Pd-CATALYZED ASSEMBLY AND MECHANISTIC ELUCIDATION OF TWISTED DONOR-ACCEPTORCARBAZOLE SCAFFOLDS

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Herein, the synthesis, mechanistic study, and computational analysis of a series of sterically twisted donor–acceptor carbazole derivatives incorporating a 3,5-bis(trifluoromethyl)benzene acceptor are reported. The target scaffolds were assembled via a modular Pd-catalyzed route combining Buchwald–Hartwig amination with Pd-mediated cyclodehydrogenation via C–H activation. Parallel experimental investigations were conducted to compare Pd(0)- and Pd(II)-based catalytic protocols. Under the conditions examined, higher isolated yields and cleaner conversions were obtained using the Pd(0) pathway. Density functional theory (DFT) calculations were employed to probe the reaction mechanism, and the energetic preference of the Pd(0) manifold was demonstrated, with oxidative addition and reductive elimination steps shown to be kinetically and thermodynamically more accessible than the corresponding processes in the Pd(II) cycle. Taken together, the experimental and theoretical results define an efficient strategy for the construction of highly twisted donor–acceptor carbazole frameworks and provide mechanistic insight for further optimization of Pd-catalyzed C–H annulation chemistries for the preparation of optoelectronically active materials.

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