

## Novel $C_2$ -symmetric chiral 18-crown-6 derivatives with two aromatic sidearms as chiral NMR discriminating agents

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**Abstract**—Novel  $C_2$ -symmetric chiral 18-crown-6 derivatives with two aromatic sidearms **2–4** were prepared, and their enantiomeric recognition abilities as chiral NMR discriminating agents towards primary ammonium salts were examined. Among these chiral crown ethers, the most effective enantiomeric discrimination of racemic ammonium salts in the  $^1\text{H}$  NMR spectra was attained by the derivative with two pyrenylmethyl sidearms.

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In the field of supramolecular chemistry, a variety of chiral host compounds have recently been developed for discriminating the molecular chirality of organic compounds, such as ammonium salts and carboxylic acids, with good enantioselectivity.<sup>1</sup> Optically pure chiral reagents can be used for the determination of both the absolute configuration and the enantiomeric excess of chiral compounds in NMR spectroscopy.<sup>2</sup> In particular, chiral crown ethers are known to be effective chiral solvating agents (CSAs) towards protonated primary amines and amino acid methyl ester salts.<sup>3</sup> The use of these CSAs is one of the most effective and convenient methods for the assessment of the enantiomeric composition of chiral compounds in NMR spectroscopy. In many CSAs, a ring current effect of the aromatic ring in the chiral host has been utilized to induce a difference in the chemical shift changes between the guest enantiomers upon complexation with the host compound.<sup>4</sup> Thus, the introduction of aromatic sidearms into a chiral crown ether bearing a C-pivot methyl group is regarded as a useful strategy for the design of novel CSAs because such aromatic sidearm, of which move-

ment is restricted by the methyl group on the C-pivot carbon atom,<sup>5</sup> should affect the enantiomeric discrimination by the combination of steric and electrical factors. So far, there have been no reports on the use of this C-pivot type of chiral crown ether as CSAs. In this paper, we describe the design and synthesis of novel  $C_2$ -symmetric chiral crown ethers with two aromatic sidearms **2–4**, and their enantiomeric recognition abilities as chiral NMR discriminating agents towards primary ammonium salts **5–9** (Fig. 1). To the best of our knowledge, this is the first example of the use of C-pivot type chiral crown ethers as CSAs.

Chiral crown ethers **2–4** were prepared according to the procedures shown in Scheme 1. (2*R*,12*R*)-2,12-Bis(hydroxymethyl)-2,12-dimethyl-18-crown-6, (*R,R*)-**1**, was synthesized according to our previously reported procedure.<sup>6</sup> Two hydroxyl groups of (*R,R*)-**1** were tosylated to give (*S,S*)-**10**. The reaction of (*S,S*)-**10** with 1-naphthol generated (*S,S*)-**2**.<sup>5f</sup> Chiral crown ethers (*R,R*)-**3** and (*R,R*)-**4** were obtained by the reactions of (*R,R*)-**1** with 1-chloromethylnaphthalene and 1-bromomethylpyrene, respectively.<sup>5i</sup> The structures of the compounds obtained were ascertained by  $^1\text{H}$  NMR and IR spectroscopy, mass spectrometry and elemental analysis.<sup>7</sup>

The abilities of these host compounds as chiral NMR discriminating agents towards protonated primary

**Keywords:** Chiral crown ethers; Chiral NMR discriminating agents; Ring current effect; C-pivot lariat ether; Enantiomeric splitting.

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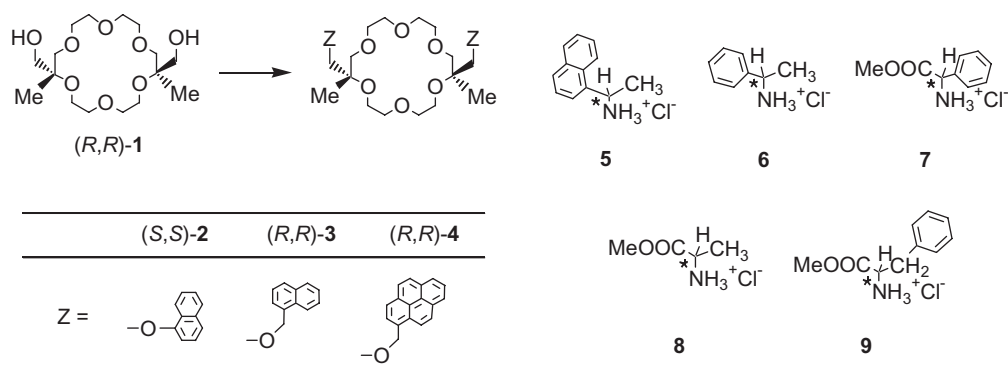
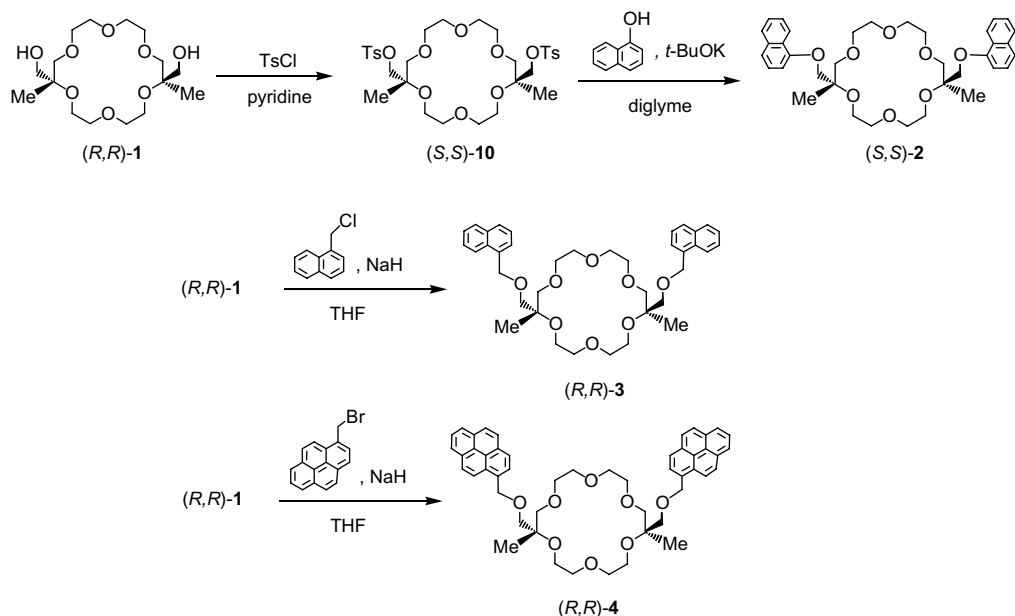


Figure 1. Structures of chiral crown ethers **1–4** and ammonium salts **5–9**.



Scheme 1.

amines and amino acid methyl ester salts<sup>8</sup> were examined. Figure 2 shows the methyl proton signals of racemic naphthylethylammonium chloride **5** ( $1.25 \times 10^{-3}$  M) in the absence and presence of chiral crown ethers **2–4** ( $2.50 \times 10^{-3}$  M) in a mixed solvent of  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (9:1). A comparison of the results obtained in the presence of (*S,S*)-**2** bearing naphthyl sidearms and (*R,R*)-**3** bearing naphthylmethyl sidearms gave an interesting suggestion for the design of effective chiral discriminating agents. Chiral crown ether (*R,R*)-**3** caused a significant splitting as well as a large upfield shift of the methyl proton signal of **5**, in sharp contrast to the case of (*S,S*)-**2**, where only a slight downfield shift of the methyl proton signal of **5** and no splitting of the signal were obtained. This indicates that the naphthalene ring of (*R,R*)-**3** is located near the methyl group of **5**, whereas the naphthalene ring of (*S,S*)-**2** is not. These results may be explained by the higher mobility of the aromatic sidearms of (*R,R*)-**3** caused by the presence of the methylene spacer between the oxygen atom and the naphthalene ring in the sidearm. On the basis of this assumption, we introduced pyrenylmethyl groups, which possess a

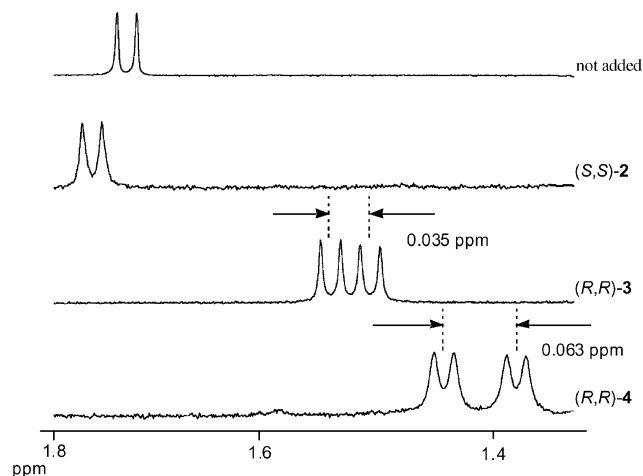
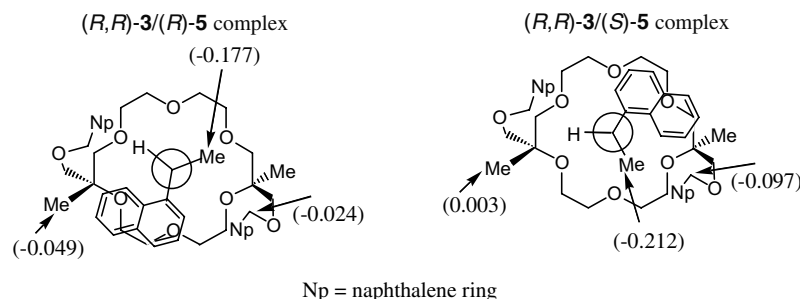


Figure 2. Methyl proton signals of **5** ( $1.25 \times 10^{-3}$  M) before and after the addition of **2–4** ( $2.50 \times 10^{-3}$  M) in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (9:1) at 25 °C.

stronger ring current effect and a greater bulkiness than naphthylmethyl groups, into the host compound to gen-



**Figure 3.** Plausible structures for the  $(R,R)$ -3/( $R$ )-5 complex and the  $(R,R)$ -3/( $S$ )-5 complex. The values in parentheses indicate the chemical shift changes based on the complexation between  $(R,R)$ -3 with  $(R)$ -5 and  $(S)$ -5.

erate more effective splitting. As expected,  $(R,R)$ -4 gave a larger chemical shift change and splitting of the methyl signal of **5** than  $(R,R)$ -3.

It is known that a difference in the stability and/or predominant geometry between the diastereomeric complexes consisting of a chiral host and racemic guests can cause the enantiomeric splitting of the guest NMR signals.<sup>9</sup> The stability constants between  $(R,R)$ -3 and the chiral ammonium salts of  $(R)$ -5 and  $(S)$ -5 in a mixed solvent of  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (3:7), which were examined by the  $^1\text{H}$  NMR titration method,<sup>1g,10</sup> showed that the difference in the stability constant between the  $(R,R)$ -3/( $R$ )-5 complex and the  $(R,R)$ -3/( $S$ )-5 complex was relatively small ( $\log K = 3.61$  for the  $(R,R)$ -3/( $R$ )-5 complex, and  $\log K = 3.67$  for the  $(R,R)$ -3/( $S$ )-5 complex). These results suggest that a difference in the predominant complex structure, rather than the stability constant, between those diastereomeric complexes was mainly responsible for the enantiomeric splitting of the guest signals. Figure 3 shows plausible structures for the  $(R,R)$ -3/( $R$ )-5 complex and the  $(R,R)$ -3/( $S$ )-5 complex, which were derived from the chemical shift changes based on the complexation of  $(R,R)$ -3 with  $(R)$ -5 and  $(S)$ -5, respectively. The conformations of the guest compounds in the complex were determined by assuming the

following two points: (i) in the  $(R,R)$ -3/( $R$ )-5 complex, the naphthalene ring of  $(R)$ -5 was located near the methyl group of  $(R,R)$ -3, far from the naphthalene ring of  $(R,R)$ -3 because the methyl proton signal of  $(R,R)$ -3 was shifted more upfield than the methylene proton signal next to the naphthalene ring of  $(R,R)$ -3; (ii) in the  $(R,R)$ -3/( $S$ )-5 complex, the naphthalene ring of  $(S)$ -5 was located near the naphthalene ring of  $(R,R)$ -3, far from the methyl group of  $(R,R)$ -3 because the methylene proton signal next to the naphthalene ring of  $(R,R)$ -3 was shifted more upfield than the methyl proton signal of  $(R,R)$ -3. The structures of these complexes are consistent with the result that, in the  $^1\text{H}$  NMR spectra of  $(R,R)$ -3 and a racemic mixture of **5**, the methyl proton signals of both  $(S)$ -5 and  $(R)$ -5 were shifted upfield.

Table 1 lists the chemical shift changes ( $\Delta\delta^R$  and  $\Delta\delta^S$ ) and the enantiomeric splitting ( $\Delta\Delta\delta^{R-S}$ ) observed in the NMR spectra of racemic ammonium salts **5–9** in the presence of chiral crown ethers **1–4**. In the cases of ammonium salts **6–9**, the effective enantiomeric splitting of those signals was observed only in the presence of chiral crown ethers having the methylene spacer between the oxygen atom and the aromatic ring in the sidearm [ $(R,R)$ -3 and  $(R,R)$ -4]. This result clearly demonstrates that the presence of the methylene spacer is essential

**Table 1.** Differences in the chemical shifts [ $\Delta\Delta\delta^{R-S}$  (ppm)] between enantiomers in the  $^1\text{H}$  NMR spectra of guests **5–9** ( $1.25 \times 10^{-3}$  M) in the presence of chiral crown ethers **1–4** ( $2.50 \times 10^{-3}$  M) in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (9/1) at 25 °C

Host		Guest resonance				
		<b>5 (Me)</b>	<b>6 (Me)</b>	<b>7 (COOMe)</b>	<b>8 (COOMe)</b>	<b>9 (COOMe)</b>
$(R,R)$ -1	$\Delta\delta^{Ra}$	–0.009	–0.011	–0.010	–0.001	–0.057
	$\Delta\delta^{Sa}$	–0.009	–0.011	–0.010	–0.001	–0.057
	$\Delta\Delta\delta^{R-Sb}$	0	0	0	0	0
$(S,S)$ -2	$\Delta\delta^{Ra}$	0.029	0.031	–0.009	0.004	–0.045
	$\Delta\delta^{Sa}$	0.029	0.031	–0.002	0.004	–0.045
	$\Delta\Delta\delta^{R-Sb}$	0	0	0.007	0	0
$(R,R)$ -3	$\Delta\delta^{Ra}$	–0.177	–0.224	–0.136	–0.074	–0.184
	$\Delta\delta^{Sa}$	–0.212	–0.237	–0.109	–0.064	–0.184
	$\Delta\Delta\delta^{R-Sb}$	0.035	0.013	0.027	0.010	0
$(R,R)$ -4	$\Delta\delta^{Ra}$	–0.276	–0.348	–0.213	–0.187	–0.222
	$\Delta\delta^{Sa}$	–0.339	–0.377	–0.194	–0.153	–0.238
	$\Delta\Delta\delta^{R-Sb}$	0.063	0.029	0.019	0.034	0.016

<sup>a</sup> (Chemical shift values of the methyl protons specified in bold in the presence of chiral crown ethers) – (chemical shift values in the absence of chiral crown ethers).

<sup>b</sup>  $\Delta\Delta\delta^{R-S}$  (ppm) =  $|\Delta\delta^R - \Delta\delta^S|$ .

for the use of this type of crown ether as a chiral NMR shift reagent. In addition, it is noteworthy that (*R,R*)-**4** showed a remarkable  $\Delta\delta^{R-S}$  towards all of the guest compounds examined in this study, including the phenylalanine methyl ester ammonium chloride **9**, whose proton signals could not be split even in the presence of a conventional chiral NMR shift reagent, (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid.<sup>3b</sup> Thus, (*R,R*)-**4** is highly effective as a chiral NMR shift reagent.

In conclusion, we prepared novel chiral crown ethers with two aromatic sidearms, and tested these host compounds as chiral NMR shift reagents. Among these chiral crown ethers, (*R,R*)-**4** bearing two pyrenylmethyl groups was found to be an excellent chiral NMR shift reagent for all the ammonium salts examined in this study. The pyrene rings linked to the oxygen atom in the sidearm through the methylene spacer strongly affected the chiral recognition of the ammonium salts. Lanthanide shift reagents are the most famous chiral NMR shift reagents,<sup>11</sup> but their use has been limited because they cause the paramagnetic line broadening.<sup>12</sup> In contrast, when the chiral crown ethers were used as CSAs for NMR spectroscopy, line broadening of the guest signals was rarely observed. Accordingly, (*R,R*)-**4** is potentially useful as a widely applicable chiral NMR shift reagent. The further design of chiral crown ethers for chiral recognition and enantiomeric separation is currently in progress in our laboratory.

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### Supplementary data

Experimental procedures, characterization data (<sup>1</sup>H NMR, IR, MS and elemental analysis) for all newly prepared compounds are provided. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2005.04.086](https://doi.org/10.1016/j.tetlet.2005.04.086).

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- Spectroscopic data: (*S,S*)-**2**:  $[\alpha]_D^{27} -8.17$  (*c* 0.30, CHCl<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.41 (s, 6H), 3.60–3.87 (m, 20H), 4.03 (d, 2H, *J* = 9.2 Hz), 4.24 (d, 2H, *J* = 9.2 Hz), 6.84 (d, 2H, *J* = 7.7 Hz), 7.33–7.50 (m, 8H), 7.78 (d, 2H, *J* = 7.3 Hz), 8.22 (d, 2H, *J* = 7.7 Hz). IR (neat, cm<sup>-1</sup>) 3050, 2880, 1720, 1580, 1460, 1360, 1270, 1110, 770, 730. MS (FAB) (*m/z*) 605

- ( $M^+ + 1$ ). Anal. Calcd for  $C_{36}H_{44}O_8$ : C, 71.50; H, 7.33. Found: C, 71.32; H, 7.11; (*R,R*)-**3**:  $[\alpha]_D^{26} -6.97$  (*c* 0.30,  $CHCl_3$ ).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.12 (s, 6H), 3.38–3.66 (m, 24H), 4.92 (d, 2H,  $J = 12.1$  Hz), 4.97 (d, 2H,  $J = 12.1$  Hz), 7.37–7.51 (m, 8H), 7.75–7.84 (m, 4H), 8.10 (d, 2H,  $J = 8.4$  Hz). IR (neat,  $cm^{-1}$ ) 3040, 2820, 1720, 1600, 1450, 1370, 1100, 800, 740. MS (FAB) ( $m/z$ ) 633 ( $M^+ + 1$ ). Anal. Calcd for  $C_{38}H_{48}O_8$ : C, 72.13; H, 7.65. Found: C, 71.87; H, 7.47; (*R,R*)-**4**:  $[\alpha]_D^{26} +19.5$  (*c* 0.30,  $CHCl_3$ ).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.11 (s, 6H), 3.38–3.63 (m, 24H), 5.18 (d, 2H,  $J = 11.7$  Hz), 5.23 (d, 2H,  $J = 11.7$  Hz), 7.93–8.39 (m, 18H). IR (neat,  $cm^{-1}$ ) 3050, 2850, 1710, 1630, 1450, 1360, 1240, 1100, 840, 710. MS (FAB) ( $m/z$ ) 780 ( $M^+$ ). Anal. Calcd for  $C_{50}H_{52}O_8$ : C, 76.90; H, 6.71. Found: C, 77.17; H, 6.44.
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