Directing group assisted alkylations with unactivated olefins were operationally simplified using tetraalkylammonium salts, which undergo an in-situ Hoffmann elimination to the corresponding olefin. This methodology allows the dosage of these gaseous compounds in stoichiometric amounts in (sub)–millimolar scale. For reactions that are not compatible with the basic conditions needed for the elimination, an operational simple separation of the olefin-production and the alkylation reaction is shown. During this approach the truly active species of a rhodium catalyzed alkylation reaction was identified.
