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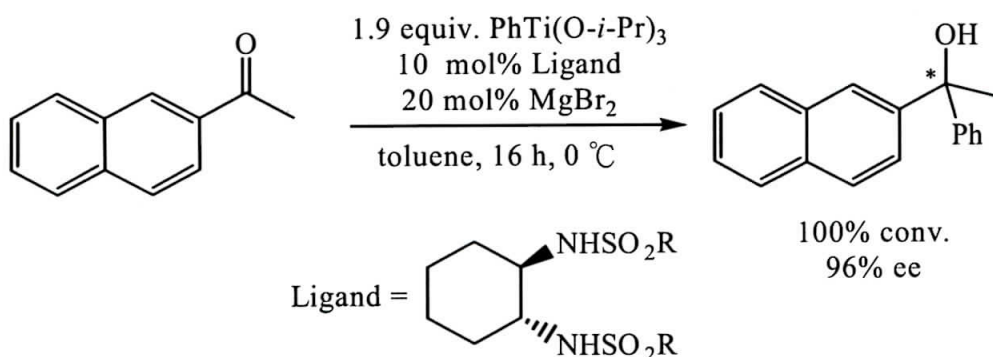
Catalytic Asymmetric Phenyl Addition of $\text{PhTi}(\text{O}^i\text{Pr})_3$ to 2'-Acetonaphthone by Titanium Catalyst of Disulfonamide Ligands

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Abstract

One of the most important challenges in organic synthesis is the enantioselective synthesis of chiral compounds with the quaternary stereocenter. There are a few reports of asymmetric catalytic aryl additions of organometallic reagents to ketones.^[1] Recently, we reported asymmetric $\text{AlAr}_3(\text{THF})$ additions to ketones catalyzed by titanium catalysts of chiral C_2 -symmetric ligands.^[2] We found that the disulfonamide ligand derived from camphor has shown excellent enantioselectivities in aryl addition to ketones. Thus, in this study, we prepared a series of disulfonamide derivatives of *trans*-1,2-diaminocyclohexane as ligands in titanium-catalyzed asymmetric phenyl addition reactions. The enantioselective phenylations of 2'-acetonaphthone were successfully performed using the phenyltitanium reagent, magnesium bromide and disulfonamides ligands **1-10**, giving the enantiomeric excesses of the product up to 96%.



R = 4-Me- C_6H_4 (**1**); 4- CF_3 - C_6H_4 (**2**); 4- NO_2 - C_6H_4 (**3**); 2-Br- C_6H_4 (**4**);
2,4,6-Me- C_6H_2 (**5**); 2,4,6- i -Pr- C_6H_2 (**6**); C_6H_5 (**7**); C_6F_5 (**8**); CH_3 (**9**); CF_3 (**10**)

References:

- [1] (a) Dosa, P. I.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 445-446; (b) Yus, M.; Ramon, D. J.; Prieto, O. *Tetrahedron: Asymmetry* **2002**, *13*, 2291-2293.; (c) Garia, C.; LaRochelle, L. K.; Walsh, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 10970-10971.
- [2] (a) Chen, C.-A.; Wu, K.-H.; Gau, H.-M. *Angew. Chem. Int. Ed.* **2007**, *46*, 5373-5376; (b) Chen, C.-A.; Wu, K.-H.; Gau, H.-M. *Adv. Synth. Catal.* **2008**, in press.