Studies concerning experimental and mechanistic aspects of the domino allylstannylation/Heck reaction of ortho-iodobenzaldehydes and related structures are described. (1) After the development of general reaction conditions structurally modified substrates were used and a broad spectrum of 3-methylene-1-indanols could be synthesised. Beside iodides, triflate and bromides in situ generated imines also proved to be suitable substrates. (2) Mechanistic investigations using in situ NMR-spectroscopy and X-ray diffractometry showed strong evidence for an intermediate palladacycle. A new intramolecular, electrophilic activation mode was postulated which consists of an activation of the aldehyde function through an adjacent Lewis-acidic PdII-center. Using control experiments it was shown that alkoxystannanes proved to be possible base equivalents in Heck reactions. (3) An enantioselective protocol using a model system could be developed by application of chiral ligands. A systematic ligand screening revealed Taniaphos to be the optimal chiral ligand with an induced enantiomeric excess of 96%. The established conditions could be applied to structural modified substrates. (4) The first steps in the synthesis of the natural product mutisianthol using the domino allylstannylation/Heck reaction as the key step demonstrates that this transformation generally serves to build up the required indan structural motif.