



# The Diels-Alder reaction of *para*-benzoquinones and simple dienes under catalysis with FeCl<sub>3</sub> on Aerosil<sup>®</sup> silica

Maria C. Donatoni,<sup>1</sup> Gilmar A. B. Junior,<sup>1</sup> Alcindo A. Dos Santos,<sup>2\*</sup> Kleber T. de Oliveira<sup>1</sup> and Timothy J. Brocksom<sup>1\*</sup>

<sup>1</sup>Departamento de Química, Universidade Federal de São Carlos, São Carlos-SP, 13565-905, Brazil.

<sup>2</sup> Instituto de Química, Universidade de São Paulo, São Paulo-SP, 05508-000, Brazil

\*e-mail corresponding author: brocksom@terra.com.br. www.lqbo.ufscar.br

Keywords: Diels-Alder, solvent-free, catalysis, iron(III) chloride, Aerosil<sup>®</sup> silica

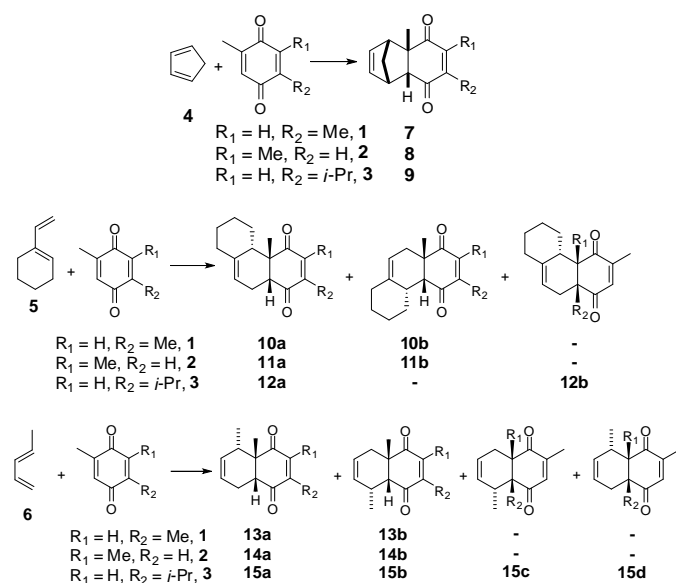
## INTRODUCTION

The Diels-Alder reactions of *para*-benzoquinones and simple dienes produce cycloadducts which serve as important intermediates for the synthesis of bioactive terpenes.<sup>1</sup> These cycloadditions are usually conducted in organic solvents (such as MeOH and CH<sub>2</sub>Cl<sub>2</sub>), for several days, or with Lewis acid catalysis in CH<sub>2</sub>Cl<sub>2</sub>. The usual Lewis acid catalysts are very efficient, but require anhydrous and oxygen-free conditions. Thus, there is ample scope for improved methodologies for the efficient execution of the Diels-Alder reaction.

We have now developed a mild *solvent-free* protocol for the promotion of these Diels-Alder reactions, catalysed by a mixture of FeCl<sub>3</sub> on Aerosil<sup>®</sup> silica (AS<sup>®</sup>).

## RESULTS AND DISCUSSION

Herein we report our results of the Diels-Alder reactions of the *para*-benzoquinones **1**, **2** and **3** with dienes **4**, **5** and **6** (see Scheme 1), catalysed by a mixture of FeCl<sub>3</sub> (4 mol% or 10 mol%) on AS<sup>®</sup>.



Scheme 1

The Diels-Alder reactions are conducted with a 2:1 ratio of diene to *para*-benzoquinone,<sup>2,3</sup> and 4 and 10% mol equivalents of catalyst, at room temperature, without solvent. Simple mortar and pestle mixture of a cheap grade of FeCl<sub>3</sub> and Aerosil<sup>®</sup> silica produces the catalyst.

All the reactions were tested first without FeCl<sub>3</sub>, or the silica, or the catalyst mixture, and then with 4% and 10% mol equivs. of the catalyst. In all the cases studied, the reaction times were reduced by factors of at least 50 to 100, and yields were increased to at least 80%, in the presence of the catalyst. 10% mol equivs of catalyst provokes a further reduction of reaction times when compared to 4% mol equivs. The orientation regioselectivity is modified or even reversed, and the site regioselectivity can reverse from the methyl double bond to the isopropyl double bond. The Raman spectrum of the catalyst confirms modification of the FeCl<sub>3</sub> species.

## CONCLUSION

The results clearly demonstrate the tremendous rate increase in all the Diels-Alder reactions studied, when catalysed by FeCl<sub>3</sub> supported on Aerosil<sup>®</sup> silica in solvent-free conditions. Also, the complexation of the *para*-benzoquinone oxygen atoms by the catalyst causes lowering of the LUMO orbital energy, and modification of the coefficients of the atomic orbitals, thus affecting regioselectivities.

## ACKNOWLEDGEMENTS

To FAPESP (2011/13993-2, 2013/06532-4), CAPES and CNPq.

## REFERENCES

1. Brocksom, T. J.; et. al. "Diels-Alder Reactions in the Synthesis of Higher Terpenes," in *Organic Synthesis: Theory and Applications*, T. Hudlicky (ed). JAI/Elsevier, Vol. 5, 39-87, 2001.
2. Dockal, E. R.; Cass, Q. B.; Brocksom, T. J.; Brocksom, U.; Corrêa, A. G. *Synth. Commun.* **1985**, 15, 1033-1036.
3. Uliana, M. P.; Vieira, Y. W.; Donatoni, M. C.; Corrêa, A. G.; Brocksom, U.; Brocksom, T. J. *J. Braz. Chem. Soc.* **2008**, 19, 1484-1489.