



HAL
open science

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

Aurélien Adenot, Joëlle Char, Niklas von Wolff, Guillaume Lefèvre, Thibault Cantat

► **To cite this version:**

Aurélien Adenot, Joëlle Char, Niklas von Wolff, Guillaume Lefèvre, Thibault Cantat. S02 Conversion to Sulfones: Development and Mechanistic Insights of a Sulfonylative Hiyama Cross-Coupling Reaction. ISySyCat 2019, Sep 2019, Evora, Portugal. cea-02329649

HAL Id: cea-02329649

<https://hal-cea.archives-ouvertes.fr/cea-02329649>

Submitted on 23 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

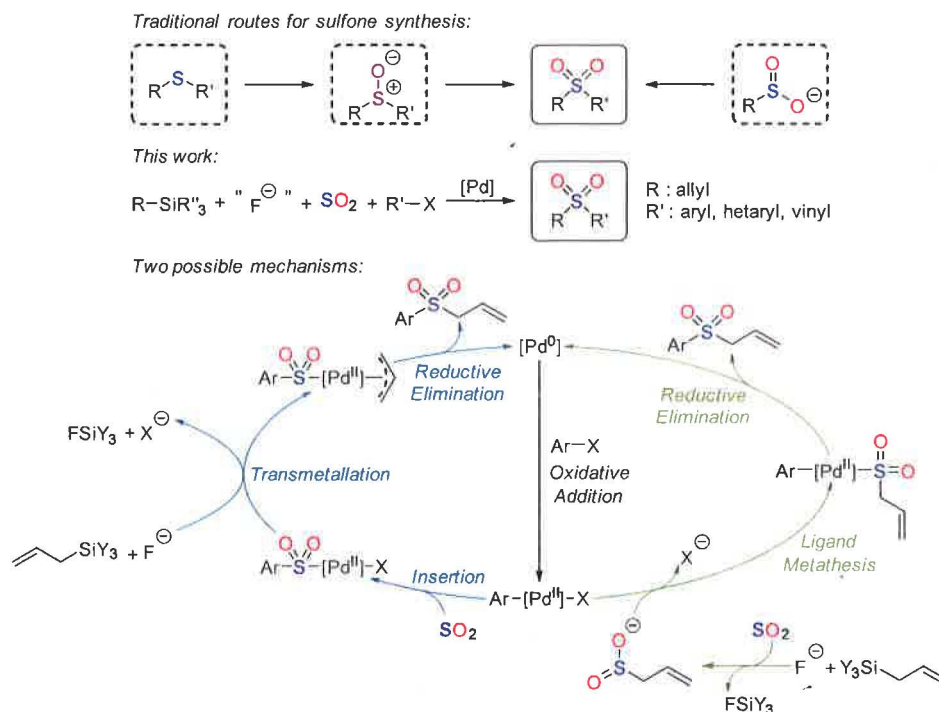
SO₂ Conversion to Sulfones: Development and Mechanistic Insights of a Sulfonylative Hiyama Cross-Coupling Reaction

Aurélien ADENOT,^a Joëlle CHAR,^a Niklas VON WOLFF,^a Guillaume LEFEVRE,^a Thibault CANTAT^{a,*}

^a NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette cedex, France

Email: aurelien.adenot@cea.fr

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 SO₂ or SO₂ surrogates, developed routes are limited to the formation of an intermediate sulfinate anion that undergoes S-alkylation and therefore to sp³-hybridized electrophiles only.³ Herein we report the first Hiyama cross-coupling, enabling the synthesis of sulfones in a direct single-step from organosilanes, SO₂ and sp²-hybridized electrophiles. Different mechanistic pathways were envisaged and discussed both from an experimental and theoretical standpoint.



References:

- Liu N.-W.; Liang S.; Manolikakes G *Synthesis* **2016**, *48*, 1939.
- a) Deeming A. S.; Russel C. J.; Hennessy A. J.; Willis M. C. *Org. Lett.* **2014**, *16*, 150. b) Rocke B. N.; Bahnck K. B.; Herr M.; Lavergne S.; Mascitti V.; Perreault C.; Polivkova J.; Shavnya A *Org. Lett.* **2014**, *16*, 154. c) Chen Y.; Willis M. C. *Chem. Sci.* **2017**, *8*, 3249.
- a) Bouchez L.; Vogel P. *Synthesis* **2002**, *2*, 225. b) Zheng D.; Mao R.; Li Z.; Wu J. *Org. Chem. Front.* **2016**, *3*, 359. c) Zheng D.; Chen M.; Yao L.; Wu J. *Org. Chem. Front.* **2016**, *3*, 985. d) von Wolff N.; Char J.; Frogneux X.; Cantat, T. *Angew. Chem. Int. Ed.* **2017**, *56*, 5616.