

Short communication

Synthesis and Characterization of BINOL Based Axially Chiral Nitronyl Nitroxide Radicals

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Abstract

Four novel axially chiral nitronyl nitroxides derived from *S*- or *R*-1,1'-bi-2-naphthol were synthesized and their crystal structures discussed. Circular dichroism spectra of these compounds showed significant Cotton effects between 200 and 400 nm, and also confirmed the optical activity of these enantiomers. The magnetic properties of the two pairs of nitronyl nitroxide radicals were characterized by magnetic susceptibility measurements. The results showed that in these four radicals exist antiferromagnetic interactions in all cases at low temperatures.

Keywords: Nitronyl nitroxide radical; chirality; magnetic properties; organic ferromagnet

1. Introduction

During the two last decades, magnetic materials based on purely organic molecules have attracted increasing interest, as their properties can be subtly modified by an adequate selection of substituents.¹ Since Kinoshita's discovery of the first purely organic ferromagnet, different arrangements of spin carriers have been achieved by several strategies, among which the purely organic and the metal-organic approaches based on nitronyl nitroxide free radicals have proven particularly rewarding.^{2–5} In 1997 Rikken and Raupach discovered a small chiral paramagnetic material magnetochiral dichroism (MChD) in a chiral paramagnetic material. This combination of magnetic properties and optical activity has attracted increasing attention because the potential magneto-optical effects of the organic spin carriers, such as nitroxides, are well suited as potential precursors of such structures.⁶ Enantiopure nitroxides would afford materials crystallizing in chiral space groups and would give opportunities to characterize new exchange pathways. However, at there are few reports on pure chiral nitronyl nitroxides.^{7–14} Herein, we have designed and synthesized a series of enantiomerically pure axially chiral nitronyl nitroxides (Figure 1). Their structure, magnetic properties, and optical characterization were investigated.

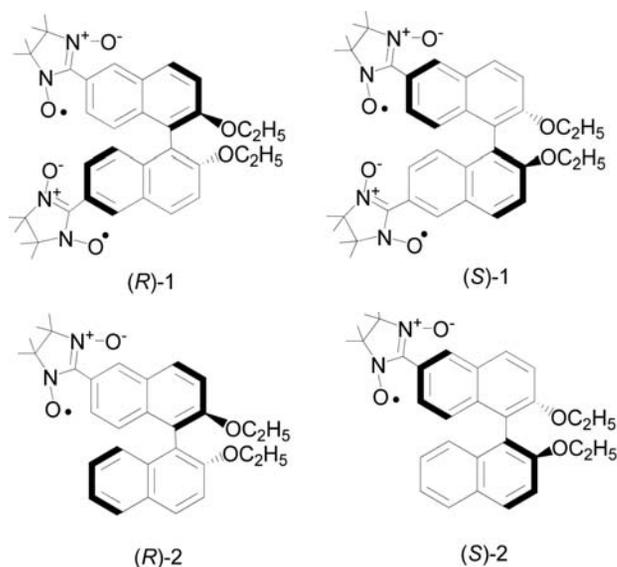


Figure 1. Structures of synthesized chiral nitronyl nitroxides.

2. Experimental

2.1. General Remarks

All experiments sensitive to moisture or air were carried out in a nitrogen atmosphere. Commercial re-

gents were used as received without further purification unless otherwise noted. THF was distilled under N₂ from Na/benzophenone, DMF was distilled from CaH₂, and CH₂Cl₂ was redistilled before use. Compounds **5–7** were prepared according to reported procedures from commercially available (*R*)-BINOL or (*S*)-BINOL. The chiral nitronyl nitroxides (*R*)-**1**/*S*-**1** and (*R*)-**2**/*S*-**2** were prepared according to Ullman's method.¹⁵

Melting points were measured with an X-5 precision micro-melting point apparatus and were uncorrected. IR was collected on an FTIR-8400S spectrophotometer. ¹H and ¹³C NMR were recorded on a Bruker AV-500 spectrometer in CDCl₃ with TMS as an internal standard. Electrospray ionization (ESI) HRMS analyses were obtained using Bio TOF IIIQ mass-spectrograph or Varian 7.0T ESI-FTICR-MS. Elemental analyses were performed on a VarioEL III Elemental Analyzer.

2. 2. Synthesis

The synthetic route to chiral compounds is outlined in Scheme 1. Compounds **5–7** were prepared according to the reported literature.¹⁶ For the synthesis of new compounds, see Supporting Information.

2. 3. X-ray Crystallography

Crystal structure determinations were carried out on a Bruker SMART 1000CCD system (Mo/K α , $\lambda = 0.71073$ nm, graphite monochromator). The data were processed by use of the *SNINT*³ data reduction software, and the structure was solved with the aid of the *SHELXTL-97* software package. Anisotropic thermal factors were ap-

plied for non-hydrogen atoms, and hydrogen atoms with isotropic thermal factors were refined with Full-matrix least-squares using the *F*² refinement method.

2. 4. Physical Measurements

Circular dichroism spectra were recorded with a JASCO-715 spectropolarimeter, and were processed by use of the associated software.

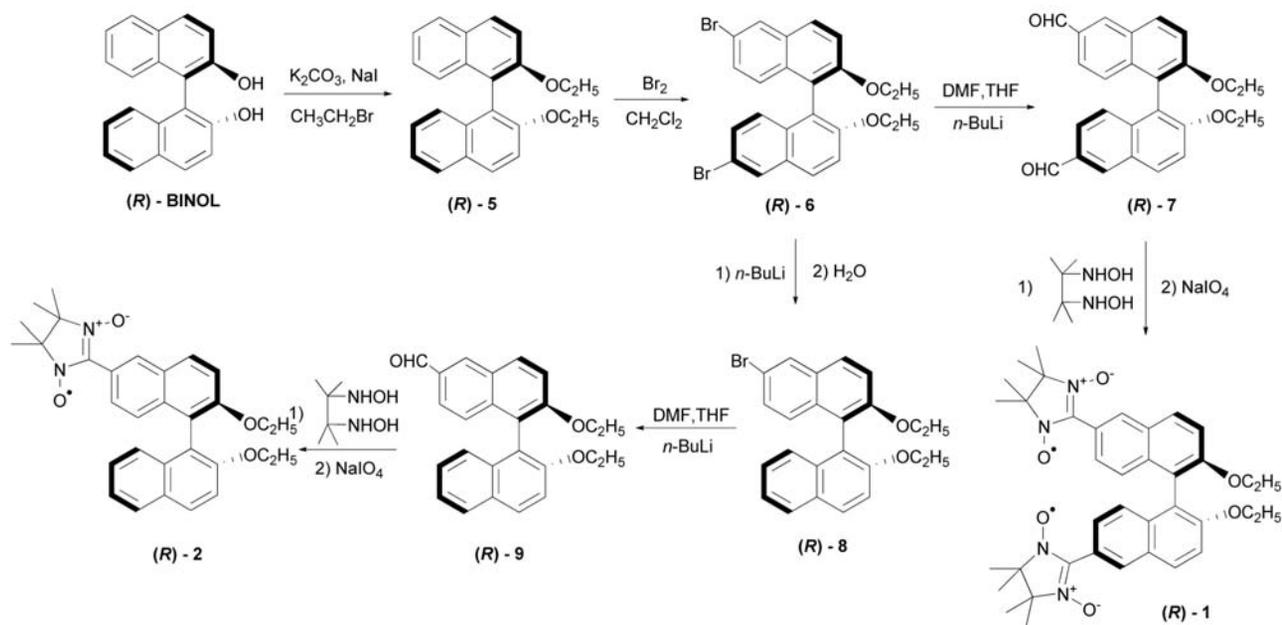
ESR spectra were recorded in solution in DMF with an EMX-10/12 EPR spectrometer. Emission spectra were recorded on a Hitachi F-2500 fluorescence spectrophotometer.

The magnetic susceptibility of the chiral radicals was measured for randomly oriented polycrystalline samples on a Quantum Design SQUID magnetometer MPMS-XL with an applied magnetic field of 0.1 T in the temperature range of 1.9–300K.

3. Results and Discussion

3. 1. Synthesis of Compounds

The synthetic route to chiral compounds is outlined in Scheme 1. The commercially available (*R*)-1,1'-bi-2,2'-naphthol (BINOL) was reacted with bromoethane to give (*R*)-**5** in a high yield (98%). Selective bromination of (*R*)-**5** also gave (*R*)-**6** in good yield, which is purified by recrystallization. Lithiated (*R*)-**6** was reacted with DMF to give (*R*)-**7**. Effects of the reaction temperature and water content were significant for the yield of (*R*)-**7**. Very little water can lead to a low yield of (*R*)-**7**. The title radical compound (*R*)-**1** was obtained through condensation with 2,3-dihy-



Scheme 1. Synthesis of chiral nitronyl nitroxides.

droxylammonium-2,3-dimethylbutane, and the subsequent oxidation of the adducts with sodium periodate, following Ullman's classic procedure.¹⁵ (*R*)-**2** can be obtained from (*R*)-**6** using multistep synthesis. The enantiomers of these compounds were obtained in the same way. The nitronyl nitroxide (*R*)/(*S*)-**1** and (*R*)/(*S*)-**2** are both dark blue solids. Crystals suitable for X-ray diffraction in the form of small needles were obtained through slow evaporation from a dichloromethane/hexane solution.

3. 2. X-ray Structure Determination

The molecular structures of (*R*)-**1** were shown in Figure 2 and Table 1. The enantiopure radical (*R*)-**1** crystallizes in the tetragonal $P4(3)2(1)2$ space group (Table 1), in which the imidazolidine heterocycle moiety was directly bound to a great conjugate π bond system. All atoms in the naphthyl ring are almost coplanar. Steric hindrance of two ethoxy groups and two O-N-C-N-O groups lead to a large dihedral angle between two naphthyl rings (86.09), and two planes of naphthyl moiety in same molecule are almost vertical to each other, producing axial chirality. Two vertical moieties are likely to weaken the intramolecular exchange interaction through the p - π conjugation in (*R*)-**1**. The dihedral angle between the N-C-N unit in the imidazolyl ring and the naphthyl ring is 38.434. The torsion angle of C(15)-N(2)-C(13)-N(1) and N(1)-C(14)-C(15)-N(2) are $-5.4(2)$ and $-20.65(18)$, respectively, which indicates that the imidazolyl ring is twisted. The distance between C(14)-C(15) is 1.554(3), which is slightly larger compared to 1.543 for the C-C bond length in the cyclopentane. The N(1)-C(14) bond length and N(2)-C(15) bond length are 1.489(3) and 1.503(3), respectively. The distances between C(13) and its neighboring N atoms (N1 and N2) are 1.340(2) and 1.346(3), which are shorter than those of N(1)-C(14) and N(2)-C(15). The molecules are linked into a two-dimensional network by the intermolecular van der Waals. The data of lengths, angles and dihedral angles in (*S*)-**1** are consistent with the data of (*R*)-**1**.

Table 1. X-ray crystallographic data of chiral nitronyl nitroxides.

Compound	(<i>R</i>)- 1	(<i>R</i>)- 2
Formula	$C_{38}H_{44}N_4O_6$	$C_{31}H_{33}N_2O_4$
<i>M</i>	652.77	497.59
Crystal system	Tetragonal	Orthorhombic
Space group	$P4(3)2(1)2$	$P2(1)2(1)2(1)$
<i>a</i> [Å]	14.0950(14)	9.2308 (7)
<i>b</i> [Å]	14.0950(14)	12.1004 (10)
<i>c</i> [Å]	17.883(3)	24.048 (2)
$\alpha = \beta = \gamma$	90 deg	90 deg
<i>V</i> [Å ³]	3552.8(7)	2686.0(4)
<i>Z</i>	4	4
Calculate density	1.220	1.230
<i>R</i> (<i>I</i>)	0.0374	0.0764
<i>R</i> _w (<i>I</i>)	0.1051	0.1860

The molecular structure of (*R*)-**2** is shown in Figure 2 and Table 1. The enantiopure radical (*R*)-**2** crystallizes in the orthorhombic $P2(1)2(1)2(1)$ space group (Table 1). In (*R*)-**2** is only one imidazolidine heterocycle moiety bound to a naphthyl ring. As shown in Figure 2, the torsion angle between the naphthyl ring and the O-N-C-N-O group is 20.9 in (*R*)-**2**, relatively smaller than that of (*R*)-**1**. The dihedral angle between the two naphthyl rings is 79.70, and is also smaller than that of (*R*)-**1**, which can lead to a stronger intramolecular exchange interaction through the π -conjugation. The results show that the number of nitronyl nitroxide moiety not only affects the torsion angles between the naphthyl ring and the O-N-C-N-O group, but also affects the dihedral angles between the two naphthyl rings in a 1,1'-binaphthalene moiety.

3. 3. CD Spectrum

The CD spectrum of (*S*)-**1** exhibits a negative Cotton effect at $\lambda_{\max} = 230, 295$ and 330 nm, and a positive dichroic signal centered at $\lambda_{\max} = 265$ nm, while (*R*)-**1**

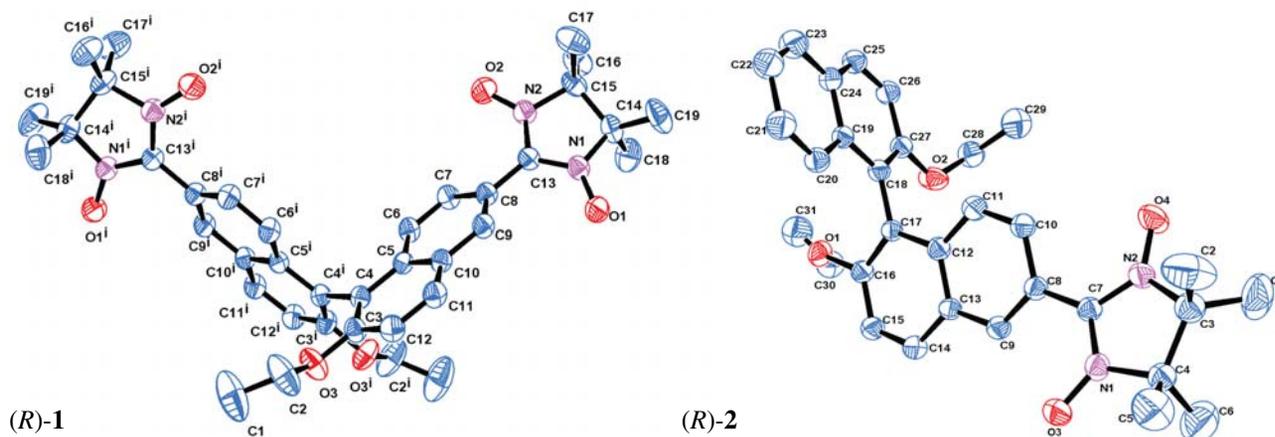


Figure 2. ORTEP views of (*R*)-**1** and (*R*)-**2** at the 50% probability level. The hydrogen atoms are omitted.

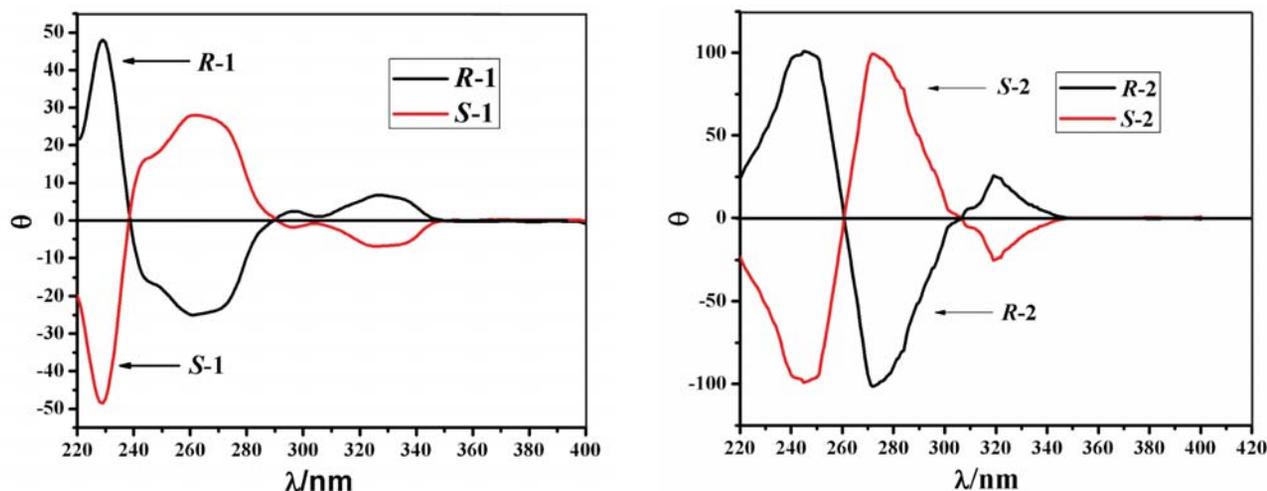


Figure 3. CD spectra of two pairs of chiral nitronyl nitroxides in CH_2Cl_2 .

shows Cotton effects of the opposite sign at the same wavelengths (Figure 3). The solution state CD spectra of the two enantiomers reveals a broad Cotton effect of moderate intensity centered at 330 nm, followed by an intense exciton coupled effect at approximately 265 nm, which coincides with the absorption maximum for the $\pi\text{-}\pi^*$ transition. There are no detectable Cotton effects in the region corresponding to the $n\text{-}\pi^*$ transition at 640 nm. It should be pointed out that the magnitudes of the Cotton effects are much greater than those observed for the chiral radicals prepared to date in which the stereogenic center is located on the phenyl substituent at the 2-position of the imidazolyl ring.

3. 4. Magnetic Susceptibility Data

Compounds (*R*)-1 and (*S*)-1 show the same magnetic behaviors because they are a pair of enantiomers. The temperature dependence of $\chi_M T$ values of (*R*)-1 and (*S*)-1 is displayed in Figure 4 in the range 3–300 K at 2,000 Oe. The $\chi_M T$ value for the (*R*)-1 radical at room temperature is $0.740 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is close to the expected value for an uncorrelated $S = 1/2$ spin ($0.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$), as shown in Figure 4. As the temperature decreases, $\chi_M T$ gradually decreases, which indicates the presence of intramolecular antiferromagnetic interactions in crystals. When the temperature is below 20 K, the $\chi_M T$ value decreases dramatically. Upon further cooling, the $\chi_M T$ value abruptly decreases to a minimum value of $0.12 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 1.9 K. This is confirmed with the fitting results according to the Curie-Weiss law, $\chi_m = C/T - \theta$. The Curie constant is $C = 0.345 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, and the Weiss constant is $\theta = -0.46 \text{ K}$. The negative Weiss constant may be ascribed to the intermolecular antiferromagnetic interaction.

The data were therefore simulated applying the Heisenberg-Dirac-Van Vleck hamiltonian $\hat{H} = -2J\hat{S}_{R1}\hat{S}_{R2}$, with the expression for the magnetic susceptibility,¹⁷

$$\chi_M = f \frac{2Ng^2\beta^2}{k_B(T - \theta)[3 + \exp(-2J/k_B T)]} \quad (1)$$

with N , g , β , k_B , f and J having their usual meanings in equations: g is Lande constants, k_B is Boltzmann constant, β is Bohr magneton, N is Avogadro's constant, f is modifying factor, and J is coupling constant. A least-square fit to the magnetic susceptibility data gives the values $J/k_B = -0.65 \text{ K}$, $g = 1.90$, $\theta = -1.53 \text{ K}$, and $f = 0.95$.

The temperature dependence of $\chi_M T$ and χ_M^{-1} for (*R*)-2 in the range 3–300 K at 2,000 Oe is shown in Figure 5. The $\chi_M T$ value for the (*R*)-2 radical at room temperature is $0.730 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is slightly less than that of $S = 1/2$ spins system ($0.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). When the temperature is at 2 K, the $\chi_M T$ value decreases dramatically to a minimum value of $0.50 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. This is confirmed with the fitting results by the Curie-Weiss law. The Curie constant is $C = 0.381 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, and the Weiss constant is $\theta = -0.53 \text{ K}$. According to the equation (1) the best fit-

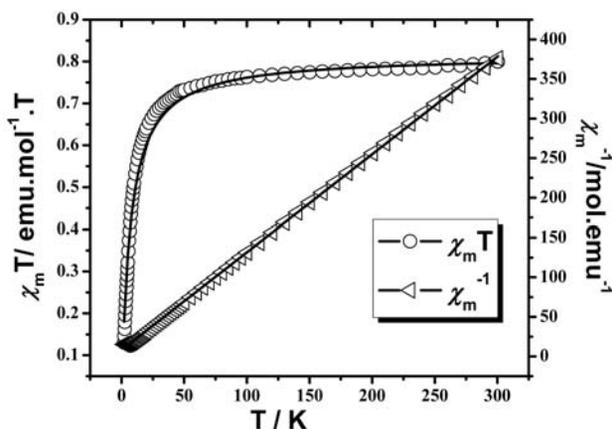


Figure 4. Temperature dependence of $\chi_M T$ and χ_M^{-1} for (*R*)-1 and their corresponding theoretical curves (solid lines).

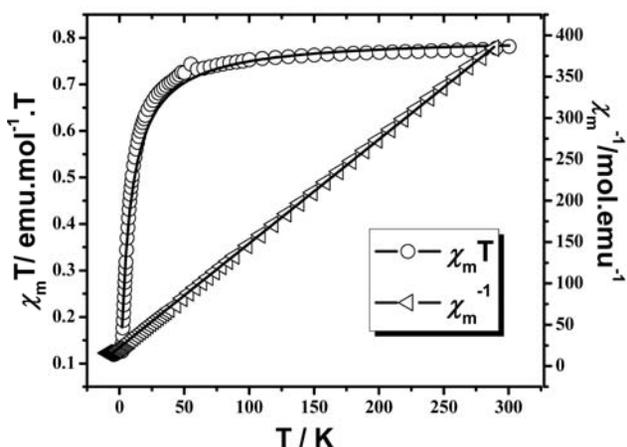


Figure 5. Temperature dependence of $\chi_m T$ and χ_m^{-1} for (R)-2 and their corresponding theoretical curves (solid lines).

ting for the data gives $J/k_B = -0.59$ K, $g = 2$, $f = 0.95$, and $\theta = -1.28$ K.

4. Conclusions

In summary, four enantiomorphous chiral nitronyl nitroxide radicals were synthesized and the molecular structures of (R)-/(S)-1 and (R)-/(S)-2 were discussed. The circular dichroism (CD) spectra confirms the optical activity and enantiomeric nature of these chiral radicals. They also showed antiferromagnetic interactions at low temperatures. Further investigation of the magnetic properties of metal complexes of these chiral nitronyl nitroxide radicals is underway.

5. Acknowledgments

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6. Appendix A. Supplementary data

CCDC 807907, 807908, 807909, 807910 contain the supplementary crystallographic data for (R)-1, (S)-1, (R)-2, and (S)-2. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or

from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Povzetek

V prispevku je predstavljena sinteza štirih novih aksialno kiralnih nitronil nitroksidov, pripravljenih iz S- oziroma R-1,1'-bi-2-naftola, in analiza njihovih kristalnih struktur. CD spektri teh spojin kažejo precejšen Cottonov efekt med 200 in 400 nm in potrjujejo optično aktivnost vseh enantiomer. Magnetne lastnosti obeh parov nitronil nitroksidnih radikalov so bile ugotovljene s pomočjo meritev magnetne susceptibilnosti. Rezultati kažejo, da v vseh štirih spojinah obstajajo antiferromagnetne interakcije pri nizkih temperaturah.

Electronic Supporting Information

1. General remarks

All experiments sensitive to moisture or air were carried out in a nitrogen atmosphere. Commercial reagents were used as received without further purification unless otherwise noted. THF was distilled under N₂ from Na/benzophenone, DMF was distilled from CaH₂, and CH₂Cl₂ was redistilled before use. Compounds 5-7 were prepared according to reported procedures from commercially available (*R*)-BINOL or (*S*)-BINOL.¹ The chiral nitronyl nitroxides (*R*)-1/(*S*)-1 and (*R*)-2/(*S*)-2 were prepared according to Ullman's method.²

Melting points were measured with an X-5 precision micro-melting point apparatus and were uncorrected. IR was collected on an FTIR-8400S spectrophotometer. ¹H and ¹³C NMR were recorded on a Bruker AV-500 spectrometer in CDCl₃ with TMS as an internal standard. Electrospray ionization (ESI) HRMS analyses were obtained using Bio TOF IIIQ mass-spectrograph or Varian 7.0T ESI-FTICR-MS. Elemental analyses were performed on a VarioEL III Elemental Analyzer.

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Crystal structure determinations were carried out with the aid of a Bruker SMART 1000CCD system (Mo/Kα, λ = 0.71073 nm, graphite monochromator). The data were processed by use of the SNINTP^{3P} data reduction software, the structure was solved with the aid of the

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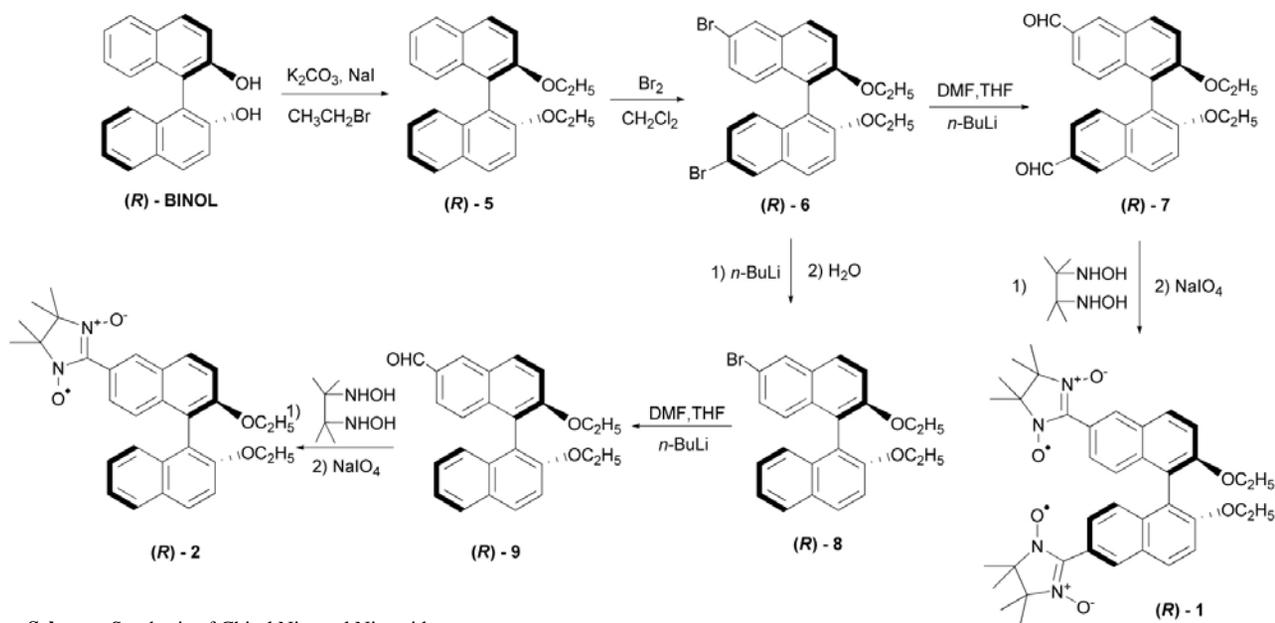
The magnetic susceptibility of the chiral radicals we obtained is measured for randomly oriented polycrystalline samples on a Quantum Design SQUID magnetometer MPMS-XL with an applied magnetic field of 0.1 T in the temperature range of 1.9–300 K.

Circular dichroism spectra were recorded with a JASCO-715 spectropolarimeter, and were processed by use of the associated software.

2. Synthesis of Chiral Nitronyl Nitroxides

2.1. Synthesis of Compound (*R*)-8 or (*S*)-8

To a stirred solution of (*R*)-6 or (*S*)-6 (2.0 g, 4.0 mmol) in 30 mL dry THF under NB_{2B} atmosphere was added *n*-BuLi (2.75 mL, 4.4 mmol, 1.6 M in hexane) over 30 min at –78 °C. The mixture was stirred for 2 h at the same temperature. Then saturated aqueous NHB_{4B}Cl was added to quench the reaction. The reaction mixture was extracted with CHB_{2B}CIB_{2B} several times. The combined organic layer was washed subsequently with water and brine and then dried over MgSOB_{4B}. Evaporation of solvent gave the crude product, which was further purified by flash



Schema: Synthesis of Chiral Nitronyl Nitroxides

column chromatography on silica gel (petroleum ether /ethyl acetate, 4:1) to yield a white solid.

(*R*)-**8**: 1.18 g, 70%. mp: 77–78 °C. IR (ν_{maxB} , $\text{cmP}^{-1\text{P}}$): 2927, 1549–1614, 1216 (C-O), 1066. $\text{P}^{1\text{H}}$ NMR (500 Hz, CDCl_3): δ 1.03–1.07 (m, 6H), 4.00–7.06 (m, 4H), 6.99–7.08 (m, 1H), 7.12–7.20 (m, 1H), 7.21–7.29 (m, 2H), 7.30–7.32 (m, 1H), 7.40–7.43 (m, 2H), 7.82–7.86 (m, 2H), 7.92–7.94 (m, 1H), 8.00 (s, 1H). $\text{P}^{13\text{C}}$ NMR (125 Hz, CDCl_3): δ 15.06, 15.13, 65.27, 65.29, 115.78, 116.88, 117.36, 120.02, 121.05–123.65, 125.36, 126.35, 127.57, 128.02, 128.59, 129.37, 129.43, 129.49, 129.86, 130.45, 132.86, 134.17, 154.43, 154.77. HRMS: m/z (ESI) calcd for $\text{CB}_{24\text{B}}\text{HB}_{21\text{B}}\text{BrOB}_2$ $[\text{M}+\text{H}]^{\text{P}+\text{P}}$: 421.0798, found: 421.0790. Elemental analysis, found: C, 68.13; H, 5.16, calcd for $\text{CB}_{24\text{B}}\text{HB}_{21\text{B}}\text{BrOB}_2$: C, 68.42; H, 5.02%.

The enantiomer (*S*)-**8** was obtained by the same method and had NMR spectra identical to that of the (*R*)-**8**.

2. 2. Synthesis of Compound (*R*)-**9** or (*S*)-**9**

To a stirred solution of (*R*)-**8** (0.84 g, 2.0 mmol) in 30 mL dry THF under $\text{NB}_{2\text{B}}$ atmosphere was added *n*-BuLi (2.5 mL, 4.0 mmol, 1.6 M in hexane) over 30 min at –78 °C. After 5 h of stirring at this temperature, 0.51 mL of dry DMF (6.6 mmol) was added slowly so that the temperature remained below –50 °C. After stirring for 45 min at this temperature, 5 mL water was added to quench the reaction. The reaction mixture was extracted with $\text{CHB}_{2\text{B}}\text{ClB}_{2\text{B}}$ several times. The combined organic layer was washed subsequently with water and brine and then dried over $\text{MgSOB}_{4\text{B}}$. Evaporation of solvent gave the crude product, which was further purified by flash column chromatography on silica gel (petroleum ether /ethyl acetate, 7:3) to yield a white solid. (*R*)-**9**: 0.54 g, 73%. mp: 118–119 °C. IR (ν_{maxB} , $\text{cmP}^{-1\text{P}}$): 2929, 1681, 1234. $\text{P}^{1\text{H}}$ NMR (500 Hz, CDCl_3): δ 1.05 (t, $J = 7.0$ Hz, 3H), 1.09 (t, $J = 7.0$ Hz, 3H), 4.00–4.15 (m, 4H), 7.09 (d, $J = 8.5$ Hz, 1H), 7.21–7.23 (m, 2H), 7.30–7.33 (m, 1H), 7.43 (d, $J = 9.0$ Hz, 1H), 7.50 (d, $J = 9.0$ Hz, 1H), 7.65–7.67 (m, 1H), 7.87 (d, $J = 8.2$ Hz, 1H), 7.97 (d, $J = 9.0$ Hz, 1H), 8.09 (d, $J = 9.0$ Hz, 1H), 8.35 (d, $J = 1.3$ Hz, 1H), 10.09 (s, 1H). $\text{P}^{13\text{C}}$ NMR (125 Hz, CDCl_3): δ 14.95, 15.10, 65.01, 65.22, 115.64, 116.09, 119.63, 121.03, 123.20, 123.69, 125.18, 126.43, 126.68, 128.12, 128.19, 129.37, 129.68, 131.21, 132.25, 134.04, 135.01, 137.74, 154.41, 157.23, 192.25. HRMS: m/z (ESI) calcd for $\text{CB}_{25\text{B}}\text{HB}_{22\text{B}}\text{OB}_3$ $[\text{M}+\text{H}]^{\text{P}+\text{P}}$: 371.1642, found 371.1642. Elemental analysis, found: C, 80.88; H, 5.89, calcd for $\text{CB}_{25\text{B}}\text{HB}_{22\text{B}}\text{OB}_3$: C, 81.06; H, 5.99%.

The enantiomer (*S*)-**9** was synthesized by the same method and had NMR spectra identical to that of the (*R*)-**9**.

2. 3. Synthesis of Nitronyl Nitroxide (*R*)-**2** or (*S*)-**2**

A mixture of (*R*)-**9** (370 mg, 1.0 mmol) and 2,3-bis (hydroxyamino)-2,3-dimethylbutane (150 mg, 1.0 mmol) in 20 mL dry MeOH was refluxed for 24 h under an argon atmosphere. The solvent was removed under reduced pressure to afford a yellow solid. The residue was taken up in $\text{CHB}_{2\text{B}}\text{ClB}_2$ (20 mL), cooled to 0 °C, and then $\text{NaIOB}_{4\text{B}}$ (0.3 g, 1.4 mmol) in water (5 mL) was added with stirring. The reaction mixture was stirred for 0.5 h. The organic layer was washed with water and brine and then dried over $\text{MgSOB}_{4\text{B}}$. Evaporation of solvent gave the crude product, which was further purified by flash column chromatography on silica gel (petroleum ether /ethyl acetate, 1:1) to yield a dark blue solid. Single crystals of (*R*)-**2** were obtained from the mixed solution of *n*-heptane and dichloromethane (the ratio of volume is 1 to 1).

(*R*)-**2**: 199 mg, 40%. mp: 185–186 °C. IR (ν_{maxB} , $\text{cmP}^{-1\text{P}}$): 2988, 2937, 1618, 1506, 1367, 1328, 1232, 1134, 1089, 816. ESR (DMF) seven lines, $g = 2.0074$, $|a_{\text{N}}| = 7.57\text{G}$. HRMS: m/z (ESI) calcd for $\text{CB}_{31\text{B}}\text{HB}_{33\text{B}}\text{NB}_{2\text{B}}\text{OB}_{4\text{B}}$ $[\text{M}+\text{H}]^{\text{P}+\text{P}}$: 498.2513, found: 498.2513. Elemental analysis, found: C, 74.76; H, 6.70; N, 5.59. calcd for $\text{CB}_{31\text{B}}\text{HB}_{33\text{B}}\text{NB}_{2\text{B}}\text{OB}_{4\text{B}}$: C, 74.82; H, 6.68; N, 5.63%.

The enantiomer (*S*)-**2** was synthesized by the same method as enantiomer (*R*)-**2**.

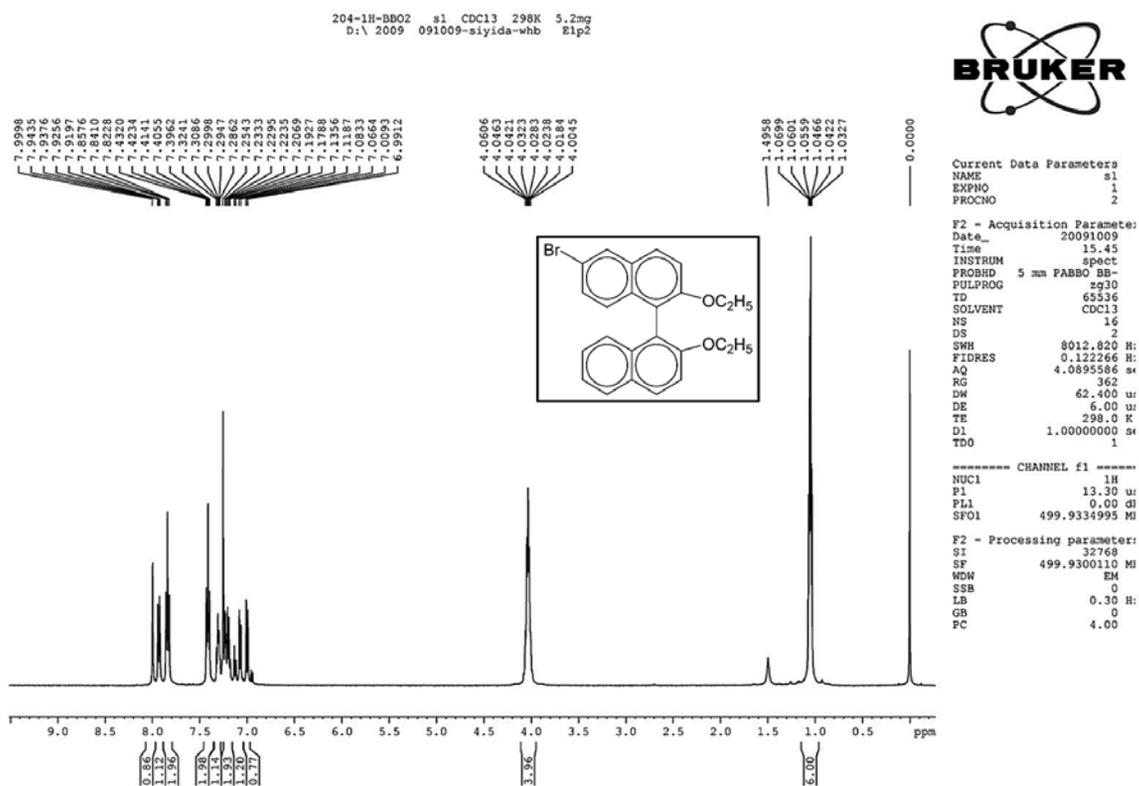
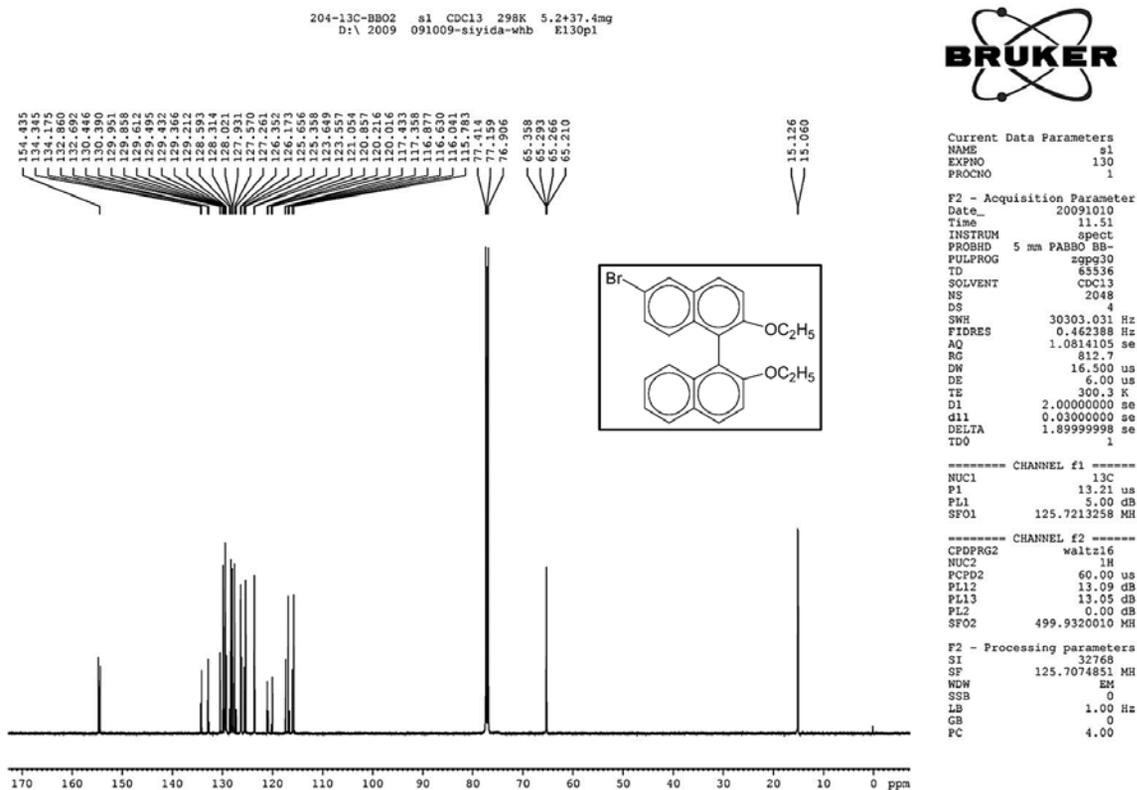
2. 4. Synthesis of Nitronyl Nitroxide (*R*)-**1** or (*S*)-**1**

A mixture of (*R*)-**7** (398 mg, 1.0 mmol) and 2,3-bis (hydroxylamino)-2,3-dimethylbutane (0.3 g, 2.0 mmol) in 20 mL dry MeOH was refluxed for 24 h under an argon atmosphere. The solvent was removed under reduced pressure to afford a yellow solid. The residue was taken up in $\text{CHB}_{2\text{B}}\text{ClB}_{2\text{B}}$ (20 mL), cooled to 0 °C, and then $\text{NaIOB}_{4\text{B}}$ (0.6 g, 2.8 mmol) in water (5 mL) was added with stirring. The reaction mixture was stirred for 0.5 h. The organic layer was washed with water and brine and then dried over $\text{MgSOB}_{4\text{B}}$. Evaporation of solvent gave the crude product, which was further purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 3:7) to yield a dark blue solid. Single crystals of (*R*)-**1** were obtained from the mixed solution of *n*-heptane and dichloromethane (the ratio of volume is 1 to 1).

(*R*)-**1**: 294 mg, 45%. mp: 220–221 °C. IR (ν_{maxB} , $\text{cmP}^{-1\text{P}}$): 2982, 2939, 1623, 1495, 1369, 1340, 1246, 1134, 1089, 822. ESR (DMF) nine lines, $g = 2.0037$, $|a_{\text{N}}| = 3.81\text{G}$. HRMS: m/z (ESI) calcd for $\text{CB}_{38\text{B}}\text{HB}_{44\text{B}}\text{NB}_{4\text{B}}\text{OB}_{6\text{B}}$ $[\text{M}+\text{Na}]^{\text{P}+\text{P}}$: 675.3153, found: 675.3150. Elemental analysis, found: C, 69.89; H, 6.82; N, 8.60, calcd for $\text{CB}_{38\text{B}}\text{HB}_{44\text{B}}\text{NB}_{4\text{B}}\text{OB}_{6\text{B}}$: C, 69.92; H, 6.79; N, 8.58%.

The enantiomer (*S*)-**1** was synthesized by the same method as enantiomer (*R*)-**1**.

3. Spectroscopic data

Figure S1. ¹H NMR spectrum of compound (R)-8.Figure S2. ¹³C NMR spectrum of compound (R)-8.

Sample Name	LC/MS	Position	Vial 3	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	JING-5.d	ACQ Method		Comment		Acquired Time	10/13/2009 10:31:02 AM

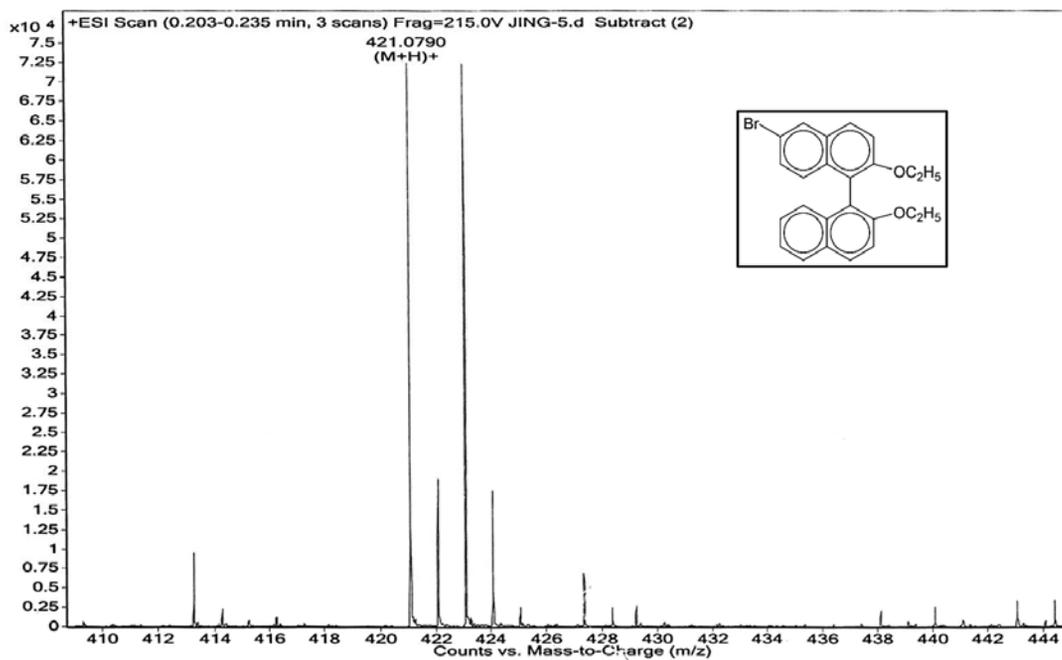
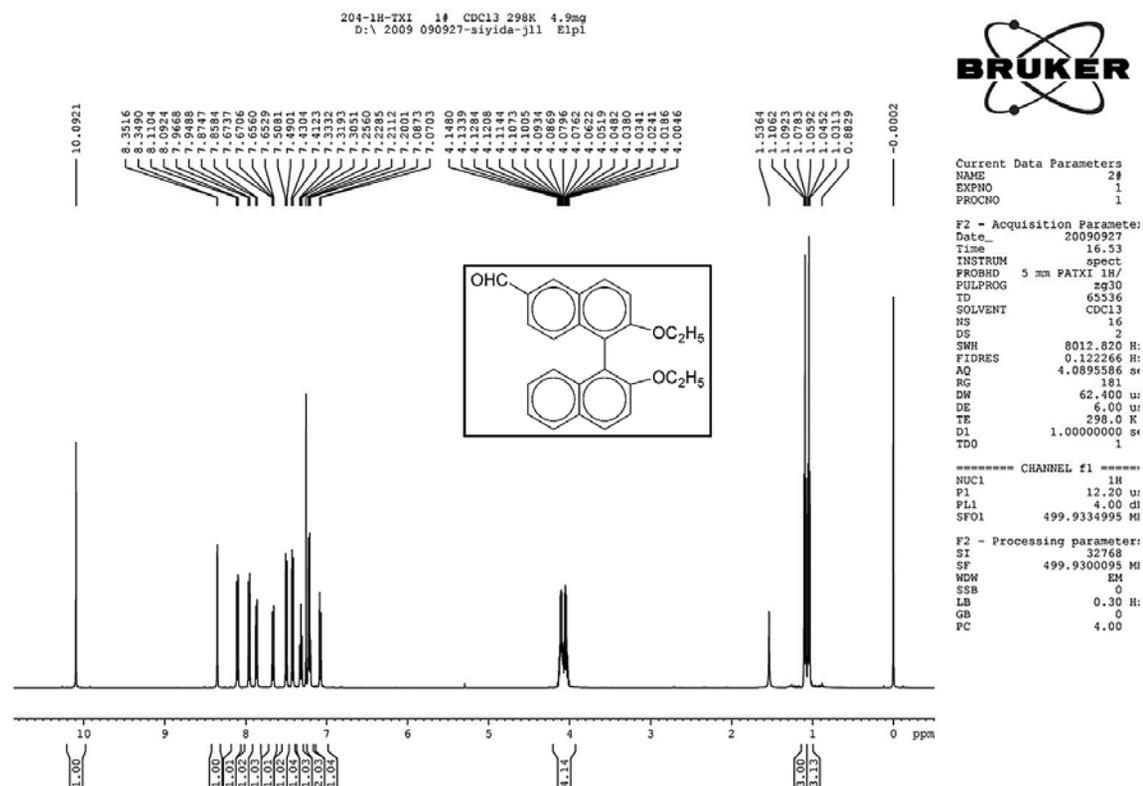
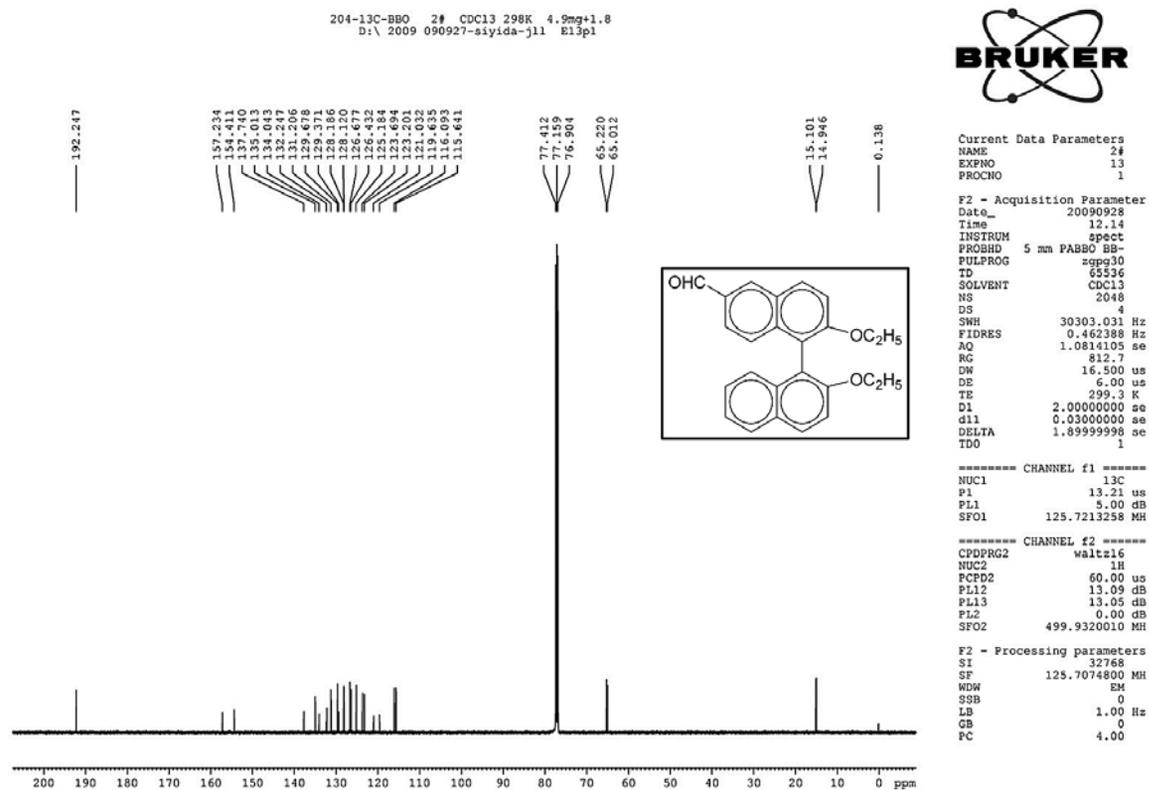


Figure S3. HRMS spectrum of compound (R)-8.

Figure S4. ¹H NMR spectrum of compound (R)-9.

Figure S5. ^{13}C NMR spectrum of compound (R)-9.

Sample Name	LC/MS	Position	Vial 3	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	JING-4.d	ACQ Method		Comment		Acquired Time	10/13/2009 10:24:50 AM

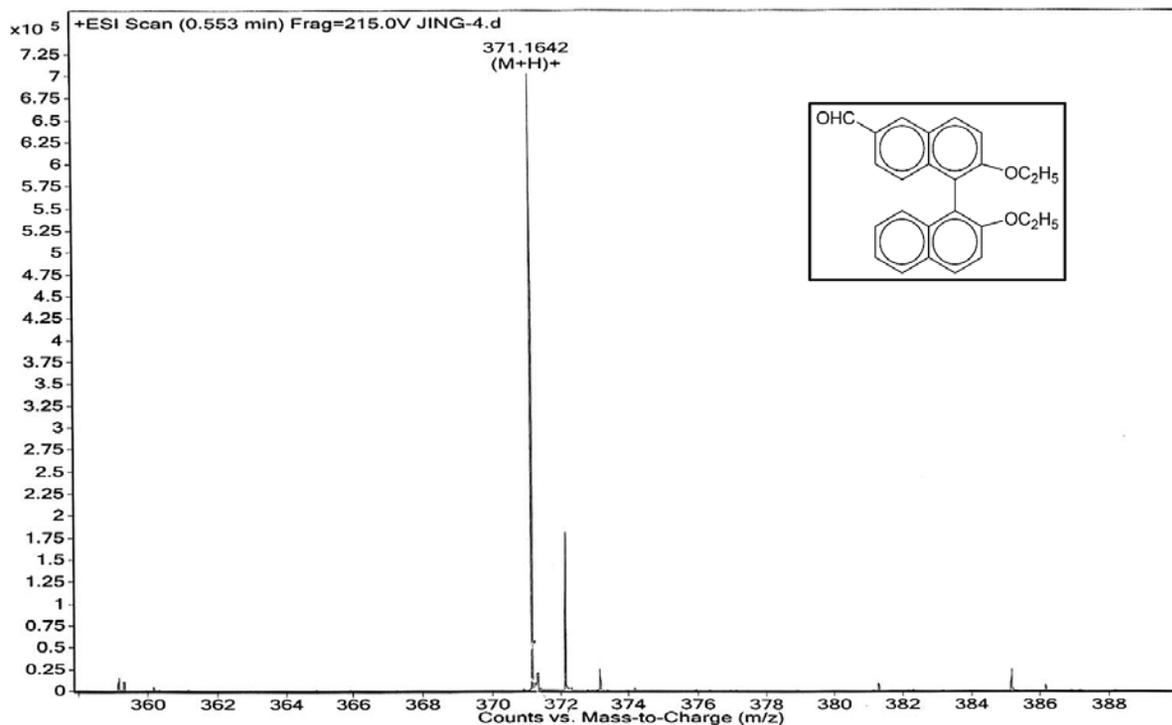


Figure S6. HRMS spectrum of compound (R)-9.

Sample Name	LC/MS	Position	Vial 3	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	COM-2.d	ACQ Method		Comment		Acquired Time	9/28/2009 3:20:49 PM

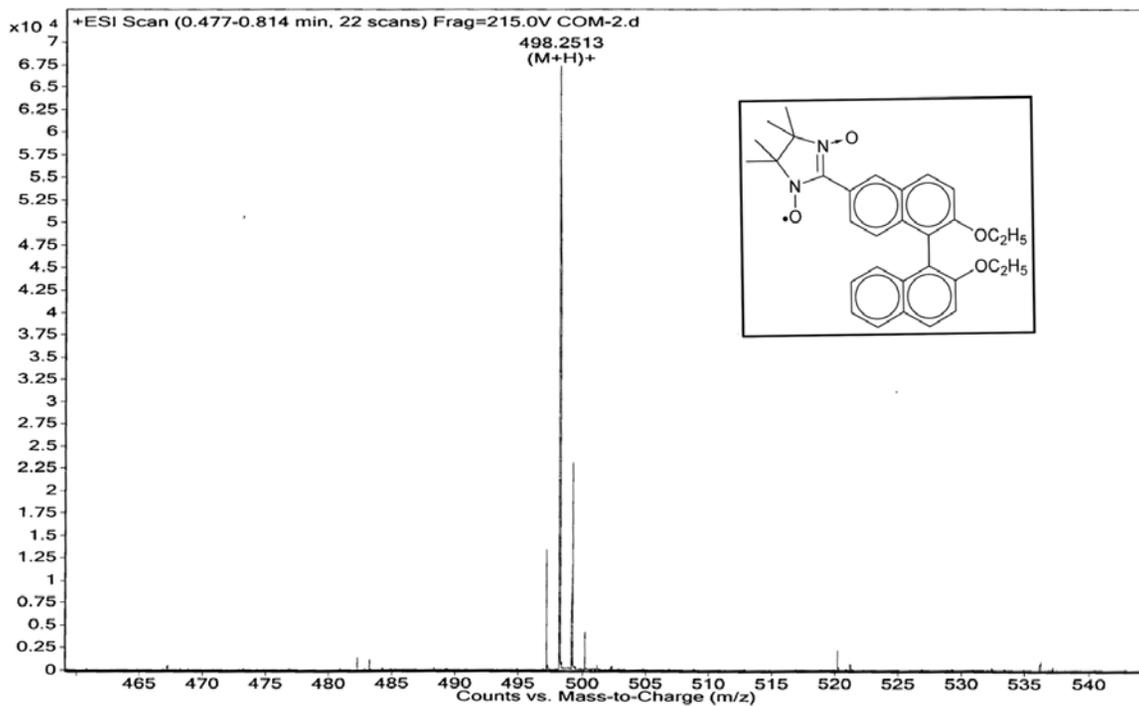


Figure S7. HRMS spectrum of compound (R)-2.

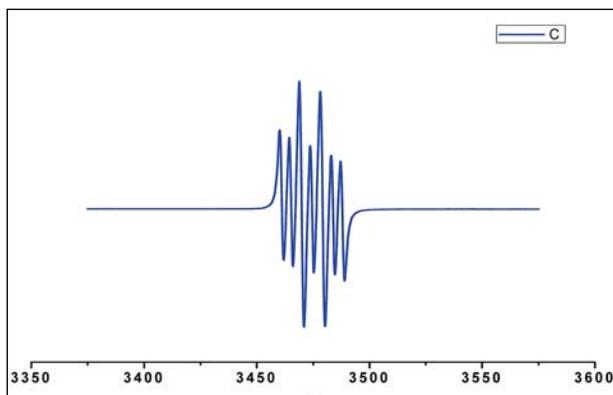


Figure S8. ESR spectra of compound (R)-2.

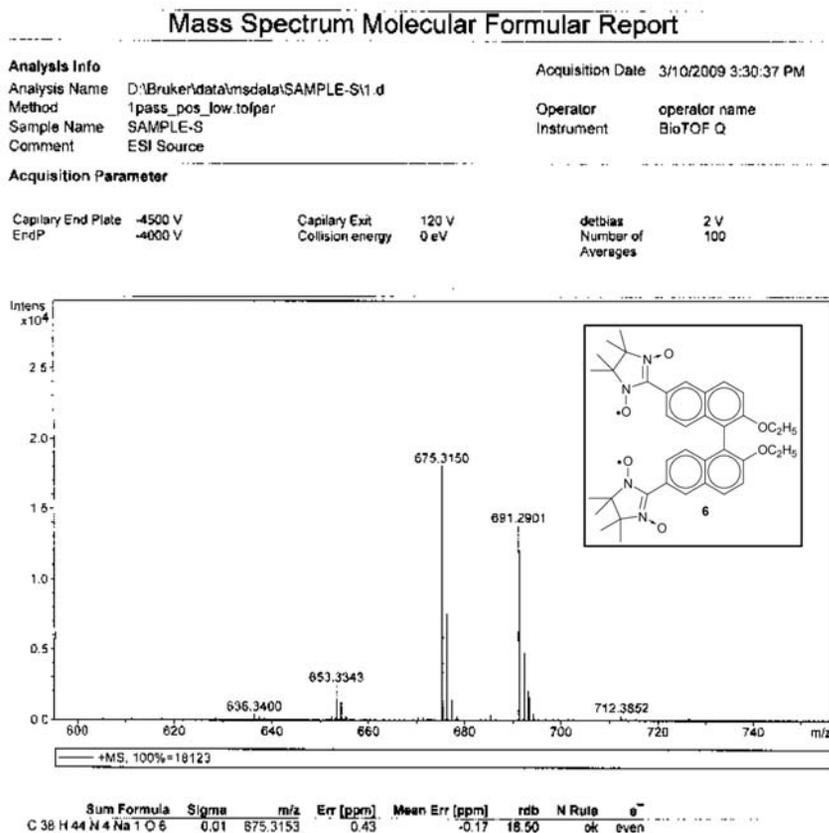


Figure S9. HRMS spectra of compound (R)-1.

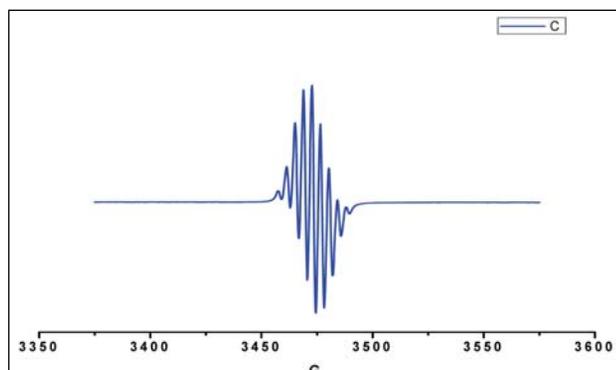


Figure S10. ESR spectra of compound (R)-1.

4. References

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