Special Issue Article

Synthesis and Application of C2 and C3 Symmetric (R)-Phenylglycinol-Derived Chiral Stationary Phases

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ABSTRACT A C3 symmetric (R)-phenylglycinol N-1,3,5-benzenetricarboxylic acid-derived chiral stationary phase (CSP) and three C2 symmetric (R)-phenylglycinol CSPs were newly synthesized using o-, m-, and p-phthaloyl dichlorides.
These CSPs were used to compare the resolution of 25 chiral samples using a previously reported 3,5-dinitrobenzoyl (R)-phenylglycinol-derived CSP. Even though all CSPs have the same chiral moiety, the C3 symmetric CSP showed the best resolution. *Chirality 28:186–191, 2016.*

KEY WORDS: 1,3,5-benzenetricarboxylic acid; C2 symmetry; C3 symmetry; (R)-phenylglycinol CSP; chiral HPLC

Various types of high-performance liquid chromatography (HPLC) chiral stationary phases (CSPs) such as brush/Pirkle-type stationary phases,[1] crown ethers,[2] ligand exchange,[3] proteins,[4] polysaccharides,[5] cyclodextrin,[6] and cyclofructan[7] have been developed.[8,9] Many amino acid-based CSPs have been reported as chiral selectors; for example, (S)-leucine and (R)-phenylglycine-derived brush/Pirkle-type CSP,[10] (S)-proline- and (S)-lysine-derived ligand-exchange CSPs,[11] and a protein CSP.[12] Various aminoalcohol-derived CSPs have also been synthesized using (R)-phenylglycinol, (S)-alaninol, (S)-leucinol, and (S)-tert-leucinol. These aminoalcohol-derived CSPs have some merits compared with amino acid-derived CSPs in short and simple synthetic processes. Among the various amino-alcohol-derived CSPs, (R)-phenylglycinol- and (S)-leucinol-derived CSPs showed better results in the resolution of many chiral samples.[13–16] A CSP derived from a synthetic amino alcohol, (S)-1-anilino-3-propyl-2-propanol, has also been reported.[17]

Some compounds with both chirality and a symmetric element have been used as chiral catalysts in the Diels-Alder reaction,[18,19] ethylation of benzaldehyde,[20] and addition reaction of β-ketoester.[21] Mechanistic studies of the asymmetric synthesis process of some of these compounds have been reported.[22,23] Many studies have investigated the simultaneous application of cyclodextrins as a chiral selector and a chiral catalyst.[24,25] Many chiral symmetric compounds have also been used as chiral catalysts[18–23]; it is assumed that these compounds can also be used as powerful chiral selector candidates.

1,3,5-Benzenetricarboxylic acid has been used as an important cross-linker for fabricating metal-organic frameworks (MOFs).[26,27] Recently, we reported the preparation of some chiral MOFs by using 1,3,5-benzenetricarboxylic acid as a cross-linker and used them in chiral recognition tests.[28–30]

(R)-Phenylglycinol N-3,5-dinitrobenzoyl amide-derived CSP (CSP 1) has been used in the resolution of various chiral analytes with moderate efficiency.[14,15] There are only two reports related to symmetric CSPs. Gasparrini et al. reported the chiral separation of several amino acid derivatives on a C3 symmetric CSP in 1995.[31] Tichy et al. reported a C2 symmetric CSP for the resolution of chiral amino alcohol derivatives in 1994.[32] In this study, a new (R)-phenylglycinol *N*-1,3,5-benzenetricarboxylic acid-derived CSP (CSP 2) with C3 symmetry was synthesized and used for the resolution of various chiral samples. In addition, three C2 symmetric CSPs were prepared by using both (R)-phenylglycinol and o-, m-, and p-phthaloyl dichlorides. The previously reported CSP 1 was also prepared for comparison with newly prepared CSPs (CSP 2–5) using the same chiral samples under the same separation conditions. Twenty-five chiral samples (five π-basic, six π-acidic, and 14 antibiotic oxazolidinones) were used in this study.

MATERIALS AND METHODS

General Methods

1H-NMR spectra were measured with a Bruker (Billerica, MA) AVANCE digital 400 spectrometer (400 MHz). Elemental analysis data were obtained using a ThermoFisher (Waltham, MA) Flash 2000 Elemental analyzer. All reagents used in this study were purchased from Tokyo Chemical Industry (Tokyo, Japan). The spherical silica gel (5 μm) was purchased from Fuji Silysia Chemical (Tokyo, Japan).

Preparation of CSP 2

N1,N3,N5-Tris(2-hydroxy-1-phenylethyl)benzene-1,3,5-tricarboxamide (2a). Thionyl chloride (7.00 mmol) and 3 drops of dimethylformamide (DMF) were gradually added to a stirred solution of 1,3,5-benzenetricarboxylic acid (2.26 mmol) in 40 mL of tetrahydrofuran (THF), and the mixture was refluxed for 18 h. After reaction, the solvent and excess thionyl chloride in the reaction mixture were removed by a rotary evaporator.[33] The resulting product was gradually

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Received for publication 21 October 2015; Accepted 3 December 2015
DOI: 10.1002/chir.22572
Published online 20 January 2016 in Wiley Online Library (wileyonlinelibrary.com).

added to a solution of (R)-phenylglycinol (1.76 mmol) and triethylamine (1 mL) in 30 mL of methylene chloride at 0°C. The reaction mixture was stirred at room temperature under nitrogen for 36 h, and then washed successively with 1.2 N HCl and saturated $NaHCO_3$. The solvent was removed after drying over anhydrous $MgSO_4$. The reaction mixture was first dissolved in a solution of methanol and methylene chloride, and then n-hexane was added to it. A white solid product was obtained, which was recrystallized and dried in a vacuum oven. **2a**; Yield 48.2%, 1H NMR (DMSO-d6) δ: 3.63–3.67 (dd, 1H), 3.71–3.76 (dd, 1H), 5.07–5.12 (m, 2H), 7.21–7.25 (tt, 1H), 7.30–7.33 (t, 2H), 7.38–7.40 (d, 2H), 8.49 (s, 1H), 9.09–9.12 (d, 1H).

N1,N3,N5-Tris(2-hydroxy-1-phenylethyl)benzene-1,3,5-tricarboxamide (triethoxysilyl) propyl carbamate (2b) and **CSP 2**. A solution of 3-(triethoxysilyl)propyl isocyanate (5.81 mmol), *N1,N3,N5*-tris(2-hydroxy-1-phenylethyl)benzene-1,3,5-tricarboxamide (triethoxysilyl) propyl carbamate (1.76 mmol), and triethylamine (1 mL) in 100 mL of 1,4-dioxane was stirred at reflux for 72 h. After cooling, the mixture was evaporated under reduced pressure, and directly added to a flask containing 5-μm silica gel (4.00 g) in 100 mL of toluene dehydrated by the Dean-Stark trap. The mixture was heated to reflux for 72 h with stirring magnetically. The modified silica gel was washed with toluene, methylene chloride, ethyl acetate, ethyl alcohol, and ethyl ether, and then dried in a vacuum oven.

Preparation of CSP 3–5

N,N-Bis((R)-2-hydroxy-1-phenylethyl)phthalamide (3a–5a). To a stirred solution of each phthaloyl chloride (ortho-, meta-, para-; 3.21 mmol) and triethylamine (7.85 mmol), 30 mL of methylene chloride was considerately added to a solution of (R)-phenylglycinol (7.14 mmol) in 70 mL of methylene chloride at 0°C. The reaction mixture was stirred for 24 h and then washed with 1.2 N HCl and saturated $NaHCO_3$. The solvent was removed after drying over anhydrous $MgSO_4$. The reaction product was first dissolved in a small amount of the mixed solution of

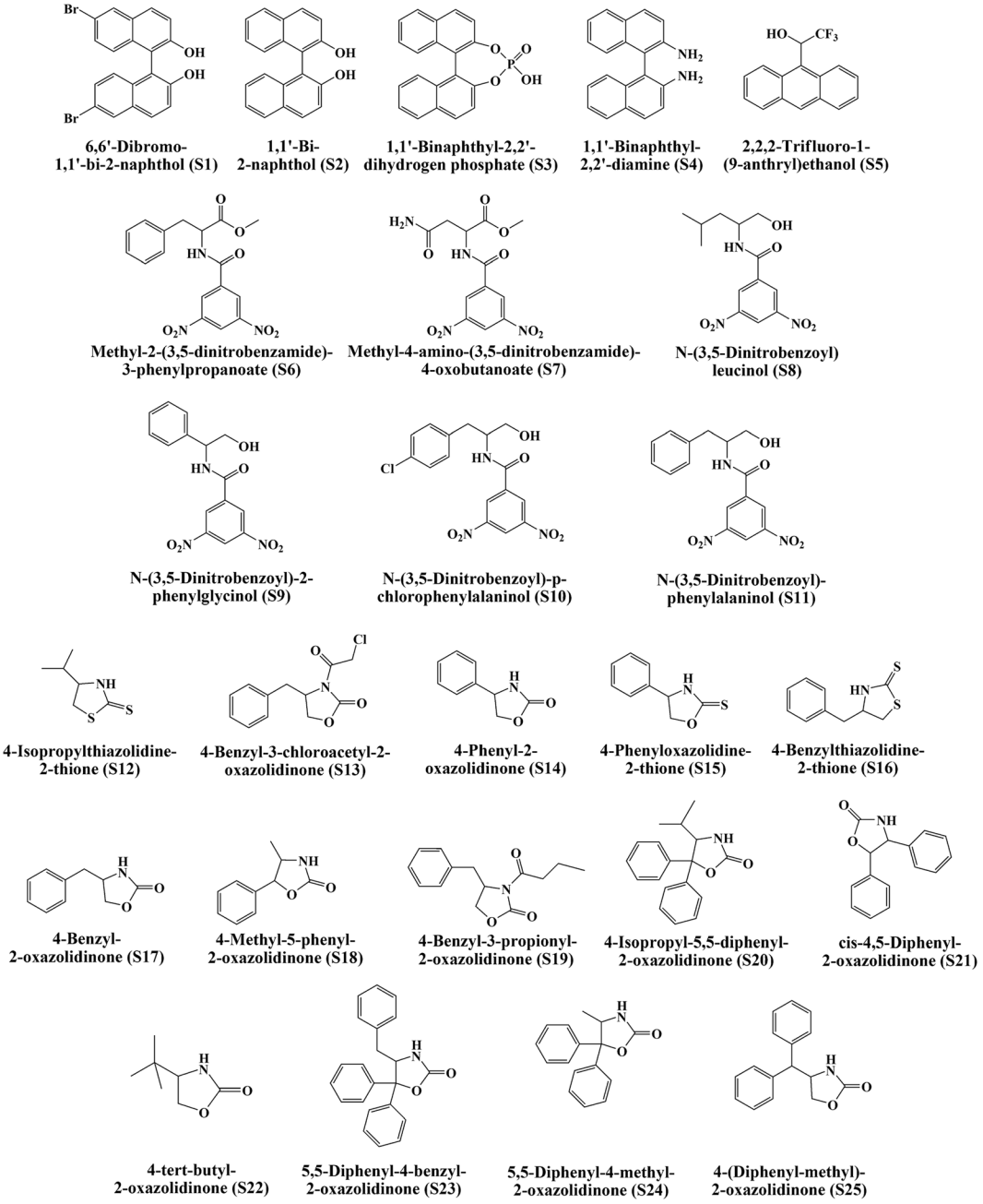
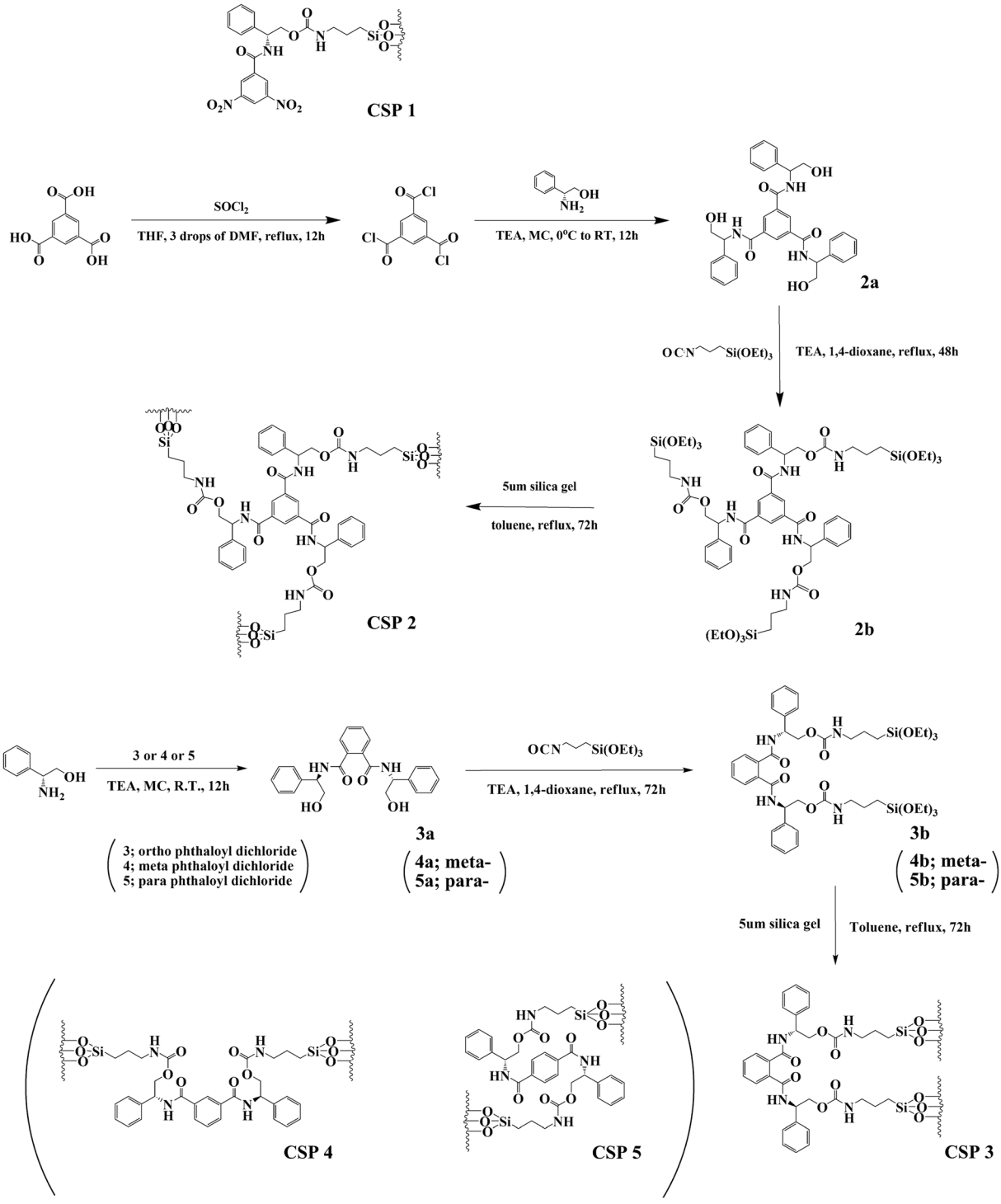


Fig. 1. Structure of racemic analytes investigated in this study.



Scheme 1. Synthetic procedures for CSP 2-5.

methanol and methylene chloride, and then n-hexane was added to the solution. A white solid product appeared, which was recrystallized and filtered and dried in a vacuum oven. **3a**; Yield 69.0%, 1H NMR (DMSO-d6) δ: 3.57–3.66 (m, 2H), 4.82–4.85 (t, 1H), 5.00–5.06 (q, 1H), 7.22–7.25 (tt, 1H), 7.28–7.32 (tt, 2H), 7.38–7.40 (d, 2H), 7.52–7.55 (m, 1H), 7.56–7.59 (m, 1H), 8.70–8.72 (d, 1H).**4a**; Yield 64.5%, 1H NMR (DMSO-d6) δ: 3.65–3.78 (m, 4H), 4.97–5.00 (t, 2H), 5.01–5.13 (td, 2H), 7.22–7.26 (tt, 2H), 7.30–7.35 (t, 4H), 7.40–7.42 (d, 4H), 7.57–7.61 (t, 1H), 8.04–8.06 (dd, 2H), 8.40–8.41 (s, 1H), 8.88–8.90 (d, 2H). **5a**; Yield 69.0%, 1H NMR (DMSO-d6) δ: 3.64–3.77 (m, 2H), 4.97–5.00 (t, 1H), 5.06–5.12 (m, 1H), 7.22–7.26 (tt, 1H), 7.31–7.35 (t, 2H), 7.40–7.41 (d, 2H), 8.00 (s, 2H), 8.85–8.86 (d, 1H).

***N,N-Bis*((*R*)-*2-hydroxy-1-phenylethyl*)*phthalamide* (*triethoxysilyl*) *propylcarbamate* (*3b–5b*)**. A solution of 3-(triethoxysily)propyl isocyanate (2.48 mmol), (*N,N*-bis((R)-2-hydroxy-1-phenylethyl)phthalamide (**3a–5a**) (5.46 mmol), and triethylamine (5.46 mmol) in 100 mL of 1,4-dioxane was stirred at reflux for 72 h. After cooling, the mixture was evaporated under reduced pressure, and directly added to a flask containing 5-μm silica gel (4.00 g) in 100 mL of toluene dehydrated by the

TABLE 1. Elemental analysis of chiral stationary phases (CSPs)

	C (%)	N (%)	Based on C	Based on N
CSP 1	2.055	0.528	0.086 mmol/g	0.094 mmol/g
CSP 2	12.65	1.679	0.167 mmol/g	0.200 mmol/g
CSP 3	6.156	0.923	0.122 mmol/g	0.165 mmol/g
CSP 4	2.173	0.380	0.043 mmol/g	0.068 mmol/g
CSP 5	0.959	0.111	0.019 mmol/g	0.020 mmol/g

Dean-Stark trap. The mixture was heated to reflux for 72 h with stirring magnetically. The modified silica gel was washed with toluene, methylene chloride, ethyl acetate, ethyl alcohol, and ethyl ether, and dried in a vacuum oven.

Chromatography

The HPLC system comprised a Waters 2690 Separation Module, which consists of a Waters 996 photodiode array detector and an auto sampler (Waters, Milford, MA). HPLC-grade solvents were obtained from J.T. Baker (Phillipsburg, NJ). The mobile phase consisted of 2-propanol: n-hexane (10:90) and 2-propanol:n-hexane:trifluoroacetic acid (10:90:0.1) at a flow rate of 1.2 mL/min. Twenty-five samples (S1–S25) were used in this study. Samples S1–S5 are π-basic, samples S6–S11 are π-acidic amino acid derivatives, and samples S12–S25 are oxazolidinone series of chiral medicines. The sample structures are shown in Figure 1. The chiral samples were purchased from Sigma-Aldrich (Seoul, Korea) and Tokyo Chemical Industry (Tokyo, Japan). The sample structures are shown in Figure 1.

RESULTS AND DISCUSSION

Synthetic procedures for CSP 2–5 are shown in Scheme 1. CSP 1 was prepared using a previously reported method.[15] The synthesis of CSP 2 includes four steps, including acylation, whereas the synthesis of CSP 3–5 requires only three steps. All products (**2b, 3a, 4a,** and **5a**) were in the form of a white solid, with very poor solubility in all solvents except for DMF and DMSO. Because of the poor solubility, the product yields were low.

The obtained compounds were identified by comparing the obtained NMR data with those of previously prepared similar compounds. Elemental analyses were carried out to determine the extent of bonding between chiral selectors and the silica gel; the results are shown in Table 1.

As shown in Table 1, silica gel in CSP 2 and CSP 3 contained more than 0.1 mmol/g of chiral selectors, whereas CSP 4 and CSP 5 contained only 0.02–0.04 mmol/g. Even though we conducted additional synthetic experiments for CSP 4 and CSP 5, the extent of covalent binding ratio between each chiral selector to silica gel did not increase. It is believed that the low covalent binding ratio was caused by the low solubility of the precursors of CSP 4 and CSP 5.

Several chromatograms for the resolution of the first sample, 6,6′-dibromo-1,1′-bi-2-naphthol (S1), on CSP 1–5 are shown in Figure 2. S1 separated on CSP 2 and CSP 3, but not on others.

Analyses were performed with the remaining 24 samples, and the results are shown in Table 2.

It was expected that π-acidic CSP 1 would perform better than the others in the resolution of the π-basic chiral samples (S1–S5). However, all of the π-basic chiral samples separated on CSP 2, but only two (S4, S5) separated on π-acidic CSP 1, one each on CSP 4 and CSP 5, and none on CSP 3. Therefore, some structural interactions occur between CSP 2 and S1–S5 that are more important than the general face-to-face π–π interactions between π-acidic CSP and π-basic samples.

In the chiral resolution of the π-acidic amino acid derivatives (S6–S11) on CSP 1–5, S9–S11 separated on both CSP 1 and CSP 2, but only S8 separated on CSP 3, and none on CSP 4 and CSP 5. CSP 1 showed a slightly better resolution from the selectivity point of view than CSP 2 for the separation of S9–S11, which have a phenyl group in common.

In the case of 14 oxazolidinone samples (S12–S25), three samples (S20, S21, and S24) resolved on CSP 1, six (S13, S14, S18, S21, S23, S24, and S25) on CSP 2, only S12 on CSP 3, and S16 and S22 on CSP 4 and CSP 5, respectively. Chiral separation results on CSP 2 are much better than those on CSP 1 and are slightly worse than those obtained with the

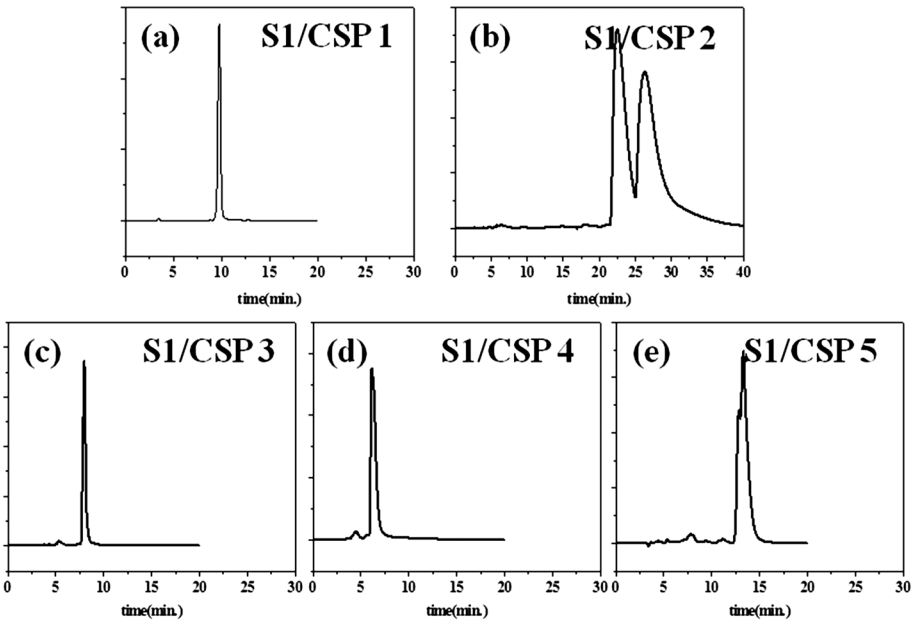


Fig. 2. Representative chromatograms of 6,6′-dibromo-1,1′-bi-2-naphthol (S1) on (**a**) CSP 1, (**b**) CSP 2, (**c**) CSP 3, (**d**) CSP 4, and (**e**) CSP 5 (CSP: chiral stationary phase).

TABLE 2. Resolution of chiral samples on chiral stationary phases (CSPs)

		CSP 1		CSP 2		CSP 3		CSP 4		CSP 5		
Sample		k_1	α	k_1	α	k_1	α	k_1	α	k_1	α	No.[b]
π-Basic compounds	S1	1.35	1.00	9.53[a]	1.17[a]	5.31	1.03	5.04	1.00	2.06	1.00	2
	S2	1.08	1.00	6.47[a]	1.13[a]	3.66	1.00	3.49	1.17	1.70	1.00	2
	S3	1.07	1.00	3.16	1.10	1.62	1.00	1.78	1.00	1.48	1.00	1
	S4	2.56	1.08	8.70[a]	1.07[a]	4.83	1.00	1.74	1.00	2.77	1.00	2
	S5	0.82	1.16	3.34[a]	1.07[a]	2.51	1.00	3.06	1.00	1.50	1.00	2
π-Acidic compounds	S6	0.95	1.00	4.34[a]	1.00[a]	2.16	1.00	1.70	1.00	1.54	1.00	0
	S7	0.97	1.00	4.28[a]	1.00[a]	2.16	1.00	1.71	1.00	1.58	1.00	0
	S8	1.64	1.00	4.52[a]	1.00[a]	3.85	1.02	2.82	1.00	2.46	1.00	1
	S9	2.52	1.47	9.64	1.06	6.57	1.00	3.35	1.00	2.74	1.00	2
	S10	3.32	1.16	9.89	1.11	2.90	1.00	4.57	1.00	3.56	1.00	2
	S11	2.26	1.14	7.57	1.06	6.52	1.00	3.62	1.00	2.92	1.00	2
Oxazolidinone	S12	5.19	1.00	6.58[a]	1.00[a]	2.81[a]	1.02[a]	2.26	1.00	2.02	1.00	1
	S13	5.20	1.00	8.67[a]	1.03[a]	5.90[a]	1.00[a]	4.72	1.00	4.47	1.00	1
	S14	9.49	1.00	6.21	1.03	5.35[a]	1.00[a]	4.10	1.00	3.83	1.00	1
	S15	7.60	1.00	2.21[a]	1.00[a]	5.31[a]	1.00[a]	3.52	1.00	3.02	1.00	0
	S16	9.14	1.00	5.76[a]	1.00[a]	3.35[a]	1.00[a]	2.30	1.04	2.00	1.02	2
	S17	4.82	1.00	7.01[a]	1.00[a]	5.93[a]	1.00[a]	5.40	1.00	4.48	1.00	0
	S18	15.4	1.00	4.44[a]	1.14[a]	5.44[a]	1.00[a]	5.42	1.00	4.55	1.00	1
	S19	2.29	1.00	4.00[a]	1.00[a]	5.90[a]	1.00[a]	4.74	1.00	4.49	1.00	0
	S20	4.64	1.16	6.78[a]	1.00[a]	2.87[a]	1.00[a]	5.90	1.00	4.00	1.00	1
	S21	9.25	1.11	7.95	1.17	5.93[a]	1.00[a]	3.23	1.00	2.96	1.00	2
	S22	2.23	1.00	5.76	1.00	5.53[a]	1.00[a]	2.32	1.04	2.26	1.03	2
	S23	16.2	1.00	9.05	1.11	1.44	1.00	3.80	1.00	3.23	1.00	1
	S24	16.7	1.10	8.08	1.11	3.07[a]	1.00[a]	ND	ND	ND	ND	2
	S25	26.5	1.00	7.26	1.11	3.86[a]	1.00[a]	2.13	1.00	1.79	1.00	1
No.[c]		8		15		3		3		2		31

Detection at 210–400 nm; flow rate, 1.2 mL/min; eluent, IPA:*n*-hexane = 10:90.
[a]IPA:hexane:TFA = 10:90:0.1.
[b]Number of CSPs giving separation.
[c]Number of separated samples.

commercially available Whelk-O-1 column. (Nine from eleven oxazolidinones were separated on Whelk-O-1 column.)[34]

CONCLUSION

A C3 symmetric (R)-phenylglycinol N-1,3,5-benzenetricarboxylic acid-derived chiral stationary phase (CSP 2) and three C2 symmetric (R)-phenylglycinol CSPs (CSP 3–5) prepared with o-, m-, p-phthaloyl dichlorides were synthesized to compare the resolution of 25 chiral samples with a previously reported 3,5-dinitrobenzoyl (R)-phenylglycinol-derived CSP (CSP 1). Eight enantiomeric samples were separated on CSP 1, 15 on CSP 2, 3 on CSP 3 and CSP 4 each, and 2 on CSP 5. Even though all CSPs have the same chiral moiety, C3 symmetric CSP 2 showed the best resolution among all the 25 chiral samples. It is believed that a structural interaction derived from the C3 symmetry led to an additional interaction between the CSP and chiral samples, which in turn led to improved resolution. Chiral symmetric CSPs should be further investigated to understand their properties.

ACKNOWLEDGMENTS

This work was supported by a grant from the National Research Foundation of Korea (NRF) (2014R1A1A2054325).

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