Supporting Information

Tether-entangled conjugated helices

Ke Jin,[ab] Zuo Xiao,[*ab] Huidong Xie,[ab] Xingxing Shen,[*c] Jizheng Wang,[d] Xiangyu Chen,[e] Zhijie Wang,[f] Zujin Zhao,[g] Keyou Yan,[h] Yong Ding[i] and Liming Ding[*ab]

1. General characterization

^{1}H, ^{13}C and 2D NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry was done by using a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous CH_2Cl_2 solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). Compounds were dissolved into the solution. A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag^+ electrode was used as the reference electrode. All potentials were corrected against Fc/Fc^+. Single-crystal X-ray diffraction data were collected on a Bruker D8 VENTURE diffractometer. Circular dichroism (CD) spectra were recorded on a JASCO J-1500 spectrophotometer. Circularly polarized luminescence (CPL) spectra were measured by using a JASCO CPL-200 spectrophotometer. The absolute quantum yields and emission spectra were measured on a HORIBA FluoroMax Plus spectrophotometer. The fluorescence lifetimes were measured on a HORIBA Jobin Yvon NanoLog-TCSPC spectrofluorometer. The dynamic light scattering (DLS) spectra were measured on a Zetasizer Nano ZS spectrometer.

2. Computational details

Molecular geometries of the ground state were optimized by PM7 or density functional theory (DFT) by using Gaussian16 software at the M06-2X(D3)/6-31G(d,p) level in gas phase.[1] The excited-state properties were calculated by time-dependent DFT (TD-DFT) theory at the PBE0(D3)/6-31G(d,p) level. The geometries of the S_1 state were optimized by TD-DFT theory at the PBE0(D3)/6-31G(d,p) level. NMR chemical shifts and NICS values were calculated at revTPSS/def2TZVPP level, with chloroform as the solvent and TMS as the reference. For **(*P*)-T2 dimer** and **(*P*)-T3 dimer**, the structural optimization was done at the M06-2X(D3)/6-31G(d,p) level, and the interaction energies (ΔE_{int}) between two monomer fragments was calculated at the M06-2X(D3)/def2TZVP level with BSSE correction. For **(*P*)-T2** and **(*P*)-T3** monomers, the structural optimization was done at the M06-2X(D3)/6-31G(d,p) level, and the single point energies (SPE) were calculated at the M06-2X(D3)/def2TZVP level. For **(*P*)-T4 dimer** and **(*P*)-T5 dimer**, the structural optimization was done at the r^{2}SCAN-3c level by using ORCA 5.0.4 software. ΔE_{int} between two monomer fragments was calculated at the ωB97M-V/def2-TZVP level with BSSE correction. Electronic CD spectra were fitted by Multiwfn software[2] and Visual Molecular Dynamics (VMD) software[3] was used to provide the directions of transition electronic dipole moment and magnetic dipole moment, and the angel between them. IGMH and IRI isosurfaces were drawn with the aid of Multiwfn and VMD.

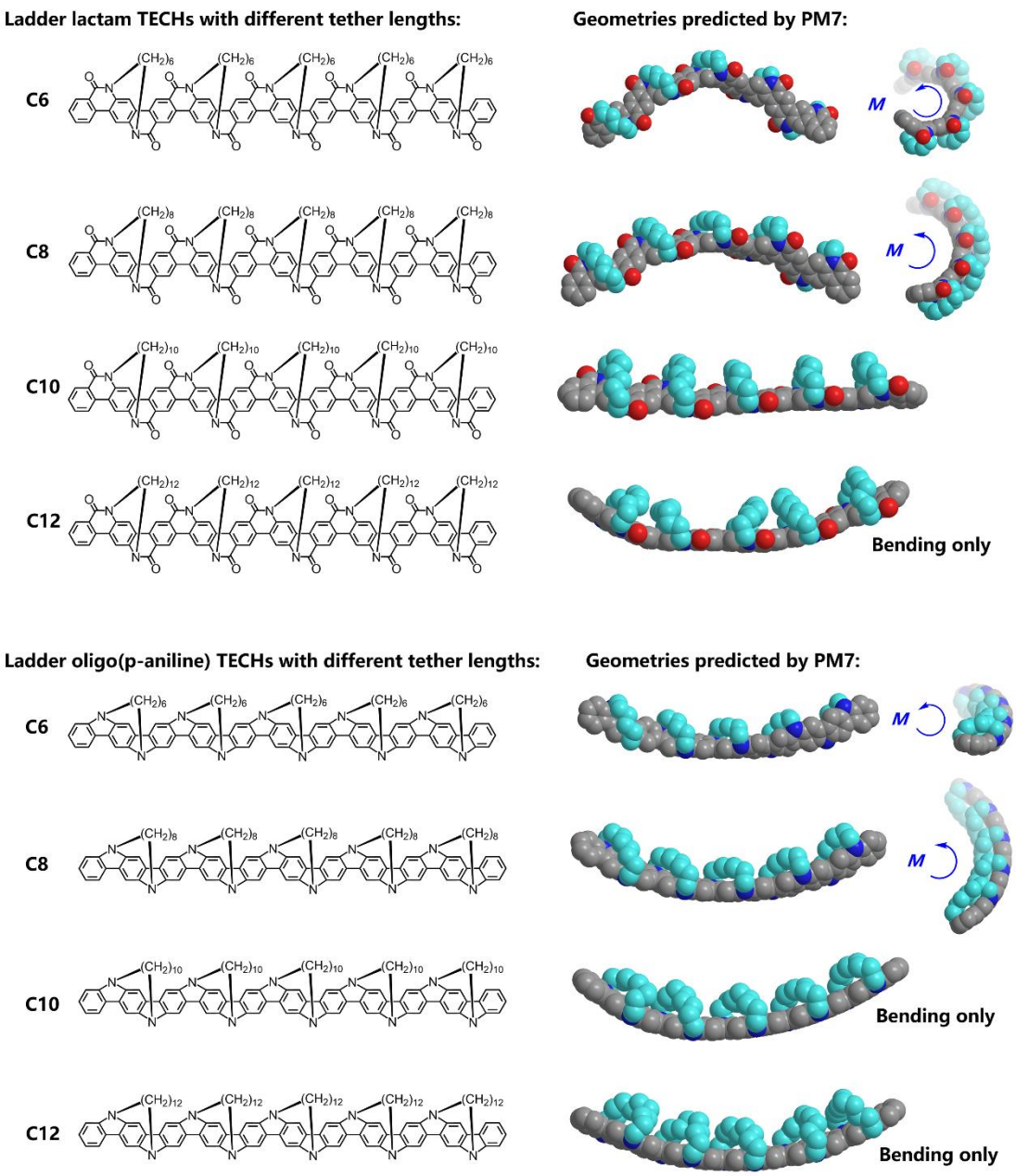


Fig. S1. The influence of tether length to the structures of TECHs. Note: the geometries were optimized at PM7 level; hydrogens are omitted for clarity; the tethers are highlighted in sky blue; for simplification, only the *M*-helices were presented.

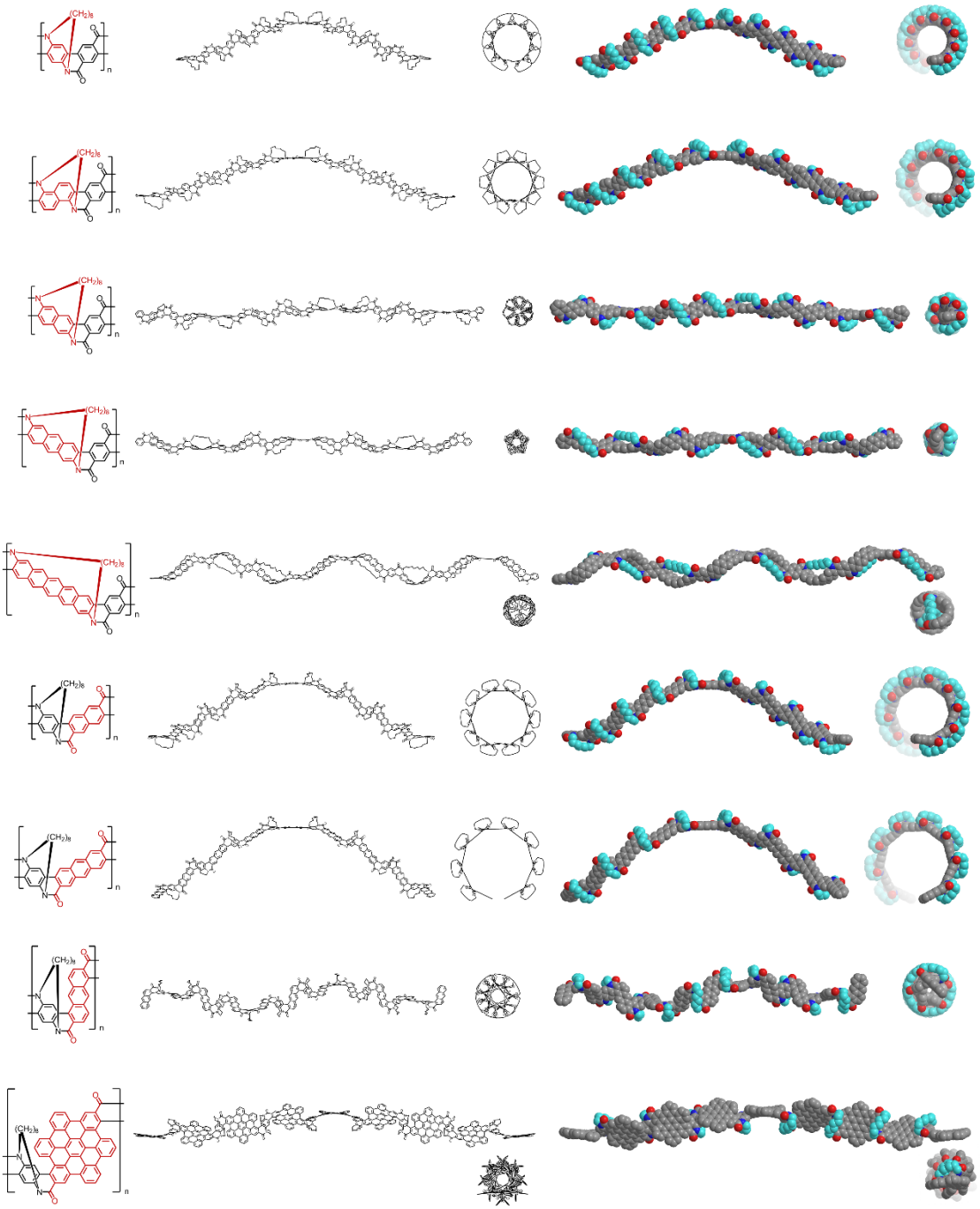
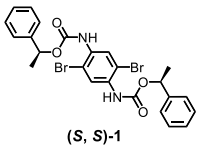


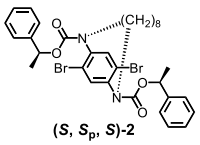
Fig. S2. Some designed TECHs with different chiral tethering units and docking units. Note: the tether length is fixed at C8; the geometries were optimized at PM7 level; hydrogens are omitted for clarity; tethers are highlighted in sky blue; for simplification, only the *M*-helices were presented.

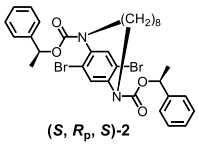
3. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co., Derthon Co., SunaTech Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques.


(*S*, *S*)-1

(*S*, *S*)-1. To a solution of 2,5-dibromoterephthalic acid (600 mg, 1.85 mmol) in toluene (12 mL) was added diphenylphosphoryl azide (1.20 mL, 5.57 mmol), triethylamine (0.77 mL, 5.54 mmol) and (S)-1-phenylethanol (1.12 mL, 9.26 mmol) under nitrogen The reaction mixture was heated to 80 °C and stirred for 30 min. The reaction solution was poured into methanol and sonicated. After filtration, **(*S*, *S*)-1** was obtained as a white powdered solid (833 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.37 (s, 2H), 7.39-7.31 (m, 10H), 7.05 (q, 2H), 5.87 (q, J = 6.6 Hz, 2H), 1.62 (d, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 152.40, 141.27, 131.78, 128.62, 128.13, 126.05, 122.86, 111.70, 74.11, 22.24. MALDI-TOF HRMS (m/z): $C_{24}H_{22}Br_2N_2O_4Na$ [M + Na^+] calc. 582.9844, found 582.9848.


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

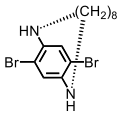

(*S*, R_p, *S*)-2

(*S*, S_p, *S*)-2 and (*S*, R_p, *S*)-2. To a solution of (*S*, *S*)-1 (100 mg, 0.18 mmol), Cs_2CO_3 (232 mg, 0.71 mmol) and KI (118 mg, 0.71 mmol) in DMF (33 mL) was added 1,8-dibromooctane (97 μL, 0.53 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 15 min and then stirred at 80 °C for 1 h. After removal of the solvent under reduced pressure, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:3) as eluent to give **(*S*, S_p, *S*)-2** as a white solid (31 mg, 26%) and **(*S*, R_p, *S*)-2** as a white solid (16 mg, 13%). The Rf values for (*S*, S_p, *S*)-2 and (*S*, R_p, *S*)-2 on TLC are 0.19 and 0.16, respectively, with CH_2Cl_2 as the eluent.

(*S*, S_p, *S*)-2: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.51-7.19 (m, 12H), 5.88 (m, 2H), 3.88-3.61 (m, 4H), 1.66-1.26 (m, 10H), 0.94-0.70 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 154.53, 154.00, 153.88, 142.15, 142.07, 141.98, 139.64, 139.56, 135.89, 135.21, 128.44, 127.76, 127.64, 125.94, 125.85, 125.54, 123.56, 123.15, 74.31, 74.22, 74.10, 47.21, 26.67, 26.43, 26.28, 26.20, 25.80, 25.50, 23.14, 22.75, 22.65. MALDI-TOF HRMS (m/z): $C_{32}H_{36}Br_2N_2O_4Na$ [M + Na^+] calc. 693.0940, found 693.0944. Single crystals of (*S*, S_p, *S*)-2 were obtained by diffusion of hexane into the (*S*, S_p, *S*)-2 solution in CH_2Cl_2. Formula: $C_{32}H_{36}Br_2N_2O_4$; formula weight: 672.45; crystal system: monoclinic; space group: P 2_1; color of crystal: colorless; unit cell parameters: a = 9.0653(2) Å, b = 8.3658(2) Å, c = 20.4585(5) Å, α = 90°, β = 94.228(2)°, γ = 90°, V = 1547.32(6) Å^3; temperature for data collection: 293(2) K; Z = 2; final R indices [I >2σ(I)]: R_1 = 0.0753, wR_2 = 0.2080; GOF on F^2: 1.072; Flack parameter: -0.04(2). The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (**CCDC-2354646**).

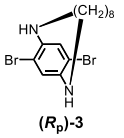
(*S*, R_p, *S*)-2: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.58-7.22 (m, 12H), 5.95-5.85 (m, 2H), 3.88-3.69 (m, 4H), 1.65-1.45 (m, 10H), 0.88-0.75 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 154.46, 154.13, 154.06, 141.91, 141.83, 141.75, 139.75, 139.54, 135.81, 135.65, 135.43, 128.57, 128.23, 127.90, 127.51, 126.09, 126.04, 125.62, 123.40, 123.22, 74.37, 74.24, 74.10, 47.35, 46.96, 26.65, 26.37, 26.16, 25.77, 25.46, 23.07, 22.75, 22.62. MALDI-TOF HRMS (m/z): $C_{32}H_{36}Br_2N_2O_4Na$ [M + Na^+] calc. 693.0940, found 693.0941. Single crystals of (*S*, R_p, *S*)-2 were obtained by diffusion of hexane into the (*S*, R_p, *S*)-2 solution in CH_2Cl_2. Formula: $C_{32}H_{36}Br_2N_2O_4$; formula weight: 672.45; crystal system: monoclinic; space group: P 2_1; color of crystal: colorless; unit cell parameters: a =

11.6760(5) Å, b = 9.3251(4) Å, c = 13.9069(5) Å, α = 90°, β = 93.0360(10)°, γ = 90°, V = 1512.06(11) Å^3; temperature for data collection: 100 K; Z = 2; final R indices [I >2σ(I)]: R_1 = 0.0279, wR_2 = 0.0687; GOF on F^2: 1.046; Flack parameter: 0.053(8). The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (**CCDC-2354656**).



(S_p)-3

(S_p)-3. To a solution of (*S*, S_p, *S*)-2 (200 mg, 0.30 mmol) in CH_2Cl_2 (20 mL) was added trifluoroacetic acid (1 mL, 13 mmol). The reaction mixture was stirred at room temperature for 2 d. The reaction mixture was neutralised with aqueous sodium bicarbonate and extratcted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2 as eluent to give **(S_p)-3** as a white solid (105 mg, 94%, 98.4% ee). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.10 (s, 2H), 3.46 (br, 2H), 3.24-3.21 (m, 4H), 1.69-1.67 (m, 2H), 1.17-1.15 (m, 2H), 1.03-0.94 (m, 4H), 0.73-0.64 (m, 2H), 0.58-0.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 141.17, 124.11, 115.48, 48.57, 28.25, 26.71, 23.90. MALDI-TOF HRMS (m/z): $C_{14}H_{20}Br_2N_2$ [M^+] calc. 373.9993, found 373.9988.



(R_p)-3

(R_p)-3. To a solution of (*S*, R_p, *S*)-2 (400 mg, 0.60 mmol) in CH_2Cl_2 (40 mL) was added trifluoroacetic acid (2 mL, 26 mmol). The reaction mixture was stirred at room temperature for 2 d. The reaction mixture was neutralised with aqueous sodium bicarbonate and extratcted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2 as eluent to give **(R_p)-3** as a white solid (213 mg, 95%, 99.7% ee). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.10 (s, 2H), 3.69 (br, 2H), 3.24-3.22 (m, 4H), 1.74-1.64 (m, 2H), 1.20-1.10 (m, 2H), 1.03-0.94 (m, 4H), 0.73-0.65 (m, 2H), 0.61-0.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 141.19, 124.11, 115.49, 48.58, 28.27, 26.72, 23.90. MALDI-TOF HRMS (m/z): $C_{14}H_{20}Br_2N_2$ [M^+] calc. 373.9993, found 373.9994.

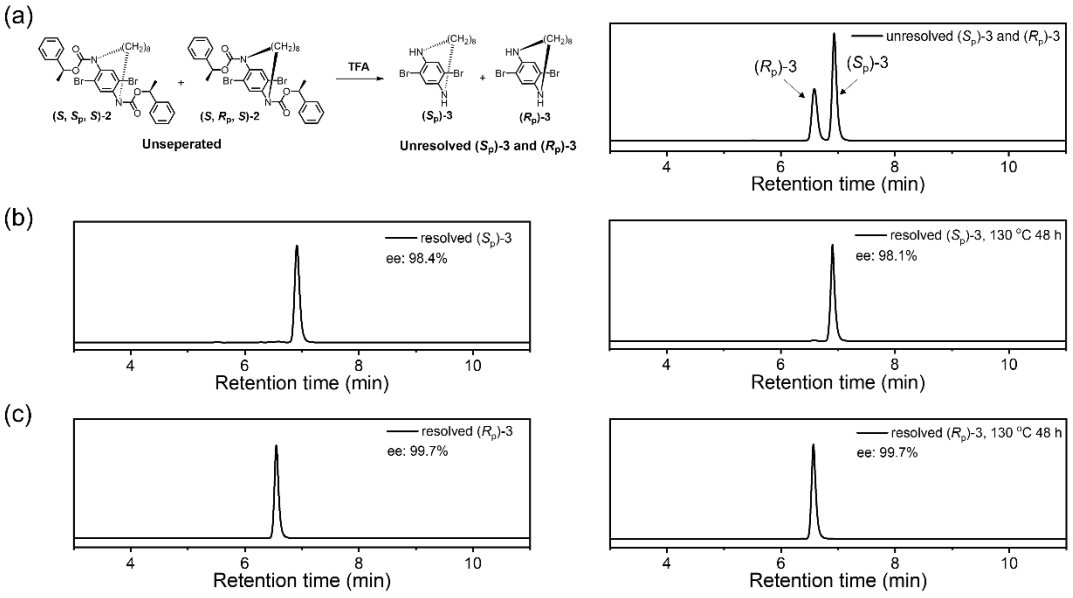
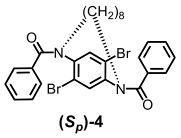


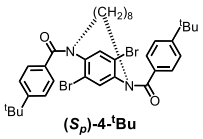
Fig. S3. (a) Preparation of the unresolved **(S_p)-3** and **(R_p)-3** sample and its chiral HPLC profile; (b) HPLC profiles of the resolved **(S_p)-3** before and after the thermal treatment (130 °C, 48 h, in

chlorobenzene); (c) HPLC profiles of the resolved **(R_p)-3** before and after the thermal treatment (130 °C, 48 h, in chlorobenzene). Chiral HPLC analysis conditions: column: CHIRALPAK IB N-3 (IBN3CE-VI007); column size: 0.46 cm × 25 cm; mobile phase: MeOH/DCM = 60/40 (V/V); flow rate: 0.6 mL/min; temperature: 25 °C.



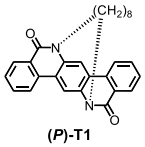
(S_p)-4

(S_p)-4. To a solution of (S_p)-3 (52 mg, 0.14 mmol) in THF (1 mL) was added benzoyl chloride (39 μL, 0.34 mmol) and triethylamine (192 μL, 1.38 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 30 min. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:20) as eluent to give **(S_p)-4** as a white solid (79 mg, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.32-7.18 (br, 12H), 4.15 (br, 2H), 3.78 (br, 2H), 1.58 (br, 2H), 1.40 (br, 2H), 0.87-0.80 (br, 8H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 169.92, 141.40, 136.84, 135.35, 133.26, 130.17, 130.02, 128.34, 128.21. 127.81. 122.76. 45.96, 26.12, 25.87. MALDI-TOF HRMS (m/z): $C_{28}H_{29}Br_2N_2O_2$ [M + H^+] calc. 583.0596, found 583.0595.



(S_p)-4-^{t}Bu

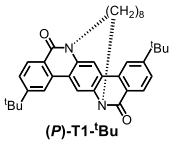
(S_p)-4-^{t}Bu. To a solution of (S_p)-3 (70 mg, 0.19 mmol) in THF (2 mL) was added 4-tert-butylbenzoyl chloride (111 μL, 0.56 mmol) and triethylamine (268 μL, 1.93 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 5 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:20) as eluent to give **(S_p)-4-^{t}Bu** as a white solid (126 mg, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.38 (br, 10H), 4.20-3.72 (br, 4H), 1.59 (br, 2H), 1.45 (br, 2H), 1.30 (s, 18H), 0.86 (br, 8H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 170.39, 153.86, 141.91, 136.71, 132.32, 129.98, 128.41, 125.40, 125.02, 122.12, 34.83, 31.14, 26.01, 25.93. MALDI-TOF HRMS (m/z): $C_{36}H_{45}Br_2N_2O_2$ [M + H^+] calc. 695.1848, found 695.1849.



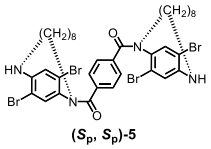
(*P*)-T1

(*P*)-T1. To a solution of (S_p)-4 (50 mg, 0.086 mmol) in DMA (1.5 mL) was added palladium diacetate (8 mg, 0.036 mmol), tricyclohexylphosphonium tetrafluoroborate (19 mg, 0.052 mmol) and cesium carbonate (112 mg, 0.34 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 10 min. The color of the reaction mixture turned black. The reaction mixture was washed with water and extracted with petroleum ether for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:8) as eluent to give **(*P*)-T1** as a yellow solid (34 mg, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.55-8.52 (m, 2H), 8.18 (s, 2H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.80 (t, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 2H), 5.17 (m, 2H), 4.19 (m, 2H), 1.75 (m, 2H), 1.48-1.22 (m, 2H), 0.84 (m, 4H), 0.57 (m, 2H), -(0.25-0.33) (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.78, 133.99, 132.71, 132.42, 129.23, 128.74, 126.50, 122.05, 121.93, 111.34, 44.97, 28.97, 27.02, 26.47. MALDI-TOF HRMS (m/z): $C_{28}H_{26}N_2O_2$ [M^+] calc. 422.1994, found 422.1993. Single crystals of (*P*)-T1 were obtained by diffusion of methanol into the (*P*)-T1 solution in CH_2Cl_2. Formula: $C_{28}H_{26}N_2O_2$; formula weight: 422.51; crystal system: monoclinic; space group: P 2_1; color of crystal: yellow; unit cell parameters: *a* = 8.6414(4) Å, *b* = 10.4890(5) Å,

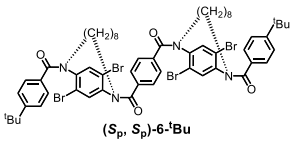
c = 11.9877(6) Å, α = 90°, β = 95.388(2)°, γ = 90°, V = 1081.76(9) Å^3; temperature for data collection: 100.0 K; Z = 2; final R indices [I >2σ(I)]: R_1 = 0.0500, wR_2 = 0.1304; GOF on F^2: 1.051; Flack parameter: 0.06(18). The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (**CCDC-2354657**).


(*P*)-T1-^{t}Bu

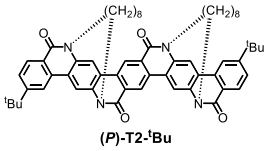
(*P*)-T1-^{t}Bu. To a solution of (S_p)-4-^{t}Bu (100 mg, 0.14 mmol) in DMA (3 mL) was added palladium diacetate (13 mg, 0.058 mmol), tricyclohexylphosphonium tetrafluoroborate (32 mg, 0.087 mmol) and cesium carbonate (187 mg, 0.57 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 10 min. The color of the reaction mixture turned black. The reaction mixture was washed with water and extracted with petroleum ether for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(*P*)-T1-^{t}Bu** as a yellow solid (65 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.46 (d, J = 8.4 Hz, 2H), 8.16 (s, 2H), 8.08 (d, J = 1.7 Hz, 2H), 7.70 (dd, J = 8.4, 1.8 Hz, 2H), 5.21-5.15 (m, 2H), 4.23-4.16 (m,2H), 1.81-1.75 (m, 2H), 1.52-1.42 (m, 20H), 0.88-0.83 (m, 4H), 0.64-0.57 (m, 2H), -(0.15-0.24) (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.84, 156.32, 134.18, 132.26, 129.04, 126.71, 124.20, 122.35, 117.90, 111.10, 44.96, 35.51, 31.26, 29.05, 27.08, 26.47. MALDI-TOF HRMS (m/z): $C_{36}H_{42}N_2O_2$ [M^+] calc. 534.3246, found 534.3240.


(S_p, S_p)-5

(S_p, S_p)-5. To a solution of (S_p)-3 (1.07 g, 2.85 mmol) and terephthaloyl chloride (288 mg, 1.42 mmol) in CH_2Cl_2 (110 mL) was added triethylamine (2.13 mL, 15.35 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(S_p, S_p)-5** as a white solid (1.20 g, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.64-7.43 (br, 4H), 7.12-6.88 (m, 4H), 4.34 (br, 0.6H), 4.17-4.12 (m, 2H), 3.65-3.60 (m, 2H), 3.51-3.48 (m, 2H), 3.20-3.14 (m, 2H), 1.84-1.82 (br, 2H), 1.47 (br, 4H), 1.16-0.90 (m, 12H), 0.70 (br, 2H), 0.43 (br, 2H), 0.08 (br, 2H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 169.90, 146.65, 137.38, 135.06, 131.21, 127.84, 123.15, 121.43, 111.78, 47.57, 45.01, 27.56, 27.00, 26.52, 26.06, 25.15, 22.05. MALDI-TOF HRMS (m/z): $C_{36}H_{43}Br_4N_4O_2$ [$M + H^+$] calc. 879.0120, found 879.0120.


(S_p, S_p)-6-^{t}Bu

(S_p, S_p)-6-^{t}Bu. To a solution of (S_p, S_p)-5 (82 mg, 0.093 mmol) in THF (2 mL) was added 4-tert-butylbenzoyl chloride (55 μL, 0.28 mmol) and triethylamine (134 μL, 0.97 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 5 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(S_p, S_p)-6-^{t}Bu** as a white solid (95 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.31 (br, 16H), 4.12-3.77 (br, 8H), 1.57-1.45 (br, 8H), 1.30 (s, 18H), 0.86 (br, 16H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 153.92, 140.99, 136.98, 136.77, 136.52, 136.14, 132.24, 128.40, 128.02, 124.94, 122.93, 46.84, 34.87, 31.21, 26.02, 25.92. MALDI-TOF HRMS (m/z): $C_{58}H_{67}Br_4N_4O_4$ [$M + H^+$] calc. 1199.1896, found 1199.1897.

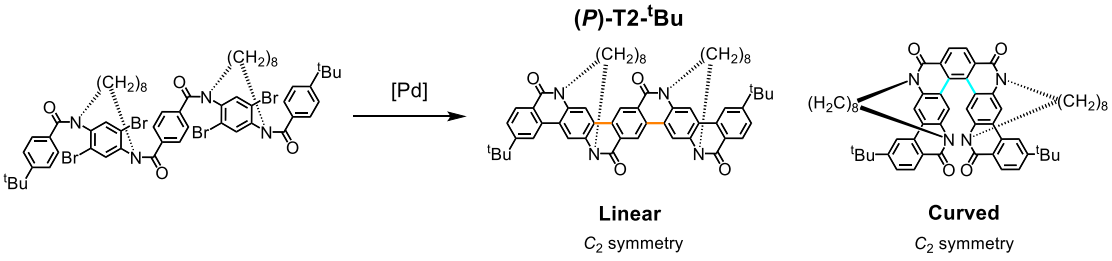


(*P*)-T2-^{t}Bu

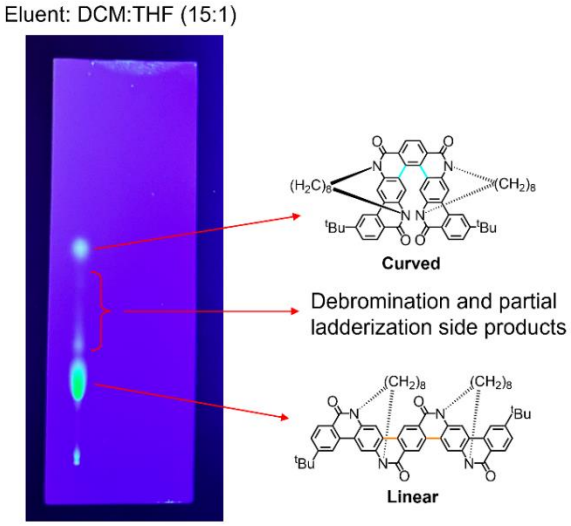
(*P*)-T2-^{t}Bu. To a solution of (S_p, S_p)-6-^{t}Bu (70 mg, 0.058 mmol) in DMA (2 mL) was added palladium diacetate (12 mg, 0.053 mmol), tricyclohexylphosphonium tetrafluoroborate (29 mg, 0.079 mmol) and cesium carbonate (174 mg, 0.53 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:6) as eluent to give **(*P*)-T2-^{t}Bu** as a yellow solid (40 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.06 (s, 2H), 8.38 (d, J = 8.5 Hz, 2H), 8.18 (s, 2H), 8.14 (s, 2H), 8.09 (d, J = 1.5 Hz, 2H), 7.71 (dd, J = 8.5, 1.6 Hz, 2H), 5.25-5.21 (m, 2H), 5.03-4.99 (m, 2H), 4.30-4.25 (m, 2H), 4.12-4.07 (m, 2H), 1.08 (br, 2H), 1.71-1.68 (br, 2H), 1.52 (s, 18H), 1.46-1.36 (br, 4H), 0.87-0.79 (br, 8H), 0.61-0.55 (br, 4H), -(0.24-0.25) (br, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.40, 161.21, 156.41, 134.74, 133.58, 131.85, 131.74, 129.17, 128.89, 127.07, 124.30, 123.45, 123.12, 121.27, 117.84, 111.61, 111.38, 45.57, 44.45, 35.56, 31.31, 29.14, 29.04, 27.08, 26.92, 26.57, 26.33. MALDI-TOF HRMS (m/z): $C_{58}H_{62}N_4O_4$ [M^+] calc. 878.4771, found 878.4765. Single crystals of (*P*)-T2-^{t}Bu were obtained by diffusion of methanol into the (*P*)-T2-^{t}Bu solution in CH_2Cl_2. Formula: $C_{119}H_{140}N_8O_{13}$; formula weight: 1890.38 (two (*P*)-T2-^{t}Bu and, three CH_3OH two H_2O were included in a cell); crystal system: monoclinic; space group: P 2_1; color of crystal: yellow; unit cell parameters: a = 13.8368(13) Å, b = 22.1444(19) Å, c = 17.5091(16) Å, α = 90°, β = 110.064(4)°, γ = 90°, V = 5039.3(8) Å^3; temperature for data collection: 170 K; Z = 2; final R indices [I >2σ(I)]: R_1 = 0.0676, wR_2 = 0.1690; GOF on F^2: 1.090; Flack parameter: 0.11(12). The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (**CCDC-2354658**).

Isolation of the curved isomer from the side products of (*P*)-T2-^{t}Bu.

The ring-closing reaction for **(*P*)-T2-^{t}Bu** would generate two possible isomers (linear and curved). See below:



The curved isomer shows much lower polarity than the dominate linear isomer as indicated by the TLC plate of the ring-closing reaction below. The structure of the curved isomer was confirmed by comparison of its 2D NMR data with that of the linear isomer (see Fig. S149).



TLC for the ladderization reaction toward **(*P*)-T2-^{t}Bu**

Two possible isomers for (*P*)-T2-^{t}Bu:

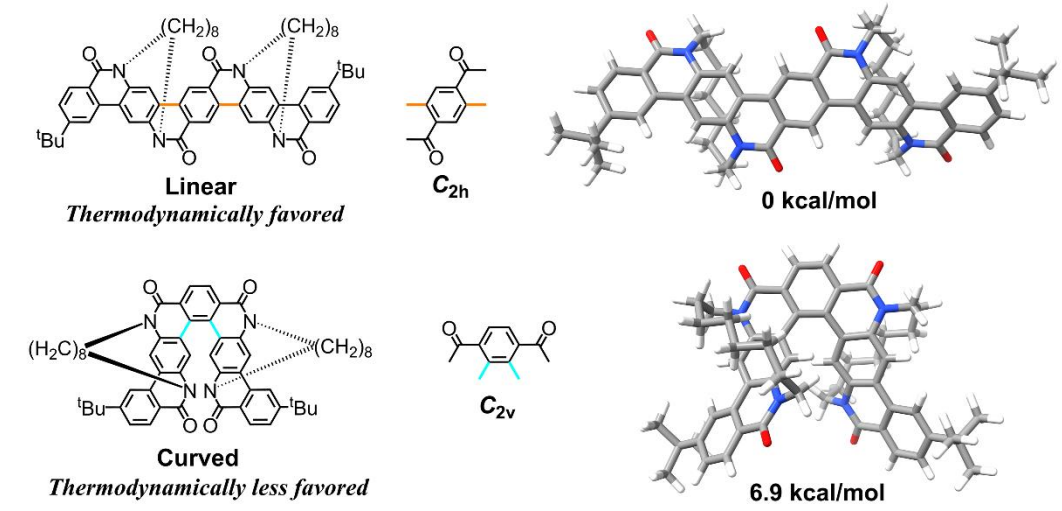
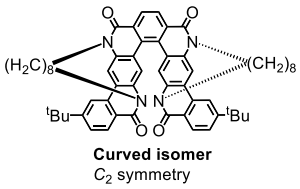
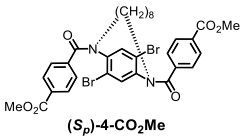


Fig. S4. Two isomers for **(*P*)-T2-^{t}Bu** and their optimized structures and relative Gibbs free energies (DFT, M06-2X(D3)/6-31G(d,p) level). Note: the bonds in orange denote the desired linear ladderization for TECHs, whereas the bonds in cyan denote the undesired curved ladderization.



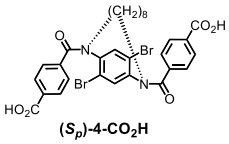
The curved isomer was isolated from the side products mixture via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:15) as eluent (3.6 mg, 7%). There are only 6 aromatic proton peaks and 17 sp^2-carbon peaks found for the curved isomer in the ^{1}H-NMR and ^{13}C-NMR spectra, respectively, suggesting its C_2-symmetry. **Curved isomer of (*P*)-T2-^{t}Bu**: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.76 (s, 2H), 8.38 (d, J = 8.4 Hz, 2H), 8.24 (s, 2H), 8.12 (d, J = 1.5 Hz, 2H), 7.73 (dd, J = 8.4, 1.7 Hz, 2H), 7.62 (s, 2H), 5.20-5.15 (m, 2H), 4.71-4.66 (m, 2H), 4.38-4.33 (m, 2H), 3.31-3.26 (m, 2H), 1.81-1.68 (br, 4H), 1.52 (s, 18H), 1.45-1.36 (br, 2H), 1.14 (br, 2H), 0.88 (br, 4H), 0.69 (br, 2H), 0.51 (br, 6H), -0.36 (br, 2H), -0.65 (br, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.64, 161.03, 156.55, 134.61, 131.88, 131.79,

130.12, 130.10, 129.23, 128.39, 127.36, 124.47, 123.74, 118.51, 118.01, 116.56, 110.00, 44.71, 44.05, 35.56, 31.29, 29.69, 28.47, 28.39, 26.74, 26.06, 26.02, 25.93. MALDI-TOF HRMS (m/z): $C_{58}H_{62}N_4O_4$ [M^+] calc. 878.4771, found 878.4763.



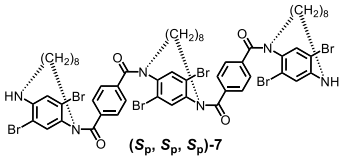
(*S*$_p$)-4-CO_2Me

(*S*$_p$)-4-CO_2Me. To a solution of (*S*$_p$)-3 (450 mg, 1.20 mmol) in THF (7 mL) was added methyl 4-(chlorocarbonyl)benzoate (714 mg, 3.59 mmol) and triethylamine (1.70 mL, 12.25 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 1.5 h. The reaction was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(*S*$_p$)-4-CO_2Me** as a white solid (738 mg, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.11-7.23 (br, 10H), 4.15-3.46 (br, 10H), 1.59 (br, 2H), 1.40 (br, 2H), 0.89-0.73 (br, 8H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 168.85, 166.08, 141.24, 139.34, 136.85, 131.77, 129.00, 128.24, 122.93, 52.36, 46.07, 26.11, 25.90, 25.78. MALDI-TOF HRMS (m/z): $C_{32}H_{33}Br_2N_2O_6$ [M + H^+] calc. 699.0705, found 699.0704.



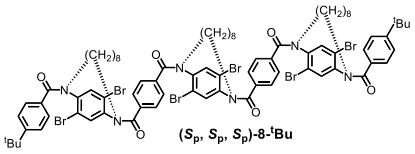
(*S*$_p$)-4-CO_2H

(*S*$_p$)-4-COOH. To a solution of (*S*$_p$)-4-CO_2Me (590 mg, 0.84 mmol) in THF (12 mL) was added KOH (142 mg, 2.54 mmol), ethanol (12 mL) and H_2O (3 mL). The reaction mixture was stirred at 70 °C for 1 h. The reaction mixture was neutralised with dilute hydrochloric acid. Then, THF in the mixture was removed under reduced pressure. After filtration, **(*S*$_p$)-4-COOH** was obtained as a white solid (550 mg, 97%). ^{1}H NMR (DMSO-d6, 400 MHz, δ/ppm): 13.19 (br, 1.5H), 8.23-7.41 (br, 10H), 3.93 (br, 2H), 3.56 (br, 2H), 1.48 (br, 4H), 0.91-0.82 (br, 8H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 166.20, 156.59, 140.26, 140.06, 139.10, 136.15, 134.97, 133.60, 131.98, 129.30, 128.03, 127.89, 126.46, 123.02, 25.58, 25.35, 24.99. MALDI-TOF HRMS (m/z): $C_{30}H_{29}Br_2N_2O_6$ [M + H^+] calc. 671.0392, found 671.0393.

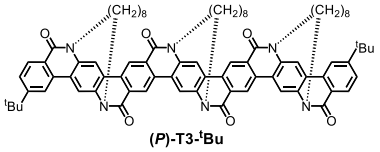


(*S*$_p$, *S*$_p$, *S*$_p$)-7

(*S*$_p$, *S*$_p$, *S*$_p$)-7. To a solution of (*S*$_p$)-4-COOH (100 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) was added oxalyl chloride (2 M in CH_2Cl_2, 0.60 mL, 1.20 mmol) and 1 drop of DMF under nitrogen. After stirring at room temperature for 30 min, the solvent was removed under reduced pressure. To the resulting solid was sequentially added CH_2Cl_2 (5 mL), triethylamine (0.21 mL, 1.52 mmol) and (*S*$_p$)-3 (118 mg, 0.31 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:4) as eluent to give **(*S*$_p$, *S*$_p$, *S*$_p$)-7** as a white solid (196 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.44-6.90 (br, 14H), 4.28-3.11 (br, 14H), 1.82-1.81 (br, 2H), 1.50 (br, 8H), 1.23-0.74 (br, 22H), 0.42 (br, 2H), 0.13 (br, 2H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 169.59, 169.01, 146.66, 141.26, 138.28, 136.33, 135.89, 135.44, 135.00, 131.13, 128.42, 127.70, 123.37, 123.13, 121.55, 121.25, 111.87, 47.45, 46.66, 45.00, 27.62, 27.06, 26.49, 26.07, 25.89, 25.49, 25.21, 22.08. MALDI-TOF HRMS (m/z): $C_{58}H_{65}Br_6N_6O_4$ [M + H^+] calc. 1383.0168, found 1383.0180.



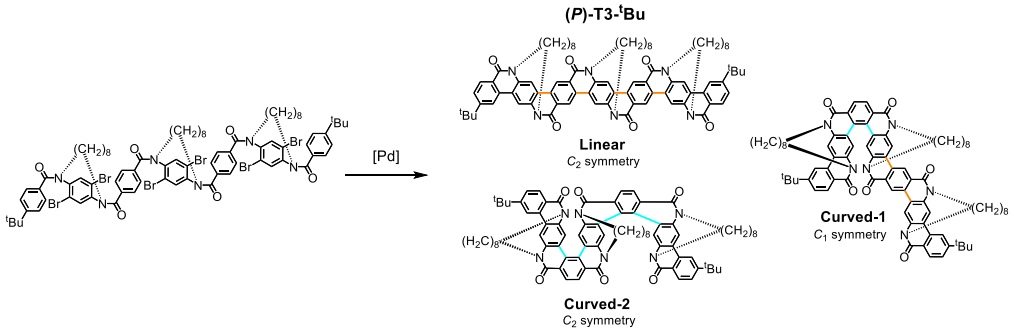
(*S*p, *S*p, *S*p)-8-^{t}Bu. To a solution of (*S*p, *S*p, *S*p)-7 (150 mg, 0.11 mmol) in THF (3 mL) was added 4-tert-butylbenzoyl chloride (64 μL, 0.32 mmol) and triethylamine (156 μL, 1.12 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 34 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:4) as eluent to give **(*S*p, *S*p, *S*p)-8-^{t}Bu** as a white solid (178 mg, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.46-7.15 (br, 22H), 4.15-3.79 (br, 12H), 1.76-1.44 (br, 12H), 1.28 (s, 18H), 0.84 (br, 24H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 169.73, 168.99, 169.59, 153.81, 142.25, 141.29, 140.66, 137.18, 136.98, 136.75, 136.55, 136.35, 132.11, 128.35, 127.79, 125.23, 124.89, 123.30, 122.89, 46.39, 34.82, 31.17, 25.93, 25.49. MALDI-TOF HRMS (m/z): $C_{80}H_{89}Br_6N_6O_6$ [M + H$^+$] calc. 1703.1944, found 1703.1960.



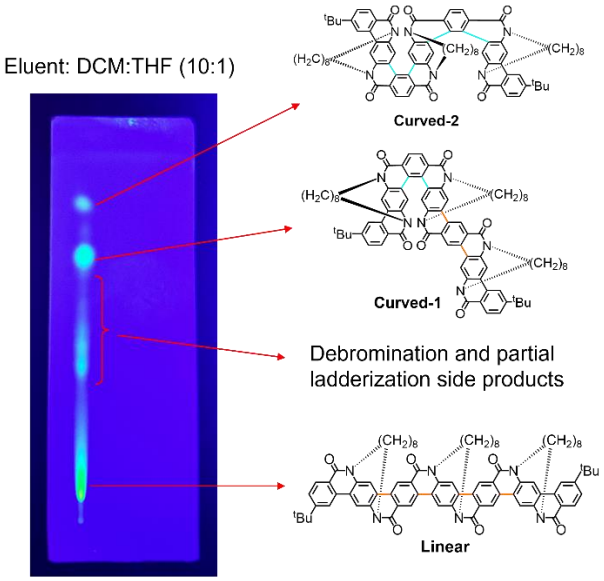
(*P*)-T3-^{t}Bu. To a solution of (*S*p, *S*p, *S*p)-8-^{t}Bu (50 mg, 0.029 mmol) in DMA (2 mL) was added palladium diacetate (8 mg, 0.036 mmol), tricyclohexylphosphonium tetrafluoroborate (19 mg, 0.052 mmol) and cesium carbonate (114 mg, 0.35 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:6) as eluent to give **(*P*)-T3-^{t}Bu** as a yellow solid (22 mg, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.95 (s, 2H), 8.41 (s, 2H), 8.26 (d, *J* = 8.5 Hz, 2H), 8.22 (s, 2H), 8.15 (d, *J* = 1.1 Hz, 2H), 8.04 (s, 2H), 7.69 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.62 (s, 2H), 5.30-5.26 (m, 2H), 5.09-5.05 (m, 2H), 4.57-4.53 (m, 2H), 4.35-4.29 (m, 2H), 4.23-4.17 (m, 2H), 3.70-3.64 (m, 2H), 1.79 (br, 4H), 1.67 (br, 2H), 1.58 (s, 18H), 1.44-1.23 (br, 6H), 0.77-0.64 (br, 12H), 0.48 (br, 6H), -(0.38-0.45) (br, 4H), -(0.55-0.56) (br, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.00, 160.84, 160.38, 156.39, 134.46, 133.73, 133.58, 131.74, 131.72, 130.91, 129.26, 128.78, 128.03, 127.01, 124.21, 123.35, 123.29, 123.12, 121.76, 120.85, 117.86, 111.71, 111.59, 111.25, 45.67, 45.01, 43.72, 35.62, 31.37, 29.04, 28.90, 27.03, 26.77, 26.62, 26.54, 26.45, 26.28. MALDI-TOF HRMS (m/z): $C_{80}H_{82}N_6O_6$ [M$^+$] calc. 1222.6296, found 1222.6295.

Isolation of the curved-1 and curved-2 isomers from the side products of (*P*)-T3-^{t}Bu.

The ring-closing reaction for **(*P*)-T3-^{t}Bu** would generate three possible isomers (linear, curved-1 and curved-2). See below:



The curved-1 and curved-2 isomers shows much lower polarity than the dominate linear isomer as indicated by the TLC plate of the ring-closing reaction below:



TLC for the ladderization reaction toward **(*P*)-T3-^{t}Bu**

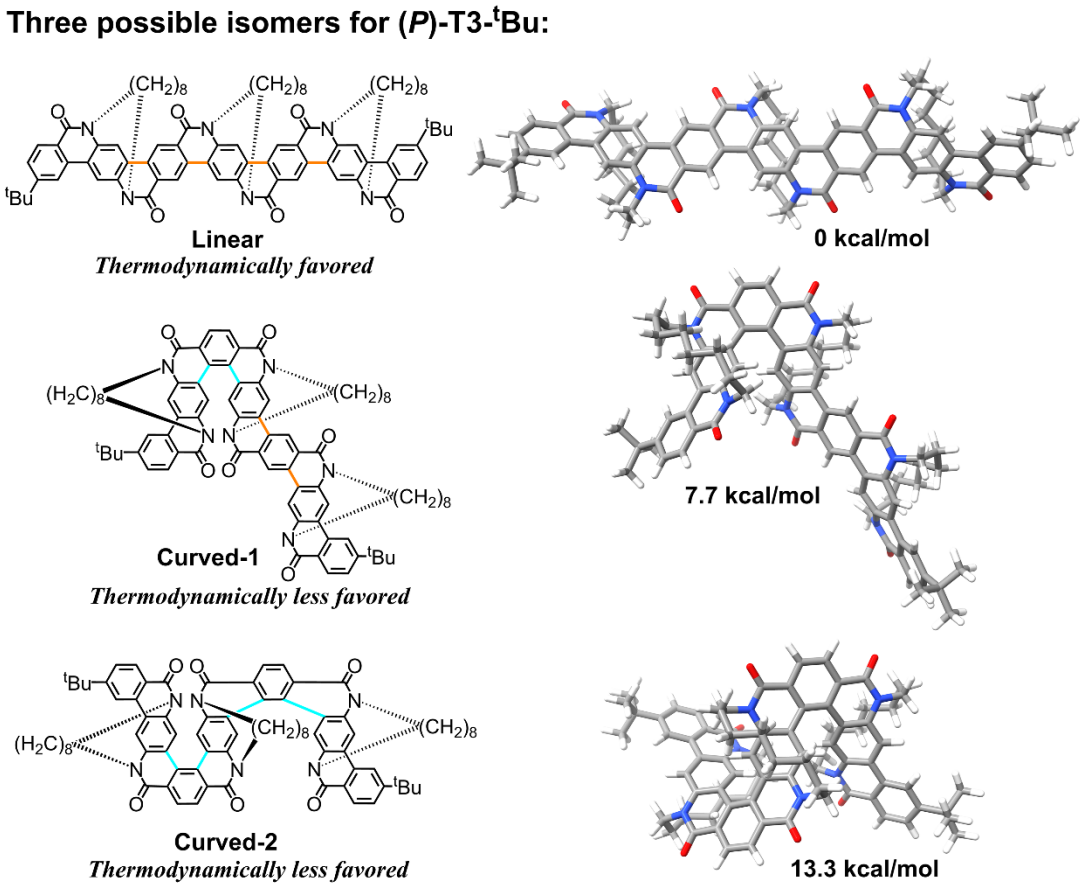
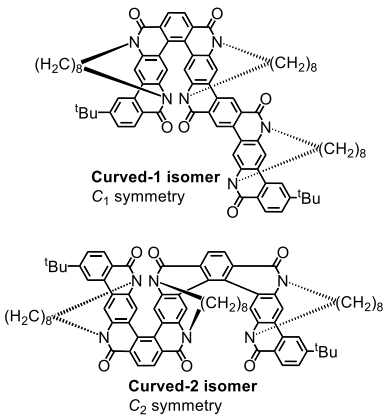
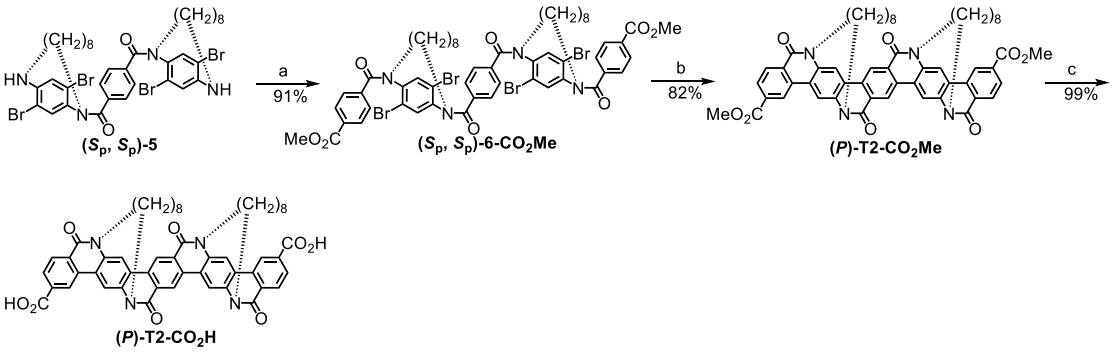


Fig. S5. Three isomers for **(*P*)-T3-^{t}Bu** and their optimized structures and relative Gibbs free energies (DFT, M06-2X(D3)/6-31G(d,p) level). Note: the bonds in orange denote the desired linear ladderization for TECHs, whereas the bonds in cyan denote the undesired curved ladderization.

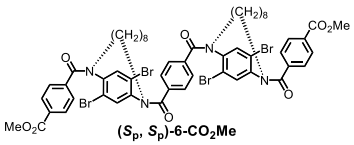


The curved-1 and curved-2 isomers were isolated from the side products mixture via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent (curved-1: 5.4 mg, 15%; curved-2: 2.5 mg, 7%). The NMR spectra indicate the C_1-symmetry and C_2-symmetry of curved-1 and curved-2 isomers, respectively (Fig.s S40-S43). For example, 15 aromatic proton peaks (two singlets overlapped) are observed for curved-1 isomer, but only 8 aromatic proton peaks are observed for curved-2 isomer. **Curved-1 isomer of (*P*)-T3-^{t}Bu**: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.39 (s, 1H), 9.25 (s, 1H), 8.79 (s, 2H), 8.53 (s, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.40 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.25 (s, 1H), 8.24 (s, 1H), 8.12 (d, *J* =1.3 Hz, 1H), 8.10 (d, *J* =1.3 Hz, 1H), 7.73 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.68 (s, 1H), 7.62 (s, 1H), 5.30-5.16 (m, 4H), 4.78-4.74 (m, 1H), 4.67-4.62 (m, 1H), 4.48-4.42 (m, 1H), 4.38-4.24 (m, 3H), 3.40– 3.35 (m, 1H), 3.28 – 3.23 (m, 1H). 1.85-1.65 (m, 8H), 1.51 (s, 9H), 1.50 (s, 9H), 1.24-1.11 (m, 2H), 0.93-0.49 (m, 20H), -(0.15-0.25) (m, 3H), -0.40 (m, 1H), -(0.59-0.65) (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.72, 161.57, 161.44, 161.25, 160.99, 160.93, 156.58, 156.43, 135.36, 134.91, 134.71, 133.71, 132.60, 131.99, 131.75, 131.52, 131.42, 130.42, 130.18, 130.13, 129.84, 129.60, 129.27, 129.17, 128.78, 128.47, 127.37, 127.12, 124.44, 124.38, 124.00, 123.73, 123.28, 122.83, 121.45, 119.27, 118.47, 118.04, 117.99, 116.87, 116.48, 111.91, 111.57, 110.72, 110.11, 45.63, 44.77, 44.71, 44.57, 44.10, 35.55, 31.27, 31.26, 29.20, 29.09, 28.67, 28.50, 28.45, 27.12, 27.01, 26.70, 26.57, 26.42, 26.17, 26.13, 26.01, 25.96. MALDI-TOF HRMS (m/z): $C_{80}H_{82}N_6O_6$ [M^+] calc. 1222.6296, found 1222.6279. **Curved-2 isomer of (*P*)-T3-^{t}Bu**: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.79 (d, *J* = 8.4 Hz, 2H), 8.74 (d, *J* = 8.4 Hz, 2H), 8.43 (d, *J* = 8.4 Hz, 2H), 8.33 (s, 2H), 8.19 (d, *J* = 1.4 Hz, 2H), 7.95 (s, 2H), 7.86 (s, 2H), 7.78 (dd, *J* = 8.4, 1.6 Hz, 2H), 5.22-5.19 (m, 2H), 4.90-4.86 (m, 2H), 4.71-4.67 (m, 2H), 4.40-4.34 (m, 2H), 3.56-3.51 (m, 2H), 3.30-3.25 (m, 2H). 1.84-1.71 (br, 6H), 1.55 (s, 18H), 1.39-1.29 (br, 8H), 0.93 (br, 6H), 0.61 (br, 6H), 0.46-0.36 (br, 4H), -0.29 (br, 2H), -0.48 (br, 2H), -0.78 (br, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.55, 161.02, 160.79, 156.81, 134.86, 132.48, 131.83, 131.70, 130.79, 130.53, 129.99, 129.53, 129.24, 129.09, 128.97, 127.58, 124.39, 123.61, 119.82, 118.43, 117.99, 116.23, 115.78, 110.32, 44.75, 44.36, 43.89, 35.63, 31.30, 29.69, 28.56, 27.86, 26.52, 26.46, 26.39, 26.13, 25.95, 25.09. MALDI-TOF HRMS (m/z): $C_{80}H_{82}N_6O_6$ [M^+] calc. 1222.6296, found 1222.6280.

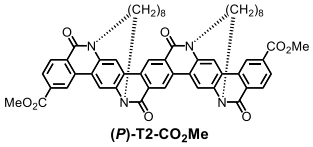


Scheme S1. Synthetic route for **(*P*)-T2-CO_2H**. Reaction conditions: a) Et_3N/ArCOCl, THF, 70 °C;

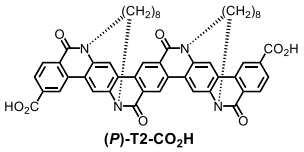
b) $Pd(OAc)_2/PCy_3{\cdot}HBF_4/Cs_2CO_3$, DMA, 130 °C; c) KOH, THF/EtOH/water, 70 °C.



(S_p, S_p)-6-CO_2Me. To a solution of (S_p, S_p)-5 (1.10 g, 1.25 mmol) and methyl 4-(chlorocarbonyl)benzoate (0.74 g, 3.74 mmol) in THF (20 mL) was added triethylamine (1.80 mL, 12.97 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 1.5 h. After cooling to room temperature, the reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(S_p, S_p)-6-CO_2Me** as a white solid (1.36 g, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.85-7.03 (br, 16H), 4.01 (br, 8H), 3.96 (s, 6H), 1.55-1.44 (br, 8H), 0.88-0.78 (16H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 168.78, 168.11, 166.19, 141.61, 140.92, 139.50, 136.77, 136.43, 131.45, 128.97, 128.40, 127.99, 123.74, 123.36, 52.43, 46.92, 46.33, 26.21, 25.87, 25.79. MALDI-TOF HRMS (m/z): $C_{54}H_{55}Br_4N_4O_8$ [M + H^+] calc. 1203.0753, found 1203.0753.

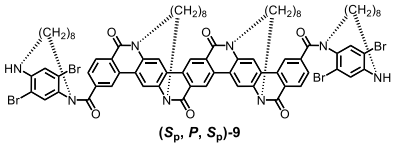


(*P*)-T2-CO_2Me. To a solution of (S_p, S_p)-6-CO_2Me (200 mg, 0.17 mmol) in DMA (10 mL) was added palladium diacetate (30 mg, 0.13 mmol), tricyclohexylphosphonium tetrafluoroborate (73 mg, 0.20 mmol) and cesium carbonate (432 mg, 1.33 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:4) as eluent to give **(*P*)-T2-CO_2Me** as a yellow solid (120 mg, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.83 (s, 2H), 8.82 (d, J = 1.0 Hz, 2H), 8.48 (d, J = 8.3 Hz, 2H), 8.24 (s, 2H), 8.24 (dd, J = 8.3, 1.4 Hz, 2H), 7.98 (s, 2H), 5.20-5.16 (m, 2H), 4.83-4.79 (m, 2H), 4.32-4.26 (m, 2H), 4.10 (s, 6H), 3.98-3.92 (br, 2H), 1.78 (br, 2H), 1.65-1.62 (br, 2H), 1.45-1.31 (br, 4H), 0.86-0.71 (br, 8H), 0.53-0.52 (br, 4H), -(0.39-0.44) (br, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 166.20, 160.81, 160.46, 134.43, 133.83, 132.02, 131.49, 129.76, 129.34, 129.17, 128.76, 123.71, 123.41, 122.03, 121.70, 111.77, 111.64, 52.82, 45.41, 44.57, 29.13, 29.01, 26.99, 26.76, 26.52, 26.40. MALDI-TOF HRMS (m/z): $C_{54}H_{50}N_4O_8$ [M^+] calc. 882.3629, found 882.3630.

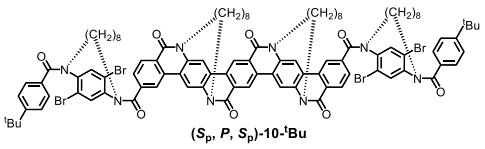


(*P*)-T2-CO_2H. To a solution of (*P*)-T2-CO_2Me (92 mg, 0.10 mmol) in THF (3 mL) was added KOH (18 mg, 0.32 mmol), ethanol (3 mL) and H_2O (1 mL). The reaction mixture was stirred at 70 °C for 1 h. The reaction mixture was neutralised with dilute hydrochloric acid. Then, THF in the mixture was removed under reduced pressure. After filtration, **(*P*)-T2-CO_2H** was obtained as a yellow solid (88 mg, 99%). ^{1}H NMR (DMSO-d6, 400 MHz, δ/ppm): 9.08 (s, 2H), 8.73 (s, 2H), 8.67 (s, 2H), 8.15-8.14 (br, 6H), 4.84 (br, 2H), 4.61 (br, 2H), 4.44 (br, 2H), 4.25 (br, 2H). 1.64-1.48 (br, 4H), 1.17-1.06 (br, 4H), 0.71-0.58 (br, 8H), 0.30 (br, 4H), -(0.62-0.68) (br, 4H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 167.26, 159.74, 133.78, 133.60, 132.21, 131.15, 128.68, 128.59, 128.13, 124.62, 123.51,

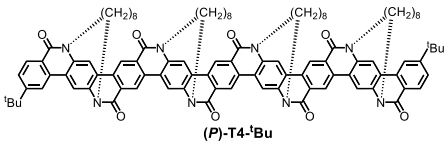
121.62, 121.15, 112.41, 111.98, 44.36, 43.76, 28.83, 26.77, 26.51, 26.19, 26.14. MALDI-TOF HRMS (m/z): $C_{52}H_{46}N_4O_8$ [M^+] calc. 854.3316, found 854.3318.


(S_p, P, S_p)-9

(S_p, P, S_p)-9. To a solution of (P)-T2-CO_2H (88 mg, 0.10 mmol) in CH_2Cl_2 (3 mL) was added oxalyl chloride (2 M in CH_2Cl_2, 412 μL, 0.82 mmol) and 1 drop DMF under nitrogen. After stirring at room temperature for 30 min, the solvent was removed under reduced pressure. To the resulting solid was sequentially added CH_2Cl_2 (8 mL), triethylamine (150 μL, 1.08 mmol) and (S_p)-3 (81 mg, 0.22 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:10) as eluent to give **(S_p, P, S_p)-9** as a yellow solid (130 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.07 (s, 2H), 8.42 (d, 2H), 8.39 (s, 2H), 8.13 (s, 2H), 8.01 (s, 2H), 7.86 (d, 2H), 7.16 (s, 2H), 7.08 (s, 2H), 5.23-5.19 (m, 2H), 5.01-4.98 (m, 2H), 4.32 (br, 2H), 4.22-4.16 (m, 2H), 4.11-4.00 (m, 6H), 3.54-3.50 (m, 2H), 3.23-3.17 (m, 2H). 1.86-0.30 (br, 44H), -(0.44-0.57) (br, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 169.07, 161.02, 160.95, 139.65, 135.66, 134.60, 133.65, 131.68, 129.27, 128.99, 128.60, 127.28, 123.54, 122.53, 122.42, 122.16, 121.63, 121.25, 111.98, 111.73, 47.40, 45.38, 45.05, 44.97, 29.12, 28.85, 27.66, 27.27, 26.68, 26.63, 26.56, 26.25, 26.11, 26.05, 22.64. MALDI-TOF HRMS (m/z): $C_{80}H_{82}Br_4N_8O_6$ [M^+] calc. 1566.3091, found 1566.3110.

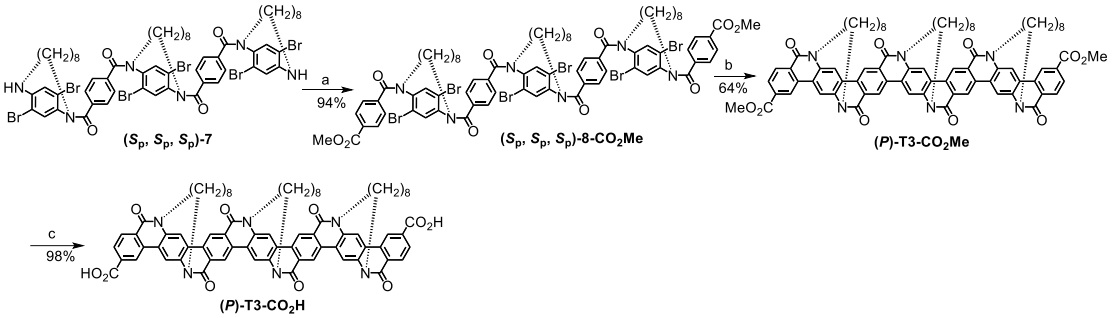

(S_p, P, S_p)-10-^{t}Bu

(S_p, P, S_p)-10-^{t}Bu. To a solution of (S_p, P, S_p)-9 (130 mg, 0.083 mmol) in THF (3 mL) was added 4-tert-butylbenzoyl chloride (49 μL, 0.25 mmol) and triethylamine (84 μL, 0.83 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:10) as eluent to give **(S_p, P, S_p)-10-^{t}Bu** as a yellow solid (140 mg, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.24-7.40 (br, 22H), 5.22-5.09 (br, 4H), 4.40-3.75 (br, 12H), 1.77-1.47 (br, 18H), 1.32 (s, 18), 0.86 (br, 24H), 0.60 (br, 4H), -0.29 (br, 4H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 161.13, 160.63, 142.44, 139.46, 136.90, 134.78, 133.88, 132.04, 128.13, 124.94, 123.70, 122.89, 121.98, 111.85, 45.41, 44.94, 34.86, 31.14, 29.12, 28.98, 26.98, 26.37, 26.16, 25.94. MALDI-TOF HRMS (m/z): $C_{102}H_{106}Br_4N_8O_8$ [M^+] calc. 1886.4867, found 1886.4872.

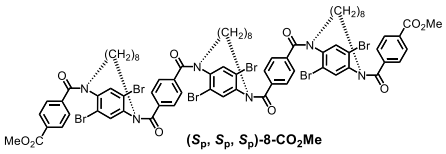

(P)-T4-^{t}Bu

(P)-T4-^{t}Bu. To a solution of (S_p, P, S_p)-10-^{t}Bu (90 mg, 0.048 mmol) in DMA (2 mL) was added palladium diacetate (9 mg, 0.040 mmol), tricyclohexylphosphonium tetrafluoroborate (21 mg, 0.057 mmol) and cesium carbonate (123 mg, 0.38 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:4) as

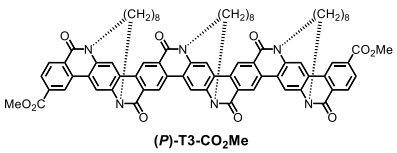
eluent to give **(*P*)-T4-^{t}Bu** as a yellow solid (32 mg, 43%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.14 (s, 2H), 8.70 (s, 2H), 8.40 (s, 2H), 8.20 (s, 2H), 8.19 (s, 2H), 8.16 (d, *J* = 8.5 Hz, 2H), 8.16 (d, *J* = 1.4 Hz, 2H) 7.81 (s, 2H), 7.64 (dd, *J* = 8.8, 1.5 Hz, 2H), 7.62 (s, 2H), 5.32-5.28 (m, 2H), 5.24-5.20 (m, 2H), 4.99-4.95 (m, 2H), 4.69-4.65 (m, 2H), 4.35-4.29 (m, 4H), 4.10-4.05 (m, 2H), 3.74-3.69 (m, 2H), 1.81-1.71 (br, 4H), 1.58 (s, 18H), 1.50-1.37 (br, 8H), 1.30-1.24 (br, 4H), 1.26 (br, 4H), 0.86-0.60 (br, 16H), 0.45 (br, 8H), -0.46 (br, 4H), -0.61 (br, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.00, 160.95, 160.44, 160.27, 156.37, 134.33, 133.94, 133.67, 133.58, 131.81, 131.77, 131.23, 131.00, 129.08, 128.78, 128.27, 128.08, 126.92, 124.14, 123.58, 123.47, 123.40, 123.21, 121.90, 121.50, 120.84, 117.97, 111.96, 111.70, 111.62, 111.30, 45.62, 45.23, 44.84, 43.83, 35.59, 31.36, 28.97, 28.83, 27.01, 26.76, 26.56, 26.40, 26.24. MALDI-TOF HRMS (m/z): $C_{102}H_{102}N_8O_8$ [M^+] calc. 1566.7821, found 1566.7822.



Scheme S2. Synthetic route for **(*P*)-T3-CO_2H**. Reaction conditions: a) Et_3N/ArCOCl, THF, 70 °C; b) $Pd(OAc)_2$/PCy_3·HBF_4/Cs_2CO_3, DMA, 130 °C; c) KOH, THF/EtOH/water, 70 °C.

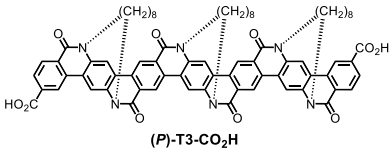


(S_p, S_p, S_p)-8-CO_2Me. To a solution of (S_p, S_p, S_p)-7 (500 mg, 0.36 mmol) and methyl 4-(chlorocarbonyl)benzoate (215 mg, 1.08 mmol) in THF (10 mL) was added triethylamine (519 μL, 3.74 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 1.5 h. After cooling to room temperature, the reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:4) as eluent to give **(S_p, S_p, S_p)-8-CO_2Me** as a white solid (581 mg, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.83-7.04 (br, 22H), 4.04-3.95 (br, 18H), 1.52-1.44 (br, 12H), 0.86-0.76 (br, 24H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 168.71, 168.53, 166.29, 141.12, 139.22, 137.10, 137.02, 136.61, 136.53, 136.26, 131.48, 128.98, 128.53, 128.13, 127.65, 123.92, 123.30, 52.29, 46.70, 46.31, 26.28, 26.11, 25.82, 25.65. MALDI-TOF HRMS (m/z): $C_{76}H_{77}Br_6N_6O_{10}$ [M + H^+] calc. 1707.0801, found 1707.0817.

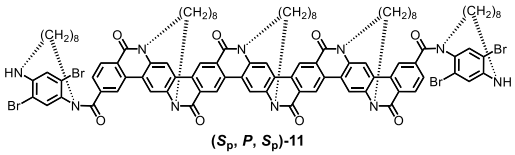


(*P*)-T3-CO_2Me. To a solution of (S_p, S_p, S_p)-8-CO_2Me (100 mg, 0.058 mmol) in DMA (3 mL) was added palladium diacetate (16 mg, 0.071 mmol), tricyclohexylphosphonium tetrafluoroborate (39 mg, 0.11 mmol) and cesium carbonate (228 mg, 0.70 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl

aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:6) as eluent to give **(*P*)-T3-CO_2Me** as a yellow solid (46 mg, 64%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.99 (s, 2H), 8.91 (d, *J* = 0.6 Hz, 2H), 8.43 (d, *J* = 8.4 Hz, 2H), 8.36 (s, 2H), 8.31 (s, 2H), 8.26 (dd, *J* = 8.4, 1.3 Hz, 2H), 8.06 (s, 2H), 7.63 (s, 2H), 5.30-5.26 (m, 2H), 5.07-5.03 (m, 2H), 4.55-4.52 (m, 2H), 4.38-4.33 (m, 2H), 4.22-4.17 (m, 2H), 4.12 (s, 6H), 3.67-3.61 (m, 2H), 1.79-1.78 (br, 2H), 1.66-1.65 (br, 2H), 1.53-1.42 (br, 4H), 1.33-1.20 (br, 4H), 0.84-0.45 (br, 18H), -(0.44-0.57) (br, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 166.24, 160.84, 160.28, 160.25, 134.28, 133.97, 133.84, 132.02, 131.38, 131.28, 129.37, 128.80, 128.15, 123.78, 123.56, 122.07, 121.68, 121.55, 112.03, 111.81, 111.43, 52.84, 45.54, 45.05, 44.16, 29.02, 28.90, 26.99, 26.74, 26.50, 26.42, 26.35. MALDI-TOF HRMS (m/z): $C_{76}H_{70}N_6O_{10}$ [M^+] calc. 1226.5153, found 1226.5157.

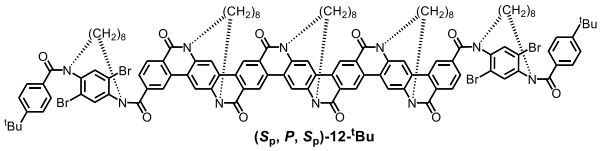

(*P*)-T3-CO_2H

(*P*)-T3-CO_2H. To a solution of (*P*)-T3-CO_2Me (210 mg, 0.17 mmol) in THF (6 mL) was added KOH (29 mg, 0.52 mmol), ethanol (6 mL) and H_2O (1.5 mL). The reaction mixture was stirred at 70 °C for 1 h. The reaction mixture was neutralised with dilute hydrochloric acid. Then, THF in the mixture was removed under reduced pressure. After filtration, **(*P*)-T3-CO_2H** was obtained as a yellow solid (202 mg, 98%). ^{1}H NMR (DMSO-d6, 400 MHz, δ/ppm): 8.88-7.61 (br, 16H), 4.83-3.84 (br, 12H), 1.57-(-1.40) (br, 36H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 166.54, 159.26, 158.96, 158.89, 158.72, 133.14, 132.96, 131.62, 130.39, 127.56, 127.08, 124.10, 122.71, 120.89, 120.45, 111.95, 43.96, 28.67, 28.11, 25.94, 25.53. MALDI-TOF HRMS (m/z): $C_{74}H_{66}N_6O_{10}$ [M^+] calc. 1198.4840, found 1198.4851.


(S_p, *P*, S_p)-11

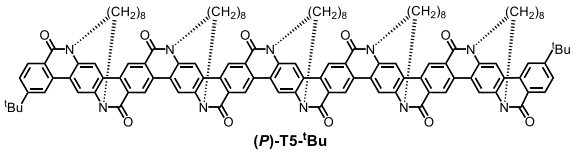
(S_p, *P*, S_p)-11. To a solution of (*P*)-T3-CO_2H (140 mg, 0.12 mmol) in CH_2Cl_2 (3 mL) was added oxalyl chloride (2 M in CH_2Cl_2, 412 μL, 0.82 mmol) and 1 drop DMF under nitrogen. After stirring at room temperature for 30 min, the solvent was removed under reduced pressure. To the resulting solid was sequentially added CH_2Cl_2 (14 mL), triethylamine (168 μL, 1.21 mmol) and (S_p)-3 (92 mg, 0.24 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:6) as eluent to give **(S_p, *P*, S_p)-11** as a yellow solid (180 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.08 (s, 2H), 8.75 (s, 2H), 8.43 (s, 2H), 8.28 (d, *J* = 8.0 Hz, 2H), 8.11 (s, 2H), 8.00 (s, 2H), 7.86 (s, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.18 (s, 2H), 7.09 (s, 2H), 5.27-5.23 (m, 2H), 5.11-5.07 (m, 2H), 4.85-4.81 (m, 2H), 4.25-4.16 (m, 4H), 4.08 (br, 4H), 3.92-3.87 (m, 2H), 3.56-3.54 (m, 2H), 3.23-3.18 (m, 2H), 1.81-0.29 (m, 54H), -(0.47-0.68) (br, 6H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 168.99, 160.88, 160.66, 147.23, 139.58, 135.63, 134.45, 133.94, 133.53, 131.70, 131.54, 131.44, 131.36, 129.17, 128.78, 128.57, 128.51, 127.19, 123.59, 122.57, 122.19, 121.78, 131.33, 121.22, 121.20, 112.05, 111.97, 111.63, 47.49, 45.34, 45.09, 44.76, 29.04, 28.79, 27.70, 27.25, 26.86, 26.59, 26.50, 26.41, 26.29, 26.13, 26.01, 22.56. MALDI-TOF HRMS (m/z): $C_{102}H_{102}Br_4N_{10}O_8$ [M^+] calc. 1910.4616,

found 1910.4646. Single crystals of (S_p, *P*, S_p)-11 were obtained by diffusion of acetonitrile into the (S_p, *P*, S_p)-11 solution in CH_2Cl_2. Formula: $C_{103}H_{104}Br_4Cl_2N_{10}O_8$ (one (S_p, *P*, S_p)-11 and one CH_2Cl_2 were included in a cell); formula weight: 2000.50; crystal system: monoclinic; space group: C 2; unit cell parameters: a = 40.326(2) Å, b = 20.5209(11) Å, c = 16.0320(9) Å, α = 90°, β = 110.733(2)°, γ = 90°, V = 12407.7(12) Å^3; temperature for data collection: 170.0 K; Z = 4; final R indices [I >2σ(I)]: R_1 = 0.0713, wR_2 = 0.1927; GOF on F^2: 0.976; Flack parameter: 0.089(10). The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (**CCDC-2354659**).



(S_p, *P*, S_p)-12-^{t}Bu

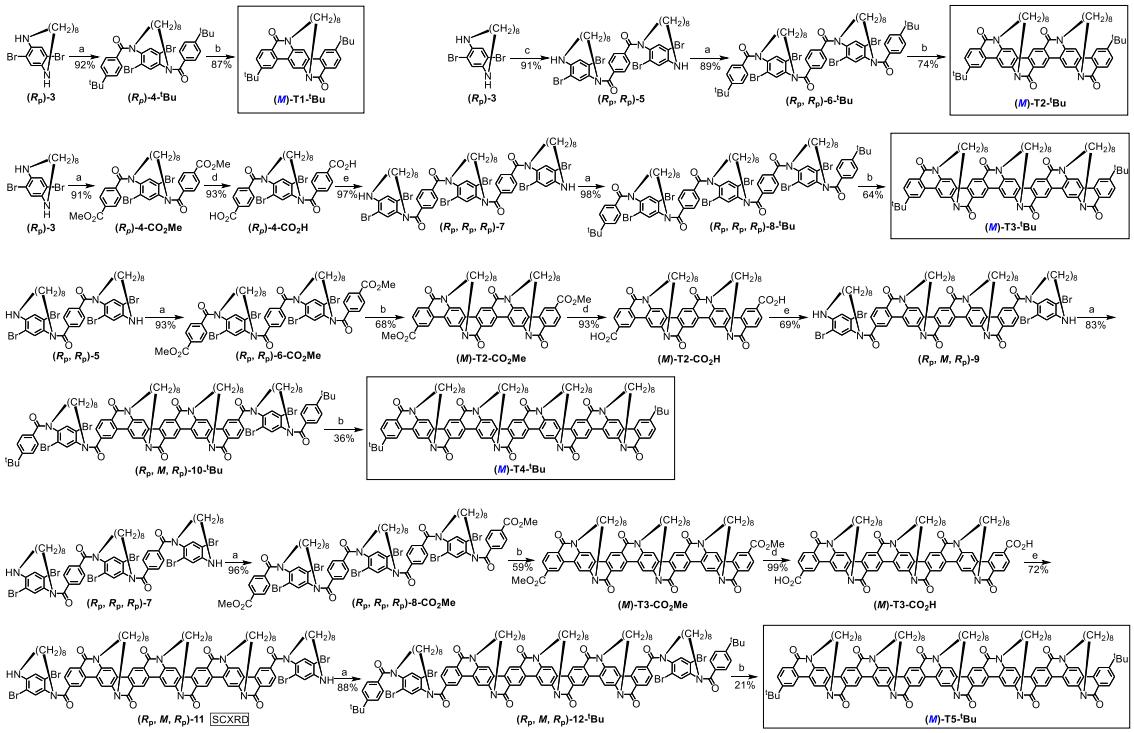
(S_p, *P*, S_p)-12-^{t}Bu. To a solution of (S_p, *P*, S_p)-11 (100 mg, 0.052 mmol) in THF (3 mL) was added 4-tert-butylbenzoyl chloride (31 μL, 0.16 mmol) and triethylamine (75 μL, 0.54 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:6) as eluent to give **(S_p, *P*, S_p)-12-^{t}Bu** as a yellow solid (106 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.21-7.32 (br, 28H), 5.24-3.79 (br, 20H), 1.83-0.55 (br, 72H), -0.35 (br, 6H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 161.04, 160.44, 142.34, 139.54, 136.68, 134.10, 133.83, 132.51,, 132.14, 131.80, 131.54, 128.95, 125.26, 123.72, 122.56, 121.78, 111.98, 45.48, 34.91, 31.18, 29.69, 29.08, 28.89, 27.00, 26.83, 26.41, 26.03, 25.95. MALDI-TOF HRMS (m/z): $C_{124}H_{126}Br_4N_{10}O_{10}$ [M^+] calc. 2230.6392, found 2230.6400.



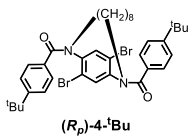
(*P*)-T5-^{t}Bu

(*P*)-T5-^{t}Bu. To a solution of (S_p, *P*, S_p)-12-^{t}Bu (30 mg, 0.014 mmol) in DMA (1 mL) was added palladium diacetate (3 mg, 0.013 mmol), tricyclohexylphosphonium tetrafluoroborate (6 mg, 0.016 mmol) and cesium carbonate (36 mg, 0.11 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:2) as eluent to give **(*P*)-T5-^{t}Bu** as an orange solid (6 mg, 23%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.26 (s, 2H), 8.97 (s, 2H), 8.59 (s, 2H), 8.42 (s, 2H), 8.29 (s, 2H), 8.22 (s, 2H), 8.18 (s, 2H), 8.15 (d, J = 8.5 Hz, 2H), 8.02 (s, 2H), 7.72 (s, 2H), 7.62 (s, 2H), 7.62 (d, J = 7.4 Hz, 2H), 5.32-5.26 (m, 4H), 5.19-5.15 (m, 2H), 4.95-4.91 (m, 2H), 4.72-4.69 (m, 2H), 4.41-4.24 (m, 6H), 4.05-4.00 (m, 2H), 3.76-3.70 (m, 2H), 1.79 (br, 10H), 1.59 (s, 18H), 1.50 (br, 10H), 0.77-0.61 (br, 20H), 0.47 (br, 10H), -0.46 (br, 4H), -(0.60-0.63) (br, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.05, 161.03, 160.60, 160.34, 160.30, 156.38, 134.31, 134.08, 133.84, 133.66, 133.63, 131.88, 131.83, 131.30, 131.24, 131.17, 129.06, 128.83, 128.37, 128.19, 128.14, 126.91, 124.15, 123.71, 123.59, 123.45, 123.27, 122.03, 121.59, 121.51, 120.87, 118.04, 112.16, 112.00, 111.70, 111.68, 111.38, 45.64, 45.30, 45.17, 44.79, 43.87, 35.61, 31.38,

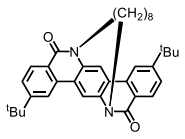
29.01, 28.94, 28.83, 27.05, 26.82, 26.68, 26.56, 26.43, 26.38, 26.24. MALDI-TOF HRMS (m/z): $C_{124}H_{122}N_{10}O_{10}$ [M^+] calc. 1910.9345, found 1910.9355.



Scheme S3. Synthesis of *M*-chirality concave-type TECHs starting from **(R_p)-3**. Reaction conditions: a) Et_3N/ArCOCl, THF, 70 °C; b) $Pd(OAc)_2$/$PCy_3{\cdot}HBF_4$/Cs_2CO_3, DMA, 130 °C; c) Et_3N/terephthaloyl chloride, CH_2Cl_2, r.t.; d) KOH, THF/EtOH/water, 70 °C; e) 1. oxalyl chloride, CH_2Cl_2, r.t.; 2. Et_3N/**(R_p)-3**, CH_2Cl_2, r.t.

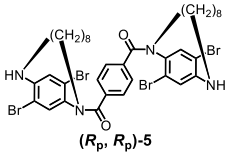


(R_p)-4-^{t}Bu. To a solution of (R_p)-3 (70 mg, 0.19 mmol) in THF (2 mL) was added 4-tert-butylbenzoyl chloride (111 μL, 0.56 mmol) and triethylamine (268 μL, 1.93 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 5 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:20) as eluent to give **(R_p)-4-^{t}Bu** as a white solid (119 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.40 (br, 10H), 4.22-3.74 (br, 4H), 1.61 (br, 2H), 1.48 (br, 2H), 1.32 (s, 18H), 0.89 (br, 8H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 170.04, 153.84, 141.88, 136.68, 132.33, 128.41, 125.02, 122.18, 46.29, 34.82, 31.13, 26.01, 25.92. MALDI-TOF HRMS (m/z): $C_{36}H_{45}Br_2N_2O_2$ [M + H^+] calc. 695.1848, found 695.1848.

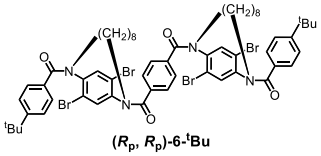


(*M*)-T1-^{t}Bu. To a solution of (R_p)-4-^{t}Bu (42 mg, 0.060 mmol) in DMA (2 mL) was added palladium diacetate (7 mg, 0.031 mmol), tricyclohexylphosphonium tetrafluoroborate (17 mg, 0.046 mmol) and cesium carbonate (102 mg, 0.31 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 10 min. The color of the reaction mixture turned black. The reaction mixture was washed with water and extracted with petroleum ether for three times. After removal of the solvent, the crude product was

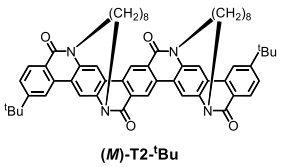
purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(*M*)-T1-^{t}Bu** as a yellow solid (28 mg, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.46 (d, *J* = 8.4 Hz, 2H), 8.16 (s, 2H), 8.08 (d, *J* = 1.6 Hz, 2H), 7.70 (dd, *J* = 8.4, 1.7 Hz, 2H), 5.21-5.15 (m, 2H), 4.23-4.16 (m, 2H), 1.81-1.75 (m, 2H), 1.52-1.42 (m, 20H), 0.88-0.83 (m, 4H), 0.64-0.57 (m, 2H), -(0.15-0.21) (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.86, 156.34, 134.17, 132.26, 129.03, 126.73, 124.17, 122.34, 117.90, 111.10, 44.96, 35.51, 31.25, 29.04, 27.06, 26.46. MALDI-TOF HRMS (m/z): $C_{36}H_{42}N_2O_2$ [M^+] calc. 534.3246, found 534.3246.


(R_p, R_p)-5

(R_p, R_p)-5. To a solution of (R_p)-3 (800 mg, 2.13 mmol) and terephthaloyl chloride (216 mg, 1.06 mmol) in CH_2Cl_2 (80 mL) was added triethylamine (1.48 mL, 10.67 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(R_p, R_p)-5** as a white solid (856 mg, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.64-7.43 (br, 4H), 7.12-6.88 (m, 4H), 4.33 (br, 1H), 4.17-4.12 (m, 2H), 3.65-3.60 (m, 2H), 3.52-3.48 (m, 2H), 3.20-3.15 (m, 2H), 1.82 (br, 2H), 1.47 (br, 4H), 1.12-0.90 (m, 12H), 0.69 (br, 2H), 0.44 (br, 2H), 0.08 (br, 2H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 169.89, 146.67, 137.39, 135.07, 131.24, 127.86, 123.18, 121.44, 111.79, 47.57, 45.02, 27.58, 27.00, 26.53, 26.07, 25.14, 22.05. MALDI-TOF HRMS (m/z): $C_{36}H_{43}Br_4N_4O_2$ [$M + H^+$] calc. 879.0120, found 879.0121.

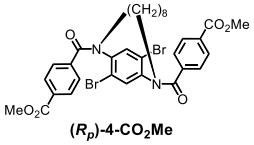

(R_p, R_p)-6-^{t}Bu

(R_p, R_p)-6-^{t}Bu. To a solution of (R_p, R_p)-5 (100 mg, 0.11 mmol) in THF (2 mL) was added 4-tert-butylbenzoyl chloride (67 μL, 0.34 mmol) and triethylamine (162 μL, 1.17 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 5 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(R_p, R_p)-6-^{t}Bu** as a white solid (122 mg, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.31 (br, 16H), 4.13-3.76 (br, 8H), 1.57-1.45 (br, 8H), 1.29 (s, 18H), 0.86 (br, 16H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 168.40, 153.93, 142.16, 141.01, 137.00, 136.16, 132.26, 128.41, 128.09, 124.97, 122.89, 46.87, 34.89, 31.23, 26.04, 25.95. MALDI-TOF HRMS (m/z): $C_{58}H_{67}Br_4N_4O_4$ [$M + H^+$] calc. 1199.1896, found 1199.1900.


(*M*)-T2-^{t}Bu

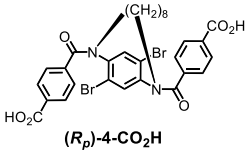
(*M*)-T2-^{t}Bu. To a solution of (R_p, R_p)-6-^{t}Bu (91 mg, 0.076 mmol) in DMA (2 mL) was added palladium diacetate (14 mg, 0.062 mmol), tricyclohexylphosphonium tetrafluoroborate (33 mg, 0.090 mmol) and cesium carbonate (197 mg, 0.60 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:6) as eluent to give **(*M*)-T2-^{t}Bu** as a yellow solid (49 mg, 74%). ^{1}H NMR

($CDCl_3$, 400 MHz, δ/ppm): 8.99 (s, 2H), 8.36 (d, *J* = 8.5 Hz, 2H), 8.17 (s, 2H), 8.08 (d, *J* = 1.6 Hz, 2H), 8.08 (s, 2H), 7.70 (dd, *J* = 8.5, 1.7 Hz, 2H), 5.24-5.20 (m, 2H), 4.98-4.94 (m, 2H), 4.30-4.25 (m, 2H), 4.07-4.02 (m, 2H), 1.80 (br, 2H), (1.67 (br, 2H), 1.53 (s, 18H), 1.45-1.37 (br, 4H), 0.86-0.76 (br, 8H), 0.60-0.53 (br, 4H), -(0.24-0.28) (br, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.36, 161.19, 156.42, 134.67, 133.52, 131.82, 131.68, 129.14, 128.79, 127.07, 124.25 123.41, 123.09, 121.21, 117.83, 111.58, 111.36, 45.57, 44.39, 35.56, 31.30, 29.12, 29.02, 27.06, 26.89, 26.56, 26.30. MALDI-TOF HRMS (m/z): $C_{58}H_{62}N_4O_4$ [M^+] calc. 878.4771, found 878.4773.



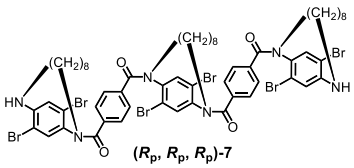
(*R*$_p$)-4-CO_2Me

(*R*$_p$)-4-CO_2Me. To a solution of (*R*$_p$)-3 (700 mg, 1.86 mmol) in THF (10 mL) was added 4-tert-butylbenzoyl chloride (1.11 g, 5.58 mmol) and triethylamine (2.69 mL, 19.39 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 1.5 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(*R*$_p$)-4-CO_2Me** as a white solid (1.18 g, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.11-7.23 (br, 10H), 4.16-3.46 (br, 10H), 1.59 (br, 2H), 1.40 (br, 2H), 0.89-0.73 (br, 8H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 166.08, 141.26, 139.33, 136.85, 131.77, 129.01, 128.24, 122.92, 52.37, 46.04, 26.12, 25.91, 25.79. MALDI-TOF HRMS (m/z): $C_{32}H_{33}Br_2N_2O_6$ [M + H^+] calc. 699.0705, found 699.0707.



(*R*$_p$)-4-CO_2H

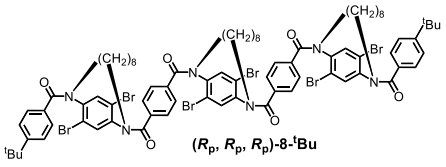
(*R*$_p$)-4-COOH. To a solution of (*R*$_p$)-4-CO_2Me (920 mg, 1.31 mmol) in THF (16 mL) was added KOH (221 mg, 3.95 mmol), ethanol (16 mL) and H_2O (4 mL). The reaction mixture was stirred at 70 °C for 1 h. The reaction mixture was neutralised with dilute hydrochloric acid. Then, THF in the mixture was removed under reduced pressure. After filtration, **(*R*$_p$)-4-COOH** was obtained as a white solid (823 mg, 93%). ^{1}H NMR (DMSO-d6, 400 MHz, δ/ppm): 13.16 (br, 2H), 8.22-7.41 (br, 10H), 3.92 (br, 2H), 3.55 (br, 2H), 1.47 (br, 4H), 0.91-0.82 (br, 8H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 167.42, 166.18, 140.28, 140.00, 139.16, 136.16, 134.96, 131.84, 129.31, 128.52, 128.06, 127.89, 126.46, 123.03, 45.96, 25.57, 25.37, 25.00. MALDI-TOF HRMS (m/z): $C_{30}H_{29}Br_2N_2O_6$ [M + H^+] calc. 671.0392, found 671.0393.



(*R*$_p$, *R*$_p$, *R*$_p$)-7

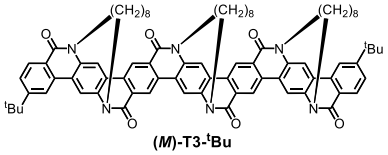
(*R*$_p$, *R*$_p$, *R*$_p$)-7. To a solution of (*R*$_p$)-4-COOH (100 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) was added was added oxalyl chloride (2 M in CH_2Cl_2, 0.60 mL, 1.20 mmol) and 1 drop DMF under nitrogen. After stirring at room temperature for 30 min, the solvent was removed under reduced pressure. To the resulting solid was sequentially added CH_2Cl_2 (5 mL), triethylamine (0.21 mL, 1.52 mmol) and (*R*$_p$)-3 (118 mg, 0.31 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:4) as eluent to give **(*R*$_p$, *R*$_p$, *R*$_p$)-7** as a white solid (201 mg, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.54-6.97 (br, 14H), 4.16-3.16 (br, 14H), 1.85 (br, 2H), 1.54 (br, 8H), 1.19-0.79

(br, 22H), 0.48 (br, 2H), 0.19 (br, 2H). MALDI-TOF HRMS (m/z): $C_{58}H_{65}Br_6N_6O_4$ [M + H^+] calc. 1383.0168, found 1383.0172.



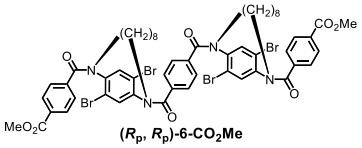
(R_p, R_p, R_p)-8-^{t}Bu

(R_p, R_p, R_p)-8-^{t}Bu. To a solution of (R_p, R_p, R_p)-7 (80 mg, 0.058 mmol) in THF (2 mL) was added 4-tert-butylbenzoyl chloride (34 μL, 0.17 mmol) and triethylamine (83 μL, 0.60 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 34 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:4) as eluent to give **(R_p, R_p, R_p)-8-^{t}Bu** as a white solid (96 mg, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.49-7.15 (br, 22H), 4.16-3.79 (br, 12H), 1.68-1.45 (br, 12H), 1.29 (s, 18H), 0.85 (br, 24H). MALDI-TOF HRMS (m/z): $C_{80}H_{89}Br_6N_6O_6$ [M + H^+] calc. 1703.1944, found 1703.1958.



(*M*)-T3-^{t}Bu

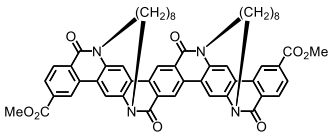
(*M*)-T3-^{t}Bu. To a solution of (R_p, R_p, R_p)-8-^{t}Bu (70 mg, 0.041 mmol) in DMA (3 mL) was added palladium diacetate (11 mg, 0.049 mmol), tricyclohexylphosphonium tetrafluoroborate (27 mg, 0.073 mmol) and cesium carbonate (160 mg, 0.49 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:6) as eluent to give **(*M*)-T3-^{t}Bu** as a yellow solid (32 mg, 64%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.00 (s, 2H), 8.53 (s, 2H), 8.30 (d, *J* = 8.5 Hz, 2H), 8.23 (s, 2H), 8.14 (d, *J* = 1.3 Hz, 2H), 8.10 (s, 2H), 7.73 (s, 2H), 7.71 (dd, *J* = 8.7, 1.6 Hz, 2H), 5.31-5.26 (m, 2H), 5.12-5.08 (m, 2H), 4.65-4.61 (m, 2H), 4.35-4.29 (m, 2H), 4.25-4.20 (m, 2H), 3.78-3.72 (m, 2H), 1.81 (br, 2H), 1.70 (br, 4H), 1.57 (s, 18H), 1.41-1.25 (br, 6H), 0.80-0.68 (br, 12H), 0.51 (br, 6H), -(0.34-0.38) (br, 4H), -0.49 (br, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.12, 160.99, 160.53, 156.43, 134.50, 133.80, 133.56, 131.80, 131.77, 131.05, 129.22, 128.76, 128.15, 127.02, 124.20, 123.44, 123.42, 123.15, 121.80, 120.91, 117.92, 111.87, 111.61, 111.36, 45.69, 45.07, 43.86, 35.61, 31.36, 29.07, 28.93, 27.05, 26.81, 26.66, 26.55, 26.47, 26.30. MALDI-TOF HRMS (m/z): $C_{80}H_{82}N_6O_6$ [M^+] calc. 1222.6296, found 1222.6299.



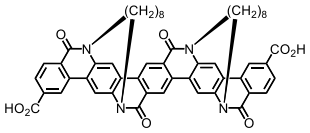
(R_p, R_p)-6-CO_2Me

(R_p, R_p)-6-CO_2Me. To a solution of (R_p, R_p)-5 (812 mg, 0.92 mmol) and methyl 4-(chlorocarbonyl)benzoate (548 g, 2.77 mmol) in THF (12 mL) was added triethylamine (1.33 mL, 9.59 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 1.5 h. After cooling to room temperature, the reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:10) as eluent to give **(R_p, R_p)-6-CO_2Me** as a white solid (1.03 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.86-7.04 (br, 16H), 4.02 (br, 8H), 3.97 (s, 6H), 1.57-1.45 (br, 8H), 0.90-0.79 (16H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 166.23, 141.66, 140.97,

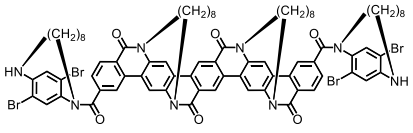
139.54, 136.77, 136.48, 131.49, 128.99, 128.43, 128.04, 123.37, 52.46, 46.94, 46.33, 26.25, 25.92. MALDI-TOF HRMS (m/z): $C_{54}H_{55}Br_4N_4O_8$ [M + H^+] calc. 1203.0753, found 1203.0752.


(*M*)-T2-CO_2Me

(*M*)-T2-CO_2Me. To a solution of (R_p, R_p)-6-CO_2Me (200 mg, 0.17 mmol) in DMA (10 mL) was added palladium diacetate (30 mg, 0.13 mmol), tricyclohexylphosphonium tetrafluoroborate (73 mg, 0.20 mmol) and cesium carbonate (432 mg, 1.33 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:4) as eluent to give **(*M*)-T2-CO_2Me** as a yellow solid (100 mg, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.87 (s, 2H), 8.82 (d, *J* = 1.0 Hz, 2H), 8.49 (d, *J* = 8.3 Hz, 2H), 8.25 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.25 (s, 2H), 8.02 (s, 2H), 5.22-5.16 (m, 2H), 4.86-4.82 (m, 2H), 4.32-4.27 (m, 2H), 4.10 (s, 6H), 4.01-3.95 (br, 2H), 1.81-1.63 (br, 4H), 1.46-1.32 (br, 4H), 0.87-0.73 (br, 8H), 0.54-0.53 (br, 4H), -(0.34-0.43) (br, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 166.20, 160.85, 160.51, 134.46, 133.86, 133.83, 132.04, 131.53, 129.77, 129.36, 129.18, 128.82, 123.72, 123.45, 122.05, 121.73, 111.79, 111.67, 52.82, 45.42, 44.62, 29.14, 29.02, 27.00, 26.78, 26.52, 26.42. MALDI-TOF HRMS (m/z): $C_{54}H_{50}N_4O_8$ [M^+] calc. 882.3629, found 882.3630.

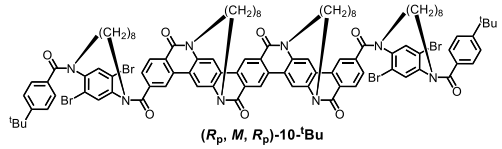

(*M*)-T2-CO_2H

(*M*)-T2-CO_2H. To a solution of (*M*)-T2-CO_2Me (400 mg, 0.45 mmol) in THF (3 mL) was added KOH (76 mg, 1.36 mmol), ethanol (3 mL) and H_2O (1 mL). The reaction mixture was stirred at 70 °C for 1 h. The reaction mixture was neutralised with dilute hydrochloric acid. Then, THF in the mixture was removed under reduced pressure. After filtration, **(*M*)-T2-CO_2H** was obtained as a yellow solid (377 mg, 97%). ^{1}H NMR (DMSO-d6, 400 MHz, δ/ppm): 13.51 (br, 1.7H), 9.04 (s, 2H), 8.64 (s, 2H), 8.63 (s, 2H), 8.09-8.06 (br, 6H), 4.84 (br, 2H), 4.64 (br, 2H), 4.36 (br, 2H), 4.18 (br, 2H). 1.63-1.40 (br, 4H), 1.20-1.00 (br, 4H), 0.70-0.54 (br, 8H), 0.25 (br, 4H), -(0.67-0.76) (br, 4H). MALDI-TOF HRMS (m/z): $C_{52}H_{46}N_4O_8$ [M^+] calc. 854.3316, found 854.3316.

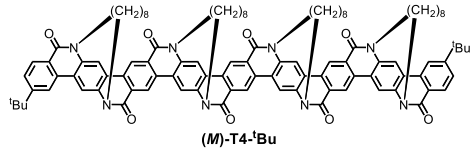

(R_p, *M*, R_p)-9

(R_p, *M*, R_p)-9. To a solution of (*M*)-T2-CO_2H (260 mg, 0.30 mmol) in CH_2Cl_2 (5 mL) was added oxalyl chloride (2 M in CH_2Cl_2, 1.22 mL, 2.44 mmol) and 1 drop DMF under nitrogen. After stirring at room temperature for 30 min, the solvent was removed under reduced pressure. To the resulting solid was sequentially added CH_2Cl_2 (26 mL), triethylamine (442 μL, 3.19 mmol) and (R_p)-3 (241 mg, 0.64 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:10) as eluent to give **(R_p, *M*, R_p)-9** as a yellow solid (332 mg, 69%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.13 (s, 2H), 8.39 (br, 4H), 8.21 (s, 2H), 8.02 (s, 2H), 7.86 (s, 2H), 7.15 (s, 2H), 7.10 (s, 2H), 5.24-5.20 (m, 2H), 5.06-5.03 (m, 2H), 4.36 (br, 2H), 4.22-4.05 (m, 8H), 3.54-3.50 (m, 2H), 3.23 (br, 2H). 1.84-0.32 (br, 44H), -(0.42-0.54) (br, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 169.02, 161.00, 139.62, 135.69,

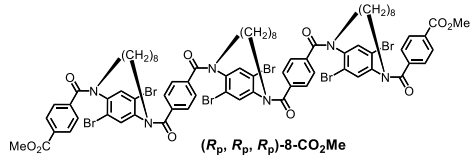
134.63, 133.71, 131.74, 131.52, 129.27, 129.06, 128.62, 127.29, 123.61, 122.53, 122.17, 121.67, 111.96, 111.84, 49.68, 47.41, 45.04, 29.12, 28.87, 27.27, 26.55, 26.29, 26.10, 22.68. MALDI-TOF HRMS (m/z): $C_{80}H_{82}Br_4N_8O_6$ [M^+] calc. 1566.3091, found 1566.3093.


(*R*p, *M*, *R*p)-10-^{t}Bu

(*R*p, *M*, *R*p)-10-^{t}Bu. To a solution of (*R*p, *M*, *R*p)-9 (60 mg, 0.038 mmol) in THF (2 mL) was added 4-tert-butylbenzoyl chloride (23 μL, 0.12 mmol) and triethylamine (55 μL, 0.40 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:10) as eluent to give **(*R*p, *M*, *R*p)-10-^{t}Bu** as a yellow solid (60 mg, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.30-7.35 (br, 22H), 5.25-5.13 (br, 4H), 4.40-3.75 (br, 12H), 1.82-1.47 (br, 18H), 1.32 (s, 18H), 0.88 (br, 24H), 0.64-0.62 (br, 4H), -(0.15-0.25) (br, 4H). MALDI-TOF HRMS (m/z): $C_{102}H_{106}Br_4N_8O_8$ [M^+] calc. 1886.4867, found 1886.4858.

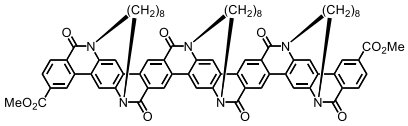

(*M*)-T4-^{t}Bu

(*M*)-T4-^{t}Bu. To a solution of (*R*p, *M*, *R*p)-10-^{t}Bu (50 mg, 0.027 mmol) in DMA (2 mL) was added palladium diacetate (5 mg, 0.022 mmol), tricyclohexylphosphonium tetrafluoroborate (12 mg, 0.033 mmol) and cesium carbonate (69 mg, 0.21 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:4) as eluent to give **(*M*)-T4-^{t}Bu** as a yellow solid (15 mg, 36%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.15 (s, 2H), 8.73 (s, 2H), 8.46 (s, 2H), 8.22 (s, 4H), 8.20 (d, 2H), 8.16 (d, *J* = 1.1 Hz, 2H), 7.85 (s, 2H), 7.68 (s, 2H), 7.67 (dd, *J* = 8.7, 1.4 Hz, 2H), 5.33-5.22 (m, 4H), 5.02-4.98 (m, 2H), 4.71-4.68 (m, 2H), 4.36-4.30 (m, 4H), 4.13-4.08 (m, 2H), 3.78-3.73 (m, 2H), 1.81 (br, 4H), 1.59 (s, 18H), 1.54-1.43 (br, 8H), 1.28 (br, 4H), 0.88-0.64 (br, 16H), 0.48 (br, 8H), -0.42 (br, 4H), -0.56 (br, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.06, 161.02, 160.51, 160.34, 156.42, 134.39, 134.00, 133.74, 133.63, 131.87, 131.81, 131.29, 131.05, 129.12, 128.84, 128.35, 128.17, 126.99, 124.18, 123.63, 123.52, 123.46, 123.24, 121.95, 121.57, 120.91, 118.00, 112.00, 111.74, 111.65, 111.36, 45.66, 45.28, 44.90, 43.89, 35.62, 31.38, 29.02, 28.88, 27.03, 26.79, 26.61, 26.43, 26.28. MALDI-TOF HRMS (m/z): $C_{102}H_{102}N_8O_8$ [M^+] calc. 1566.7821, found 1566.7828.


(*R*p, *R*p, *R*p)-8-CO_2Me

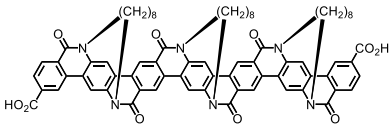
(*R*p, *R*p, *R*p)-8-CO_2Me. To a solution of (*R*p, *R*p, *R*p)-7 (1.00 g, 0.72 mmol) and methyl 4-(chlorocarbonyl)benzoate (430 mg, 2.16 mmol) in THF (20 mL) was added triethylamine (1.03 mL, 7.42 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 1.5 h. After cooling to room temperature, the reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:4) as eluent to give **(*R*p, *R*p, *R*p)-8-CO_2Me** as a white solid (1.18

g, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.84-7.05 (br, 22H), 4.05-3.95 (br, 18H), 1.85-1.44 (br, 12H), 0.86-0.77 (br, 24H). MALDI-TOF HRMS (m/z): $C_{76}H_{77}Br_6N_6O_{10}$ [M + H^+] calc. 1707.0801, found 1707.0801.



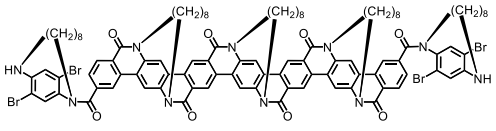
(*M*)-T3-CO_2Me

(*M*)-T3-CO_2Me. To a solution of (R_p, R_p, R_p)-8-CO_2Me (100 mg, 0.058 mmol) in DMA (3 mL) was added palladium diacetate (16 mg, 0.071 mmol), tricyclohexylphosphonium tetrafluoroborate (39 mg, 0.11 mmol) and cesium carbonate (228 mg, 0.70 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:6) as eluent to give **(*M*)-T3-CO_2Me** as a yellow solid (42 mg, 59%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.00 (s, 2H), 8.91 (d, *J* = 0.6 Hz, 2H), 8.42 (d, *J* = 8.4 Hz, 2H), 8.34 (s, 2H), 8.32 (s, 2H), 8.25 (dd, *J* = 8.4, 1.2 Hz, 2H), 8.06 (s, 2H), 7.63 (s, 2H), 5.29-5.26 (m, 2H), 5.06-5.02 (m, 2H), 4.54-4.50 (m, 2H), 4.38-4.33 (m, 2H), 4.22-4.17 (m, 2H), 4.12 (s, 6H), 3.65-3.60 (m, 2H), 1.79-1.78 (br, 2H), 1.66-1.65 (br, 2H), 1.48-1.43 (br, 4H), 1.42-1.21 (br, 4H), 0.84-0.44 (br, 18H), -(0.46-0.59) (br, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 166.25, 160.86, 160.27, 160.23, 134.25, 133.93, 133.83, 133.80, 132.02, 131.35, 131.28, 129.73, 129.34, 129.17, 128.75, 128.10, 123.80, 123.59, 123.31, 122.05, 121.64, 121.53, 112.04, 111.84, 111.41, 52.84, 45.54, 45.04, 44.14, 29.04, 29.01, 28.89, 26.98, 26.73, 26.49, 26.41, 26.34, 26.13, 25.93. MALDI-TOF HRMS (m/z): $C_{76}H_{70}N_6O_{10}$ [M^+] calc. 1226.5153, found 1226.5154.



(*M*)-T3-CO_2H

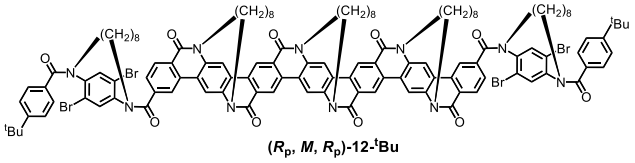
(*M*)-T3-CO_2H. To a solution of **(*M*)-T3-CO_2Me** (160 mg, 0.13 mmol) in THF (6 mL) was added KOH (21 mg, 0.38 mmol), ethanol (6 mL) and H_2O (1.5 mL). The reaction mixture was stirred at 70 °C for 1 h. The reaction mixture was neutralised with dilute hydrochloric acid. Then, THF in the mixture was removed under reduced pressure. After filtration, **(*M*)-T3-CO_2H** was obtained as a yellow solid (155 mg, 99%). ^{1}H NMR (DMSO-d6, 400 MHz, δ/ppm): 13.49 (br, 0.3H), 8.88-7.30 (br, 16H), 4.84-3.87 (br, 12H), 1.58-(-1.38) (br, 36H). MALDI-TOF HRMS (m/z): $C_{74}H_{66}N_6O_{10}$ [M^+] calc. 1198.4840, found 1198.4838.



(R_p, *M*, R_p)-11

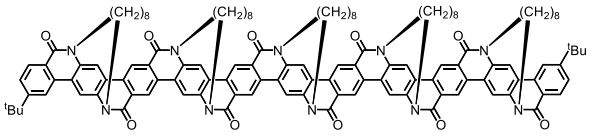
(R_p, *M*, R_p)-11. To a solution of (*M*)-T3-CO_2H (80 mg, 0.067 mmol) in CH_2Cl_2 (2 mL) was added oxalyl chloride (2 M in CH_2Cl_2, 0.27 mL, 0.53 mmol) and 1 drop DMF under nitrogen. After stirring at room temperature for 30 min, the solvent was removed under reduced pressure. To the resulting solid was sequentially added CH_2Cl_2 (8 mL), triethylamine (93 μL, 0.67 mmol) and (R_p)-3 (53 mg, 0.14 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:6) as eluent to give **(R_p, *M*, R_p)-11** as a yellow solid (92 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.08 (s, 2H), 8.74 (s, 2H), 8.44 (s, 2H), 8.27 (d, *J* = 7.0 Hz, 2H), 8.10 (s, 2H),

8.00 (s, 2H), 7.85 (s, 2H), 7.78 (d, J = 7.0 Hz, 2H), 7.19 (s, 2H), 7.09 (s, 2H), 5.27-5.23 (m, 2H), 5.11-5.07 (m, 2H), 4.85-4.81 (m, 2H), 4.25-4.16 (m, 4H), 4.08 (br, 4H), 3.92-3.86 (m, 2H), 3.56-3.52 (m, 2H), 3.21 (br, 2H), 1.68-0.30 (br, 54H), -(0.48-0.68) (br, 6H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 168.99, 160.88, 160.76, 160.66, 139.58, 135.63, 134.42, 133.92, 133.52, 131.68, 131.35, 129.42, 129.14, 128.76, 128.54, 127.17, 123.57, 122.59, 122.18, 121.77, 121.32, 112.06, 111.65, 47.49, 45.10, 44.72, 29.03, 28.79, 27.67, 27.24, 26.84, 26.58, 26.40, 26.29, 26.12, 26.00, 22.57. MALDI-TOF HRMS (m/z): $C_{102}H_{102}Br_4N_{10}O_8$ [M^+] calc. 1910.4616, found 1910.4605. Single crystals of (R_p, M, R_p)-11 were obtained by diffusion of methanol into the (R_p, M, R_p)-11 solution in CH_2Cl_2. Formula: $C_{104}H_{110}Br_4N_{10}O_{10}$ (one (R_p, M, R_p)-11 and two CH_3OH were included in a cell); formula weight: 1979.65; crystal system: triclinic; space group: P 1; unit cell parameters: a = 15.9913(15) Å, b = 19.7892(19) Å, c = 21.961(2) Å, α = 112.136(4)°, β = 107.694(4)°, γ = 95.621(4)°, V = 5952.6(10) Å^3; temperature for data collection: 170(2) K; Z = 2; final R indices [I >2σ(I)]: R_1 = 0.0674, wR_2 = 0.1804; GOF on F^2: 0.947; Flack parameter: 0.093(5). The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (**CCDC-2354661**).



(R_p, M, R_p)-12-^{t}Bu

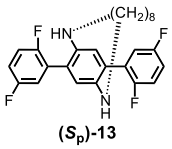
(R_p, M, R_p)-12-^{t}Bu. To a solution of (R_p, M, R_p)-11 (60 mg, 0.031 mmol) in THF (2 mL) was added 4-tert-butylbenzoyl chloride (19 μL, 0.096 mmol) and triethylamine (45 μL, 0.32 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:6) as eluent to give **(R_p, M, R_p)-12-^{t}Bu** as a yellow solid (60 mg, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.18-7.34 (br, 28H), 5.25-3.71 (br, 20H), 1.81-0.54 (br, 72H), -0.39 (br, 6H). MALDI-TOF HRMS (m/z): $C_{124}H_{126}Br_4N_{10}O_{10}$ [M^+] calc. 2230.6392, found 2230.6394.



(M)-T5-^{t}Bu

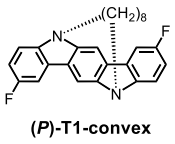
(M)-T5-^{t}Bu. To a solution of (R_p, M, R_p)-12-^{t}Bu (50 mg, 0.023 mmol) in DMA (2 mL) was added palladium diacetate (4 mg, 0.018 mmol), tricyclohexylphosphonium tetrafluoroborate (10 mg, 0.027 mmol) and cesium carbonate (60 mg, 0.18 mmol) under nitrogen. The reaction mixture was stirred at 130 °C for 2 min. The color of the reaction mixture turned black. After cooling to room temperature, saturated NaCl aqueous solution was added into the reaction mixture. The mixture was filtered with the aid of silica gel and then washed with water for three times. After drying, the crude product absorbed in silica gel was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:2) as eluent to give **(M)-T5-^{t}Bu** as an orange solid (9 mg, 21%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.26 (s, 2H), 8.97 (s, 2H), 8.59 (s, 2H), 8.45 (s, 2H), 8.30 (s, 2H), 8.24 (s, 2H), 8.19 (d, J = 6.4 Hz, 2H), 8.19 (s, 2H), 8.03 (s, 2H), 7.73 (s, 2H), 7.67 (s, 2H), 7.66 (d, J = 8.9 Hz, 2H), 5.34-5.27 (m, 4H), 5.20-5.16 (m, 2H), 4.95-4.92 (m, 2H), 4.73-4.70 (m, 2H), 4.41-4.24 (m, 6H), 4.04-3.99 (m, 2H), 3.78-3.72 (m, 2H), 1.81 (br, 10H), 1.60 (s, 18H), 1.52 (br, 10H), 0.78-0.63 (br, 20H), 0.48 (br, 10H), -0.43 (br, 4H), -(0.57, 0.60) (br, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.14, 161.11, 160.73, 160.49, 160.44, 156.45, 134.31,

134.06, 133.83, 133.67, 133.61, 131.90, 131.87, 131.36, 134.34, 131.27, 129.06, 128.76, 128.35, 128.20, 128.13, 126.88, 124.12, 123.81, 123.71, 123.52, 123.30, 122.05, 121.61, 121.50, 120.88, 118.04, 112.32, 112.16, 111.83, 111.71, 111.46, 45.64, 45.30, 45.13, 44.84, 43.89, 35.63, 31.40, 29.04, 28.99, 28.85, 27.04, 26.87, 26.72, 26.59, 26.47, 26.41, 26.26. MALDI-TOF HRMS (m/z): $C_{124}H_{122}N_{10}O_{10}$ [M^+] calc. 1910.9345, found 1910.9370.



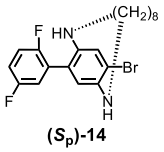
(S_p)-13

(S_p)-13. To a solution of 2-(2,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (57 mg, 0.24 mmol), (S_p)-3 (30 mg, 0.080 mmol) in THF (1 mL) was added $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), K_2CO_3 (110 mg, 0.80 mmol) and H_2O (0.5 mL) under nitrogen. The reaction mixture was stirred at 70 °C for 12 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate:CH_2Cl_2 (1:40) as eluent to give **(S_p)-13** as a white solid (30 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.20-7.11 (m, 4H), 7.09-7.03 (m, 2H), 6.96 (d, *J* = 0.9 Hz, 2H), 3.34 (br, 2H), 3.26-3.20 (m, 2H), 3.01-2.95 (m, 2H), 1.77-1.66 (m, 2H), 1.10-1.09 (br, 4H), 0.95-0.90 (m, 2H), 0.67-0.65 (m, 2H), 0.55-0.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 159.90, 159.88, 157.48, 157.46, 157.06, 157.04, 154.64, 154.62, 139.76, 127.38, 127.30, 127.20, 127.13, 122.78, 118.30, 118.27, 118.07, 118.03, 117.63, 117.54, 117.37, 117.28, 116.28, 116.19, 116.04, 115.95, 48.28, 28.13, 26.48, 23.78. MALDI-TOF HRMS (m/z): $C_{26}H_{26}F_4N_2$ [M^+] calc. 442.2032, found 442.2031.



(*P*)-T1-convex

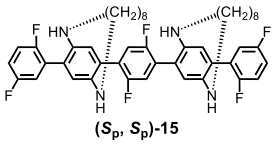
(*P*)-T1-convex. To a solution of (S_p)-13 (30 mg, 0.068 mmol) in DMF (2 mL) was added potassium tert-butoxide (0.45 M in DMF, 0.46 mL, 0.21 mmol) under nitrogen. The reaction mixture was stirred at 80 °C for 30 min. The reaction mixture was washed with water and extracted with petroleum ether for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether:CH_2Cl_2 (2:1) as eluent to give **(*P*)-T1-convex** as a yellow solid (23 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.08 (s, 2H), 7.79 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.34-7.31 (m, 2H), 7.19 (td, *J* = 8.9, 2.5 Hz, 2H), 4.53-4.46 (m, 2H), 4.42-4.36 (m, 2H), 1.51-1.45 (m, 2H), 1.04-0.84 (m, 6H), 0.50-0.42 (m, 2H), 0.15-0.03 (m, 2H), -(1.84-1.94) (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 158.79, 156.44, 141.58, 140.67, 127.34, 127.30, 126.63, 126.54, 113.82, 113.57, 112.11, 112.02, 106.57, 106.33, 104.37, 48.17, 28.93, 27.61, 27.26. MALDI-TOF HRMS (m/z): $C_{26}H_{24}F_2N_2$ [M^+] calc. 402.1908, found 402.1902.



(S_p)-14

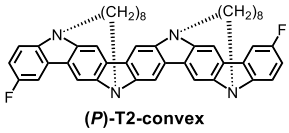
(S_p)-14. To a solution of 2-(2,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (179 mg, 0.75 mmol), (S_p)-3 (200 mg, 0.53 mmol) in THF (4 mL) was added $Pd(PPh_3)_4$ (37 mg, 0.032 mmol), K_2CO_3 (732 mg, 5.32 mmol) and H_2O (2 mL) under nitrogen. The reaction mixture was stirred at 70 °C for 6 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate: petroleum ether (1:20) as eluent to give **(S_p)-14** as a white solid (120 mg, 55%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.19 (s, 1H), 7.16-7.12 (m, 1H), 7.08-7.04 (m, 2H), 6.86 (d, *J* = 1.0 Hz, 1H), 3.35-2.93 (m, 6H), 1.84-1.80 (m, 1H), 1.60-1.25 (m, 1H), 1.20-1.16 (m, 1H), 1.10-0.97 (m, 4H), 0.89-0.57 (m, 4H), 0.42-0.38 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 159.91, 159.89, 157.49, 157.46, 156.96, 156.94, 154.54, 154.51, 141.04, 139.98, 127.01, 126.93, 126.83, 126.75,

126.55, 124.65, 122.39, 122.38, 118.19, 118.15, 117.95, 117.92, 117.69, 117.60, 117.44, 117.35, 116.47, 116.41, 116.33, 116.18, 116.09, 48.58, 48.29, 28.65, 27.79, 26.58, 23.92, 23.73. MALDI-TOF HRMS (m/z): $C_{20}H_{23}BrF_2N_2$ [M^+] calc. 408.1013, found 408.1012.



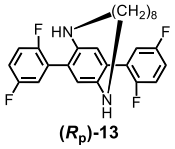
(S_p, S_p)-15

(S_p, S_p)-15. To a solution of 2,5-difluorobenzene-1,4-diboronicacidbis(pinacol)ester (64 mg, 0.17 mmol), (S_p)-14 (106 mg, 0.26 mmol) in THF (2 mL) was added $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), K_2CO_3 (241 mg, 1.75 mmol) and H_2O (1 mL) under nitrogen. The reaction mixture was stirred at 70 °C for 12 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:5) as eluent to give **(S_p, S_p)-15** as a white solid (70 mg, 52%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.29 (t, J = 7.8 Hz, 2H), 7.22-7.13 (m, 4H), 7.11-7.06 (m, 2H), 7.02 (br, 2H), 6.99 (br, 2H), 3.43 (br, 4H), 3.29-3.01 (m, 8H), 1.75 (br, 4H), 1.13-0.93 (br, 12H), 0.73-0.57 (br, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 159.95, 159.93, 157.53, 157.51, 157.10, 157.08, 157.02, 154.65, 154.60, 139.96, 127.23, 126.83, 122.92, 122.72, 119.31, 119.03, 118.33, 118.30, 118.10, 118.06, 117.69, 117.60, 117.44, 117.35, 116.37, 116.29, 116.13, 116.05, 48.31, 30.29, 29.68, 28.21, 26.53, 23.90, 23.78. MALDI-TOF HRMS (m/z): $C_{46}H_{48}F_6N_4$ [M^+] calc. 770.3783, found 770.3783.



(*P*)-T2-convex

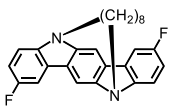
(*P*)-T2-convex. To a solution of (S_p, S_p)-15 (71 mg, 0.092 mmol) in DMF (2 mL) was added potassium tert-butoxide (0.45 M in DMF, 1 mL, 0.46 mmol) under nitrogen. The reaction mixture was stirred at 100 °C for 30 min. The reaction mixture was washed with water and extracted with petroleum ether for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether:CH_2Cl_2 (1:1) as eluent to give **(*P*)-T2-convex** as a yellow solid (11 mg, 17%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.12-7.19 (br, 12H), 4.44 (br, 4H), 1.57-0.57 (br, 18H), 0.15-0.05 (br, 4H), -(1.64-1.82) (br, 4H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 113.09, 106.12, 47.81, 31.92, 29.70, 29.36, 28.97, 28.81, 27.73, 27.55, 22.69, 14.11. MALDI-TOF HRMS (m/z): $C_{46}H_{44}F_2N_4$ [M^+] calc. 690.3534, found 690.3527. Single crystals of (*P*)-T2-convex were obtained by diffusion of methanol into the (*P*)-T2-convex solution in CH_2Cl_2. Formula: $C_{48}H_{48}Cl_{3.5}F_2N_4$ (one (*P*)-T2-convex and disordered solvent molecules were included in a cell); formula weight: 842.98; crystal system: tetragonal; space group: P 4_3 2_1 2; color of crystal: yellow; unit cell parameters: a = 15.9463(3) Å, b = 15.9463(3) Å, c = 35.1878(11) Å, α = 90°, β = 90°, γ = 90°, V = 8947.7(4) Å^3; temperature for data collection: 170(2) K; Z = 8; final R indices [I >2σ(I)]: R_1 = 0.0757, wR_2 = 0.2198; GOF on F^2: 1.072; Flack parameter: 0.034(16). The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (**CCDC-2354660**).



(R_p)-13

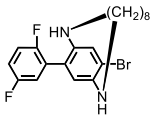
(R_p)-13. To a solution of 2-(2,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (57 mg, 0.24 mmol), (R_p)-3 (30 mg, 0.080 mmol) in THF (1 mL) was added $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), K_2CO_3 (110 mg, 0.80 mmol) and H_2O (0.5 mL) under nitrogen. The reaction mixture was stirred at 70 °C for 12 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl

acetate:CH_2Cl_2 (1:40) as eluent to give **(R_p)-13** as a white solid (33 mg, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.17-7.11 (m, 4H), 7.09-7.03 (m, 2H), 6.95 (d, *J* = 0.7 Hz, 2H), 3.11 (br, 2H), 3.27-3.21 (m, 2H), 3.02-2.95 (m, 2H), 1.74-1.70 (m, 2H), 1.10-1.09 (br, 4H), 0.94-0.91 (m, 2H), 0.70-0.64 (m, 2H), 0.56-0.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 159.92, 159.90, 157.50, 157.48, 157.09, 157.06, 154.66, 154.64, 139.87, 127.44, 127.37, 127.26, 127.15, 122.78, 118.33, 118.30, 118.10, 118.06, 117.64, 117.55, 117.39, 117.30, 116.28, 116.20, 116.04, 115.96, 48.32, 28.23, 26.52, 23.83. MALDI-TOF HRMS (m/z): $C_{26}H_{26}F_4N_2$ [M^+] calc. 442.2032, found 442.2030.



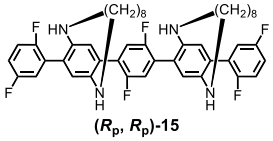
(*M*)-T1-convex

(*M*)-T1-convex. To a solution of (R_p)-13 (30 mg, 0.068 mmol) in DMF (2 mL) was added potassium tert-butoxide (0.45 M in DMF, 0.46 mL, 0.21 mmol) under nitrogen. The reaction mixture was stirred at 70 °C for 30 min. The reaction mixture was washed with water and extracted with petroleum ether for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether:CH_2Cl_2 (2:1) as eluent to give **(*M*)-T1-convex** as a white solid (25 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.08 (s, 2H), 7.79 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.34-7.30 (m, 2H), 7.19 (td, *J* = 8.9, 2.5 Hz, 2H), 4.53-4.46 (m, 2H), 4.42-4.36 (m, 2H), 1.51-1.45 (m, 2H), 1.04-0.85 (m, 6H), 0.50-0.42 (m, 2H), 0.15-0.02 (m, 2H), -(1.85-1.95) (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 158.78, 156.44, 141.59, 140.67, 127.34, 127.30, 126.62, 126.53, 113.81, 113.56, 112.10, 112.01, 106.57, 106.33, 104.36, 48.17, 28.94, 27.62, 27.27. MALDI-TOF HRMS (m/z): $C_{26}H_{24}F_2N_2$ [M^+] calc. 402.1908, found 402.1906.



(R_p)-14

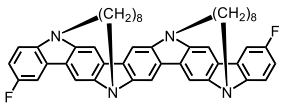
(R_p)-14. To a solution of 2-(2,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (179 mg, 0.75 mmol), (R_p)-3 (200 mg, 0.53 mmol) in THF (4 mL) was added $Pd(PPh_3)_4$ (37 mg, 0.032 mmol), K_2CO_3 (732 mg, 5.32 mmol) and H_2O (2 mL) under nitrogen. The reaction mixture was stirred at 70 °C for 6 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using ethyl acetate: petroleum ether (1:20) as eluent to give **(R_p)-14** as a white solid (102 mg, 47%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.19 (s, 1H), 7.16-7.12 (m, 1H), 7.08-7.04 (m, 2H), 6.86 (d, *J* = 0.9 Hz, 1H), 3.44 (br, 2H), 3.32-2.93 (m, 4H), 1.85-1.79 (m, 1H), 1.63-1.56 (m, 1H), 1.22-1.14 (m, 1H), 1.11-0.97 (m, 4H), 0.89-0.56 (m, 4H), 0.44-0.37 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 159.89, 159.87, 157.47, 157.45, 156.94, 156.92, 154.52, 154.50, 141.01, 139.95, 126.99, 126.91, 126.81, 126.73, 126.54, 124.65, 122.38, 122.36, 118.17, 118.14, 117.94, 117.90, 117.68, 117.59, 117.43, 117.34, 116.45, 116.40, 116.32, 116.16, 116.08, 48.58, 48.28, 28.64, 27.78, 26.58, 23.92, 23.72. MALDI-TOF HRMS (m/z): $C_{20}H_{23}BrF_2N_2$ [M^+] calc. 408.1013, found 408.1011.



(R_p, R_p)-15

(R_p, R_p)-15. To a solution of 2,5-difluorobenzene-1,4-diboronicacidbis(pinacol)ester (76 mg, 0.21 mmol), (R_p)-14 (126 mg, 0.31 mmol) in THF (2 mL) was added $Pd(PPh_3)_4$ (14 mg, 0.012 mmol), K_2CO_3 (286 mg, 2.07 mmol) and H_2O (1 mL) under nitrogen. The reaction mixture was stirred at 70 °C for 12 h. The reaction mixture was washed with water and extracted with CH_2Cl_2 for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using THF:CH_2Cl_2 (1:5) as eluent to give **(R_p, R_p)-15** as a white solid (72 mg, 45%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.29 (t, *J* = 7.9 Hz, 2H), 7.22-7.14

(m, 4H), 7.12-7.06 (m, 2H), 7.02-6.98 (4H), 3.45 (br, 4H), 3.28-2.98 (m, 8H), 1.75 (br, 4H), 1.12-0.92 (br, 12H), 0.72-0.57 (br, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 159.95, 159.93, 157.52, 157.50, 157.07, 154.65, 154.63, 139.99, 127.07, 122.98, 122.79, 119.38, 119.11, 118.30, 118.27, 118.06, 118.04, 117.74, 117.66, 117.49, 117.40, 116.47, 116.38, 116.23, 116.15, 48.27, 30.29, 29.67, 28.14, 27.86, 26.47, 23.83. MALDI-TOF HRMS (m/z): $C_{46}H_{48}F_6N_4$ [M^+] calc. 770.3783, found 770.3785.



(*M*)-T2-convex

(*M*)-T2-convex. To a solution of (R_p, R_p)-15 (62 mg, 0.080 mmol) in DMF (2 mL) was added potassium tert-butoxide (0.45 M in DMF, 1 mL, 0.46 mmol) under nitrogen. The reaction mixture was stirred at 100 °C for 30 min. The reaction mixture was washed with water and extracted with petroleum ether for three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether:CH_2Cl_2 (1:1) as eluent to give **(*M*)-T2-convex** as a yellow solid (9 mg, 15%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.13-7.20 (br, 12H), 4.44 (br, 6H), 1.54-0.53 (br, 18H), 0.15-0.02 (br, 4H), -(1.59-1.74) (br, 4H). ^{13}C NMR (only partial peaks were recorded due to the significant broadening. $CDCl_3$, 100 MHz, δ/ppm): 113.23, 111.95, 106.39, 104.14, 47.94, 29.70, 28.97, 28.81, 27.73, 27.53. MALDI-TOF HRMS (m/z): $C_{46}H_{44}F_2N_4$ [M^+] calc. 690.3534, found 690.3532.

4. ^{1}H and ^{13}C NMR spectra

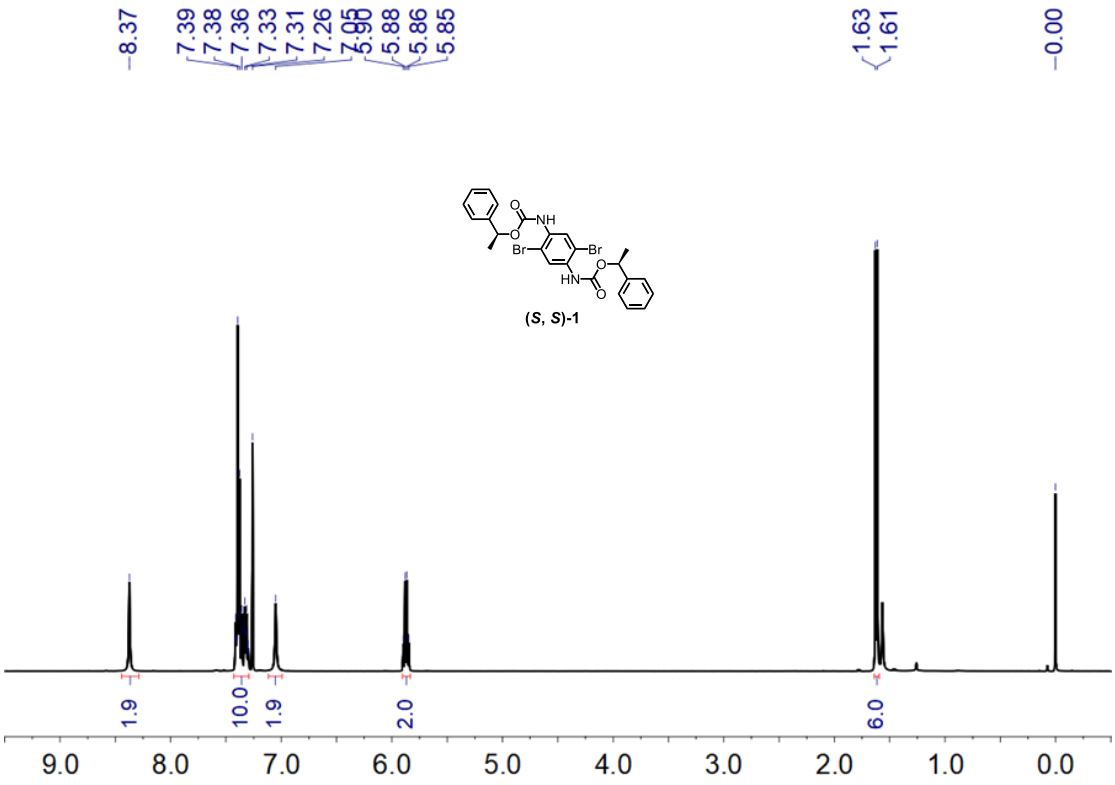


Fig. S6. ^{1}H NMR spectrum for **(*S*, *S*)-1** ($CDCl_3$, 298 K)

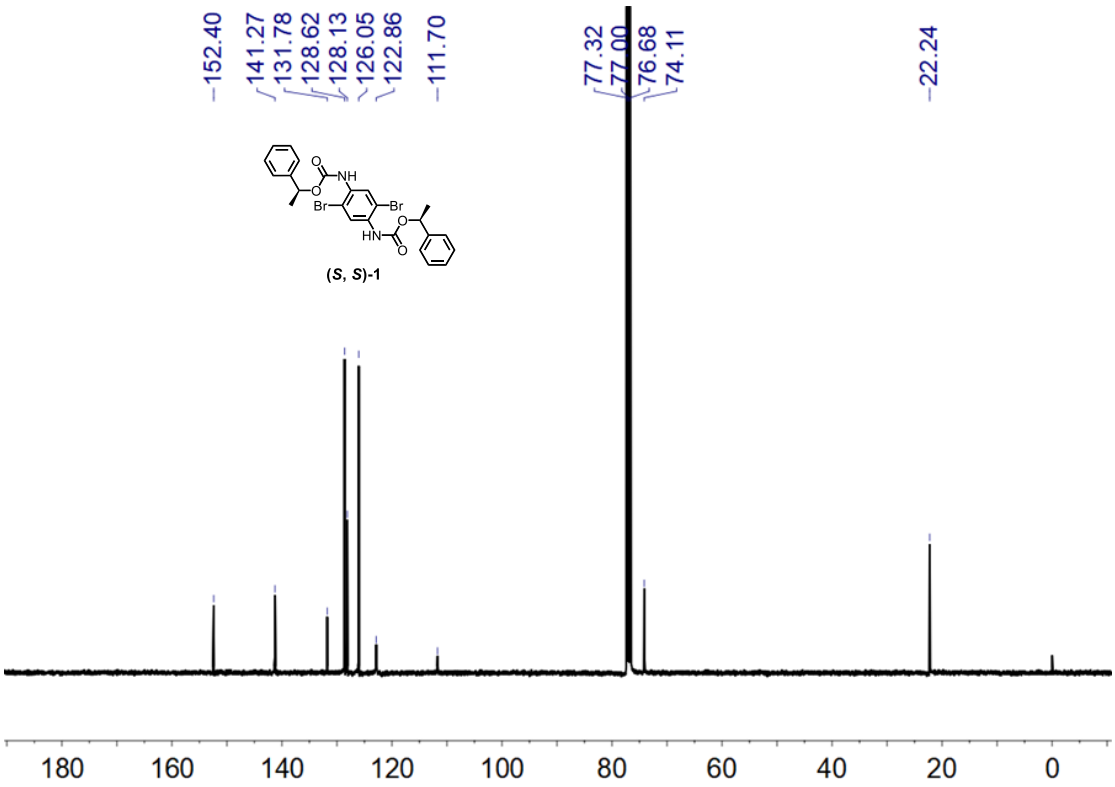


Fig. S7. ^{13}C NMR spectrum for **(*S*, *S*)-1** ($CDCl_3$, 298 K)

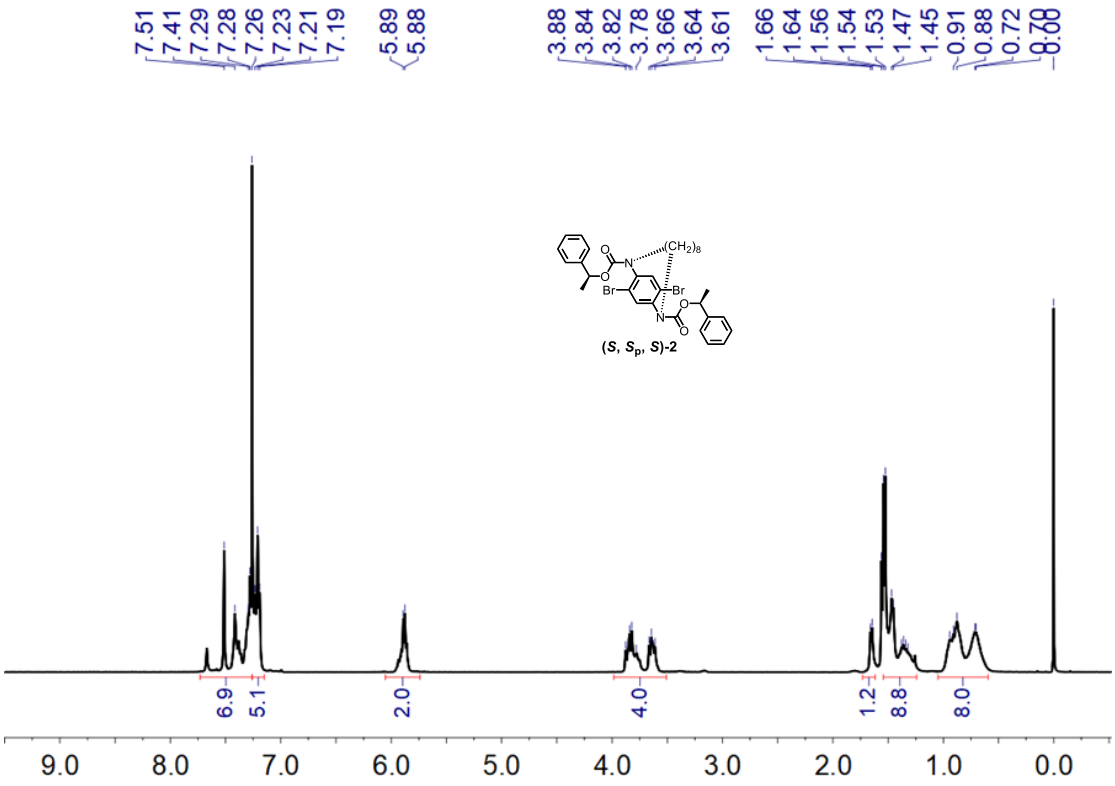


Fig. S8. ^{1}H NMR spectrum for **(*S*, *S*$_p$, *S*)-2** ($CDCl_3$, 298 K)

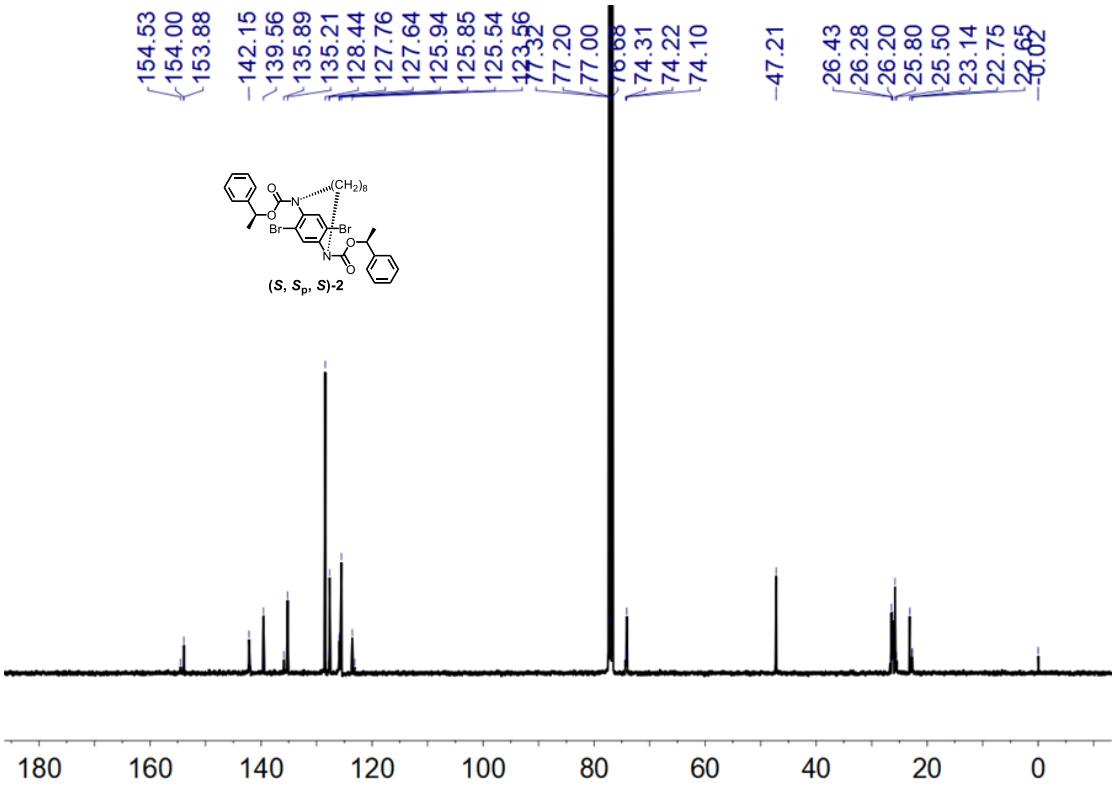


Fig. S9. ^{13}C NMR spectrum for **(*S*, *S*$_p$, *S*)-2** ($CDCl_3$, 298 K)

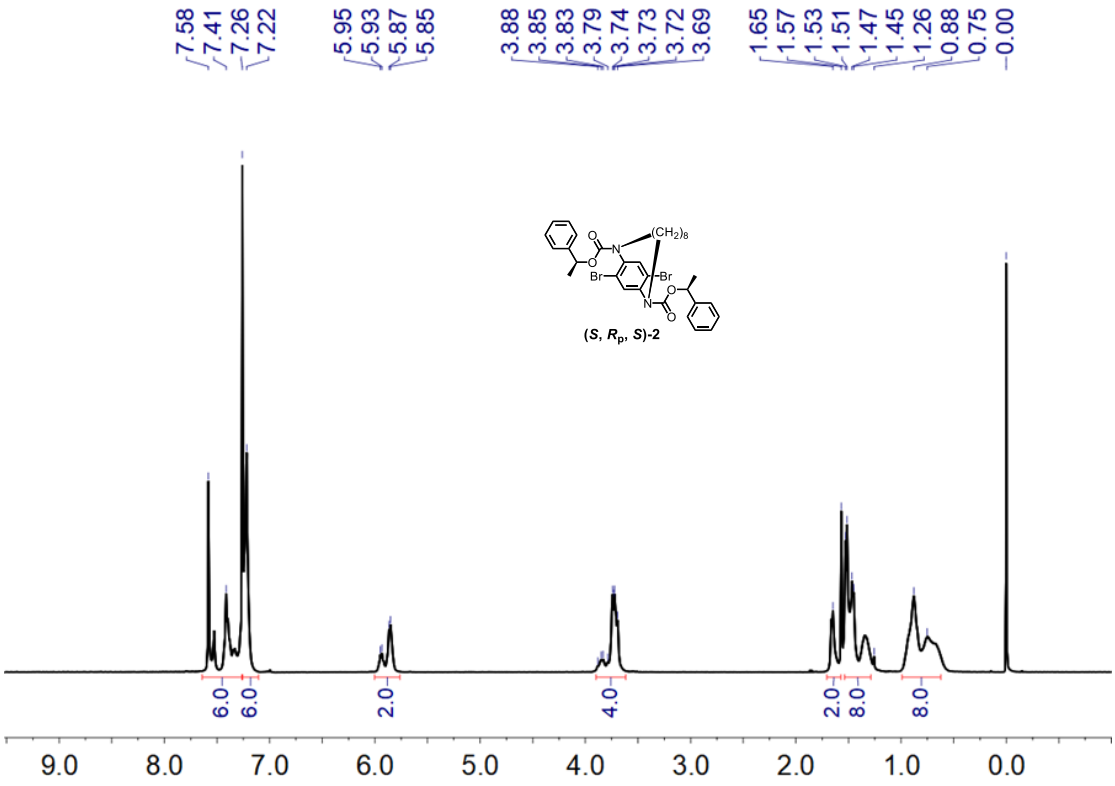


Fig. S10. ^{1}H NMR spectrum for **(*S*, *R*$_p$, *S*)-2** ($CDCl_3$, 298 K)

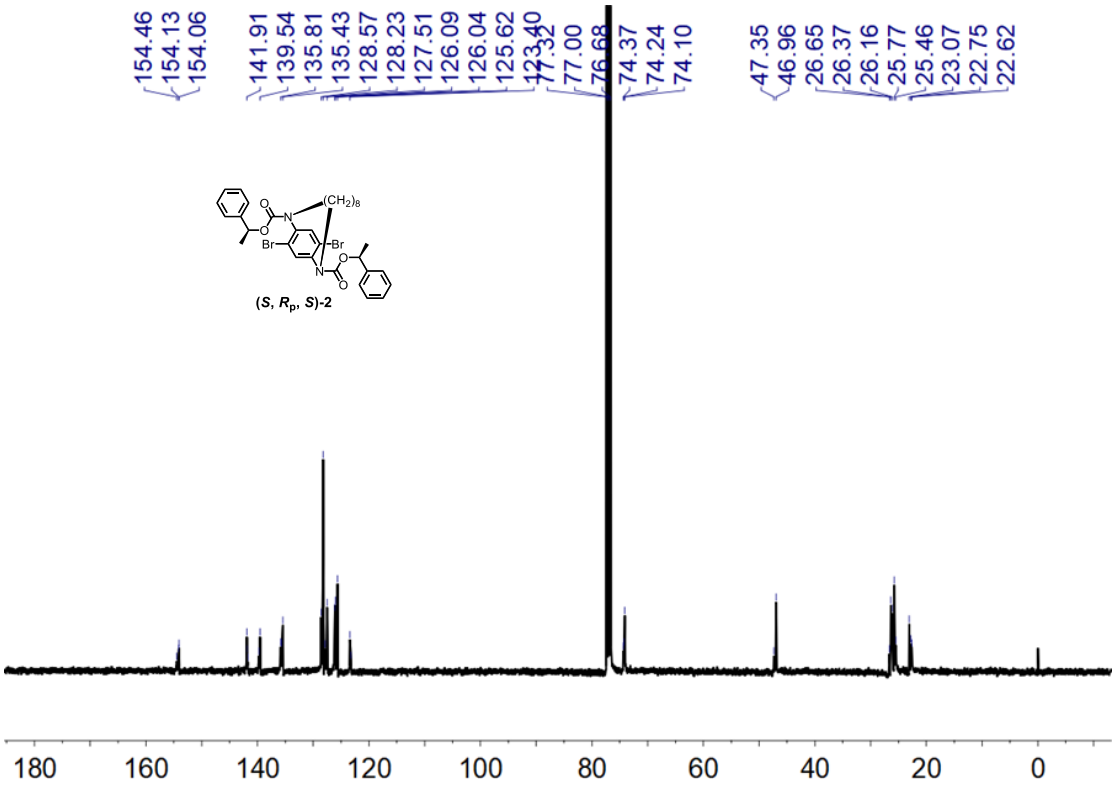


Fig. S11. ^{13}C NMR spectrum for **(*S*, *R*$_p$, *S*)-2** ($CDCl_3$, 298 K)

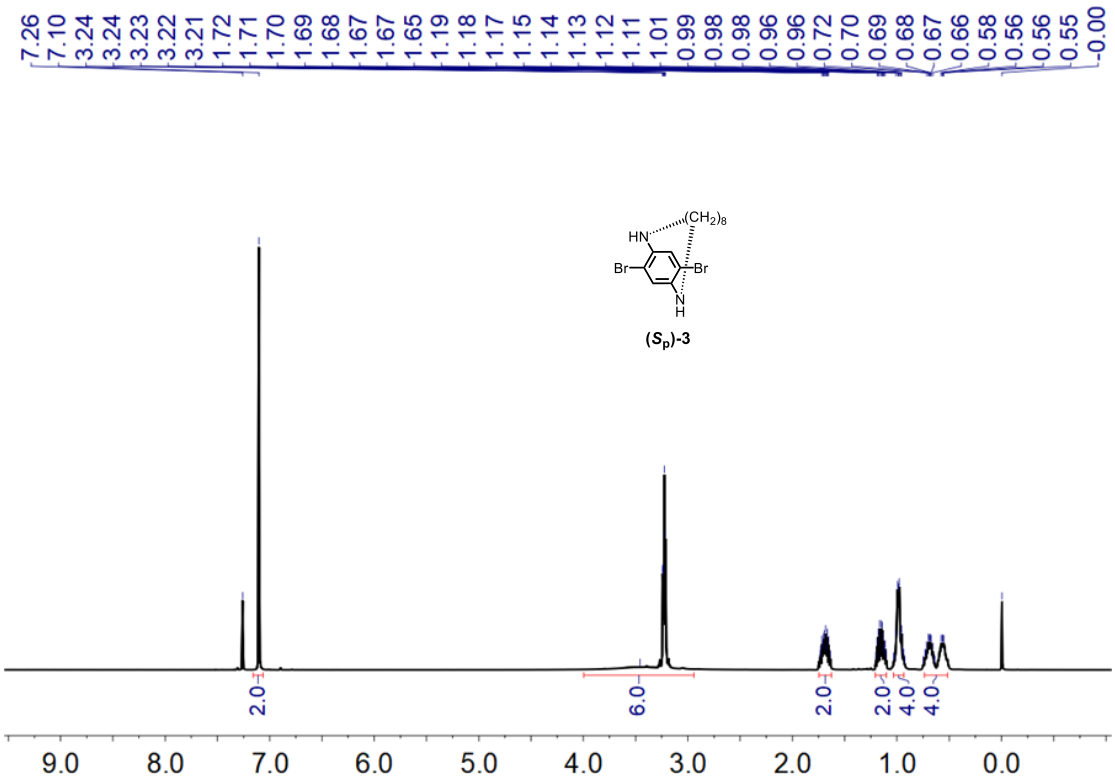


Fig. S12. ^{1}H NMR spectrum for **(S_p)-3** ($CDCl_3$, 298 K)

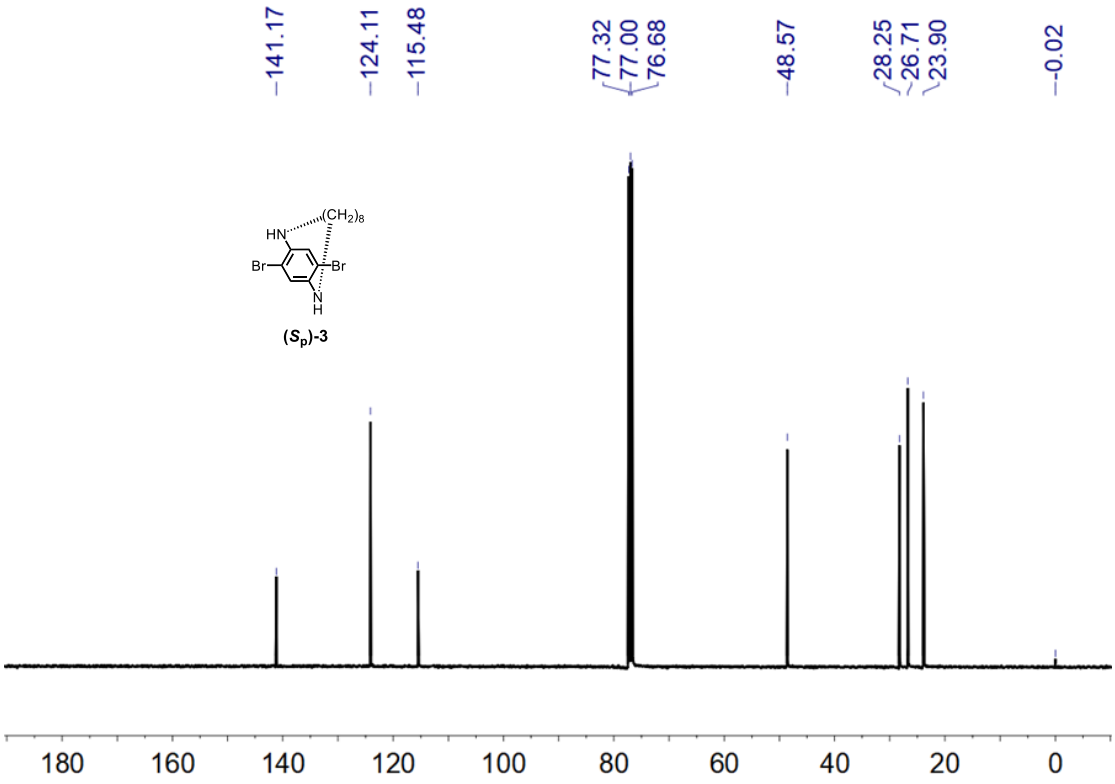


Fig. S13. ^{13}C NMR spectrum for **(S_p)-3** ($CDCl_3$, 298 K)

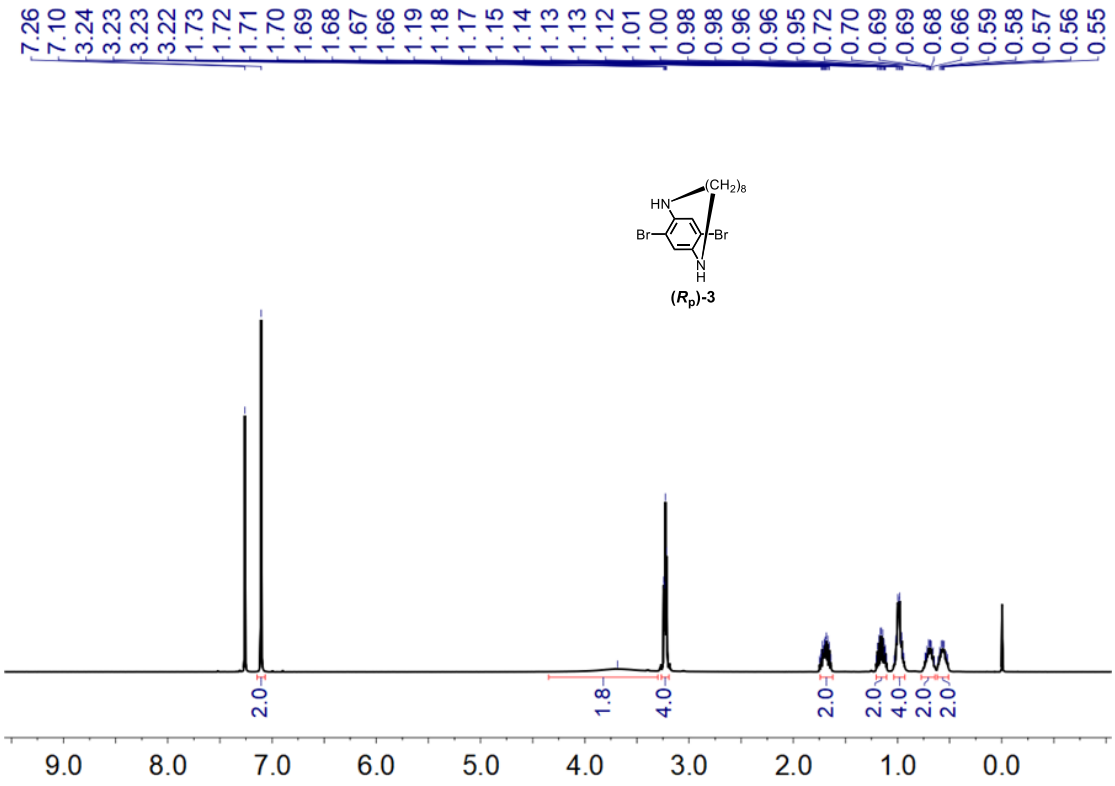


Fig. S14. ^{1}H NMR spectrum for **(R_p)-3** ($CDCl_3$, 298 K)

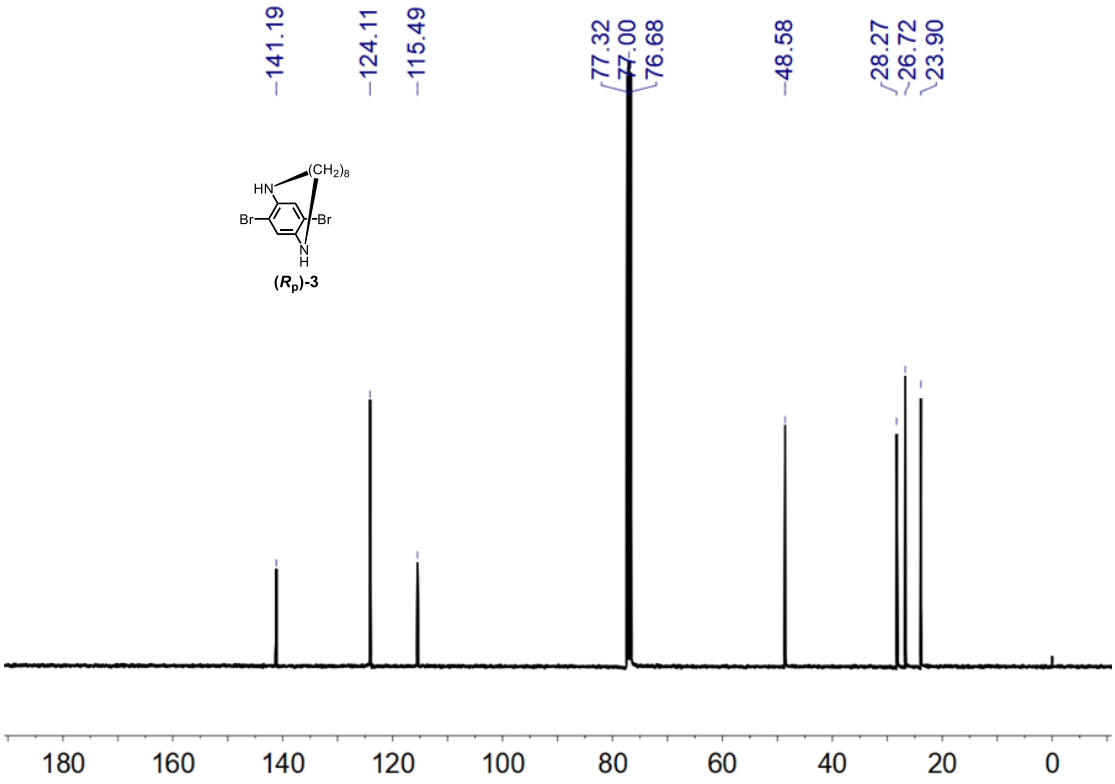


Fig. S15. ^{13}C NMR spectrum for **(R_p)-3** ($CDCl_3$, 298 K)

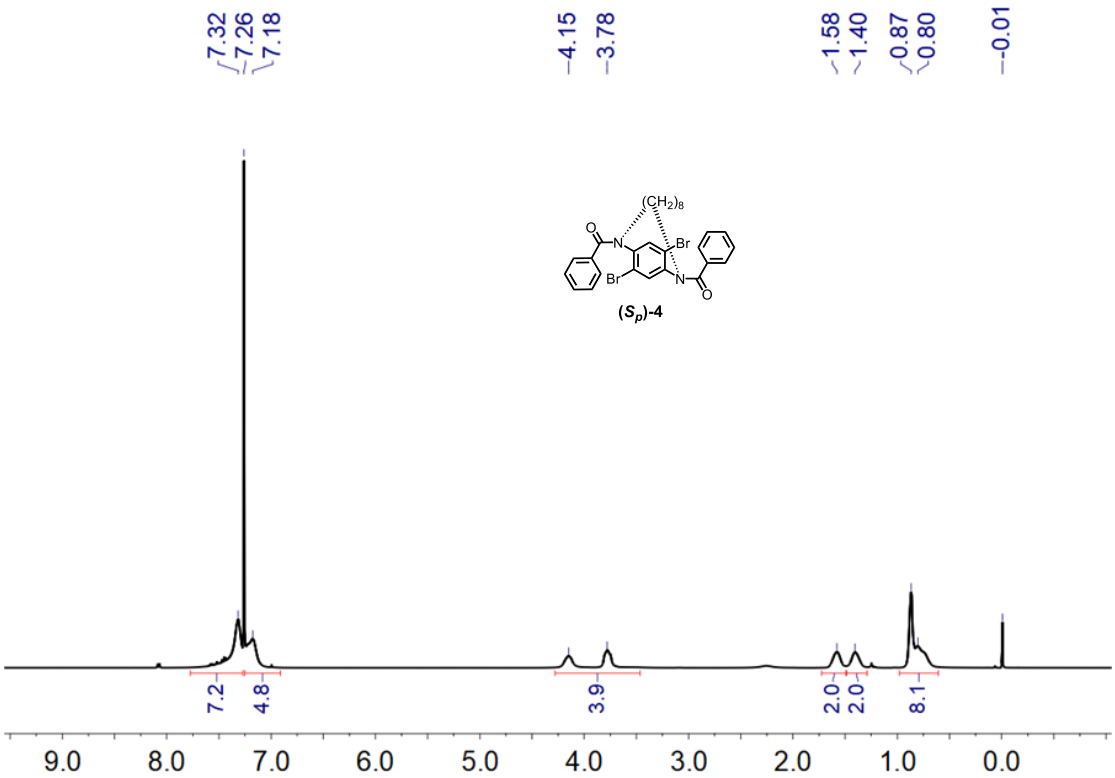


Fig. S16. ^{1}H NMR spectrum for **(S_p)-4** ($CDCl_3$, 298 K)

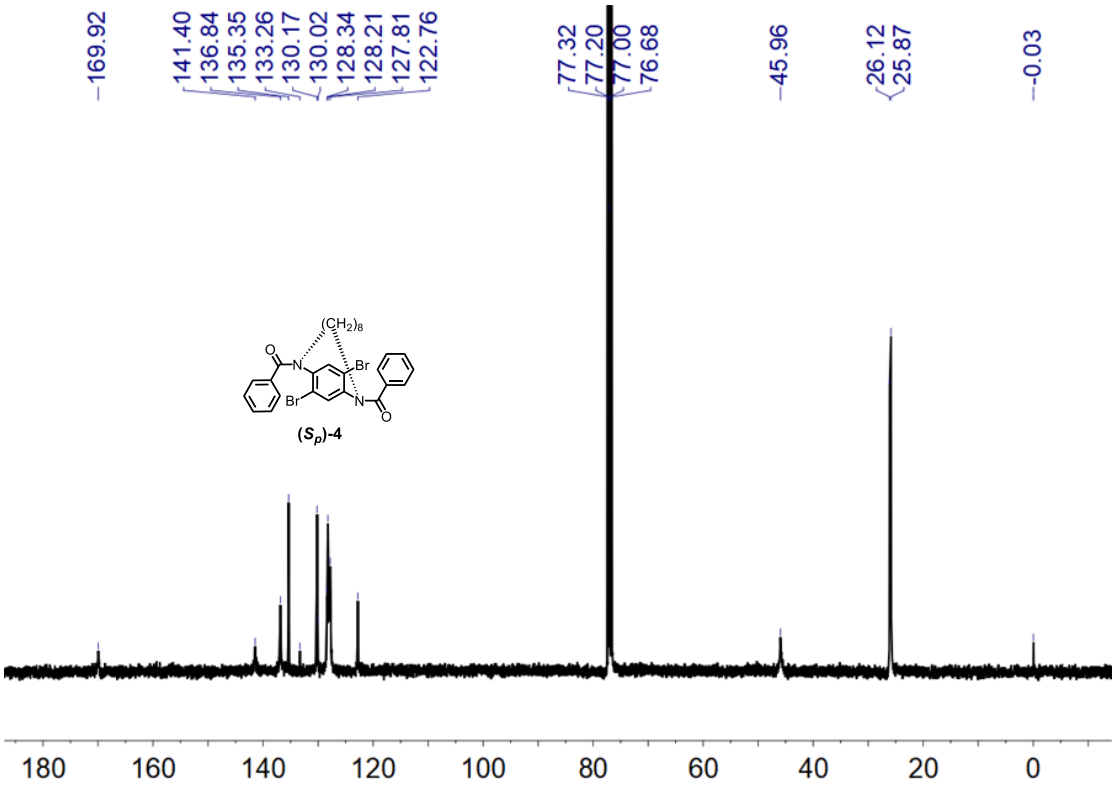


Fig. S17. ^{13}C NMR spectrum for **(S_p)-4** ($CDCl_3$, 298 K)

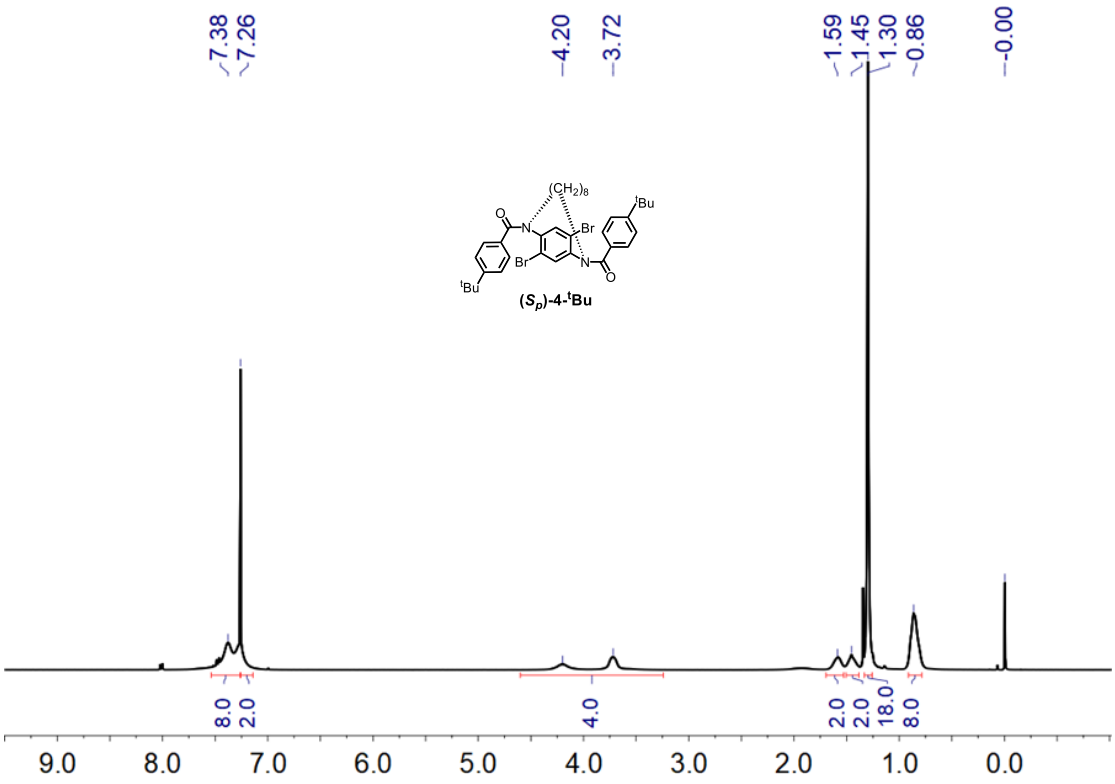


Fig. S18. ^{1}H NMR spectrum for **(S_p)-4-^{t}Bu** ($CDCl_3$, 298 K)

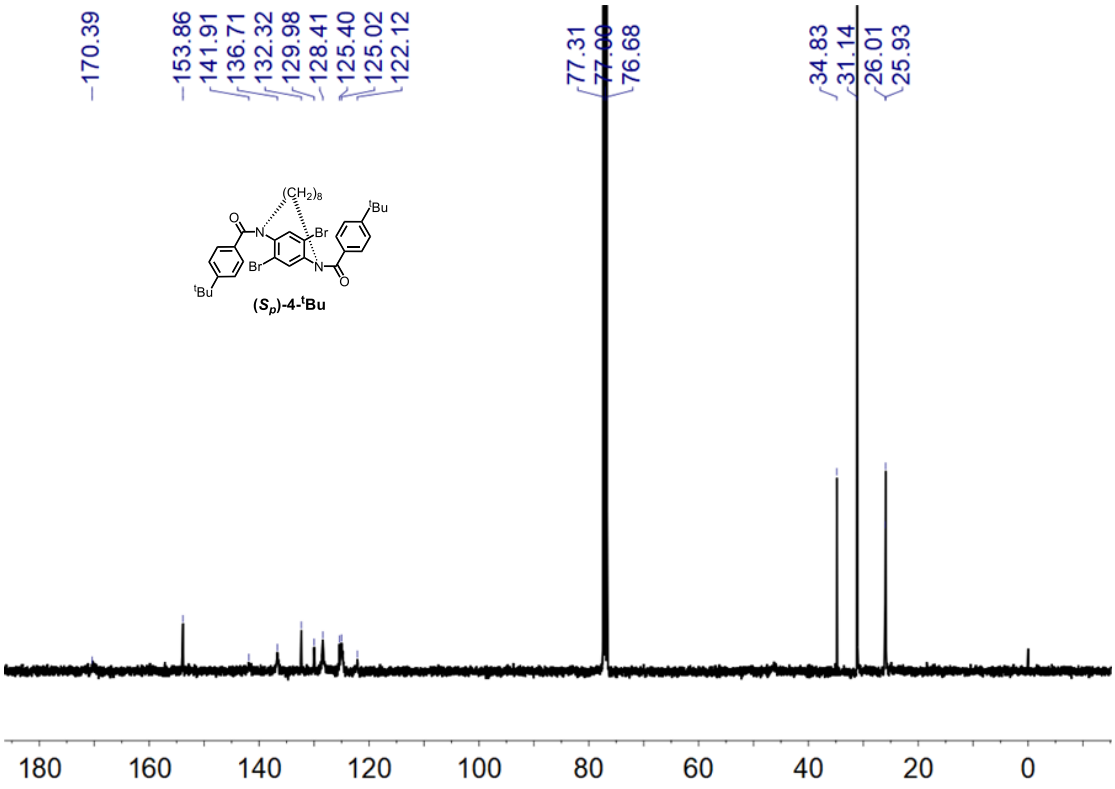


Fig. S19. ^{13}C NMR spectrum for **(S_p)-4-^{t}Bu** ($CDCl_3$, 298 K)

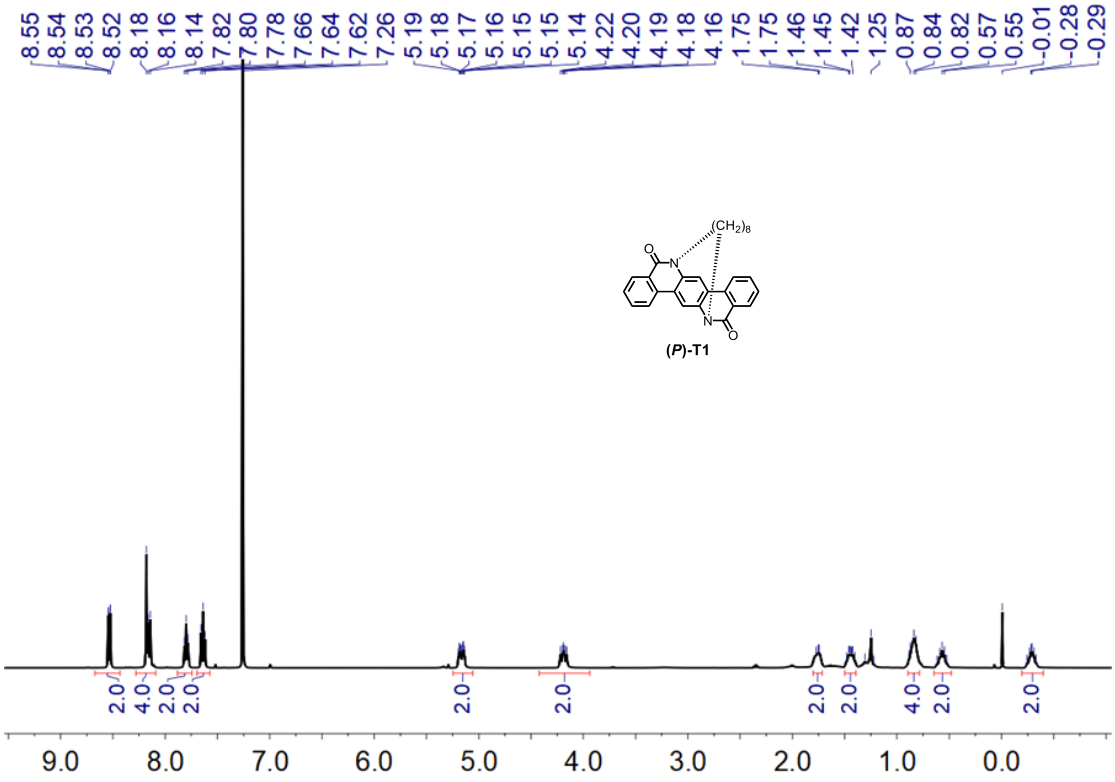


Fig. S20. ^{1}H NMR spectrum for **(*P*)-T1** ($CDCl_3$, 298 K)

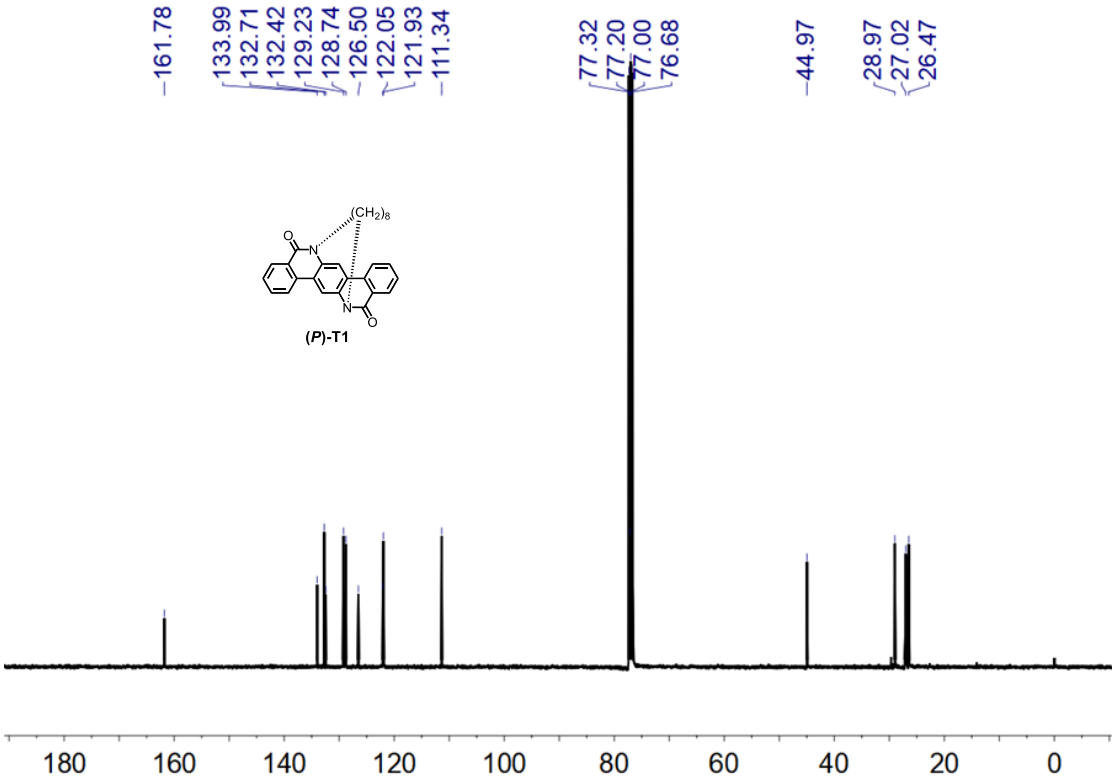


Fig. S21. ^{13}C NMR spectrum for **(*P*)-T1** ($CDCl_3$, 298 K)

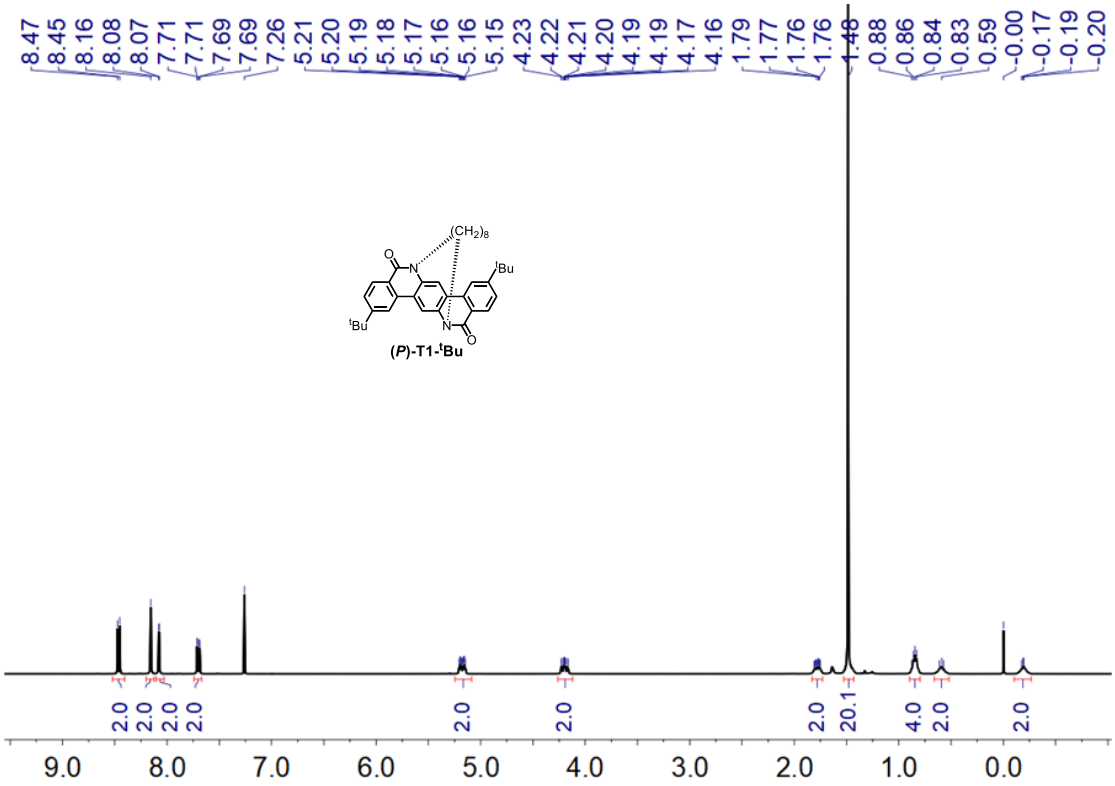


Fig. S22. ^{1}H NMR spectrum for **(*P*)-T1-^{t}Bu** ($CDCl_3$, 298 K)

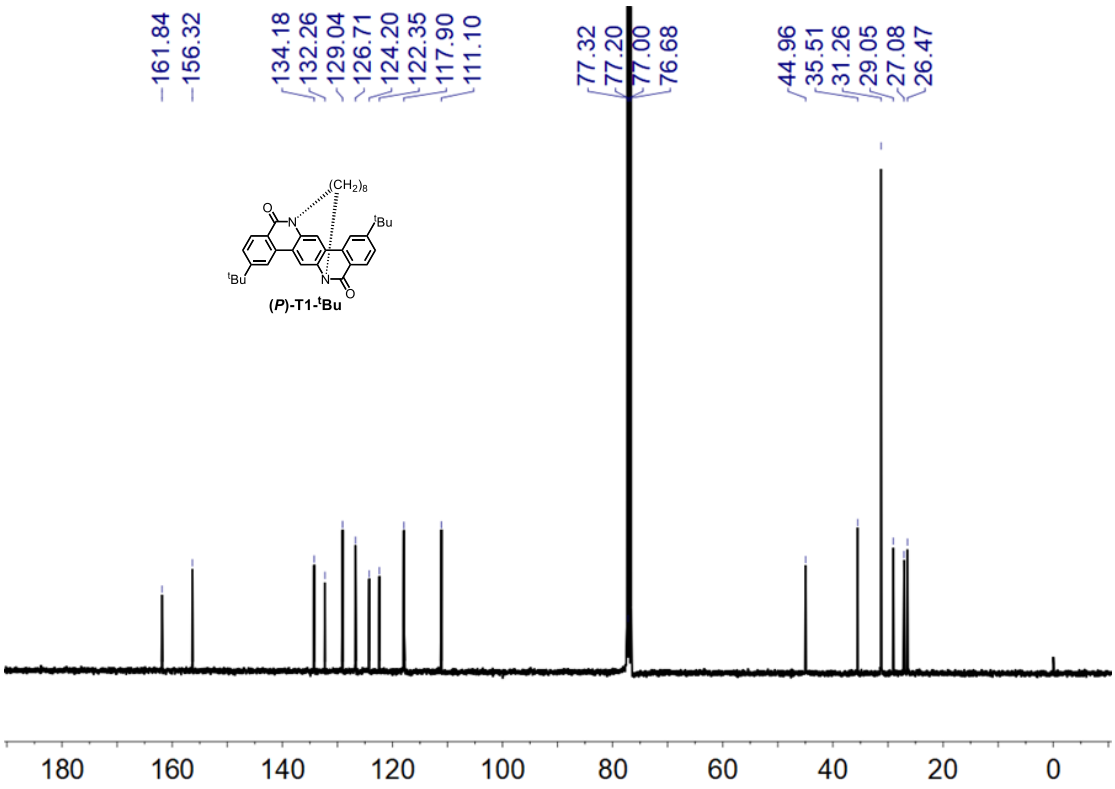


Fig. S23. ^{13}C NMR spectrum for **(*P*)-T1-^{t}Bu** ($CDCl_3$, 298 K)

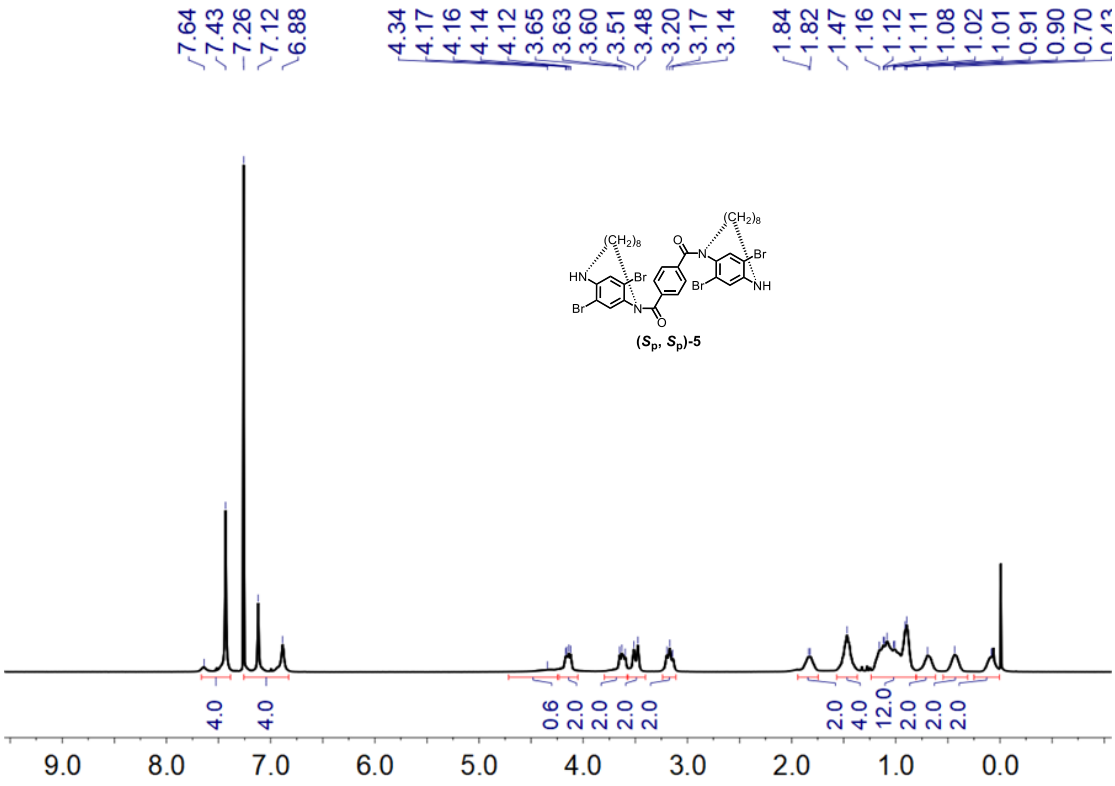


Fig. S24. ^{1}H NMR spectrum for **(S_p, S_p)-5** ($CDCl_3$, 298 K)

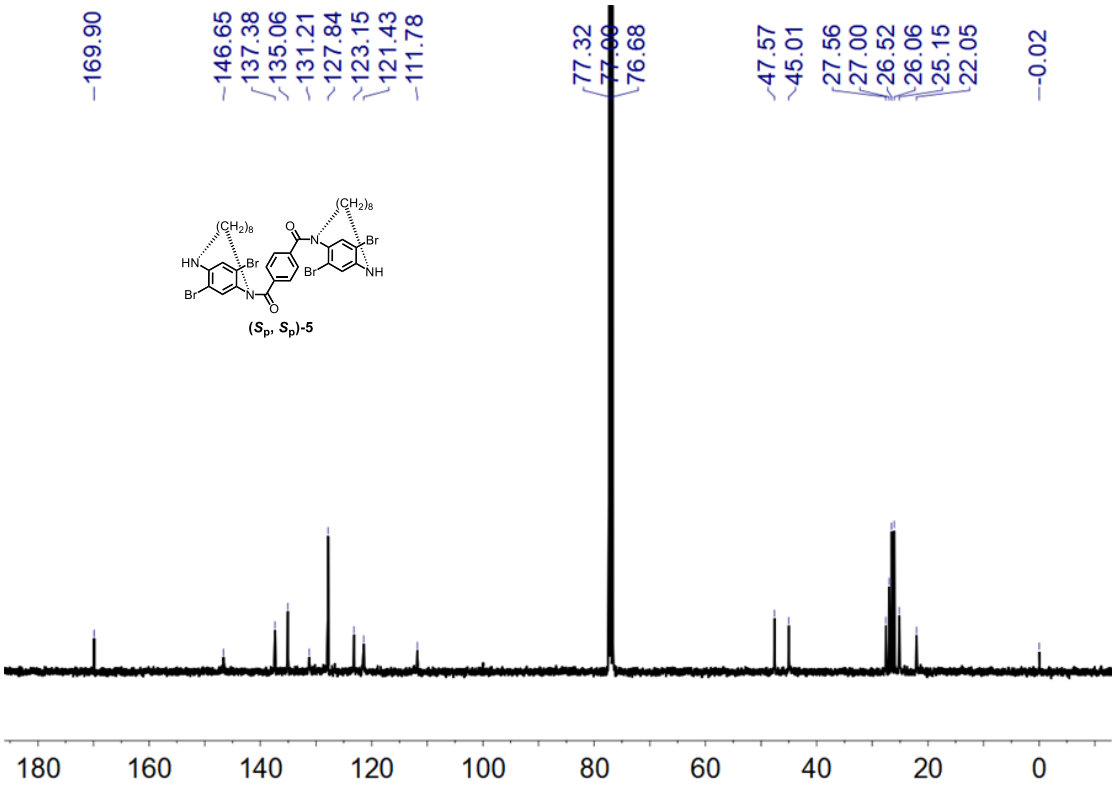


Fig. S25. ^{13}C NMR spectrum for **(S_p, S_p)-5** ($CDCl_3$, 298 K)

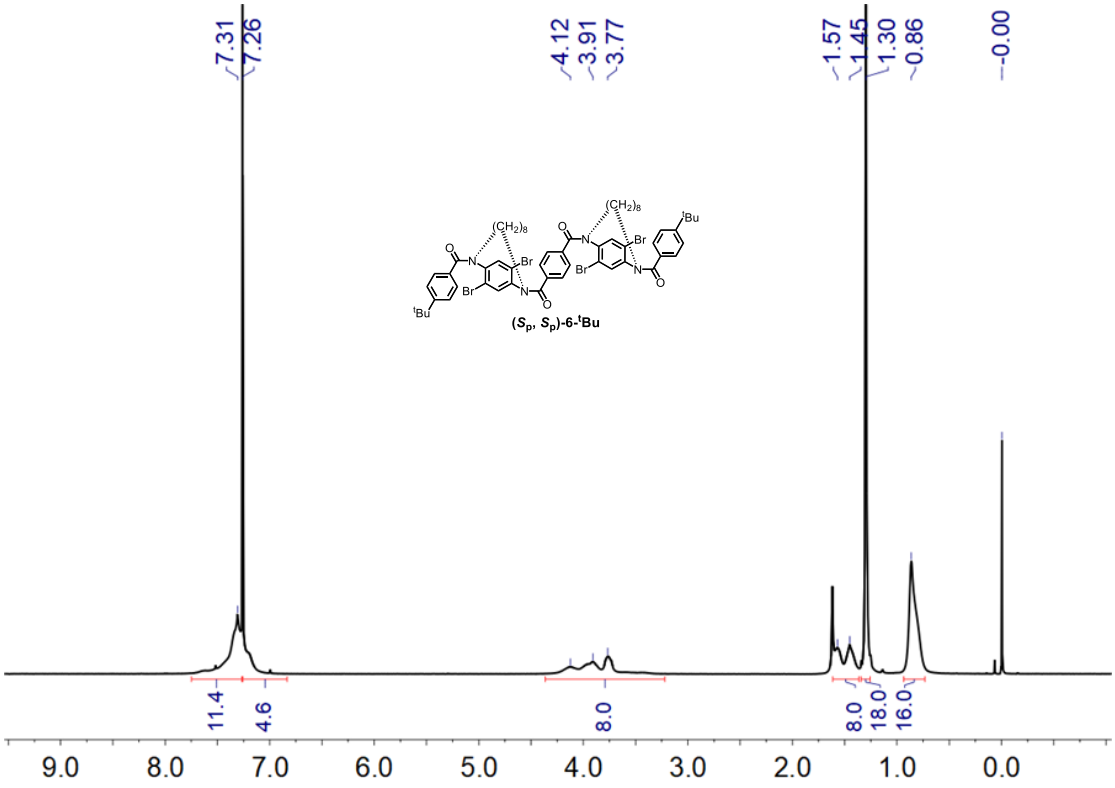


Fig. S26. ^{1}H NMR spectrum for **(S_p, S_p)-6-^{t}Bu** ($CDCl_3$, 298 K)

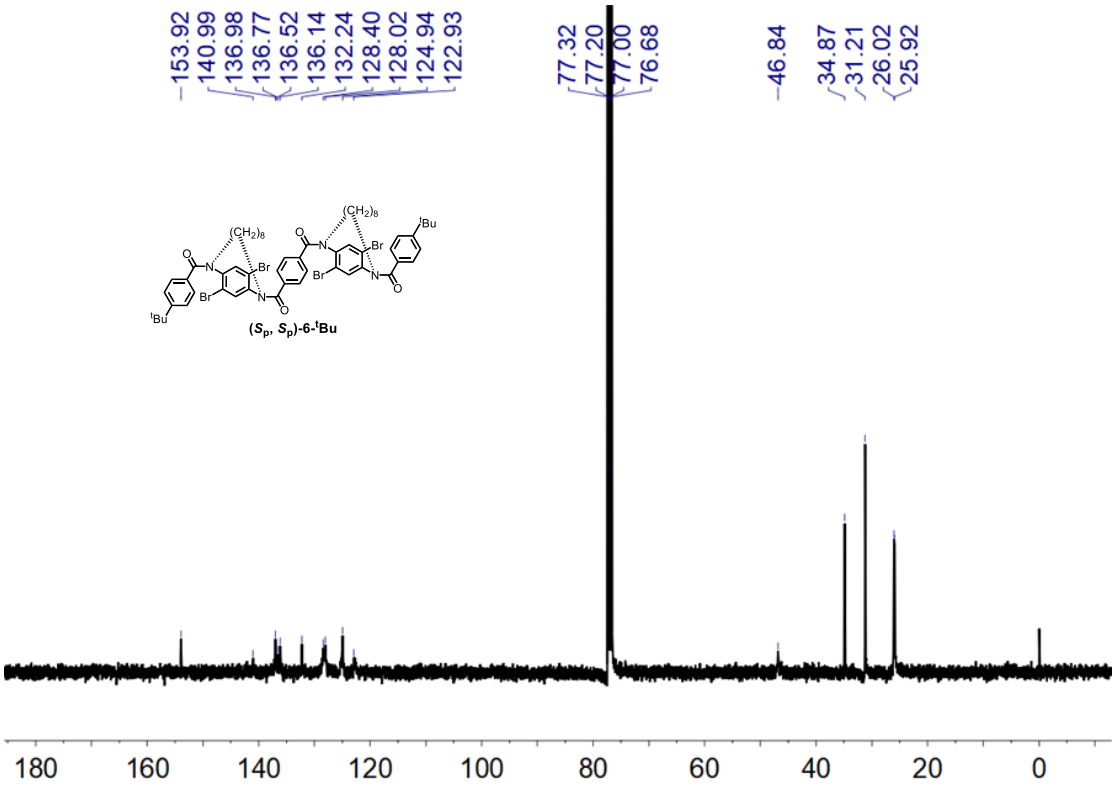


Fig. S27. ^{13}C NMR spectrum for **(S_p, S_p)-6-^{t}Bu** ($CDCl_3$, 298 K)

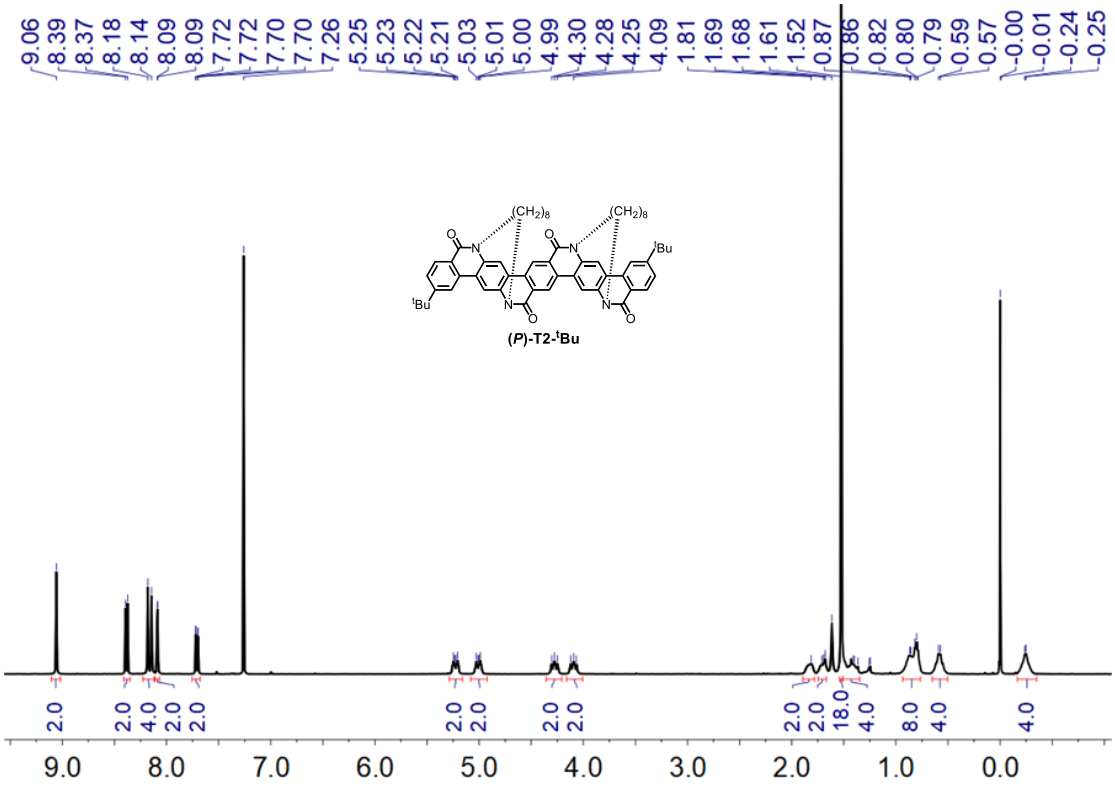


Fig. S28. ^{1}H NMR spectrum for **(*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

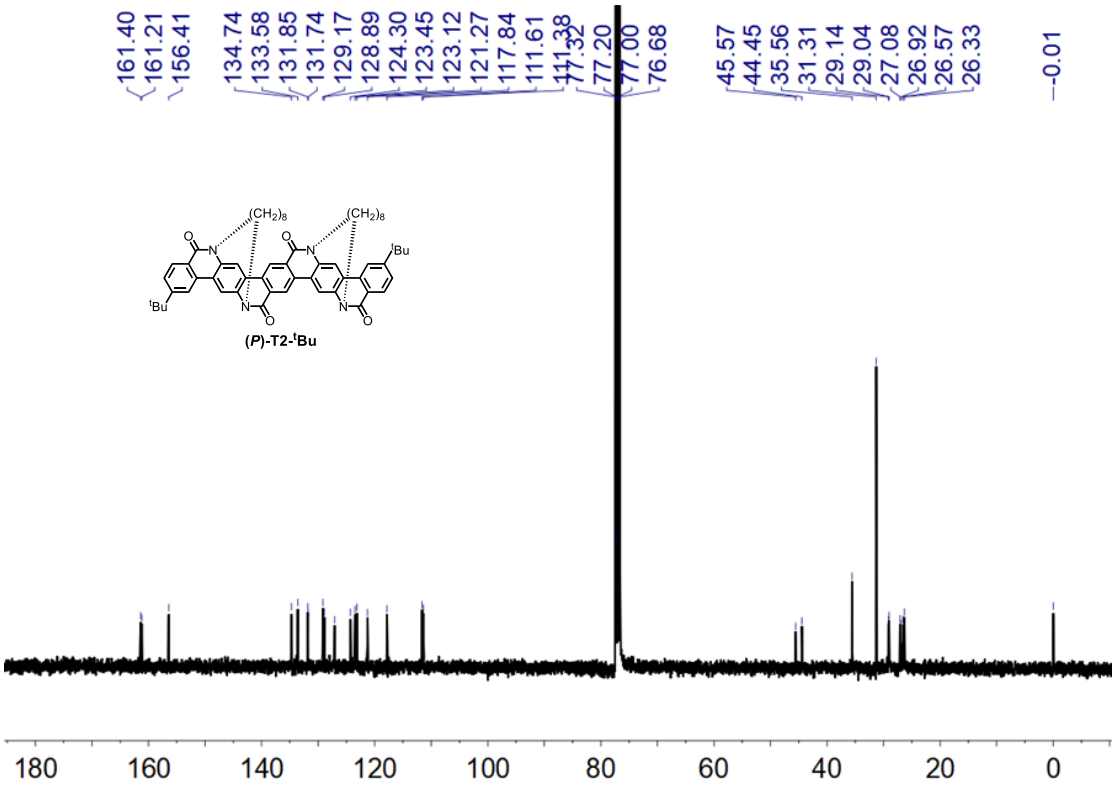


Fig. S29. ^{13}C NMR spectrum for **(*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

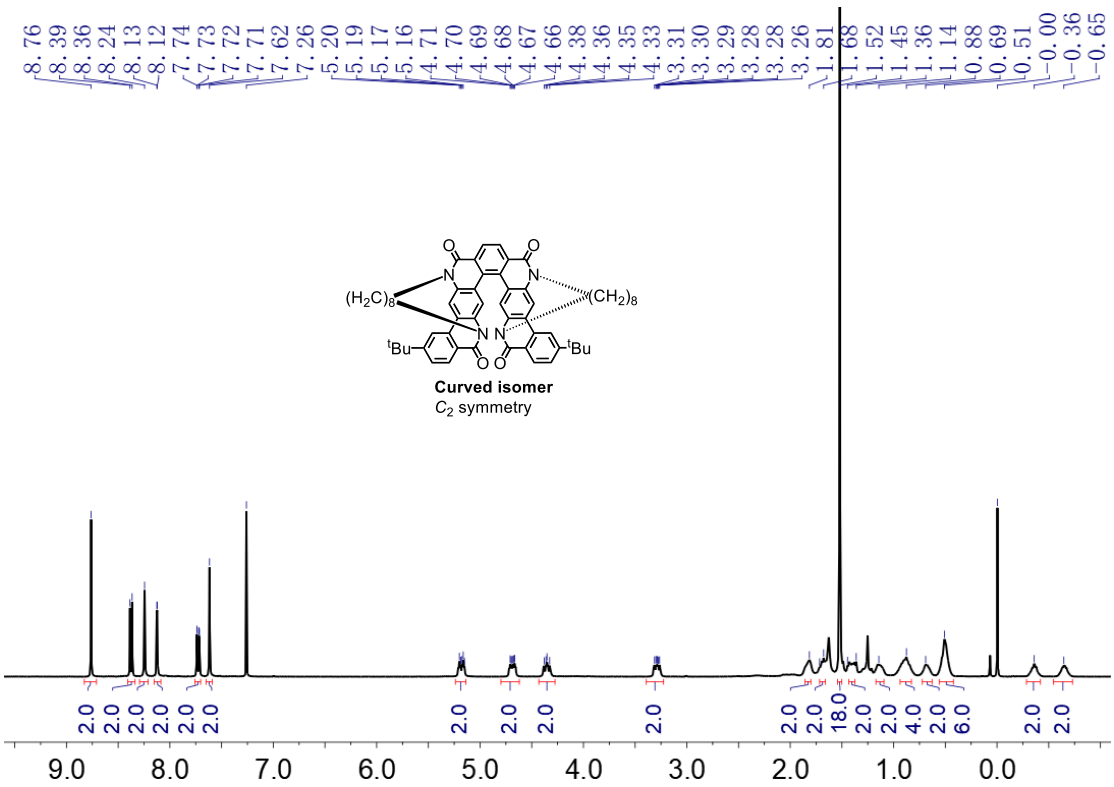


Fig. S30. ^{1}H NMR spectrum for **curved isomer of (*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

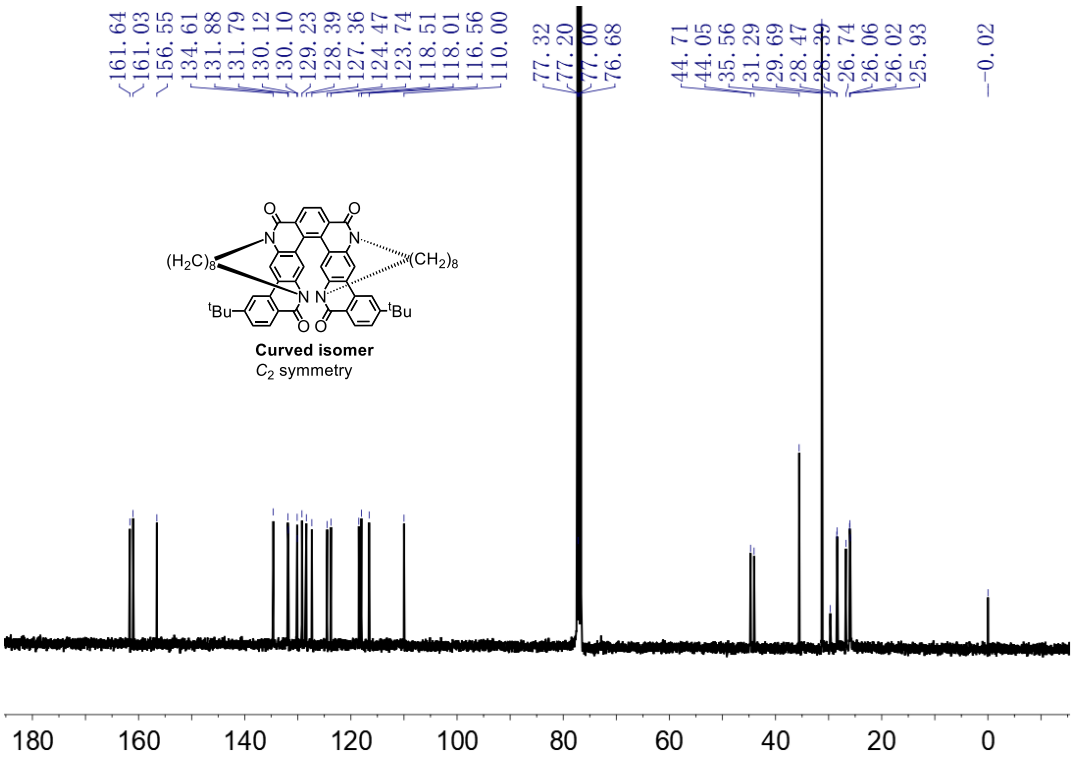


Fig. S31. ^{13}C NMR spectrum for **curved isomer of (*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

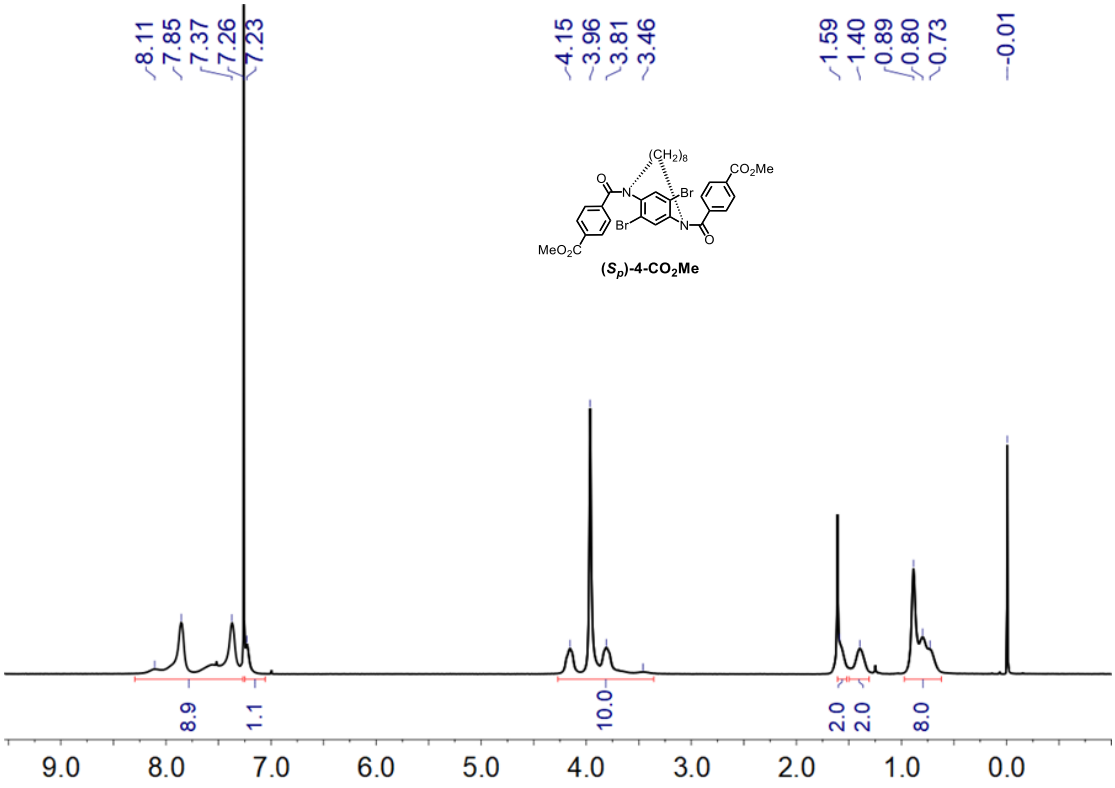


Fig. S32. ^{1}H NMR spectrum for **(S_p)-4-CO_2Me** ($CDCl_3$, 298 K)

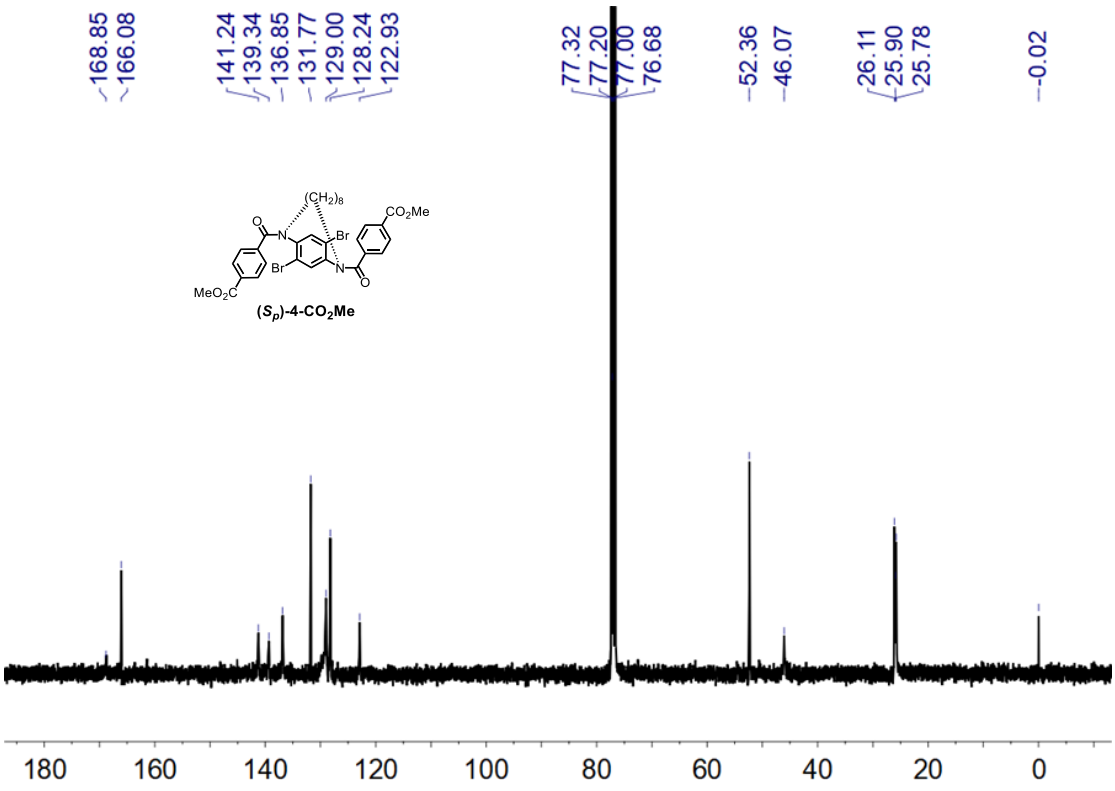


Fig. S33. ^{13}C NMR spectrum for **(S_p)-4-CO_2Me** ($CDCl_3$, 298 K)

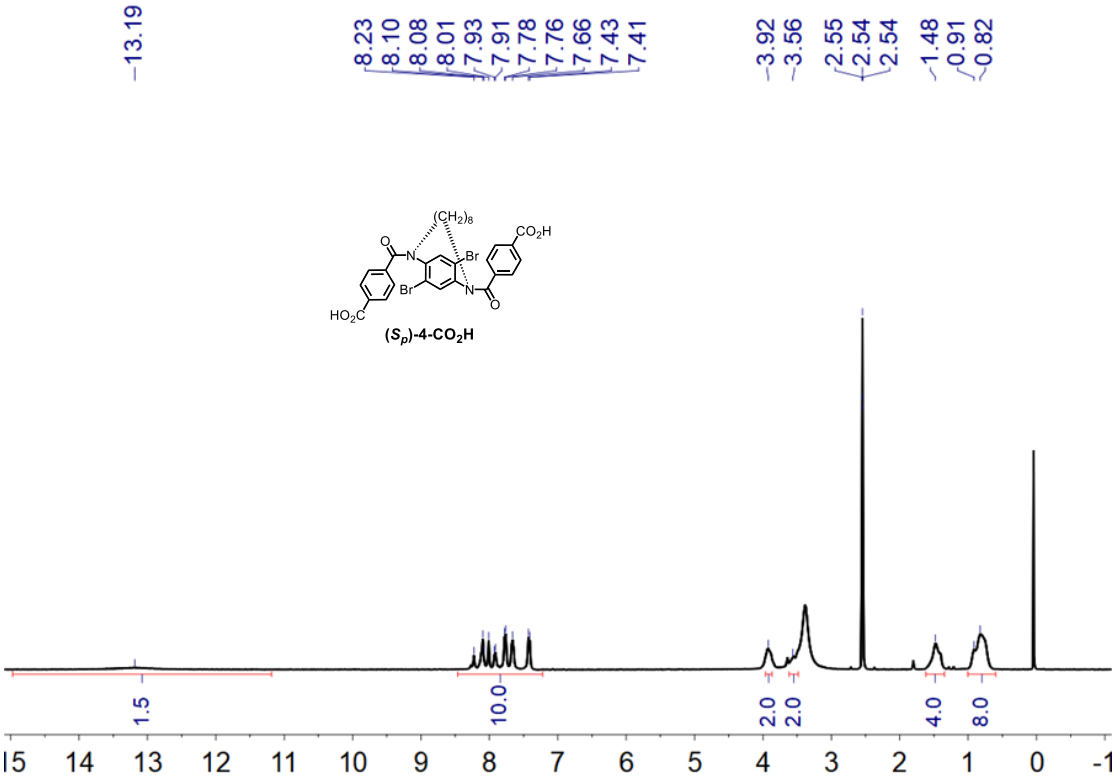


Fig. S34. ^{1}H NMR spectrum for **(S_p)-4-COOH** ($CDCl_3$, 298 K)

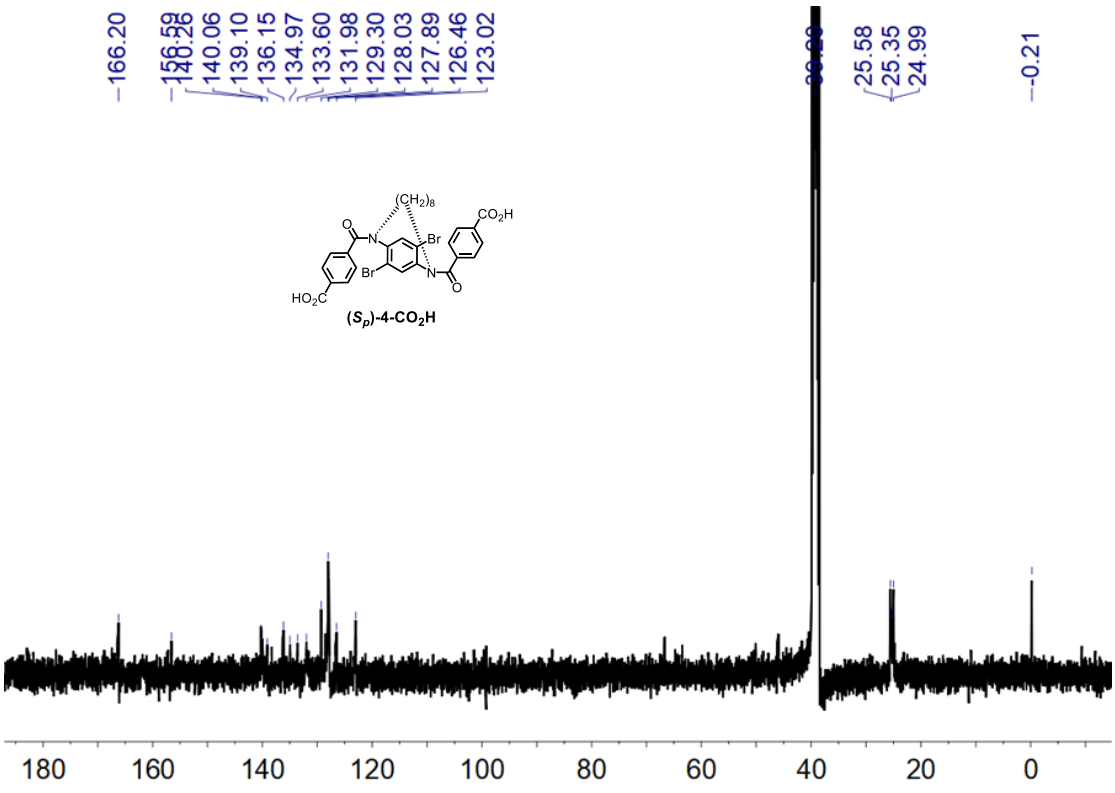


Fig. S35. ^{13}C NMR spectrum for **(S_p)-4-COOH** ($CDCl_3$, 298 K)

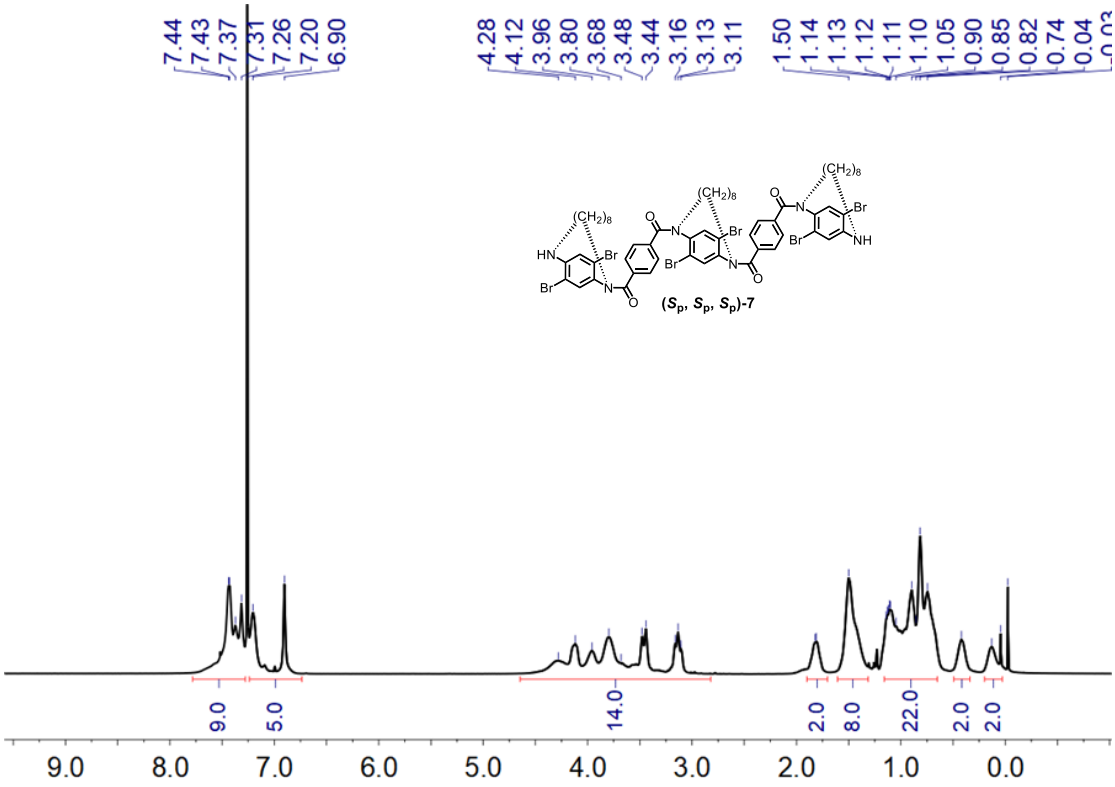


Fig. S36. ^{1}H NMR spectrum for **(S_p, S_p, S_p)-7** ($CDCl_3$, 298 K)

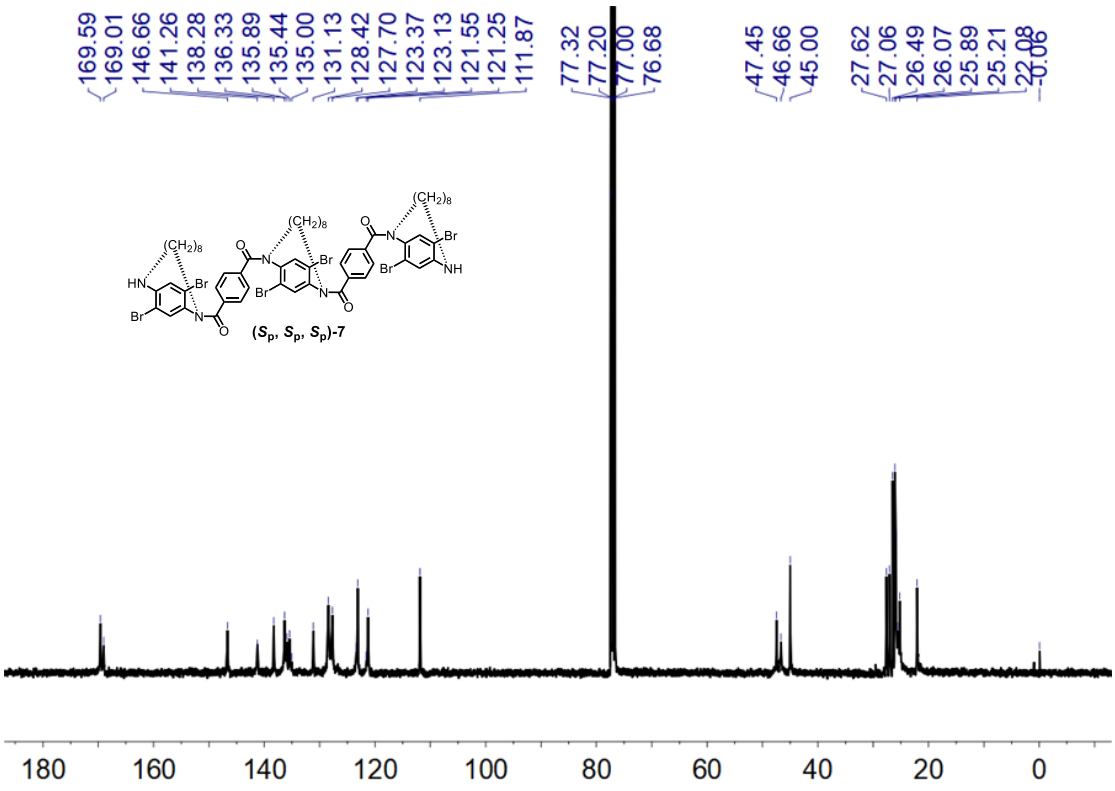


Fig. S37. ^{13}C NMR spectrum for **(S_p, S_p, S_p)-7** ($CDCl_3$, 298 K)

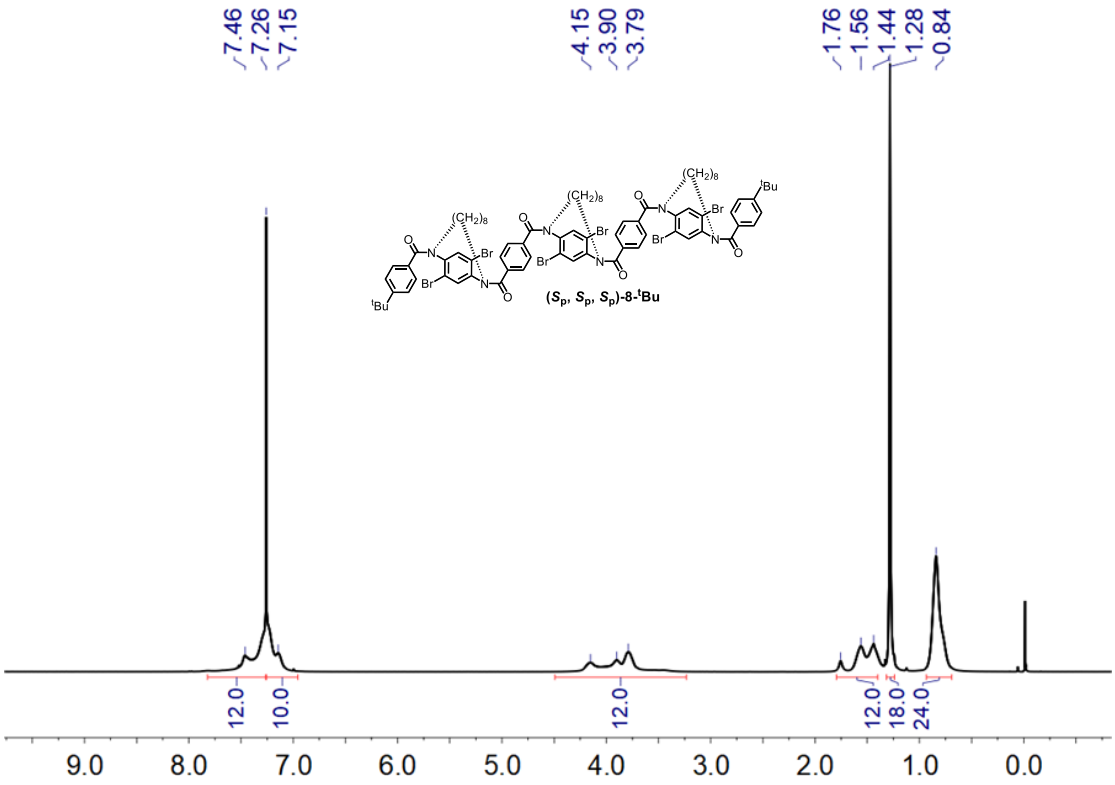


Fig. S38. ^{1}H NMR spectrum for **(S_p, S_p, S_p)-8-^{t}Bu** ($CDCl_3$, 298 K)

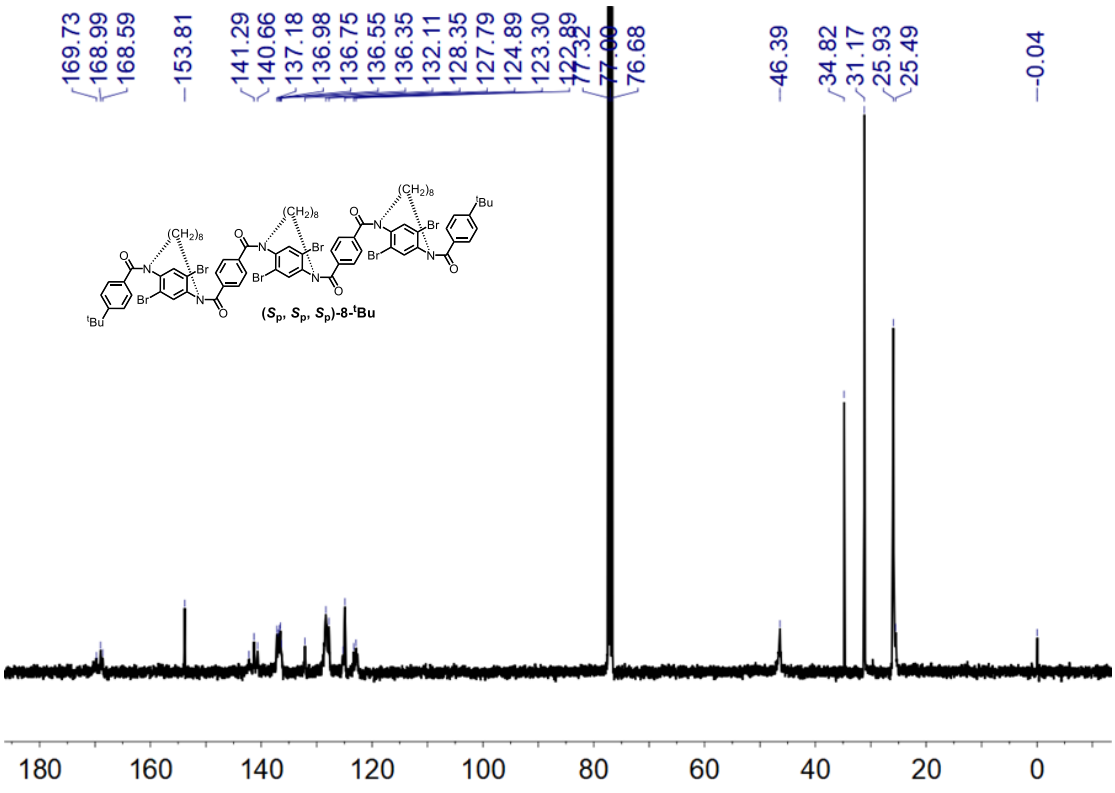


Fig. S39. ^{13}C NMR spectrum for **(S_p, S_p, S_p)-8-^{t}Bu** ($CDCl_3$, 298 K)

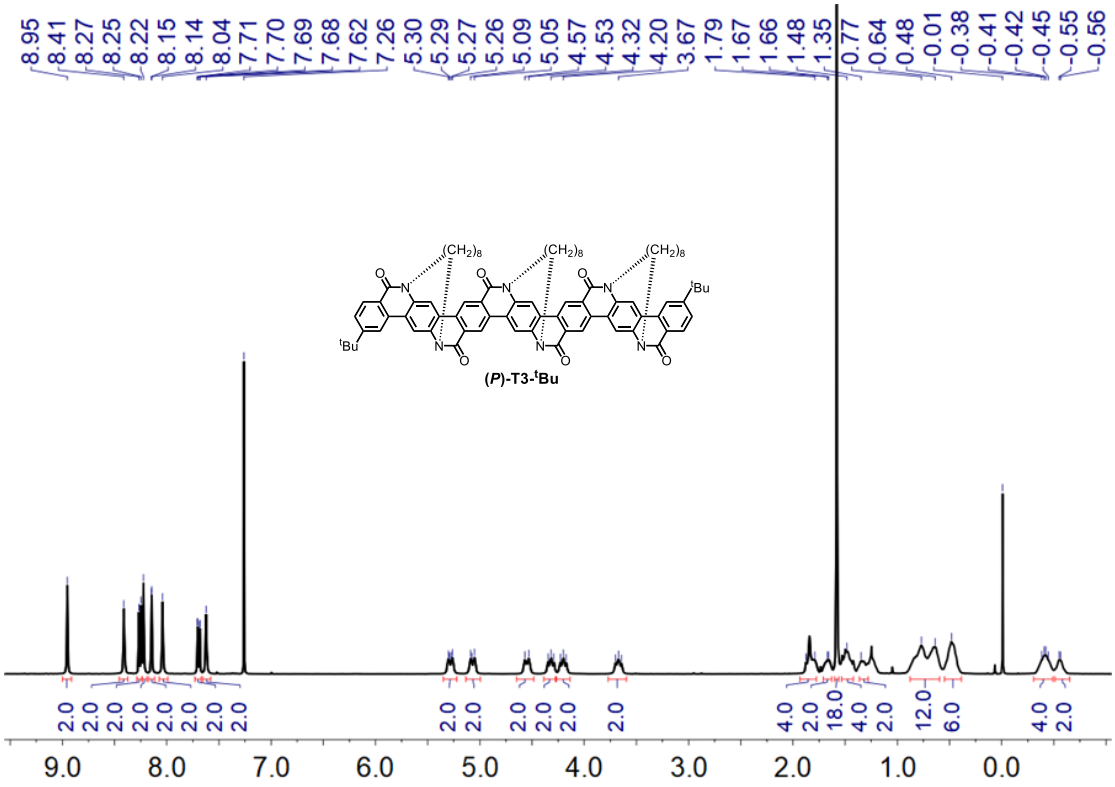


Fig. S40. ^{1}H NMR spectrum for **(*P*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

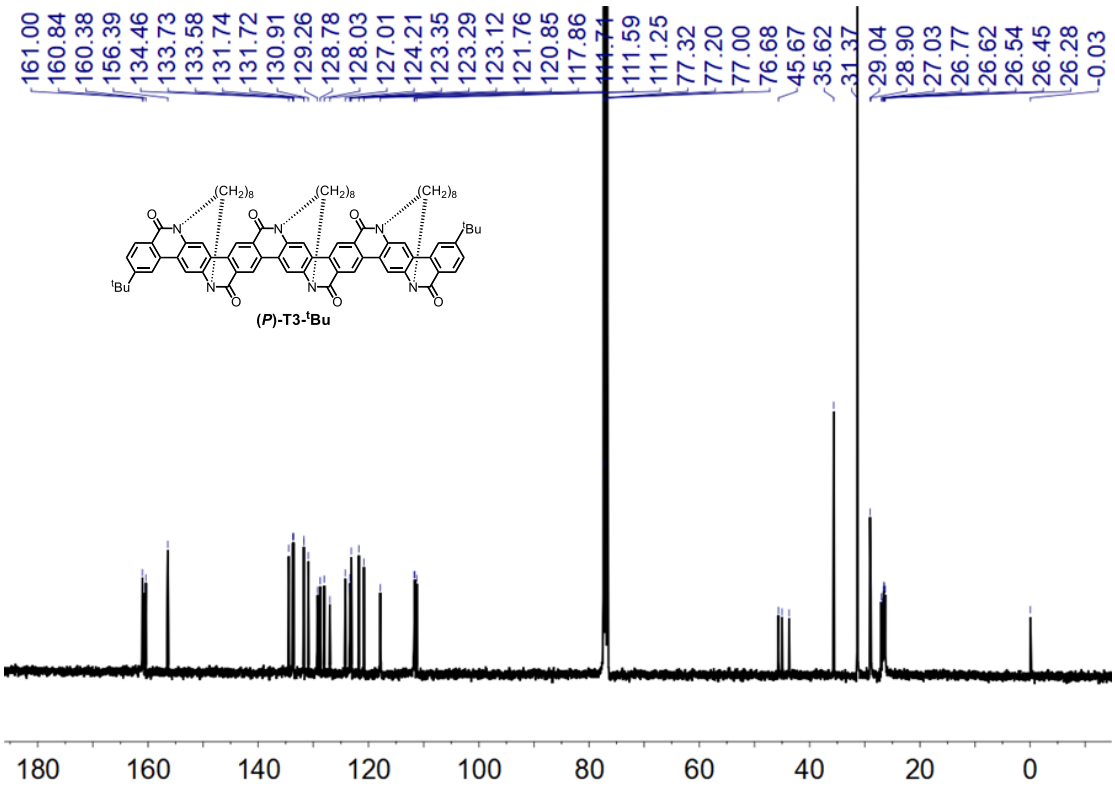


Fig. S41. ^{13}C NMR spectrum for **(*P*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

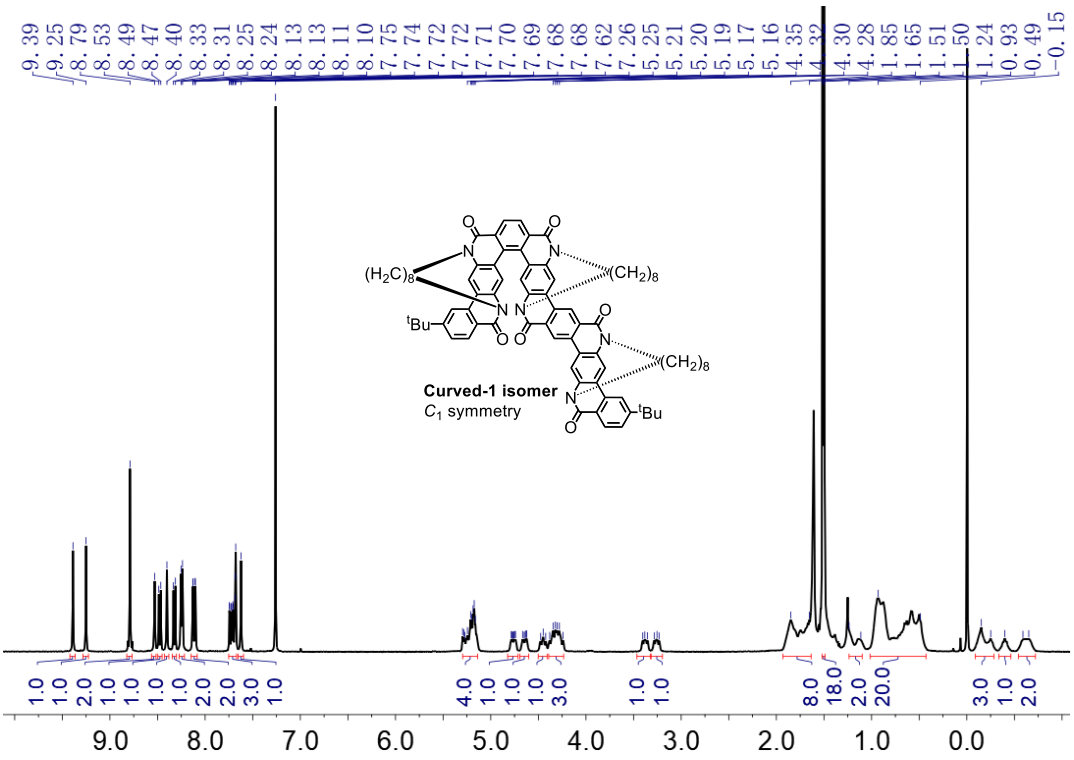


Fig. S42. ^{1}H NMR spectrum for **curved-1 isomer of (*P*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

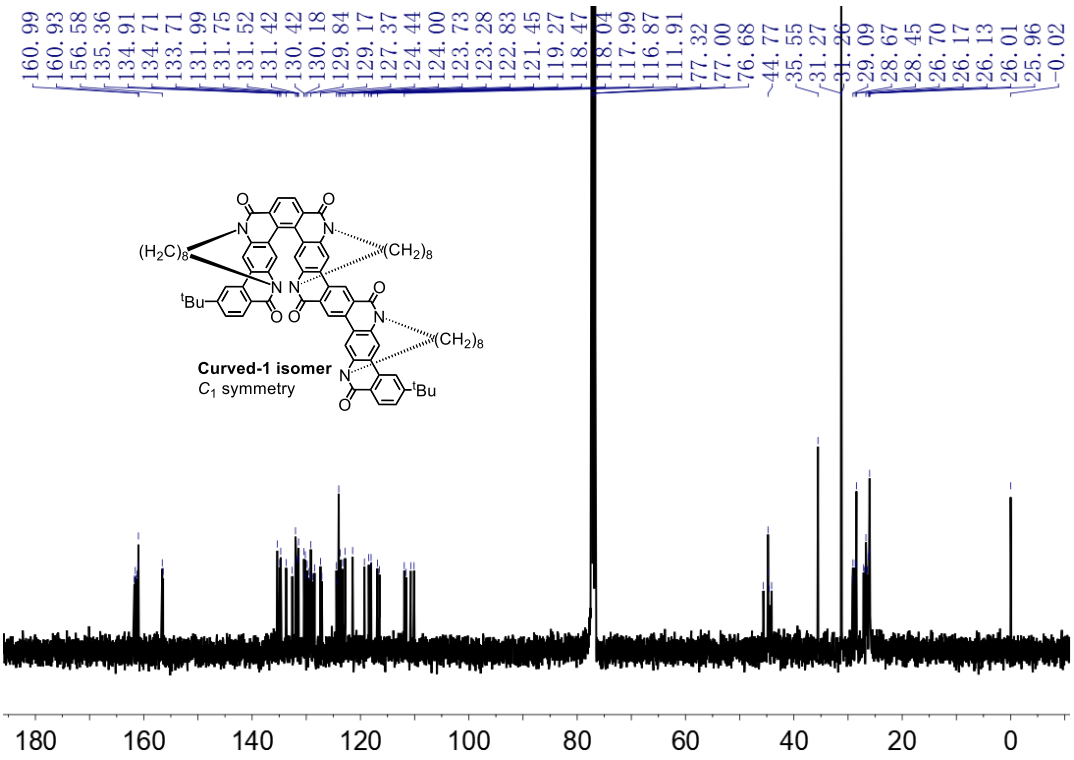


Fig. S43. ^{13}C NMR spectrum for **curved-1 isomer of (*P*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

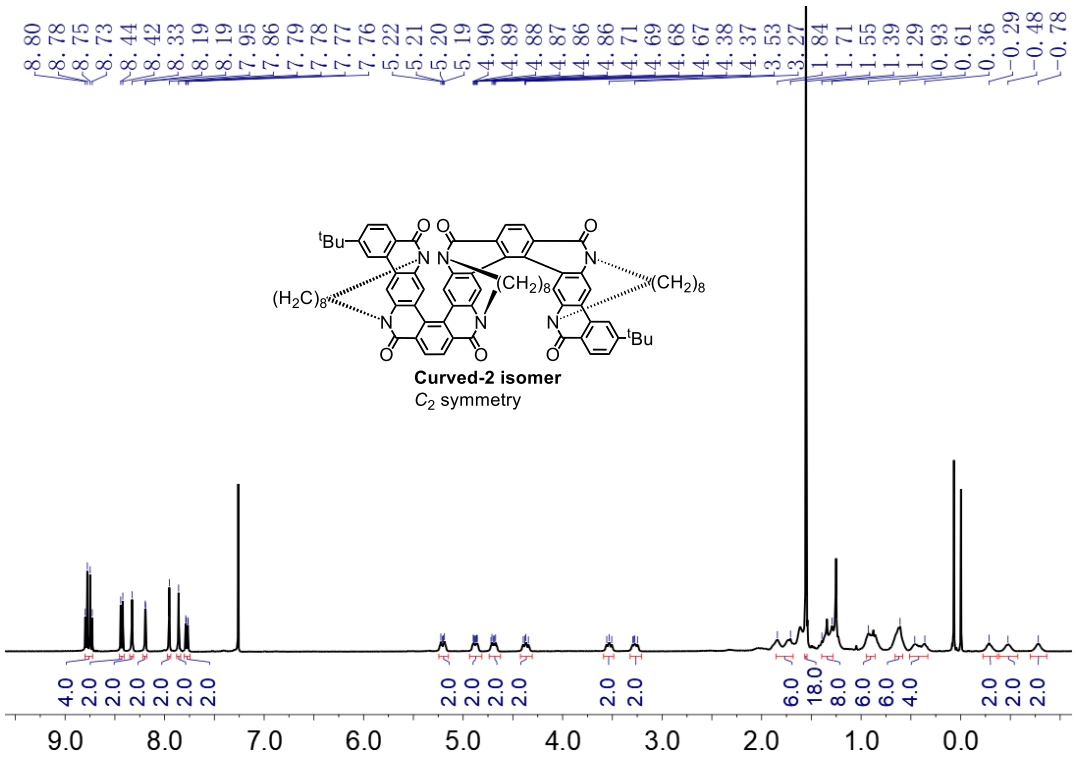


Fig. S44. ^{1}H NMR spectrum for **curved-2 isomer of (*P*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

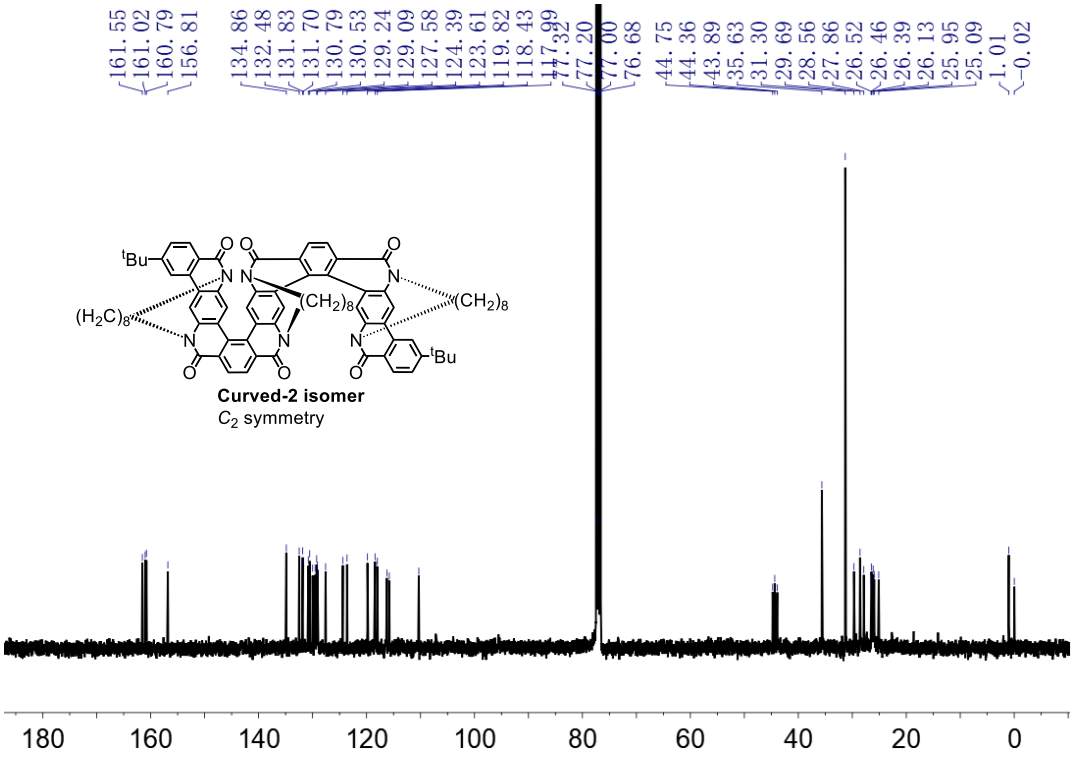


Fig. S45. ^{13}C NMR spectrum for **curved-2 isomer of (*P*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

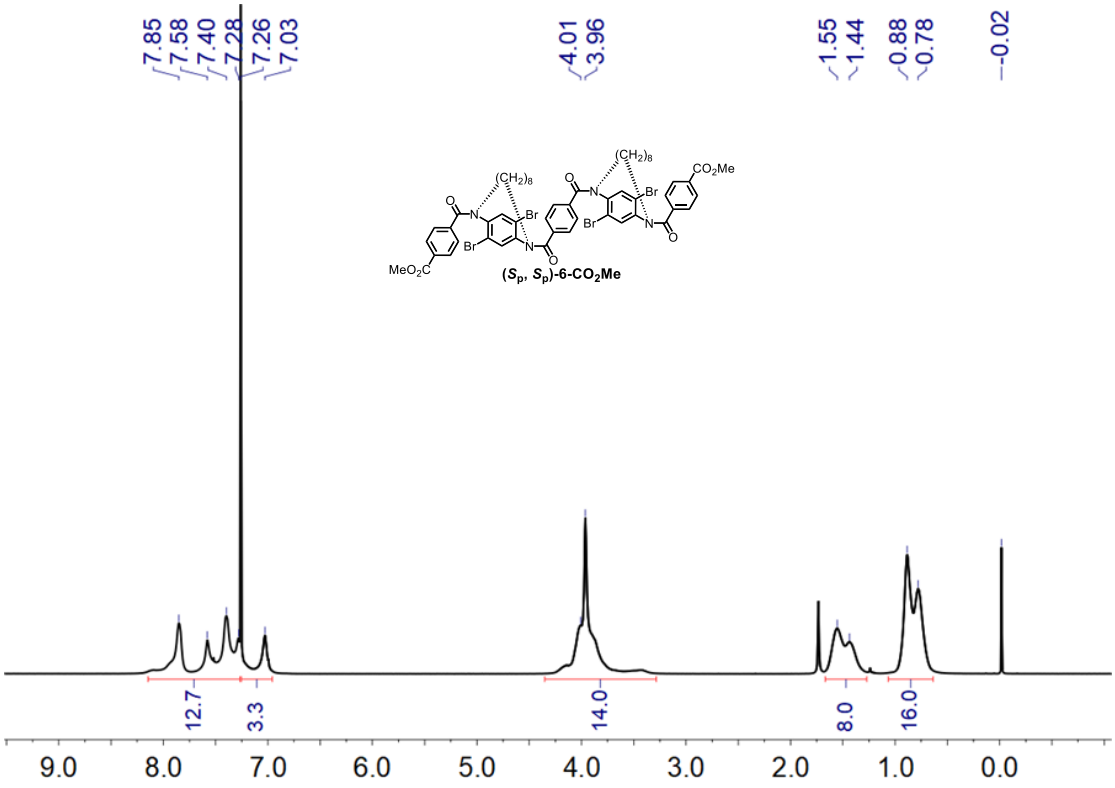


Fig. S46. ^{1}H NMR spectrum for **(S_p, S_p)-6-CO_2Me** ($CDCl_3$, 298 K)

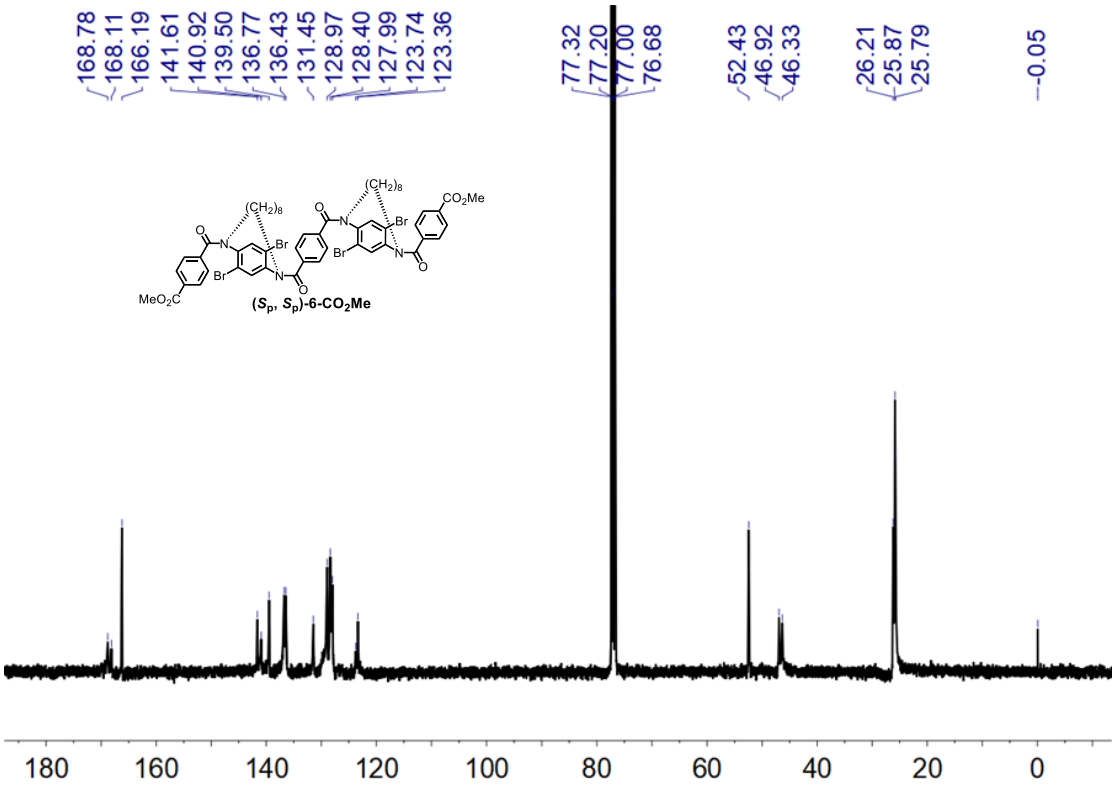


Fig. S47. ^{13}C NMR spectrum for **(S_p, S_p)-6-CO_2Me** ($CDCl_3$, 298 K)

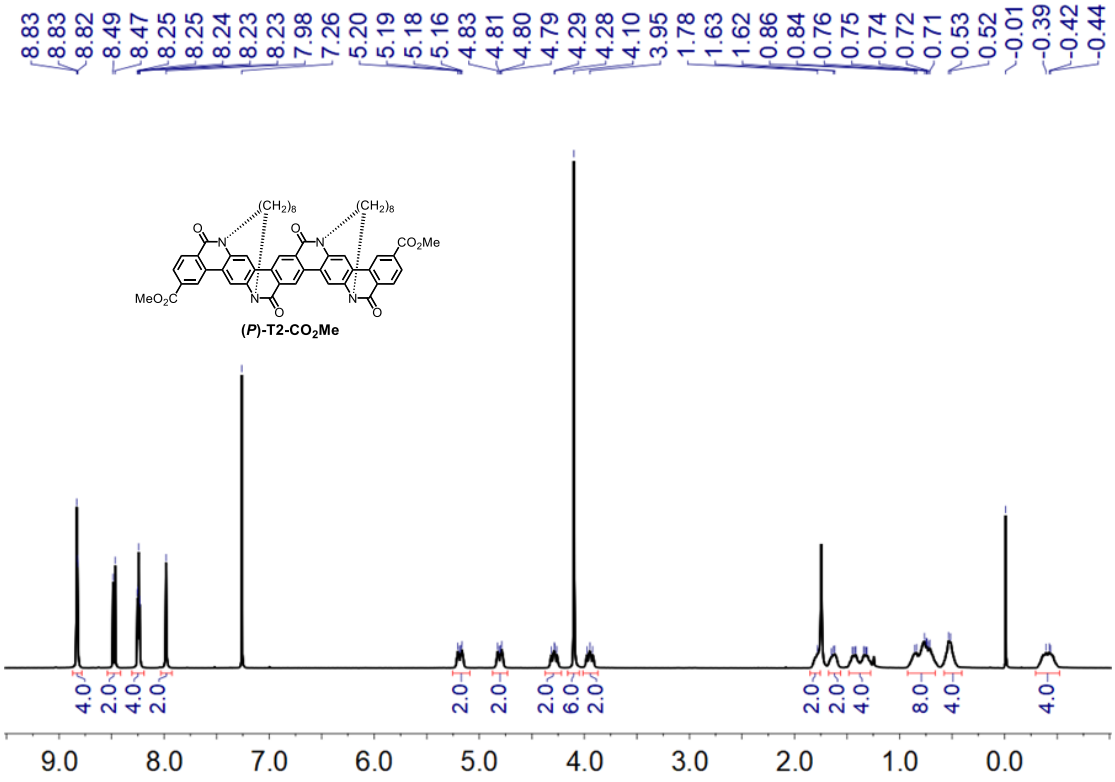


Fig. S48. ^{1}H NMR spectrum for **(*P*)-T2-CO$_2$Me** ($CDCl_3$, 298 K)

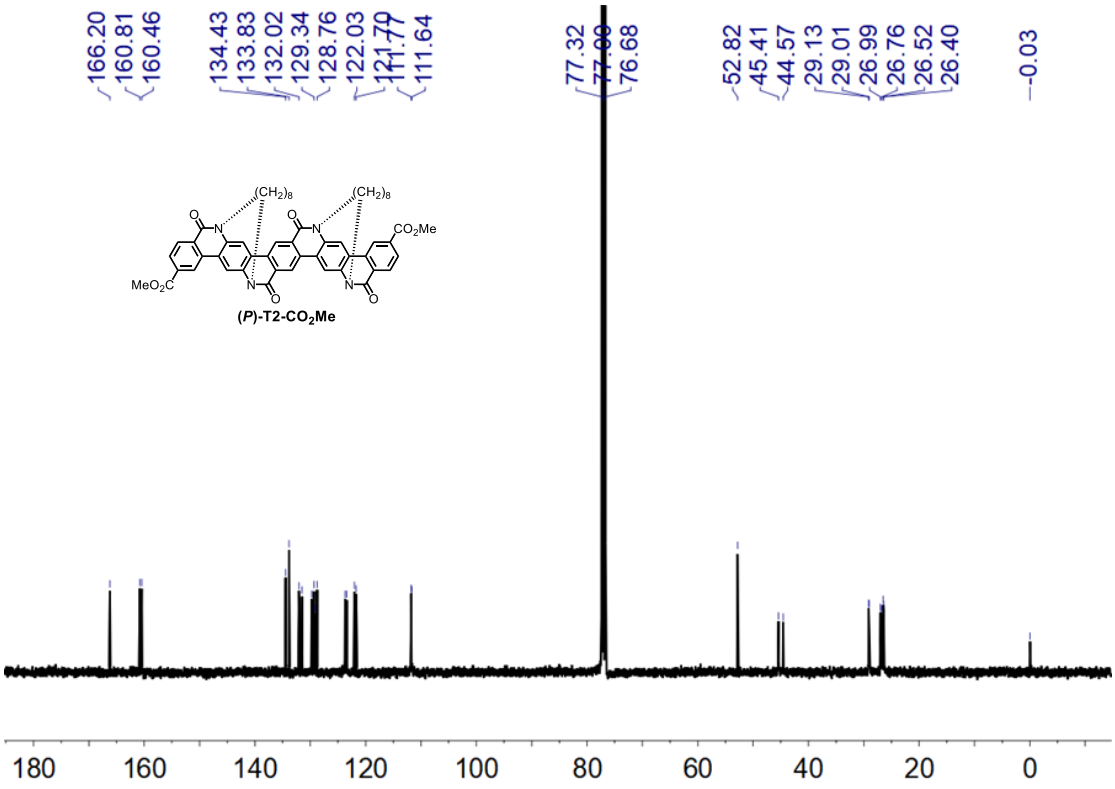


Fig. S49. ^{13}C NMR spectrum for **(*P*)-T2-CO$_2$Me** ($CDCl_3$, 298 K)

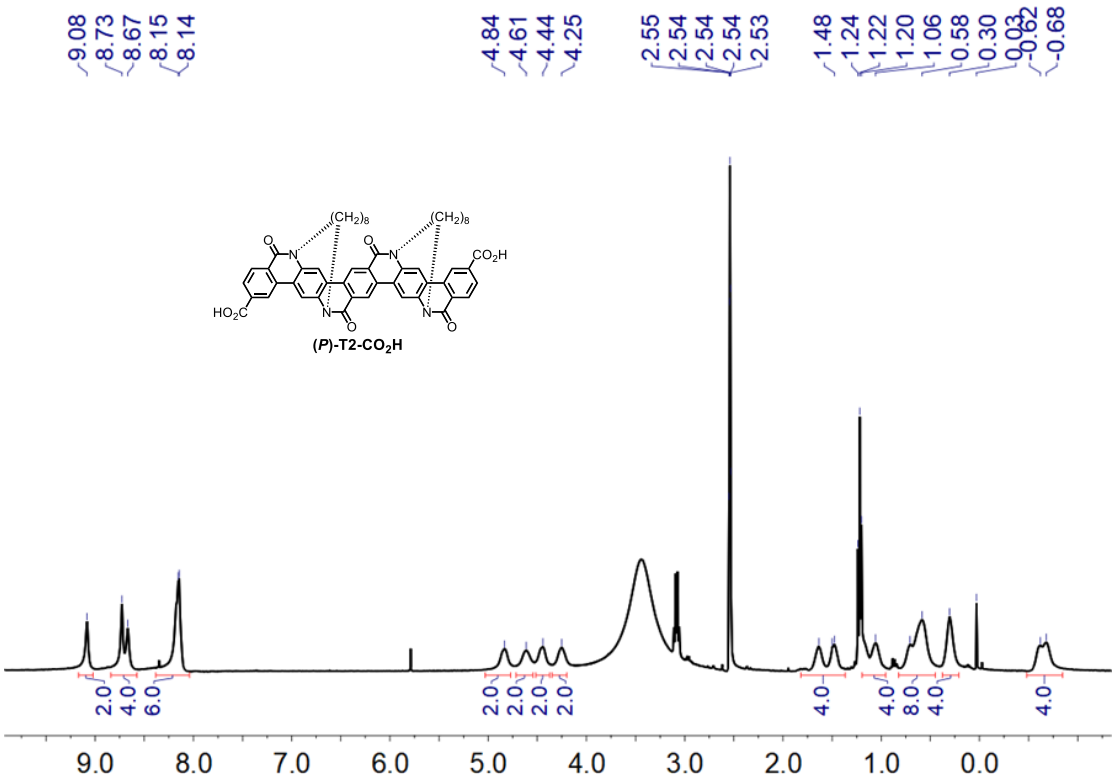


Fig. S50. ^{1}H NMR spectrum for **(*P*)-T2-CO$_2$H** (CDCl$_3$, 298 K)

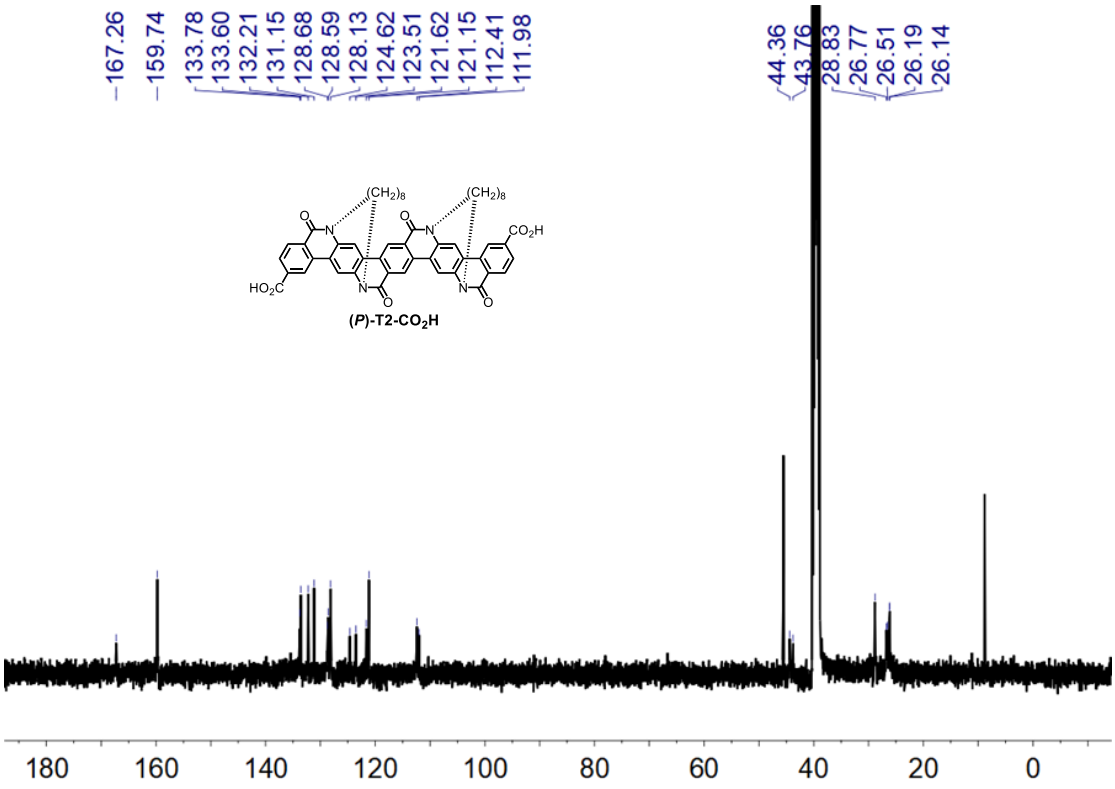


Fig. S51. ^{13}C NMR spectrum for **(*P*)-T2-CO$_2$H** (CDCl$_3$, 298 K)

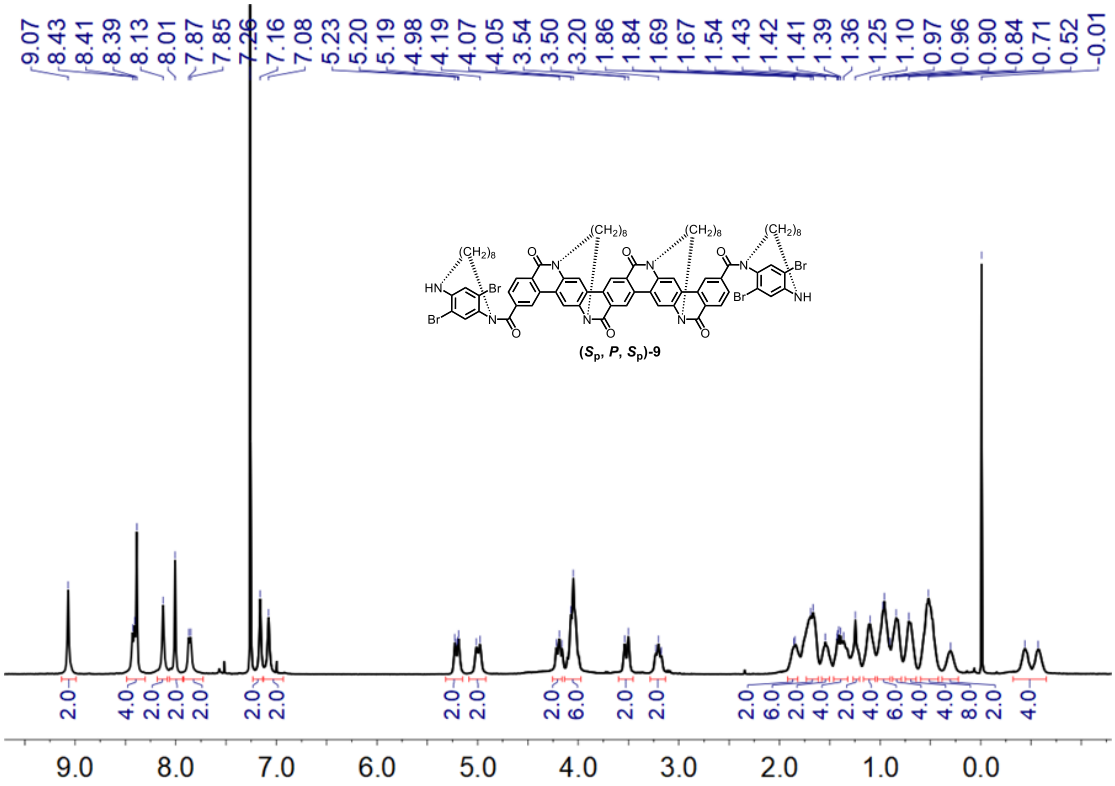


Fig. S52. ^{1}H NMR spectrum for **(S_p, *P*, S_p)-9** ($CDCl_3$, 298 K)

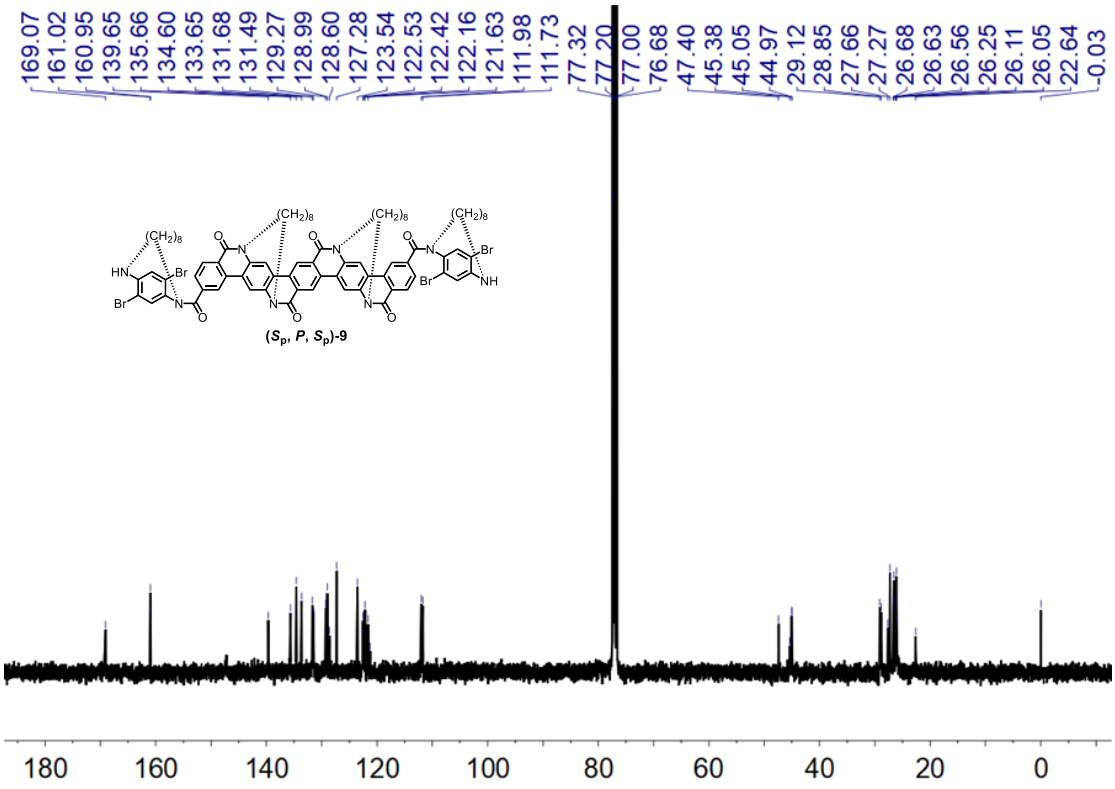


Fig. S53. ^{13}C NMR spectrum for **(S_p, *P*, S_p)-9** ($CDCl_3$, 298 K)

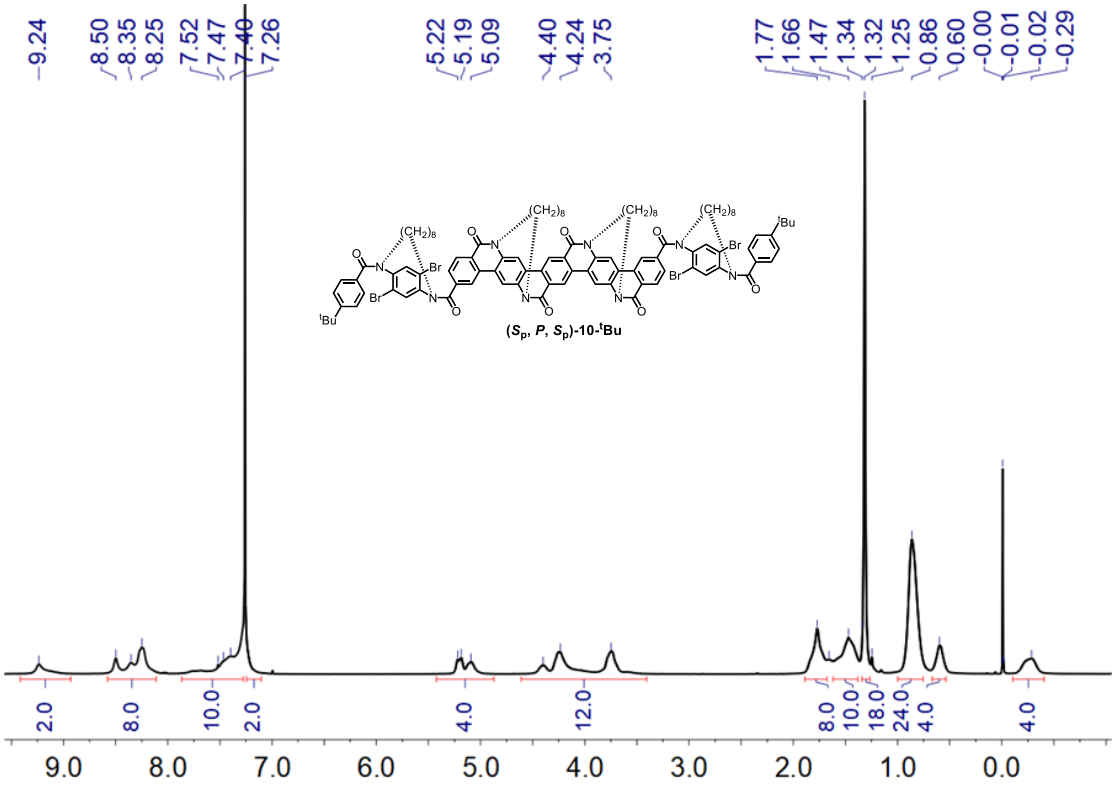


Fig. S54. ^{1}H NMR spectrum for **(S_p, *P*, S_p)-10-^{t}Bu** ($CDCl_3$, 298 K)

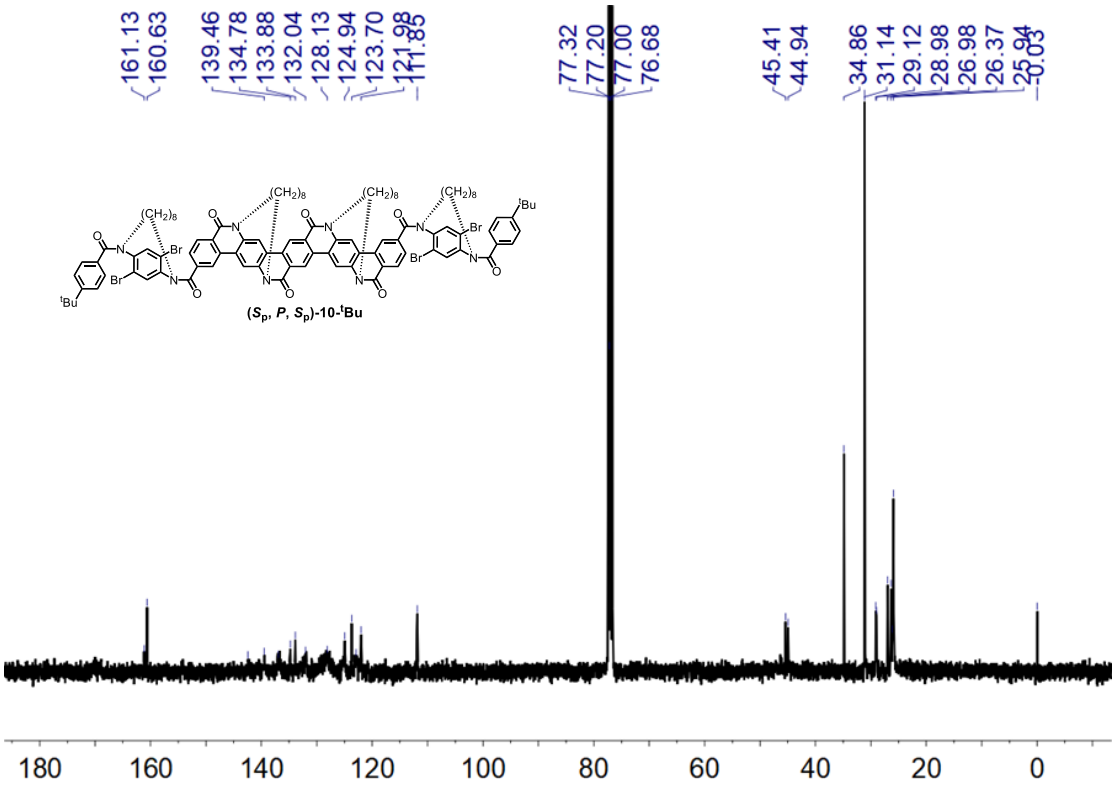


Fig. S55. ^{13}C NMR spectrum for **(S_p, *P*, S_p)-10-^{t}Bu** ($CDCl_3$, 298 K)

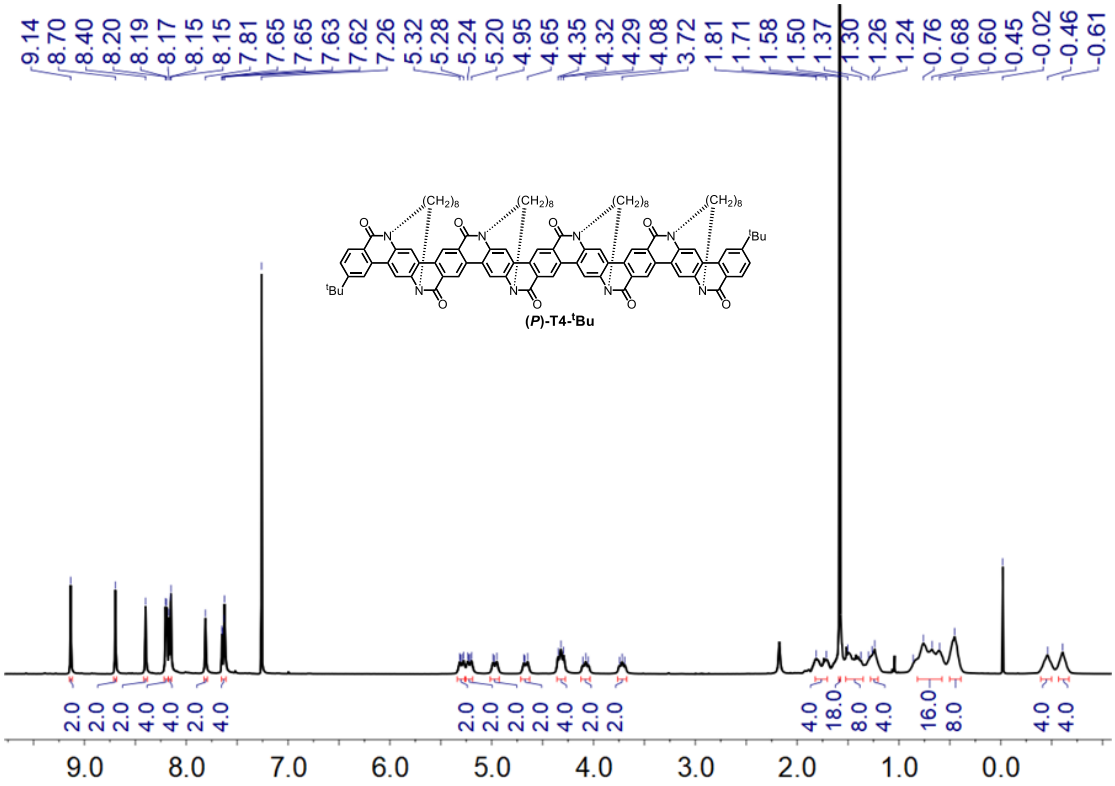


Fig. S56. ^{1}H NMR spectrum for **(*P*)-T4-^{t}Bu** ($CDCl_3$, 298 K)

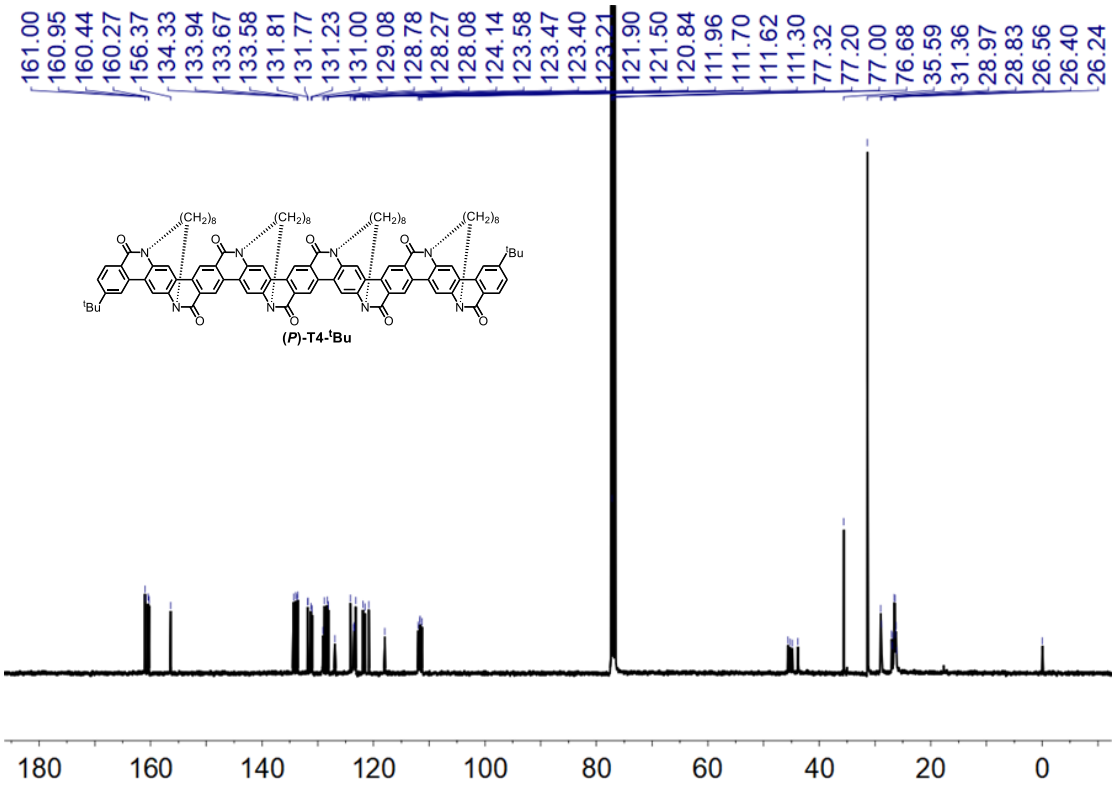


Fig. S57. ^{13}C NMR spectrum for **(*P*)-T4-^{t}Bu** ($CDCl_3$, 298 K)

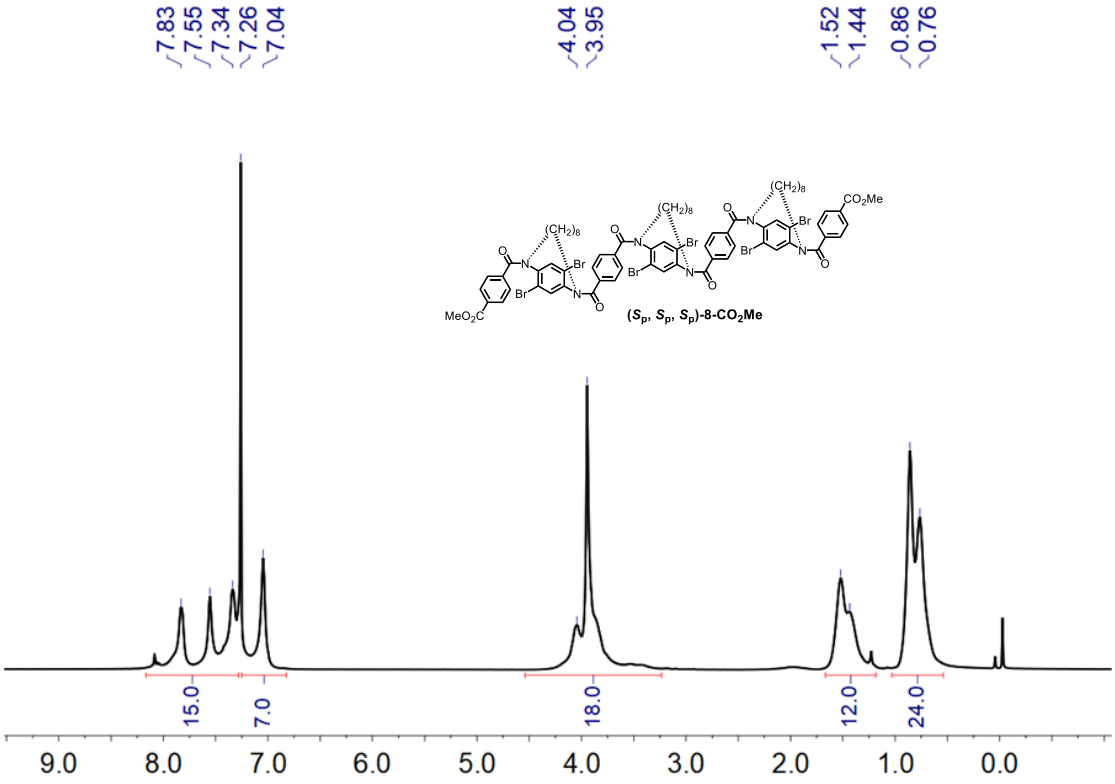


Fig. S58. ^{1}H NMR spectrum for **(S_p, S_p, S_p)-8-CO_2Me** ($CDCl_3$, 298 K)

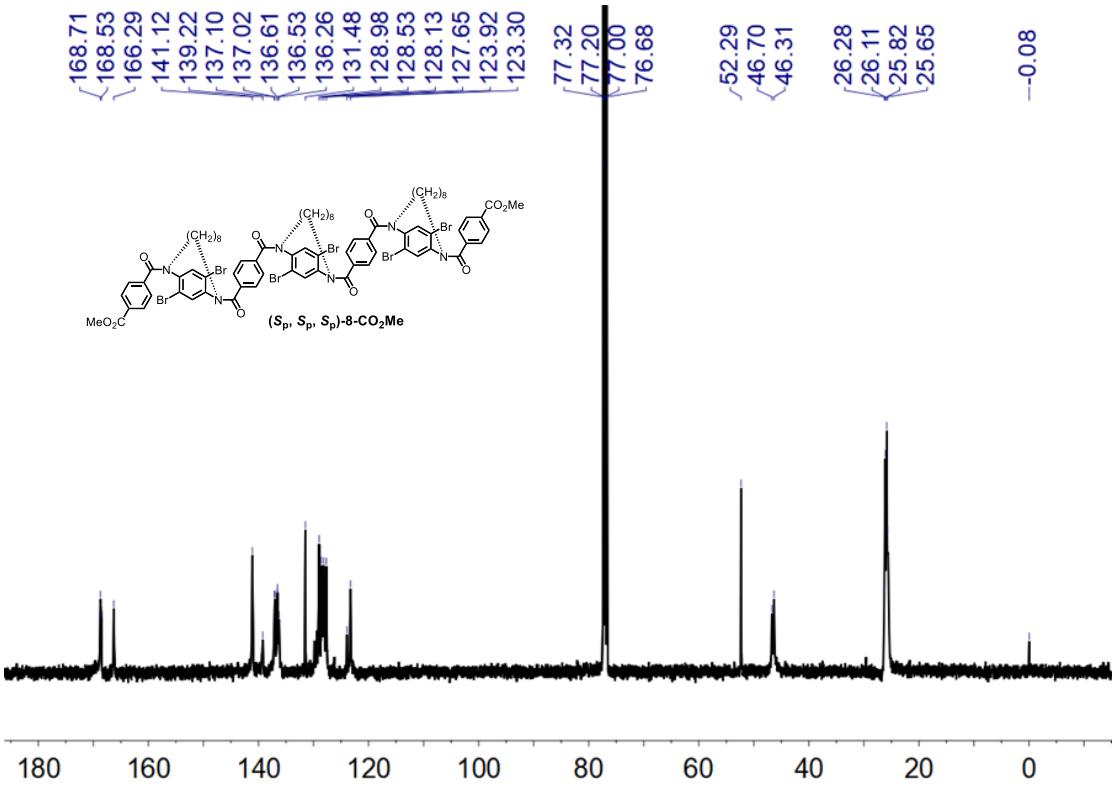


Fig. S59. ^{13}C NMR spectrum for **(S_p, S_p, S_p)-8-CO_2Me** ($CDCl_3$, 298 K)

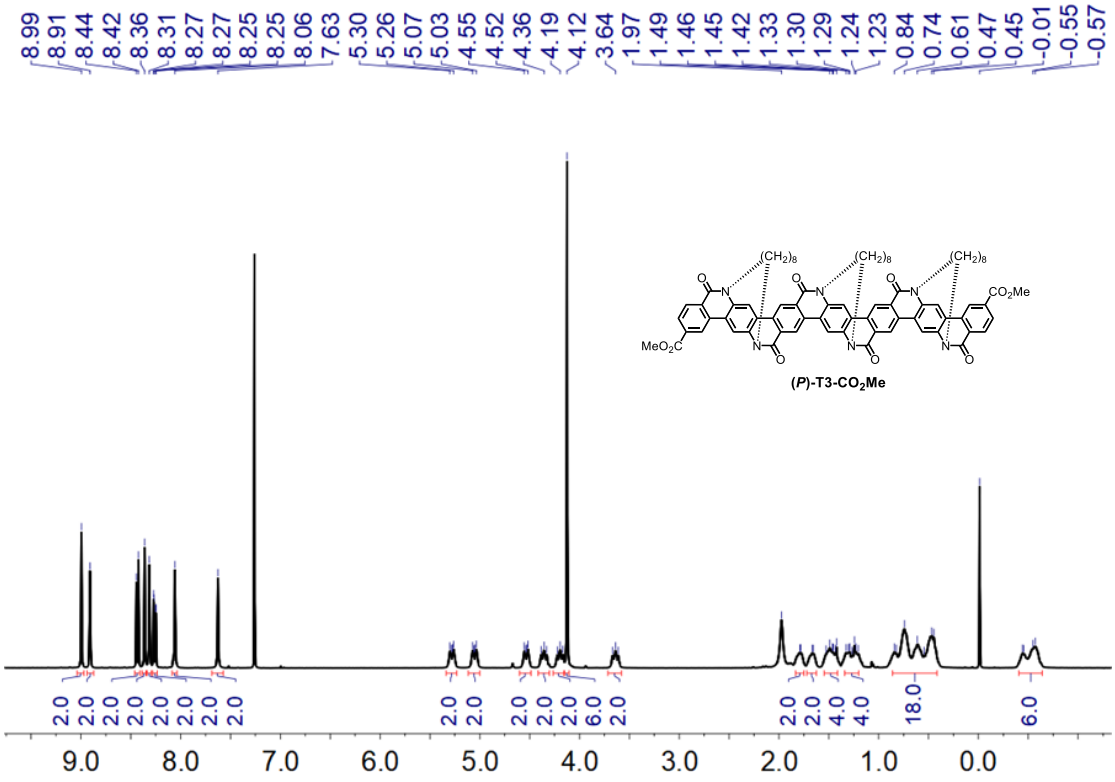


Fig. S60. ^{1}H NMR spectrum for **(*P*)-T3-CO$_2$Me** ($CDCl_3$, 298 K)

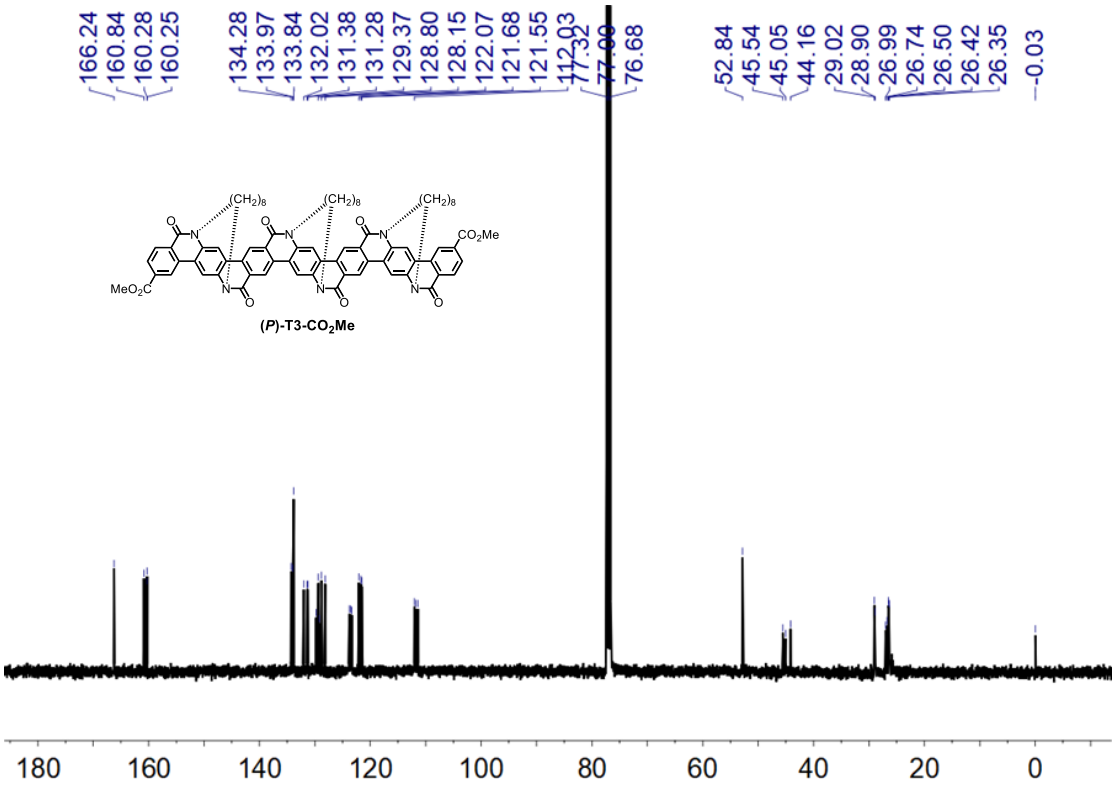


Fig. S61. ^{13}C NMR spectrum for **(*P*)-T3-CO$_2$Me** ($CDCl_3$, 298 K)

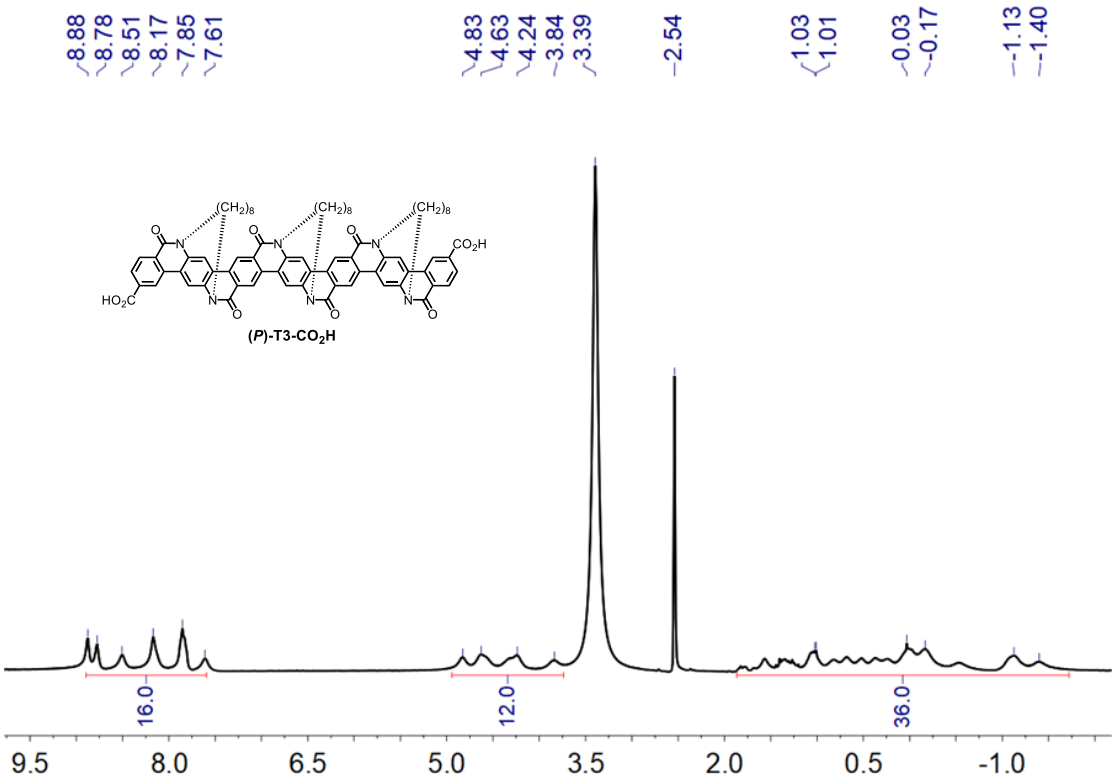


Fig. S62. ^{1}H NMR spectrum for **(*P*)-T3-CO$_2$H** (CDCl$_3$, 298 K)

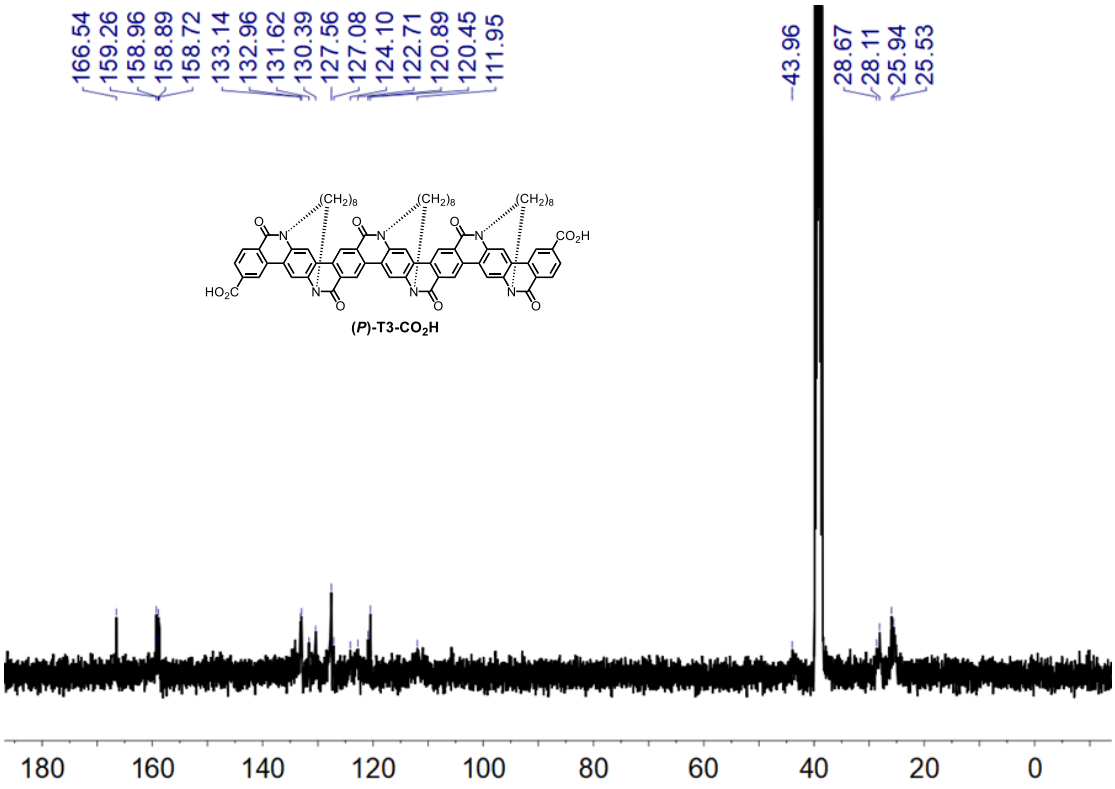


Fig. S63. ^{13}C NMR spectrum for **(*P*)-T3-CO$_2$H** (CDCl$_3$, 298 K)

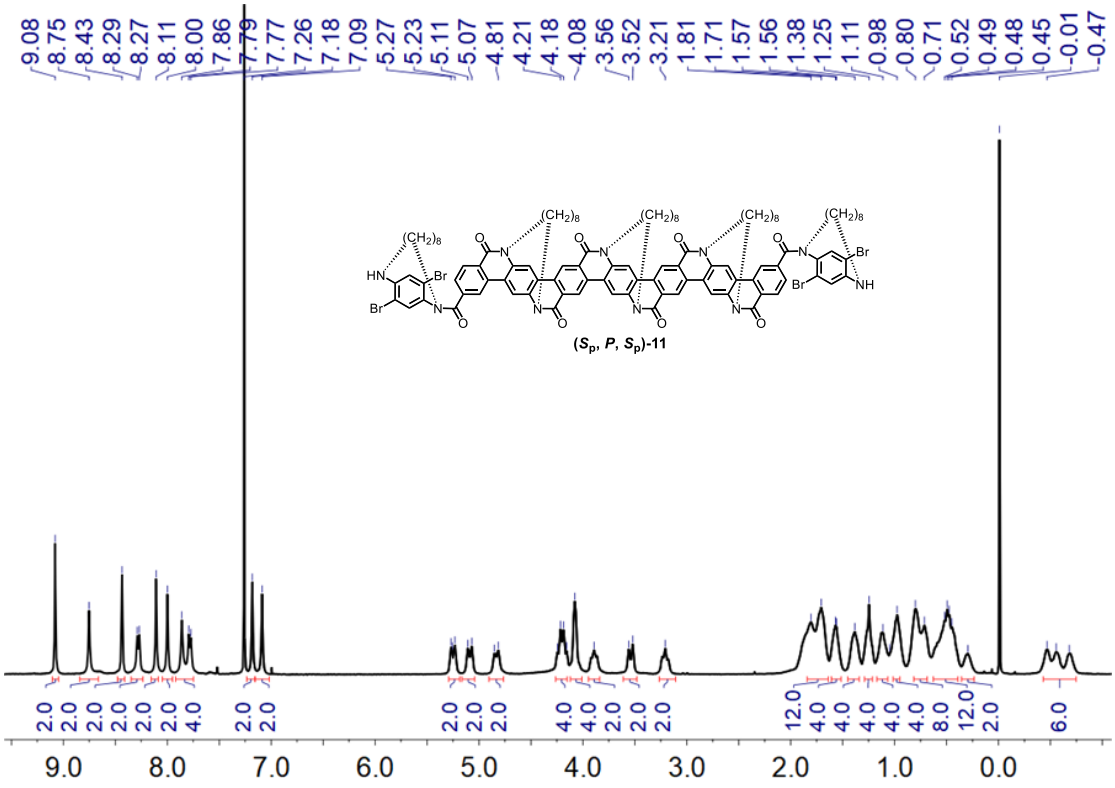


Fig. S64. ^{1}H NMR spectrum for **(S_p, *P*, S_p)-11** ($CDCl_3$, 298 K)

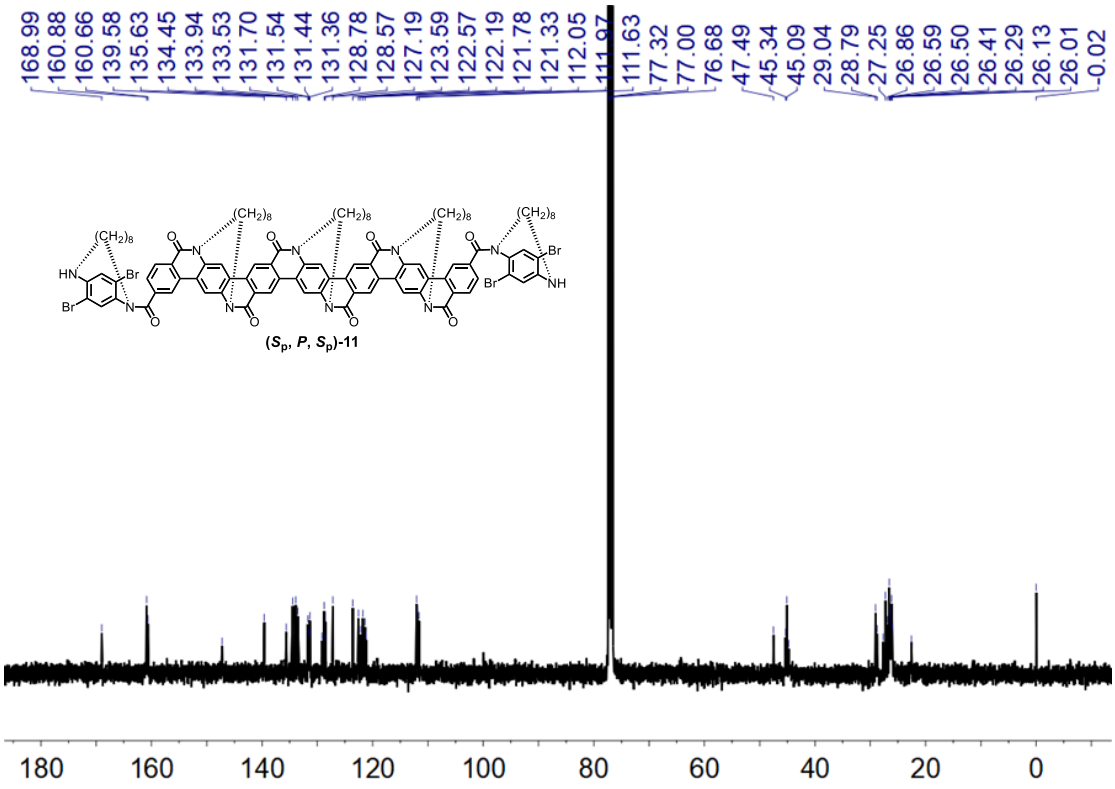


Fig. S65. ^{13}C NMR spectrum for **(S_p, *P*, S_p)-11** ($CDCl_3$, 298 K)

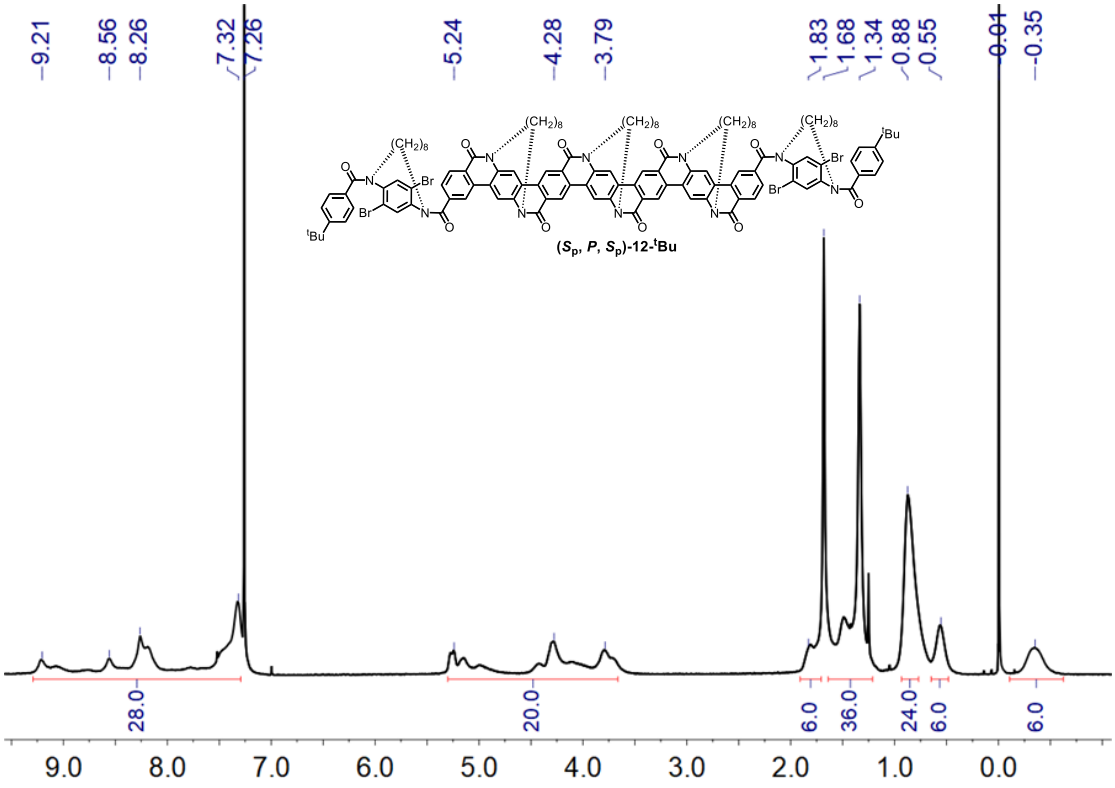


Fig. S66. ^{1}H NMR spectrum for **(S_p, *P*, S_p)-12-^{t}Bu** ($CDCl_3$, 298 K)

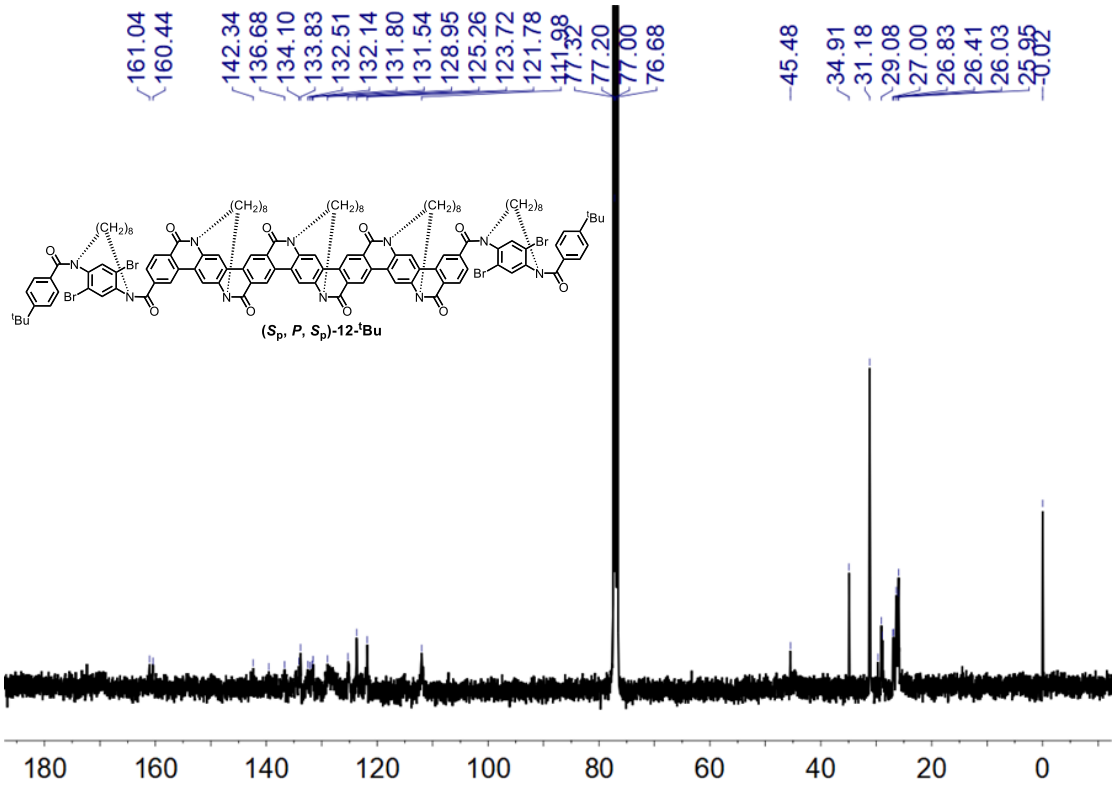


Fig. S67. ^{13}C NMR spectrum for **(S_p, *P*, S_p)-12-^{t}Bu** ($CDCl_3$, 298 K)

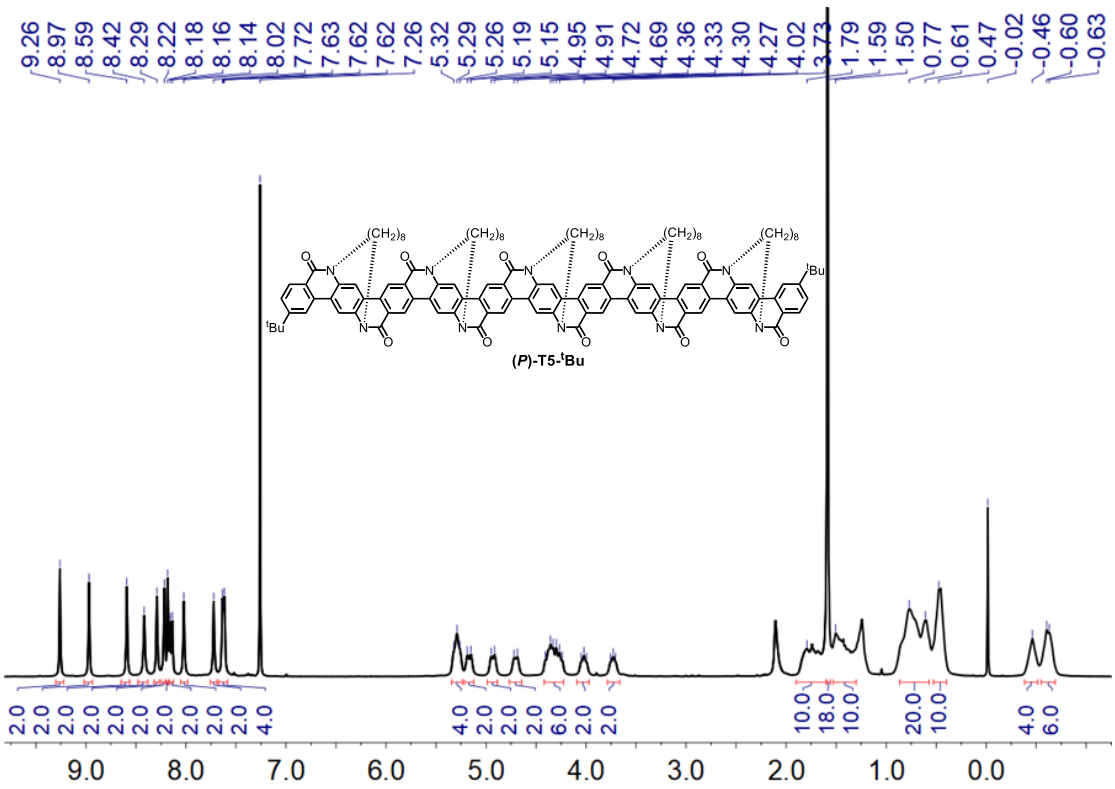


Fig. S68. ^{1}H NMR spectrum for **(*P*)-T5-^{t}Bu** ($CDCl_3$, 298 K)

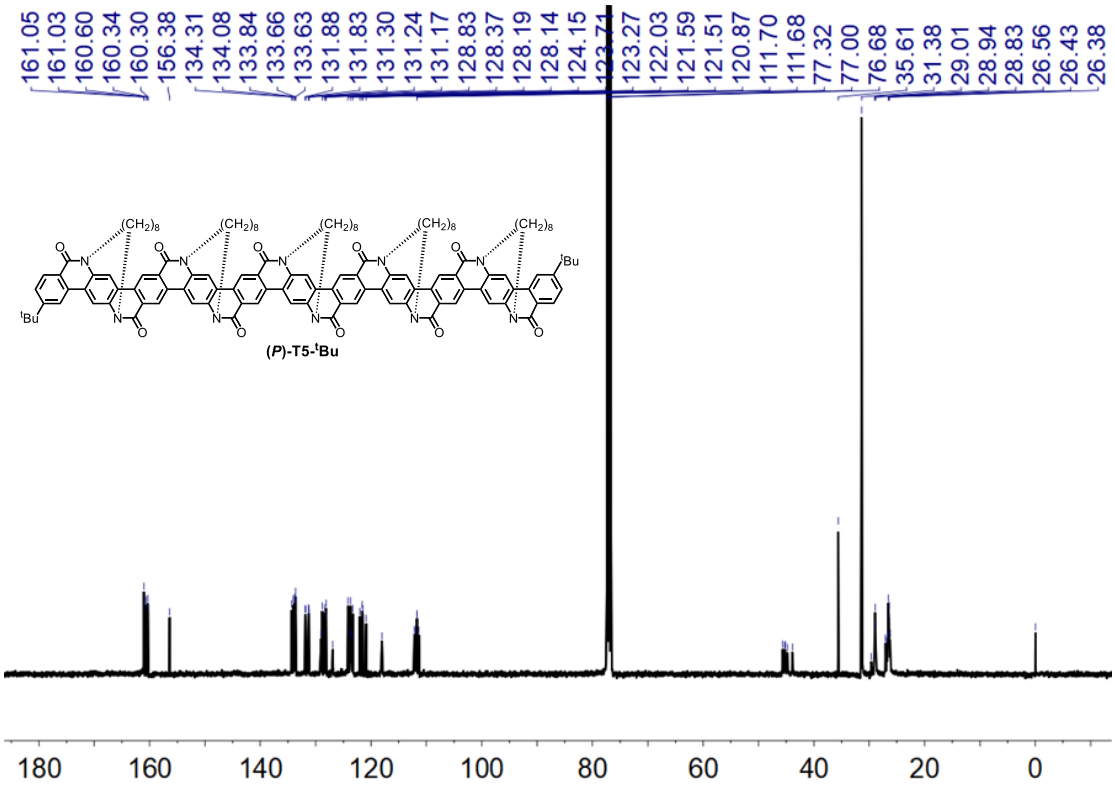


Fig. S69. ^{13}C NMR spectrum for **(*P*)-T5-^{t}Bu** ($CDCl_3$, 298 K)

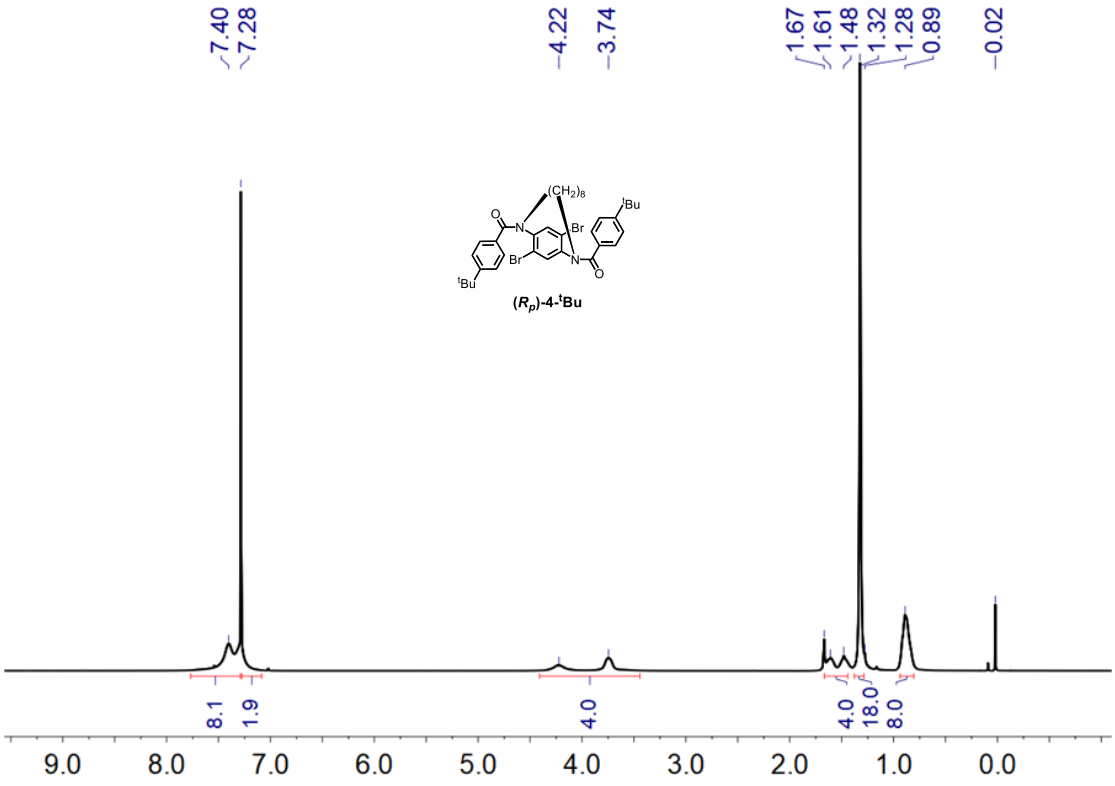


Fig. S70. ^{1}H NMR spectrum for **(R_p)-4-^{t}Bu** ($CDCl_3$, 298 K)

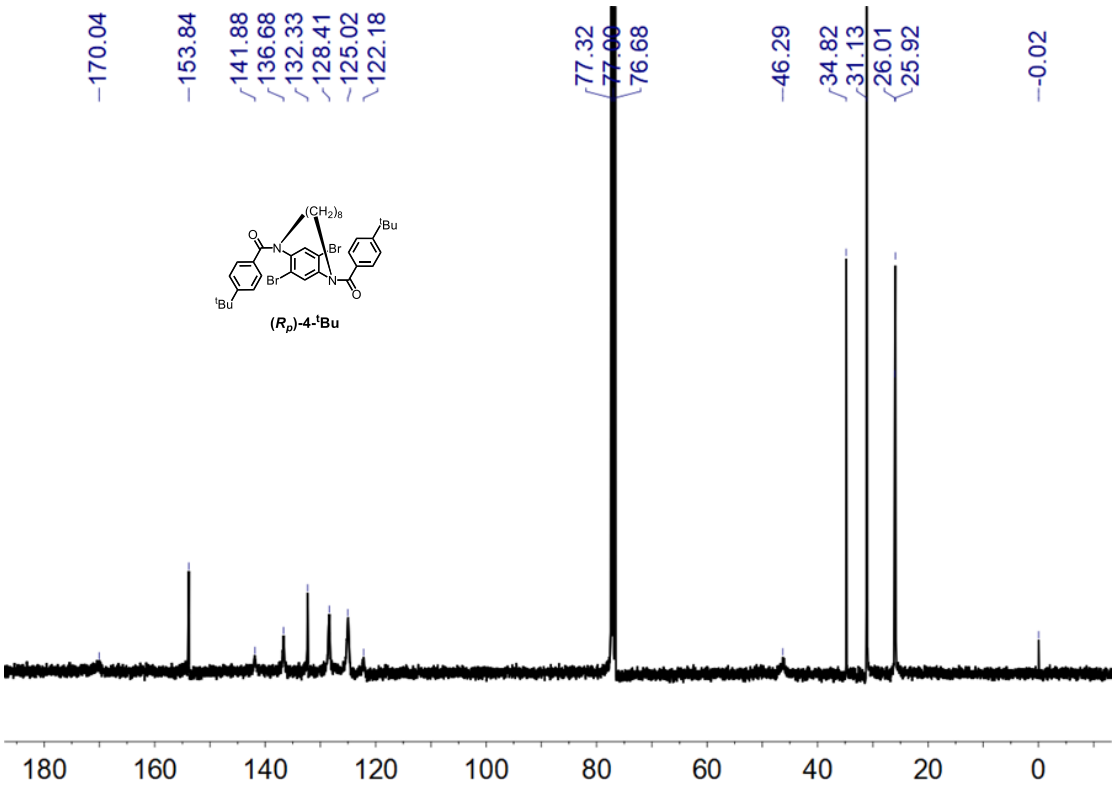


Fig. S71. ^{13}C NMR spectrum for **(R_p)-4-^{t}Bu** ($CDCl_3$, 298 K)

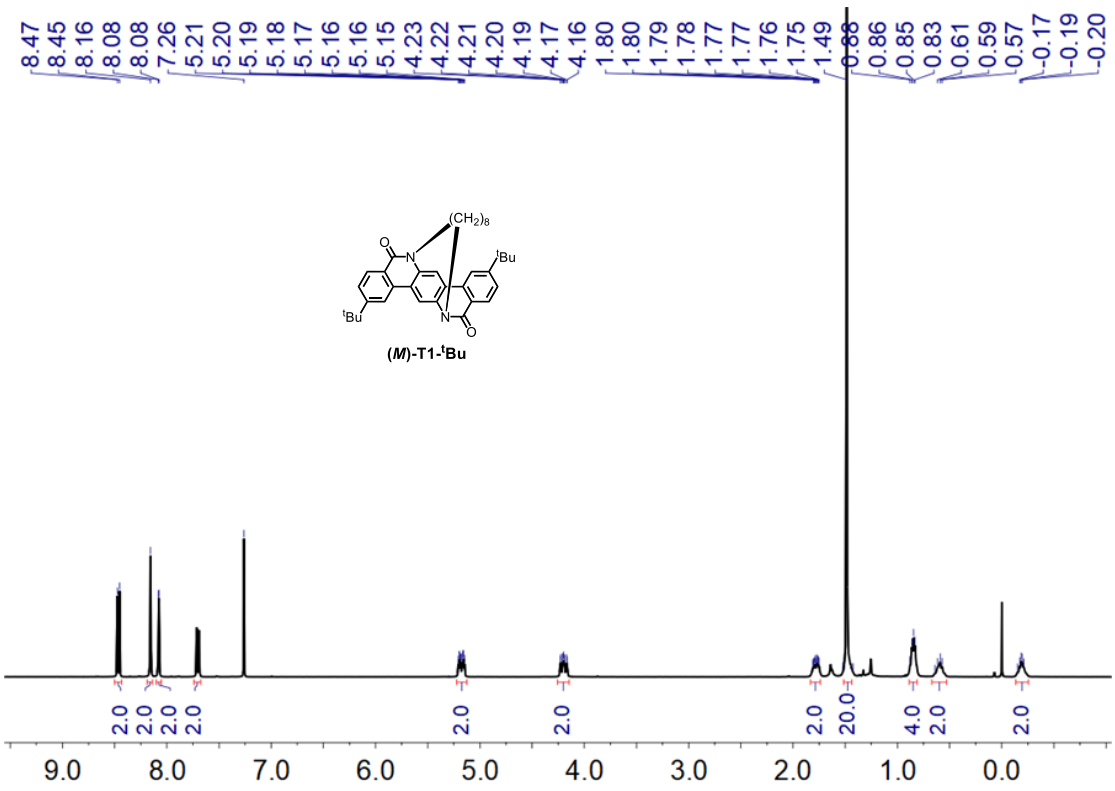


Fig. S72. ^{1}H NMR spectrum for **(*M*)-T1-^{t}Bu** ($CDCl_3$, 298 K)

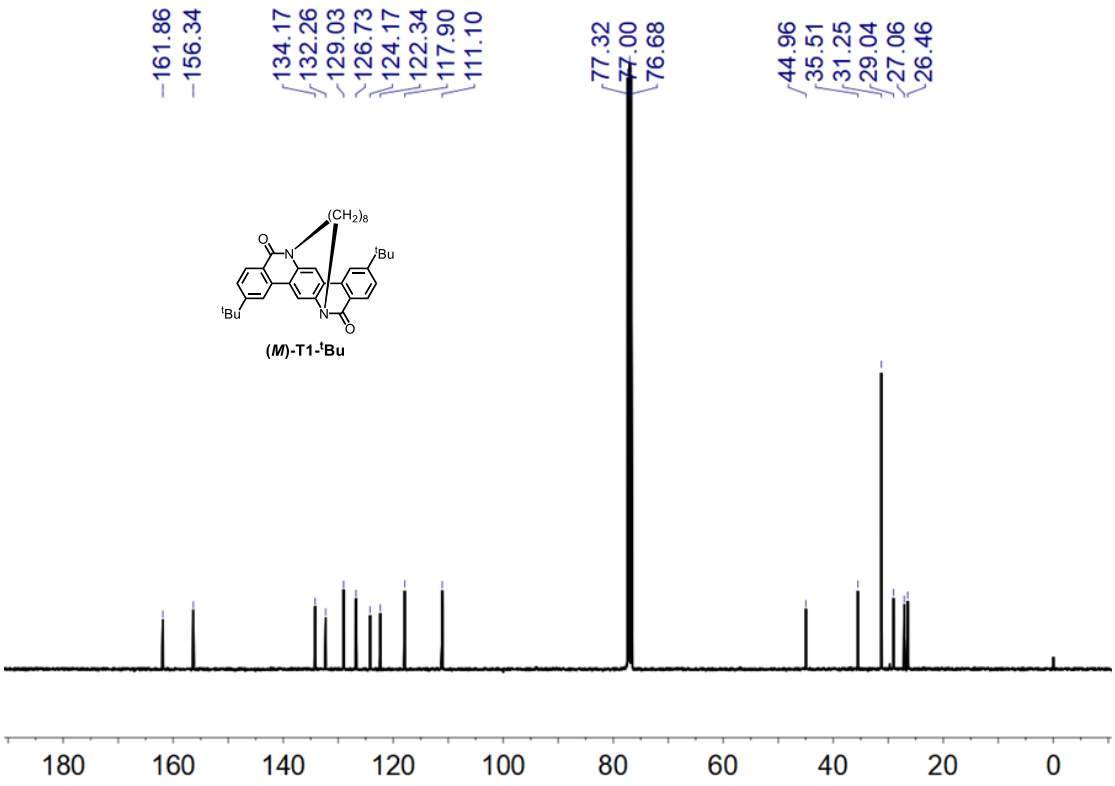


Fig. S73. ^{13}C NMR spectrum for **(*M*)-T1-^{t}Bu** ($CDCl_3$, 298 K)

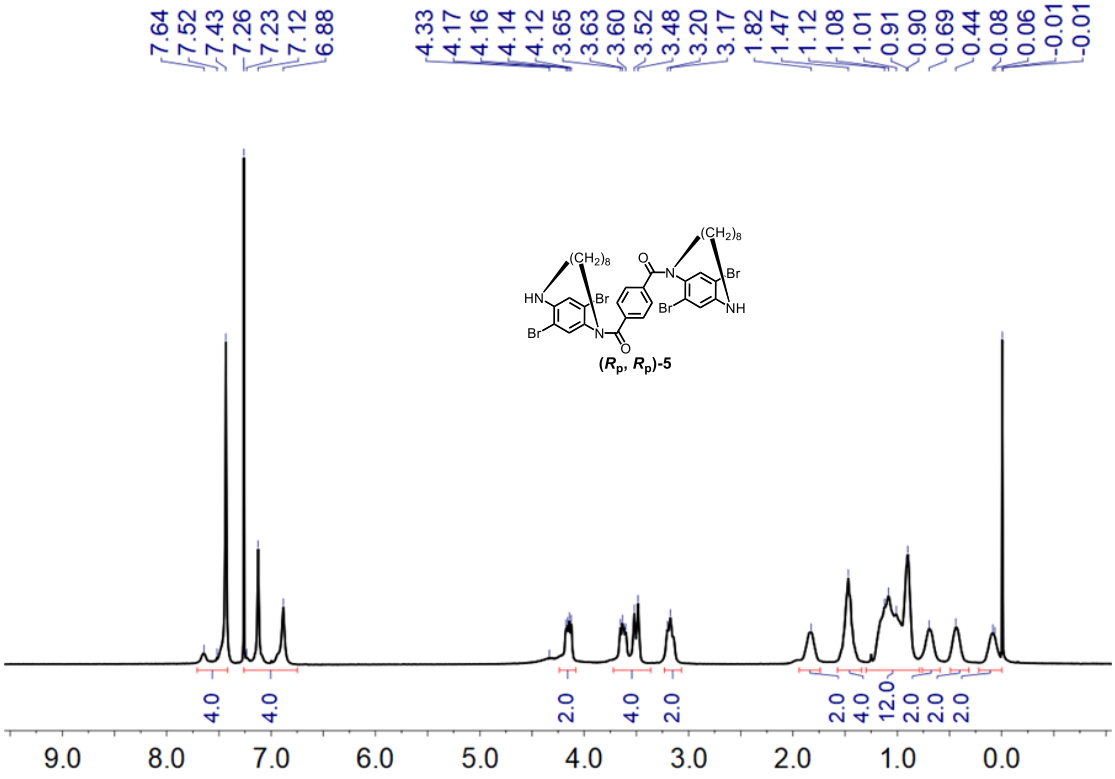


Fig. S74. ^{1}H NMR spectrum for **(R_p, R_p)-5** ($CDCl_3$, 298 K)

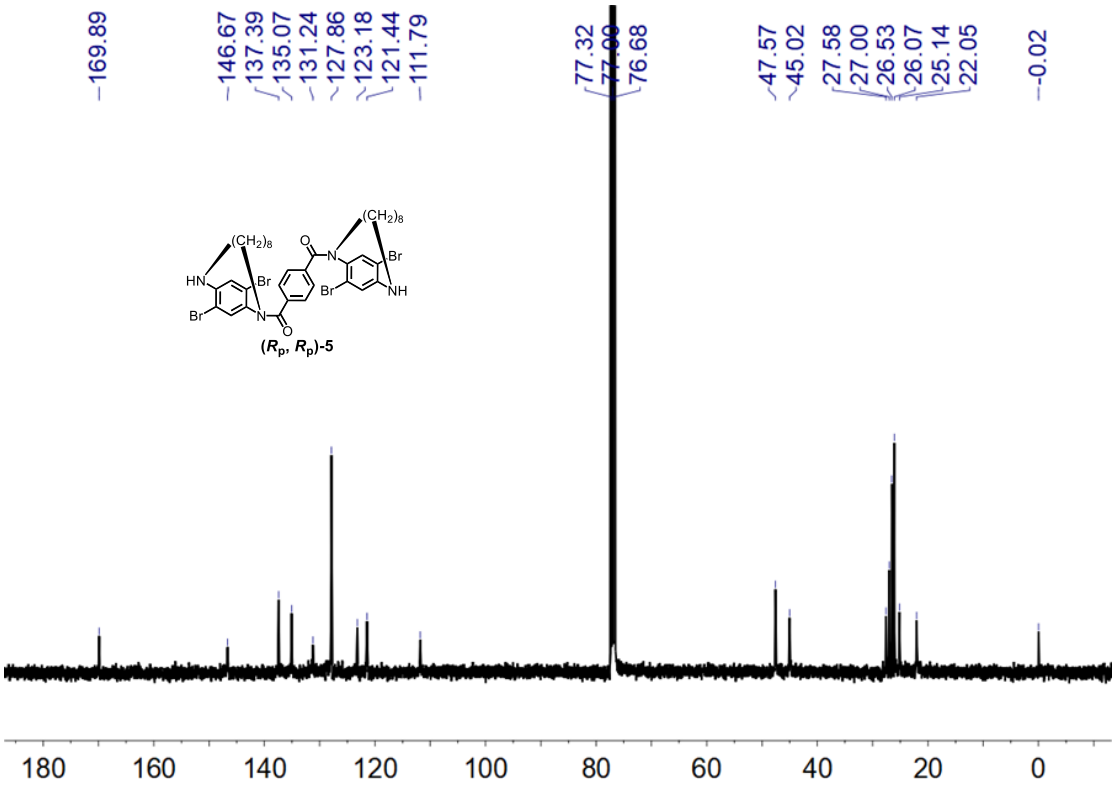


Fig. S75. ^{13}C NMR spectrum for **(R_p, R_p)-5** ($CDCl_3$, 298 K)

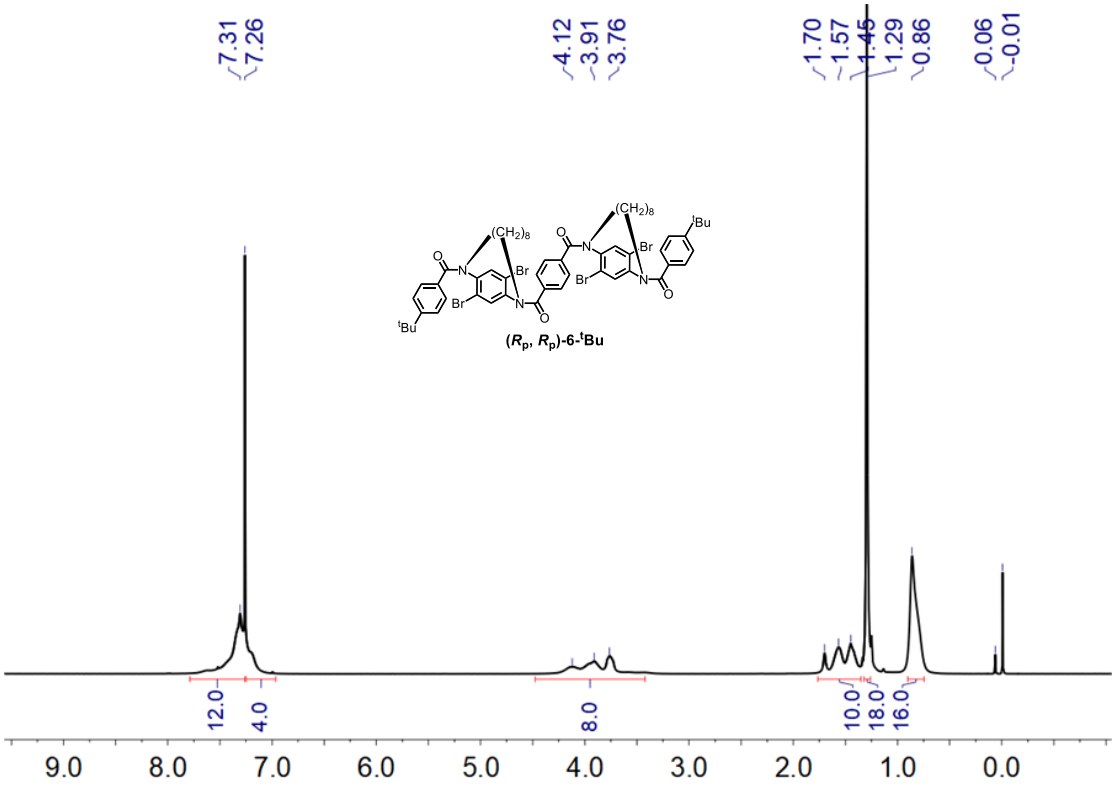


Fig. S76. ^{1}H NMR spectrum for **(R_p, R_p)-6-^{t}Bu** ($CDCl_3$, 298 K)

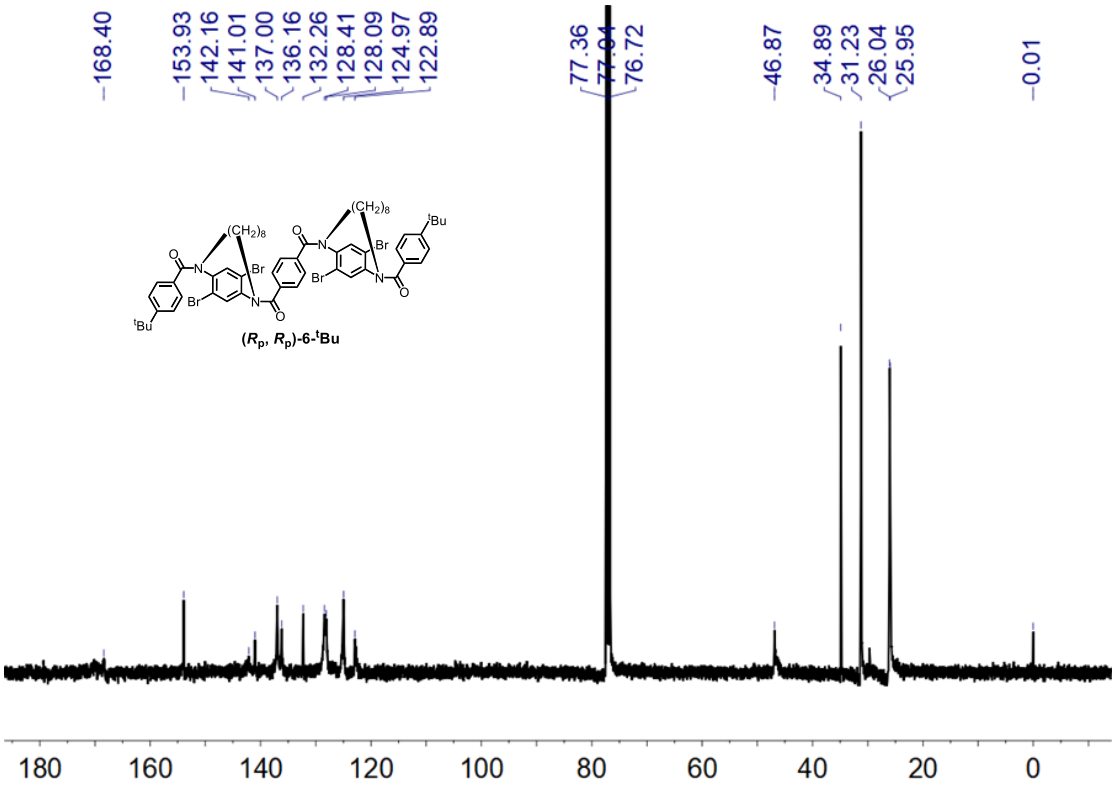


Fig. S77. ^{13}C NMR spectrum for **(R_p, R_p)-6-^{t}Bu** ($CDCl_3$, 298 K)

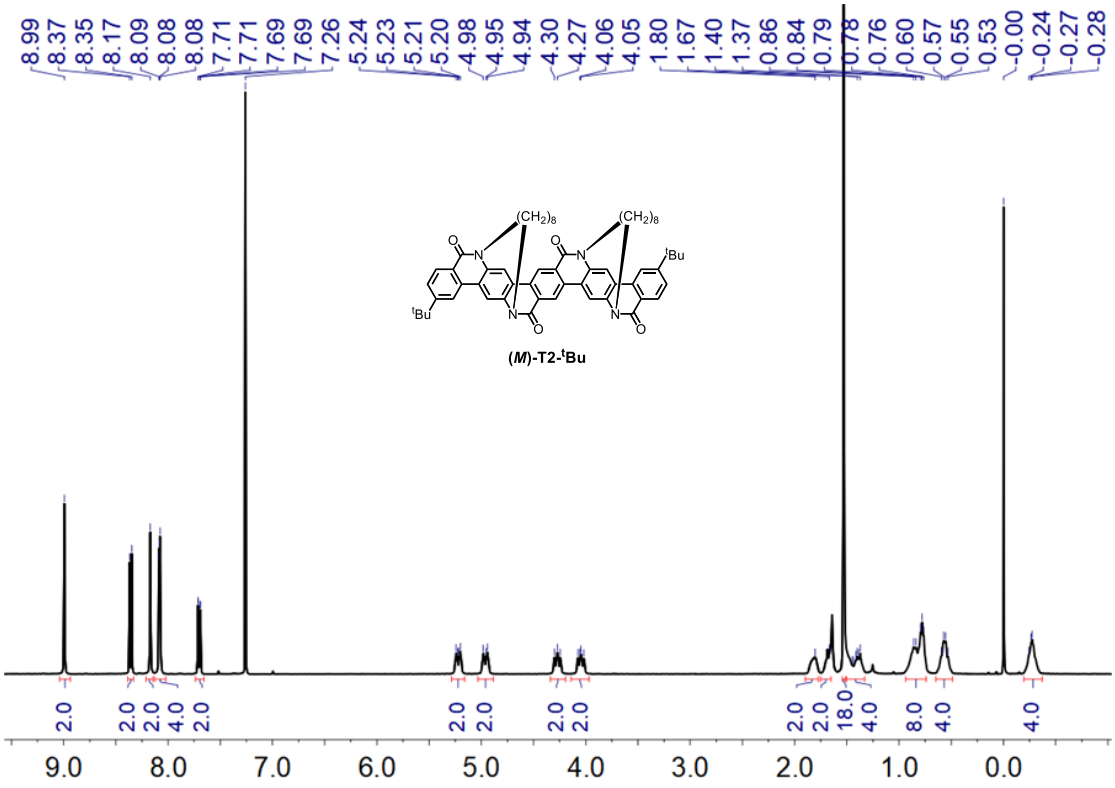


Fig. S78. ^{1}H NMR spectrum for **(*M*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

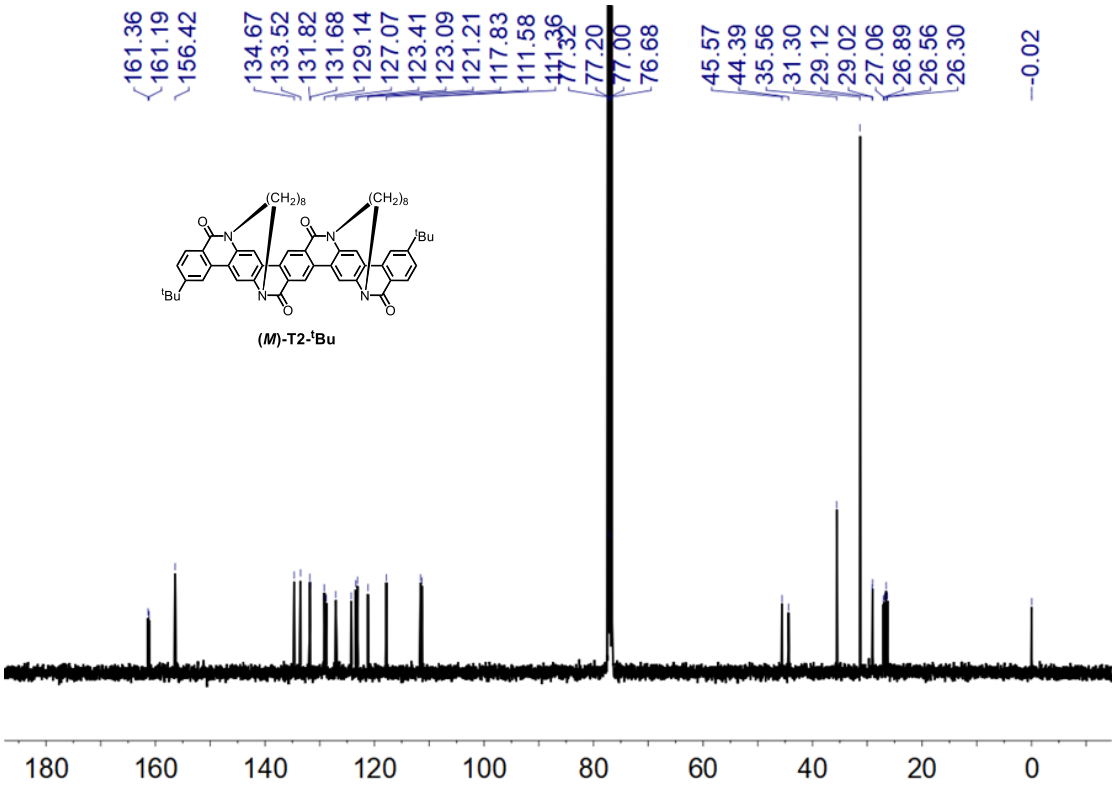


Fig. S79. ^{13}C NMR spectrum for **(*M*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

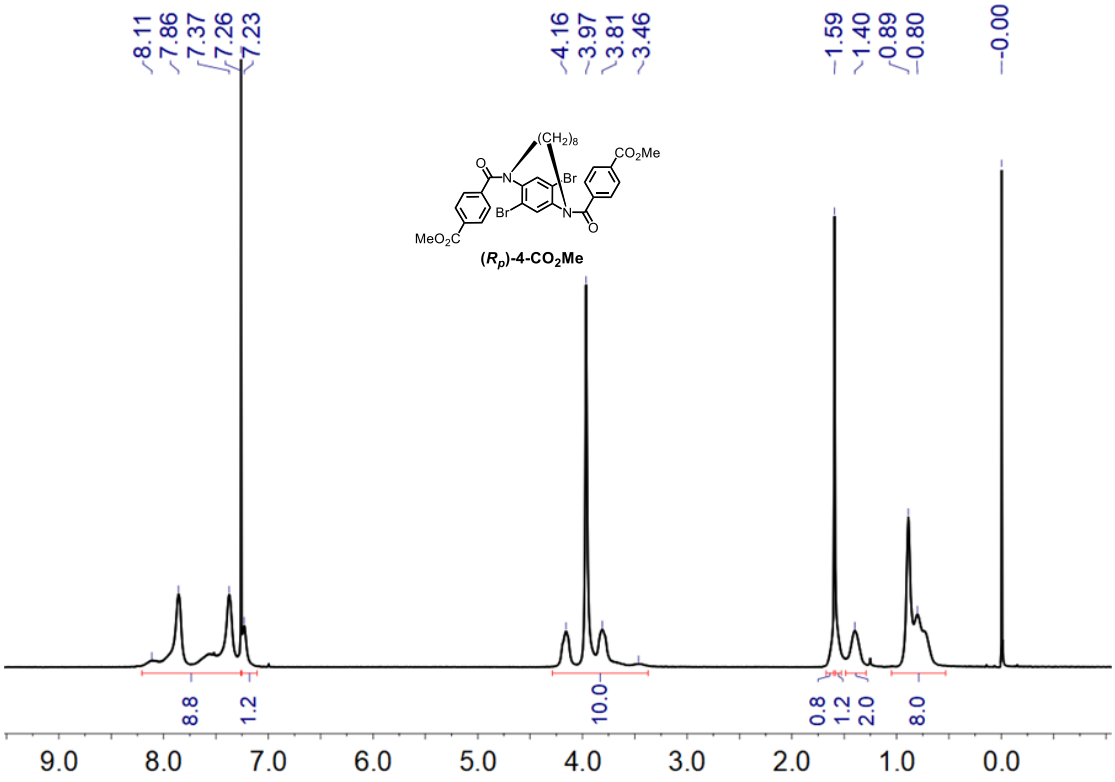


Fig. S80. ^{1}H NMR spectrum for **(R_p)-4-CO_2Me** ($CDCl_3$, 298 K)

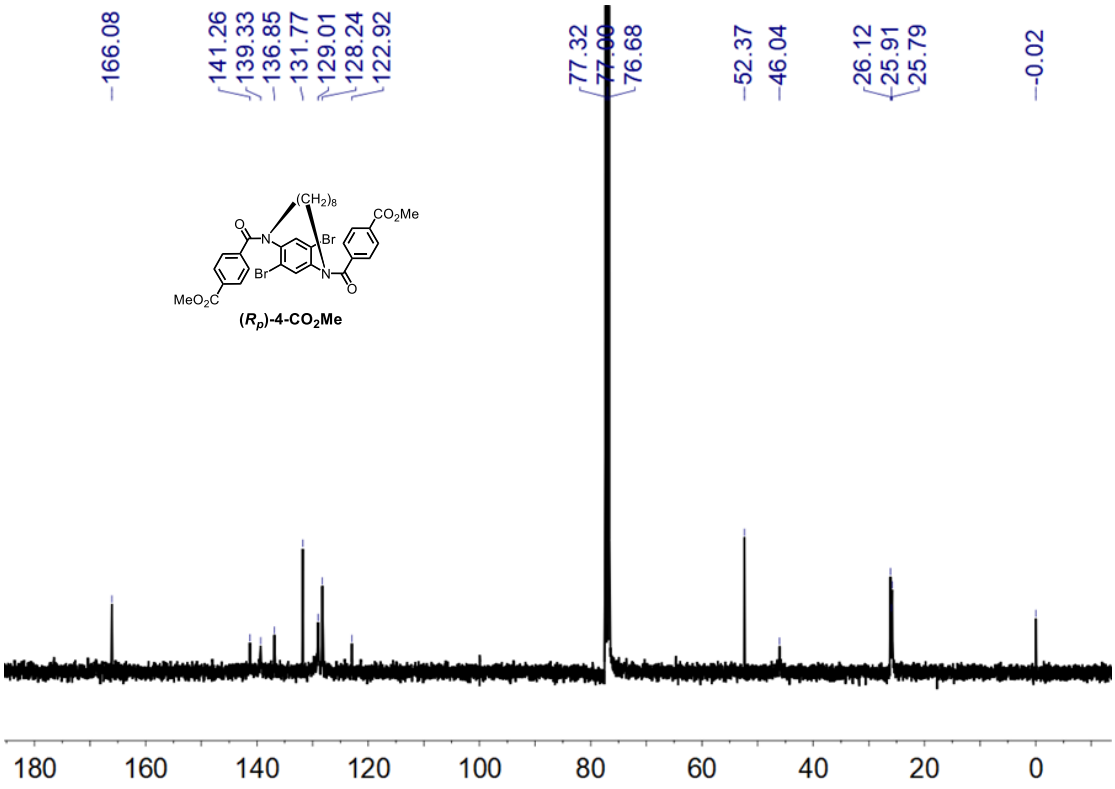


Fig. S81. ^{13}C NMR spectrum for **(R_p)-4-CO_2Me** ($CDCl_3$, 298 K)

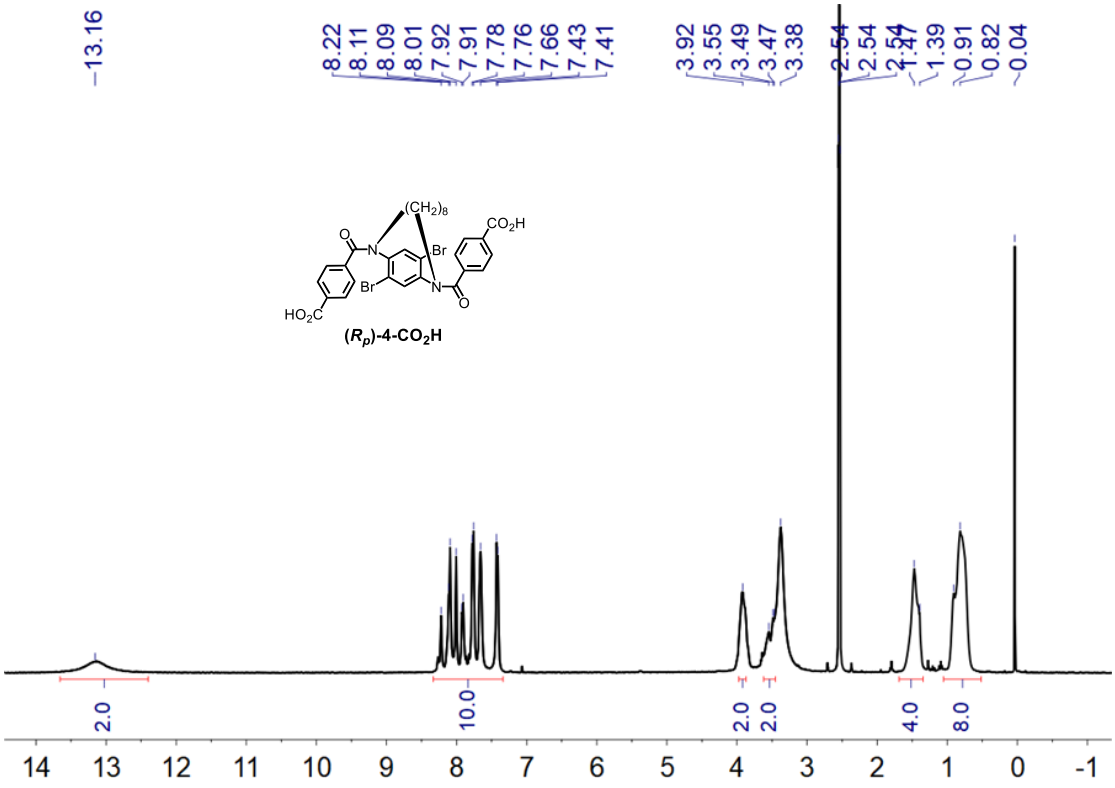


Fig. S82. ^{1}H NMR spectrum for **(R_p)-4-COOH** ($CDCl_3$, 298 K)

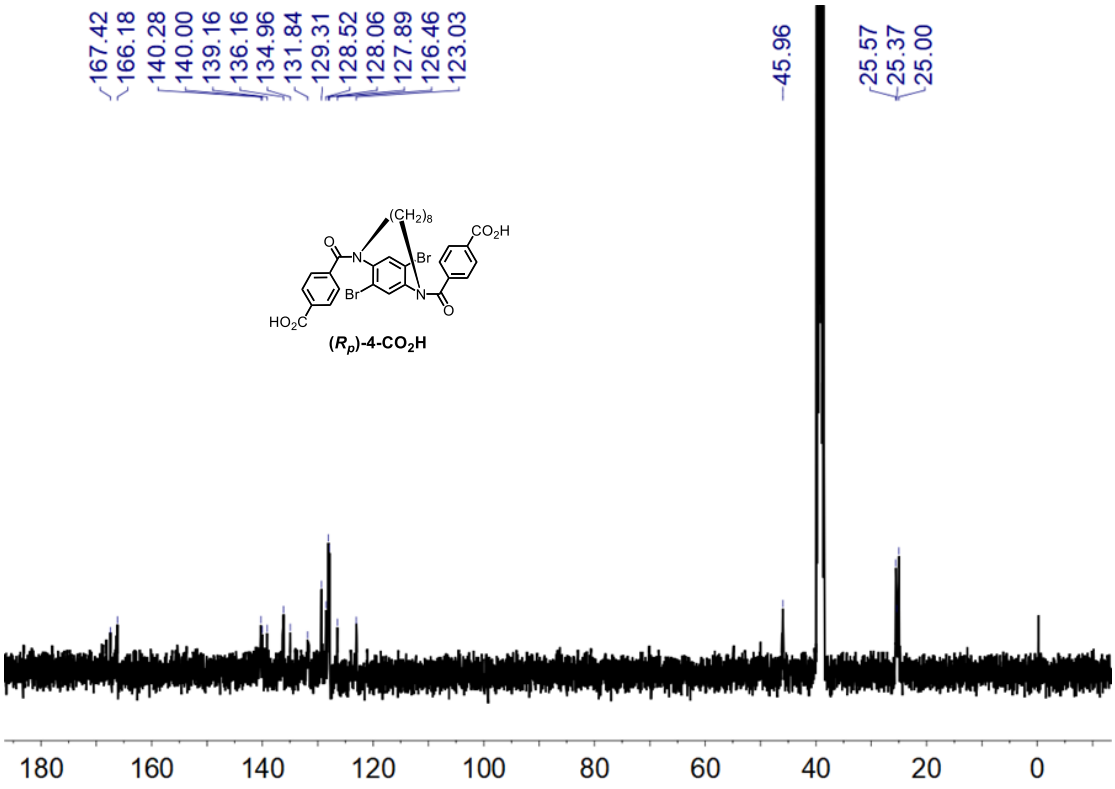


Fig. S83. ^{13}C NMR spectrum for **(R_p)-4-COOH** ($CDCl_3$, 298 K)

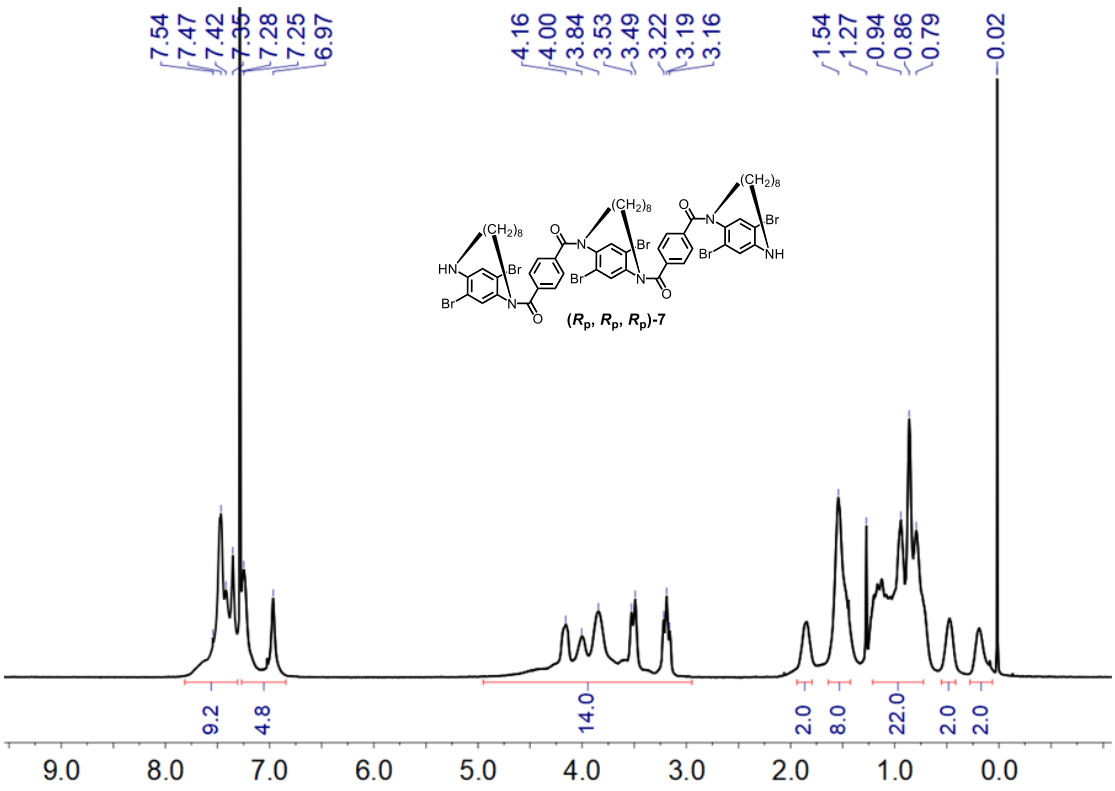


Fig. S84. ^{1}H NMR spectrum for **(R_p, R_p, R_p)-7** ($CDCl_3$, 298 K)

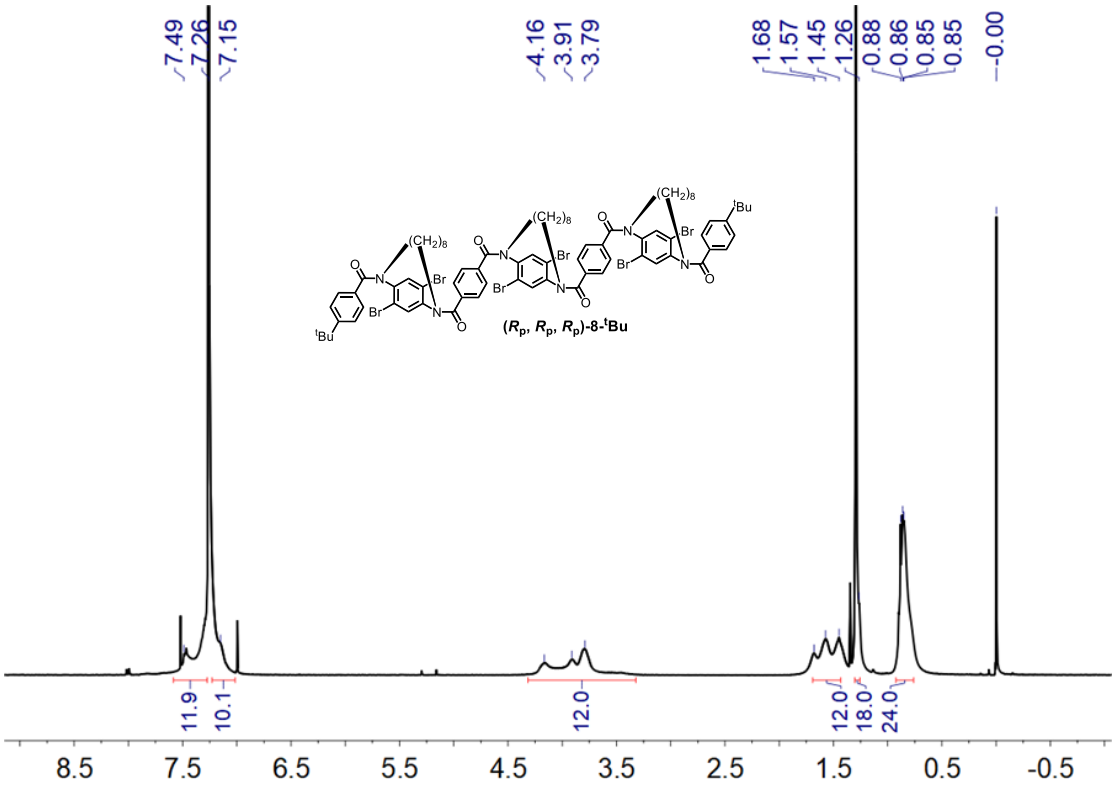


Fig. S85. ^{1}H NMR spectrum for **(R_p, R_p, R_p)-8-^{t}Bu** ($CDCl_3$, 298 K)

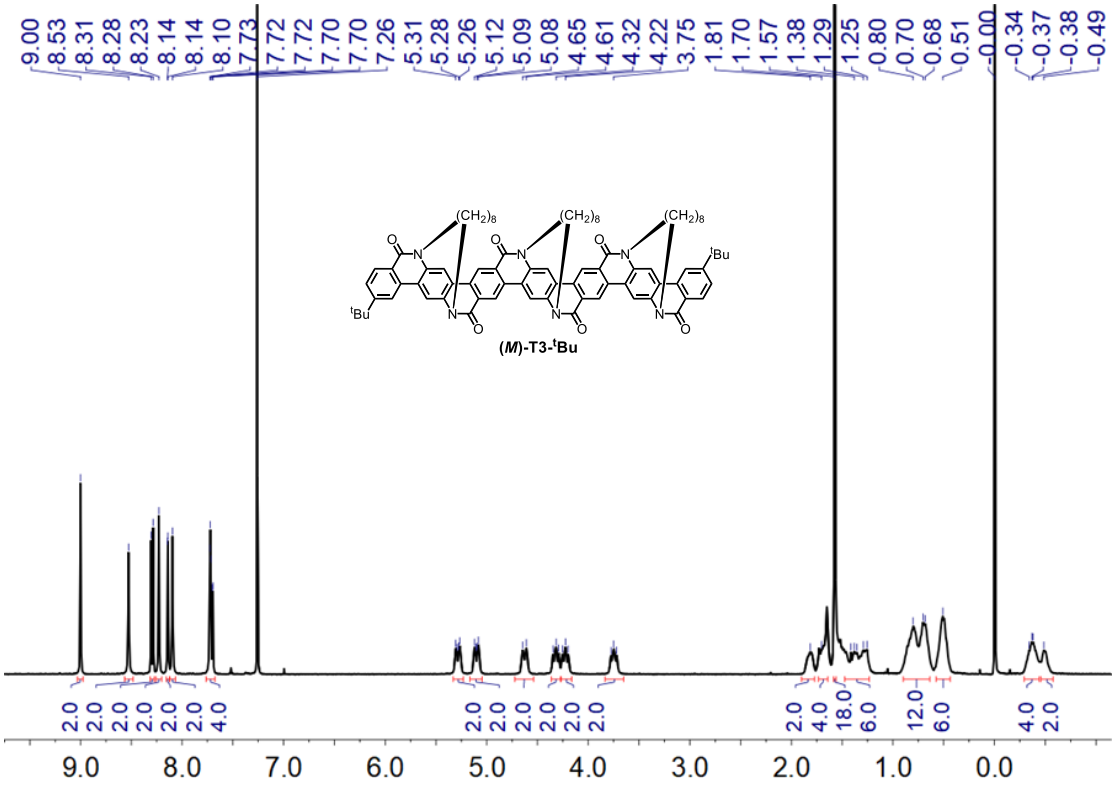


Fig. S86. ^{1}H NMR spectrum for **(*M*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

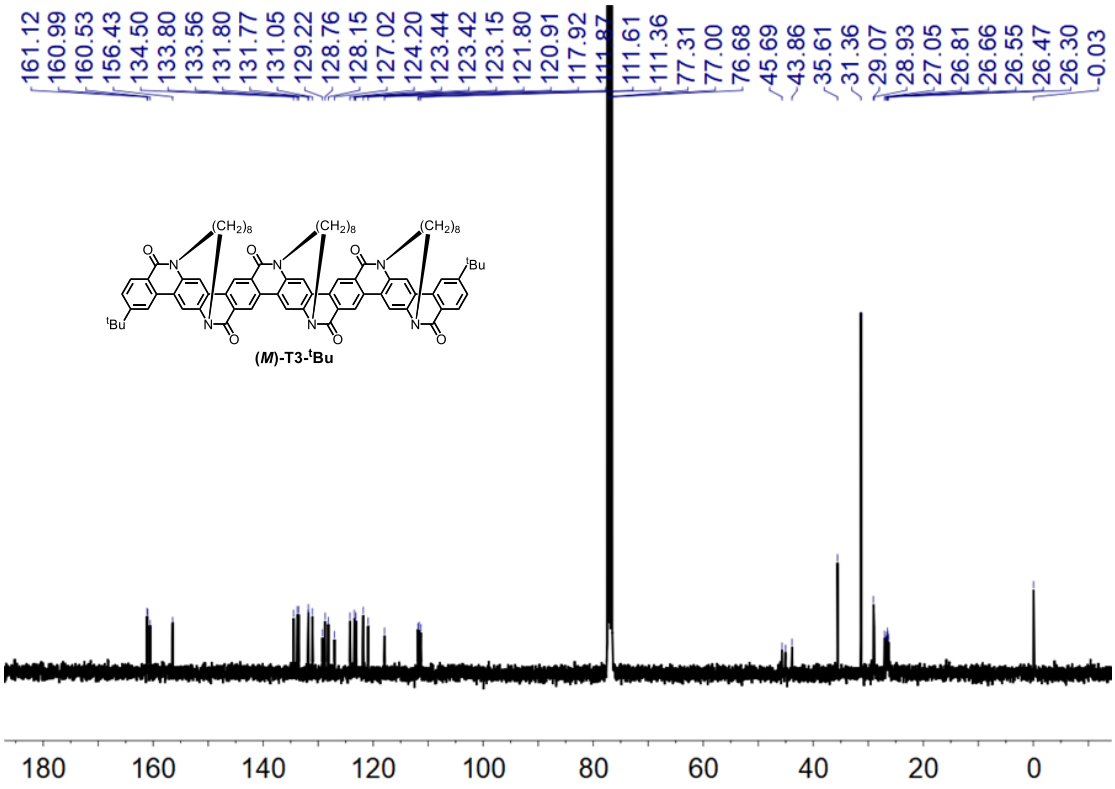


Fig. S87. ^{13}C NMR spectrum for **(*M*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

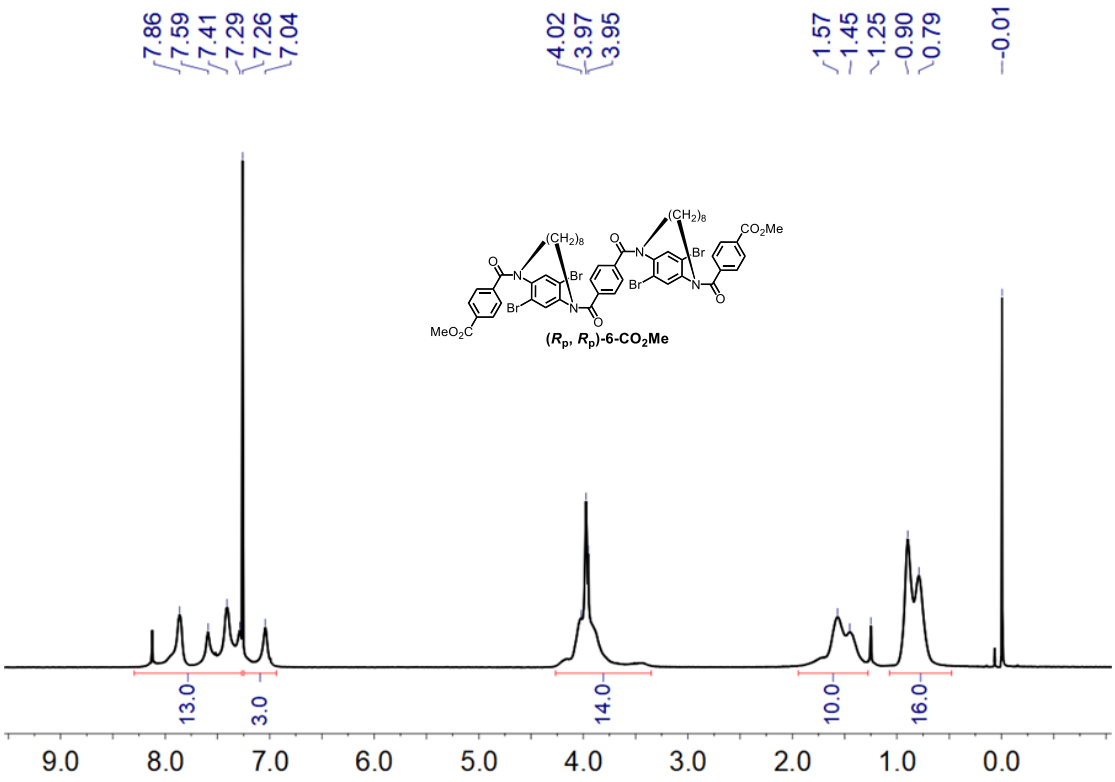


Fig. S88. ^{1}H NMR spectrum for **(R_p, R_p)-6-CO_2Me** ($CDCl_3$, 298 K)

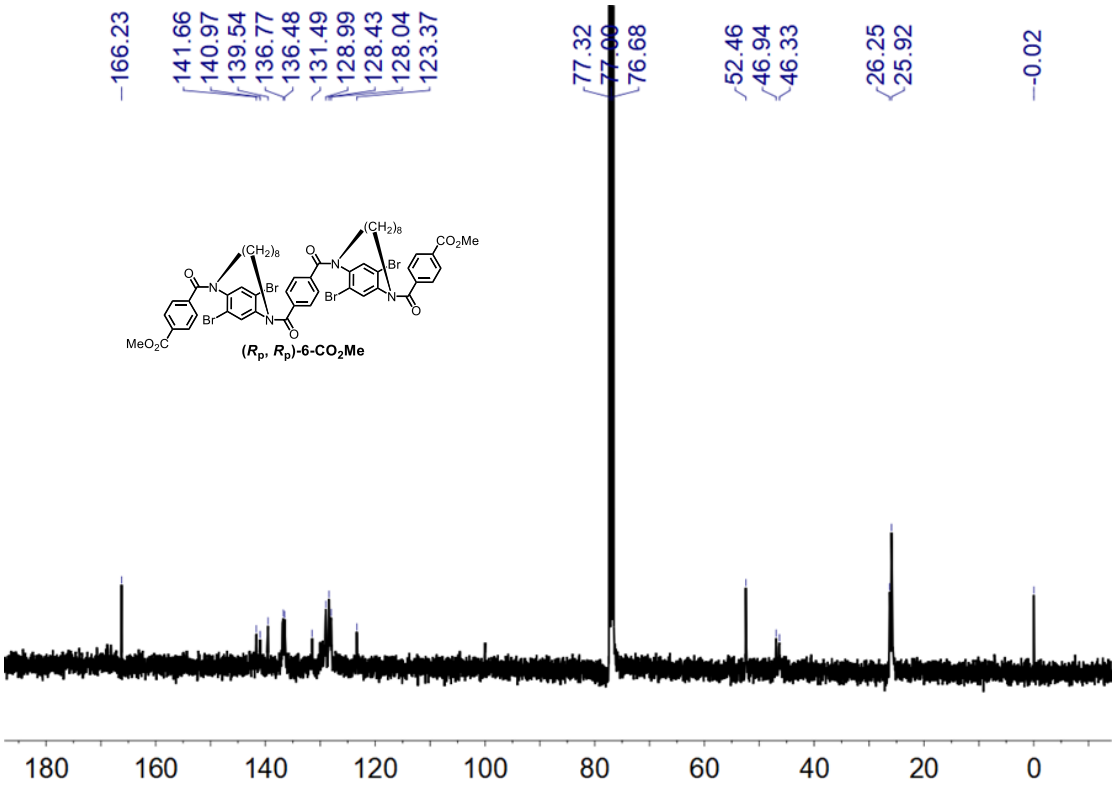


Fig. S89. ^{13}C NMR spectrum for **(R_p, R_p)-6-CO_2Me** ($CDCl_3$, 298 K)

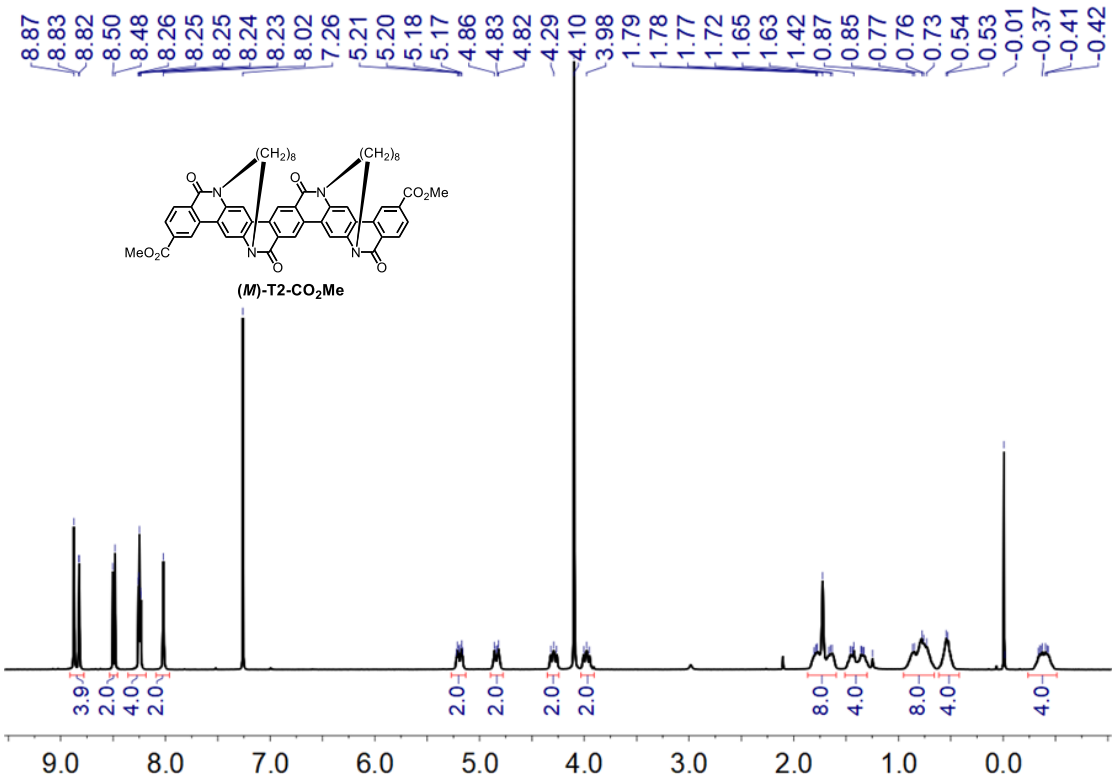


Fig. S90. ^{1}H NMR spectrum for **(*M*)-T2-CO$_2$Me** ($CDCl_3$, 298 K)

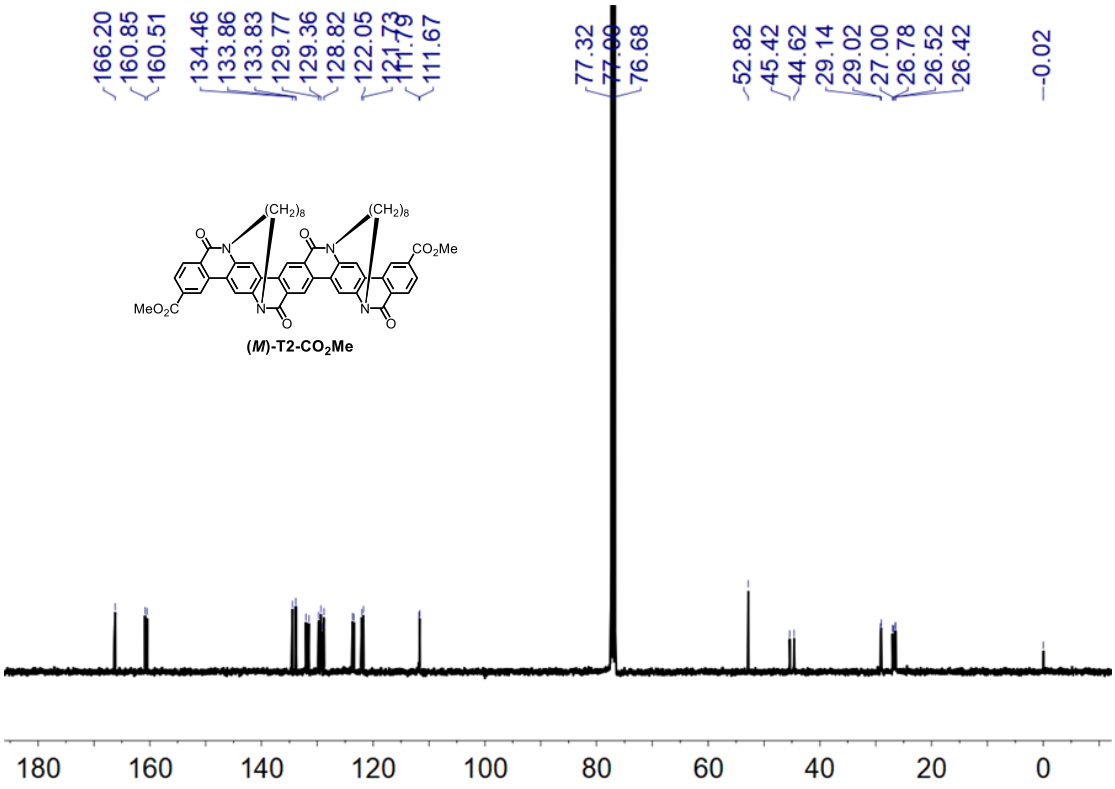


Fig. S91. ^{13}C NMR spectrum for **(*M*)-T2-CO$_2$Me** ($CDCl_3$, 298 K)

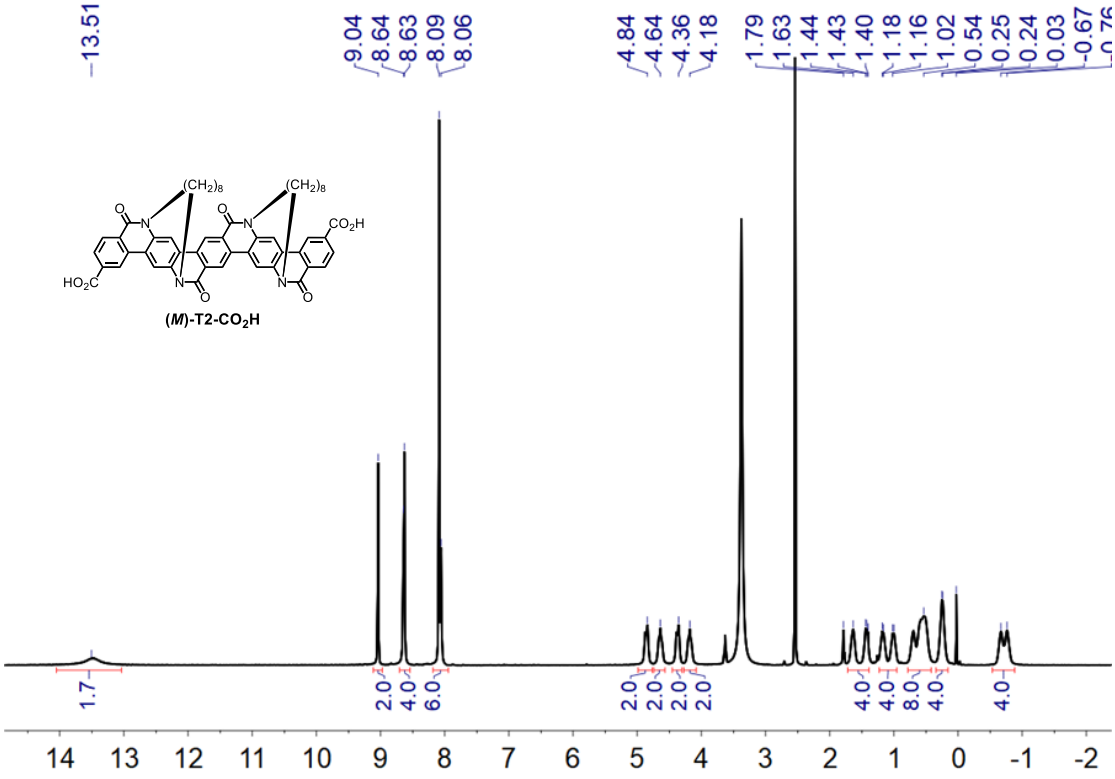


Fig. S92. ^{1}H NMR spectrum for **(*M*)-T2-CO$_2$H** ($CDCl_3$, 298 K)

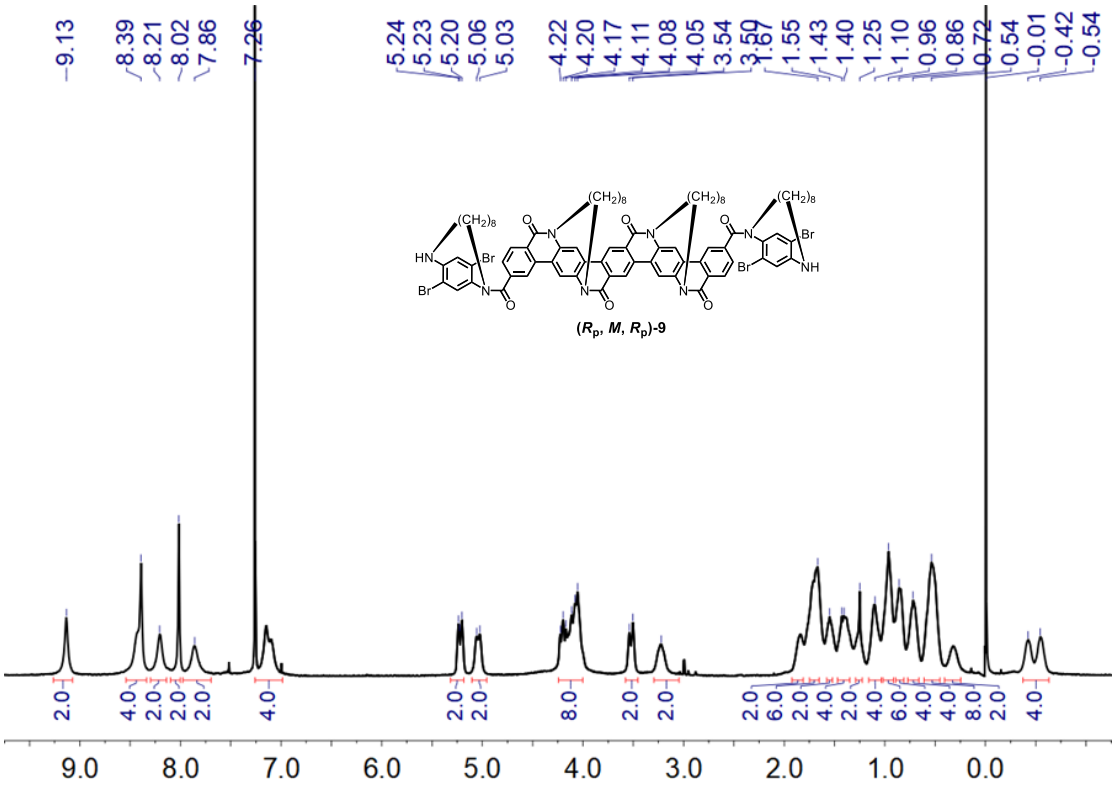


Fig. S93. ^{1}H NMR spectrum for **(R_p, *M*, R_p)-9** ($CDCl_3$, 298 K)

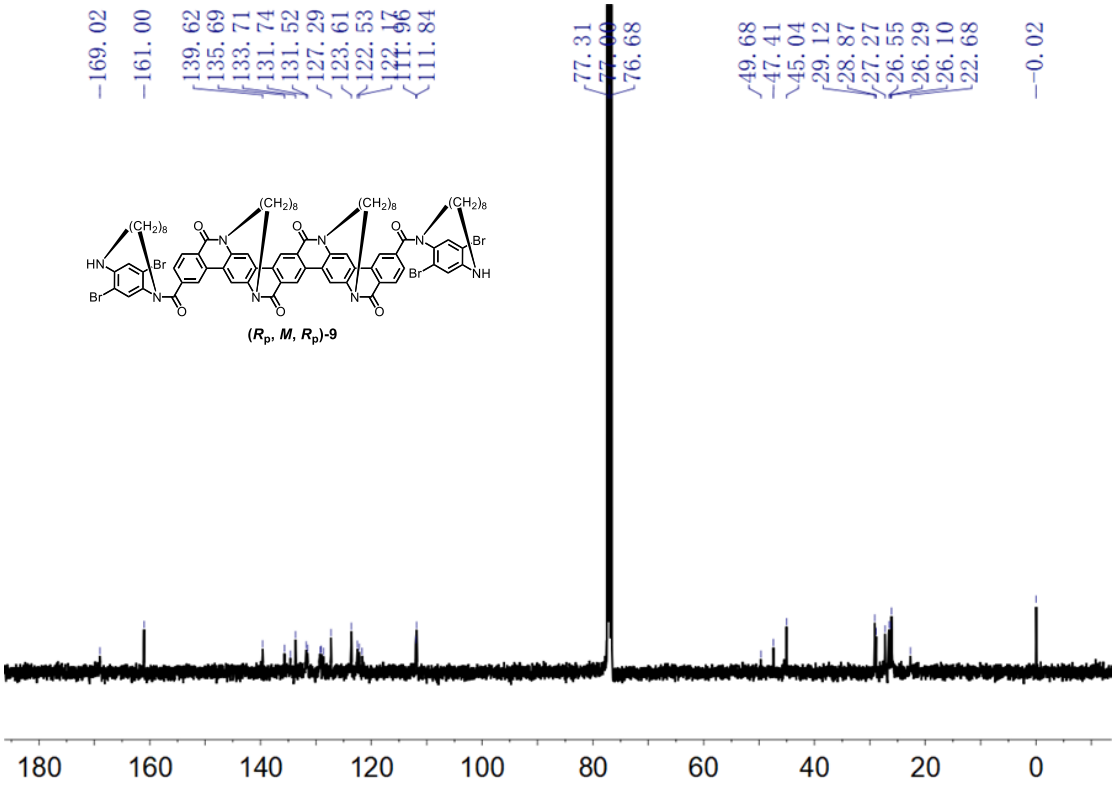


Fig. S94. ^{13}C NMR spectrum for **(R_p, *M*, R_p)-9** ($CDCl_3$, 298 K)

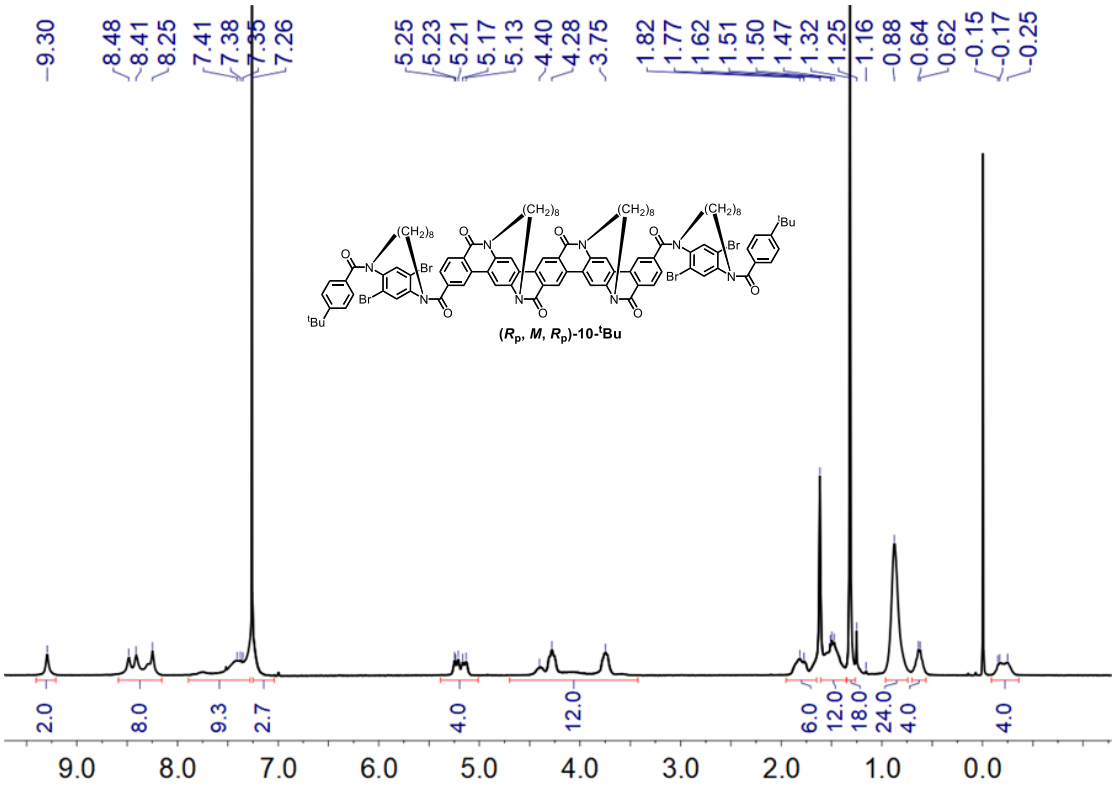


Fig. S95. ^{1}H NMR spectrum for **(R_p, *M*, R_p)-10-^{t}Bu** ($CDCl_3$, 298 K)

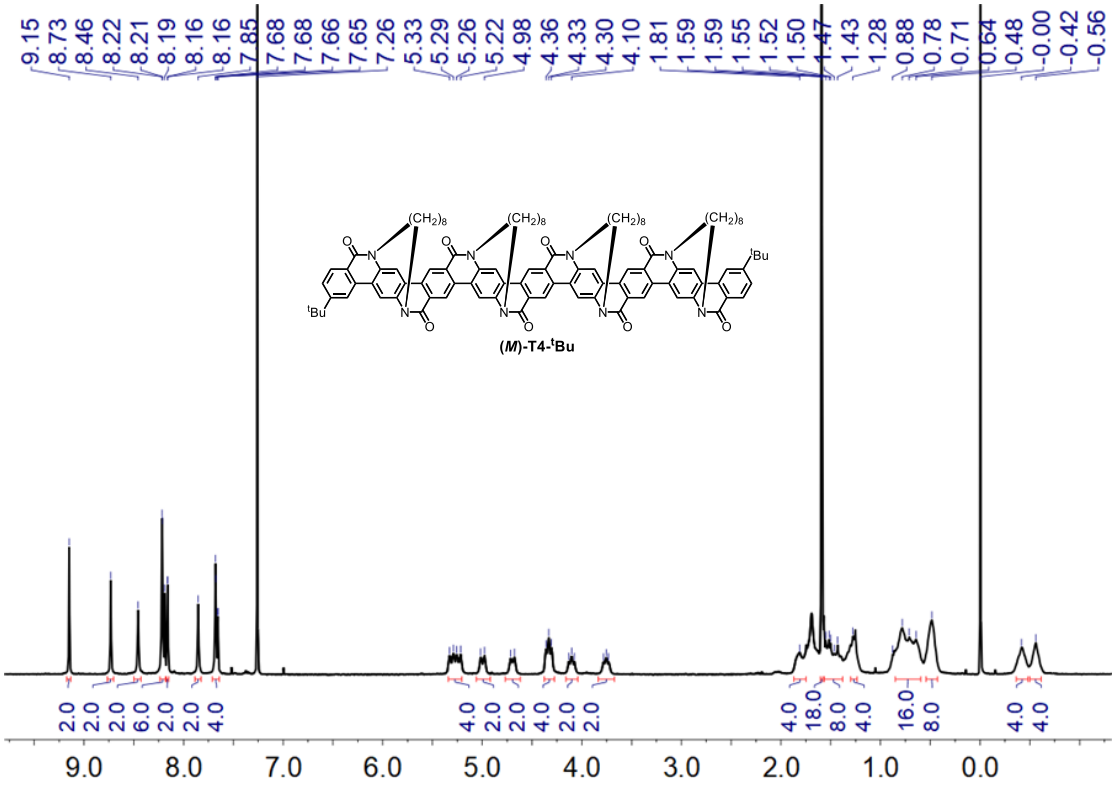


Fig. S96. ^{1}H NMR spectrum for **(*M*)-T4-^{t}Bu** ($CDCl_3$, 298 K)

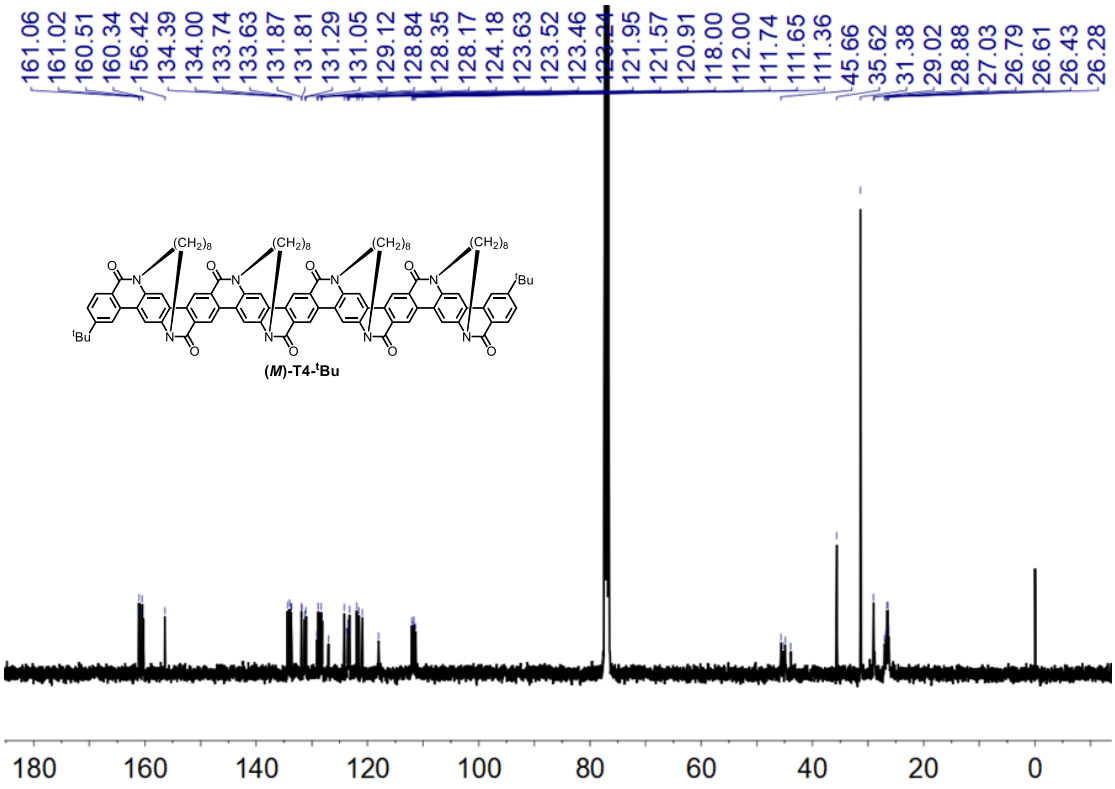


Fig. S97. ^{13}C NMR spectrum for **(*M*)-T4-^{t}Bu** ($CDCl_3$, 298 K)

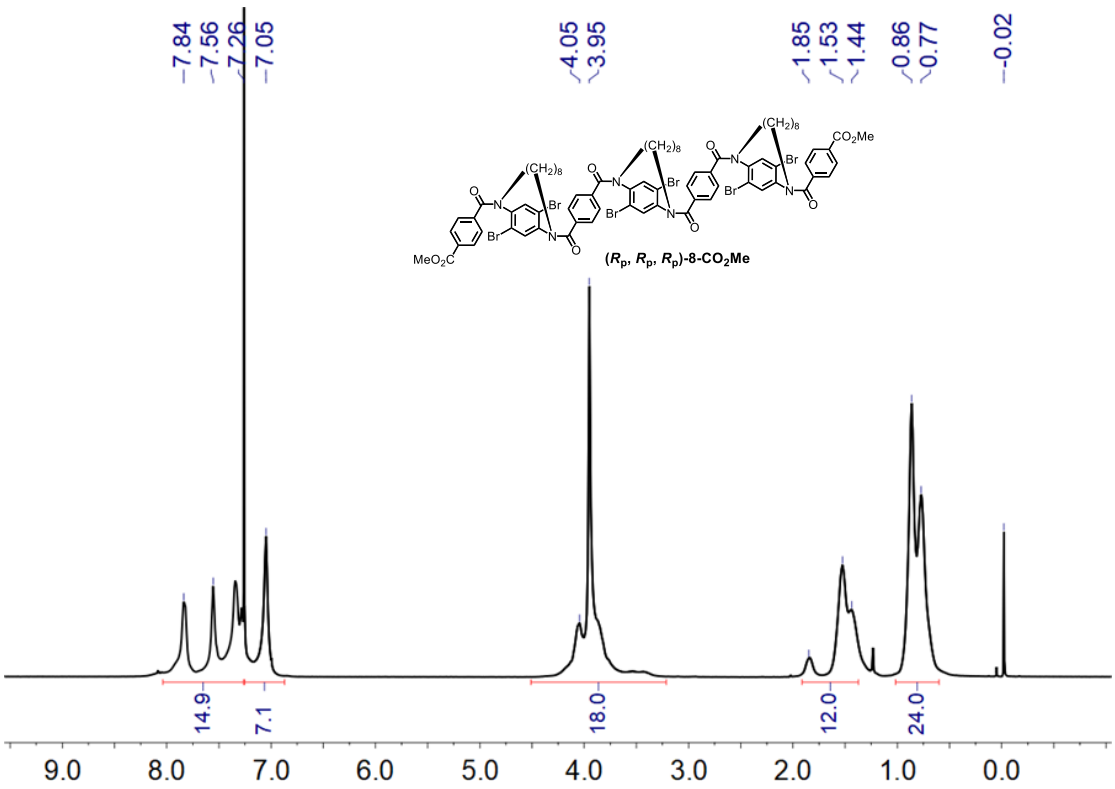


Fig. S98. ^{1}H NMR spectrum for **(R_p, R_p, R_p)-8-CO_2Me** ($CDCl_3$, 298 K)

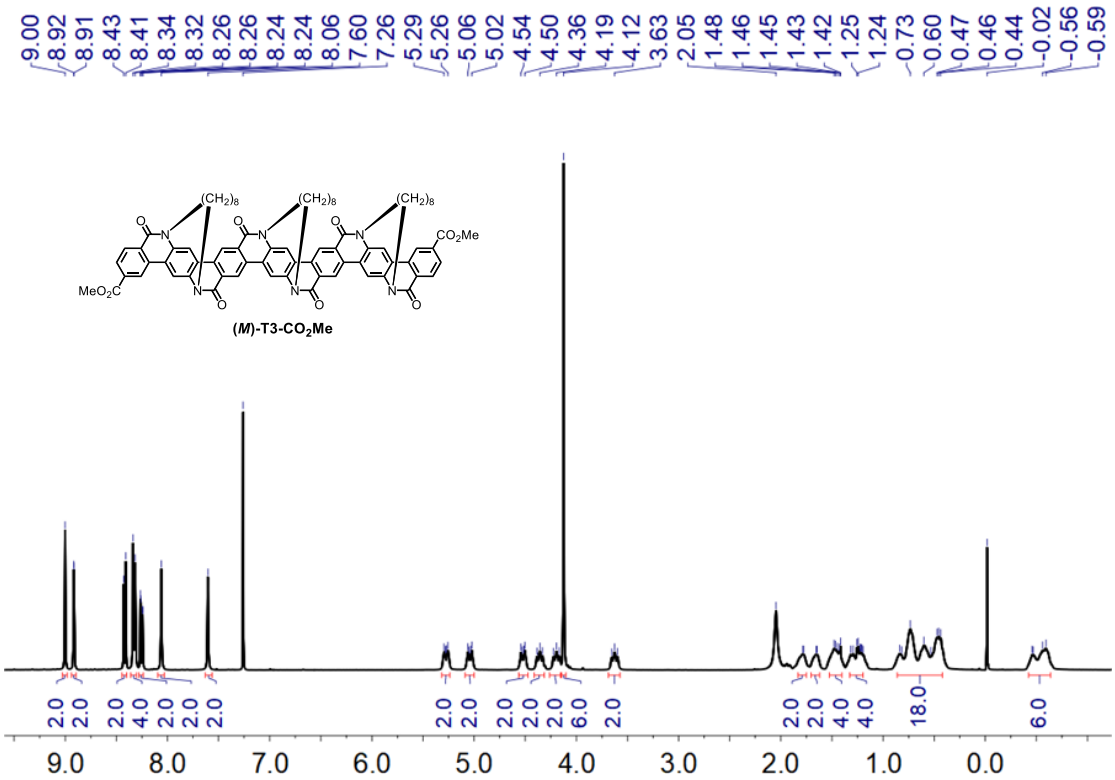


Fig. S99. ^{1}H NMR spectrum for **(*M*)-T3-CO_2Me** ($CDCl_3$, 298 K)

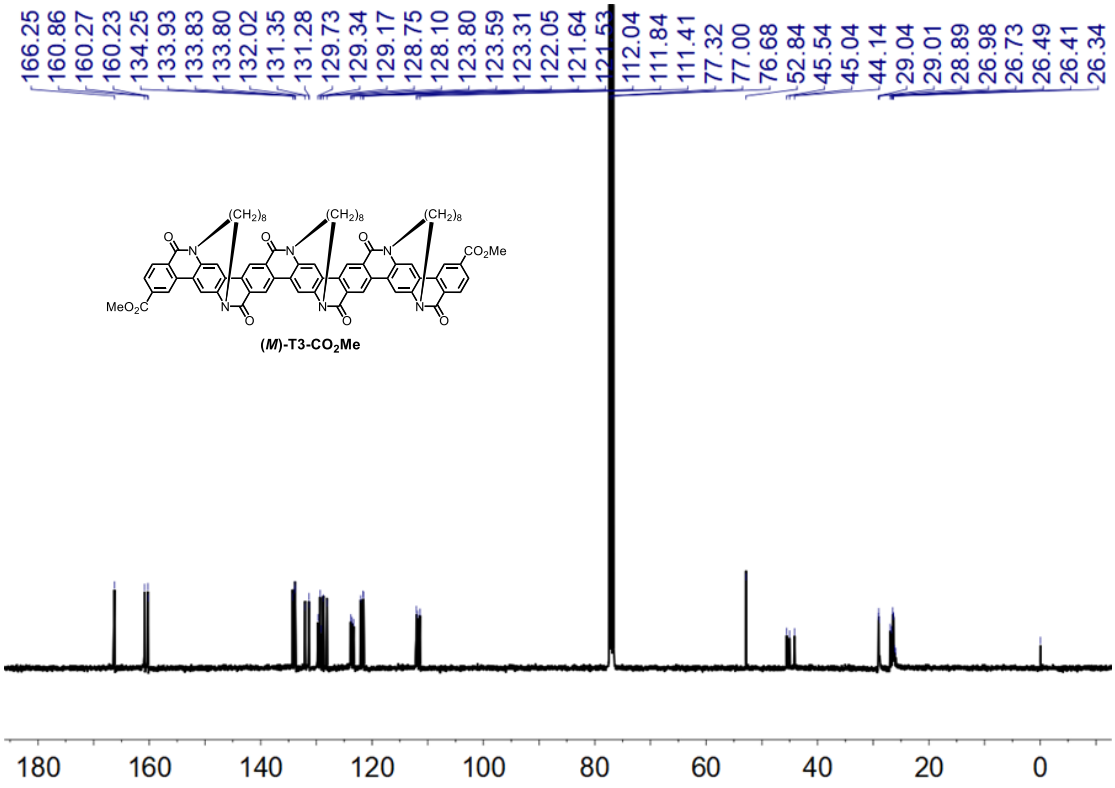


Fig. S100. ^{13}C NMR spectrum for **(*M*)-T3-CO$_2$Me** ($CDCl_3$, 298 K)

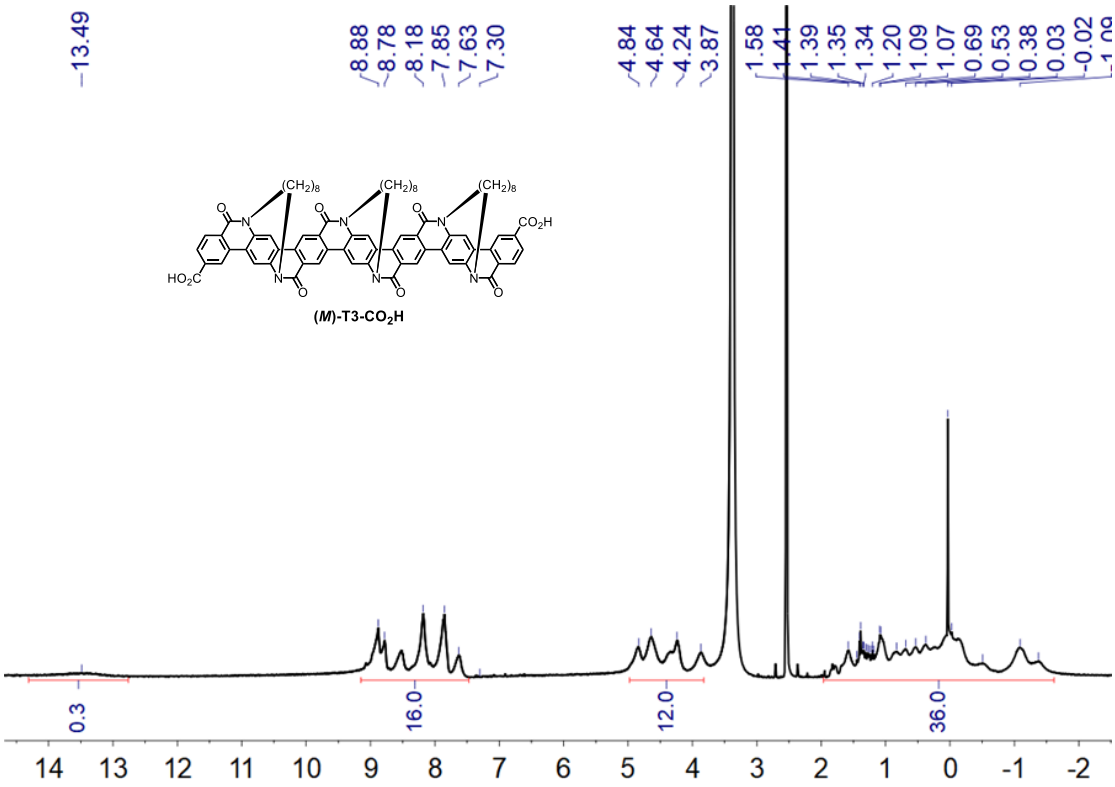


Fig. S101. ^{1}H NMR spectrum for **(*M*)-T3-CO$_2$H** ($CDCl_3$, 298 K)

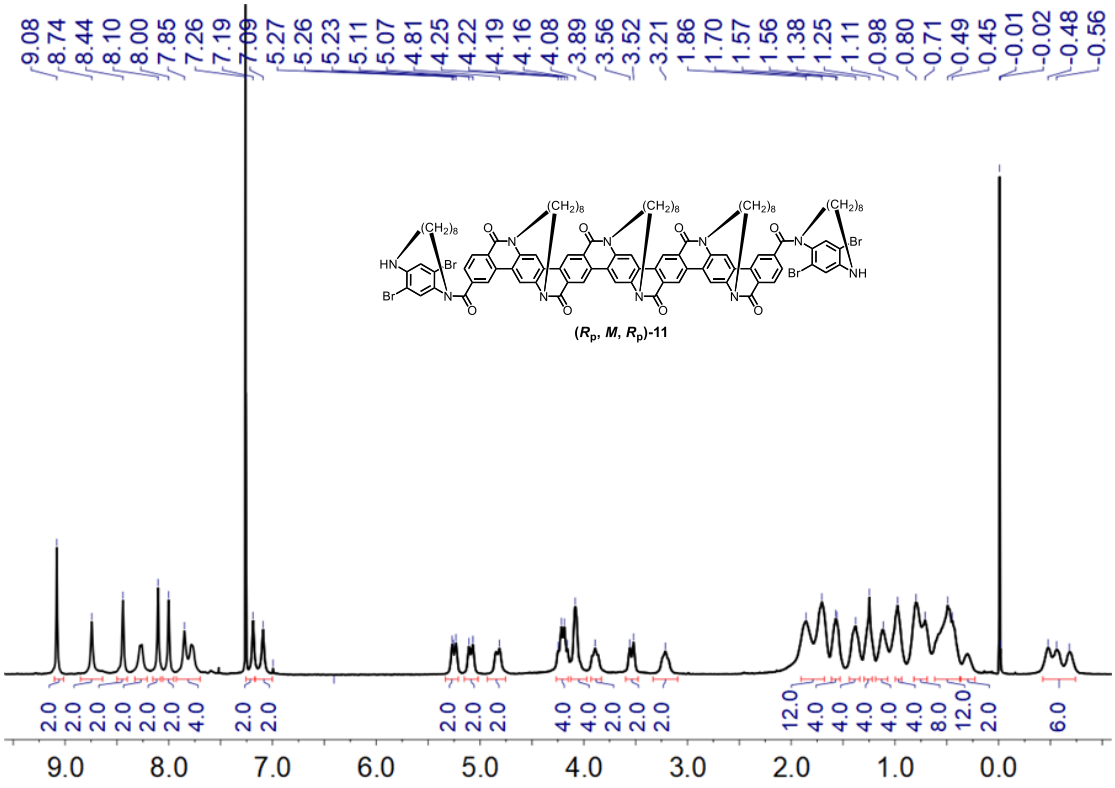


Fig. S102. ^{1}H NMR spectrum for **(R_p, *M*, R_p)-11** ($CDCl_3$, 298 K)

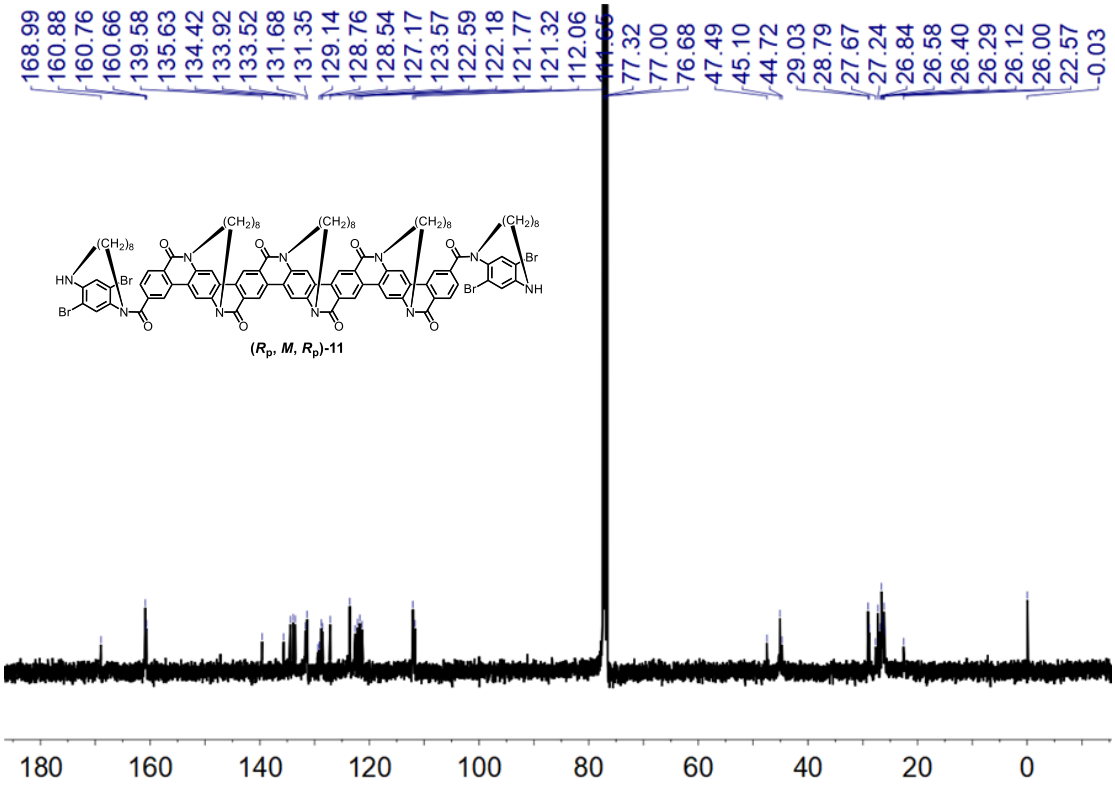


Fig. S103. ^{13}C NMR spectrum for **(R_p, *M*, R_p)-11** ($CDCl_3$, 298 K)

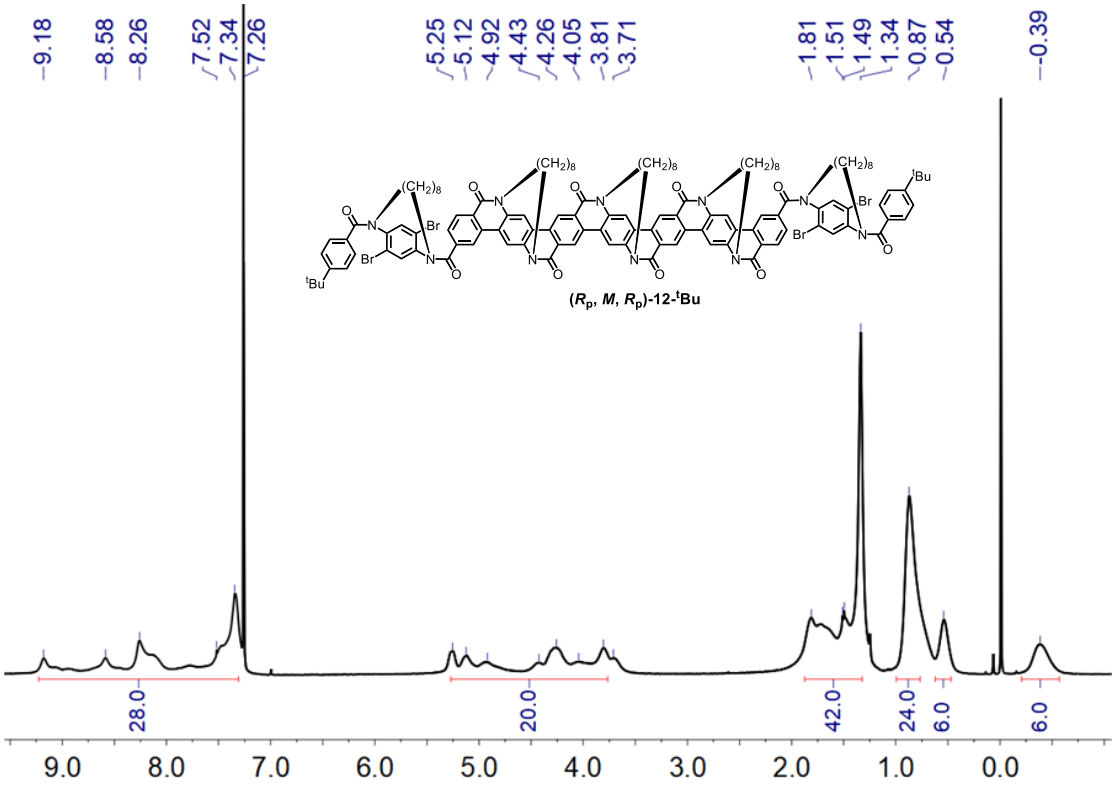


Fig. S104. ^{1}H NMR spectrum for **(R_p, *M*, R_p)-12-^{t}Bu** ($CDCl_3$, 298 K)

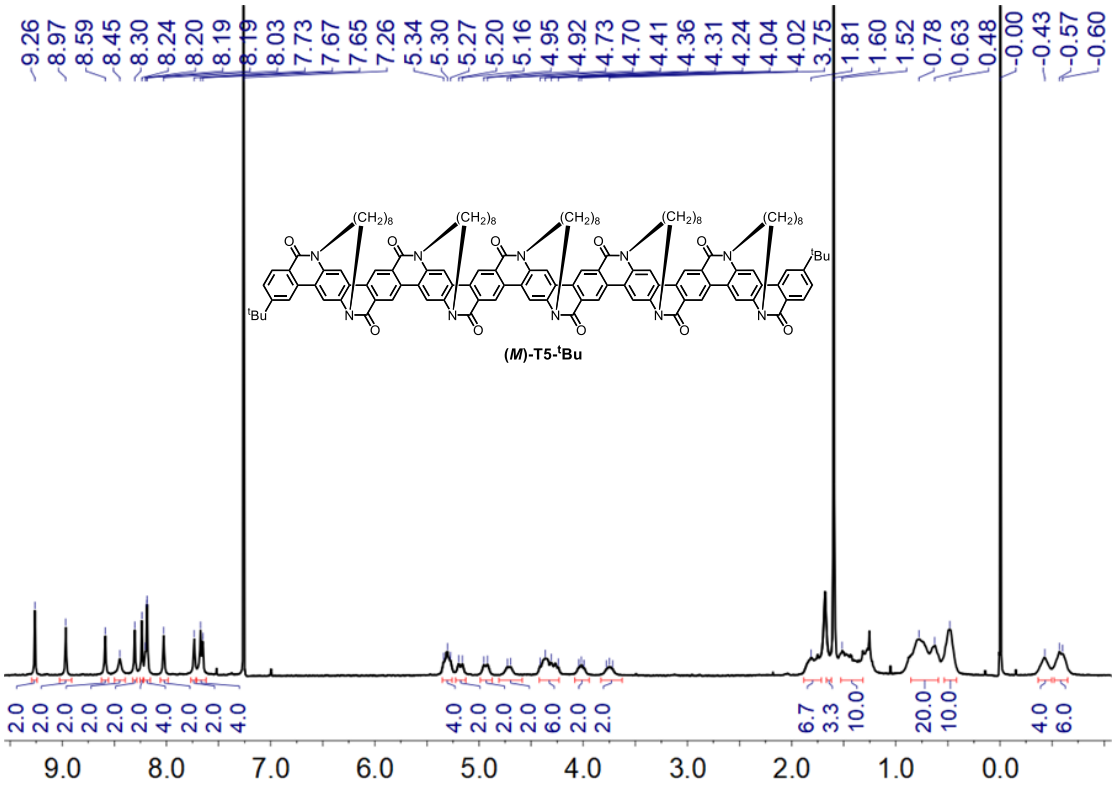


Fig. S105. ^{1}H NMR spectrum for **(*M*)-T5-^{t}Bu** ($CDCl_3$, 298 K)

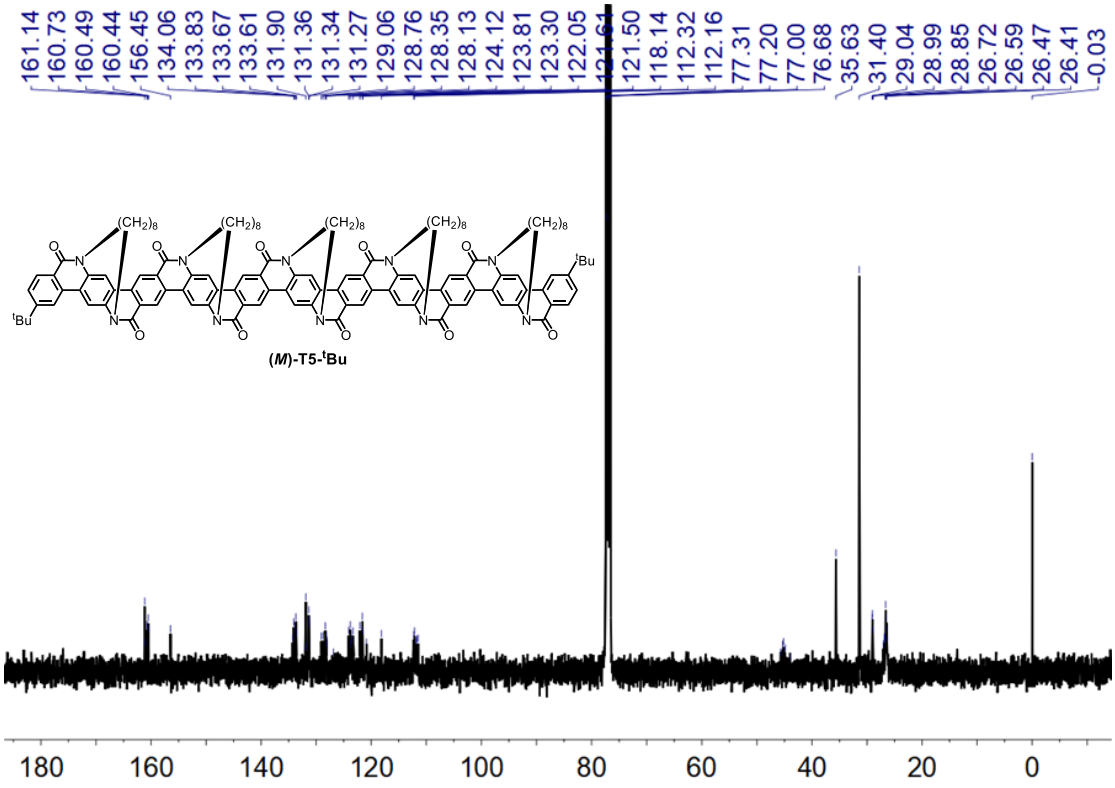


Fig. S106. ^{13}C NMR spectrum for **(*M*)-T5-^{t}Bu** ($CDCl_3$, 298 K)

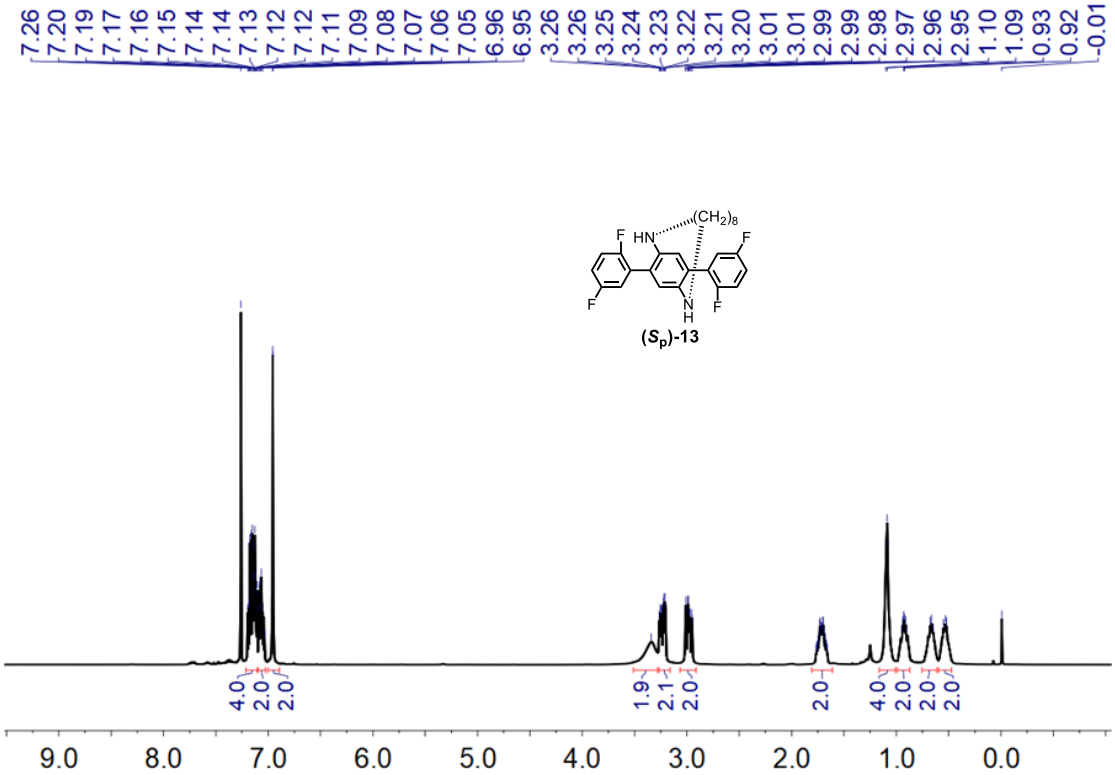


Fig. S107. ^{1}H NMR spectrum for **(S_p)-13** ($CDCl_3$, 298 K)

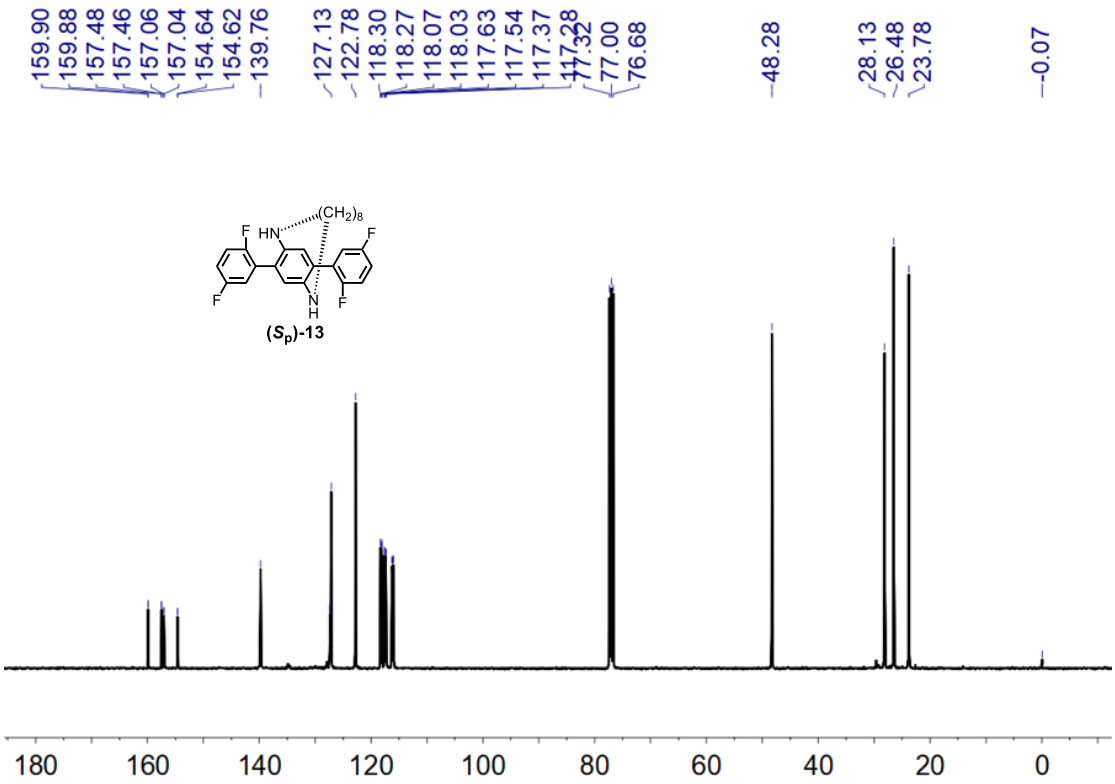


Fig. S108. ^{13}C NMR spectrum for **(S_p)-13** ($CDCl_3$, 298 K)

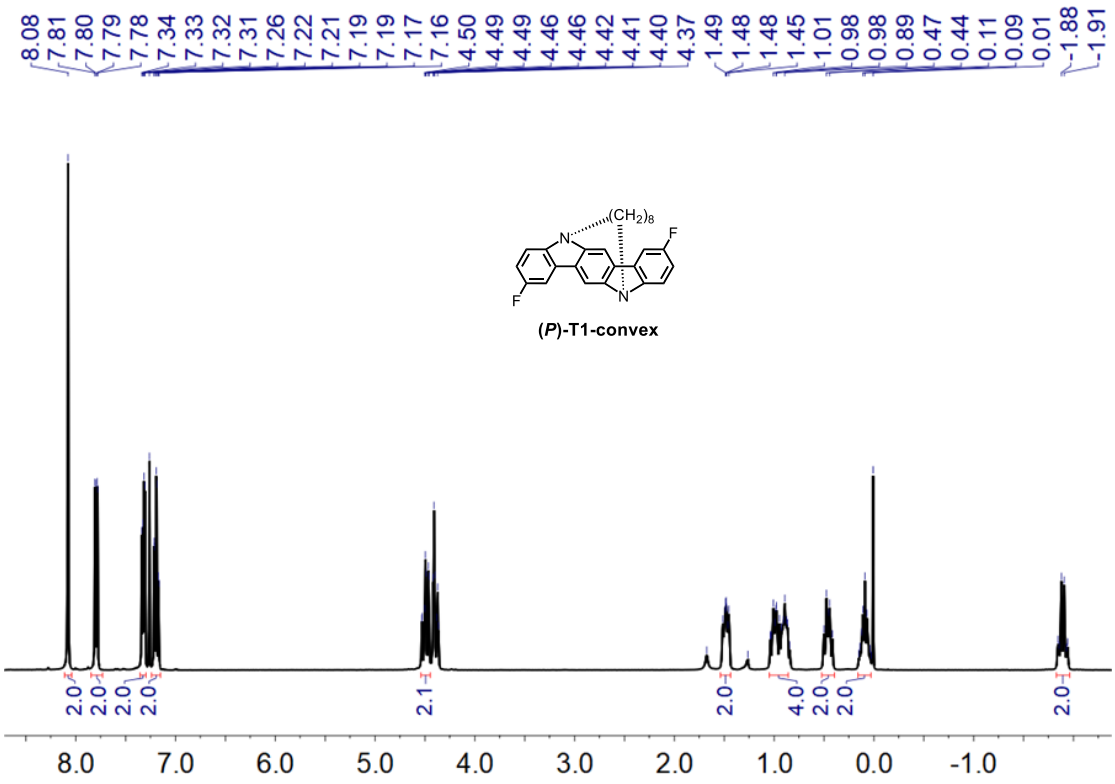


Fig. S109. ^{1}H NMR spectrum for **(*P*)-T1-convex** ($CDCl_3$, 298 K)

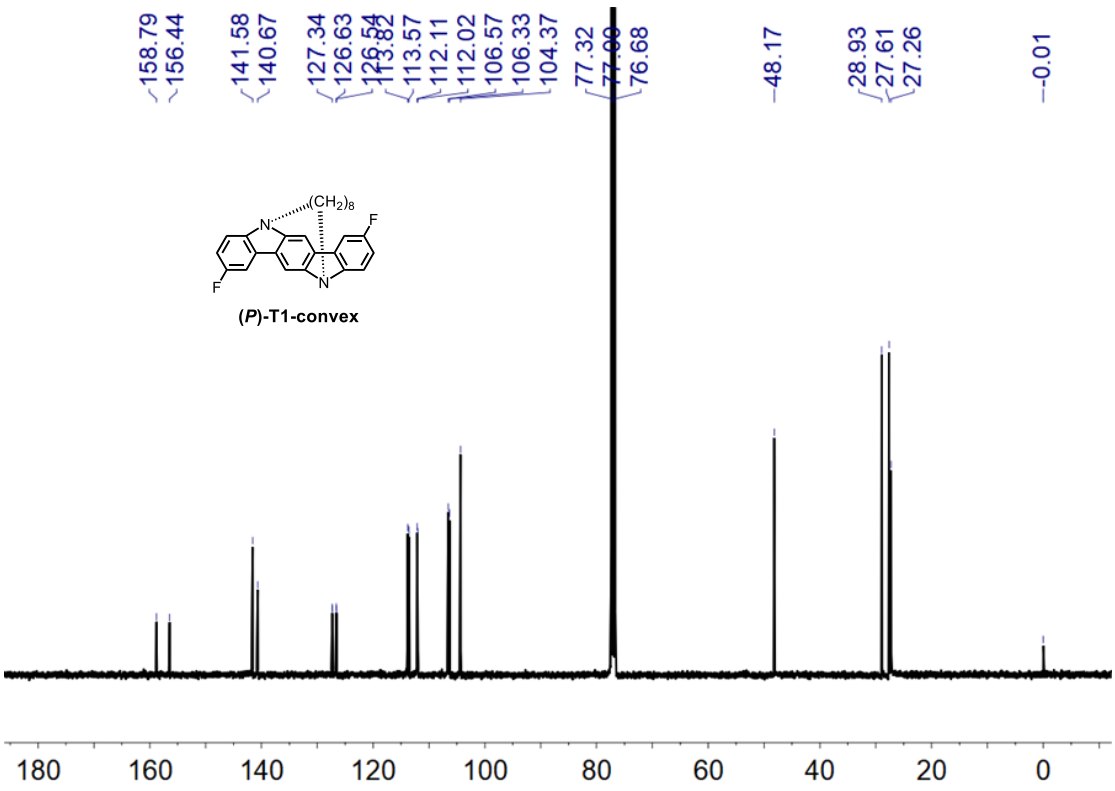


Fig. S110. ^{13}C NMR spectrum for **(*P*)-T1-convex** ($CDCl_3$, 298 K)

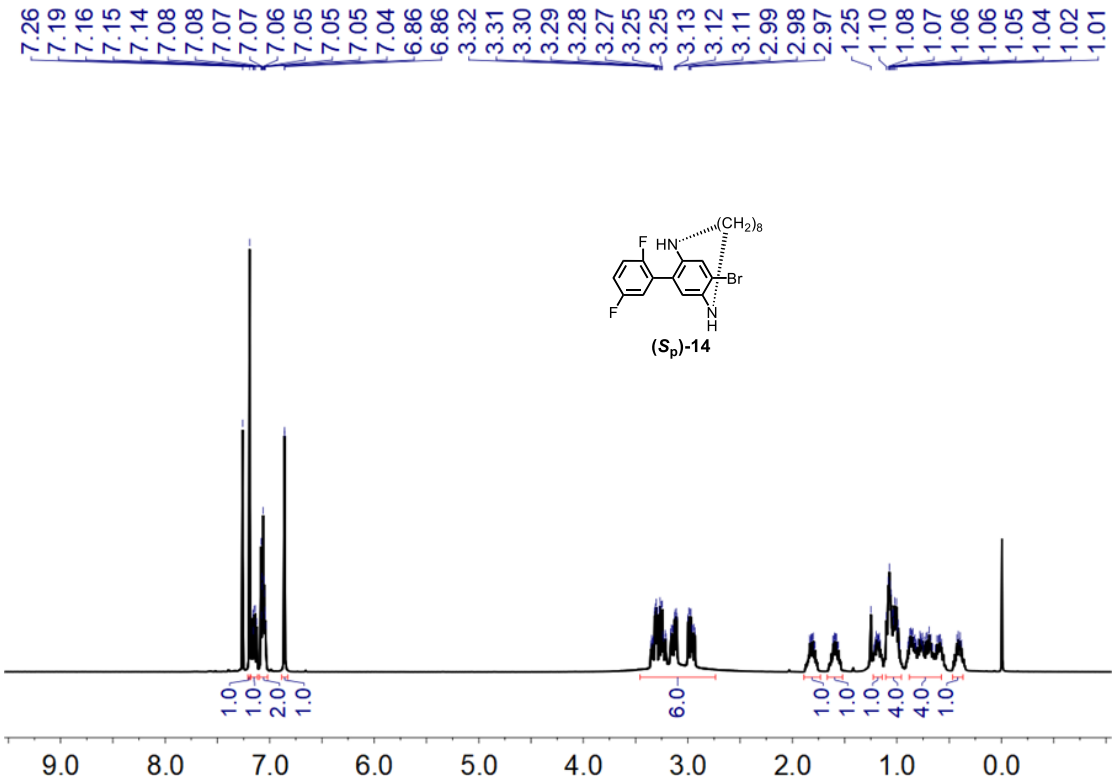


Fig. S111. ^{1}H NMR spectrum for **(S_p)-14** ($CDCl_3$, 298 K)

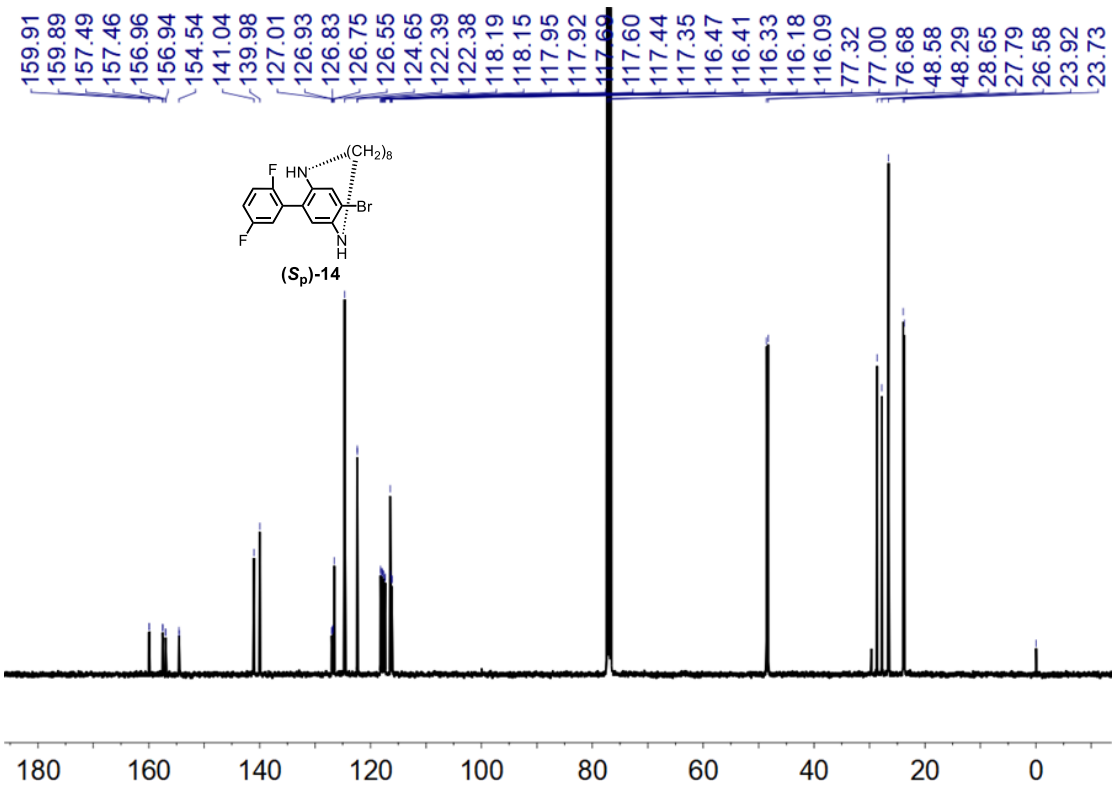


Fig. S112. ^{13}C NMR spectrum for **(S_p)-14** ($CDCl_3$, 298 K)

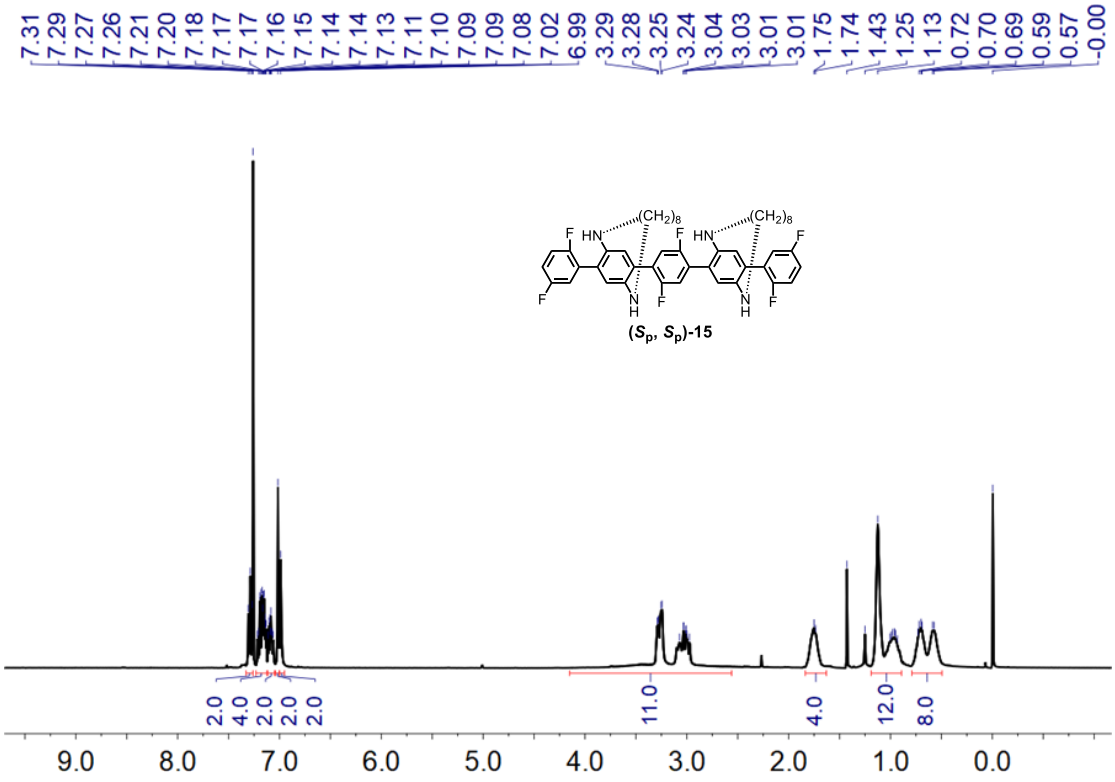


Fig. S113. ^{1}H NMR spectrum for **(S_p, S_p)-15** ($CDCl_3$, 298 K)

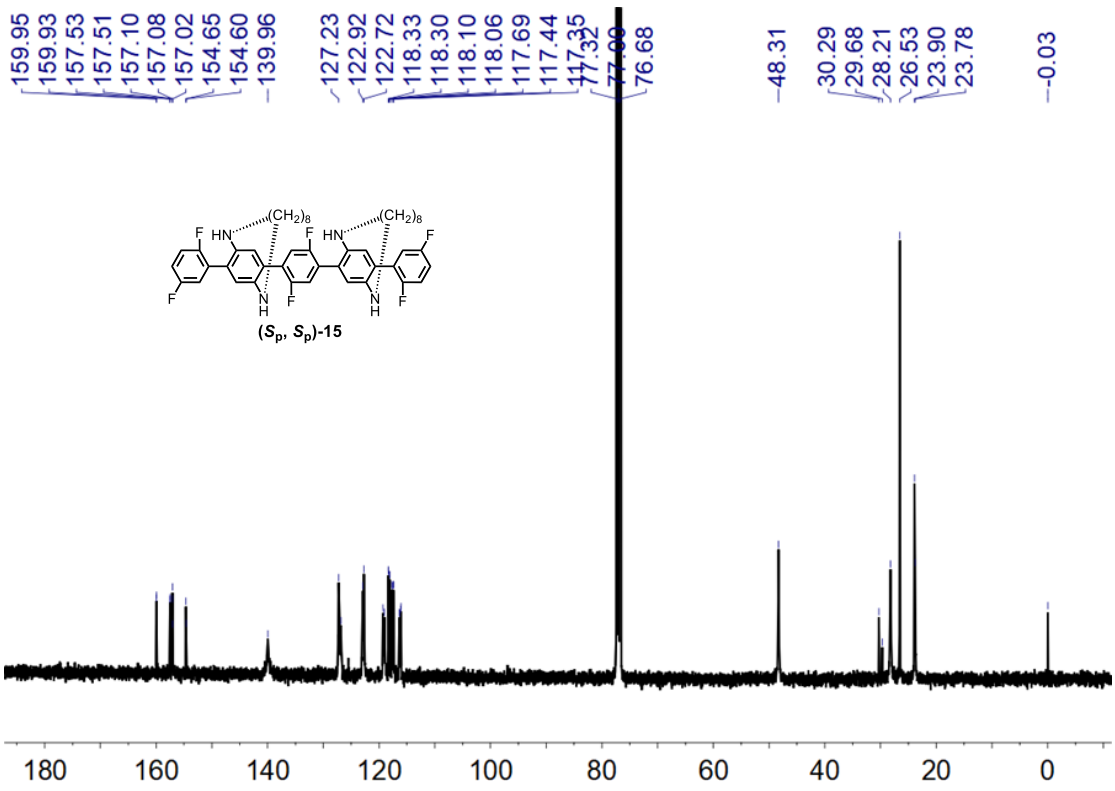


Fig. S114. ^{13}C NMR spectrum for **(S_p, S_p)-15** ($CDCl_3$, 298 K)

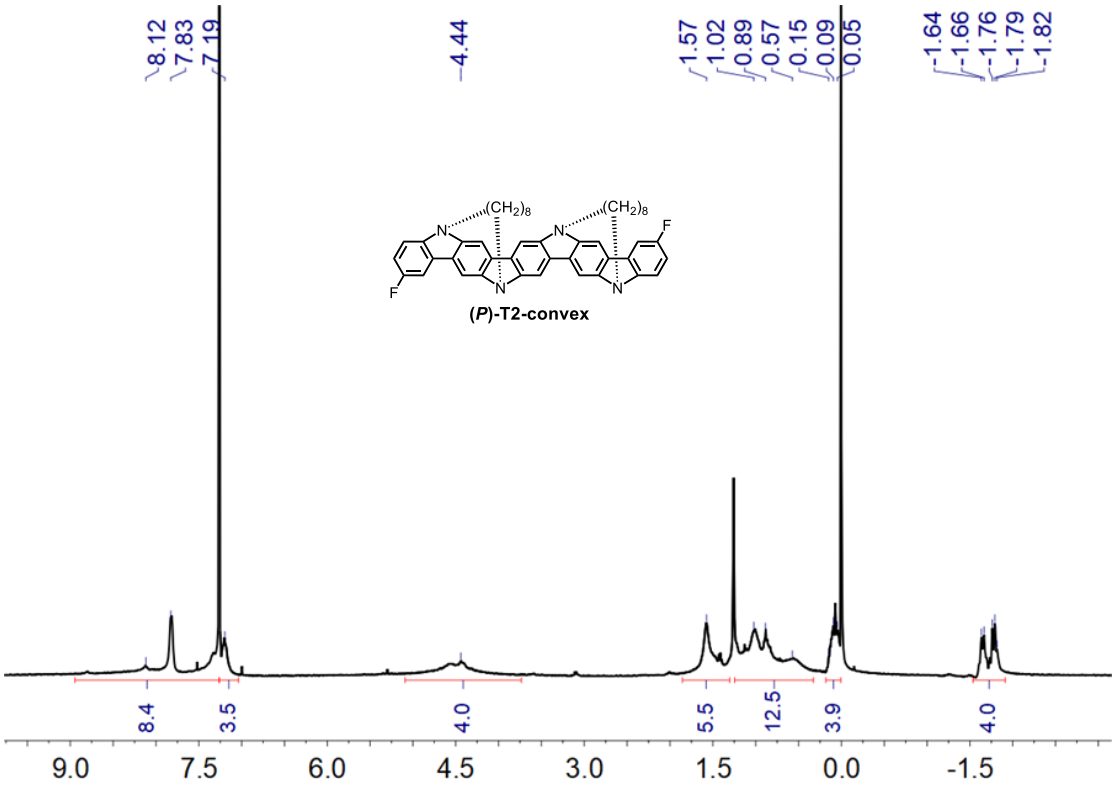


Fig. S115. ^{1}H NMR spectrum for **(*P*)-T2-convex** ($CDCl_3$, 298 K)

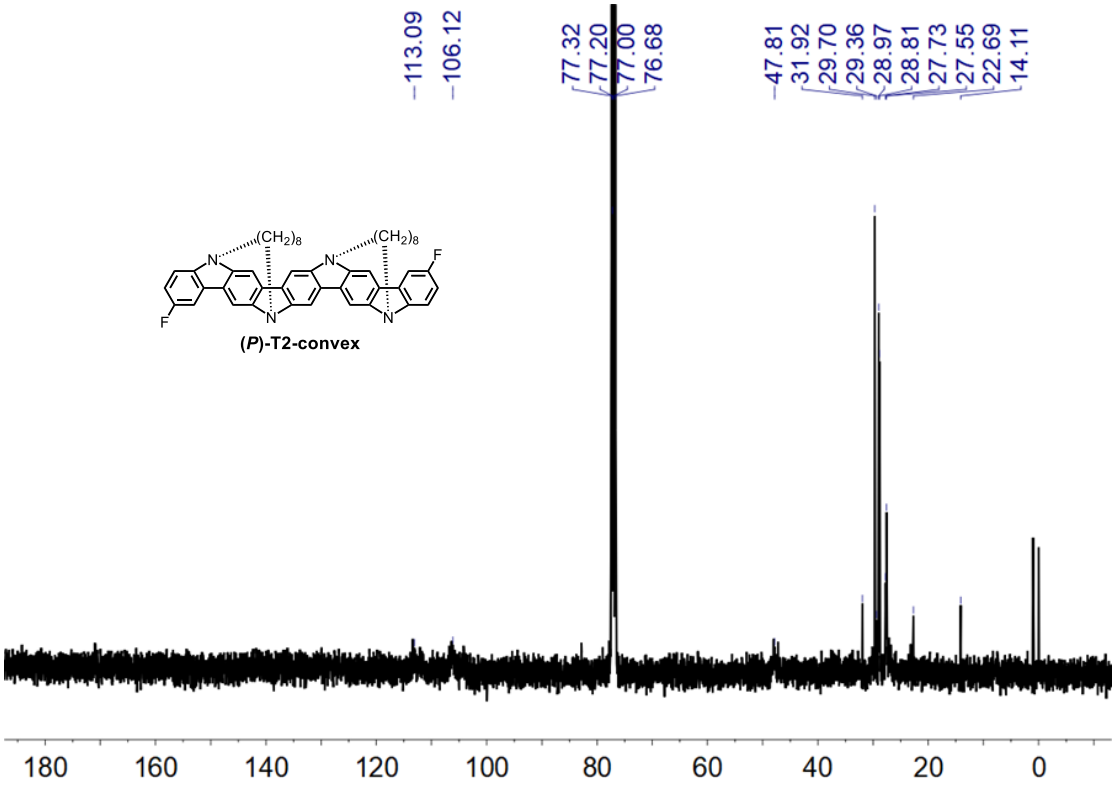


Fig. S116. ^{13}C NMR spectrum for **(*P*)-T2-convex** ($CDCl_3$, 298 K)

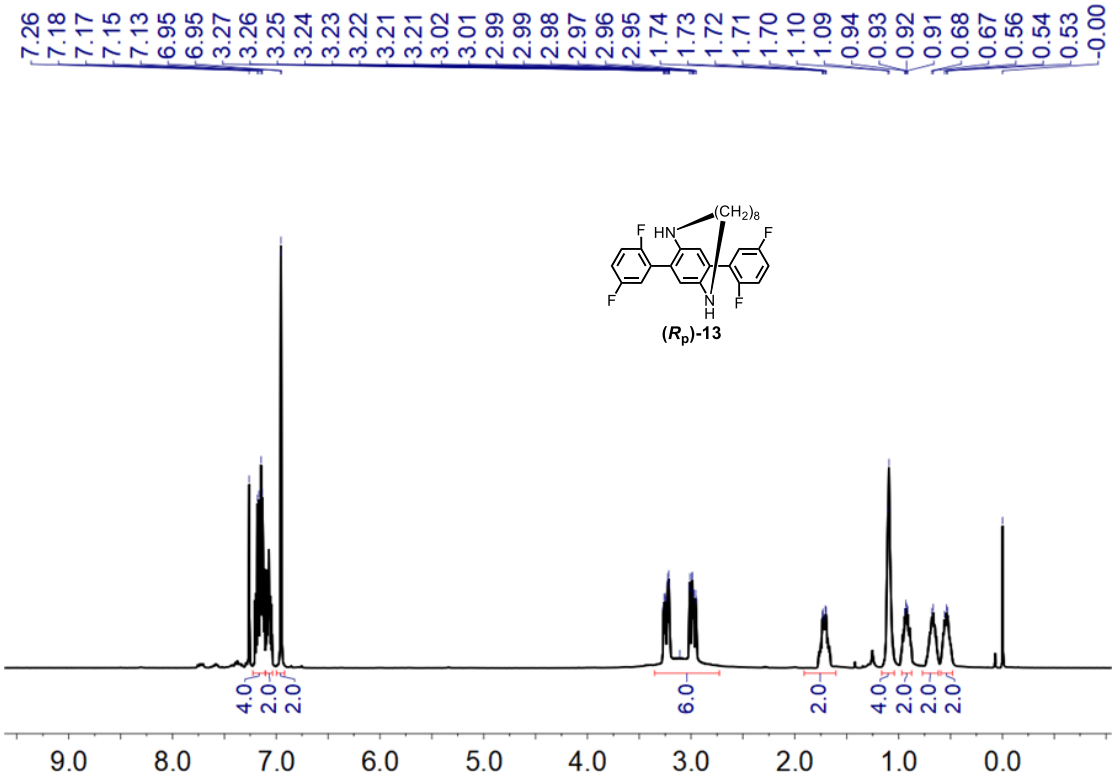


Fig. S117. ^{1}H NMR spectrum for **(R_p)-13** ($CDCl_3$, 298 K)

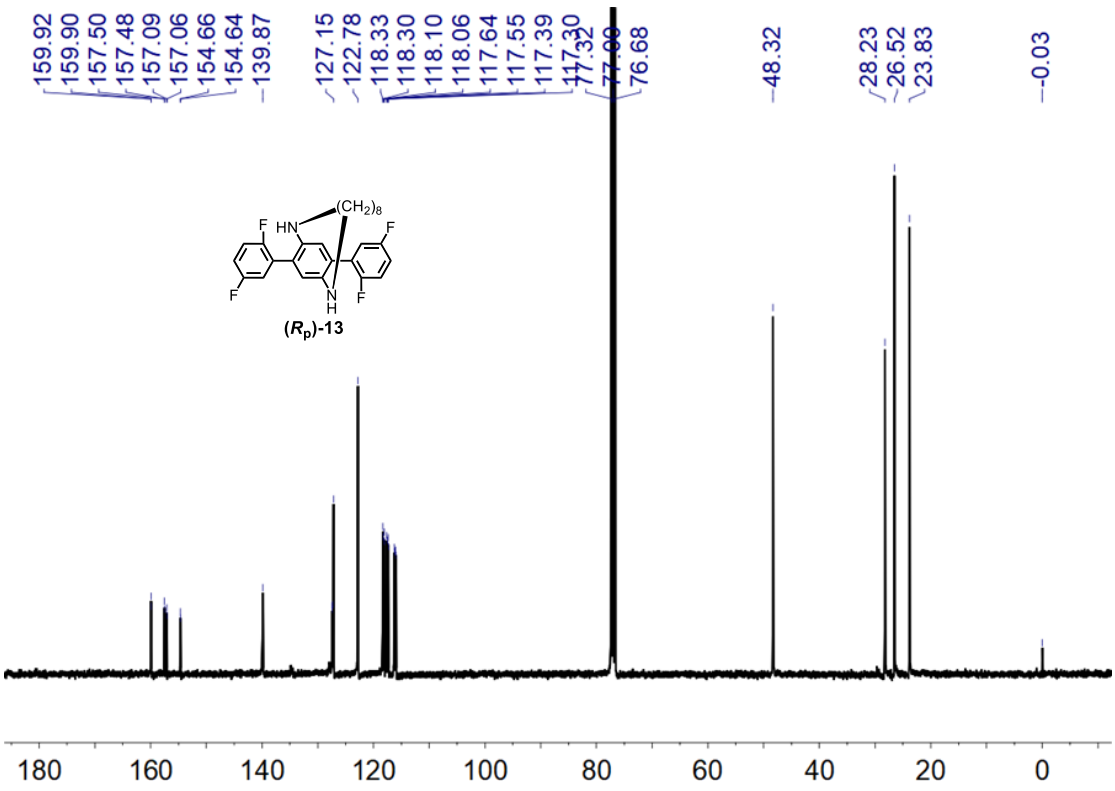


Fig. S118. ^{13}C NMR spectrum for **(R_p)-13** ($CDCl_3$, 298 K)

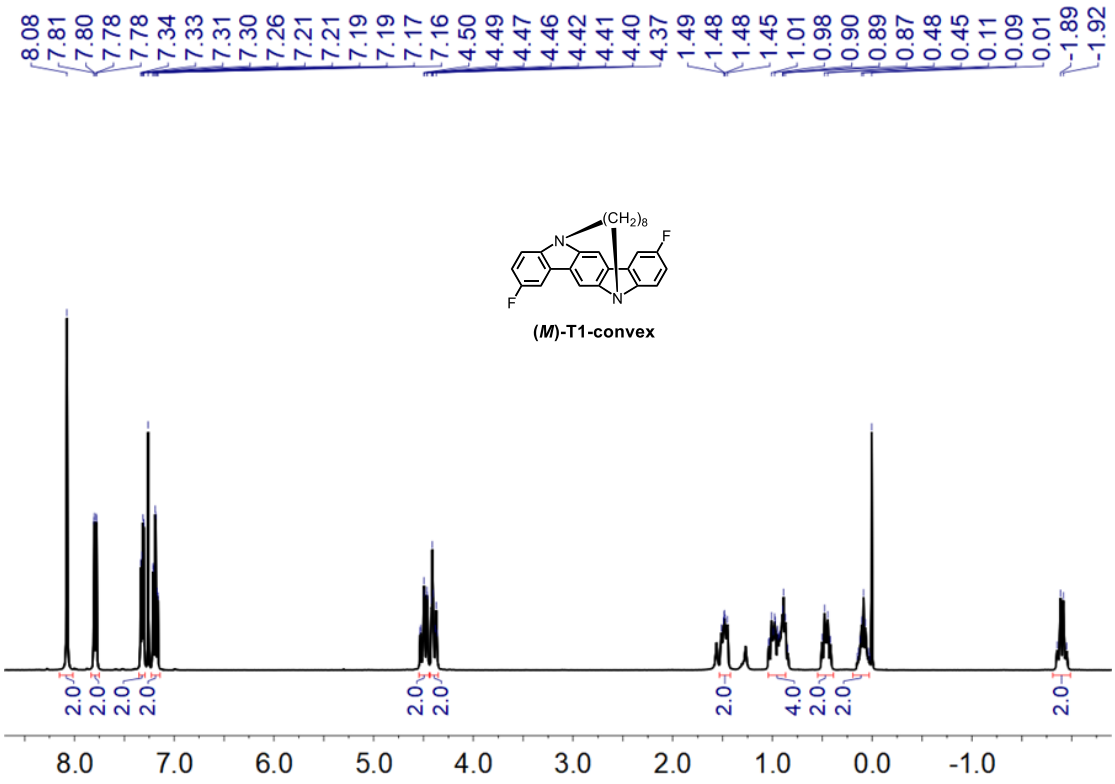


Fig. S119. ^{1}H NMR spectrum for **(*M*)-T1-convex** ($CDCl_3$, 298 K)

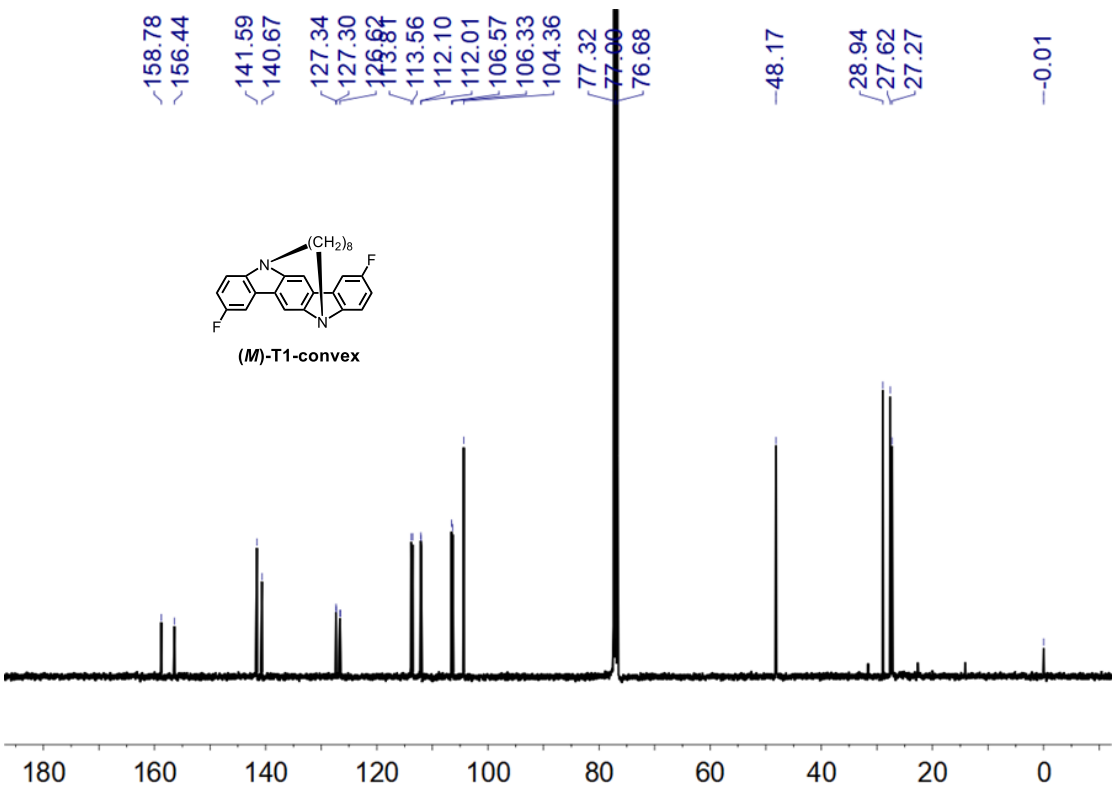


Fig. S120. ^{13}C NMR spectrum for **(*M*)-T1-convex** ($CDCl_3$, 298 K)

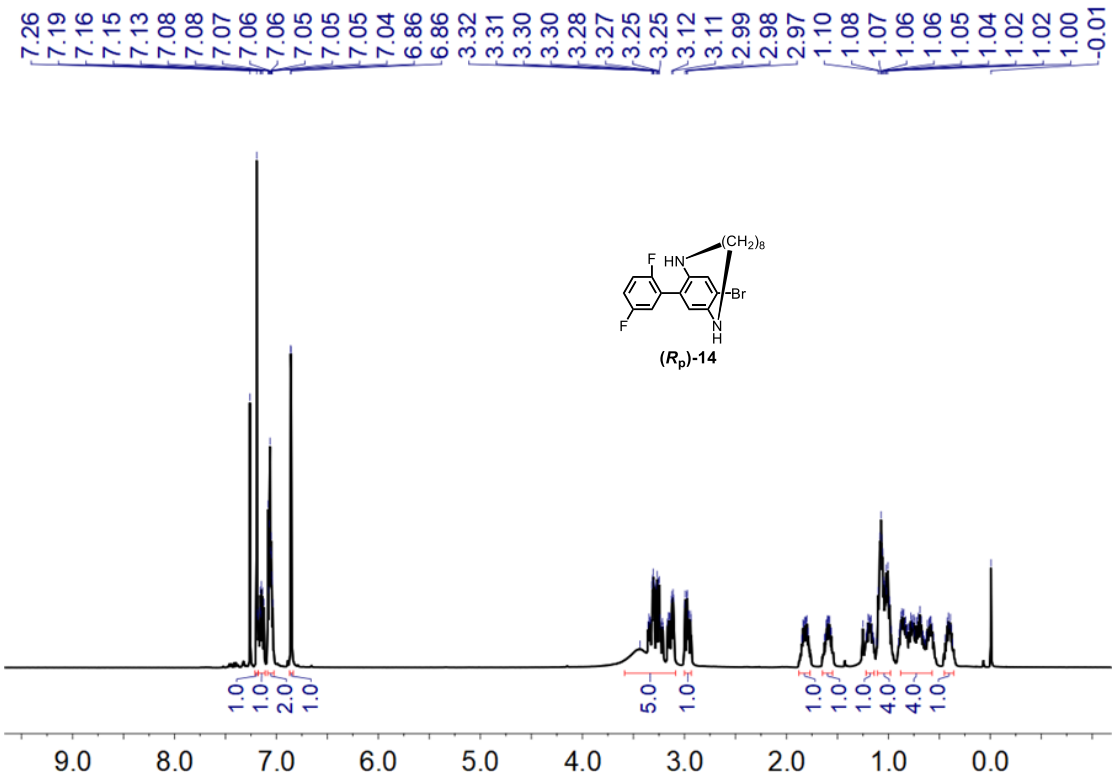


Fig. S121. ^{1}H NMR spectrum for **(R_p)-14** ($CDCl_3$, 298 K)

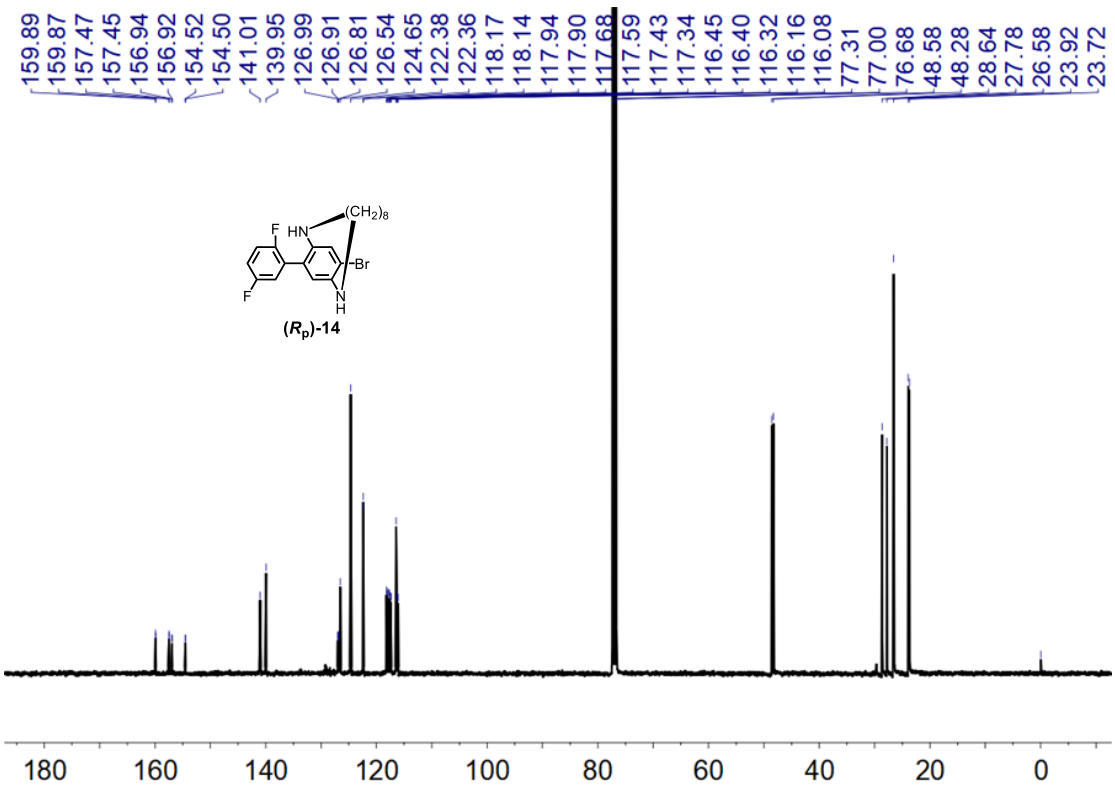


Fig. S122. ^{13}C NMR spectrum for **(R_p)-14** ($CDCl_3$, 298 K)

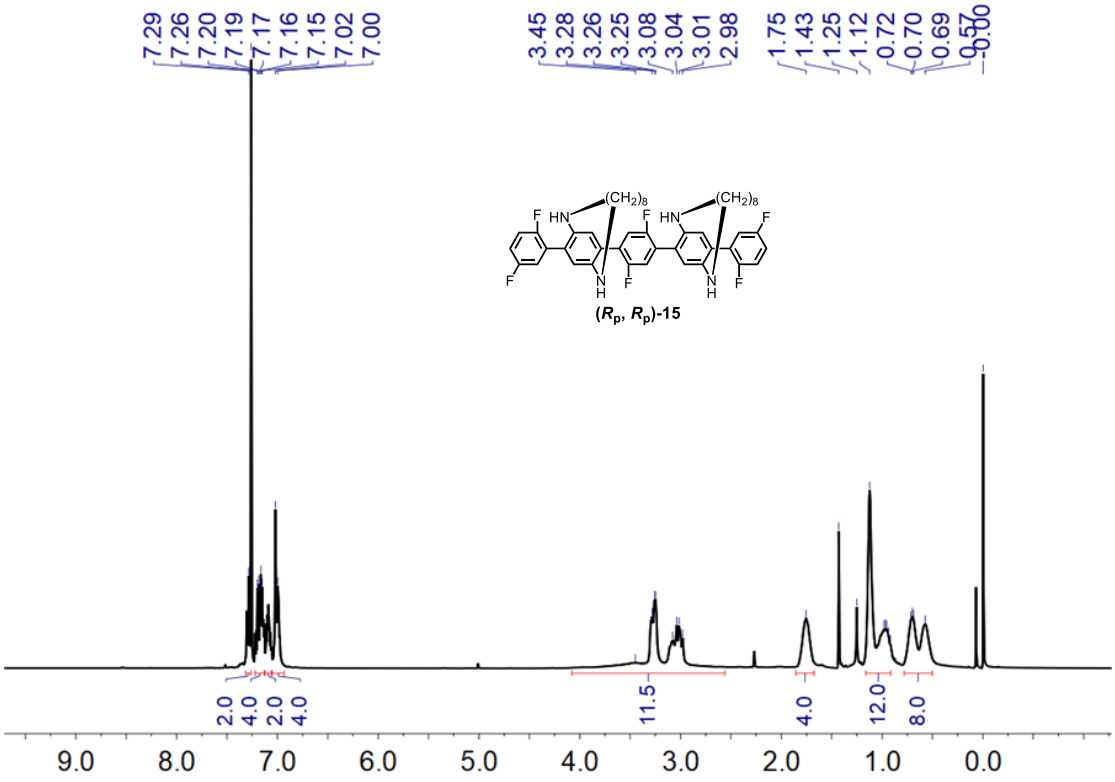


Fig. S123. ^{1}H NMR spectrum for **(R_p, R_p)-15** ($CDCl_3$, 298 K)

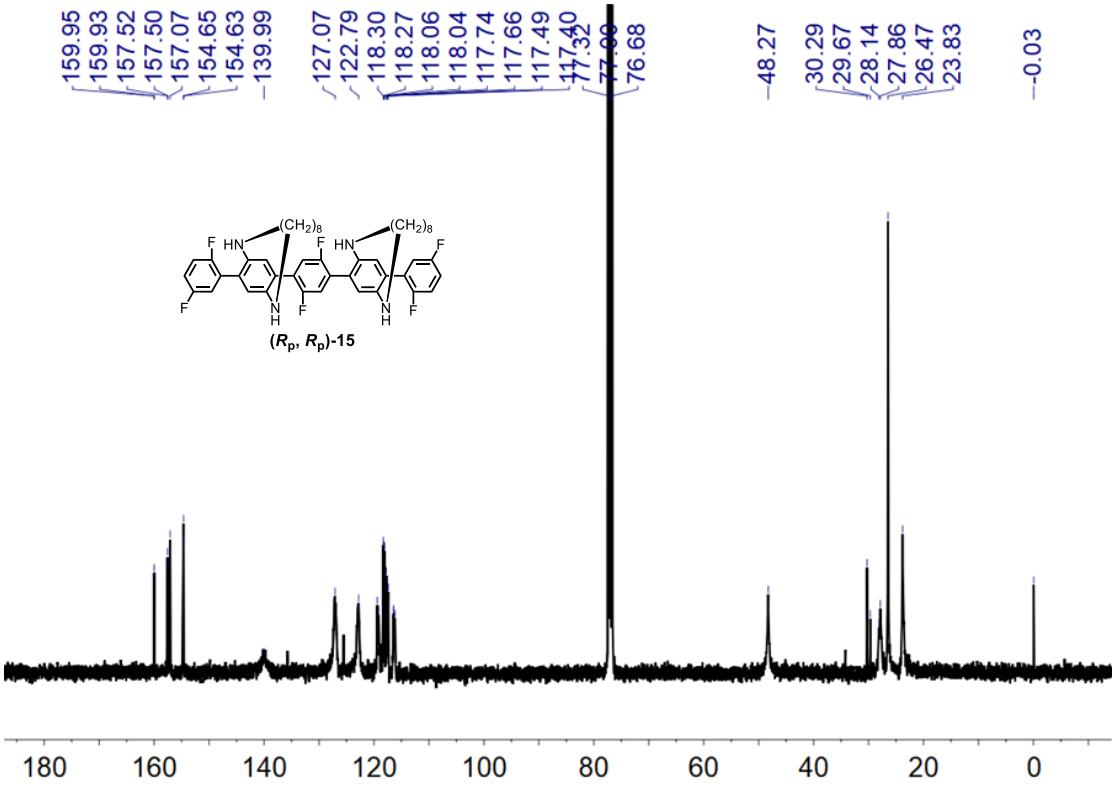


Fig. S124. ^{13}C NMR spectrum for **(R_p, R_p)-15** ($CDCl_3$, 298 K)

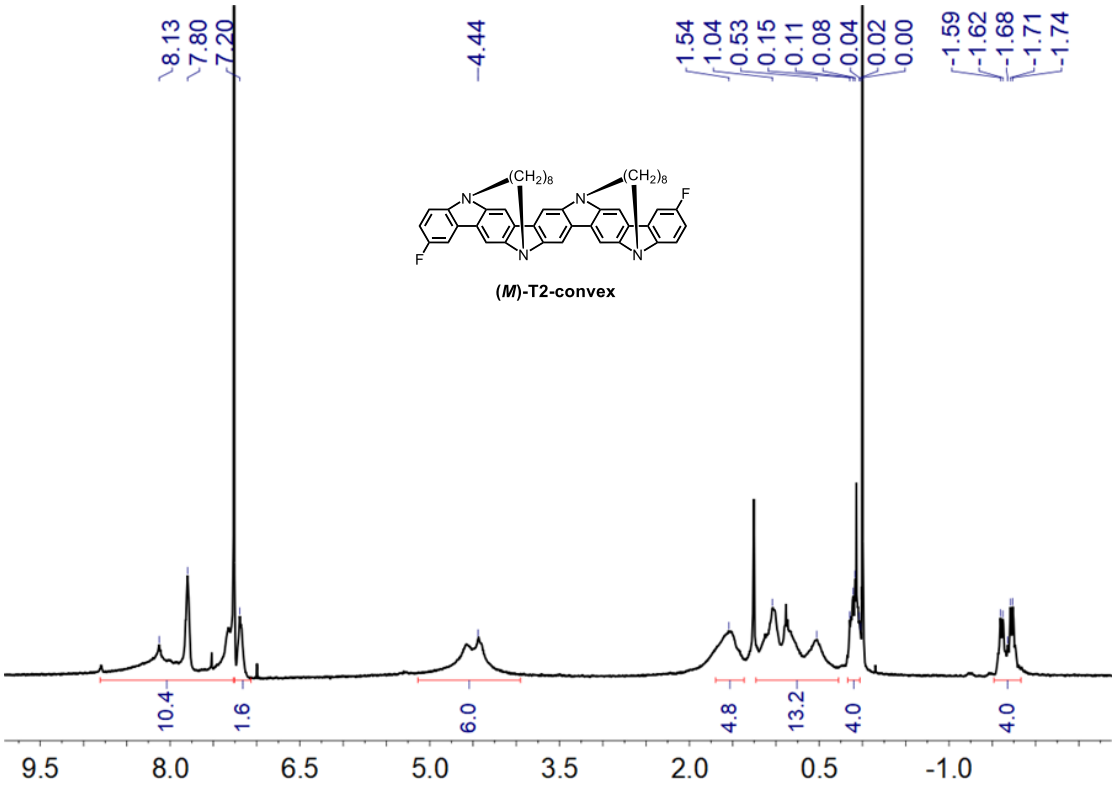


Fig. S125. ^{1}H NMR spectrum for **(*M*)-T2-convex** ($CDCl_3$, 298 K)

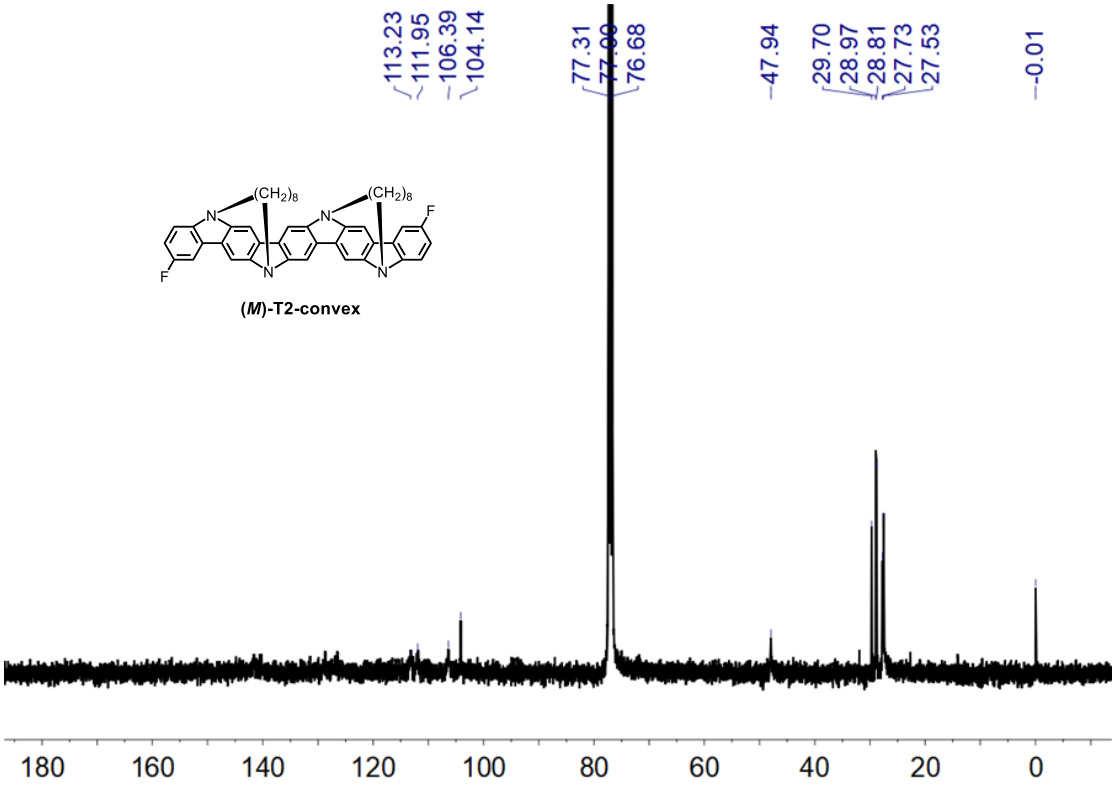


Fig. S126. ^{13}C NMR spectrum for **(*M*)-T2-convex** ($CDCl_3$, 298 K)

5. 2D-NMR spectra for (*P*)-T1-^{t}Bu, (*P*)-T2-^{t}Bu, curved isomer of (*P*)-T2-^{t}Bu, (*P*)-T3-^{t}Bu, (*P*)-T4-^{t}Bu, (*P*)-T5-^{t}Bu and (*P*)-T1-convex

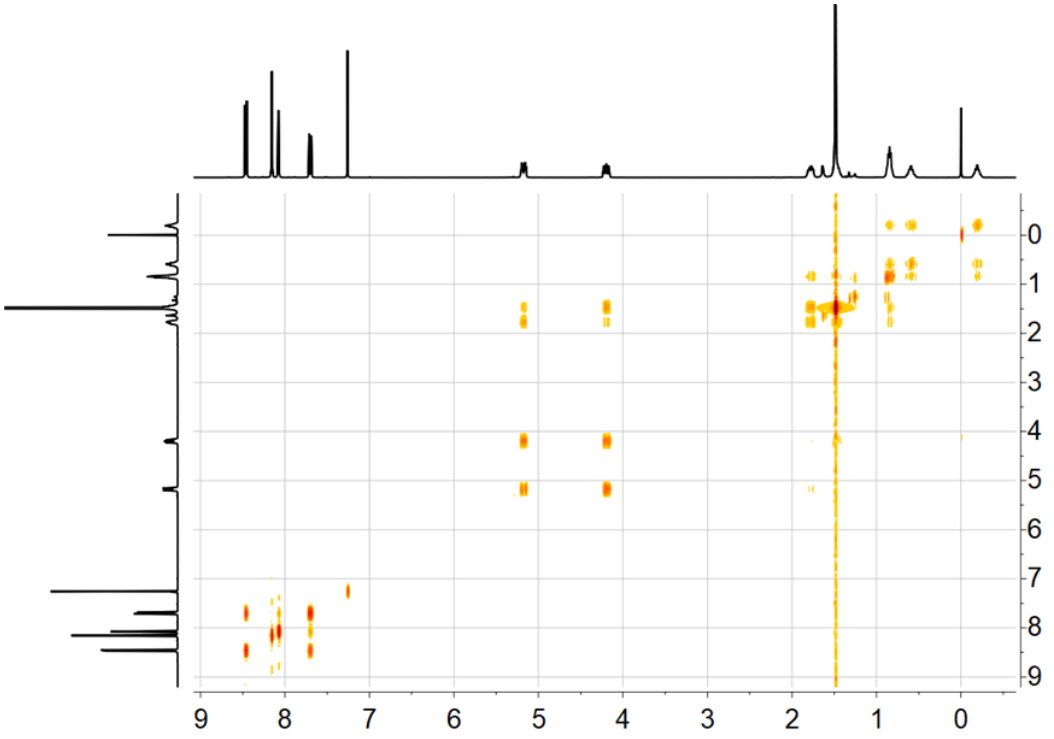


Fig. S127. COSY spectrum for **(*P*)-T1-^{t}Bu** ($CDCl_3$, 298 K)

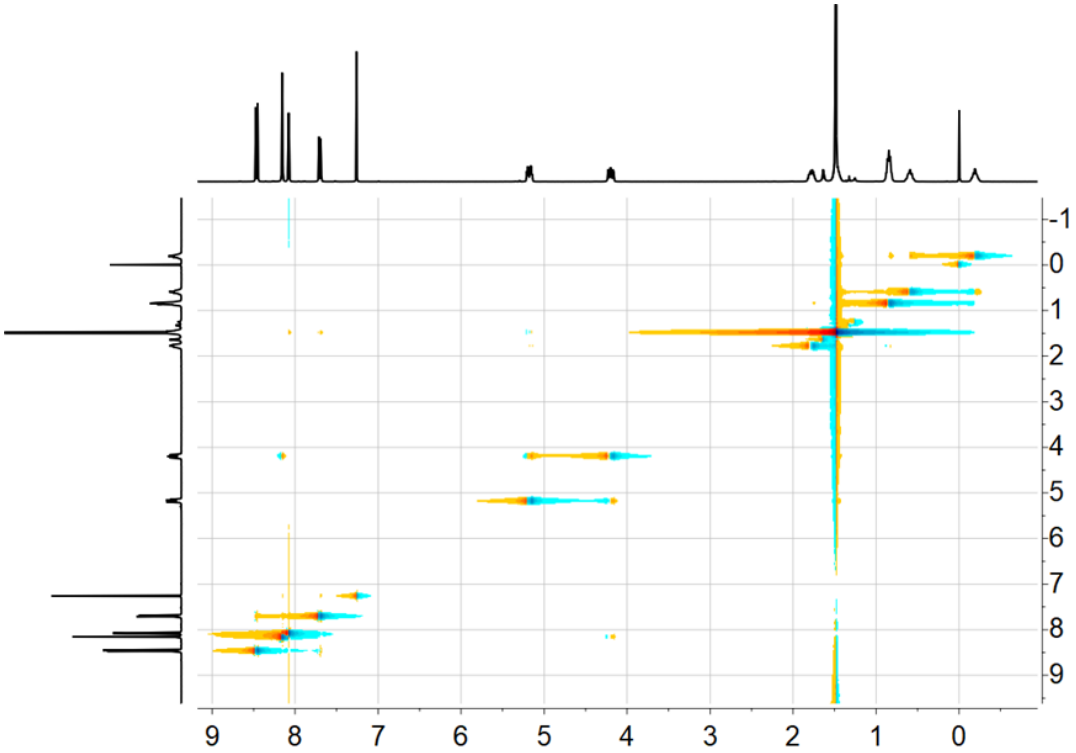


Fig. S128. NOESY spectrum for **(*P*)-T1-^{t}Bu** ($CDCl_3$, 298 K)

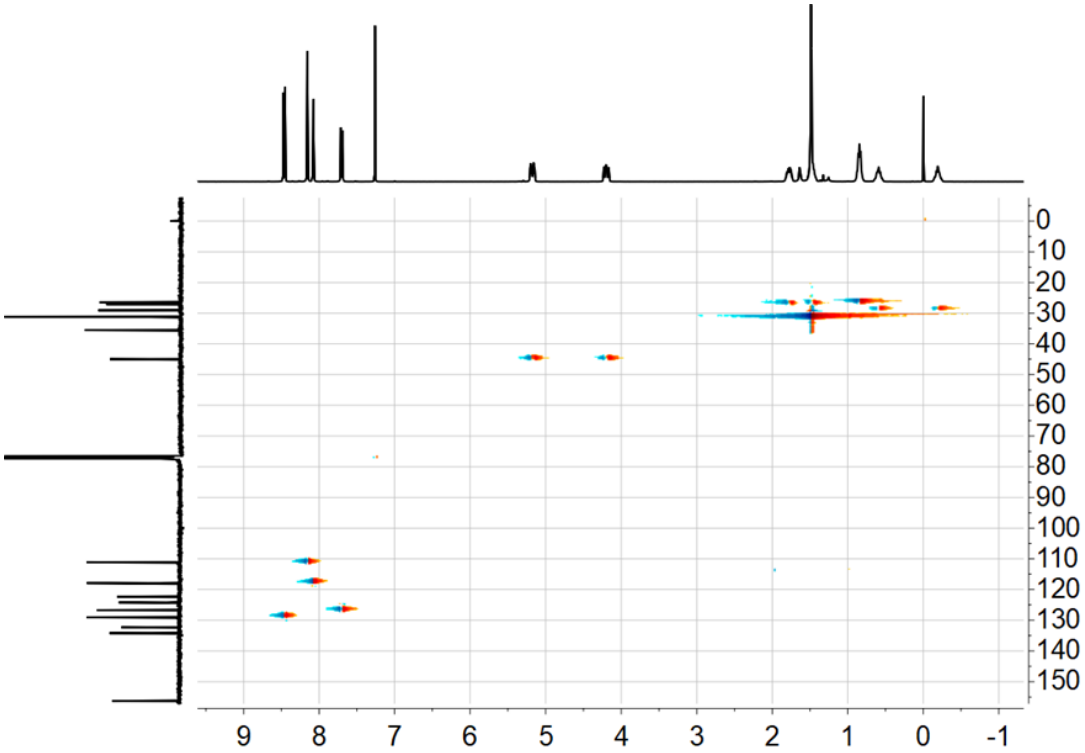


Fig. S129. HSQC spectrum for **(*P*)-T1-^{t}Bu** ($CDCl_3$, 298 K)

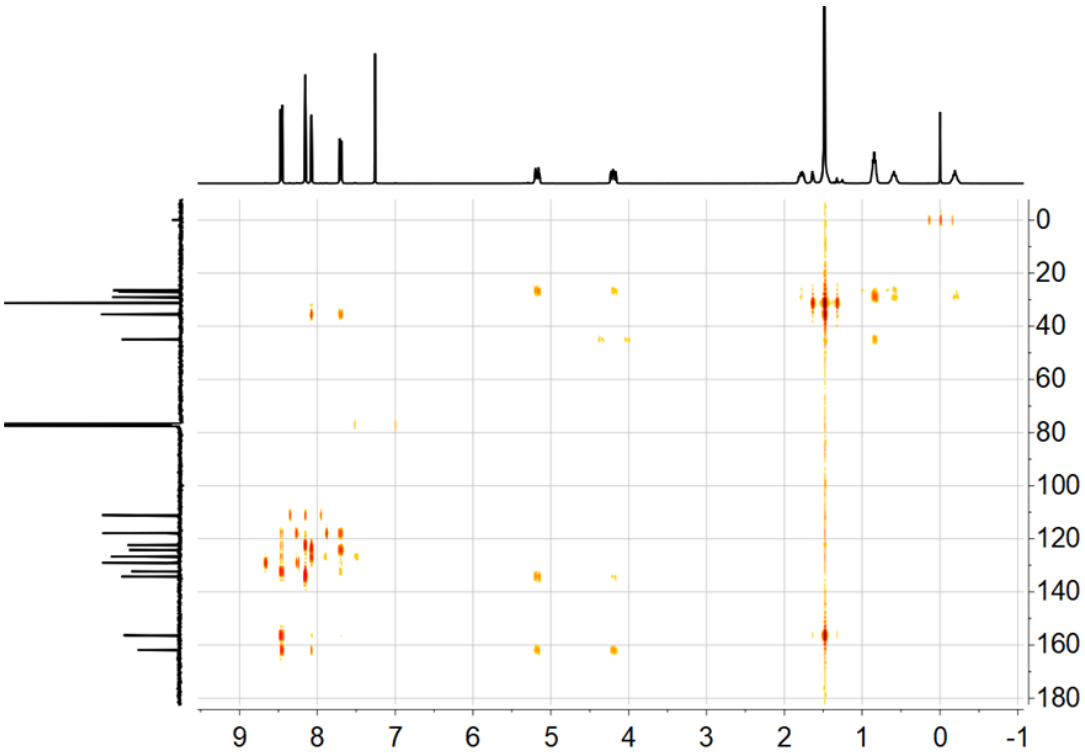


Fig. S130. HMBC spectrum for **(*P*)-T1-^{t}Bu** ($CDCl_3$, 298 K)

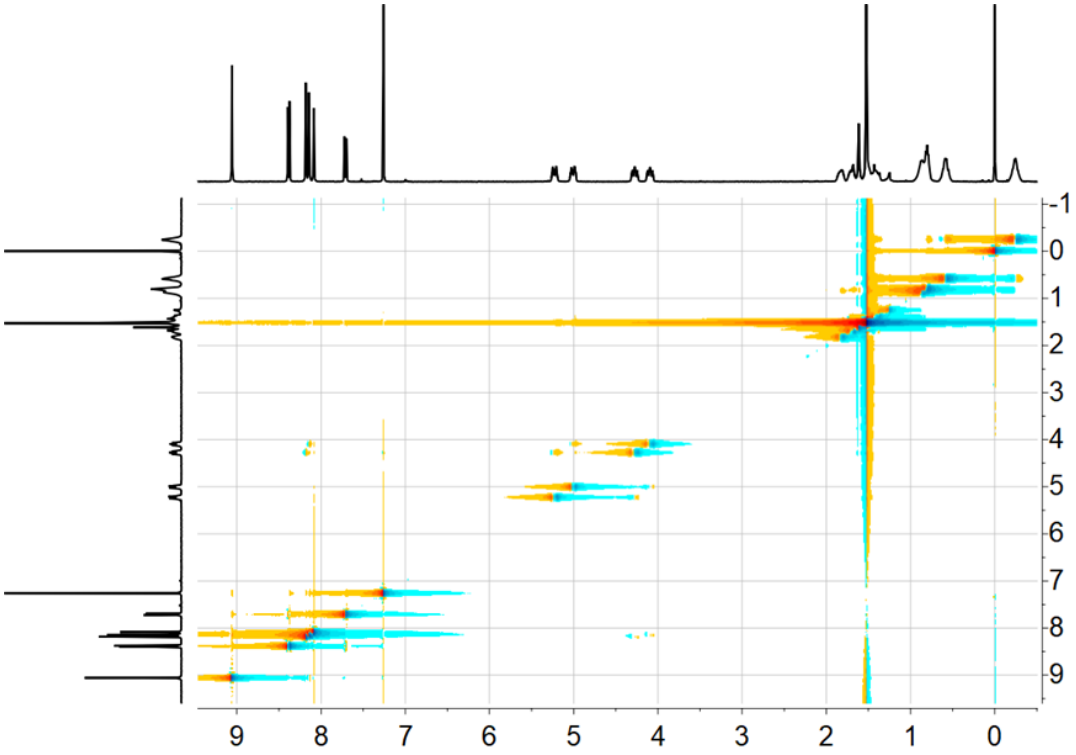


Fig. S131. NOESY spectrum for **(*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

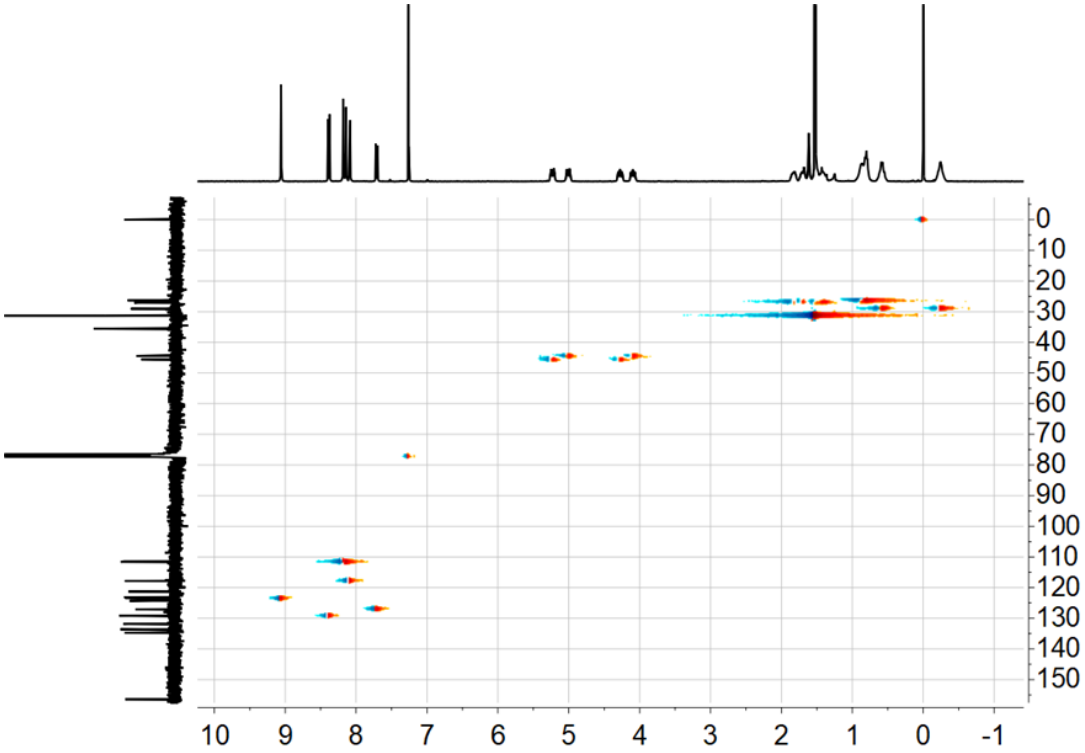


Fig. S132. HSQC spectrum for **(*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

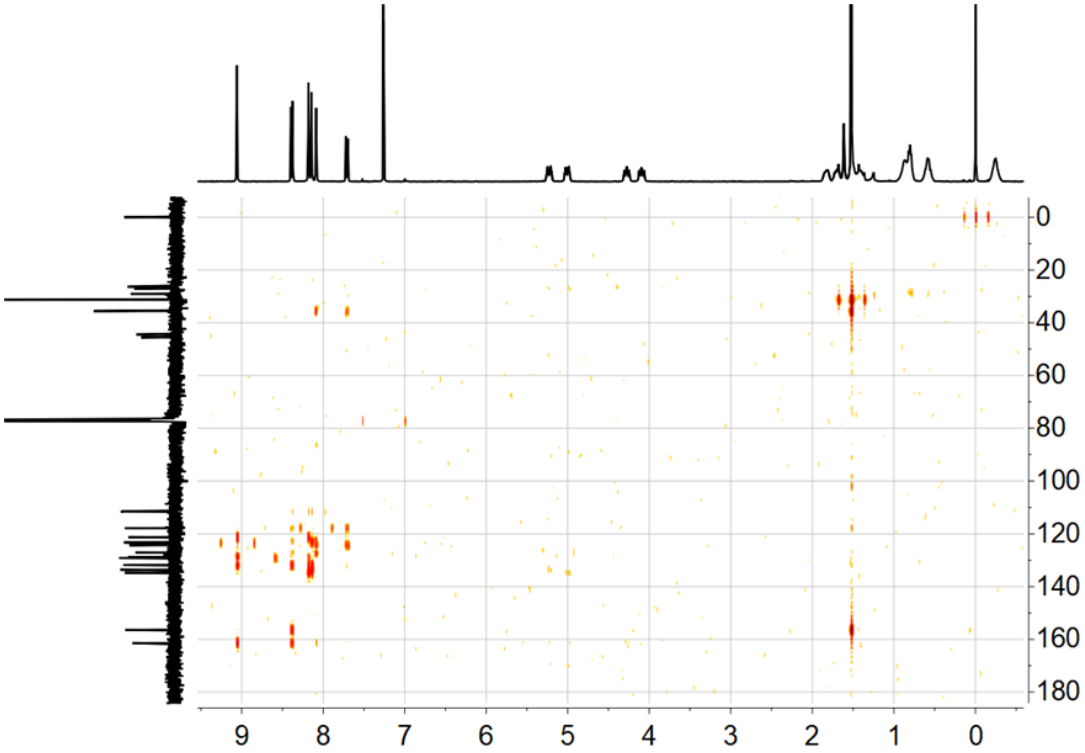


Fig. S133. HMBC spectrum for **(*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

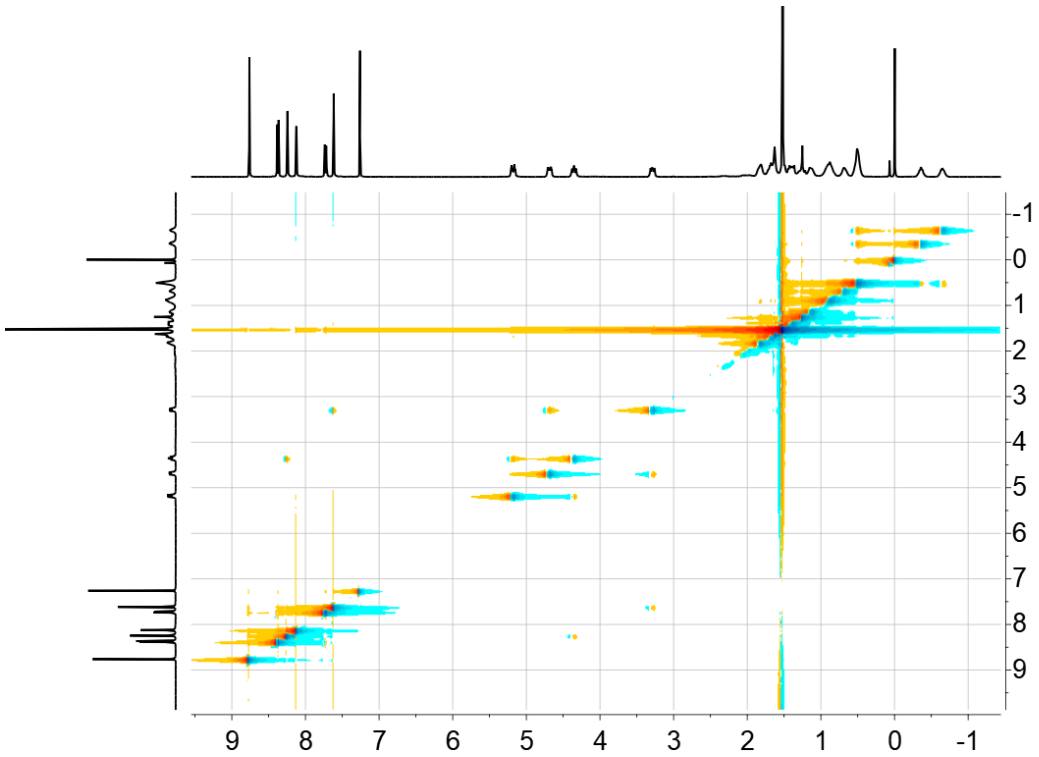


Fig. S134. NOESY spectrum for the **curved isomer of (*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

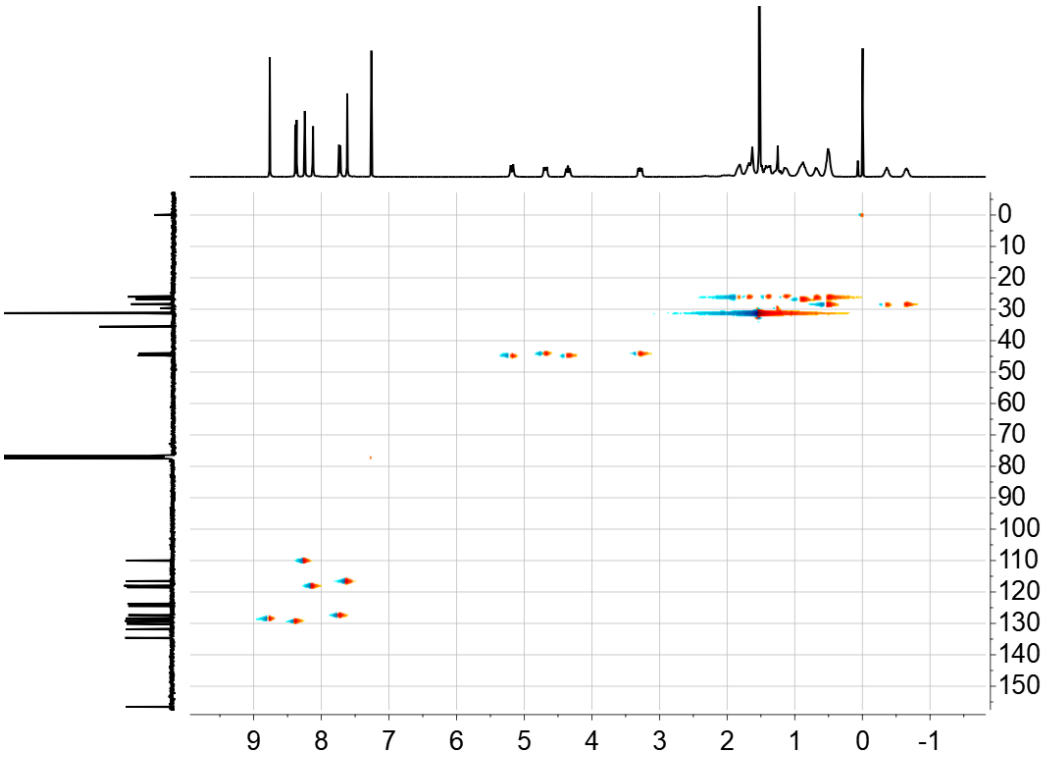


Fig. S135. HSQC spectrum for **curved isomer of (*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

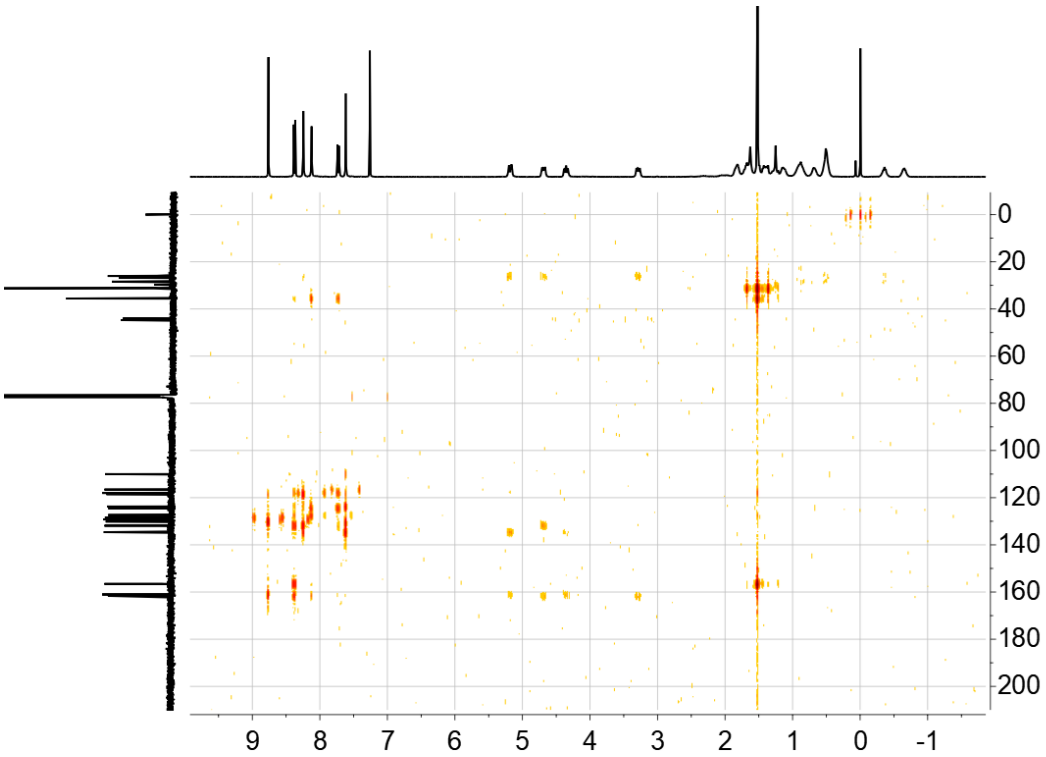


Fig. S136. HMBC spectrum for **curved isomer of (*P*)-T2-^{t}Bu** ($CDCl_3$, 298 K)

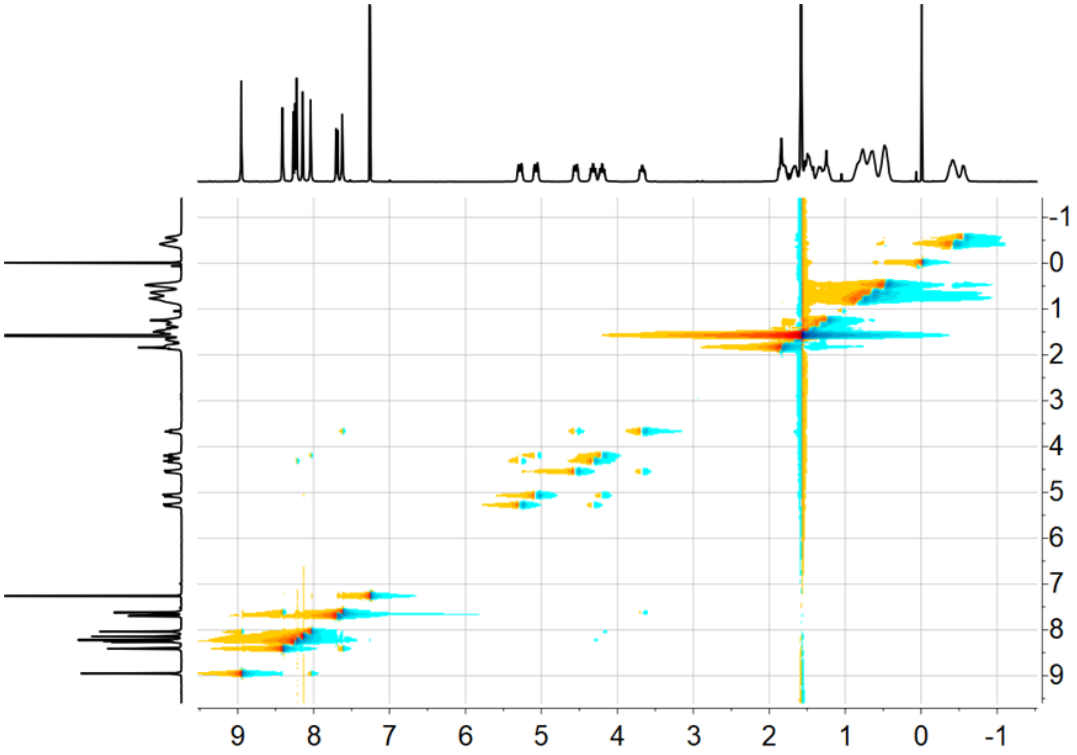


Fig. S137. NOESY spectrum for **(*P*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

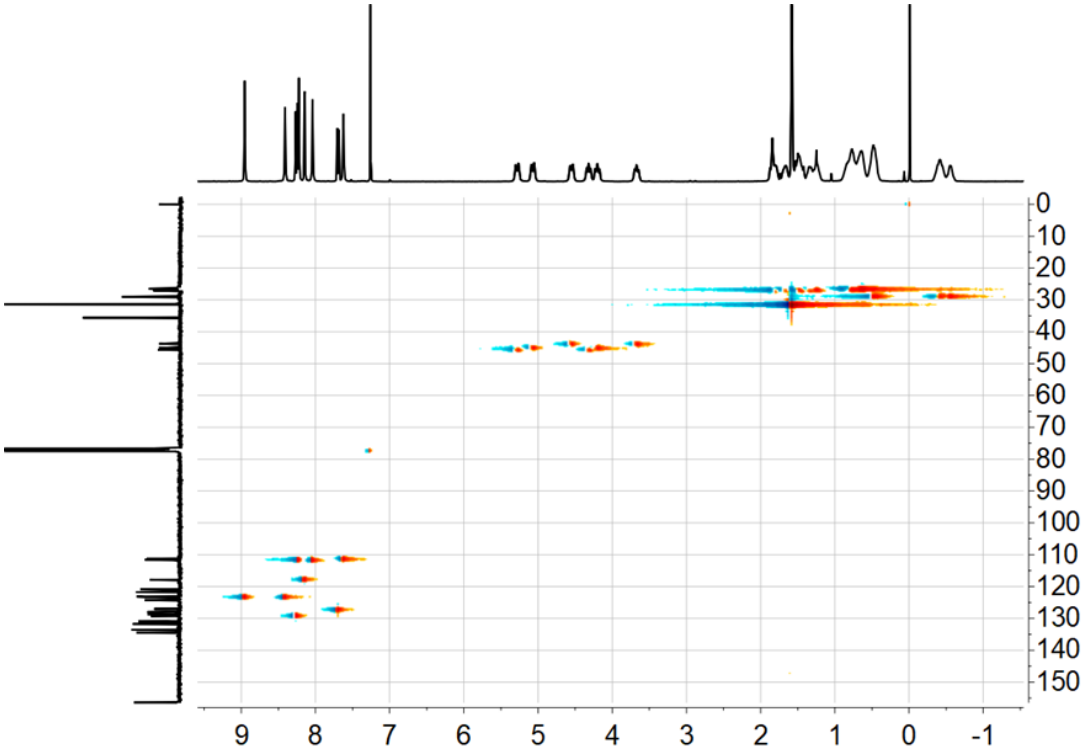


Fig. S138. HSQC spectrum for **(*P*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

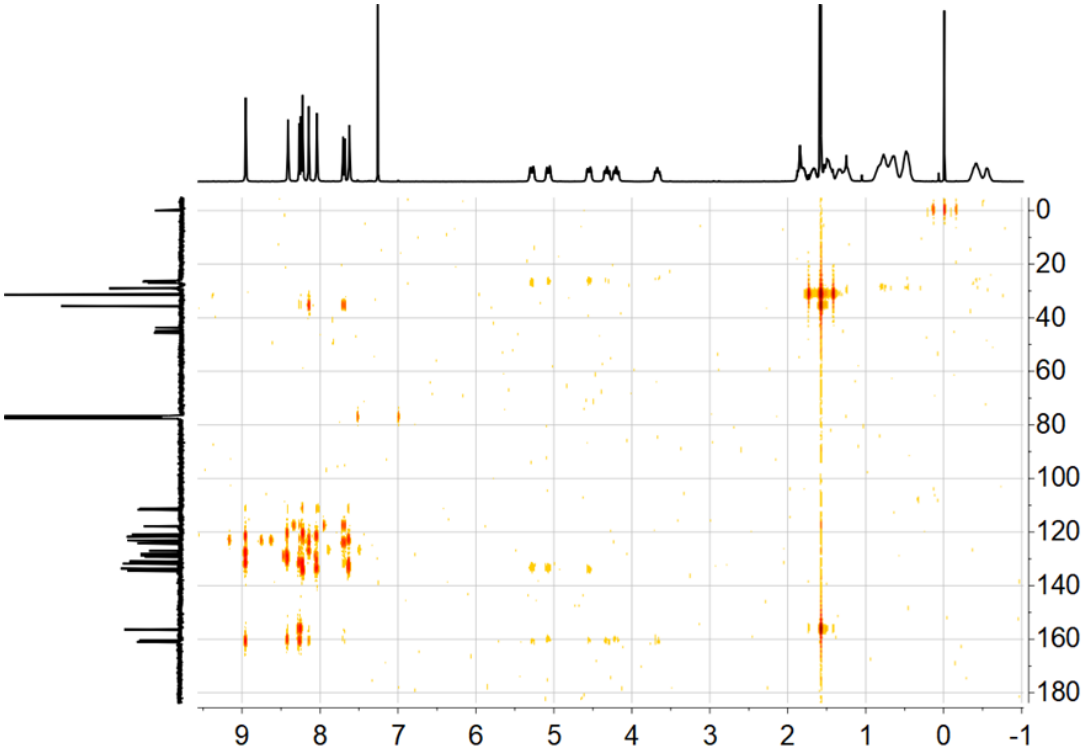


Fig. S139. HMBC spectrum for **(*P*)-T3-^{t}Bu** ($CDCl_3$, 298 K)

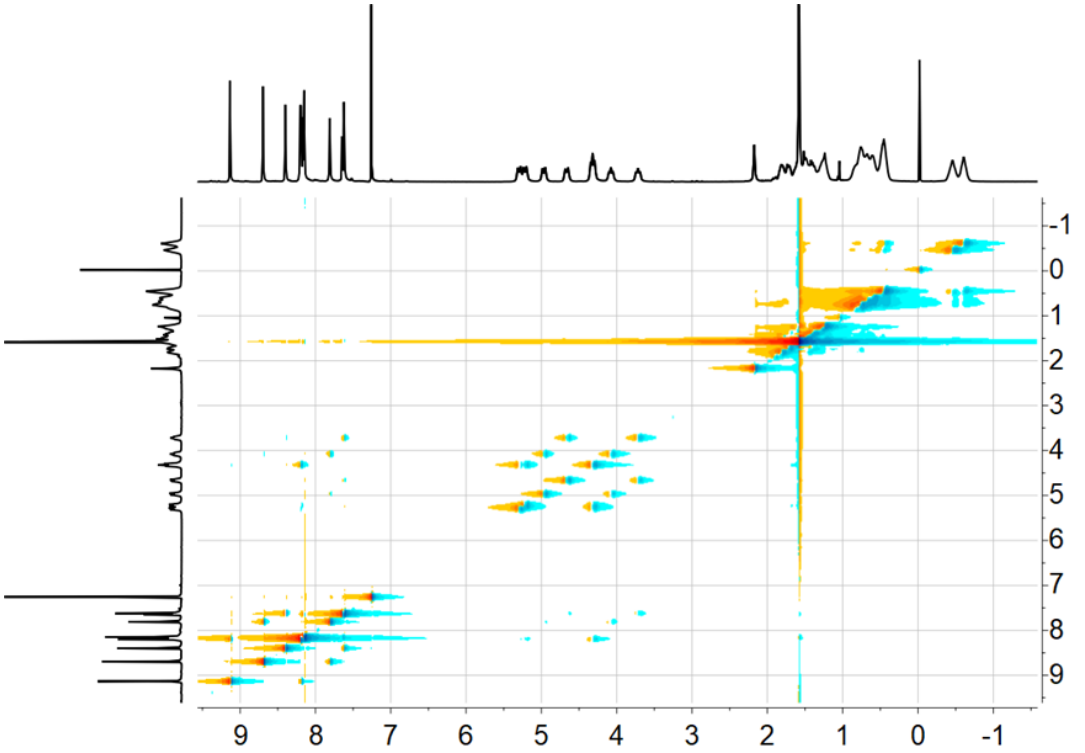


Fig. S140. NOESY spectrum for **(*P*)-T4-^{t}Bu** ($CDCl_3$, 298 K)

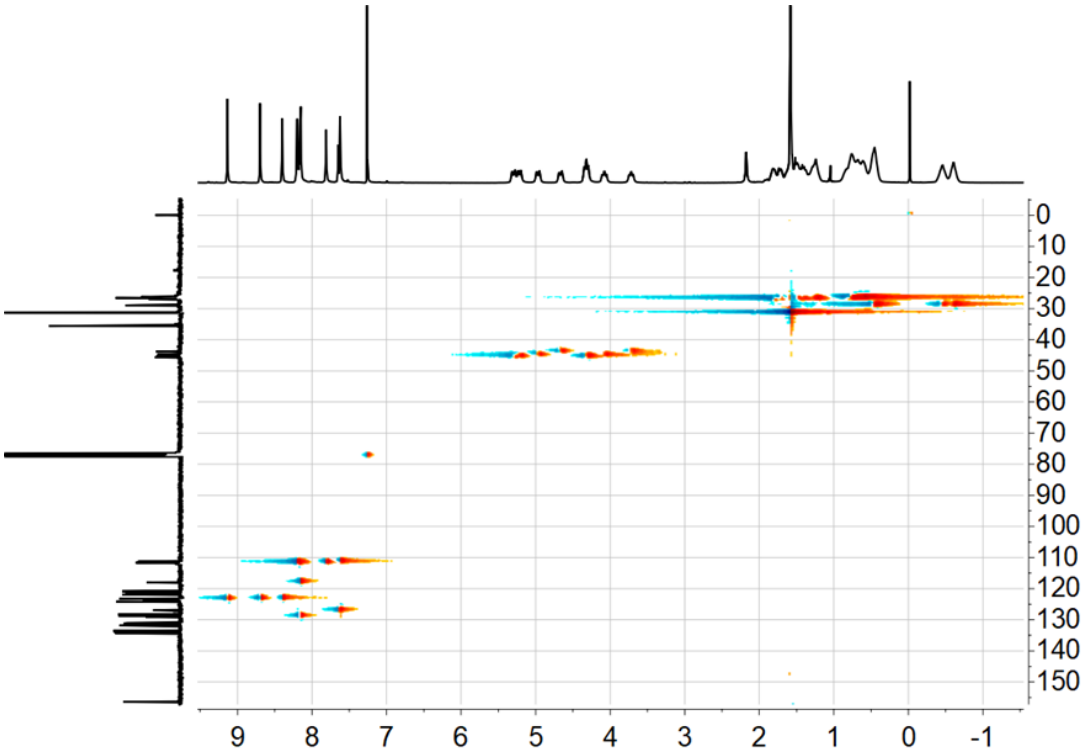


Fig. S141. HSQC spectrum for **(*P*)-T4-^{t}Bu** ($CDCl_3$, 298 K)

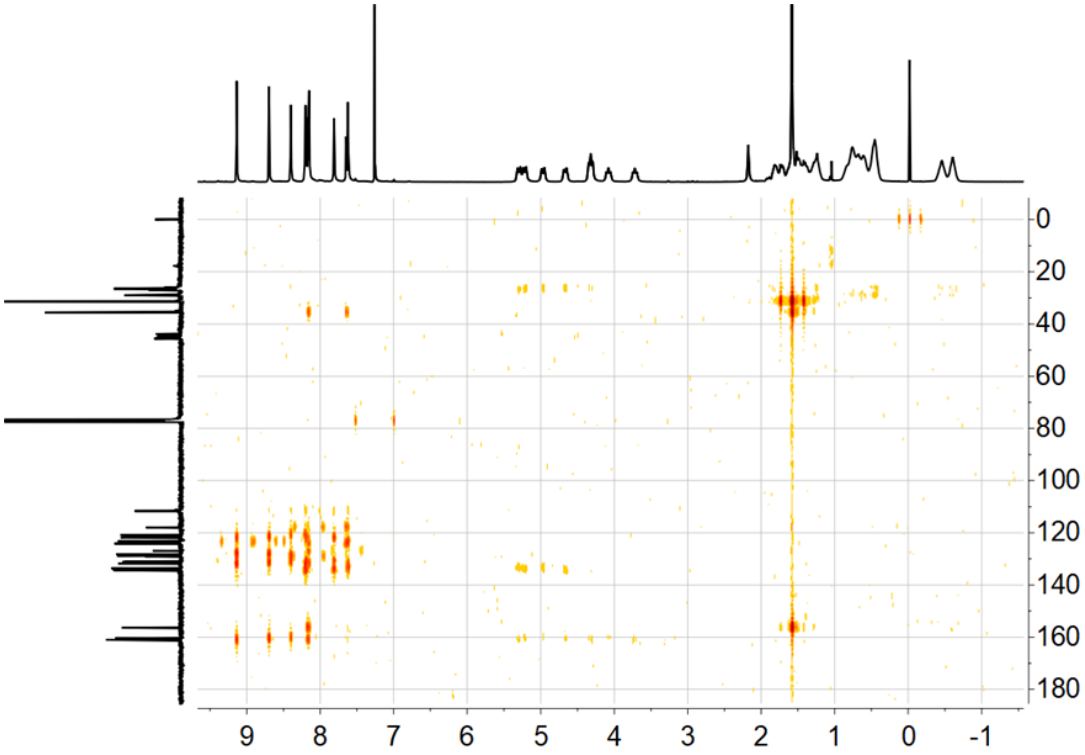


Fig. S142. HMBC spectrum for **(*P*)-T4-^{t}Bu** ($CDCl_3$, 298 K)

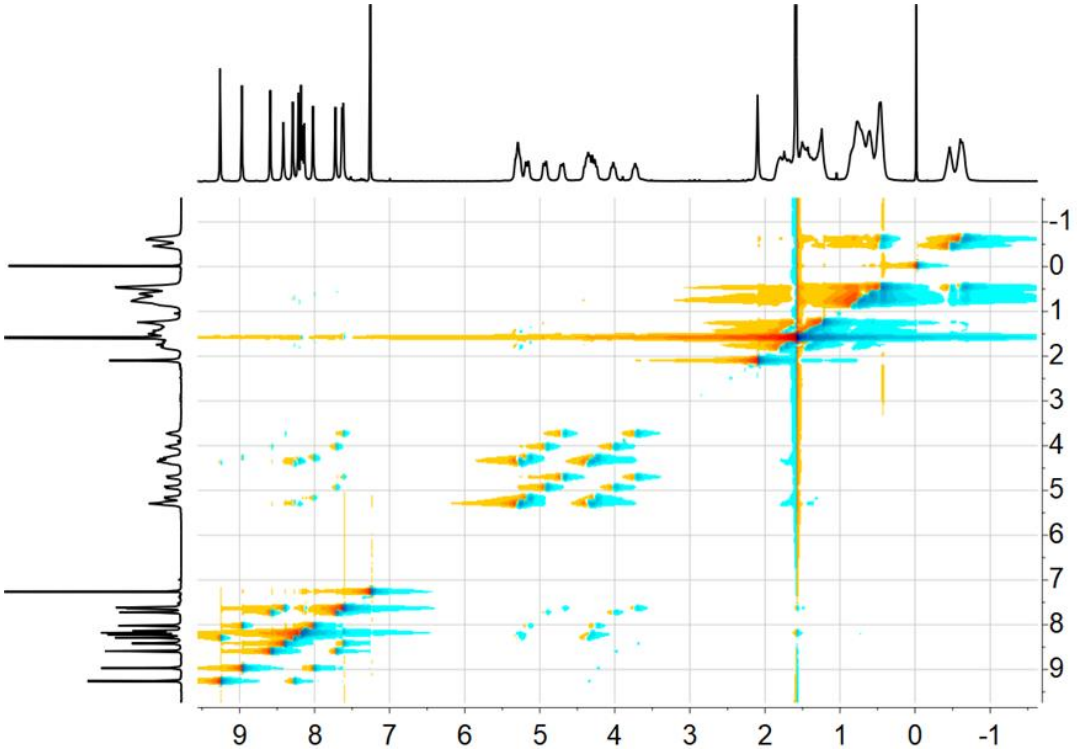


Fig. S143. NOESY spectrum for **(*P*)-T5-^{t}Bu** ($CDCl_3$, 298 K)

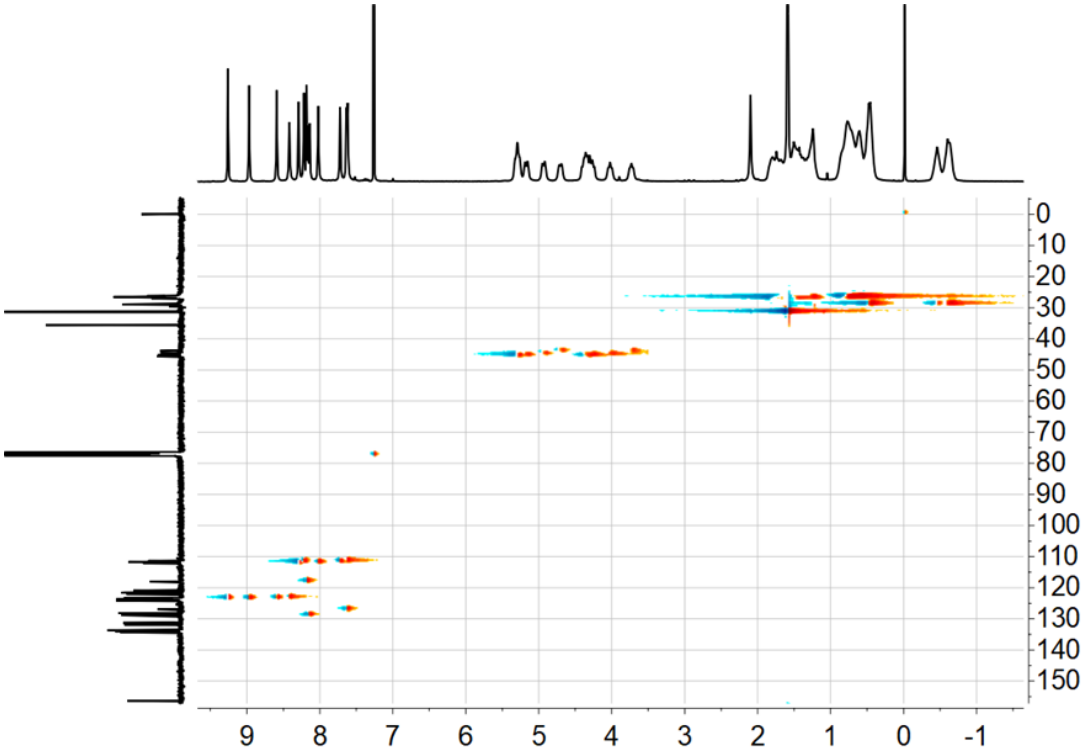


Fig. S144. HSQC spectrum for **(*P*)-T5-^{t}Bu** ($CDCl_3$, 298 K)

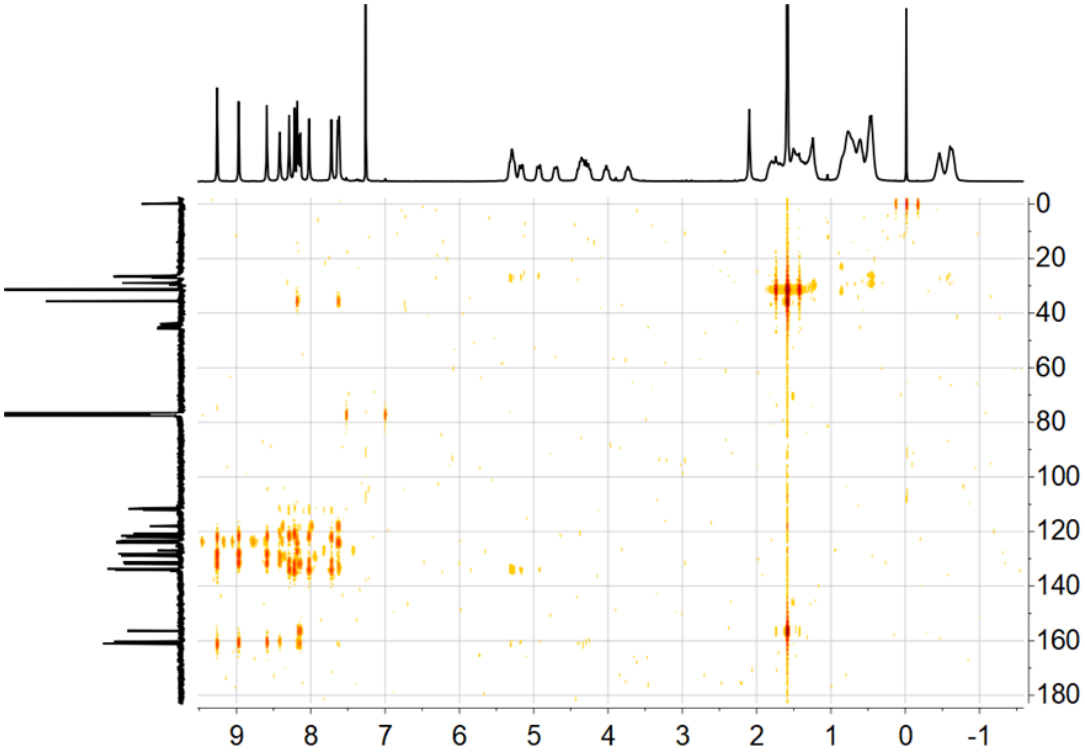


Fig. S145. HMBC spectrum for **(*P*)-T5-^{t}Bu** ($CDCl_3$, 298 K)

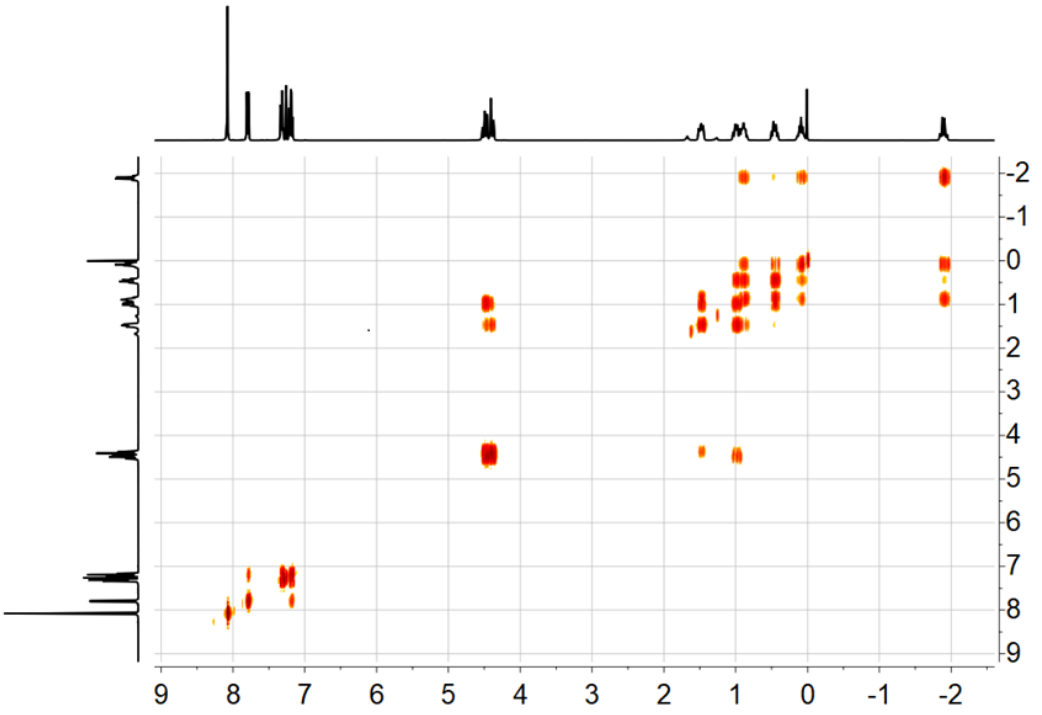


Fig. S146. COSY spectrum for **(*P*)-T1-convex** ($CDCl_3$, 298 K)

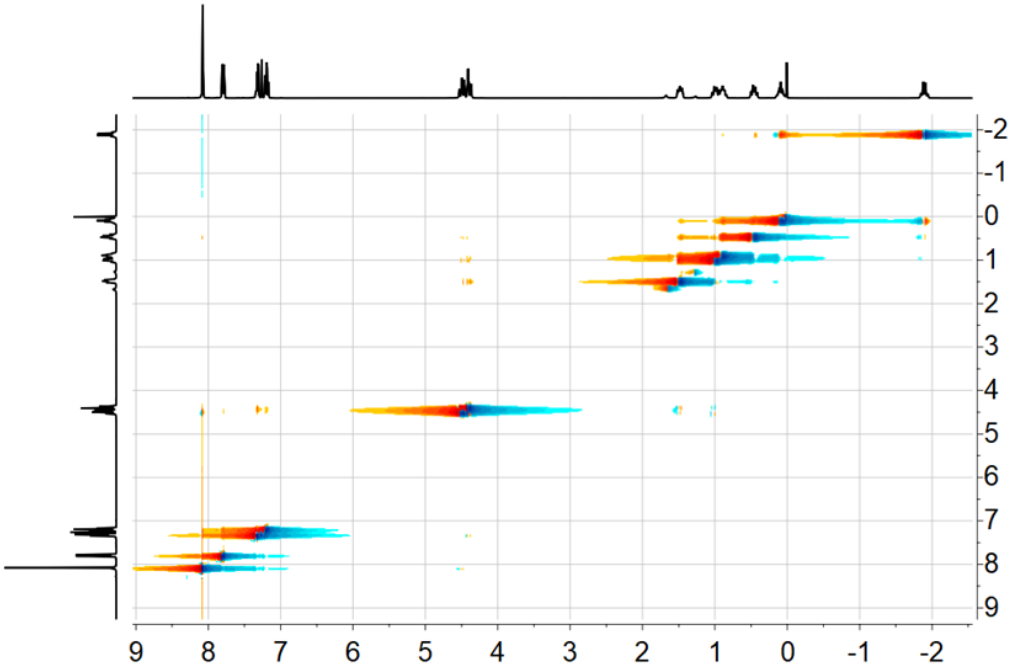


Fig. S147. NOESY spectrum for **(*P*)-T1-convex** ($CDCl_3$, 298 K)

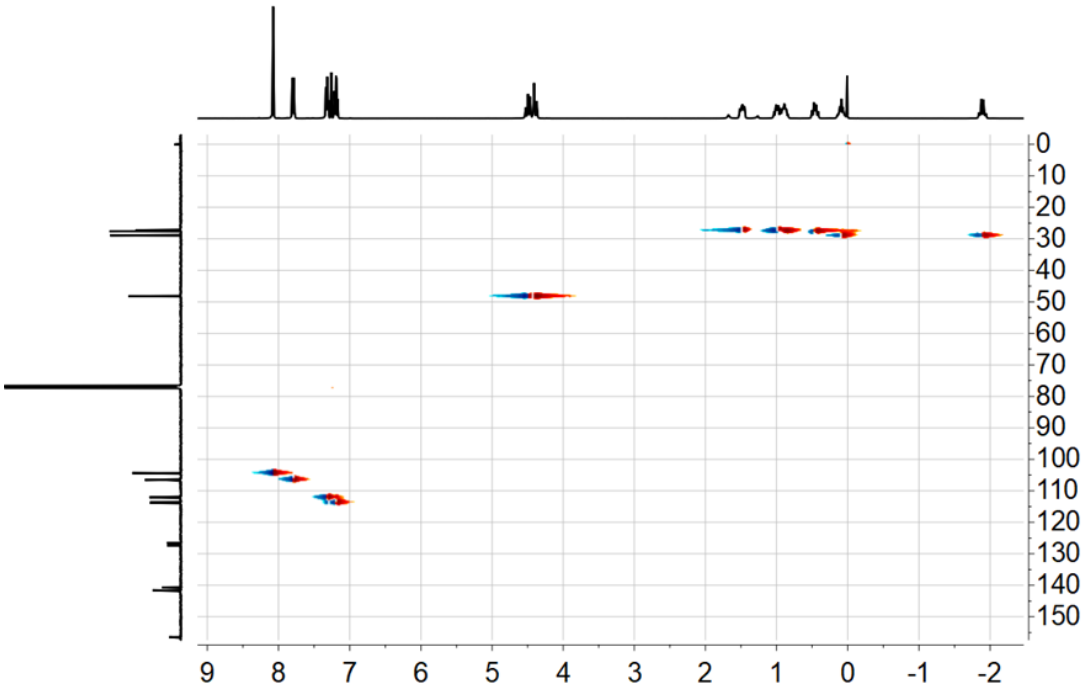


Fig. S148. HSQC spectrum for **(*P*)-T1-convex** ($CDCl_3$, 298 K)

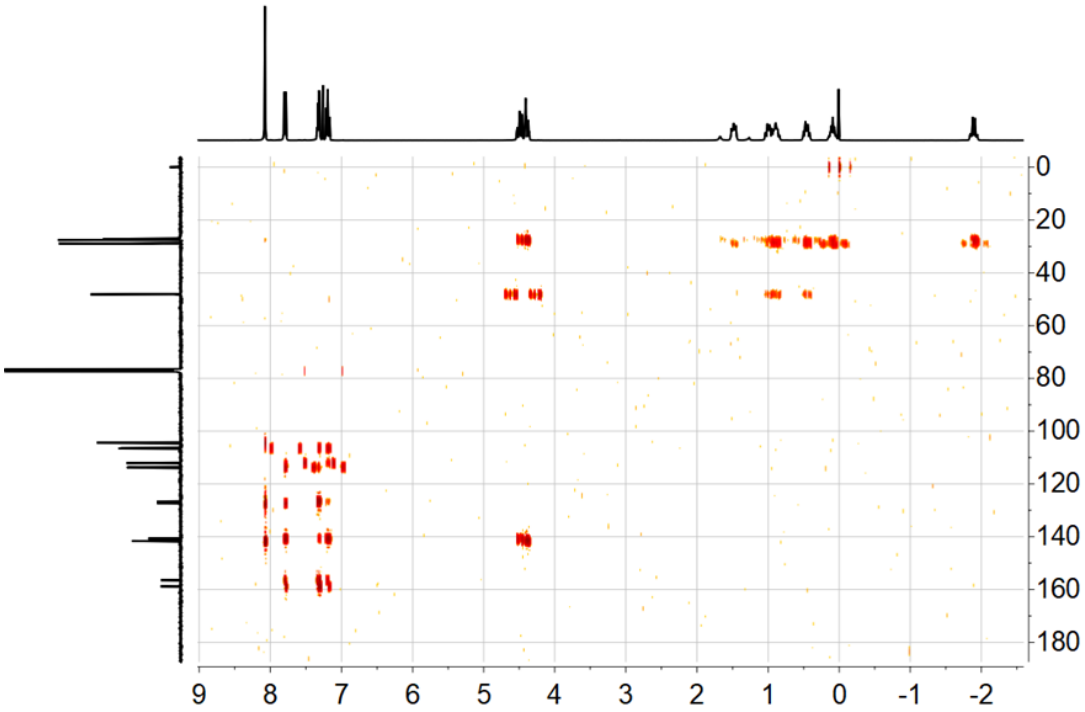


Fig. S149. HMBC spectrum for **(*P*)-T1-convex** ($CDCl_3$, 298 K)

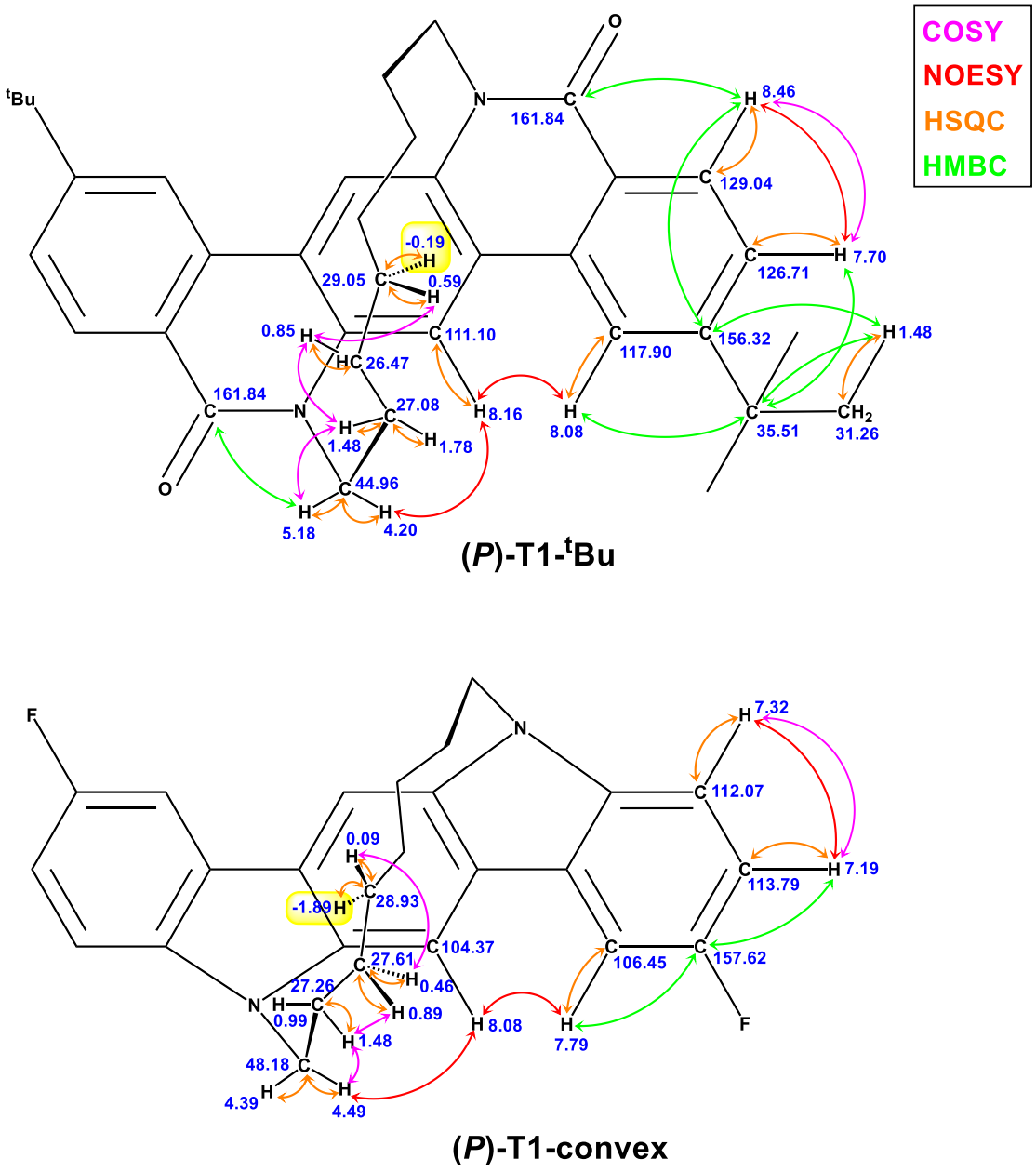


Fig. S150. A summary of the key correlations and assigned chemical shifts for **(*P*)-T1-^{t}Bu** and **(*P*)-T1-convex**

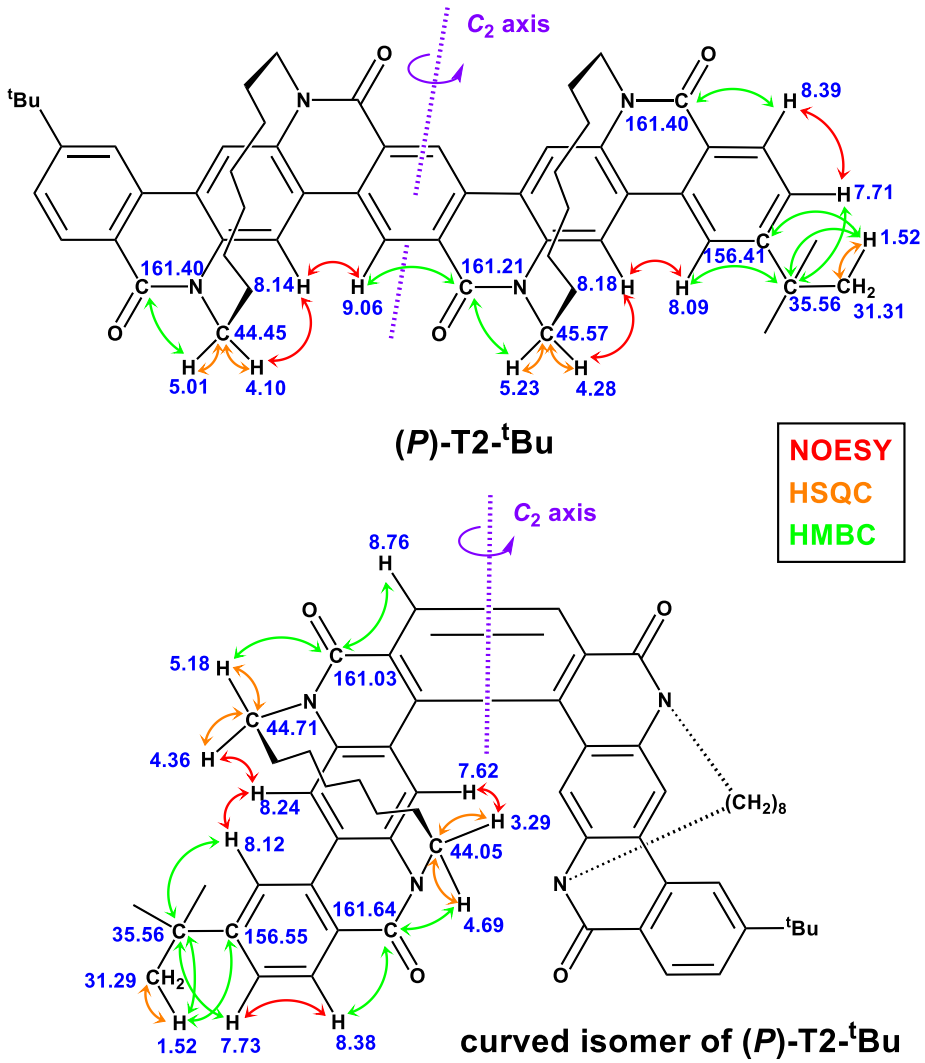
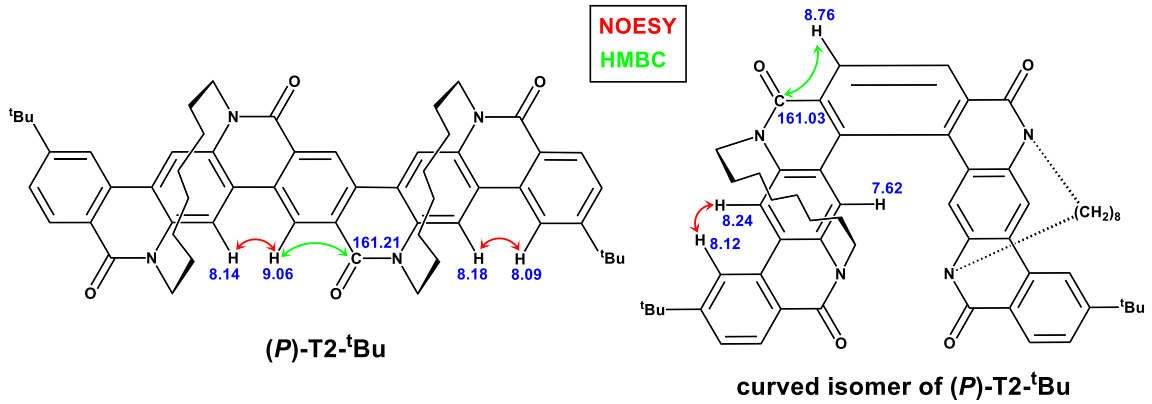


Fig. S151. A summary of the key correlations and assigned chemical shifts for **(*P*)-T2-^{t}Bu** and the **curved isomer of (*P*)-T2-^{t}Bu**

The major difference between **(*P*)-T2-^{t}Bu** and the curved isomer is that there are two sets of NOESY correlation (8.14↔9.06, 8.18↔8.09) found for the aromatic protons at the bay region of **(*P*)-T2-^{t}Bu**, while there is only one set of NOESY correlation (8.12↔8.24) found for the curved isomer. There is no correlation between the aromatic protons at 8.76 ppm and 7.62 ppm for the curved isomer, because these protons are spatially far away from each other. See below:



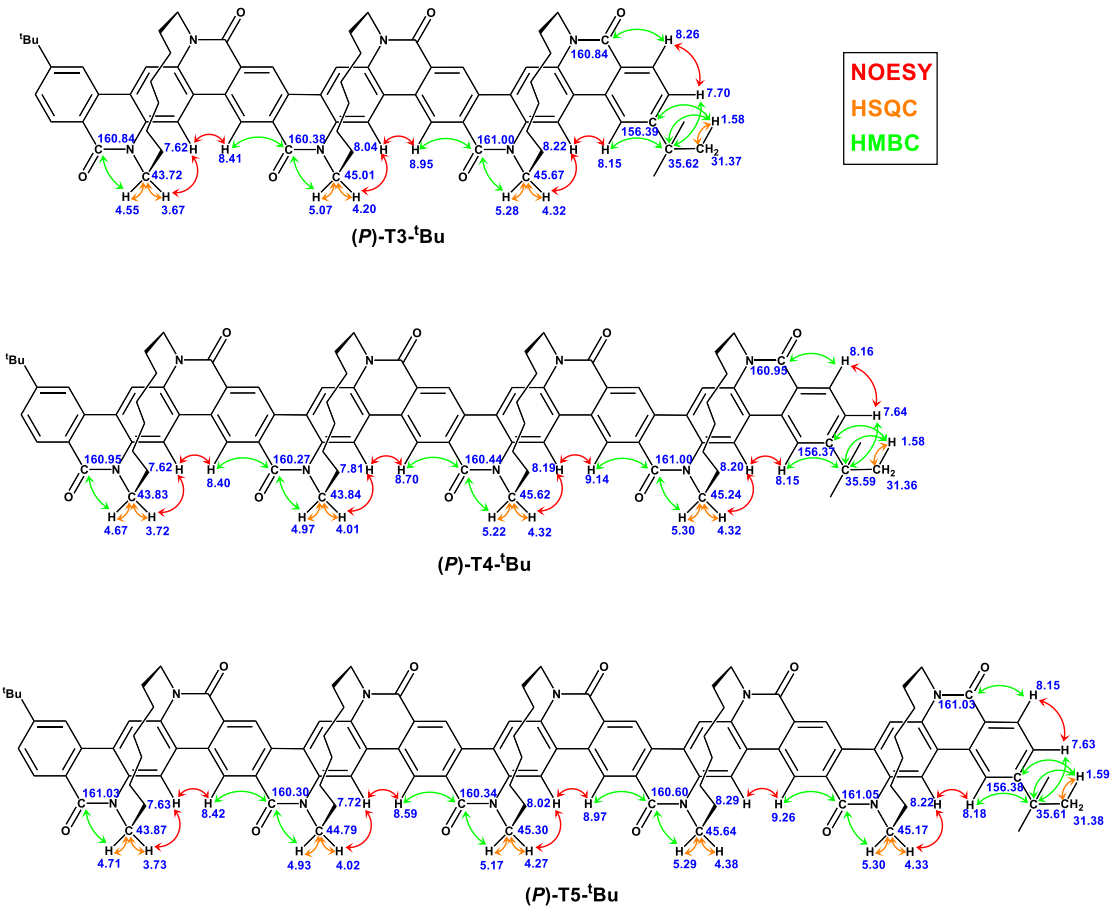


Fig. S152. A summary of the key correlations and assigned chemical shifts for **(*P*)-T3-^{t}Bu**, **(*P*)-T4-^{t}Bu** and **(*P*)-T5-^{t}Bu**

6. DFT-predicted chemical shifts and NICS values for (*P*)-T1-^{t}Bu and (*P*)-T1-convex

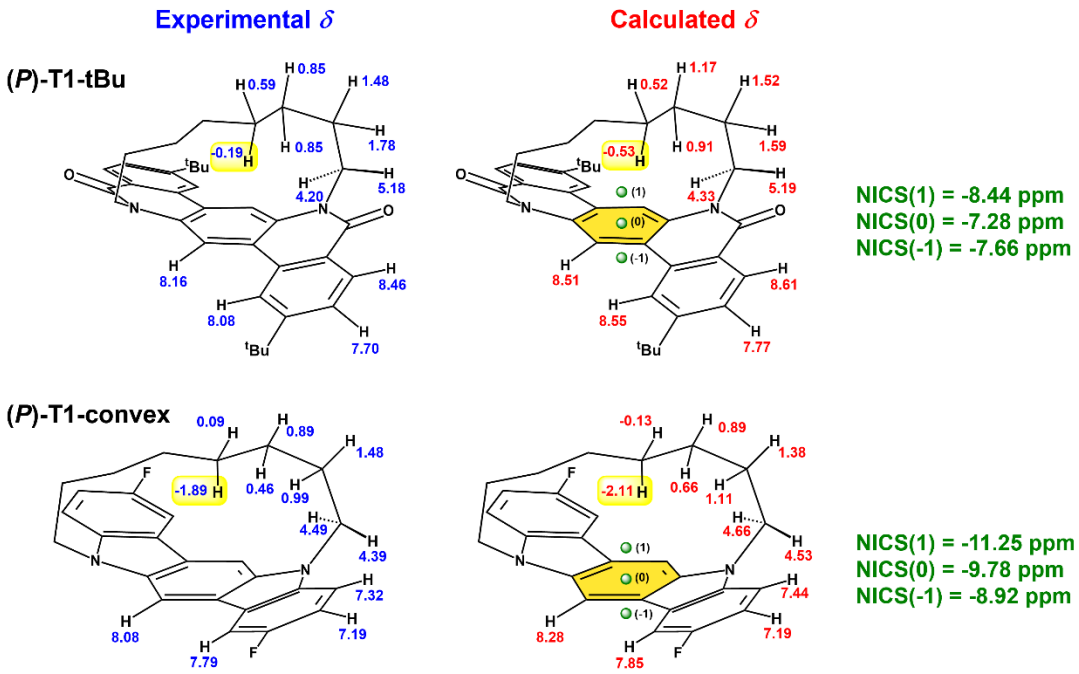
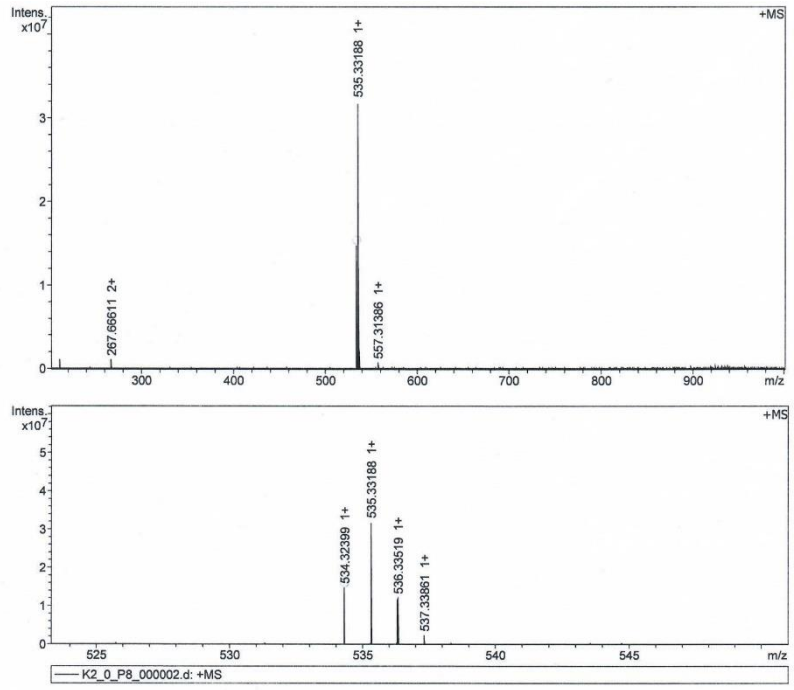


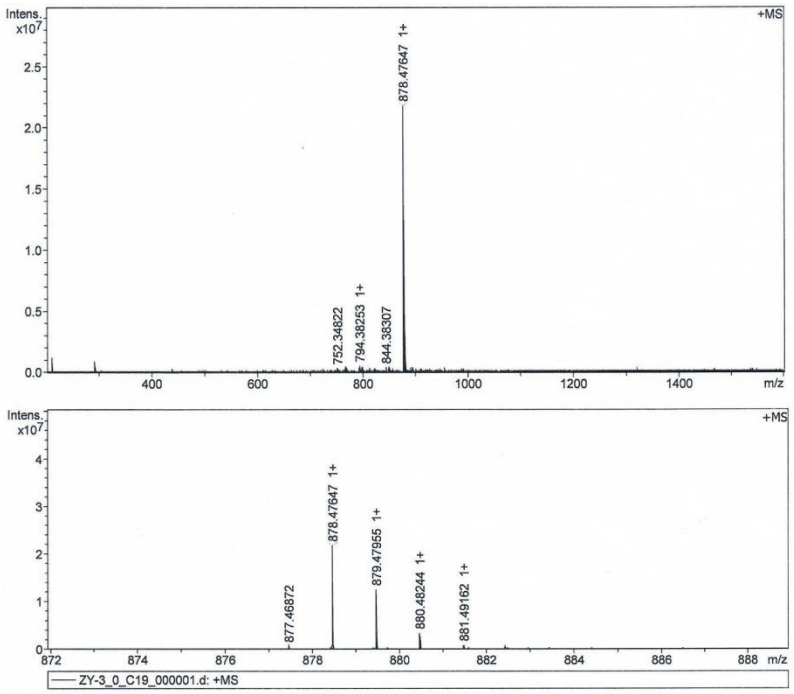
Fig. S153. DFT-predicted chemical shifts and NICS values for **(*P*)-T1-^{t}Bu** and **(*P*)-T1-convex**. Note: the molecular structures of **(*P*)-T1-^{t}Bu** and **(*P*)-T1-convex** were optimized at M06-2X(D3)/6-31G(d,p) level; NMR chemical shifts and NICS values were calculated at revTPSS/def2TZVPP level, with chloroform as the solvent and TMS as the reference.

7. HRMS spectra



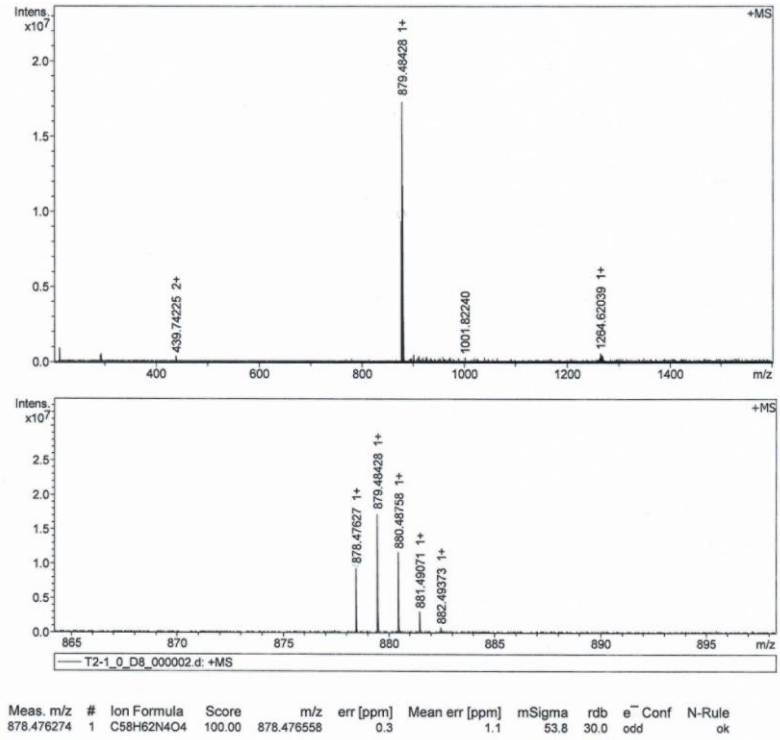
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
534.323993	1	C36H42N2O2	100.00	534.324080	-0.2	0.1	53.8	17.0	odd	ok

Fig. S154. MALDI-TOF HRMS spectrum for **(*P*)-T1-^{t}Bu**



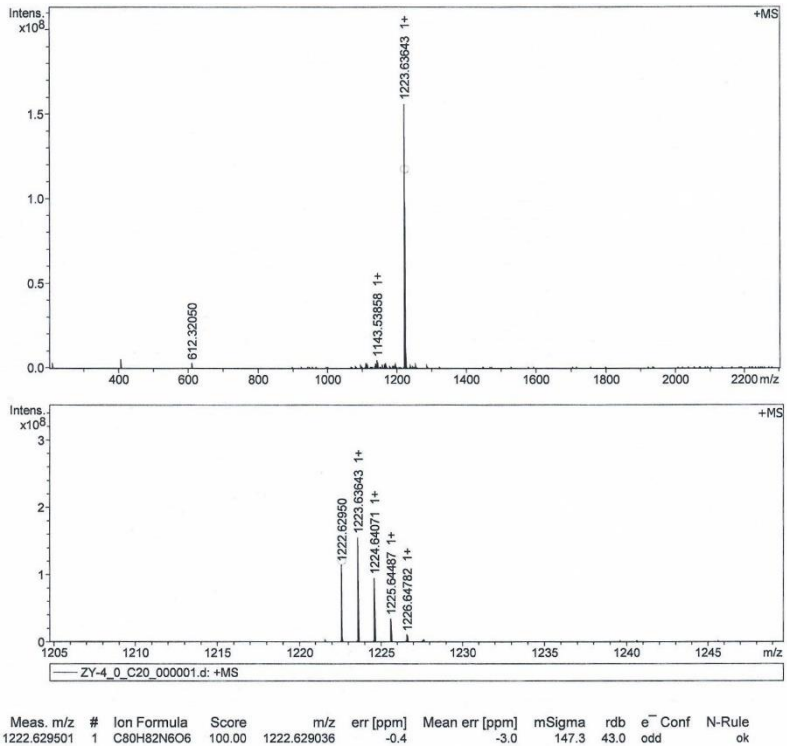
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
878.476469	1	C58H62N4O4	100.00	878.476558	0.1	0.2	44.6	30.0	odd	ok

Fig. S155. MALDI-TOF HRMS spectrum for **(*P*)-T2-^{t}Bu**



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
878.476274	1	C58H62N4O4	100.00	878.476558	0.3	1.1	53.8	30.0	odd	ok

Fig. S156. MALDI-TOF HRMS spectrum for the **curved isomer of (*P*)-T2-^{t}Bu**



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1222.629501	1	C80H82N6O6	100.00	1222.629036	-0.4	-3.0	147.3	43.0	odd	ok

Fig. S157. MALDI-TOF HRMS spectrum for **(*P*)-T3-^{t}Bu**

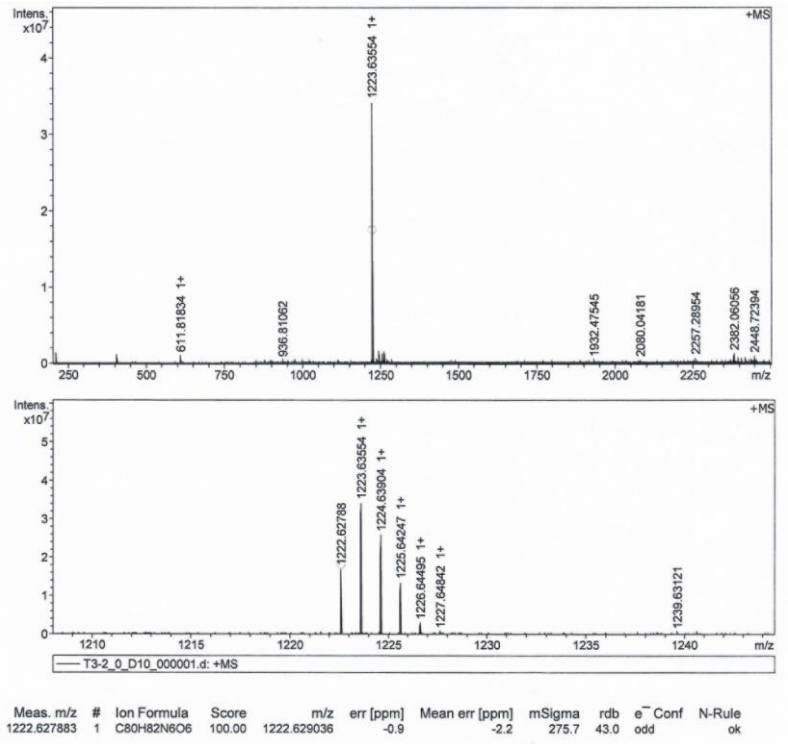


Fig. S158. MALDI-TOF HRMS spectrum for **curved-1 isomer of (*P*)-T3-^{t}Bu**

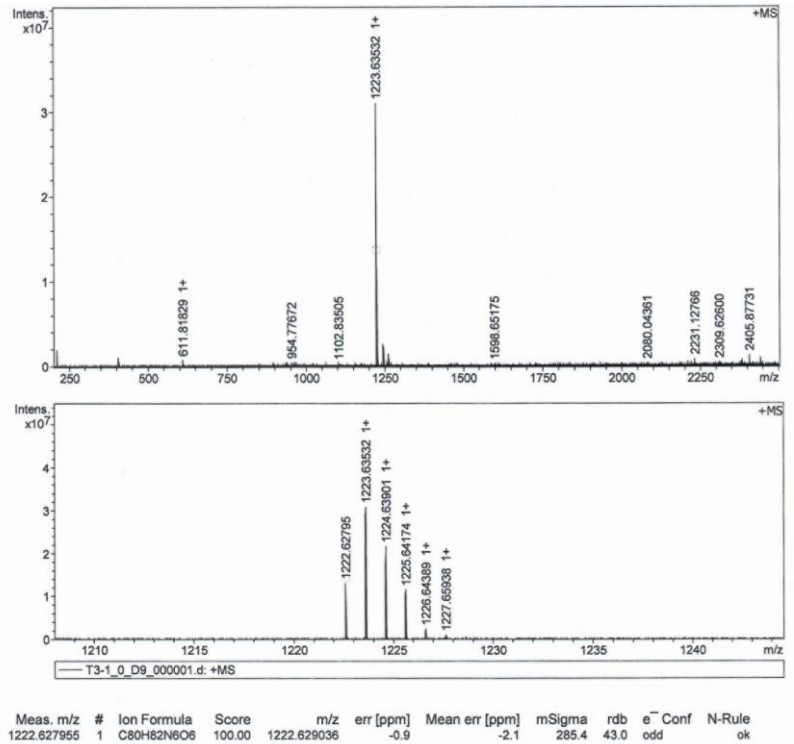
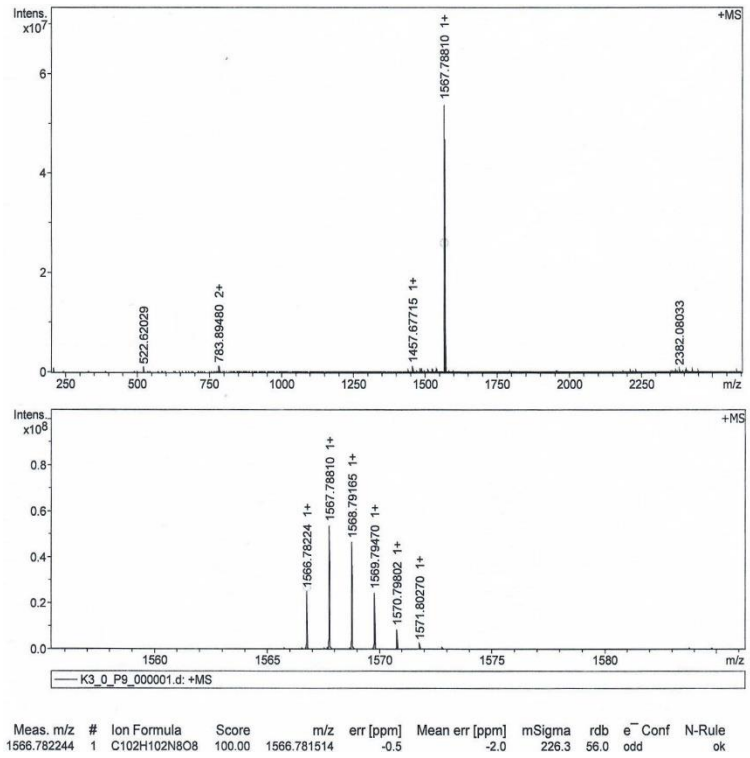
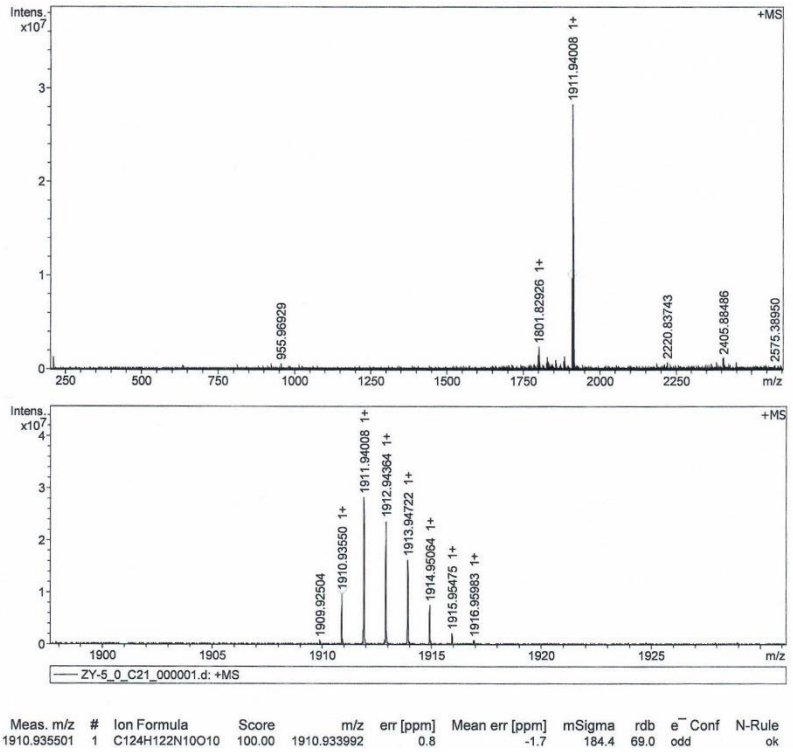


Fig. S159. MALDI-TOF HRMS spectrum for **curved-2 isomer of (*P*)-T3-^{t}Bu**



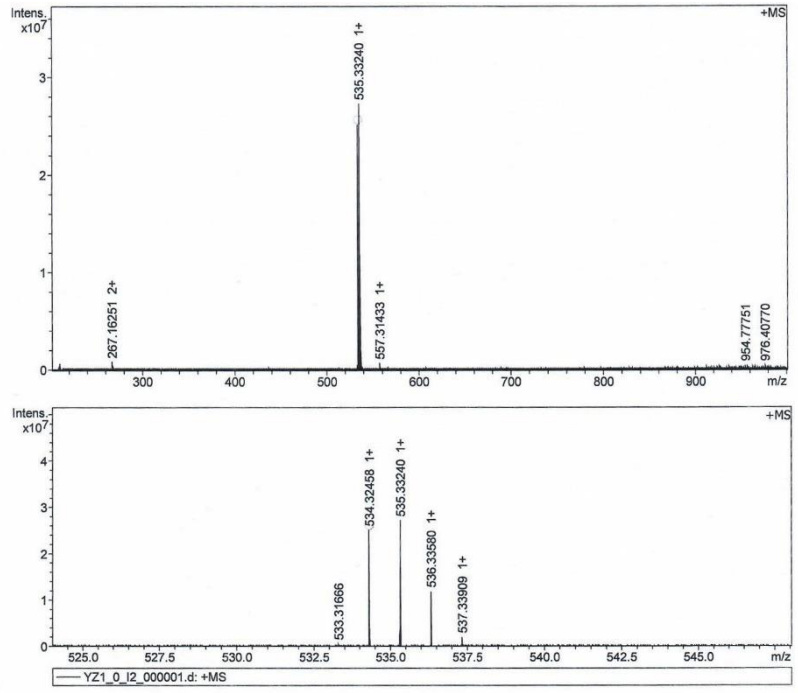
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
1566.782244	1	C102H102N8O8	100.00	1566.781514	-0.5	-2.0	226.3	56.0	odd	ok

Fig. S160. MALDI-TOF HRMS spectrum for **(*P*)-T4-^{t}Bu**



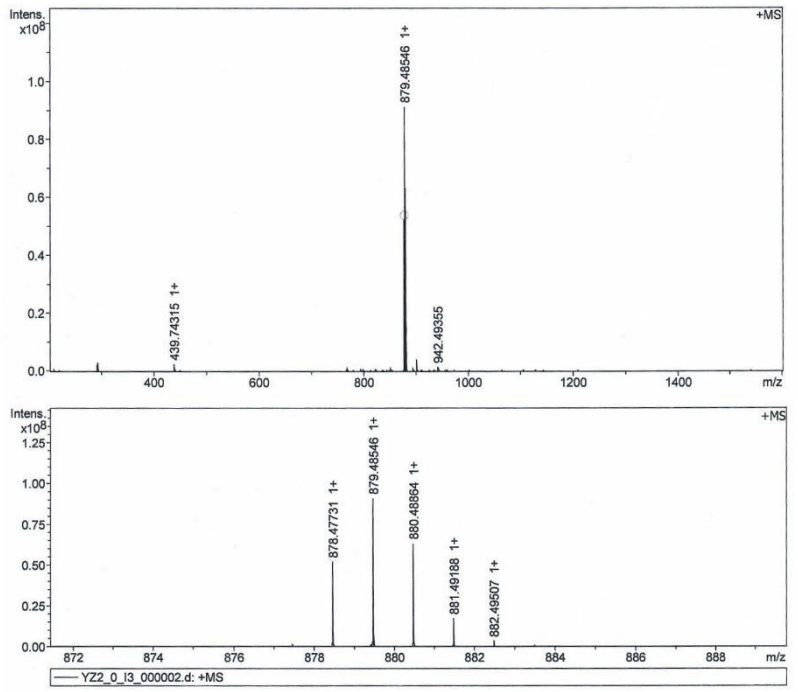
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
1910.935501	1	C124H122N10O10	100.00	1910.933992	0.8	-1.7	184.4	69.0	odd	ok

Fig. S161. MALDI-TOF HRMS spectrum for **(*P*)-T5-^{t}Bu**



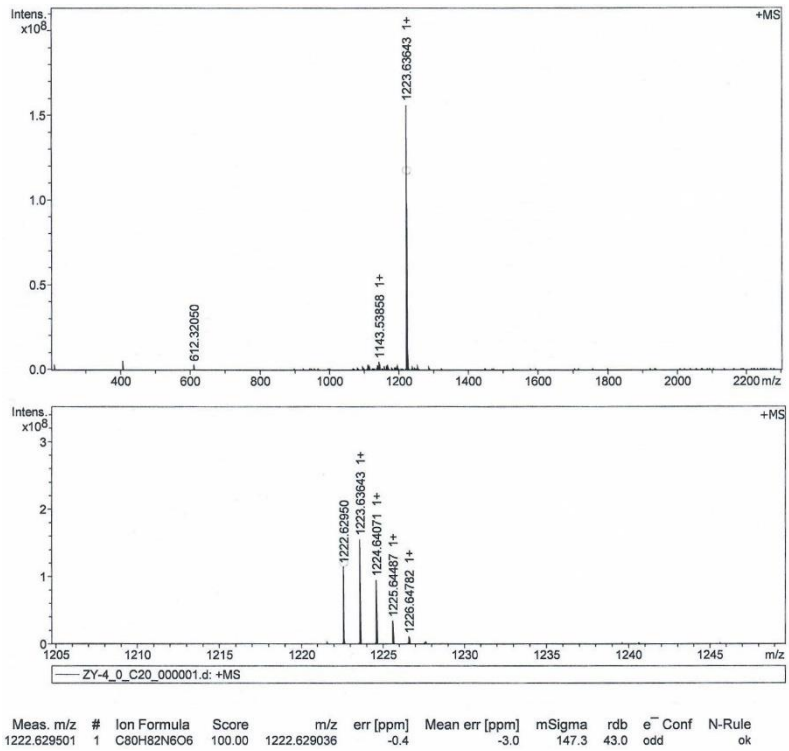
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
534.324584	1	C36H42N2O2	100.00	534.324080	-0.9	-1.0	31.1	17.0	odd	ok

Fig. S162. MALDI-TOF HRMS spectrum for **(*M*)-T1-^{t}Bu**



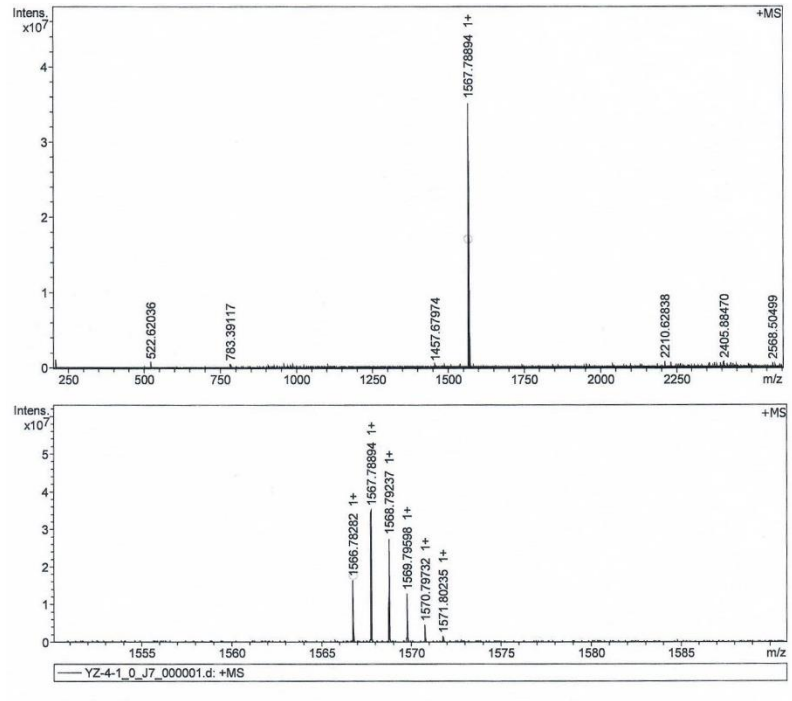
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
878.477307	1	C58H62N4O4	100.00	878.476558	-0.9	-0.1	46.4	30.0	odd	ok

Fig. S163. MALDI-TOF HRMS spectrum for **(*M*)-T2-^{t}Bu**



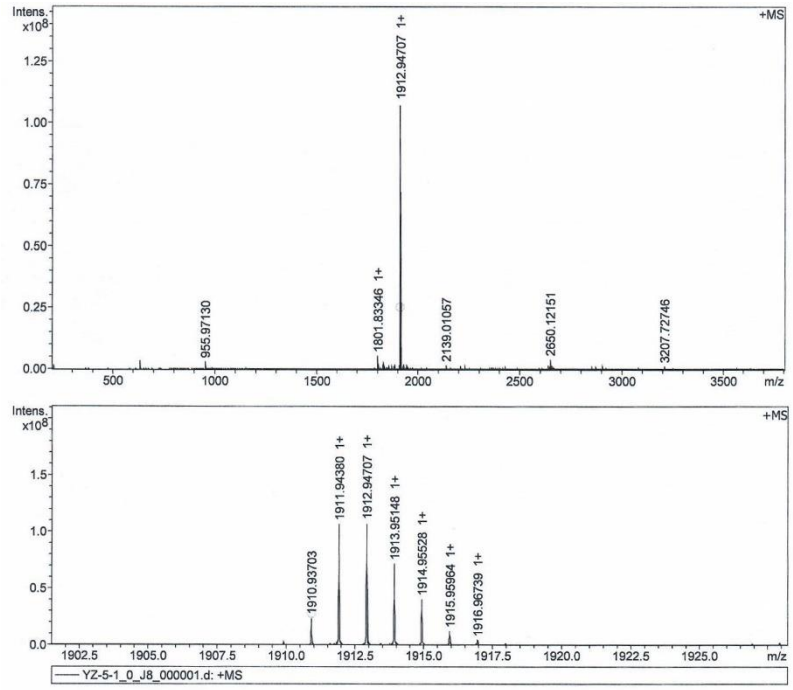
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1222.629501	1	C80H82N6O6	100.00	1222.629036	-0.4	-3.0	147.3	43.0	odd	ok

Fig. S164. MALDI-TOF HRMS spectrum for **(*M*)-T3-^{t}Bu**



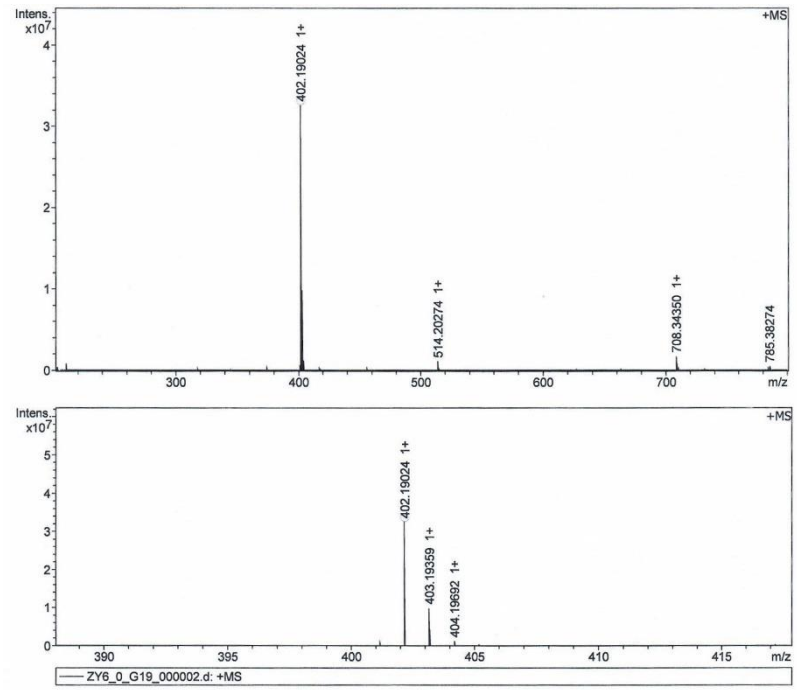
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1566.782821	1	C102H102N8O8	100.00	1566.781514	0.8	-2.5	194.8	56.0	odd	ok

Fig. S165. MALDI-TOF HRMS spectrum for **(*M*)-T4-^{t}Bu**



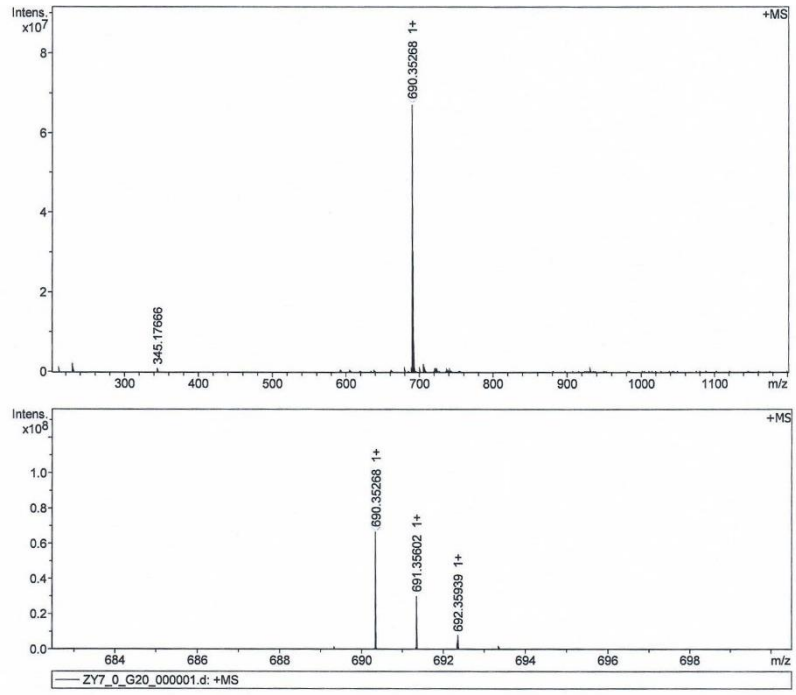
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
1910.937033	1	C124H122N10O10	100.00	1910.933992	1.6	-3.7	270.7	69.0	odd	ok

Fig. S166. MALDI-TOF HRMS spectrum for **(*M*)-T5-^{t}Bu**



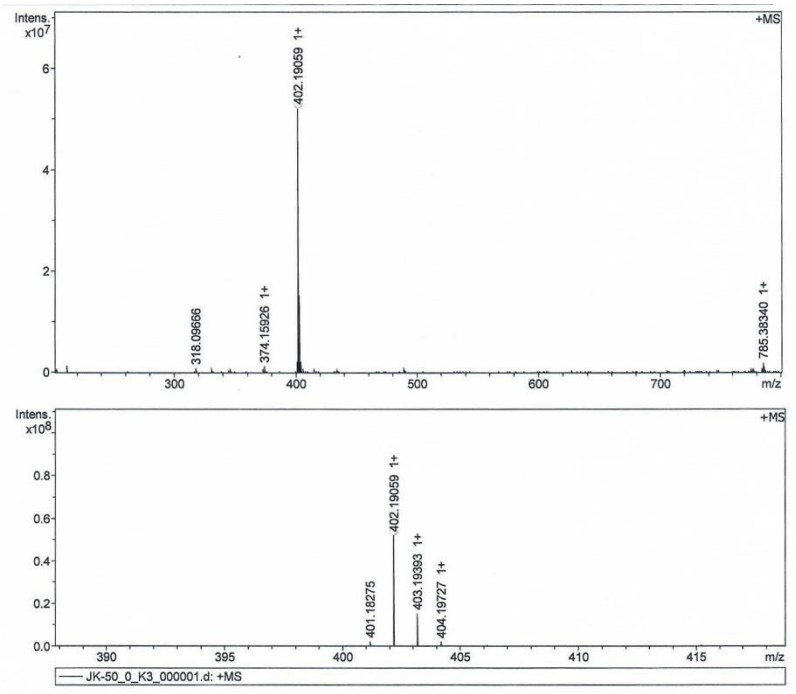
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
402.190240	1	C26H24F2N2	100.00	402.190207	0.1	-0.2	6.4	15.0	odd	ok

Fig. S167. MALDI-TOF HRMS spectrum for **(*P*)-T1-convex**



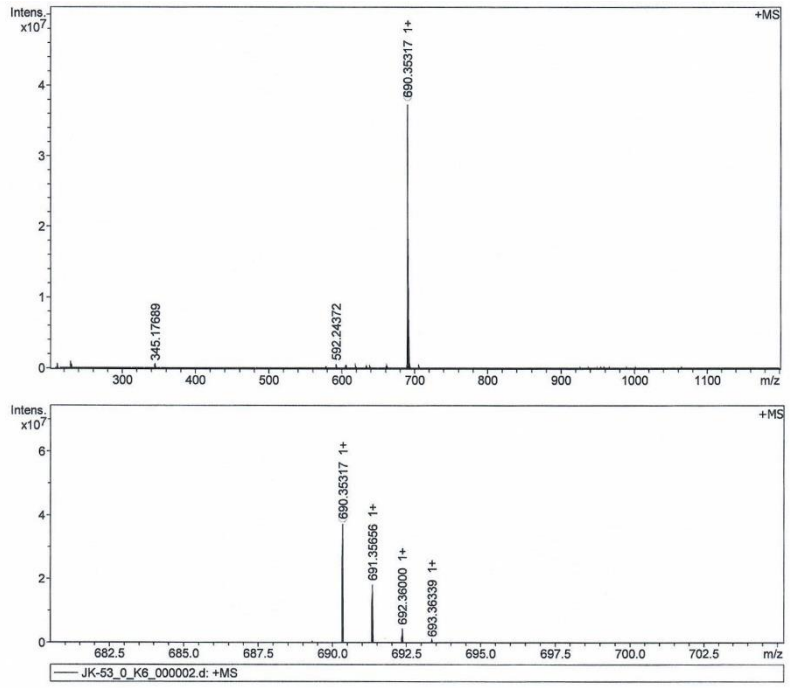
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
690.352683	1	C46H44F2N4	100.00	690.352855	0.2	0.2	33.5	26.0	odd	ok

Fig. S168. MALDI-TOF HRMS spectrum for **(*P*)-T2-convex**



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
402.190585	1	C26H24F2N2	100.00	402.190207	0.9	-1.0	1.0	15.0	odd	ok

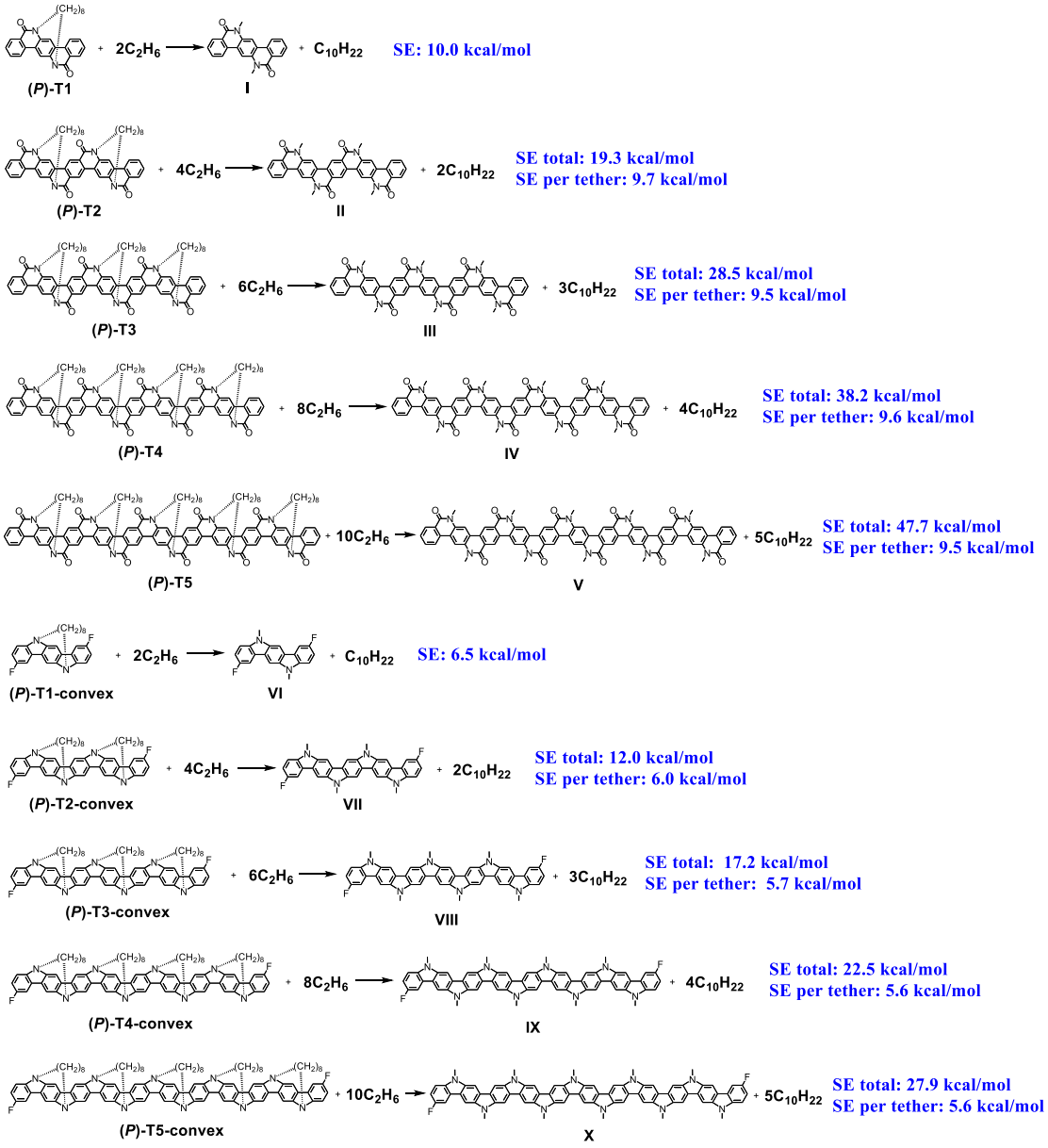
Fig. S169. MALDI-TOF HRMS spectrum for **(*M*)-T1-convex**



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
690.353170	1	C46H44F2N4	100.00	690.352855	0.5	-0.6	16.1	26.0	odd	ok

Fig. S170. MALDI-TOF HRMS spectrum for **(*M*)-T2-convex**

8. Quantification of the chiral strain caused by tethering by using the homodesmotic reaction method



Scheme S4. The homodesmotic reactions and calculated strain energies for **(*P*)-T1**, **(*P*)-T2**, **(*P*)-T3**, **(*P*)-T4**, **(*P*)-T5**, **(*P*)-T1-convex**, and **(*P*)-T2-convex**.

Table S1 Uncorrected and thermal-corrected (298 K) energies (Hartree)

Compound	E	E+ZPE	H
(*P*)-T1	-1342.159307	-1341.670739	-1341.645510
(*P*)-T2	-2452.176415	-2451.300860	-2451.255144
(*P*)-T3	-3562.193395	-3560.931337	-3560.864970

(*P*)-T4	-4672.209764	-4670.560803	-4670.473925
(*P*)-T5	-5782.226206	-5780.190856	-5780.083384
(*P*)-T1-convex	-1313.945823	-1313.496139	-1313.472212
(*P*)-T2-convex	-2197.339490	-2196.525607	-2196.484332
(*P*)-T3-convex	-3080.733162	-3079.555304	-3079.496598
(*P*)-T4-convex	-3964.126767	-3962.585133	-3962.508932
(*P*)-T5-convex	-4847.520356	-4845.614330	-4845.520839
C_2H_6	-79.778395	-79.702821	-79.698404
$C_{10}H_{22}$	-394.138742	-393.833001	-393.818283
I	-1107.595494	-1107.260518	-1107.240049
II	-1983.046960	-1982.479036	-1982.442905
III	-2858.498604	-2857.697667	-2857.645892
IV	-3733.950247	-3732.916346	-3732.848918
V	-4609.401873	-4608.135042	-4608.051948
VI	-1079.375902	-1079.080923	-1079.061117
VII	-1728.197792	-1727.693585	-1727.660445
VIII	-2377.019578	-2376.306137	-2376.259657
IX	-3025.841331	-3024.918653	-3024.858832
X	-3674.663073	-3673.531169	-3673.457999

E: electronic energy; ZPE: zero-point energy; H (E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT): sum of electronic and thermal enthalpies. All calculations were done at the M06-2X(D3)/6-31G(d,p) level.

9. IRI analysis for (*P*)-T2 dimer and (*P*)-T3 dimer

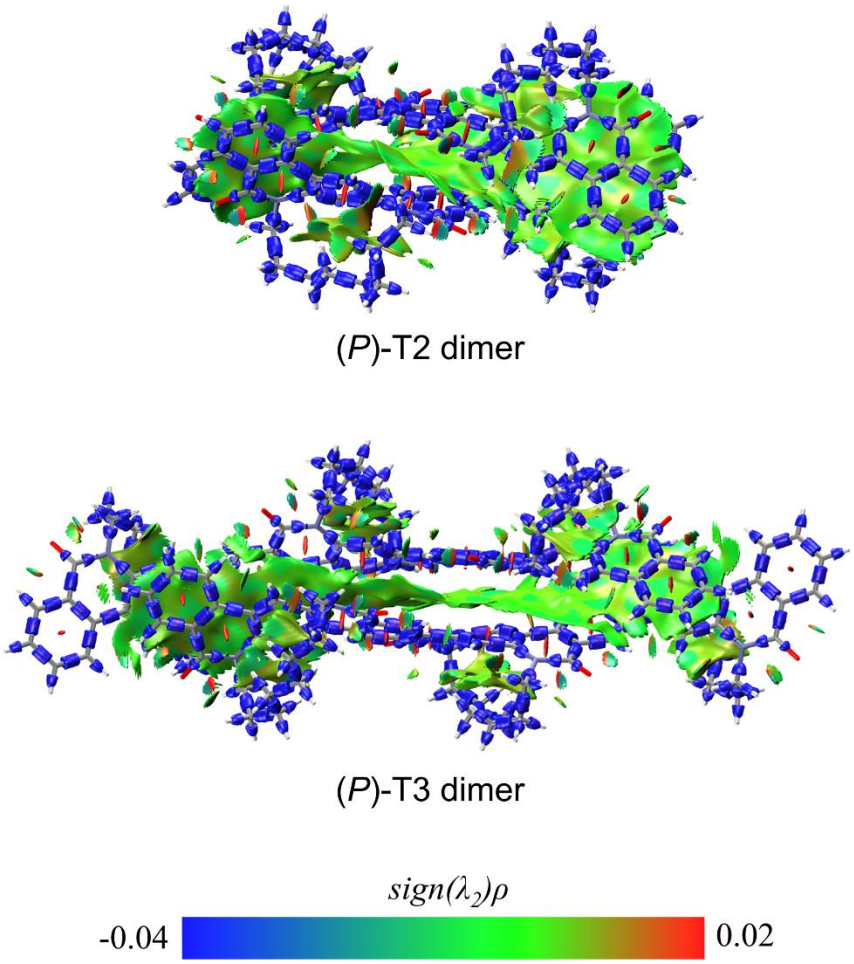


Fig. S171. The interaction region indicator (IRI) analysis for **(*P*)-T2 dimer** and **(*P*)-T3 dimer**. Note: the isosurfaces were drawn at a IRI value of 1.1; the IRI isosurfaces were colored by the sign(λ_2)ρ index; the IRI isosurfaces in blue, green and red represent strong attraction (eg. chemical bond), van der Waals interaction (eg. π-π interaction) and strong repulsion (eg. steric repulsion) regions, respectively.

10. A comparison of interaction energies (ΔE_{int}), binding energies (ΔE_b) and deformation energies (ΔE_d) in the double-helix π-dimers ((*P*)-T2 dimer and (*P*)-T3 dimer) and conventional π-dimers (planar-T2 dimer and planar-T3 dimer)

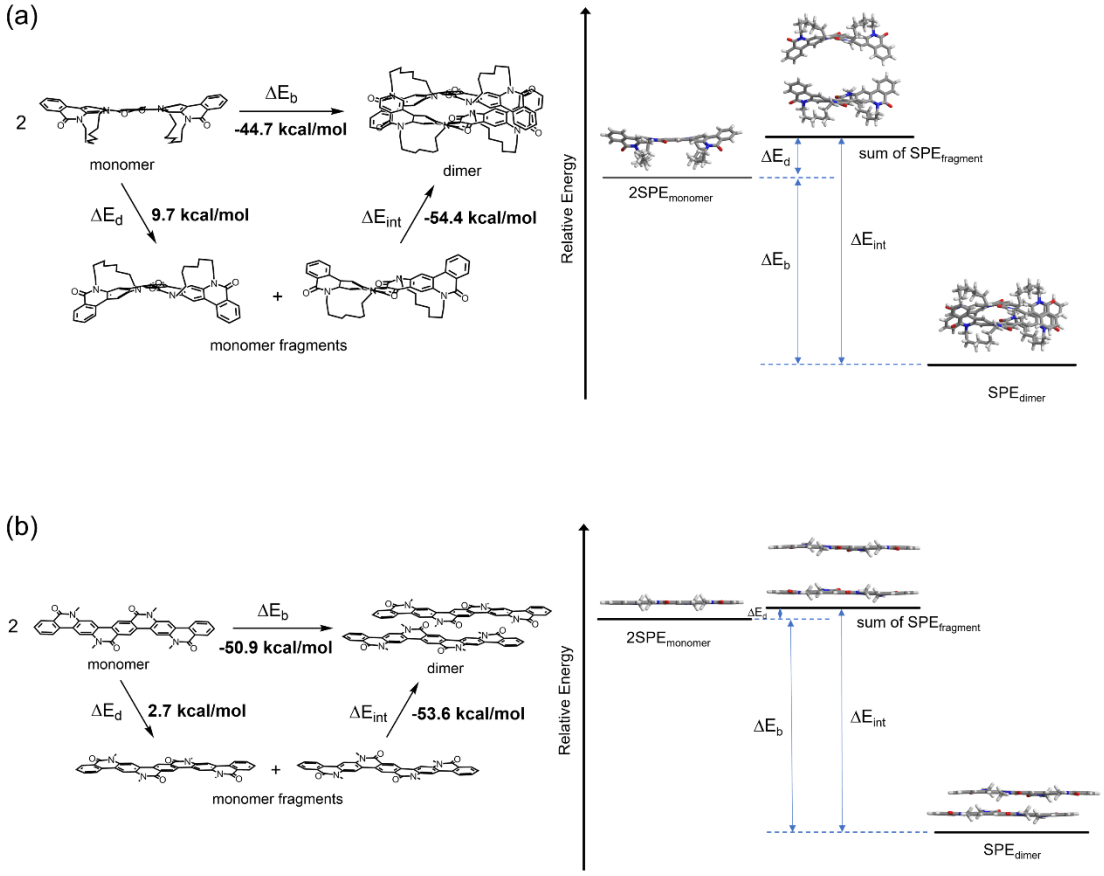


Fig. S172. A comparison of ΔE_{int}, ΔE_b and ΔE_d in (a) **(*P*)-T2 dimer** and (b) **planar-T2 dimer**. Note: the structural optimization for dimers and monomers was done at the M06-2X(D3)/6-31G(d,p) level, and the ΔE_{int} between two monomer fragments in dimer was calculated at the M06-2X(D3)/def2TZVP level with BSSE correction; single point energies (SPE) were calculated at the M06-2X(D3)/def2TZVP level; ΔE_b for dimers were calculated according to: $\Delta E_b = SPE_{dimer} - 2SPE_{monomer}$; ΔE_d were calculated according to: $\Delta E_d = \Delta E_b - \Delta E_{int}$.

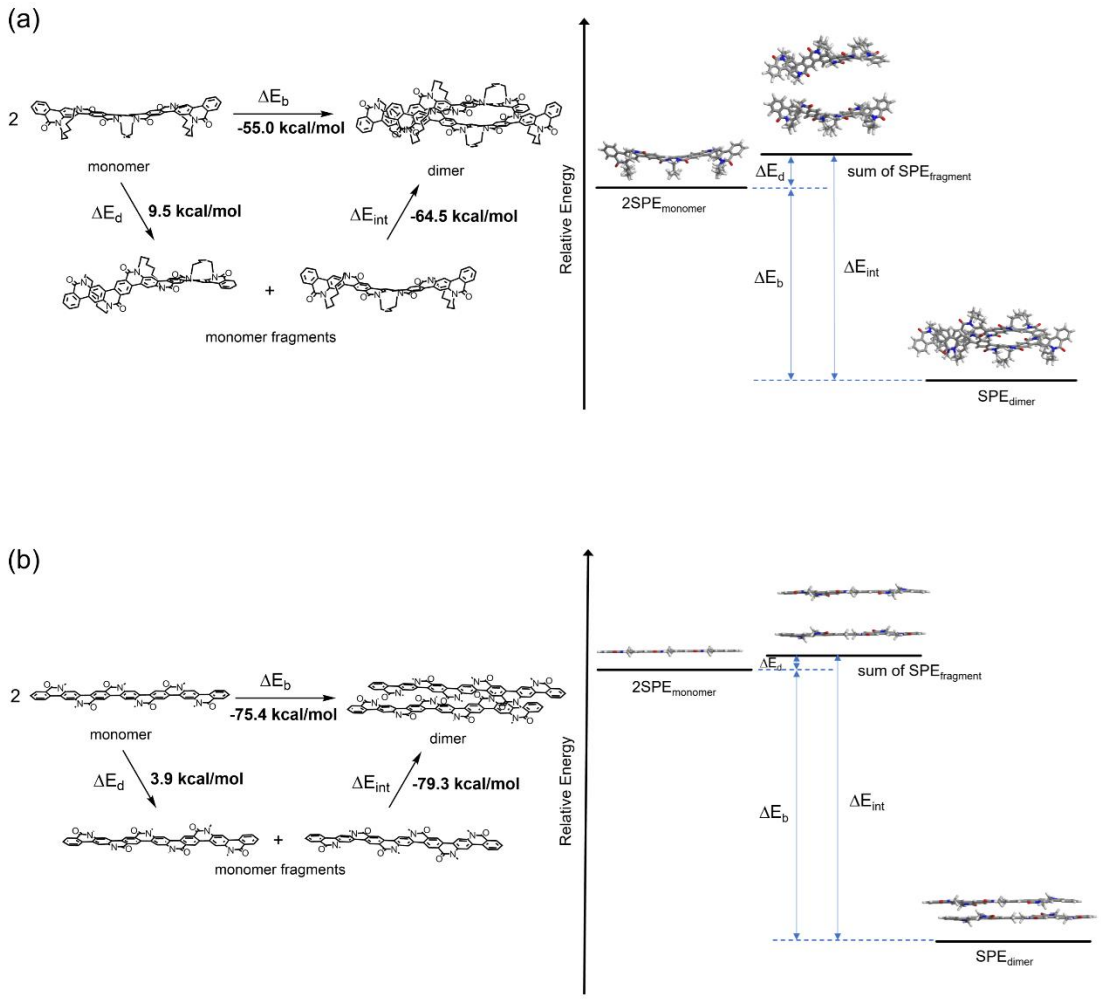


Fig. S173. A comparison of ΔE_{int}, ΔE_b and ΔE_d in (a) **(*P*)-T3 dimer** and (b) **planar-T3 dimer**. Note: the structural optimization for dimers and monomers was done at the M06-2X(D3)/6-31G(d,p) level, and the ΔE_{int} between two monomer fragments in dimer was calculated at the M06-2X(D3)/def2TZVP level with BSSE correction; single point energies (SPE) were calculated at the M06-2X(D3)/def2TZVP level; ΔE_b for dimers were calculated according to: $\Delta E_b = SPE_{dimer} - 2SPE_{monomer}$; ΔE_d were calculated according to: $\Delta E_d = \Delta E_b - \Delta E_{int}$.

11. The optimized structures and IGMH analysis for (*P*)-T4 dimer and (*P*)-T5 dimer

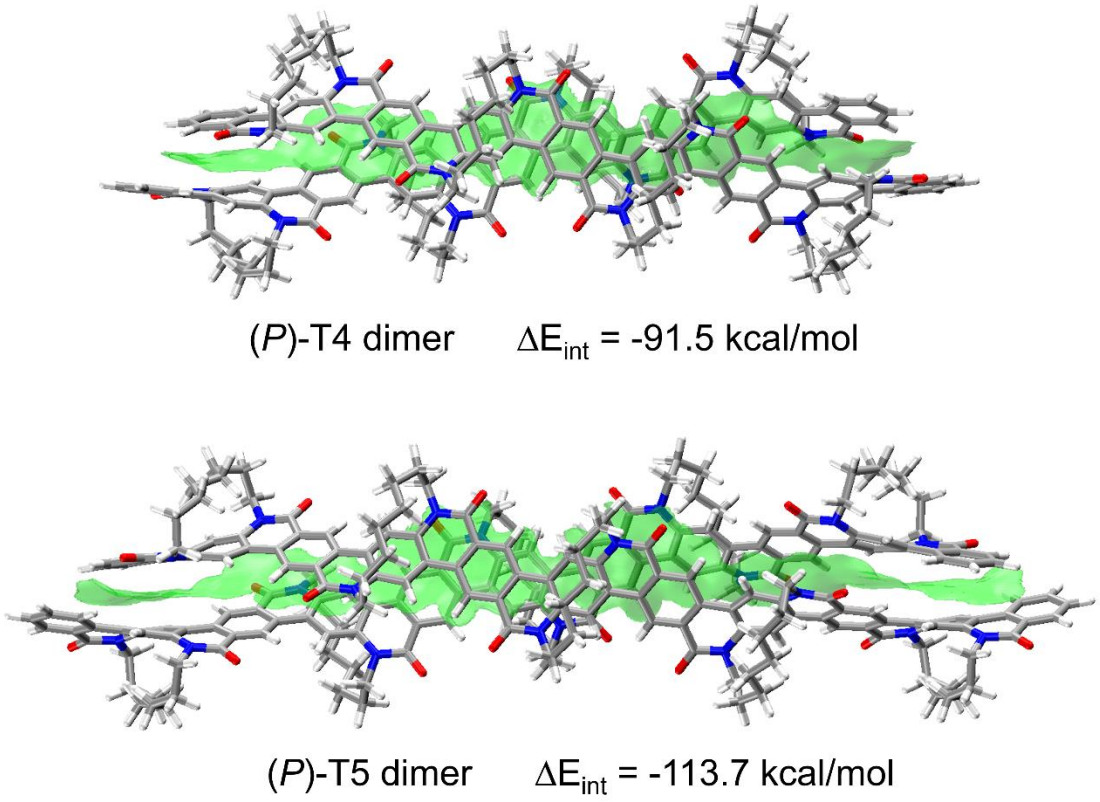


Fig. S174. The optimized structures and IGMH analysis for **(*P*)-T4 dimer** and **(*P*)-T5 dimer**. Note: the structural optimization was done at the r^2SCAN-3c level by using ORCA 5.0.4 software; ΔE_{int} between two monomer fragments was calculated at the ωB97M-V/def2-TZVP level with BSSE correction; the green isosurfaces representing the interfragment interactions were drawn at a δg^{inter} value of 0.003.

12. Comparison of the experimental and theoretical absorption spectra for TECHs

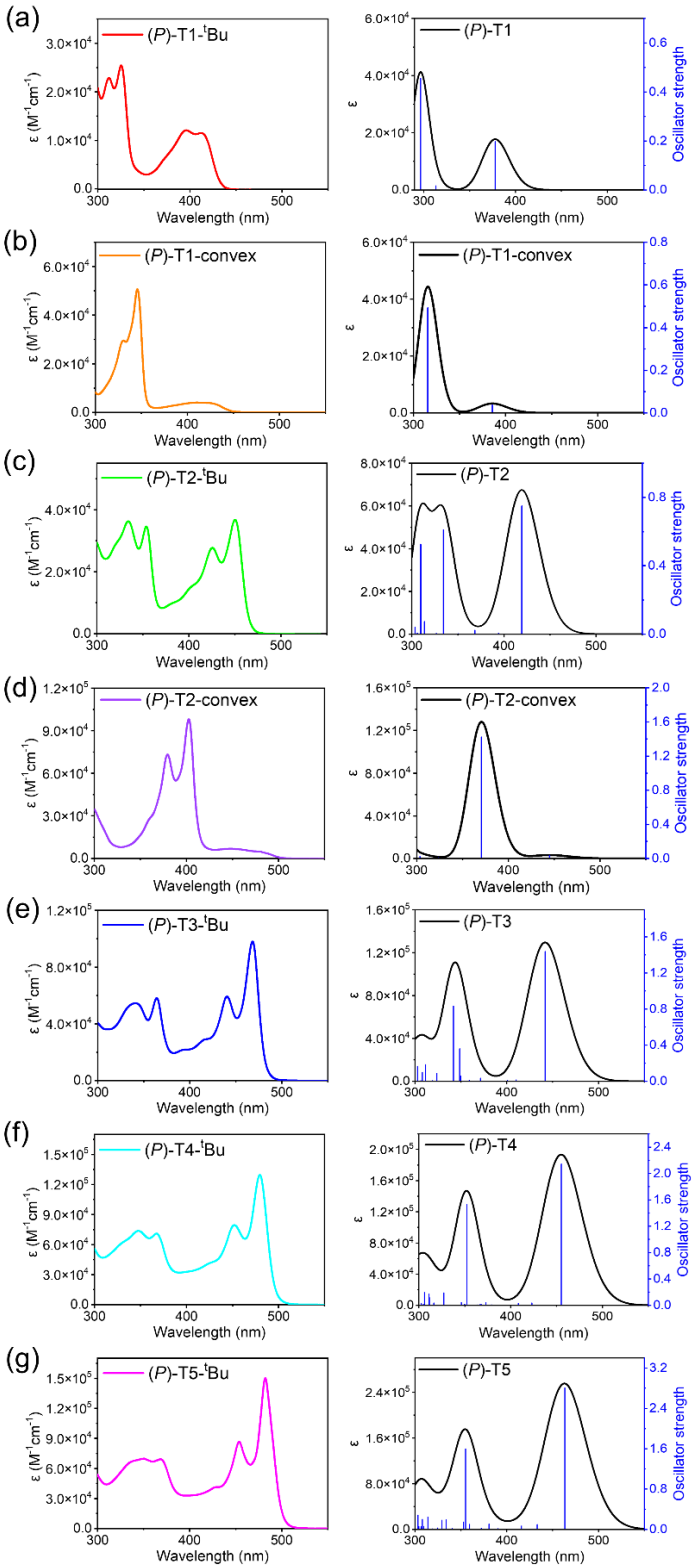


Fig. S175. The experimental (left) and theoretical (right) absorption spectra for TECHs: (a) **(*P*)-T1-^{t}Bu**; (b) **(*P*)-T1-convex**; (c) **(*P*)-T2-^{t}Bu**; (d) **(*P*)-T2-convex**; (e) **(*P*)-T3-^{t}Bu**; (f) **(*P*)-T4-^{t}Bu**; (g) **(*P*)-T5-^{t}Bu**. Note: theoretical absorption spectra were calculated by TD-DFT theory at the PBE0(D3)/6-31G(d,p) level.

13. Calculated properties for the optimized S_1 state of TECHs

Table S2 Calculated properties for the optimized S_1 state of TECHs

TECHs	E (Hartree)	$E_{S1\rightarrow S0}$ (eV)	$\lambda_{S1\rightarrow S0}$ (nm)	$f_{S1\rightarrow S0}$
(*P*)-T1	-1341.2053	2.73	454	0.18
(*P*)-T2	-2450.4510	2.60	477	0.70
(*P*)-T2 dimer	-4900.9837	2.29	542	0.04
(*P*)-T3	-3559.6935	2.49	498	1.57
(*P*)-T3 dimer	-7119.4894	2.06	601	0.03
(*P*)-T4	-4668.9348	2.43	510	2.31
(*P*)-T5	-5778.1759	2.40	518	2.93
(*P*)-T1-convex	-1313.0326	2.92	425	0.04
(*P*)-T2-convex	-2195.8070	2.56	484	0.04

E: electronic energy of the S_1 state; $E_{S1\rightarrow S0}$: emission energy of the $S_1\rightarrow S_0$ transition; $\lambda_{S1\rightarrow S0}$: emission wavelength of the $S_1\rightarrow S_0$ transition; $f_{S1\rightarrow S0}$: oscillator strength of the $S_1\rightarrow S_0$ transition.
Note: the geometry of the S_1 state was optimized at the PBE0(D3)/6-31G(d,p) level.

14. Fluorescence decay measurements for TECHs

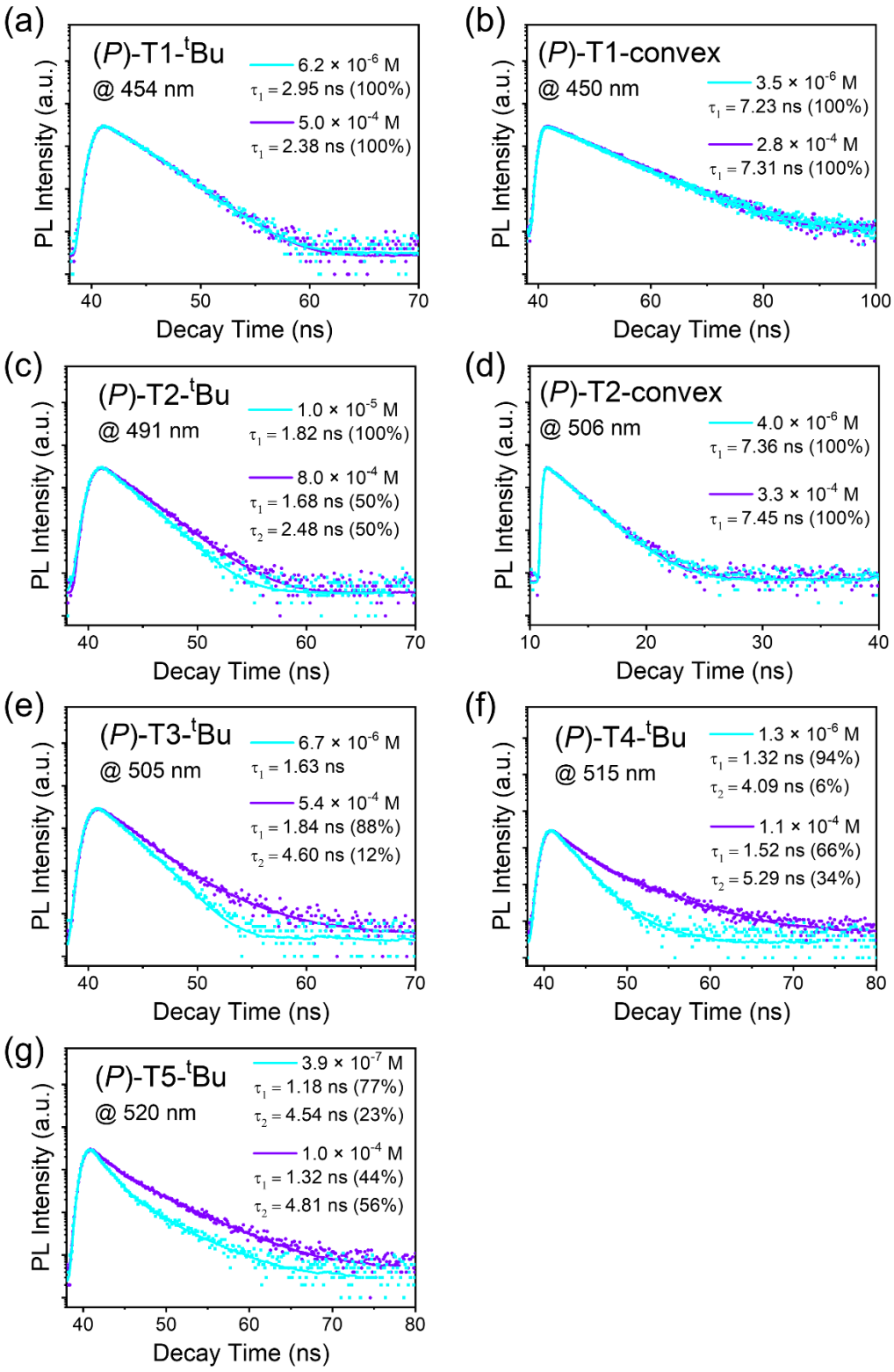


Fig. S176. Fluorescence decay plots for low-concentration (cyan) and high-concentration (violet) solutions of (a) **(*P*)-T1-^{t}Bu**, (b) **(*P*)-T1-convex**, (c) **(*P*)-T2-^{t}Bu**, (d) **(*P*)-T2-convex**, (e) **(*P*)-T3-^{t}Bu**, (f) **(*P*)-T4-^{t}Bu**, and (g) **(*P*)-T5-^{t}Bu**.

15. CV measurements for TECHs

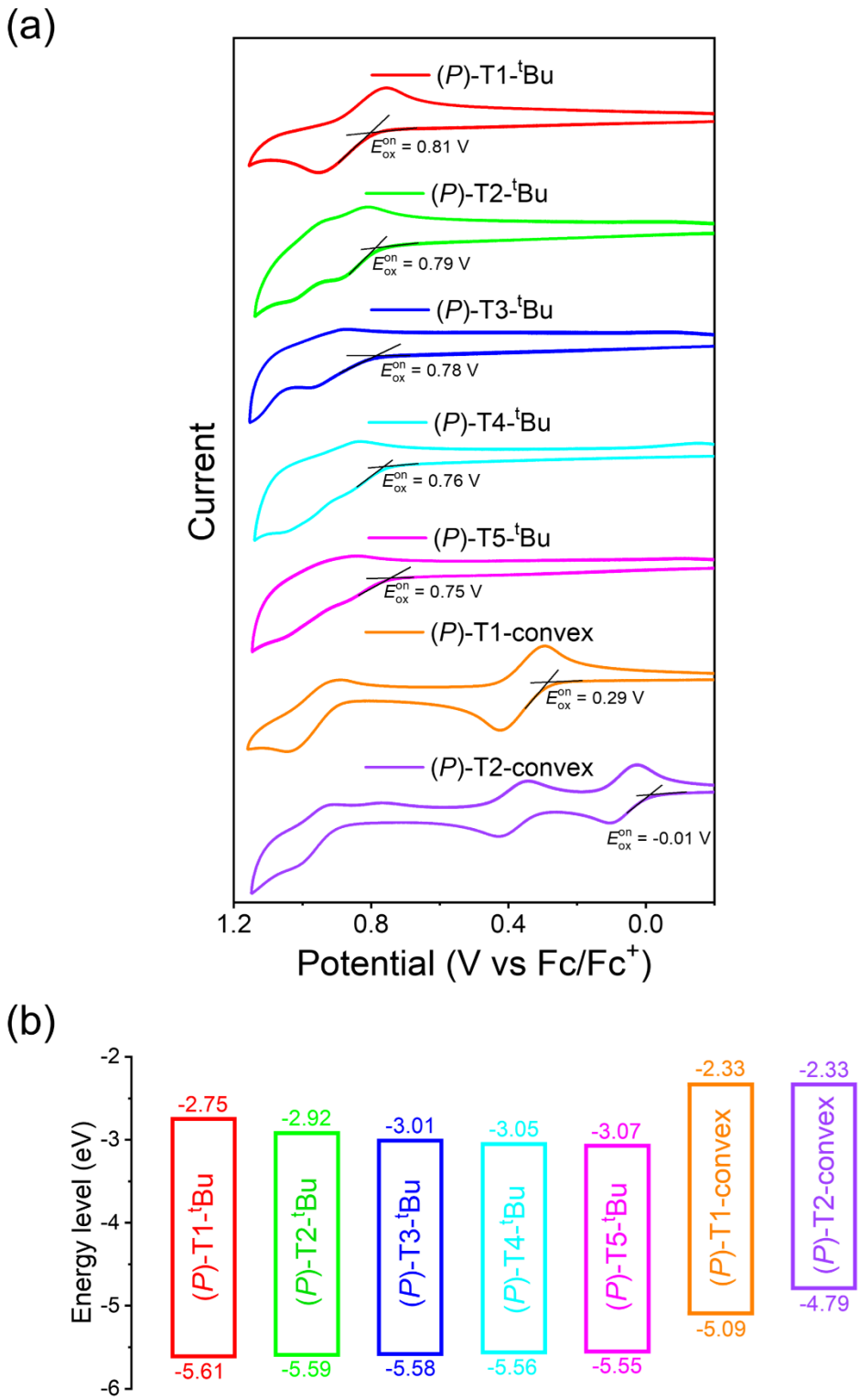


Fig. S177. (a) CV and (b) energy level diagram for TECHs. Note: HOMO levels were calculated from E_{ox}^{on} by using the empirical equation: HOMO = - (E_{ox}^{on} + 4.8); LUMO levels were calculated by using the equation: LUMO = HOMO + E_g^{opt}.

16. DFT-calculated HOMO/LUMO levels for TECHs

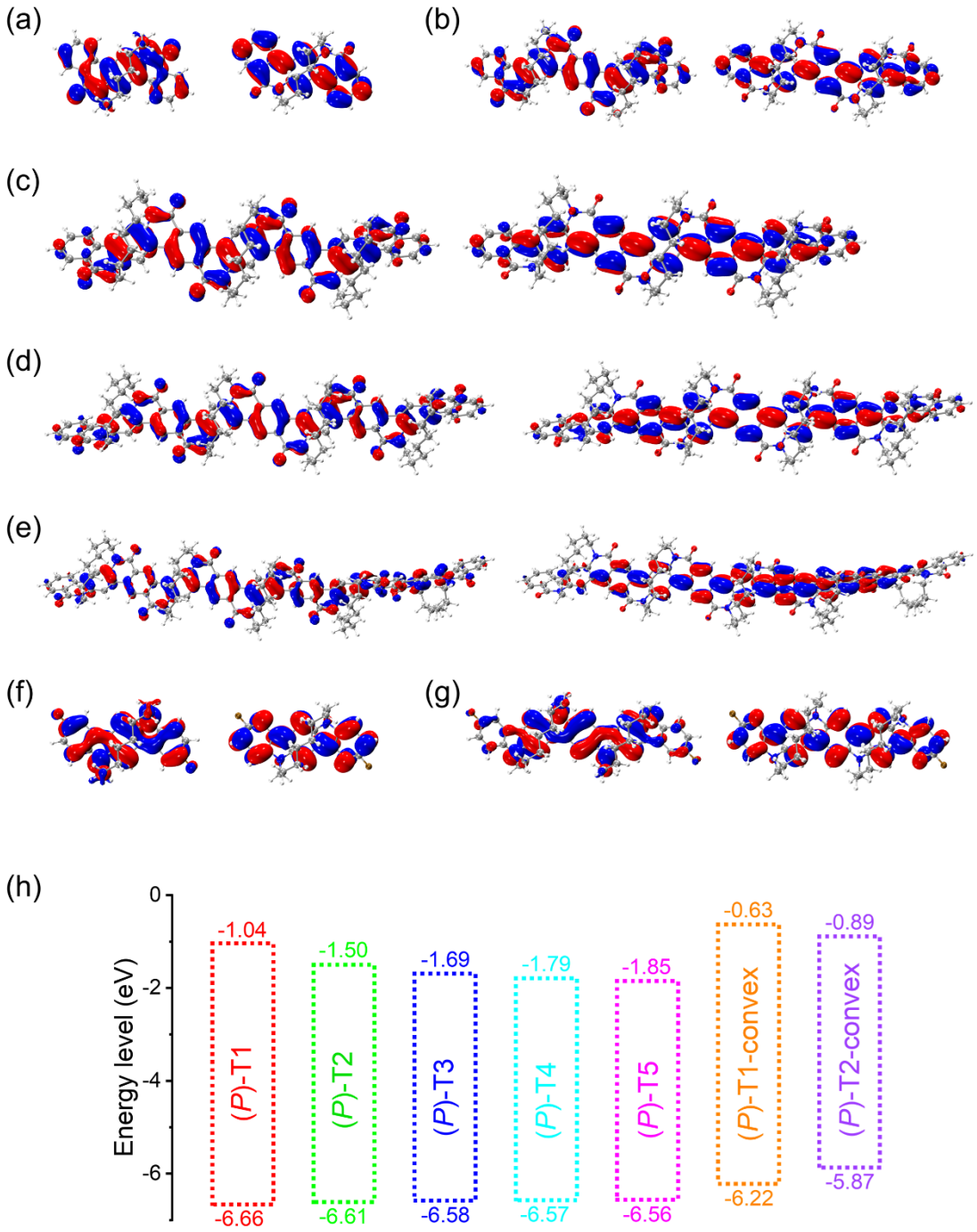
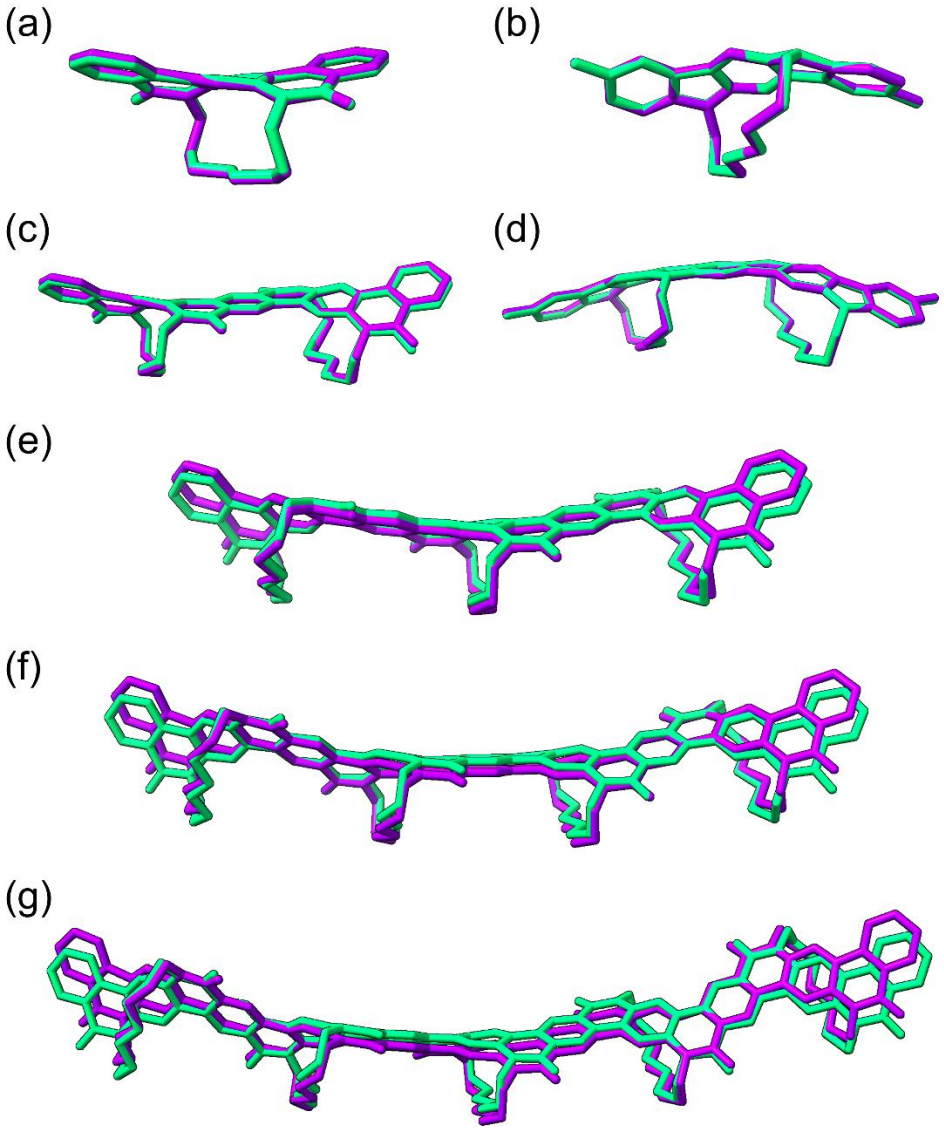


Fig. S178. DFT-calculated HOMO (left) and LUMO (right) orbitals for (a) **(*P*)-T1**, (b) **(*P*)-T2**, (c) **(*P*)-T3**, (d) **(*P*)-T4**, (e) **(*P*)-T5**, (f) **(*P*)-T1-convex** and (g) **(*P*)-T2-convex**. (h) A summary of the DFT-calculated HOMO/LUMO levels for TECHs.

17. Comparison of the optimized geometries of ground and excited states for TECHs



(h)

TECHs	g_{abs}^{cal}	g_{lum}^{cal}	$g_{lum}^{cal}/g_{abs}^{cal}$
(*P*)-T1	-8.9×10^{-4}	-1.3×10^{-3}	1.5
(*P*)-T1-convex	-1.5×10^{-3}	-1.3×10^{-3}	0.9
(*P*)-T2	-5.7×10^{-4}	-5.3×10^{-4}	0.9
(*P*)-T2-convex	-3.9×10^{-3}	-4.2×10^{-3}	1.1
(*P*)-T3	-4.7×10^{-4}	-3.9×10^{-4}	0.8
(*P*)-T4	-4.3×10^{-4}	-3.4×10^{-4}	0.8
(*P*)-T5	-3.7×10^{-4}	-2.6×10^{-4}	0.7

Fig. S179. Comparison of the optimized geometries of S_0 (green) and S_1 (violet) states for (a) **(*P*)-T1**, (b) **(*P*)-T1-convex**, (c) **(*P*)-T2**, (d) **(*P*)-T2-convex**, (e) **(*P*)-T3**, (f) **(*P*)-T4** and (g) **(*P*)-T5**. (h) A summary of the calculated g_{abs} ($S_0 \rightarrow S_1$) and g_{lum} ($S_1 \rightarrow S_0$). Note: g_{abs}^{cal} and g_{lum}^{cal} were calculated according to the equation $g = 4\cos\theta|m|/|\mu|$, where μ is the electric transition dipole moment, m is the magnetic transition dipole moment, and θ is the angle between μ and m.

18. CPL and g_{lum} for *P*-TECHs at different concentrations

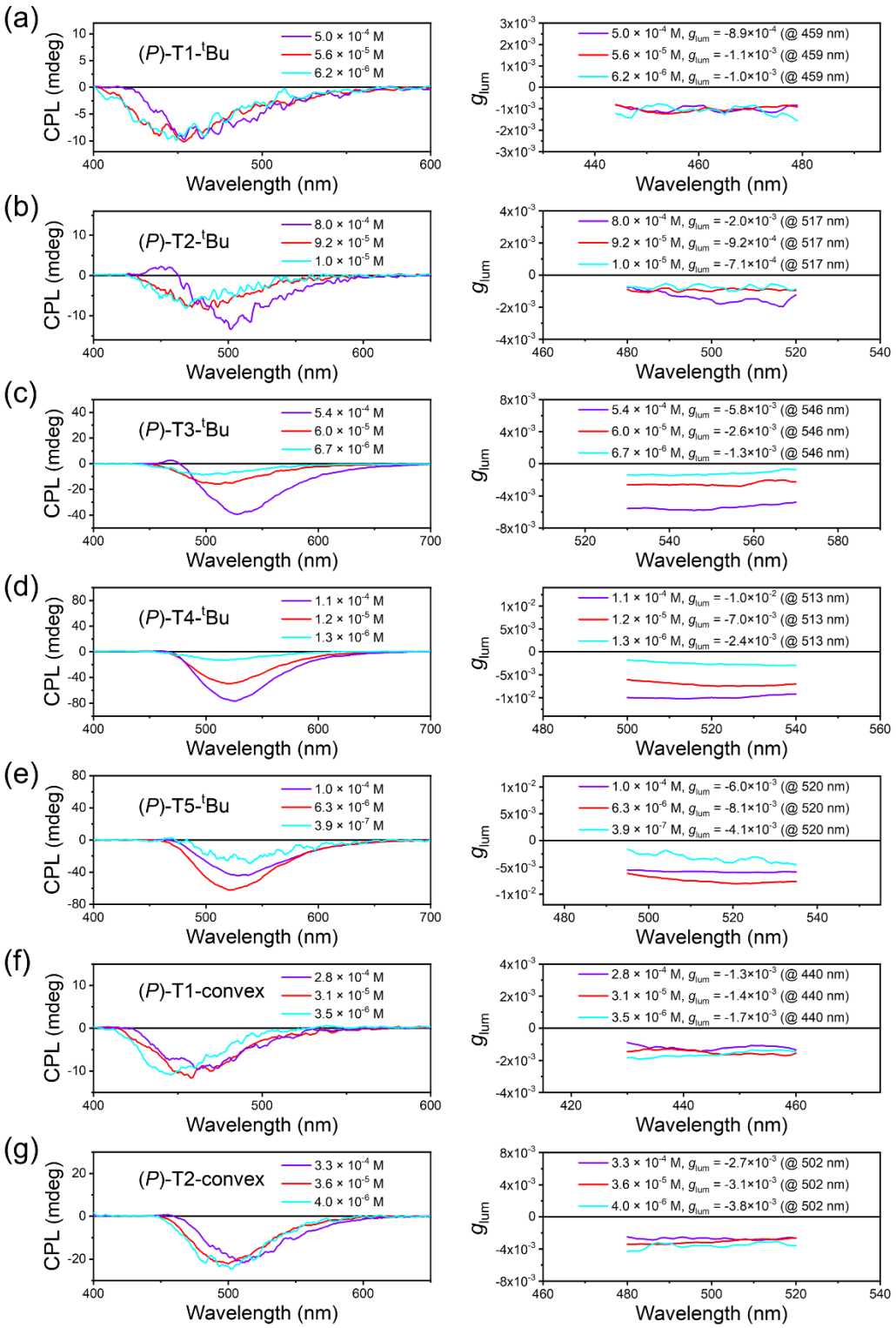


Fig. S180. CPL and g_{lum} for *P*-TECHs at low (cyan), medium (red), and high (violet) concentrations: (a) **(*P*)-T1-^{t}Bu**, (b) **(*P*)-T2-^{t}Bu**, (c) **(*P*)-T3-^{t}Bu**, (d) **(*P*)-T4-^{t}Bu**, (e) **(*P*)-T5-^{t}Bu**, (f) **(*P*)-T1-convex**, and (g) **(*P*)-T2-convex**.

19. CPL and g_{lum} for *M*-TECHs at different concentrations

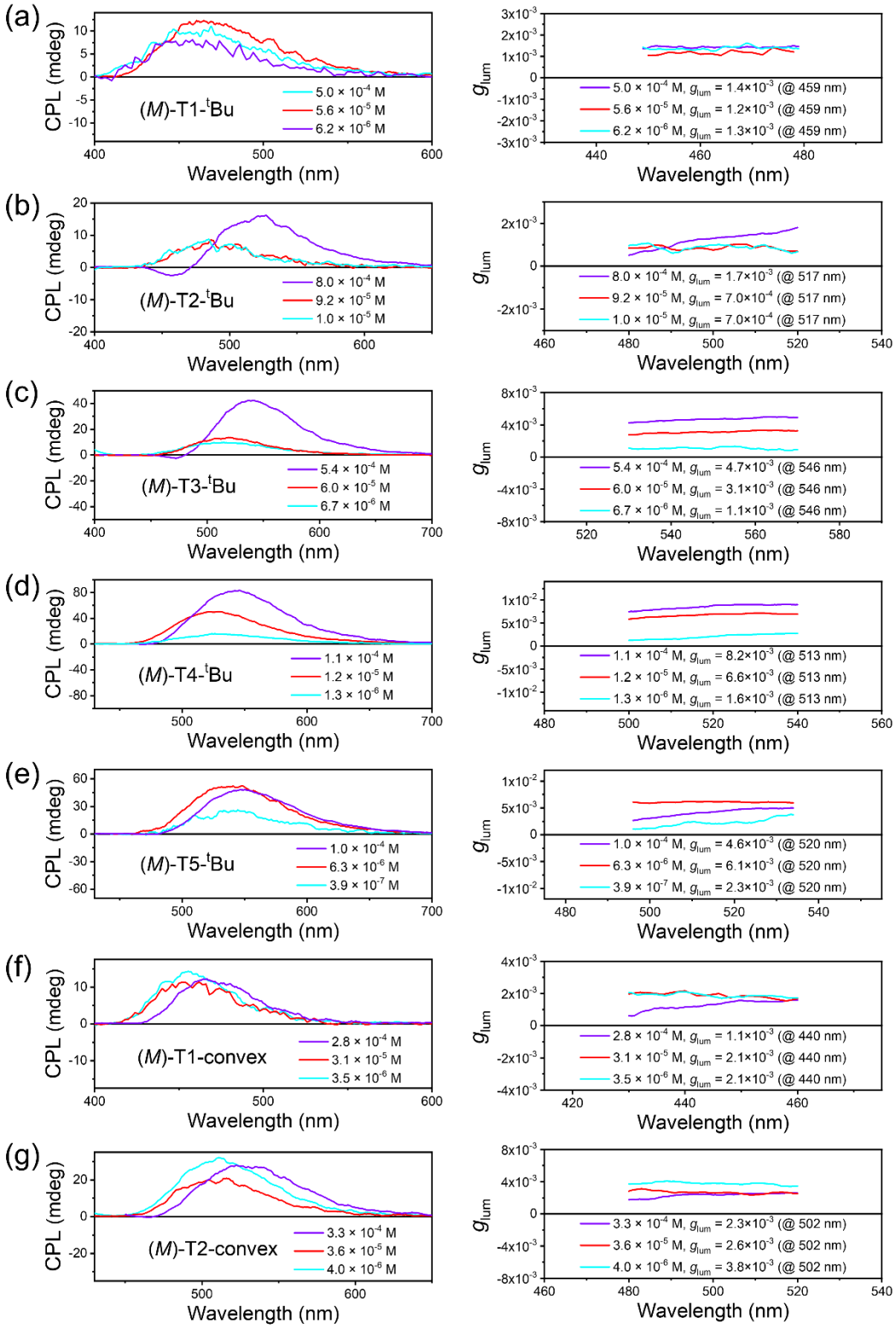


Fig. S181. CPL and g_{lum} for *M*-TECHs at low (cyan), medium (red), and high (violet) concentrations: (a) **(*M*)-T1-^{t}Bu**, (b) **(*M*)-T2-^{t}Bu**, (c) **(*M*)-T3-^{t}Bu**, (d) **(*M*)-T4-^{t}Bu**, (e) **(*M*)-T5-^{t}Bu**, (f) **(*M*)-T1-convex**, and (g) **(*M*)-T2-convex**.

20. DLS measurements for *P*-TECHs at high concentrations

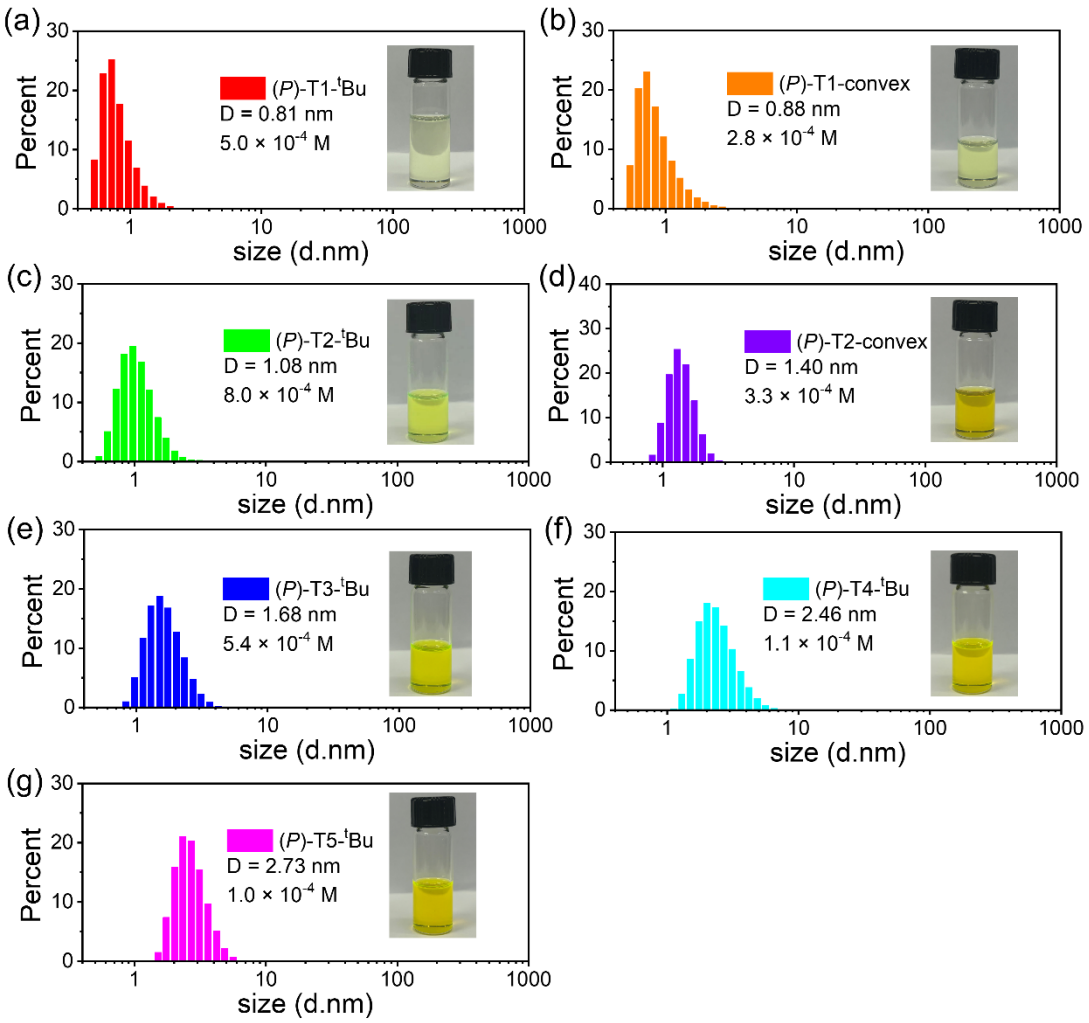


Fig. S182. Dynamic light scattering (DLS) measurements for high-concentration solutions of (a) **(*P*)-T1-^{t}Bu**, (b) **(*P*)-T1-convex**, (c) **(*P*)-T2-^{t}Bu**, (d) **(*P*)-T2-convex**, (e) **(*P*)-T3-^{t}Bu**, (f) **(*P*)-T4-^{t}Bu**, and (g) **(*P*)-T5-^{t}Bu**.

21. Normalized absorptions spectra for *P*-TECHs with different concentrations

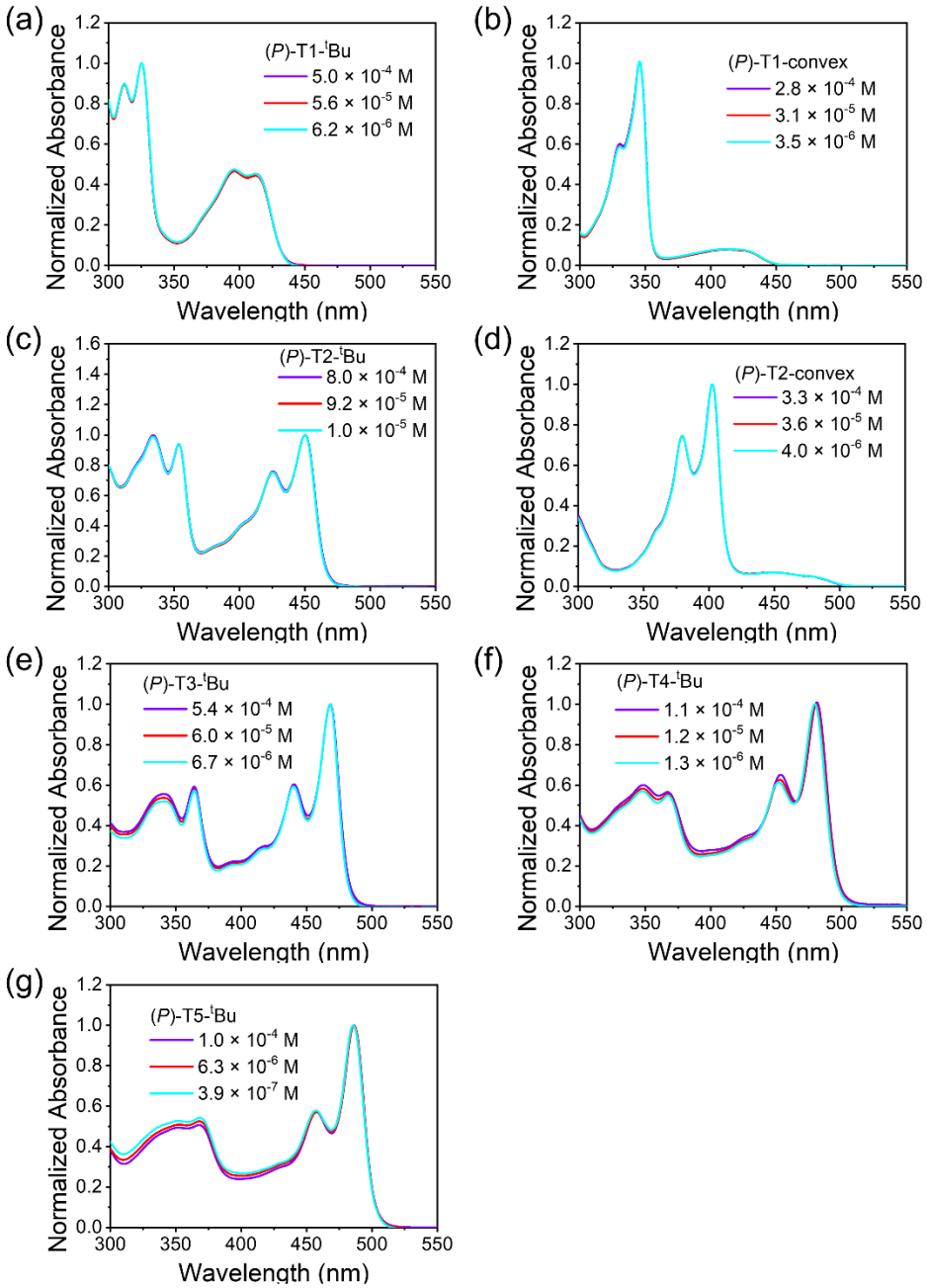


Fig. S183. Normalized absorptions spectra for (a) **(*P*)-T1-^{t}Bu**, (b) **(*P*)-T1-convex**, (c) **(*P*)-T2-^{t}Bu**, (d) **(*P*)-T2-convex**, (e) **(*P*)-T3-^{t}Bu**, (f) **(*P*)-T4-^{t}Bu**, and (g) **(*P*)-T5-^{t}Bu** with different concentrations.

22. CPL brightnesses for *P*-TECHs

The CPL brightnesses (B_{CPL}) were calculated according to the definition[4]:

$$B_{CPL} = \varepsilon \times \phi \times |g_{lum}| / 2$$

where ε is the molar extinction coefficient measured at the excitation wavelength, ϕ is the emission quantum yield, and $|g_{lum}|$ is the luminescence dissymmetric factor.

Table S3 Calculated B_{CPL} for *P*-TECHs

P-TECHs	ε (M^{-1} cm^{-1})	ϕ	$\lvert g_{lum}\rvert$ ($\times10^{-3}$)	B_{CPL} (M^{-1} cm^{-1})
(*P*)-T1-^{t}Bu	1.21×10^4	0.22 (0.29)	0.89 (1.0)	1 (2)
(*P*)-T2-^{t}Bu	3.67×10^4	0.36 (0.43)	2.0 (0.71)	13 (6)
(*P*)-T3-^{t}Bu	9.80×10^4	0.41 (0.57)	5.8 (1.3)	117 (36)
(*P*)-T4-^{t}Bu	1.29×10^5	0.49 (0.71)	10.0 (2.4)	316 (110)
(*P*)-T5-^{t}Bu	1.50×10^5	0.50 (0.46)	6.0 (4.1)	225 (141)
(*P*)-T1-convex	5.07×10^4	0.19 (0.27)	1.3 (1.7)	6 (12)
(*P*)-T2-convex	9.80×10^4	0.12 (0.21)	2.7 (3.8)	16 (39)

Note: the values in the parentheses are measured from dilute solutions.

23. Chiroptical stability tests for TECHs

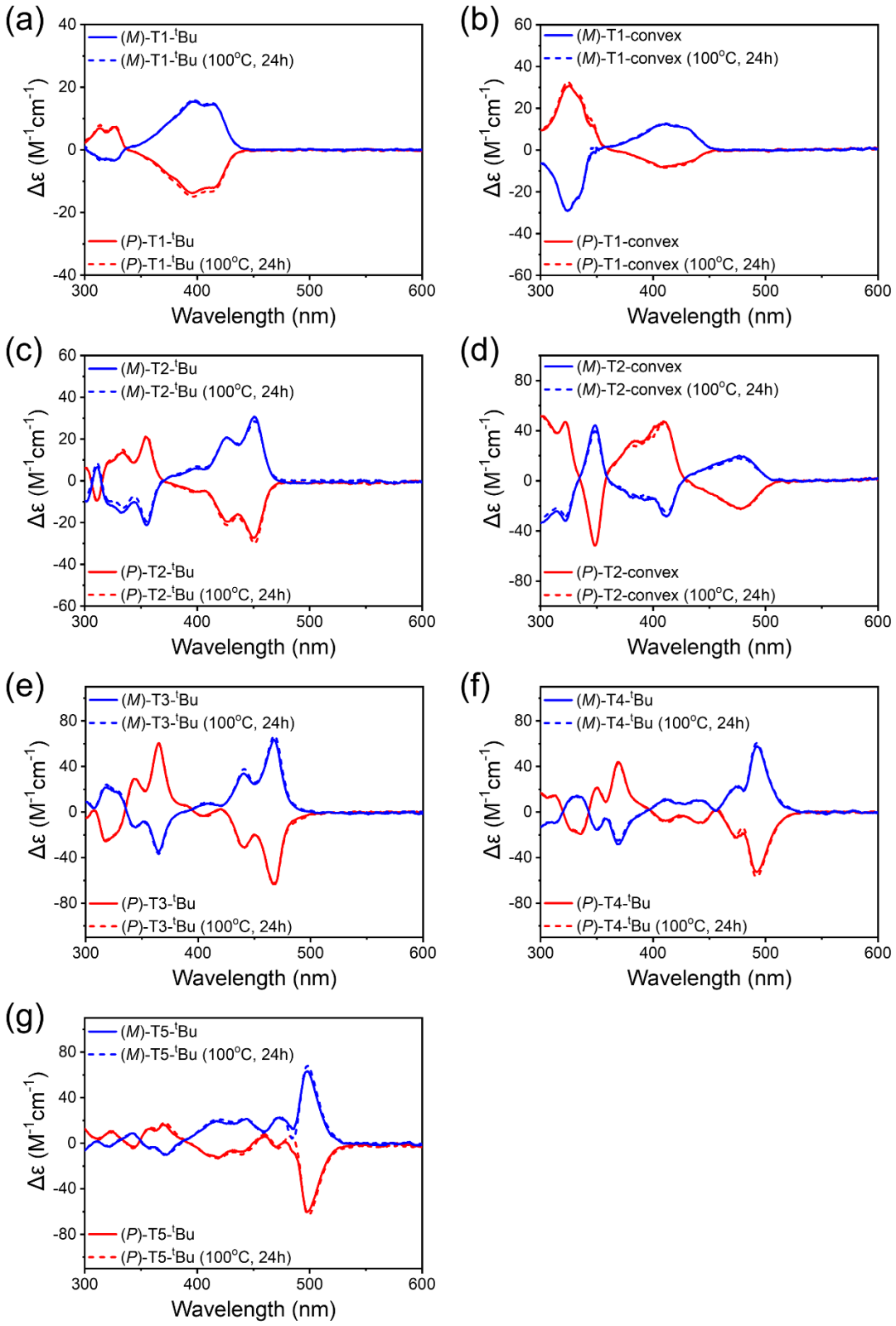


Fig. S184. CD spectra for the *P*-TECHs before and after being heated in toluene at 100 °C for 24 hours: (a) **(*P*)-T1-^{t}Bu**, (b) **(*P*)-T1-convex**, (c) **(*P*)-T2-^{t}Bu**, (d) **(*P*)-T2-convex**, (e) **(*P*)-T3-^{t}Bu**, (f) **(*P*)-T4-^{t}Bu**, and (g) **(*P*)-T5-^{t}Bu**.

References:

1. Gaussian 16, Revision C.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., Jr. Montgomery, 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, Millam, J. M. M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, 2016, *Gaussian, Inc., Wallingford* CT.
2. T. Lu and F. Chen, Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem.,* 2012, **33**, 580-592.
3. W. Humphrey, A. Dalke and K. Schulten, VMD: Visual molecular dynamics, *J. Mol. Graph. Model.,* 1996, **14**, 33-38.
4. L. Arrico, L. Di Bari and F. Zinna, Quantifying the Overall Efficiency of Circularly Polarized Emitters, *Chem. Eur. J.*, 2021, **27**, 2920-2934.