Abstract

In the first part of the present work chiral and nonchiral phosphonates and phosphinates were synthesized as Umpolung precatalysts in the Benzoin-reaction. New or improved *ortho*-lithiation protocols were developed for the synthesis of terpenone-based diols, including novel diols with flexible biaryl-axes. Employing the phosphonates derived from these diols as pre-catalysts in cross-benzoin reaction enantiomeric excesses of up to 72% could be achieved. In analogy achiral and chiral phosphinates were tested in Umpolung-catalysis for the first time.

In the main part of the present work novel hydrogen bonding (HB) structural motivs were designed, synthesized and tested in multiple applications. Four novel (thio)phosphorus diamides with different substitution-patterns based on (*S*)-BINOL were evaluated as HB-catalysts in the 1,4-addition of indole to *β*-nitrostyrene. These compounds revealed good catalytic activity with isolated yields of up to 82%, albeit with low selectivity (up to 14% ee). The catalytic activity of these catalysts could be attributed to acidity of the NH-protons as a direct correlation between the downfield-shift of these protons in ^{1}H-NMR and the isolated product-yields in catalysis was observed. Furthermore a novel class of HB-catalysts, four cyclodiphosph(V)azanes and ten phosphorus triamides were designed and synthesized. These catalysts were evaluated in the 1,4-addition of 2-hydroxy-naphthoquinone to *β*-nitrostyrene, with isolated yields of up to 98% and enantiomeric excess of up to 75%. Cyclodiphosph(V)azanes were found to act as superior catalysts, and DFT-computations on the binding of model-compound nitro benzene confirmed improved HB-donor characteristics of this structural motif when compared to standard thiourea (ΔE = 7.2 kcal mol^{-1} vs. ΔE = 6.5 kcal mol^{-1}, respectively). Further DFT-computations gave insight into the mechanism of catalysis.

Cyclodiphosph(V)azanes were then tested as novel anion-receptors and revealed improved affinity for spherical chloride (logK = 5.43) and equivalent affinity to trigonal acetate (logK = 6.72) compared to a classic urea anion-receptor (logK = 4.25 and logK = 6.91 respectively). Following experimental, crystallographic and computational studies the binding-mode of cyclodiphosph(V)azanes can be ascribed to their geometrical structure, which resembles that of squaramides. The canted cyclodiphosph(V)azane-structure results in greater substrate proximity to the C_{α}-H on the aryl-moieties on the catalyst, which increases the effects of *meta*-substitution by CF_3-groups. The results presented in this work will be key to the design of further novel organocatalysts based on the cyclodiphosph(V)azane core.