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Classically, the practice of chemical synthesis has focused on building hydrocarbon scaffolds while concurrently introducing oxygen, nitrogen, and carbon functionality. We have discovered and commercialized palladium/sulfoxide catalysts for allylic C-H functionalizations, iron(PDP) catalysts for aliphatic C-H hydroxylations, and manganese phthalocynine catalysts for intramolecular C(sp³)-H aminations. These catalysts proceed with unprecedented levels of reactivity and tunable selectivities in complex molecule settings, without the need for directing groups. We have delineated site-selectivity rules based on the physical organic properties of C-H bonds (electronic, steric, and stereoelectronic) that have proven general across a variety of aliphatic C-H functionalization reactions. Using these novel transition metal catalysts we have validated late stage C-H oxidation, i.e. direct introduction of oxidized functionality into C(sp³)-H bonds of molecule scaffolds, as a powerful approach for streamlining synthetic sequences and directly diversifying natural products, including complex peptides. This lecture aims to provide an overview of these areas in addition to current advances in chemoselective and asymmetric C-H oxidations.

