

Electronic Supplementary Material (ESI)

Influence of Ag(I)-coordinated supramolecular architectures by conformation isomers in alkyl chains

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Contents

<i>Methods</i>	<i>S2</i>
<i>Material synthesis</i>	<i>S3</i>
<i>Supplementary Scheme and Figures</i>	<i>S4</i>
<i>References</i>	<i>S20</i>

Methods

General characterization. The ^1H and ^{13}C NMR spectra were taken on a Bruker DRX 300, and Bruker DRX 500. Mass spectroscopy samples were analyzed on a JEOL JMS-700 mass spectrometer. The high resolution mass spectra (HR MS) were measured by electrospray ionization (ESI) with a micro TOF Focus spectrometer from SYNAPT G2 (Waters, U.K.). A UV-visible spectrophotometer (Jasco V-750) was used to obtain the absorption spectra. IR spectra were observed over the range $500\text{-}4000\text{ cm}^{-1}$, with a Thermo scientific Nicolet iS 10 instrument. Powder X-ray pattern (XRD) was recorded on a Rigaku model NANOPIX X-ray diffractometer with a Cu K_α radiation source.

Preparation of silver complexes. Different concentrations (0.5 and 1.0 equiv.) of Ag^+ solution (water) were added to the ligand *trans*-**L** and *cis*-**L** (6.0 mM) solution in a mixture of DMSO and H_2O (4:1 v/v).

SEM observation. FE-SEM images were observed using a JEOL (JSM-7900F). The images of samples using an accelerating voltage 10 kV and an emission current of $8\mu\text{A}$. Samples were prepared by dropping dilute solution of supramolecular nanostructure formed in a mixture of DMSO and H_2O (4:1 v/v) on glasses following by spinning, drying and coating them with a thin layer of Pt to increase the contrast.

Circular dichroism studies. The CD and UV-vis spectra were recorded on a Jasco J-815 CD spectrophotometer. CD and UV-vis spectra were determined over the range of 200-500 nm using a quartz cell with 0.1 mm path length. Scans were taken at rate of 500 nm/min with a sampling interval of 0.5 nm and response time of 0.5s. The scans were acquired for the supramolecular nanostructure directly at $25\text{ }^\circ\text{C}$.

Calculation of thermodynamic parameter. The thermodynamic parameters governing the supramolecular aggregation of *trans*-**L** and *cis*-**L** were obtained by the global fitting of the melting curves. This global fitting is performed by using the equilibrium (EQ) model reported by ten Eikelder and coworkers.¹ The values for the elongation enthalpy (ΔH_e) and the entropy (ΔS_e), and elongation binding constant (K_e) used in the cooperative supramolecular polymerization models were determined by the global fitting of the heating curves,²⁻⁴ which were obtained by plotting the degree of aggregation (α_{agg}) of *trans*-**L** and *cis*-**L** (6 mM) without and with AgNO_3 (0.5 equiv.) at 275 nm against temperature with heating experiments. An elongation binding constant (K_e) for aggregation at 293 K was estimated according to eq. 1, from which the enthalpy change (ΔH), and the entropy change (ΔS) were determined:

$$K_e = e^{-(\Delta H_e - T\Delta S)/RT} \quad (\text{eq. 1})$$

Material synthesis

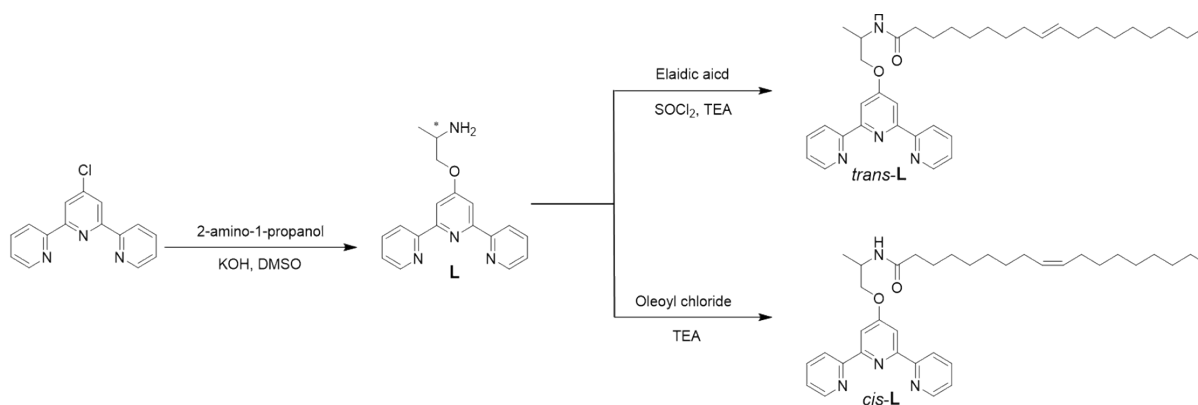
trans-L and *cis*-L were synthesized according to the procedure shown in Scheme S1. All chemical reagents were purchased commercially without further purification, unless otherwise noted.

Synthesis of compound L. (*R*)-(-)-2-amino-1-propanol (0.28 g, 3.7 mmol) was put into a stirred suspension of powdered KOH (1.05 g, 18.7 mmol) in dry DMSO (20 mL) at 60 °C. After 30 min, 4'-chloro-2,2':6',2''-terpyridine (1.00 g, 3.7 mmol) was put into the mixture. The mixture was then stirred for 4 h at 70 °C and poured into 600 mL of distilled water thereafter. CH₂Cl₂ (3 × 200 mL) was used to extract the aqueous phase. Residual water in dichloromethane was dried over Na₂SO₄ and CH₂Cl₂ was removed in vacuum, and the desired product was purified by recrystallization with ethyl acetate. Yield: 72%; Mp = 118.3 °C; IR (KBr pellet): 3375, 2964, 2926, 2846, 1577, 1565, 1473, 1439, 1403, 1353, 1204, 799 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆): δ 8.70 (tdd, *J* = 4.8, 1.8, 0.9 Hz, 2H), 8.62 (dt, *J* = 8.0, 1.1 Hz, 2H), 8.02 (s, 2H), 7.84 (td, *J* = 7.7, 1.8 Hz, 2H), 7.33 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 2H), 4.14 (dd, *J* = 9.0, 4.1 Hz, 1H), 3.94 (dd, *J* = 9.1, 7.6 Hz, 1H), 3.41 (dddd, *J* = 10.6, 7.6, 6.6, 4.2 Hz, 1H), 1.21 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125 MHz, DMSO-d₆): δ 167.2, 157.1, 155.3, 149.7, 137.9, 125.0, 121.3, 107.3, 75.1, 46.2, 20.43; HR-Mass (*m/z*) calculated for C₁₈H₁₈N₄O [M]⁺: 306.3690, Found [M]⁺: 306.3690.

Synthesis of compound *trans*-L. L (0.5 g, 2 mmol), elaidic acid (0.5 g, 2 mmol), SOCl₂ (1 mL, 20 mmol), and triethylamine (TEA, 2.5 mL, 20 mmol) were added to a 50-mL flask. Anhydrous toluene (10 mL) was then injected, and the reaction mixture was stirred for 2 hours at 80 °C. Then solvents were removed using a rotary evaporator. After the crude product was partitioned in CH₂Cl₂/H₂O, the organic layer was separated and dried over Na₂SO₄. Then, the organic solvent was removed using a rotary evaporator. The desired product was recrystallized from ethyl ether and MeOH. Yield: 52%; ¹H NMR (300 MHz, DMSO-d₆) δ 8.71 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 2H), 8.62 (dt, *J* = 8.0, 1.1 Hz, 2H), 8.06 – 7.96 (m, 4H), 7.89 (d, *J* = 7.4 Hz, 1H), 7.50 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 2H), 5.36 – 5.18 (m, 2H), 4.32 – 4.06 (m, 3H), 2.07 (t, *J* = 7.2 Hz, 2H), 1.85 (dd, *J* = 13.1, 5.5 Hz, 4H), 1.47 (s, 2H), 1.21 (d, *J* = 5.5 Hz, 24H), 0.84 (s, 3H); HR-Mass (*m/z*): Calculated for C₃₆H₅₀N₄O₂ [M]⁺ 571.401, Found [M]⁺ 571.4018 and [M+H]⁺ 572.4050.

Synthesis of compound *cis*-L. L (0.25 g, 0.8 mmol), oleoyl chloride (0.36 g, 1.2 mmol), and triethylamine (TEA, 2.5 mL, 20 mmol) were added to a 50 mL flask. Anhydrous CH₂Cl₂ (10 mL) was then injected, and the reaction mixture was stirred for 1 days at room temperature. Then solvents were

removed using a rotary evaporator. After the crude product was partitioned in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$, the organic layer was separated and dried over Na_2SO_4 . Then, the organic solvent was removed using a rotary evaporator. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.76 – 8.57 (m, 4H), 8.07 – 7.86 (m, 6H), 7.50 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 2H), 5.31 – 5.19 (m, 2H), 4.28 – 4.12 (m, 3H), 2.07 (t, $J = 7.1$ Hz, 2H), 1.89 (dd, $J = 10.5, 5.8$ Hz, 4H), 1.47 (s, 2H), 1.21 (d, $J = 6.7$ Hz, 23H), 0.88 – 0.77 (m, 4H); HR-Mass (m/z): Calculated for $\text{C}_{36}\text{H}_{50}\text{N}_4\text{O}_2$ $[\text{M}]^+$ 571.401, Found $[\text{M}]^+$ 571.4017 and $[\text{M}+\text{H}]^+$ 572.4047.



Scheme S1 Synthetic method of *trans*-L and *cis*-L

Table S1. Thermodynamic parameters of *trans*- and *cis*-L with AgNO₃ (0.5 equiv.) in a mixture of DMSO/H₂O (4:1 v/v) after 72 h.

	ΔG (kJ mol ⁻¹)	ΔH_e (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)	K_e (L mol ⁻¹)	T_e (K)
trans	-18.87	-39.98	-70.84	2.0×10^3	352.64
cis	-18.02	-64.05	-154.46	1.4×10^3	325.15

^aGibbs free energy. ^bElongation enthalpy. ^cEntropy. ^dElongation binding constant. ^eElongation Temperature.

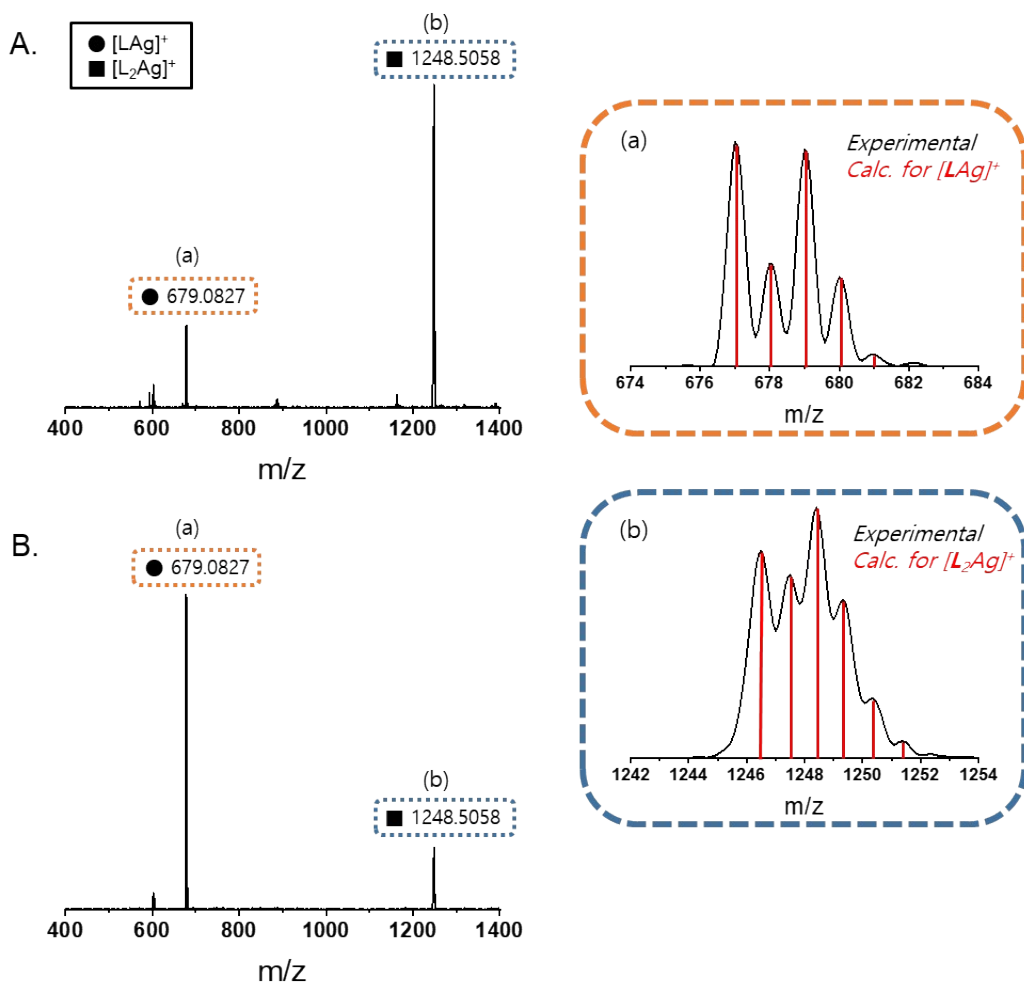


Fig. S1 HR-ESI-MS spectra of *trans*-**L** (6.0 mM) with AgNO₃ (A) 0.5 equiv. and (B) 1.0 equiv. in H₂O and DMSO (1:4 v/v) after 10 h.

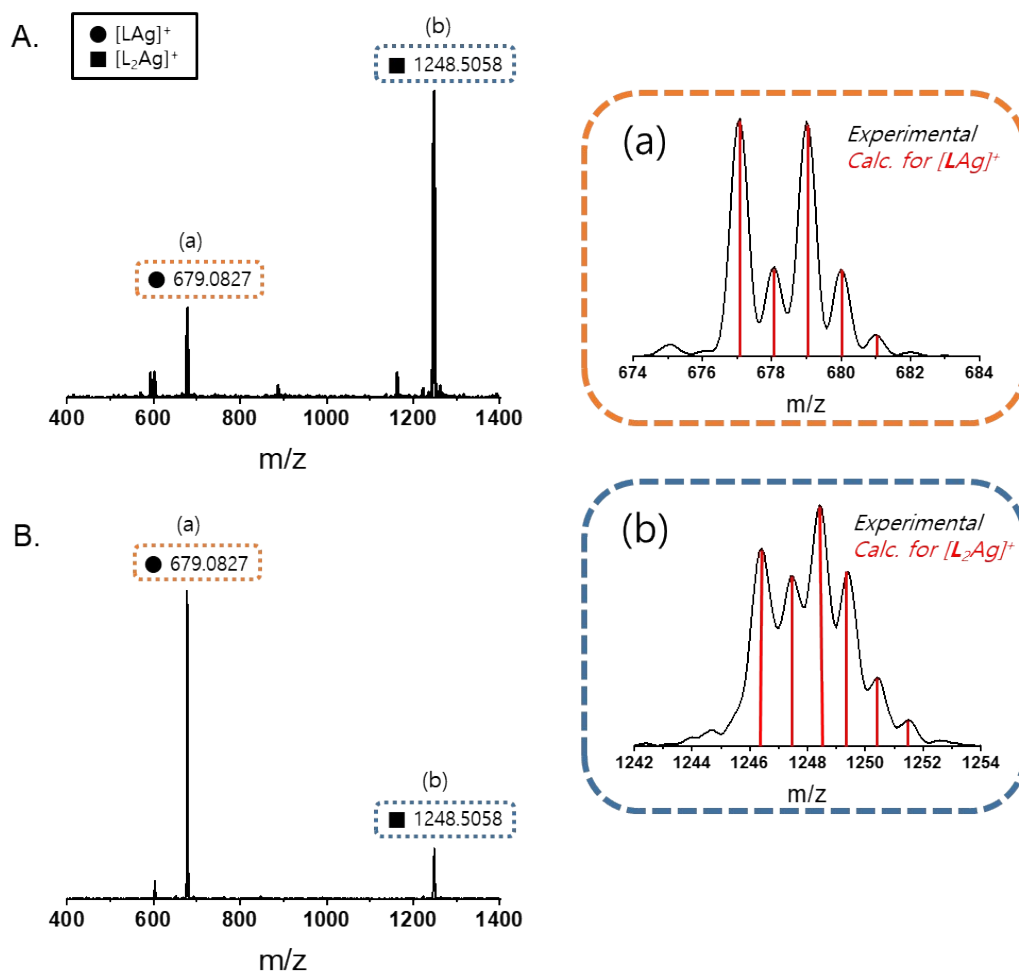


Fig. S2 HR-ESI-MS spectra of *cis*-L (6.0 mM) with AgNO₃ (A) 0.5 equiv. and (B) 1.0 equiv. in H₂O and DMSO (1:4 v/v) after 10 h.

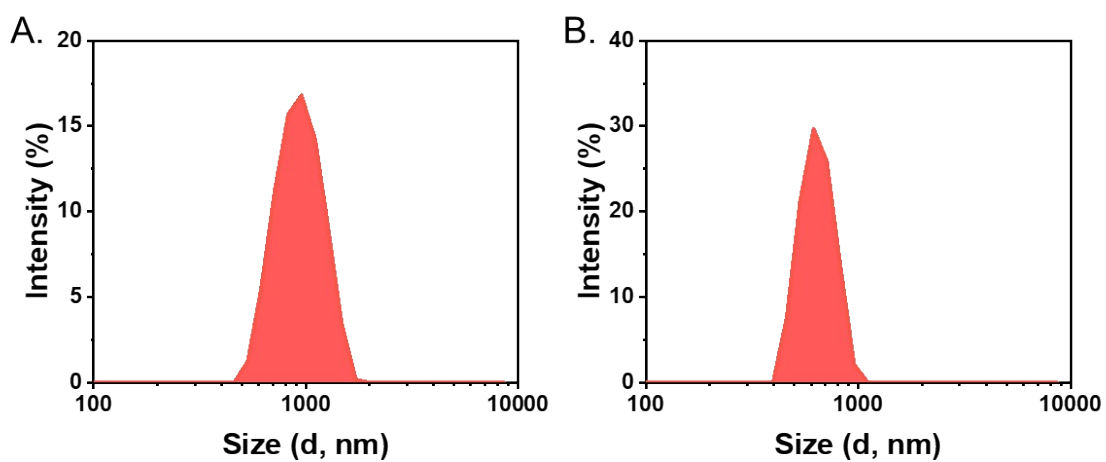


Fig. S3 Intensity percentage dynamic light scattering size distributions of (A) *trans*-L and (B) *cis*-L (6.0 mM) with AgNO₃ (0.5 equiv.) in a mixed H₂O and DMSO (1:4 v/v) after 72 h. Since DLS will consider the supramolecular architectures as spherical aggregates and hence the obtained values will not be accurate and can only be utilized to show the trend.

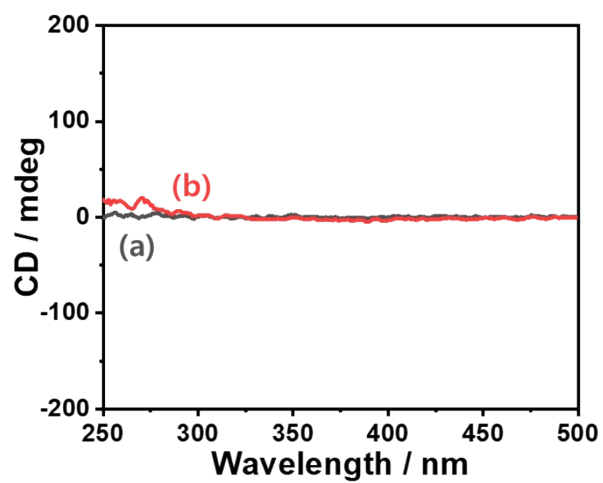


Fig. S4 CD spectra of *cis*-L (6.0 mM) with AgNO₃ (a) 0.5 equiv. and (b) 1.0 equiv. in H₂O and DMSO (1:4 v/v).

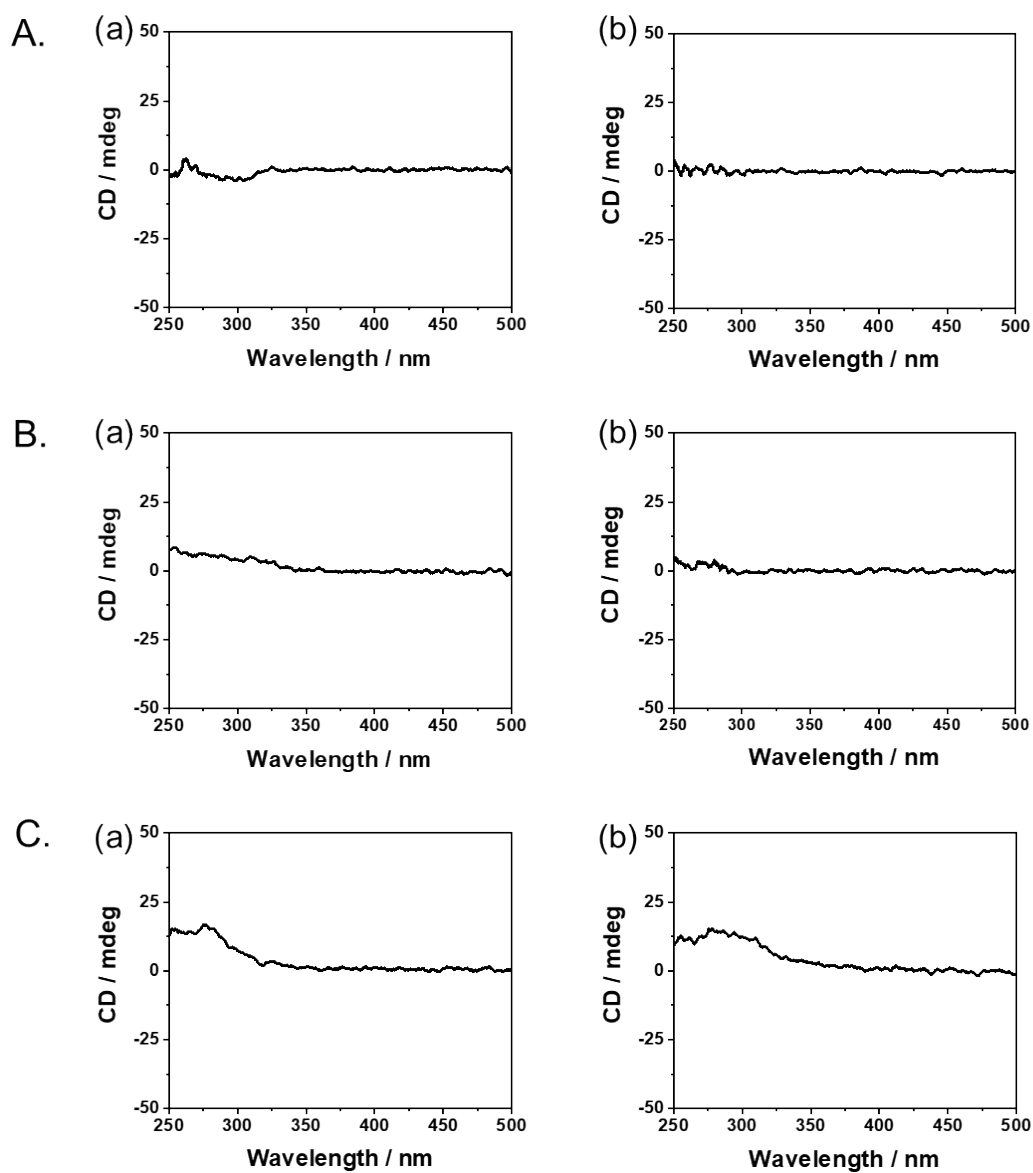


Fig. S5 CD spectra of *cis*-L (6.0 mM) with AgNO_3 (a) 0.5 equiv. and (b) 1.0 equiv. in (A) MeOH, (B) H_2O and DMSO (1:1 v/v) and (C) H_2O and DMSO (2:1 v/v).

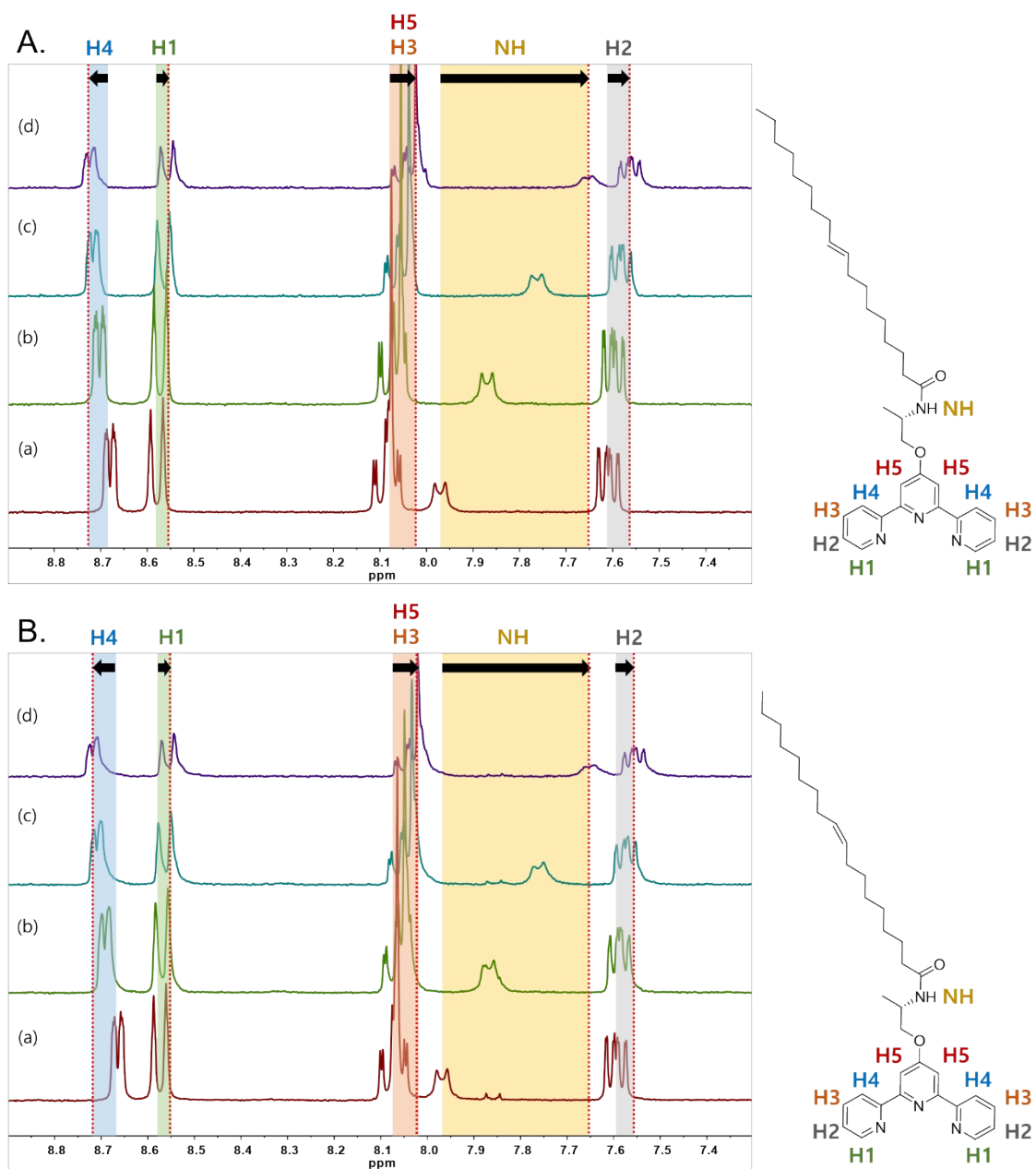


Fig. S6 Temperature-dependent ^1H NMR spectra of (A) *trans*-L and (B) *cis*-L with AgNO_3 (0.5 equiv.) in D_2O and DMSO-d_6 (1:4 v/v); (a) 293 K, (b) 313 K, (c) 333 K, (d) 353 K.

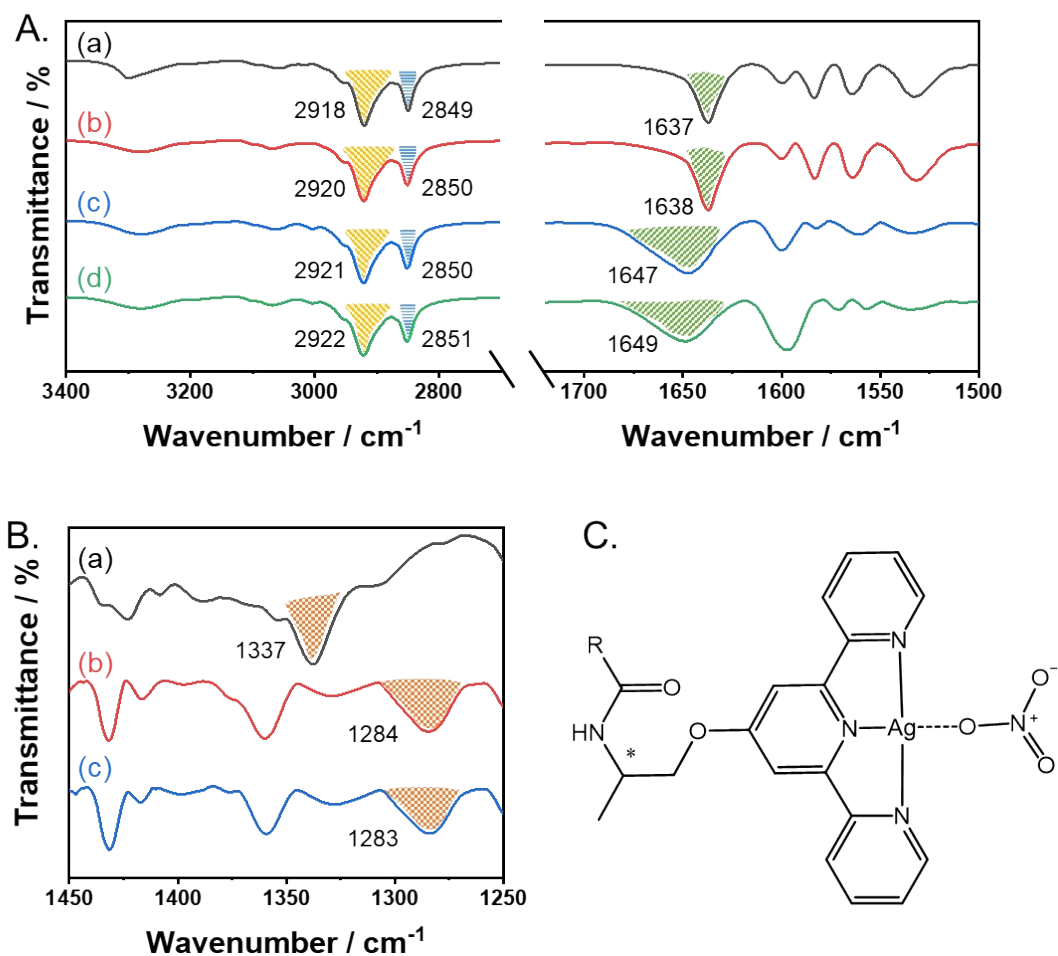


Fig. S7 (A) FT-IR spectra of (a) *trans*-**L** and (b) *cis*-**L**, (c) *trans*-**L** + AgNO₃ (0.5 equiv.), and (d) *cis*-**L** + AgNO₃ (0.5 equiv.). (B) FT-IR spectra of (a) AgNO₃ (black line), (b) *trans*-**L** + AgNO₃ (0.5 equiv.; red line) (c) *cis*-**L** + AgNO₃ (0.5 equiv.; blue line). (C) Proposed complex structure of *trans*-**L** or *cis*-**L** with AgNO₃.

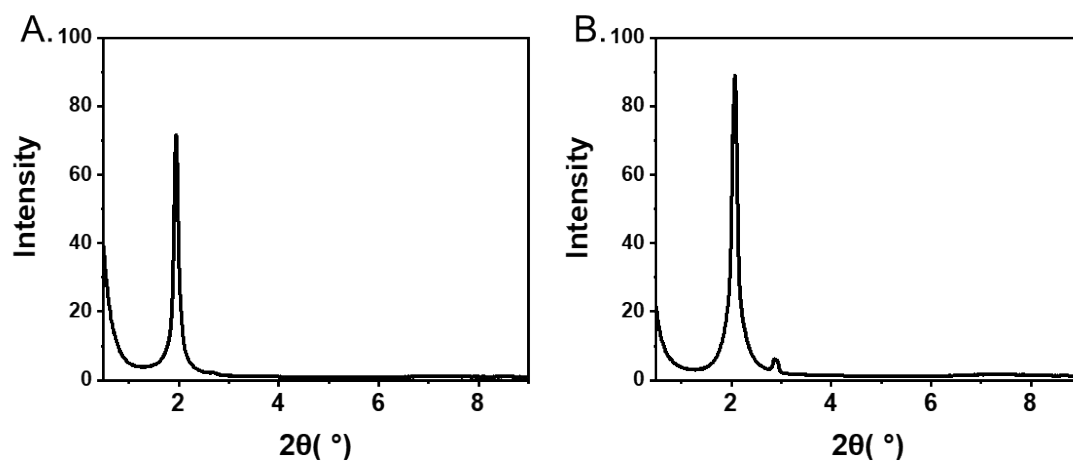


Fig. S8 SAXS patterns of (A) *trans*-L and (B) *cis*-L (6.0 mM) with AgNO_3 (0.5 equiv.) in a mixed H_2O and DMSO (1:4 v/v) after 72 h.

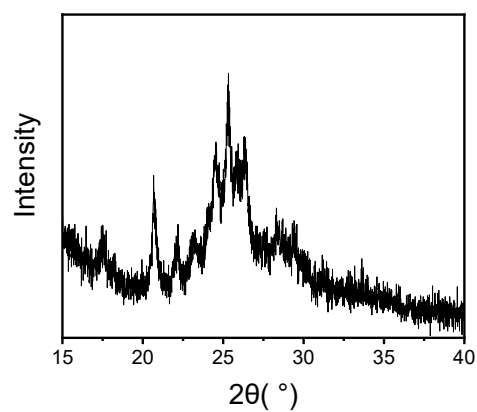


Fig. S9 WARD pattern of *trans*-L (6.0 mM) with AgNO₃ (0.5 equiv.) in a mixed H₂O and DMSO (1:4 v/v) after 72 h.

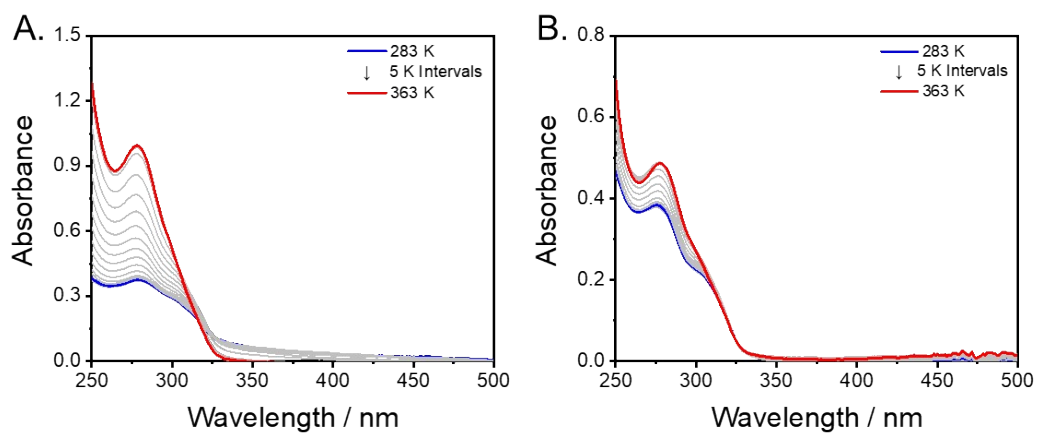


Fig. S10 Temperature-dependent UV spectra of (A) *trans*- and (B) *cis*-L (6.0 mM) with AgNO₃ (0.5 equiv.) in H₂O and DMSO (1:4 v/v).

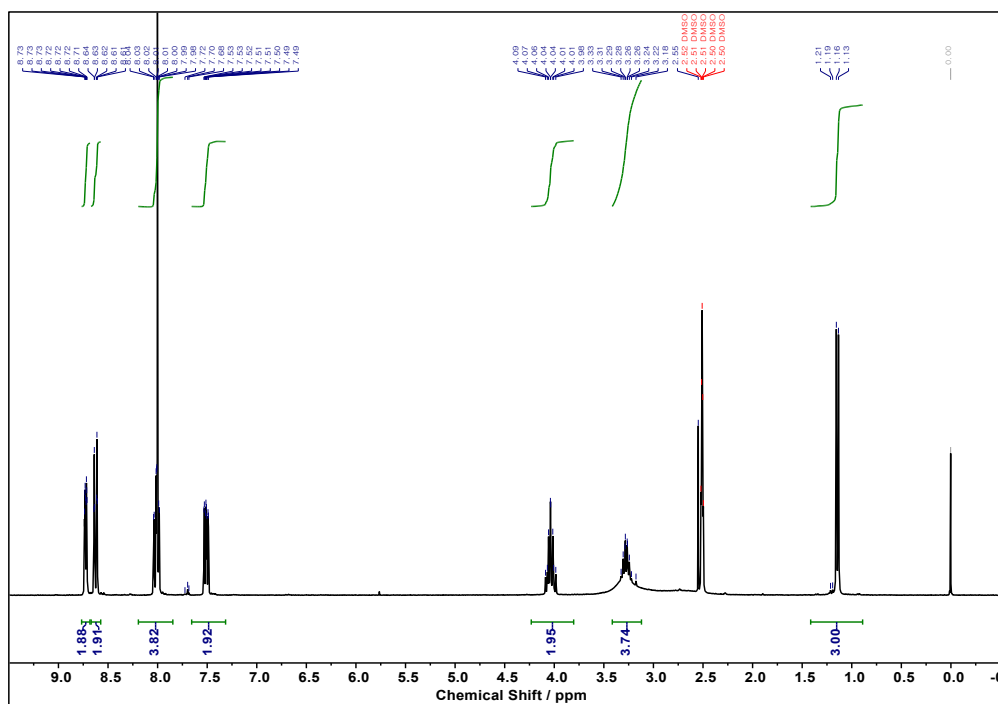


Fig. S11 ^1H NMR spectrum (300 MHz) of L in $\text{DMSO-}d_6$ at 25 $^\circ\text{C}$.

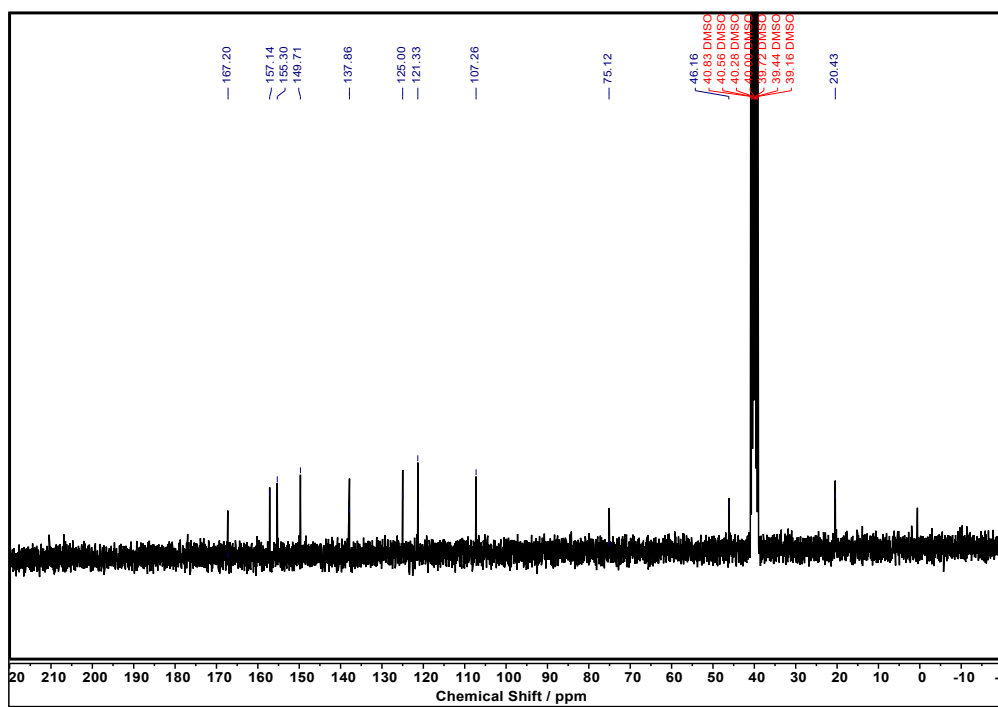


Fig. S12 ^{13}C NMR spectrum (125 MHz) of L in $\text{DMSO-}d_6$ at 25 $^\circ\text{C}$.

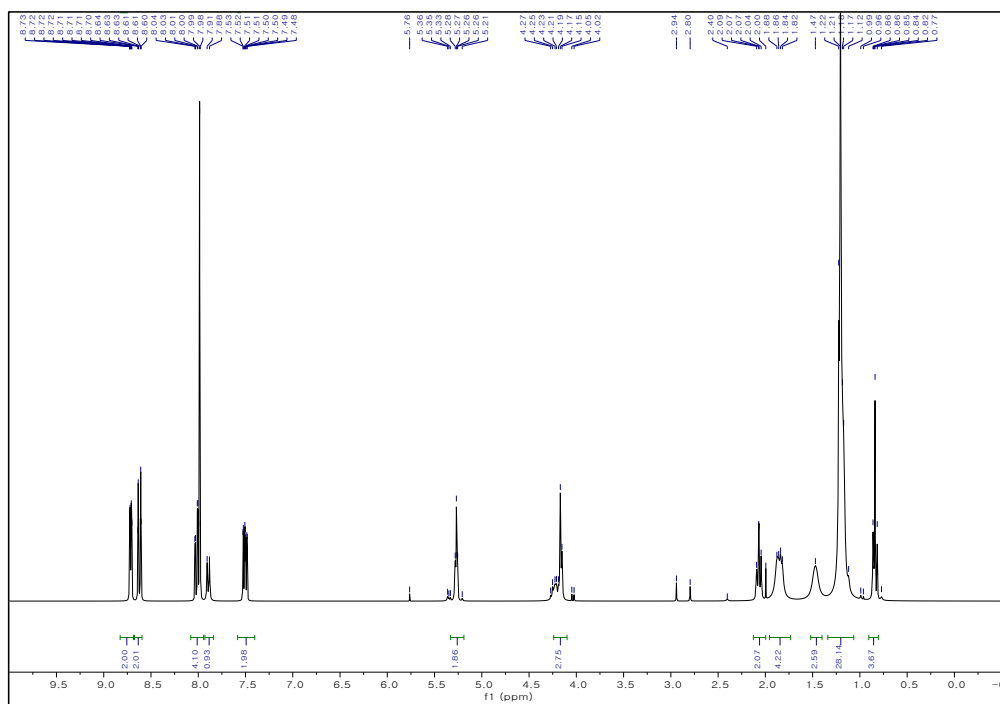


Fig. S13 ^1H NMR spectrum (300 MHz) of *trans*-L in $\text{DMSO-}d_6$ at 25 °C.

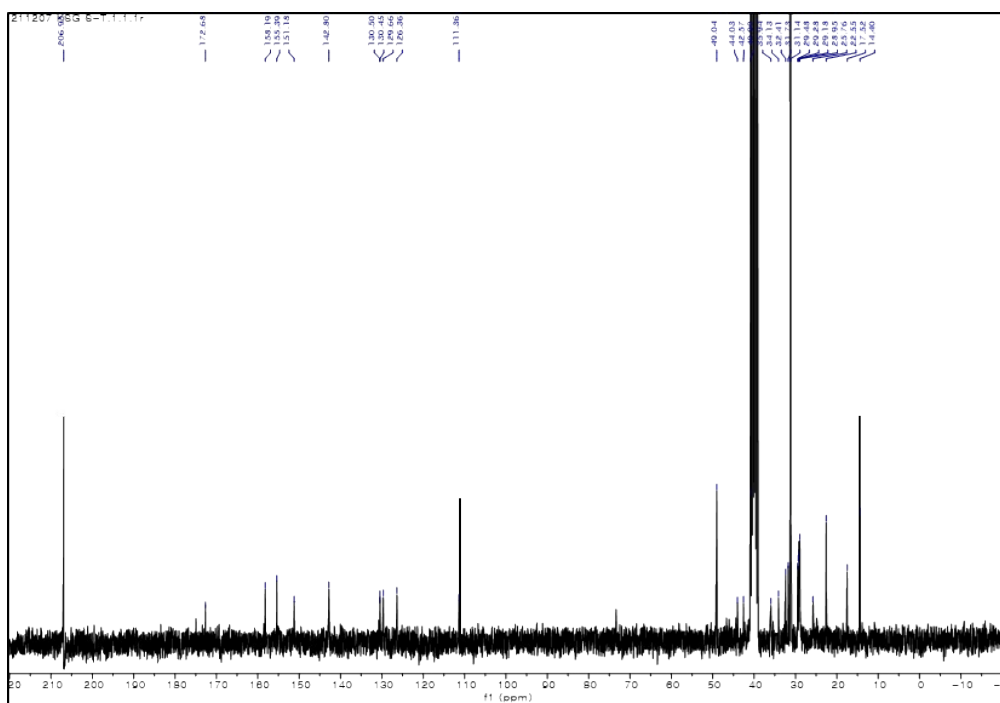


Fig. S14 ^{13}C NMR spectrum (75 MHz) of *trans*-L in $\text{DMSO-}d_6$ at 25 °C.

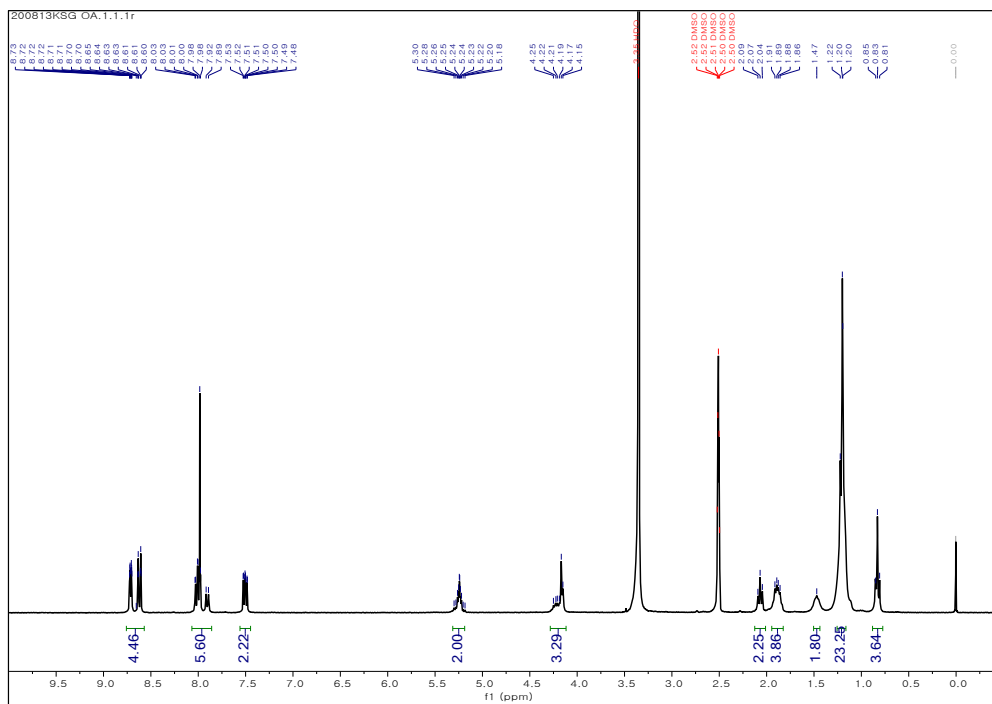


Fig. S15 ^1H NMR spectrum (300 MHz) of *cis*-L in $\text{DMSO-}d_6$ at 25 °C.

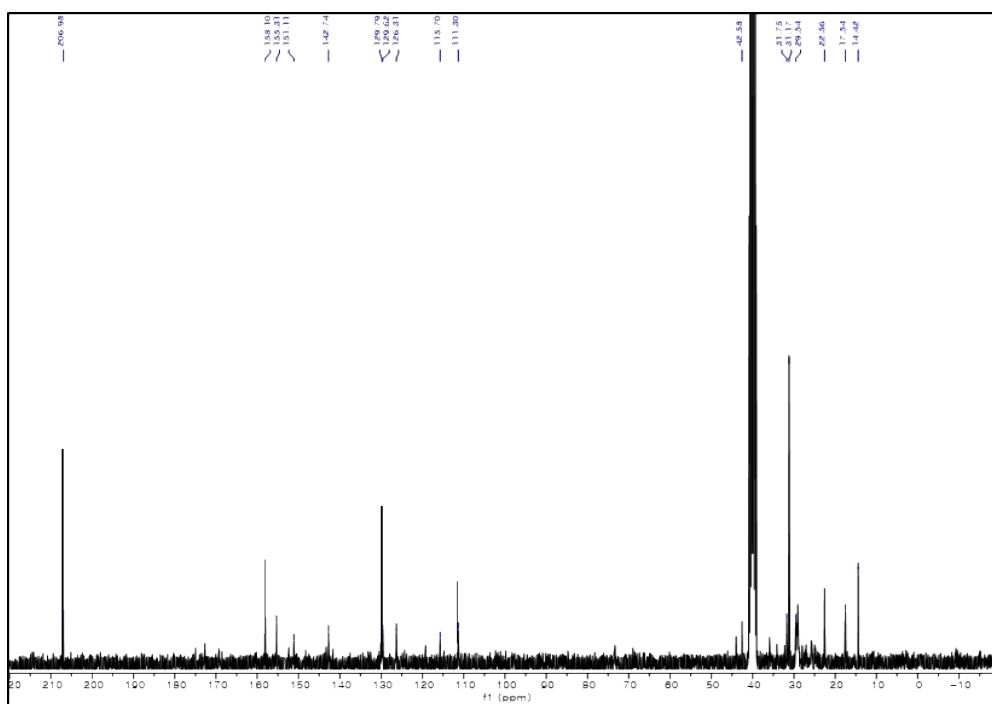


Fig. S16 ^{13}C NMR spectrum (75 MHz) of *cis*-L in $\text{DMSO-}d_6$ at 25 °C.

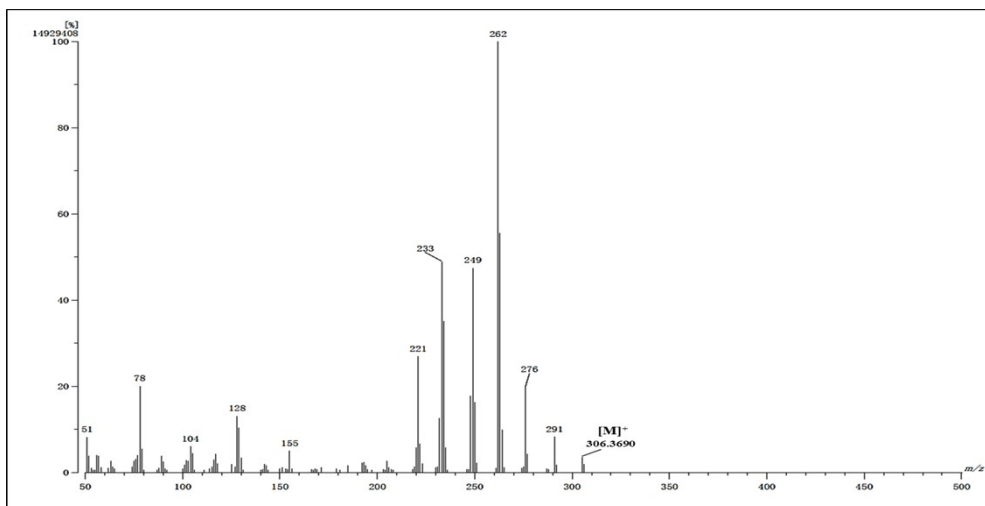


Fig. S17 HR EI-MS spectrum of **L** in MeOH.

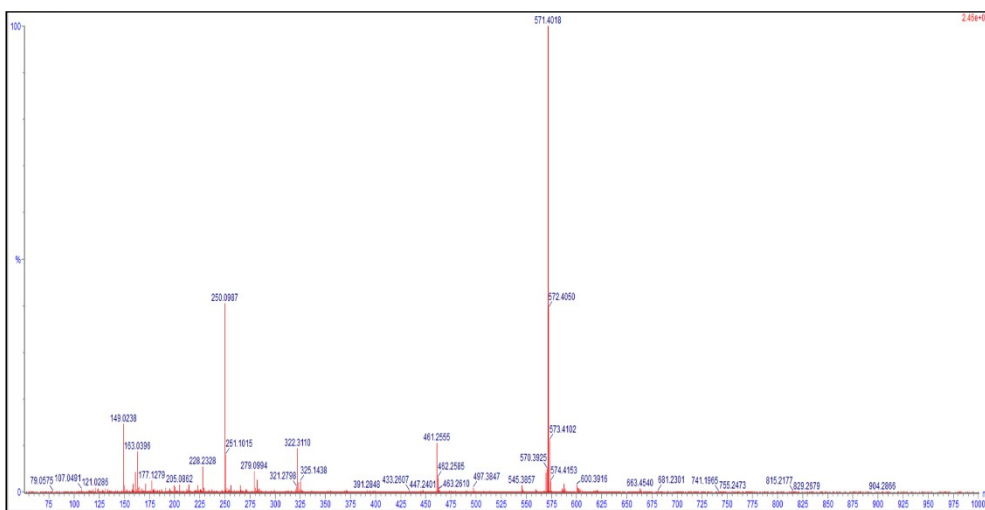


Fig. S18 HR FAB-MS spectrum of *trans*-L in MeOH.

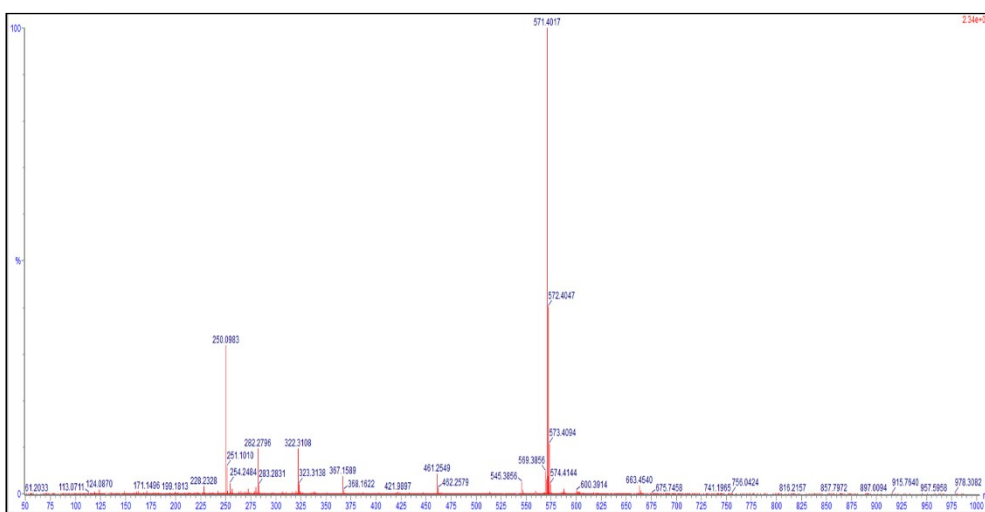


Fig. S19 HR FAB-MS spectrum of *cis*-L in MeOH.

References

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