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AZIRIDINES -- EPOXIDES AS NEW SUBSTRATES FOR VISIBLE-LIGHT TRIGGERED GENERATION OF RADICALS -- SCOPE AND LIMITATIONS OF THE REDUCTIVE RING-OPENING METHODOLOGY -- UTILIZATION OF THE PHOTOGENERATED RADICALS IN CARBON-CARBON BOND FORMATIONS -- SUPPORTING INFORMATION -- GENERAL REMARKS -- GENERAL PROCEDURES -- EPOXIDE, AZIRIDINES AND CYCLOPROPANES PRECURSORS -- REDUCTIVE RING-OPENING PRODUCTS -- ALLYLATION PRODUCTS 246 -- PART C: NEW DEVELOPMENTS IN ARYL-ARYL COUPLINGS VIA PALLADIUM/NORBORNENE DUAL CATALYSIS: SYNTHESIS OF PHENANTHRIDINES AND PHENANTHRENES -- BIBLIOGRAPHICAL BACKGROUND: THE ORTHO EFFECT IN THE CATELLANI REACTION -- THE CATELLANI REACTION -- SYNTHETIC APPLICATIONS OF THE ORTHO EFFECT -- MECHANISTIC EXPLANATIONS FOR THE ORTHO EFFECT -- RESULTS: NEW PARTNERS FOR ORTHO-SUBSTITUTED ARYL IODIDES IN PALLADIUM/NORBORNENE COCATALYSIS -- COUPLING OF ORTHO-SUBSTITUTED ARYL IODIDES AND BROMOBENZYL AMINES: FIRST REPORTED CATELLANI SEQUENCE TERMINATED BY N-ARYL COUPLING WITH UNPROTECTED AMINES -- COUPLING OF ORTHO-SUBSTITUTED ARYL IODIDES AND 2-BROMOPHENYL ACETAMIDES: AN EXCEPTION TO THE ORTHO EFFECT -- SUPPORTING INFORMATION -- GENERAL REMARKS -- COUPLING OF ORTHO-SUBSTITUTED ARYL IODIDES AND BROMOBENZYL AMINES -- COUPLING OF ORTHO-SUBSTITUTED ARYL IODIDES AND 2-BROMOPHENYL ACETAMIDES.

Sommario/riassunto

In this dissertation, Marie-Hélène Larraufie develops original radical and pallado-catalyzed methodologies to enable the synthesis of several classes of bioactive nitrogen-containing heterocycles. New radical cascades employing the N-acylcyanamide moiety offer straightforward routes to quinazolinones and guanidines, as well as new insights into the mechanism of homolytic aromatic substitutions. In parallel, Larraufie expands the scope of visible light photoredox catalysis to the ring opening of epoxides and aziridines, thus providing new sustainable alternatives for the generation of radicals. Furthermore, in a collaborative effort with the Catellani group, the author investigates dual palladium/norbornene catalysis. First, she develops a C-amination coupling variant of the Catellani reaction with unprotected amines which provides an expeditious route to phenanthridines. Then, she examines the influence of the chelating effect on Pd(IV) intermediates reactivity with the help of experimental studies and DFT calculations. The work in this thesis has resulted in numerous publications in high impact journals. The clarity and depth of the experimental section will be useful for students and researchers working in this field. .
