Electronic Supplementary Information

Optically Active Cyclic Compounds Based on Planar Chiral [2.2]Paracyclophane: Extension of the Conjugated Systems and Chiroptical Properties

Masayuki Gon, Yasuhiro Morisaki* and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Katsura, Kyoto 615-8510, Japan.

E-mail: ymo@chujo.synchem.kyoto-u.ac.jp or chujo@chujo.synchem.kyoto-u.ac.jp

Contents:

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 $CDCl_3$, 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. High-resolution mass (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI), a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI), and a Thermo Fisher Scientific orbitrapXL spectrometer for matrix assisted laser desorption/ionization (MALDI) using 1,8-dihydroxy-9,10-dihydroanthracen-9-one (DIT) 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) using $CHCl_3$ as an eluent. UV-vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Photoluminescence (PL) spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and samples were analyzed in $CHCl_3$ at room temperature. The PL lifetime measurement was performed on a Horiba FluoreCube spectrofluorometer system; excitation was carried out using a UV diode laser (NanoLED 375 nm). Specific rotations ($[\alpha]^{t}_{D}$) were measured with a HORIBA SEPA-500 polarimeter. 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 Organic Elemental Analysis Research Center, Kyoto University.

Materials

Commercially available compounds used without purification:

4-*tert*-Butylphenylacetylene (**1**)

$PdCl_2(PPh_3)_2$

PPh_3

1,1'-Bis(diphenylphosphino)ferrocene (dppf)

CuI

Trimethylsilylacetylene (TMS-acetylene)

$NaNO_2$

98% H_2SO_4

KI

$Pd_2(dba)_3$ (dba = dibenzylideneacetone)

Di(1-adamantyl)-*n*-butylphosphine (cataCXium® A)

Tetra-*n*-butylammonium fluoride (1 M in THF)

p-Bromoiodobenzene

K_2CO_3

Commercially available solvents:

CH_3CN and MeOH, used without purification

H_2O was purified by demineralizer

THF and Et_3N, purified by passage through solvent purification columns under Ar pressure.[1]

Compounds prepared as described in the literatures:

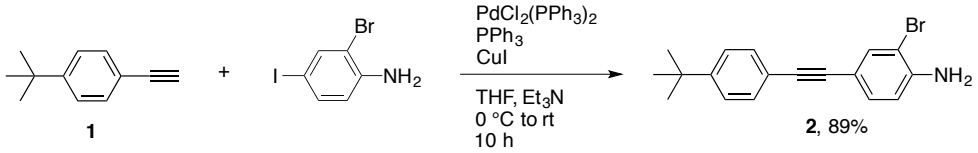
2-Bromo-4-iodoaniline[2]

3,5-Di-*tert*-butylphenylacetylene (**5**)[3]

(R_p)- and (S_p)-4,7,12,15-Tetraethynyl[2.2]paracyclophane ((R_p)- and (S_p)-**12**)[4]

Synthetic Procedures and Characterization

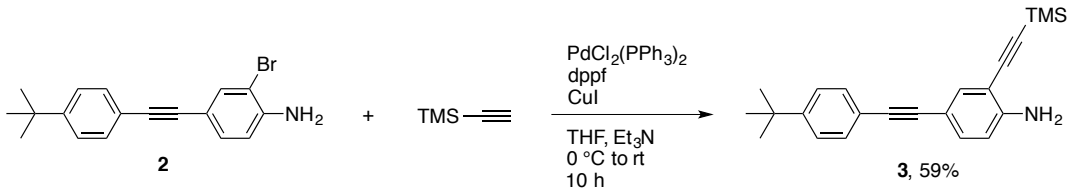
Synthesis of 2



1 **2**, 89%

A mixture of 2-bromo-4-iodoaniline (4.16 g, 14.0 mmol), $PdCl_2(PPh_3)_2$ (0.490 g, 0.70 mmol), PPh_3 (0.366 g, 1.40 mmol), CuI (0.133 g, 0.70 mmol), THF (80 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, the mixture was cooled to 0 °C. 4-*t*-Butylphenylacetylene (**1**) (2.61 mL, 14.7 mmol) was added to the mixture via syringe. The reaction was carried out at room temperature for 10 h with stirring. Precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 (EtOAc/hexane = 1/6 v/v as an eluent) to afford **2** (4.06 g, 12.4 mmol, 89%) as a pale brown crystal (R_f = 0.34 (EtOAc/hexane = 1/6 v/v)). Compound **2** was used for the next reaction without further purification.

Synthesis of 3



2 **3**, 59%

A mixture of **2** (2.29 g, 7.0 mmol), $PdCl_2(PPh_3)_2$ (0.245 g, 0.35 mmol), dppf (0.194 g, 0.35 mmol), CuI (0.067 g, 0.35 mmol), THF (45 mL) and Et_3N (15 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, TMS-acethylene (1.97 mL, 14.0 mmol) was added to the mixture via syringe. The reaction was carried out at 60 °C for 10 h with stirring. After the reaction mixture was cooled to room

temperature, precipitates were removed by filtration. The solvent was removed with a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 (EtOAc/hexane = 1/6 v/v as an eluent). Further purification was carried out by recrystallization with hexane to afford **3** (1.42 g, 4.11 mmol, 59%) as a light brown crystal.

R_f = 0.43 (EtOAc/hexane = 1/6 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.26 (s, 9H), 1.32 (s, 9H), 4.38, (s, 2H), 6.64 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 1.9 Hz, 1H) 7.34 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 1.9 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.1, 31.2, 34.7, 87.5, 88.6, 100.3, 100.8, 107.8, 112.4, 114.0, 120.7, 125.3, 131.1, 133.2, 135.6, 148.0, 151.0 ppm. HRMS (ESI) calcd. for $C_{23}H_{28}NSi$ $[M+H]^+$: 346.1986, found 346.1977. Elemental analysis calcd. for $C_{23}H_{27}NSi$: C 79.94 H 7.88 N 4.05, found: C 79.86 H 7.94 N 4.03.

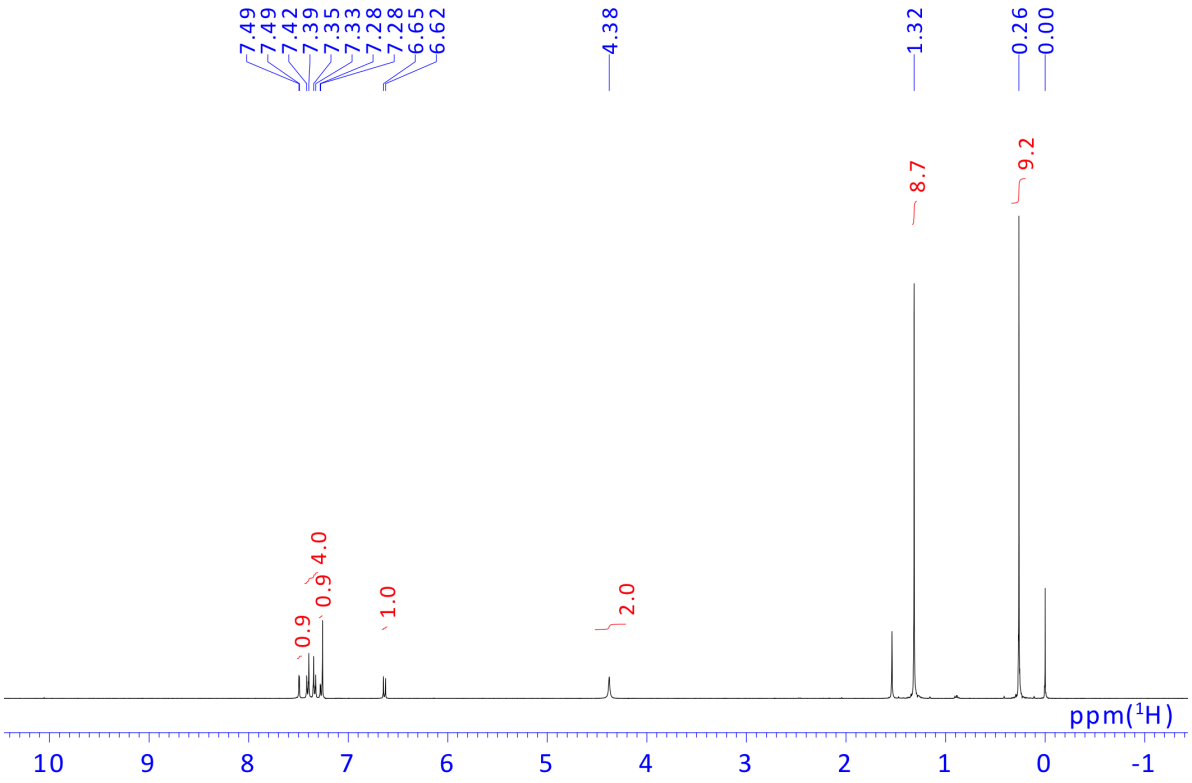


Figure S1. ^{1}H NMR spectrum of **3**.

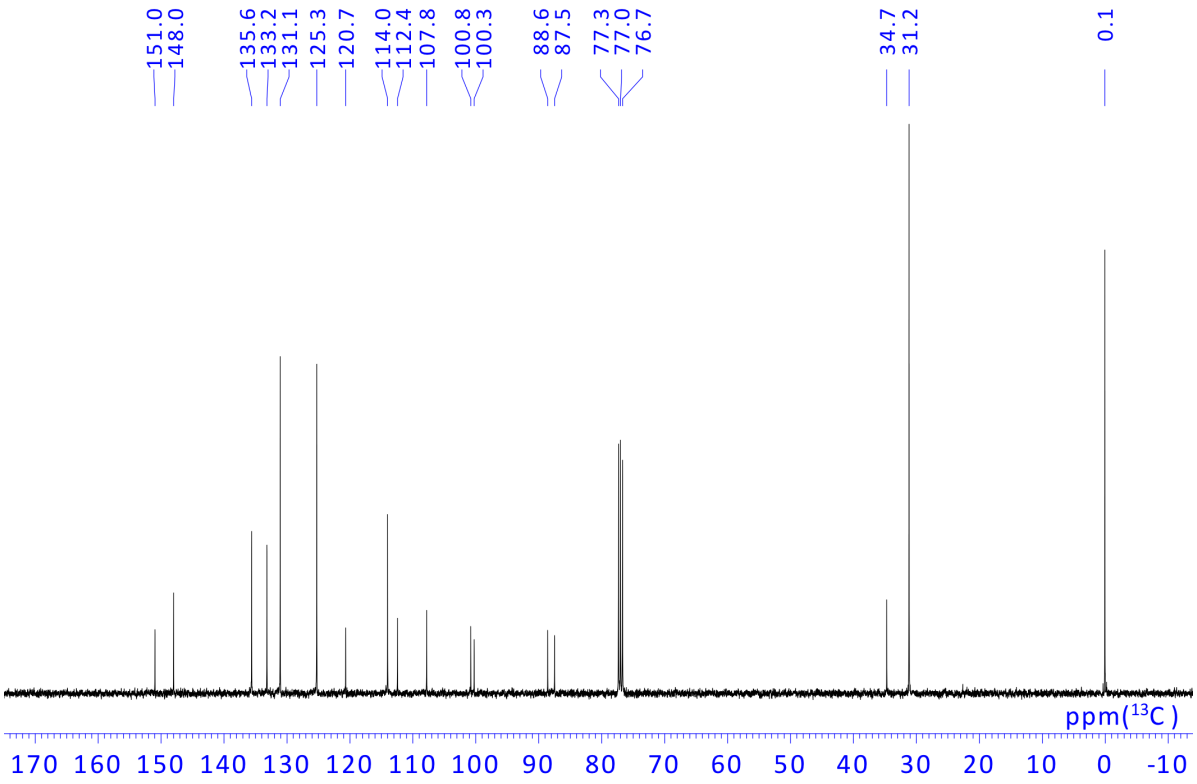
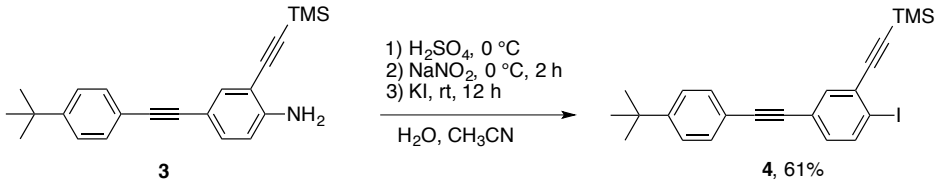


Figure S2. ^{13}C NMR spectrum of **3**.

Synthesis of 4



3 **4**, 61%

A mixture of **3** (0.628 g, 1.82 mmol), CH_3CN (100 mL), H_2O (30 mL) and concentrated H_2SO_4 (8.0 mL) was placed in a round-bottom flask at 0 °C, equipped with a magnetic stirring bar. To the reaction mixture, $NaNO_2$ (0.163 g, 2.36 mmol) in H_2O (4 mL) was slowly added at 0 °C. After stirring for 2 h, the mixture was added into a solution of KI (1.87 g, 11.3 mmol) in CH_3CN (50 mL) and H_2O (50 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h. The mixture was quenched by the addition of aqueous $NaHSO_3$ solution, and the organic layer was extracted three times with CH_2Cl_2. 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 (hexane as an eluent). Further purification was carried out by recrystallization with $CHCl_3$ and MeOH (good and poor solvent, respectively) to afford **4** (0.734 g, 1.62 mmol, 61%) as a colorless crystal.

R_f = 0.23 (hexane). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.29 (s, 9H), 1.30 (s, 9H), 7.08, (dd, J = 8.2 Hz, J = 2.1 Hz, 1H), 7.34 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 2.1 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ –0.1, 31.2, 34.8, 87.1, 91.4, 99.4, 100.5, 105.8, 119.6, 123.5, 125.3, 129.9, 131.3, 132.0, 135.3, 138.6, 151.8 ppm. HRMS (APCI) calcd. for $C_{23}H_{26}ISi$ $[M+H]^+$: 457.0843, found 457.0840. Elemental analysis calcd. for $C_{23}H_{25}ISi$: C 60.52 H 5.52 I 27.80, found: C 60.49 H 5.57 I 27.79.

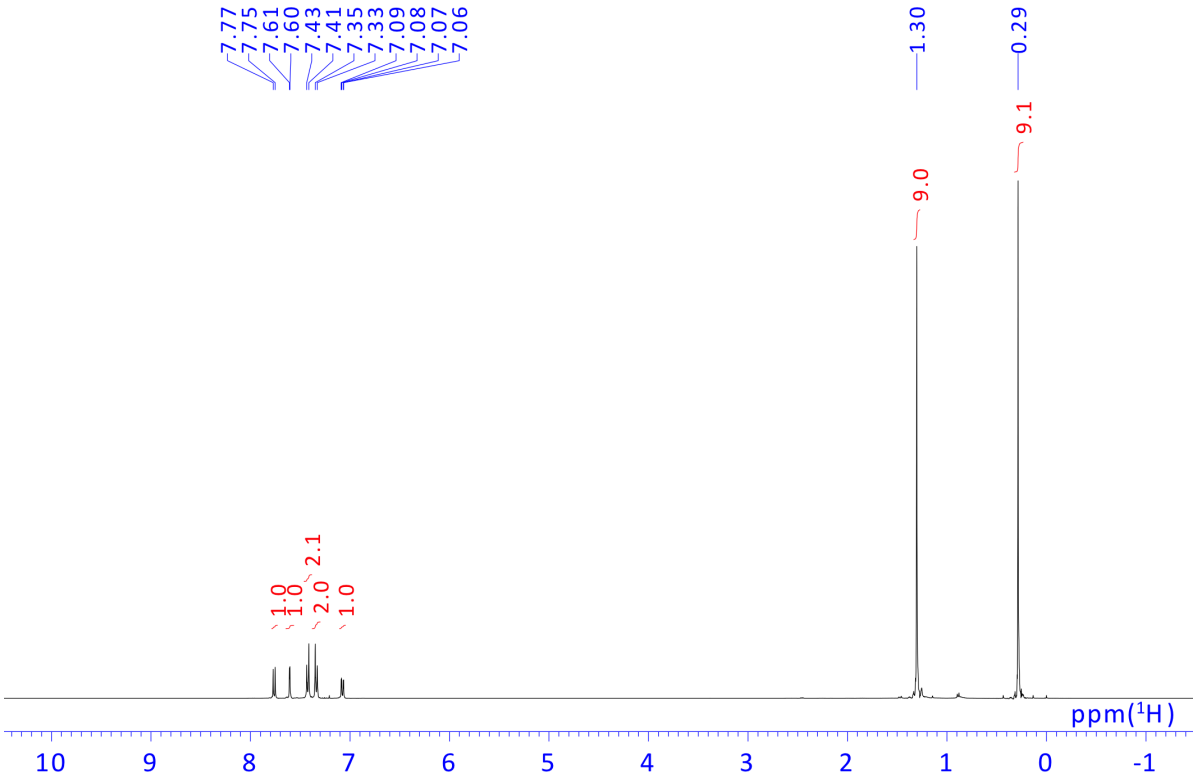


Figure S3. ^{1}H NMR spectrum of **4**.

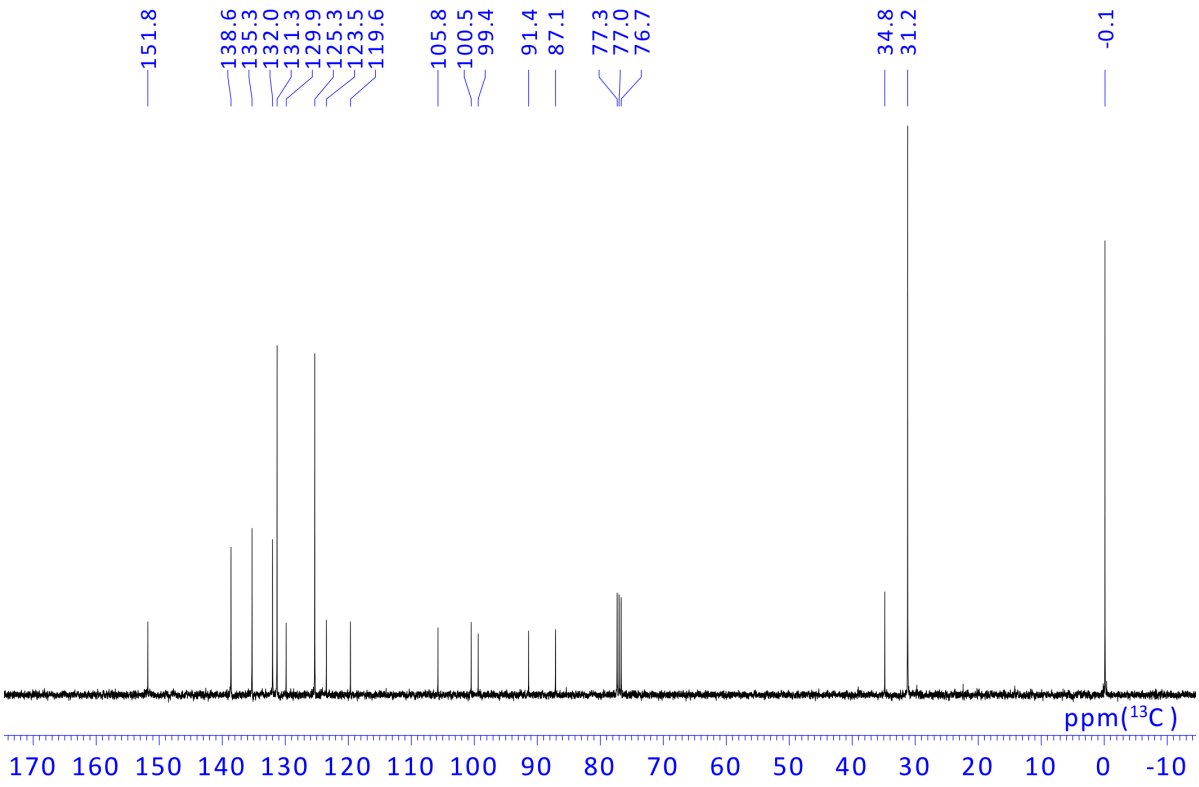
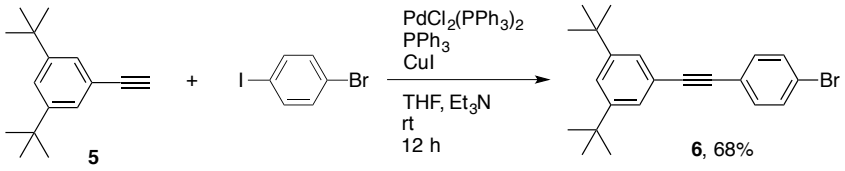


Figure S4. ^{13}C NMR spectrum of **4**.

Synthesis of 6



A mixture of **5** (3.79 g, 17.7 mmol), *p*-bromoiodobenzene (5.26 g, 18.6 mmol), $PdCl_2(PPh_3)_2$ (0.621 g, 0.885 mmol), PPh_3 (0.464 g, 1.77 mmol), CuI (0.169 mg, 0.885 mmol), THF (75 mL) and Et_3N (25 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 room temperature for 12 h with stirring. After the reaction, precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 (hexane as an eluent). Further purification was carried out by recrystallization with $CHCl_3$ and MeOH (good and poor solvent, respectively) to afford **6** (4.45 g, 12.0 mmol, 68%) as a colorless block crystal.

R_f = 0.39 (hexane). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (s, 18H), 7.37-7.41 (m, 5H), 7.47 (d, J = 8.8 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.3, 34.8, 87.0, 91.7, 121.9, 122.2, 122.5, 123.0, 125.8, 131.6, 133.0, 150.9 ppm. HRMS (APCI) calcd. for $C_{22}H_{26}Br$ $[M+H]^+$: 369.1212, found 369.1206. Elemental analysis calcd. for $C_{22}H_{25}Br$: C 71.54 H 6.82, found: C 71.48 H 6.81.

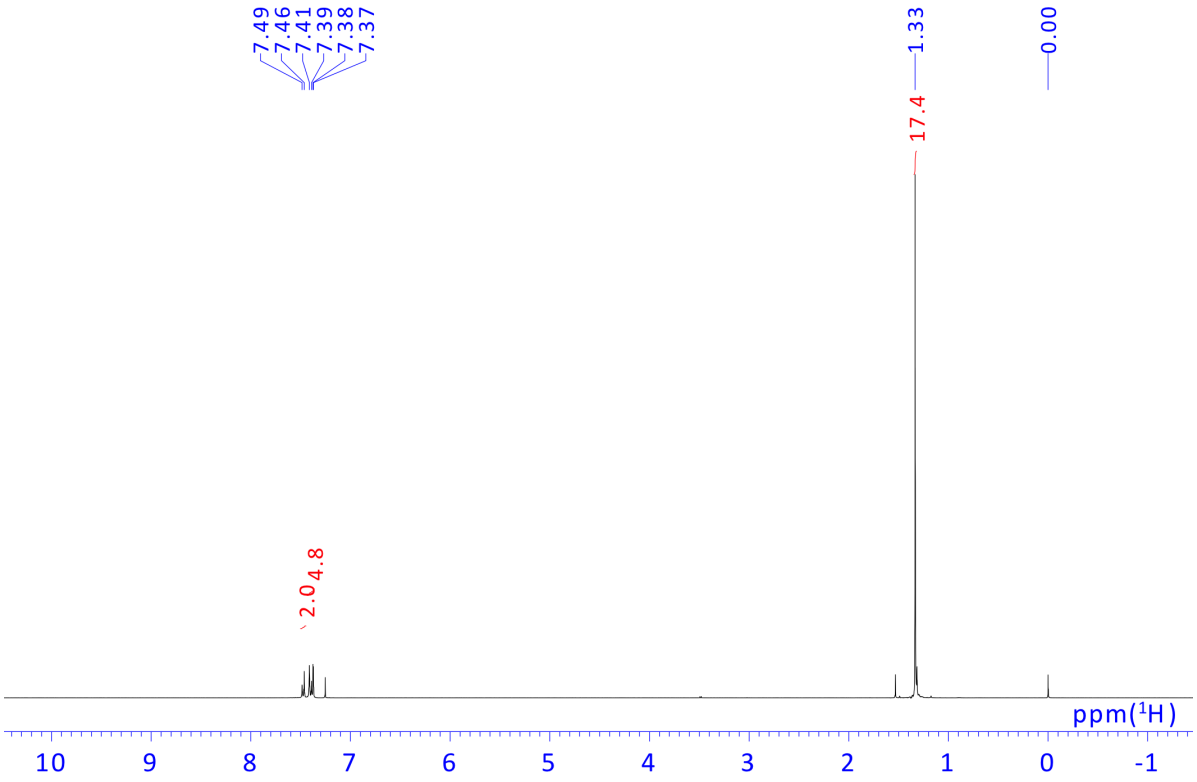


Figure S5. ^{1}H NMR spectrum of **6**.

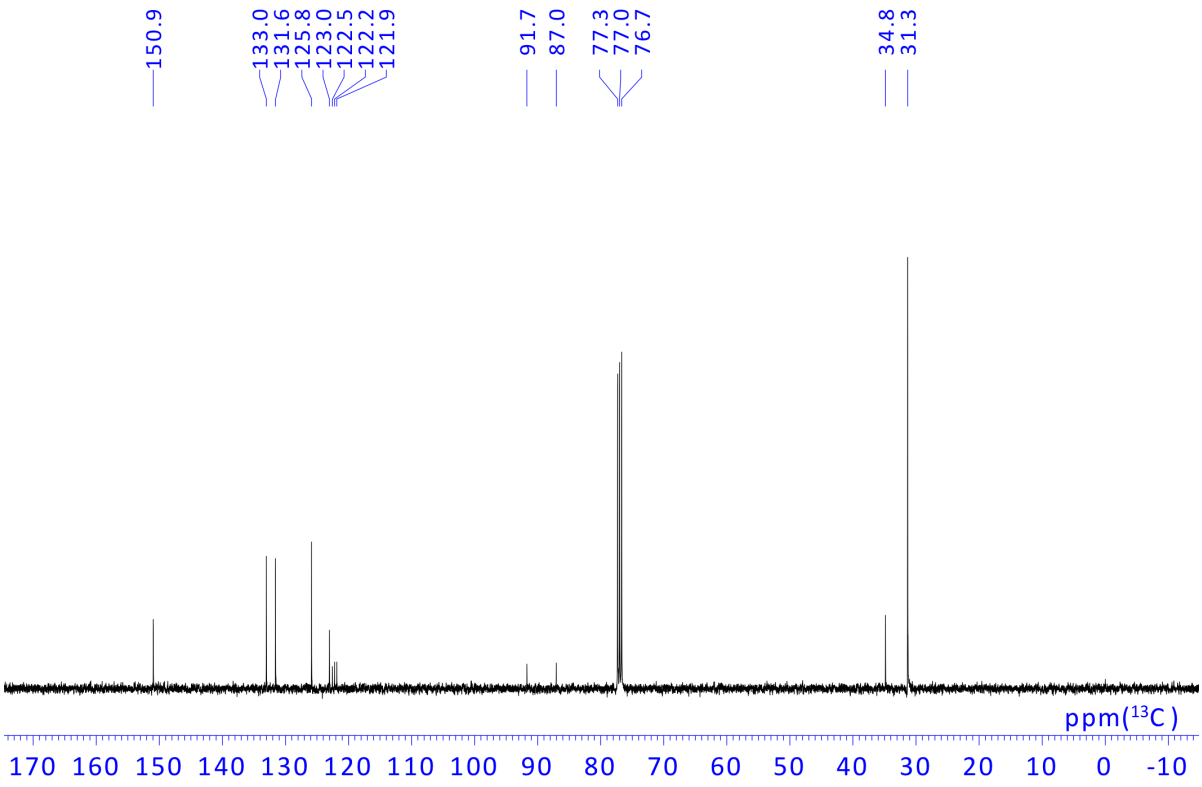
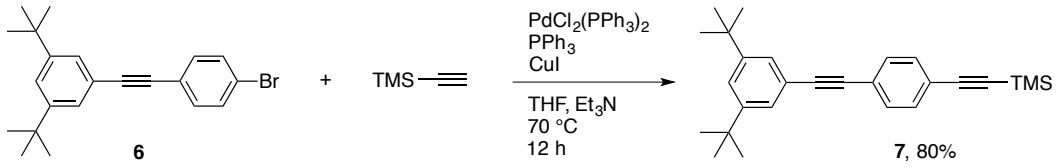


Figure S6. ^{13}C NMR spectrum of **6**.

Synthesis of 7



6 **7**, 80%

A mixture of **6** (4.21 g, 11.4 mmol), $PdCl_2(PPh_3)_2$ (0.400 g, 0.57 mmol), PPh_3 (0.299 g, 1.14 mmol), CuI (0.109 g, 0.57 mmol), THF (40 mL) and Et_3N (40 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, TMS-acethylene (2.42 mL, 17.1 mmol) was added to the mixture via syringe. The reaction was carried out at 70 °C for 12 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration. The solvent was removed with a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/9 v/v as an eluent). Further purification was carried out by recrystallization with $CHCl_3$ and MeOH (good and poor solvent, respectively) to afford **7** (3.54 g, 9.15 mmol, 80%) as a light yellow needle crystal.

R_f = 0.50 ($CHCl_3$/hexane = 1/9 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.25 (s, 9H), 1.33 (s, 18H), 7.38-7.48 (m, 7H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ –0.1, 31.3, 34.8, 87.8, 92.5, 96.1, 104.7, 121.9, 122.7, 123.0, 123.6, 125.9, 131.4, 131.9, 150.9 ppm. HRMS (APCI) calcd. for $C_{27}H_{35}Si$ $[M+H]^+$: 387.2503, found 387.2491. Elemental analysis calcd. for $C_{27}H_{34}Si$: C 83.87 H 8.86, found: C 83.71 H 8.79.

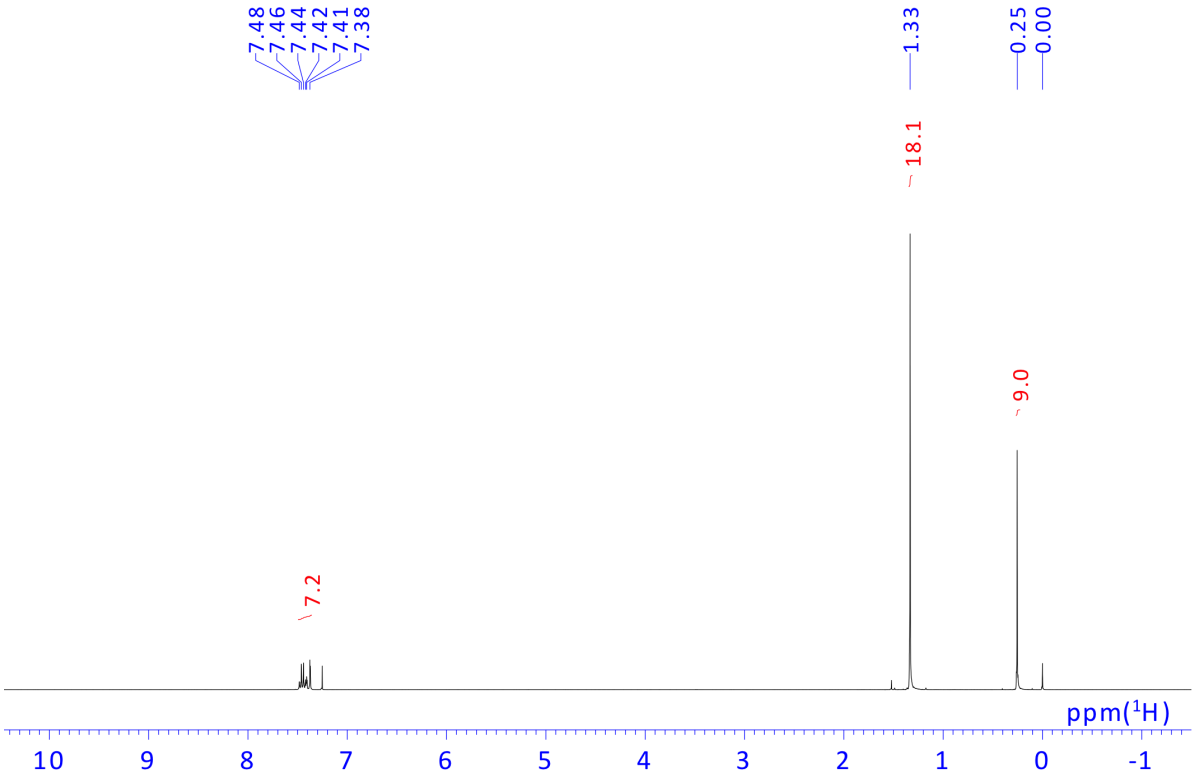


Figure S7. ^{1}H NMR spectrum of **7**.

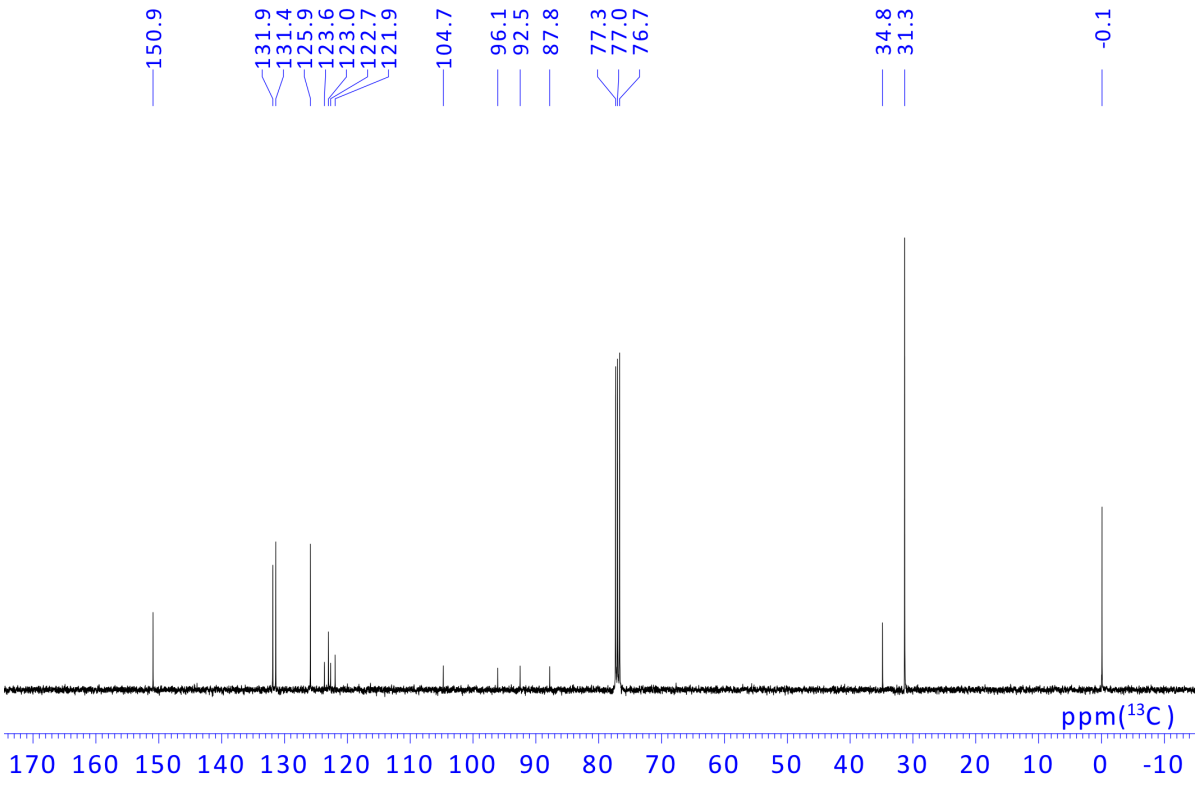
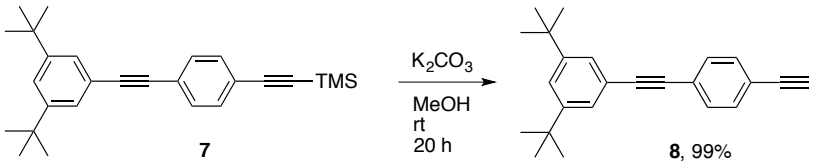


Figure S8. ^{13}C NMR spectrum of **7**.

Synthesis of 8



K_2CO_3 (1.80 g, 13.1 mmol) was added to a suspension of **7** (3.36 g, 8.70 mmol) in MeOH (100 mL). After the mixture was stirred for 20 h at room temperature, H_2O was 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 crude residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/9 v/v as an eluent) to afford **8** (2.71 g, 8.62 mmol, 99%) as a colorless crystal.

R_f = 0.48 ($CHCl_3$/hexane = 1/9 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.25 (s, 9H), 1.33 (s, 18H), 7.38 (d, J = 2.0 Hz, 2H), 7.41 (t, J = 1.8 Hz, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.4, 34.9, 78.7, 83.4, 87.6, 92.6, 121.6, 121.8, 123.0, 124.0, 125.8, 131.4, 132.0, 150.9 ppm. HRMS (APCI) calcd. for $C_{24}H_{27}$ $[M+H]^+$: 315.2107, found 315.2102. Elemental analysis calcd. for $C_{24}H_{26}$: C 91.67 H 8.33, found: C 91.43 H 8.56.

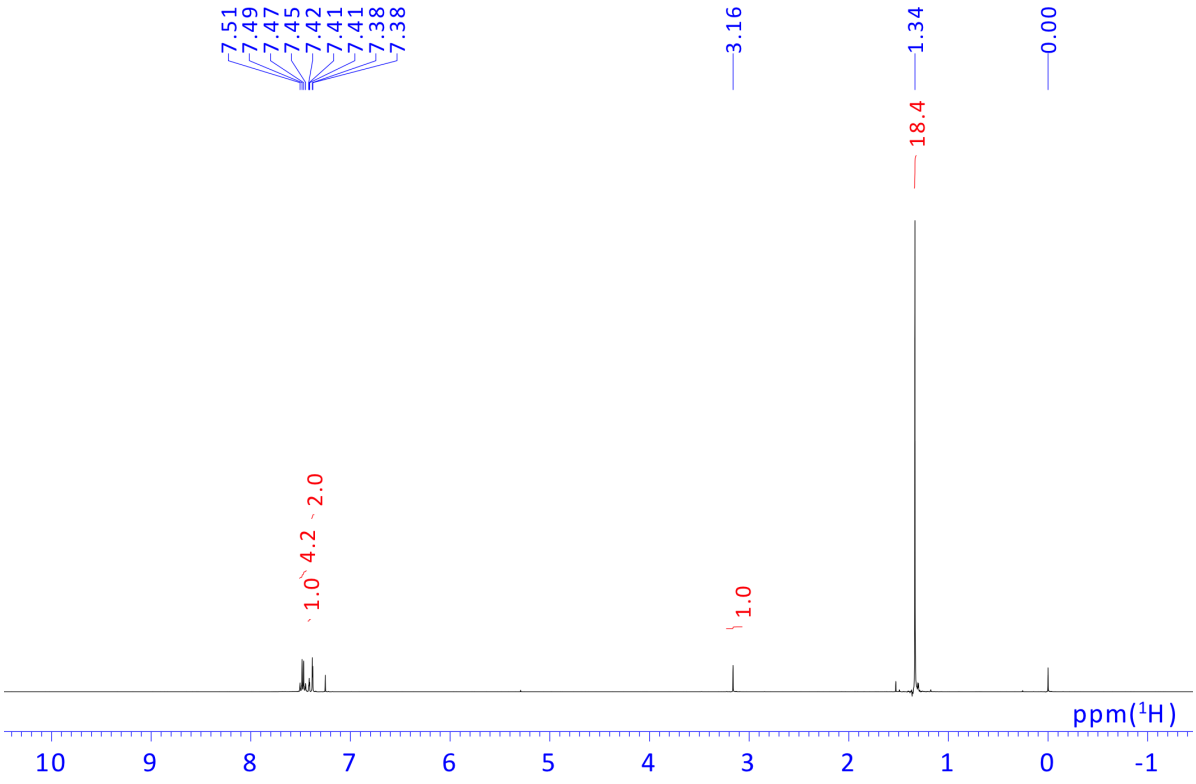


Figure S9. ^{1}H NMR spectrum of **8**.

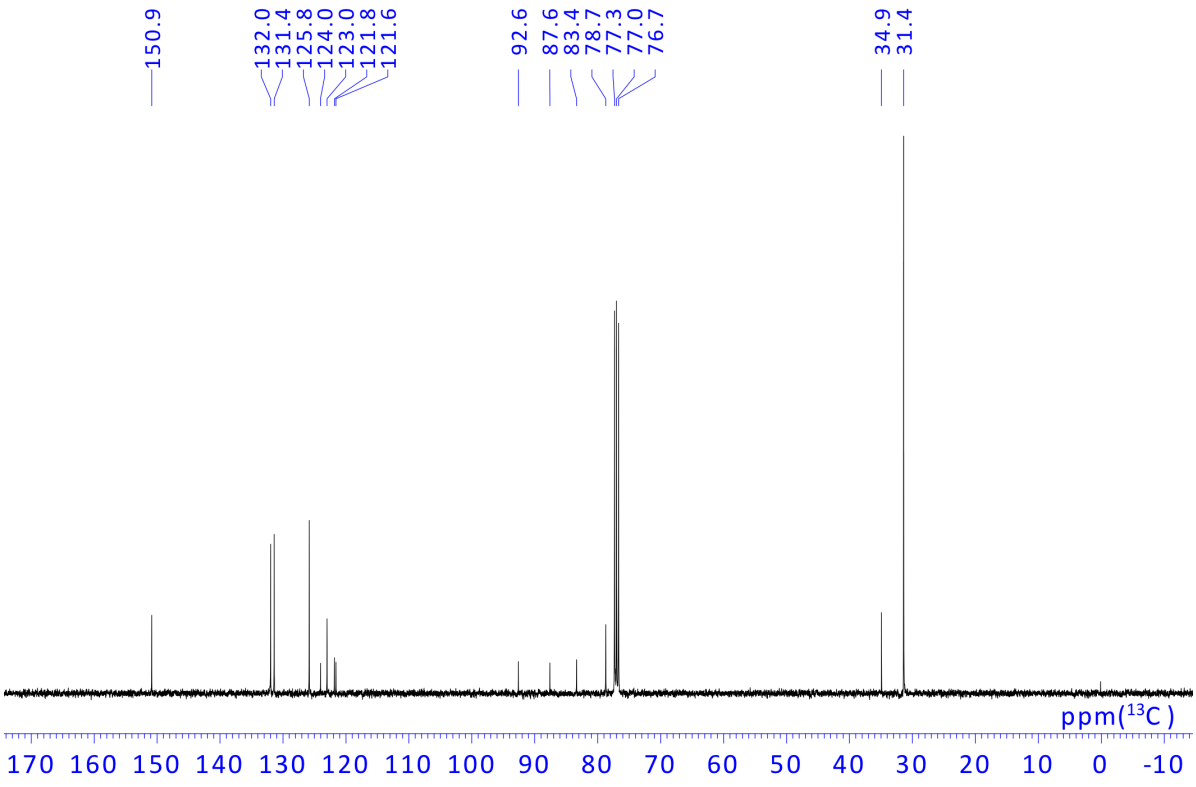
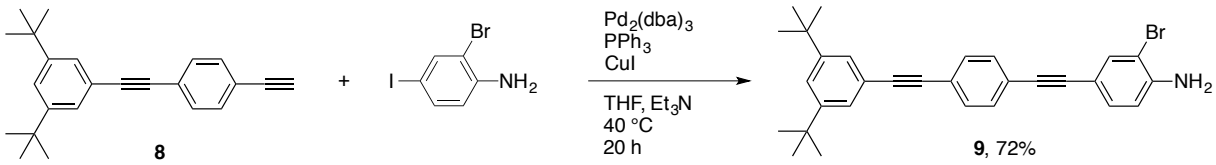


Figure S10. ^{13}C NMR spectrum of **8**.

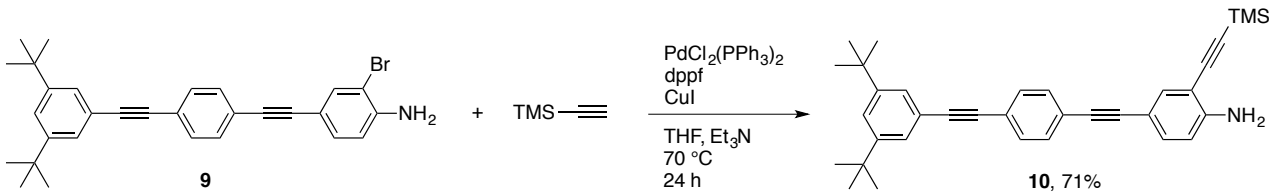
Synthesis of 9



8 **9**, 72%

A mixture of 2-bromo-4-iodoaniline (2.34 g, 7.88 mmol), **8** (2.48 g, 7.88 mmol), $Pd_2(dba)_3$ (0.180 g, 0.197 mmol), PPh_3 (0.207 g, 0.788 mmol), CuI (0.075 g, 0.39 mmol), THF (40 mL) and Et_3N (40 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 40 °C for 20 h with stirring. Precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 (EtOAc/hexane = 1/4 v/v as an eluent) to afford **9** (2.74 g, 5.65 mmol, 72%) as a pale brown crystal (R_f = 0.48 (EtOAc/hexane = 1/6 v/v)). The compound **9** was used for the next reaction without further purification.

Synthesis of 10



9 **10**, 71%

A mixture of **9** (2.74 g, 5.65 mmol), $PdCl_2(PPh_3)_2$ (0.270 g, 0.385 mmol), dppf (0.213 g, 0.385 mmol), CuI (0.073 g, 0.39 mmol), THF (40 mL) and Et_3N (40 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, trimethylsilylacethylene (2.17 mL, 15.4 mmol) was added to the mixture via syringe. The reaction was carried out at 70 °C for 24 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration. The solvent was removed with a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 (EtOAc/hexane = 1/4 v/v as an eluent). Further purification was carried out by recrystallization with hexane to

afford **10** (2.01 g, 4.00 mmol, 71%) as a light brown needle crystal.

R_f = 0.59 (EtOAc/hexane = 1/4 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.27 (s, 9H), 1.34 (s, 18H), 4.42, (s, 2H), 6.64 (d, J = 8.6 Hz, 1H), 7.28 (dd, J = 8.6 Hz, J = 2.0 Hz, 1H) 7.38-7.45 (m, 5H), 7.49-7.51 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.1, 31.3, 34.8, 87.3, 88.0, 91.2, 92.2, 100.4, 100.6, 107.9, 111.9, 114.0, 122.0, 122.8, 122.9, 123.4, 125.9, 131.2, 131.5, 133.2, 135.7, 148.3, 150.9 ppm. HRMS (ESI) calcd. for $C_{35}H_{40}NSi$ $[M+H]^+$: 502.2925, found 502.2911. Elemental analysis calcd. for $C_{35}H_{39}NSi$: C 83.78 H 7.83 N 2.79, found: C 83.52 H 7.85 N 2.53.

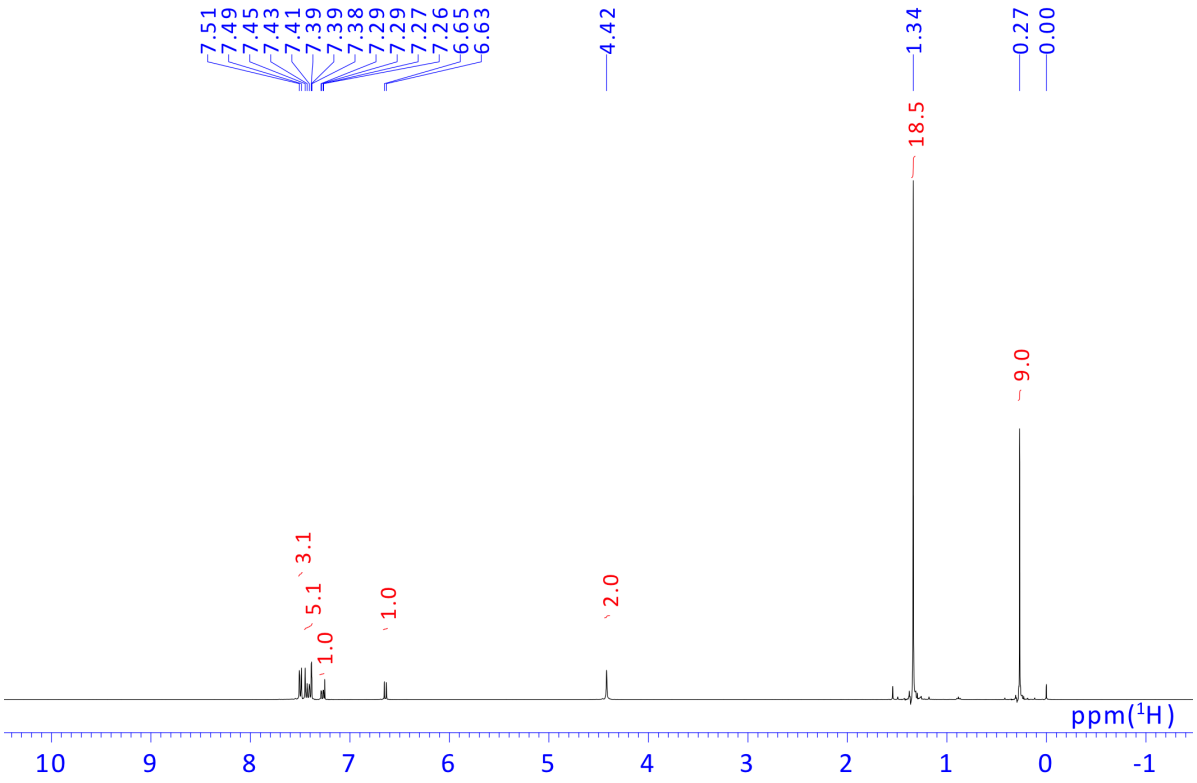


Figure S11. ^{1}H NMR spectrum of **10**.

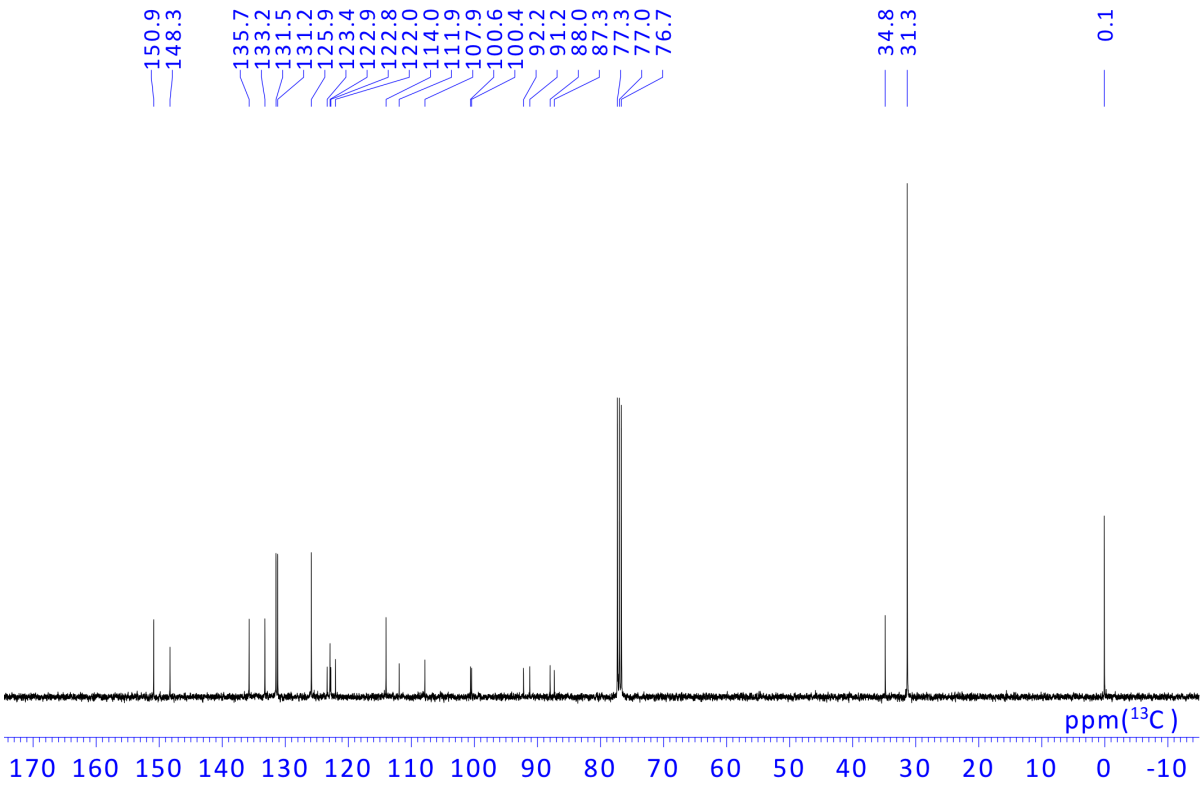
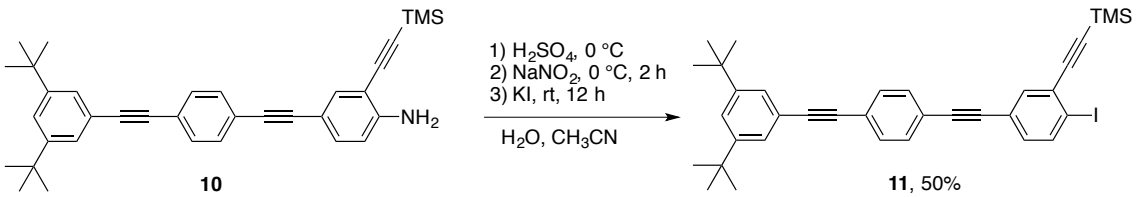


Figure S12. ^{13}C NMR spectrum of **10**.

Synthesis of 11



A mixture of **10** (0.878 g, 1.75 mmol), CH_3CN (150 mL), H_2O (50 mL) and concentrated H_2SO_4 (24 mL) was placed in a round-bottom flask at 0 °C, equipped with a magnetic stirring bar. To the reaction mixture, $NaNO_2$ (0.224 g, 3.25 mmol) in H_2O (4 mL) was slowly added at 0 °C. After stirring for 2 h, the mixture was added into a solution of KI (2.57 g, 15.5 mmol) in CH_3CN (50 mL) and H_2O (50 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h. The mixture was quenched by the addition of aqueous $NaHSO_3$ solution, and the organic layer was extracted three times with CH_2Cl_2. 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 ($CHCl_3$/hexane = 1/7 v/v as an eluent). Further purification was carried out by recrystallization with $CHCl_3$ and MeOH (good and poor solvent, respectively) to afford **11** (0.443 g, 0.883 mmol, 50%) as a colorless crystal.

R_f = 0.44 ($CHCl_3$/hexane = 1/7 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.29 (s, 9H), 1.34 (s, 18H), 7.11, (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.39 (d, J = 1.7 Hz, 2H), 7.42 (d, J = 1.7 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 2.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ –0.3, 31.3, 34.8, 87.8, 89.4, 90.9, 92.7, 99.6, 101.0, 105.6, 121.9, 122.2, 123.0, 123.1, 123.8, 125.9, 130.0, 131.5, 131.6, 132.0, 135.4, 138.8, 150.9 ppm. HRMS (ESI) calcd. for $C_{35}H_{37}ISi$ $[M]^+$: 612.1704, found 612.1688. Elemental analysis calcd. for $C_{35}H_{37}ISi$: C 68.62 H 6.09, found: C 68.31 H 5.99.

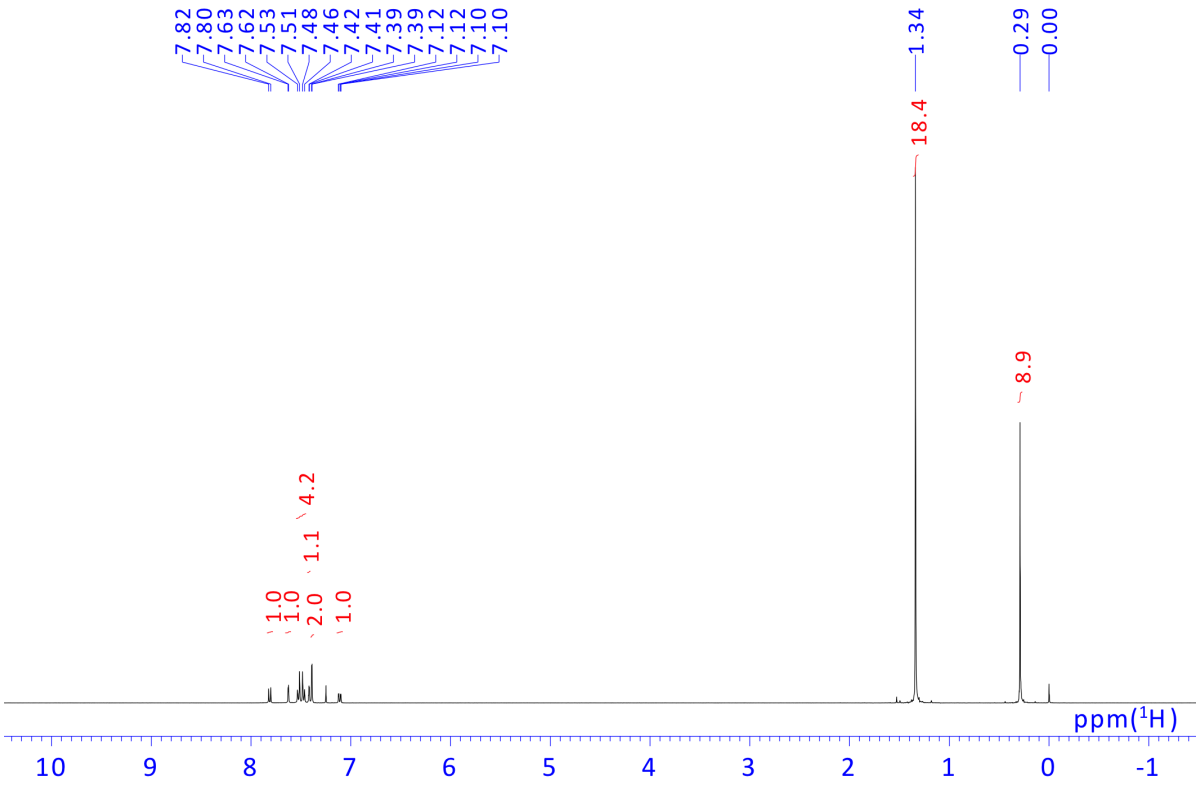


Figure S13. ^{1}H NMR spectrum of **11**.

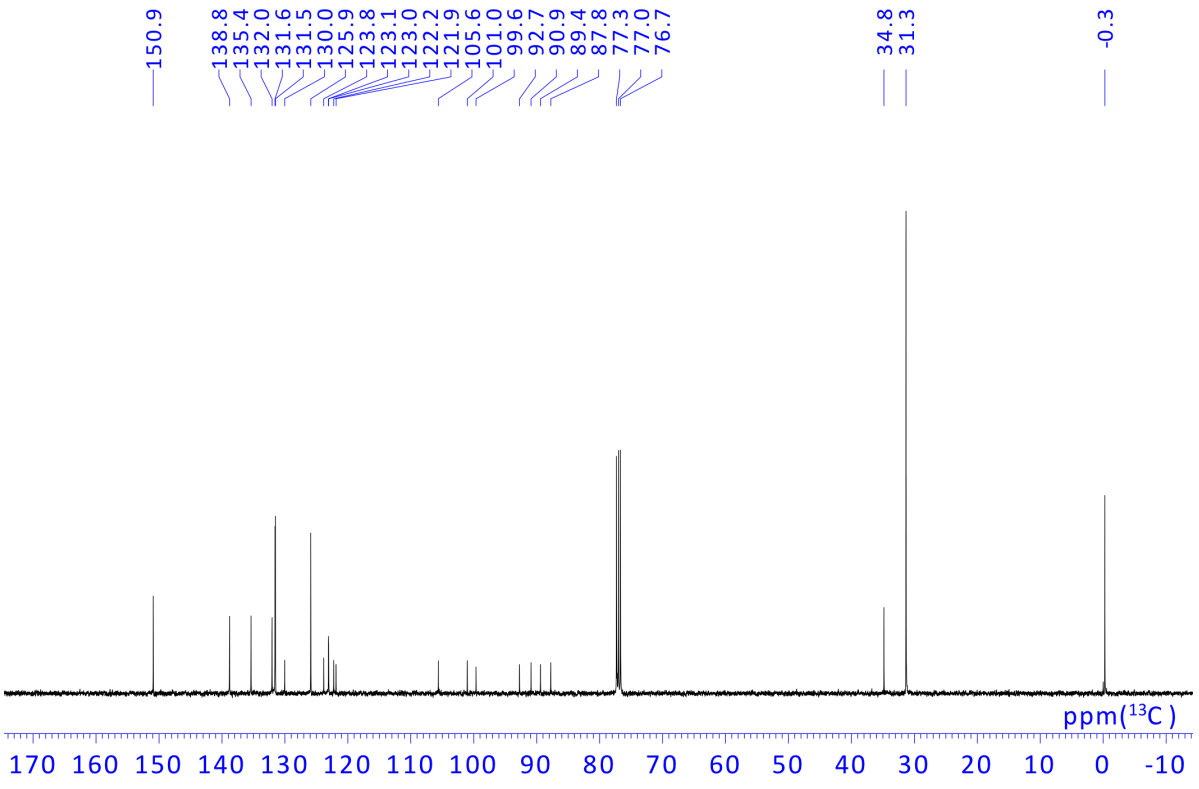
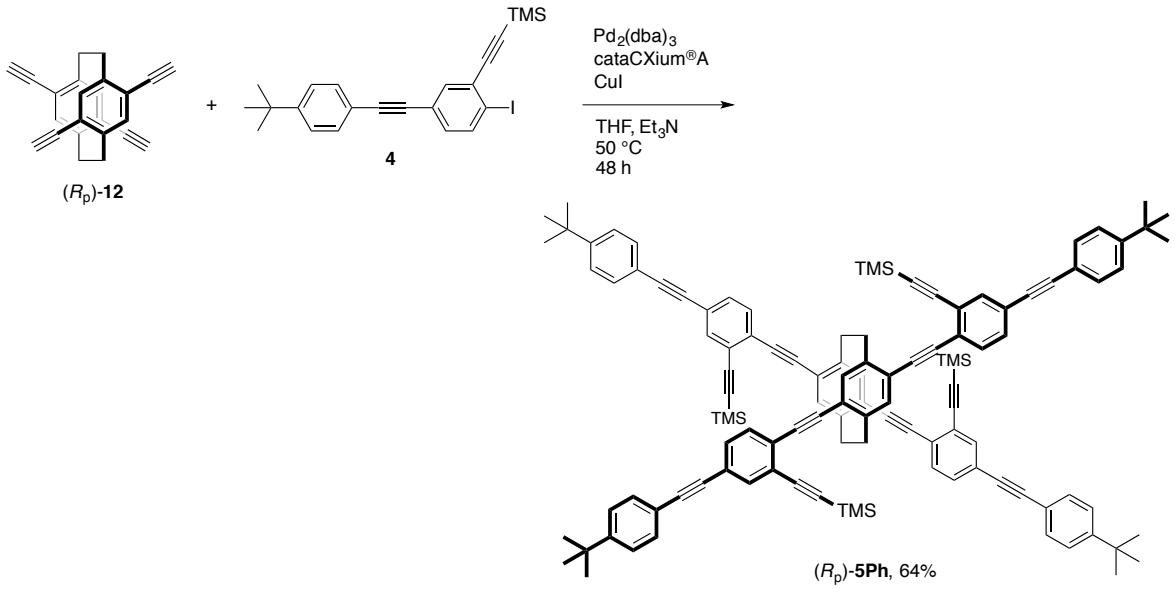


Figure S14. ^{13}C NMR spectrum of **11**.

Synthesis of 5Ph



A mixture of (R_p)-**12** (20 mg, 0.0657 mmol), **4** (132 mg, 0.289 mmol), $Pd_2(dba)_3$ (6.0 mg, 0.066 mmol), cataCXium® A (9.4 mg, 0.026 mmol), CuI (2.5 mg, 0.013 mmol), THF (2 mL) and Et_3N (2 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 48 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration. The solvent was removed with a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/2 v/v as an eluent). Further purification was carried out by HPLC to afford (R_p)-**5Ph** (68 mg, 0.042 mmol, 64%) as a light yellow solid.

R_f = 0.53 ($CHCl_3$/hexane = 1/3 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 36H), 1.33 (s, 36H), 3.19, (m, 4H), 3.73 (m, 4H), 7.26 (s, 4H) 7.38 (d, J = 8.6 Hz, 8H), 7.45 (dd, J = 8.0 Hz, 1.6 Hz, 4H), 7.48 (d, J = 8.6 Hz, 8H), 7.52 (d, J = 8.0 Hz, 4H), 7.73 (d, J = 1.6 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.1, 31.2, 32.8, 34.9, 87.8, 92.0, 93.4, 94.8, 99.2, 103.0, 119.8, 123.3, 125.3, 125.4, 125.4, 125.4, 131.0, 131.4, 132.3, 135.2, 135.7, 141.9, 151.9 ppm. HRMS (ESI) calcd. for $C_{116}H_{116}Si_4N$ $[M+NH_4]^+$: 1634.8179, found 1634.8173. Elemental analysis calcd. for $C_{116}H_{112}Si_4$: C 86.08 H 6.98, found: C 86.06 H 6.93.

(S_p)-**5Ph** was obtained by the same procedure in 69% isolated yield.

(R_p)-**5Ph**: $[\alpha]^{23}_D$ = –42.5 (*c* 0.1, $CHCl_3$). (S_p)-**5Ph**: $[\alpha]^{23}_D$ = +42.6 (*c* 0.1, $CHCl_3$).

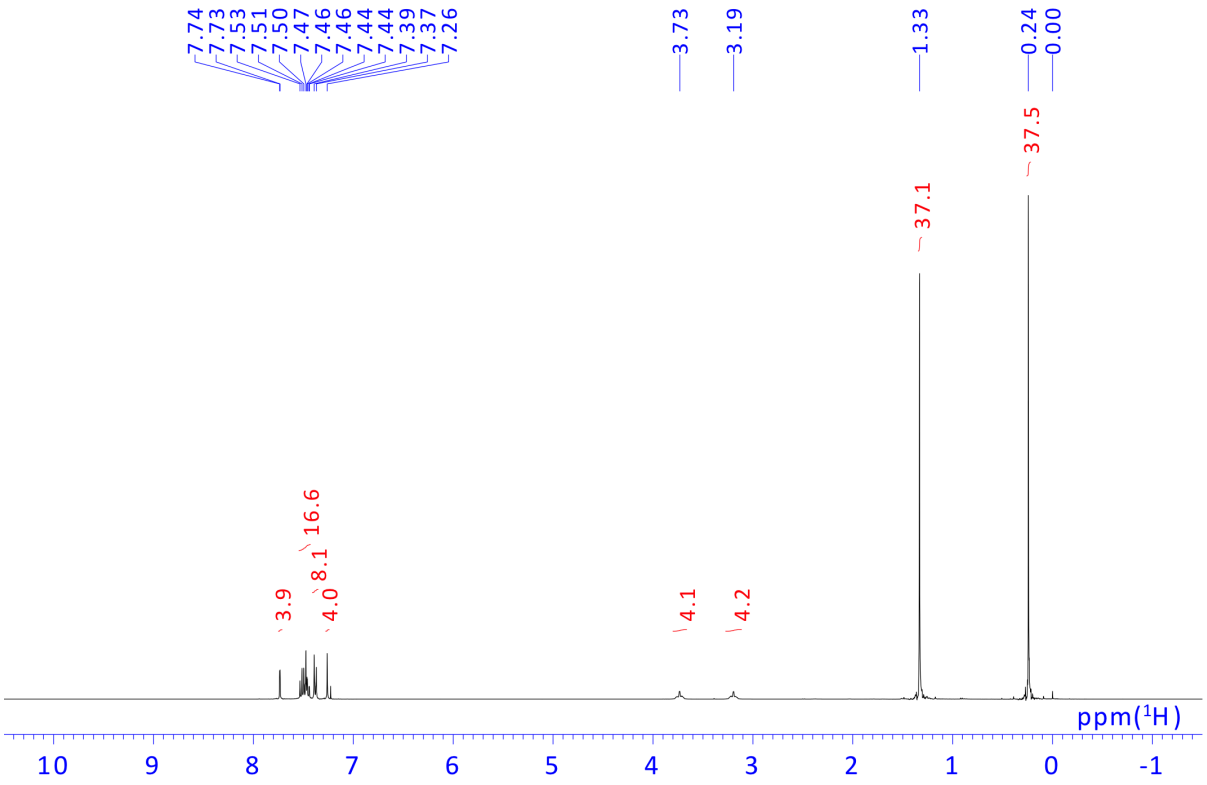


Figure S15. ^{1}H NMR spectrum of (R_p)-**5Ph**.

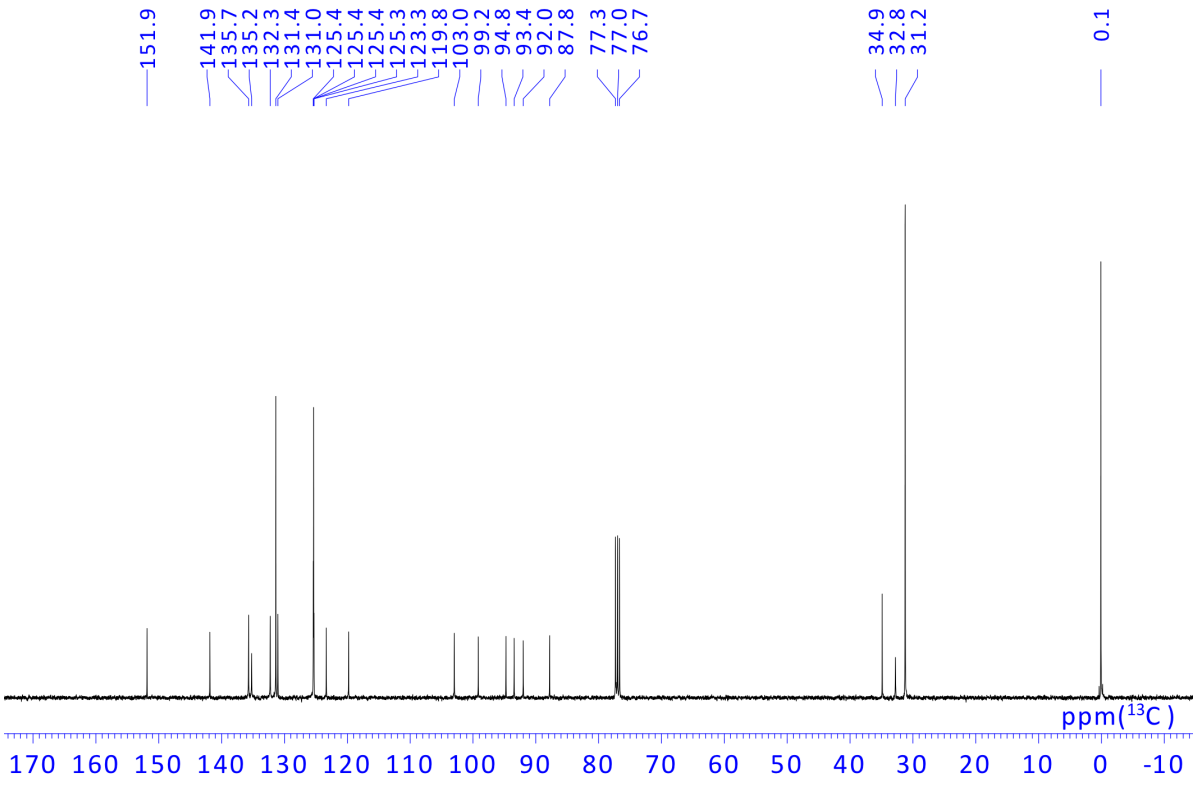
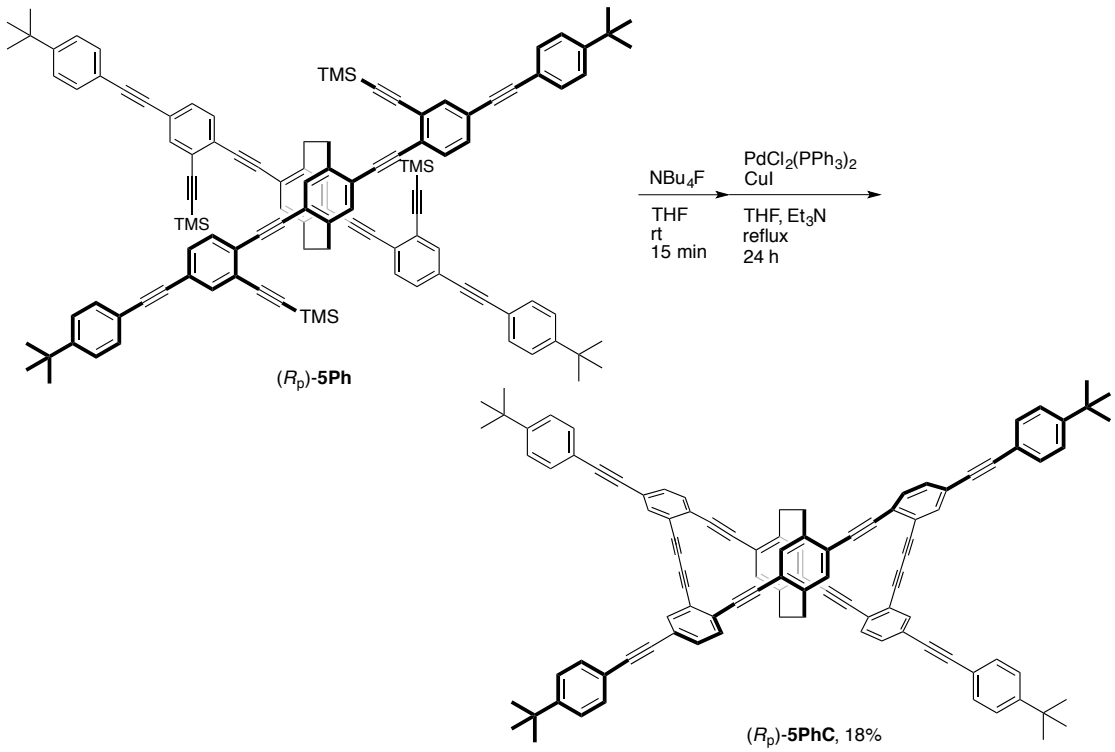


Figure S16. ^{13}C NMR spectrum of (R_p)-**5Ph**.

Synthesis of 5PhC



(R_p)-**5Ph** (53.6 mg, 0.0331 mmol) in THF (5.0 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing several times, NBu_4F (1 M in THF, 0.2 mL, 0.2 mmol) was added to the solution at room temperature for 15 min with stirring. The mixture was quenched by the addition of H_2O, and the organic layer was extracted three times with $CHCl_3$. 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 product was purified by column chromatography on SiO_2 ($CHCl_3$ as an eluent). To this product in a round-bottom flask equipped with a magnetic stirring bar, $PdCl_2(PPh_3)_2$ (217 mg, 0.309 mmol), CuI (58.8 mg, 0.309 mmol), THF (200 mL) and Et_3N (50 mL) was added. The mixture was heated at reflux temperature for 24 h under air. After the reaction mixture was cooled to room temperature, the solvent was evaporated. The residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/2 v/v as an eluent). Further purification was carried out by HPLC to afford (R_p)-**5PhC** (7.7 mg, 0.0058 mmol, 18%) as a light yellow solid.

R_f = 0.30 ($CHCl_3$/hexane = 1/3 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 36H), 3.13, (m, 4H), 3.55 (m, 4H), 7.21 (s, 4H) 7.40 (d, J = 8.6 Hz, 8H), 7.50 (d, J = 8.6 Hz, 8H), 7.51 (m, 8H),

7.69 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.2, 33.2, 34.9, 79.0, 81.5, 87.5, 92.5, 93.0, 94.8, 119.6, 123.7, 124.2, 124.3, 125.4, 127.7, 131.4, 131.8, 132.2, 133.9, 133.9, 143.3, 152.1 ppm. HRMS (APCI) calcd. for $C_{104}H_{77}$ $[M+H]^+$: 1325.6020, found 1325.6032.

(S_p)-**5PhC** was obtained by the same procedure in 18% isolated yield.

(R_p)-**5PhC**: $[\alpha]^{23}_D$ = +855.59 (*c* 0.1, $CHCl_3$). (S_p)-**5PhC**: $[\alpha]^{23}_D$ = –849.61 (*c* 0.1, $CHCl_3$).

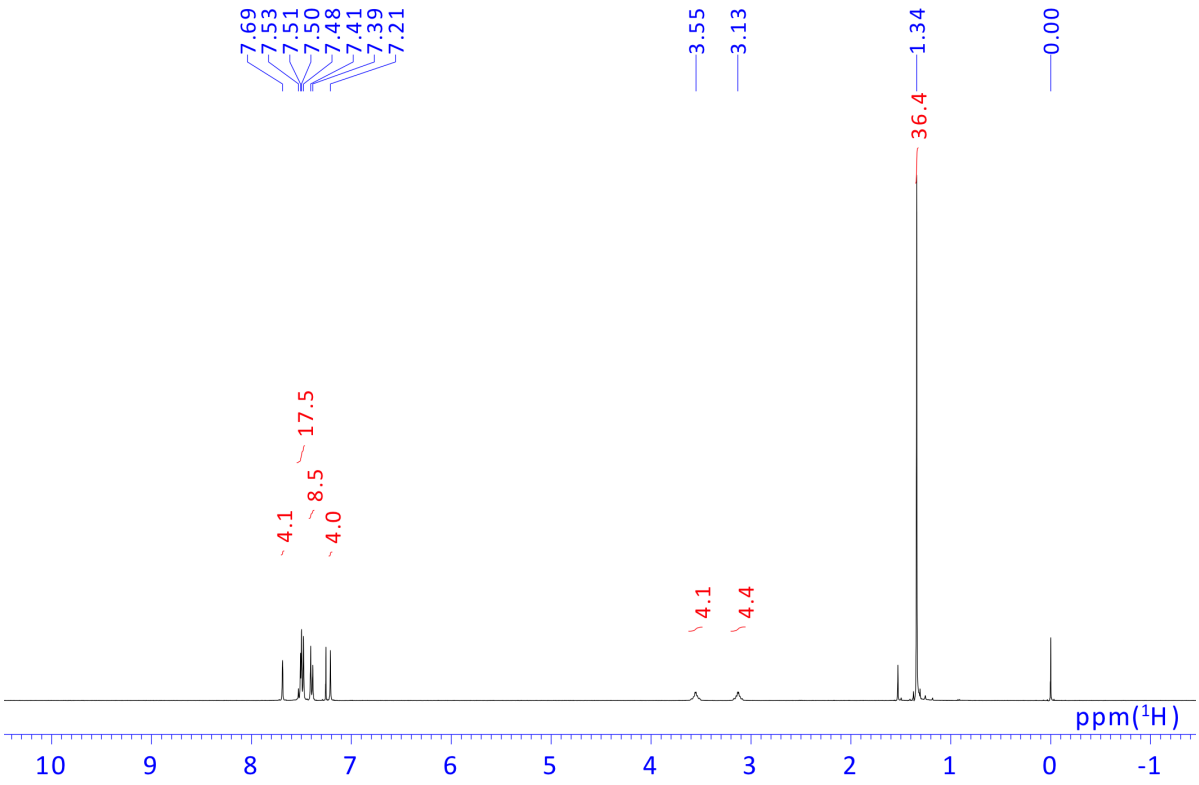


Figure S17. ^{1}H NMR spectrum of (R_p)-**5PhC**.

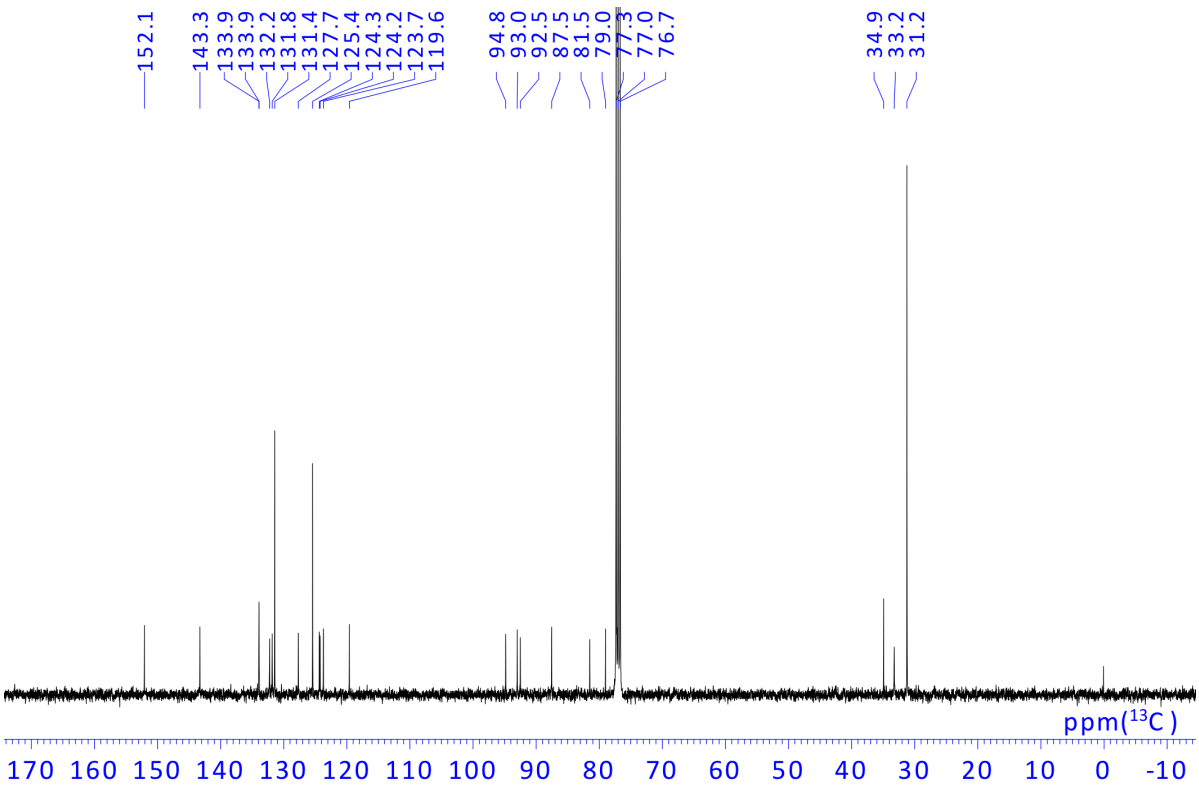
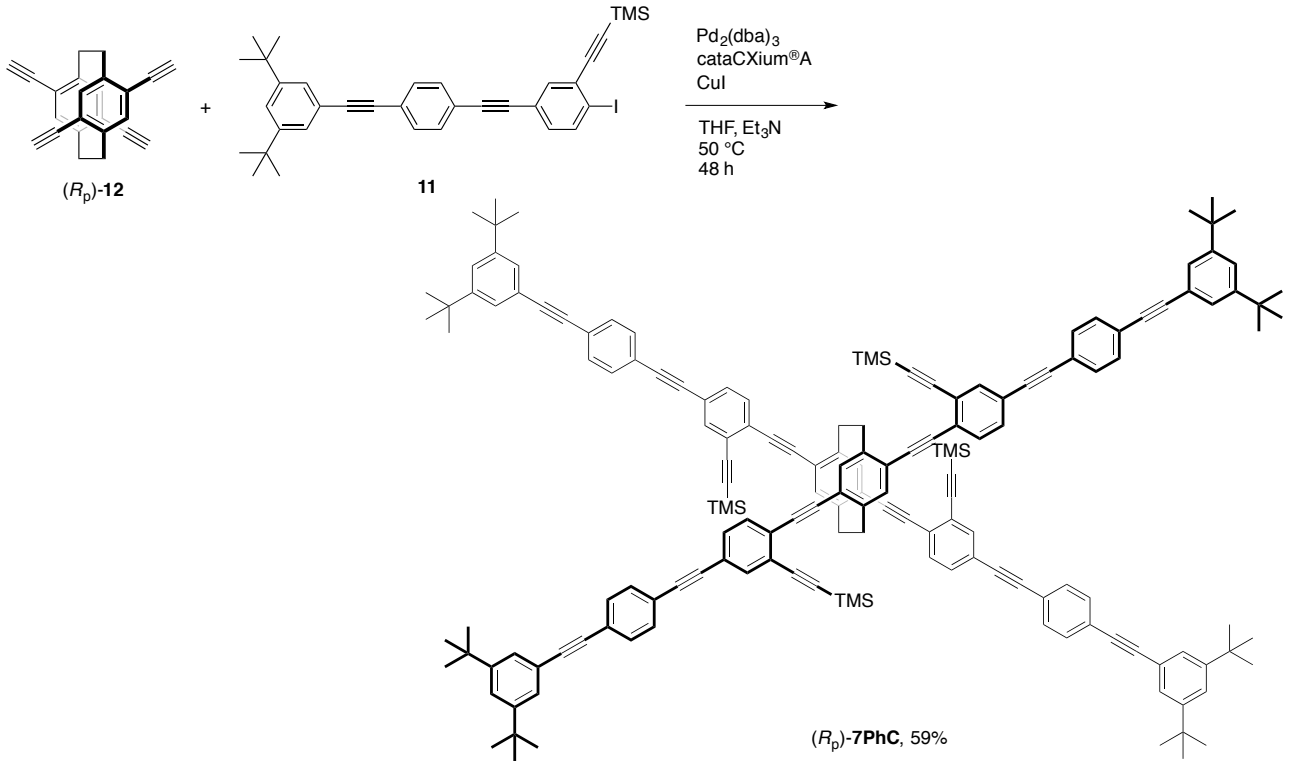


Figure S18. ^{13}C NMR spectrum of (R_p)-**5PhC**.

Synthesis of 7Ph



A mixture of (R_p)-**12** (20 mg, 0.0657 mmol), **11** (177 mg, 0.289 mmol), $Pd_2(dba)_3$ (6.0 mg, 0.066 mmol), cataCXium® A (9.4 mg, 0.026 mmol), CuI (2.5 mg, 0.013 mmol), THF (2 mL) and Et_3N (2 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 48 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration. The solvent was removed with a rotary evaporator. The crude residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/3 v/v as an eluent). Further purification was carried out by HPLC to afford (R_p)-**7Ph** (87 mg, 0.039 mmol, 59%) as a light yellow solid.

R_f = 0.26 ($CHCl_3$/hexane = 1/3 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.25 (s, 36H), 1.34 (s, 72H), 3.21, (m, 4H), 3.75 (m, 4H), 7.28 (s, 4H) 7.41-7.43 (m, 12H), 7.47 (dd, J = 8.2 Hz, 1.5 Hz, 4H), 7.51-7.57 (m, 20H), 7.76 (d, J = 1.6 Hz, 4H), ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.0, 31.3, 32.7, 34.8, 87.8, 90.1, 91.6, 92.8, 93.4, 95.0, 99.4, 102.9, 121.9, 122.3, 122.9, 123.0, 123.8, 125.5, 125.6, 125.7, 125.9, 131.1, 131.6, 131.6, 132.4, 135.3, 135.9, 142.0, 150.9 ppm. HRMS (APCI) calcd. for $C_{164}H_{161}Si_4$ $[M+H]^+$: 2242.1670, found 2242.1710. Elemental analysis calcd. for $C_{164}H_{160}Si_4$: C 87.80 H 7.19, found: C 87.70 H 7.16.

(S_p)-**7Ph** was obtained by the same procedure in 63% isolated yield.

(R_p)-**7Ph**: $[\alpha]^{23}_D = -62.9$ (*c* 0.1, $CHCl_3$). (S_p)-**7Ph**: $[\alpha]^{23}_D = +59.6$ (*c* 0.1, $CHCl_3$).

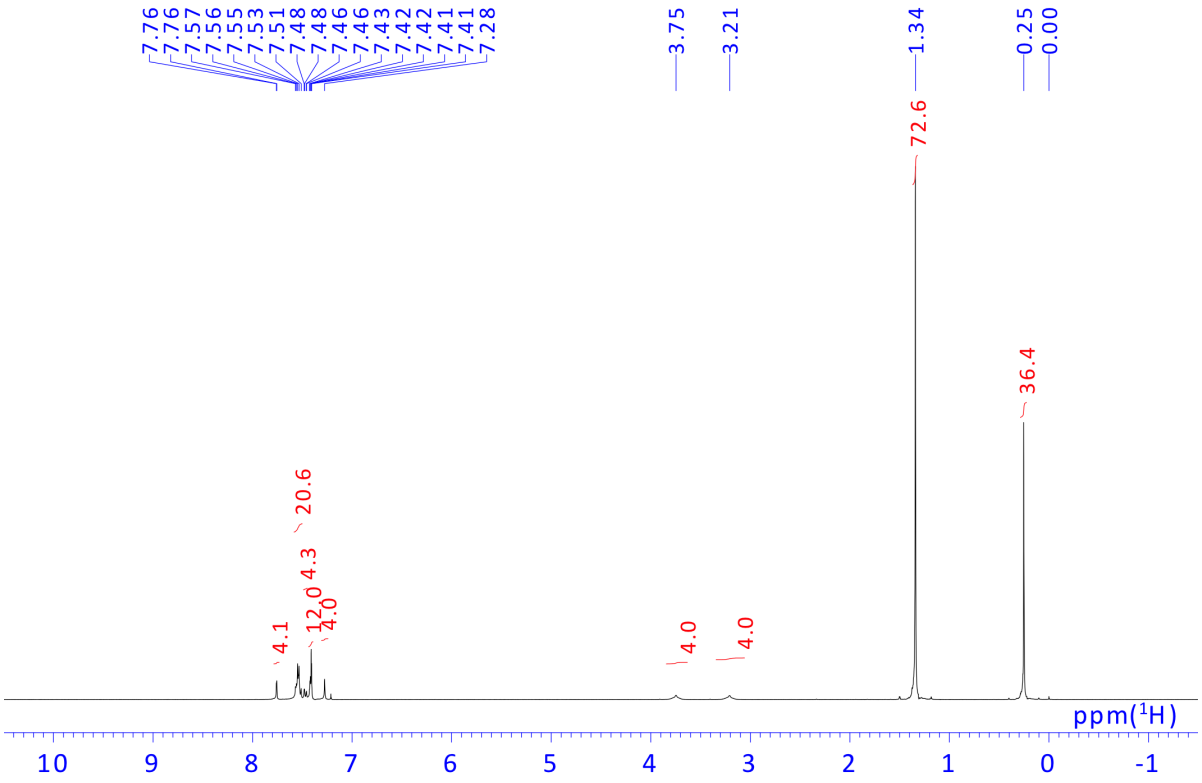


Figure S19. ^{1}H NMR spectrum of (R_p)-**7Ph**.

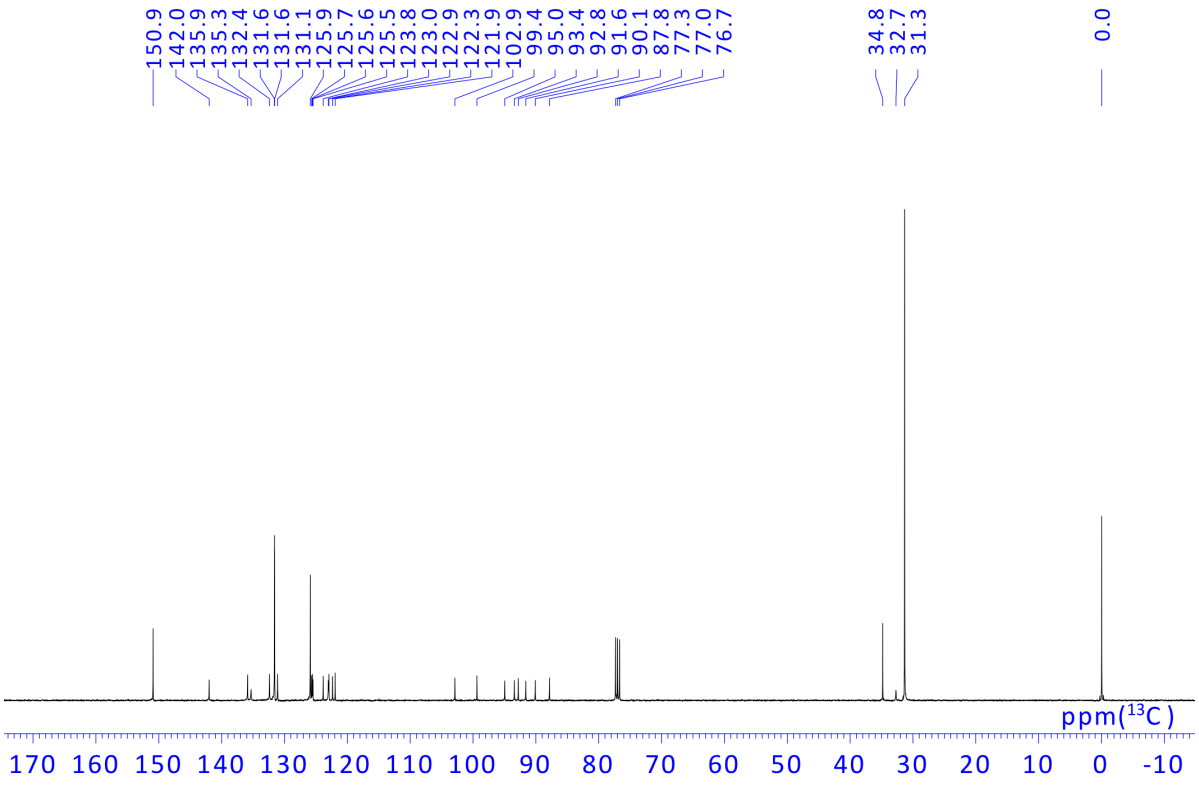
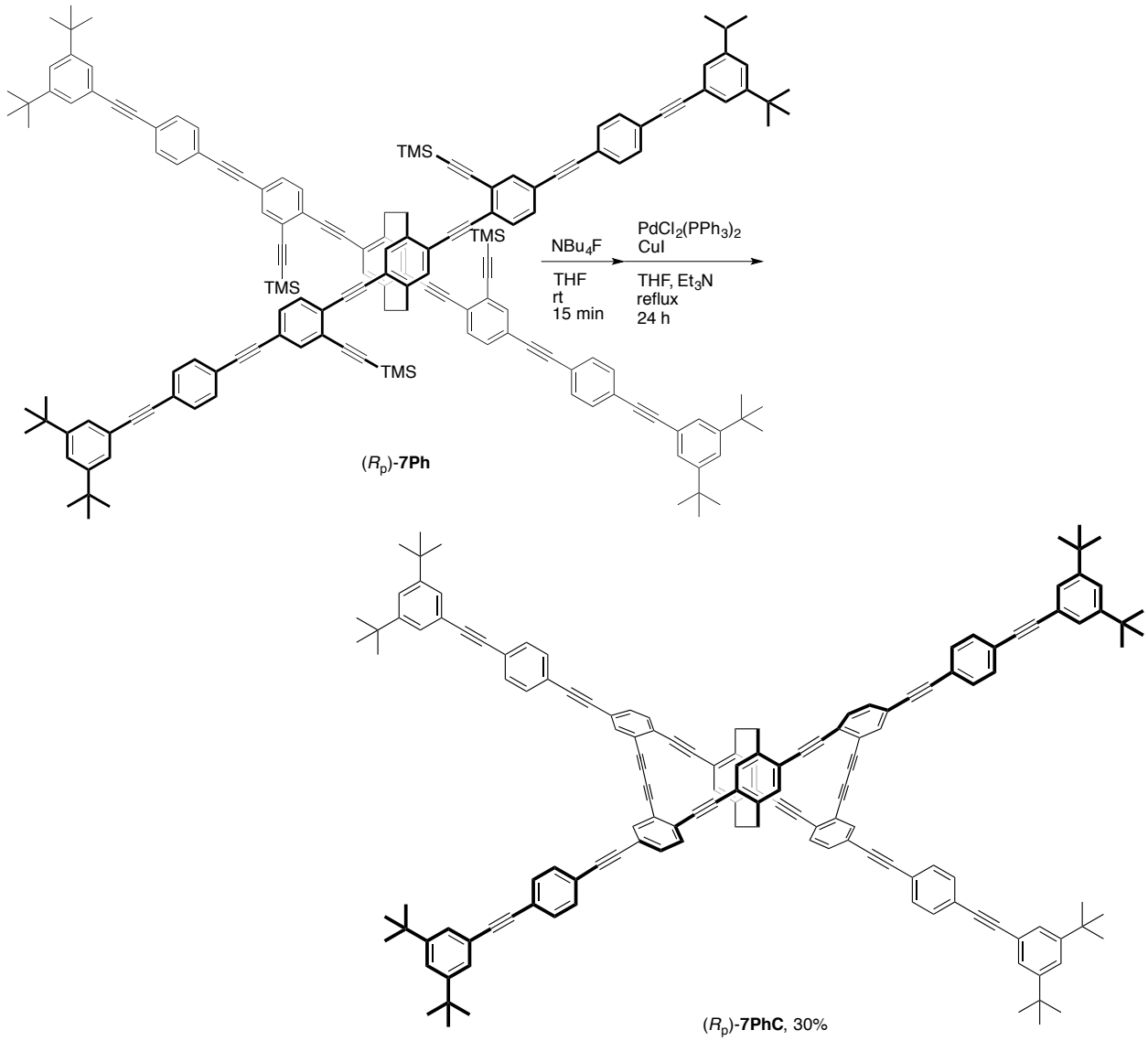


Figure S20. ^{13}C NMR spectrum of (R_p)-**7Ph**.

Synthesis of 7PhC



(R_p)-**7Ph** (70.0 mg, 0.0312 mmol) in THF (5.0 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing several times, NBu_4F (1 M in THF, 0.3 mL, 0.3 mmol) was added to the solution at room temperature for 15 min with stirring. The mixture was quenched by the addition of H_2O, and the organic layer was extracted three times with $CHCl_3$. 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). A mixture of the product, $PdCl_2(PPh_3)_2$ (219 mg, 0.312 mmol), CuI (59.4 mg, 0.312 mmol), THF (300 mL) and Et_3N (50 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. The mixture was heated at reflux

temperature for 24 h under air. After the reaction mixture was cooled to room temperature, the solvent was evaporated. The residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/1 v/v as an eluent). Further purification was carried out by HPLC to afford (R_p)-**7PhC** (18.1 mg, 0.00928 mmol, 30%) as a light yellow solid.

R_f = 0.26 ($CHCl_3$/hexane = 1/3 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (s, 72H), 3.14, (m, 4H), 3.56 (m, 4H), 7.21 (s, 4H) 7.40-7.43 (m, 12H), 7.48-7.56 (m, 24H), 7.69 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.3, 33.2, 34.8, 79.1, 81.5, 87.8, 89.8, 92.1, 92.9, 93.0, 95.0, 121.9, 122.2, 123.1, 123.3, 124.0, 124.3, 124.4, 125.9, 128.1, 131.6, 131.6, 131.9, 132.4, 134.0, 134.0, 143.4, 150.9 ppm. HRMS (MALDI, DIT) calcd. for $C_{152}H_{124}$ $[M]^+$: 1948.9703, found 1948.9756.

(S_p)-**7PhC** was obtained by the same procedure in 27% isolated yield.

(R_p)-**7PhC**: $[\alpha]^{23}_D$ = +467.90 (*c* 0.1, $CHCl_3$). (S_p)-**7PhC**: $[\alpha]^{23}_D$ = –463.35 (*c* 0.1, $CHCl_3$).

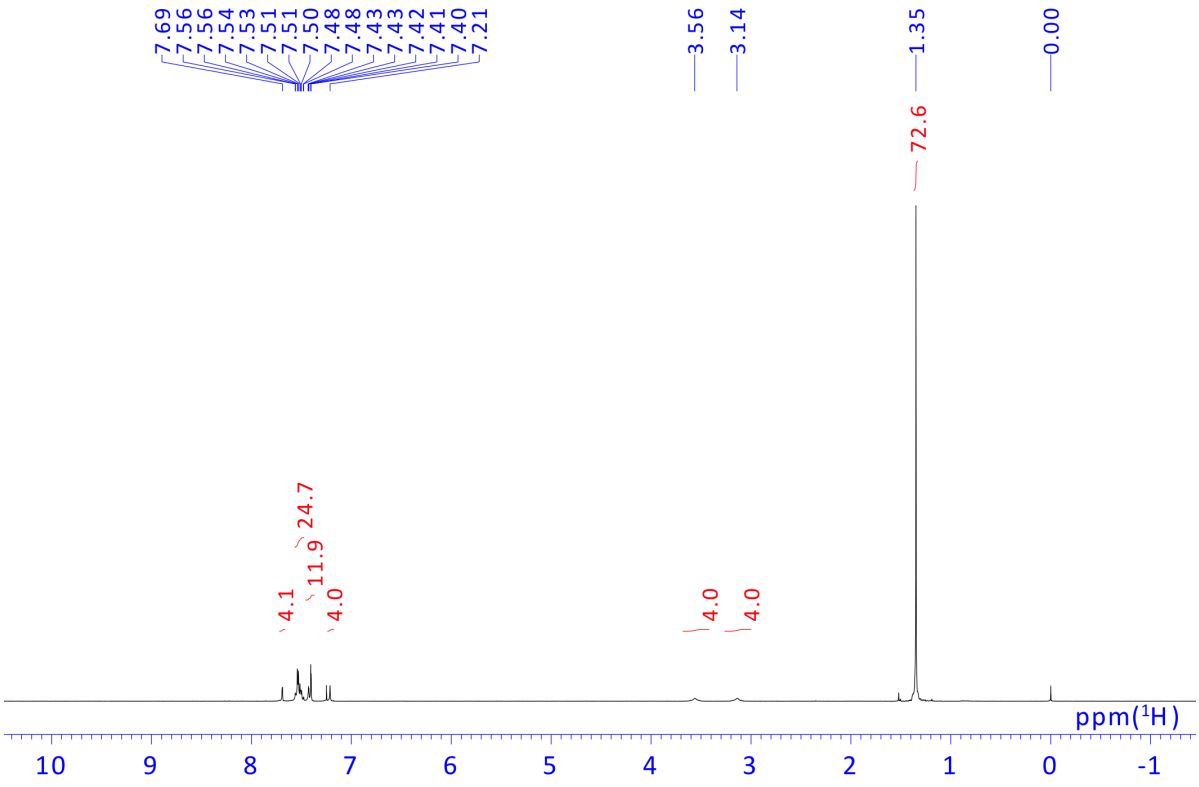


Figure S21. ^{1}H NMR spectrum of (R_p)-**7PhC**.

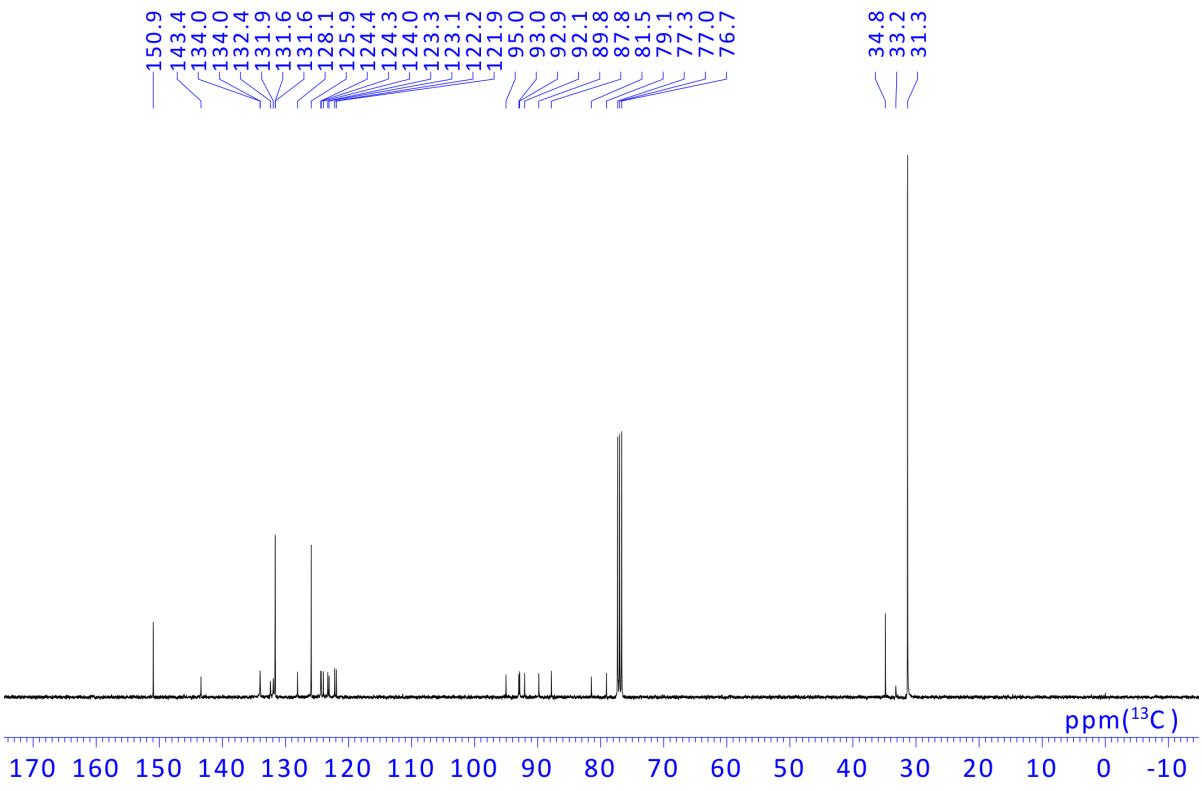


Figure S22. ^{13}C NMR spectrum of (R_p)-**7PhC**.

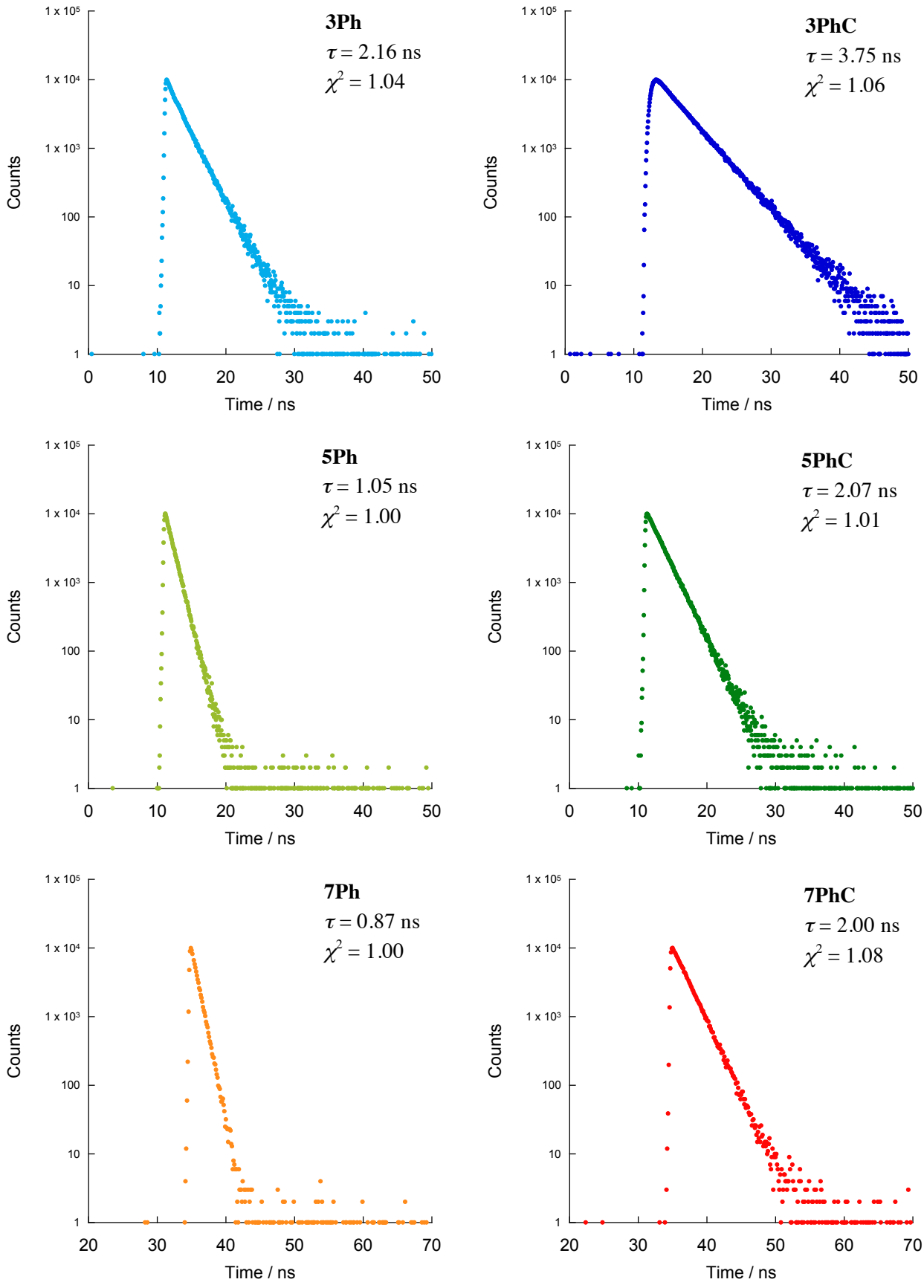


Figure S23. PL lifetime decay curves of (R_p)-isomers in $CHCl_3$ (1.0×10^{-6} M) at room temperature, excited at 375 nm with LED laser. Their PL peak tops were monitored. (S_p)-Isomers exhibited identical profiles.

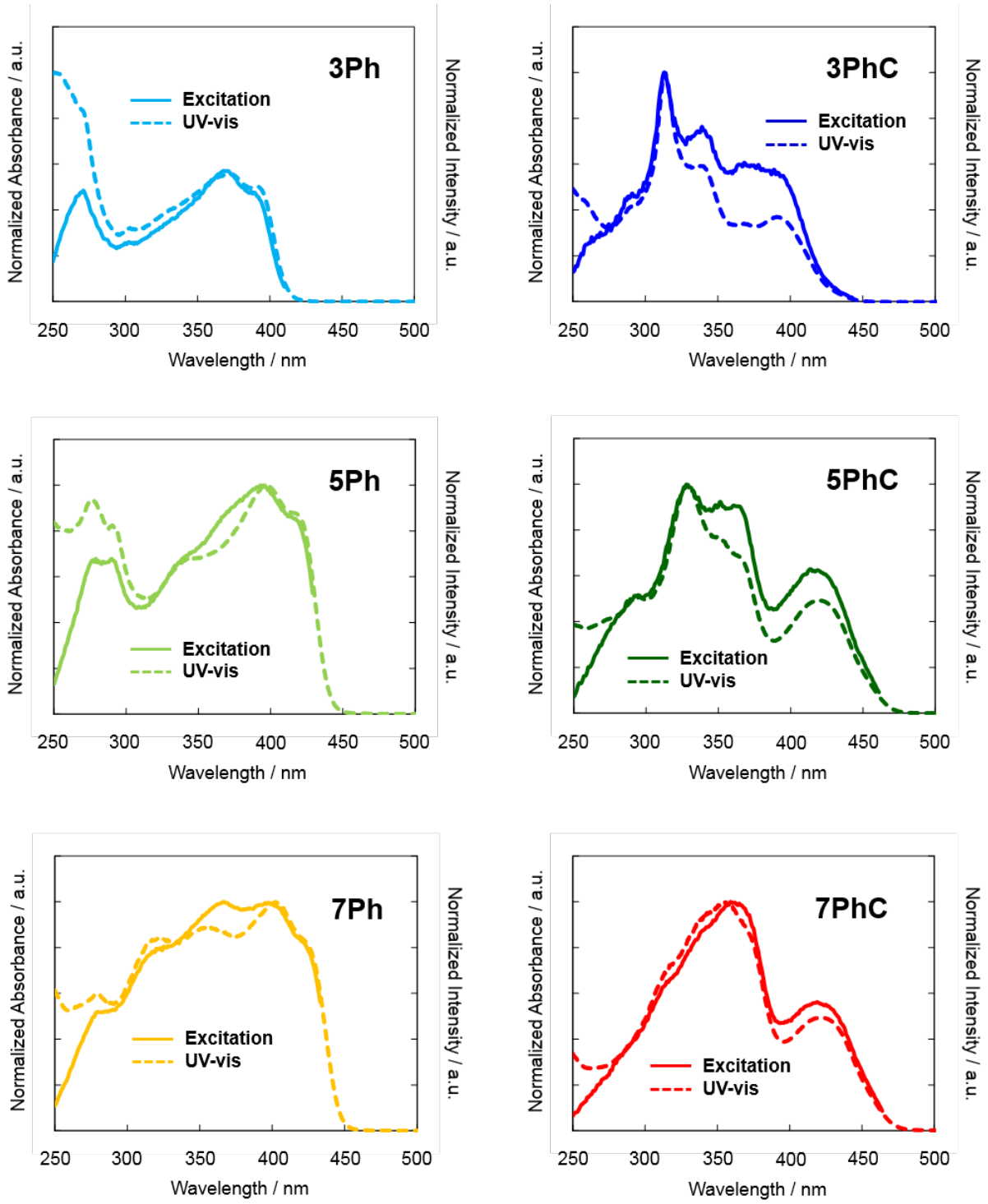
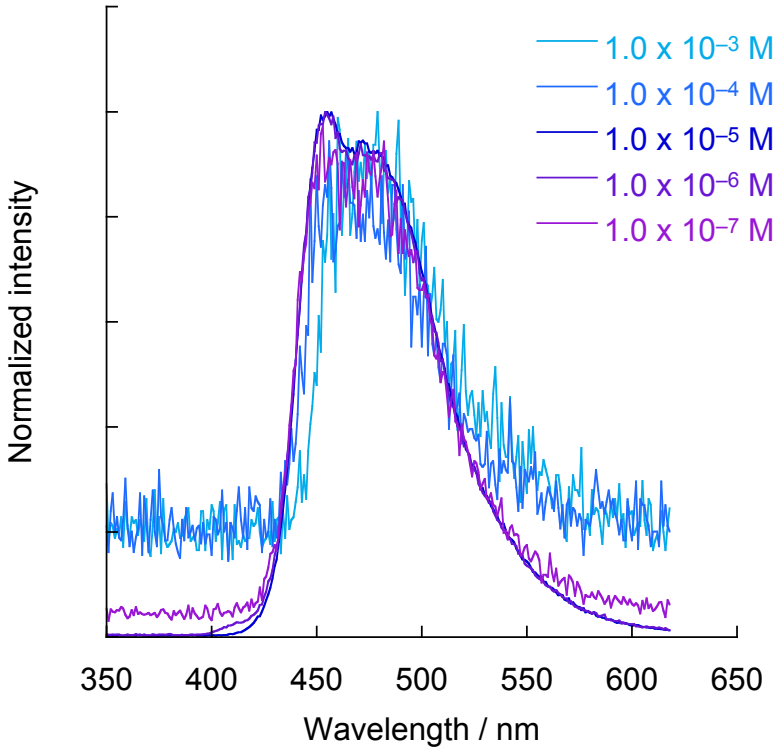


Figure S24. Excitation spectra of (R_p)-isomers in $CHCl_3$ (1.0×10^{-6} M); spectra was detected at each wavelength of maximum PL intensity. (S_p)-Isomers exhibited identical profiles.

(A)



(B)

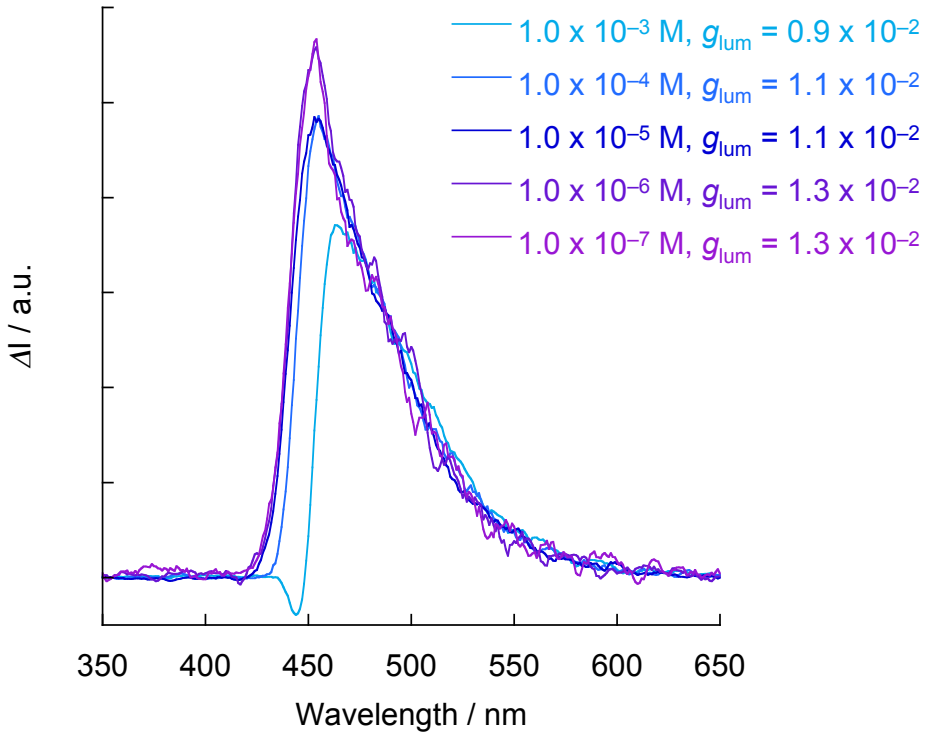


Figure S25. Concentration effect on (A) PL and (B) CPL spectra of (R_p)-**3PhC** in $CHCl_3$, excited at 314 nm.

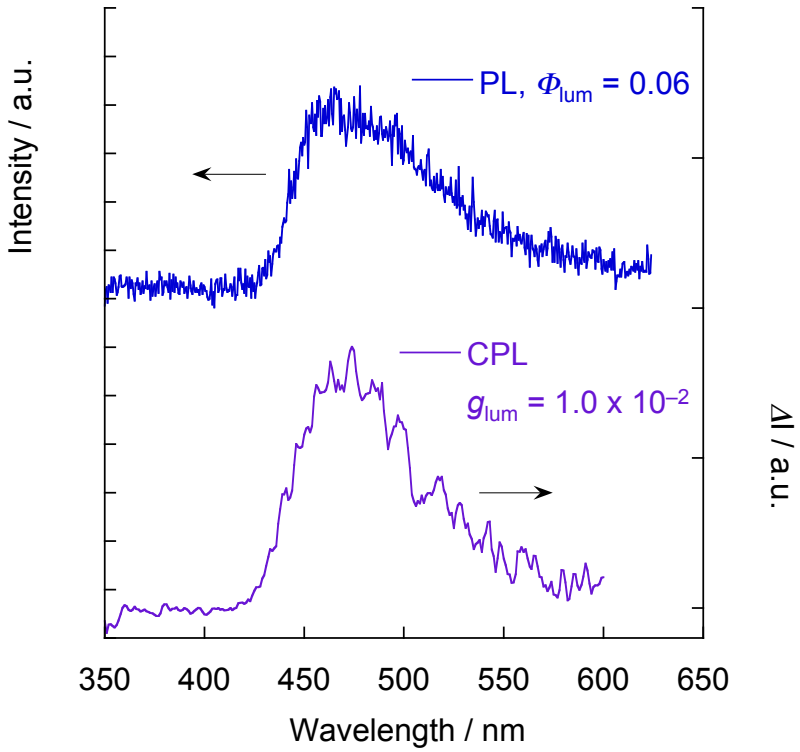


Figure S26. PL and CPL spectra of the (R_p)-**3PhC** cast film from the $CHCl_3$ solution (1.0×10^{-3} M), excited at 316 nm.

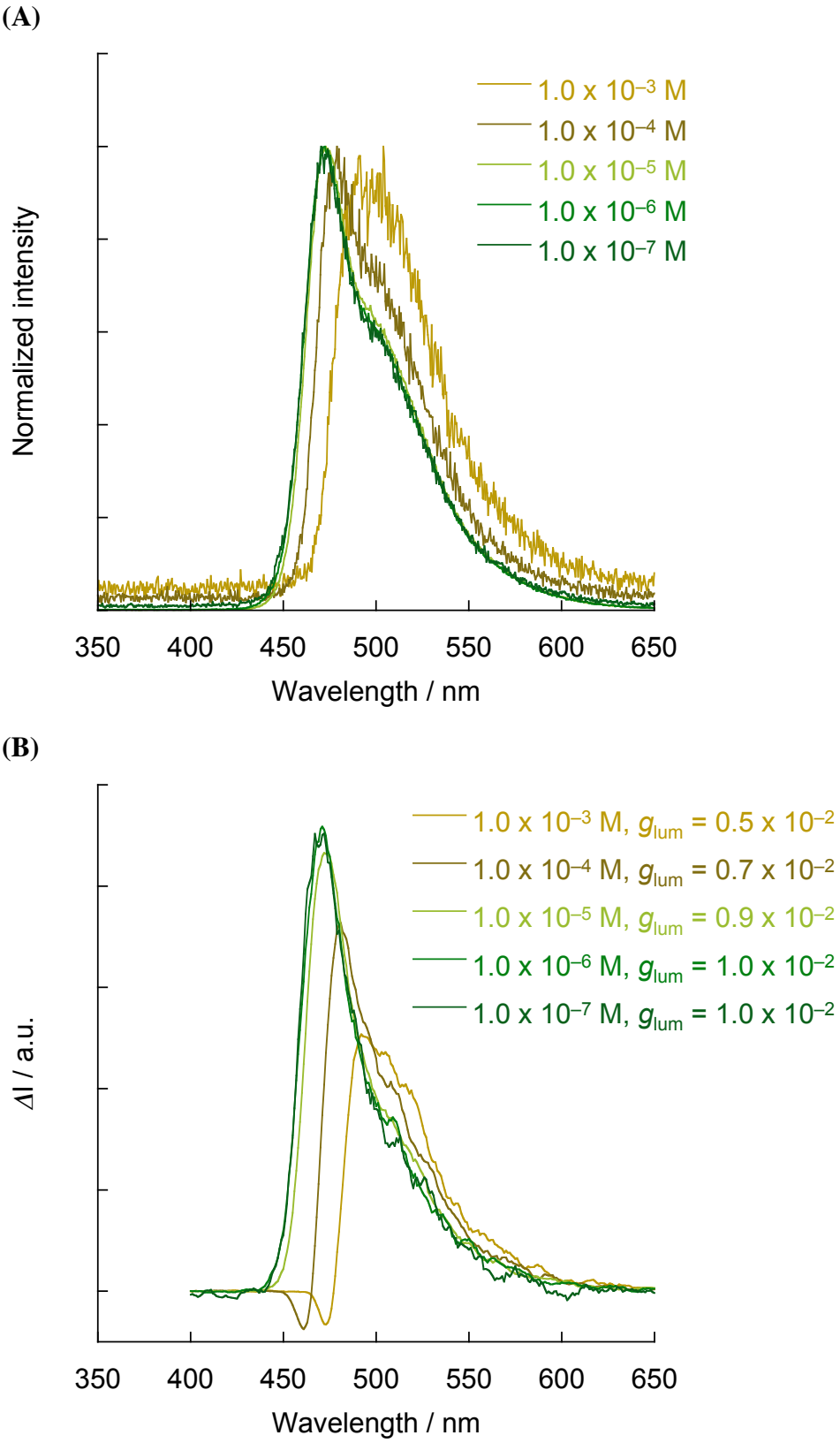


Figure S27. Concentration effect on (A) PL and (B) CPL spectra of (R_p)-**5PhC** in $CHCl_3$, excited at 330 nm.

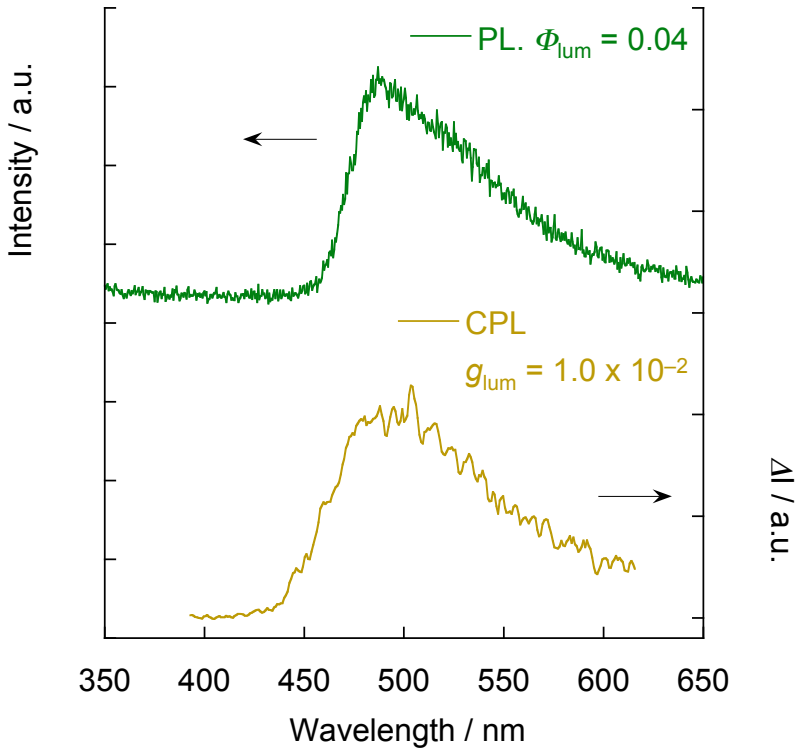
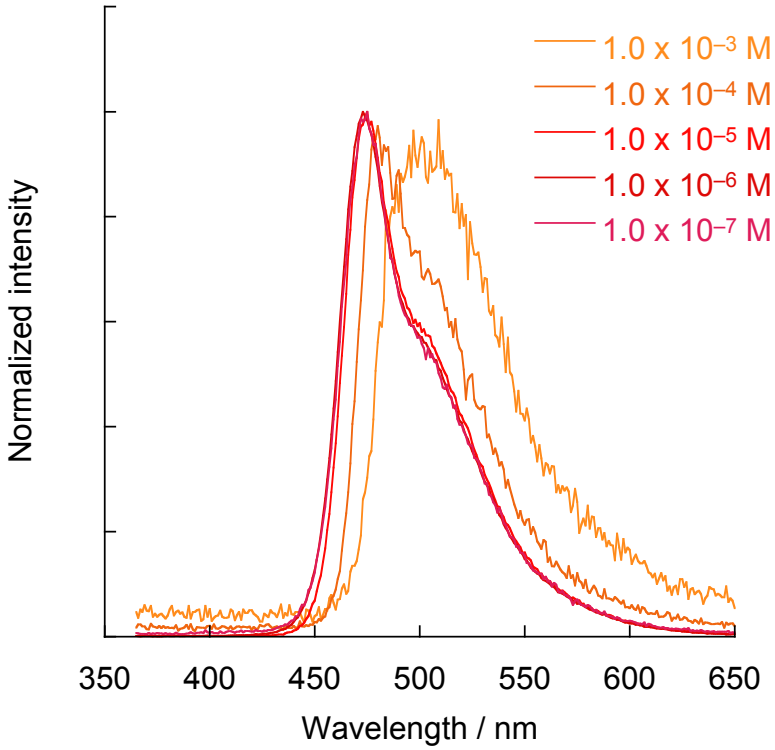


Figure S28. PL and CPL spectra of the (R_p)-**5PhC** cast film from the $CHCl_3$ solution (1.0×10^{-3} M), excited at 333 nm.

(A)



(B)

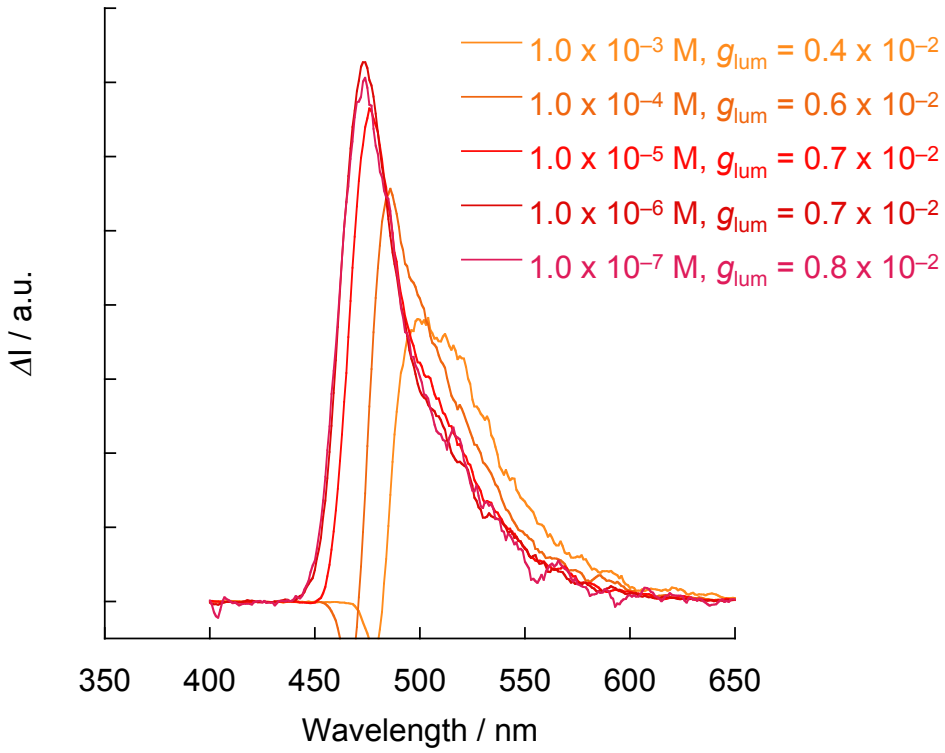


Figure S29. Concentration effect on (A) PL and (B) CPL spectra of (R_p)-**7PhC** in $CHCl_3$, excited at 355 nm.

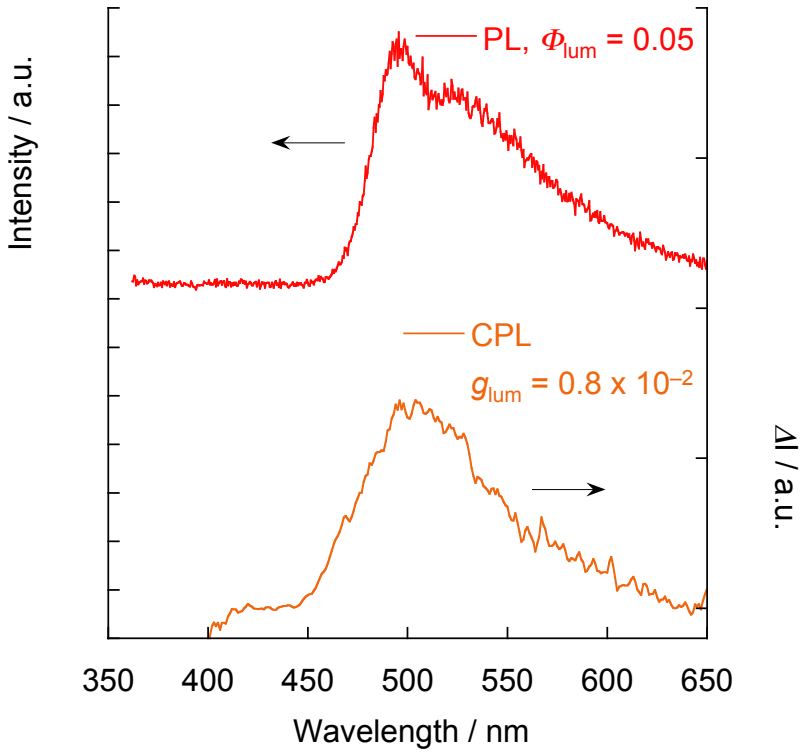


Figure S30. PL and CPL spectra of the (R_p)-**7PhC** cast film from the $CHCl_3$ solution (1.0×10^{-3} M), excited at 333 nm, excited at 352 nm.

References

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[3] Y. Miura, M. Matsumoto and Y. Ushitani, *Macromolecules*, 1993, **26**, 6673-6675.

[4] Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh and Y. Chujo, *J. Am. Chem. Soc.*, 2014, **136**, 3350-3353.