

Supporting Information

Construction of Helical Structures with Planar Chiral [2.2]Paracyclophane: Fusing Helical and Planar Chiralities

Motoki Tsuchiya, Hazuki Maeda, Ryo Inoue, Yasuhiro Morisaki

Department of Applied Chemistry for Environment,
School of Biological and Environmental Sciences,
Kwansei Gakuin University
2-1 Gakuen, Sanda, Hyogo 669-1337, Japan.

ymo@kwansei.ac.jp (Yasuhiro Morisaki)

General

^1H and ^{13}C spectra were recorded on a JEOL JNM ECZ-500R instrument at 500 and 125 MHz, respectively. Samples were analyzed in CDCl_3 or CD_2Cl_2 , and the chemical shift values were expressed relative to Me_4Si as an internal standard. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F_{254} plates. Column chromatography was performed with Wakogel C-300 SiO_2 . Flush column chromatography and recyclable preparative high-performance liquid chromatography (HPLC) were carried out on a YMC LC Forte/R. Diastereomer ratio (dr) was confirmed by a HPLC (TOSOH UV-8020) equipped with a Daicel Chiralpak® IA column (0.46 cm \times 25 cm, solvent flow rate 0.5 mL/min). High-resolution mass (HRMS) spectra were obtained on a JEOL JMS-S3000 spectrometer for matrix assisted desorption/ionization (MALDI) with α -cyano-4-hydroxycubbanic acid (CHCA), or *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix. In addition, high-resolution mass (HRMS) spectra were obtained on a Bruker Daltonics microTOF II for atmospheric pressure chemical ionization (APCI). UV-vis spectra were recorded on a JASCO V-730 spectrophotometer, and samples were analyzed in CHCl_3 at room temperature. Photoluminescence (PL) spectra were recorded on a JASCO FP-8500 spectrofluorometer, and samples were analyzed in CHCl_3 at room temperature. Absolute PL quantum efficiency was calculated on a JASCO FP8500 with an ILF-835 integrating sphere. The PL lifetime measurement was performed on a Hamamatsu Photonics Quantaaurus-Tau fluorescence lifetime system. Circular dichroism (CD) spectra were recorded on a JASCO J-1500 spectropolarimeter with CHCl_3 as a solvent at room temperature; two scans were accumulated. Circularly polarized luminescence (CPL) spectra were recorded on a JASCO CPL-300 with CHCl_3 as a solvent at room temperature. All samples for CPL were excited around 290 nm, and five scans were accumulated. Specific rotations ($[\alpha]_D$) were measured with a HORIBA SEPA-500 polarimeter.

Materials

Commercially available compounds used without purification:

B(OMe)₃, (1*S*,4*R*)-camphanoyl chloride, Tf₂O, 2-vinylnaphthalene, styrene

n-BuLi (1.55 M in hexane), Pd(OAc)₂

2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos)

NaOH, H₂O₂ (30% in H₂O), NH₄Cl, MgSO₄, KOH, conc HCl, NaHCO₃, I₂, NaHSO₃

Et₂O (dehydrated), CHCl₃, CH₂Cl₂, pyridine (dehydrated), hexane, EtOH, DMF, toluene (dehydrated),

THF (dehydrated)

Compounds prepared as described in the literature:

(*rac*)-**1**: H. Maeda, M. Kameda, T. Hatakeyama, Y. Morisaki, *Polymers* **2018**, *10*, 1140/1-10.

X-ray structure determination

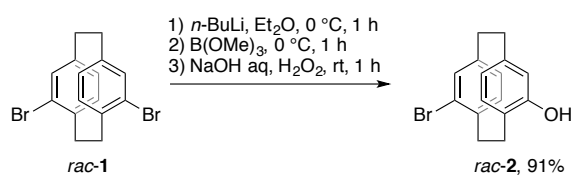
Crystals suitable for X-ray diffraction studies were analyzed using a Rigaku MicroMax-007HFM MoK α rotating anode generator equipped with VariMax optics, an AFC1 goniometer, and Saturn 724+ detector. The reflection data for them was integrated, scaled and averaged using Rigaku CrysAlis^{PRO}. The structures were solved by a direct method (SHELXT) and refined using a full-matrix least-squares method on F² for all reflections (SHELXL-2018/3). The calculations were performed on Yadokari-XG or Olex2 program package. Crystallographic data are given in Table S1–S4. CCDC-2084825 ((*R*_p,1*S*,4*R*)-**3**), 2084826 ((*S*_p,1*S*,4*R*)-**3**), 2084827 ((*R*_p)-**7**), 2084828 ((*R*_p)-**8**), 2087318 ((*S*_p)-**5**), and 2087319 ((*S*_p)-**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>

Computational methods

All calculations were carried out by using the Gaussian 16 program package.¹ Optimized geometries in singlet ground state, molecular orbitals, and CD properties were estimated by DFT and TD-DFT calculations^{2–7} with MN15⁸ functionals and 6-31G(d)^{9–11} basis set. Optimized geometries in S₁ state were obtained by SS-CASSCF(16e,14o) calculation^{12–13} with 6-31G basis set. The CPL properties were estimated by using CIS(D) calculation^{14–15} based on the optimized geometry obtained by SS-CASSCF calculation. Cartesian coordinates of all optimized structures are given in Tables S5–S8.

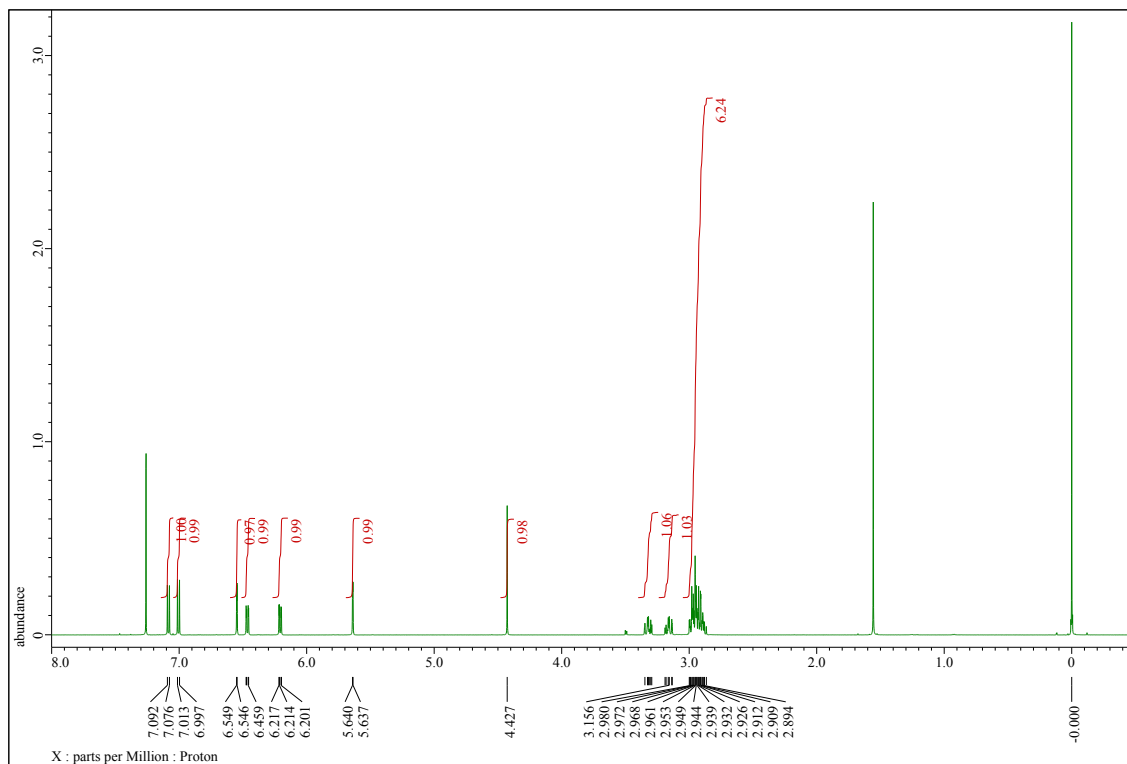
- 1) Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- 2) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439–4449.
- 3) R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1998**, *109*, 8218–8224.
- 4) R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454–464.
- 5) A. C. Tsipis, *Coord. Chem. Rev.* **2014**, *272*, 1–29.
- 6) C. Adamo, D. Jacquemin, *Chem. Soc. Rev.* **2013**, *42*, 845–856.
- 7) C. Adamo, T. Le Bahers, M. Savarese, L. Wilbraham, G. García, R. Fukuda, M. Ehara, N. Rega, I. Ciofini, *Coord. Chem. Rev.* **2015**, *304–305*, 166–178.
- 8) H. S. Yu, X. He, S. L. Li, D. G. Truhlar, *Chem. Sci.* **2016**, *7*, 5032–5051.
- 9) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654–3665.
- 10) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213–222.
- 11) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294–0.
- 12) D. Hegarty and M. A. Robb, *Mol. Phys.* **1979**, *38*, 1795–1812.
- 13) R. H. E. Eade and M. A. Robb, *Chem. Phys. Lett.* **1981**, *83*, 362–368.
- 14) J. A. Pople, R. Seeger, and R. Krishnan, *Int. J. Quantum Chem.* **1977**, 149–163.
- 15) K. Raghavachari, H. B. Schlegel, and J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 4654–4655.
- 16) K. Raghavachari and J. A. People, *Int. J. Quantum Chem.* **1981**, *20*, 1067–1071.

Synthesis of *rac-2*

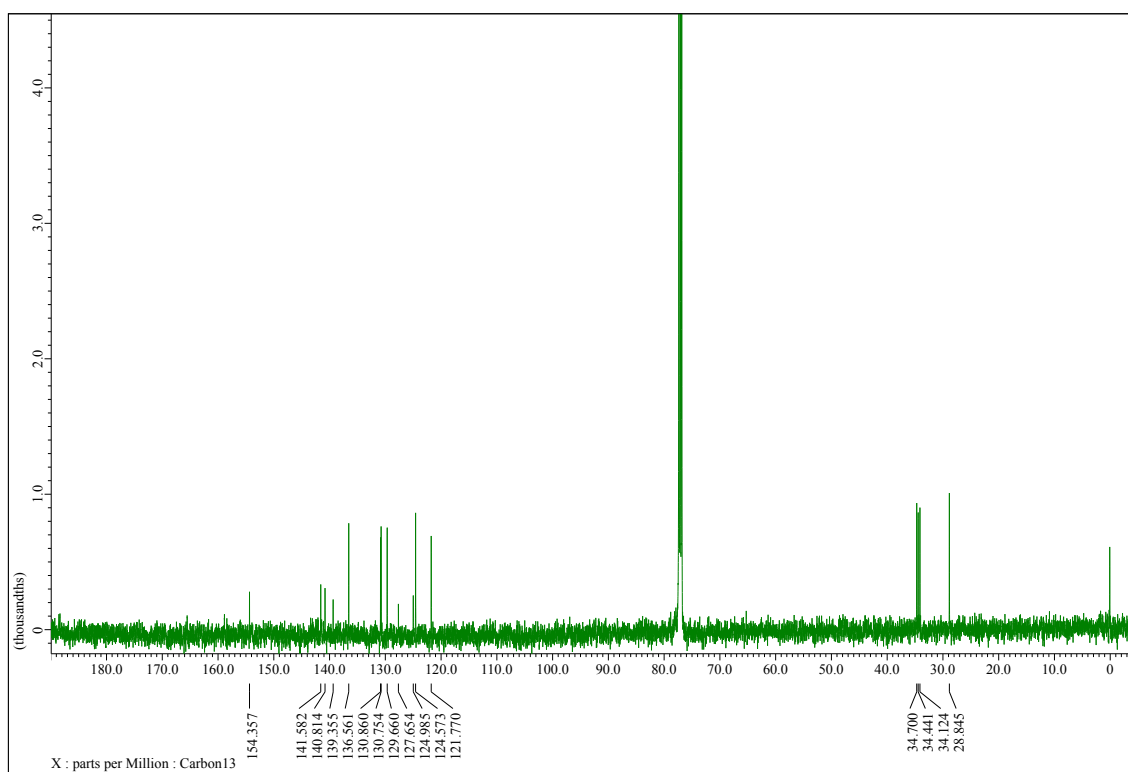


A solution of *n*-BuLi (1.55 M in hexane, 8.4 mL, 13.0 mmol) was slowly added to a solution of *rac-1* (3.68 g, 10.0 mmol) in Et₂O (80 mL) at 0 °C. After 1 h, B(OMe)₃ (2.2 mL, 19.7 mmol) was added, and then the mixture was warmed to room temperature. After 1 h, aqueous NaOH (1.0 M, 4.0 mL, 4.0 mmol) and aqueous H₂O₂ (30%, 6.0 mL, 58.8 mmol) were added, and the mixture was stirred for 1 h at room temperature. After the saturated aqueous NH₄Cl solution was added to the reaction mixture, the organic layer was extracted with CH₂Cl₂ three times. The combined organic layer was washed with brine and dried over MgSO₄. MgSO₄ was removed by filtration, and the solvent was evaporated. The residue was purified by column chromatography on SiO₂ (CHCl₃ as an eluent) to afford *rac-2* (2.78 g, 9.2 mmol, 91%) as a pale yellowish green crystal.

$R_f = 0.29$ (CHCl₃ as an eluent). ¹H NMR (CDCl₃, 500 MHz) δ 2.89-3.16 (m, 6H), 3.12-3.18 (m, 1H), 3.28-3.34 (m, 1H), 4.42 (m, 1H), 5.64 (d, $J = 1.5$ Hz, 1H), 6.21 (dd, $J = 1.5, 8.0$ Hz, 1H), 6.46 (dd, $J = 1.5, 8.0$ Hz, 1H), 6.55 (d, $J = 1.5$ Hz, 1H), 7.00 (d, 8.0 Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 1H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 28.8, 34.1, 34.4, 34.7, 121.7, 124.5, 124.9, 127.6, 129.6, 130.7, 130.8, 136.5, 139.3, 140.8, 141.5, 154.3 ppm. HRMS (MALDI, DCTB) calcd. for C₁₆H₁₅OBr, M^+ : 302.0306, found 302.0360.

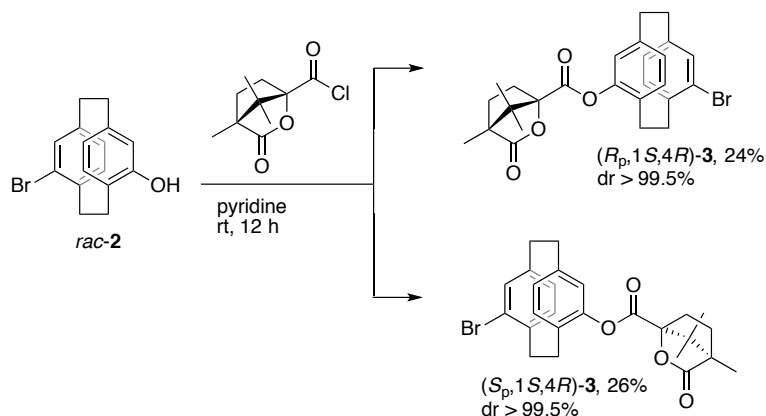


^1H NMR spectrum of *rac*-2.



^{13}C NMR spectrum of *rac*-2.

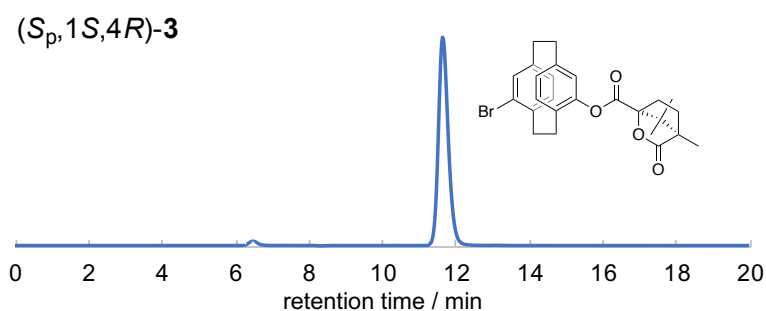
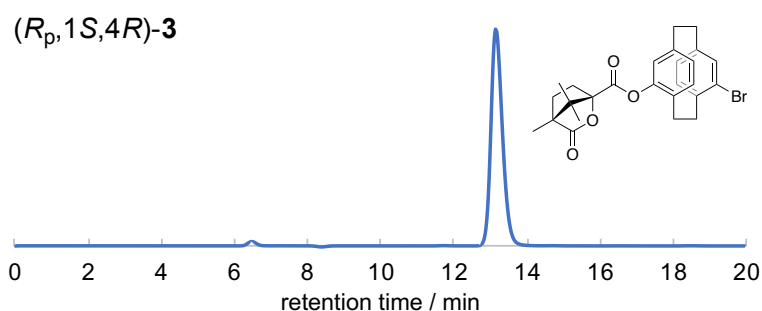
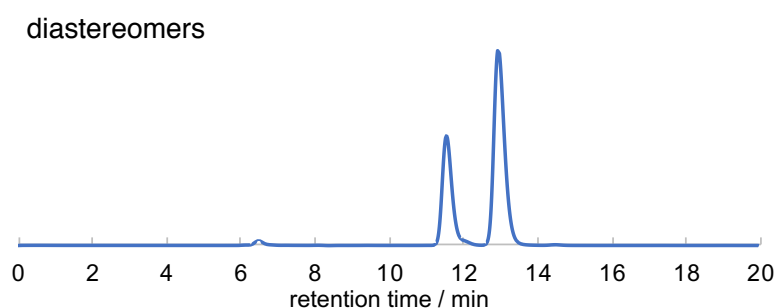
Optical resolution: synthesis of (*R_p*,1*S*,4*R*)- and (*S_p*,1*S*,4*R*)-**3**



A mixture of *rac*-**2** (1.82 g, 6.0 mmol) and (*1S*,4*R*)-camphanoyl chloride (2.25 g, 10.4 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, dry pyridine (50 mL) was added to the mixture at 0 °C, and the reaction was carried out at room temperature for 24 h with stirring. After the reaction mixture was cooled to 0 °C, 6 M HCl (100 mL) was added, and organic species were extracted with CH₂Cl₂ three times. The combined organic layer was washed with 1 M HCl, aqueous NaHCO₃, and brine. The organic layer was dried over MgSO₄. MgSO₄ was removed, and the solvent was evaporated. The residue was separated by SiO₂ column chromatography (CHCl₃/hexane = 12/1 v/v as an eluent) to afford (*S_p*,1*S*,4*R*)-**3** (*R_f* = 0.23) and (*R_p*,1*S*,4*R*)-**3** (*R_f* = 0.29) as white powders. Each diastereomer was purified by recrystallization from CHCl₃/MeOH to afford (*S_p*,1*S*,4*R*)-**3** (740.0 mg, 1.5 mmol, 26%) and (*R_p*,1*S*,4*R*)-**3** (693.3 mg, 1.4 mmol, 24%).

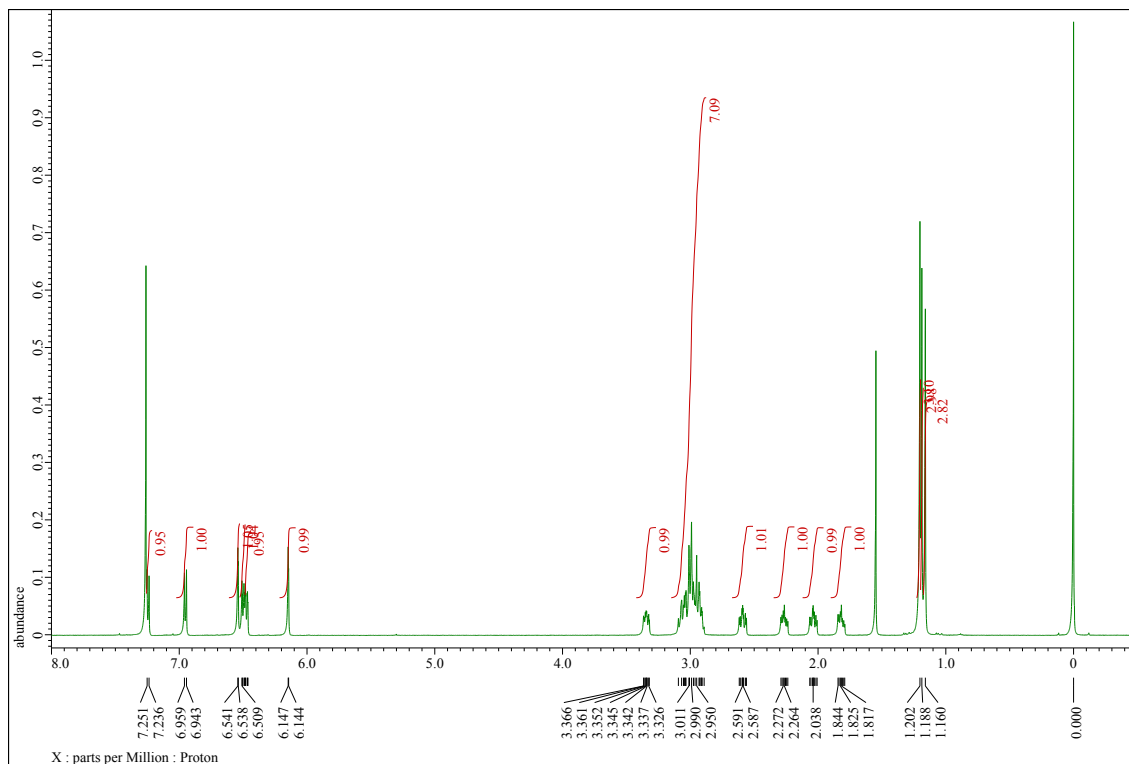
(*S_p*,1*S*,4*R*)-**3**: ¹H NMR (CDCl₃, 500 MHz) δ 1.15 (s, 3H), 1.18 (s, 3H), 1.21 (s, 3H), 1.73-1.89 (m, 1H), 1.95-2.10 (m, 1H), 2.15-2.30 (m, 1H), 2.51-2.66 (m, 1H), 2.85-3.14 (m, 7H), 3.28-3.42 (m, 1H), 6.11 (d, *J* = 2.0 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 6.50 (d, *J* = 2.0 Hz, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 9.8, 16.8, 17.0, 29.0, 29.6, 31.0, 34.4, 34.5, 34.6, 54.6, 55.0, 90.9, 127.2, 127.6, 130.0, 130.6, 130.9, 130.9, 131.6, 136.8, 139.2, 141.0, 141.5, 149.0, 165.5, 178.3 ppm. HRMS (MALDI, CHCA) calcd. for C₂₆H₂₇BrO₄ + Na⁺: 505.0985, found 505.0919. [α]_D²⁵ = +100.18 (*c* 0.25, CHCl₃).

(*R_p*,1*S*,4*R*)-**3**: ¹H NMR (CDCl₃, 500 MHz) δ 1.16 (s, 3H), 1.19 (s, 3H), 1.20 (s, 3H), 1.74-1.90 (m, 1H), 1.96-2.12 (m, 1H), 2.19-2.35 (m, 1H), 2.51-2.66 (m, 1H), 2.88-3.14 (m, 7H), 3.28-3.42 (m, 1H), 6.15 (d, *J* = 2.0 Hz, 1H), 6.47 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.50 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.54 (d, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 9.9, 16.9, 16.9, 29.0, 29.7, 31.2, 34.4, 34.5, 34.7, 54.6, 55.0, 90.9, 127.2, 127.6, 130.0, 130.6, 130.9, 130.9, 131.5, 136.8, 139.1, 141.1, 141.5, 148.9, 165.4, 178.1 ppm. HRMS (MALDI, CHCA) calcd. for C₂₆H₂₇BrO₄ + Na⁺ : 505.0985, found 505.0919. [α]_D²⁵ = -100.21 (*c* 0.25, CHCl₃).

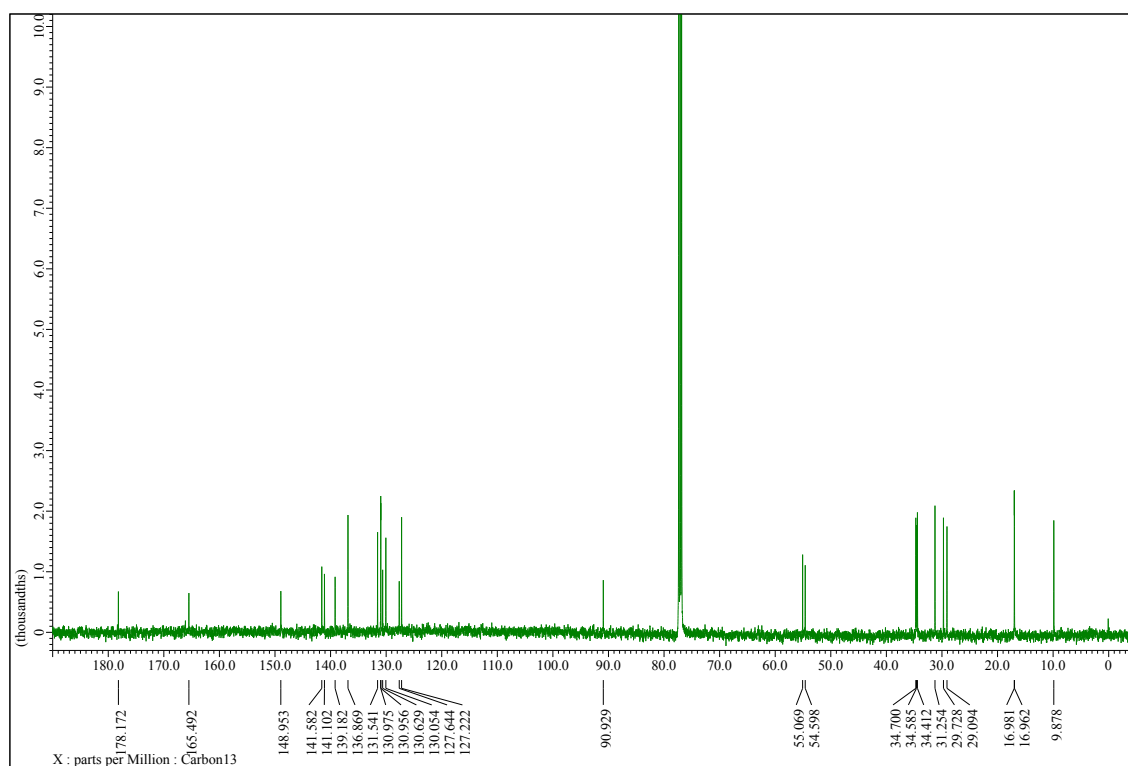


Colum: Chiralpak[®] IA, 0.46 cm × 25 cm
 Eluent: hexane/THF = 8/2 v/v
 Flow rate: 0.5 mL/min

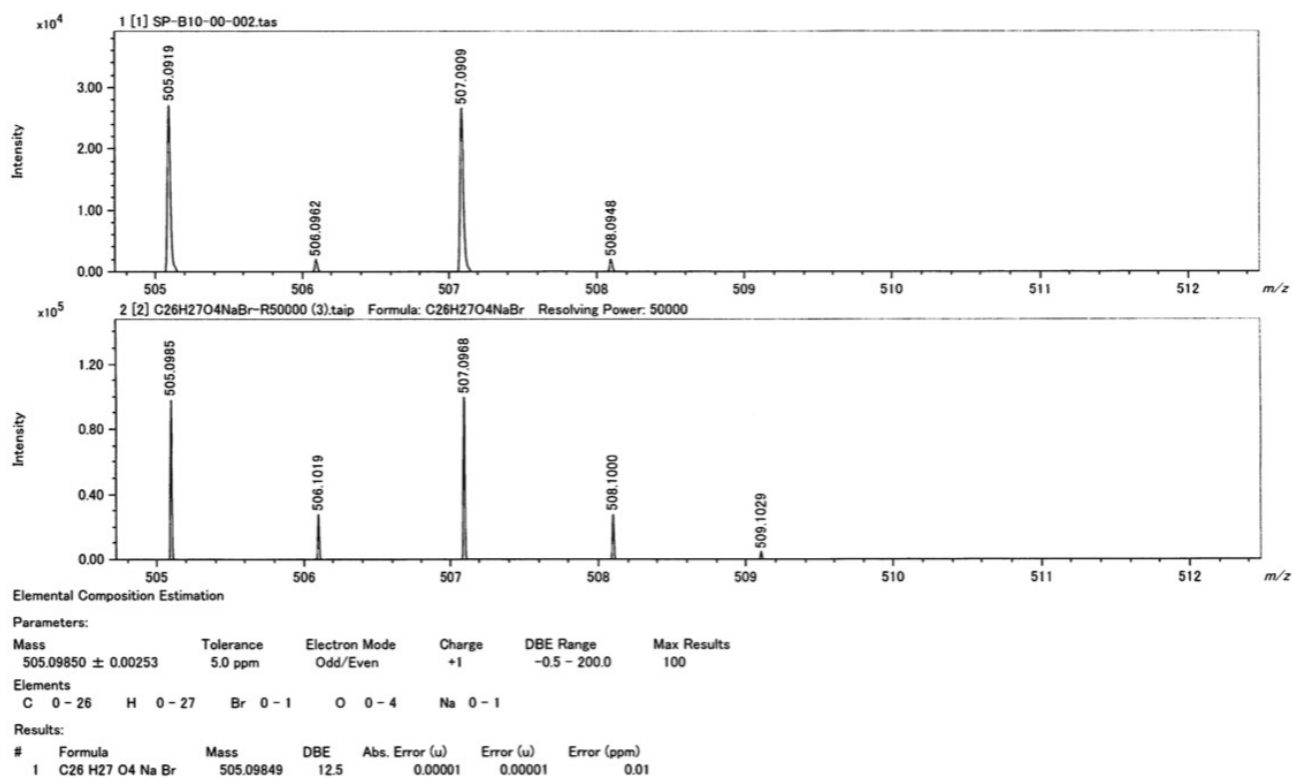
Figure S1. Chromatograms of diastereomers, (*R_p*,1*S*,4*R*)-**3**, and (*S_p*,1*S*,4*R*)-**3**



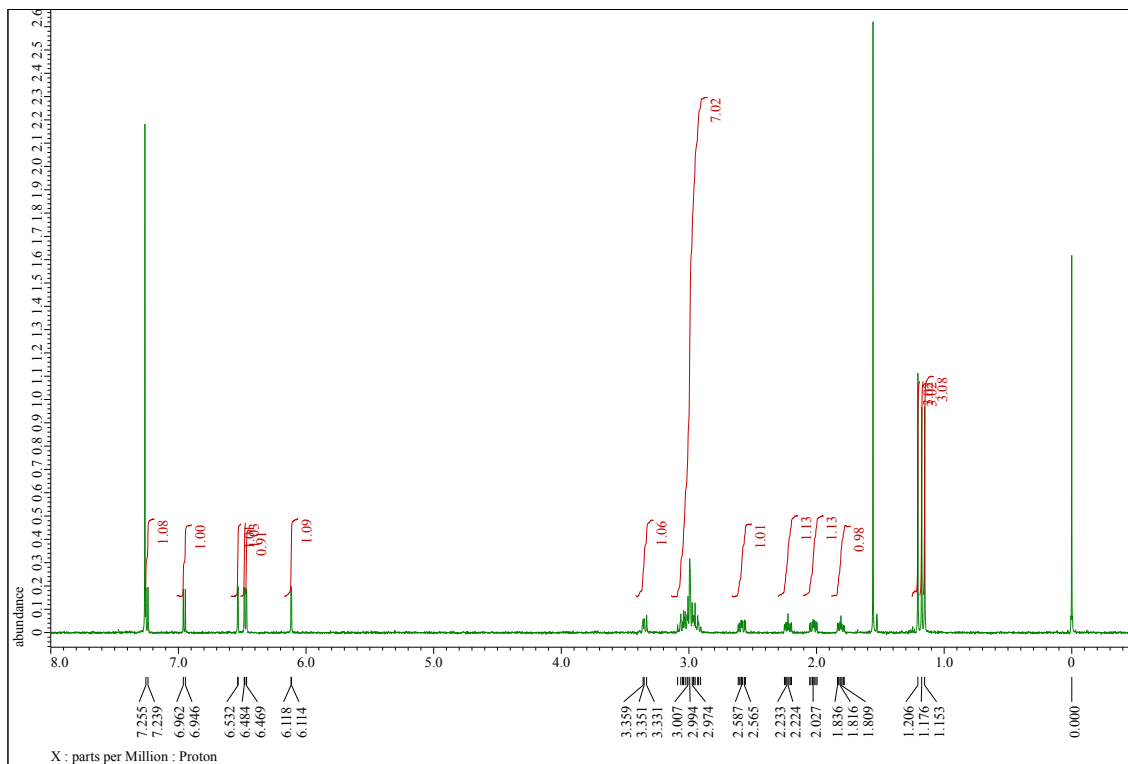
¹H NMR spectrum of (*R*_p,1*S*,4*R*)-3.



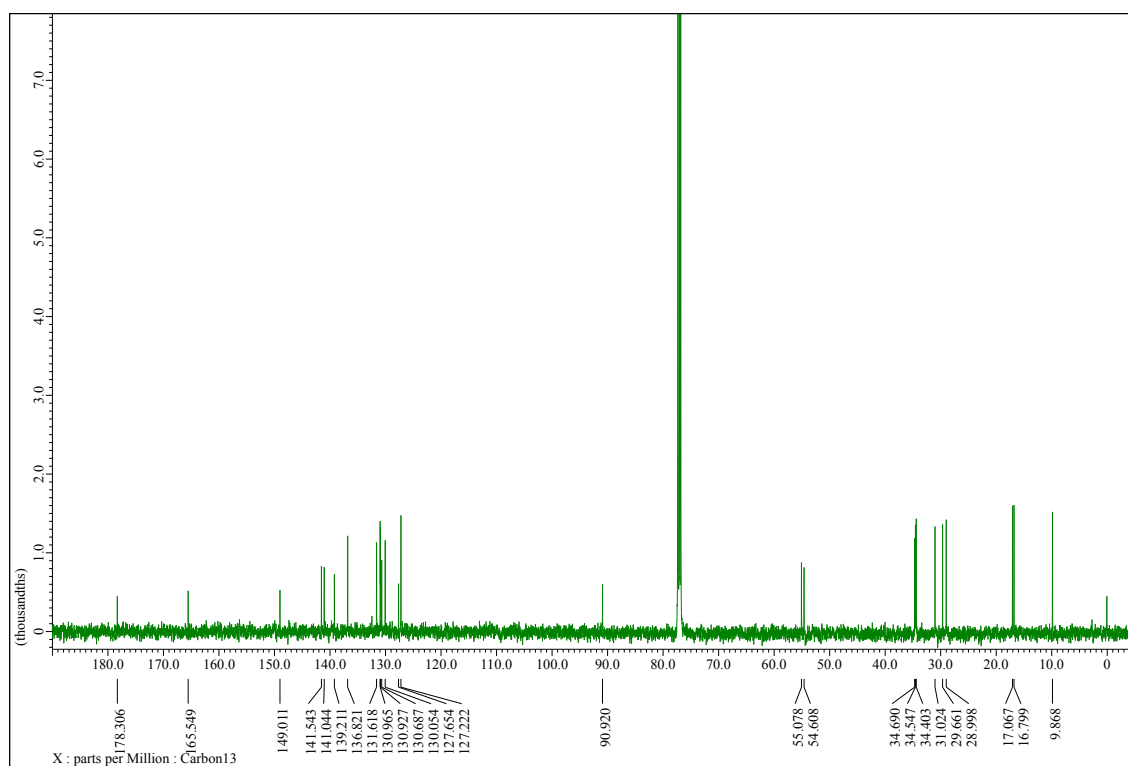
¹³C NMR spectrum of (*R*_p,1*S*,4*R*)-3.



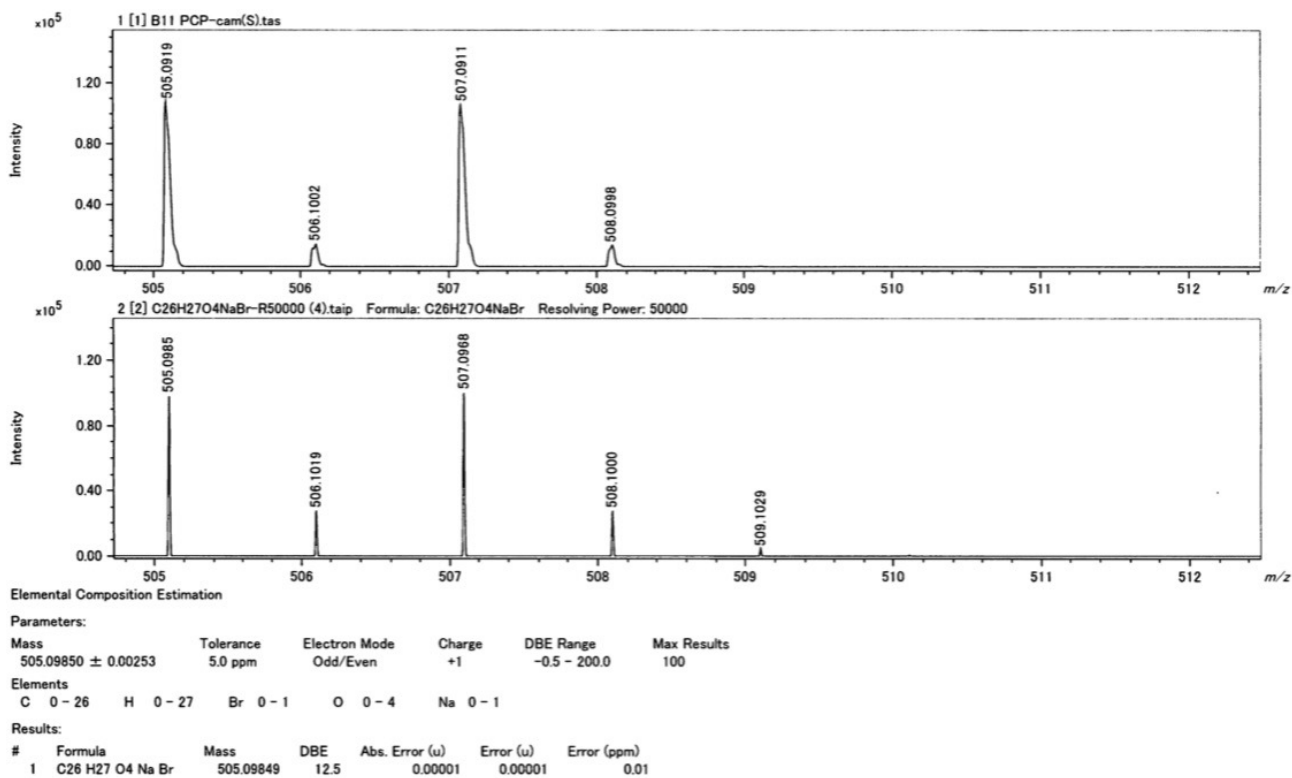
Results of mass spectrometry of $(R_p,1S,4R)$ -**3**; upper and lower Mass spectra indicate experimental and theoretical spectra, respectively.



¹H NMR spectrum of (S_p,1S,4R)-3.

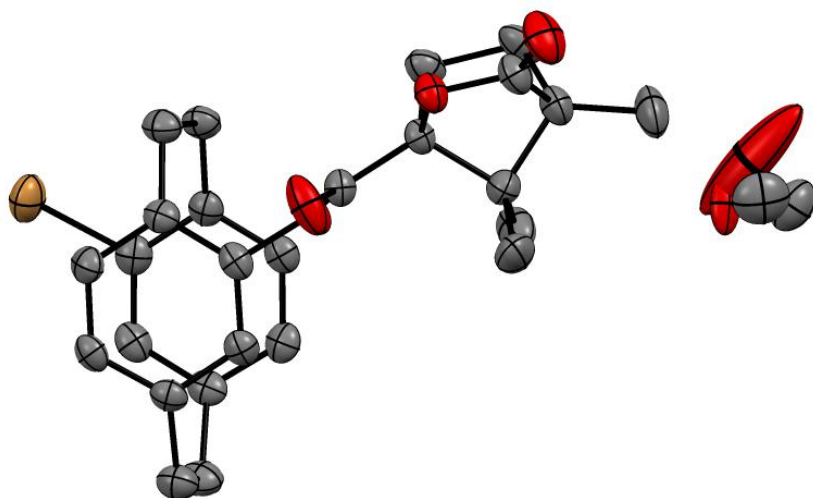


¹³C NMR spectrum of (S_p,1S,4R)-3.



Results of mass spectrometry of (*S_p*,1*S*,4*R*)-**3**; upper and lower Mass spectra indicate experimental and theoretical spectra, respectively.

(A)



(B)

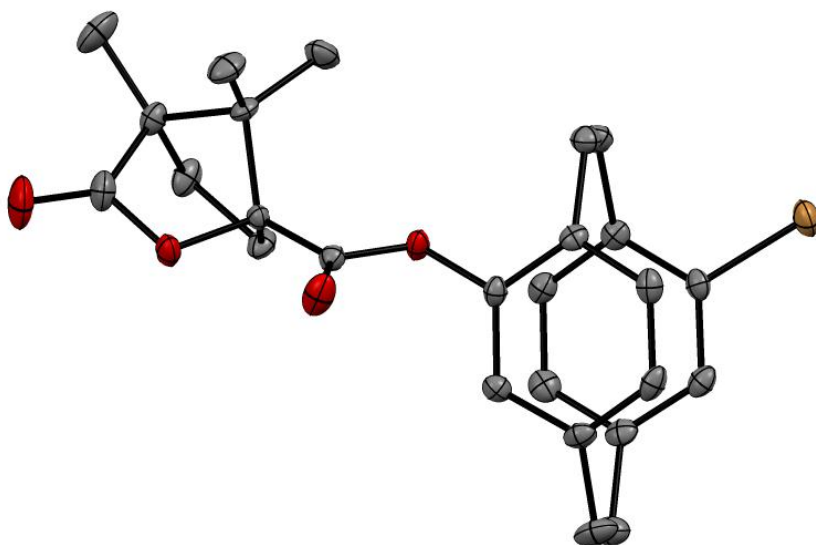


Figure S2. ORTEP drawings of (A) $(R_p,1S,4R)$ -**3**·EtOH: CCDC-2084825 and (B) $(S_p,1S,4R)$ -**3**: CCDC-2084826. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

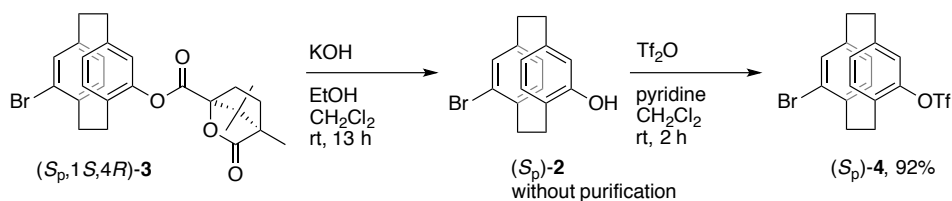
Table S1. Crystallographic data for (A) (*R_p,1S,4R*)-**3**·EtOH and (B) (*S_p,1S,4R*)-**3**

	(<i>R_p,1S,4R</i>)- 3 ·EtOH	(<i>S_p,1S,4R</i>)- 3
Formula	C ₂₆ H ₂₇ BrO ₄ , C ₂ H ₆ O	C ₂₆ H ₂₇ BrO ₄
Formula weight	529.45	483.38
Temperature (K)	150	150
Crystal color, habit	colorless, plate	colorless, needle
Crystal size, mm	0.20 × 0.10 × 0.05	0.50 × 0.20 × 0.05
Crystal system	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)	<i>P</i> 12 ₁ 1(#4)
<i>a</i> , Å	7.946(9)	9.1381(3)
<i>b</i> , Å	8.073(10)	7.2746(2)
<i>c</i> , Å	39.47(5)	16.3470(5)
<i>α</i> , deg	90	90
<i>β</i> , deg	90	91.457(3)
<i>γ</i> , deg	90	90
<i>V</i> , Å ³	2532 (5)	1086.33(6)
<i>Z</i> value	4	2
<i>D</i> _{calcd} , g cm ⁻³	1.389	1.478
<i>μ</i> (MoKα), cm ⁻¹	1.659	1.923
<i>F</i> (000)	1104	1544.00
2 θ _{max} , deg	54.97	62.32
No. of reflections measured	26196	10203
No. of observed reflections	5754	6149
No. of variables	324	283
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^[a]	0.0427(5336)	0.0372(5699)
w <i>R</i> ₂ (all reflns) ^[b]	0.1088(5754)	0.0880(6149)
Goodness of fit	1.100	1.017
Flack parameter	-0.001(5)	-0.009(6)

[a] $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$.

Recrystallization solvent : chloroform / methanol

Synthesis of (*S_p*)-4

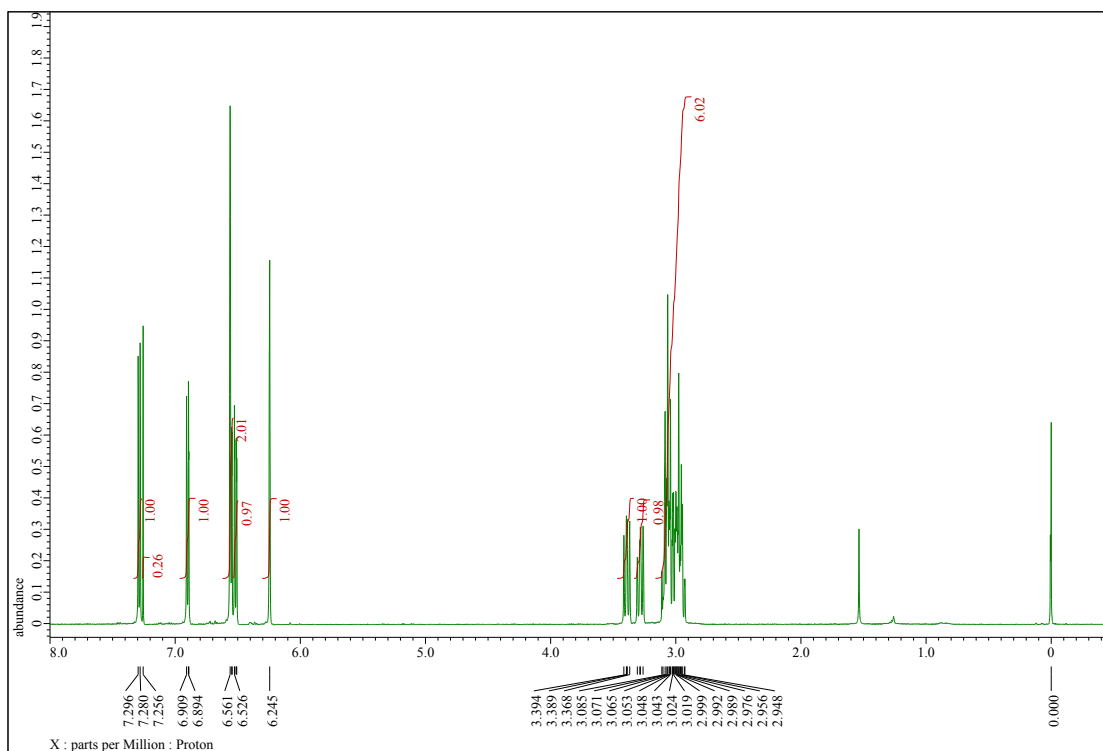


(*S_p*,1*S*,4*R*)-**3** (733.7 mg, 1.5 mmol), EtOH (40 mL) and CH₂Cl₂ (30 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, an aqueous solution of KOH (872.2 mg in H₂O (7 mL)) was added to the mixture. After stirring for 13 h, 6 M HCl (3.5 mL) was added to the reaction mixture. The organic layer was separated and extracted with CH₂Cl₂ three times. The combined organic layer was washed with aqueous NaHCO₃ and brine, and then dried over MgSO₄. MgSO₄ was removed by filtration, and the solvent was evaporated. The solid of (*S_p*)-**2** was used for the next reaction without further purification.

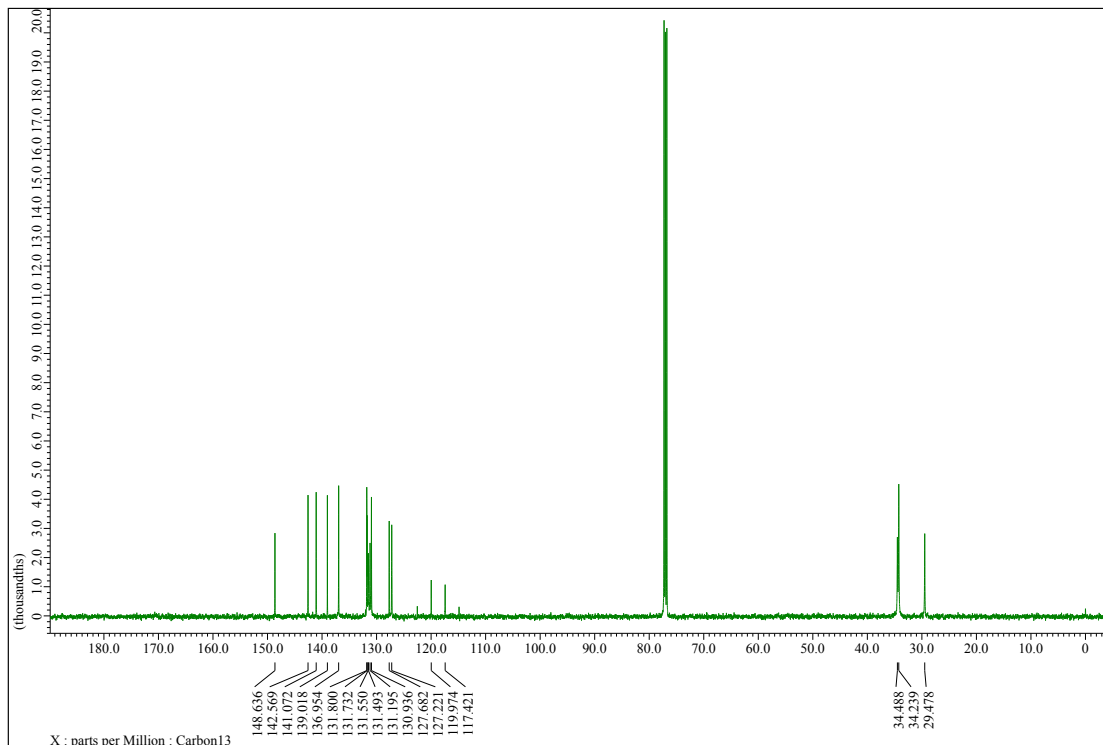
To a solution of (*S_p*)-**2** in CH₂Cl₂ (18 mL) were added pyridine (1.2 mL, 14.9 mmol) and Tf₂O (0.6 mL, 3.57 mmol) at 0 °C. After being stirred for 2 h at room temperature, 6 M HCl (3.5 mL) was added to the reaction mixture. The organic layer was separated and extracted with CH₂Cl₂ three times. The combined organic layer was washed with aqueous NaHCO₃ and brine, and then dried over MgSO₄. MgSO₄ was removed by filtration, and the solvent was evaporated. The residue was purified by column chromatography on SiO₂ (AcOEt/hexane = 1/2 v/v as an eluent) to afford (*S_p*)-**4** (609.5 mg, 1.4 mmol, 92%) as a colorless liquid. *R_f* = 0.77 (AcOEt / hexane = 1/2 v/v as an eluent).

R_f = 0.31 (CHCl₃/hexane = 1/2 v/v). ¹H NMR (CDCl₃, 500 MHz) δ 2.92-3.11 (m, 6H), 3.26-3.30 (m, 1H), 3.36-3.41 (m, 1H), 6.51 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.54 (dd, *J* = 1.5, 7.5 Hz, 2H), 6.89 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 29.4, 34.2, 34.4, 118.7 (q, *J* = 319 Hz), 127.6, 130.9, 131.2, 131.4, 131.5, 131.8, 136.9, 139.0, 141.0, 142.5, 148.6 ppm. HRMS (APCI) calcd. for C₁₇H₁₄BrF₃O₃S M⁺: 433.9794, found 433.9793. [α]_D²⁵ = -100.90 (*c* 0.25, CHCl₃).

(*R_p*)-**4** was obtained in 90% yield by the same procedure of (*S_p*)-**4**. HRMS (APCI) calcd. for C₁₇H₁₄BrF₃O₃S M⁺: 433.9794, found 433.9794. [α]_D²⁵ = +100.02 (*c* 0.25, CHCl₃).

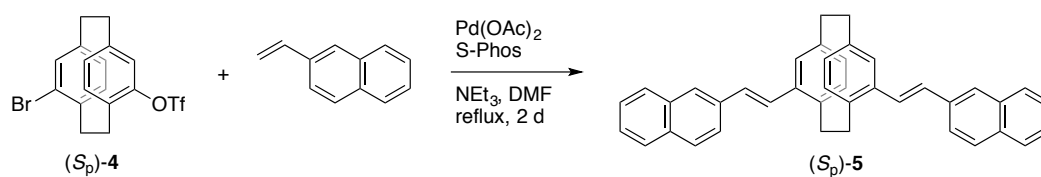


¹H NMR spectrum of (S_p)-4.



¹³C NMR spectrum of (S_p)-4.

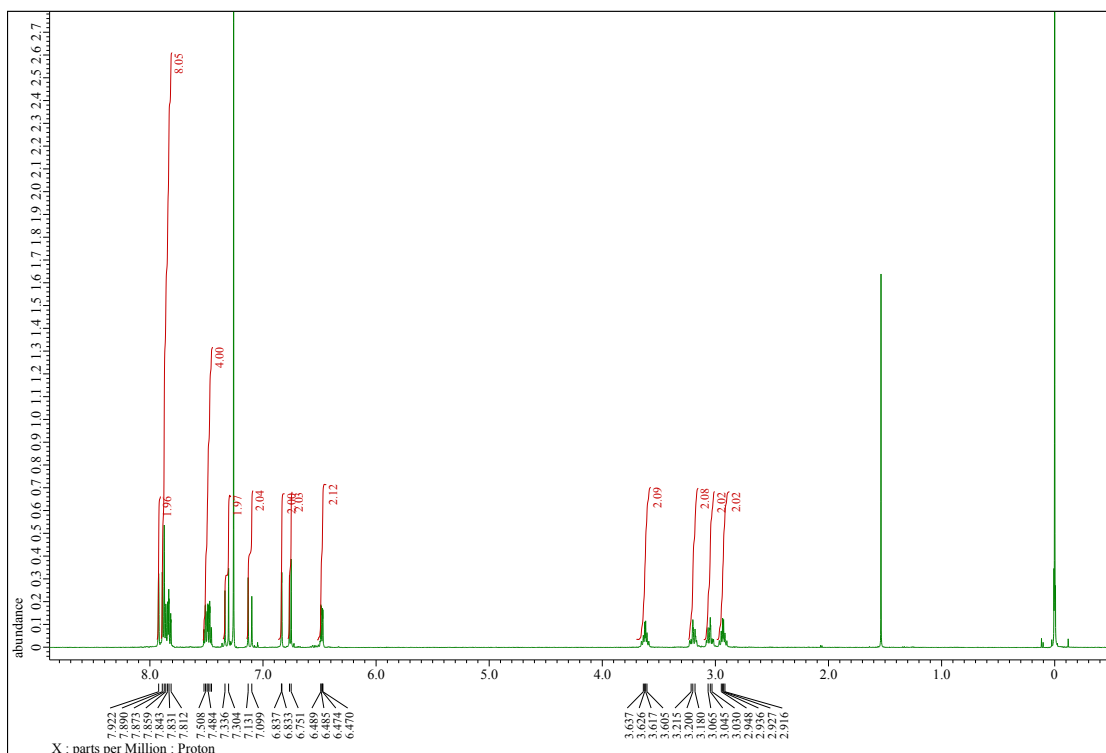
Synthesis of (*S_p*)-**5**



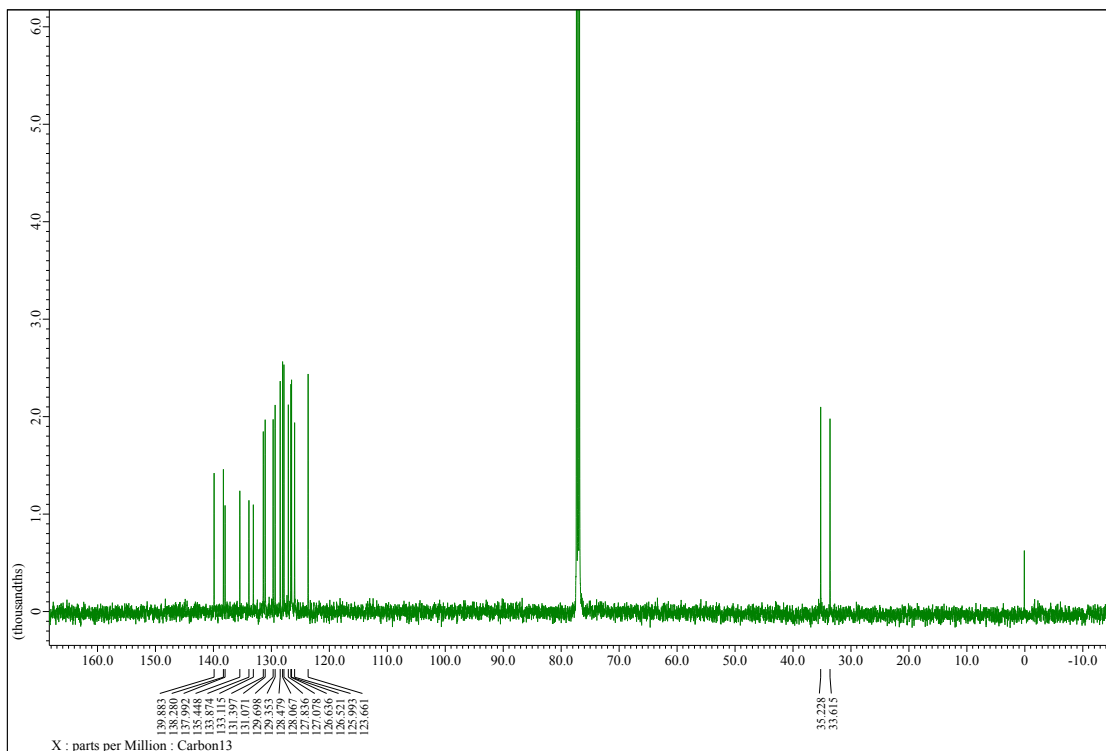
A mixture of (*S_p*)-**4** (201.4 mg, 0.462 mmol), Pd(OAc)₂ (11.1 mg, 4.9×10⁻³ mmol) and S-Phos (62.6 mg, 0.015 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, DMF (9.0 mL), Et₃N (2.0 mL) and 2-vinylnaphthalene (157.3 mg, 1.02 mmol) were added, and the reaction was carried out at reflux temperature for 48 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration. The organic layer was separated, and then aqueous layer was extracted with CH₂Cl₂. The organic layer was washed with H₂O and brine, and dried over MgSO₄. MgSO₄ was removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO₂ (CHCl₃/hexane = 1/2 v/v as an eluent) and recrystallization from CHCl₃/MeOH (v/v = 1/1) to afford (*R_p*)-**5** (92.3 mg, 0.18 mmol, 39%) as a light yellow solid.

$R_f = 0.34$ (CHCl₃/hexane = 1/2 v/v). ¹H NMR (CDCl₃, 500 MHz) δ 2.89-1.96 (m, 2H), 3.01-3.07 (m, 2H), 3.16-3.22 (m, 2H), 3.58-3.64 (m, 2H), 6.47 (dd, $J = 1.72, 7.45$ Hz, 2H), 6.75 (d, $J = 7.45$ Hz, 2H), 6.82 (d, $J = 1.72$ Hz, 2H), 7.12 (d, $J = 16.04$ Hz, 2H), 7.32 (d, $J = 16.04$ Hz, 2H), 7.47 (ddd, $J = 1.15, 6.87, 8.02$ Hz, 2H), 7.51 (ddd, $J = 1.15, 6.87, 8.02$ Hz, 2H), 7.81-7.89 (m, 8H), 7.92 (s, 2H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 33.6, 35.2, 123.6, 126.0, 126.5, 126.6, 127.1, 127.8, 128.1, 128.5, 129.4, 129.7, 131.1, 131.4, 133.1, 133.9, 135.4, 138.0, 138.3, 139.9 ppm. HRMS (APCI) calcd. for C₄₀H₃₂ + H⁺: 513.2577, found 513.2567. $[\alpha]_D^{25} = +1103.2$ (c 0.258, CHCl₃).

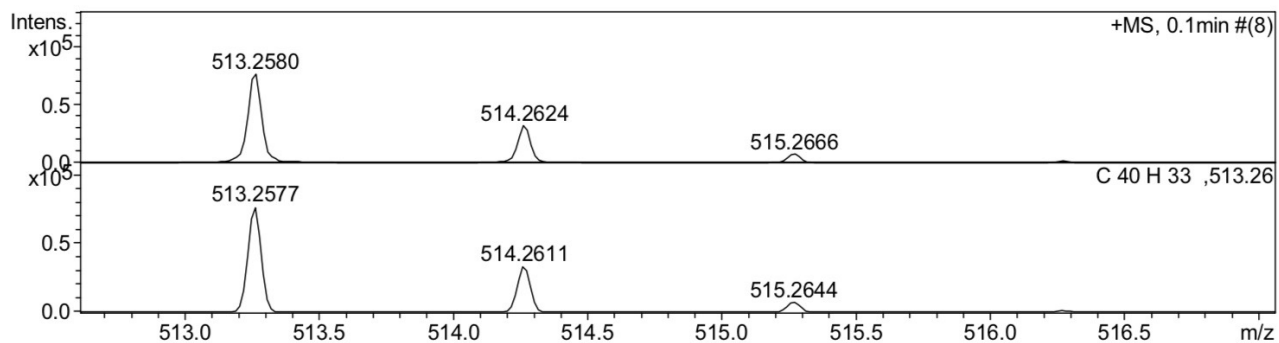
(*R_p*)-**5** was obtained in 32% yield by the same procedure of (*S_p*)-**5**. HRMS (APCI) calcd. for C₄₀H₃₂ + H⁺: 513.2577, found 513.2580. $[\alpha]_D^{25} = -1103.2$ (c 0.051, CHCl₃).



^1H NMR spectrum of (S_p)-**5**.



^{13}C NMR spectrum of (S_p)-**5**.



#	m/z	Res.	S/N	I	FWHM
1	513.2580	9711	4967.8	77012	0.0529
2	514.2624	10162	2068.1	32109	0.0506
3	515.2666	9712	480.7	7476	0.0531

Sum	Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e ⁻
C 40	H 33	0.012	513.2577	-0.56	-1.36	-0.29	24.50	ok	even

Results of mass spectrometry of (*S_p*)-**5**; upper and lower Mass spectra indicate experimental and theoretical spectra, respectively.

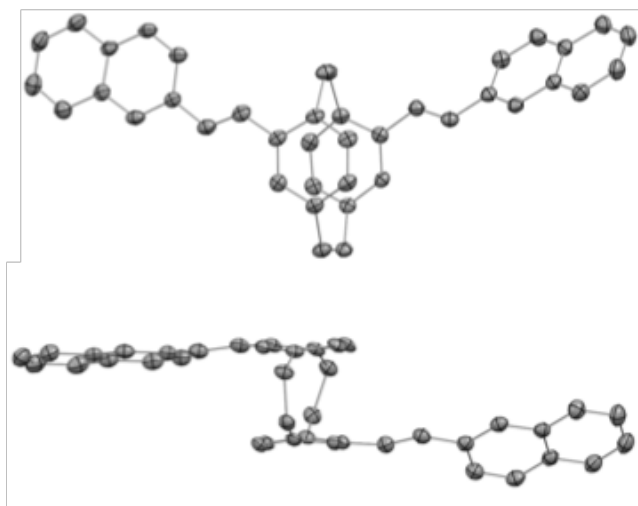


Figure S3. ORTEP drawings (top and side views) of (*S_p*)-**5**; CCDC-2087318. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S2. Crystallographic data and structure refinements for (*S_p*)-**5**.

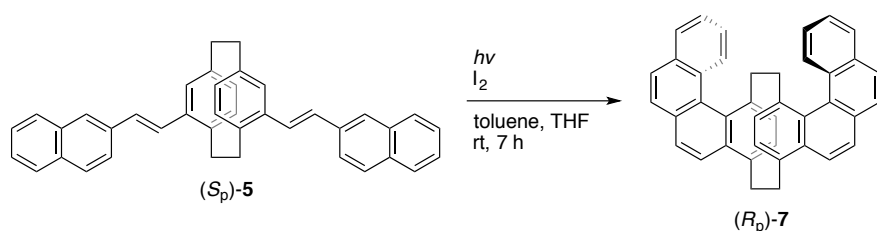
Formula	C ₄₀ H ₃₂
Formula weight	512.65
Temperature (K)	150
Crystal color, habit	colorless, needle
Crystal size, mm	0.4×0.1×0.05
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)
<i>a</i> , Å	8.3890(2)
<i>b</i> , Å	21.6023(6)
<i>c</i> , Å	30.9026(8)
<i>α</i> , deg	90
<i>β</i> , deg	90
<i>γ</i> , deg	90
<i>V</i> , Å ³	5600.2(3)
<i>Z</i> value	8
<i>D</i> _{calcd} , g cm ⁻³	1.216
<i>μ</i> (MoKα), cm ⁻¹	0.690
<i>F</i> (000)	2176
2 θ _{max} , deg	60.7440
No. of reflections measured	109620
No. of observed reflections	16867
No. of variables	721
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^[a]	0.0676(8550)
w <i>R</i> ₂ (all reflns) ^[b]	0.1250(16867)
Goodness of fit	1.000
Flack parameter	1.9(10)

[a] $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$.

Recrystallization solvent : chloroform / methanol

The single crystal X-ray experimental data above do not support the determination of the absolute structure, which was determined by the corresponding diastereomer precursor.

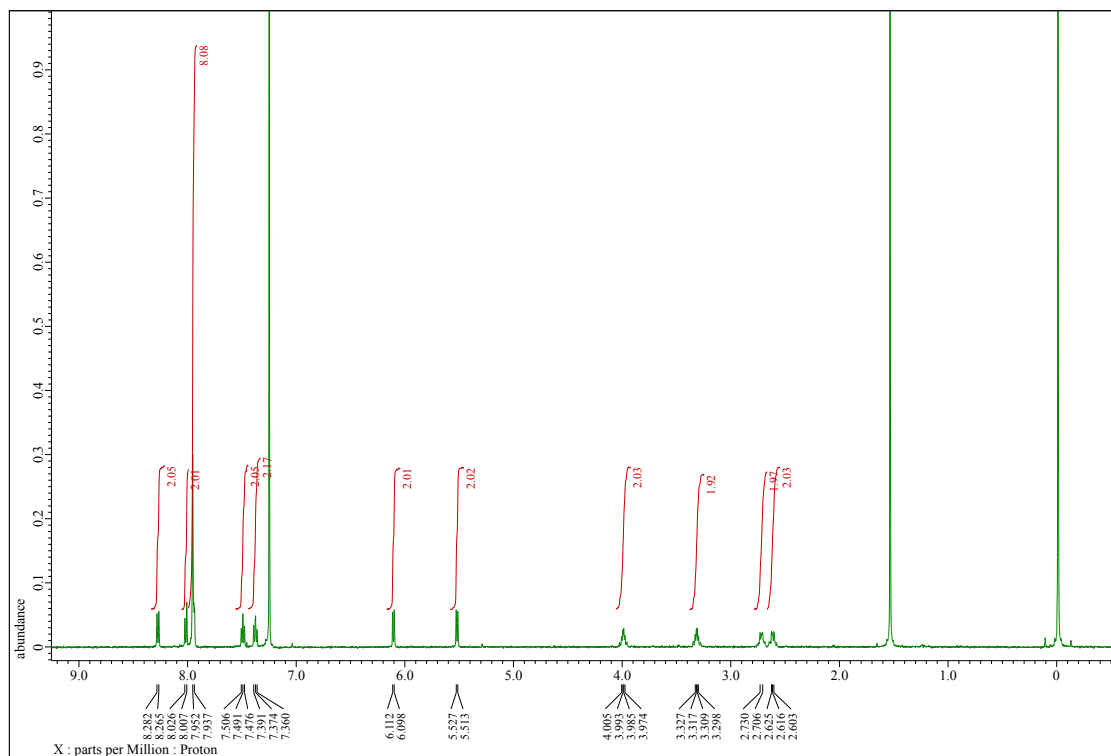
Synthesis of (*S_p*)-7



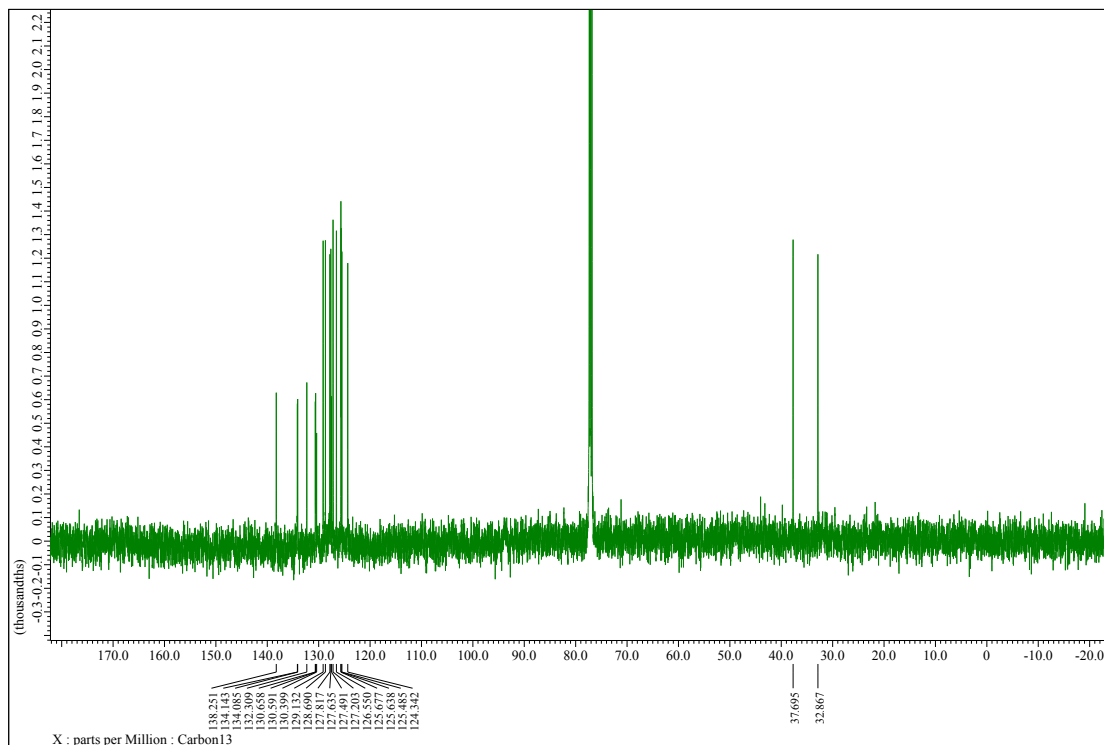
(*S_p*)-5 (26.3 mg, 0.051 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After toluene (50 mL), THF (1.0 mL), and I_2 (6.9 mg, 0.025 mmol) were added, the mixture was irradiated from a UV lamp (LED $\lambda = 365$ nm), and the reaction was carried out at room temperature for 7 h with stirring under air. H_2O and $NaHSO_3$ were added in the reaction mixture. The organic layer was separated, and then aqueous layer was extracted with CH_2Cl_2 . The organic layer was washed with H_2O and brine, and dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by recycled HPLC (eluent: CH_2Cl_2) to afford (*R_p*)-7 (4.6 mg, 0.009 mmol, 18%) as a colorless solid.

$R_f = 0.56$ ($CHCl_3$ /hexane = 1/2 v/v). 1H NMR ($CDCl_3$, 500 MHz) δ 2.59-2.66 (m, 2H), 2.67-2.77 (m, 2H), 3.30-3.36 (m, 2H), 3.97-4.04 (m, 2H), 5.53 (d, $J = 6.87$ Hz, 2H), 6.12 (d, $J = 6.87$ Hz, 2H), 7.38 (dd, $J = 6.87, 8.59$ Hz, 2H), 7.50 (dd, $J = 7.45, 7.45$ Hz, 2H), 7.95-7.96 (m, 8H), 8.03 (d, $J = 9.16$ Hz, 2H), 8.28 (d, $J = 8.59$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.9, 37.7, 124.3, 125.5, 125.6, 125.7, 126.6, 127.2, 127.5, 127.6, 127.8, 128.7, 129.1, 130.4, 130.6, 130.7, 132.3, 134.09, 134.14, 138.3 ppm. HRMS (APCI) calcd. for $C_{40}H_{28} + H^+$: 509.2264, found 509.2266. $[\alpha]^{25}_D = +878.0$ (c 0.041, $CHCl_3$).

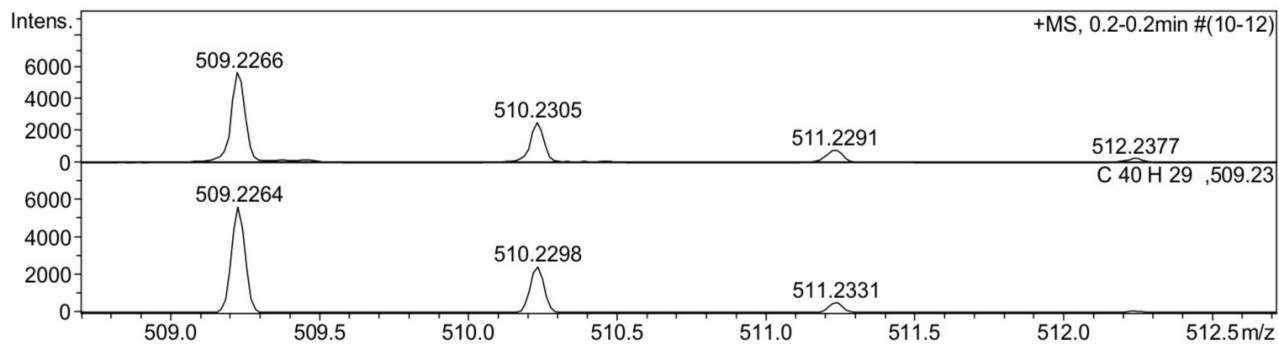
(*S_p*)-7 was obtained in 14% yield by the same procedure of (*R_p*)-7. HRMS (APCI) calcd. for $C_{40}H_{28} + H^+$: 509.2264, found 509.2264. $[\alpha]^{25}_D = -878.4$ (c 0.050, $CHCl_3$).



¹H NMR spectrum of (*R_p*)-7.



¹³C NMR spectrum of (*R_p*)-7.



#	m/z	Res.	S/N	I	FWHM
1	509.2266	10168	875.8	5607	0.0501
2	510.2305	10522	388.3	2488	0.0485
3	511.2291	8532	119.0	764	0.0599
4	512.2377	7533	38.1	245	0.0680

Sum	Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e ⁻
C 40 H 29		0.027	509.2264	-0.51	-0.21	-0.26	26.50	ok	even

Results of mass spectrometry of (*R_p*)-**7**.; upper and lower Mass spectra indicate experimental and theoretical spectra, respectively.

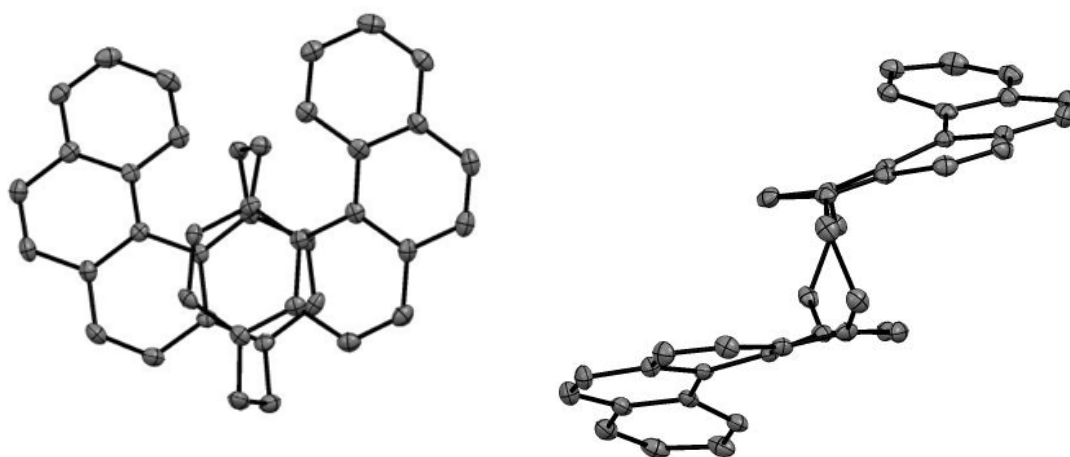


Figure S4. ORTEP drawings (top and side views) of (*R_p*)-**7**; CCDC-2084827. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

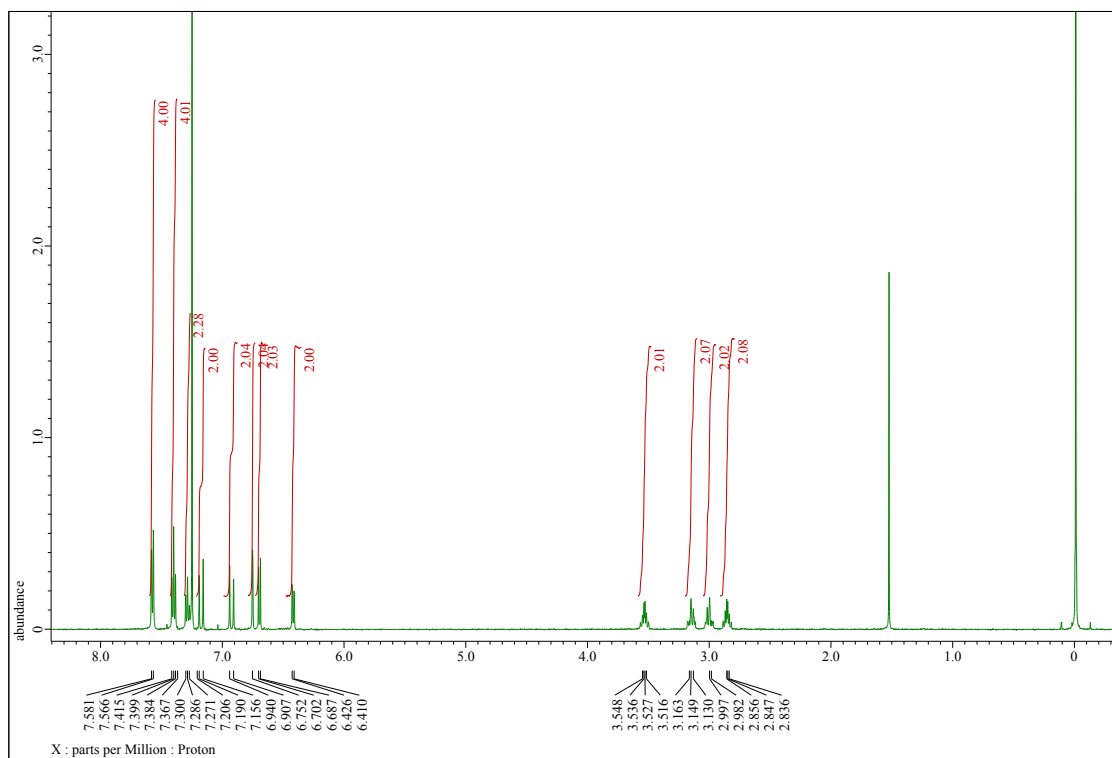
Table S3. Crystallographic data and structure refinements for (*R_p*)-**7**.

Formula	C ₄₀ H ₂₈
Formula weight	508.62
Temperature (K)	123
Crystal color, habit	colourless, plate
Crystal size, mm	0.10×0.05×0.01
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)
<i>a</i> , Å	11.0786(7)
<i>b</i> , Å	15.0781(9)
<i>c</i> , Å	15.4237(9)
<i>α</i> , deg	90
<i>β</i> , deg	90
<i>γ</i> , deg	90
<i>V</i> , Å ³	2576.4(3)
<i>Z</i> value	4
<i>D</i> _{calcd} , g cm ⁻³	1.311
<i>μ</i> (MoKα), cm ⁻¹	0.74
<i>F</i> (000)	1072
2 θ _{max} , deg	62.228
No. of reflections measured	12553
No. of observed reflections	6631
No. of variables	361
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^[a]	0.0630
w <i>R</i> ₂ (all reflns) ^[b]	0.1219
Goodness of fit	1.015
Flack parameter	2.5(10)

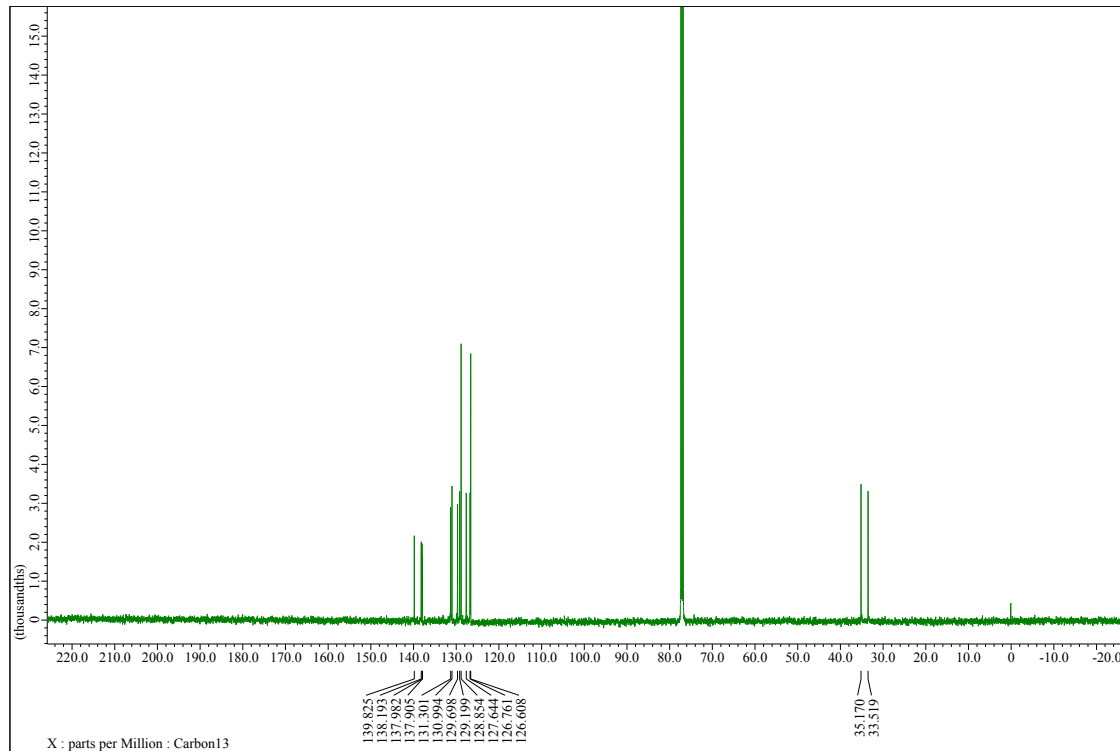
[a] $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$.

Recrystallization solvent: toluene

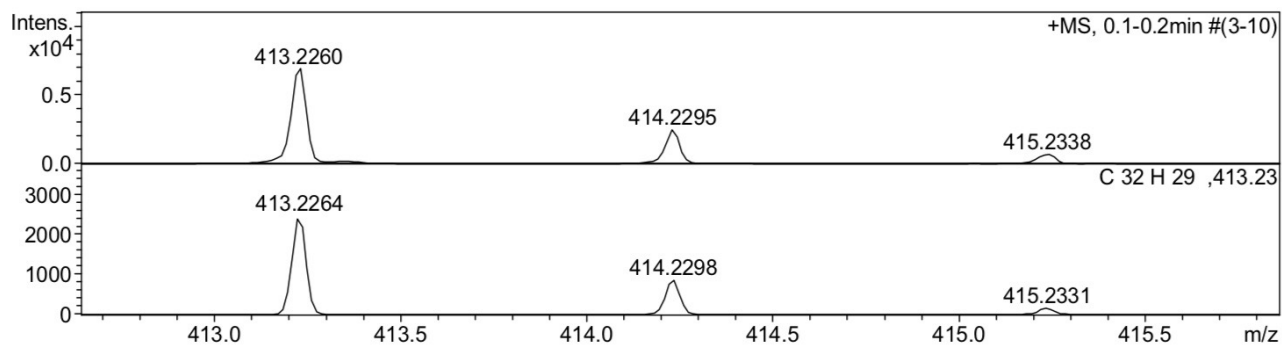
The single crystal X-ray experimental data above do not support the determination of the absolute structure, which was determined by the corresponding diastereomer precursor.



¹H NMR spectrum of (S_p)-6.



¹³C NMR spectrum of (S_p)-6.



#	m/z	Res.	S/N	I	FWHM
1	413.2260	9607	1322.1	6927	0.0430
2	414.2295	10092	472.0	2464	0.0410
3	415.2338	7926	134.1	698	0.0524

Sum	Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e ⁻
C 32	H 29	0.024	413.2264	1.02	0.81	0.42	18.50	ok	even

Results of mass spectrometry of (*R_p*)-**6**; upper and lower Mass spectra indicate experimental and theoretical spectra, respectively.

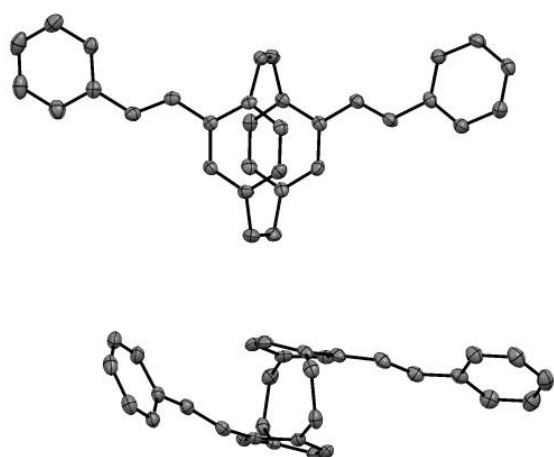


Figure S5. ORTEP drawings (top and side views) of (*S_p*)-**6**; CCDC-2087319. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S4. Crystallographic data and structure refinements for (*S_p*)-**6**.

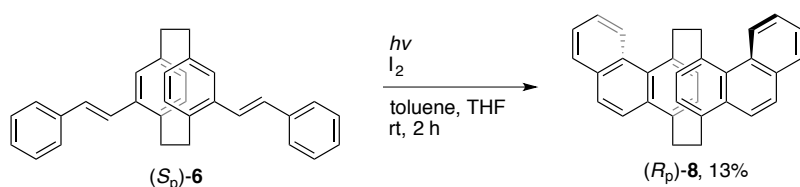
Formula	C ₃₂ H ₂₈
Formula weight	412.54
Temperature (K)	123
Crystal color, habit	colorless, platelet
Crystal size, mm	0.40 × 0.20 × 0.10
Crystal system	monoclinic
Space group	<i>P</i> 1 2 ₁ 1 (#4)
<i>a</i> , Å	14.7972(6)
<i>b</i> , Å	8.0733(3)
<i>c</i> , Å	18.9373(7)
<i>α</i> , deg	90
<i>β</i> , deg	96.319(4)
<i>γ</i> , deg	90
<i>V</i> , Å ³	2248.55(15)
<i>Z</i> value	4
<i>D</i> _{calcd} , g cm ⁻³	1.219
<i>μ</i> (MoKα), cm ⁻¹	0.69
<i>F</i> (000)	880.0
2 θ _{max} , deg	62.3520
No. of reflections measured	21741
No. of observed reflections	12890
No. of variables	577
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^[a]	0.0572(9411)
w <i>R</i> ₂ (all reflns) ^[b]	0.1263(12690)
Goodness of fit	1.008
Flack parameter	1.8(10)

[a] $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$.

Recrystallization solvent : chloroform / methanol

The single crystal X-ray experimental data above do not support the determination of the absolute structure, which was determined by the corresponding diastereomer precursor.

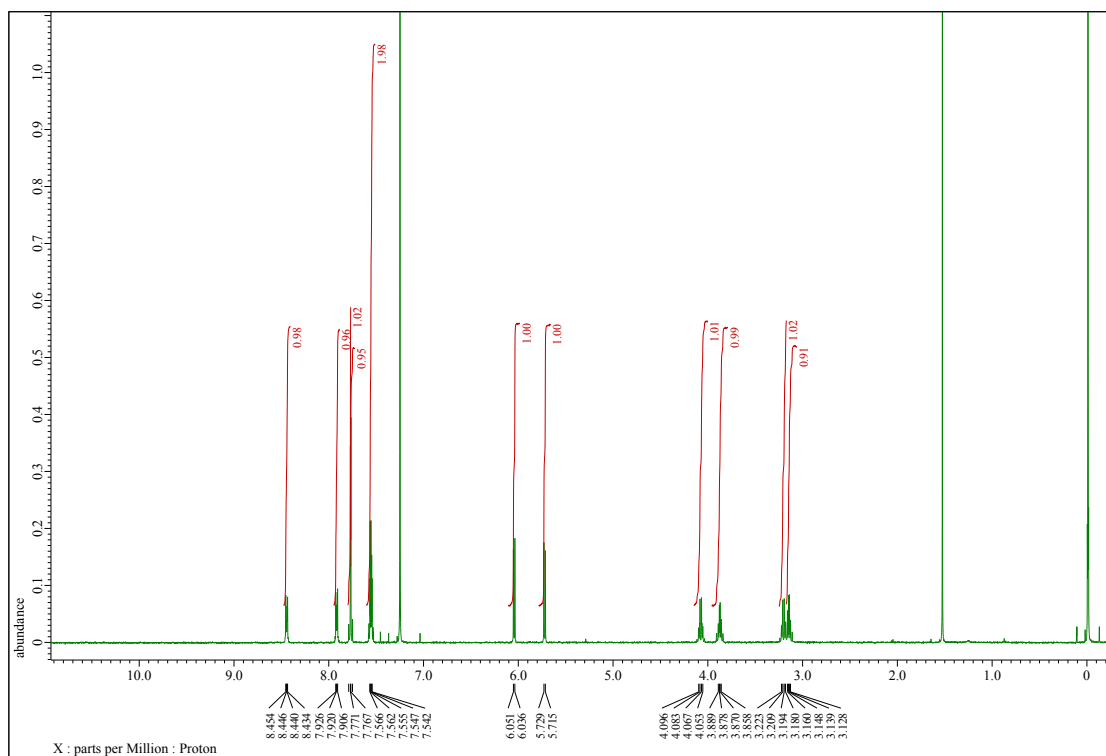
Synthesis of (*S_p*)-**8**



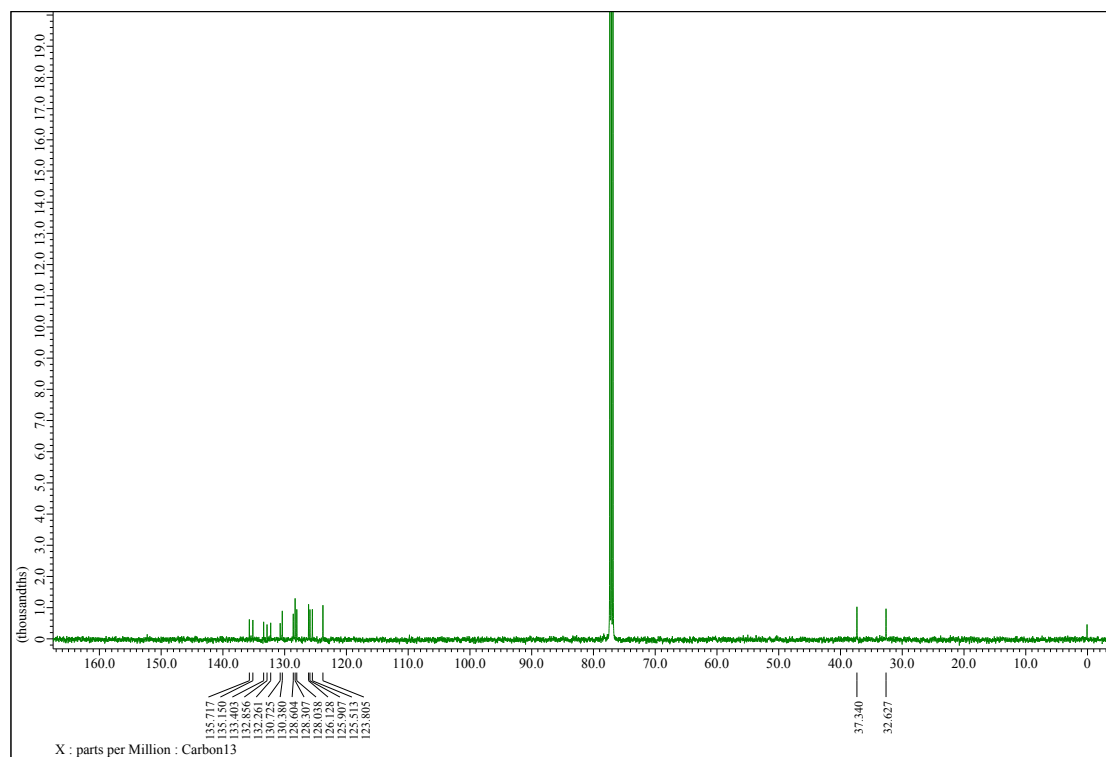
(*S_p*)-**6** (51.3 mg, 0.12 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After toluene (100 mL), THF (1.0 mL), and I₂ (13.8 mg, 0.05 mmol) were added, the mixture was irradiated from a UV lamp (LED $\lambda = 365$ nm), and the reaction was carried out at room temperature for 2 h with stirring under air. H₂O and NaHSO₃ were added in the reaction mixture. The organic layer was separated, and then aqueous layer was extracted with CH₂Cl₂. The organic layer was washed with H₂O and brine, and dried over MgSO₄. MgSO₄ was removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by GPC (CH₂Cl₂) to afford (*R_p*)-**8** (6.6 mg, 0.016 mmol, 13%) as a colorless solid.

$R_f = 0.46$ (CHCl₃/hexane = 1/2 v/v). ¹H NMR (CDCl₃, 500 MHz) δ 3.14 (dd, $J = 10.31, 5.15$, 2H), 3.20 (dd, $J = 14.32, 7.16$ Hz, 2H) 3.87 (dd, $J = 9.74, 4.87$ Hz, 2H), 4.08 (dd, $J = 15.46, 6.87$ Hz, 2H), 5.72 (d, $J = 7.45$ Hz, 2H), 6.04 (d, $J = 7.45$ Hz, 2H), 7.55 (dd, $J = 6.87, 2.29$ Hz, 2H), 7.56 (dd, $J = 6.87, 2.29$ Hz, 2H), 7.58 (d, $J = 8.59$ Hz, 2H), 7.78 (d, $J = 8.59$ Hz, 2H), 7.92 (dd, $J = 6.87, 2.29$ Hz, 2H), 8.44 (dd, $J = 6.87, 2.29$ Hz, 2H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 32.5, 37.3, 123.7, 125.4, 125.8, 126.1, 128.0, 128.2, 128.5, 130.3, 130.6, 132.2, 132.8, 133.3, 135.1, 135.6 ppm. HRMS (APCI, [M+H]⁺) calcd. for C₃₂H₂₄ + H⁺: 409.1951, found 409.1959. $[\alpha]_D^{25} = +713.3$ (c 0.02, CHCl₃).

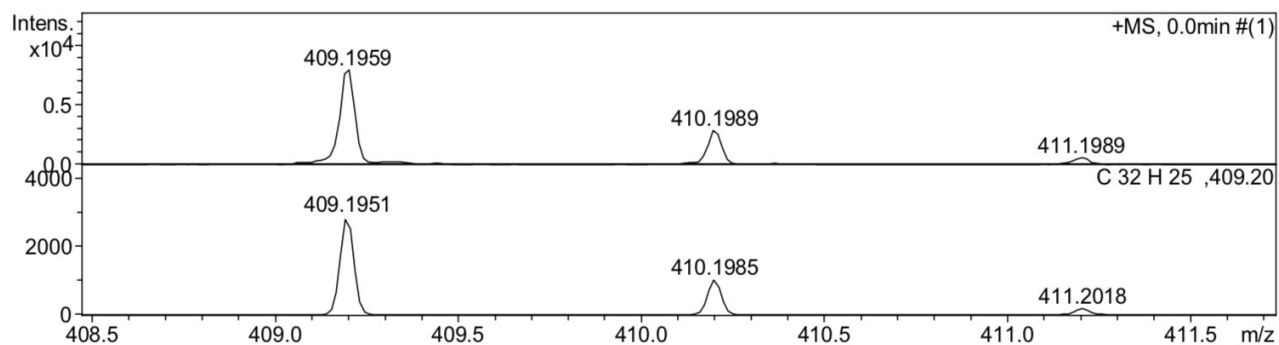
(*S_p*)-**8** was obtained in 12% yield by the same procedure of (*R_p*)-**8**. HRMS (APCI) calcd. for C₃₂H₂₄ + H⁺: 409.1951, found 409.1963. $[\alpha]_D^{25} = -713.3$ (c 0.03, CHCl₃).



^1H NMR spectrum of (*R*_p)-8.



^{13}C NMR spectrum of (*R*_p)-8.



#	m/z	Res.	S/N	I	FWHM
1	409.1959	9665	125.2	7961	0.0423
2	410.1989	10174	45.2	2870	0.0403
3	411.1989	8746	8.6	546	0.0470

Sum	Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e ⁻
C 32	H 25	0.009	409.1951	-2.02	-1.40	-0.83	20.50	ok	even

Results of mass spectrometry of (*R_p*)-**8**; upper and lower Mass spectra indicate experimental and theoretical spectra, respectively.

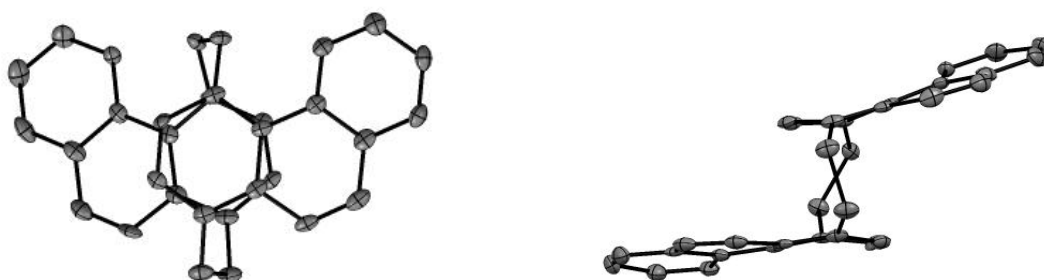


Figure S6. ORTEP drawings (top and side views) of (*R_p*)-**8**; CCDC-2084828. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S5. Crystallographic data and structure refinements for (*R_p*)-**8**.

Formula	C ₃₂ H ₂₄
Formula weight	408.51
Temperature (K)	123
Crystal color, habit	colourless, plate
Crystal size, mm	0.01×0.01×0.005
Crystal system	monoclini
Space group	<i>P</i> 1 2 ₁ 1(#4)
<i>a</i> , Å	8.2667(12)
<i>b</i> , Å	12.9527(18)
<i>c</i> , Å	9.9631(16)
<i>α</i> , deg	90
<i>β</i> , deg	102.109(15)
<i>γ</i> , deg	90
<i>V</i> , Å ³	1043.1(3)
<i>Z</i> value	2
<i>D</i> _{calcd} , g cm ⁻³	1.301
<i>μ</i> (MoKα), cm ⁻¹	0.073
<i>F</i> (000)	432.0
2 <i>θ</i> _{max} , deg	62.112
No. of reflections measured	5071
No. of observed reflections	4589
No. of variables	289
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^[a]	0.0800(2719)
w <i>R</i> ₂ (all reflns) ^[b]	0.1571(4589)
Goodness of fit	1.038
Flack parameter	1.9(10)

[a] $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$.

Recrystallization solvent: toluene

The single crystal X-ray experimental data above do not support the determination of the absolute structure, which was determined by the corresponding diastereomer precursor.

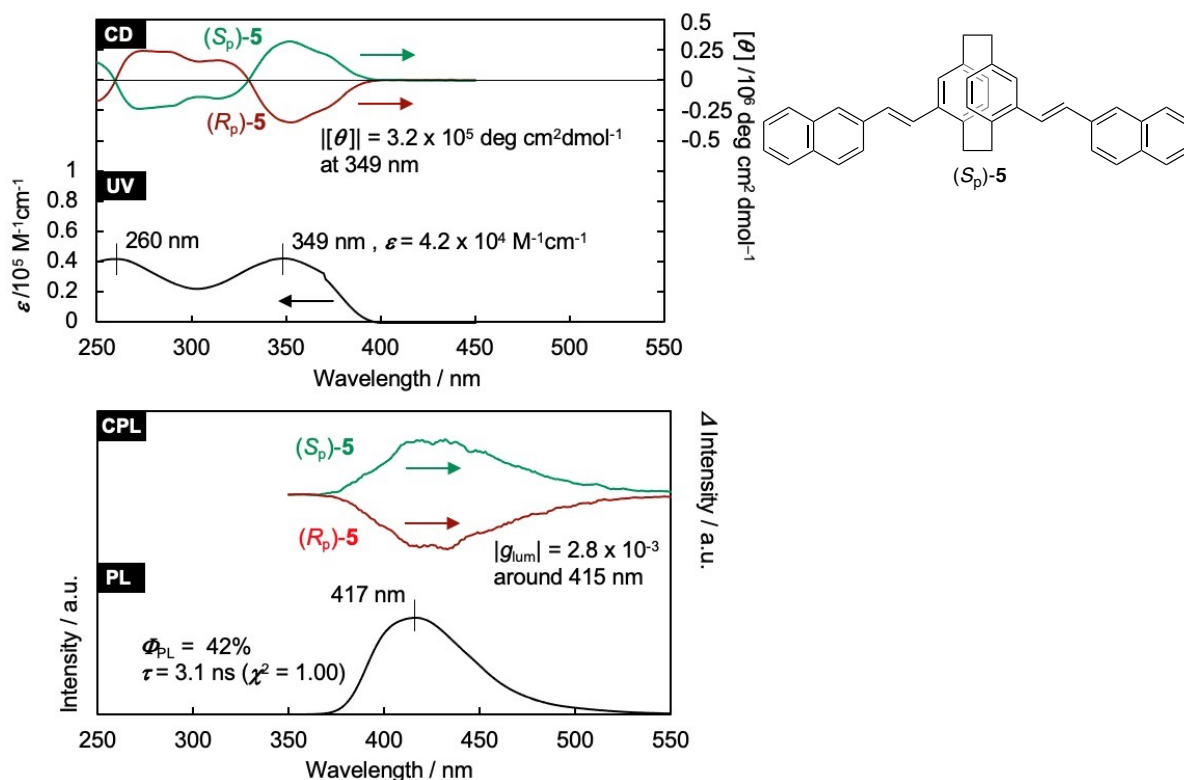


Figure S7. UV-vis absorption, CD, PL, and CPL spectra of (*R_p*)- and (*S_p*)-**5** in dilute CHCl₃ (1.0×10^{-5} M); excitation wavelength = 349 nm for PL and 290 nm for CPL.

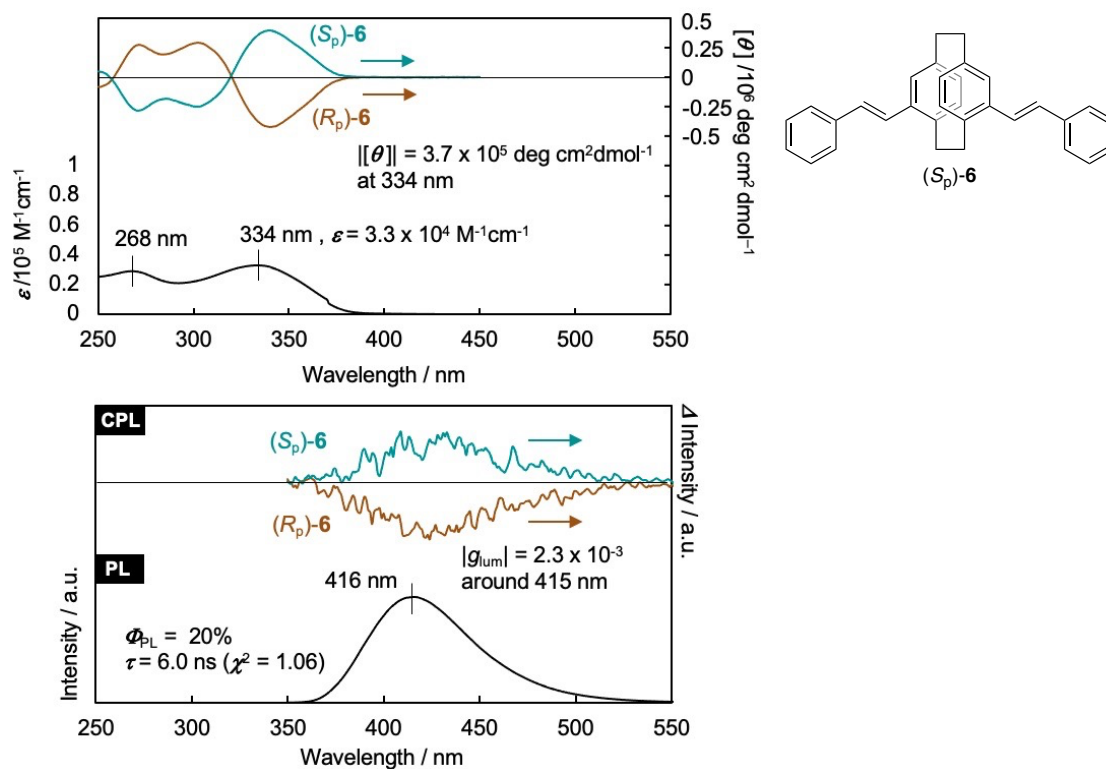


Figure S8. UV-vis absorption, CD, PL, and CPL spectra of (*R_p*)- and (*S_p*)-**6** in dilute CHCl₃ (1.0×10^{-5} M); excitation wavelength = 349 nm for PL and 290 nm for CPL.

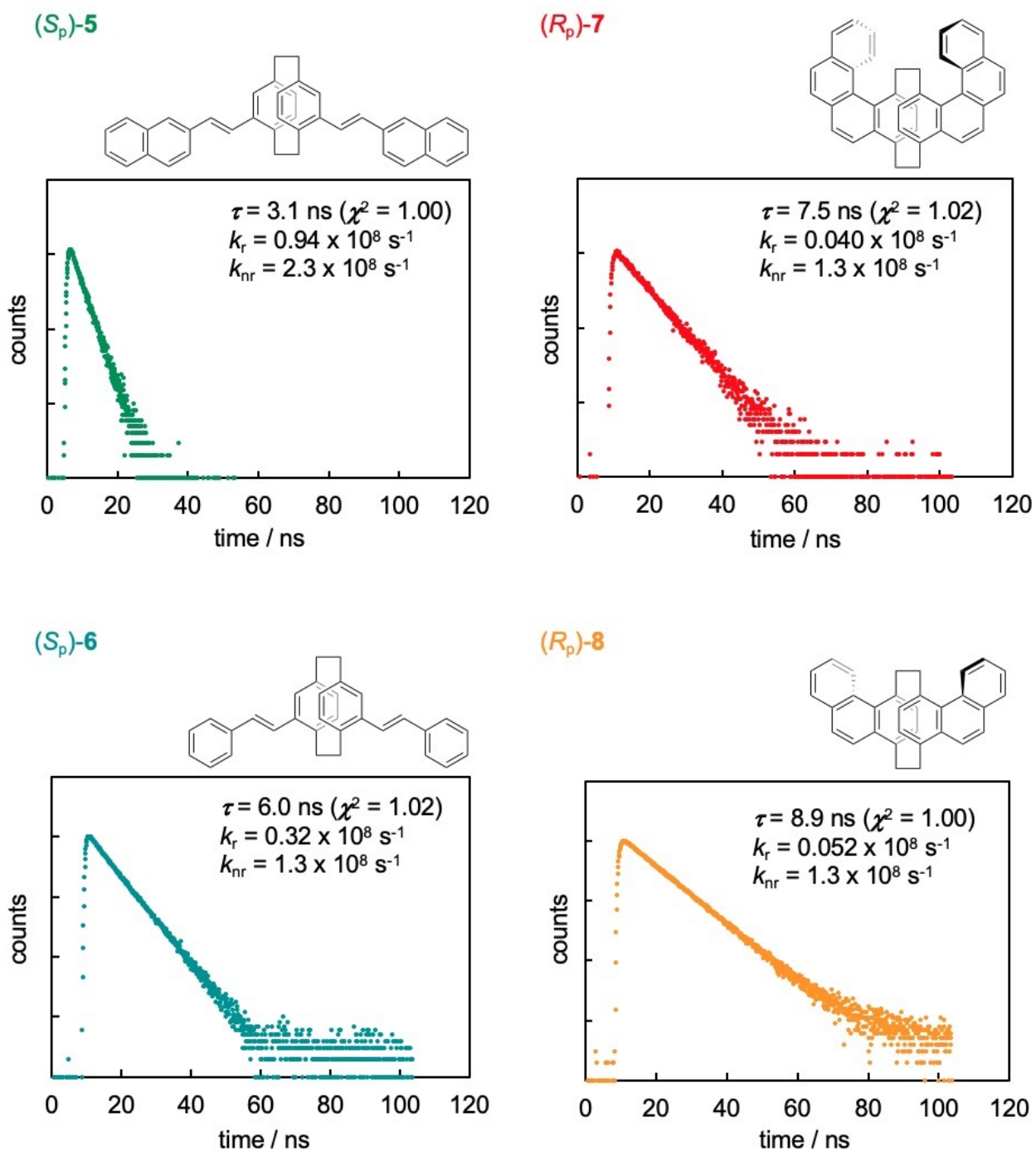
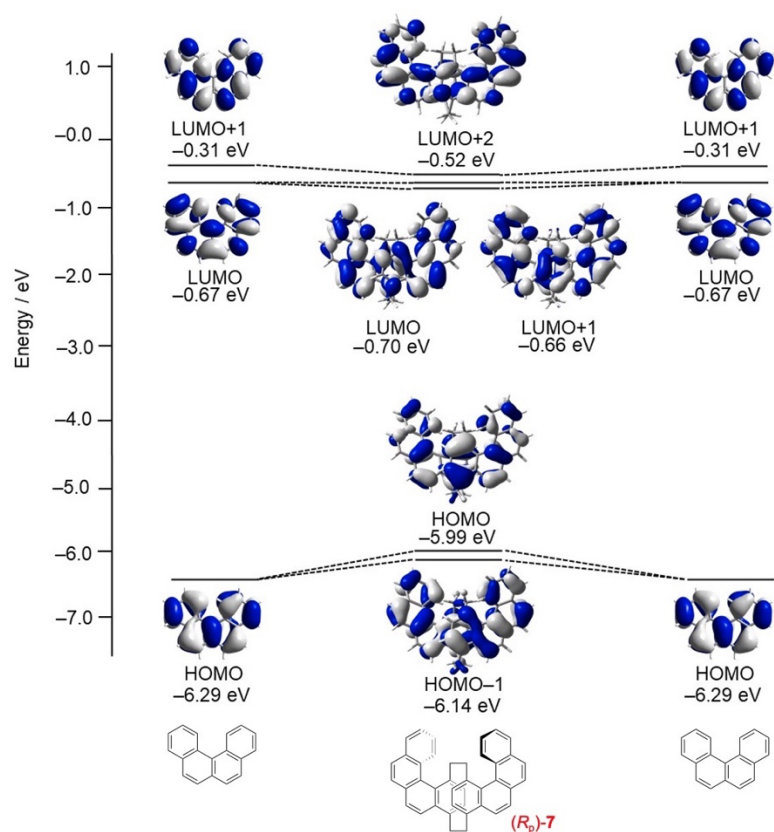


Figure S9. PL decay curves and the data (τ = PL lifetime, k_r = radiative decay rate, and k_{nr} = non-radiative decay rate). The decay curves were obtained in their CHCl_3 solution ($1.0 \times 10^{-5} \text{ M}$), and monitored at each PL peak top. All PL decay profiles were fitted with a single exponential function.

(A)



(B)

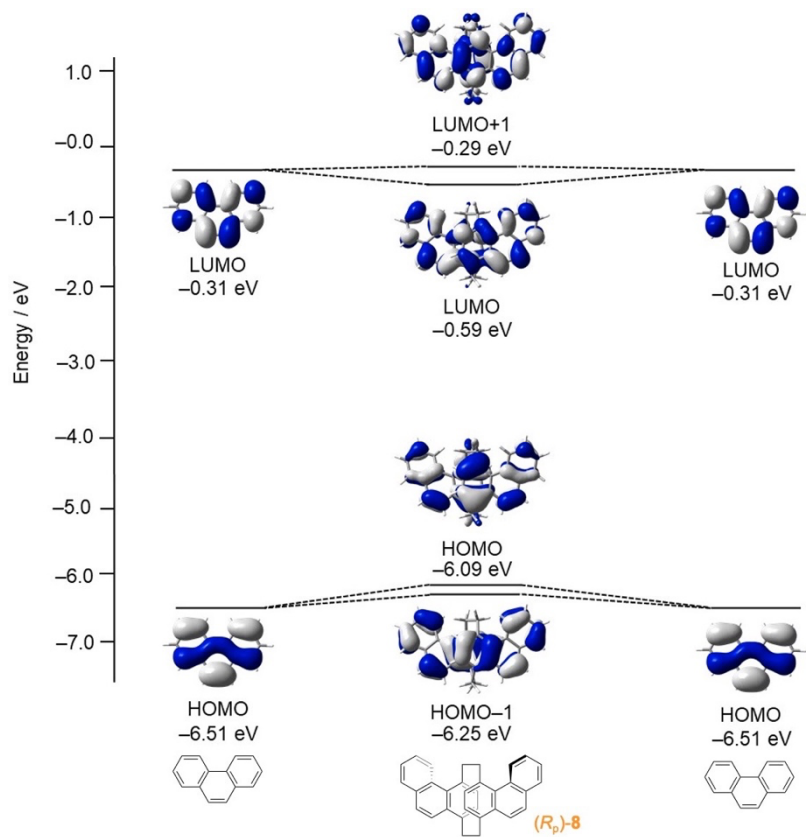


Figure S10. Molecular orbitals of (A) (R_p) -7 and (B) (R_p) -8 with monomeric units (MN15/6-31G(d)).

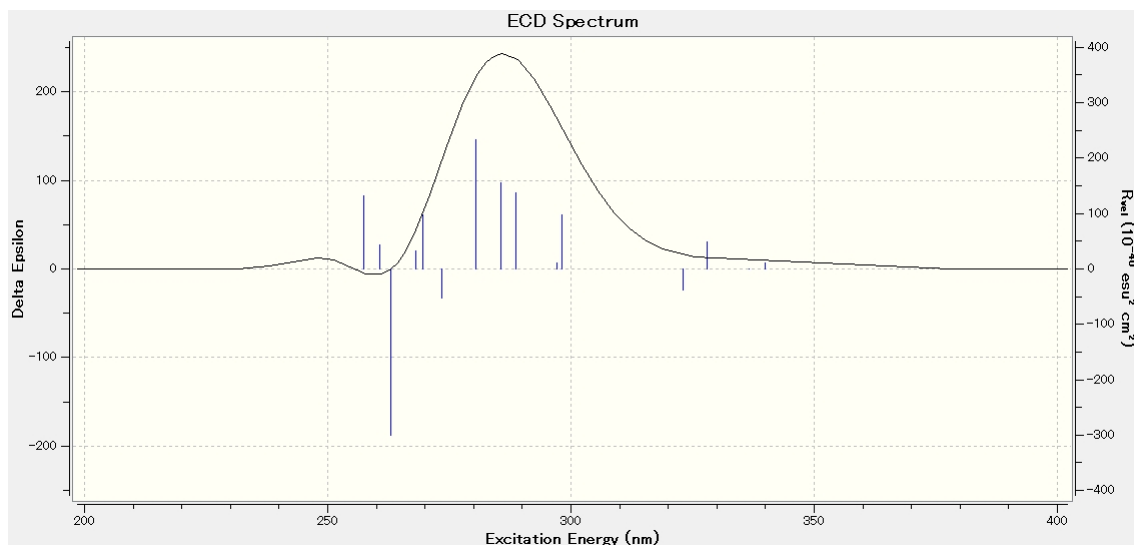


Figure S11. Calculated ECD spectra of (*R_p*)-7 estimated by TD-DFT calculation (TD-MN15/6-31G(d)//MN15/6-31G(d)).

Table S6. Selected data for excitation energy, major configuration, coefficient, oscillator strength, and rotatory strengths for (*R_p*)-7.^a

State	Excitation energy / eV (/ nm)	Major Configuration	Coefficient	Oscillator strength	Rotatory Strengths / 10 ⁻⁴⁰ esu ² cm ²
S ₁	3.65 (340)	H→L+2	0.4128	0.0072	9.9302
S ₂	3.68 (337)	H-1→L+2	0.2977	0.0000	0.2658
S ₃	3.78 (328)	H→L+1	0.5240	0.0039	49.1631
S ₄	3.84 (323)	H→L	0.5150	0.0425	-37.5011
S ₅	4.16 (298)	H-1→L+1	0.5577	0.0245	97.2531
S ₆	4.17 (297)	H-2→L	0.3838	0.0089	11.3506
S ₇	4.29 (289)	H→L+2	0.4367	0.0587	137.9363
S ₈	4.34 (286)	H-1→L+2	0.4929	0.9610	156.3373
S ₉	4.42 (280)	H-2→L+2	0.3955	0.1525	233.2631
S ₁₀	4.53 (274)	H-2→L+1	0.3949	0.1662	-52.7694

^a Estimated from TD-DFT calculations (TD-MN15 /6-31G(d)) based on optimized structures determined by DFT calculation (MN15/6-31G(d)). H and L denote HOMO and LUMO.

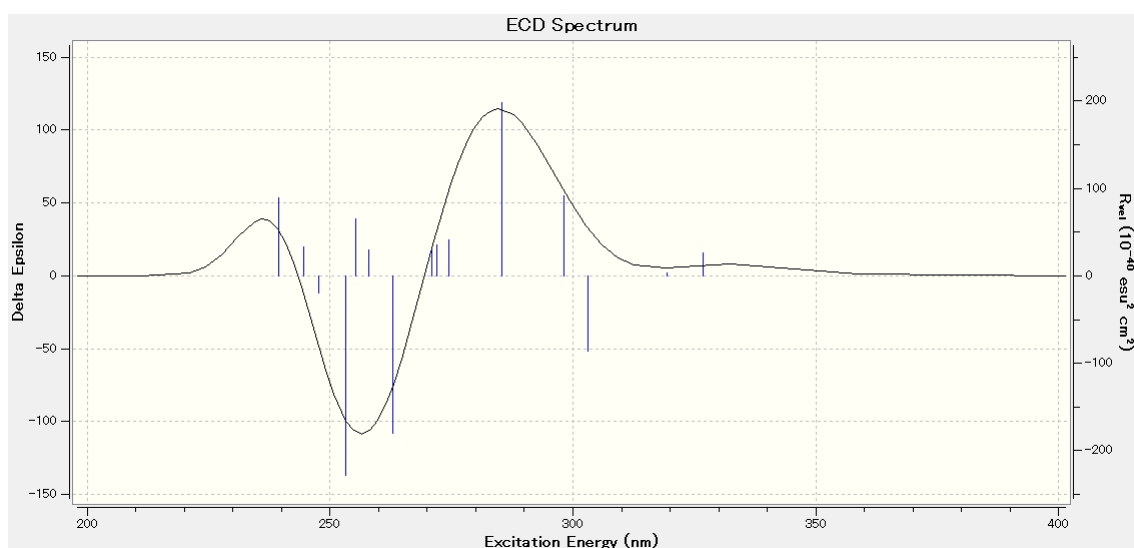


Figure S12. Calculated ECD spectra of (*R_p*)-**8** estimated by TD-DFT calculation (TD-MN15/6-31G(d)//MN15/6-31G(d)).

Table S7. Selected data for excitation energy, major configuration, coefficient, oscillator strength, and rotatory strengths for (*R_p*)-**8**.^a

State	Excitation energy / eV (/ nm)	Major Configuration	Coefficient	Oscillator strength	Rotatory Strengths / 10^{-40} esu ² cm ²
S ₁	3.79 (327)	H→L	0.5216	0.0036	26.5888
S ₂	3.88 (319)	H-2→L	0.4026	0.0015	2.7175
S ₃	4.09 (303)	H→L+2	0.4549	0.0914	-86.0892
S ₄	4.16 (298)	H→L+2	0.4114	0.0373	90.9670
S ₅	4.34 (285)	H-1→L	0.4843	0.1082	197.6851
S ₆	4.52 (274)	H-2→L+1	0.4743	0.0025	40.8013
S ₇	4.56 (272)	H-2→L	0.4624	0.0008	35.7537
S ₈	4.57 (271)	H→L+2	0.4638	0.0021	33.0991
S ₉	4.72 (263)	H→L+3	0.4574	0.2597	-179.5021
S ₁₀	4.80 (258)	H-2→L+2	0.5731	0.8068	29.4767

^a Estimated from TD-DFT calculations (TD-MN15 /6-31G(d)) based on optimized structures determined by DFT calculation (MN15/6-31G(d)). H and L denote HOMO and LUMO.

Table S8. Cartesian coordinate of (R_p)-7 in the ground state (MN15/6-31G(d)).

atom	x	y	z
C	5.62526	-0.94375	1.23681
C	5.26244	0.35763	1.39375
C	4.13911	0.90112	0.69272
C	3.3391	0.07746	-0.1269
C	3.85309	-1.24111	-0.45733
C	4.96227	-1.76221	0.26956
H	6.46353	-1.36507	1.78821
H	5.8139	1.01541	2.06303
C	2.09862	0.61386	-0.65465
C	0.98487	-0.20495	-1.04023
C	1.90769	2.03243	-0.64099
C	-0.02263	0.38421	-1.78181
C	0.72362	2.60679	-1.18709
C	-0.13396	1.78241	-1.88987
H	-0.86634	-0.22303	-2.11016
H	-1.03121	2.20213	-2.34226
C	2.83207	2.85005	0.08371
C	3.85724	2.29728	0.7895
H	4.52059	2.91714	1.38991
H	2.67798	3.9261	0.10208
C	0.69046	-1.5405	-0.36525
H	1.4798	-1.74966	0.3634
H	0.69796	-2.38514	-1.06676
C	0.22216	3.9686	-0.75572
H	0.95579	4.77174	-0.90267
H	-0.64459	4.21812	-1.37978
C	-0.22257	3.9688	0.75518
C	-0.724	2.60709	1.18689
H	-0.95622	4.77196	0.90193
H	0.64417	4.2185	1.37918
C	-1.90805	2.03257	0.64091
C	0.13363	1.78289	1.88983
C	-2.09885	0.61399	0.65475
C	-2.83255	2.85002	-0.08383
C	0.02236	0.38466	1.78206
H	1.03087	2.20274	2.34213
C	-3.3392	0.07738	0.12696
C	-0.98509	-0.20469	1.04057
C	-3.8577	2.29708	-0.78951
H	-2.67858	3.92608	-0.10231
H	0.86608	-0.22248	2.11058
C	-4.13938	0.90088	-0.69264
C	-3.85283	-1.24136	0.45729
C	-0.69069	-1.54041	0.36596
H	-4.52115	2.91681	-1.38993
C	-5.26267	0.3572	-1.39359
C	-4.96197	-1.76264	-0.26952
H	-1.48004	-1.74977	-0.36263
H	-0.69819	-2.38486	1.0677
C	-5.62524	-0.94426	-1.23665
H	-5.81429	1.01487	-2.06283
H	-6.46347	-1.36573	-1.78801
C	-5.44832	-3.06006	0.02158
C	-3.37189	-2.00767	1.55036
C	-3.88337	-3.25557	1.83802
H	-3.50018	-3.8101	2.69095
C	-4.91288	-3.80648	1.04708
H	-5.30235	-4.7966	1.26933
C	5.44896	-3.05948	-0.02161
C	3.37257	-2.00737	-1.55062
C	3.88439	-3.25511	-1.83835
H	3.5015	-3.80961	-2.69144
C	4.91386	-3.8059	-1.04729
H	5.30361	-4.7959	-1.26961
H	-6.27921	-3.44277	-0.56859
H	6.27985	-3.44206	0.56863
H	2.60607	-1.5819	-2.19143
H	-2.60533	-1.58212	2.19105

Table S9. Cartesian coordinate of (R_p)-**8** in ground state (MN15/6-31G(d)).

atom	x	y	z
C	5.8615	-1.66499	0.42284
C	5.5447	-0.33584	0.61035
C	4.29991	0.18339	0.18752
C	3.33446	-0.67977	-0.39686
C	3.71586	-2.02295	-0.63727
C	4.94342	-2.50909	-0.23051
H	6.82461	-2.05158	0.74594
H	6.26	0.34485	1.06887
H	3.04379	-2.67141	-1.19198
H	5.20779	-3.54373	-0.43391
C	2.04191	-0.15015	-0.80237
C	0.91755	-0.98468	-1.09353
C	1.85972	1.2644	-0.81015
C	-0.15029	-0.40644	-1.75876
C	0.62475	1.82662	-1.23836
C	-0.2872	0.98807	-1.85331
H	-1.00666	-1.02344	-2.03048
H	-1.22533	1.39793	-2.22553
C	2.87861	2.10322	-0.23902
C	4.02443	1.58742	0.27784
H	4.77874	2.23526	0.72059
H	2.71216	3.17774	-0.21794
C	0.67561	-2.32007	-0.39414
H	1.48973	-2.50601	0.31251
H	0.66545	-3.17357	-1.0868
C	0.14954	3.18642	-0.77252
H	0.85428	3.99855	-0.99247
H	-0.77769	3.41934	-1.31058
C	-0.14953	3.18646	0.77249
C	-0.62482	1.82671	1.2384
H	-0.85424	3.99864	0.99238
H	0.7777	3.41938	1.31056
C	-1.85972	1.26445	0.81005
C	0.28704	0.98822	1.85358
C	-2.04194	-0.1501	0.80243
C	-2.87849	2.10322	0.23864
C	0.15012	-0.4063	1.75916
H	1.2251	1.39812	2.2259
C	-3.33446	-0.67973	0.39684
C	-0.91762	-0.9846	1.09384
C	-4.02425	1.58738	-0.27832
H	-2.71201	3.17773	0.21742
H	1.00645	-1.02327	2.03108
C	-4.29979	0.18338	-0.18782
C	-3.71597	-2.02284	0.63745
C	-0.67558	-2.32006	0.39461
H	-4.77848	2.23518	-0.72128
C	-5.54454	-0.33588	-0.61074
C	-4.9435	-2.50899	0.23061
H	-3.04403	-2.67123	1.1924
H	-1.48967	-2.50613	-0.31204
H	-0.66539	-3.17348	1.08736
C	-5.86144	-1.66497	-0.42304
H	-6.25975	0.34478	-1.06948
H	-5.20796	-3.54358	0.43417
H	-6.82452	-2.05157	-0.7462

Table S10. Cartesian coordinate of (R_p)-7 in S_1 state (SS-CASSCF(16e,14o)/6-31G).

atom	x	y	z
C	5.850078	-0.919742	1.174836
C	5.445165	0.339489	1.414223
C	4.284150	0.883368	0.772601
C	3.496133	0.065917	-0.081019
C	4.036601	-1.240849	-0.466483
C	5.180904	-1.735014	0.193080
H	6.709657	-1.325036	1.674169
H	5.982123	0.962917	2.104459
C	2.215514	0.580014	-0.523996
C	1.061913	-0.236488	-0.892923
C	1.976291	2.069372	-0.453932
C	0.138399	0.358448	-1.808261
C	0.830118	2.591638	-1.127130
C	0.058122	1.711981	-1.938703
H	-0.572406	-0.267119	-2.315724
H	-0.703859	2.134495	-2.565167
C	2.816023	2.827769	0.314562
C	3.916706	2.254481	0.988204
H	4.533448	2.863197	1.620535
H	2.645995	3.880896	0.419116
C	0.686996	-1.508751	-0.151702
H	1.423770	-1.689656	0.618715
H	0.725235	-2.372953	-0.809942
C	0.258666	3.955700	-0.801037
H	1.011782	4.734742	-0.858072
H	-0.485705	4.197680	-1.549831
C	-0.415264	4.026390	0.626236
C	-0.928466	2.674381	1.083693
H	-1.186819	4.787400	0.602614
H	0.321223	4.364491	1.344002
C	-2.062991	2.029243	0.454208
C	-0.156671	1.927579	1.938799
C	-2.239233	0.640851	0.559971
C	-2.967345	2.787644	-0.343042
C	-0.223496	0.506940	1.901430
H	0.661562	2.384939	2.459632
C	-3.457067	0.048757	0.042366
C	-1.124205	-0.139906	1.091028
C	-3.970522	2.187002	-1.021591
H	-2.826591	3.845391	-0.433048
H	0.588342	-0.043735	2.339288
C	-4.241914	0.805031	-0.841197
C	-3.965896	-1.255697	0.435313
C	-0.739896	-1.494619	0.496486
H	-4.610384	2.756976	-1.668627
C	-5.336145	0.202691	-1.534174
C	-5.035590	-1.823503	-0.271525
H	-1.461425	-1.770218	-0.257358
H	-0.761030	-2.284596	1.239114
C	-5.683038	-1.079161	-1.303345
H	-5.873014	0.795756	-2.250273
H	-6.490084	-1.537108	-1.843114
C	-5.528093	-3.113084	0.089266
C	-3.511189	-1.952658	1.603545
C	-4.024959	-3.172721	1.953788
H	-3.679694	-3.664291	2.843028
C	-5.034336	-3.781507	1.159163
H	-5.417470	-4.746920	1.427946
C	5.702219	-2.993131	-0.158554
C	3.515182	-2.001058	-1.531932
C	4.051946	-3.218300	-1.875163
H	3.636233	-3.771057	-2.695707
C	5.144929	-3.733354	-1.169578
H	5.555717	-4.688663	-1.433759
H	-6.320693	-3.535862	-0.499417
H	6.563598	-3.359867	0.367836
H	2.699633	-1.612878	-2.104534
H	-2.787585	-1.489788	2.239056

Table S11. Cartesian coordinate of (R_p)-**8** in S_1 state (SS-CASSCF(16e,14o)/6-31G).

atom	x	y	z
C	-5.94169	-1.74278	-0.46234
C	-5.63654	-0.42682	-0.70642
C	-4.41010	0.11977	-0.29507
C	-3.45373	-0.69264	0.33656
C	-3.81662	-2.02251	0.62691
C	-5.02745	-2.54022	0.23147
H	-6.88362	-2.14957	-0.77608
H	-6.34680	0.20935	-1.20082
H	-3.15450	-2.63983	1.19656
H	-5.27599	-3.55642	0.47048
C	-2.16681	-0.11463	0.75459
C	-1.04328	-0.91608	1.16730
C	-2.00558	1.28554	0.70636
C	-0.05244	-0.29162	1.89773
C	-0.80167	1.88632	1.19695
C	0.05058	1.11555	1.92765
H	0.76961	-0.86604	2.28087
H	0.92552	1.55356	2.36787
C	-3.02720	2.09070	0.06939
C	-4.15046	1.53428	-0.44618
H	-4.89434	2.14278	-0.92517
H	-2.88470	3.15039	0.00417
C	-0.72686	-2.27360	0.54338
H	-1.47398	-2.51231	-0.19721
H	-0.74289	-3.07841	1.27373
C	-0.32405	3.23998	0.71451
H	-1.07100	4.02040	0.80360
H	0.51240	3.54552	1.33063
C	0.14576	3.16395	-0.78809
C	0.71085	1.81745	-1.18957
H	0.85986	3.96423	-0.95901
H	-0.70333	3.37434	-1.42778
C	1.95872	1.29726	-0.63349
C	-0.10259	0.90054	-1.93924
C	2.17171	-0.18486	-0.63913
C	2.95370	2.10640	-0.08397
C	0.02894	-0.44224	-1.82903
H	-0.90083	1.30434	-2.53416
C	3.50552	-0.70074	-0.35871
C	1.01150	-1.03736	-0.95090
C	4.16513	1.57828	0.36143
H	2.79808	3.16595	-0.01682
H	-0.66580	-1.08581	-2.33818
C	4.48449	0.16733	0.17613
C	3.86694	-2.02860	-0.60990
C	0.67158	-2.29189	-0.15900
H	4.91319	2.22078	0.78416
C	5.74972	-0.32377	0.48184
C	5.13466	-2.49927	-0.30735
H	3.15789	-2.69218	-1.06144
H	1.43774	-2.45121	0.58700
H	0.68979	-3.16962	-0.80411
C	6.07844	-1.65028	0.25090
H	6.48305	0.34385	0.89475
H	5.38435	-3.52261	-0.51255
H	7.05946	-2.01205	0.49121

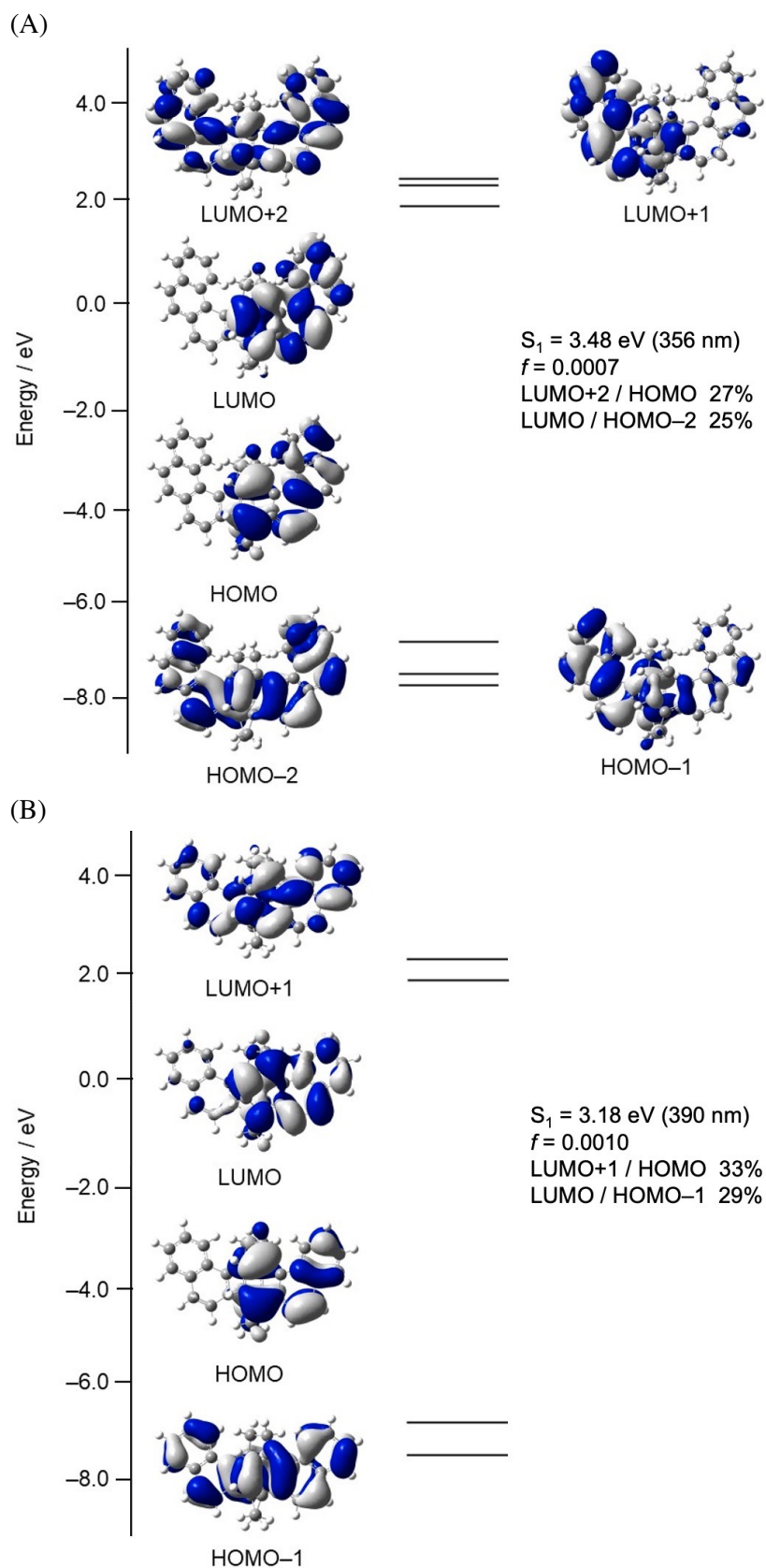


Figure S13. Selected Molecular orbitals of (A) (*R_p*)-**7** and (B) (*R_p*)-**8** and their data for S_1 excitation energy, oscillator strength, major configuration, and coefficient (CIS(D)/6-31G//SS-CASSCF(16e,14o)/6-31G).