HETEROCYCLES, Vol. 80, No. 1, 2010, pp. 527 - 535. © The Japan Institute of Heterocyclic Chemistry
Received, 22nd July, 2009, Accepted, 31st August, 2009, Published online, 1st September, 2009
DOI: 10.3987/COM-09-S(S)64

PREPARATION AND FERROELECTRIC PROPERTIES OF NEW CHIRAL LIQUID CRYSTALLINE ORGANIC RADICAL COMPOUNDS

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Abstract – We have synthesized new chiral liquid crystalline (LC) organic radical compounds **2** and **3**, which are the derivatives of the previously reported compounds **1** containing a chiral cyclic nitroxide unit and an ester group in the mesogen core, and their ferroelectric properties have been studied. The enantiomerically enriched (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3** showed an SmC* phase for which their ferroelectric properties such as spontaneous polarization (*P*s) and tilt angle (θ) were compared with those of (2*S*,5*S*)-**1**.

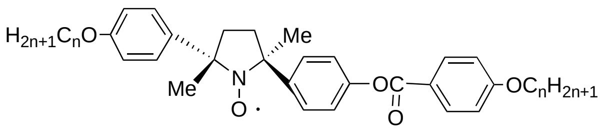
INTRODUCTION

Recently, we have shown that a 2,2,5,5-tetrasubstituted pyrrolidin-1-yloxy (PROXYL) structure is stable enough for repeated heating and cooling cycles below 150°C in the air and thereby this radical unit can serve as the excellent source of the magnetic spin (S = 1/2) and spontaneous polarization (*P*s) for elaborating paramagnetic as well as ferroelectric all-organic liquid crystals (LCs), which can combine the optical and electric properties of conventional ferroelectric LCs (FLCs) with the magnetic properties of paramagnetic compounds.[1-9] For example, it is quite interesting to know whether magneto-electric effects can be observed in the FLC state of paramagnetic materials. The magneto-electric effects are well known to arise from the intra- and intermolecular interactions between magnetic and electric dipole moments and to be observed in ferroelectric rare earth metal manganite crystals such as $YMnO_3$, $TbMnO_3$, and

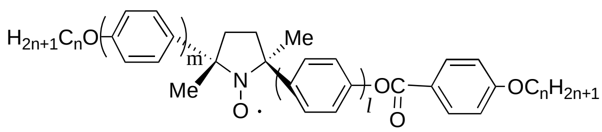
$HoMnO_3$ with magnetic order at low temperatures.[10-12] Experimentally, the effects can be detected as the influence of a magnetic (electric) field on the polarization (magnetization) of a material and *vice versa*.[13-15]

In this context, we successfully obtained the prototypic all-organic chiral LC radical compounds **1** which have a PROXYL group with a large electric dipole moments (3 Debye) in the mesogen core as well as a polar ester group (1.8 Debye) used very often for the preparation of conventional FLCs.[16] Indeed, (2*S*,5*S*)-**1** (n=11–15) showing an SmC* phase exhibited ferroelectricity in a thin sandwich cell (4 µm thickness); the highest *P*s value of 24 nC cm^{-2} was recorded for (2*S*,5*S*)-**1** (n=13).[2,3]

In order to improve the *P*s value which should become a crucial factor for observing magneto-electric effects in the paramagnetic FLCs, we have designed compounds (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3** with an additional benzene ring on either 2 or 5 position of the PROXYL ring, compared to (2*S*,5*S*)-**1** (Chart 1). This structural modification is expected to result in the strong intra-layer interactions in the SmC* phase and hence to increase the overall *P*s value.[17] Here we report the synthesis, LC characterization and ferroelectric properties of (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3**.

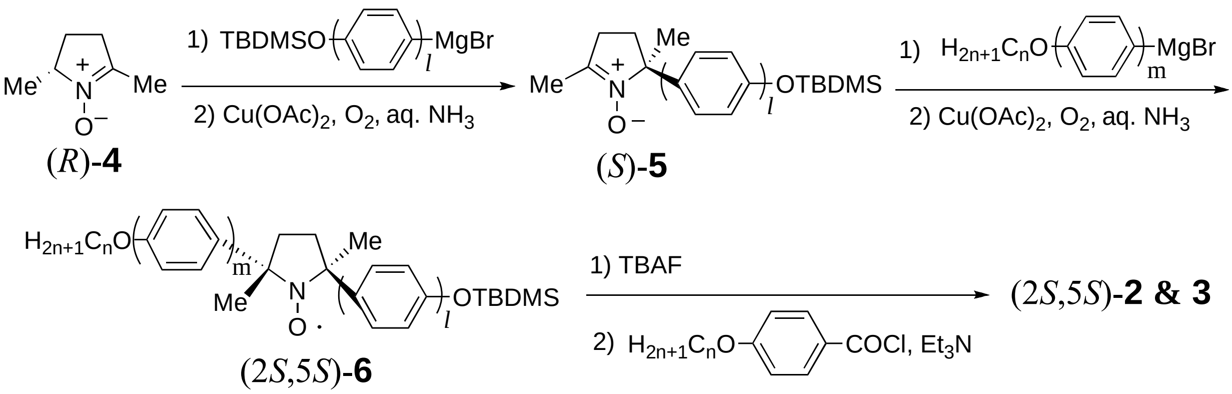


(2*S*,5*S*)-**1**



(2*S*,5*S*)-**2a**; *l* = 1, m = 2, n = 12 (2*S*,5*S*)-**3a**; *l* = 2, m = 1, n = 13
(2*S*,5*S*)-**2b**; *l* = 1, m = 2, n = 13 (2*S*,5*S*)-**3b**; *l* = 2, m = 1, n = 14
(2*S*,5*S*)-**2c**; *l* = 1, m = 2, n = 14
(2*S*,5*S*)-**2d**; *l* = 1, m = 2, n = 15

Chart 1. PROXYL type of LC compounds (2*S*,5*S*)-**1**–**3** showing an SmC* phase.



Scheme 1. Preparation of (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3**.

RESULTS AND DISCUSSION

*Synthesis of (2S,5S)-**2** and (2S,5S)-**3**.* (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3** were synthesized with high stereoselectivity by repeating the addition of an appropriate Grignard reagent to nitrones [**4** (*ca*. 90% *ee*) and **5**] and the subsequent oxidation twice, followed by benzoylation of the phenolic hydroxy group after desilylation, similarly to the synthesis of (2*S*,5*S*)-**1** (Scheme 1).[1-3,18-23]

Characterization of LC phases. The phase transition behavior of (2*S*,5S)-**2** and (2*S*,5*S*)-**3** was characterized by DSC, POM, and XRD analyses, which were measured below 160°C because these compounds instantly decompose in the isotropic phase above 160°C (Table 1, Figure 1 and 2).

Table 1. Phase transition temperatures of (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3** on the first heating run.

		Transition temperature (°C) and Δ*H* (in parentheses, kJ/mol)						
(2*S*,5*S*)-**2** or **3**	*ee* (%)	Cr		SmC*		N*		I
2a (n=12)	89.3	•	105.9 (30.6)	•	129.7 (0.4)	•	163.8 (2.2)	•
2b (n=13)	91.0	•	105.5 (33.2)	•	150.1 (1.2)	•	167.4 (2.2)	•
2c (n=14)	90.9	•	106.5 (36.9)	•	154.9 (1.7)	•	164.8 (3.3)	•
2d (n=15)	90.8	•	106.2 (38.1)	•	155.0 (7.1)[a]	•	159.8 (7.1)[a]	•
3a (n=13)	91.2	•	105.6 (22.8)	•	154.4 (2.1)	•	165.2 (2.0)	•
3b (n=14)	89.0	•	107.2 (37.3)	•	159.7 (8.6)[a]	•	164.5 (8.6)[a]	•

[a] Two peaks were overlapped.

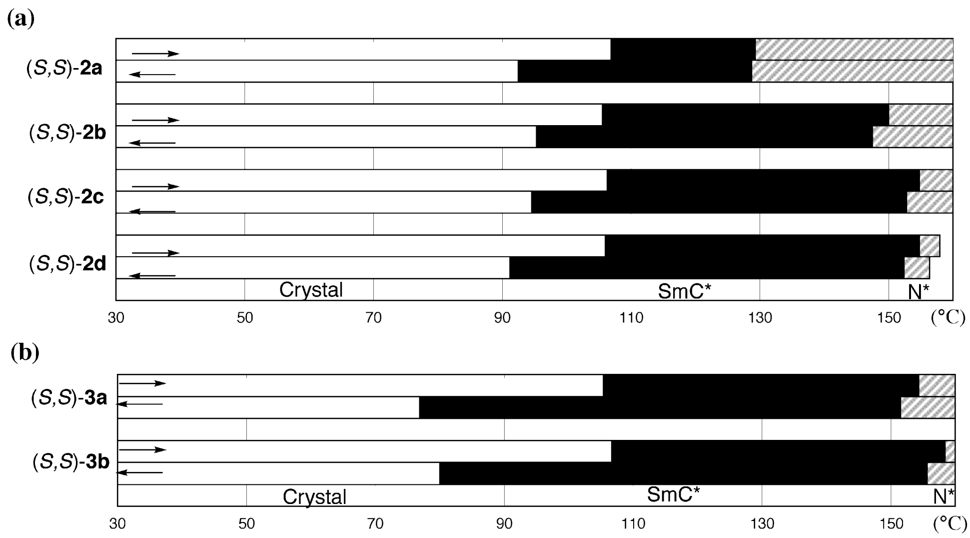


Figure 1. LC behavior of (a) (2*S*,5*S*)-**2** and (b) (2*S*,5*S*)-**3**. Transition temperatures determined by DSC analysis at a scanning rate of 5°C min^{-1} upon the first heating and cooling processes. Heating was turned down at 160°C for the subsequent cooling run.

As expected, (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3** showed stable LC phases over wide temperature ranges and at higher temperatures than (2*S*,5*S*)-**1** due most likely to the stronger inter-layer interactions.[17] Similarly to the case of (2*S*,5*S*)-**1**, (2*S*,5*S*)-**2** with C12 to C15 chains and (2*S*,5*S*)-**3** with C13 and C14 chains exhibited SmC* and N* phases, with respective broken fan-shaped and oily-streak textures observed on the cooling run (Table 1, Figure 1 and 2). Variable temperature XRD analysis verified the existence of the SmC* and N* phases (Figure 3).

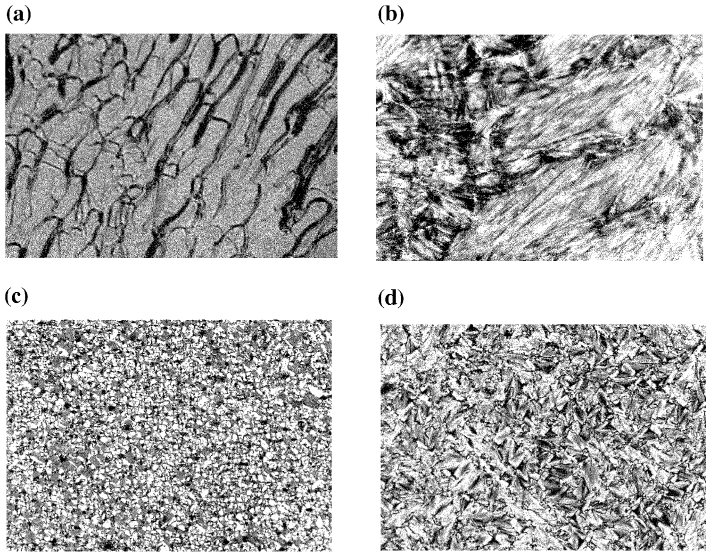


Figure 2. Polarized optical micrographs showing (a) oily-streaks texture (N*) under random conditions at 158°C and (b) broken fan-shaped texture (SmC*) in a thin sandwich cell (4 mm) under homogeneous planar boundary conditions at 130°C for (2*S*,5*S*)-**2b**, and (c) oily-streaks texture (N*) under random conditions at 160°C and (d) broken fan-shaped texture (SmC*) in a thin sandwich cell (4 μm) under homogeneous planar boundary conditions at 150°C for (2*S*,5*S*)-**3b**.

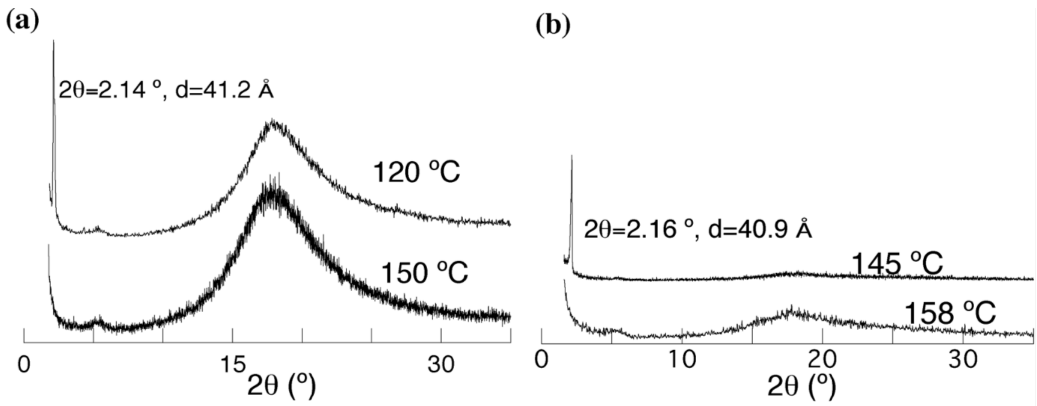


Figure 3. XRD patterns of (a) (2*S*,5*S*)-**2a** at 120 (SmC*) and 150°C (N*) and (b) (2*S*,5*S*)-**3a** at 145 (SmC*) and 158°C (N*).

Ferroelectric properties. The magnitude of *P*s and the optical and calculated tilt angles [θ and $\cos^{-1}(d/l)$] of (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3** are summarized in Figures 4 and 5 and Table 2. On the cooling run from the N*-to-SmC* transition temperature, the *P*s values rapidly increased (Figure 4). On the whole, the *P*s values of (2*S*,5*S*)-**2** were larger than those of the corresponding (2*S*,5*S*)-**1** and (2*S*,5*S*)-**3**; (2*S*,5*S*)-**2d** showed the highest *P*s(–10°) value of 32 nC cm^{-2} (Figure 4a and Table 2). Such high *P*s values observed for (2*S*,5*S*)-**2** can be interpreted in terms of the increased intra-layer interactions.[17] The tilt angles of (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3** were too large to measure the optical response time (Figure 5 and Table 2); only a bright-dark-bright or dark-bright-dark texture change was observed upon switching the polarity of the applied electric field.

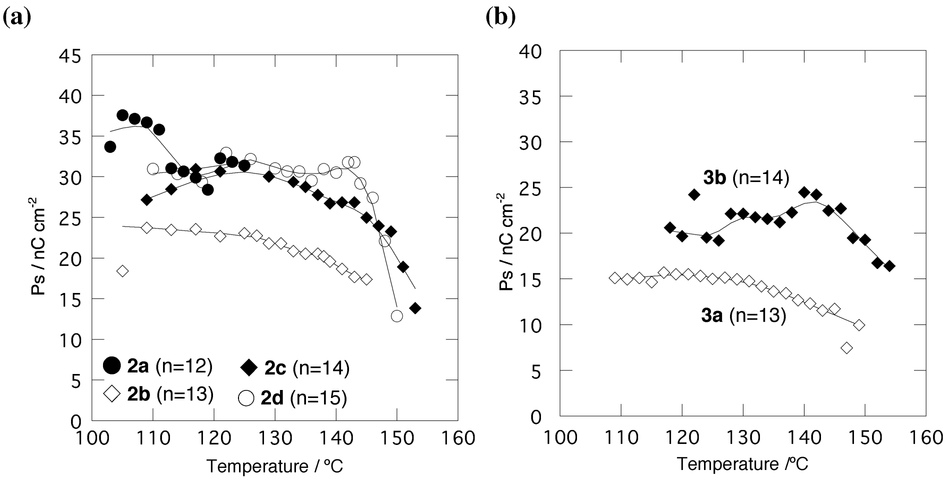


Figure 4. Temperature dependence of the *P*s value in the SmC* phases of (a) (2*S*,5*S*)-**2** and (b) (2*S*,5*S*)-**3**.

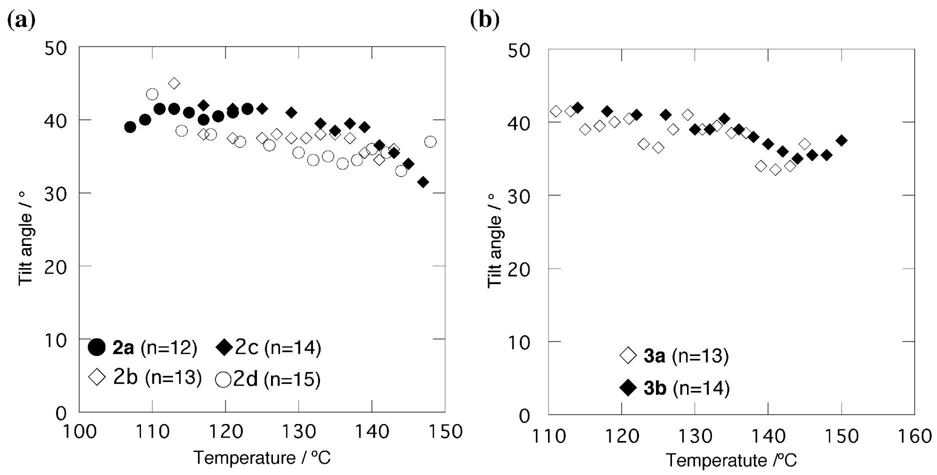


Figure 5. Temperature-dependence of the tilt angle (θ) of (a) (2*S*,5*S*)-**2** and (b) (2*S*,5*S*)-**3** measured by hot-stage POM.

Moreover, in contrast to the case of (2*S*,5*S*)-**1**, we observed the relaxation of the ferroelectric state of (2*S*,5*S*)-**2a** and (2*S*,5*S*)-**2b** in the same type of FLC cell, i.e., POM texture change by turning off the electric fields (Figure 6). At the same time, the textures in the two field-free states of (2*S*,5*S*)-**2a** or (2*S*,5*S*)-**2b** considerably differed from each other, suggesting the short-pitch SmC* nature and the incomplete formation of a helical superstructure in the FLC cell used (Figures 6b and d).

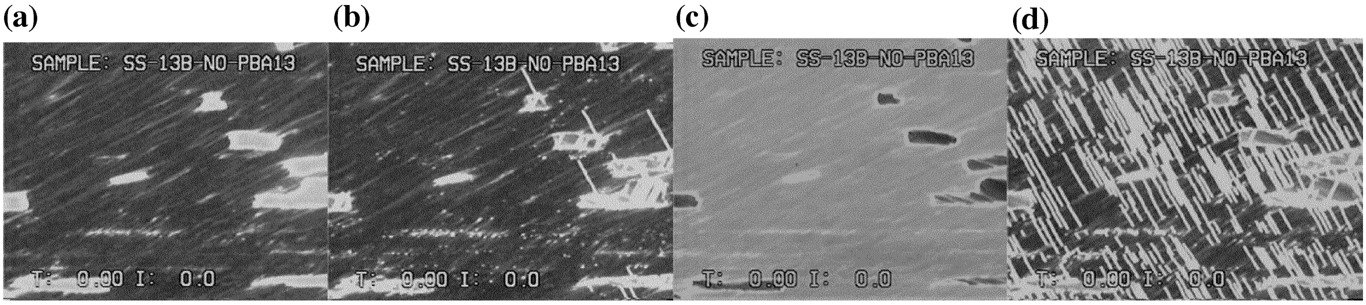


Figure 6. Ferroelectric switching modes of (2*S*,5*S*)-**2b** in a sandwich cell (4 μm) at 130°C under homogeneous planar boundary conditions between crossed polarizers. Applied DC voltage dependence of texture change in the same area at 110°C: Electric field sweeping in the order of (a) +12 V, (b) 0 V, (c) –12 V, and (d) 0V.

Table 2. Ferroelectric properties measured in the SmC* phases of (2*S*,5*S*)-**2** and (2*S*,5*S*)-**3**, layer distances, calculated molecular length, and geometrical tilt angles.

Compound	*P*s(–10°)[a,b] [nC cm^{-2}]	θ(–10°)[b,c] [deg]	*d* [d] [Å]	*l* [e] [Å]	$\cos^{-1}(d/l)$ [f] [deg]
2a (n=12)	28 (119°C)	41	41.2 (120°C)	50.6	35
2b (n=13)	21 (137°C)	38	40.3 (120°C)	53.1	41
2c (n=14)	27 (143°C)	36	41.5 (120°C)	54.8	41
2d (n=15)	32 (142°C)	36	43.7 (130°C)	57.4	40
3a (n=13)	12 (141°C)	34	40.9 (145°C)	55.4	42
3b (n=14)	23 (146°C)	36	42.6 (145°C)	57.7	42

[a]Spontaneous polarization. [b]Measured at a temperature 10°C below the phase transition from the N* phase to the SmC* phase during the cooling process. [c]Tilt angle measured by hot-stage POM. [d]Layer distance from XRD data. [e]Molecular length determined by a PM3 semiemprical calculation (PC Spartan'02). [f]Calculated geometrical tilt angle from *d* and *l* values.

In summary, we could obtain new chiral organic radical compounds with strong inter-layer interactions which showed FLC properties at high temperatures and over wide temperature ranges. Above all, (2*S*,5*S*)-**2d** showed the highest *P*s(–10°) value of 32 nC cm^{-2}, which was larger than that (24 nC cm^{-2}) of (2*S*,5*S*)-**1** (n=13) previously reported.[2,3]

EXPERIMENTAL

General. Transition temperatures refer to the peak top of each transition curve by DSC analysis, which was performed at a scanning rate of 5 °C min^{-1}. Enantiomeric excess (*ee*) were determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD, 0.46 x 25 cm), a mixture of hexane and 2-PrOH (9:1) as the mobile phase at a flow rate of 1.0 mL min^{-1}, and a UV-vis spectrometer (254 nm) as the detector. *P*s was measured by the triangular wave method at a frequency of 20 Hz in a thin sandwich cell (EHC Co., Japan; thickness of 4 μm) coated with ITO electrodes and covered with antiparallel-rubbed polyimide films in an electric field of 10 V peak to peak. Tilt angles were measured by polarized optical microscopy (POM). Their *g* values and hyperfine coupling constants (a_N) were determined by electron paramagnetic resonance (EPR) spectroscopy in THF at 25 ºC. The variable temperature X-ray diffraction (XRD) patterns were recorded at a continuous scanning rate of 2° 2θ min^{-1} at a heating and cooling rate of 4 °C min^{-1} using CuKα radiation (40 kV, 20 mA), with the intensity of the diffracted X-rays being collected at intervals of 0.02° 2θ.

*General synthetic procedure for (2S,5S)-**2** and (2S,5S)-**3**.* Enantiomerically enriched nitrone (*R*)-**4** (*ca*. 90% *ee*) was prepared according to the published procedure.[18,19] The nitrone (*R*)-**4** (0.452 g, 4.0 mmol) was reacted with the first Grignard reagent (8.0 mmol) in THF (5 mL) at –78 ºC. The reaction temperature was slowly raised to 25 ºC. After being stirred overnight, the reaction mixture was poured into saturated aqueous NH_4Cl solution (50 mL), followed by extraction with CH_2Cl_2 (2 x 50 mL) and concentration in vacuo. The residue was dissolved in MeOH (20 mL) and oxidized by treatment with $Cu(OAc)_2 \cdot H_2O$(0.13 g), conc. NH_3 solution (1.1 mL), and O_2 bubbling until dark blue color developed in solution. The solution was evapolated in vacuo, and the residue extracted by $CHCl_3$ (50 mL). The organic phase was washed with saturated aqueous $NaHCO_3$ solution (50 mL), dried over $MgSO_4$, and concentrated in vacuo to give the crude nitrone (*S*)-**5**. The crude (*S*)-**5** was reacted with the second Grignard reagent (8.0 mmol) and the resulting crude addition product was oxidized by the same procedure. The crude (2*S*,5*S*)-**6** was roughly purified by column chromatography on silica gel (hexane:CH_2Cl_2:Et_2O 6/4/0~6/3/1) to remove mainly the less polar impurities. Then to this crude (2*S*,5*S*)-**6** dissolved in THF (20 mL) was added a THF solution of Bu_4NF (1 M solution, 1.0 mL) at 0 ºC. After being stirred at 0 °C for 20 min, the reaction mixture was poured into saturated aqueous NH_4Cl solution (30 mL), followed by extraction with CH_2Cl_2 (2 x 50 mL), drying over $MgSO_4$, and concentration in vacuo. The crude product was purified by column chromatography on silica gel (hexane:CH_2Cl_2:Et_2O 6/3/1~5/3/2) to give the pure desilylated product of (2*S*,5*S*)-**6** as yellow solid in ca. 10% yield from (*R*)-**4**.

To a mixture of the desilylated product (0.3 mmol) and Et_3N (0.9 mL) in THF (10 mL) was added an appropriate *p*-alkoxybenzoyl chloride (0.9 mmol) in THF (3 mL) at 0°C. The reaction mixture was slowly warmed to 25 °C and stirred for 40 h. Then the mixture was poured into a saturated aqueous $NaHCO_3$ solution (20 mL) and the aqueous mixture was extracted with Et_2O (2 x 50 mL). The combined organic phase was dried over $MgSO_4$ and evaporated in vacuo. Column chromatography on silica gel (hexane:CH_2Cl_2:Et_2O 8/2/0~7/2/1) of the residue gave pure (2*S*,5*S*)-**2** or (2*S*,5*S*)-**3** as yellow solid in 70-80% yield from (2*S*,5*S*)-**6**.

(2*S*,5*S*)-**2a**: $[\alpha]_D^{24}$ –71.49 (89.3% *ee*, c 1.001, THF). EPR (THF): g = 2.0057, a_N = 1.33 mT. IR (KBr): 2923, 2850, 1734, 1607, 1507, 1395, 1254, 1164, 1071, 813, 764. Anal. Calcd for $C_{55}H_{77}NO_5$: C, 79.47; H, 9.22; N, 1.69. Found: C, 79.39; H, 9.44; N, 1.70.

(2*S*,5*S*)-**2b**: $[\alpha]_D^{25}$ –72.91 (91.0% *ee*, c 0.982, THF). EPR (THF): g = 2.0060, a_N = 1.34 mT. IR (KBr): 2849, 1735, 1604, 1507, 1395, 1250, 1164, 1078, 820, 765. Anal. Calcd for $C_{57}H_{81}NO_5$: C, 79.68; H, 9.38; N, 1.63. Found: C, 79.69; H, 9.41; N, 1.60.

(2*S*,5*S*)-**2c**: $[\alpha]_D^{25}$ –70.40 (90.9% *ee*, c 0.991, THF). EPR (THF): g = 2.0058, a_N = 1.33 mT. IR (KBr): 2915, 1731, 1607, 1498, 1371, 1254, 1201, 1165, 1077, 819, 764. Anal. Calcd for $C_{59}H_{85}NO_5$: C, 79.86; H, 9.54; N, 1.58. Found: C, 79.90; H, 9.60; N, 1.55.

(2*S*,5*S*)-**2d**: $[\alpha]_D^{25}$ –67.13 (90.8% *ee*, c 0.984, THF). EPR (THF): g = 2.0059, a_N = 1.33 mT. IR (KBr): 2922, 2851, 1730, 1606, 1511, 1371, 1254, 1201, 1164, 1977, 823, 764. Anal. Calcd for $C_{61}H_{89}NO_5$: C, 80.04; H, 9.69; N, 1.53. Found: C, 80.23; H, 9.52; N, 1.57.

(2*S*,5*S*)-**3a**: $[\alpha]_D^{25}$ –71.27 (91.2% *ee*, c 1.006, THF). EPR (THF): g = 2.0055, a_N = 1.33 mT. IR (KBr): 2917, 2853, 1731, 1605, 1509, 1372, 1256, 1206, 1169, 1079, 850, 767. Anal. Calcd for $C_{57}H_{81}NO_5$: C, 79.68; H, 9.38; N, 1.63. Found: C, 79.44; H, 9.39; N, 1.65.

(2*S*,5*S*)-**3b**: $[\alpha]_D^{25}$ –67.84 (89.0% *ee*, c 1.003, THF). EPR (THF): g = 2.0056, a_N = 1.32 mT. IR (KBr): 2921, 2851, 1730, 1605, 1510, 1372, 1255, 1206, 1169, 1079, 876, 767. Anal. Calcd for $C_{59}H_{85}NO_5$: C, 79.86; H, 9.54; N, 1.58. Found: C, 79.76; H, 9.53; N, 1.63.

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