

Reactivity Studies of β -Alkene-type Porphyrins with Vinyl-Triazoles by Cross Metathesis Reactions

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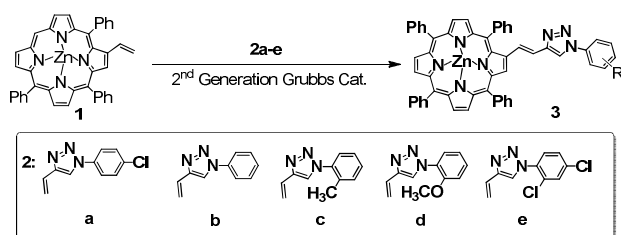
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INTRODUCTION

The search for new tetrapyrrolic macrocycles with adequate features for specific applications (e.g. cancer photodynamic therapy, microorganisms photoinactivation, catalysis, electronics, solar cells production, *etc.*) has become a target for several research groups.¹ Recently several approaches were explored for developing, or improving, methods to obtain novel porphyrin derivatives. Diels-Alder, 1,3-dipolar cycloadditions, electrocyclization and cyclopropanation reactions are examples of that.² In this communication we will report our studies on the reactivity of β -alkene-type porphyrins with several vinyl-triazoles through metathesis methodologies.

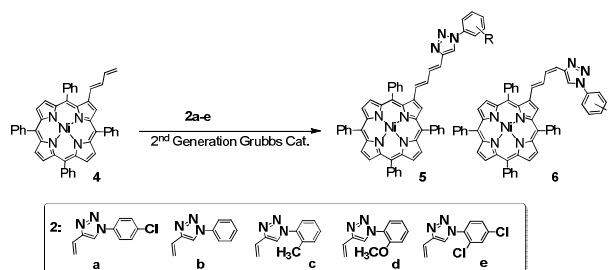
RESULTS AND DISCUSSION

We decided to start this study with the reaction of the zinc complex of β -vinyl-5,10,15,20-tetraphenylporphyrin **1** with vinyl-triazoles **2a-e** in the presence of 2nd Generation Grubbs Catalyst. In these reactions we were able to isolate the triazole-substituted porphyrins **3a-e** (Scheme 1).



Scheme 1. Metathesis reaction of porphyrin **1** with vinyl-triazoles **2a-e** in the presence of 2nd Generation Grubbs Catalyst.

We observed that the yields of these reactions are usually low (9-26%). So we have decided to use a different porphyrin with two conjugated double bonds in a β -pyrrolic position, the nickel complex of 2-(1,3-butadienyl)-5,10,15,20-tetraphenylporphyrin, **4**, in the metathesis reaction with vinyl-triazoles **2a-e**. In this way the reactions afforded the isomeric triazole-substituted porphyrins **5** (*trans,trans*) and **6** (*trans,cis*) with global yields higher than those obtained for porphyrin **1** (table 1).



Scheme 2. Metathesis reaction of porphyrin **4** with vinyl-triazoles **2a-e** in the presence of 2nd generation Grubbs catalyst.

Table 1. Results obtained in the metathesis reaction of porphyrin **4** with vinyl-triazoles **2a-e**.

4	5	6	Global \square (%)
a	21	13	34
b	19	16	34
c	9	12	21
d	21	19	40
e	9	-	9

CONCLUSION

In this work we looked at the reactivity of two β -alkene-type porphyrins with several vinyl-triazoles under metathesis conditions in the presence of the 2nd Generation Grubbs Catalyst. We observed that porphyrin **4** is more reactive than porphyrin **1** affording isomeric compounds **5** and **6** in acceptable yields. This methodology allows the synthesis of novel triazole-substituted porphyrin derivatives which might exhibit important biological activities.

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