

Supporting Information for:

Synthesis of Metallo-Polymers and Direct Visualization of Single Polymer Chain

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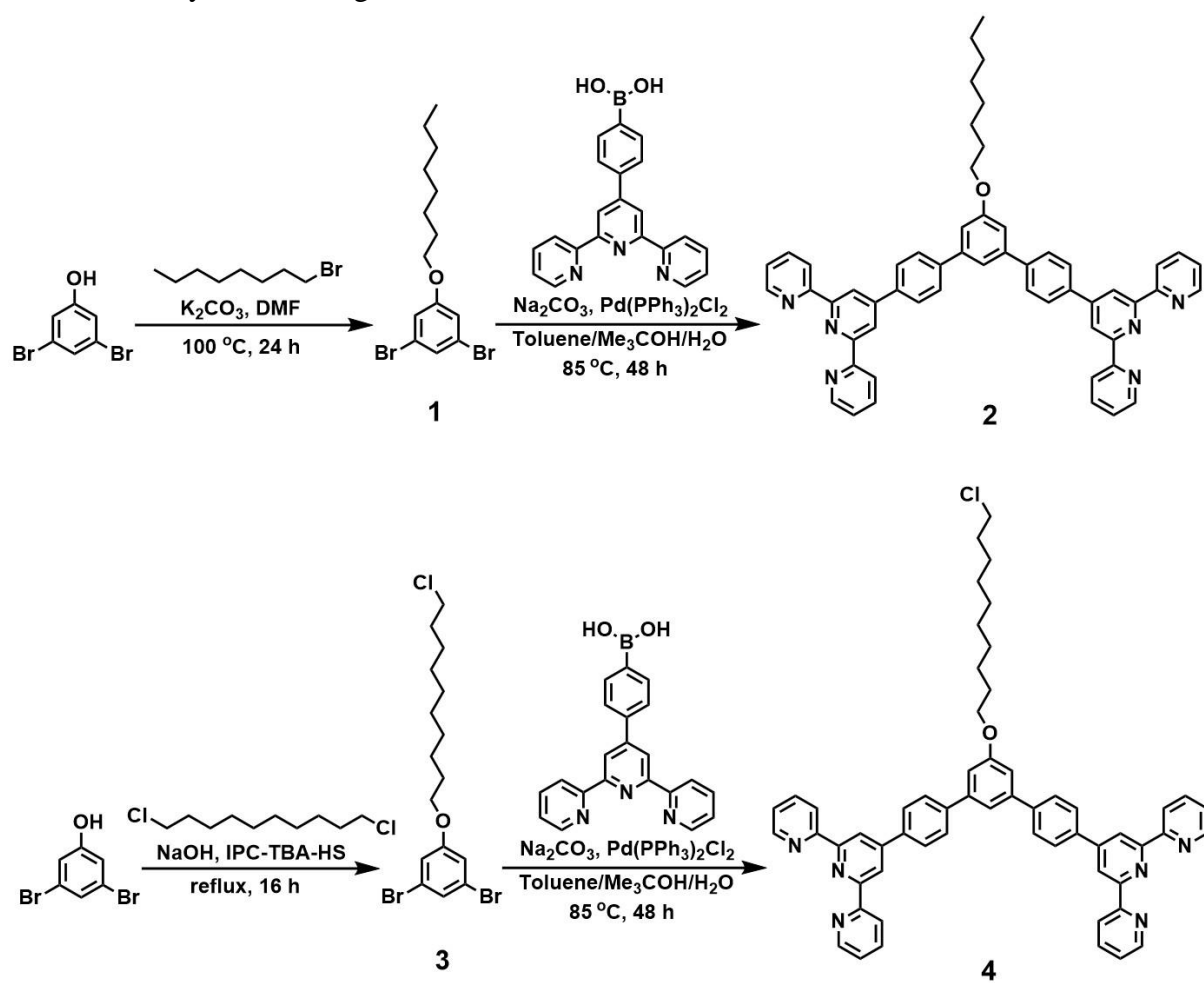
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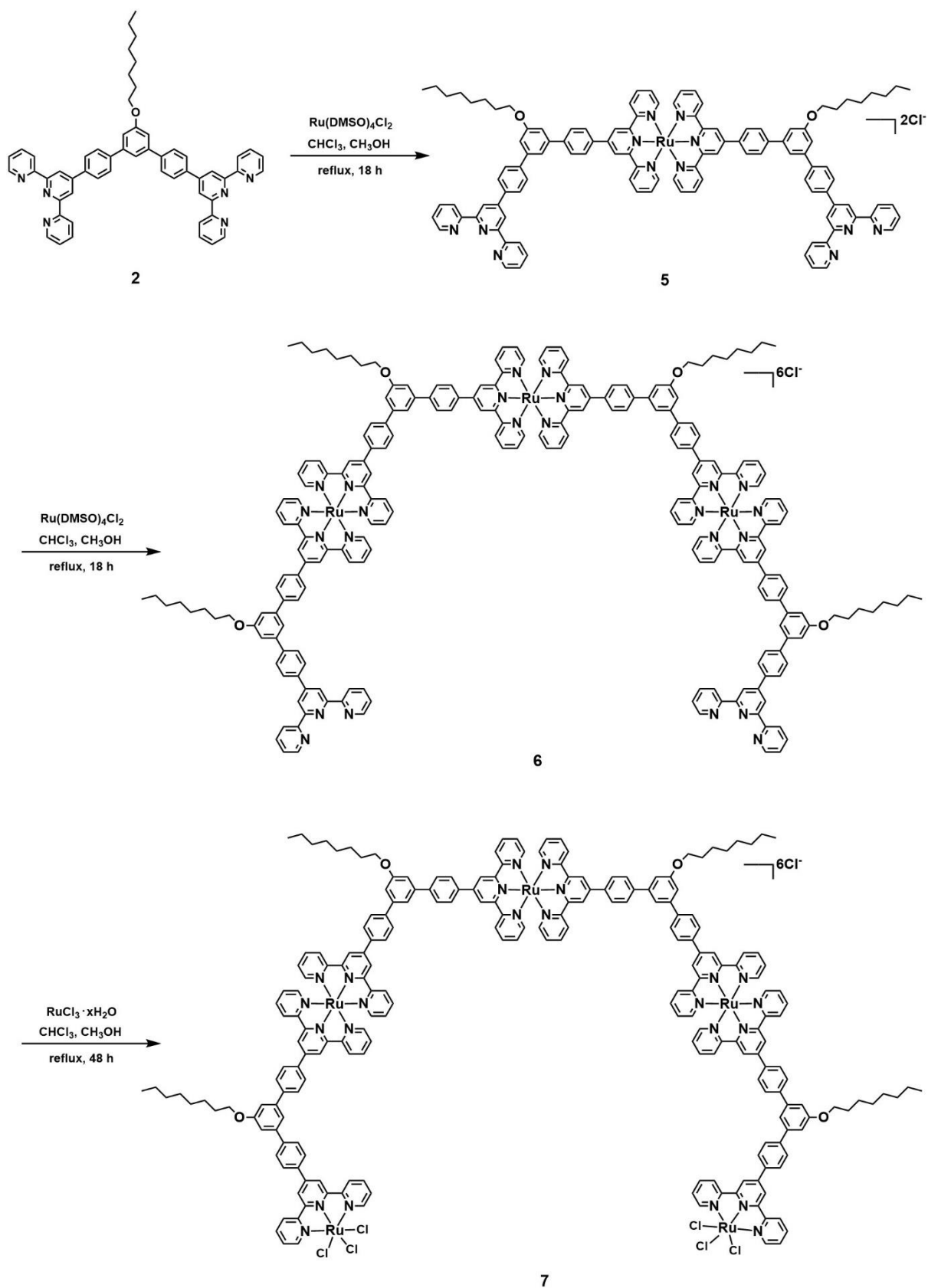
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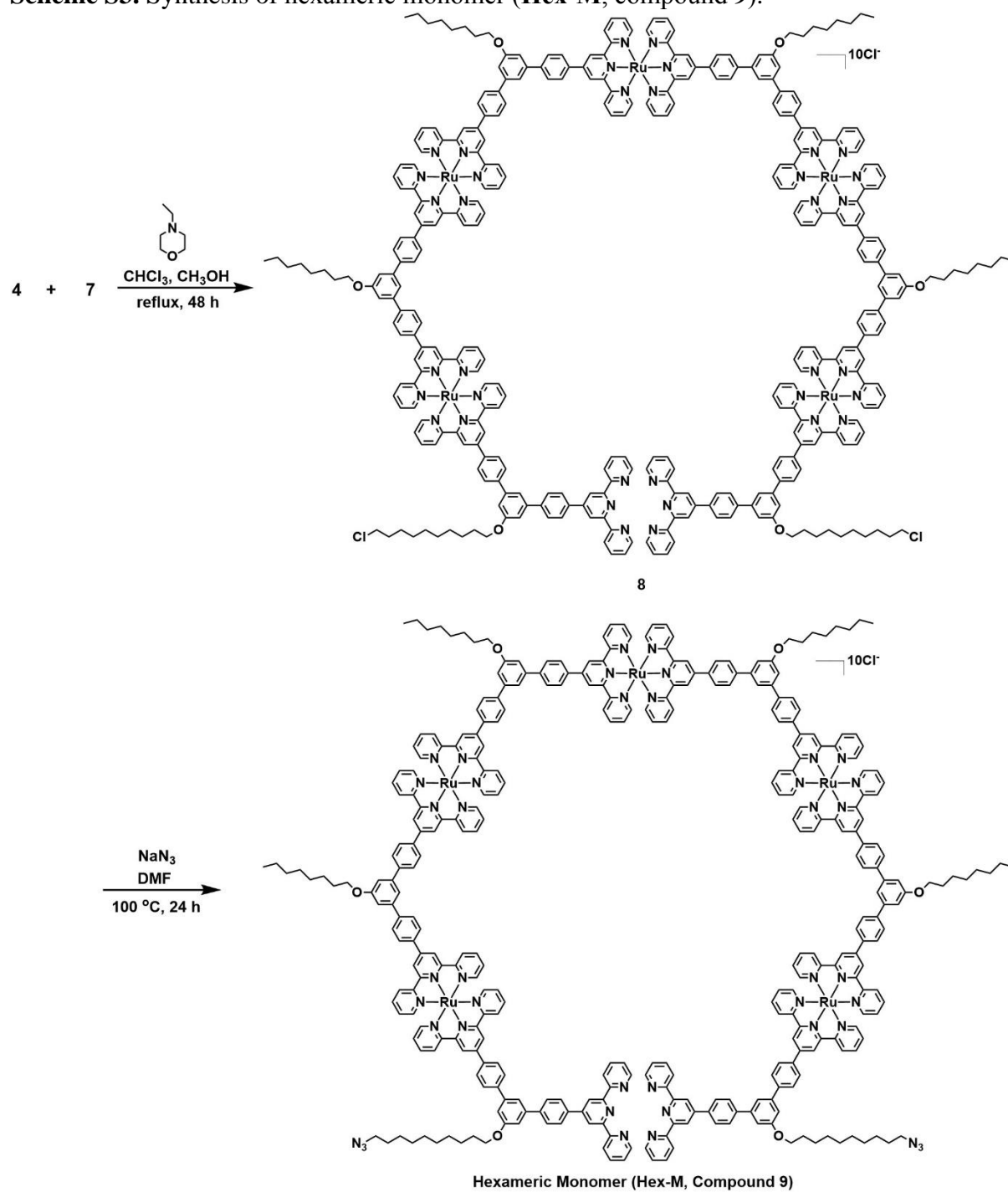
Scheme S1. Synthesis of ligands **2** and **4**.



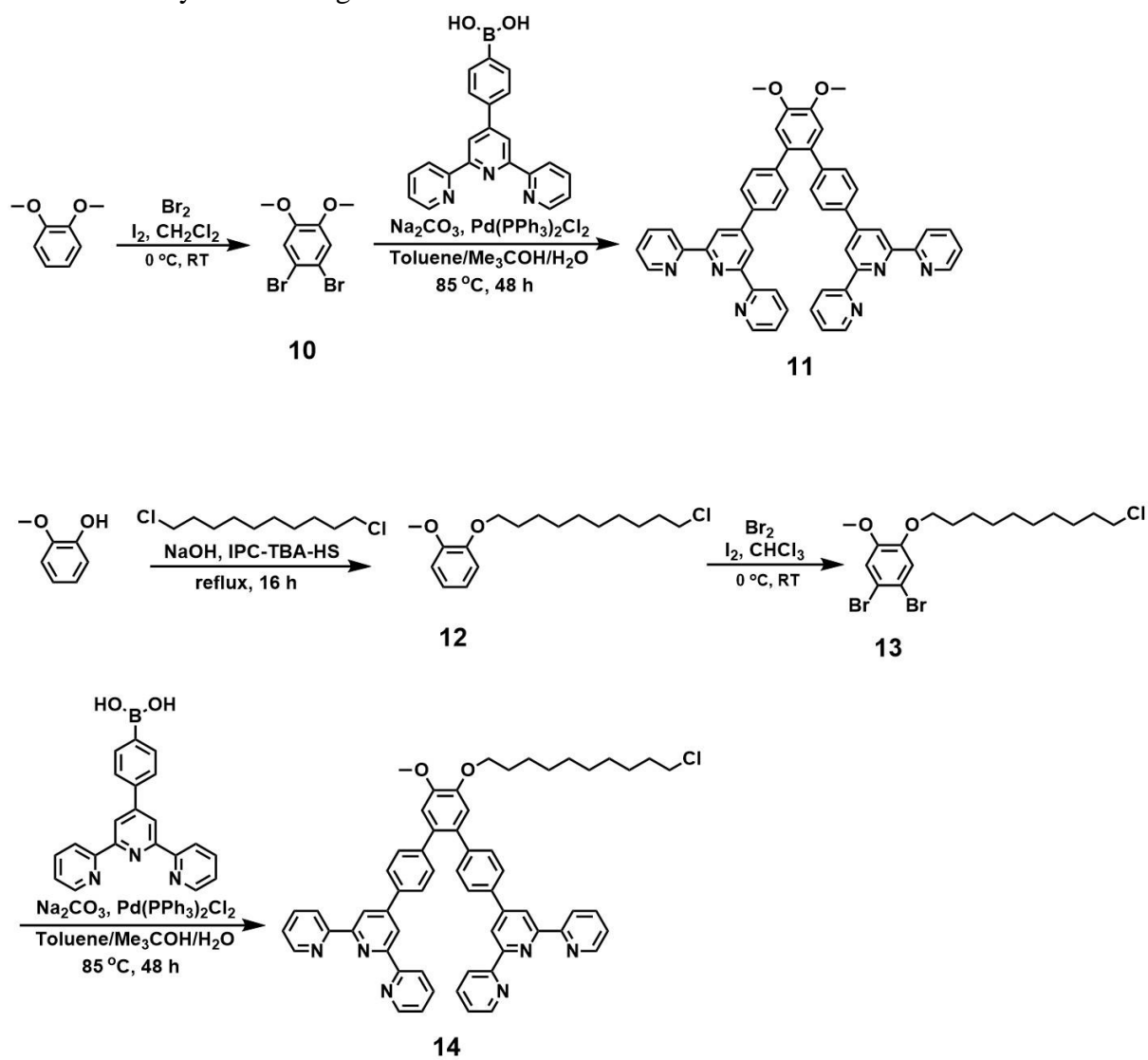
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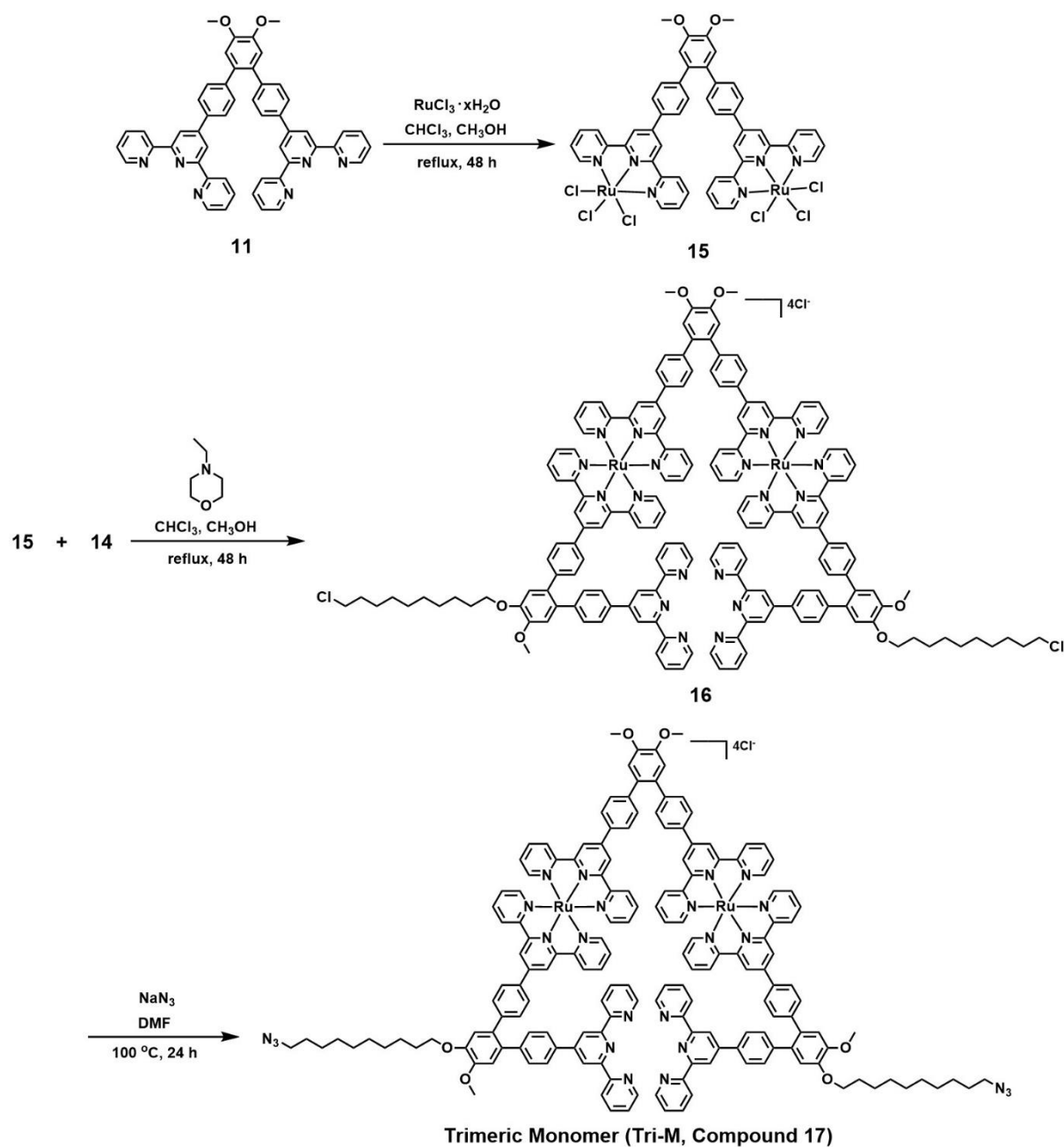
Scheme S3. Synthesis of hexameric monomer (**Hex-M**, compound **9**).



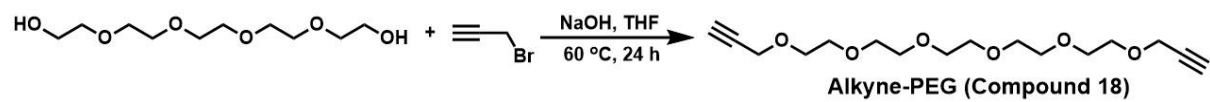
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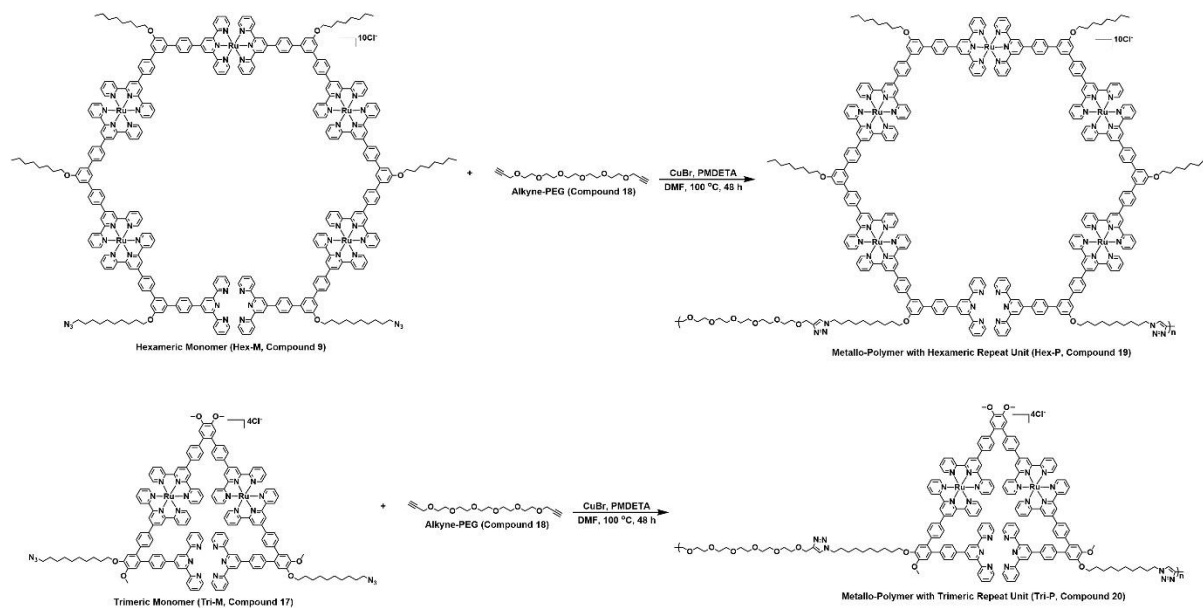
Scheme S5. Synthesis of trimeric monomer (**Tri-M**, compound **17**).



Scheme S6. Synthesis of alkyne-terminated pentaethylene glycol (**Alkyne-PEG**).



Scheme S7. Synthesis of metallo-polymer with hexameric repeat unit (**Hex-P**, compound **19**) and metallo-polymer with trimeric repeat unit (**Tri-P**, compound **20**).



Materials and Methods

All reagents were purchased from Sigma-Aldrich, Fisher, Acros, and Alfa Aesar. And they were used as received unless noted otherwise. Column chromatography was conducted using neutral Al_2O_3 (Brockman I, activity, 58 Å) or SiO_2 (VWR, 40-60 μm , 60 Å) and the separated products were visualized by UV light.

Nuclear magnetic resonance (NMR) spectra data were recorded on an Agilent Technologies 600 MHz nuclear magnetic resonance instrument and a Bruker 400 MHz nuclear magnetic resonance instrument using CDCl_3 and CD_3CN as the solvents with tetramethylsilane (TMS) as the internal standard at 25 °C.

Electrospray ionization mass spectrometry (ESI-MS) and travelling wave ion mobility mass spectrometry (TWIM-MS) spectra were collected on a Waters Synapt G2 mass spectrometer, using solutions of 0.01 mg sample in 1 mL of $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1:3, v/v) or acetonitrile for the intermediate compounds and ligands. The TWIM-MS experiments were performed under the following conditions: ESI capillary voltage, 1-3 kV; sample cone voltage, 20-30 V; extraction cone voltage, 3 V; source temperature 100 °C; desolvation temperature, 200 °C; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (N_2); source gas control, 0 mL/min; trap gas control, 2 mL/min; helium cell gas control, 100 mL/min; ion mobility (IM) cell gas control, 30 mL/min; sample flow rate, 5 $\mu\text{L}/\text{min}$; IM traveling wave height, 25 V; and IM traveling wave velocity, 1000 m/s.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass characterization was conducted on a Bruker UltrafleXtreme TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd: YAG laser (355 nm). Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, Aldrich, >99%) was

served as matrix. The matrix dissolved in CHCl_3 at 20 mg mL^{-1} and the metallo-polymers (**Hex-P** and **Tri-P**) were dispersed in DMF at 10 mg mL^{-1} . Sample was prepared by depositing $0.5 \mu\text{L}$ of matrix on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing $0.5 \mu\text{L}$ of the sample on a spot of dry matrix, and adding another $0.5 \mu\text{L}$ of matrix on top of the dry sample. The plate was inserted into the MALDI source after drying. The sample was conducted in linear mode. And the data analysis was conducted with Bruker's FlexAnalysis software.

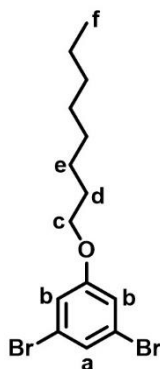
Ultraviolet visible (UV-vis) spectra were recorded on a HORIBA Scientific FluoroMax-4 spectrofluorometer at room temperature.

Scanning tunneling microscope (STM). UHV-LT-STM experiments were performed at 4 K using a home-built system with a Besoke-Beetle type STM scanner. The Ag(111) substrate was cleaned by repeated cycles of sputtering and annealing up to 1000 K. An electrochemically etched polycrystalline tungsten wire was used for the STM tip. The tip apex was prepared by using a controlled tip-crash procedure. The samples were deposited onto the cleaned Ag(111) surface at 25°C , and then cooled to 4 K inside the STM system.

Molecular modeling. Energy minimization was conducted with Materials Studio version 4.2, using the Anneal and Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The effects of the counterions were omitted in the modeling. Geometry optimization was conducted using a universal force field with atom-based summation and cubic spline truncation for both the electrostatic and van der Waals parameters.

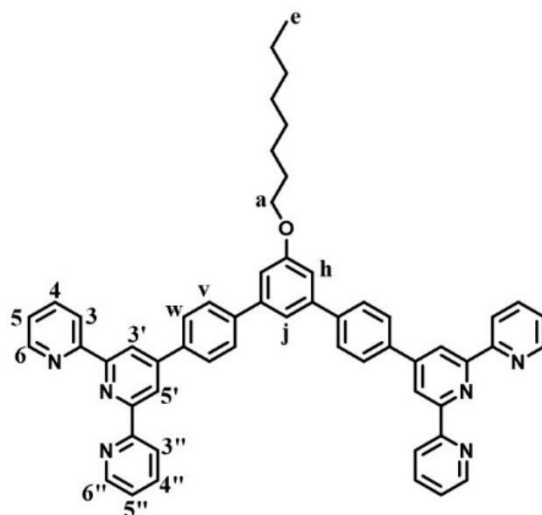
Experimental Section

Counterion exchange. For samples, the counterion was exchanged from Cl^- to PF_6^- for better solubility before the NMR and MS characterization. The general procedure of counterion exchange was as follows. First, sample was dissolved in a mixed solvent of $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1/1, v/v) or DMF, and then the mixture was added into a solution of excess NH_4PF_6 in CH_3OH (the volume of CH_3OH was 5 times of the sample solution), which afforded the corresponding precipitate. Then, the precipitate was collected through centrifugation, washed by methanol repeatedly and dried in vacuum.



Compound 1.¹ 3,5-dibromophenol (20 mmol, 5.0 g) and K_2CO_3 (120 mmol, 16.6 g) were added into a 200 mL Schlenk flask and degassed for three times. 1-bromooctane (30 mmol, 5.8 g) and DMF (120 mL) were added under N_2 . The solution was stirred at 100 °C for 24 h under N_2 . After that, the mixture was cooled to room temperature. Then 200 mL distilled water was added and extracted with CH_2Cl_2 . The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4 . After concentrated by rotary evaporator, the crude product was purified by column chromatography on silica gel with hexanes. 6.6 g pure product was obtained with high purity (Yield 91%), which was proved by ^1H NMR. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.22 (s, 1H, H^a), 6.98 (s, 2H, H^b), 3.91 (t, 2H, $J = 6.3$ Hz, H^c), 1.79-1.72 (m, 2H, H^d),

1.46-1.39 (m, 2H, H^e), 1.36-1.27 (m, 8H, $-CH_2$), 0.89 (t, 3H, $J = 6.7$ Hz, H^f). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 160.51, 126.28, 123.19, 117.07, 68.78, 31.94, 29.41, 29.35, 29.14, 26.06, 22.80, 14.25.



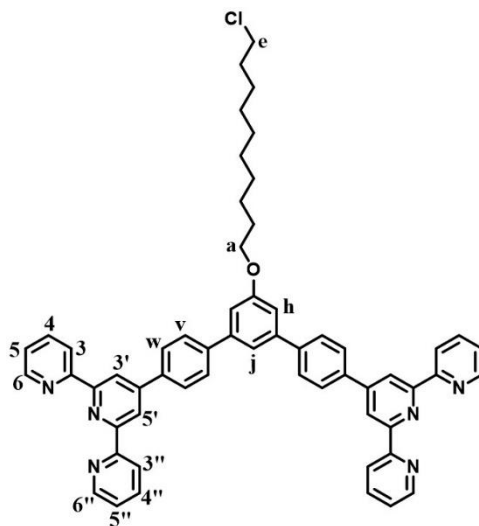
Compound 2.¹ A mixture of compound **1** (18.3 mmol, 6.7 g), 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (73.2 mmol, 28.1 g), Na_2CO_3 (219.6 mmol, 23.3 g) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (1.0 g) was added into a 500 mL Schlenk flask and degassed for three times. Under N_2 atmosphere, 200 mL toluene, 50 mL tert-butyl alcohol and 100 mL H_2O were added. The mixture was stirred at 85 °C for 48 h. After cooling to room temperature, the mixture was poured into 200 mL H_2O and extracted with CHCl_3 . The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated by rotary evaporator. The crude product was purified by column chromatography on silica gel with the eluent from CH_2Cl_2 to $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 100/1$ (v/v, gradient) to afford a white solid. After dried in vacuum, 10.5 g product was obtained, and the yield was 70%. ^1H NMR (600 MHz, CDCl_3) δ (ppm) 8.81 (s, 4H, $H^{3',5'}$), 8.76 (d, 4H, $J = 4.3$ Hz, $H^{6,6''}$), 8.69 (d, 4H, $J = 7.9$ Hz, $H^{3,3''}$), 8.04 (d, 4H, $J = 8.2$ Hz, H^w), 7.89 (td, 4H, $J = 7.8$ Hz, 1.3 Hz, $H^{4,4''}$), 7.82 (d, 4H, $J = 8.2$ Hz, H^v), 7.52 (s, 1H, H^j), 7.39-7.33 (m, 4H, $H^{5,5''}$),

7.21 (s, 2H, H^h), 4.13 (t, 2H, $J = 6.5$ Hz, H^a), 1.93-1.83 (m, 2H, alkyl chain $-CH_2$), 1.59-1.49 (m, 2H, alkyl chain $-CH_2$), 1.44-1.26 (m, 8H, alkyl chain $-CH_2$), 0.90 (t, 3H, $J = 6.6$ Hz, H^e). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 160.19, 156.35, 156.06, 149.88, 149.23, 142.56, 141.90, 137.69, 137.06, 127.92, 127.88, 123.98, 121.55, 118.90, 118.70, 112.80, 68.48, 31.98, 29.55, 29.54, 29.42, 26.28, 22.82, 14.26. ESI-MS (m/z): Calcd. for $[\text{C}_{56}\text{H}_{48}\text{N}_6\text{O} + 2\text{H}^+]^{2+}$: 411.20, Found: 411.13; Calcd. for $[\text{C}_{56}\text{H}_{48}\text{N}_6\text{O} + \text{H}^+]^+$: 821.40, Found: 821.40.



Compound 3.² A two-phase mixture of 3,5-dibromophenol (5 mmol, 1.3 g), 1,10-dichlorodecane (10 mmol, 2.1 g), tetrabutylammonium hydrogen sulfate (IPC-TBA-HS, 0.1 mmol, 34.0 mg) and 3 M NaOH (3 mL) was heated to reflux for 16 h. After cooling to room temperature, the mixture was washed by water and extracted by CHCl_3 . After dried by anhydrous Na_2SO_4 , the organic layer was concentrated by rotary evaporator. The crude product was purified by column chromatograph on silica gel with the eluent from hexanes to ethyl acetate/hexanes = 1/10 (v/v, gradient). After dried in vacuum, 1.1 g product was obtained, and the yield was 52%. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.22 (s, 1H, H^a), 6.98 (s, 2H, H^b), 3.91 (t, 2H, $J = 5.8$ Hz, H^c), 3.53 (t, 2H, $J = 6.3$ Hz, H^d), 1.79-1.73 (m, 4H, alkyl chain $-CH_2$), 1.46-1.40 (m, 4H, alkyl chain $-CH_2$), 1.34-1.28 (m, 8H, alkyl chain $-CH_2$). ^{13}C NMR (100

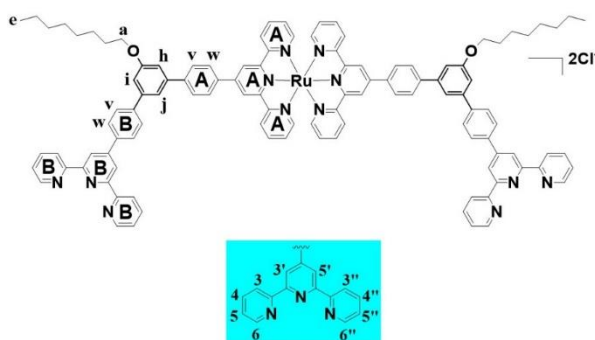
The chemical structure is a complex molecule featuring several fused and linked rings. It includes a central benzene ring with various substituents. A long, zigzag chain with a terminal chlorine atom (Cl) is attached to the central ring via an oxygen atom (O). The chain is labeled 'e' at the chlorine end and 'a' at the oxygen end. The central ring is also labeled with 'h' and 'j'. Other rings include a pyridine ring, a benzene ring, and a pyridine ring. The structure is labeled with various letters and numbers: 'a', 'e', 'h', 'j', 'v', 'w', '3', '3'', '3''', '4', '4'', '5', '5'', '5'''', '6', '6''', '6'''', 'N', 'N', 'N', 'O', 'Cl'. The labels '3', '3'', '3'''', '4', '4'', '5', '5'', '5'''', '6', '6''', '6'''', 'N', 'N', 'N', 'O', 'Cl' are used to identify specific atoms and positions within the rings.



S13

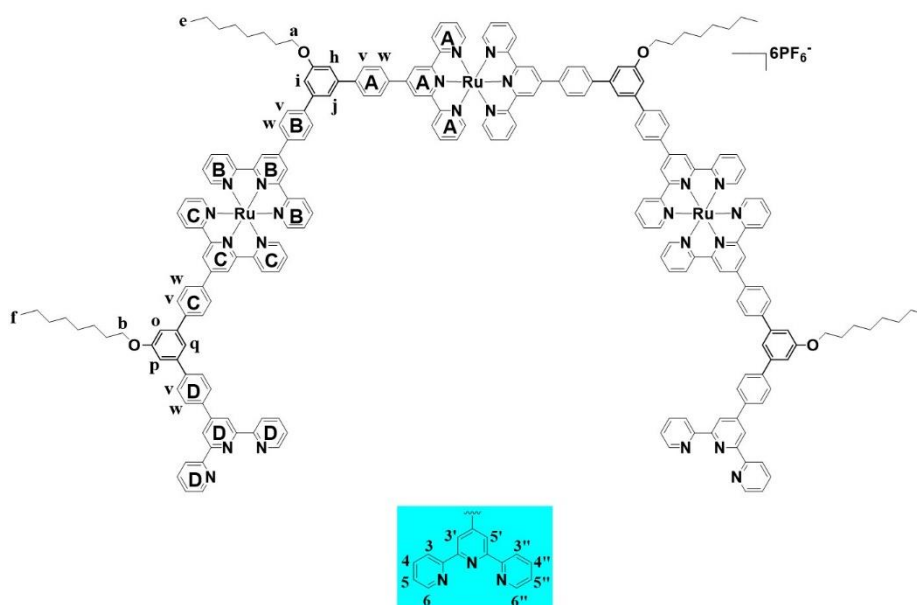
chain $-CH_2$), 1.80-1.74 (m, 2H, alkyl chain $-CH_2$), 1.57-1.50 (m, 2H, alkyl chain $-CH_2$), 1.47-1.38 (m, 4H, alkyl chain $-CH_2$), 1.37-1.30 (m, 6H, alkyl chain $-CH_2$). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 160.19, 156.35, 156.07, 149.89, 149.23, 142.58, 141.90, 137.72, 137.08, 127.93, 127.89, 123.99, 121.56, 118.91, 118.73, 112.81, 68.44, 45.32, 32.79, 29.62, 29.55, 29.53, 29.03, 27.03, 26.25. ESI-MS (m/z): Calcd. for $[C_{58}H_{51}N_6OCl + 2H^+]^{2+}$: 442.20, Found: 442.18; Calcd. for $[C_{58}H_{51}N_6OCl + H^+]^+$: 883.39, Found: 883.49.

Ru(DMSO) $_4$ Cl $_2$. To a 100 mL Schlenk flask, a mixture of $RuCl_3 \cdot xH_2O$ (7.7 mmol, 1.6 g) and DMSO (5 mL) were added and degassed for 20 min. Then 17.5 mL isopropanol was added under N_2 . After heating at 85 °C for 48 h, the mixture was cooled to room temperature. A yellow solid product was obtained after filtering and washing with acetone, toluene and diethyl ether in turn. After dried in vacuum, 2.5 g product was obtained, and the yield was 67%. The product was used directly without further purification.



Compound 5.³ To a 1000 mL round bottom flask, a mixture of compound **2** (1.2 mmol, 1.0 g), $Ru(DMSO)_4Cl_2$ (0.2 mmol, 100.0 mg), 400 mL $CHCl_3$ and 400 mL CH_3OH were added. After refluxing for 18 h, the mixture was cooled to room temperature and concentrated by rotary evaporator. And the crude product was purified by column chromatography on Al_2O_3 with the

eluent from CH₂Cl₂ to CH₂Cl₂/CH₃OH = 100/1.5 (v/v, gradient) to afford a red solid. After dried in vacuum, 223.3 mg product was obtained, and the yield was 60%. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 9.56 (s, 4H, *HA*^{3',5'}), 9.39 (s, 4H, *HA*^{3,3''}), 8.79 (s, 4H, *HB*^{3',5'}), 8.77-8.68 (m, 8H, *HB*^{6,6'',A^w}), 8.63 (d, 4H, *J* = 7.6 Hz, *HB*^{3,3''}), 7.96 (d, 4H, *J* = 7.4 Hz, *HB*^w), 7.89-7.81 (m, 8H, *HA*^{4,4'',B^{4,4''}}), 7.65 (d, 4H, *J* = 5.4 Hz, *HA*^v), 7.58 (d, 4H, *J* = 6.8 Hz, *HB*^v), 7.39-7.33 (m, 4H, *HB*^{5,5''}), 7.28-7.22 (4H, *HA*^{5,5''}), 7.05 (s, 6H, *H^h*, *A*^{6,6''}), 6.91 (s, 2H, *Hⁱ*), 6.86 (s, 2H, *H^j*), 4.02 (t, 4H, *J* = 5.9 Hz, *H^a*), 1.85-1.79 (m, 4H, alkyl chain -CH₂), 1.52-1.46 (m, 4H, alkyl chain -CH₂), 1.40-1.35 (m, 4H, alkyl chain -CH₂), 1.34-1.27 (m, 12H, alkyl chain -CH₂), 0.87 (t, 6H, *J* = 6.5 Hz, *H^e*). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 160.16, 158.15, 155.90, 155.87, 155.24, 151.25, 149.51, 149.03, 148.98, 148.20, 142.24, 142.11, 141.70, 141.48, 138.47, 137.59, 137.42, 137.34, 134.64, 128.91, 128.26, 128.17, 127.84, 126.59, 124.23, 121.76, 118.86, 117.88, 113.10, 112.39, 68.58, 31.98, 29.84, 29.59, 29.44, 26.27, 22.82, 14.26. ESI-MS (*m/z*): Calcd. for [C₁₁₂H₉₆N₁₂O₂RuCl₂ - 2Cl]²⁺: 871.34, Found: 871.34.



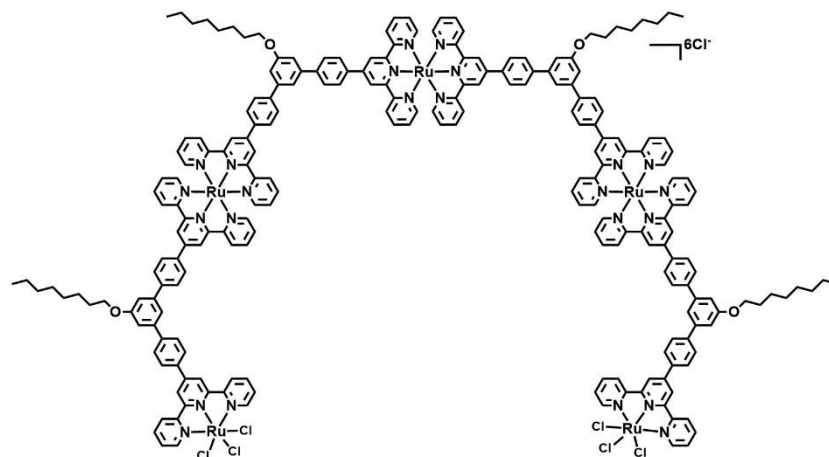
Compound 6.³ To a 1000 mL round bottom flask, a mixture of compound **5** (0.55 mmol, 1.0

S15

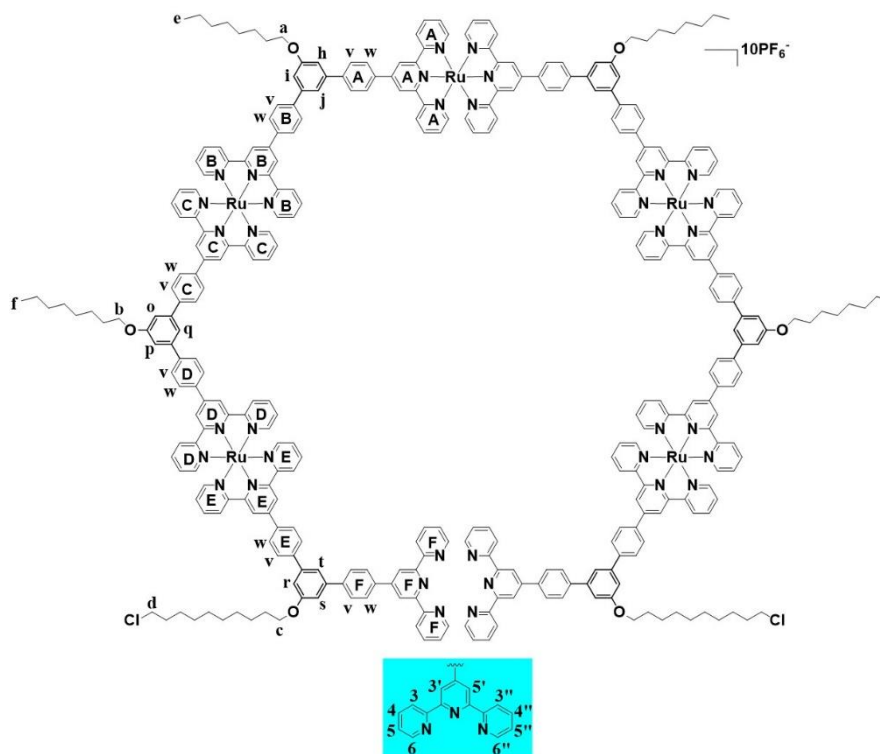
g), Ru(DMSO)₄Cl₂ (0.1 mmol, 48.5 mg), 400 mL CHCl₃ and 400 mL CH₃OH were added. After refluxing for 18 h, the mixture was cooled to room temperature. The solvent was removed by rotary evaporator and the crude product was purified by column chromatography on Al₂O₃ with the eluent from CH₂Cl₂ to CH₂Cl₂/CH₃OH=100/2.5 (v/v, gradient) to afford a red solid. After dried in vacuum, 187.3 mg product was obtained, and the yield was 49%. The counterion was exchanged from Cl⁻ to PF₆⁻ for better solubility before the NMR and MS characterization.

¹H NMR (600 MHz, CD₃CN) δ (ppm) 9.12 (s, 4H, *HA*^{3',5'}), 9.10 (s, 4H, *HB*^{3',5'}), 9.07 (s, 4H, *HC*^{3',5'}), 8.80 (s, 4H, *HD*^{3',5'}), 8.77-8.66 (m, 20H, *HA*^{3,3''}, *B*^{3,3''}, *C*^{3,3''}, *D*^{3,3''}, *D*^{6,6''}), 8.40 (t, 8H, *J* = 7.7 Hz, *HA*^w, *B*^w), 8.35 (d, 4H, *J* = 7.8 Hz, *HC*^w), 8.24-8.18 (m, 8H, *HA*^v, *B*^v), 8.14 (d, 4H, *J* = 7.8 Hz, *HC*^v), 8.05-7.93 (m, 24H, *HA*^{4,4''}, *B*^{4,4''}, *C*^{4,4''}, *D*^{4,4''}, *D*^w, *D*^v), 7.86 (s, 2H, *H*^p), 7.71 (s, 2H, *H*^q), 7.53-7.48 (m, 12H, *HA*^{6,6''}, *B*^{6,6''}, *C*^{6,6''}), 7.48-7.42 (m, 8H, *H*^{h,i}, *D*^{5,5''}), 7.38 (s, 2H, *H*^o), 7.32 (s, 2H, *H*^p), 7.27-7.21 (m, 12H, *HA*^{5,5''}, *B*^{5,5''}, *C*^{5,5''}), 4.30 (t, 4H, *J* = 5.8 Hz, *H*^a), 4.22 (t, 4H, *J* = 6.2 Hz, *H*^b), 1.93-1.89 (m, 4H, alkyl chain -CH₂), 1.89-1.83 (m, 4H, alkyl chain -CH₂), 1.63-1.57 (m, 4H, alkyl chain -CH₂), 1.57-1.52 (m, 4H, alkyl chain -CH₂), 1.49-1.32 (m, 32H, alkyl chain -CH₂), 0.94 (t, 6H, *J* = 6.1 Hz, *H*^e), 0.91 (t, 6H, *J* = 6.4 Hz, *H*^f). ¹³C NMR (150 MHz, CD₃CN) δ (ppm) 161.42, 161.33, 159.21, 159.19, 159.17, 157.22, 157.19, 157.17, 156.68, 156.66, 156.48, 156.46, 156.43, 153.42, 153.40, 150.33, 150.29, 148.63, 148.61, 143.51, 143.19, 142.95, 142.73, 142.72, 142.37, 139.05, 138.54, 138.17, 137.07, 137.04, 136.87, 129.39, 129.38, 129.30, 129.29, 129.28, 129.20, 129.05, 129.03, 129.02, 129.01, 128.50, 128.48, 125.57, 125.27, 125.26, 122.47, 122.43, 122.38, 122.06, 122.05, 119.31, 119.24, 119.23, 119.22, 119.13, 119.12, 114.07, 113.83, 113.65, 69.38, 69.31, 69.29, 32.59, 32.58, 30.09, 30.08, 30.07, 30.03, 30.02, 26.82, 26.80, 23.39, 23.37, 14.39, 14.38. ESI-MS

(*m/z*): Calcd. for $[\text{C}_{224}\text{H}_{192}\text{N}_{24}\text{O}_4\text{Ru}_3\text{P}_6\text{F}_{36} - 6\text{PF}_6^- + \text{H}^+]^{7+}$: 512.61, Found: 512.60; Calcd. for $[\text{C}_{224}\text{H}_{192}\text{N}_{24}\text{O}_4\text{Ru}_3\text{P}_6\text{F}_{36} - 6\text{PF}_6^-]^{6+}$: 597.88, Found: 597.88; Calcd. for $[\text{C}_{224}\text{H}_{192}\text{N}_{24}\text{O}_4\text{Ru}_3\text{P}_6\text{F}_{36} - 5\text{PF}_6^-]^{5+}$: 746.45, Found: 746.44; Calcd. for $[\text{C}_{224}\text{H}_{192}\text{N}_{24}\text{O}_4\text{Ru}_3\text{P}_6\text{F}_{36} - 4\text{PF}_6^-]^{4+}$: 969.30, Found: 969.29.

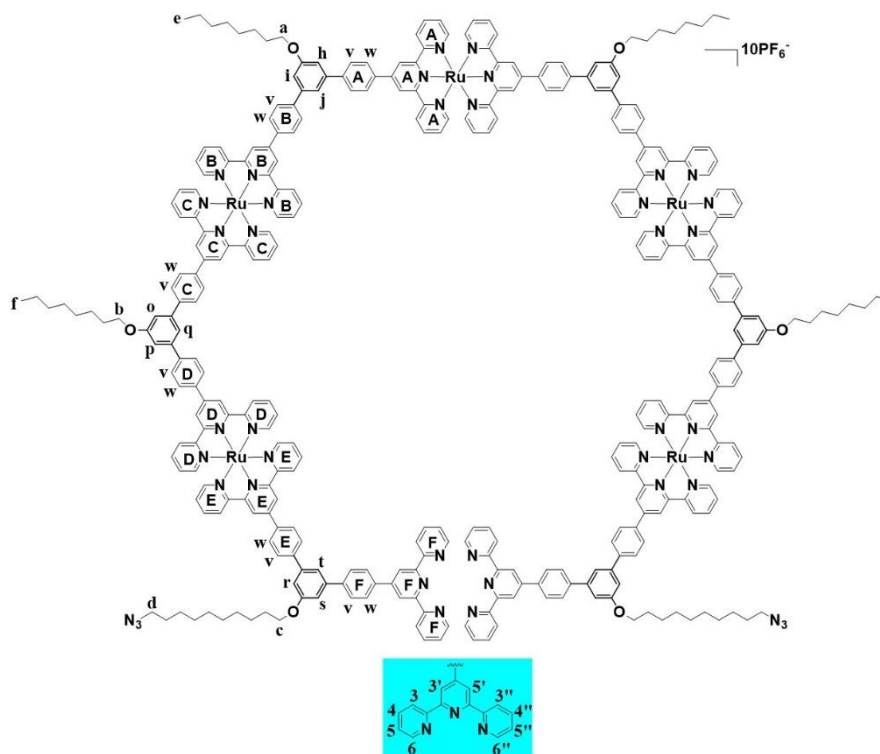


Compound 7.¹ To a 1000 mL round bottom flask, a mixture of compound **6** (0.15 mmol, 570.0 mg), $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.6 mmol, 124.5 mg), 400 mL CHCl_3 and 400 mL CH_3OH was added. After refluxing for 48 h, the mixture was cooled to room temperature. The mixture was concentrated by rotary evaporator and washed by methanol and distilled water, respectively. After dried in vacuum, 300.9 mg product was obtained, and the yield was 48%. Due to the extremely poor solubility, the product was directly used for the following step without further characterization.



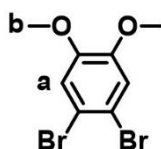
Compound 8.¹ A mixture of compound 4 (0.29 mmol, 256.2 mg), compound 7 (0.07 mmol, 300.9 mg), *N*-ethylmorpholine (2 mL), 400 mL CHCl₃ and 400 mL CH₃OH was added to a 1000 mL round bottom flask. After refluxing for 48 h, the mixture was cooled to room temperature. The mixture was concentrated by rotary evaporator and the crude product was purified by column chromatography on Al₂O₃ with the eluent from CHCl₃ to CHCl₃/CH₃OH = 10/1 (v/v, gradient) to afford a red solid. After dried in vacuum, 189.2 mg product was obtained, and the yield was 46%. The counterion was exchanged from Cl⁻ to PF₆⁻ for better solubility before the NMR and MS characterization. ¹H NMR (600 MHz, CD₃CN) δ (ppm) 9.14-9.10 (m, 20H, *HA*^{3',5'}, *B*^{3',5'}, *C*^{3',5'}, *D*^{3',5'}, *E*^{3',5'}), 8.86 (s, 4H, *HF*^{3',5'}), 8.78-8.68 (m, 28H, *HA*^{3,3''}, *B*^{3,3''}, *C*^{3,3''}, *D*^{3,3''}, *E*^{3,3''}, *F*^{3,3''}, *F*^{6,6''}), 8.42-8.38 (m, 16H, *HA*^w, *B*^w, *C*^w, *D*^w), 8.37 (d, 4H, *J* = 8.0 Hz, *HE*^w), 8.23 (d, 16H, *J* = 7.3 Hz, *HA*^v, *B*^v, *C*^v, *D*^v), 8.18 (d, 4H, *J* = 7.4 Hz, *HE*^v), 8.09 (s, 4H, *HF*^w), 8.03-7.95 (m, 28H, *HA*^{4,4''}, *B*^{4,4''}, *C*^{4,4''}, *D*^{4,4''}, *E*^{4,4''}, *F*^{4,4''}, *F*^v), 7.88 (s, 4H, *H*^{i,q}), 7.77 (s, 2H, *H*^r), 7.51-7.46 (m, 32H, *HA*^{6,6''}, *B*^{6,6''}, *C*^{6,6''}, *D*^{6,6''}, *E*^{6,6''}, *F*^{5,5''}, *h,i,o,p*), 7.42 (s, 2H, *H*^r), 7.39 (s,

$2H, H^f$), 7.25-7.21 (m, 20H, $HA^{5,5''}, B^{5,5''}, C^{5,5''}, D^{5,5''}, E^{5,5''}$), 4.30 (t, 8H, $J = 6.1$ Hz, $H^{a,b}$), 4.25 (t, 4H, $J = 6.4$ Hz, H^e), 3.59 (t, 4H, $J = 6.8$ Hz, H^d), 1.92-1.86 (m, 12H, alkyl chain $-CH_2$), 1.80-1.74 (m, 4H, alkyl chain $-CH_2$), 1.62-1.56 (m, 12H, alkyl chain $-CH_2$), 1.50-1.45 (m, 12H, alkyl chain $-CH_2$), 1.42-1.33 (m, 40H, alkyl chain $-CH_2$), 0.94 (t, 12H, $J = 6.5$ Hz, H^{ef}). ^{13}C NMR (150 MHz, CD_3CN) δ (ppm) 161.43, 159.22, 159.20, 156.48, 156.44, 153.45, 153.43, 153.42, 150.38, 148.66, 148.64, 148.63, 148.62, 148.60, 143.52, 143.50, 143.49, 142.97, 142.96, 142.95, 139.09, 139.06, 139.04, 137.09, 137.07, 129.44, 129.43, 129.37, 129.34, 129.30, 129.21, 128.49, 125.71, 125.45, 122.59, 122.36, 114.07, 69.38, 69.36, 69.29, 69.28, 46.30, 46.27, 33.37, 33.35, 32.58, 30.18, 30.17, 30.10, 30.08, 30.07, 30.02, 30.00, 29.52, 29.51, 27.53, 27.52, 26.81, 26.74, 26.72, 23.38, 14.39. ESI-MS (m/z): Calcd. for $[C_{340}H_{294}N_{36}O_6Ru_5Cl_2P_{10}F_{60} - 10PF_6^-]^{10+}$: 555.58, Found: 555.58; Calcd. for $[C_{340}H_{294}N_{36}O_6Ru_5Cl_2P_{10}F_{60} - 9PF_6^-]^{9+}$: 633.42, Found: 633.42; Calcd. for $[C_{340}H_{294}N_{36}O_6Ru_5Cl_2P_{10}F_{60} - 8PF_6^-]^{8+}$: 730.72, Found: 730.72; Calcd. for $[C_{340}H_{294}N_{36}O_6Ru_5Cl_2P_{10}F_{60} - 7PF_6^-]^{7+}$: 855.82, Found: 855.82; Calcd. for $[C_{340}H_{294}N_{36}O_6Ru_5Cl_2P_{10}F_{60} - 6PF_6^-]^{6+}$: 1022.62, Found: 1022.62; Calcd. for $[C_{340}H_{294}N_{36}O_6Ru_5Cl_2P_{10}F_{60} - 5PF_6^-]^{5+}$: 1256.13, Found: 1256.15.



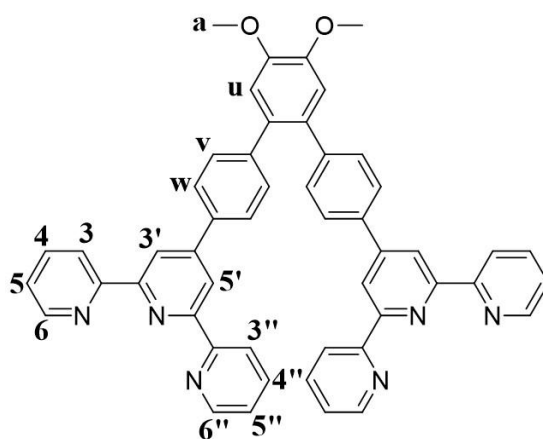
Compound 9 (hexameric monomer, Hex-M).⁴ A mixture of compound **8** (0.02 mmol, 118.2 mg), NaN₃ (1 mmol, 65.0 mg) and DMF (50 mL) was added to a 100 mL round flask and stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was concentrated under reduced pressure. Then the product was washed by distilled water to remove the excess NaN₃ and collected through centrifugation. After dried in vacuum, 69.1 mg product was obtained, and the yield was 58%. The counterion was exchanged from Cl⁻ to PF₆⁻ for better solubility before the NMR and MS characterization. ¹H NMR (600 MHz, CD₃CN) δ (ppm) 9.14-9.10 (m, 20H, *HA*^{3',5'}, *B*^{3',5'}, *C*^{3',5'}, *D*^{3',5'}, *E*^{3',5'}), 8.86 (s, 4H, *HF*^{3',5'}), 8.77-8.70 (m, 28H, *HA*^{3,3''}, *B*^{3,3''}, *C*^{3,3''}, *D*^{3,3''}, *E*^{3,3''}, *F*^{3,3''}, *F*^{6,6''}), 8.42-8.38 (m, 16H, *HA*^w, *B*^w, *C*^w, *D*^w), 8.38 (d, 4H, *J* = 8.3 Hz, *HE*^w), 8.23 (d, 16H, *J* = 7.4 Hz, *HA*^v, *B*^v, *C*^v, *D*^v), 8.19 (d, 4H, *J* = 8.0 Hz, *HE*^v), 8.10 (d, 4H, *J* = 7.9 Hz, *HF*^w), 8.04-7.97 (m, 28H, *HA*^{4,4''}, *B*^{4,4''}, *C*^{4,4''}, *D*^{4,4''}, *E*^{4,4''}, *F*^{4,4''}, *F*^v), 7.88 (s, 4H, *H*^{i,q}), 7.77 (s, 2H, *H*^r), 7.51-7.46 (m, 32H, *HA*^{6,6''}, *B*^{6,6''}, *C*^{6,6''}, *D*^{6,6''}, *E*^{6,6''}, *F*^{5,5''}, *h,i,o,p*), 7.42 (s, 2H, *H*^r), 7.38 (s, 2H, *H*^s), 7.25-7.20 (m, 20H, *HA*^{5,5''}, *B*^{5,5''}, *C*^{5,5''}, *D*^{5,5''}, *E*^{5,5''}), 4.30 (t, 8H, *J* = 6.2 Hz,

$H^{a,b}$), 4.25 (t, 4H, $J = 6.5$ Hz, H^c), 3.28 (t, 4H, $J = 7.0$ Hz, H^d), 1.92-1.86 (m, 12H, alkyl chain $-CH_2$), 1.61-1.55 (m, 16H, alkyl chain $-CH_2$), 1.50-1.45 (m, 12H, alkyl chain $-CH_2$), 1.42-1.35 (m, 40H, alkyl chain $-CH_2$), 0.94 (t, 12H, $J = 6.5$ Hz, $H^{e,f}$). ^{13}C NMR (150 MHz, CD_3CN) δ (ppm) 161.43, 161.37, 159.21, 159.20, 157.20, 156.67, 156.48, 153.42, 150.32, 148.63, 143.52, 142.96, 142.77, 139.05, 138.19, 137.08, 136.92, 129.39, 129.29, 129.21, 129.08, 128.49, 125.58, 125.29, 122.47, 122.06, 119.30, 114.09, 113.88, 113.66, 69.38, 69.28, 52.10, 32.59, 30.17, 30.12, 30.08, 30.03, 30.00, 29.79, 29.43, 29.31, 27.38, 26.81, 26.72, 23.38, 14.39. ESI-MS (m/z): Calcd. for $[\text{C}_{340}\text{H}_{294}\text{N}_{42}\text{O}_6\text{Ru}_5\text{P}_{10}\text{F}_{60} - 10\text{PF}_6]^{10+}$: 556.99, Found: 556.99; Calcd. for $[\text{C}_{340}\text{H}_{294}\text{N}_{42}\text{O}_6\text{Ru}_5\text{P}_{10}\text{F}_{60} - 9\text{PF}_6]^{9+}$: 634.99, Found: 634.99; Calcd. for $[\text{C}_{340}\text{H}_{294}\text{N}_{42}\text{O}_6\text{Ru}_5\text{P}_{10}\text{F}_{60} - 8\text{PF}_6]^{8+}$: 732.48, Found: 732.49; Calcd. for $[\text{C}_{340}\text{H}_{294}\text{N}_{42}\text{O}_6\text{Ru}_5\text{P}_{10}\text{F}_{60} - 7\text{PF}_6]^{7+}$: 857.83, Found: 857.84; Calcd. for $[\text{C}_{340}\text{H}_{294}\text{N}_{42}\text{O}_6\text{Ru}_5\text{P}_{10}\text{F}_{60} - 6\text{PF}_6]^{6+}$: 1024.96, Found: 1024.97.



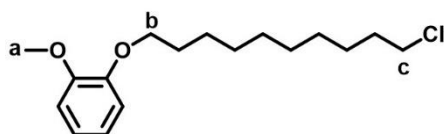
Compound 10.⁵⁻⁶ A mixture of 1,2-dimethoxybenzene (0.12 mol, 16.6 g) and I_2 (catalytic amount) was dissolved in CH_2Cl_2 (300 mL) to a 1000 mL round flask. Liquid bromine (0.28 mol, 44.1 g) was dissolved in 100 mL CH_2Cl_2 to a 125 mL constant pressure funnel. Under 0 $^\circ\text{C}$, liquid bromine solution was added into the round flask drop by drop. After it finished, the temperature was returned to room temperature gradually. Then the mixture was stirred under room temperature for another 12 hours. The reaction was quenched by the aqueous solution of sodium sulfite. And the product was extracted by CHCl_3 . Subsequently, the organic phase was

washed by distilled water and dried by anhydrous Na₂SO₄. After filtration, the filtrate was concentrated by rotary evaporator. Then, 300 mL isopropanol was added into the mixture. The mixture was kept at -20 °C for 24 hours to afford a white crystal. After dried in vacuum, 18.4 g product was obtained, and the yield was 51%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.06 (s, 2H, *H^a*), 3.86 (s, 6H, *H^b*). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 148.68, 115.69, 114.54, 56.10.

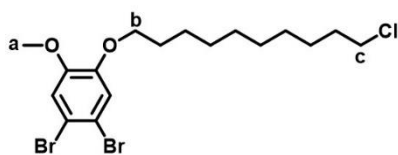


Compound 11.^{1, 5} A mixture of compound **10** (0.02 mol, 5.9 g), 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (0.06 mol, 21.2 g), Na₂CO₃ (0.24 mol, 25.4 g) and Pd(PPh₃)₂Cl₂ (2.4 mmol, 1.7 g) was added into 500 mL Schlenk flask and degassed for three times. Under N₂ atmosphere, 200 mL toluene, 40 mL *tert*-butyl alcohol and 100 mL H₂O were added. The mixture was stirred at 85 °C for 48 h. After cooling to room temperature, the mixture was poured into 300 mL H₂O and extracted with CHCl₃. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and then concentrated by rotary evaporator. The crude product was purified by column chromatography on silica gel with the eluent from CH₂Cl₂ to CH₂Cl₂/CH₃OH = 100/1 (v/v, gradient) to afford a white solid. After dried in vacuum, 7.5 g product was obtained, and the yield was 50%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.74 (s, 4H, *H^{3',5'}*), 8.68 (d, 4H, *J* = 4.2 Hz, *H^{6,6''}*), 8.65 (d, 4H, *J* = 7.9 Hz, *H^{3,3''}*), 7.87-7.80 (m, 8H, *H^w*,

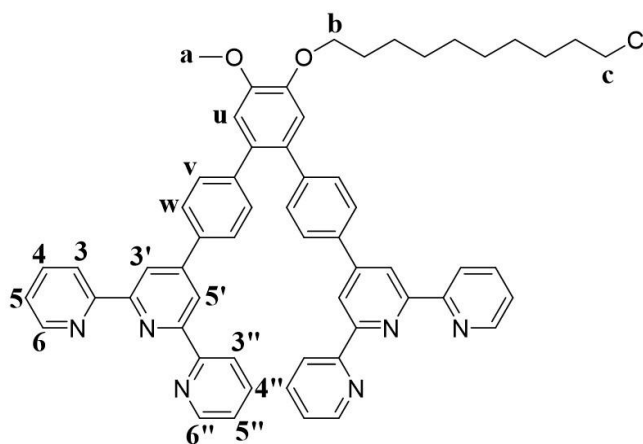
^{4,4''}), 7.35-7.29 (m, 8H, *H^{v,5,5''}*), 7.03 (s, 2H, *H^u*), 4.01 (s, 6H, *H^a*). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 156.41, 155.99, 149.85, 149.20, 148.66, 142.33, 136.89, 136.49, 132.63, 130.61, 127.16, 123.83, 121.42, 118.87, 113.82, 56.30. ESI-MS (*m/z*): Calcd. for [C₅₀H₃₆N₆O₂ + 2H⁺]²⁺: 377.15, Found: 377.15; Calcd. for [C₅₀H₃₆N₆O₂ + H⁺]⁺: 753.30, Found: 753.30.



Compound 12.² A two-phase mixture of 2-methoxyphenol (20 mmol, 2.5 g), 1,10-dichlorodecane (40 mmol, 8.5 g), tetrabutylammonium hydrogen sulfate (IPC-TBA-HS, 1 mmol, 340 mg) and 3 M NaOH (15 mL) was heated to reflux for 16 h. After cooling to room temperature, the mixture was washed by water and extracted by CHCl₃. After dried by anhydrous Na₂SO₄, the organic layer was concentrated by rotary evaporator. The crude product was purified by column chromatograph on silica gel with the eluent from hexanes to ethyl acetate/hexanes = 1/10 (v/v, gradient). After dried in vacuum, 5.0 g product was obtained, and the yield was 83%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.89 (s, 4H, aromatic region -*H*), 4.01 (t, 2H, *J* = 6.9 Hz, *H^b*), 3.86 (s, 3H, *H^a*), 3.53 (t, 2H, *J* = 6.9 Hz, *H^c*), 1.86-1.74 (m, 4H, alkyl chain -*CH*₂), 1.48-1.40 (m, 4H, alkyl chain -*CH*₂), 1.35-1.28 (m, 8H, alkyl chain -*CH*₂). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 149.51, 148.66, 120.88, 120.86, 113.16, 111.91, 69.01, 55.99, 45.20, 32.70, 29.49, 29.44, 29.41, 29.27, 28.92, 26.93, 26.02.



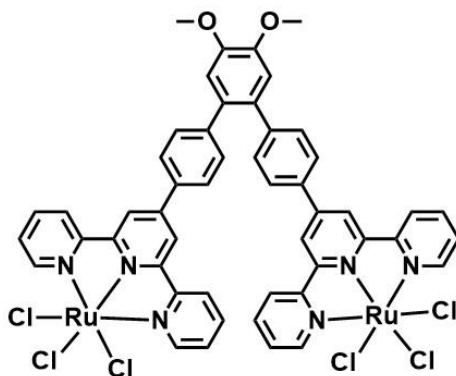
Compound 13.⁵⁻⁶ A mixture of compound **12** (16.4 mmol, 4.9 g) and I₂ (catalytic amount) was dissolved in CHCl₃ (200 mL) to a 500 mL round flask. Liquid bromine (32.8 mmol, 5.2 g) was dissolved in 100 mL CHCl₃ to a 125 mL constant pressure funnel. Under 0 °C, liquid bromine solution was added into the round flask drop by drop. After it finished, the temperature was returned to room temperature gradually. Then the mixture was stirred under room temperature for another 12 hours. The reaction was quenched by the aqueous solution of sodium sulfite. And the product was extracted by CHCl₃. Subsequently, the organic phase was washed by distilled water and dried by anhydrous Na₂SO₄. After filtration, the filtrate was concentrated by rotary evaporator. After dried in vacuum, the product was used directly for the following step without further purification. And the yield was 98% (7.3 g). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.05 (d, 2H, *J* = 1.2 Hz, aromatic region -*H*), 3.95 (t, 2H, *J* = 6.8 Hz, *H*^b), 3.83 (s, 3H, *H*^a), 3.53 (t, 2H, *J* = 6.8 Hz, *H*^c), 1.84-1.75 (m, 4H, alkyl chain -CH₂), 1.46-1.40 (m, 4H, alkyl chain -CH₂), 1.34-1.28 (m, 8H, alkyl chain -CH₂). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 149.37, 148.61, 117.39, 116.35, 114.79, 114.66, 69.53, 56.42, 45.25, 32.72, 29.48, 29.45, 29.35, 29.03, 28.95, 26.96, 25.94.



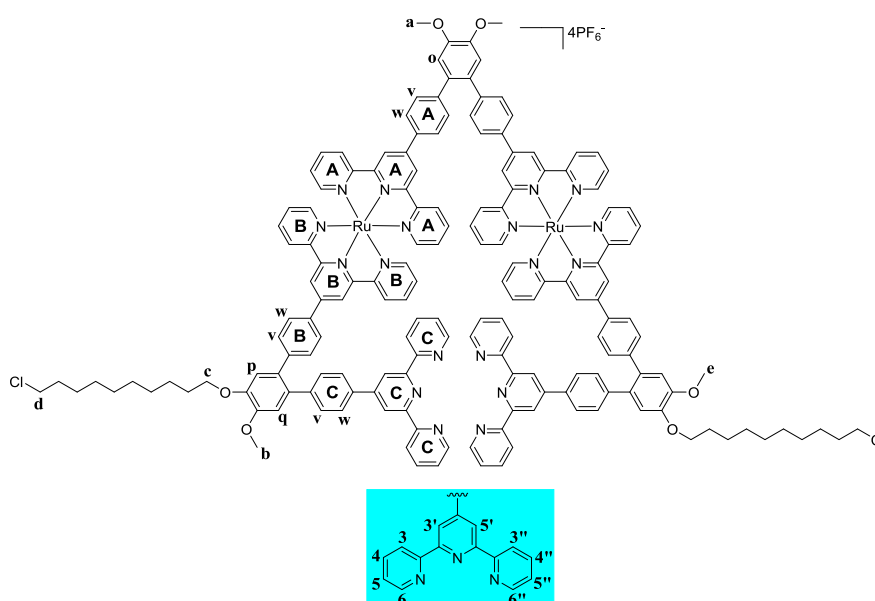
Compound 14.¹ A mixture of compound **13** (15 mmol, 6.9 g), 4'-(4-boronatophenyl)-2,2':6',2''-

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terpyridine (60 mmol, 21.2 g), Na₂CO₃ (180 mmol, 19.1 g) and Pd(PPh₃)₂Cl₂ (1.8 mmol, 1.3 g) was added into 500 mL Schlenk flask and degassed for three times. Under N₂ atmosphere, 200 mL toluene, 40 mL *tert*-butyl alcohol and 100 mL H₂O were added. The mixture was stirred at 85 °C for 48 h. After cooling to room temperature, the mixture was poured into 300 mL H₂O and extracted with CHCl₃. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and then concentrated by rotary evaporator. The crude product was purified by column chromatography on silica gel with the eluent from CH₂Cl₂ to CH₂Cl₂/CH₃OH = 100/1 (v/v, gradient) to afford a white solid. After dried in vacuum, 7.2 g product was obtained, and the yield was 53%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.74 (s, 4H, *H*^{3',5'}), 8.68 (d, 4H, *J* = 4.4 Hz, *H*^{6,6''}), 8.65 (d, 4H, *J* = 8.0 Hz, *H*^{3,3''}), 7.87-7.80 (m, 8H, *H*^{w, 4,4''}), 7.35-7.28 (m, 8H, *H*^{v, 5,5''}), 7.03 (s, 2H, *H*^u), 4.14 (t, 2H, *J* = 6.8 Hz, *H*^b), 3.99 (s, 3H, *H*^a), 3.53 (t, 2H, *J* = 6.8 Hz, *H*^c), 1.96-1.88 (m, 2H, alkyl chain -CH₂), 1.82-1.73 (m, 2H, alkyl chain -CH₂), 1.58-1.48 (m, 2H, alkyl chain -CH₂), 1.45-1.30 (m, 10H, alkyl chain -CH₂). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 156.27, 155.88, 149.70, 149.08, 148.99, 148.20, 142.32, 136.77, 136.34, 132.52, 132.45, 130.55, 127.05, 123.73, 121.30, 118.73, 115.33, 114.18, 69.32, 56.32, 45.22, 32.68, 29.49, 29.43, 29.40, 29.29, 28.91, 26.92, 26.04. ESI-MS (*m/z*): Calcd. for [C₅₉H₅₃N₆O₂Cl + 2H⁺]²⁺: 457.20, Found: 457.20; Calcd. for [C₅₉H₅₃N₆O₂Cl + H⁺]⁺: 913.40, Found: 913.41.

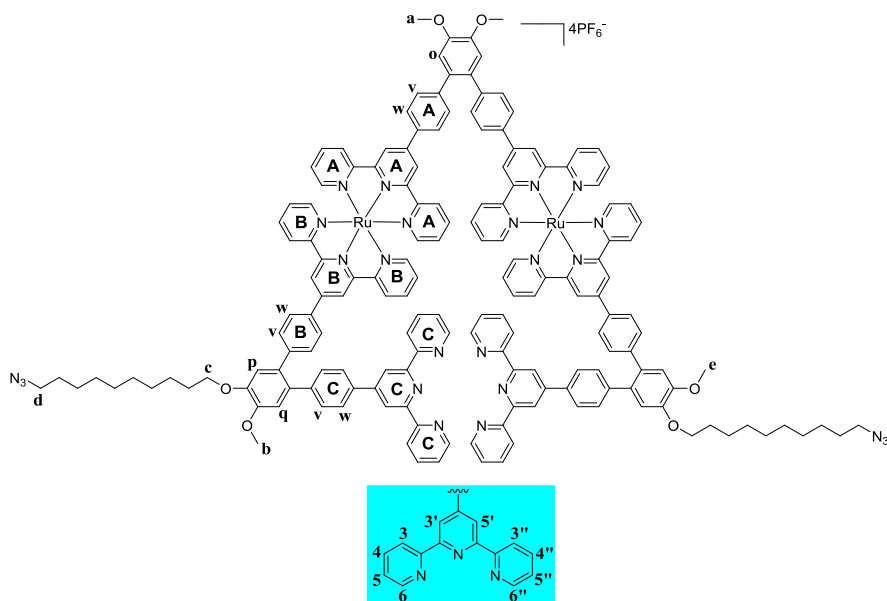


Compound 15.¹ To a 1000 mL round bottom flask, a mixture of compound **11** (0.66 mmol, 500.0 mg), $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (2.89 mmol, 600.0 mg), 400 mL CHCl_3 and 400 mL CH_3OH was added. After refluxing for 48 h, the mixture was cooled to room temperature. The mixture was concentrated by rotary evaporator and washed by methanol and distilled water, respectively. After dried in vacuum, 467.1 mg product was obtained, and the yield was 60%. Due to the extremely poor solubility, the product was directly used for the following step without further characterization.



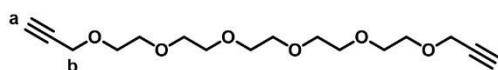
Compound 16.¹ A mixture of compound **15** (0.43 mmol, 0.50 g), compound **14** (2.55 mmol, 2.33 g), *N*-ethylmorpholine (4 mL), 400 mL CHCl_3 and 400 mL CH_3OH was added to a 1000

mL round bottom flask. After refluxing for 48 h, the mixture was cooled to room temperature. The mixture was concentrated by rotary evaporator and the crude product was purified by column chromatography on Al₂O₃ with the eluent from CHCl₃ to CHCl₃/CH₃OH = 100/2.5 (v/v, gradient) to afford a red solid. After dried in vacuum, 0.64 g product was obtained, and the yield was 52%. The counterion was exchanged from Cl⁻ to PF₆⁻ for better solubility before the NMR and MS characterization. ¹H NMR (400 MHz, CD₃CN) δ (ppm) 9.01 (s, 4H, *HA*^{3',5'}), 8.98 (s, 4H, *HB*^{3',5'}), 8.75 (s, 4H, *HC*^{3',5'}), 8.70-8.65 (m, 8H, *HC*^{3,3''}, *C*^{6,6''}), 8.65-8.58 (m, 8H, *HA*^{3,3''}, *B*^{3,3''}), 8.19 (d, 4H, *J* = 8.3 Hz, *HA*^w), 8.13 (d, 4H, *J* = 7.3 Hz, *HB*^w), 7.97-7.91 (m, 4H, *HC*^{4,4''}), 7.90-7.82 (m, 12H, *HA*^{4,4''}, *B*^{4,4''}, *C*^w), 7.69 (d, 4H, *J* = 8.3 Hz, *HA*^v), 7.63-7.56 (m, 4H, *HB*^v), 7.50-7.45 (m, 4H, *HC*^v), 7.43-7.37 (m, 12H, *HC*^{5,5''}, *A*^{6,6''}, *B*^{6,6''}), 7.21 (s, 2H, *H*^o), 7.17 (d, 2H, *J* = 3.8 Hz, *H*^q), 7.15-7.09 (m, 10H, *HP*, *A*^{5,5''}, *B*^{5,5''}), 4.21-4.11 (m, 4H, *H*^c), 4.01 (s, 6H, *H*^a), 3.98 (s, 3H, *H*^e), 3.95 (s, 3H, *H*^b), 3.58 (t, 4H, *J* = 6.7 Hz, *H*^d), 1.89-1.83 (m, 4H, alkyl chain -CH₂), 1.79-1.71 (m, 4H, alkyl chain -CH₂), 1.58-1.48 (m, 4H, alkyl chain -CH₂), 1.47-1.39 (m, 8H, alkyl chain -CH₂), 1.38-1.32 (m, 12H, alkyl chain -CH₂). ¹³C NMR (150 MHz, CD₃CN) δ (ppm) 159.11, 157.12, 156.58, 156.39, 156.35, 153.37, 153.30, 150.33, 150.31, 150.27, 150.22, 150.17, 150.11, 149.52, 149.37, 148.52, 148.49, 144.87, 144.79, 143.59, 143.58, 138.92, 138.90, 138.16, 137.20, 135.69, 135.39, 133.34, 133.27, 132.92, 132.81, 132.71, 132.28, 132.24, 131.98, 128.39, 128.35, 128.22, 128.20, 127.57, 125.48, 125.44, 125.22, 122.19, 122.14, 121.96, 119.04, 116.41, 116.25, 115.39, 115.36, 115.30, 69.96, 69.84, 56.76, 56.74, 56.66, 46.28, 46.26, 33.35, 30.14, 30.08, 30.03, 29.98, 29.96, 29.49, 27.50, 26.72, 26.69. ESI-MS (*m/z*): Calcd. for [C₁₆₈H₁₄₂N₁₈O₆Ru₂Cl₂P₄F₂₄ - 4PF₆]⁴⁺: 695.22, Found: 695.22; Calcd. for [C₁₆₈H₁₄₂N₁₈O₆Ru₂Cl₂P₄F₂₄ - 3PF₆]³⁺: 975.28, Found: 975.29.



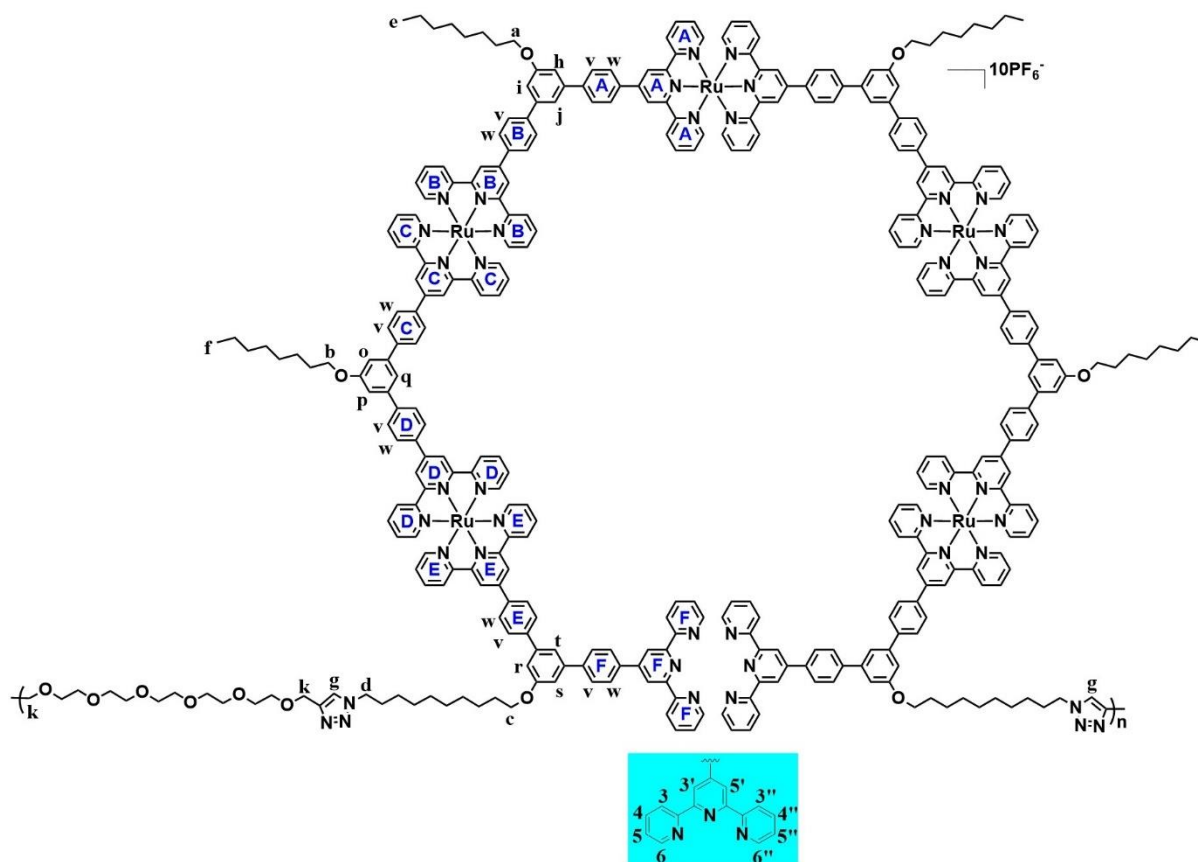
Compound 17 (trimeric monomer, Tri-M).⁴ A mixture of compound **16** (0.22 mmol, 0.64 g), NaN₃ (7.69 mmol, 0.50 g) and DMF (100 mL) was added to a 200 mL round flask and stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was concentrated under reduced pressure. Then the product was washed by distilled water to remove the excess NaN₃ and collected through centrifugation. After dried in vacuum, 0.49 g product was obtained, and the yield was 77%. The counterion was exchanged from Cl⁻ to PF₆⁻ for better solubility before the NMR and MS characterization. ¹H NMR (400 MHz, CD₃CN) δ (ppm) 9.01 (s, 4H, *HA*^{3',5'}), 8.98 (s, 4H, *HB*^{3',5'}), 8.75 (s, 4H, *HC*^{3',5'}), 8.69-8.66 (m, 8H, *HC*^{3,3''}, *C*^{6,6''}), 8.65-8.58 (m, 8H, *HA*^{3,3''}, *B*^{3,3''}), 8.19 (d, 4H, *J* = 8.3 Hz, *HA*^w), 8.13 (d, 4H, *J* = 7.3 Hz, *HB*^w), 7.97-7.92 (m, 4H, *HC*^{4,4''}), 7.90-7.82 (m, 12H, *HA*^{4,4''}, *B*^{4,4''}, *C*^w), 7.69 (d, 4H, *J* = 8.3 Hz, *HA*^v), 7.63-7.55 (m, 4H, *HB*^v), 7.51-7.45 (m, 4H, *HC*^v), 7.43-7.37 (m, 12H, *HC*^{5,5''}, *A*^{6,6''}, *B*^{6,6''}), 7.21 (s, 2H, *H*^o), 7.17 (d, 2H, *J* = 3.8 Hz, *H*^q), 7.16-7.09 (m, 10H, *H*^p, *A*^{5,5''}, *B*^{5,5''}), 4.22-4.12 (m, 4H, *H*^e), 4.01 (s, 6H, *H*^a), 3.98 (s, 3H, *H*^e), 3.96 (s, 3H, *H*^b), 3.28 (t, 4H, *J* = 6.7 Hz, *H*^d), 1.89-1.83 (m, 4H, alkyl chain -CH₂), 1.61-1.47 (m, 8H, alkyl chain -CH₂), 1.44-1.32 (m, 20H, alkyl chain -CH₂). ¹³C NMR

(150 MHz, CD₃CN) δ (ppm) 159.11, 157.14, 156.59, 156.39, 156.36, 153.38, 153.30, 150.35, 150.33, 150.29, 150.23, 150.17, 150.12, 149.53, 149.37, 148.55, 148.53, 148.48, 144.88, 144.80, 143.60, 143.59, 138.93, 138.90, 138.16, 137.23, 137.21, 135.69, 135.40, 135.39, 133.35, 133.28, 132.92, 132.81, 132.71, 132.28, 132.24, 131.98, 128.39, 128.36, 128.35, 128.22, 128.20, 127.60, 127.58, 125.48, 125.45, 125.22, 122.19, 122.15, 122.13, 121.95, 119.05, 116.42, 116.27, 115.40, 115.37, 115.31, 69.97, 69.85, 56.76, 56.74, 56.67, 52.10, 30.14, 30.10, 30.03, 29.99, 29.96, 29.77, 29.43, 27.36, 26.73, 26.69. ESI-MS (m/z): Calcd. for [C₁₆₈H₁₄₂N₂₄O₆Ru₂P₄F₂₄ - 4PF₆]⁴⁺: 698.74, Found: 698.75; Calcd. for [C₁₆₈H₁₄₂N₂₄O₆Ru₂P₄F₂₄ - 3PF₆]³⁺: 979.98, Found: 979.98.



Compound 18 (Alkyne-PEG).⁷ A solution of propargyl bromide in toluene (80% by weight) (20 mmol) was added to a mixture of pentaethylene glycol (2 mmol, 0.48 g) and NaOH (20 mmol, 0.80 g) in THF (30 mL). The mixture was heated at 60 °C for 24 h under ambient atmosphere. Then, the mixture was washed by 1 M NH₄Cl (100 mL) and extracted by ethyl acetate. The combined organic phase was washed by brine and distilled water. After dried by anhydrous Na₂SO₄, the solvent was concentrated by rotary evaporator, and the crude product was purified by column chromatography on silica gel with the eluent from CHCl₃ to CHCl₃/CH₃OH = 20/1 (v/v, gradient). After being dried in vacuum, 0.38 g product was obtained, and the yield was 60%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 4.21 (d, 4H, J = 2.2 Hz, HA^b), 3.75-3.60 (m, 20H, -OCH₂), 2.43 (t, 2H, J = 2.0 Hz, HA^a). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 79.74, 74.68, 70.68, 70.64, 70.55, 70.47, 69.19, 58.49. ESI-MS (m/z): Calcd. for [C₁₆H₂₆O₆ +

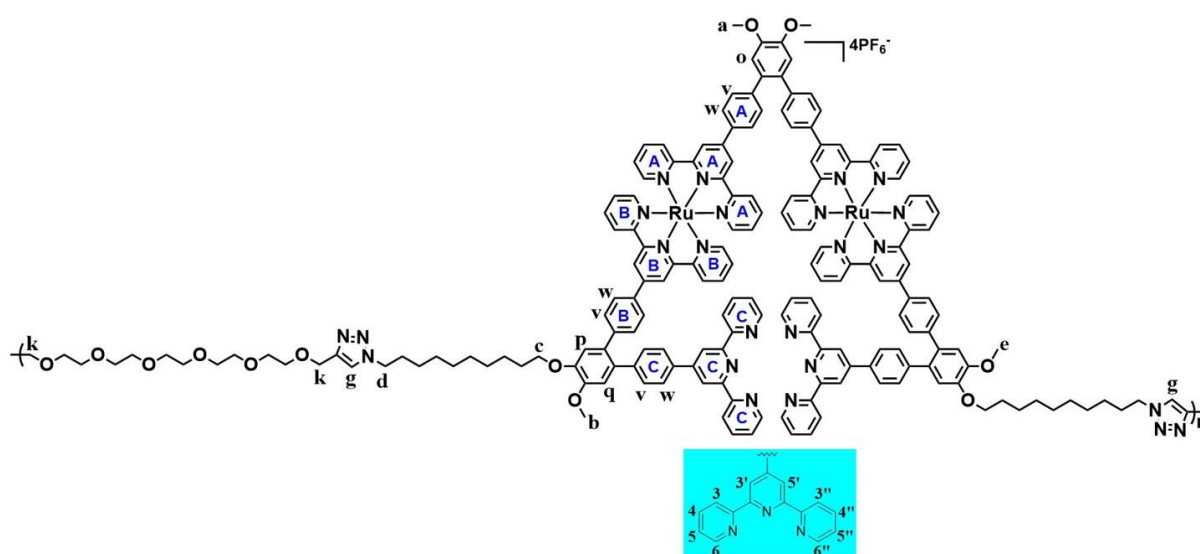
$\text{Na}^+]$: 337.16, Found: 337.18.



Compound 19 (metallo-polymer with hexameric repeat unit, Hex-P). A mixture of hexameric monomer (Compound 9, **Hex-M**) (30.0 mg, 5.1×10^{-3} mmol), alkyne-terminated pentaethylene glycol (Compound 18, **Alkyne-PEG**) (1.6 mg, 5.1×10^{-3} mmol), PMDETA (0.1 mmol, 17.3 mg) and DMF (1 mL, DMF was purified by distillation under reduced pressure) was added to a 25 mL Schlenk flask. The flask underwent three freeze/pump/thaw cycles. Upon an additional freeze, CuBr (0.1 mmol, 14.3 mg, CuBr was washed several times before use with a mixture of water and acetic acid) was added to the frozen mixture. Then another three freeze/pump/thaw cycles were undergoing. Subsequently, the reaction mixture was stirred at 100 °C for 48 h. After that, the mixture was exposed to O₂, 1 mL PMDETA and 5 mL DMF were added. Then the mixture was stirred for another 24 h at 100 °C to remove the Cu ions.

After that, the mixture was poured into a solution of excess NH_4PF_6 in methanol to exchange the counterion from Cl^- to PF_6^- . A dark red precipitate was formed, and the solution turned blue. Then, the precipitate was collected through centrifugation and washed by fresh methanol repeatedly. After being dried in vacuum, 33.4 mg product was obtained, and the yield was 90%.

^1H NMR (600 MHz, CD_3CN) δ (ppm) 9.17-9.08 (m, 20H, $HA^{3',5'}, B^{3',5'}, C^{3',5'}, D^{3',5'}, E^{3',5'}$), 8.90-8.68 (m, 32H, $HA^{3,3'}, B^{3,3'}, C^{3,3'}, D^{3,3'}, E^{3,3'}, F^{3,3'}, F^{6,6'}, F^{3',5'}$), 8.43-8.36 (m, 20H, HA^w, B^w, C^w, D^w, E^w), 8.25-8.17 (m, 20H, HA^v, B^v, C^v, D^v, E^v), 8.08-7.93 (m, 32H, $HA^{4,4'}, B^{4,4'}, C^{4,4'}, D^{4,4'}, E^{4,4'}, F^v, F^w$), 7.88 (s, 4H, $H^{i,q}$), 7.78 (s, 2H, H^i), 7.72 (s, 2H, H^s), 7.51-7.38 (m, 36H, $HA^{6,6'}, B^{6,6'}, C^{6,6'}, D^{6,6'}, E^{6,6'}, F^{5,5'}, h,i,o,p,r,s$), 7.26-7.20 (m, 20H, $HA^{5,5'}, B^{5,5'}, C^{5,5'}, D^{5,5'}, E^{5,5'}$), 4.68-4.43 (m, 4H, H^d), 4.41-4.10 (m, 16H, $H^{a,b,c,k}$), 3.58-3.44 (m, 20H, ether chain $-\text{OCH}_2\text{CH}_2\text{O}-$), 1.89-1.77 (m, 12H, alkyl chain $-\text{CH}_2$), 1.66-1.53 (m, 16H, alkyl chain $-\text{CH}_2$), 1.51-1.45 (m, 12H, alkyl chain $-\text{CH}_2$), 1.45-1.33 (m, 40H, alkyl chain $-\text{CH}_2$), 0.94 (t, 12H, $J = 6.5$ Hz, $H^{e,f}$).



Compound 20 (metallo-polymer with trimeric repeat unit, Tri-P). A mixture of trimeric

monomer (Compound **17**, **Tri-M**) (30.0 mg, 10.2×10^{-3} mmol), alkyne-terminated pentaethylene glycol (Compound **18**, **Alkyne-PEG**) (3.2 mg, 10.2×10^{-3} mmol), PMDETA (0.1 mmol, 17.3 mg) and DMF (0.5 mL, DMF was purified by distillation under reduced pressure) was added to a 25 mL Schlenk flask. The flask underwent three freeze/pump/thaw cycles. Upon an additional freeze, CuBr (0.1 mmol, 14.3 mg, CuBr was washed several times before use with a mixture of water and acetic acid) was added to the frozen mixture. Then another three freeze/pump/thaw cycles were undergoing. Subsequently, the reaction mixture was stirred at 100 °C for 48 h. After that, the mixture was exposed to O₂, 1 mL PMDETA and 5 mL DMF were added. Then the mixture was stirred for another 24 h at 100 °C to remove the Cu ions. After that, the mixture was poured into a solution of excess NH₄PF₆ in methanol to exchange the counterion from Cl⁻ to PF₆⁻. A dark red precipitate was formed, and the solution turned blue. Then, the precipitate was collected through centrifugation and washed by fresh methanol repeatedly. After being dried in vacuum, 34.7 mg product was obtained, and the yield was 92%. ¹H NMR (400 MHz, CD₃CN) δ (ppm) 9.06-8.91 (m, 8H, *HA*^{3',5'}, *B*^{3',5'}), 8.87-8.37 (m, 20H, *HA*^{3,3''}, *B*^{3,3''}, *C*^{3,3''}, *C*^{3',5'}, *C*^{6,6''}), 8.23-8.15 (m, 4H, *HA*^w), 8.14-8.05 (m, 4H, *HB*^w), 8.02-7.75 (m, 16H, *HA*^{4,4''}, *B*^{4,4''}, *C*^{4,4''}, *C*^w), 7.72-7.64 (m, 6H, *HA*^{v,g}), 7.60-7.51 (m, 4H, *HB*^v), 7.49-7.32 (m, 16H, *HC*^v, *C*^{5,5''}, *A*^{6,6''}, *B*^{6,6''}), 7.23-7.05 (m, 14H, *H*^{o,q,p}, *A*^{5,5''}, *B*^{5,5''}), 4.56-4.45 (m, 4H, *H*^d), 4.33-4.22 (m, 4H, *H*^c), 4.14-3.88 (m, 16H, *H*^{k,a,b,e}), 3.56-3.45 (m, 20H, ether chain -OCH₂CH₂O-), 1.86-1.75 (m, 4H, alkyl chain -CH₂), 1.38-1.19 (m, 28H, alkyl chain -CH₂).

Coordination with Fe(II). A general experimental procedure for the coordination with Fe(II) is given below: in a 150 mL heavy-wall pressure vessel, 5 mg metallo-polymers (**Hex-P** or **Tri-**

M) dissolved in a mixed solvents of 1 mL DMSO and 20 mL CH₃CN and equivalent FeSO₄•7H₂O dissolved in 4 mL CH₃OH were added. The mixture was stirred at 80 °C for 8 h and then cooled to room temperature. Upon addition of excess NH₄PF₆ (100 mg) in CH₃OH, a dark red-brown precipitate was formed. Then, the precipitate was collected through centrifugation, washed by fresh CH₃OH repeatedly and dried in vacuum. The yield was 94% for hexagonal system and 91% for triangular system, respectively.

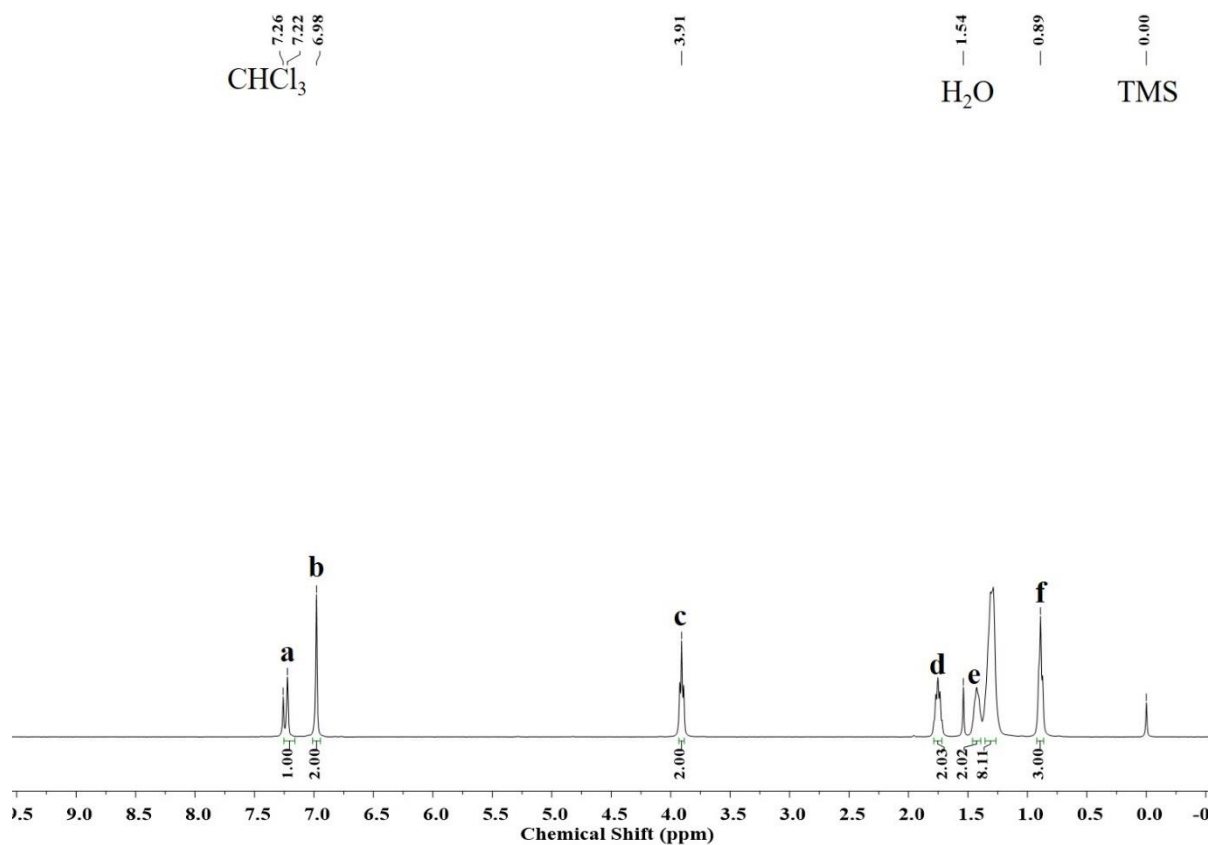


Figure S1. ¹H NMR (400 MHz, CDCl₃) spectrum of compound **1**.

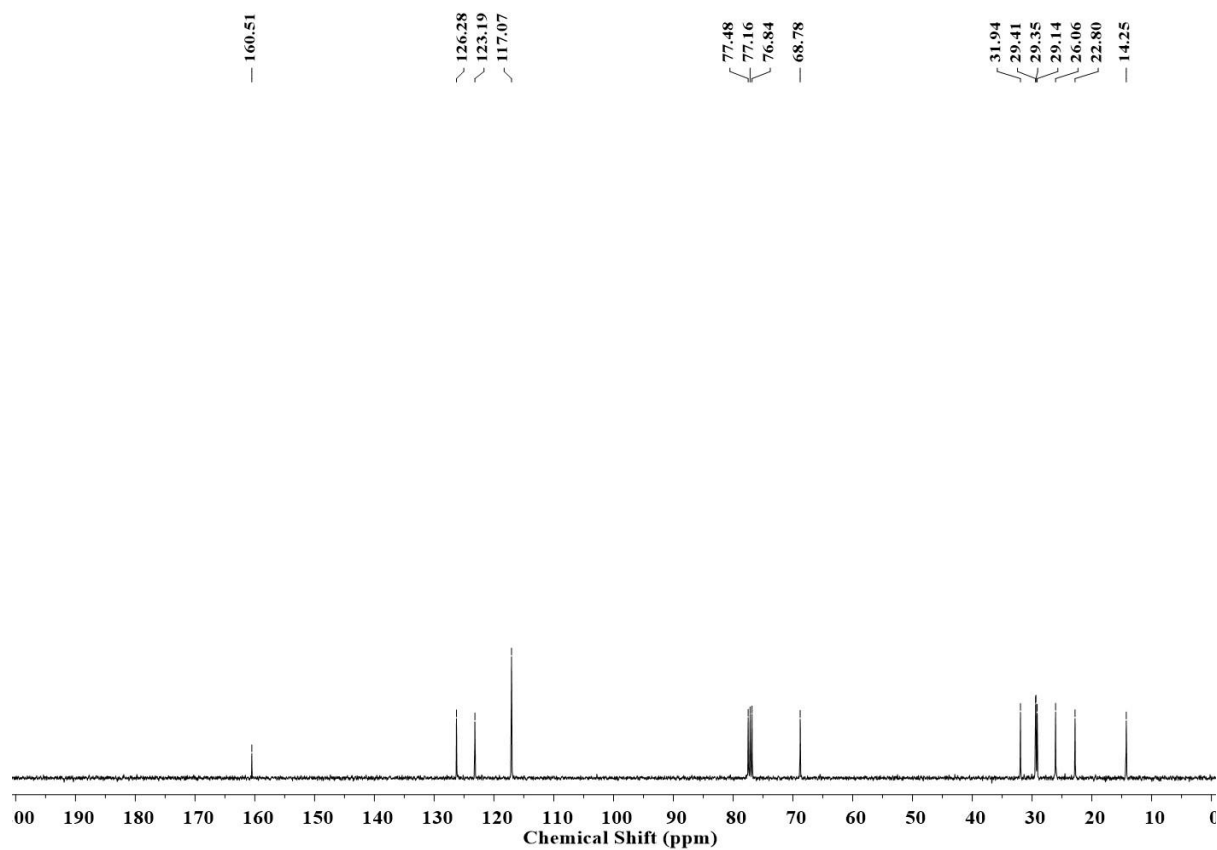


Figure S2. ¹³C NMR (100 MHz, CDCl₃) spectrum of compound **1**.

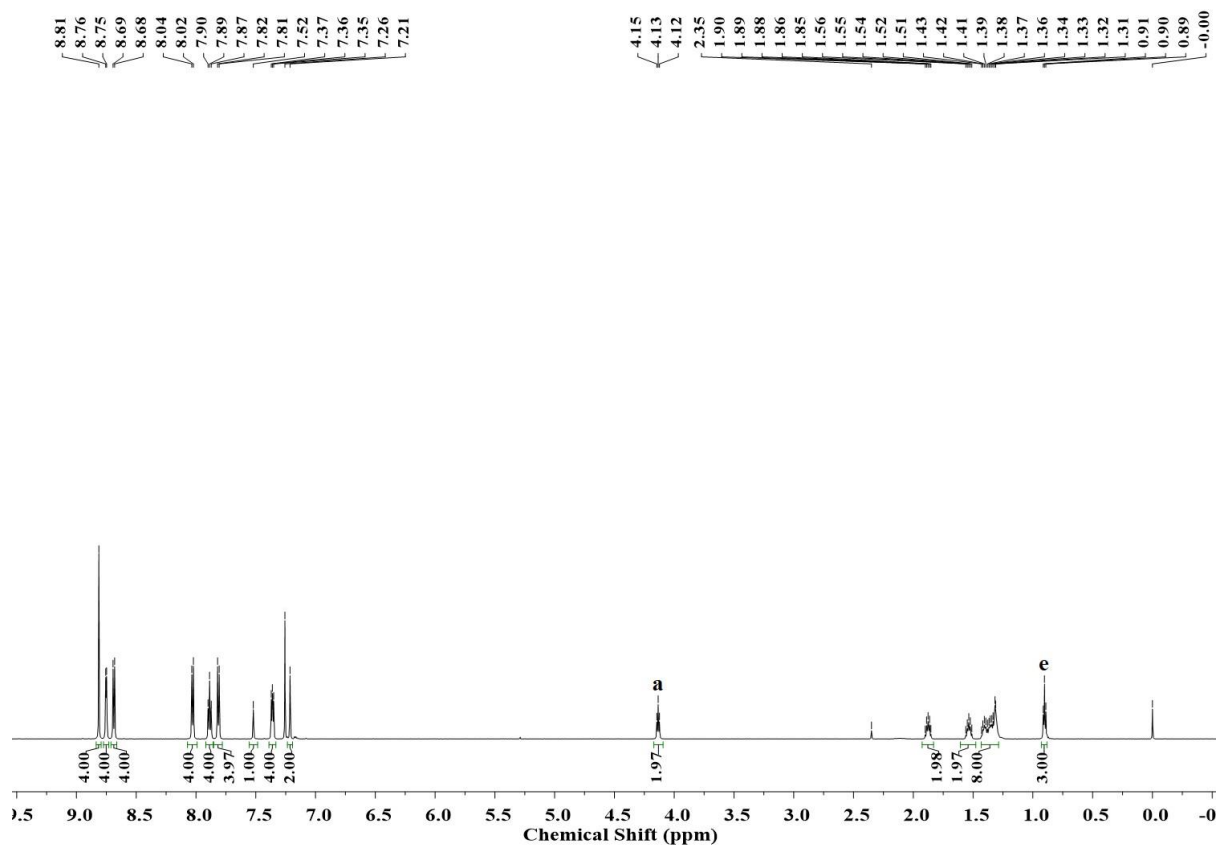


Figure S3. ^1H NMR (600 MHz, CDCl_3) spectrum of compound **2**.

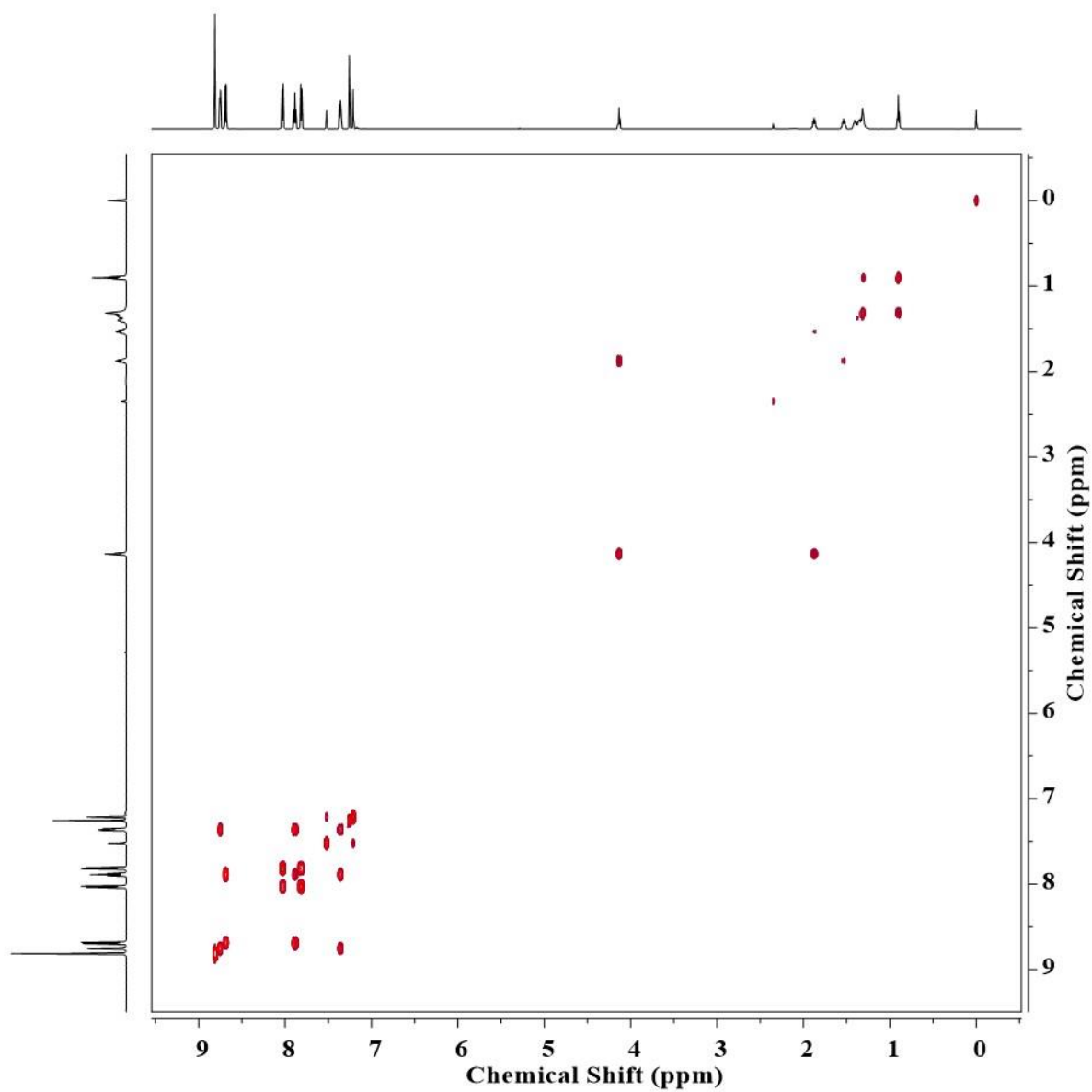


Figure S4. 2D COSY NMR (600 MHz, CDCl₃) spectrum of compound **2**.

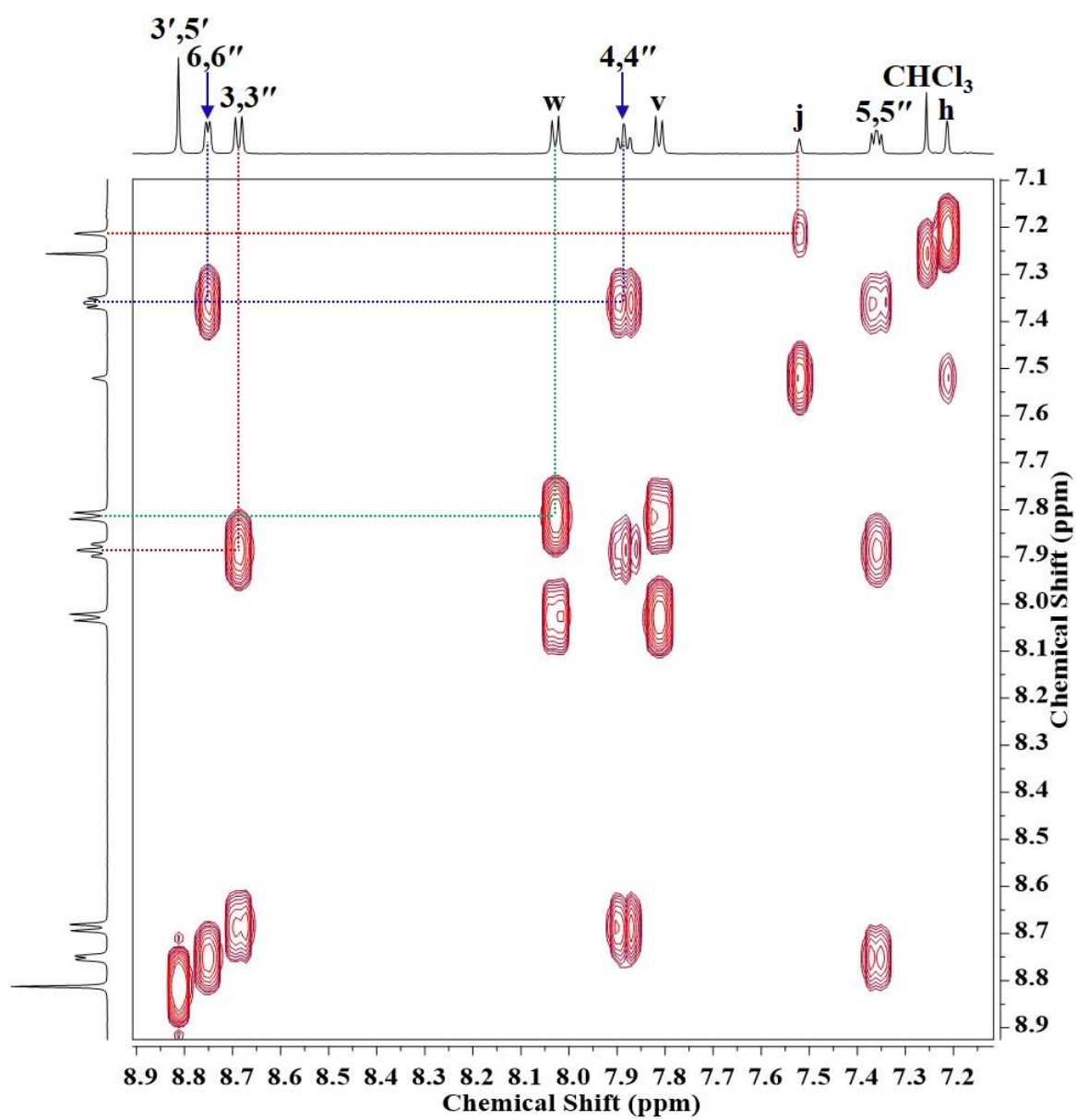


Figure S5. 2D COSY NMR (600 MHz, CDCl₃) spectrum of compound **2** (aromatic region).

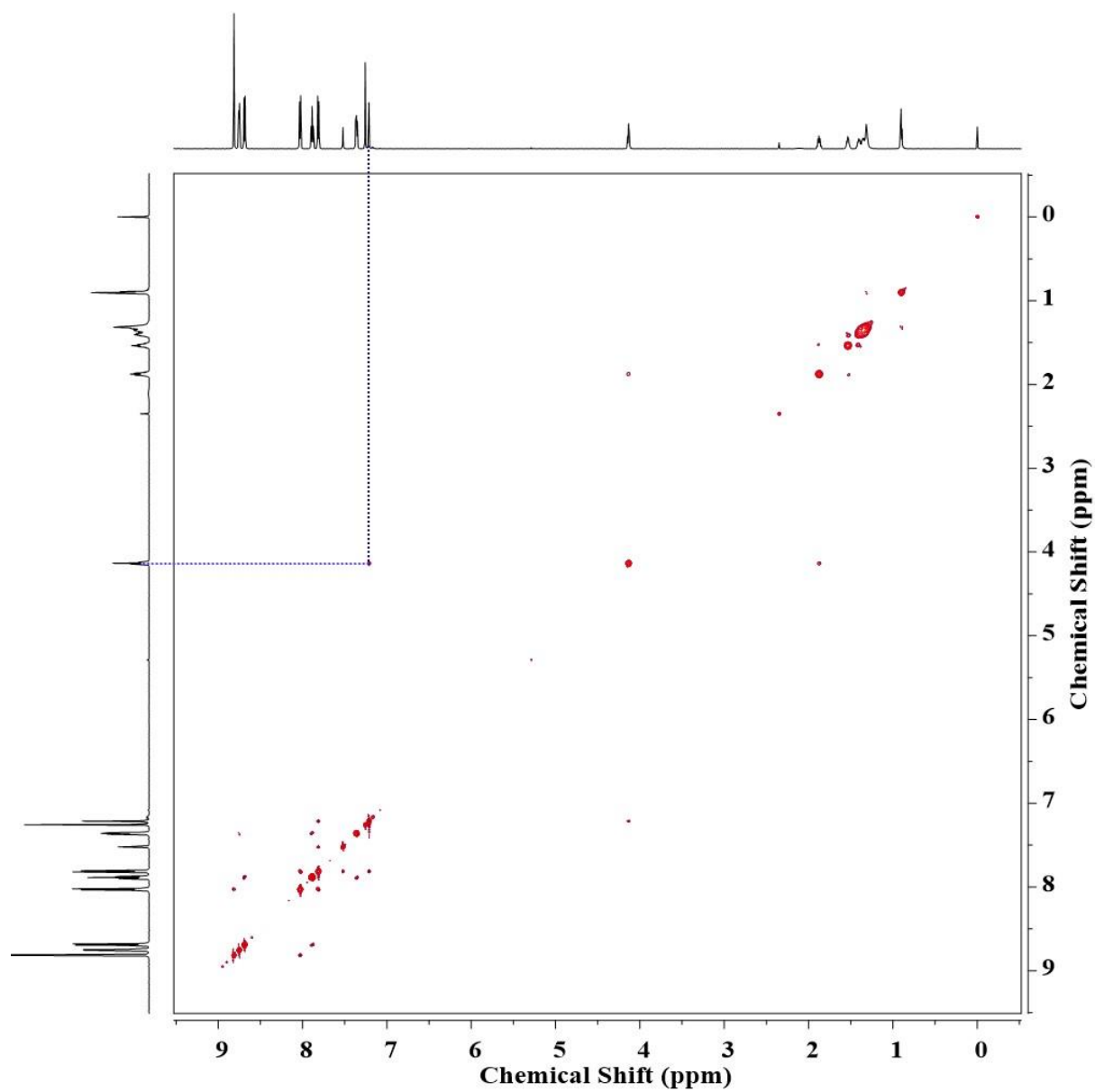


Figure S6. 2D NOESY NMR (600 MHz, CDCl₃) spectrum of compound 2.

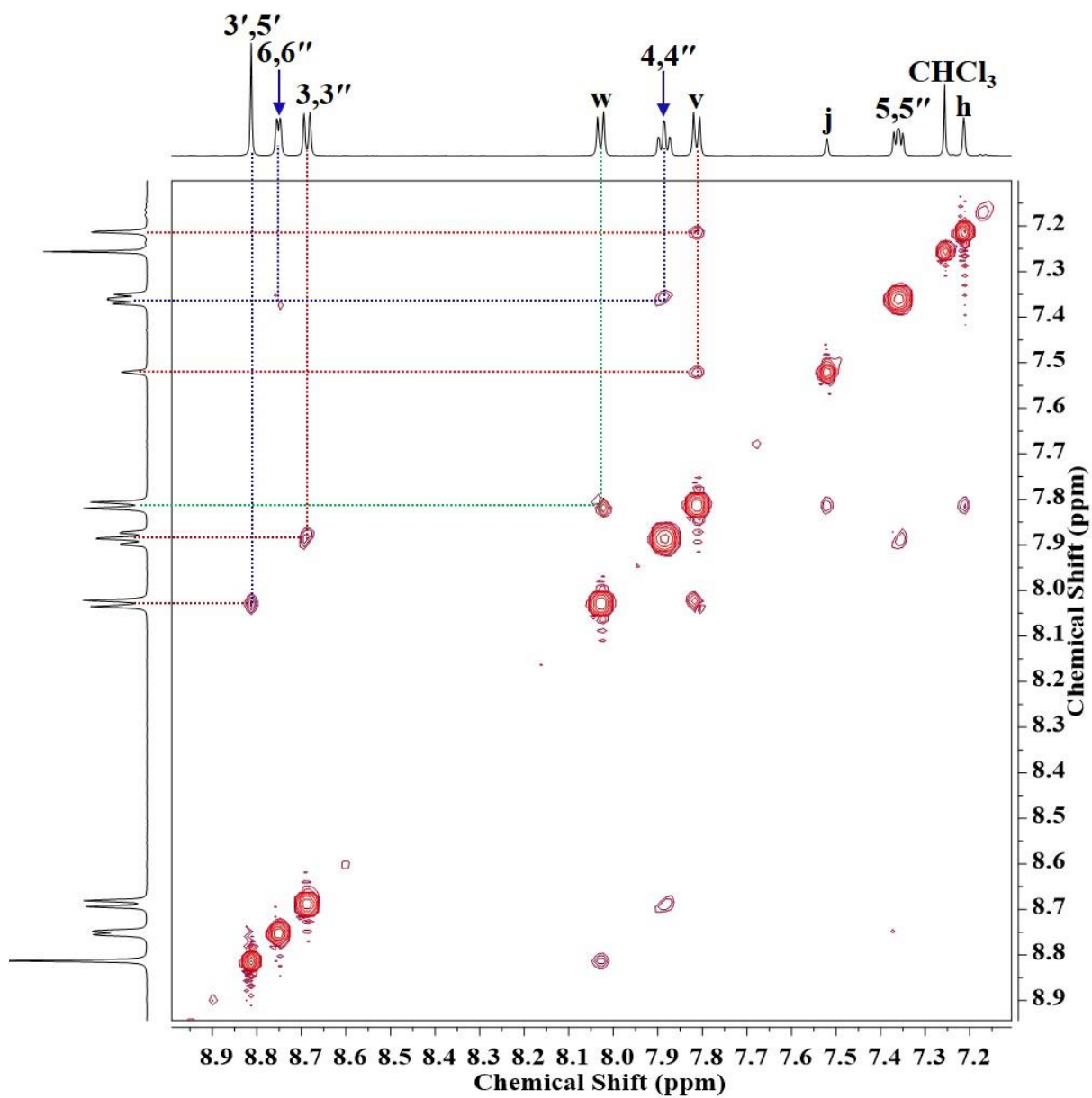


Figure S7. 2D NOESY NMR (600 MHz, CDCl₃) spectrum of compound **2** (aromatic region).

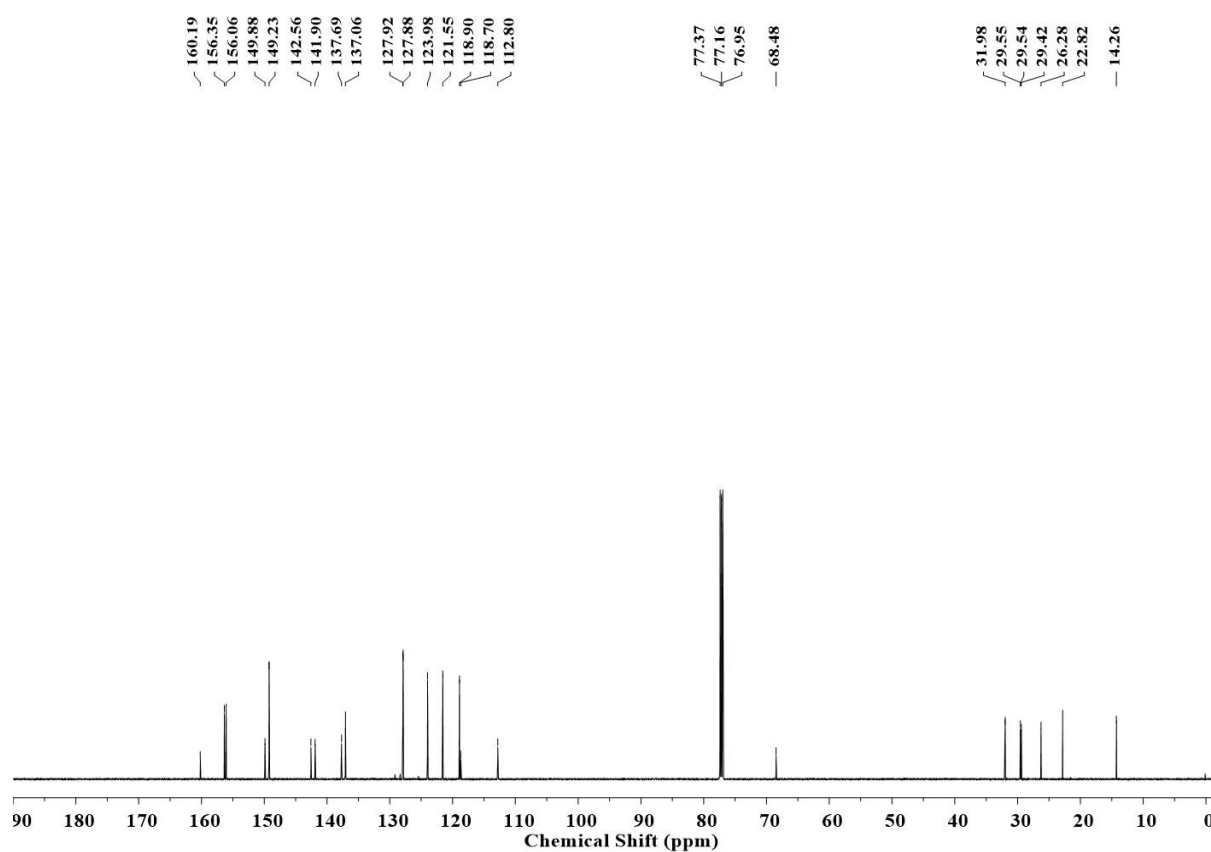


Figure S8. ¹³C NMR (150 MHz, CDCl₃) spectrum of compound **2**.

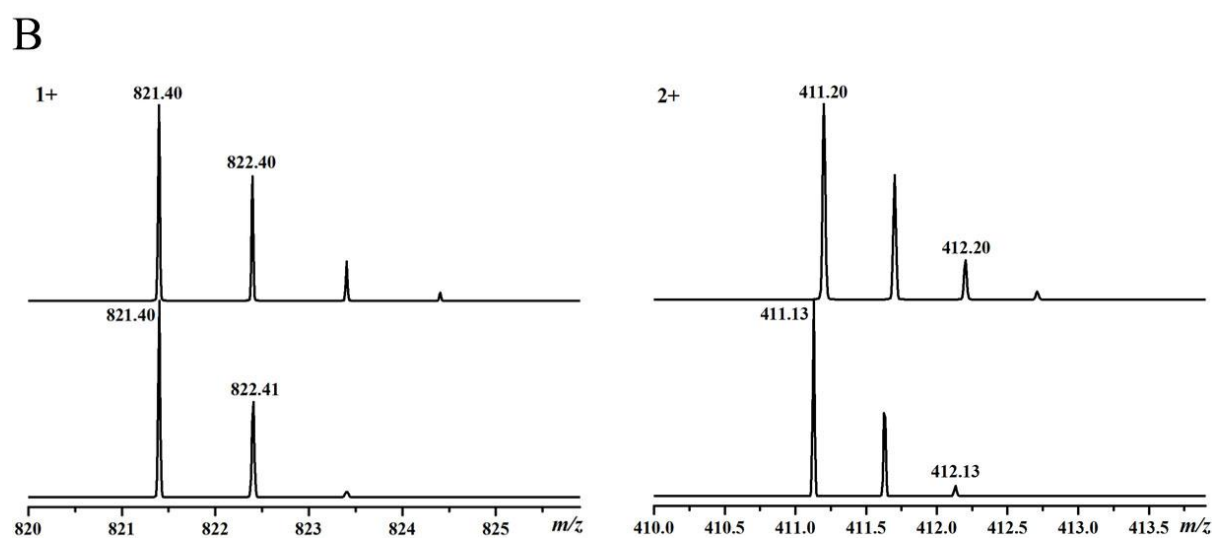
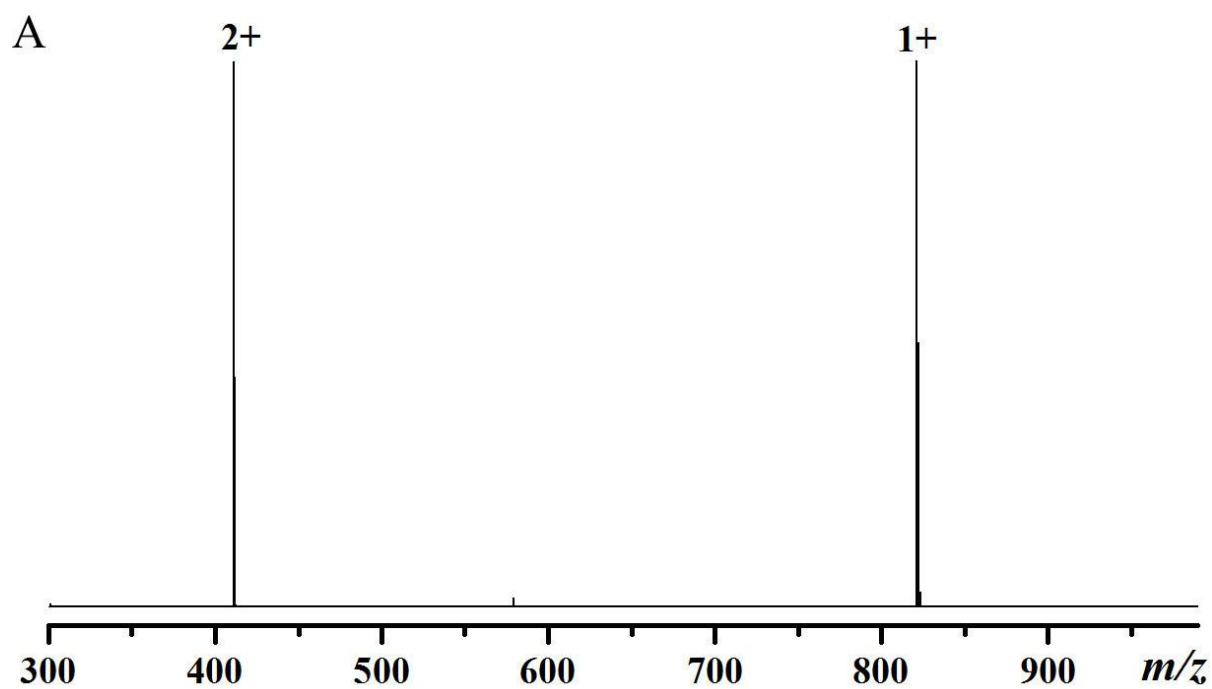


Figure S9. ESI-MS spectrum of compound **2** in $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1/3) (A). Experimental (bottom) and calculated (top) isotope patterns for different charge states (B).

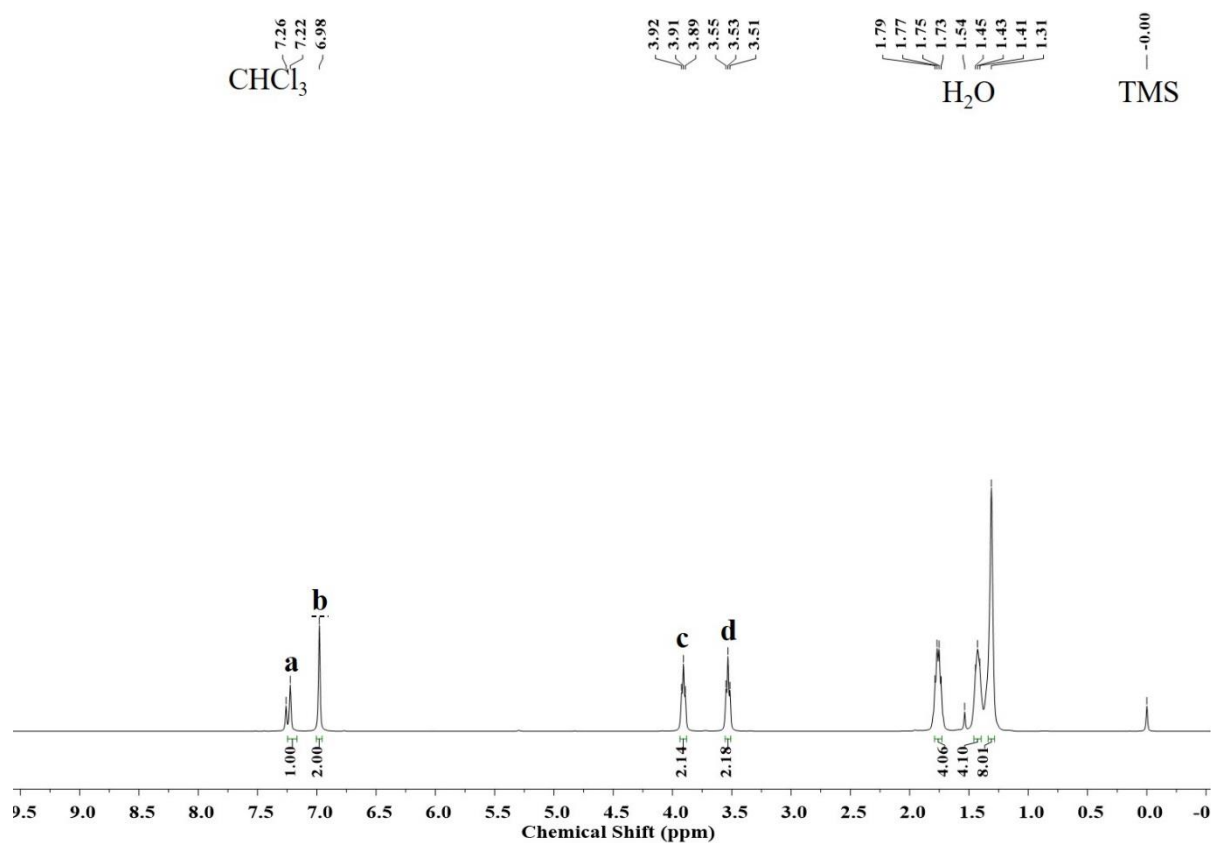


Figure S10. ¹H NMR (400 MHz, CDCl₃) spectrum of compound **3**.

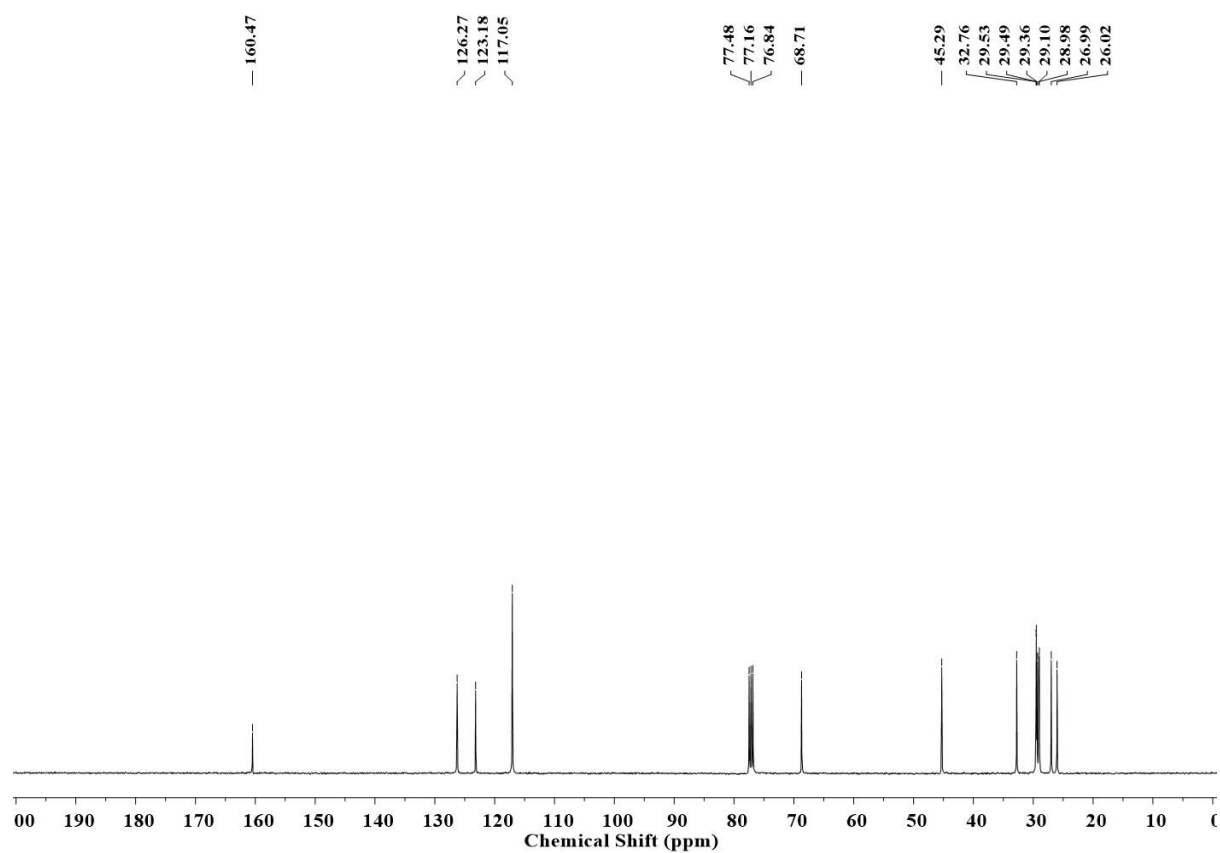


Figure S11. ¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3**.

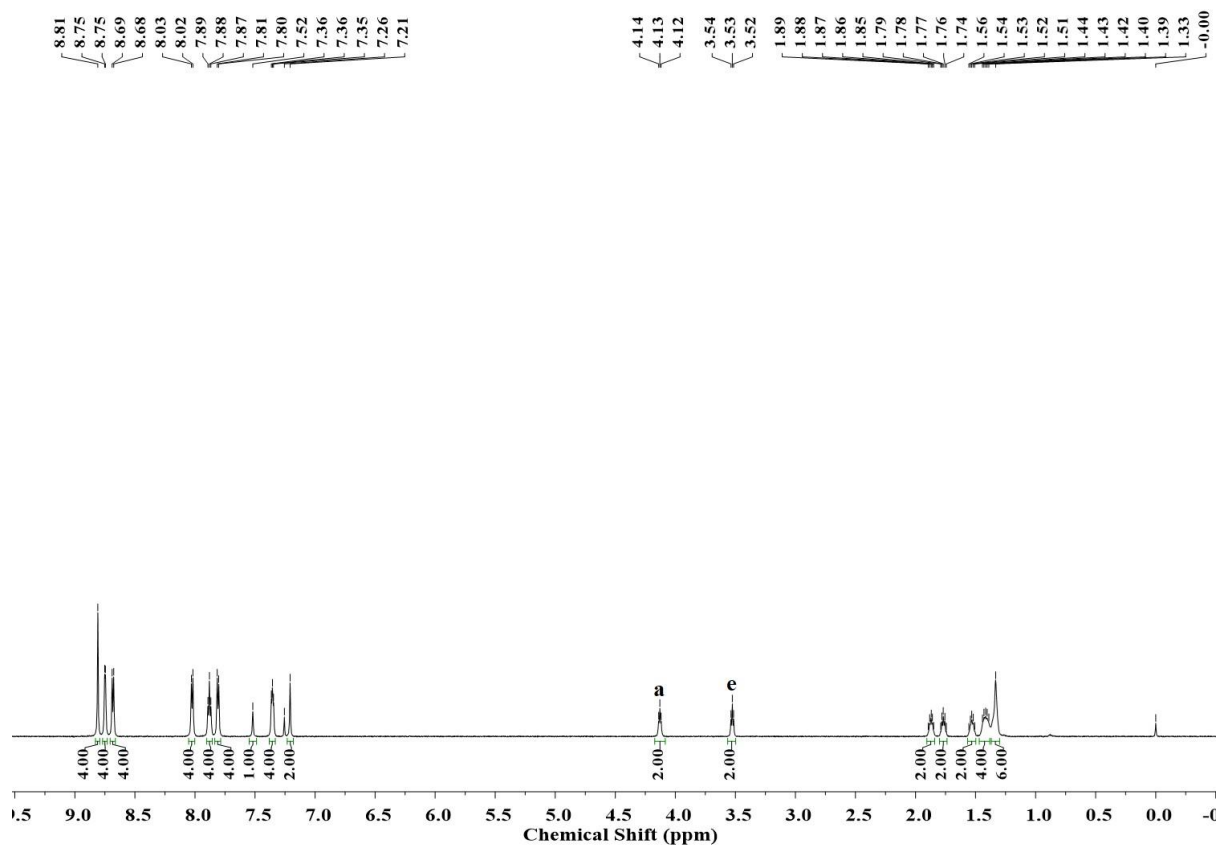


Figure S12. ^1H NMR (600 MHz, CDCl_3) spectrum of compound **4**.

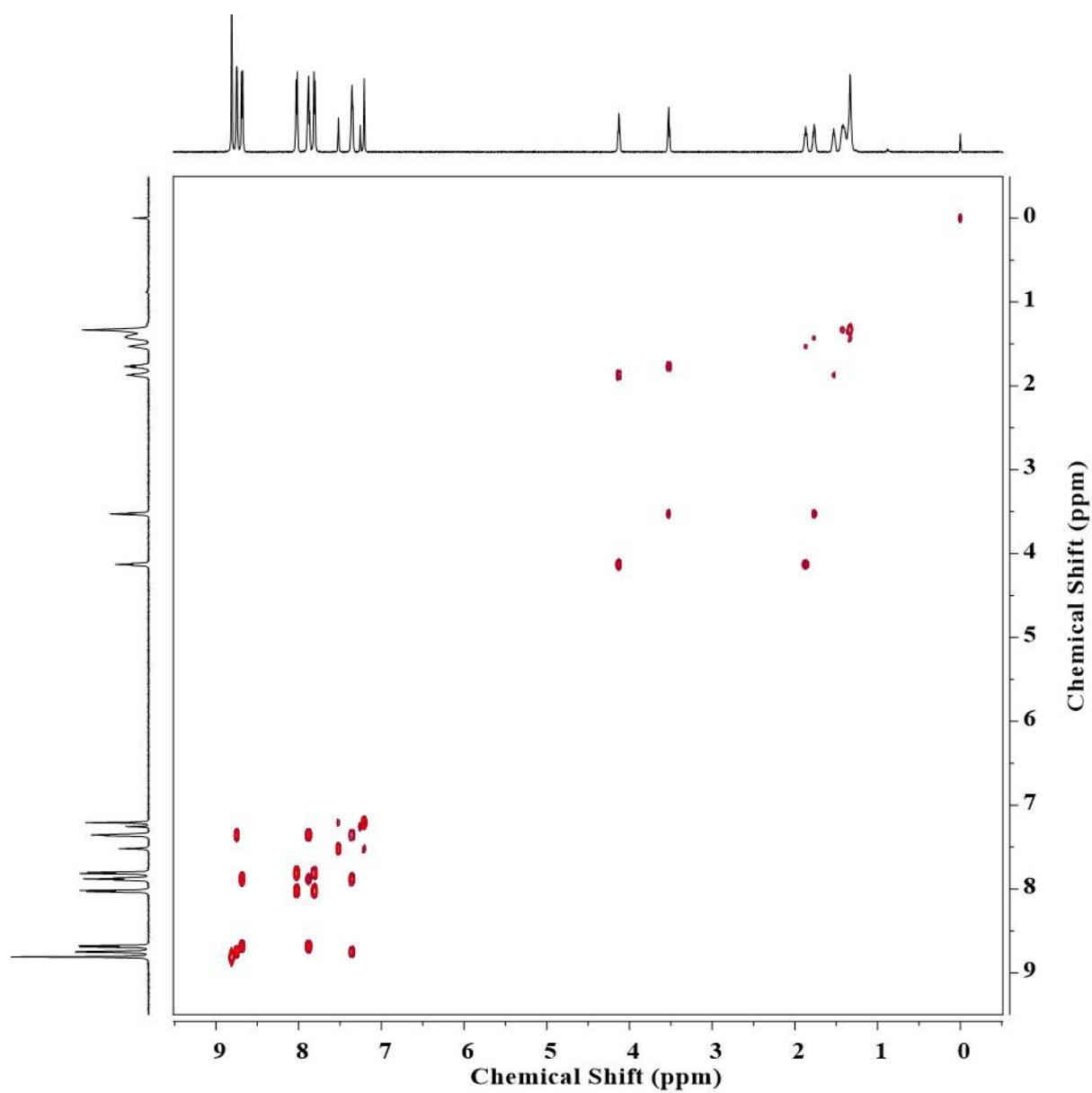


Figure S13. 2D COSY NMR (600 MHz, CDCl_3) spectrum of compound **4**.

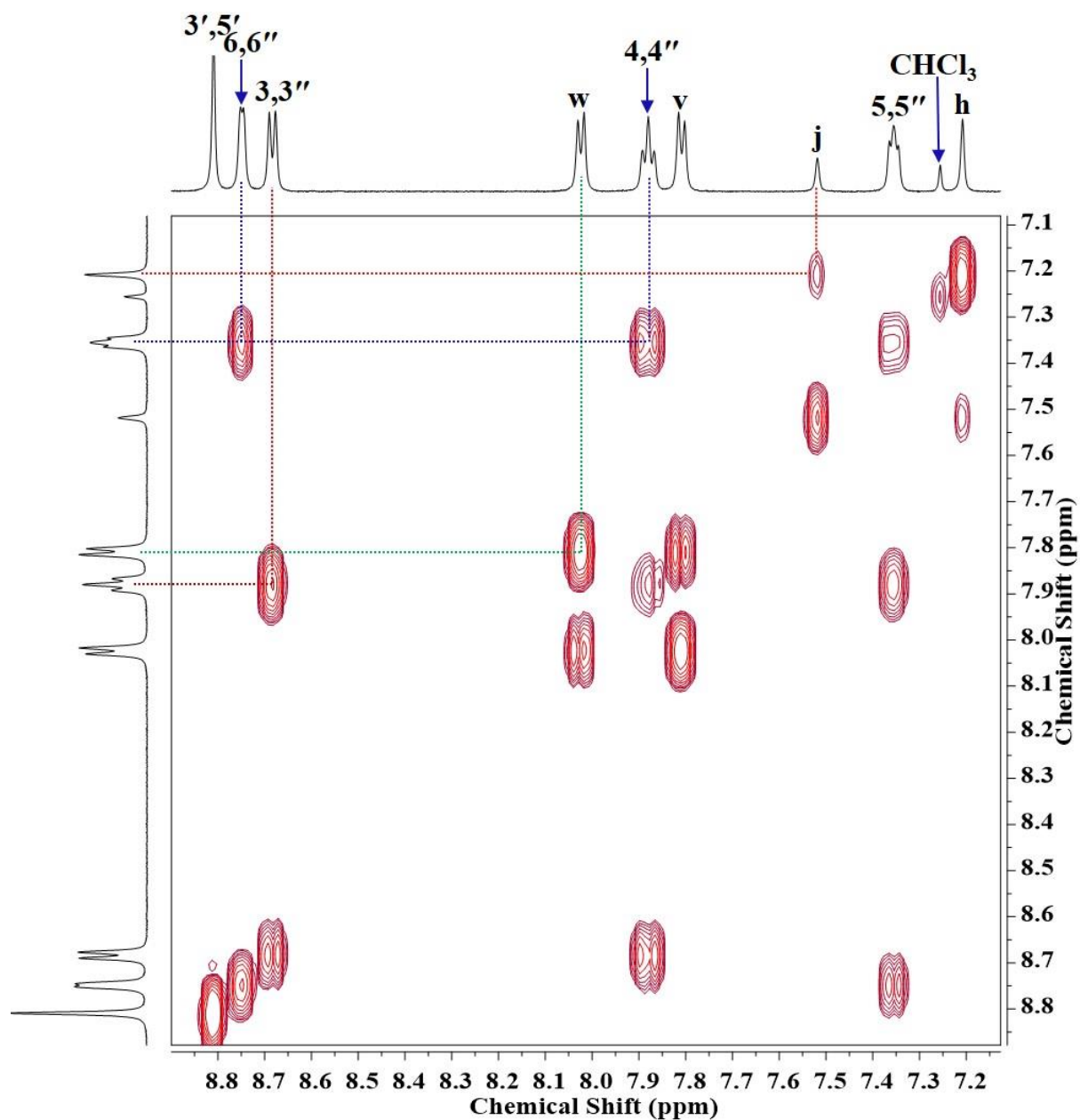


Figure S14. 2D COSY NMR (600 MHz, CDCl₃) spectrum of compound **4** (aromatic region).

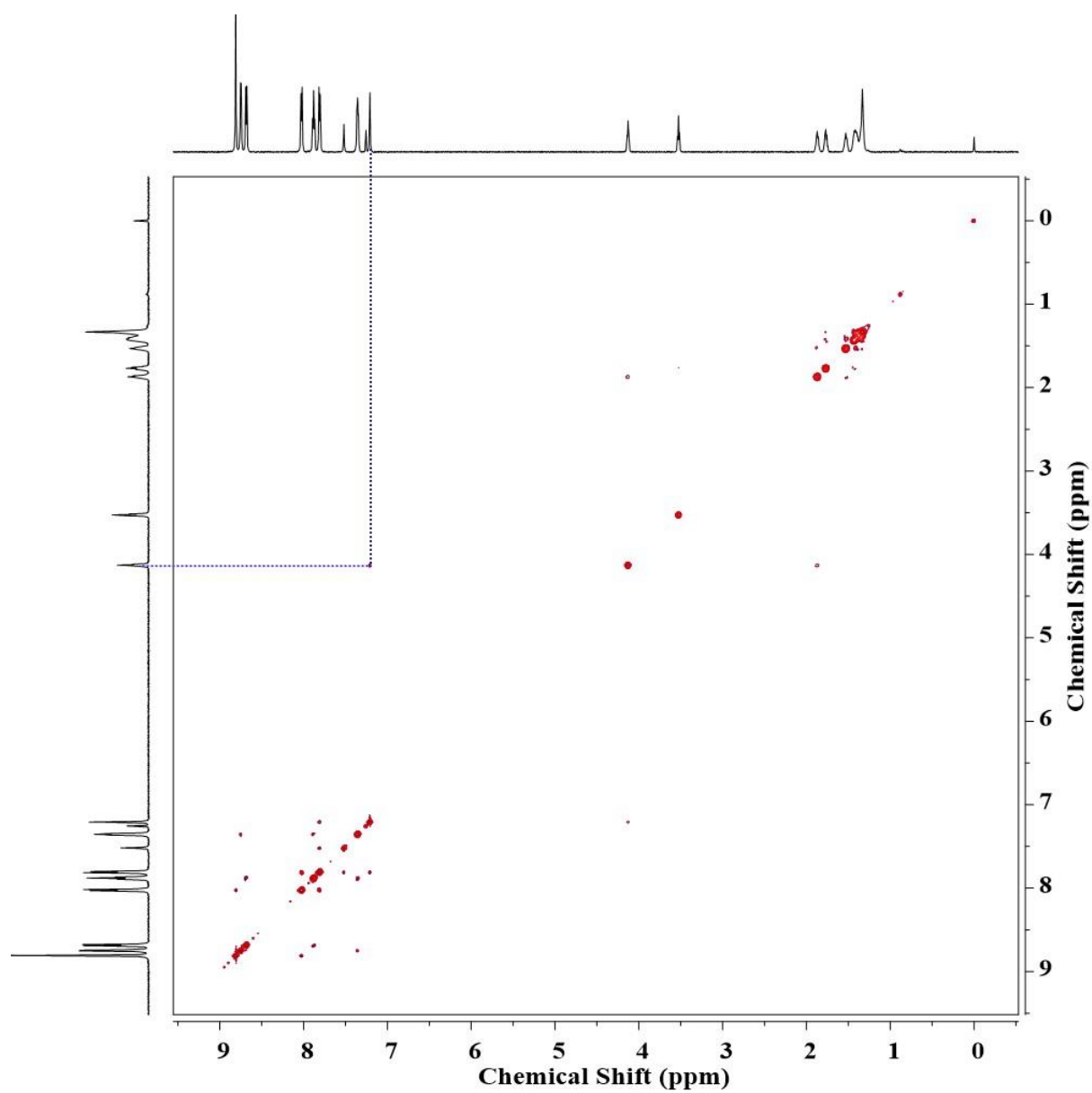


Figure S15. 2D NOESY NMR (600 MHz, CDCl₃) spectrum of compound 4.

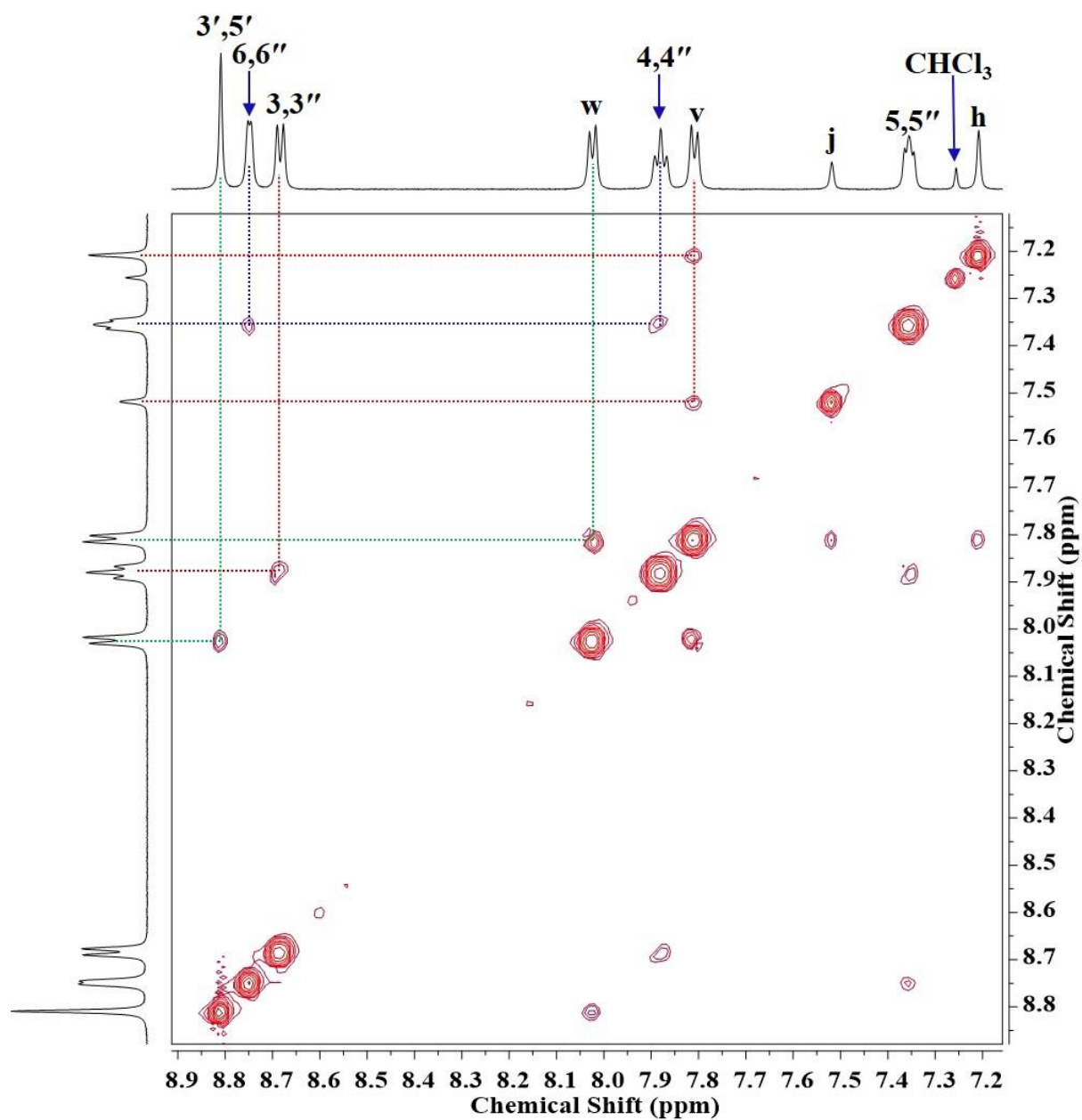


Figure S16. 2D NOESY NMR (600 MHz, CDCl₃) spectrum of compound 4 (aromatic region).

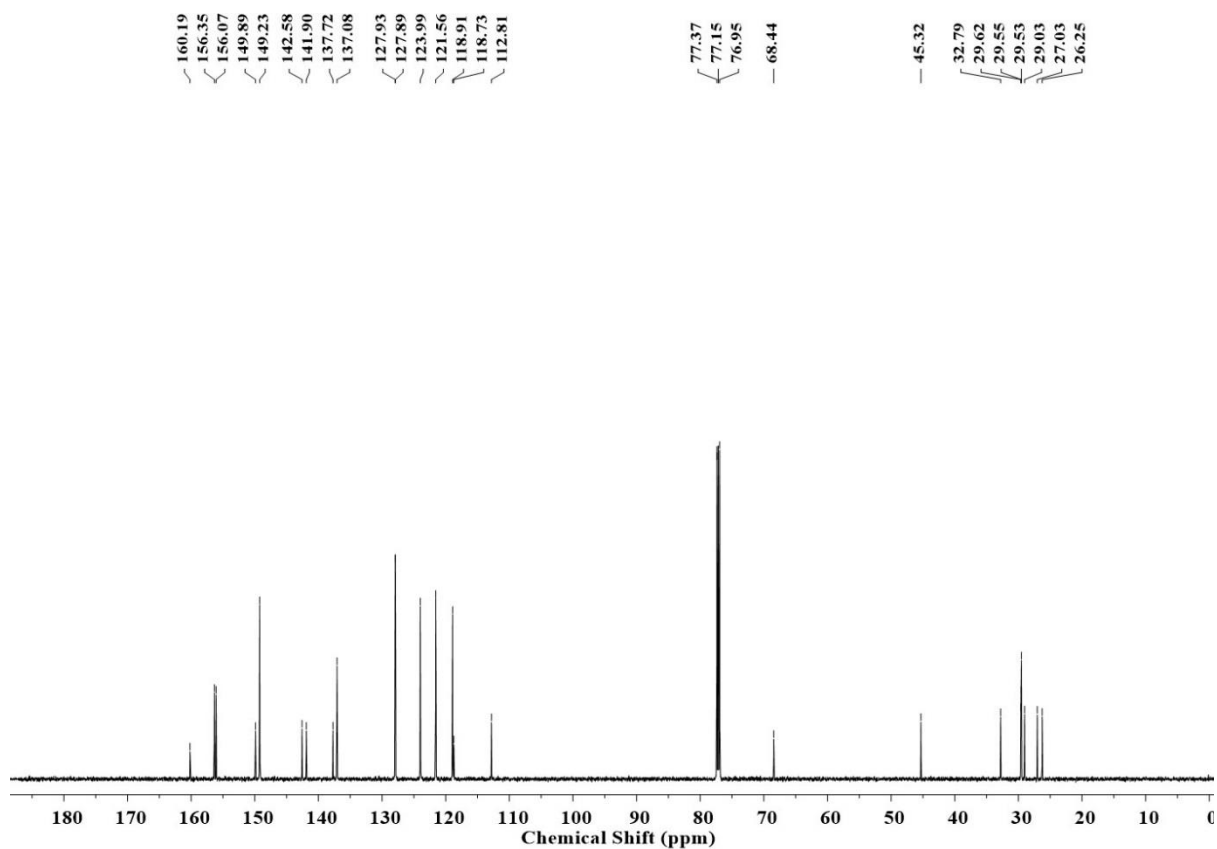


Figure S17. ^{13}C NMR (150 MHz, CDCl_3) spectrum of compound **4**.

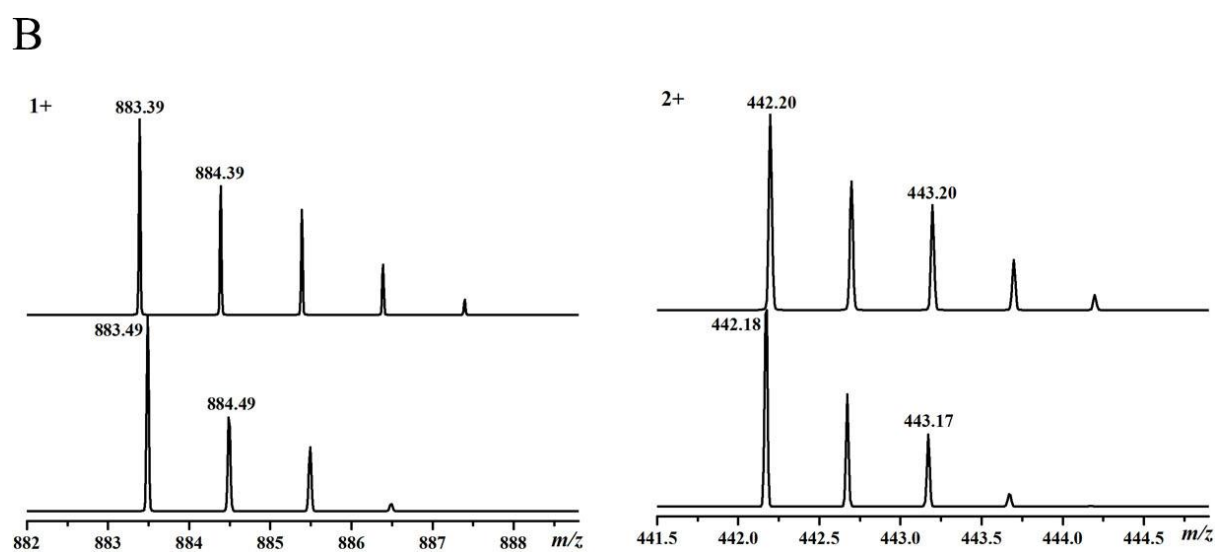
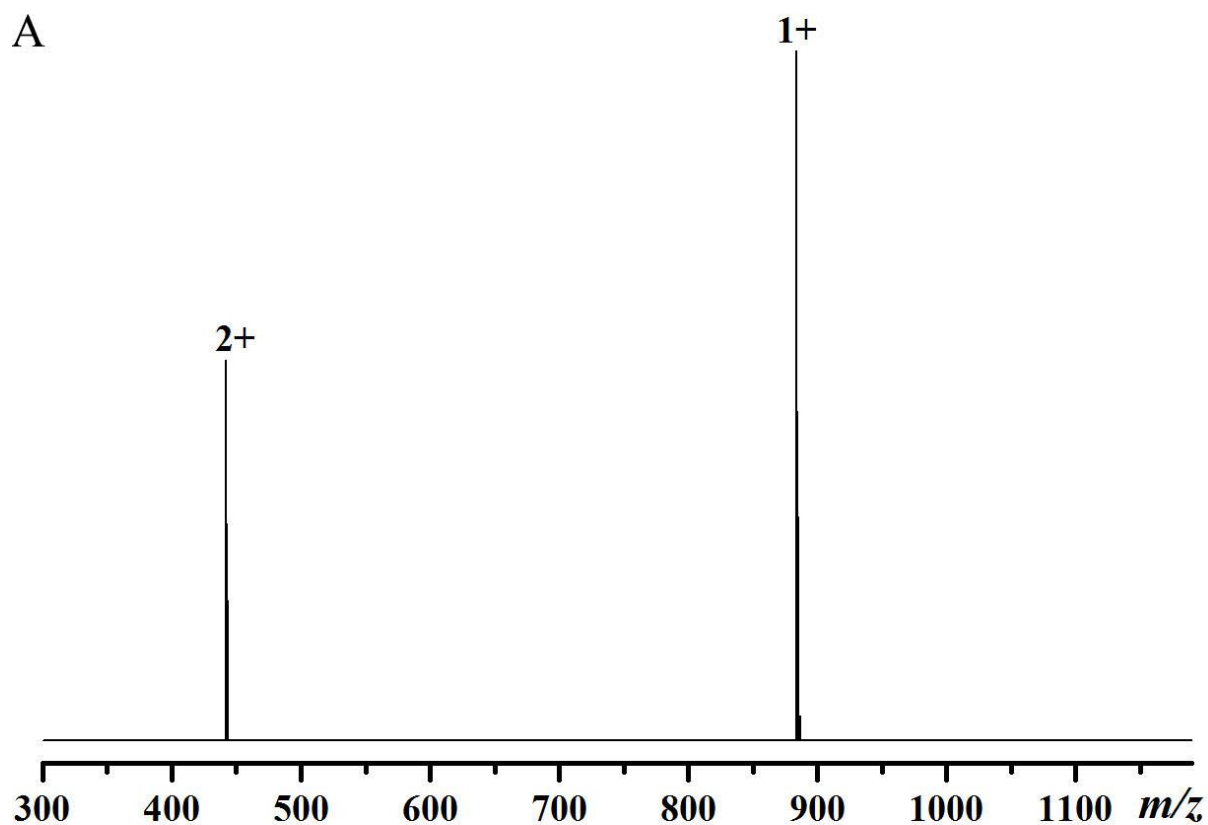


Figure S18. ESI-MS spectrum of compound **4** in $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1/3) (A). Experimental (bottom) and calculated (top) isotope patterns for different charge states (B).

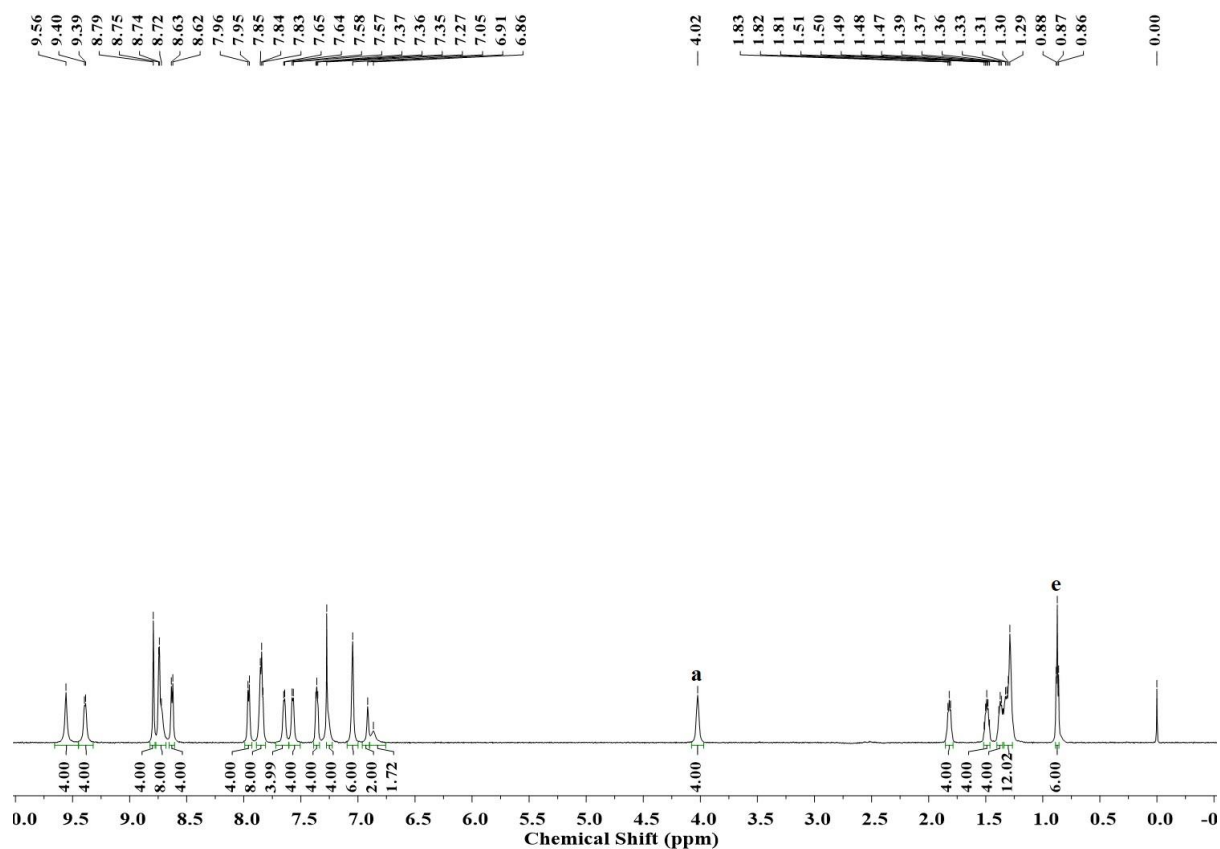


Figure S19. ^1H NMR (600 MHz, CDCl_3) spectrum of compound **5**.

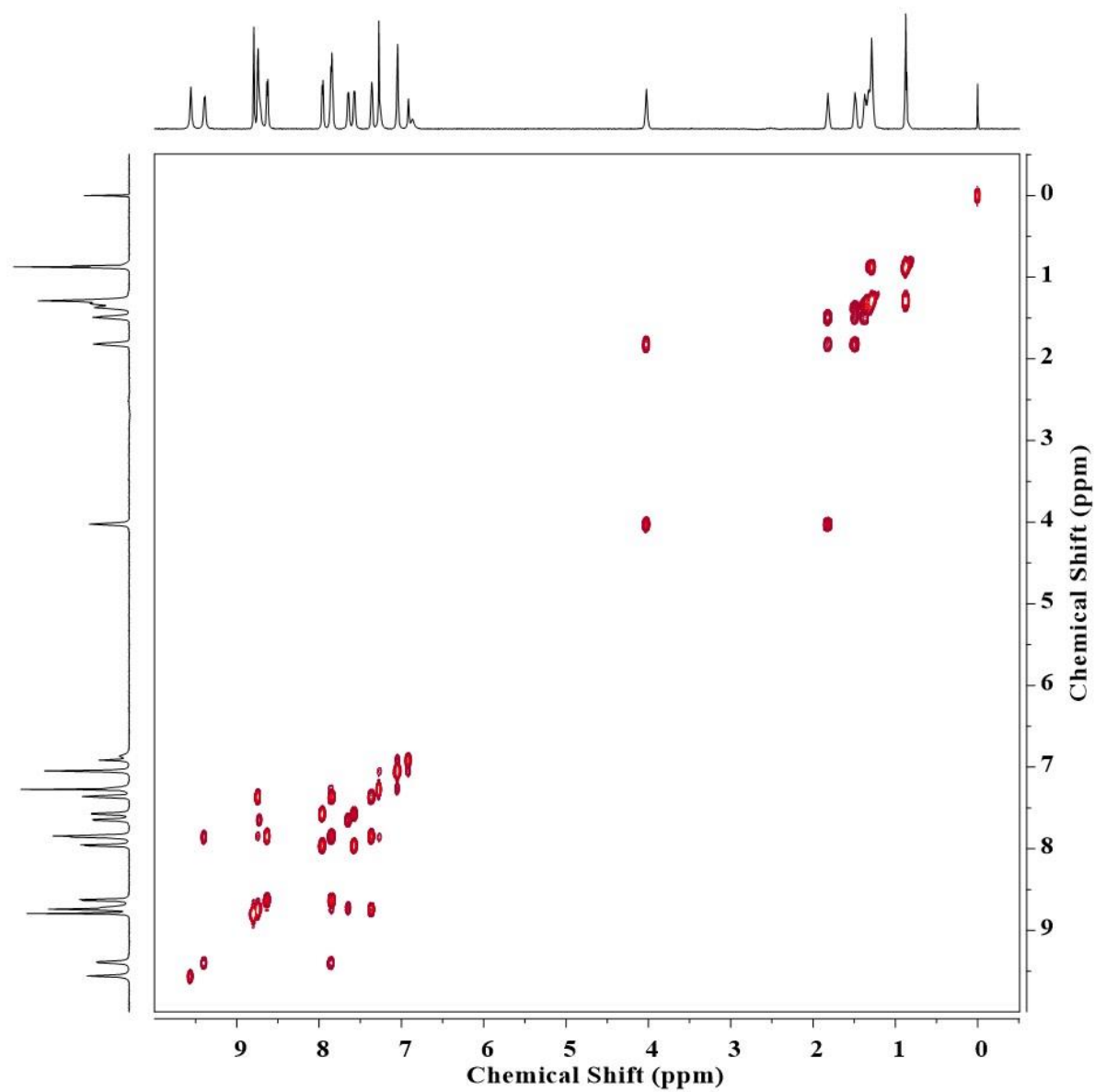


Figure S20. 2D COSY NMR (600 MHz, CDCl₃) spectrum of compound **5**.

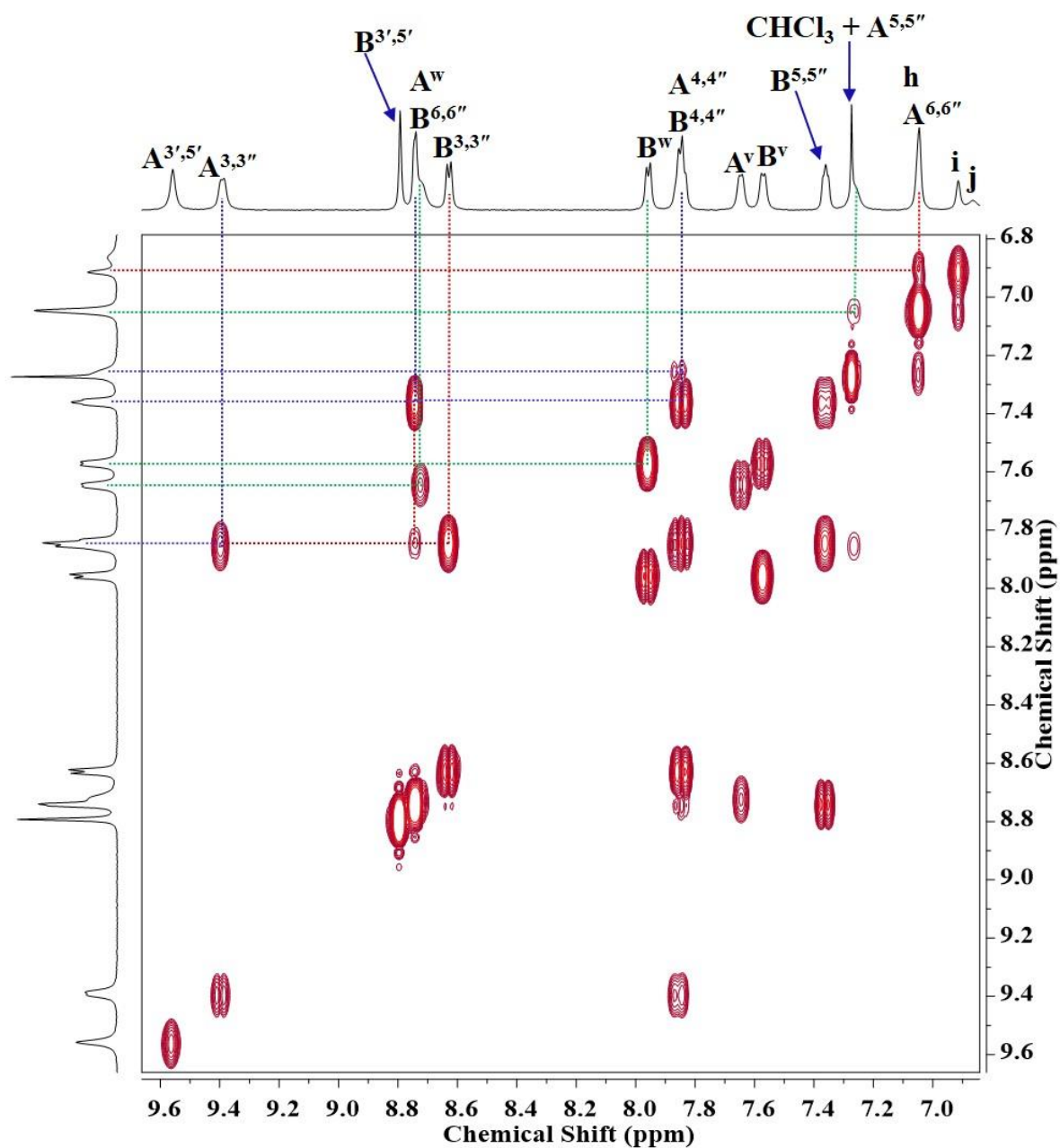


Figure S21. 2D COSY NMR (600 MHz, CDCl_3) spectrum of compound **5** (aromatic region).

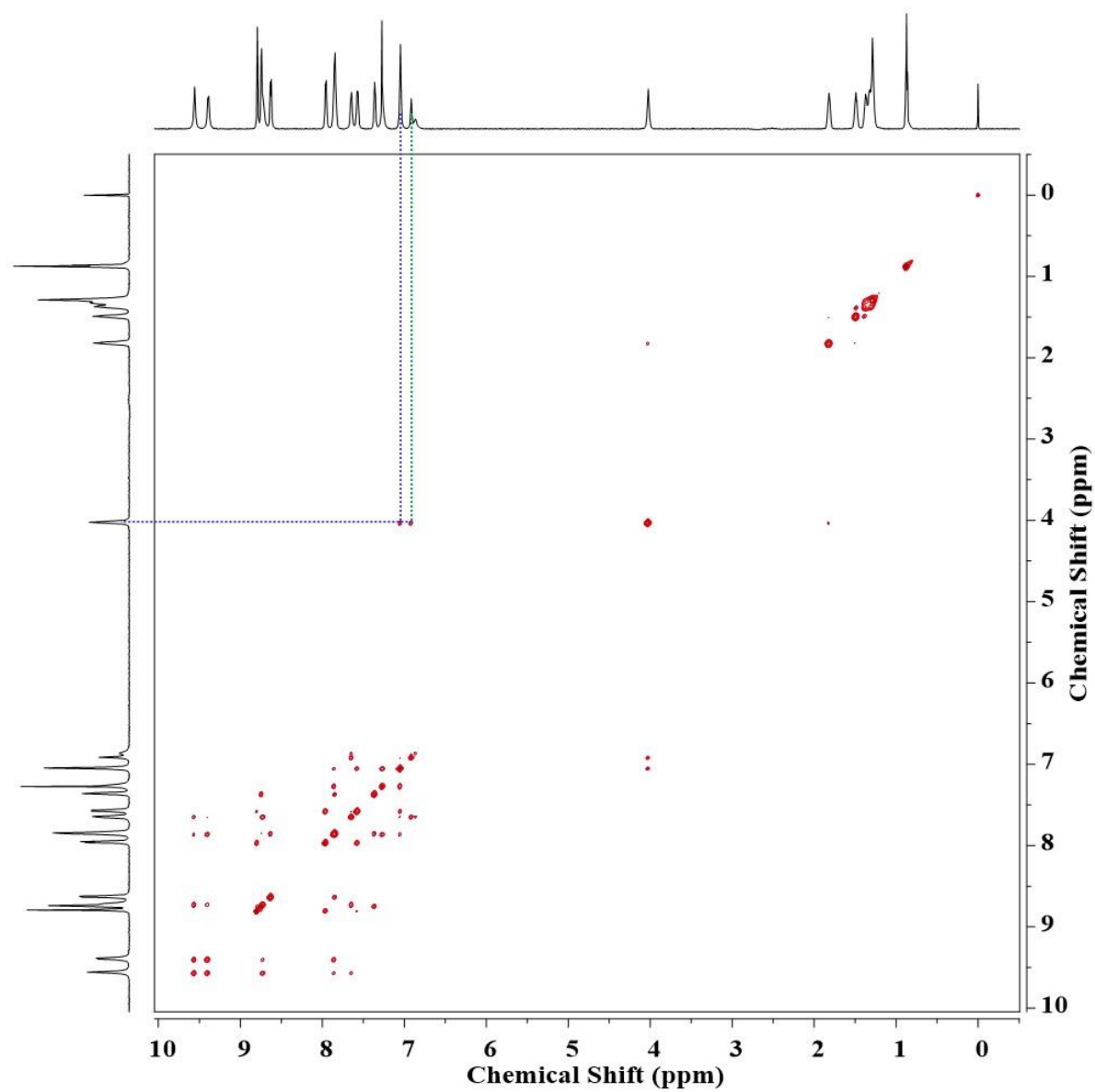


Figure S22. 2D NOESY NMR (600 MHz, CDCl_3) spectrum of compound **5**.

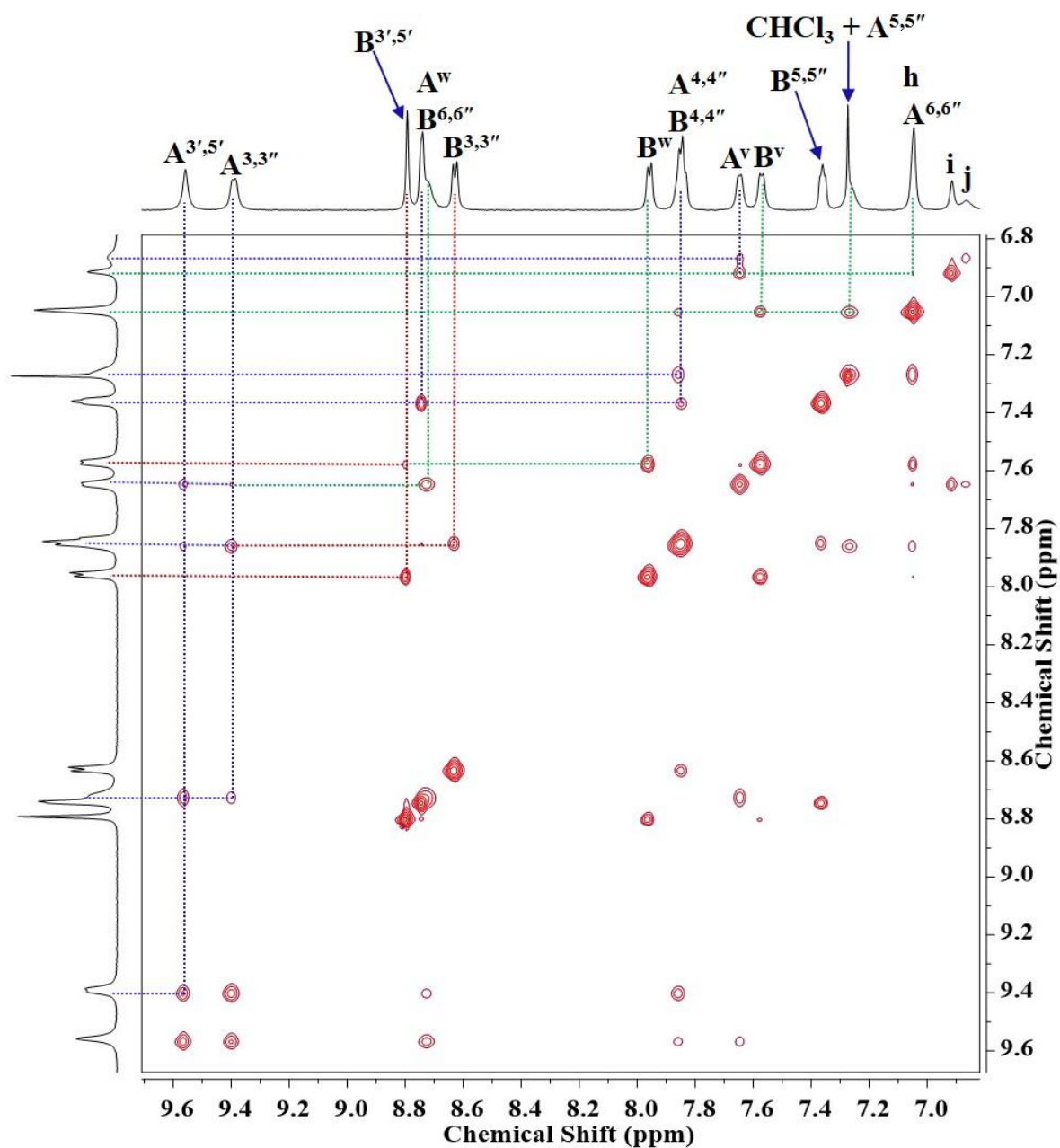


Figure S23. 2D NOESY NMR (600 MHz, CDCl_3) spectrum of compound **5** (aromatic region).

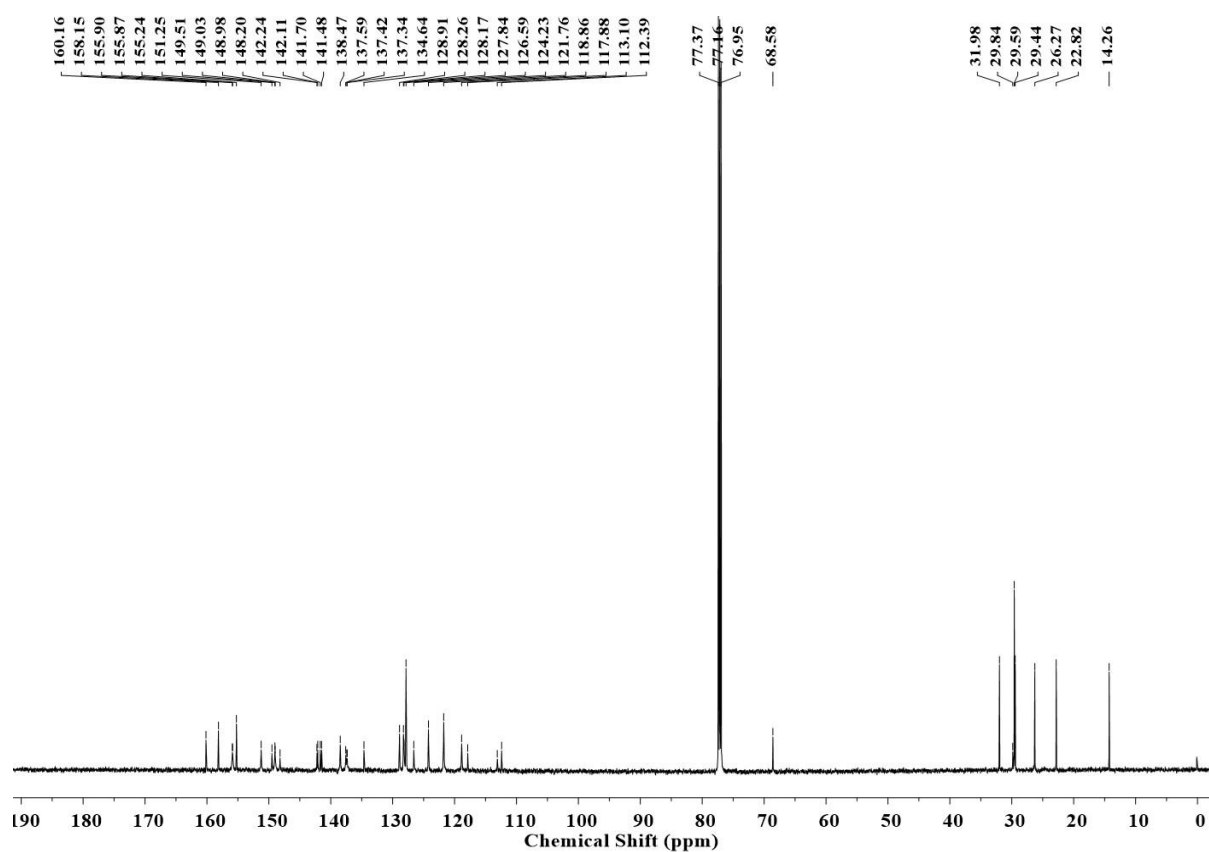


Figure S24. ¹³C NMR (150 MHz, CDCl₃) spectrum of compound **5**.

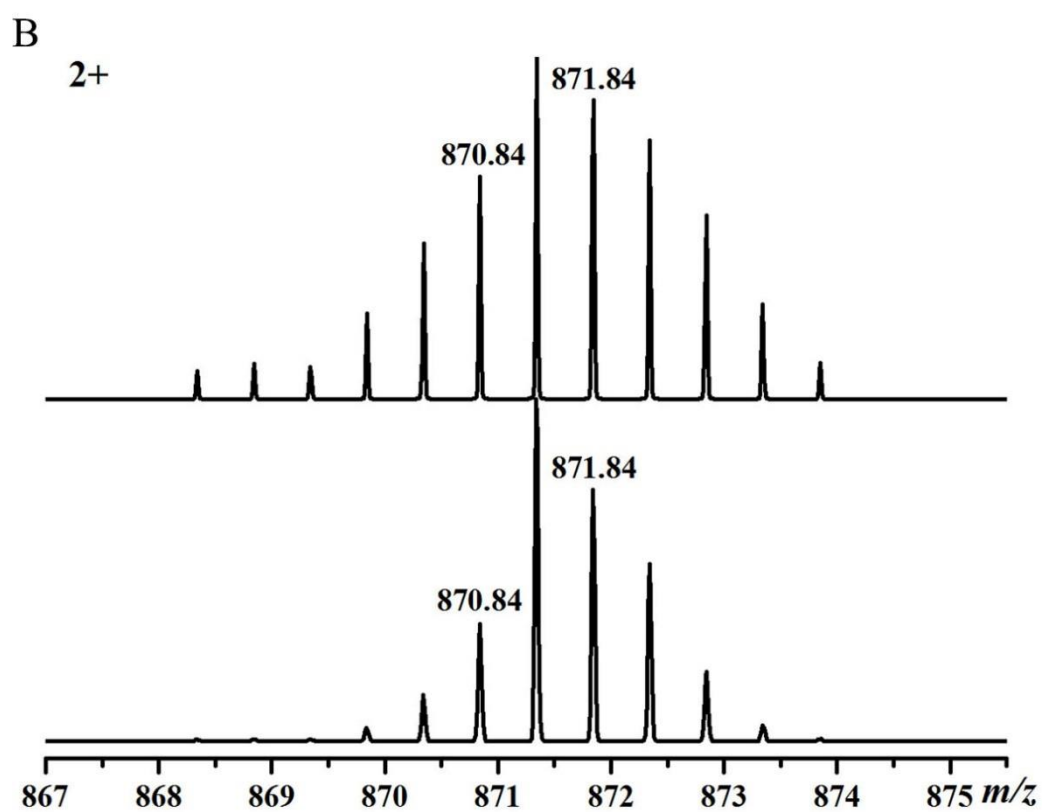
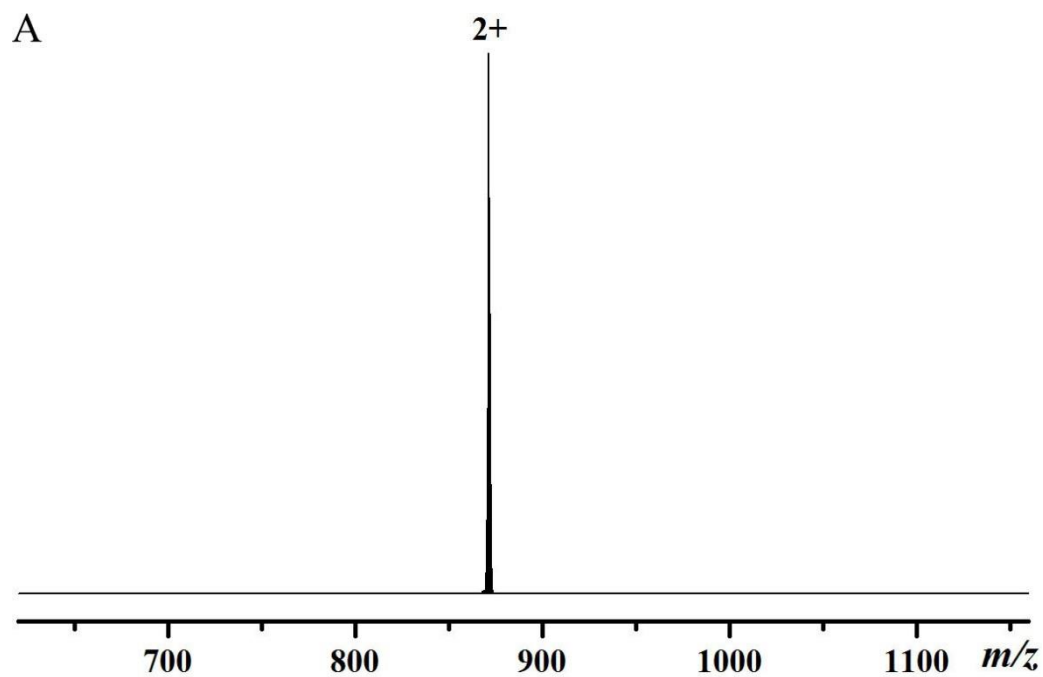


Figure S25. ESI-MS spectrum of compound **5** in $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1/3) (A). Experimental (bottom) and calculated (top) isotope patterns (B).

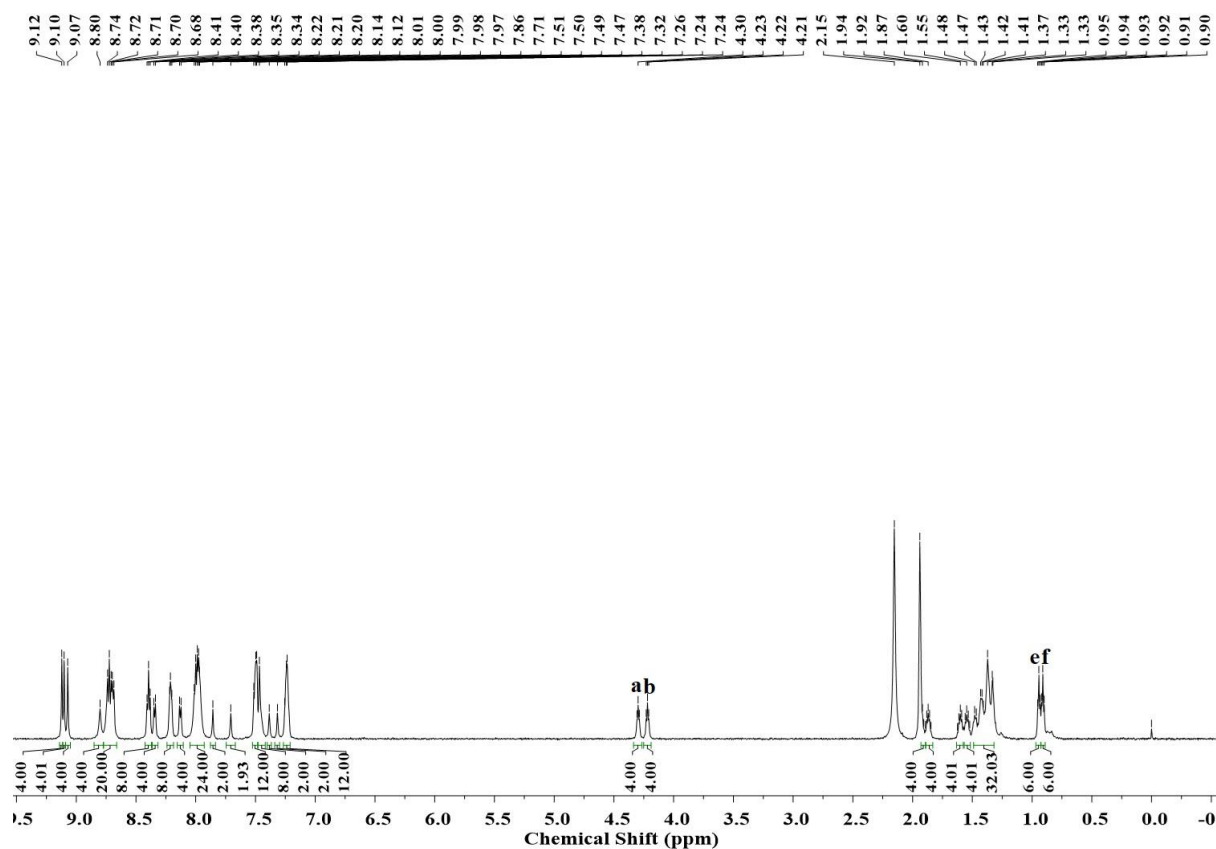


Figure S26. ^1H NMR (600 MHz, CD_3CN) spectrum of compound **6**.

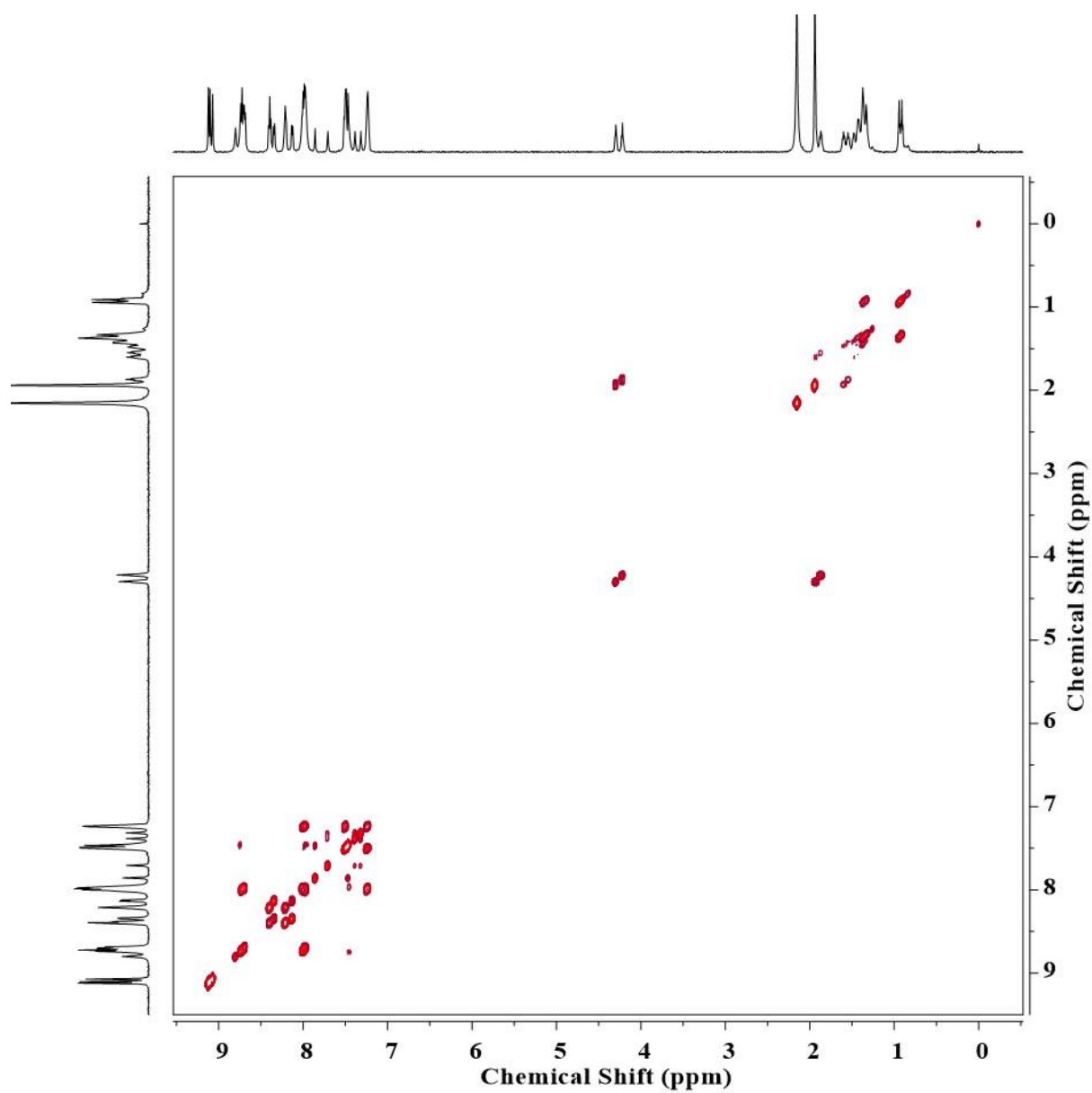


Figure S27. 2D COSY NMR (600 MHz, CD₃CN) spectrum of compound **6**.

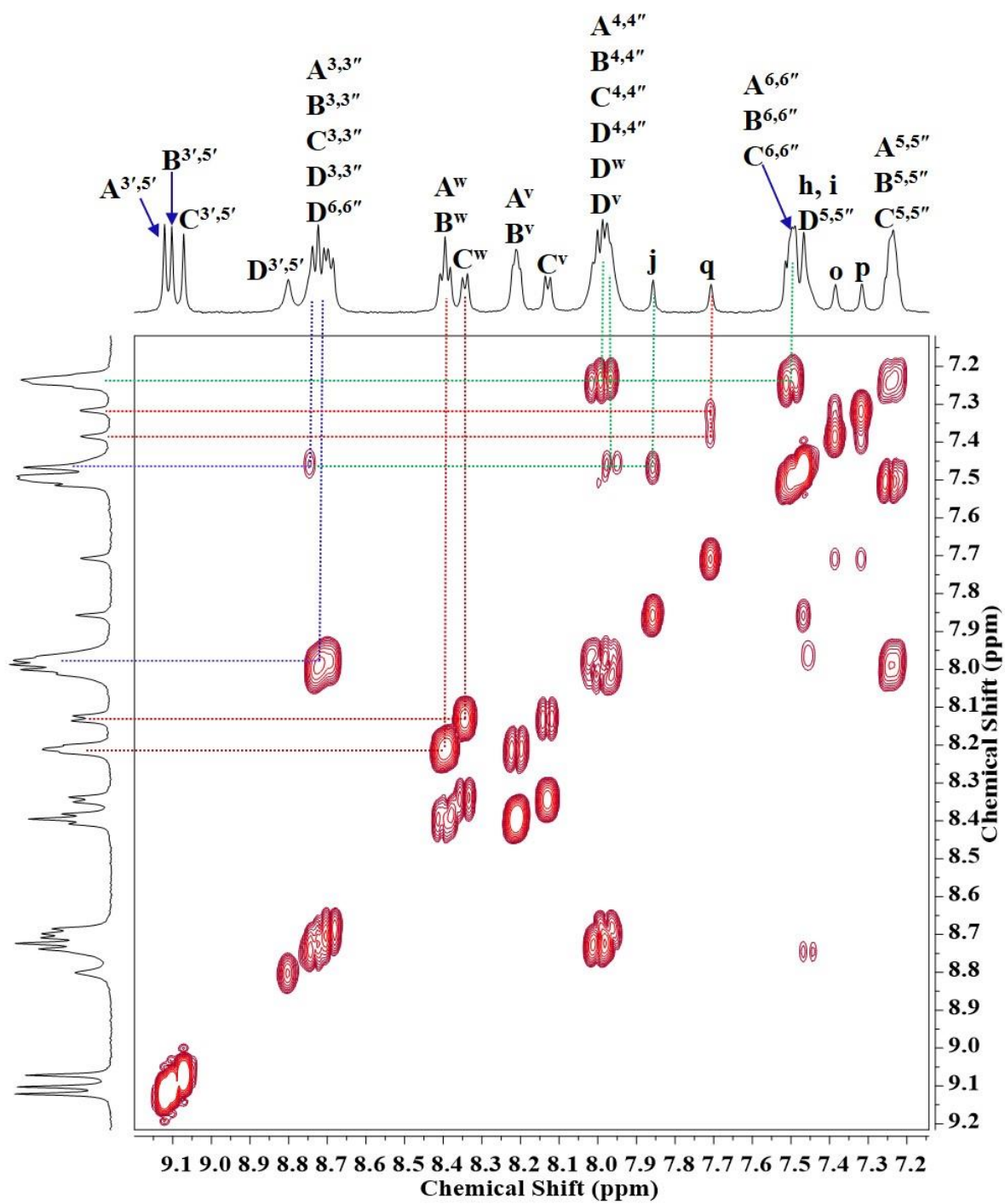


Figure S28. 2D COSY NMR (600 MHz, CD_3CN) spectrum of compound **6** (aromatic region).

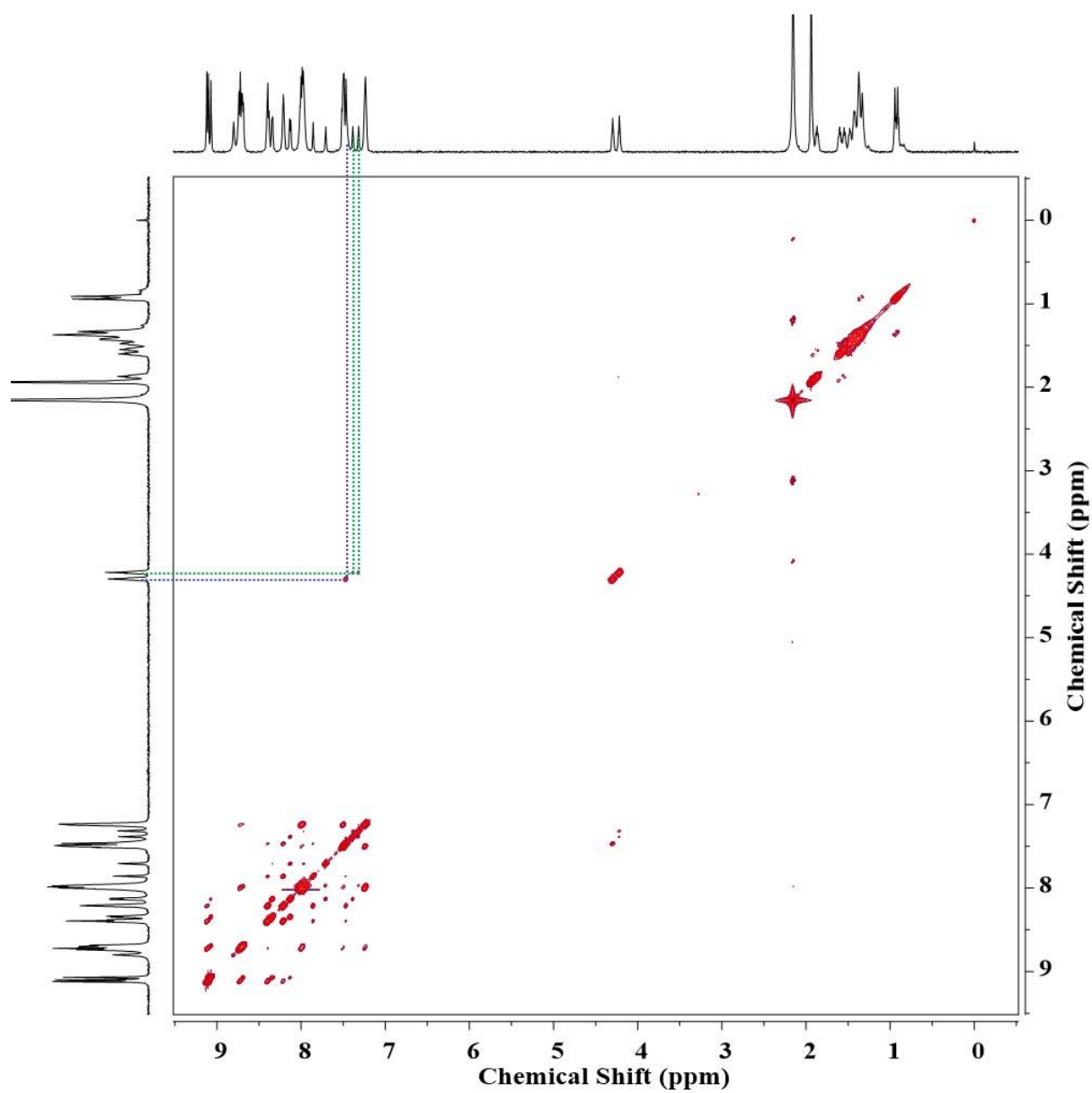


Figure S29. 2D NOESY NMR (600 MHz, CD₃CN) spectrum of compound **6**.

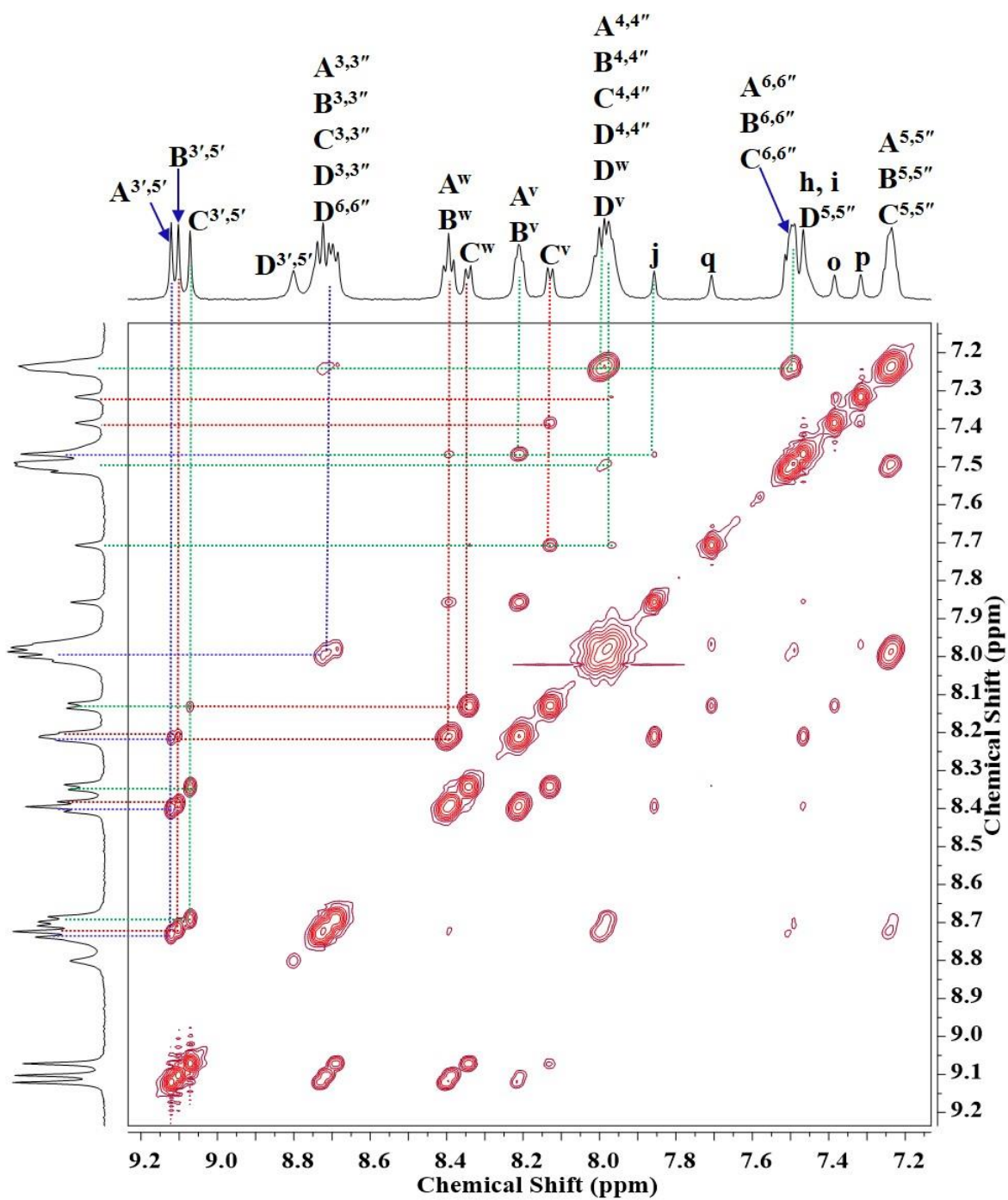


Figure S30. 2D NOESY NMR (600 MHz, CD_3CN) spectrum of compound **6** (aromatic region).

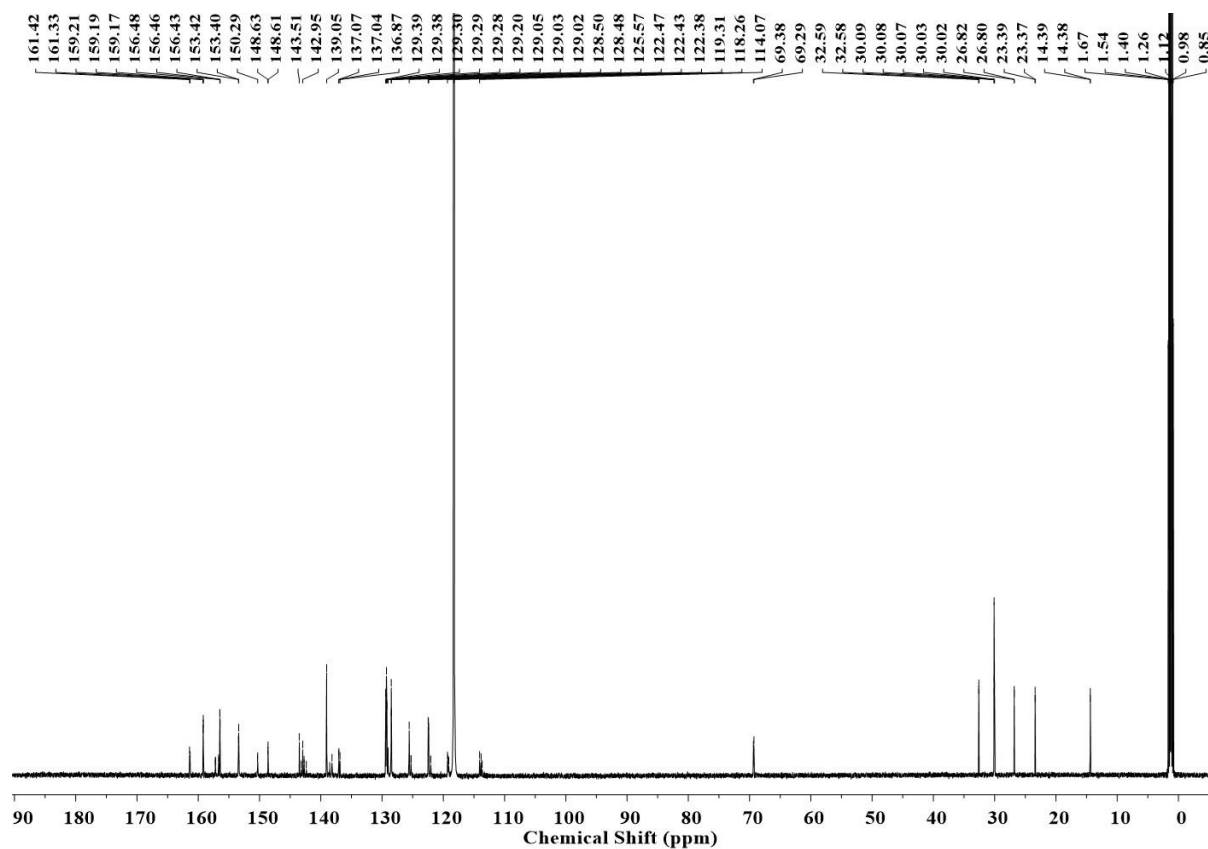


Figure S31. ^{13}C NMR (150 MHz, CD_3CN) spectrum of compound **6**.

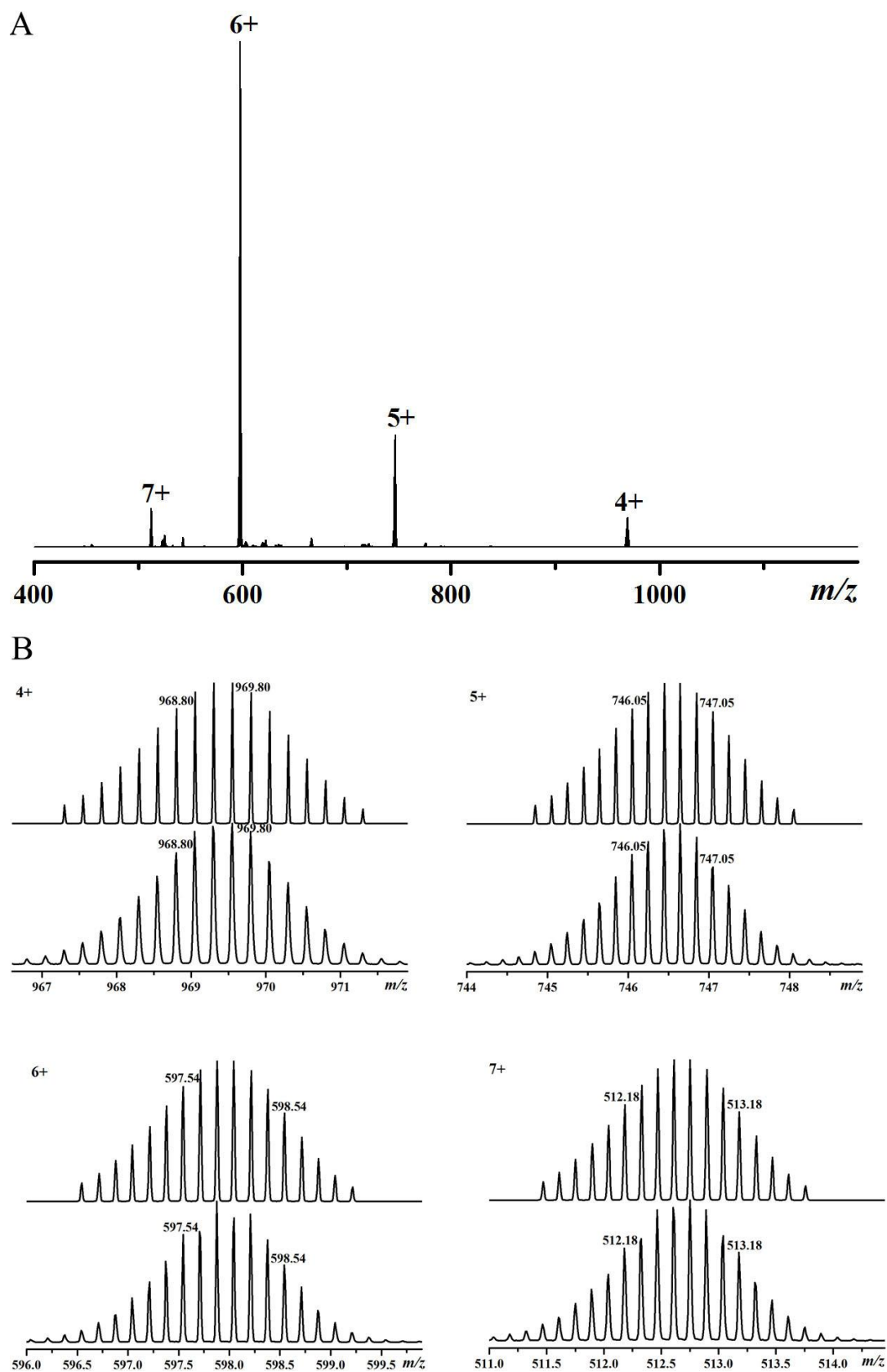


Figure S32. ESI-MS spectrum of compound **6** in CH₃CN (A). Experimental (bottom) and calculated (top) isotope patterns for different charge states (B).

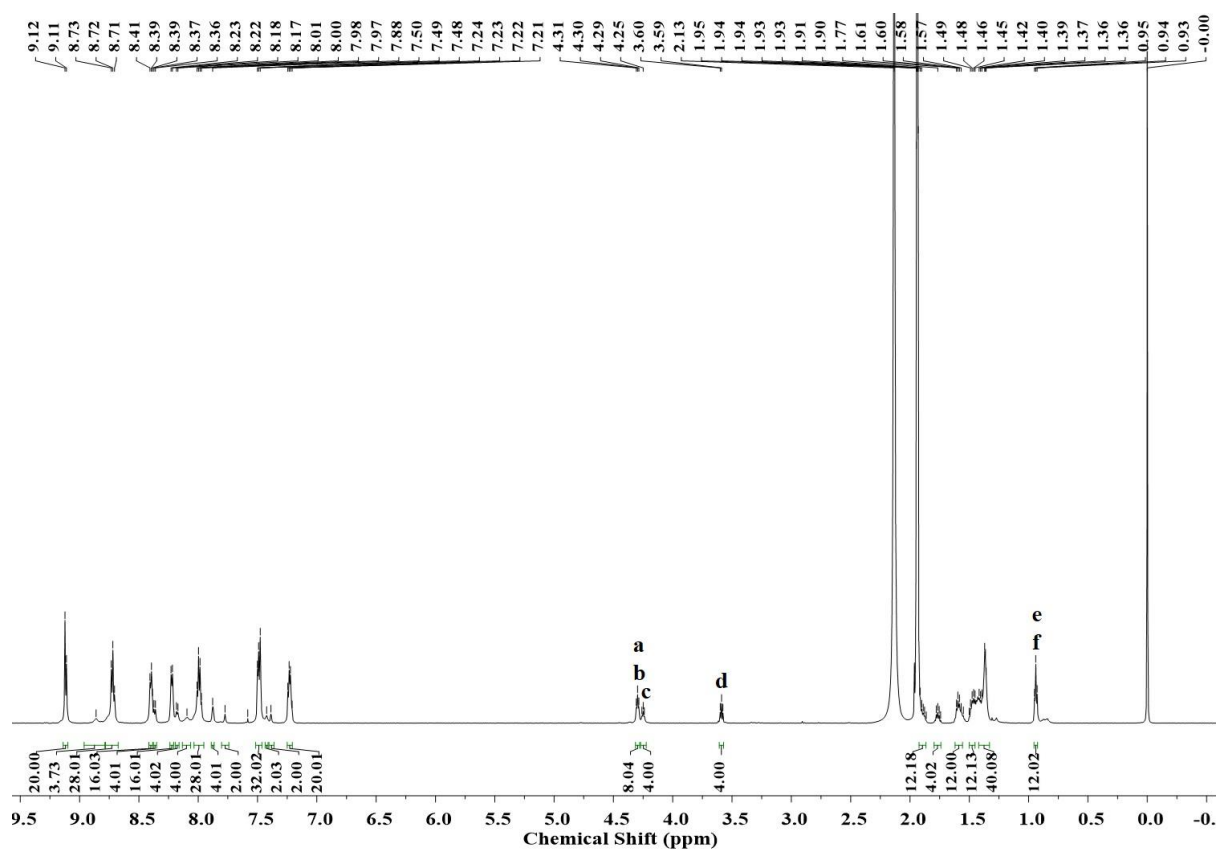


Figure S33. ^1H NMR (600 MHz, CD_3CN) spectrum of compound **8**.

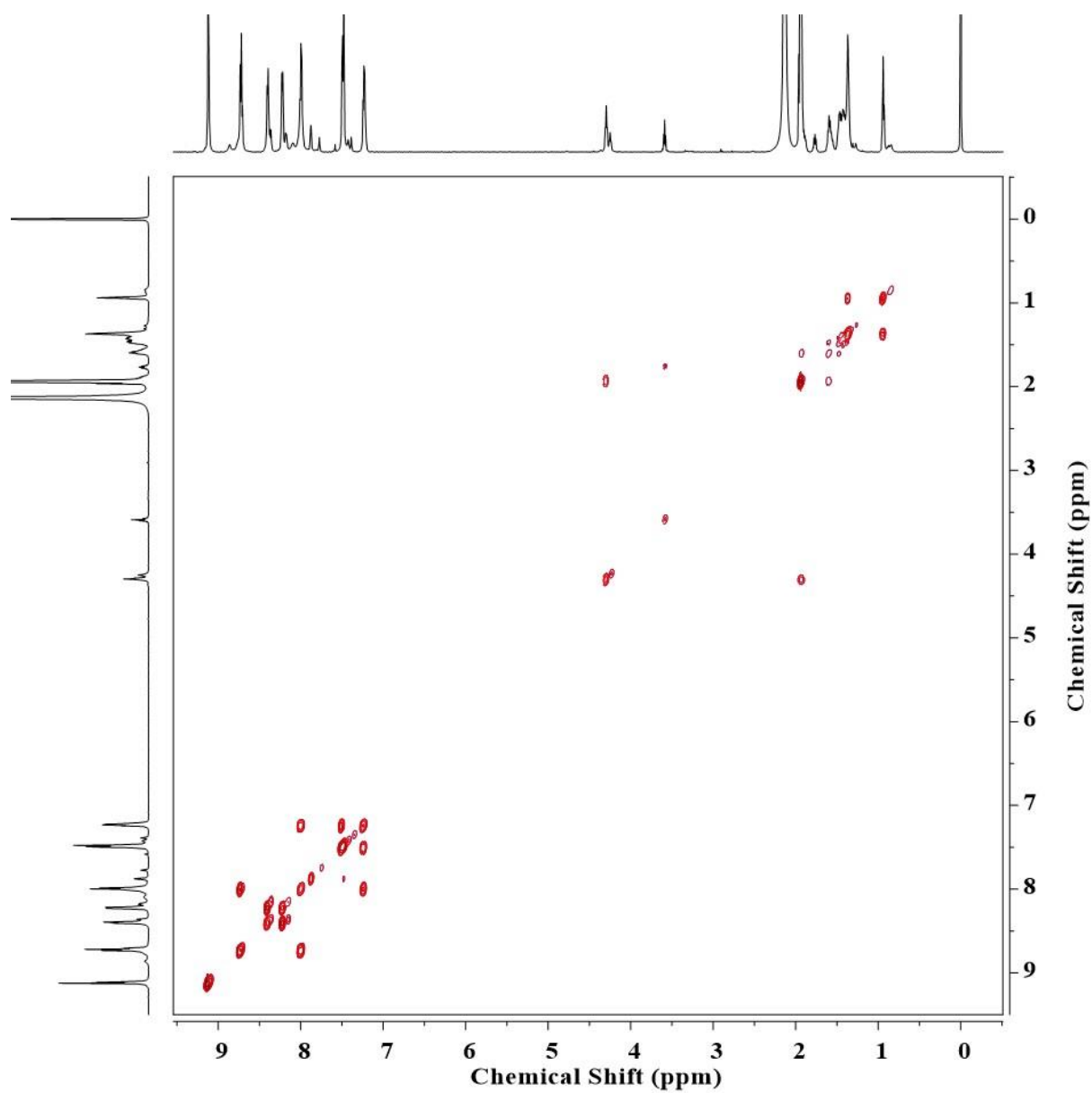


Figure S34. 2D COSY NMR (600 MHz, CD₃CN) spectrum of compound **8**.

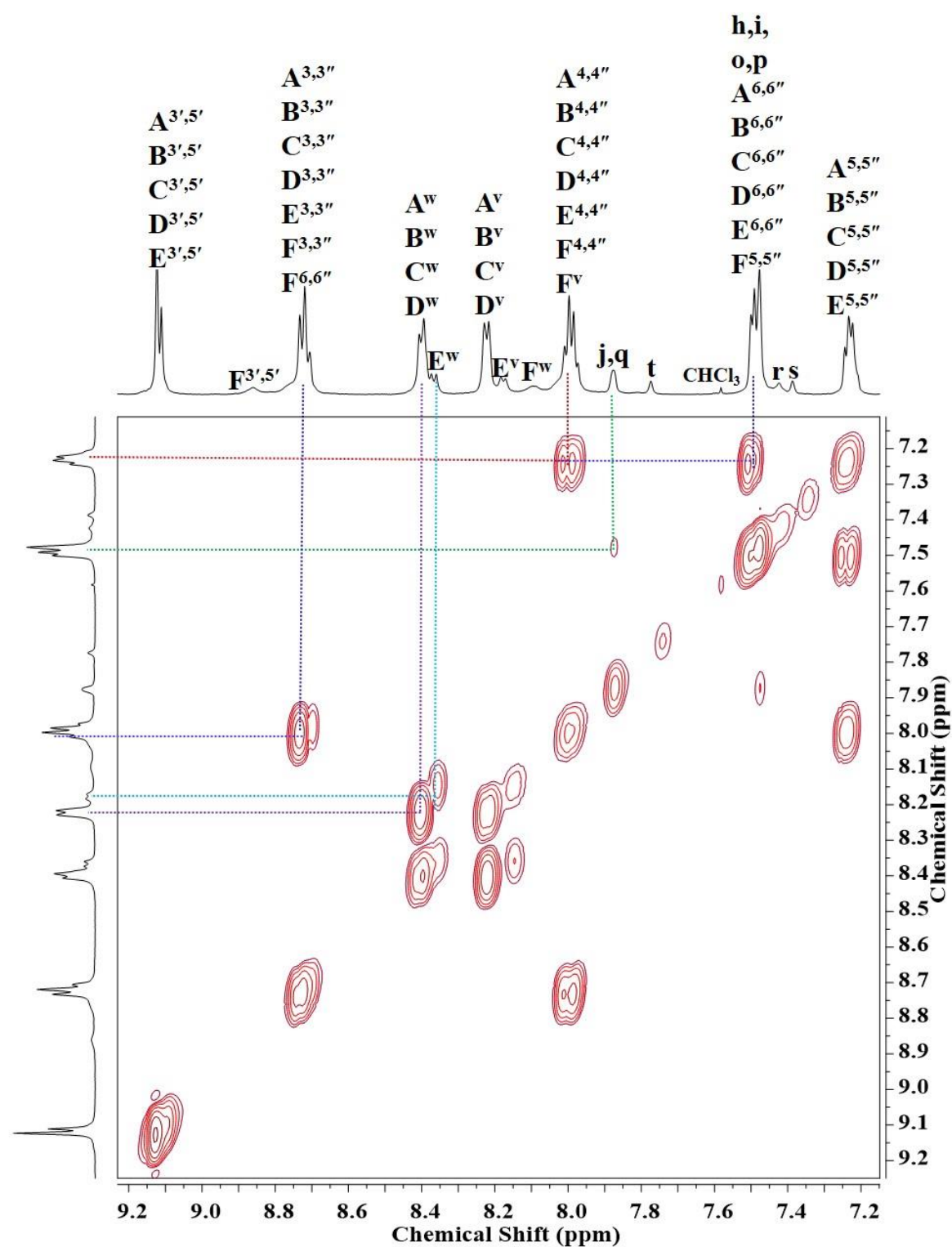


Figure S35. 2D COSY NMR (600 MHz, CD₃CN) spectrum of compound **8** (aromatic region).

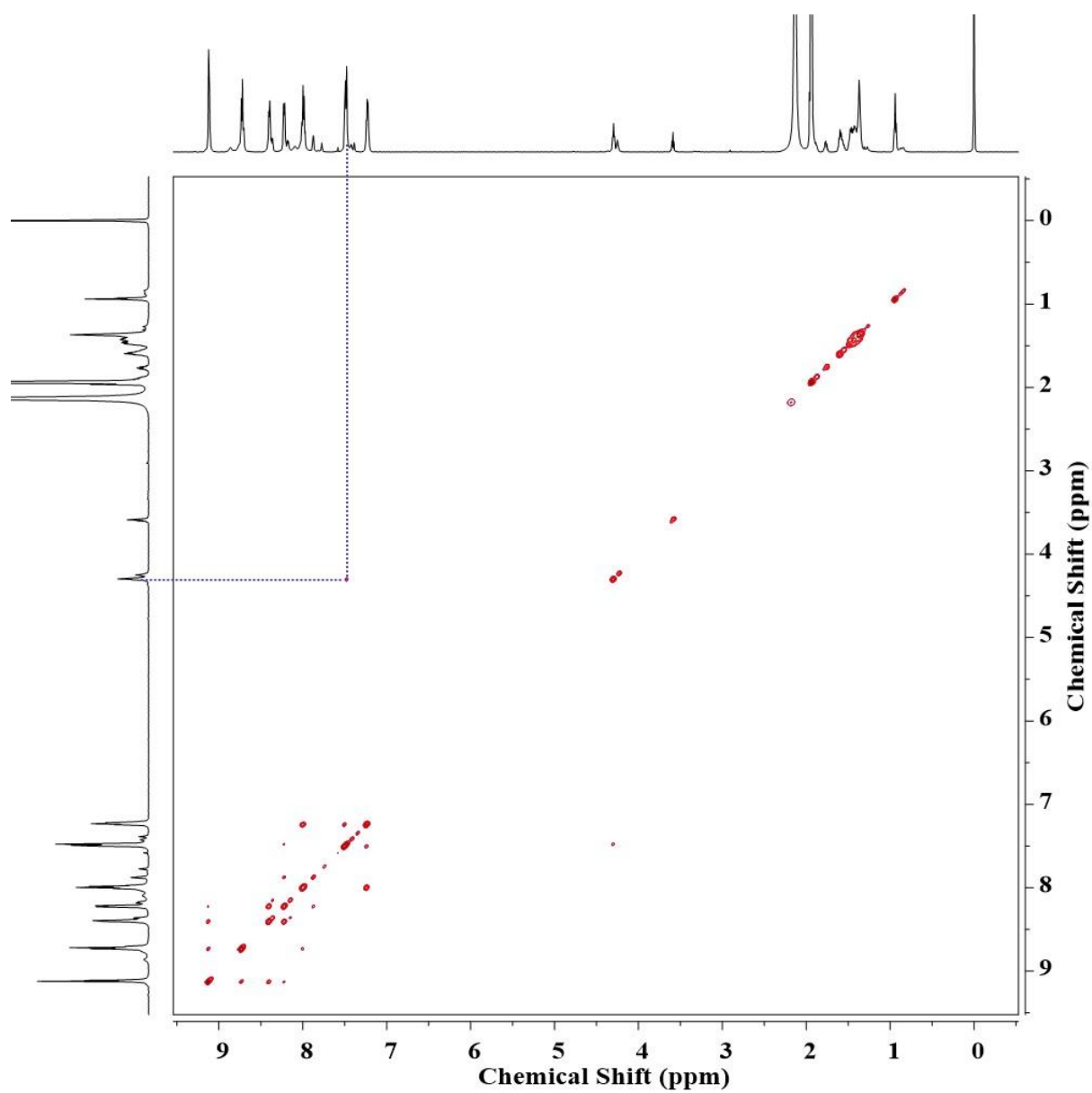


Figure S36. 2D NOESY NMR (600 MHz, CD₃CN) spectrum of compound **8**.

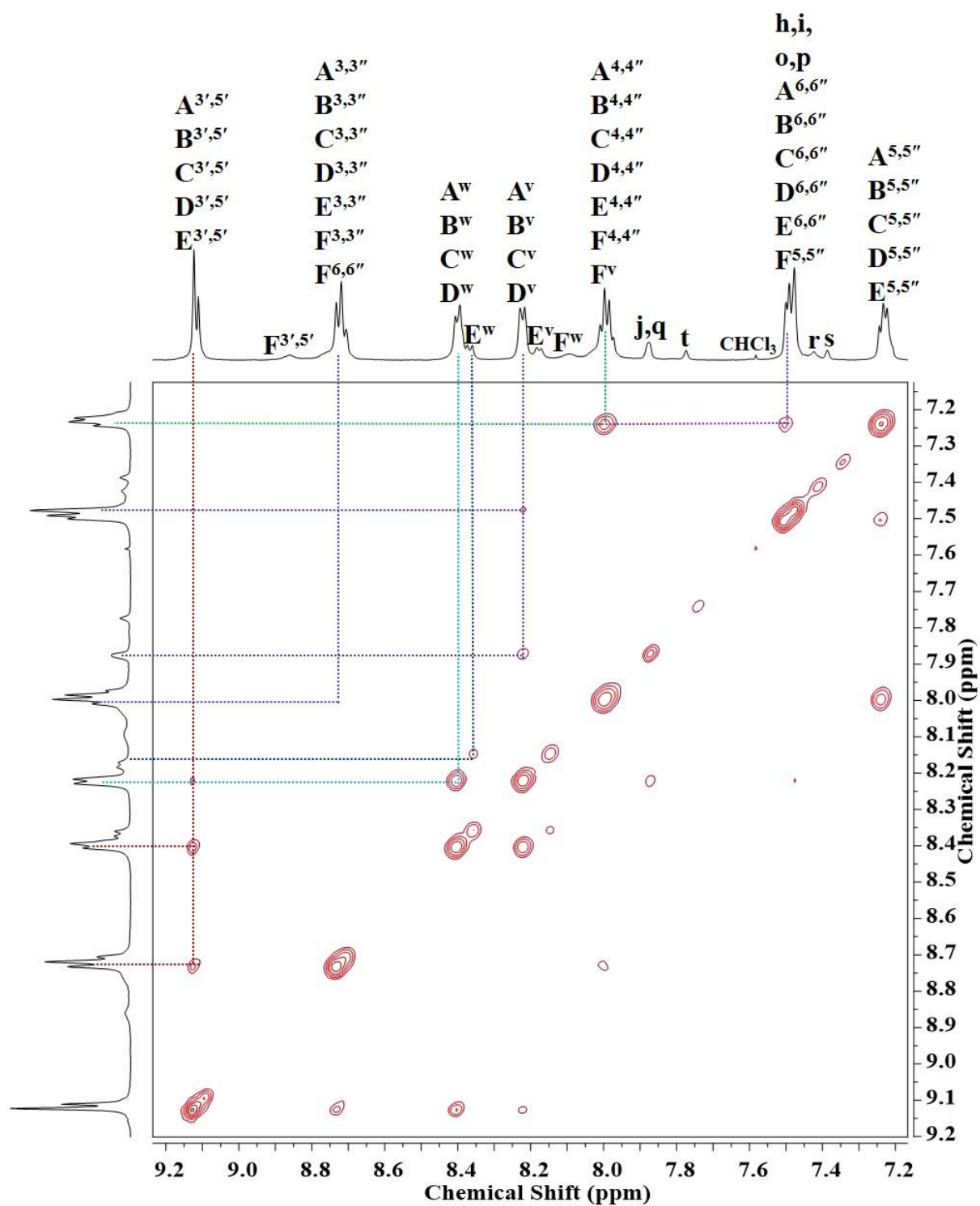


Figure S37. 2D NOESY NMR (600 MHz, CD₃CN) spectrum of compound **8** (aromatic region).

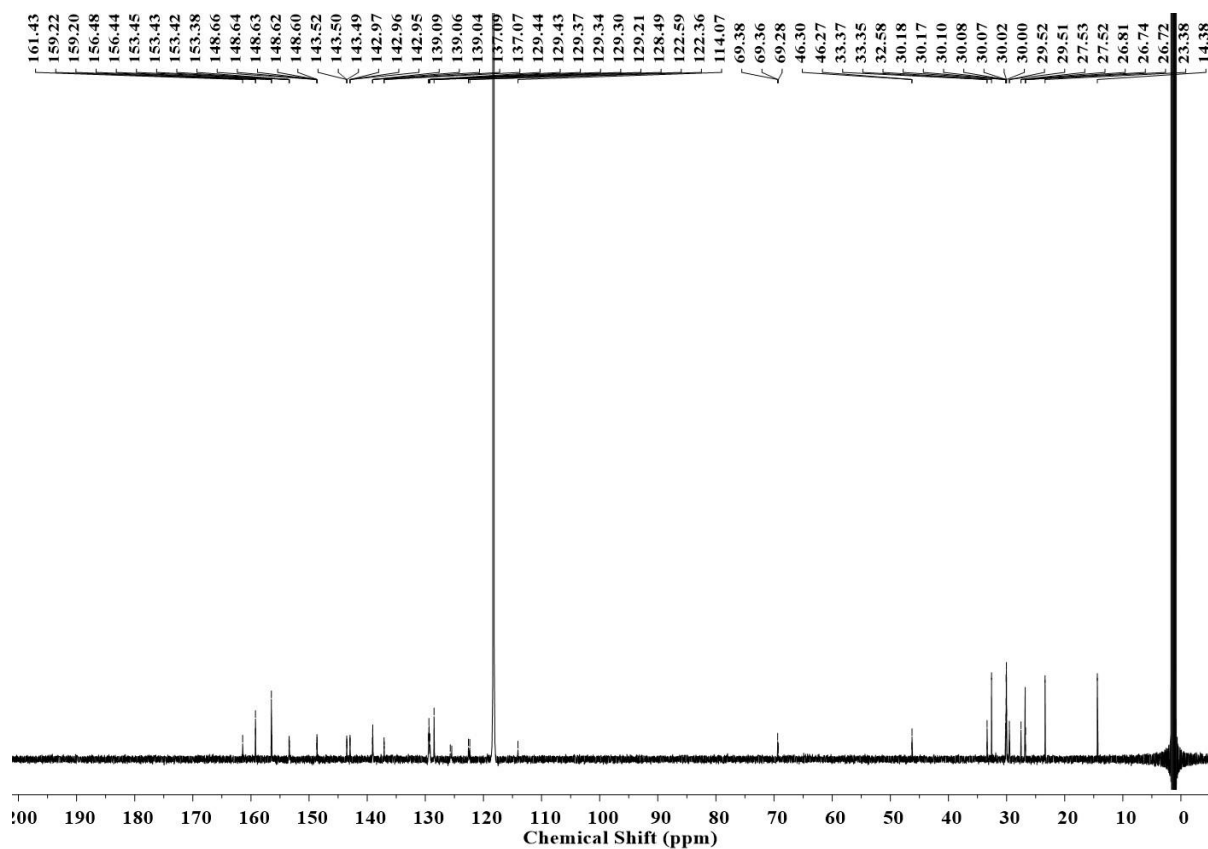


Figure S38. ^{13}C NMR (150 MHz, CD_3CN) spectrum of compound **8**.

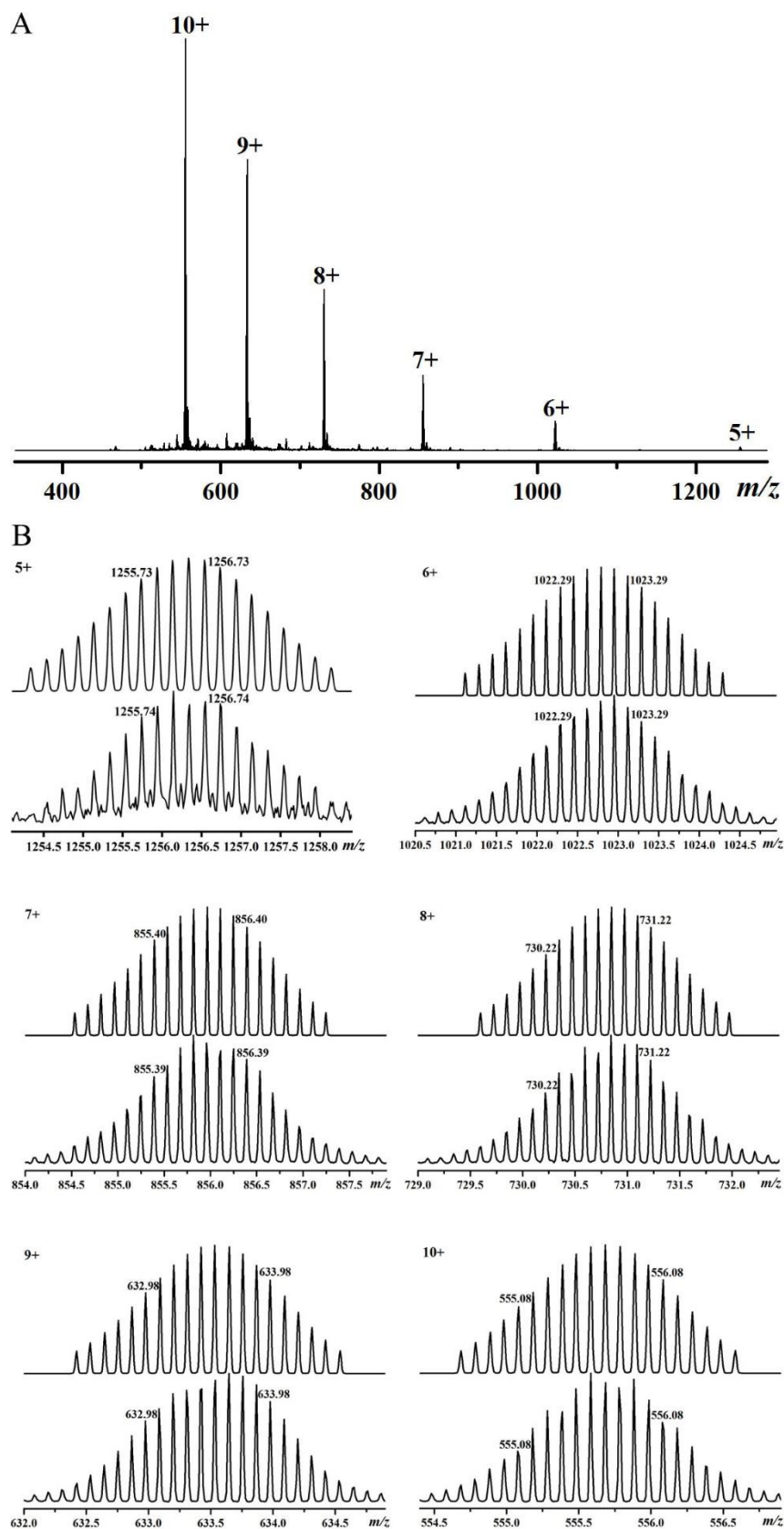


Figure S39. ESI-MS spectrum of compound **8** in CH₃CN (A). Experimental (bottom) and calculated (top) isotope patterns for different charge states (B).

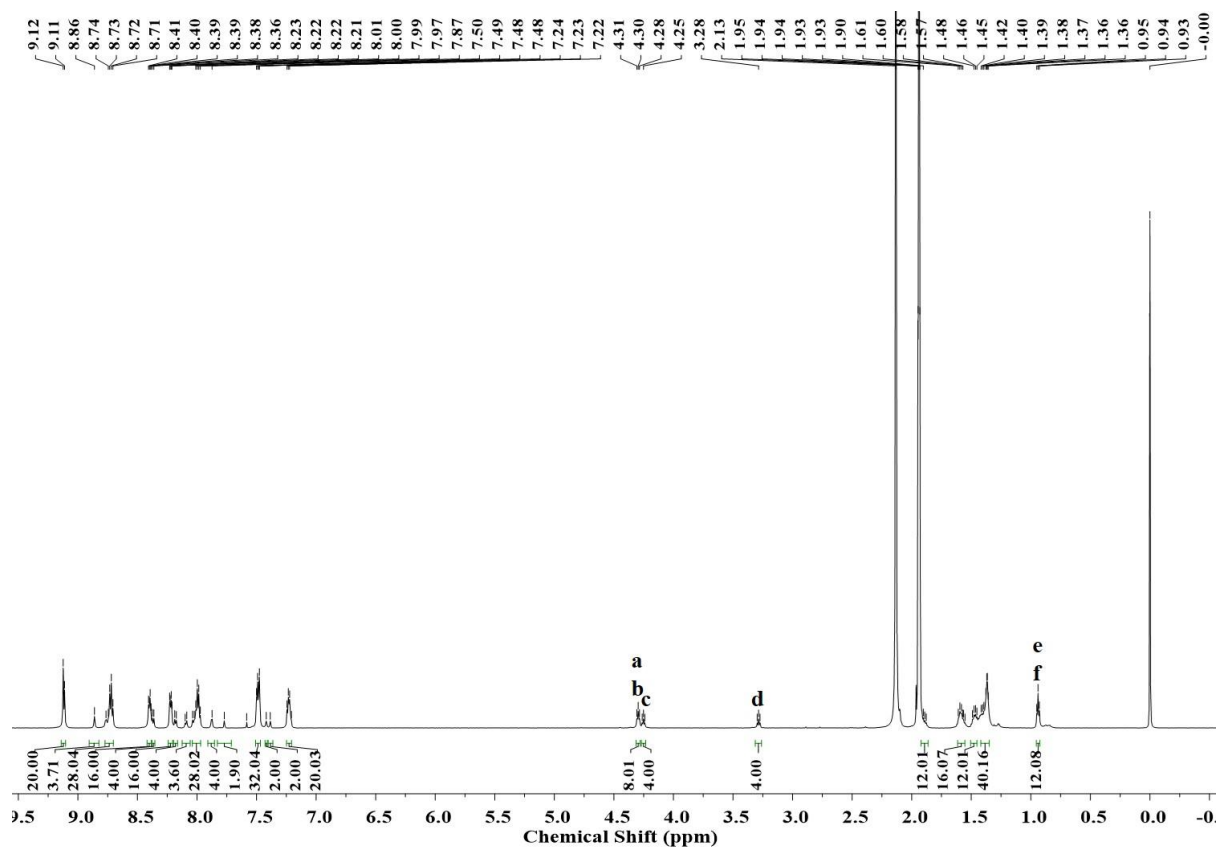


Figure S40. ^1H NMR (600 MHz, CD_3CN) spectrum of compound **9** (Hex-M).

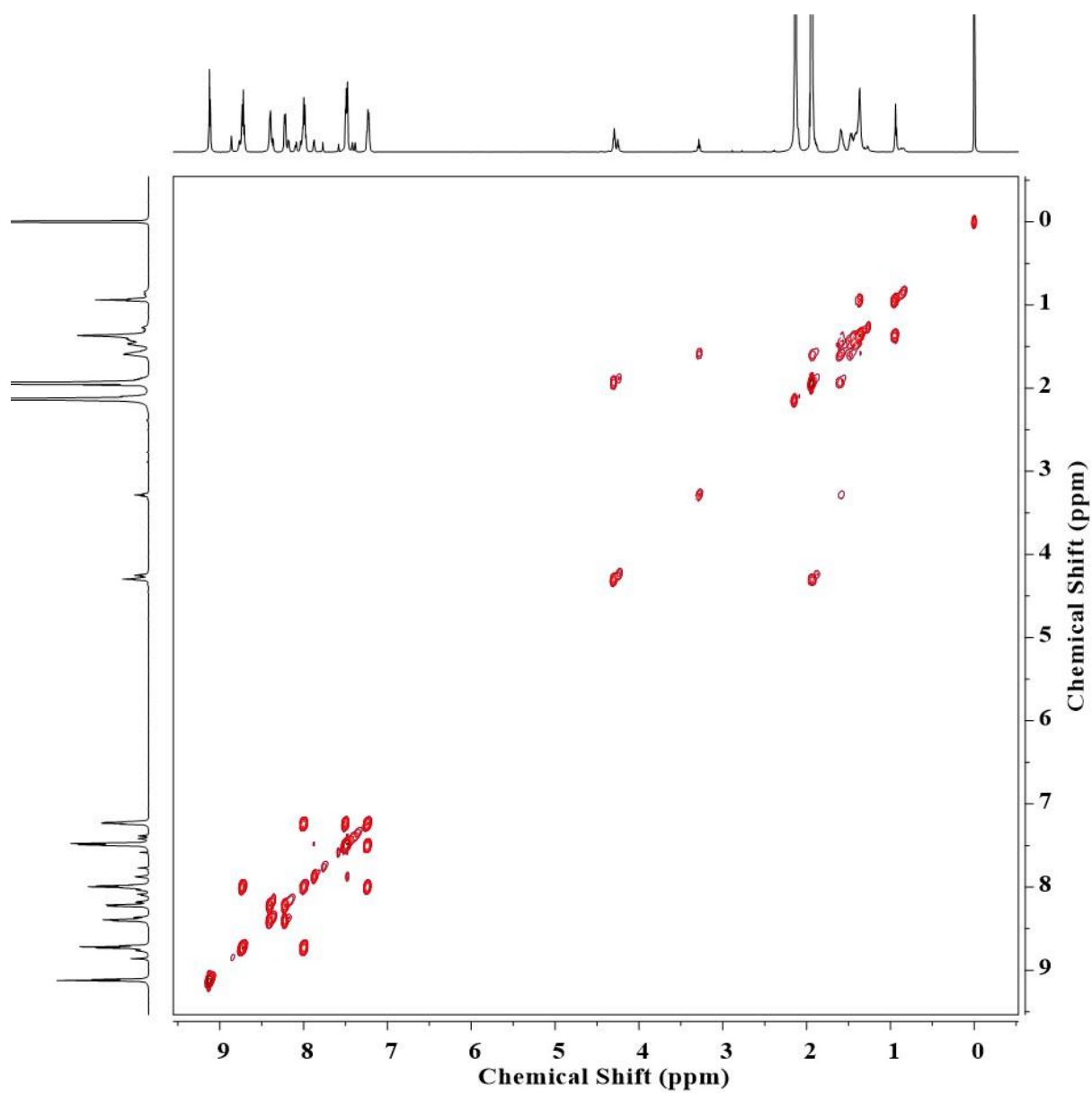


Figure S41. 2D COSY NMR (600 MHz, CD₃CN) spectrum of compound **9** (Hex-M).

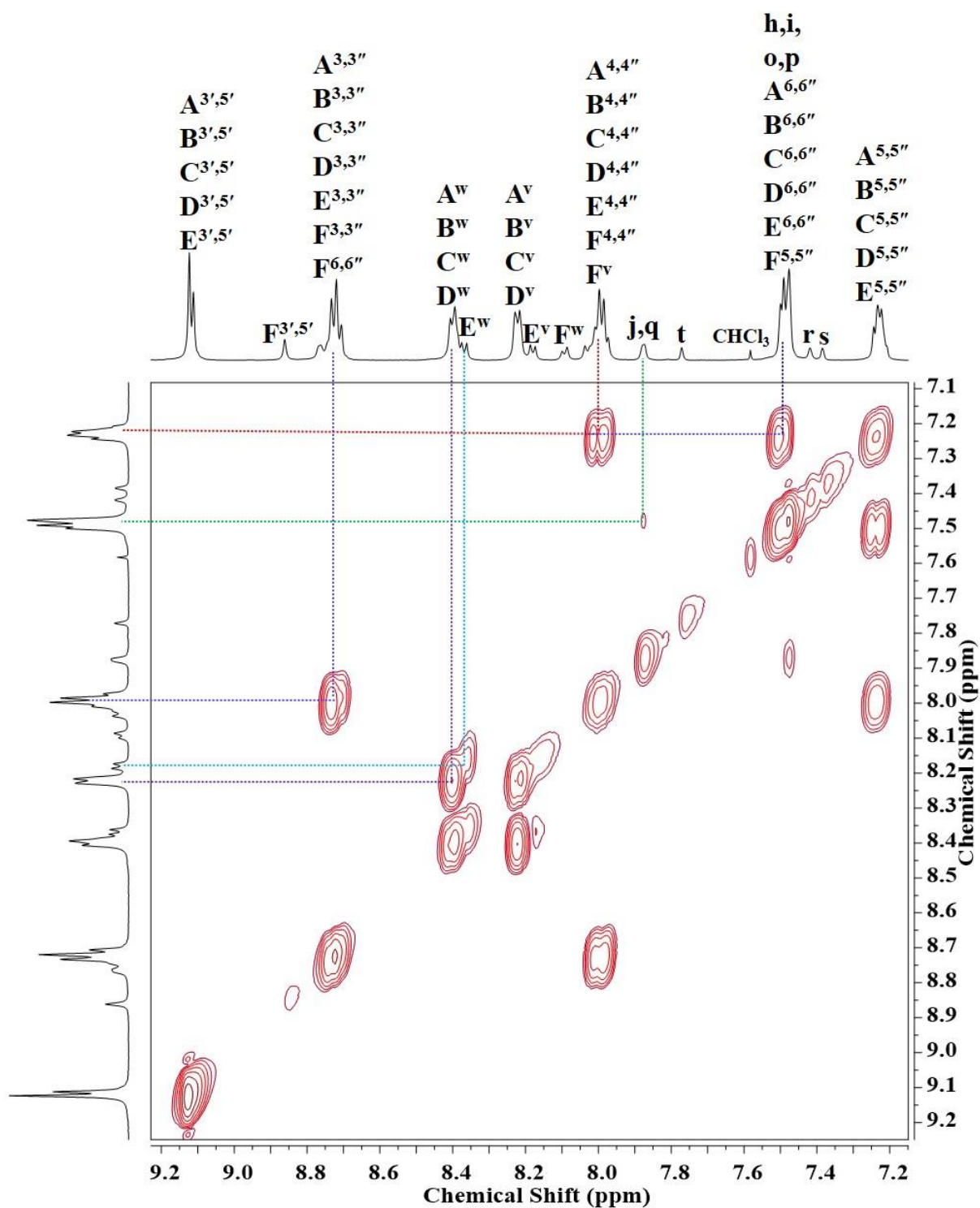


Figure S42. 2D COSY NMR (600 MHz, CD_3CN) spectrum of compound **9** (Hex-M) (aromatic region).

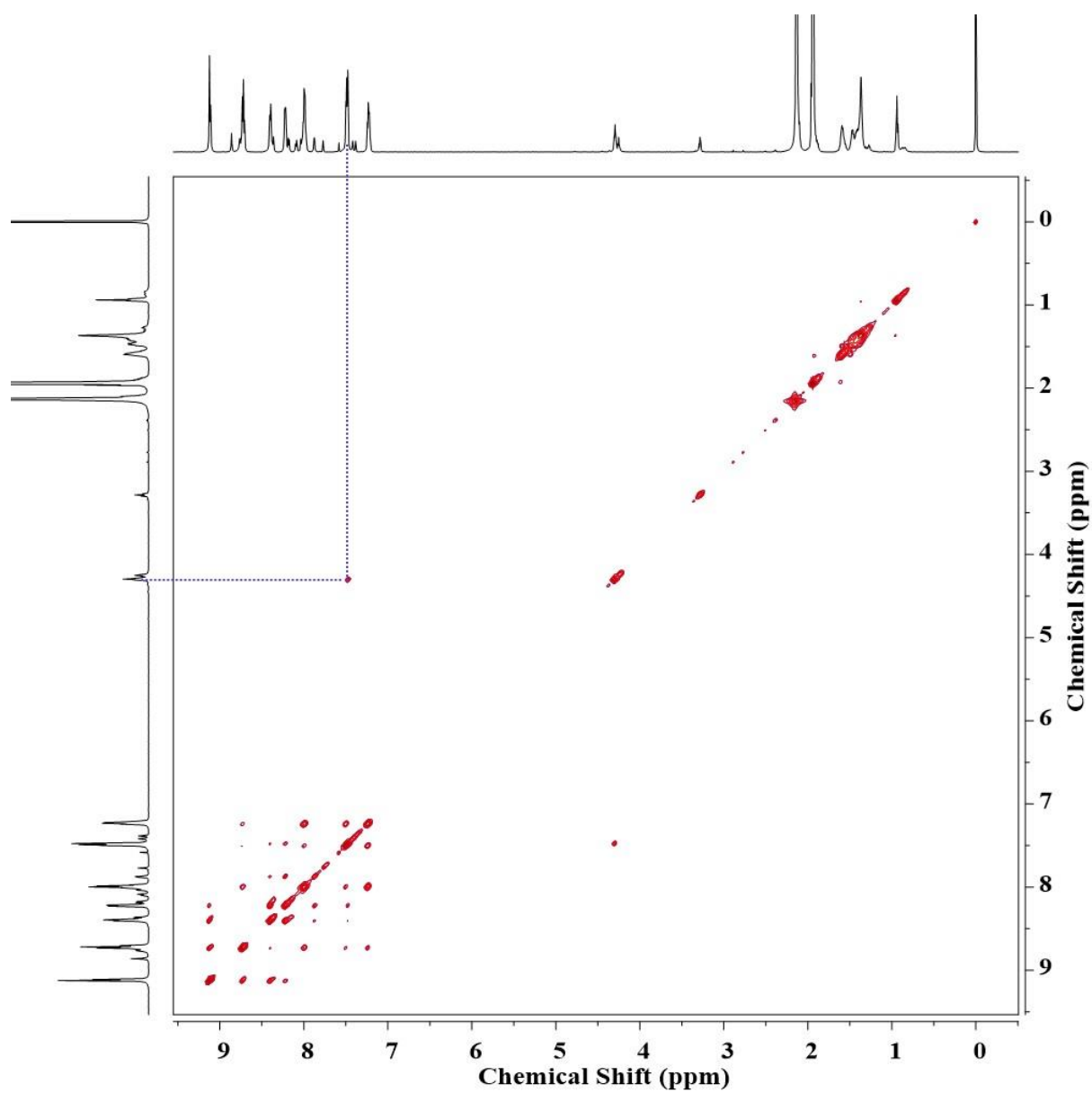


Figure S43. 2D NOESY NMR (600 MHz, CD₃CN) spectrum of compound **9** (Hex-M).

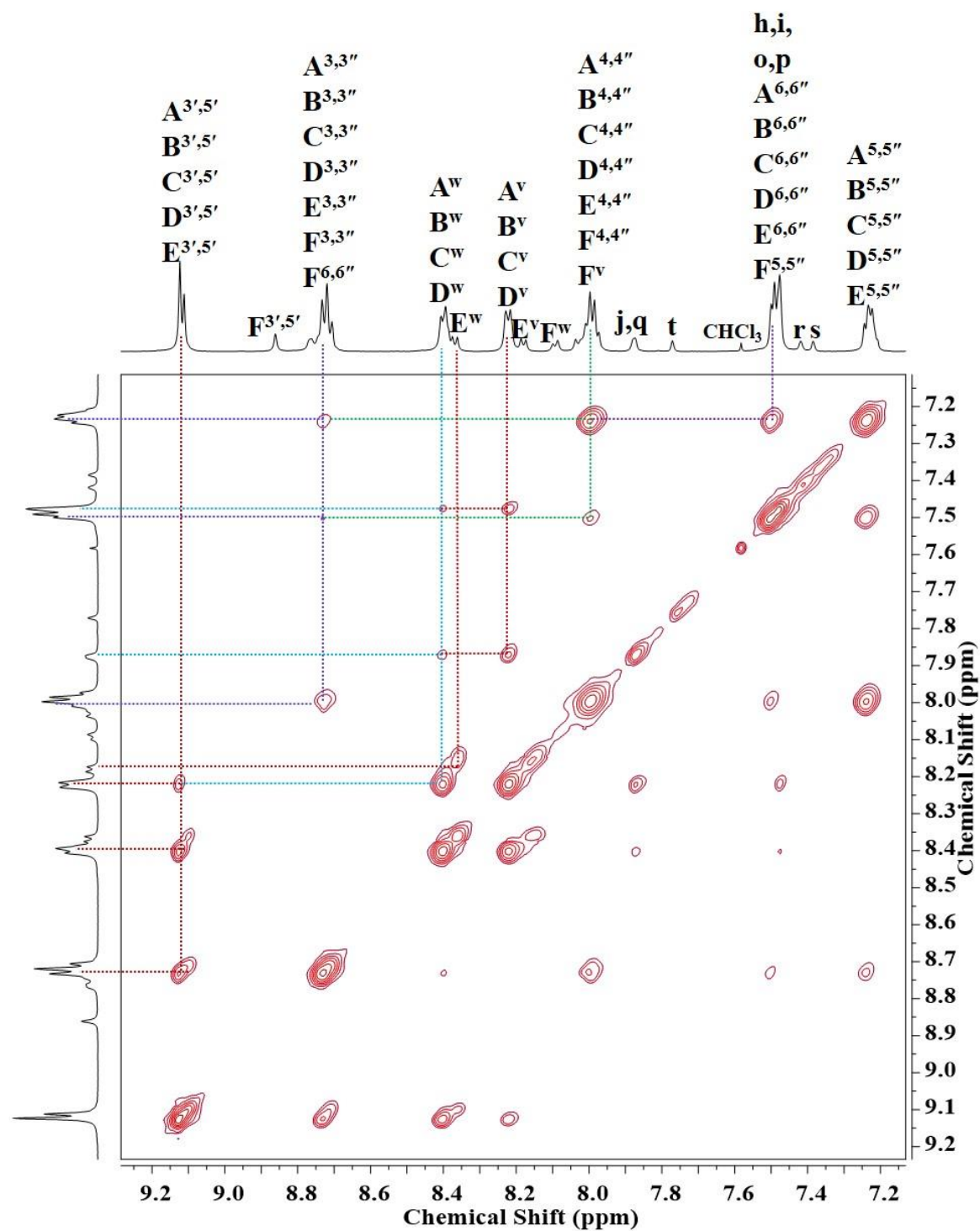


Figure S44. 2D NOESY NMR (600 MHz, CD_3CN) spectrum of compound 9 (Hex-M) (aromatic region).

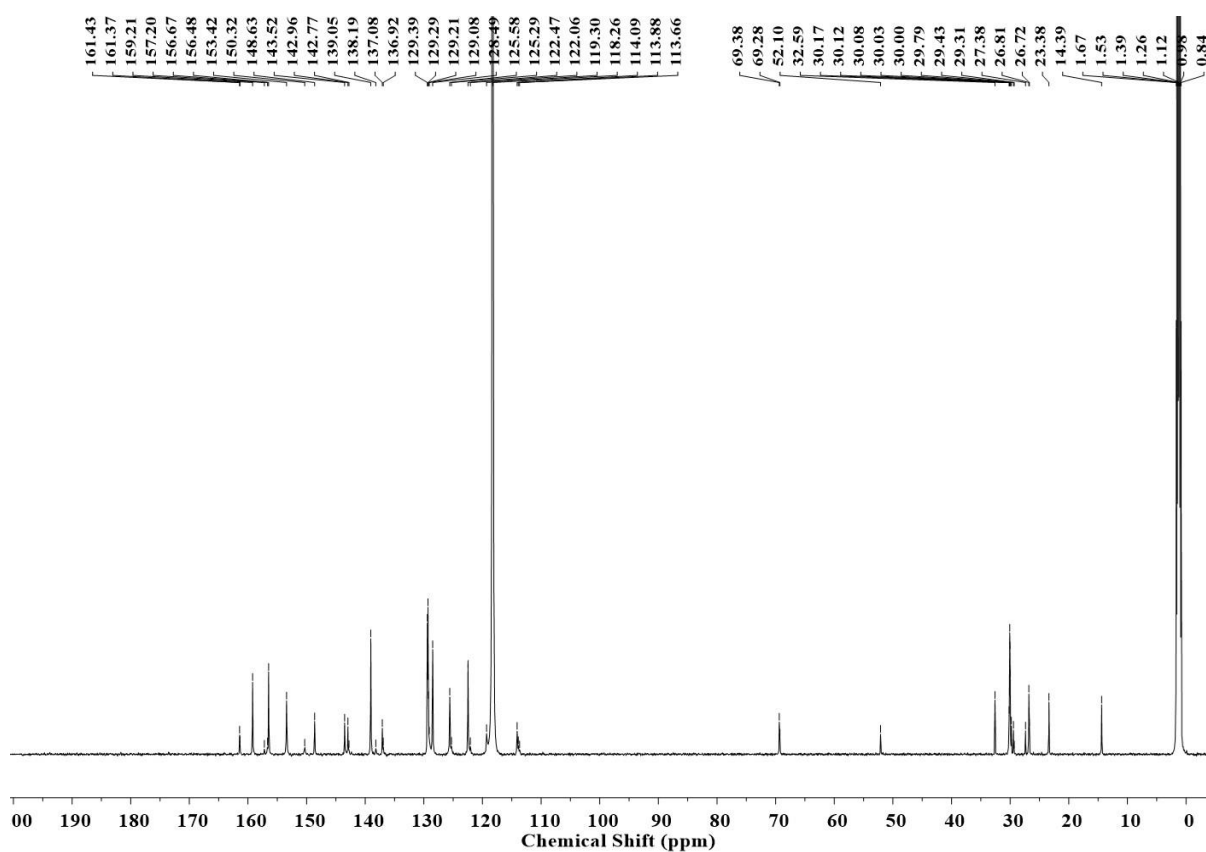


Figure S45. ^{13}C NMR (150 MHz, CD_3CN) spectrum of compound **9** (Hex-M).

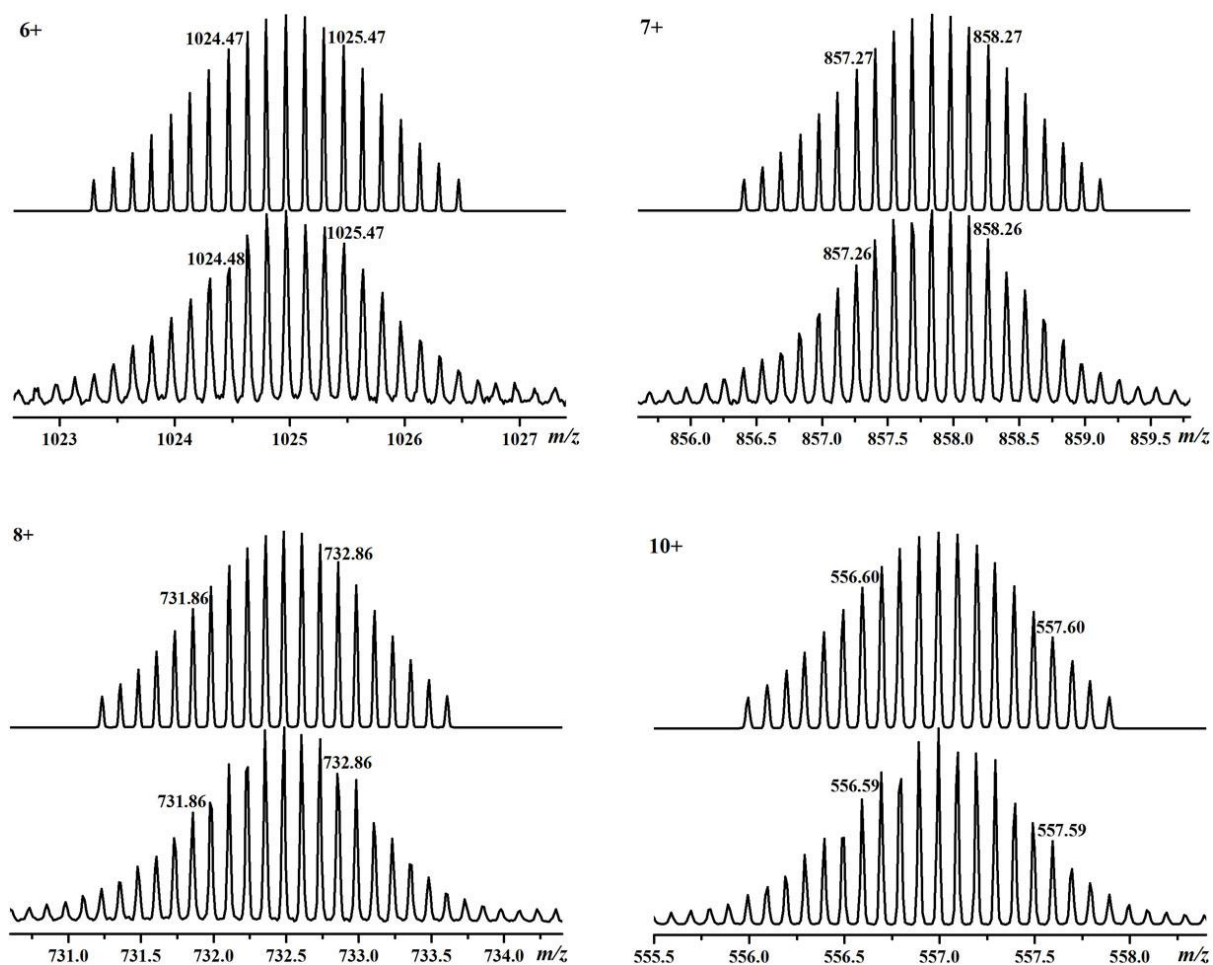


Figure S46. Experimental (bottom) and calculated (top) isotope patterns of compound **9** (Hex-M) in CH₃CN for different charge states.

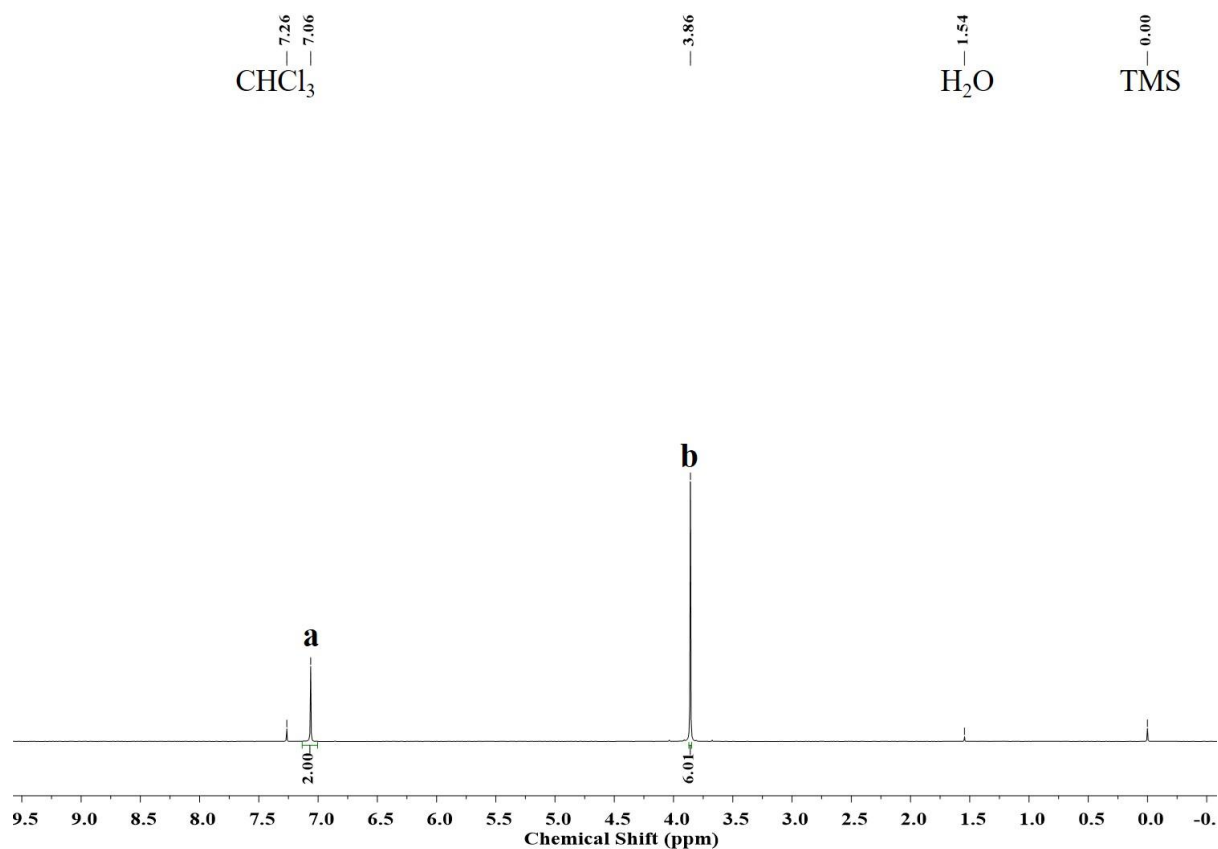


Figure S47. ^1H NMR (400 MHz, CDCl_3) spectrum of compound **10**.

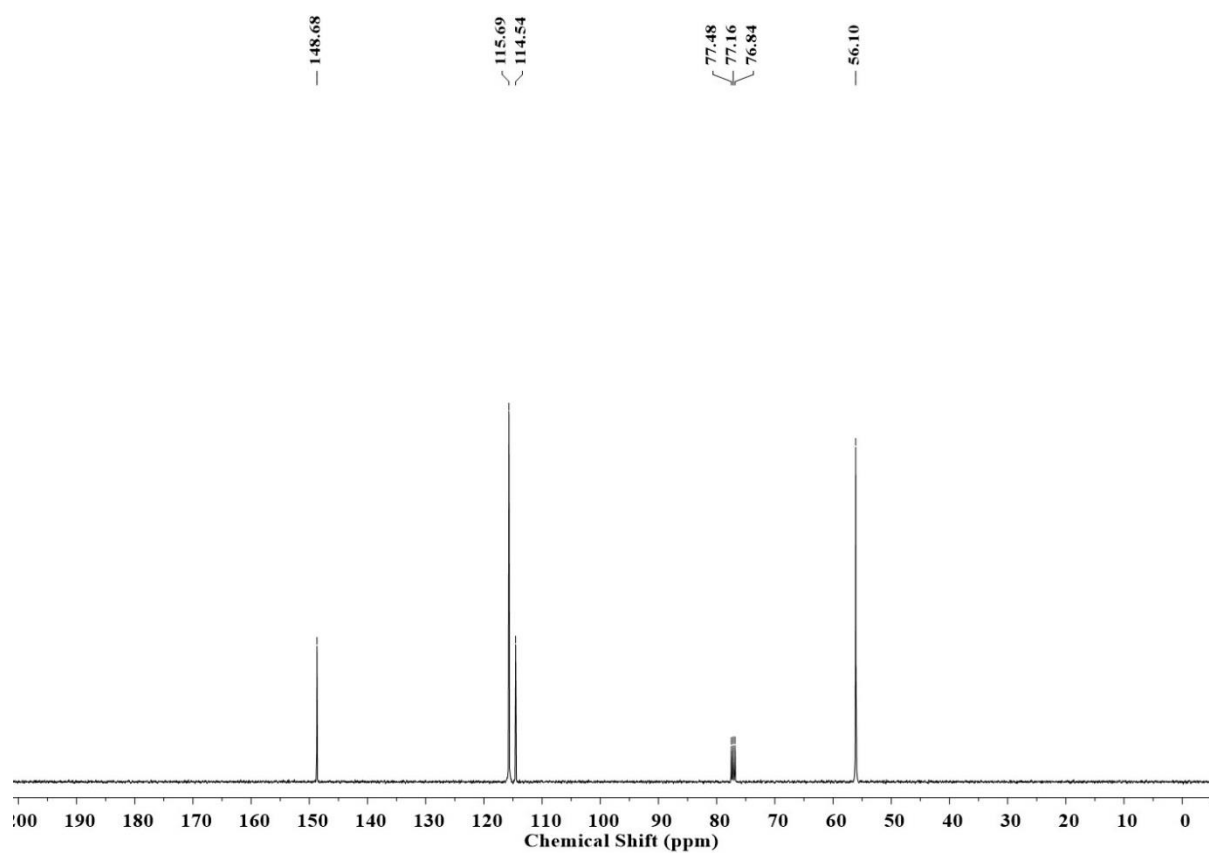


Figure S48. ^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **10**.

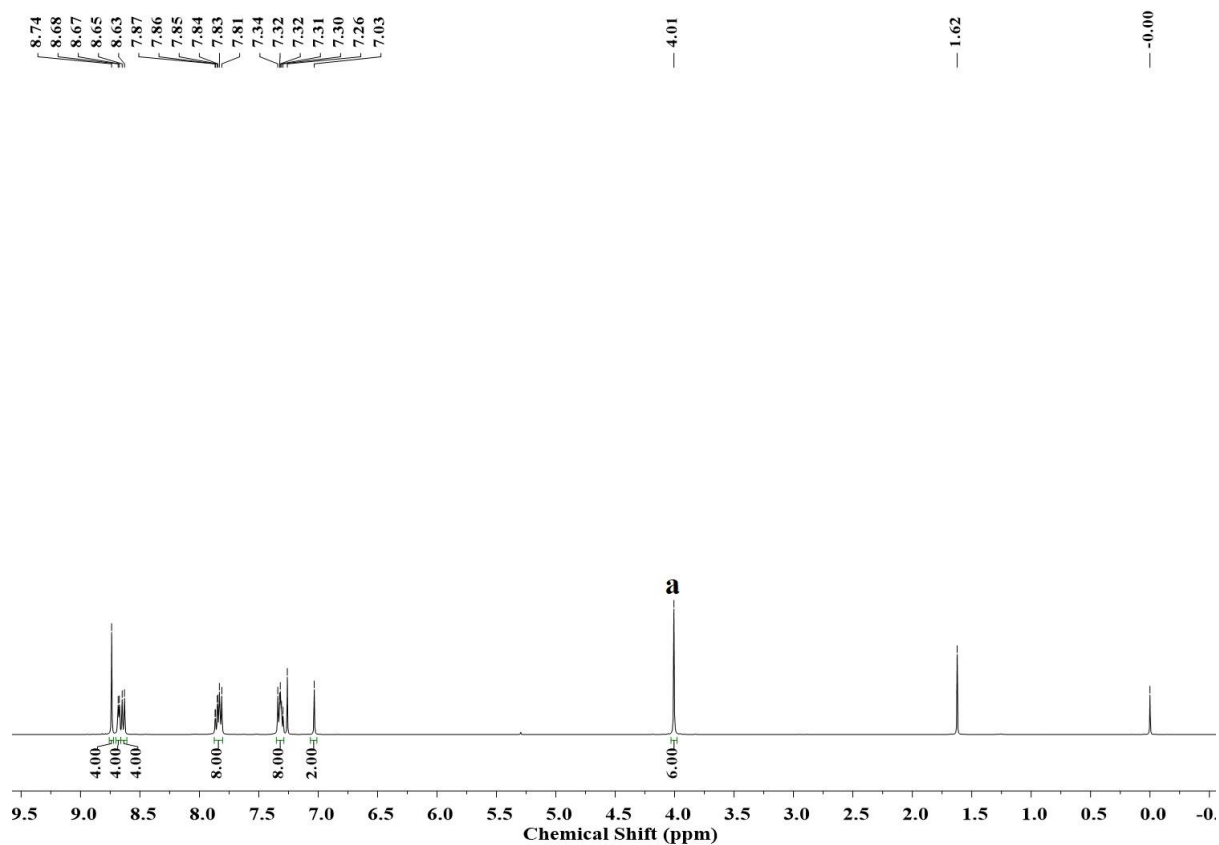


Figure S49. ^1H NMR (400 MHz, CDCl_3) spectrum of compound **11**.

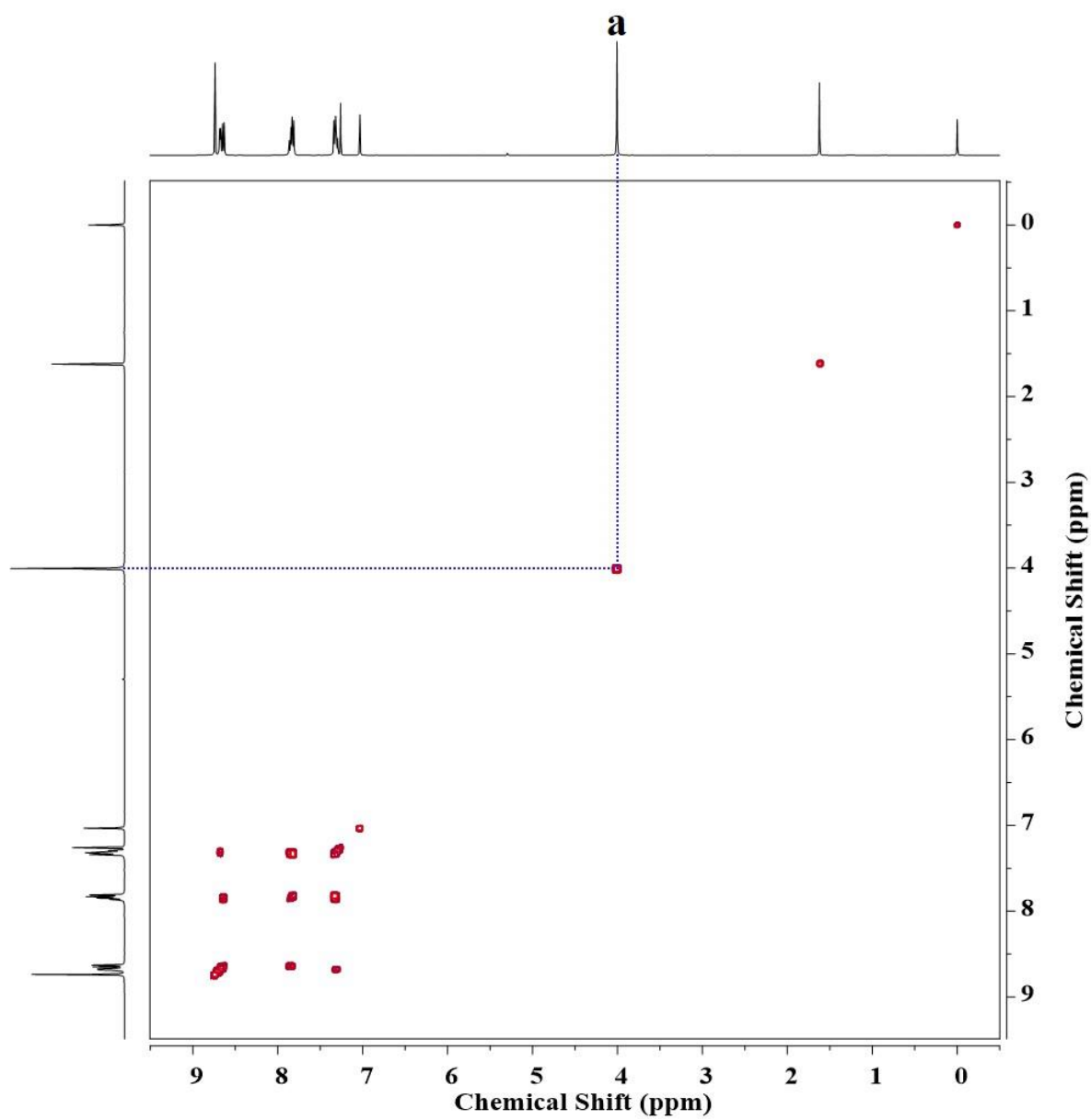


Figure S50. 2D COSY NMR (400 MHz, CDCl₃) spectrum of compound 11.

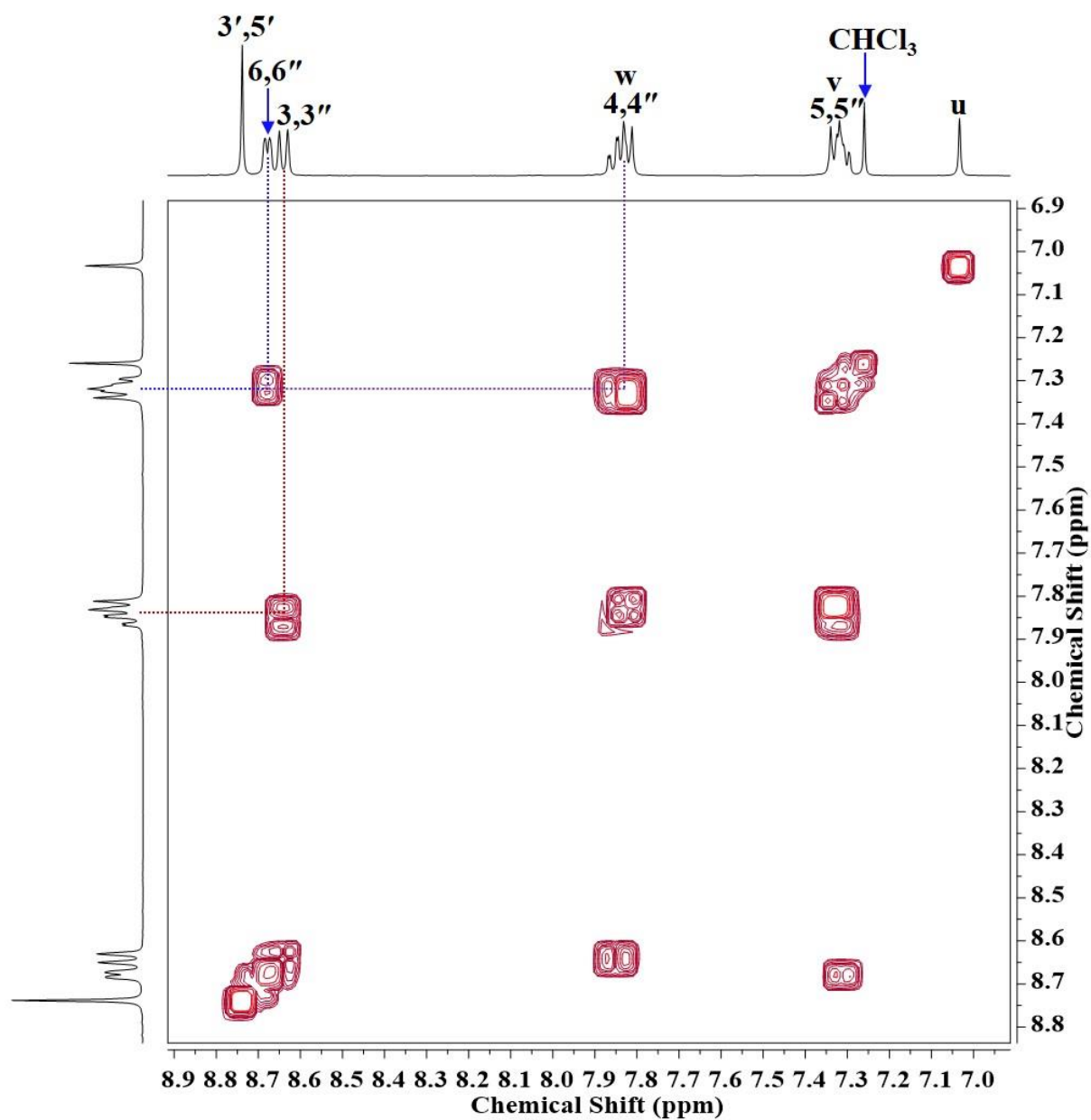


Figure S51. 2D COSY NMR (400 MHz, CDCl₃) spectrum of compound **11** (aromatic region).

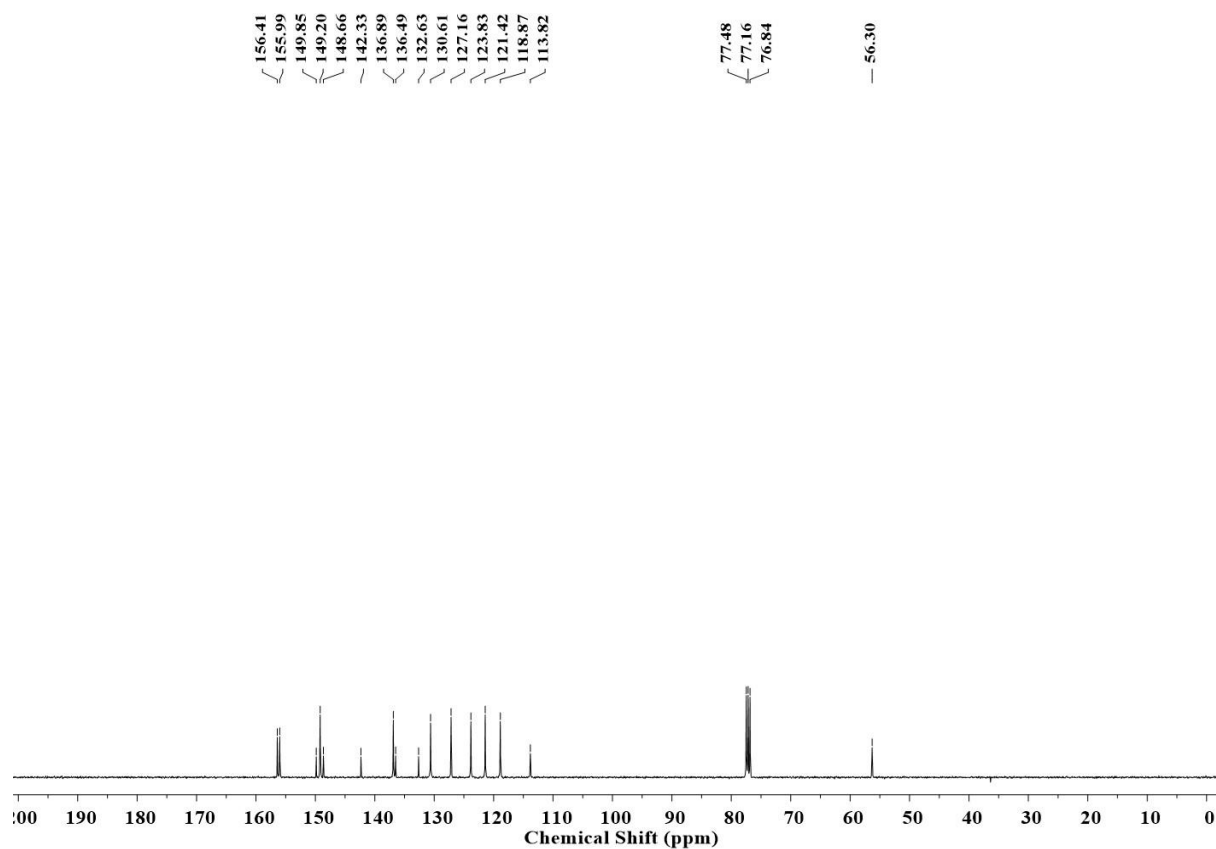


Figure S52. ^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **11**.

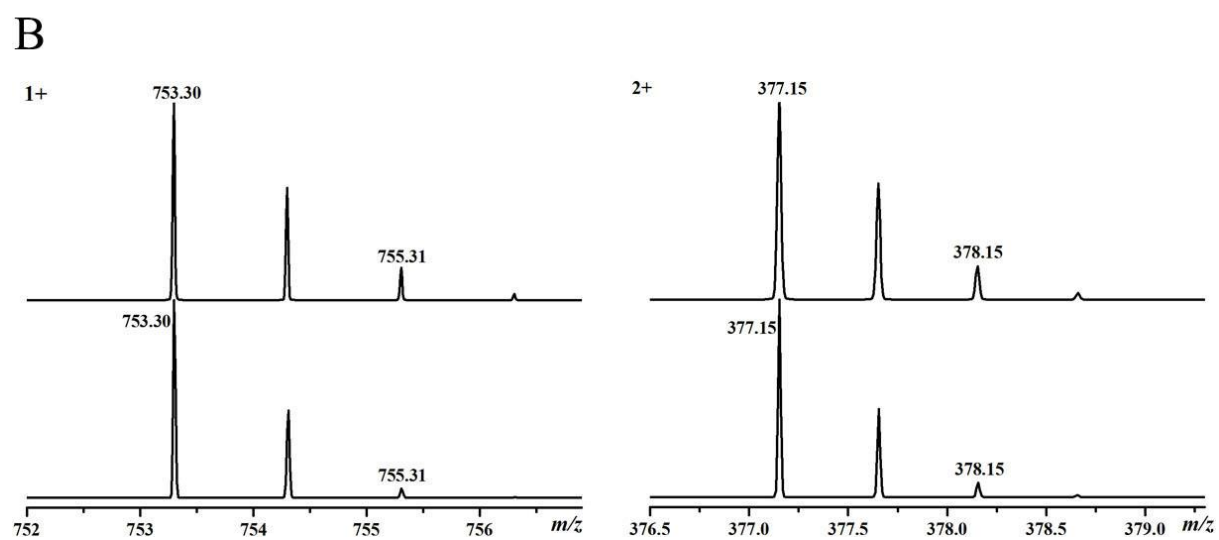
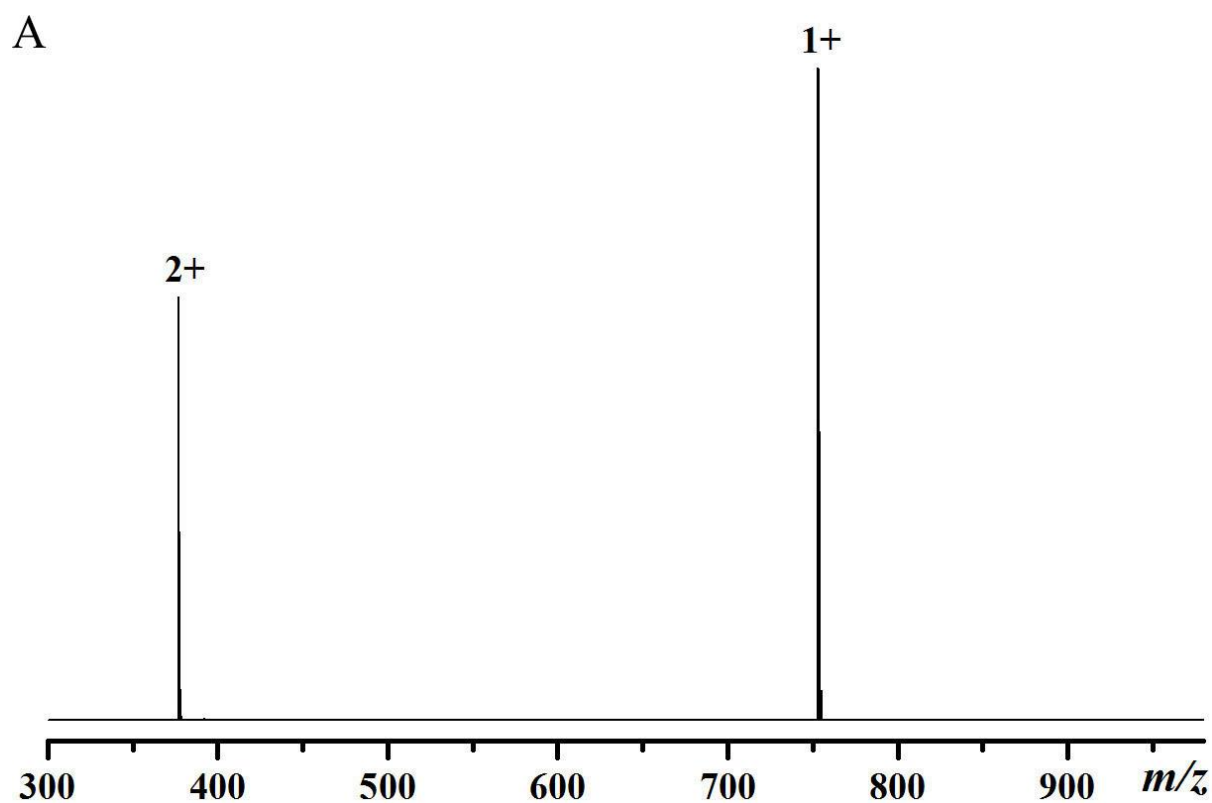


Figure S53. ESI-MS spectrum of compound **11** in CHCl_3 (A). Experimental (bottom) and calculated (top) isotope patterns for different charge states (B).

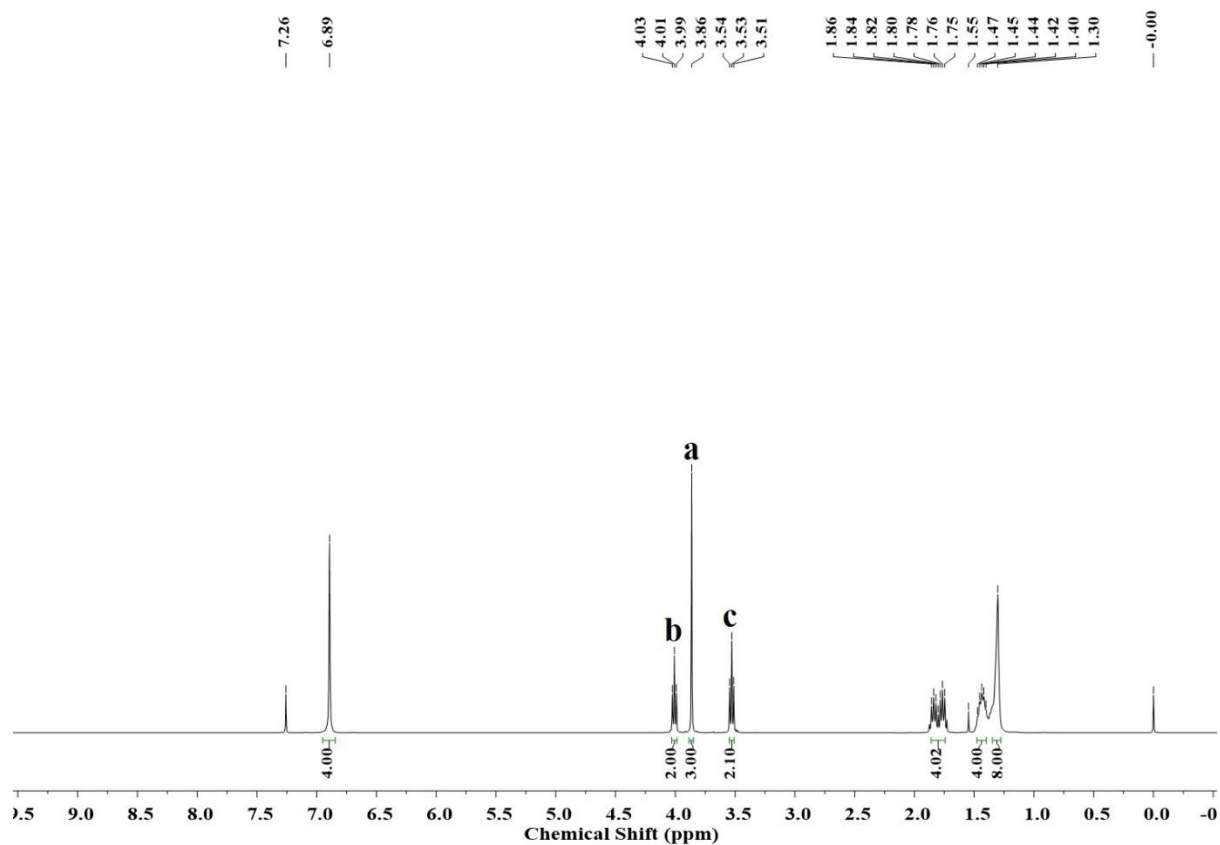


Figure S54. ^1H NMR (400 MHz, CDCl_3) spectrum of compound **12**.

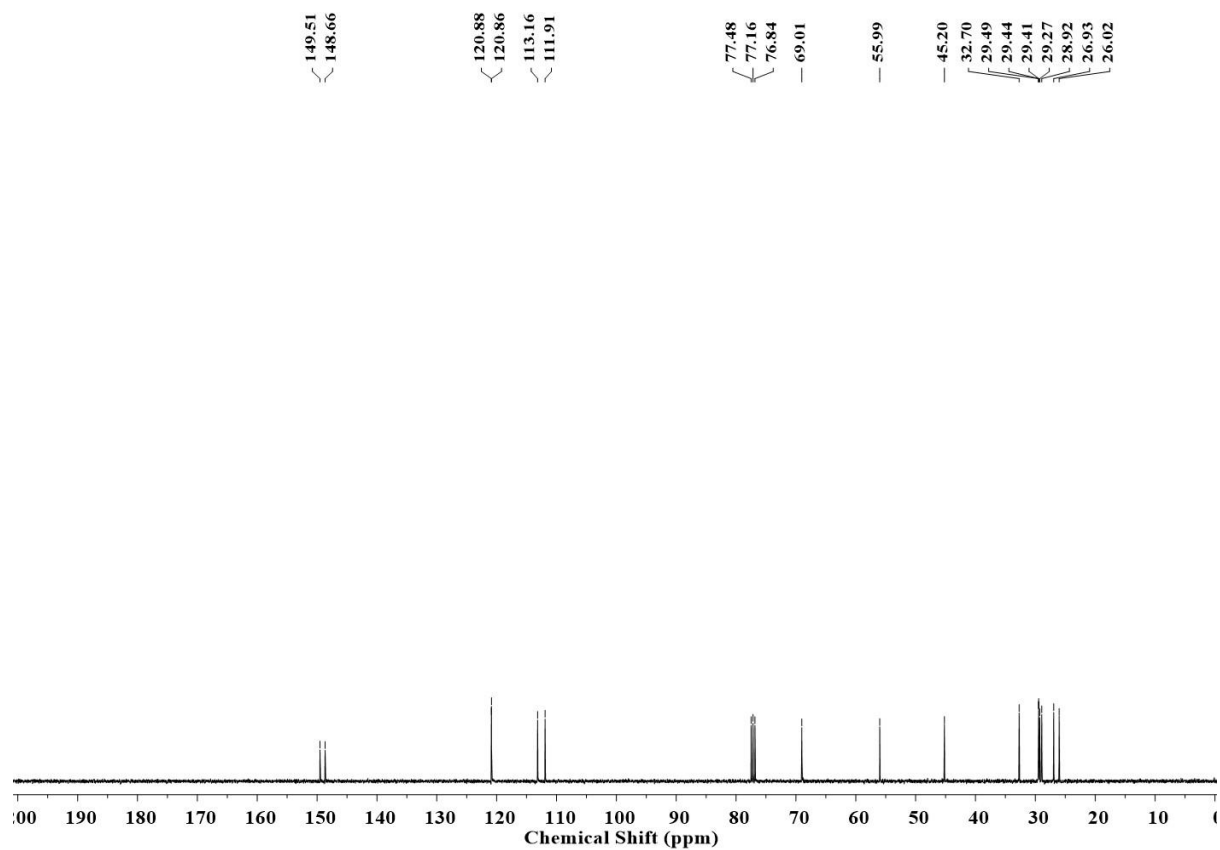


Figure S55. ^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **12**.

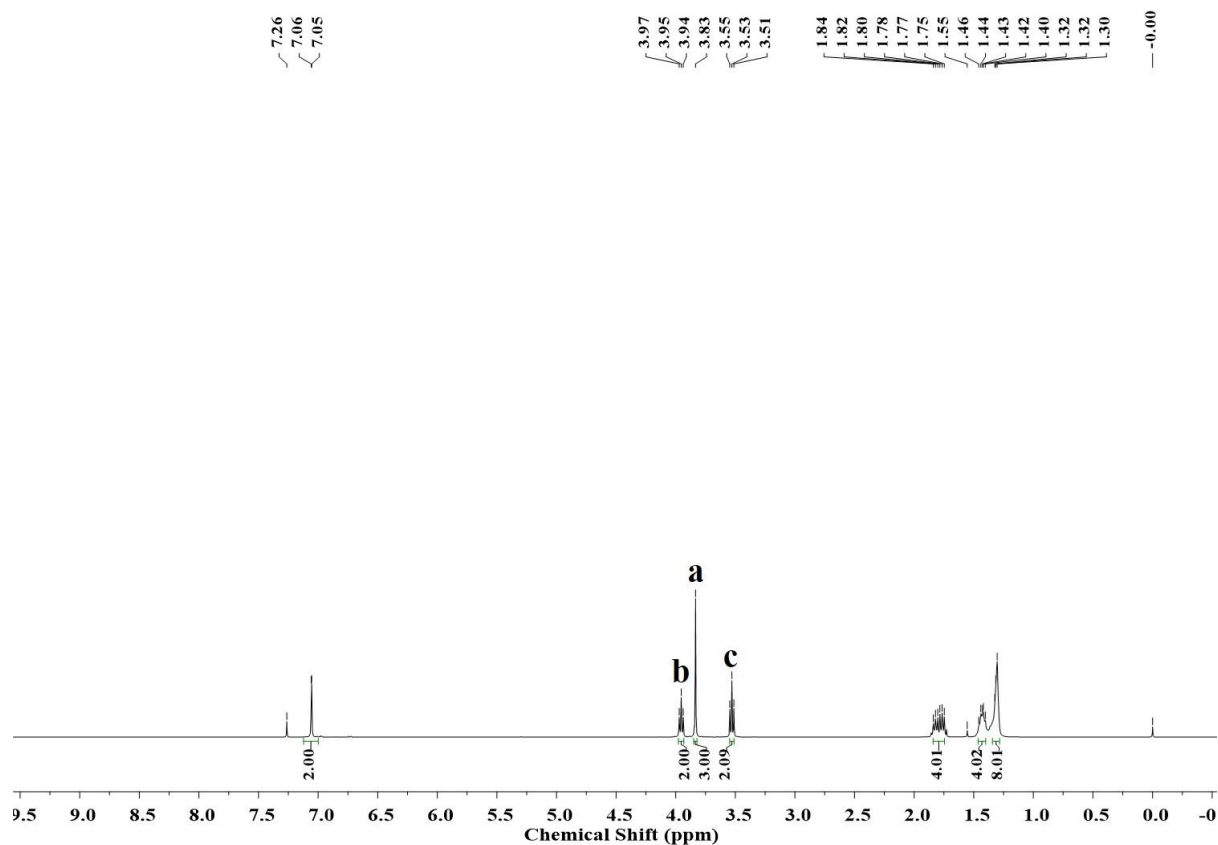


Figure S56. ^1H NMR (400 MHz, CDCl_3) spectrum of compound **13**.

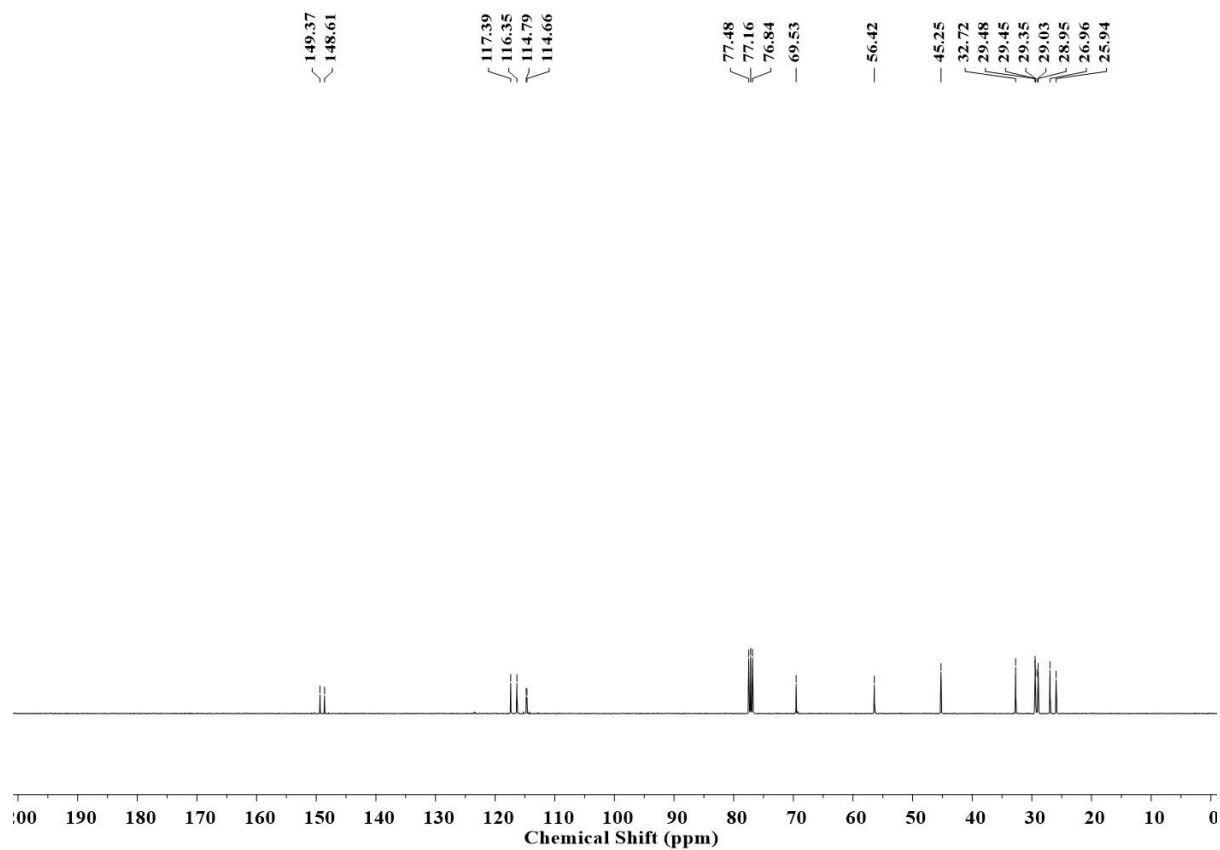


Figure S57. ^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **13**.

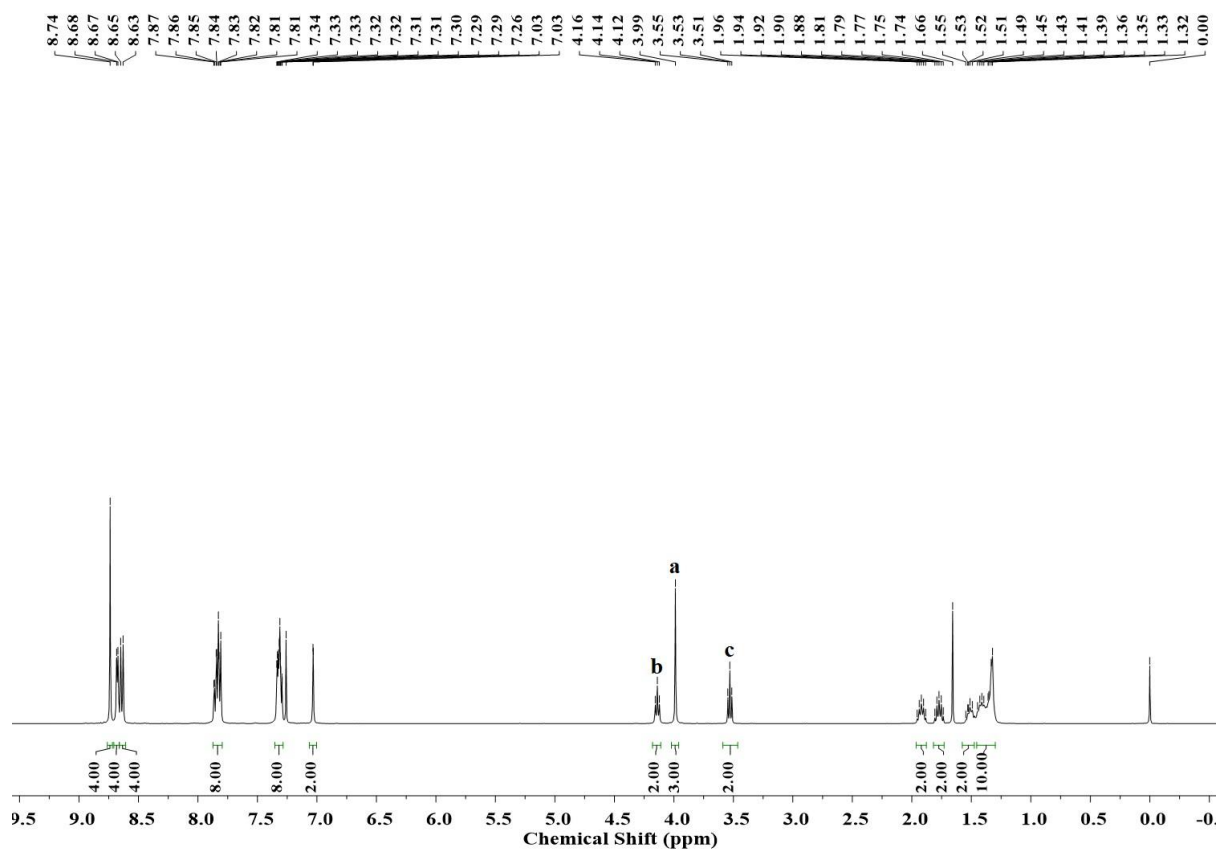


Figure S58. ^1H NMR (400 MHz, CDCl_3) spectrum of compound 14.

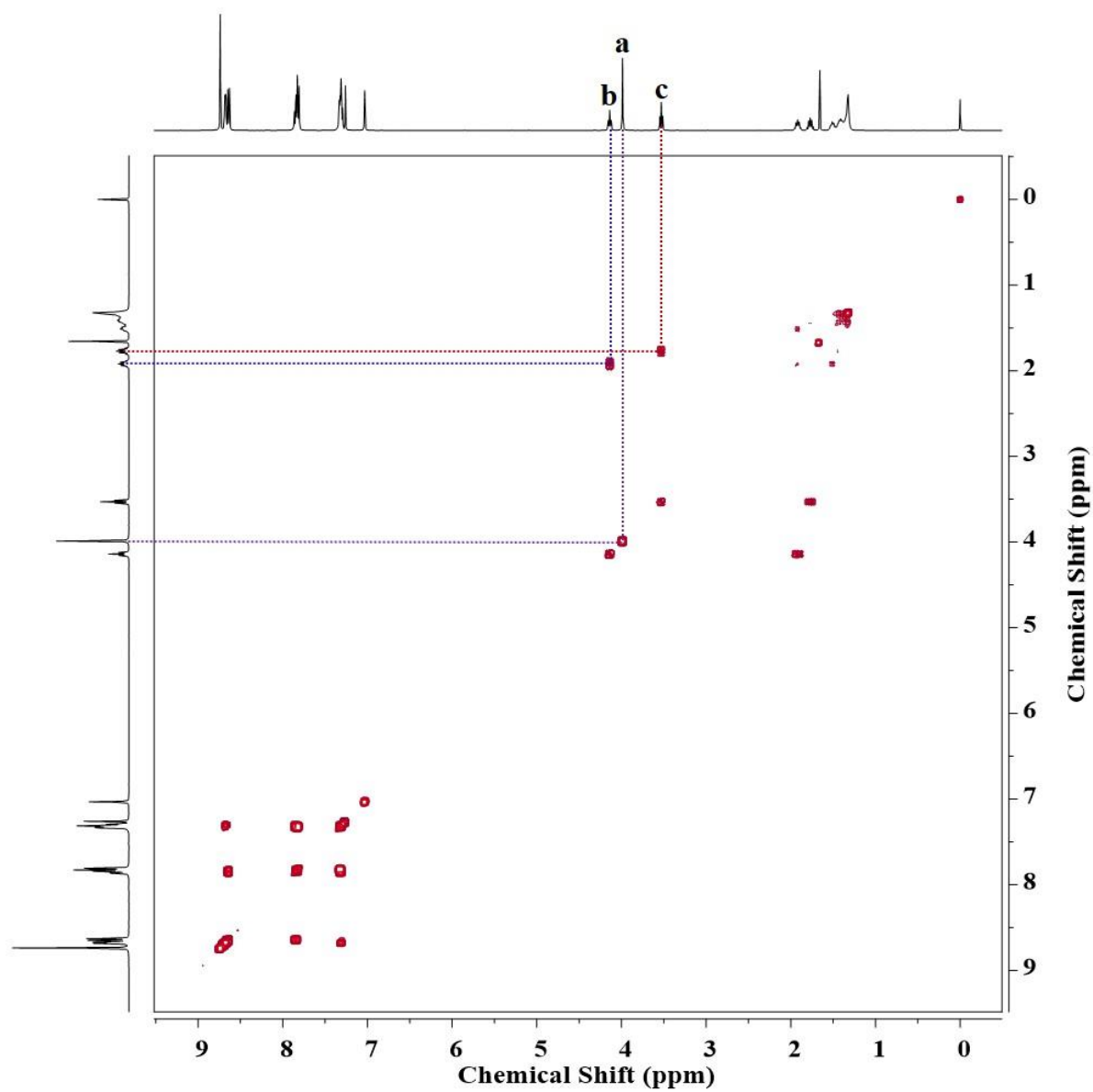


Figure S59. 2D COSY NMR (400 MHz, CDCl_3) spectrum of compound **14**.

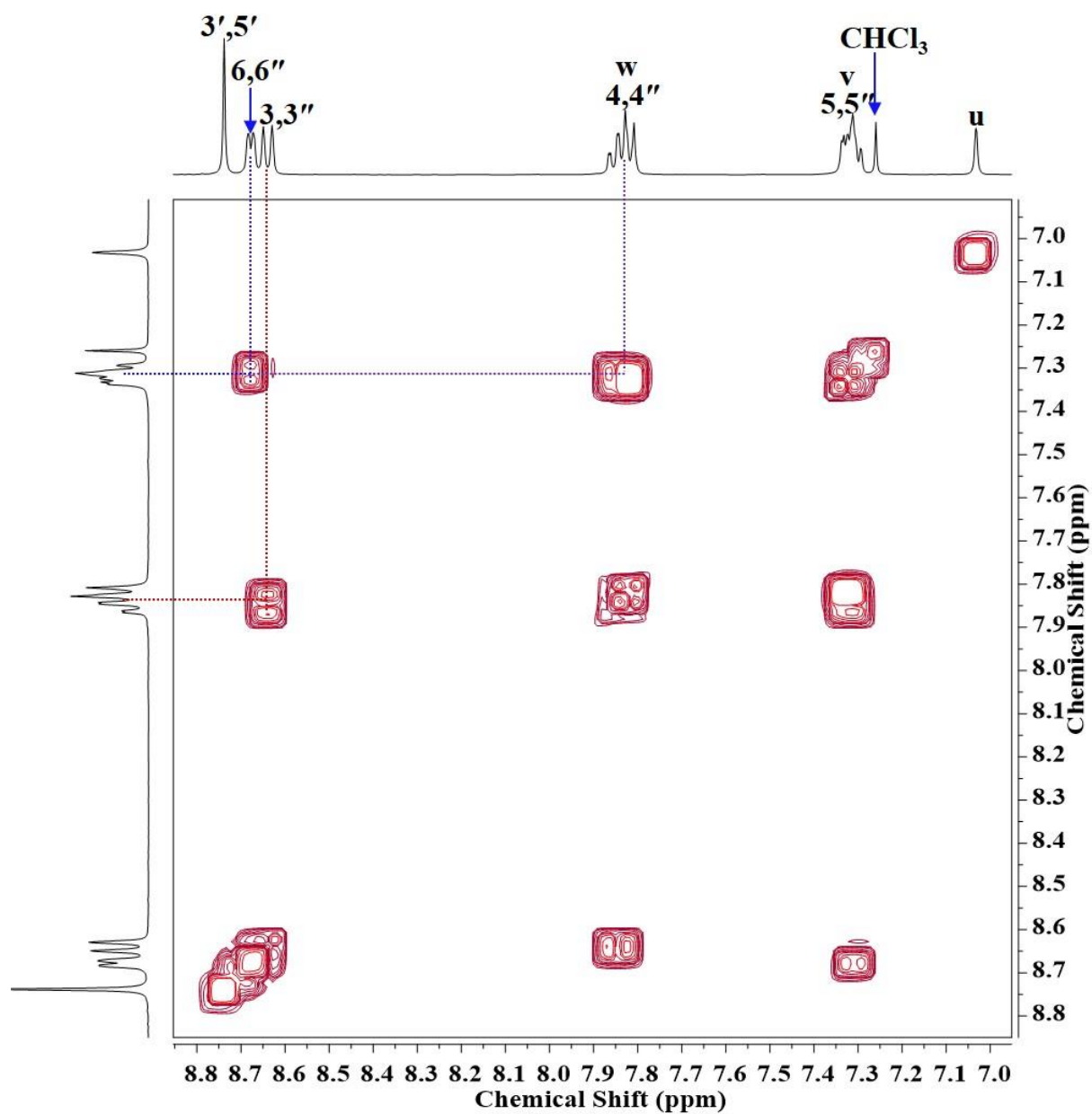


Figure S60. 2D COSY NMR (400 MHz, CDCl₃) spectrum of compound **14** (aromatic region).

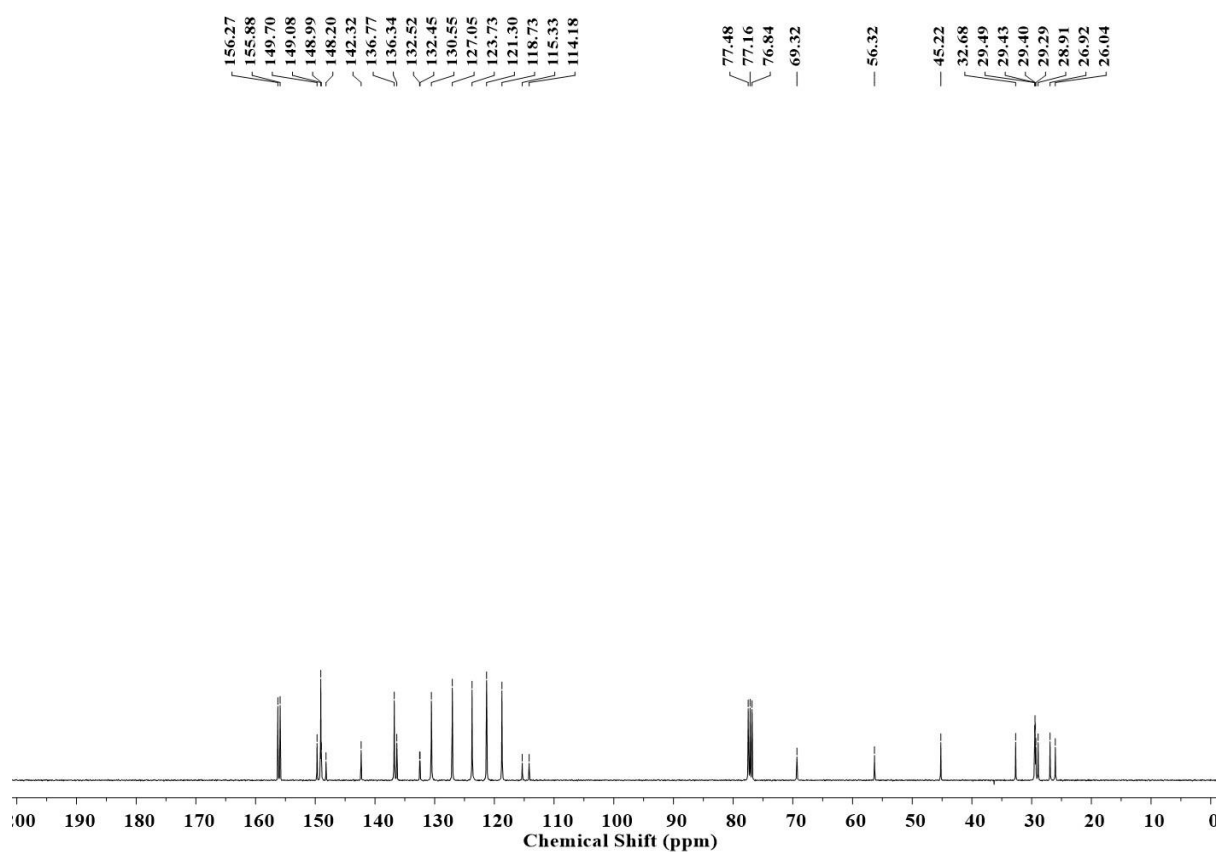


Figure S61. ^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **14**.

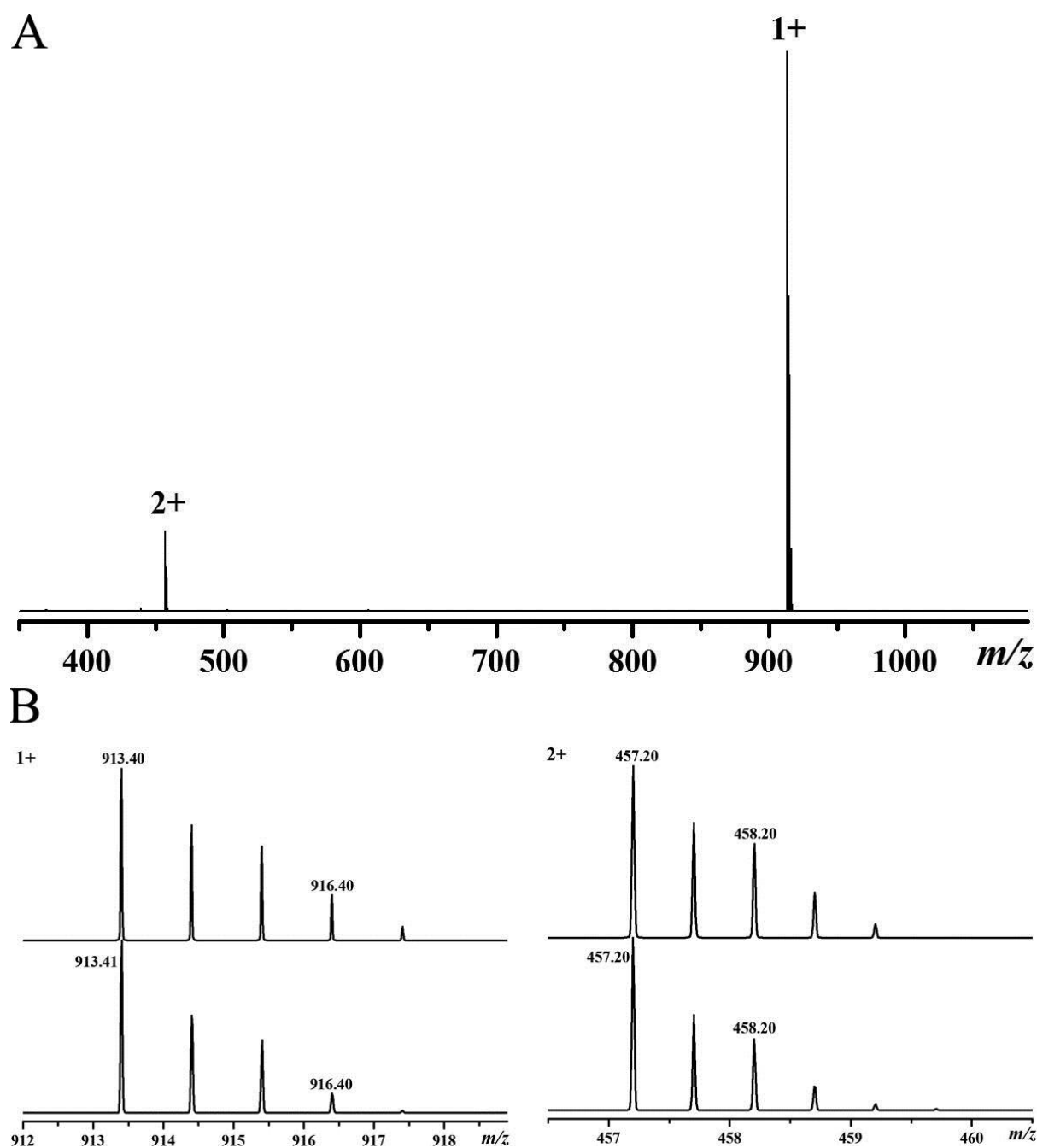


Figure S62. ESI-MS spectrum of compound **14** in CHCl_3 (A). Experimental (bottom) and calculated (top) isotope patterns for different charge states (B).

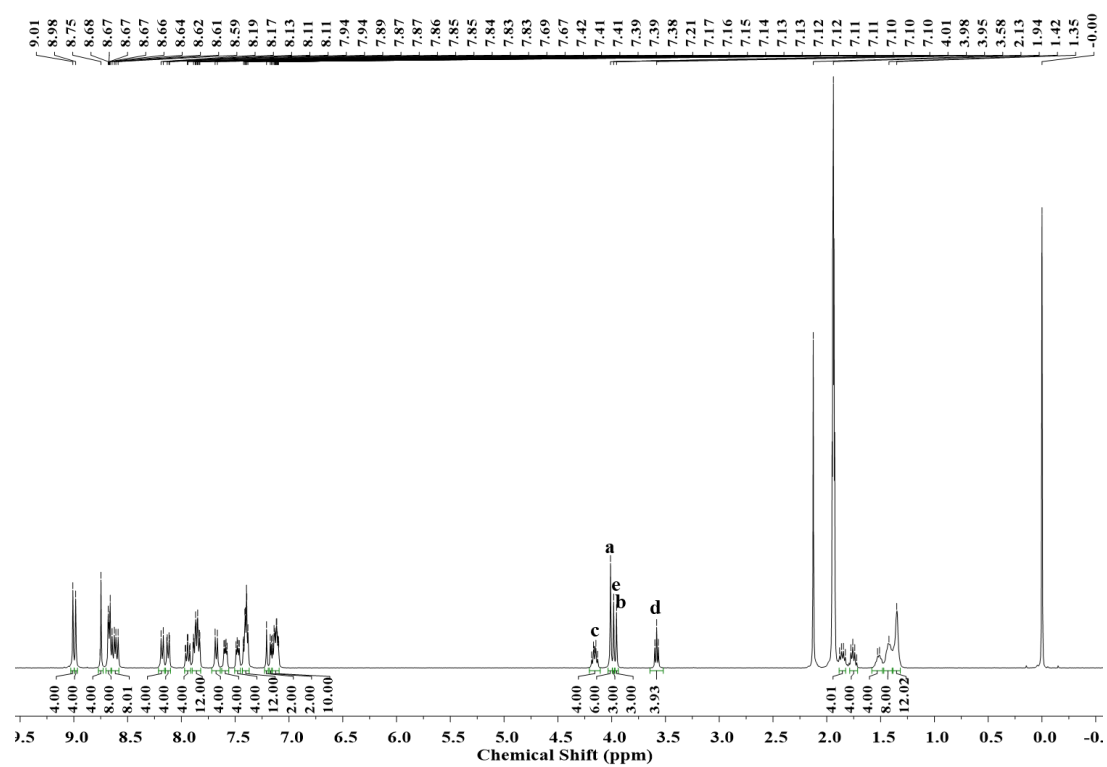


Figure S63. ^1H NMR (400 MHz, CD_3CN) spectrum of compound **16**.

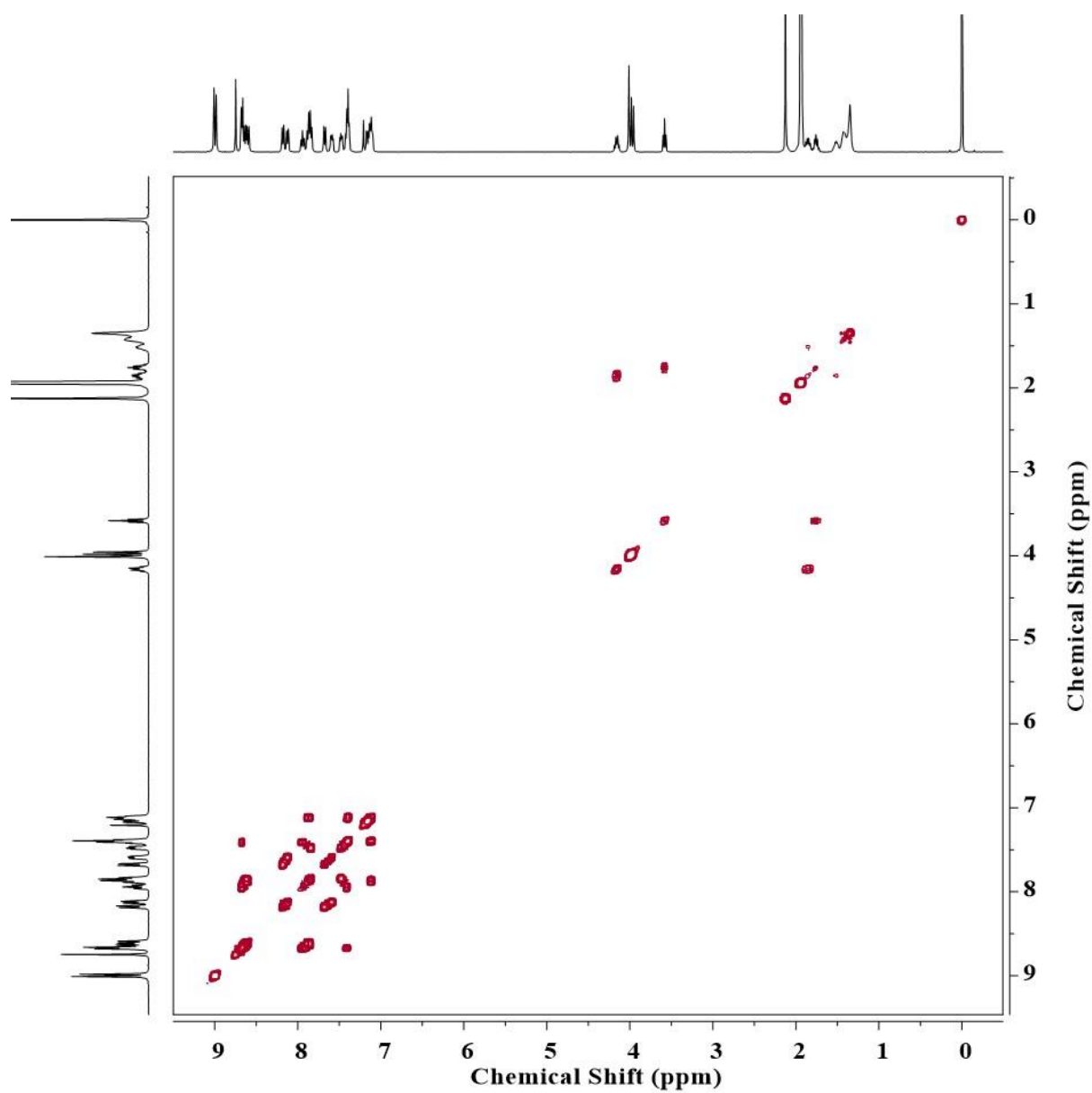


Figure S64. 2D COSY NMR (400 MHz, CD₃CN) spectrum of compound **16**.

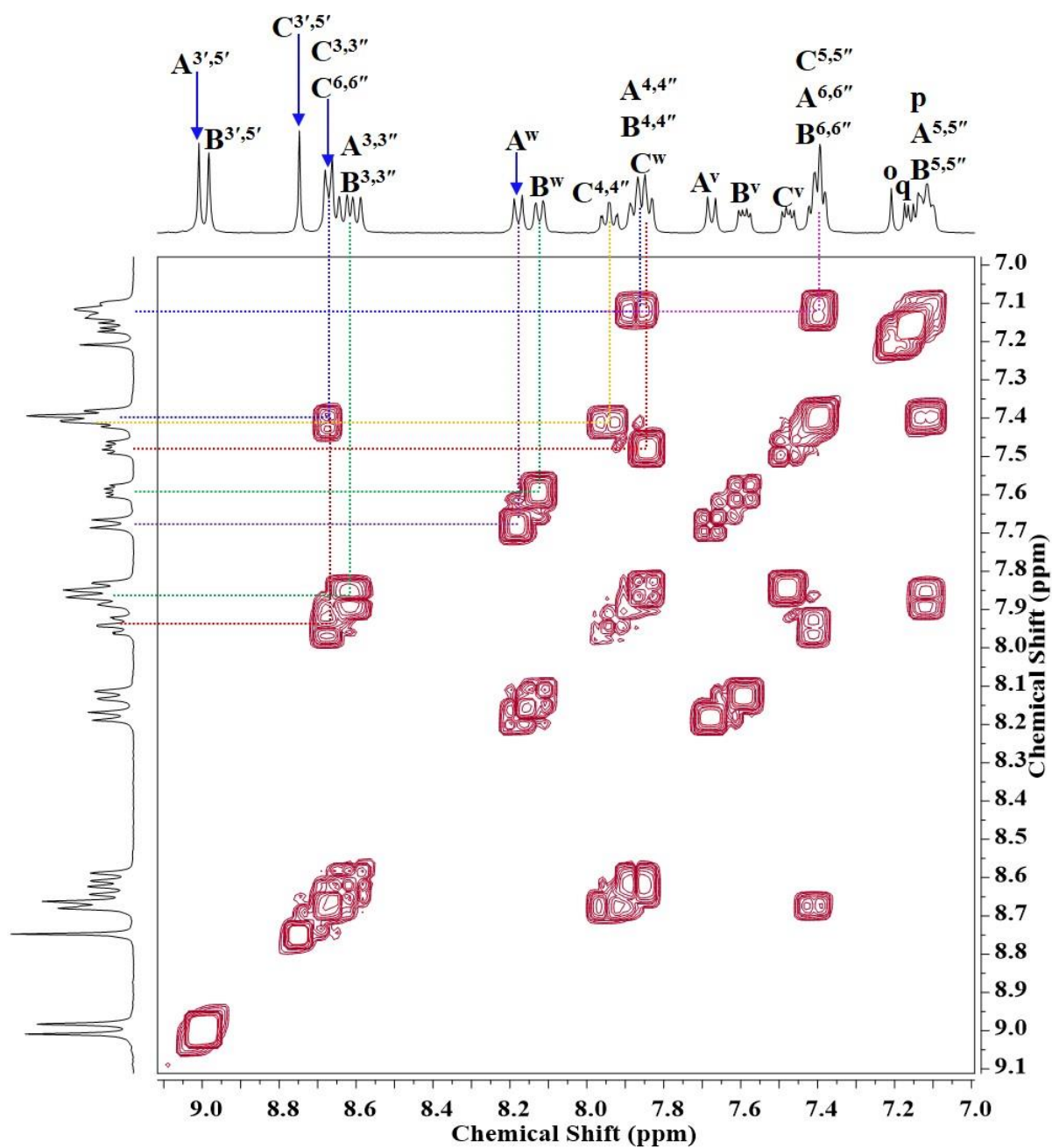


Figure S65. 2D COSY NMR (400 MHz, CD₃CN) spectrum of compound **16** (aromatic region).

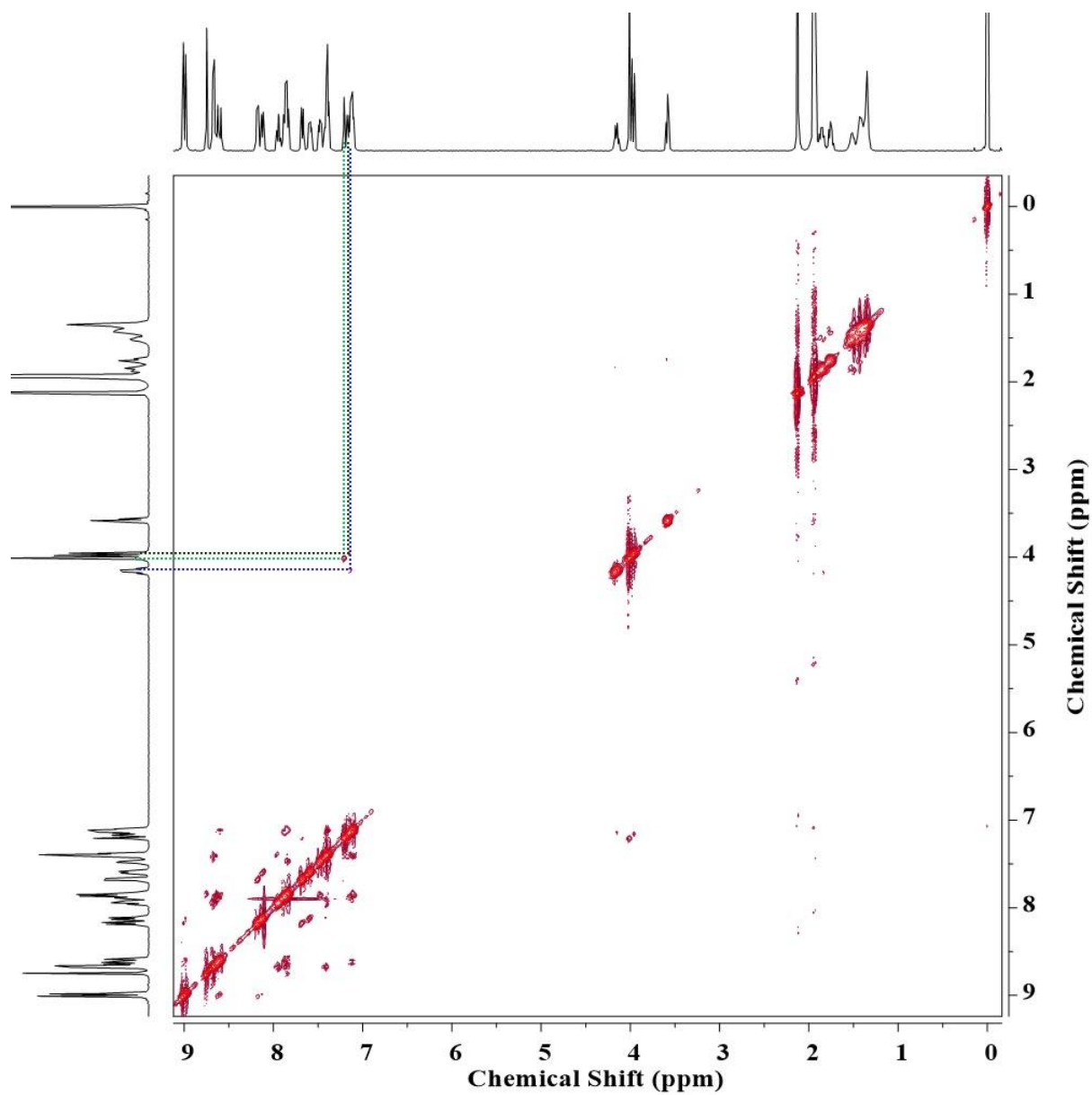


Figure S66. 2D NOESY NMR (400 MHz, CD₃CN) spectrum of compound 16.

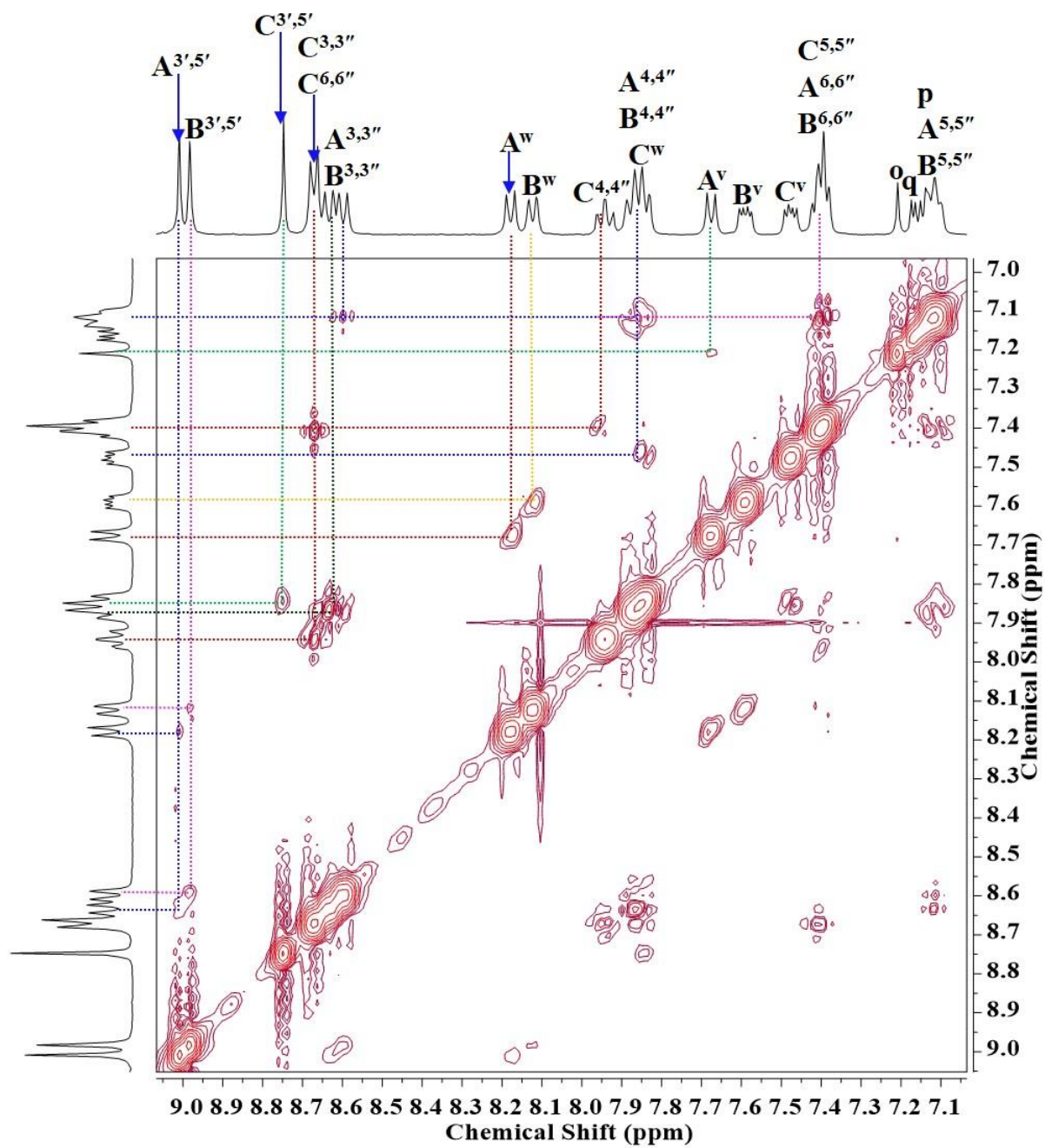


Figure S67. 2D NOESY NMR (400 MHz, CD₃CN) spectrum of compound 16 (aromatic region).

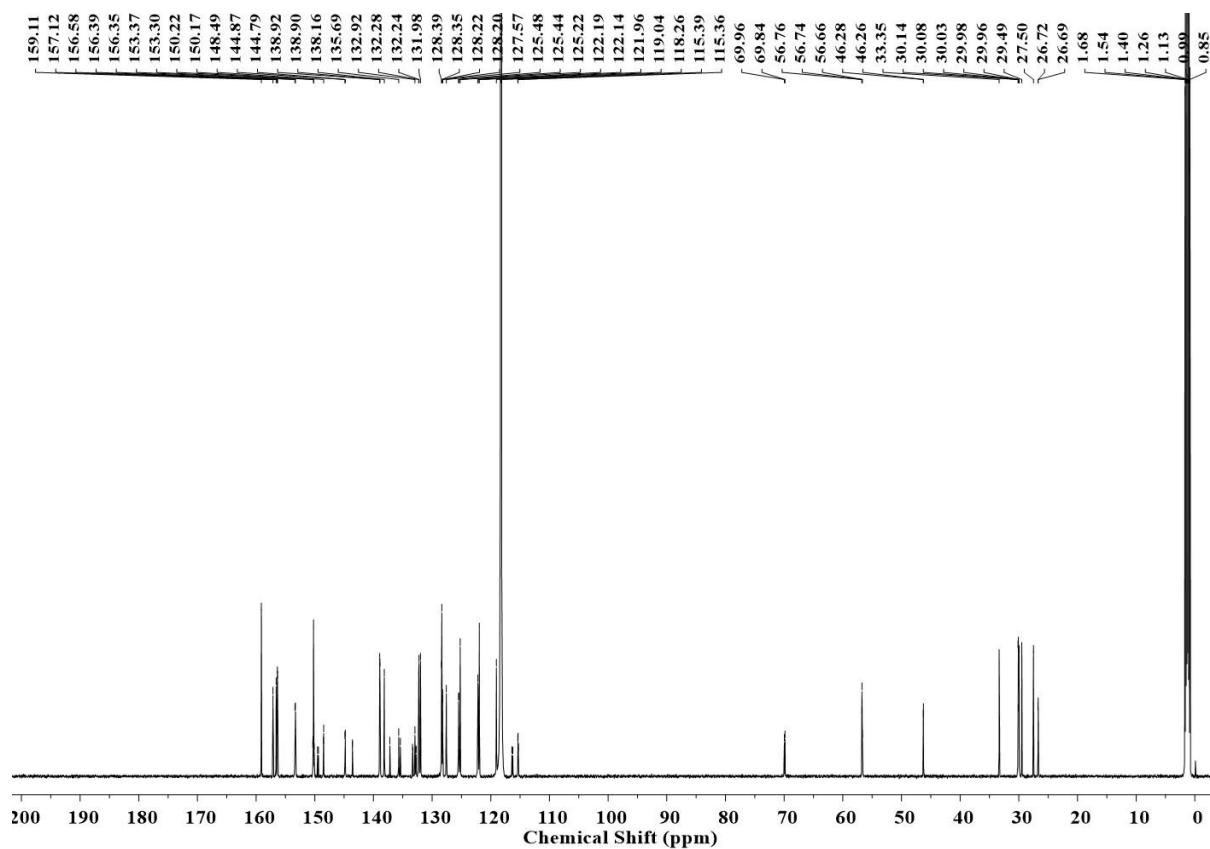


Figure S68. ^{13}C NMR (150 MHz, CD_3CN) spectrum of compound **16**.

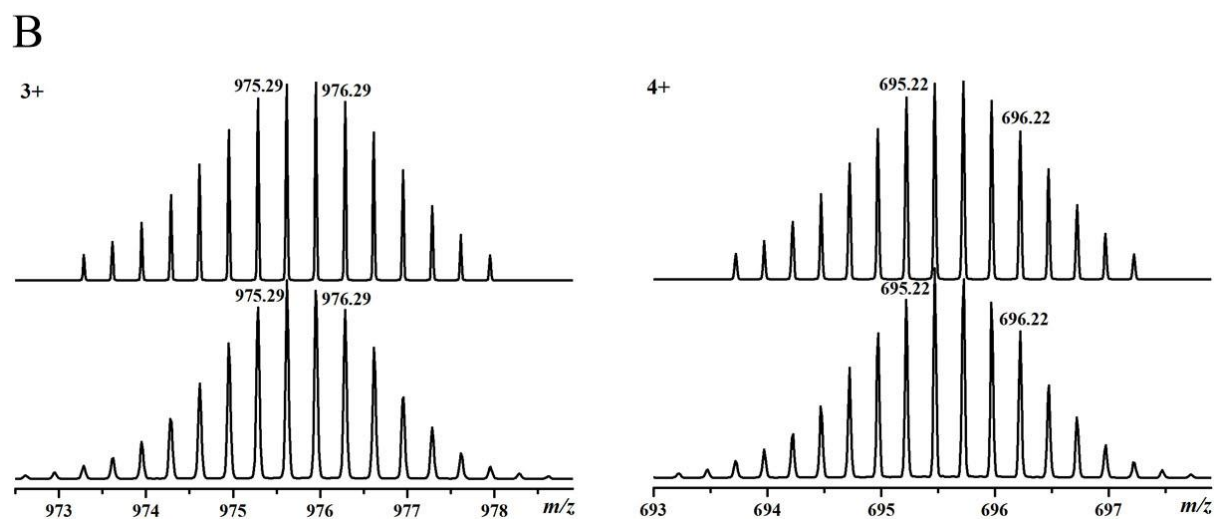
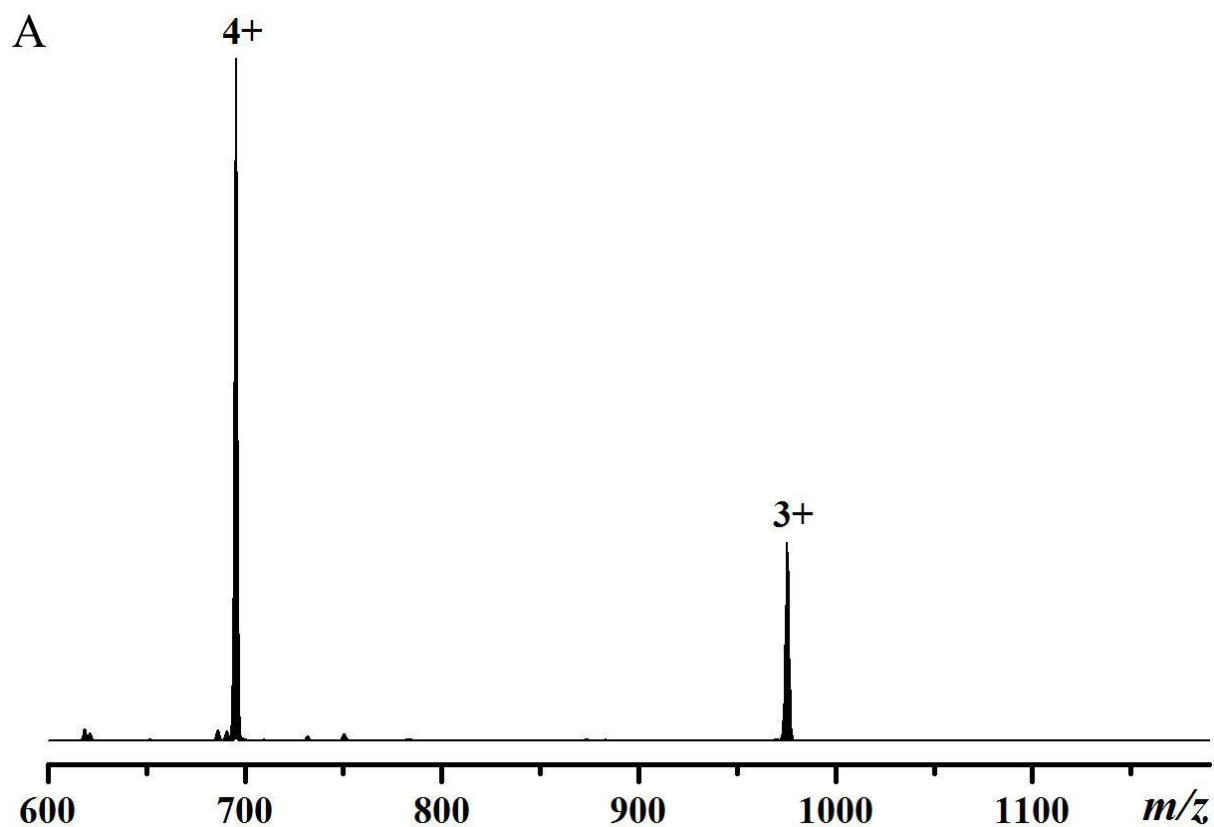


Figure S69. ESI-MS spectrum of compound **16** in CH_3CN (A). Experimental (bottom) and calculated (top) isotope patterns for different charge states (B).



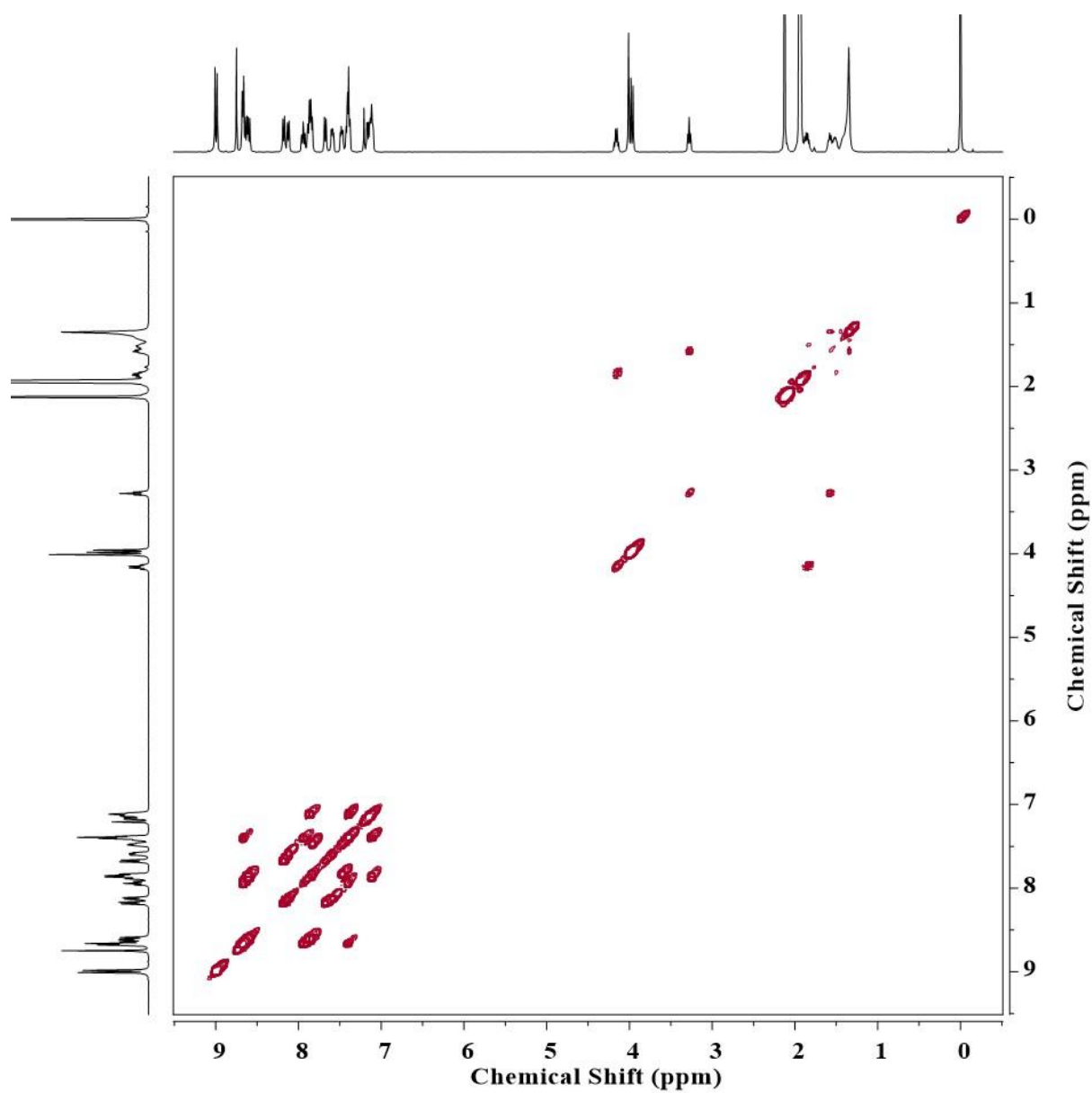


Figure S71. 2D COSY NMR (400 MHz, CD₃CN) spectrum of compound **17** (Tri-M).

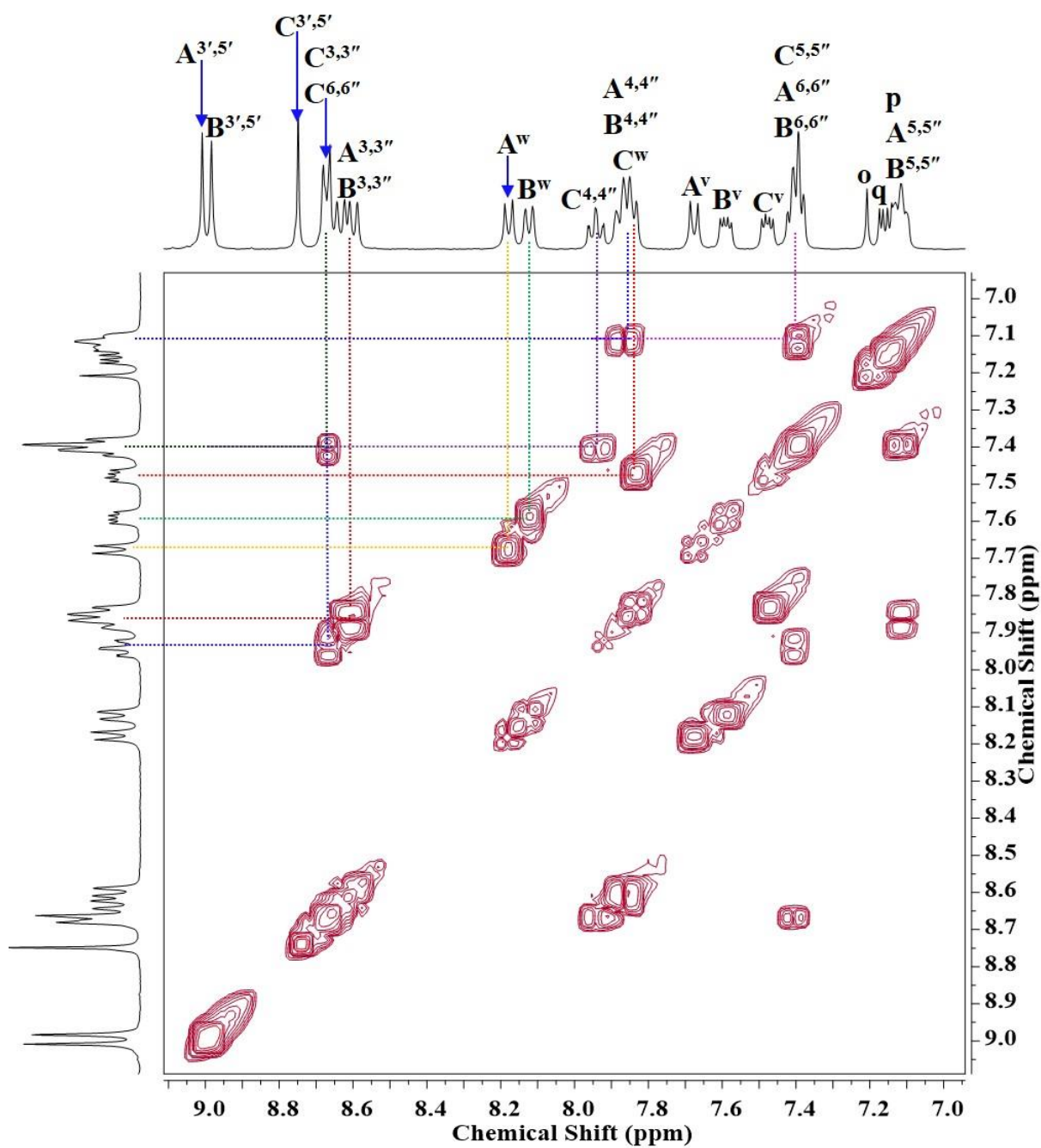


Figure S72. 2D COSY NMR (400 MHz, CD₃CN) spectrum of compound 17 (Tri-M) (aromatic region).

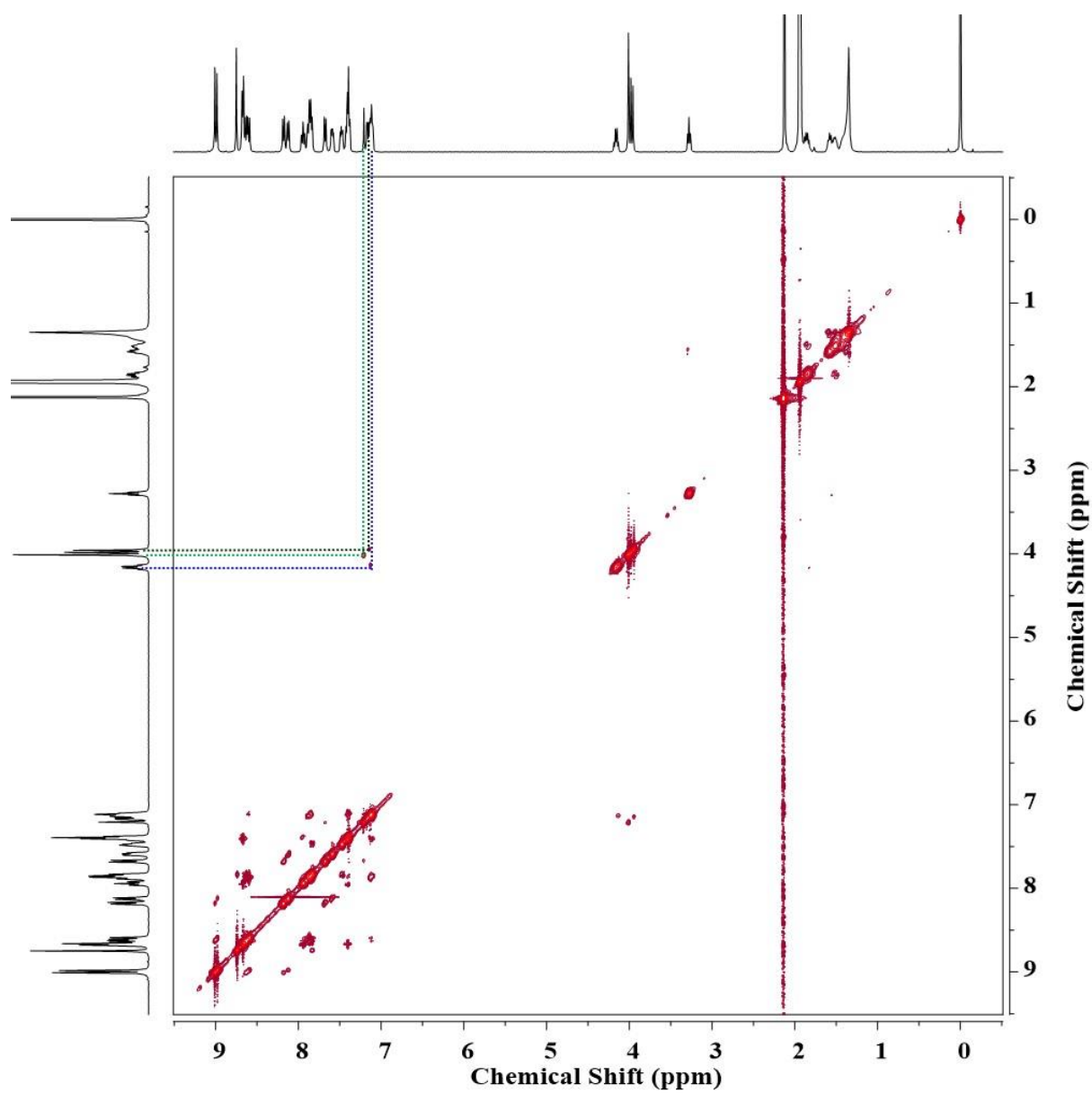


Figure S73. 2D NOESY NMR (400 MHz, CD₃CN) spectrum of compound **17** (Tri-M).

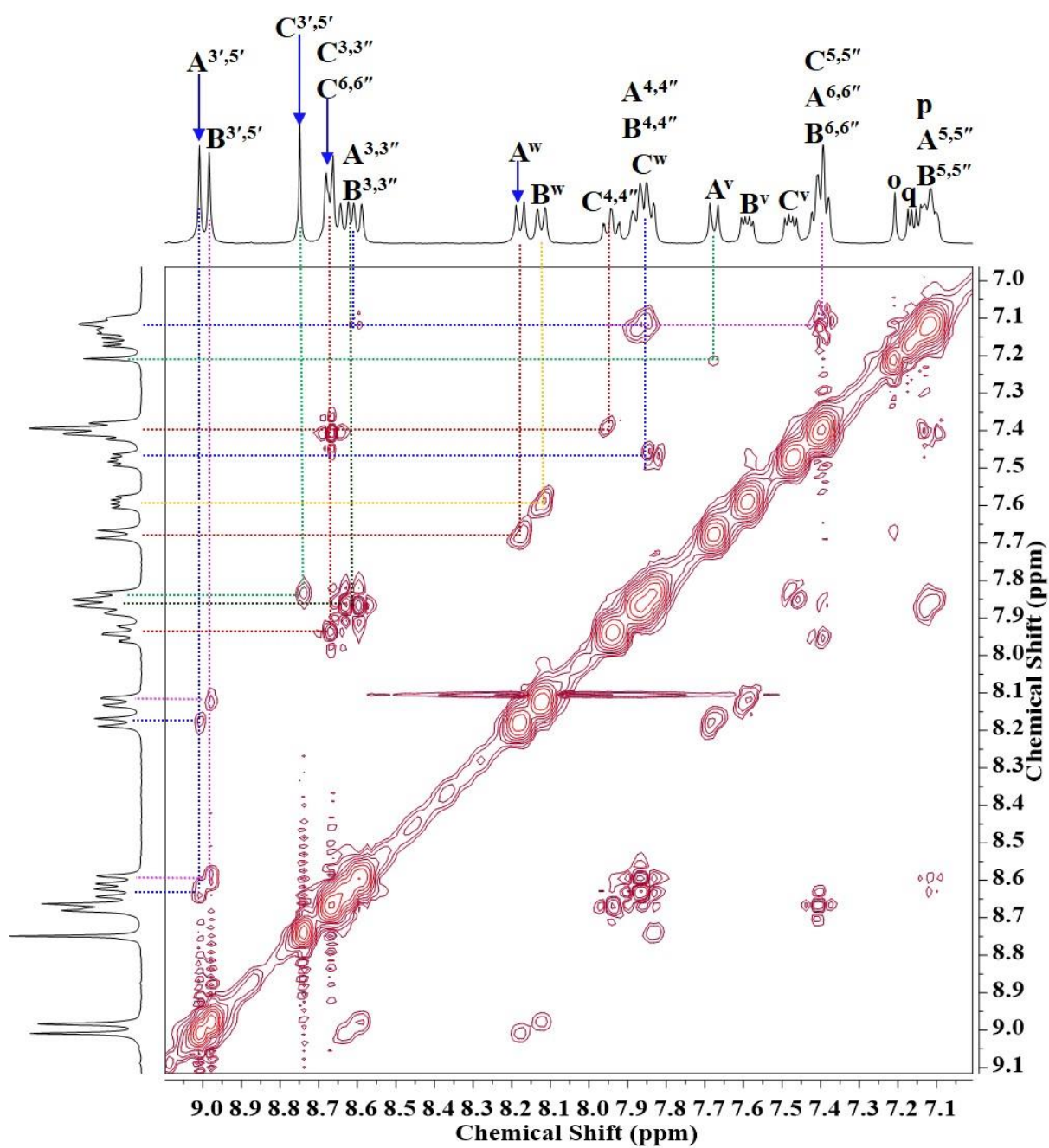


Figure S74. 2D NOESY NMR (400 MHz, CD₃CN) spectrum of compound **17** (Tri-M) (aromatic region).

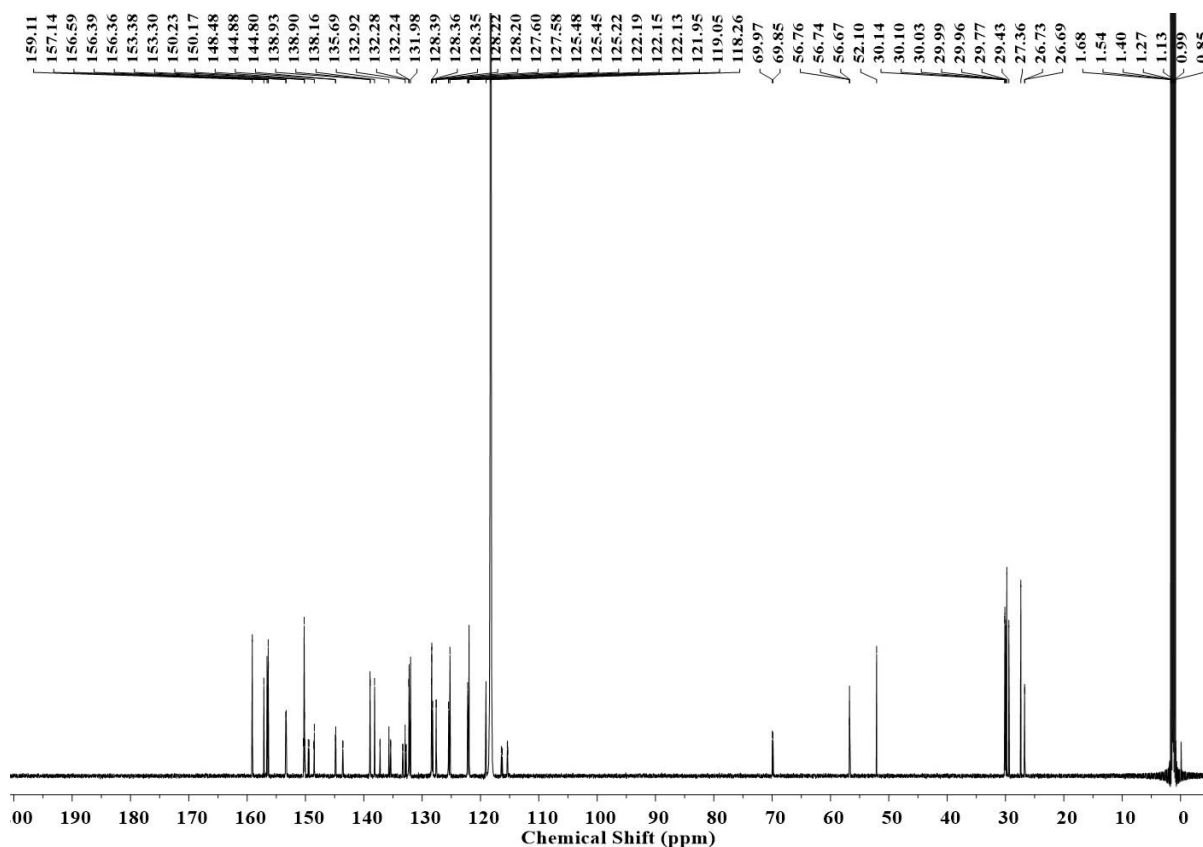


Figure S75. ^{13}C NMR (150 MHz, CD_3CN) spectrum of compound **17** (**Tri-M**).

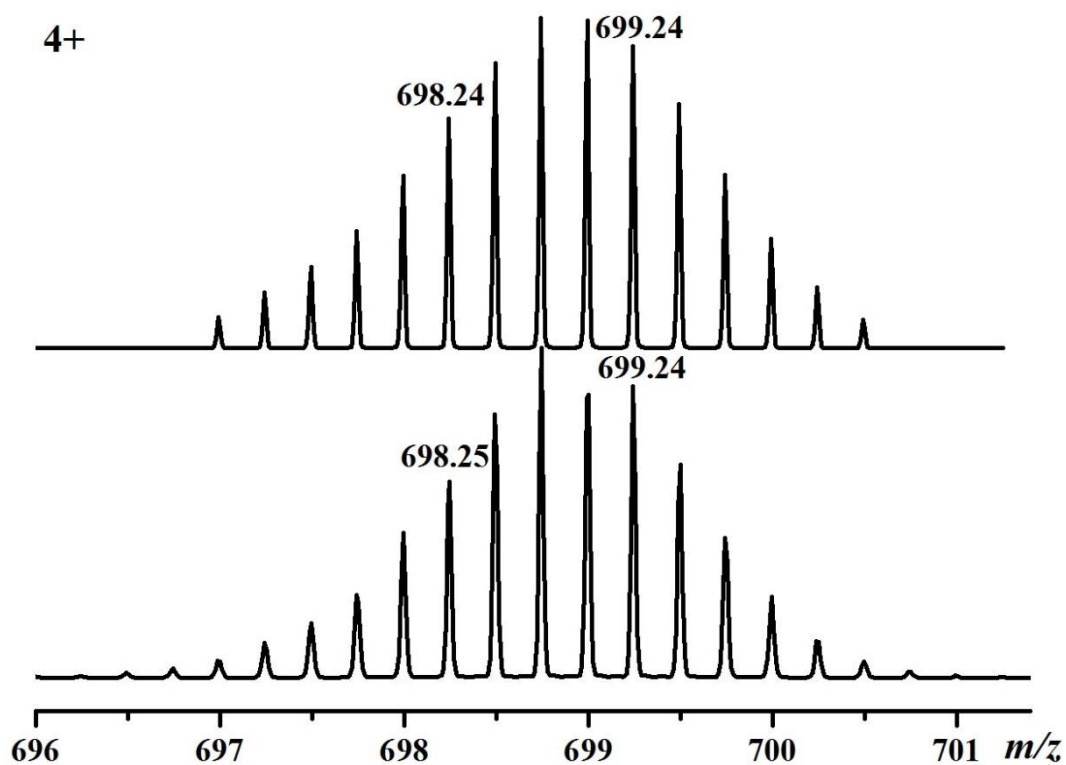


Figure S76. Experimental (bottom) and calculated (top) isotope patterns for charge state 4+ observed from compound **17** (**Tri-M**) (PF_6^- as counterion).

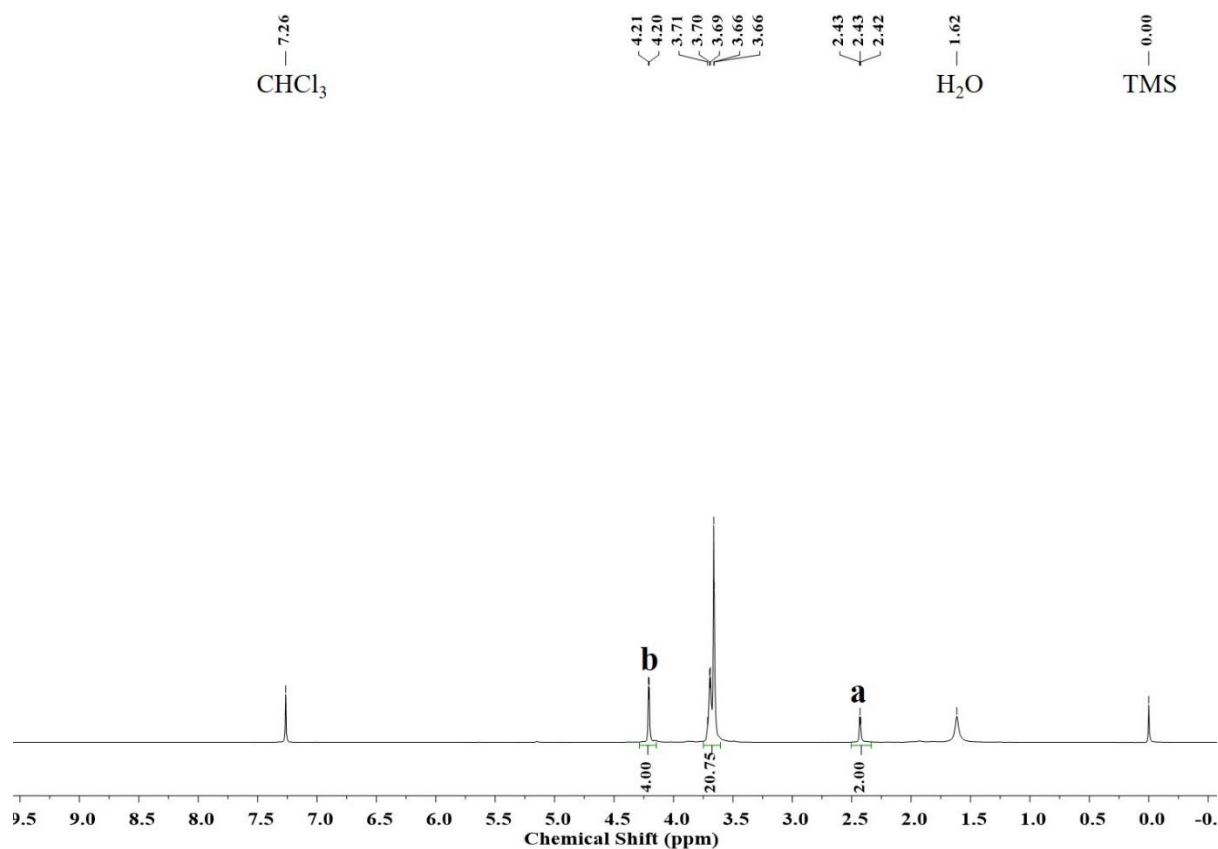


Figure S77. ¹H NMR (400 MHz, CDCl₃) spectrum of compound **18** (Alkyne-PEG).

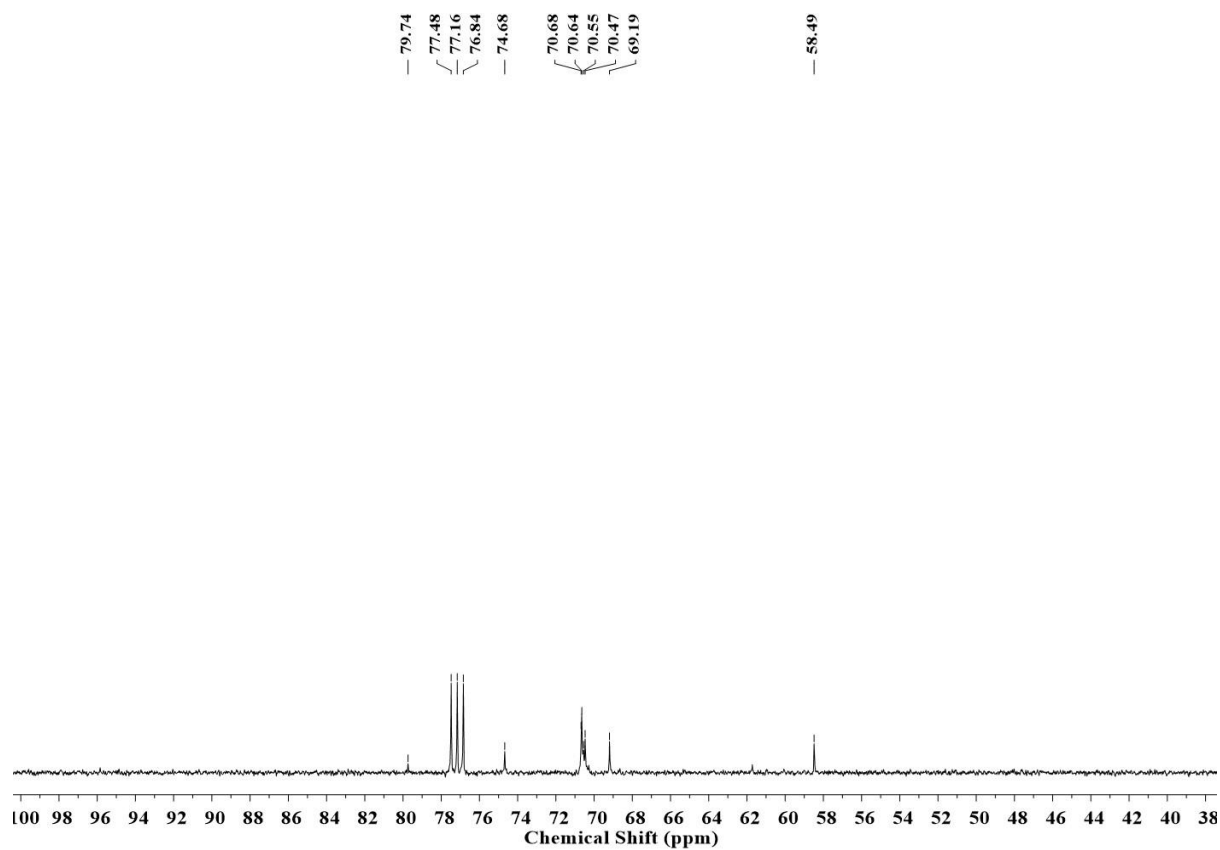


Figure S78. ¹³C NMR (100 MHz, CDCl₃) spectrum of compound **18** (Alkyne-PEG).

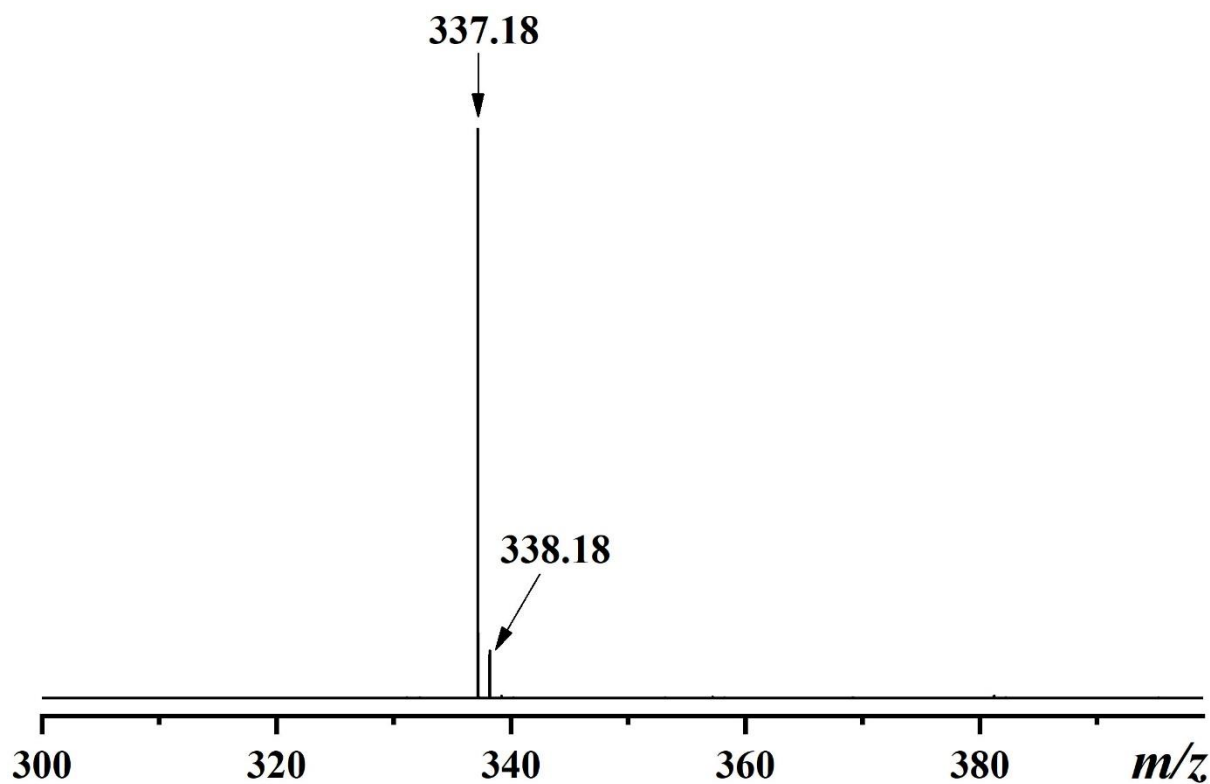


Figure S79. ESI-MS spectrum of compound 18 (Alkyne-PEG) in CHCl₃/CH₃OH (1/3).

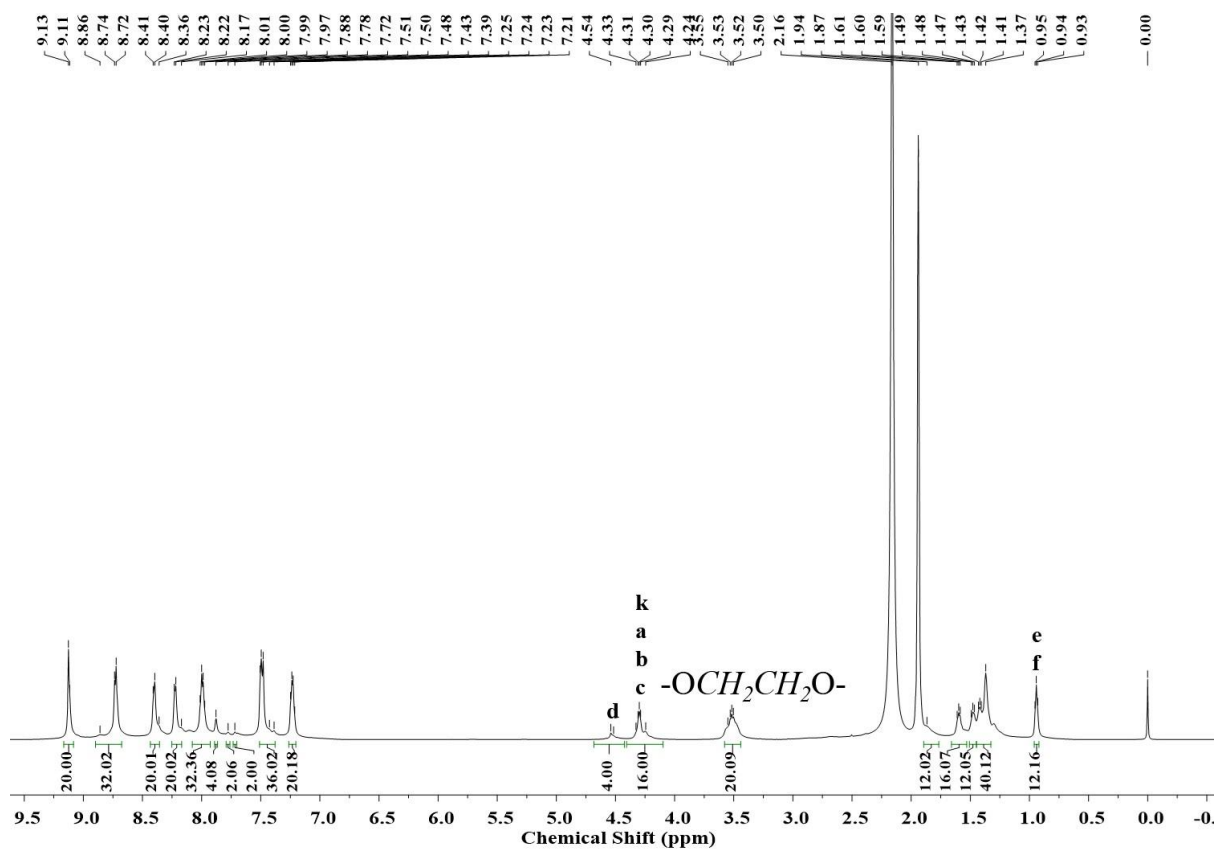


Figure S80. ¹H NMR (600 MHz, CD₃CN) spectrum of compound 19 (Hex-P).

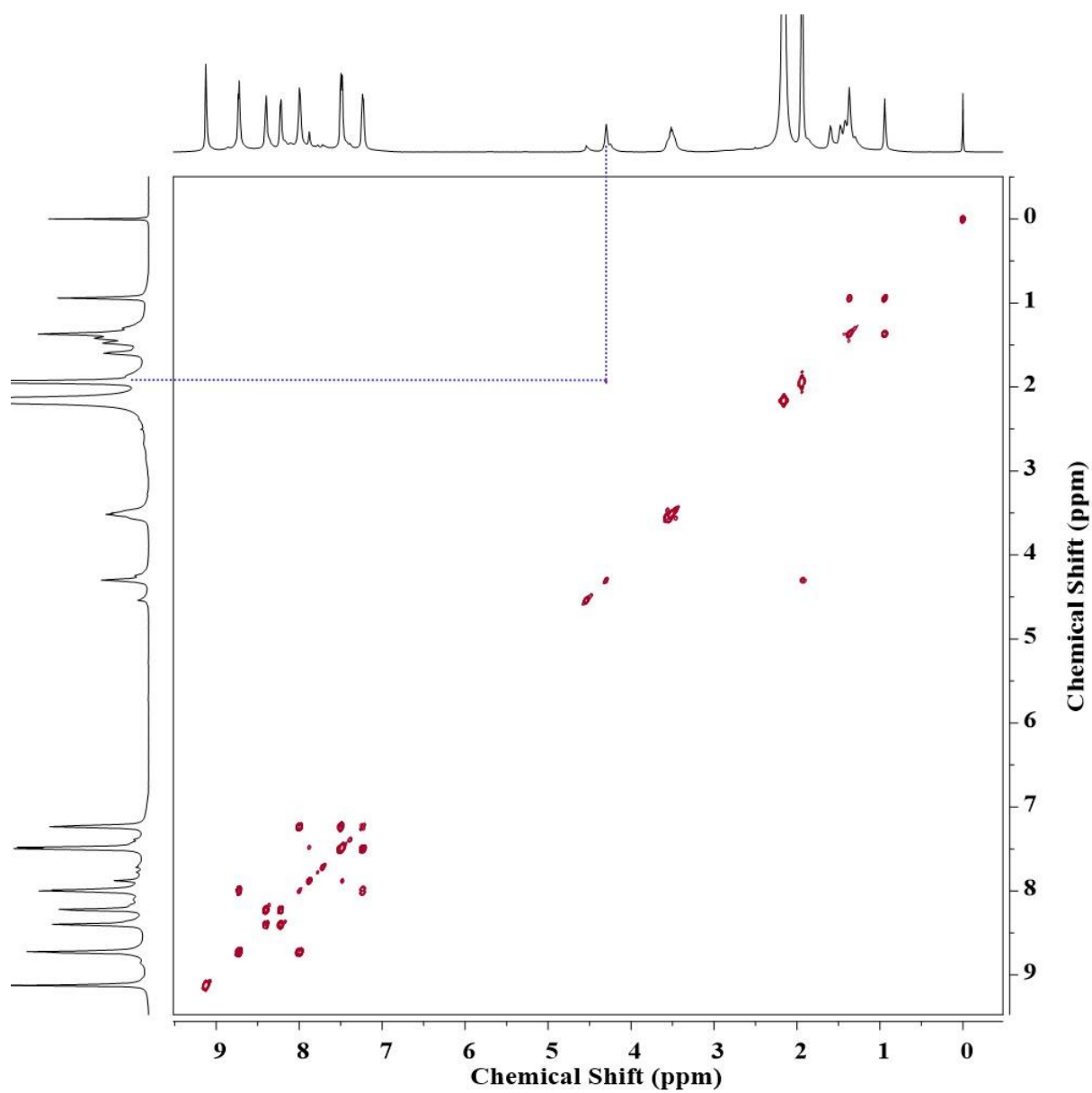


Figure S81. 2D COSY NMR (600 MHz, CD₃CN) spectrum of compound **19** (Hex-P).

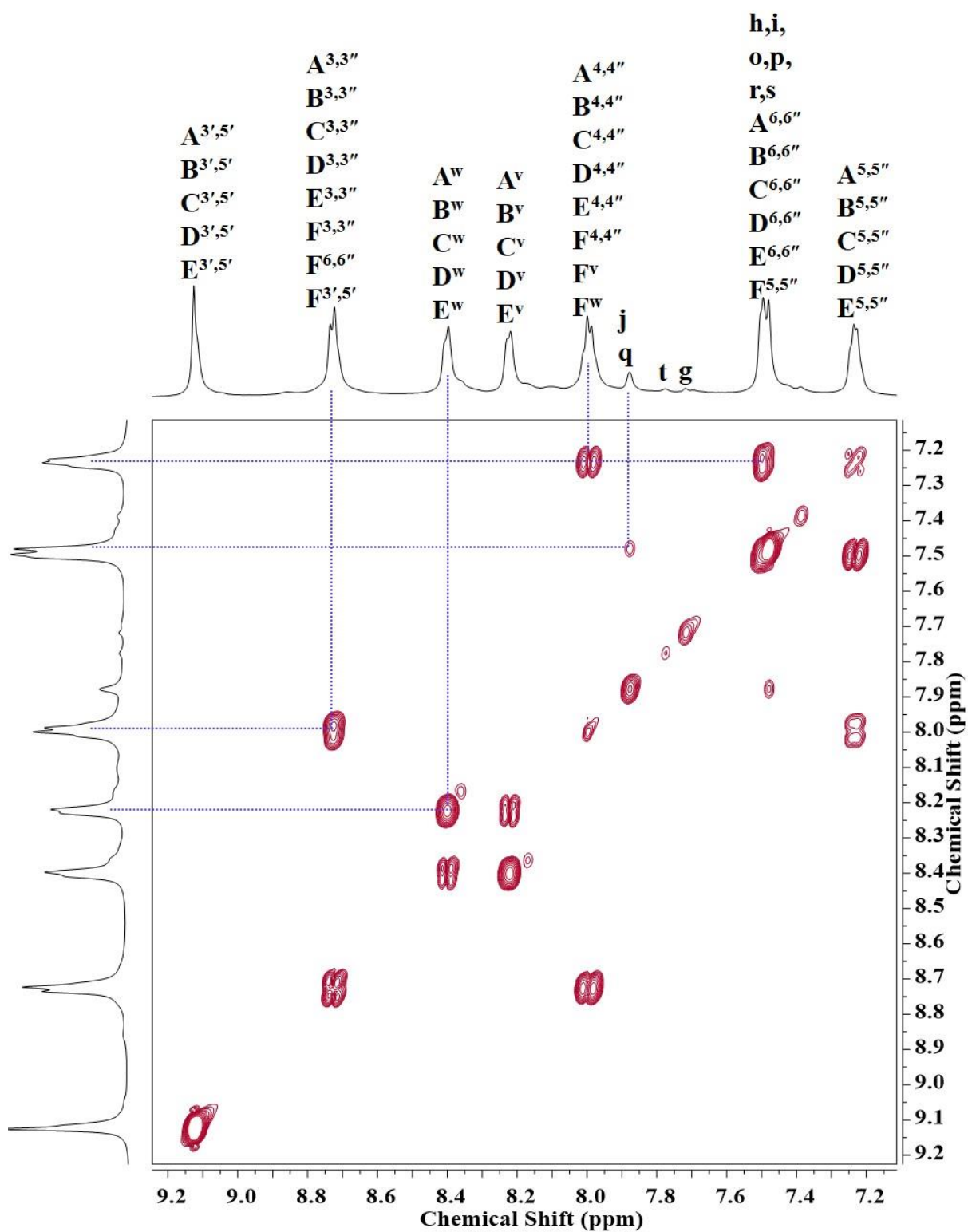


Figure S82. 2D COSY NMR (600 MHz, CD_3CN) spectrum of compound **19** (Hex-P) (aromatic region).

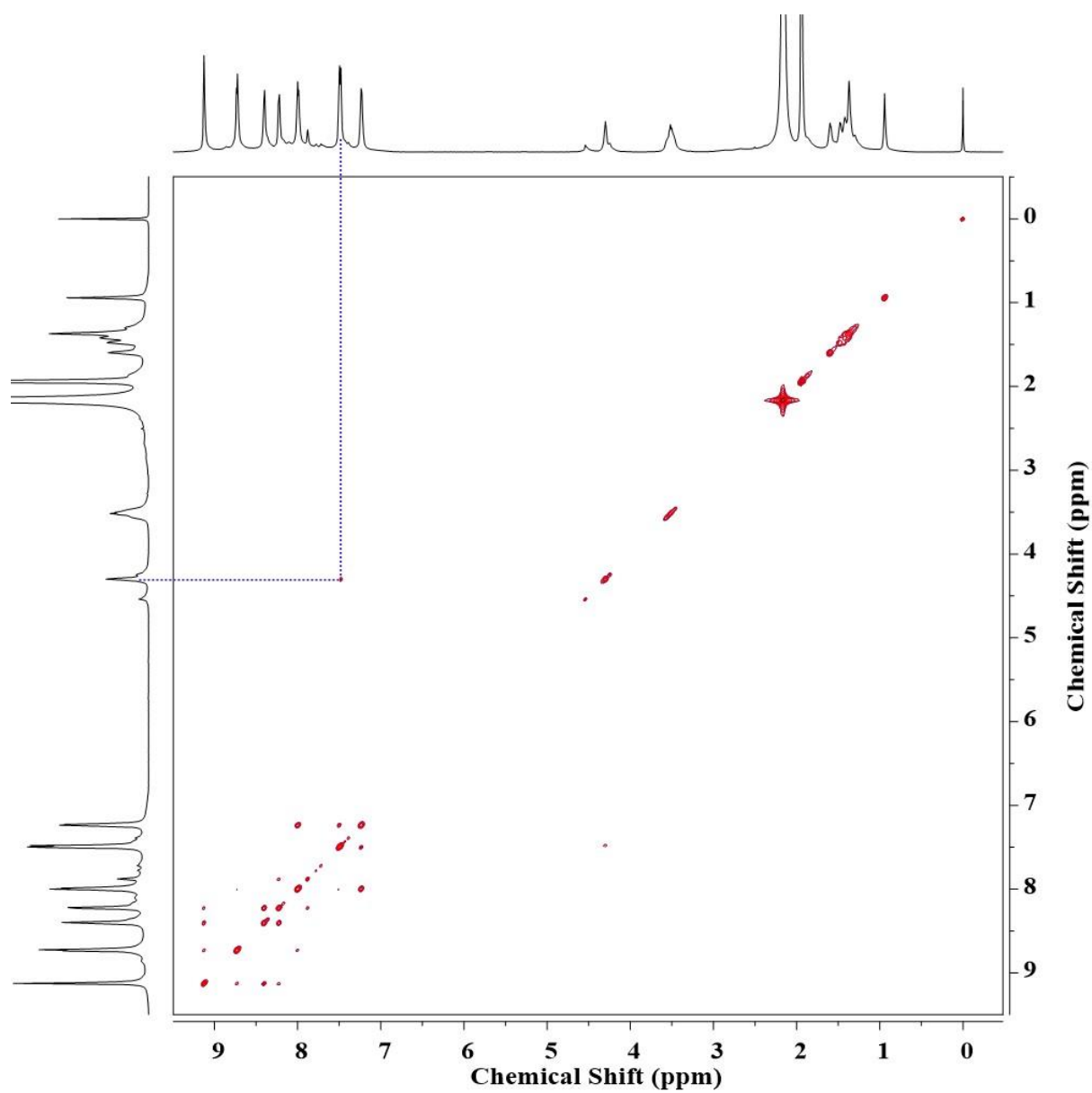


Figure S83. 2D NOESY NMR (600 MHz, CD₃CN) spectrum of compound **19 (Hex-P)**.

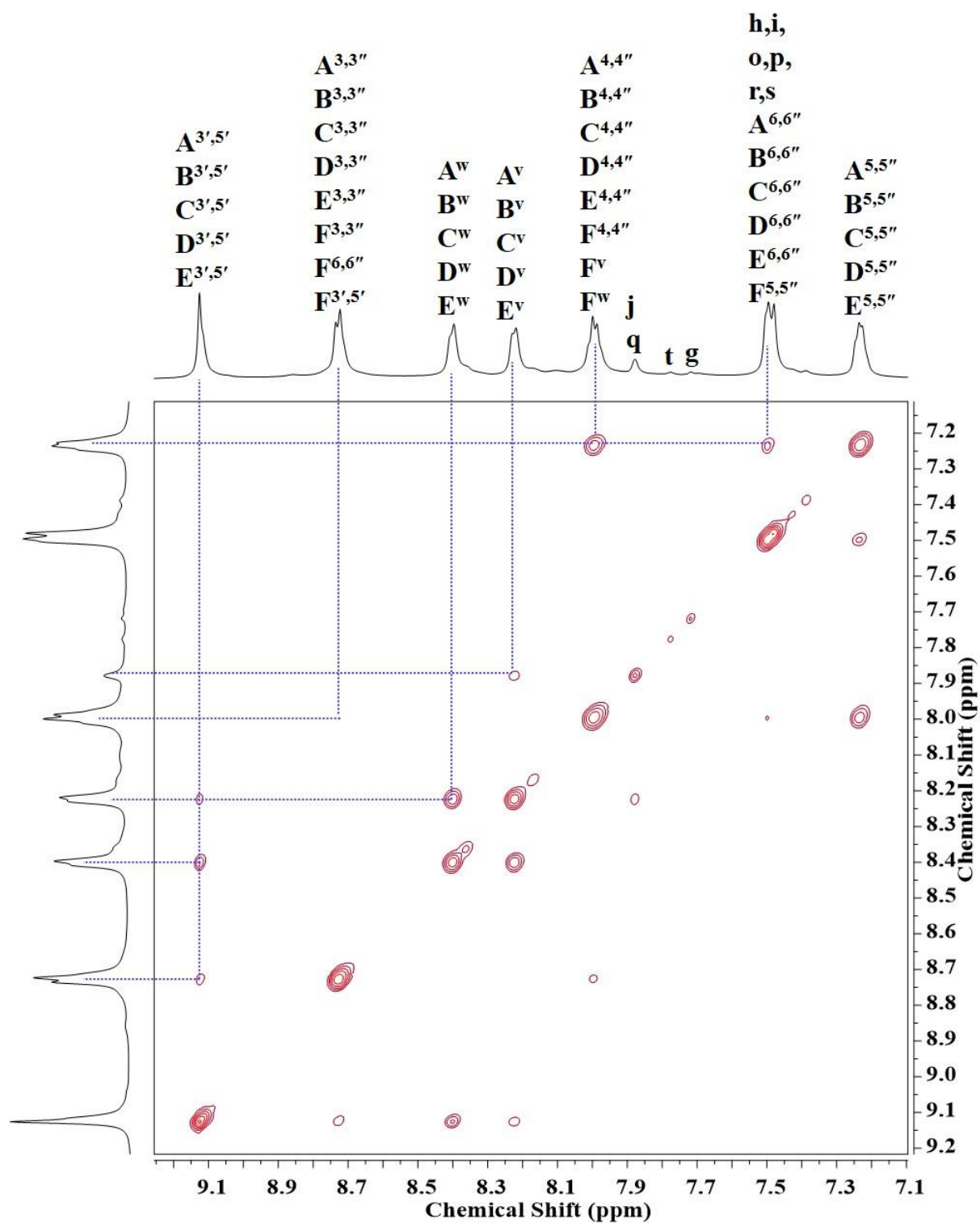


Figure S84. 2D NOESY NMR (600 MHz, CD₃CN) spectrum of compound **19** (Hex-P) (aromatic region).

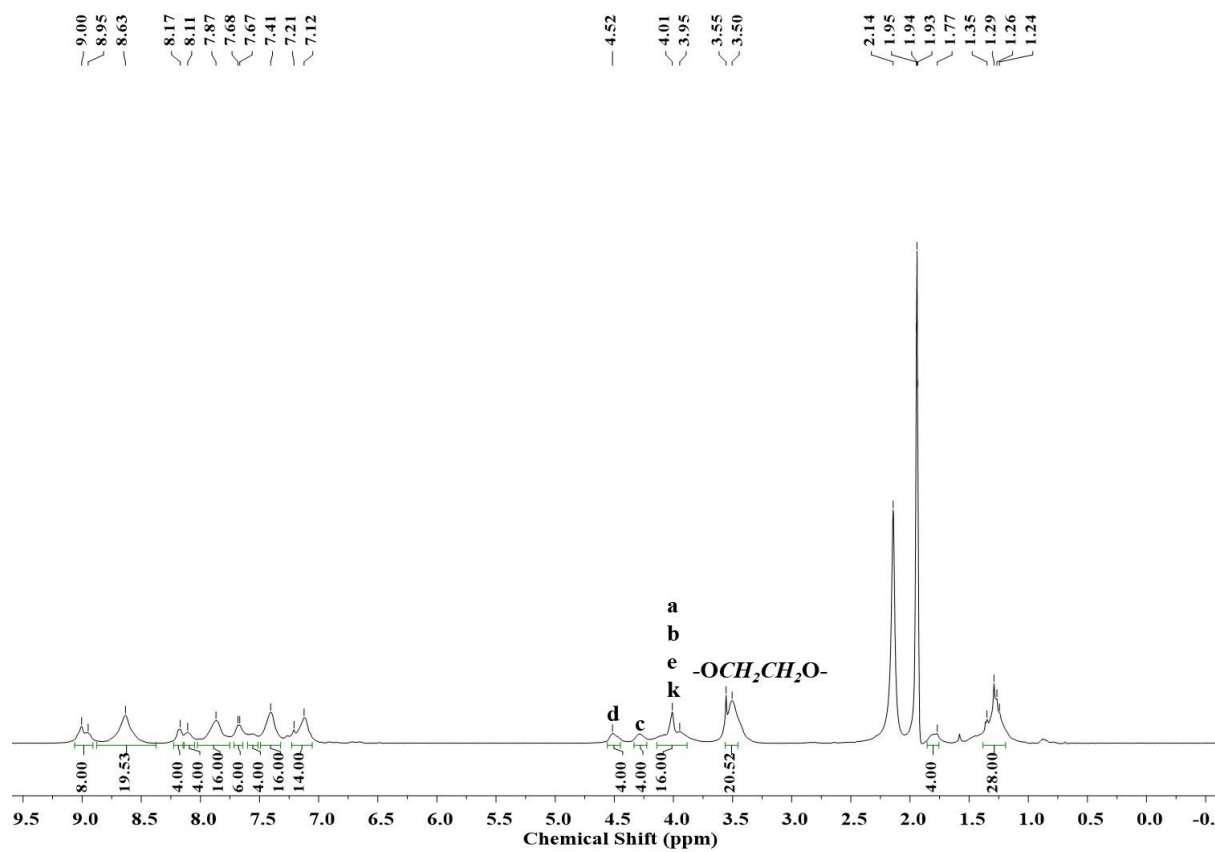


Figure S85. ¹H NMR (400 MHz, CD₃CN) spectrum of compound **20** (Tri-P).

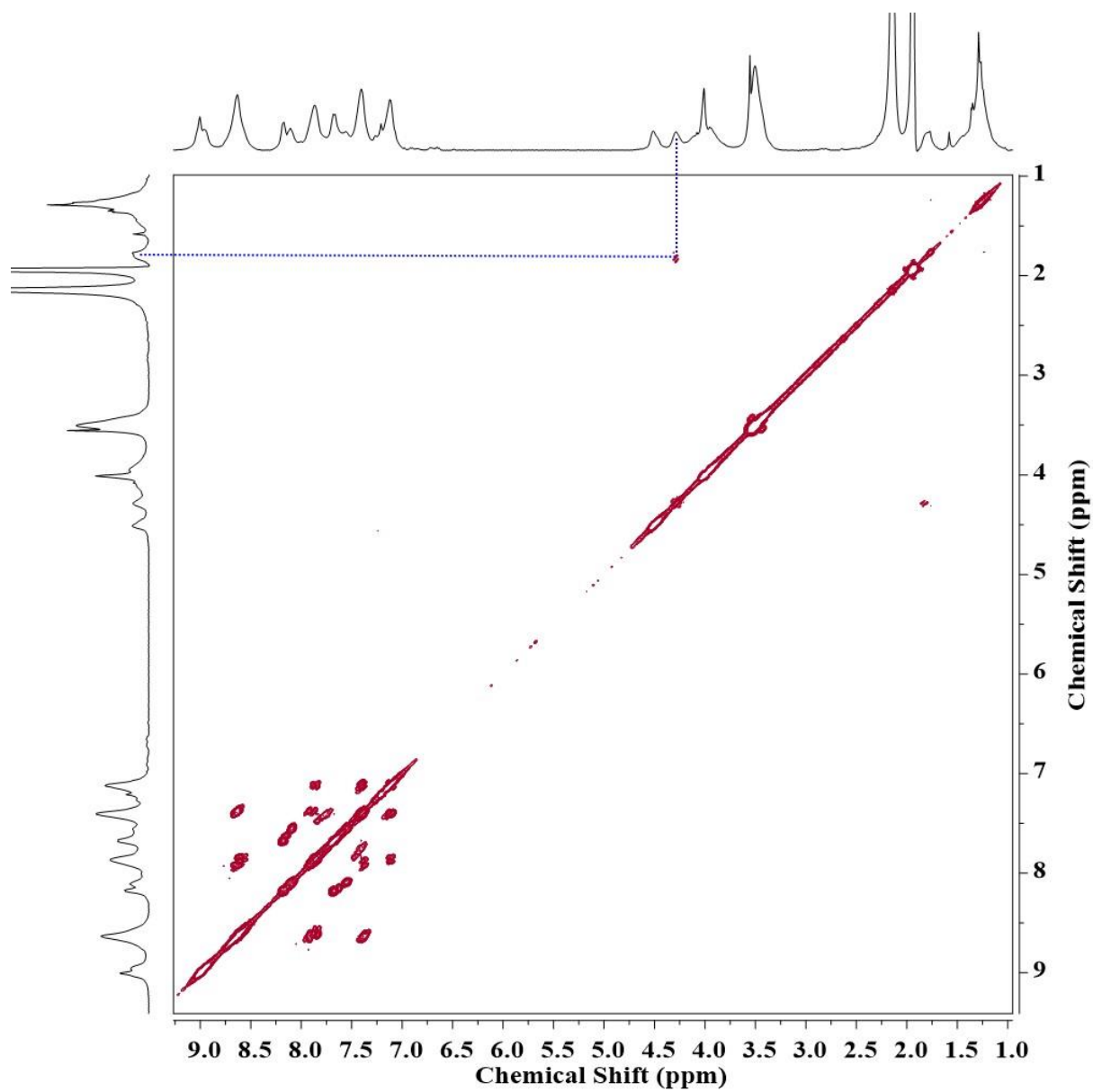


Figure S86. 2D COSY NMR (400 MHz, CD₃CN) spectrum of compound **20** (Tri-P).

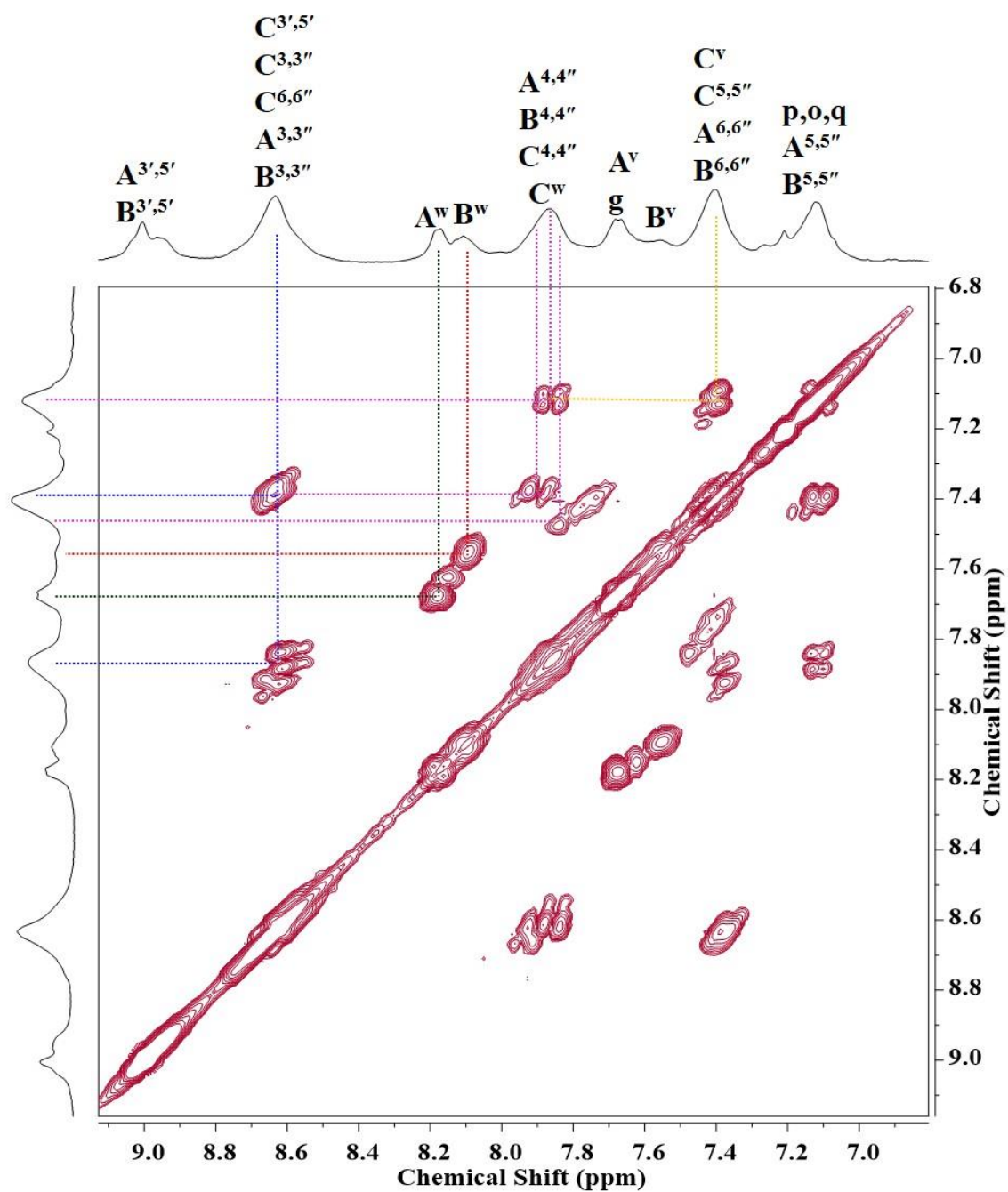


Figure S87. 2D COSY NMR (400 MHz, CD_3CN) spectrum of compound **20** (Tri-P) (aromatic region).

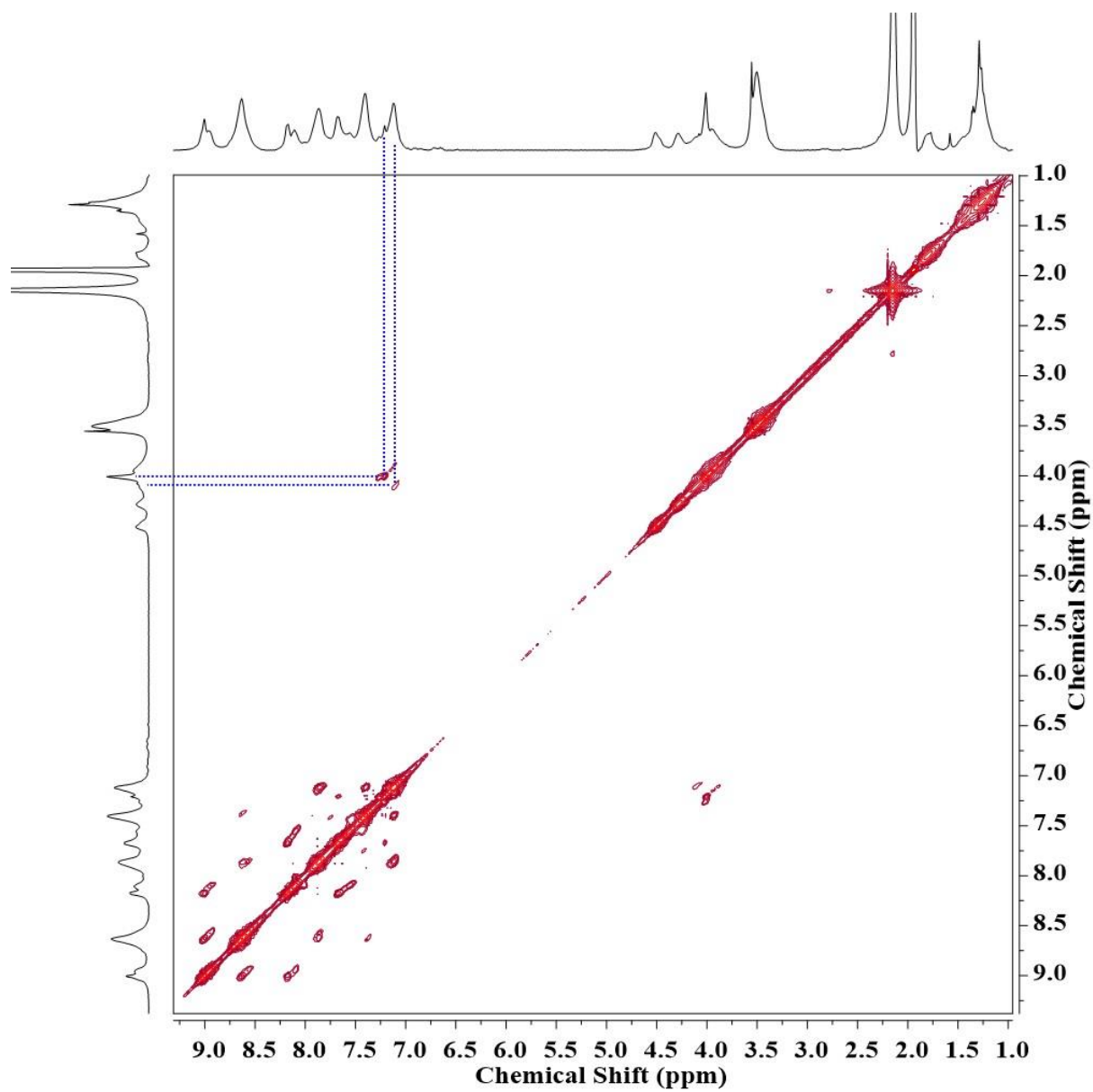


Figure S88. 2D NOESY NMR (400 MHz, CD₃CN) spectrum of compound **20** (Tri-P).

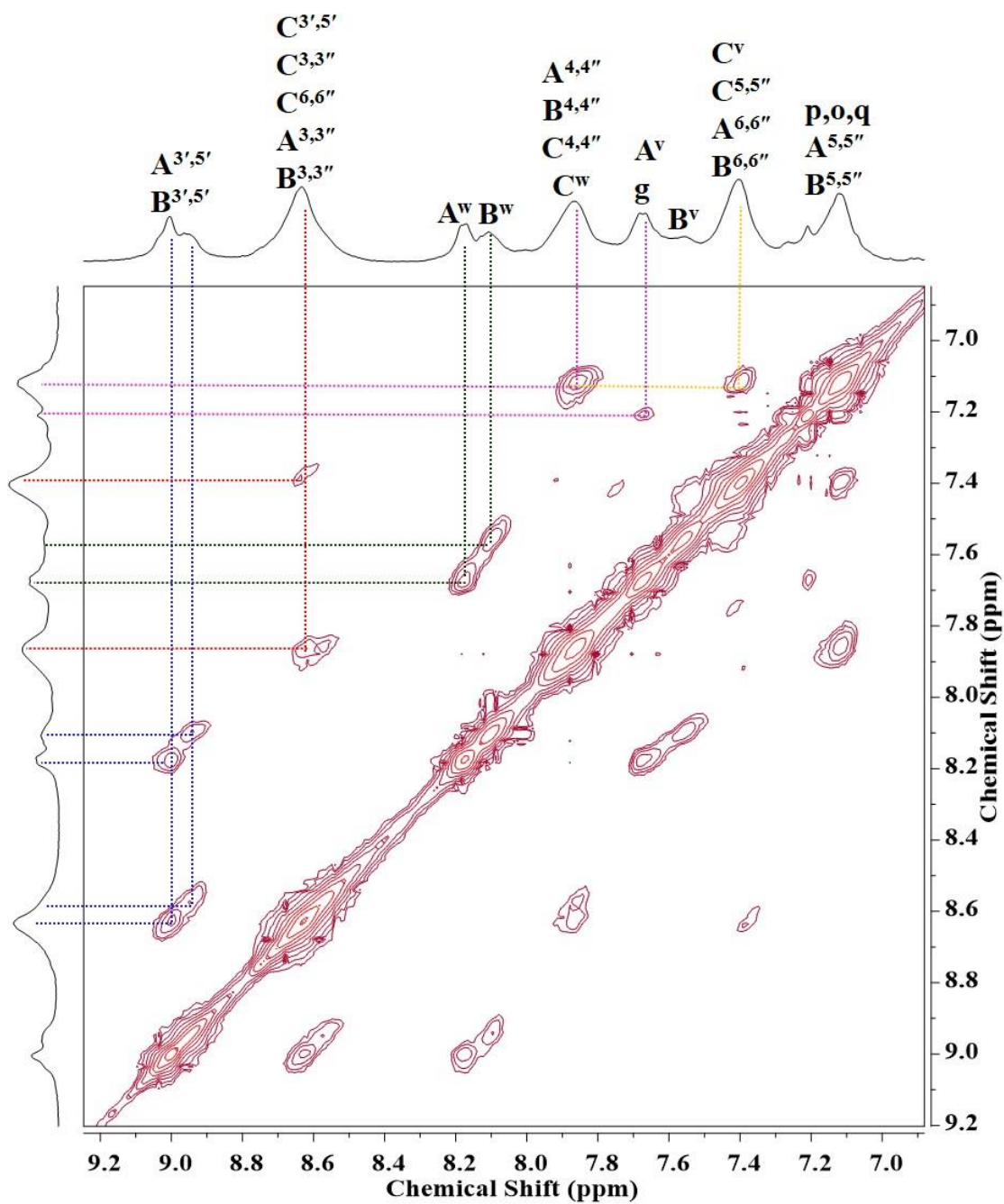


Figure S89. 2D NOESY NMR (400 MHz, CD₃CN) spectrum of compound **20** (Tri-P) (aromatic region).

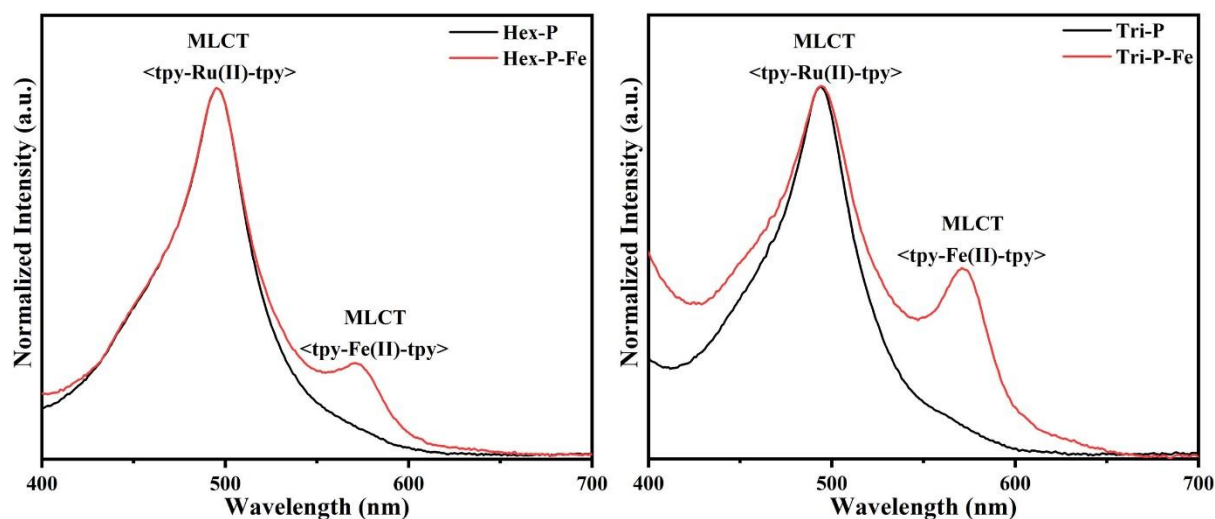


Figure S90. UV-vis absorption spectra in CH₃CN of metallo-polymer with hexameric repeat unit (**Hex-P**) before and after metalation by Fe(II) (Left), and metallo-polymer with trimeric repeat unit (**Tri-P**) before and after metalation by Fe(II) (Right).

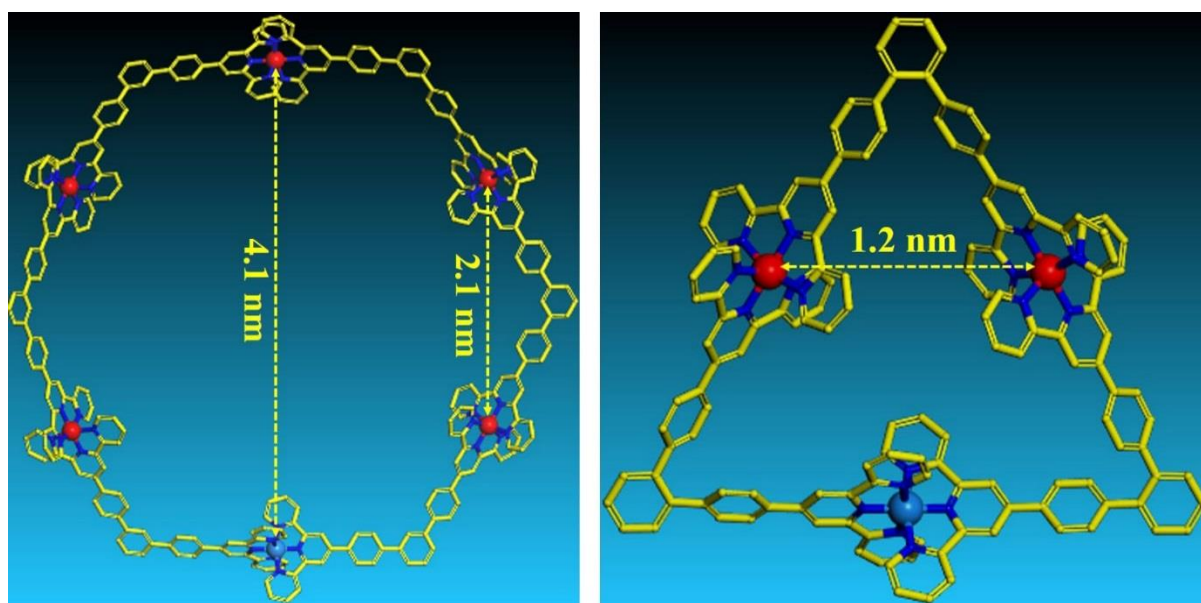


Figure S91. Representative energy-minimized structures of hexagon (right) and triangle (left) with all alkyl chains omitted for clarity.

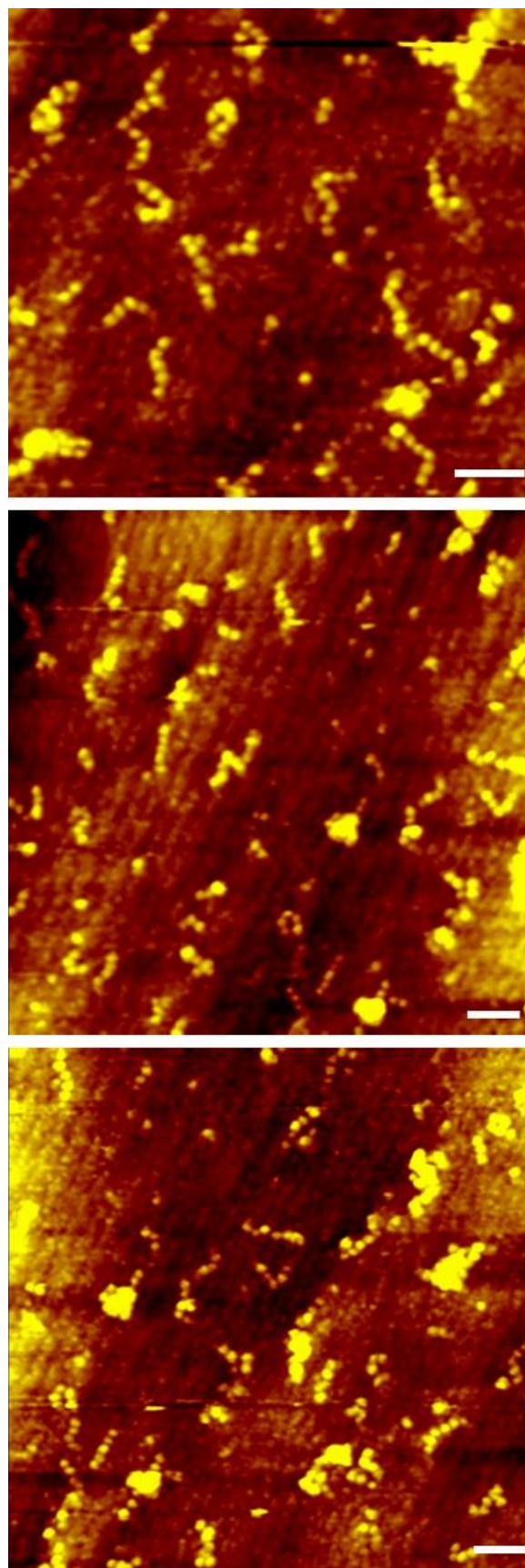


Figure S92. STM images of **Hex-P** on the supporting Ag(111) surface (scale bar: 20 nm).

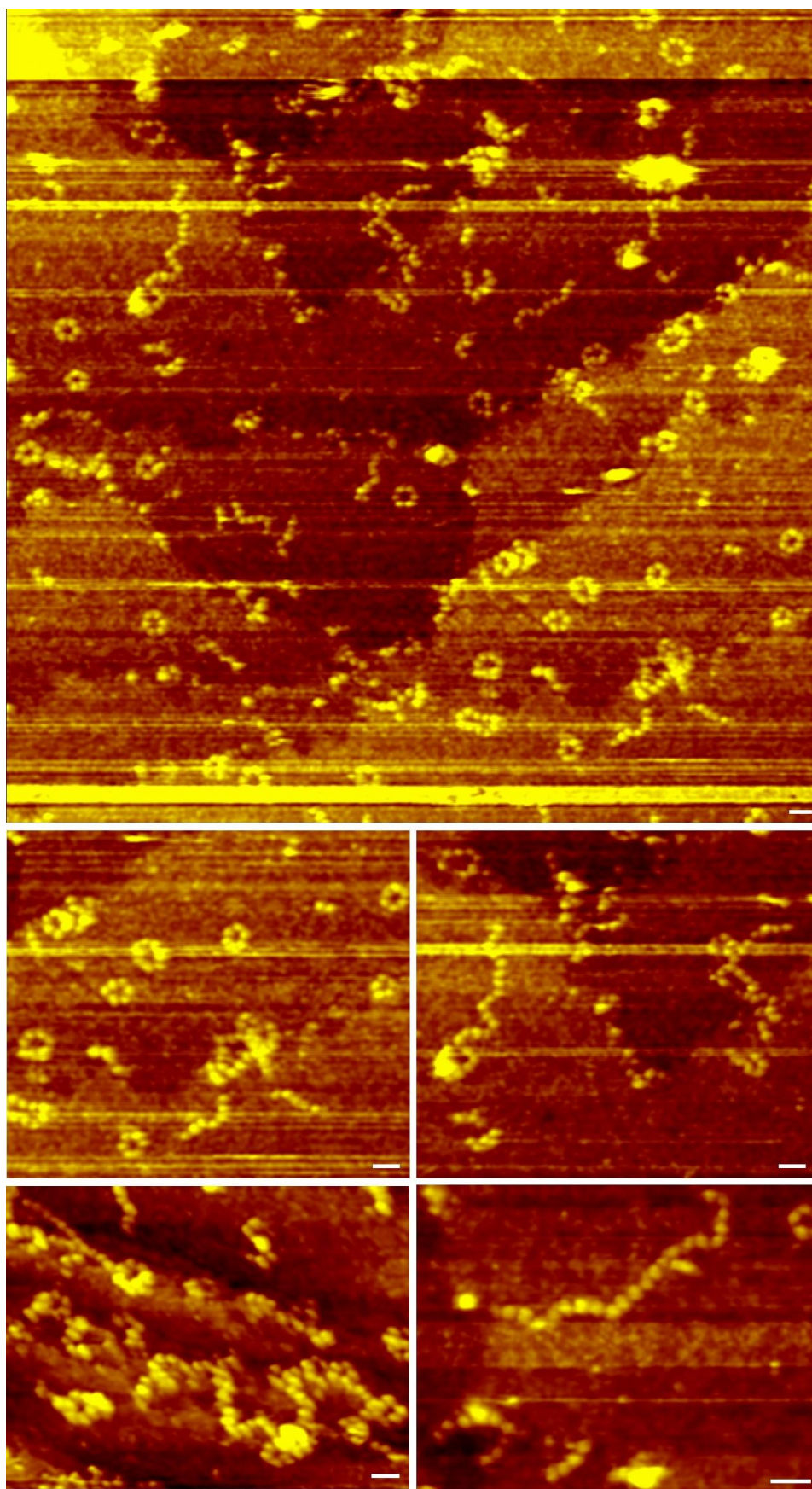


Figure S93. STM images of **Hex-P-Fe** (**Hex-P-C** and **Hex-P-L**) on the supporting Ag(111) surface (scale bar: 10 nm).

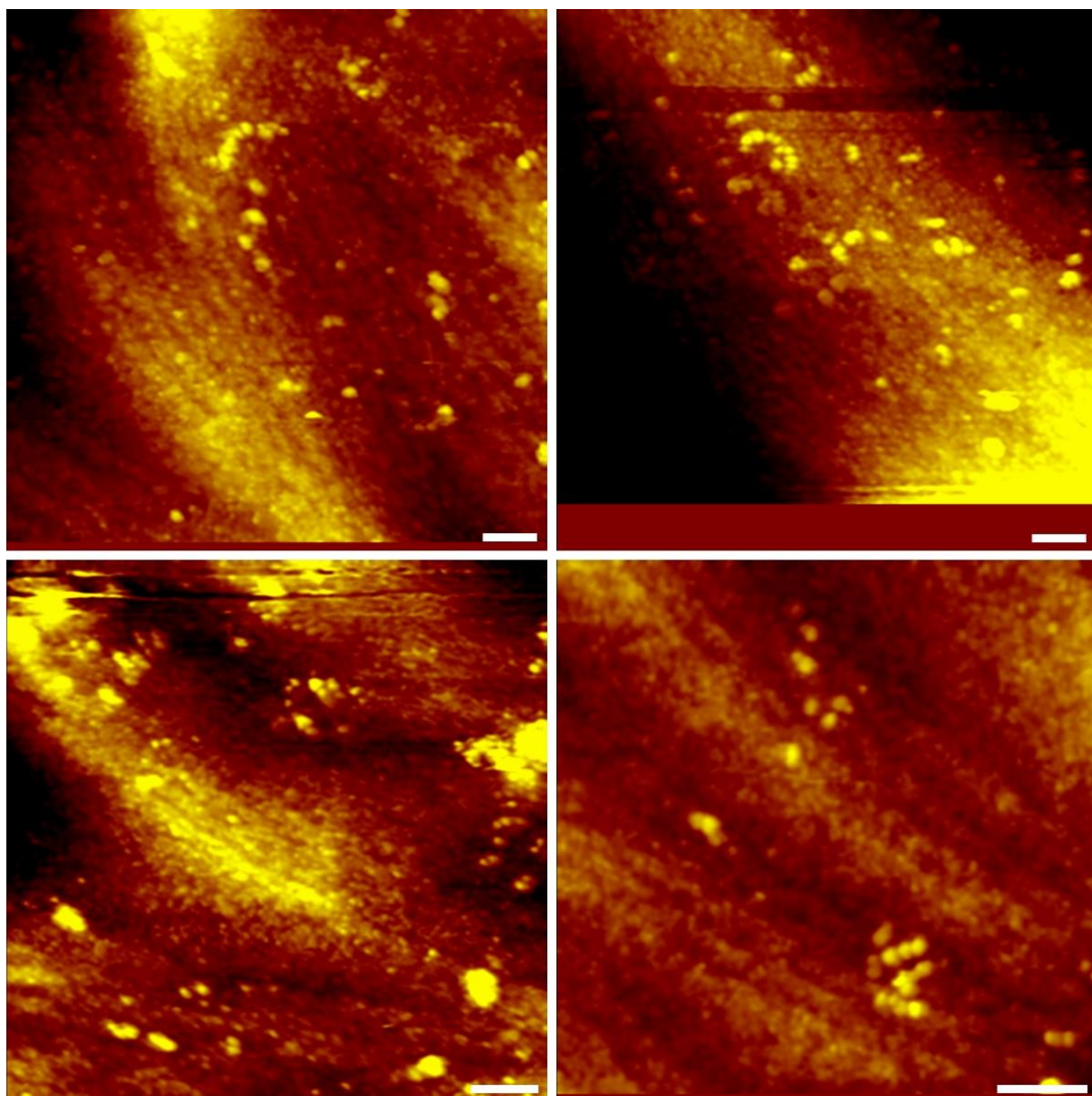


Figure S94. STM images of **Tri-P** on the supporting Ag(111) surface (scale bar: 10 nm).

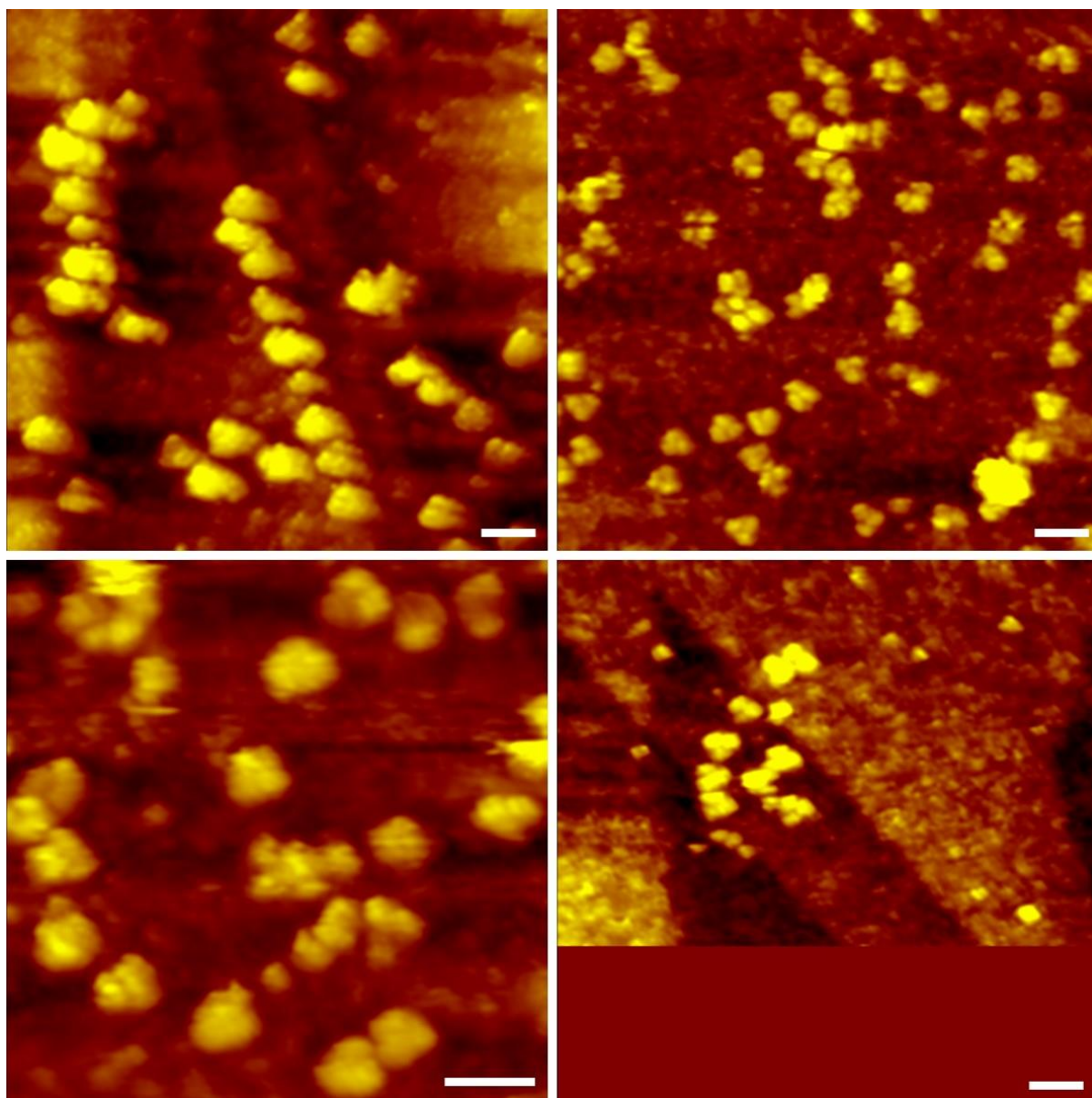


Figure S95. STM images of **Tri-P-Fe (Tri-P-C)** on the supporting Ag(111) surface (scale bar: 5 nm).

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