

# Photocatalytic Dehydrogenative Amination of Cyclohexanones

Category

Polymer-Supported Synthesis

Key words

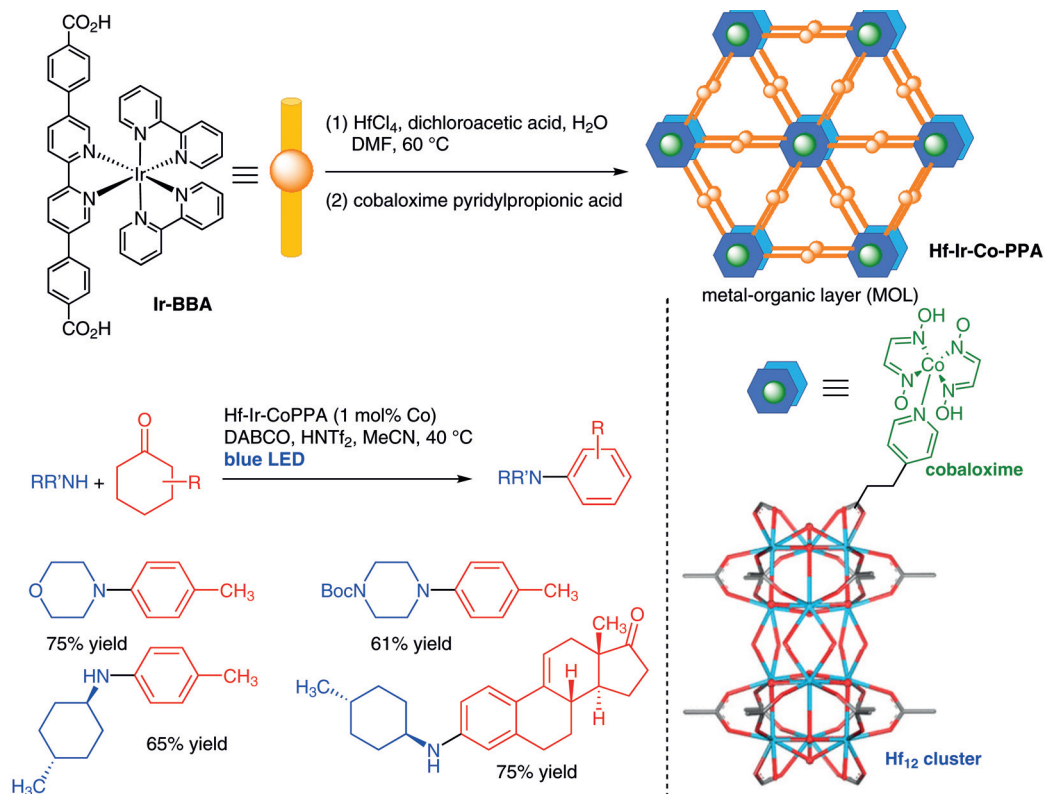
photocatalysis

metal-organic layer

cobalt catalyst

dehydrogenative amination

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**Significance:** A metal organic layer (MOL) Hf–Ir composite was prepared from a photosensitizing Ir–BBA complex and  $\text{HfCl}_4$  under solvothermal conditions. A cobaloxime unit was added to the resulting Hf–Ir MOL with a pyridylpropionate (PPA) tether to give Hf–Ir–CoPPA. The Hf–Ir–CoPPA promoted a dehydrogenative amination of cyclohexanones to give the corresponding *N*-alkyl anilines with photo irradiation by blue LED. The amination of a steroidal 3,17-diketone took place with excellent chemoselectivity to give the corresponding A-ring amination product exclusively.

**Comment:** ICP analysis of Hf–Ir–CoPPA revealed that the MOL composite had a Hf/Ir/Co ratio of 1.0/0.54/0.40. A 2D-monolayered double-decker structure of Hf–Ir–CoPPA was constructed with  $\text{Hf}_{12}$  cluster units and bridging-ligand units Ir–BBA. Hf–Ir–CoPPA was recovered by centrifugation and reused 8 times without significant loss of its catalytic performance. Hf–Ir–CoPPA also catalyzed the Heck-type coupling of alkyl iodides with styrenes to give the corresponding  $\beta$ -substituted styrenes.