



## CHAPTER V

### CONCLUSION

Forty-six racemic phenoxy acid methyl esters with different type, position, and number of substituents were enantioseparated by gas chromatography using two chiral selectors: hexakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)- $\alpha$ -cyclodextrin (or ASiMe) and octakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)- $\gamma$ -cyclodextrin (or GSiMe). Both derivatized cyclodextrins possess identical substituents at C2, C3 and C6 carbons, but have different ring size. Most analytes could be completely enantioresolved by ASiMe derivative with higher degree of separation than by GSiMe derivative. The higher enantioresolution of ASiMe is probably ascribed to the appropriate orientation of cyclodextrin derivative and analyte structure.

To obtain more information about the influence of analyte structure on the enantioseparation on both of ASiMe and GSiMe phases systematically, three groups of analytes with closely related structure were selected and thermodynamic data were acquired using van't Hoff equation. The  $-\Delta H_2$  and  $-\Delta S_2$  values acquired from each chiral column are quite similar, stating that the main analyte contributions toward the interaction arise from ester and phenyl groups. Nonetheless, the interaction strength does not necessarily correlate with the discrimination of enantiomers, since some analytes showing strong interaction with stationary phase do not exhibit high enantioseparation.

On ASiMe phase, the position of substituent has great effect to enantioseparation as seen from mono-substituted analytes. The substitution at *meta*-position of the aromatic ring seems to enhance the enantio-recognition. However, type of substituent also plays a major role in enantiomeric separations, such as halogen-substituted analytes. Among all tested analytes, methyl 2-(3',5'-dichlorophenoxy)

propanoate (**3,5Cl**) shows the highest degree of enantioseparation (largest  $-\Delta\Delta H$  and  $-\Delta\Delta S$  values).

On GSiMe column, the *meta*-substituted analytes still plays the key role on enantioseparation while most of the *ortho*- and *para*-substitution poorly exhibit enantioseparation. However, the type of substitution also had a significant effect to enantioseparation, as all three isomers of only trifluoromethyl- and cyano-substituted phenoxy acid methyl esters could be enantioseparated on this column. The  $-\Delta\Delta H$  and  $-\Delta\Delta S$  values of each analyte on this column were lower than those on ASiMe column. Comparing the enantioseparation on three chiral columns, GSiMe showed lowest  $-\Delta\Delta H$  and  $-\Delta\Delta S$  values. It indicates that the most of phenoxy acid methyl esters could not form stable complex with the large-sized cyclodextrin derivative.

All the above results demonstrated that the differences in retention and degree of enantioseparation of all phenoxy acid methyl esters on ASiMe and GSiMe columns depended on several factors, e.g. type, position and number of substituent on the aromatic ring as well as the size of cyclodextrin ring. Due to the unavailability of many poly-substituted analytes, the complete effect of number of substituent on the enantioseparation could not be achieved. Hopefully, further study with larger number of phenoxy acid methyl ester analytes with various substitution patterns should be explored. In addition, molecular modeling experiments should be performed to better understand the analyte-selector interaction and that leads to enantioselective recognition mechanism.