

Supporting Information

Red circularly polarized luminescence from intramolecular excimers restricted by chiral aromatic oligoamide foldamers

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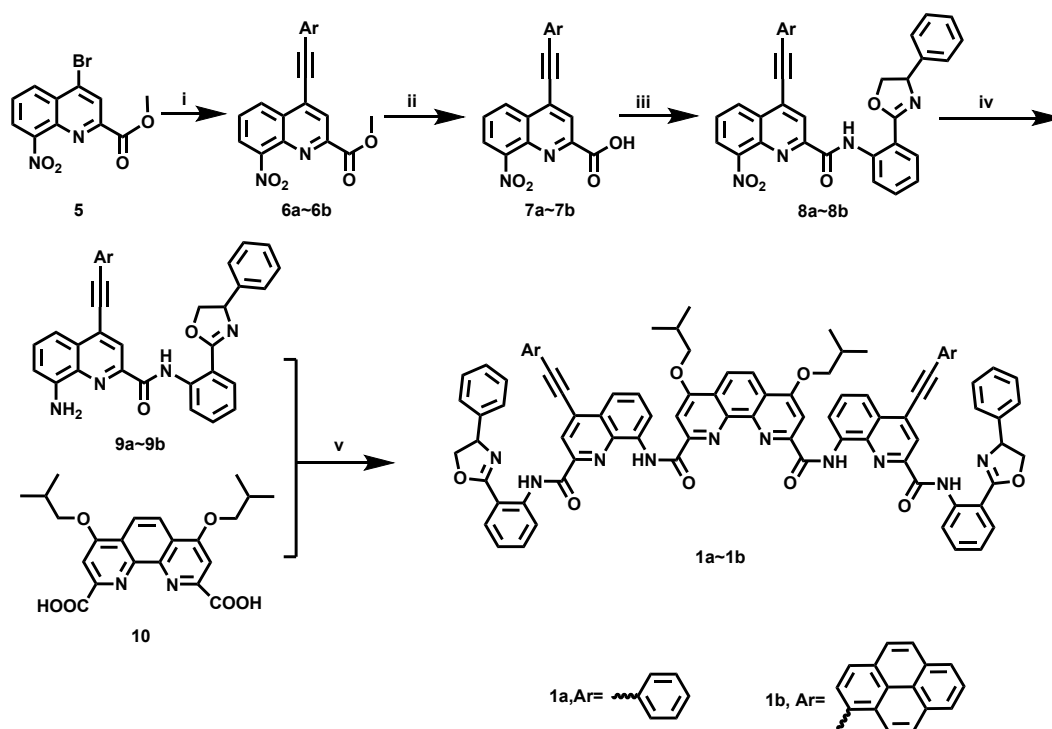
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General Procedures and Materials.

Anhydrous dichloromethane, tetrahydrofuran and dimethyl formamide were gained from PureSolv MD 5 (Inert solvent purification system). Anhydrous chlorobenzene and triethylamine were distilled over calcium hydride (CaH_2) under Ar atmosphere. *S/R*- CQ_n -**b** ($n=0, 1, 2, 3$) were prepared according to our previous work.¹ Column chromatography was carried out on flash grade silica gel, using 0 - 20 psig pressure. Analytical TLC was carried out using tapered silica plates with a preadsorbent zone. NMR spectra were obtained with a Bruker spectrometer (400 MHz) and JEOL Delta (400 MHz and 600 MHz) using chloroform- d (CDCl_3) as solvents. The chemical shift references were as follows: (^1H) chloroform- d , 7.26 ppm; (^{13}C) chloroform- d , 77.00 ppm (chloroform- d), (^1H) dichloromethane- d_2 , 5.32 ppm. Mass spectra (ESI, MALDI) were acquired on GCT and FT-ICR spectrometer (Bruker Daltonics Inc. APEXII, BIFLEX III), respectively. CD spectra were recorded on a Chirascan TM Circular Dichroism spectrometer (Applied Photophysics Ltd, Surrey, United Kingdom). CPL spectra were gained with JACSO CPL-300.

Synthesis

Synthesis of helicities of *S/R*-**1a~1b**.



Scheme S1 Synthesis of compound *S/R*-**1a~1b**. Conditions: i. $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , anhydrous THF and anhydrous Et_3N , aromatic acetylene, room temperature; ii. NaOH, THF/MeOH, 40°C; iii. HATU, DIEA, anhydrous DMF, *S*- or *R*- chiral amines; iv. Iron powder, CH_3COOH , MeOH, reflux; v. $\text{C}_2\text{Cl}_2\text{O}_2$, dry DCM, room temperature; DIEA, anhydrous DCM, room temperature.

General procedure for compound **6a~6b**: The general Sonogashira coupling procedure described above was used to prepare this compound. 500 mg of 4-bromo-8-nitro-2-quinoline carboxylate (compound **5**) (1.61 mmol, 1.0 equiv.), aromatic acetylene (1.93 mmol, 1.2 eq.), 56 mg of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.08 mmol, 0.05 eq.), and 0.1 equivalents of CuI (31 mg, 0.16 mmol) were combined in a Schlenk flask with 5 mL dry THF and 5 mL dry Et_3N . Once dissolved, the solution

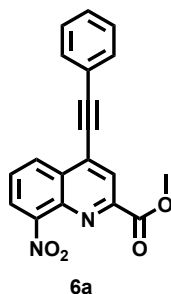
turned into black immediately. Then the solution was stirred at room temperature for overnight. Once done, the solvent was removed at vacuum and the product was soluted in DCM then washed by NH₄Cl saturated solution and NaCl solution for three times. The organic layer was dried by MgSO₄ and then purified by flash chromatography(SiO₂, Hexane/DCM stepwise elution, 15:1 to 3:1).

General procedures for **compound 7a~7b**: 1.0 mmol **compound 6a~6b** was dissolved in 5 mL THF and 1 mL MeOH, and 100 mg **sodium hydroxide** (2.5 mmol, 2.5 equiv.) was dissolved in 1 mL water which was then added to above solution dropwise. The solution was then stirred at 40 °C for about 40 min until TLC monitored that compound 6a~6f completely disappeared. After the solution was cooled into room temperature, dilute hydrochloric acid was added to make the solution pH around 1~4. After that, wash the solution with dichloromethane and the organic layer was dried by sodium sulfate powders. Compound 7a~7f was gained after solvent removed.

General procedures for **compound S/R-8a~8b**: 0.5 mmol **compound 7a~7b** and 0.5 mmol **compound chiral amine**, 0.52 mmol (1.2 equiv.) **2-(7-Azabenzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HATU)** was dissolved in 3 mL anhydrous DMF, and then 1.0 mmol (2.0 equiv.) **N,N-Diisopropylethylamine** was added. The mixture was stirred at room temperature for overnight. Then the solution was dissolved in 20 mL DCM, and was washed by saturated NH₄Cl solution. After the organic layer was dried and solute was removed, the crude was purified by column chromatography(SiO₂, Hexane/DCM stepwise elution, 10:1 to 5:1).

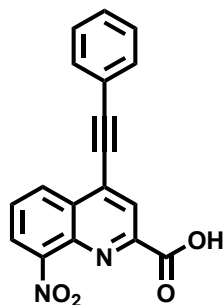
General procedures for **compound S/R-9a~9b**: 0.5 mmol **compound S/R-8a~8b** was dissolved in 20 ml methyl alcohol in a 100 mL round flask and 3 ml glacial acetic acid was added. This heterogeneous mixture turned to homogeneous as the temperature increased. After the temperature of solution increased to 75 °C, 2.0 mmol (4.0 equiv.) **Fe powder** was added to the solution with stirring in three portions within 30 minutes, poured over the mixture of ice and water, and then extracted with DCM. The organic phase was washed three times with saturated aqueous NaHCO₃ and brine respectively, dried over sodium sulfate and concentrated in vacuo to give brown red residue which was then purified by column chromatography(SiO₂, Hexane/DCM stepwise elution, 10:1 to 5:1).

General procedures for **compound S/R-1a~1b**: 0.1 mmol (1.0 equiv.) **compound 10** was suspended in anhydrous CH₂Cl₂ (2 mL) under argon. 0.5 mmol (5 equiv.) **oxalyl chloride** were added carefully to the mixture because of gas evolution. The reaction slowly turned to a yellow homogeneous solution over 2 h. The solution was concentrated in vacuo to give the acid chloride as a yellow solid, which was pumped dry for 2 h. 0.2 mmol (2.0 equiv.) **compound S/R-9a~9b** and 0.5 mmol (5.0 equiv.) **N, N-diisopropylethylamine** were dissolved in anhydrous CH₂Cl₂ (3 mL) under argon with stirring. The acid chloride was dissolved in anhydrous CH₂Cl₂ (5 mL), then were added into amine liquor immediately. After stirring for overnight, TLC analysis indicated completion of the reaction. The mixture extracted with CH₂Cl₂. The resultant crude material was purified by column chromatography (SiO₂, Hexane/DCM stepwise elution, 10:1 to 2:1) to give compounds Cod-68 as a light-yellow solid.



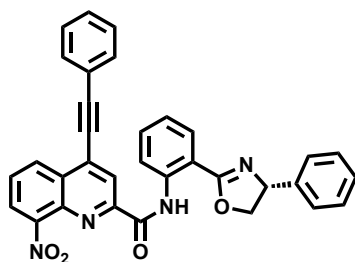
Compound 6a: 491 mg compound **6a** was gained as a brown solid, yield 92%. ¹HNMR (400 MHz, CDCl₃) δ 8.63 (d, *J*=8.4 Hz, 1H), 8.45 (s, 1H), 8.15 (d, *J*=7.6 Hz, 1H), 7.80 (t, *J*=7.6 Hz, 1H), 7.69 (dd, *J*=1.5, 7.3 Hz, 1H), 7.46-7.49 (m, 3H), 3.97 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 165.1, 149.6, 149.0, 139.2, 132.2, 132.03, 130.2, 129.3, 128.8, 127.7,

125.1, 125.1, 121.4, 101.7, 83.9, 77.3, 77.1, 76.9, 53.5, 50.9, 50.8. MS(ESI) calcd C₁₉H₁₂N₂O₄Na for [M+Na]⁺: 355.0689, found 355.0689.



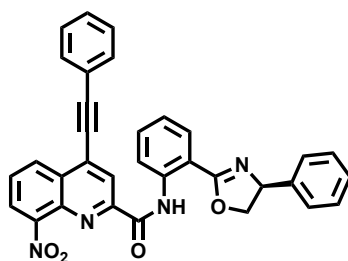
7a

Compound of 7a: 400 mg compound **6a** was put into reaction, and 350 mg light-yellow solid was gained as product, yield: 92%. ¹H NMR (400 MHz, CDCl₃) δ 10.84(br, 1H), 8.73 (dd, *J*=0.8, 7.4 Hz, 1H), 8.56 (s, 1H), 8.30 (dd, *J*=0.8, 7.4 Hz, 1H), 7.89 (t, *J*=8.0 Hz, 1H), 7.0 (dd, *J*=1.3, 7.6 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 162.9, 147.8, 147.5, 137.6, 134.1, 132.4, 131.0, 130.6, 130.1, 128.9, 128.3, 126.4, 123.3, 121.1, 103.4, 83.7, 77.3, 77.1, 76.9. MS(ESI) calcd C₁₈H₁₀N₂O₄ for [M+H]⁺: 319.0713, found 319.0716.



R-8a

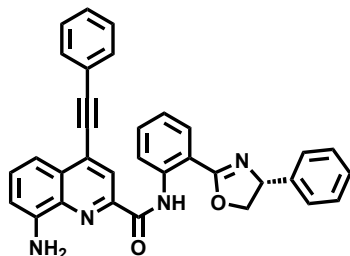
Compound R-8a: 150 mg compound **6a** was put into reaction, and 230 mg yellow solid was gained as product, yield: 88%. ¹H NMR (400 MHz, CDCl₃) δ 13.52 (s, 1H), 9.01 (d, *J*=8.4 Hz, 1H), 8.62 (s, 1H), 8.52 (dd, *J*=0.6, 8.4 Hz, 1H), 8.00 (dd, *J*=1.3, 7.8 Hz, 1H), 7.9 (d, *J*=0.9, 8.4 Hz, 1H), 7.61-7.65 (m, 3H), 7.55 (td, *J*=1.2, 8.4 Hz, 1H), 7.37-7.45 (m, 3H), 7.27 (s, 1H), 7.10-7.20 (m, 4H), 5.91 (dd, *J*=6.4, 9.9 Hz, 1H), 4.79 (dd, *J*=9.9, 8.2 Hz, 1H), 4.29 (dd, *J*=6.7, 8.0 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 164.0, 162.8, 152.6, 148.5, 143.2, 139.3, 138.2, 132.4, 132.2, 132.0, 130.2, 130.0, 129.7, 129.2, 128.8, 128.4, 127.2, 126.9, 126.5, 125.0, 123.8, 123.4, 121.6, 120.8, 115.3, 101.3, 84.2, 77.4, 77.1, 76.9, 74.0, 69.8, 60.5. MS(ESI) calcd C₃₃H₂₃N₄O₄ for [M+H]⁺: 537.1568, found 537.1569.



S-8a

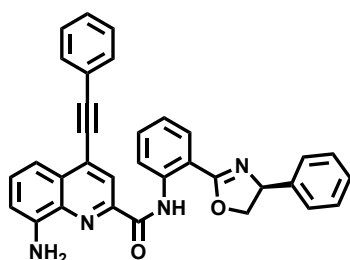
Compound S-8a: 170 mg compound **7a** was put into reaction, and 250 mg yellow solid was gained as product, yield: 87%. ¹H NMR (400 MHz, CDCl₃) δ 13.52 (s, 1H), 9.01 (d, *J*=8.4 Hz, 1H), 8.62 (s, 1H), 8.52 (dd, *J*=0.6, 8.4 Hz, 1H), 8.00 (dd, *J*=1.3, 7.8 Hz, 1H), 7.9 (d, *J*=0.9, 8.4 Hz, 1H), 7.61-7.65 (m, 3H), 7.55 (td, *J*=1.2, 8.4 Hz, 1H), 7.37-7.45 (m, 3H),

7.27 (s, 1H), 7.10-7.20 (m, 4H), 5.91 (dd, $J=6.4, 9.9$ Hz, 1H), 4.79 (dd, $J=9.9, 8.2$ Hz, 1H), 4.29 (dd, $J=6.7, 8.0$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 164.0, 162.9, 152.6, 148.5, 143.1, 139.2, 138.3, 132.5, 132.2, 132.0, 130.2, 130.0, 129.7, 129.3, 128.8, 128.4, 127.2, 126.9, 126.5, 125.0, 123.8, 123.4, 121.6, 120.8, 115.4, 101.3, 84.3, 77.3, 77.1, 76.9, 74.0, 69.7. MS(ESI) calcd $\text{C}_{33}\text{H}_{23}\text{N}_4\text{O}_4$ for $[\text{M}+\text{H}]^+$: 539.1713, found 539.1719.



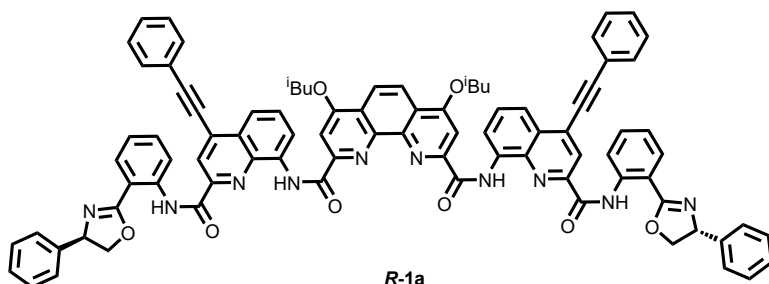
R-9a

Compound R-9a: 230 mg compound R-8a was put into reaction, and 140 mg yellow solid was gained as product, yield: 65%. ^1H NMR (600 MHz, CDCl_3) δ 13.57 (s, 1H), 9.13 (d, $J=8.0$ Hz, 1H), 8.50 (s, 1H), 8.05 (d, $J=8.0$ Hz, 1H), 7.65 (d, $J=6.9$ Hz, 2H), 7.60 (d, $J=8.6$ Hz, 1H), 7.35-7.42 (m, 9H), 7.260 (dd, $J=6.9, 8.0$ Hz, 1H), 6.71 (d, $J=6.9$ Hz, 1H), 5.66 (dd, $J=8.0$ Hz, 1H), 4.76 (dd, $J=8.0$ Hz, 1H), 4.56 (s, 2H), 4.19 (t, $J=8.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 163.7, 146.6, 145.4, 142.4, 139.7, 136.2, 133.0, 132.3, 130.2, 130.2, 129.3, 129.1, 128.1, 126.6, 125.6, 123.0, 122.6, 120.8, 114.4, 113.1, 110.3, 96.9, 87.8, 77.4, 77.1, 76.8, 73.7, 70.8, 32.0, 29.8, 22.8, 14.2. MS(ESI) calcd $\text{C}_{33}\text{H}_{24}\text{N}_4\text{O}_2$ for $[\text{M}+\text{H}]^+$: 509.1978, found 509.1974.



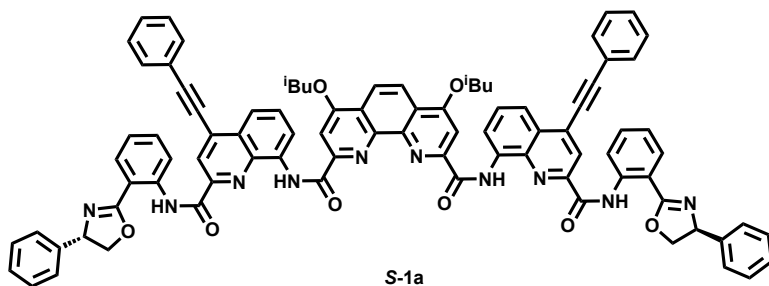
S-9a

Compound S-9a: 250 mg compound S-8a was put into reaction, and 160 mg yellow solid was gained as product, yield: 67%. ^1H NMR (600 MHz, CDCl_3) δ 13.57 (s, 1H), 9.13 (d, $J=8.0$ Hz, 1H), 8.50 (s, 1H), 8.05 (d, $J=8.0$ Hz, 1H), 7.65 (d, $J=6.9$ Hz, 2H), 7.60 (d, $J=8.6$ Hz, 1H), 7.35-7.42 (m, 9H), 7.260 (dd, $J=6.9, 8.0$ Hz, 1H), 6.71 (d, $J=6.9$ Hz, 1H), 5.66 (dd, $J=8.0$ Hz, 1H), 4.76 (dd, $J=8.0$ Hz, 1H), 4.56 (s, 2H), 4.19 (t, $J=8.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 163.8, 163.7, 144.5, 144.2, 142.4, 139.4, 136.3, 132.8, 132.7, 132.1, 131.1, 130.1, 130.1, 129.8, 129.5, 129.4, 129.1, 128.9, 128.6, 128.5, 127.8, 127.4, 126.6, 126.0, 125.8, 123.2, 123.1, 122.7, 122.6, 121.2, 120.8, 114.6, 113.8, 113.4, 108.0, 107.8, 99.2, 77.4, 77.3, 77.1, 76.8, 75.8, 73.8, 73.2, 69.8, 69.6, 54.1. MS(ESI) calcd $\text{C}_{33}\text{H}_{23}\text{N}_4\text{O}_2$ for $[\text{M}+\text{H}]^+$: 507.1827, found 507.1826.

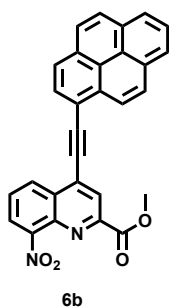


R-1a

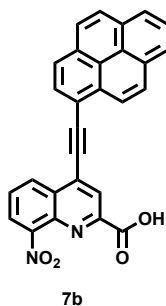
Compound R-1a: 50 mg compound **S-9a** was put into reaction, and 105 mg yellow solid was gained as product, yield: 61%. ¹H NMR (600 MHz, CDCl₃) δ 13.01(s, 1H), 12.90 (s, 1H), 8.89 (d, *J*=6.9 Hz, 1H), 8.86 (d, *J*=8.0 Hz, 1H), 8.28 (s, 1H), 7.96 (d, *J*=8.0 Hz, 1H), 7.79 (dd, *J*=6.9, 8.0 Hz, 1H), 7.60 (d, *J*=6.9, 8.0 Hz, 1H), 7.56 (s, 1H), 7.44 (d, *J*=6.9 Hz, 2H), 7.36 (s, 1H), 7.329 (dd, *J*=6.9, 8.0 Hz, 1H), 7.19 (d, *J*=6.9 Hz, 1H), 7.18 (d, *J*=8.0 Hz, 1H), 7.06 (d, *J*=8.0 Hz, 1H), 6.91, 6.90, 6.89 (d, *J*=6.9, 8.0 Hz, 1H), 6.82 (d, *J*=6.9 Hz, 1H), 6.80 (d, *J*=6.9 Hz, 1H), 6.79 (d, *J*=8.0 Hz, 1H), 6.51(d, *J*=8.0 Hz, 2H), 4.11 (dd, *J*=6.9, 8.0 Hz, 1H), 4.01 (dd, *J*=6.9, 8.0 Hz, 1H), 3.44 (t, *J*=8.0 Hz, 1H), 3.31 (dd, *J*=6.9, 8.0 Hz, 1H), 2.88 (dd, *J*=6.9, 8.0 Hz, 1H), 2.36 (m, 1H), 1.25 (dd, *J*=6.9, 5.8 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 162.9, 162.3, 162.1, 161.7, 150.9, 147.3, 144.5, 141.3, 139.0, 137.1, 134.8, 132.3, 132.1, 130.4, 129.5, 129.1, 128.4, 128.2, 127.7, 127.2, 126.0, 122.3, 122.0, 121.8, 121.3, 120.4, 119.8, 118.4, 114.1, 100.6, 99.2, 85.2, 77.3, 77.1, 76.9, 75.6, 72.2, 69.3, 29.8, 28.3, 19.4, 19.3, 14.3. MS(ESI) calcd C₈₈H₆₉N₁₀O₈F₆ for [M+H]⁺: 1393.5294, found 1393.5289.



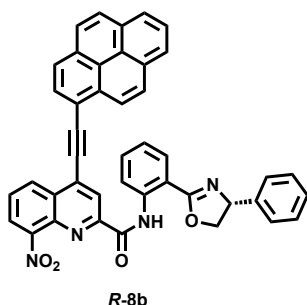
Compound S-1a: 50 mg compound **S-9a** was put into reaction, and 115 mg yellow solid was gained as product, yield: 69%. ¹H NMR (600 MHz, CDCl₃) δ 13.01(s, 1H), 12.90 (s, 1H), 8.89 (d, *J*=6.9 Hz, 1H), 8.86 (d, *J*=8.0 Hz, 1H), 8.28 (s, 1H), 7.96 (d, *J*=8.0 Hz, 1H), 7.79 (dd, *J*=6.9, 8.0 Hz, 1H), 7.60 (d, *J*=6.9, 8.0 Hz, 1H), 7.56 (s, 1H), 7.44 (d, *J*=6.9 Hz, 2H), 7.36 (s, 1H), 7.329 (dd, *J*=6.9, 8.0 Hz, 1H), 7.19 (d, *J*=6.9 Hz, 1H), 7.18 (d, *J*=8.0 Hz, 1H), 7.06 (d, *J*=8.0 Hz, 1H), 6.91, 6.90, 6.89 (d, *J*=6.9, 8.0 Hz, 1H), 6.82 (d, *J*=6.9 Hz, 1H), 6.80 (d, *J*=6.9 Hz, 1H), 6.79 (d, *J*=8.0 Hz, 1H), 6.51(d, *J*=8.0 Hz, 2H), 4.11 (dd, *J*=6.9, 8.0 Hz, 1H), 4.01 (dd, *J*=6.9, 8.0 Hz, 1H), 3.44 (t, *J*=8.0 Hz, 1H), 3.31 (dd, *J*=6.9, 8.0 Hz, 1H), 2.88 (dd, *J*=6.9, 8.0 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 162.9, 162.2, 162.1, 161.7, 150.9, 147.3, 144.5, 141.3, 139.0, 137.1, 134.8, 132.2, 132.1, 131.0, 130.4, 129.5, 129.1, 128.9, 128.4, 128.3, 128.2, 127.7, 127.1, 126.0, 122.3, 122.0, 121.8, 121.3, 120.4, 119.8, 118.4, 114.1, 100.6, 99.2, 85.2, 77.3, 77.1, 76.9, 75.6, 72.2, 69.3, 65.6, 30.7, 28.3, 19.4, 19.3, 19.3, 13.8. MS(ESI) calcd C₈₈H₆₉N₁₀O₈F₆ for [M+H]⁺: 1393.5294, found 1393.5282.



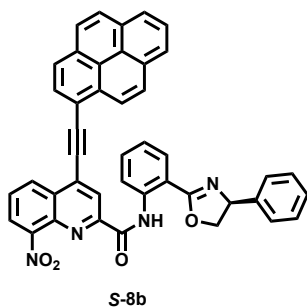
Compound 6b: 350 mg compound **5** was put into reaction, and 276 mg orange solid was gained as product, yield: 81%. ¹H NMR (400 MHz, CDCl₃) δ 8.85 (d, *J*=8.5 Hz, 1H), 8.71 (d, *J*=9.1 Hz, 1H), 8.64 (s, 1H), 8.36 (d, *J*=8.4 Hz, 1H), 8.29 (d, *J*=7.6 Hz, 1H), 8.19-8.24 (m, 3H), 8.10-8.12 (m, 2H), 7.88 (t, *J*=6.9 Hz, 1H), 4.11 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 149.6, 149.0, 139.2, 132.7, 132.1, 131.2, 130.9, 130.3, 130.2, 129.5, 129.4, 129.2, 127.7, 127.2, 126.7, 126.4, 125.1, 125.0, 125.0, 124.7, 124.5, 115.4, 101.2, 89.5, 77.4, 77.1, 76.8, 53.5. MS(ESI) calcd C₂₈H₁₃N₂O₄ for [M-CH₃]⁻: 441.0880, found 441.0883.



Compound 7b: 270 mg compound **6b** was put into reaction, and 230 mg black solid was gained as product, yield: 88%. ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.97 (s, 1H), 8.91 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.81 (d, *J* = 9.0 Hz, 1H), 8.66 (s, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.52 – 8.49 (m, 2H), 8.48 (d, *J* = 7.4 Hz, 1H), 8.45 (d, *J* = 7.9 Hz, 2H), 8.37 (d, *J* = 8.9 Hz, 1H), 8.31 (d, *J* = 8.9 Hz, 1H), 8.20 (t, *J* = 7.6 Hz, 1H), 8.13 – 8.07 (m, 1H). MS(ESI) calcd C₂₈H₁₅N₂O₄ for [M+H]⁺: 443.1026, found 443.1021.

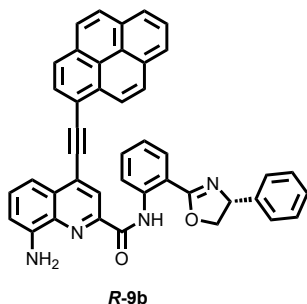


Compound R-8b: 100 mg compound **7b** was put into reaction, and 120 mg orange solid was gained as product, yield: 79%. ¹H NMR (600 MHz, CDCl₃) δ 13.53 (s, 1H), 9.07 (d, *J* = 8.0 Hz, 1H), 8.65 (s, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.23-8.27 (m, 3H), 8.13 (t, *J* = 9.2 Hz, 2H), 7.97-8.05 (m, 6H), 7.65 (t, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20-7.25 (m, 3H), 7.16 (d, *J* = 6.9 Hz, 2H), 5.96 (t, *J* = 6.9 Hz, 1H), 4.84 (t, *J* = 8.0 Hz, 2H), 4.33 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 162.8, 152.1, 148.2, 143.3, 139.3, 137.9, 132.4, 131.6, 130.9, 130.7, 130.3, 129.9, 129.8, 129.2, 129.1, 128.6, 127.4, 127.0, 126.7, 126.5, 126.3, 126.2, 125.0, 124.7, 124.6, 124.2, 123.8, 123.3, 120.7, 115.6, 115.2, 100.6, 89.7, 77.4, 77.1, 76.8, 74.1, 69.9, 36.5, 31.5. MS(ESI) calcd C₄₃H₂₆N₄O₄ for [M+H]⁺: 663.2027, found 663.2027.

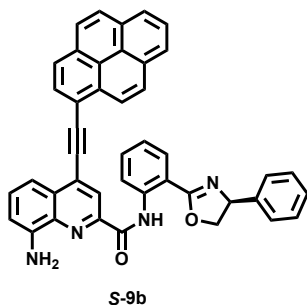


Compound S-8b: 100 mg compound **7b** was put into reaction, and 114 mg orange solid was gained as product, yield: 75%. ¹H NMR (600 MHz, CDCl₃) δ 13.53 (s, 1H), 9.07 (d, *J* = 8.0 Hz, 1H), 8.65 (s, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.23-8.27 (m, 3H), 8.13 (t, *J* = 9.2 Hz, 2H), 7.97-8.05 (m, 6H), 7.65 (t, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20-7.25 (m, 3H), 7.16 (d, *J* = 6.9 Hz, 2H), 5.96 (t, *J* = 6.9 Hz, 1H), 4.84 (t, *J* = 8.0 Hz, 2H), 4.33 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 164.0, 162.9, 152.4, 148.4, 143.2, 139.3, 138.2, 132.6, 132.6, 132.5, 132.0, 131.1, 130.9, 130.3, 130.1, 129.8, 129.4, 129.3, 129.0, 128.5, 127.3, 127.1, 126.8, 126.6, 126.3, 125.1.

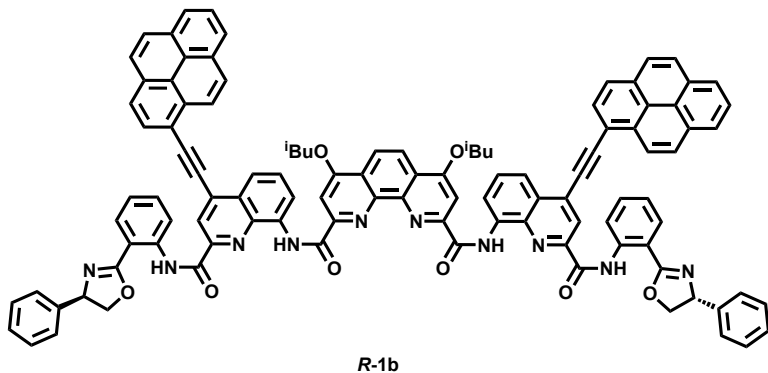
124.9, 124.7, 124.4, 124.1, 123.6, 123.4, 120.8, 115.6, 115.4, 100.8, 89.8, 77.3, 77.1, 76.9, 74.1, 69.8. MS(ESI) calcd $C_{43}H_{26}N_4O_4$ for $[M+H]^+$: 663.2027, found 663.2029.



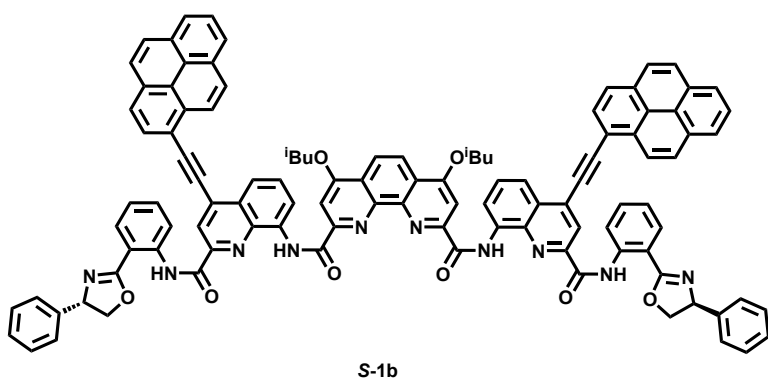
Compound R-9b: 100 mg compound **R-8b** was put into reaction, and 65 mg orange solid was gained as product, yield: 68%. 1H NMR (400 MHz, $CDCl_3$) δ 13.59 (s, 1H), 9.17 (d, $J=7.6$ HZ, 1H), 8.75 (d, $J=8.4$ HZ, 1H), 8.66 (s, 1H), 8.31 (d, $J=7.6$ HZ, 1H), 8.22-8.27 (m, 3H), 8.17 (d, $J=7.6$ HZ, 1H), 8.13 (d, $J=9.2$ HZ, 1H), 8.03-8.08 (m, 3H), 7.81 (d, $J=7.6$ HZ, 1H), 7.64 (t, $J=7.6$ HZ, 1H), 7.34-7.48 (m, 6H), 7.22 (t, $J=7.6$ HZ, 1H), 6.75 (d, $J=6.1$ HZ, 1H), 5.68 (d, $J=8.4$ HZ, 1H), 4.78 (d, $J=8.4$ HZ, 1H), 4.20 (t, $J=7.6$ HZ, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.2, 163.9, 146.6, 145.4, 142.5, 139.8, 136.4, 133.0, 132.4, 132.1, 131.3, 131.1, 130.2, 130.1, 130.1, 129.5, 129.1, 129.0, 128.8, 128.1, 127.3, 126.6, 126.5, 126.1, 126.0, 125.4, 124.7, 124.6, 124.3, 122.9, 122.4, 120.7, 116.7, 114.4, 113.5, 110.3, 98.4, 91.5, 77.3, 77.1, 76.9, 73.8, 70.8. MS(ESI) calcd $C_{33}H_{29}N_4O_2$ for $[M+H]^+$: 633.2278, found 633.2285.



Compound S-9b: 120 mg compound **S-8b** was put into reaction, and 89 mg orange solid was gained as product, yield: 78%. 1H NMR (400 MHz, $CDCl_3$) δ 13.59 (s, 1H), 9.17 (d, $J=7.6$ HZ, 1H), 8.75 (d, $J=8.4$ HZ, 1H), 8.66 (s, 1H), 8.31 (d, $J=7.6$ HZ, 1H), 8.22-8.27 (m, 3H), 8.17 (d, $J=7.6$ HZ, 1H), 8.13 (d, $J=9.2$ HZ, 1H), 8.03-8.08 (m, 3H), 7.81 (d, $J=7.6$ HZ, 1H), 7.64 (t, $J=7.6$ HZ, 1H), 7.34-7.48 (m, 6H), 7.22 (t, $J=7.6$ HZ, 1H), 6.75 (d, $J=6.1$ HZ, 1H), 5.68 (d, $J=8.4$ HZ, 1H), 4.78 (d, $J=8.4$ HZ, 1H), 4.20 (t, $J=7.6$ HZ, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.2, 163.8, 146.6, 145.4, 142.5, 139.8, 136.3, 133.4, 133.0, 133.0, 132.4, 131.0, 130.9, 130.1, 123.0, 129.5, 129.1, 128.9, 128.4, 128.4, 128.1, 127.9, 127.3, 126.9, 126.6, 122.9, 122.3, 120.7, 119.7, 114.4, 113.4, 110.3, 99.4, 86.2, 77.3, 77.1, 76.9, 73.7, 70.8, 65.6, 53.5, 30.7, 19.3, 13.82. MS(ESI) calcd $C_{33}H_{29}N_4O_2$ for $[M+H]^+$: 633.2278, found 633.2277.

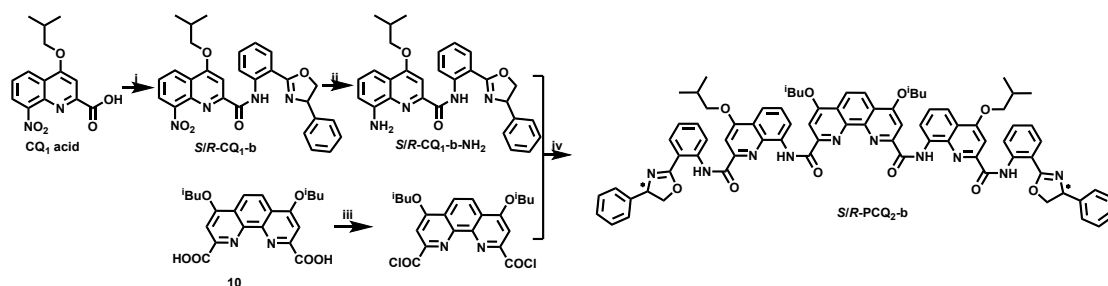


Compound R-1b: 30 mg compound **10** was put into reaction, and 35 mg orange solid was gained as product, yield: 30%. ¹H NMR (400 MHz, CDCl₃) δ 13.11 (s, 1H), 12.88 (s, 1H), 9.0 (d, *J*=7.3 Hz, 1H), 8.94 (d, *J*=8.3 Hz, 1H), 8.33 (s, 1H), 8.31 (d, *J*=7.3 Hz, 1H), 8.29 (d, *J*=11.0 Hz, 1H), 8.04 (t, *J*=8.7 Hz, 1H), 7.83 (d, *J*=7.3 Hz, 1H), 7.72-7.78 (m, 4H), 7.68 (d, *J*=7.3 Hz, 1H), 7.5 (dd, *J*=2.8, 8.3 Hz, 1H), 7.44 (s, 1H), 7.23 (dd, *J*=1.8, 9.2 Hz, 1H), 7.18 (d, *J*=7.3 Hz, 1H), 7.10 (dd, *J*=1.83, 7.3 Hz, 1H), 6.94 (t, *J*=7.3 Hz, 1H), 6.81-6.85 (m, 3H), 6.57 (dd, *J*=1.8, 7.3 Hz, 2H), 4.15 (t, *J*=9.2 Hz, 1H), 4.06 (d, *J*=9.2 Hz, 1H), 3.53 (dd, *J*=4.6, 10.1 Hz, 1H), 3.34 (dd, *J*=8.3, 7.3 Hz, 1H), 2.88 (dd, *J*=8.3, 7.3 Hz, 1H), 2.42 (m, 1H), 1.26 (d, *J*=6.4 Hz, 7H). ¹³C NMR (150 MHz, CDCl₃) δ 162.9, 162.3, 162.2, 161.8, 151.0, 147.3, 144.6, 141.4, 139.1, 137.4, 135.0, 132.4, 131.5, 131.1, 130.8, 130.5, 130.3, 129.6, 129.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.2, 126.2, 126.0, 125.6, 125.4, 124.7, 123.5, 123.2, 122.0, 122.0, 121.8, 121.0, 120.5, 120.0, 118.5, 115.9, 114.2, 100.7, 99.3, 90.9, 77.3, 77.1, 76.9, 75.6, 72.2, 69.4, 29.8, 28.3, 19.4, 19.4. MS(ESI) calcd C₁₀₈H₇₇N₈O₁₀ for [M+H]⁺: 1641.5920, found 1641.5918.



Compound S-1b: 30 mg compound **10** was put into reaction, and 58 mg orange solid was gained as product, yield: 50%. ¹H NMR (400 MHz, CDCl₃) δ 13.11 (s, 1H), 12.88 (s, 1H), 9.0 (d, *J*=7.3 Hz, 1H), 8.94 (d, *J*=8.3 Hz, 1H), 8.33 (s, 1H), 8.31 (d, *J*=7.3 Hz, 1H), 8.29 (d, *J*=11.0 Hz, 1H), 8.04 (t, *J*=8.7 Hz, 1H), 7.83 (d, *J*=7.3 Hz, 1H), 7.72-7.78 (m, 4H), 7.68 (d, *J*=7.3 Hz, 1H), 7.5 (dd, *J*=2.8, 8.3 Hz, 1H), 7.44 (s, 1H), 7.23 (dd, *J*=1.8, 9.2 Hz, 1H), 7.18 (d, *J*=7.3 Hz, 1H), 7.10 (dd, *J*=1.83, 7.3 Hz, 1H), 6.94 (t, *J*=7.3 Hz, 1H), 6.81-6.85 (m, 3H), 6.57 (dd, *J*=1.8, 7.3 Hz, 2H), 4.15 (t, *J*=9.2 Hz, 1H), 4.06 (d, *J*=9.2 Hz, 1H), 3.53 (dd, *J*=4.6, 10.1 Hz, 1H), 3.34 (dd, *J*=8.3, 7.3 Hz, 1H), 2.88 (dd, *J*=8.3, 7.3 Hz, 1H), 2.42 (m, 1H), 1.26 (d, *J*=6.4 Hz, 7H). ¹³C NMR (150 MHz, CDCl₃) δ 162.9, 162.3, 162.1, 161.8, 151.0, 147.3, 144.6, 141.4, 139.0, 137.4, 135.0, 132.4, 131.5, 131.1, 130.8, 130.5, 130.3, 129.6, 129.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.2, 126.3, 126.0, 125.6, 125.4, 124.7, 123.6, 123.2, 122.0, 121.9, 121.8, 121.0, 120.5, 120.1, 118.5, 115.9, 114.2, 100.7, 99.3, 90.9, 77.3, 77.1, 76.9, 75.6, 72.2, 69.4, 30.7, 29.8, 29.4, 28.3, 22.8, 19.4, 19.4, 19.3, 14.2, 13.8. MS(ESI) calcd C₁₀₈H₇₇N₈O₁₀ for [M+H]⁺: 1641.5920, found 1641.5911.

Synthesis of helicities of *S/R*-PCQ₂-b.

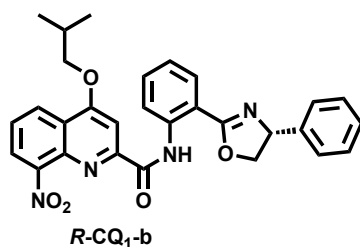


Scheme S2 Synthesis of compound *S/R*-PCQ₂-b. Conditions: i. HATU, DIEA, anhydrous DMF, *S*- or *R*- chiral amines; ii. Iron powder, CH₃COOH, MeOH, reflux; iii. C₂Cl₂O₂, dry DCM, room temperature; iv. DIEA, anhydrous DCM, room temperature.

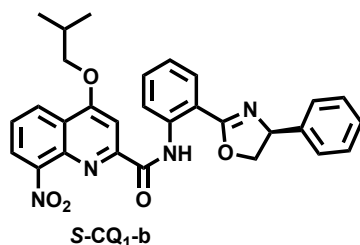
General procedures for Compound *S/R*-CQ₁-b: 0.2 mmol compound CQ₁ acid and 0.2 mmol compound chiral amine, 0.24 mmol (1.2 equiv.) 2-(7-Azabenzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HATU) was dissolved in 3 mL anhydrous DMF, and then 0.4 mmol (2.0 equiv.) N,N-Diisopropylethylamine was added. The mixture was stirred at room temperature for overnight. Then the solution was dissolved in 20 mL DCM, and was washed by saturated NH₄Cl solution. After the organic layer was dried and solute was removed, the crude was purified by column chromatography (SiO₂, Hexane/DCM stepwise elution, 10:1 to 5:1).

General procedures for **compound *S/R*-CQ₁-b-NH₂**: 0.15mmol compound *S/R*-CQ₁-b was dissolved in 5 mL ethyl acetate with 80 mg **10% wt. Palladium on activated carbon**. The solution was stirred at hydrogen atmosphere at room temperature for overnight. After the catalyst was filtered with silica and solvent removed at vacuum, the target product was gained without further purification.

General procedures for compound *S/R*-PCQ₂-b: 0.1 mmol (1.0 equiv.) **compound 10** was suspended in anhydrous CH₂Cl₂ (2 mL) under argon. 0.5 mmol (5 equiv.) **oxalyl chloride** were added carefully to the mixture because of gas evolution. The reaction slowly turned to a yellow homogeneous solution over 2 h. The solution was concentrated in vacuo to give the acid chloride as a yellow solid, which was pumped dry for 2 h. 0.2 mmol (2.0 equiv.) **compound *S/R*-CQ₁-b-NH₂** and 0.5 mmol (5.0 equiv.) **N, N-diisopropylethylamine** were dissolved in anhydrous CH₂Cl₂ (3 mL) under argon with stirring. The acid chloride was dissolved in anhydrous CH₂Cl₂ (5 mL), then were added into amine liquor immediately. After stirring for overnight, TLC analysis indicated completion of the reaction. The mixture extracted with CH₂Cl₂. The resultant crude material was purified by column chromatography (SiO₂, Hexane/DCM stepwise elution, 10:1 to 2:1) to give compounds Cod-68 as a light-yellow solid.

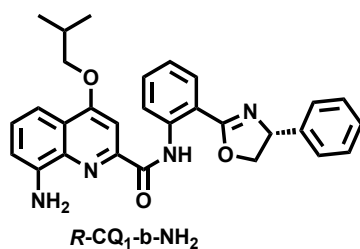


Compound *R*-CQ₁-b: 85 mg **compound *R*-CQ₁-b** was gained as pale white solid, yield 84%. ¹H NMR (600 MHz, CDCl₃) δ 13.49 (s, 1H), 9.02 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.45 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.99 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.88 (s, 1H), 7.60 – 7.54 (m, 2H), 7.27 (d, *J* = 1.7 Hz, 1H), 7.26 (d, *J* = 1.0 Hz, 1H), 7.22 – 7.17 (m, 3H), 7.16 – 7.12 (m, 1H), 5.91 (dd, *J* = 10.0, 6.4 Hz, 1H), 4.81 (dd, *J* = 10.0, 8.1 Hz, 1H), 4.31 (dd, *J* = 8.1, 6.4 Hz, 1H), 4.23 – 4.06 (m, 2H), 2.31 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.14 (dd, *J* = 6.7, 0.8 Hz, 7H). ¹³C NMR (150 MHz, CDCl₃) δ 163.9, 163.6, 163.1, 154.6, 148.1, 143.2, 139.3, 132.4, 129.8, 128.4, 127.1, 126.6, 126.4, 125.3, 124.9, 123.4, 123.3, 120.8, 115.5, 100.6, 77.3, 77.2, 77.1, 77.0, 76.9, 75.7, 74.0, 69.7, 28.2, 19.3. MS(ESI) calcd C₂₉H₂₇N₄O₅ for [M+H]⁺: 511.1975, found 511.1979.

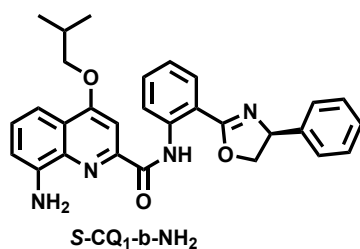


Compound *S*-CQ₁-b: ¹H NMR (400 MHz, Chloroform-*d*) δ 13.49 (s, 1H), 9.02 (dd, *J* = 8.6, 1.2 Hz, 1H), 8.45 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.99 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.88 (s, 1H), 7.61 – 7.53 (m, 2H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.24 – 7.16 (m, 4H), 7.14 (d, *J* = 7.1 Hz, 1H), 5.91 (dd, *J* = 10.0, 6.4 Hz, 1H), 4.81 (dd, *J* = 10.0, 8.1 Hz, 1H), 4.31 (dd, *J* = 8.2, 6.5 Hz, 2H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.30 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.18 – 1.11 (m, 7H). ¹³C

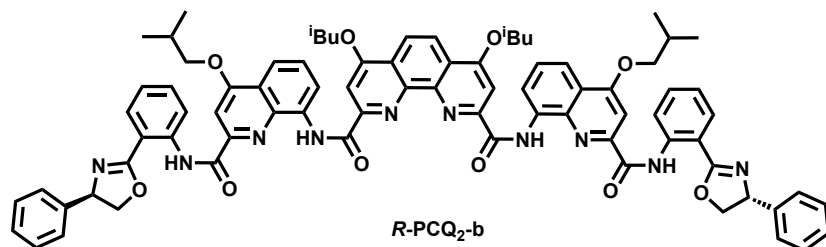
NMR (100 MHz, CDCl₃) δ 163.9, 163.6, 163.1, 143.2, 139.3, 132.4, 129.8, 128.4, 127.2, 126.6, 126.4, 125.3, 124.9, 123.4, 123.3, 120.8, 115.5, 100.6, 77.4, 77.1, 76.8, 75.7, 74.0, 69.7, 28.2, 19.3. MS(ESI) calcd C₂₉H₂₇N₄O₅ for [M+H]⁺: 511.1975, found 511.1980.



Compound **R-CQ₁-b-NH₂**: 80 mg **compound R-CQ₁-b** was gained as pale white solid, yield 79%. ¹H NMR (400 MHz, CDCl₃) δ 13.50 (s, 1H), 9.02 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.94 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.59 (s, 1H), 7.50 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.36 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.32 – 7.19 (m, 7H), 7.19 – 7.11 (m, 2H), 7.11 – 7.07 (m, 2H), 7.07 – 7.02 (m, 1H), 6.65 (s, 1H), 6.59 (d, *J* = 1.2 Hz, 1H), 6.57 – 6.55 (m, 1H), 5.55 (dd, *J* = 10.1, 7.7 Hz, 1H), 4.63 (dd, *J* = 10.2, 8.2 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 1H), 4.08 – 4.03 (m, 1H), 3.93 (d, *J* = 6.5 Hz, 3H), 2.15 (dt, *J* = 13.3, 6.6 Hz, 1H), 1.01 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 164.6, 163.1, 148.7, 144.7, 142.5, 139.8, 137.4, 132.9, 130.1, 129.4, 129.1, 129.0, 128.0, 126.6, 122.8, 120.6, 118.6, 115.2, 114.5, 110.5, 109.6, 98.8, 77.5, 77.2, 76.8, 75.0, 73.7, 70.8, 29.8, 28.3, 19.3. MS(ESI) calcd C₂₉H₂₉N₄O₃ for [M+H]⁺: 481.2234, found 481.2230.

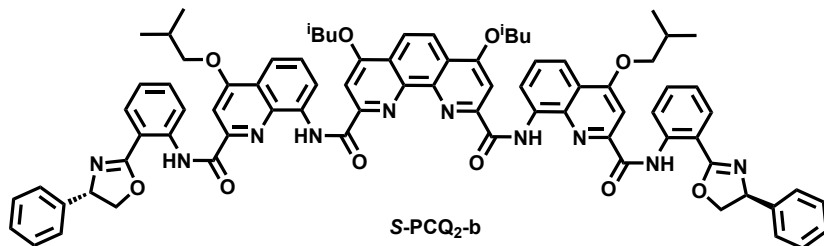


Compound **S-CQ₁-b-NH₂**: ¹H NMR (400 MHz, CDCl₃) δ 13.60 (s, 1H), 9.11 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.05 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.70 (s, 1H), 7.61 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.46 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.42 – 7.30 (m, 6H), 7.23 – 7.18 (m, 1H), 7.18 – 7.14 (m, 1H), 6.79 – 6.73 (m, 1H), 6.71 – 6.68 (m, 1H), 6.67 (dd, *J* = 2.7, 1.1 Hz, 1H), 5.67 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.76 (dd, *J* = 10.2, 8.2 Hz, 1H), 4.48 (s, 2H), 4.18 (t, *J* = 8.0 Hz, 1H), 4.06 (d, *J* = 6.5 Hz, 2H), 2.26 (dt, *J* = 13.3, 6.6 Hz, 1H), 1.12 (d, *J* = 6.7 Hz, 7H). ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 164.6, 163.1, 148.7, 144.7, 142.5, 139.9, 137.4, 132.9, 130.1, 129.4, 129.1, 128.8, 128.0, 126.6, 122.9, 122.8, 120.6, 115.2, 114.5, 110.4, 109.5, 98.8, 77.5, 77.2, 76.8, 75.0, 73.7, 70.8, 28.3, 19.4. MS(ESI) calcd C₂₉H₂₉N₄O₃ for [M+H]⁺: 481.2234, found 481.2229.



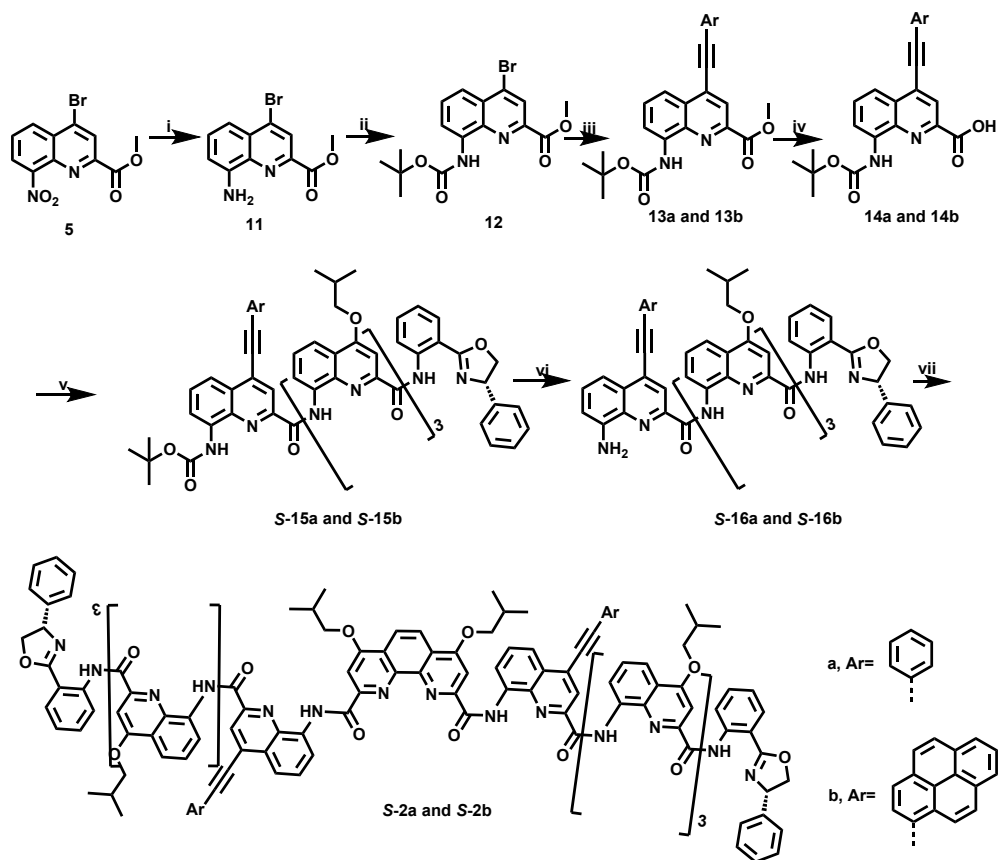
Compound **R-PCQ₂-b**: ¹H NMR (600 MHz, CDCl₃) δ 12.97 (s, 1H), 12.93 (s, 1H), 8.87 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.79 (dd, *J* = 7.5, 1.4 Hz, 1H), 8.26 (s, 1H), 7.66 (s, 1H), 7.64 – 7.60 (m, 1H), 7.58 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.30 (s, 1H), 7.05 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.87 (td, *J* = 7.5, 1.2 Hz, 1H), 6.85 – 6.82 (m, 1H), 6.82 – 6.78 (m, 3H), 6.53 (d, *J* = 1.2 Hz, 1H), 6.51 (d, *J* = 1.7 Hz, 1H), 4.31 (t, *J* = 6.7 Hz, 1H), 4.08 (dd, *J* = 8.6, 6.3 Hz, 1H), 3.99 (dd, *J* = 8.6, 6.7 Hz, 1H), 3.87 (dd, *J* = 8.7, 6.1 Hz, 1H), 3.74 (dd, *J* = 8.7, 7.3 Hz, 1H), 3.41 (dd, *J* = 9.9, 8.0 Hz, 1H), 3.28 (t, *J* = 7.8 Hz, 1H), 2.85 (dd,

$J = 9.9, 7.6$ Hz, 1H), 2.37 (dt, $J = 13.3, 6.6$ Hz, 1H), 2.23 (dt, $J = 13.4, 6.7$ Hz, 1H), 1.24 (dd, $J = 11.4, 6.8$ Hz, 9H), 1.14 (dd, $J = 10.6, 6.7$ Hz, 7H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.8, 163.0, 162.8, 162.0, 161.9, 161.5, 151.0, 149.4, 144.5, 141.4, 139.1, 138.4, 134.4, 132.4, 132.2, 131.0, 128.9, 128.4, 128.2, 127.4, 127.1, 126.0, 121.8, 121.8, 121.7, 121.1, 120.3, 118.2, 115.4, 114.1, 100.4, 98.3, 77.3, 77.1, 76.9, 75.5, 75.0, 72.1, 69.3, 65.6, 30.7, 28.3, 28.2, 19.4, 19.4, 19.3, 19.3, 19.3, 13.8. MS(ESI) calcd $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br}$ for $[\text{M}+\text{H}]^+$: 310.9662, found 310.9667.

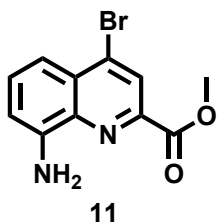


Compound **S-PCQ₂-b**: ^1H NMR (600 MHz, CDCl_3) δ 12.97 (s, 1H), 12.93 (s, 1H), 8.87 (d, $J = 8.0$ Hz, 1H), 8.79 (d, $J = 6.9$ Hz, 1H), 8.25 (s, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 9.2$ Hz, 1H), 7.30 (s, 1H), 7.05 (d, $J = 9.2$ Hz, 1H), 6.88 (d, $J = 6.9$ Hz, 1H), 6.84 (d, $J = 86.9$ Hz, 1H), 6.78-6.81 (m, 3H), 6.52 (s, 1H), 6.51 (s, 1H), 4.07 (dd, $J = 8.0, 6.9$ Hz, 1H), 3.99 (t, $J = 6.9$ Hz, 1H), 3.87 (dd, $J = 5.8, 5.8$ Hz, 1H), 3.74 (t, $J = 8.0$ Hz, 1H), 3.41 (dd, $J = 8.0, 9.2$ Hz, 1H), 3.28 (t, $J = 8.0$ Hz, 1H), 2.86 (t, $J = 8.0$ Hz, 1H), 2.834-3.41 (m, 1H), 2.20-2.67 (m, 1H), 1.22 (dd, $J = 6.9, 5.8$ Hz, 1H), 1.15 (dd, $J = 10.3, 6.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 162.8, 161.9, 161.5, 151.00, 149.3, 144.4, 141.4, 139.1, 138.4, 134.4, 132.1, 128.3, 128.2, 127.4, 127.1, 126.0, 121.8, 121.0, 120.3, 118.2, 115.4, 114.1, 100.4, 98.3, 77.4, 77.1, 76.8, 75.5, 75.0, 72.1, 69.3, 28.3, 28.2, 19.5, 19.4, 19.3. MS(ESI) calcd $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br}$ for $[\text{M}+\text{H}]^+$: 310.9662, found 310.9659.

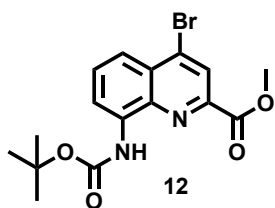
Synthesis of helicities of *S*-2a and *S*-2b.



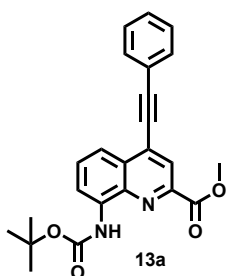
Scheme S3 Synthesis of compound *S/R*-1a~1b. Conditions: i. Iron powder, CH₃COOH, MeOH, reflux; ii. (BOC)₂O, 1,2-dioxane, 100 °C; iii. Pd(PPh₃)₂Cl₂, CuI, anhydrous THF and anhydrous Et₃N, **aromatic acetylene**, room temperature; iv. NaOH, THF/MeOH, 40°C; v. C₂Cl₂O₂, dry DCM, room temperature; DIEA, anhydrous DCM, Q3-NH₂-b-NH₂, room temperature; vi. CF₃COOH, DCM, room temperature; vii. C₂Cl₂O₂, dry DCM, room temperature; DIEA, anhydrous DCM, room temperature.



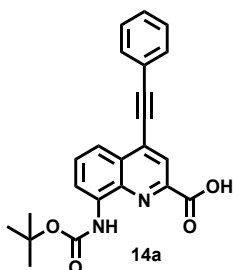
Compound 11: a dark red solid. Yield: 78 %. ¹H NMR (600 MHz, CDCl₃) δ 8.40 (s, 1H), 7.50 (d, *J* = 6.9 Hz, 1H), 7.46 (d, *J* = 6.9 Hz, 1H), 6.97 (d, *J* = 6.9 Hz, 1H), 5.24 (s, 2H), 4.03 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.99, 145.67, 143.98, 137.66, 134.75, 131.28, 129.75, 125.33, 114.31, 111.09, 77.42, 77.10, 76.78, 53.02. MS(ESI) calcd C₁₁H₈N₂O₄Br for [M+H]⁺: 310.9662, found 310.9659.



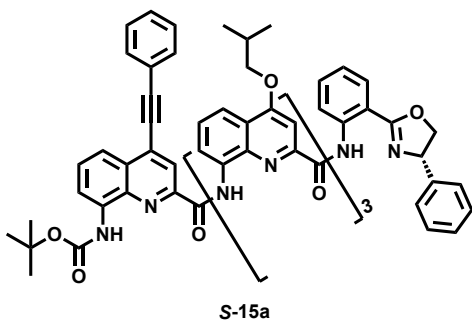
Compound 12: 190 mg (yield: 78%) compound 12 was gained as light-yellow solid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.99 (s, 1H), 8.56 (d, $J = 7.5$ Hz, 1H), 8.45 (s, 1H), 7.78 (d, $J = 8.1$ Hz, 1H), 7.70 (t, $J = 8.1$ Hz, 1H), 4.07 (s, 3H), 1.59 (s, 9H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 164.6, 152.7, 144.9, 137.9, 136.7, 135.4, 131.1, 129.0, 125.5, 118.9, 116.0, 81.2, 77.3, 77.1, 76.9, 53.2, 28.4. MS(ESI) calcd $\text{C}_{80}\text{H}_{77}\text{N}_{10}\text{O}_{10}$ for $[\text{M}+\text{H}]^+$: 1337.5819, found 1337.5801.



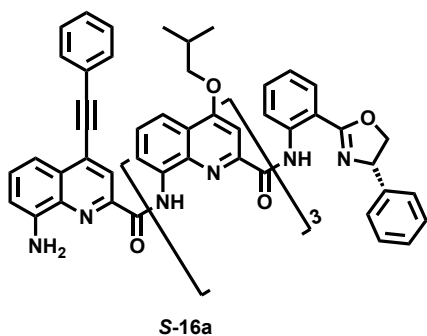
Compound 13b: 185 mg **compound 13a** was gained, yield: 86%. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 9.02 (s, 1H), 8.54 (d, $J = 8.0$ Hz, 1H), 8.33 (s, 1H), 7.97 (d, $J = 9.2$ Hz, 1H), 7.73 – 7.64 (m, 3H), 7.48 – 7.40 (m, 3H), 4.08 (s, 3H), 1.60 (s, 10H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 165.4, 152.8, 145.0, 137.7, 136.7, 132.1, 131.4, 130.4, 129.7, 128.9, 128.7, 124.1, 122.0, 118.1, 115.6, 100.0, 85.0, 81.0, 77.3, 77.1, 76.9, 53.1, 28.5. MS(ESI) calcd $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_4$ for $[\text{M}+\text{H}]^+$: 403.1652, found 403.1646.



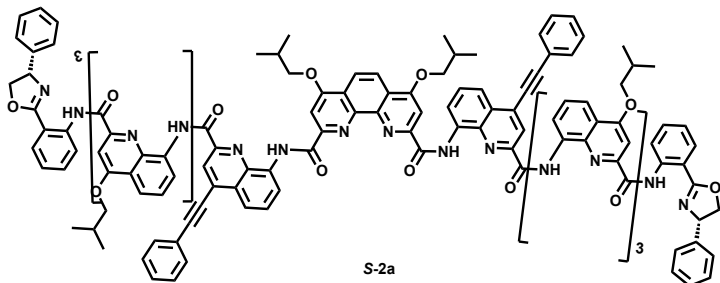
Compound 14a: 110 mg brown solid was gained as product. Yield: 95%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.60 (d, $J = 7.9$ Hz, 1H), 8.54 (s, 1H), 8.47 (s, 1H), 8.07 (dd, $J = 8.4, 1.3$ Hz, 1H), 7.76 (t, $J = 8.1$ Hz, 1H), 7.71 – 7.66 (m, 2H), 7.48 – 7.42 (m, 3H), 1.62 (s, 3H). MS(ESI) calcd $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}_4$ for $[\text{M}-\text{H}]^-$: 387.1350, found 387.1352.



Compound **S-15a**: 220 mg Yellow solid was gained. Yield: 65%. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 13.11 (s, 1H), 12.33 (s, 1H), 11.69 (s, 1H), 11.67 (s, 1H), 8.83 (d, $J=7.6$ Hz, 1H), 8.64 (d, $J=8.3$ Hz, 1H), 8.57 (d, $J=7.8$ Hz, 1H), 8.12 (s, 1H), 8.10 (s, 1H), 8.06 (d, $J=7.6$ Hz, 1H), 8.04 (d, $J=7.6$ Hz, 1H), 8.02 (d, $J=7.6$ Hz, 1H), 8.00 (d, $J=7.6$ Hz, 1H), 7.98 (d, $J=7.6$ Hz, 1H), 7.82 (d, $J=2.2$ Hz, 1H), 7.68 (s, 1H), 7.66 (s, 1H), 7.53 (s, 1H), 7.51 (d, $J=6.4$ Hz, 1H), 7.46 – 7.42 (m, 2H), 7.33 (d, $J=8.1$ Hz, 1H), 7.31 (d, $J=8.1$ Hz, 1H), 6.85 (s, 1H), 6.84 (s, 1H), 6.77 (d, $J=7.0$ Hz, 1H), 6.71 (d, $J=7.8$ Hz, 1H), 6.42 (s, 1H), 6.41 (s, 1H), 4.44 – 4.33 (m, 1H), 4.20 – 4.12 (m, 1H), 4.03 – 3.97 (m, 1H), 3.97 – 3.84 (m, 4H), 3.43 – 3.36 (m, 1H), 3.14 – 3.06 (m, 1H), 2.89 – 2.84 (m, 1H), 2.52 (m, 1H), 2.33 (m, 1H), 1.44 – 1.12 (m, 70H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 163.6, 163.3, 163.2, 162.7, 162.7, 162.2, 160.9, 160.5, 151.7, 150.5, 149.6, 149.4, 147.7, 141.2, 139.0, 138.4, 137.9, 135.9, 135.0, 134.5, 133.8, 133.45, 132.4, 132.3, 131.8, 129.7, 129.5, 129.1, 128.7, 128.5, 128.2, 127.4, 127.1, 127.0, 125.8, 123.0, 122.6, 122.5, 122.4, 121.9, 121.5, 120.4, 118.6, 117.3, 116.8, 116.3, 115.8, 114.7, 114.2, 99.9, 99.7, 98.7, 97.8, 85.8, 80.8, 77.3, 77.1, 76.9, 75.6, 75.5, 75.2, 72.3, 69.2, 32.0, 29.8, 29.4, 28.4, 28.3, 28.3, 27.9, 22.8, 19.6, 19.5, 19.5, 19.4, 19.4, 14.2. MS(ESI) calcd $\text{C}_{80}\text{H}_{75}\text{N}_{10}\text{O}_{10}$ for $[\text{M-H}]^-$: 1335.5662, found 1335.5654.

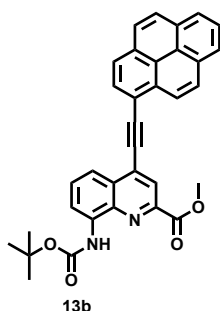


Compound **S-16a**: 220 mg compound cod-137(S) (0.165 mmol, 1equiv.). Yield: 70%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.05 (s, 1H), 12.29 (s, 1H), 11.67 (s, 1H), 11.55 (s, 1H), 8.75 (d, $J=7.6$ Hz, 1H), 8.58 (d, $J=8.3$ Hz, 1H), 8.46 (d, $J=7.6$ Hz, 1H), 8.06 (d, $J=6.8$ Hz, 1H), 8.02 – 7.97 (m, 3H), 7.94 (dd, $J=8.3, 1.1$ Hz, 1H), 7.79 – 7.74 (m, 2H), 7.69 (d, $J=8.1$ Hz), 7.67 (d, $J=5.0$ Hz, 1H), 7.65 (d, $J=3.6$ Hz, 1H), 7.62 (d, $J=8.1$ Hz, 1H), 7.53 (dd, $J=11.2, 4.1$ Hz, 1H), 7.47 – 7.43 (m, 3H), 7.32 (s, 1H), 7.28 (t, $J=8.0$ Hz, 1H), 7.19 (dd, $J=11.1, 4.1$ Hz, 1H), 7.13 (t, $J=7.9$ Hz, 2H), 6.94 (s, 1H), 6.84 (s, 1H), 6.74 (d, $J=7.0$ Hz, 1H), 6.69 (t, $J=7.3$ Hz, 1H), 6.44 (s, 1H), 6.43 (s, 1H), 5.97 (d, $J=7.6$ Hz, 1H), 4.36 – 4.26 (m, 1H), 4.15 – 4.08 (m, 1H), 4.04 – 3.94 (m, 1H), 3.94 – 3.81 (m, 3H), 3.79 (s, 2H), 3.39 (t, $J=7.8$ Hz, 1H), 3.24 (t, $J=8.7$ Hz, 1H), 2.95 (t, $J=8.9$ Hz, 1H), 2.54 – 2.41 (m, 1H), 2.31 (m, 2H), 1.31 – 1.13 (m, 32H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 163.5, 163.3, 163.2, 162.8, 162.7, 160.9, 160.8, 150.3, 150.1, 149.4, 146.6, 144.0, 141.1, 138.7, 138.4, 137.9, 135.3, 134.8, 133.8, 133.7, 132.3, 131.8, 131.2, 129.8, 129.6, 129.3, 128.8, 128.6, 128.2, 127.4, 127.1, 125.8, 122.9, 122.5, 122.3, 121.9, 121.6, 120.4, 117.5, 116.8, 116.7, 116.1, 116.0, 115.6, 114.2, 114.0, 109.4, 99.7, 98.9, 98.7, 98.2, 86.2, 77.3, 77.1, 76.9, 75.6, 75.5, 75.2, 72.3, 69.3, 32.0, 29.8, 29.4, 28.4, 28.3, 22.8, 19.6, 19.5, 19.4, 19.3, 14.2. MS(ESI) calcd $\text{C}_{75}\text{H}_{66}\text{N}_{10}\text{O}_8$ for $[\text{M-H}]^-$: 1257.4957, found 1257.4958.

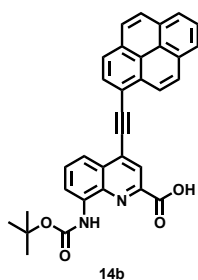


Compound **S-2a**: Yellow solid was gained. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 12.36 (s, 1H), 12.03 (s, 1H), 11.01 (s, 1H), 10.94 (s, 1H), 10.71 (s, 1H), 8.07 (d, $J=8.0$ Hz, 1H), 8.05 (d, $J=9.2$ Hz, 1H), 8.01 (d, $J=8.0$ Hz, 1H), 7.93 (d, $J=8.0$ Hz, 1H), 7.89 (d, $J=8.0$ Hz, 1H), 7.81 (d, $J=8.0$ Hz, 1H), 7.75 (s, 1H), 7.74 (s, 1H), 7.71 (dd, $J=3.5, 9.2$ Hz, 1H), 7.52–7.54 (m, 3H), 7.50 (d, $J=8.0$ Hz, 1H), 7.49 (s, 1H), 7.44 (t, $J=8.0$ Hz, 1H), 7.41 (d, $J=8.0$ Hz, 1H), 7.38 (d, $J=8.0$ Hz, 1H), 7.35

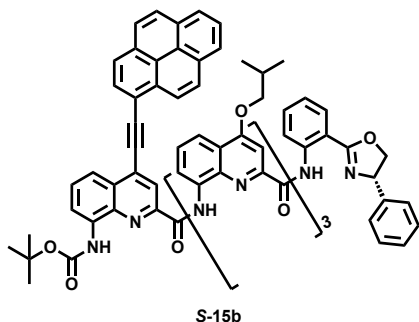
(t, $J=8.0$ Hz, 1H), 7.32 (d, $J=6.9$ Hz, 1H), 7.30 (d, $J=6.9$ Hz, 1H), 7.29 (d, $J=6.9$ Hz, 1H), 7.16 (d, $J=8.0, 6.9$ Hz, 1H), 7.08 (t, $J=6.9$ Hz, 1H), 6.91 (s, 1H), 6.88 (t, $J=6.9$ Hz, 1H), 6.57 (s, 1H), 6.56 (t, $J=6.9$ Hz, 1H), 6.48 (d, $J=8.0$ Hz, 1H), 6.46 (d, $J=6.9$ Hz, 1H), 6.43 (s, 1H), 6.26 (s, 1H), 6.12 (s, 1H), 6.11 (s, 1H), 6.10 (s, 1H), 3.85-3.88 (m, 4H), 3.79 (t, $J=6.9$ Hz, 1H), 3.76 (t, $J=6.9$ Hz, 1H), 3.63-3.68 (m, 2H), 3.08 (d, $J=6.9$ Hz, 1H), 2.70 (t, $J=9.2$ Hz, 1H), 2.57 (dd, $J=5.8, 6.9$ Hz, 1H), 2.35-2.44 (m, 2H), 2.26-2.30 (m, 1H), 2.21-2.23 (m, 1H), 2.13-2.18 (m, 1H), 1.23-1.30 (m, 33H), 1.19 (d, $J=6.9$ Hz, 3H), 1.12 (d, $J=6.9$ Hz, 3H), 1.09 (d, $J=6.9$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.8, 162.8, 162.6, 162.2, 161.9, 161.6, 160.4, 159.8, 159.6, 159.1, 148.8, 148.6, 147.5, 146.1, 142.5, 141.0, 138.6, 137.9, 137.7, 136.6, 135.7, 133.7, 133.5, 133.2, 133.0, 132.4, 131.2, 131.0, 130.4, 129.2, 128.9, 128.4, 127.9, 127.7, 127.3, 126.8, 126.5, 125.6, 123.0, 122.3, 121.6, 121.4, 120.8, 120.1, 119.8, 119.6, 119.1, 117.2, 116.8, 116.7, 116.6, 116.5, 116.1, 115.2, 113.7, 99.7, 98.8, 98.5, 98.1, 97.7, 85.7, 77.4, 77.3, 77.1, 76.8, 75.3, 75.1, 74.8, 71.9, 68.8, 68.2, 65.6, 38.8, 32.0, 30.7, 30.4, 29.8, 29.4, 29.0, 28.3, 28.2, 28.1, 23.8, 23.1, 22.8, 19.8, 19.7, 19.6, 19.5, 19.4, 19.3, 19.3, 14.2, 14.1, 13.8, 11.0. MS(ESI) calcd $\text{C}_{172}\text{H}_{152}\text{N}_{22}\text{O}_{20}$ for $[\text{M}+\text{H}]^+$: 2848.1693, found 2848.1702.



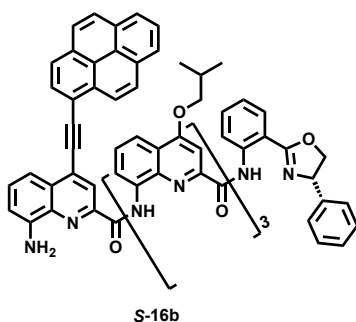
Compound 13b: Yield: 81%. ^1H NMR (600 MHz, CDCl_3) δ 9.04 (s, 1H), 8.68 (d, $J=9.0$ Hz, 1H), 8.56 (d, $J=6.9$ Hz, 1H), 8.44 (s, 1H), 8.29 (d, $J=7.9$ Hz, 1H), 8.24 (m, 3H), 8.17 – 8.10 (m, 3H), 8.09 – 8.02 (m, 3H), 7.74 (t, $J=8.0$ Hz, 1H), 4.11 (s, 3H), 1.63 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 165.4, 152.8, 145.0, 137.7, 136.7, 132.4, 132.3, 131.6, 131.2, 131.0, 130.5, 130.2, 129.2, 129.0, 128.8, 128.5, 127.3, 126.5, 126.2, 126.2, 125.2, 124.7, 124.5, 124.2, 124.1, 118.2, 116.2, 115.6, 99.5, 90.6, 81.0, 77.3, 77.1, 76.9, 53.1, 28.5. MS(ESI) calcd $\text{C}_{34}\text{H}_{27}\text{N}_2\text{O}_4$ for $[\text{M}+\text{H}]^+$: 527.1965, found 527.1959.



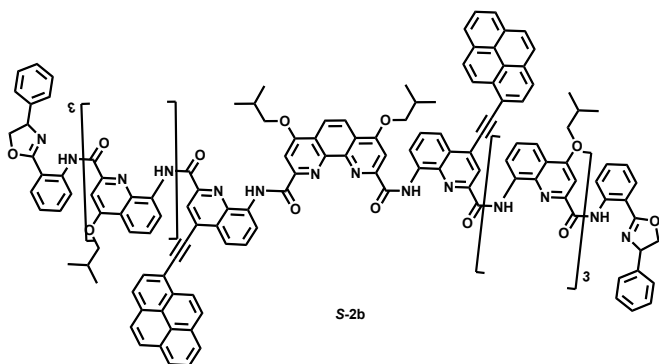
Compound 14b: ^1H NMR (400 MHz, CDCl_3) δ 8.73 (d, $J=9.1$ Hz, 1H), 8.66 (s, 1H), 8.36 (d, $J=7.9$ Hz, 1H), 8.32 (d, $J=8.8$ Hz, 1H), 8.29 (dd, $J=8.6, 3.5$ Hz, 2H), 8.22 (d, $J=7.9$ Hz, 1H), 8.20 (d, $J=8.9$ Hz, 1H), 8.12 (d, $J=5.9$ Hz, 1H), 8.10 (d, $J=4.6$ Hz, 1H), 7.85 (t, $J=8.1$ Hz, 1H), 7.65 (s, 1H), 7.52 (s, 1H), 6.99 (d, $J=6.7$ Hz, 1H), 1.64 (s, 13H). Yield: 89 %. MS(ESI) calcd $\text{C}_{33}\text{H}_{24}\text{N}_2\text{O}_4$ for $[\text{M}-\text{H}]^-$: 511.1654, found 511.1660.



Compound 15b: 220 mg Yellow solid was gained. Yield: 30%. ^{13}C NMR (600 MHz, CDCl_3) δ 13.13 (s, 1H), 12.34 (s, 1H), 11.70 (s, 1H), 11.69 (s, 1H), 8.91 (d, $J=9.0$ Hz, 1H), 8.88 (d, $J=7.6$ Hz, 1H), 8.68 (d, $J=7.5$ Hz, 1H), 8.65 (d, $J=8.2$ Hz, 1H), 8.48 (d, $J=7.5$ Hz, 1H), 8.37 (d, $J=9.1$ Hz, 1H), 8.32 (d, $J=7.4$ Hz, 1H), 8.28 – 8.23 (m, 3H), 8.20 (d, $J=8.2$ Hz, 1H), 8.17 (t, $J=4.1$ Hz, 2H), 8.12 (d, $J=8.7$ Hz, 1H), 8.11 – 8.04 (m, 3H), 8.01 (t, $J=8.5$ Hz, 2H), 7.76 (t, $J=7.9$ Hz, 1H), 7.71 (d, $J=6.9$ Hz, 1H), 7.69 (d, $J=7.8$ Hz, 1H), 7.63 – 7.54 (m, 2H), 7.44 (s, 1H), 7.41 (t, $J=7.8$ Hz, 1H), 7.32 (t, $J=7.9$ Hz, 1H), 7.24 (d, $J=7.5$ Hz, 1H), 6.92 (s, 1H), 6.87 (s, 1H), 6.75 (t, $J=7.0$ Hz, 1H), 6.70 (t, $J=7.4$ Hz, 2H), 6.44 (d, $J=7.6$ Hz, 1H), 6.43 (s, 1H), 4.45 – 4.34 (m, 1H), 4.18 (t, $J=7.7$ Hz, 1H), 4.06 – 3.98 (m, 1H), 3.94 (td, $J=8.3, 3.6$ Hz, 2H), 3.86 (d, $J=7.8$ Hz, 1H), 3.39 (t, $J=7.6$ Hz, 1H), 3.16 – 3.07 (m, 1H), 2.91 – 2.84 (m, 1H), 2.53 (m, 1H), 2.35 (m, 2H), 1.40 – 1.28 (m, 13H), 1.28 – 1.18 (m, 37H). ^{13}C NMR (150 MHz, CDCl_3) δ 163.6, 163.3, 163.2, 162.7, 162.7, 162.3, 160.9, 160.5, 151.7, 150.5, 149.6, 149.5, 147.7, 141.2, 139.0, 138.4, 137.9, 136.0, 135.1, 134.5, 133.8, 133.5, 132.7, 132.5, 132.3, 131.8, 131.3, 131.2, 130.5, 129.7, 129.1, 129.0, 128.9, 128.6, 128.2, 128.2, 127.4, 127.1, 127.0, 126.5, 126.2, 126.1, 125.8, 125.6, 124.7, 124.6, 124.4, 123.0, 122.5, 121.9, 121.6, 120.4, 118.7, 117.4, 117.3, 116.9, 116.3, 115.9, 115.8, 114.8, 114.2, 99.8, 99.3, 98.7, 97.9, 91.5, 80.8, 77.3, 77.1, 76.9, 75.6, 75.2, 72.3, 69.2, 29.8, 28.4, 28.3, 28.3, 28.0, 22.7, 19.6, 19.5, 19.5, 19.4, 19.4. MS(ESI) calcd $\text{C}_{90}\text{H}_{79}\text{N}_{10}\text{O}_{10}$ for $[\text{M}+\text{H}]^+$: 1459.5975, found 1459.5944.



Compound S-16b: 140 mg **compound S-16b** was gained. Yield: 70%. ^1H NMR (600 MHz, CDCl_3) δ 13.02 (s, 1H), 12.13 (s, 1H), 11.62 (s, 1H), 11.50 (s, 1H), 8.97 (d, $J=6.9$ Hz, 1H), 8.93 (d, $J=5.6$ Hz, 1H), 8.88 (d, $J=9.2$ Hz, 1H), 8.51 (d, $J=8.0$ Hz, 1H), 8.48 (d, $J=8.0$ Hz, 1H), 8.42 (d, $J=9.2$ Hz, 1H), 8.37 (d, $J=8.0$ Hz, 1H), 8.31 (d, $J=6.9$ Hz, 1H), 8.30 (s, 1H), 8.26 (d, $J=6.9$ Hz, 1H), 8.23 (d, $J=9.2$ Hz, 1H), 8.17 (d, $J=8.0$ Hz, 1H), 8.14 (d, $J=6.9$ Hz, 1H), 8.05 (s, 1H), 8.04 (s, 1H), 7.76 (t, $J=8.0$ Hz, 1H), 7.2-7.69 (m, 4H), 7.44 (s, 1H), 7.36 (t, $J=6.9$ Hz, 1H), 7.19-7.22 (m, 2H), 6.99 (s, 1H), 6.94 (s, 1H), 6.73 (t, $J=5.8$ Hz, 1H), 6.68 (d, $J=6.9$ Hz, 1H), 6.67 (d, $J=8.0$ Hz, 1H), 6.42 (s, 1H), 6.41 (s, 1H), 4.15 (t, $J=8.0$ Hz, 1H), 3.94-4.04 (m, 4H), 3.89 (t, $J=6.9$ Hz, 1H), 3.52 (br, 2H), 3.38 (t, $J=8.0$ Hz, 1H), 3.11 (t, $J=5.8$ Hz, 1H), 3.00 (t, $J=6.9$ Hz, 1H), 2.47-2.52 (m, 1H), 2.32-2.38 (m, 3H), 1.21-1.31 (m, 47H). ^{13}C NMR (150 MHz, CDCl_3) δ 163.6, 163.2, 162.7, 161.0, 160.9, 149.5, 146.7, 144.1, 141.1, 138.8, 138.4, 137.9, 135.5, 134.8, 133.8, 132.6, 132.2, 131.8, 131.4, 131.2, 130.4, 129.8, 129.6, 129.0, 128.8, 128.2, 127.4, 127.1, 126.5, 126.1, 126.0, 125.8, 125.7, 124.7, 124.4, 122.9, 122.5, 122.0, 121.7, 120.4, 117.6, 117.2, 116.8, 116.8, 116.2, 116.1, 115.7, 114.2, 109.5, 99.7, 98.8, 98.4, 92.0, 77.3, 77.1, 76.9, 75.6, 75.5, 75.2, 72.3, 69.3, 28.4, 28.3, 19.6, 19.49, 19.4, 19.4. MS(ESI) calcd $\text{C}_{85}\text{H}_{71}\text{N}_{10}\text{O}_8$ for $[\text{M}+\text{H}]^+$: 1359.5451, found 1359.5425.



Compound S-2b: compounds **S-2b** as a yellow solid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 12.39 (s, 1H), 12.08 (s, 1H), 11.07 (s, 1H), 10.99 (s, 1H), 10.82 (s, 1H), 8.55 (d, $J = 8.4$ Hz, 1H), 8.25 (d, $J = 7.9$ Hz, 1H), 8.10 – 8.03 (m, 4H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.90 (t, $J = 7.4$ Hz, 1H), 7.85 (d, $J = 7.9$ Hz, 1H), 7.81 (t, $J = 8.5$ Hz, 2H), 7.67 (d, $J = 7.2$ Hz, 1H), 7.56 (s, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 8.6$ Hz, 1H), 7.46 (d, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 7.1$ Hz, 1H), 7.26 (s, 1H), 7.23 (d, $J = 7.5$ Hz, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.15 (s), 7.13 (d, $J = 7.3$ Hz, 1H), 6.89 (t, $J = 7.0$ Hz, 1H), 6.65 (s, 1H), 6.51 (t, $J = 7.3$ Hz, 1H), 6.46 (s, 1H), 6.43 (t, $J = 7.4$ Hz, 2H), 6.32 (s, 1H), 6.14 (s, 1H), 6.11 (s, 1H), 6.10 (s, 1H), 3.90 (m, 6H), 3.80 (t, $J = 7.4$ Hz, 1H), 3.69 (d, $J = 6.6$ Hz, 1H), 3.66 (d, $J = 6.2$ Hz, 1H), 3.10 – 3.07 (m, 1H), 2.71 (t, $J = 8.8$ Hz, 1H), 2.60 (dd, $J = 9.6, 6.4$ Hz, 1H), 2.39 (m, 3H), 2.18 (m, 1H), 1.34 – 1.20 (m, 33H), 1.15 (d, $J = 6.8$ Hz, 3H), 1.11 (d, $J = 6.7$ Hz, 3H), 0.92 – 0.82 (m, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 162.8, 162.6, 162.2, 161.9, 161.6, 160.4, 159.9, 159.8, 159.2, 148.8, 148.7, 147.6, 146.2, 142.7, 140.9, 138.6, 138.0, 137.8, 136.8, 136.0, 133.8, 133.2, 133.0, 131.8, 131.2, 130.8, 130.7, 130.6, 129.7, 129.2, 128.7, 128.1, 127.9, 127.8, 127.3, 126.8, 126.7, 126.6, 125.9, 125.5, 125.2, 123.8, 123.6, 122.3, 121.7, 121.5, 121.2, 120.9, 120.3, 119.9, 119.2, 117.3, 117.0, 116.8, 116.6, 116.1, 115.3, 113.7, 99.8, 98.8, 98.5, 98.1, 97.8, 91.6, 77.3, 77.1, 76.9, 75.4, 75.1, 74.8, 71.9, 68.8, 29.8, 29.4, 28.4, 28.3, 28.22, 28.1, 19.8, 19.7, 19.6, 19.4, 19.4, 19.4. MS(ESI) calcd $\text{C}_{192}\text{H}_{160}\text{N}_{22}\text{O}_{20}\text{Na}$ for $[\text{M}+\text{Na}]^+$: 3118.2139, found 3118.2124.

Chiroptical Properties:

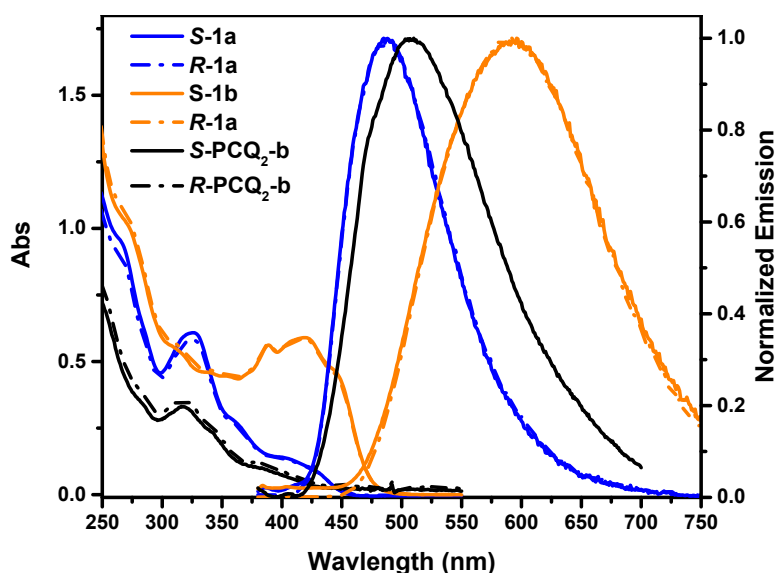


Figure S1 Uv-vis absorption and normalized emission spectra of *S/R*-1a/1b and *S/R*-PCQ₂-b (1.0×10^{-5} M, DCM at 298 K, $\lambda_{\text{exc}}=360$ nm).

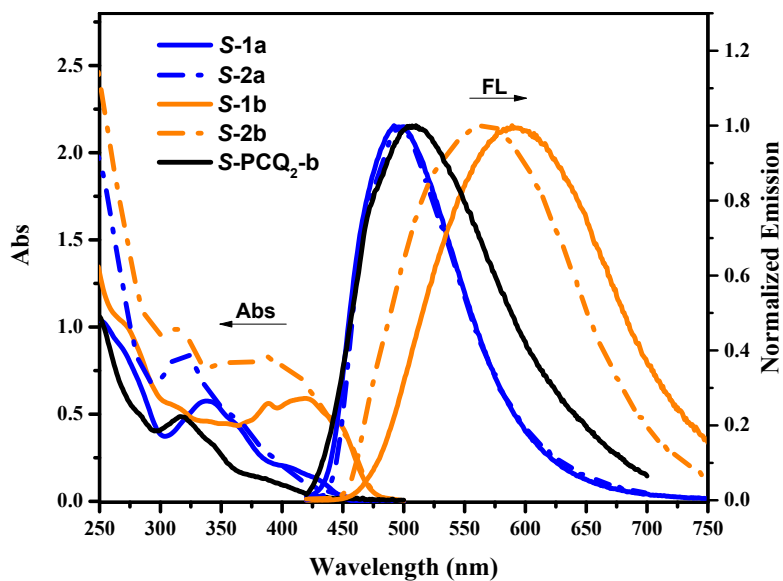


Figure S2 Uv-vis absorption and normalized emission spectra of *S-1a/1b* and *S-2a/2b* (1.0×10^{-5} M, DCM at 298 K, $\lambda_{\text{ex}}=360$ nm).

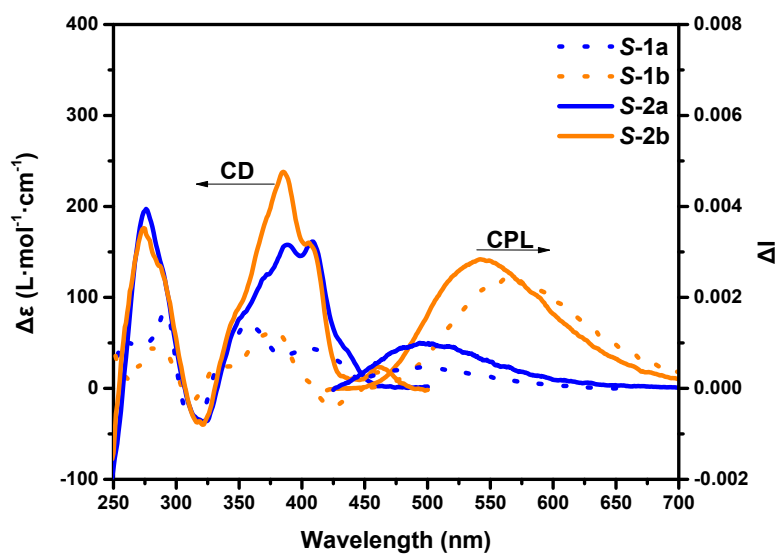


Figure S3 CD and CPL spectra of *S-1a/1b* and *S-2a/2b* (1.0×10^{-5} M, DCM at 298 K).

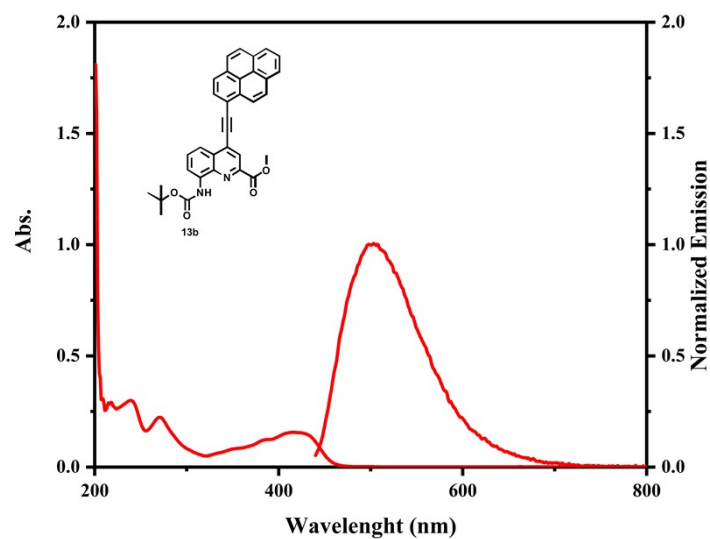


Figure S4 Uv-vis absorption and normalized emission spectra of **13b** (1.0×10^{-5} M, DCM at 298 K, $\lambda_{\text{ex}}=430$ nm, $\lambda_{\text{em}}=500$ nm). The quantum yield was determined to be 0.2 by using a calibrated integrating sphere.

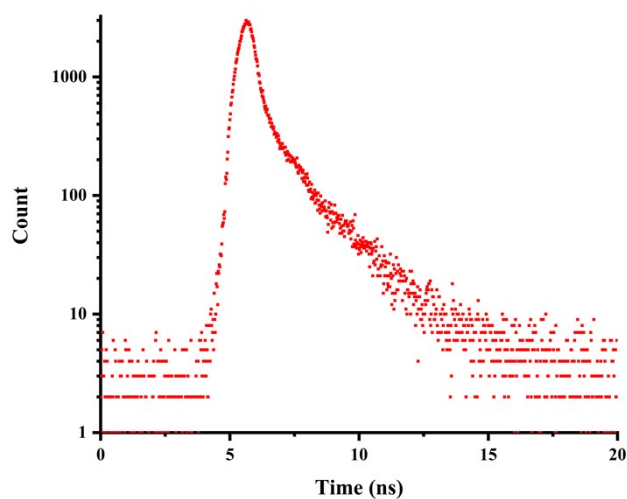


Figure S5 Emission lifetime of **13b** ($\tau=1.44$ ns, 1.0×10^{-5} M, DCM at 298 K).

Table S1 Optical properties of *S/R*-**1a**~**1b**, **S-2a** and **S-2b**.

Compd.	$\lambda_{\text{Abs}}/\text{nm}$	$\epsilon_{\text{m}}(\times 10^4)$	$\epsilon_{360 \text{ nm}}(\times 10^4)$	$\Phi^a/\%$	$g_{\text{lum}}/10^{-3}(\text{nm})$	$B^b/\text{M}^{-1} \cdot \text{cm}^{-1}$
S-1a	327	5.8	2.5	56.1	1.4 (490)	9.9

R-1a	327	6.0	2.6	56.8	-1.2 (490)	9.3
S-1b	418	5.9	4.4	45.1	5.0 (550)	49.1
R-1b	418	5.9	4.5	44.2	-4.8(550)	47.4
S-PCQ₂-b	316	3.2	2.0	5.8	3.6 (480)	2.0
R-PCQ₂-b	316	2.9	1.9	5.4	-3.1(480)	1.7
S-2a	320	8.6	4.9	36.0	3.3 (485)	29.2
S-2b	386	9.9	8.0	44.4	6.2 (520)	109.8

^a Φ is measured using a calibrated integrating sphere, excited at 360 nm. ^b B_{CPL} refers to the resulting brightness which is calculated by $B_{CPL} = \epsilon_{ex} \cdot \Phi \cdot \frac{|g_{lum}|}{2}$, while ϵ_{λ} is the extinction coefficient at the excitation wavelength. ²

NMR & MS Spectra:

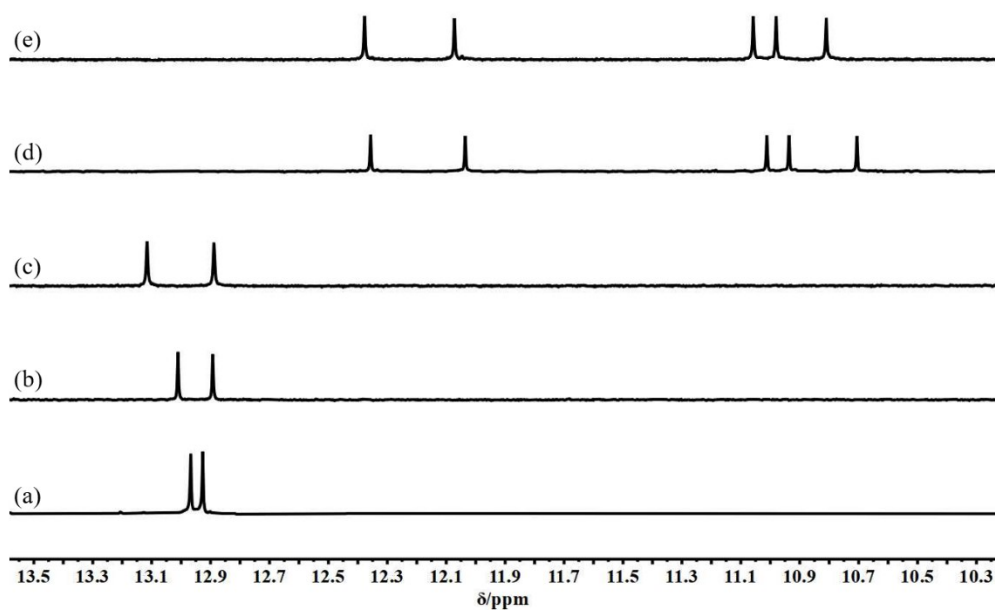


Figure S6 Parts of ¹H NMR of (a) **S-PCQ₂-b**, (b) **S-1a**, (c) **S-1b**, (d) **S-2a** and (e) **S-2b** in CDCl₃ at 298 K.

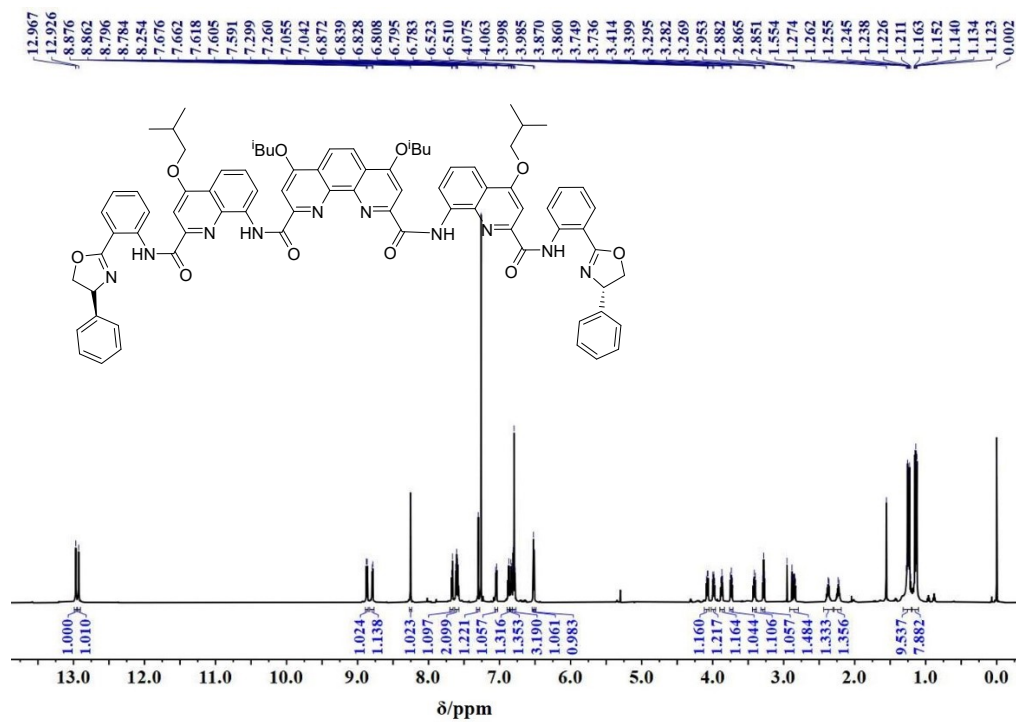


Figure S7 ¹H NMR of *S*-PCQ₂-b(CDCl₃)

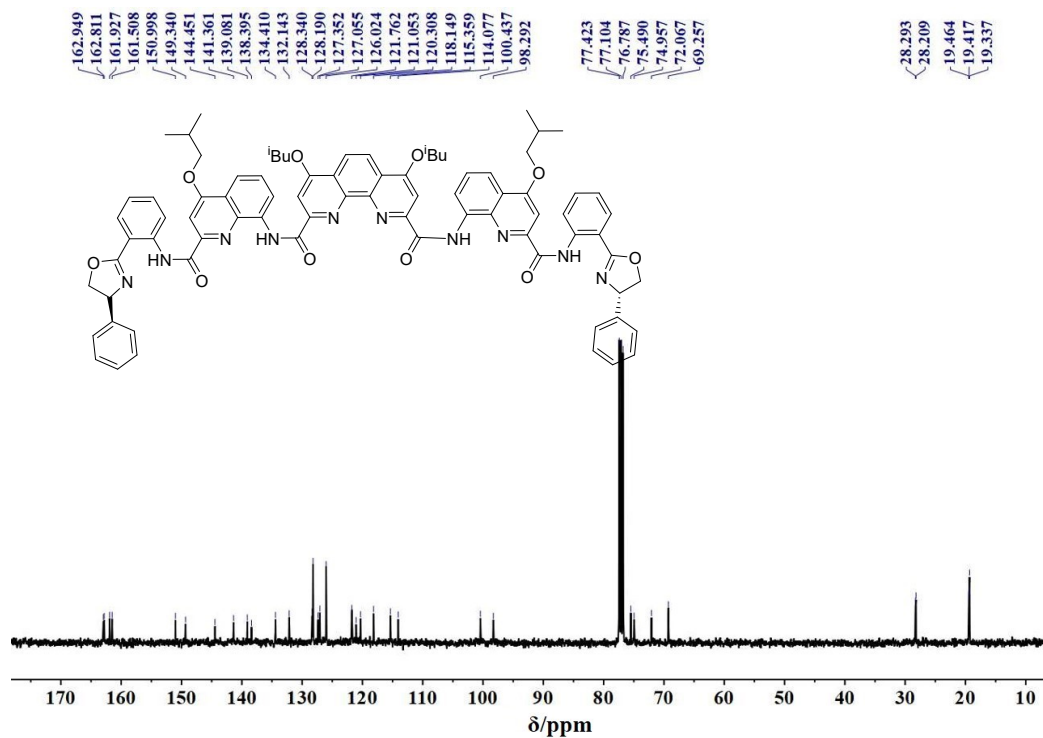


Figure S8 ¹³C NMR of *S*-PCQ₂-b(CDCl₃)

116S #23 RT: 0.39 AV: 1 NL: 1.03E3
 T: FTMS (1,1) + p ESI Full ms [200.00-2000.00]

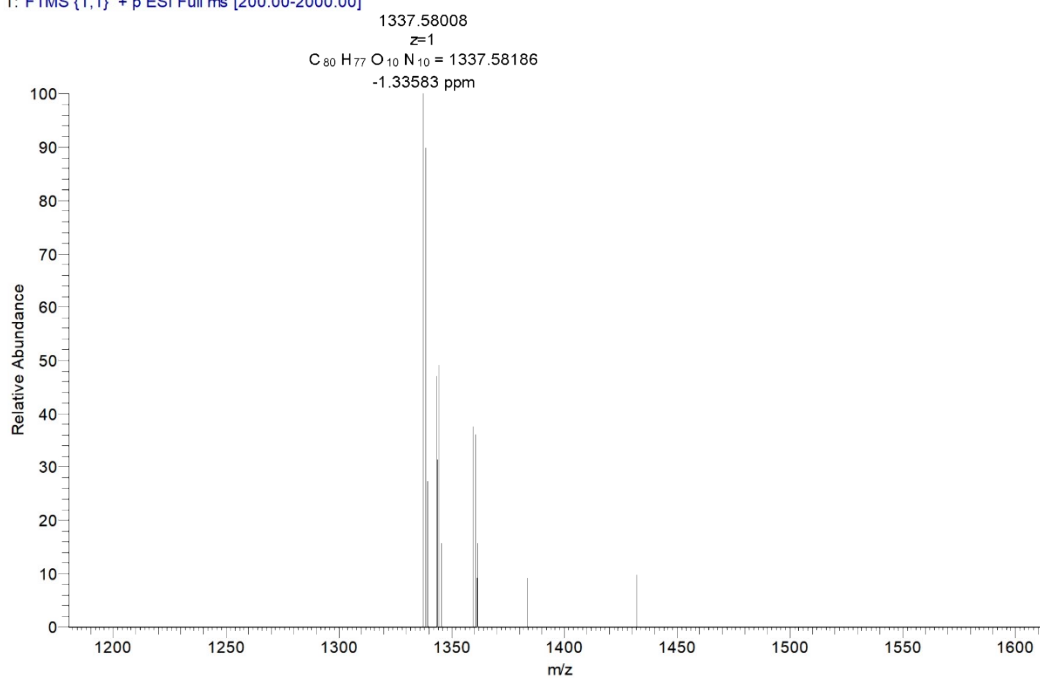


Figure S9 ESI-MS of **S-PCQ₂-b**(CDCl₃)

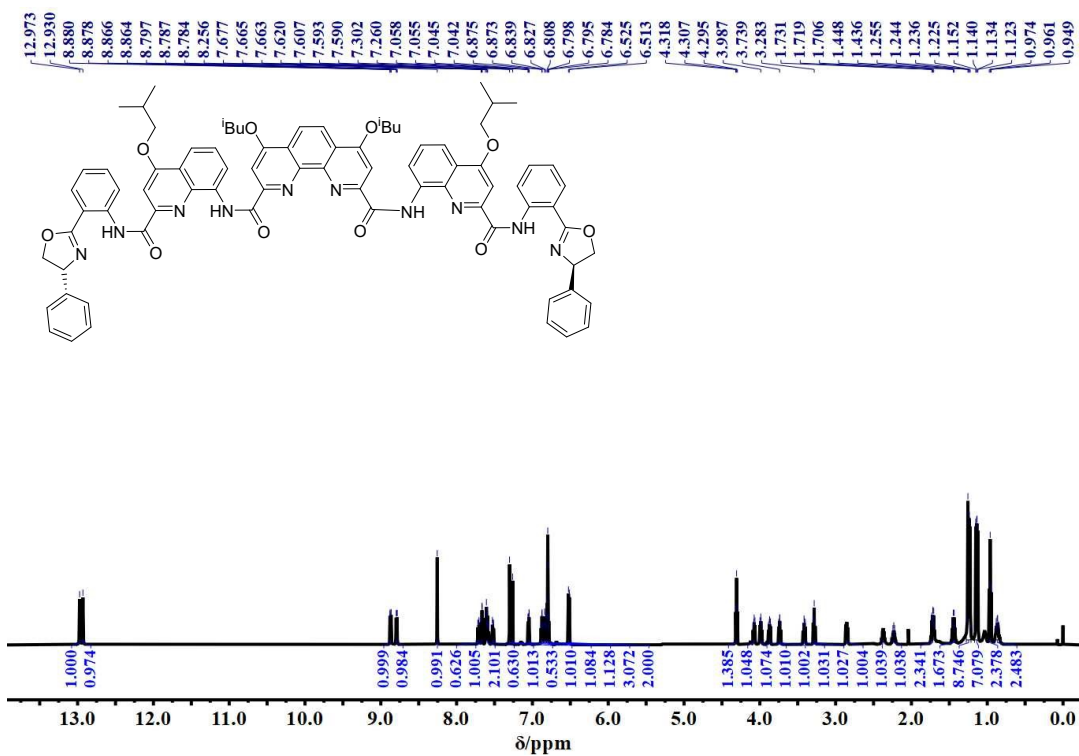


Figure S10 ¹H NMR of **R-PCQ₂-b**(CDCl₃)

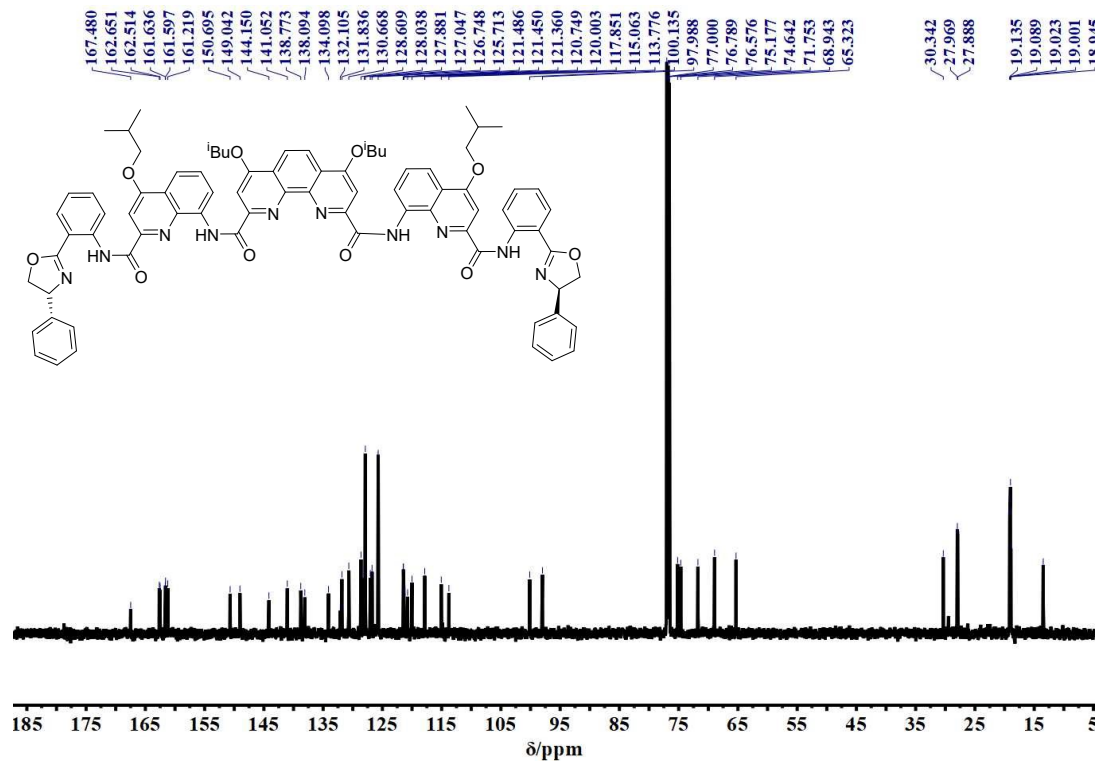


Figure S11 ¹³C NMR of *R*-PCQ₂-b(CDCl₃)

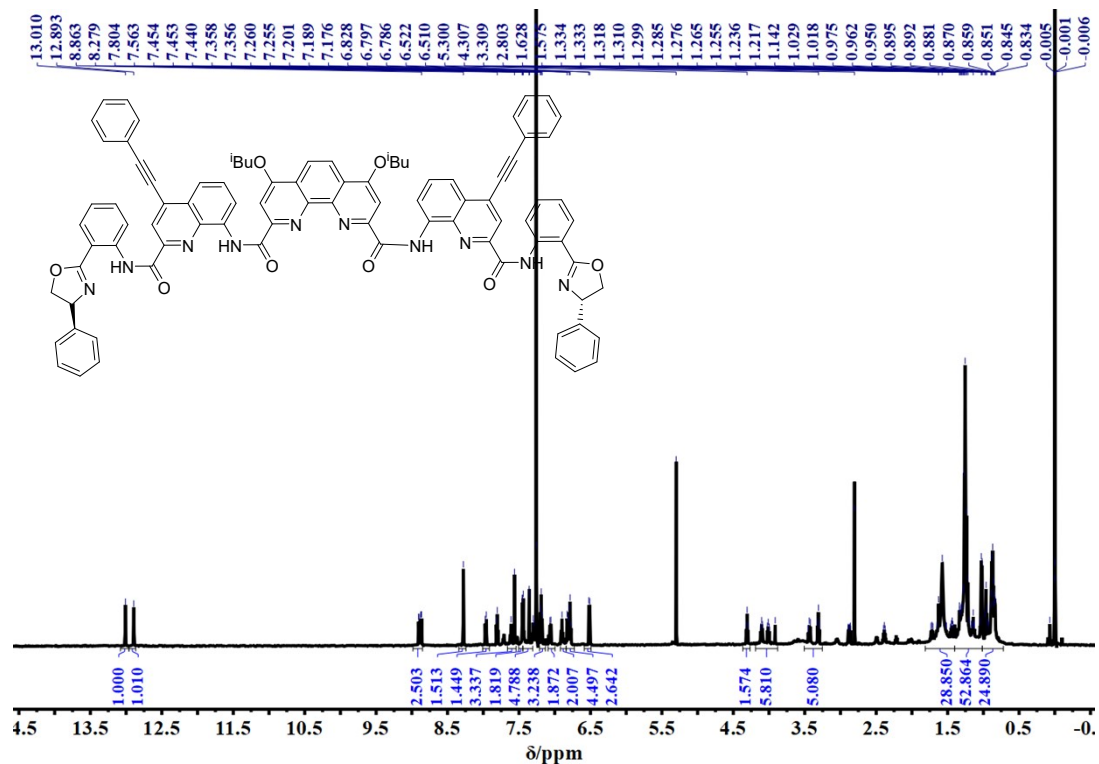


Figure S12 ¹H NMR of *S*-1a(CDCl₃)

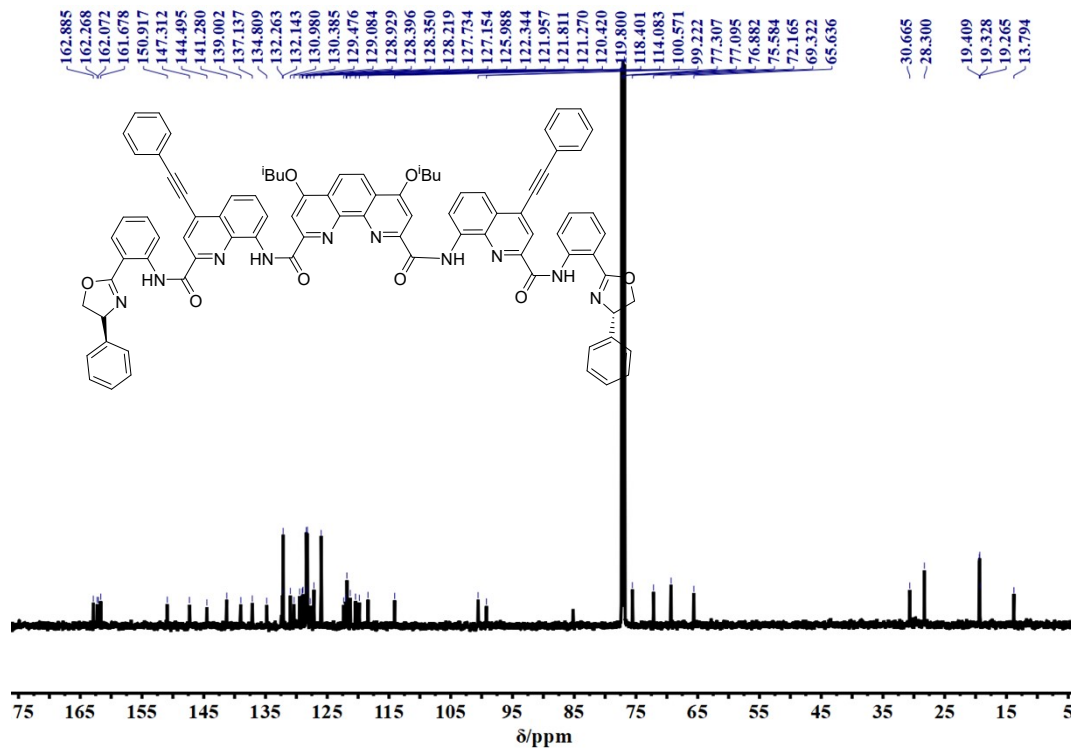


Figure S13 ¹³C NMR of **S-1a**(CDCl₃)

COD-94S #23 RT: 0.36 AV: 1 NL: 2.76E5
T: FTMS (1,1) + p ESI Full ms [200.00-2000.00]

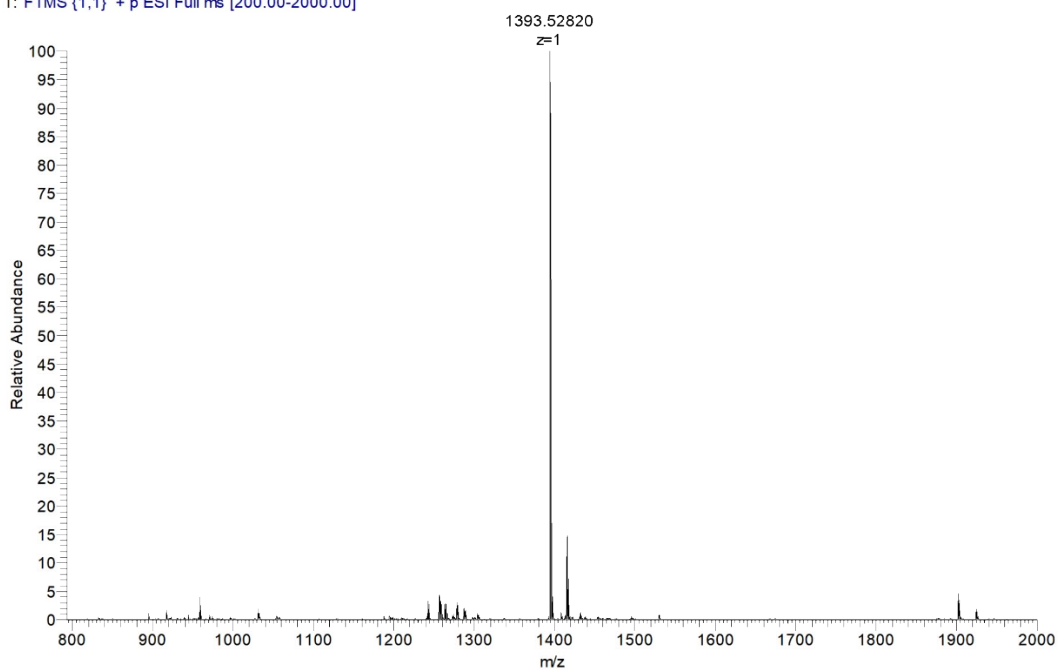


Figure S14 ESI-MS of **S-1a**

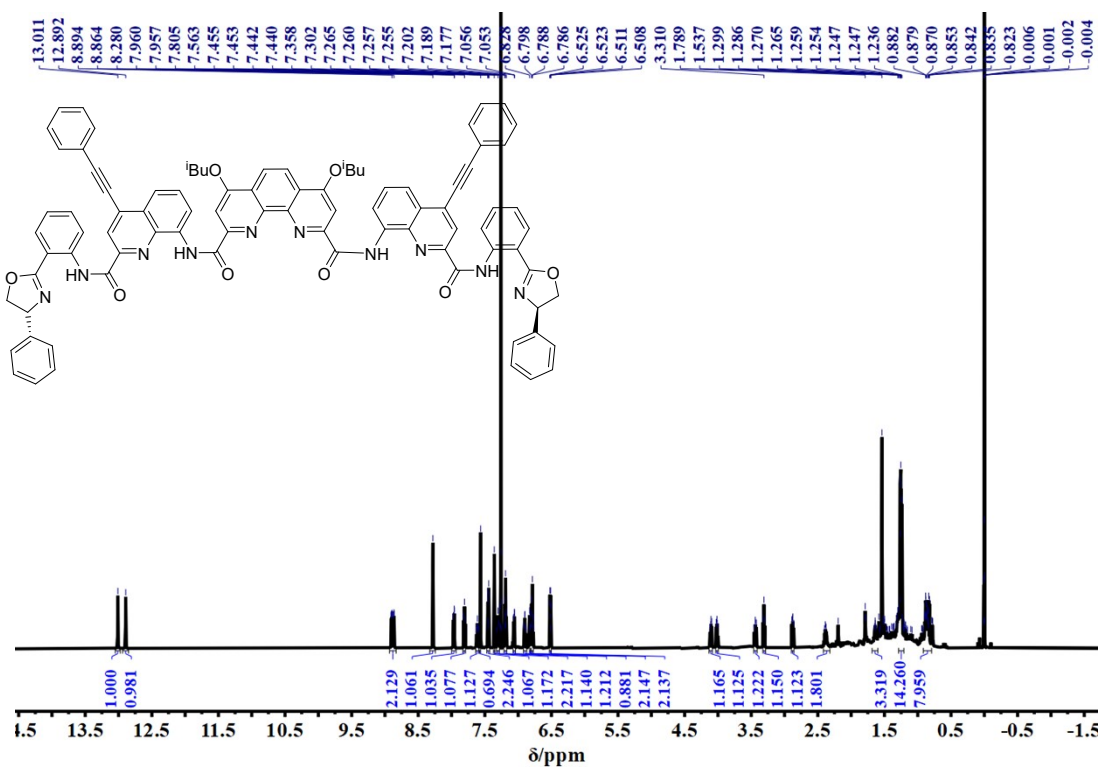


Figure S15 $^1\text{H NMR}$ of **R-1a**(CDCl₃)

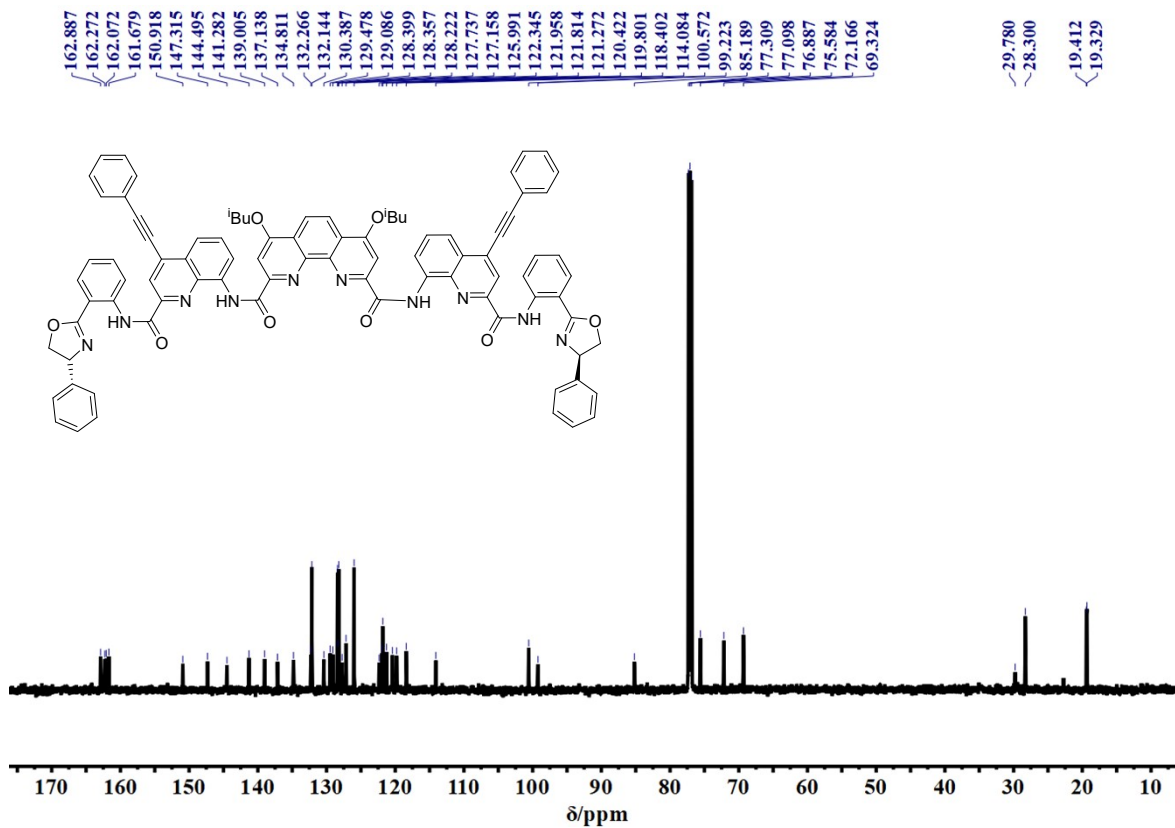


Figure S16 $^{13}\text{C NMR}$ of **R-1a**(CDCl₃)

COD-94R #31 RT: 0.46 AV: 1 NL: 1.76E5
T: FTMS {1,1} + p ESI Full ms [200.00-2000.00]

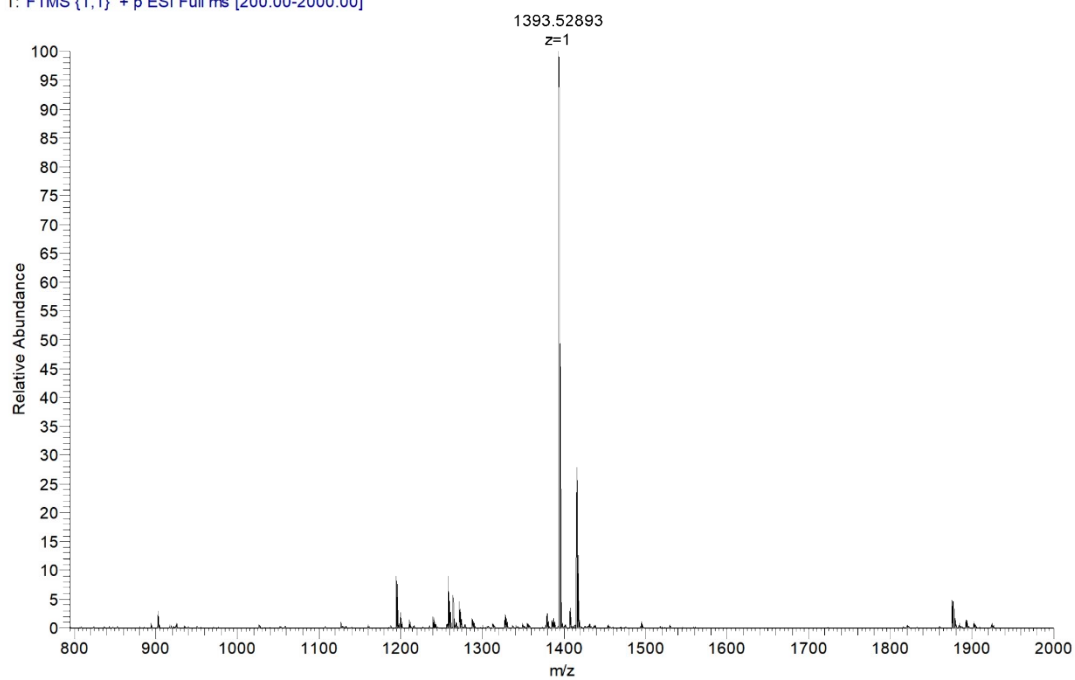


Figure S17 ESI-MS of **R-1a**

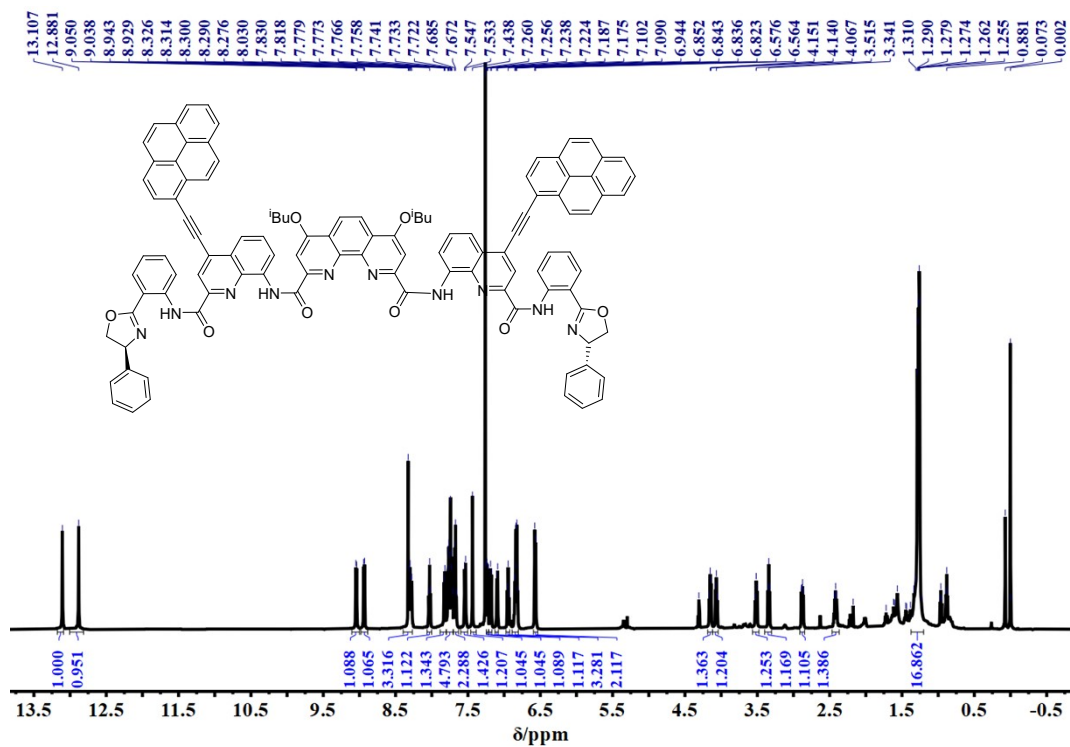


Figure S18 ¹H NMR of **S-1b** (CDCl₃)

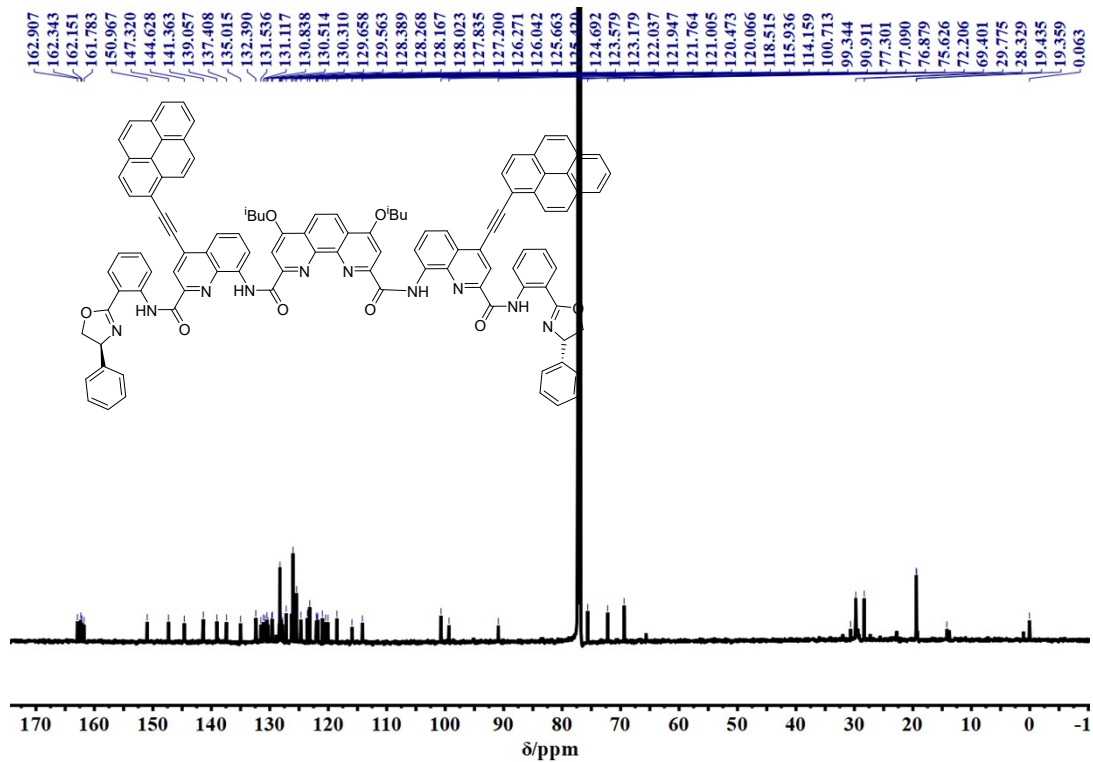


Figure S19 ¹³C NMR of **S-1b** (CDCl₃)

COD-98S #53 RT: 0.86 AV: 1 NL: 2.01E4
T: FTMS (1,1) + p ESI Full ms [200.00-2000.00]

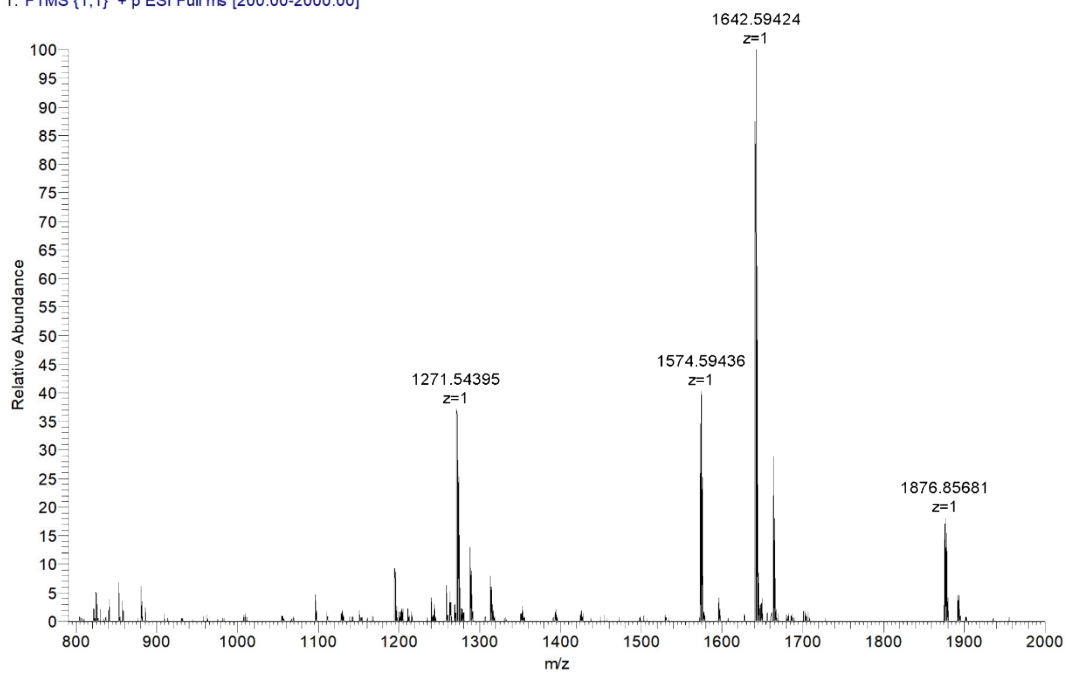


Figure S20 ESI-MS of **S-1b**

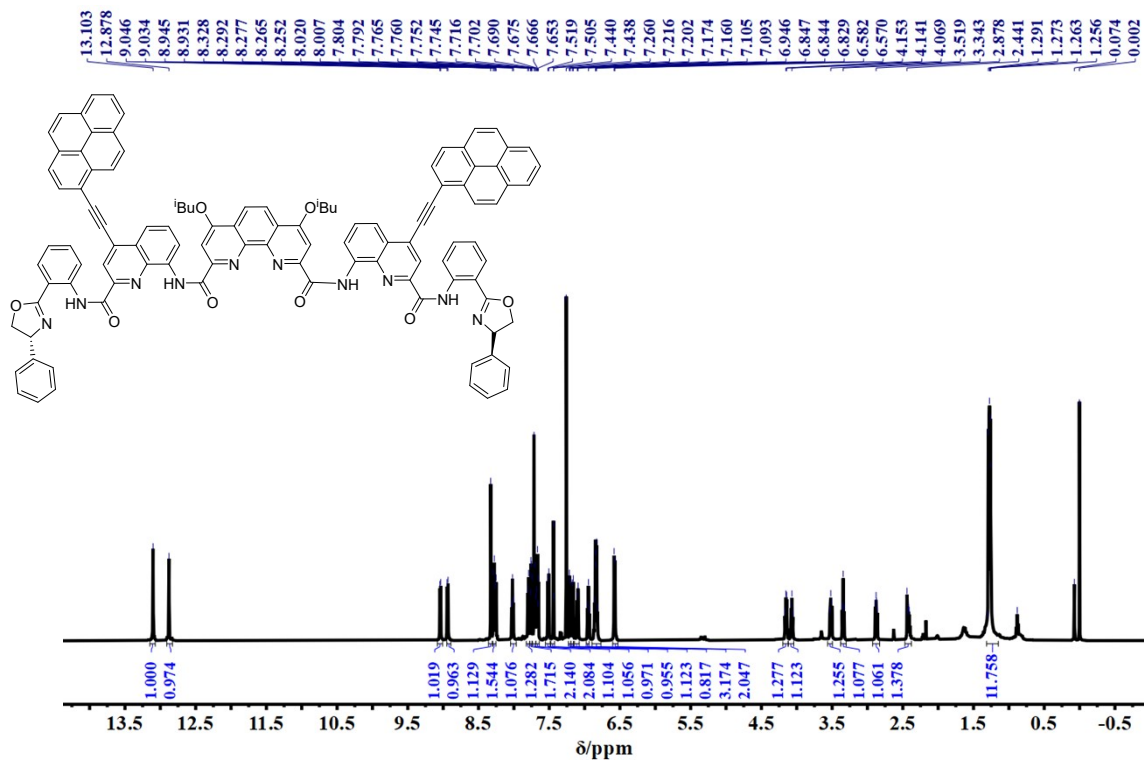


Figure S21 ¹H NMR of *R-1b* (CDCl₃)

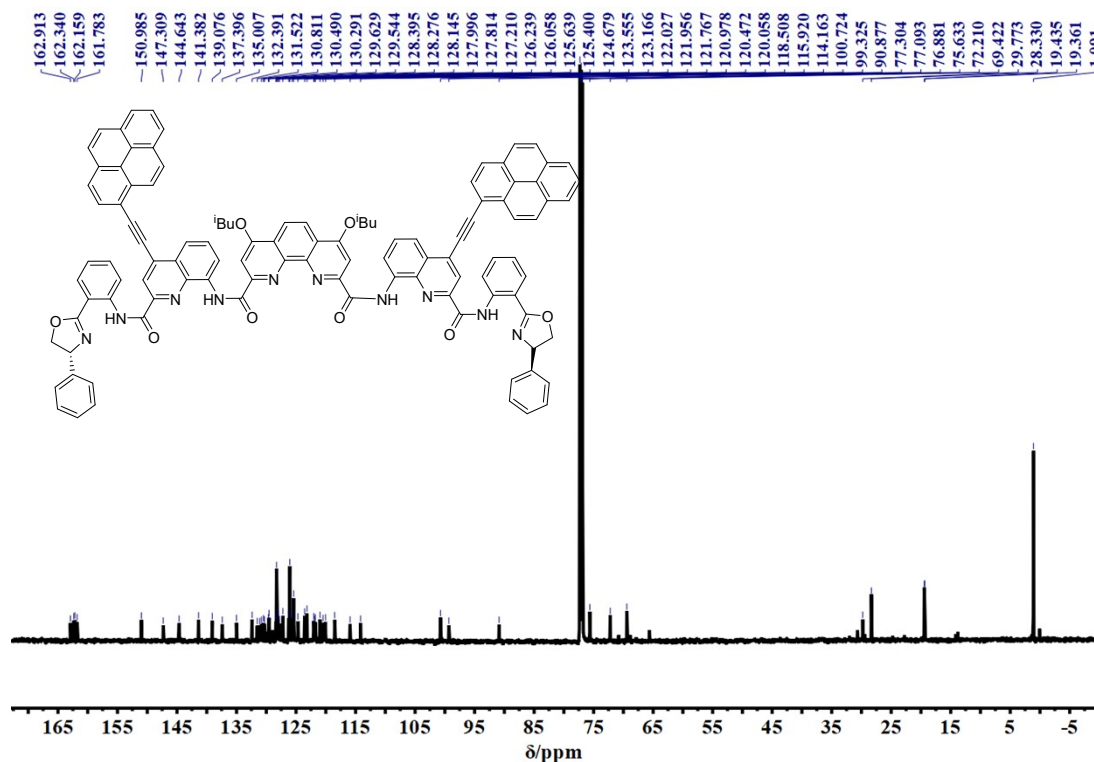


Figure S22 ¹³C NMR of *R-1b* (CDCl₃)

COD-98R #55 RT: 0.86 AV: 1 NL: 4.84E4
T: FTMS (1,1) + p ESI Full ms [200.00-2000.00]

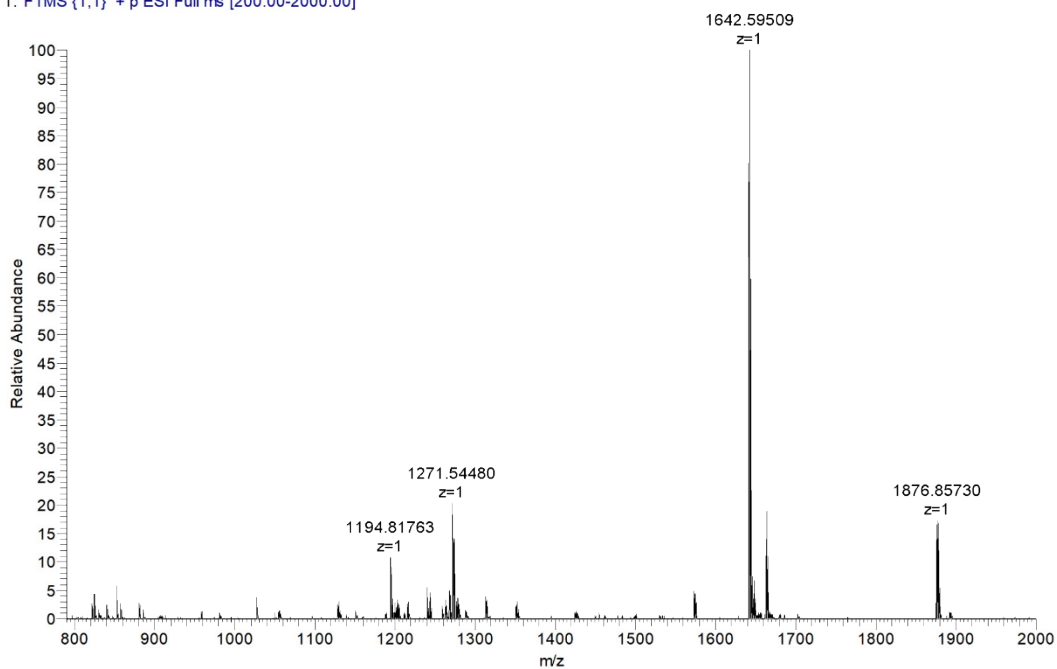


Figure S23 ESI-MS of **R-1b**

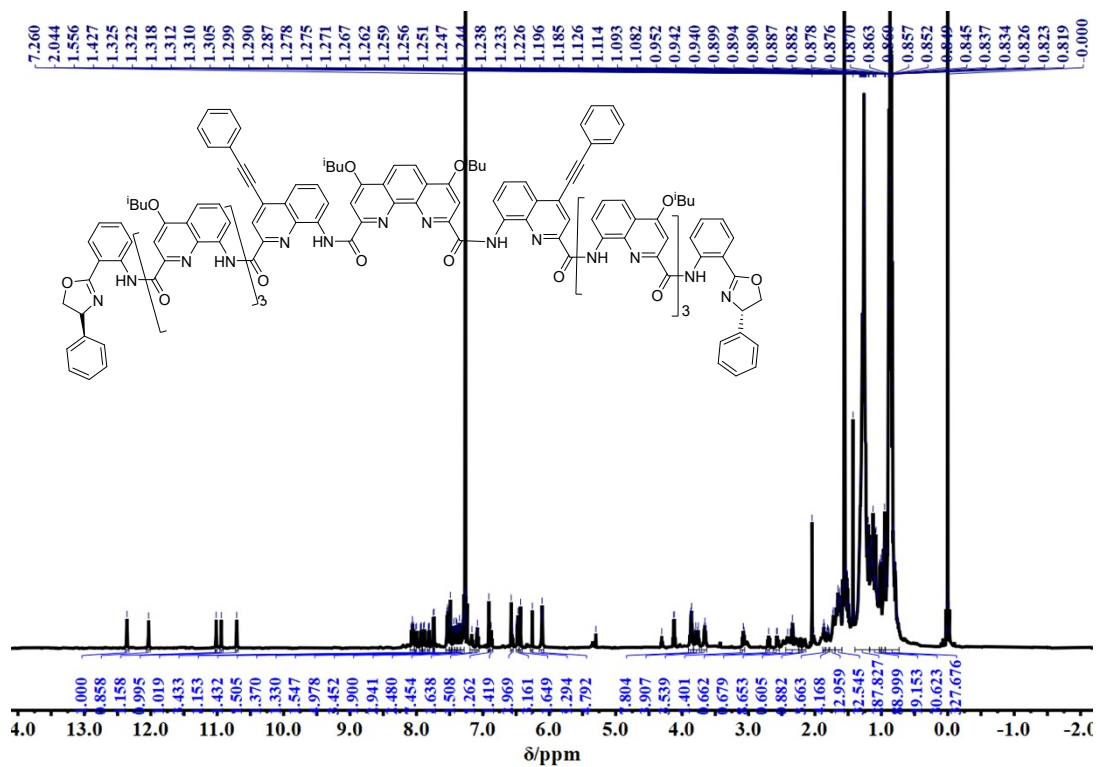


Figure S24 ¹H NMR of **S-2a** (CDCl₃)

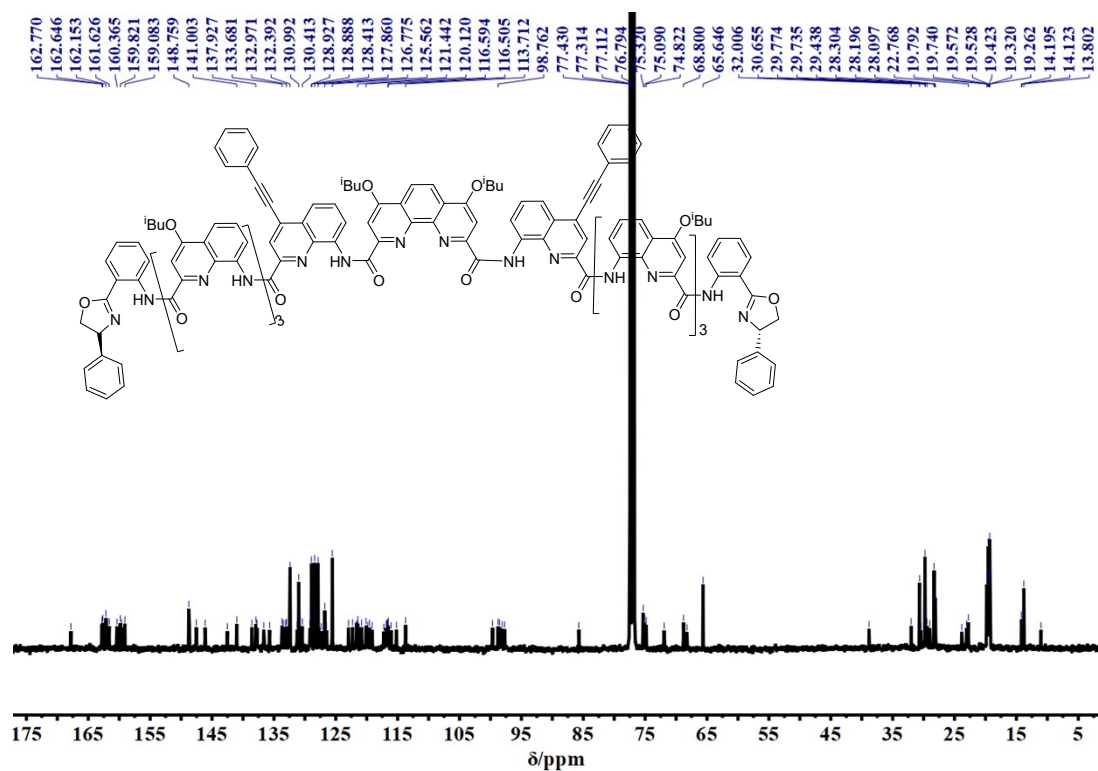


Figure S25 ^{13}C NMR of **S-2a** (CDCl_3)

COD-117S #7 RT: 0.13 AV: 1 NL: 2.63E4
 T: FTMS (1,1) + p ESI Full ms [400.00-3000.00]
 1424.08594

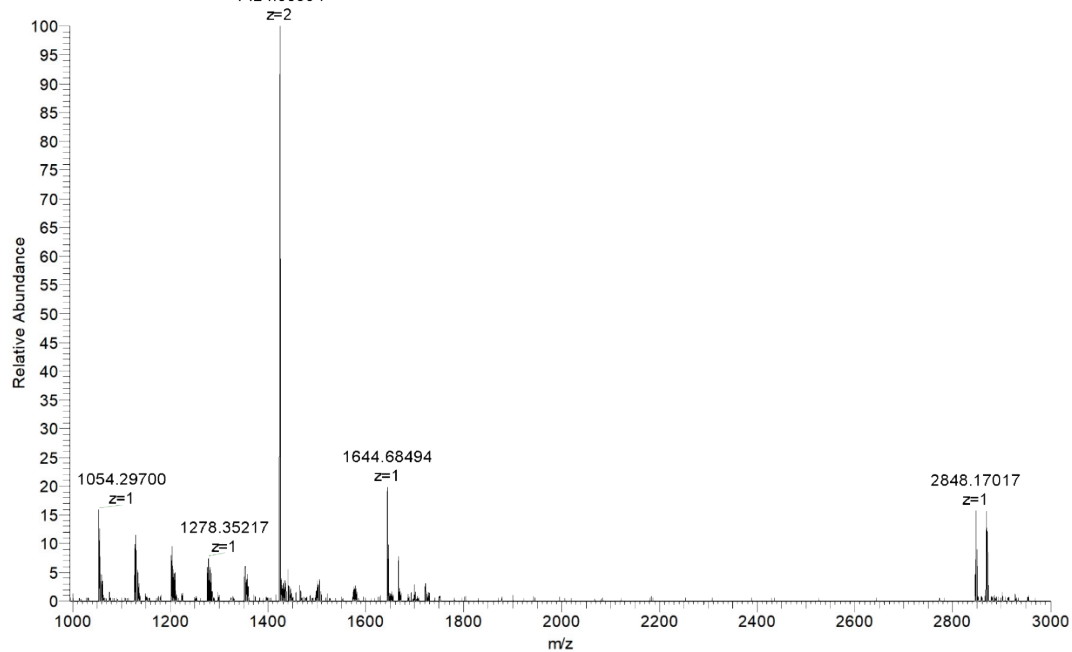


Figure S26 ESI-MS of **S-2a**

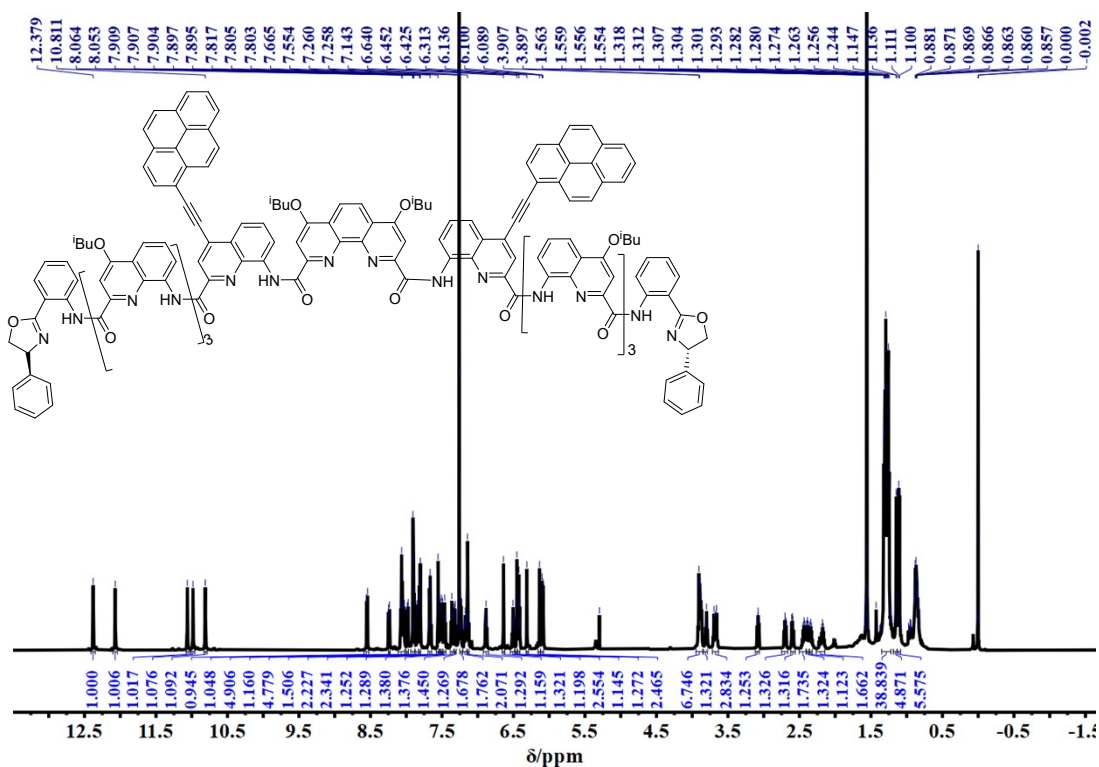


Figure S27 ^1H NMR of *S-2b*(CDCl_3)

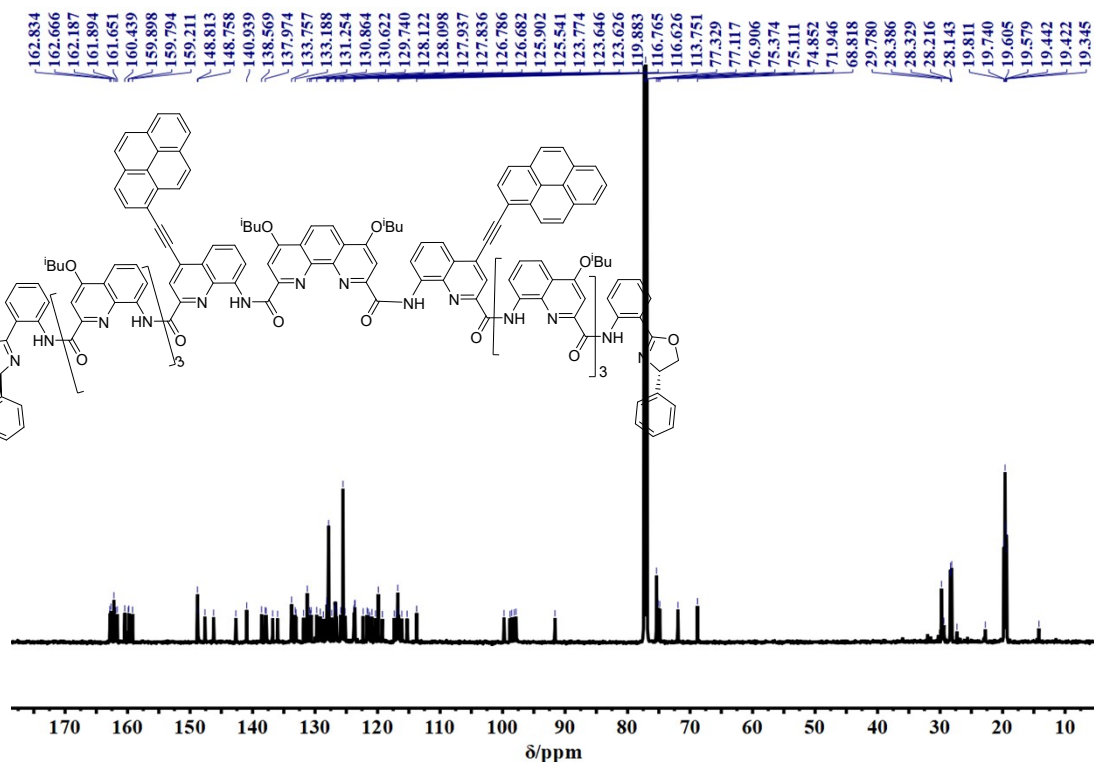


Figure S28 ^{13}C NMR of *S-2b*(CDCl_3)

110S #15 RT: 0.32 AV: 1 NL: 1.23E3
T: FTMS (1,1) + p ESI Full ms [500.00-4000.00]

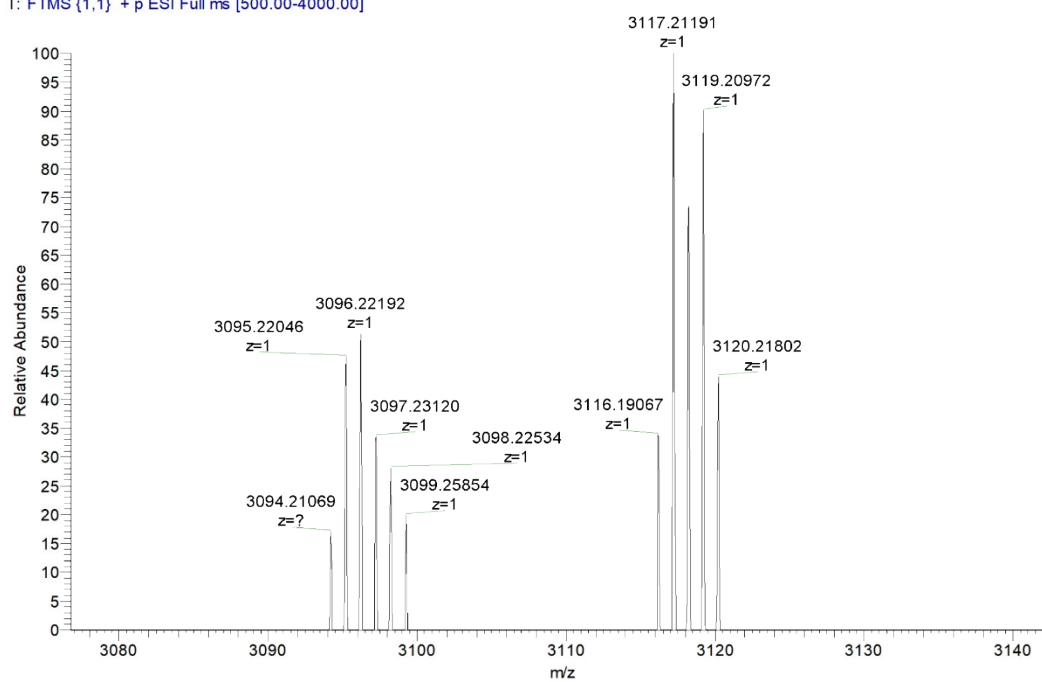


Figure S29 ESI-MS of **S-2b**

Reference:

- 1 (a)D. Zheng, C. Yu, L. Zheng, Y. Zhan and H. Jiang, *Chin. Chem. Lett.*, 2020, **31**, 673-676; (b)D. Zheng, L. Zheng, C. Y. Yu, Y. L. Zhan, Y. Wang and H. Jiang, *Org. Lett.*, 2019, **21**, 2555-2559.
- 2 (a)T. Mori, *Circularly Polarized Luminescence of Isolated Small Organic Molecules*, Springer Nature Singapore Pte Ltd., Singapore, 2020; (b) L. Arrico, L.Di Bari, and F. Zinna, *Chem. Eur. J.* 2021, 27, 2920 – 2934.