

C(sp³)-*gem*-Bimetallic Compounds for Asymmetric Sequential Reactions

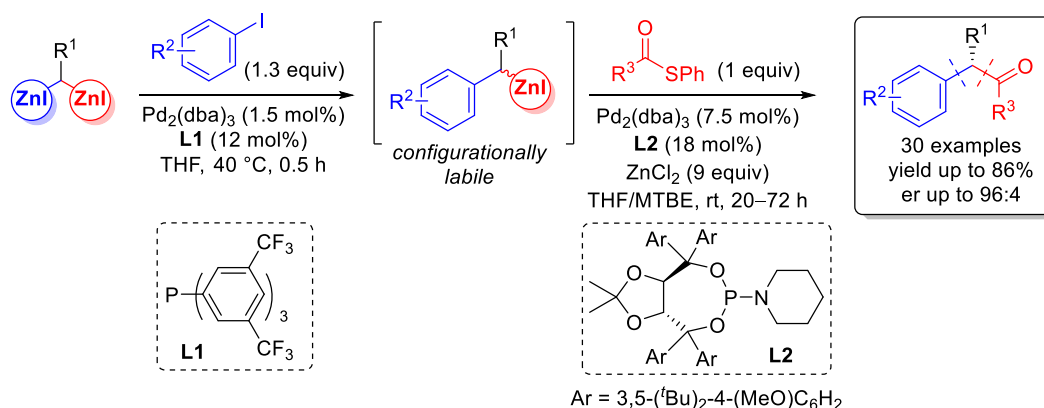
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Developing tools to achieve the efficient and selective assembly of complex molecular structures with a minimum of chemical steps is a key endeavour in organic synthesis. In this context, geminated C(sp³)-organodimetallics attracted pursued interest,^[1] and the opportunity to be engaged in consecutive reactions with two different electrophiles is well established. However, their use for the development of asymmetric sequential reactions remains a relevant challenge.

The case of *gem*-dizinc reagents is particularly interesting because this type of readily accessible linchpin has shown versatile reactivity with reasonable stability and environmental benignity. However, only one enantioselective transformation involving two sequential cross-coupling reactions of an achiral *gem*-dizinc reagent was reported, but the enantiomeric excess was low (33% *ee*).^[2]

We have thus engaged a general program to develop the use of *gem*-dizinc reagents in the context of enantioselective one-pot bi-directional functionalization through two distinct palladium-based catalytic systems.^[3] First, the non-enantioselective mono-arylation of 1,1-dizincioalkanes by reaction with several (hetero)aryl iodides was achieved leading to configurationally labile secondary benzylzinc species and leaving intact the second C(sp³)-Zn bond.^[4] Then, acylation with thioesters through an enantioconvergent Fukuyama coupling exploiting a highly efficient dynamic kinetic resolution of the racemic benzyl zinc intermediates was performed to furnish enantioenriched acyclic α -disubstituted ketones bearing potentially enolizable tertiary stereocenters.^[5]



References:

[1] I. Marek, J.-F. Normant, *Chem. Rev.* **1996**, 96, 3241–3268. [2] S. Matsubara, N. Toda, M. Kobata, K. Utimoto, *Synlett* **2000**, 987–988. [3] F. Banchini, B. Leroux, E. Le Gall, M. Presset, O. Jackowski, F. Chemla, A. Perez-Luna, *Chem. Eur. J.* **2023**, 29, e202301084. [4] Y. Shimada, R. Haraguchi, S. Matsubara, *Synlett* **2015**, 26, A–D. [5] R. Oost, A. Misale, N. Maulide, *Angew. Chem.* **2016**, 128, 4663–4666.

