Electronic Supplementary Material (ESI) for Soft Matter.

From Helical Supramolecular Arrays to Gel-forming 3D-Networks: Lattice-restructuring and Aggregation-control in Peptide-based Sulfamides to Integrate New Functional Attributes

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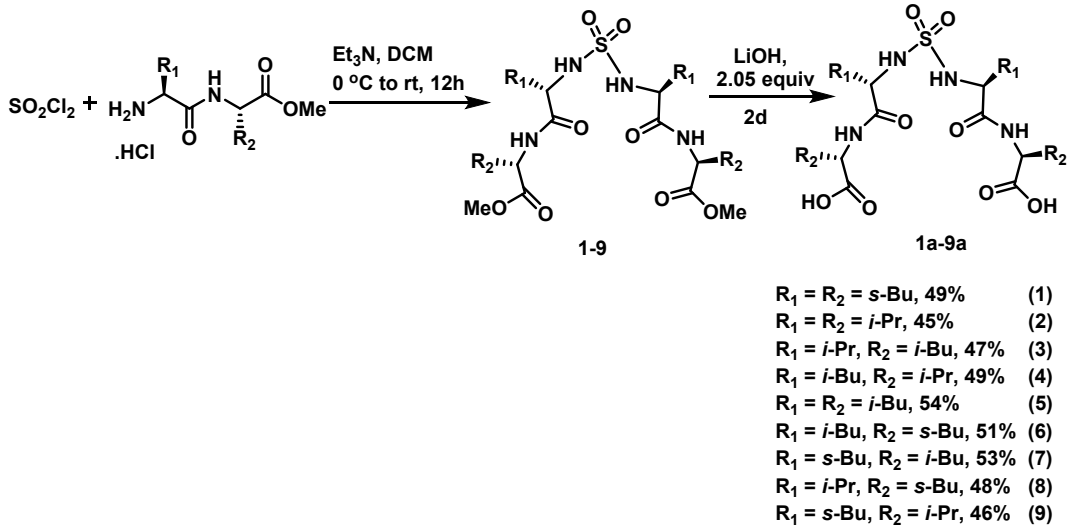
General experimental information:

All reactions were carried out under nitrogen atmosphere using dry solvents under anhydrous conditions, unless otherwise mentioned. The amino acid based sulfamides **1-9** were prepared according to our previously reported protocol (*CrystEngComm,* **2014**, *16*, 10371; Tetrahedron, 2000, 56, 9781). They were further subjected to alkaline hydrolysis to get the required acids (**1a-9a**) in quantitative yields. Reaction steps which required anhydrous conditions were carried out under nitrogen atmosphere in dry dichloromethane. Thin-layer chromatography (TLC) was performed on 0.25 mm silica gel plates (60 F254 grade) from Merck, and were analysed using 254 nm UV light. Chromatographic separation was carried out on 100-200 mesh silica gel in gravity mode. High-resolution mass spectra (HRMS) were recorded on a Waters Q-Tof *micro*™ spectrometer with lock spray source. Infrared spectra were recorded using a Nicolet 6700 FT-IR spectrophotometer. Powder X-Ray diffraction data was obtained on BRUKER D8-Advance diffractometer using CuKα radiation (λ=1.5418 Å) over the range of $0.5° < 2\theta < 15°$ at room temperature. Samples for SEM imaging were coated with Au-Pd (Gatan precision etching coating system (model No. 682) operating at 5 KeV) and analysed by FEI Quanta FEG 200 High Resolution Scanning Electron Microscope operating at 10-30 kV. Rheological measurements were performed with a stress-controlled rheometer (MCR 301) equipped with steel-coated parallel-plate geometry (25 mm diameter). The gap distance was fixed at 1 mm and a solvent-trapping device was placed above the plate to prevent solvent evaporation. All measurements were done at 25°C.

Single crystal X-Ray crystallography: The intensity data collection during X-ray crystallographic analysis was carried out on a Bruker AXS (kappa apex II) diffractometer equipped with graphite monochromated Mo (Ka) radiation. The data were collected for θ up to 25° for Mo (Kα) radiation. ω and ϕ scans were employed to collect the data. The frames were integrated and data were reduced for Lorentz and polarization correction using SAINT-Plus. The multi-scan absorption correction was applied to the data. All structures were solved using SIR-92 and refined using SHELXL-2014/7. The molecular and packing diagrams were drawn using ORTEP-34 and Mercury 3.1. The non-hydrogen atoms were refined with anisotropic displacement parameter. All hydrogen atoms could be located in the difference Fourier map. However, the hydrogen atoms bonded to carbons were fixed at chemically meaningful positions and were allowed to ride with parent atom during the refinement.



Scheme 1. Synthesis of amino acid-based sulfamides **1-9** and **1a-9a.**

General procedure for the syntheses of compounds 1-9

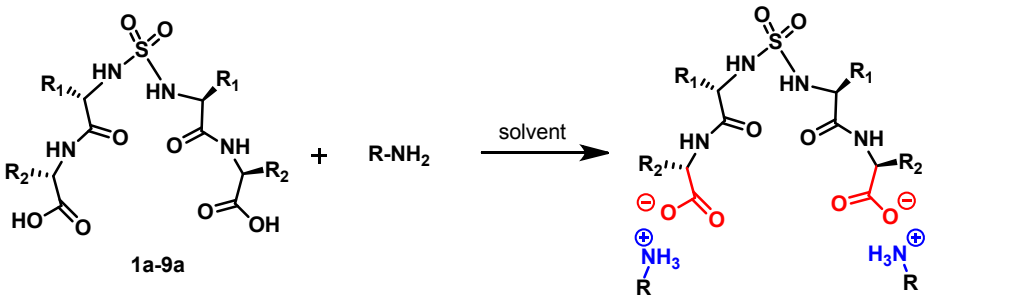
To a stirred solution of the dipeptide of amino acid methyl ester hydrochloride (1 equiv.) in dry DCM at 0 °C, in a two necked RB flask under nitrogen atmosphere was added triethylamine (2-3 equiv.). A dilute solution of sulfuryl chloride (0.45-0.5 equiv.) in dry DCM (40-80 mL) was then added drop-wise to this using an addition funnel during about 30-45 min, the mixture was allowed to warm to room temperature and stirring was continued for an additional 12 h. The reaction mixture was washed with water and 5% HCl solution, extracted with DCM, dried over Na_2SO_4 and solvents were evaporated to get a residue which was chromatographed using EtOAc-Hexanes mixture to get the compounds **1-9** in 40-50% yields as white crystalline solids.

General procedure for the synthesis of sulfamido-peptides 1a-9a

At first, the diesters **1-9** were subjected to alkaline hydrolysis (1N LiOH in 3:1 of THF and water) to get the corresponding diacids **1a-9a** in quantitative yields.

Gelation studies:

Gelation ability of salts **DA1a-DA9a**, **DDA1a-DDA9a**, **TDA1a-TDA9a**, **ODA1a-ODA9a** was studied by vial inversion method. The sulfamide diacid (**1a-9a**) and the desired amine R-NH_2 (molar ratio of 1:2) were mixed in an organic solvent (1mL) in a 5 mL vial and the components were dissolved by gentle heating. It was then allowed to reach room temperature. Gelation was evidenced by decreased mobility of the solvent and the system later became stable on vial inversion.



Scheme 2. Formation of salts from **1a-9a**.

Details of secondary interactions in crystal structures of 7 and 8:

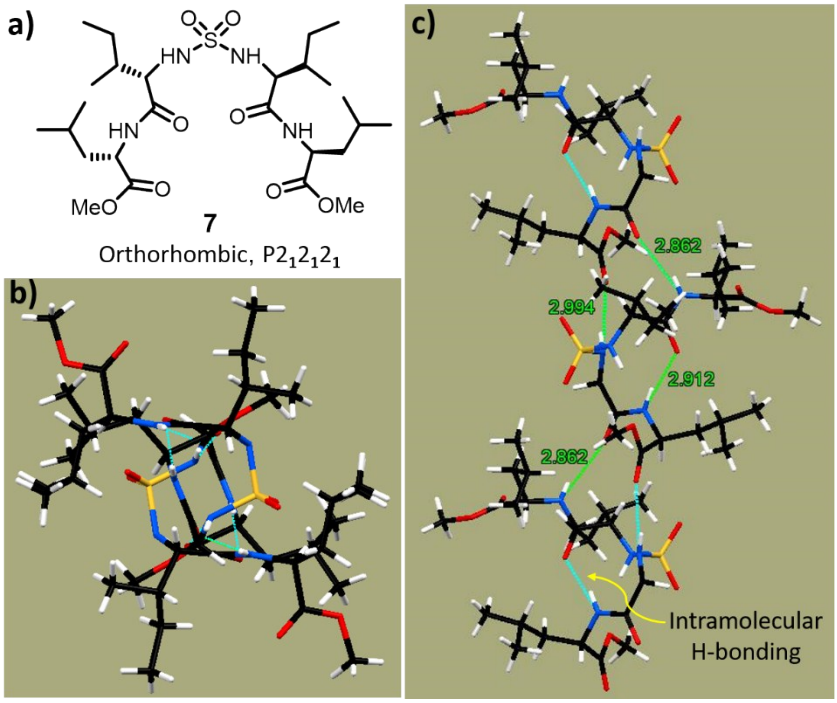


Figure S1. a) Chemical structure of **7**, b) View along b axis, C) Helical stacking in peptide **7**.

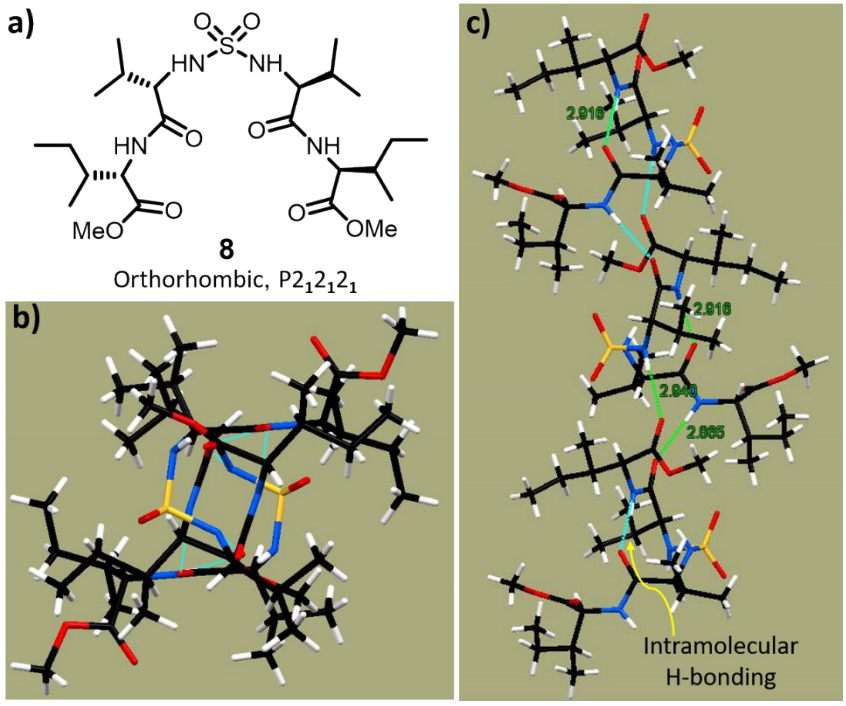
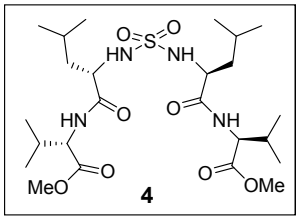


Figure S2. a) Chemical structure of **8**, b) View along b axis, C) Helical stacking in peptide **8**.

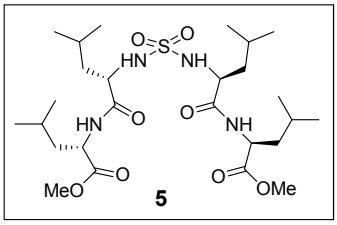
Sulfamido peptide 4



4

Analytical data for **4**: Rf: 0.4 (90% EtOAc-Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, 1H, *J* = 8.9 Hz), 5.6 (d, 1H, *J*= 7.6 Hz), 4.58 (dd, 1H, *J* = 8.9, 5.3 Hz), 4.08 (dd, 1H, *J* = 14.92, 7.8 Hz), 3.74 (s, 3H), 2.26-2.17 (m, 1H), 1.84-1.74 (m, 1H), 1.57-1.53 (m, 2H,), 0.96-0.91 (m,12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 172.9, 57.3, 52.2, 41.8, 31.0, 24.4, 22.8, 21.5, 19.0, 17.9; HRMS(ESI) exact mass calcd. for $C_{24}H_{46}N_4O_8SNa$ $[M+Na]^+$ 573.2934, found $[M+Na]^+$ 573.2956.

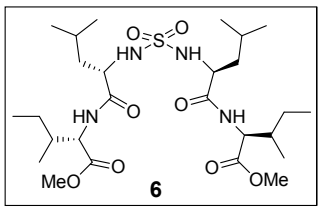
Sulfamido peptide 5



5

Analytical data for **5**: Rf: 0.5 (75% EtOAc-Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (t, 1H, *J* = 6.4 Hz), 5.88 (dd, 1H, *J*= 5.5, 3.3 Hz), 4.6-4.55 (m, 1H), 4.10-4.05 (m, 1H), 3.71 (s, 3H), 1.82-1.70 (m, 2H), 1.67-1.59 (m, 2H), 1.50 (t, 2H, *J* = 5.7 Hz), 0.93-0.91 (m,12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 173.0, 57.5, 52.4, 50.8, 41.6, 40.2, 24.9, 24.3, 22.9, 22.8, 21.5, 21.3; HRMS(ESI) exact mass calcd. for $C_{26}H_{50}N_4O_8SNa$ [M+Na]+ 601.3247, found [M+Na]+ 601.3236.

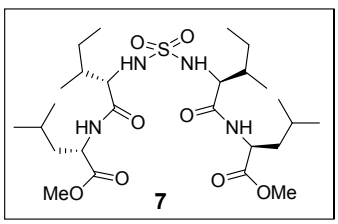
Sulfamido peptide 6



6

Analytical data for **6**: Rf: 0.4 (65% EtOAc-Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, 1H, *J* = 8.6 Hz), 5.49 (d, 1H, *J*= 7.4 Hz), 4.61 (dd, 1H, *J* = 8.7, 5.4 Hz), 4.07 (dd, 1H, *J* = 15, 7.6 Hz), 3.76 (s, 3H), 1.99-1.92 (m, 1H), 1.84-1.77 (m, 1H), 1.55 (t, 2H, *J* = 7.0 Hz),1.46-1.38 (m, 1H), 1.26-1.19 (m, 1H), 0.96-0.89 (m,12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 172.8, 57.4, 56.6, 52.2, 41.8, 37.5, 25.2, 24.4, 22.9, 21.5, 15.6, 11.4; HRMS(ESI) exact mass calcd. for $C_{26}H_{50}N_4O_8SNa$ [M+Na]+ 601.3247, found [M+Na]+ 601.3233.

Sulfamido peptide 7

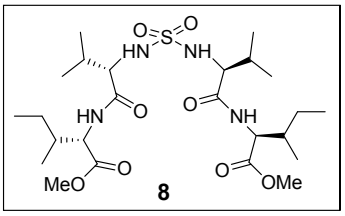


7

Analytical data for **7**: Rf: 0.3 (68% EtOAc-Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.2 (d, 1H, *J* = 6.8 Hz), 5.63 (d, 1H, *J*= 6.0 Hz), 4.62 (dd, 1H, *J* = 4.4, 3.2 Hz), 3.91 (dd, 1H, *J* = 6.0, 5.2 Hz), 3.72 (s, 3H), 1.80-1.78 (m, 1H), 1.75-1.70 (m, 2H), 1.69-1.62 (m, 1H),1.55-1.53 (m, 1H), 1.20-1.16 (m, 1H), 0.98-0.88 (m,12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 171.9, 63.3, 52.3, 50.9, 40.2, 37.5, 27.3, 25.0, 24.8, 22.8, 21.3, 15.5, 11.3;

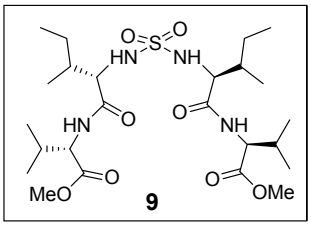
HRMS(ESI) exact mass calcd. for $C_{26}H_{50}N_4O_8SNa$ [M+Na]+ 601.3247, found [M+Na]+ 601.3234.

Sulfamido peptide 8



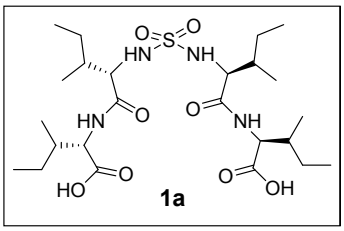
Analytical data for **8**: Rf: 0.4 (75% EtOAc-Hexanes); ^{1}H NMR (400 MHz, CDCl3): δ 7.04 (d, 1H, *J* = 8.5 Hz), 5.45 (d, 1H, *J*= 7.8 Hz), 4.6 (dd, 1H, *J* = 8.5, 5.2 Hz), 3.85 (dd, 1H, *J* = 7.7, 5.8 Hz), 3.73 (s, 3H), 2.15-2.07 (m, 1H), 1.97-1.93 (m, 1H), 1.49-1.39 (m, 1H), 1.27-1.16 (m, 1H), 2.0(d, 3H, *J* = 6.8 Hz), 0.95-0.88 (m,9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 171.4, 63.5, 56.7, 52.2, 37.5, 31.1, 25.2, 19.1, 17.9, 15.5, 11.4; HRMS(ESI) exact mass calcd. for $C_{24}H_{47}N_4O_8S$ $[M+H]^+$ 551.3115, found $[M+H]^+$ 551.3104.

Sulfamido peptide 9



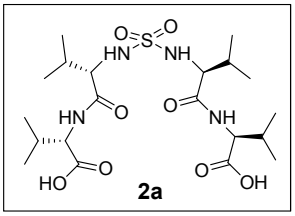
Analytical data for **9**: Rf: 0.5 (70% EtOAc-Hexanes); ^{1}H NMR (400 MHz, CDCl3): δ 7.07 (d, 1H, *J* = 8.2 Hz), 5.50 (d, 1H, *J*= 6.8 Hz), 4.57 (dd, 1H, *J* = 8.72, 5.28 Hz), 3.90 (dd, 1H, *J* = 7.7, 6.08 Hz), 3.73 (s, 3H), 2.25-2.17 (m, 1H), 1.86-1.80 (m, 1H), 1.60-1.52 (m, 1H), 1.24-1.13 (m, 1H), 0.98-0.90 (m,12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 171.5, 62.8, 57.4, 52.2, 37.6, 30.9, 24.9, 19.0, 18.0, 15.5, 11.3; HRMS(ESI) exact mass calcd. for $C_{24}H_{46}N_4O_8SNa$ $[M+Na]^+$ 573.2934, found $[M+Na]^+$ 573.2939.

Sulfamido peptide 1a



Analytical data for **1a**: ^{1}H NMR (400 MHz, CD_3OD) δ 4.39 (dd, 1H, *J* = 11.0, 5.5 Hz), 3.82 (dd, 1H, *J* = 12.1, 5.8 Hz), 1.96-1.87 (m, 1H), 1.77-1.71 (m, 1H), 1.61-1.53 (m, 1H), 1.31-1.24 (m, 1H), 1.20-1.13 (m, 1H), 0.98-0.88 (m,12H); ^{13}C NMR (100 MHz, CD_3OD) δ 174.8, 174.2, 62.8, 58.2, 39.2, 38.3, 26.3, 26.0, 16.0, 15.8, 11.8, 11.7; HRMS(ESI) exact mass calcd. for $C_{22}H_{46}N_4O_8SNa$ $[M+Na]^+$ 573.2934, found $[M+Na]^+$ 573.2956.

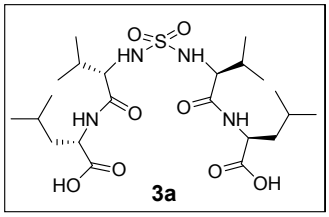
Sulfamido peptide 2a



Analytical data for **2a**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.01 (d, 1H, *J* = 7.9 Hz), 6.48 (d, 1H, *J*= 9.0 Hz), 4.12 (dd, 1H, *J* = 7.6, 5.8 Hz), 3.67 (dd, 1H, *J* = 8.8, 5.7 Hz), 2.06-2.03 (m, 1H), 1.92-1.89 (m, 1H), 1.92-1.89 (m, 1H), 0.88 (brs, 9H,) 0.79 (d, 3H, *J* = 6.4); ^{13}C NMR (125 MHz, DMSO-d_6) δ 172.9, 171.4, 61.0, 57.4, 31.1, 29.9, 19.2, 19.1, 18.1, 17.9;

HRMS(ESI) exact mass calcd. for $C_{20}H_{38}N_4O_8SNa$ $[M+Na]^+$ 517.2308, found $[M+Na]^+$ 517.2280.

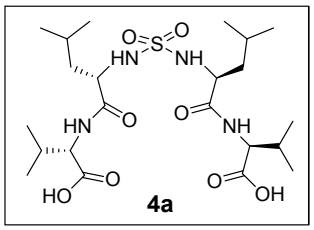
Sulfamido peptide 3a



3a

Analytical data for **3a**: ^{1}H NMR (500 MHz, CD_3OD): δ 4.81 (dd, 1H, *J* = 10.3, 4.9 Hz), 3.77 (dd, 1H, *J* = 12.0, 6.2 Hz), 2.07-2.0 (m, 1H), 1.81-1.72 (m, 2H), 1.65-1.60 (m, 1H), 1.01 (d, 3H, *J* = 6.8), 0.97-0.92 (m, 9H);13C NMR (125 MHz, CD_3OD) δ 176.1, 174.2, 64.0, 52.1, 41.3, 32.5, 25.8, 23.4, 21.7, 19.7, 18.5; HRMS(ESI) exact mass calcd. for $C_{22}H_{43}N_4O_8S$ $[M+H]^+$ 523.2802, found $[M+H]^+$ 523.2806.

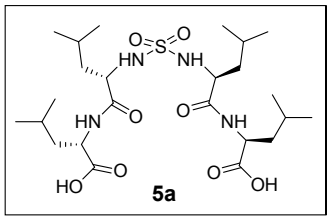
Sulfamido peptide 4a



4a

Analytical data for **4a**: ^{1}H NMR (500 MHz, CD_3OD): δ 4.3 (dd, 1H, *J* = 10.8, 5.2 Hz), 3.94 (dd, 1H, *J* = 8.8, 6.2 Hz), 2.18-2.12 (m, 1H), 1.74-1.69 (m, 1H), 1.53-1.4 (m, 2H), 0.94-0.89 (m,12H); ^{13}C NMR (125 MHz, CD_3OD) δ 175.4, 174.8, 58.9, 56.8, 43.1, 31.8, 25.5, 23.2, 22.4, 19.5, 18.4; HRMS(ESI) exact mass calcd. for $C_{22}H_{43}N_4O_8S$ $[M+H]^+$ 523.2802, found $[M+H]^+$ 523.2819.

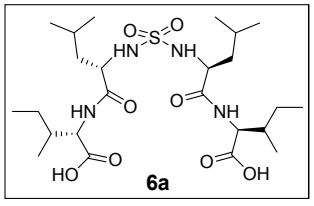
Sulfamido peptide 5a



5a

Analytical data for **5a**: ^{1}H NMR (500 MHz, CD_3OD): δ 4.4 (dd, 1H, *J* = 10.2, 5.3 Hz), 4.9 (dd, 1H, *J* = 9.0, 6.0 Hz), 1.77-1.65 (m, 3H), 1.60-1.53 (m, 1H), 1.49-1.39 (m, 2H) , 0.90-0.84 (m,12H); ^{13}C NMR (125 MHz, CD_3OD) δ 176.3, 175.4, 57.5, 52.0, 42.9, 41.3, 27.7, 25.9, 25.4, 23.4, 23.2, 22.1, 21.7; HRMS(ESI) exact mass calcd. for $C_{24}H_{47}N_4O_8S$ $[M+H]^+$ 551.3115, found $[M+H]^+$ 551.3096.

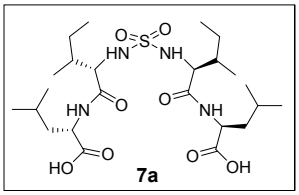
Sulfamido peptide 6a



6a

Analytical data for **6a**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.9 (d, 1H, *J* = 8.3 Hz), 6.8 (d, 1H, *J*= 8.7 Hz), 4.2 (dd, 1H, *J* = 8.3, 5.9 Hz), 3.8 (dd, 1H, *J* = 15.3, 8.2Hz), 1.80-1.75 (m, 1H), 1.66-1.59 (m, 1H), 1.45-1.39 (m, 2H), 1.36-1.30 (m, 1H), 1.22-1.15 (m, 1H), 0.87-0.84 (m,12H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 172.9, 172.1, 56.1, 54.7, 41.7, 36.6, 24.7, 23.9, 22.6, 22.3, 15.4, 11.3; HRMS(ESI) exact mass calcd. for $C_{24}H_{46}N_4O_8SNa$ $[M+Na]^+$ 573.2934, found $[M+Na]^+$ 573.2928.

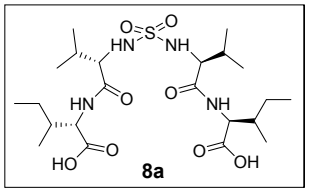
Sulfamido peptide 7a



7a

Analytical data for **7a**: ^{1}H NMR (400 MHz, CD_3OD): δ 4.4 (dd, 1H, *J* = 10.0, 4.8 Hz), 3.8 (dd, 1H, *J* = 11.4, 5.32 Hz), 1.76-1.68 (m, 3H), 1.62-1.49 (m, 2H), 1.24-1.08 (m, 1H), 0.94-0.84 (m,12H); ^{13}C NMR (100 MHz, CD_3OD) δ 176.5, 174.1, 63.4, 52.4, 41.6, 39.0, 25.9(2C), 23.5, 21.8, 16.0, 11.7; HRMS(ESI) exact mass calcd. for $C_{24}H_{46}N_4O_8SNa$ $[M+Na]^+$ 573.2934, found $[M+Na]^+$ 573.2958.

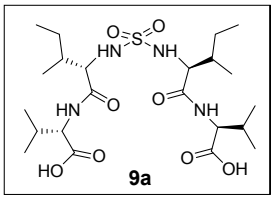
Sulfamido peptide 8a



8a

Analytical data for **8a**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.0 (d, 1H, *J* = 8.0 Hz), 6.4 (d, 1H, *J*= 9.3 Hz), 4.17 (dd, 1H, *J* = 7.8, 5.8 Hz), 3.67 (dd, 1H, *J* = 9.2, 5.6 Hz), 1.93-1.87 (m, 1H), 1.80-1.75 (m, 1H), 1.46-1.41 (m, 1H), 1.24-1.15 (m, 1H), 0.88-0.78 (m,12H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 172.9, 171.3, 61.0, 56.4, 36.4, 31.1, 24.8, 19.1, 17.8, 15.5, 11.4;; HRMS(ESI) exact mass calcd. for $C_{22}H_{42}N_4O_8SNa$ $[M+Na]^+$ 545.2621, found $[M+Na]^+$ 545.2629.

Sulfamido peptide 9a



9a

Analytical data for **9a**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.99 (d, 1H, *J* = 8.2 Hz), 6.5 (d, 1H, *J*= 9.3 Hz), 4.14 (dd, 1H, *J* = 8.2, 5.6 Hz), 3.71 (dd, 1H, *J* = 9.2, 6.0 Hz), 2.08-2.01 (m, 1H), 1.66-1.61 (m, 1H), 1.47-1.39 (m, 1H), 1.06-0.96 (m, 1H), 0.90-0.77 (m,12H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 172.9, 171.4, 60.4, 57.3, 37.6, 29.9, 24.2, 19.1, 18.2, 15.3, 11.4; HRMS(ESI) exact mass calcd. for $C_{22}H_{42}N_4O_8SNa$ $[M+Na]^+$ 545.2621, found $[M+Na]^+$ 545.2615.

Table 1. Gelation profile of salts from **1a**

S.no	Solvent	DEA	DA	TDA	ODA
1	Toulene	WG	G	G	G
2	Mesitylene	WG	G	G	G
3	Xylene	WG	G	G	G
4	Ethanol	S	P	P	P
5	IPA	S	P	P	P
6	tert-butanol	P	P	P	P
7	THF	G	WG	G	G
8	2-Butanone	P	P	G	G
9	Dibromoetahne	P	P	P	P
10	Chlorobenzene	P	P	P	P
11	Chloroform	PP	WG	WG	P
12	Nitrobenzene	P	P	P	P
13	NMP	S	S	S	P
14	DMF	S	P	P	P
15	H_2O	P	P	P	P

Table 2. Gelation profile of salts from **2a**

S.no	Solvent	DEA	DA	TDA	ODA
1	Toulene	WG	WG	G	G
2	Mesitylene	WG	G	G	G
3	Xylene	WG	WG	WG	G
4	Ethanol	S	S	S	S
5	IPA	P	P	P	P
6	tert-butanol	P	P	P	P
7	THF	WG	WG	G	G
8	2-Butanone	P	P	P	P
9	Dibromoetahne	P	P	P	P
10	Chlorobenzene	P	P	P	G
11	Chloroform	WG	WG	WG	WG
12	Nitrobenzene	P	P	P	P
13	NMP	S	S	S	P
14	DMF	S	P	P	P
15	H_2O	P	P	P	P

Table 3. Gelation profile of salts from **3a**

S.no	Solvent	DEA	DA	TDA	ODA
1	Toulene	G	G	G	G
2	Mesitylene	G	G	G	G
3	Xylene	G	G	G	G
4	Ethanol	S	S	S	S
5	IPA	S	P	P	P
6	tert-butanol	S	WG	P	G
7	THF	G	G	WG	G
8	2-Butanone	P	P	P	P
9	Dibromoetahne	P	P	P	P
10	Chlorobenzene	WG	WG	WG	G
11	Chloroform	G	G	G	G
12	Nitrobenzene	P	P	P	P
13	NMP	S	S	P	S
14	DMF	P	S	P	P
15	H_2O	P	P	P	P

Table 4. Gelation profile of salts from **4a**

S.no	Solvent	DEA	DA	TDA	ODA
1	Toulene	WG	WG	G	G
2	Mesitylene	WG	WG	G	G
3	Xylene	WG	WG	G	G
4	Ethanol	S	S	S	P
5	IPA	P	P	P	P
6	tert-butanol	P	P	P	P
7	THF	P	P	G	G
8	2-Butanone	P	P	P	P
9	Dibromoetahne	P	P	P	P
10	Chlorobenzene	WG	P	WG	P
11	Chloroform	P	WG	G	G
12	Nitrobenzene	P	P	P	P
13	NMP	S	CS	S	P
14	DMF	P	P	P	P
15	H_2O	P	P	P	P

Table 5. Gelation profile of salts from **5a**

S.no	Solvent	DEA	DA	TDA	ODA
1	Toulene	WG	G	G	G
2	Mesitylene	WG	G	G	G
3	Xylene	WG	G	G	G
4	Ethanol	S	P	S	P
5	IPA	P	P	P	P
6	tert-butanol	P	P	P	P
7	THF	P	P	G	G
8	2-Butanone	G	P	P	P
9	Dibromoetahne	P	P	P	P
10	Chlorobenzene	P	WG	P	P
11	Chloroform	P	WG	P	G
12	Nitrobenzene	P	P	G	G
13	NMP	S	S	S	P
14	DMF	S	P	S	P
15	H_2O	P	P	P	P

Table 6. Gelation profile of salts from **6a**

S.no	Solvent	DEA	DA	TDA	ODA
1	Toulene	WG	WG	WG	G
2	Mesitylene	WG	WG	WG	G
3	Xylene	WG	WG	WG	G
4	Ethanol	S	S	S	S
5	IPA	S	S	S	P
6	tert-butanol	P	P	P	P
7	THF	P	P	P	G
8	2-Butanone	P	P	P	P
9	Dibromoetahne	P	P	P	P
10	Chlorobenzene	WG	WG	WG	WG
11	Chloroform	WG	WG	WG	G
12	Nitrobenzene	P	P	P	P
13	NMP	P	P	P	P
14	DMF	P	P	P	P
15	H_2O	P	P	P	P

Table 7. Gelation profile of salts from **7a**

S.no	Solvent(ileu-leu)	DEA	DA	TDA	ODA
1	Toulene	G	G	G	G
2	Mesitylene	G	G	G	G
3	Xylene	G	G	G	G
4	Ethanol	S	P	PP	G
5	IPA	P	P	P	P
6	tert-butanol	P	P	P	P
7	THF	WG	WG	WG	WG
8	2-Butanone	P	P	P	P
9	Dibromoetahne	P	P	P	P
10	Chlorobenzene	G	G	G	WG
11	Chloroform	WG	WG	G	G
12	Nitrobenzene	P	P	P	WG
13	NMP	S	S	P	P
14	DMF	P	P	P	P
15	H_2O	P	P	P	P

Table 8. Gelation profile of salts from **8a**

S.no	Solvent(val-ileu)	DEA	DA	TDA	ODA
1	Toulene	G	G	G	G
2	Mesitylene	G	G	G	G
3	Xylene	G	G	G	G
4	Ethanol	S	S	S	P
5	IPA	S	S	S	P
6	tert-butanol	S	S	P	P
7	THF	G	G	G	G
8	2-Butanone	P	P	P	P
9	Dibromoetahne	P	P	P	P
10	Chlorobenzene	WG	WG	G	G
11	Chloroform	WG	WG	G	G
12	Nitrobenzene	P	P	P	P
13	NMP	S	S	S	P
14	DMF	S	S	P	P
15	H_2O	P	P	P	P

Table 9. Gelation profile of salts from **9a**

S.no	Solvent	DEA	DA	TDA	ODA
1	Toulene	WG	WG	WG	G
2	Mesitylene	WG	WG	WG	G
3	Xylene	WG	WG	WG	G
4	Ethanol	S	S	S	P
5	IPA	P	P	P	P
6	tert-butanol	P	P	P	P
7	THF	P	P	P	P
8	2-Butanone	P	P	P	P
9	Dibromoethane	P	P	P	P
10	Chlorobenzene	WG	WG	WG	WG
11	Chloroform	WG	WG	G	WG
12	Nitrobenzene	P	P	P	P
13	NMP	S	S	S	P
14	DMF	P	P	P	P
15	H_2O	P	P	P	P

Table 10. Gelation profile of Sulfamide **4**

S.no	Solvent	4
1	Toulene	G
2	Mesitylene	G
3	Xylene	G
4	Ethanol	S
5	IPA	S
6	tert-butanol	S
7	THF	S
8	2-Butanone	S
9	Dibromoethane	S
10	Chlorobenzene	G
11	Chloroform	S
12	Nitrobenzene	S
13	NMP	S
14	DMF	S
15	H_2O	P

G= Gel, PG=partial Gel (partially immobilized solvent which flows down on vial inversion); P= precipitate, S=solution.

Gel pictures of salts in various solvents:

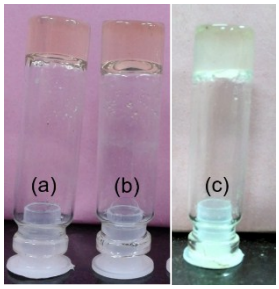


Figure S3. Gel pictures of
a) DDA**1a**/Toulene
b) DDA**1a**/ Mesitylene
c) ODA**1a**/ Toulene

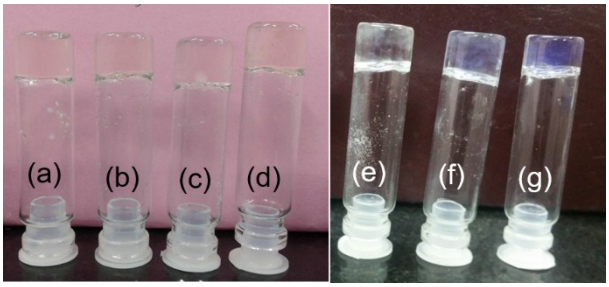


Figure S4. Gel pictures of a) TDA**3a**/$CHCl_3$, b) TDA**3a**/Toulene, c) TDA**3a**/Mesitylene, d) TDA**3a**/Xylene, e**)** ODA**3a**/Xylene, f) ODA**3a**/Mesitylene, g) ODA**3a**/Toulene

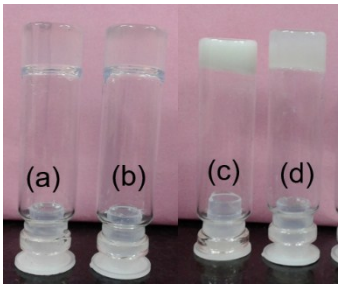


Figure S5. Gel pictures of a) TDA**4a**/ Mesitylene, b) TDA**4a**/Xylene, c) TDA**4a**/ THF, d) TDA**4a**/ $CHCl_3$

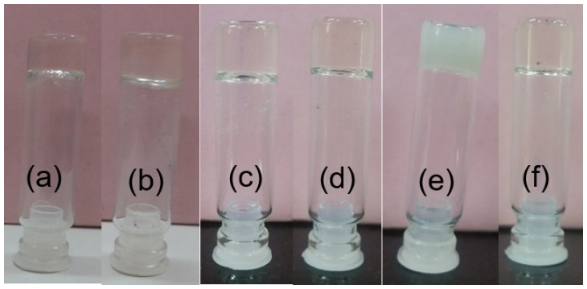


Figure S6. Gel pictures of a) DA**5a**/ Xylene, b) DA**5a**/Mesitylene, c) TDA**5a**/Mesitylene, d) TDA**5a**/ Xylene, e) TDA**5a**/THF, f) ODA**5a**/ Xylene

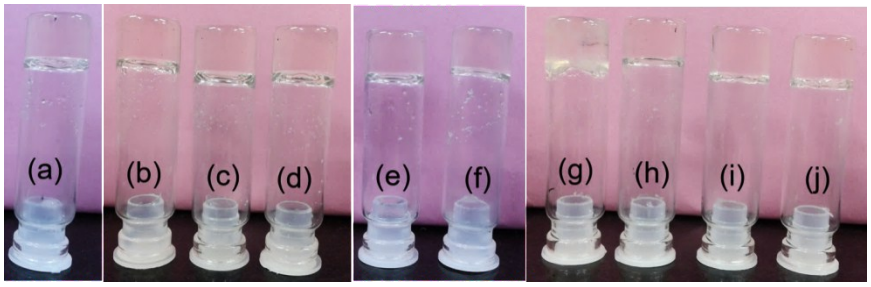


Figure S7. Gel pictures of a) **D**DA**7a**/Xylene, b) TDA**7a**/Toulene, c) TDA**7a**/Mesitylene, d) TDA**7a**/Xylene, e) DDA**7a**/Mesitylene, f) DDA**7a**/Xylene, g) DA**7a**/Chlorobenzene, h) DA**7a**/Toulene, i) DA**7a**/Mesitylene, j) DA**7a**/Xylene

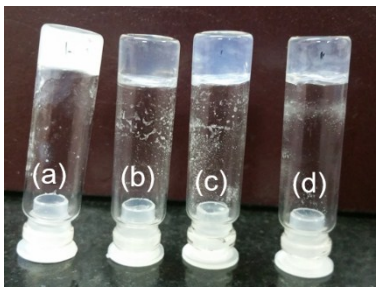


Figure S8. Gel pictures of a) TDA**9a**/Mesitylene, b) TDA**9a**/Xylene, c) TDA**9a**/THF

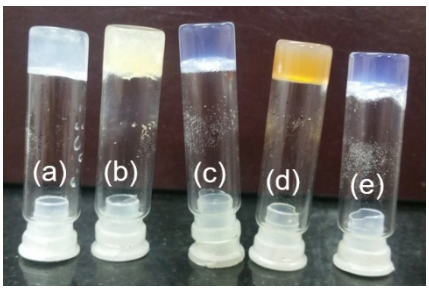


Figure S9. Gel pictures of a) **4**/Dodecanol, b) **4**/Bromobenzene, c) **4**/Xylene, d) **4**/Tetralin, e) **4**/Mesitylene.

SEM images of various Xerogels:

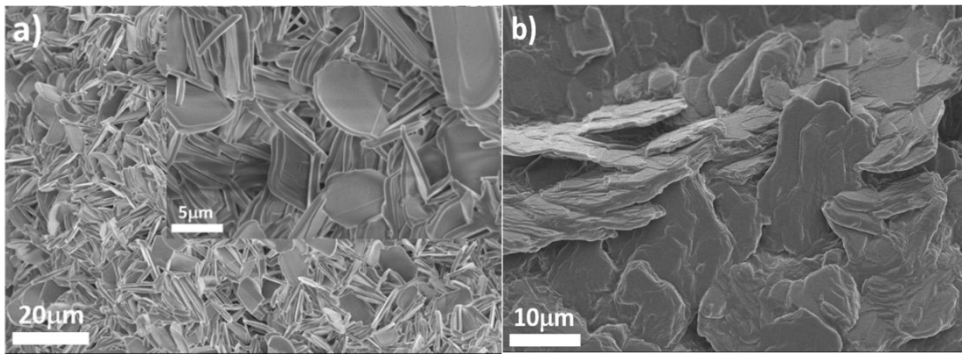


Figure S10. SEM images of a) TDA**1a**/Xylene, b) TDA**4a**/$CHCl_3$

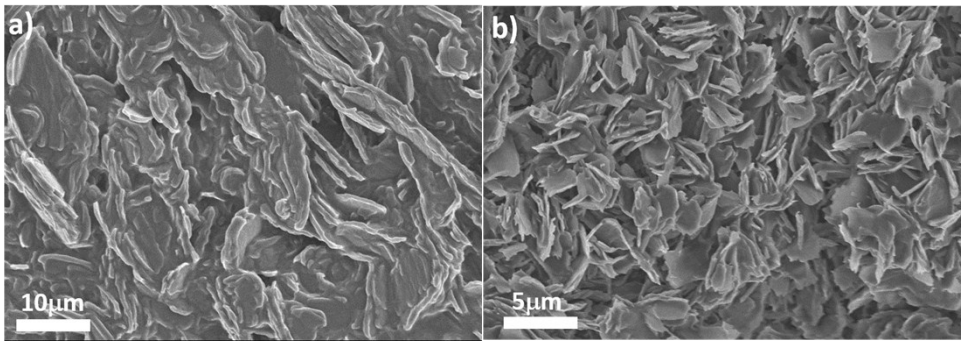


Figure S11. SEM images of a) TDA**8a**/Chlorobenzene, b) ODA**8a**/THF

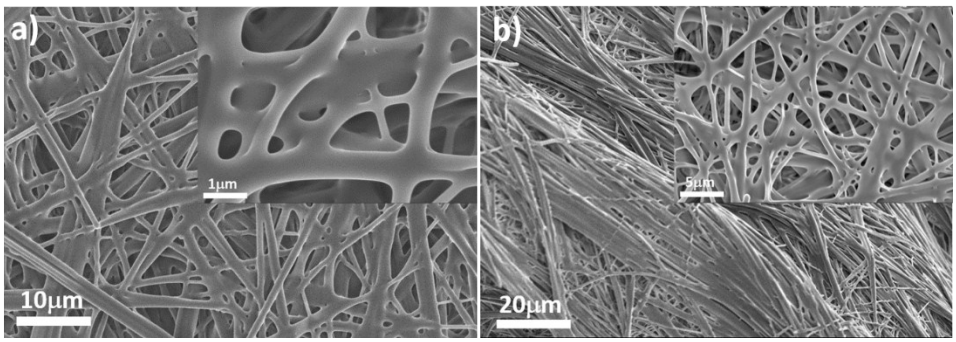


Figure S12. SEM images of a) **4**/Bromobenzene, b) **4**/Toulene

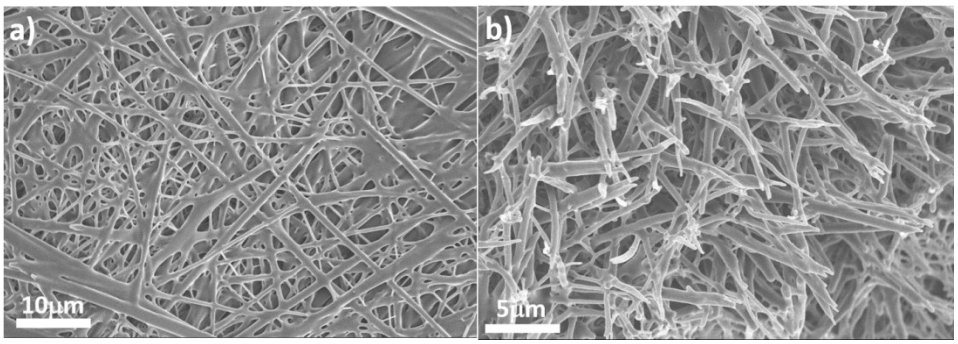


Figure S13. SEM images of a) **4**/Xylene, b) **4**/EtOAc:Hexane(1:1)

SEM imaging of xerogels of ODA8a at concentrations below its CGC

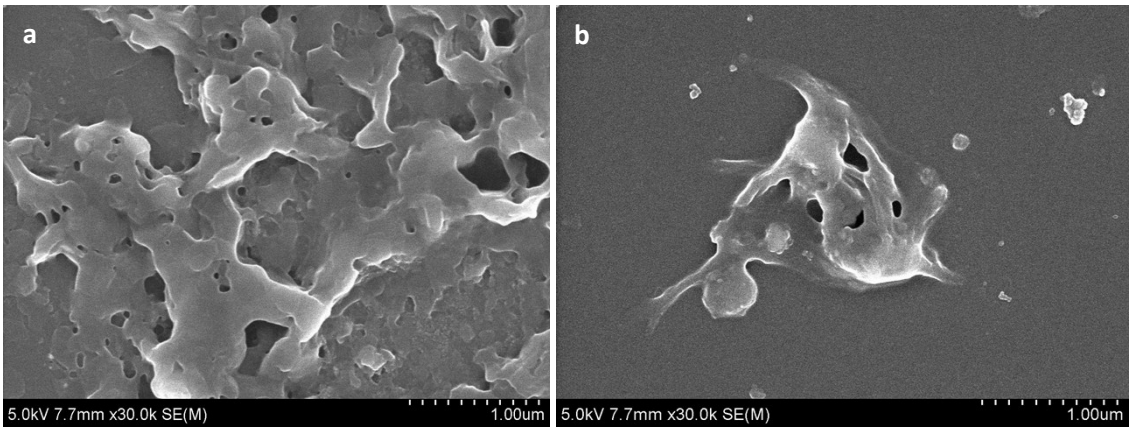


Figure S14. SEM images of a) **ODA8a** (0.1 wt% 8a with 2 equiv. of ODA in 1 mL THF);
b) ODA**8a** (0.01 wt% 8a with 2 equiv. of ODA in1 mL THF).

IR data:

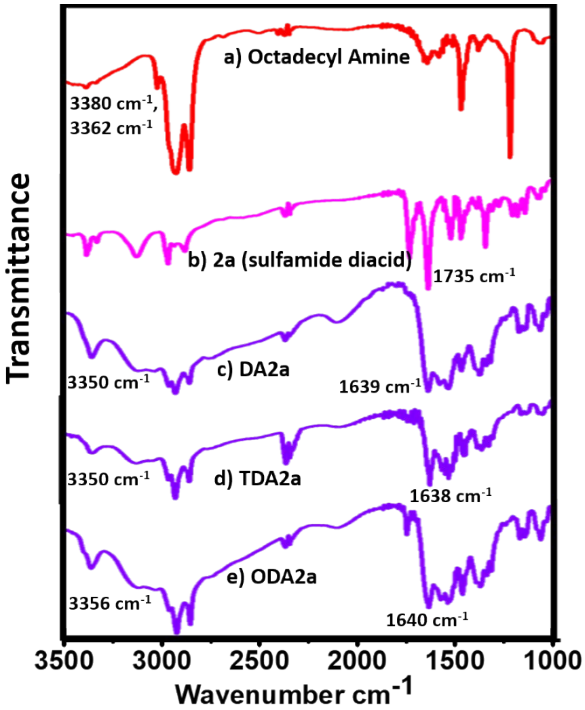


Figure S15. a) IR spectrum (neat) of simple octadecylamine (drop-casted from from $CHCl_3$) b) IR spectrum of **2a** (neat) drop-casted from $CHCl_3$ c) IR spectrum (KBr pellet) of the xerogel of **DA2a**. **TDA2a**, **ODA2a.**

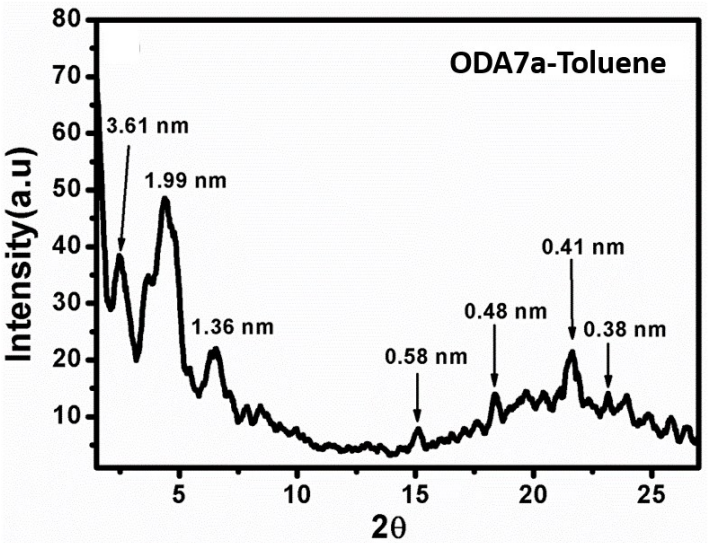


Figure S16. Results from PXRD analysis of **ODA7a** from Toluene showing evidence of layered arrangement.

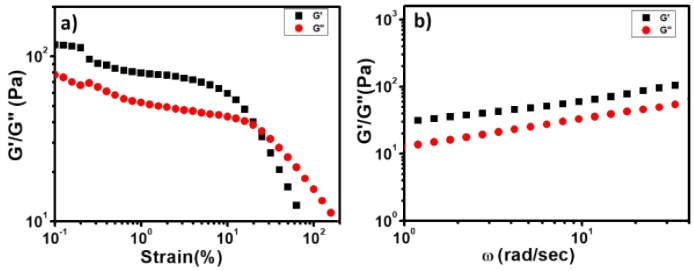


Figure S17. a) Strain sweep experiment with the gel of **TDA5a** in xylene; b) Result from Frequency sweep experiment (1-50 rad/s).

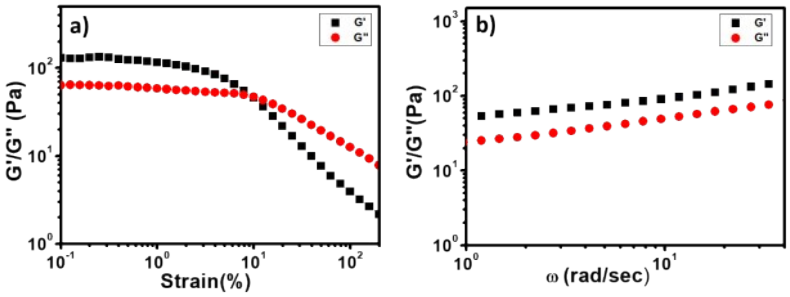


Figure S18. a) Strain sweep experiment with the gel of **ODA5a** in xylene; b) Result from Frequency sweep experiment (1-50 rad/s).

As can be seen from Figure S17a, G' in the case of **TDA5a** remained greater than G'' between 0.1-20% strain and then crossed each other giving a % yield strain value of 20.05%. In frequency sweep experiment of **TDA5a** (done at 1% strain), G' and G'' remained steady over the frequency range of 1-50 rad/s which is an indication of good stability of this material (Figure S17b). In the case of **ODA5a**, the rheological behaviour was similar and G' remained greater than the loss modulus G'' between 0.1-10% strain and then crossed each other at yield strain value of 8.0%. In frequency sweep experiment it showed a similar trend from 1-50 rad/s (Figure S18 a-b).

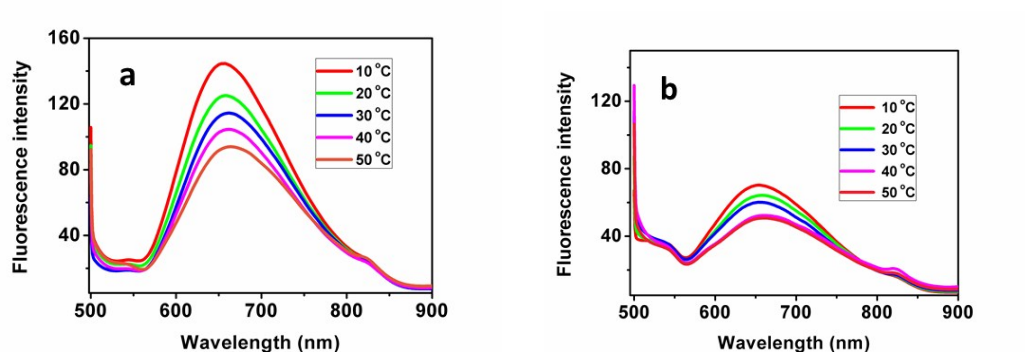
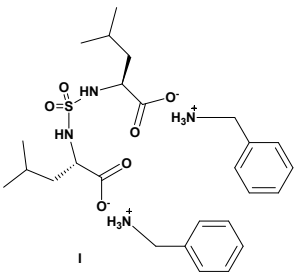


Figure S19. Temperature dependant changes in fluorescence intensity of Ag nanoparticle solution in $CHCl_3$ containing: a) 0.5 wt% of **8a** and 2 equiv of ODA; b) 2 wt% of **8a** and 2 equiv of ODA (slit: 5 nm/ 2.5 nm).

Study of 'matrix effect using the gel prepared from the lower homologue of peptide-based sulfamide

In order to see whether the nature of gel matrix is having any significance in the emission enhancement, we have done additional experiments with gel created from the lower homologue of the sulfamides studied here. This is based on the dipeptide analog from leucine and benzylamine (I, Figure 20). Interestingly, gel from this dipeptide analog was not efficient in fluorescence enhancement as shown below. As mentioned, ODA8a is based on tetrapeptide analog whereas the one shown in Figure S20 is taken for comparative assessment and is a dipeptide analog. Because of the difference in size, conformation and the secondary interaction possibilities, their supramolecular network and nature of solvent interfaces would be different. Further, the silver nanoparticles used here are initially capped with glutatione and then CTAB (Cetyl trimethylammonium bromide) is added to partition them to chloroform layer, and hence will have both these entitties in their periphery. Since our studies show noticeable emission enhancement only in the case of tetrapepetide analog, it is logical to assume that the nanoparticles are finding better stability and 'confinement' in this case compared to the other.



I

Figure S20. Temperature dependent changes in fluorescence intensity of Ag nanoparticle solution in $CHCl_3$ containing: a) 0.5 wt% of **I** with 2 equiv. of benzylamine; b) 3 wt% of **1** and 2 equiv of benzylamine (slit: 5 nm/ 2.5 nm).

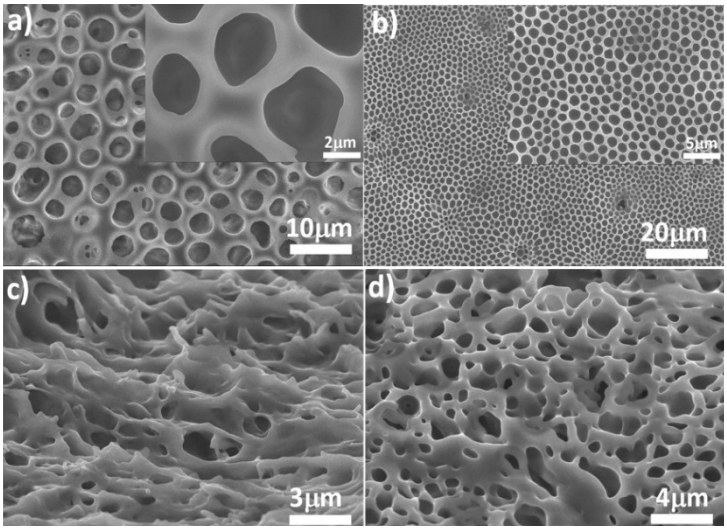


Figure S21. SEM images of **ODA8a** in combination of a) 1 mg of F-127, b) 2 mg of F-127, c) 4mg of F-127, d) 5mg of F-127 in THF.

Table 12. Crystallographic summary for compounds **5** and **7-9**

Compound	**5**	**7**	**8**	**9**
Chemical	$C_{26}H_{50}N_4O_8S$	$C_{26}H_{50}N_4O_8S$	$C_{24}H_{46}N_4O_8S$	$C_{24}H_{46}N_4O_8S$
Formula weight	578.76	578.76	550.71	550.71
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
a (Å)	10.0952(13)	10.2919(8)	9.5629(6)	9.5100(9)
b (Å)	16.406(2)	15.7509(9)	15.7440(9)	15.8715(12)
c (Å)	10.2489(14)	20.9127(15)	21.1445(13)	10.7748(11)
α (°)	90	90	90	90
β (°)	90.105(3)	90	90	105.503(3)
γ (°)	90	90	90	90
Temperature	RT	RT	RT	RT
V (Å ^{3})	1697.4(4)	3390.1(4)	3183.5(3)	1567.2(2)
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
Z	2	4	4	2
Total reflections	17341	37722	54270	18505
Independent	5633	6256	6251	18505
Final R value	0.0700	0.0457	0.0484	0.0603
CCDC Number	1583457	1583446	1583458	1583456

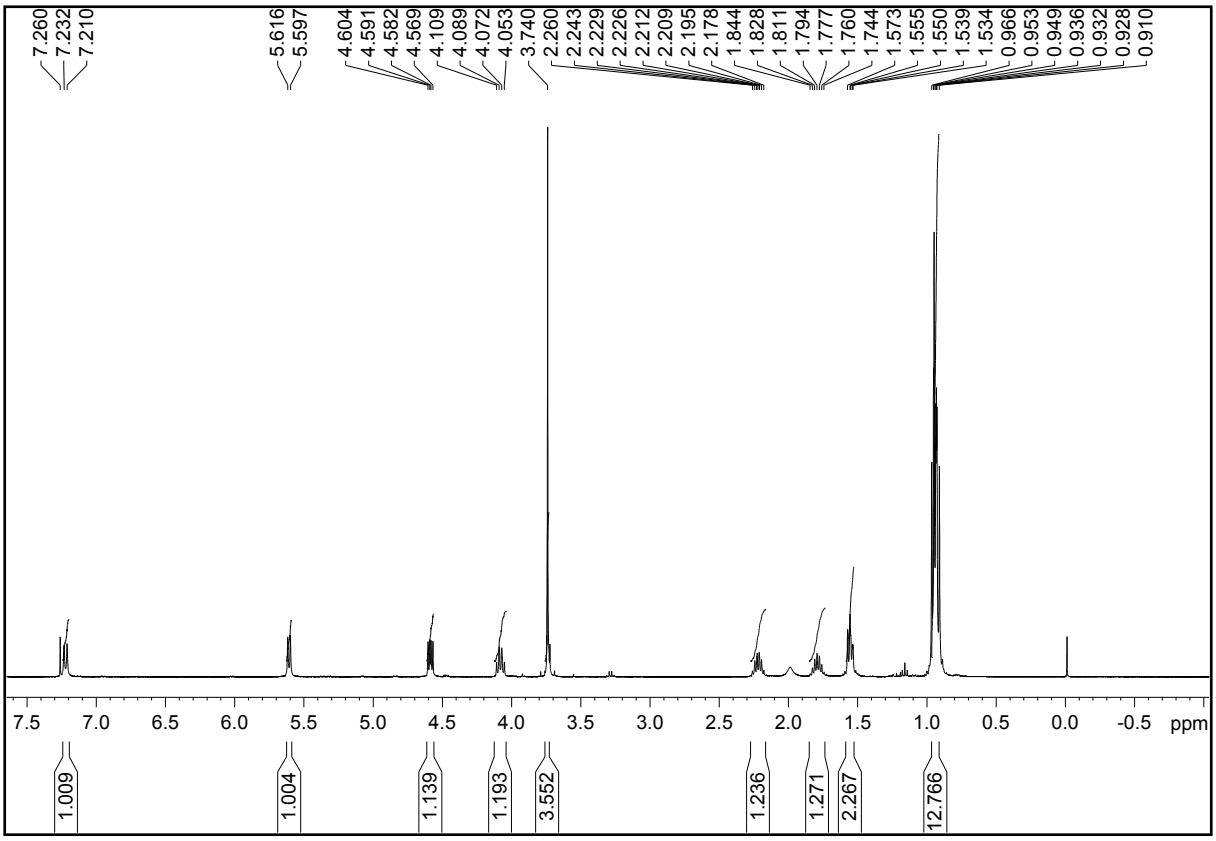


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **4**.

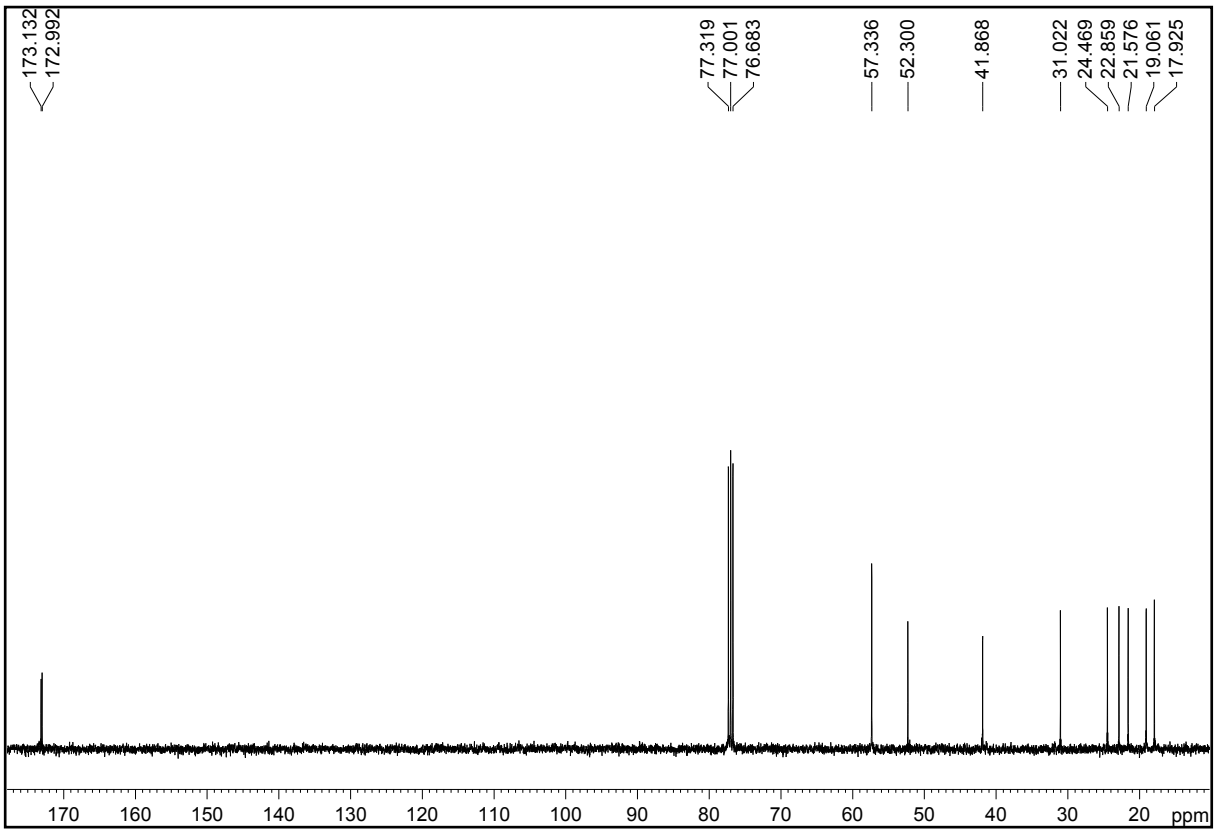


Figure S23. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the compound **4**.

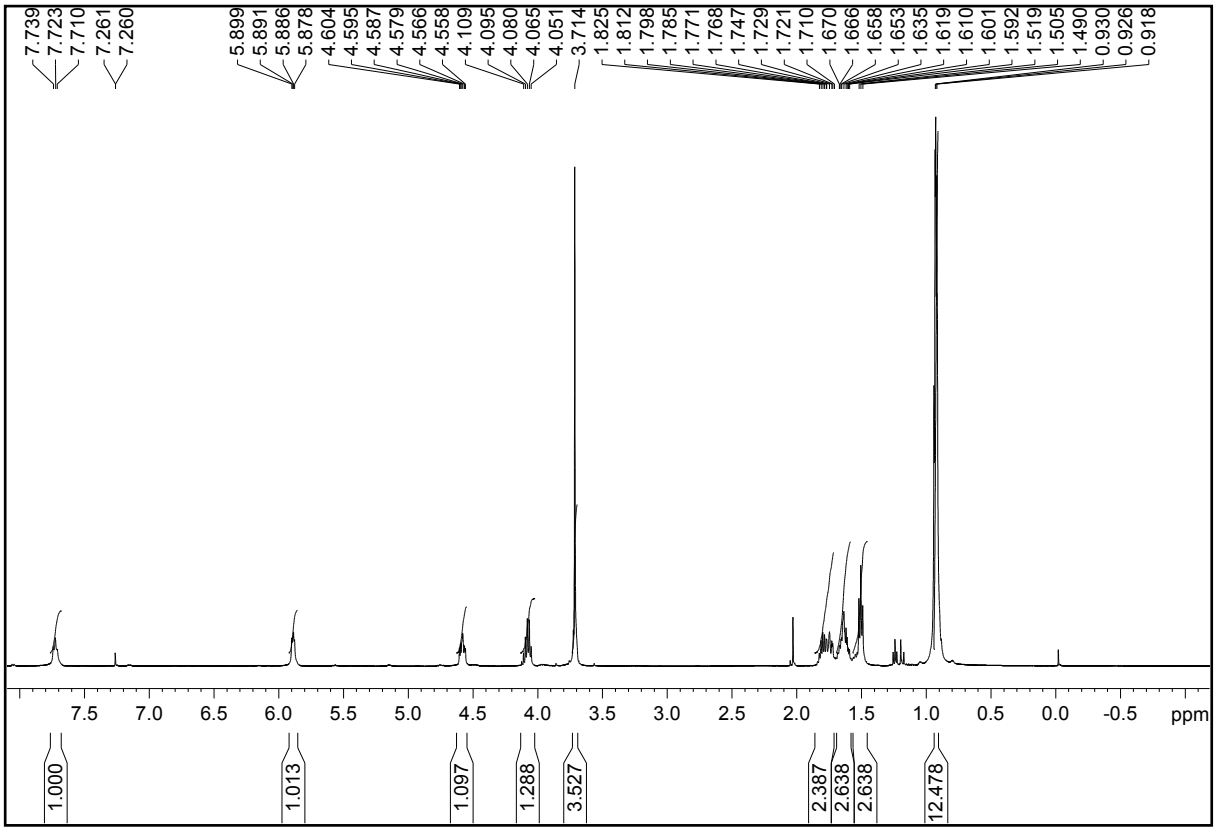


Figure S24. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the compound **5**.

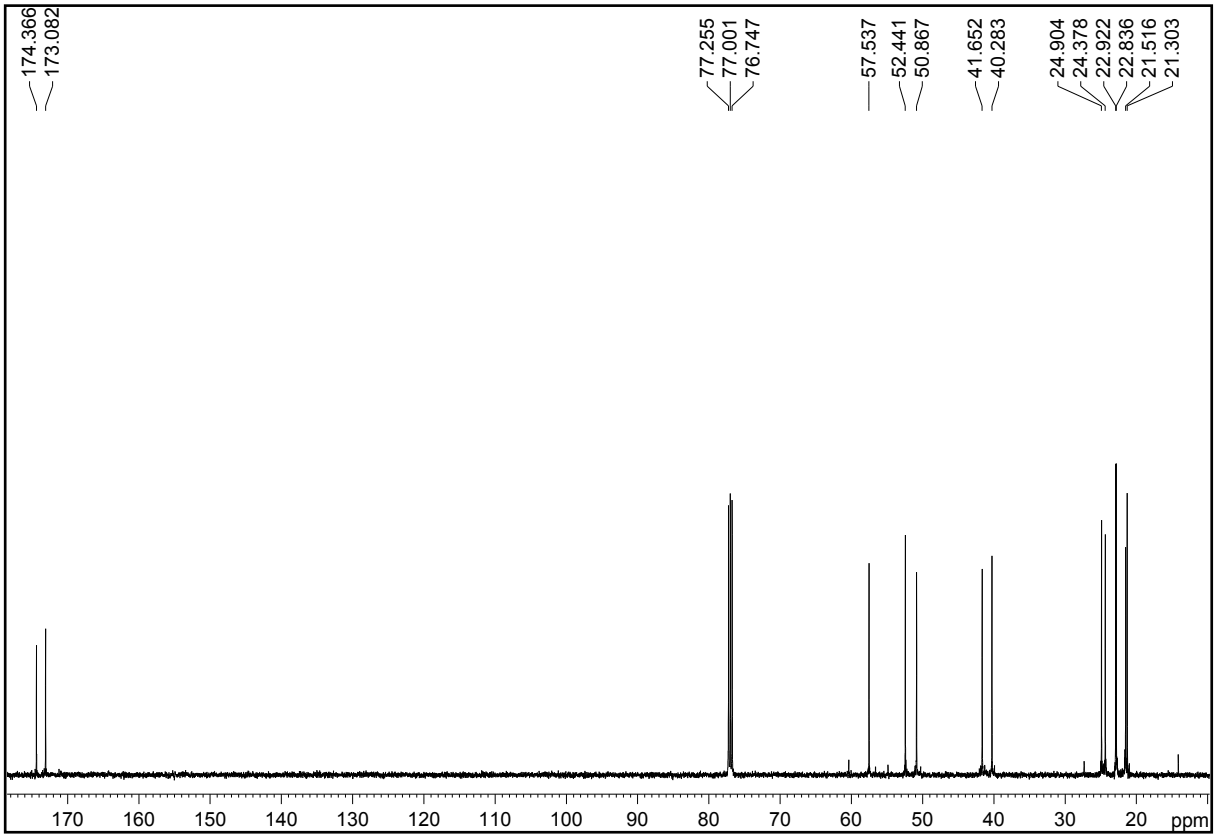


Figure S25. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **5**.

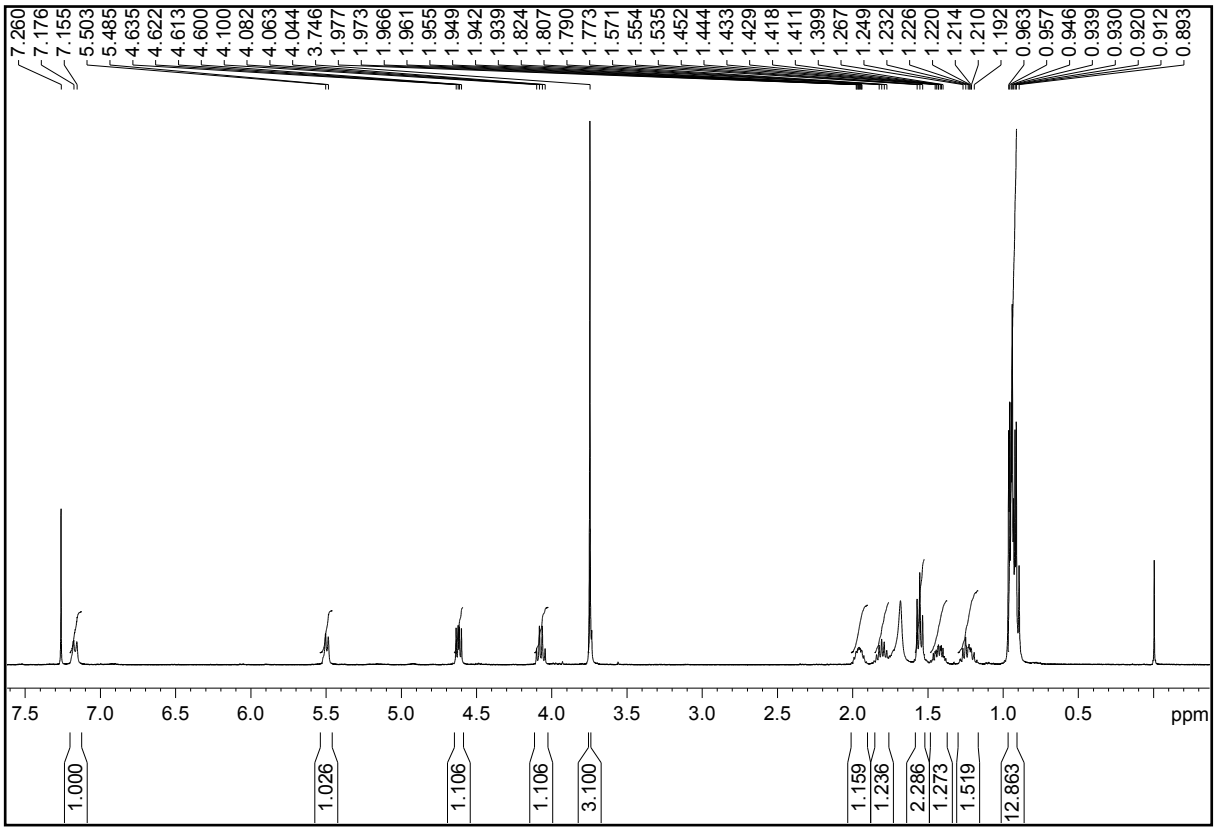


Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **6**.

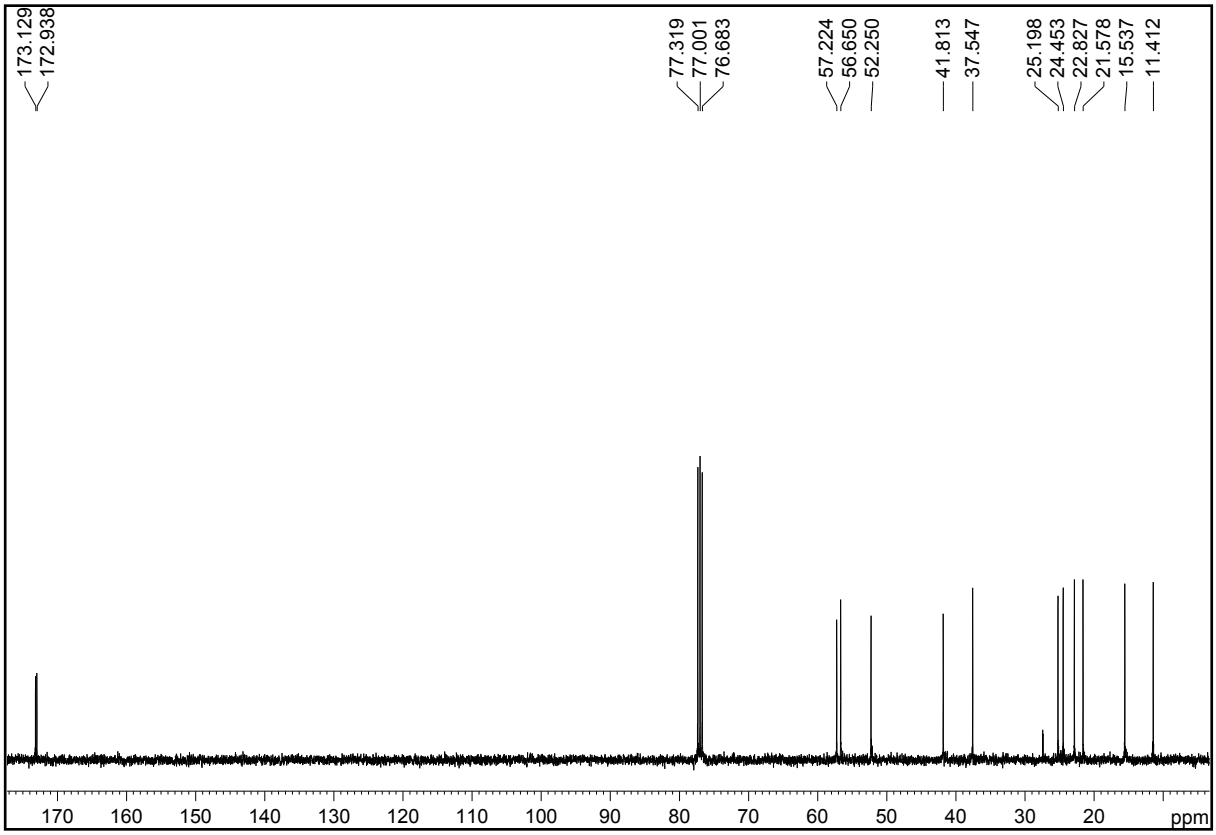


Figure S27. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the compound **6**.

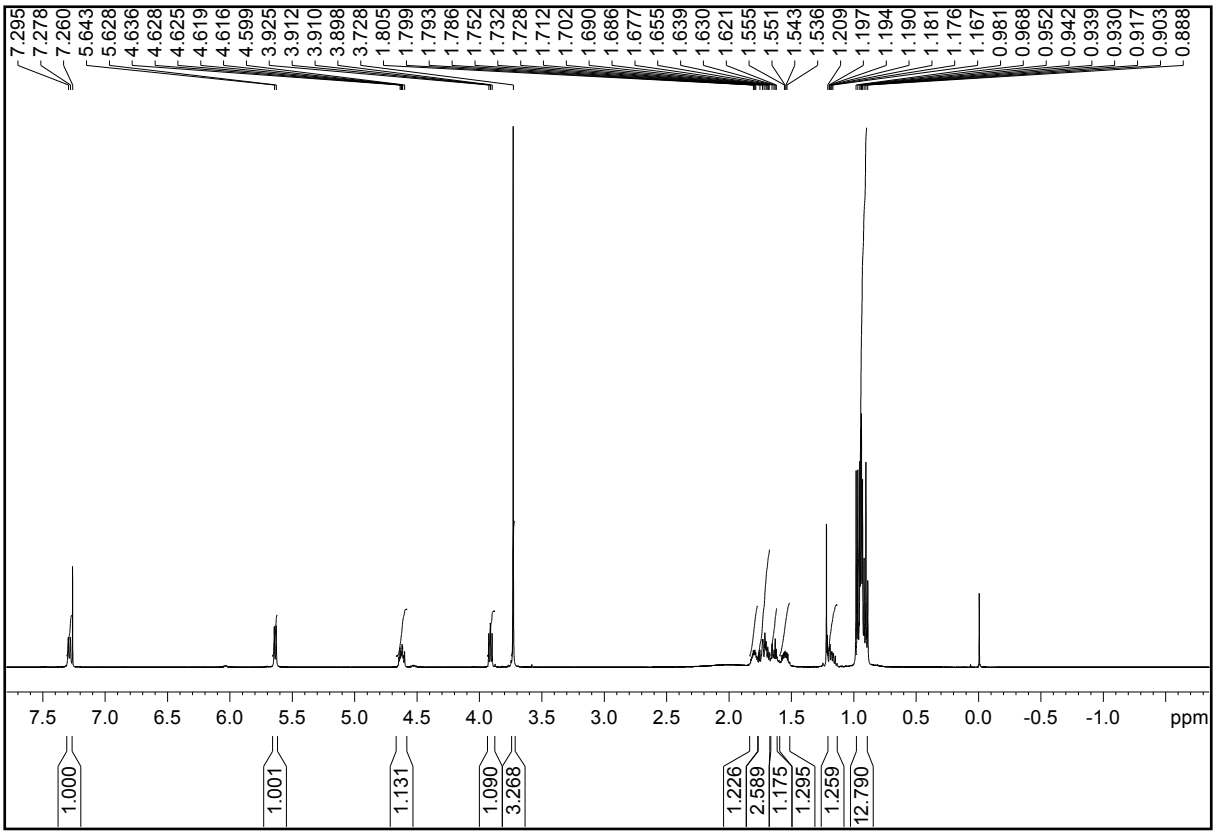


Figure S28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the compound **7**

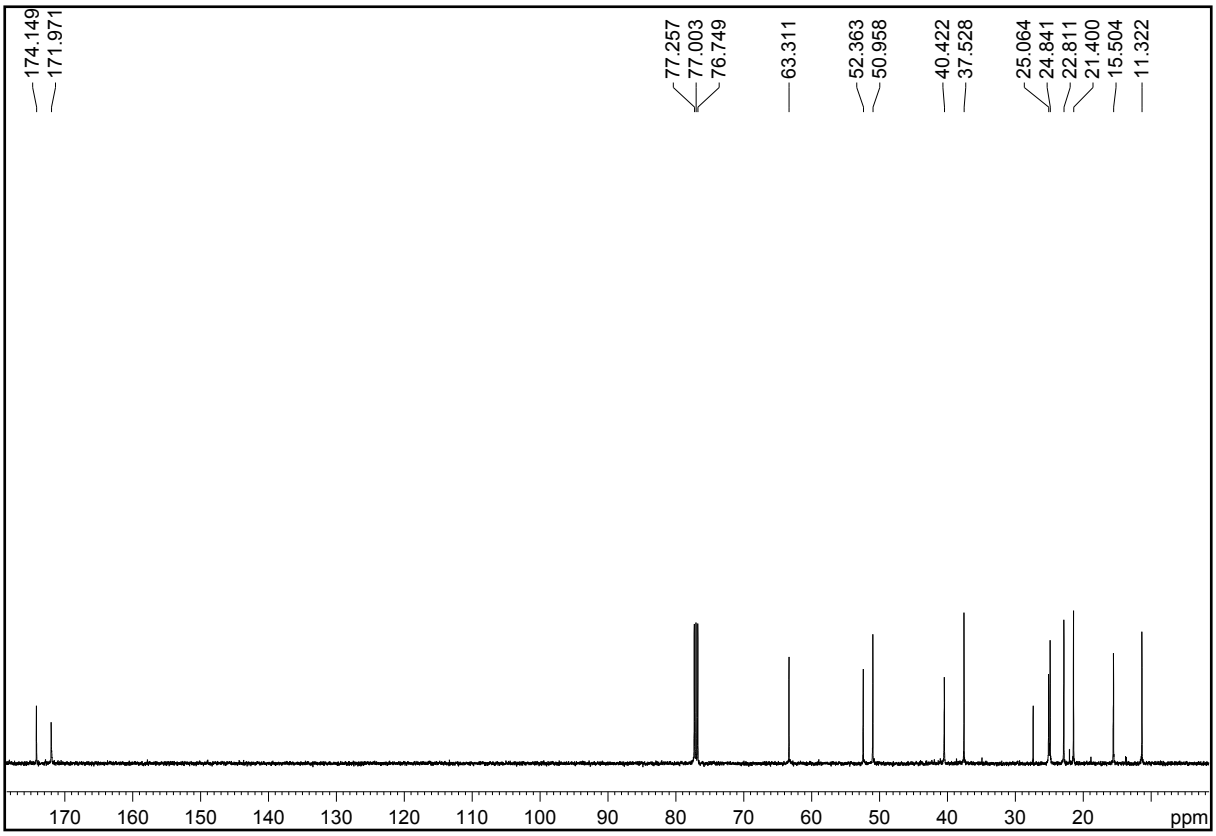


Figure S29. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **7**.

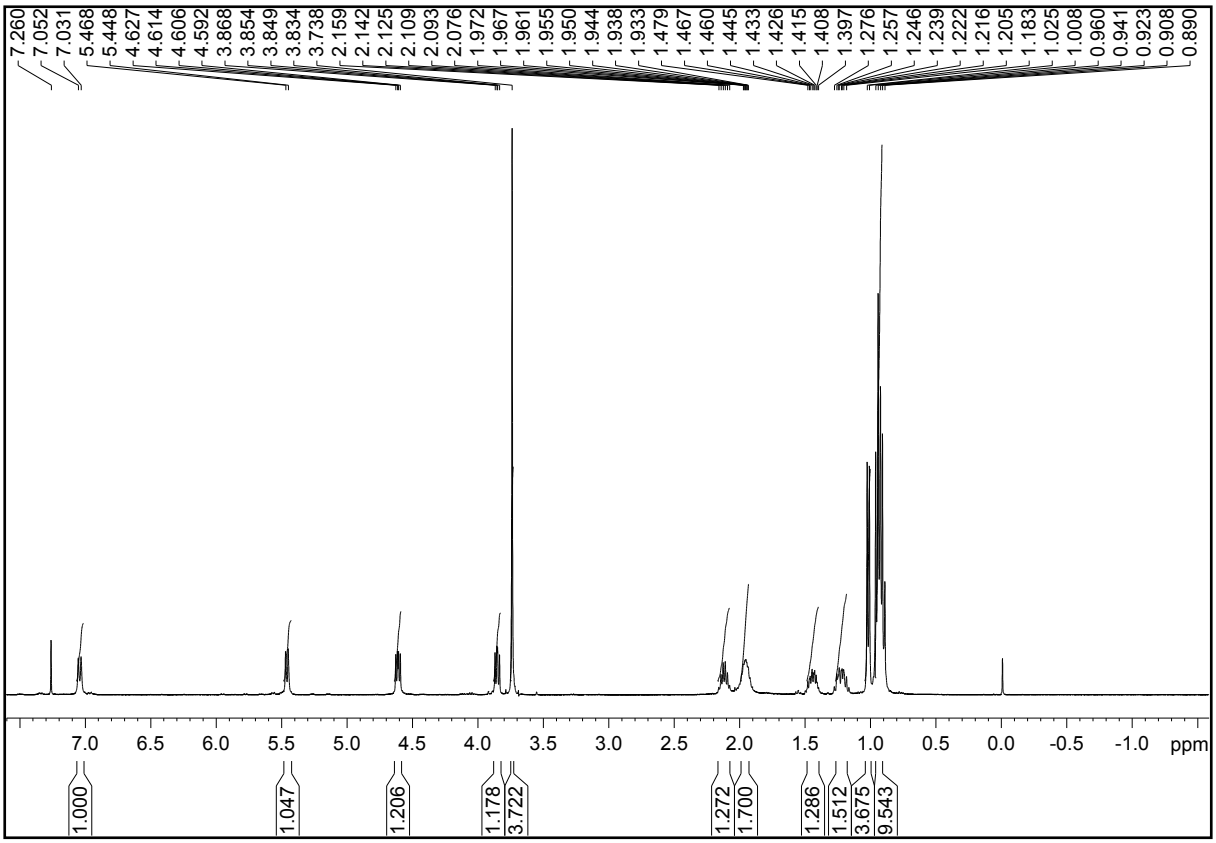


Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **8**.

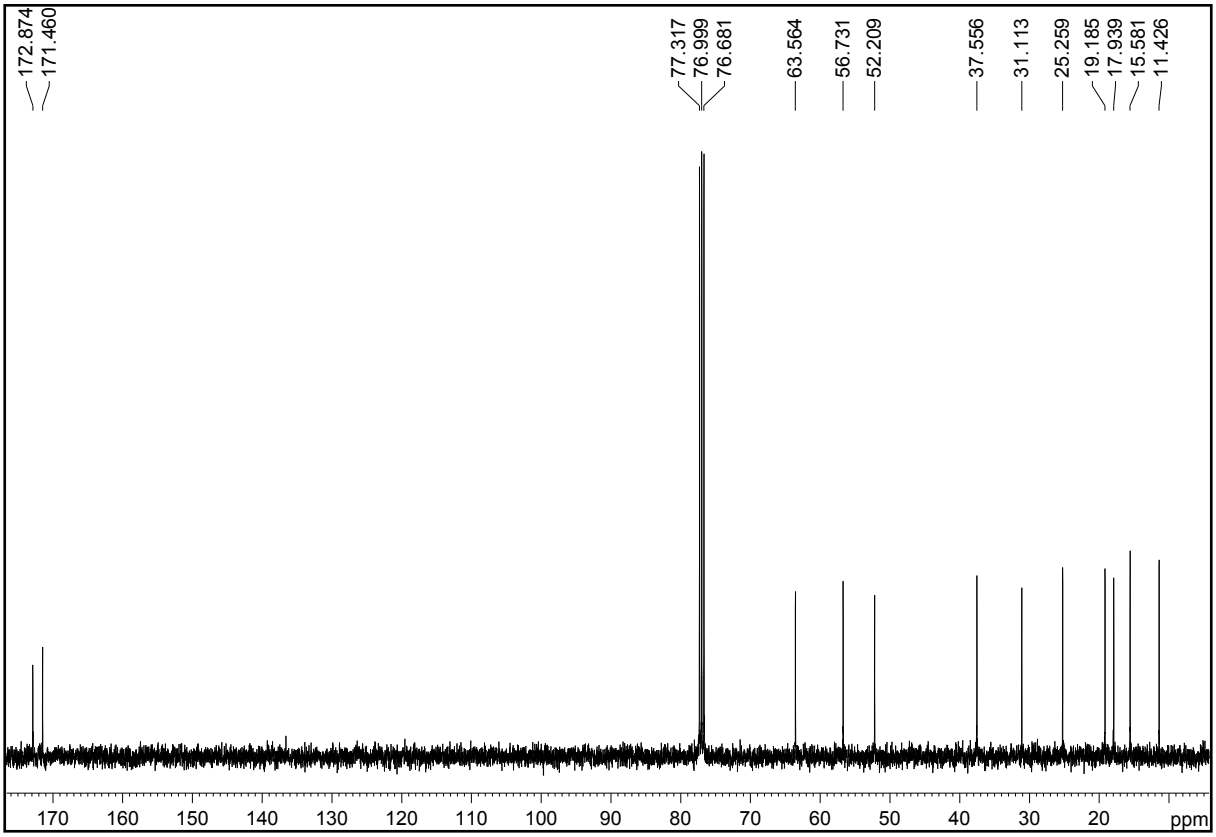


Figure S31. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the compound **8**.

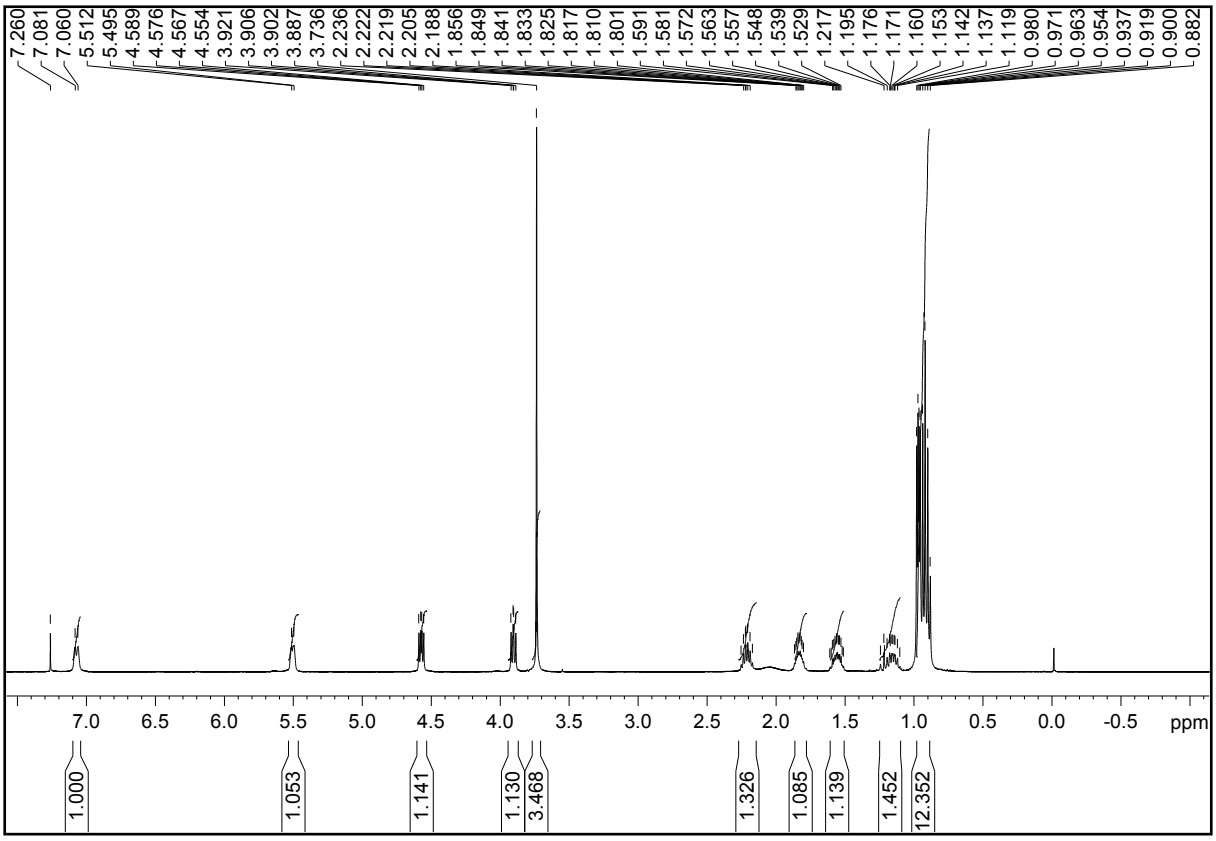


Figure S32. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **9**.

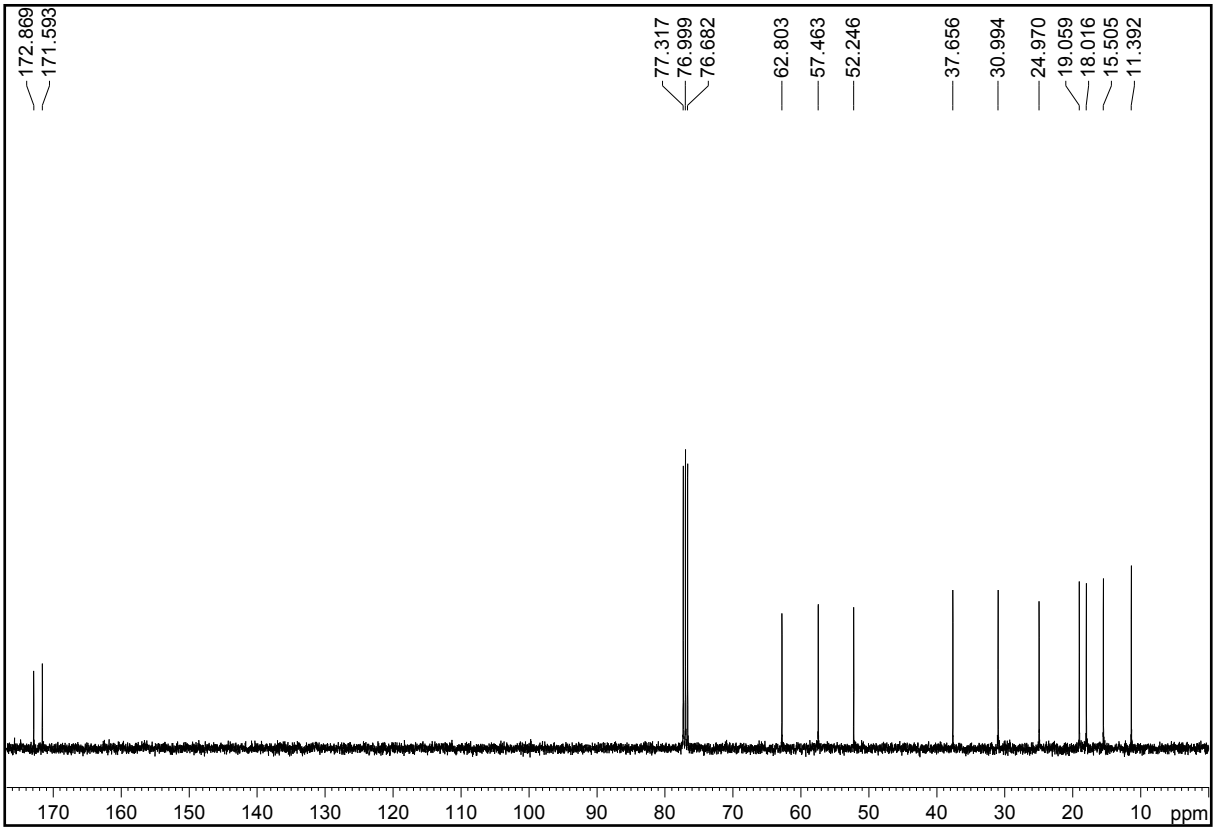


Figure S33. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the compound **9**.

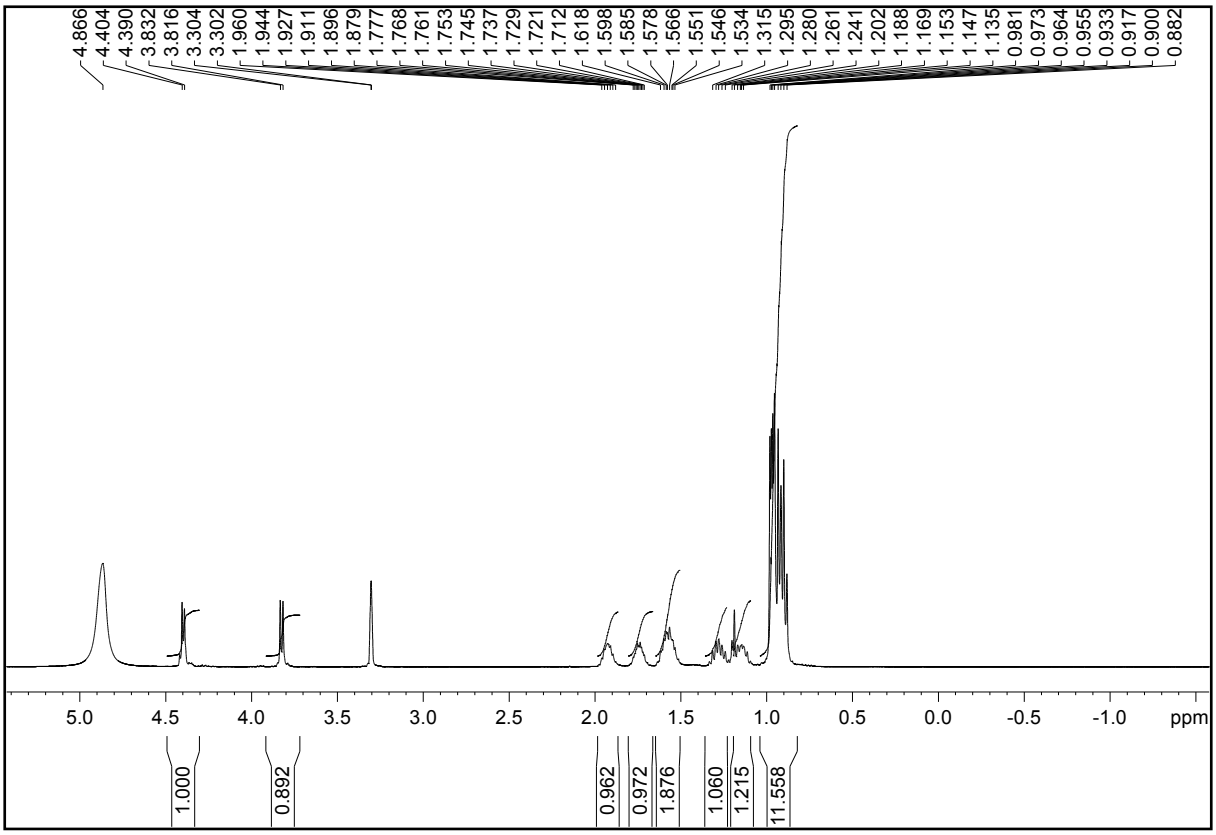


Figure S34. ^{1}H NMR spectrum (400 MHz, CD_3OD) of the compound **1a**.

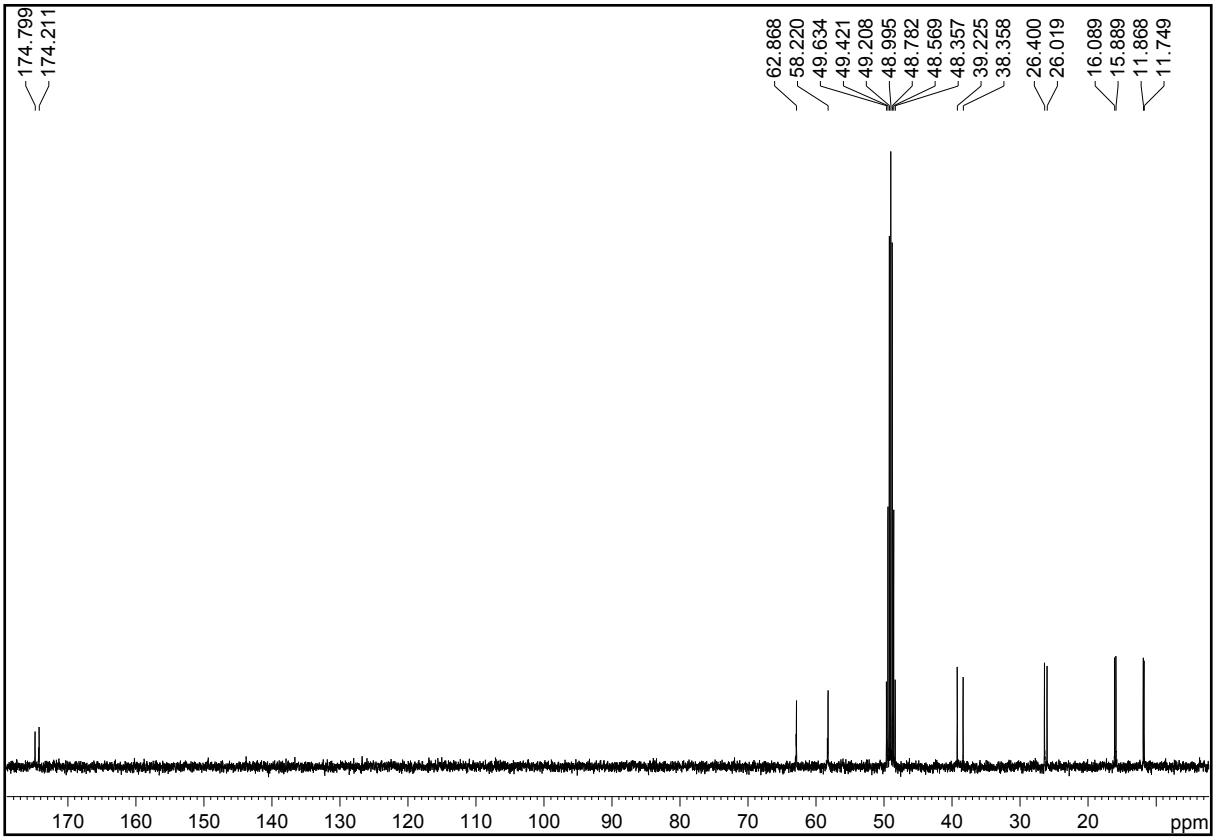


Figure S35. ^{13}C NMR spectrum (100 MHz, CD_3OD) of the compound **1a**.

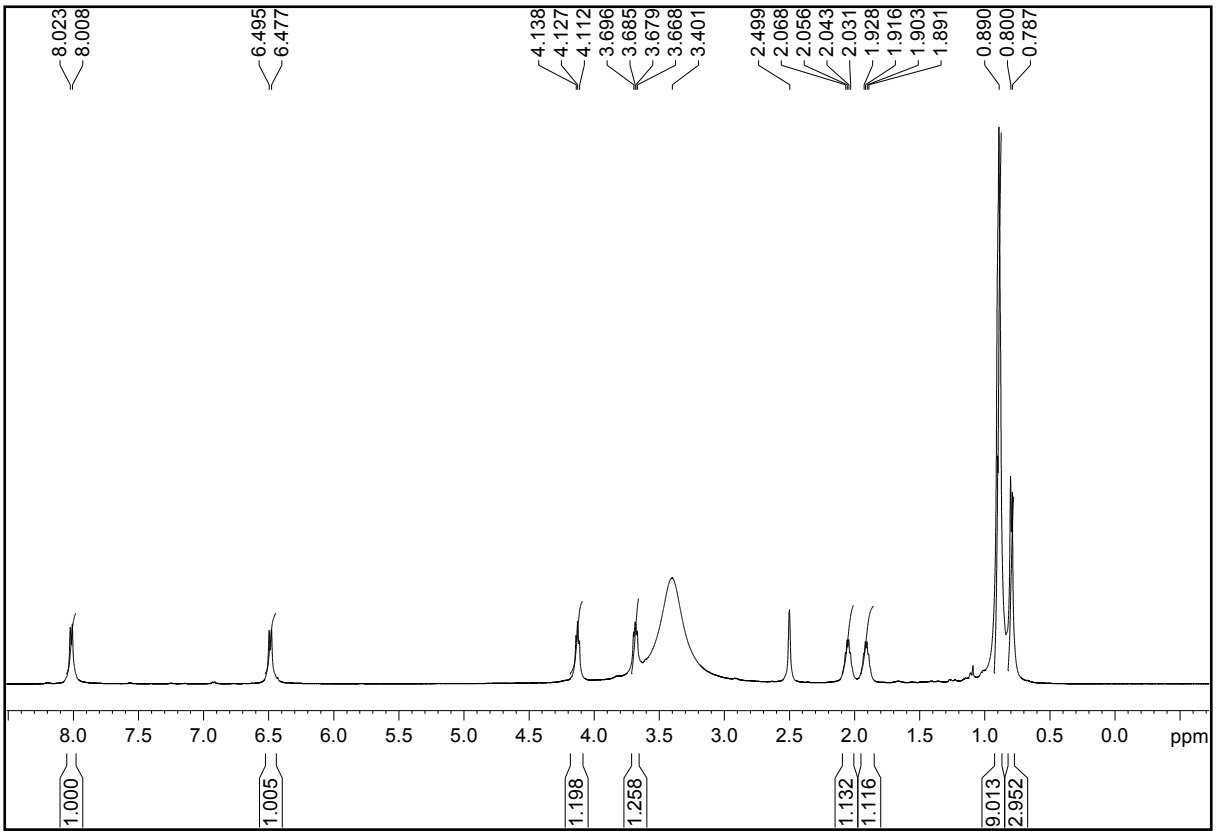


Figure S36. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the compound **2a**.

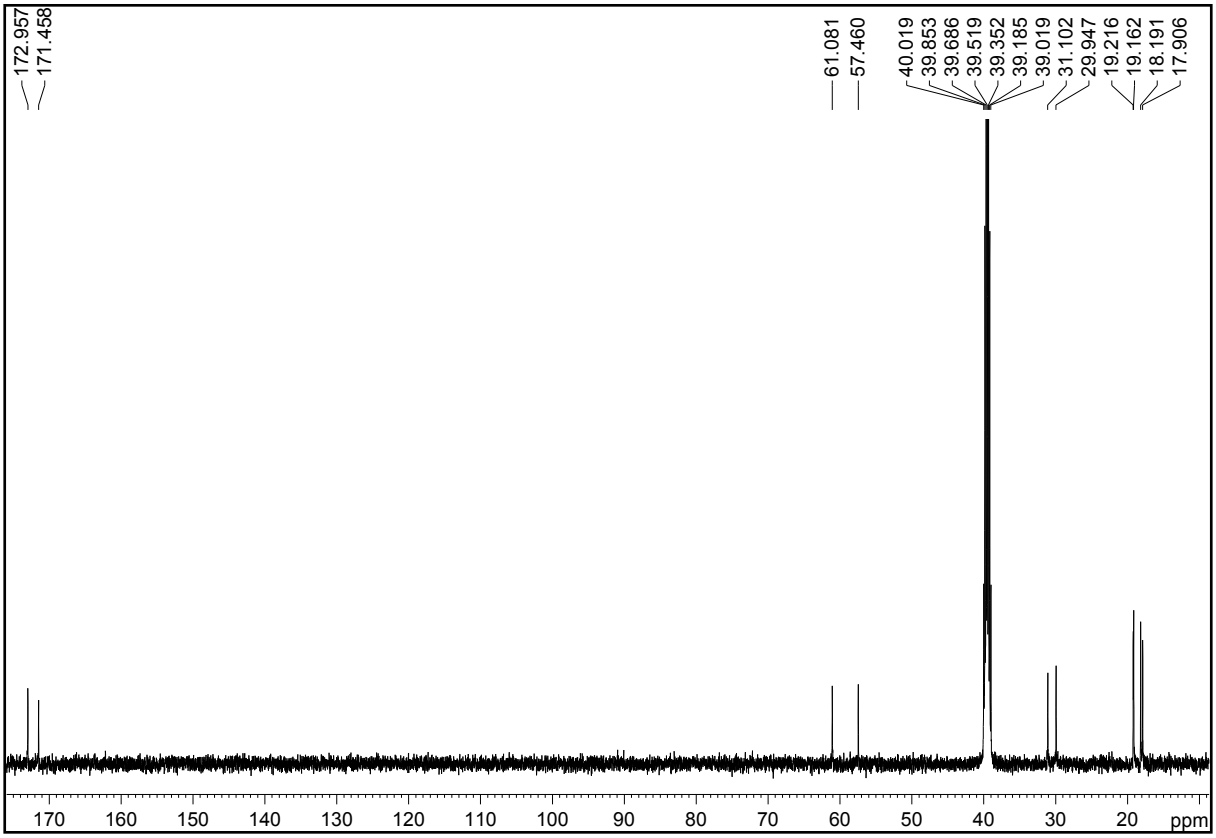


Figure S37. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of the compound **2a**.

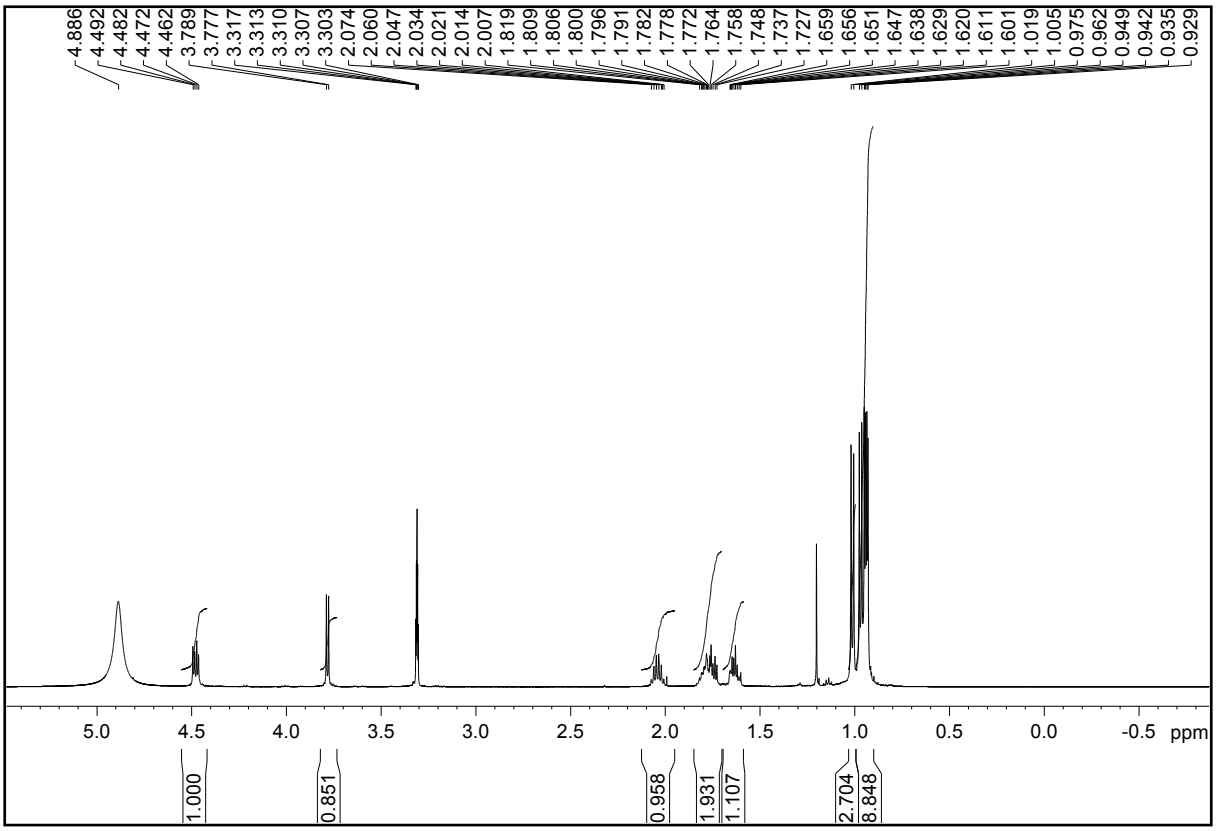


Figure S38. ^{1}H NMR spectrum (500 MHz, CD_3OD) of the compound **3a**.

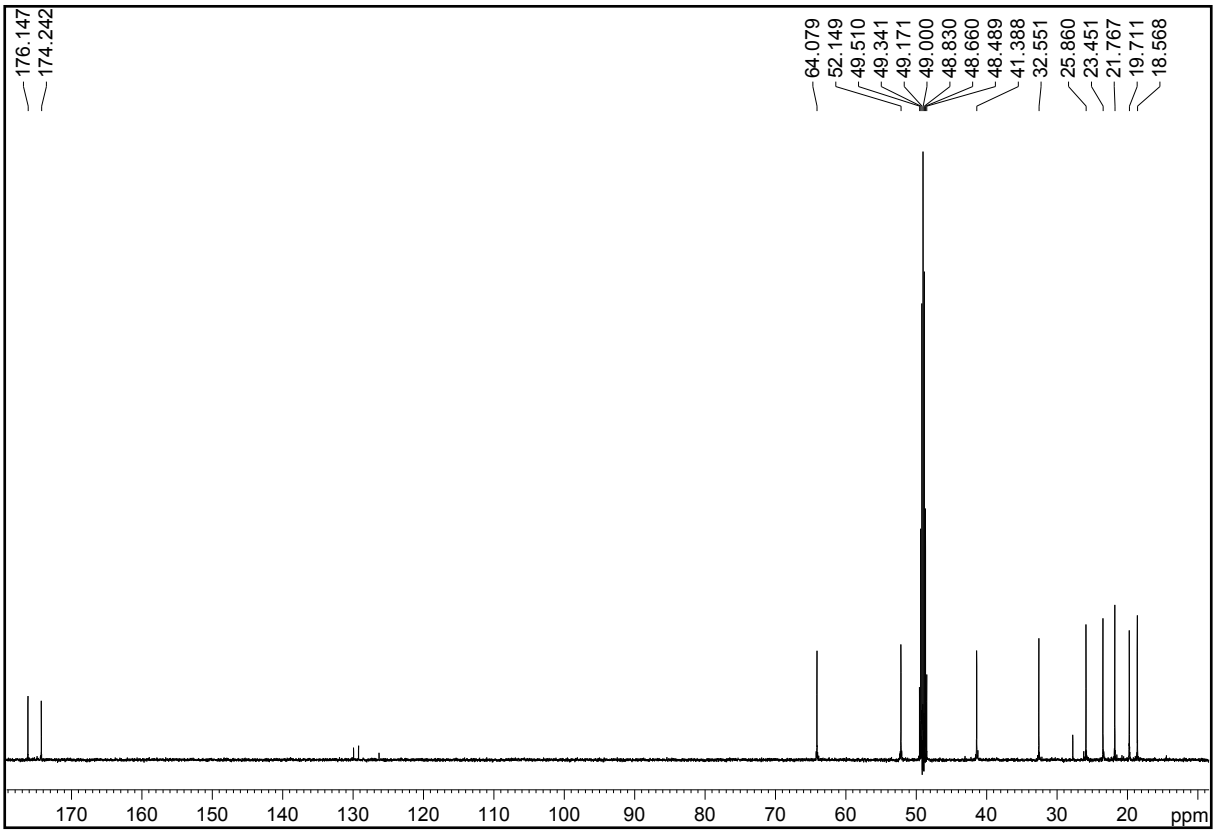


Figure S39. ^{13}C NMR spectrum (125 MHz, CD_3OD) of the compound **3a**.

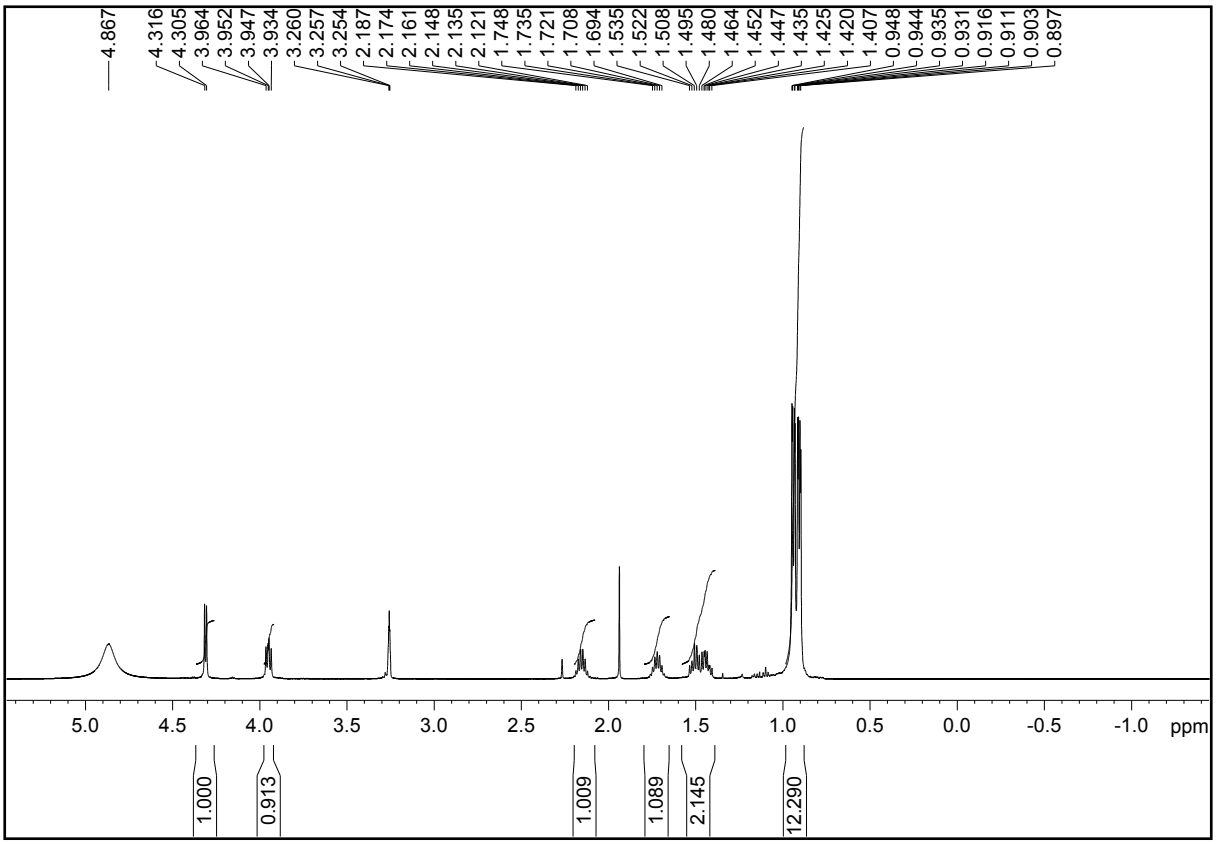


Figure S40. ^{1}H NMR spectrum (500 MHz, CD_3OD) of the compound **4a**.

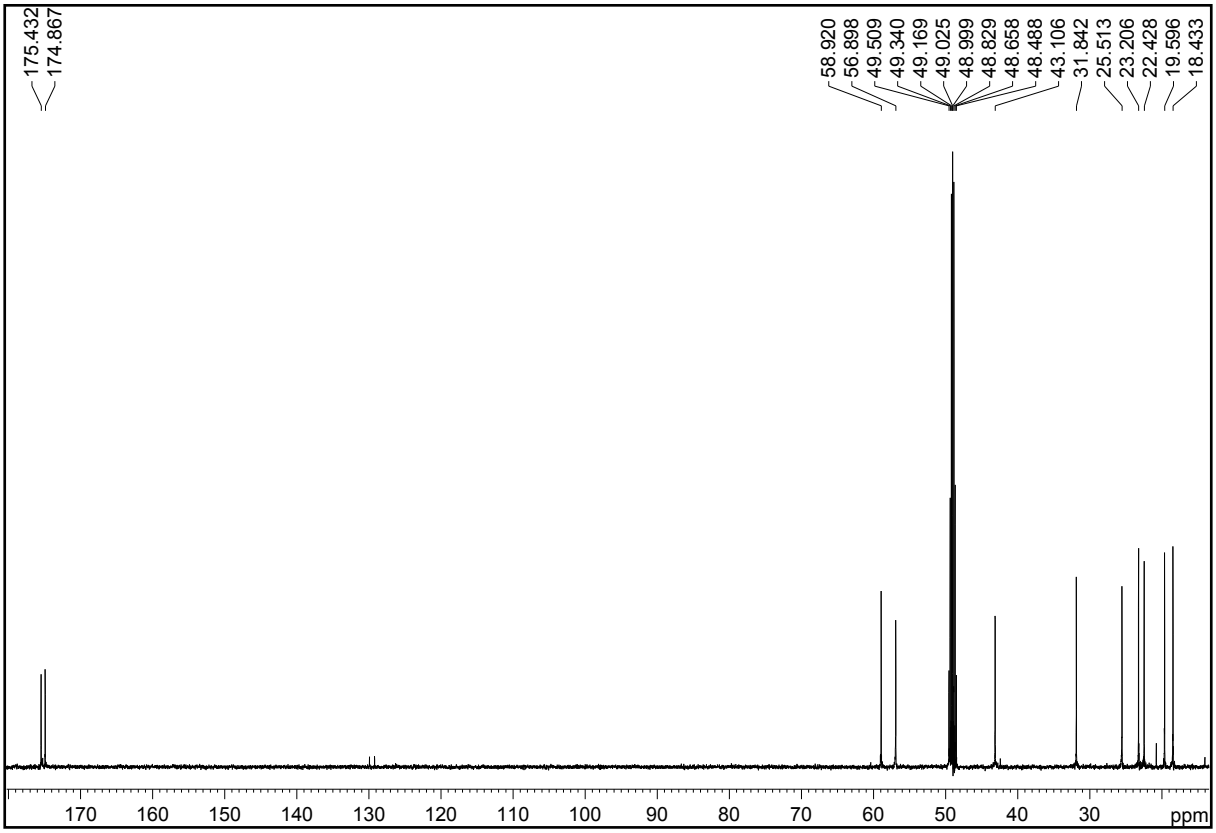


Figure S41. ^{13}C NMR spectrum (125 MHz, CD_3OD) of the compound **4a**.

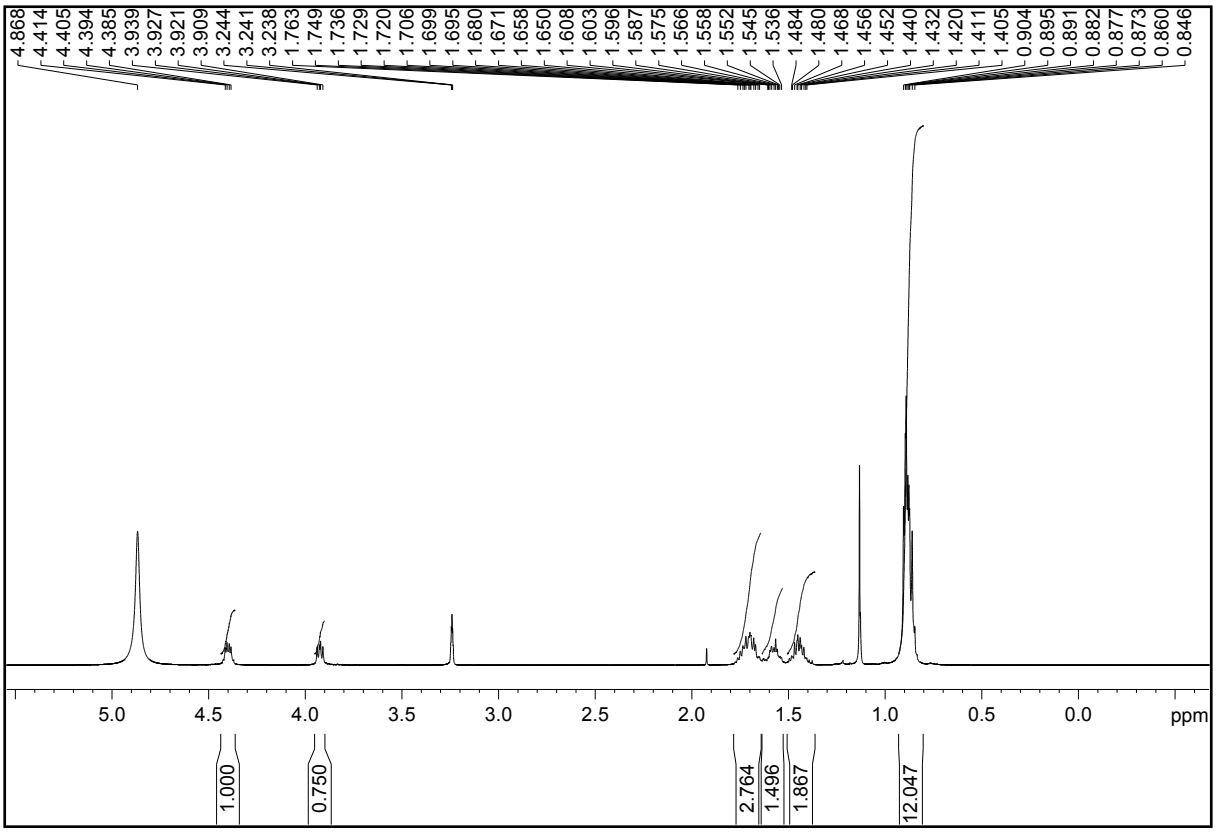


Figure S42. ^{1}H NMR spectrum (500 MHz, CD_3OD) of the compound **5a**.

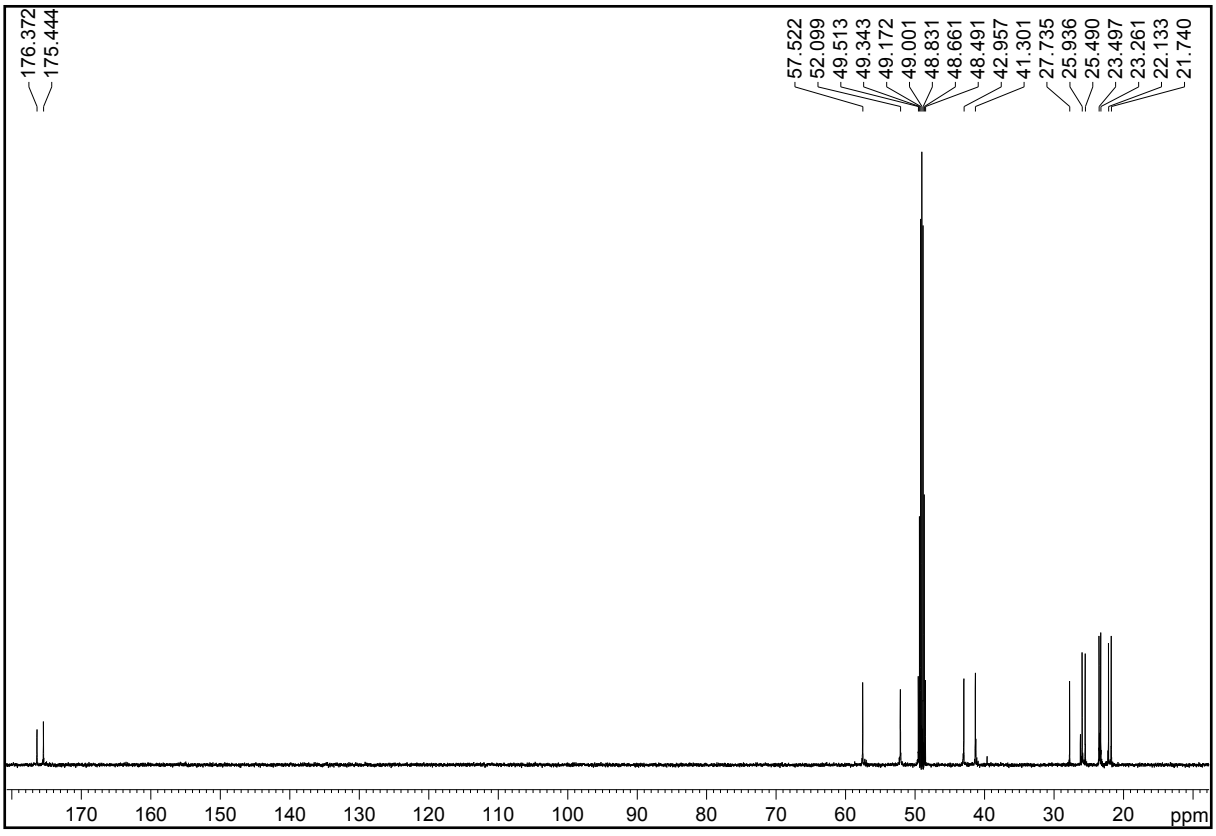


Figure S43. ^{13}C NMR spectrum (125 MHz, CD_3OD) of the compound **5a**

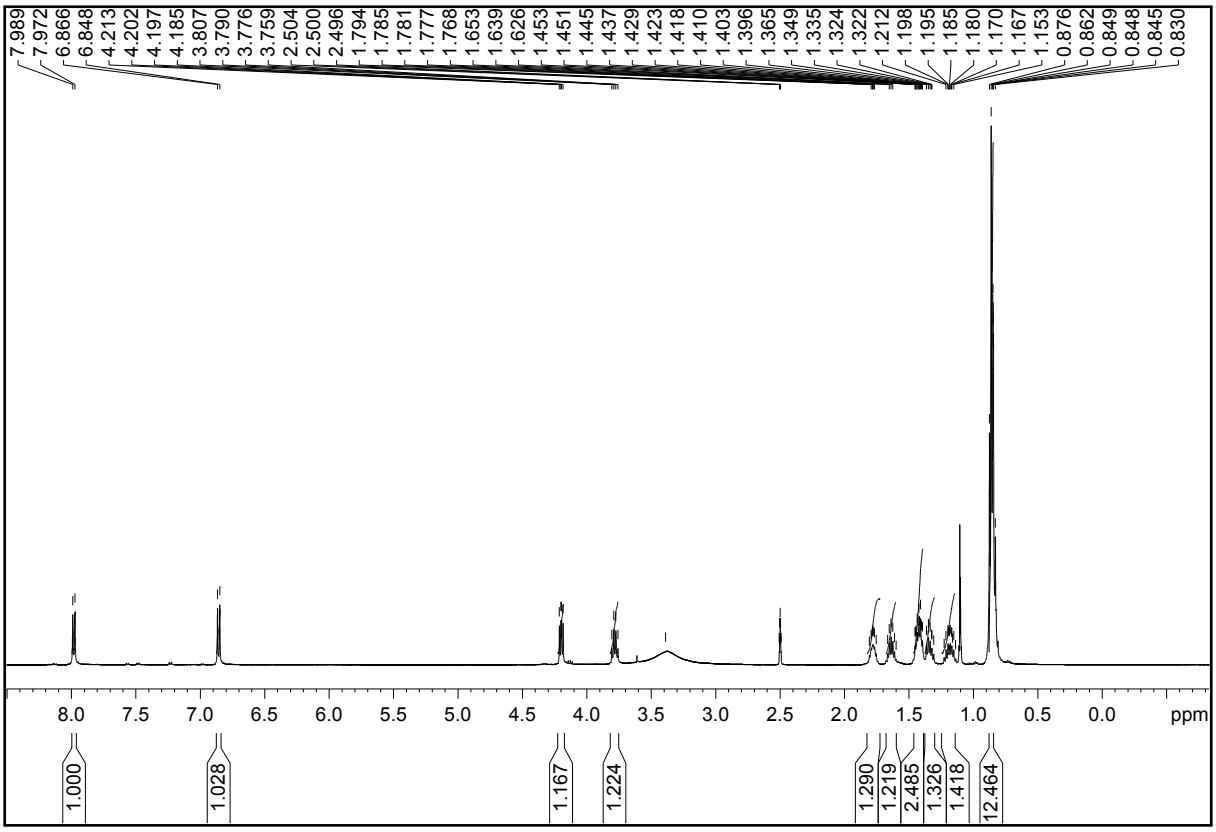


Figure S44. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the compound **6a**.

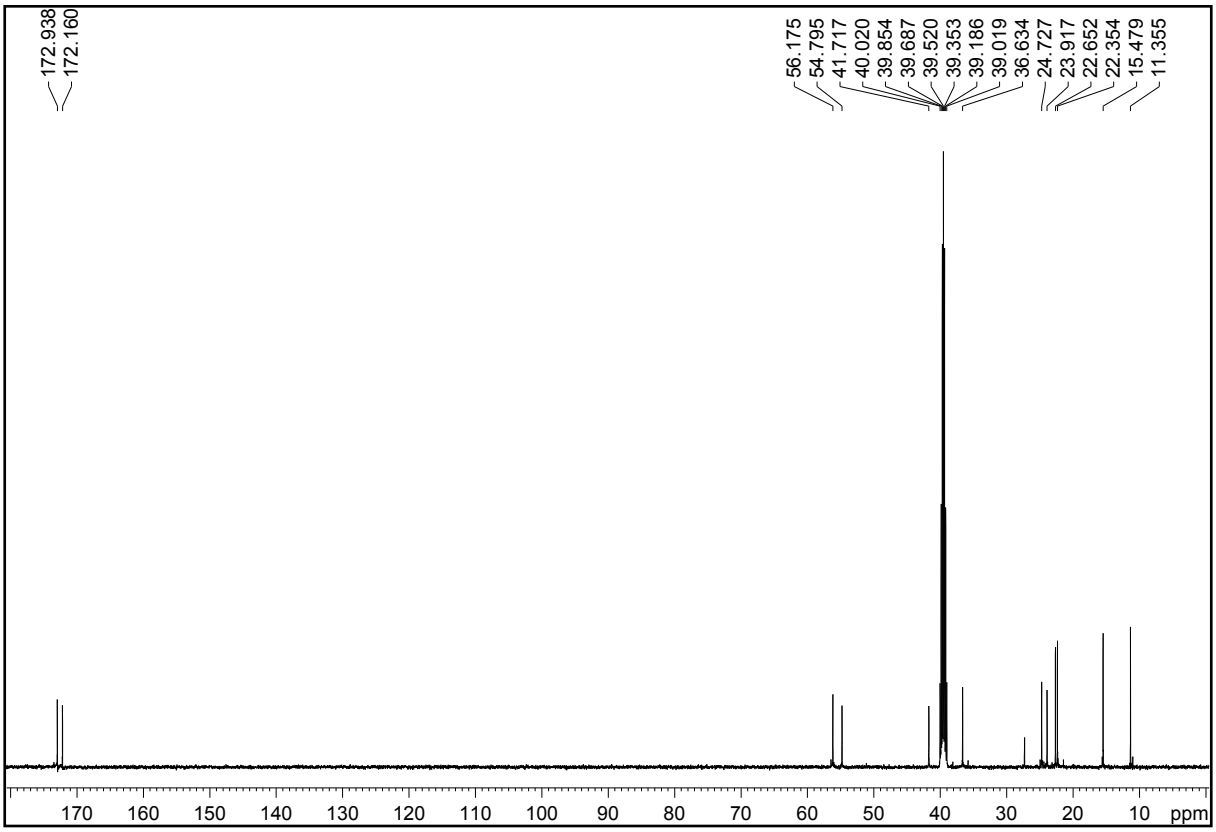


Figure S45. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of the compound **6a**

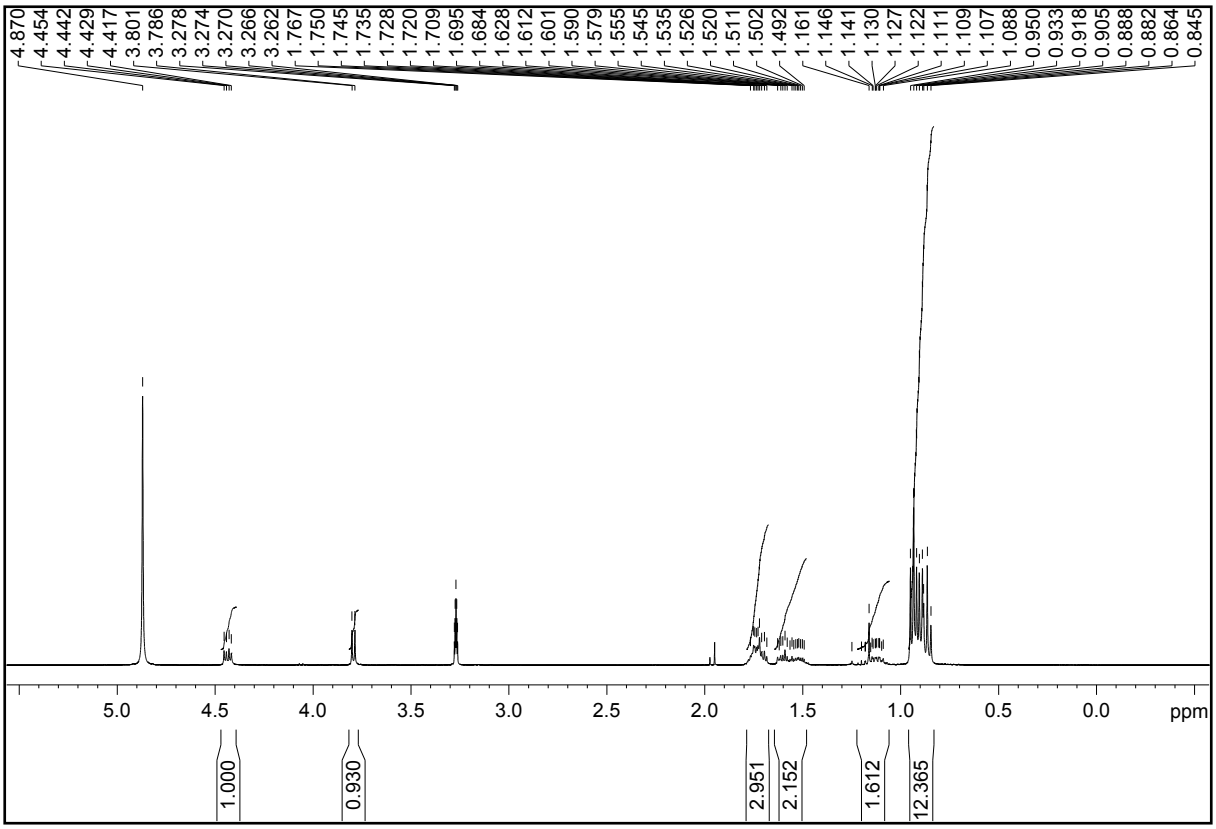


Figure S46. ^{1}H NMR spectrum (400 MHz, CD_3OD) of the compound **7a**.

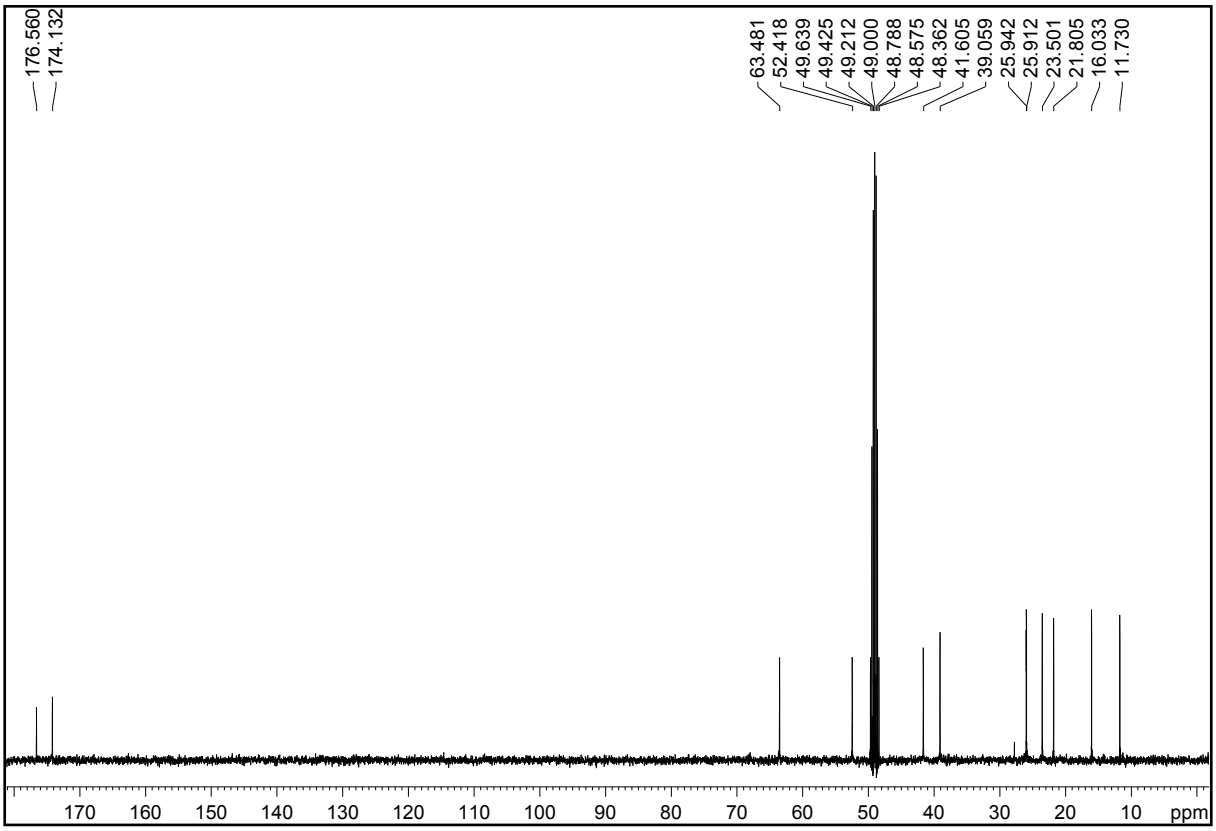


Figure S47. ^{13}C NMR spectrum (100 MHz, CD_3OD) of the compound **7a**

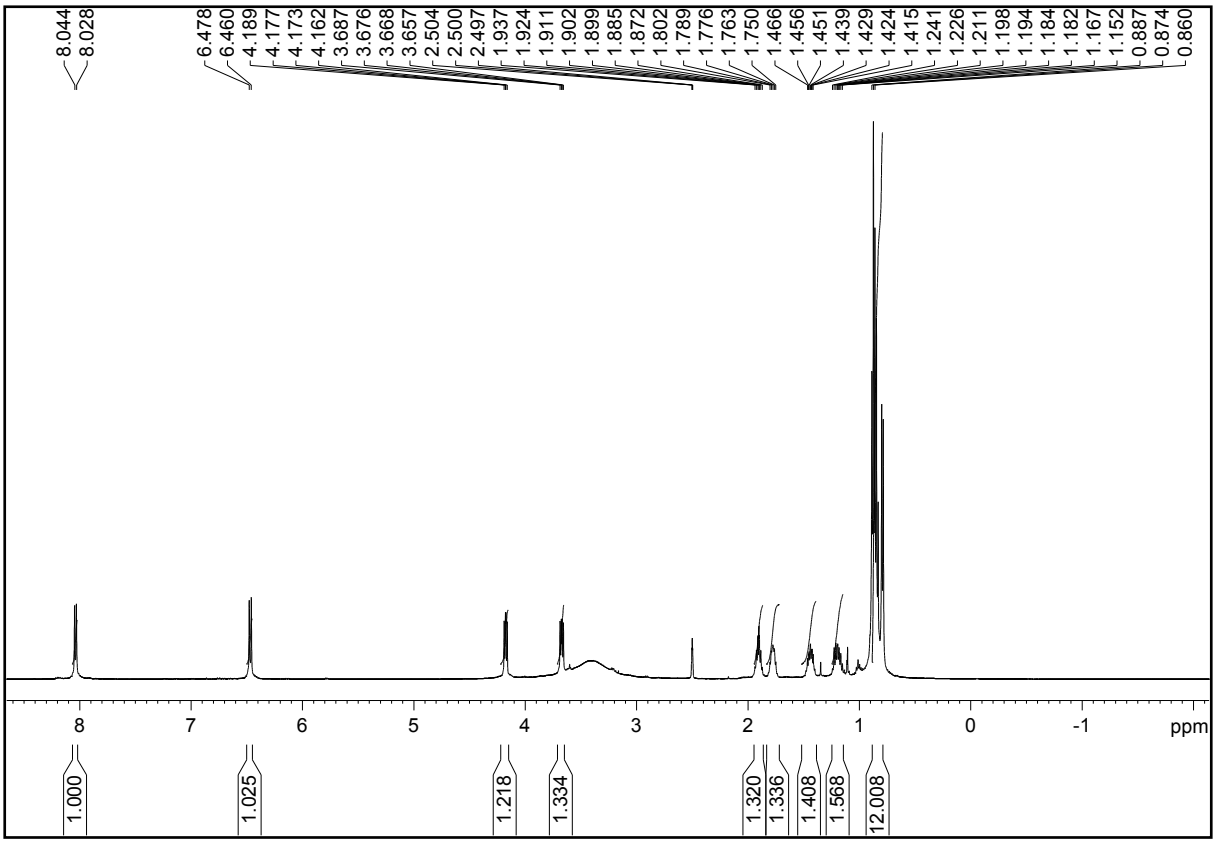


Figure S48. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the compound **8a**.

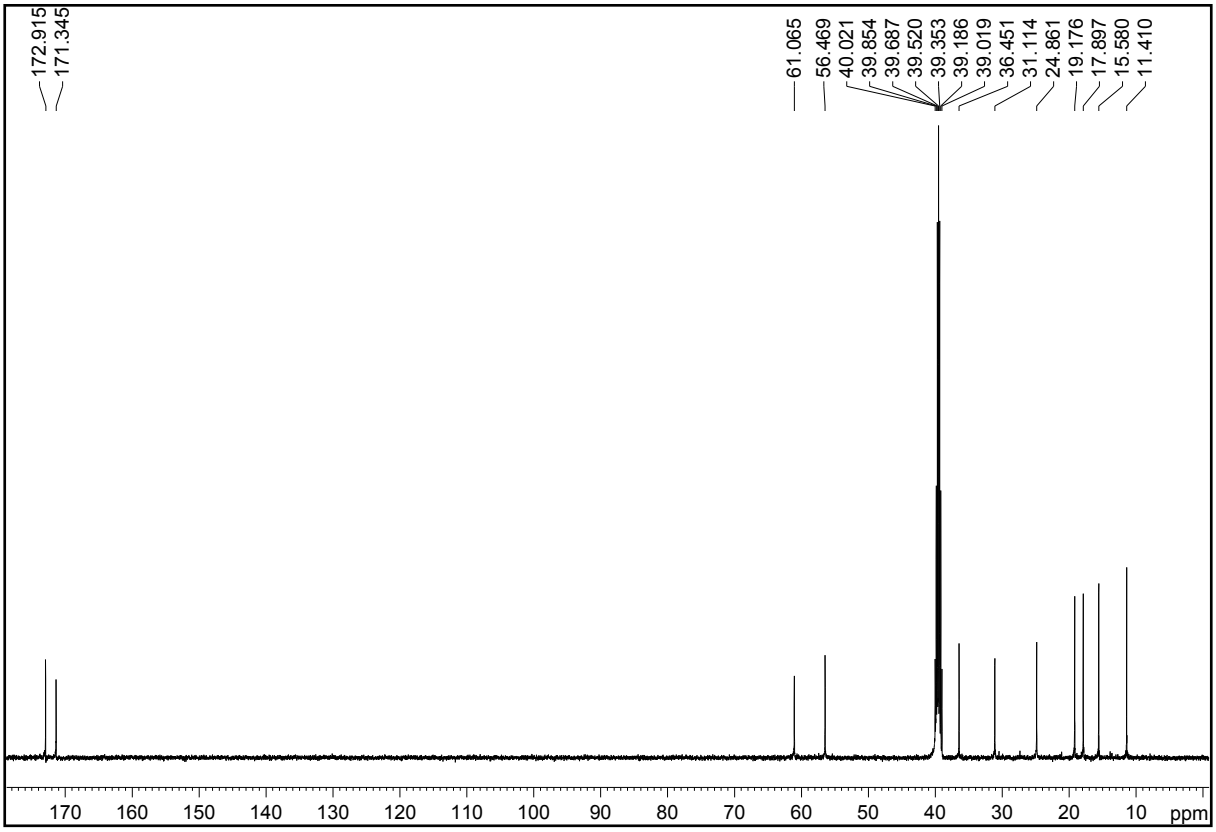


Figure S49. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of the compound **8a**

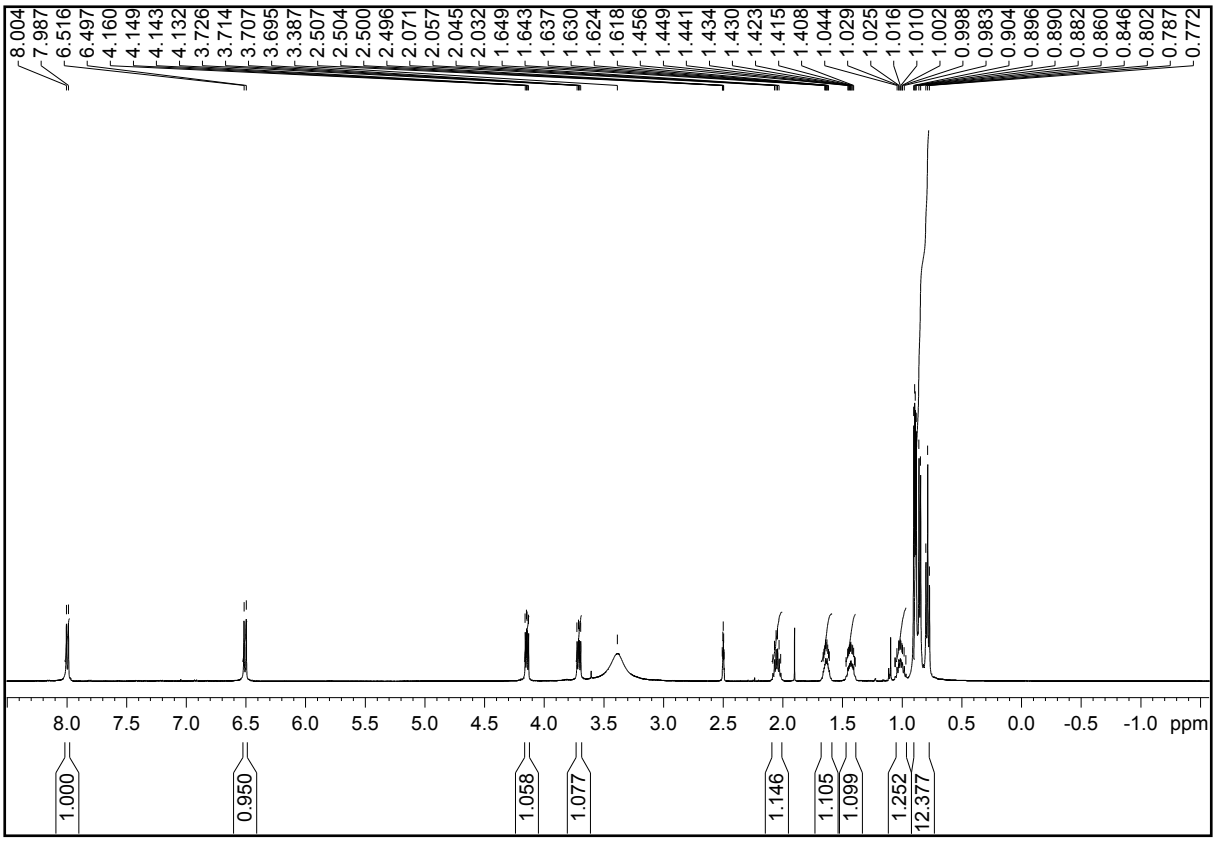


Figure S50. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the compound **9a**.

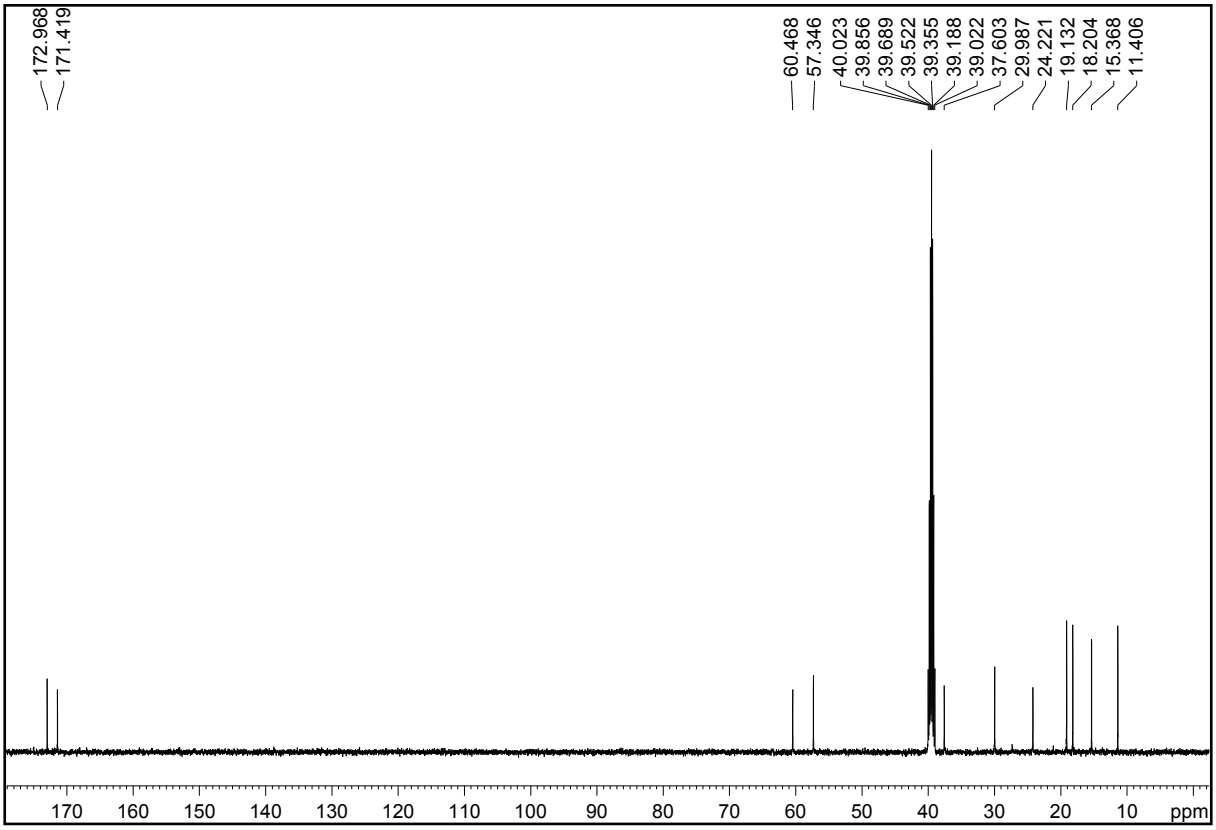


Figure S51. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **9a**.