

Extended anthracenes and their use as dienes in Diels-Alder reactions

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9,10-Disubstituted anthracenes have interesting electro-optical applications and usage as sensor materials. These include polymers with 9,10-disubstituted anthranyl subunits.

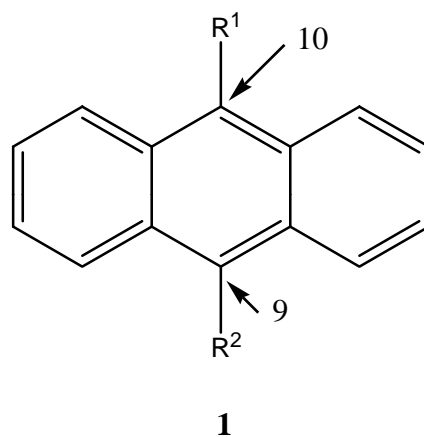
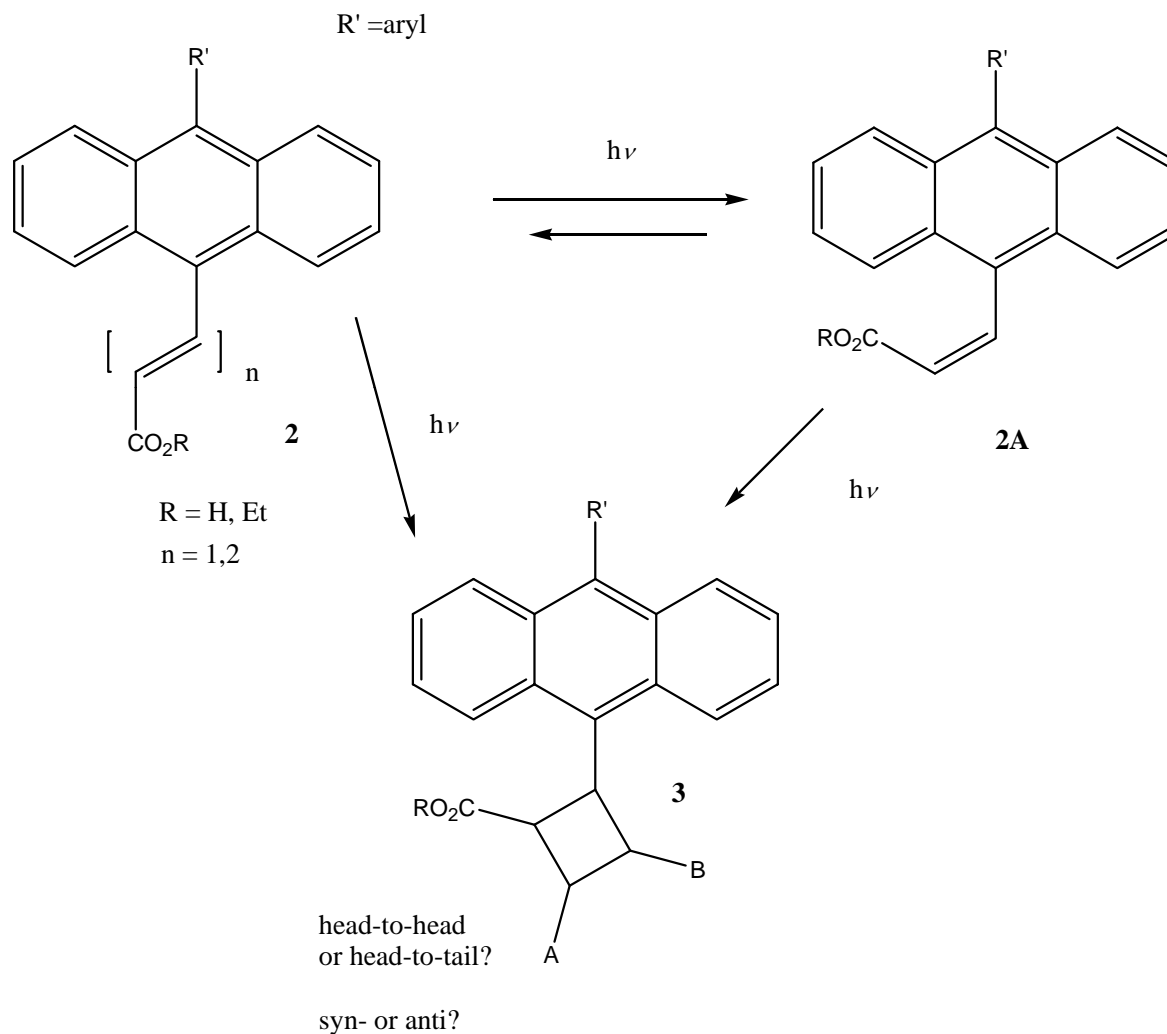


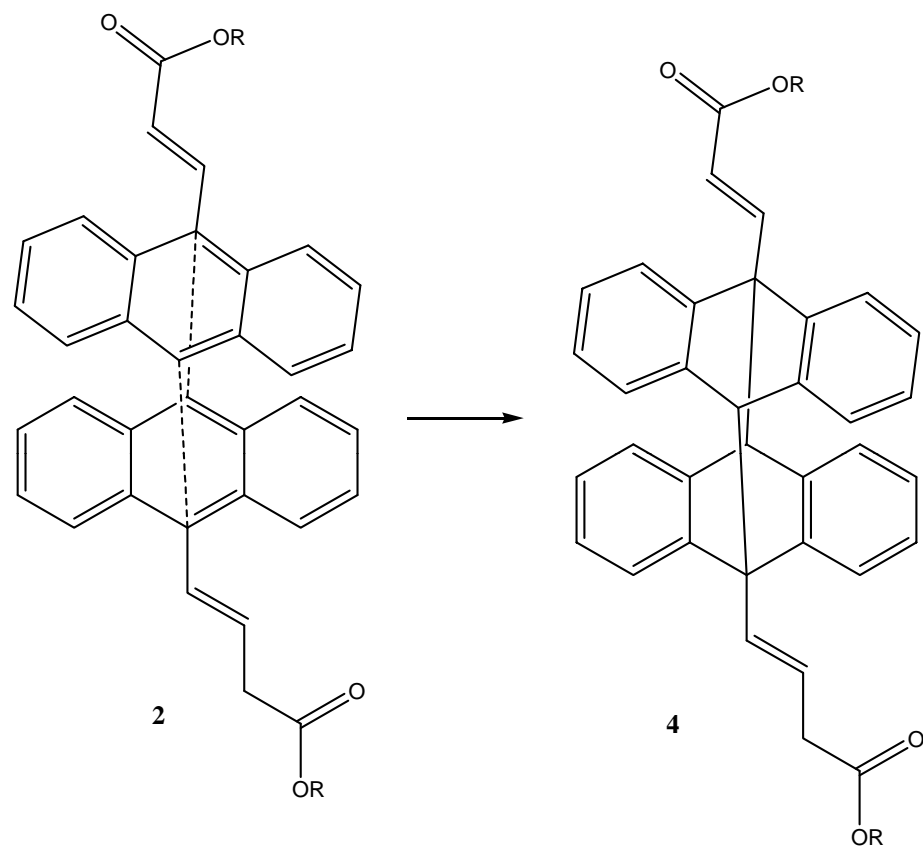
Figure 1. Disubstituted anthracene with carbon-numbering

In our endeavor to produce interlinked 9,10-disubstituted anthran-9-yl-containing materials photochemically, be it by photochemical dimerisation or photochemical polymerization, the photochemistry of 3-(anthran-9-yl)acrylates was studied. Possible photochemical pathways for these molecules were envisaged to be *E*-/*Z*-isomerisation of the acrylate moiety and photodimerisation of the acrylate moiety



Scheme 1. Possible photodimerisation products of anthran-9-ylacrylates

as well as a possible competing [4+4]-photodimerisation of the anthranly unit.



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

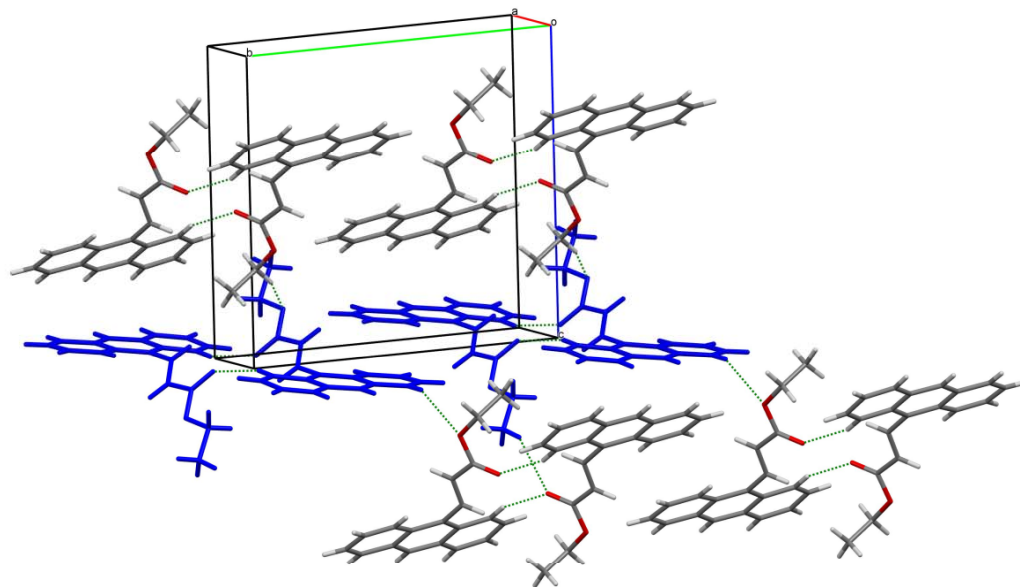


Figure 2. Crystal packing of ethyl 3-(anthran-9-yl)acrylate showing intermolecular distances that are too large for photochemical dimerisation reactions in the crystal.

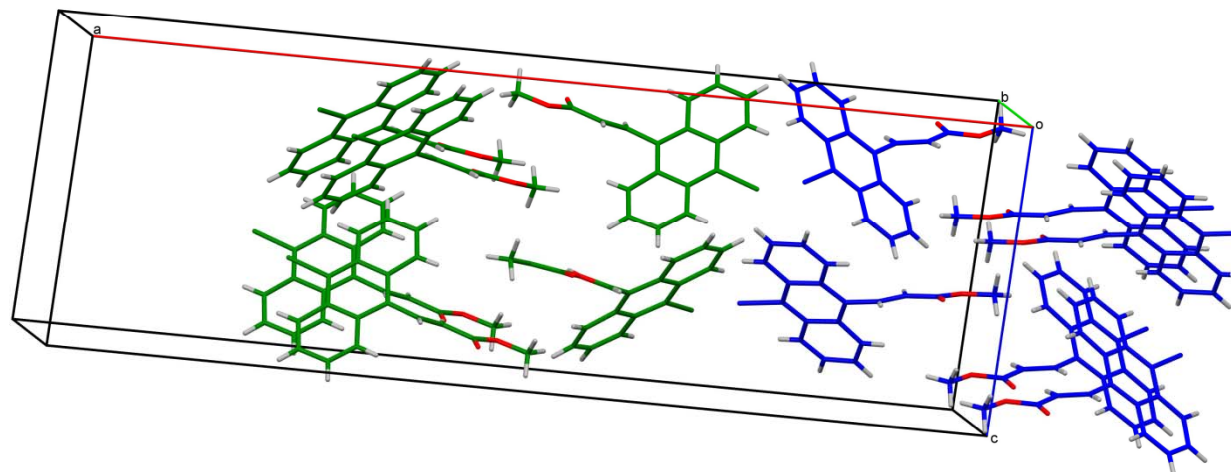
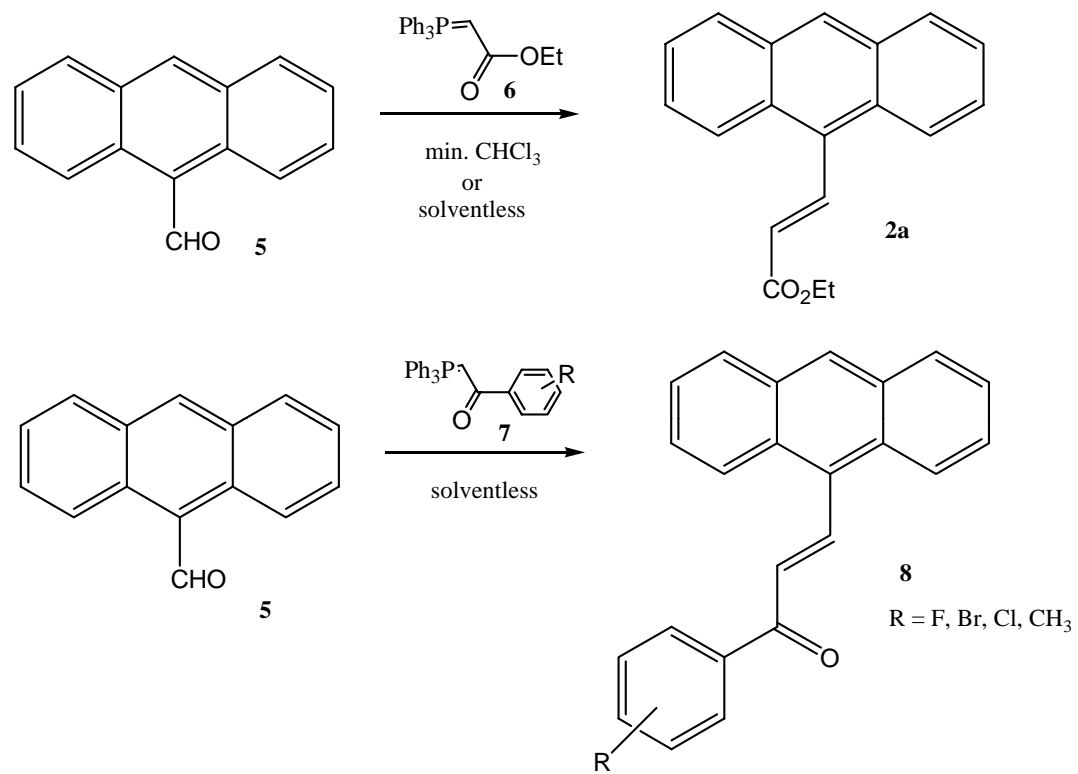


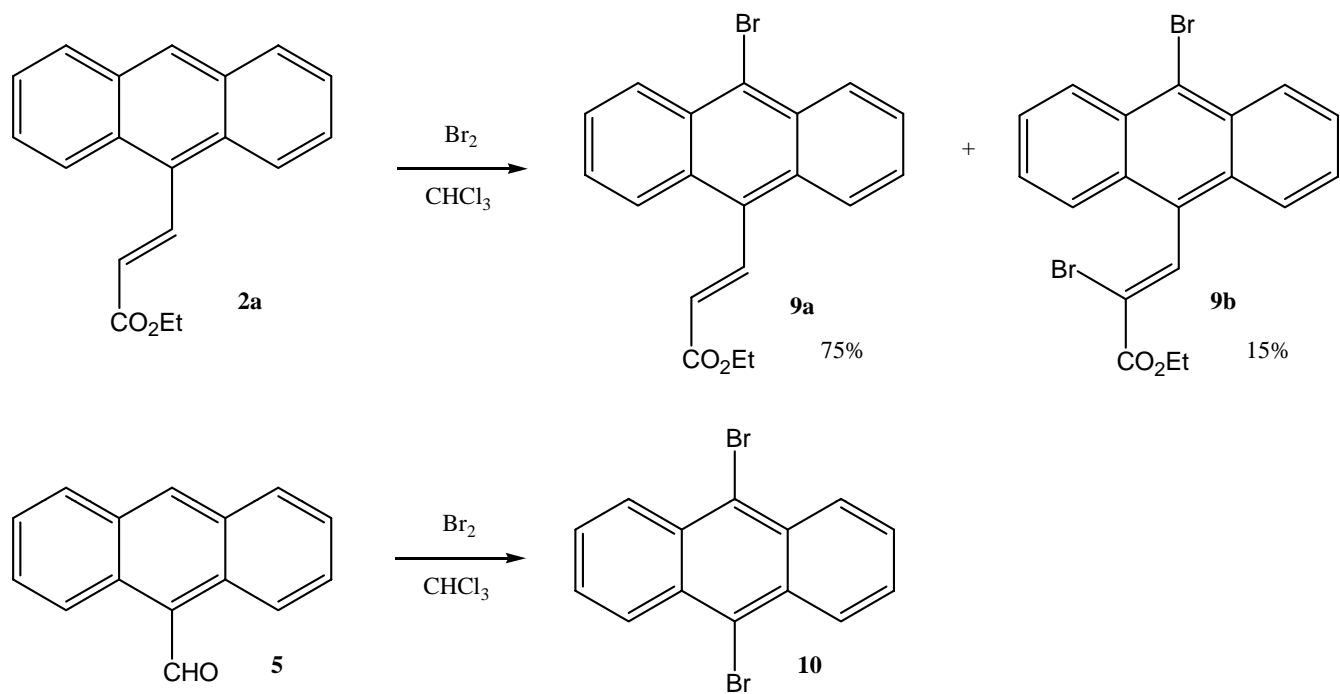
Figure 3. Crystal packing of ethyl 3-(9-bromoanthran-10-yl)acrylate showing intermolecular distances that are too large for photochemical dimerisation reactions in the crystal.

This would mean that a photochemical dimerisation of molecules in the crystal would be unlikely. In solution, however, the photochemistry of the molecules is very complex. Therefore, it was decided to cycloadd across the anthran-10-yl units, carry out the photochemistry of the vinyl group, and subsequently subject the molecules to a Retro-Diels Alder reaction.

In the following, the authors show the preparation of the anthran-10-ylacrylates and aroylethenanthracenes and their Diels–Alder reactivity.

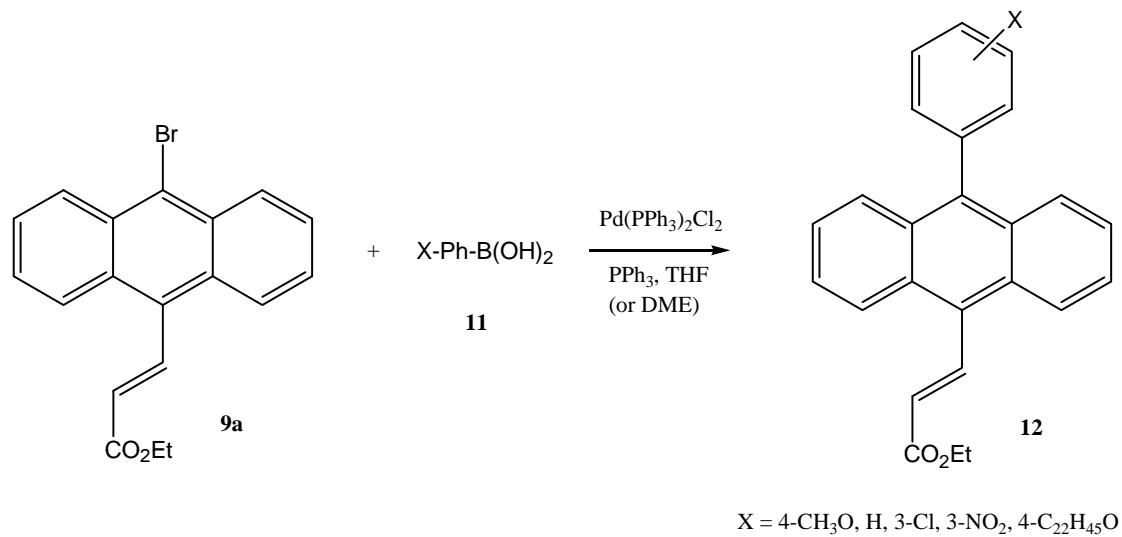


Scheme 3. Solventless Wittig-olefination reactions to anthranylacrylate **2** and aroylethenyl-anthracenes **8**

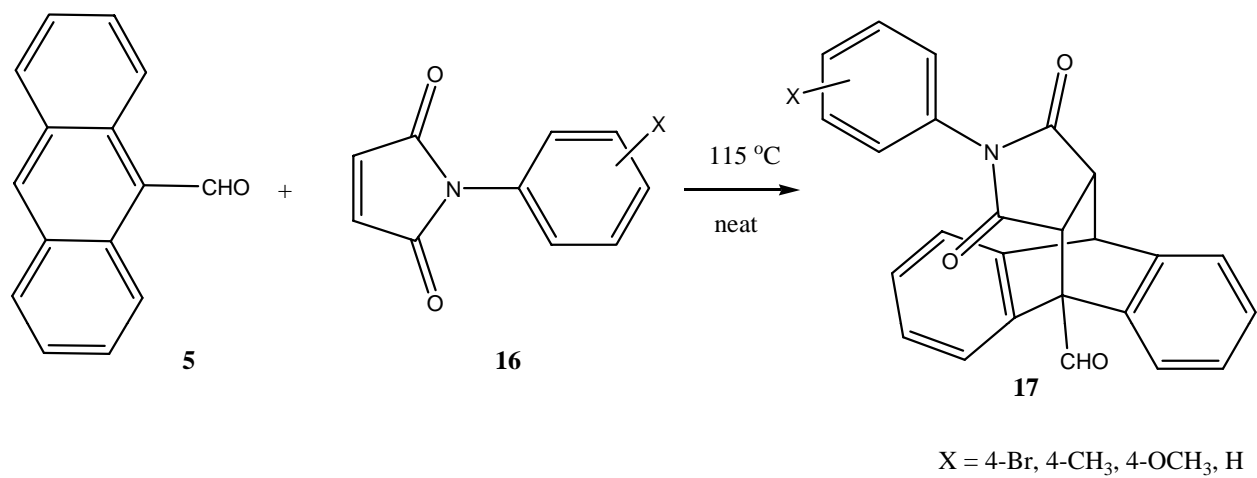


Scheme 4. Bromination of anthranylacrylate **2a** and anthranylcarbaldehyde **5**

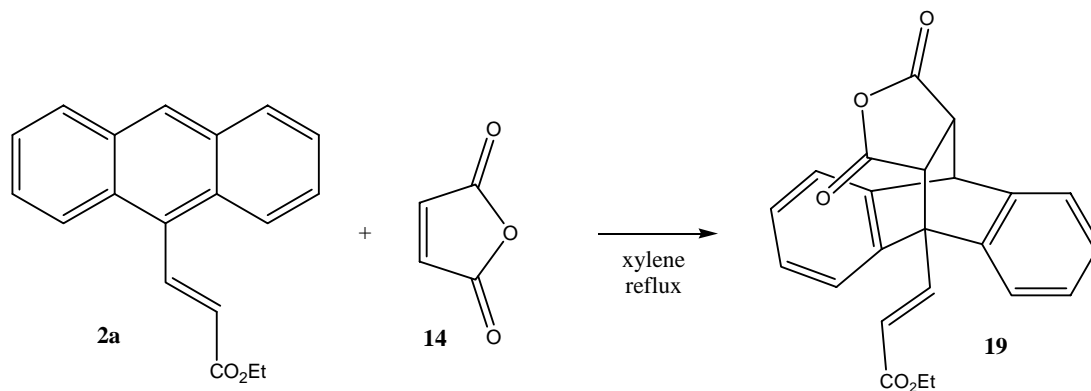
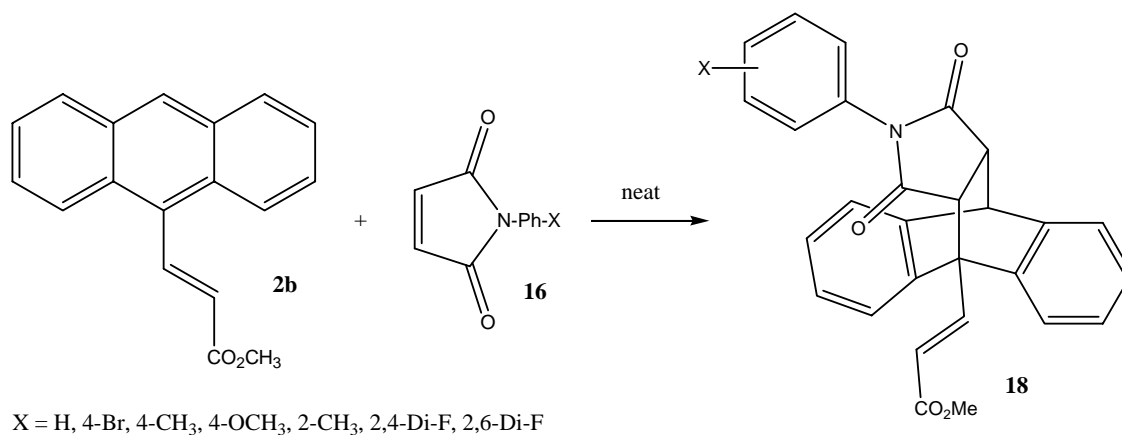
Bromination of anthranylacrylates of type **2** leads mainly to bromination of the central ring system of the anthracene.



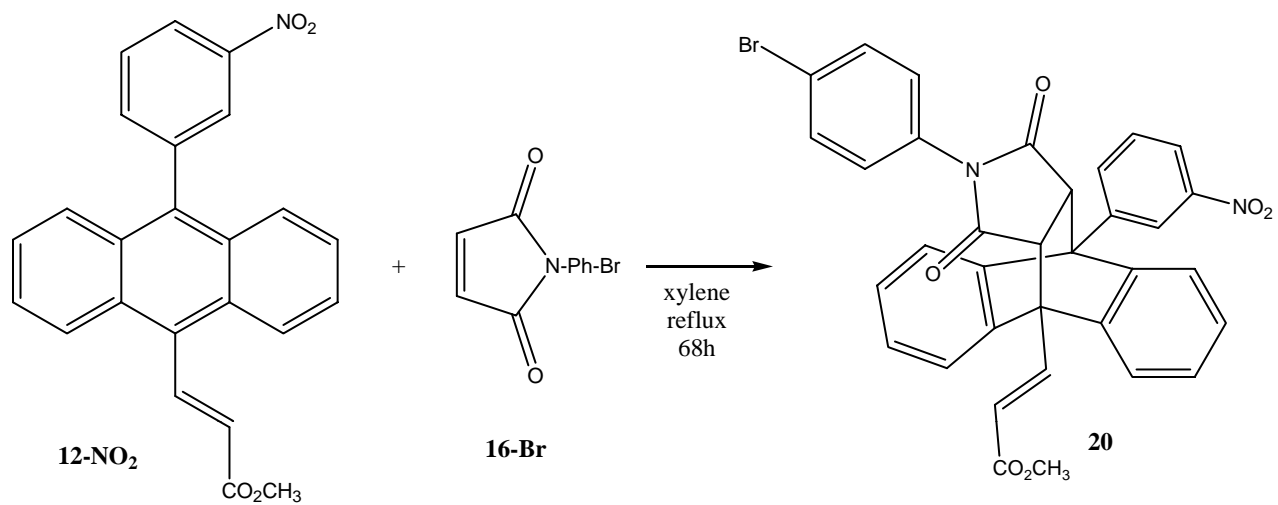
Scheme 5. Pi-extension of anthranylethyl acrylate **9a** by Suzuki-Miyaura cross-coupling reaction.



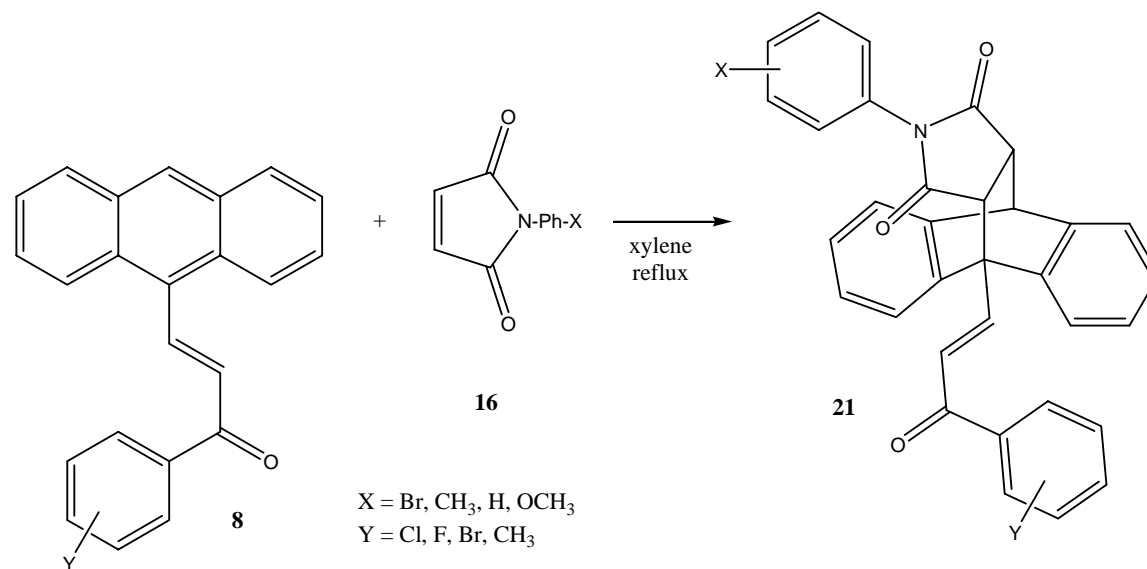
Scheme 6. Solventless cycloaddition of 9-anthracenecarbaldehyde **5** to maleimides **16**



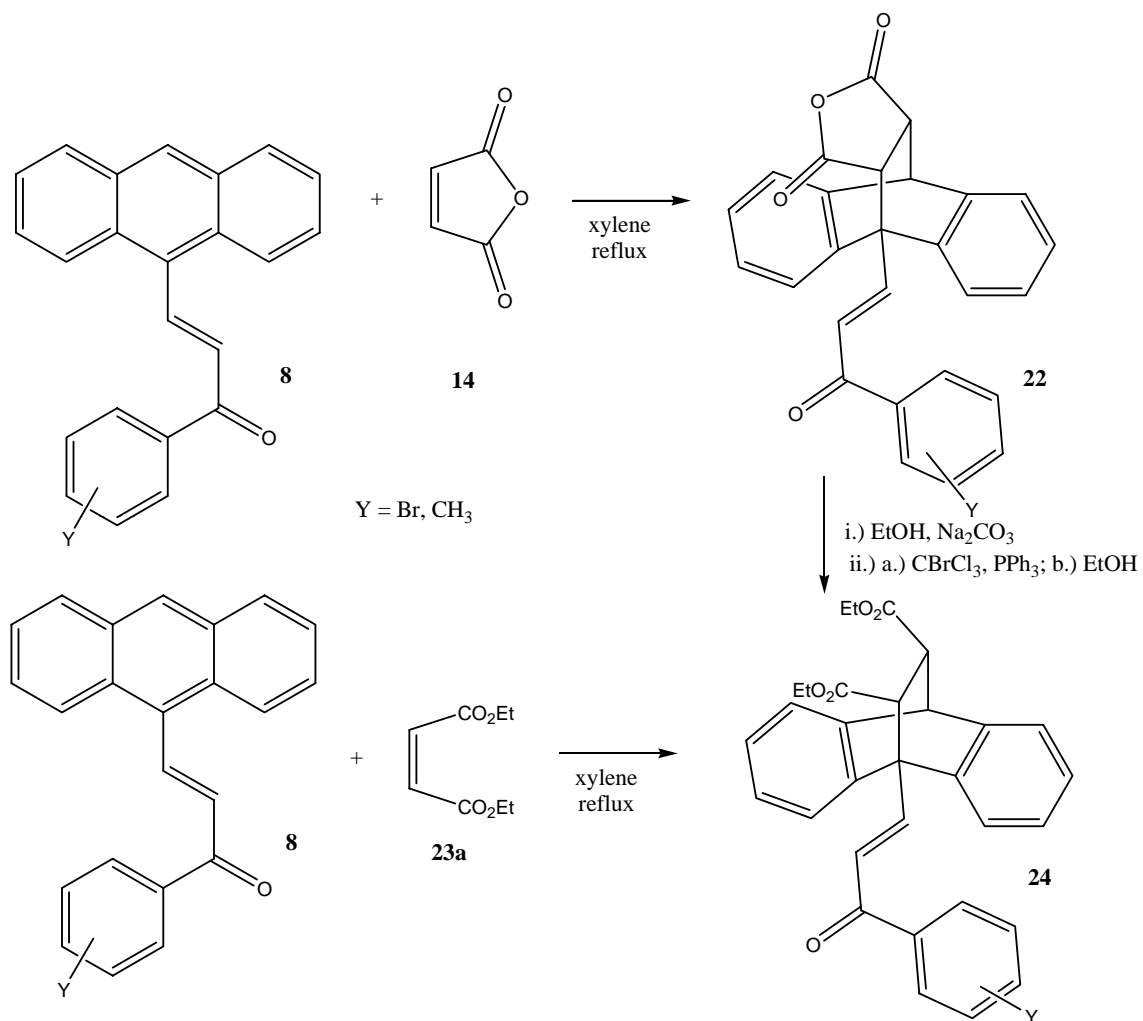
Scheme 7. [4+2]-Cycloaddition of anthranilacrylates **2a/2b** with maleimides and maleic anhydride



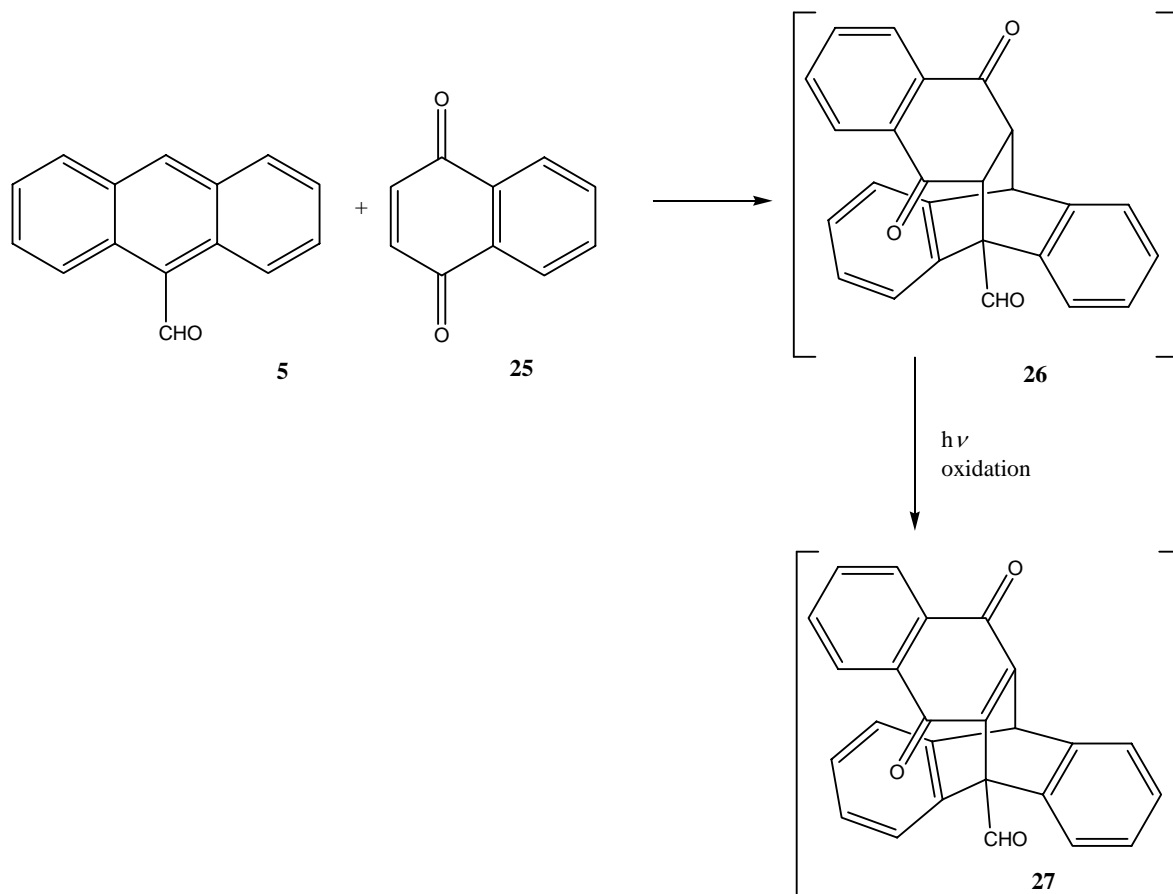
Scheme 8. Cycloaddition reactions of pi-extended anthracenes **12** with maleimides **16**.



Scheme 9. Cycloaddition reactions of aroylethenylanthracenes **8** with maleimides **16**



Scheme 10. Cycloaddition reactions of aroylethenylantracenes **8** and maleic anhydride (**14**) and diethyl maleate (**23a**).



Scheme 11. Cycloaddition of anthranilcarbaldehyde (**5**) and benzoquinone (**25**) with subsequent photochemically aided oxidative dehydrogenation of the cycloadduct.

Conclusions:

3-(Anthran-9-yl)acrylates and 9-arylethenylanthracenes can be produced easily by *solventless* Wittig reaction.

3-(Anthran-9-yl)acrylates can be brominated selectively to produce 3-(9-bromoanthran-10-yl)acrylates, which can be used as substrates to produce pi-extended anthracenes by Suzuki-Miyaura cross-coupling reaction.

3-(Anthran-9-yl)acrylates, 9-anthranilcarbaldehyde and 9-arylethenylanthracenes easily undergo Diels Alder type cycloaddition reactions with a variety of bisactivated enes. Of these, 3-(anthran-9-yl)acrylates and 9-anthranilcarbaldehyde undergo *solventless* Diels-Alder reactions with maleimides.

Thank you very much for your kind interest!

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