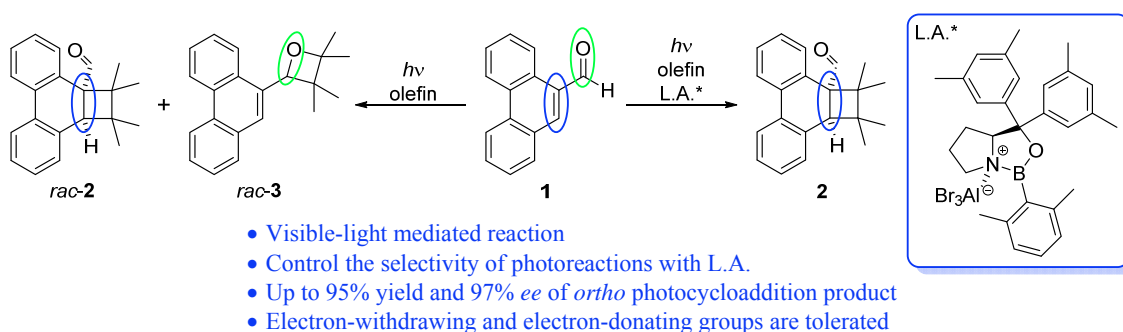


CHROMOPHORE ACTIVATION AT ITS BEST – INFLUENCING THE SELECTIVITY OF PHOTOREACTIONS BY ADDITION OF LEWIS ACIDS

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Enantioselective catalysis of photochemical reactions is a challenge that many groups have faced in recent years. Several approaches have been developed to control the selectivity in the excited state [1]. Among others, it has been shown that chiral Lewis acids can be used to promote enantioselective intra- and intermolecular [2+2] photocycloaddition reactions of enones [2]. However, photocycloaddition reactions of aromatic aldehydes with olefins have not been thoroughly explored. Herein, the intermolecular *ortho* photocycloaddition reaction of phenanthrene carboxaldehyde (**1**) was studied, with a focus on the use of achiral and chiral Lewis acids in order to influence the selectivity of the reaction [3].



Without Lewis acids both expected products, the *ortho* photocycloaddition product **rac-2** and the oxetane **rac-3** were formed. The addition of Lewis acids led to an extensive bathochromic shift of the absorption band with π,π^* character and therefore selective excitation of the Lewis acid substrate complex was possible. Irradiation of this complex with visible light led to exclusive population of the π,π^* state and consequently to the formation of the *ortho* photocycloaddition product **2** as the only photoproduct.

Currently, the photochemical reactivity of 1-naphthaldehyde and 2-naphthaldehyde with olefins is under investigation. It is known that when irradiated with light of short wavelength, both aldehydes only show reactivity at the carbonyl group [4]. However, there are indications that the aromatic ring can be activated by catalytic amounts of Lewis acids and as a result the type selectivity of photoreactions can be reversed.

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