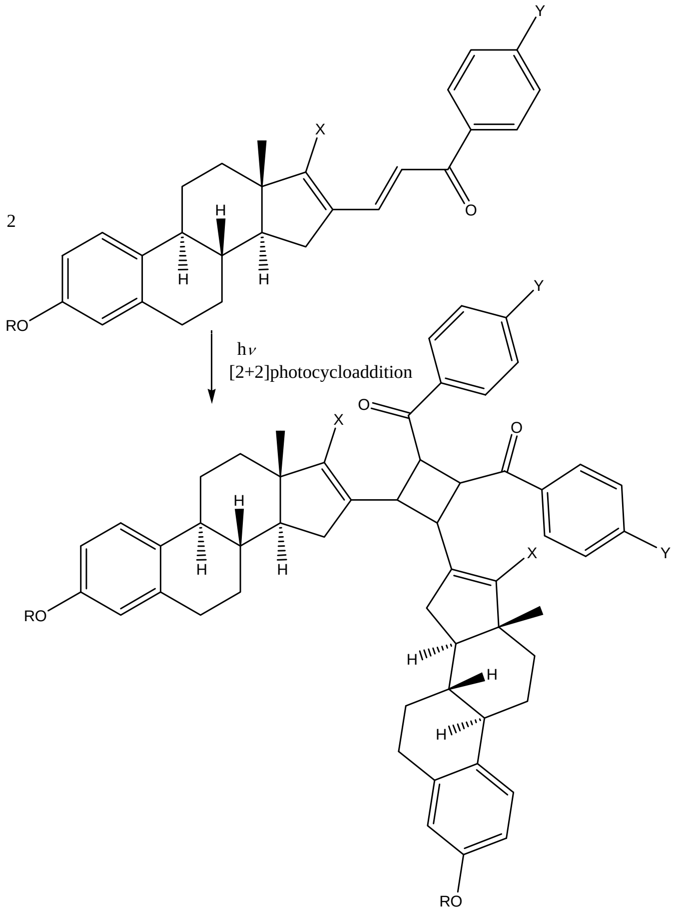
Photochemistry of 9-vinyl substituted anthracenes, of their reduced derivatives and of Diels Alder type adducts of 9-vinylanthracenes with activated dienophiles

Hasnaa Sadeq,[1] Thies Thiemann,[1]* John P Graham,[1] Yosef Al Jasem,[2] Bernhard Bugenhagen,[3]
Nathir Al-Rawashdeh[4]

[1]Department of Chemistry, United Arab Emirates University, Al Ain, Abu Dhabi, United Arab Emirates
[2]Department of Chemical Engineering, United Arab Emirates University, Al Ain, Abu Dhabi, United Arab Emirates
[3]Department of Inorganic Chemistry, University of Hamburg, Hamburg, Germany
[4]Department of Applied Chemical Sciences, Jordan University of Science and Technology, Irbid, Jordan

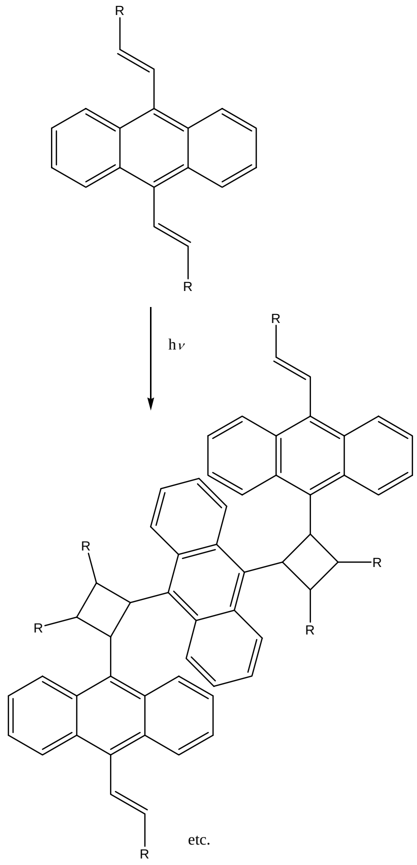
Introduction

[2+2]-Photocycloaddition published previously

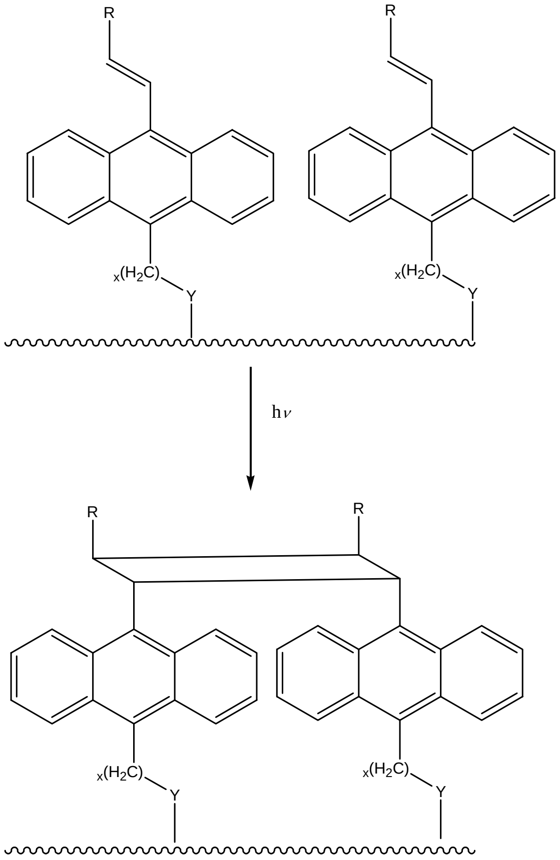


T. Thiemann, C. Thiemann, S. Sasaki, V. Vill, S. Mataka, M. Tashiro,
J. Chem. Res., **1997**, *21*(*S*) 248 - 249; **1997**, *21*(*M*) 1736 - 1750

What could be done, if [2+2]-photocycloaddition of 9-ethenylanthracenes were possible.



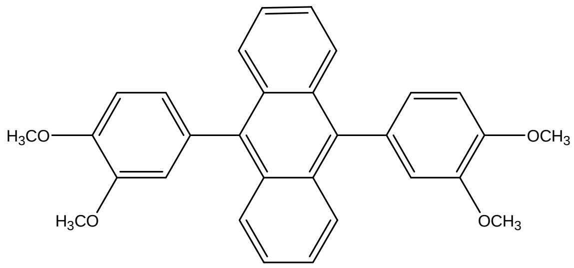
Oligo-/polymerisation of bis(ethenyl)anthracenes

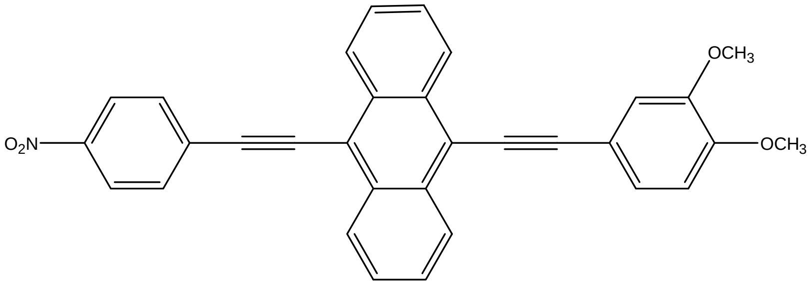


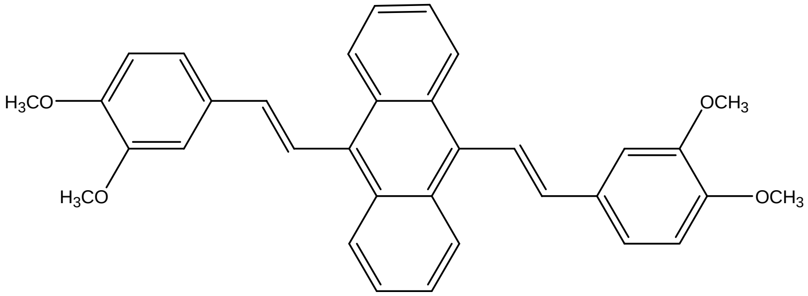
Cross-linking of ethenyl-substituted anthracenes on a solid support

Introduction (continued)

In 2010, A. Marrocchi et al.[1] have studied 9,10-diaryl-, 9,10-diarylethenyl, and 9,10-diarylethynylanthracenes as potential semiconducting materials.



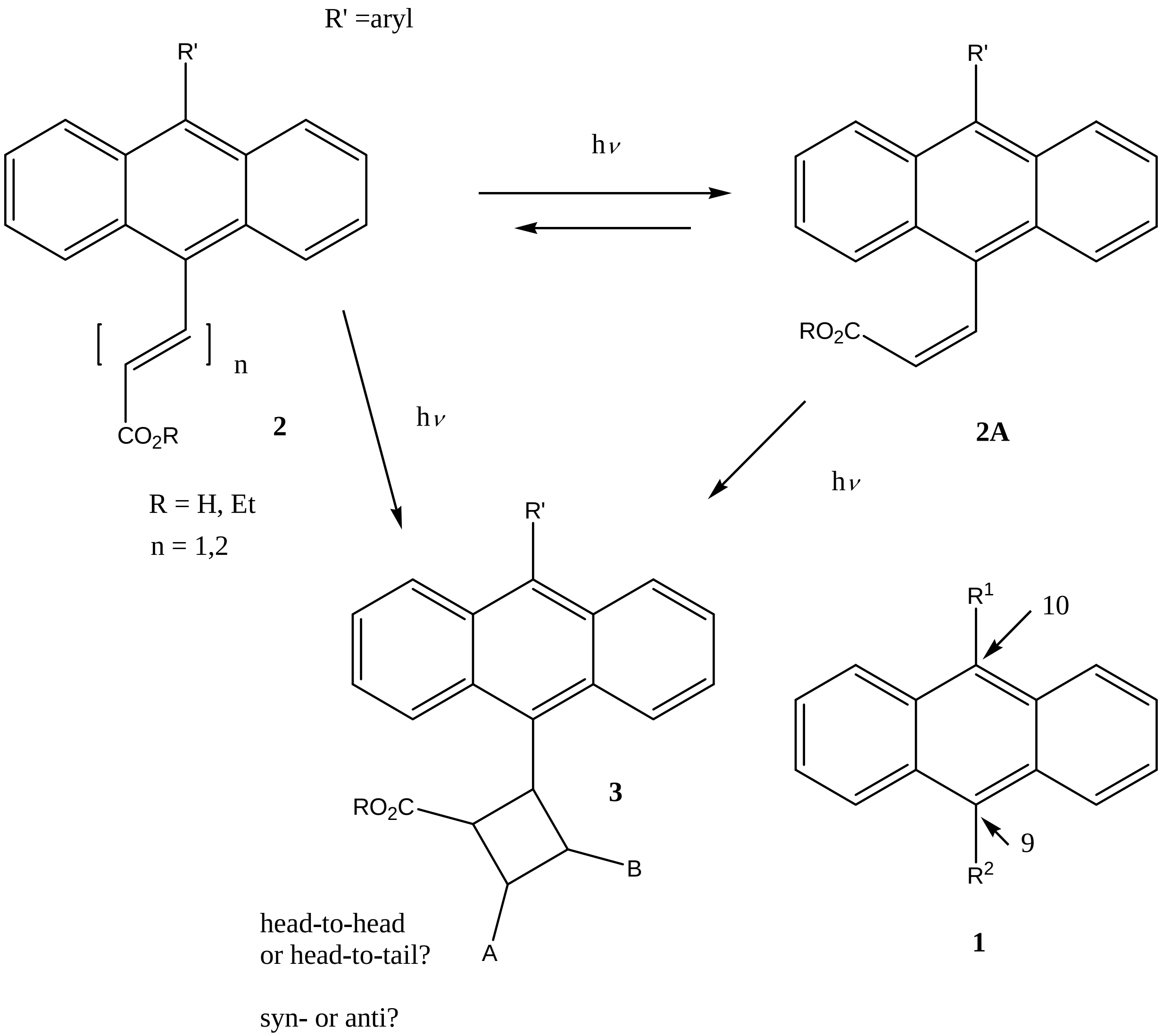




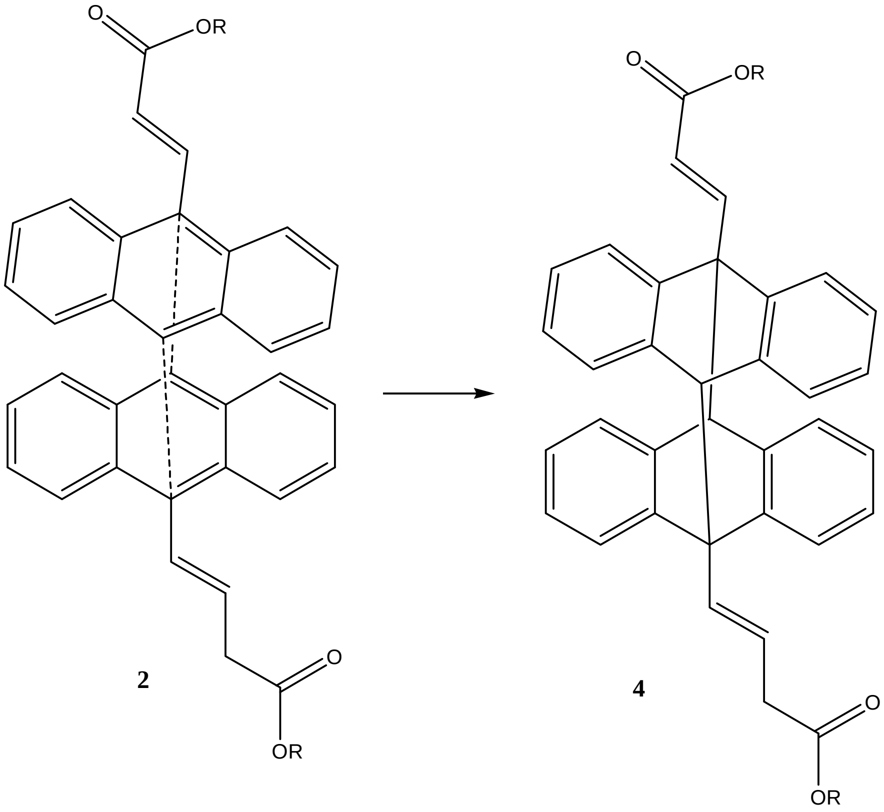
In recent times, 9,10-diaryl and 9,10-diarylethenyl substituted anthracenes have been forwarded as potential constituent molecules in light-harvesting devices for organic solar cell applications.[2]

So, it is of importance to understand whether such 9,10-substituted anthracenes are stable under photoirradiation for a longer time and what type of reactions they could undergo.

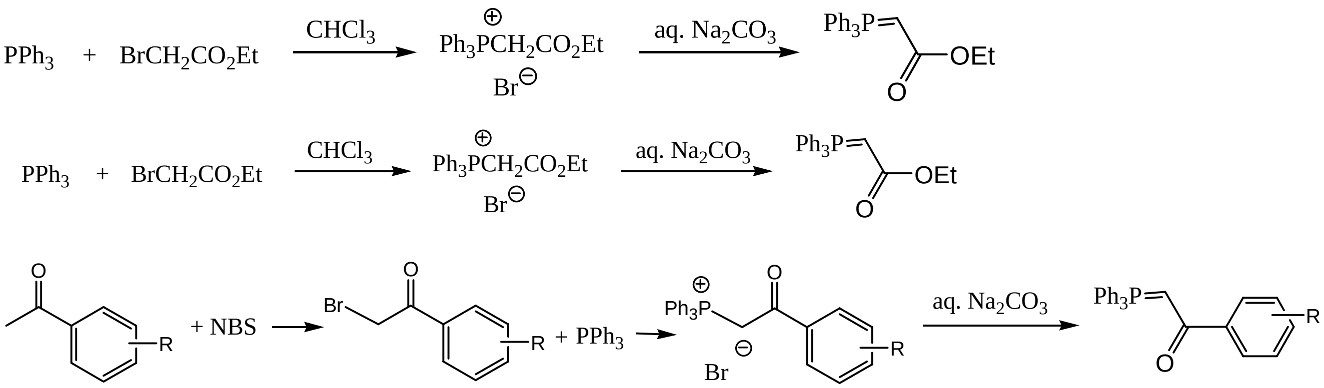
References: 1. A. Marrocchi et al., *J. Photochem. Photobiol.* **2010**, *211*, 162.
2. N. Belghiti et al., *Mat. Environ. Sci.* **2014**, *5*, 2191



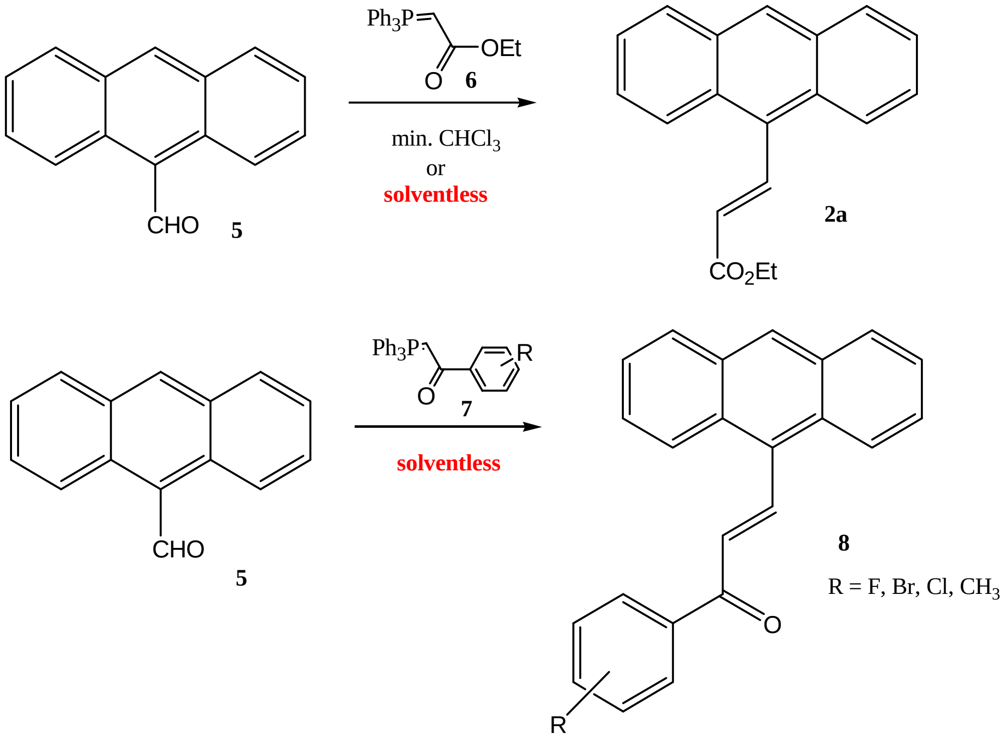
Scheme 1. Possible photodimerisation products of anthranylacrylates



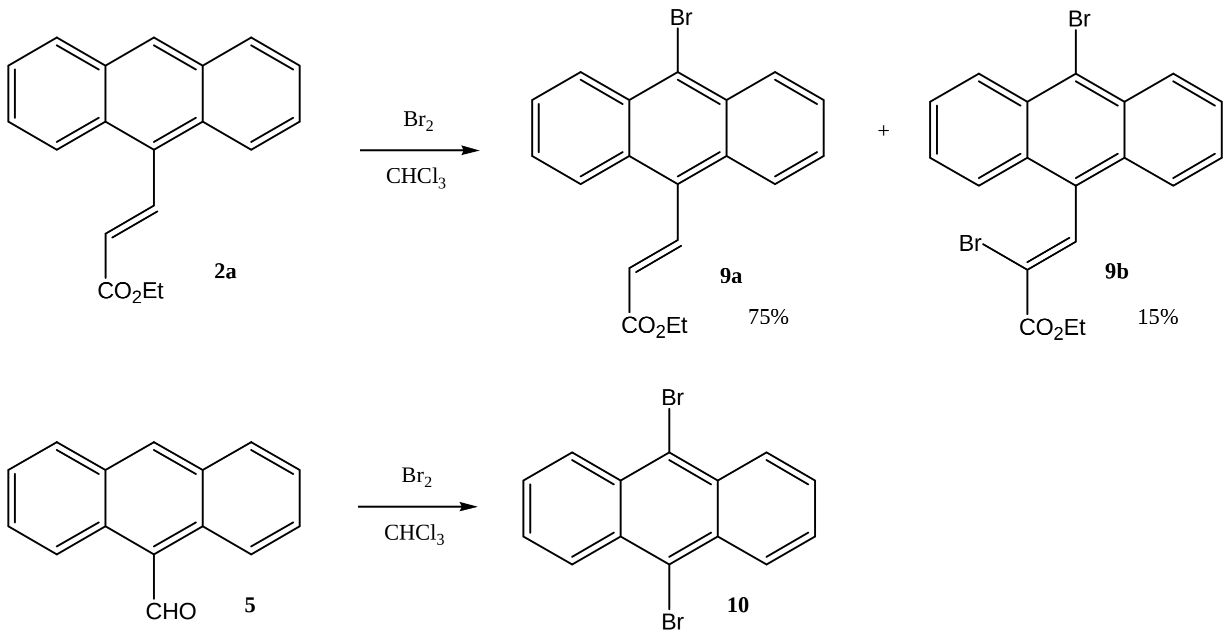
Scheme 2. Possible competing [4+4]-photodimerisation of anthranylacrylates



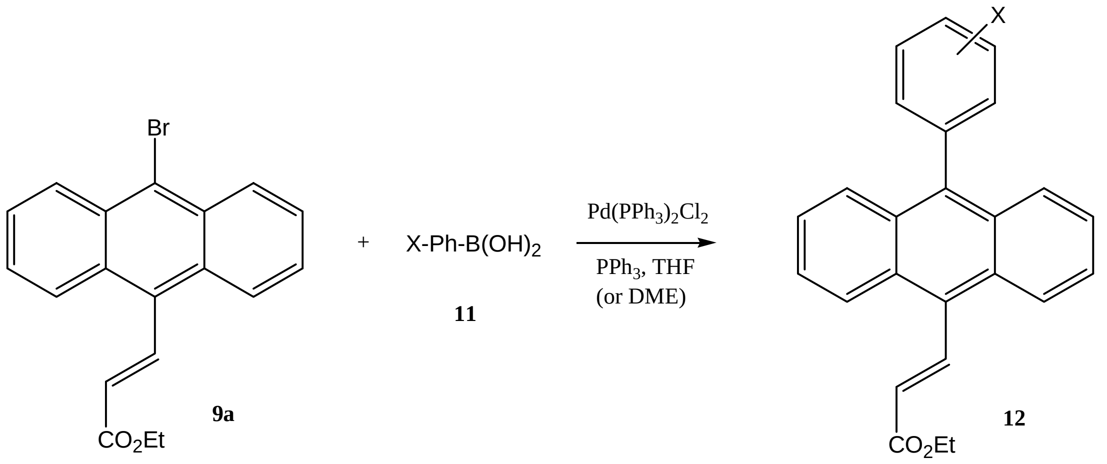
Preparation of the phosphorane reagents



Scheme 3. Synthesis of 9-aroylethenylanthracenes **8** and anthranylacrylates **2**

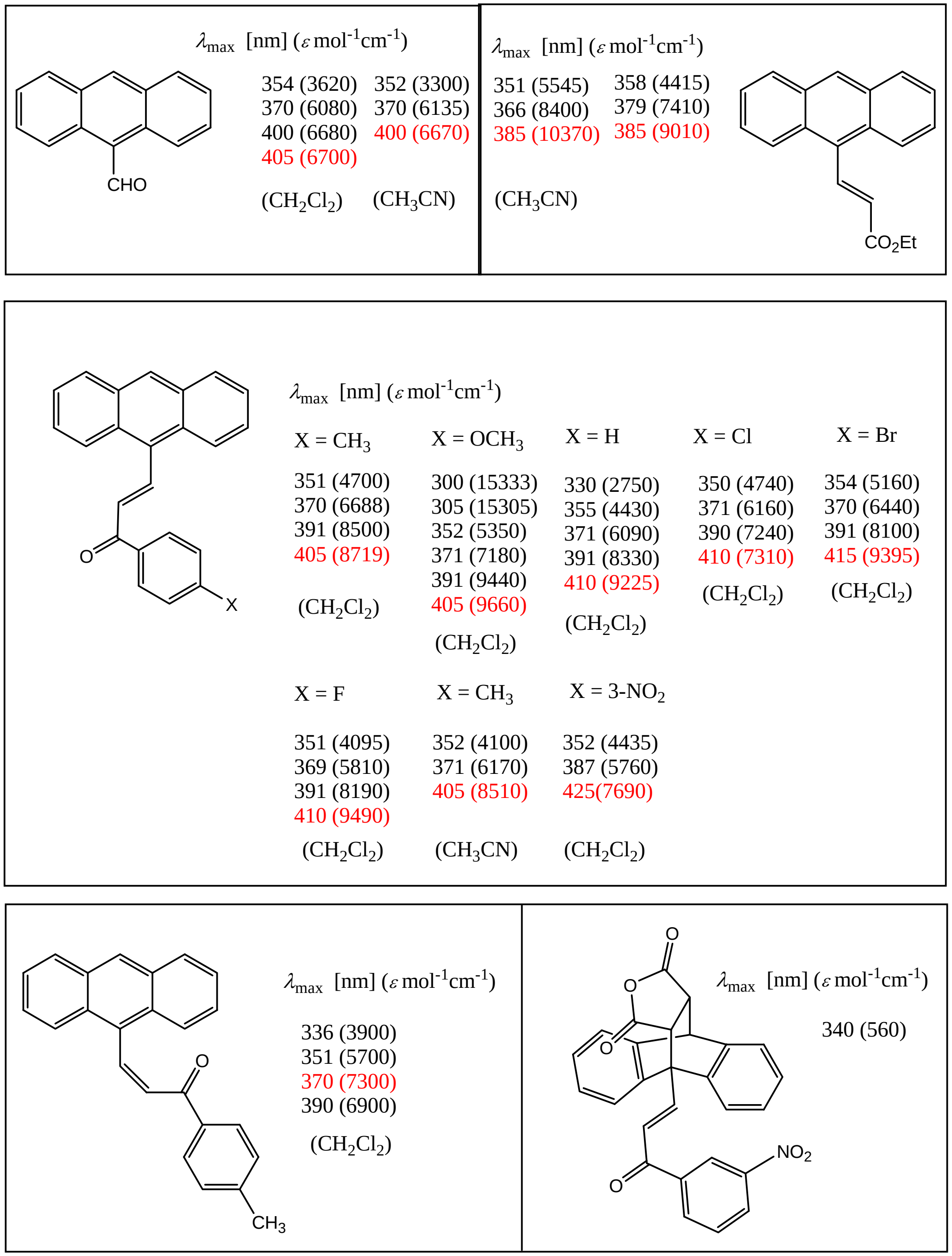


Scheme 4. Bromination 9-substituted anthracenes **2a** and **5**



X = 4-CH_3O, H, 3-Cl, 3-NO_2, 4-$C_{22}H_{45}O$

Scheme 5. Suzuki cross-coupling reactions to extended anthracenes



λ_{max} [nm] (ε mol^{-1}cm^{-1})

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

λ_{max} [nm] (ε mol^{-1}cm^{-1})

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

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)	(CH_2Cl_2)	(CH_2Cl_2)
(CH_2Cl_2)	405 (9660)	(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)

λ_{max} [nm] (ε mol^{-1}cm^{-1})

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

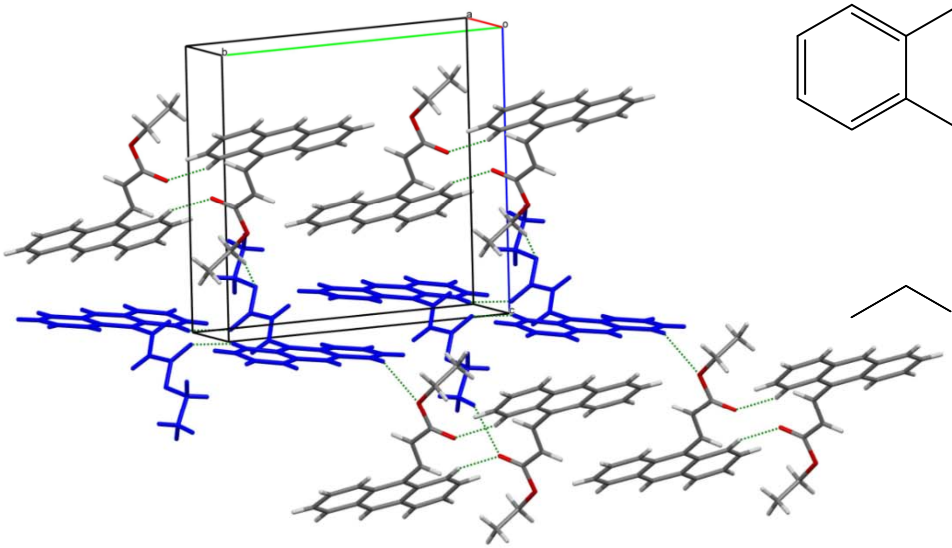
(CH_2Cl_2)

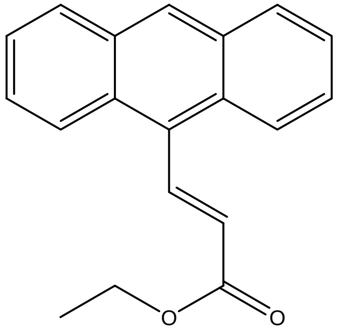
λ_{max} [nm] (ε mol^{-1}cm^{-1})

340 (560)

Fig. 1

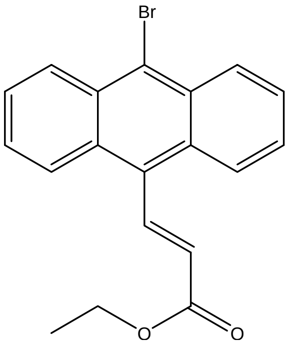
UV band maxima of selected compounds in CH_2Cl_2 and CH_3CN.





2a

Fig 2. Crystal packing of ethyl 3-(anthran-9-yl)acrylate showing intermolecular distances that are too large for photochemical dimerisation reactions in the crystal.



9a

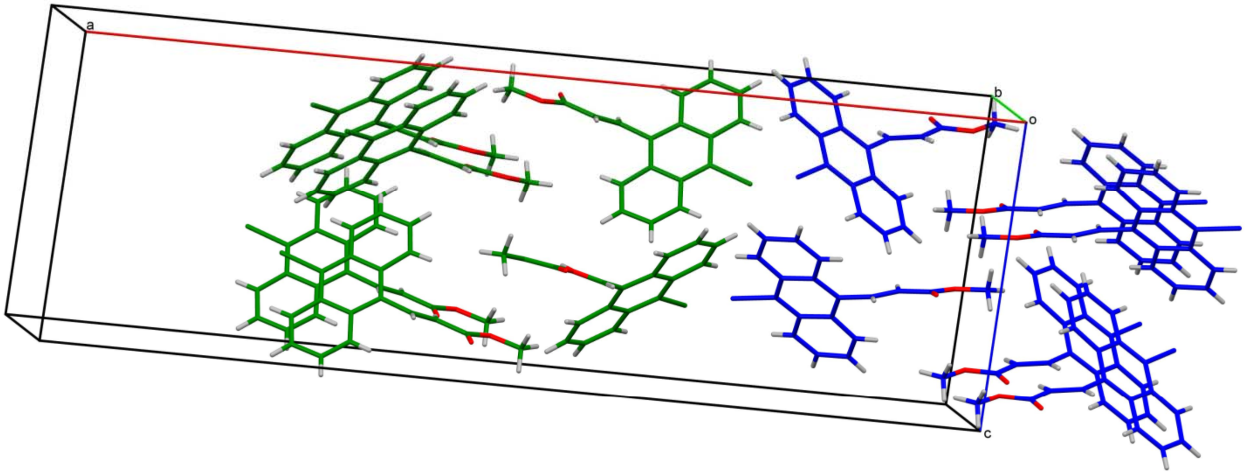
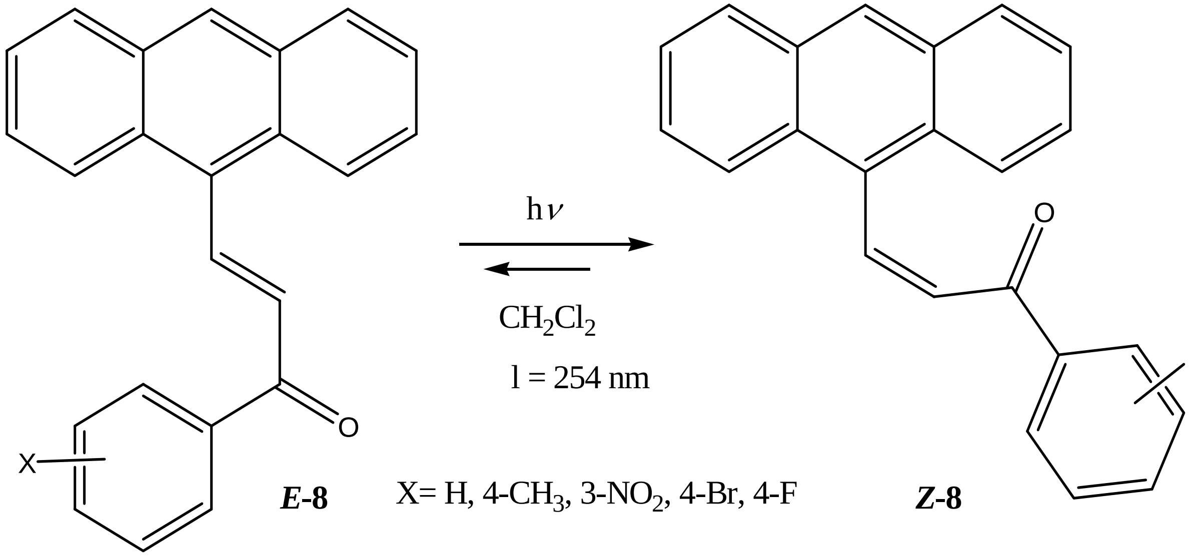
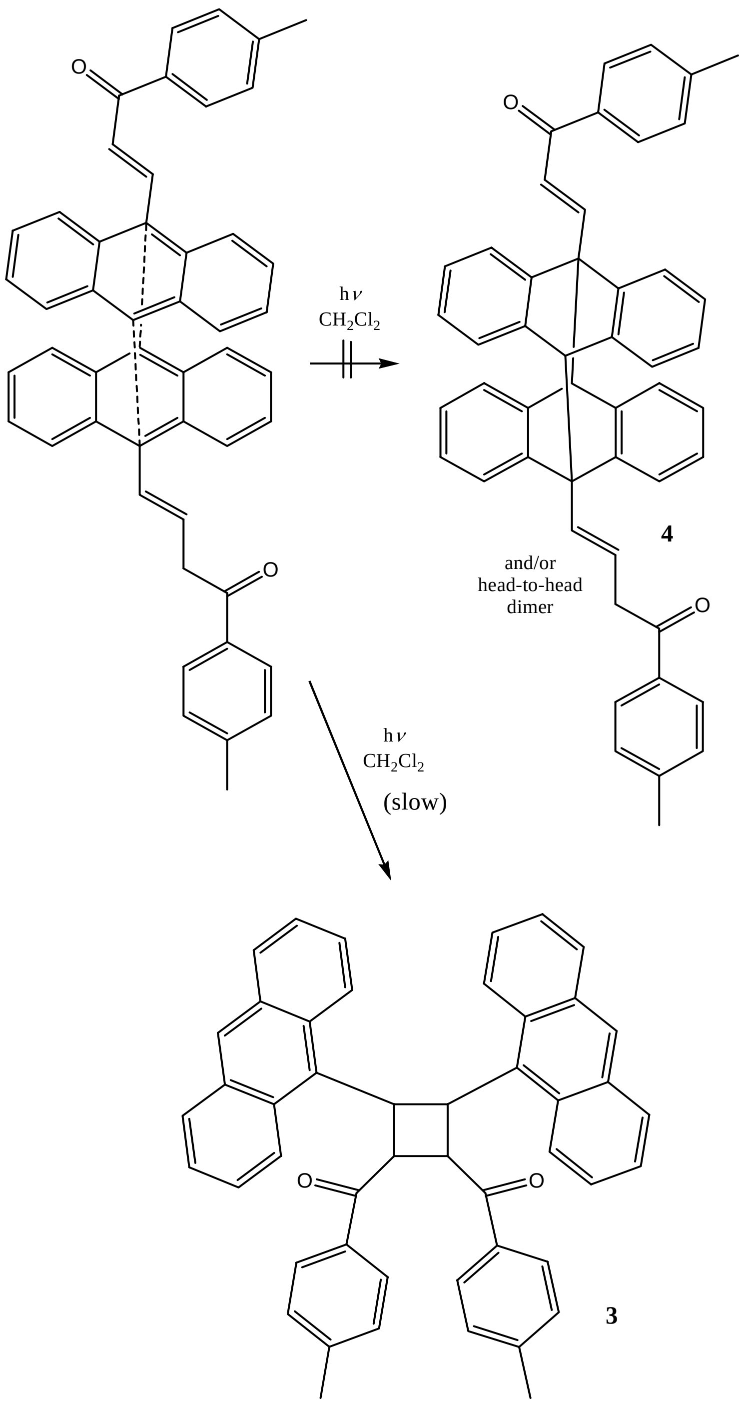


Fig 3. Crystal packing of ethyl 3-(9-bromoanthran-10-yl)acrylate showing intermolecular distances that are too large for photochemical dimerisation reactions in the crystal.



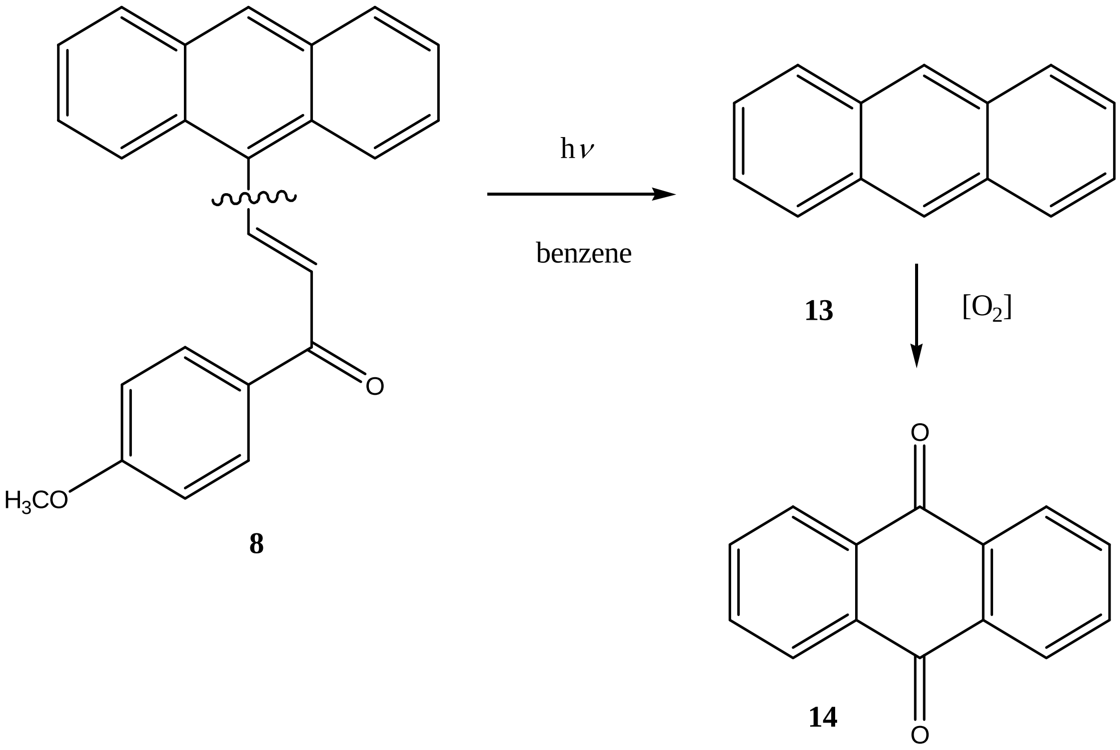
Scheme 6. Photochemical *cis-trans* isomerisation of 9-aroylethenylanthracenes

See also: H.-D. Becker, H. C. Becker, K. Sandros, K. Andersson, *Tetrahedron Lett.*, **1985**, *26*, 1589.
H. Bouas-Laurent, A. Castellan, J. P. Desvergne, and R. Lapouyade,, *Chem. Soc. Rev.*, **2000**, 29, 43 (review).
H. Bouas-Laurent, A. Castellan, J. P. Desvergne, and R. Lapouyade, *Chem. Soc. Rev.*, **2001**, *30*, 248 (review).

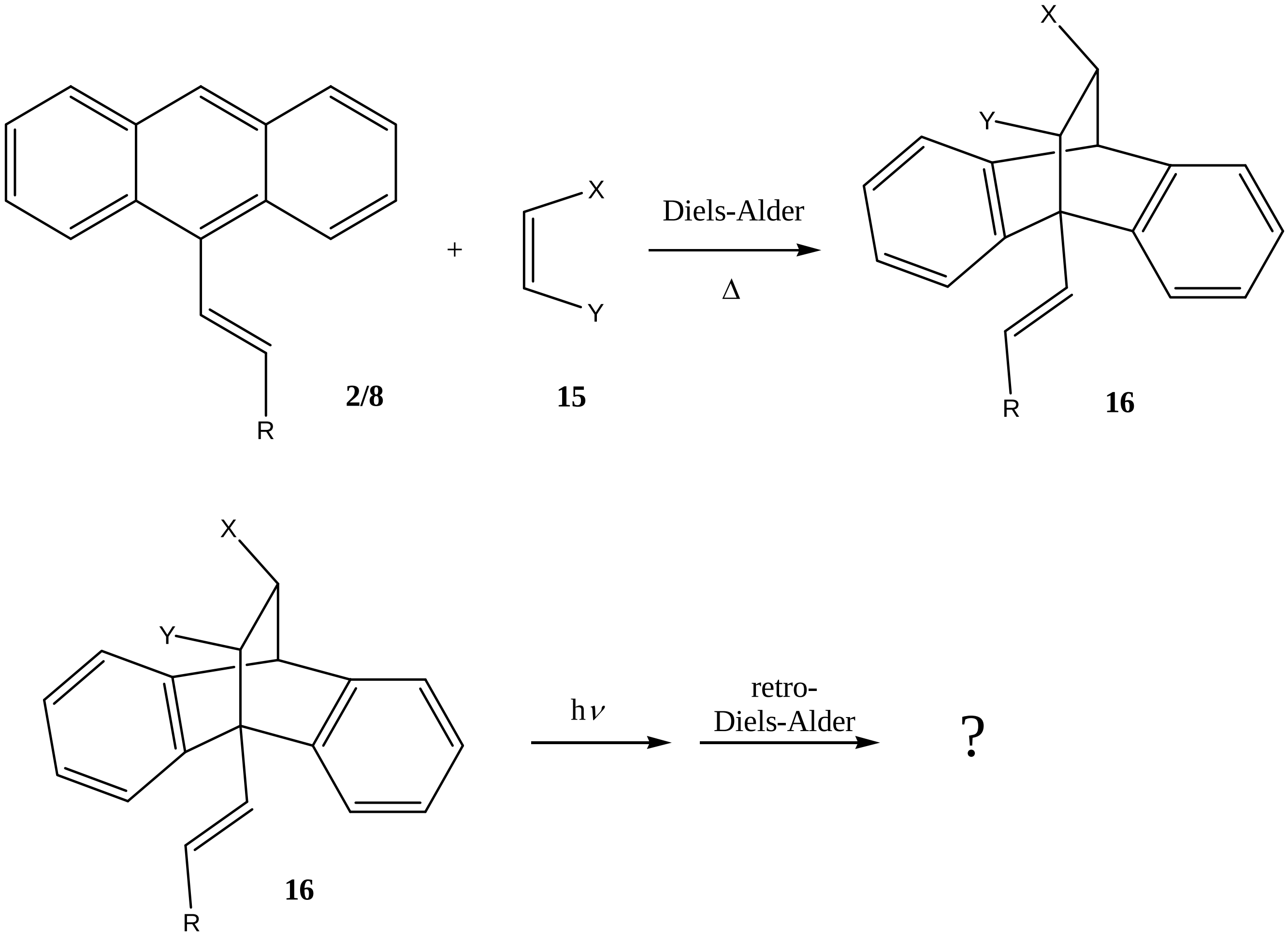


Scheme 7.

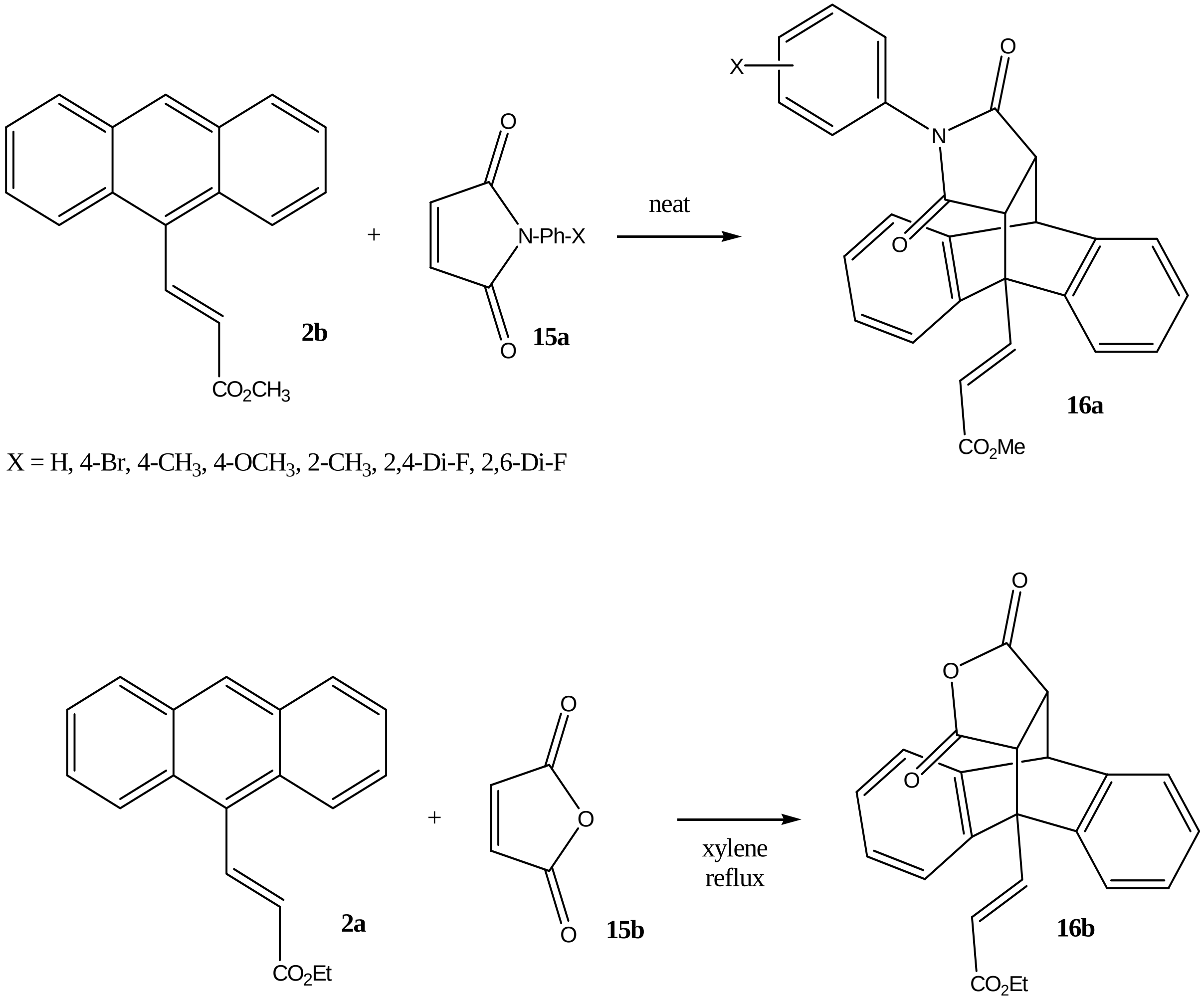
Slow build-up of a [2+2] photodimer in CH_2Cl_2



Scheme 8. Long-time Photoirradiation of aroylethenylanthracene (**8**) in benzene in presence of air oxygen at λ = 352 nm.

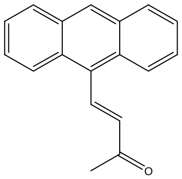
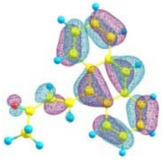
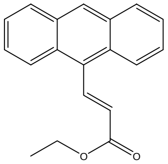
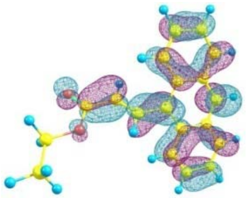
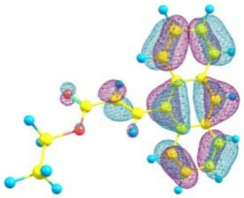
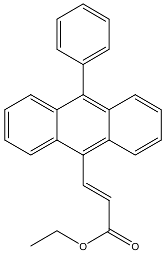
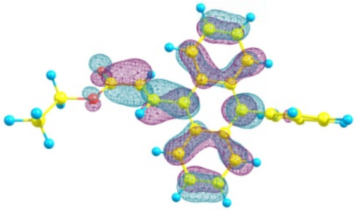
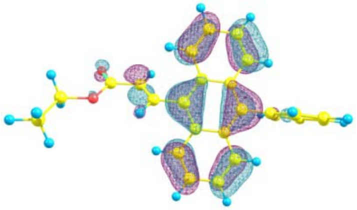
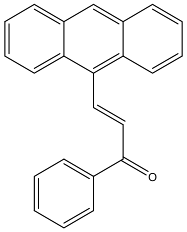
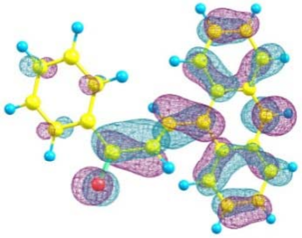
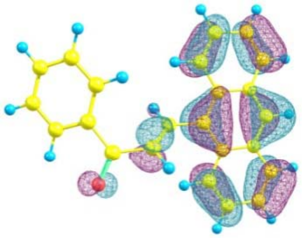


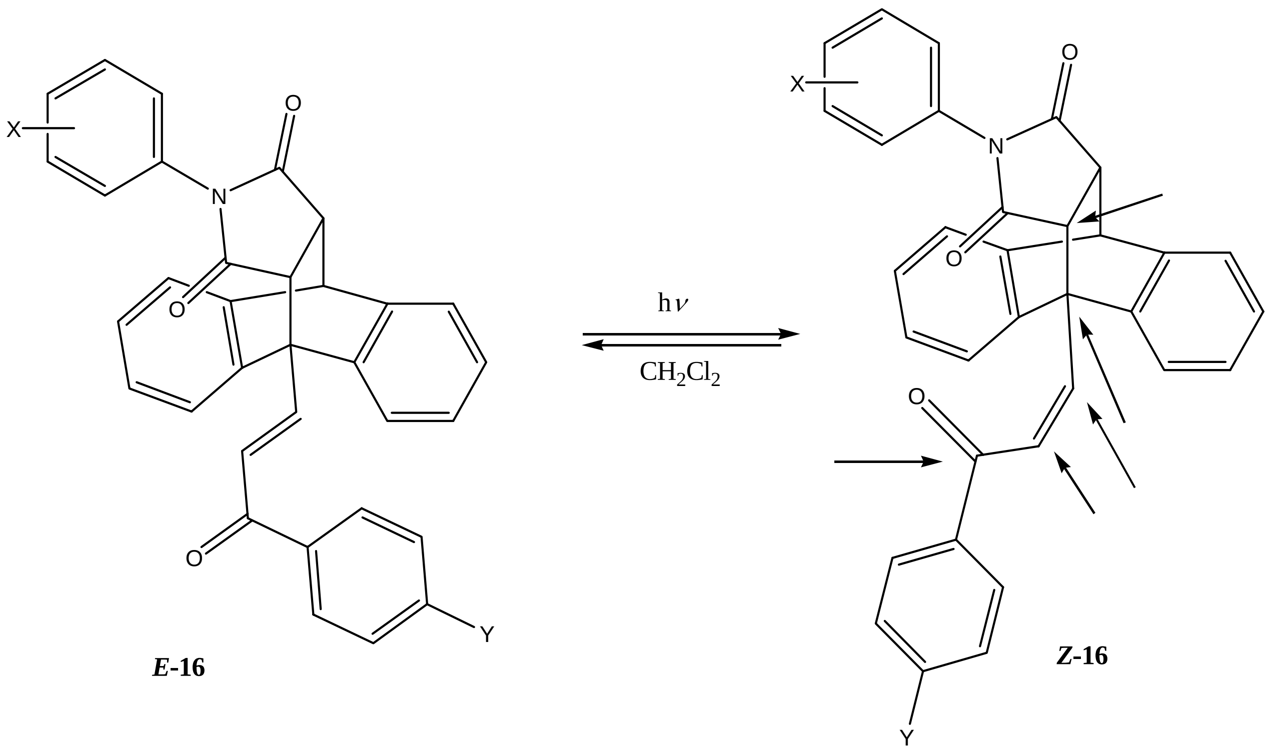
Scheme 7. Plan to produce [2+2]-cycloadducts from the ethenylanthracenes: First “protect” the anthranyl unit in a Diels-Alder reaction, then carry out the photochemistry, then “deprotect” the anthranyl unit in a retro-Diels-Alder reaction.



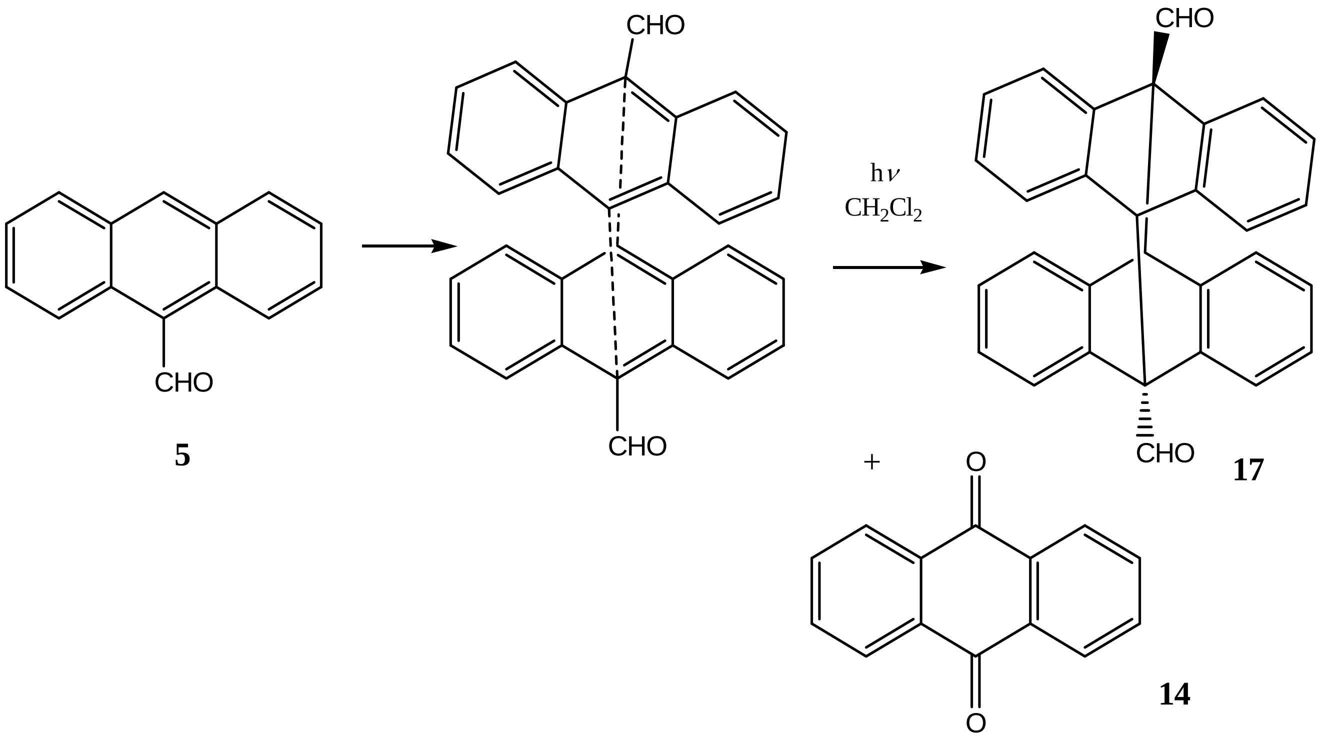
Scheme 8. Facile Diels-Alder reactions of 9-substituted anthracenes with doubly activated dienophiles.

Fig 4. Spatial distribution and energies of HOMO – LUMO for representative anthranylacrylates and phenacyl and acetylethenylanthracenes. 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. Geometry optimizations for the each molecule were performed without symmetry constraints in the gas-phase using the B3LYP hybrid functional and 6-31G(d) basis set. Optimized structures were confirmed to be energy minima through vibrational frequency calculations Orbital energies and isosurfaces were calculated using the same functional and basis set.

	LUMO (eV)	HOMO (eV)
Str1 	-2.17 	-5.39 
Str2 	-2.05 	-5.32 
Str3 	-2.02 	-5.25 
Str4 	-2.12 	-5.33 



Scheme 9. *E*-/*Z*-isomerisation of **16** upon photoirradiation at λ = 254 nm. Arrows indicate disappearing ^{1}H and ^{13}C NMR peaks due extreme broadening.

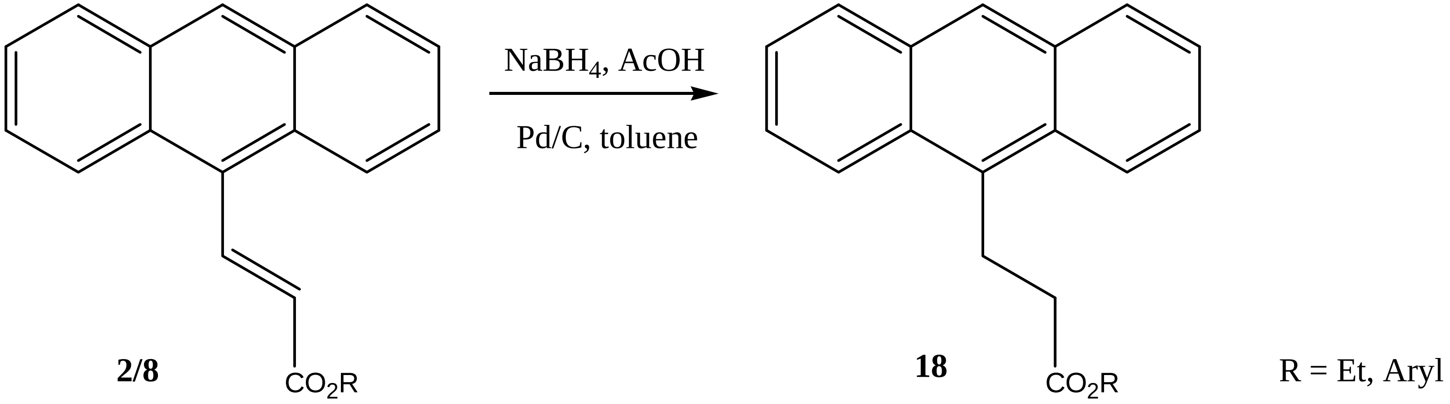


5

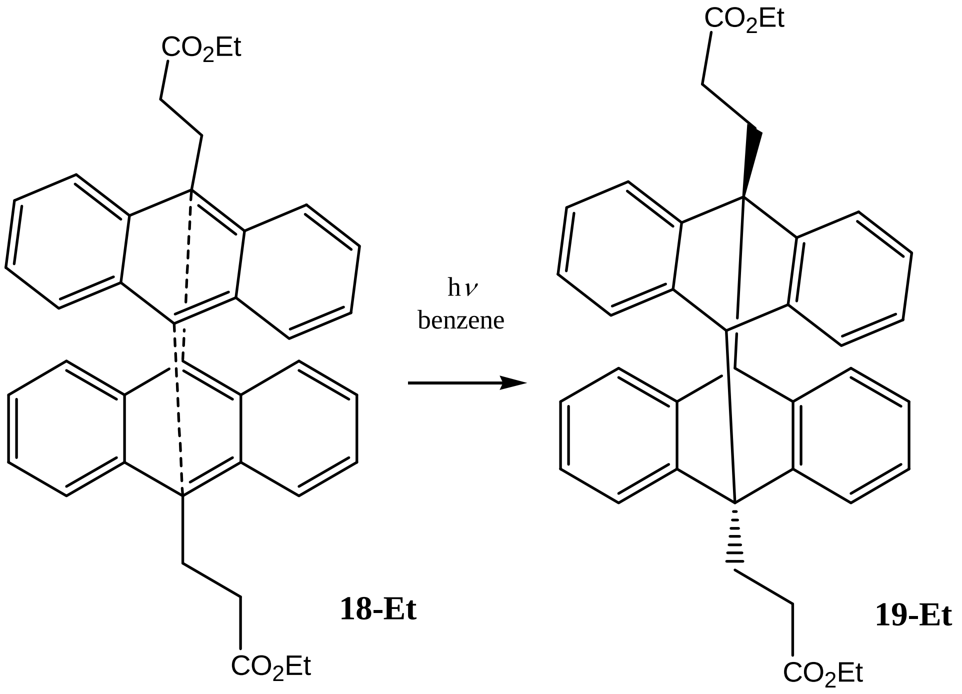
17

14

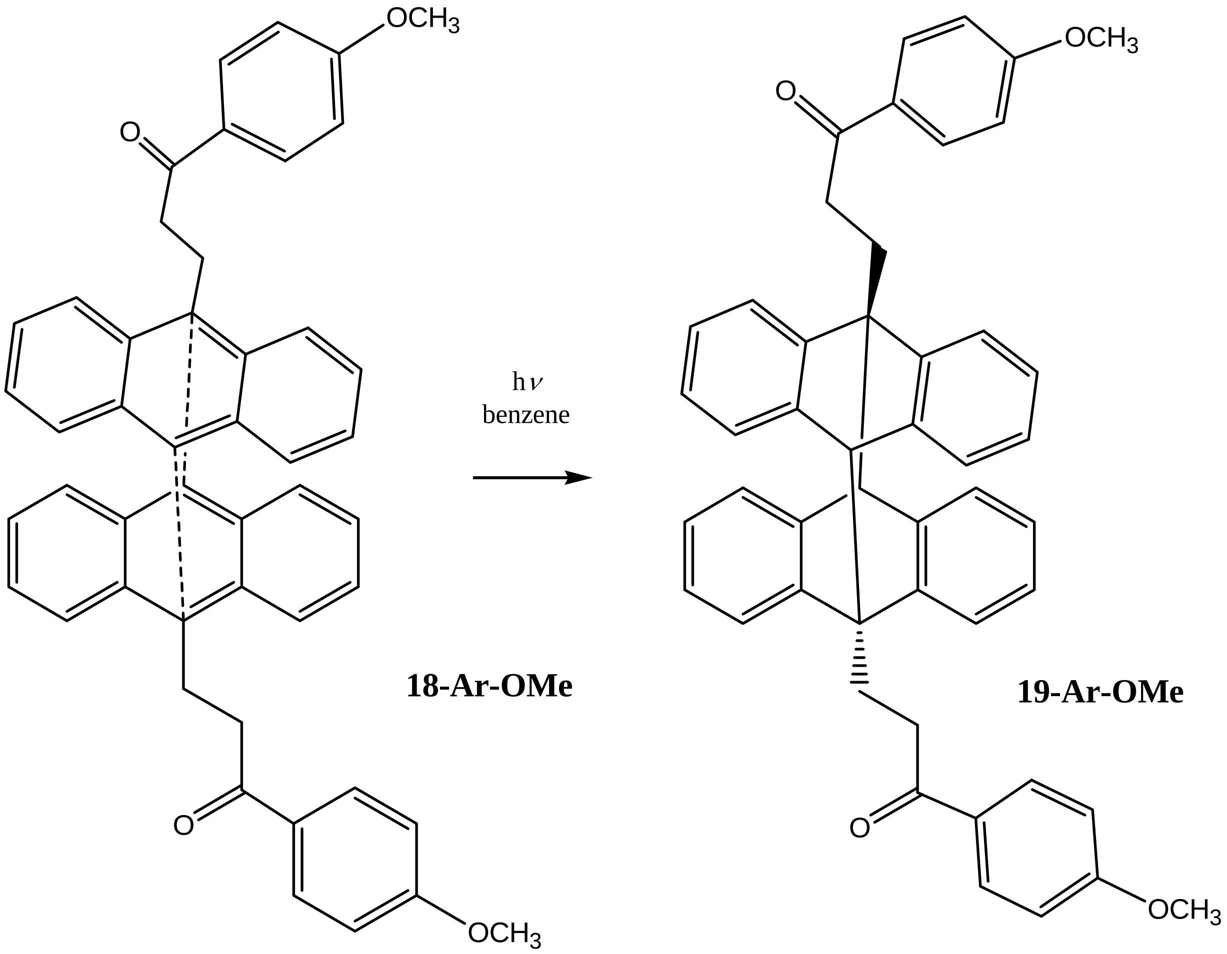
Scheme 10. Known photodimerisation of 9-formylanthracene in CH_2Cl_2 at λ = 352 nm.



Scheme 11. Hydrogenation of anthranyl acrylates and aroylethenylanthracenes with $NaBH_4$, AcOH, Pd/C



Scheme 12. Photodimerisation of ethyl anthranylpropionate (**18-Et**) at λ = 352 nm

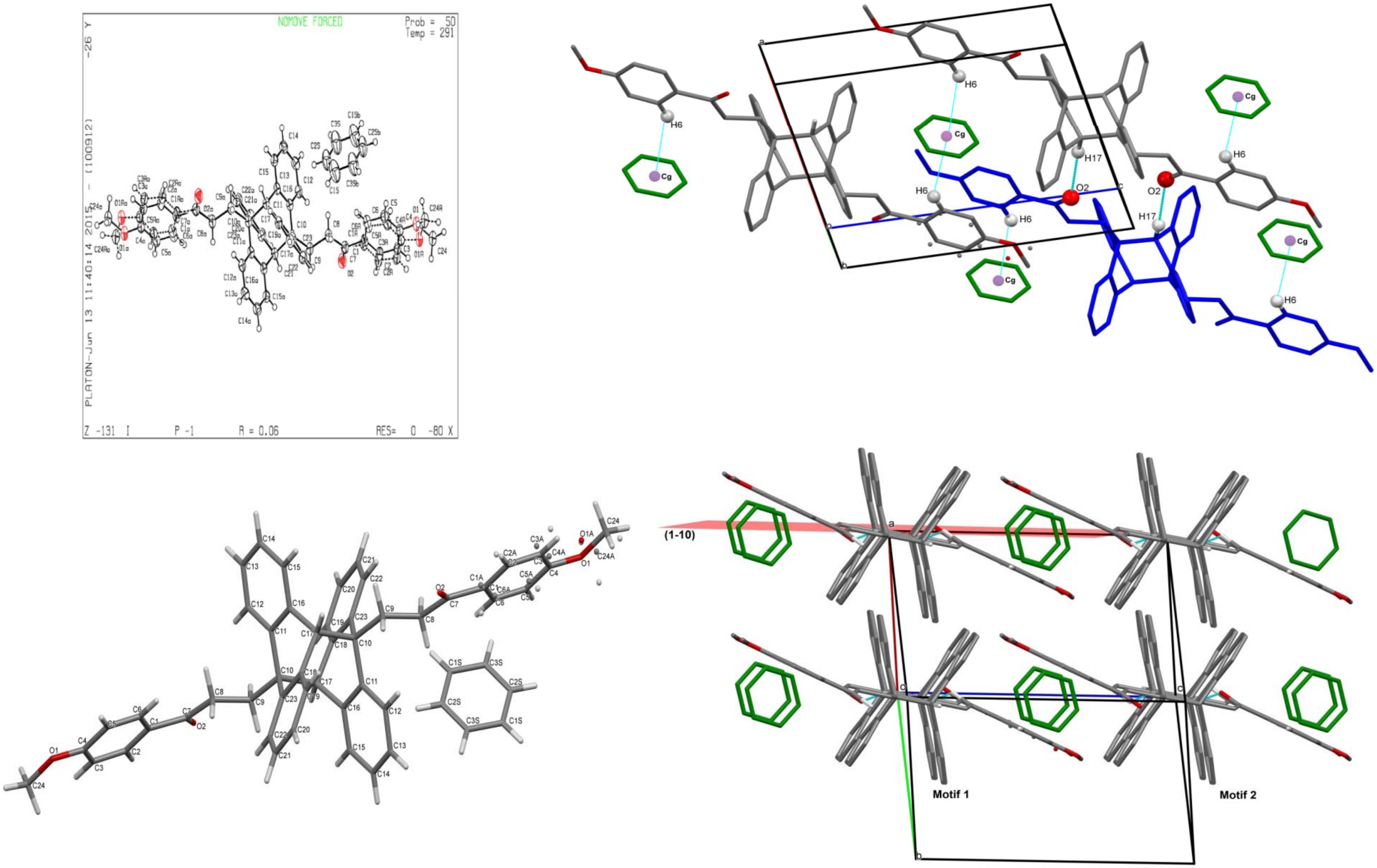


Scheme 13. Photodimerisation of 4-methoxybenzoylethylanthracene (**18-Ar-OMe**) at λ = 352 nm

see also:

H. Bouas-Laurent, A. Castellan, J. P. Desvergne, and R. Lapouyade,, *Chem. Soc. Rev.*, **2000**, 29, 43 (review).

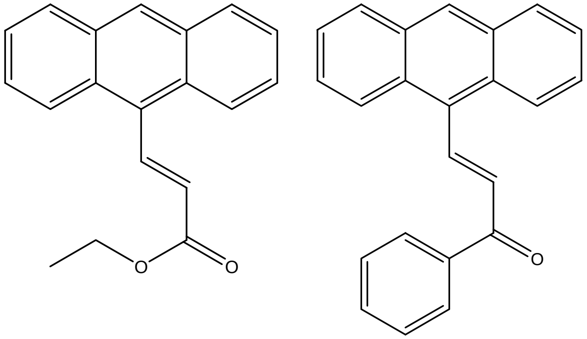
H. Bouas-Laurent, A. Castellan, J. P. Desvergne, and R. Lapouyade, *Chem. Soc. Rev.*, **2001**, *30*, 248 (review).



A view of the molecular structure of the molecule **19-Ar-OMe**, with non-hydrogen atom labelling. Displacement ellipsoids are shown at the 50% probability level. Disorder is clear at only one methoxyphenyl group.

Conclusions:

1.) A larger number of aroyl and ester substituted 9-ethenylanthracenes could be synthesized via solventless Wittig-olefination.



2.) X-ray crystal structures of two of them showed the molecules too far apart in the crystal for them to photodimerize.

3.) The keto substituted 9-ethenylanthracenes undergo photochemical E-/Z-isomerisation at λ = 254 nm, the ester substituted molecules undergo a slow polymerisation. The 9-aroyl-ethenylanthracenes undergo a slow [2+2]-cycloaddition, but in very low yield.

4.) 9-Ethenylanthracenes were submitted facilely to Diels- Alder reactions with maleimides. The photoreaction of the cycloadducts, which still carry an α,β-enone or an α,β-unsaturated ester functionality, leads mainly to rapid *E*/*Z*-isomerisation.

5.) When photoirradiated at λ = 352 nm, 9-ketoethylanthracenes (ie., the hydrogenated 9-ethenylanthracenes) undergo [4+4]-cycloaddition with the formation of head-to-tail cycloadducts.

6.) 9-Ethenylanthracenes are photoreactive under UV-irradiation. This can lead to aging of such ethenylanthracene containing material and should be taken into account when using these in organic solar cells.

Who we are

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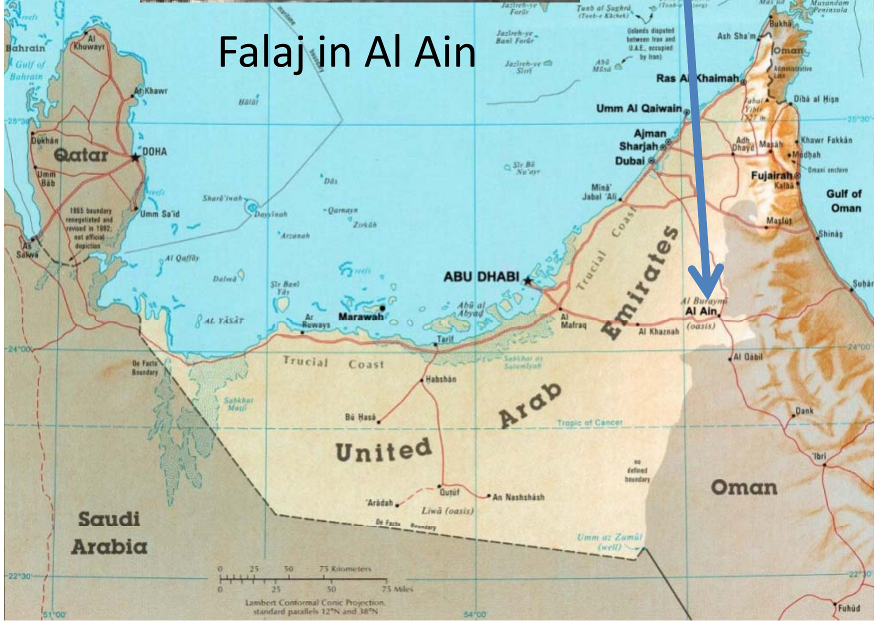
Administrative building of the United Arab Emirates University



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Chemistry research building

Thank you very much for your attention!