An Efficient Asymmetric Olefin Aziridination Using a Newly Designed Ru(CO)(salen) Complex as Catalyst

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This report describes that highly enantioselective aziridination of conjugated and non-conjugated terminal olefins and cyclic olefins could be achieved using a newly designed Ru(CO)(salen) complex as the catalyst under mild conditions in the presence of $SESN_3$. Asymmetric aziridination (AA) using azides as nitrene precursors has been intensively studied, because of its high atom efficiency and the high utility of aziridine products as building blocks. Besides, AA is the most straightforward tranformation of olefins to chiral aziridines. Several groups including our group have reported efficient AA using azides, but further reduction of catalyst loading, improvement of molecular ratio between olefin and azide and increase of the chemical yields in the aziridination of non-conjugated olefins are required. Recently, we synthesized 'robust Ru-salen complex' and reported that this robust Ru(CO)-salen complex bearing 3,5-dichloro-4-trimethylsilylphenyl group at C2" as a stereocontrolling unit catalyzes highly enantioselective aziridination. However, substrate scopes are limited to conjugated olefins. To develop and improve the catalytic reactivity, we designed and synthesized new Ru(CO)(salen) complex **3** having 3,5-di(trifluoromethyl)phenyl group at C2" position. Our expectation based on the previous report is that the introduction of trifluoromethyl group can deliver the good catalytic activity through an interaction between the lone pair electrons on the sulfonyl oxygen atom and a low-lying anti-bonding orbital of C-F bond and increase the durability of the complex by the interaction between C-F antibonding orbital and π-orbital of the C2" phenyl group. As our hypothesis, newly designed Ru(CO)(salen) complex bearing 3,5-trifluoromethylphenyl group at C2" is more durable and catalytically active and catalyzes aziridination of 1-alkenes with high enantioselectivity (up to 99% ee) and acceptable yields at low catalyst loading (0.5~3 mol %) under mild conditions. Conjugated terminal and *cis*-disubstituted olefins also undergoes aziridination in high enantioselectivity and good to high yields. We developed less waste-forming AA.