Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Optical resolution of pseudo-*para*-disubstituted [2.2]paracyclophane: chiral building block for optically active helicene-stacked molecules emitting circularly polarized luminescence

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General

^{1}H and ^{13}C spectra were recorded on a JEOL JNM ECZ-500R instrument at 500 and 125 MHz, respectively. Samples were analyzed in $CDCl_3$, 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 or Japan Analytical Industry LaboACE LC-5060. Diastereomer ratio (dr) was confirmed by a HPLC (TOSOH UV-8020) equipped with a Daicel Chiralpak® IA column (0.46 cm × 25 cm, solvent flow rate 0.5 mL/min). High-resolution mass (HRMS) spectra were obtained on a Bruker Daltonics microTOF II for atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI). 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. 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 ($[\alpha]^{t}_{D}$) were measured with a HORIBA SEPA-500 polarimeter.

All reactions were carried out under N_2 atmosphere.

Materials

Commercially available compounds used without purification:

(1*S*,4*R*)-Camphanoyl chloride (1*S*,4*R*)-**3**, Tf_2O, styrene **6**, 2-vinylnaphthalene **8**

n-BuLi (1.55 M in hexane), $B(OMe)_3$

NaOH, KOH, 30% H_2O_2, I_2

$Pd(OAc)_2$, $Pd_2(dba)_3$

P(*o*-tol)$_3$, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos)

Et_2O, CH_2Cl_2, EtOH

Pyridine (dehydrated), toluene (dehydrated), THF (dehydrated), DMF (dehydrated)

Et_3N was purchased and distilled over KOH under N_2.

Compounds prepared as described in the literature:

Pseudo-*para*-dibromo[2.2]paracyclophane **1**:

Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527–3533.

(S_p)- and (R_p)-**11**:

Tsuchiya, M.; Maeda, H.; Inoue, R.; Morisaki, Y. *Chem. Commun.* **2021**, *57*, 9256–9259.

X-ray structure determination

Crystals suitable for X-ray diffraction studies were analyzed using a Rigaku MicroMax-007HFM MoKa 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 Olex2 program package. Crystallographic data are given in Tables S1–S5. Deposition numbers 2214406 ((S_p,1*S*,4*R*)-**4**), 2214407 ((R_p,1*S*,4*R*)-**4**), 2214408 ((S_p)-**9**), 2214409 ((R_p)-**10**), and 2214410 ((R_p)-**14**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Computational methods

DFT and TD-DFT calculations[1–5] were carried out by using the Gaussian 16 program package[6], with the 6-31G(d)[7–9] basis set for C and H atoms. Optimized geometries and their molecular orbitals in the ground and S_1 states were determined by DFT and TD-DFT calculations with the CAM-B3LYP[10] functional and integral equation formalism polarizable continuum model (IEF-PCM)[11] method for solvation effect. Cartesian coordinates of all optimized structures are given in Tables S8–S11. The energy levels, electronic configurations, CD, and CPL properties in the singlet excited states were estimated from TD-DFT calculations with the same level of theory.

1. M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439–4449.
2. R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1998**, *109*, 8218–8224.
3. R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, 256, 454–464.
4. C. Adamo, D. Jacquemin, *Chem. Soc. Rev.* **2013**, *42*, 845–856.
5. 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.
6. Gaussian 16, Revision B.01, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2016.

7. 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.

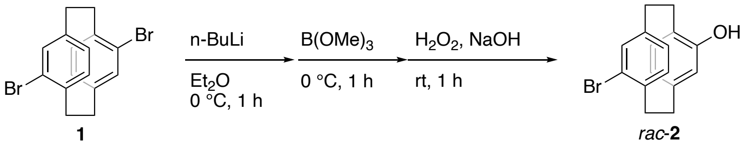
8. P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213–222.

9. T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294–0.

10. T. Yanai, D. Tew, N. Handy, *Chem. Phys. Lett.* **2004**, *393*, 51–57.

11. M. T. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997,** *107*, 3032–3041.

Synthesis of *rac*-**2**



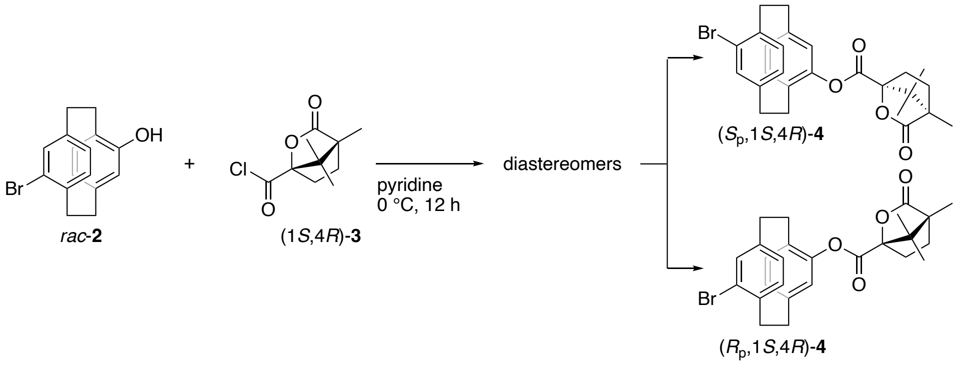
A solution of *n*-BuLi (1.55 M in hexane, 11.3 mL, 17.5 mmol) was slowly added to a solution of **1** (4.94 g, 13.5 mmol) in Et_2O (21 mL) at 0 °C. After 1 h, $B(OMe)_3$ (3.0 mL, 26.8 mmol) was added, and then the mixture was warmed to room temperature. After 1 h, aqueous NaOH (1.0 M, 8.7 mL, 8.7 mmol) and aqueous H_2O_2 (30%, 5.7 mL, 55.9 mmol) were added, and the mixture was stirred for 1 h at room temperature. After the saturated aqueous $NaHCO_3$ solution was added to the reaction mixture, the organic layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine and dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was evaporated. The residue was purified by column chromatography on SiO_2 ($CHCl_3$ as an eluent) to afford *rac*-**2** (2.89 g, 9.5 mmol, 71%) as a pale yellow crystal.

$R_f = 0.35$ ($CHCl_3$ as an eluent).

^1H and ^{13}C NMR spectra were matched with the literature's data.

Delcourt, M.-L.; Reynaud, C.; Turcaud, S.; Favereau, L.; Crassous, J.; Micouin, L.; Benedetti, E. *J. Org. Chem.* **2019**, *84*, 888–899.

Optical resolution: synthesis of (S_P,1S,4R)- and (R_P,1S,4R)-**4**

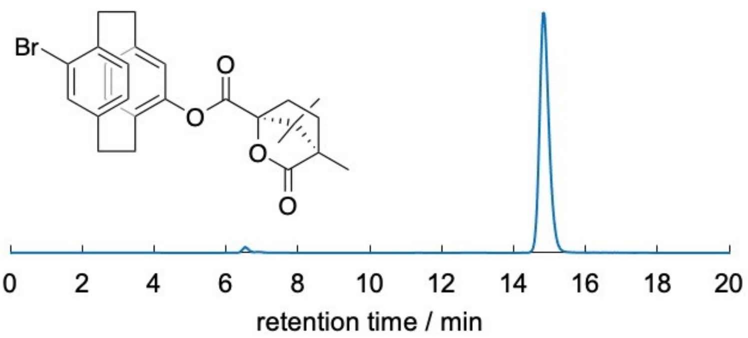


A mixture of *rac*-**2** (3.67 g, 12.1 mmol) and (1S,4R)-camphanoyl chloride (5.25 g, 24.2 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, dry pyridine (101 mL) was added to the mixture at 0 °C, and the reaction was carried out at room temperature for 12 h with stirring. After the reaction mixture was cooled to 0 °C, 6 M HCl was added, and organic species were extracted with CH_2Cl_2 three times. The combined organic layer was washed with aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$. $MgSO_4$ was removed, and the solvent was evaporated. The residue was separated by SiO_2 column chromatography ($CHCl_3$/EtOAc = 1000/2.5 v/v as an eluent) to afford (S_P,1S,4R)-**4** (R_f= 0.38) and (R_P,1S,4R)-**4** (R_f = 0.28) as white powders. Each diastereomer was purified by recrystallization from $CHCl_3$/MeOH to afford (S_p,1S,4R)-**4** (2.17 g, 4.5 mmol, 37%) and (R_p,1S,4R)-**4** (2.20 g, 4.6 mmol, 38%).

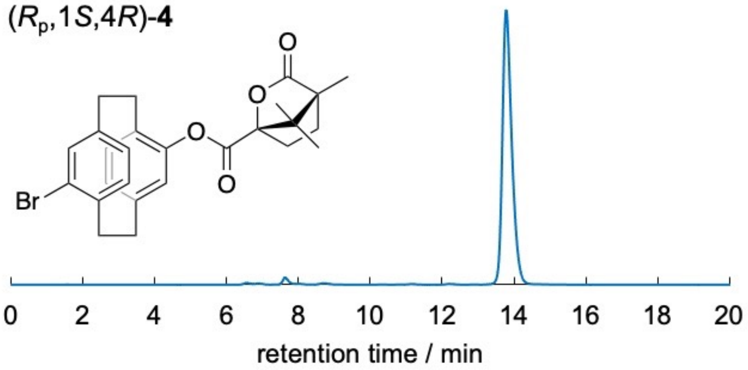
(R_P,1S,4R)-**4**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.15 (s, 3H), 1.18 (s, 3H), 1.21 (s, 3H), 1.77–1.84 (m, 1H), 1.99–2.06 (m, 1H), 2.19–2.26 (m, 1H), 2.56–2.63 (m, 1H), 2.72–2.86 (m, 2H), 2.93–3.03 (m, 2H), 3.07–3.21 (m, 3H), 3.46–3.53 (m, 1H), 6.04 (d, J = 1.7 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 6.48 (d, J = 1.7 Hz, 1H), 6.52 (d, J = 8.0 Hz, 1H), 6.94 (dd, J = 1.7, 1.7 Hz, 1H), 7.12 (dd, J = 1.7, 1.7 Hz, 1H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 9.8, 16.8, 17.0, 28.9, 30.9, 31.1, 32.7, 33.5, 35.3, 54.6, 55.0, 90.9, 126.7, 127.7, 127.8, 127.8, 129.1, 130.4, 134.1, 134.1, 134.4, 137.5, 138.6, 141.3, 148.5, 165.6, 178.3 ppm. HRMS (ESI+) calcd for $C_{26}H_{27}BrO_4+Na^+$: 505.0985, found 505.0987. $[\alpha]^{25}_{\mathrm{D}} = -55.28$ (*c* 0.20, $CHCl_3$).

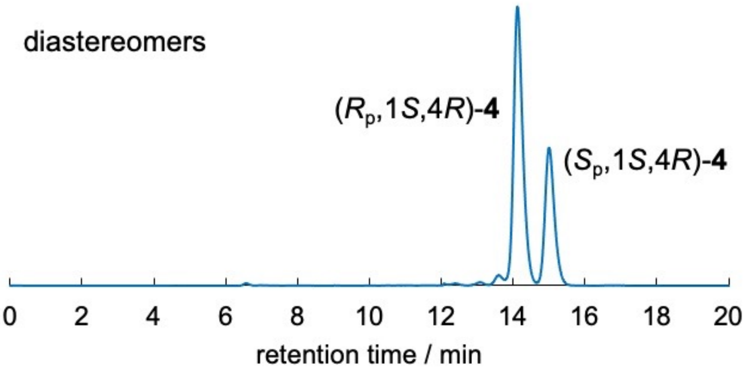
(S_P,1S,4R)-**4**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.17 (s, 3H), 1.20 (s, 3H), 1.21 (s, 3H), 1.79–1.86 (m, 1H), 2.00–2.08 (m, 1H), 2.23–2.31 (m, 1H), 2.56–2.64 (m, 1H), 2.71–2.87 (m, 2H), 2.93–3.22 (m, 5H), 3.46–3.53 (m, 1H), 6.07 (d, *J* = 1.7 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 1.7 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 1.7, 1.7 Hz, 1H), 7.12 (dd, *J* = 1.7, 1.7 Hz, 1H) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) δ = 9.8, 16.9, 16.9, 29.0, 31.1, 31.2, 32.7, 33.5, 35.3, 54.5, 55.0, 90.9, 126.8, 127.7, 127.8, 129.1, 130.4, 134.1, 134.4, 137.5, 138.6, 141.2, 141.3, 148.5, 165.5, 178.1 ppm. HRMS (ESI+) calcd for $C_{26}H_{27}BrO_4+Na^+$: 505.0985, found 505.0969. $[\alpha]^{25}_{D}$ = +55.48 (*c* 0.20, $CHCl_3$).

(S_p,1*S*,4*R*)-**4**



(R_p,1*S*,4*R*)-**4**





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

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

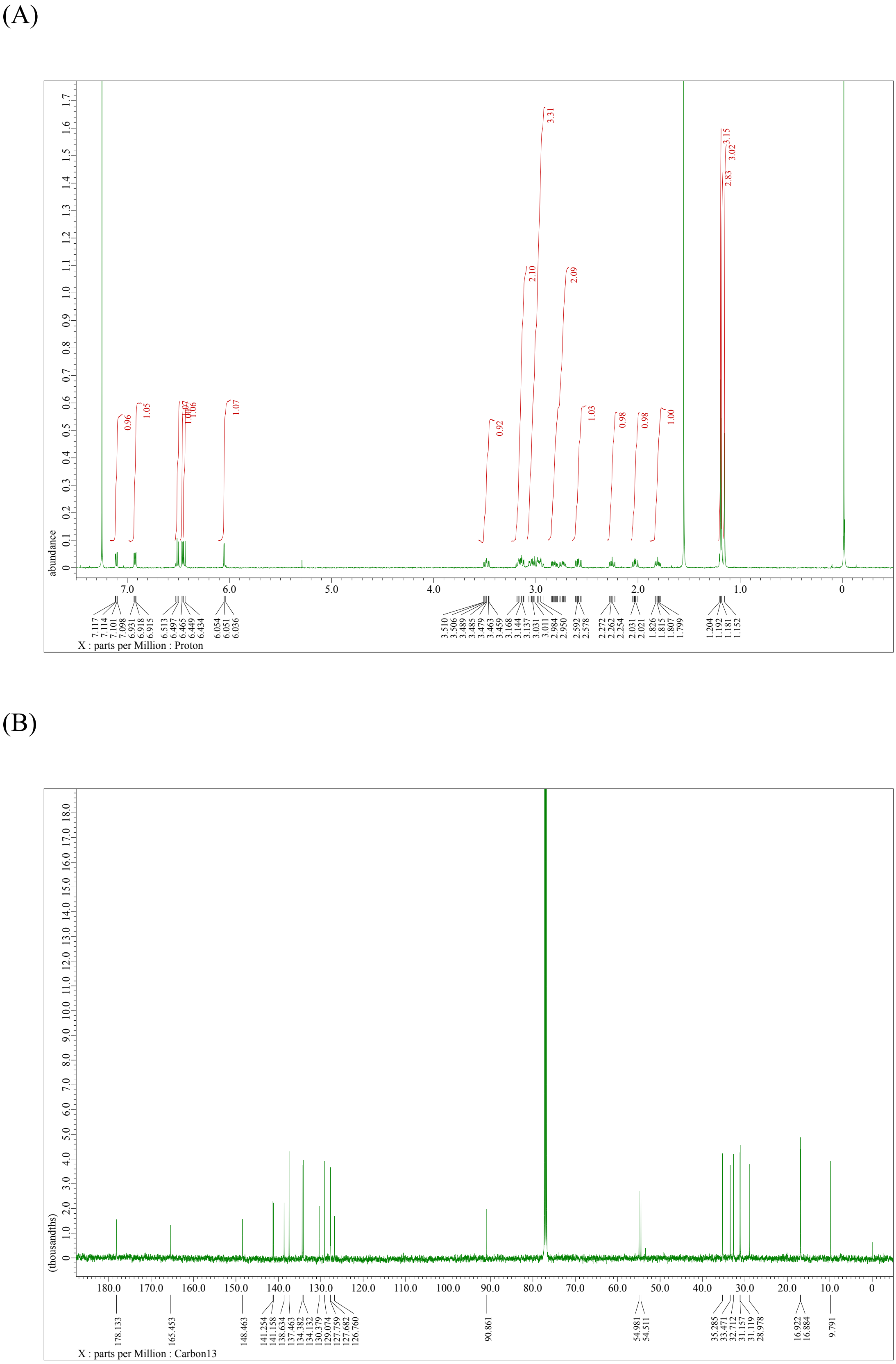


Fig. S2. (A) ^{1}H NMR spectrum and (B) ^{13}C{^{1}H} NMR spectrum of (S_p,1*S*,4*R*)-**4** in $CDCl_3$.

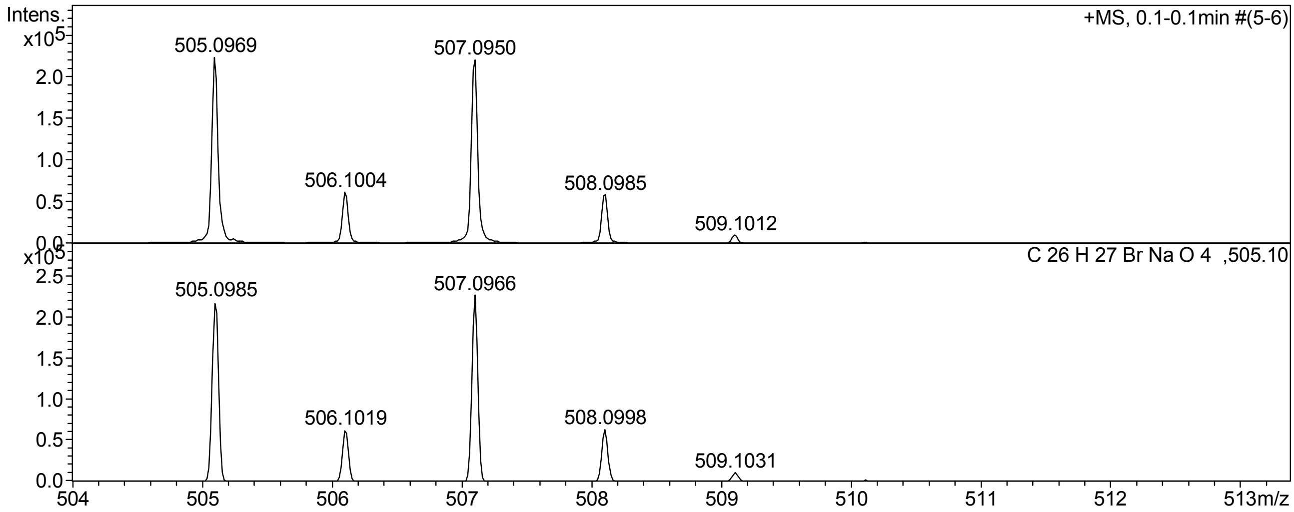
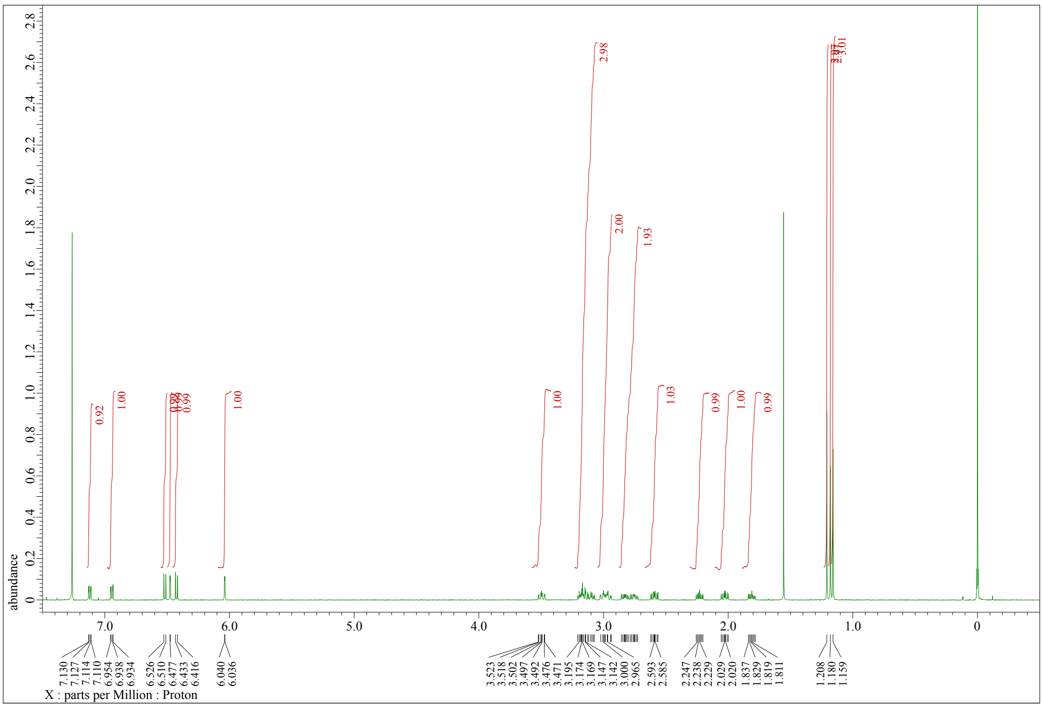


Fig. S3. Mass spectra of (S_p,1S,4R)-**4**. Upper and lower show observed and calculated spectra, respectively.

(A)



(B)

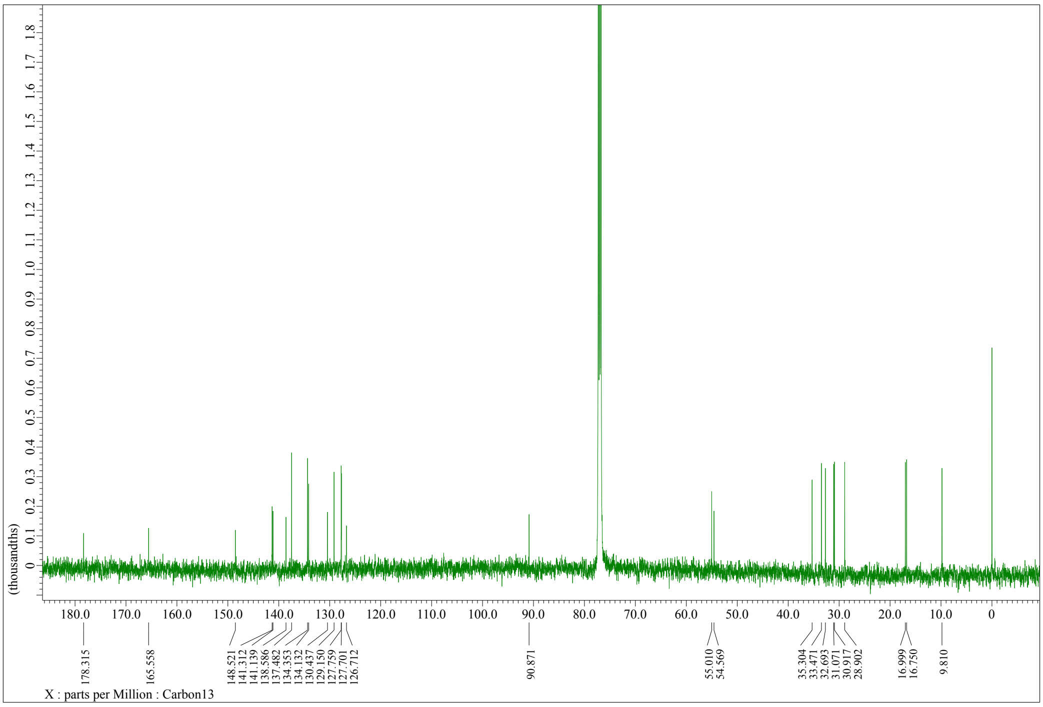


Fig. S4. (A) ^{1}H NMR spectrum and (B) ^{13}C{^{1}H} NMR spectrum of (R_p,1*S*,4*R*)-**4** in $CDCl_3$.

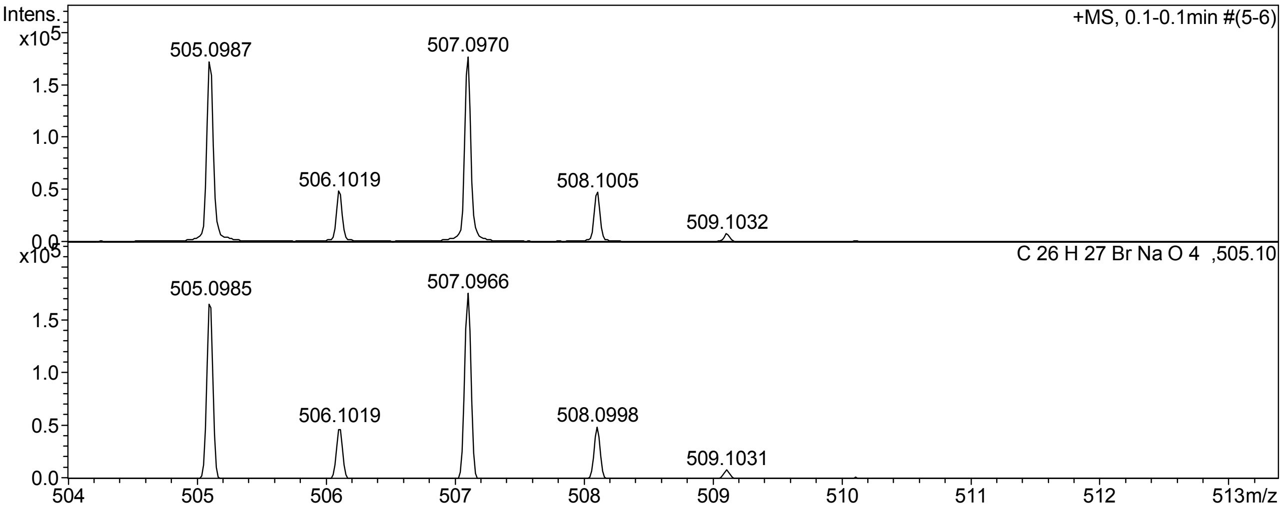


Fig. S5. Mass spectra of (R_p,1*S*,4*R*)-**4**. Upper and lower show observed and calculated spectra, respectively.

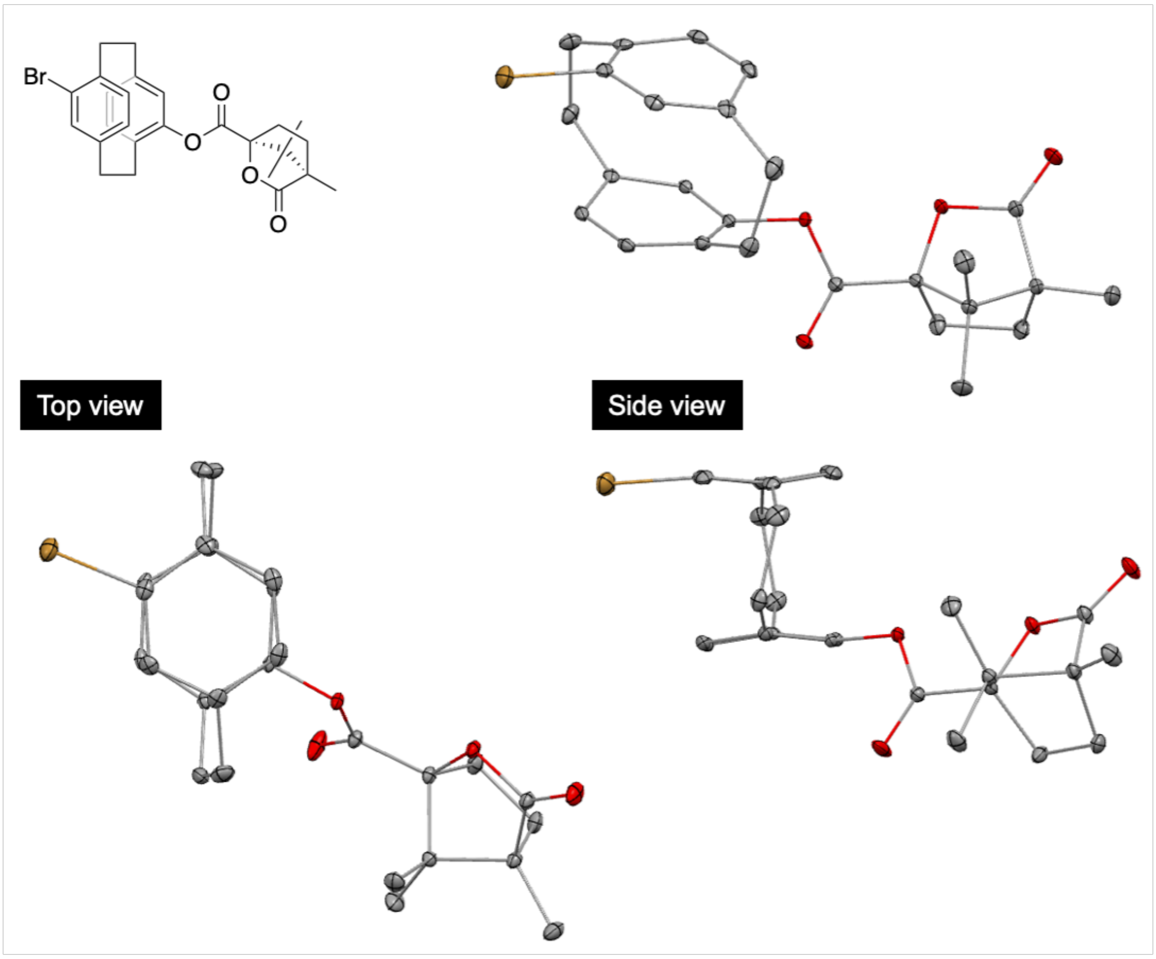


Fig. S6. ORTEP drawings of (S_p,1*S*,4*R*)-**4** (CCDC-2214406). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S1. Crystallographic data for (S_p,1S,4R)-**4**.

Formula	$C_{26}H_{27}BrO_4$
Formula weight	483.38
Temperature (K)	150
Crystal color, habit	colourless, plate
Crystal size, mm	0.3 × 0.3 × 0.05
Crystal system	monoclinic
Space group	$P2_1$ (#4)
a, Å	7.4207(2)
b, Å	10.8719(2)
c, Å	13.8261(4)
α, deg	90
β, deg	105.401(3)
γ, deg	90
V, Å^3	1075.39(5)
Z value	2
D_{calcd}, g cm^{-3}	1.493
μ (MoKα), cm^{-1}	19.43
F(000)	500
$2\theta_{\text{max}}$, deg	62.322
No. of reflections measured	7744
No. of observed reflections	4450
No. of variables	283
R_1 (I > 2σ(I))[a]	0.0368(4337)
wR_2 (all reflns)[b]	0.1049(4450)
Goodness of fit	1.078
Flack Parameter	0.008(9)

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.
Recrystallization solvent: chloroform / methanol

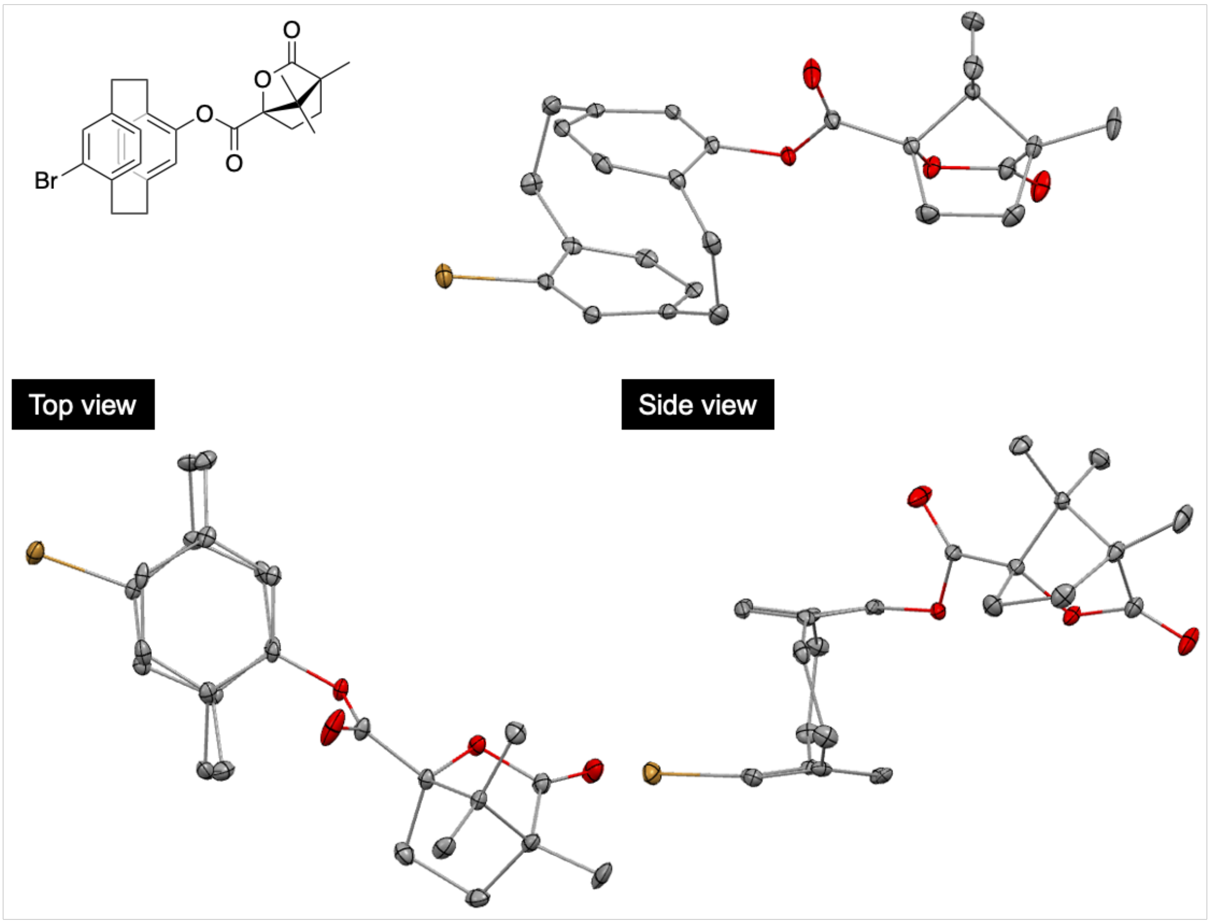


Fig. S7. ORTEP drawings of (R_p,1S,4R)-**4** (CCDC-2214407). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

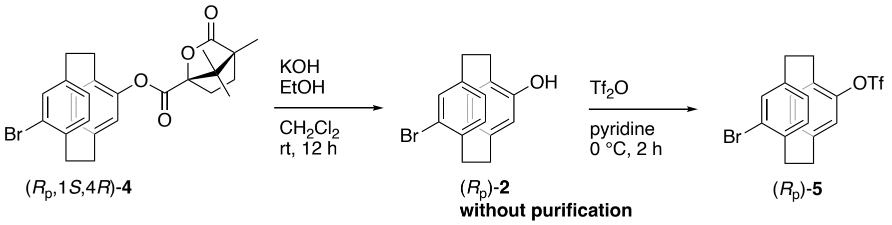
Table S2. Crystallographic data for (R_p,1S,4R)-**4**.

Formula	$C_{26}H_{27}BrO_4$
Formula weight	483.38
Temperature (K)	150
Crystal color, habit	colourless, plate
Crystal size, mm	0.4 × 0.4 × 0.1
Crystal system	monoclinic
Space group	$P2_1$(#4)
a, Å	7.4466(3)
b, Å	10.9055(7)
c, Å	13.5554(6)
α, deg	90
β, deg	99.584(4)
γ, deg	90
V, Å^3	1085.45(10)
Z value	2
D_{calcd}, g cm^{-3}	1.479
μ (MoKα), cm^{-1}	19.25
F(000)	500
$2\theta_{\max}$, deg	62.188
No. of reflections measured	5212
No. of observed reflections	4724
No. of variables	283
R_1 (I > 2σ(I))[a]	0.0577(4560)
wR_2 (all reflns)[b]	0.1589 (4724)
Goodness of fit	1.067
Flack Parameter	-0.005(12)

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

Recrystallization solvent : chloroform / methanol

Synthesis of (R_P)-**5**



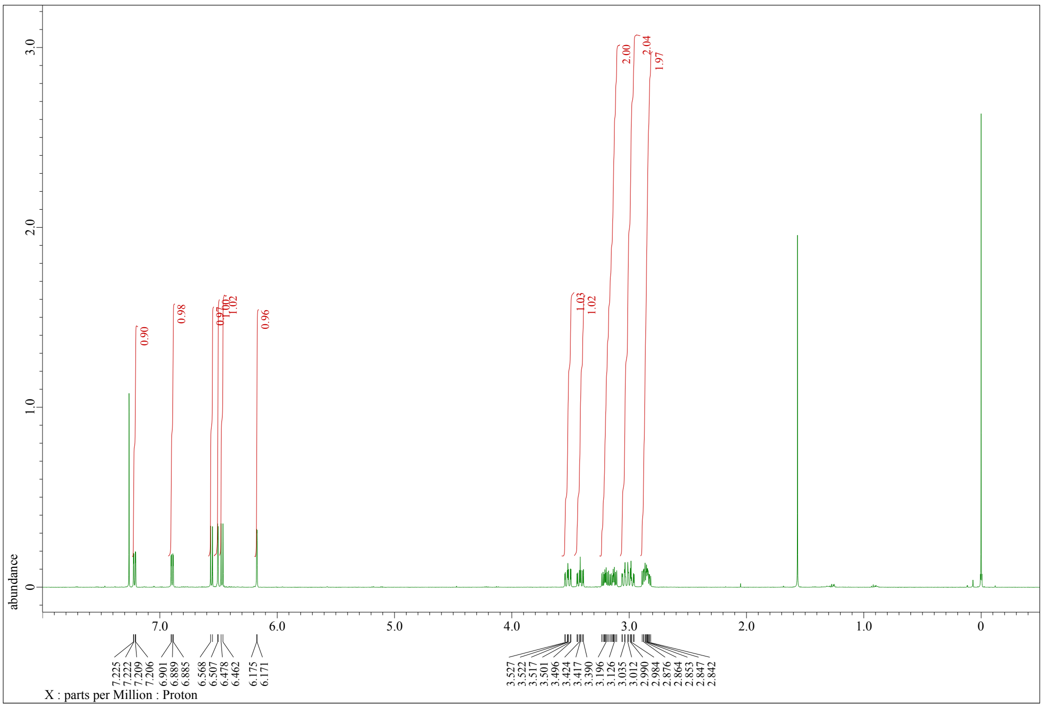
(R_P,1*S*,4*R*)-**4** (2.00 g, 4.1 mmol), EtOH (116 mL) and CH_2Cl_2 (72 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, an aqueous solution of KOH (2.9 g) was added to the mixture. After stirring for 12 h, 6 M HCl (16 mL) was added to the reaction mixture. The organic layer was separated and extracted with CH_2Cl_2 three timers. The combined organic layer was washed with aqueous $NaHCO_3$ and brine, and then dried over $MgSO_4$. $MgSO_4$ 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 (R_p)-**2** in CH_2Cl_2 (44 mL) were added pyridine (4.4 mL, 54.6 mmol) and Tf_2O (2.2 mL, 13.1 mmol) at 0 °C. After being stirred for 2 h at room temperature, 6 M HCl was added to the reaction mixture. The organic layer was separated and extracted with CH_2Cl_2 three timers. The combined organic layer was washed with aqueous $NaHCO_3$ and brine, and then dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was evaporated. The residue was purified by column chromatography on SiO_2 (AcOEt/hexane = 2/1 v/v as an eluent) to afford (R_p)-**5** (1.75 g, 4.0 mmol, 97%) as a yellow liquid.

R_f = 0.88 (AcOEt / hexane = 2/1 v/v as an eluent). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.81–2.90 (m, 2H), 2.95–3.07 (m, 2H), 3.10–3.24 (m, 2H), 3.38–3.45 (m, 1H), 3.49–3.56 (m, 1H), 6.17 (d, *J* = 1.7 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 1.7 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.89 (dd, *J* = 2.3, 1.7 Hz, 1H), 7.22 (dd, *J* = 1.7, 1.7 Hz, 1H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 31.0, 32.6, 33.5, 35.4, 117.6, 120.0, 127.0, 127.9, 128.8, 129.5, 131.6, 134.3, 135.1, 137.7, 138.8, 141.3, 142.3, 148.5 ppm. HRMS (APCI) calcd for $C_{17}H_{14}BrF_3O_3S+H^+$: 434.9872, found 434.9866. $[\alpha]^{25}_\mathrm{D}$ = –91.79 (*c* 0.20, $CHCl_3$).

(S_p)-**5** was obtained in 91% yield by the same procedure of (R_p)-**4**. HRMS (APCI) calcd. for $C_{17}H_{14}BrF_3O_3S+H^+$: 434.9872, found 434.9868. $[\alpha]^{25}_\mathrm{D}$ = +91.61 (*c* 0.25, $CHCl_3$).

(A)



(B)

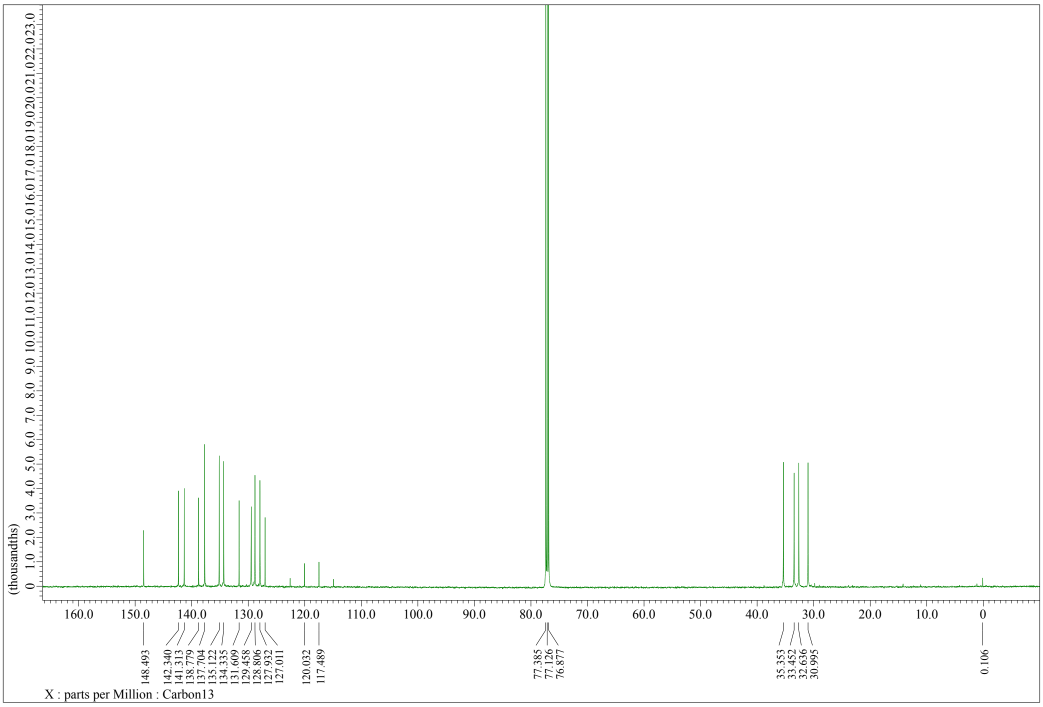


Fig. S8. (A) ^{1}H NMR spectrum and (B) ^{13}C{^{1}H} NMR spectrum of (R_p)-**5** in $CDCl_3$.

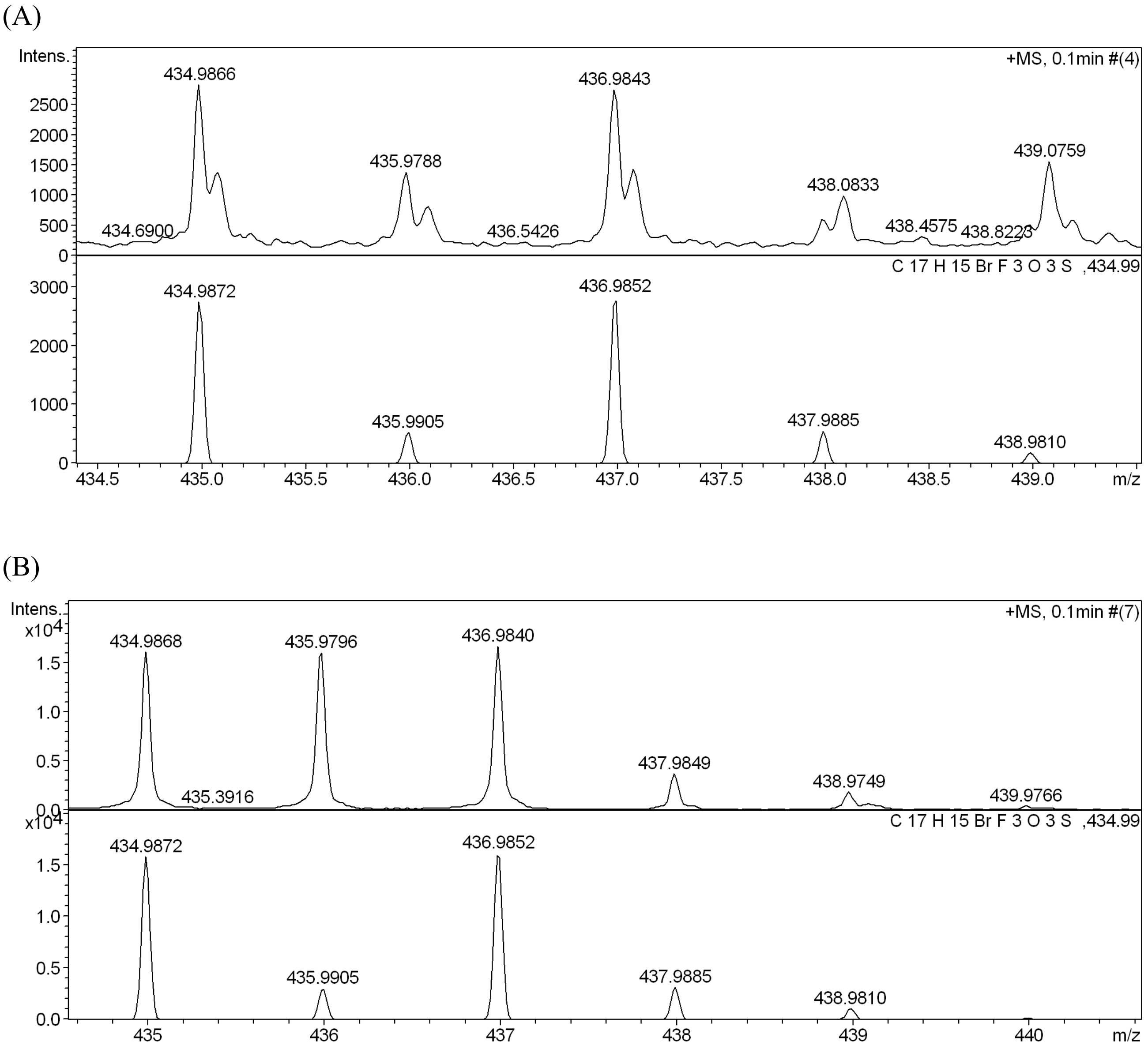
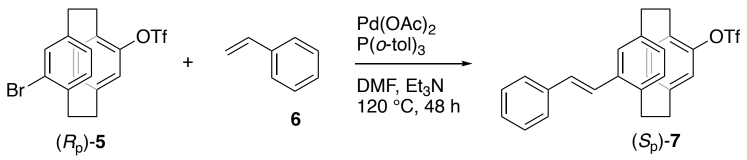


Fig. S9. Mass spectra of (A) (R_p)-**5** and (S_p)-**5**; upper and lower spectra show observed and calculated spectra, respectively.

Synthesis of (S_P)-**7**

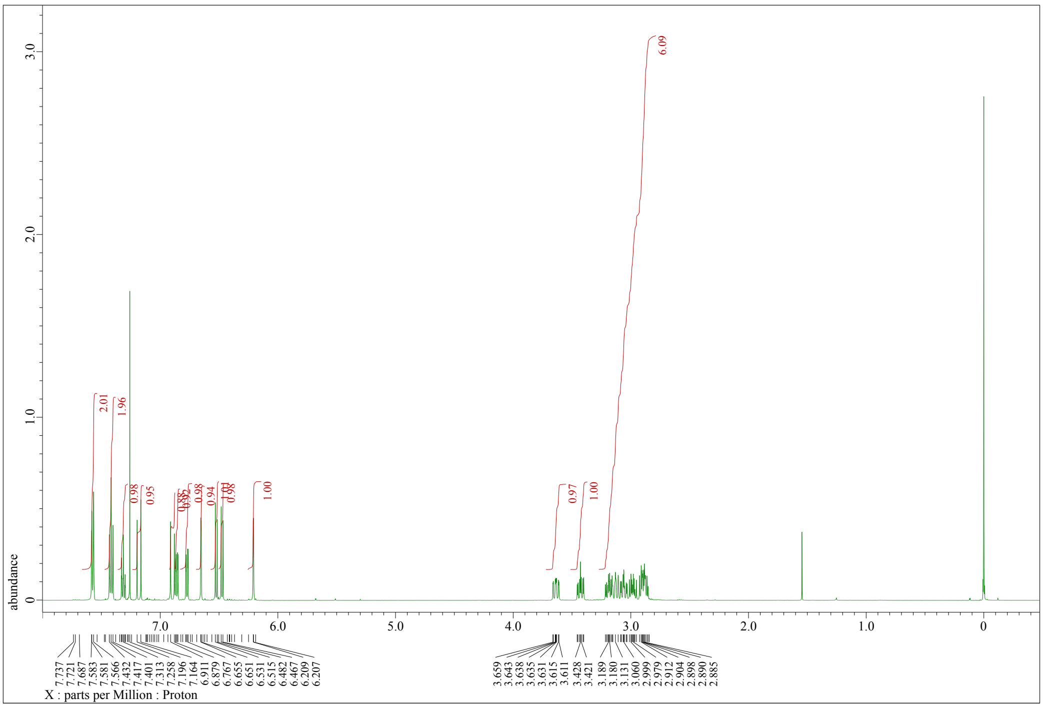


A mixture of (R_p)-**5** (1.75 g, 4.0 mmol), Pd(OAc)$_2$ (46.9 mg, 0.20 mmol) and P(*o*-tol)$_3$ (232.9 mg, 0.76 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, DMF (12 mL), Et$_3$N (62 mL) and styrene **6** (0.65 mL, 613.2 mg, 5.63 mmol) were added, and the reaction was carried out at 120 ºC 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 CH$_2$Cl$_2$. The organic layer was washed with H$_2$O 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 column chromatography on SiO$_2$ (CHCl$_3$/hexane = 1/2 v/v as an eluent) to afford (S_p)-**7** (1.49 g, 4.03 mmol, 81%) as a yellow oil.

R_f = 0.45 (CHCl$_3$/hexane = 1/2 v/v). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 2.82–3.21 (m, 6H), 3.39–3.48 (m, 1H), 3.60–3.69 (m, 1H), 6.21 (d, *J* = 1.7 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 1.7 Hz, 1H), 6.78 (dd, *J* = 1.7, 1.7 Hz, 1H), 6.85 (dd, *J* = 2.3, 1.7 Hz, 1H), 6.90 (d, *J* = 16.0 Hz, 1H), 7.18 (d, *J* = 16.0 Hz, 1H), 7.31 (t, *J* = 7.5, 7.5 Hz, 1H), 7.42 (t, *J* = 7.5, 8.0 Hz, 2H), 7.57 (d, *J* = 6.9 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) δ 30.8, 33.3, 33.8, 33.9, 117.5, 120.1, 126.3, 126.5, 127.6, 127.8, 128.8, 128.9, 129.8, 130.2, 130.4, 131.8, 134.2, 134.6, 137.5, 137.6, 137.8, 139.5, 142.3, 148.3 ppm. HRMS (ESI+) calcd for $C_{25}H_{21}BrF_3O_3S+Na^+$: 481.1056, found 481.1063. $[\alpha]^{25}_D = -60.51$ (*c* 0.11, CHCl$_3$).

(R_p)-**7** was obtained in 80% yield by the same procedure of (S_p)-**7**. HRMS (APCI) calcd. for $C_{25}H_{21}BrF_3O_3S+H^+$: 459.1236, found 459.1227. $[\alpha]^{25}_D = +60.37$ (*c* 0.11, CHCl$_3$).

(A)



(B)

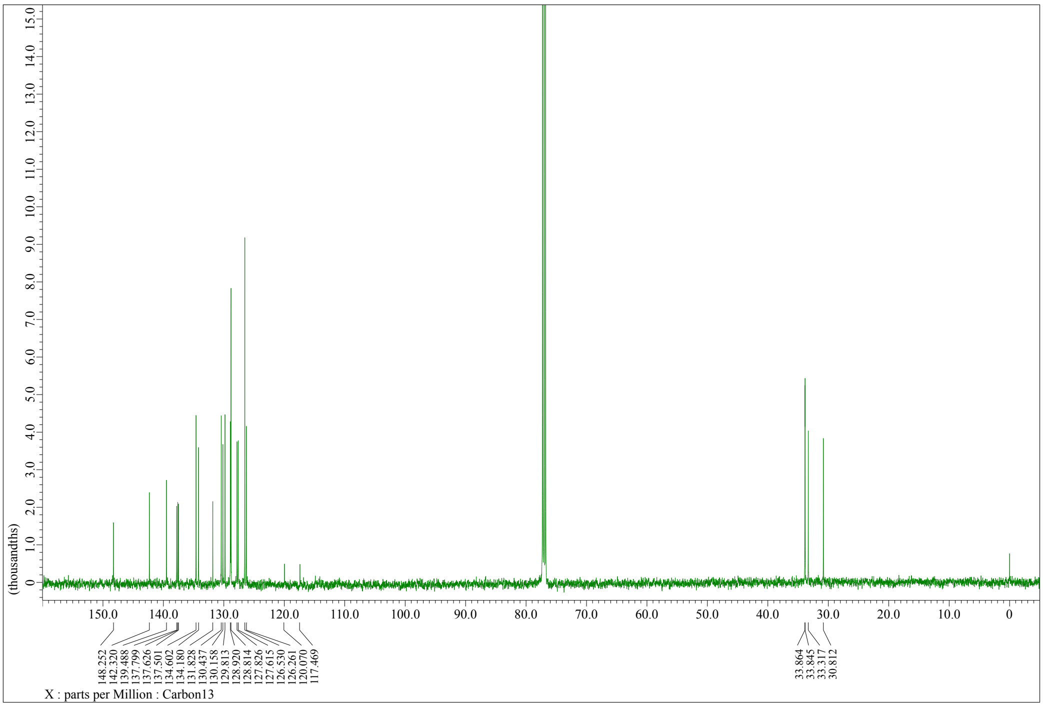


Fig. S10. (A) ^{1}H NMR spectrum and (B) ^{13}C{^{1}H} NMR spectrum of (S_p)-**7** in $CDCl_3$.

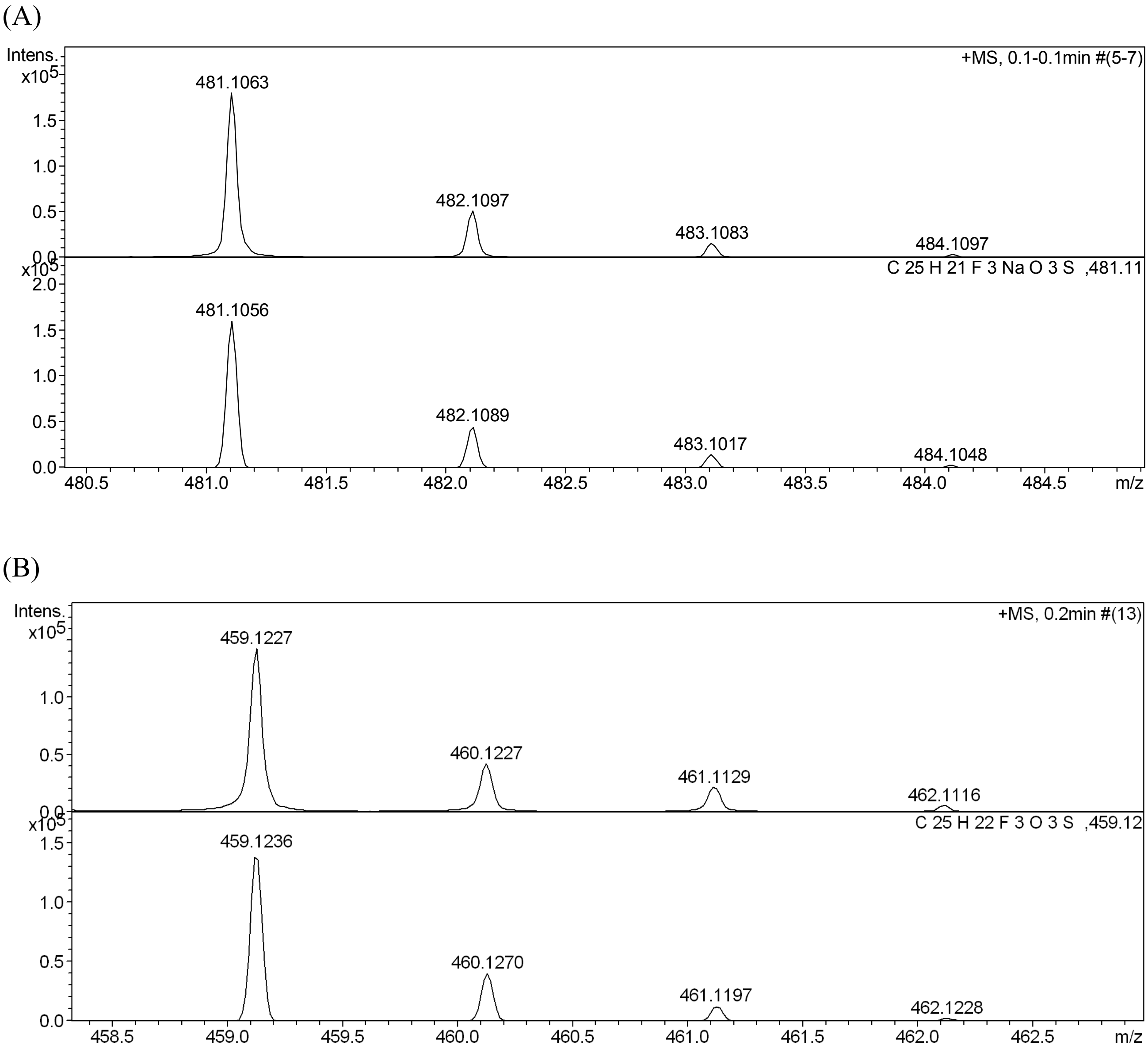
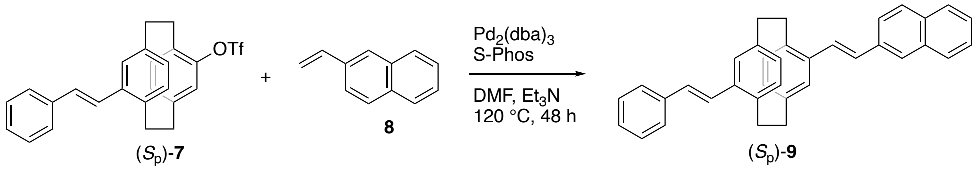


Fig. S11. Mass spectra of (A) (S_p)-**7** and (R_p)-**7**; upper and lower spectra show observed and calculated spectra, respectively.

Synthesis of (S_P)-**9**



A mixture of (S_p)-**7** (252.5 mg, 0.55 mmol), $Pd_2(dba)_3$ (51.0 mg, 0.056 mmol) and S-Phos (79.8 mg, 0.19 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, DMF (81 mL), Et_3N (1.5 mL) and 2-vinylnaphthalene **8** (120.0 mg, 0.78 mmol) were added, and the reaction was carried out at 120 ºC 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 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 column chromatography on SiO_2 ($CHCl_3$/hexane = 1/2 v/v as an eluent) and recrystallization from $CHCl_3$/MeOH (v/v = 1/1) to afford (S_p)-**9** (154.5 mg, 0.33 mmol, 81%) as a light yellow solid.

R_f = 0.40 ($CHCl_3$/hexane = 1/2 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.88–3.09 (m, 4H), 3.10–3.19 (m, 2H), 3.56–3.69 (m, 2H), 6.45 (t, J = 8.0, 5.7 Hz, 2H), 6.66–6.77 (m, 4H), 6.90 (d, J = 16.0 Hz, 1H), 7.06 (d, J = 16.0 Hz, 1H), 7.23 (s, 1H), 7.31 (t, J = 7.5, 7.5 Hz, 1H), 7.36 (d, J = 16.6 Hz, 1H), 7.43 (t, J = 7.5, 7.5 Hz, 2H), 7.46–7.54 (m, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.81–7.91 (m, 4H), 7.92 (s, 1H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 33.4, 33.4, 34.5, 123.5, 125.9, 126.4, 126.5, 127.0, 127.3, 127.5, 127.7, 128.0, 128.4, 128.8, 129.3, 129.4, 129.5, 129.5, 130.1, 130.2, 133.6, 133.6, 139.5, 139.5 ppm. HRMS (APCI) calcd for $C_{36}H_{30}+H^+$: 463.2420, found 463.2410. $[\alpha]^{25}_D = -91.24$ (c 0.20, $CHCl_3$).

(R_p)-**9** was obtained in 70% yield by the same procedure of (S_p)-**9**. HRMS (APCI) calcd. for $C_{36}H_{30}+H^+$: 463.2420, found 463.2414. $[\alpha]^{25}_D = +91.84$ (c 0.20, $CHCl_3$).

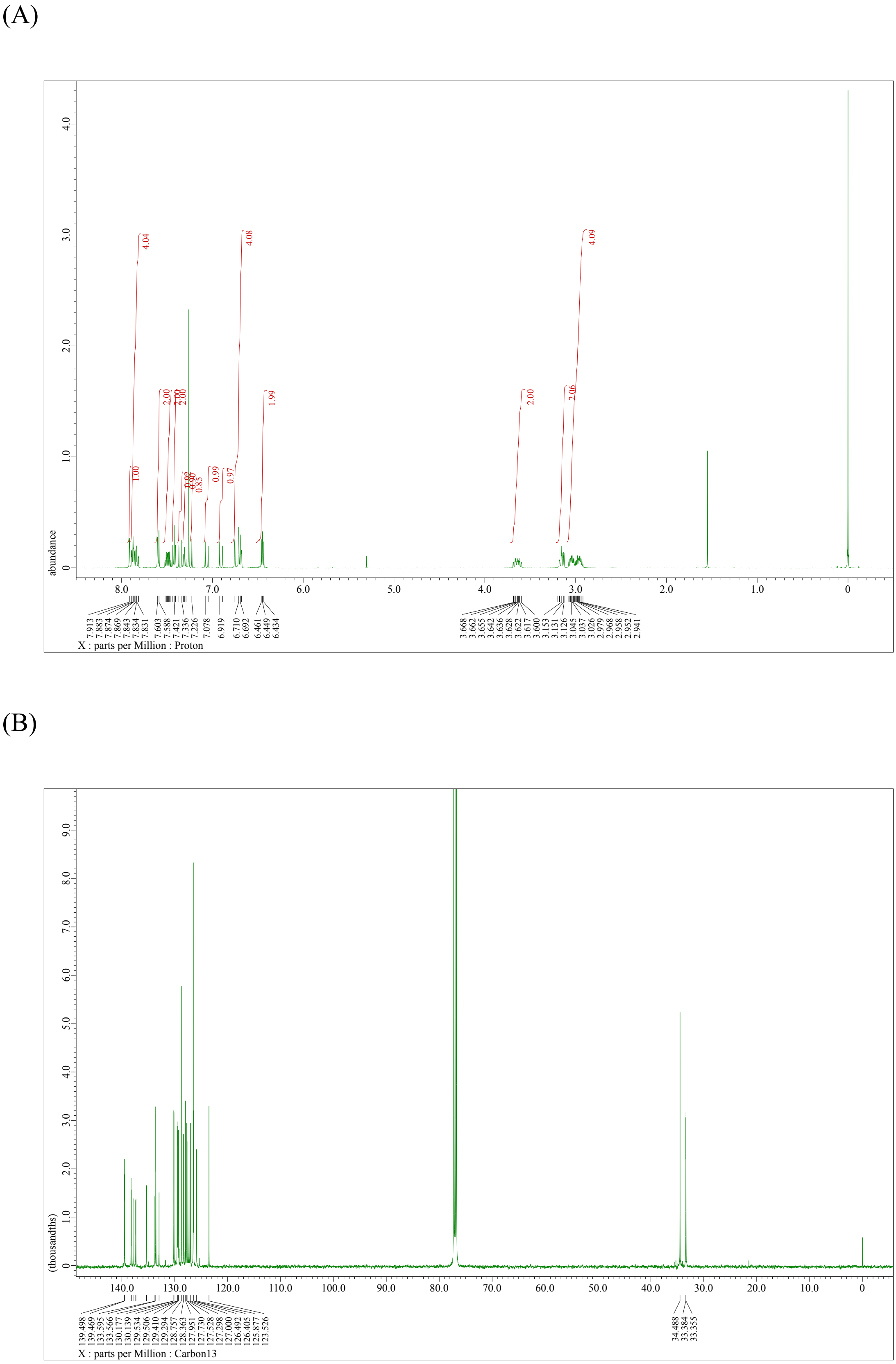


Fig. S12. (A) ^{1}H NMR spectrum and (B) $^{13}C\{^{1}H\}$ NMR spectrum of (S_p)-**9** in $CDCl_3$.

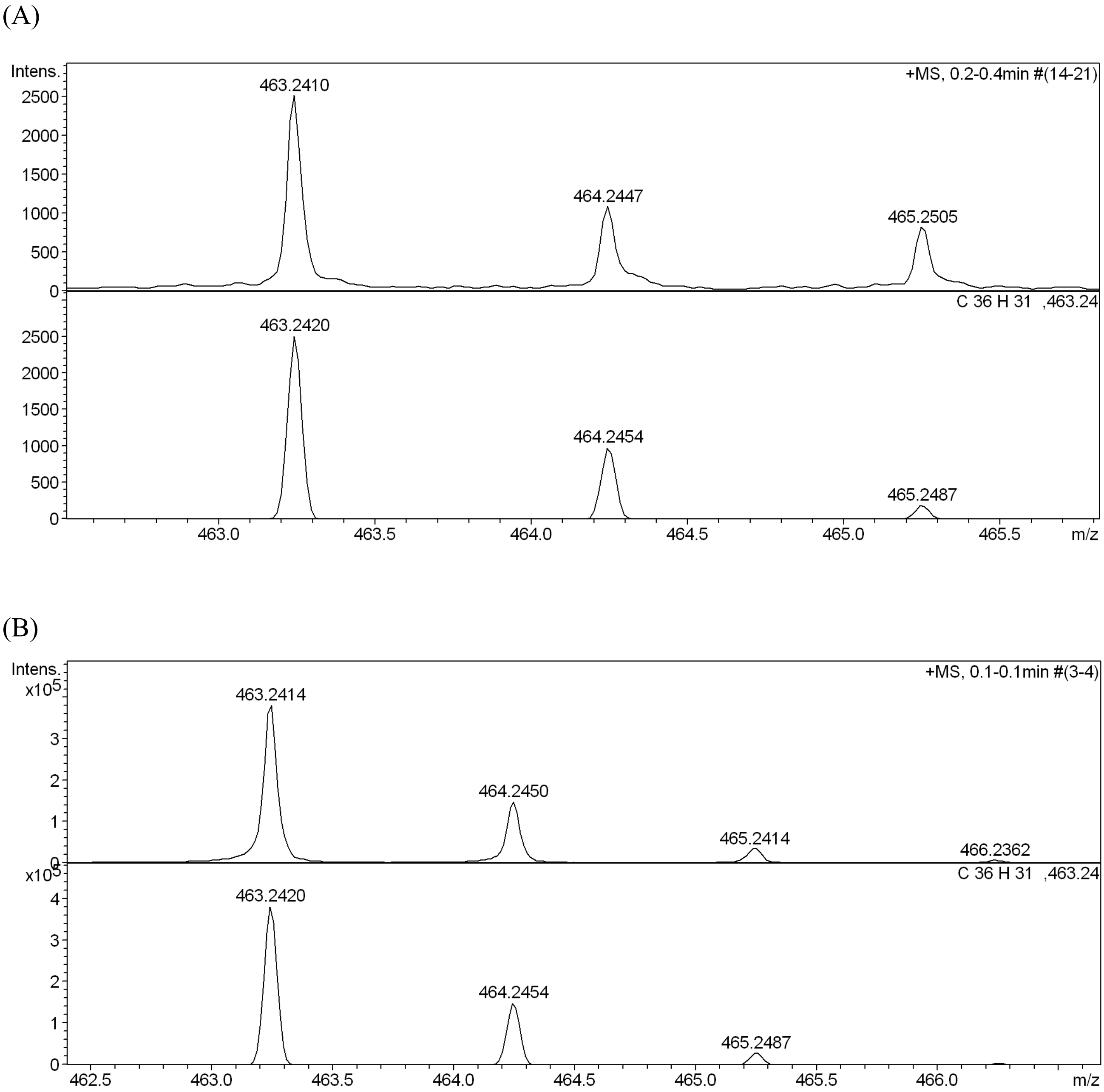


Fig. S13. Mass spectra of (A) (S_p)-**9** and (R_p)-**9**; upper and lower spectra show observed and calculated spectra, respectively.

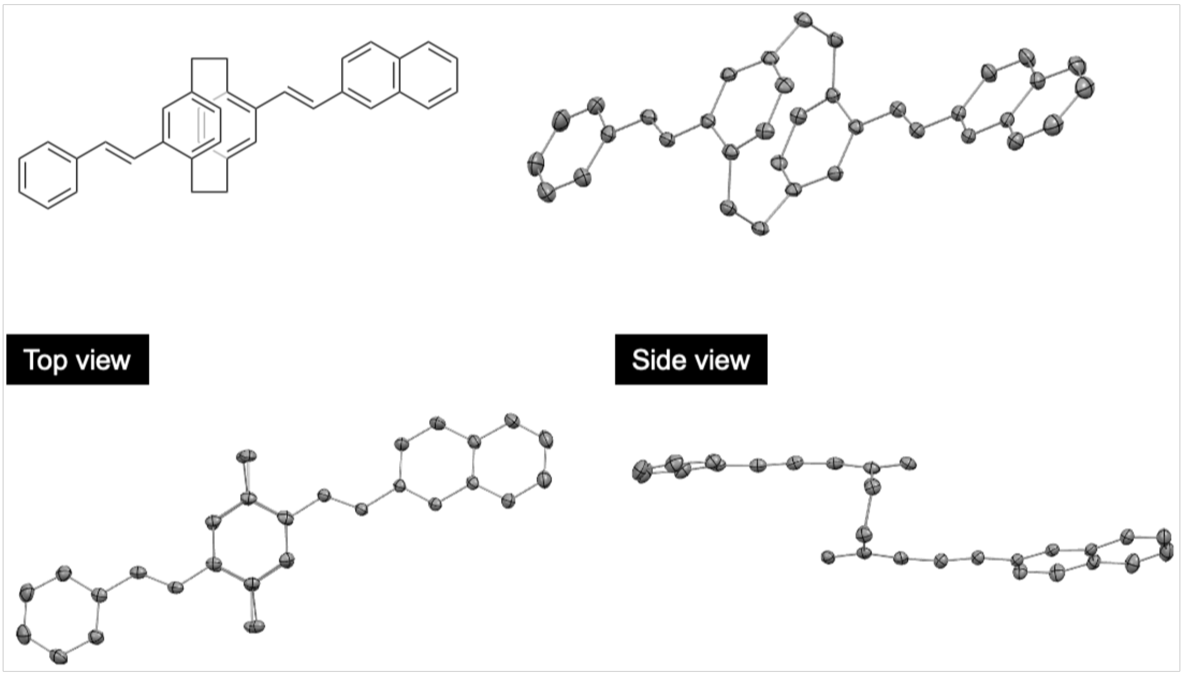


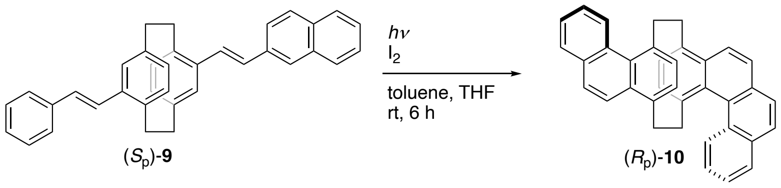
Fig. S14. ORTEP drawings of (S_p)-**9** (CCDC-2214408). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S3. Crystallographic data for (S_p)-**9**.

Formula	$C_{36}H_{30}$
Formula weight	462.639
Temperature (K)	150
Crystal color, habit	clear, light yellow
Crystal size, mm	0.1×0.1×0.05
Crystal system	monoclinic
Space group	$P2_1$(#4)
a, Å	11.7851(8)
b, Å	8.4229(4)
c, Å	14.0354(9)
α, deg	90
β, deg	113.748(8)
γ, deg	90
V, Å^3	1275.25(15)
Z value	2
D_{calcd}, g cm^{-3}	1.205
μ (MoKα), cm^{-1}	0.68
F(000)	492.248
$2\theta_{\mathrm{max}}$, deg	62.26
No. of reflections measured	12303
No. of observed reflections	6459
No. of variables	325
R_1 ($I > 2\sigma(I)$)[a]	0.0577(4855)
wR_2 (all reflns)[b]	0.1757(6459)
Goodness of fit	1.0511
Flack Parameter	3(3)

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.
Recrystallization solvent : chloroform/acetonitrile

Synthesis of (R_P)-**10**



(S_p)-**9** (50.5 mg, 0.11 mmol) was placed in a round-bottom flask equipped with a magnetic stirring After toluene (94 mL), THF (2.0 mL), and I_2 (6.81 mg, 0.05 mmol) were added, the mixture was irradiated with a UV lamp (LED λ = 365 nm), and the reaction was carried out at room temperature for 6 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 recyclable HPLC (CH_2Cl_2) and column chromatography on SiO_2 ($CHCl_3$/hexane = 1/2 v/v as an eluent) to afford (R_P)-**10** (2.5 mg, 0.0054 mmol, 5%) as a white solid.

R_f = 0.30 ($CHCl_3$/hexane = 1/2 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.91–1.99 (m, 1H), 2.86–2.90 (m, 1H), 3.27–3.29 (m, 2H), 3.48–3.51 (m, 1H), 3.69–3.73 (m, 2H), 4.62–4.66 (m, 1H), 5.25 (d, *J* = 6.9 Hz, 1H), 5.60 (d, *J* = 6.9 Hz, 1H), 6.42 (dd, *J* = 6.9, 6.9 Hz, 2H), 7.54–7.63 (m, 5H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.90–7.97 (m, 4H), 8.01 (dd, *J* = 1.7, 1.2 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.80–8.81 (m, 1H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 32.0, 32.1, 37.7, 38.4, 124.1, 124.5, 125.5, 125.7, 125.8, 126.0, 126.5, 126.5, 127.1, 127.2, 127.7, 127.9, 128.4, 128.6, 128.8, 129.3, 129.7, 130.5, 130.5, 131.2, 131.4, 132.1, 132.5, 132.5, 133.4, 134.2, 134.4, 135.4, 136.0, 136.6 ppm. HRMS (APCI): m/z calcd for $C_{36}H_{26}+H^+$: 459.2107; found: 459.2092. $[\alpha]^{25}_\mathrm{D}$ = +304.43 (*c* 0.060, $CHCl_3$).

(S_p)-**10** was obtained in 6% yield by the same procedure of (R_p)-**10**. HRMS (APCI) calcd. for $C_{36}H_{26}+H^+$: 459.2107, found 459.2114. $[\alpha]^{25}_\mathrm{D}$ = –304.23 (*c* 0.060, $CHCl_3$).

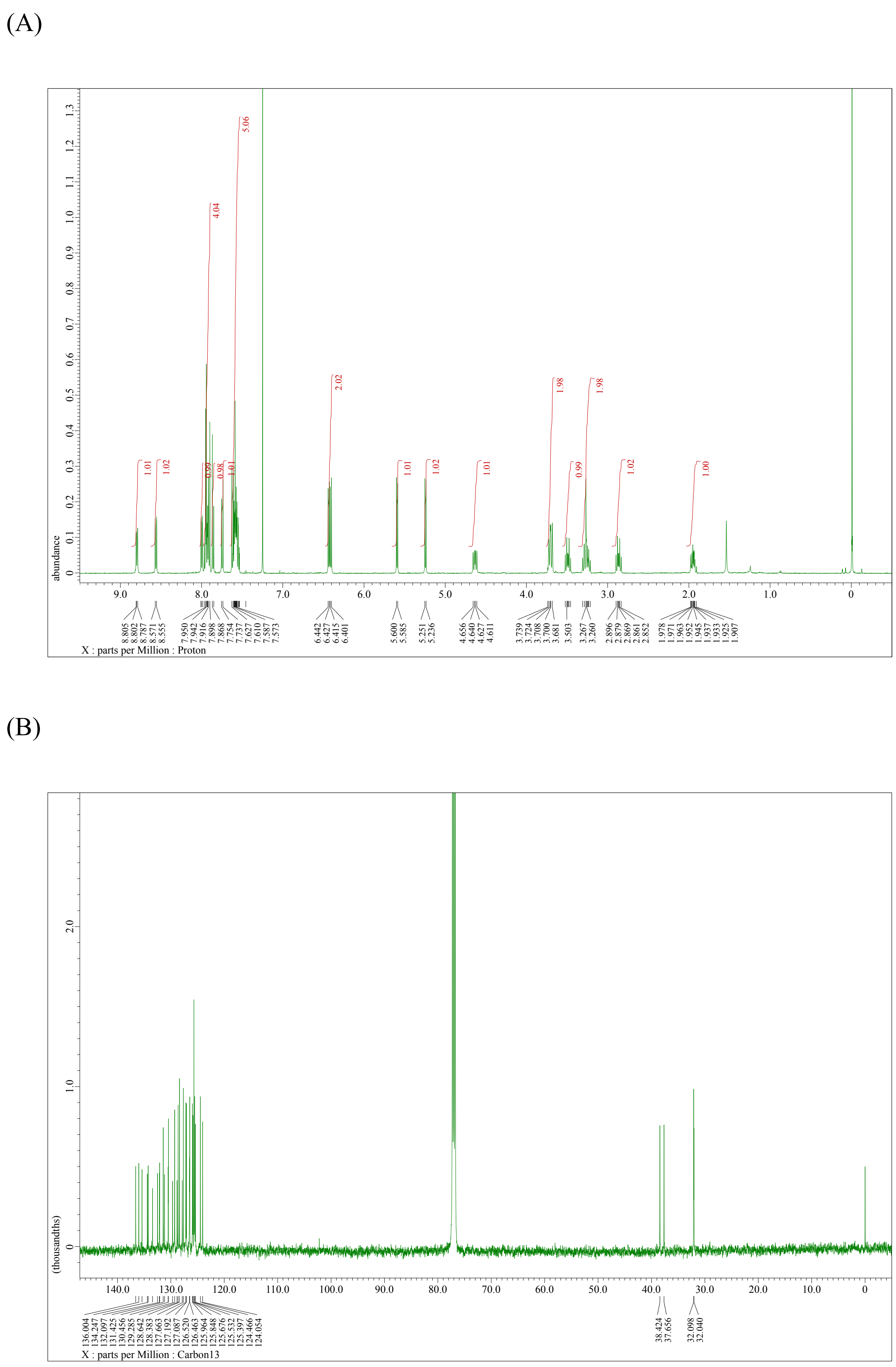
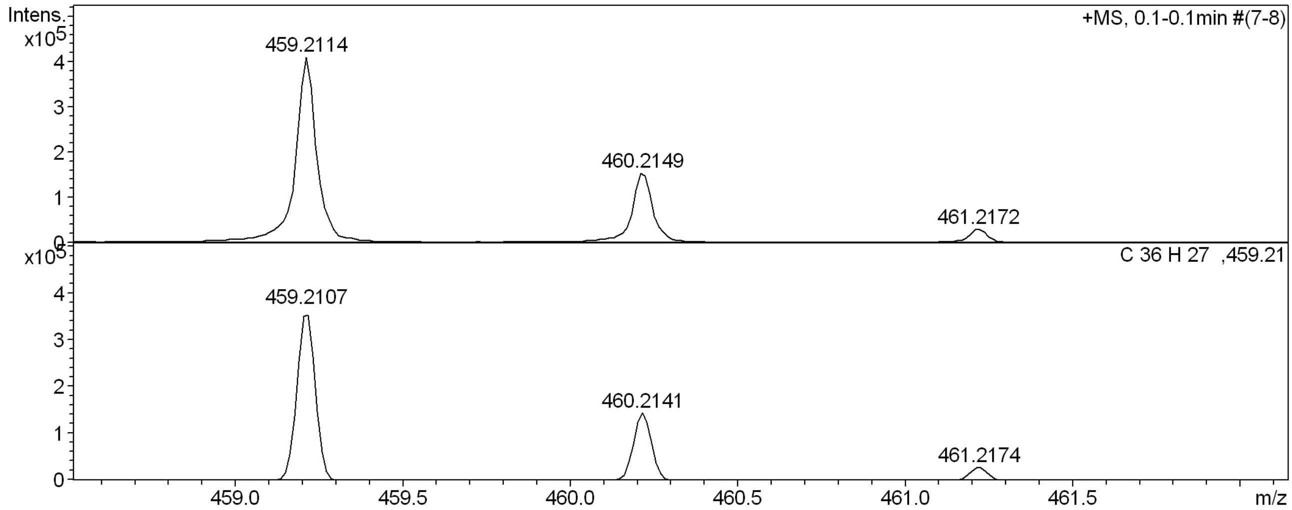


Fig. S15. (A) ^{1}H NMR spectrum and (B) ^{13}C{^{1}H} NMR spectrum of (S_p)-**10** in $CDCl_3$.

(A)



(B)

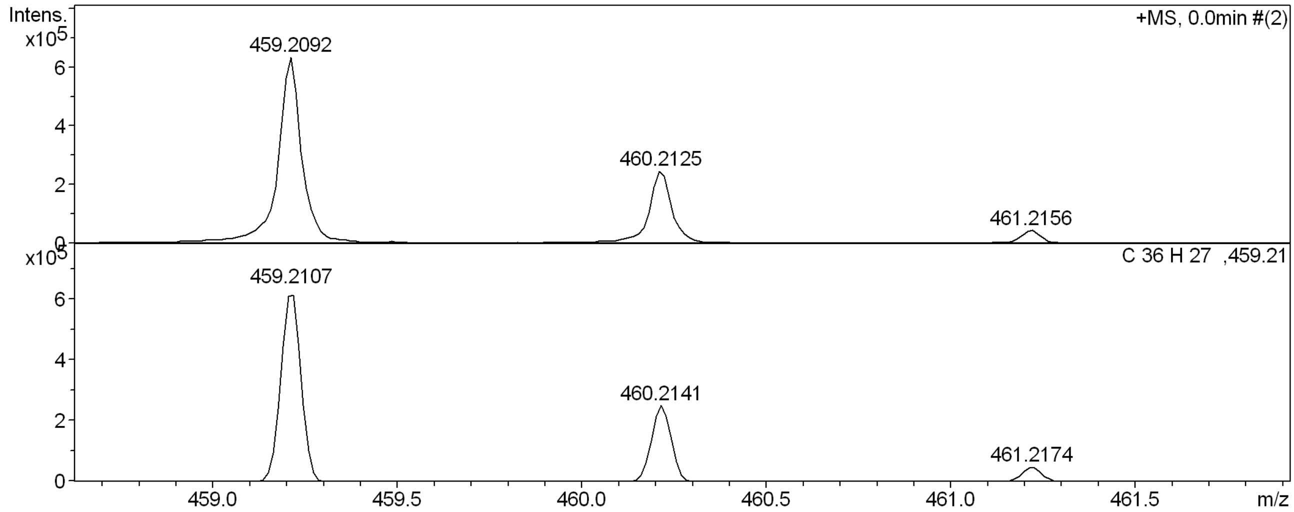


Fig. S16. Mass spectra of (A) (S_p)-**10** and (R_p)-**10**; upper and lower spectra show observed and calculated spectra, respectively.

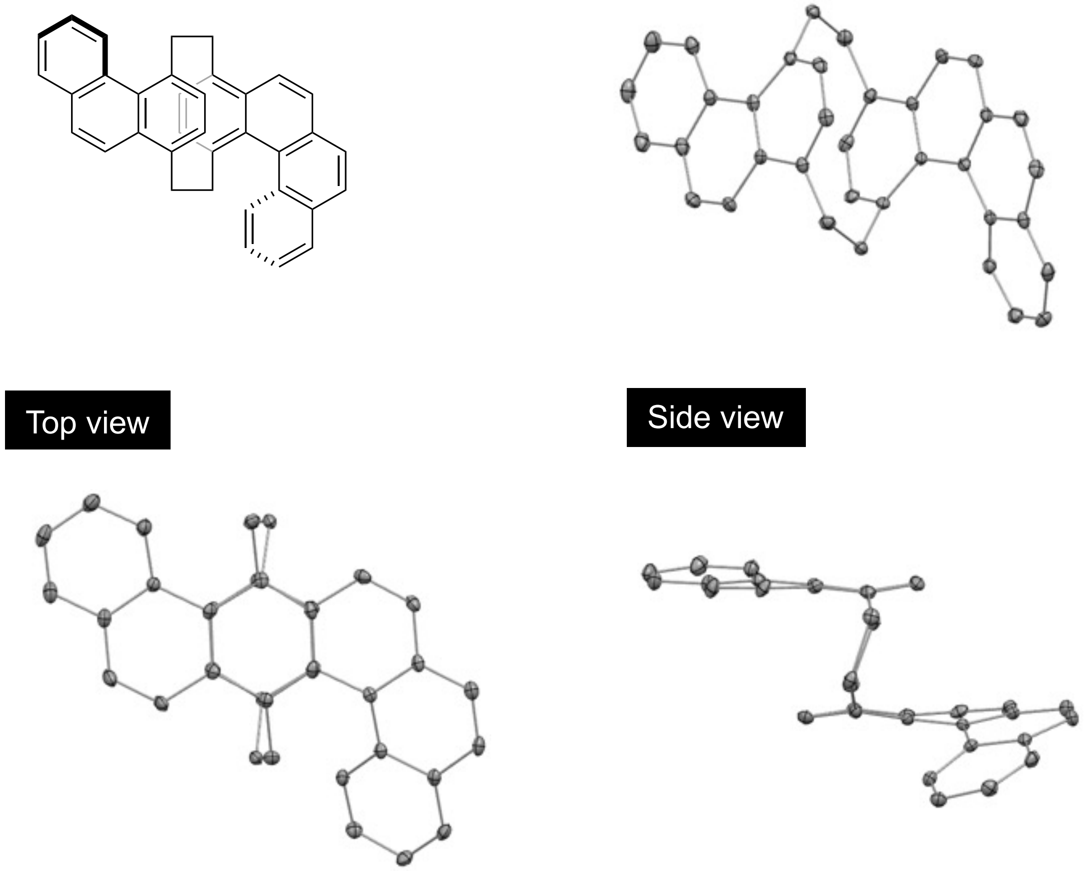


Fig. S17. ORTEP drawings of (R_p)-**10** (CCDC-2214409). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

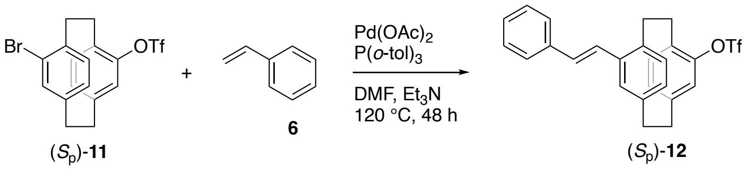
Table S4. Crystallographic data for (R_p)-**10**.

Formula	$C_{36}H_{26}$
Formula weight	458.57
Temperature (K)	150
Crystal color, habit	clear, colourless, needle
Crystal size, mm	0.2 × 0.1 × 0.05
Crystal system	monoclinic
Space group	$P2_1$(#4)
a, Å	10.4112(8)
b, Å	8.1076(7)
c, Å	14.6075(11)
α, deg	90
β, deg	102.802(8)
γ, deg	90
V, Å^3	1202.37(17)
Z value	2
D_{calcd}, g cm^{-3}	1.267
μ (MoKα), cm^{-1}	0.72
F(000)	484
$2\theta_{\mathrm{max}}$, deg	62.398
No. of reflections measured	11308
No. of observed reflections	6766
No. of variables	325
R_1 ($I > 2\sigma(I)$)[a]	0.0747(4037)
wR_2 (all reflns)[b]	0.2091(6766)
Goodness of fit	0.919
Flack Parameter	4.7(10)

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

Recrystallization solvent : chloroform / acetonitrile

Synthesis of (S_p)-**12**



A mixture of (S_p)-**11** (534.1mg, 1.227 mmol), $Pd(OAc)_2$ (27.6 mg, 0.123 mmol) and P(*o*-tol)$_3$ (131.0mg, 0.430 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, DMF (18.7 mL), Et_3N (4 mL) and styrene **6** (0.183 mL, 166.1 mg, 1.6 mmol) were added, and the reaction was carried out at 120 °C 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 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 column chromatography on SiO_2 ($CHCl_3$/hexane = 1/6 v/v as an eluent) and recrystallization from $CHCl_3$/MeOH (v/v = 1/1) to afford (S_p)-**12** (433.6 mg, 0.946 mmol, 77%) as a white solid.

R_f = 0.42 (CH_2Cl_2/hexane = 1/2 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.73–2.81 (m, 1H), 2.98–3.19 (m, 5H), 3.37 (dd, *J* = 9.2, 4.6 Hz, 1H), 3.54 (dd, *J* = 9.7, 4.0 Hz, 1H), 6.24 (s, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.89–6.93 (m, 2H), 7.11 (d, *J* = 16.0 Hz 1H), 7.31 (t, *J* = 6.9 Hz, 1H), 7.41 (dd, *J* = 8.0, 6.9 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 31.4, 32.2, 34.5, 34.8, 126.0, 126.6, 127.3, 127.9, 128.8, 129.6, 129.9, 131.2, 131.5, 131.7, 132.4, 137.5, 138.1, 138.2, 139.4, 141.2, 142.9, 148.5 ppm. HRMS (APCI) calcd. for $C_{25}H_{21}F_3O_3S+Na^+$: 481.1056, found 481.1068. $[\alpha]^{25}_D$ = +295.13 (*c* 0.078, $CHCl_3$).

(R_p)-**12** was obtained in 12% yield by the same procedure of (R_p)-**12**. HRMS (APCI) calcd. for $C_{25}H_{21}F_3O_3S+Na^+$: 481.1056, found 481.1062. $[\alpha]^{25}_D$ = –295.17 (*c* 0.102, $CHCl_3$).

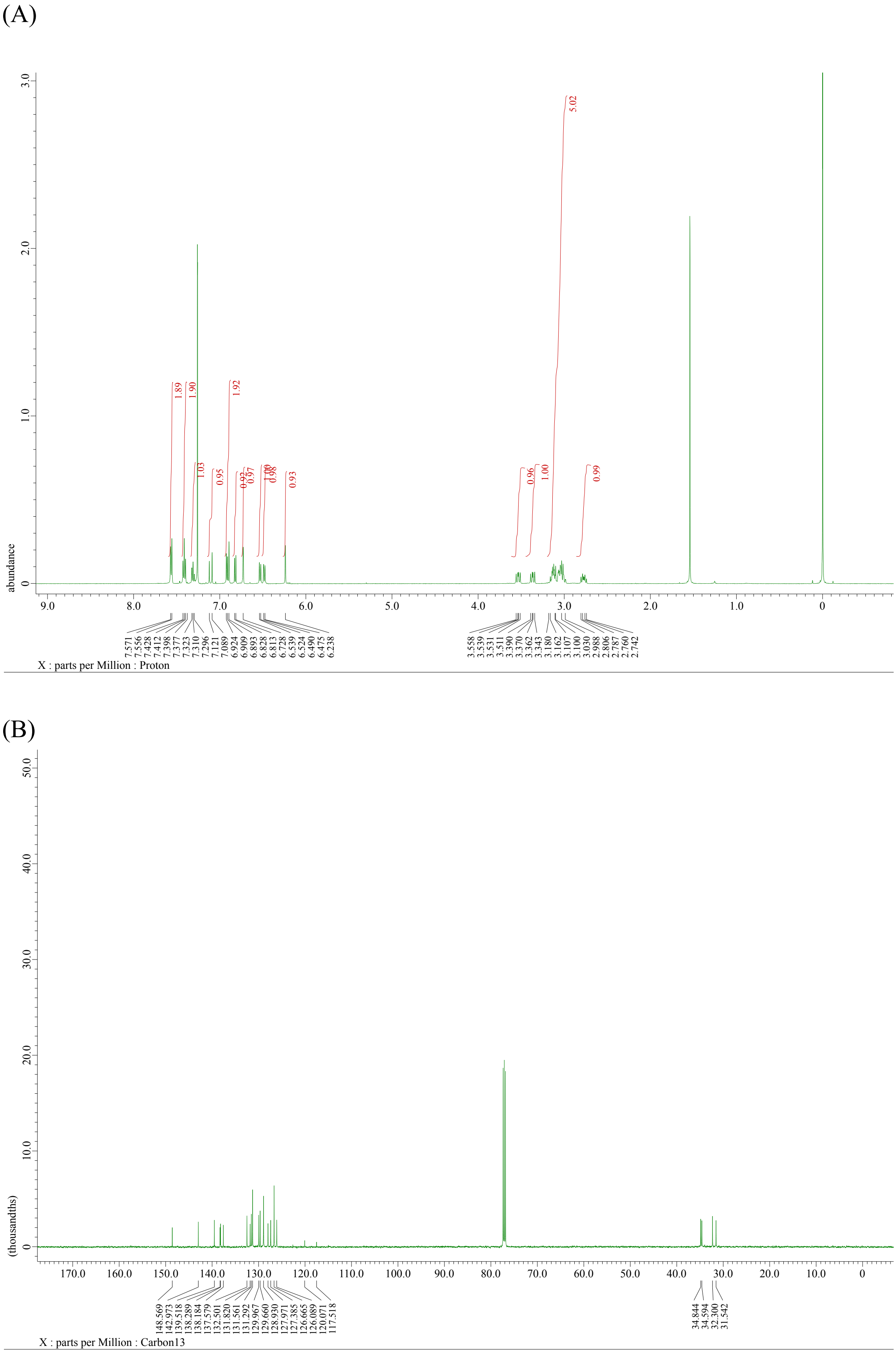


Fig. S18. (A) ^{1}H NMR spectrum and (B) ^{13}C{^{1}H} NMR spectrum of (S_p)-**12** in $CDCl_3$.

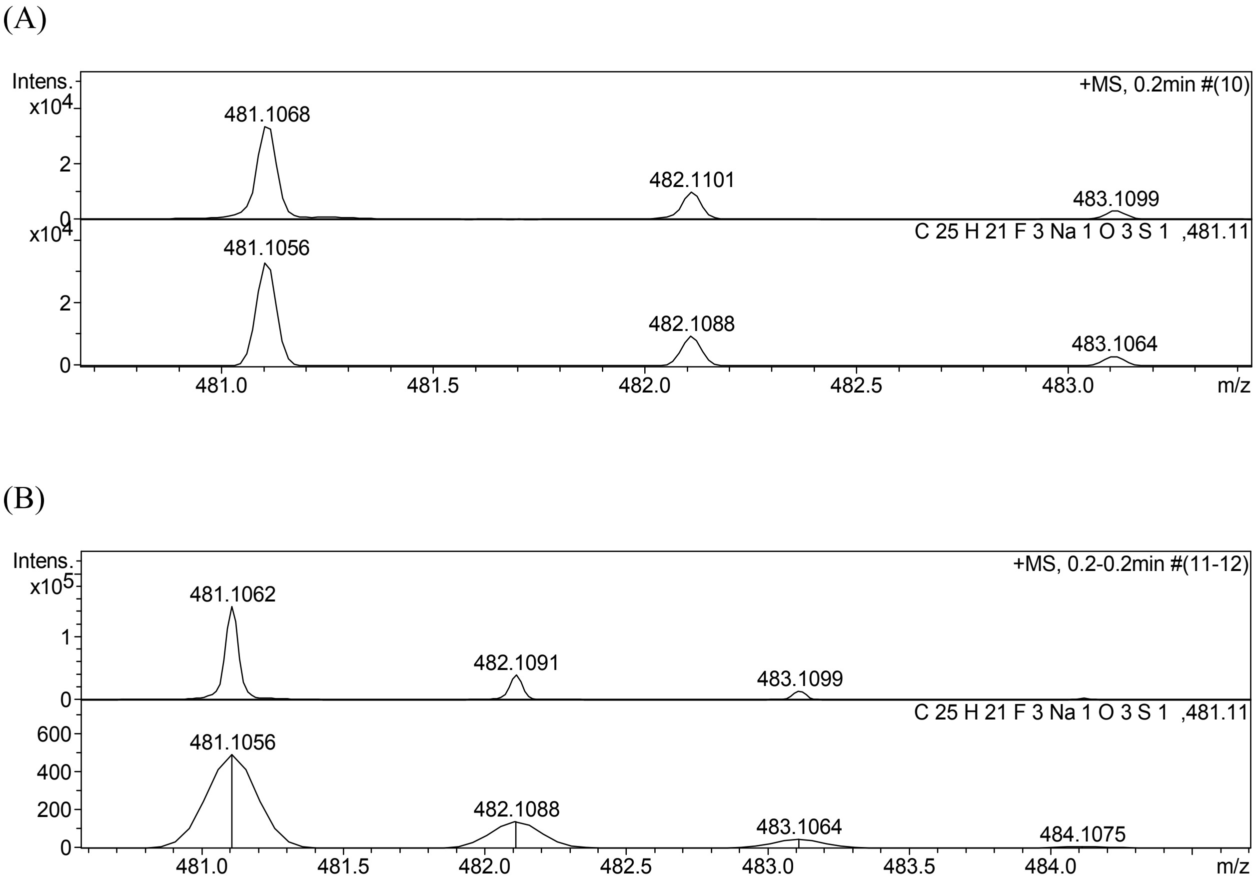
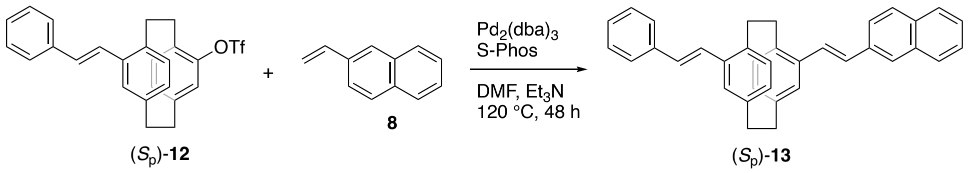


Fig. S19. Mass spectra of (A) (S_p)-**12** and (R_p)-**12**; upper and lower spectra show observed and calculated spectra, respectively.

Synthesis of (S_p)-**13**



A mixture of (S_p)-**12** (221.9 mg, 0.48 mmol), $Pd(OAc)_2$ (10.8 mg, 0.048 mmol) and S-Phos (69.0 mg, 0.17 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, DMF (7.3 mL), Et_3N (1.6 mL) and 2-vinylnaphthalene (89.4 mg, 0.58 mmol) were added, and the reaction was carried out at 120 °C 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 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 column chromatography on SiO_2 ($CHCl_3$/hexane = 1/3 v/v as an eluent) and recrystallization from $CHCl_3$/MeOH (v/v = 1/1) to afford (S_p)-**13** (78.7 mg, 0.17 mmol, 35%) as a light yellow solid.

R_f = 0.31 (CH_2Cl_2/hexane = 1/2 v/v). ^{1}H NMR (CDCl3, 500 MHz) δ 2.86–2.93 (m, 2H), 2.99–3.06 (m, 2H), 3.15–3.20 (m, 2H), 3.53–3.63 (m, 2H), 6.45 (dd, J = 7.5 Hz, 2H), 6.72–6.74 (m, 2H), 6.78 (s, 1H), 6.82 (s, 1H), 6.94 (d, J = 16.0 Hz, 1H), 7.10(d, J = 16.61 Hz, 1H), 7.20 (d, J = 16.0 Hz, 1H), 7.29–7.32 (m, 2H), 7.42 (dd, J = 7.5 Hz, 2H), 7.45–7.52 (m, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.81–7.88 (m, 4H), 7.91 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 33.5, 35.1, 123.5, 125.9, 126.4, 126.5, 126.7, 127.0, 127.6, 127.7, 128.0, 128.4,128.8, 129.1, 129.2, 129.6, 130.9, 131.0, 131.2, 133.0, 133.8, 135.3, 137.8, 137.9, 138.1, 138.2 139.7, 139.8 ppm. HRMS (APCI) calcd. for $C_{36}H_{30}+H^+$: 463.2420, found 463.2417. $[\alpha]^{25}_\mathrm{D}$ = +902.2 (c 0.204, $CHCl_3$).

(R_p)-**13** was obtained in 34% yield by the same procedure of (S_p)-**13**. HRMS (APCI) calcd. for $C_{36}H_{30}+H^+$: 463.2420, found 463.2420. $[\alpha]^{25}_\mathrm{D}$ = –902.4 (c 0.126, $CHCl_3$).

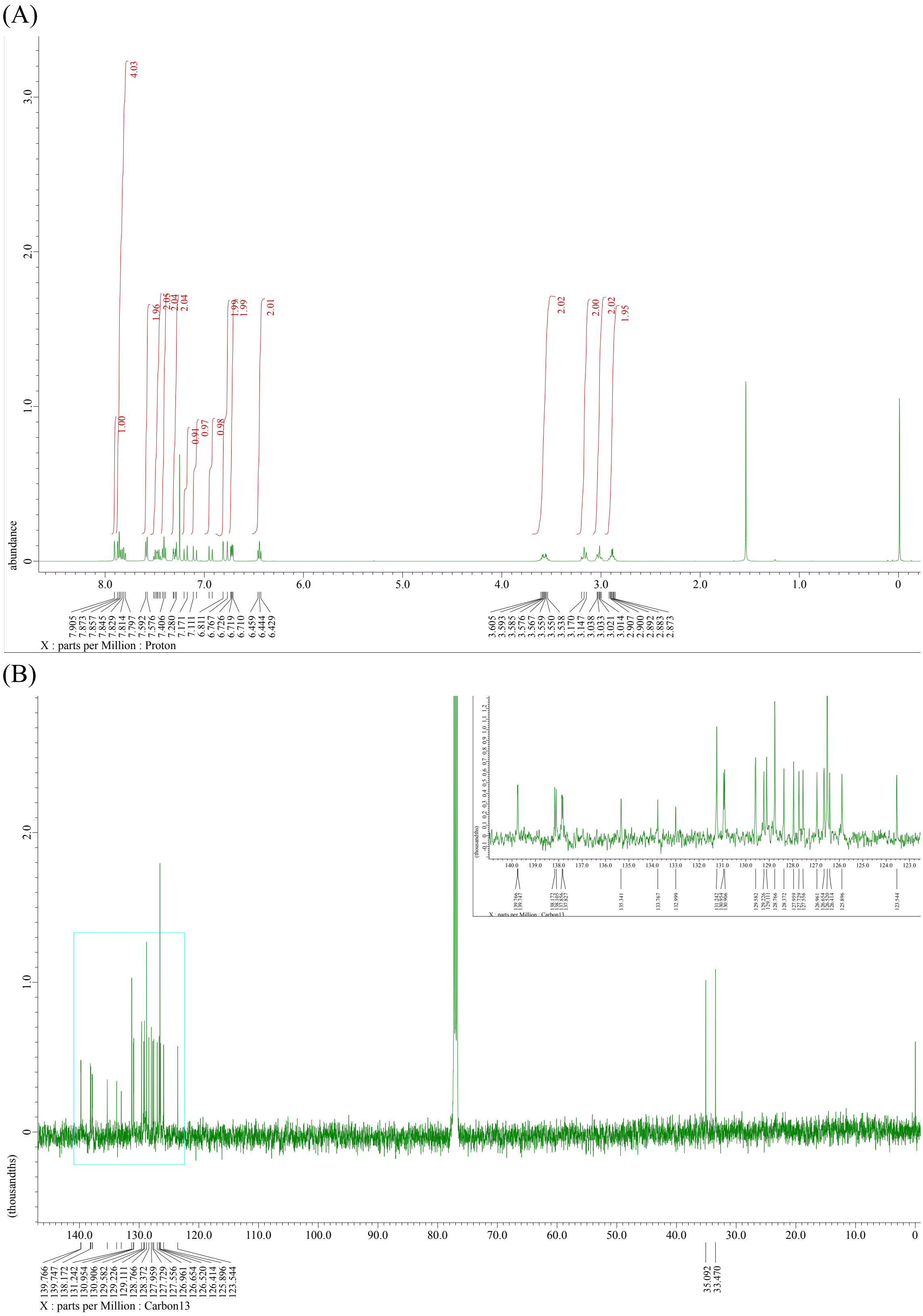


Fig. S20. (A) ^{1}H NMR spectrum and (B) ^{13}C{^{1}H} NMR spectrum of (S_p)-**13** in CDCl$_3$.

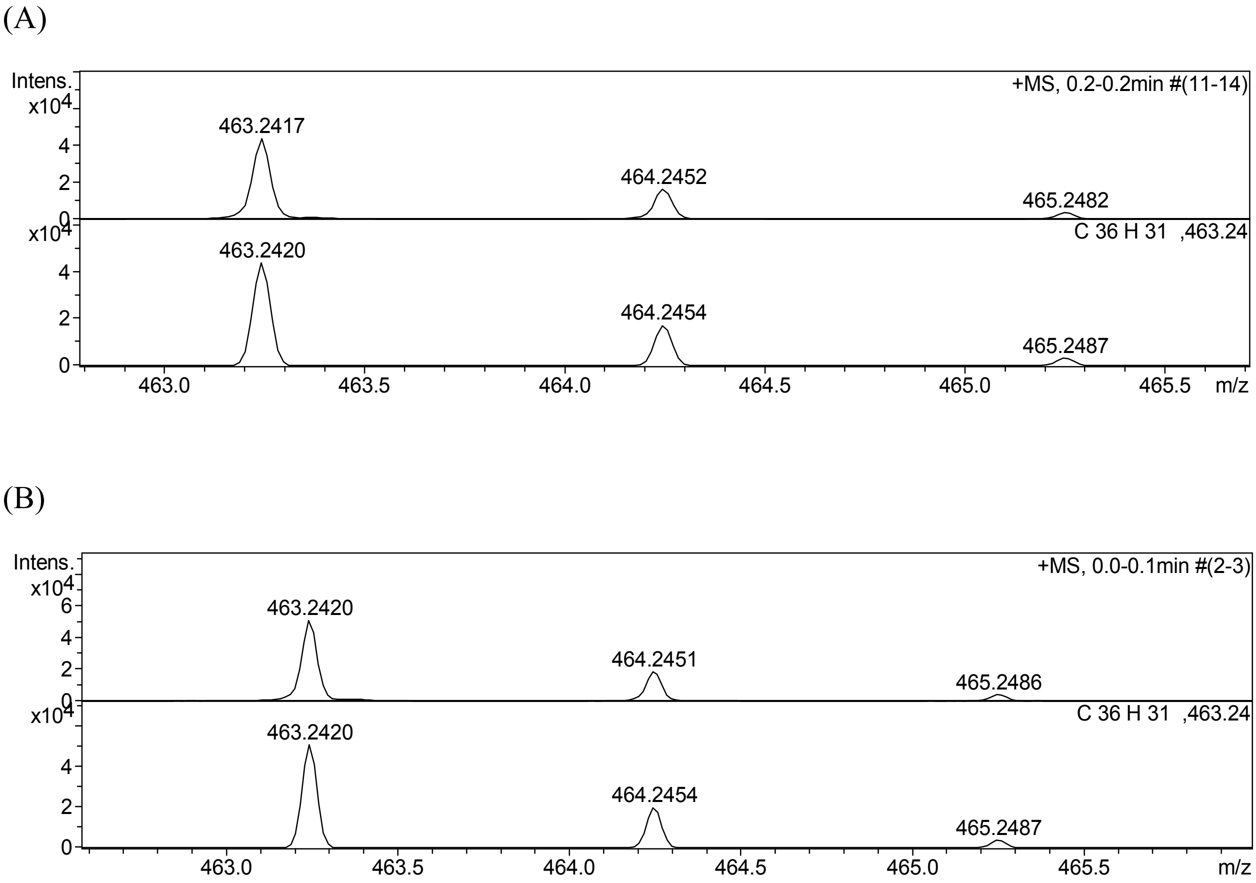
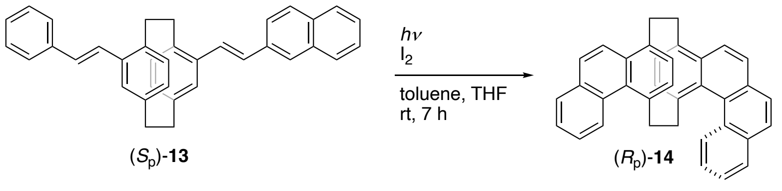


Fig. S21. Mass spectra of (A) (S_p)-**13** and (R_p)-**13**; upper and lower spectra show observed and calculated spectra, respectively.

Synthesis of (*R*$_p$)-**14**



(*S*$_p$)-**13** (78.7 mg, 0.17 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After toluene (170 mL), THF (6 mL) and I_2 (21.6 mg, 0.085 mmol) were added, the mixture was irradiated with a UV lamp (LED λ = 365 nm), and the reaction was carried out at room temperature for 7 h with stirring. 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 recyclable HPLC (CH_2Cl_2) to afford (*R*$_p$)-**14** (7.2 mg, 0.016 mmol, 9%) as a colorless solid.

R_f = 0.39 (CH_2Cl_2/hexane = 1/2 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.70–2.75 (m, 1H), 2.94–3.00 (m, 1H), 3.12–3.27 (m, 3H), 3.72–3.78 (m, 1H), 3.90–3.98 (m, 2H), 5.44 (d, *J* = 8.02 Hz, 1H), 5.86 (d, *J* = 7.5 Hz, 1H), 6.04 (d, *J* = 8.0 Hz, 1H), 6.13 (d, *J* = 7.5 Hz, 1H), 7.46–7.59 (m, 4H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.92–8.01 (m, 5H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.44 (d, *J* = 8.6 Hz, 1H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 32.6, 32.7, 36.6, 38.0, 123.4, 124.4, 125.2, 125.5, 125.6, 125.66, 125.73, 125.9, 126.5, 127.2, 127.5, 127.6, 128.1, 128.2, 128.4, 128.7, 128.8, 129.2, 129.5, 130.2, 130.3, 130.4, 130.5, 132.2, 132.3, 132.8, 133.0, 134.2, 134.4, 134.6, 136.0, 137.8 ppm. HRMS (APCI) calcd. for $C_{36}H_{26}+H^+$: 459.2107, found 459.2100. $[\alpha]^{25}_D$ = + 508.4 (*c* 0.042, $CHCl_3$).

(*S*$_p$)-**14** was obtained in 10% yield by the same procedure of (*R*$_p$)-**14**. HRMS (APCI) calcd. for $C_{36}H_{26}+H^+$: 459.2107, found 459.2106. $[\alpha]^{25}_D$ = –508.3 (*c* 0.02, $CHCl_3$).

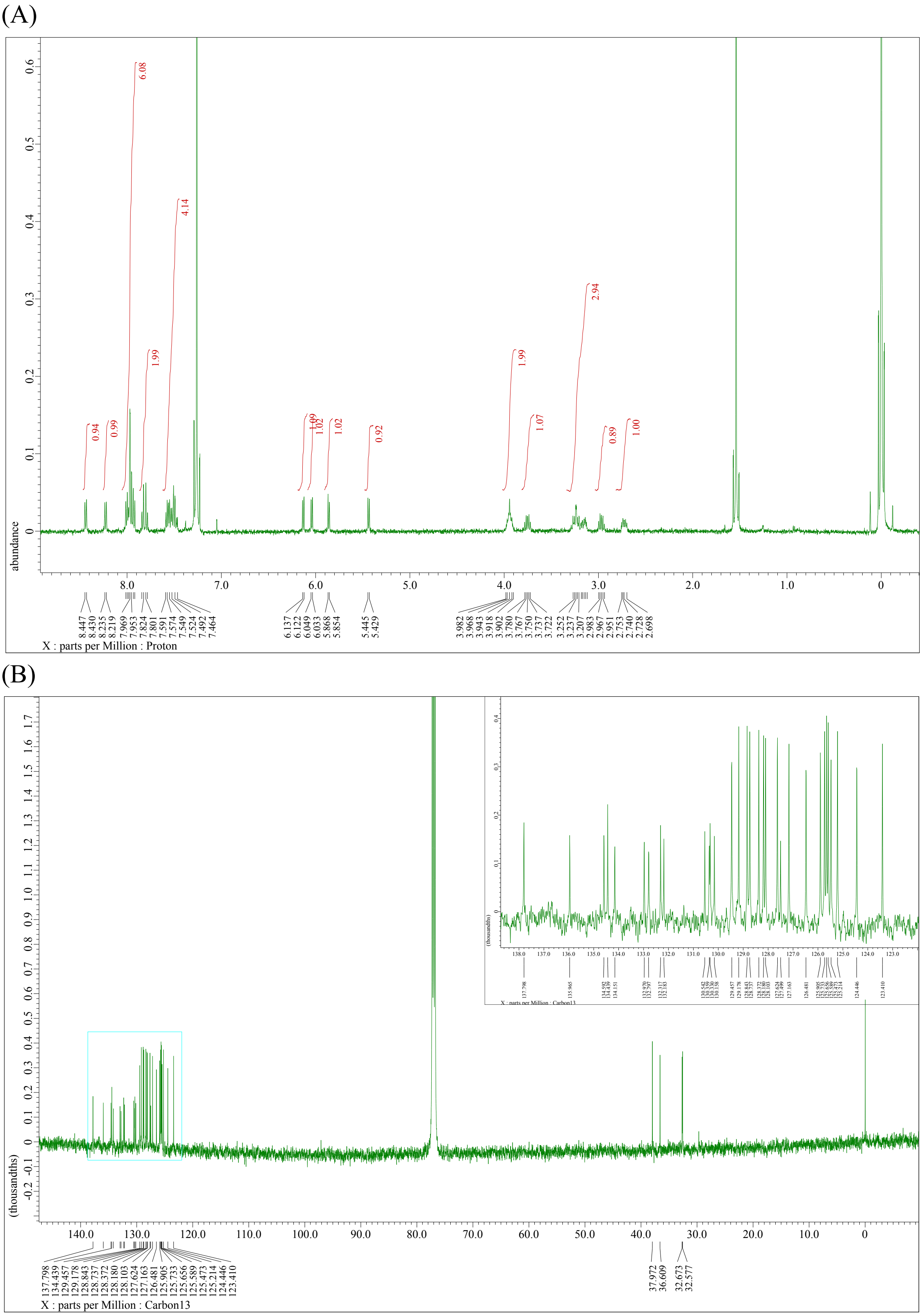
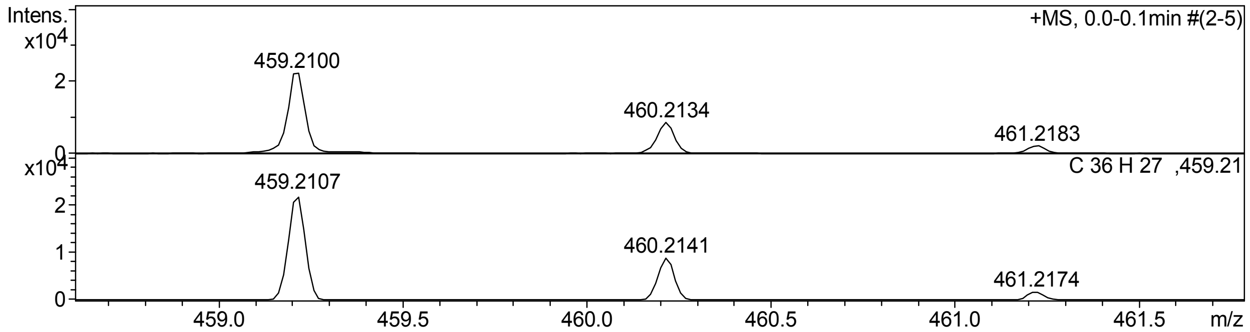


Fig. S22. (A) ^{1}H NMR spectrum and (B) ^{13}C{^{1}H} NMR spectrum of (R_p)-**14** in $CDCl_3$.

(A)



(B)

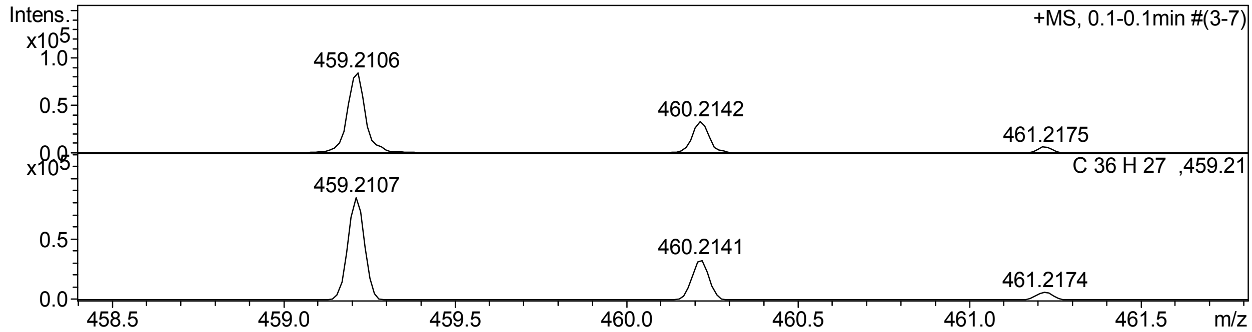


Fig. S23. Mass spectra of (A) (R_p)-**14** and (S_p)-**14**; upper and lower spectra show observed and calculated spectra, respectively.

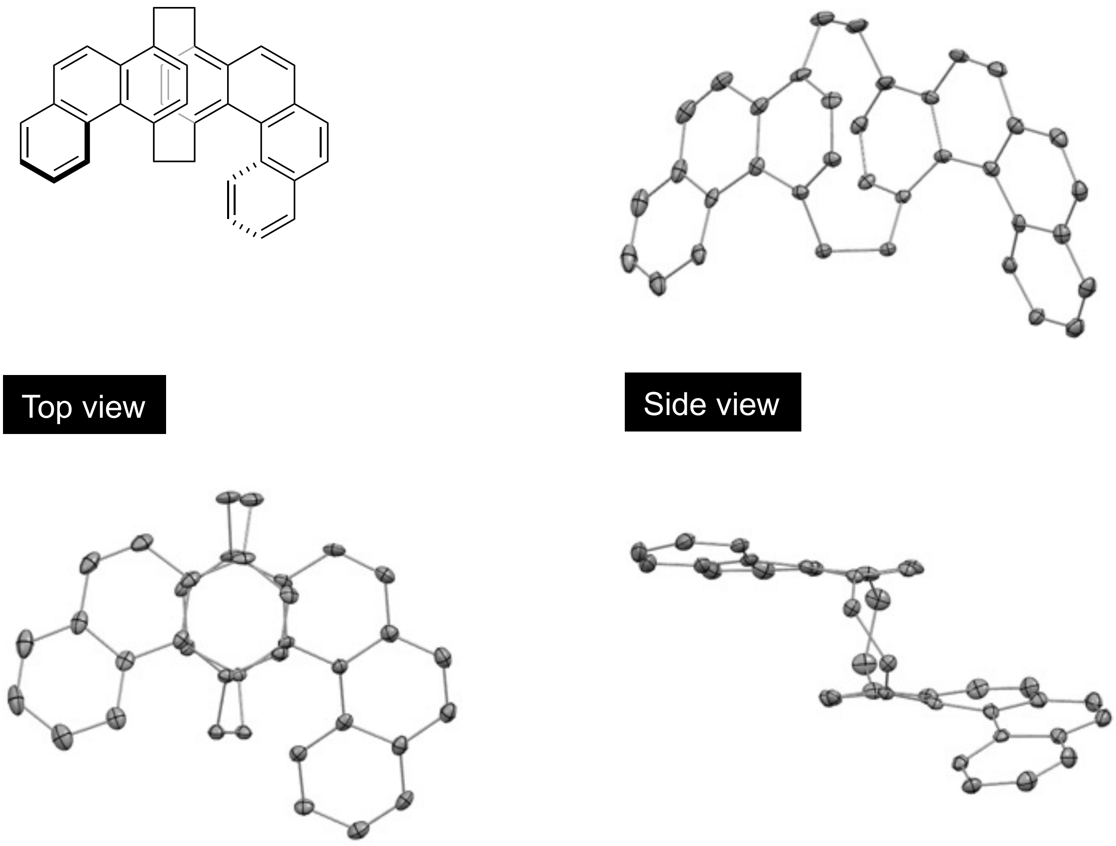


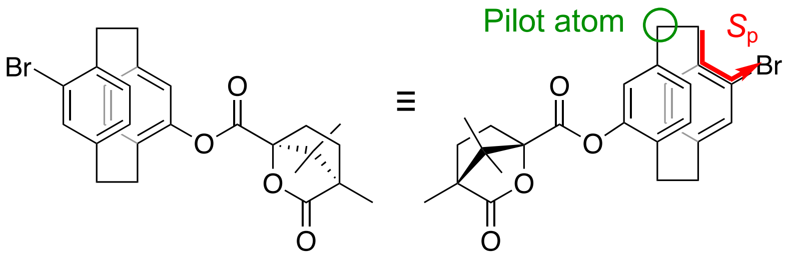
Fig. S24. ORTEP drawings of (R_p)-**14** (CCDC-2214410). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S5. Crystallographic data for (R_p)-**14**.

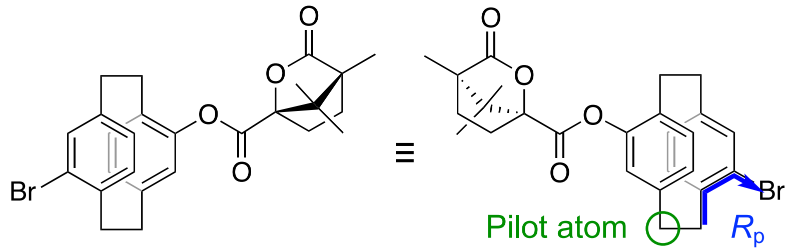
Formula	$C_{36}H_{26}$
Formula weight	458.57
Temperature (K)	123
Crystal color, habit	colourless,plate
Crystal size, mm	0.05×0.02×0.01
Crystal system	monoclinic
Space group	$P2_1$(#4)
a, Å	9.1321(8)
b, Å	9.8490(9)
c, Å	13.2407(12)
α, deg	90
β, deg	98.635(9)
γ, deg	90
V, Å^3	1177.40(19)
Z value	2
D_{calcd}, g cm^{-3}	1.293
μ (MoKα), cm^{-1}	0.073
F(000)	484.0
$2\theta_{\mathrm{max}}$, deg	62.254
No. of reflections measured	11438
No. of observed reflections	6335
No. of variables	325
R_1 ($I > 2\sigma(I)$)[a]	0.0776(3684)
wR_2 (all reflns)[b]	0.1748(6335)
Goodness of fit	1.015
Flack Parameter	2.0 (10)

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.
Recrystallization solvent : chloroform / methanol

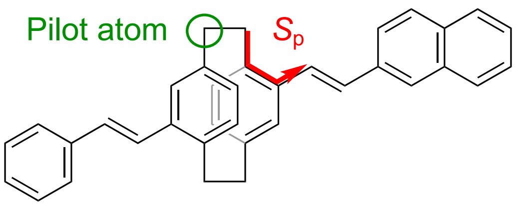
(S_p,1S,4R)-**4**



(R_p,1S,4R)-**4**



(S_p)-**7**



(R_p)-**9**

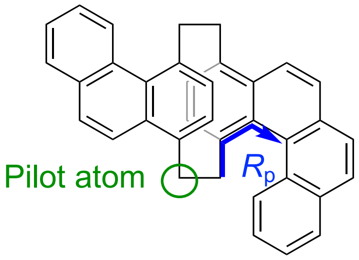


Fig. S25. Absolute configurations of planar chiral molecules **4**, **7**, and **9**.

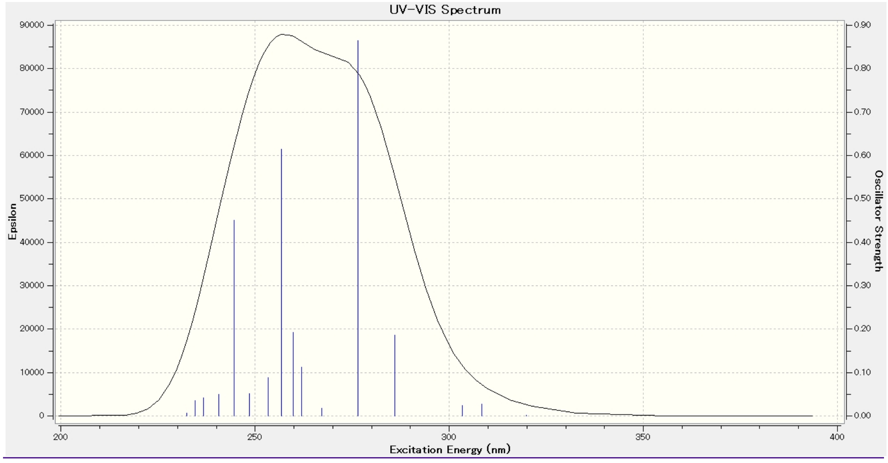


Fig. S26. Simulated UV-vis spectrum (half-width at half height = 0.20 eV) of (*R*$_p$)-**10** by TD-DFT calculation (TD-CAM-B3LYP(CHCl$_3$)/6-31G(d)//CAM-B3LYP(CHCl$_3$)/6-31G(d)).

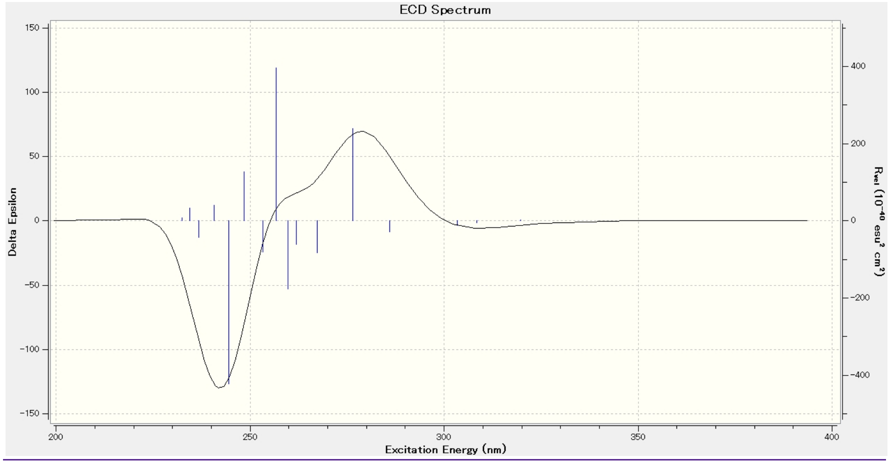


Fig. S27. Simulated ECD spectrum (half-width at half height = 0.20 eV) of (*R*$_p$)-**10** by TD-DFT calculation (TD-CAM-B3LYP(CHCl$_3$)/6-31G(d)//CAM-B3LYP(CHCl$_3$)/6-31G(d)).

Table S6. Selected data for excitation energy, major configuration, coefficient, oscillator strength, and rotatory strengths for (*R*$_p$)-**10**.[a]

State	Excitation energy / eV (/ nm)	Major Configuration	Coefficient	Oscillator strength	Rotatory Strengths / 10^{-40} esu^2 cm^2
S_1	3.88 (319)	H→L+1	0.42351	0.0020	1.8037
S_2	4.02 (308)	H→L	0.60759	0.0267	-5.2450
S_3	4.09 (303)	H−1→L+1	0.38266	0.0242	-11.3387
S_4	4.33 (286)	H−1→L+2	0.39231	0.1865	-27.7546
S_5	4.48 (277)	H−2→L	0.43331	0.8645	239.2795
S_6	4.64 (267)	H−2→L+1	0.39029	0.0179	-82.8554
S_7	4.73 (262)	H−1→L	0.29806	0.1275	-60.8531
S_8	4.77 (260)	H−1→L+2	0.25041	0.1921	-176.4591
S_9	4.83 (257)	H-2→L+1	0.32718	0.6152	397.3696
S_{10}	4.90 (253)	H→L+2	0.49447	0.0878	-81.2049
S_{11}	4.99 (249)	H−4→L	0.41195	0.0261	128.1694
S_{12}	5.07 (245)	H−3→L+1	0.38603	0.4512	-421.8813
S_{13}	5.15 (241)	H→L+1	0.30093	0.0503	39.7007
S_{14}	5.24 (237)	H→L+3	0.33265	0.0413	-42.7019
S_{15}	5.29 (234)	H−3→L	0.39183	0.0356	33.5135
S_{16}	5.33 (232)	H→L+4	0.27819	0.0072	8.2541

[a] Estimated from TD-DFT calculations (TD-CAM-B3LYP/6-31G(d)) based on optimized structures determined by DFT calculation (CAM-B3LYP/6-31G(d)). H and L denote HOMO and LUMO.

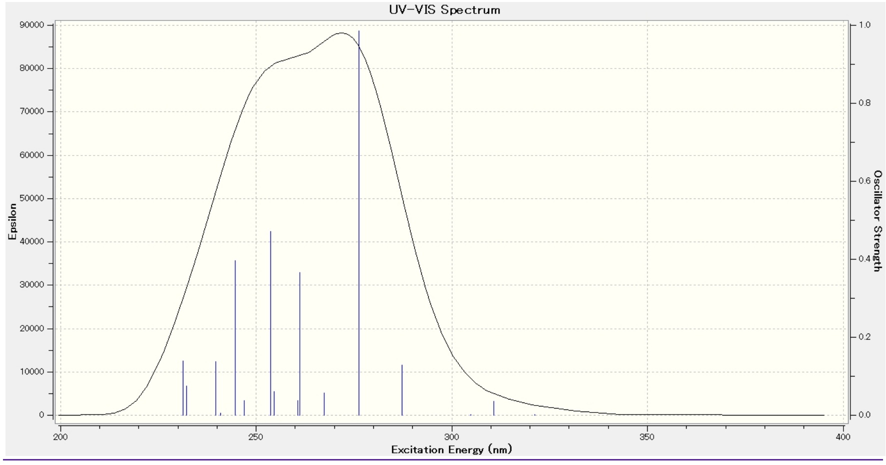


Fig. S28. Simulated UV-vis spectrum (half-width at half height = 0.20 eV) of (R_p)-**14** by TD-DFT calculation (TD-CAM-B3LYP($CHCl_3$)/6-31G(d)//CAM-B3LYP($CHCl_3$)/6-31G(d)).

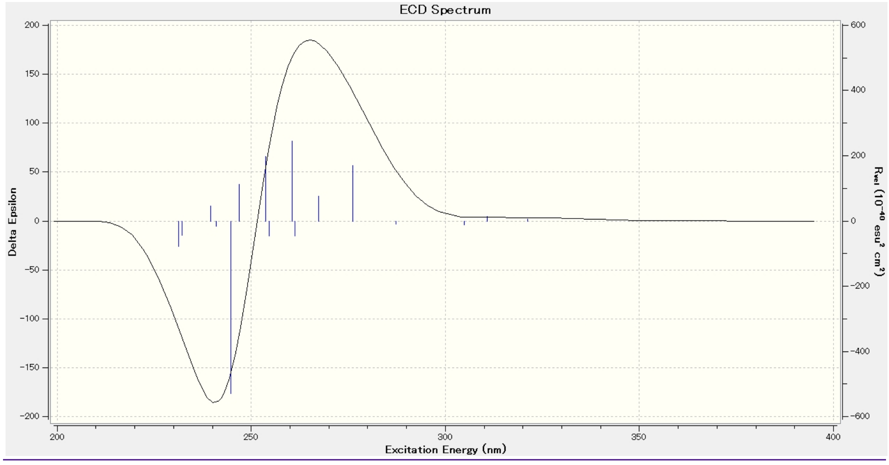
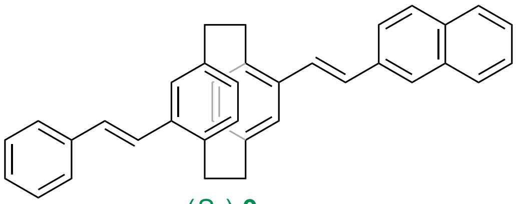


Fig. S29. Simulated ECD spectrum (half-width at half height = 0.20 eV) of (R_p)-**14** by TD-DFT calculation (TD-CAM-B3LYP($CHCl_3$)/6-31G(d)//CAM-B3LYP($CHCl_3$)/6-31G(d)).

Table S7. Selected data for excitation energy, major configuration, coefficient, oscillator strength, and rotatory strengths for (R_p)-**14**.[a]

State	Excitation energy / eV (/ nm)	Major Configuration	Coefficient	Oscillator strength	Rotatory Strengths / 10^{-40} esu^2 cm^2
S_1	3.86 (321)	H→L+1	0.39875	0.0014	4.8528
S_2	3.99 (311)	H→L	0.57099	0.0367	13.6274
S_3	4.07 (305)	H-1→L+3	0.27297	0.0016	-11.0044
S_4	4.32 (287)	H–1→L+2	0.33622	0.1288	-8.6206
S_5	4.49 (276)	H–2→L	0.43620	0.9858	170.3518
S_6	4.64 (267)	H–1→L	0.39372	0.0570	76.7423
S_7	4.75 (261)	H–4→L+1	0.21301	0.3658	-45.8299
S_8	4.76 (261)	H–2→L+1	0.41314	0.0369	245.0402
S_9	4.87 (255)	H-2→L+2	0.38008	0.0612	-46.4189
S_{10}	4.89 (254)	H→L+2	0.29599	0.4712	198.0918
S_{11}	5.02 (247)	H-4→L	0.39104	0.0383	112.3381
S_{12}	5.07 (245)	H–3→L+1	0.35699	0.000	-528.3133
S_{13}	5.15 (241)	H→L+3	0.45459	0.0058	-16.3965
S_{14}	5.17 (240)	H–1→L+3	0.29850	0.1382	45.7511
S_{15}	5.34 (232)	H-3→L	0.35620	0.0751	-44.5018
S_{16}	5.36 (231)	H-4→L	0.45069	0.1397	-77.9917

[a] Estimated from TD-DFT calculations (TD-CAM-B3LYP/6-31G(d)) based on optimized structures determined by DFT calculation (CAM-B3LYP/6-31G(d)). H and L denote HOMO and LUMO.



(S_P)-**9**

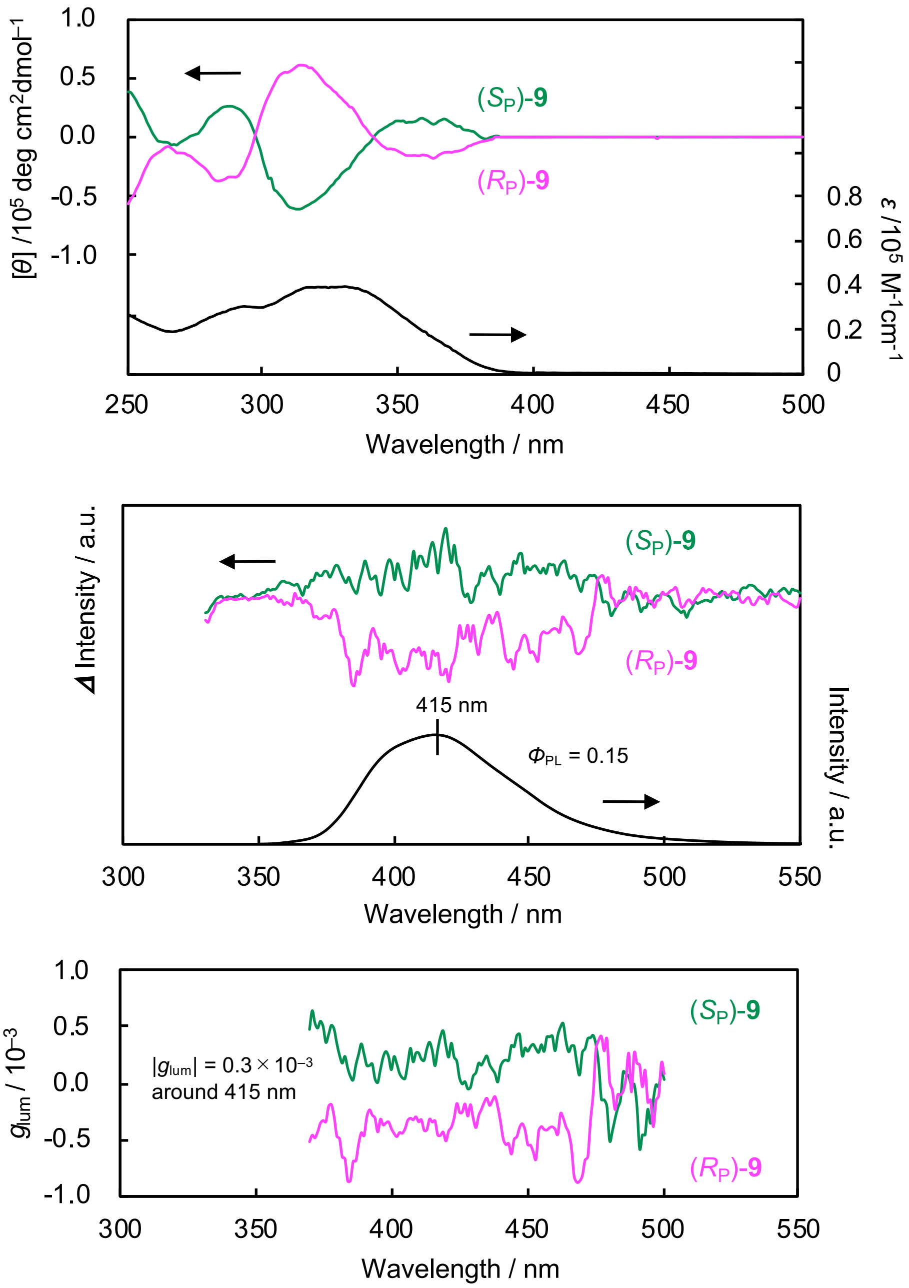
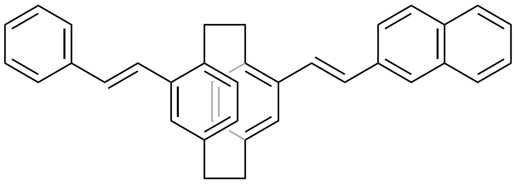


Fig. S30. UV, CD, PL, CPL spectra, and g_{lum} charts of (S_p)- and (R_p)-**9** in $CHCl_3$ (1.0×10^{-5} M). Excitation wavelength: 345 nm and 300 nm for PL and CPL, respectively.



(S_P)-**13**

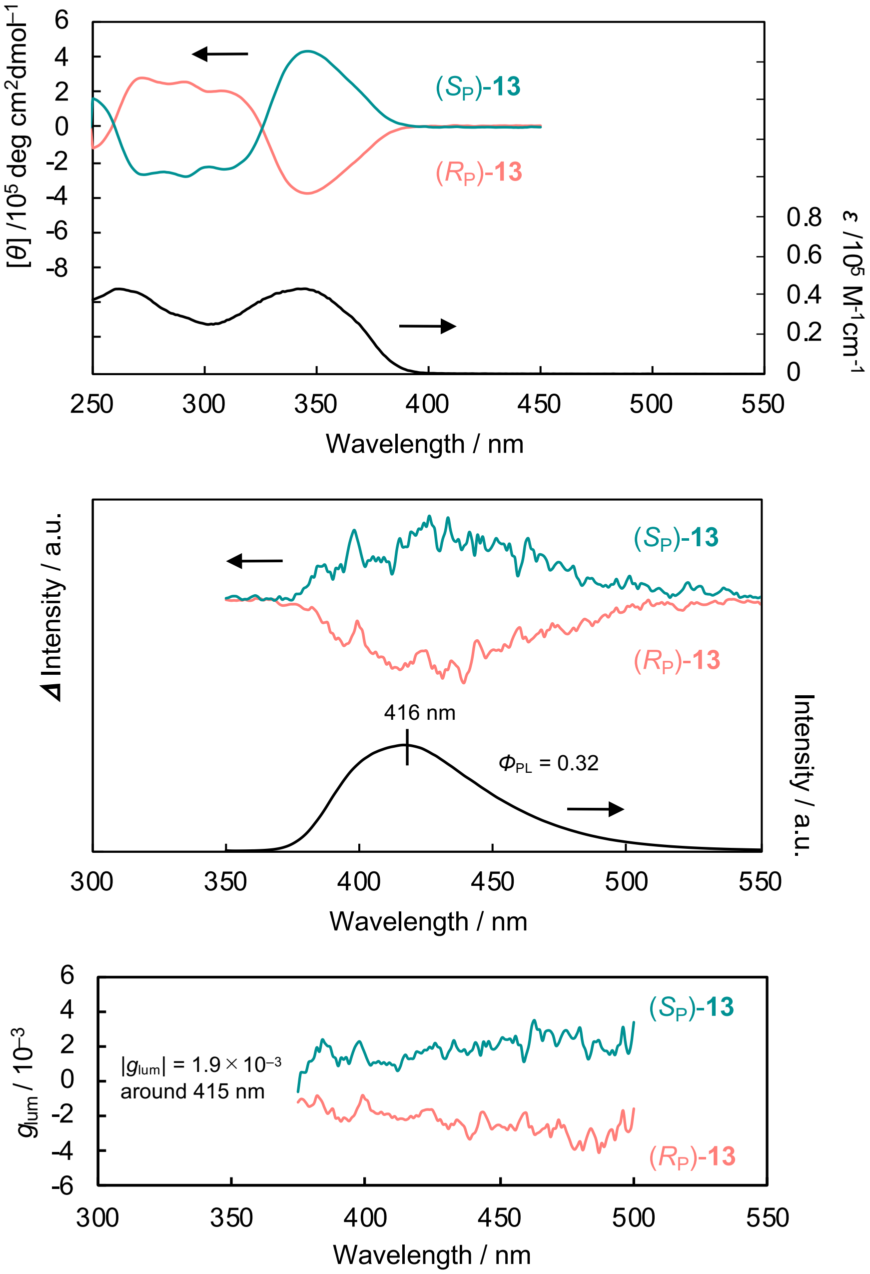


Fig. S31. UV, CD, PL, CPL spectra, and g_{lum} charts of (S_p)- and (R_p)-**13** in $CHCl_3$ (1.0×10^{-5} M). Excitation wavelength: 345 nm and 300 nm for PL and CPL, respectively.

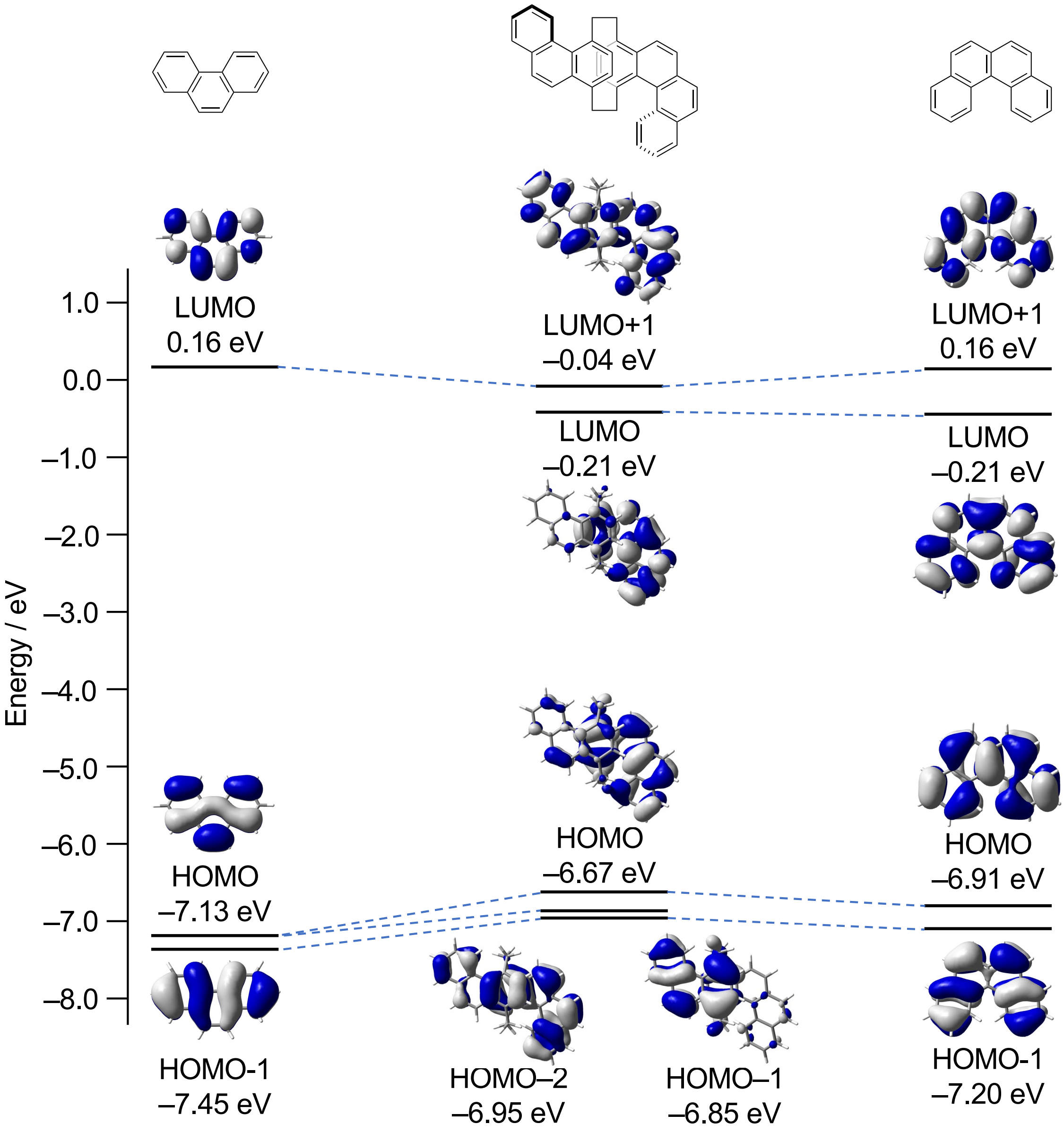


Fig. S32. Molecular orbitals of (R_p)-**10** with monomeric π-electron systems, phenanthrene and benzo[*c*]phenanthrene ((TD)-CAM-B3LYP($CHCl_3$)/6-31G(d)).

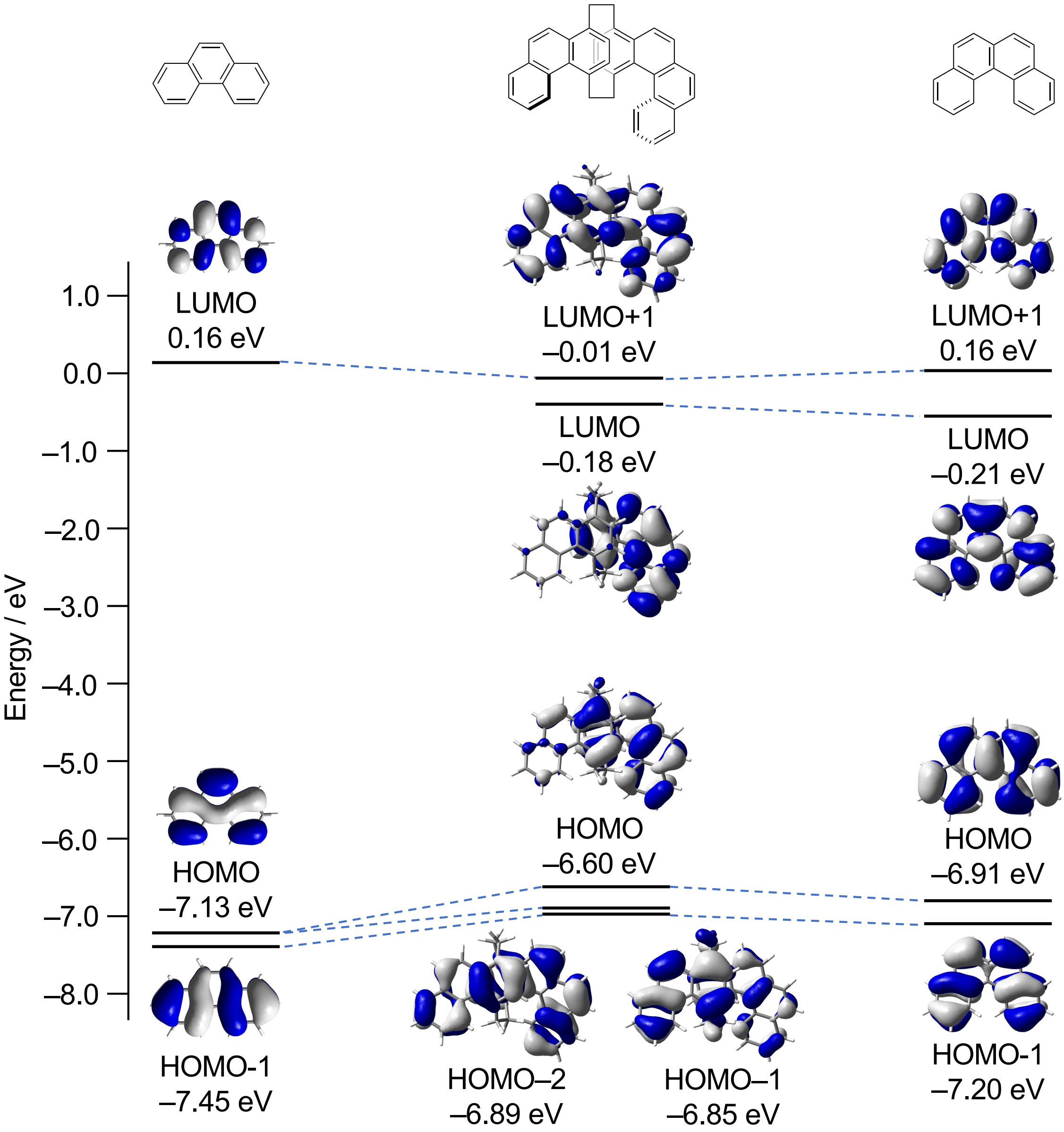


Fig. S33. Molecular orbitals of (R_p)-**14** with monomeric π-electron systems, phenanthrene and benzo[*c*]phenanthrene ((TD)-CAM-B3LYP($CHCl_3$)/6-31G(d)).

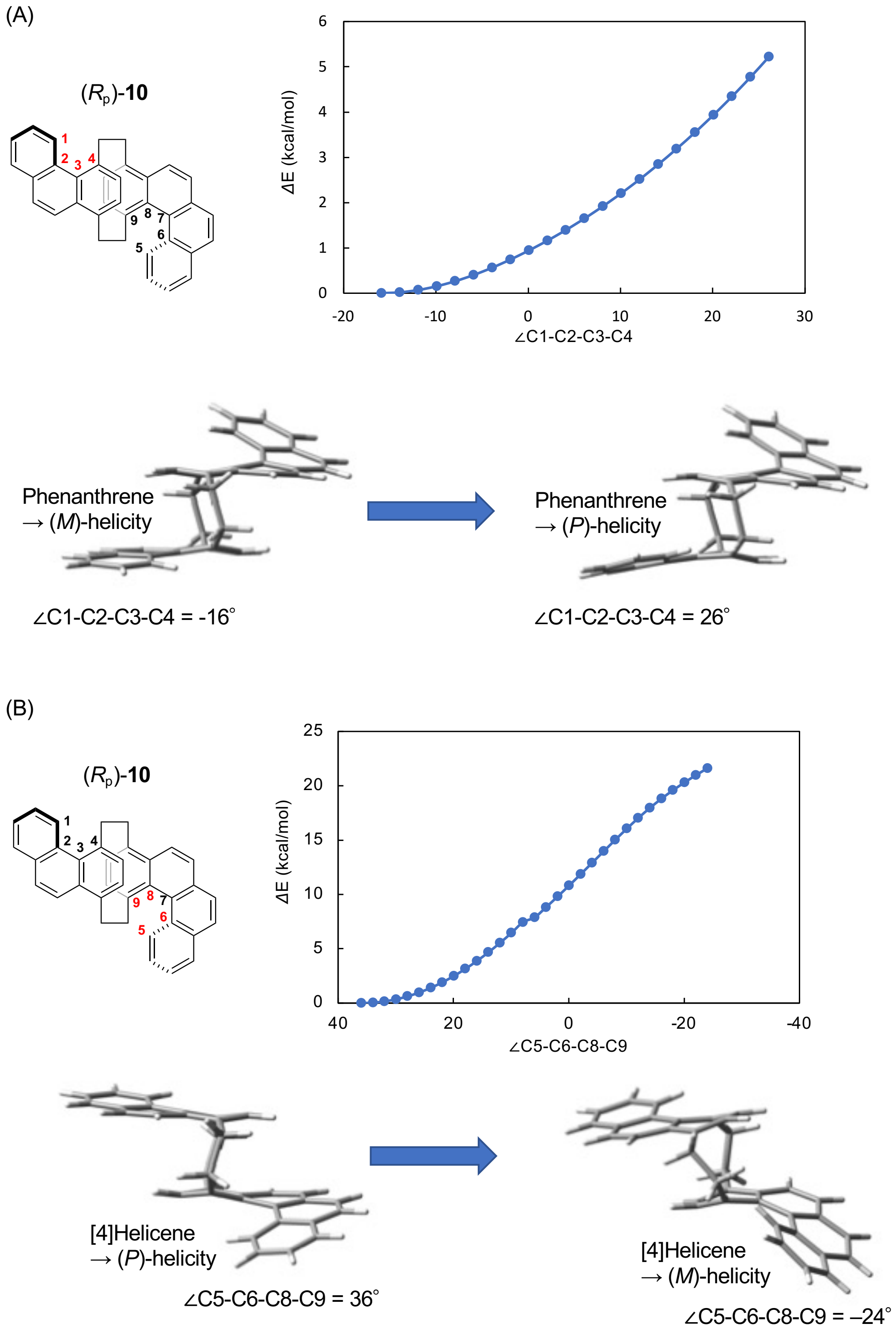


Fig. S34. Energy calculations of (A) flipped phenanthrere (from (*M*)-helicity to (*P*)-helicity) and (B) flipped [4]helicene (from (*P*)-helicity to (*M*)-helicity) in (R_p)-**10**.

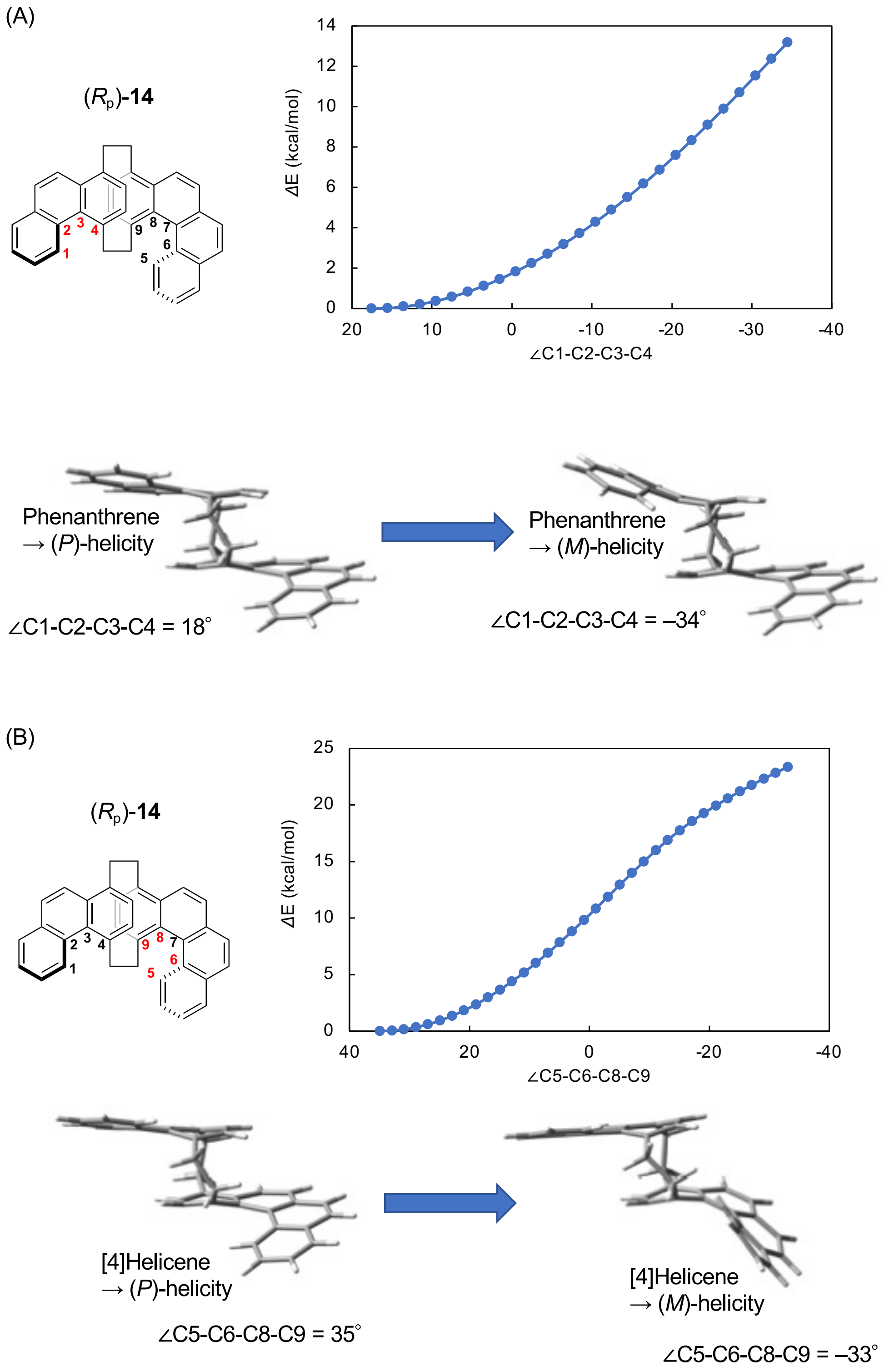


Fig. S35. Energy calculations of (A) flipped phenanthrere (from (*P*)-helicity to (*M*)-helicity) and (B) flipped [4]helicene (from (*P*)-helicity to (*M*)-helicity) in (R_p)-**14**.

Table S8. Cartesian coordinate of (R_p)-**10** in ground state (CAM-B3LYP($CHCl_3$)/6-31G(d)).

atom	x	y	z
C	-6.543641	-0.758407	-0.643855
C	-5.624462	-1.757745	-0.43634
C	-4.342371	-1.474232	0.080925
C	-3.963823	-0.134412	0.352451
H	-7.528443	-0.988654	-1.037924
H	-5.878255	-2.792531	-0.649599
C	-2.627249	0.153043	0.858739
C	-2.06845	1.4706	0.932886
C	-1.800073	-0.943476	1.230809
C	-0.948813	1.635703	1.722515
C	-0.493912	-0.726427	1.7554
C	-0.170536	0.550738	2.146603
H	-0.539956	2.633146	1.851164
H	0.7906	0.747174	2.613237
C	-2.247452	-2.282241	0.974808
C	-3.441506	-2.538855	0.395538
H	-3.756059	-3.560097	0.199896
H	-1.598159	-3.10587	1.250167
C	0.602356	-1.766296	1.688619
H	0.324398	-2.709979	2.170471
H	1.456568	-1.378019	2.250281
C	-6.208589	0.561244	-0.301808
H	-6.9441	1.352502	-0.408886
C	-4.957569	0.858238	0.189593
H	-4.753396	1.872389	0.500123
C	1.085423	-2.10427	0.225355
C	0.790327	-0.996672	-0.776959
H	2.136692	-2.380894	0.293702
H	0.553369	-2.996114	-0.118545
C	1.379498	0.312907	-0.739627
C	-0.347179	-1.155284	-1.537768
C	0.535421	1.420965	-1.057035
C	2.731441	0.581165	-0.287432
C	-1.111435	-0.059927	-1.970976
H	-0.781632	-2.145909	-1.633177
C	-0.775408	1.21359	-1.581137
C	0.970115	2.738442	-0.724226
C	3.047504	1.877238	0.159583
C	3.820679	-0.379902	-0.358996
H	-2.07855	-0.247537	-2.42864
C	-1.864323	2.264337	-1.512123
C	2.139566	2.948988	-0.07052
H	0.327764	3.578825	-0.962031
C	4.297235	2.139709	0.802808
C	5.049094	-0.093987	0.295859
C	3.77199	-1.547453	-1.158445
H	-1.577658	3.204588	-1.996112
H	-2.723487	1.881896	-2.070177
H	2.431864	3.949659	0.2348
C	5.237955	1.173813	0.926071
H	4.4698	3.136741	1.198028
C	6.106927	-1.028997	0.24946
C	4.828398	-2.425662	-1.221072
H	2.891122	-1.735527	-1.759796
H	6.17631	1.368801	1.437048
C	6.000682	-2.184325	-0.484026
H	7.024386	-0.797798	0.783553
H	4.758739	-3.304115	-1.855077
H	6.825544	-2.888692	-0.523831
C	-2.336608	2.606671	-0.047499
H	-3.369757	2.944771	-0.114817
H	-1.76496	3.468311	0.307086

Table S9. Cartesian coordinate of (R_p)-**10** in S_1 state (TD-CAM-B3LYP($CHCl_3$)/6-31G(d)).

atom	x	y	z
C	-6.5642944	-0.7789578	-0.6991692
C	-5.6403358	-1.7721071	-0.478473
C	-4.3658226	-1.4786735	0.05007602
C	-3.9977883	-0.1349527	0.31716987
C	-7.5436595	-1.0173872	-1.1018607
C	-5.8860739	-2.8093598	-0.6892096
H	-2.6662197	0.1632571	0.83330515
H	-2.1142049	1.48254318	0.89990185
C	-1.841165	-0.927869	1.23467065
C	-0.9994319	1.66387051	1.69369884
C	-0.5495239	-0.6990913	1.78618901
C	-0.2274496	0.58751238	2.14973009
C	-0.5961946	2.66470519	1.81222571
C	0.72367821	0.79137575	2.63317333
H	-2.2791439	-2.2703698	0.98010943
H	-3.4625669	-2.5366715	0.38331839
C	-3.7685778	-3.5607647	0.18920952
C	-1.6311431	-3.0896419	1.27111327
H	0.54546668	-1.741521	1.78322458
H	0.23760211	-2.6848456	2.24591428
C	1.36735579	-1.3567493	2.3928916
H	-6.2418649	0.54321232	-0.3577244
H	-6.9819425	1.32910409	-0.4725171
C	-4.9965641	0.84999966	0.14423314
H	-4.8028513	1.8658928	0.45632933
H	1.11053143	-2.0690873	0.34588429
C	0.81025531	-0.9831383	-0.6698747
C	2.17432747	-2.2762857	0.45720205
H	0.64721764	-2.9931836	-0.0123225
H	1.42070567	0.31196667	-0.6730628
C	-0.3300374	-1.1630396	-1.4516927
C	0.54683018	1.45114214	-1.0028963
C	2.77589305	0.57335092	-0.2985155
C	-1.0814706	-0.0761561	-1.917523
C	-0.7452909	-2.1609394	-1.5515179
H	-0.7448438	1.22182718	-1.5439372
C	0.9853212	2.74513477	-0.664363
C	3.11863869	1.90789673	0.16205395
C	3.84974623	-0.3780844	-0.4079635
H	-2.0330695	-0.2631425	-2.4051538
H	-1.835868	2.2675983	-1.5331644
C	2.20750928	2.96132481	-0.0498154
C	0.33784062	3.59194697	-0.8620189
C	4.36026986	2.1310375	0.79369269
H	5.10635632	-0.1119022	0.25118635
C	3.77262529	-1.5466195	-1.2022049
C	-1.5201529	3.20586587	-2.0028923
H	-2.6661787	1.88635578	-2.133825
H	2.49654566	3.96581309	0.24459273
C	5.3098359	1.13672019	0.88444384
H	4.55942844	3.11571264	1.20669544
H	6.13181486	-1.0812122	0.20337854
C	4.80739845	-2.4566137	-1.2625788
C	2.88010603	-1.7168942	-1.7934437
C	6.25483047	1.32325221	1.38566058
H	5.99070864	-2.2388906	-0.5295771
C	7.05603372	-0.8805165	0.73830302
H	4.71112716	-3.3395957	-1.8862292
H	6.7958831	-2.965548	-0.5661679
H	-2.3783579	2.60873441	-0.092171
H	-3.4176278	2.91267864	-0.2037479
H	-1.8469353	3.4891241	0.27823617

Table S10. Cartesian coordinate of (R_p)-**14** in ground state (CAM-B3LYP($CHCl_3$)/6-31G(d)).

atom	x	y	z
C	-5.420369	0.119258	-1.175829
C	-4.781778	1.313285	-1.150618
C	-3.53883	1.472865	-0.463493
C	-2.911996	0.371263	0.145828
C	-3.696797	-0.843645	0.299012
C	-4.922477	-0.976986	-0.40839
H	-6.351681	-0.004776	-1.720731
H	-5.198183	2.176094	-1.662629
C	-1.564527	0.533498	0.658847
C	-0.653214	-0.555638	0.861405
C	-1.063541	1.856923	0.853185
C	0.441828	-0.325691	1.66379
C	0.221151	2.06479	1.43097
C	0.859125	0.976513	1.980625
H	1.120346	-1.145195	1.885583
H	1.81521	1.108898	2.478651
C	-1.804399	2.959091	0.328408
C	-2.953785	2.767777	-0.365238
H	-3.479776	3.60849	-0.808465
H	-1.415179	3.96272	0.457834
C	-0.645442	-1.791008	-0.034712
H	-1.463399	-1.71497	-0.75184
H	-0.819459	-2.717392	0.523083
C	1.018238	3.333616	1.211517
H	0.46597	4.241854	1.473747
H	1.888344	3.300581	1.873318
C	1.523217	3.476511	-0.276183
C	1.706915	2.130125	-0.941816
H	2.431313	4.087509	-0.27036
H	0.778356	4.037031	-0.847939
C	2.736187	1.222738	-0.571882
C	0.692713	1.651365	-1.742607
C	2.578555	-0.172154	-0.801271
C	3.896989	1.685522	0.135442
C	0.483349	0.272613	-1.877401
H	-0.07397	2.331296	-2.102013
C	3.690819	-1.056503	-0.48649
C	1.310745	-0.643247	-1.262746
C	4.867891	0.838666	0.547255
H	3.989385	2.746034	0.342376
H	-0.458659	-0.062324	-2.303516
C	4.810141	-0.554142	0.222844
C	3.753101	-2.395359	-0.937847
C	0.703665	-1.967781	-0.814035
H	5.733764	1.209693	1.088306
C	5.881647	-1.412304	0.546881
C	4.815374	-3.213716	-0.62435
H	1.406039	-2.480978	-0.157739
H	0.512688	-2.648971	-1.652381
C	5.883358	-2.72716	0.146136
H	6.720963	-1.005996	1.104673
H	6.716619	-3.376442	0.395795
C	-5.679688	-2.163756	-0.288172
C	-3.362302	-1.873017	1.21179
C	-4.133224	-3.003738	1.340268
H	-3.851849	-3.766084	2.060151
C	-5.290591	-3.170389	0.559559
H	-5.887318	-4.072233	0.653197
H	-6.598201	-2.250688	-0.862
H	-2.495136	-1.750699	1.847557
H	4.832772	-4.235676	-0.990361
H	2.968747	-2.778892	-1.578391

Table S11. Cartesian coordinate of (*R*$_p$)-**14** in S$_1$ state (TD-CAM-B3LYP(CHCl$_3$)/6-31G(d)).

atom	x	y	z
C	-5.413134	0.075369	-1.175816
C	-4.772988	1.294574	-1.181456
C	-3.562833	1.496247	-0.482315
C	-2.916804	0.368703	0.163566
C	-3.695016	-0.827523	0.345988
C	-4.926375	-0.99448	-0.387448
H	-6.336128	-0.060997	-1.731598
H	-5.196903	2.130177	-1.730837
C	-1.570377	0.527114	0.615563
C	-0.650952	-0.554587	0.796444
C	-1.048695	1.888103	0.812688
C	0.444917	-0.345818	1.632939
C	0.221099	2.066926	1.41756
C	0.856855	0.953246	1.964659
H	1.102017	-1.177073	1.871173
H	1.796441	1.086204	2.491957
C	-1.777546	2.967215	0.277659
C	-2.970877	2.772202	-0.397926
H	-3.487697	3.616086	-0.84481
H	-1.383297	3.972524	0.373912
C	-0.654274	-1.777669	-0.105879
H	-1.479628	-1.692319	-0.814226
H	-0.828547	-2.704381	0.452786
C	1.023817	3.335044	1.241621
H	0.459269	4.236038	1.504102
H	1.878085	3.294752	1.923185
C	1.557472	3.496304	-0.233942
C	1.725761	2.153154	-0.909388
H	2.477091	4.088703	-0.204591
H	0.832933	4.077976	-0.809955
C	2.736683	1.228384	-0.534016
C	0.710489	1.698649	-1.723534
C	2.571202	-0.162184	-0.795205
C	3.890363	1.665444	0.201148
C	0.487029	0.323877	-1.880678
H	-0.042056	2.393849	-2.082488
C	3.675424	-1.060938	-0.48897
C	1.307868	-0.611979	-1.282637
C	4.847952	0.801759	0.608754
H	3.988656	2.720139	0.433183
H	-0.449977	0.002603	-2.327179
C	4.786593	-0.583135	0.249564
C	3.73943	-2.385903	-0.977523
C	0.692736	-1.948658	-0.886799
H	5.707895	1.153722	1.171492
C	5.848457	-1.454748	0.566492
C	4.793457	-3.218356	-0.670404
H	1.386939	-2.491582	-0.246447
H	0.49843	-2.595716	-1.750994
C	5.85044	-2.758831	0.129898
H	6.68112	-1.067973	1.147617
H	6.676807	-3.418652	0.37477
C	-5.651318	-2.19873	-0.262921
C	-3.358603	-1.837838	1.27733
C	-4.106904	-2.989732	1.403288
H	-3.817853	-3.739928	2.132557
C	-5.250443	-3.19039	0.605538
H	-5.826308	-4.105459	0.697345
H	-6.55631	-2.319177	-0.852208
H	-2.503394	-1.687681	1.925506
H	4.812376	-4.229377	-1.065285
H	2.964622	-2.747337	-1.642006