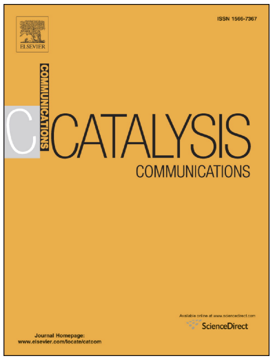

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Chiral calixarene and resorcinarene derivatives. Conical cavities substituted at their upper rim by two phosphito units and their use as ligands in Rh-catalysed hydroformylation

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Abstract:

Two chiral diphosphites, (*S*,*S*)-5,17-bis(1,1'-binaphthyl-2,2'-dioxyphosphanyloxy)-25,26,27,28-tetrapropyloxycalix[4]arene (**1**) and (*S*,*S*)-5,11-bis(1,1'-binaphthyl-2,2'-dioxyphosphanyloxy)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (**2**), each based on a conical cavity, were synthesised and assessed in the rhodium-catalysed hydroformylation of vinyl arenes. Under optimised conditions, both ligands led to high proportions of branched aldehyde (b/l = 8.1) in the hydroformylation of styrene. The observed enantioselectivity was considerably higher for **1** than **2** (ee 89 % *vs.* 50 %), this being consistent with the easy formation of chelated intermediates with **1** (chelate formation is prevented with **2**), in which the embracing ligand enables an efficient chirality transfer to the catalytic centre.

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