Supporting Information

Through-space Conjugated Polymers Consisting of Planar Chiral Pseudo-*ortho*-linked [2.2]Paracyclophane

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General

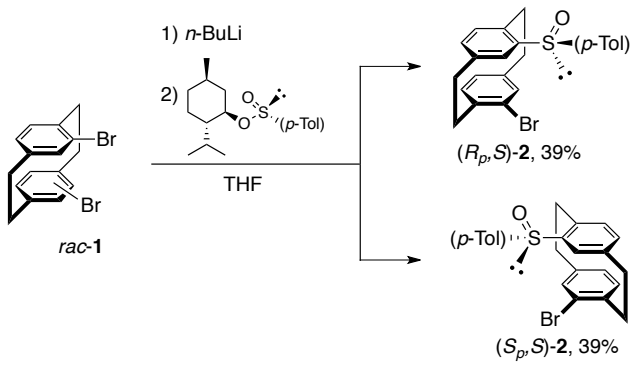
^{1}H and ^{13}C spectra were recorded on a JEOL EX400 or AL400 instrument at 400 and 100 MHz, respectively. Samples were analyzed in $CDCl_3$ or CD_2Cl_2, and the chemical shift values were expressed relative to Me_4Si as an internal standard. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-200 SiO_2. Flash column chromatorgraphy was performed with a Yamazen Science YFLC AI-580 using a Hi-flash column SiO_2 (size 2L, 2.6 cm × 15 cm). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. MALDI experiments were performed on a Thermo Scientific MALDI LTQ Orbitrap XL hybrid mass spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix. Recyclable preparative high-performance liquid chromatography (HPLC) was carried out on a Japan Analytical Industry Model LC918R (JAIGEL-1H and 2H columns) and LC9204 (JAIGEL-2.5H and 3H columns) using $CHCl_3$ as an eluent. Gel permeation chromatography (GPC) was carried out on a TOSOH 8020 (TSK gel α-4000, α-3000, and α-2500 columns) instrument using THF as an eluent at 40 °C after calibration with standard polystyrene. UV-vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and samples were analyzed in $CHCl_3$ at room temperature. Specific rotations ($[\alpha]^{t}_{D}$) were measured with a Rudolph Research Analytical ATUTOPOL IV polarimeter or HORIBA SEPA-500 polarimeter. Enantiomeric purity was confirmed by a HPLC (TOSOH UV-8020) equipped with a Daicel Chiralpak IA column (0.46 cm × 25 cm, flow rate 0.5 mL/min). Circular dichroism (CD) spectra were recorded on a JASCO J-820 spectropolarimeter with $CHCl_3$ as a solvent at room temperature. Circularly polarized luminescence (CPL) spectra were recorded on a JASCO CPL-200S with $CHCl_3$ as a solvent at room temperature. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials

rac-Pseudo-*ortho*-dibromo[2.2]paracyclophane (*rac*-**1**) was purchased from Strem Chemicals Inc. and used without further purification. *n*-BuLi (1.59 M in hexane) and *t*-BuLi (1.54 M in pentane) were purchased from Kanto Chemical Co., Inc. and used without further purification. (1*R*,2*S*,5*R*)-(–)-Menthyl (*S*)-*p*-toluenesulfinate, dimethyl-1-diazo-2-oxopropylphosphonate, and $Pd_2(dba)_3$ were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. P(*t*-Bu)$_3$, CuI, dehydrated *N,N*-dimethylformamide (DMF), and dehydrated toluene were purchased from Wako Pure Chemical Industries and used without further purification. THF and Et_3N were purchased from Kanto Chemical Co., Inc. and purified by passage through solvent purification columns under Ar pressure.[1] 2,5-Didodecyloxy-1,4-diiodobenzene was prepared as described in the literature.[2]

Synthetic Procedures and Characterization

(R_p,*S*)-2 and (S_p,*S*)-2



To a solution of *rac*-pseudo-*ortho*-dibromo[2.2]paracyclophane *rac*-**1** (385 mg, 1.05 mmol) in THF (10 mL) at –78 °C was added *n*-BuLi (1.59 M in hexane; 0.8 mL, 1.3 mmol) under Ar atmosphere. The yellow solution was stirred for 1 h at –78 °C. The solution was added to (1*R*,2*S*,5*R*)-(–)-menthyl (*S*)-*p*-toluenesulfinate (465 mg, 1.58 mmol) in THF (5.0 mL) at –78 °C. The yellow solution was warmed to room temperature and stirred for 11 h. To the reaction mixture was added saturated aqueous NH_4Cl solution, and the organic layer was extracted three times with EtOAc. The combined organic layer was washed with brine and dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was removed with a rotary evaporator. The crude residue was purified by flash column chromatography on SiO_2 (eluent: hexane/EtOAc = 4/1 v/v) to give (R_p,*S*)-**2** (176 mg, 0.41 mmol, 39%) and (S_p,*S*)-**2** (172 mg, 0.40 mmol, 39%) as colorless crystals. Recrystallization from toluene and hexane (good and poor solvent, respectively) was carried out to obtain single crystals of (R_p,*S*)-**2** and (S_p,*S*)-**2**.

(R_p,*S*)-**2**. Yield: 39%.

R_f = 0.31 (hexane/EtOAc = 4/1 v/v).

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 2.38 (s, 3H), 2.75 (m, 1H), 2.85 (m, 1H), 3.15 (m, 4H), 3.48 (m, 1H), 3.81 (m, 1H), 6.59 (m, 4H), 6.93 (s, 1H), 7.25 (m, 3H), 7.39 (d, J = 8.1 Hz, 2H) ppm.

^{13}C NMR (CD_2Cl_2, 100 MHz) δ 21.9, 33.0, 33.7, 35.3, 36.3, 125.7, 127.6, 129.6, 130.2, 132.0, 135.3, 137.5, 137.6, 138.0, 139.5, 141.0, 141.2, 141.6, 142.5, 142.7, 142.9 ppm.

HRMS (EI) calcd. for $C_{23}H_{21}OBrS$ $[M]^+$: 424.0496, found 424.0493.

Elemental analysis calcd. for $C_{23}H_{21}OBrS$: C 64.94; H 4.98; S 7.54; Br 18.78, found: C 65.14; H 4.87; S 7.49; Br 18.49.

$[\alpha]^{27}_{D} = -136.6$ (*c* 0.25, $CHCl_3$).

Retention time of HPLC: t = 10.5 min (Chiralpak IA, 0.46 cm × 25 cm, hexane/THF = 6/4 v/v, rate 0.5 mL/min).

(S_p,*S*)-**2**. Yield: 39%.

R_f = 0.28 (hexane/EtOAc = 4/1 v/v).

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 2.32 (s, 3H), 2.86 (m, 2H), 3.16 (m, 3H), 3.28 (m, 1H), 3.52 (m, 2H), 6.56 (m, 2H), 6.62 (m, 2H), 6.94 (d, J = 1.7 Hz, 1H), 7.20 (m, 2H), 7.39 (m, 2H), 7.59 (d, J = 1.7 Hz, 1H) ppm.

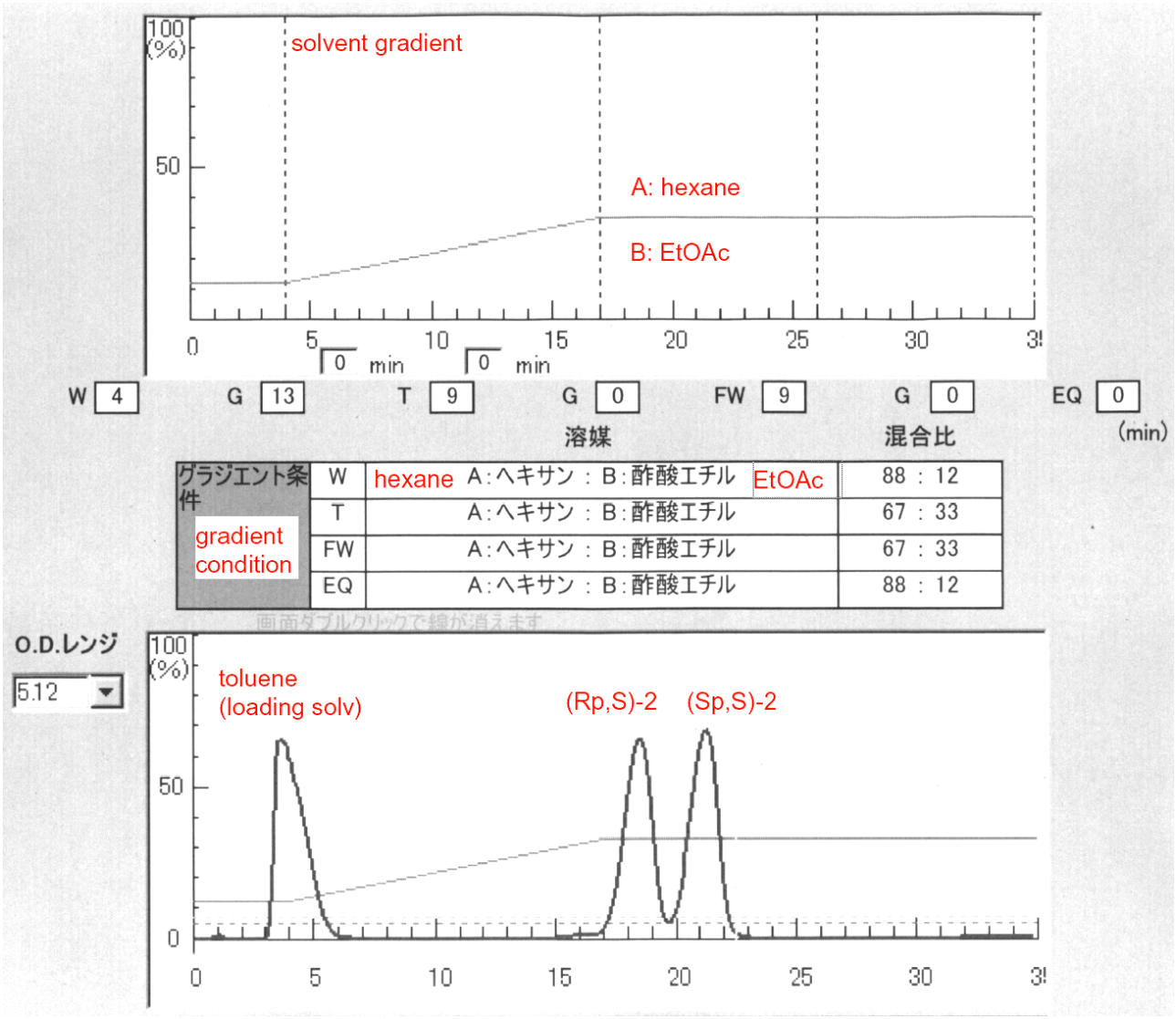
^{13}C NMR (CD_2Cl_2, 100 MHz) δ 21.8, 33.3, 34.0, 34.4, 36.5, 124.7, 126.0, 127.5, 130.6, 132.2, 135.9, 136.3, 136.4, 136.8, 137.3, 139.9, 142.0, 142.3 (overlapping signals), 143.6, 145.2 ppm.

HRMS (EI) calcd. for $C_{23}H_{21}OBrS$ $[M]^+$: 424.0496, found 424.0499.

Elemental analysis calcd. for $C_{23}H_{21}OBrS$: C 64.94; H 4.98; S 7.54; Br 18.78, found: C 65.22; H 4.97; S 7.55; Br 18.49.

$[\alpha]^{25}_{D} = +128.5$ (*c* 0.25, $CHCl_3$).

Retention time of HPLC: t = 13.7 min (Chiralpak IA, 0.46 cm × 25 cm, hexane/THF = 6/4 v/v, rate 0.5 mL/min).



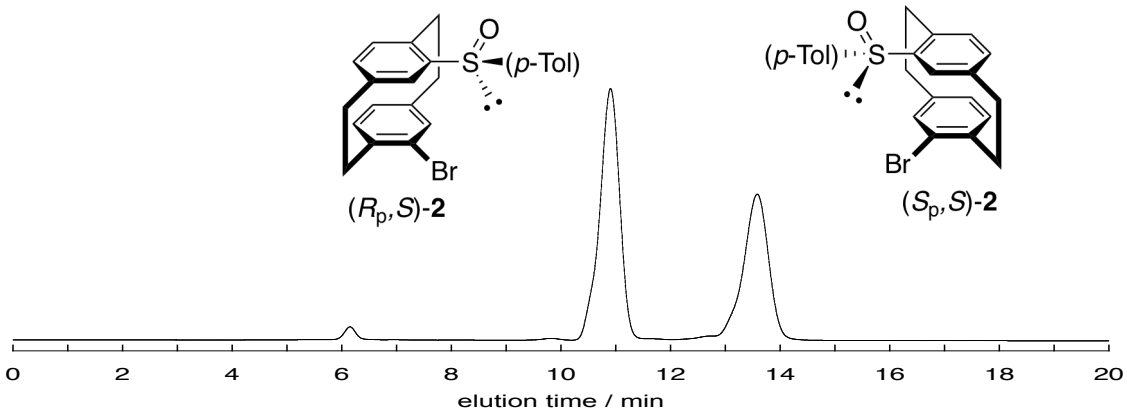
Column: Hi-flash column 2L SiO_2, 2.6 × 15 cm

Eluent: hexane/EtOAc gradient

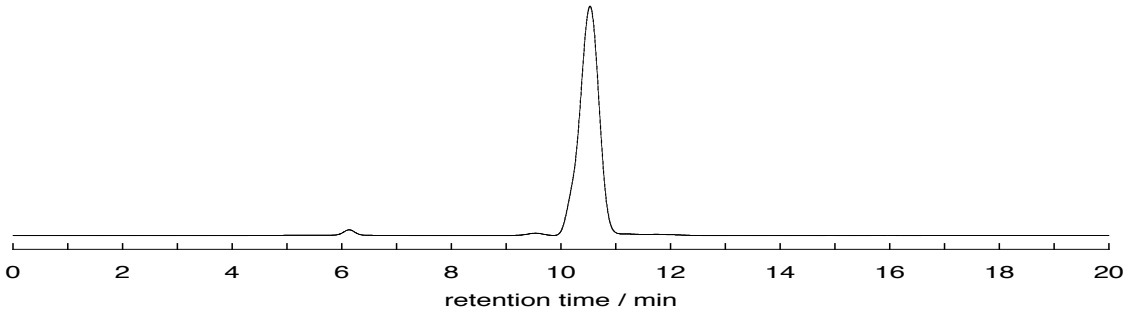
Flow rate: 20 mL/min

Figure S1. HPLC chart of (R_p,*S*)-**2** and (S_p,*S*)-**2**.

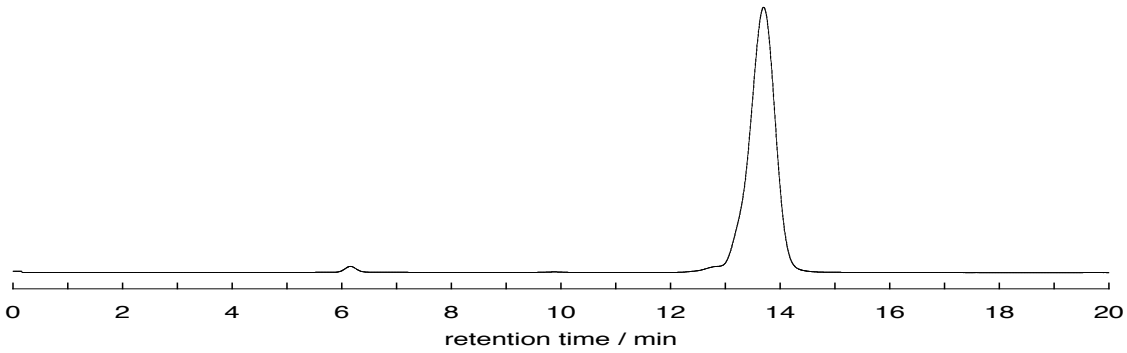
Diastereomers



(R_p,S)-**2**



(S_p,S)-**2**



Column: Chiralpak IA, 0.46 cm × 25 cm
Eluent: hexane/THF = 6/4 v/v
Flow rate: 0.5 mL/min

Figure S2. HPLC charts of mixture of the diastereomers, (R_p,S)-**2**, and (S_p,S)-**2**.

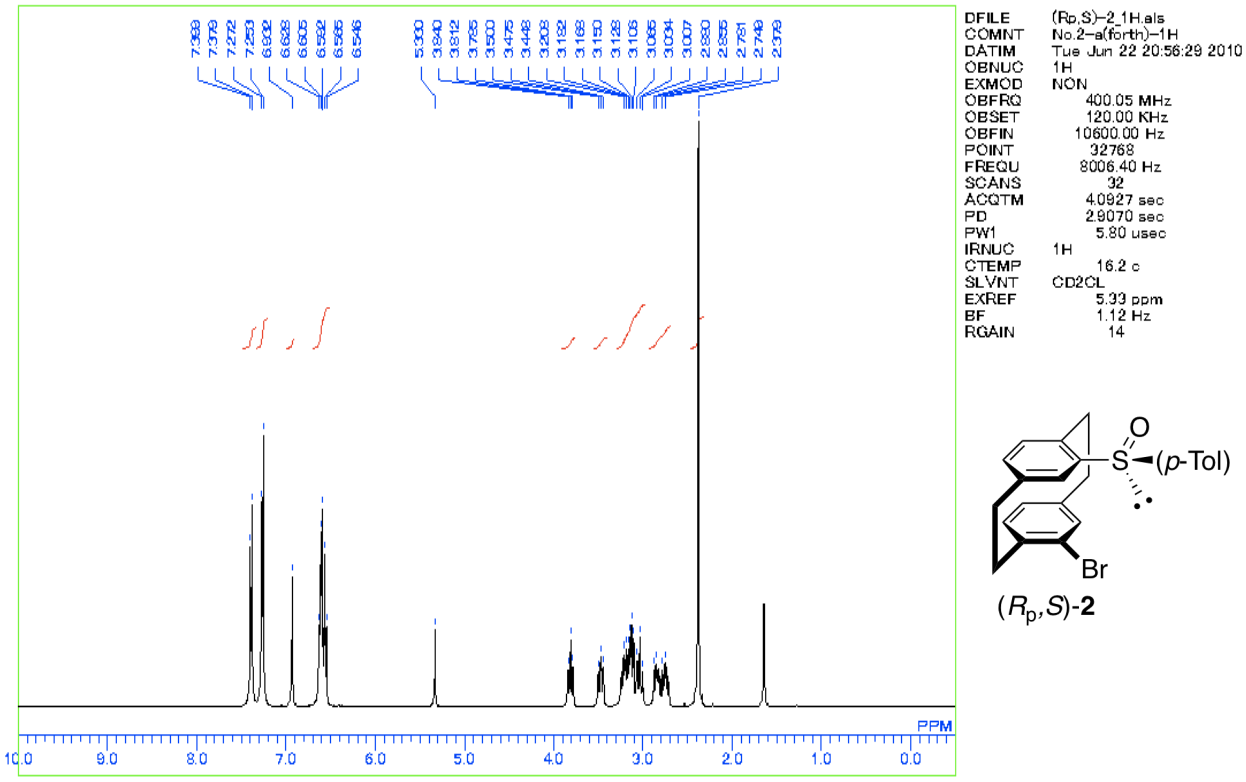


Figure S3. ^{1}H NMR spectrum of (R_p,S)-**2**, 400 MHz, CD_2Cl_2.

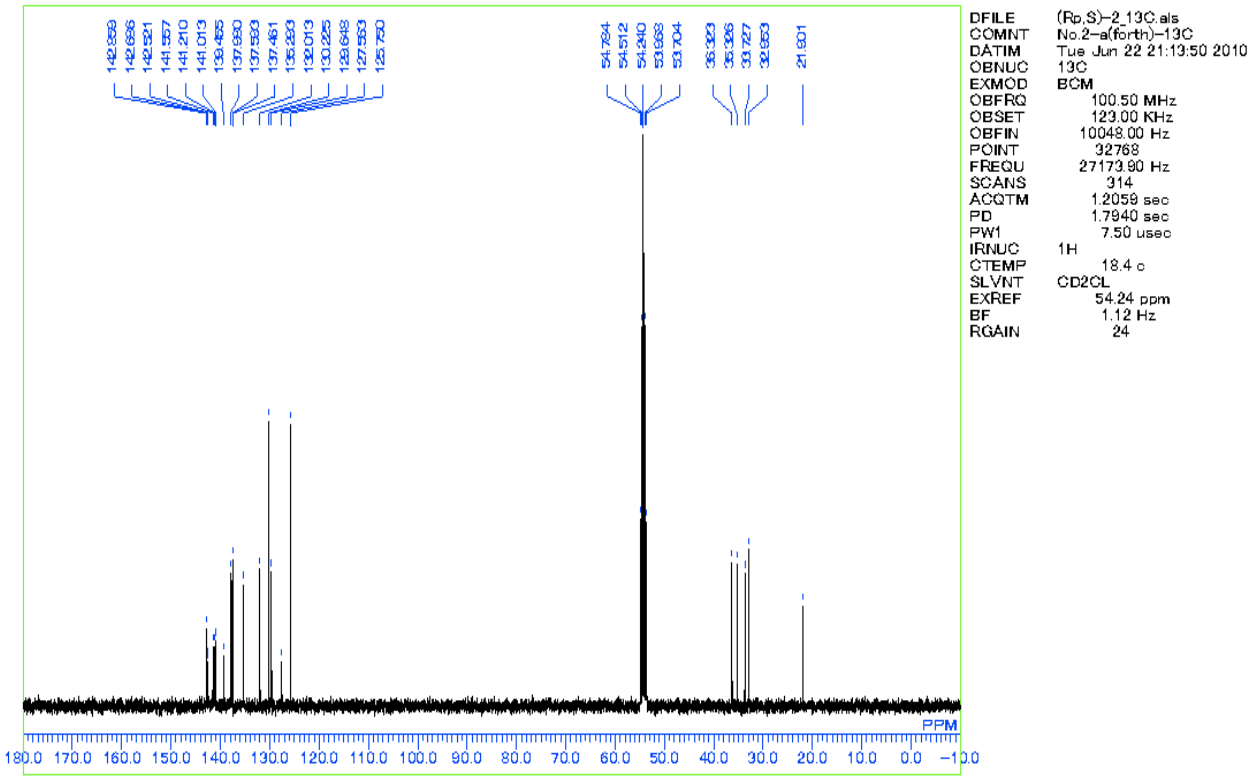


Figure S4. ^{13}C NMR spectrum of (R_p,S)-**2**, 100 MHz, CD_2Cl_2.

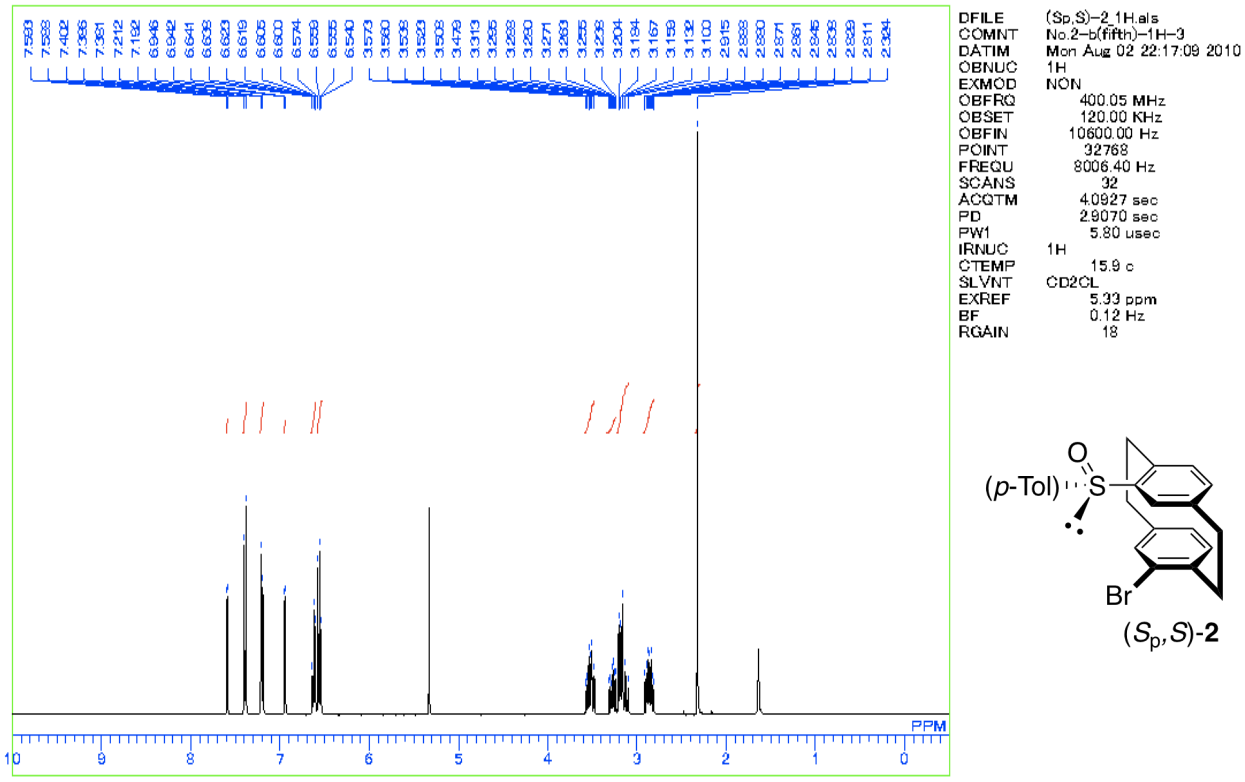


Figure S5. ^{1}H NMR spectrum of (S_p,S)-**2**, 400 MHz, CD_2Cl_2.

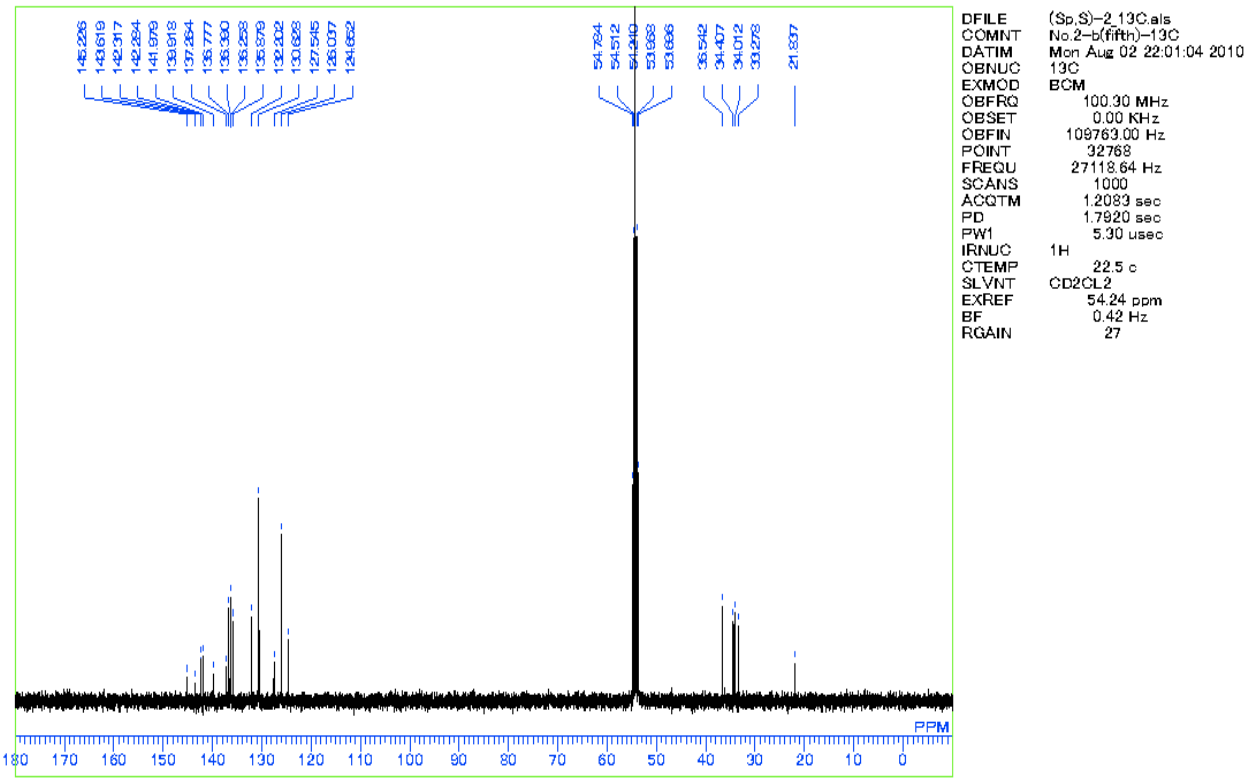
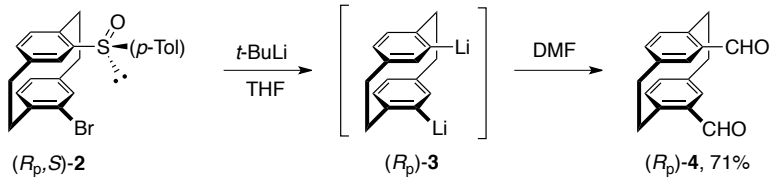


Figure S6. ^{13}C NMR spectrum of (S_p,S)-**2**, 100 MHz, CD_2Cl_2.

(R_p)-4



(R_p,*S*)-**2** (R_p)-**3** (R_p)-**4**, 71%

To a stirred solution of (R_p,*S*)-**2** (156 mg, 0.37 mmol) in THF (10 mL) was added *t*-BuLi (1.54 M in pentane, 1.9 mL, 3.0 mmol) at –78 °C under Ar atmosphere. The solution turned orange immediately and was stirred for 30 min. Dehydrated DMF (1.1 ml, 14.3 mmol) was added to the reaction mixture at –78 °C, and it was allowed to warm to room temperature. The resulting colorless solution was stirred for 9 h. To the reaction mixture was added H_2O to quench the reaction, and the organic layer was extracted three times with EtOAc. The combined organic layer was washed with brine, and dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was removed by a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 (eluent: hexane/EtOAc = 4/1 v/v) to give (R_p)-**4** (69.6 mg, 0.26 mmol, 71%) as colorless crystals.

Yield: 71%.

R_f = 0.30 (hexane/EtOAc = 4/1 v/v).

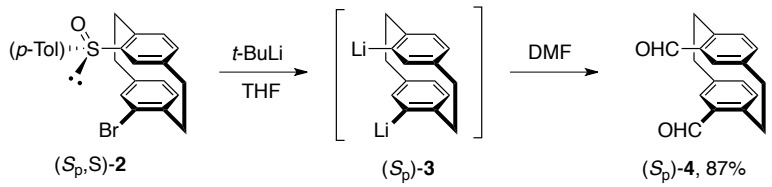
^{1}H and ^{13}C NMR spectral data were matched with the reported values of the racemic compound.[3]

HRMS (EI) calcd. for $C_{18}H_{16}O_2$ $[M]^+$: 264.1150, found 264.1154.

$[\alpha]^{27}_D$ = –67.4 (*c* 0.25, $CHCl_3$).

Retention time of HPLC: *t* = 25.3 min (Chiralpak IA, hexane/*i*-PrOH = 9/1 v/v).

(S_p)-4



(S_p,S)-**2** (S_p)-**3** (S_p)-**4**, 87%

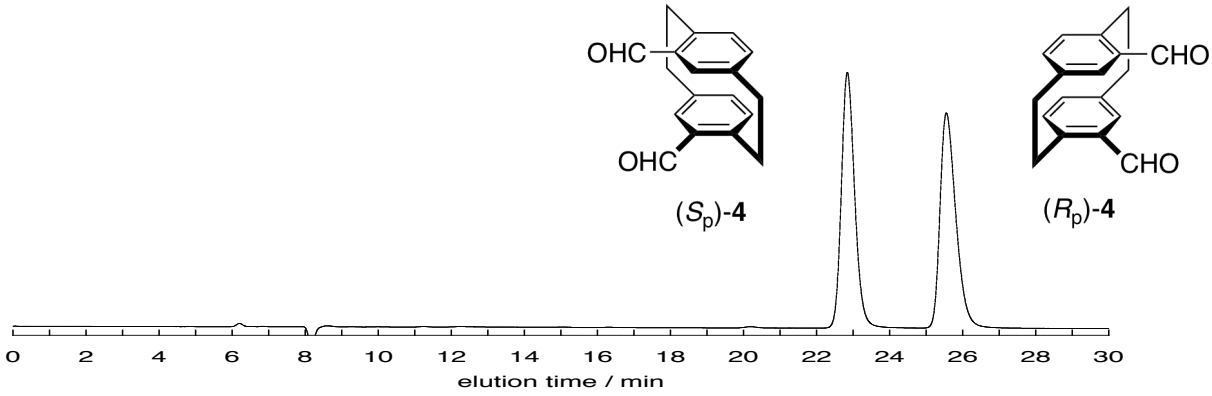
The synthetic procedure is the same as that of (R_p)-**4**.

Yield: 87 %.

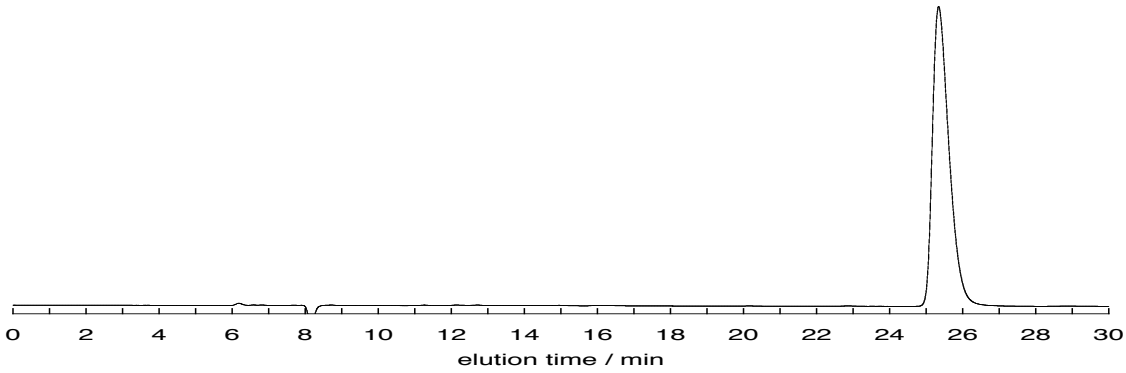
$[\alpha]^{27}_D$ = +66.1 (*c* 0.25, $CHCl_3$).

Retention time of HPLC: *t* = 22.3 min (Chiralpak IA, hexane/*i*-PrOH = 9/1 v/v).

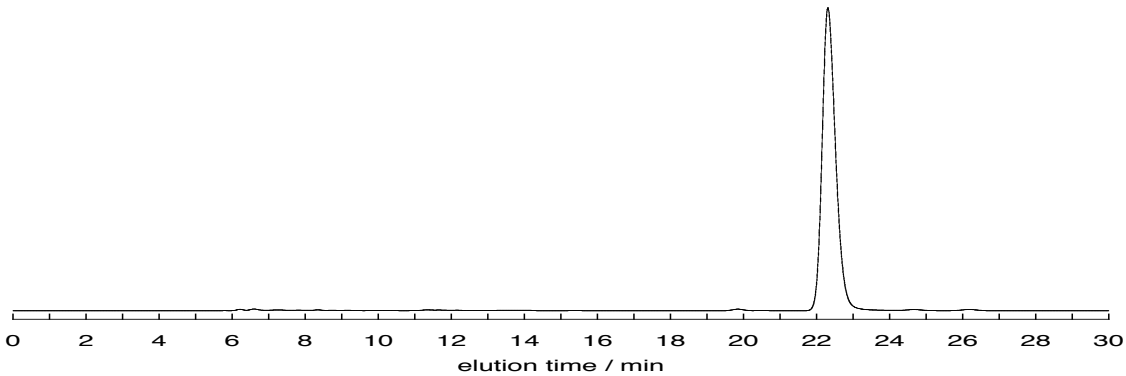
rac-**4**



(R_p)-**4**



(S_p)-**4**



Column: Chiralpak IA, 0.46 cm × 25 cm
Eluent: hexane/*i*-PrOH = 9/1 v/v
Flow rate: 0.5 mL/min

Figure S7. HPLC charts of *rac*-**4**, (R_p)-**4**, and (S_p)-**4**.

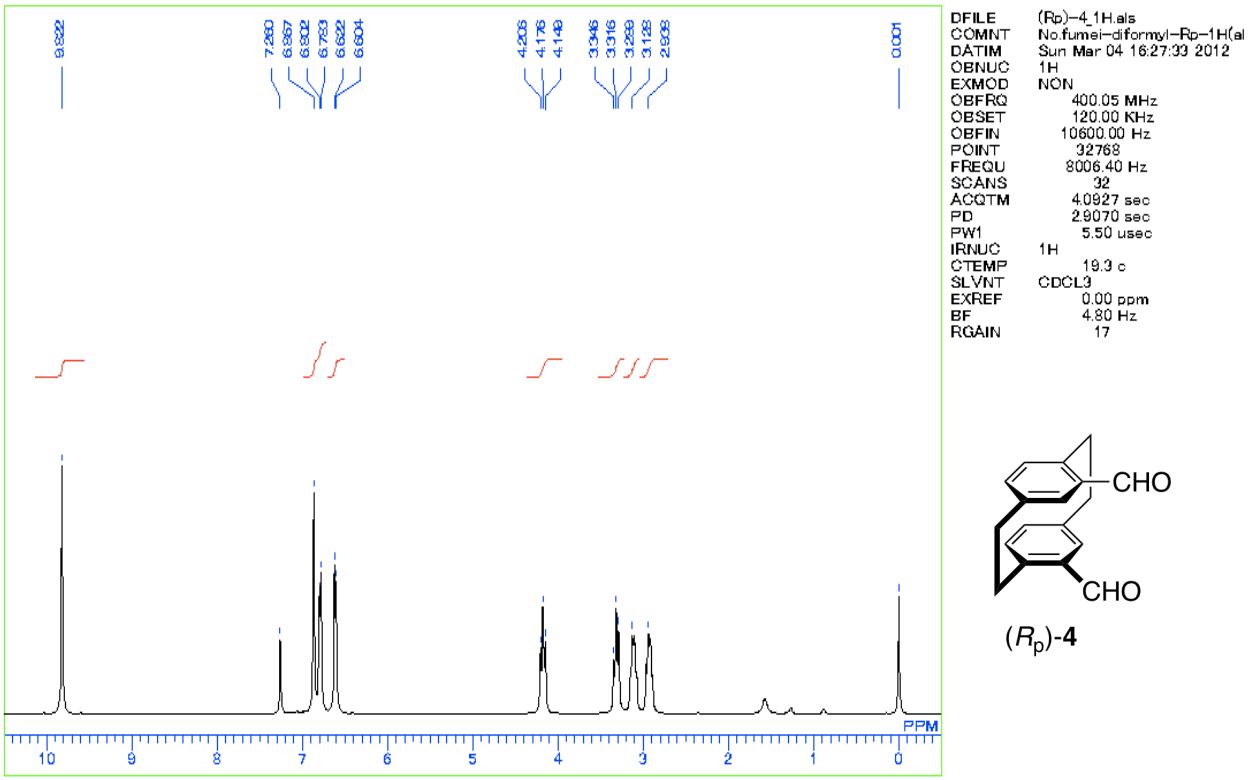


Figure S8. ^{1}H NMR spectrum of (R_p)-**4**, 400 MHz, $CDCl_3$.

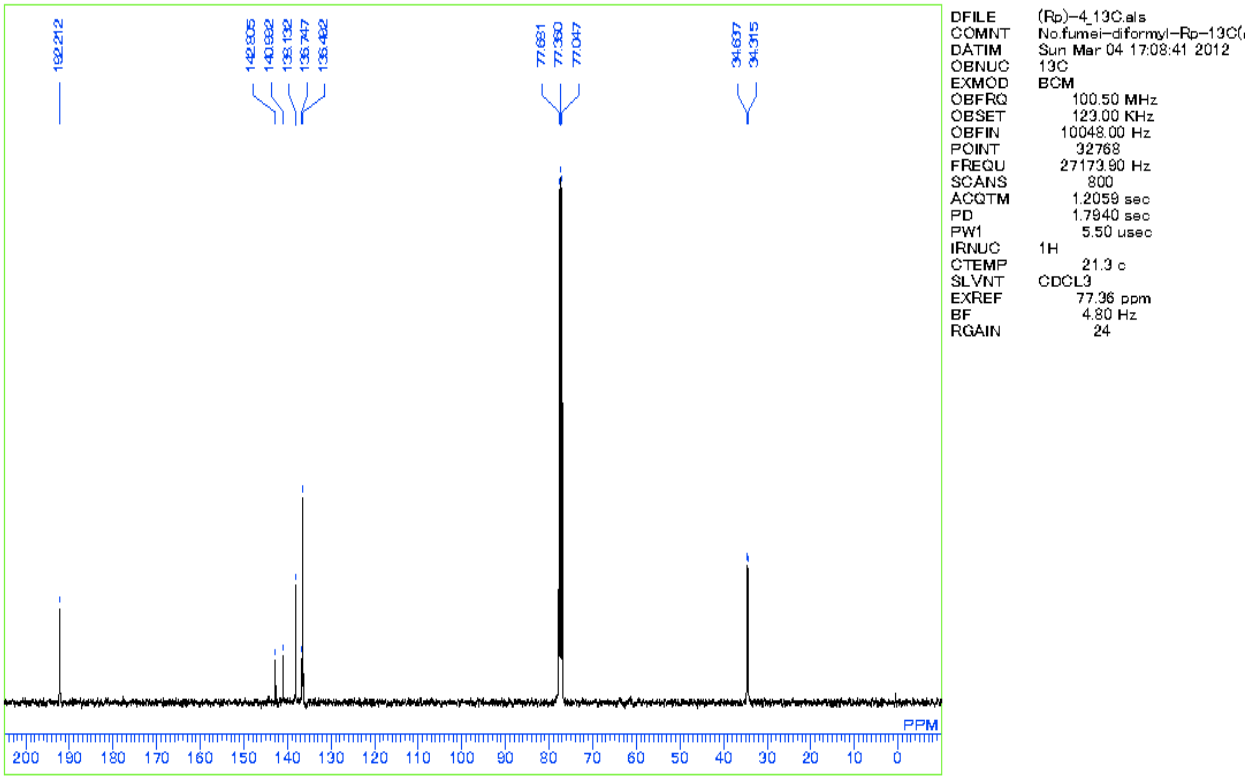
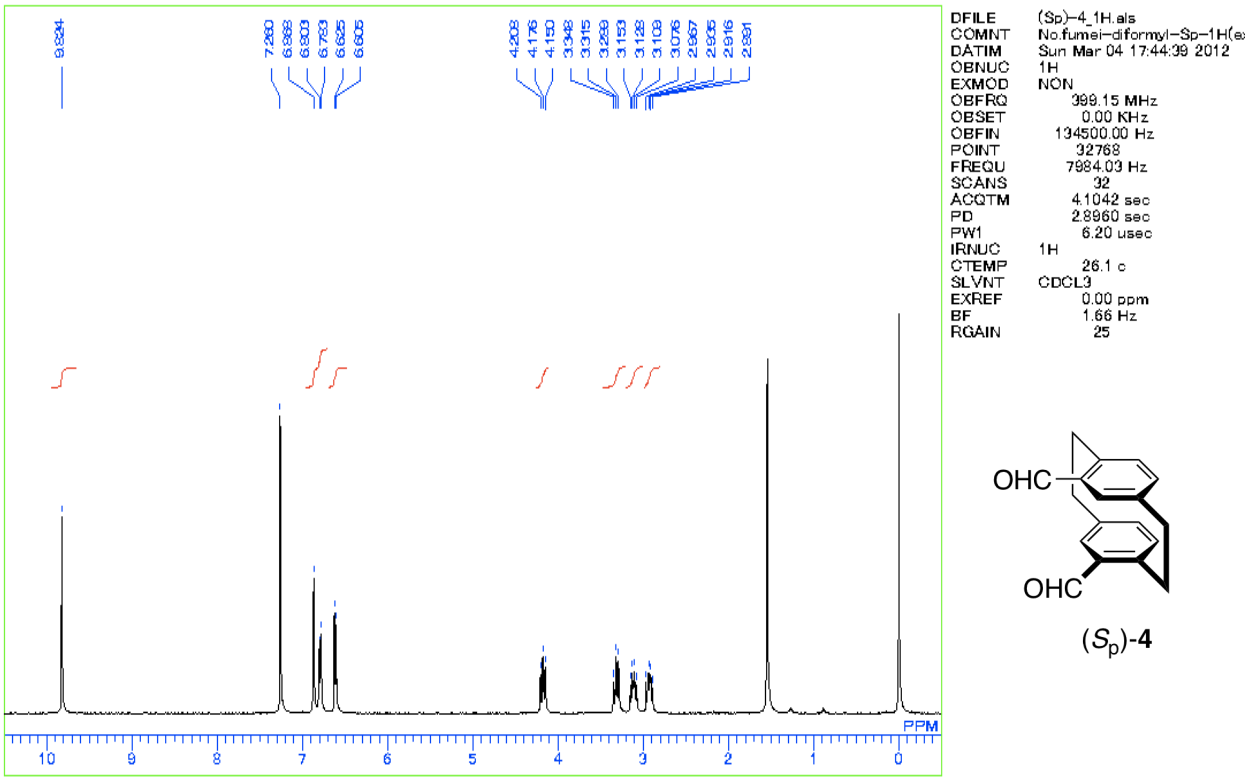


Figure S9. ^{13}C NMR spectrum of (R_p)-**4**, 100 MHz, $CDCl_3$.



(S_p)-**4**

Figure S10. ^{1}H NMR spectrum of (S_p)-**4**, 400 MHz, $CDCl_3$.

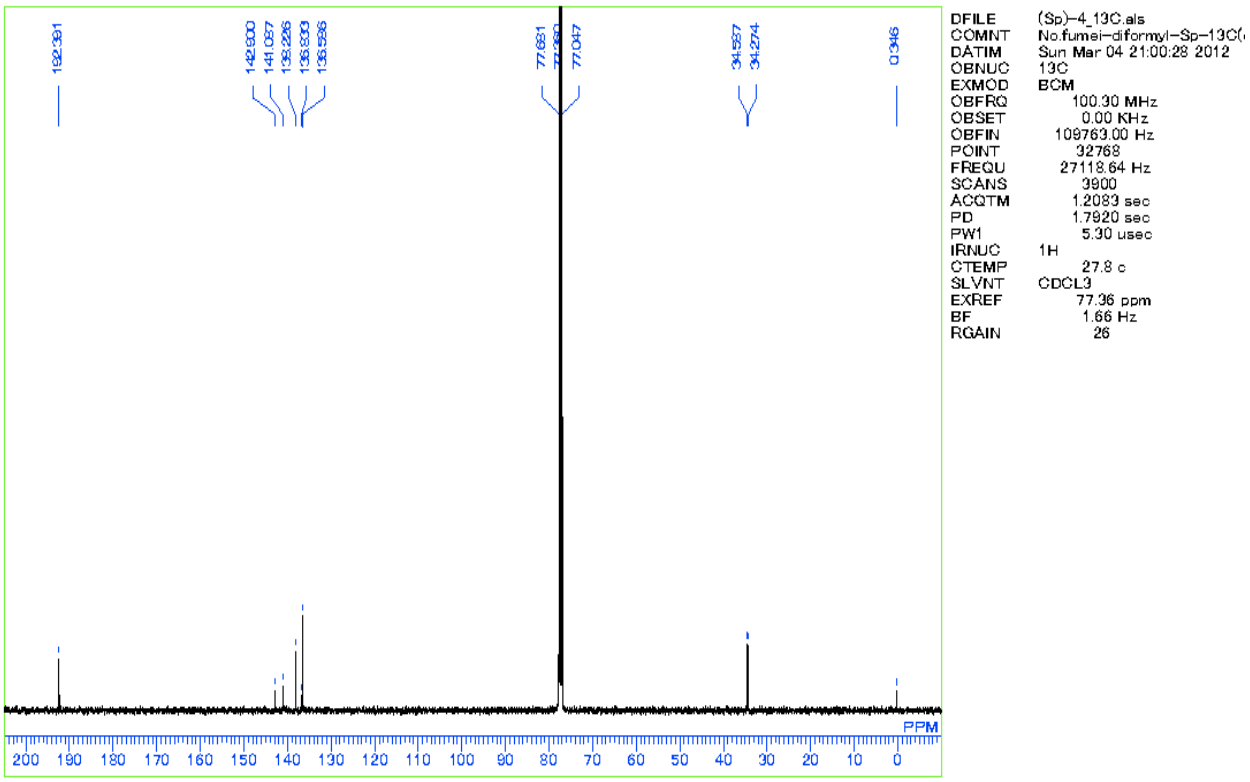
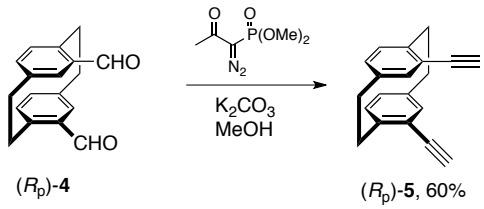


Figure S11. ^{13}C NMR spectrum of (S_p)-**4**, 100 MHz, $CDCl_3$.

(R_p)-5



(R_p)-**4** (R_p)-**5**, 60%

The mixture of (R_p)-**4** (70.2 mg, 0.27 mmol), K_2CO_3 (388 mg, 2.8 mmol), and dimethyl-1-diazo-2-oxopropylphosphonate (300 mg, 1.6 mmol) were dissolved in CH_2Cl_2 (5.0 mL). To the solution was added MeOH (10 mL) at room temperature under air. The resulting yellow solution was warmed to 50 °C and stirred for 14 h. The solution color turned pink after stirring, and H_2O was added to the solution. The organic layer was extracted three times with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was removed by a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 (eluent: hexane/EtOAc = 20/1 v/v) to give (R_p)-**5** (41.4 mg, 0.16 mmol, 60%) as colorless crystals.

Yield: 60%.

R_f = 0.35 (hexane/EtOAc = 20/1 v/v).

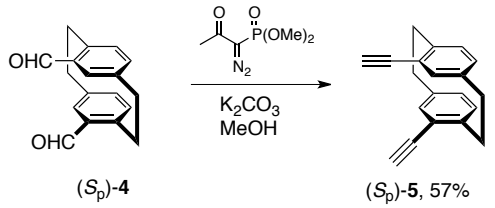
^{1}H and ^{13}C NMR spectral data were matched with the reported values of the racemic compound.[3]

HRMS (EI) calcd. for $C_{20}H_{16}$ $[M]^+$: 256.1252, found 256.1254.

$[\alpha]^{27}_D$ = –45.3 (*c* 0.25, $CHCl_3$).

Retention time of HPLC: *t* = 13.8 min (Chiralpak IA, hexane/THF = 50/1 v/v).

(S_p)-5



(S_p)-**4** (S_p)-**5**, 57%

The synthetic procedure is the same as that of (R_p)-**5**.

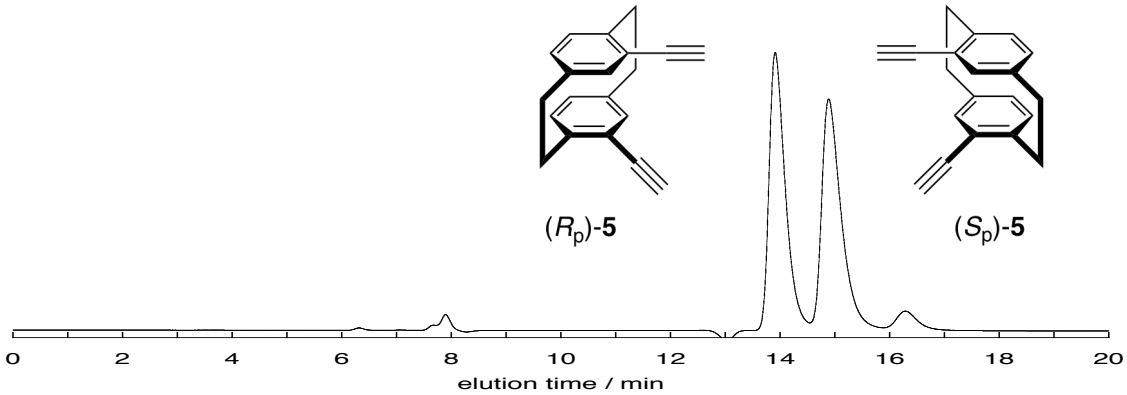
Yield: 57 %.

HRMS (EI) calcd. for $C_{20}H_{16}$ $[M]^+$: 256.1252, found 256.1254.

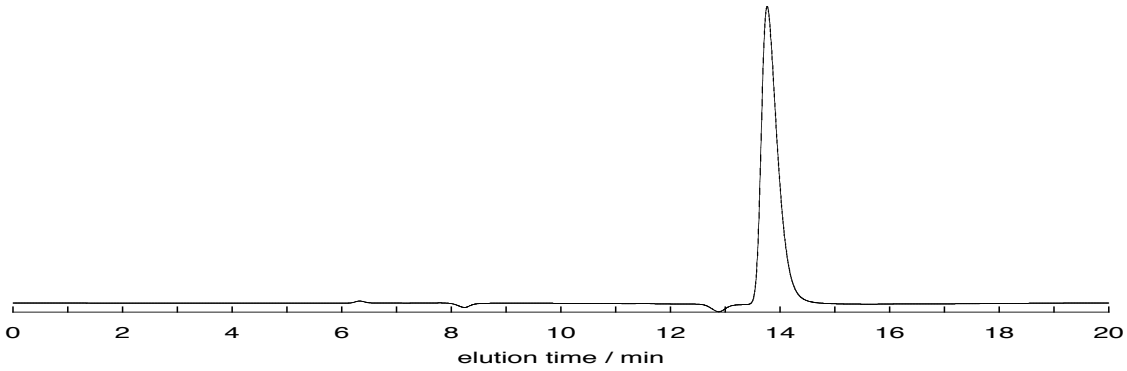
$[\alpha]^{27}_D$ = +44.5 (*c* 0.25, $CHCl_3$).

Retention time of HPLC: *t* = 14.9 min (Chiralpak IA, hexane/THF = 50/1 v/v).

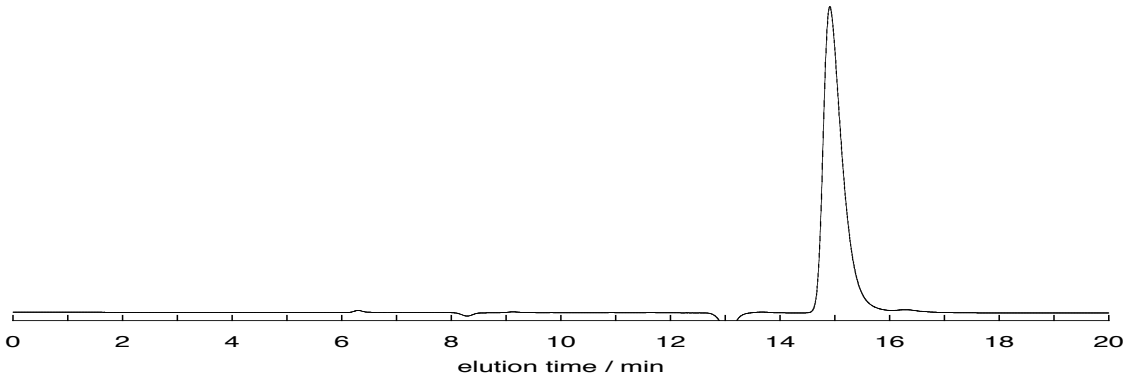
rac-**5**



(R_p)-**5**



(S_p)-**5**



Column: Chiralpak IA, 0.46 cm × 25 cm
Eluent: hexane/THF = 50/1 v/v
Flow rate: 0.5 mL/min

Figure S12. HPLC charts of *rac*-**5**, (R_p)-**5**, and (S_p)-**5**.

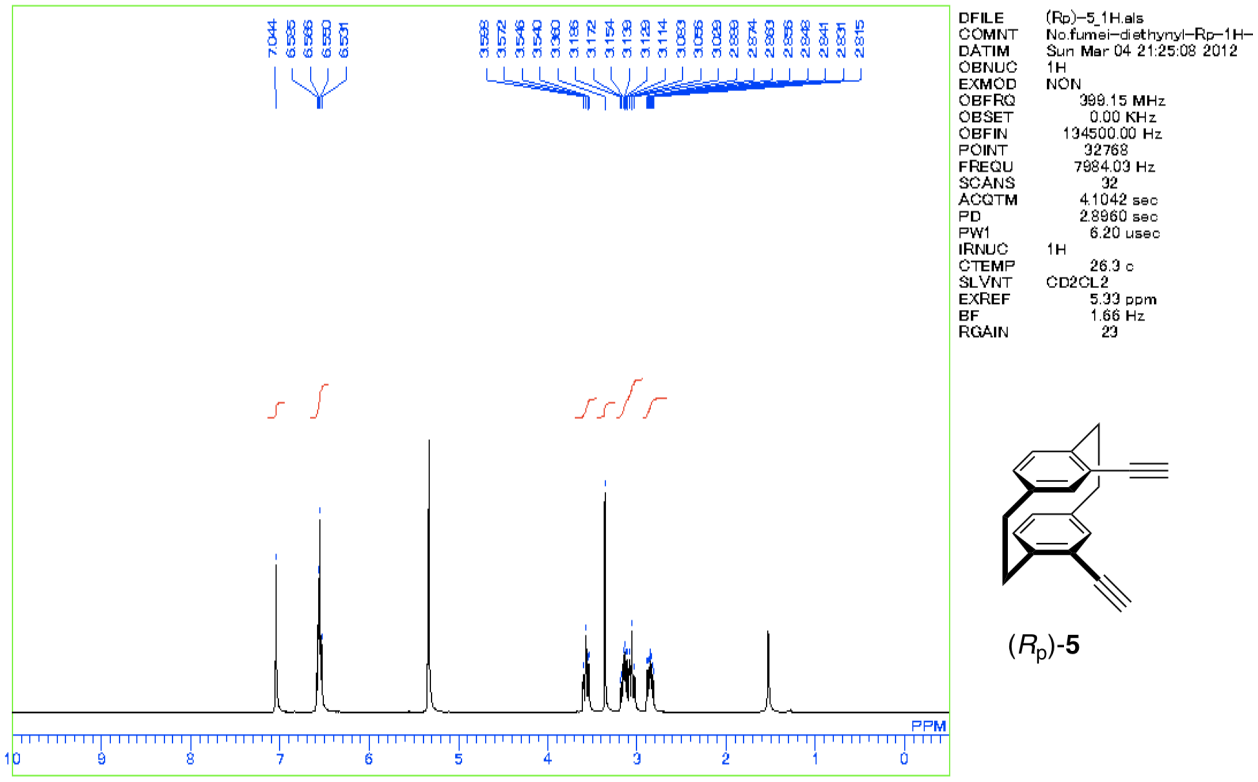


Figure S13. ^{1}H NMR spectrum of (R_p)-**5**, 400 MHz, CD_2Cl_2.

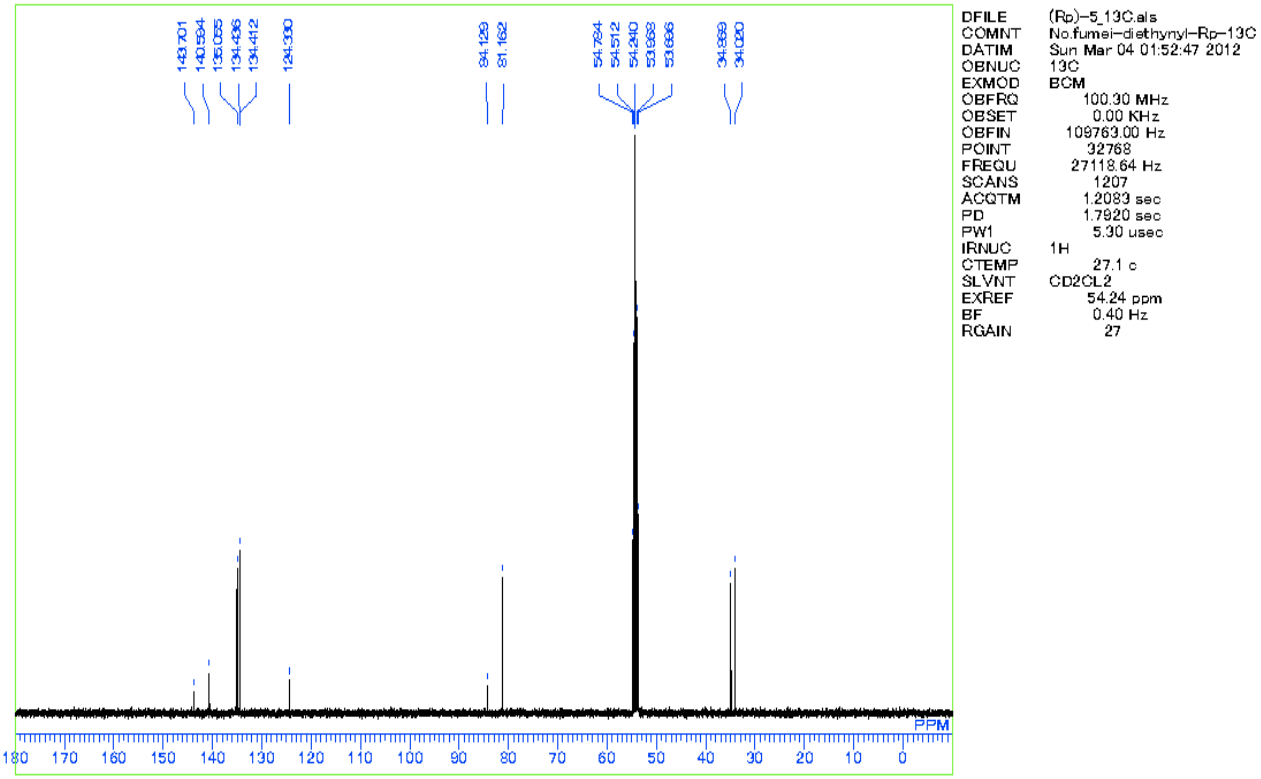


Figure S14. ^{13}C NMR spectrum of (R_p)-**5**, 100 MHz, CD_2Cl_2.

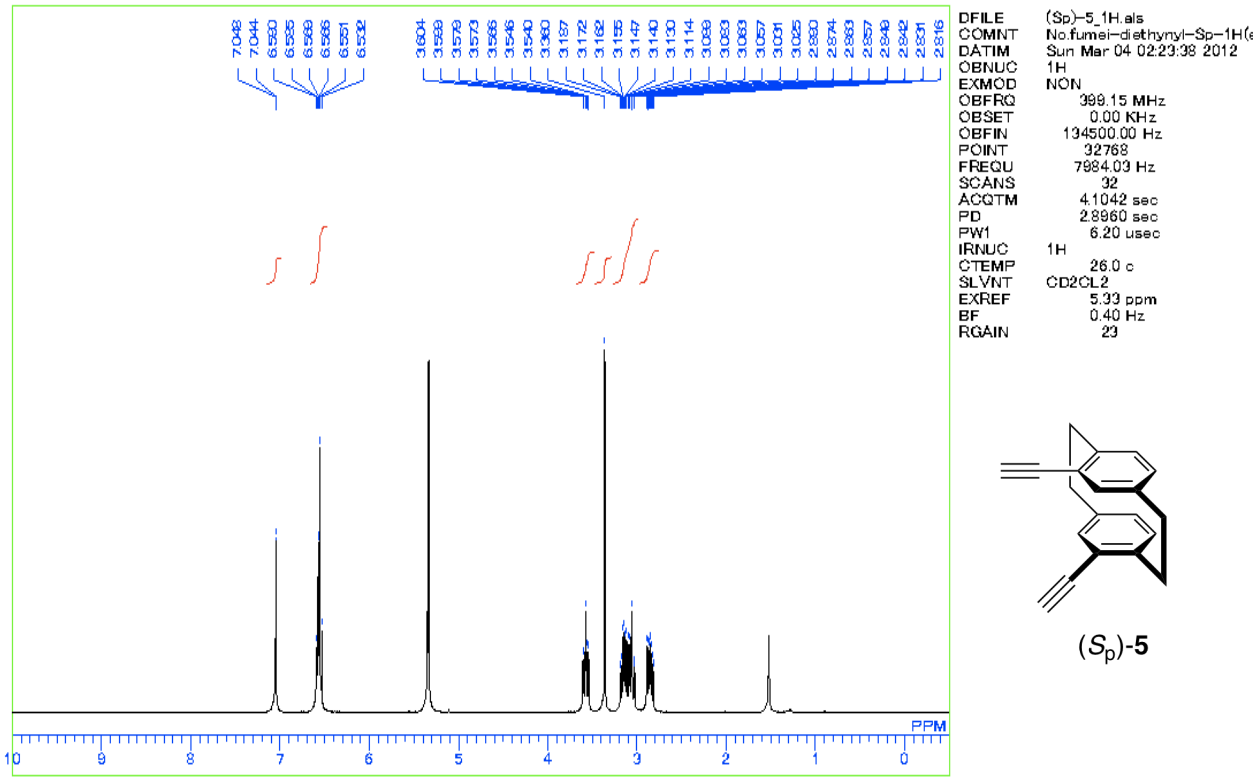


Figure S15. ^{1}H NMR spectrum of (S_p)-**5**, 400 MHz, CD_2Cl_2.

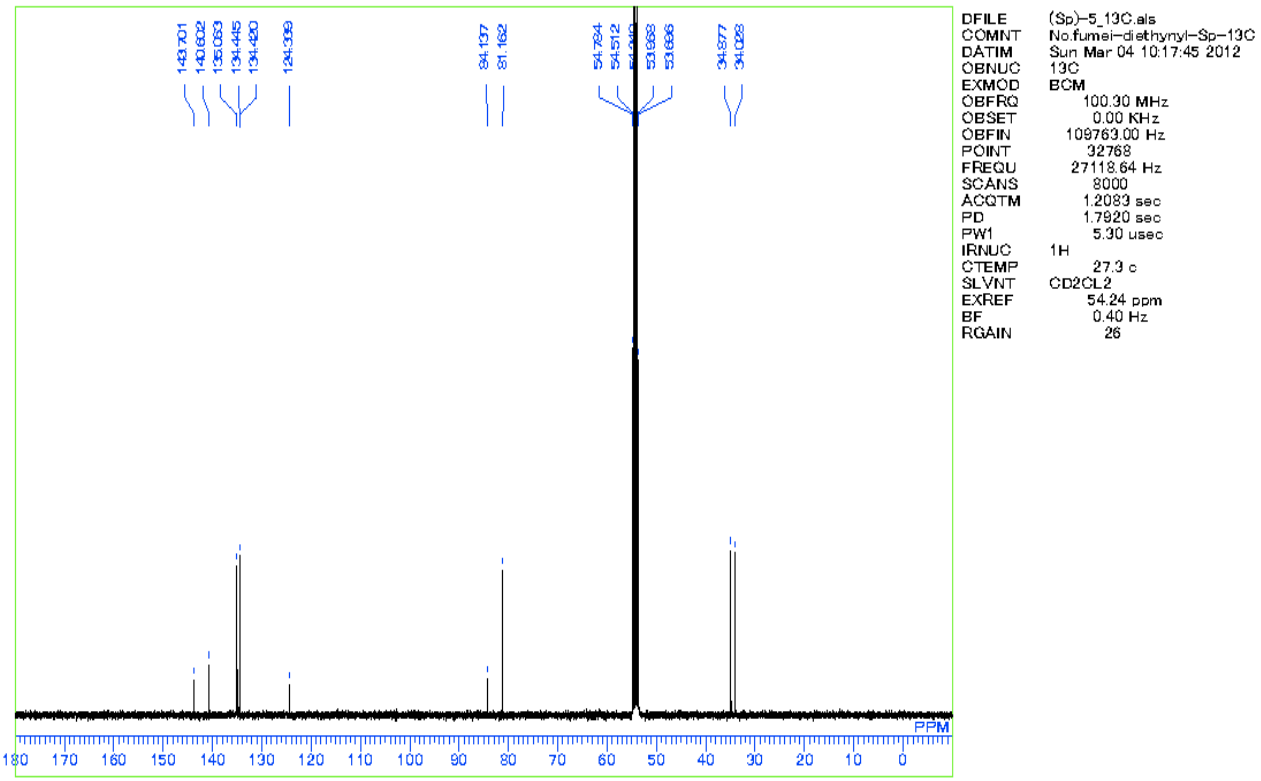
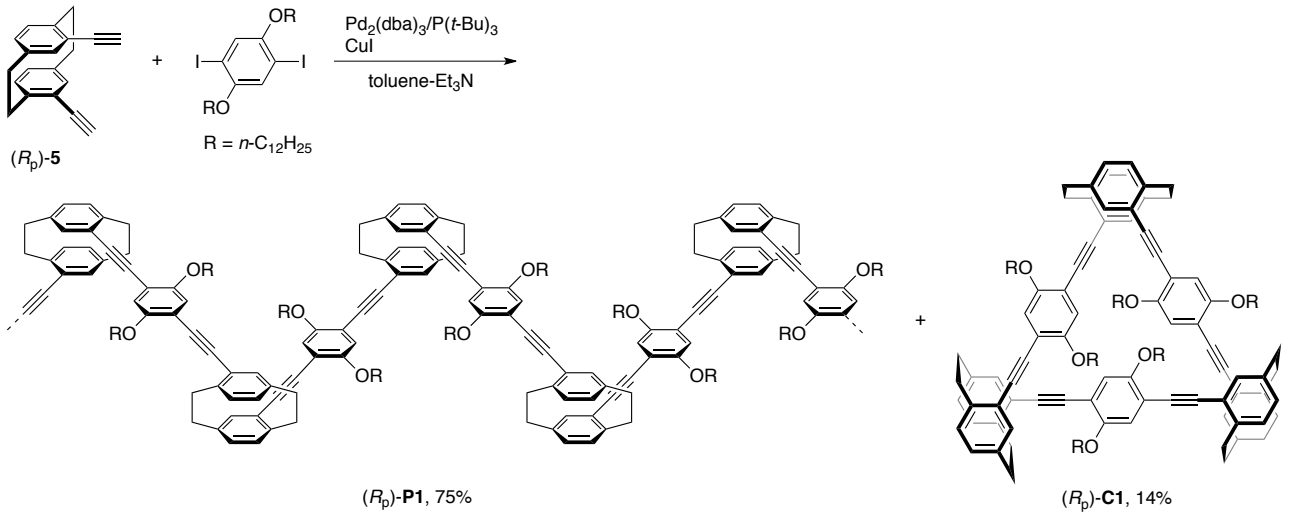


Figure S16. ^{13}C NMR spectrum of (S_p)-**5**, 100 MHz, CD_2Cl_2.

Polymerization



All of the solid reagents (R_p)-**5** (25.6 mg, 0.10 mmol), 2,5-didodecyloxy-1,4-diiodobenzene (69.9 mg, 0.10 mmol), $Pd_2(dba)_3$ (5.5 mg, 0.0060 mmol), P(*t*-Bu)$_3$ (4.2 mg, 0.021 mmol), and CuI (2.0 mg, 0.011 mmol) were placed in a Schlenk tube equipped with a magnetic stirring bar and a three-way cock. This tube was purged with Ar, followed by introducing toluene (0.50 ml) and Et_3N (0.50 mL). The reaction was carried out at 70 °C for 24 h. After the reaction mixture was cooled to room temperature, 28% aqueous NH_3 solution was added to the reaction mixture. The organic layer was extracted three times with $CHCl_3$ and washed with brine. The combined organic solution was filtered with Celite and washed with $CHCl_3$. The solvent was removed by a rotary evaporator. The residue was subjected to column chromatography (HPLC, eluent: $CHCl_3$) to separate (R_p)-**P1** (52.6 mg, 75%) as an orange solid and (R_p)-**C1** (9.8 mg, 14%) as a yellow solid.

(R_p)-**P1**. Yield: 75%. M_n = 7800 (PDI = 1.8).

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 0.87 (m, 6H), 1.21 (m, 32H), 1.46 (m, 4H), 1.80 (m, 4H), 2.88 (m, 2H), 3.07 (m, 2H), 3.30 (m, 2H), 3.78 (m, 2H), 3.94 (m, 4H), 6.57 (m, 4H), 7.05 (m, 2H), 7.16 (m, 2H) ppm.

^{13}C NMR (CD_2Cl_2, 100 MHz) δ 14.8, 23.6, 27.3, 30.3, 30.6 (overlapping signals), 32.9, 34.5, 35.3, 70.4, 90.7, 95.7, 115.0, 117.2, 125.9, 133.8, 134.2, 134.7, 140.6, 143.1, 154.4 ppm.

(R_p)-**C1**. Yield: 14%.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 0.86 (m, 18H), 1.23 (m, 64H), 1.28 (m, 32H), 1.46 (m, 12H), 1.87 (m, 12H), 2.89 (m, 6H), 3.11 (m, 6H), 3.30 (m, 6H), 3.74 (m, 6H) 4.07 (t, J = 6.8 Hz, 12H), 6.60 (m, 12H), 7.09 (m, 6H), 7.24 (m, 6H) ppm.

^{13}C NMR (CD_2Cl_2, 100 MHz) δ 14.7, 23.5, 27.1, 30.2, 30.4 (overlapping signals), 30.5 (overlapping signals), 32.7, 34.2, 35.4, 70.6, 90.4, 95.2, 115.0, 117.6, 125.7, 133.8, 134.4, 134.9, 140.8, 143.2, 154.5 ppm.

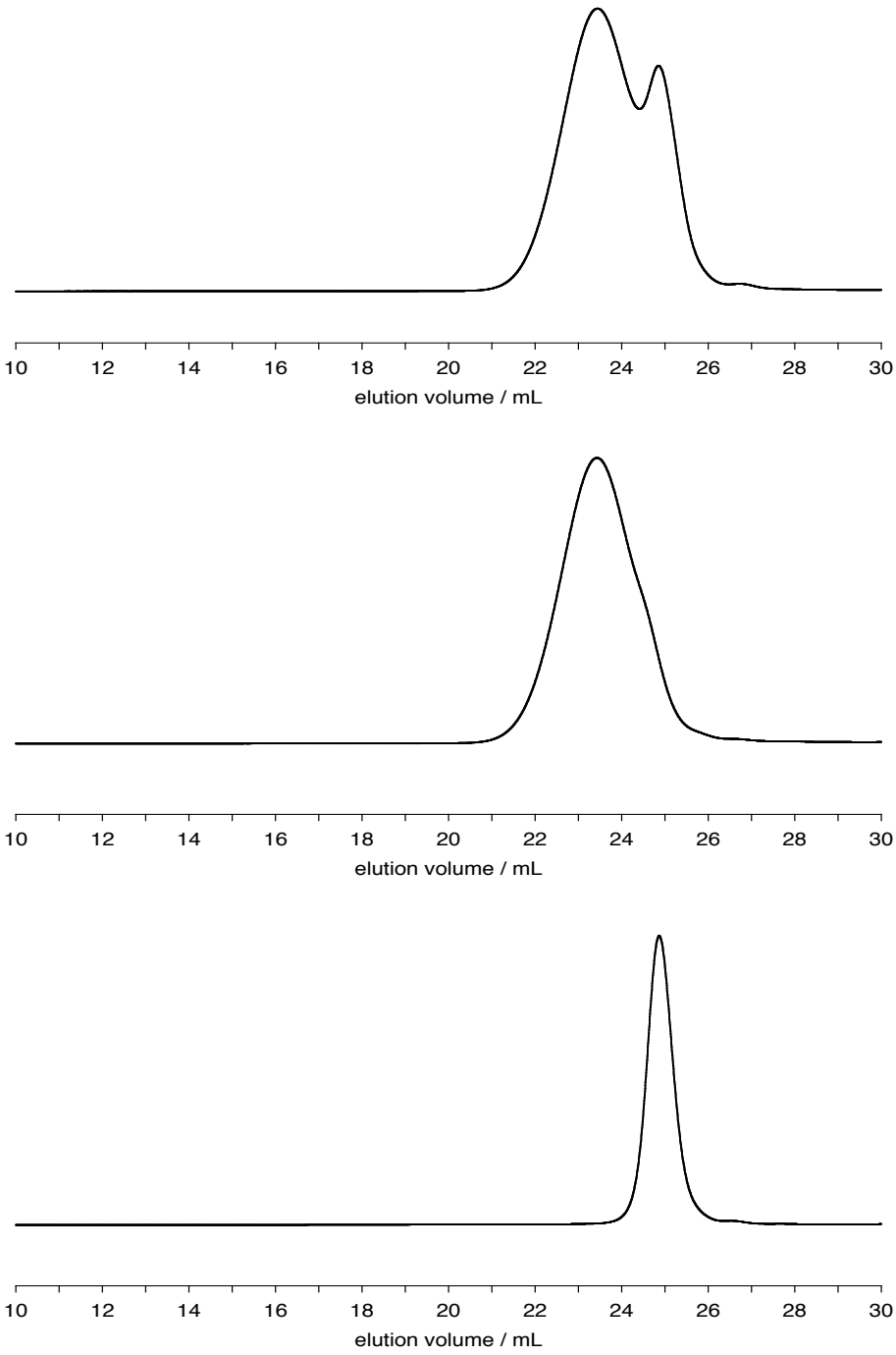
HRMS (MALDI, matrix: DCTB) calcd. for $C_{150}H_{198}O_6$ $[M]^+$: 2095.5188, found 2095.5184.

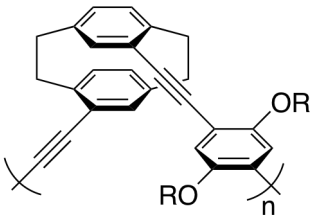
Polymer (S_p)-**P1** and compound (S_p)-**C1** were obtained by the same procedure above using monomer (S_p)-**5**.

(S_p)-**P1**. Yield: 66%. M_n = 8500 (PDI = 1.4).

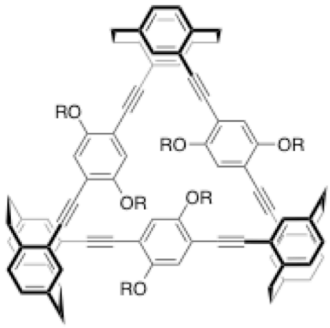
(S_p)-**C1**. Yield: 8%.

HRMS (MALDI, matrix: DCTB) calcd. for $C_{150}H_{198}O_6$ $[M]^+$: 2095.5188, found 2095.5193.





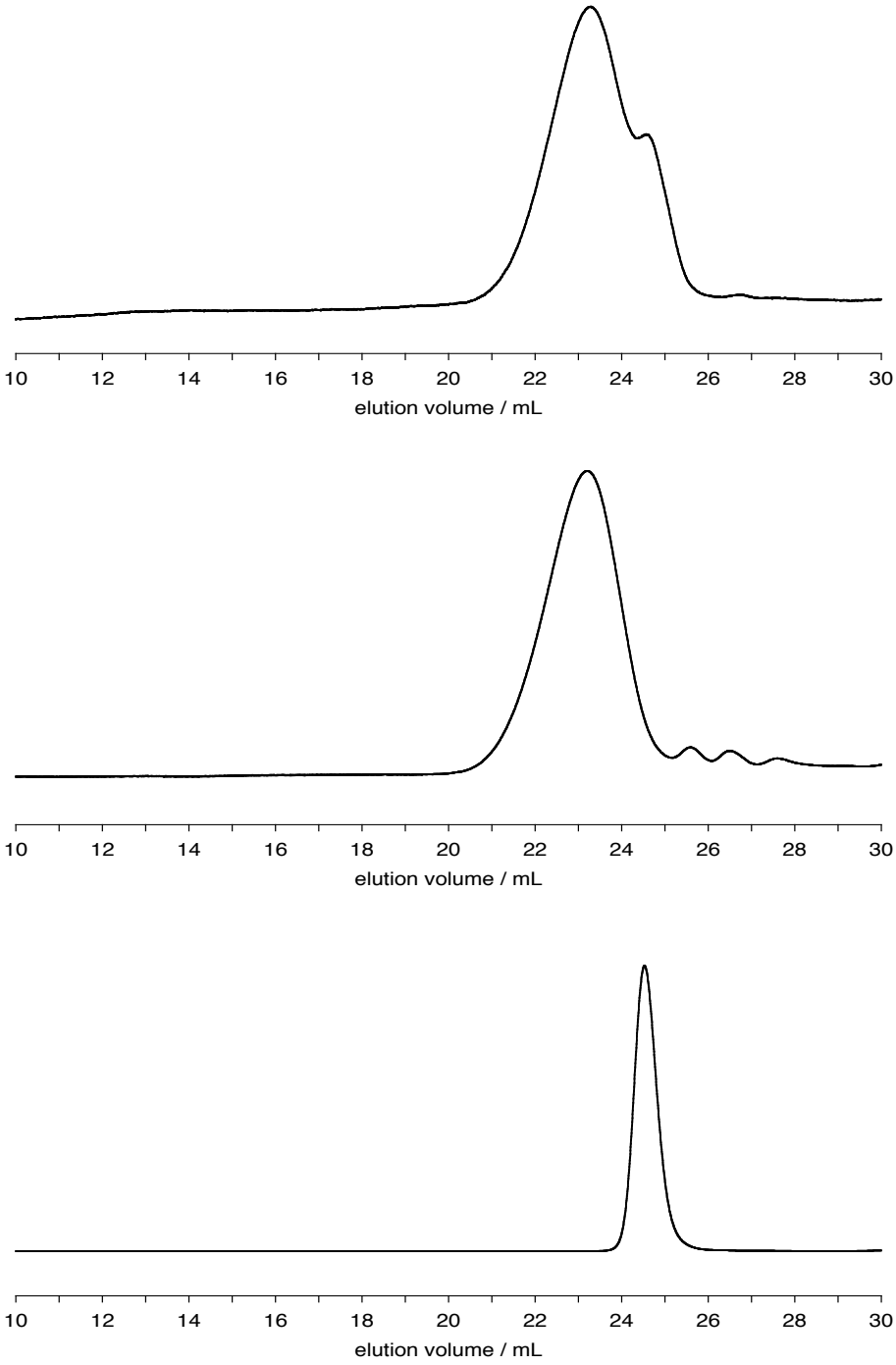
(R_p)-**P1**

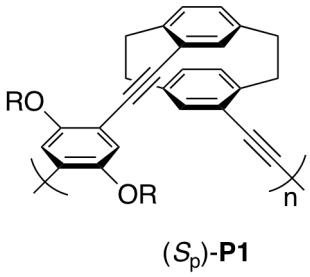


(R_p)-**C1**

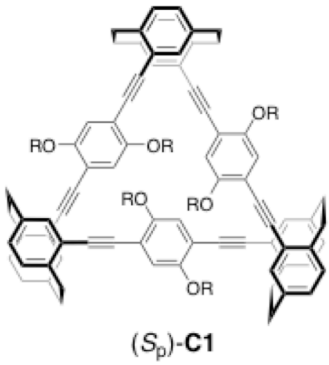
Column: TSK gel α-4000 + α-3000 + α-2500
Eluent: THF
Temperature: 40 °C
Flow rate: 1.0 mL / min

Figure S17. GPC charts: after polymerization from (R_p)-**5**, separated (R_p)-**P1** and (R_p)-**C1**.





(S_p)-**P1**



(S_p)-**C1**

Column: TSK gel α-4000 + α-3000 + α-2500
Eluent: THF
Temperature: 40 °C
Flow rate: 1.0 mL / min

Figure S18. GPC charts: after polymerization from (S_p)-**5**, separated (S_p)-**P1** and (S_p)-**C1**.

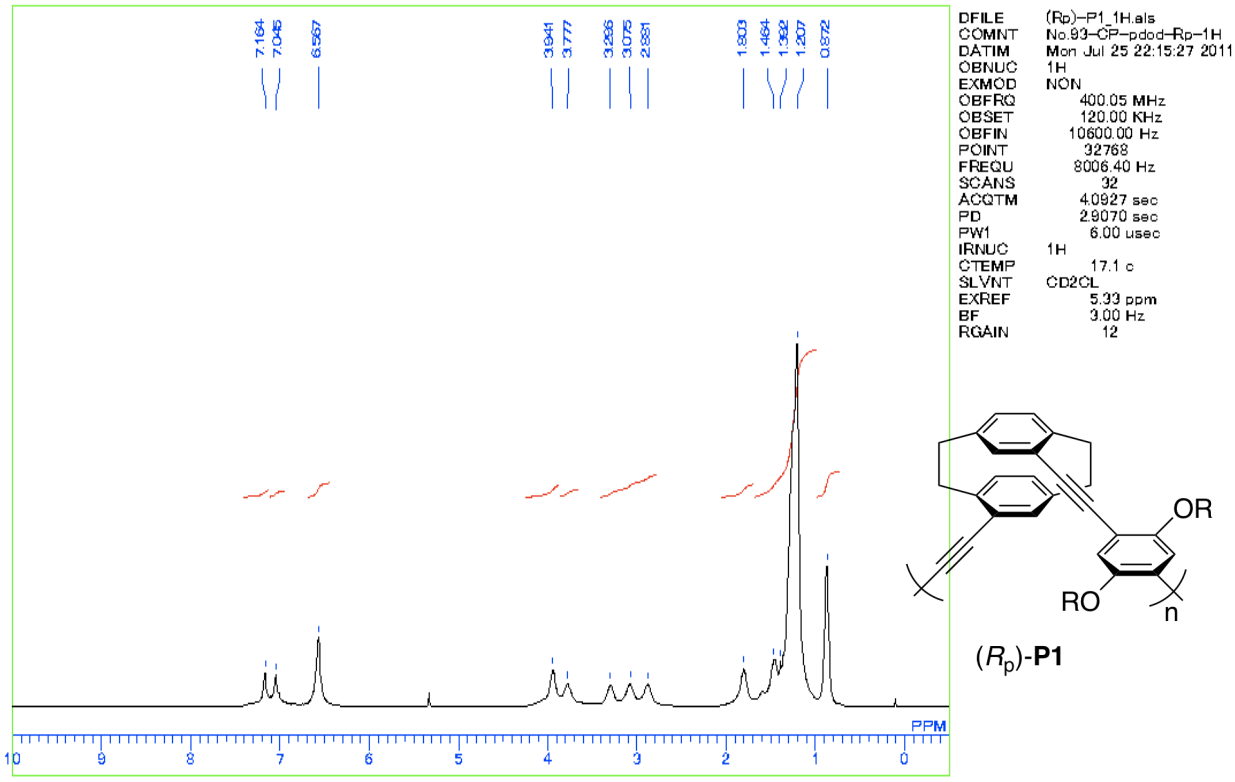


Figure S19. ^{1}H NMR spectrum of (R_p)-**P1**, 400 MHz, CD_2Cl_2.

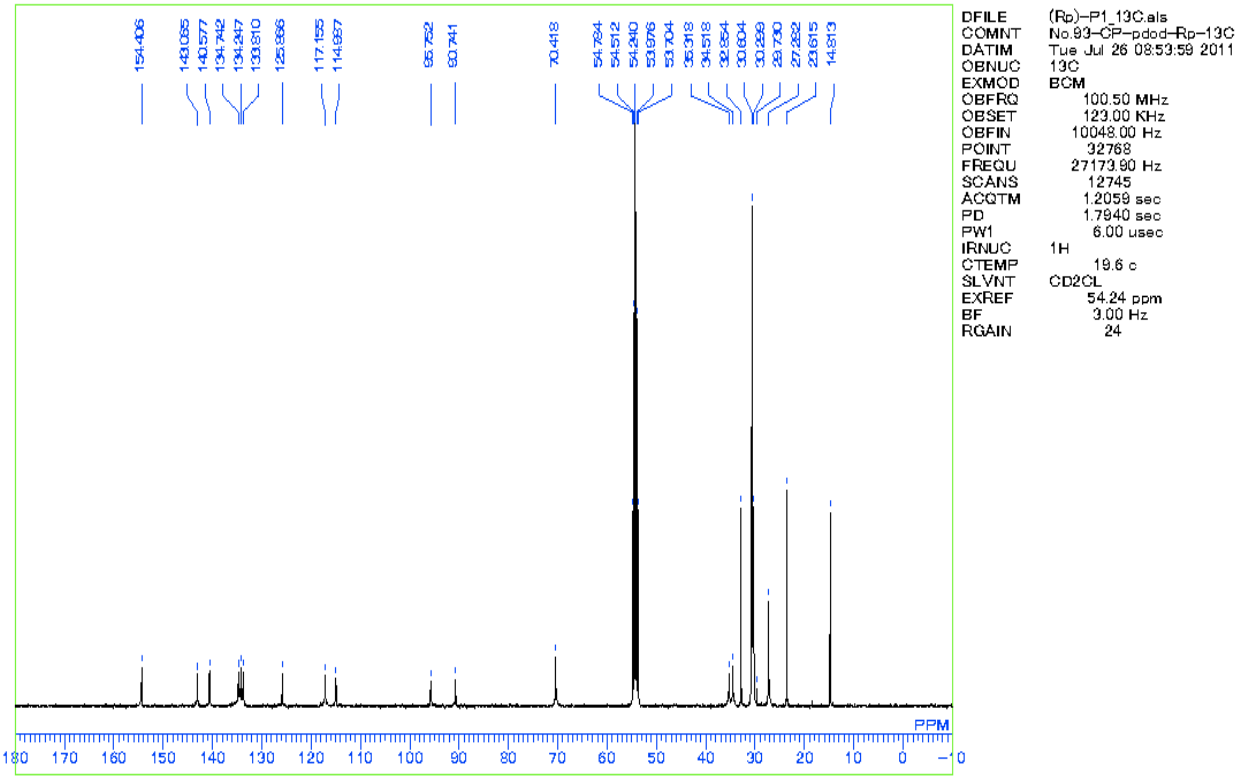


Figure S20. ^{13}C NMR spectrum of (R_p)-**P1**, 100 MHz, CD_2Cl_2.

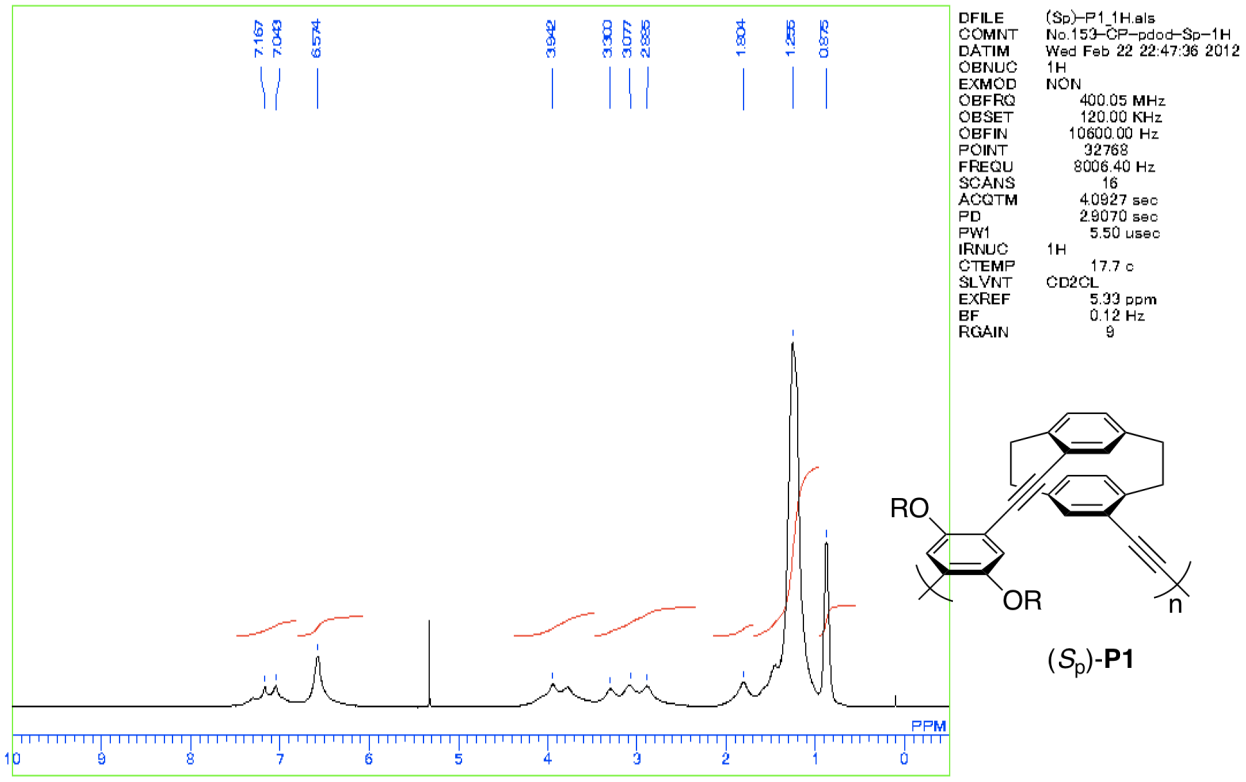


Figure S21. ^{1}H NMR spectrum of (S_p)-**P1**, 400 MHz, CD_2Cl_2.

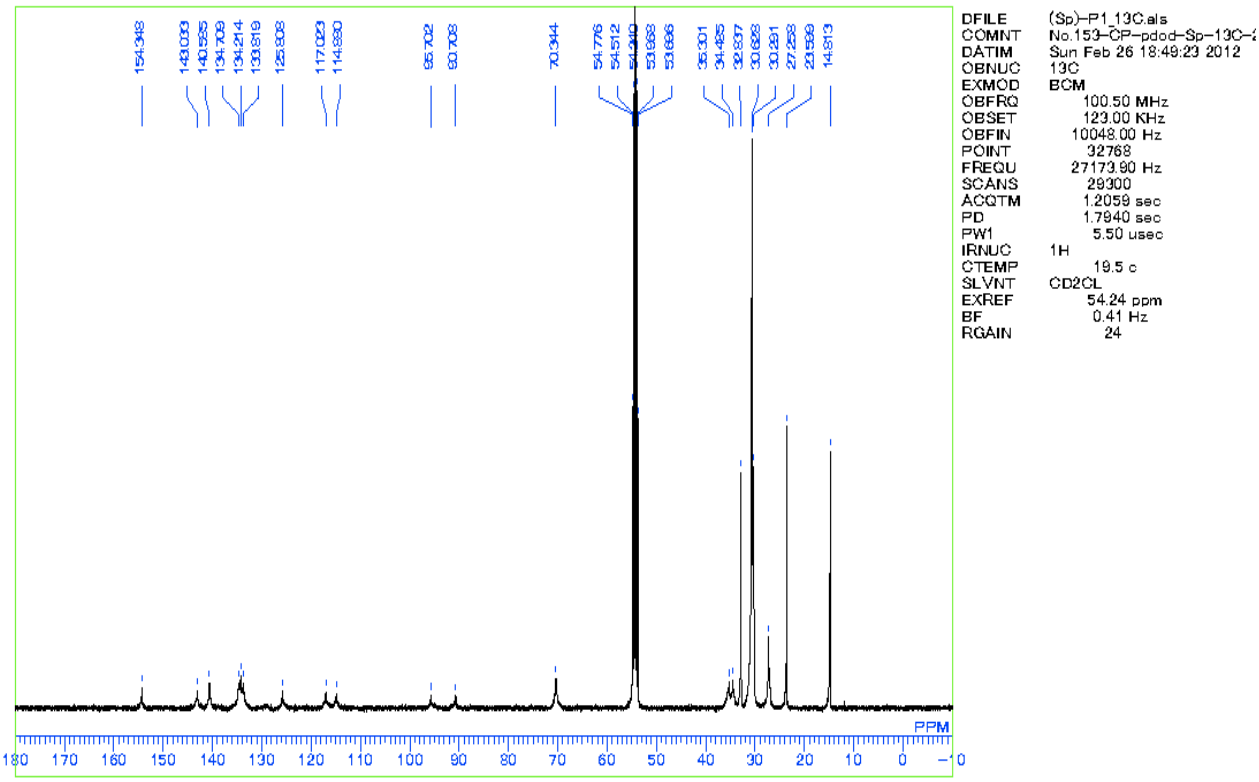


Figure S22. ^{13}C NMR spectrum of (S_p)-**P1**, 100 MHz, CD_2Cl_2.

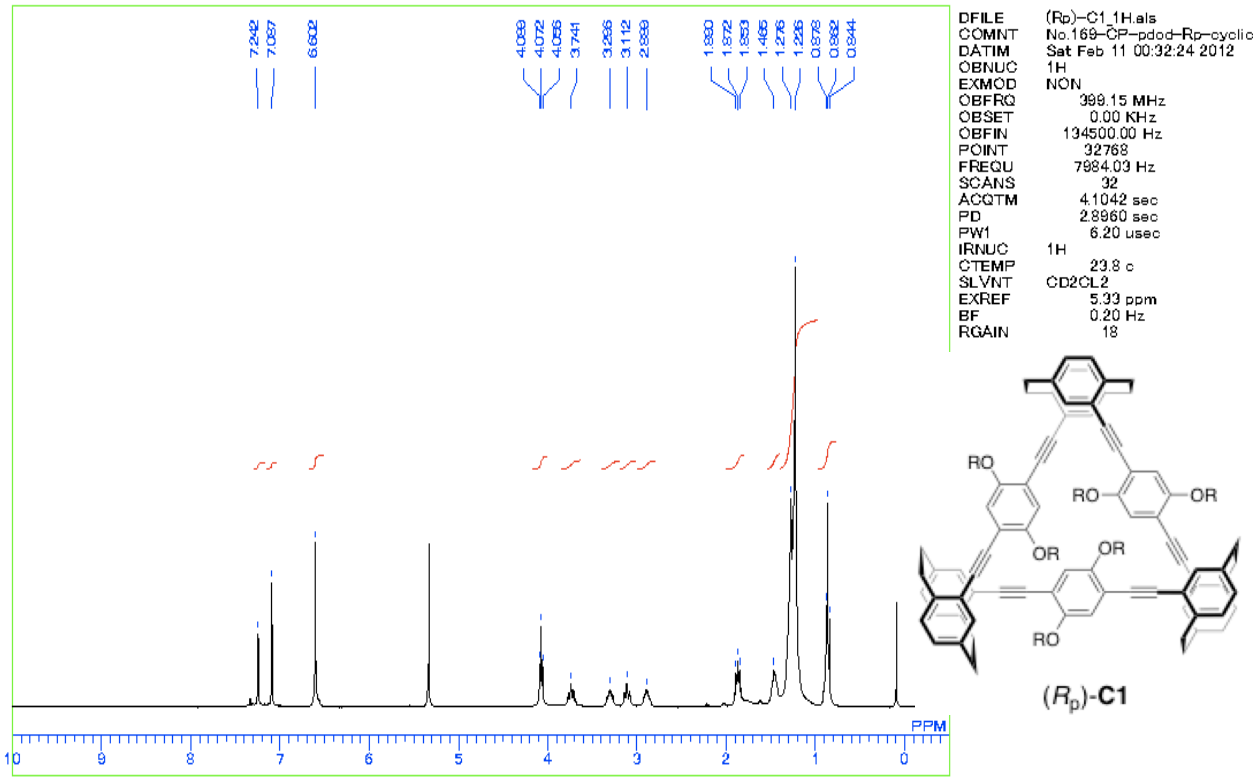


Figure S23. ^{1}H NMR spectrum of (R_p)-**C1**, 400 MHz, CD_2Cl_2.

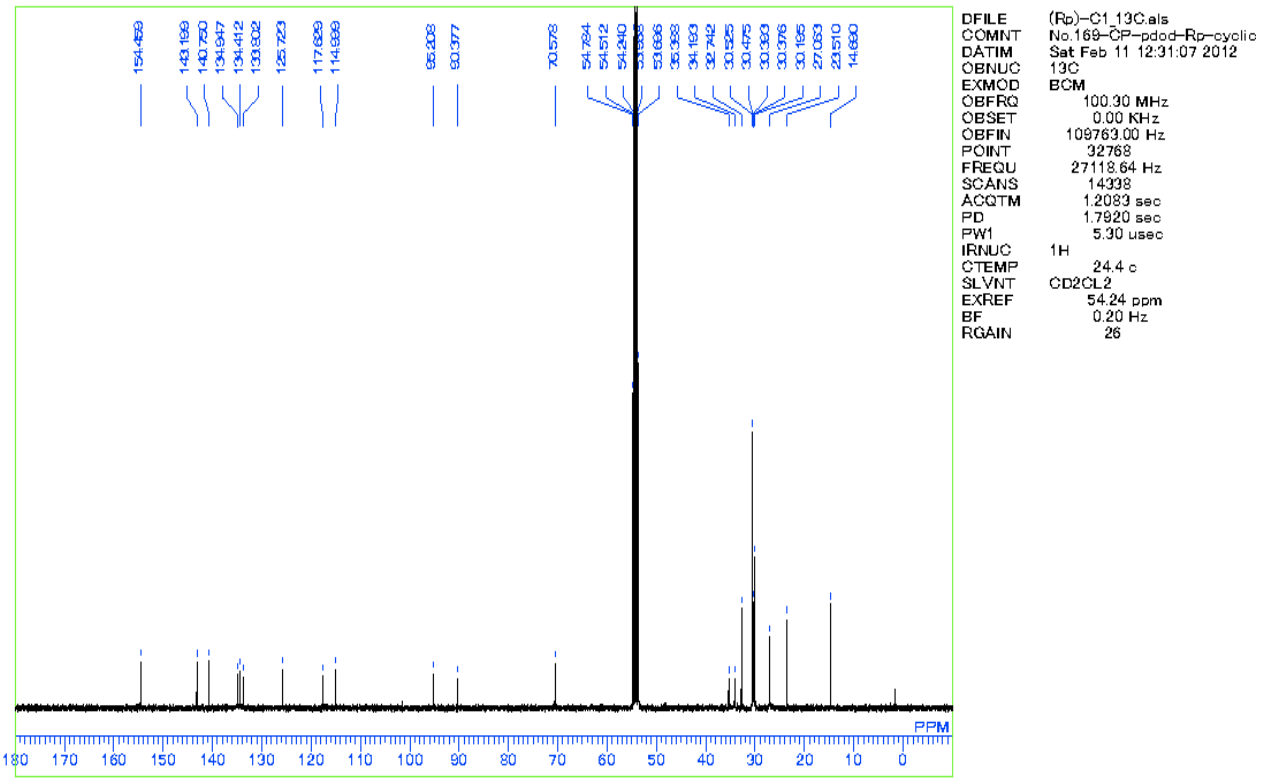


Figure S24. ^{13}C NMR spectrum of (R_p)-**C1**, 100 MHz, CD_2Cl_2.

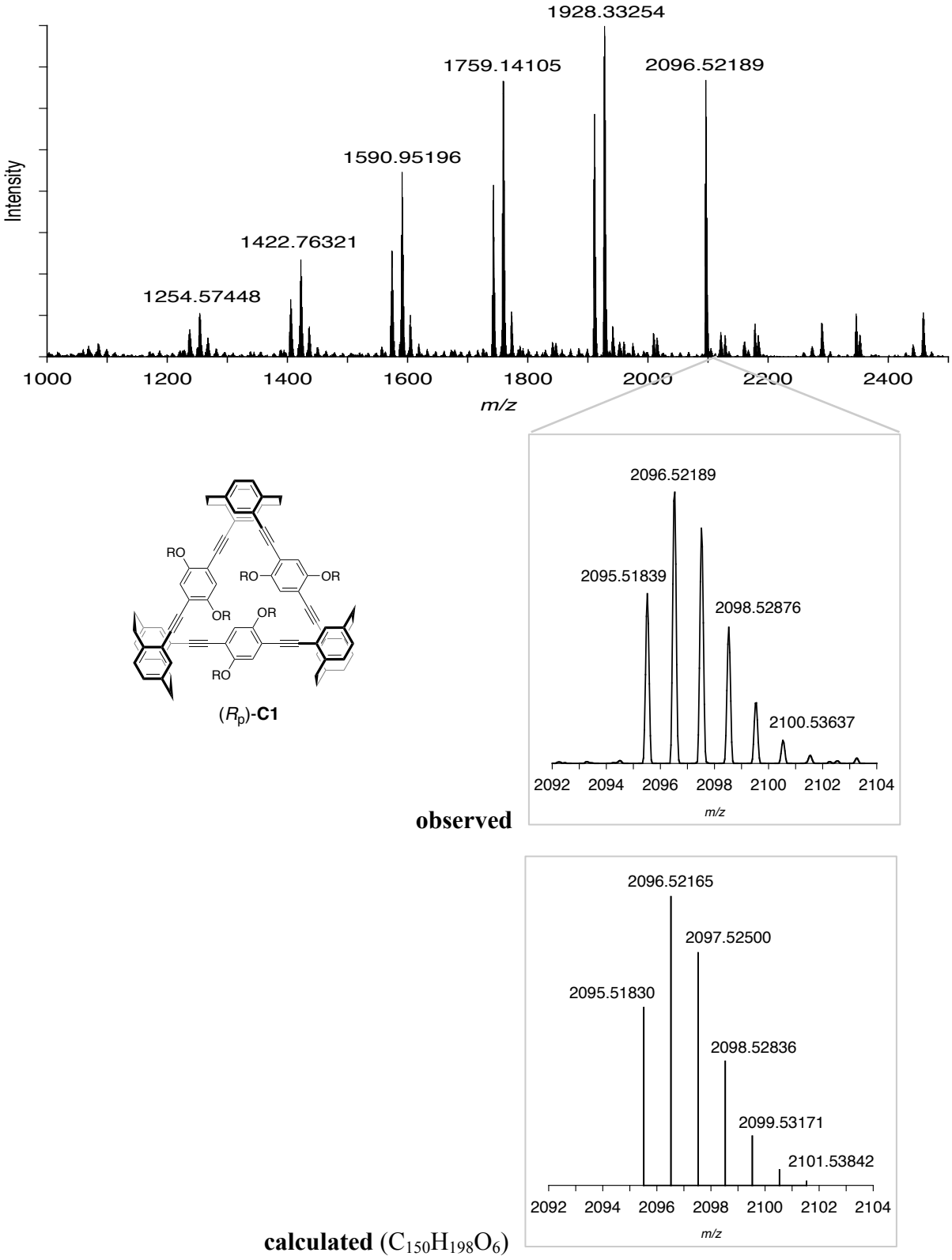


Figure S25. High-resolution mass spectra (MALDI, matrix: DCTB) of (R_p)-**C1**,

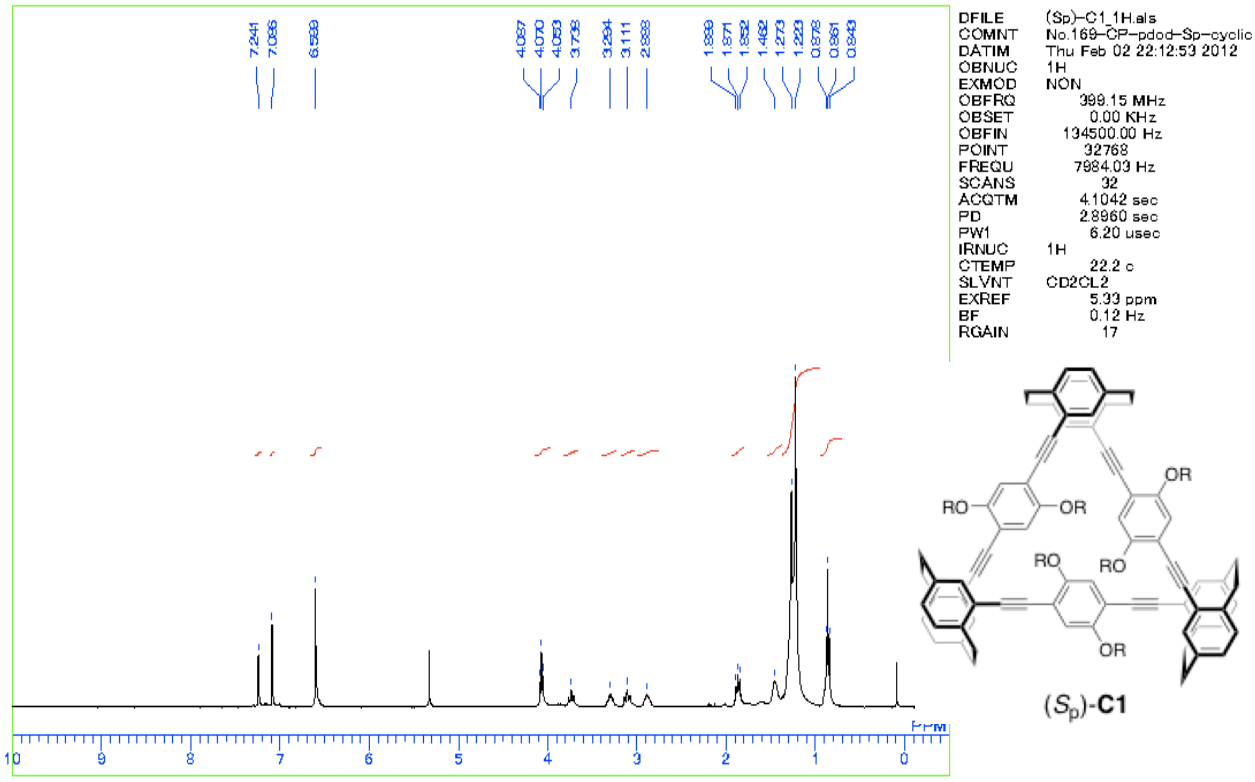


Figure S26. ^{1}H NMR spectrum of (S_p)-**C1**, 400 MHz, CD_2Cl_2.

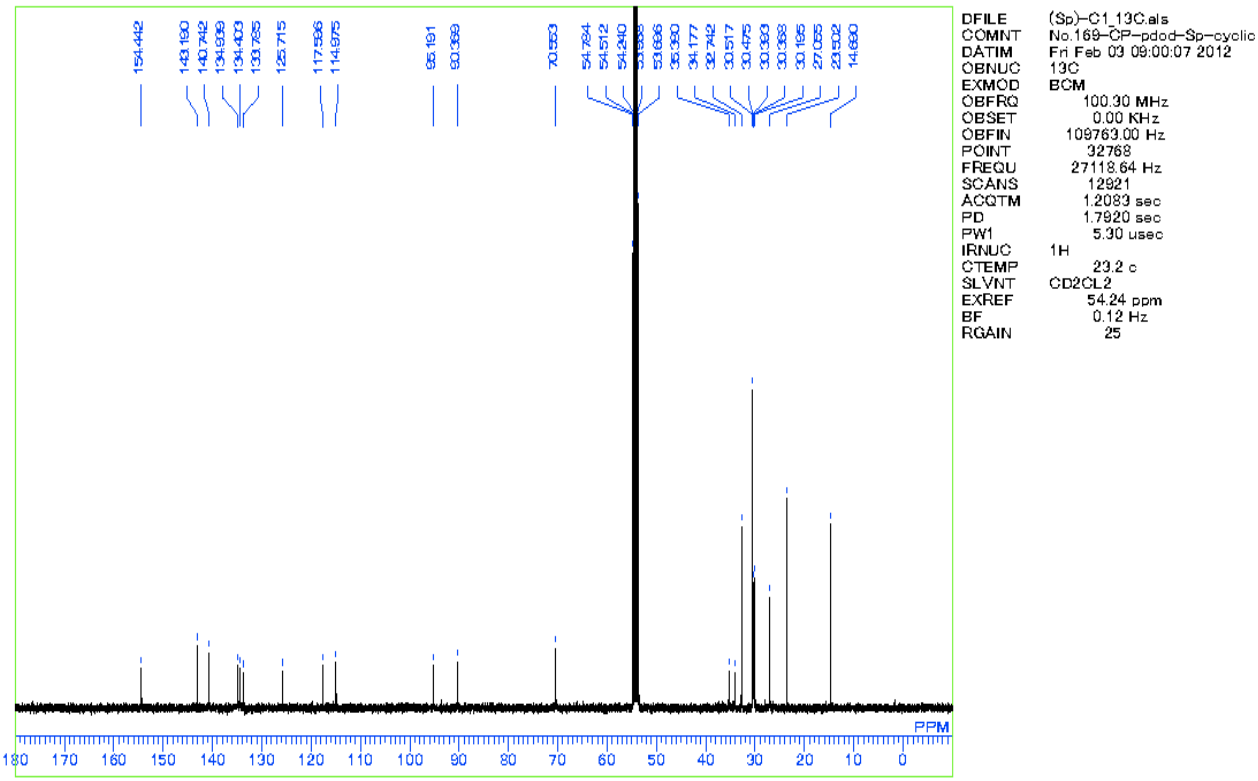


Figure S27. ^{13}C NMR spectrum of (S_p)-**C1**, 100 MHz, CD_2Cl_2.

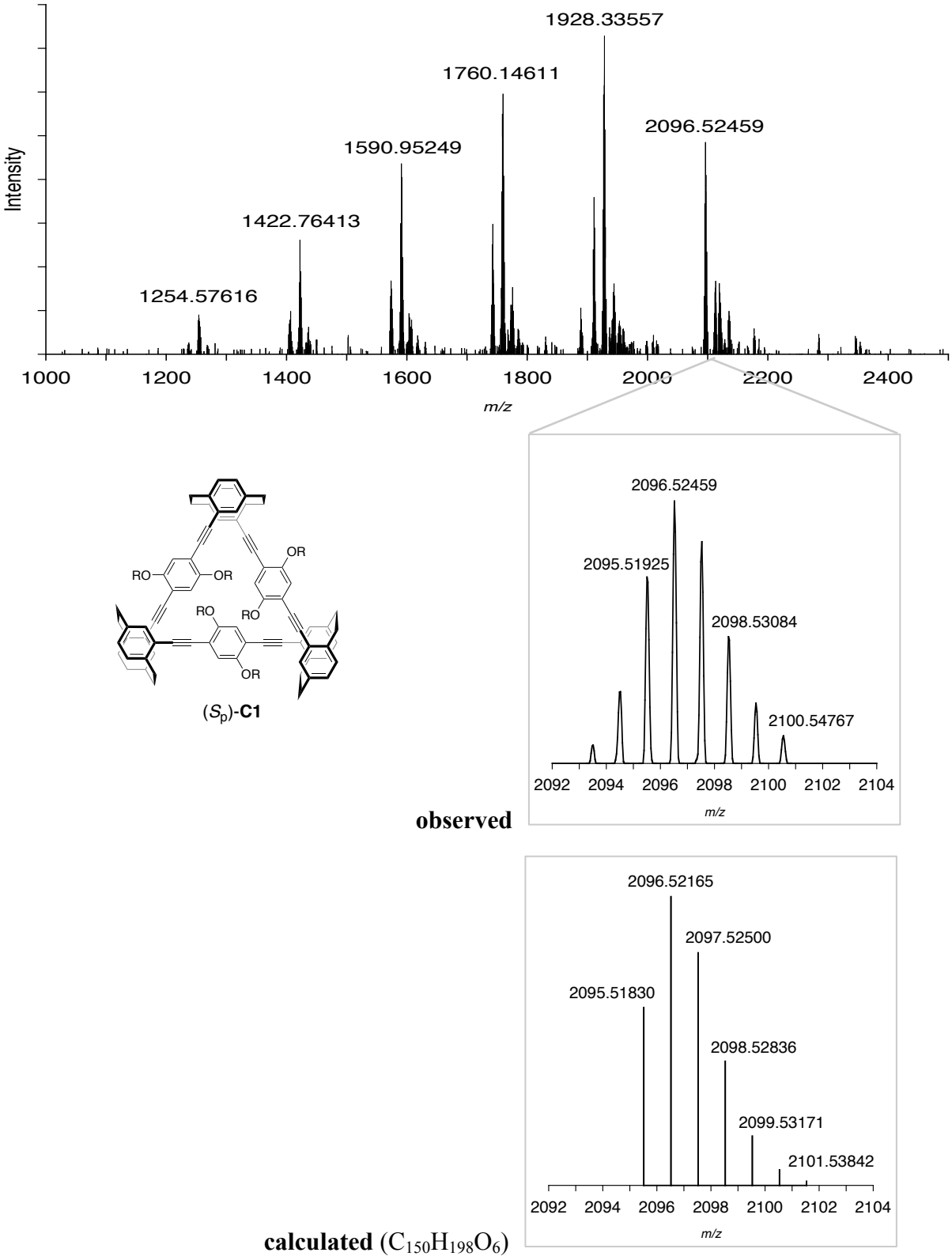


Figure S28. High-resolution mass spectra (MALDI, matrix: DCTB) of (S_p)-**C1**,

Optical properties of (R_p)-5 and (S_p)-5

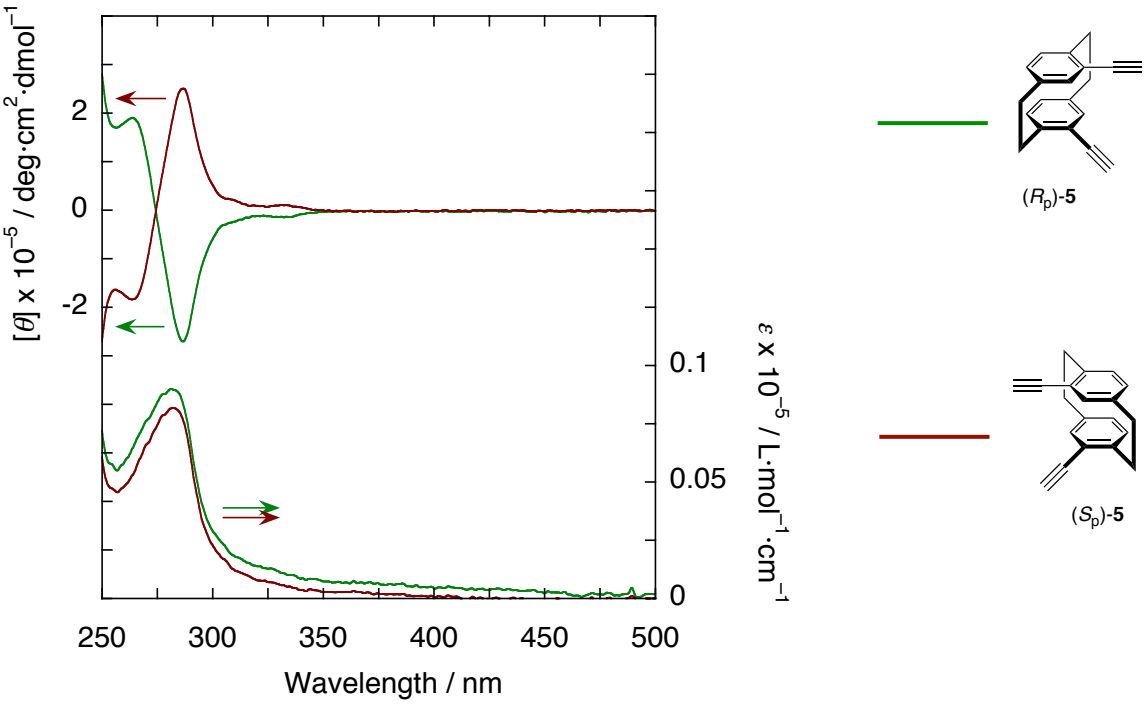


Figure S29. UV-vis absorption and CD spectra of (R_p)-**5** and (S_p)-**5** in $CHCl_3$ (1.0×10^{-5} M) at room temperature.

Optical properties of (R_p)-C1 and (S_p)-C1

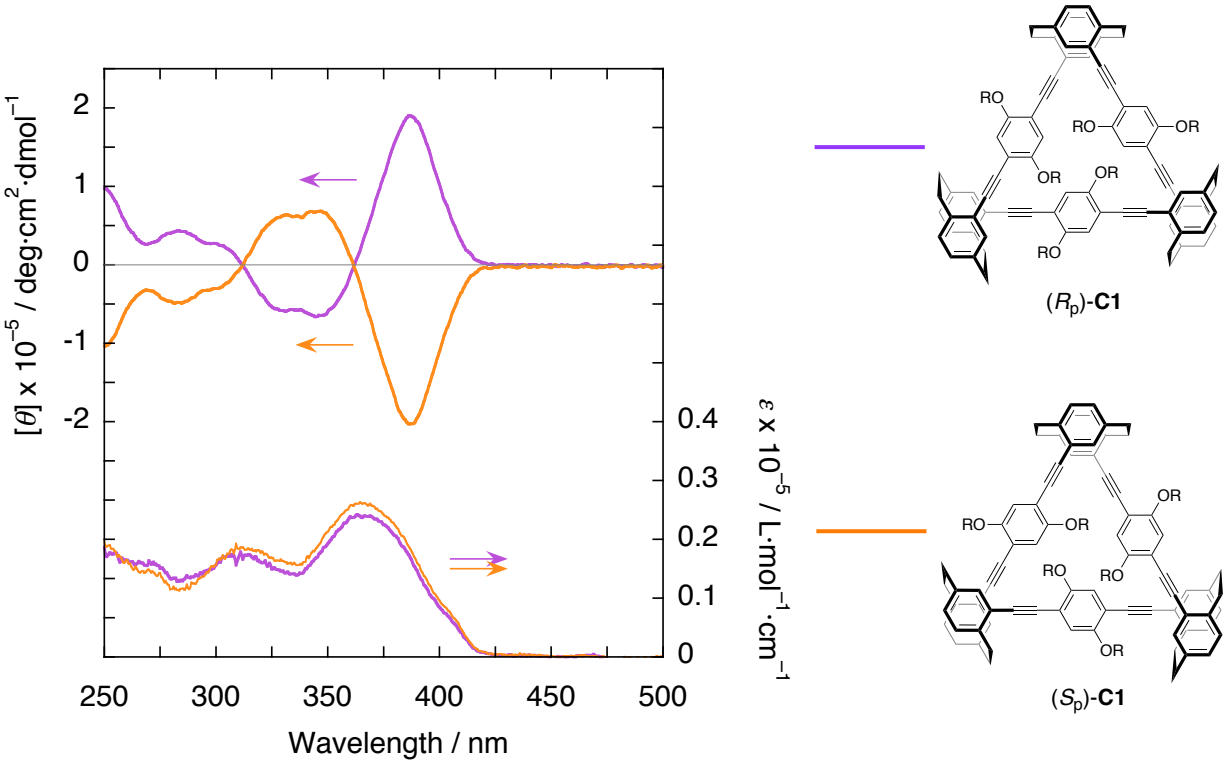


Figure S30. UV-vis absorption and CD spectra of (R_p)-**C1** and (S_p)-**C1** in $CHCl_3$ (1.0×10^{-5} M) at room temperature.

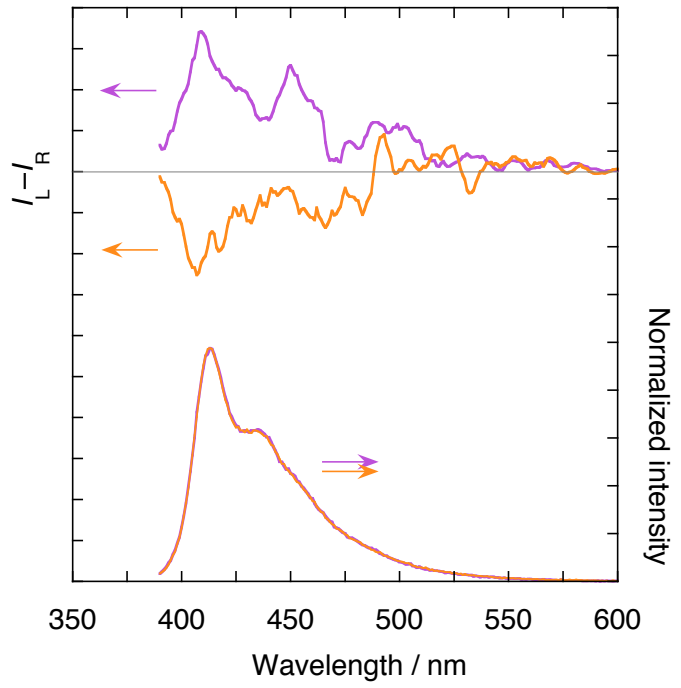


Figure S31. Photoluminescence spectra in $CHCl_3$ (1.0×10^{-6} M, excited at 370 nm) and CPL spectra in $CHCl_3$ (1.0×10^{-5} M, excited at 320 nm) of (R_p)-**C1** and (S_p)-**C1** at room temperature.

References

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(2) Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52–58.

(3) Bondarenko, L.; Dix, I.; Hinrichs, H.; Hopf, H. *Synthesis* **2004**, 2751–2759.