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Title: Conversion of 2,3-Dihydrobenzo[b][1,4]dioxine-2-carboxamides to 3-Oxoquinolin-2(1H)-ones via

Ring-Opening and Formal 6-endo-trig Cyclization-Involved Heck Reactions

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 $Abstract: \qquad \text{We report the conversion of 2,3-dihydrobenzo[b][1,4] dioxine-2-carboxamides, (derived from 2,4] dioxine-2-carboxamides, (derived from 2,4] dioxine-2-carboxamides, (derived from 2,4] dioxine-2-carboxamide$

dihydrobenzo[b][1,4]dioxine-2-carboxylic acid and 2-haloanilines) to 3-oxoquinolin-2(1H)-one motifs using catalytic amounts of Pd(OAc)2, PPh3, BINOL and Cs2CO3 (1.5 equiv). This conversion occurred via the less common formal 6-endo-trig cyclization and chelation-controlled β -arylation (Heck-type reaction) pathways. Initially, a base-mediated ring-opening of the 2,3-dihydrobenzo[b][1,4]dioxine moiety generates an acrylamide intermediate in situ, which then undergoes a formal 6-endo-trig cyclization-involved Heck-type reaction to afford 3-oxoquinolin-2(1H)-one motif. The proposed acrylamide intermediate was isolated, characterized by the X-ray structure analysis and then, it was also treated under the experimental conditions, which afforded the expected 3-oxoquinolin-2(1H)-one; thus, providing a strong support for the proposed mechanism. Various 3-oxoquinolin-2(1H)-one motifs were synthesized in moderate to good yields.

Representative 3-oxoquinolin-2(1H)-one motifs were characterized by X-ray analysis.

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