

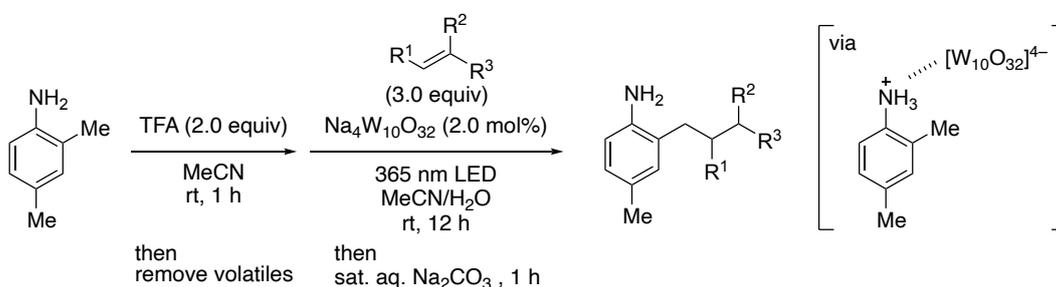
Decatungstate-catalyzed Site-selective C(sp³)-H Alkylation of 2-Methylanilinium Salts Controlled by Noncovalent Interactions

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Regioselective C(sp³)-H functionalization is one of the most significant issues in organic synthesis. Although radical chemistry is a powerful tool for the activation of C(sp³)-H bonds, it is still difficult to convert C(sp³)-H bonds in a similar environment with high selectivity because the selectivity of hydrogen atom abstraction is generally determined by the steric and the electronic properties of the C(sp³)-H bonds. We have reported iridium-catalyzed *meta*-selective C(sp²)-H borylation, which was controlled by hydrogen bonds between the designed ligand and the functional group of substrates.¹ To develop regioselective C(sp³)-H functionalization through radical pathway, we focused on the noncovalent interactions between the substrate and the catalyst. We envisioned the anionic decatungstate photocatalyst, which is known as an efficient catalyst for C(sp³)-H functionalization, should interact with the cationic functional group of substrates.² Herein, we report a site-selective C(sp³)-H alkylation of 2-methylanilinium salts via radical intermediates.

The TFA salt of 2,4-dimethylaniline was reacted with electron-deficient alkenes in the presence of the decatungstate photocatalyst under UV irradiation. The C(sp³)-H alkylation proceeded at the proximal methyl group with high selectivity. A variety of 2-methylanilines could be applied to this reaction, and the synthetic conversion of the product was also successful. Mechanistic studies indicated the existence of the interaction between the ammonium group of substrates and the decatungstate photocatalyst.



1) Y. Kuninobu, H. Ida, M. Nishi, M. Kanai, *Nature Chem.* **2015**, 7, 712. 2) J. Zeng, T. Torigoe, Y. Kuninobu, The 100th CSJ Annual Meeting, 3H8-04.