Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Synthesis of Optically Active π-Stacked Compounds Based on Planar Chiral Tetrasubstituted [2.2]Paracyclophane

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General

^{1}H and ^{13}C spectra were recorded on a JEOL JNM ECX-500II instrument at 500 and 125 MHz, respectively. Samples were analyzed in CD_2Cl_2 or $CDCl_3$, 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. High-resolution mass (HRMS) spectra were obtained on a JEOL JMS-S3000 spectrometer for matrix assisted desorption/ionization (MALDI) with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix. 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 a ILF-835 integrating sphere. Fluorescence decays in this study were measured by a picosecond time-correlated single-photon counting system with a response function of ~ 40 ps. The samples were excited by a second harmonic (~ 385 nm) of a cavity-dumped Ti:sapphire laser (Cascade, KM Labs, 4 MHz, ~ 770 nm). The fluorescence signal was collimated into a monochromator (JASCO, CT-10) and detected by a microchannel-plate photomultiplier (MCP) tube (Hamamatsu, R3809U). Fluorescence lifetimes were analyzed with a nonlinear least-squares iterative convolution method based on a Marquardt algorithm. Statistical fitting parameters used to evaluate the goodness of fit were reduced chi-squares (χ^2) and Durbin-Watson statistics (DW). Specific rotations ($[\alpha]^t_D$) were measured with a HORIBA SEPA-500 polarimeter. 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 at 280 nm, and five scans were accumulated.

Materials

Commercially available compounds used without purification:

Trimethylsilylacetylene, *p*-methoxyphenylacetylene, phenylacetylene

Iodobenzene, *p*-iodoanisole

$Pd_2(dba)_3$, $PdCl_2(dppf)\cdot CH_2Cl_2$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene)

$(t\text{-Bu})_3P\cdot HBF_4$, dppf

CuI, K_2CO_3

THF (dehaydrated), MeOH

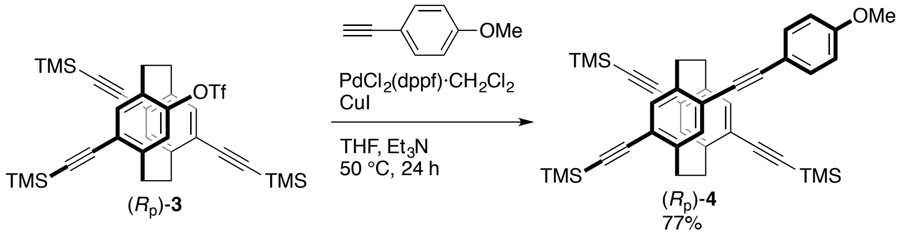
Et_3N was purchased and purified by distillation using KOH.

Compounds prepared as described in the literature:

(R_p)- and (S_p)-**2** and (R_p)- and (S_p)-**3**

Morisaki, Y.; Gon, M.; Sasamori, T.; Tokitoh, N.; Chujo Y. *J. Am. Chem. Soc.* **2014**, *136(9)*, 3350-3353.

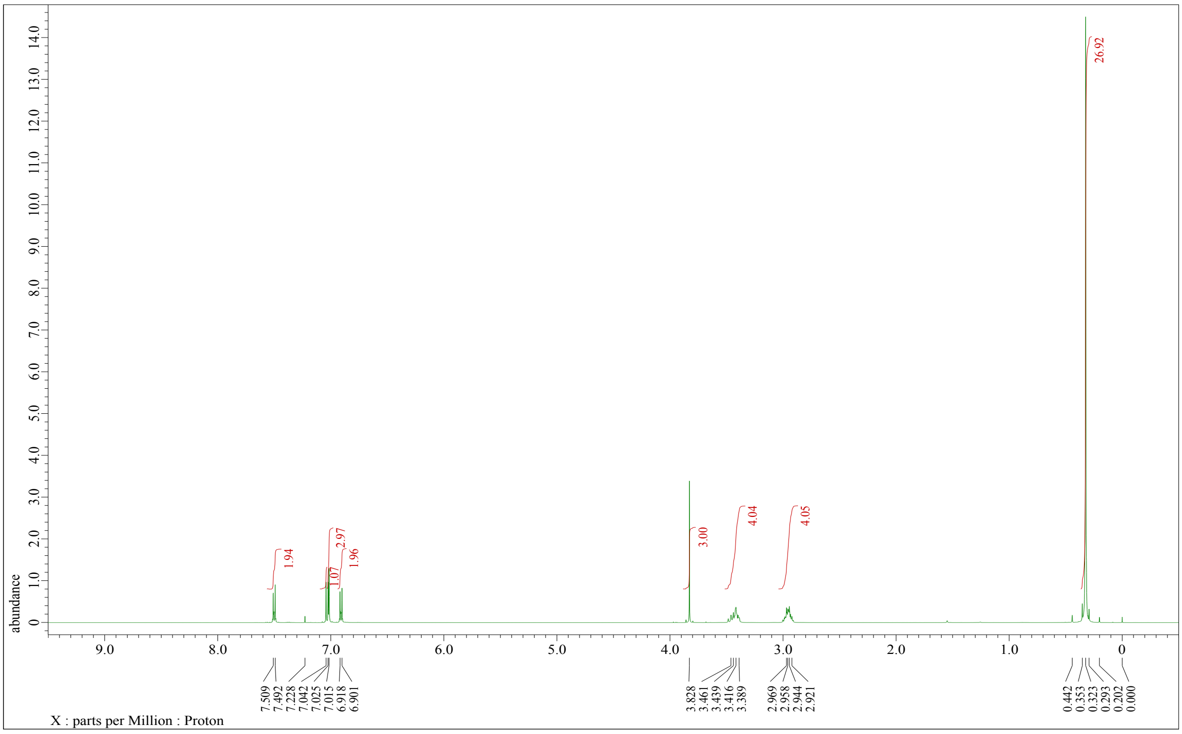
Synthesis of (R_p)-**4**



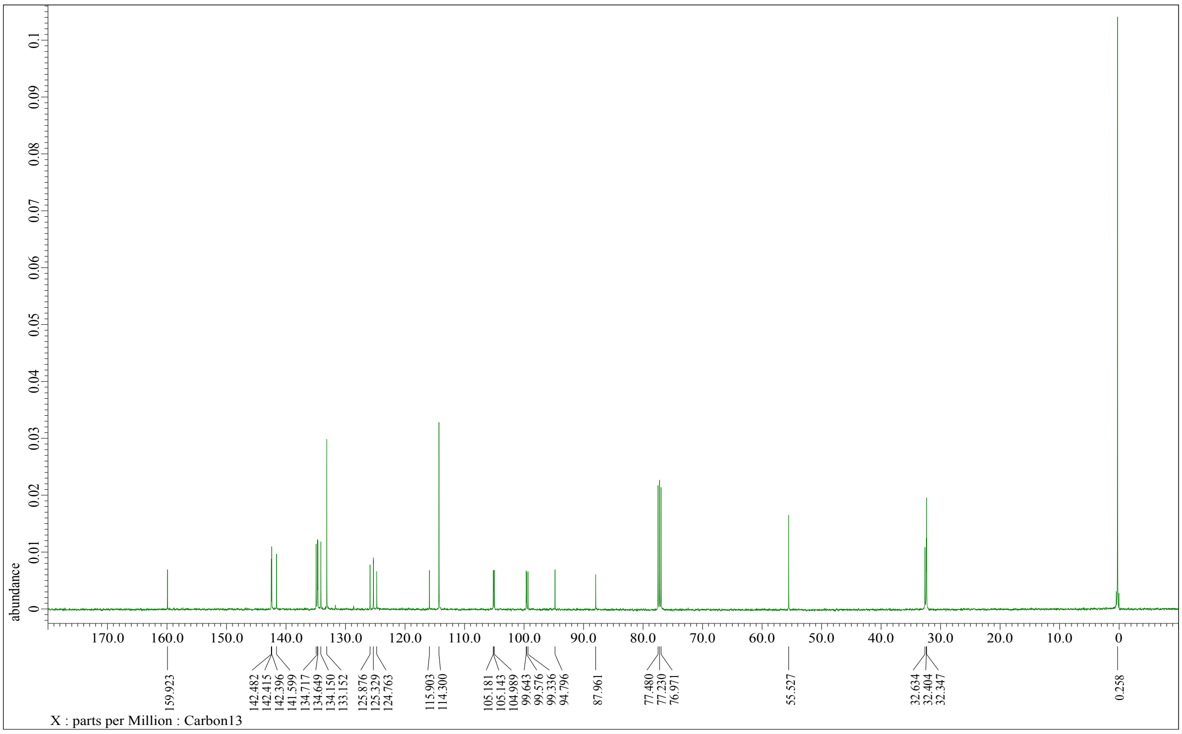
A mixture of (R_p)-**3** (1.10 g, 1.70 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (254 mg, 0.31 mmol), CuI (53 mg, 0.28 mmol), THF (20 mL) and Et_3N (20 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, *p*-methoxyphenylacetylene (1.53 mg, 11.6 mmol) was added to the mixture. The reaction was carried out at 50 °C for 24 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were 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 = 1/4 v/v as an eluent) to afford (R_p)-**4** (822 mg, 1.31 mmol, 77%) as a light yellow solid.

R_f = 0.25 ($CHCl_3$/hexane = 1/4 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.32 (three singlet peaks, 27H), 2.95 (m, 4H), 3.42 (m, 4H), 3.83 (s, 3H), 6.91 (d, J = 8.5 Hz, 2H), 7.01 (two singlet peaks, 2H), 7.02 (s, 1H), 7.04 (s, 1H), 7.50 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.3 (two peaks), 32.4, 32.6, 55.5, 87.9, 94.7, 99.3, 99.5, 99.6, 104.9, 105.14, 105.18, 114.3, 115.9, 124.7, 125.3 (two peaks), 125.8, 133.1, 134.1, 134.6 (two peaks), 134.7, 141.5, 142.3, 142.4, 142.8, 159.9 ppm. HRMS (MALDI) calcd. for $C_{40}H_{46}OSi_3$ M$^+$: 626.2851, found 626.2841. $[\alpha]^{25}_{D}$ = +44.8 (c = 0.5, $CHCl_3$).

(S_p)-**4** was obtained in 69% yield by the same procedure of (R_p)-**5**. HRMS (MALDI) calcd. for $C_{40}H_{46}OSi_3$ M$^+$: 626.2851, found 626.2839. $[\alpha]^{25}_{D}$ = –44.2 (c = 0.5, $CHCl_3$).

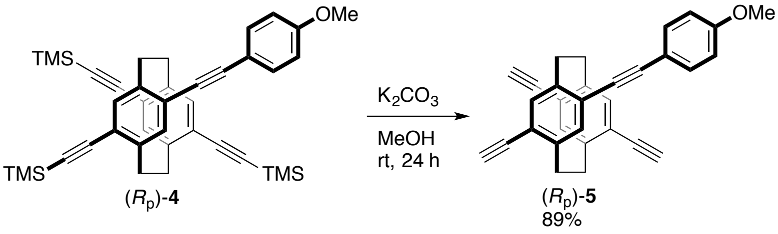


^{1}H NMR spectrum of (R_p)-**4**.



^{13}C NMR spectrum of (R_p)-**4**.

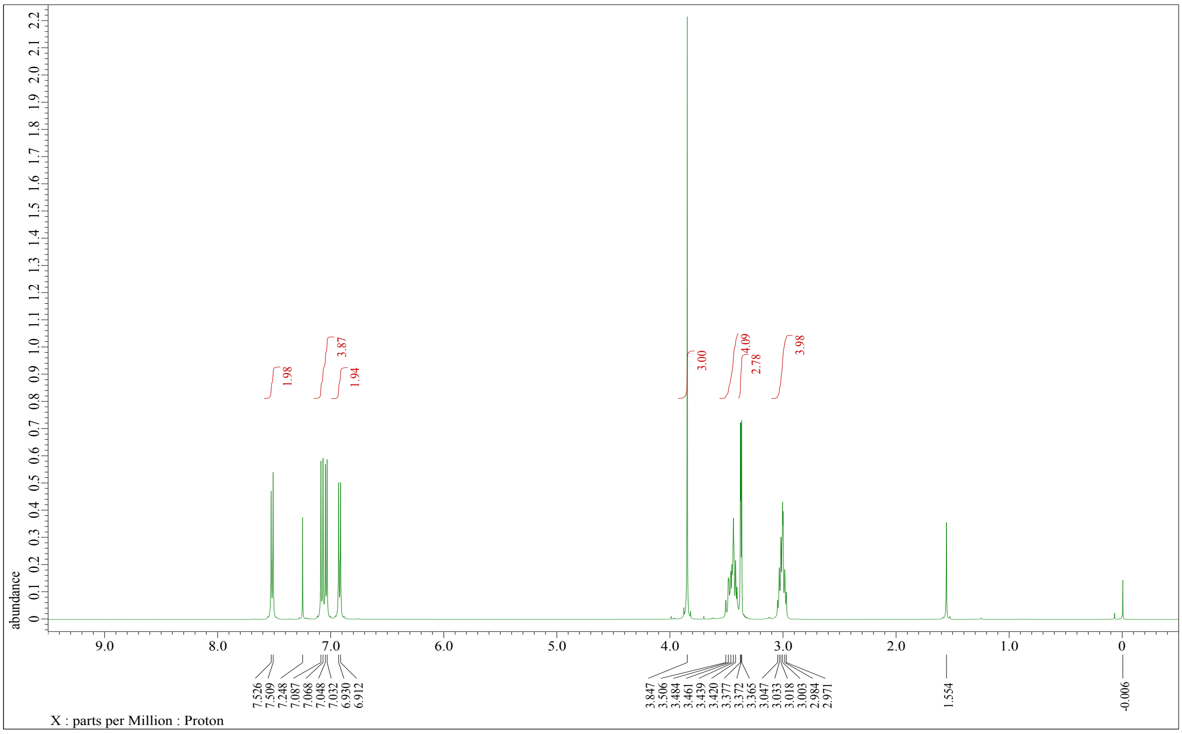
Synthesis of (R_p)-**5**



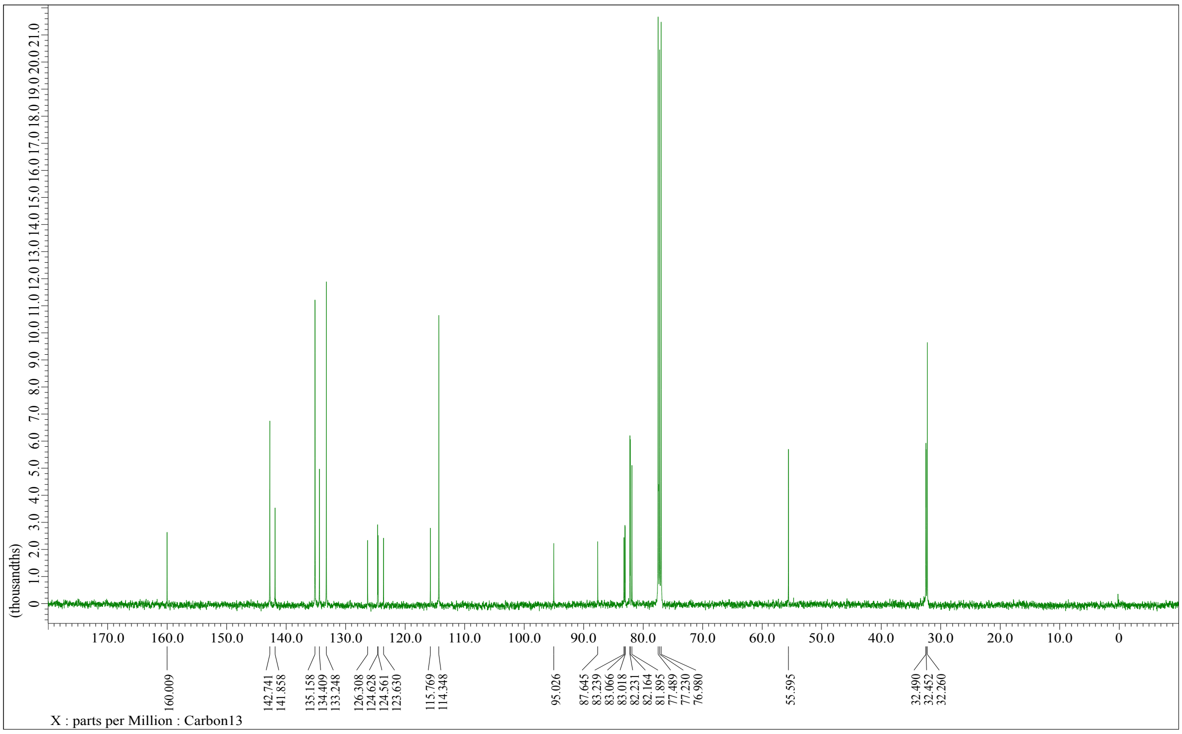
K_2CO_3 (1.03 g, 7.48 mmol) was added to a suspension of (R_p)-**4** (822 mg, ?1.31 mmol) in MeOH (40 mL). After the mixture was stirred for 24 h at room temperature, H_2O and $CHCl_3$ were added to the reaction mixture. The organic layer was extracted with $CHCl_3$ and washed with brine. The combined organic layer was 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 (R_p)-**5** (480 mg, 1.17 mmol, 89%) as a pale yellow solid.

$R_f = 0.35$ ($CHCl_3$/hexane = 1/2 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.0 (m, 4H), 3.36 (s, 1H), 3.372 (s, 1H), 3.378 (s, 1H), 1.94 (d, J = 8.5 Hz, 2H), 7.03 (s, 1H), 7.04 (s, 1H), 7.06 (s, 1H), 7.08 (s, 1H), 7.51 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.2 (two peaks), 32.45, 32.49, 81.8, 82.1, 82.2, 83.01, 83.06, 83.2, 87.6, 95.0, 114.3, 115.7, 123.6, 124.5, 124.6, 126.3, 133.2, 134.4, 135.1, 141.8, 142.7, 160.0 ppm. HRMS (MALDI) calcd. for $C_{31}H_{22}O$ M^+: 410.1671, found 410.1697. $[\alpha]^{25}_D = -69.2$ (c = 0.5, $CHCl_3$).

(S_p)-**5** was obtained in 71% yield by the same procedure of (R_p)-**5**. HRMS (MALDI) calcd. for $C_{31}H_{22}O$ M^+: 410.1671, found 410.1692. $[\alpha]^{25}_D = +68.8$ (c = 0.5, $CHCl_3$).

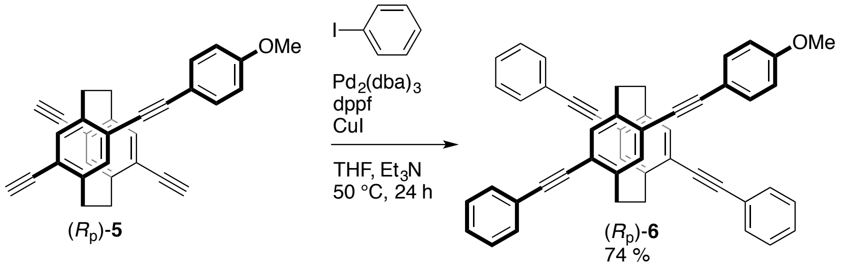


^{1}H NMR spectrum of (R_p)-**5**.



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

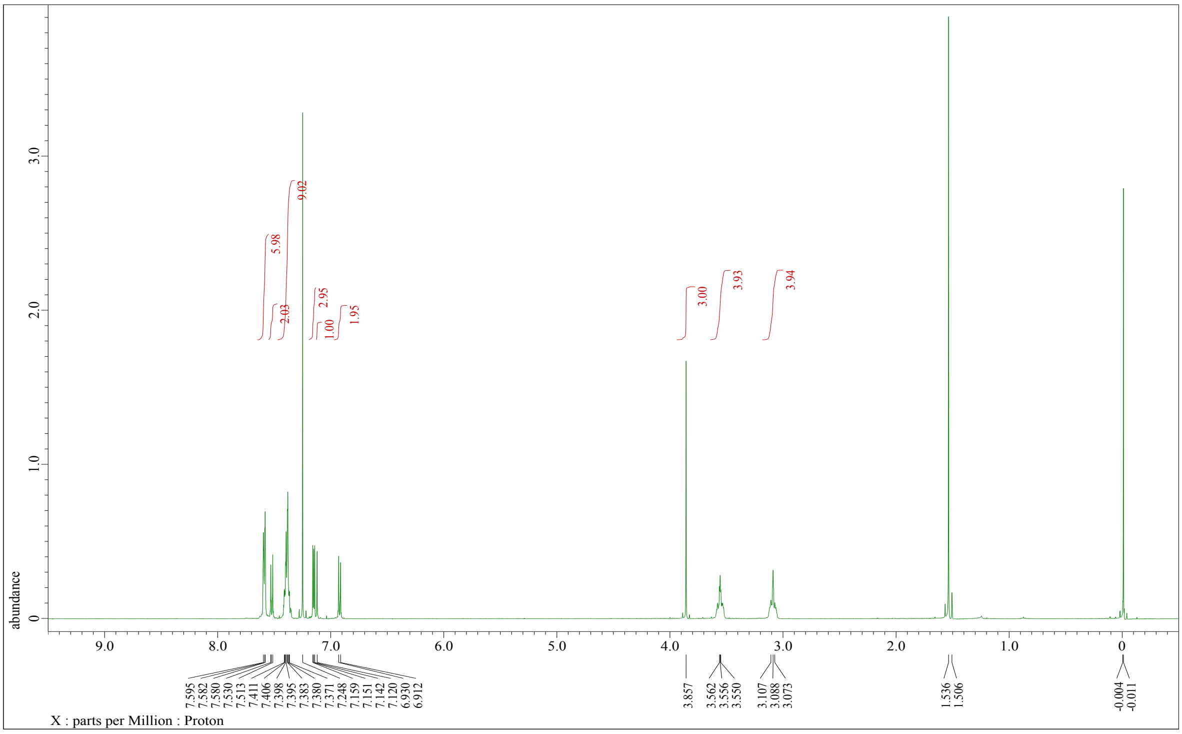
Synthesis of (R_p)-**6**



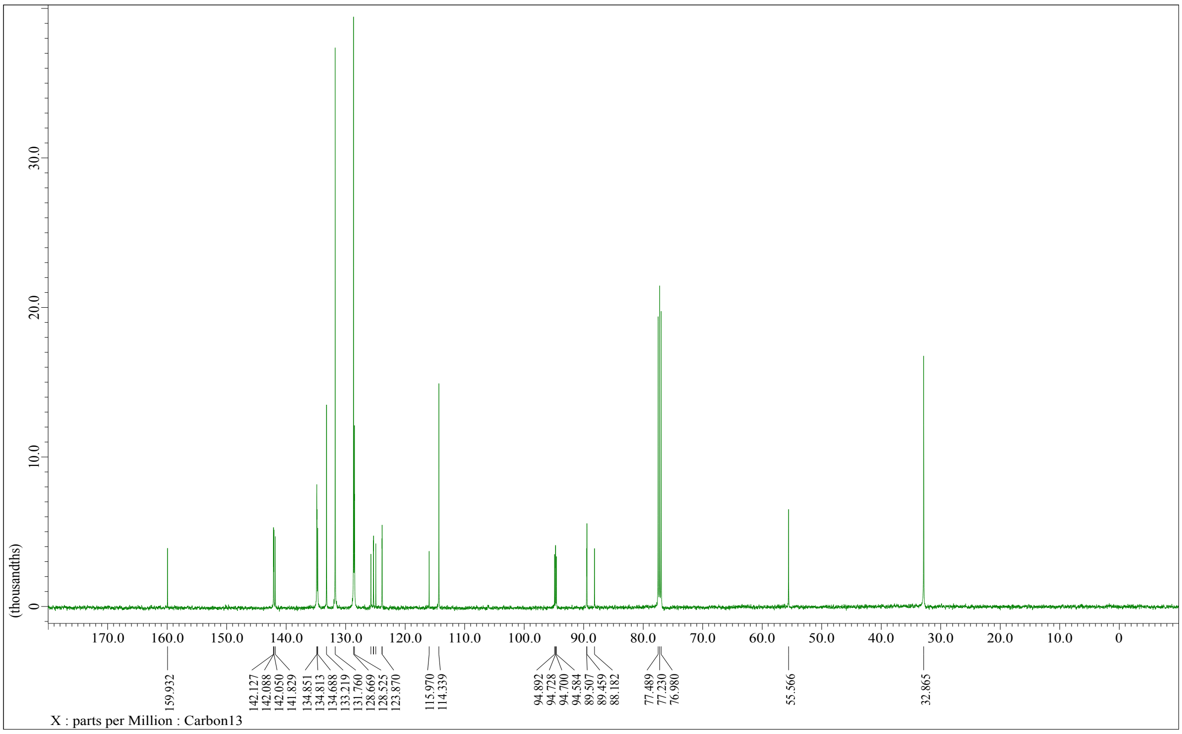
A mixture of (R_p)-**5** (20.1 mg, 0.05 mmol), $Pd_2(dba)_3$ (5.9 mg, 0.006 mmol), dppf (8.0 mg, 0.012 mmol), CuI (4.0 mg, 0.021 mmol), THF (3.0 mL) and Et_3N (3.0 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, iodobenzene (91.5 mg, 0.45 mmol) was added, and the reaction was carried out at 50 °C for 24 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were 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 = 1/1 v/v as an eluent) to afford (R_p)-**6** (23.1 mg, 0.036 mmol, 74%) as a light yellow solid.

R_f = 0.32 ($CHCl_3$/hexane = 3/7 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.09 (m, 4H), 3.55 (m, 4H), 3.85 (s, 3H), 6.92 (d, J = 8.5 Hz, 2H), 7.12 (s, 1H), 7.14 (s, 1H), 7.15 (s, 1H), 7.16 (s, 1H), 7.39 m, 9H), 7.52 (d, J = 8.5 Hz, 2H), 7.59 (m, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.8 (four peaks), 55.5, 88.1, 89.4 (two peaks), 89.5, 94.5, 94.70, 94.72, 94.8, 114.3, 115.9, 123.80, 123.82, 124.87, 125.24, 125.27, 125.6, 128.5, 128.6, 131.7, 133.2, 134.6, 134.81, 134.85, 141.8, 142.05, 142.08, 142.1, 159.9 ppm. HRMS (MALDI) calcd. for $C_{49}H_{34}O$ M^+: 638.2610, found 638.2620. $[\alpha]^{25}_D$ = +84.7 (c = 0.25, $CHCl_3$).

(S_p)-**6** was obtained in 81% yield by the same procedure of (R_p)-**6**. HRMS (MALDI) calcd. for $C_{49}H_{34}O$ M^+: 638.2610, found 638.2621. $[\alpha]^{25}_D$ = –85.3 (c = 0.25, $CHCl_3$).

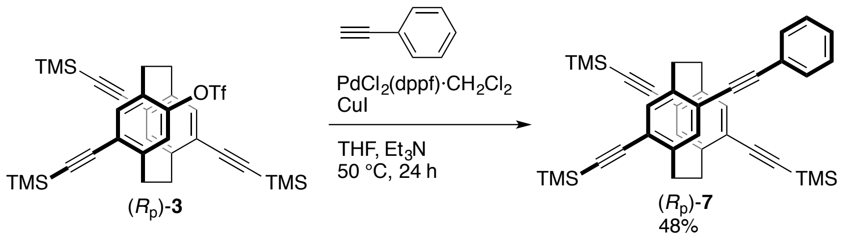


^{1}H NMR spectrum of (R_p)-**6**.



^{13}C NMR spectrum of (R_p)-**6**.

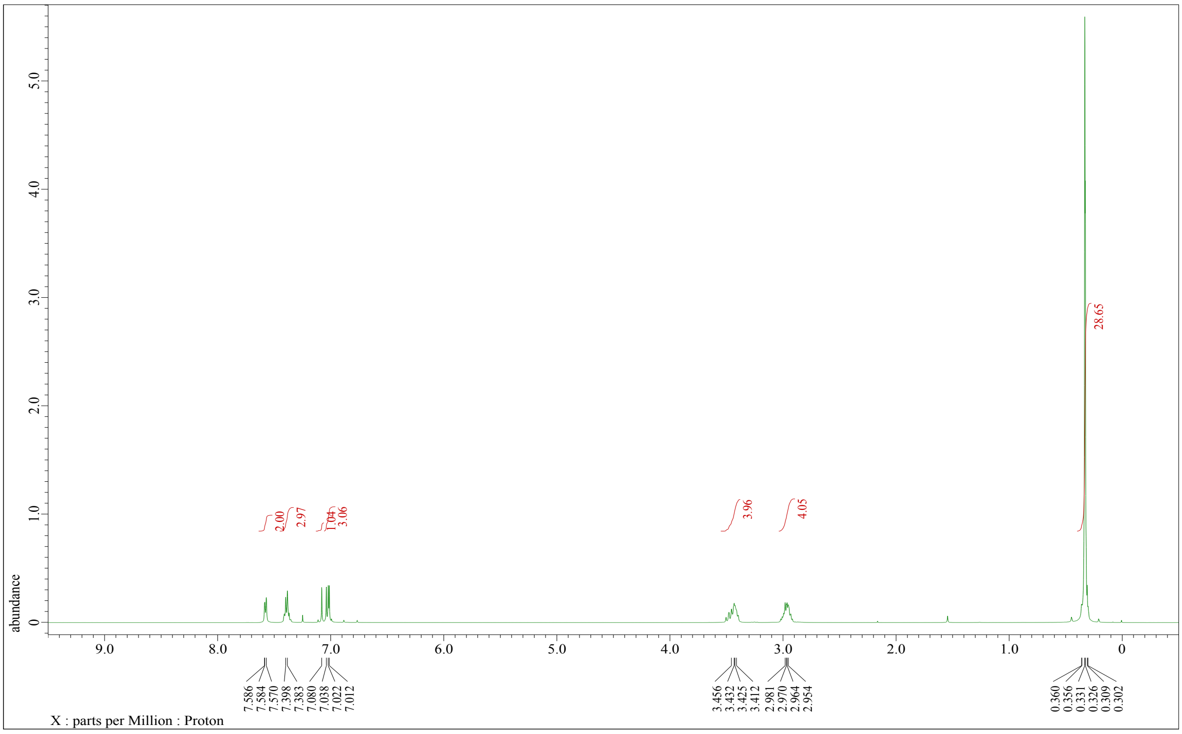
Synthesis of (*R*$_p$)-**7**



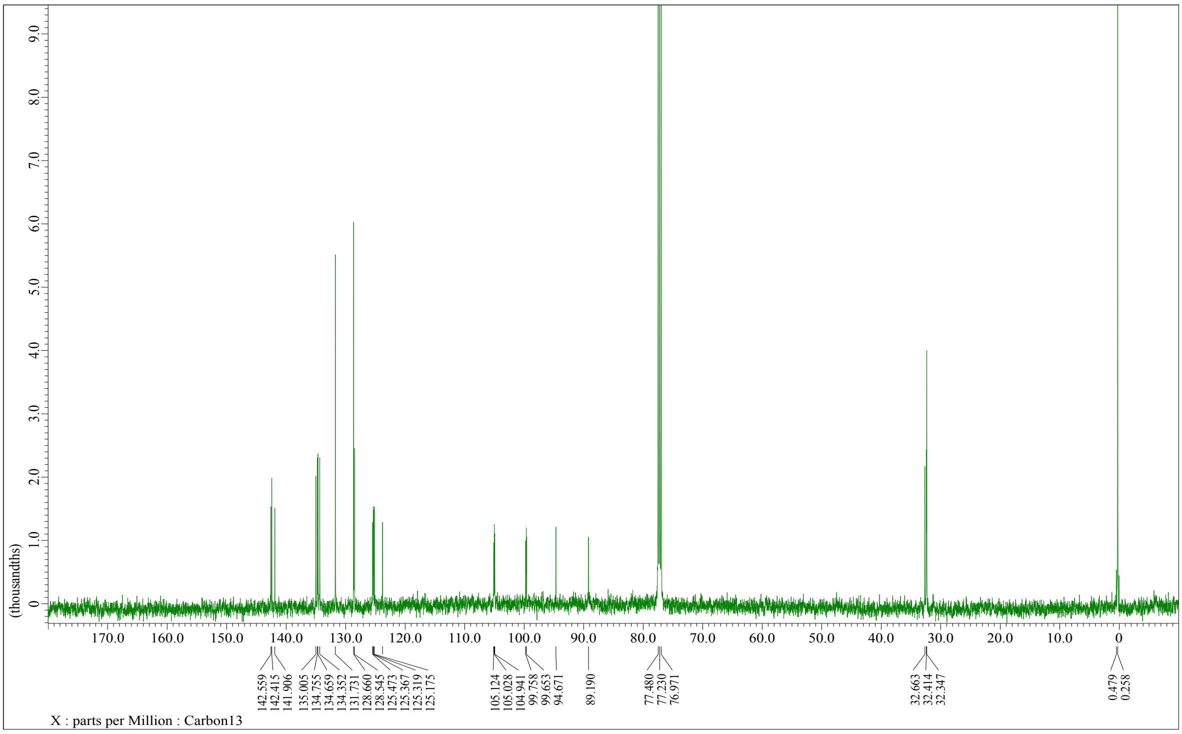
A mixture of (*R*$_p$)-**3** (566.3 mg, 0.88 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (140.0 mg, 0.17 mmol), CuI (40 mg, 0.21 mmol), THF (7.5 mL) and Et_3N (7.5 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, phenylacetylene (484 mg, 4.7 mmol) was added to the mixture. The reaction was carried out at 50 °C for 24 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were 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 = 1/9 v/v as an eluent) to afford (*R*$_p$)-**7** (250.6 mg, 0.42 mmol, 48%) as a light yellow solid.

R_f = 0.51 ($CHCl_3$/hexane = 1/9 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.33 (three singlet peaks, 27H), 2.96 (m, 4H), 3.42 (m, 4H), 7.01 (s, 1H). 7.02 (s, 1H), 7.03 (s, 1H), 7.08 (s, 1H), 7.38 (m, 3 H), 7.57 (d, J = 7.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.3 (two peaks), 32.4, 32.6, 89.1, 94.6, 99.6 (two peaks), 99.7, 104.9, 105.0, 105.1, 123.6, 125.1, 125.31, 125.36, 125.4, 128.5, 128.6, 131.6, 134.3, 134.6, 134.7, 135.0, 141.9, 142.4 (two peaks), 142.5 ppm. HRMS (MALDI) calcd. for $C_{39}H_{44}Si_3$ M^+: 596.2751, found 596.2744. $[\alpha]^{25}_D$ = +58.9 (c = ?0.5, $CHCl_3$).

(*S*$_p$)-**7** was obtained in 66% yield by the same procedure of (*R*$_p$)-**7**. HRMS (MALDI) calcd. for $C_{39}H_{44}Si_3$ M^+: 626.2856, found 596.2769. $[\alpha]^{25}_D$ = –58.7 (c = 0.5, $CHCl_3$).

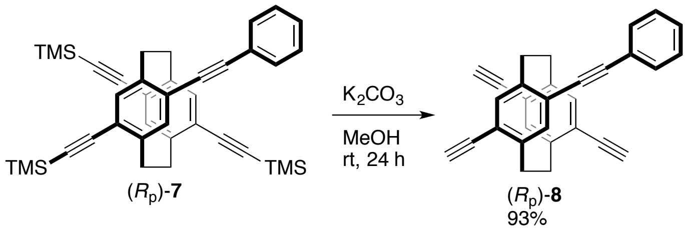


^{1}H NMR spectrum of (R_p)-**7**.



^{13}C NMR spectrum of (R_p)-**7**.

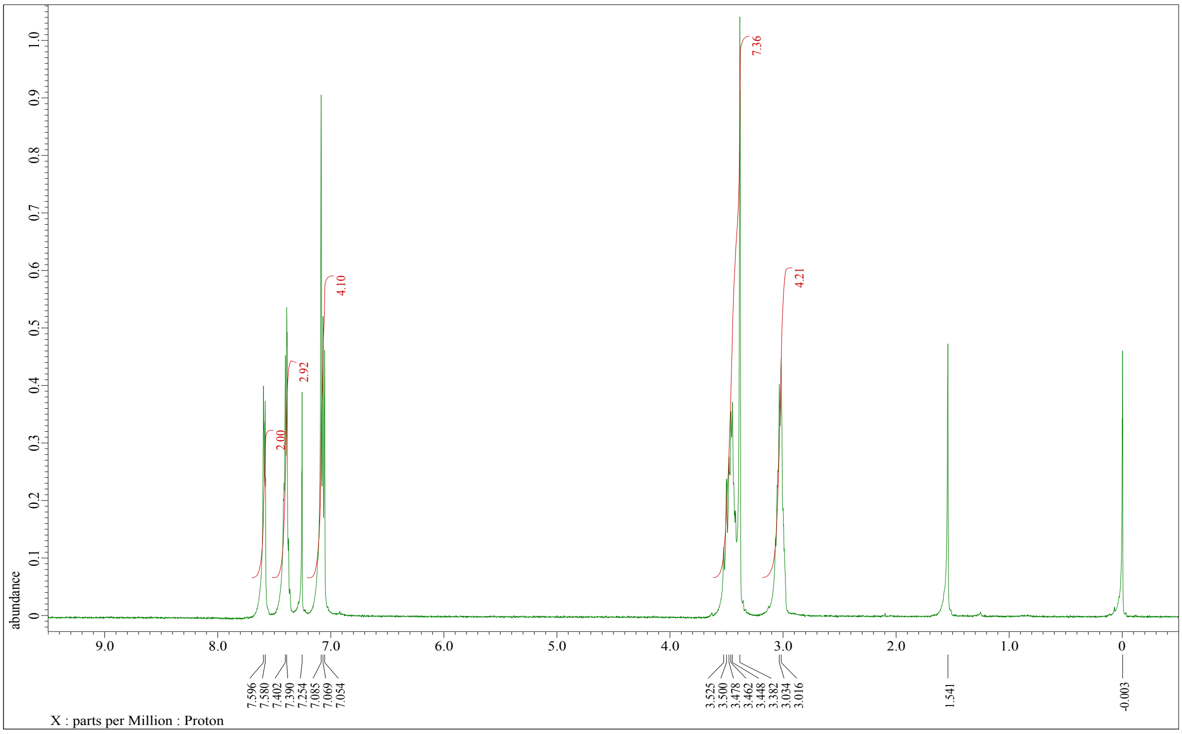
Synthesis of (*R*p)-**8**



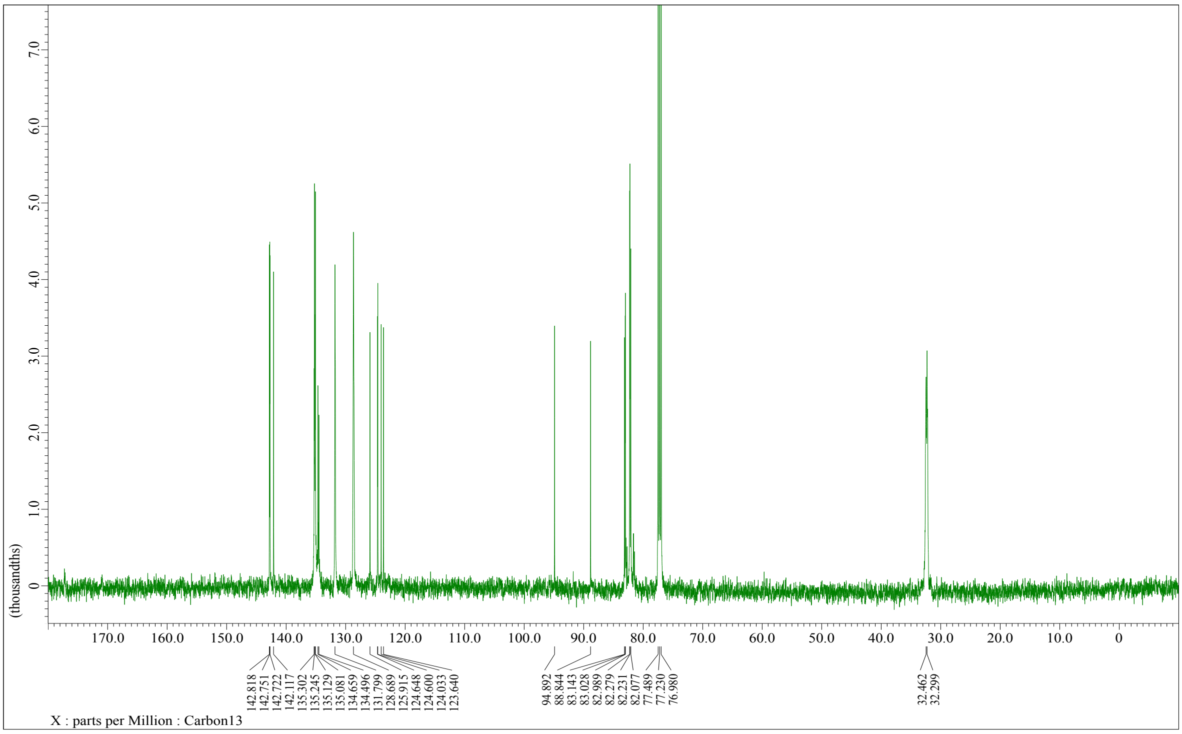
K_2CO_3 (281.2 mg, 2.03 mmol) was added to a suspension of (*R*p)-**7** (187.3 mg, 0.31 mmol) in MeOH (10 mL). After the mixture was stirred for 24 h at room temperature, H_2O and $CHCl_3$ were added to the reaction mixture. The organic layer was extracted with $CHCl_3$ and washed with brine. The combined organic layer was 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 = 1/4 v/v as an eluent) to afford (*R*p)-**8** (111.0 mg, 0.29 mmol, 93%) as a pale yellow solid.

R_f = 0.38 ($CHCl_3$/hexane = 1/4 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.02 (m, 4H), 3.38 (three singlet peaks, 3H), 3.48 (m, 4H), 7.07 (m, 4H), 7.40 (m, 3H), 7.59 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.3-32.5 (four peaks), 82.0, 82.23, 82.27, 82.9, 83.0, 83.1, 88.8, 94.8, 123.6, 124.0, 124.6, 125.9, 128.6, 131.7, 134.4, 134.6, 135.0, 135.1, 135.2, 135.3, 142.1, 142.72, 142.75, 142.8 ppm. HRMS (MALDI) calcd. for $C_{30}H_{20}$ M^+: 380.1565, found 380.1553. $[\alpha]^{25}_D$ = –76.0 (c = ?0.25, $CHCl_3$).

(*S*p)-**8** was obtained in 75% yield by the same procedure of (*R*p)-**8**. HRMS (MALDI) calcd. for $C_{31}H_{22}O$ M^+: 380.1565, found 380.1546. $[\alpha]^{25}_D$ = +76.0 (c = 0.25, $CHCl_3$).

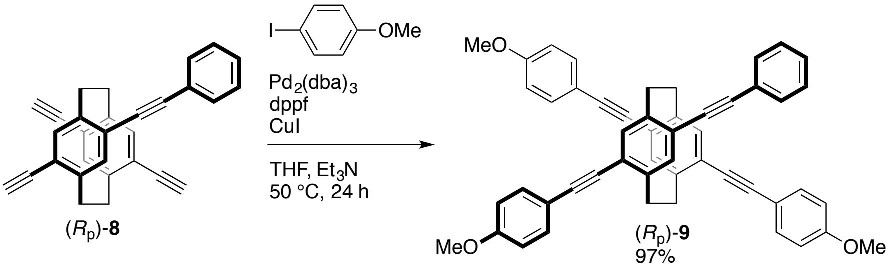


^{1}H NMR spectrum of (R_p)-**8**.



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

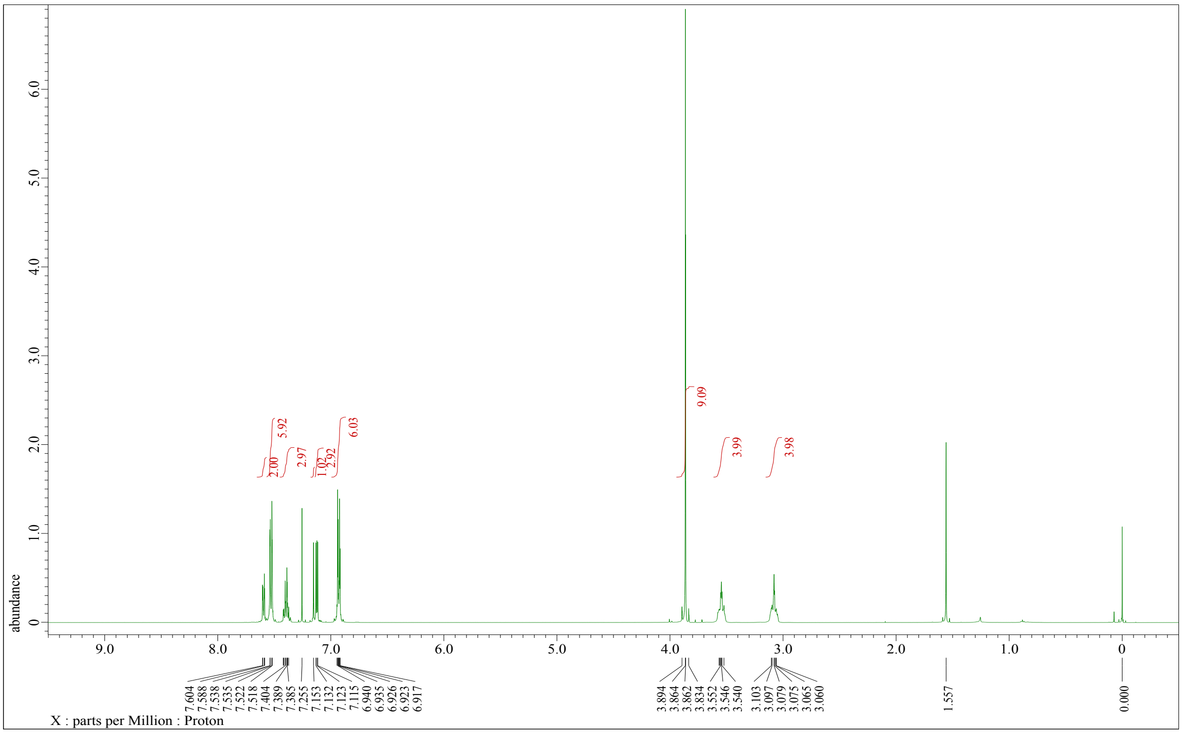
Synthesis of (R_p)-**9**



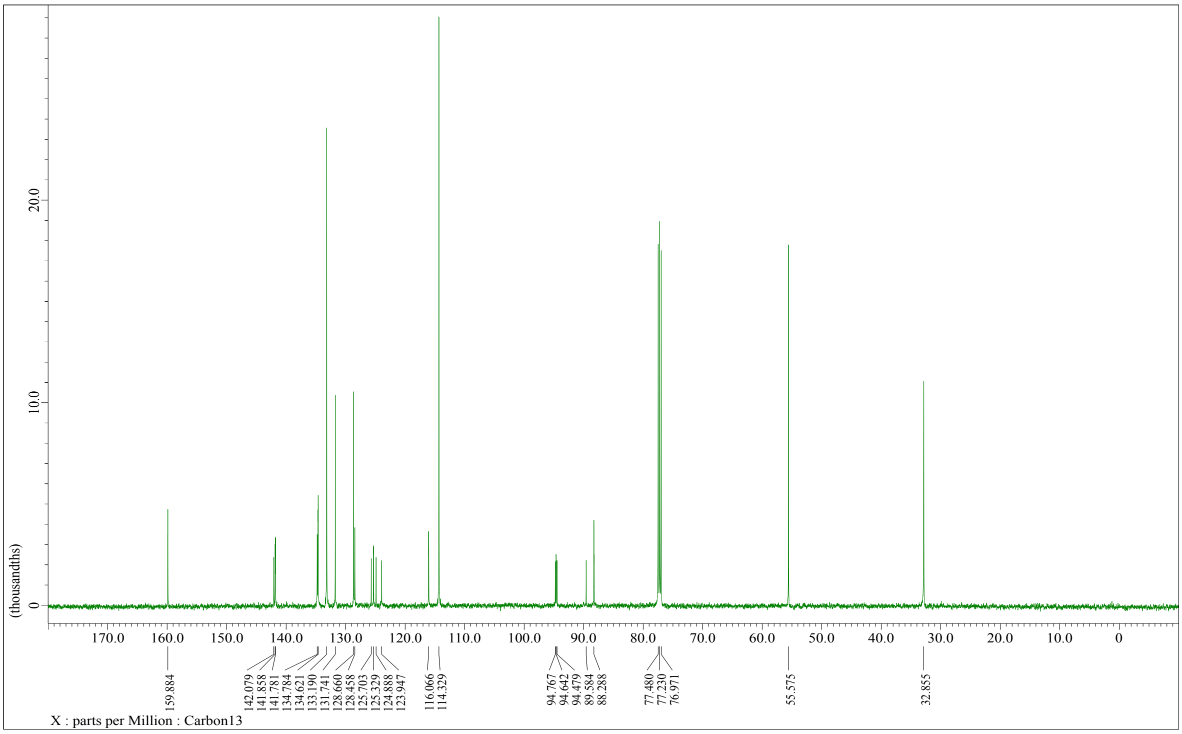
A mixture of (R_p)-**8** (111.0 mg, 0.29 mmol), *p*-iodoanisole (212.3 mg, 0.91 mmol), $Pd_2(dba)_3$ (27.5 mg, 0.03 mmol), dppf (35.1 mg, 0.06 mmol), CuI (20.0 mg, 0.11 mmol), THF (10 mL) and Et_3N (10 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, the reaction was carried out at 50 °C for 24 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were 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 = 4/1 v/v as an eluent) to afford (R_p)-**9** (197.6 mg, ?0.28 mmol, 97%) as a light yellow solid.

R_f = 0.45 ($CHCl_3$/hexane = 1/1 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.07 (m, 4H), 3.54 (m, 4H), 3.86 (three singlet peaks, 3H), 6.92 (m, 6H), 7.11 (s, 1H), 7.12 (s, 1H), 7.13 (s, 1H), 7.15 (s, 1H), 7.39 (m, 3H), 7.53 (m, 5H), 7.58 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.8 (four peaks), 55.5 (three peaks), 88.2 (three peaks), 89.5, 94.4, 94.6 (two peaks), 94.7, 114.3, 116.0, 123.9, 124.8, 125.3, 125.7, 128.4, 128.6, 131.7, 133.1, 134.6, 134.7, 141.7, 141.8, 142.0, 159.8 ppm. HRMS (MALDI) calcd. for $C_{51}H_{38}O_3$ M$^+$: 698.2821, found 698.2919. $[\alpha]^{25}_D$ = +77.0 (c = 0.25, $CHCl_3$).

(S_p)-**9** was obtained in 95% yield by the same procedure of (R_p)-**9**. HRMS (MALDI) calcd. for $C_{40}H_{46}OSi_3$ M$^+$: 698.2821, found 698.2824. $[\alpha]^{25}_D$ = –77.2 (c = 0.25, $CHCl_3$).

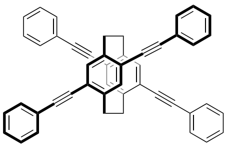
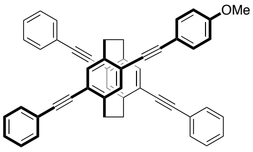
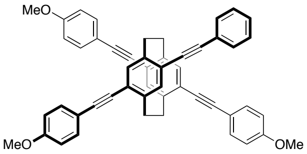
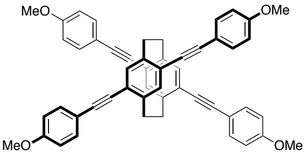


^{1}H NMR spectrum of (R_p)-**9**.



^{13}C NMR spectrum of (R_p)-**9**.

Table S1. Optical properties of X-shaped compounds

	UV-vis [a] λ_{max} /nm (ε /10^5 cm^{-1}M^{-1})	PL [b] λ_{max} /nm	τ[c] /ns	Φ_{lum}[d]	CPL[e] $\lvert g_{lum}\rvert$ /10^{-3}
[f] 	349 (0.63)	412	3.67	0.60	1.1
This work: compound **6** 	352 (0.60)	420	3.57	0.71	1.5
This work: compound **9** 	357 (0.56)	424	3.00	0.73	1.7
[g] 	361 (0.68)	427	2.21	0.75	1.7

[a] In $CHCl_3$ (1.0×10^{-5} M).

[b] In $CHCl_3$ (1.0×10^{-5} M), excited around absorption maxima.

[c] Emission lifetime around PL λ_{max}. All PL decay curves could be fitted to a single-exponential equation.

[d] Absolute PL quantum efficiency.

[e] Absolute g_{lum} value between enantiomers. $g_{lum} = 2(I_{left} - I_{right})/(I_{left} + I_{right})$, where I_{left} and I_{right} indicate luminescence intensities of left- and right-handed CPL, respectively.

[f] Gon, M.; Morisaki, Y.; Chujo Y. *Eur. J. Org. Chem.* **2015**, *(35)*, 7756-7762.

[g] Gon, M.; Morisaki, Y.; Sawada, R.; Chujo Y. *Chem.–Eur. J.* **2016**, *22(7)*, 2291-2298. The enantiomers were prepared, and data were collected again for this work.