Allylboration of Aldehydes by Immobilized TRIP

Selected examples:

- 96% yield, er = 97.5:2.5
- 70% yield, er = 72.5:27.5
- 86% yield, er = 98:2
- 95% yield, er = 91.5:8.5
- >99% yield, er = 91.5:8.5

Catalyst preparation:

1. styrene, divinylbenzene
2. POCl₃, py
3. H₂O

Significance: The Pericàs and Rodríguez-Escrich groups report an enantioselective allylboration of aldehydes catalyzed by polystyrene-immobilized TRIP phosphoric acid. The catalyst was prepared by copolymerization of the BINOL derivative B with styrene and divinylbenzene, resulting in a functionalization level of 0.20–0.23 mmol/g. The desired homoallylic alcohols were obtained in generally good yields (≥99%), enantioselectivities (er ≤ 99:1), and diastereoselectivities (dr ≤ 99:1). Interestingly, the scope was explored by using a single sample of the catalyst regenerated by simply washing the resin with a solution of HCl in EtOAc.

Comment: Heterogeneous catalysts offer the advantages of easy recyclability and simplified work-up procedures. Although methods for the immobilization of chiral phosphoric acids have been described, immobilization of the most successful acid (TRIP) had not previously been achieved. The authors applied their system to the continuous-flow catalytic enantioselective allylation of benzaldehyde, giving the corresponding product in 92% yield and an enantiomeric ratio of 95.5:4.5 with a turnover number of 282 and a productivity of 2.22 mmol/(h·g resin).