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Synthesis and characterizations of one-handed helical oligo(o-phenylene)s: control of axial chirality by the planar chiral [2.2]paracyclophane

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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 $CDCl_3$ (or CD_2Cl_2 for VT-NMR) 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. Recyclable preparative high-performance liquid chromatography (HPLC) was carried out on a YMC LC Forte/R. High-resolution mass (HRMS) spectra were obtained on a Bruker Daltonics microTOF II spectrometer (APCI) using sodium formate and tuning mix as internal standards. IR spectra were recorded on a JASCO FT/IR-4600 spectrometer using an ATR (attenuated total reflection) PRO ONE attachment. 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 Quantaurus-Tau fluorescence lifetime spectrometer. Specific rotation values ($[\alpha]^t_D$) were measured with a HORIBA SEPA-500 polarimeter. Circular dichroism (CD) spectra were recorded on a JASCO J-1500 spectropolarimeter with THF as a solvent at room temperature. Circular dichroism (CD) spectra were recorded on a JASCO J-1500 spectropolarimeter with $CHCl_3$ as a solvent at room temperature. Circularly polarized luminescence (CPL) spectra were recorded on a JASCO CPL-300 with $CHCl_3$ as a solvent at room temperature.

All reactions were carried out under N_2 atmosphere.

Materials

Commercially available compounds used without purification:

$Pd_2(dba)_3$, $Pd(PPh_3)_4$, S-Phos (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl)

K_3PO_4, *sec*-BuLi (1.04 M in hexane)

1,4-Dioxane (dehydrated), Et_2O (dehydrated)

1-Bromo-2-(2-phenylphenyl)benzene **s1**

2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **s2**

Compounds prepared as described in the literature:

(R_p)- and (S_p)-**1**:

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

4:

C. Zhu, Y. Zhao, D. Wang, W.-Y. Sun, Z. Shi, *Sci. Rep.*, **2016**, *6*, 33131.

X-ray structure determination

Crystals suitable for X-ray diffraction studies were analyzed using a Rigaku MicroMax-007HFM MoKα 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 CrysAlisPRO. 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. Deposition number 2297220 (*rac*-**5**), 2297221 (*rac*-**6**), and 2297222 ((*M*,S_p,*M*)-**7**) 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 MN15[10] functional and integral equation formalism polarizable continuum model (IEFPCM)[11] method for solvation effect. Cartesian coordinates of all optimized structures are given in Tables S3–S4.

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6 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.
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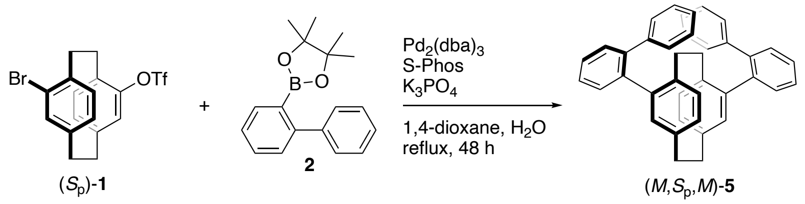
Synthesis of (*M*,*S*$_\mathrm{p}$,*M*)-**5**



A mixture of (*S*$_\mathrm{p}$)-**1** (192.5 mg, 0.44 mmol), **2** (370.6 mg, 1.32 mmol), $Pd_2(dba)_3$ (80.8 mg, 0.088 mmol), S-Phos (108.4 mg, 0.26 mmol), and K_3PO_4 (569.8 mg, 2.68 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, 1,4-dioxane (18 mL) and H_2O (2.0 mL) 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, H_2O was added to the reaction mixture. The organic layer was separated, and then aqueous layer was extracted three times with CH_2Cl_2. The organic layer was washed with H_2O and brine, and dried over $MgSO_4$. $MgSO_4$ was removed by the filtration, and the solvent was removed by a rotary evaporator. The residue was purified by column chromatography on SiO_2 (CH_2Cl_2/hexane = 2/1 v/v as an eluent) and by recyclable HPLC (CH_2Cl_2 as an eluent) to afford (*M*,*S*$_\mathrm{p}$,*M*)-**5** (179.0 mg, 0.44 mmol, 79%) as a colorless solid. R_f = 0.62 (CH_2Cl_2/hexane = 2/1 v/v).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.78−1.87 (m, 2H), 2.09−2.18 (m, 2H), 3.07−3.23 (m, 4H), 6.12 (d, *J* = 7.5 Hz, 2H), 6.41 (d, *J* = 8.6 Hz, 2H), 6.75 (s, 2H), 6.83 (d, *J* = 6.9 Hz, 4H), 6.96−7.04 (m, 6H), 7.31 (d, *J* = 6.9 Hz, 2H), 7.39 (t, *J* = 6.9 Hz, 2H), 7.48 (t, *J* = 6.9 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 2H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 32.9, 35.2, 126.0, 127.1, 127.4, 127.6, 130.0, 130.1, 130.4, 130.7, 131.5, 132,1, 138.5, 138.5, 139.6, 140.0, 140.5, 141.8, 142.3 ppm. IR (ATR) $\tilde{\nu}$ = 3045, 3014, 2924, 2853, 1589, 1472, 1434, 1277, 987, 849, 766, 750 cm^{-1}. HRMS (APCI) calcd. for $C_{40}H_{33}$ $[M+H]^+$: 513.2577, found 513.2563. $[\alpha]^{25}_\mathrm{D}$ = –171.82 (*c* 0.102, $CHCl_3$).

(*P*,*R*$_\mathrm{p}$,P)-**5** was obtained in 68% yield by the same procedure of (*M*,*S*$_\mathrm{p}$,*M*)-**5**. HRMS (APCI) calcd. for $C_{40}H_{33}$ $[M+H]^+$: 513.2577, found 513.2571. $[\alpha]^{25}_\mathrm{D}$ = +174.83 (*c* 0.066, $CHCl_3$).

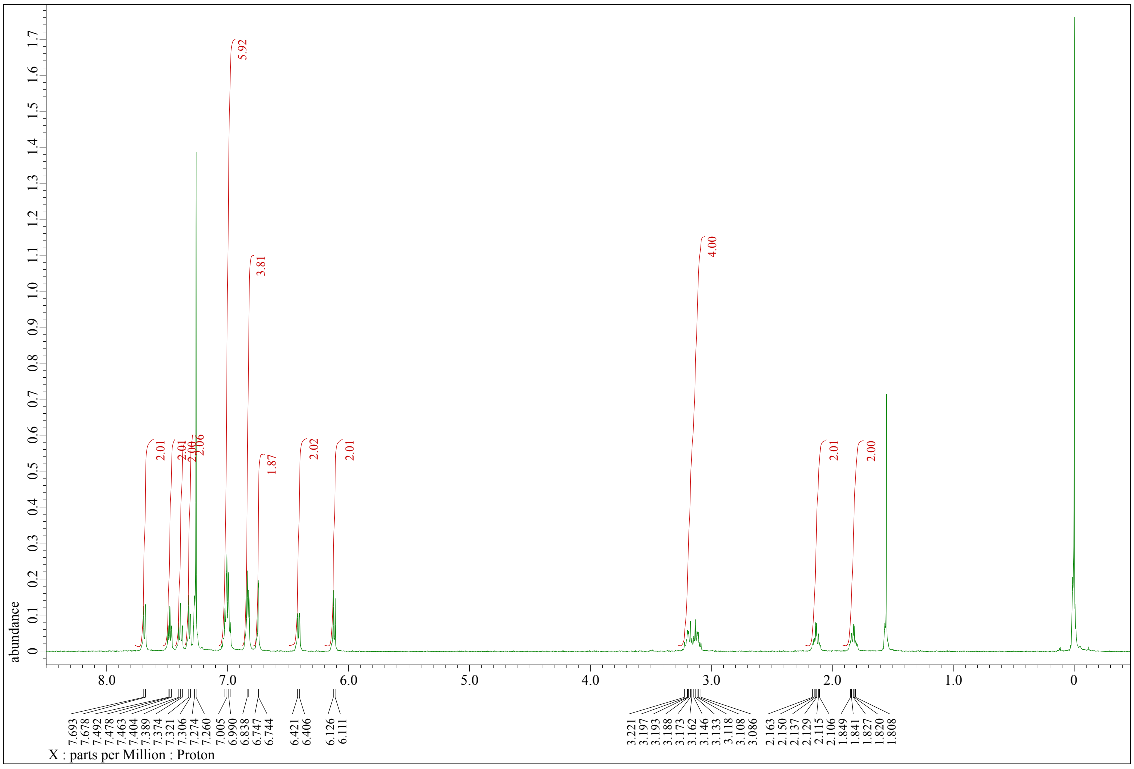


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of (*M*,*S*$_p$,*M*)-**5**.

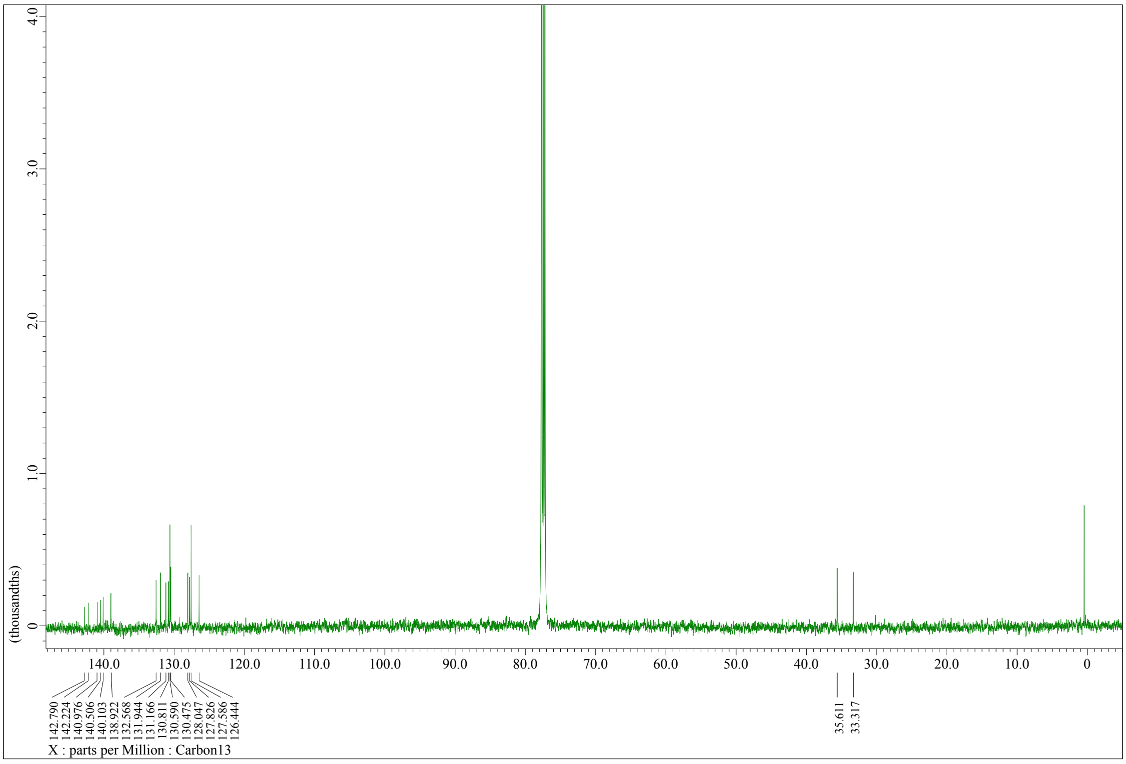


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz) of (*M*,*S*$_p$,*M*)-**5**.

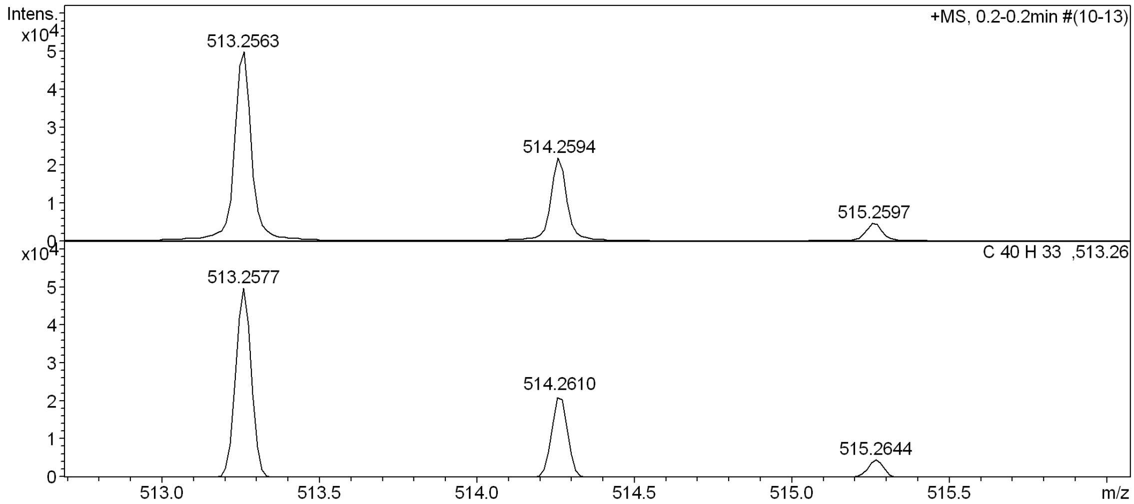


Figure S3. Mass spectra of (*M*,S_{p},*M*)-**5**. Upper and lower show observed and calculated spectra, respectively.

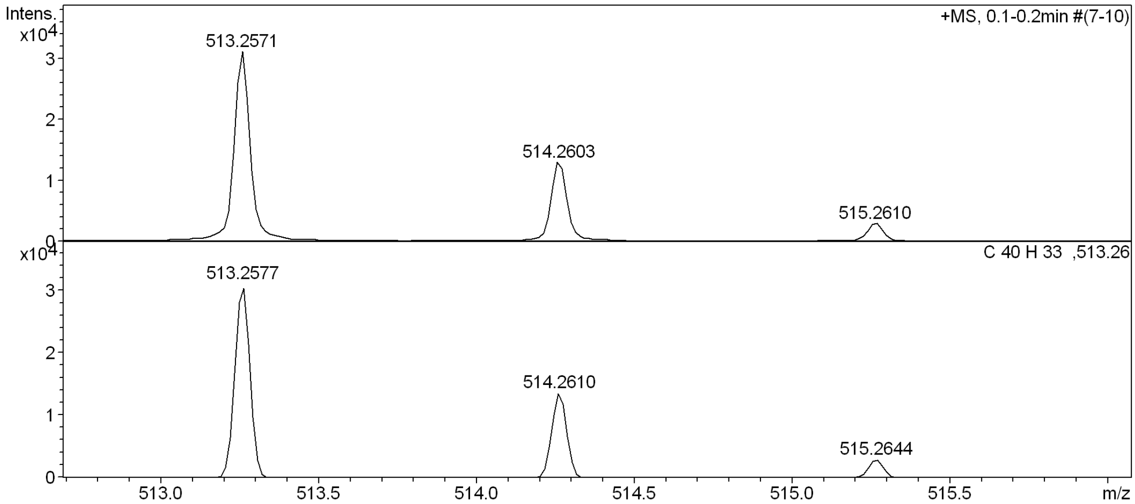


Figure S4. Mass spectra of (*P*,R_{p},P)-**5**. Upper and lower show observed and calculated spectra, respectively.

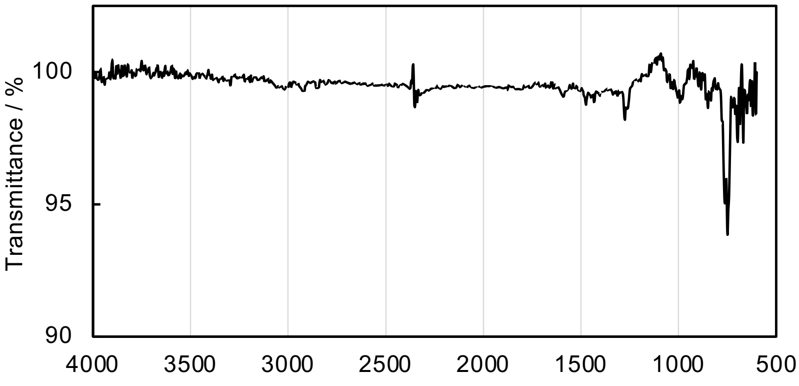
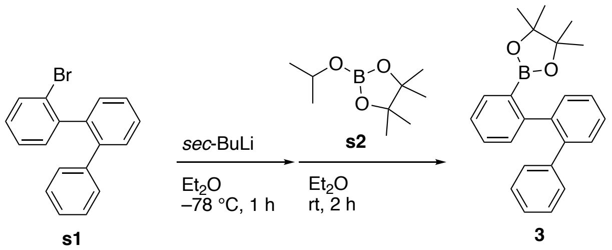


Figure S5. IR spectrum (ATR) of (*M*,S_{p},*M*)-**5**.

Synthesis of **3**

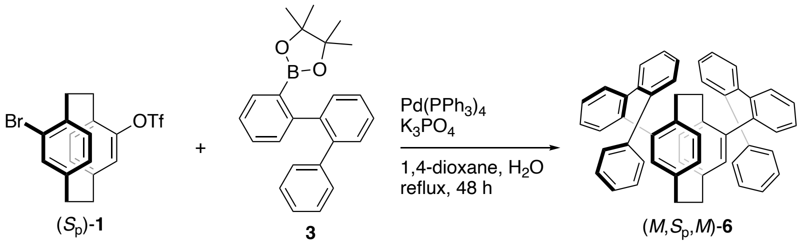


A solution of *sec*-BuLi (1.04 M in hexane, 12.0 mL, 12.5 mmol) was slowly added to a solution of 1-bromo-2-(2-phenylphenyl)benzene **s1** (3.50 g, 11.3 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **s2** (2.5 mL, 12.5 mmol) in Et_2O (34 mL) at –78 °C. After 1 h, the mixture was warmed up to room temperature. After stirring for 2 h at room temperature, the reaction mixture was quenched by 1 M HCl (1.0 M, 15 mL, 15 mmol). 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 **3** (3.67 g, 11.3 mmol, 91%) as a colorless solid.

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

R. R. A. Freund, P. Gobrecht, Z. Rao, J. Gerstmeier, R. Schlosser, H. Gorls, O. Werz, D. Fischer, H-D. Arndt, *Chem. Sci*, **2019**, *10*, 7358-7364.

Synthesis of (M,S_p,M)-**6**



A mixture of (S_p)-**1** (51.3 mg, 0.12 mmol), **3** (138.5 mg, 0.39 mmol), $Pd(PPh_3)_4$ (31.2 mg, 0.027 mmol), and K_3PO_4 (181.6 mg, 0.86 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, 1,4-dioxane (6 mL) and H_2O (0.6 mL) 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, H_2O was added to the reaction mixture. The organic layer was separated, and then aqueous layer was extracted three times with CH_2Cl_2. The organic layer was washed with H_2O and brine, and dried over $MgSO_4$. $MgSO_4$ was removed by the filtration, and the solvent was removed by a rotary evaporator. The residue was purified by column chromatography on SiO_2 (EtOAc/hexane = 1/1 v/v as an eluent) and by recyclable HPLC (CH_2Cl_2 as an eluent) to afford (M,S_p,M)-**6** (27.6 mg, 0.14 mmol, 29%) as a colorless solid. R_f = 0.93 (EtOAc/hexane = 1/1 v/v).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.75–1.89 (m, 2H), 1.93–2.06 (m, 2H), 2.63–2.76 (m, 4H), 5.48 (s, 2H), 5.84 (d, J = 7.5 Hz, 2H), 6.03 (d, J = 7.5 Hz, 2H), 6.13 (d, J = 7.5 Hz, 4H), 6.69 (t, J = 7.5Hz, 4H), 6.81 (d, J = 7.5 Hz, 2H), 6.87 (t, J = 7.5 Hz, 2H), 7.13 (dd, J = 7.5, 7.5 Hz, 2H), 7.21 (dd, J = 7.5, 7.5 Hz, 2H), 7.28–7.35 (m, 4H), 7.35–7.47 (m, 6H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 33.6, 34.7, 125.3, 126.5, 126.9, 127.1, 127.5, 128.7, 129.0, 129.6, 129.9, 130.9, 131.6, 131.6, 131.7, 137.7, 140.6, 140.7, 142.2 ppm. IR (ATR) $\tilde{\nu}$ = 3052, 3018, 2925, 2853, 1593, 1476, 1431, 1273, 1007, 849, 762, 750, 694 cm^{-1}. HRMS (APCI) calcd. for $C_{52}H_{41}$ [M+H]$^+$: 665.3203, found 665.3209. $[\alpha]^{25}_{D}$ = –108.33 (c 0.040, $CHCl_3$).

(P,R_p,P)-**6** was obtained in 35% yield by the same procedure of (M,S_p,M)-**6**. HRMS (APCI) calcd. for $C_{40}H_{33}$ [M+H]$^+$: 665.3203, found 665.3196. $[\alpha]^{25}_{D}$ = +108.22 (c 0.040, $CHCl_3$).

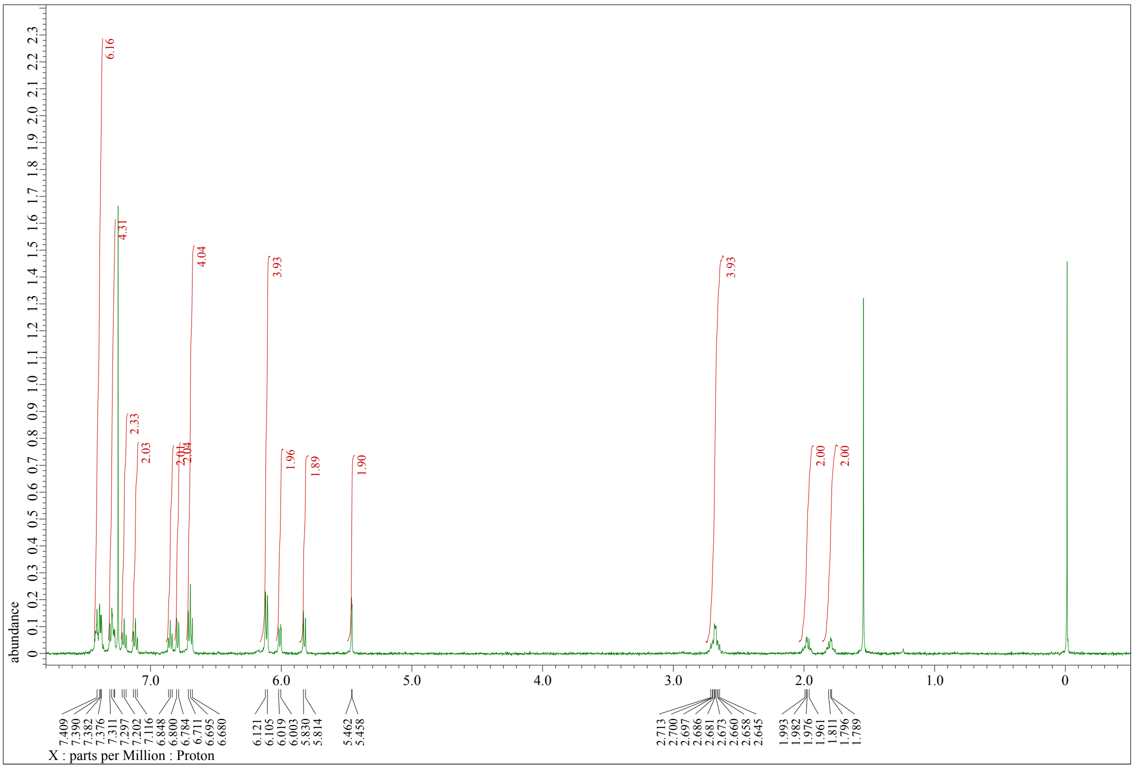


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of (*M*,*S*$_p$,*M*)-**6**.

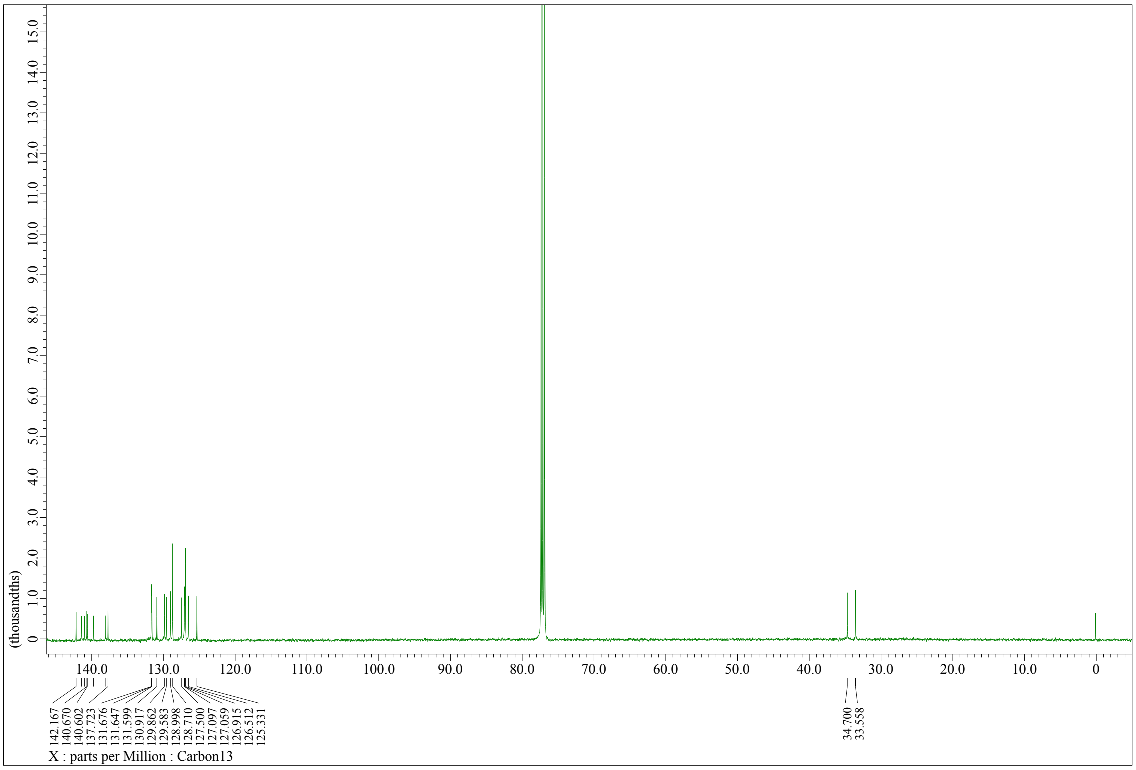


Figure S7. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 125 MHz) of (*M*,*S*$_p$,*M*)-**6**.

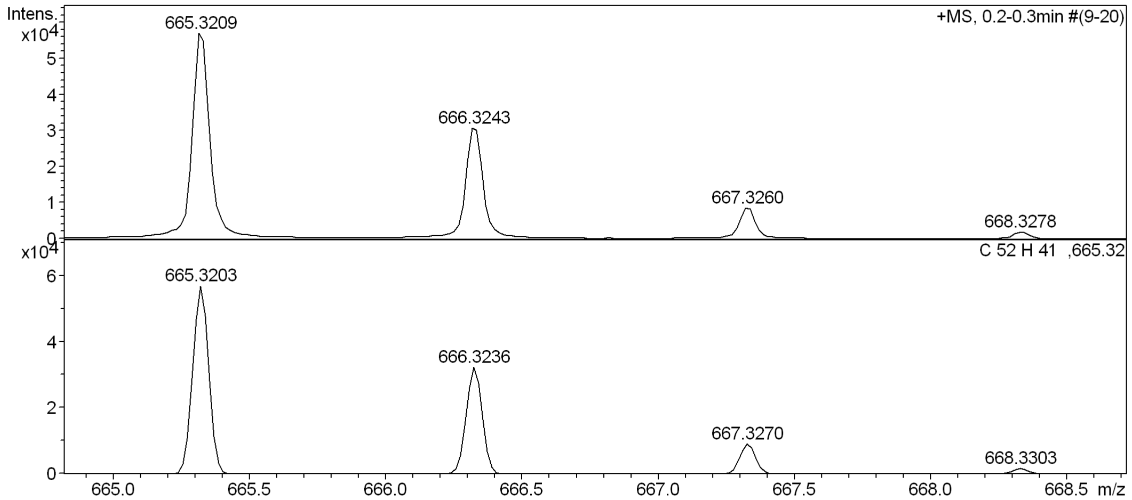


Figure S8. Mass spectra of (M,S_p,M)-**6**. Upper and lower show observed and calculated spectra, respectively.

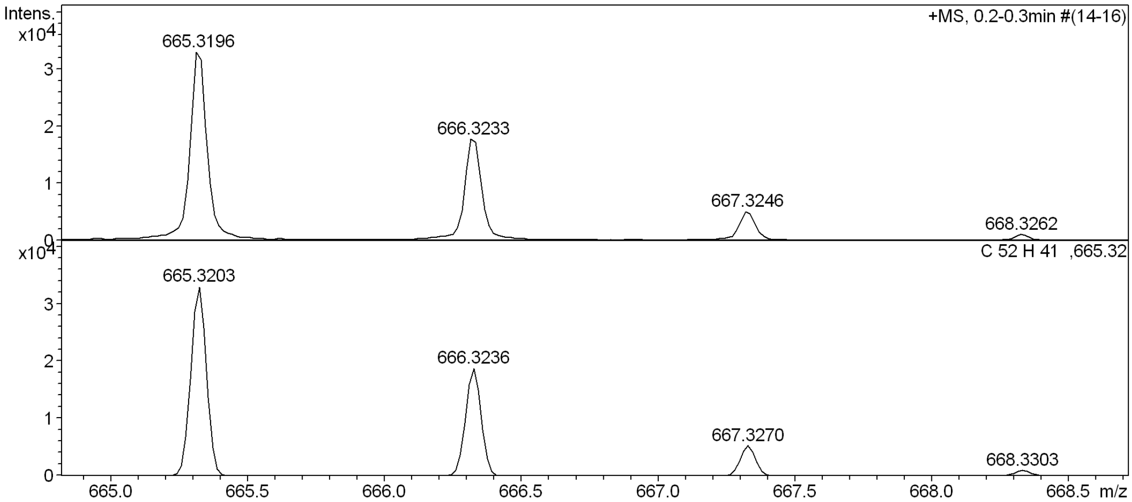


Figure S9. Mass spectra of (P,R_p,P)-**6**. Upper and lower show observed and calculated spectra, respectively.

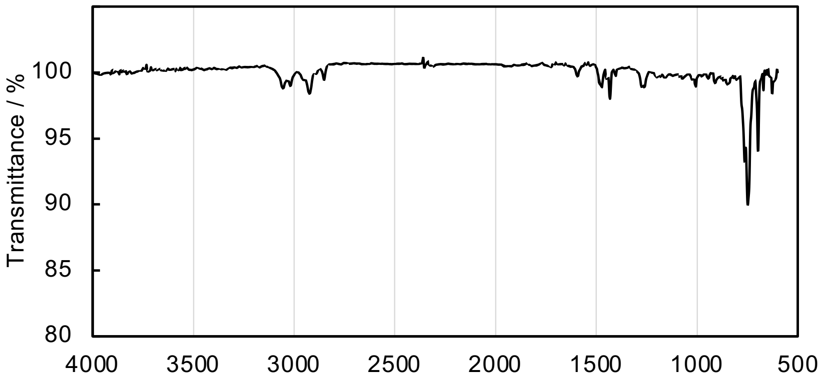
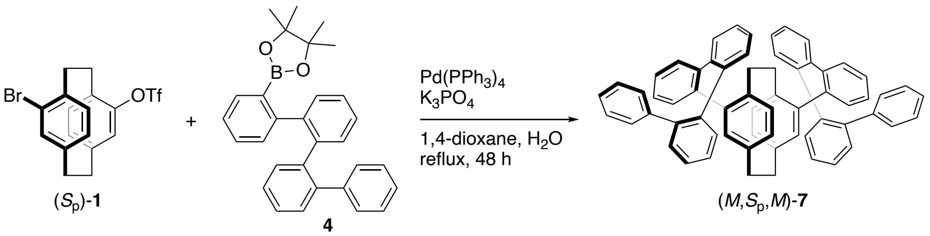


Figure S10. IR spectrum (ATR) of (M,S_p,M)-**6**.

Synthesis of (*M*,*S*$_p$,*M*)-**7**



A mixture of (*S*$_p$)-**1** (50.6 mg, 0.12 mmol), **4** (148.5 mg, 0.34 mmol), Pd(PPh$_3$)$_4$ (26.6 mg, 0.023 mmol), and K_3PO_4 (48.8 mg, 0.23 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, 1,4-dioxane (5 mL) and H_2O (0.5 mL) 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, H_2O was added to the reaction mixture. The organic layer was separated, and then aqueous layer was extracted three times with CH_2Cl_2. The organic layer was washed with H_2O and brine, and dried over $MgSO_4$. $MgSO_4$ was removed by the filtration, and the solvent was removed by a rotary evaporator. The residue was purified by column chromatography on SiO_2 (CH_2Cl_2/hexane = 1/3 v/v as an eluent) and by recyclable HPLC (CH_2Cl_2 as an eluent) to afford (*M*,*S*$_p$,*M*)-**7** (9.7 mg, 0.12 mmol, 10%) as a colorless solid. R_f = 0.25 (CH_2Cl_2/hexane = 1/3 v/v).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.63−1.69 (m, 2H), 1.74−1.81 (m, 2H), 2.80−2.89 (m, 4H), 5.64 (d, *J* = 6.9 Hz, 2H), 5.76 (s, 2H), 5.78 (d, *J* = 7.5 Hz, 2H), 5.83 (d, *J* = 6.9 Hz, 2H), 6.10 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 6.9 Hz, 4H), 6.60 (dd, *J* = 7.2, 7.2 Hz, 2H), 6.78−6.85 (m, 4H), 6.89−7.00 (m, 10H), 7.01−7.07 (t, *J* = 7.5 Hz, 2H), 7.12−7.22 (m, 8H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 33.7, 34.8, 125.7, 125.8, 126.1, 126.2, 126.5, 126.9, 127.4, 128.6, 129.1, 129.7, 129.8, 130.7, 130.9, 130.9, 131.2, 131.7, 131.9, 131.9, 137.7, 138.2, 139.4, 140.1, 140.2, 141.3, 141.4, 141.6 ppm. IR (ATR) $\tilde{\nu}$ = 3056, 3014, 2925, 2853, 1593, 1480, 1431, 1266, 1029, 1007, 946, 742, 702 cm^{-1}. HRMS (APCI) calcd. for $C_{64}H_{49}$ [M+H]$^+$: 817.8329, found 817.3804. $[\alpha]^{25}_D$ = –71.70 (*c* 0.020, $CHCl_3$).

(*P*,*R*$_p$,P)-**7** was obtained in 7% yield by the same procedure of (*M*,*S*$_p$,*M*)-**7**. HRMS (APCI) calcd. for $C_{64}H_{49}$ [M+H]$^+$: 817.8329, found 817.3833. $[\alpha]^{25}_D$ = +71.55 (*c* 0.020, $CHCl_3$).

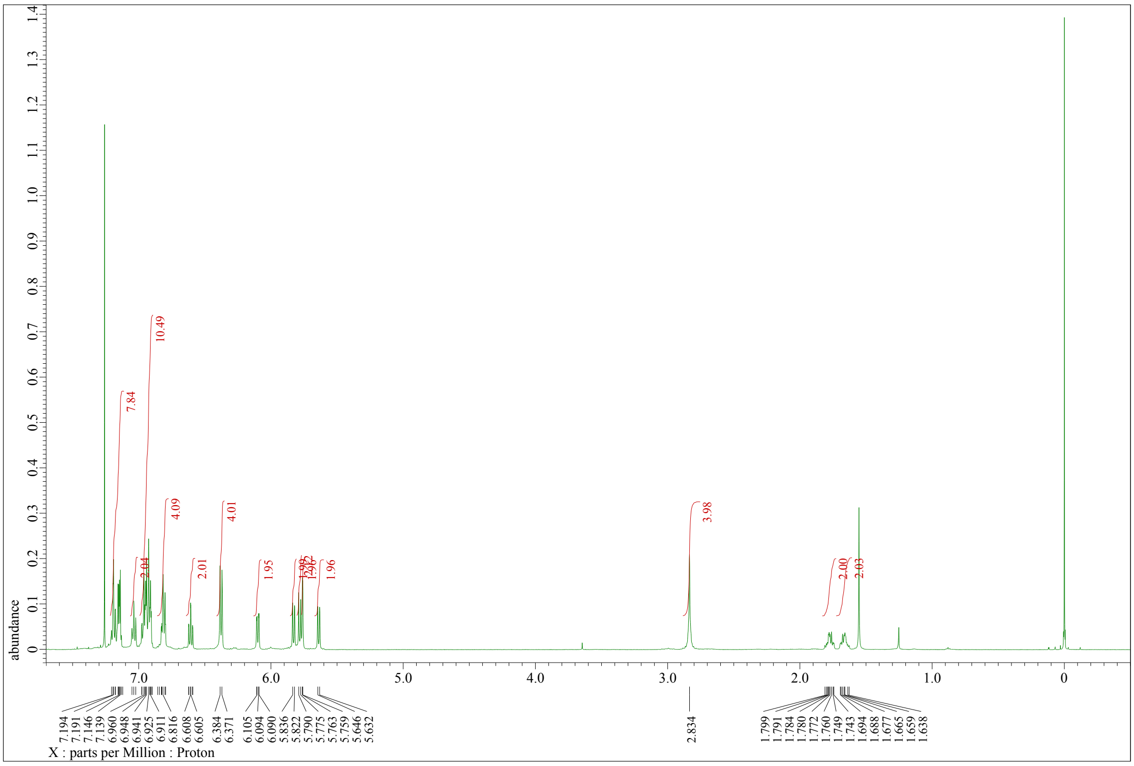


Figure S11. ^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of (*M*,*S*$_p$,*M*)-**7**.

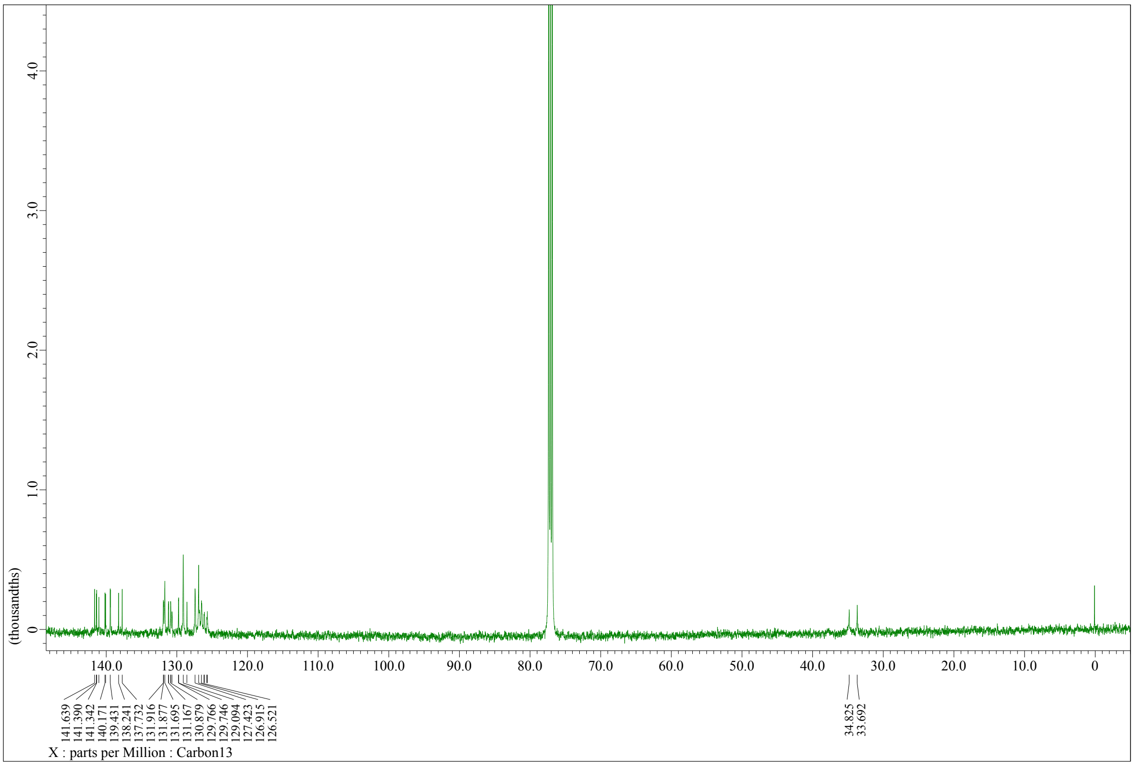


Figure S12. ^{13}C{^{1}H} NMR spectrum (CDCl$_3$, 125 MHz) of (*M*,*S*$_p$,*M*)-**7**.

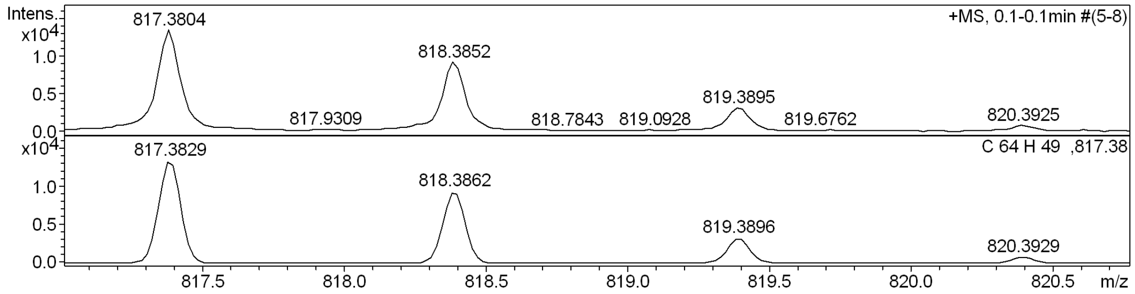


Figure S13. Mass spectra of (M,S_p,M)-**7**. Upper and lower show observed and calculated spectra, respectively.

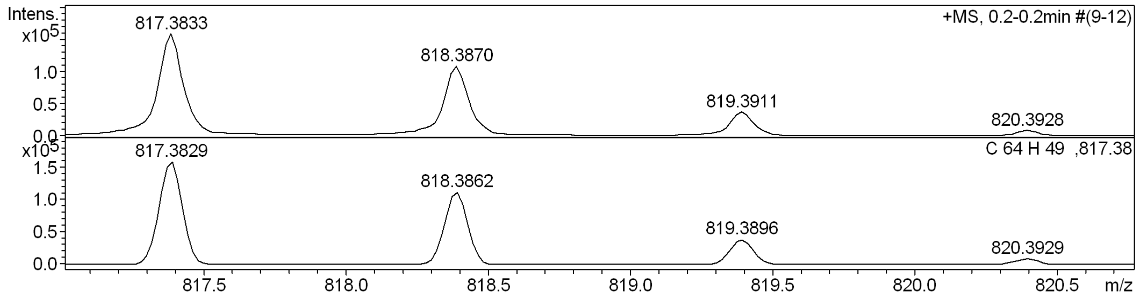


Figure S14. Mass spectra of (P,R_p,P)-**7**. Upper and lower show observed and calculated spectra, respectively.

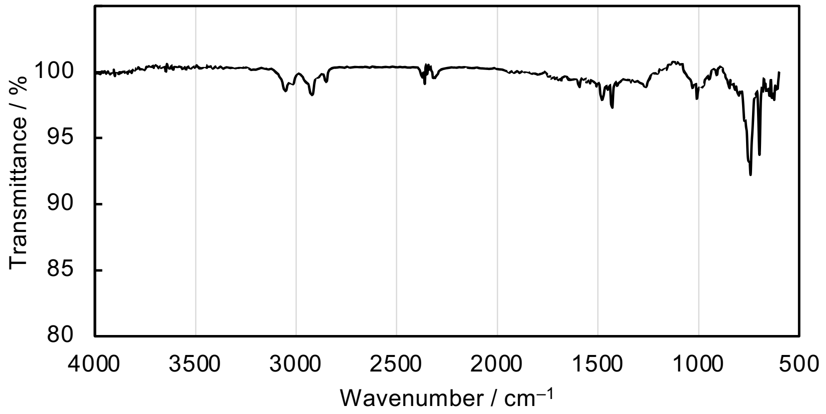


Figure S15. IR spectrum (ATR) of (M,S_p,M)-**7**.

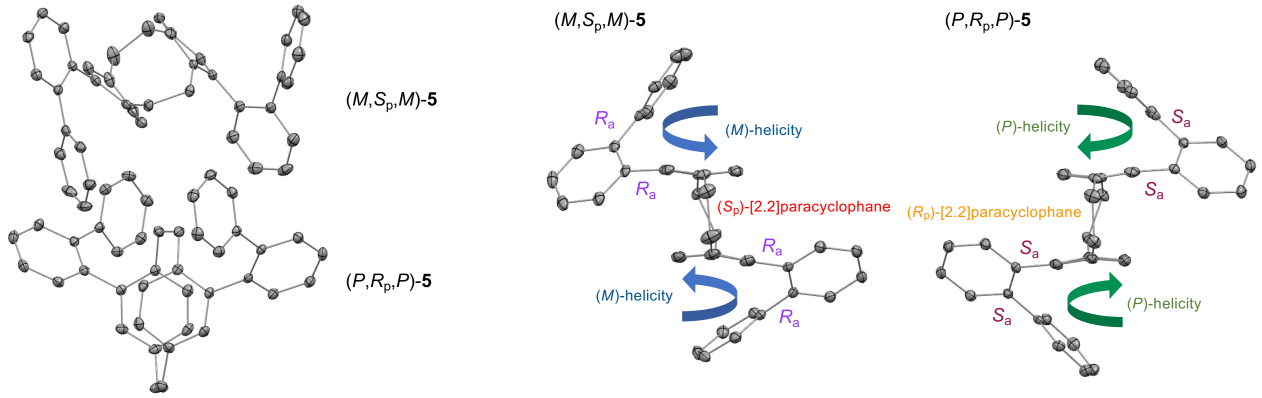


Figure S16. ORTEP drawings of *rac*-**5** and each isomer extracted. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

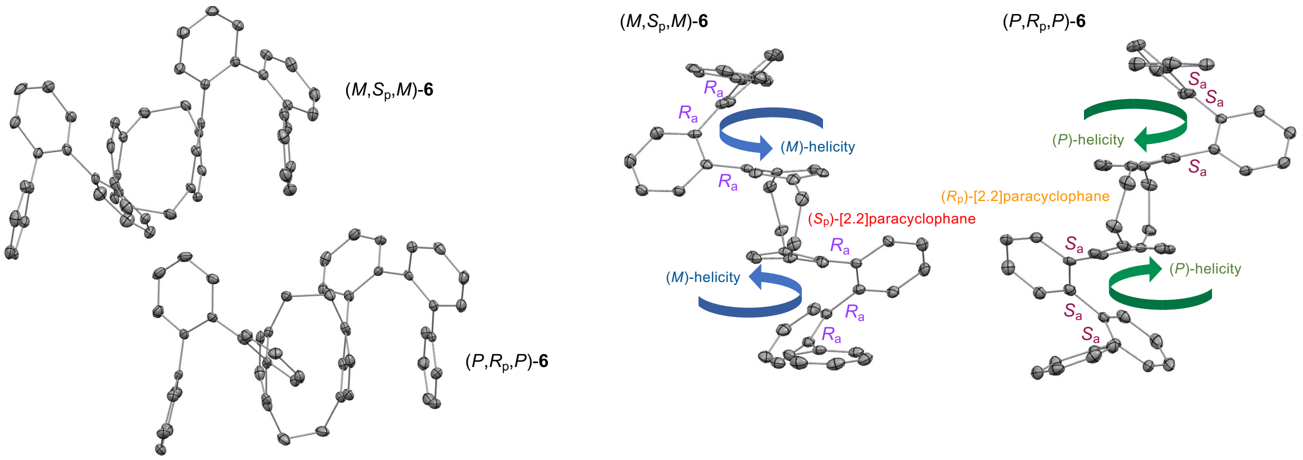


Figure S17. ORTEP drawings of *rac*-**6** and each isomer extracted. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and one of two molecules in a cell are omitted for clarity.

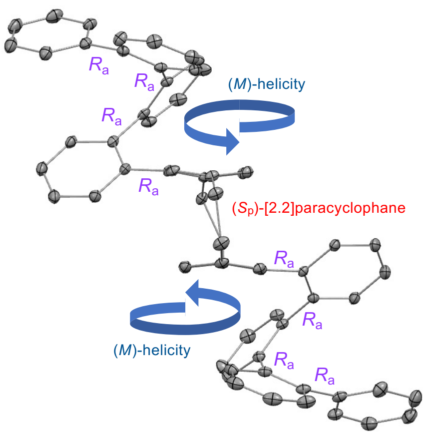


Figure S18. ORTEP drawing of (M,S_p,M)-**7**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and two $CHCl_3$ are omitted for clarity.

Table S1. Crystallographic data and structure refinements for *rac*-**5**, *rac*-**6**, and (*M*,*S*p,*M*)-**7**.

Parameter	*rac*-**5**	*rac*-**6**	(*M*,*S*p,*M*)-**7**
Formula	$C_{40}H_{32}$	$C_{52}H_{40}$	$C_{64}H_{48}\cdot 2(CHCl_3)$
Formula weight	512.65	664.84	1055.848
Tenperature(K)	150	150	150
Crystal color, habit	colourless, plate	colourless, plate	colourless, plate
Crystal size, mm	0.05 × 0.05 × 0.02	0.2 × 0.2 × 0.02	1.0 × 1.0 × 0.5
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*-1 (#2)	$P2_1/c$ (#14)	*P*1 (#1)
a, Å	12.8595(8)	18.2403(6)	9.6478(3)
b, Å	13.7903(8)	26.1062(8)	10.0343(3)
c, Å	17.4417(11)	15.1270(6)	14.7985(6)
α, deg	91.863(5)	90	104.808(3)
β, deg	108.767(5)	90.475(3)	99.837(3)
γ, deg	103.412(5)	90	101.640(3)
V, $Å^3$	2829.4(3)	7203.0(4)	1318.61(9)
Z value	4	8	1
D_{calcd}, g cm^{-3}	1.203	1.226	1.330
μ (MoKα), cm^{-1}	0.68	0.69	3.69
F(000)	1088	2816	549.124
$2\theta_{max}$, deg	62.384	62.472	62.40
No. of reflections measured	27692	68461	12809
No. of observed reflections	15546	21384	9994
No. of variables	721	937	649
R_1(I>2δ(I))[a]	0.0801(6360)	0.1868(13056)	0.0754(8808)
wR_2(all reflns)[b]	0.1509(15546)	0.5066(21384)	0.2271(9994)
Goodness of fit	0.963	1.055	1.0384
Recrystallization solvents	$CHCl_3$ / MeOH	$CHCl_3$ / MeOH	$CHCl_3$ / MeOH

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

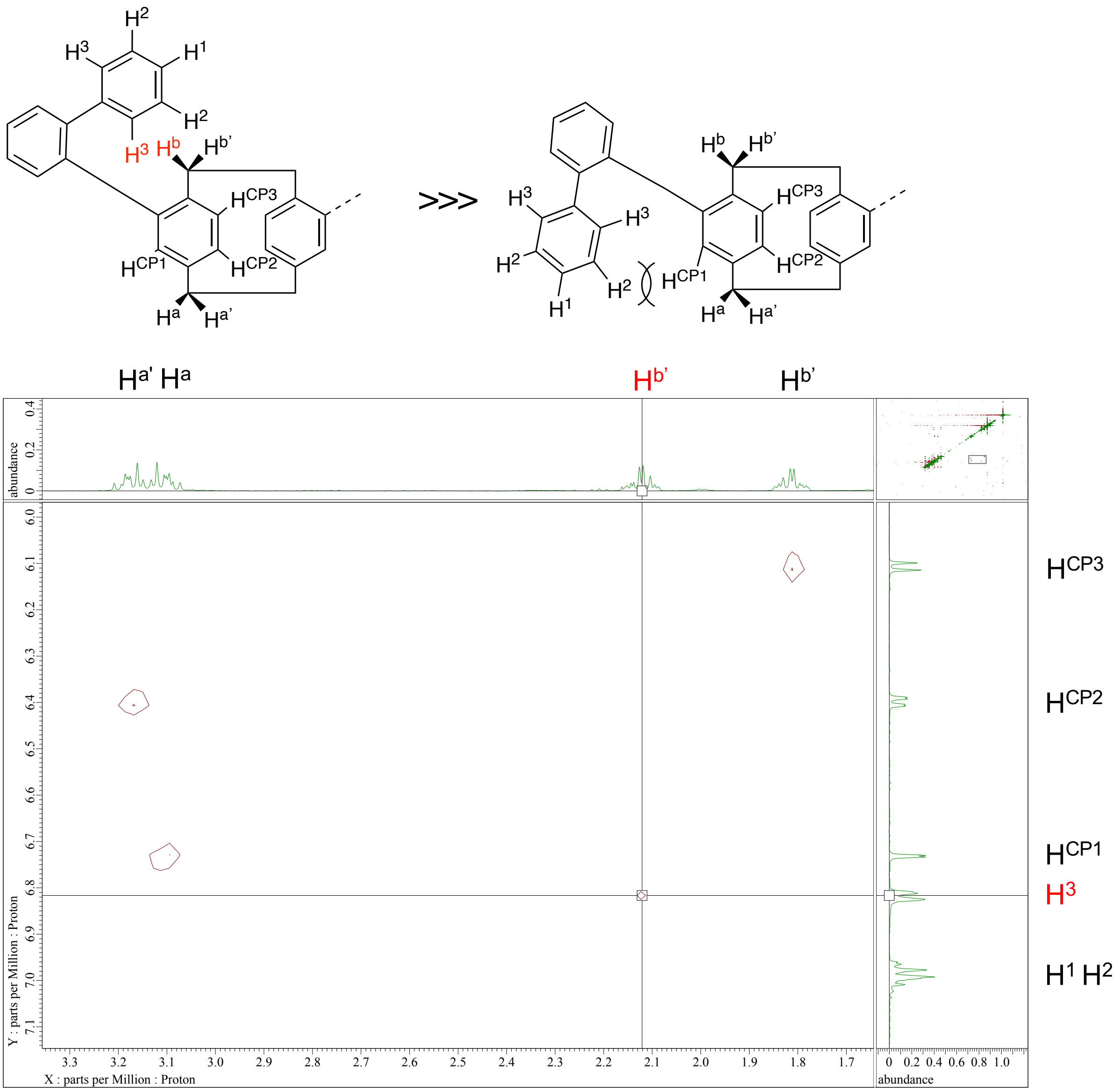


Figure S19. ^{1}H-^{1}H NOESY spectrum (CDCl$_3$, 500 MHz) of (M,S_p,M)-**5**.

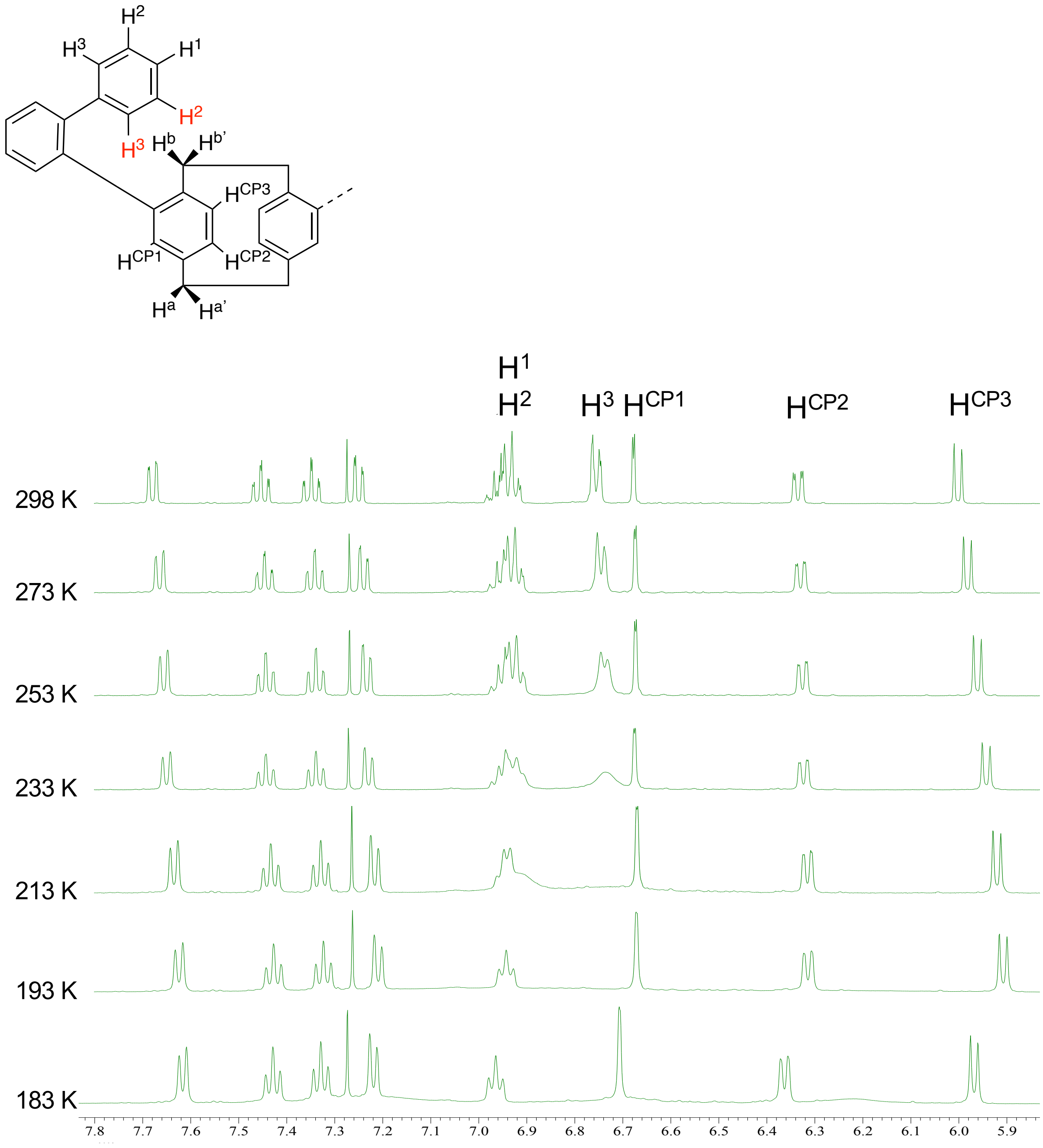


Figure S20. VT-NMR spectra (CD_2Cl_2, 500 MHz) of (M,S_p,M)-**5**.

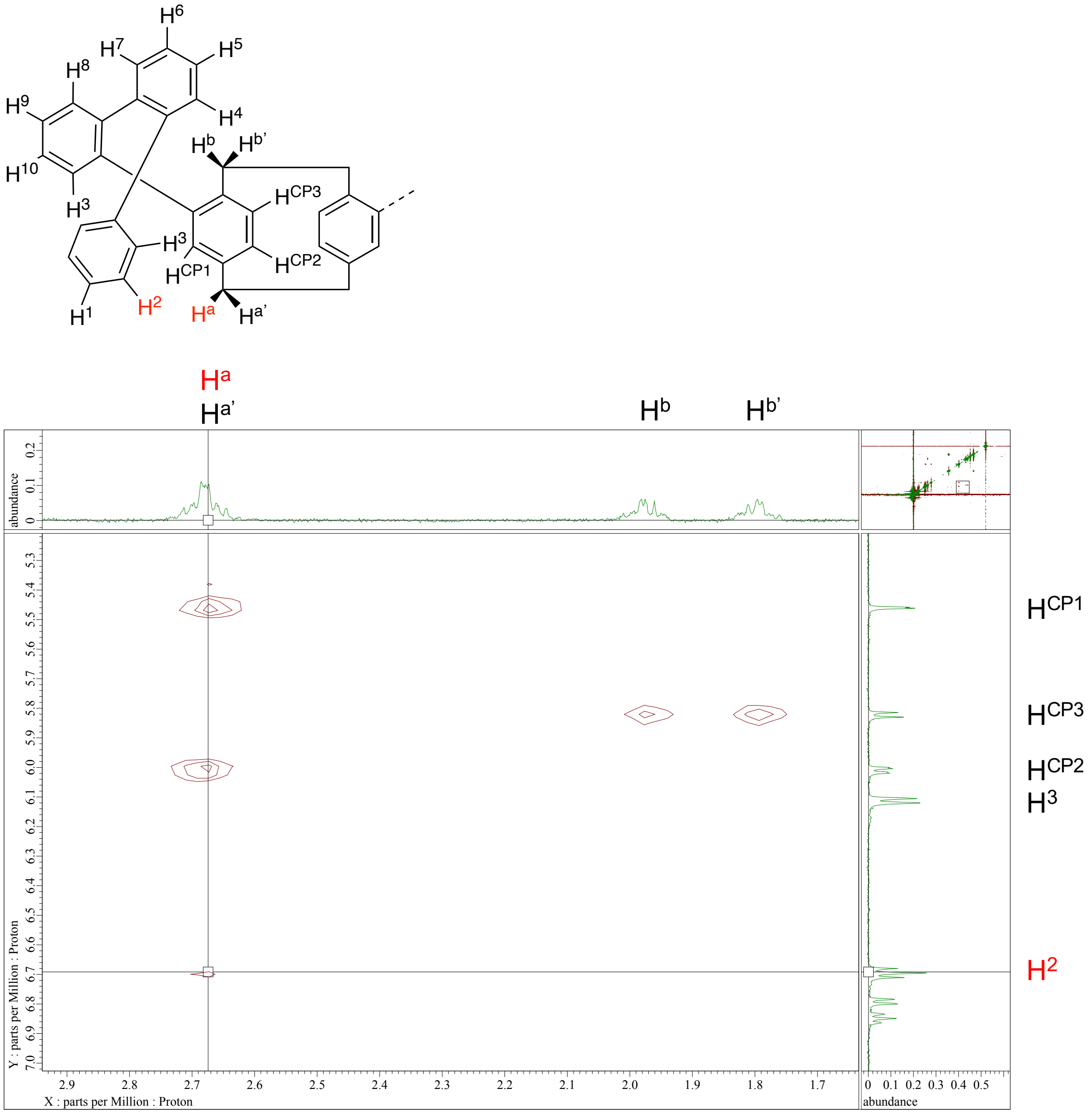


Figure S21. ^{1}H-^{1}H NOESY spectrum (CDCl$_3$, 500 MHz) of (*M*,*S*$_\text{p}$,*M*)-**6**.

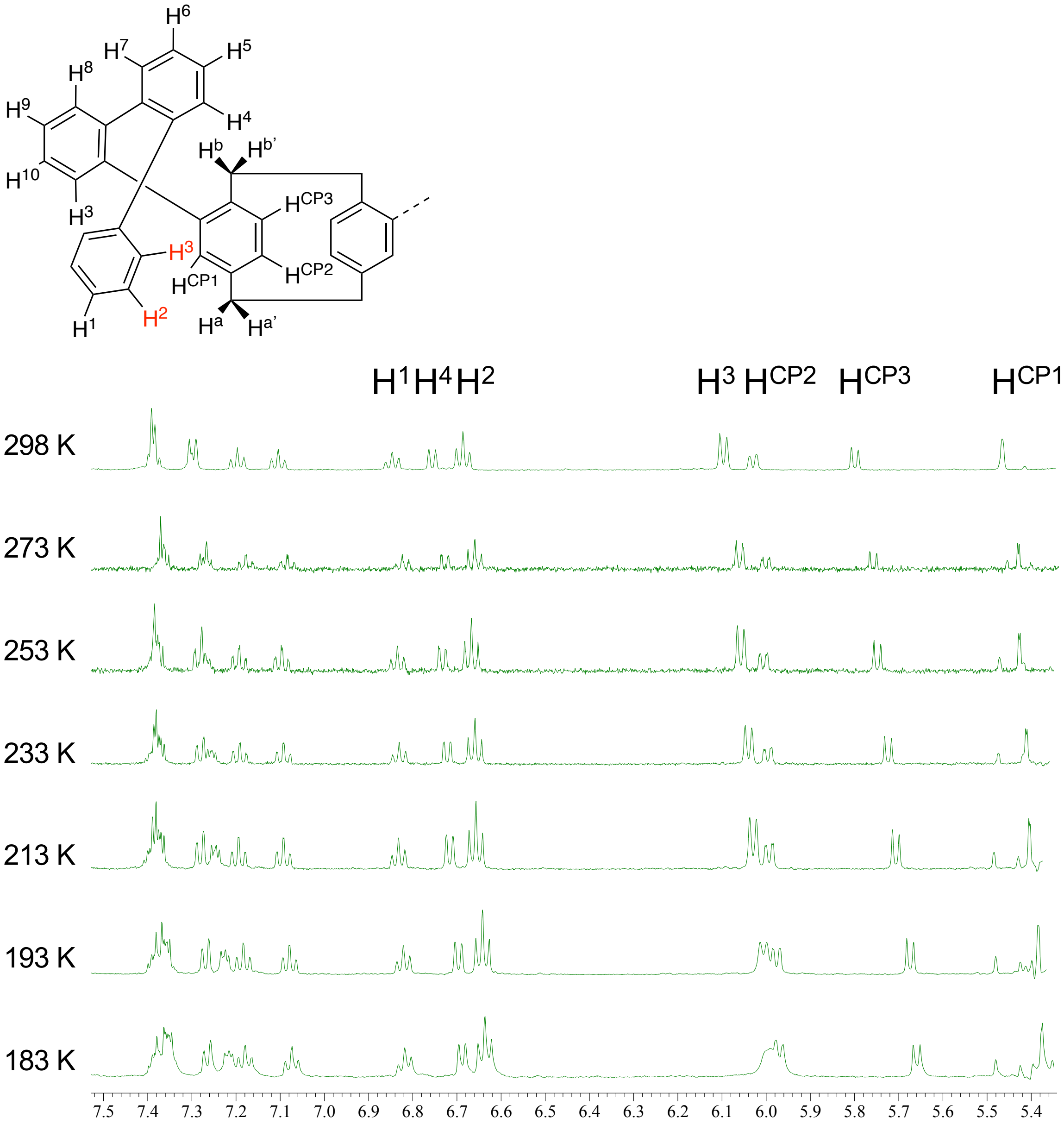


Figure S22. VT-NMR spectra (CD_2Cl_2, 500 MHz) of (M,S_p,M)-**6**.

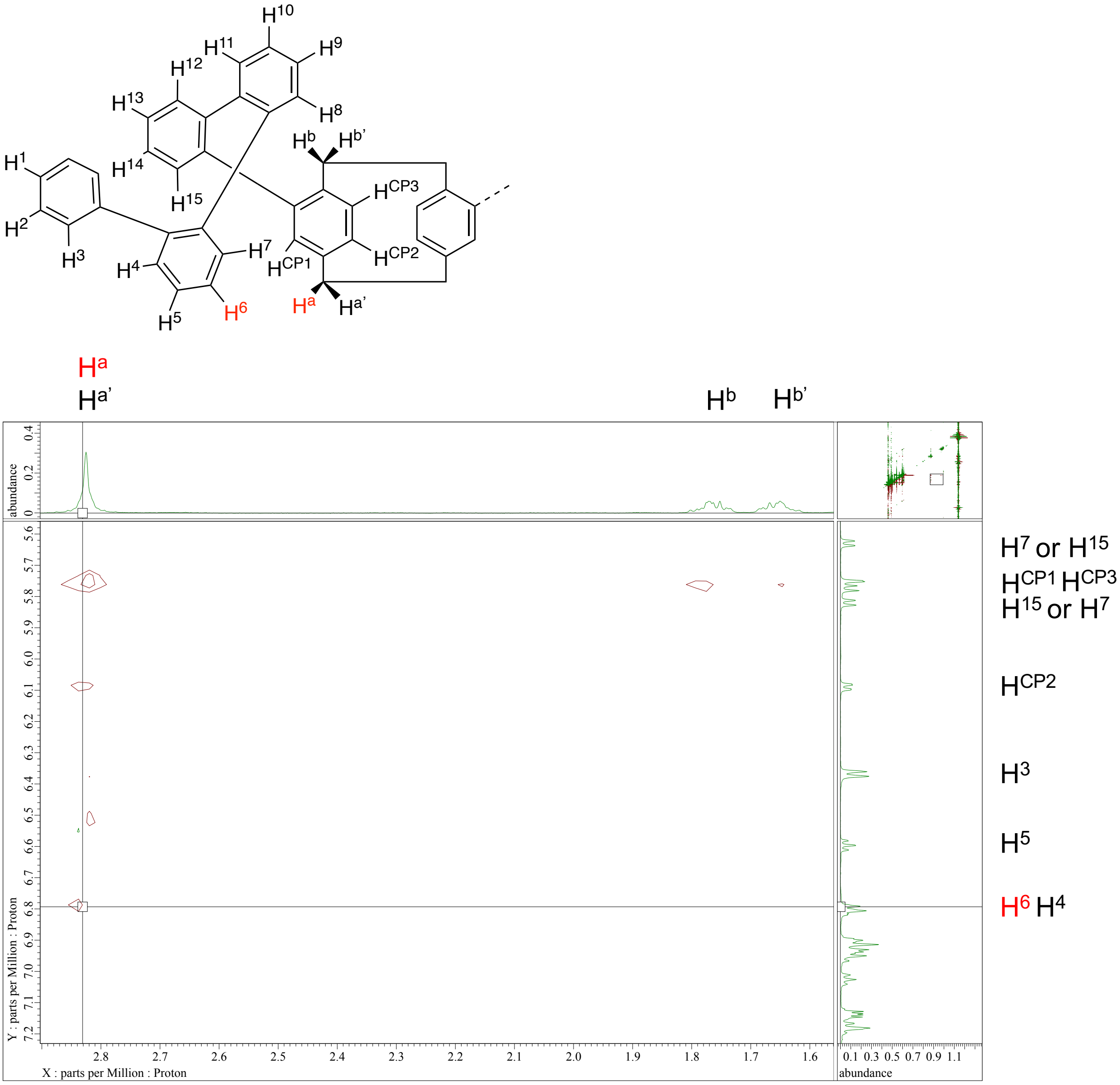


Figure S23. ^{1}H-^{1}H NOESY spectrum (CDCl$_3$, 500 MHz) of (*M*,*S*$_p$,*M*)-**7**.

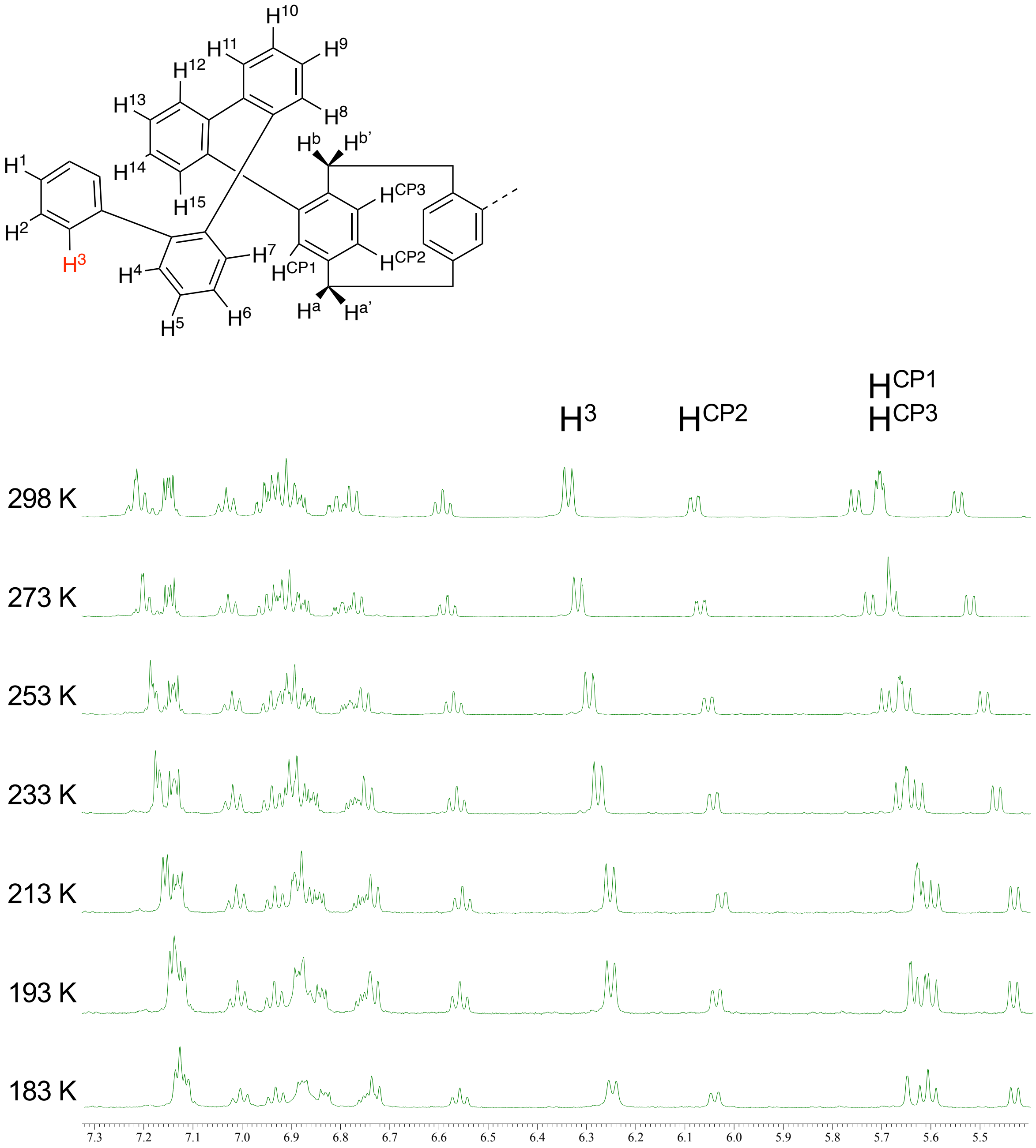


Figure S24. VT-NMR spectra (CD_2Cl_2, 500 MHz) of (M,S_p,M)-**7**.

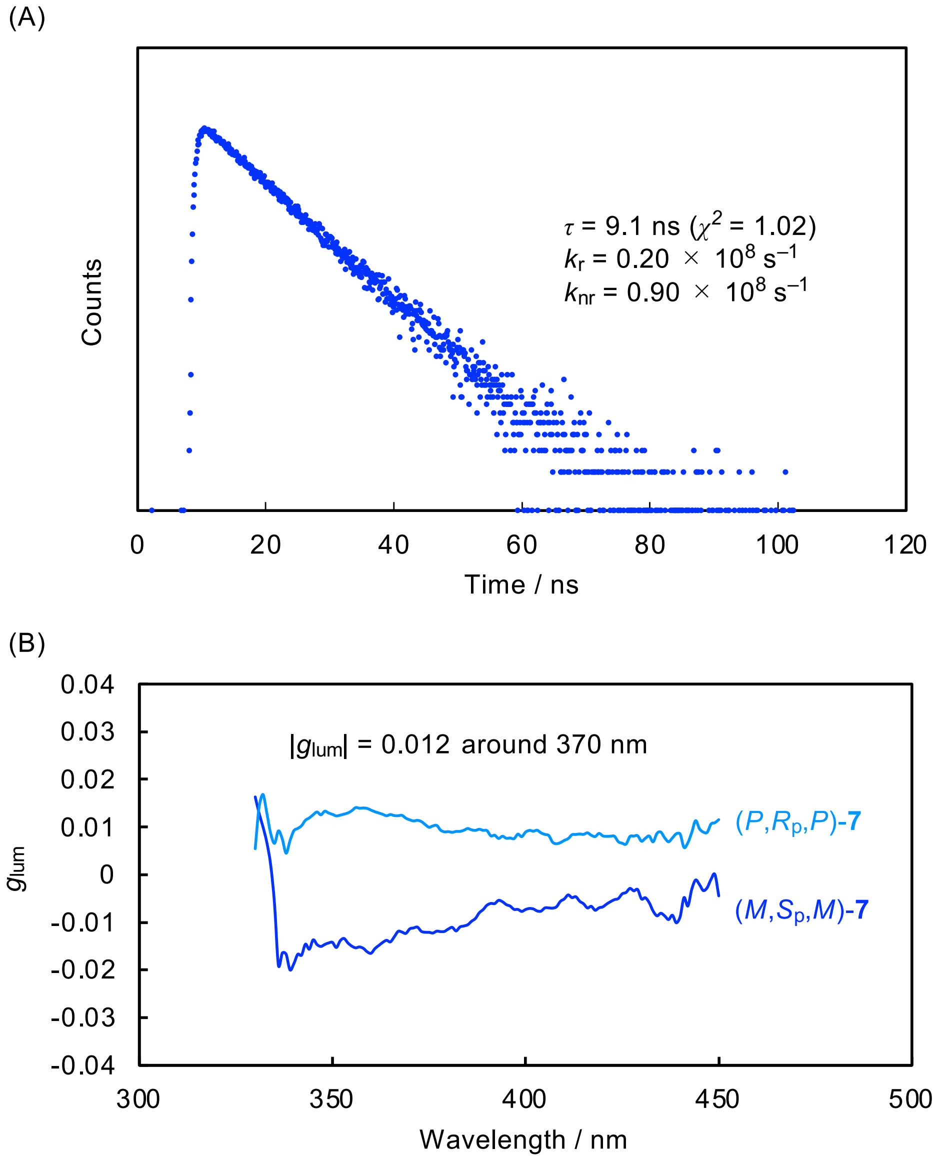


Figure S25. (A) PL decay study and the parameter of (*M*,*S*$_p$,*M*)-**7** in cyclohexane (1.0 × 10^{-5} M) monitored at the PL peak top 372 nm. (B) g_{lum} charts of (*M*,*S*$_p$,*M*)- and (*P*,*R*$_p$,*P*)-**7** in cyclohexane (1.0 × 10^{-5} M) excited at 220 nm.

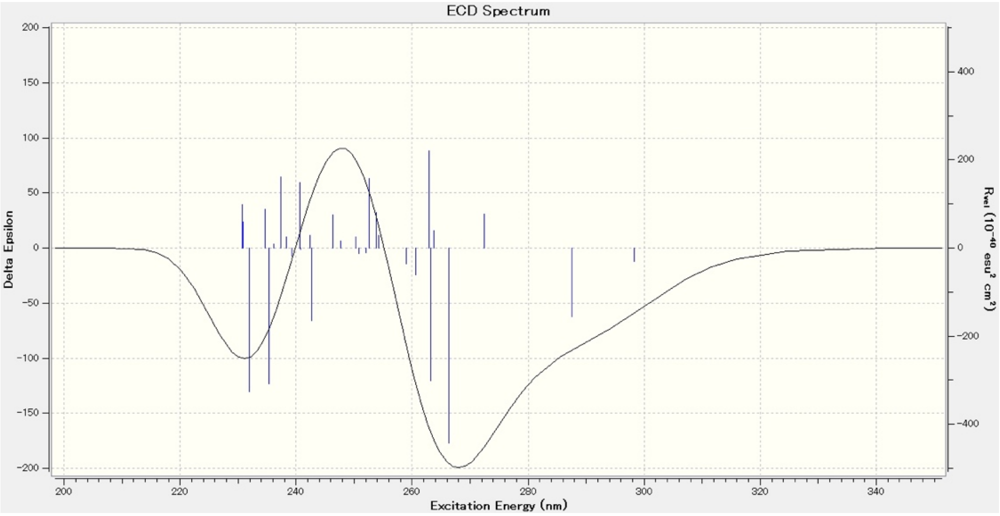


Figure S26. Calculated ECD spectrum of (*M*,S_p,*M*)-**7** estimated by TD-DFT calculation ((TD-)MN15/6-31G(d) with IEFPCM (cyclohexane)). Half-width at half height = 0.20 eV.

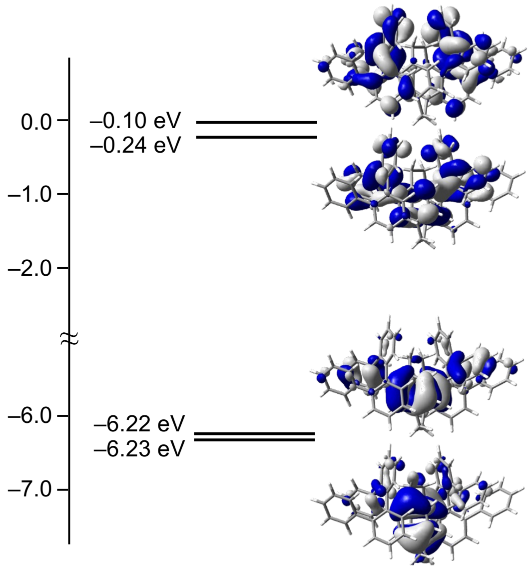


Figure S27. Selected molecular orbitals of (*M*,S_p,*M*)-**7** in the ground state.

Table S2. Selected data for excitation energy, major configuration, coefficient, oscillator strength, and rotatory strengths for (*M*,S_p,*M*)-**7**.[a]

State	Excitation energy / eV (/ nm)	Major Configuration	Coefficient	Oscillator strength	Rotatory Strengths / 10^{-40} esu^2 cm^2
S_1	4.16 (298)	H−1→L	0.57370	0.0119	-30.1752
S_2	4.31 (288)	H→L	0.57132	0.1719	-155.2505
S_3	4.55 (272)	H→L+1	0.43057	0.0195	77.7504
S_4	4.67 (266)	H→L+7	0.32931	0.1273	-442.9029
S_5	4.70 (264)	H–1→L+1	0.30574	0.0203	38.5966
S_6	4.71 (263)	H→L+2	0.35824	0.2088	-301.1879
S_7	4.71 (263)	H–2→L+1	0.43613	0.0457	220.8455
S_8	4.76 (261)	H–1→L+2	0.37316	0.0244	-60.7224
S_9	4.79 (259)	H–1→L+3	0.42762	0.0157	-36.6184
S_{10}	4.88 (254)	H–3→L+3	0.34915	0.1208	28.0287

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

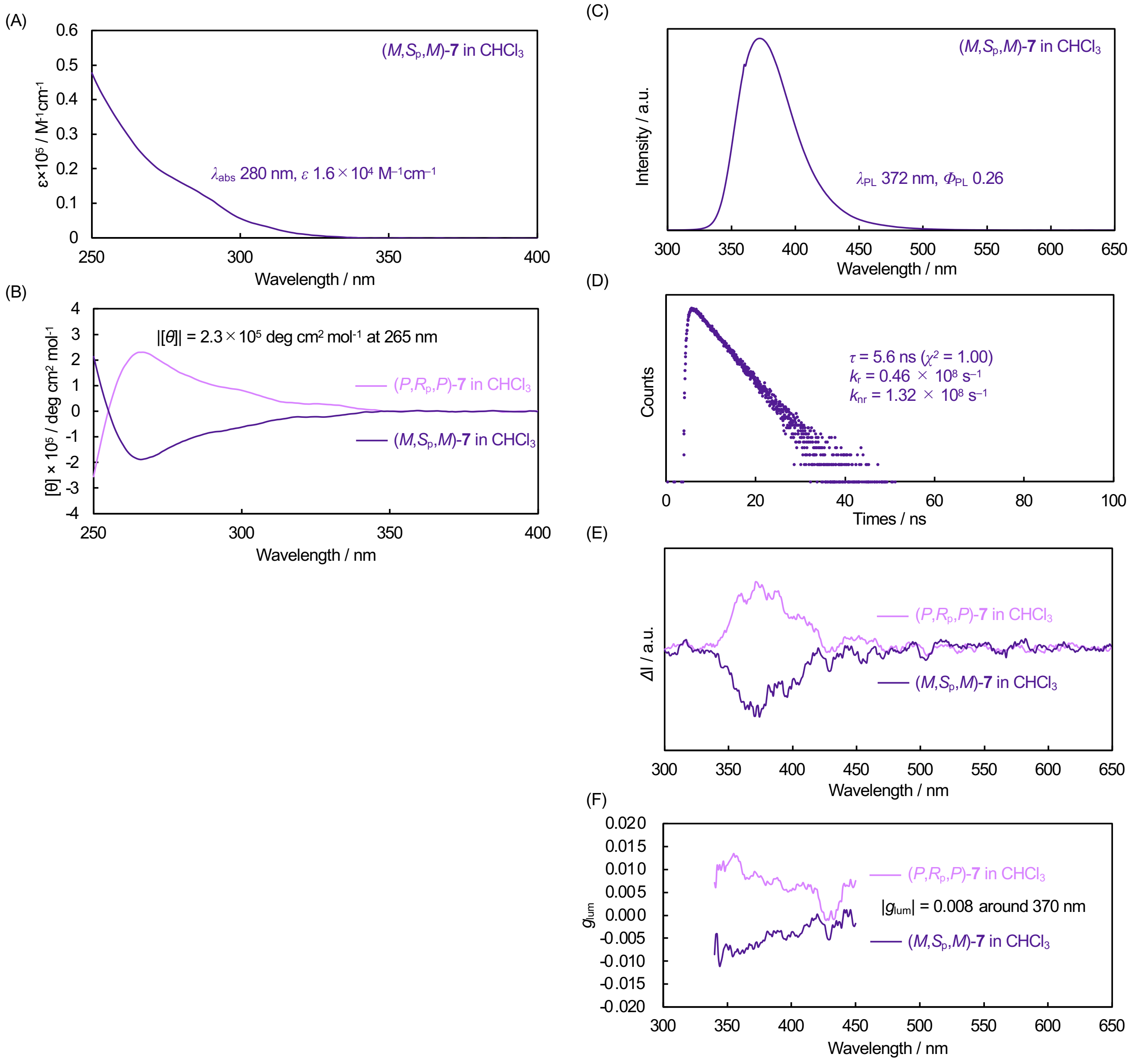


Figure S28. (A) UV-vis absorption spectrum of (M,S_p,M)-**7** in CHCl₃ (1.0×10^{-5} M). (B) CD spectra of (M,S_p,M)- and (P,R_p,P)-**7** in CHCl₃ (1.0×10^{-5} M). (C) PL spectrum of (M,S_p,M)-**7** in CHCl₃ (1.0×10^{-5} M), excited at 250 nm. (D) PL decay study and the parameter of (M,S_p,M)-**7** in CHCl₃ (1.0×10^{-5} M) monitored at the PL peak top 372 nm. (E) CPL spectra of (M,S_p,M)- and (P,R_p,P)-**7** in CHCl₃ (1.0×10^{-5} M), excited at 250 nm. (F) g_{lum} charts of (M,S_p,M)- and (P,R_p,P)-**7** in CHCl₃ (1.0×10^{-5} M) excited at 250 nm.

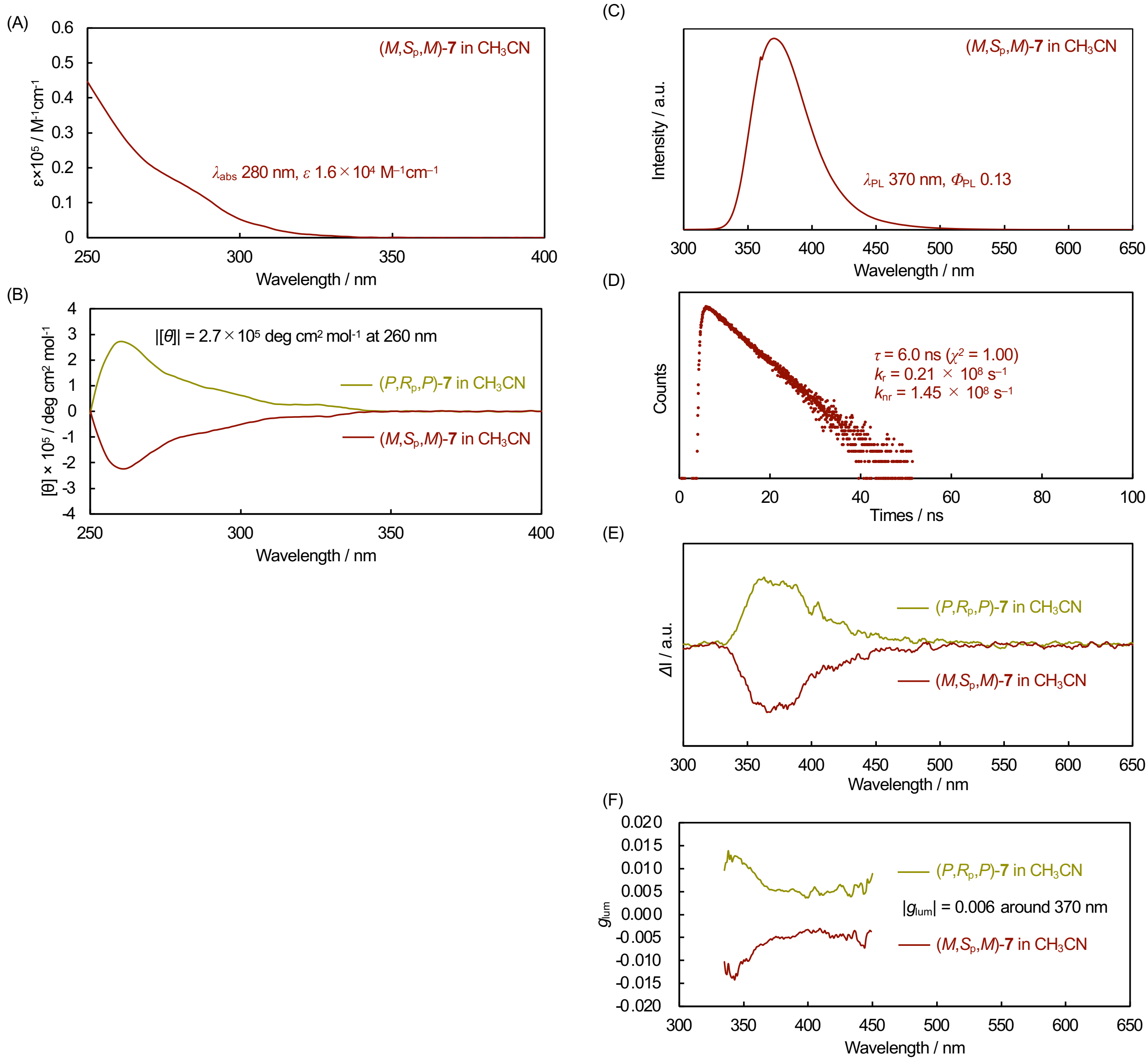
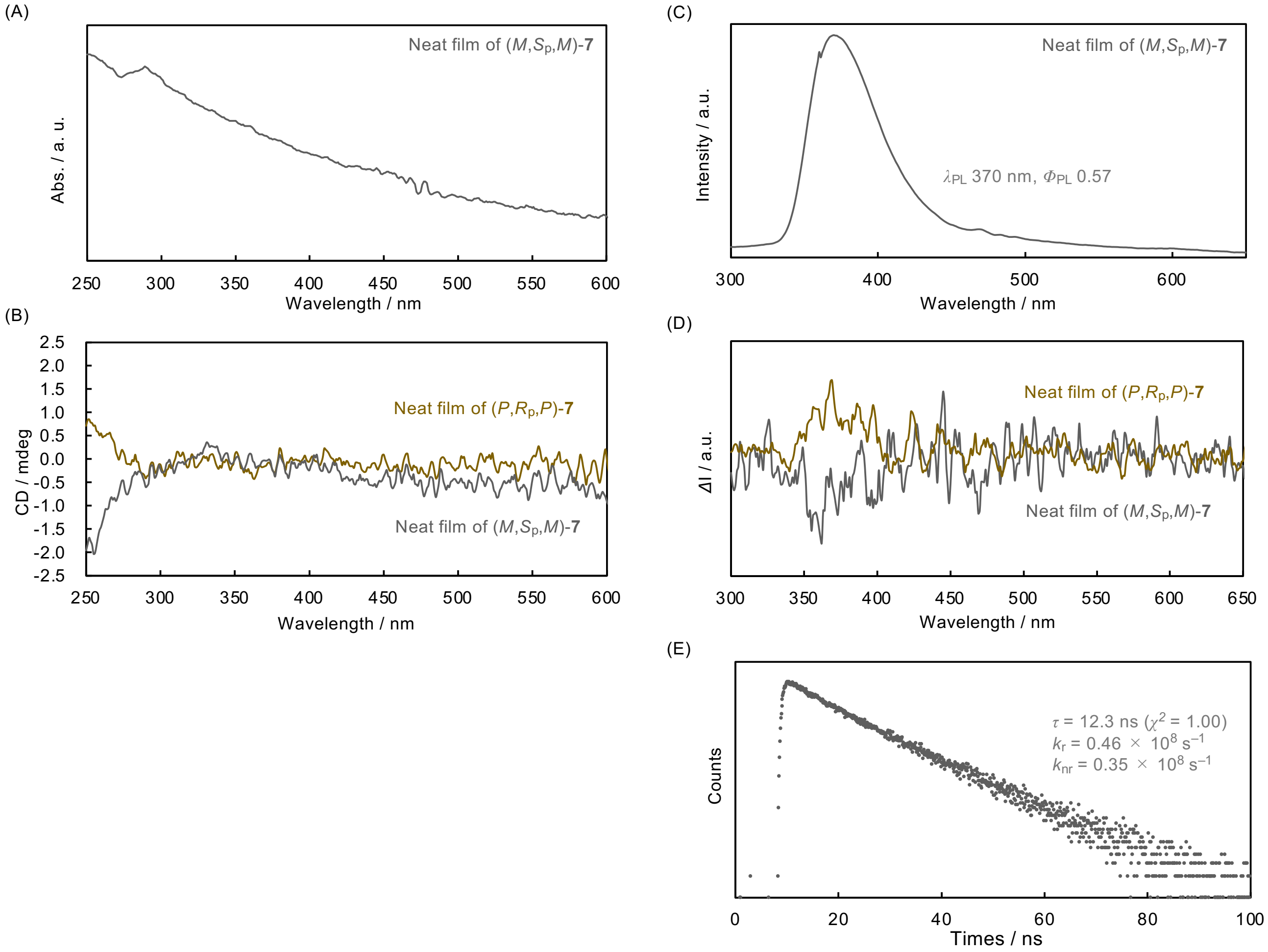


Figure S29. (A) UV-vis absorption spectrum of (*M*,*S*$_p$,*M*)-**7** in CH$_3$CN (1.0×10^{-5} M). (B) CD spectra of (*M*,*S*$_p$,*M*)- and (*P*,*R*$_p$,*P*)-**7** in CH$_3$CN (1.0×10^{-5} M). (C) PL spectrum of (*M*,*S*$_p$,*M*)-**7** in CH$_3$CN (1.0×10^{-5} M), excited at 250 nm. (D) PL decay study and the parameter of (*M*,*S*$_p$,*M*)-**7** in CH$_3$CN (1.0×10^{-5} M) monitored at the PL peak top 370 nm. (E) CPL spectra of (*M*,*S*$_p$,*M*)- and (*P*,*R*$_p$,*P*)-**7** in CH$_3$CN (1.0×10^{-5} M), excited at 250 nm. (F) g_{lum} charts of (*M*,*S*$_p$,*M*)- and (*P*,*R*$_p$,*P*)-**7** in CH$_3$CN (1.0×10^{-5} M) excited at 250 nm.



Neat films of **7** were fabricated on a quartz plate by a drop-casting method from the corresponding $CHCl_3$ solution (2.0×10^{-4} M).

Figure S30. (A) UV-vis absorption spectrum of the neat film of (M,S_p,M)-**7**. (B) CD spectra of the neat film of (M,S_p,M)- and (P,R_p,P)-**7**. (C) PL spectrum of the neat film of (M,S_p,M)-**7**, excited at 250 nm. (D) CPL spectra of the neat film of (M,S_p,M)- and (P,R_p,P)-**7**, excited at 250 nm. (E) PL decay study and the parameter of the neat film of (M,S_p,M)-**7** monitored at the PL peak top 370 nm.

Table S3. Cartesian coordinate of (*M*,S_p,*M*)-**7** in the ground state (MN15/6-31G(d) with IEFPCM(cyclohexane)).

atom	x	y	z
C	1.103757	2.531764	0.844024
C	0.476186	1.721238	1.795089
C	0.543159	0.334028	1.698543
C	1.242518	-0.282274	0.656569
C	2.134363	0.521359	-0.090571
C	2.040441	1.918162	0.00836
H	-0.19599	2.178143	2.521927
H	-0.112472	-0.270545	2.327269
H	2.64458	2.527549	-0.665212
C	0.768783	-1.642956	0.17438
H	0.954465	-2.430963	0.916045
H	1.338098	-1.92032	-0.720084
C	-0.768652	-1.642902	-0.174693
C	-1.24235	-0.282121	-0.656638
H	-0.954357	-2.43077	-0.916498
H	-1.337975	-1.92041	0.719723
C	-0.542984	0.334341	-1.698514
C	-2.134155	0.521415	0.090658
C	-0.475961	1.721566	-1.794814
H	0.112613	-0.270145	-2.327358
C	-2.040172	1.918231	-0.008019
C	-1.103481	2.531947	-0.843593
H	0.196218	2.178575	-2.521584
H	-2.644267	2.527521	0.665681
C	-0.549054	3.911608	-0.57527
H	-1.338945	4.619422	-0.296331
H	-0.084916	4.291124	-1.493713
C	0.549383	3.911491	0.575934
H	1.3393	4.619322	0.297117
H	0.085257	4.290868	1.49444
C	3.037165	-0.060832	-1.12012
C	3.887842	-1.158474	-0.858136
C	3.022746	0.477172	-2.417089
C	4.647409	-1.697133	-1.907367
C	3.797811	-0.055159	-3.444793
H	2.356079	1.312756	-2.620528
C	4.609125	-1.159366	-3.190376
H	5.315497	-2.527214	-1.686748
H	3.754958	0.382108	-4.439342
H	5.223219	-1.589002	-3.977813
C	4.017954	-1.81607	0.475756
C	3.818262	-3.204544	0.519495
C	4.368907	-1.145194	1.669331
C	3.938242	-3.932611	1.700541
H	3.537531	-3.710322	-0.402781
C	4.480883	-1.892257	2.852005
C	4.27092	-3.268841	2.879407
H	3.769019	-5.006358	1.697797
H	4.759244	-1.368939	3.764631
H	4.372166	-3.815758	3.813356
C	4.590138	0.327662	1.774347
C	3.836111	1.008219	2.74216
C	5.494992	1.061539	0.976205
C	3.928776	2.386251	2.909016
H	3.124127	0.437592	3.334406
C	5.566699	2.452553	1.148208
C	4.793841	3.116981	2.096539
H	3.314164	2.885123	3.654036
H	6.27857	3.010936	0.543582
H	4.879723	4.195013	2.208445
C	-3.036923	-0.060915	1.120159
C	-3.887626	-1.158518	0.858074
C	-3.02241	0.476896	2.417208
C	-4.647086	-1.697351	1.907293
C	-3.797389	-0.055593	3.444894
H	-2.355726	1.312449	2.620721
C	-4.608704	-1.159777	3.19038
H	-5.315175	-2.527414	1.686607
H	-3.754459	0.381525	4.439505
H	-5.222724	-1.589542	3.977804
C	-4.017817	-1.815969	-0.475883
C	-3.818047	-3.204428	-0.519765
C	-4.36893	-1.145011	-1.669369
C	-3.938066	-3.932397	-1.700866
H	-3.537216	-3.710271	0.402445
C	-4.480922	-1.891976	-2.852104
C	-4.270862	-3.268542	-2.879649
H	-3.768772	-5.006134	-1.698231
H	-4.759383	-1.368594	-3.764663
H	-4.372135	-3.815379	-3.813642
C	-4.590291	0.327835	-1.774271
C	-3.836306	1.008513	-2.742032
C	-5.495274	1.061582	-0.97615
C	-3.929099	2.386543	-2.908826
H	-3.124248	0.437983	-3.334282
C	-5.56711	2.452598	-1.148093
C	-4.794268	3.11715	-2.096351
H	-3.314506	2.88551	-3.653799
H	-6.279078	3.010879	-0.543487
H	-4.880257	4.195177	-2.208212
C	-6.414266	0.435383	0.011092
C	-7.157863	-0.711374	-0.304459
C	-6.584456	1.020434	1.273466
C	-8.037939	-1.263068	0.624658
H	-7.047512	-1.164731	-1.286759
C	-7.467461	0.471803	2.201256
H	-5.984759	1.889934	1.536927
C	-8.195497	-0.67445	1.881133
H	-8.61012	-2.150016	0.362894
H	-7.575229	0.931694	3.180791
H	-8.883221	-1.10605	2.604328
C	6.413936	0.435467	-0.011162
C	7.157667	-0.711237	0.304262
C	6.583899	1.020556	-1.273549
C	8.03767	-1.262832	-0.624982
H	7.047476	-1.164632	1.286563
C	7.466829	0.472022	-2.201468
H	5.984085	1.890004	-1.536915
C	8.195013	-0.674171	-1.881464
H	8.60996	-2.149738	-0.363315
H	7.574424	0.931941	-3.181008
H	8.882678	-1.105695	-2.60476

Table S4. Cartesian coordinate of (M,S_p,M)-**7** in the S_1 state (TD-MN15/6-31G(d) with IEFPCM(cyclohexane).

atom	x	y	z
C	-0.986714	2.512083	-0.842217
C	-0.383676	1.703843	-1.821973
C	-0.459011	0.308236	-1.704593
C	-1.170546	-0.275917	-0.629297
C	-2.055924	0.533875	0.147399
C	-1.907181	1.931422	0.059132
H	0.260186	2.164407	-2.568673
H	0.170105	-0.326286	-2.327618
H	-2.485443	2.577872	0.717825
C	-0.758166	-1.665567	-0.179351
H	-0.955412	-2.412567	-0.960826
H	-1.348058	-1.957753	0.694407
C	0.757945	-1.66564	0.178884
C	1.170392	-0.276122	0.629181
H	0.955161	-2.412835	0.960181
H	1.347823	-1.957641	-0.694944
C	0.45887	0.307792	1.704604
C	2.055831	0.533831	-0.147328
C	0.383535	1.703375	1.822274
H	-0.17031	-0.326853	2.32744
C	1.907127	1.931367	-0.058734
C	0.986638	2.511827	0.842704
H	-0.260316	2.163793	2.569072
H	2.485417	2.577956	-0.717268
C	0.475337	3.917601	0.622901
H	1.297156	4.627194	0.462882
H	-0.07585	4.243611	1.512296
C	-0.475342	3.917778	-0.622074
H	-1.297116	4.627384	-0.46188
H	0.075863	4.24397	-1.511391
C	-2.969698	-0.042128	1.150792
C	-3.792135	-1.164962	0.87722
C	-3.039956	0.537081	2.433616
C	-4.566297	-1.710566	1.913247
C	-3.829715	-0.004023	3.441758
H	-2.414414	1.401947	2.6446
C	-4.589367	-1.149273	3.186172
H	-5.204463	-2.562667	1.686419
H	-3.840587	0.455867	4.42705
H	-5.215608	-1.582856	3.961674
C	-3.890896	-1.813096	-0.461673
C	-3.719633	-3.207681	-0.511022
C	-4.192206	-1.13048	-1.666338
C	-3.810192	-3.926486	-1.699842
H	-3.478949	-3.726279	0.415407
C	-4.267471	-1.869057	-2.85814
C	-4.079962	-3.249395	-2.888765
H	-3.662917	-5.003381	-1.696791
H	-4.505867	-1.337199	-3.777151
H	-4.152195	-3.787908	-3.83
C	-4.424271	0.341824	-1.76962
C	-3.663936	1.038455	-2.720397
C	-5.356927	1.060311	-0.986802
C	-3.761383	2.418763	-2.873237
H	-2.940608	0.480358	-3.310531
C	-5.430424	2.453265	-1.140145
C	-4.639393	3.135777	-2.062134
H	-3.140457	2.928626	-3.605573
H	-6.157155	3.001799	-0.544209
H	-4.727369	4.214971	-2.159329
C	2.969634	-0.041957	-1.150789
C	3.792104	-1.164828	-0.877424
C	3.039953	0.537547	-2.433483
C	4.566315	-1.710184	-1.913547
C	3.829752	-0.003322	-3.441712
H	2.41442	1.402462	-2.644297
C	4.589418	-1.14862	-3.18635
H	5.20451	-2.562306	-1.686879
H	3.840653	0.456789	-4.4269
H	5.215698	-1.582018	-3.961921
C	3.890925	-1.813178	0.461354
C	3.719751	-3.207786	0.510471
C	4.19224	-1.130757	1.666134
C	3.810384	-3.926792	1.699161
H	3.479058	-3.726238	-0.416036
C	4.267583	-1.869542	2.857804
C	4.08015	-3.249896	2.888197
H	3.663171	-5.003696	1.695924
H	4.505998	-1.337837	3.776897
H	4.152448	-3.788571	3.829334
C	4.424274	0.341535	1.769662
C	3.663866	1.038006	2.7205
C	5.356875	1.060185	0.986925
C	3.761172	2.418309	2.873466
H	2.940571	0.479788	3.31056
C	5.430211	2.453136	1.140378
C	4.6391	3.135487	2.062417
H	3.140186	2.928044	3.605839
H	6.156898	3.001799	0.544506
H	4.726961	4.214683	2.159704
C	6.307908	0.413965	0.043264
C	7.028715	-0.734507	0.4053
C	6.54335	0.984833	-1.215192
C	7.947858	-1.302772	-0.474996
H	6.870989	-1.175887	1.386847
C	7.465578	0.419937	-2.094626
H	5.967272	1.857955	-1.515853
C	8.169466	-0.728136	-1.728948
H	8.501134	-2.190259	-0.177099
H	7.624386	0.869719	-3.071814
H	8.887311	-1.171928	-2.414288
C	-6.307848	0.413911	-0.043153
C	-7.028297	-0.734801	-0.405135
C	-6.543541	0.984832	1.21523
C	-7.947327	-1.303258	0.475157
H	-6.870366	-1.17623	-1.386628
C	-7.465669	0.419755	2.094652
H	-5.96773	1.858146	1.515848
C	-8.169191	-0.728563	1.729037
H	-8.500319	-2.190937	0.177309
H	-7.624679	0.869585	3.071785
H	-8.886954	-1.172499	2.41437