Influence of the bite natural angle of bidentate diphosphine ligands in the syngas-free branched hydroformylation of ?-functionalized olefins

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© 2018 Elsevier B.V. The correlation between the activity, regio- and chemoselectivity of Rh-diphosphine catalyst and the ligand bite natural angle (?n) in the syngas-free hydroformylation of allyl cyanide was investigated. A screening of Xantphos type and diphosphine alkyl ligands with different bite natural angles was studied. Interesting, a switch in the linear to the branch regioselectivity was found. Wide ?n favour a linear regioselectivity whereas smaller ?n allow the formation of the branched aldehyde as the major product. Modification of the substituents at the phosphorus atoms of the diphosphine ligands produced a dramatic change in the hydroformylation. Others ?-functionalized olefins were also branched hydroformylated.