



Photocontrol of an enantioselective reaction using a chiral supramolecular catalyst

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Abstract

We have developed a supramolecular photoswitchable crown ether which can work as a chiral phase transfer catalyst for the first time. The crown ether bearing a wide variety of ring sizes can be prepared in a short step from commercially available chemicals. The developed catalyst was applied to the asymmetric synthesis of chiral amino acid precursors. Under the irradiation of UV, the photoswitchable crown ether promoted the asymmetric reaction to afford the desired product in a good yield and high enantioselectivity. In contrast, the catalyst activity greatly dropped in the absence of light irradiation.

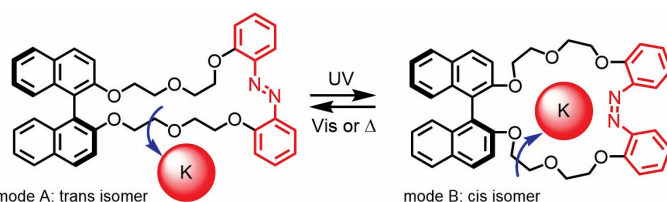
Background & Results

The development of green catalytic asymmetric processes has been important for the efficient synthesis of optically active compounds toward SDGs. In recent, photo-responsive chiral catalysts using a light as a clean energy have also attracted much attention. These catalysts can switch the reactivity and selectivity on the enantioselective reaction through the control of the period and wavelength of light irradiation. Although acid-base and metal catalysts have been investigated to date, the development of chiral phase transfer catalysts, which is useful for asymmetric synthesis of unnatural amino acid derivatives, has been unexplored. Moreover, conventional light-responsive asymmetric catalysts often require a multi-step synthesis, being a barrier for a practical use. This time, we developed a photoresponsive chiral phase transfer catalysts that can be synthesized in a short step from commercially available chemicals such as BINOL and azobenzene. Polyethylene glycol linkages between chiral BINOL backbone and azobenzene as a photoresponsive unit led to formation of the designed crown ether. The NMR and UV-Vis studies of the catalyst structure indicated that the reversibly change by irradiation of UV and visible lights. When the catalyst with KOH was applied to the enantioselective reaction of glycine Schiff bases with benzyl bromides, under the UV irradiation the desired amino acid precursor was obtained in high yields and high stereoselectivities. In contrast, the reactivity was decreased in the absence of light or under visible light irradiation. The photoisomerization made a change of the catalyst structure, resulting in control of the reactivity.

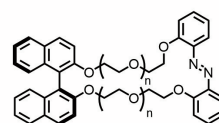
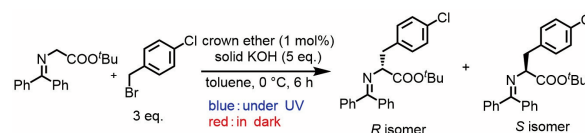
Significance of the research and Future perspective

Toward the SDGs, environmentally friendly, energy- and resource-saving synthetic methodologies of fine chemicals have been highly demanded. The present photoswitchable organocatalyst could express multiple functions for on-demand synthesis of optically active compounds as well as saving cost for development of catalyst. Although we focus on the reactivity switching with the external stimulus at this moment, the chemo- and stereoselectivities could be controlled by just irradiation of various light wave-

length in near future.



Photoswitchable chiral phase transfer catalyst (Azobenzene binaphthyl crown ether)



n = 0	45%, R:S = 58:42 (ON)
(O: 4)	trace, R:S = no data (OFF)
n = 1	75%, R:S = 92:8 (Fast)
(O: 6)	11%, R:S = 92:8 (Slow)
n = 2	59%, R:S = 52:48 (R major)
(O: 8)	80%, R:S = 46:54 (S major)

Photocontrol of reactivity for enantioselective alkylation of glycine Schiff base

Patent

Kondo, Masaru; Takizawa, Shinobu; Sasai, Hiroaki et al. Photoswitchable Chiral Phase Transfer Catalyst. ACS Catalysis. 2021; 11 (3): 1863-1867. doi: 10.1021/acscatal.1c00057

Treatise

Kondo, Masaru; Takizawa, Shinobu; Sasai, Hiroaki et al. Azopyridine-based Chiral Oxazolines with Rare-earth Metals for Photoswitchable Catalysis. Chem. Commun. 2021; 57 (60): 7414-7417. doi: 10.1039/D1CC02602J

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<https://www.thieme-connect.de/products/ejournals/abstract/10.1055/s-0040-1706168>

Keyword

photoswitchable catalyst, asymmetric reaction, amino acid synthesis, crown ether