Abstract
We are engaged in the first systematic efforts to develop “C-C bond forming hydrogenations” beyond hydroformylation - processes in which two or more reactants are hydrogenated to form a single, more complex product. Using cationic rhodium and iridium catalysts, diverse π-unsaturated reactants reductively couple to carbonyl compounds and imines under hydrogenation conditions, offering a byproduct-free alternative to stoichiometric organometallics in a range of classical C=X (X = O, NR) addition processes. This concept is extended further via “C-C bond forming transfer hydrogenation.” In such processes, the exchange of hydrogen between alcohols and π-unsaturated reactants triggers the generation of aldehyde-organometal pairs that combine to give products of carbonyl addition. Direct alcohol CH-functionalization in this manner is byproduct-free. This new pattern of reactivity enables direct C-C coupling of methanol and other renewable alcohols (ethanol and glycerol) to abundant π-unsaturated reactants (α-olefins, styrene, butadiene and isoprene) to furnish higher alcohols, and has been used to construct diverse polyketide natural products (bryostatin, roxaticin, 6-deoxy erythronolide).