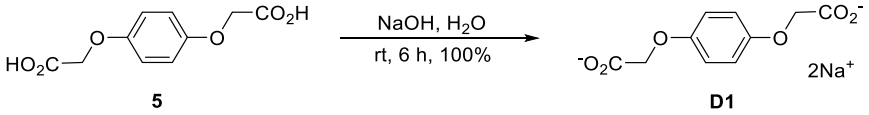
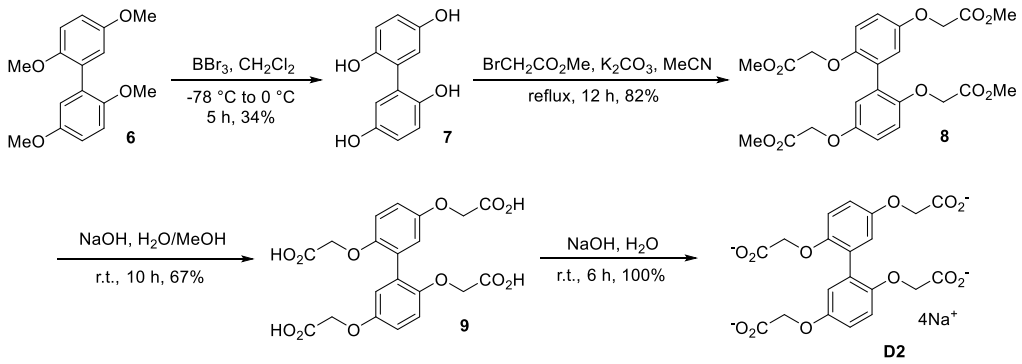
General Procedures. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C using a 400 MHz Bruker Avance III HD spectrometer. 2D NMR spectra were recorded on a 500 MHz Bruker Avance III HD spectrometer. Melting points were measured on a SGW X-4 microscopic melting point instrument. UV-Vis spectra were recorded on Perkin Almer 750s spectrophotometer. High-resolution ESI mass spectra were obtained on a Bruker McriOTOF 11 mass spectrometer. Crystallographic data were collected on Bruker APEX-II CCD diffractometer using graphite-monochromated Cu Kα radiation (λ=1.54178 Å) at 190(2) K.



5 D1

Compound D1. A solution of compound **5** (1.0 g, 4.4 mmol) and sodium hydroxide (0.35 g, 8.8 mmol) in distilled water (10 mL) was stirred at room temperature 5 minutes. Water was removed under reduced pressure to give **D1** (1.19 g, 100%) as a white solid. M.p. > 300 °C. ^{1}H NMR (400 MHz, D_2O): δ 6.92 (s, 4 H), 4.45 (s, 4 H). ^{13}C NMR (100 MHz, D_2O): δ 176.98, 152.12, 115.42, 67.23. HRMS (ESI): calcd for $C_{10}H_9O_6Na_2$ $[M+H]^+$: 271.0189. Found: 271.0196.

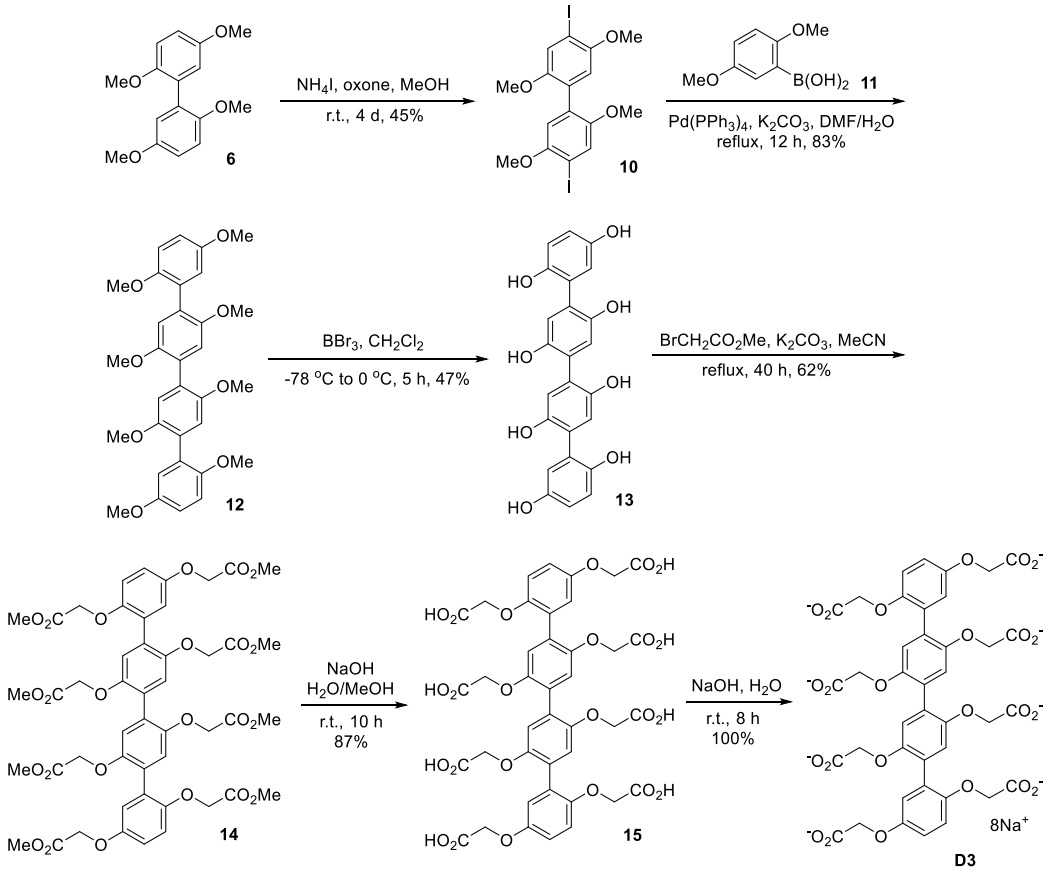


6 7 8 9 D2

Compound 8. BBr_3 (0.75 mL) was dropwise added to a solution of compound **6**[1] (0.5 g, 1.8 mmol) in dichloromethane (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and left at room temperature for 4h. The mixture was poured onto icy water and the resulting precipitate was filtered, washed with water (5 mL × 2) and dried under vacuum to give tetraol **7** (0.13 g, 34%) as white solid. A mixture of **7** (0.25 g, 1.0 mmol) and anhydrous potassium carbonate (1.59 g, 10 mmol) in acetonitrile (15 mL) was stirred at 50 °C for 0.5 h and then methyl bromoacetate (1.4 g, 9.0 mmol) was added dropwise. The reaction mixture was stirred under reflux for 20 h and then concentrated with a rotavapor. The resulting residue was washed with water (15 mL) and ether (20 mL × 3) to give compound **8** (0.47 g, 82%) as ivory solid. M.p. 126-128 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.84-6.92 (m, 6 H), 4.74 (s, 4 H), 4.67 (s, 4 H), 3.69 (s, 6 H), 3.66 (s, 6 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 169,98, 152.05, 150.04, 128.04, 118.27, 114.65, 114.11, 66.09, 65.52, 52.12. HRMS (ESI): calcd for $C_{24}H_{30}NO_{12}$ $[M+NH_4]^+$: 524.1763. Found: 524.1774.

Compound D2. A solution of compound **8** (50 mg, 0.10 mmol) and sodium hydroxide (48 mg, 1.2 mmol) in methanol (7 mL) and distilled water (1.5 mL) was stirred for 10 h. The mixture was concentrated under reduced pressure, diluted with distilled water (2 mL), and then acidified with dilute hydrochloride (1 N). The precipitate formed was collected by filtration, washed by

cold water, and then dried under vacuum to give compound **9** as a white solid (30 mg, 67%). This tetraacid was suspended in water (7 mL). To the mixture was added sodium hydroxide (10.6 mg, 0.28 mmol). The solution was stirred at room temperature for 5 minutes and then concentrated under reduced pressure to give **D2** (37 mg, 100%) as a white solid. M.p. > 300 °C. ^{1}H NMR (400 MHz, D_2O): δ 6.80-6.84 (m, 6 H), 4.35 (s, 4 H), 4.24 (s, 4 H). ^{13}C NMR (100 MHz, D_2O): δ 177.10, 176.87, 151.97, 150.08, 128.20, 117.69, 114.56, 114.51, 68.65, 67.33. HRMS (ESI): calcd for $C_{20}H_{18}NaO_{12}$ $[M-3Na+4H]^+$: 473.0690. Found: 473.0692.



Compound 10. A mixture of compound **6** (2.54 g, 9.0 mmol) and ammonium iodide (2.92 g, 20 mmol) in methanol (50 mL) was stirred at room temperature for 0.5 h and then oxone (6.26 g, 20 mmol) was added slowly. The mixture was stirred for 96 hours and then concentrated under reduced pressure and triturated with dichloromethane (50 mL). The organic phase was washed by aqueous sodium hyposulfite (0.5 N, 15 mL×3) and brine (15 mL) and dried over anhydrous sodium sulphate. After the solvent was removed under reduced pressure, the resulting residue was subject to column chromatography (n-hexane/dichloromethane 1:2) to give compound **10** (2.2 g, 45%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.41 (s, 2 H), 6.81 (s, 2 H), 3.75 (s, 6 H), 3.66 (s, 6 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.28, 151.79, 128.18, 122.49, 114.57, 85.44, 57.34, 56.78. HRMS (ESI): calcd for $C_{16}H_{16}O_4I_2Na$ $[M+Na]^+$: 548.9030. Found: 548.9028.

Compound 12. A mixture of compounds **10** (0.5 g, **11** (0.46 g, 2.5 mmol), tetrakis(triphenyl-phosphine)palladium (0.17 g, 0.15 mmol) and anhydrous potassium carbonate (2.21 g, 16 mmol) in *N*,*N*-dimethylformamide (15 mL) and water (7.5 mL) was slowly stirred under reflux

for 12 hours and then cooled to room temperature. Water (15 mL) was added slowly, the resulting mixture was quickly filtered off and the filtrate was diluted in dichloromethane (500 mL). After filtration, the organic layer was concentrated under reduced pressure. After workup, the crude product was subject to column chromatography (chloroform) to give compound **12** (0.43 g, 83%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87-7.00 (m, 10 H), 3.76-3.81 (m, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.32, 151.35, 150.68, 128.67, 127.29, 127.14, 117.33, 115.28, 115.07, 113.38, 112.46, 56.52, 56.49, 55.74. HRMS (ESI): calcd for $C_{32}H_{35}O_8$ $[M+H]^+$: 547.2326. Found: 547.2348.

Compound 14. To a solution of compound **12** (1 g, 1.8 mmol) in dichloromethane (15 mL) at 0 °C was added BBr_3 dropwise (1.4 mL). The reaction mixture was stirred at 0 °C for 2 h and left at room temperature for 4h. The mixture was poured onto ice water and the precipitate formed was filtered, washed with water (20 mL × 2), and dried under vacuum to give compound **13** (0.37 g, 47%) as a purple solid. A mixture of **13** (0.37 g, 0.9 mmol) and anhydrous potassium carbonate (2.85 g, 20.6 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at room temperature for 0.5 h and then methyl bromoacetate (2.1 g, 11.4 mmol) was added dropwise. The reaction mixture was stirred at 100 °C for 40 h. After cooling, water (30 mL) was added. The precipitate formed was collected by filtration, washed by water and dried under vacuum to give compound **14** as a pale white solid (0.52 g, 62%). M.p. 178-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (s, 2H), 7.01 (s, 2H), 6.93-6.98 (m, 4 H), 6.85-6.88 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.80, 169.60, 152.45, 150.40, 149.73, 149.69, 128.35, 127.16, 127.01, 118.40, 117.35, 117.13, 115.21, 114.64, 66.94, 66.61, 66.03, 52.21, 52.03, 51.98, 51.97. HRMS (ESI): calcd for $C_{48}H_{50}O_{24}$ $[M+H]^+$: 1011.2765. Found: 1011.2783.

Compound D3. A solution of **14** (50 mg, 0.05 mmol) and sodium hydroxide (48 mg, 1.2 mmol) in methanol (7 mL) and distilled water (1.5 mL) was stirred for 10 h. The mixture was concentrated under reduced pressure. The resulting residue was triturated with distilled water (2 mL) and then acidified with dilute hydrochloride (1N) to pH = 4. The precipitate formed was collected by filtration, washed by cold water and dried under vacuum to give compound **15** as a pale yellow solid (39 mg, 87%). M.p. > 245 °C (decomp.).^{1}H NMR (400 MHZ, DMSO-d_6): δ 7.10 (s, 1H), 7.02 (s, 1H), 6.98-6.99 (m, 1 H), 6.90-6.92 (m, 1 H), 6.80-6.85 (m, 4 H), 6.74-6.78 (m, 2 H), 4.54-4.63 (m, 16 H). ^{13}C NMR (100 MHz, D_2O): δ 171.10, 171.01, 170.89, 170.81, 151.95, 150.10, 149.19, 149.12, 127.77, 126.45, 126.18, 118.39, 116.36, 116.40, 114.36, 113.78, 65.89, 65.74, 65.66, 65.38. HRMS (ESI): calcd for $C_{40}H_{33}O_{24}$[M-H]$^-$: 897.1356. Found: 897.1385. Compound **15** (37 mg, 0.044 mmol) and sodium hydroxide (13.9 mg, 0.35 mmol) were added to distilled water (7 mL) and stirred at room temperature for 5 minutes. Upon concentration and dryness under reduced pressure, compound **D3** was obtained as a white solid (46.7 mg, 100%). M.p. > 300 °C. ^{1}H NMR (400 MHZ, D_2O): δ 6.87-7.03 (m, 10 H), 4.39-4.46 (m, 16 H). ^{13}C NMR (100 MHz, D_2O): δ 177.31, 176.88, 176.74, 151.94, 150.27, 150.04, 149.79, 128.13, 127.78, 127.54, 117.97, 117.23, 116.86, 114.36, 68.91, 68.88, 68.76, 67.37.

UV-vis Dilution experiments: For the determination of association constants (K_a) for 1:1 the complexes using the UV-vis dilution method, charge-transfer (CT) absorption bands within 400 and 500 nm were recorded at different concentrations and the data were fitted using the following nonlinear binding equation[2]:

$$\Delta A = \Delta A_\infty\{1+0.5/(K_a[\text{acceptor}])-((0.5/(K_a[\text{acceptor}]))^2+1/(K_a[\text{acceptor}]))^{1/2}\}$$

In this equation, ΔA was the change defined as the difference between the observed (A_{obs}) and the initial (A_0) absorbance of the samples and [acceptor] was the concentration of **A1-A3** after each dilution. The values of ΔA_∞ and K_a was calculated after nonlinear regression.

Isothermal titration calorimetry (ITC): The experiments were carried out using a MicroCal PEAQ-ITC instrument. Association constants and associated thermodynamic parameters were obtained through computer simulations (curve fitting) using MicroCal ITC analyze software[3-5].

References:

1) R. J. Bushby, D. R. McGill, K. M. Ng and N. Taylor, *J. Mater. Chem.*, 1997, **7**, 2343-2354.
2) Y.-C. Zhang, Y. Qin, H. Wang, D.-W. Zhang, G.-Y. Yang and Z.-T. Li, *Chem. Asian J.*, 2016, **11**, 1065-1070.
3) B. Yang, L.-M. Zheng, Z.-Z. Gao, X. Xiao, Q.-J. Zhu, S.-F. Xue, Z. Tao, J.-X. Liu, G. Wei, *J. Org. Chem.*, 2014, **79**, 11194-11198.
4) G. Wu, M. Olesińska, Y.-C. Wu, D. Matakvinkovic, O.-A. Scherman, *J. Am. Soc.*, 2017, **139**, 3202-3208.
5) L. Chen, H.-Y. Zhang, Y. Liu, *J. Org. Chem.*, 2012, **77**, 9766-9773.

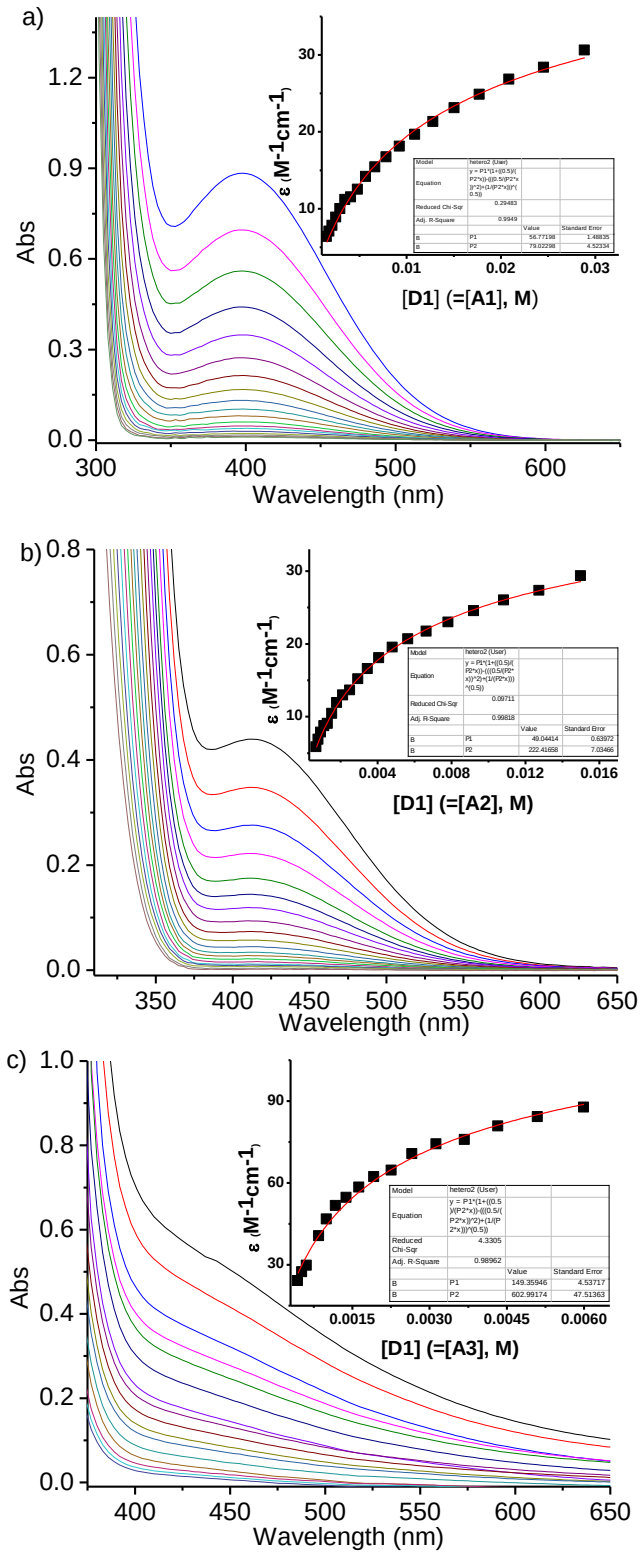


Fig. S1 Absorption spectra of the solution of a) **A1** and **D1** ([**D1**] = [**A1**] = 30-0.6 mM), b) **A2** and **D1** ([**D1**] = [**A2**] = 15-0.6 mM), and c) **A3** and **D1** ([**D1**] = [**A3**] = 6-0.4 mM) in water at 25 °C. Inset: Plot of a) ε (402 nm), and b) ε (413 nm), and c) ε (450 nm).

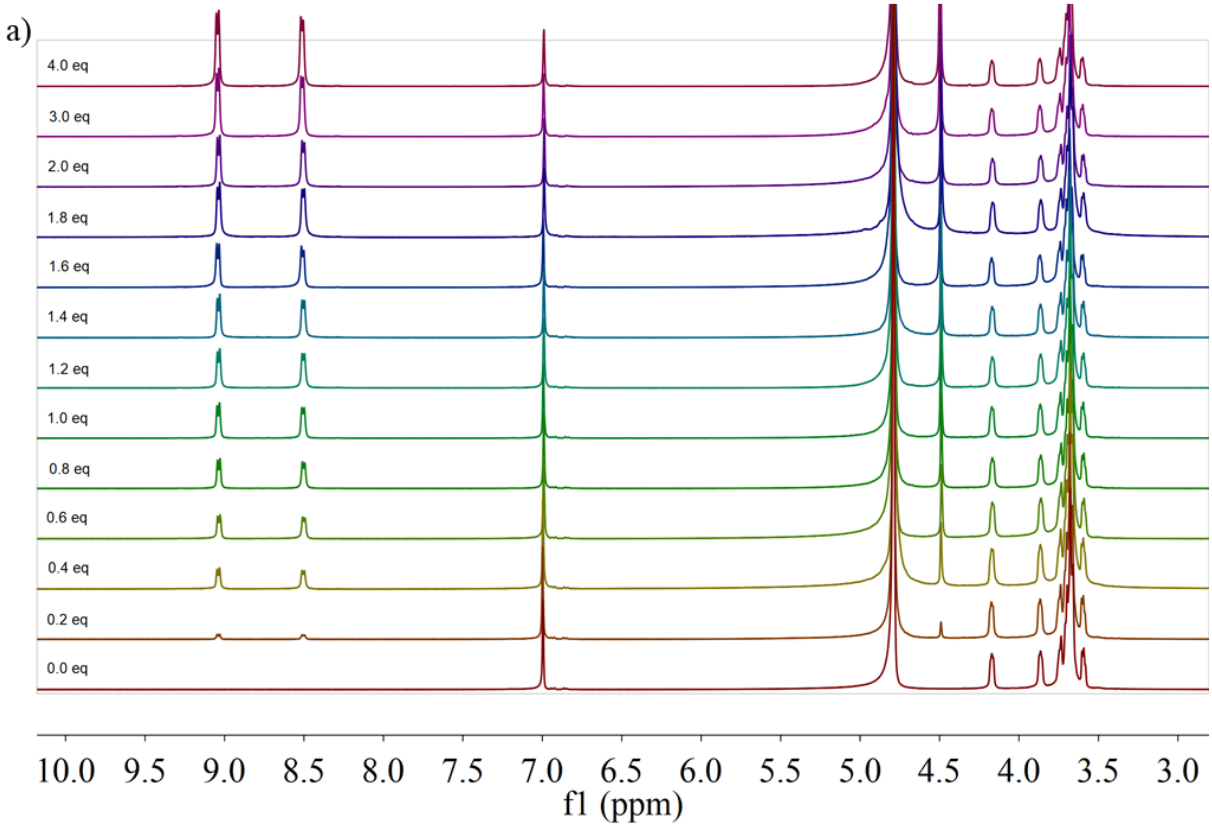


Fig. S2 Partial ^{1}H NMR spectra (400 MHz) of **D1'** (9.0 mM) and **A1** of varying amounts (0-36.0 mM) in D_2O at 25 ºC.

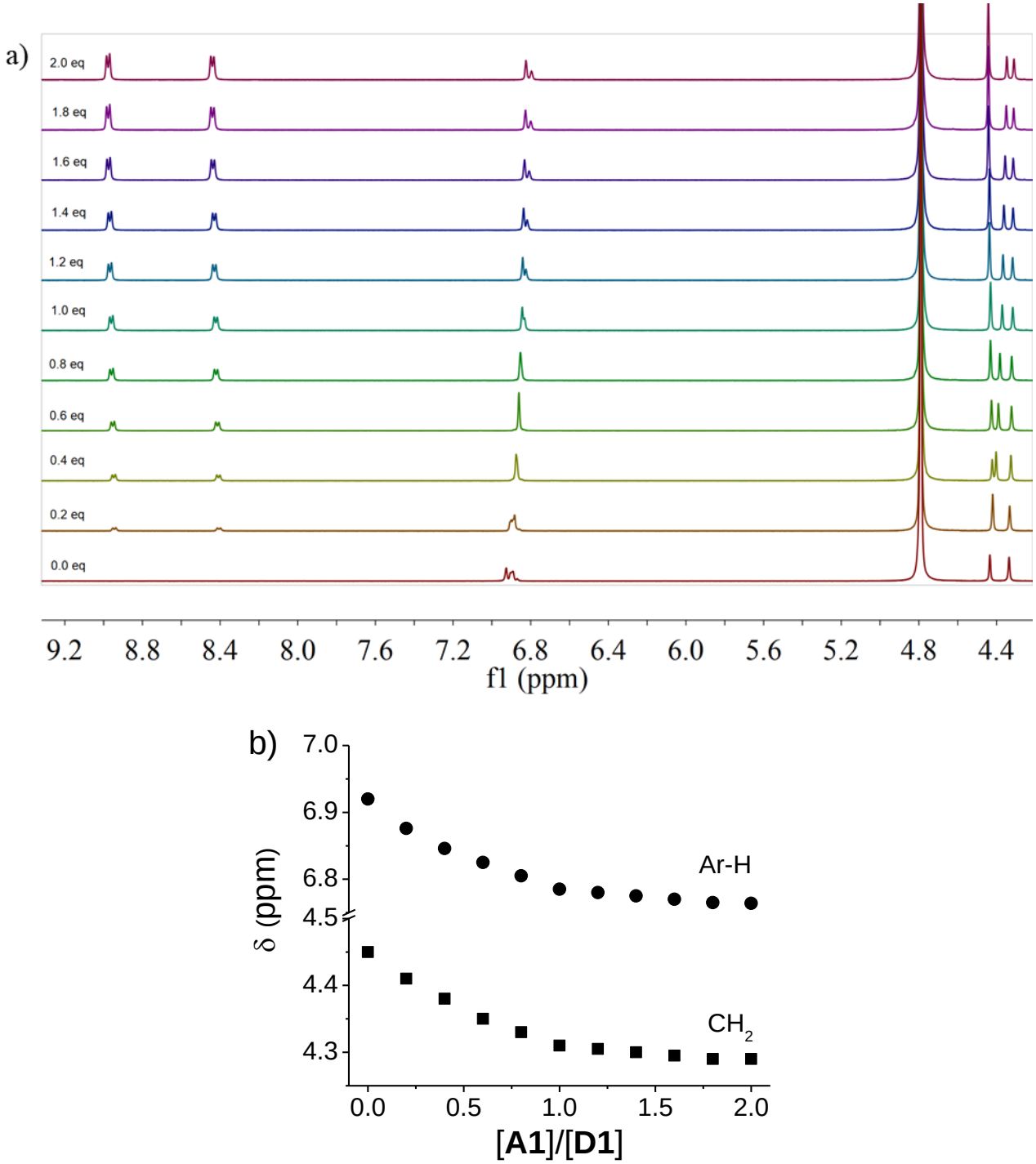


Fig. S3 a) Partial ^{1}H NMR spectra of the mixture of **D1** (0.14 M) and **A1** of varying amount (0-0.28 M) in D_2O at 25 °C. b) Plot of the chemical shift of the Ar-H and CH_2 signals of **D1** versus [**A1**]/[**D1**].

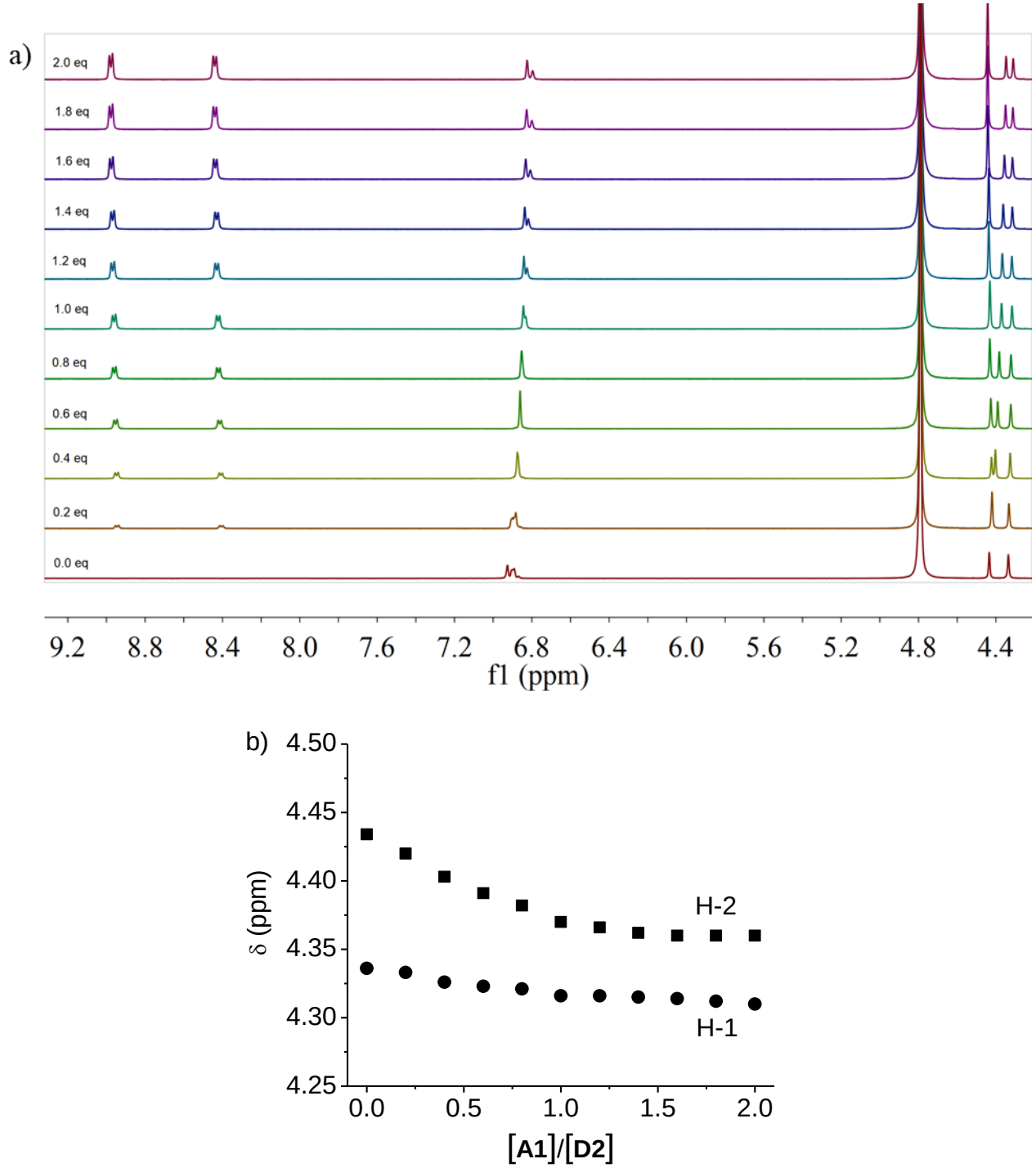


Fig. S4 a) Partial ^{1}H NMR spectra of the mixture of **D2** (2.0 mM) and **A1** of varying amount (0-4.0 mM) in D_2O at 25 °C. b) Plot of the chemical shift of the two C*H*$_2$ signals of **D2** versus [**A1**]/[**D2**].

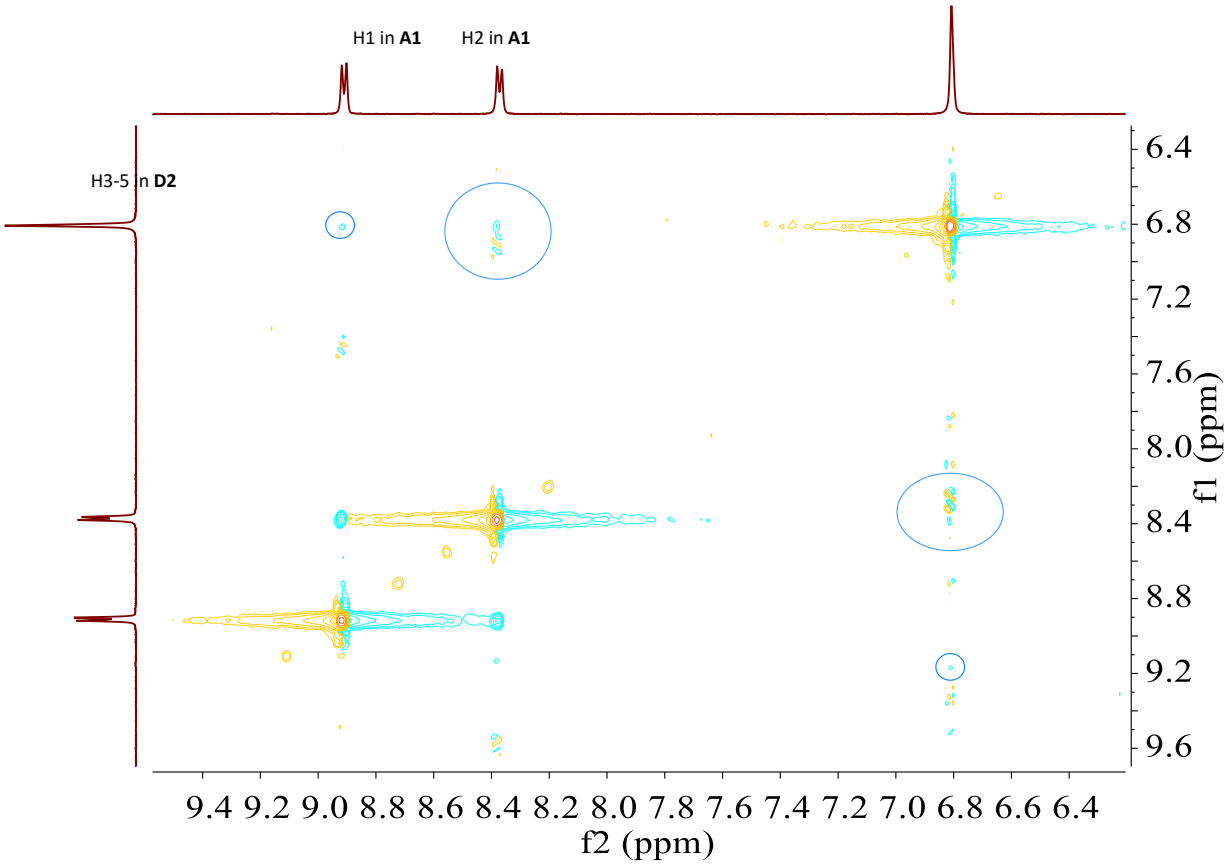


Fig. S5 Partial 2D NOESY NMR spectrum of the mixture of **D2** and **A1** (1:1, 1.0 mM) in D_2O at 25 °C.

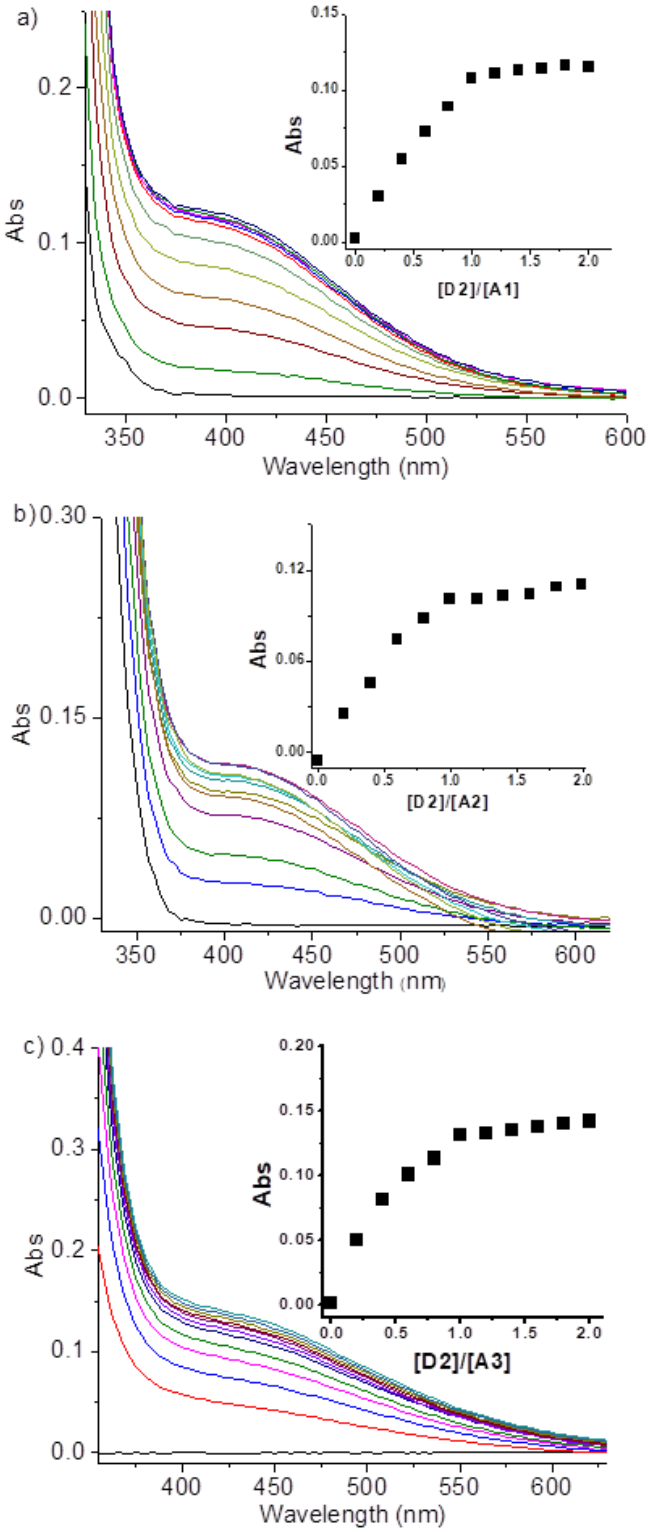


Fig. S6 Absorption spectra of the mixtures of a) **A1**, b) **A2**, and c) **A3** with **D2** of incrementally increased concentration (0–3.0 mM) in water at 25 °C ([**A1**] = [**A2**] = [**A3**] = 1.5 mM). Inset: Plot of the CT absorption at a) 408, b) 416, and c) 425 nm.

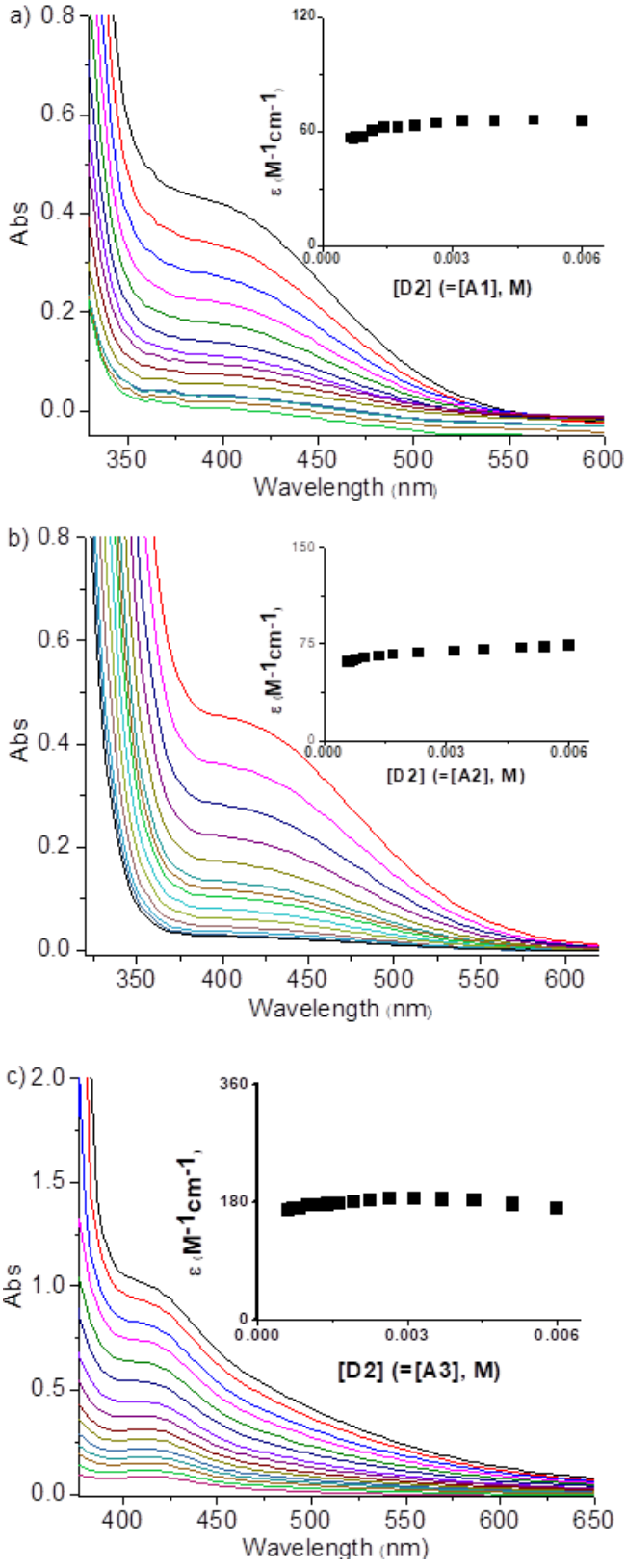


Fig. S7 Absorption spectra of the solutions of a) **A1** and **D2** ([**D2**] = [**A1**] = 6-0.6 mM), b) **A2** and **D2** ([**D2**] = [**A2**] = 6-0.6 mM) and c) **A3** and **D2** ([**D2**] = [**A3**] = 6-0.6 mM) in water at 25 °C. Inset: Plot of ε a) at 408 nm, b) at 416 nm and c) at 425 nm, respectively.

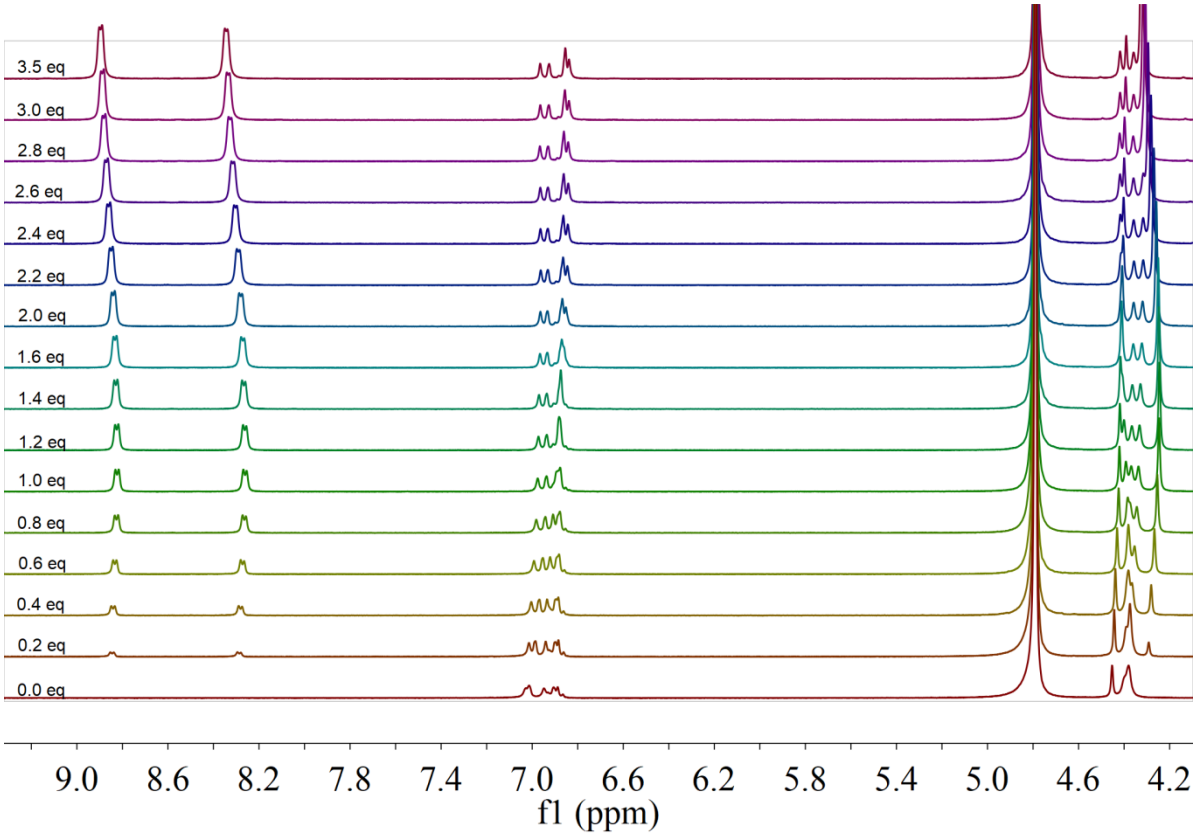


Fig. S8 Partial ^{1}H NMR spectra of the mixture of **D3** (2.0 mM) and **A1** of varying amount (0-4.0 mM) in D_2O at 25 °C.

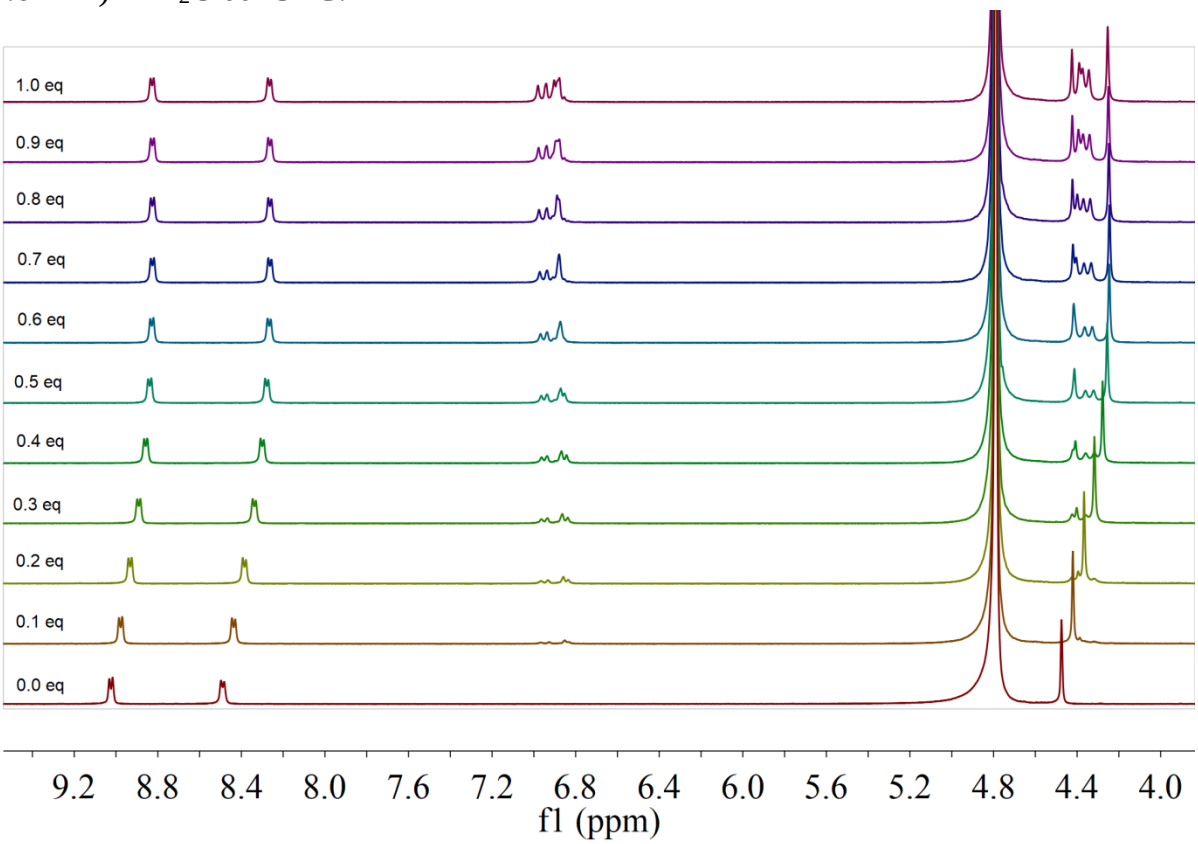


Fig. S9 Partial ^{1}H NMR spectra of the mixture of **A1** (2.0 mM) and **D3** of varying amount (0-2.0 mM) in D_2O at 25 °C.

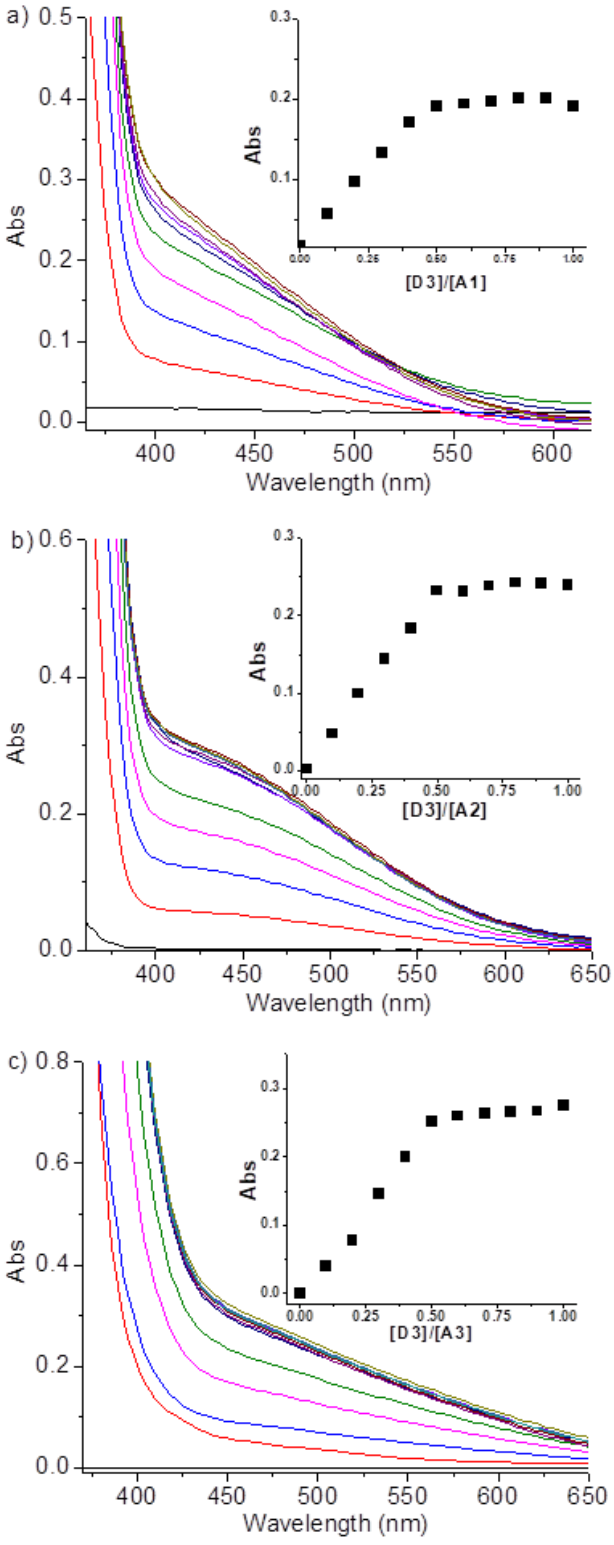


Fig. S10 Absorption spectra of the mixture of a) **A1**, b) **A2** and c) **A3** with **D3** of incrementally increased concentration (0–1.5 mM) in water at 25 °C ([**A1**] = [**A2**] = [**A3**] = 1.5 mM). Inset: Plot of the CT absorption at a) 443, b) 450 and c) 472 nm.

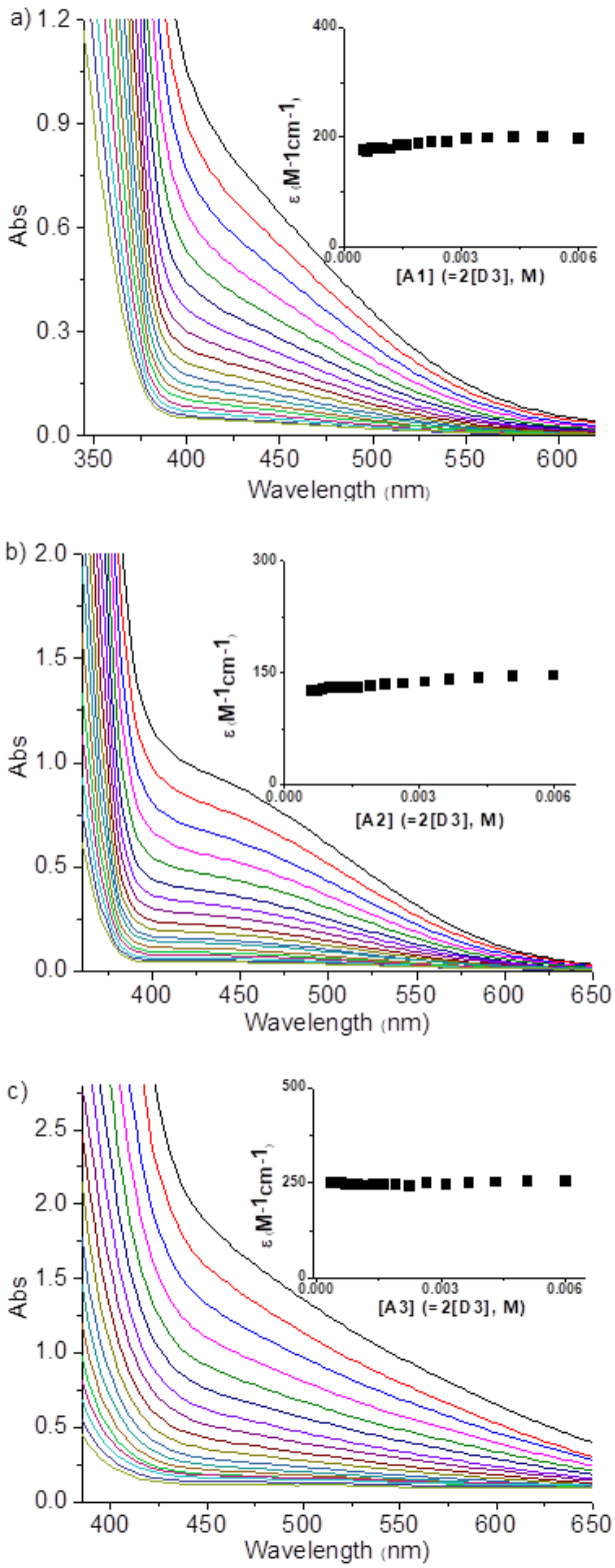


Fig. S11 Absorption spectra of the solution of a) **A1** and **D3** (2[**D3**] = [**A1**] = 6-0.6 mM), b) **A2** and **D3** ([2**D3**] = [**A2**] = 6-0.6 mM) and c) **A3** and **D3** (2[**D3**] = [**A3**] = 6-0.6 mM) in water at 25 °C. Inset: Plot of ε a) at 443 nm, b) at 460 nm, and c) at 472 nm, respectively.

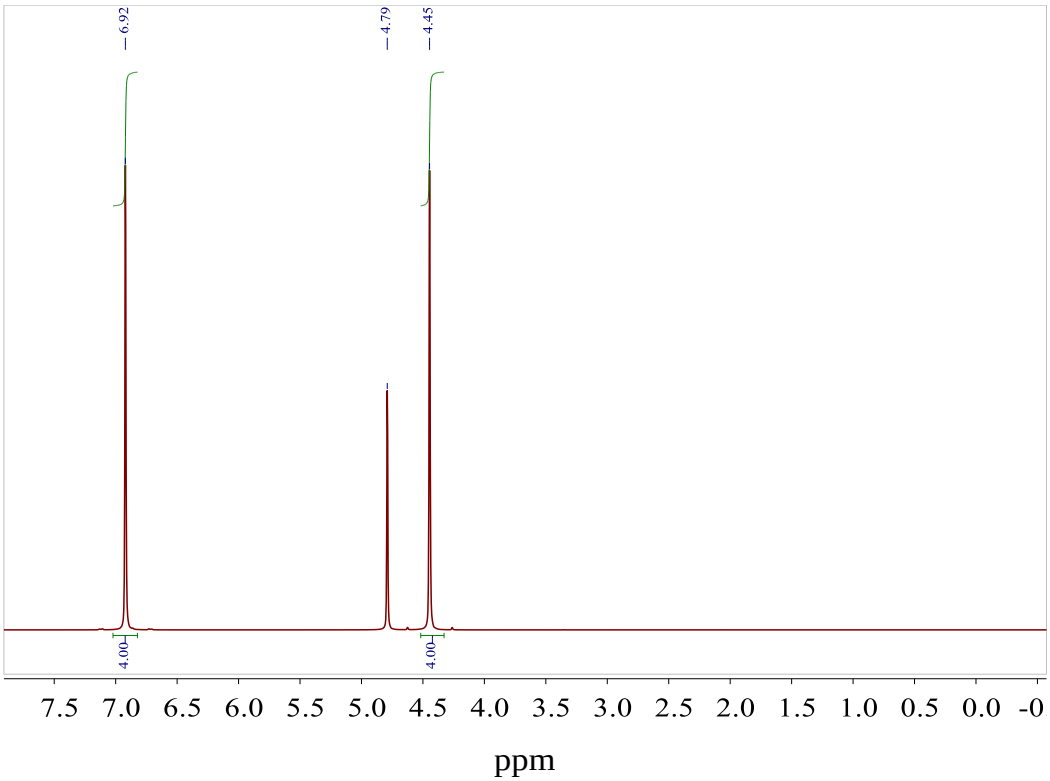


Fig. S12 ^{1}H NMR spectrum of compound **D1** in D_2O at 25 °C.

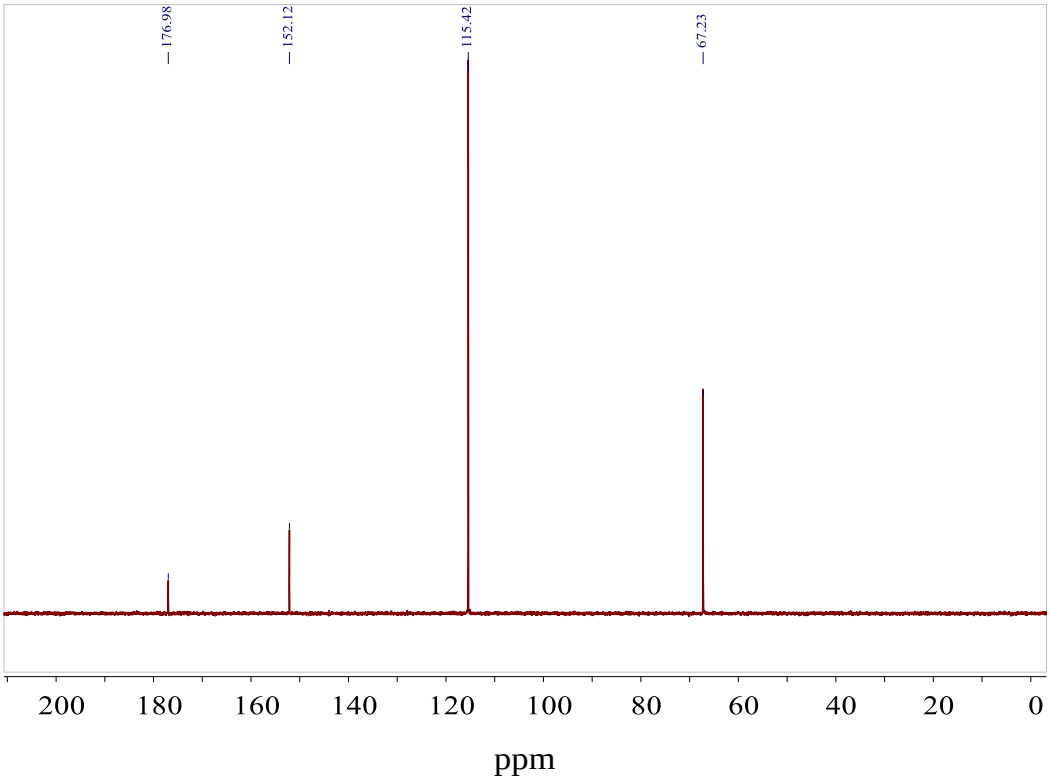


Fig. S13 ^{13}C NMR spectrum of compound **D1** in D_2O at 25 °C.

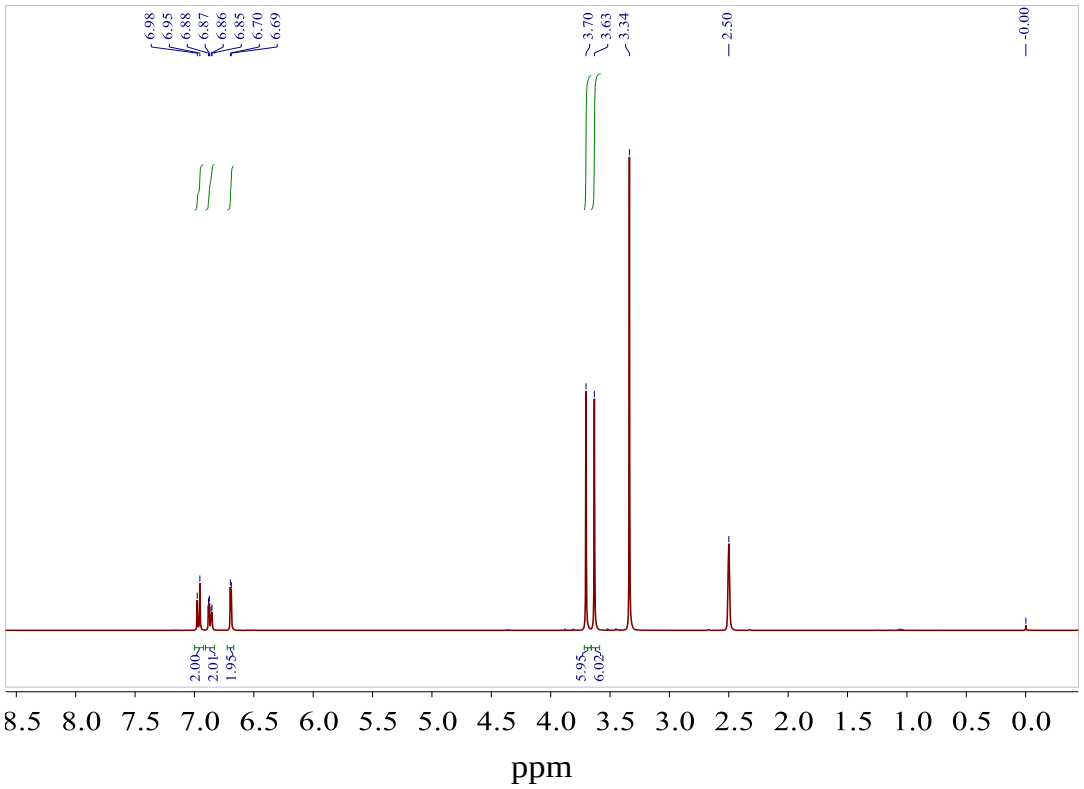


Fig. S14 ^{1}H NMR spectrum of compound **6** in DMSO-d_6 at 25 °C.

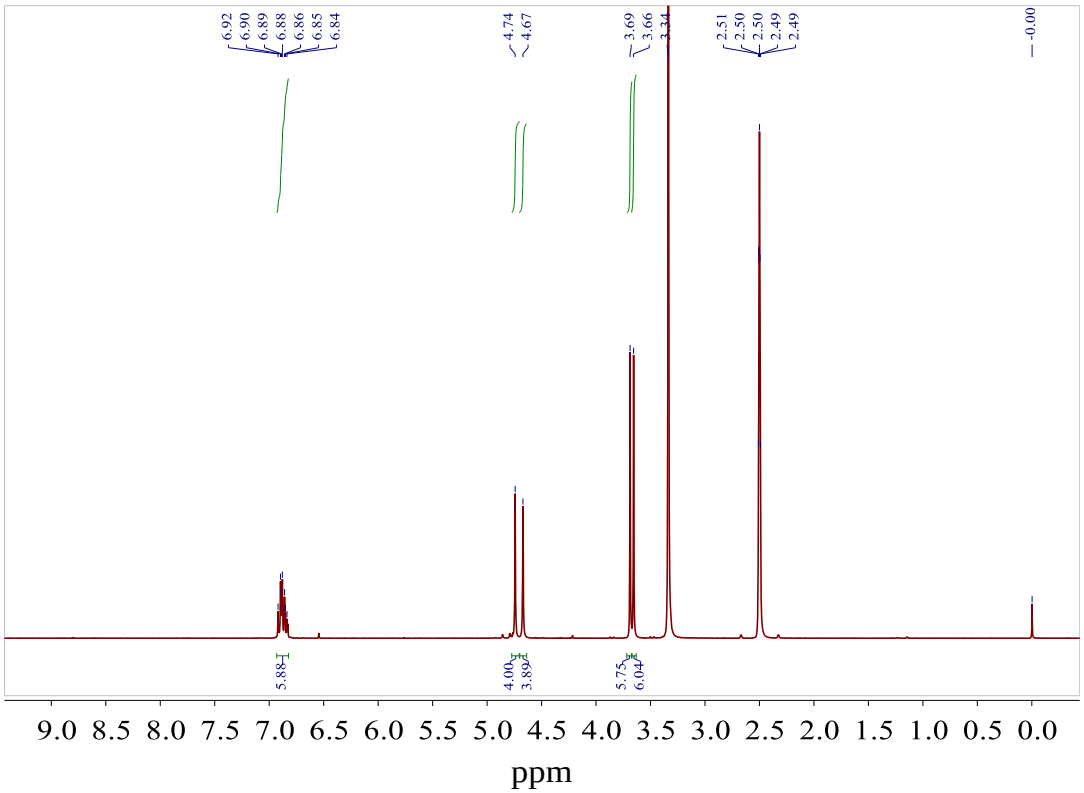


Fig. S15 ^{1}H NMR spectrum of compound **8** in DMSO-d_6 at 25 °C.

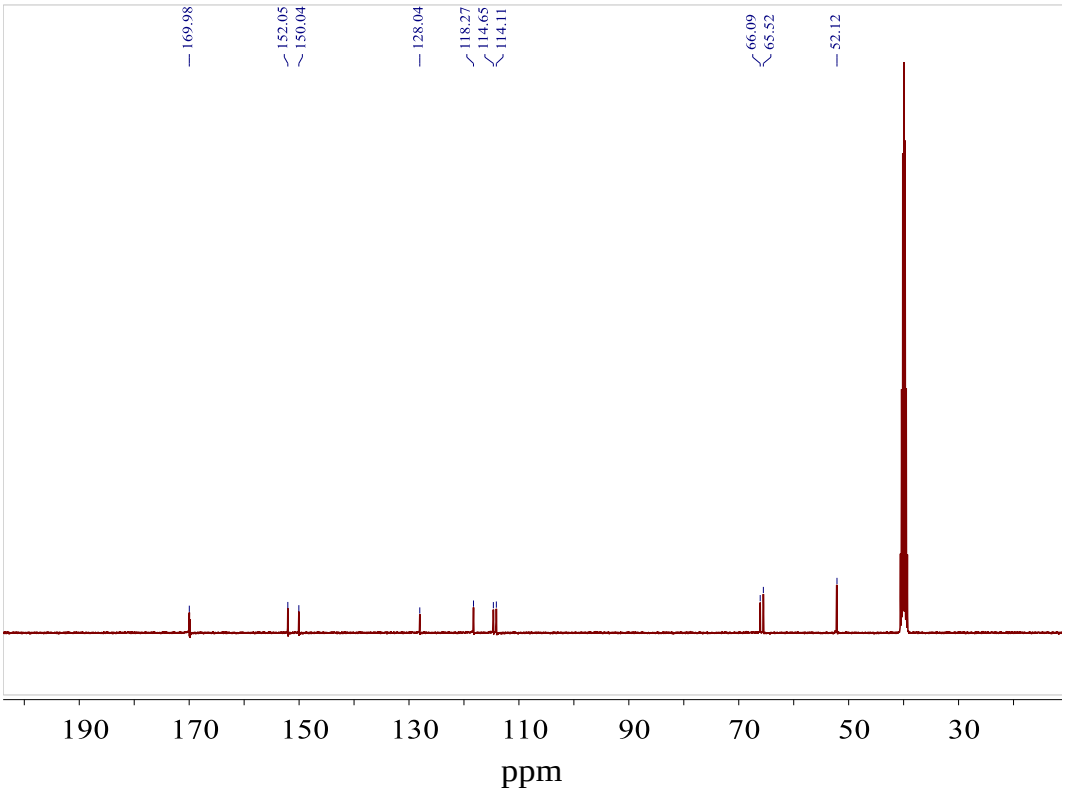


Fig. S16 ^{13}C NMR spectrum of compound **8** in DMSO-d_6 at 25 °C.

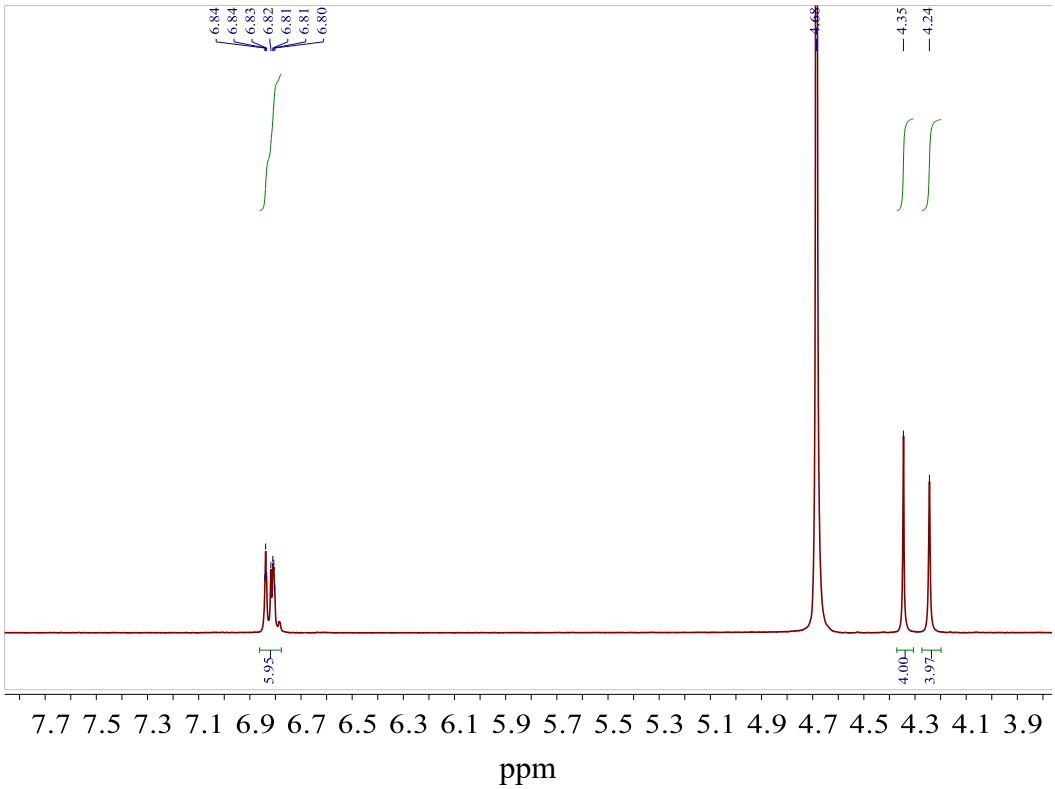


Fig. S17 ^{1}H NMR spectrum of compound **D2** in D_2O at 25 °C

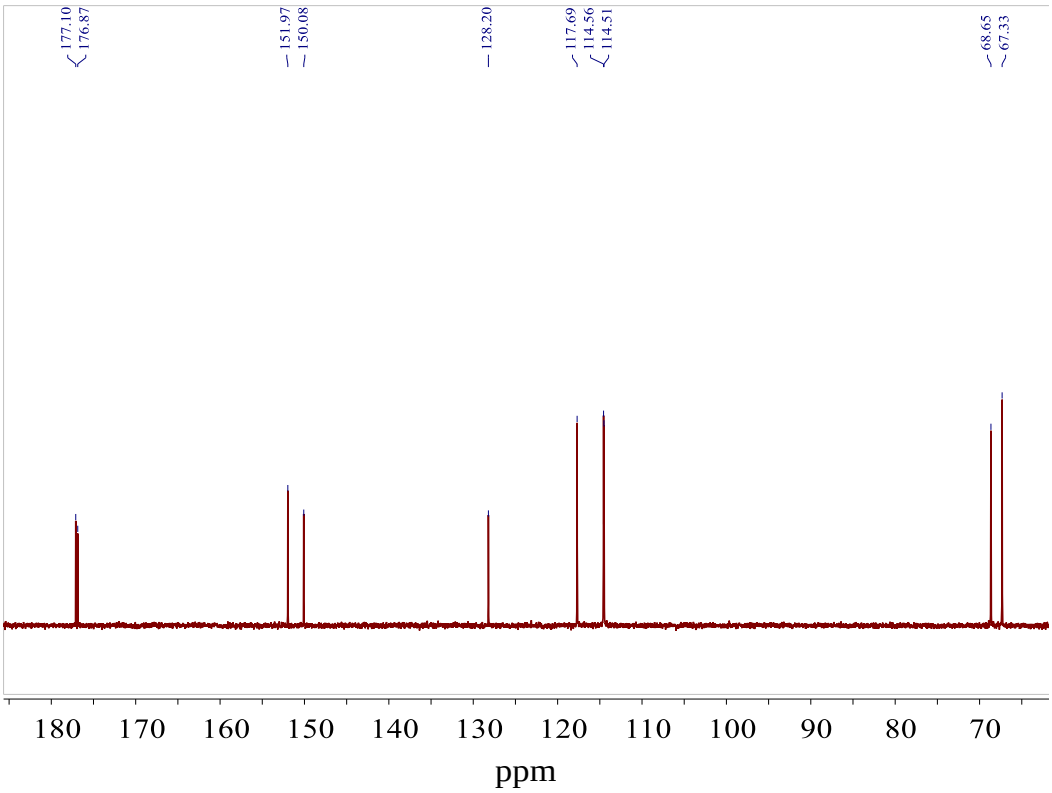


Fig. S18 ^{13}C NMR spectrum of compound **D2** in D_2O at 25 °C.

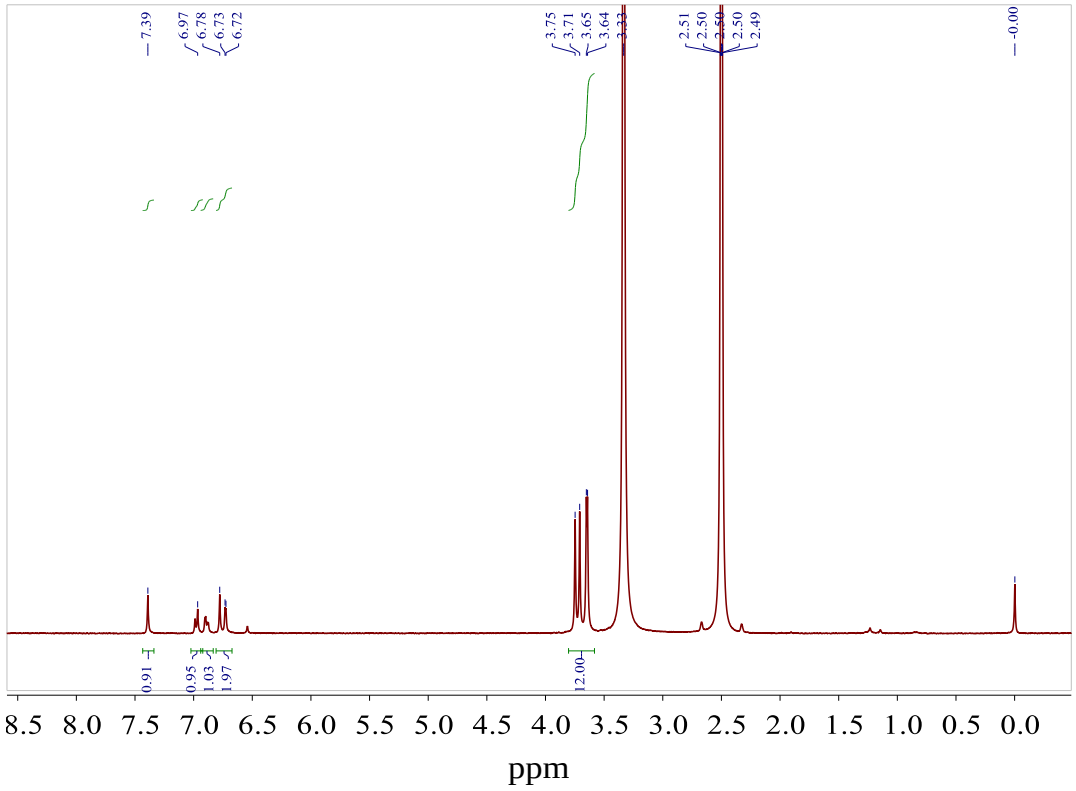


Fig. S19 ^{1}H NMR spectrum of compound **10** in DMSO-d_6 at 25 °C.

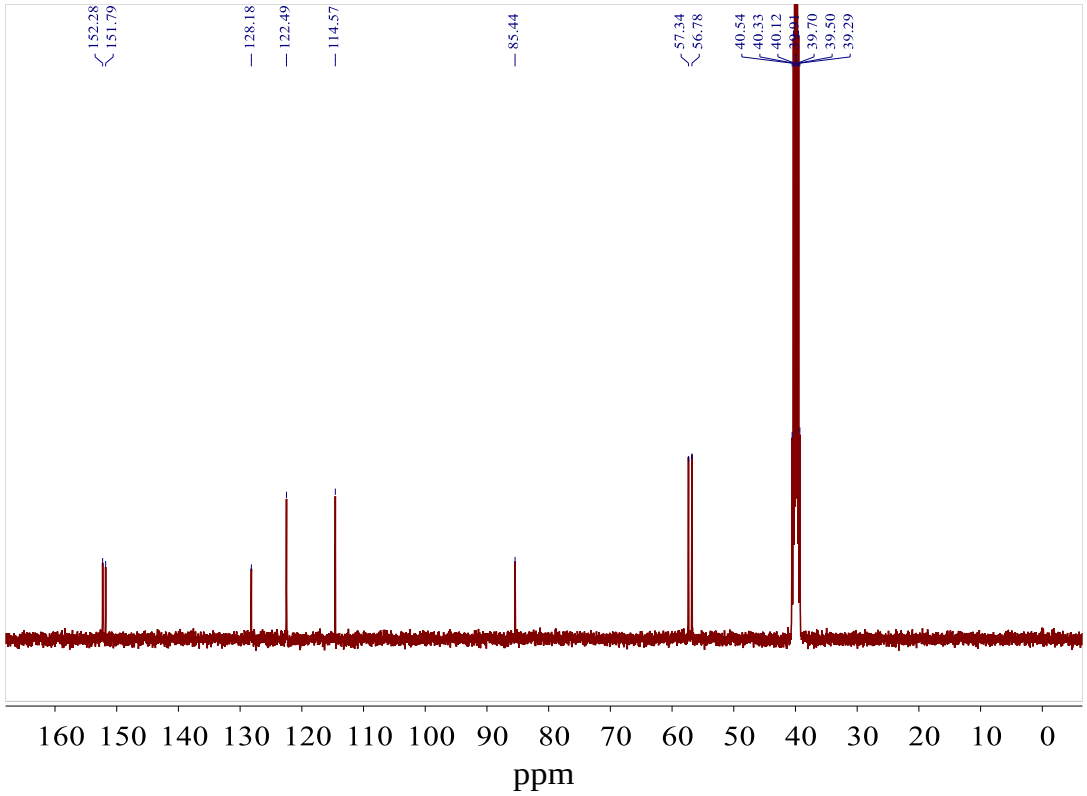


Fig. S20 ^{13}C NMR spectrum of compound **10** in DMSO-d_6 at 25 °C.

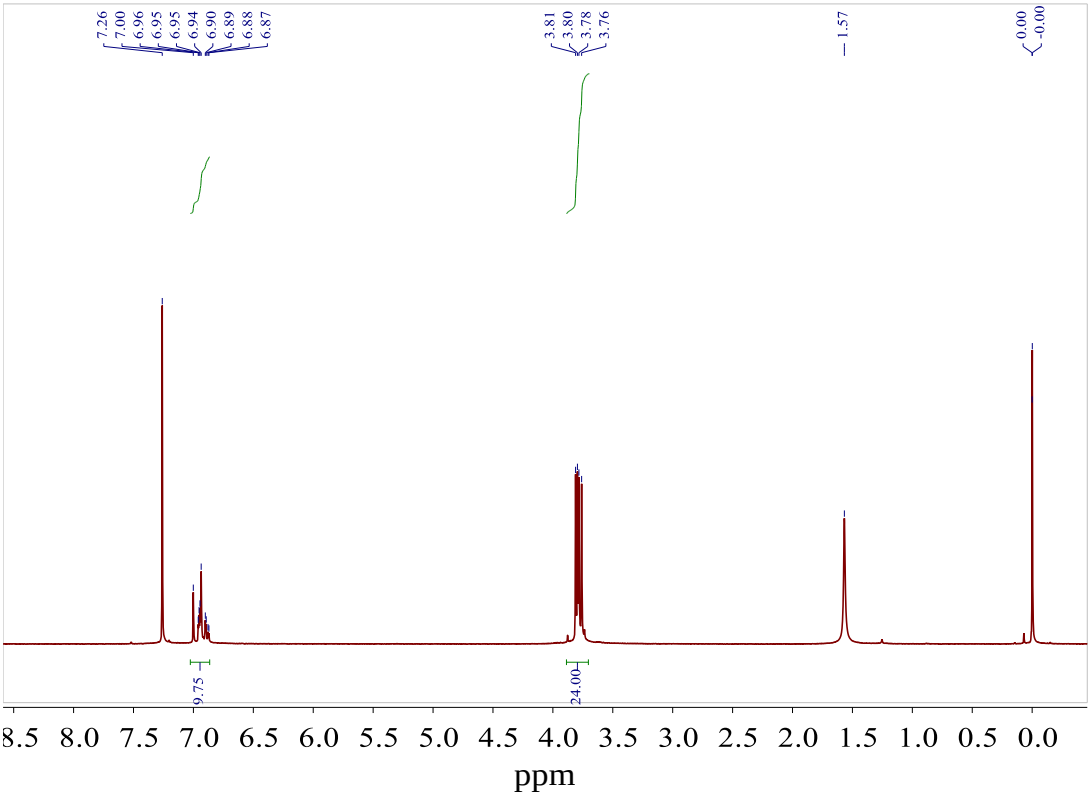


Fig. S21 ^{1}H NMR spectrum of compound **12** in $CDCl_3$ at 25 °C.

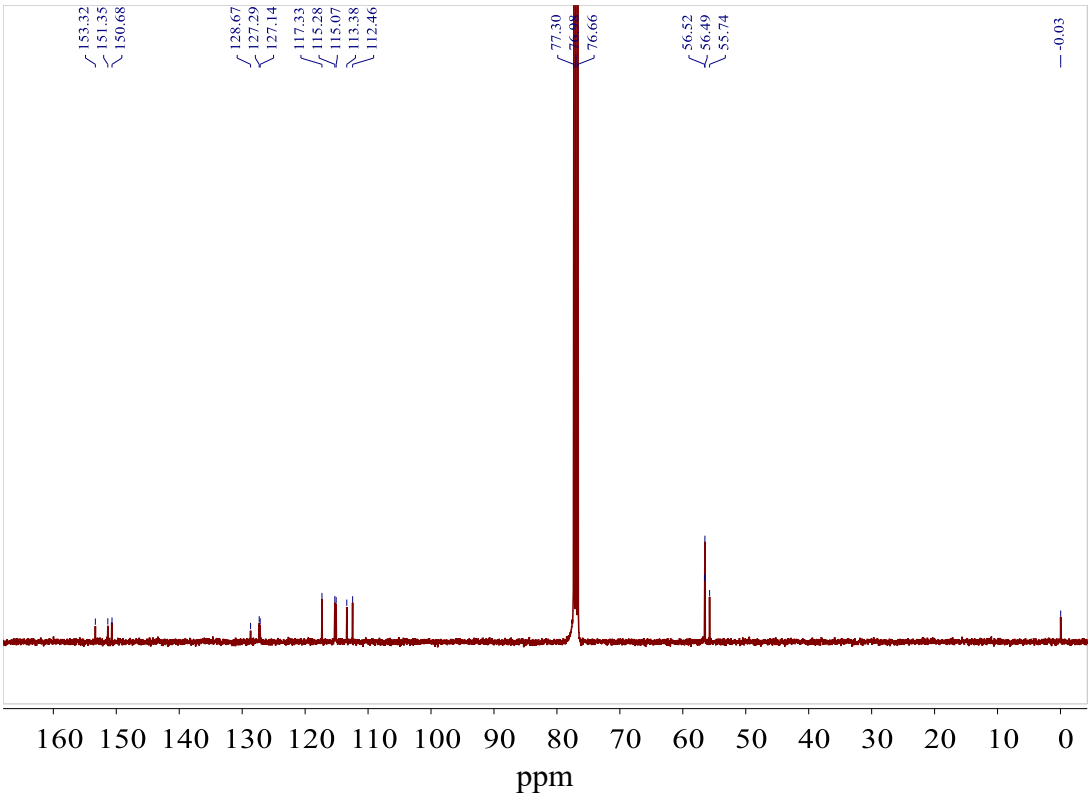


Fig. S22 ^{13}C NMR spectrum of compound **12** in $CDCl_3$ at 25 °C.

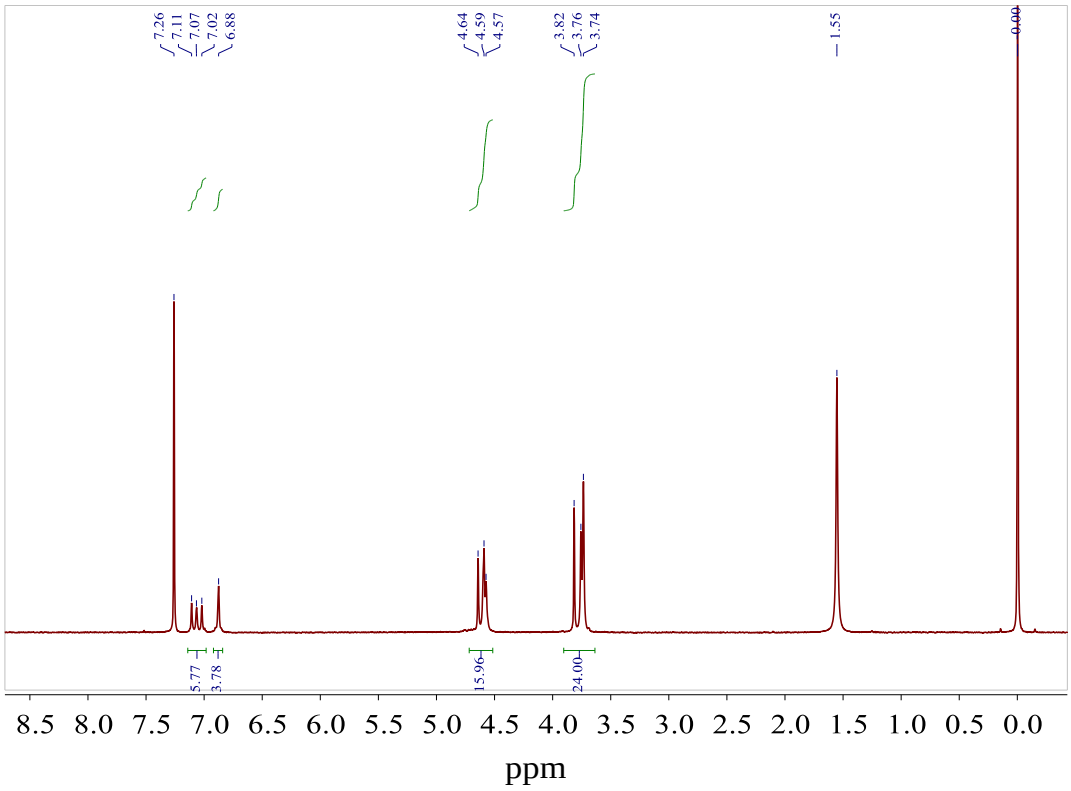


Fig. S23 ^{1}H NMR spectrum of compound **14** in $CDCl_3$ at 25 °C.

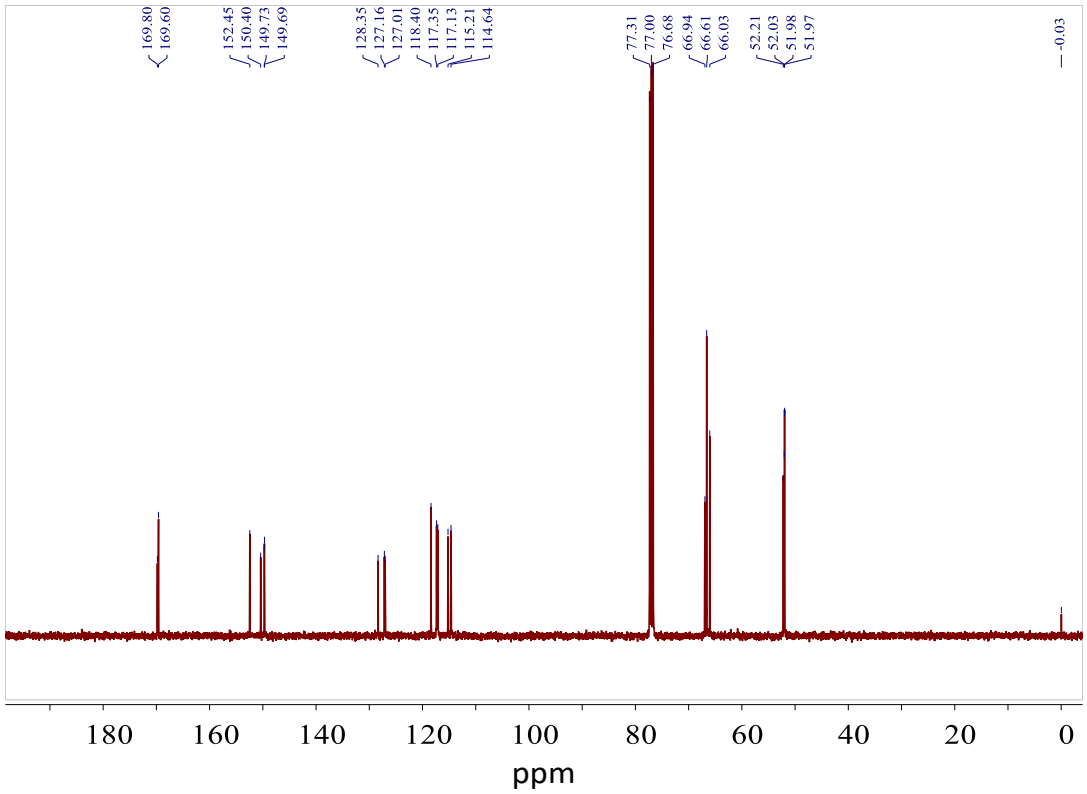


Fig. S24 ^{13}C NMR spectrum of compound **14** in $CDCl_3$ at 25 °C.

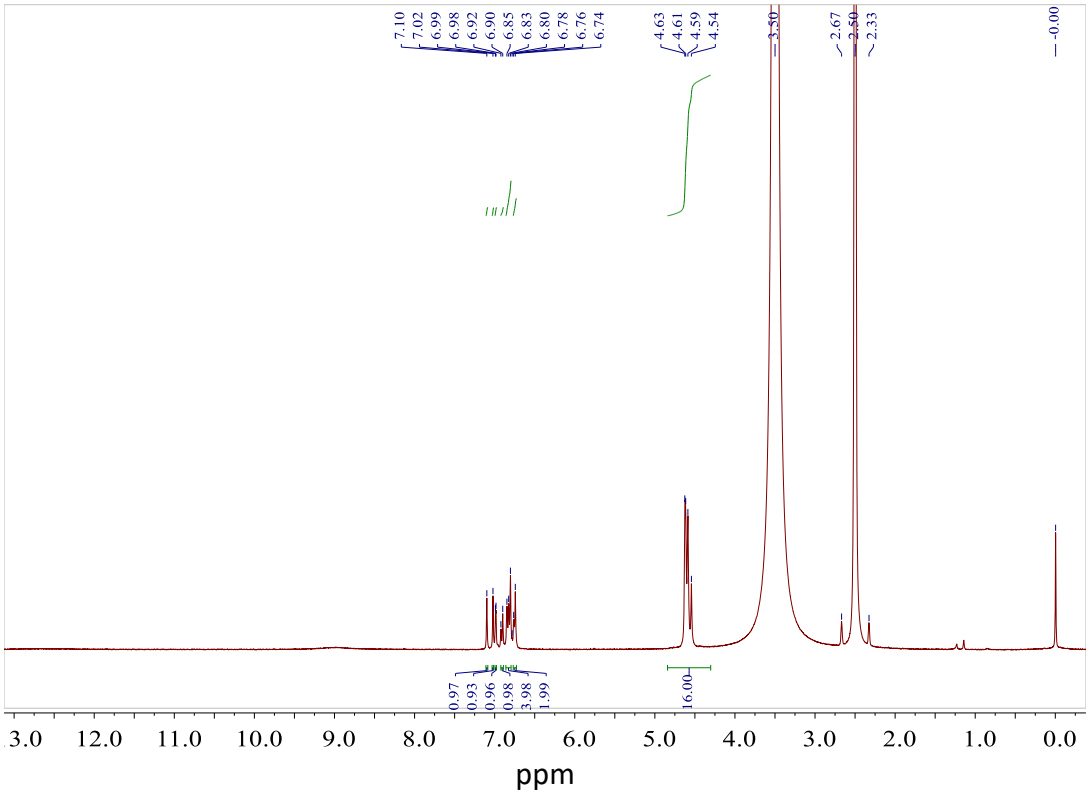


Fig. S25 ^{1}H NMR spectrum of compound **15** in DMSO-d_6 at 25 °C.

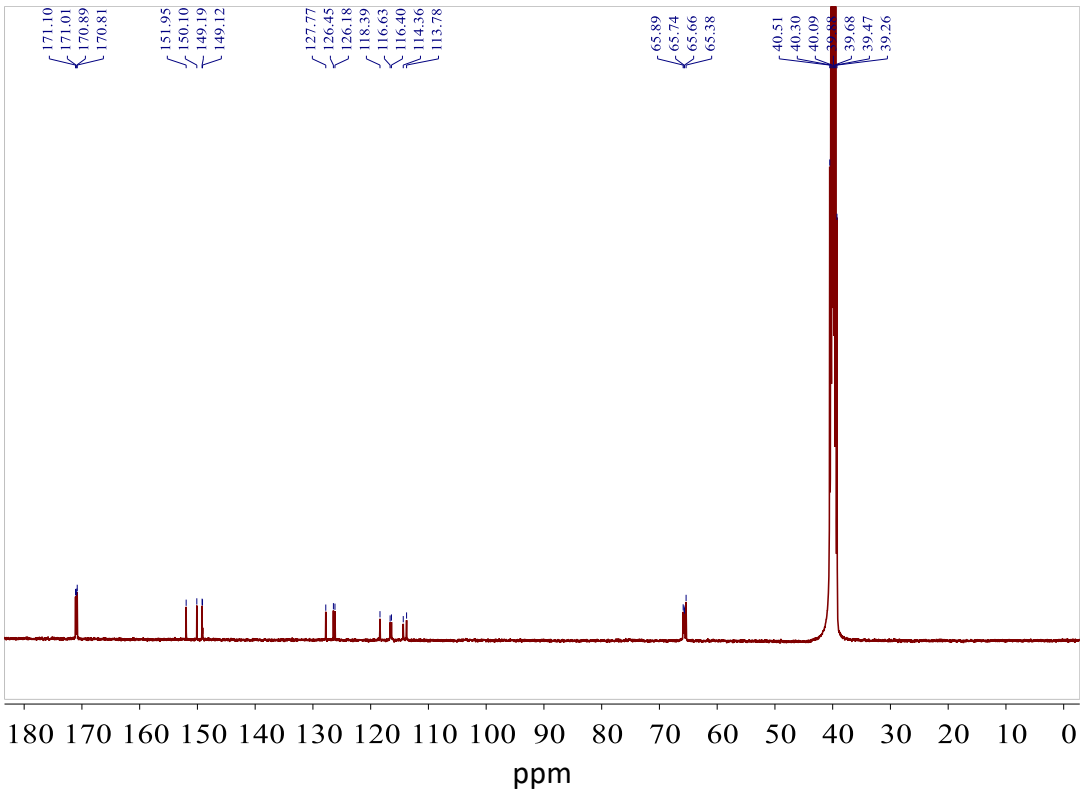


Fig. S26 ^{13}C NMR spectrum of compound **15** in DMSO-d_6 at 25 °C.

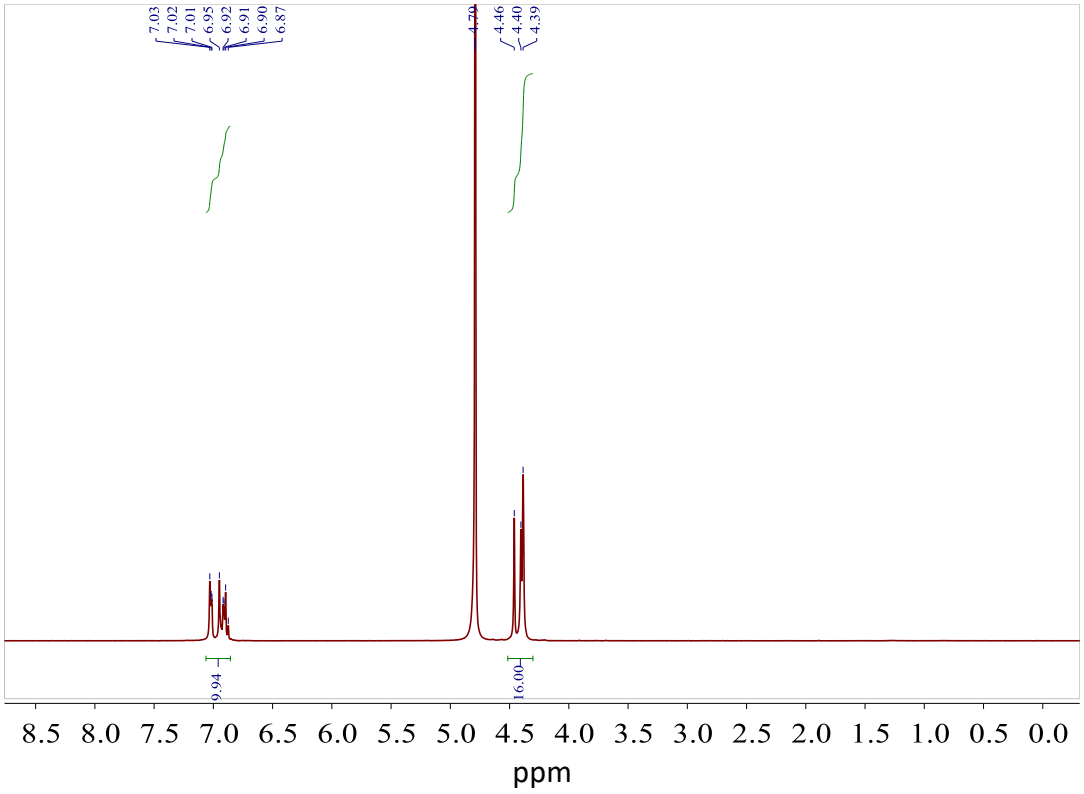


Fig. S27 ^{1}H NMR spectrum of compound **D3** in D_2O at 25 °C.

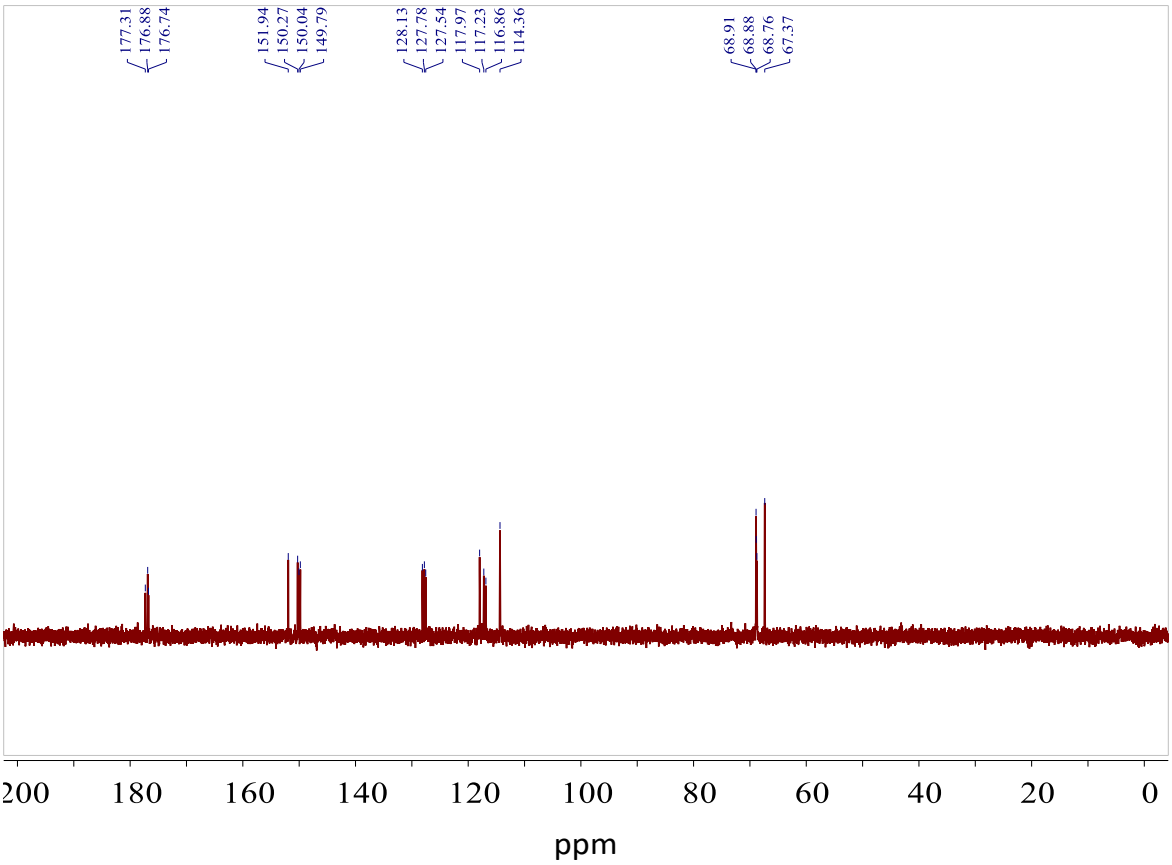


Fig. S28 ^{13}C NMR spectrum of compound **D3** in D_2O at 25 °C.

Table S1 Crystallographic parameters and the details of the structure refinements of the cocrystal **D2·A1**.

Crystal data and structure refinement for the crystal of **D2·A1**	
Empirical formula	$C_{64}H_{100}N_4Na_4O_{46}$
Formula weight	1753.43
Temperature	190(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 29.1539(5) Å = 90°. b = 14.0671(3) Å = 126.1560(10)°. c = 24.2333(7) Å = 90°.
Volume	8024.3(3) $Å^3$
Z, calculated density	4, 1.451 Mg/m^3
Absorption coefficient	1.249 mm^{-1}
F(000)	3696
Crystal size	0.250 x 0.220 x 0.180 mm^3
Theta range for data collection	3.660 to 67.499°.
Index ranges	-34<=h<=34, -16<=k<=16, -26<=l<=29
Reflections collected	42503
Independent reflections	7081 [R(int) = 0.0422]
Completeness to theta = 67.499°	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.637
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7081 / 27 / 588
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.1053, wR2 = 0.2954
R indices (all data)	R1 = 0.1207, wR2 = 0.3094
Extinction coefficient	n/a
Largest diff. peak and hole	3.329 and -1.166 $e.Å^{-3}$