

Metal-free aryl cross-coupling directed by traceless linkers.

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Abstract

The metal-free, highly selective synthesis of biaryls poses a major challenge in organic synthesis. We report the scope and mechanism of a promising new approach to (hetero)biaryls by the photochemical fusion of aryl substituents tethered to a traceless sulfonamide linker (photosplicing). Interrogating photosplicing with varying reaction conditions and comparison of diverse synthetic probes (40 examples, including a suite of heterocycles) showed that the reaction has a surprisingly broad scope and involves neither metals nor radicals. Quantum chemical calculations revealed that the C-C bond is formed by an intramolecular photochemical process that involves an excited singlet state and the traverse of a five-membered transition state, thus warranting consistent ipso ipso coupling fidelity. These results demonstrate that photosplicing is a unique aryl cross-coupling method in the excited state that can be applied to synthesize a broad range of biaryls.

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