HETEROCYCLES, Vol. 85, No. 2, 2012, pp. 345 - 353. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 11th November, 2011, Accepted, 15th December, 2011, Published online, 22nd December, 2011
DOI: 10.3987/COM-11-12389

# SYNTHESIS AND OPTICAL PROPERTIES OF ZINCKE SALTS HAVING CHIRAL ANIONS

**Isao Yamaguchi,* Mikihiko Minamitani, and Sachiko Jonai**

Department of Material Science, Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan; E-mail: iyamaguchi@riko.shimane-u.ac.jp

**Abstract** – Zincke salts having chiral anions were obtained by the anion exchange reaction of Zincke salts having a chloride anion with *R*-(-)- or *S*-(+)-binaphthylphospholic acid sodium salts (*R*-BINAP-$PO_4$Na and *S*-BINAP-$PO_4$Na). The anion exchange behavior was investigated by photoluminescence measurements. The circular dichroism (CD) spectra of the Zincke salts having *R*-BINAP-$PO_4^-$ or *S*-BINAP-$PO_4^-$ showed relatively strong negative and positive Cotton effects, respectively.

## INTRODUCTION

Zincke salts, a highly electrophilic species formed by reaction between a pyridine derivative and 1-chloro-2,4-dinitrobenzene, are versatile compounds that can afford various *N*-substituted pyridinium salts as a result of reaction with amines. Pyridinium salts are an important class of compounds that are used as initiators of cationic polymerization,[1] cationic surfactants,[2] non-linear optical materials,[3] and phase transfer catalysts.[4] Pyridinium salts containing a chiral *N*-alkyl group[5a] have been synthesized through the Zincke reaction and are widely used as starting materials in asymmetric synthesis. However, the synthetic method previously reported for pyridinium salts having a chiral *N*-alkyl group requires expensive chiral amines. Furthermore, the number of chiral amines is limited. In contrast, many achiral amines exist, and most of them are less expensive than chiral amines. Thus, the reaction of Zincke salts having chiral anions with achiral amines can afford various chiral pyridinium salts at lower cost. We recently reported the synthesis of π-conjugated oligomers and polymers consisting of 5-piperazinium-penta-2,4-dienylideneammonium chloride units as a result of the ring-opening reaction of the pyridinium ring of the Zincke salts with piperazines.[6] Additionally, the anion exchange reaction between chloride anion in the polymers and *R*-(-)- or *S*-(+)-binaphthylphospholic acid anions yielded helical π-conjugated polymers.[7] These results suggest that Zincke salts having chiral anions will be useful starting materials for the synthesis of helical π-conjugated polymers. To the best of our knowledge,

however, there has been no report on Zincke salts having chiral anions. An investigation of the structures and optical properties of Zincke salts containing chiral anions will afford fundamental information for the development of new functional chiral materials.

Herein, we report the synthesis and optical properties of Zincke salts produced via anion exchange reactions between *N*-(2,4-dinitrophenyl)-4-arylpyridinium (aryl = H: **1**, phenyl: **2**, and 4-pyridyl: **3**) or *N*-(2,4-dinitrophenyl)isoquinolinium (**4**) chlorides and *R*-(-)-, *S*-(+)-, or (±)-binaphthylphospholic acid sodium salts (*R*-BINAP-$PO_4$Na, *S*-BINAP-$PO_4$Na, and BINAP-$PO_4$Na).

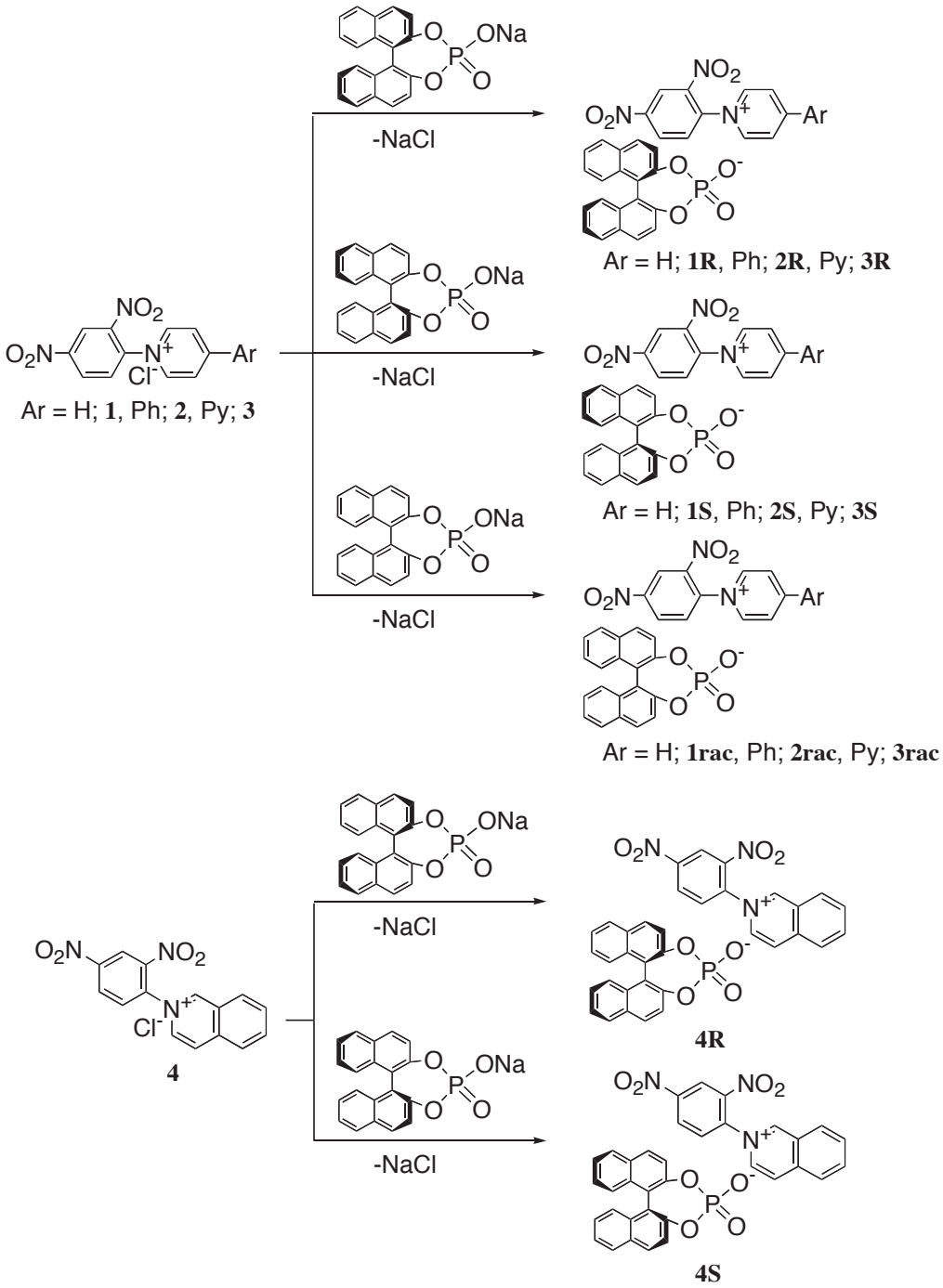
## RESULTS AND DISCUSSION

The reaction of **1**, **2**, **3**, or **4** with *R*-BINAP-$PO_4$Na or *S*-BINAP-$PO_4$Na in EtOH caused anion exchange between $Cl^-$ and *R*- or *S*-BINAP-$PO_4^-$ to yield Zincke salts containing chiral anions **1R**, **1S**, **2R**, **2S**, **3R**, **3S**, **4R**, and **4S** in 71%, 90%, 99%, 96%, 82%, 99%, 85%, and 80% yields, respectively (Scheme 1). The reaction of **1**, **2**, and **3** with BINAP-$PO_4$Na yielded **1rac**, **2rac**, and **3rac** containing a racemic binaphthylphospholic acid anion in 87%, 75%, and 74% yields, respectively (Scheme 1). The results of these reactions are summarized in Table 1. The anion-exchanged Zincke salts were soluble in acetone, EtOH, dimethyl sulfoxide (DMSO), and water, although the original Zincke salts (**1**-**4**) were insoluble in acetone and chloroform. The solubility in acetone of the anion exchanged products facilitated their purification.

**Table 1**. Synthesis results and UV-vis data

| | yield (%) | absorption/ nm[a] | CD peak position/ nm ($\theta \times 10^{-4}$ degree•cm$^2$•dmol$^{-1}$)[b] |
|---|---|---|---|
| **1R** | 71 | 216 (5.03), 226 (4.95), 260 (4.32) | 227 (-29), 215 (14) |
| **1S** | 90 | 216 (4.96), 226 (4.81), 260 (4.04) | 227 (19), 215 (-25) |
| **1rac** | 87 | 215 (4.91), 225 (4.81), 260 (4.61) | |
| **2R** | 99 | 216 (5.08), 225 (4.98), 311 (4.65) | 227 (-30), 214 (11) |
| **2S** | 96 | 215 (4.96), 225 (4.82), 311 (4.05) | 227 (20), 214 (-23) |
| **2rac** | 75 | 215 (5.00), 225 (4.92), 311 (4.45) | |
| **3R** | 82 | 216 (5.27), 225 (5.21), 274 (4.79) | 227 (-33), 214 (11) |
| **3S** | 99 | 216 (4.99), 225 (4.82), 272 (4.44) | 226 (16), 215 (-26) |
| **3rac** | 74 | 215 (5.01), 224 (4.92), 273 (4.49) | |
| **4R** | 85 | 215 (5.01), 224 (4.92), 300 (4.59) 309 (4.40), 317 (4.39), 324 (4.51) | 227 (-30), 215 (12) |
| **4S** | 80 | 215 (5.00), 224 (4.90), 300 (4.55) 309 (4.48), 317 (4.42), 323 (4.49) | 227 (18), 215 (-27) |

[a] In methanol. log$\varepsilon$ value is shown in parenthesis ($\varepsilon$ = molar absorption coefficient). [b] Molar ellipticity value ($\theta$) is shown in the parenthesis.




**Scheme 1**. Synthesis of Zincke salts containing chiral phosphate anions

The NMR and elemental analysis data supported the anion-exchanged structures of **1R**-**4S**. The $^{1}$H NMR peak integral between the protons of the pyridinium or isoquinolinium rings and the binaphthyl group suggested that the anion exchange reaction proceeded to completion. The $^{1}$H NMR chemical shifts of protons corresponding to *R*- and *S*-BINAP-$PO_4^-$ in **1R**-**4S** were almost the same as those of *R*- and *S*-BINAP-$PO_4$Na. However, the $^{31}$P NMR spectra of **1R** and **1S** showed peaks corresponding to phosphate anions at different chemical shifts ($\delta$ = 5.02 for **1R** and 5.39 for **1S**) from that of *R*- and *S*-BINAP-$PO_4$Na

(δ = 5.87 for *R*-BINAP-$PO_4$Na and *S*-BINAP-$PO_4$Na). The reason for the difference between the chemical shifts corresponding to the P atoms in **1R** and **1S** is unclear. However, the content of water molecules in **1R** and **1S** may affect the $^{31}$P NMR chemical shifts. Elemental analysis and following IR data supported the hydrated structures of the Zincke salts.

The IR spectra of the obtained Zincke salts exhibited strong absorption corresponding to the stretching vibrations of P=O and P-O bonds around 1260 $cm^{-1}$ and 1100 $cm^{-1}$, respectively, and the asymmetrical and symmetrical stretching vibrations of the $NO_2$ group at 1543 $cm^{-1}$ and 1342 $cm^{-1}$, respectively. The obtained Zincke salts were hygroscopic. Absorption corresponding to hydrated water molecules was observed around 3420 $cm^{-1}$.

The optical properties of the obtained Zincke salts are summarized in Table 1. Their UV-vis spectra showed absorption corresponding to the *R*- or *S*-BINAP-$PO_4^-$ groups at 216 or 225 nm, respectively. These wavelengths are almost the same as those of *R*- or *S*-BINAP-$PO_4$Na. In addition to these peaks, the salts containing Ar = H, Ph, or Py substituents showed absorption peaks corresponding to the pyridinium component at 260, 311, and 274 nm, respectively. Figure 1 shows the UV-vis spectra of **1R**, **2R**, and **3R** in MeOH. The appearance of absorption features corresponding to the pyridinium components of **2R**, **2S**, **2rac**, **3R**, **3S**, and **3rac** at longer wavelengths than those of **1R**, **1S**, and **1rac** is due to the presence of phenyl and pyridyl substituents in **2R**, **2S**, **2rac**, **3R**, **3S**, and **3rac**. The fact that the wavelengths at which absorption corresponding to the pyridinium component of **2R**, **2S**, and **2rac** was observed were longer than those of **3R**, **3S**, and **3rac** is apparently due to intramolecular charge transfer between the phenyl and pyridinium rings in **2R**, **2S**, and **2rac**.

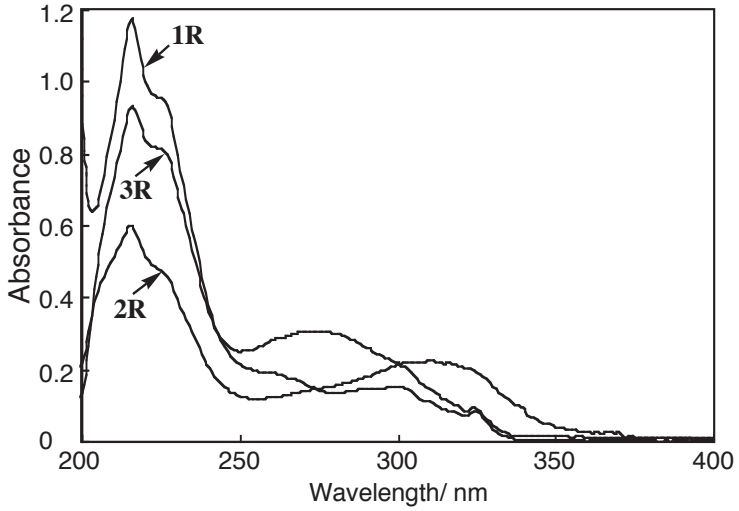



**Figure 1**. UV-vis spectra of **1R**, **2R**, and **3R** in MeOH. $c = 1.0 \times 10^{-4}$ M (**1R** and **3R**) and $0.5 \times 10^{-4}$ M (**2R**).

*R*- and *S*-BINAP-$PO_4$Na were photoluminescent in solution, whereas the anion-exchanged Zincke salts showed no photoluminescence (PL) in solution. To compare the quenching effect of **1** on BINAP-$PO_4$Na

and BINAP-$PO_4$H, PL measurements of the methanol solutions of BINAP-$PO_4$Na or BINAP-$PO_4$H were conducted at a series of **1**/methanol concentrations. As shown in Figure 1, the PL intensities of BINAP-$PO_4$Na/methanol solutions decreased with increasing **1** content. In contrast, the PL intensities of the BINAP-$PO_4$H/methanol solutions were almost unchanged regardless of the amount of **1** used. These results suggest that the quenching effect of **1** on BINAP-$PO_4$Na is pronounced when BINAP-$PO_4^-$ was replaced with $Cl^-$ from **1**. A quantitative measurement of the PL quenching can be achieved by determining the Stern-Volmer constant, $K_{SV}$:

$$I_0/I = 1 + K_{SV}[\text{quencher}],$$

where $I_0$ is the intensity of the PL in the absence of the quencher and $I$ is the intensity of the PL in the presence of the quencher. The equation reveals that $I_0/I$ increases in direct proportion to the concentration of the quenching moiety, and the constant $K_{SV}$ defines the efficiency of quenching. Stern-Volmer plots for PL quenching by **1** for BINAP-$PO_4$Na are insetted in Figure 2. The $K_{SV}$ value of BINAP-$PO_4$Na was $8.8 \times 10^4$ $M^{-1}$. The result that the $K_{SV}$ value for the **1**/BINAP-$PO_4$Na quenching system is considerably greater than that for pyridinium chloride/anthracene quenching system ($K_{SV}$ = 42 $M^{-1}$)[8] corresponds to the fact that the static interaction between *N*-(2,4-dinitrophenyl)-4-pyridinium cation and BINAP-$PO_4^-$ facilitates the formation of the quencher/fluorophore adduct. The $K_{SV}$ values for the **2**/BINAP-$PO_4$Na and **3**/BINAP-$PO_4$Na quenching system was $6.2 \times 10^4$ $M^{-1}$ and $3.5 \times 10^4$ $M^{-1}$, respectively.

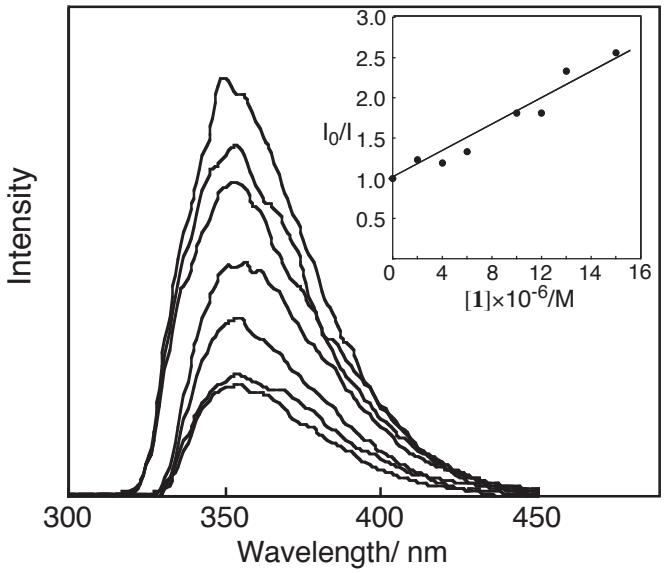



**Figure 2**. Changes of PL spectra of methanol solutions of BINAP-$PO_4$Na ($1.0 \times 10^{-5}$ M) in the presence of a series of concentrations of the **1**/methanol solution. The excitation wavelengths for **1**/BINAP-$PO_4$Na, **2**/BINAP-$PO_4$Na, and **3**/BINAP-$PO_4$Na system were 240 nm, 239 nm, and 240 nm, respectively. The inset is a Stern-Volmer plot.

The CD spectra of *R*-BINAP-$PO_4$Na and *S*-BINAP-$PO_4$Na showed complicated signals in the range of 170-200 nm in methanol. In contrast, the CD spectra of methanol solutions of **1R**, **2R**, **3R**, and **4R** as well as **1S**, **2S**, **3S**, and **4S** showed relatively strong negative and positive Cotton effects in the range of 205-240 nm, respectively, with a zero-crossing centered at approximately 220 nm, as shown in Figure 3. This wavelength is largely consistent with the λmax positions of *R*-BINAP-$PO_4$Na and *S*-BINAP-$PO_4$Na. The difference in the CD signals between *R*- and *S*-BINAP-$PO_4$Na and the anion-exchanged Zincke salts is attributed to the difference in the cationic species in these compounds. The peak positions of CD signals of the obtained Zincke salts are summarized in Table 1. In contrast, **1rac**, **2rac**, and **3rac** showed no CD signal.

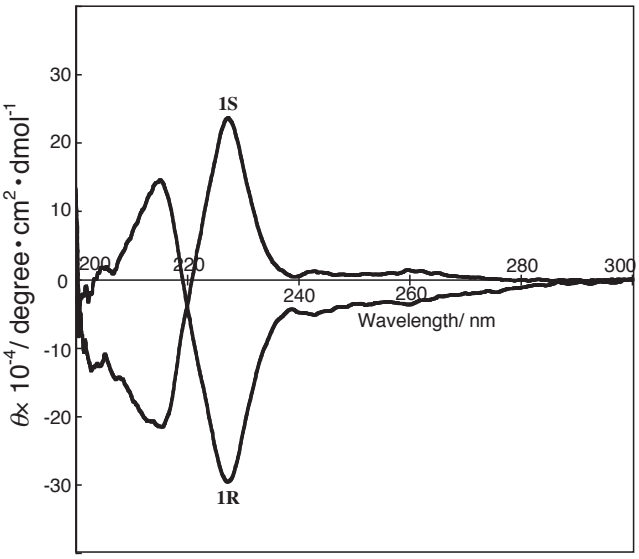



**Figure 3**. CD spectra of **1R** and **1S** in methanol at 25 ˚C ($c$ = 1.0 × $10^{-5}$ M)

## EXPERIMENTAL

**1**, **2**, **3**, and **4** were prepared according to the literatures.[9,10] Other reagents were purchased and used without further purification. Solvents were dried, distilled, and stored under $N_2$. Reactions were carried out with standard Schlenk technique under nitrogen.

IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer and JEOL AL-400 and ECX-500 spectrometers, respectively. $^{13}$C NMR measurements were carried out with gated decoupling technique. Elemental analysis was carried out on a Yanagimoto MT-5 CHN corder. UV-vis and CD spectra were obtained with a JASCO V-560 spectrometer and a JASCO J-720WS, respectively.

**Synthesis of 2R. 2** (0.53 g, 1.0 mmol) and *R*-BINAP-$PO_4$Na (0.37 g, 1.5 mmol) were dissolved in 50 mL of EtOH. After the solution was stirred for 24 h at room temperature, NaCl precipitated from the reaction solution was removed by filtration. The solvent was evaporated under vacuum and the resulting solid was

extracted with acetone (150 mL). The solvent was removed under vacuum and resulting solid was dissolved in MeOH (4 mL). The solution was poured in $Et_2O$ (400 mL) to give a precipitate, which was collected by filtration and dried under vacuum to obtain **2R** as a yellow powder (0.67 g, 99%).

Other Zincke salts were synthesized in an analogous manner.

**1R**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.38 (d, $J$ = 5.6 Hz, 2H), 9.12 (d, $J$ = 2.4 Hz, 1H), 8.92-8.98 (m, 2H), 8.40-8.44 (m, 3H), 8.03 (t, $J$ = 8.4 Hz, 4H), 7.44 (d, $J$ = 6.8 Hz, 2H), 7.40 (d, $J$ = 9.2 Hz, 2H), 7.30 (t, $J$ = 8.0 Hz, 2H), 7.21 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 150.0, 149.2, 149.1, 148.8, 146.1, 143.0, 138.7, 131.9, 131.93, 131.85, 130.3, 130.2, 129.7, 128.4, 128.0, 126.1, 126.0, 124.4, 122.57, 122.55, 121.67, 121.66, 121.1. $^{31}$P NMR (203 MHz, DMSO-$d_6$) δ 5.02. IR (KBr, cm$^{-1}$) 3420, 3116, 3072, 1614, 1543, 1343, 1242, 1100, 960, 836, 754. Anal. Calcd for $C_{31}H_{20}N_3O_8P$•0.25$H_2O$: C, 62.26; H, 3.46; N, 7.03. Found: C, 62.29; H, 3.89; N, 6.63.

**2R**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.40 (d, $J$ = 6.8 Hz, 2H), 9.14 (d, $J$ = 2.4 Hz, 1H), 8.97 (dd, $J$ = 8.8, 2.0 Hz, 1H), 8.82 (d, $J$ = 6.4 Hz, 2H), 8.43 (d, $J$ = 8.4 Hz, 2H), 8.25 (d, $J$ = 7.2 Hz, 2H), 8.02 (t, $J$ = 8.4 Hz, 2H), 7.70-7.76 (m, 3H), 7.38-7.44 (m, 4H), 7.29 (t, $J$ = 8.0 Hz, 2H), 7.20 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 157.3, 150.0, 149.9, 149.0, 145.9, 143.2, 138.5, 133.1, 133.0, 132.0, 131.9, 130.3, 130.2, 130.0, 129.7, 128.7, 128.4, 126.1, 126.0, 124.4, 124.1, 122.6, 121.7, 121.5. $^{31}$P NMR (203 MHz, DMSO-$d_6$) δ 5.76. IR (KBr, cm$^{-1}$) 3442, 3116, 3058, 1636, 1610, 1541, 1342, 1260, 1243, 1099, 960, 837. Anal. Calcd for $C_{37}H_{24}N_3O_8P$•0.3$H_2O$: C, 65.84; H, 3.67; N, 6.23. Found: C, 65.80; H, 3.84; N, 6.47.

**3R**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.55 (d, $J$ = 6.4 Hz, 2H), 9.15 (d, $J$ = 2.0 Hz, 1H), 9.00 (dd, $J$ = 8.4, 2.8 Hz, 1H), 8.91-8.94 (m, 4H), 8.44 (d, $J$ = 8.4 Hz, 2H), 8.18 (d, $J$ = 5.2 Hz, 2H), 8.06 (t, $J$ = 8.4 Hz, 2H), 7.45 (t, $J$ = 7.6 Hz, 2H), 7.43 (d, $J$ = 8.8 Hz, 2H), 7.31 (t, $J$ = 8.0 Hz, 2H), 7.20 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 155.1, 151.2, 149.9, 149.8, 149.2, 146.6, 143.1, 140.4, 138.4, 131.99, 131.92, 130.4, 130.2, 129.8, 128.4, 126.1, 126.0, 125.2, 124.5, 122.53, 122.51, 122.2, 121.66, 121.64, 121.5. $^{31}$P NMR (203 MHz, DMSO-$d_6$) δ 5.44. IR (KBr, cm$^{-1}$) 3447, 3114, 3066, 1637, 1610, 1543, 1342, 1260, 1242, 1100, 961, 837, 817. Anal. Calcd for $C_{36}H_{23}N_4O_8P$•0.6$H_2O$: C, 63.46; H, 3.58; N, 8.22. Found: C, 63.50; H, 3.54; N, 7.66.

**4R**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.47 (s, 1H), 9.15 (d, $J$ = 2.4 Hz, 1H), 9.05 (d, $J$ = 6.8 Hz, 1H), 8.99 (dd, $J$ = 8.6, 1.8 Hz, 1H), 8.79 (d, $J$ = 6.8 Hz, 1H), 8.59 (d, $J$ = 8.4 Hz, 1H), 8.48 (d, $J$ = 8.8 Hz, 2H), 8.42 (t, $J$ = 8.0 Hz, 1H), 8.16 (t, $J$ = 8.0 Hz, 1H), 8.03 (d, $J$ = 8.8 Hz, 4H), 7.44 (d, $J$ = 7.2 Hz, 2H), 7.41 (d, $J$ = 8.4 Hz, 2H), 7.30 (t, $J$ = 8.0 Hz, 2H), 7.21 (d, $J$ = 8.4 Hz, 2H). $^{31}$P NMR (203 MHz, DMSO-$d_6$) δ 5.73. Anal. IR (KBr, cm$^{-1}$) 3445, 3114, 3066, 1637, 1612, 1591, 1580, 1543, 1345, 1260, 1242, 1100, 961, 840, 817. Calcd for $C_{35}H_{22}N_4O_8P$•0.2$H_2O$: C, 64.96; H, 3.49; N, 6.49. Found: C, 64.90; H, 3.53; N, 6.80.

**1S**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.38 (d, $J$ = 5.6 Hz, 2H), 9.12 (d, $J$ = 2.4 Hz, 1H), 8.92-8.98 (m,

2H), 8.40-8.44 (m, 3H), 8.03 (t, *J* = 8.8 Hz, 4H), 7.45 (d, *J* = 6.8 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H). $^{31}$P NMR (203 MHz, DMSO-$d_6$) δ 5.39. Anal. Calcd for $C_{31}H_{20}N_3O_8P$•0.4$H_2O$: C, 61.98; H, 3.49; N, 7.00. Found: C, 61.98; H, 3.61; N, 6.62.

**2S**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.40 (d, *J* = 7.2 Hz, 2H), 9.14 (d, *J* = 2.4 Hz, 1H), 8.98 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.82 (d, *J* = 7.2 Hz, 2H), 8.43 (d, *J* = 8.4 Hz, 2H), 8.25 (d, *J* = 6.8 Hz, 2H), 8.01 (t, *J* = 8.8 Hz, 2H), 7.70-7.77 (m, 3H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H). $^{31}$P NMR (203 MHz, DMSO-$d_6$) δ 5.81. Anal. Calcd for $C_{37}H_{24}N_3O_8P$•0.3$H_2O$: C, 65.84; H, 3.67; N, 6.23. Found: C, 65.88; H, 3.81; N, 6.59.

**3S**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.55 (d, *J* = 6.4 Hz, 2H), 9.15 (d, *J* = 2.4 Hz, 1H), 8.98 (dd, *J* = 8.8, 2.8 Hz, 1H), 8.92-8.94 (m, 4H), 8.43 (d, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 6.4 Hz, 2H), 8.01 (t, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H). $^{31}$P NMR (203 MHz, DMSO-$d_6$) δ 5.65. Anal. Calcd for $C_{36}H_{23}N_4O_8P$•0.6$H_2O$: C, 63.46; H, 3.58; N, 8.22. Found: C, 63.42; H, 3.58; N, 8.20.

**4S**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.47 (s, 1H), 9.15 (d, *J* = 2.4 Hz, 1H), 9.05 (d, *J* = 6.8 Hz, 1H), 8.99 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.79 (d, *J* = 6.8 Hz, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.48 (d, *J* = 8.8 Hz, 2H), 8.42 (t, *J* = 8.0 Hz, 1H), 8.16 (t, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 4H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H). Anal. Calcd for $C_{35}H_{22}N_4O_8P$•0.2$H_2O$: C, 64.96; H, 3.49; N, 6.49. Found: C, 64.88; H, 3.59; N, 6.67.

**1rac**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.38 (d, *J* = 6.4 Hz, 2H), 9.12 (d, *J* = 2.8 Hz, 1H), 8.91-8.97 (m, 2H), 8.40-8.44 (m, 3H), 8.02 (t, *J* = 8.4 Hz, 4H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 150.0, 149.9, 149.1, 148.8, 146.1, 143.0, 138.7, 131.9, 131.8, 130.3, 130.2, 129.7, 128.4, 128.0, 126.1, 126.0, 124.4, 122.5, 121.7, 121.4. $^{31}$P NMR (203 MHz, DMSO-$d_6$) δ 5.49. Anal. Calcd for $C_{31}H_{20}N_3O_8P$•0.2$H_2O$: C, 62.36; H, 3.44; N, 7.04. Found: C, 62.35; H, 3.92; N, 6.75.

**2rac**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.41 (d, *J* = 6.8 Hz, 2H), 9.14 (d, *J* = 2.4 Hz, 1H), 8.99 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.83 (d, *J* = 5.6 Hz, 2H), 8.42 (d, *J* = 8.4 Hz, 2H), 8.25 (d, *J* = 7.2 Hz, 2H), 8.00 (t, *J* = 8.8 Hz, 2H), 7.70-7.76 (m, 3H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H). $^{31}$P NMR (203 MHz, DMSO-$d_6$) δ 5.87. Anal. Calcd for $C_{37}H_{24}N_3O_8P$•0.2$H_2O$: C, 62.36; H, 3.44; N, 7.04. Found: C, 65.96; H, 3.61; N, 6.32.

**3rac**: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.54 (d, *J* = 6.4 Hz, 2H), 9.15 (d, *J* = 2.0 Hz, 1H), 8.99 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.92-8.95 (m, 4H), 8.43 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 6.4 Hz, 2H), 8.03 (t, *J* = 9.2 Hz, 2H), 7.45 (d, *J* = 6.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H). Anal. Calcd for $C_{36}H_{23}N_4O_8P$•0.6$H_2O$: C, 63.46; H, 3.58; N, 8.22. Found: C, 63.55; H, 3.62; N, 7.59.

**ACKNOWLEDGEMENT**

This work was supported by Grant-in-Aid for Scientific Research (C) from Ministry of Education, Science, Culture, and Sports Japan (No. 21550173).

**REFERENCES**

1. (a) E. Takahashi, F. Sanda, and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 1037; (b) M. Onciu, A. Onen, and Y. Yagci, *Polym. Int.*, 2001, **50**, 144; (c) W. Schnabel, *Macromol. Rapid Commun.*, 2000, 628.
2. (a) N. O. Mchedlov-Petrossyan, N. A. Vodolazkaya, A. A. Kornienko, E. L. Karyakina, and C. Reichardt, *Langmuir*, 2005, **21**, 7090; (b) J. Pernak, J. Kalewska, H. Ksycińska, and J. Cybulski, *Eur. J. Med. Chem.*, 2001, **36**, 899.
3. (a) H. Umezawa, S. Okada, H. Oikawa, H. Matsuda, and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 344; (b) B. J. Coe, J. A. Harris, I. Asselberghs, K. Wostyn, K. Clays, A. Persoons, B. S. Brunschwig, S. J. Coles, T. Gelbrich, M. E. Light, M. B. Hursthouse, and K. Nakatani, *Adv. Funct. Mater.*, 2002, **12**, 110.
4. (a) D. Wang, M. Wang, X. Wang, R. Zhang, J. Ma, and L. Sun, *J. Mol. Cat. A: Chem.*, 2007, **270**, 278; (b) R. T. Dere, R. R. Pal, P. S. Patil, and M. M. Salunkhe, *Tetrahedron Lett.*, 2003, **44**, 5351.
5. (a) G. H. R. Viana, I. C. Santos, R. B. Alves, L. Gil, C. Marazano, and R. P. F. Gil, *Tetrahedron Lett.*, 2005, **46**, 7773; (b) M. Eda, M. J. Kurth, and M. H. Nantz, *J. Org. Chem.*, 2000, **65**, 5131; (c) D. Urban, E. Duval, and Y. Langlois, *Tetrahedron Lett.*, 2000, **41**, 9251; (d) D. Gnecco, J. Juárez, A. Galindo, C. Marazano, and R. G. Enríquez, *Synth. Commun.*, 1999, **29**, 281; (e) J. Levillain, D. Paquer, A. Sene, and M. Vazeux, *Synthesis*, 1998, 99; (f) S. Kunugi, T. Okubo, and N. Ise, *J. Am. Chem. Soc.*, 1976, **98**, 2282; (g) E. N. Marvell, G. Caple, and I. Shahidi, *J. Am. Chem. Soc.*, 1970, **92**, 5641; (h) E. N. Marvell and I. Shahidi, *J. Am. Chem. Soc.*, 1970, **92**, 5646.
6. (a) I. Yamaguchi, Y. Matsuda, and M. Sato, *Polym. Int.*, 2011, **60**, 78; (b) I. Yamaguchi, A. Kado, T. Fukuda, H. Fukumoto, T. Yamamoto, and M. Sato, *Eur. Polym. J.*, 2010, **46**, 1119; (c) I. Yamaguchi, S. Shingai, and M. Sato, *Macromolecules*, 2008, **41**, 6292.
7. I. Yamaguchi, S. Jonai, and Y. Matsuda, *Macromolecules*, 2011, **44**, 1273.
8. H. J. Pownall and L. C. Smith, *Biochemistry*, 1974, **13**, 2594.
9. (a) T. H. Zincke, G. Heuser, and W. I. U. Möller, *Justus Liebigs Ann Chem.,* 1904, **333**, 296; (b) I. Yamaguchi, H. Higashi, S. Shigesue, S. Shingai, and M. Sato, *Tetrahedron Lett.*, 2007, **48**, 7778.
10. D. Barbier, C. Marazano, B. C. Das, and P. Potier, *J. Org. Chem.*, 1996, **61**, 9596.