Pergamon

Tetrahedron: *Asymmetry* 9 (1998) 563–574

TETRAHEDRON: *ASYMMETRY*

Preparation and temperature-dependent enantioselectivities of homochiral phenolic crown ethers having aryl chiral barriers: thermodynamic parameters for enantioselective complexation with chiral amines

Koichiro Naemura,* Kazuyuki Nishioka, Kazuko Ogasahara, Yasushi Nishikawa, Keiji Hirose and Yoshito Tobe

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560 Japan

Received 6 November 1997; accepted 4 December 1997

Abstract

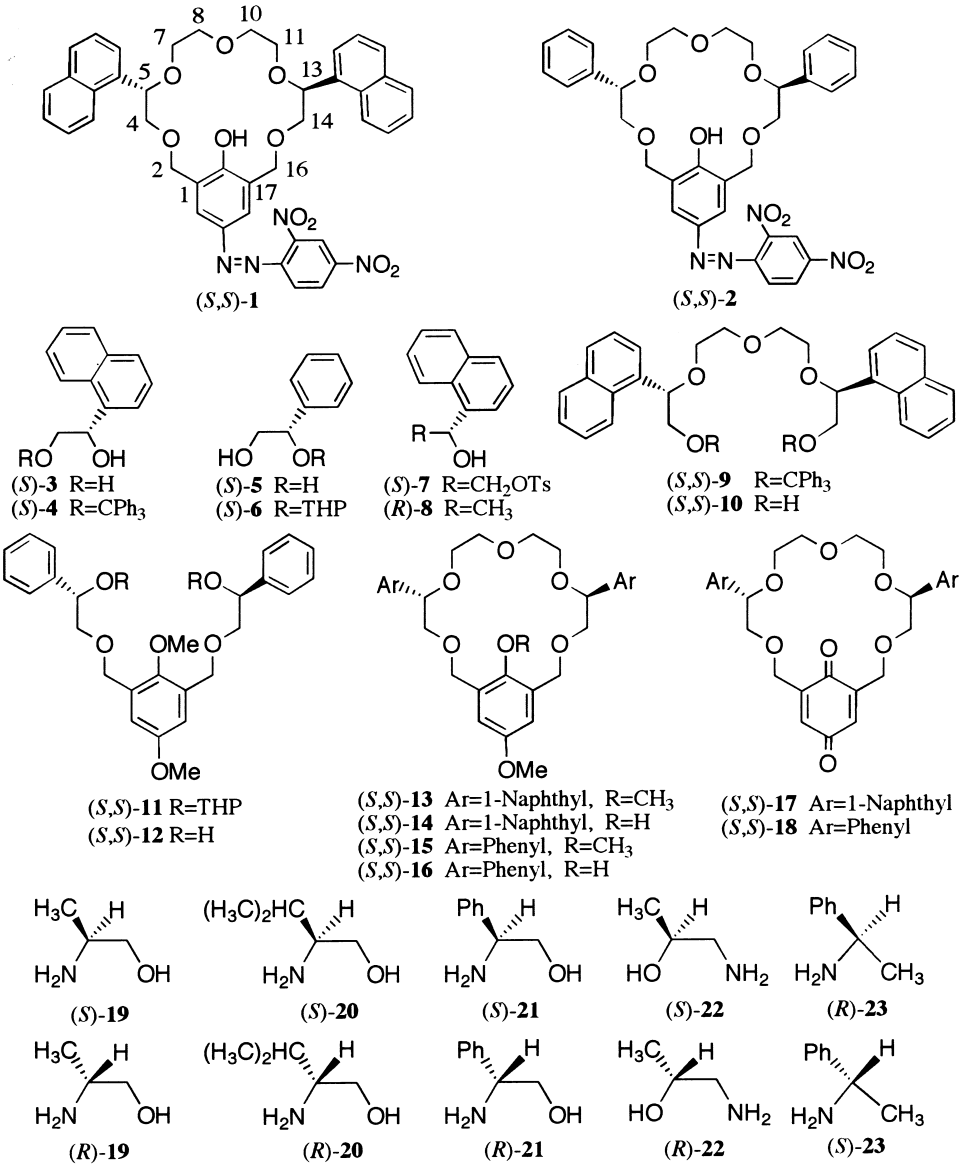
Homochiral crown ether (*S*,*S*)-**1** containing 1-naphthyl groups as chiral barriers together with the phenol moiety was prepared by using (*S*)-**3** as a chiral subunit which was resolved in enantiomerically pure form by lipase-catalyzed enantioselective acylation of (±)-**3**. Homochiral phenolic crown ether (*S*,*S*)-**2**, containing phenyl groups as chiral barriers, was also prepared from (*S*)-**5** which was derived from (*S*)-mandelic acid. The association constants for their complexes with chiral amines in $CHCl_3$ were determined at various temperatures by the UV–visible spectroscopic method demonstrating that the crown ethers (*S*,*S*)-**1** and (*S*,*S*)-**2** displayed the large $\Delta_{R-S}\Delta G$ values of 6.2 and 6.4 kJ mol^{-1}, respectively, towards the amine **21** at 15°C. Thermodynamic parameters for complex formation were also determined and a linear correlation between $T\Delta_{R-S}\Delta S$ and $\Delta_{R-S}\Delta H$ values was observed.

A large number of homochiral crown ethers have been prepared by using various types of homochiral compounds as chiral subunits.[1] In regard to their chiral recognition on complexation, it is a generally accepted view that an increase in the size of substituents at stereogenic centers usually increases the degree of enantiomeric recognition. On the other hand, large repulsive interactions between host and guest molecules may reduce the stability of the complex. Recently, in order to seek information on how the size of the substituents at stereogenic centers might affect the enantioselectivity in complexation with amines, we have prepared homochiral azophenolic crown ethers possessing the alkyl substituents as chiral barriers and examined the temperature dependent enantioselectivity and thermodynamic parameters for complexation.[2] In this paper, we report the preparation of homochiral crown ethers (*S*,*S*)-**1** and (*S*,*S*)-**2** containing the 1-naphthyl substituents and the phenyl substituents, respectively, as chiral barriers together with the *p*-(2,4-dinitrophenylazo)phenol moiety and the association constants of their complexes with

* Corresponding author. E-mail: hirose@chem.es.osaka-u.ac.jp

0957-4166/98/$19.00
PII: S0957-4166(97)00638-1

neutral amines determined on the basis of the UV–visible spectrum of the complexes collected in $CHCl_3$ at various temperatures. Further, thermodynamic parameters for complex formation were also determined from the van't Hoff plots of the K_a values.



1. Results and discussion

The enantioselective acylation of (±)-**3** with isopropenyl acetate as an acylating agent was carried out using lipase QL from *Alcaligenes* sp. In order to prepare directly homochiral **3** of high e.e., the reaction was terminated at the esterification point of >50%. Silica gel chromatography of the products gave (+)-**3** of 96% e.e. (by HPLC) in 33% yield together with the mixture of the monoacetates. Recrystallization of (+)-**3** of 96% e.e. from diethyl ether gave the partially resolved (+)-**3** of 48% e.e. as a sparingly soluble

solid and enantiomerically pure (+)-**3**, $[\alpha]_D$ +75.8 (10^{-1} deg cm^2 g^{-1}) ($CHCl_3$), was isolated in 31% yield based on (±)-**3** from the mother liquor. The absolute configuration of (+)-**3** was determined by chemical correlation with **8** of known absolute configuration.[3] The primary hydroxy group of (+)-**3** was selectively tosylated to give (+)-**7**, $[\alpha]_D$ +123 ($CHCl_3$), in 60% yield. Treatment of (+)-**7** with $LiAlH_4$ gave (*R*)-(+)-**8**, $[\alpha]_D$ +81.6 (MeOH), in 81% yield leading to the assignment of (*S*)-(+)-**3**.

Our previous results[4] demonstrated that location of the phenyl substituents near the diethylene glycol bridge resulted in a higher degree of enantiomeric recognition than is the case when the substituents are located near the phenol moiety; in the phenolic crown ether having stereogenic centers at C-4 and C-14 positions, the substituent at the stereogenic center and 'ethyleneoxy barrier'[2] recognize opposite enantiomers of the amine resulting in a reduction of the degree of enantiomeric recognition in the complexation of amines. In order to prepare the phenolic crown ether exhibiting a higher degree of chiral recognition, the aryl substituents of the crown ethers (*S*,*S*)-**1** and (*S*,*S*)-**2** were located at the C-5 and C-13 positions.

Treatment of (*S*)-**3** with triphenylmethyl chloride gave regioselectively (*S*)-**4**, $[\alpha]_D$ +50.0 ($CHCl_3$), in 72% yield. Condensation of two molar equivalents of (*S*)-**4** with diethylene glycol bis(*p*-toluenesulfonate) in the presence of NaH in THF gave (*S*,*S*)-**9**, $[\alpha]_D$ +39.6 ($CHCl_3$), which was deprotected with methanol and *p*-toluenesulfonic acid to give (*S*,*S*)-**10**, $[\alpha]_D$ +102 ($CHCl_3$), in 57% overall yield for the two steps. Ring closure of (*S*,*S*)-**10** with 1,3-bis(bromomethyl)-2,5-dimethoxybenzene in the presence of NaH in THF under high-dilution conditions gave (*S*,*S*)-**13**, $[\alpha]_D$ +133 ($CHCl_3$), in 78% yield. Treatment of (*S*,*S*)-**13** with sodium ethanethiolate in DMF cleaved selectively the inner methoxy group to give (*S*,*S*)-**14**, $[\alpha]_D$ +139 ($CHCl_3$), in 94% yield. Oxidation of (*S*,*S*)-**14** with cerium(IV) ammonium nitrate (CAN) in acetonitrile gave (*S*,*S*)-**17**, which was immediately treated with 2,4-dinitrophenylhydrazine in a mixture of ethanol, chloroform and conc. H_2SO_4 to give (*S*,*S*)-**1** in 69% overall yield for the two steps.

Next, (*S*,*S*)-**2** containing (*S*)-**5** as a chiral subunit was prepared. Two molar equivalents of (*S*)-**6**, which was derived from (*S*)-mandelic acid according to the reported procedure,[5] were reacted with 1,3-bis(bromomethyl)-2,5-dimethoxybenzene in the presence of NaH to give (*S*,*S*)-**11**, deprotection of which with pyridinium *p*-toluenesulfonate and ethanol gave (*S*,*S*)-**12**, $[\alpha]_D$ +34.2 ($CHCl_3$), in 80% overall yield for the two steps. High-dilution condensation of (*S*,*S*)-**12** with diethylene glycol bis(*p*-toluenesulfonate) in the presence of NaH and KBF_4 in THF gave (*S*,*S*)-**15**, $[\alpha]_D$ +104 ($CHCl_3$), in 42% yield. Demethylation of (*S*,*S*)-**15** gave (*S*,*S*)-**16**, $[\alpha]_D$ +109 ($CHCl_3$), in 77% yield, oxidation of which followed by treatment with 2,4-dinitrophenylhydrazine afforded (*S*,*S*)-**2** in 32% overall yield *via* (*S*,*S*)-**18**.

The association constants, K_a, of the complexes of the crown ethers (*S*,*S*)-**1** and (*S*,*S*)-**2** with chiral amines; 2-aminopropan-1-ol **19**, 2-amino-3-methylbutan-1-ol **20**, 2-amino-2-phenylethanol **21**, 1-aminopropan-2-ol **22** and 1-phenylethylamine **23** were determined by the Rose–Drago method[7] on the basis of the UV–visible spectrum of the complexes in $CHCl_3$ collected at various temperatures and the observed K_a values are summarized in Table 1. The thermodynamic parameters, ΔH, ΔS and ΔG, for complex formation were determined from the van't Hoff plots of the K_a values and are listed in Table 2.

Table 2 shows that large repulsive interactions between host and guest molecules slightly reduced the stability of the complex; all complexes of (*S*,*S*)-**1** with the amines, except the (*S*,*S*)-**1**: (*S*)-**21** complex, showed a little less negative ΔG value at 298 K than did the corresponding complexes of (*S*,*S*)-**2** with the amines.

In Figs 1 and 2, we plot $\Delta_{R-S}\Delta G$ ($=\Delta G_R - \Delta G_S$) values for complexation of the crown ethers (*S*,*S*)-**1** and (*S*,*S*)-**2**, respectively, with the amines as a function of temperature. The plots indicate that the enantioselectivities of the crown ethers (*S*,*S*)-**1** and (*S*,*S*)-**2** towards the amines; the (*R*)-selectivities of both crown ethers towards the amines **19**, **20**, **21** and **22** and the (*S*)-selectivities of both crown ethers towards **23** were substantially contributed to by $\Delta_{R-S}\Delta H$. In Fig. 3, using the data in Table 2, plotting

Table 1
The association constants for the complexes of the crown ethers (*S*,*S*)-**1** and (*S*,*S*)-**2** with amines in chloroform

Crown ether	Amine	*Ka* (°C) mol^{-1}			
1	(*R*)-**19**	(4.57±0.60)x10^4(16)	(1.78±0.09)x10^4(26)	(5.04±0.23)x10^3(34)	(2.09±0.38)x10^3(43)
1	(*S*)-**19**	(8.53±0.79)x10^3(16)	(4.68±0.45)x10^3(26)	(1.96±0.07)x10^3(34)	(9.22±0.44)x10^2(43)
1	(*R*)-**20**	(1.31±0.14)x10^4(14)	(4.16±0.36)x10^3(26)	(1.94±0.19)x10^3(35)	(9.14±0.90)x10^2(43)
1	(*S*)-**20**	(2.77±0.27)x10^3(14)	(9.01±0.64)x10^2(26)	(4.62±0.58)x10^2(35)	(2.18±0.20)x10^2(43)
1	(*R*)-**21**	(5.03±0.27)x10^4(15)	(1.74±0.25)x10^4(25)	(5.87±0.25)x10^3(35)	(2.34±0.35)x10^3(43)
1	(*S*)-**21**	(3.77±0.34)x10^3(15)	(1.41±0.19)x10^3(25)	(6.09±0.45)x10^2(35)	(3.02±0.15)x10^2(43)
1	(*R*)-**22**	(3.05±0.34)x10^4(17)	(1.19±0.13)x10^4(26)	(3.93±0.29)x10^3(35)	(2.12±0.12)x10^3(43)
1	(*S*)-**22**	(1.11±0.04)x10^4(17)	(4.66±0.58)x10^3(26)	(2.05±0.15)x10^3(35)	(1.18±0.07)x10^3(43)
1	(*R*)-**23**	(1.31±0.18)x10^3(15)	(5.32±0.47)x10^2(26)	(2.23±0.08)x10^2(35)	(1.30±0.17)x10^2(43)
1	(*S*)-**23**	(3.41±0.39)x10^3(15)	(1.34±0.11)x10^3(26)	(5.48±0.13)x10^2(35)	(2.87±0.37)x10^2(43)
2	(*R*)-**19**[a]	(1.66±0.16)x10^5(14)	(3.82±0.22)x10^4(25)	(1.03±0.07)x10^4(34)	(4.32±0.33)x10^3(44)
2	(*S*)-**19**[a]	(2.84±0.25)x10^4(14)	(7.77±0.64)x10^3(25)	(2.44±0.23)x10^3(34)	(1.12±0.10)x10^3(44)
2	(*R*)-**20**	(1.93±0.07)x10^4(17)	(7.53±0.66)x10^3(25)	(2.58±0.12)x10^3(36)	(1.07±0.11)x10^3(44)
2	(*S*)-**20**	(3.32±0.33)x10^3(17)	(1.69±0.35)x10^3(25)	(6.12±0.29)x10^2(36)	(2.85±0.24)x10^2(44)
2	(*R*)-**21**	(5.31±0.59)x10^4(16)	(1.95±0.13)x10^4(26)	(7.15±0.32)x10^3(36)	(2.83±0.18)x10^3(44)
2	(*S*)-**21**	(3.68±0.14)x10^3(16)	(1.66±0.09)x10^3(26)	(6.56±0.07)x10^2(36)	(3.12±0.30)x10^3(44)
2	(*R*)-**22**[a]	(8.37±0.57)x10^5(14)	(1.79±0.22)x10^4(26)	(6.60±0.34)x10^3(34)	(1.36±0.11)x10^3(45)
2	(*S*)-**22**[a]	(3.06±0.16)x10^5(14)	(6.78±0.39)x10^3(26)	(2.94±0.14)x10^3(34)	(7.04±0.61)x10^2(45)
2	(*R*)-**23**	(1.21±0.08)x10^3(17)	(7.64±0.62)x10^2(25)	(2.81±0.14)x10^2(35)	(1.54±0.13)x10^2(44)
2	(*S*)-**23**	(4.08±0.36)x10^3(17)	(2.39±0.07)x10^3(25)	(7.64±0.45)x10^2(35)	(3.49±0.16)x10^2(44)

[a] Part of the data have been reported in our previous communication.[6]

$T\Delta S$ at 298 K against ΔH affords two types of linear correlations; $T\Delta S$=0.739ΔH +1.54, R=0.897 for the complexations of (*S*,*S*)-**1** and $T\Delta S$=0.757ΔH +2.12, R=0.959 for those of (*S*,*S*)-**2**. Judging from the slopes of the plot of α=0.739 and α=0.757, we infer that the processes of complexation of the crown ethers (*S*,*S*)-**1** and (*S*,*S*)-**2** with the amines were accompanied with the same extent of conformational changes.[8]

In Fig. 4, we plot $T\Delta_{R-S}\Delta S$ values at 298 K against $\Delta_{R-S}\Delta H$ values giving a linear correlation; $T\Delta_{R-S}\Delta S$=0.742$\Delta_{R-S}\Delta H$−0.459, R=0.915. The data demonstrate that the complexation showing the larger $\Delta_{R-S}\Delta H$ value is accompanied by the larger $\Delta_{R-S}\Delta S$ value and the larger $\Delta_{R-S}\Delta S$ value results in the greater slope of the plot of $\Delta_{R-S}\Delta G$ against temperature. Therefore, relative merits of the enantioselectivity in the complexation may reverse at a certain temperature. For instance, on the basis of the observed thermodynamic parameters, it is predictable that the $\Delta_{R-S}\Delta G$ value for the (*S*,*S*)-**1**:**21** complexation is larger below ca −40°C than that for the (*S*,*S*)-**2**:**21** complexation. The enantioselectivity observed at 15°C for the (*S*,*S*)-**1**:**21** complexation ($\Delta_{R-S}\Delta G$=−6.2 kJ mol^{-1}) was lower than that for the (*S*,*S*)-**2**:**21** complexation ($\Delta_{R-S}\Delta G$=−6.4 kJ mol^{-1}). Thus (*S*,*S*)-**1** having the larger substituents showed a larger $\Delta_{R-S}\Delta H$ value for the complexation with **21** than did (*S*,*S*)-**2** but the large $\Delta_{R-S}\Delta H$ value was compensated for by the large $\Delta_{R-S}\Delta S$ value sharply reducing its $\Delta_{R-S}\Delta G$ value with increasing temperature.

We have previously described that the more stable complex shows the λ_{max} value at a shorter wavelength than the less stable diastereomeric complex.[9] Among the present data, the largest difference in the λ_{max} value between diastereomeric complexes was found for the (*S*,*S*)-**1**:**21** complexes. The more stable complex with (*R*)-**21** showed λ_{max} at a shorter wavelength; 553 nm (at 15°C) and 552 nm (at

Table 2
Thermodynamic parameters for complexation of the crown ethers (*S*,*S*)-**1** and (*S*,*S*)-**2** with amines in chloroform

Crown ether	Amine	ΔH kJ mol^{-1}	ΔS J mol^{-1} K^{-1}	ΔG (at 298K) kJ mol^{-1}	$\Delta_{R\text{-}S}\Delta H$ [a] kJ mol^{-1}	$\Delta_{R\text{-}S}\Delta S$ [b] J mol^{-1} K^{-1}
1	(*R*)-**19**	-88.6±4.0	-217±13	-23.9	-25.1	-73
1	(*S*)-**19**	-63.5±5.8	-144±19	-20.6		
1	(*R*)-**20**	-69.8±6.4	-164±21	-20.9	-3.6	+1
1	(*S*)-**20**	-66.2±6.1	-165±20	-17.0		
1	(*R*)-**21**	-85.7±5.0	-207±17	-23.8	-15.6	-32
1	(*S*)-**21**	-70.1±3.8	-175±13	-17.9		
1	(*R*)-**22**	-83.1±7.4	-200±25	-23.5	-14.3	-40
1	(*S*)-**22**	-68.8±3.9	-160±13	-21.1		
1	(*R*)-**23**	-62.4±1.2	-157±4	-15.6	+3.9	+5
1	(*S*)-**23**	-66.3±4.4	-162±15	-18.0		
2	(*R*)-**19**	-89.2±2.4	-211±8	-26.3	-10.2	-20
2	(*S*)-**19**	-79.0±2.1	-191±7	-22.1		
2	(*R*)-**20**	-80.6±3.4	-196±11	-22.2	-12.1	-27
2	(*S*)-**20**	-68.5±3.4	-169±11	-18.1		
2	(*R*)-**21**	-80.3±4.1	-187±28	-24.6	-12.1	-17
2	(*S*)-**21**	-68.2±4.9	-170±7	-17.2		
2	(*R*)-**22**	-91.4±7.6	-225±25	-24.3	-8.0	-20
2	(*S*)-**22**	-83.4±2.1	-205±7	-22.3		
2	(*R*)-**23**	-58.9±8.5	-144±14	-16.0	+10.9	+23
2	(*S*)-**23**	-69.8±2.2	-167±16	-20.0		

[a] $\Delta_{R\text{-}S}\Delta H = \Delta H_R - \Delta H_S$ [b] $\Delta_{R\text{-}S}\Delta S = \Delta S_R - \Delta S_S$

6

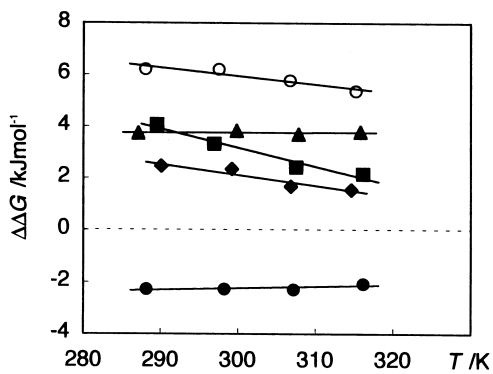


Fig. 1. Temperature dependent enantioselectivity for the complexation of (*S*,*S*)-**1** with amines; **19** (■), **20** (▲), **21** (○), **22** (◆) and **23** (●)

42°C) in $CHCl_3$ than did the less stable complex with (*S*)-**21** showing λ_{max} at 566 nm (at 15°C) and 563 nm (at 42°C). Similar correlations between $\Delta_{R-S}\Delta G$ and $\Delta_{R-S}\lambda_{max}$ values were observed for all other diastereomeric complexes.

As mentioned above, the present results demonstrate that the combination of the crown ether and the amine showing the larger $\Delta_{R-S}\Delta H$ value does not always display the higher degree of enantiomeric recognition at any temperature than the combination having the smaller $\Delta_{R-S}\Delta H$ value because the large $\Delta_{R-S}\Delta H$ value is usually accompanied by a large $\Delta_{R-S}\Delta S$ value.

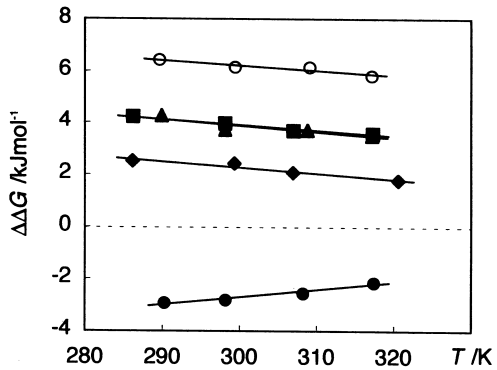


Fig. 2. Temperature dependent enantioselectivity for the complexation of (*S*,*S*)-**2** with amines; **19** (■), **20** (▲), **21** (○), **22** (◆) and **23** (●)

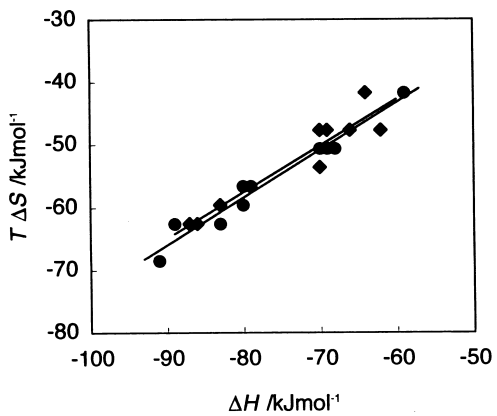


Fig. 3. Enthalpy–entropy compensation plot for complexation of (*S*,*S*)-**1** (◆) and (*S*,*S*)-**2** (●) with amines. The $T\Delta S$ terms were evaluated at T=298 K

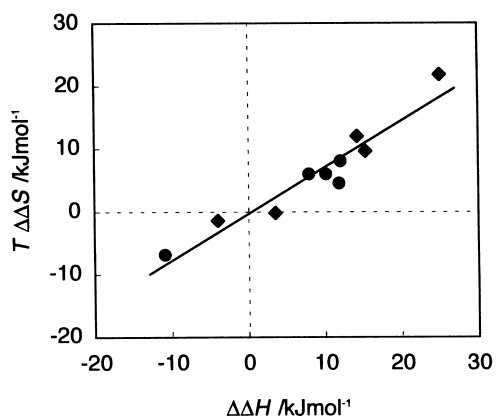


Fig. 4. $T\Delta_{R-S}\Delta S-\Delta_{R-S}H$ compensation plot for complexation of (*S*,*S*)-**1** (◆) and (*S*,*S*)-**2** (●) with amines. The $T\Delta_{R-S}\Delta S$ terms were evaluated at T=298 K

2. Experimental section

2.1. General

^{1}H NMR spectra were recorded at 270 MHz on a JEOL JNM-MH-270 spectrometer for solutions in $CDCl_3$ with $SiMe_4$ as an internal standard and *J* values are given in hertz. Mass spectra were recorded with 3-nitrobenzyl alcohol as a matrix on a JEOL-DX-303-HF spectrometer. IR spectra were measured on a JASCO FT-IR-410 spectrometer. UV and visible spectra were measured on a HITACHI 260-10 spectrometer. Optical rotations were measured using a JASCO DIP-40 polarimeter and $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. HPLC analyses were carried out on a Shimadzu LC-6A using a chiral column CHIRAL PAK AD (250×4.6 mm) (DAICEL). Elemental analysis data were collected with a Perkin-Elmer 2400 II CHNS. All melting points are uncorrected. Lipase QL was supplied by Meito Sangyo and used without further purification. The homochiral amines were purchased from the Aldrich Chemical Company, Inc. The amine (*S*)-**21** was used after recrystallization from benzene–hexane[10] and the other amines were used without further purification.

2.2. (±)-1-(1-Naphthyl)ethane-1,2-diol *3*

A solution of 1-ethenylnaphthalene[11] (5.02 g, 32.4 mmol) was added dropwise to a mixture of *N*-methylmorpholine *N*-oxide (5.30 g, 45.3 mmol) and osmiumtetroxide (106 mg, 0.417 mmol) in 1,1-dimethylethanol (80 cm^3) and water (8 cm^3) and the resulting mixture was then stirred for 4 h at room temperature. After 0.2 M aq. sodium hydrogen sulfite (50 cm^3) had been added to the reaction mixture with ice-cooling, the solvent was removed under reduced pressure. The residue was extracted with chloroform and the combined extracts were washed with water and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure gave (±)-**3** (4.98 g, 83% yield); mp 145–146°C (recrystallized from hexane–ethyl acetate) (lit.[12] mp 146–147°C); IR (KBr) 3230, 2942, 2856, 1653, 1595, 1109, 1067, 1030, 905, 865, 802 and 777 cm^{-1}; δ_H ($CDCl_3$), 3.45–3.54 (1H, m, CH_2), 3.60–3.68 (1H, m, CH_2), 4.79 (1H, t, *J*=5.2, primary OH), 5.28–5.35 (1H, m, CH), 5.37 (1H, d, *J*=2.0, secondary OH) and 7.43–8.16 (7H, m, ArH).

2.3. Resolution of (±)-*3*

A mixture of (±)-**3** (10.0 g, 53.1 mmol), lipase QL (from *Alcaligenes* sp.) (5.3 g) and isopropenyl acetate (15.7 g, 0.157 mol) in acetonitrile (1000 cm^3) was stirred for 4 days at 30°C. The reaction was terminated at the esterification point of 65% (by GLC) by filtration of the enzyme and volatile materials were evaporated under reduced pressure. Silica gel chromatography of the residue (hexane:ethyl acetate=4:1 as eluent) gave a mixture of monoacetates (7.86 g, 64%) and **3** (3.27 g, 33%) (96% e.e. by HPLC, hexane:ethyl acetate=4:1). Recrystallization of **3** from diethyl ether gave the partially resolved diol **3** (48% e.e. by HPLC) (0.156 g, 1.6%) as a sparingly soluble solid and removal of the solvent gave (+)-**3** (>99% e.e. by HPLC) (3.10 g, 31%); mp 79–81°C (recrystallized from hexane–ethyl acetate); $[\alpha]_D^{24}$ +75.8 (c 0.225, CH_3OH); spectral data were in accord with those of (±)-**3**. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57%; H, 6.43%. Found: C, 76.45%; H, 6.55%.

2.4. (S)-(+)-1-(1-Naphthyl)-2-(triphenylmethoxy)ethanol **4**

To a solution of triethylamine (900 mg, 8.84 mmol) in dry DMF were added successively triphenylmethyl chloride (820 mg, 2.94 mmol), 4-(dimethylamino)pyridine (16 mg, 0.13 mmol) and (+)-**3** (>99% e.e.) (500 mg, 2.65 mmol) and the resulting mixture was then stirred for 15 h at room temperature. After water had been added to the reaction mixture, the reaction mixture was extracted with chloroform. Customary work-up, followed by silica gel chromatography of the products (hexane:ethyl acetate=4:1) gave (+)-**4** (820 mg, 72%); mp 187–189°C (recrystallized from hexane–ethyl acetate); $[\alpha]_D^{23}$ +50.0 (c 0.095, CH_3OH); IR (KBr) 3581, 3061, 2923, 2869, 1951, 1489, 1447, 1201, 1167, 1055, 981, 899, 775 and 699 cm^{-1}; δ_H ($CDCl_3$), 2.95 (1H, d, *J*=2.5, OH), 3.45 (1H, dd, *J*=8.7 and 10.3, CH_2), 3.62 (1H, dd, *J*=3.2 and 10.3, CH_2), 5.57–5.64 (1H, m, CH) and 7.19–7.82 [22H, m, $C_{10}H_7$ and $C(C_6H_5)_3$]; MS (FAB) *m*/*z* (relative intensity) 430 (M^+, 10) and 115 (100). Anal. Calcd for $C_{31}H_{26}O_2$: C, 86.48%; H, 6.09%. Found: C, 86.39%; H, 5.89%.

2.5. (S)-(+)-1-(1-Naphthyl)-2-(p-toluenesulfonyloxy)ethanol **7**

To a solution of (+)-**3** (>99% e.e.) (1.02 g, 5.31 mmol) in pyridine (7 cm^3) was added *p*-toluenesulfonyl chloride (810 mg, 4.25 mmol) and the mixture was then stirred for 5 h at 0–5°C. The reaction mixture was poured onto ice–water, acidified (pH 2) with hydrochloric acid and extracted with chloroform. Customary work-up, followed by silica gel chromatography of the products (hexane:ethyl acetate=4:1) gave (+)-**7** (1.09 g, 60%); mp 84–85 (recrystallized from hexane–ethyl acetate); $[\alpha]_D^{27}$ +123 (c 0.944, $CHCl_3$); IR (KBr) 3531, 3062, 2986, 2949, 2924, 1932, 1595, 1509, 1351, 1174, 967, 912, 877, 818 and 754 cm^{-1}; δ_H ($CDCl_3$), 2.43 (3H, s, CH_3), 2.72 (1H, d, *J*=2.9, OH), 4.13 (1H, dd, *J*=8.8 and 10.7, CH_2), 4.38 (1H, dd, *J*=2.4 and 10.7, CH_2), 5.79 (1H, ddd, *J*=2.4, 2.9 and 8.7, CH), 7.29 (2H, d, *J*=8.3, tosyl moiety ArH), 7.44–7.52 (3H, m, tosyl moiety ArH and $C_{10}H_7$), 7.69 (1H, d, *J*=7.3, $C_{10}H_7$) and 7.76–7.91 (5H, m, $C_{10}H_7$). Anal. Calcd for $C_{19}H_{18}O_4S$: C, 66.65%; H, 5.30%. Found: C, 66.62%; H, 5.19%.

2.6. (R)-(+)-1-(1-Naphthyl)ethanol **8**

To a suspension of $LiAlH_4$ (110 mg, 2.92 mmol) in dry THF (10 cm^3) was added a solution of (+)-**7** (500 mg, 1.46 mmol) in dry THF (5 cm^3) and the mixture was then stirred for 2 h at room temperature. To the reaction mixture was carefully added aq. ammonium chloride with ice-cooling. The deposited solids were removed by filtration and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane:ethyl acetate=9:1) to give (+)-**8** (205 mg, 81%) as an oil; $[\alpha]_D^{27}$ +81.6 (c 0.303, CH_3OH); IR (neat film) 3374, 3049, 2973, 1596, 1509, 1371, 1169, 1109, 1066, 1011, 800 and 778 cm^{-1}; δ_H ($CDCl_3$), 1.68 (3H, d, *J*=6.4, CH_3), 1.89 (1H, d, *J*=2.9, OH), 5.68 (1H, dq, *J*=3.2 and 12.7, CH) and 7.46–8.16 (7H, m, $C_{10}H_7$). HPLC analysis of (+)-**8** showed a single peak of R_t=42.4 min [CHIRAL PAK AD (250×4.6 mm) hexane:ethanol=98:2 (0.5 cm^3 min^{-1})] for the (*R*)-enantiomer.[13] A peak of R_t=39.0 min for the (*S*)-enantiomer[13] was not found.

2.7. (2S,10S)-(+)-2,10-Di(1-naphthyl)-1,11-bis(triphenylmethoxy)-3,6,9-trioxaundecane **9**

A solution of (*S*)-**4** (1.02 g, 2.32 mmol) in dry THF (10 cm^3) was added slowly to a suspension of NaH (223 mg, 9.29 mmol) in dry THF (30 cm^3) and the resulting mixture was then refluxed for 1.5 h. After the reaction mixture had been cooled to room temperature, a solution of diethylene glycol bis(*p*-toluenesulfonate) (790 mg, 1.71 mmol) in dry THF (20 cm^3) was added dropwise to the mixture

and then the reaction mixture was gently refluxed for 6 days under a nitrogen atmosphere. After a small amount of chilled water had been carefully added to the reaction mixture with ice-cooling, the solvent was removed under reduced pressure. The residue was extracted with chloroform and the combined extracts were washed with water, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane:ethyl acetate=19:1) to give (*S*,*S*)-**9** (687 mg, 64%); mp 72–73°C (recrystallized from hexane–ethyl acetate); $[\alpha]_D^{24}$ +39.6 (c 0.716, $CHCl_3$); IR (KBr) 3056, 2868, 1596, 1489, 1448, 1223, 1073, 776 and 705 cm^{-1}; δ_H ($CDCl_3$) 3.34 (2H, dd, *J*=4.8 and 9.7, CH_2OPh_3), 3.53 (2H, dd, *J*=7.1 and 9.7, CH_2OPh_3), 3.57–4.14 (8H, m, OCH_2CH_2O), 5.20 (2H, dd, *J*=4.8 and 7.1, CH), 6.99–7.91 [44H, m, $C_{10}H_7$ and $C(C_6H_5)_3$]; MS (FAB) *m*/*z* (relative intensity) 929 [(M^+-1), 3] and 73 (100). Anal. Calcd for $C_{66}H_{58}O_5$: C, 85.13%; H, 6.28%. Found: C, 84.80%; H, 6.43%.

*2.8. (2*S*,10*S*)-(+)-2,10-Di(1-naphthyl)-3,6,9-trioxaundecane-1,11-diol **10***

A solution of (*S*,*S*)-**9** (502 mg, 0.537 mmol) and *p*-toluenesulfonic acid (410 mg, 2.15 mmol) in methanol (20 cm^3) was stirred for 6 h at room temperature. After aq. sodium hydrogen carbonate had been added to the reaction mixture, the volatile materials were removed under reduced pressure and the residue was extracted with chloroform. Customary work-up, followed by silica gel chromatography of the products (ethyl acetate) gave (*S*,*S*)-**10** (217 mg, 94%) as an oil; $[\alpha]_D^{28}$ +102 (c 0.853, $CHCl_3$); IR (neat film) 3434, 3049, 2869, 1644, 1595, 1112, 1000, 803 and 737 cm^{-1}; δ_H ($CDCl_3$), 3.67–3.93 (12H, m, CH_2), 4.54 (2H, dd, *J*=2.9 and 9.3, OH), 5.35 (2H, dd, *J*=3.3 and 8.2, CH) and 7.47–8.19 (14H, m, $C_{10}H_7$). The high-resolution mass spectrum could not be recorded because of the very weak molecular ion peak. MS (FAB) *m*/*z* (relative intensity) 469 [($M+Na^+$), 4], 447 [(M^++1), 5] and 90 (100).

*2.9. (+)-1,3-Bis[(4*S*)-4-hydroxy-4-phenyl-2-oxabutyl]-2,5-dimethoxybenzene **12***

A solution of (*S*)-**6**[6] (10.0 g, 45.0 mmol) in dry THF (150 cm^3) was added to a suspension of NaH (2.16 g, 90.0 mmol) in dry THF (150 cm^3) and the resulting mixture was then stirred for 1.5 h at 60°C. The reaction mixture was cooled to room temperature and to the mixture was slowly added a solution of 1,3-bis(bromomethyl)-2,5-dimethoxybenzene (7.30 g, 22.5 mmol) in dry THF (250 cm^3). After the reaction mixture had been refluxed for 15 h, a similar work-up to that described for the preparation of **9** gave **11** as an oil, which was stirred with pyridinium *p*-toluenesulfonate (1.13 g, 4.50 mmol) in ethanol (350 cm^3) for 12 h at 60°C. Customary work-up, followed by silica gel chromatography of the products (chloroform) gave (*S*,*S*)-**12** (7.90 mg, 80%) as an oil; $[\alpha]_D^{25}$ +34.2 (c 1.98, $CHCl_3$); IR (neat film) 3443, 2904, 1650, 1482, 1359, 1321, 1213, 1174, 1151, 1108, 1005, 903, 760 and 701 cm^{-1}; δ_H ($CDCl_3$), 3.78 (2H, s, OH), 3.71 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 4.56 (2H, br s, benzylic CH_2), 4.65 (2H, br s, benzylic CH_2), 4.74 (4H, dd, *J*=3.2 and 9.9, CH_2), 4.94 (2H, dd, *J*=3.2 and 8.7, CH), 6.89 [2H, s, $(MeO)_2ArH$] and 7.28–7.40 (10H, m, C_6H_5); MS (FAB) *m*/*z* (relative intensity) 438 (M^+, 18) and 136 (100).

*2.10. (5*S*,13*S*)-(+)-19,21-Dimethoxy-5,13-di(1-naphthyl)-3,6,9,12,15-pentaoxabicyclo[15.3.1]-henicosane-1(21),17,19-triene **13***

A solution of (*S*,*S*)-**10** (2.36 g, 5.29 mmol) and 1,3-bis(bromomethyl)-2,5-dimethoxybenzene (1.72 g, 5.30 mmol) in dry THF (500 cm^3) was slowly added to a suspension of NaH (127 mg, 5.28 mmol) in dry THF (300 cm^3) over a 26 h period under reflux and the mixture was refluxed for a further 18 h under a nitrogen atmosphere. After a small amount of chilled water had been added to the reaction mixture with

ice-cooling, the solvent was removed under reduced pressure. The residue was extracted with chloroform and the combined extracts were washed with water, dried over $MgSO_4$ and evaporated under reduced pressure. Silica gel chromatography of the products (hexane:ethyl acetate=4:1) gave (*S*,*S*)-**13** (1.96 g, 78%); mp 155–156°C (recrystallized from hexane–ethyl acetate); $[\alpha]_D^{29}$ +133 (c 1.04, $CHCl_3$); IR (KBr) 3047, 2863, 1595, 1510, 1483, 1352, 1245, 1227, 1097, 1003, 955, 866, 801 and 745 cm^{-1}; δ_H ($CDCl_3$) 3.45–3.59 (8H, m, CH_2), 3.71–3.88 (4H, m, CH_2), 3.75 (3H, s, C-19 OCH_3), 4.36 (3H, s, C-21 OCH_3), 4.53 (2H, d, *J*=10.9, benzylic CH_2), 4.78 (2H, d, *J*=10.9, benzylic CH_2), 5.37 (2H, dd, *J*=2.2 and 8.7, CH), 6.85 [2H, s, $(MeO)_2$ArH] and 7.43–8.13 (14H, m, $C_{10}H_7$); MS (FAB) *m*/*z* (relative intensity) 647 [($M+K^+$), 3], 631 [($M+Na^+$), 8], 447 (M^+, 29) and 107 (100).

2.11. (5S,13S)-(+)-21-Hydroxy-19-methoxy-5,13-di(1-naphthyl)-3,6,9,12,15-pentaoxabicyclo[15.3.1]-henicosane-1(21),17,19-triene ***14***

To a suspension of NaH (150 mg, 6.25 mmol) in dry DMF (4 cm^3) was slowly added ethanethiol (480 mg, 7.80 mmol) and then a solution of (*S*,*S*)-**13** (190 mg, 312 mmol) in dry DMF (7 cm^3) was added to the resulting clear solution. The reaction mixture was stirred for 4 h at 90°C and cooled to 0–5°C. After a small amount of hydrochloric acid had been added to the chilled reaction mixture, the volatile materials were evaporated under reduced pressure and the residue was extracted with chloroform. The combined extracts were washed with water, dried over $MgSO_4$ and evaporated under reduced pressure. Silica gel chromatography of the products (hexane:ethyl acetate=1:1) gave (*S*,*S*)-**14** (174 mg, 94%); mp 70–71°C (recrystallized from hexane–ethyl acetate); $[\alpha]_D^{29}$ +139 (c 1.04, $CHCl_3$); IR (KBr) 3388, 3049, 2865, 1486, 1354, 1249, 1098, 870, 802 and 780 cm^{-1}; δ_H ($CDCl_3$), 3.67–3.89 (13H, m, CH_2 and OH), 3.75 (3H, s, OCH_3), 4.79 (2H, d, *J*=10.9, benzylic CH_2), 4.91 (2H, d, *J*=10.9, benzylic CH_2), 5.47 (2H, dd, *J*=4.2 and 7.1, CH), 6.77 [2H, s, (HO)ArH] and 7.41–8.12 (14H, m, $C_{10}H_7$); MS (FAB) *m*/*z* (relative intensity) 647 [($M+K^+$), 3], 631 [($M+Na^+$), 10], 447 (M^+, 21) and 91 (100).

2.12. (5S,13S)-(+)-19,21-Dimethoxy-5,13-diphenyl-3,6,9,12,15-pentaoxabicyclo[15.3.1]henicosane-1(21),17,19-triene ***15***

A solution of (*S*,*S*)-**12** (3.95 g, 9.01 mmol) and diethylene glycol bis(*p*-toluenesulfonate) (3.73 g, 9.01 mmol) in dry THF (500 cm^3) was slowly added to a mixture of NaH (864 mg, 36.0 mmol) and KBF_4 (1.13 mg, 9.01 mmol) in dry THF (200 cm^3) over a 9 h period under reflux and the mixture was refluxed for further 20 h under a nitrogen atmosphere. After a similar work-up to that described above, silica gel chromatography of the products (chloroform) gave (*S*,*S*)-**15** (1.90 g, 42%); mp 83–85°C; $[\alpha]_D^{25}$ +104 (c 0.615, $CHCl_3$); IR (KBr) 3030, 2893, 2857, 1611, 1487, 1357, 1243, 1230, 1170, 1099, 1053, 1023, 957, 923, 849, 763, 704, 666 and 579 cm^{-1}; δ_H ($CDCl_3$), 3.40–3.74 (12H, m, CH_2), 3.79 (3H, s, C-19 OCH_3), 4.19 (3H, s, C-21 OCH_3), 4.52 (2H, dd, *J*=2.6 and 8.5, CH), 4.48 (2H, d, *J*=10.8, benzylic CH_2), 4.71 (2H, d, *J*=10.8, benzylic CH_2), 6.84 [2H, s, $(MeO)_2$ArH] and 7.27–7.37 (10H, m, C_6H_5); MS (FAB) *m*/*z* (relative intensity) 531 [($M+Na^+$), 4], 508 (M^+, 35) and 165 (100). Anal. Calcd for $C_{30}H_{36}O_7$: C, 70.84%; H, 7.14%. Found: C, 70.64%; H, 7.06%.

2.13. (5S,13S)-(+)-21-Hydroxy-19-methoxy-5,13-diphenyl-3,6,9,12,15-pentaoxabicyclo[15.3.1]-henicosane-1(21),17,19-triene ***16***

In a similar manner to that described above, demethylation of (*S*,*S*)-**15** (1.00 g, 1.97 mmol) was carried out using NaH (943 mg, 0.393 mmol) and ethanethiol (2.90 g, 0.472 mmol). Silica gel chromatography

of the products (hexane:ethyl acetate=1:1) gave (*S*,*S*)-**16** (751 mg, 77%) as an oil; $[\alpha]_D^{25}$ +109 (c 0.850, $CHCl_3$); IR (neat film) 3372, 2850, 1600, 1492, 1358, 1320, 1248, 1200, 1100, 1028, 950, 860, 762, 735 and 700 cm^{-1}; δ_H ($CDCl_3$), 3.58–3.81 (12H, m, CH_2), 3.75 (3H, s, OCH_3), 4.68 (2H, dd, *J*=2.9 and 8.6, CH), 4.73 (2H, d, *J*=11.1, benzylic CH_2), 4.76 (2H, d, *J*=11.1, benzylic CH_2), 6.73 [2H, s, (HO)ArH], 7.28–7.36 (10H, m, C_6H_5) and 7.66 (1H, s OH); MS (FAB) *m*/*z* (relative intensity) 517 [($M+Na^+$), 4], 494 (M^+, 49) and 121 (100).

*2.14. (5S,13S)-5,13-Di(1-naphthyl)-3,6,9,12,15-pentaoxabicyclo[15.3.1]-henicosane-17,20-diene-19,21-dione **17***

A solution of (*S*,*S*)-**14** (101 mg, 0.168 mmol) in acetonitrile (7 cm^3) was added to a solution of CAN (180 mg, 0.328 mmol) in acetonitrile (10 cm^3) and then the resulting mixture was stirred for 1 h at room temperature. After the reaction mixture had been cooled to 0–5°C, water was added to the reaction mixture and the solvent was evaporated under reduced pressure. The residue was extracted with chloroform and customary work-up followed by silica gel chromatography of the products (hexane:ethyl acetate=4:1) gave (*S*,*S*)-**17** (94 mg, 96%) as a yellow solid; δ_H ($CDCl_3$), 3.54–3.87 (12H, m, CH_2), 4.68 (2H, d, *J*=14.8, benzylic CH_2), 4.81 (2H, d, *J*=14.8, benzylic CH_2), 5.39 (2H, dd, *J*=3.2 and 7.4, CH), 6.85 (2H, s, quinone moiety CH) and 7.44–8.16 (14H, m, $C_{10}H_7$). This was used for the next reaction without further purification.

*2.15. (5S,13S)-5,13-Diphenyl-3,6,9,12,15-pentaoxabicyclo[15.3.1]-henicosane-17,20-diene-19,21-dione **18***

In a similar manner to that described above, (*S*,*S*)-**16** (500 mg, 1.01 mmol) was oxidized with CAN (1.10 g, 2.00 mmol). Silica gel chromatography of the products (chloroform) gave (*S*,*S*)-**18** (474 mg, 98%) as a yellow solid; δ_H ($CDCl_3$), 3.42–3.79 (12H, m, CH_2), 4.60 (2H, d, *J*=14.8, benzylic CH_2), 4.61 (2H, dd, *J*=2.8 and 7.5, CH), 4.69 (2H, d, *J*=14.8, benzylic CH_2), 6.78 (2H, s, quinone moiety CH) and 7.28–7.38 (10H, m, C_6H_5). This was used for the next reaction without further purification.

*2.16. (5S,13S)-21-Hydroxy-19-(2′,4′-dinitrophenylazo)-5,13-di(1-naphthyl)-3,6,9,12,15-pentaoxabicyclo[15.3.1]-henicosane-1(21),17,19-triene **1***

A solution of 2,4-dinitrophenylhydrazine (1.90 g, 9.60 mmol) in ethanol (100 cm^3) containing conc. H_2SO_4 (8.4 cm^3) was added to a solution of (*S*,*S*)-**17** (1.10 g, 1.90 mmol) in a mixture of chloroform (50 cm^3) and ethanol (50 cm^3) and the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was diluted with water and extracted with chloroform. Customary work-up, followed by silica gel chromatography of the products (hexane:ethyl acetate=1:1) gave (*S*,*S*)-**1** (1.09 g, 76%) as a red glass; λ_{max} ($CHCl_3$) 403 nm (ε 2.34×10^4); IR (KBr) 3291, 3059, 2866, 1597, 1532, 1466, 1430, 1344, 1292, 1113, 906, 832, 802, 780 and 745 cm^{-1}; δ_H ($CDCl_3$), 3.68–3.96 (12H, m, CH_2), 4.92 (2H, d, *J*=11.1, benzylic CH_2), 4.98 (2H, d, *J*=11.1, benzylic CH_2), 5.39 (2H, dd, *J*=4.3 and 6.6, CH), 7.46–7.55 (6H, m, $C_{10}H_7$), 7.67 (2H, d, *J*=7.1, $C_{10}H_7$), 7.80–7.82 [3H, m, $C_{10}H_7$ and $(NO_2)_2ArH$], 7.88–7.90 [4H, m, $C_{10}H_7$ and (HO)ArH], 8.14 (2H, d, *J*=7.9, $C_{10}H_7$), 8.48 [1H, dd, *J*=2.3 and 8.9, $(NO_2)_2ArH$], 8.75 [1H, d, *J*=2.2, $(NO_2)_2ArH$] and 9.28 (1H, s, OH). The high-resolution mass spectrum could not be recorded because of the very weak molecular ion peak. MS (FAB) *m*/*z* (relative intensity) 797 [($M+K^+$), 3], 781 [($M+Na^+$), 7], 766 [($M+Li^+$), 3], 756 [(M^++1), 4] and 245 (100).

2.17. (5S,13S)-21-Hydroxy-19-(2′,4′-dinitrophenylazo)-5,13-diphenyl-3,6,9,12,15-pentaoxabicyclo-[15.3.1]-henicosane-1(21),17,19-triene ***2***

In a similar manner to that described above, (*S*,*S*)-**18** (484 mg, 1.01 mmol) was treated with 2,4-dinitrophenylhydrazine (1.00 g, 5.05 mmol) and the product was purified by silica gel chromatography (chloroform) followed by preparative recycling HPLC (JAIGEL 1H and 2H column, chloroform) to give (*S*,*S*)-**2** (210 mg, 32%) as a red solid; mp 73–75°C; λ_{max} ($CHCl_3$) 402 nm (ε 2.29×10^4); IR (KBr) 3292, 2867, 1600, 1534, 1466, 1430, 1345, 1290, 758 and 701 cm^{-1}; δ_H ($CDCl_3$), 3.58–3.81 (12H, m, CH_2), 4.70 (2H, br s, CH), 4.85 (4H, br s, benzylic CH_2), 7.28–7.40 (10H, m, C_6H_5), 7.84 [2H, s, (HO)ArH], 7.85 [1H, d, *J*=8.8, $(NO_2)_2$ArH], 8.47 [1H, dd, *J*=2.5 and 8.8, $(NO_2)_2$ArH], 8.74 [1H, d, *J*=2.5, $(NO_2)_2$ArH] and 9.16 (1H, s, OH). The high-resolution mass spectrum could not be recorded because of the very weak molecular ion peak. MS (FAB) *m*/*z* (relative intensity) 697 [($M+K^+$), 2], 681 [($M+Na^+$), 15], 659 [(M^++1), 20] and 135 (100).

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

1. G. W. Gokel and S. H. Korezeniowski, *Macrocyclic Polyether Syntheses*; Springer-Verlag: New York, 1982; J. F. Stoddart, Chiral Crown Ethers. In *Topics in Stereochemistry*; E. L. Eliel and S. H. Wilen Eds.; Wiley-Interscience: New York, 1988; Vol. 17, p. 207; J.-M. Lehn, *Supramolecular Chemistry*; VCH Verlagsgesellachaft, Weinheim, 1955.
2. K. Hirose, J. Fuji, K. Kamada, Y. Tobe and K. Naemura, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 1649.
3. W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc*., **1967**, *89*, 5485.
4. K. Naemura, K. Ogasahara, K. Hirose and Y. Tobe, *Tetrahedron: Asymmetry*, **1997**, *8*, 19.
5. P. Huszthy, J. S. Bradshaw, C. Y. Zhu and R. M. Izatt, *J. Org. Chem*., **1991**, *56*, 3330; K. Naemura, Y. Nishikawa, J. Fuji, K. Hirose and Y. Tobe, *Tetrahedron: Asymmetry*, **1997**, *8*, 873.
6. K. Naemura, J. Fuji, K. Ogasahara, K. Hirose and Y. Tobe, *J. Chem. Soc., Chem. Commun*., **1996**, 2749.
7. N. J. Rose and R. S. Drago, *J. Am. Chem. Soc*., **1959**, *81*, 6138.
8. Y. Inoue and T. Hakushi, *J. Chem. Soc., Perkin Trans. 2*, **1985**, 935; Y. Inoue, F. Amano, H. Inada, M. Ouchi, A. Tai, T. Hakushi, Y. Liu and L.-H. Tong, *J. Chem. Soc., Perkin Trans. 2*, **1990**, 1239; Y. Inoue, T. Hakushi, Y. Liu, L.-H. Tong, B.-J. Shen and D.-S. Jin, *J. Am. Chem. Soc*., **1993**, *115*, 475.
9. K. Naemura, K. Ueno, S. Takeuchi, Y. Tobe, T. Kaneda and Y. Sakata, *J. Am. Chem. Soc*., **1993**, *115*, 8475.
10. K. Saigo, H. Miura, K. Ishizaki and H. Nohira, *Bull. Chem. Soc. Jpn*, **1982**, *55*, 1188.
11. A. Cohen and F. L. Warren, *J. Chem. Soc*., **1937**, 1315.
12. G. A. Russell and G. J. Mikol, *J. Am. Chem. Soc*., **1966**, *88*, 5498.
13. The authentic samples of both enantiomers of **8** were prepared according to the reported method; K. Naemura, M. Murata, R. Tanaka, M. Yano, K. Hirose and Y. Tobe, *Tetrahedron: Asymmetry*, **1996**, *7*, 3285.