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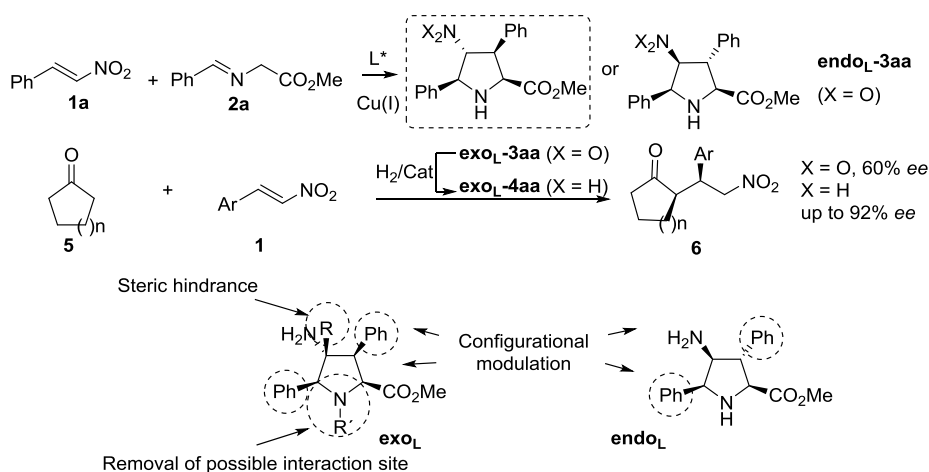
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### Synthesis and reactivity in the Michael reaction of unnatural densely functionalized Proline-derived organocatalysts

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Our group have developed an offspring of densely substituted unnatural L- and D- pyrrolidine derivatives **3** and **4** with endo- or exo- diastereoselectivity, respectively, in high enantioselectivities.<sup>1</sup> Encouraged by the efficiency of Proline-based organocatalysts in several C-C bond transformations, these novel densely substituted pyrrolidines (**3** and **4**) have been used as organocatalysts in the Michael reaction yielding the corresponding addition adduct **6**.<sup>2</sup> These products may possess the same or opposite stereochemistry obtained under natural L-Proline organocatalysis depending on the stereochemistry of the catalyst used (**endo<sub>L</sub>-3,4aa** or L-Proline vs. **exo<sub>L</sub>-3,4aa**). Computational studies have been performed in order to gain insight into the mechanism and also, the influence of the substituents' nature and additional side groups in the catalysts have been studied. As a *coda*, reactivity of the catalysts against a novel double electrophile is shown.



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<sup>1</sup> Conde, E.; Bello, D.; de Cózar, A.; Sánchez, M.; Vázquez, M. A.; Cossío, F. P. *Chem. Sci.* **2012**, *3*, 1486-1491

<sup>2</sup> a) Xu, L. W.; Luo, J.; Lu, Y. *Chem. Comm.* **2009**, 1807-1821. b) Vicario, J. L.; Badía, D.; Carrillo, L.; Reyes, E. *Organocatalytic Enantioselective Conjugate Additions Reactions*, RSC Publishing: Cambridge UK **2010**