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TiO_2-catalyzed direct diazenylation of active methylene compounds with diazonium salts

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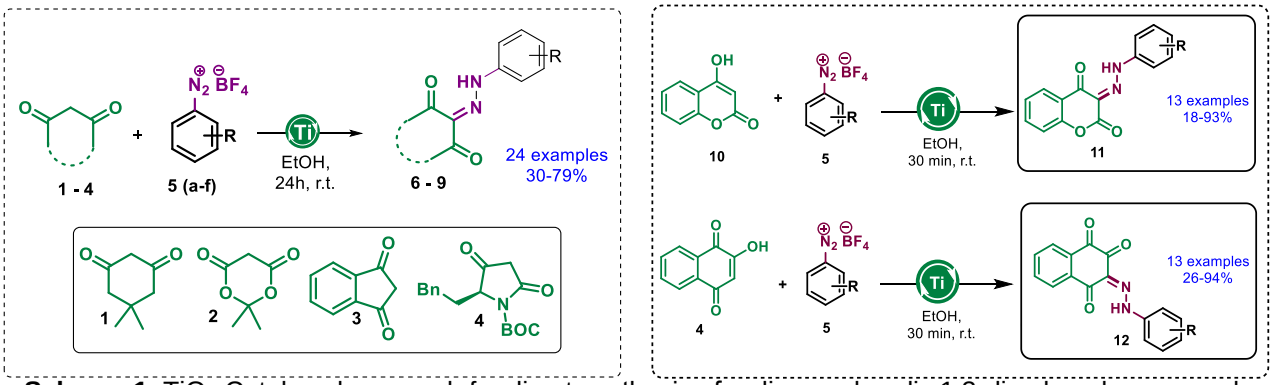
ABSTRACT

Azo compounds play a crucial role in medicinal chemistry, serving as fundamental building blocks for substances with diverse bioactivities.[1,2] Direct diazenylation via active methylene species emerges as an efficient strategy for incorporating the azo group into the structure of cyclic 1,3-dicarbonyl compounds (or in its enol form). Moreover, 1,3-carbonyl structures, such as coumarins and naphthoquinones are recognized pharmacophores of bioactive compounds, exhibiting remarkable antioxidant properties and actively participating in redox reactions.[3,4] These hallmarks make them highly valuable targets in pharmaceutical research focused on therapeutic development. Within this scope, his work reports a rapid, and scalable direct diazenylation of cyclic 1,3-dicarbonyl compounds, 4-hydroxycoumarin, and lawsone, employing an accessible and recyclable, heterogeneous catalyst (TiO_2) (Scheme 1). This transformation showed high compatibility with both electron-rich and electron-poor diazonium salts, and the corresponding products were isolated in good yields using eco-friendly solvents at room temperature.



Scheme 1. TiO_2-Catalyzed approach for direct synthesis of α-diazoaryl cyclic 1,3-dicarbonyl compounds.

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