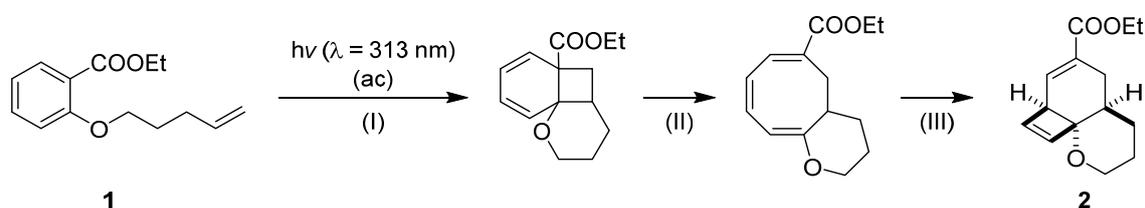


# PHOTOCHEMICAL REACTION CASCADE FROM O-PENT-4-ENYL-SUBSTITUTED SALICYLATES TO COMPLEX MULTIFUNCTIONAL SCAFFOLDS

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In 1995 Wagner reported on the photochemical transformation of ethyl 2-(pent-4-en-1-yloxy)benzoate (**1**) to ethyl 2,3,4,4a,5,7a-hexahydrocyclobuta[*i*]chromene-6-carboxylate (**2**). The complex polycyclic product is the result of three consecutive reactions which take place in a cascade fashion (Scheme 1) [1]. However, this is the only example that existed on that kind of reaction cascade and no further studies were conducted. Thus we were interested in the scope and synthetic utility of the above described transformation.



Scheme 1: Reaction cascade from **1** to **2** consisting of an *ortho* photocycloaddition (I), a thermal ring opening (II), and a [4 $\pi$ ] cyclization (III).

During our investigations we could show that a photosensitizer is not necessary for a successful outcome of the reaction [2]. In fact, in our experiments direct excitation at  $\lambda = 300 \text{ nm}$  in methanol gave better results than sensitization with acetone. Furthermore, a wide variety of compounds sharing the salicylic acid backbone could be utilized in this photochemical reaction cascade. The ethyl ester could be substituted with other alkyl esters of which the *tert*-butyl ester was sterically most demanding. When other electron withdrawing groups were tested only nitriles gave satisfactory results, whereas the analogous amides gave no reaction due to short wavelength absorption. Regarding the *O*-pent-4-enyl side chain, substituents in the 1-, 2-, 3-, 4- and 5-position were tolerated. The diastereoselectivity induced by the stereogenic centers being present upon substitution is moderate to good (*dr* = 65/35 to 82/18). The reaction being stereoconvergent in regard to *E* / *Z* in case of substitution in the 5-position is in agreement with a triplet mechanism. The future goal is to implement this reaction cascade into natural product synthesis.

[1] P. J. Wagner, R. P. Smart, *Tetrahedron Lett.* **1995**, 36, 5135–5138.

[2] A. Zech, T. Bach, *J. Org. Chem.* **2018**, 83, 3069-3077.