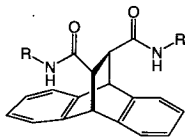


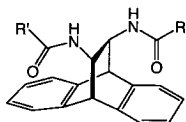
# Abstract

Five  $C_2$ -symmetric chiral selectors with their stereogenic centres incorporated into rigid structures have been synthesised. The selectors were crosslinked and immobilised to a vinyl-silica by hydrosilylation reactions with a multifunctional hydrosilane. The new stationary phases were evaluated by chromatography of a series of structurally different racemates. Compared to the commercially available Kromasil CHI-DMB and CHI-TBB sorbents, based on quite flexible selectors, the new chiral stationary phases showed improved enantioselectivity for certain groups of compounds. The influence from the length of the achiral spacer was studied by chromatography on the stationary phases based on the selectors (+)-(*S,S*)-7, (+)-(*S,S*)-8, (+)-(*5R,6S,11R,12S*)-10 and (-)-(*5S,6R,11S,12R*)-11. The effects from reversed orientation of the amide groups of the selectors were demonstrated by comparison of the chromatographic results from the phases based on (+)-(*S,S*)-7 and (+)-(*S,S*)-9. It has been shown that hydrogen bonds between the selectors and the analytes are crucial for the enantiodiscrimination.

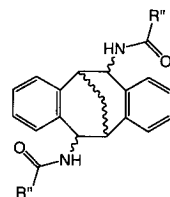


(+)-(*S,S*)-7 R:  $-\text{CH}_2\text{-CH=CH}_2$

(+)-(*S,S*)-8 R:  $-(\text{CH}_2)_9\text{-CH=CH}_2$



(+)-(*S,S*)-9 R':  $-\text{CH}_2\text{-CH=CH}_2$



(+)-(*5R,6S,11R,12S*)-10 R'':  $-\text{CH}_2\text{-CH=CH}_2$

(-)-(*5S,6R,11S,12R*)-11 R'':  $-(\text{CH}_2)_8\text{-CH=CH}_2$

The equilibrium constants for formation of the diastereomeric complexes between a chiral selector in the absence of the stationary support and the enantiomers of an analyte have been determined by NMR spectroscopy. The selectivity factors obtained from chromatographic and NMR spectroscopic experiments were compared. A concentration dependence of the chemical shift for protons in the chiral selector (+)-(*S,S*)-7 indicated the existence of self-association in solution.

**Keywords:** chiral stationary phases, enantioselective liquid chromatography,  $C_2$ -symmetric bicyclic selectors, amide group orientation, dual hydrogen bonding, NMR spectroscopy, enantioselective complexation, chemical shift displacement, self-association

ISBN: 91-628-6107-7