NOVEL CARBAMATE-BASED *P,O*-LIGANDS IN ASYMMETRIC ALLYLIC ALKYLATIONS

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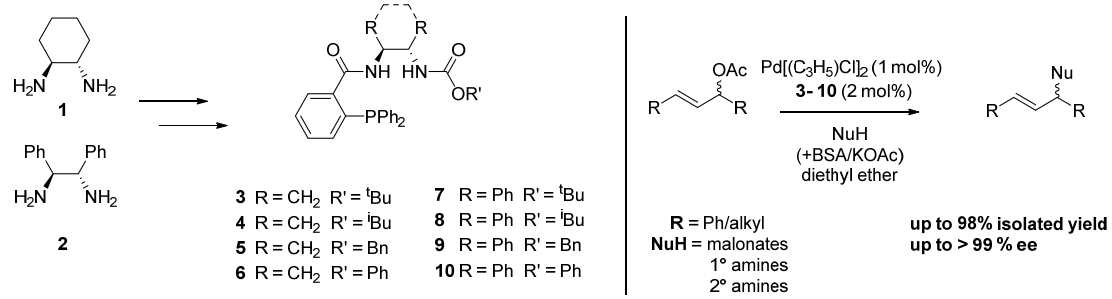
Highly functionalized allylic compounds are invaluable intermediates for the synthesis of biologically active molecules. Since the early discovery of *B. Trost* and *J. Tsuji*, the concept of asymmetric allylic allylation (AAA) has been rapidly growing and is still one of the most relevant strategies for the formation of chiral allylic compounds [1]. While chiral diamine-based *P,P*-ligands have proven to be efficient for AAA reactions, monophosphine-analogues featuring *P,O*-chelation have not yet been studied.

Encouraged by our previous results with carbamate-based ligands in transition-metal catalysis [2], a small library of carbamate-monophosphine ligands (**3**-**10**) has been prepared in a straightforward two-step procedure. These ligands were used in the AAA reaction of (±)-diphenylallyl acetate and dimethyl malonate as a benchmark reaction. After optimization of the reaction conditions, a series of different soft nucleophiles were successfully applied to the asymmetric allylic alkylation of aromatic and aliphatic allylic acetates under mild reaction conditions, enabling high catalytic activity with excellent enantioselectivities.



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[1] Trost, B. M.; Chisholm, J. D.; Wrobleski, S. J.; Jung, M. J. Am. Chem. Soc. **2002**, 124, 12420.

[2] Pálvölgyi, Á. M.; Bitai, J.; Zeindlhofer, V.; Schröder, C.; Bica, K. ACS Sustainable Chem. Eng. **2019**, 7, 3414.