oxygen (Juaristi, E.; Cuevas, G. *The Anomeric Effect*; CRC Press: Boca Raton, 1995; pp. 208-209.).
8. Equatorial orientation of the sulfoxide oxygen could be inferred from the NMR data (see Ref. 6). For ketone **3a** the axial proton at C-2, *cis* to oxygen suffered an upfield shift from δ 5.97 ppm to δ 5.37 ppm upon oxidation. Also, C-5 of sulfoxide **4a** appeared at lower field than C-5 of sulfide **3a** (δ 50.8, 42.9 ppm, respectively).
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11. Addition of CH_3MgBr to sulfide **3b** and sulfoxide **4b** proceeded with a high (96% de) and moderate (40% de) diastereoselectivities, respectively. Even though the absolute configuration of the Grignard addition product has not been determined yet, the lower selectivity in Grignard addition to **4b** suggests that Mg ion chelates with ring oxygen more strongly than Li ion does.

Liquid Chromatographic Resolution of *N*-1- and 2-Naphthylamide Derivatives of 2-Aryloxypropionic Acids

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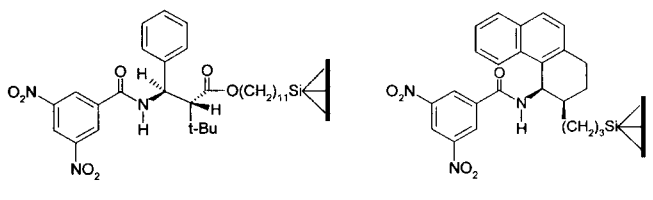
2-Aryloxypropionic acids and their ester or amide derivatives have proven to be essential herbicides and some of them are sold as the racemic mixtures.[1,2] It has been reported that the R-isomers show the herbicidal activity, the S-isomers being inactive.[3] Therefore, a few of these compounds are marketed as the single R-enantiomers.[1] Also, the most biologically active 2-aryloxypropionic acids and their derivatives have been developed. Owing to the importance of determining the enantiomeric purity of these compounds and to the dependence of their biological activities on stereochemistry, a number of studies for the resolution of 2-aryloxypropionic acids and/or their derivatives have been reported. Gas chromatographic chiral stationary phases (CSPs) based on modified cyclodextrins to resolve the ester derivatives of three 2-aryloxypropionic acids were reported.[4] Several liquid chromatographic methods using CSPs derived from *N*-3,5-dinitrobenzoylphenylglycine,[5-8] α_1-acid glycoprotein,[6,8] tartaric acid,[9] cellulose derivatives[10] and diaminocyclohexane[11,12] were investigated to separate the enantiomers of these various analytes. Recently, brush-type synthetic CSPs[13] 1 and 2 (Figure 1) were also employed to resolve several 2-aryloxypropionic acids and their derivatives.[14] Although these compounds showed generally good enantioseparation on CSPs 1 and 2, some analytes showed poor resolution, as seen in Table 1.[14] For example, 2-(2,4-dichlorophenoxy) propionic acid,[2,8] one of the important herbicides of this class in Europe and 2-(2-chlorophenoxy)propionic acid showed little enantioselectivity on CSPs 1 and 2 in the previous study. Even the enantiomers of their ester or *N*-n-butyl amide derivatives were poorly resolved on CSP 1 and/or CSP 2. In these cases, derivatization of the analyte with a proper achiral reagent which sometimes provides the necessary interaction sites for chiral recognition may improve the resolution.[15]



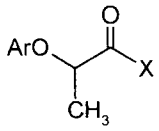
(R,R) CSP 1 (R,R) CSP 2

Figure 1. Structures of commercially available CSPs 1 and 2 used in this study.

Therefore, racemic 2-aryloxypropionic acids were derivatized with a strong π-basic 1- or 2-naphthylamine which is expected to allow an enantioselective π-π interaction with a π-acidic 3,5-dinitrobenzoyl (DNB) group of CSP. In this study, the enantioseparation of 2-aryloxypropionic acids as their *N*-1- and 2-naphthylamide derivatives was investigated on CSP 1 or CSP 2. The presence of *N*-naphthyl derivatizing moiety serves also to provide strong UV adsorption to aid detection, which affords an advantage of a lower limit of detection of 2-aryloxypropionic acids.

As good enantioseparation of the *N*-1- and 2-naphthylamide derivatives of 2-aryloxypropionic acids is observed on CSP 1, chromatographic data of these analytes on CSP 1 are presented in Tables 2 and 3. The enantiomers of *N*-1-naphthylamide derivatives of 2-aryloxypropionic acids were base-line separated on CSP 1 in all cases. Especially, fairly good enantioselectivity (α=1.37-1.66) was observed for the resolution of *N*-1-naphthylamide derivatives of 2-(2,4-dichloro- and 2-chlorophenoxy)propionic acids. The separation factors of the enantiomers of all analytes are superior to those of the corresponding *N*-n-butyl amides.[14] The degree of enantioselectivity of the *N*-1-naphthylamide derivatives of 2-aryloxypropionic acids is greater than that of the corresponding *N*-2-naphthylamide derivatives. These observed results are considered to arise from the

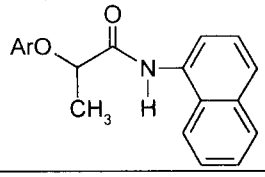
Table 1. Separation of enantiomers of 2-(2,4-dichloro- and 2-chlorophenoxy)propionic acids and their derivatives*



Ar	X	(R,R) CSP 1			(R,R) CSP 2		
		α	k'_1	Ret[a]	α	k'_1	Ret[a]
2,4-dichlorophenyl	OH	1.00	0.69[b]		1.00	0.78[b]	
2-chlorophenyl	OH	1.00	0.94[b]		1.05	0.91[b]	
2,4-dichlorophenyl	OEt	1.11	0.80[c]	(+)(R)	1.00	1.88[c]	
2-chlorophenyl	OEt	1.16	1.07[c]	(+)	1.06	2.44[c]	(+)
2,4-dichlorophenyl	O-n-Bu	1.11	0.60[c]		1.00	1.41[c]	
2-chlorophenyl	O-n-Bu	1.15	0.81[c]		1.00	1.62[c]	
2,4-dichlorophenyl	NH-n-Bu	1.00	2.36[d]		1.33	2.31[d]	(-)(R)
2-chlorophenyl	NH-n-Bu	1.00	2.78[d]		1.26	2.88[d]	(-)

*All of the data were taken from reference 14.; Flow rate=2.0 mL/min; UV 254 nm; [a] absolute configuration and/or the sign of optical rotation of the second eluted enantiomer. [b] 5% 2-propanol/hexane (V/V) with 0.1% trifluoroacetic acid as a mobile phase. [c] 0.5% 2-propanol/hexane (V/V). [d] 5% 2-propanol/hexane (V/V).

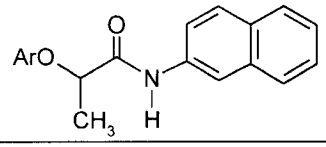
Table 2. Separation of enantiomers of *N*-1-naphthylamide derivatives of 2-aryloxypropionic acids on (R,R) CSP 1*



Entry	Ar	α	k'_1	Retained**
1	1-naphthyl	1.64	12.10	(-)(R)
2	2-naphthyl	1.40	11.55	(+)(R)
3	phenyl	1.33	5.68	(+)
4	4-methylphenyl	1.32	5.58	(+)
5	4-n-butoxyphenyl	1.40	5.68	(+)
6	4-chlorophenyl	1.45	6.54	(+)(R)
7	2,4-dichlorophenyl	1.66	4.26	(-)(R)
8	3-chlorophenyl	1.33	6.28	(+)
9	2-chlorophenyl	1.37	4.28	(-)

*Chromatography was performed at room temperature using an HPLC consisting of a Waters model 510 pump, a Rheodyne model 7125 injector with a 20 μL loop, a variable wavelength detector Dynamax UV-1 detector and a Waters 746 data module integrating recorder.; Flow rate=2.0 mL/min; UV 254 nm; Mobile phase=40% 2-propanol/hexane (V/V); **absolute configuration and/or the sign of optical rotation of the second eluted enantiomer.

Table 3. Separation of enantiomers of *N*-2-naphthylamide derivatives of 2-aryloxypropionic acids on (R,R) CSP 1



Entry	Ar	α	k'_1	Retained*
1	1-naphthyl	1.27	14.54	(-)(R)
2	2-naphthyl	1.36	11.82	(+)(R)
3	phenyl	1.10	6.01	(-)
4	4-methylphenyl	1.11	5.75	
5	4-n-butoxyphenyl	1.17	5.61	(+)
6	4-chlorophenyl	1.28	6.23	(+)(R)
7	2,4-dichlorophenyl	1.56	4.31	(-)(R)
8	3-chlorophenyl	1.15	5.98	(-)
9	2-chlorophenyl	1.31	4.14	(-)

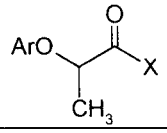
Flow rate=2.0 mL/min; UV 254 nm; Mobile phase=40% 2-propanol/hexane (V/V); *absolute configuration and/or the sign of optical rotation of the second eluted enantiomer.

conformational rigidity of the *N*-1-naphthyl derivatives engendered by the peri-hydrogen of the *N*-1-naphthyl moiety.[16] The conformationally rigid *N*-1-naphthyl derivatives without the substantial deviation from the heavily populated conformation with a lower energy are more favorable for formation of the stable diastereomeric adsorbate than the conformationally flexible *N*-2-naphthyl derivatives.[17]

A consistent elution order for the enantiomers of *N*-1- or 2-naphthyl-2-aryloxypropionamides examined was observed on (R,R) CSP 1, where the R-isomers were selectively retained. Two principal competing recognition processes are expected to occur during diastereomeric complexation between the enantiomers of *N*-1- or 2-naphthyl-2-aryloxypropionamides and the chiral selector. From the study of CPK molecular models, one chiral recognition mechanism of the *N*-naphthylamide derivatives of 2-aryloxypropionic acids is proposed, which utilizes 1) a π-π interaction between the DNB group of the chiral selector and *N*-naphthyl derivatizing moiety of the analyte and 2) a hydrogen bonding interaction between the DNB N-H hydrogen of the chiral selector and the carbonyl oxygen of the analyte. The other competing chiral recognition process is similar to the previously proposed mechanistic rationale: a π-π interaction between the DNB moiety of the CSP and the 2-aryloxy group of the analyte and a hydrogen bonding interaction between the DNB N-H hydrogen of the CSP and the carbonyl oxygen of the analyte.[14]

For the *N*-naphthylamide derivatives of 1- or 2-naphthoxy substituted 2-propionic acids, the π-electron rich *N*-naphthyl derivatizing group competes strongly with the π-electron rich naphthoxy group for a π-π interaction with the DNB

Table 4. Separation of enantiomers of *N*-1- and 2-naphthylamide and *N*-3,5-dimethylanilide derivatives of some 2-aryloxypropionic acids



Ar	X	(R,R) CSP 1			(R,R) CSP 2		
		α	k'_1[a]	Ret[b]	α	k'_1[a]	Ret[b]
2,4-dichlorophenyl	NH-1-naphthyl	1.66	4.26	(-)(R)	1.12	3.92	(-)(R)
4-chlorophenyl	NH-1-naphthyl	1.45	6.54	(+)(R)	1.14	5.25	(+)(R)
2-chlorophenyl	NH-1-naphthyl	1.37	4.28	(-)	1.10	4.13	(-)
2,4-dichlorophenyl	NH-2-naphthyl	1.56	4.31	(-)(R)	1.13	2.93	(+)(S)
4-chlorophenyl	NH-2-naphthyl	1.28	6.23	(+)(R)	1.22	3.15	(-)(S)
2-chlorophenyl	NH-2-naphthyl	1.31	4.14	(-)	1.14	3.05	(+)
2,4-dichlorophenyl	NH-3,5-DNP*	1.38	1.86[c]	(-)	1.05	1.48[c]	(+)
4-chlorophenyl	NH-3,5-DNP*	1.14	3.60[c]	(+)	1.12	1.94[c]	(-)
2-chlorophenyl	NH-3,5-DNP*	1.17	1.84[c]	(-)	1.00	1.70[c]	

Flow rate=2.0 mL/min; UV 254 nm; *DNP=3,5-dimethylphenyl; [a]40% 2-propanol/hexane (V/V) as a mobile phase. [b]absolute configuration and/or the sign of optical rotation of the second eluted enantiomer. [c]20% 2-propanol/hexane (V/V).

group of the chiral selector. Therefore, two chiral recognition processes mentioned above compete strongly with each other in these analytes. In case of the *N*-naphthylamide derivatives of other aryloxy substituted 2-propionic acids, however, the π-electron rich *N*-naphthyl derivertizing moiety of the analyte is expected to interact more preferentially with the DNB group of the chiral selector than π-electron poor 2-aryloxy group. Consequently, the former chiral recognition process predominates over the latter in this case. The greatest enantioseparation of the *N*-1- and 2-naphthylamide derivatives of 2-(2,4-dichlorophenoxy)propionic acid can be explained by the most predominant π-π interaction between the DNB group of the chiral selector and the π-electron rich *N*-naphthyl derivatizing moiety, which competes least with 2,4-dichlorophenoxy group for a π-π interaction with the DNB group. It should be pointed out that when two competing chiral recognition mechanisms occur, the relative contribution of each process to the overall time-averaged chiral recognition can be influenced by certain structural features in the analyte.[18]

On the other hand, the enantiomers of *N*-2-naphthyl amide derivatives of some 2-aryloxypropionic acids show the inverted elution orders on CSP 2, as shown in Table 4. As a result, the signs of optical rotation for the preferentially retained enantiomers of *N*-2-naphthylamide derivatives of these analytes on CSP 2 are the opposite of those on CSP 1. The reason for the observed reversal of elution order depending upon *N*-1- or 2-naphthyl derivatizing group on CSP 2 is not clear yet, because both CSP 1 and CSP 2 are expected to have similar patterns of chiral recognition, judging from two X-ray crystallographic data of similar spatial orientation of the essential interaction sites.[19,20] Presumably, the conformationally flexibility of the *N*-2-naphthylamides resulting from the absence of the peri-hydrogen might be responsible for the inversion of elution orders of these analytes. The same results are observed for the resolution of *N*-3,5-dimethylanilide derivatives of these analytes (Table 4). The enantiomers of the *N*-3,5-dimethylanilide derivatives lacking the peri-hydrogen show the inverted elution order on CSP 2. It is also noted that lower enantioselectivity of the *N*-3,5-dimethylanilide derivatives than that of the *N*-1- or 2-naphthylamide derivatives is due to the less strong π-basic nature of the former derivatizing group than that of the latter.

In summary, liquid chromatographic enantioseparation of 2-aryloxypropionic acids as their *N*-1- or 2-naphthylamide derivatives was investigated with two proposed competing chiral recognition processes in this study. CSP 1 showed the base-line resolution of all *N*-1-naphthylamide derivatives of 2-aryloxypropionic acids used in this study. Especially, CSP 1 afforded good enantioselectivity (α=1.31-1.66) for the resolution of the enantiomers of *N*-1- or 2-naphthyl-2-(2,4-dichloro- and 2-chlorophenoxy)propionamides. CSP 1 is expected to be useful for a lower limit of enantiomeric detection of the *N*-1- or 2-naphthylamide derivatives of several 2-aryloxypropionic acids owing to a strong UV adsoption of *N*-naphthyl derivatizing moiety. Consequently, either CSP 1 or CSP 2 proved to be capable of separating the enantiomers of a variety of 2-aryloxypropionic acids and their derivatives.

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Easy Preparation of (*Z*)-γ-Trimethylsilyl Allylic Alcohol from 3-(Trimethylsilyl)-1-propyne for the Stereoselective Synthesis of *syn*-1,2-Diols

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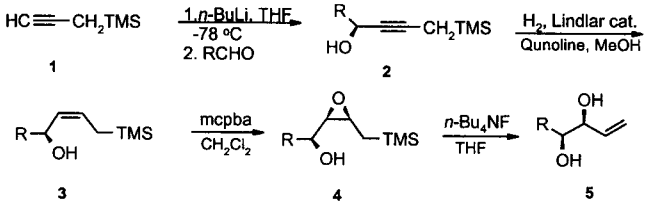
Stereoselective synthesis of 1,2-diols and 1,3-diols[1] has been well utilized by synthetic chemists who are interested in polyoxygenated natural products. As part of our efforts to develop methods for the stereoselective synthesis of 1,2-diols, we describe herein a simple approach to *syn*-1,2-diols *via* (*Z*)-γ-trimethylsilyl allylic alcohols **3**.

In 1988, Matsumoto *et al.* reported the utilization of compound **3** for the synthesis of *syn*-diol **5**, which was prepared from (*Z*)-γ-allylic alcohols.[2] Their synthesis involved complicate sequences. In contrast, our approach in Scheme 1 is relatively concise and straightforward.

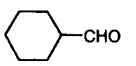
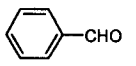
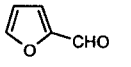
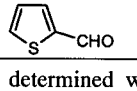
In our synthetic route, first of all, the carbanion of 3-(trimethylsily)-1-propyne (**1**) was reacted with aldehyde to give compound **2**. Subsequently **2** was partially hydrogenated to *cis*-allylic alcohol **3**[3] utilizing Lindlar catalyst. Then, compound **3** was converted to *threo*-epoxide **4** by treating with mcpba. The treatment of crude **4** with tetrabutylammonium fluoride provided the desired *syn*-1,2-diol **5**.



Scheme 1

We examine this reaction for several aldehydes. The results are summarized in Table 1. The yields are satisfactory and the stereoselectivities are preferentially *syn*. In a hope to change the *syn*-selectivity to *anti*-selectivity, we used $VO(acac)_2$ with *t*-butylhydroperoxide[4] for the expoxidation or *t*-butyldimethylsilyl ether derivative of **3**. But the results gave predominantly *syn*-selectivity. To expand the

Table 1. The Stereoselectivity for Various Aldehydes

Entry	Aldehyde	Yield of Diol (%)	*syn* : *anti*[a]
1	C_2H_5CHO	92	97:3
2	C_3H_7CHO	90	96:4
3		81	96:4
4		92	94:6
5		98	100:0
6		92	95:5

[a] The ratios were determined with both GC separations and ^1H NMR data of the acetonide of diols.[5]