

STUDY OF THE REACTIVITY AND THE SELECTIVITY OF THE DIELS-ALDER REACTIONS OF FURANYLBORON COMPOUNDS WITH MALEIMIDES

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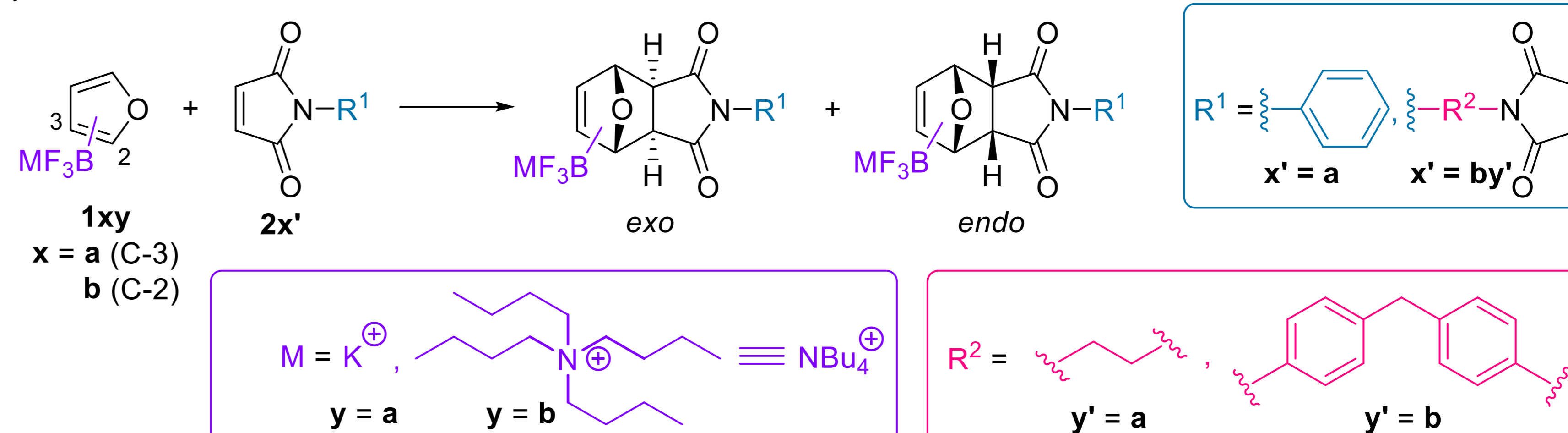
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Introduction

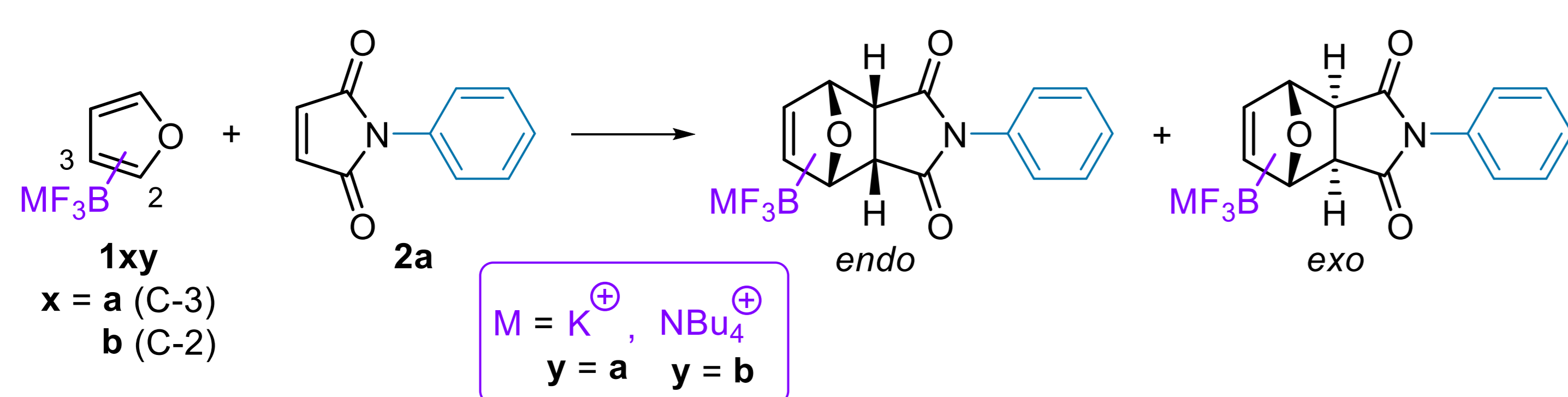
Organoboranes show high versatility, low-toxicity and wide availability. When unsaturated boranes participate in Diels-Alder (DA) reactions, they allow the formation of carbon-carbon bonds and cyclic structures with a wide variety of functional groups and high regio- and stereoselectivities.¹ Recently, our research group studied the DA reactions of boron-substituted furans, obtaining cycloadducts with excellent yields and diastereo-selectivities.² These reactions are attractive, since their precursors come from biomass and have potential for industrial applications. In recent years, the development of self-healing polymeric materials (SHPMs) capable of restoring their mechanical properties through dynamic covalent bonds has been studied.³ Given its thermal reversibility, the DA reaction has been essential in the design of SHPMs, with the reaction between furan and maleimide being a prominent example pair in the literature.

Objectives

When aimed to carry out the experimental study of the DA reactions of 2- and 3-furanyltrifluoroborates (**1xy**) with various maleimides (**2x'**). We proposed to analyze the reactivity and selectivity of **1xy** with *N*-phenylmaleimide, using potassium and tetrabutylammonium as counterions. Also, we planned to study the reactivity of 3-furanyltrifluoroborates with different bismaleimides (**2by'**), such as **2ba** and **2bb**, since these bisdienophiles could be subsequently used in reversible reactions to cross-link self-repairing polymeric networks with boron-substituted furans.



Diels-Alder reactions of furanylboron compounds with maleimides



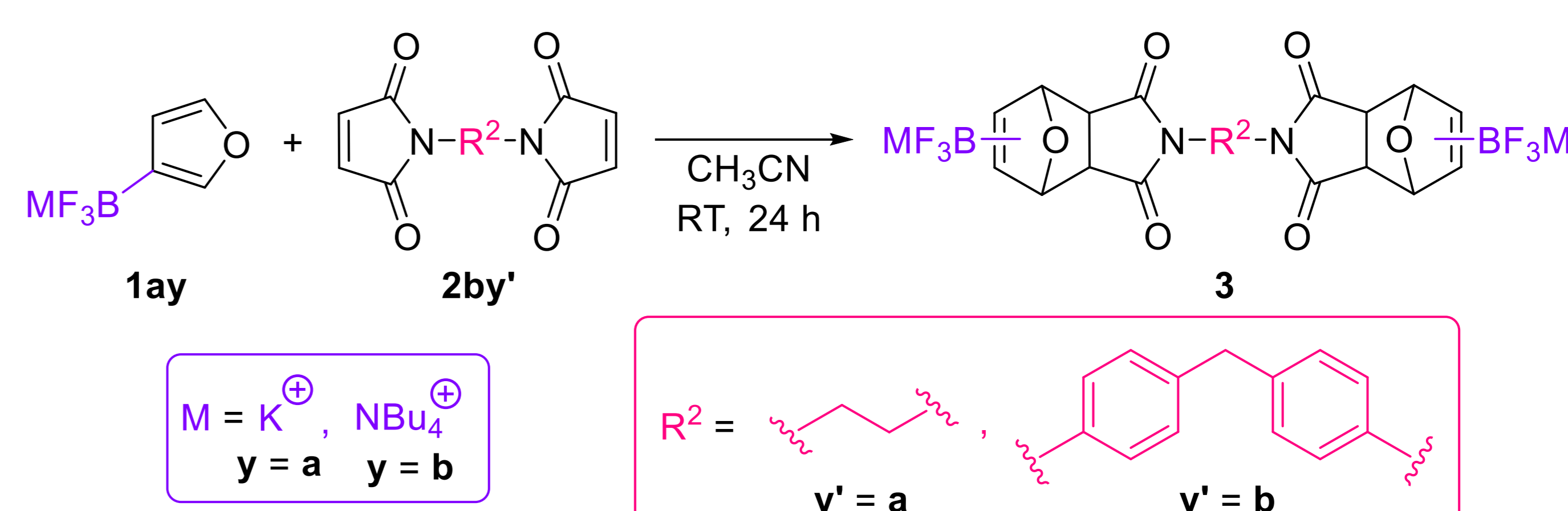
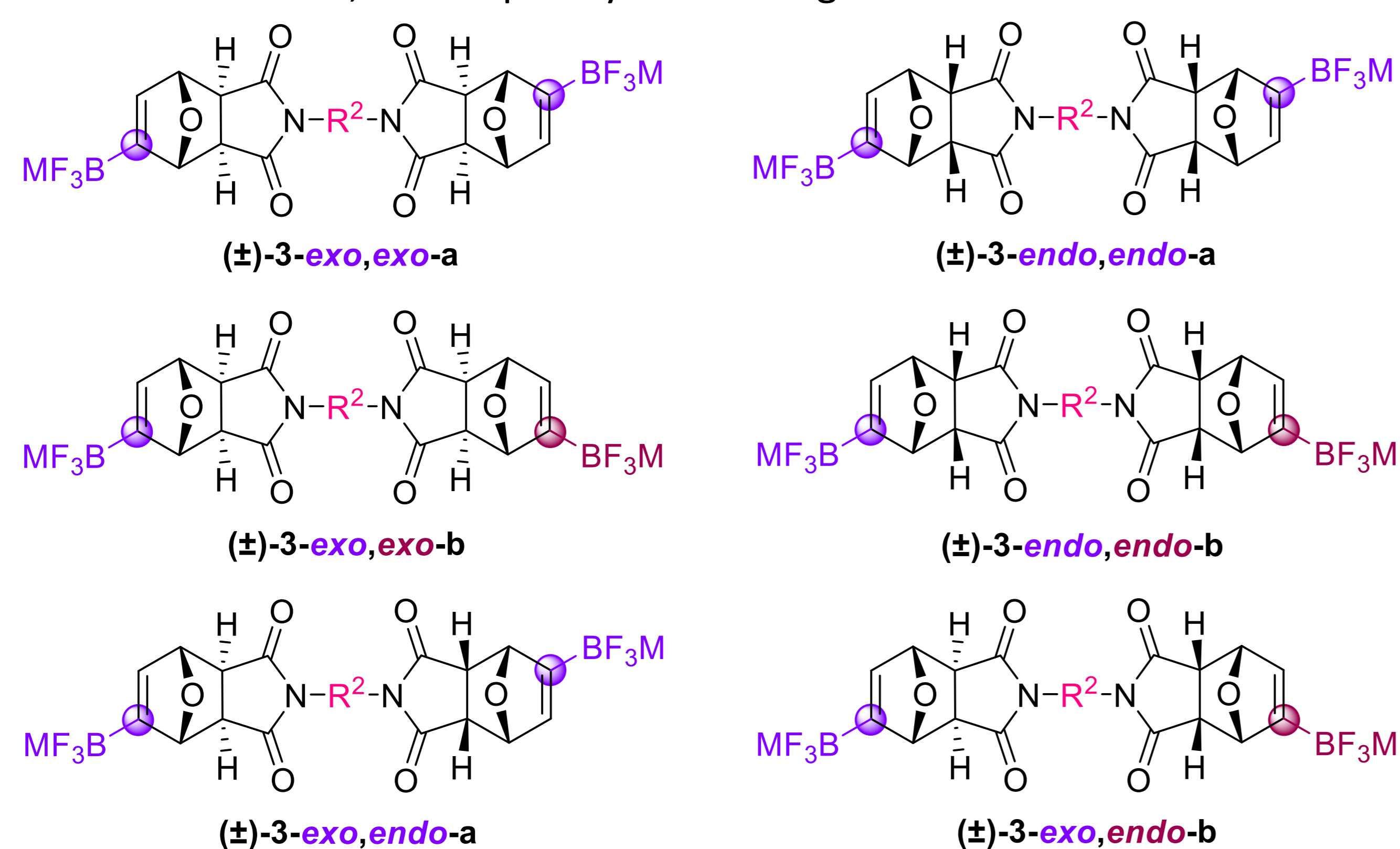
1	Conditions	Yield	Selectivity (N/X)
1aa	CH ₃ CN, RT, 1 h	99% ^a	31:69
1ab	CH ₃ CN, RT, 1 h	99% ^b	0:100
1ba	CH ₃ CN, RT, 10 d	69% ^b	0:100
1bb	CH ₃ CN, RT, 10 d	17% ^c	0:100

^a isolated yield; ^b determined by ¹H NMR of the crude reaction using internal standard; ^c determined by ¹H NMR integration (conversion).

The study of the reactions of C-2- and C-3-substituted furanyltrifluoroborates with *N*-phenylmaleimide (**2a**) in acetonitrile was carried out using two different counterions. The highly activated dienophile allowed the efficient generation of the Diels-Alder adducts under various conditions, showing good to excellent *exo*-selectivities and stable products. Thanks to this stability, the cycloadducts are not susceptible to retro-Diels-Alder at room temperature, which makes them attractive materials for future

derivatization reactions. Furthermore, the influence of the counterion on the reactivity and the selectivity of the system was demonstrated, since the use of tetrabutylammonium as counterion of trifluoroborate **1ab** lead exclusively to the *exo* cycloadduct in one hour, while its potassium analogue **1aa** produced an *endo/exo* mixture in a 31:69 ratio. Also, the *exo* product was obtained from 2-furanyl trifluoroborate for both counterions.

Motivated by such results, the study of Diels-Alder reactions with bismaleimides **2ba** and **2bb** was initiated to study their potential application in the reversible cross-linking of self-healing polymeric networks with boron-substituted furans. 3-Furanyltrifluoroborate was selected since it proved to be the most reactive. Firstly, all possible addition modes were analyzed and the structures of the possible products were proposed. Although the analysis is simplified by discarding identical structures by arising from the symmetry of the system and considering only one of the enantiomers of the racemic mixtures, its complexity remains significant.



2by'	1ay	Conversion ^a	Selectivity (N/X)
2ba	1aa	100%	57:43
2ba	1ab	100%	18:82
2bb	1aa	100%	26:74
2bb	1ab	100%	06:94

^a determined by ¹H NMR integration.

The results obtained so far are promising, since for both bismaleimides, a 100% conversion has been achieved in the double addition of 3-furanyltrifluoroborate at room temperature in 24 hours with both counterions. In addition, a notable increase in *exo*-selectivity has been observed when using bismaleimide **2bb** and also tetrabutylammonium as counterion. Currently, we are investigating the thermal reversibility of these reactions.

Conclusions

The study of the Diels-Alder reactions of 2- and 3-furanyltrifluoroborates with various bismaleimides was carried out. It was shown that the C-3 substituted furan acts as a substantially more reactive diene than its C-2 analogue, displaying good to excellent *exo*-selectivities, especially when tetrabutylammonium is used as counterion. When performing reactions of 3-furanyltrifluoroborates with bismaleimides, a complete conversion of the cycloadducts was achieved in 24 hours, with a remarkable increase in *exo*-selectivity when bismaleimide **2bb** is employed. These results are encouraging and will be further explored in a potential application in the reversible cross-linking of self-healing polymeric networks with boron-substituted furans.

Acknowledgments

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References

- (a) Eberlin, L.; Tripoteau, F.; Carreaux, F.; Whiting, A.; Carboni, B. *J. Org. Chem.*, **2014**, *10*, 237-250. (b) Hall, D. G.; Rybak, T.; Verdelet T. *Acc. Chem. Res.*, **2016**, *49*, 2489-2500. (c) Pyziak, J.; Walkowiak, J.; Marciniak, B. *Chem. Eur. J.*, **2017**, *23*, 3502-3541.
- Medrán, N. S.; Dezotti, F.; Pellegrinet, S. C. *Org. Lett.*, **2019**, *21*, 5068-5072.
- Liu, Y. L.; Chuo, T. W. *Polym. Chem.*, **2013**, *4*, 2194-2205.

