AXIALLY CHIRAL SELECTORS OF C_2 SYMMETRY BOUND TO SILICA: SYNTHESIS AND HPLC-EVALUATION

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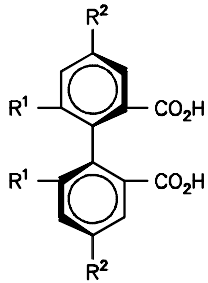
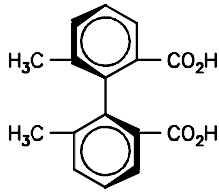
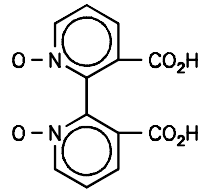
Axially chiral biaryl stationary phases (CSPs) of C_2 symmetry bound to 3-aminopropyl silica both by ionic and covalent bond were prepared. The separation effectivity of the CSPs so obtained was investigated using 2-acylamino alcohols and biaryl derivatives as analytes. Whereas ionically bound phases derived from biphenyl-2,2′-dicarboxylic or 2,2′-bipyridine-3,3′-dicarboxylic acids (CSP 1, 2, 3 and 4) generally exhibited good resolving performance for 2-acylamino alcohols, they were ineffective for biaryl derivatives. On the other hand, covalent CSPs showed poor selector properties with acylamino alcohols; the binaphthyl CSP 7 resolved some of the biaryl analytes. Phase CSP 6 was completely inactive toward all the compounds tested. Absolute configuration of 4,4′,6,6′-tetranitrobiphenyl-2,2′-dicarboxylic acid (*II*) has been derived from its CD spectrum and some speculations on configuration of bipyridine diacid *IV* are presented.

The recent boom of chromatography on chiral stationary phases (CSPs) has brought an intensive search for efficient chiral selectors (for a review see ref.[1]). Whereas the chirality of most chiral selectors is based on one or more chiral centers, much less of them possess other kinds of chirality (such as helical or axial) that may offer equally good or even better separation properties. A special group of prospective selectors are systems possessing a C_2 symmetry axis: in interaction of these systems with an analyte the number of competing diastereoisomeric situations should be strongly reduced[2].

We have recently investigated some CSPs of C_2 symmetry, based on 6,6′-dinitrobiphenyl- and 6,6′-dimethylbiphenyl-2,2′-dicarboxylic acids (*I* and *III*, respectively) ionically bound to 3-aminopropyl silica[3] (CSP 1 and 3, Fig. 1). The promising results, particularly as concerns enantiomeric separation of 2-acylamino alcohols on CSP 1, encouraged our search for other C_2-symmetrical biaryl selectors ionically or covalently bound to the silica carrier. In order to increase the number of polar groups in the selector *I* (and thus enhance its orienting power), we have tried optically active 4,4′,6,6′-tetranitrobiphenyl-2,2′-dicarboxylic acid ((+)-*II*). We also investigated another polar system, 2,2′-bipyridine-3,3′-dicarboxylic acid 1,1′-dioxide (*IV*) which is formally analogous to the biphenyl selectors *I* – *III*. Compounds (+)-*II* and (–)-*IV* were anchored ionically to 3-aminopropyl silica giving the respective phases CSP 2 and 4 (Fig. 1).

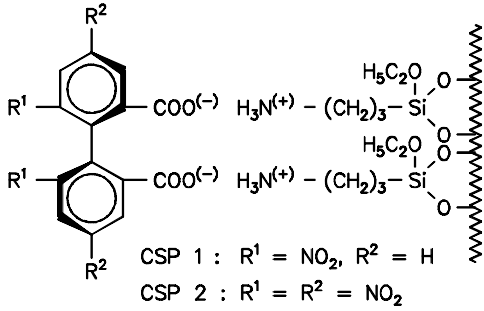


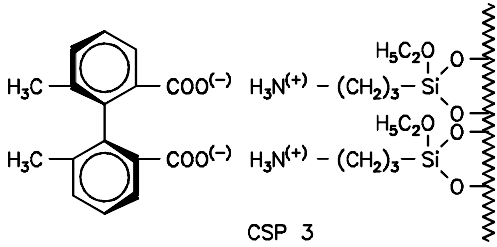




(*R*)–(+)–*I* : $R^1 = NO_2$, $R^2 = H$ (*S*)–(+)–*III* (–)–*IV*

(*R*)–(+)–*II* : $R^1 = R^2 = NO_2$





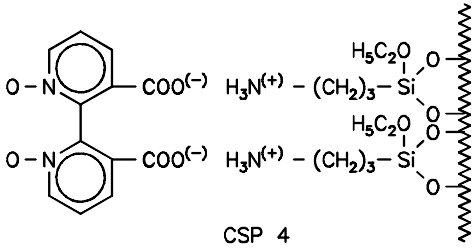


FIG. 1

Chiral diacids *I* – *IV* and the corresponding ionic phases CSPs 1 – 4 (for the configuration of acid *IV* see text)

As covalently bound phases we prepared CSPs 5 – 7 (Fig. 2). Since we are currently investigating chiral biaryl systems, it was of particular interest to study the potentialities of the obtained CSPs for the separation of biaryl analytes, making use of the great array of derivatives available in our Laboratory.

Racemic acid (±)-*II* was synthesized by nitration of biphenyl-2,2′-dicarboxylic acid[4] and resolved as described in the literature[5,6]. Racemic acid (±)-*IV* was prepared by oxidation of 2,2′-bipyridine-3,3′-dicarboxylic acid and resolved with brucine[7].

The covalently bound phases CSP 5 – 7 were obtained by reaction of the respective known chiral dibromides (–)-*V* (ref.[8]), (–)-*VI* (ref.[9]), and (–)-*VII* (ref.[10]) with 3-aminopropyl silica in benzene. Although we cannot confirm directly the cyclic structure of the products, there is ample evidence (see e.g. ref.[11]) that dibromides of the above type react with primary amines to give invariably cyclic amines as the sole products even under conditions favouring acyclic compounds (excess of the amine).

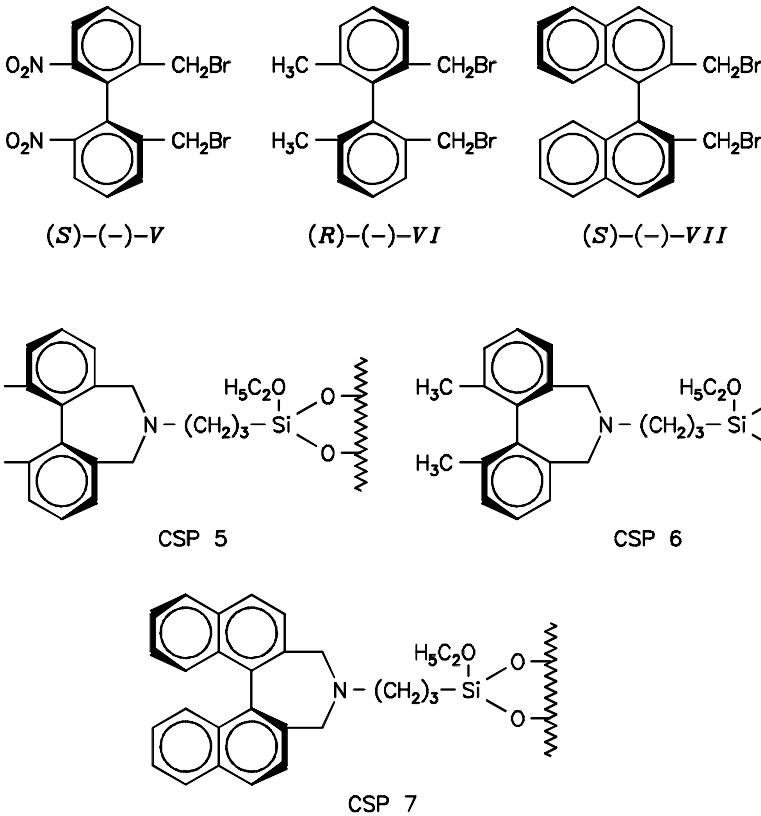


FIG. 2
Chiral dibromides *V* – *VII* and the corresponding covalent phases CSP 5 – 7

EXPERIMENTAL

Chromatography

Liquid chromatography was carried out using a Varian 2510 pump, a Varian 2550 UV-detector (detection at 254 nm) and a polarimetric detector (Chiralizer, Knauer). Analyses were performed on 250 × 4 mm stainless steel columns (slurry-packed in the usual manner) with 10% 2-propanol in heptane as the mobile phase; flow rate 0.5 ml/min. Sample solutions (about 1 mg/ml) were introduced via a 20 μl loop. Hold-up times were determined using 1,3,5-tri-*tert*-butylbenzene.

Materials

(*R*)-(+)-4,4′,6,6′-Tetranitrobiphenyl-2,2′-dicarboxylic acid ((+)-*II*), prepared and resolved as described[4,5], had $[\alpha]_D^{25}$ +124.3° (*c* 1.0, 0.1 M NaOH) (reported[6] [α] +115° (*c* 1.64, 0.1 M NaOH), and $[\alpha]_D^{20}$ +126 ± 4° (*c* 0.8, 0.1 M NaOH), ref.[12]); (–)-2,2′-bipyridine-3,3′-dicarboxylic acid 1,1′-dioxide[7] ((–)-*IV*) had $[\alpha]_D^{25}$ –52.3° (*c* 0.5, 0.1 M NaOH). The dibromide (–)-*V* had m.p. 170 – 173 °C and $[\alpha]_D^{25}$ –7.2° (*c* 2.0, tetrahydrofuran) (reported[8] m.p. 171.5 – 172.5 °C, $[\alpha]_D^{32}$ –8.9° (*c* 2.0, tetrahydrofuran)); dibromide (–)-*VI*: m.p. 51 – 53 °C, $[\alpha]_D^{25}$ –52.0° (*c* 0.5, benzene) (reported[9] m.p. 52 – 53 °C, $[\alpha]_D^{20}$ –46.9° (*c* 0.33, benzene)); (–)-*VII*: m.p. 180 – 184 °C, $[\alpha]_D^{25}$ –158.8° (*c* 1.0, benzene) (reported[10] m.p. 182 – 184 °C, $[\alpha]_D^{23}$ –159.2° (*c* 1.0, benzene)).

3-Aminopropyl silica was a Tessek product (Separon SGX-NH_2, 7 μm, found: 6.33% C, 1.55% H, 2.22% N). Stationary phases CSP 1 and CSP 3 were prepared as described previously[3]. The amino alcohol derivatives **1** – **31** (Scheme 1) were available from our previous studies; the pertinent references concerning their preparation and/or physicochemical properties are summarized in our previous paper[3]. Some of the biaryl analytes **32** – **68** (Scheme 2) are already known, some will be described elsewhere[13].

Preparation of Phase CSP 2

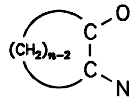
A solution of (*R*)-(+)-4,4′,6,6′-tetranitrobiphenyl-2,2′-dicarboxylic acid ((+)-*II*; 920 mg) in methanol (15 ml) was mixed with a slurry of Separon SGX-NH_2 (3.0 g, 4.44 mmol) in methanol (10 ml). The mixture was intermittantly shaken for 1 day at room temperature, filtered, the adsorbent was washed with methanol, acetone, ether and pentane (70 ml each) and dried at 50 – 60 °C in vacuo. The washings were evaporated and the recovered unreacted acid was accurately weighed. The amount of the acid retained on the adsorbent was obtained by subtracting the weight of the recovered acid (218 mg) from that originally applied. For CSP 2 the content of (+)-*II* was thus 0.45 mmol/g.

Preparation of Phase CSP 4

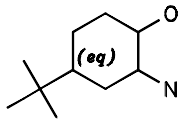
A mixture of finely dispersed (–)-2,2′-bipyridine-3,3′-dicarboxylic acid 1,1′-dioxide[7] ((–)-*IV*; 465 mg, 1.68 mmol), Separon SGX-NH_2 (7 μm; 3.0 g) and methanol (50 ml) was sonicated for 30 min at 20 °C and left aside for 4 days with intermittant gentle shaking (to allow for gradual dissolution and trapping by the aminopropyl silica). After filtration, the solid was washed with methanol (100 ml) and dried. For CSP 4 the content of (–)-*IV* was 0.47 mmol/g.

General Procedure for Preparation of Phases CSP 5 – 7

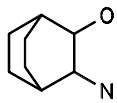
A solution of the corresponding 2,2′-bis(bromomethyl)-1,1′-biaryl ((–)-*V*, (–)-*VI* or (–)-*VII*; 4.5 mmol) in warm dry benzene (10 – 20 ml) was added to a slurry of Separon SGX-NH_2 (7 μm; 3.0 g) in dry benzene (5 ml). After addition of triethylamine (0.523 g, 5.2 mmol), the mixture was gently shaken



1, $n = 5$
2, $n = 6$
3, $n = 7$
4, $n = 9$
5, $n = 11$
6, $n = 12$
7, $n = 13$
8, $n = 14$
9, $n = 15$
10, $n = 16$
11, $n = 20$
12, $n = 26$



19, O(*ax*), N(*ax*)
20, O(*eq*), N(*eq*)
21, O(*ax*), N(*eq*)
22, O(*eq*), N(*ax*)



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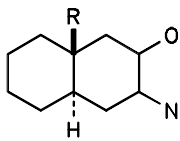
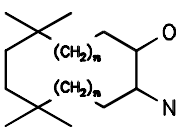
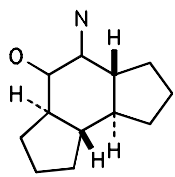


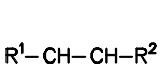
24, R = H, O(*ax*), N(*ax*)
25, R = CH_3, O(*eq*), N(*eq*)



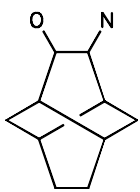
13, $n = 1$
14, $n = 2$



26, O(*ax*), N(*ax*)
27, O(*eq*), N(*eq*)



15, $R^1 = R^2 = CH_3$
16, $R^1 = R^2 = n\text{-}C_4H_9$
17, $R^1 = R^2$ = cyclohexyl
18, $R^1 = C_6H_5$; $R^2 = CH_3$



28, O(*endo*), N(*endo*), 30°
29, O(*exo*), N(*exo*), 30°
30, O(*endo*), N(*exo*), 90°
31, O(*exo*), N(*endo*), 150°

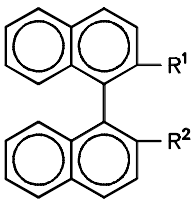
In formulae **1** – **31**:

a, N = $NHCOC_6H_5$; O = OH **b,** N = $NHCOC_6H_4\text{-}NO_2(p)$; O = OH

c, N = $NHCOC_6H_5$; O = $OCOCH_3$

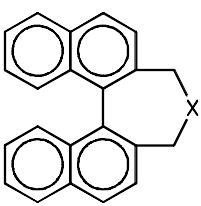
Expressions (*ax*) and (*eq*) for the conformationally homogeneous compounds **19** – **22** and **24** – **27** denote the respective *axial* and *equatorial* positions of the substituents; for compounds **28** – **31**; torsion angles between substituents are given

SCHEME 1

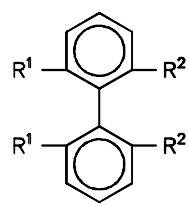


	R^1, R^2
32	OH
33	CH_2OH
34	CO_2CH_3
35	CH_3
36	CH_2NH_2
37	$CH_2NHCOCH_3$
38	CH_2Br
39	CH_2CN
41	CH_2OCOCH_3

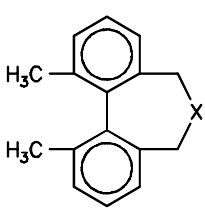
	R^1	R^2
40	CH_2N_3	CH_2OCH_3
42	CH_2Br	CH_2OCH_3
43	CH_2Br	CH_2OCOCH_3
44	CH_2I	CH_2I
45	CH_2SCH_3	CH_2SCH_3
46	CH_2SCH_3	$CH_2SC_6H_5$
47	CH_2SCH_3	CH_2N_3
48	CH_2SCH_3	$CH_2SeC_6H_5$
49	$OCOCH_3$	$OCOCH_3$
50	$CH_2CH(CO_2C_2H_5)_2$	$CH_2CH(CO_2C_2H_5)_2$



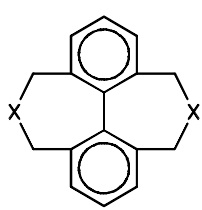
	X
51	$C(CO_2C_2H_5)_2$
52	$C(CO_2CH_3)_2$
53	$CHCO_2CH_3$
54	S
55	O
56	C = O
57	C = N − OH
58	CO − NH
59	N − CH_3



	R^1	R^2
60	CH_2OH	CH_3
61	CO_2CH_3	CH_3
62	CO_2CH_3	NO_2



	X
63	$C(CO_2C_2H_5)_2$
64	$CHCO_2CH_3$
65	C = O
66	C = N − OH



	X
67	$C(CO_2CH_3)_2$
68	$C(CO_2C_2H_5)_2$

SCHEME 2

at about 35 °C for 2 h and then left overnight at room temperature. Next day another portion of triethylamine (0.66 g, 6.5 mmol) was added and the mixture was set aside at room temperature with intermittant shaking. When no further increase in the percentage of carbon was observed (5 – 7 days), the mixture was filtered and washed successively with methanol, acetone and light petroleum (140 ml each). The analytical samples were dried in vacuo at 50 °C for 5 h. The following contents of the chiral selector (as calculated from the elemental analysis by the procedure mentioned below) have been found: CSP 5 (13.56% C, 1.81% H, 4.48% N): 0.43 mmol/g; CSP 6 (16.67% C, 2.23% H, 1.32% N): 0.54 mmol/g; CSP 7 (18.64% C, 2.15% H, 1.62% N): 0.47 mmol/g.

Calculation of the Selector Content in the Covalently Bound CSPs

The content (m_2, in mmol) of the chiral selector in one gram of the resulting modified phase was calculated by the formula

$$m_2 = 10\,(p_2 - p_1)/12\,(n_2 - n_1)\ ,$$

where $p_2 - p_1$ is the difference between the respective carbon percentages found in the modified phase and in the starting 3-aminopropyl silica, and $n_2 - n_1$ is the difference in the number of carbon atoms in the modified and starting phase.

RESULTS AND DISCUSSION

Absolute Configuration of the Selectors

The absolute configuration of the acids (+)-*I* (ref.[8]) and (+)-*III* (ref.[14]), and dibromides (–)-*V* (ref.[8]), (–)-*VI* (ref.[14]) and (–)-*VII* (ref.[15]) has been already determined (Figs 1 and 2). The hitherto unknown absolute configuration of acid (+)-*II* has been assigned by comparison of its CD spectrum with that of the dinitro acid (*R*)-(+)-*I*. As seen from Fig. 3, both the acids exhibit a positive maximum at about 330 nm which is characteristic of

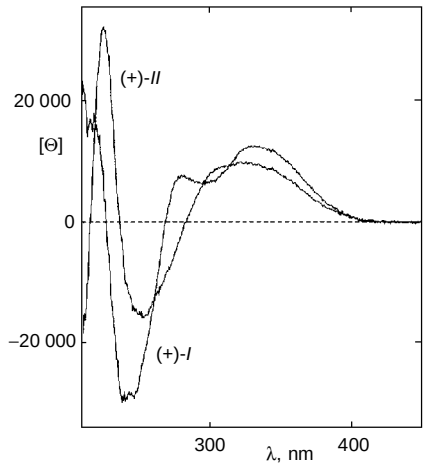


FIG. 3
CD spectra of acids (+)-*I* and (+)-*II* in dioxane (c 3.2 . 10^{-3} mol/l, cell length 0.01 cm)

6,6′-dinitrobiphenyl derivatives having (*R*)-configuration[16]. The configuration of the bipyridine diacid dioxide (–)-*IV* may be tentatively assigned on the basis of the following reasoning. Save one exception (compound **19b**), enantiomers that are eluted first on CSP 1 and CSP 2 (selectors of (*R*)-configuration) are eluted as the second on CSP 3 ((*S*)-configuration) and vice versa: this indicates analogous recognition pattern for the three phases. Since the elution order on CSP 4 is opposite to that on CSP 1 and CSP 2, the absolute configuration of the acid (–)-*IV* is thus also very likely opposite (*S*) to that of acids (*R*)-(+)-*I* and (*R*)-(+)-*II*. Further studies leading to a more reliable configurational assignment of *IV* are in progress.

Performance of the Columns

The chromatographic data are summarized in Table I. For comparison, we also included some of the already published data[3] for separation of acylamino alcohols **1** – **31** on CSP 1 and CSP 3. Since the covalently bound 6,6′-dimethylbiphenyl phase CSP 6 did not separate any of the 68 compounds tested, it was not included in the Table.

We investigated two groups of compounds that, apart from our own work, might be of more general interest: 2-acylamino alcohols (Scheme 1) and compounds with chiral biaryl axis (Scheme 2).

Acylamino Alcohols

The separation properties of phases CSP 1 and CSP 3 have already been discussed by us[3]. The tetranitro phase CSP 2, and also the bipyridyl phase CSP 4, are good separators of 2-benzamido alcohols, their performance being roughly comparable to that of CSP 1. As seen, no great effect has been achieved by introduction of additional nitro groups into the positions 4 and 4′ of the molecule *I*. The effectivity of the bipyridine phase CSP 4 indicates that for the resolution of 2-acylamino alcohols (with polar groups and many hydrogen bond possibilities) a general structural scheme of two pairs of strongly dipolar groups on a chiral biaryl system might be a sufficient condition. The dimethyl phase CSP 3, containing polar groups only on one side of the system, is far less effective. No resolution of 2-acylamino alcohols was achieved on the covalently bound CSPs 5 – 7.

Biaryl Derivatives

A different situation is encountered in the case of biaryl analytes. The ionically bound phases CSP 1 – CSP 4 are mostly inactive; some separation was observed only for compounds with relatively polar groups such as diols (**33**, **60**) or esters (**50** – **52**). The covalently bound phases CSP 5 and CSP 7 separated some cyclic compounds (**51** – **55**, **57**, **58**) in which the additional ring apparently makes the structure more rigid. Most of the ("acyclic") binaphthyl analytes bearing substituted methyl groups in positions 2,2′ (**37** – **48**) were not separated on any of the phases.

TABLE I

Capacity factors, k_1, and separation factors, α, for HPLC of compounds **1** – **68** on stationary phases CSP 1 – 5 and 7. The capacity factors k_1 refer to the first enantiomer eluted (with its sign of rotation), the separation factor, α, (in parentheses) is the ratio of capacity factors of the enantiomers. No attempts were made to optimize the analytical conditions for the individual compounds. Mobile phase: 10% 2-propanol in heptane, flow rate 0.5 ml/min

Compound	CSP 1	CSP 2	CSP 3	CSP 4	CSP 5	CSP 7
			Acylamino alcohols (see Scheme 1)			
1a *cis*	4.12(+)			7.57(–)		
	(1.09)[a]			(1.09)		
1a *trans*	9.00(–)			18.71		
	(1.14)[a]			(1.00)[b]		
2a *cis*	4.12(+)	5.92(+)	2.25	6.25(–)		5.00
	(1.15)[a]	(1.19)	(1.00)[a,b]	(1.09)		(1.00)[b]
2a *trans*	6.12(–)	9.19	2.62(+)	10.71	5.11	2.91
	(1.36)[a]	(1.38)	(1.24)[a]	(1.00)[b]	(1.00)[b]	(1.00)[b]
2c *trans*	3.25	7.68	1.75[d]			4.00
	(1.00)[a]	(1.00)[b]	(1.00)[a,b]			(1.00)[b]
3a *cis*	4.12(+)			6.57(–)		
	(1.15)[a]			(1.09)		
4a *cis*	3.62(+)	5.28(+)		5.43(–)	4.88	4.28
	(1.12)[a]	(1.17)		(1.08)	(1.00)[b]	(1.00)[b]
4a *trans*	4.25(+)	6.04			3.96	3.00
	(1.35)[a]	(1.40)			(1.00)[b]	(1.00)[b]
5a *trans*	3.37(+)			5.43(–)		
	(1.22)[a]			(1.08)		
6a *cis*	3.12(+)	4.04(+)	1.62(–)	5.14(–)	4.07	4.00
	(1.12)[a]	(1.19)	(1.15)[a]	(1.14)	(1.00)[b]	(1.00)[b]
6a *trans*	3.12(+)	4.04(+)	1.75	4.57(–)	3.62	3.28
	(1.24)[a]	(1.21)	(1.00)[a,b]	(1.09)	(1.00)[b]	(1.00)[b]
7a *cis*	2.75(+)		1.50(–)	4.42(–)		
	(1.14)[a]		(1.08)[a]	(1.10)		
7a *trans*	2.87(+)		1.62	4.00(–)		
	(1.22)[a]		(1.00)[a,b]	(1.07)		
8a *cis*	2.50(+)			3.57(–)		
	(1.20)[a]			(1.08)		
8a *trans*	2.62(+)			4.43(–)		
	(1.18)[a]			(1.10)		
9a *trans*	2.62(+)			3.57(–)		
	(1.14)[a]			(1.08)		
10a *cis*	2.25(+)	3.15(+)		3.00(–)		
	(1.11)[a]	(1.20)		(1.14)		
10a *trans*	2.37(+)	3.02(+)	1.12	3.14(–)		
	(1.21)[a]	(1.21)	(1.00)[a,b]	(1.09)		

TABLE I
(*Continued*)

Compound	CSP 1	CSP 2	CSP 3	CSP 4	CSP 5	CSP 7
11a *cis*	2.00(+)			2.71(–)	2.24	2.28
	(1.12)[a]			(1.15)	(1.00)[b]	(1.00)[b]
11a *trans*	1.87(+)			2.86(–)	2.11	2.28
	(1.20)[a]			(1.10)	(1.00)[b]	(1.00)[b]
12a *cis*	1.50(+)	2.15(+)	2.25[d]	2.00(–)		
	(1.17)[a]	(1.18)	(1.00)[a,b]	(1.21)		
12a *trans*	1.50(+)	2.02(+)	2.25[d]	1.86(–)		
	(1.17)[a]	(1.19)	(1.00)[a,b]	(1.15)		
13a *trans*	2.87(–)		1.37	3.57		
	(1.13)[a]		(1.00)[a,b]	(1.00)[b]		
14a *cis*	2.50(+)	3.40(+)	1.25	3.86(–)		
	(1.10)[a]	(1.15)	(1.00)[a,b]	(1.11)		
14a *trans*	2.37(+)	3.28	1.25	3.28(–)		
	(1.05)[a]	(1.19)	(1.00)[a,b]	(1.13)		
15b *erythro*	9.62(+)		7.00		10.07	12.85
	(1.16)[a]		(1.00)[a,b]		(1.00)[b]	(1.00)[b]
16b *erythro*	3.12(+)	1.98(+)[e]	1.87	7.57(–)		4.28
	(1.24)[a]	(1.14)	(1.00)[a,b]	(1.19)		(1.00)[b]
16b *threo*	3.12(+)		2.12	7.00(–)		4.57
	(1.16)[a]		(1.00)[a,b]	(1.14)		(1.00)[b]
17a *erythro*	2.20	3.15				
	(1.00)[a,b]	(1.00)[b]				
17a *threo*	2.12	3.28	1.12			
	(1.00)[a,b]	(1.00)[b]	(1.00)[a,b]			
18a *erythro*	5.25(–)		2.62	9.86(+)		
	(1.12)[a]		(1.00)[a,b]	(1.16)		
18a *threo*	8.12(–)		3.50(+)	14.28		
	(1.17)[a]		(1.07)[a,b]	(1.00)[b]		
18c *erythro*	8.75	7.55				
	(1.00)[a,b]	(1.00)[b]				
18c *threo*	5.00	4.66(+)				
	(1.00)[a]	(1.05)				
19a	4.87(–)		1.50	4.71	6.15(+)	
	(1.05)[a]		(1.00)[a,b]	(1.00)[b]	(1.06)	
19b	11.87(–)	6.30(–)[e]	4.62(–)			8.14
	(1.07)[a]	(1.12)	(1.05)[a]			(1.07)
20b	6.00(–)	3.66(–)[e]	3.37(+)	18.57	5.11	5.14
	(1.52)[a]	(1.31)	(1.18)[a]	(1.00)[b]	(1.00)[b]	(1.00)[b]

TABLE I
(*Continued*)

Compound	CSP 1	CSP 2	CSP 3	CSP 4	CSP 5	CSP 7
21a	2.50(+) (1.10)[a]		1.50 (1.00)[a,b]	4.00(–) (1.18)	3.15 (1.00)[b]	
21b	3.75(+) (1.23)[a]	2.40(+)[e] (1.05)	2.75 (1.00)[a,b]	11.57(–) (1.15)	6.04 (1.00)[b]	5.85 (1.00)[b]
22b	5.25(–) (2.05)[a]	3.66(–)[e] (1.69)	2.62(+) (1.24)[a]	11.25 (1.00)[b]	6.27 (1.00)[b]	4.28 (1.00)[b]
23a *cis*	3.25 (1.00)[a,b]	4.79 (1.08)	1.87 (1.00)[a,b]	4.57(–) (1.06)		
23a *trans*	8.37(+) (1.10)[a]	14.34 (1.16)	3.25 (1.00)[a,b]	14.43 (1.04)	10.54 (1.00)[b]	5.86 (1.00)[b]
24a	5.87 (1.00)[a,b]	12.21(–) (1.05)				
24b	14.62 (1.00)[a,b]	7.81(+)[e] (1.06)				
25a	5.00(–) (1.25)	6.79(–) (1.28)	2.26(+) (1.13)			
26a	2.87 (1.00)[a,b]	5.42 (1.00)[b]				
27b	5.00(+) (1.55)[a]	2.77(+)[e] (1.41)	2.50 (1.00)[a,b]			
28a	3.75 (1.00)[a,b]	5.92(–) (1.11)	2.26 (1.00)[b]	4.14 (1.00)[b]		
29a		2.15[e] (1.00)[b]	4.24(–) (1.07)			
30a	7.62(+) (1.15)[a]	13.21(+) (1.17)	3.12(–) (1.08)[a]	13.00(–) (1.09)	10.76 (1.00)[b]	6.14 (1.00)[b]
31a	7.75 (1.00)[a,b]	19.13 (1.07)	2.12(–) (1.11)[a]	7.00(–) (1.06)		
			Biaryl derivatives (see Scheme 2)			
32		2.40[e] (1.00)[b]			22.53 (1.05)	
33		4.66(+) (1.05)	4.68(–) (1.10)	12.00 (1.00)[b]	11.58 (1.00)[b]	8.75 (1.08)
34	2.46 (1.06) 8.30[c] (1.06)	2.64 (1.00)[b]	0.85 (1.00)[b]		21.21 (1.03)	2.90 (1.00)[b] 6.77[c] (1.00)[b]

TABLE I
(*Continued*)

Compound	CSP 1	CSP 2	CSP 3	CSP 4	CSP 5	CSP 7
35	0.51[c] (1.00)[b]				0.38 (1.00)[b] 0.89[c] (1.00)[b]	0.64 (1.00)[b] 0.75[c] (1.00)[b]
36					7.25(–)[c] (1.04)	4.90 (1.00)[b]
37					10.42 (1.00)[b]	
38	0.54 (1.00)[b] 1.51[c] (1.00)[b]				2.53[c] (1.00)[b]	2.33[c] (1.00)[b]
39			2.62 (1.00)[b]	2.12 (1.00)[b]		10.50 (1.00)[b]
40					2.83[c] (1.00)[b]	1.93[c] (1.00)[b]
41		1.40 (1.00)[b] 2.53[e] (1.00)[b]	0.77 (1.00)[b]		20.32[c] (1.00)[b]	7.19[c] (1.00)[b]
42	1.64[c] (1.00)[b]				3.15[c] (1.00)[b]	2.11[c] (1.00)[b]
43			0.55 (1.00)[b]		7.81[c] (1.00)[b]	4.26[c] (1.00)[b]
44					2.40[c] (1.00)[b]	2.63[c] (1.00)[b]
45		0.38 (1.00)[b]	0.34 (1.00)[b]		2.72[c] (1.00)[b]	2.53 (1.00)[b]
46					3.77[c] (1.00)[b]	3.51[c] (1.00)[b]
47					4.09[c] (1.00)[b]	2.39[c] (1.00)[b]
48					3.77[c] (1.00)[b]	3.21[c] (1.00)[b]
49		1.02[e] (1.00)[b]	0.70 (1.00)[b]	1.00 (1.00)[b]	3.38 (1.00)[b]	
50		6.42(–) (1.04)	0.85 (1.00)[b]		10.54 (1.00)[b]	

TABLE I
(*Continued*)

Compound	CSP 1	CSP 2	CSP 3	CSP 4	CSP 5	CSP 7
51	1.06 (1.00)[b]	2.26(+) (1.12)			2.34(–) (1.15) 7.25(–)[c] (1.15)	1.58 (1.12) 2.98[c] (1.15)
52	1.40 (1.00)[b]	1.26(+) (1.11)		0.47 (1.00)[b]	2.80(–) (1.13)	
53	0.86 (1.00)[b]	0.75 (1.00)[b]	0.43 (1.00)[b]		1.54(–) (1.07) 4.47[c] (1.07)	1.64(–) (1.15) 3.09[c] (1.15)
54	0.54 (1.00)[b]	0.26 (1.00)[b]	0.43 (1.00)[b]	0.43 (1.00)[b]	1.08 (1.00)[b] 2.40[c] (1.00)[b]	1.50(–) (1.13) 2.28[c] (1.10)
55	0.80 (1.00)[b] 2.26[c] (1.00)[b]	0.89 (1.00)[b]	0.49 (1.00)[b]	0.57 (1.00)[b]	1.59 (1.00)[b] 4.42[c] (1.00)[b]	1.64(–) (1.15) 2.63[c] (1.15)
56	1.14 (1.00)[b]	1.77 (1.00)[b]		2.86 (1.00)[b]		2.26 (1.00)[b]
57	2.20 (1.00)[b]	1.64 (1.00)[b]		5.86 (1.00)[b]	5.00 (1.00)[b]	6.04(+) (1.08)
58	11.66 (1.00)[b]	16.98(+) (1.06)		1.86 (1.00)[b]	12.37(–) (1.05)	7.68 (1.13)
59					9.38 (1.00)[b]	5.17 (1.00)[b]
60		1.51[e] (1.00)[b]	2.68(–) (1.06)		5.18(+) (1.03)	3.34 (1.00)[b]
61	1.26 (1.00)[b] 4.15[c] (1.00)[b]	1.64 (1.00)[b]	0.49 (1.00)[b]		6.87(+)[c] (1.03)	0.94 (1.00)[b] 1.93[c] (1.00)[b]
62	20.50[d] (1.00)[b]	5.42[e] (1.00)[b]				10.94 (1.00)[b]
63	0.60 (1.00)[b]	1.02 (1.00)[b]		0.28 (1.00)	3.21(+)[c] (1.02)	0.64 (1.00)[b]

TABLE I
(*Continued*)

Compound	CSP 1	CSP 2	CSP 3	CSP 4	CSP 5	CSP 7
64	0.46 (1.00)[b]	0.38 (1.00)[b]			0.56 (1.00)[b] 1.40[c] (1.00)[b]	0.64 (1.00)[b]
65	0.66 (1.00)[b]				1.30 (1.00)[b]	0.75 (1.00)[b]
66	1.40 (1.00)[b]				2.06 (1.00)[b]	2.08 (1.00)[b]
67		5.79(–) (1.13)				
68	2.20 (1.00)[b]	3.30(–) (1.15)	0.49 (1.00)[b]		4.88(+) (1.10)	1.59 (1.00)[b]

[a] Taken from ref.[3]. [b] No separation. [c] 1% 2-Propanol in heptane. [d] 5% 2-Propanol in heptane. [e] 20% 2-Propanol in heptane.

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