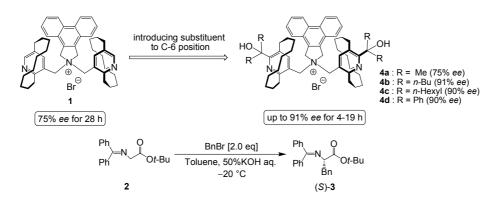
Synthesis of planar-chiral phase-transfer catalysts incorporating hydroxyl methyl pyridinophane moieties and their use for catalytic asymmetric reactions

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Various phase-transfer catalysts (PTCs) have been reported useful for asymmetric reaction, however planar-chiral PTCs have not been reported yet in literature.

We have been studying planar-chiral PTCs having [10]parapyridinophanes as planar chiral moieties and have already revealed that bispyridinophane catalyst **1** having a dibenz[*e,g*]isoindoline unit has moderate enantioselectivity for asymmetric benzylation of glycine derivatives **2** (up to 75% ee). For exploring further effective catalysts, we have synthesized novel planar-chiral PTCs **4a-d** having tertiary hydroxyl groups on their pyridine rings. With these catalysts **4a-d**, asymmetric benzylation reaction afforded phenylalanine derivatives **3** with up to 91% ee. Significant improvement of enantioselectivity was observed according to remote steric effect¹⁾ by introduction of sterically demanding substituents pushing oligo-methylene bridge out to the reaction site around a quaternary ammonium nitrogen. Reactions were also accelerated when using catalyst **4a-d** as compared to our previous ones due to increase of hydrophilicity around hydroxyl groups.



References

1) Mugishima, N.; Kanomata, N.; Akutsu, N.; Kubota, H. *Tetrahedron. Lett.* **2015**, *56*, 1898-1903.