Electronic Supporting Information
Preferential intermolecular interactions lead to chiral recognition: Enantioselective gel formation and collapsing

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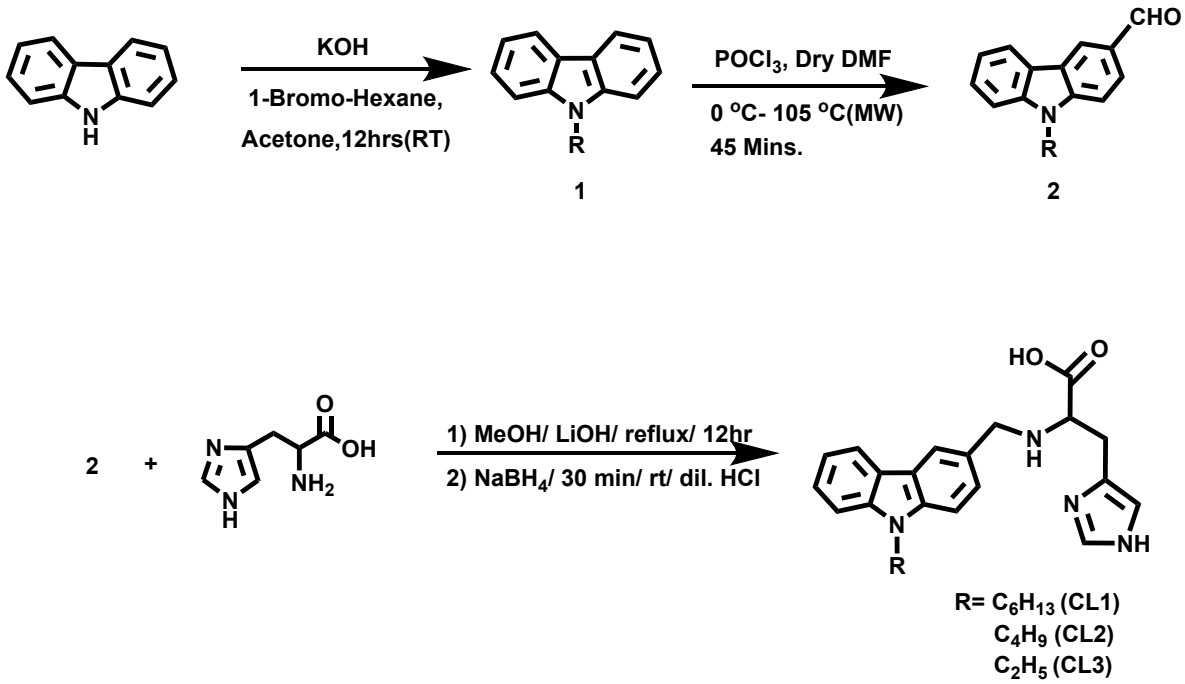
Materials: All chemicals were purchased from Merck, SD Fine, Sigma-Aldrich and Alfa Aesar and were used without further purification. Freshly distilled solvents (n-hexane and ethyl acetate) were used for column chromatography and Merck silica gel (60−120 mesh) was used as stationary phase. Merck silica gel 60-F-254 plates were used for TLC. Nitrate salt of Zn^{2+} was used for metallogel formation. Metal salts were dissolved in Milli-Q water at pH 7.0.

Instruments: FT-IR spectra were recorded on a Carry-660 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra in $CDCl_3$, methanol-d4 and DMSO-d6 were recorded on a Jeol-ECX-500 MHz spectrometer using tetra methyl silane as an internal standard. HRMS spectra were recorded on a Bruker impact-HD spectrometer. The morphology of the gel was characterized by using a field emission scanning electron microscope (FESEM) FEI Nova Nano SEM-450 and a high resolution transmission electron microscope (HRTEM) FEI Tecnai G2 20 S-twin microscope operating at 200 kV. Jasco – J1500 machine was used for Circular Dichroism spectra measurement. Rheological measurements were performed using a stress-controlled rheometer (Anton Paar Quality Control Rheometer MCR 302 instrument) equipped with stainless steel parallel plates (25 mm diameter, 1 mm gap).

DFT Studies:

The geometries of the ligand (**CL1**), dimer (D1) and its interaction with (R)-MBA, (S)-MBA and Zn(II) were optimized with the help of density functional theory (DFT) using the B3LYP/6-311G(d,p)[1] basis set using the Gaussian 09 suite of programs.[2] Frequency calculations at the same level with the same basis set were carried out to ensure that the geometries correspond to real minima. Gaussview 03 and Chemcraft software were used for visualization purposes.[3]

Synthesis Scheme of CL1 (S1):



Synthesis Procedure of compound 1:

Carbazole (1 eq) was added slowly to a solution of KOH (3.77 eq) in acetone at 0 °C and the mixture was left stirring for 30 mins at room temperature. 1-bromo-hexane (1.5 eq) in acetone was then added drop wise and stirred for 12 h at room temperature. The progress of the reaction was monitored by TLC. After completion of reaction, the organic solvent was removed under vacuum and the crude mixture was extracted with DCM. The organic layer was dried over magnesium sulfate and the volatiles were removed under vacuum. The crude product was collected and purified using column chromatography with hexane. **^{1}H-NMR (500 MHz, $CDCl_3$):** δ 8.10(d, J = 7.76, 2H), 7.48-7.44(m, 2H), 7.41-7.39(m, 2H), 7.24-7.34(m, 2H), 4.29(t, J = 8.04, 2H), 1.89-1.82(m, 2H), 1.39-1.26(m, 6H), 0.85(t, J = 6.7 Hz, 3H) ppm. **^{13}C-NMR (125 MHz, $CDCl_3$)**: δ 140, 125.53, 122.75, 120.32, 118.64, 108.62, 43.06, 31.59, 28.93, 26.98, 22.55, 14.03 ppm.

Formylation of alkylated carbazole (2)

Alkylated product **1** (1 eq) was dissolved in dry DMF at 0 °C. Following that, phosphorus oxychloride (1.5 eq) was added in the solution with vigorous stirring at 0 °C under nitrogen atmosphere. Then the reaction mixture was allowed to come to room temperature and left stirring for 20 min followed by microwave heating (P = 10, T = 105 °C) for 45 mins. The resulting mixture was then was cooled to room temperature and extracted with ethyl acetate and water. The organic layer was collected and dried over anhydrous sodium sulfate. The volatiles were removed under vacuum, the crude product was purified using column chromatography with EtOAc: Hexane (5:95).**^{1}H-NMR (500 MHz, CDCl$_3$):** δ 10.08 (s, 1H), 8.59 (d, J= 1.4 Hz, 1H), 8.15 (d, J= 5 Hz, 1H), 8.00 (dd, J= 1.4 and 8.2 Hz, 1H), 7.54-7.51 (m, 1H), 7.46-7.43 (m, 2H), 7.33-7.25 (m, 1H), 4.31 (t, J= 7.5 Hz, 2H), 1.90-1.84 (m, 2H), 1.40-1.25 (m, 6H), 0.85 (t, J= 7.5 Hz, 3H) ppm. **^{13}C-NMR (125 MHz, CDCl$_3$)**: δ 191.7, 144.0, 141.1, 128.4, 127.1, 126.6, 124.0, 123.0, 122.9, 120.7, 120.2, 109.3, 108.9, 43.4, 31.4, 28.8, 26.8, 22.4, 14.0 ppm.

Synthesis Procedure of CL1

A methanolic solution of **2** (1 eq) was added dropwise to a stirred mixture of L-histidine (1.5 eq) and LiOH·H_2O (1.5 eq) in methanol (10 mL). Then, the resulting mixture was refluxed at 80 °C for 12 h to produce a bright yellow color solution. After that, the solution was treated with sodium borohydride (4 eq) with constant stirring at room temperature for 1 h. The solvent was evaporated after completion of the reaction using a rotary evaporator. The resulting sticky residue was dissolved in water and acidified with dil. HCl to pH 5−6 under stirring. The white precipitate formed was filtered off through a sintered funnel and washed with water (20 mL) and air-dried for 1 h, and the crude product was purified by column chromatography on silica gel dichloromethane−methanol (1:9) to afford a light yellow solid as ligand (**CL1**) Yield= 65%. **^{1}H-NMR (500 MHz,**

methanol- *d*$_4$): δ :8.16 (s, 1H), 8.07 (d, J= 8.2 Hz, 1H), 7.80 (s,1H), 7.48-7.43 (m, 4H), 7.19 (t, J= 7.5 Hz, 1H), 7.00 (s, 1H), 4.40 (dd, J= 3.4 and 13.0 Hz, 1H), 4.32-4.28 (m, 3H), 3.81 (t, J= 6.8 Hz, 1H), 3.26-3.22 (m, 1H), 3.16-3.11 (m, 1H), 1.8 (s, 2H), 1.27-1.18 (m, 6H), .080 (t, J= 7.5 Hz, 3H) ppm.**^{13}C-NMR (125 MHz, methanol- *d*$_4$)**: δ 172.8, 142.4, 142.2, 136.4, 134.7, 128.4, 127.4, 124.5, 123.7, 123.2, 122.8, 121.4, 120.4, 117.2, 110.6, 110.4, 62.9, 52.0, 43.9, 32.8, 30.1, 28.3, 28.0, 23.7, 14.4 ppm. **HRMS**, m/z calculated for $C_{25}H_{30}N_4O_2$ $[M-H]^+$: 417.2369. Found: 417.2399.

Synthesis Procedure CD1:

This was synthesized following the same procedure as described for **CL1** starting with D-histidine. Yield= 62%. **^{1}H-NMR (500 MHz, methanol- *d*$_4$):** δ : 8.69 (s, 1H), 8.23 (s, 1H), 8.10 (d, J= 8.2 Hz, 1H), 7.55 (s, 2H), 7.52-7.46 (m, 2H), 7.36 (s, 1H), 7.22 (t, J= 6.8 Hz, 1H), 4.47 (d, J= 13.1 Hz, 1H), 4.37 (t, J= 6.2 Hz, 3H), 3.38-3.30 (m, 2H), 3.34-3.32 (m, 1H), 1.84-.81 (m, 2H), 1.31-1.21 (m, 6H), 0.82 (t, J= 7.0 Hz, 3H) ppm. **^{13}C-NMR (125 MHz, methanol- *d*$_4$)**: δ 142.4, 142.3, 135.4, 130.3, 128.6, 127.5, 124.6, 123.7, 123.5, 122.4, 121.4, 120.5, 118.8, 110.7, 110.5, 61.1, 52.4, 44.0, 32.8, 30.1, 28.0, 26.7, 23.7, 14.4.

Synthesis Procedure CL2 and CL3:

Ligand with alkyl chain C_4H_9 and C_2H_5 were prepared in a similar way as reported for **CL1** using 1-bromo butane and 1-bromo ethane respectively for alkylation. The remaining procedure remained the same.

Gelation Study of CL1 and CD1:

Initially, 2μL (0.082 x 10^{-3} M) of amine was added to 200 μL of water. Then, 5mg (0.06M) of **CL1/CD1** was added to that solution which was kept at room temperature. The gelation was

confirmed by “inversion method”. The same procedure was followed for (R/S)-cyclohexylethylamines.

Gelation with (R/S)-4-Methoxy-α-methylbenzylamine: To form gel, **CL1/CD1** was first dissolved in min. amount of MeOH and then amine was added followed by dropwise addition of water. The concentration of both ligand and amine were kept constant.

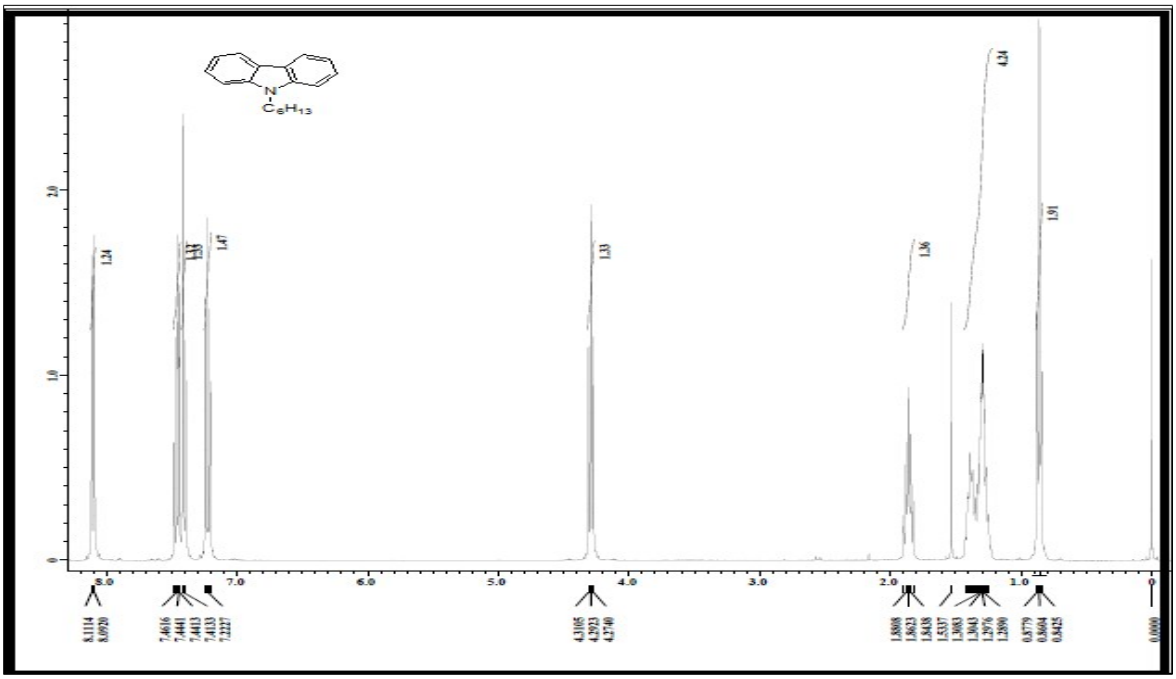


Fig. S1: ^{1}H NMR spectra of compound **1**.

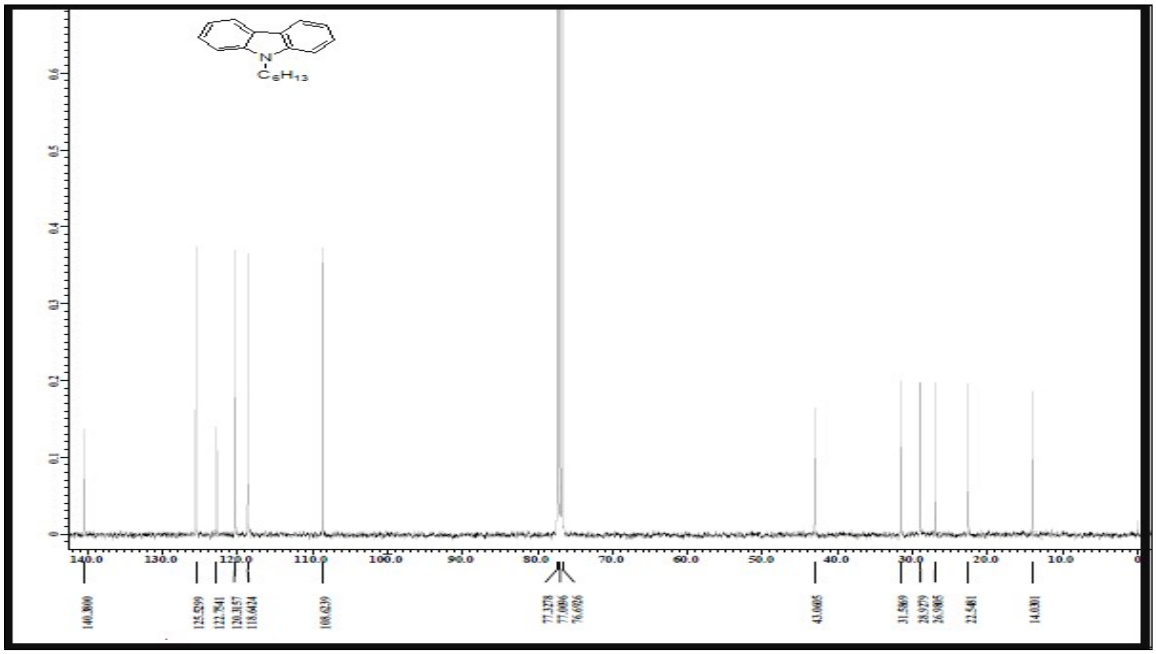


Fig. S2: ^{13}C NMR spectra of compound **1.**

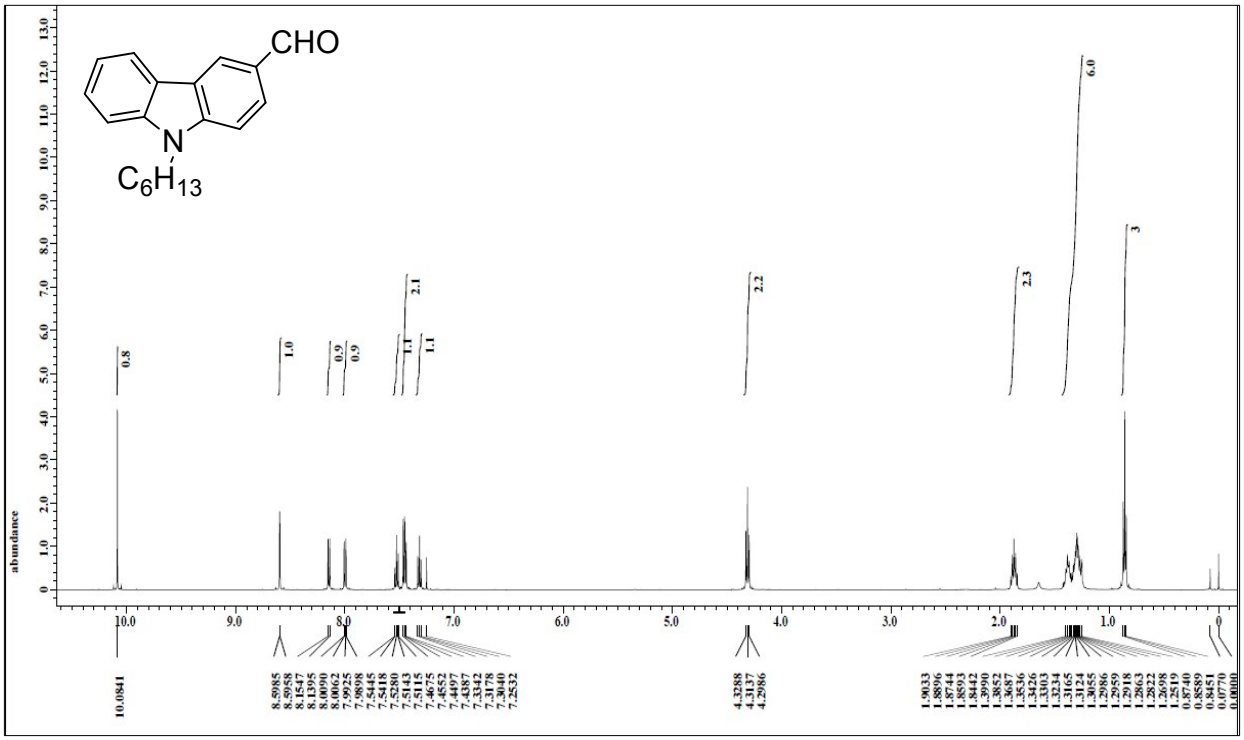
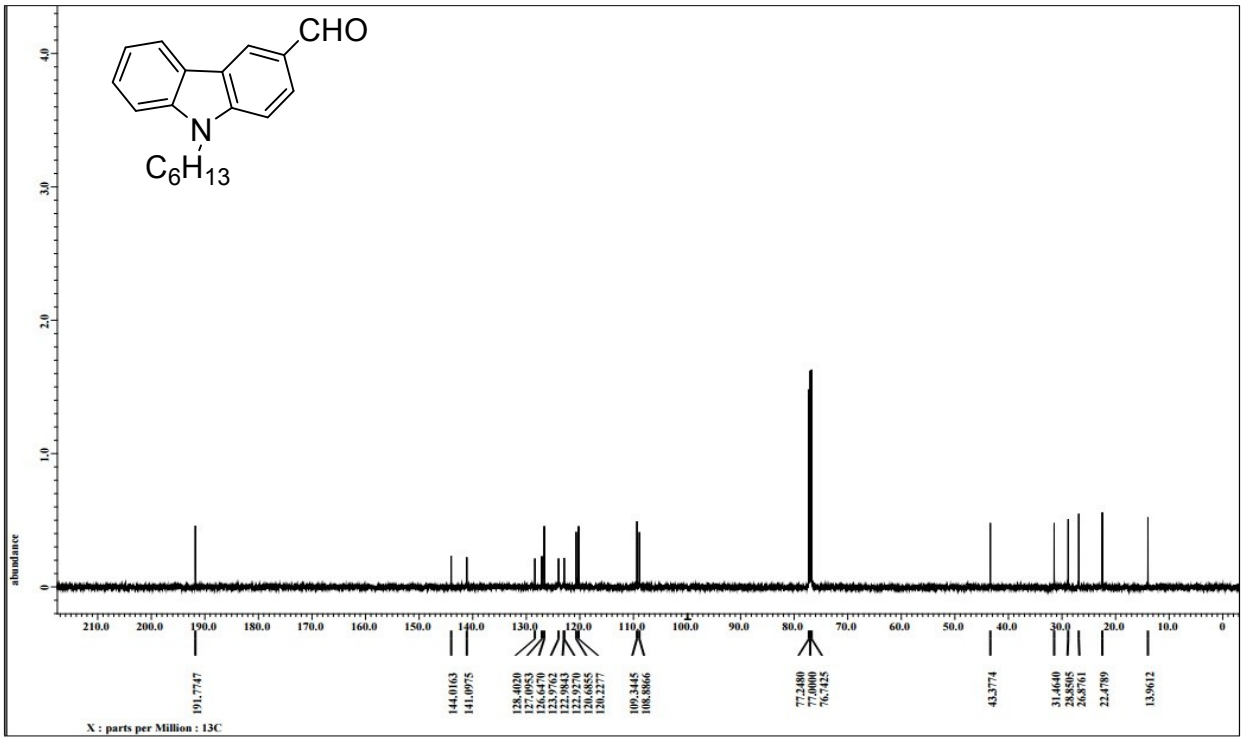


Fig. S3: ^{1}H NMR spectra of compound **2.**



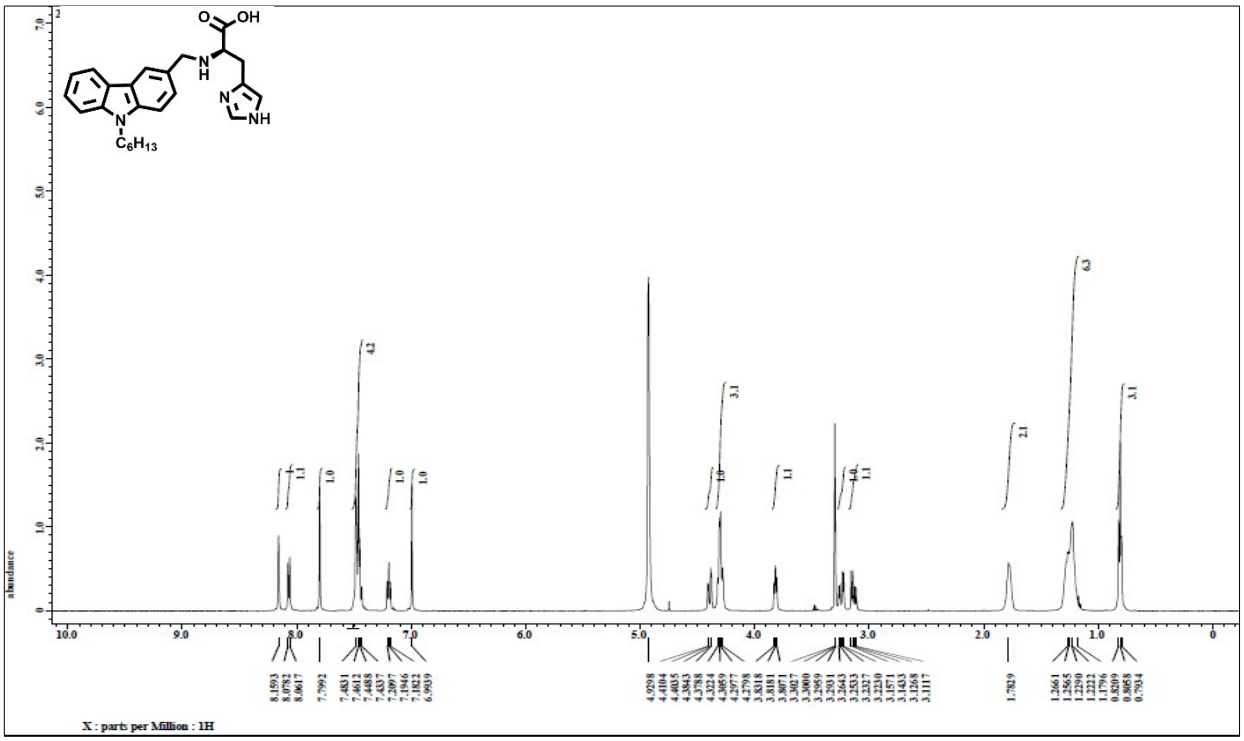


Fig. S5: ^{1}H NMR spectra of compound **CL1.**

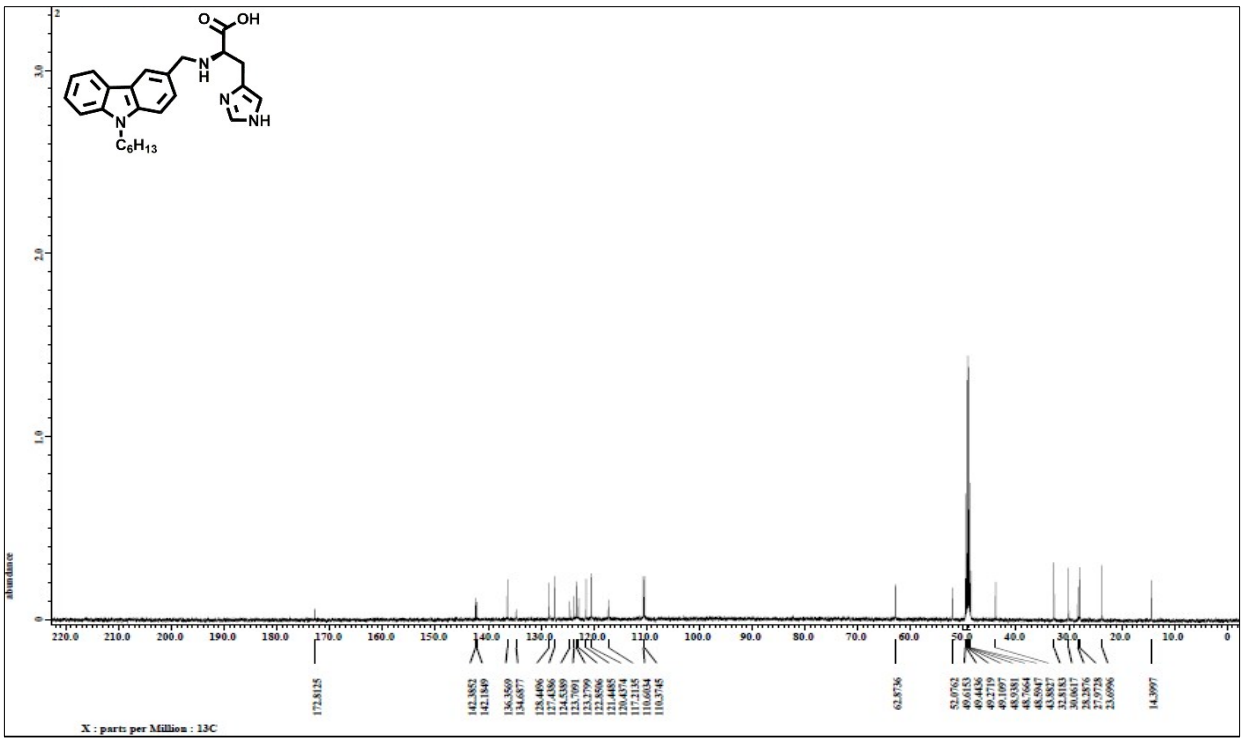


Fig. S6: ^{13}C NMR spectra of compound **CL1.**

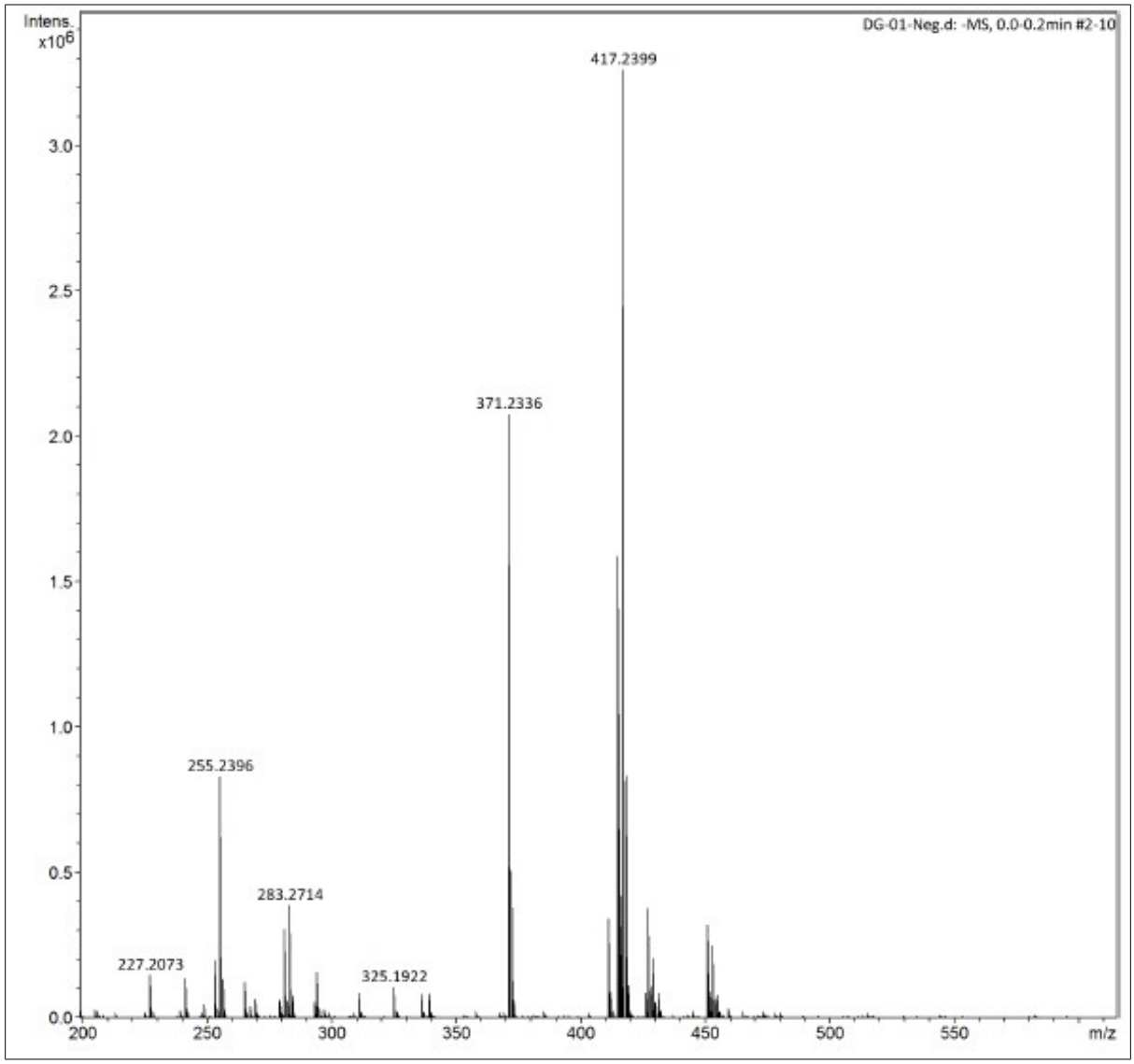


Fig. S7: HRMS spectra of compound **CL1.**

Fig. S8: Formation of gel with **CL1**:(R)-MBA (a) 1.5:1, (b) 2:1, (c) 1:1.5 and (d) 2:1

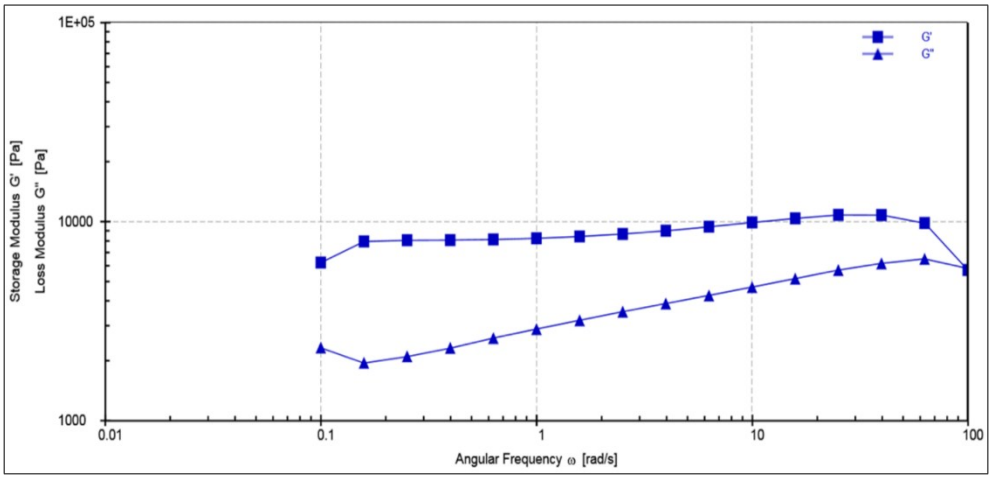


Fig S9: Angular Frequency sweep measurements of the hydrogel with **CL1** and (R)-MBA.

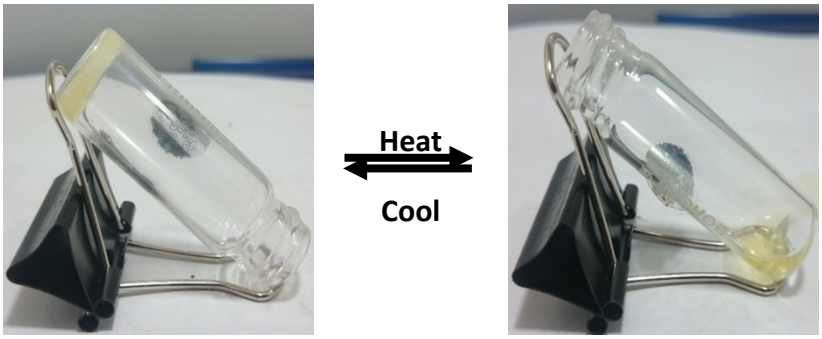


Fig. S10: Gel to sol transition in response to temperature

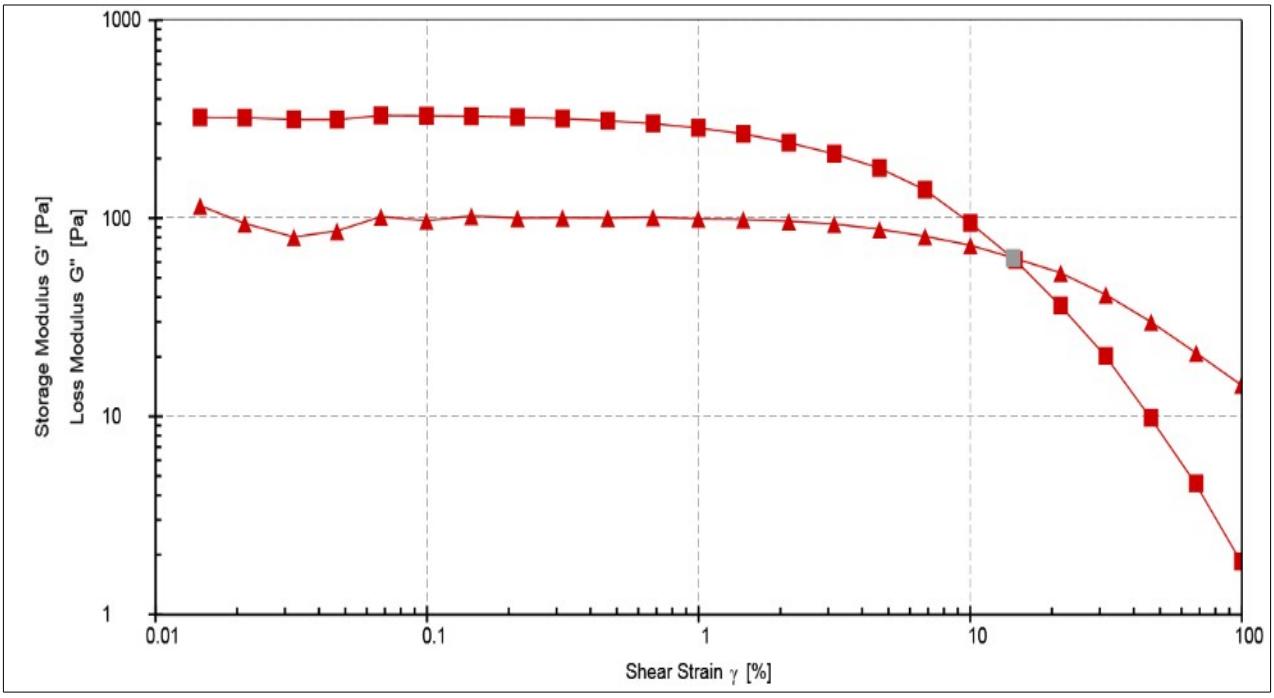


Fig S11: Angular Frequency sweep measurements of the hydrogel with **CL1** and (R)-MBA.

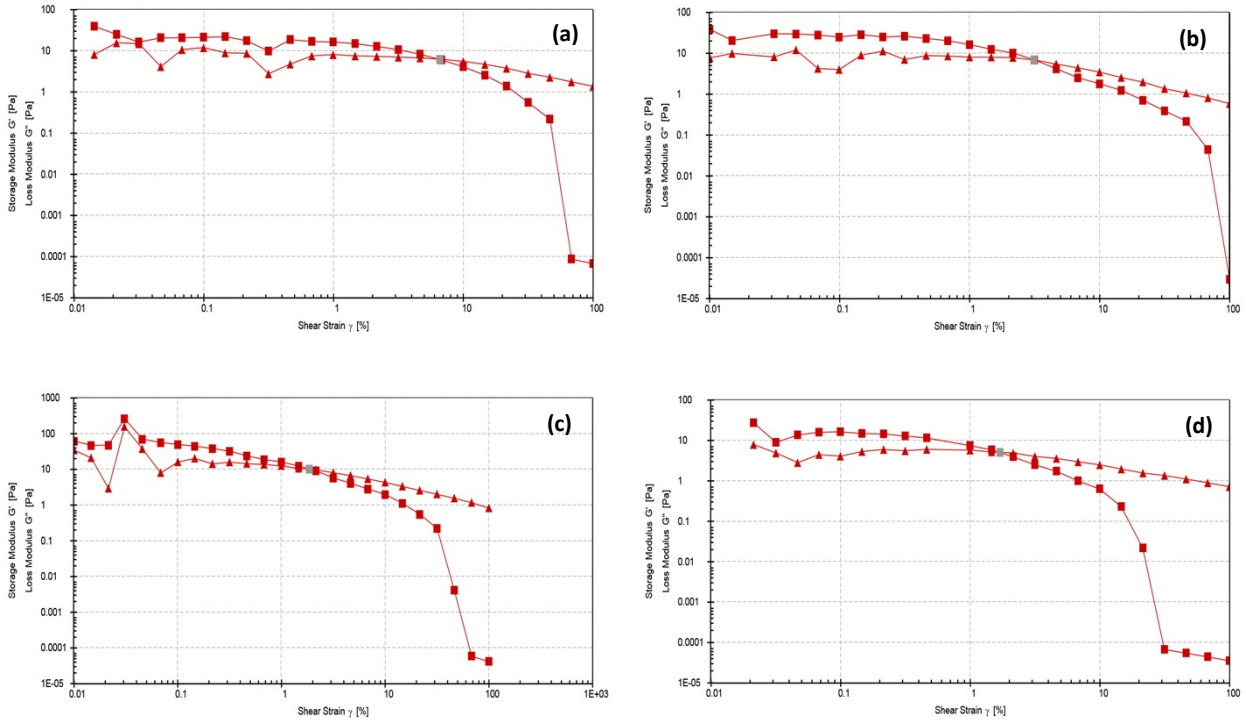


Fig. S12: Amplitude sweep measurements of thermoreversible gels after (a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle and (d) 4th cycle.

Thermoreversible cycle	**γ (%)**
Original gel	14.414
1st cycle	6.5875
2nd cycle	3.1335
3rd cycle	1.8589
4th cycle	1.6943

Table S1: Thermoreversible cycles and its mechanical strength.

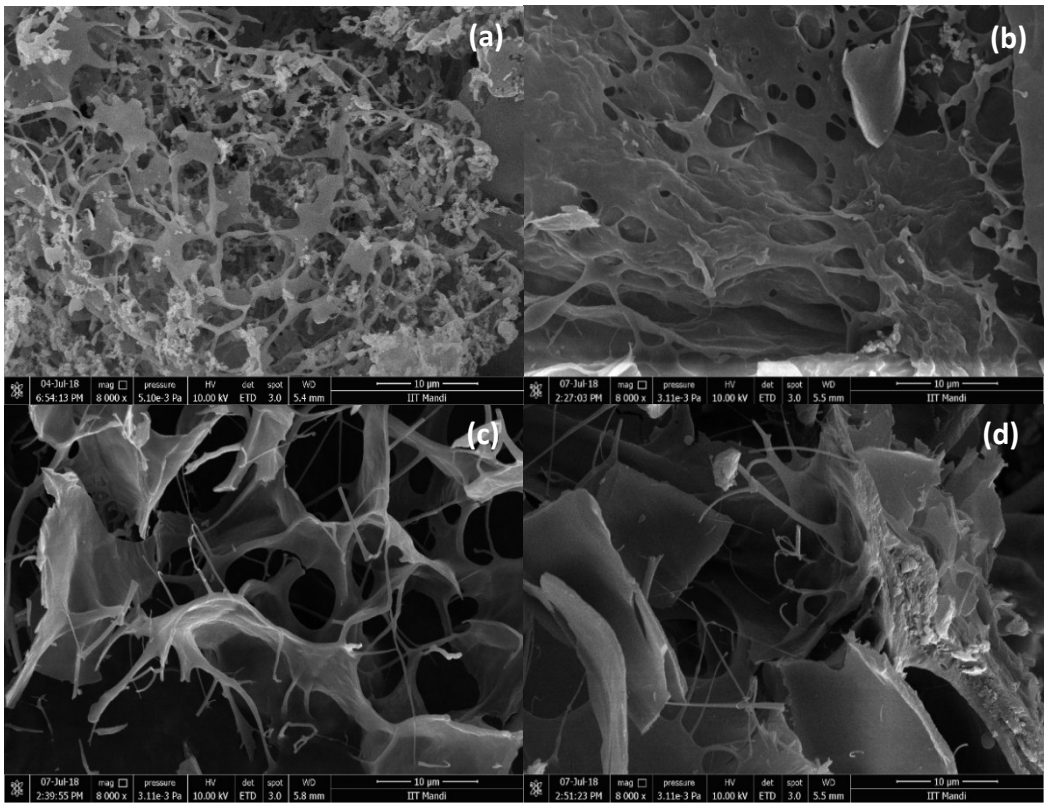


Fig. S13: SEM images of thermoreversible gels after (a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle and (d) 4th cycle.

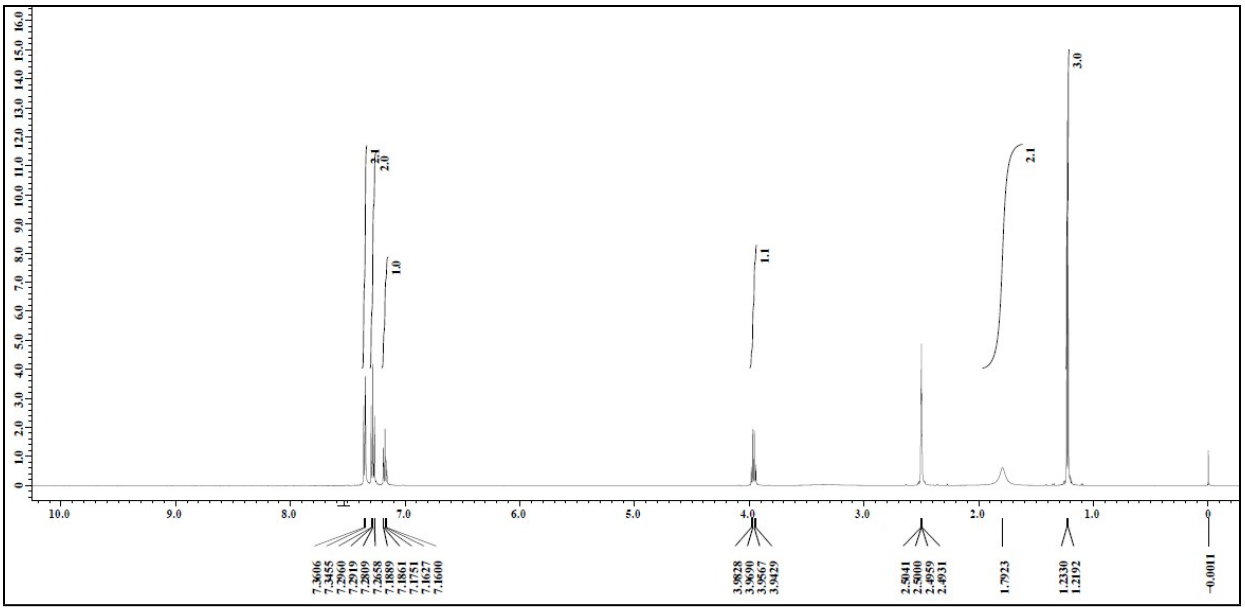


Fig. S14: ^{1}H NMR spectra of (R)-MBA.

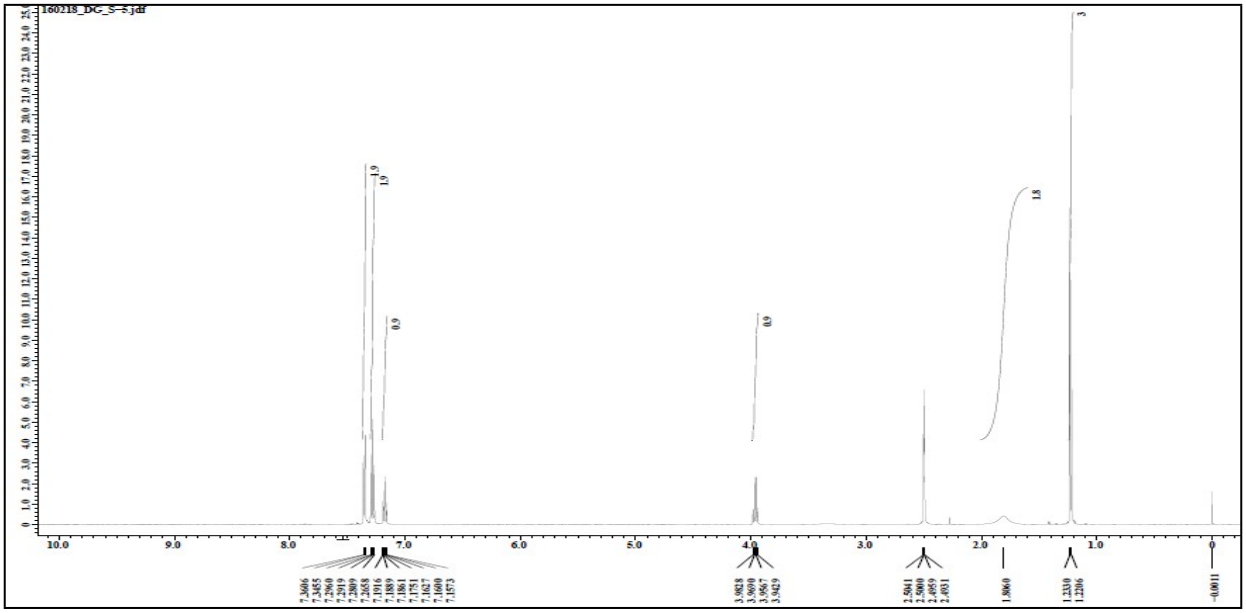


Fig. S15: ^{1}H NMR spectra of (S)-MBA.

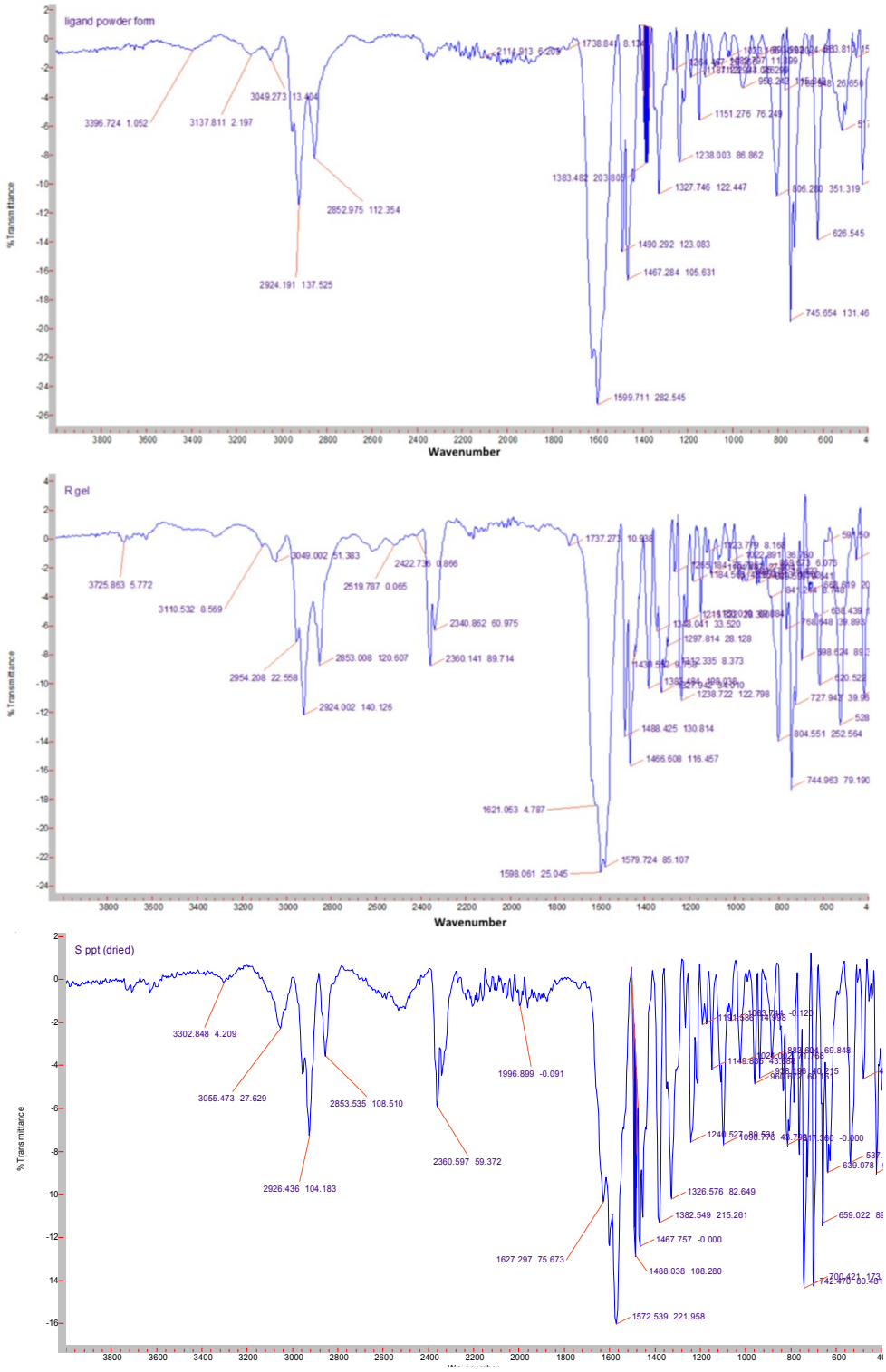


Fig. S16: FTIR spectra of CL1, xerogel with (R)-MBA and precipitate with (S)-MBA

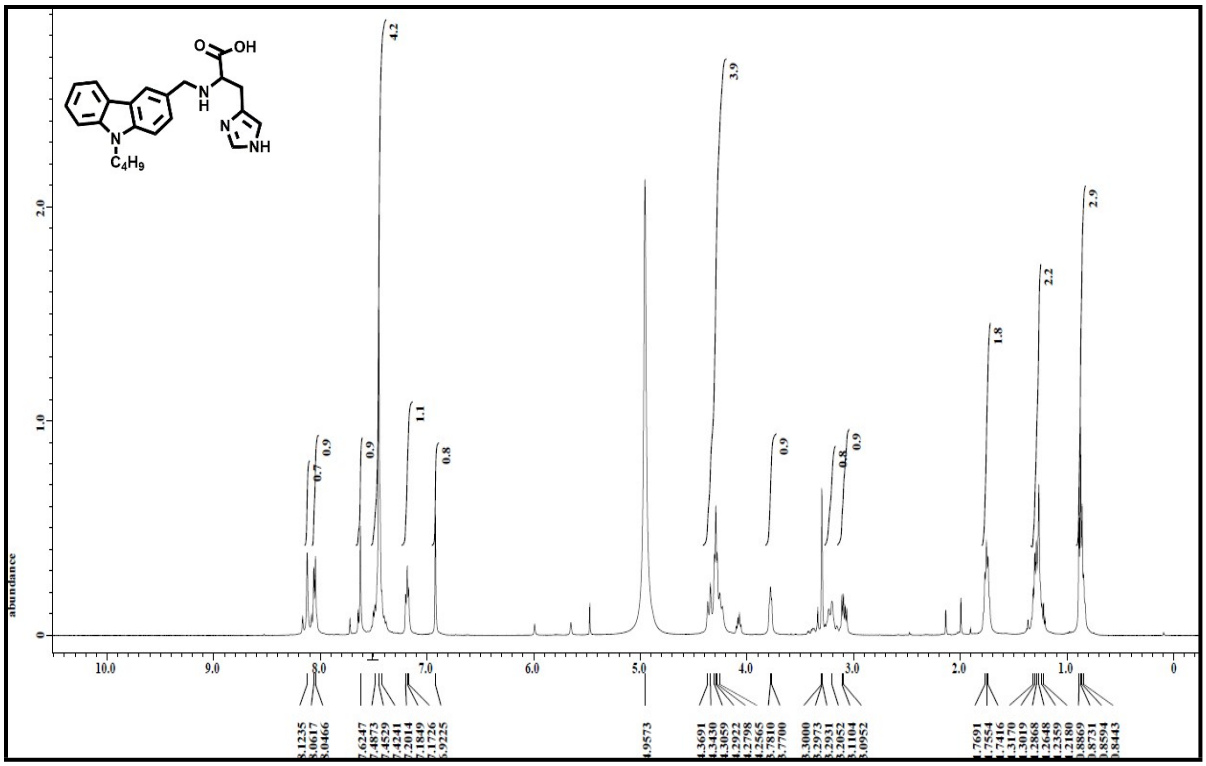


Fig. S17: ^{1}H NMR spectra of **CL2.**

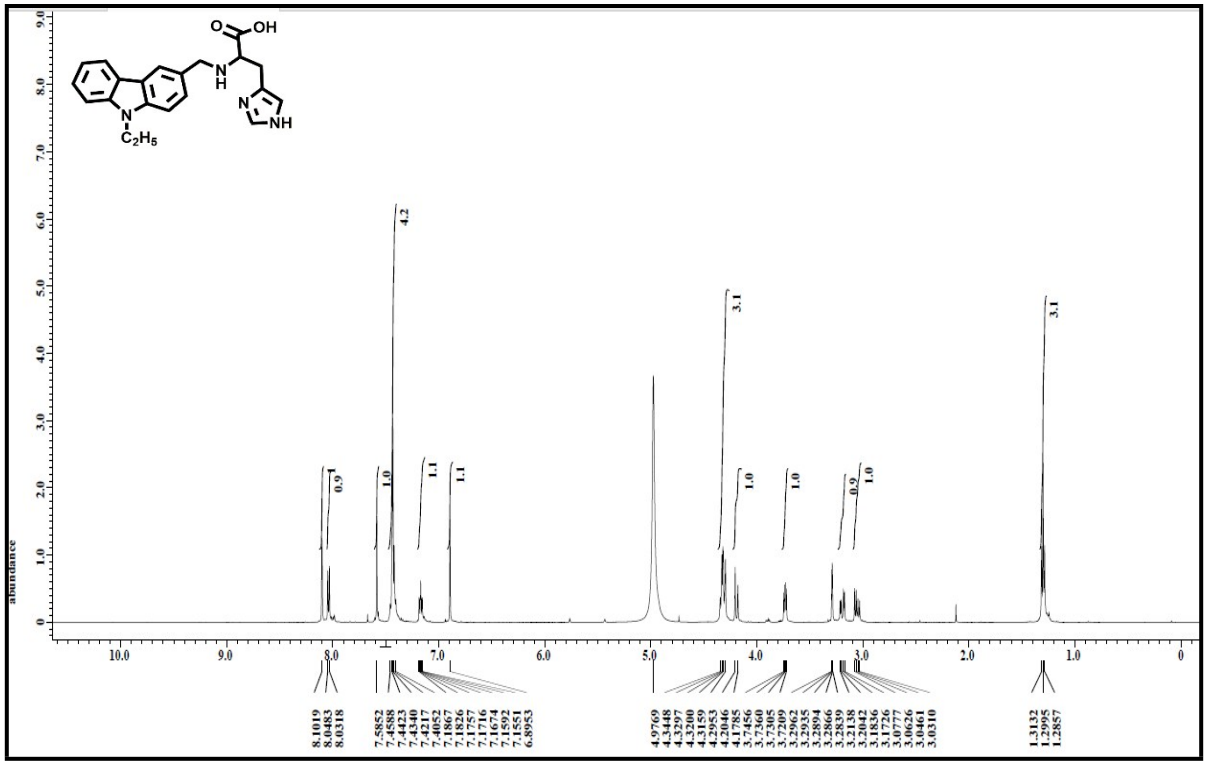


Fig. S18: ^{1}H NMR spectra of **CL3.**

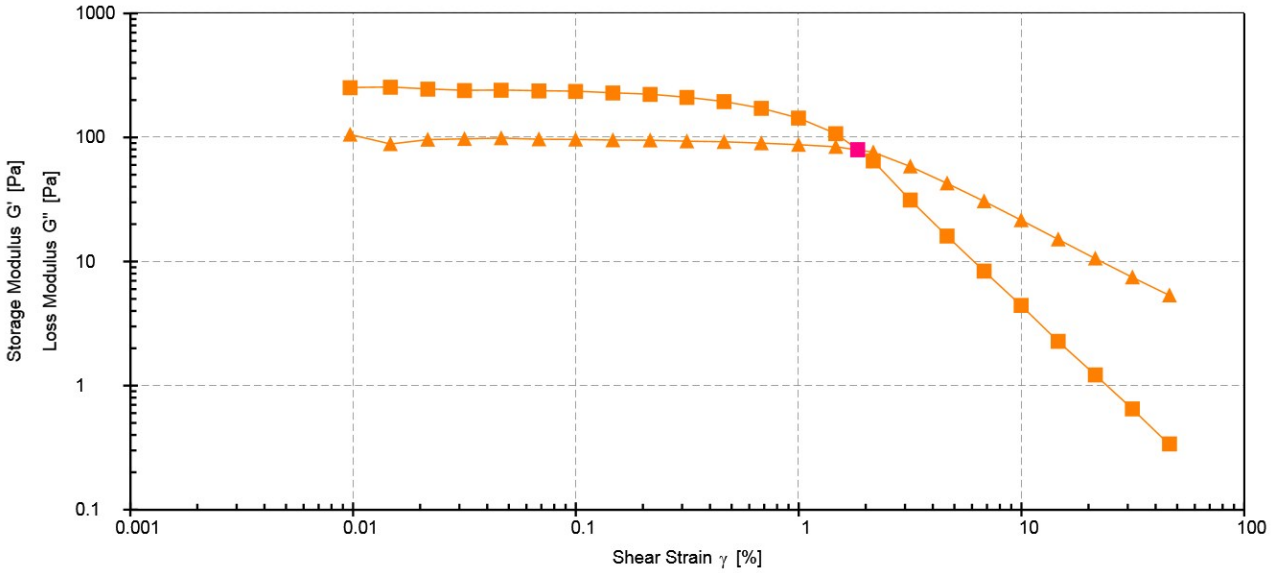


Fig S19: Angular Frequency sweep measurements of the hydrogel with **CL2** and (R)-MBA (γ (%) = 1.8418).

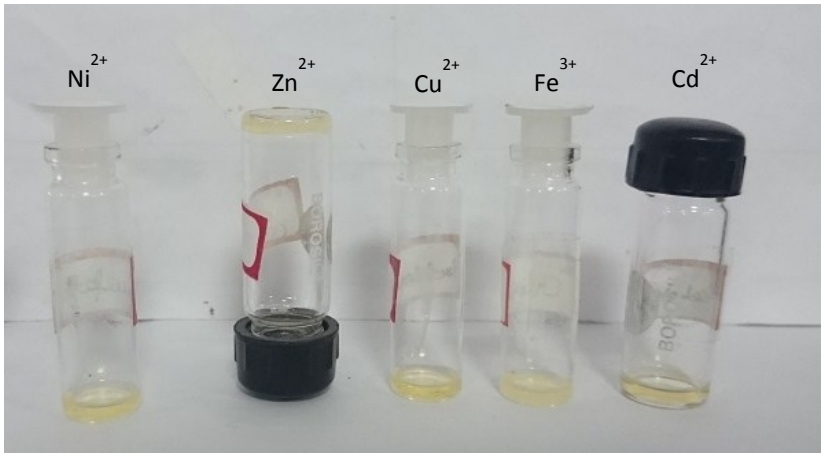


Fig. S20: Photograph of **CL1** forming gel with Zn^{2+} and solution with other bivalent metal ions

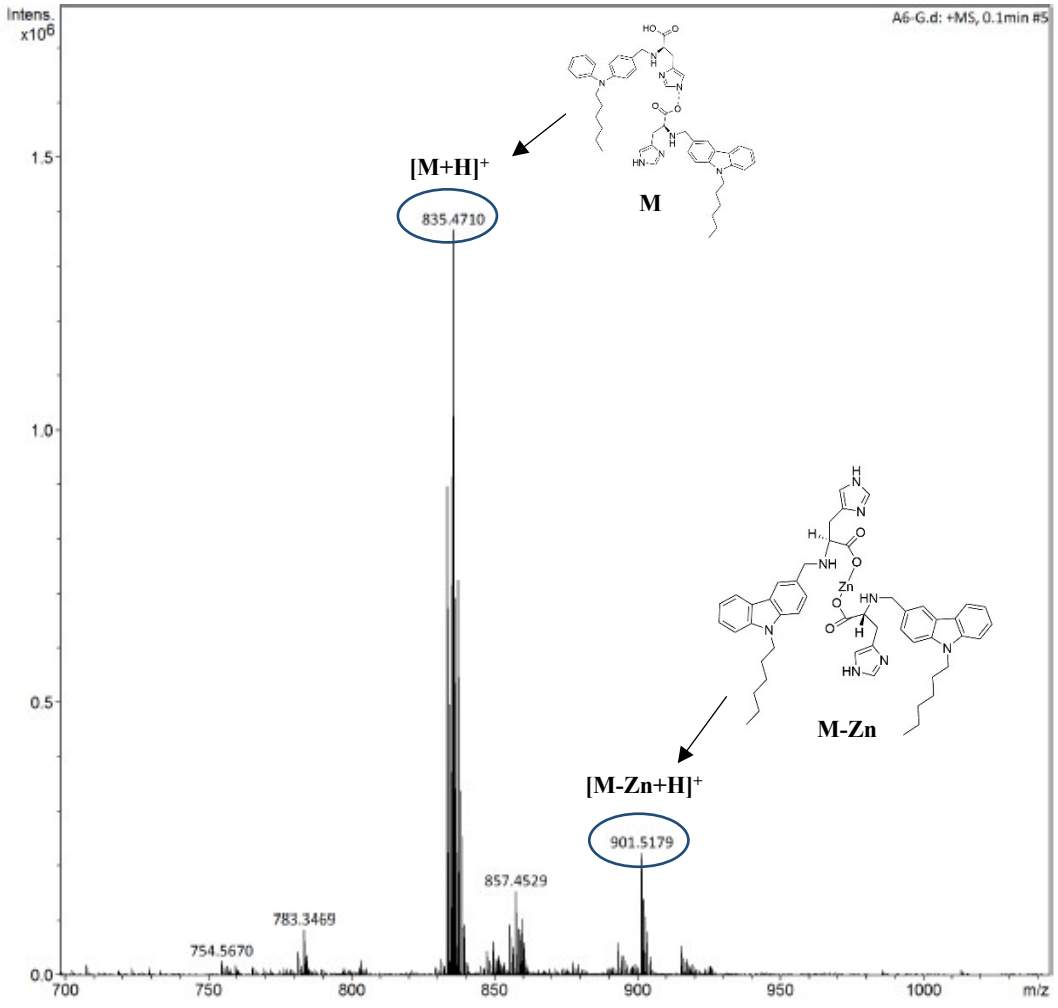


Fig. S21: HRMS spectra of Zn metallogel**.**

Ratio	**Outcome (Yield stress γ (%))**
Pure R	Gel (14.414)
90:10	Gel (4.7418)
80:20	Gel (4.556)
70:30	Gel (3.6896)
60:40	Gel (2.8644)
50:50	Gel (1.0105)
40:60	Precipitates
30:70	Precipitates
20:80	Precipitates
10:90	Precipitates
Pure S	Precipitates

Table S2: Different ratio of chiral amines and its outcome

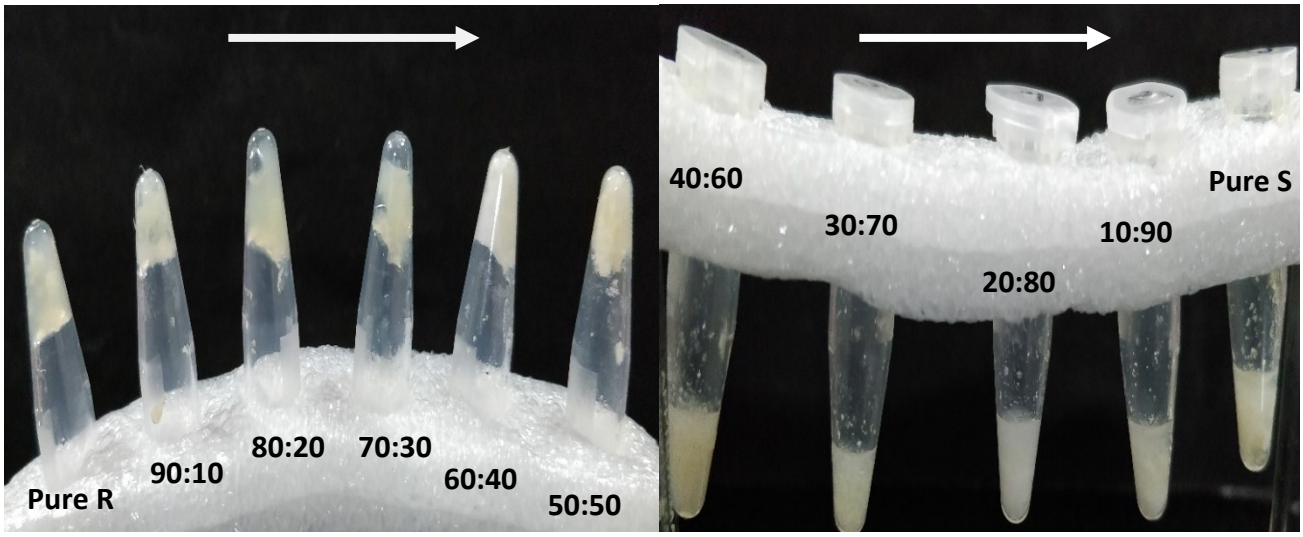


Fig S22: Photograph of gel or precipiates formed with different ratios of (R)-MBA and (S)-MBA.

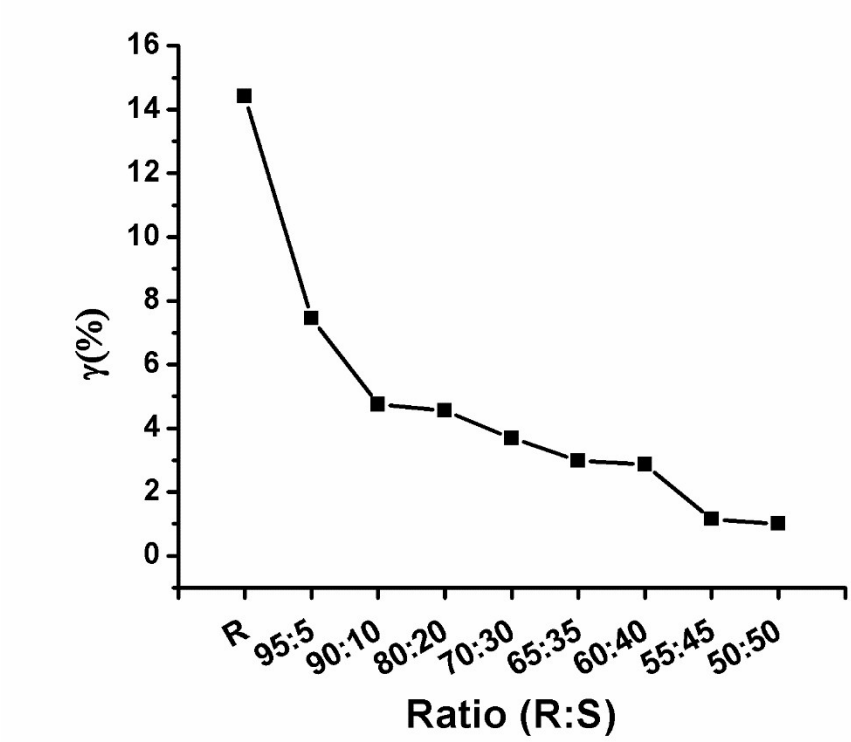


Fig. S23: Graph between different ratios of (R)-MBA : (S):MBA v/s yield strength.

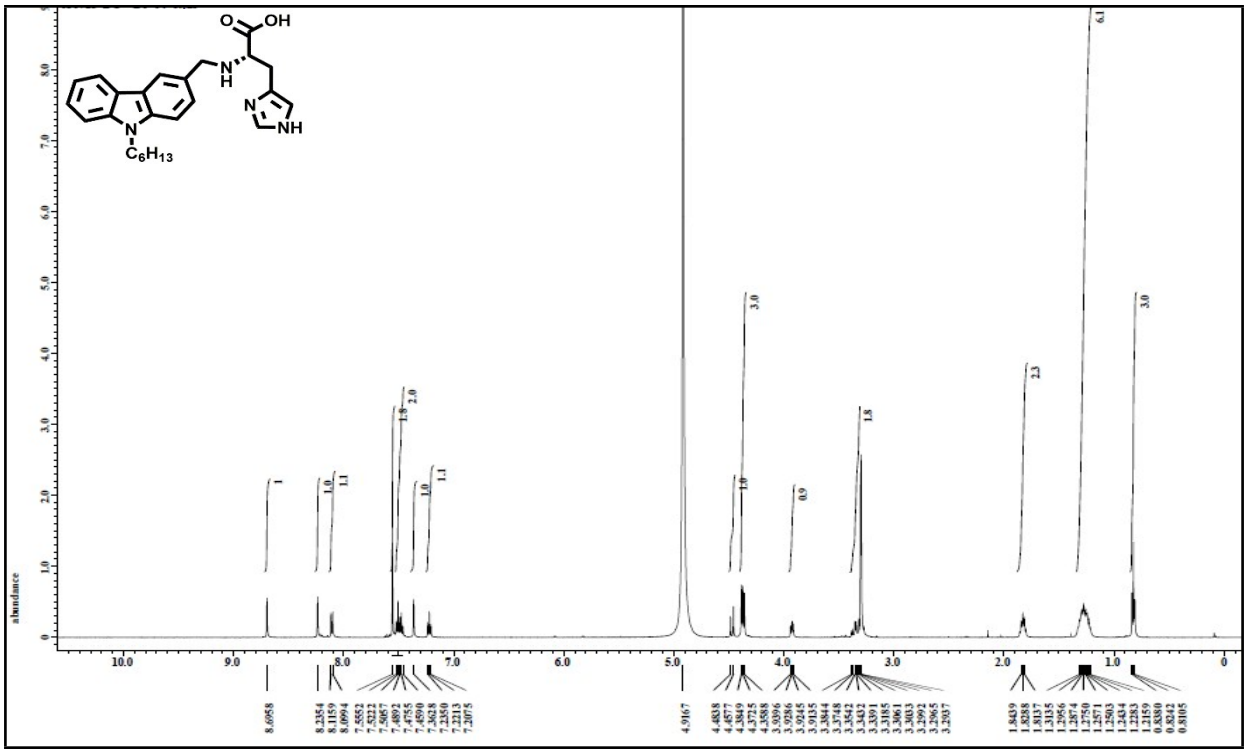


Fig. S24: ^{1}H NMR spectra of compound **CD1.**

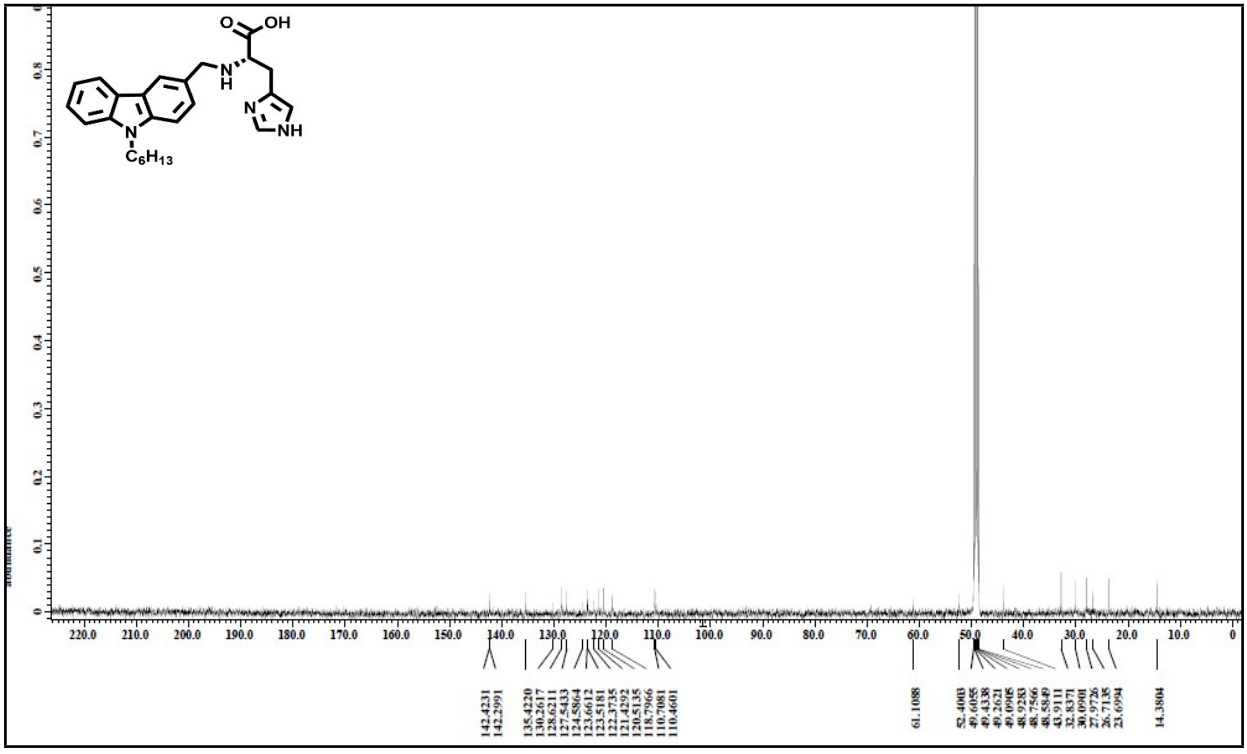


Fig. S25: ^{13}C NMR spectra of compound **CD1.**

Fig. S26: Photograph of (a) gel formed between **CD1** and (S)-MBA and (b) precipitates formed between **CD1** and (R)-MBA.

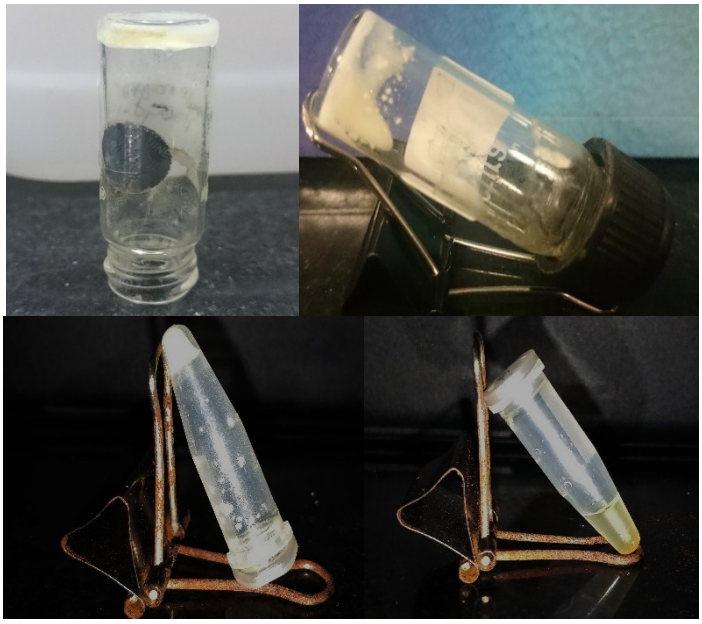


Fig S27: Photograph of (a) gel formed in presence of (R)-cyclohexylamine, (b) precipitates formed in presence of (S)-cyclohexylamine, (c) gel formed in presence of (R)-4-Methoxy-α-methylbenzylamine and (d) solution in presence of (S)-4-Methoxy-α-methylbenzylamine

References:

1 (a) A. D. Becke, *The Journal of chemical physics*, 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Physical review B*, 1988, **37**, 785.

2 R. A. Gaussian09, *Inc., Wallingford CT*, 2009.

3 R. Dennington, T. Keith and J. Millam, 2009.