# Generation of homosumanene *ortho*-quinone under photo-irradiation and its synthetic application to azaacene-fused homosumanenes

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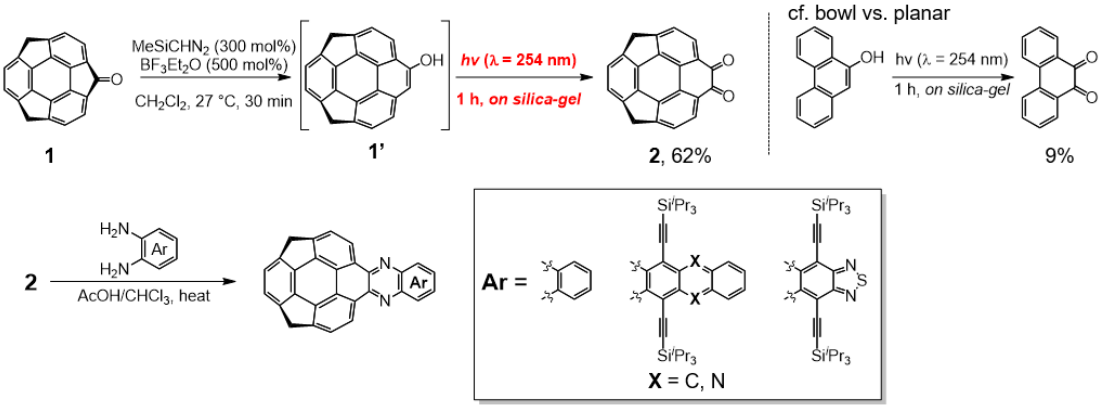
Highly strained buckybowls, such as sumanene, are suitable as a starting material to synthesize less distorted buckybowls through a series of ring-expansion reactions.[1] Recently, we have reported synthesis of C70 fragment, homosumanene via Büchner–Curtius–Schlotterbeck reaction from sumanenone (**1**).[2] In the course of our previous work, we noticed that hydroxyhomosumanene (**1'**) generated by treating **1** with $Me_3SiCHN_2$ was oxidized during the purification to give *o*-quinone (**2**) as a byproduct. In this study, we investigated the synthesis of **2** and its azaacene-fused derivatives.

Aerobic oxidation of **1'** proceeded efficiently on silica gel to give **2** in 62% yield under the irradiation of UV light (254 nm). The reaction of planar analogue having a substructure of **1'** proceeded much slower than **1'**, which was attributed to the structural difference between planer and curved π-system. The condensation reaction between **2** and aromatic diamines took place to afford azaacene-fused homosumanenes (**3**–**6**). Single crystal X-ray diffraction analyses of azaacenes showed stacked structures due to the interactions between each bowl. Cyclic voltammetry measurements suggested that they have high electron affinity due to the combination of curved buckybowl and electron-deficient azaacene structures.

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2) M. Nishimoto, Y. Uetake, Y. Yakiyama, H. Sakurai, *J. Org. Chem.* accepted.

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