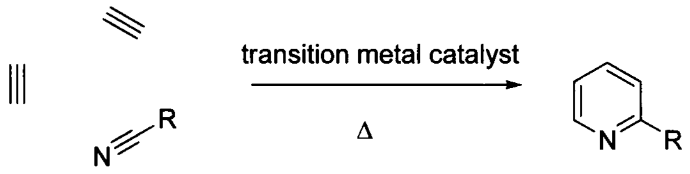
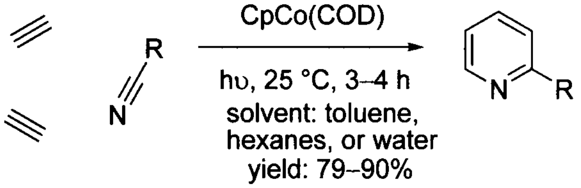
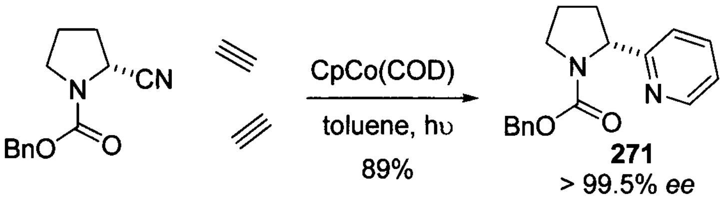


A number of transition metal complexes has been developed for the [2 + 2 + 2]-cycloaddition reaction, among which cobalt-based catalysts are most widely used. In 1973, Yamazaki and Wakatsuki reported the first synthesis of pyridines using stoichiometric and later on, catalytic cobaltacyclopentadienes.[165]

Irradiation of the reaction mixture with UV-Vis light (350–500 nm), or sunlight enabled the reaction to be carried out at room temperature.[166] The photochemistry process provided improved chemoselectivity by avoiding the homocyclotrimerization for the alkynes.[167] For example, photo-catalyzed [2 + 2 + 2]-cycloaddition of various nitriles with acetylene at room temperature in the presence of $CpCo(COD)_2$ provided the corresponding 2-pyridines such as **271** in 3–4 h in good to excellent yields.[168]





The limitation of the reaction is obvious. When terminal alkynes reacted with nitrile, they give a mixture of 2,4,6-trisubstituted and 2,3,6-trisubstituted pyridines, with the former being the dominant product. The electron density of the metal affected the yields and regioselectivity of the reaction.[164b,169,170] In general, two approaches are employed to control regioselectivity and to enhance reactivity by tethering two of the three reaction components: i) reaction of diakynes such as α,ω-diynes, cyanoalkynes and nitriles or ii) reaction of nitrilediynes with alkynes, thus, providing bicyclic or multicyclic pyridines.

Besides Co,[171] a number of transition metal complexes such as Ru,[172] Rh,[173] Ni,[174] Ti,[175] Zr/Ni[176], and Fe[177] catalyst systems, have also been