

A theoretical study on Ir(III)-catalyzed intermolecular branch-selective allylic C-H amidation

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Abstract

Herein, we report the mechanism of Ir(III)-catalyzed intermolecular branch-selective allylic C-H amidation, including the influence of substituent effect on yield and regioselectivity. The sequence of amidation reaction is alkene coordination, allylic C-H activation, oxidative addition of methyl dioxazolone, reductive elimination of allyl-Ir-nitrenoid complex, amine protonation and proto-demetalation. The apparent activation energy of amidation between hexene and methyl dioxazolone is 17.8 kcal/mol, and the energy difference between two transition state for formation amide is only 2.8 kcal/mol. The introduction of more electron-deficient groups at the allyl terminal increases the apparent activation energy, conversely, the introduction of electron-donating groups significantly reduces the apparent activation energy. Among them, the apparent activation energy of the reaction between aniline group substituted allyl and methyl dioxazolone is only 13.8 kcal/mol, which further improves the reaction yield. In addition, the introduction of more electron-withdrawing groups on dioxazolone can significantly improve the regioselectivity. When 3,4,5-trifluorophenyl substituted dioxazolone and hexene occur C-N bond coupling reaction, the energy difference of the two transition states is as high as 9.0 kcal/mol, indicating that the regioselectivity is greatly improved. The mechanism explanation of allylic C-H amidation will provide strong theoretical support for streamlined synthesis of allyl branched amides.

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