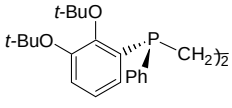
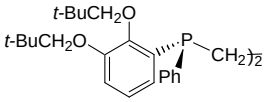
Abstract

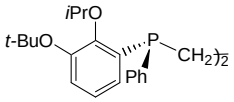
Synthesis of new *P*-stereogenic diphosphine ligands possessing bulky *P*-(*o*-RO-aryl) groups and their use as ligands in Rh(I)-catalyzed hydrogenation of olefins is described. Establishing new reliable access to *o*-di(RO)-benzenes wherein R = *t*-Bu, *t*-BuCH_2, or mixed *o*-dialkoxy-benzene derivatives, allowed their implementation in the Jugé–Stephan route toward the targeted BigFUS super-bulky ligand series.



(*R*,*R*)-**2*t*BuBigFUS**
>99% ee; dr 90:10



(*R*,*R*)-**2(*t*BuCH$_2$)BigFUS**
>99.9% ee



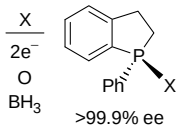
(*R*,*R*)-***i*Pr/*t*BuBigFUS**
>99.9% ee

These ligands displayed excellent performance in Rh(I)-catalyzed hydrogenation of benchmark olefins, in particular itaconates and α-acetamidostyrene, leading to virtually perfect enantioselectivity and high reaction rate.

Moreover, a knockout PCCP-type diphosphine design, wherein backbone flexibility and identical nature of *P*,*P'*-substituents of related C_2-symmetrical ethylene-bridged diphosphines were knocked out, brought a further mechanistic insight in relation to steric and electronic factors affecting the Rh(I)-catalyzed hydrogenation of olefins.

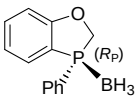
Besides, introduction of a new enantiopure cyclic phosphinite-*P*-borane key-intermediate and devising new cyclization strategies in phosphorous chemistry, allowed for the first time efficient preparation of *P*-stereogenic phosphacyclic structures with >99% ee, such as 1-phenylphosphindane, and 1-phenyl-3-oxa-phosphindane. These *P*-stereogenic-based units can serve as precursors to new generations of phosphine ligands.

1-Phenylphosphindanes



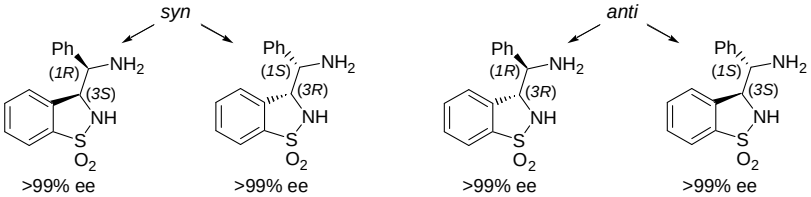
>99.9% ee

1-Phenyl-3-oxa-phosphindane-*P*-borane



>99.9% ee

In Ru(II)-catalyzed asymmetric transfer hydrogenation, new complementary synthetic strategies to chiral aminobenzyl–benzo-γ-sultames allowed their preparation in diastereomerically pure forms which enantiomers were further separated by chiral HPLC. These new ligands were evaluated on benchmark ketones.



>99% ee >99% ee >99% ee >99% ee

Keywords: asymmetric hydrogenation, asymmetric transfer hydrogenation, N-ligands, P-ligands, rhodium, ruthenium