Since its discovery in 1949 by Brown and Farthing [1], [2.2]para-cyclophanes have been intensely studied by chemists. Consisting of two benzene rings bound together by two ethano bridges, the [2.2]paracyclopahne core can undergo chemical transformations specific to both aliphatic and aromatic compounds, resulting in a wide variety of functionalized [2.2]paracyclophanes. Thus, cyclophanes are ideal model systems to investigate whether and how functionalized groups can interact and react with each other. Because of the rigid molecular framework provided by the paracyclopahne moiety and its short interannular distance, functional groups in pseudo-geminally substituted [2.2]paracyclophanes are often held in such a position as to allow highly specific reactions to take place between them. Both the parent hydrocarbon and its derivatives have been used in asymmetric catalysis, optoelectronics and polymer synthesis.

Acetylene-substituted paracyclophanes are important because of the ability of the acetylene moiety to easily undergo coupling and addition reactions, leading to new derivatives that contain one or more units of the [2.2]paracyclopahne core. Orthogonal \( \pi \)-bridges have been introduced into [2.2]paracyclophanes by the reaction of the pseudo-geminal bisacetylene with various monoacetylenes and nitriles [2]. This procedure can incorporate not only aromatic but also heteroaromatic bridges, as in pyridine-annulated cyclophane. Mono, pseudo-gem and pseudo-para ethynylcyclophanes and bis(azides) have been employed as addition partners in CuAAC reactions to design and build complex extended molecular scaffolds [3]. The reactivity of the resulting triazoles was investigated under photochemical conditions. A variety of newly substituted [2.2]paracyclophanes were identified; deazotization of pseudo-gem and pseudo-para adducts provided indolophane derivatives. An intramolecular stabilization effect was observed in the case of pseudo-gem derivatives. A photochemical rearrangement from a pseudo-para adduct to a pseudo-ortho product was identified.

\[\text{[1]} \text{ Brown CJ, Farthing AC (1949) Nature 164: 915-916.} \]
\[\text{[2]} \text{ Birsa ML, Jones PG, Hopf H (2011) Synlett: 259-261.} \]