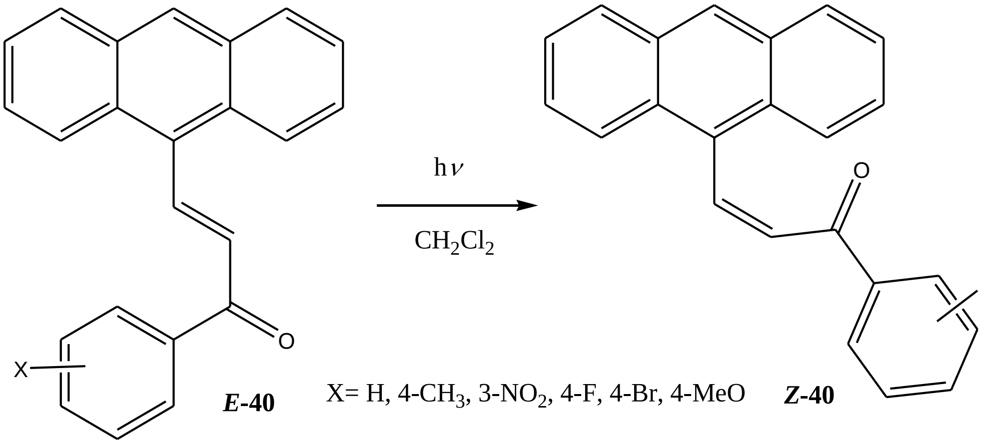


Figure 2: Crystal packing of ethyl 3-(9-bromoanthran-10-yl)-acrylate (41)

[*Showing intermolecular distances that are too large for photochemical dimerization reactions in the crystal* (Bugenhagen 2013b)]

Next step, the ethyl *E*-anthranylacrylate and *E*-aroylethenylanthracenes were photoirradiated as solutions in CH_2Cl_2 using 13 USHIO G8T5 lamps (7.2 W low-pressure mercury arc lamp with a radiation peak at= 253.7nm). It was noted that the *E*-aroylethenylanthracenes upon photoirradiation formed mixtures of close to 1:1 *E*- and *Z*-aroylethenylanthracenes after 24h. In addition, ethyl *E*-anthranylacrylate isomerized under photoirradiation, however, the acrylate showed some polymerization over time. In addition, the photoreaction mixtures of the aroylethenylanthracenes were appreciably dark so that some oligomerisation was occurring.

The *Z*-isomers as photoproducts could be isolated by column chromatography and obtained in a pure state, except for the (*Z*)-4-methoxybenzoylethenylanthracene. Interestingly, the *Z*-isomers **40** elute from the column after than *E*-isomers **40**, which is unusual. The *Z*-isomers **Z-40** was photoirradiated, and again a mixture of *E*-*Z*-isomers was noted. No rearrangement products as described by Becker et al. (Becker 1985b) were noted at this wavelength. In addition, at this short wavelength, no [4+4]-cycloaddition would have been expected, but a [2+2]-cycloaddition could have been possible (Thiemann, 1997).



***E*-40** X= H, 4-CH_3, 3-NO_2, 4-F, 4-Br, 4-MeO ***Z*-40**

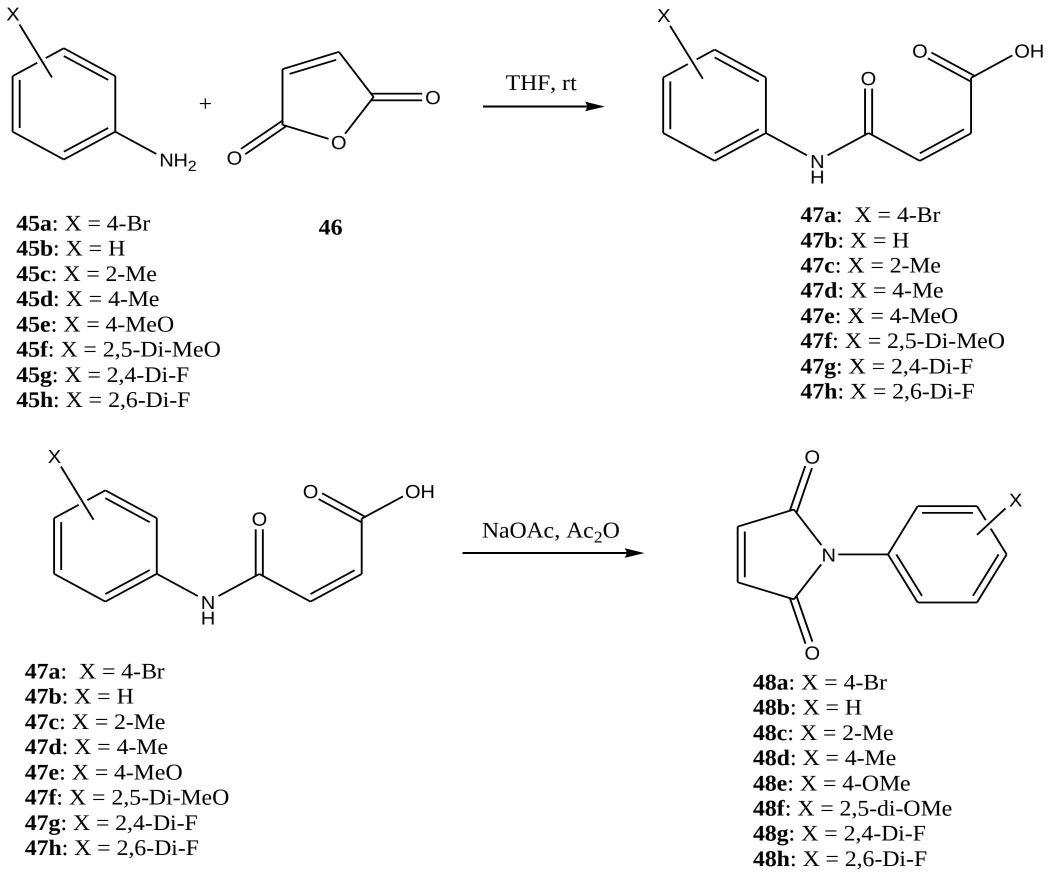
Scheme 20: E-Z-isomerisation of the aroylethyleneanthracene 40 at= 253.7nm

3.2. 9-Aroylethenylanthracenes & 3-Anthran-9-ylacrylates Cycloaddition

Cycloaddition is carried out with maleimides and maleic anhydride

3.2.1. Preparation of *N*-Arylmaleimides

In order to isolate the enone or ene-ester moiety in the molecules for a photoreaction, i.e., for [2+2]-cycloaddition, a [4+2] cycloaddition of the anthracenes with dienophiles was attempted. For this, maleimides **48** had to be prepared. They were synthesized according to a known procedure (Crivello 1976) as shown in Scheme 21.



45a: X = 4-Br
45b: X = H
45c: X = 2-Me
45d: X = 4-Me
45e: X = 4-MeO
45f: X = 2,5-Di-MeO
45g: X = 2,4-Di-F
45h: X = 2,6-Di-F

46

47a: X = 4-Br
47b: X = H
47c: X = 2-Me
47d: X = 4-Me
47e: X = 4-MeO
47f: X = 2,5-Di-MeO
47g: X = 2,4-Di-F
47h: X = 2,6-Di-F

47a: X = 4-Br
47b: X = H
47c: X = 2-Me
47d: X = 4-Me
47e: X = 4-MeO
47f: X = 2,5-Di-MeO
47g: X = 2,4-Di-F
47h: X = 2,6-Di-F

48a: X = 4-Br
48b: X = H
48c: X = 2-Me
48d: X = 4-Me
48e: X = 4-OMe
48f: X = 2,5-di-OMe
48g: X = 2,4-Di-F
48h: X = 2,6-Di-F

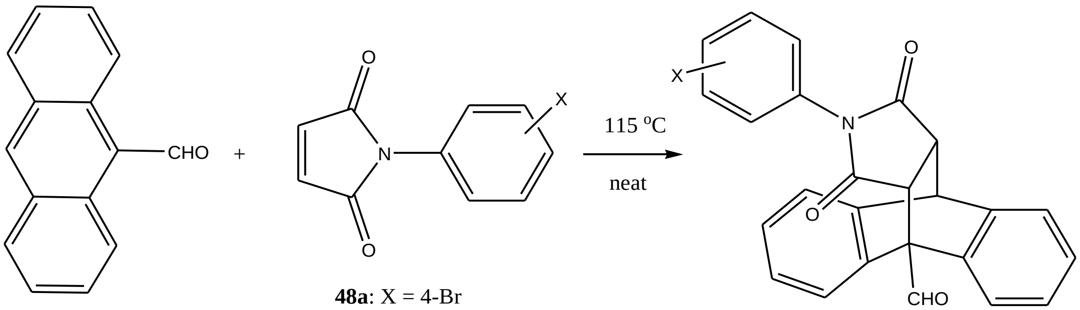
Scheme 21: Synthesis of N-arylmaleimides

Substituted anilines were reacted with maleic anhydride (MSA, **46**) to give the corresponding maleic acid monophenylamides **47**. The reactions were carried out in THF at *Rt*. While most anilines reacted within 90 min., anilines with electron-withdrawing substituents were more sluggish to react. Thus, while 2,4-difluoroaniline (**45g**) still reacted within 90 min. to give the ring opened amide in acceptable yield, 2,6-difluoroaniline (**45h**) did not. Reaction of the maleic acid monoarylamides in hot acetic anhydride in the presence of sodium acetate gave the corresponding maleimides. After the reaction was complete, the reaction mixture was cooled and subsequently added to aq. Na_2CO_3. The maleimides were purified by column chromatography.

3.2.2. Cycloaddition of Anthracenes to Maleimides and Maleic Anhydride

[4+2]-Cycloaddition with substituted anthracenes has been studied (Atherton 2003). As it was not certain whether the vinyl substituent on C9 of the anthracene would have a detrimental effect or would participate in the cycloaddition reaction of the anthracene, at first it was attempted to carry out the Diels-Alder reaction of the anthracene at the stage of the 9-anthranylcarbaldehyde (**37**) (Scheme 22), followed by a Wittig reaction of the carbaldehyde containing cycloadduct **49** as shown in Scheme 23.

9-Anthranylcarbaldehyde (**37**) has been submitted to [4+2]-cycloaddition reactions previously (Meek 1952), although not to cycloaddition reactions with maleimides **48**. In our studies, 9-anthranylcarbaldehyde (**37**) was subjected to solventless Diels Alder reactions at 110-115^{o}C with a number of maleimides **48**. After 13h, the reaction mixtures were cooled and diluted with ether/hexane, whereupon the cycloadducts crystallized. The reactions gave appreciable yields (78% - quant.), and in no instance could a concomitant decarbonylation be observed. Solventless reactions have been used previously in the cycloaddition of anthracenes with liquid mono-activated alkenes such as with alkyl acrylates or propiolates (Meek, 1952; Atherton, 2003), but not with maleimides.



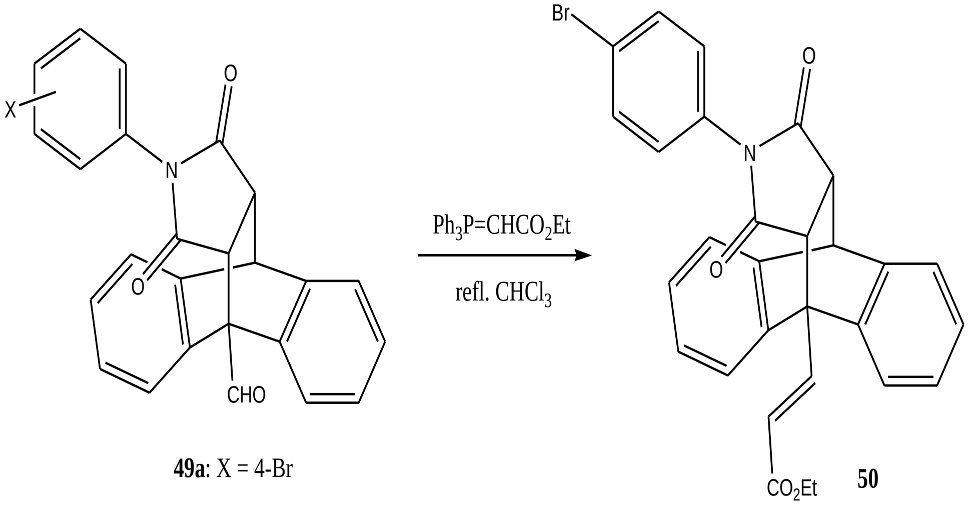
37

48a: X = 4-Br
48b: X = H
48c: X = 2-Me
48d: X = 4-Me
48e: X = 4-OMe
48f: X = 2,5-di-OMe
48g: X = 2,4-di-F
48h: X = 2,6-di-F

49a: X = 4-Br
49b: X = H
49c: X = 2 - Me
49d: X = 4-Me
49e: X = 4-OMe
49f: X = 2,5-di-OMe
49g: X = 2,4-di-F
49h: X = 2,6-di-F

Scheme 22: [4+2]-Cycloaddition of 9-anthranylcarbaldehyde (37) with arylmaleimides 48

The Wittig-olefination of the cycloadducts such as of **49a** with even relatively reactive phosphoranes**,** such as ethoxycarbonylmethylidenetriphenylphosphorane (**35**) necessitates relatively long reaction times. Thus after 90 min. in refluxing chloroform, **49a** produced the Wittig olefination product **50** in only 31% yield as shown in Scheme 23.

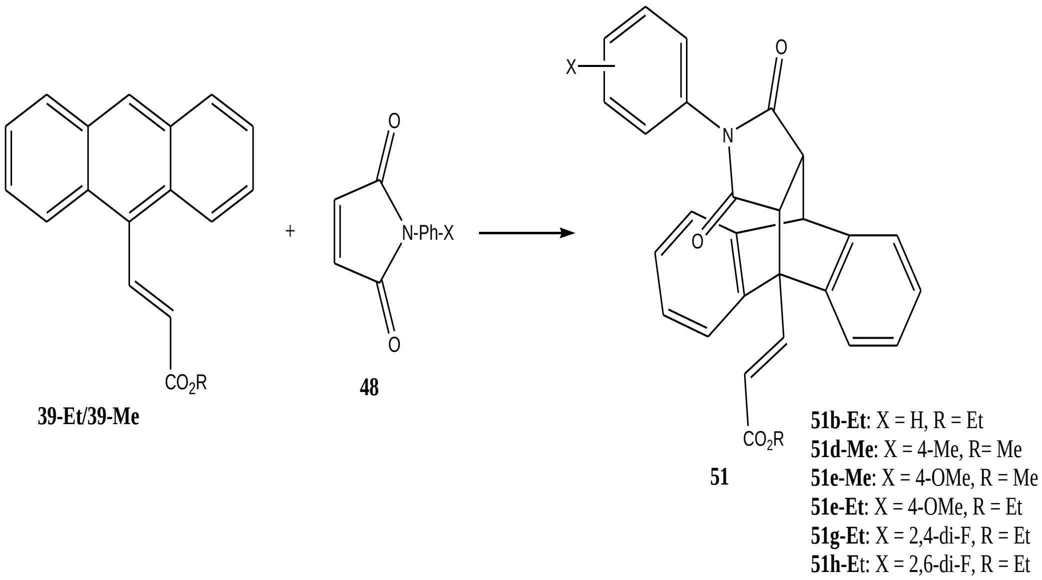


49a: X = 4-Br

50

Scheme 23: Wittig olefination of the cycloadduct 49a

Therefore, it was decided to carry out the Wittig-olefination on anthranylcarbaldehyde first and subsequently subject the acrylates to Diels Alder type reaction. This worked well, where diene **39-Me**/**39-Et** and dienophile **48** were heated under solventless conditions for the Diels Alder reaction to proceed as shown in Scheme 24.



39-Et/39-Me

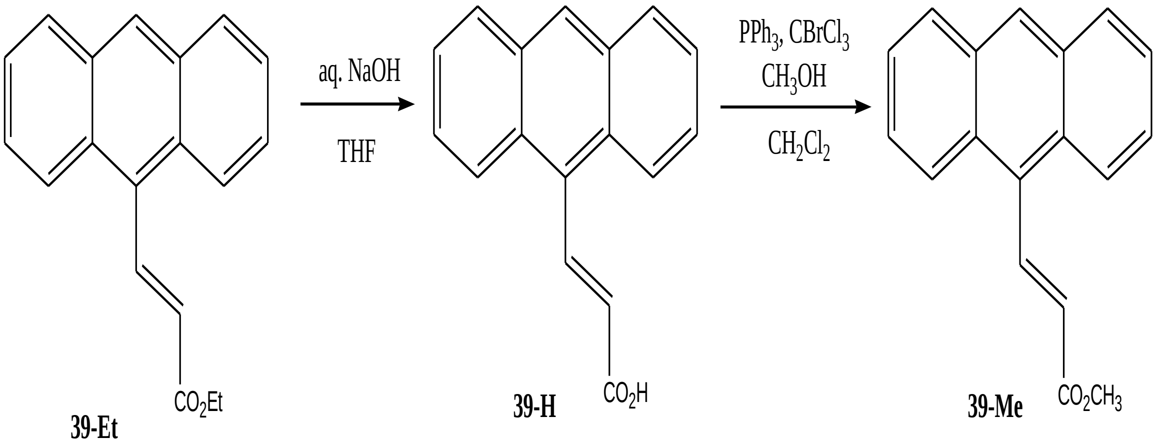
48

51

51b-Et: X = H, R = Et
51d-Me: X = 4-Me, R= Me
51e-Me: X = 4-OMe, R = Me
51e-Et: X = 4-OMe, R = Et
51g-Et: X = 2,4-di-F, R = Et
51h-Et: X = 2,6-di-F, R = Et

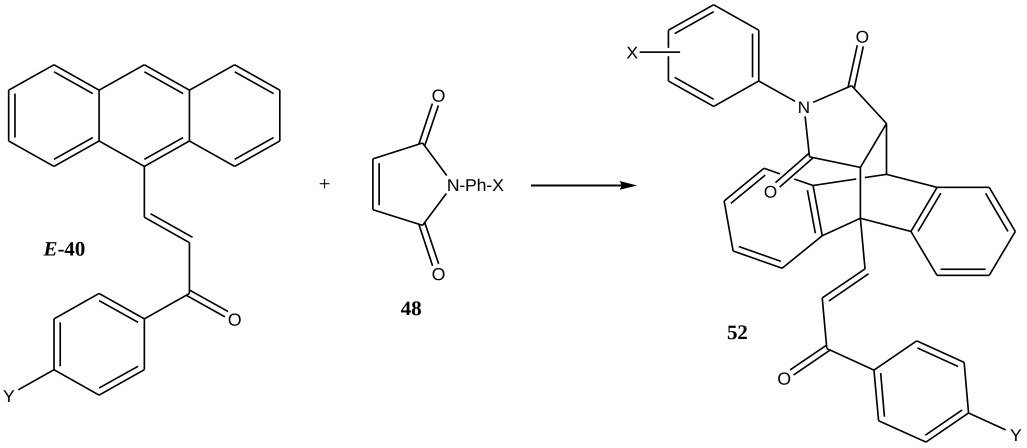
Scheme 24: Diels Alder reaction of anthranylacrylates (39*Et*/39-Me) with maleimides 48

The mixture provided a melt at the reaction temperature of 120^{o}C, which started to solidify as the reaction proceeded. Although the melting-solidification behaviour indicates that the reaction may be completed after 15-20 min., this type of reaction was run for 3-4h. Here, though, larger amounts of starting material were difficult to stir to provide a homogeneous melt, and in these cases, more starting materials remained after the reaction. The reaction product is poorly soluble in DMSO, so the product could not be adequately analysed spectroscopically.



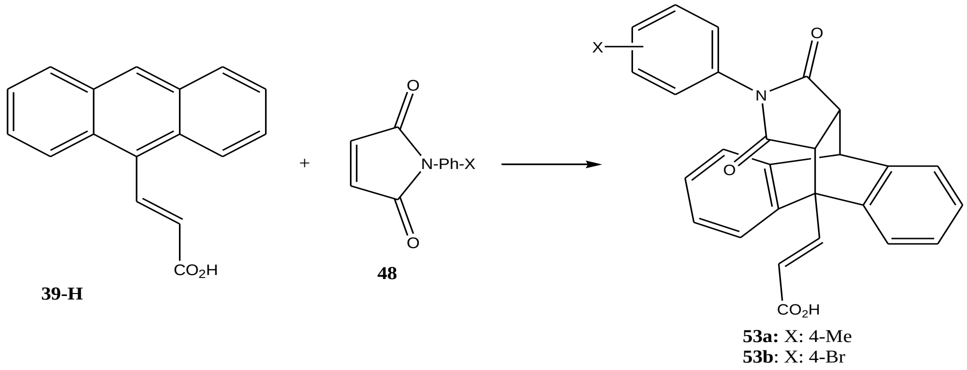
Scheme 25: Trans-esterication of 39-*Et.*

In the case of the 9-aroylethenylanthracenes, the Diels-Alder reactions were carried out in a minimum amount of xylene (usually 0.3 mL-0.5 mL) as shown in Scheme 26. The reactions were carried out in small volume round bottom flasks (5 mL and less), which were stoppered directly. Reflux condensers were not used as it was found that many of the dienophiles (such as 4-methoxyphenylmaleimide and maleic anhydride) were sublimating out of the reaction mixture.



Scheme 26: Diels Alder reaction of aroylethenylanthracenes 40 with maleimides 48

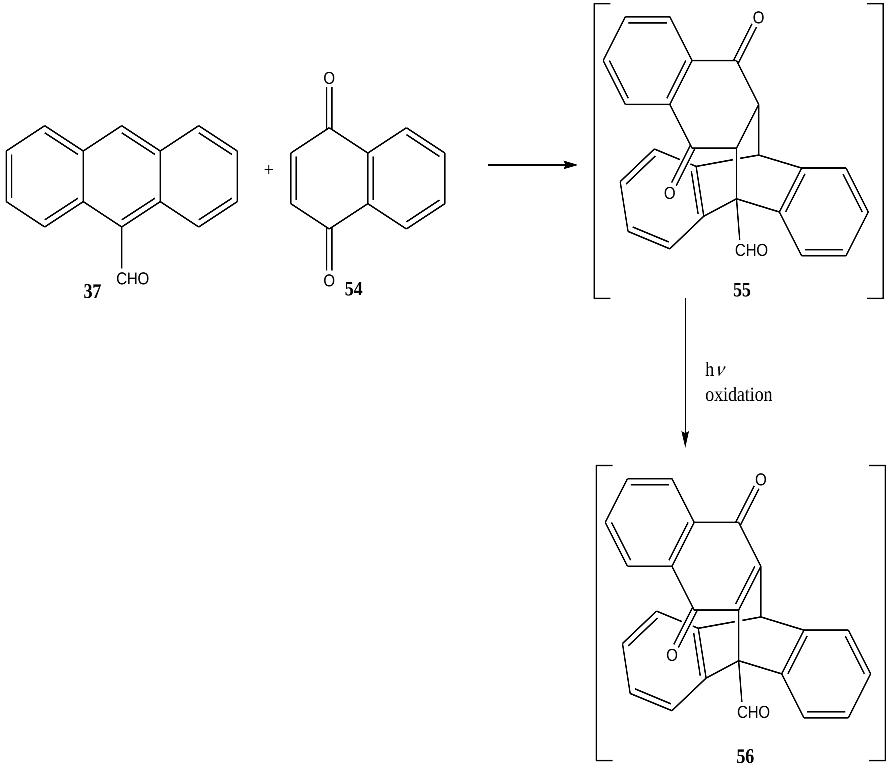
The reaction of anthranylacrylic acid, which is formed from ethyl anthranylacrylate by hydrolysis (aq. NaOH, THF, Scheme 25), and maleimides cannot be carried out solventless at temperatures of 130^{o}C or below, as melts do not form. Rather in these cases, xylene is used as solvent as shown in Scheme 27.



Scheme 27**:** Diels Alder reaction of anthranylacrylic acid 39-H with maleimides 48

Finally, maleic anhydride, diethyl maleate, and diethyl fumarate could be cycloadded to **37**, **39-Et/Me**, and ***E*-40**. In the case of the cycloaddition of naphthoquinone (**54**) to anthranylcarbaldehyde **37,** the photolysis of the primary cycloadduct **55** at λ = 254 nm led to dehydrogenative oxidation to quinoid cycloadduct **56** as shown in Scheme 28.

	LUMO (eV)	HOMO (eV)



Scheme 28: Diels-Alder reaction

[*Reaction of anthranylcarbaldehyde with naphthoquinone (**54**) and subsequent photolytic dehydrogenative oxidation to **56***]

Anthranylacrylates and phenacylethenylanthracenes seem to react equally well. The major difference in the reaction being associated with the physical property of the melting point of the starting materials rather than with significantly different electronic characteristics of the starting materials. This can also be viewed from the computational data of HOMO-LUMO of selected vinylanthracenes, where no significant differences in HOMO-LUMO data are discernible when compared the compounds as in Figure 3.

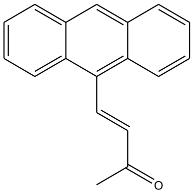
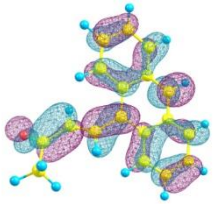
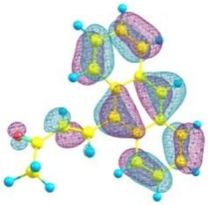
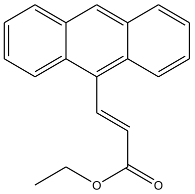
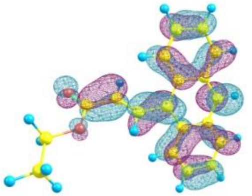
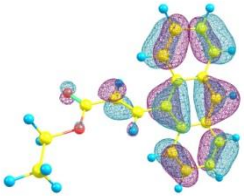
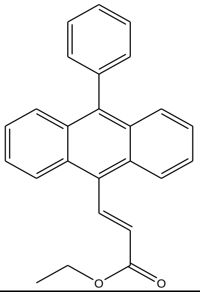
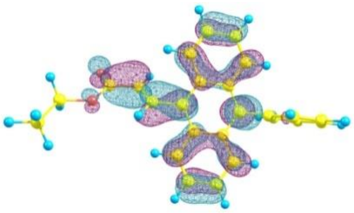
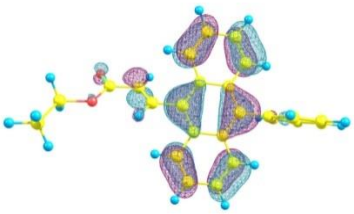
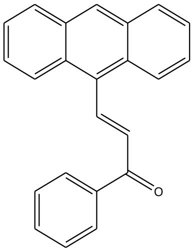
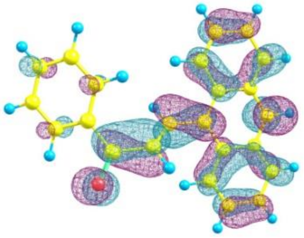
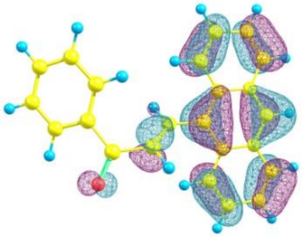
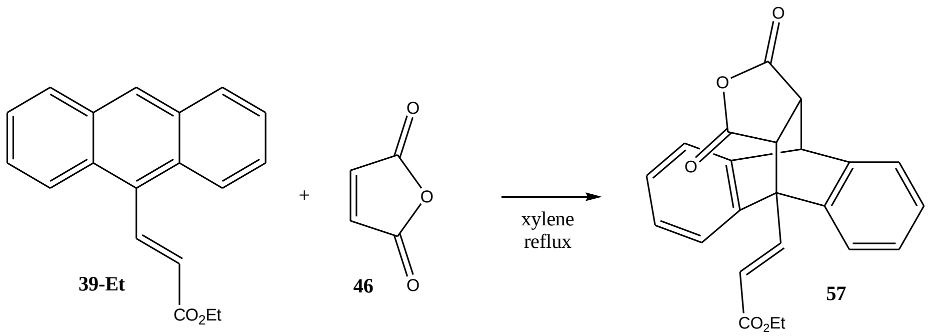
Str1 	-2.17 	-5.39 
Str2 	-2.05 	-5.32 
Str3 	-2.02 	-5.25 
Str4 	-2.12 	-5.33 

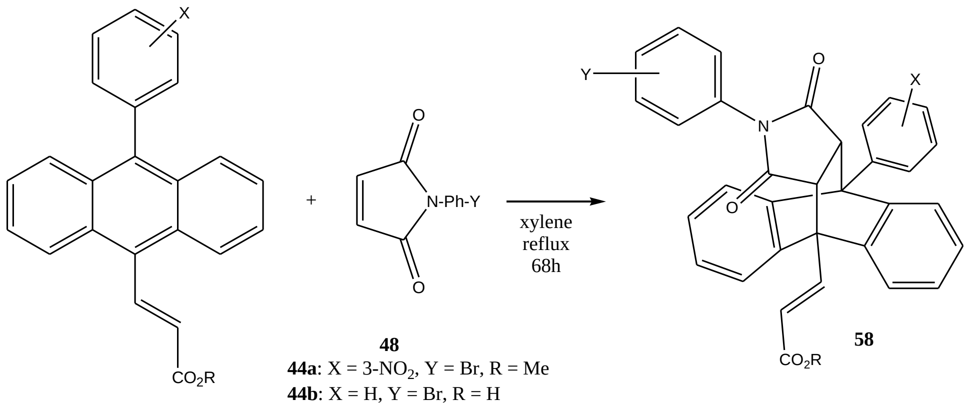
Table 1: Spatial distribution and energies of HOMO-LUMO

It can be seen that the HOMOs and the LUMOs, respectively, for the compounds are similar in energy and spatial distribution. All calculations were performed using the Gaussian 09W C01 program (Gaussian 09). Geometry optimizations for the each molecule were performed without symmetry constraints in the gas-phase using the

B3LYP (Becke 1993, Stephens 1994) hybrid functional and 6-31G(d) basis set. Optimized structures were confirmed to be energy minima through vibrational frequency calculations Orbital energies, iso-surfaces were calculated using the same functional, and basis set.



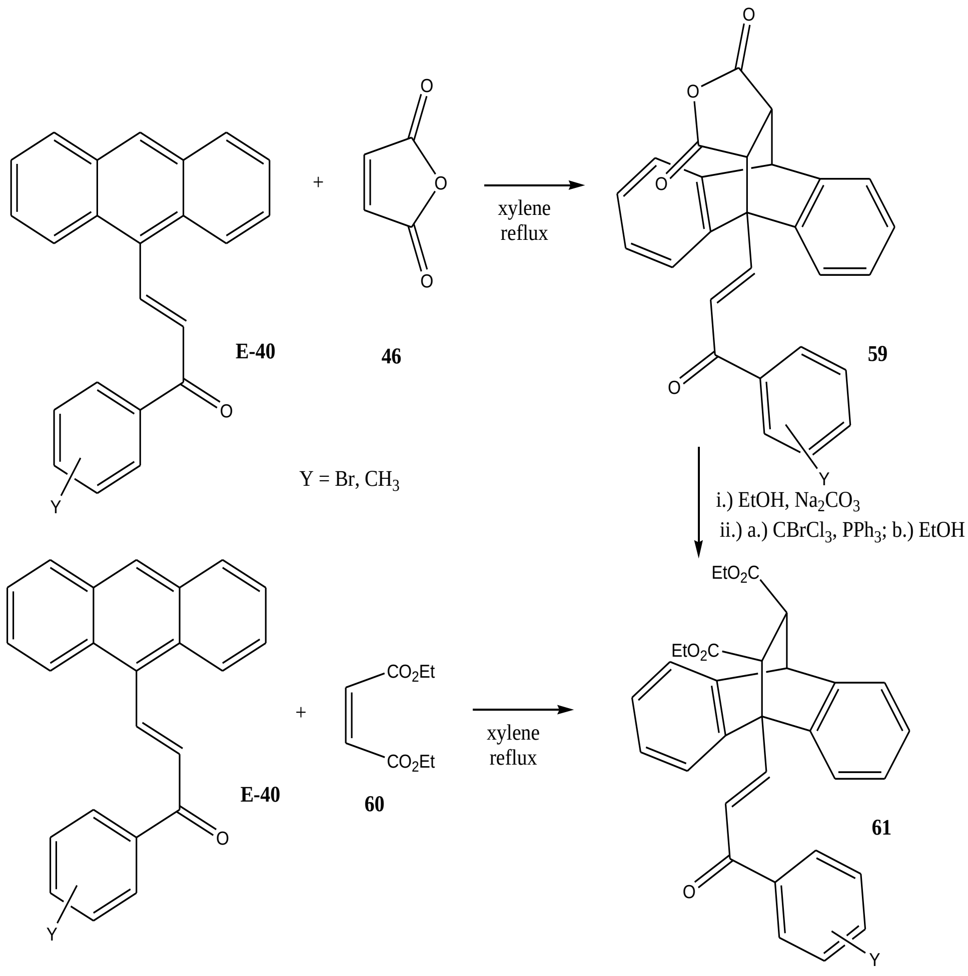
Scheme 29: Ethyl 9-anthranylacrylate (39-Et) cycloadduct with maleic anhydride (MSA, 46)



44a: X = 3-NO_2, Y = Br, R = Me
44b: X = H, Y = Br, R = H
44c: X = 3-NO_2, Y = Br, R = H

58a: X = 3-NO_2, Y = Br, R = Me
58b: X = H, Y = Br, R = H
58c: X = 3-NO_2, Y = Br, R = H

Scheme 30: 10-substituted ethylanthranylacrylates & anthranylacrylic acids cycloaddition



Scheme 31: [4+2]-cycloaddition reactions with E-40, follows reactions on cycloadduct 59

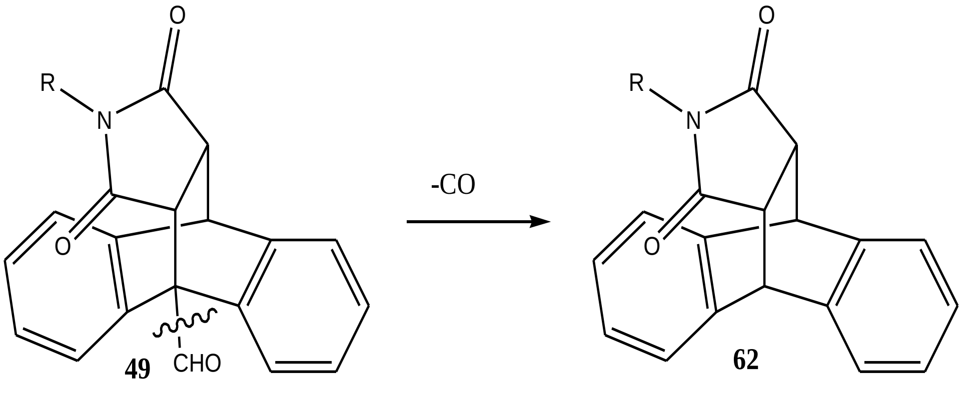
3.2.3. Follow-up Reactions of the Cycloadducts

Follow-up reactions on cycloadducts of maleic anhydride on anthracene itself are known (Gouda 2011). To have **61** in a better yield, it was tried to react ***E*-40** with the more reactive MSA first, then hydrolyse the cycloadduct to the corresponding dicarboxylic acid, and esterify the dicarboxylic acid to **61**. The dicarboxylic acid was found to be very poorly soluble. As the reaction mixture contained still some THF when applied to the column and THF lends solubility to the dicarboxylic acid, it crystallized along the column when the mixture was separated with ether/ethyl acetate 3:1.

The content of ethyl acetate in the eluent was raised accordingly. Nevertheless, even with ethyl acetate alone it took many hours for the substance to vacate the column. Thereafter, ethyl acetate was evaporated at room temperature. During the evaporation process, dicarboxylic acid precipitated readily and lent itself to esterification to **61** ($CBrCl_3$, PPh_3, CH_2Cl_2; ii. EtOH). Overall, the direct cycloaddition of ***E*-40** with diethyl maleate gives the cycloadduct **61** in a better yield (Scheme 31).

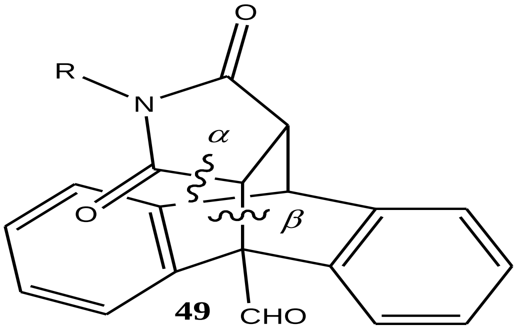
3.2.4. Photochemistry of the Cycloadducts at $\lambda < 300$ nm

An investigation of the photoreactivity of the *N*-(aryl)-9-formyl-9,10-dihydro-9,10(4,’5’)-succinimido)anthracenes was carried out. Cleavage to a carbonyl group would happen (see 1.2.2.), which would lead to a decarbonylation as shown in Scheme 32.



Scheme 32: Expected photochemical -cleavage

Also, a -cleavage to the imido carbonyl or, as the product would be aromatic, a β–cleavage to the formyl group and the imido function could be expected (Figure 4).



49

Figure 3: Possible photochemical and -cleavages

N-(aryl)-9-formyl-9,10-dihydro-9,10(4,’5’)-succinimido)anthracene **49** (100 mg, ca. 0.25 mmol) was dissolved in CH_2Cl_2 (3.5 mL) and the ensuing solution was photoirradiated in a quartz tube for 60h with 13 USHIO G8T5 lamps in a LuzChem photoreactor (7.2 W low pressure mercury arc lamp with a radiation peak at $\lambda = 253.7$ nm), where the reaction was monitored by ^{1}H NMR spectroscopy. The photoreaction of *N*-(methylphenyl)-9-formyl-9,10-dihydro-9,10(4,’5’)-succinimido)anthracene(**49d**) has revealed very little photoreactivity of the cycloadduct. Therefore, slow decarbonylation to *N*-(methylphenyl)-9,10-dihydro-9,10(4,’5’)-succinimido)anthracene (**62d**) occurred.

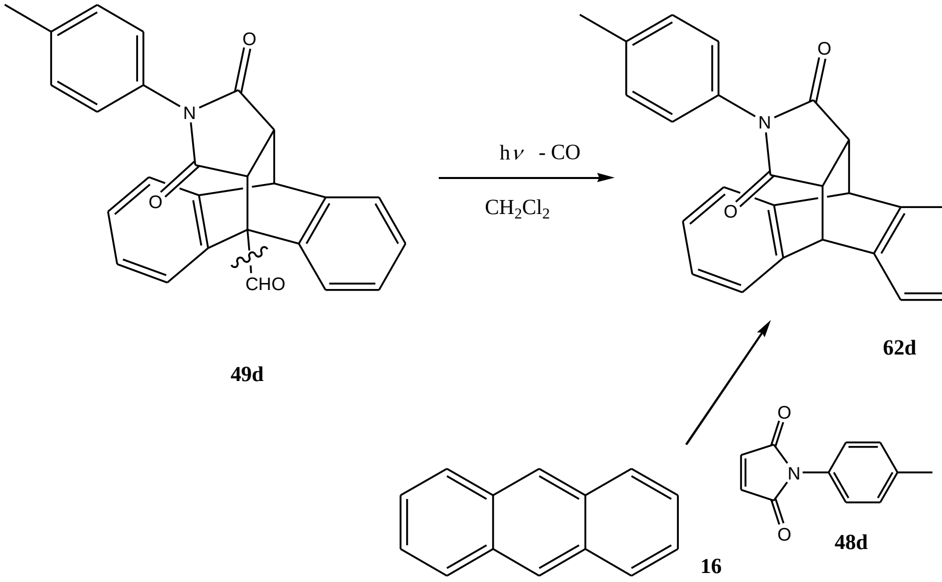
For the comparison, *N*-(methylphenyl)-9,10-dihydro-9,10(4,’5’)-succinimido)-anthracene (**62d**) was produced in an independent way by cycloaddition of *N*-(*p*-methylphenyl)maleimide and anthracene (Scheme 31). By TLC, a trace of 9-

formylanthracene (**37**) was found in the photoreaction, however, the presence of 9-formylanthracene (**37**) could not be shown by ^{1}H NMR spectrum.

A small amount of anthracene could also be identified in the photoreaction mixture. Interestingly, larger amounts of 9,10-anthraquinone could be isolated from the mixture. It may be that the anthraquinone stems from photooxygenation of anthracene, which is a known reaction, though it is mostly seen in the presence of a photocatalyst. Perhaps, anthraquinone is produced directly via the cleavage product of the 9-formylanthracene. The photoreaction of *N*-(4-methoxyphenyl)-9-formyl-9,10-dihydro-9,10(4,'5')-succinimido)anthracene produces 9-formylanthraquinone and *N*-(4-methoxyphenyl)maleimide with a trace of anthracene (Scheme 32). After 60h of photoirradiation, the ratio of 9-formylanthracene to anthracene was 2:1.4 as observed by ^{1}H NMR spectroscopy.

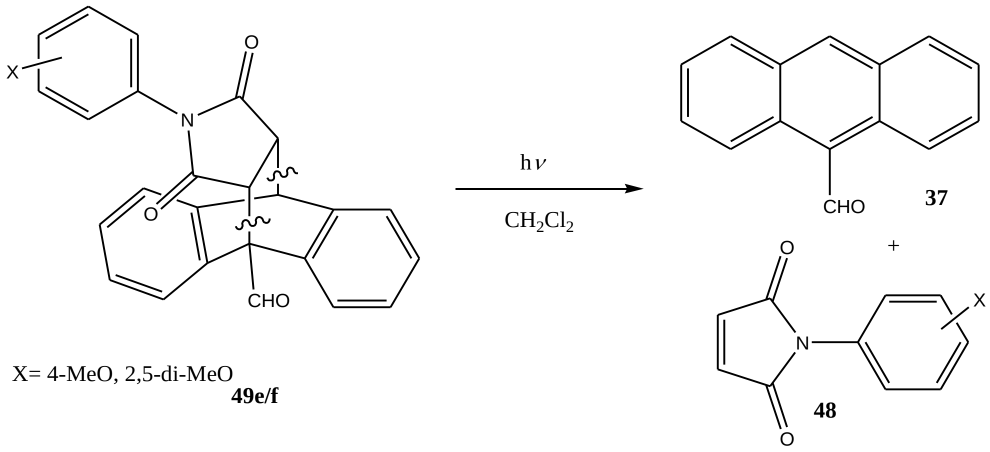
No decarbonylation product could be observed. For comparative purposes, again the decabonylation product, such as *N*-(4-methoxyphenyl)-9,10-dihydro-9,10(4,'5')-succinimido)-anthracene, was produced independently by cycloaddition of *N*-(4-methoxyphenyl)maleimide and anthracene. This retro-cycloaddition of *N*-(aryl)-9,10-dihydro-9,10(4,'5')-succinimido)-anthracenes has been noted recently by Thapaliya et al., who irradiated a series of C9-non-substituted *N*-(aryl)-9,10-dihydro-9,10(4,'5')-succinimido)anthracenes at λ =254nm (Thapaliya, 2014). Equally, the photoreaction of *N*-(2,5-dimethoxyphenyl)-9-formyl-9,10-dihydro-9,10(4,'5')succinimido)anthracene was carried out, which again produced 9-formylanthracene and anthraquinone. Decarbonylation products, *N*-(2,5-dimethoxyphenyl)-9,10-dihydro-9,10(4,'5')-

succinimido)anthracene (**62f**) was not obtained as it was ascertained by preparing **62f** separately from anthracene (**16**) and *N*-(2,5-dimethoxyphenyl)maleimide (**48f**) (Schemes 34 and 35). All the photoreactions were very slow. Additionally, some oligomers were formed and reaction mixtures turned light brown.



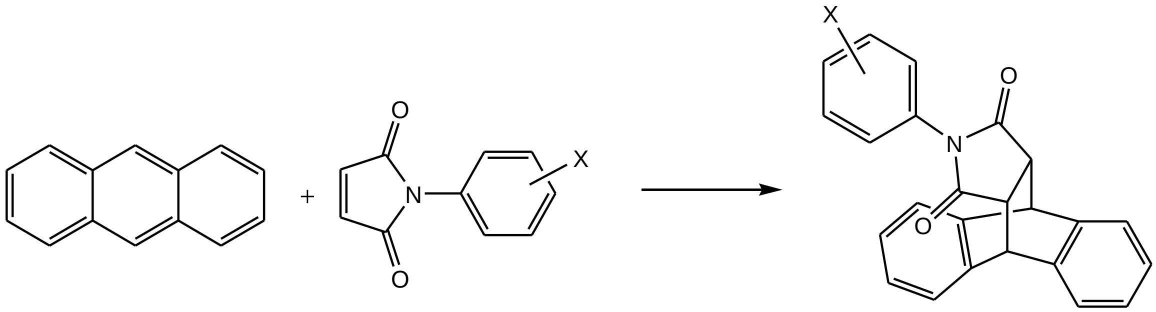
Scheme 33: Photoreaction of cycloadduct 49d at λ = 254 nm

Apart from cycloadduct **62d**, small amounts of *N*-(4-methylphenyl)maleimide, formylanthracene and anthracene, anthraquinone could be detected. For comparative purposes, cycloadduct **62d** was prepared separately from anthracene (**16**) and *N*-(4-methylphenyl)maleimide (**48d**).



Scheme 34: Photoreaction of cycloadducts 49e and 49f at λ = 254 nm.

[*9-Formylanthracene, maleimide, anthracene and anthraquinone were the major products*].



16

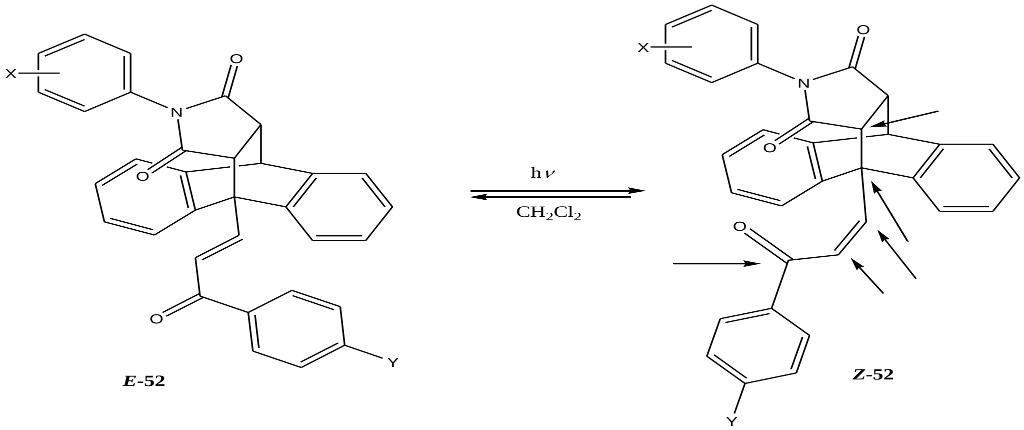
48c (X = 2-Me)
48e (X = 4-MeO)
48f (X = 2,5-di-MeO)

62c (X = 2-Me)
62e (X = 4-MeO)
62f (X= 2,5-di-MeO)

Scheme 35: Preparation of cycloadducts 62 to compare the photochemical reactions of 49.

N-(aryl)-9-(4-substituted)benzoylethenyl-9,10-dihydro-9,10(4,'5')-succinimido)-anthracenes were photoirradiated at λ = 254 nm. The first irradiation of a compound, *N*-(4-methylphenyl)-9-(*E*)-methylbenzoylethylene-9,10-dihydro-9,10-(4,'5')-succinimido)-anthracene, showed a quick accumulation of a new product with the appearance of a double set of methyl groups in the ^{1}H NMR spectrum. The newly formed product could be separated by column chromatography on silica gel (CH_2Cl_2). The ^1H NMR and the ^{13}C NMR spectrum showed a number of broadened peaks.

Initially, that seems indicating a larger ring with a fluctuating structure that could have formed by an intramolecular radicalar double bond addition of a species formed through cleavage β– to the imido function. Because of the relatively few peaks in both ^1H and ^{13}C NMR, no ring structure was found to be matching the spectroscopic data. However, it was seen that the UV irradiation of the separated photoproduct on TLC directly or in CH_2Cl_2 solution formed back the starting material. No photoinduced electrocyclic reaction pathway was evident, so that it was concluded that again **52** undergoes a rapid *E*/*Z*-isomerisation and that the benzoylethenyl substitutent at C-9 undergoes a slow rotation in NMR time. This affects the (dis)appearance of the keto carbonyl function (^{13}C), the ene protons (^1H) and Cs 9 and C4' (^{13}C) (Scheme 36). The samples should be measured at variable temperature, but this has not been done yet.



Scheme 36: E-Z-isomerisation of 52 upon photoirradiation at λ = 254 nm.

[*Arrows indicate disappearing ^1H and ^{13}C NMR peaks due extreme broadening*]

3.2.5. Absorption spectra of 9-aroylethenylanthracenes and 3-anthran-9-ylacrylates at $\lambda > 300$ nm

In benzene, there is a pair of degenerate p-orbitals, π^2 and π^3, forming the HOMOs, and a pair of degenerate orbitals, π^4* and π^5*, forming the LUMOs (M. Hesse et al. 1979a). This leads to four potential transitions from $\pi^{2/3}$ to $\pi^{*4/5}$, namely from the ground state $^1A_{1g}$ to the excited singlet states $^1B_{2u}$, $^1B_{1u}$ and $^1E_{1u}$, where $^1E_{1u}$ is a degenerate state (M. Hesse et al. 1979a). The $^1A_{1g}$ to $^1B_{2u}$ transition corresponds to the α–band (for benzene, λ =256 nm, ε_{max} 204). The $^1A_{1g}$ to $^1B_{1u}$ transition corresponds to the p-band (for benzene, λ = 203 nm, ε_{max}: 7400). The $^1A_{1g}$ to $^1E_{1u}$ transition corresponds to the β–band (184 nm, ε_{max}: 60000). The naming of the transitions is according to Clar, where transitions corresponding to the p-band are in reality symmetry-forbidden (M. Hesse et al. 1979a).

In condensed benzoid aromatic compounds, the highest occupied orbitals, p_{n-1} and p, are no longer degenerate. Also, the lowest unoccupied orbitals, p^*_{n+1} and p^*_{n+2}, are no longer degenerate (M. Hesse et al. 1979b). Between these, four different transitions are possible (see Figure 5). All α–, *p*- and β–bands shift to higher wavelengths with successive annelation steps. In the polyacenes, the p-band overtakes the □-band, which is of low intensity, and overlaps it (M. Hesse et al. 1979b). This also happens in anthracene (Jones 1947). The extinction factors of the bands at long wavelengths increase from the forbidden transition in benzene [λ= 255 nm, ε_{max} 220 ($M^{-1}cm^{-1}$)] to anthracene [λ = 357 nm, ε_{max} 10000 ($M^{-1}cm^{-1}$)]. Some of the measured maxima in the UV absorption spectra of the compounds are given below. The maximum extinction coefficients of the p-bands of our 9-substituted anthracenes lie between 7000 and 10000 ($M^{-1}cm^{-1}$), which would be normal for substituted anthracenes.

No great difference in absorption maxima can be noted in the absorption of the molecules in CH_2Cl_2 and in CH_3CN. No great influence of the aryl substituent at C4 of the aroyl function can be seen. The absorption maximum of the 3-nitro-substituted compound is shifted comparatively to longer wave numbers, which is usual for the nitro-chromophore. There is a great difference in band structure for the *E*- and *Z*-isomer of 4-methylbenzoylethenylanthracene and the absorption maximum, which is shifted to lower wavelength for the *Z*-isomer, indicating less double bond conjugation of the enone structure with the anthranyl unit than it is the case in the *E*-isomer. The cycloadduct with maleic anhydride shows absorption at 340 nm, but with a low extinction (= 560 $M^{-1}cm^{-1}$).

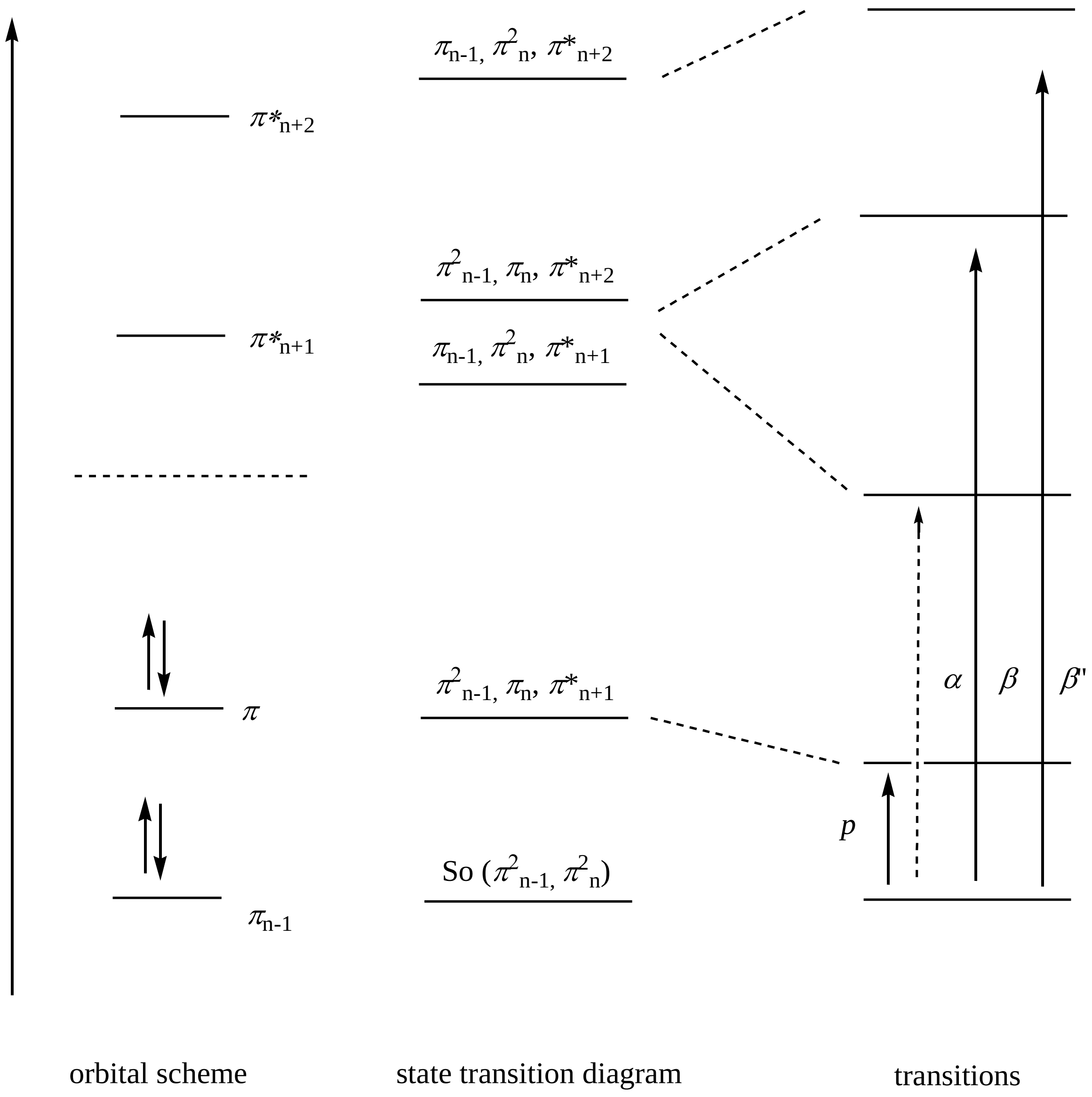
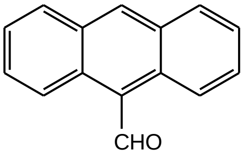


Figure 4: Electron transitions in polyacenes

(*Adopted from Hesse et al. 1979, p. 31*).



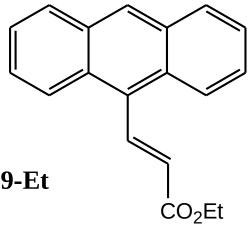
37

λ_{max} [nm] (ε mol^{-1}cm^{-1})

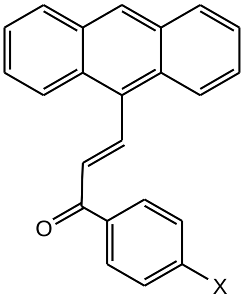
(CH_2Cl_2)	(CH_3CN)
354 (3620)	352 (3300)
370 (6080)	370 (6135)
400 (6680)	400 (6670)
405 (6700)	

λ_{max} [nm] (ε mol^{-1}cm^{-1})

(CH_3CN)	
351 (5545)	358 (4415)
366 (8400)	379 (7410)
385 (10370)	385 (9010)



39-Et

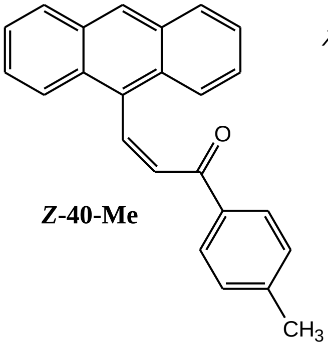


***E*-40**

λ_{max} [nm] (ε mol^{-1}cm^{-1})

X = CH_3	X = OCH_3	X = H	X = Cl	X = Br
351 (4700)	300 (15333)	330 (2750)	350 (4740)	354 (5160)
370 (6688)	305 (15305)	355 (4430)	371 (6160)	370 (6440)
391 (8500)	352 (5350)	371 (6090)	390 (7240)	391 (8100)
405 (8719)	371 (7180)	391 (8330)	410 (7310)	415 (9395)
	391 (9440)	410 (9225)		
	405 (9660)			
(CH_2Cl_2)	(CH_2Cl_2)	(CH_2Cl_2)	(CH_2Cl_2)	(CH_2Cl_2)

X = F	X = CH_3	X = 3-NO_2
351 (4095)	352 (4100)	352 (4435)
369 (5810)	371 (6170)	387 (5760)
391 (8190)	405 (8510)	425(7690)
410 (9490)		
(CH_2Cl_2)	(CH_3CN)	(CH_2Cl_2)

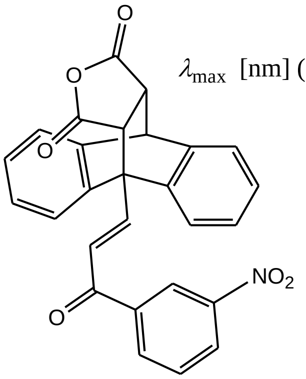


***Z*-40-Me**

λ_{max} [nm] (ε mol^{-1}cm^{-1})

336 (3900)
351 (5700)
370 (7300)
390 (6900)

(CH_2Cl_2)



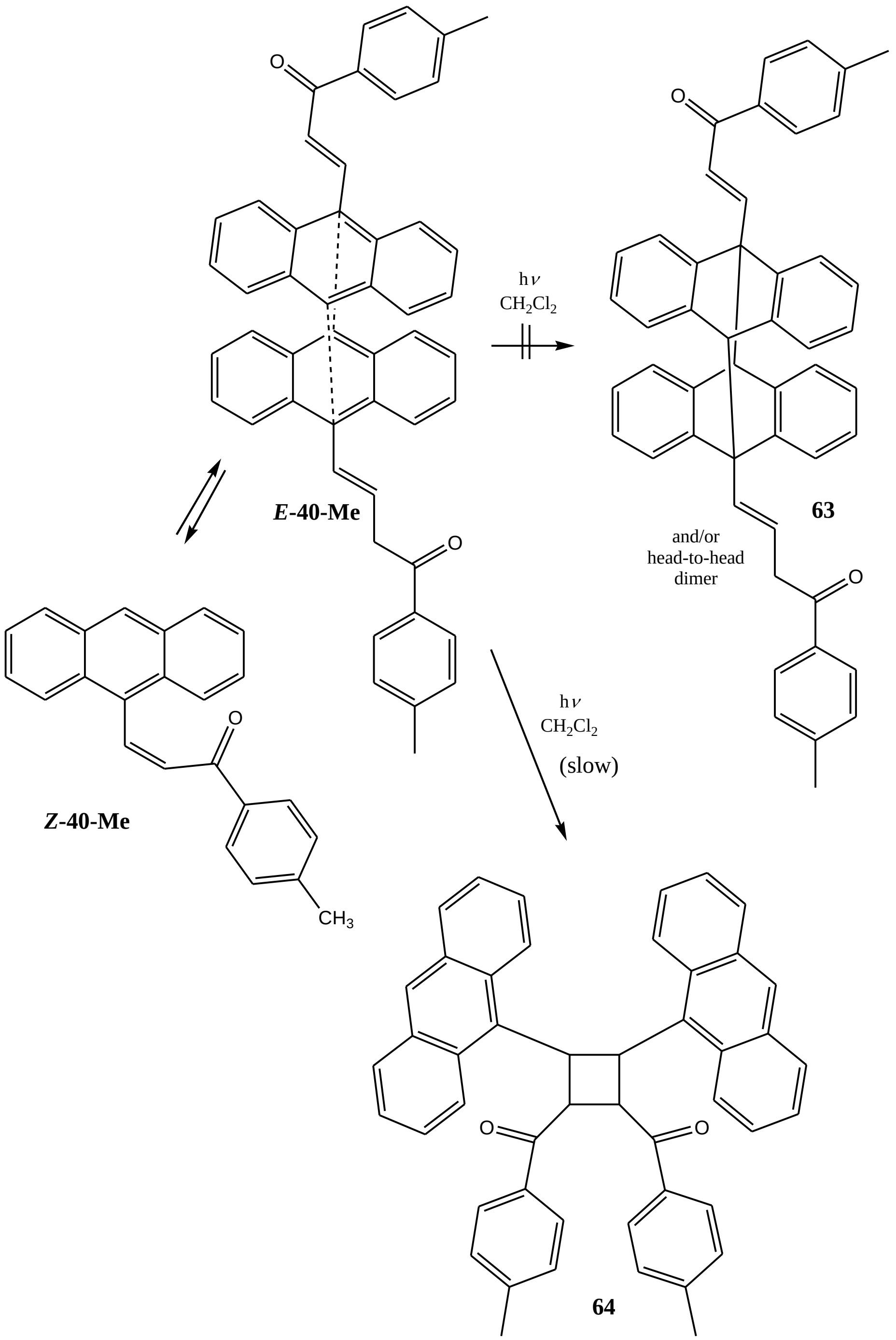
λ_{max} [nm] (ε mol^{-1}cm^{-1})

340 (560)

59-NO_2

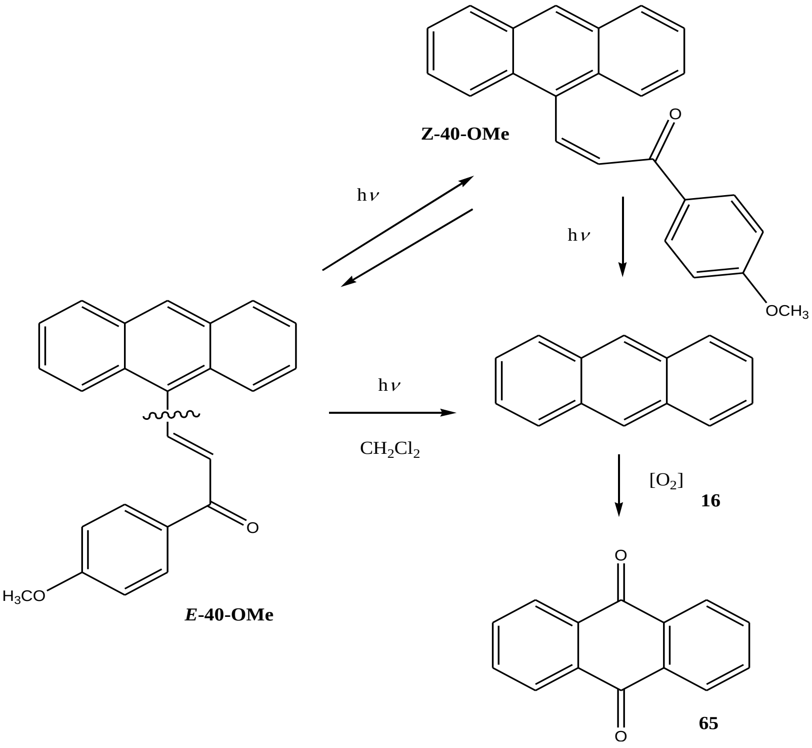
Table 2: UV band maxima of selected compounds in CH2Cl2 and CH3CN

3.2.6. Photochemistry of 9-aroylethenylanthracenes and derivatives at $\lambda > 300$ nm



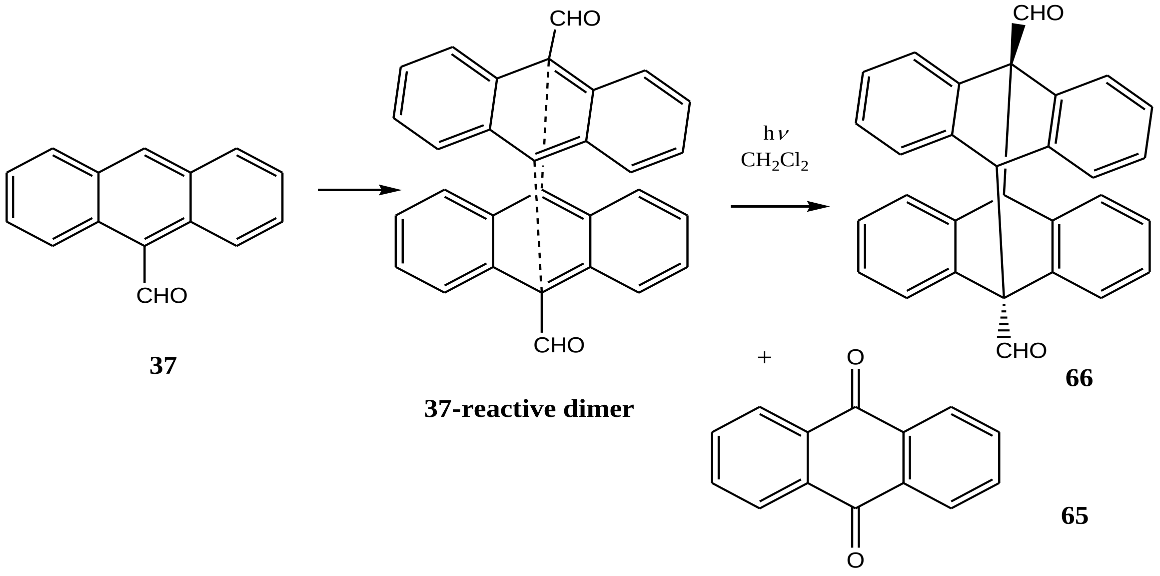
Scheme 37: Slow build-up of two isomers of HH-[2+2]-cycloadducts in aroylethenylanthracene (**E-40-Me**) photoirradiation.
[*The main reaction is shown in Scheme 20*]

Next, 9-(*E*)-aroylethenylanthracenes ***E*-40** were photoirradiated with blacklight UV radiation (λ = 352 nm peak output). In CH_2Cl_2 a rapid conversion to an equilibrium of 9-(*E*)- and 9-(Z)-aroylethenylanthracenes was observed. Additionally, over days, a build-up of two other products was observed. These were characterized by two doublets each in the aliphatic region of the NMR spectrum. Due to their coupling contants, they were attributed to the *cis*- and *trans*-isomers of the head-to-head [2+2]-cycloadduct **64** (Scheme 37). In benzene, the main product in a 3-day photoirradiation in blacklight UV (λ = 352 nm peak output) is anthraquinone (**65**) (Scheme 38).



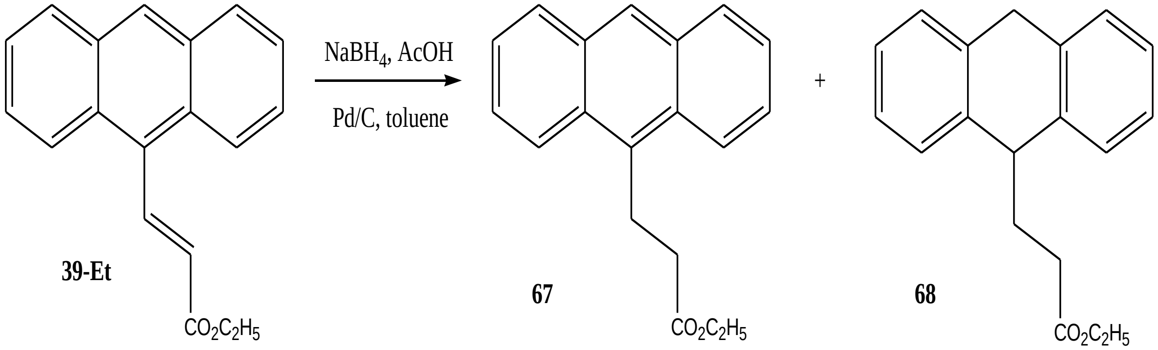
Scheme 38: Aroylethenylanthracene (E-40-OMe) photoirradiation in benzene on blacklight UV

In order to see whether the conditions used above are suitable in general to even reported photo-induced [4+4] cycloaddition reactions, the known photochemical reaction of 9-formylanthracene (**37**) was investigated both in CH_2Cl_2 and in benzene. The photochemical dimerisation proceeds more quickly in benzene than in CH_2Cl_2. It had been reported previously that halogenated solvents such as CCl_4 and bromobenzene (Bowen 1953) are detrimental to the photochemical dimerisation in comparison to THF, ether or toluene. In the present case, in a M solution of 9-formylanthracene (**37**), 50% of dimerizes photolytically within 24h, while under otherwise the same conditions only 25% of 9-formylanthracene (**37**) dimerizes to **66** in CH_2Cl_2 within 48h (Scheme 39). In either case, anthraquinone (**65**) was also produced. The product mixture was separated by column chromatography on silica gel (hexane – CH_2Cl_2: 1.5/1). The colorless dimer eluted first, followed by the yellow starting material and anthraquinone. Only one isomer of the photo-dimer was obtained, both in CH_2Cl_2 and in benzene. This had already been found by Applequist et al. (Applequist 1968) in the photoirradiation of 9-formylanthracene (**37**).



Scheme 39: 9-anthranylanthracene photodimerisation in CH2Cl2 on black light UV light.

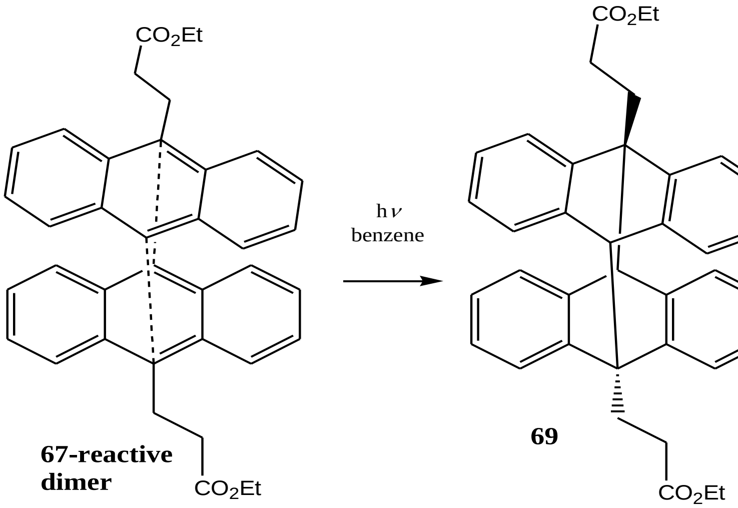
Lastly, ethyl 9-anthranylacrylate (**46-Et**) was hydrogenated to give ethyl 9-anthranylpropionate (**67**). Normal hydrogenation using H_2 gas under Pd/C was not used as this was thought to be too dangerous as there had been a previous, small laboratory fire using H_2 in presence of Pd/C. Here, it was tried to produce hydrogen *in situ* by reacting $NaBH_4$ with AcOH in the presence of Pd/C (Tran 2009, Russo 2011, Al Soom 2015). The double bond hydrogenation took a long time, and partially the anthracene core was also hydrogenated to produce ethyl 9,10-dihydroanthranylpropionate as side product (Scheme 40). The hydrogenation of the central ring system of the anthracene with hydrogen in presence of a Pd-catalyst had been reported previously, with 9,10-diphenylanthracene being reduced over Pd/C (Ma 2010). Driving force of the hydrogenation of the anthranyl moiety is the stability of the two isolated benzo groups, which are found to be more aromatic than the anthranyl unit is.



Scheme 40: Ethyl anthranylacrylate (39-Et) hydrogenation to ethyl anthranyl-propionate(67)

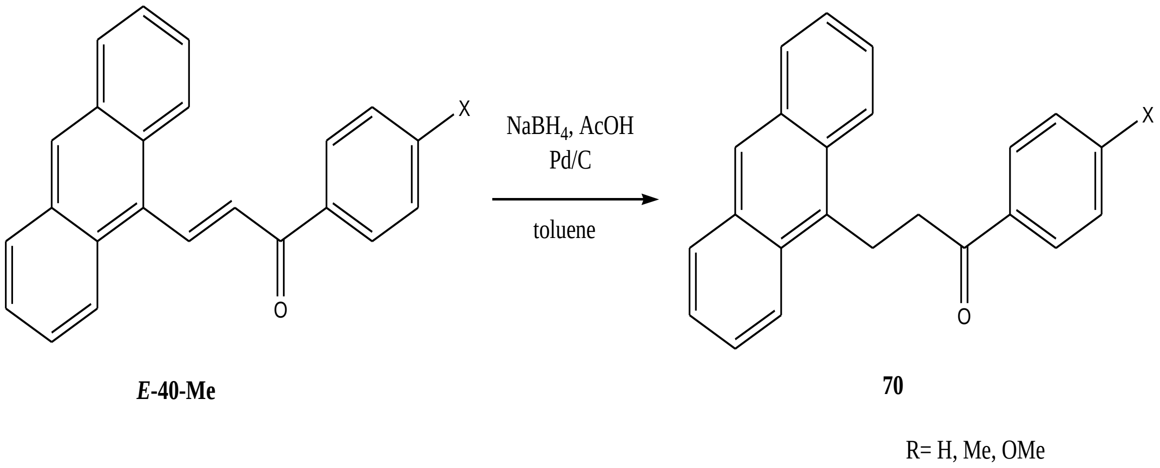
[*This reaction is made by using $NaBH_4$, AcOH, Pd/C as a reagent substitute for H_2, Pd/C*]

The photolysis of ethyl anthranylpropionate (**67**) in benzene using blacklight UV (λ = 352 nm peak output) radiation gave the [4+4]-dimer **69** rapidly (Scheme 41), which crystallized from the solution. A single crystal of the molecule is being prepared.



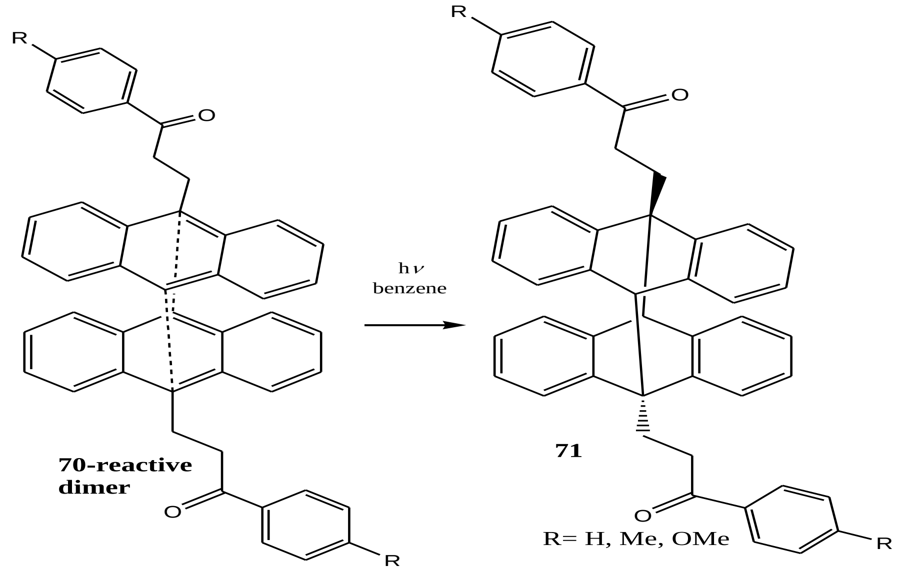
Scheme 41: Photochemical [4+4]-dimerization of ethyl 9-anthranylpropionate (67) using blacklight UV

Therefore, the exchange of an ethenyl substituent to ethanyl substituent changes the photochemical pathway from a purely *E*-*Z*- isomerisation and [2+2]-cycloaddition to a [4+4]-cycloaddition (Becker 1990, Becker 1993).



Scheme 42: (E)-9-(2-phenacylethenyl)anthracenes (E-40) to 9-(2-phenacylethyl)anthracenes

[*This Hydrogenation was made by using* $NaBH_4$*, AcOH, Pd/C as a reagent substitute for* H_2*, Pd/C*]



70-reactive dimer

71

Scheme 43: Photochemical [4+4]-dimerisation of 9-aroylethylanthracenes (70) on blacklight UV.

Chapter 4: Conclusion

9-Anthranylacrylates and 9-benzoylethenylanthracenes could be prepared from 9-anthranylcarbaldehyde by Wittig olefination using minimal amounts of solvent or solventless systems. Both 9-Anthranylacrylates and 9-benzoylethenylanthracenes were found to be good dienes in Diels-Alder reactions, where the dienophiles add exclusively over the C9 and C10 of the anthracene unit. 9-anthranylacrylates *E*-*Z*- isomerizes under photoirradiation at λ= 254 nm. Over longer periods of irradiation, oligomers form as shown by ^{1}H NMR spectroscopy.

In addition, 9-benzoylethenylanthracenes *E*/*Z*- isomerize, but the reactions are much cleaner. The photoirradiation of the cycloadducts of anthranylcarbaldehyde with maleimides leads to a number of products, stemming from decarbonylation, and from overall a Retro Diels-Alder reaction to 9-formylanthracene. Anthracene and anthraquinone can also be found as products. The cycloadducts of 9-aroylethenylanthracenes with maleimides undergo easy *E*-*Z*-isomerisation. According to the ^{1}H and ^{13}C NMR spectra of the compounds, the aroylethenyl substituent performs a rotation in NMR time that broadens peaks of the substituent and of neighboring Cs and Hs considerably.

Irradiated at λ = 352nm, 9-aroylethenylanthracenes again undergo *E*-*Z*-isomerisation. Small amounts of [2+2]-cycloadducts are formed in dichloromethane (CH_2Cl_2). Under the same conditions, 9-formylanthracene was shown to undergo the known [4+4]-cycloadditive dimerisation. When the anthranylacryates are reduced to the anthranylpropionates, these can be used in [4+4]-cycloadditive dimerisations as could be shown for compound **67**, reacting to compound **69**. The exchange of an ethenyl substituent to an ethanyl substituent changes the photochemical pathway from a purely E- Z- isomerisation and [2+2]-cycloaddition to a [4+4]-cycloaddition.

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