

ABSTRACT
SYNTHETIC AND MECHANISTIC STUDIES OF RUTHENIUM CATALYZED
C–C, C–H AND C–N BOND ACTIVATION REACTIONS

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Transition metal-catalyzed selective C–H, C–C and C–N bond activation reactions represent a challenging and synthetically important field in organic chemistry. In particular, transition-metal catalytic unreactive bond activation protocols are applicable in various stereoselective and atom economical complex organic molecule synthesis. Recently, significant research efforts have been made for utilizing catalytic C–H and C–C bond cleavage methods in the further development of commercially valuable pharmaceuticals and agrochemicals.

The well-defined cationic Ru–H complex was found to be an effective catalyst for mediating the coupling reaction of 1,2-disubstituted indoles with α,β -unsaturated aldehydes and ketones, in which the regioselective C α –C β activation of the carbonyl substrates has been achieved in forming a series of 3-alkylindole products. The analogous coupling reaction of indoles with saturated aldehydes and ketones directly led to the C α –C β cleavage of the carbonyl substrates in forming the 3-alkylindole derivatives. The cationic Ru–H complex was found to be an effective catalyst for the dehydrative C–H coupling reaction of phenols and aldehydes to form 2-alkylphenol products. The coupling reaction of phenols with branched aldehydes selectively formed 1,1-disubstituted benzofurans, while the analogous coupling reaction with salicylaldehydes yielded xanthene derivatives. The DFT calculations provided a detailed catalysis mechanism featuring an electrophilic aromatic substitution of the aldehyde followed by the hydrogenolysis of the hydroxy group. The calculations also revealed a mechanistic rationale for the strong electronic effect of the aldehyde substrates p -X-C₆H₄CHO (X = OMe, CF₃). We also developed an innovative multi-component deaminative catalytic reaction to synthesize xanthene and bicyclic dioxo-core structures efficiently. This multi-component coupling method facilitates multiple bond-breaking and forming operations in a single reaction sequence to assemble synthetically valuable complex organic molecules.