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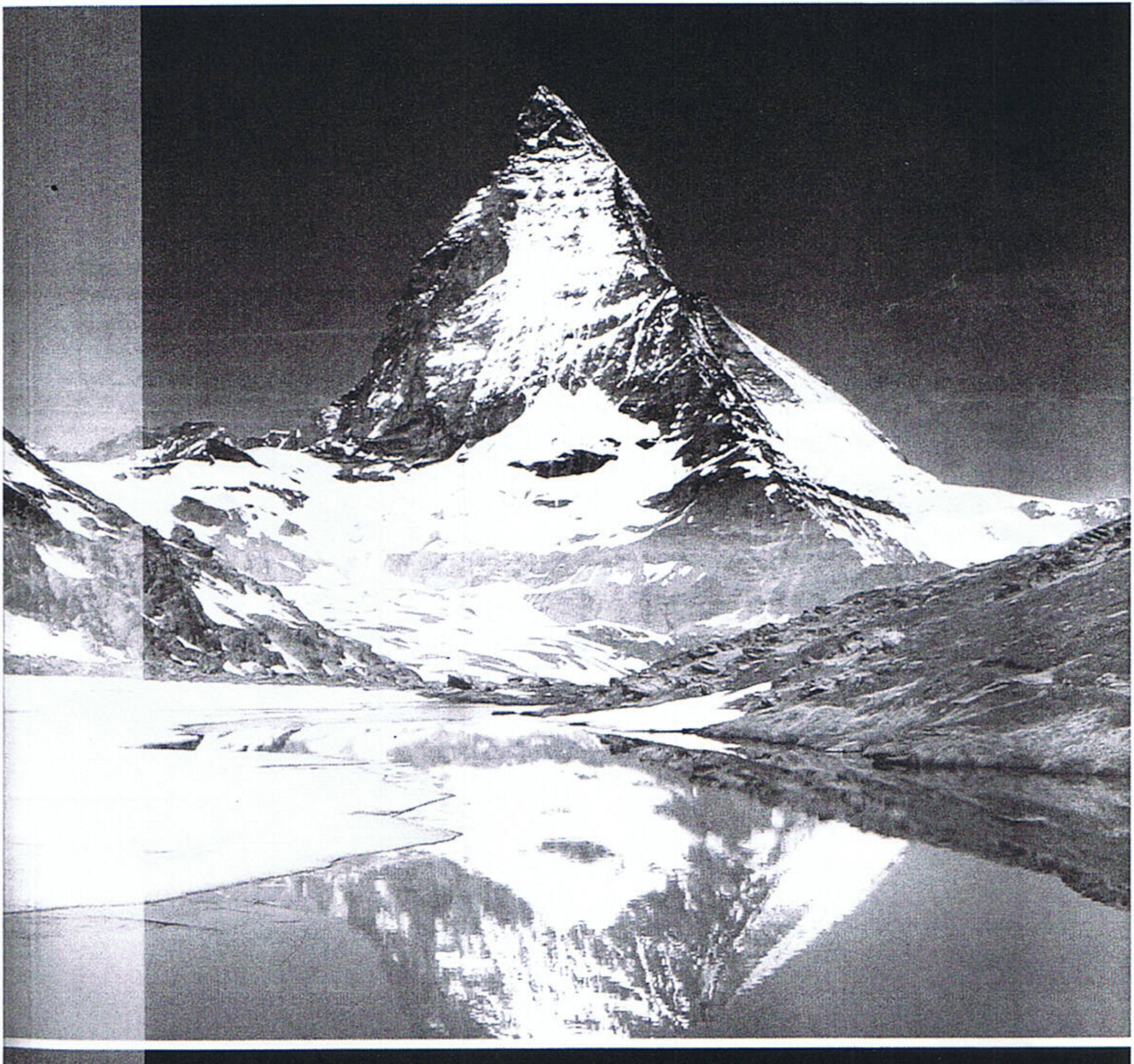

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P-148 - WALPHOS AND (R,R)-DUPHOS-IPR LIGANDS IN THE PD(0) CATALYSED ASYMMETRIC ALLYLIC ALKYLATION REACTION

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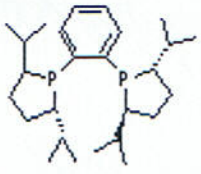
Presently asymmetric synthesis finds considerable application in providing useful enantiomerically pure compounds. One of the outstanding endeavours in this area is the creation of new C-C and C-X bonds. Since 1977 the asymmetric allylic alkylation (AAA) reaction has become a standard approach to achieve this objective [1, 2].

Two commercial ligands, (R,R)-DuPHOS-iPr 1 and Walphos 2 were tested in the Pd(0) catalysed asymmetric allylic alkylation using 1,3-diphenyl propenyl acetate as substrate, malonate as nucleophile and a variety of Pd pre-catalysts under standard conditions. Some excellent ees (> 98%) were achieved with (R,R)-DuPHOS-iPr 1 while Walphos 2 gave generally higher conversions but only when the reaction was heated [3].



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References
[1] For a key review, see: B.M. Trost, C. Lee in Catalytic Asymmetric Synthesis, I. Ojima (ed.), 2nd ed., Wiley-VCH, 2000.
[2] B.M. Trost, P.E. Strege, J. Am. Chem. Soc. 1977, 99, 1649.
[3] V.R. Marinho, J. P. Ramalho, O.M. Furtado, A.J. Burke, Eur. J. Org. Chem. submited.

P-149 - ENANTIOSELECTIVE CONJUGATE RADICAL ADDITION TO ALPHA'-PHOSPHORIC ENONES

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During the past decade, enantioselective radical reactions have been investigated with great interest. Like ionic reactions, conjugate radical addition of various precursors to alpha?beta-unsaturated carbonyl compounds was considered as the most intriguing part. In order to obtain a high enantioselectivity in the radical conjugate addition process, various kinds of bidentate templates were introduced, such as alkylidene malonates, Evans' oxazolidinones, pyrazolidinones, the imide group, and alpha'-hydroxy enones. However in the most of cases, the applications of products were limited to carboxylic acid derivatives. To extend the diversity of achiral templates, we have been interested in using alpha'-phosphoric enone template in radical conjugate addition processes. First of all, several transition metals and Box ligands complexes were screened. The combination of $Zn(OTf)_2$ and (4R,5S)-bisPh-Box in CH_2Cl_2 at -78 °C gave the product with 82% ee. Although the modification on phosphoric ester was not effective, the increased enantioselectivity up to 91% ee was obtained by changing the solvent to diethyl ether. Under present reaction condition, conjugate addition of alkyl iodides produced desired products cleanly with high enantioselectivies. In addition, when allyltributyltin was used, allylated products were obtained with high enantio- and diastereoselectivities.