Electronic Supplementary Information (ESI)

Dithienylethene-based supramolecular chiroptical switch in phosphate-coordination-driven 2:2 duplexes

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Table of contents

S1. General Information

All starting materials and solvents were obtained from commercial sources (Beijing InnoChem, Aladdin, Shanghai Bide Pharmaceutical Technology Co., Ltd, Macklin Science & Technology Co., Ltd.), which were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400/500/700 MHz spectrometer at 298 K. ^{1}H NMR chemical shifts were reported relative to residual solvent peaks (^{1}H NMR: 2.50 ppm for DMSO-d_6, 1.94 ppm for CD_3CN). Single crystal X-ray data were recorded on Bruker D8 Venture Photon II diffractometer.

Absorption spectra were recorded on Thermo Scientific Evolution One (1 cm quartz cell). Ring closing and opening experiments for the ligand and complexes were carried out using 313 nm UV lamp (8 W) and 625 nm LED lamp (20 W) irradiation. The UV-vis and CD light irradiation experiments were in - situ conducted in quartz cuvettes, while the NMR light irradiation experiments were in - situ carried out in NMR tubes.

The phosphate salts are not commercially available and were prepared by acid-base reaction from corresponding tetraalkylammonium hydroxide solution (water) and phosphoric acid. The phosphoric acid (H_3PO_4) was placed in a small vial and certain amounts of hydroxide was added. The mixture was diluted to 1 mL and the prepared solution was used directly.

($K \subset$ [18] crown-6)$_3PO_4$ (water): Three equivalents of [18] crown-6 was mixed with K_3PO_4 and diluted with water to a certain concentration.

TEA_3PO_4 (water): H_3PO_4 was mixed with three equivalents of TEAOH (25% wt, H_2O).

S2. Synthesis Procedures of ligand *o*-L[1] and *(S)-o*-L[2]

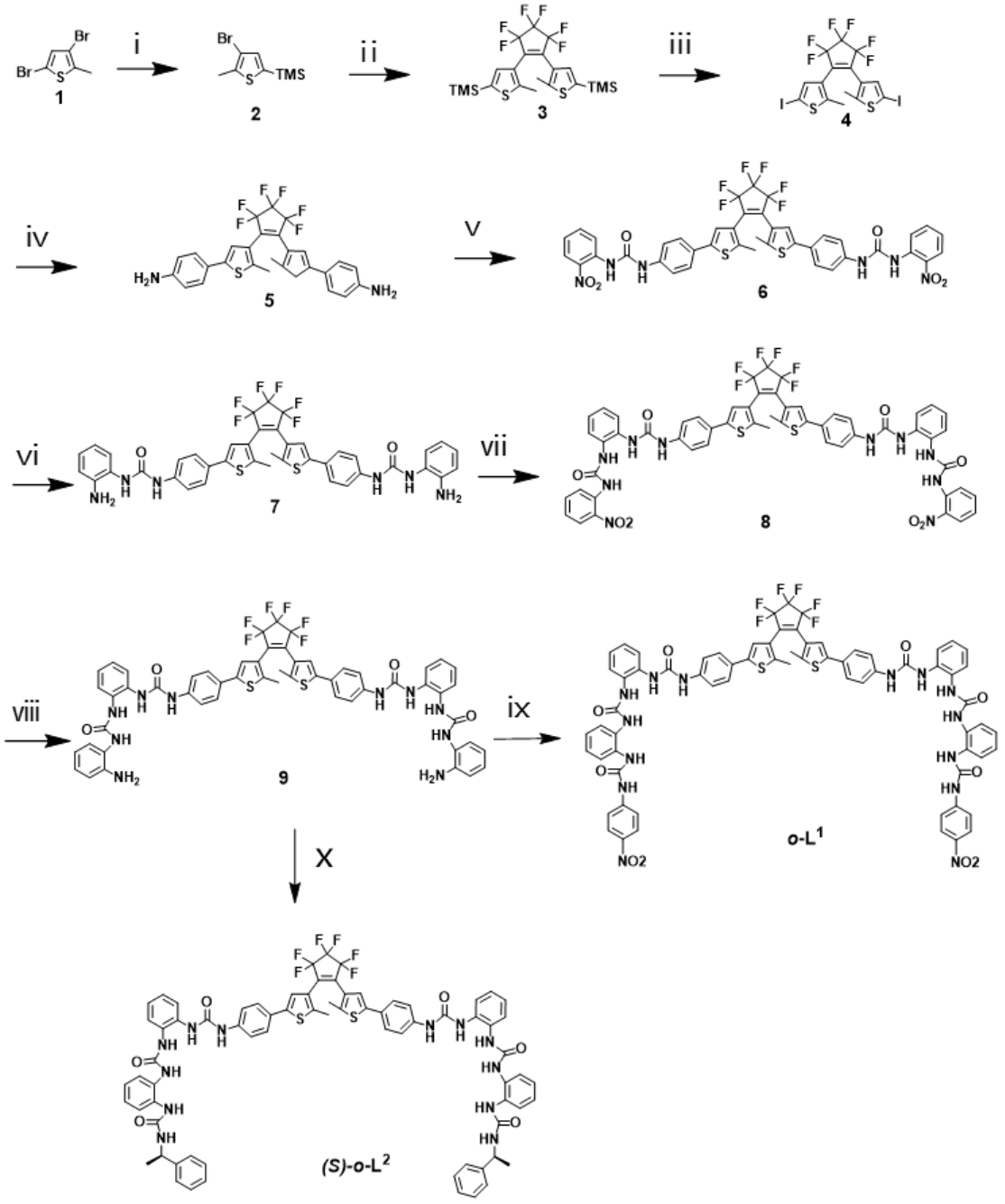


Figure S1. Synthetic scheme of ligand ***o*-L[1]** and ***(S)-o*-L[2]**. (i) n-BuLi, THF, -78℃, chlorotrimethylsilane; (ii) n-BuLi, THF, -78℃, perfluorocyclopentene; (iii) DCM, iodine monochloride, ice-salt bath; (iv) K_3CO_3, tetrakis(triphenylphosphine)palladium, 4-aminophenylboronic acid pinacol ester, THF, H_2O, 70℃; (v) 2-nitrophenyl isocyanate, THF, reflux; (vi) Pd/C 10% cat., $N_2H_4 \cdot H_2O$, EtOH, THF, reflux; (vii) 2-nitrophenyl isocyanate, THF, DMF, reflux; (viii) Pd/C 10% cat., $N_2H_4 \cdot H_2O$, EtOH, THF, reflux; (ix) 4-nitrophenyl isocyanate, THF, DMF, reflux; (x) *(S)*-(-)-1-phenylethyl isocyanate, THF, DMF, reflux.

Compound 2- 5 were prepared according to literature methods.[1-3]

Compound 2

The hexane solution of *n*-BuLi (4.2 mL, 2.5 mmol L^{-1}) was added dropwise at -78 ℃ under N_2 atmosphere to a solution of compound 1 (3.0 g, 11.7 mmol) in dry THF (100 mL). After 1 h,

chlorotrimethylsilane (1.4 mL, 1.3 mmol) was added. After stirring for 1 h, cooling was removed and the solution was allowed to room temperature. Ammonium chloride saturated aqueous solution was added to the reaction system to quench the reaction, subsequently, the reaction mixture was poured into water, and layers were separated. The aqueous layer was extracted with DCM, and merged organic layers were dried over sodium sulfate, filtered off. Column chromatography (silica, n-hexane) yielded purified product as a yellow liquid (2.3 g, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01 (s, 1H), 2.42 (s, 3H), 0.29 (s, 9H).

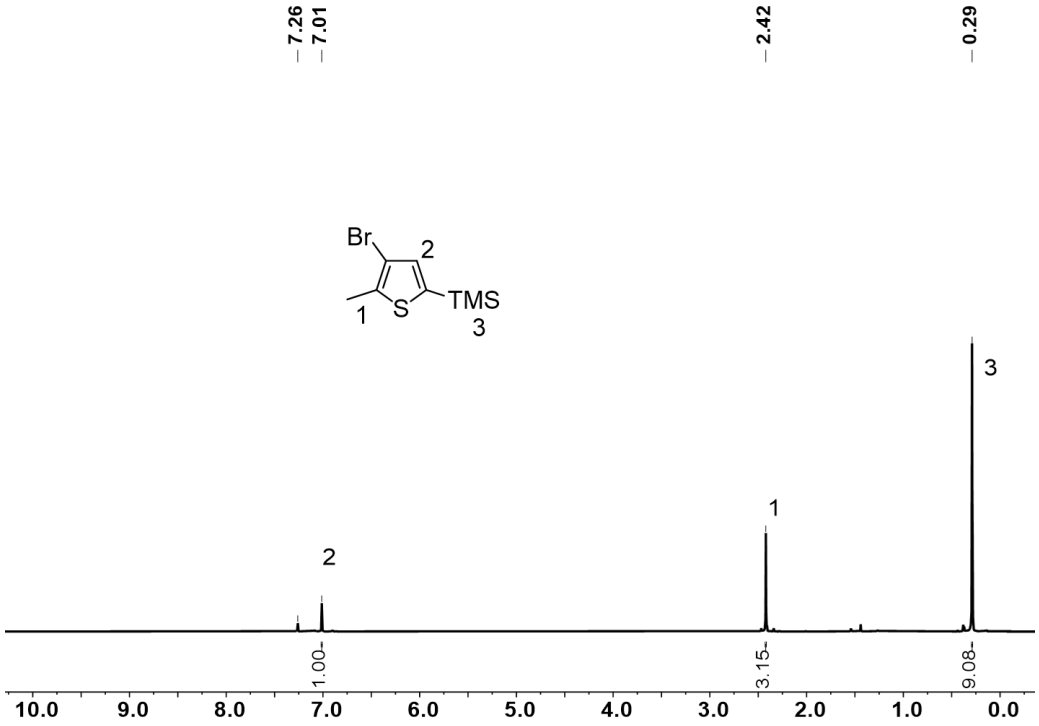


Figure S2. ^{1}H NMR spectra of compound **2** (400 MHz, $CDCl_3$, 298 K).

Compound 3

The hexane solution of *n*-BuLi (4.8 mL, 2.5 mmol L^{-1}) was added dropwise at -78 ℃ under N_2 atmosphere to a solution of compound **2** (3.1 g, 14.3 mmol) in anhydrous THF (100 mL). After 1 h, octafluorocyclopentene (0.8 mL, 5.9 mmol) was added. After stirring for 1 h, cooling was removed and the solution was allowed to room temperature. Ammonium chloride saturated aqueous solution is added to the reaction system to quench the reaction, subsequently, the reaction mixture was poured into water, and layers were separated. The aqueous layer was extracted with DCM, and merged organic layers were dried over sodium sulfate, filtered off. Column chromatography (silica, n-hexane) yielded purified product as white solid (2.0 g, 57 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.05 (s, 1H), 1.90 (s, 3H), 0.27 (s, 9H).

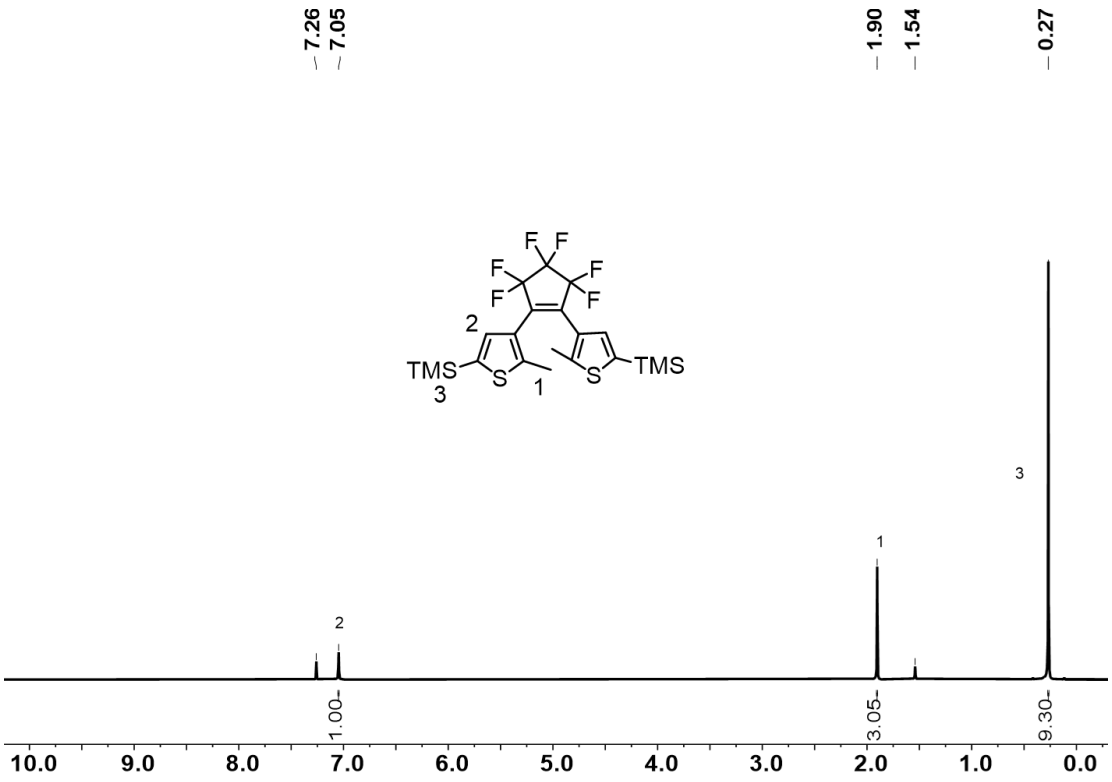


Figure S3. ^{1}H NMR spectra of compound **3** (400 MHz, $CDCl_3$, 298 K).

Compound 4

The DCM solution of ICl (1.3 g, 7.8 mmol) was added dropwise at 0 ℃ under N_2 atmosphere to a solution of compound **3** (1.0 g, 2.0 mmol) in anhydrous DCM (50 mL). After stirring for 2 h, cooling was removed and the solution was allowed to room temperature. Ammonium chloride saturated aqueous solution was added to the reaction system to quench the reaction, subsequently, the reaction mixture was poured into water, and layers were separated. The aqueous layer was extracted with DCM, and merged organic layers were dried over sodium sulfate, filtered off. Column chromatography (silica, n-hexane) yielded purified product as white solid (0.8 g, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (s, 1H), 1.90 (s, 3H).

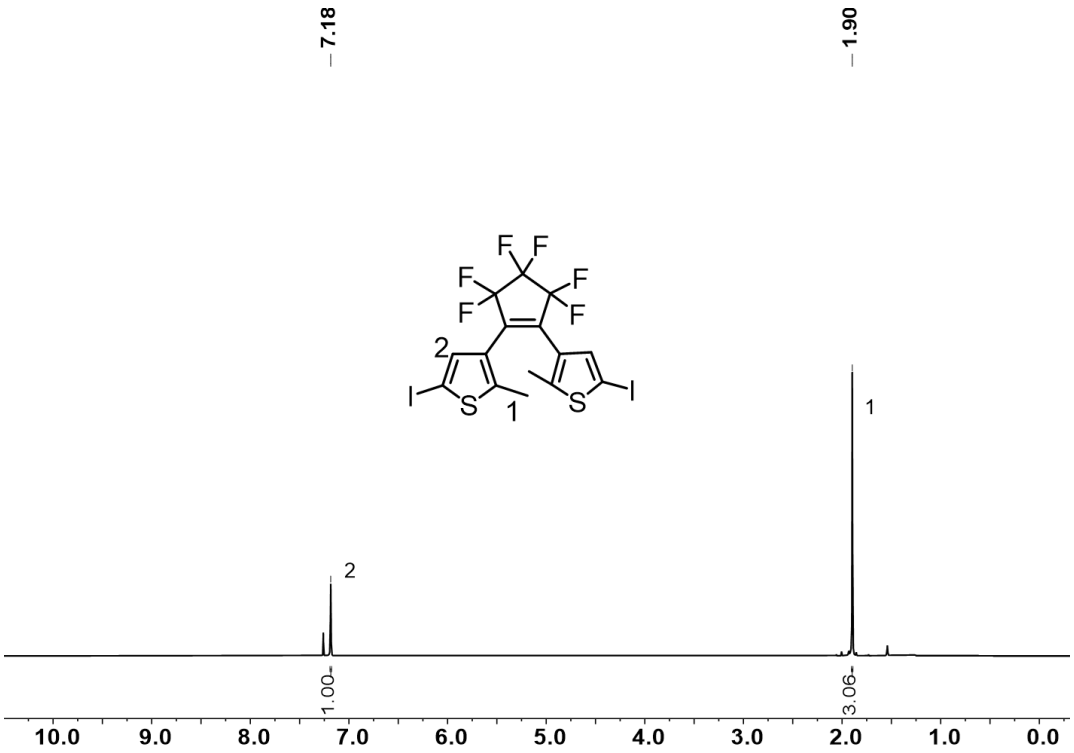


Figure S4. ^{1}H NMR spectra of compound **4** (400 MHz, $CDCl_3$, 298 K).

Compound 5

K_3CO_3 (5.1 g, 37mmol), Tetrakis(triphenylphosphine)palladium (0.3, 0.023 mmol), 4-aminophenylboronic acid pinacol ester (1.3 g, 4.8 mmol) and compound **4** (1.4 g, 2.3 mmol) were added to the mixed solution of THF (30mL) and H_2O (5 mL). The above solution was degassed with N_2 bubbling for 15 min, Subsequently, heating up to 70 ℃. After stirring for 20 h, heat was removed and the solution was allowed to cool to room temperature. Ammonium chloride saturated aqueous solution is added to the reaction system to quench the reaction, subsequently, the reaction mixture was poured into water, and layers were separated. The aqueous layer was extracted with DCM, and merged organic layers were dried over sodium sulfate, filtered off. Column chromatography (silica, hexanes/ethyl acetate 7:3) yielded purified product as green solid (1.1g, 86%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.27 (d, J = 8.6 Hz, 2H), 7.14 (s, 1H), 6.58 (d, J = 8.6 Hz, 2H), 5.41 (s, 2H), 1.91 (s, 3H).

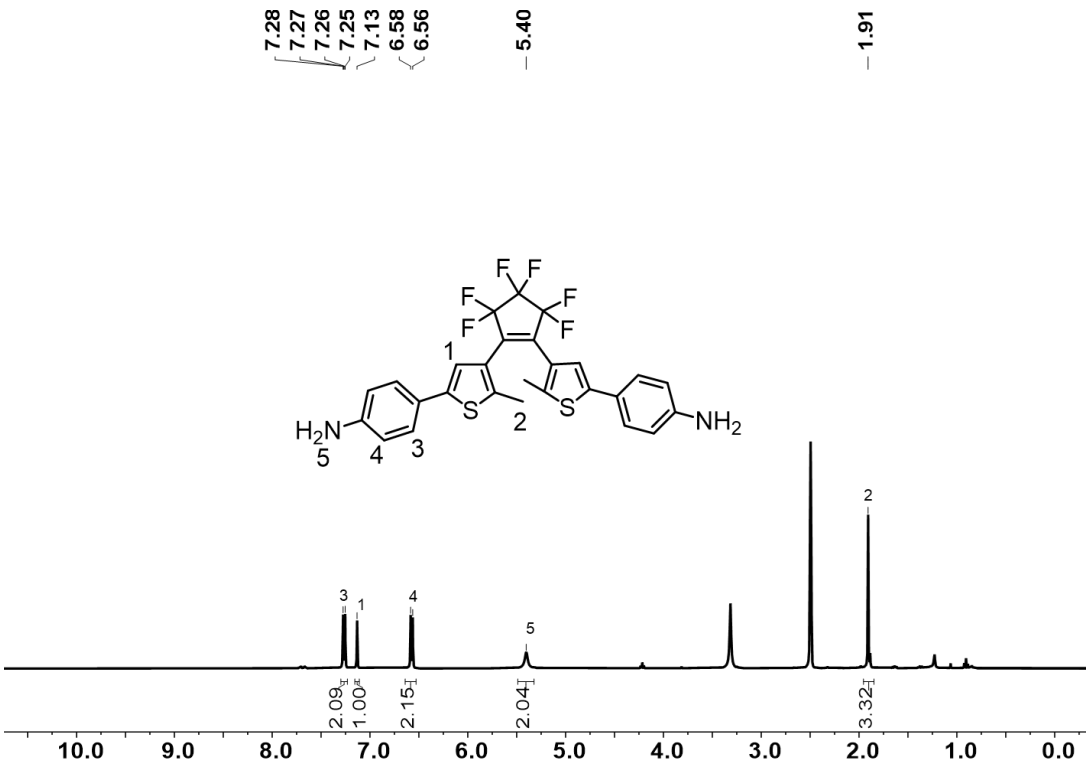


Figure S5. ^{1}H NMR spectra of compound **5** (400 MHz, DMSO-d_6, 298 K).

Compound 6

The THF solution of 2-nitrophenyl isocyanate (0.5 g, 3.25mmol) was added dropwise at 70 ℃ under N_2 atmosphere to a solution of compound **5** (0.7 g, 1.3mmol) in dry THF (50 mL). After stirring for 7 hours, the mixture was concentrated, and petroleum ether was added. The precipitable was filtered and washed several times with petroleum ether to obtain a yellow-green solid **6**（1.0 g，65 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 10.00 (s, 1H), 9.61 (s, 1H), 8.30 (d, J = 8.5, 1.3 Hz, 1H), 8.10 (d, J = 8.4, 1.6 Hz, 1H), 7.71 (t, 1H), 7.57 (m, 3H), 7.41 (s, 1H), 7.22 (t, 1H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.2, 142.2, 140.8, 139.8, 138.3, 135.5, 135.2, 127.2, 126.4, 125.9, 125.5, 123.1, 122.9, 121.9, 119.4, 56.5, 19.0, 14.5. MALDI TOF-MS (m/z): calculated for $C_{41}H_{28}F_6N_6NaO_6S_2^+$ at $[M+Na]^+$: 901.13; found: 901.16.

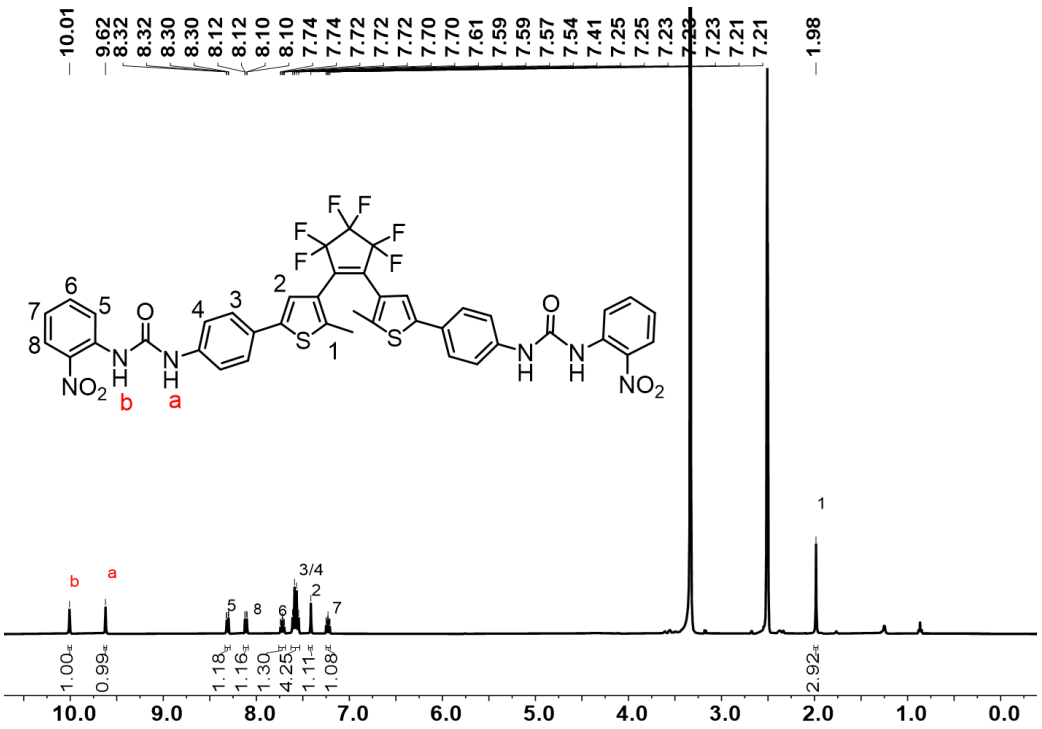


Figure S6. ^{1}H NMR spectra of compound **6** (400 MHz, DMSO-d_6, 298 K).

Compound 7

Hydrazine monohydrate (1.0 mL) was added dropwise to a suspension of compound **6** (1.40 g, 1.9 mmol) and Pd/C 10% (0.2 g, cat.) in a mixture of ethanol (150 mL) and THF (50 mL). After refluxing and stirring for 48 hours, the deposit was filtered off, dissolved in DMF (60 mL), and filtered through Celite to remove Pd/C. The DMF solution was poured in ethanol (500 mL) and the precipitate thus obtained was filtered off, washed several times with ethanol and then dried over vacuum to give compound **7** as a yellow solid (0.2g, 70 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ = ppm: 8.95 (s, 1H), 7.75 (s, 1H), 7.53 (m, 4H), 7.39 - 7.31 (m, 2H), 6.89- 6.82 (m, 1H), 6.75 (d, J = 8.0, 1.5 Hz, 1H), 6.59 (m, 1H), 4.80 (s, 2H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.4, 142.4, 141.5, 140.7, 140.5, 126.4, 126.3, 125.5, 125.0, 124.3, 121.5, 118.7, 117.3, 116.4. MALDI TOF-MS (m/z): calculated for $C_{41}H_{32}F_6N_6NaO_2S_2^+$ at $[M+Na]^+$: 841.18; found: 841.20.

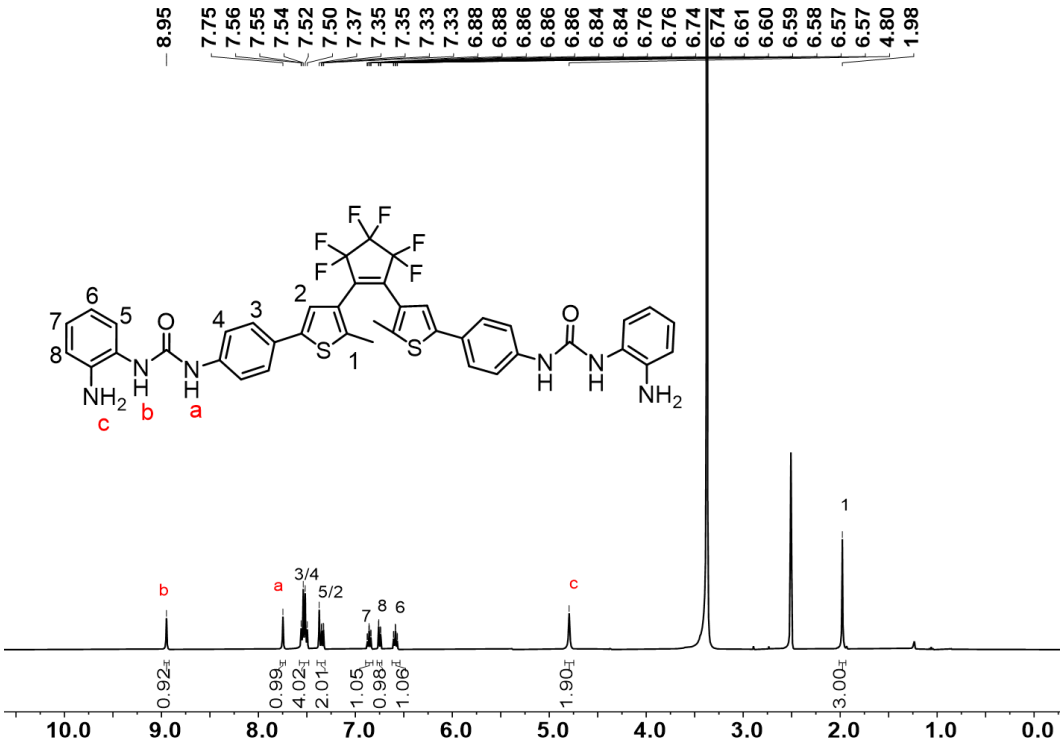


Figure S7. ^{1}H NMR spectra of compound **7** (400 MHz, DMSO-d_6, 298 K).

Compound 8

The THF solution of 2-nitrophenyl isocyanate (0.4 g，2.4 mmol) was added dropwise at 70 ℃ under N_2 atmosphere to a solution of compound **7** (0.8 g, 0.98 mmol) in a mixture of dry THF (50 mL) and dry DMF (10 mL). After stirring for 7 hours, the mixture was concentrated, and petroleum ether was added. The precipitable was filtered and washed several times with petroleum ether to obtain a yellow- brown solid **8** (0.9g, 82 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.75 (s, 1H), 9.31 (s, 1H), 9.23 (s, 1H), 8.33 (dd, J = 8.6, 1.3 Hz, 1H), 8.11 - 8.08 (m, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 8.7, 7.2, 1.6 Hz, 1H), 7.57 - 7.51 (m, 4H), 7.43 (dd, J = 8.0, 1.5 Hz, 1H), 7.37 (s, 1H), 7.23 - 7.16 (m, 2H), 7.10 - 7.05 (m, 1H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.4, 153.1, 142.3, 140.6, 140.3, 138.1, 135.5, 135.4, 133.5, 129.3, 126.6, 126.4, 126.1, 125.9, 125.5, 123.8, 123.2, 123.1, 122.8, 121.6, 118.9, 56.5, 19.0, 14.5. MALDI TOF-MS (m/z): calculated for $C_{50}H_{40}F_6N_{10}NaO_8S_2^+$ at $[M+Na]^+$: 1169.23; found: 1169.37.

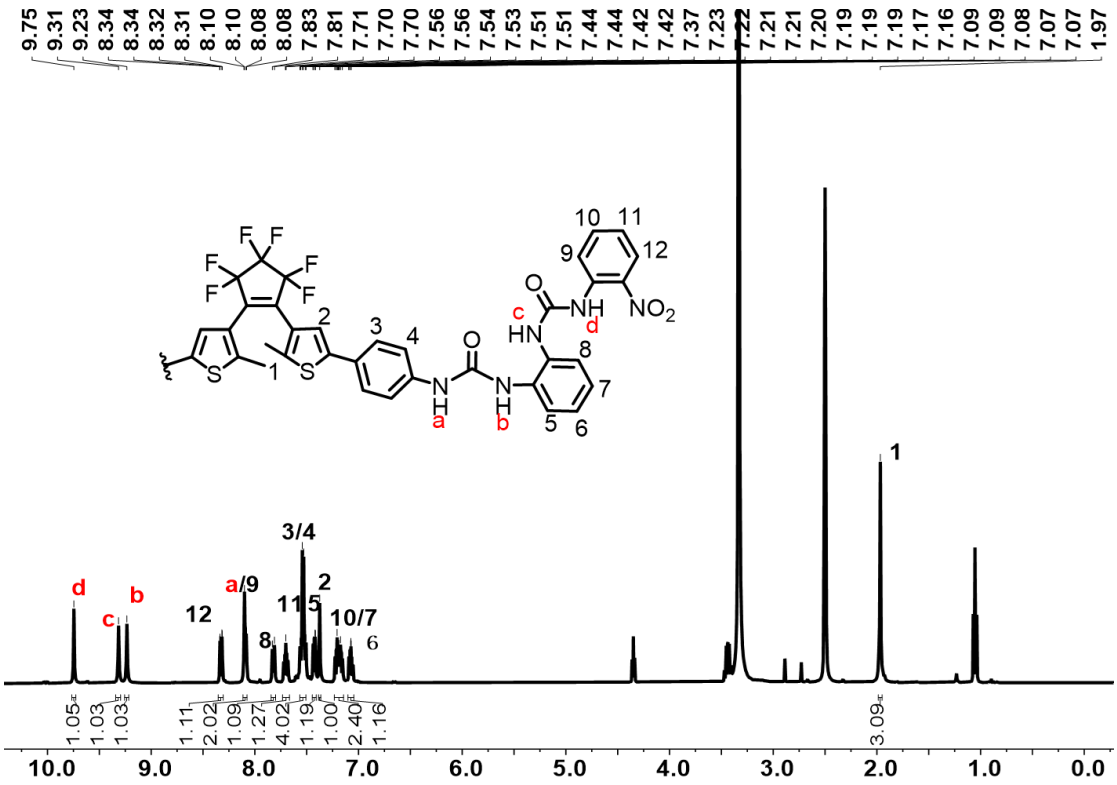


Figure S8. ^{1}H NMR spectra of compound **8** (400 MHz, DMSO-d_6, 298 K).

Compound 9

Hydrazine monohydrate (1 mL) was added dropwise to a suspension of compound **8** (0.37g, 0.32mmol) and 10% Pd/C (0.1 g, cat.) in a mixture of ethanol (200 mL) and THF (50 mL). After refluxing and stirring for 10 hours, the deposit was filtered off, dissolved in DMF (60 mL), and filtered through Celite to remove Pd/C. The DMF solution was poured in ethanol (500 mL) and the precipitate thus obtained was filtered off, washed several times with ethanol and then dried over vacuum to give compound **9** as a blue solid (0.22 g, 63 %).^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.27 (s, 1H), 8.17 (s, 1H), 8.09 (d, *J* = 2.3 Hz, 2H), 7.60 - 7.53 (m, 6H), 7.38 (s, 1H), 7.33 (d, *J* = 7.9, 1.5 Hz, 1H), 7.11 - 7.06 (m, 2H), 6.83 (d, *J* = 7.6, 1.5 Hz, 1H), 6.73 (d, *J* = 7.9, 1.5 Hz, 1H), 6.56 (m, 1H), 4.80 (s, 2H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.8, 154.4, 153.5, 142.4, 141.6, 140.5, 132.3, 131.3, 126.5, 126.4, 125.5, 125.1, 124.9, 124.8, 124.7, 124.6, 124.2, 121.6, 118.9, 117.2, 116.3, 36.3, 31.2, 14.5. MALDI TOF-MS (m/z): calculated for $C_{55}H_{44}F_6N_{10}NaO_4S_2^+$ at $[M+Na]^+$: 1109.28; found: 1109.33.

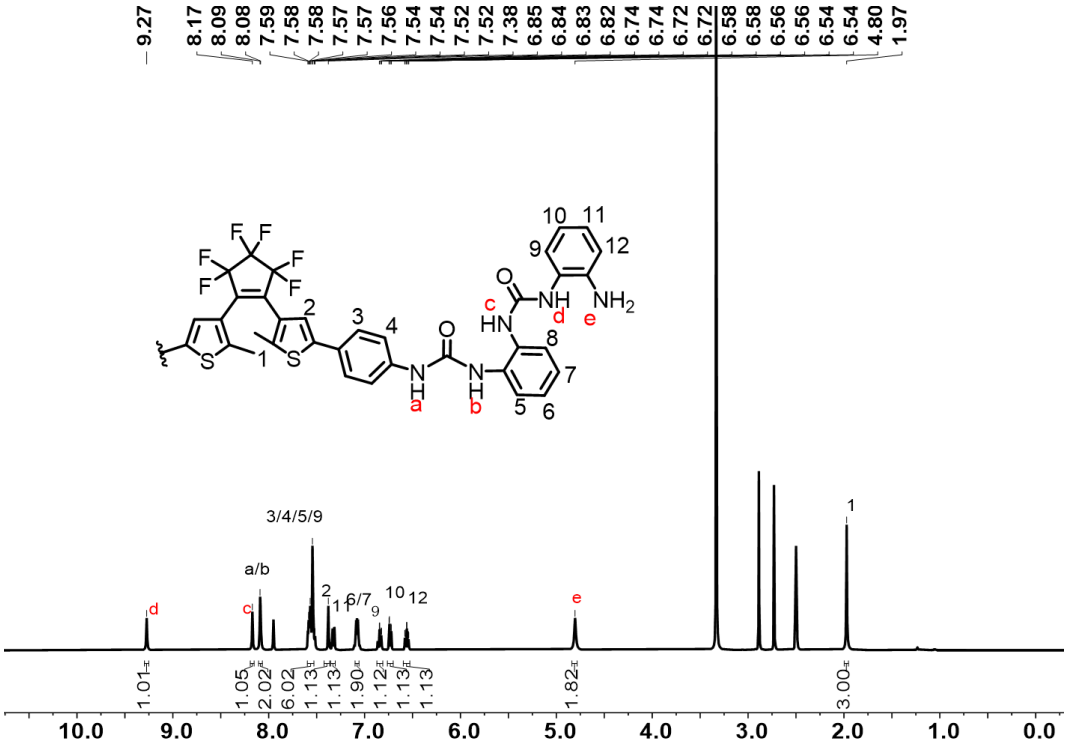


Figure S9. ^{1}H NMR spectra of compound **9** (400 MHz, DMSO-d_6, 298 K).

Compound *o*-L^{1}

The THF solution of 4-nitrophenyl isocyanate (0.13 g，0.8 mmol) was added dropwise at 70 ℃ under N_2 atmosphere to a solution of compound **9** ((0.35 g，0.32 mmol) in a mixture of dry THF (30 mL) and dry DMF (5 mL). After stirring for 7 hours, the mixture was concentrated, and petroleum ether was added. The precipitable was filtered and washed several times with petroleum ether to obtain a yellowish-brown solid ***o*-L^{1}** (0.26 g, 57 %). ^{1}H NMR (400 MHz, DMSO-d_6, 298K) δ = 9.88 (s, 1H), 9.29 (s, 1H), 8.48 (d, *J* = 13.2 Hz, 2H), 8.30 (s, 1H), 8.18 - 8.13 (m, 2H), 8.11 (s, 1H), 7.68 (d, *J* = 9.3 Hz, 2H), 7.63 - 7.54 (m, 4H), 7.53 - 7.47 (m, 4H), 7.36 (s, 1H), 7.13 - 7.07 (m, 4H), 1.96 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6, 298K) δ 154.6, 153.5, 153.2, 147.1, 142.4, 141.4, 140.6, 140.4, 132.1, 132.0, 131.5, 131.2, 126.5, 126.3, 125.6, 125.5, 125.2, 125.2, 124.8, 124.8, 124.7, 124.6, 124.5, 121.5, 119.0, 117.9, 67.5, 25.6, 14.5. MALDI TOF-MS (m/z): calculated for $C_{69}H_{52}F_6N_{14}NaO_{10}S_2^+$ at $[M+Na]^+$: 1437.32; found: 1437.61.

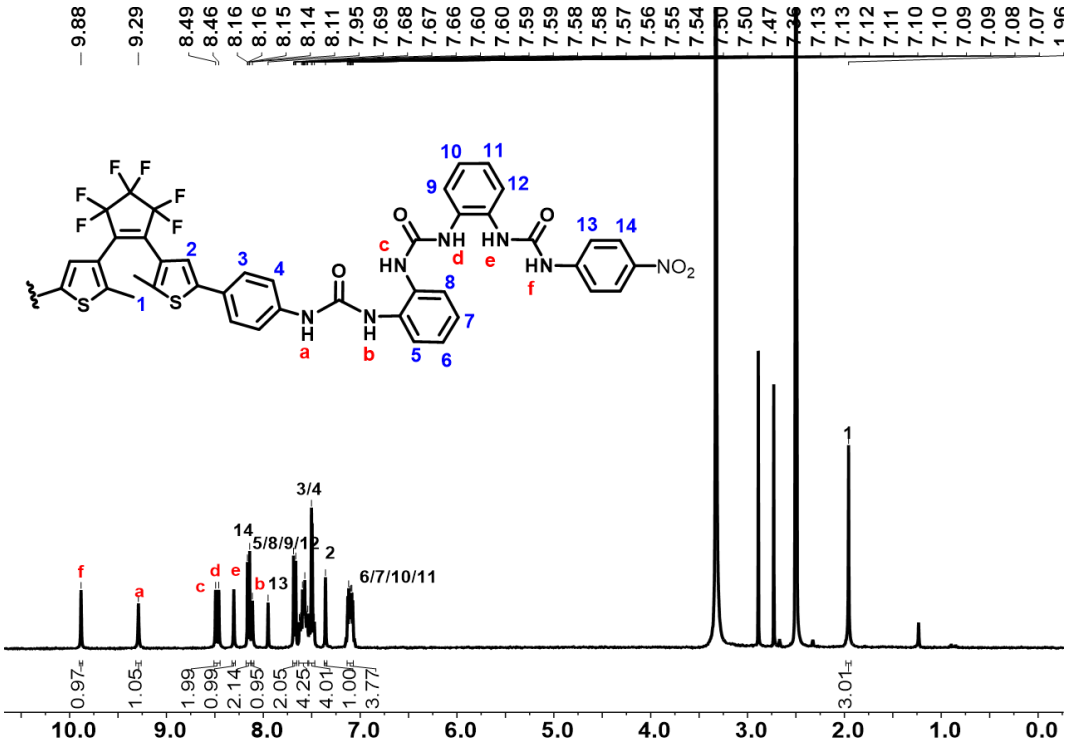


Figure S10 ^{1}H NMR spectra of compound ***o*-L^{1}** (400 MHz, DMSO-d_6, 298 K).

Compound *(S)-o*-L^{2}

The THF (30 mL) solution of *(S)*-(-)-1-Phenylethyl isocyanate (0.1 g，0.68 mmol) was added dropwise at 70 ℃ under N_2 atmosphere to a solution of compound **9** (0.22 g，0.2 mmol) in a mixture of dry THF (70 mL) and dry DMF (10 mL). After stirring for 7 hours, the mixture was concentrated, and petroleum ether was added. The precipitable was filtered and washed several times with petroleum ether to obtain a blue solid ***(S)-o*-L^{2}** (0.26 g, 93 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ= 9.30 (s, 1H), 8.42 (s, 1H), 8.36 (s, 1H), 8.08 (s, 1H), 7.86 (s, 1H), 7.62 - 7.56 (m, 3H), 7.53 (d, J = 3.9 Hz, 4H), 7.45 (d, J = 7.8, 1.7 Hz, 1H), 7.38 (s, 1H), 7.34 - 7.28 (m, 4H), 7.22 - 7.17 (m, 1H), 7.11 - 7.06 (m, 3H), 7.02 (m, 1H), 6.96 (m, 1H), 4.85 - 4.77 (m, 1H), 1.97 (s, 3H), 1.37 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.8, 155.4, 154.6, 153.5, 145.6, 142.4, 140.6, 140.5, 133.5, 131.7, 131.7, 129.8, 128.8, 128.8, 127.1, 126.5, 126.4, 125.5, 124.9, 124.6, 124.5, 124.4, 123.0, 122.6, 121.5, 118.9, 49.3, 41.9, 36.3, 31.2, 23.6, 23.6, 14.5, 11.5. MALDI TOF-MS (m/z): calculated for $C_{73}H_{62}F_6N_{12}NaO_6S_2^+$ at $[M+Na]^+$:1403.42; found:1403.98.

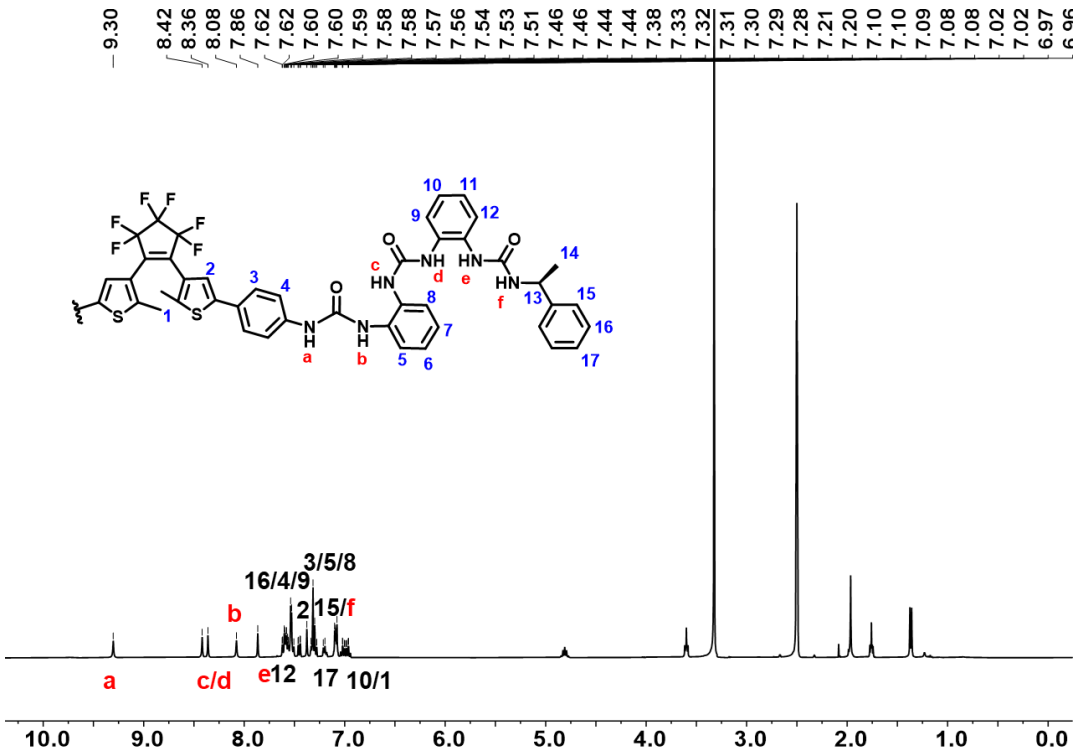


Figure S11 ^{1}H NMR spectra of compound ***(S)-o*-L^{2}** (400 MHz, DMSO-d_6, 298 K).

S3. Synthesis Procedures of complexes of *o*-H^{1} and *(S)*-o-H^{2}

(K⊂ [18] crown-6)$_6$[(*o*-L^{1})$_2$(PO$_4$)$_2$] (*o*-H^{1})

(K⊂ [18] crown-6)$_3$PO$_4$ (9.0 μL, 0.625 mol/L) was added to a suspension of ***o*-L^{1}** (8 mg) in acetonitrile (1 mL), stirring overnight at room temperature. Then the mixture was centrifugate and filtered. The clear solution followed by slow vapor diffusion of diethyl ether in two weeks, the yellow crystals of ***o*-H^{1}** was obtained (yield > 90 %). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 12.66 (s, 1H), 12.35 (s, 1H), 12.17 (s, 1H), 11.79 (d, J = 11.6 Hz, 2H), 11.52 (s, 1H), 8.40 (dd, J = 17.1, 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 9.0 Hz, 2H), 7.17 (d, J = 8.1 Hz, 1H), 7.03 (dd, J = 16.8, 8.8 Hz, 2H), 6.87 (t, J = 7.6 Hz, 1H), 6.72 (s, 1H), 6.45 (d, J = 8.3 Hz, 2H), 2.26 (s, 3H).

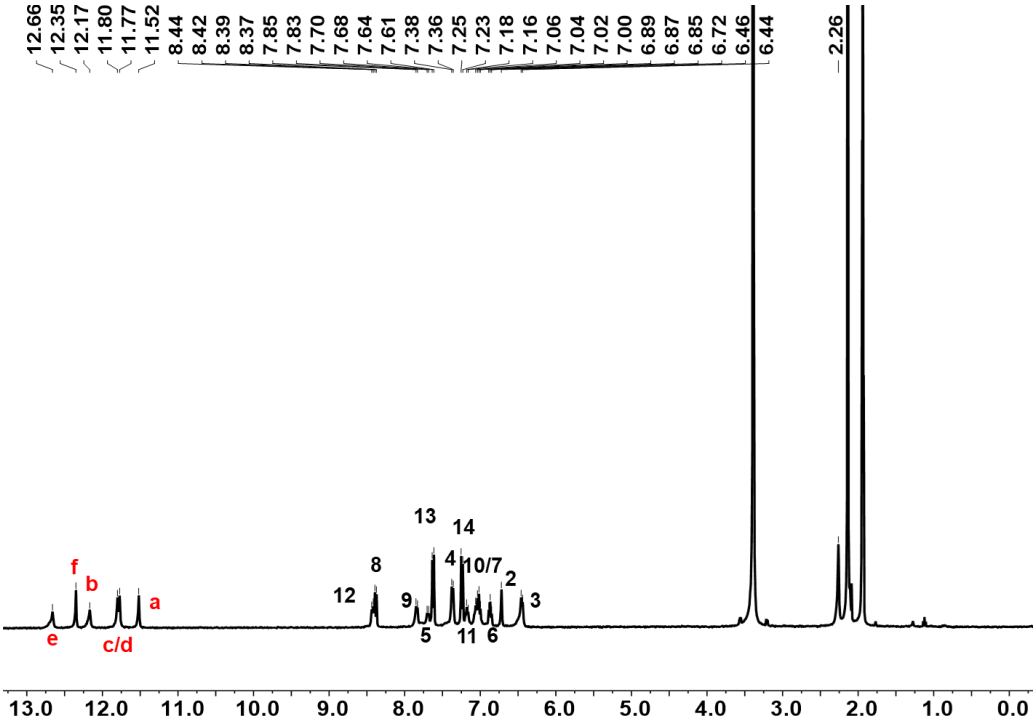


Figure S12 ^{1}H NMR spectra of compound ***o*-H^1** (400 MHz, CD_3CN, 298 K).

$TEA_6[(PO_4)_2$(*(S)*-*o*-$L^2)_2$] (*(S)*-o-H^2)

$(TEA)_3PO_4$ (5.8 μL, 0.625 mol/L) was added to a suspension of L (5 mg) in acetonitrile (1 mL). After stirring overnight at room temperature, a clear yellow solution was obtained. Diethyl ether was added to this solution to give a yellow precipitate, which was collected by centrifugation and washed with diethyl ether for several times, and dried to obtain the yellow complex of complex ***(S)*-o-H^2**. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.84 (s, 1H), 12.26 (s, 2H), 11.93 (s, 1H), 11.73 (s, 1H), 9.75 (s, 1H), 8.29 (dd, J = 8.2, 1.6 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.03 (s, 1H), 7.78 (s, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 7.2 Hz, 2H), 7.02 – 6.70 (m, 8H), 6.54 (d, J = 8.4 Hz, 2H), 4.77 – 4.67 (m, 1H), 2.28 (s, 3H).

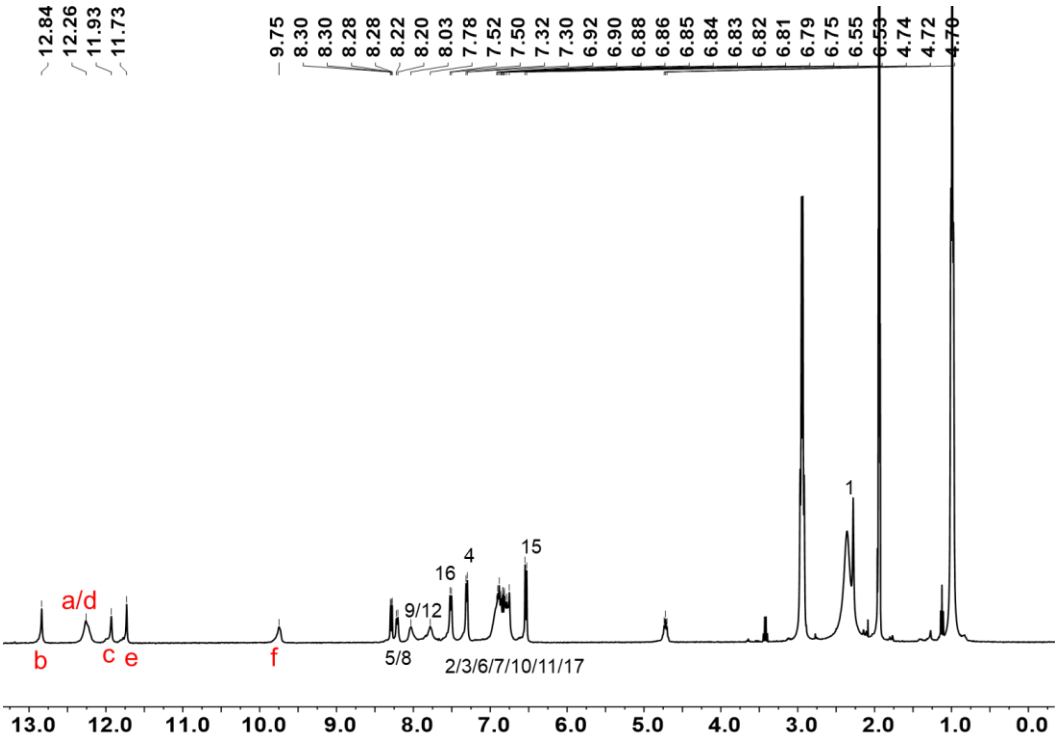


Figure S13 ^{1}H NMR spectra of compound ***(S)*-o-H^{2}** (400 MHz, CD_3CN, 298 K).

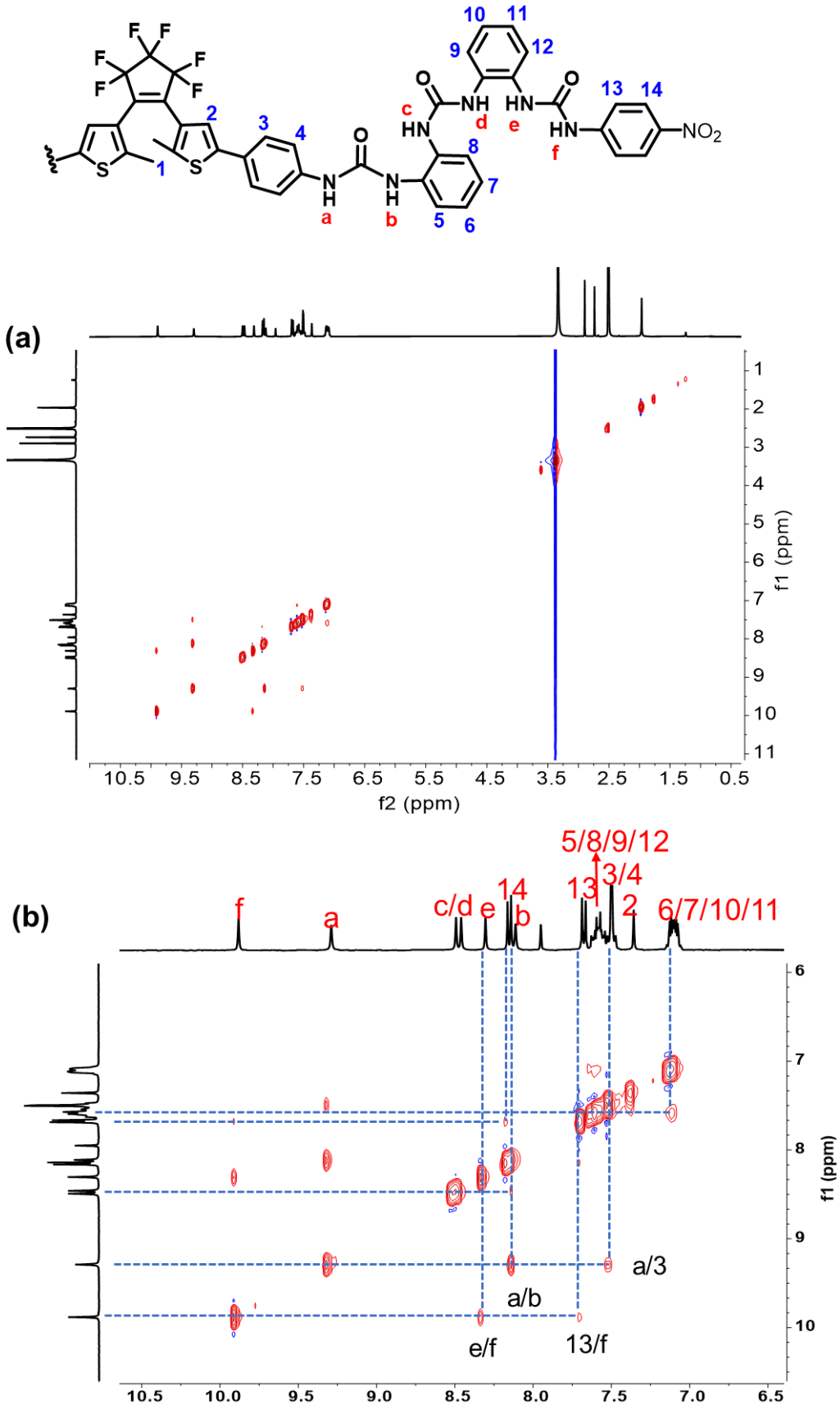


Figure S14. ^{1}H-^{1}H NOESY NMR spectrum of ***o*-L^{1}** (700 MHz, DMSO-d_6, 298 K).

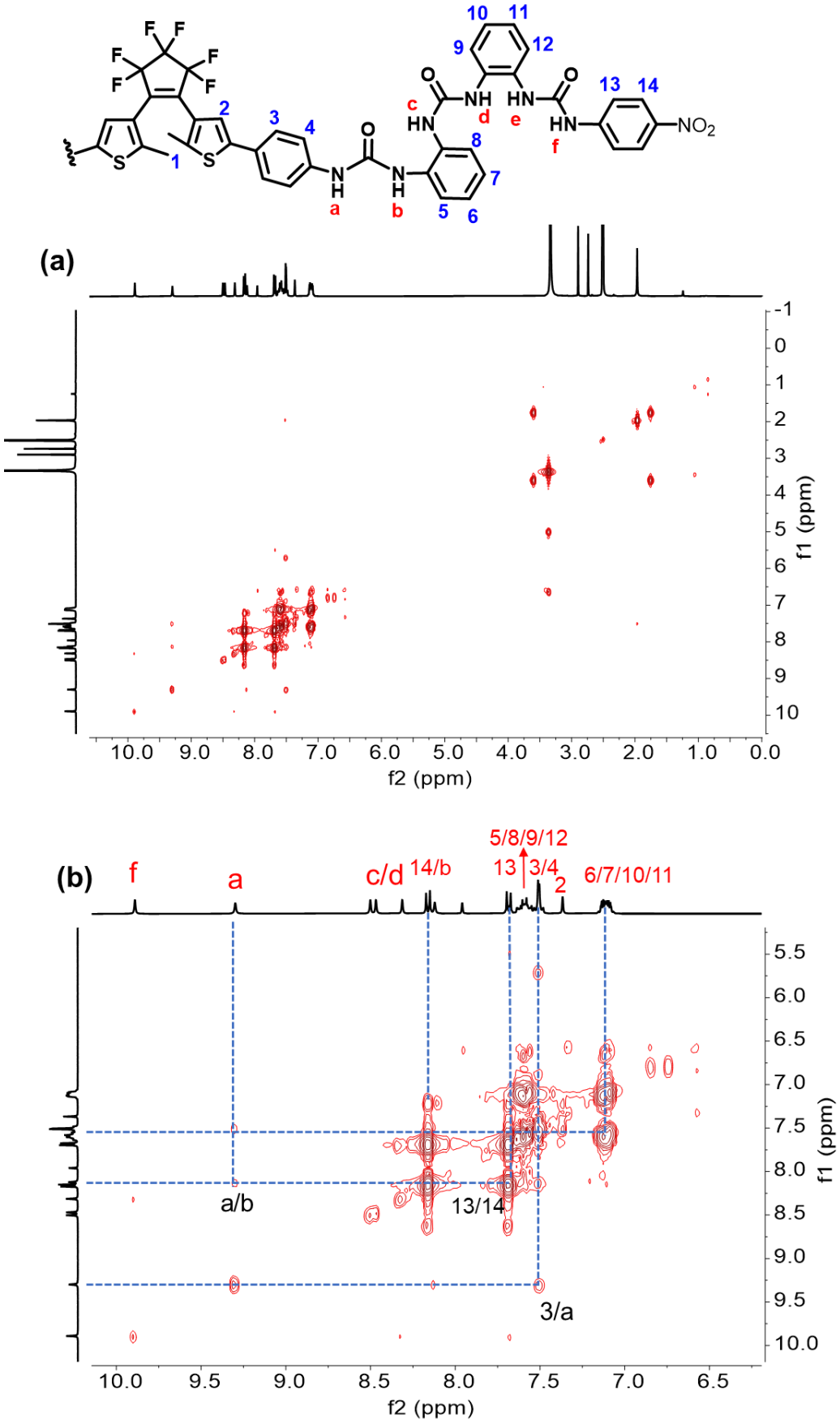


Figure S15. ^{1}H-^{1}H COSY NMR spectrum of ***o*-L^{1}** (700 MHz, DMSO-d_6, 298 K).

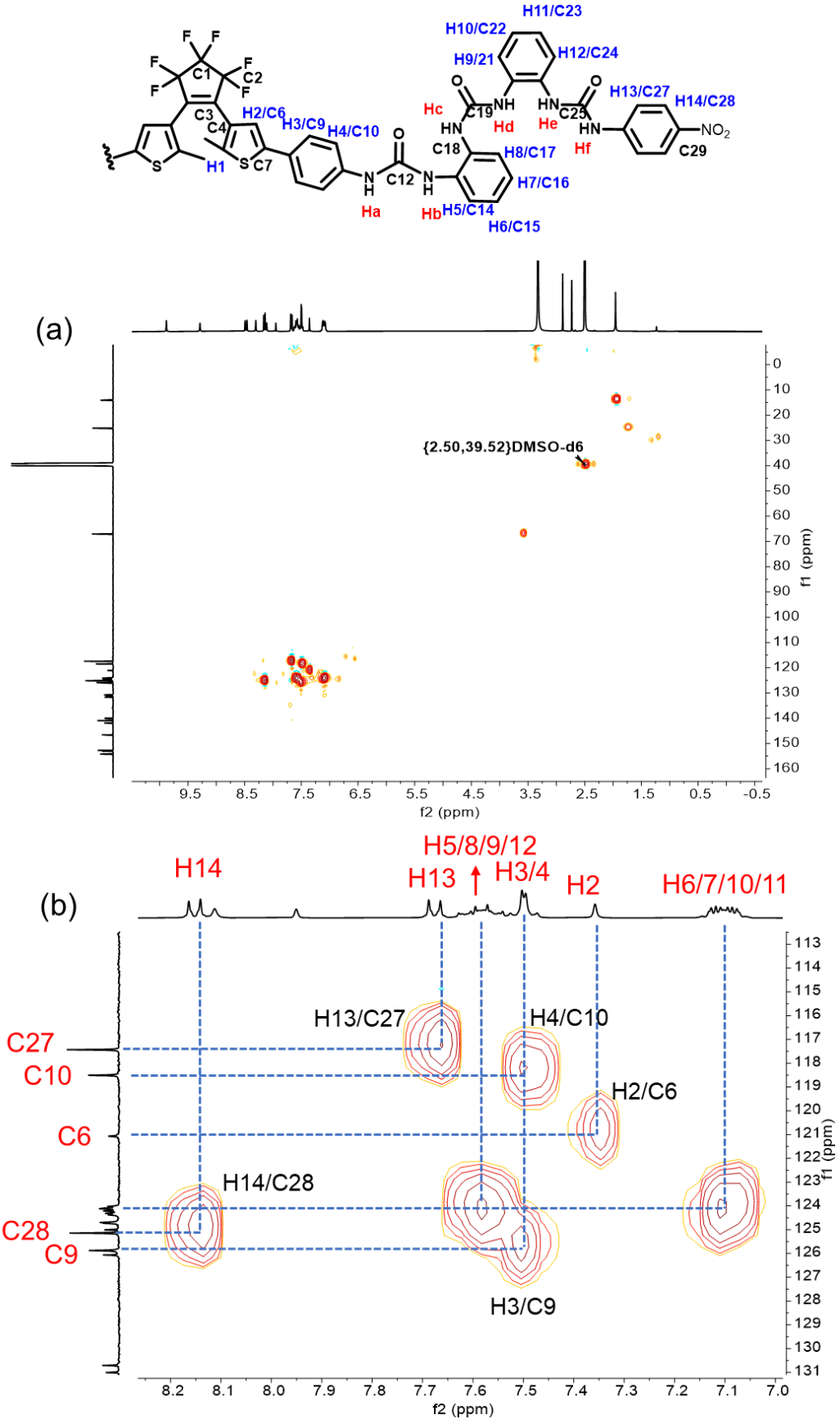


Figure S16. ^{1}H-^{13}C HSQC NMR spectrum of ***o*-L^{1}** (700 MHz, DMSO-d_6, 298 K).

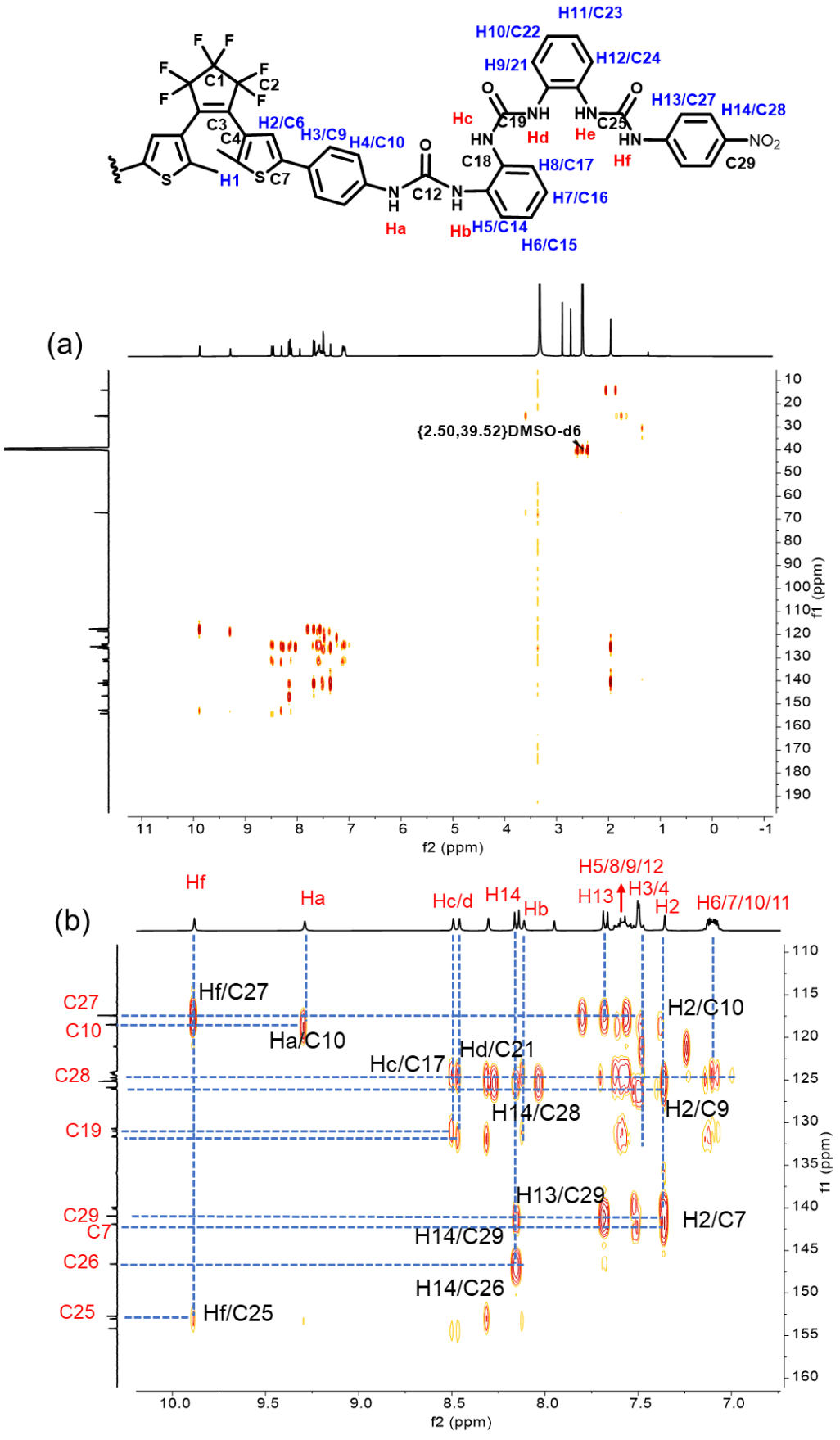


Figure S17. ^{1}H-^{13}C HMBC NMR spectrum of ***o*-L^{1}** (700 MHz, DMSO-d_6, 298 K).

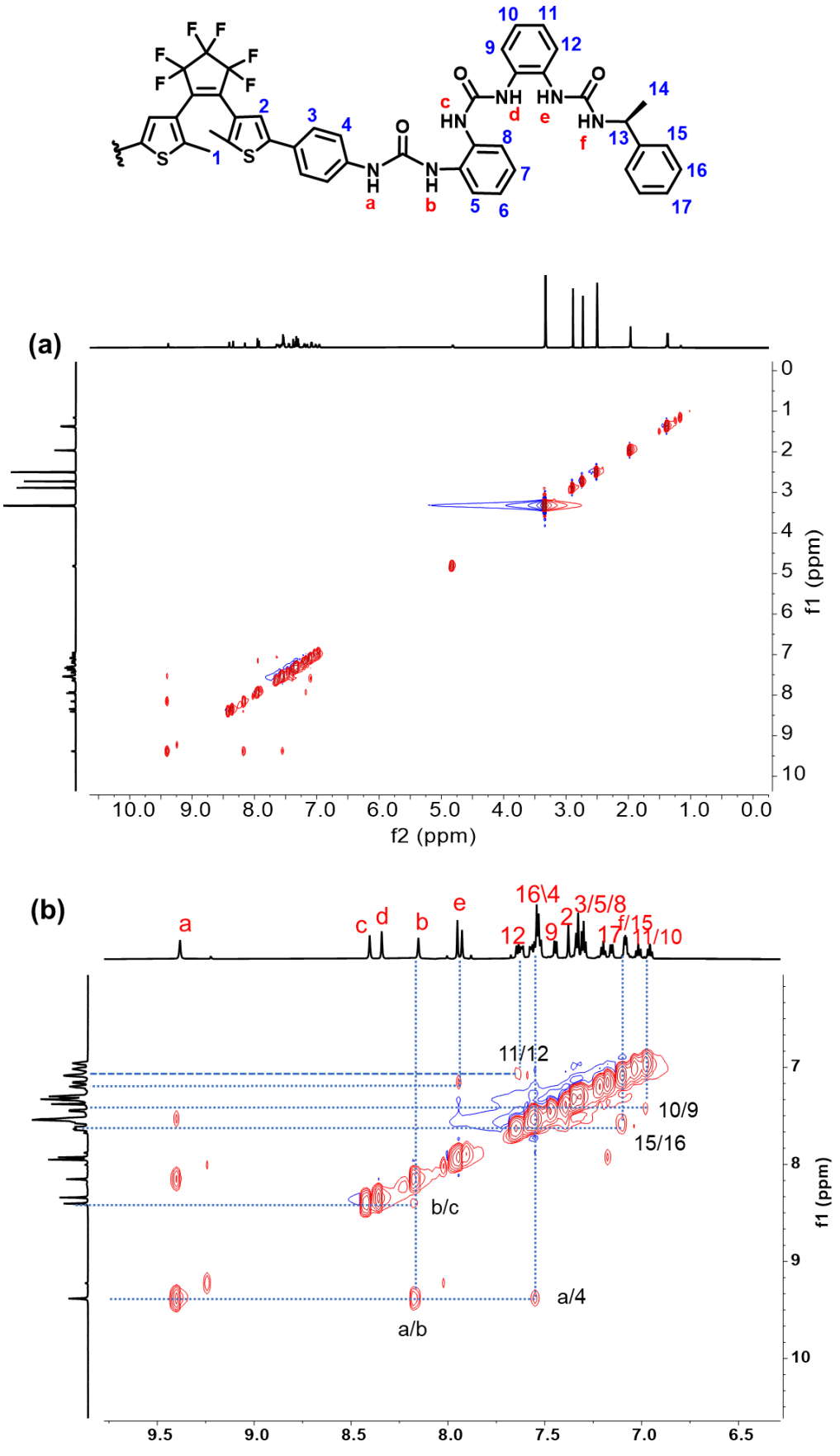


Figure S18. ^{1}H-^{1}H NOESY NMR spectrum of ***(S)-o-*L^{2}** (700 MHz, DMSO-d_6, 298 K).

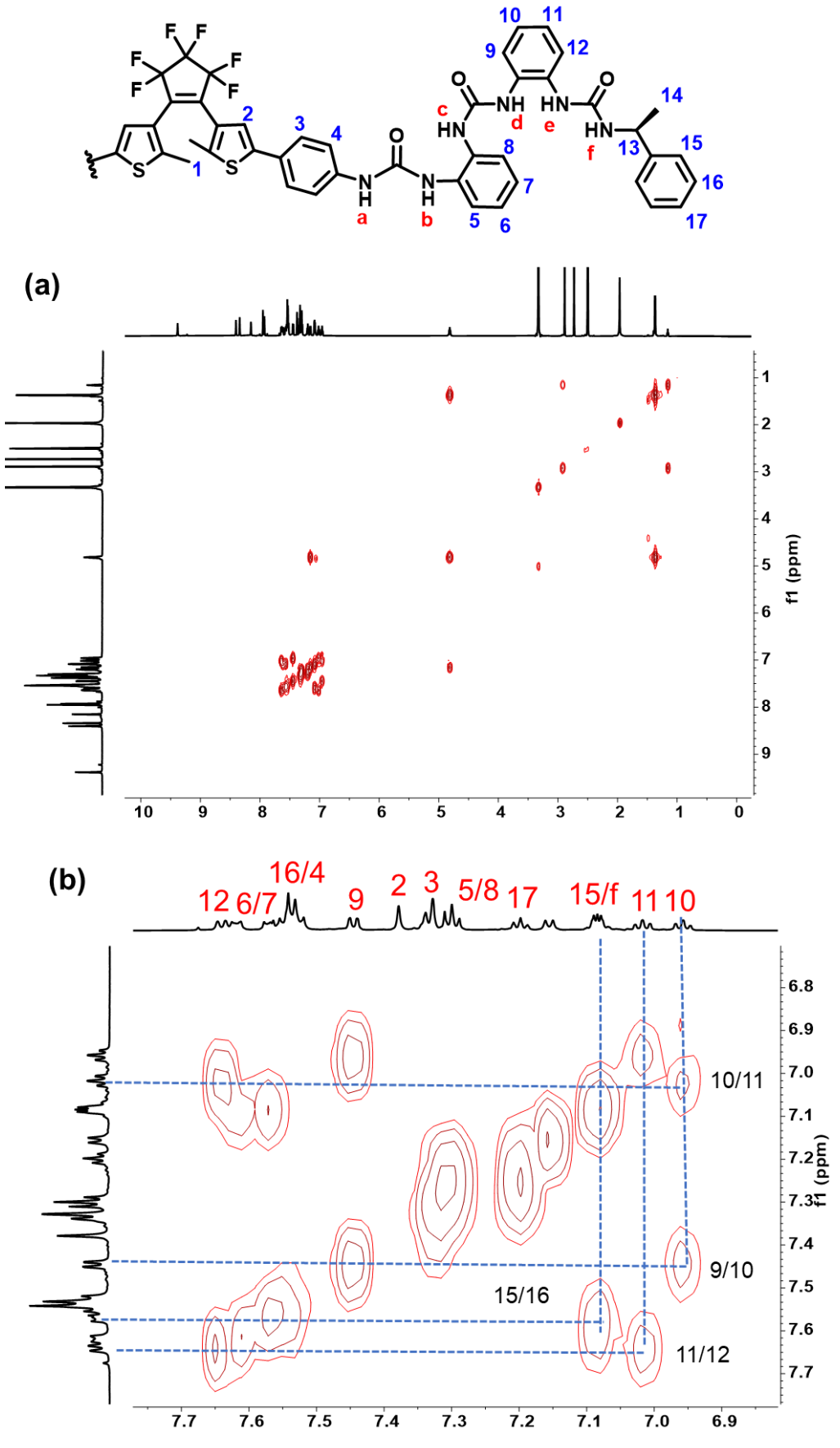


Figure S19. ^{1}H-^{1}H COSY NMR spectrum of ***(S)*-*o*-L^{2}** (700 MHz, DMSO-d_6, 298 K).

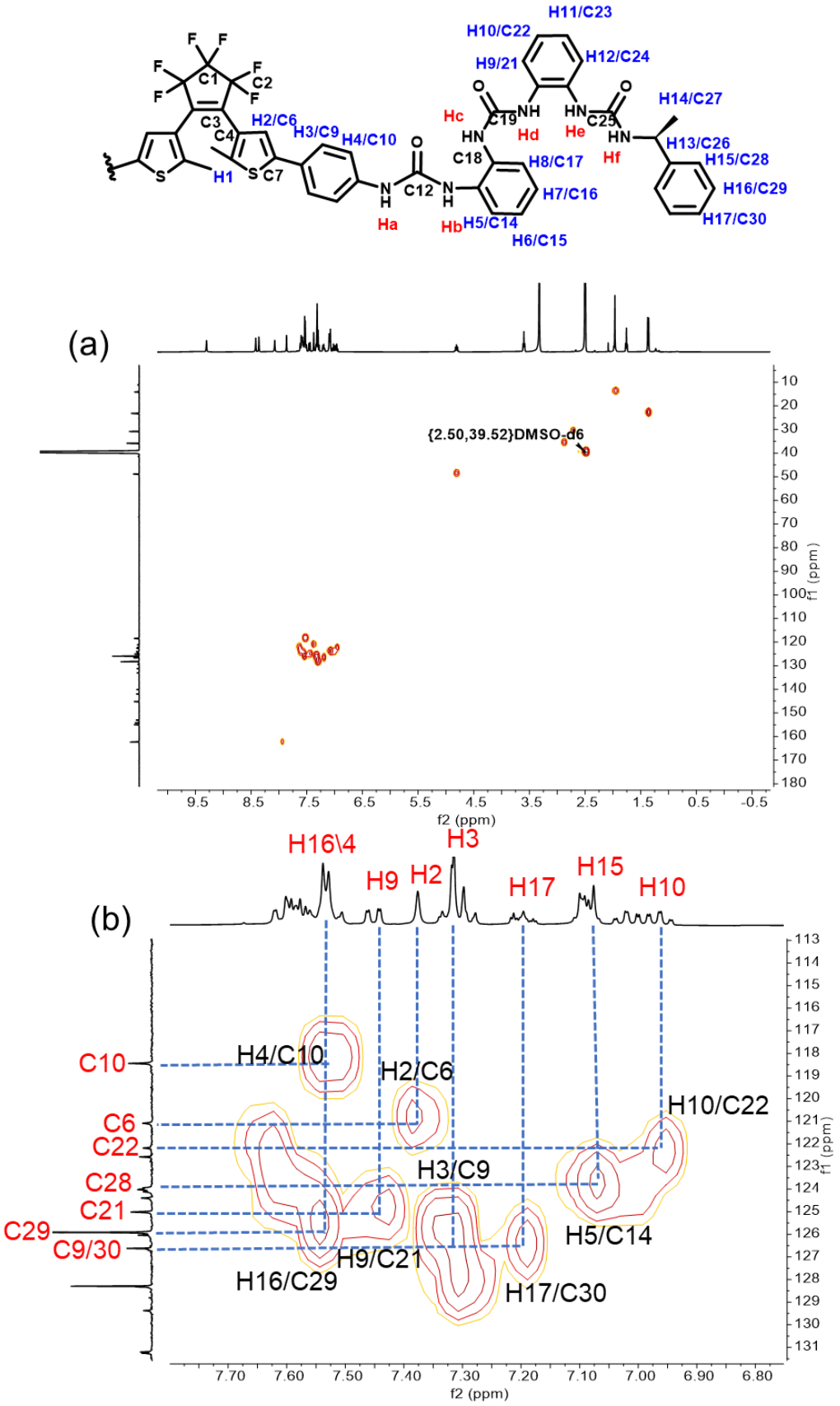


Figure S20. ^{1}H-^{13}C HSQC NMR spectrum of ***(S)-o*-L^{2}** (700 MHz, DMSO-d_6, 298 K).

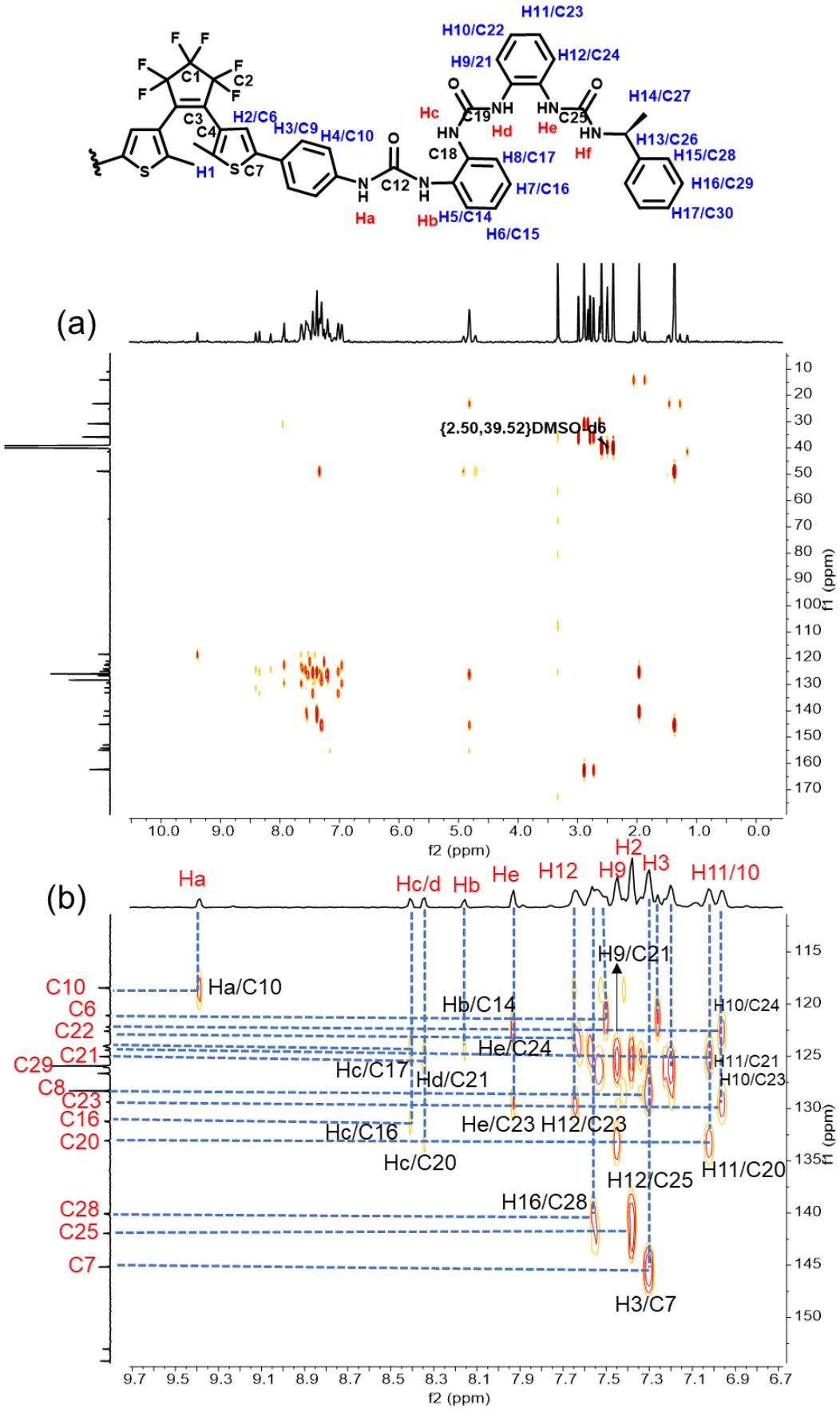
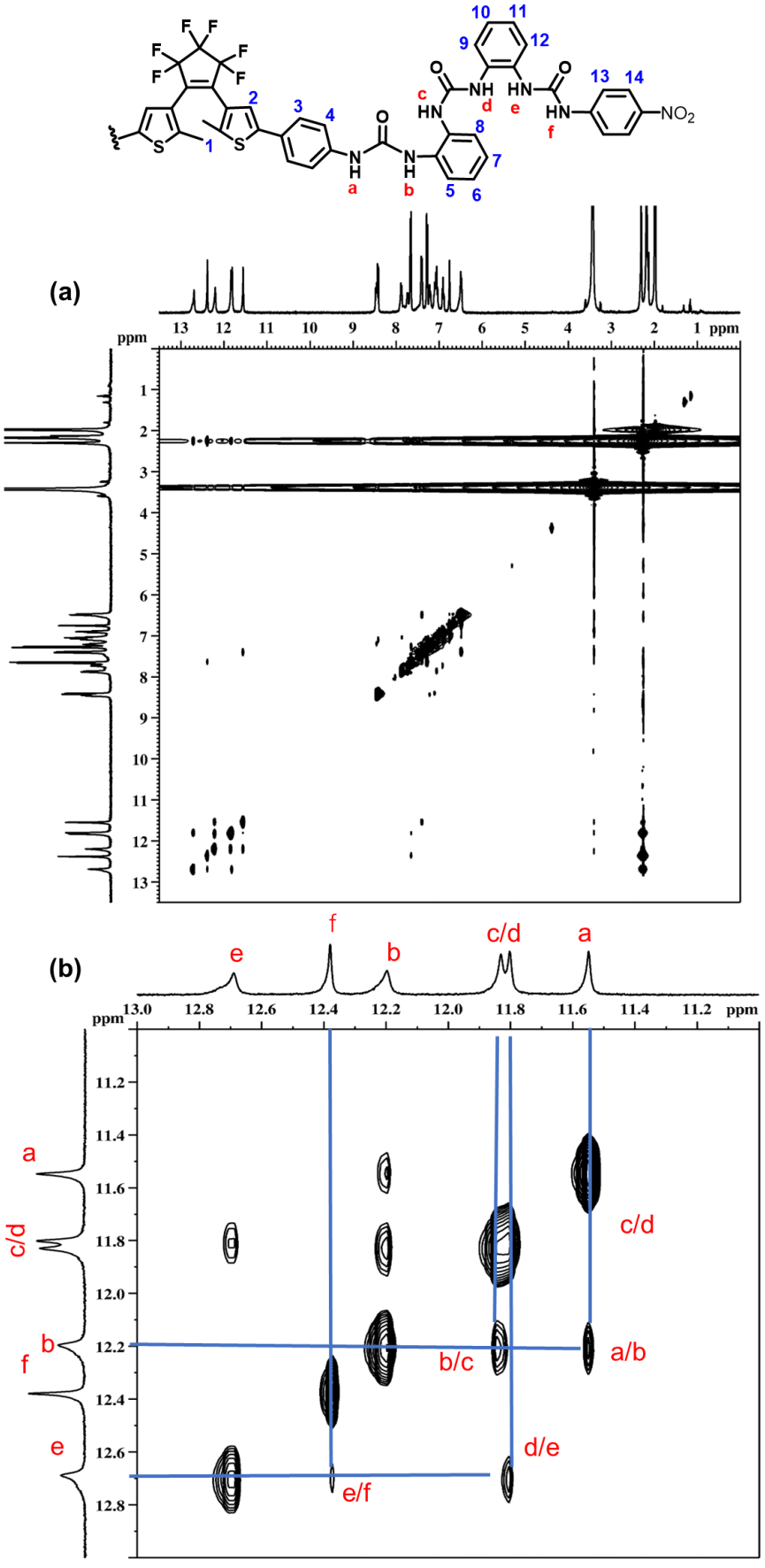


Figure S21. ^{1}H-^{13}C HMBC NMR spectrum of ***(S)*-*o*-L^{2}** (700 MHz, DMSO-d_6, 298 K).


(a)
(b)
ppm
e
f
b
c/d
a
a
c/d
b
f
e
b/c
a/b
d/e
e/f

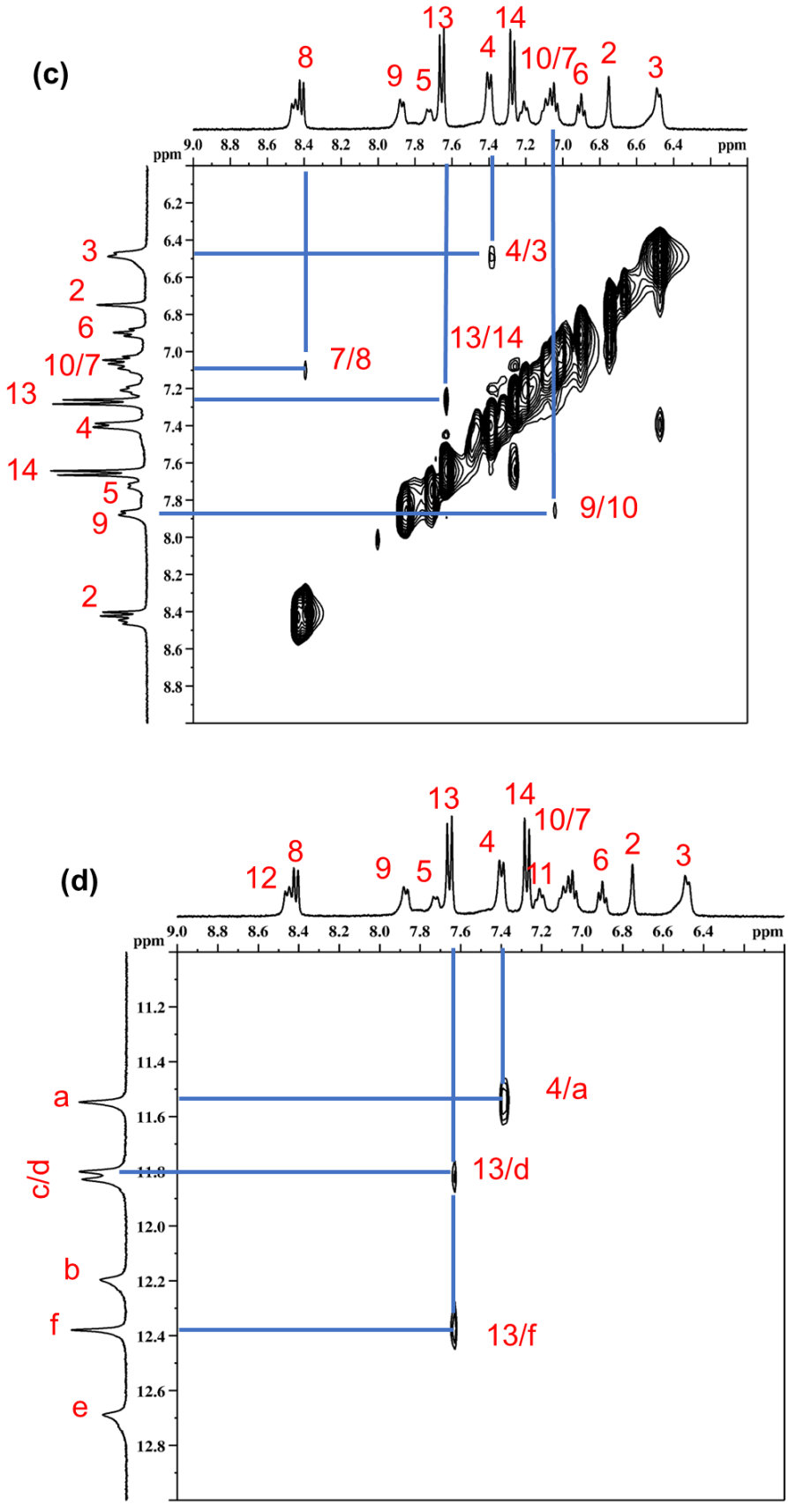


Figure S22. ^{1}H-^{1}H NOESY NMR spectrum of ***o*-H^{1}** (700 MHz, CD_3CN, 298 K).

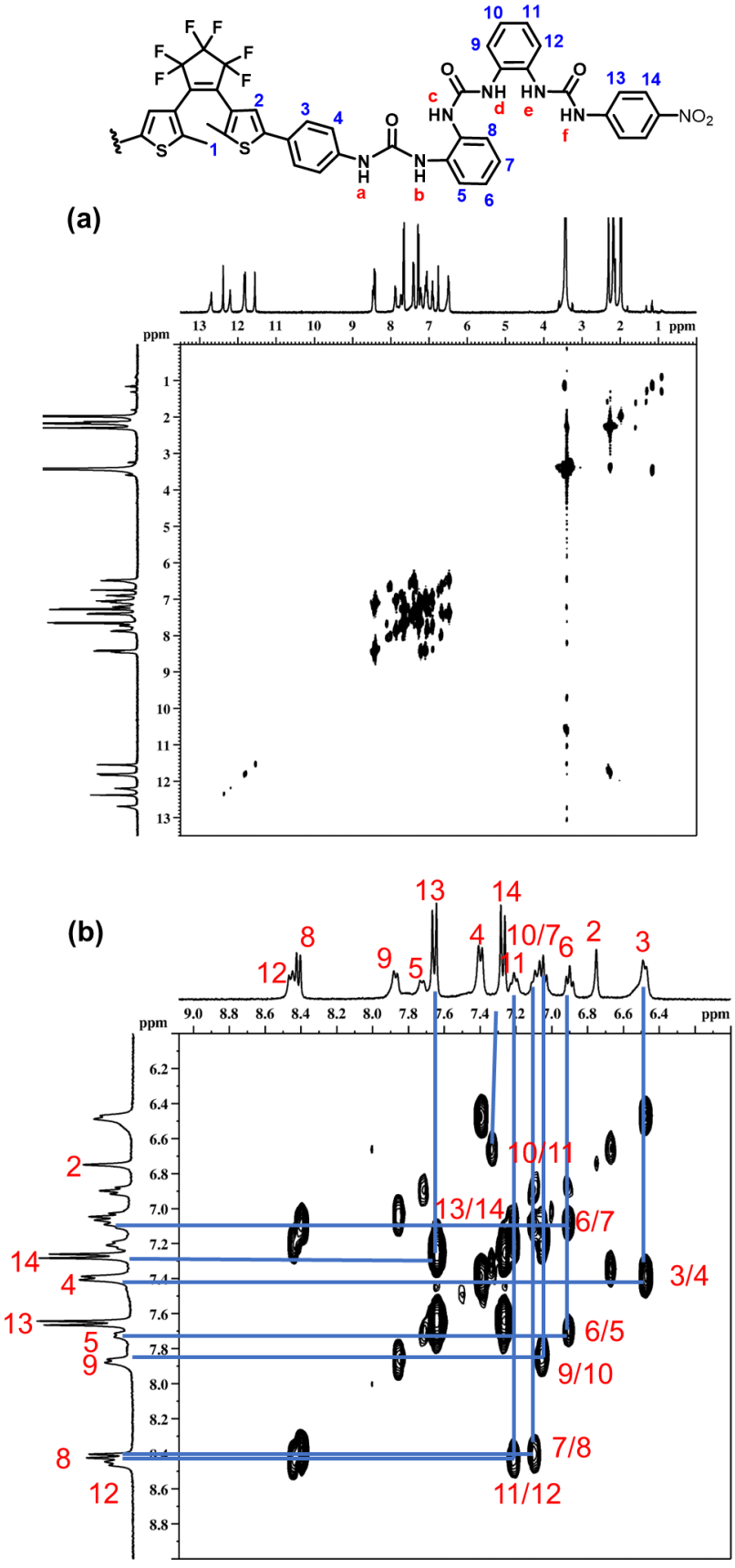


Figure S23. ^{1}H-^{1}H COSY NMR spectrum of ***o*-H^{1}** (700 MHz, CD_3CN, 298 K).

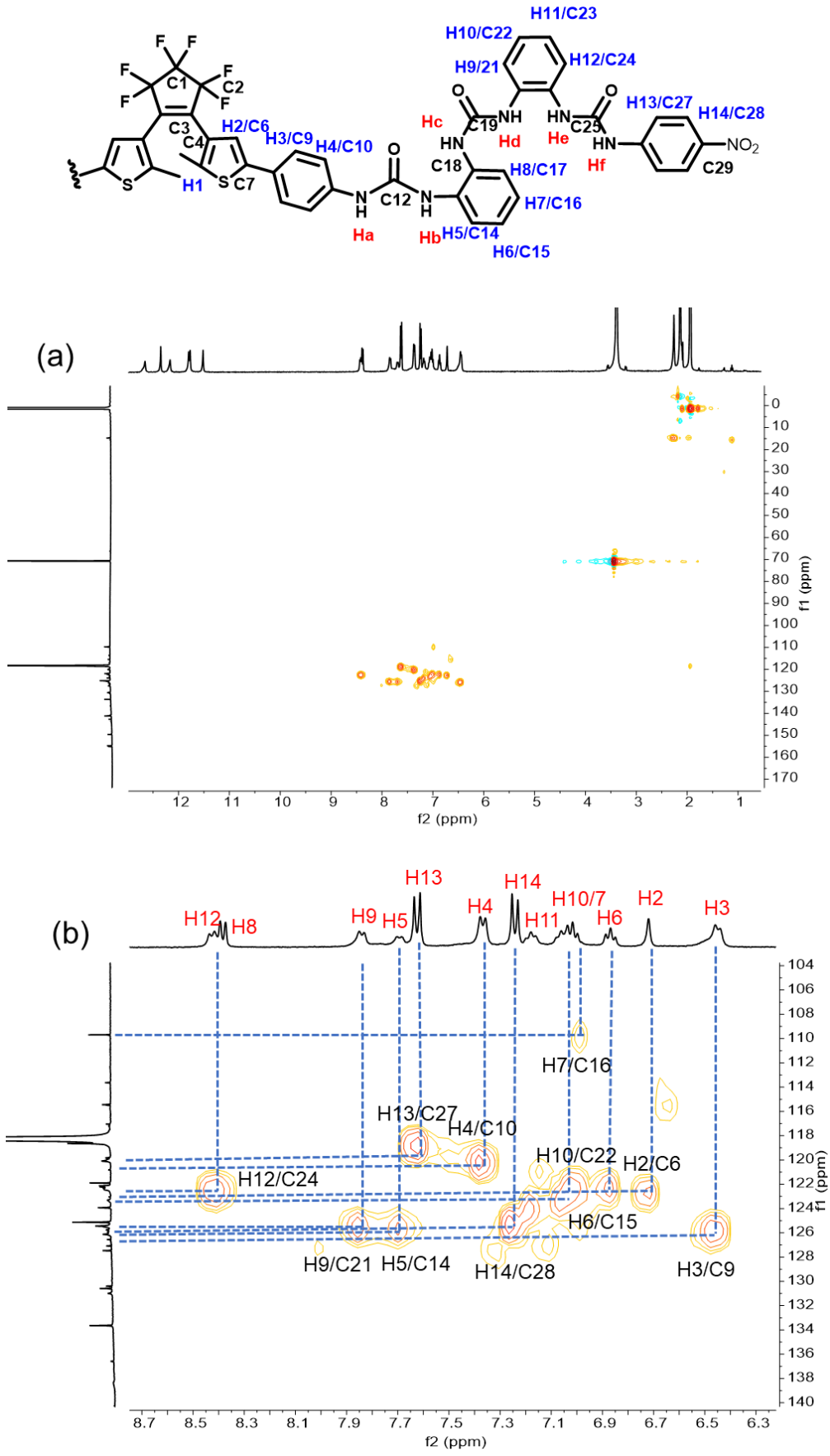


Figure S24. ^{1}H-^{13}C HSQC NMR spectrum of ***o*-H^{1}** (700 MHz, CD_3CN, 298 K).

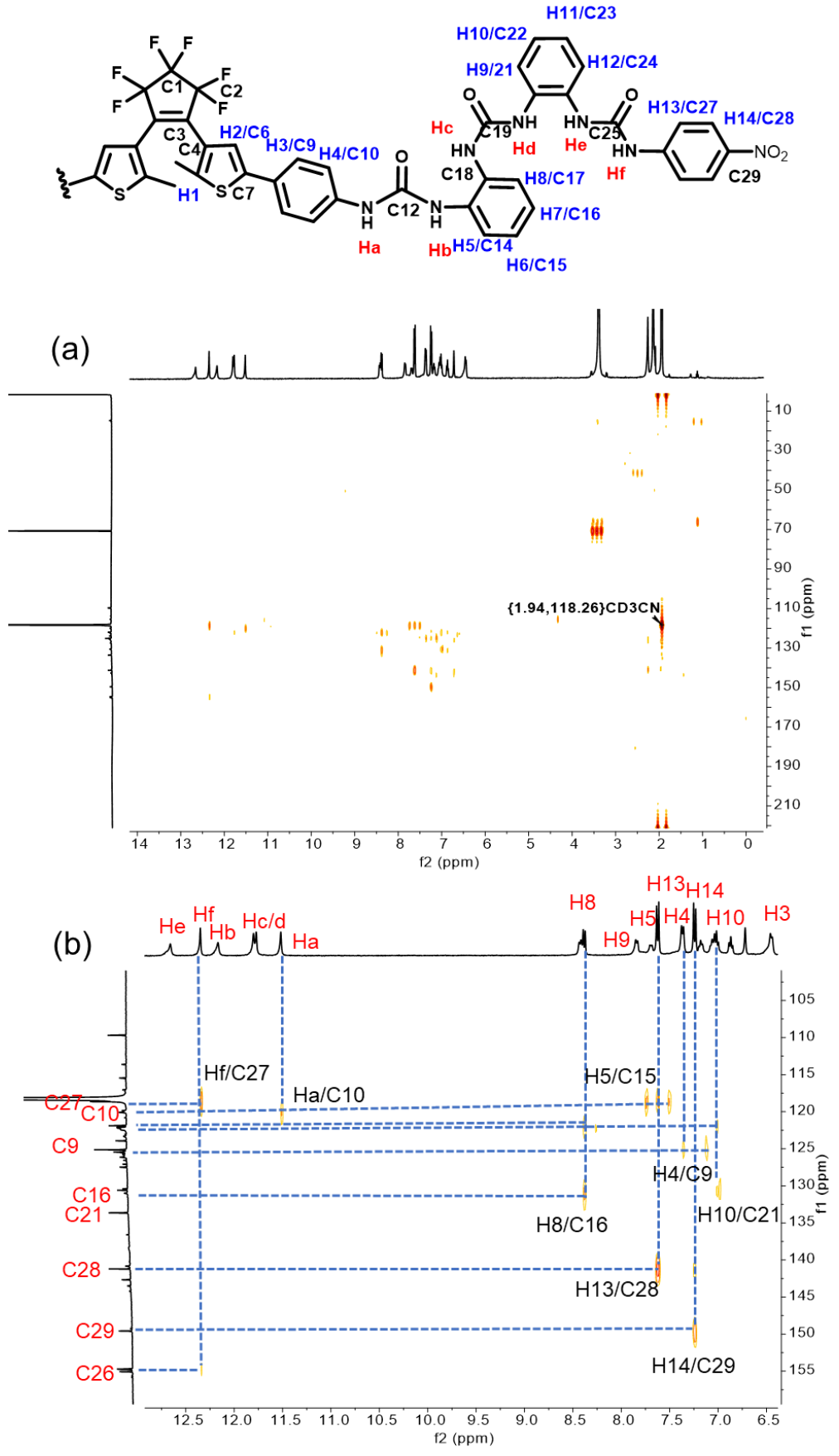


Figure S25. ^{1}H-^{13}C HMBC NMR spectrum of ***o*-H[1]** (700 MHz, CD_3CN, 298 K).

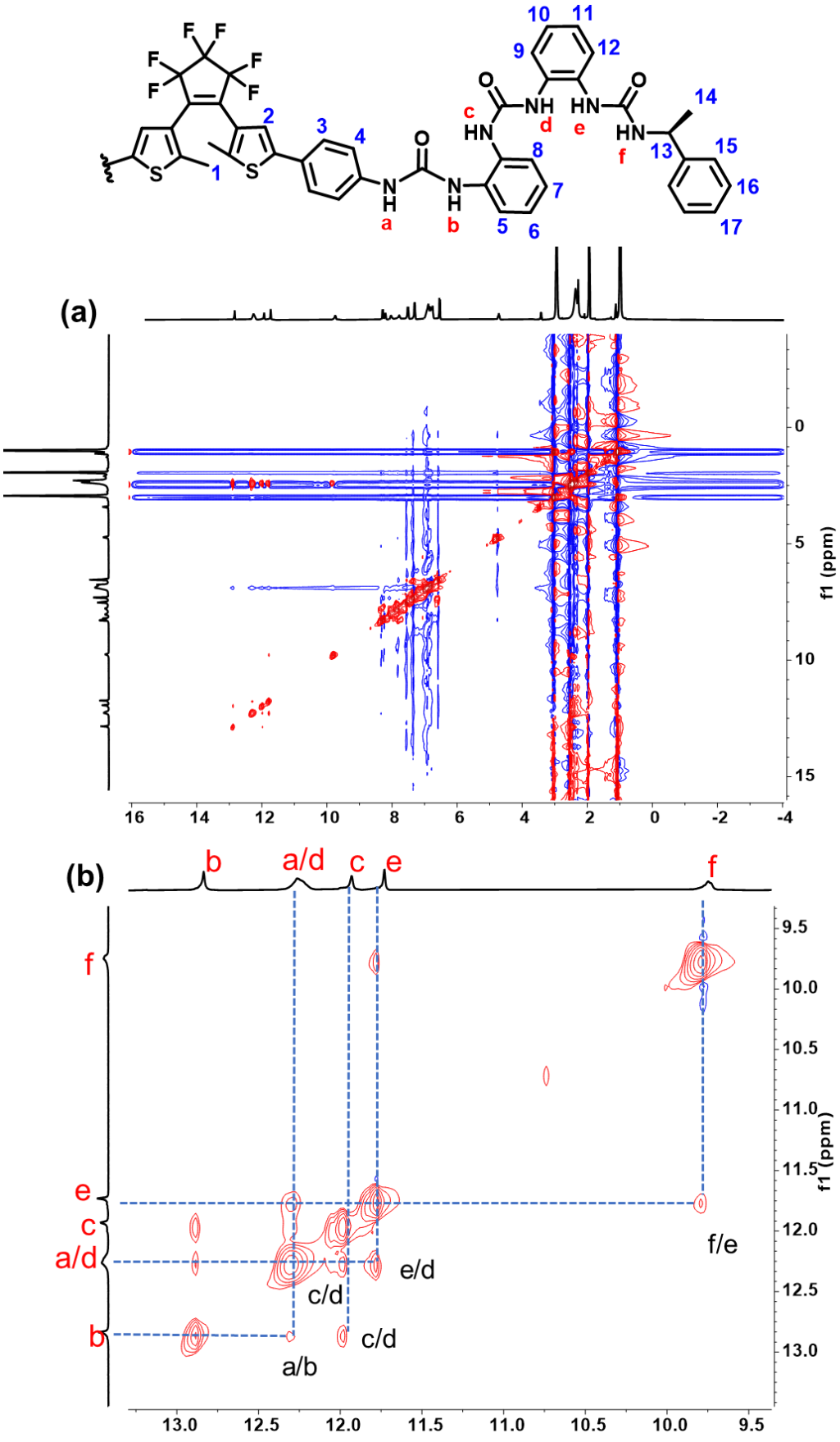


Figure S26. ^{1}H-^{1}H NOESY NMR spectrum of ***(S)-o-*H^{2}** (700 MHz, CD_3CN, 298 K).

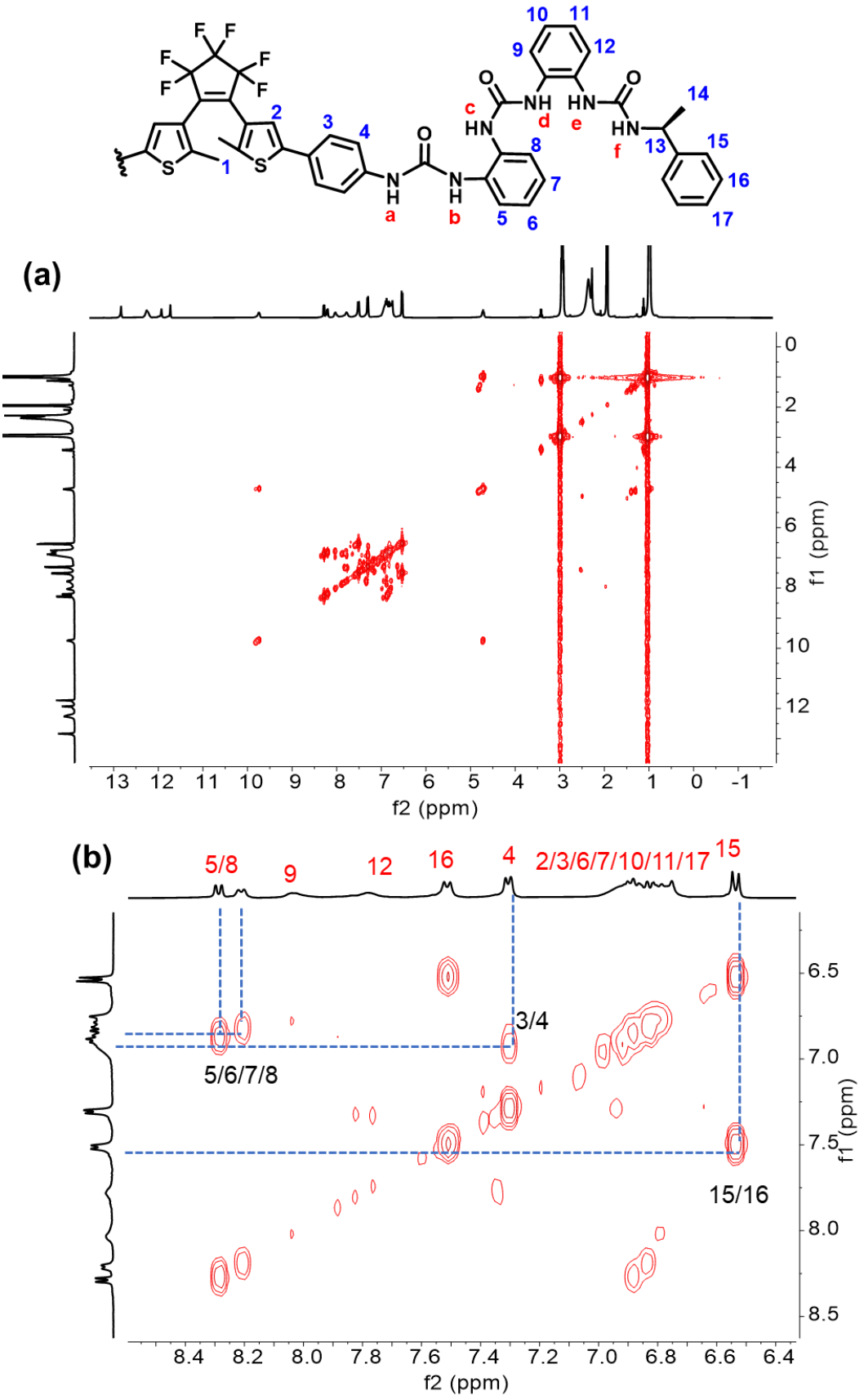


Figure S27. ^{1}H-^{1}H COSY NMR spectrum of ***(S)-o*-H²** (700 MHz, CD_3CN, 298 K).

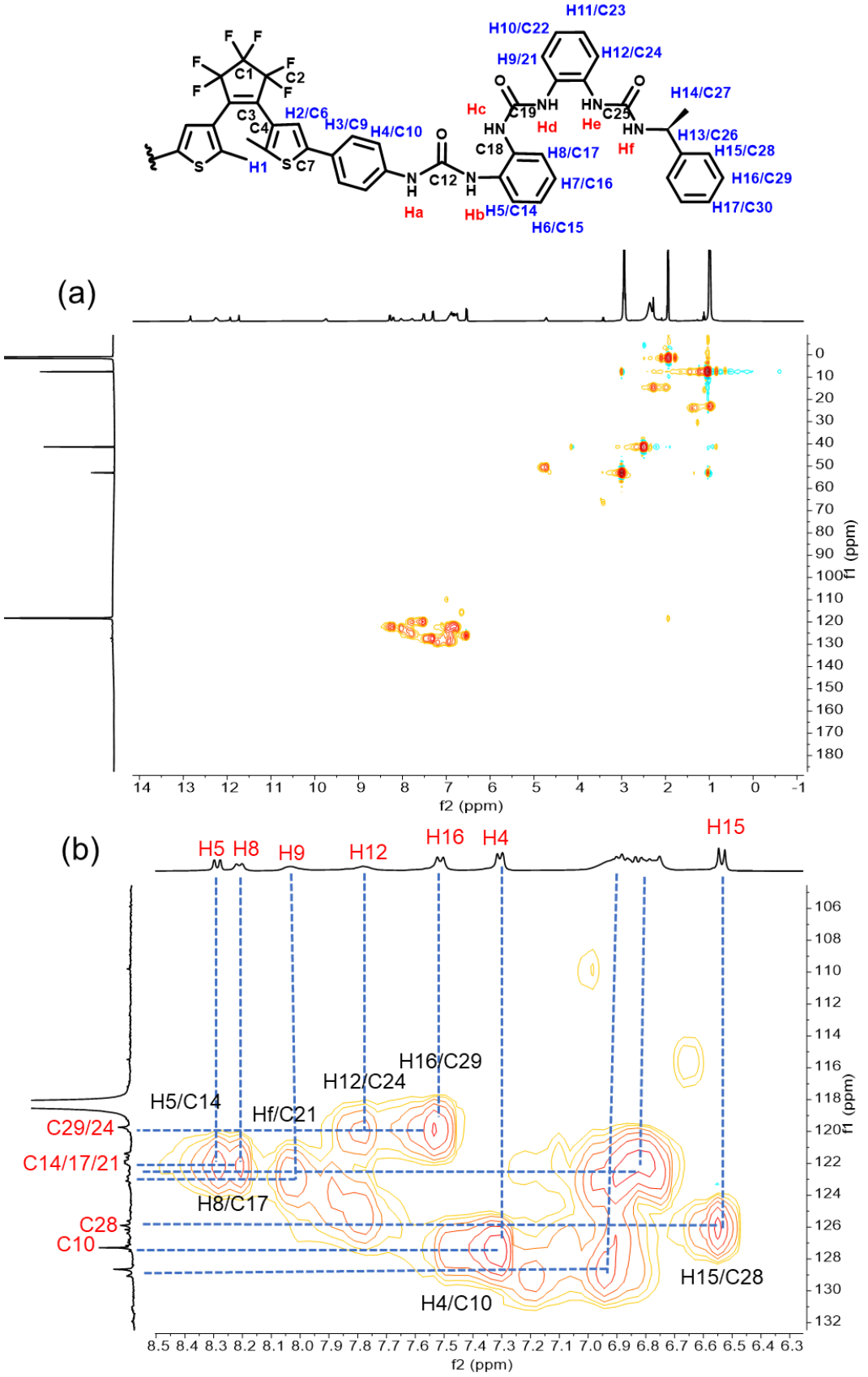


Figure S28. ^{1}H-^{13}C HSQC NMR spectrum of ***(S)-o*-H^{2}** (700 MHz, CD_3CN, 298 K).

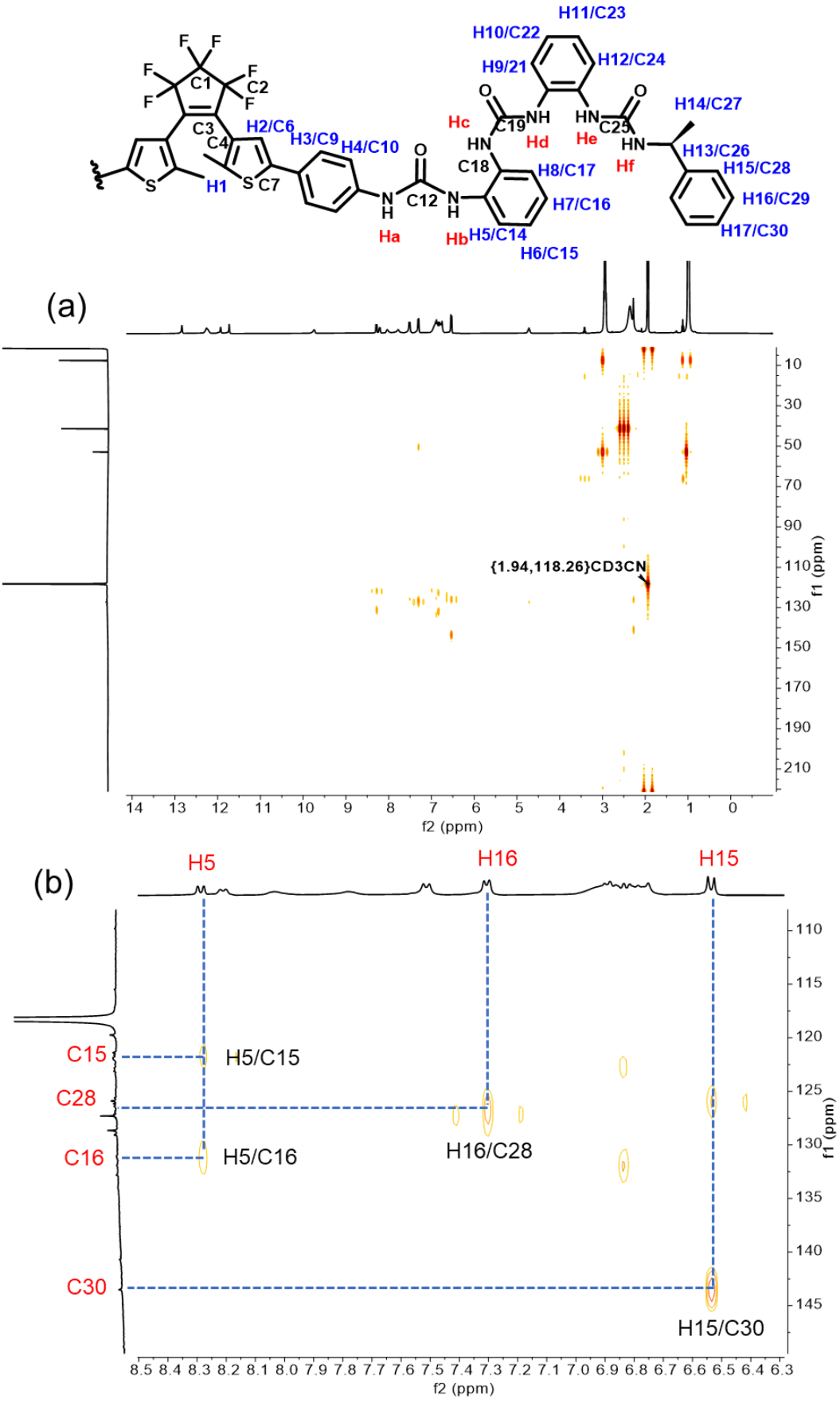


Figure S29. ^{1}H-^{13}C HMBC NMR spectrum of ***(S)-o*-H^{2}** (700 MHz, CD_3CN, 298 K).

S4. Photoisomerization properties of L^1 and *(S)* -L^2

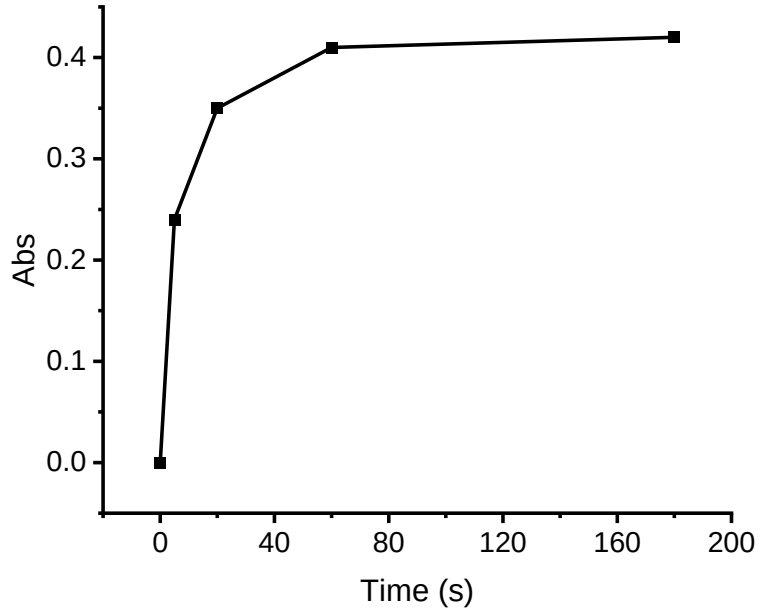


Figure S30. Absorption changes of $\mathbf{L^1}$ at 610 nm under light irradiation (20 μM, DMSO).

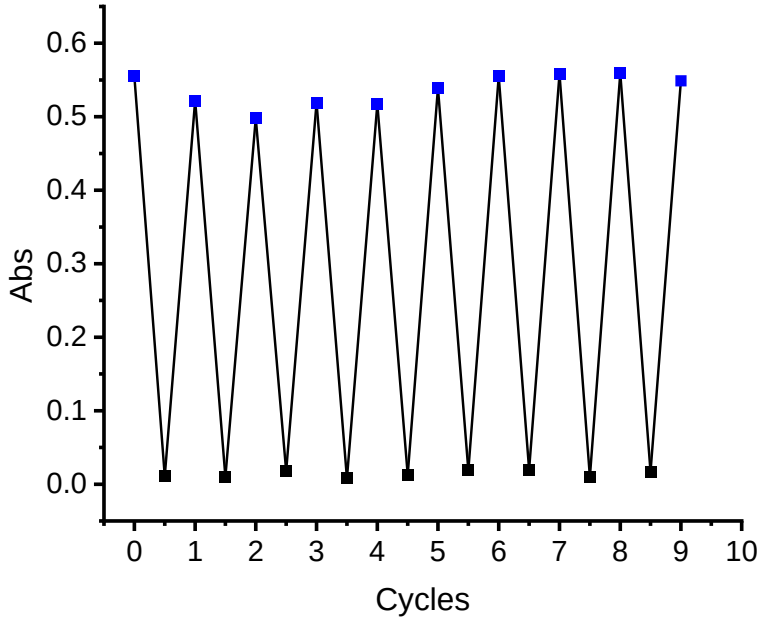


Figure S31. Plot of the absorption intensity changes at 610 nm upon alternating light irradiation for multiple cycles. ($\mathbf{L^1}$, 20 μM, DMSO).

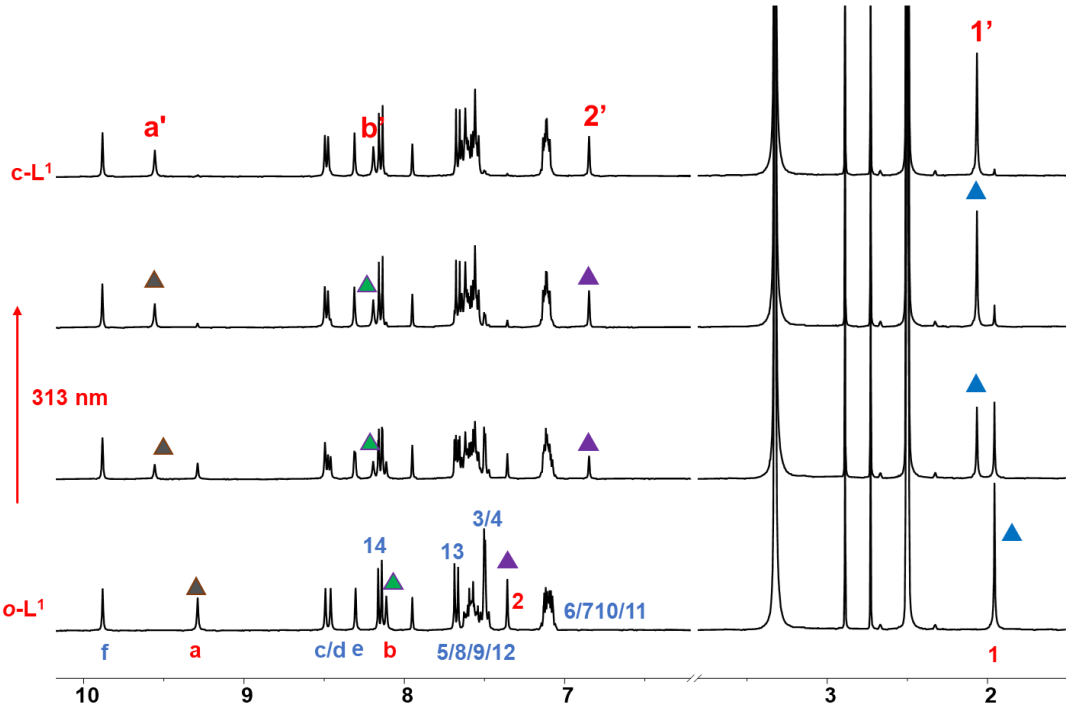


Figure S32. ^{1}H NMR spectra of ligand **L^{1}** photoisomerization process (400 MHz, DMSO-d_6, 298 K).

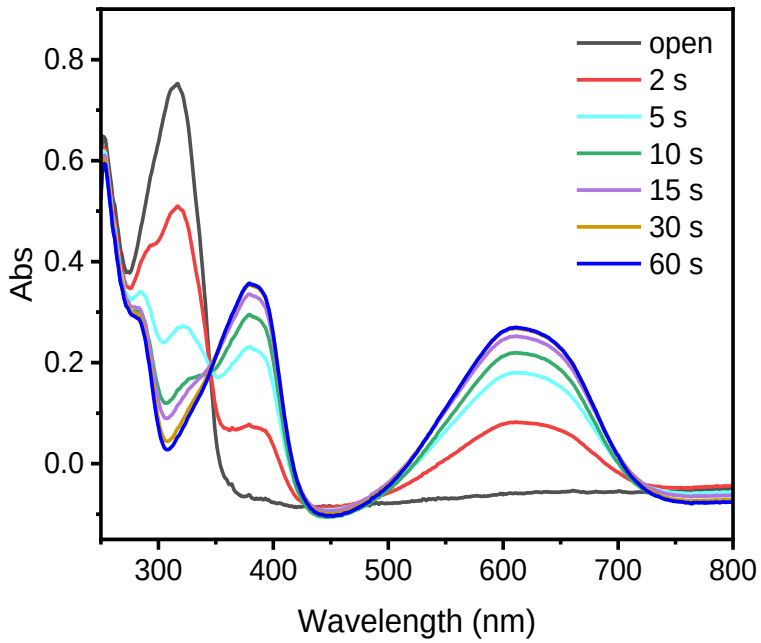


Figure S33. UV-vis spectra of ***(S)-o*-L^{2}** under light irradiation (20 μM, DMSO).

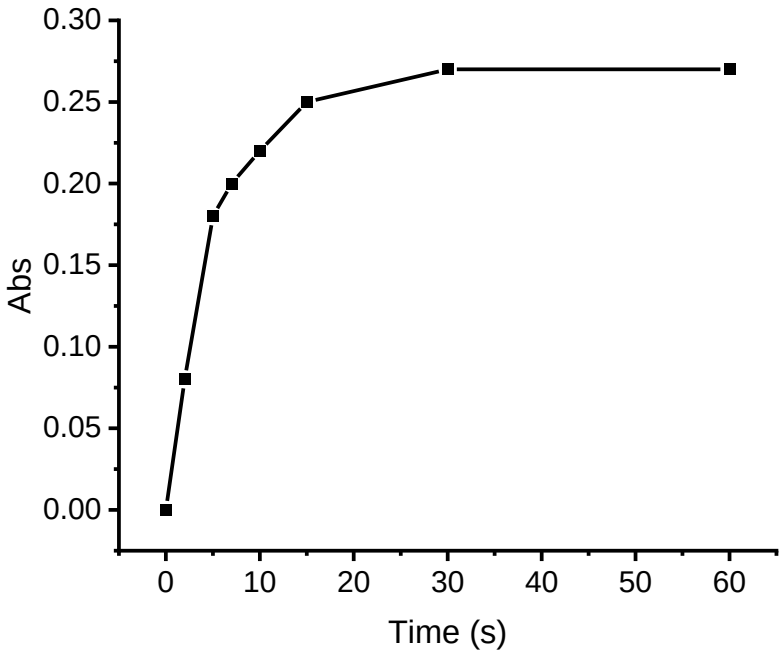


Figure S34. Absorption changes of ***(S)*-L²** at 611 nm under light irradiation (DMSO, 20 μM).

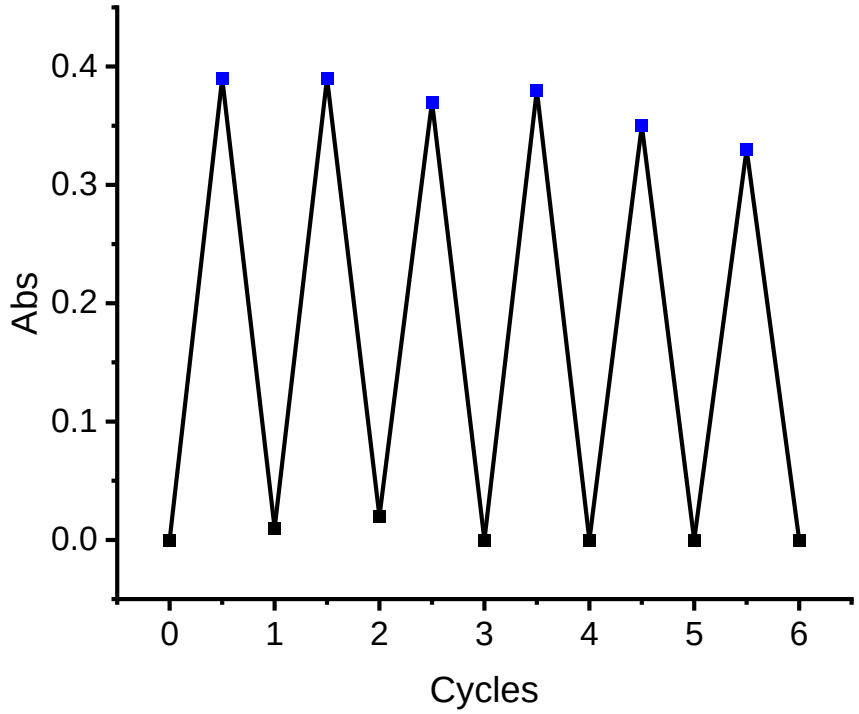


Figure S35. Plot of the absorption intensity changes at 611 nm upon alternating light irradiation for multiple cycles. (***(S)*-L²**, 20 μM, DMSO).

The characteristic absorption peak of ***(S)*-L²** is at 316 nm, and the characteristic absorption peaks of ***c*-L^S** are at 380 nm and 611 nm. Meanwhile, the isosbestic point is at 345 nm.

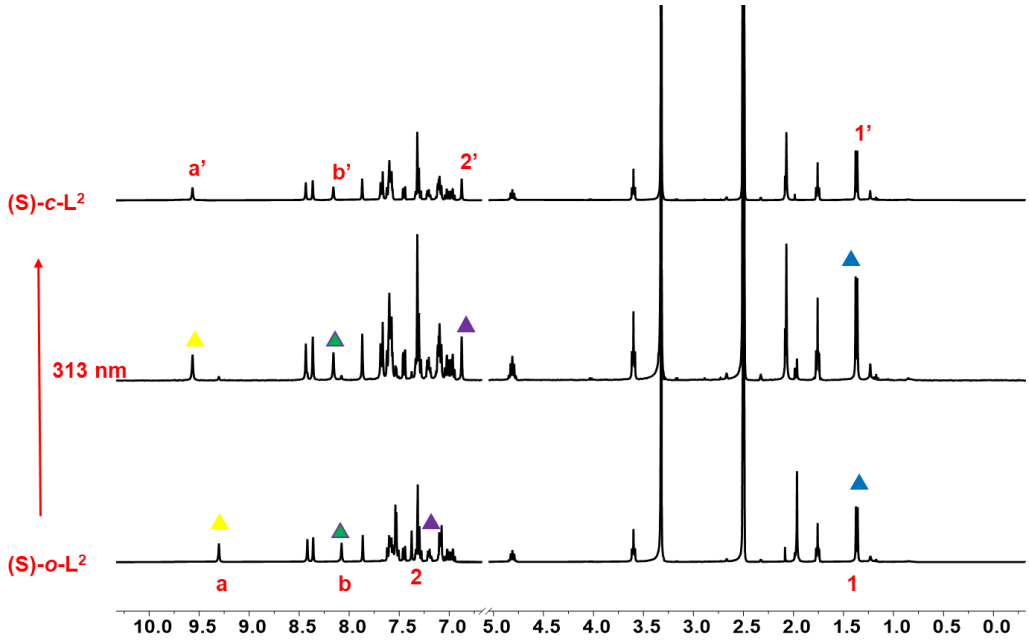


Figure S36. ^{1}H NMR spectra of ligand ***(S)*-L^{2}** photoisomerization process (500 MHz, DMSO-d_6, 298 K).

S5. Single Crystal X-ray Diffraction Structures

Table S1 Crystal data details for ***o*-H**[1].

Complex	***o*-H**[1]
CCDC	2415315
Empirical formula	$C_{242}H_{318}F_{12}K_6N_{32}O_{71}P_2S_4$
Formula weight	5464.05
Crystal system	triclinic
Space group	P-1
a(Å)	23.872(2)
b(Å)	23.947(2)
c(Å)	28.949(3)
α(deg)	91.551(2)
β (deg)	100.438(2)
γ(deg)	116.519(2)
V(Å^3)	14453(2)
Z	2
T(K)	180
F(000)	5756.0
D_{calc}, g/cm^3	1.256
Crystal size (nm)	0.15 × 0.14 × 0.13
θ range	2.128-19.98
μ /mm^{-1}	0.218
Date/restraints/parameters	26848/1267/3056
GoF on F^2	1.029
Final R indexes [I >=2σ (I)]	R_1 = 0.1054, wR_2 = 0.2632
Final R indexes [all data]	R_1 = 0.1724, wR_2 = 0.3155
Largest diff. peak/hole / e Å^{-3}	1.05/-0.61

X-ray diffraction data were collected on a Bruker D8 Venture Photon II diffractometer at 180 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data (G. M. Sheldrick, Program SADABS: Area-Detector Absorption Correction, 1996, University of Göttingen, Germany). The structures were solved by the dual methods using the SHELXS program (G. Sheldrick, Acta Cryst. A, 2008, 64, 5 112-122). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F2 using the program SHELXL, and hydrogen atoms were included in idealized positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Some remaining solvents could not be successfully resolved despite numerous attempts at modeling, and consequently the SQUEEZE function of PLATON was used to account for these highly disordered solvents. The removed void electron density corresponds to about 9.4 diethyl ether molecules for ***o*-H**[1].

There is still an A level alert for crystal *o*-H[1] and which is attributed to the quality of diffraction. The value of sin(theta_max)/wavelength is less than 0.550, calculated value is 0.4808. The high

disorder of [18] crown-6 causes an overly large difference between the maximum and minimum temperature factors of the carbon atoms of the non-solvent. Compared with the nearby atoms, the temperature factor of the K atom is relatively low and the accuracy of the C-C bond length is not precise.

The crystal data and refinement details are given in Table S1.

Table S2 Hydrogen bonding information in the crystal structure of ***o*-H**[1]

D-H···*A*	d(*D*-H)	d(H···*A*)	d(D···*A*)	∠(*D*H*A*)
N1-H1···O21	0.88	2.02	2.862(8)	161
N018-H018···O21	0.88	1.91	2.782(10)	169
N2-H2···O24	0.88	1.93	2.772(8)	160
N3-H3···O24	0.88	1.90	2.776(8)	171
N4-H4···O22	0.88	2.00	2.850(8)	162
N5-H5···O22	0.88	1.90	2.775(8)	169
N6-H6···O23	0.88	1.96	2.820(8)	165
N8-H8···O27	0.88	1.89	2.751(9)	166
N9-H9···O28	0.88	1.89	2.753(9)	166
N10-H10···O28	0.88	1.98	2.817(8)	159
N11-H11···O25	0.88	1.94	2.805(8)	165
N12-H12···O25	0.88	1.85	2.723(9)	170
N13-H13···O26	0.88	1.94	2.804(9)	168
N15-H15···O24	0.88	2.05	2.865(9)	153
N16-H16···O23	0.88	1.88	2.742(10)	168
N17-H17···O23	0.88	2.03	2.856(8)	156
N18-H18···O21	0.88	1.90	2.780(8)	172
N20-H20···O22	0.88	1.99	2.833(9)	161
N22-H22···O25	0.88	2.02	2.824(7)	152
N23-H23···O27	0.88	1.85	2.728(8)	174
N24-H24···O27	0.88	1.87	2.742(8)	172
N25-H25···O26	0.88	1.94	2.772(8)	158
N26-H26···O26	0.88	1.88	2.744(8)	166
N27-H27···O28	0.88	1.96	2.828(8)	171
average	0.88	1.94±0.11	2.792±0.073	165±13

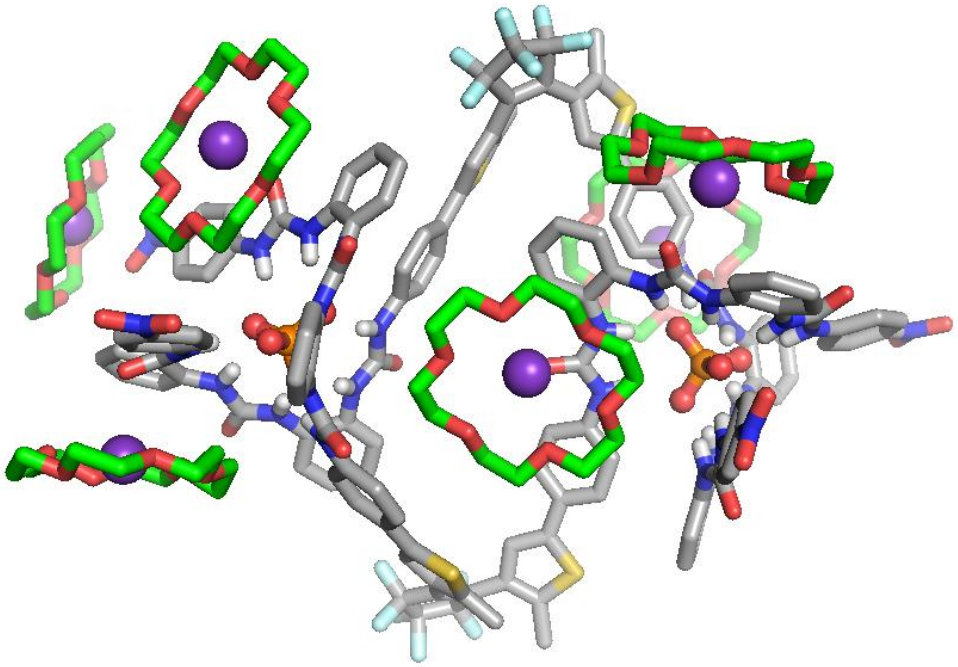


Figure S37. Crystal structure of ***o*-H[1]**.

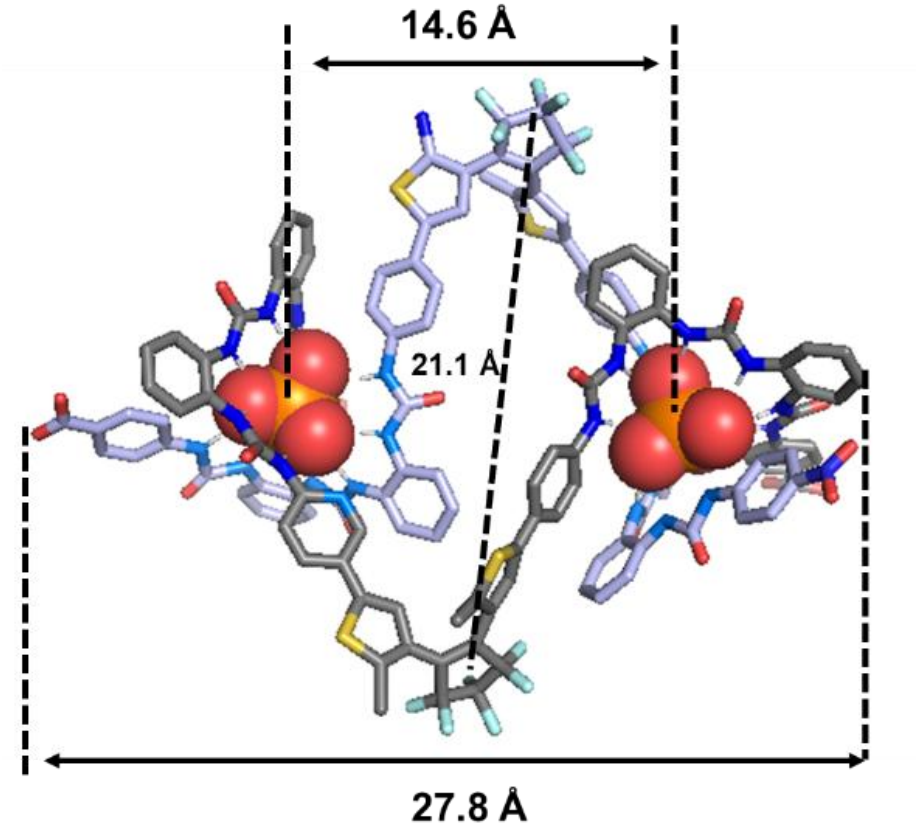


Figure S38. The length and width of the ***o*-H[1],** and the distance between the phosphate groups.

S6. Photoisomerization properties of H^1

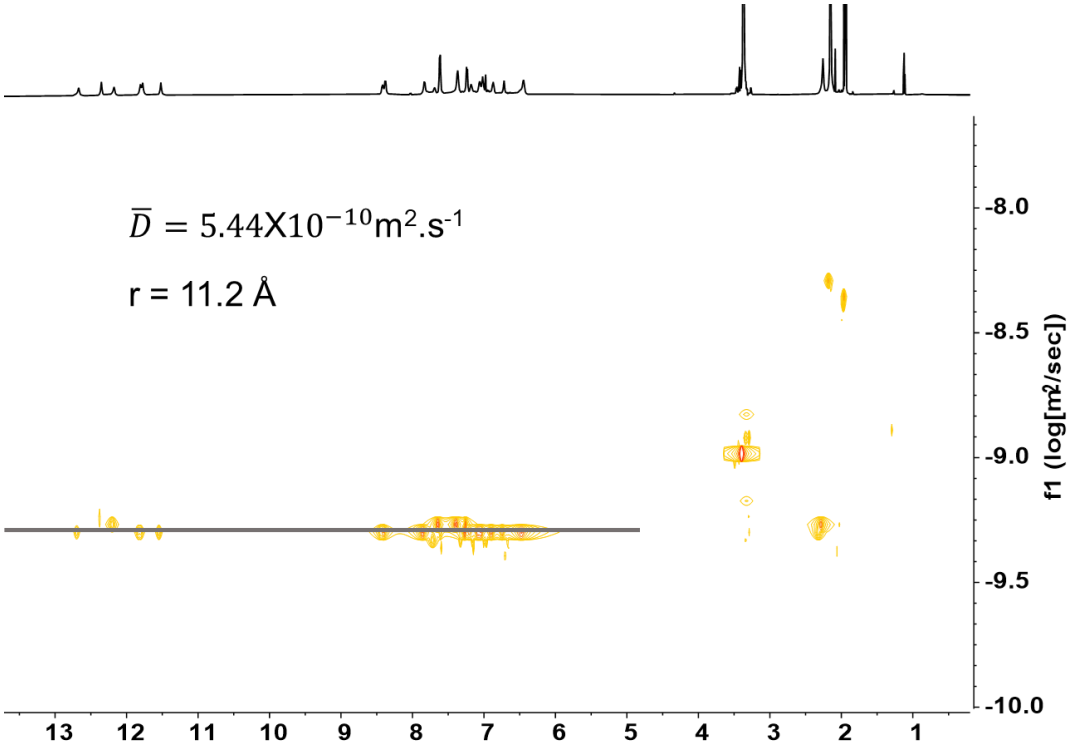


Figure S39. DOSY spectrum of ***o*-H^1** (700 MHz, CD_3CN, 298 K).

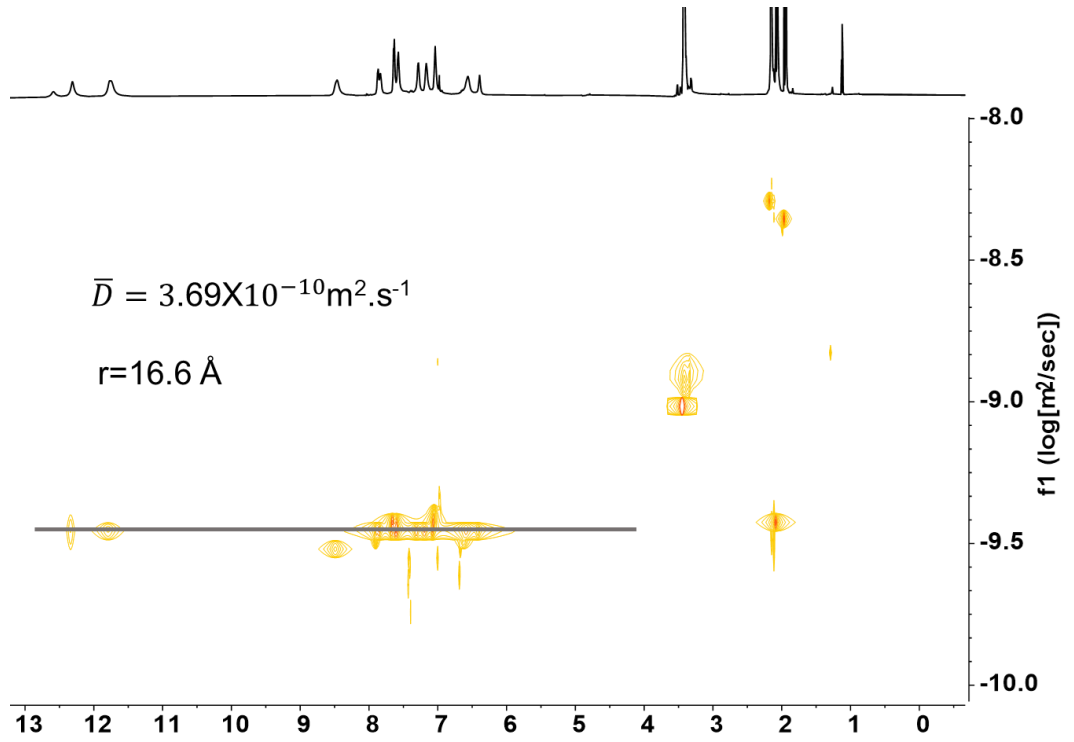


Figure S40. DOSY spectrum of ***c*-H^1** (700 MHz, CD_3CN, 298 K).

$\mu = 3.57 \times 10^{-4}$ N m^{-2} s (CD_3CN); $k = 1.38 \times 10^{-23}$ N m K^{-1}; T= 298 K;

D (***o*-H^1**) = 5.44×10^{-10} m^2/s; r (***o*-H^1**) = $kT/6\pi\mu D$ = 11.2 Å

D (***c*-H^1**) = 3.69×10^{-10} m^2/s; r (***c*-H^1**) = $kT/6\pi\mu D$ = 16.6 Å

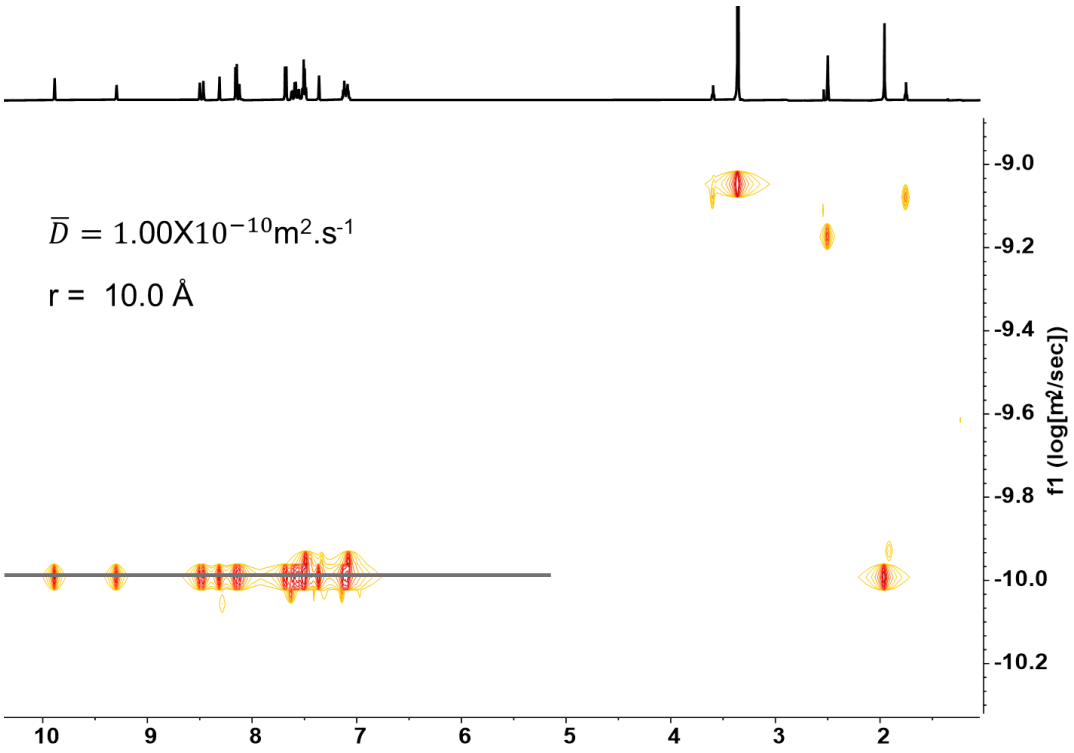


Figure S41. DOSY spectrum of ***o*-L^1** (700 MHz, DMSO-d_6, 298 K).

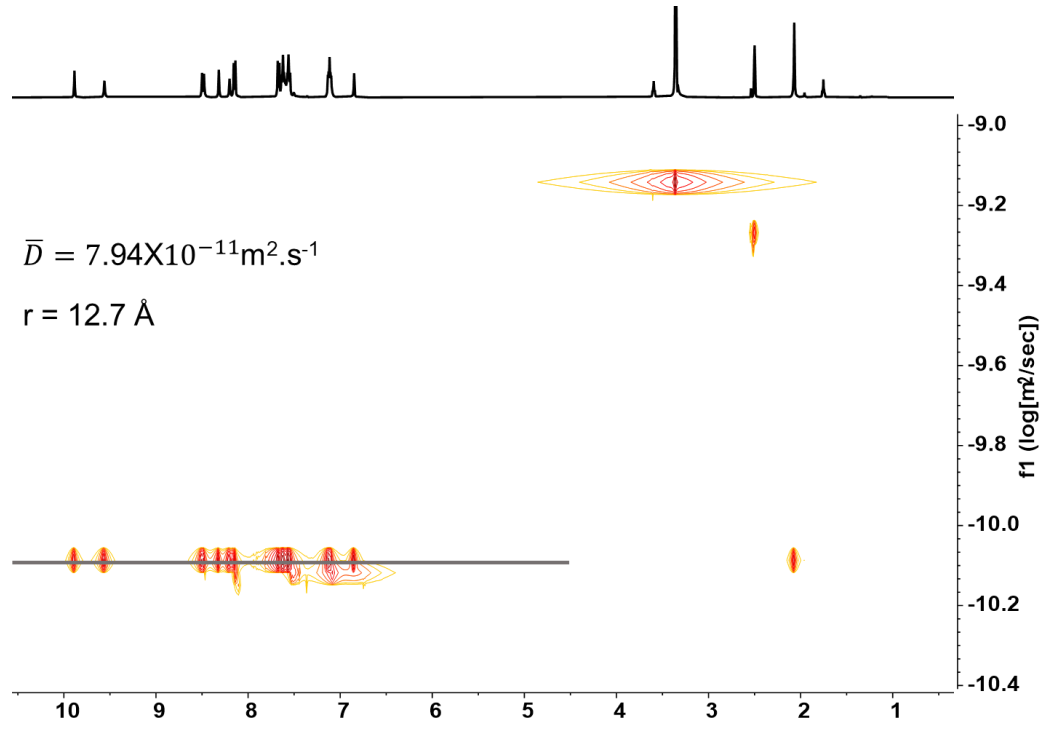


Figure S42. DOSY spectrum of ***c*-L^1** (500 MHz, DMSO-d_6, 298 K).

μ = 2.18 × 10^{-3} N m^{-2} s (DMSO-d_6); k = 1.38 × 10 $^{-23}$ N m K^{-1}; T= 298 K;
D (***o*-L^1**) = 1.00 × 10^{-10} m^2/s; r (***o*-L^1**) = $kT/6\pi\mu D$ = 10.0 Å
D (***c*-L^1**) = 7.94 × 10^{-11} m^2/s; r (***c*-L^1**) = $kT/6\pi\mu D$ = 12.7 Å

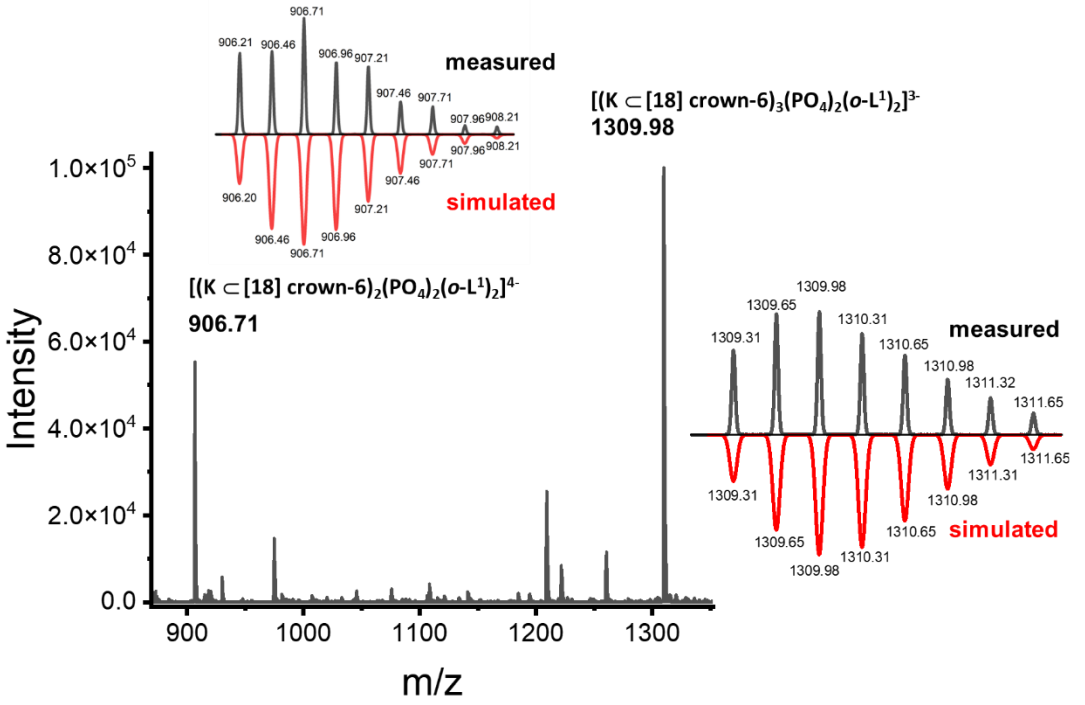


Figure S43. ESI-TOF-MS of ***o*-H^1**.

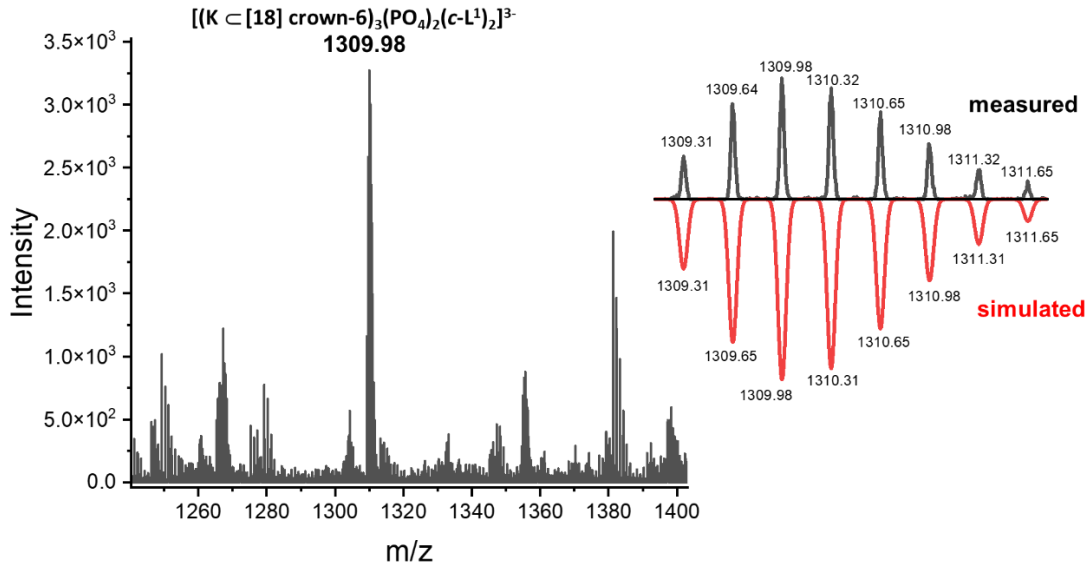


Figure S44. ESI-TOF-MS of ***c*-H^1**.

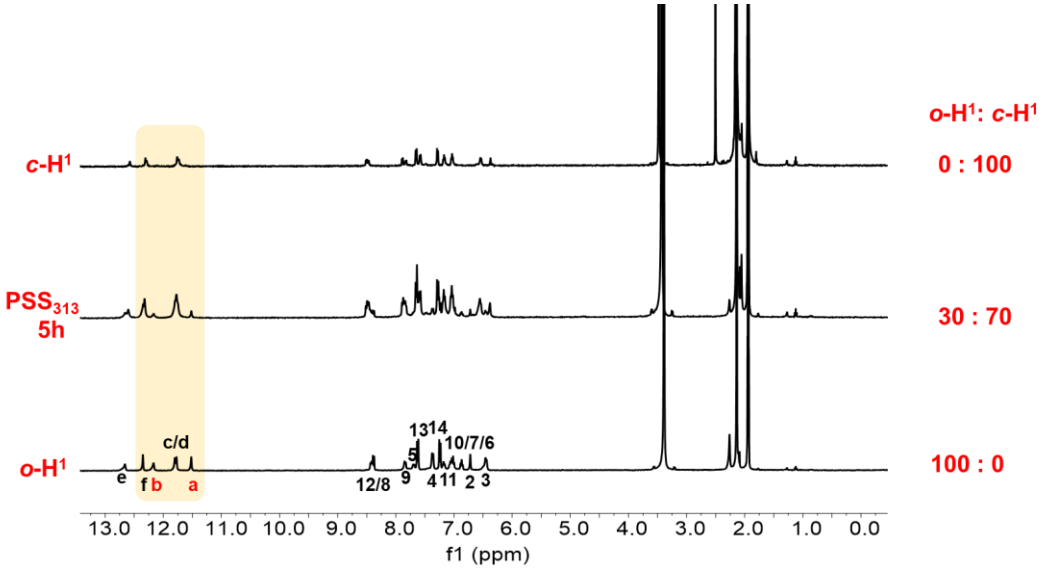


Figure S45. ^{1}H NMR spectra of $\mathbf{H^1}$ photoisomerization process (400 MHz, CD_3CN, 298 K).

***C*-H^1** is obtained by the self-assembly of ***c*-L^1** and phosphate groups, and ***o*-H^1** is obtained by the self-assembly of ***o*-L^1** and phosphate groups. **313nm-5h** is obtained by irradiating ***o*-H^1** with a 313nm ultraviolet light for 5 hours (in-situ irradiation in a nuclear magnetic resonance tube), the conversion yield is approximately 70%.

S7. Optimization and calculation of c-H^1

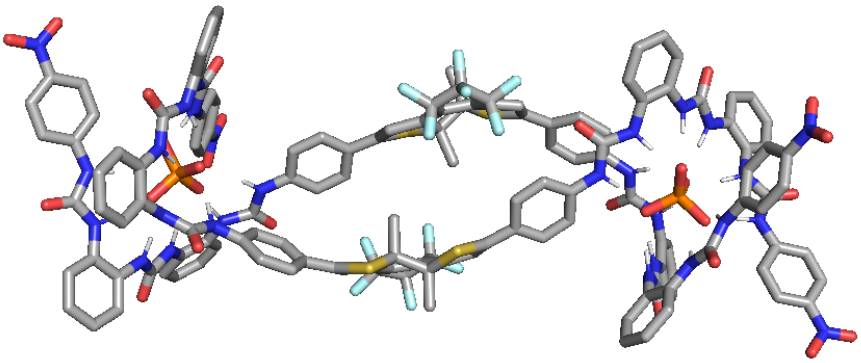


Figure S46. DFT-optimized structure of ΛΔ-***c*-H^1**.

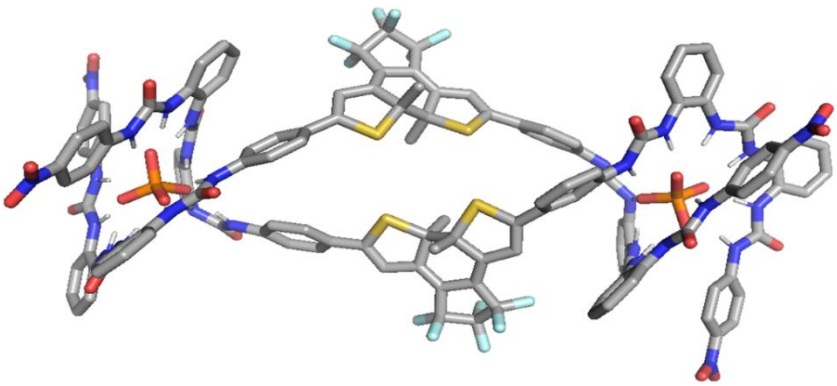


Figure S47. DFT-optimized structure of ΛΛ-***c*-H^1**.

S8. Photoisomerization properties of *(S)*-H^2

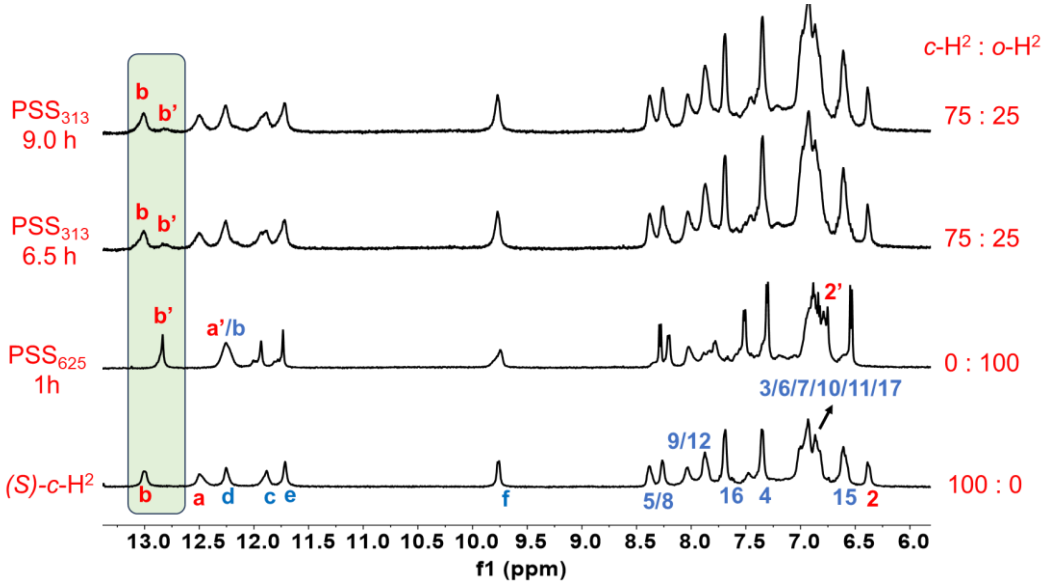


Figure S48. ^{1}H NMR spectra of ***(S)-o*-H^2** photoisomerization process (500 MHz CD_3CN, 298 K).

***(S)-c*-H^2** is obtained by the self-assembly of ***(S)-c*-L^2** and phosphate groups, and **PSS$_{625}$** is obtained by irradiating ***(S)-c*-H^2** with a 625 nm LED light for 1 hours (in-situ irradiation in a nuclear magnetic resonance tube). **313nm-6.5h** is obtained by irradiating ***(S)-o*-H^2** with a 313nm ultraviolet light for 6.5 hours (in-situ irradiation in a nuclear magnetic resonance tube), the conversion yield is approximately 75%.

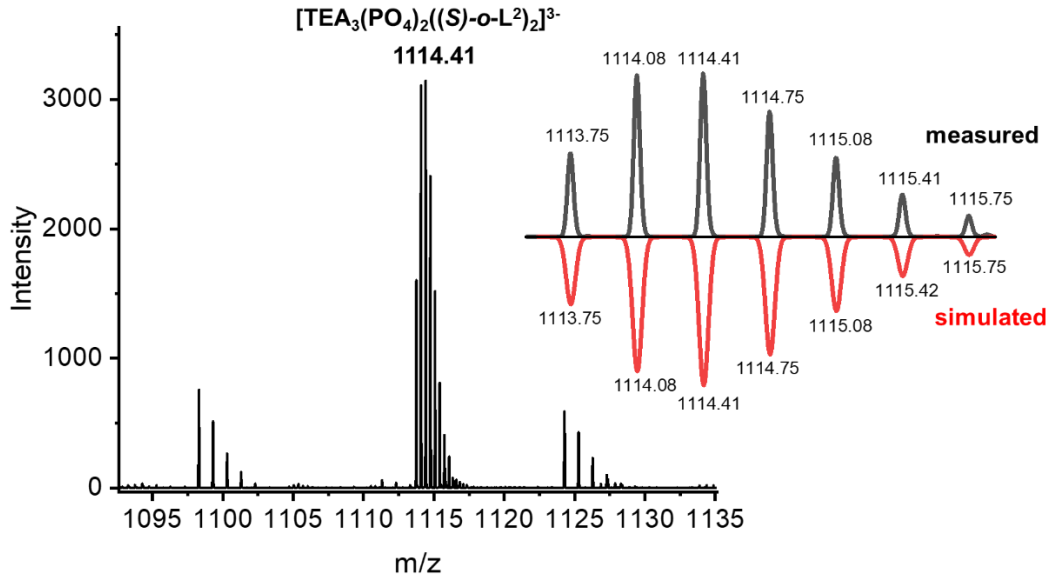


Figure S49. ESI-TOF-MS of ***(S)-o*-H^2**.

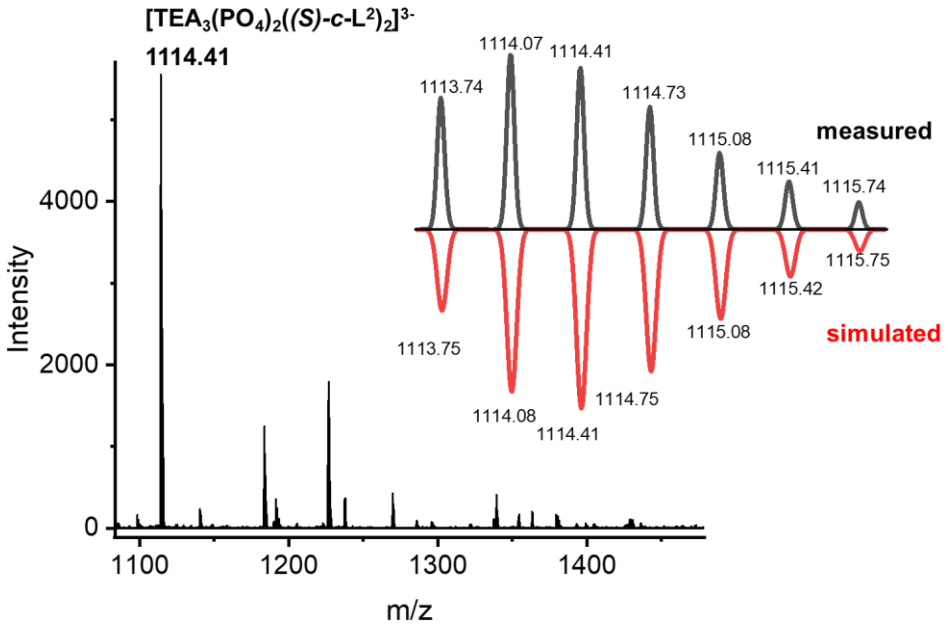


Figure S50. ESI-TOF-MS of ***(S)-c*-H²**.

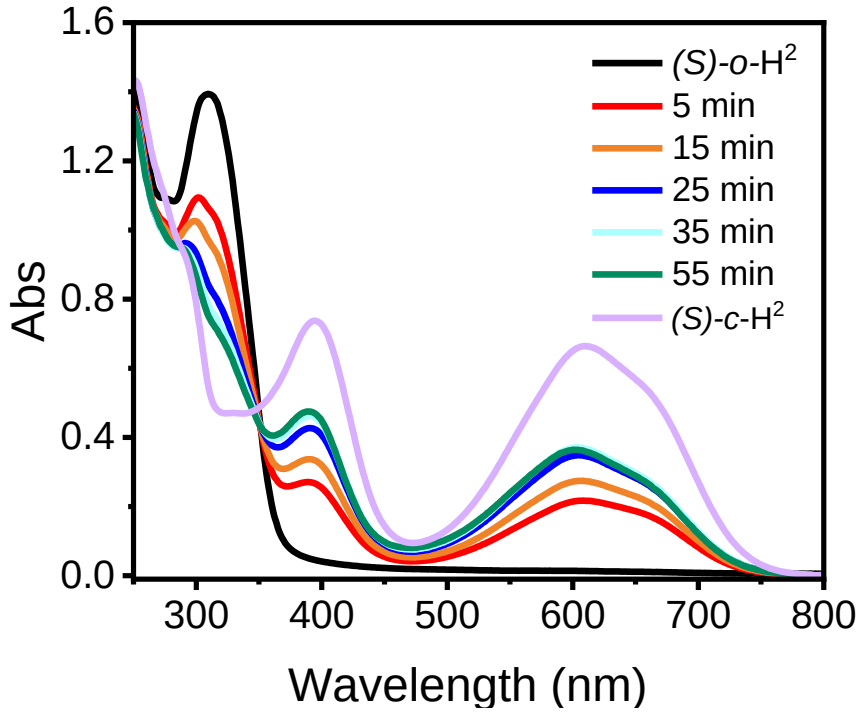


Figure S51. UV-vis spectra of ***(S)-o*-H²** under light irradiation (CH_3CN, [***(S)*-L²**] = 20 μM).

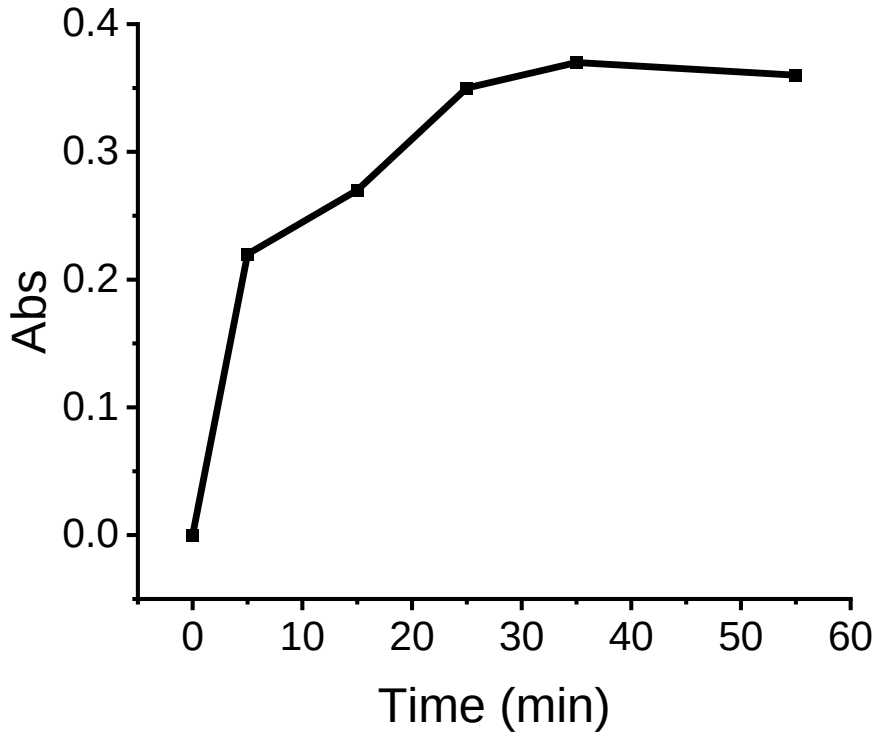


Figure S52. Absorption changes at 600 nm of ***(S)*-*o*-H^2** under light irradiation (CH_3CN, [***(S)*-L^2**] = 20 μM).

The characteristic absorption peak of ***(S)*-*o*-H^2** is at 308 nm, and the characteristic absorption peaks of ***(S)*-*c*-H^2** are 319 nm and 600 nm. Meanwhile, the isosbestic point is at 345 nm.

S9. References

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