Deciphering Regioselective *meta*-Olefination in Biaryl Systems with DFT Insights

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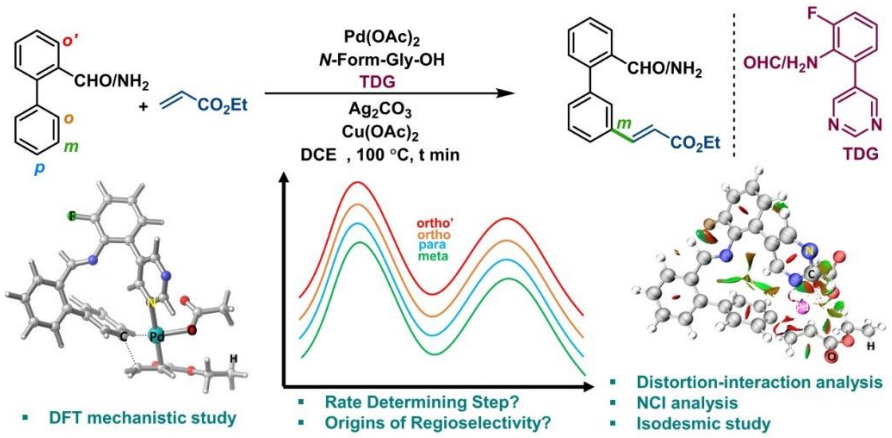
ABSTRACT

Despite the widespread utility of C–H functionalization reactions, achieving precise control over site selectivity remains a formidable challenge. In recent years, a novel palladiumcatalyzed C–(sp^2)-H olefination of 2-arylbenzaldehyde, facilitated by a temporary directing group (TDG) through reversible imine formation, has emerged as a promising approach for achieving selective meta-C–H functionalization.

This innovative strategy offers distinct advantages over the conventional covalently attached directing group (DG) approach. The focal point of this presentation will be on the computational investigations that shed light on the detailed reaction mechanism responsible for this remote meta-selectivity. Using density functional theory (DFT)-based computations, we conducted a comprehensive exploration encompassing all conceivable Pd-catalyzed templatedirected C–H olefinations (ortho', ortho, meta, para) of 2-aryl benzaldehyde/aniline.[1]

Distortion-interaction analysis (DIA), non-covalent interaction (NCI) analysis, and isodesmic studies were employed to unveil the origins of *meta*-regioselectivity. This presentation promises to provide invaluable insights into the mechanisms underlying TDG-assisted metaolefination of complex biaryl systems, offering a fresh perspective on achieving site-selective functionalization in complex systems and showcasing the potential of this innovative approach.



References

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