

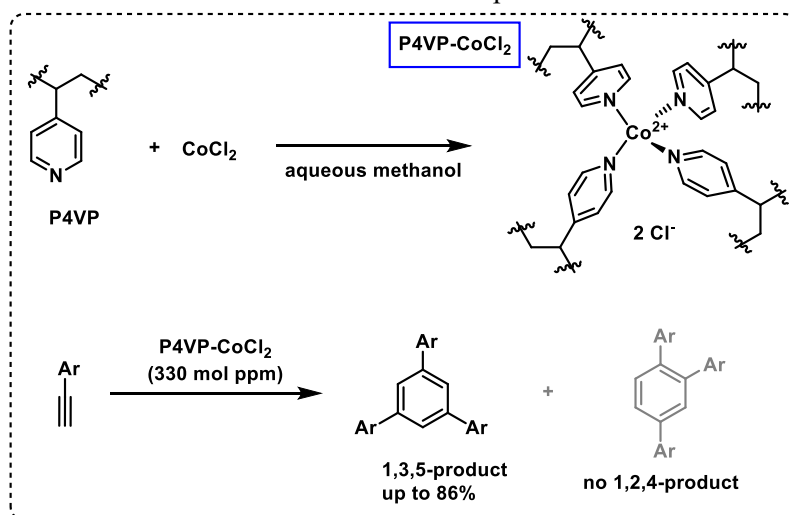
Convoluting Polymer-Supported-Cobalt-Catalyzed Regioselective Cyclotrimerization of Aryl Alkynes

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Transition metal-catalyzed cyclotrimerization of aryl alkyne is a well-known reaction.¹ Among the transition metals, cobalt is one of the most commonly used metals.² The cobalt catalyzed cyclotrimerization usually afforded a mixture of 1,2,4-triarylbenzene and 1,3,5-triarylbenzene where 1,3,5-triarylbenzene is obtained as a minor product. Contrarily, these C₃-symmetric 1,3,5-triarylbenzenes are useful because of their application as polycyclic aromatic hydrocarbons (PAHs) and functional materials.³ Unfortunately, used cobalt catalysts are not reusable and required high catalyst loading.

This time, we developed a poly(4-vinylpyridine), P4VP-self-supported novel, stable, and heterogeneous cobalt catalyst P4VP-CoCl₂ by using our molecular convolution method.⁴ The structure was determined based on theoretical and experimental calculation. When the reaction of aryl acetylenes was carried out with 330 mol ppm of P4VP-CoCl₂ under neat conditions, exclusive 1,3,5-selective cyclotrimerization proceeded with up to 86% yield whereas no 1,2,4-selective product was obtained. The catalyst was recoverable and reusable. The catalyst tolerates gram-scale reactions. Functional materials were also synthesized. Details on substrate scope and mechanistic studies will be discussed in the presentation.



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