

Abstract

The thesis entitled “**Carbon–Carbon and Carbon–Heteroatom Bond Formation from pi-Activated Alcohol using an Iridium–Tin Heterobimetallic Catalyst**” is primarily an effort towards the exploration of the catalytic activity of the heterobimetallic $[\text{Ir}(\text{COD})(\text{SnCl}_3)\text{Cl}(\mu\text{-Cl})]_2$ (here after $\text{Ir}^{\text{III}}\text{-SnCl}_3$) catalyst, which could be easily synthesized from corresponding Ir(I)-diene complex and tin(IV) chloride. The results are described in mainly three parts. They are summarized below.

The catalyst $\text{Ir}^{\text{III}}\text{-SnCl}_3$ successfully activates the propargylic alcohols, bearing both internal as well as terminal alkynes moiety, towards nucleophilic substitution of propargylic alcohols with different carbon (arene, heteroarene, allyltrimethylsilane, 1,3-dicarbonyl compound), sulfur (thiol), oxygen (alcohol), and nitrogen (sulfonamide) nucleophiles. Hammett study on propargylic alcohol resulted in a moderate negative reaction constant (ρ) value (-1.45), which supports an electrophilic mechanism for the propargylation reaction. From in situ 1D and 2D ^1H NMR studies, we tentatively conclude that the pre-activation of the propargylic alcohol across the $\text{Ir}^{\text{III}}\text{-SnCl}_3$ involves initial coordination of the alcoholic -OH group at the hard Sn(IV)–center. The tertiary propargylic alcohols with aryl substituent at the alkyne terminus produced 1,3-substituted indenenes with bulky arenes via allenyl intermediate. To establish the plausible interplay of allenyl intermediate, one of the indene formation reactions was monitored by in situ ^1H NMR spectroscopy. The ability of $\text{Ir}^{\text{III}}\text{-SnCl}_3$ complex to catalyze the direct substitution of hydroxyl groups in different propargylic alcohols by 1,3-dicarbonyl compounds was also observed. The reaction was general with respect to substitution in the 1,3-dicarbonyl framework as well as at the alkyne terminus in propargylic alcohol. In 4-hydroxycoumarin, propargylation occurred at the 3-position. Selective propargylation or allenylation took place depending on the nature of propargylic alcohols. By utilizing this methodology as the key step, a number of structurally diverse and fully decorated furans and pyrroles were synthesized from propargylic substituted 1,3-dicarbonyl derivatives in one-pot.

In continuation with the objective of the thesis, an efficient nucleophilic substitution of allylic alcohols with carbon (arene, heteroarene, allyltrimethylsilane, 1,3-

dicarbonyl compound), sulfur (thiol), oxygen (alcohol), and nitrogen (sulfonamide) nucleophiles was also demonstrated using the Ir^{III}-SnCl₃ catalyst. In the absence of any nucleophile, the activated diaryl substituted allylic alcohols underwent Ir^{III}-SnCl₃ catalyzed disproportionation reaction providing the corresponding reduced alkene and chalcone via the intermediacy of an ether. Hammett study on allylic alcohol resulted in a moderate negative reaction constant (ρ) value (-2.00), which supports an electrophilic mechanism for the allylation reaction.

The Ir^{III}-SnCl₃ motif could also activate 1° and 2° benzylic alcohols towards the benzylation of 1,3-dicarbonyl compounds with various benzylic alcohols as benzylating agent. The reaction was general with respect to substitution in the 1,3-dicarbonyl framework and aryl substituent in the benzylic alcohol skeleton. 3-Substituted coumarin analogs were synthesized through the benzylation of 4-hydroxycoumarin with various benzylic alcohols.

Keywords: Heterobimetallic, Iridium, Tin, Catalyst, Alcohol, Propargylation, Allenylation, Allylation, Benzylation, Disproportionation, Indenes, Furans, Pyrroles, Electrophilic Mechanism.