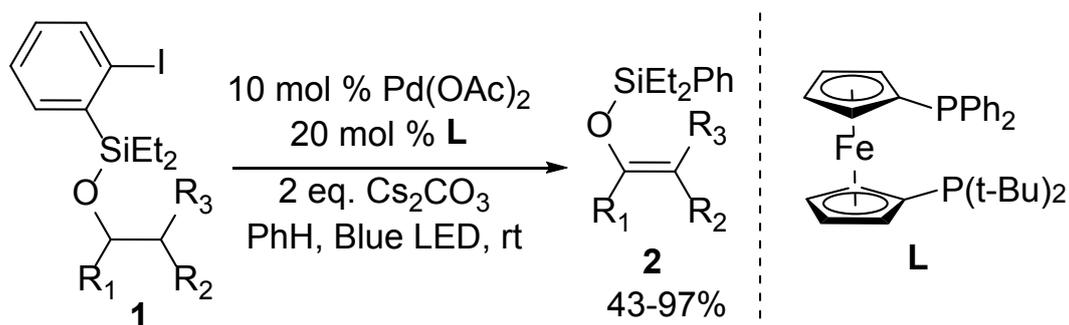


FERROCENYL COMPOUNDS IN THE PHOTOCHEMICAL REACTIONS

Since its discovery, more than 70 years ago, ferrocene has played a prominent role in nearly all aspects of synthetic chemistry from materials science to medicinal chemistry. Due to the unique properties of ferrocene and its derivatives, ferrocenyl compounds are unsurprisingly considered privileged structures in asymmetric catalysis, synthesis of biologically active compounds and components for organoelectronics. One particularly interesting and practically useful application of ferrocenes is the use as ligands and/or as catalysts in photochemical reactions. Here we provide several examples of such an application.

Work [3] presents a new method that allows the direct oxidation of silyl ethers to silyl enol ethers under mild conditions, with improved selectivity and efficiency compared to the prior art with rhodium or iridium catalysts. The scope of this reaction turned out to be relatively broad, with cyclic, acyclic and complex silyl ethers (**1**) that undergo efficient desaturation to form silyl enol ether products (**2**) with high yields (Scheme 1).

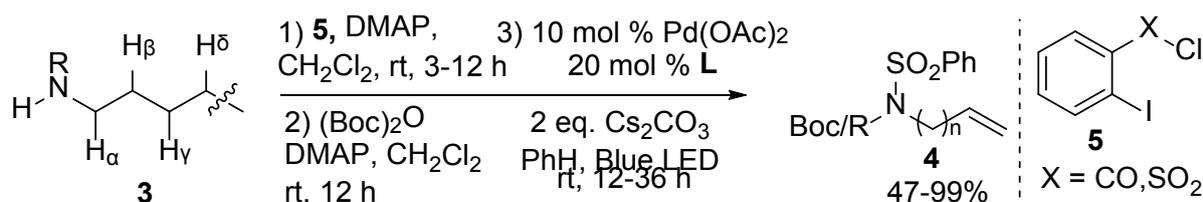


Scheme 1—Desaturation of silyl ethers (1)

Mechanistic studies, including the radical scavengers and the radical clock experiments confirmed the radical mechanism of this transformation. In addition,

isotopic labeling studies have revealed an alternative type of concerted metalation-deprotonation mechanism. The authors [3] showed combined synergism of two unique reactivities – hydrogen atom transfer (HAT) and palladium-involved the β -H-elimination event that turned on the novel remote functionalization of C(sp³)-H bonds.

Next, the same research group discovered the selective desaturation of aliphatic amines [2]. The authors showed that iodobenzamide (X=CO) and iodosulfonamide (X=SO₂) moieties were also suitable donors for the creation of hybrid palladium/aryl radical under visible light irradiation. Interestingly, these two substituents showed marked selectivity for the HAT process: 1,5-HAT for iodobenzamides and 1,7-HAT (also 1,6-HAT) for iodosulfonamides. Enamines were synthesized in good yields when using iodobenzamide. Similarly, iodosulfonamide amines (**3**) gave allylic and homoallylic amines (**4**) in good yields (Scheme 2).



Scheme 2 – Desaturation of amines (**3**)

Notably, unsaturated amines were synthesized simultaneously from aliphatic amines in semi *one-pot* synthesis, without isolation of auxiliary-protected amines. Also, mechanical studies of this work supported the radical mechanism of this transformation. Deuterium-labeling studies have provided evidence for the HAT process. In addition, photophysical studies showed that the palladium complex is the only light-absorbing species among reagents, and its excited state is quenched by aryl iodide. Based on these researches, it was proposed the similar mechanisms for silyl ethers desaturation reactions involving hybrid palladium/aryl radical species.

In 2017, Gevorgyan and co-workers [1] showed the ability of a hybrid palladium/alkyl radical species to undergo a HAT process at unactivated C(sp³)-H sites (Scheme 3). The activation of tertiary and secondary C(sp³)-H bonds

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