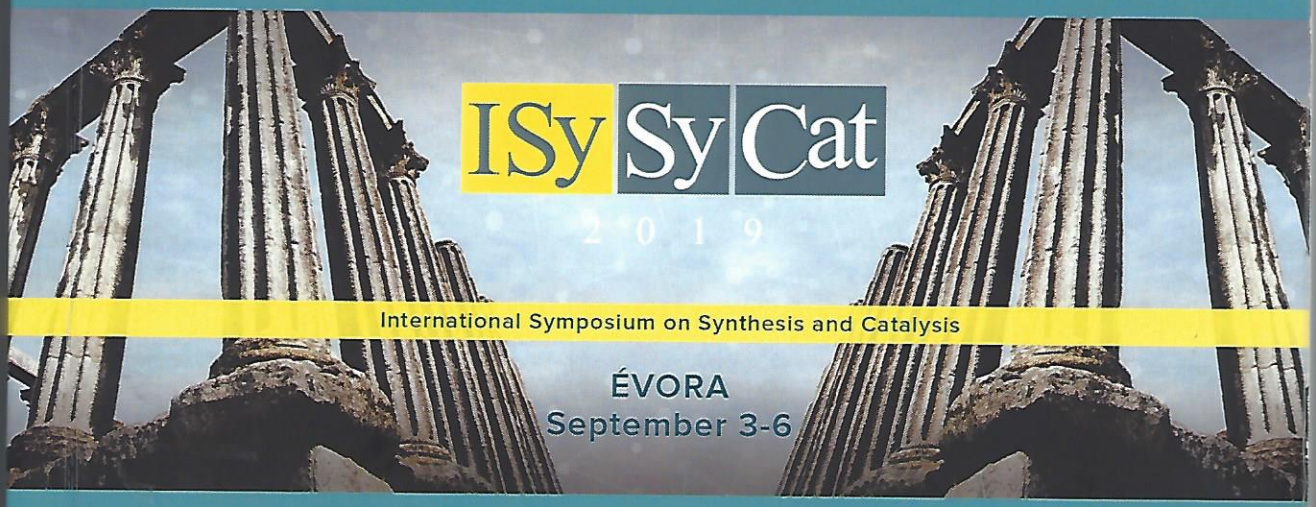

Book of Abstracts

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Contents

Liquid Sulfur Dioxide – Beneficial Solvent for Alkyne Transformations via Vinyl Carbenium Ion Intermediate

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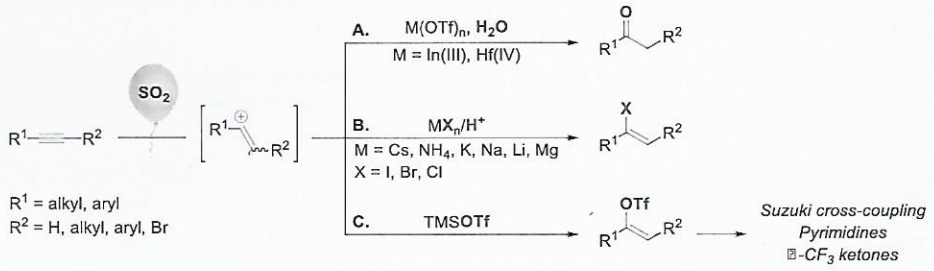
Sulfur dioxide is not only a useful building block in a synthetic organic chemistry, but due to its high polarity and Lewis acid properties liquid SO_2 can be used as a strongly ionizing solvent, especially, for organic transformations that involve ionic intermediates.[1] Herein we report application of liquid SO_2 as a reaction media for various alkyne transformations via vinyl carbenium ion intermediate that is quenched with nucleophiles like water, halide and triflate.[2]

Firstly, a combination of $In(OTf)_3$ or $Hf(OTf)_4$ as a catalyst and liquid SO_2 as a solvent allowed us to develop effective method for the hydration of electron-rich terminal and internal aryl alkynes without the direct addition of Brønsted acid (Scheme 1, **A.**). Catalyst loading can be lowered to less than 1 mol% for alkynes containing strong electron-donating groups. Besides, $Hf(OTf)_4$ has found an application in this chemical transformation for the first time.

Secondly, by employing simple reagent systems like CsI, KI, NaI, LiBr, or $LiCl/H_2O$ as well as solo reagents like NH_4I, $MgBr_2 \cdot 6H_2O$, and $MgCl_2 \cdot 6H_2O$, we have succeeded in the hydrohalogenation of electron-rich aromatic alkynes in liquid SO_2 (Scheme 1, **B.**). Most of these salts are used as halide sources in alkyne hydrohalogenation for the first time. Moreover, ammonium iodide works as both iodide and proton donor in a reaction mixture without the need for water additive.

Finally, we have found application of liquid SO_2 as a reaction media for *in situ* generation of α-vinyl triflates from aromatic alkynes by employing TMSOTf as a triflate ion source (Scheme 1, **C.**). The use of this method is demonstrated by two-step one-pot synthesis of α-CF_3 ketones, pyrimidines and Suzuki cross-coupling products.



Scheme 1: Alkyne transformations in liquid SO_2 via vinyl carbenium ion intermediate.

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References:

1. a) Posevins, D.; Suta, K.; Turks, M. *Eur. J. Org. Chem.* **2016**, 1414. b) Luginina, J.; Uzulena, J.; Posevins, D.; Turks, M. *Eur. J. Org. Chem.* **2016**, 1760. c) Luginina, J.; Turks, M. *Synlett* **2017**, *28*, 939.
2. Suta, K.; Turks, M. *ACS Omega* **2018**, *3*, 18065.