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Ruthenium(II)-Catalyzed C–H Alkenylation of SuFEx-Functionalized Quinones: A Mechanistic Approach

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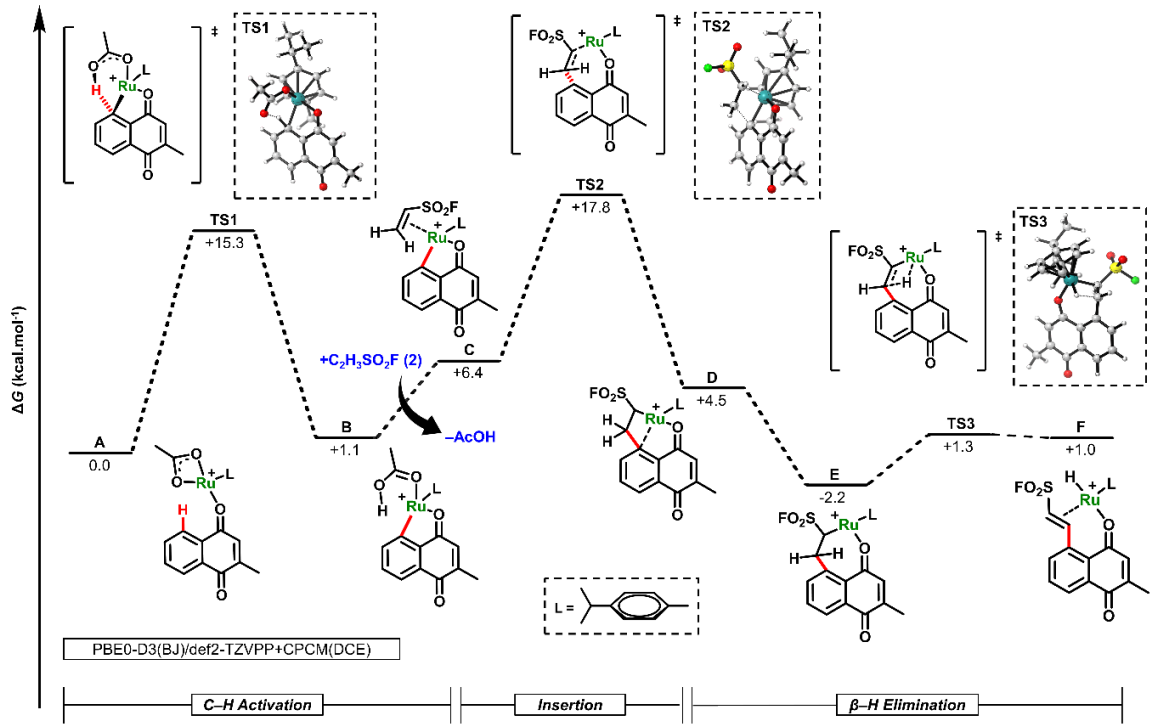
ABSTRACT

In the 21st century, the development of sustainable, selective, and modular click-reactions has revolutionized chemistry, enabling the rapid and efficient connection of molecular building blocks.[1] Within this concept, sulfur(VI) fluoride exchange (SuFEx) emerged as a second-generation click-type reaction, providing a protocol to obtain hypervalent sulfur derivatives under metal-free conditions.[2] Therefore, in pursuit of new C–H activation methodologies to afford direct functionalization of quinone motifs employing organometallic catalysis, our group has developed a ruthenium(II)-catalyzed C–H alkenylation route to access 1,4-naphthoquinone-based SuFEx–hybrids. In this work, aiming to investigate the alkenylation mechanism, we focus on a detailed computational approach using density functional theory (DFT). All free energies (ΔG) were computed at the PBE0[3]-D3(BJ)/def2-TZVPP+CPCM level of theory, following geometry optimizations and harmonic vibrational frequencies at PBE0-D3(BJ)/def2-SVP. Intrinsic reaction coordinate (IRC)[4] calculations were performed to verify the connectivity of transition states (TS), resulting in the proposed reaction pathway for the mono-methylated derivative.



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