S02 Conversion to Sulfones: Development and Mechanistic Insights of a Sulfonylative Hiyama Cross-Coupling Reaction

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SO_2 Conversion to Sulfones: Development and Mechanistic Insights of a Sulfonylative Hiyama Cross-Coupling Reaction

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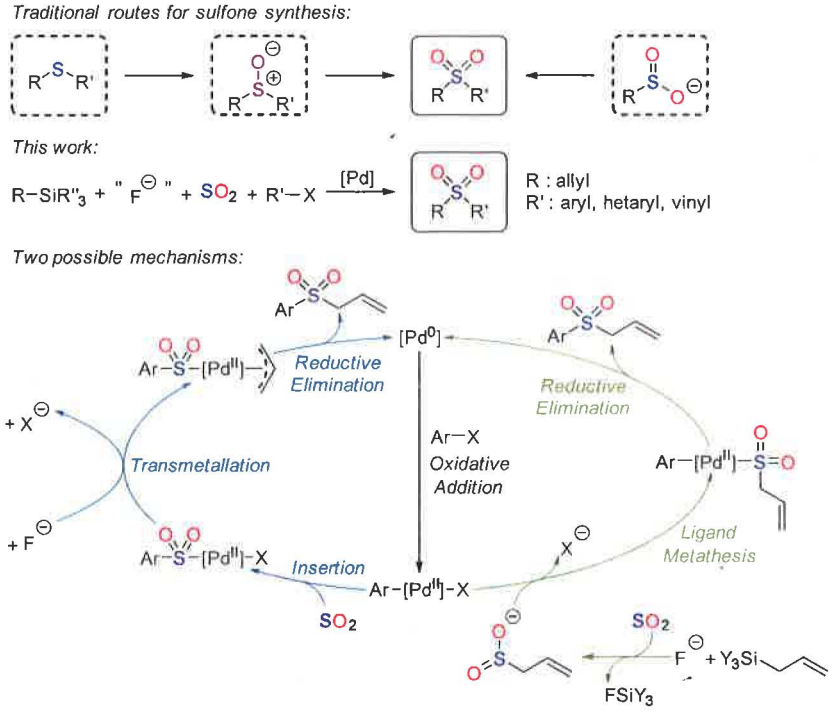
Due to distinctive structural and electronic features, sulfones have attracted a particular attention over the past few decades, making it a widespread functional group.[1] Present in many contemporary pharmaceuticals and agrochemicals, they are also used as essential intermediates in organic synthesis. Therefore, numerous methodologies have been developed for their preparation.[1] However, the most common methods (see Scheme below) suffer from significant limitations with harsh reaction conditions or regioselectivity issues. Recently, the insertion of a molecule of sulfur dioxide between two partners was investigated and reactions involving organomagnesium,[2a] organozinc[2b] and organoboron[2c] compounds were reported. As regards the use of organosilanes to produce sulfones from SO_2 or SO_2 surrogates, developed routes are limited to the formation of an intermediate sulfinate anion that undergoes S-alkylation and therefore to sp^3-hybridized electrophiles only.[3] Herein we report the first Hiyama cross-coupling, enabling the synthesis of sulfones in a direct single-step from organosilanes, SO_2 and sp^2-hybridized electrophiles. Different mechanistic pathways were envisaged and discussed both from an experimental and theoretical standpoint.



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