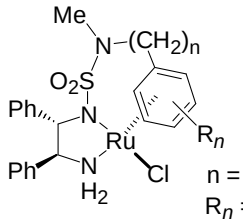
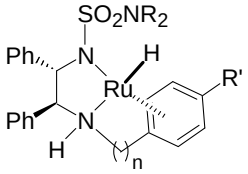
Abstract

The development of asymmetric transfer hydrogenation (ATH) *ansa*-ruthenium(II) complexes of multidentate organic ligands, wherein the η^6-arene is intra-covalently tethered to the *N*-sulfamoyl-(*S*,*S*)-DPEN (DPEN = 1,2-diphenylethylenediamine) either from the sulfamoyl terminal leading to complex series **I**, or from the amine terminal (transshifted tether) leading to complex series **II**, is described. In addition, the '$(CH_2)_n$' *ansa*-bridge length and the anchored 'η^6-aryl' substituents were varied in these series.



n = 2, 3
R_n = H, Me, *i*Pr

ansa-Ru(II) complex **I**

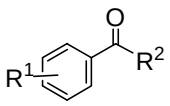


ansa-Ru(II) complex **II**

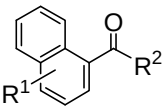
NR_2 = NMe_2, N
n = 3, 4
R' = H, Me, *i*Pr

The ATH of various classes of aryl ketones in HCO_2H/Et_3N medium employing these new *ansa*-Ru(II) complexes was studied. The beneficial effect of the *ansa*-bridge, especially the 3C long tether coupled with the anchored η^6-aryl having a *para*-Me or -*i*Pr substituent in both series was identified. Such complexes extended the catalytic species longevity and afforded increased enantioselectivity.

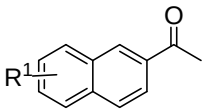
Examples of aryl ketones reduced in high enantiomeric excesses are presented:



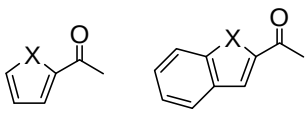
R^1 = H, OH, F, Me, OMe
R^2 = Me, Et, CH_2Bn, CH_2Cl, CH_2CN, CH_2CO_2Me, $CH_2P(O)(OEt)_2$



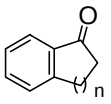
R^1 = H, 2'-OH, 4'-F, 4'-Me, 4'-OMe, 6'-OMe, etc
R^2 = Me, Et, *i*-Bu, Bn, CH_2Cl, CH_2CO_2Me



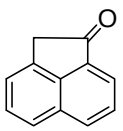
R^1 = H, 1'-OH, 6'-OMe

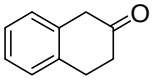


X = O, S



n = 1–3





Keywords: asymmetric catalysis, ligands, ruthenium, transfer hydrogenation