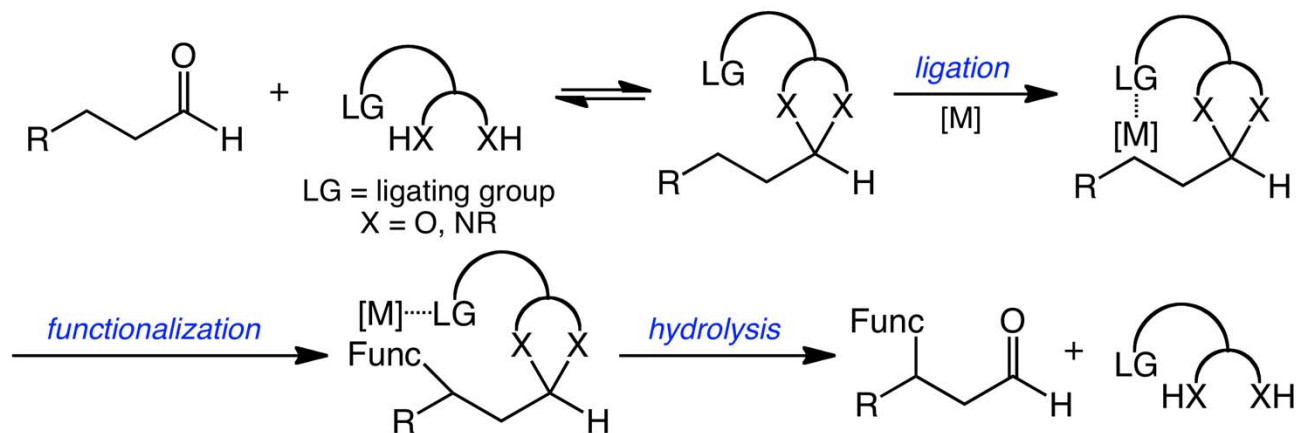


# Ligand-Linked Catalysis: Metal-Catalyzed Functionalization via Transient Directing Group Installation

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**Ligand-Linked Catalysis:** We are currently investigating a unique approach to metal-catalyzed remote functionalization, wherein we utilize covalent attachment to temporarily install a ligand framework onto a substrate. This adduct can then appropriately position the metal catalyst to functionalize the substrate in a site-specific fashion. It is anticipated that this versatile approach to functionalization will lead to transformations currently unrealized by either transition metal catalysis or organocatalysis approaches.



Our initial studies have focused on the design of a ligand framework that would be suitable for imparting the desired reactivity. To this end, we have synthesized a pyrrolidine scaffold based on readily available proline. This ligand can be condensed with aromatic and aliphatic aldehydes to form aminals such as compounds **1** and **3**. Under palladium-catalyzed oxidative conditions, arenes can be functionalized at the ortho position with high selectivity. Aminals based on aliphatic systems can also be oxidized with excellent levels of stereoselectivity, showing acetoxylation of one of the two diastereotopic methyl groups.

