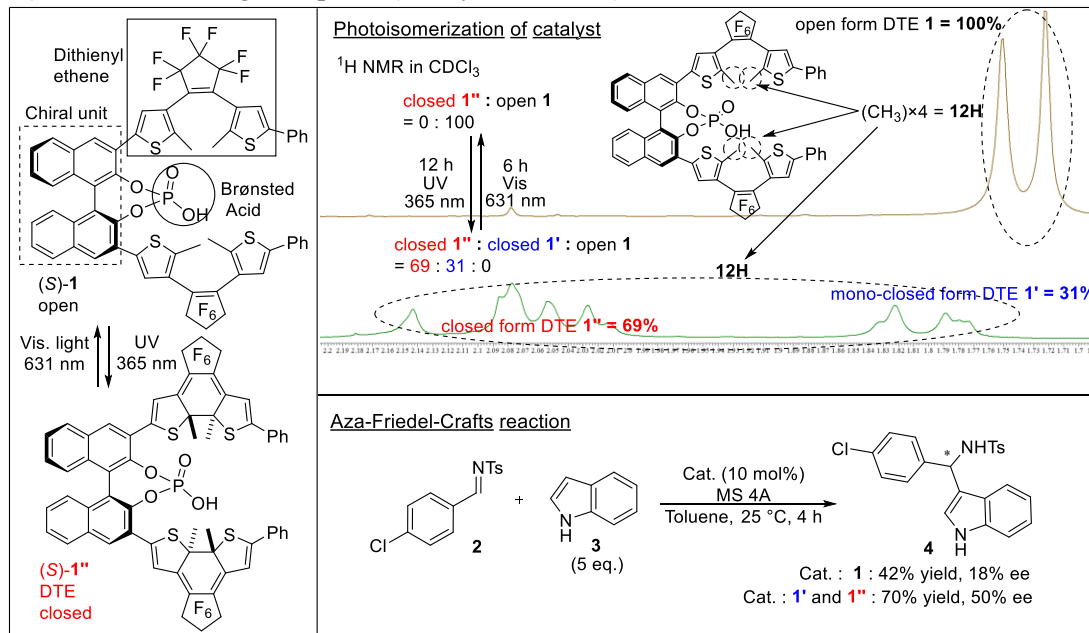


Development of Photoresponsive Chiral Brønsted Acid Catalyst

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The open/closed photoisomerization of dithienylethene (DTE) derivatives by irradiating light with arbitrary wavelength significantly switches their steric and electric properties.¹ To date, DTE derivatives have been utilized in the field of materials science. Despite their unique properties, DTE derivatives were less explored as a key unit for a photoswitchable catalyst. Herein, we report a chiral Brønsted acid catalyst **1** bearing DTE moieties as photoresponsive units. When photoisomerization of **1**, under UV irradiation for 12 h, the open form DTE **1** was completely converted into the closed form DTE **1''** and the mono-closed form DTE **1'** in the ratio of 69 to 31 as the corresponding diastereomixture. We also confirmed that the mono-closed **1'** and the closed **1''** were reversibly isomerized to open **1** under visible light irradiation for 6 h. To investigate catalytic activity between the open **1** and the closed **1'** and **1''**, aza-Friedel Crafts reaction² of aldimine **2** and indole **3** was examined; the reaction catalyzed by the closed **1'** and **1''** afforded the higher yield and enantioselectivity of product **4** (70% yield, 50% ee) than that of using the open **1** (42% yield 18% ee).



1) M. Irie, *Chem. Rev.* **2000**, *100*, 1685. 2) S.-L. You, Q. Kang, Z.-A. Zhao, *J. Am. Chem. Soc.*, **2007**, *129*, 1484.