Supporting Information

A Helix-Turn-Helix Supersecondary Structure Based on Oligo(Phenanthroline Dicarboxamide)s

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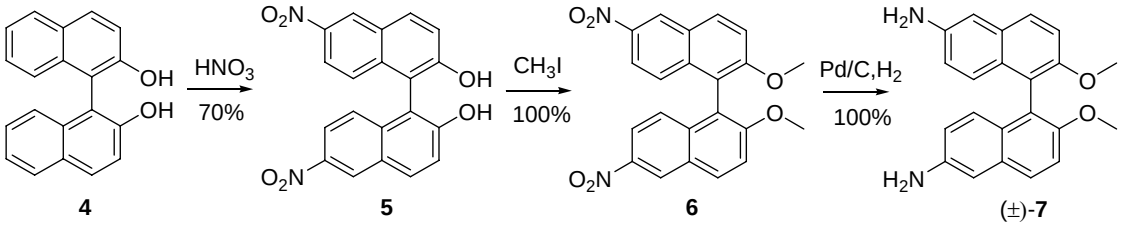
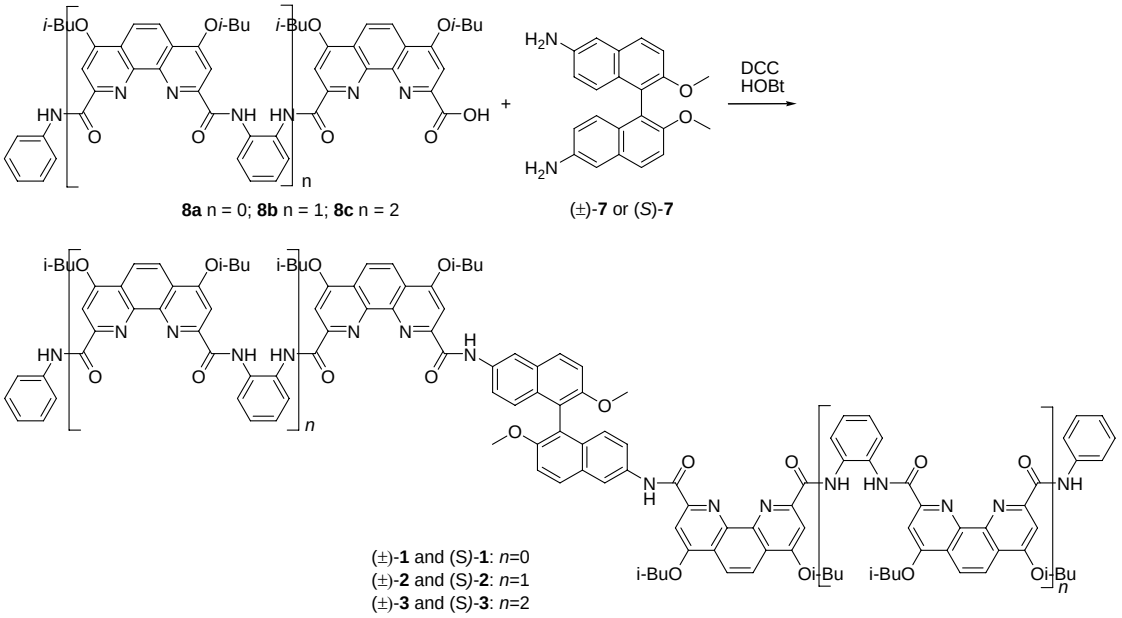
1. Experimental section



Scheme S1. Synthesis of compound (±)-**7**.



Scheme S2. Synthesis of the oligomers **1**~**3**.

Compound 5. To the solution of 1, 1'-binaphthyl-2, 2'-diol **4** (5.72 g, 20 mmol) in acetic acid and dichloromethane (50 mL, 1:1 v/v) was added dropwise nitric acid (100%, 2.58 g, 40.1 mmol) in acetic acid (2 mL). The resulting mixture was then stirred at room temperature for 16 h during which the color of the solution changed from white to black and finally to yellow. The mixture was poured into ice-water (1000 mL), filtered, and

then washed with methanol and chloroform to yield product **5** (5.74 g, 73.6%) as a yellow solid. Mp > 300 ºC. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 10.31 (s, 2H, -O*H*), 8.98 (d, J = 2.4 Hz, 2H), 8.29 (d, J = 9.0 Hz, 2H), 7.98 (dd, J = 2.4, 9.3 Hz, 2H), 7.54 (d, J = 9.0 Hz, 2H), 7.09 (d, J = 9.3 Hz, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 157.1, 142.4, 137.0, 132.1, 126.3, 125.5, 125.2, 120.6, 119.6, 115.0. EI MS: *m/z* 376 $[M]^+$. Anal. Calcd. for $C_{20}H_{12}N_2O_6 \cdot 0.5H_2O$: C, 62.34; H, 3.40; N, 7.27. Found: C, 62.62; H, 3.40; N, 7.19.

Compound 6. To a suspension of compound **5** (3.76 g, 10 mmol) in acetone (100 mL) was added potassium carbonate (5.52 g, 40 mmol) and methyl iodide (4.26 g, 30 mmol), and the reaction mixture was refluxed for 24 h. After the solvent was evaporated to leave a volume of 30 mL, the mixture was cooled to 25 °C, treated with water (160 mL), and then filtered. The resulting solid was washed with water and dried to afford 3.96 g (98%) of **6** as a yellow powder. Mp > 300 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.87 (s, 2H), 8.22 (d, J = 9.1 Hz, 2H), 7.99 (dd, J = 9.3, 2.2 Hz, 2H), 7.61 (d, J = 9.1 Hz, 2H), 7.13 (d, J = 9.3 Hz, 2H), 3.84 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.0, 143.9, 136.5, 132.5, 127.2, 126.1, 125.3, 120.1, 118.4, 115.2, 56.5. EI MS: *m/z* 404 $[M]^+$. Anal. Calcd. for $C_{22}H_{16}N_2O_6 \cdot 0.5H_2O$: C, 63.92; H, 4.15; N, 6.78. Found: C, 64.41; H, 4.01; N, 6.77.

(±)-2,2'-Dimethoxy-1,1'-binaphthyl-6,6'-diamine (±)-7. A mixture of the nitro precursor **6** (4.85 g, 8 mmol) dissolved in DMF (50 mL) and 10% Pd/C (0.29 g) was stirred at ambient temperature under a 4 bar atmosphere of hydrogen for 4 h. The reaction mixture was filtered through Celite, and concentrated. The product was characterized by

^{1}H NMR and used without further purification. Mp 217-218 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69 (d, J = 9.0 Hz, 2H), 7.34 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 2.3 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 7.13 (dd, J = 8.9, 2.3 Hz, 2H), 3.70 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.8, 142.2, 130.6, 128.5, 127.0, 126.8, 120.5, 119.0, 115.5, 109.0, 57.3. EI MS: *m/z* 344 $[M]^+$. Anal. Calcd. for $C_{22}H_{20}N_2O_2 \cdot 0.5H_2O$: C, 74.77; H, 5.99; N, 7.93. Found: C, 75.11; H, 5.79; N, 7.93.

General Method for Synthesis of Oligomers. To the solution of 2,2'-dimethoxyl-1,1'-binaphthyl-6,6'-diamine (344 mg, 1.0 mmol) in CH_2Cl_2 (50 mL) was added the acid (2.0 mmol), 1-hydroxylbenzotriazole (HOBt) (383 mg, 2.5 mmol), and DCC (515 mg, 2.5 mmol). The reaction mixture was stirred at room temperature until the starting material was completely consumed in TLC. The precipitates were removed by filtration through the Celite. The solution was concentrated, and the residue was washed with MeOH. The solid was purified by silica-gel column chromatography (ethyl acetate/petrol ether 1:1) to give the product as a yellow solid.

(±)-1. Yield: 83%. Mp 279-284 ºC. ^{1}H NMR ($CDCl_3$, 600MHz): δ 10.94 (s, 2H, N*H*), 10.68 (s, 2H, N*H*), 8.71-7.01 (m, 28H), 4.17 (d, J = 5.0 Hz, 4H), 4.09 (d, 4H, J = 4.1 Hz), 3.88 (s, 6H), 2.34-2.26 (m, 4H), 1.17-1.14 (m, 24H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.2, 163.1, 161.94, 161.89, 154.7, 150.84, 150.76, 144.4, 137.8, 133.6, 131.5, 129.8, 129.4, 129.1, 126.4, 124.3, 122.5, 120.6, 120.3, 119.7, 119.5, 116.5, 115.0, 101.4, 75.4, 57.0,

28.1, 19.2. TOF MS: *m/z* 1284 $[M+H]^+$. Anal. Calcd. for $C_{78}H_{74}N_8O_{10}\cdot 2H_2O$: C, 71.00; H, 5.96; N, 8.49. Found: C, 70.93; H, 5.91; N, 8.34.

(±)-2. Yield: 75%. Mp 273-276 ºC. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.24 (s, 2H, N*H*), 10.87 (s, 2H, N*H*) 10.74 (s, 2H, N*H*), 10.10 (s, 2H, N*H*), 8.50-6.98 (m, 44H), 4.01 (bs, 4H), 3.81 (s, 6H), 3.72-3.21 (m, 12H), 2.31-2.02 (m, 6H), 1.96-1.92 (m, 2H), 1.25-0.94 (m, 48H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.0, 162.8, 162.7, 162.6, 162.3 162.2, 161.7, 161.2, 154.5, 151.0, 150.6, 150.5, 149.7, 144.7, 144.6, 144.3, 144.0, 137.6, 133.6, 131.2, 129.9, 129.5, 129.4, 128.8, 126.3, 125.7, 124.6, 123.9, 123.7, 122.6, 122.3, 122.0, 121.7, 120.6, 120.3, 120.0, 119.5, 119.3, 116.4, 114.9, 101.7, 101.2, 100.7, 75.4, 75.1, 75.0, 74.5, 57.0, 28.2, 28.12, 28.07, 28.0, 19.3 19.2, 19.14, 19.10, 19.0. TOF MS: *m/z* 2252 $[M+H]^+$. Anal. Calcd. for $C_{134}H_{130}N_{16}O_{18}\cdot 2H_2O$: C, 70.32; H, 5.90; N, 9.79. Found: C, 70.42; H, 5.95; N, 9.77.

(±)-3. Yield: 50%. Mp 296-298 ºC. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.91-10.27 (m, 12H, N*H*), 8.21-6.90 (m, 60H), 4.14-3.52 (m, 30H), 2.37-2.00 (m, 12H), 1.22-0.93 (m, 72H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.1, 163.0, 162.8, 162.5, 162.2, 161.8, 154.5, 150.5, 150.3, 150.1, 144.9, 144.8, 144.5, 137.6, 131.5, 131.2, 129.4, 129.3, 128.6, 126.0, 125.5, 125.2, 124.8, 123.7, 122.9, 122.8, 122.4, 122.1, 120.7, 120.1, 119.5, 119.3, 114.6, 101.6, 101.1, 75.4, 74.8, 56.9, 28.3, 28.11, 28.08, 19.3, 19.2, 19.09, 19.06. TOF MS: *m/z* 3322 $[M+H]^+$. Anal. Calcd. for $C_{190}H_{186}N_{24}O_{26}\cdot 2H_2O$: C, 70.05; H, 5.88; N, 10.32. Found: C, 69.70; H, 5.89; N, 10.29.

(*S*)-1. Yield: 86%. Mp 276-278 ºC. $[\alpha]^{20}_{D}$ = +90 (c=1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.89 (s, 2H, N*H*), 10.61 (s, 2H, N*H*), 8.71-7.00 (m, 28H), 4.14 (d, *J* = 6.5 Hz, 4H), 4.09 (d, 4H, *J* = 6.5 Hz), 3.86 (s, 6H), 2.37-2.27 (m, 4H), 1.17-1.12 (m, 24H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.4, 163.3, 162.1, 162.0, 154.8, 150.9, 144.6, 137.8, 133.5, 131.5, 129.8, 129.4, 129.1, 126.5, 124.4, 122.7, 120.7, 120.5, 119.7, 119.6, 116.5, 115.1, 101.5, 101.4, 75.5, 57.0, 28.1, 19.20, 19.18. TOF MS: *m/z* 1284 $[M+H]^+$. Anal. Calcd. for $C_{78}H_{74}N_8O_{10}\cdot 2H_2O$: C, 71.00; H, 5.96; N, 8.49. Found: C, 70.93; H, 5.81; N, 8.48.

(*S*)-2. Yield: 74%. Mp 274-275 ºC. $[\alpha]^{20}_{D}$ = +54 (c=1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.29 (s, 2H, N*H*), 10.85-10.80 (m, 4H, N*H*), 10.14 (s, 2H, N*H*), 8.52-6.96 (m, 44H), 4.09-4.08 (m, 8H), 3.79 (s, 6H), 3.52-3.48 (m, 4H), 3.21-3.20 (m, 4H), 2.36-1.89 (m, 8H), 1.18-0.92 (m, 48H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.9, 162.72, 162.67, 162.5, 162.4, 162.1, 161.6, 161.1, 154.5, 151.0, 150.7, 150.4, 149.8, 144.6, 144.5, 144.3, 144.0, 137.6, 133.6, 131.2, 129.8, 129.7, 129.5, 129.4, 128.7, 126.2, 125.7, 124.5, 123.8, 122.5, 122.3, 121.9, 121.7, 120.6, 120.5, 120.3, 119.9, 119.6, 119.2, 116.5, 114.9, 101.8, 101.2, 100.8, 75.3, 75.1, 74.9, 74.5, 56.9, 28.2, 28.1, 28.0, 19.23, 19.18, 19.11, 19.07, 19.0. TOF MS: *m/z* 2252 $[M+H]^+$. Anal. Calcd. for $C_{134}H_{130}N_{16}O_{18}\cdot 2H_2O$: C, 70.32; H, 5.90; N, 9.79. Found: C, 69.00; H, 5.87; N, 9.35.

(*S*)-3. Yield: 62%. Mp 303-304 ºC. $[\alpha]^{20}_{D}$ = +258 (c=2.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.02-10.17 (m, 12H, N*H*), 8.43-6.99 (m, 60H), 4.12 (d, *J* = 6.0 Hz, 4H), 3.98 (d, *J* = 5.2 Hz, 4H), 3.85 (s, 6H), 3.60-3.32 (m, 16H), 2.67-1.99 (m, 12H), 1.22-0.92 (m,

72H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.5, 163.4, 162.71, 162.66, 162.5, 162.4, 162.1, 161.4, 161.2, 160.7, 160.2, 159.0, 154.4, 153.7, 151.3, 151.1, 150.9, 150.8, 150.3, 149.7, 145.0, 144.8, 144.7, 144.6, 144.4, 144.0, 143.2, 138.5, 137.6, 134.1, 133.7, 131.7, 131.1, 130.8, 129.4, 128.4, 127.7, 125.9, 125.8, 125.4, 125.0, 124.3, 123.4, 122.9, 122.8, 122.4, 122.1, 122.02, 121.99, 121.6, 121.4, 121.0, 120.7, 120.6, 120.4, 120.2, 119.9, 119.7, 119.3, 119.1, 117.1, 114.4, 102.2, 102.1, 101.8, 101.2, 75.4, 74.8, 57.1, 56.8, 28.5, 28.3, 28.1, 27.6, 27.2, 19.7, 19.5, 19.4, 19.3, 19.2, 19.10, 19.05, 18.9, 18.5, 18.1. MALDI-TOF MS: *m/z* 3221 $[M+H]^+$. Anal. Calcd. for $C_{190}H_{186}N_{24}O_{26}\cdot 4H_2O$: C, 69.28; H, 5.94; N, 10.21. Found: C, 69.24; H, 5.91; N, 10.13.

2. ^{1}H NMR and ^{13}C NMR spectra of new compounds

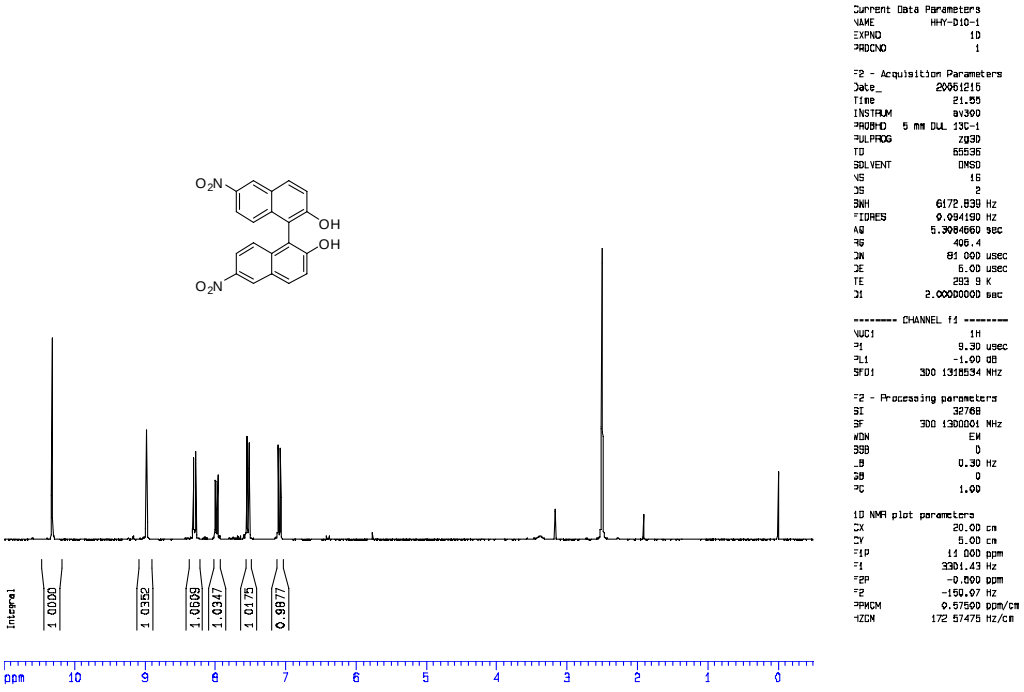


Figure S1. The ^{1}H NMR spectrum of compound 5.

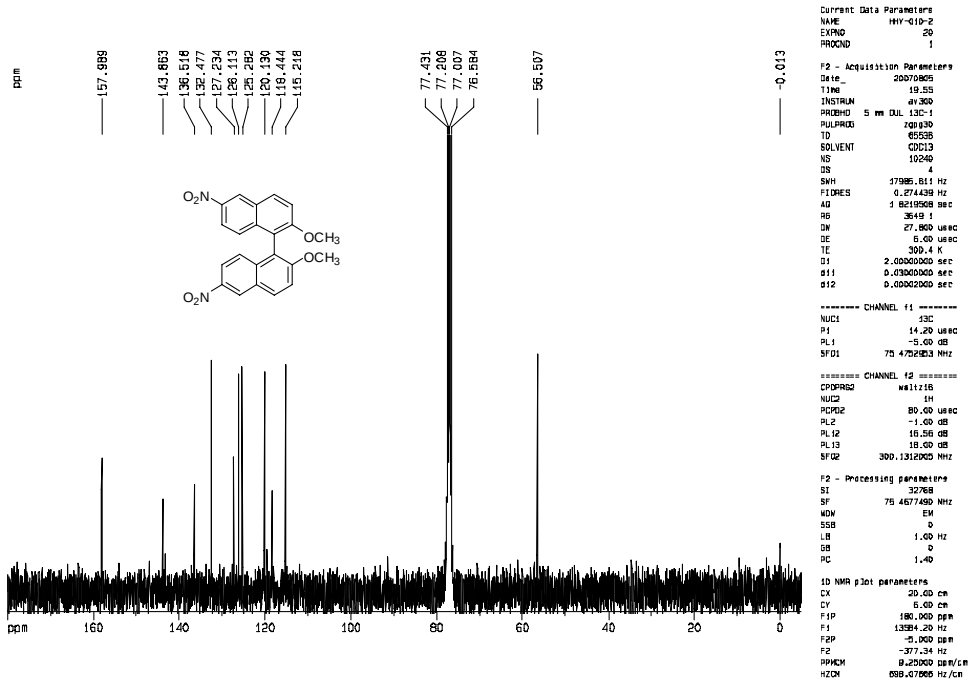


Figure S2. The ^{13}C NMR spectrum of compound 5.

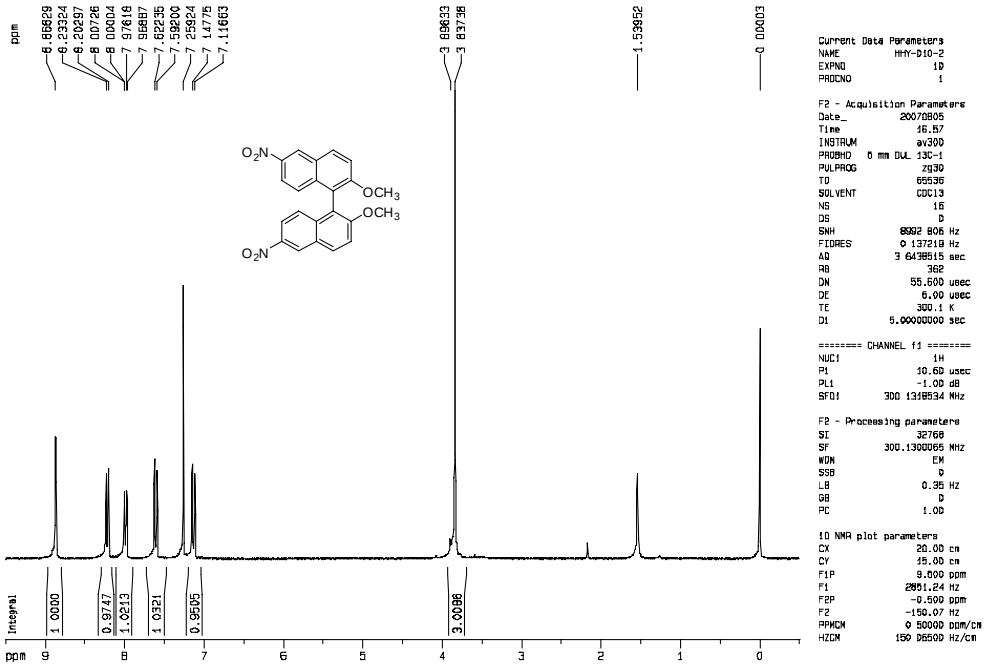


Figure S3. The ^{1}H NMR spectrum of compound 6.

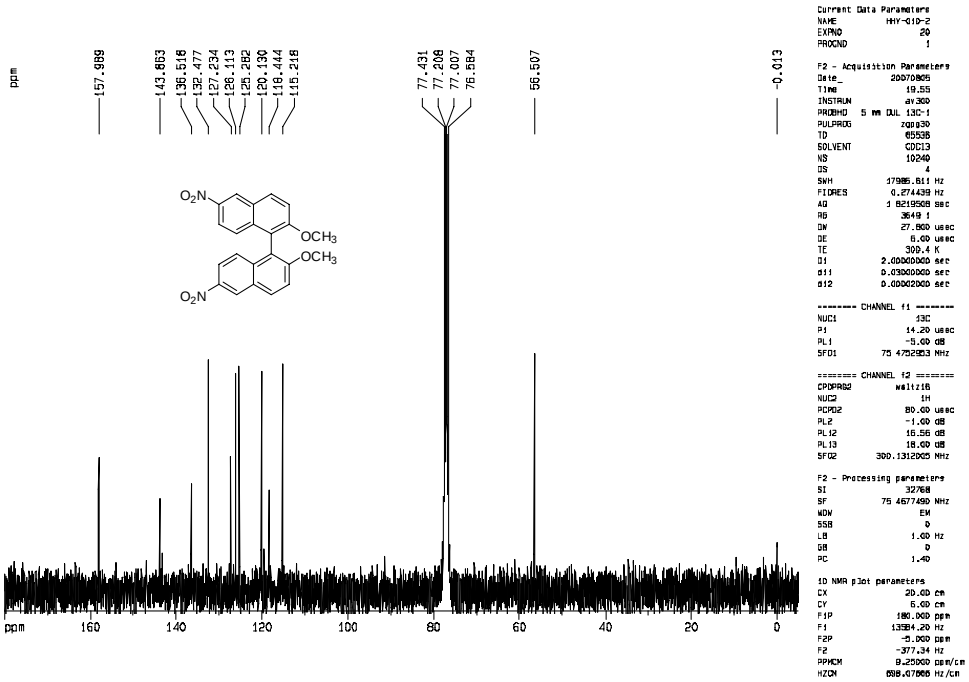


Figure S4. The ^{13}C NMR spectrum of compound 6.

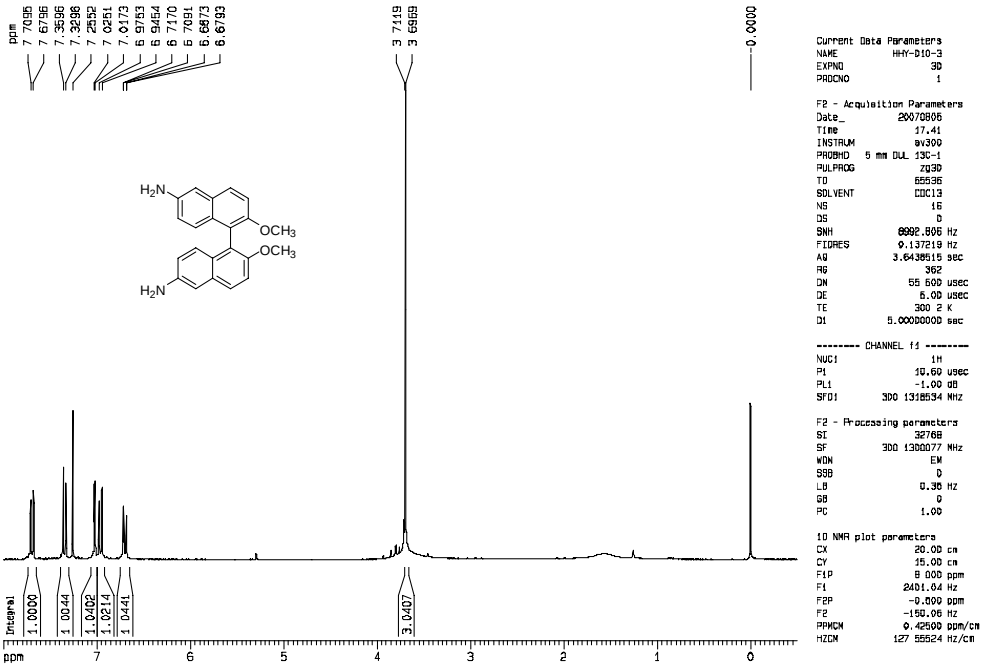


Figure S5. The ^{1}H NMR spectrum of compound 7.

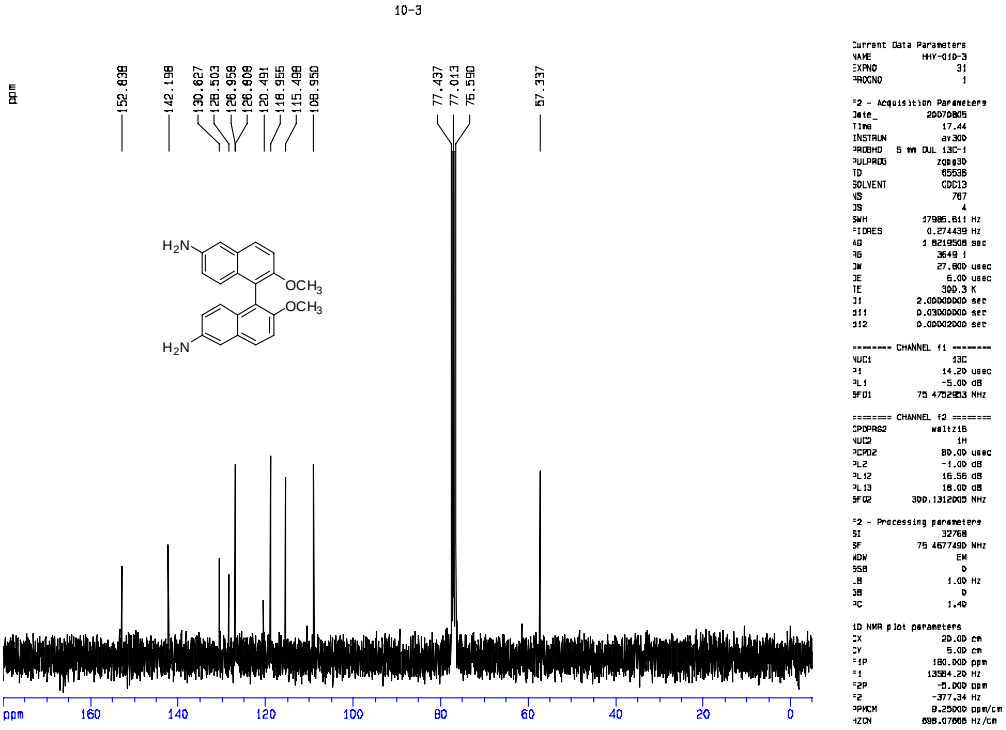


Figure S6. The ^{13}C NMR spectrum of compound 7.

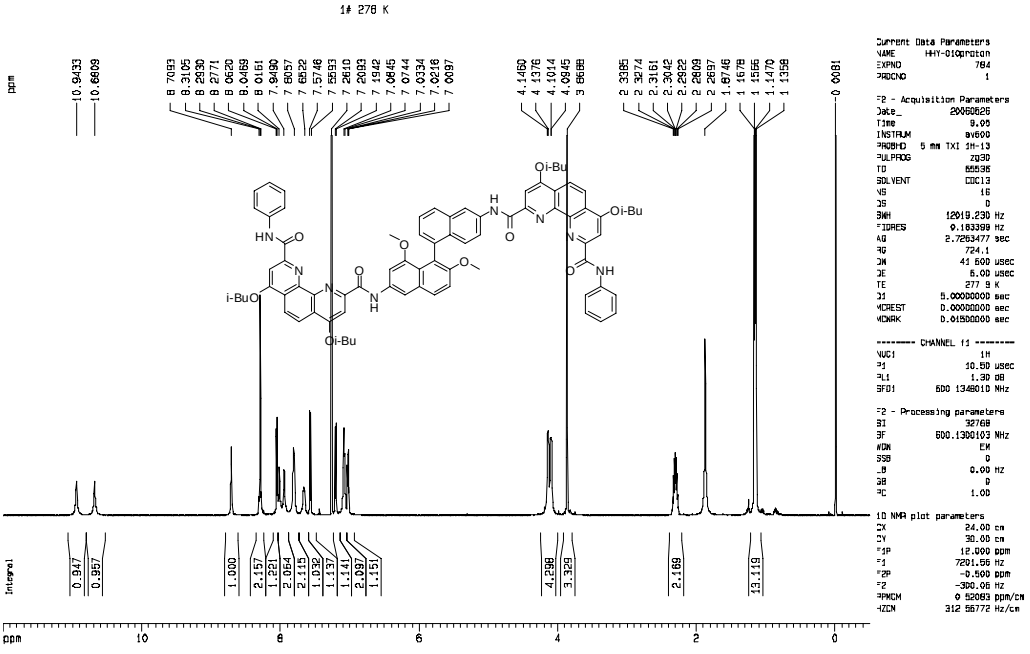


Figure S7. The ^{1}H NMR spectrum of compound (±)-1.

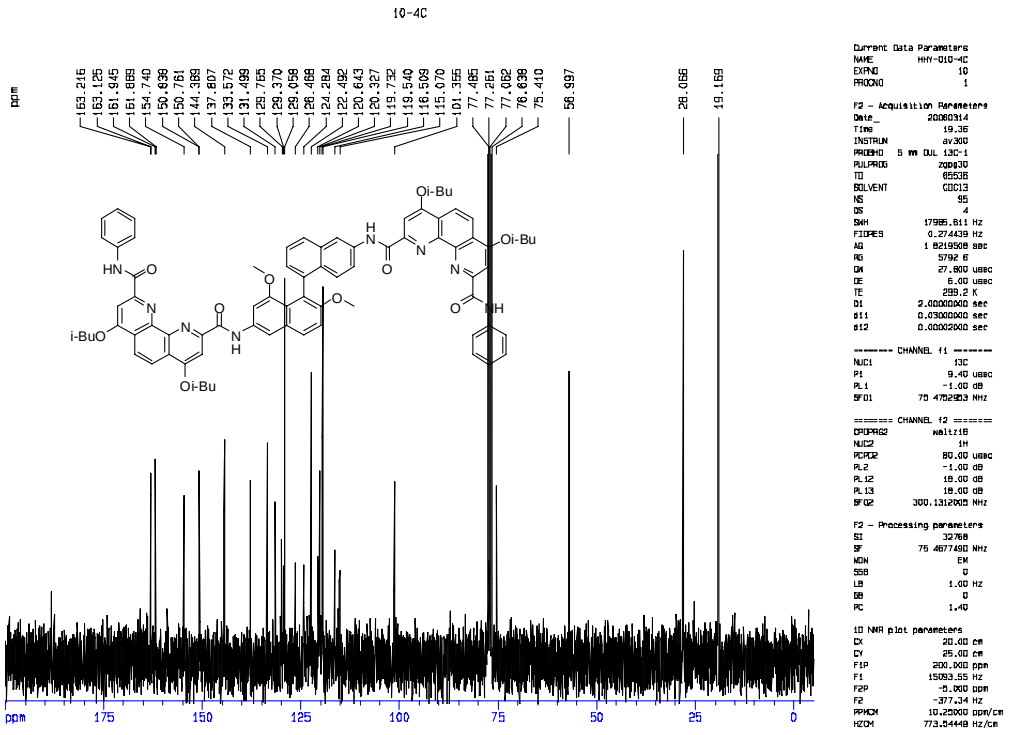


Figure S8. The ^{13}C NMR spectrum of compound (±)-1.

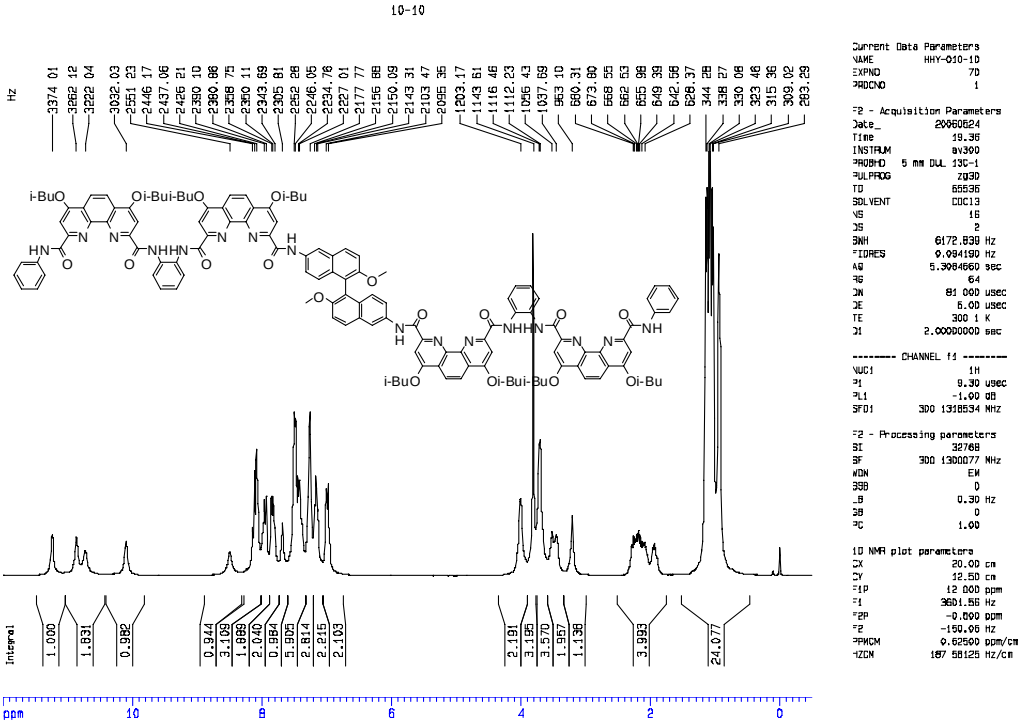


Figure S9. The ^{1}H NMR spectrum of compound (±)-2.

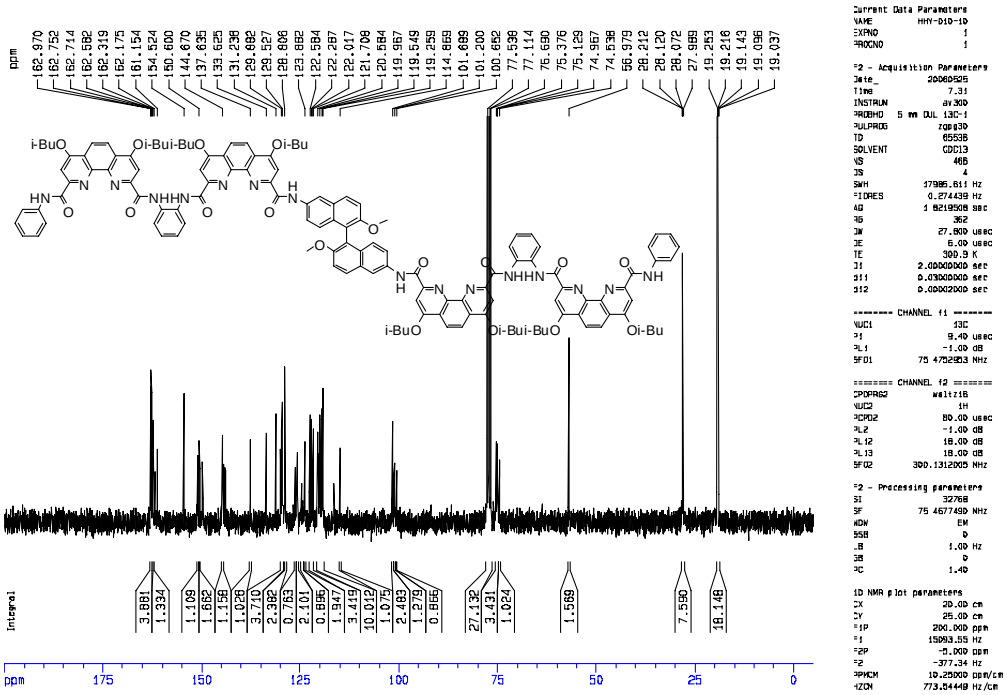


Figure S10. The ^{13}C NMR spectrum of compound (±)-2.

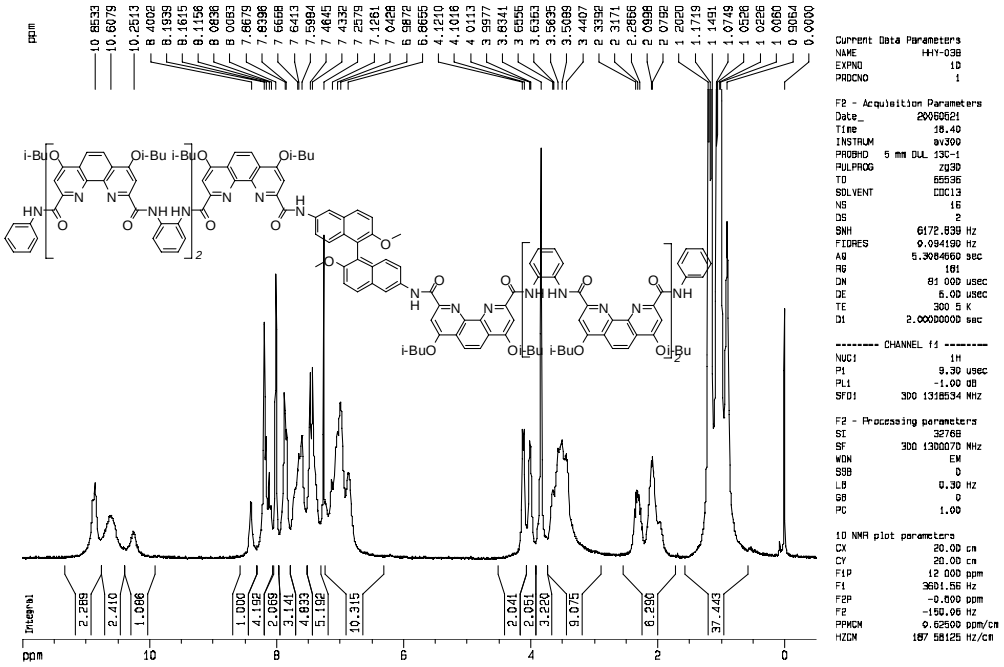


Figure S11. The ^{1}H NMR spectrum of compound (±)-3.

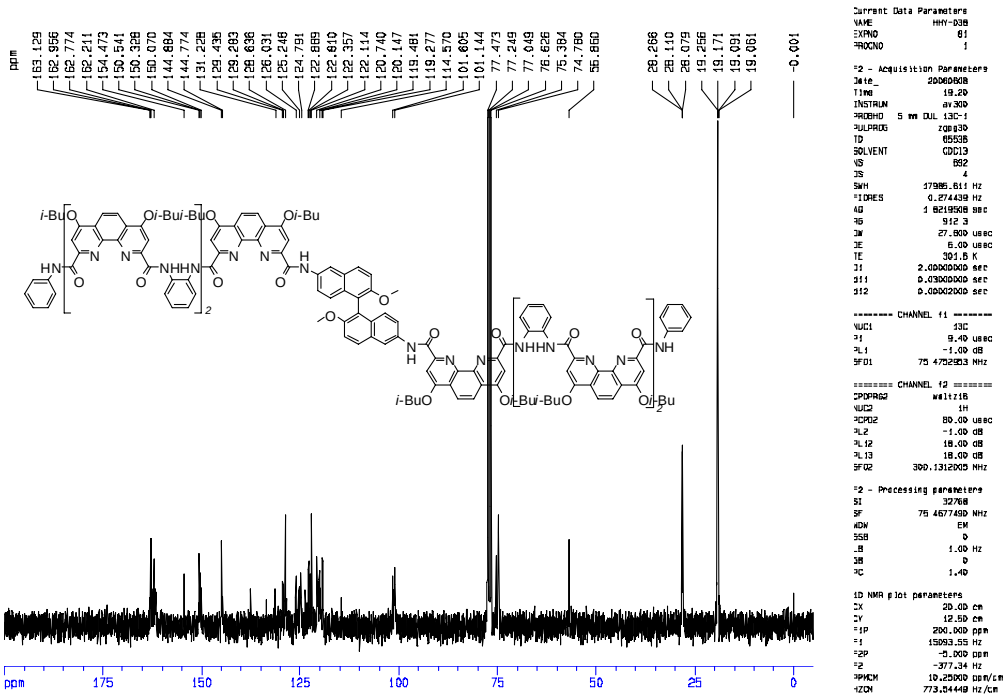


Figure S12. The ^{13}C NMR spectrum of compound (±)-3.

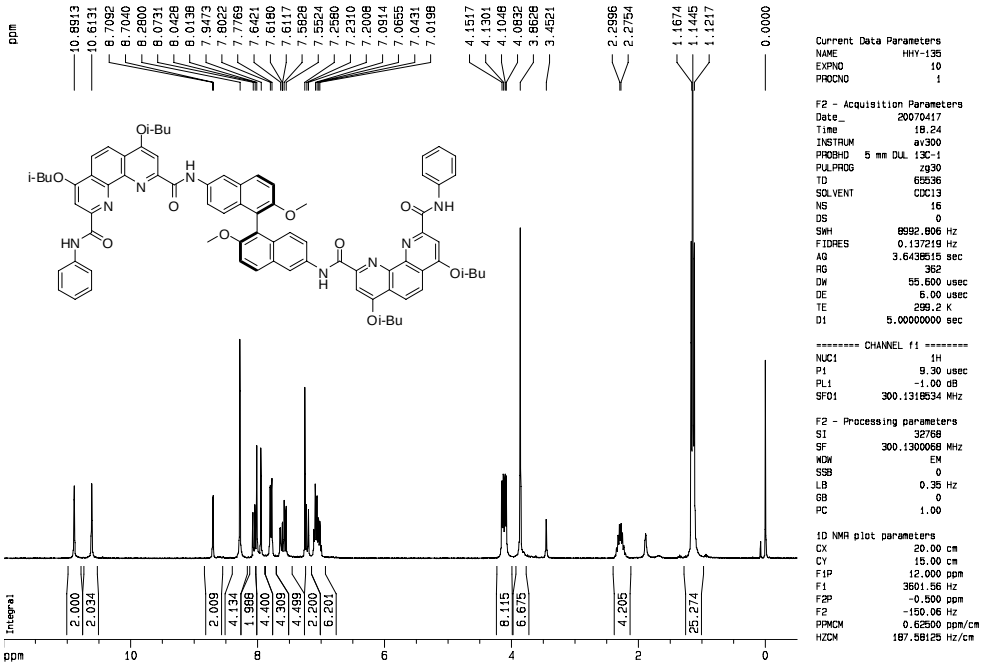


Figure S13. The ^{1}H NMR spectrum of compound (*S*)-1.

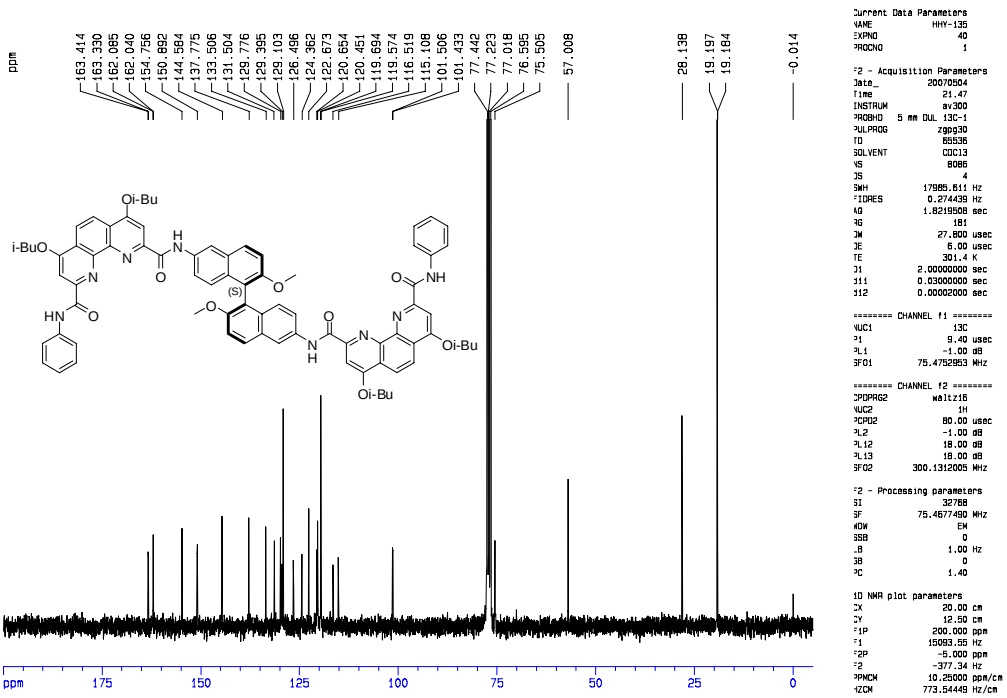


Figure S14. The ^{13}C NMR spectrum of compound (*S*)-1.

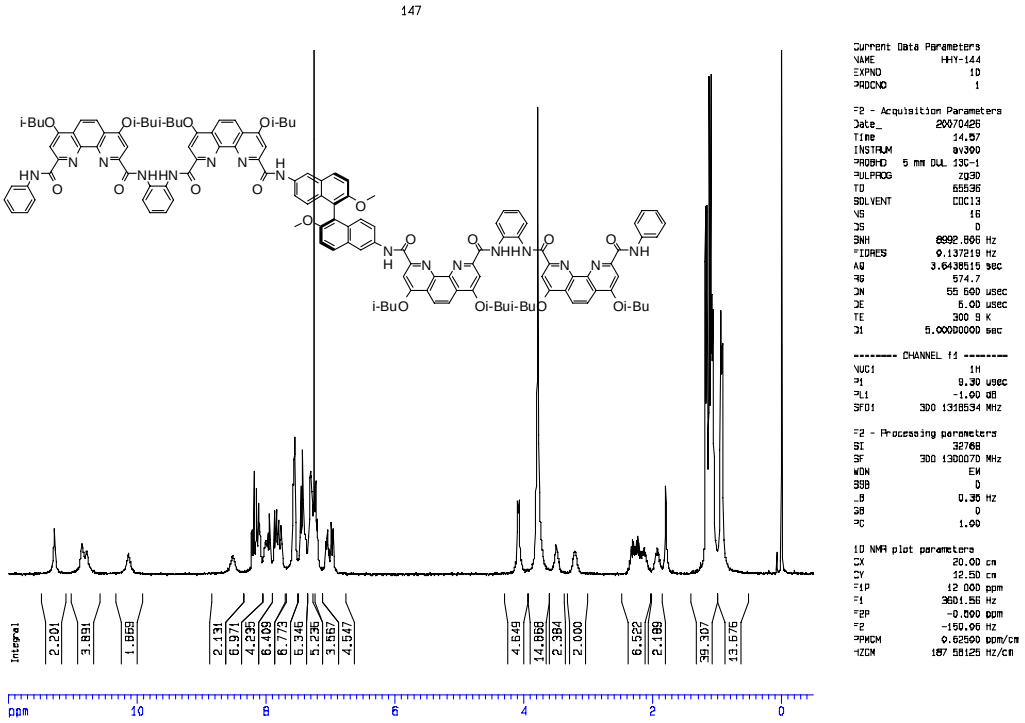


Figure S15. The ^{1}H NMR spectrum of compound (*S*)-2.

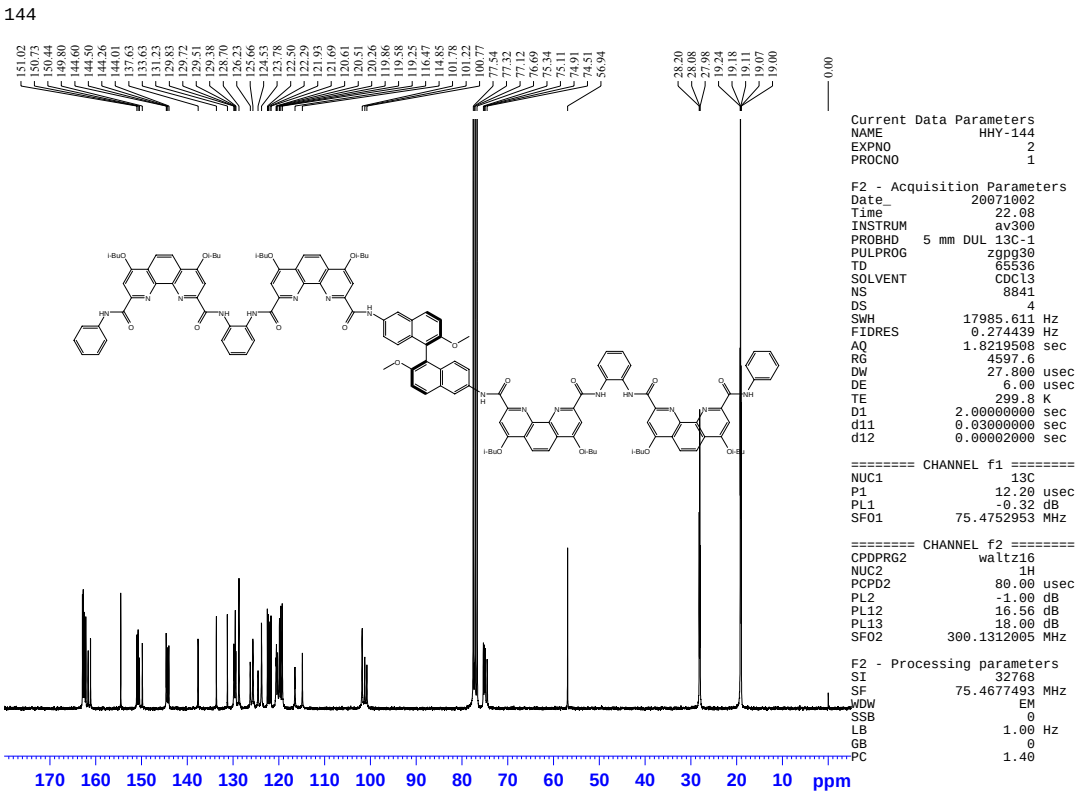


Figure S16. The ^{13}C NMR spectrum of compound (*S*)-2.

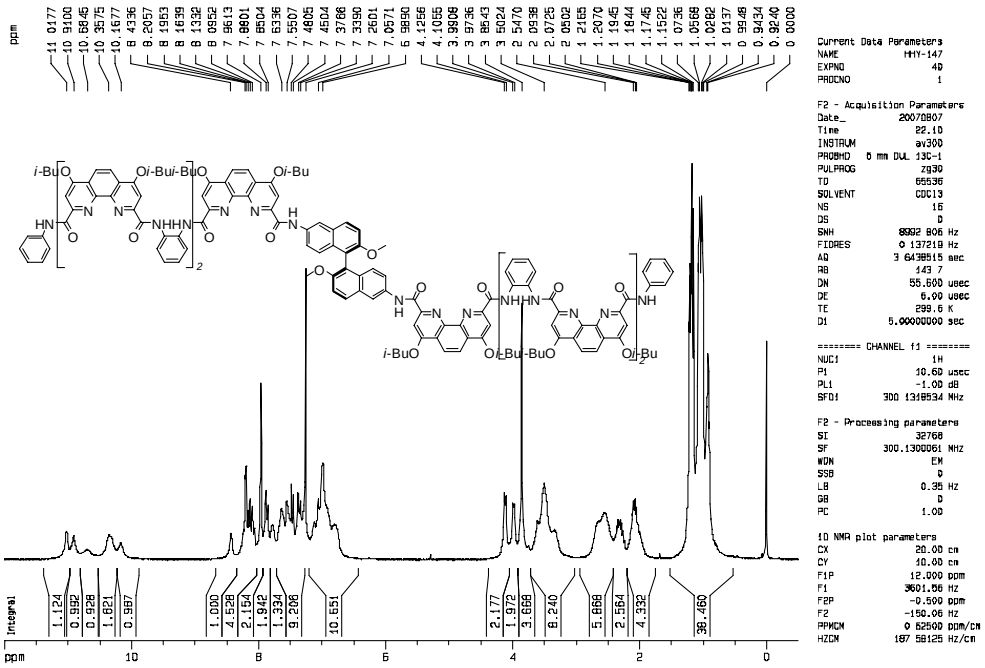


Figure S17. The ^{1}H NMR spectrum of compound (*S*)-3.

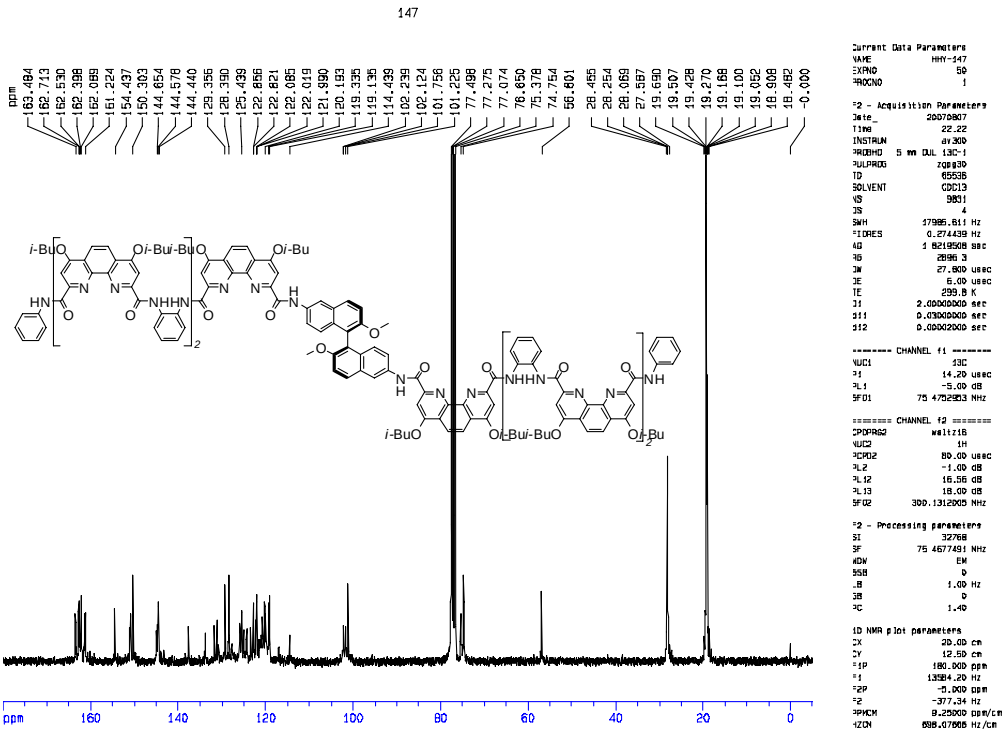


Figure S18. The ^{13}C NMR spectrum of compound (*S*)-3.

3. TOCSY and NOESY spectra of compounds (*S*)-1 and (*S*)-2

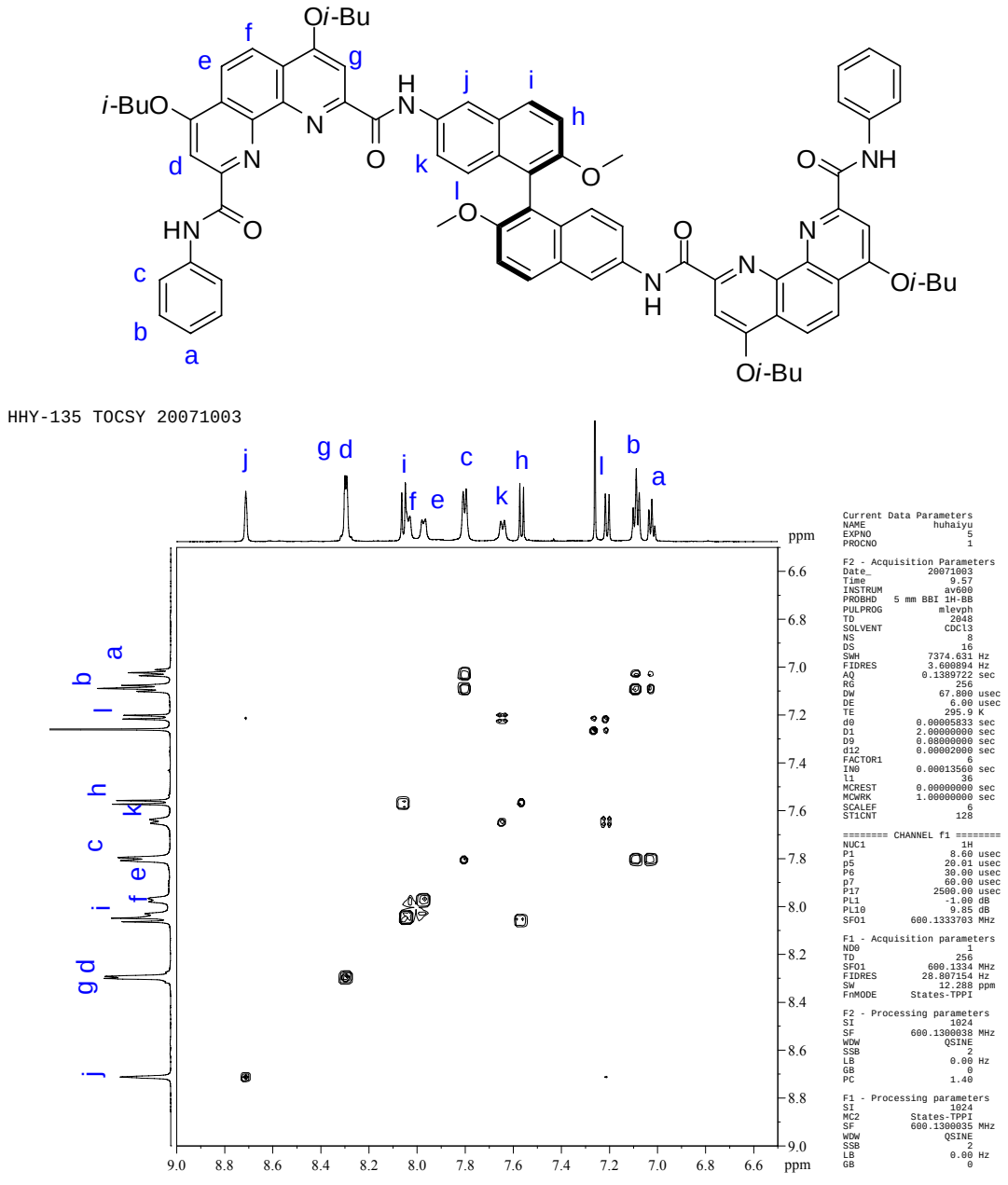
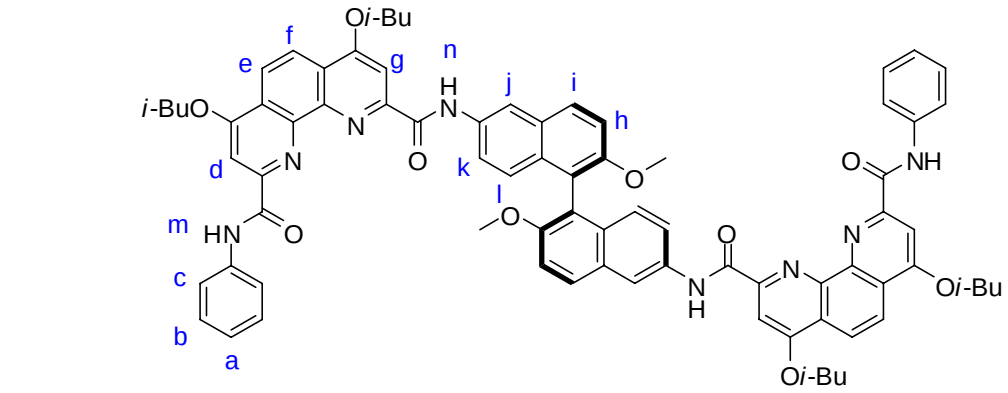


Figure S19. The TOCSY spectrum of compound (*S*)-1.



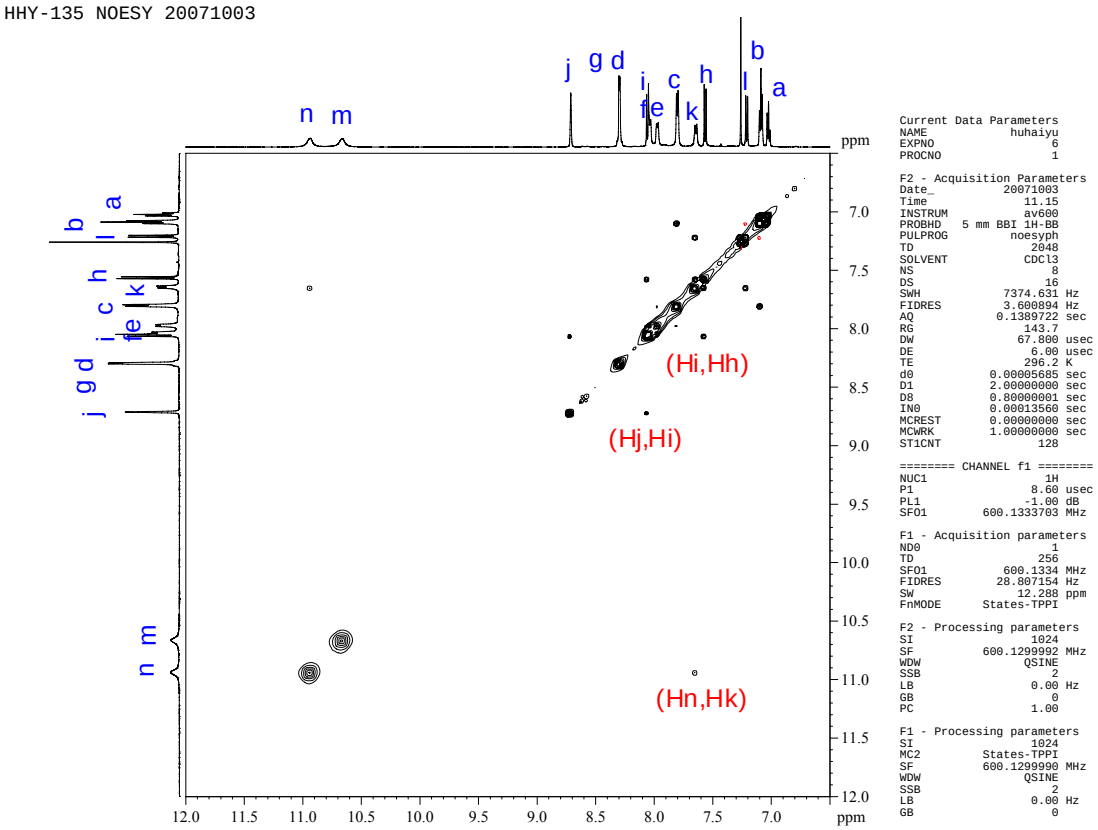


Figure S20. The NOESY spectrum of compound (*S*)-1.

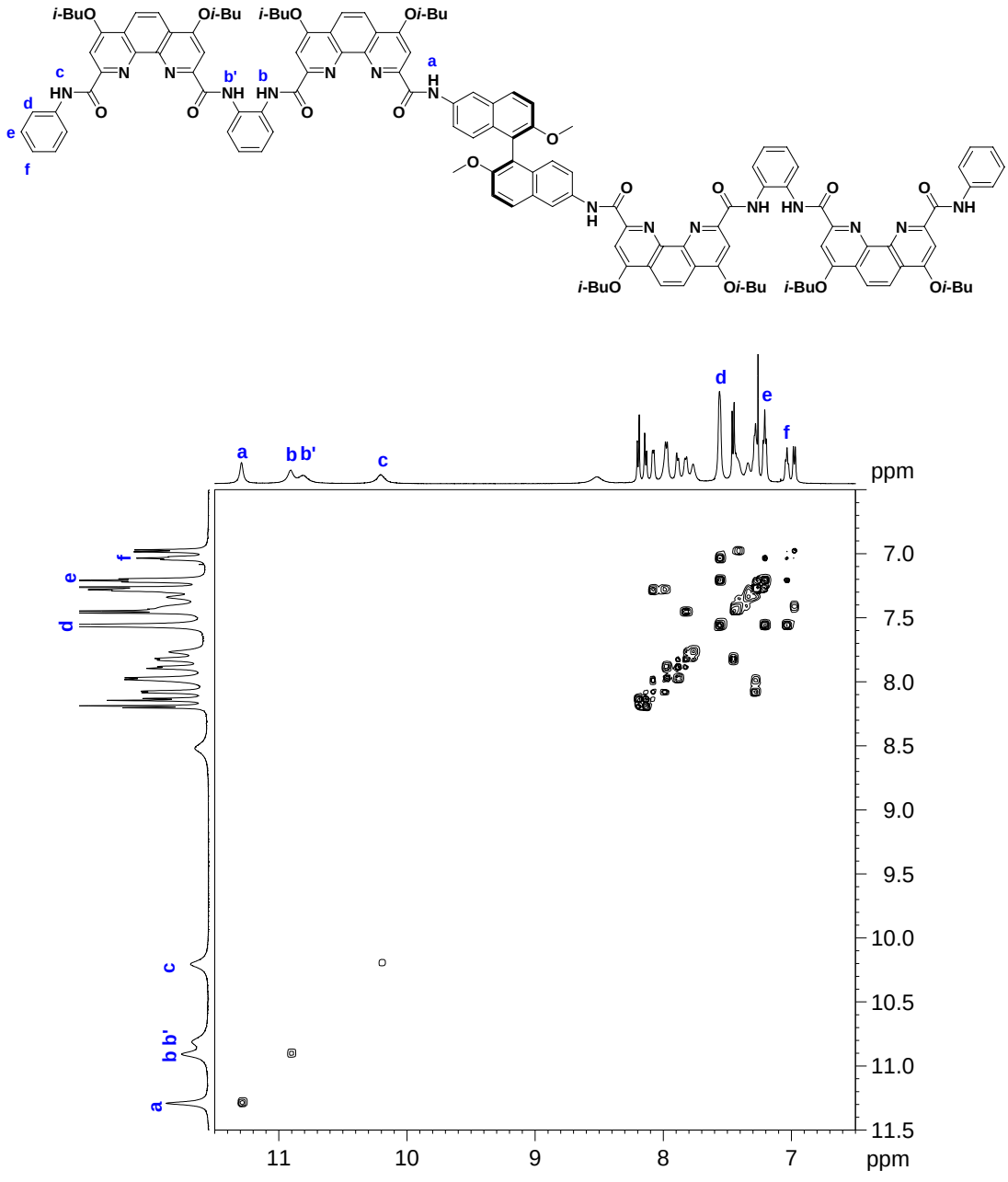


Figure S21. The TOCSY spectrum of compound (*S*)-2.

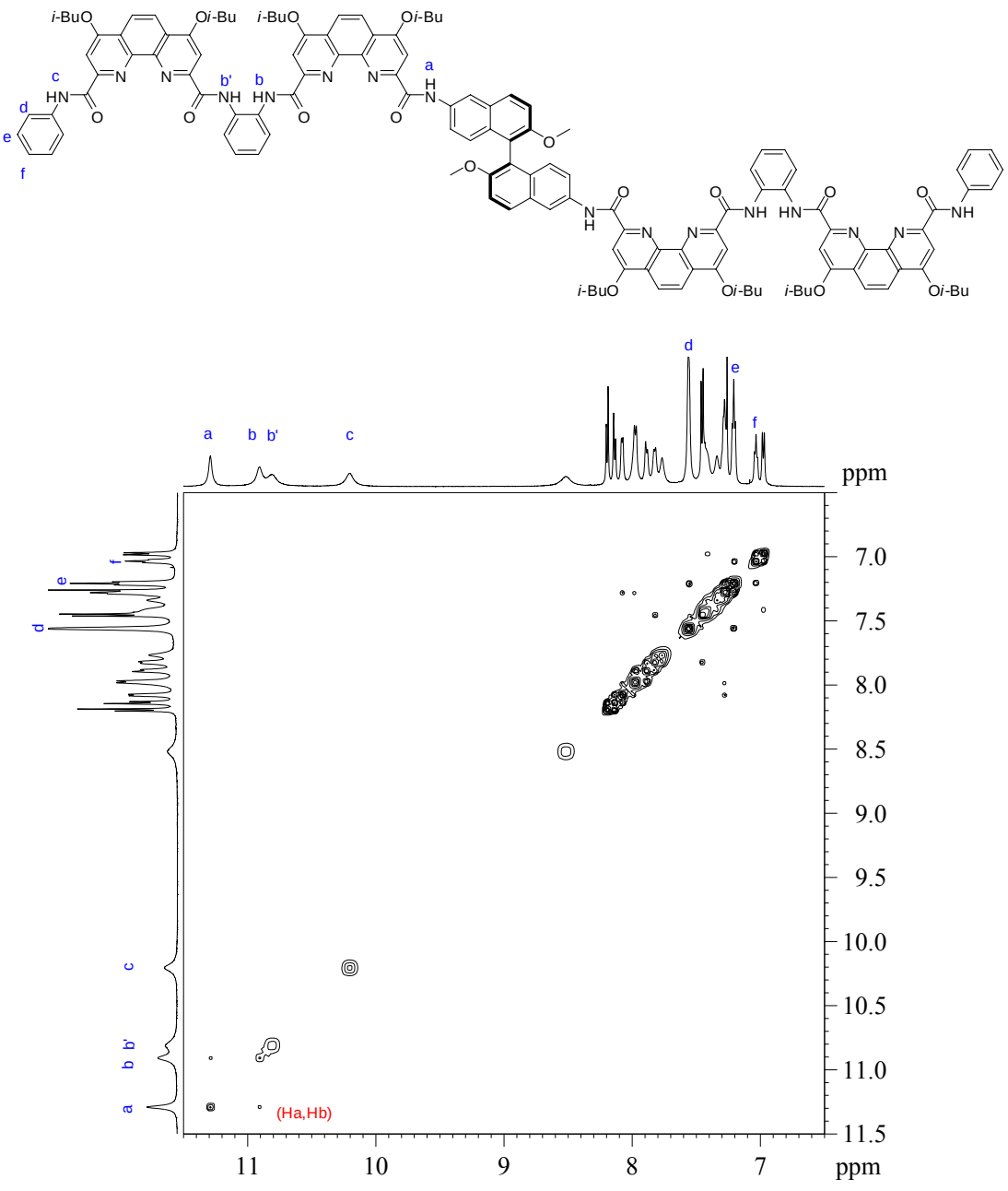


Figure S22. The NOESY spectrum of compound (*S*)-2.

4. Comparison of partial ^{1}H NMR spectra for (*S*)-1 and (*S*)-2 in $CDCl_3$

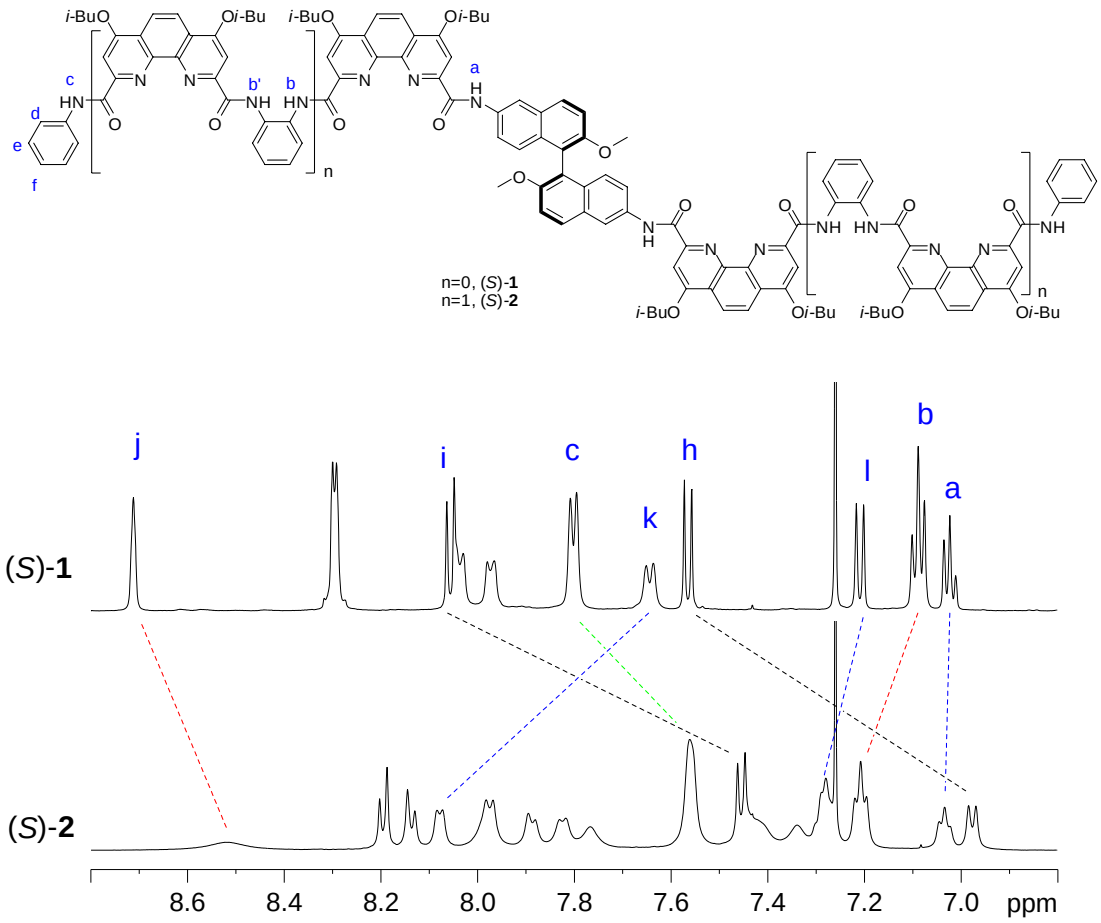


Figure S23. Partial ^{1}H NMR spectra (600 MHz) of (*S*)-1 and (*S*)-2 in $CDCl_3$.

5. UV-vis spectra of compounds (±)-1-3 and (*S*)-7

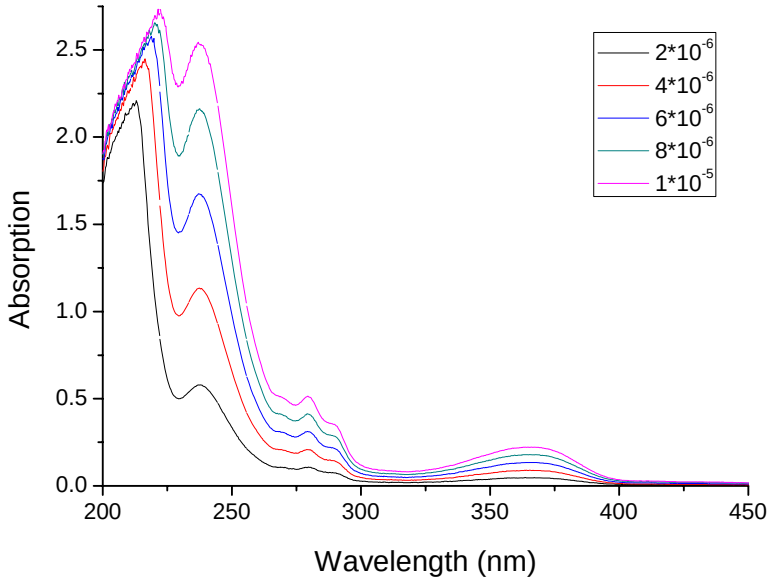


Figure S24. Representative UV spectra for compound (±)-7 in CH_3CN at various concentrations.

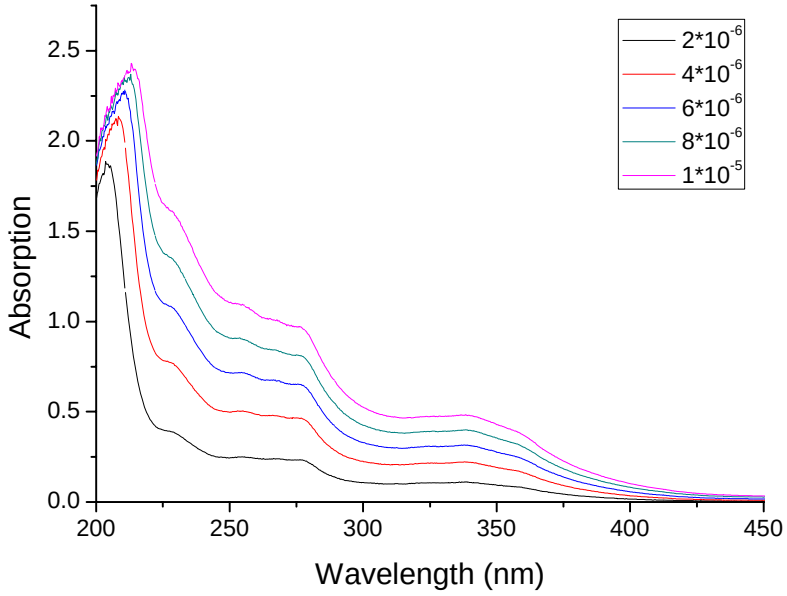


Figure S25. Representative UV spectra for compound (±)-1 in CH_3CN at various concentrations.

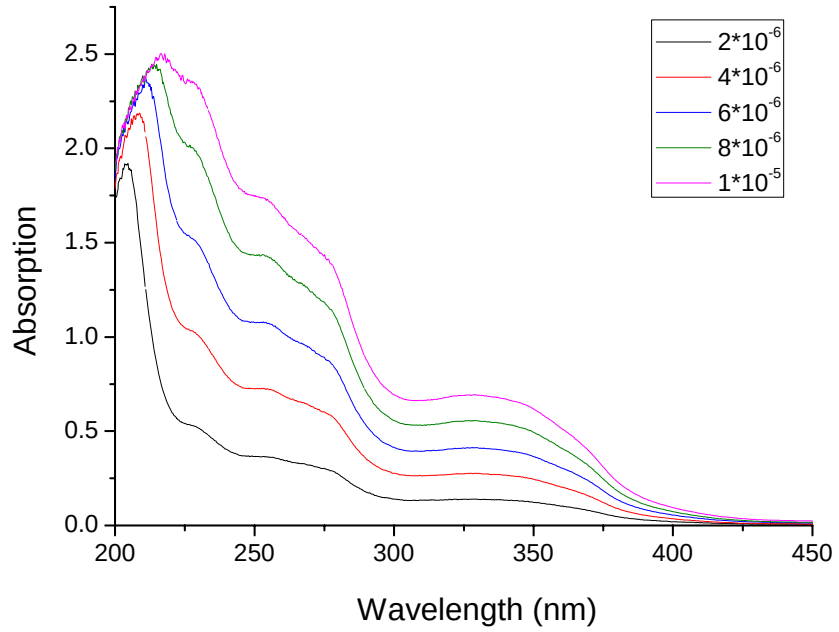


Figure S26. Representative UV spectra for compound (±)-2 in CH_3CN at various concentrations.

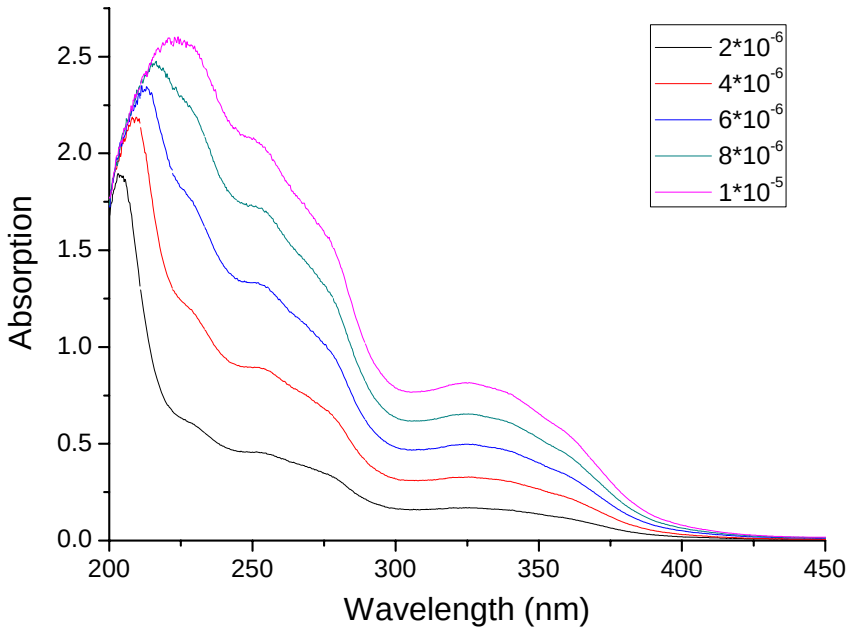


Figure S27. Representative UV spectra for compound (±)-3 in CH_3CN at various concentrations.

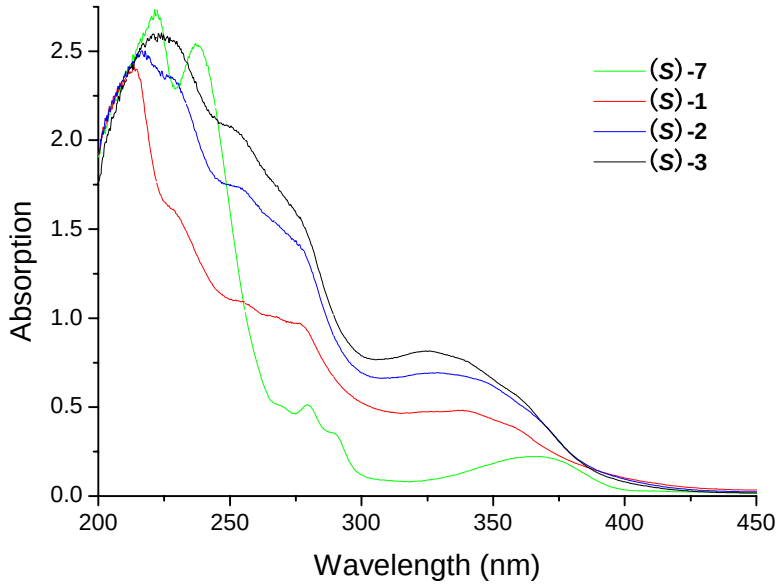


Figure S28. UV spectra of the molecular strands (±)-1 (red), (±)-2 (blue), (±)-3 (black) and (±)-7 (green) in CH_3CN ($c = 10^{-5}$ M).

6. CD spectra of compounds (S)-1-3 and (*S*)-7

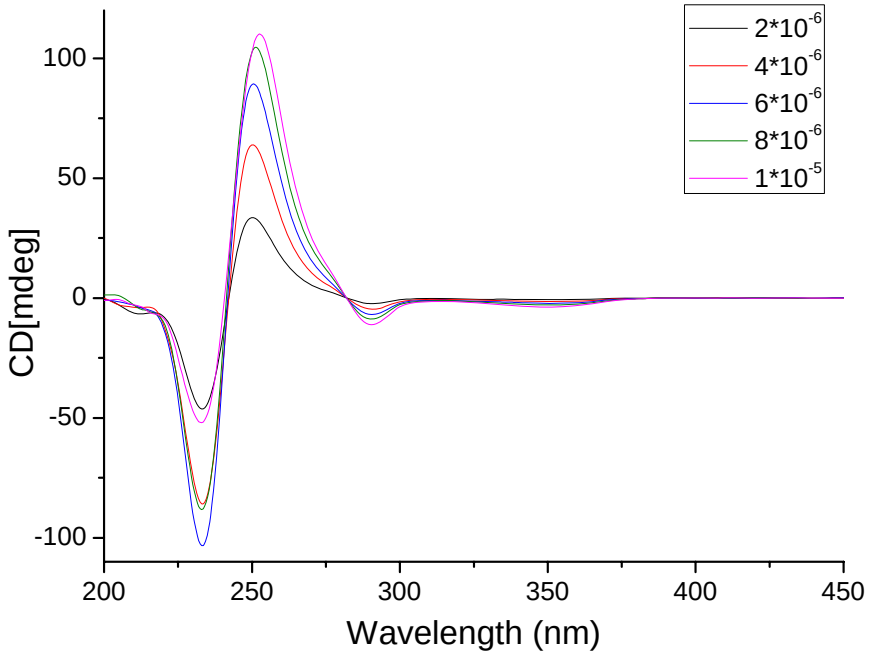


Figure S29. CD spectra for (*S*)-7 in CH_3CN at various concentrations.

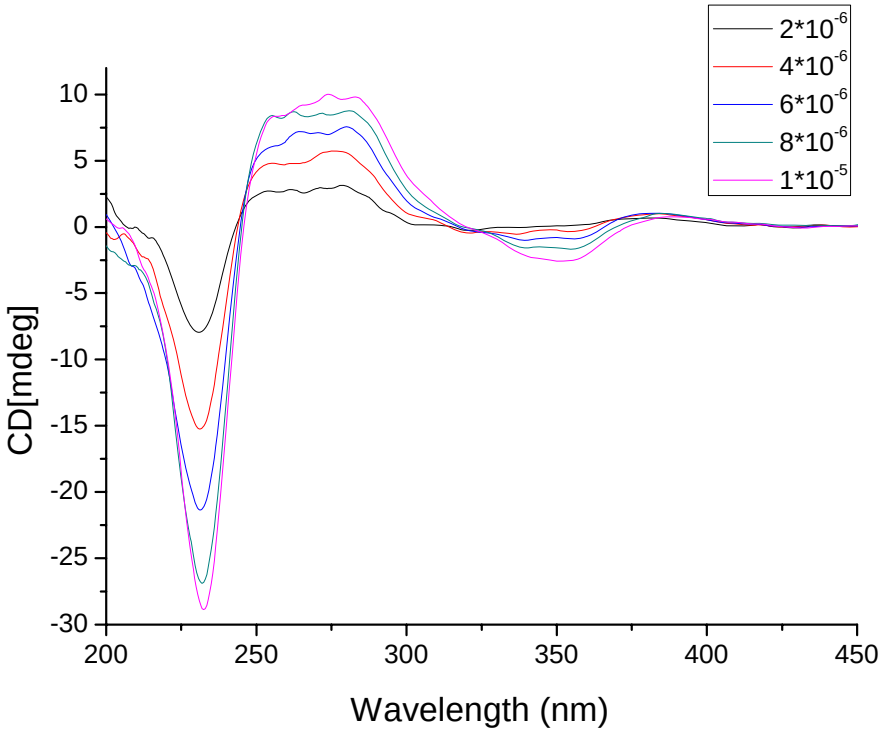


Figure S30. CD spectra for (*S*)-1 in CH_3CN at various concentrations.

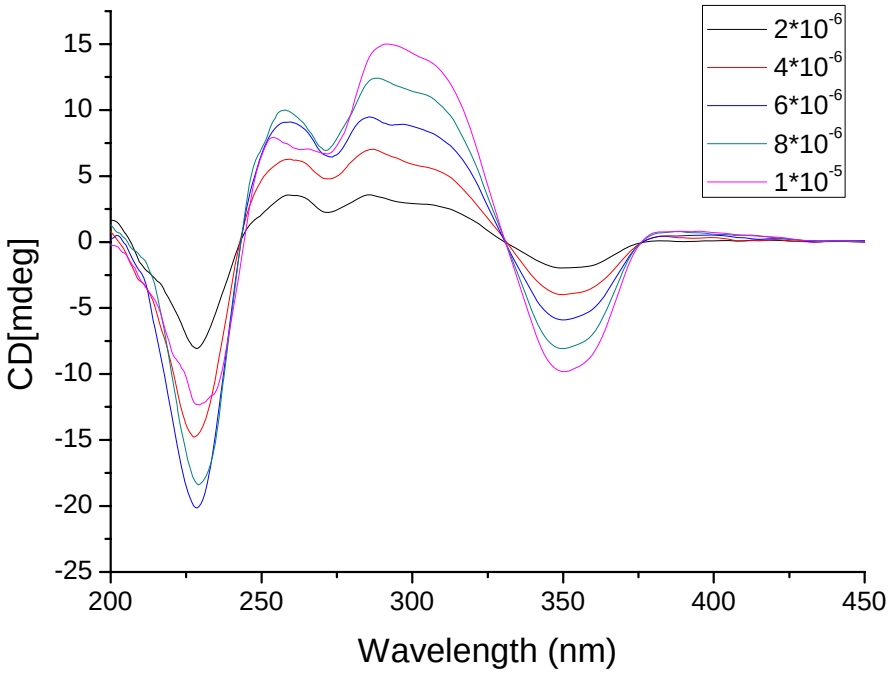


Figure S31. CD spectra for (*S*)-2 in CH_3CN at various concentrations.

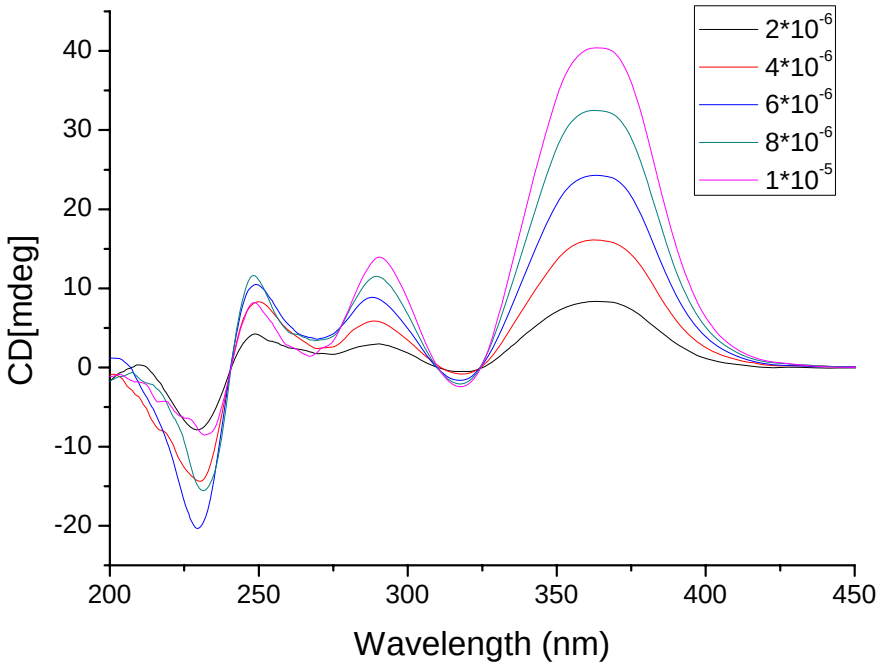


Figure S32. CD spectra for (*S*)-3 in CH_3CN at various concentrations.

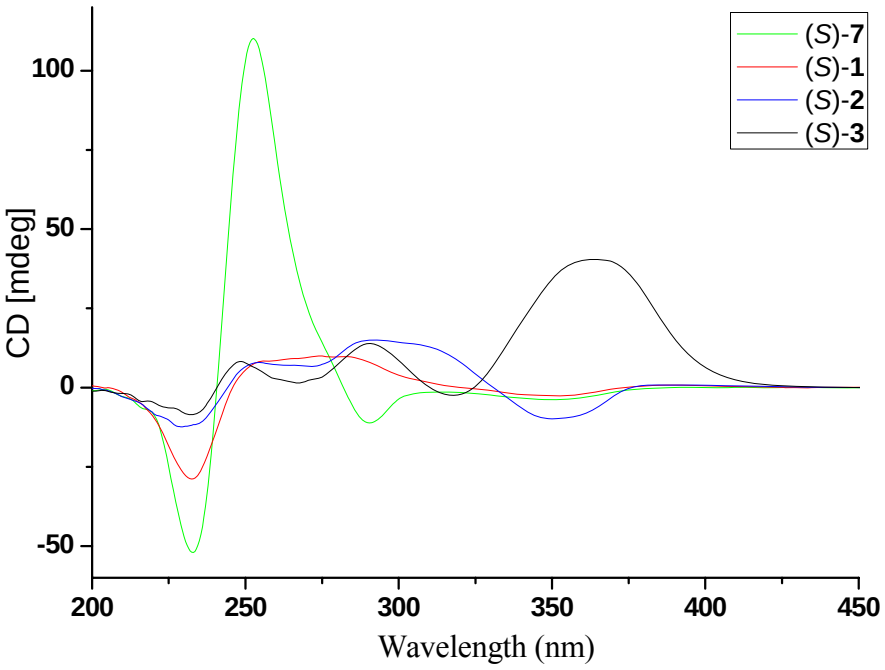
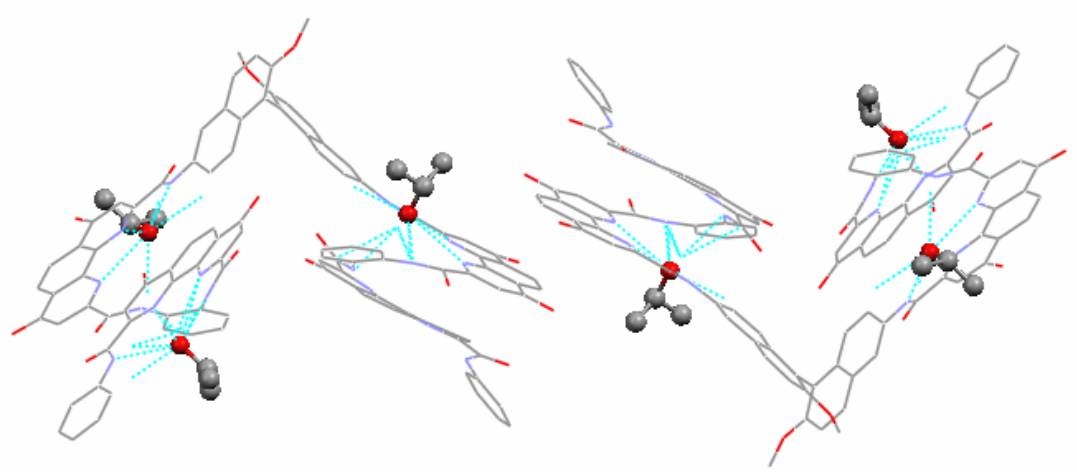


Figure S33. Circular dichroism spectra of the molecular strands (*S*)-1 (red), (*S*)-2, (blue) (*S*)-3 (black) and (*S*)-7 (green) in CH_3CN (c = 10^{-5} M).

7. Crystal packing of (±)-2

(a)



(b)

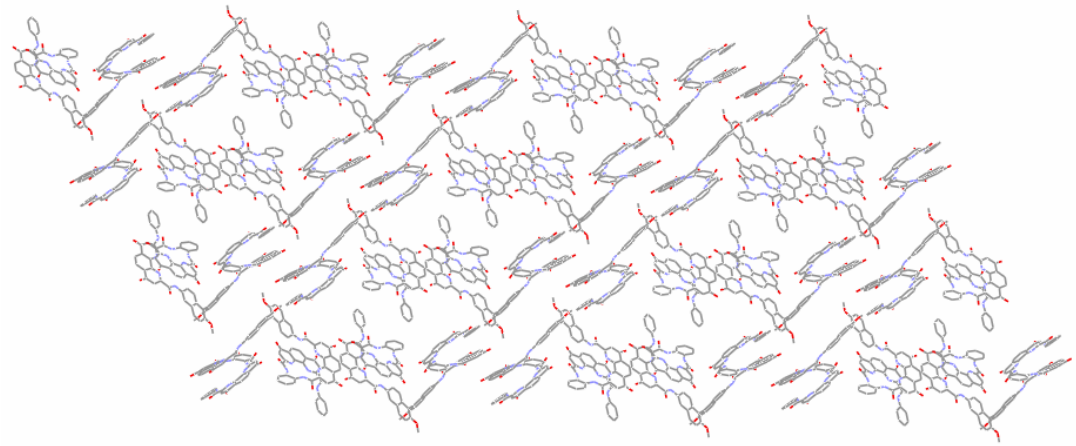


Figure S34. (a) Crystal packing of (±)-2 with the hydrogen bonding interactions between the oligomer and 2-propanol molecules (blue dotted lines); (b) view of a 2D layer structure of (±)-2. Solvent molecules not involved in the interactions, isobutyl chains, and hydrogen atoms were omitted for clarity.