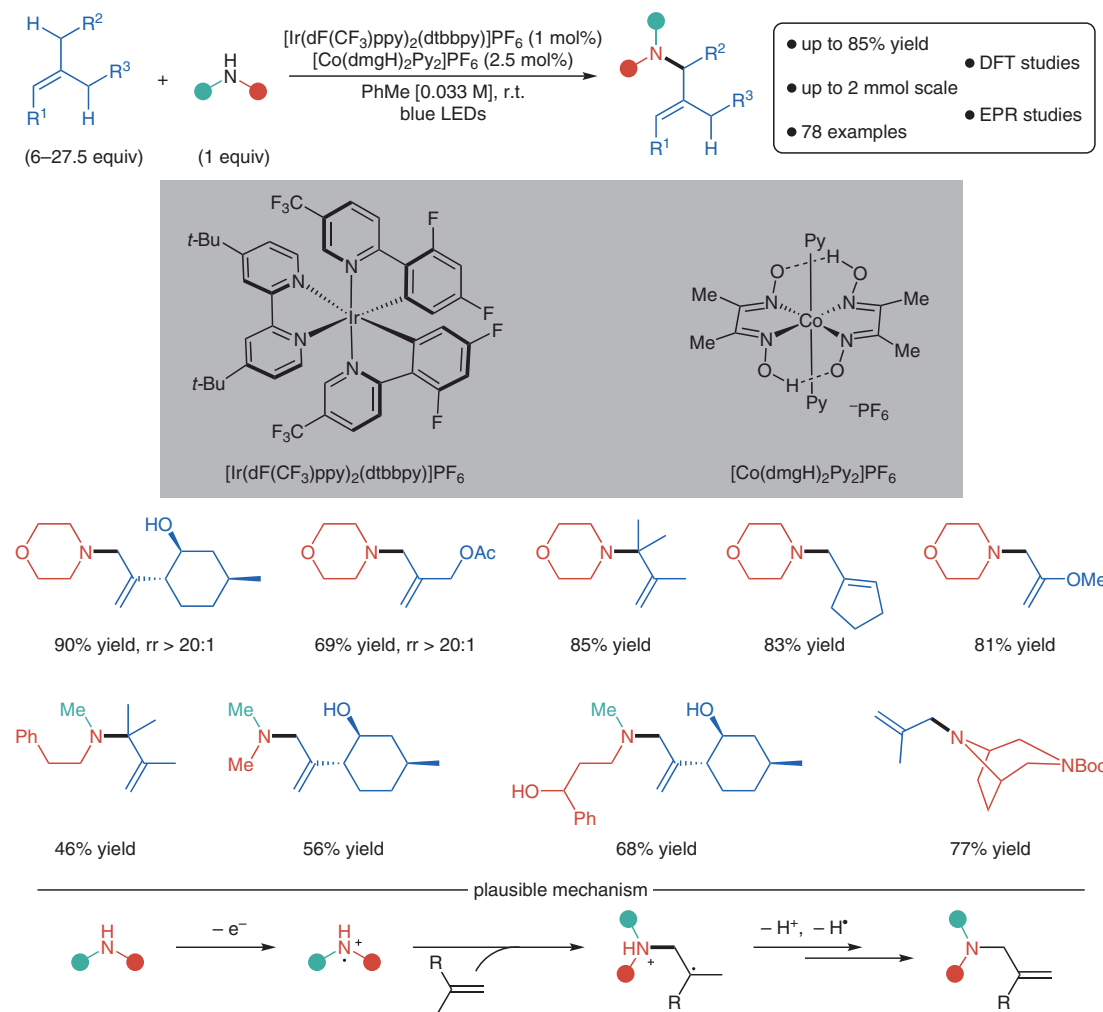


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Site-Selective Amination towards Tertiary Aliphatic Allylamines

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Site-Selective Allylic C–H Amination of Alkenes Enabled by Formation of an Aminium Radical Cation



Significance: The groups of Qi and Lei have developed a cobalt-catalyzed photoredox approach for the site-selective amination of alkenes bearing allylic hydrogens. The reaction proceeds with high regioselectivity for the primary allylic C–H bond over secondary or tertiary C–H bonds. The reaction displayed high functional group tolerance and was compatible with natural products, pharmaceuticals, and tetrasubstituted olefins.

Comment: X-ray fine-absorption spectroscopy revealed that the cobalt catalyst was not coordinated to the alkene or reduced by amines. Furthermore, spin trapping experiments led to an observed EPR signal, suggesting the formation of a radical intermediate. In combination, these results support a hydrogen-atom transfer pathway that involves the cobalt catalyst. Density functional theory (DFT) indicated that the preferred pathway involved an aminium radical cation and not an N-centered radical.

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