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## ACCEPTED MANUSCRIPT

# 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:**

(S,S)-5,17-bis(1,1)-binaphthyl-2,2 $^{\circ}$ -dioxyphosphanyloxy)diphosphites, Two chiral (S,S)-5,11-bis(1,1'-binaphthyl-2,2'-25,26,27,28-tetrapropyloxycalix[4]arene **(1)** and dioxyphosphanyloxy)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylre sorcin[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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