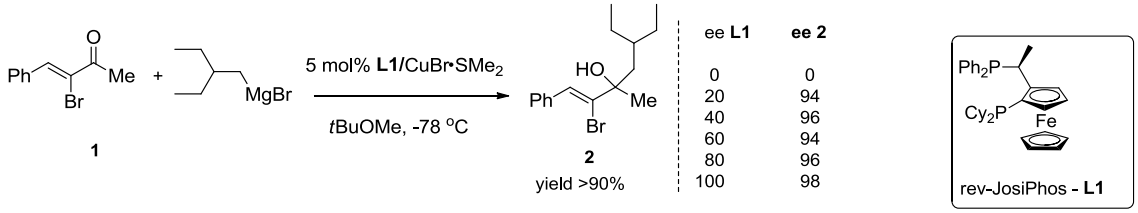
Asymmetric Amplification due to Differences in Phase Behaviour of Cu-Diphosphine Based Chiral Complexes

Francesca Caprioli , Ashoka V. R. Madduri, Martin Lutz, Adriaan J. Minnaard, S*yuzanna R. Harutyunyan*,

Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands
f.caprioli@rug.nl

Asymmetric amplification is a beneficial situation which allows using non-enantiopure chiral catalyst to achieve the same level of enantioselectivity as one would obtain using enantiopure analogue.[1] Here we report that asymmetric 1,2-addition of Grignard reagents to enones catalysed by chiral copper complex of ferrocenyl diphosphine ligand **L1** displays a strong asymmetric amplification affording high levels of enantioselectivities using nearly racemic catalyst.[2] We found that the amplification is not specific to this particular reaction but is in fact due to significant differences in the solubility of the racemic and enantiopure catalyst. During our studies we have observed that complexation of a transition metals (Cu, Pd) with chiral diphosphine ligands, induces an extreme difference in the solubility between the racemates and the single enantiomers, an effect which is not present in case of the free ligands. This allows the efficient separation of racemic and enantiopure complexes from a scalemic mixture by simple filtration. The metal can be readily removed from the separated racemic and enantiopure complexes, thus leading quantitatively to the pure free ligands. This discovery is of particular importance for the use of scalemic mixtures in the case of new chiral ligands for which asymmetric synthesis is deficient.



[1] For reviews on asymmetric amplifications see: (a) T. Satyanarayana, S. Abraham, H. B. Kagan *Angew. Chem. Int. Ed.*, 2009, **48**, 456;.
[2] F. Caprioli, A. V. R. Madduri, A. J. Minnard, S. R. Harutyunyan, *Chem. Commun*. **2013**, *49*, 5450.