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## Chiral Monothiosquaramides as Efficient Catalysts for the Enantioselective Imine Reduction of Dihydro- $\beta$ -carbolines

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### ABSTRACT

The search for new sustainable chiral organometallic complexes by substituting expensive and toxic metals with non-toxic and cost-effective metals with higher catalytic efficiency is a good concept from both environmental and commercial. Thus, we developed various chiral monothiosquaramide<sup>1</sup> catalysts **4-6** (Pd- or Fe-MTSQs) for the enantioselective reduction of dihydro- $\beta$ -carboline imines (DHBCs), as shown in Figure 1.<sup>2-4</sup> Optimized reaction conditions revealed selectivities ranging from 90%-98% ee, and good yields. The substituents at the 1-position of THBC played a critical role in obtaining stereoselectivities and their configurations (*R* or *S*, Figure 1) when Pd-MTSQs were employed. Alkyl groups at the 1-position of chiral **2a-c** were isolated with excellent enantioselectivities (90%-98% ee), and it was confirmed that their major isomer had a *R* configuration, using 5 mol% of catalysts. Surprisingly, *S* configuration was observed in the case of aryl groups at the 1-position of **1d,e**, yielding (*S*)-aryl-**2d,e** with 95%-96% ee.<sup>5</sup>

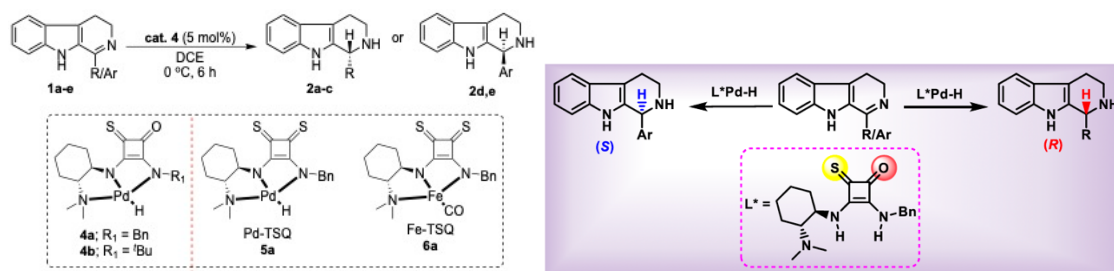


Figure 1: Pd- and Fe-monothiosquaramides catalyzed enantioselective imine reduction of imines.

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