SUPPORTING INFORMATION

Experimental Correlation between Apparent pKa and Gelation Propensity in Amphiphilic Hydrogelators Derived from L-Dopa

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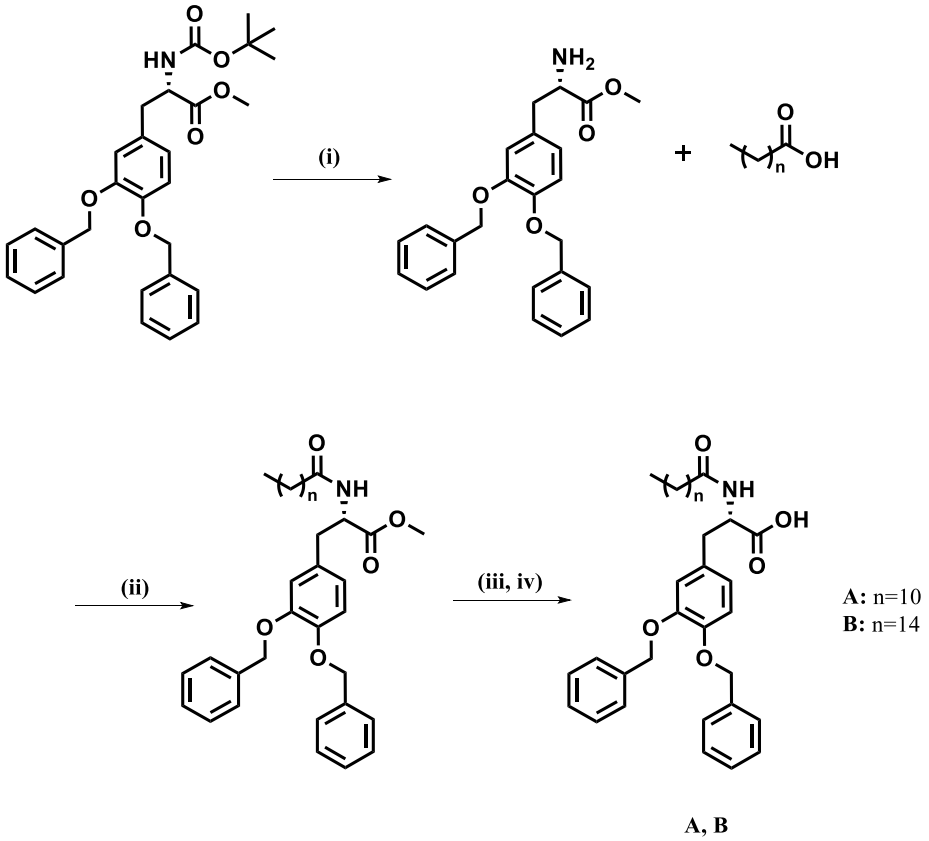
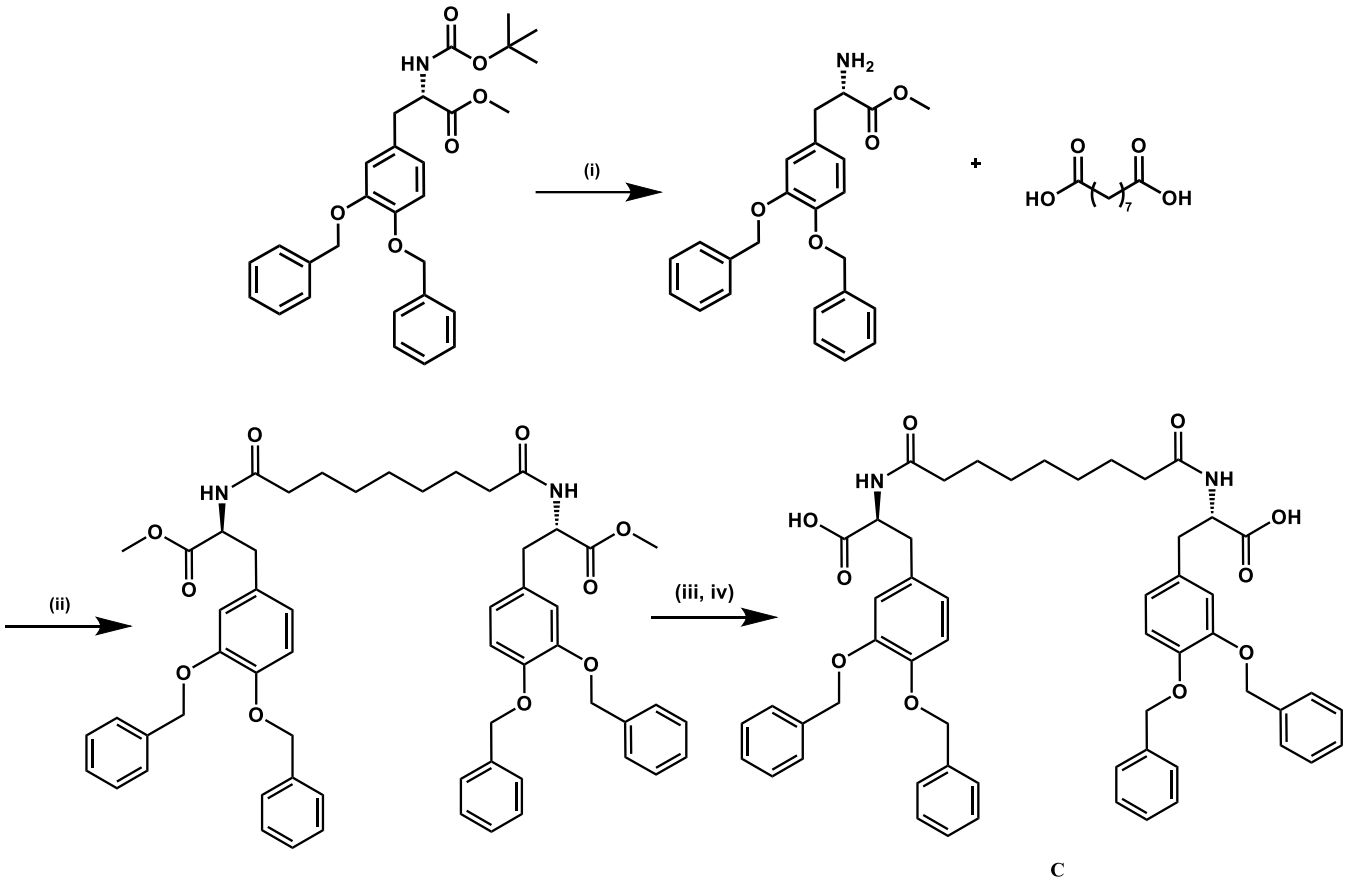
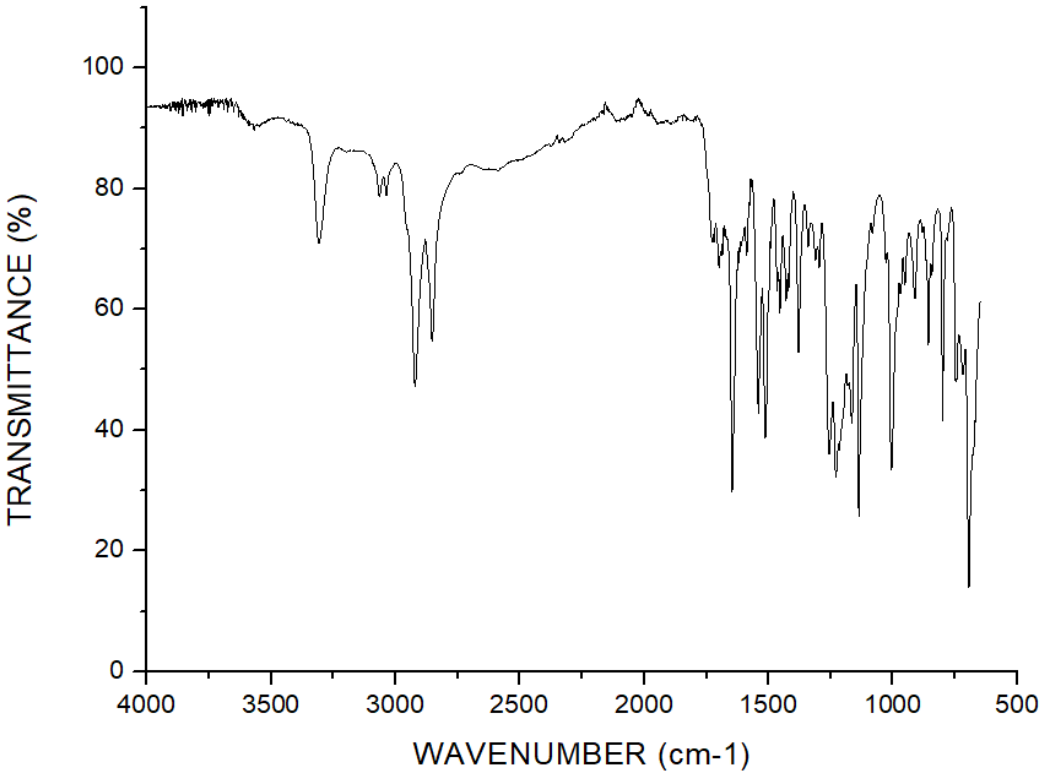


Scheme S1. Reagents and conditions: (i) TFA (18 equiv.), dry CH_2Cl_2, r.t., 4 h; (ii) fatty acid (n=10, n=14) (1 equiv.), HBTU (1.1 equiv.), DIEA (2.1 equiv.), dry ACN, r.t., 4 h; (iii) 1M NaOH (1.25 equiv.), MeOH/THF, r.t., 18 h; (iv) 1M HCl (1.35 equiv.), r.t., 10 min.

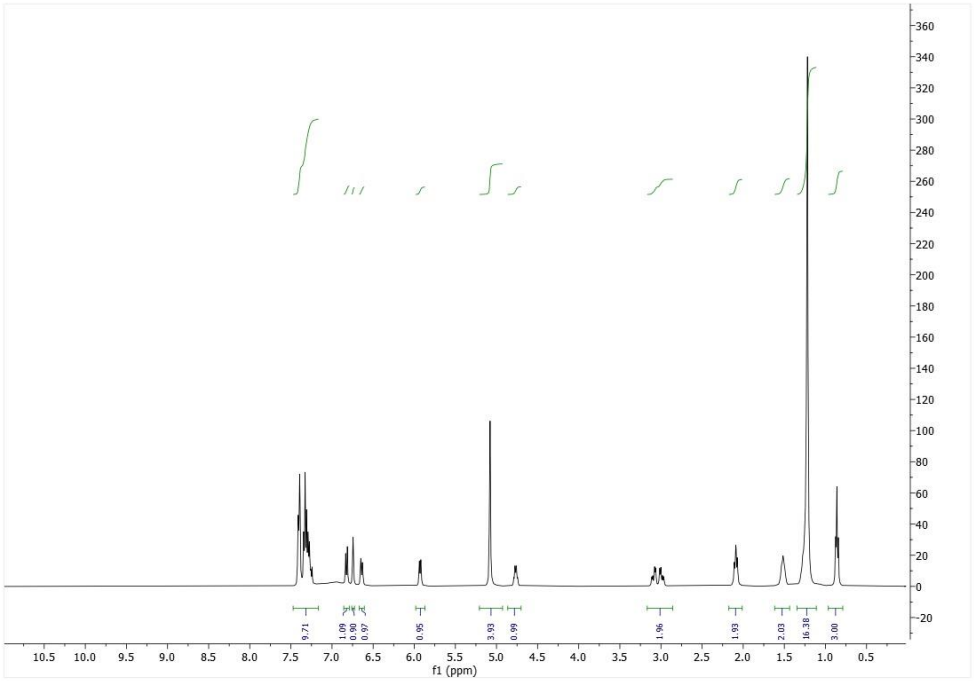


Scheme S2. Reagents and conditions: (i) TFA (18 equiv.), CH_2Cl_2, r.t., 4 h; (ii) Azelaic acid (1 equiv.), HBTU (2.2 equiv.), DIEA (4.2 equiv.), dry ACN, r.t., 4 h; (iii) 1M NaOH (2.5 equiv.), MeOH/THF, r.t., 18 h; (iv) 1M HCl (2.7 equiv.), r.t., 10 min.

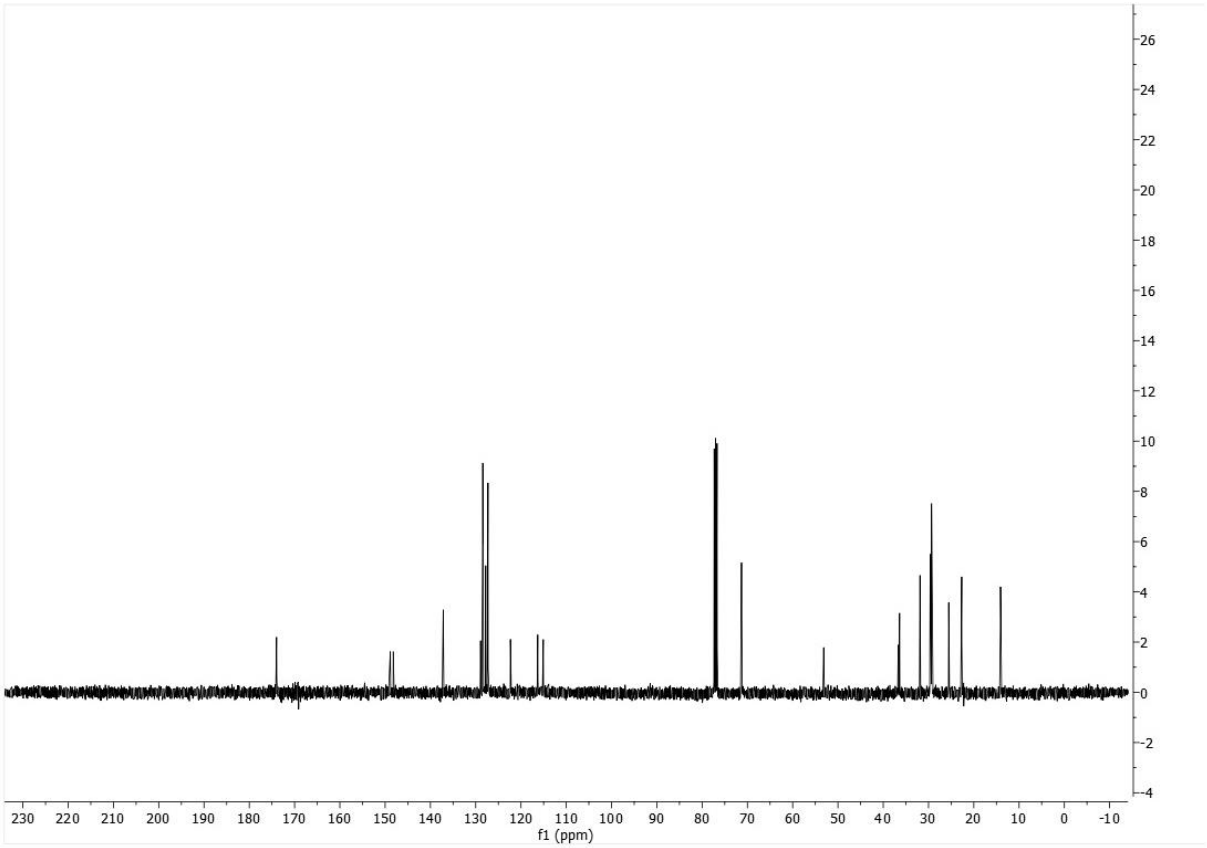
IR spectrum of Lau-L-DOPA(Bn)$_2$OH **A**



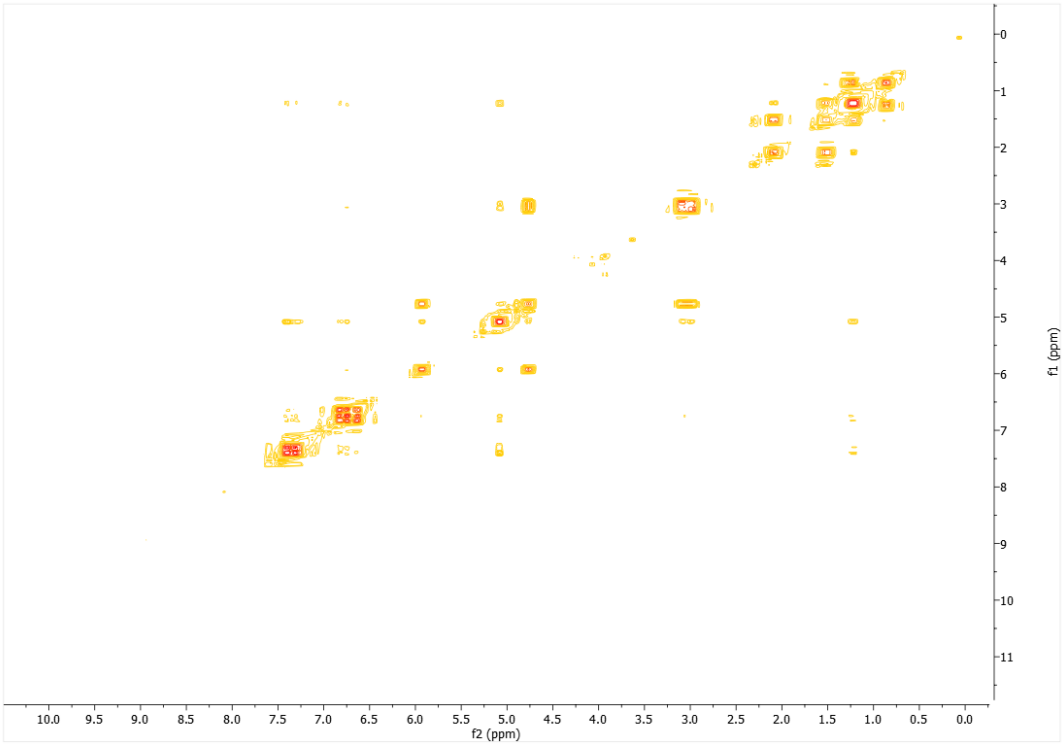
^{1}H-NMR spectrum of Lau-L-DOPA(Bn)$_2$OH **A** ($CDCl_3$)



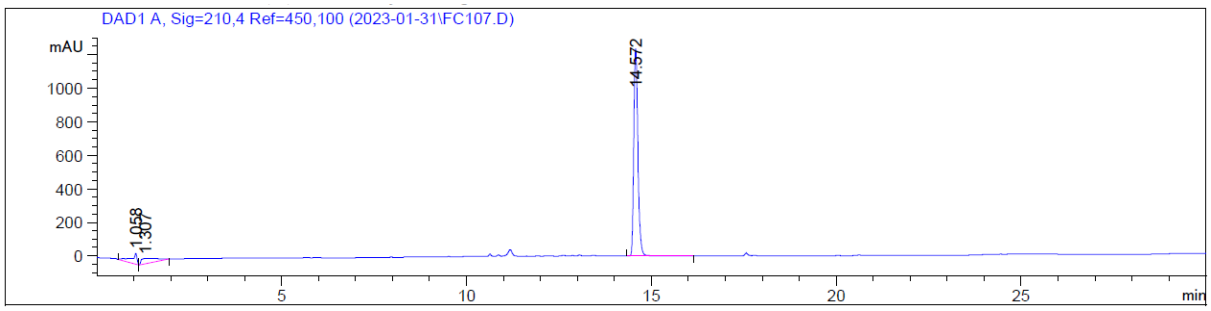
^{13}C-NMR spectrum of Lau-L-DOPA(Bn)$_2$OH **A** ($CDCl_3$)

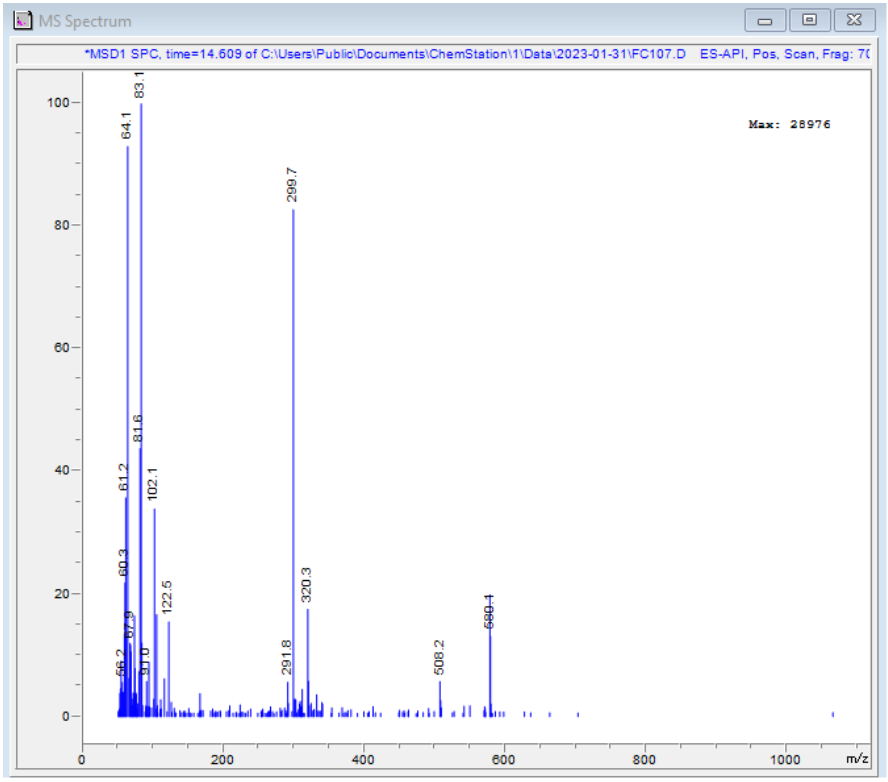


COSY spectrum of Lau-L-DOPA(Bn)$_2$OH **A** ($CDCl_3$)

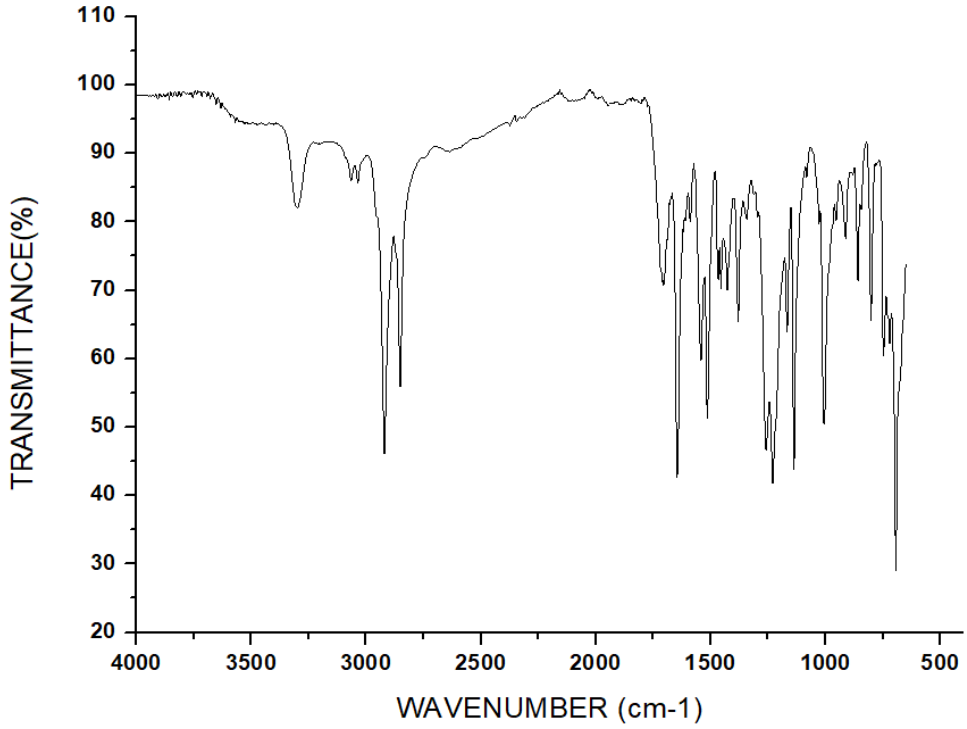


HPLC-MS of Lau-L-DOPA(Bn)$_2$OH **A**

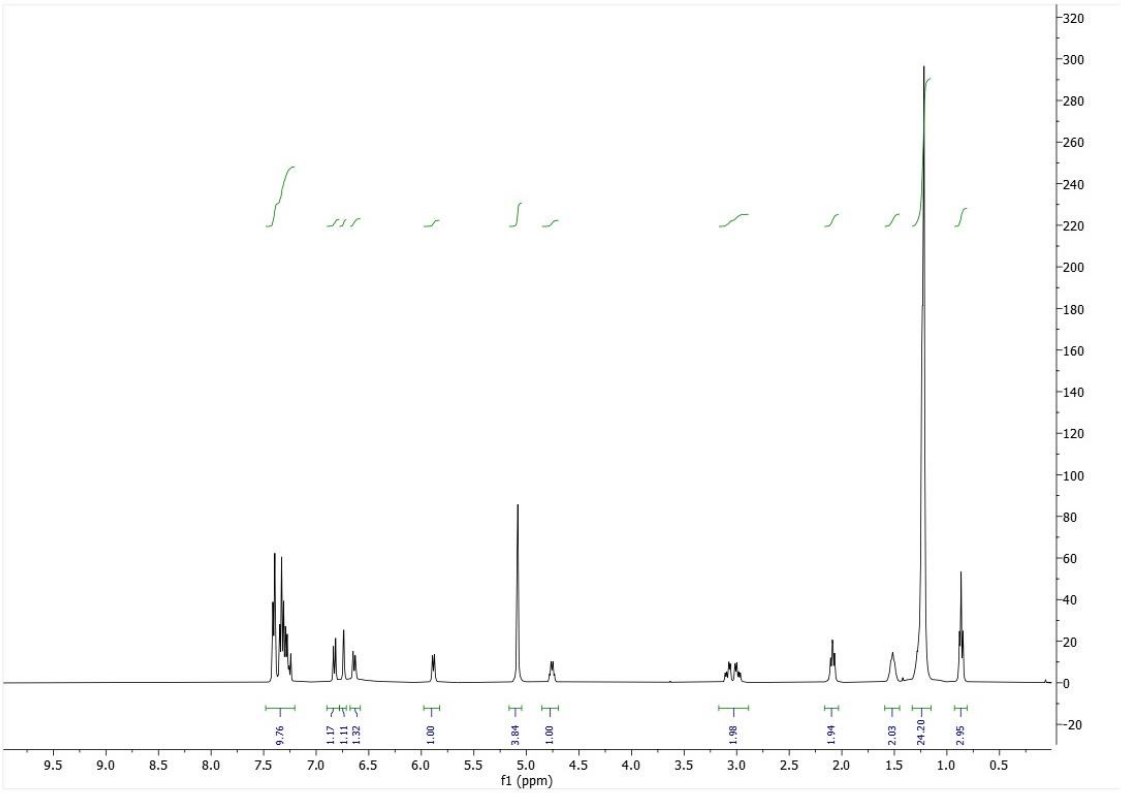




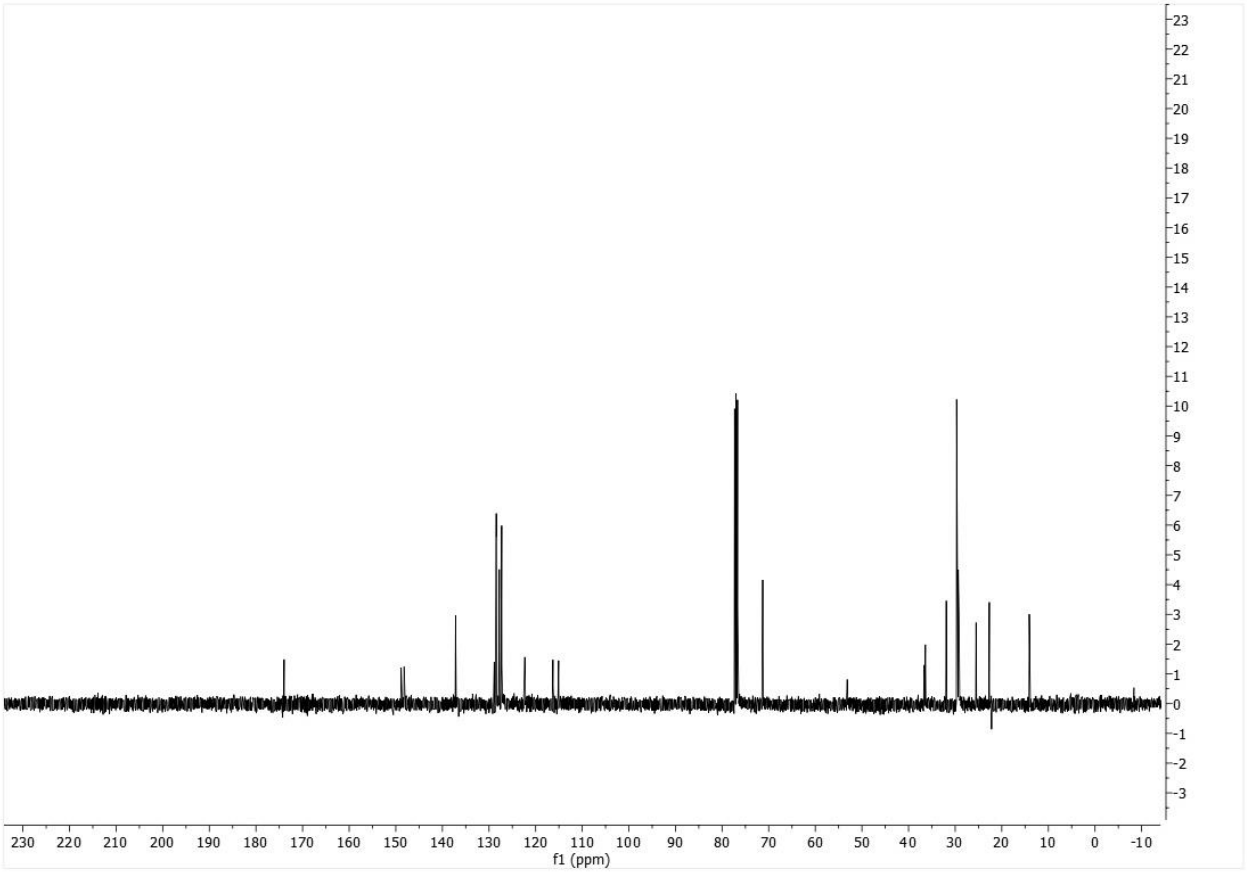
IR spectrum of Pal-L-DOPA(Bn)$_2$OH **B**



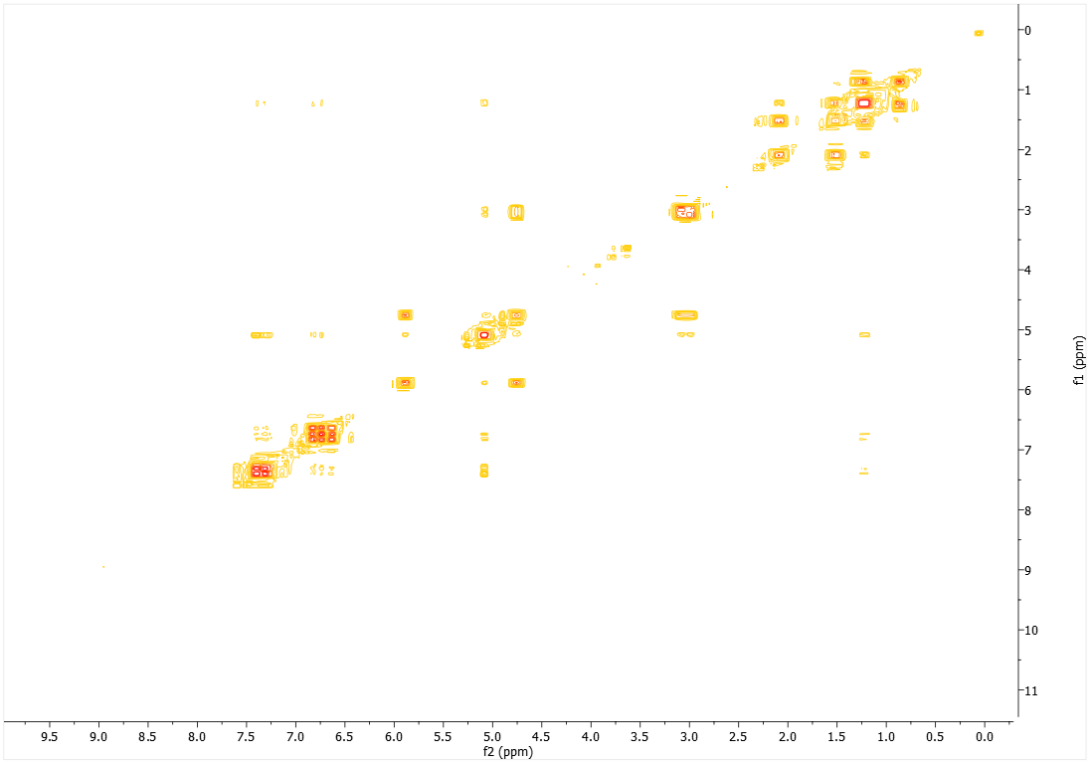
^{1}H-NMR spectrum of Pal-L-DOPA(Bn)$_2$OH **B** ($CDCl_3$)



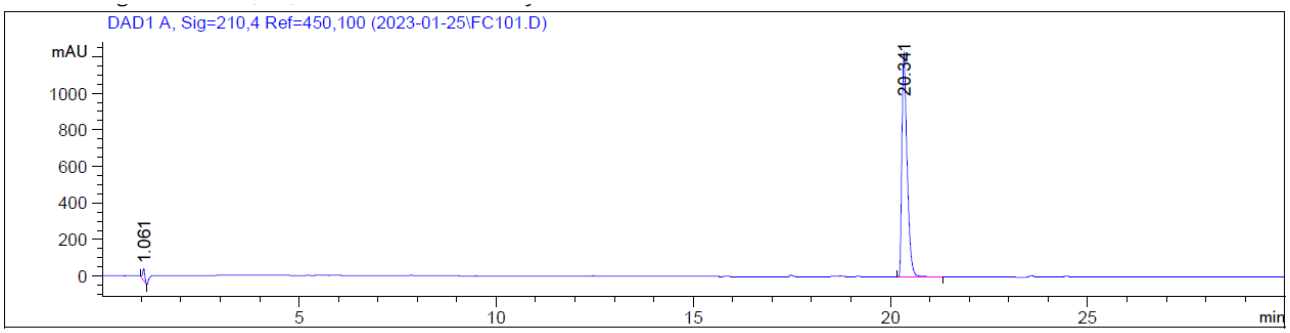
^{13}C-NMR spectrum of Pal-L-DOPA(Bn)$_2$OH **B** ($CDCl_3$)



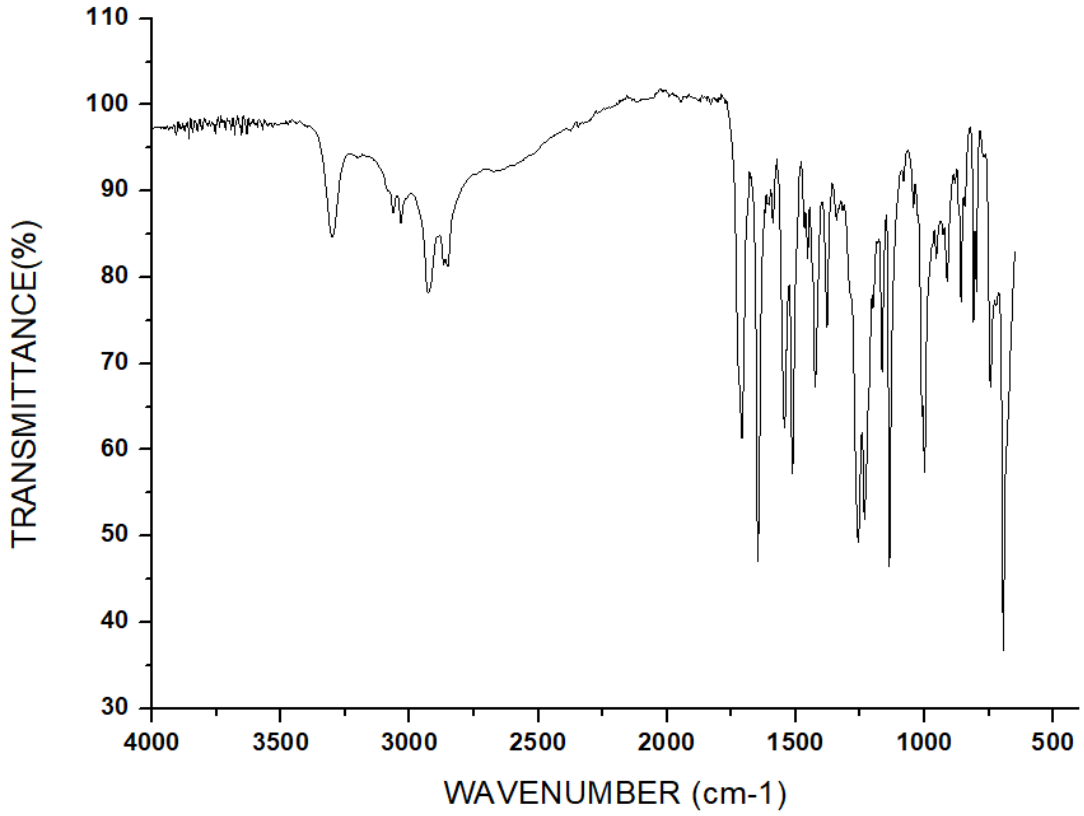
COSY spectrum of Pal-L-DOPA(Bn)$_2$OH **B** ($CDCl_3$)



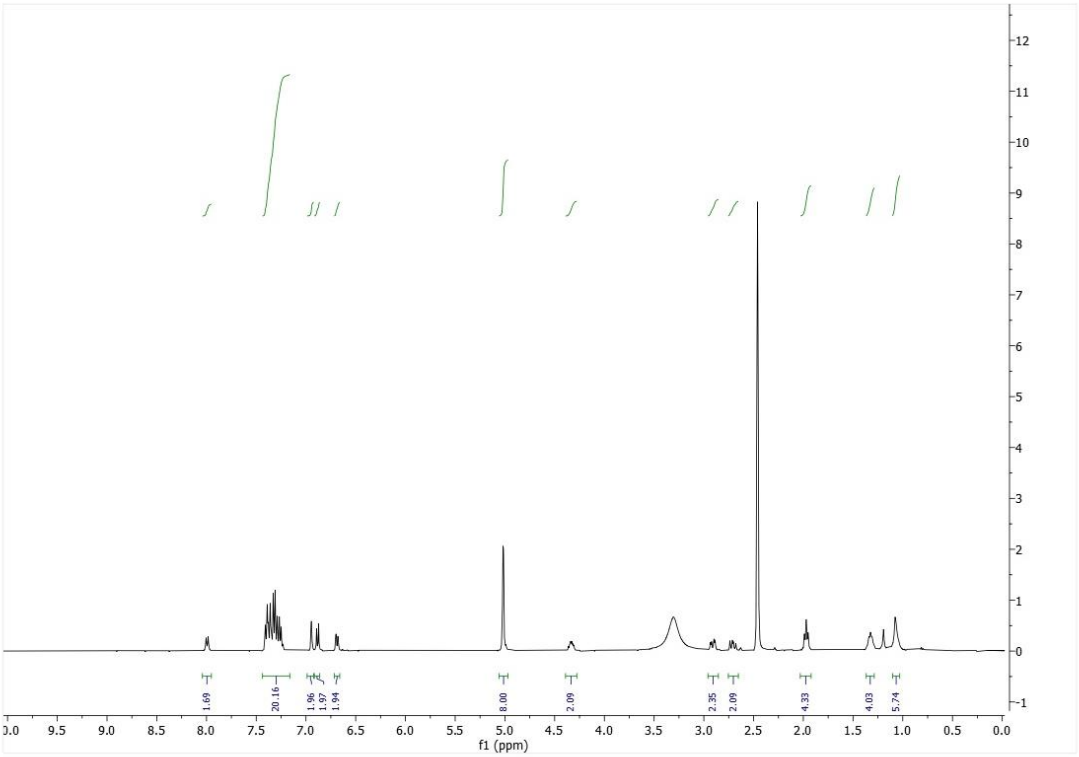
HPLC-MS of Pal-L-DOPA(Bn)$_2$OH **B**



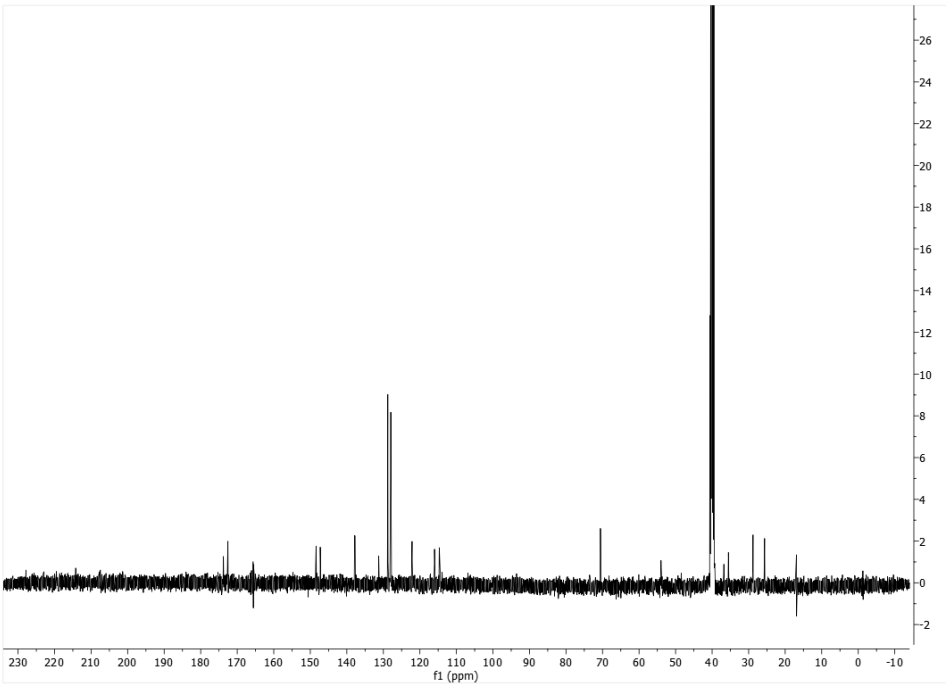
IR spectrum of Az-(L-DOPA(Bn)$_2$OH)$_2$ **C**



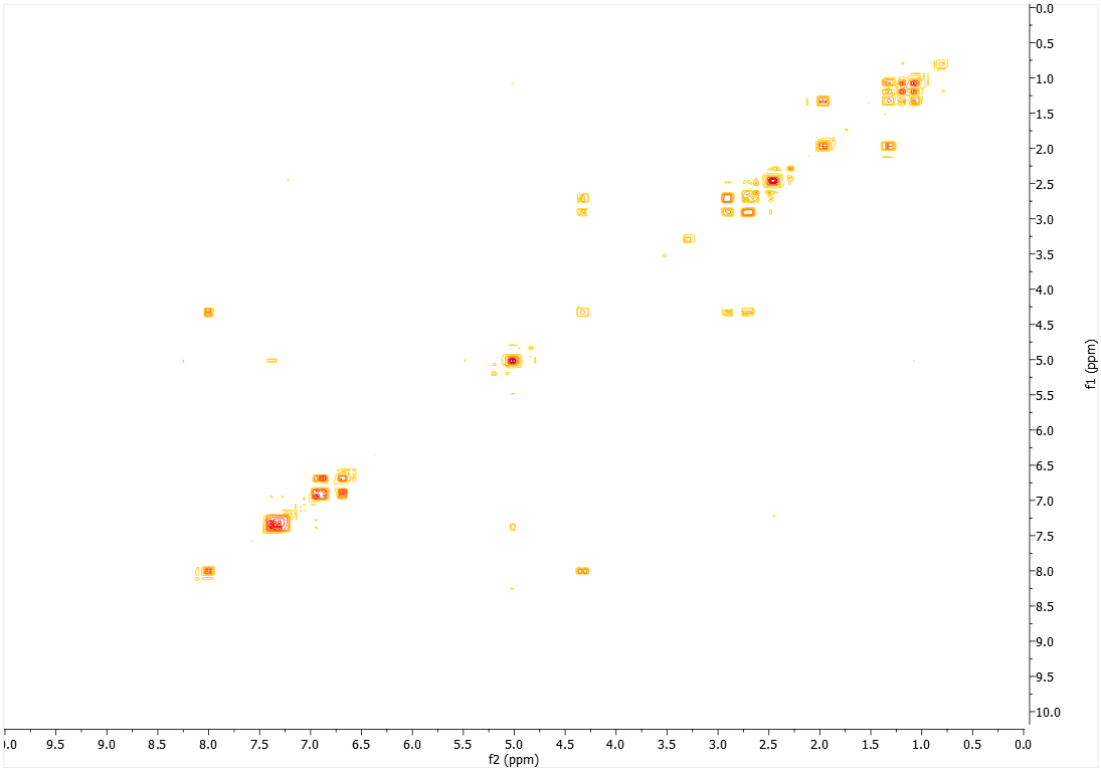
^{1}H-NMR spectrum of Az-(L-DOPA(Bn)$_2$OH)$_2$ **C** (DMSO-d6)



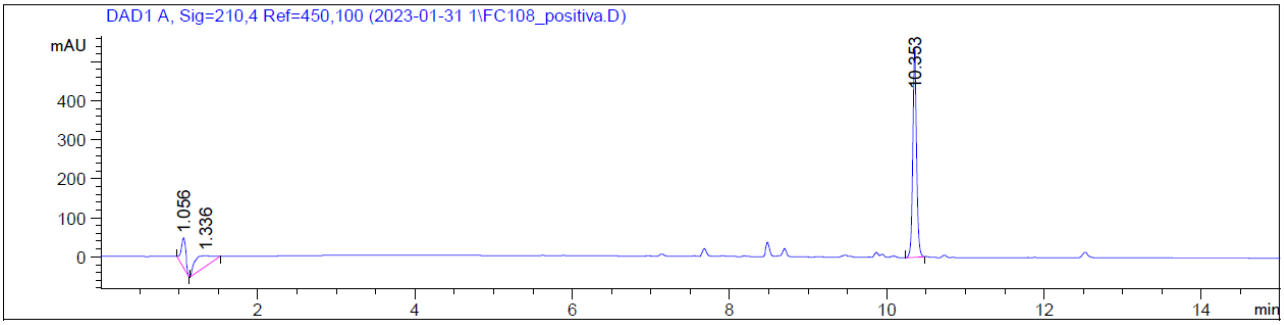
^{13}C-NMR spectrum of Az-(L-DOPA(Bn)$_2$OH)$_2$ **C** (DMSO-d$_6$)

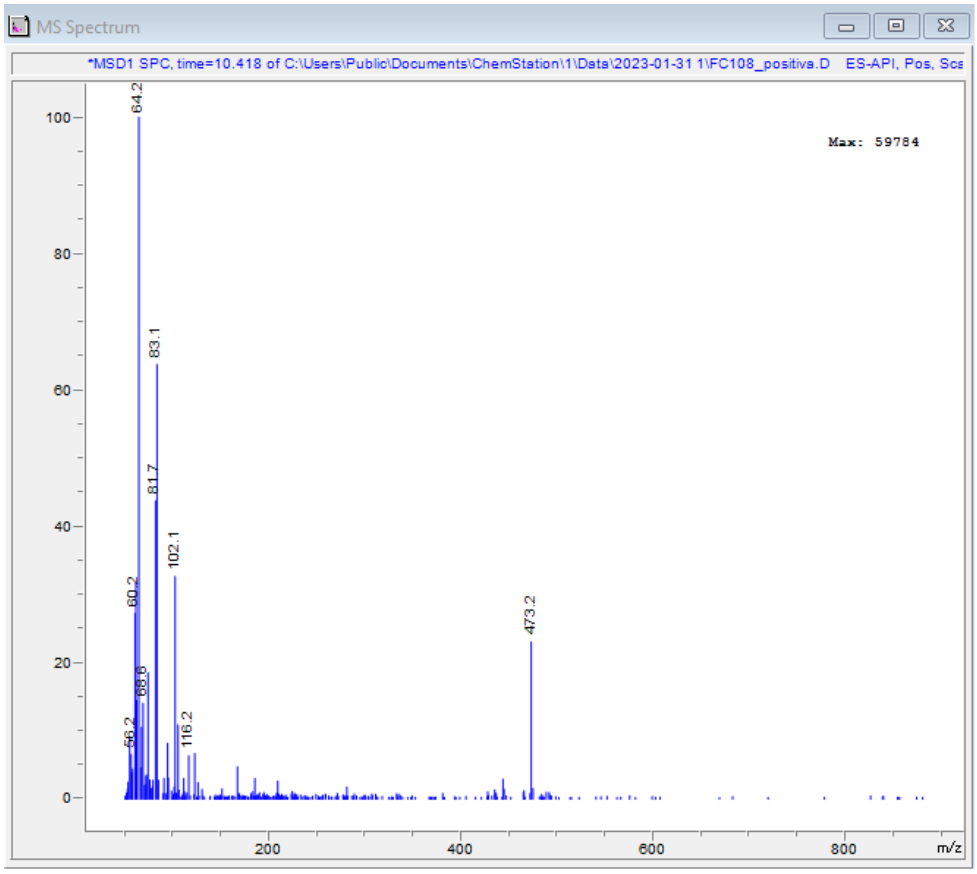


COSY spectrum of Az-(L-DOPA(Bn)$_2$OH)$_2$ **C** (DMSO-d$_6$)



HPLC-MS of Az-(L-DOPA(Bn)$_2$OH)$_2$ **C**





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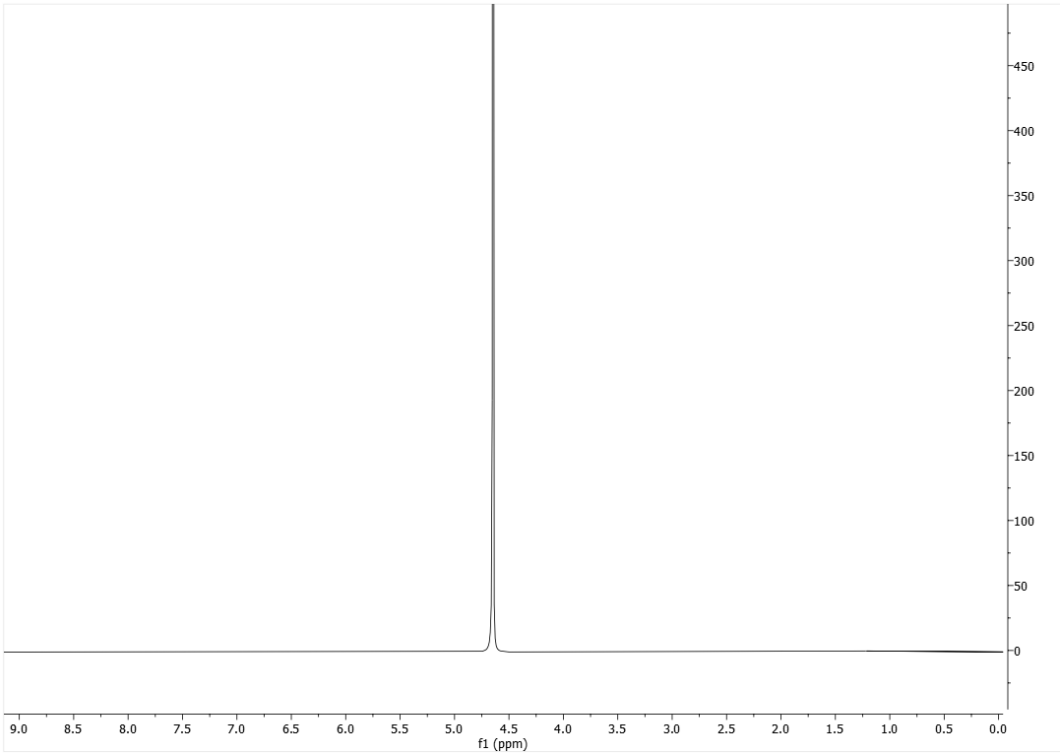
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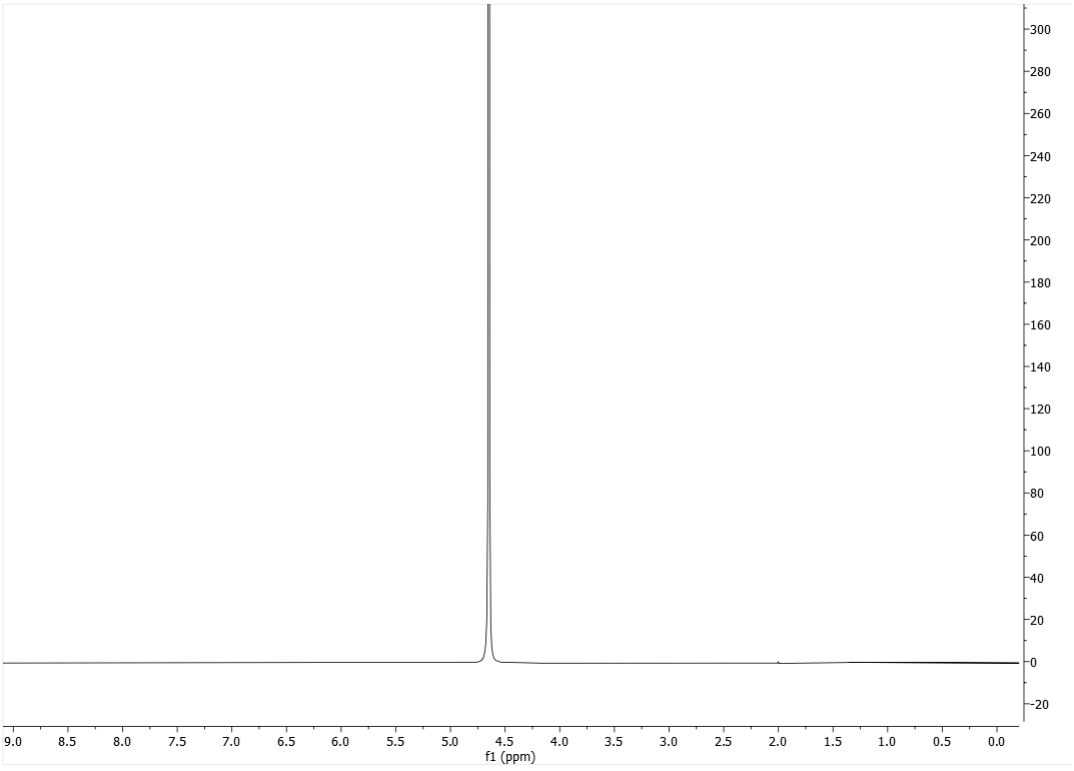
f1 (ppm)

b)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9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

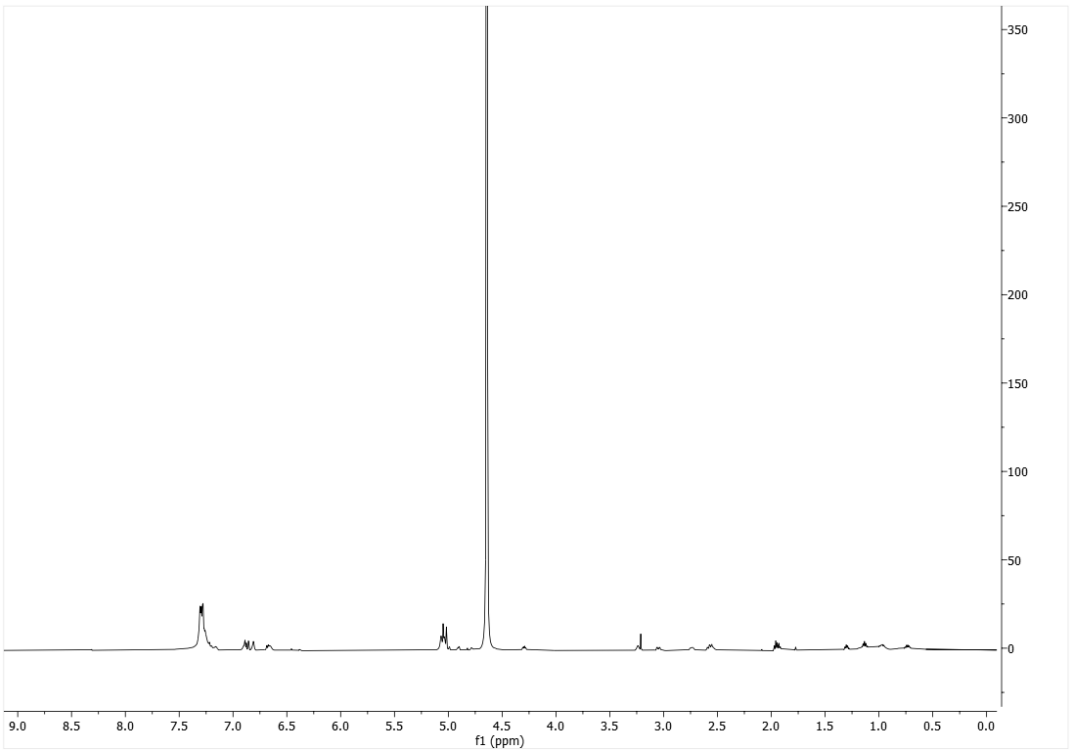
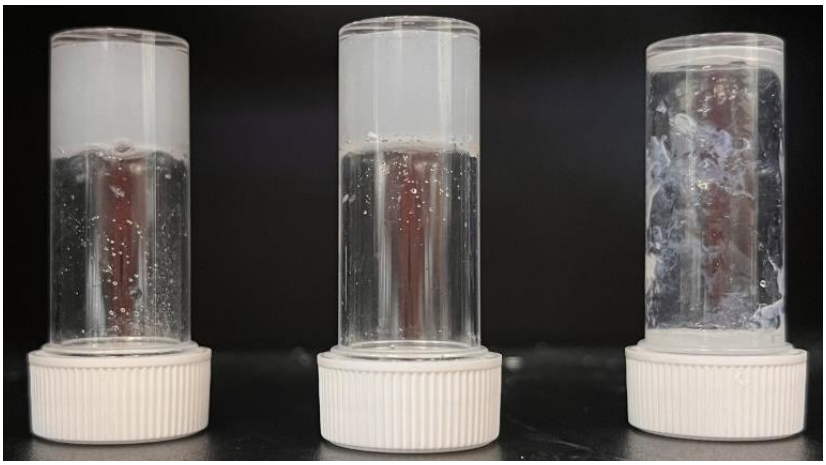
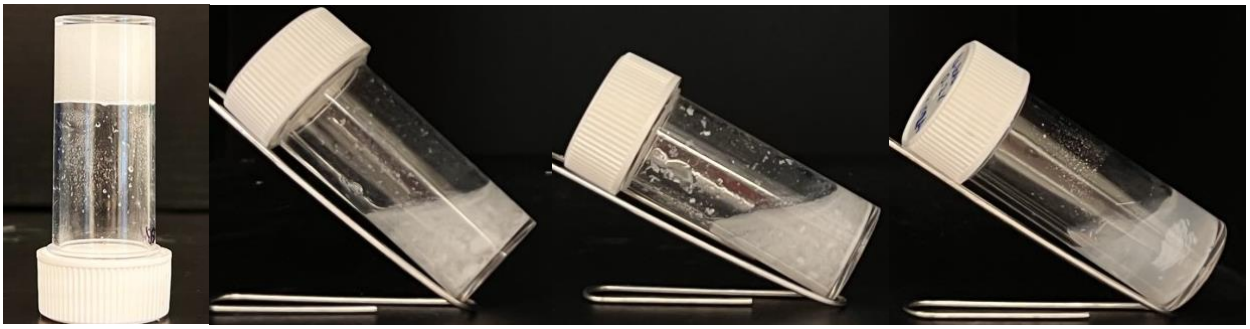
c) 

Figure S1. ^{1}H NMR spectra of **A** (a)**, B** (b) and **C** (c) in D_2O and NaOD.

A)



B)



C)

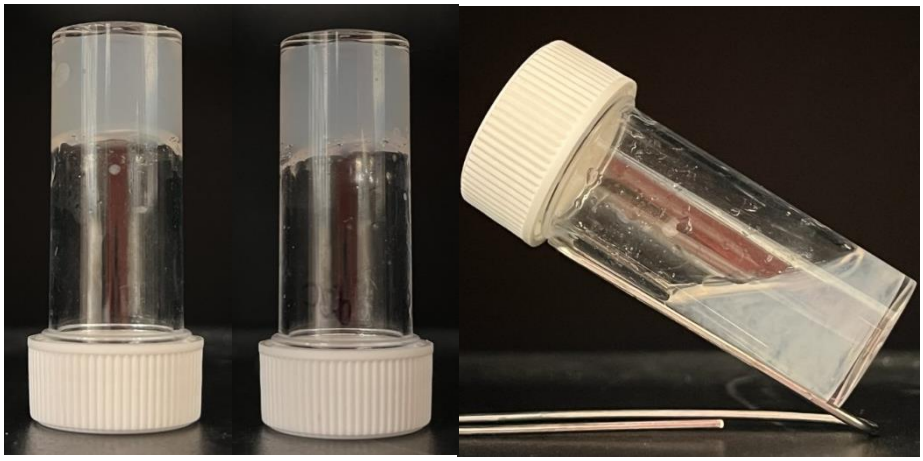
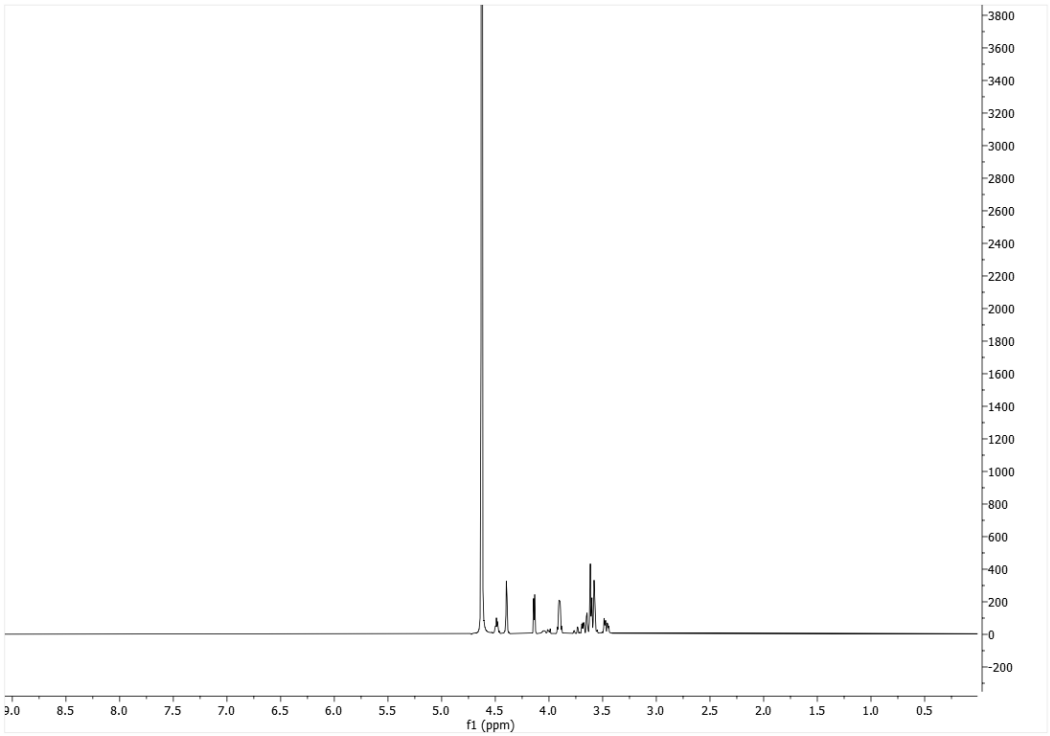


Figure S2. Photographs of the trials for the measurement of the MGC. From left to right: **A)** Lau-Dopa **A**, 0.4-0.3-0.2% w/V (MGC 0.3% w/V); **B)** Pal-Dopa **B**, 0.5-0.4-0.3-0.2% w/V (MGC 0.5% w/V); **C)** Az-Dopa **C**, 0.4-0.3-0.2% w/V (MGC 0.3% w/V).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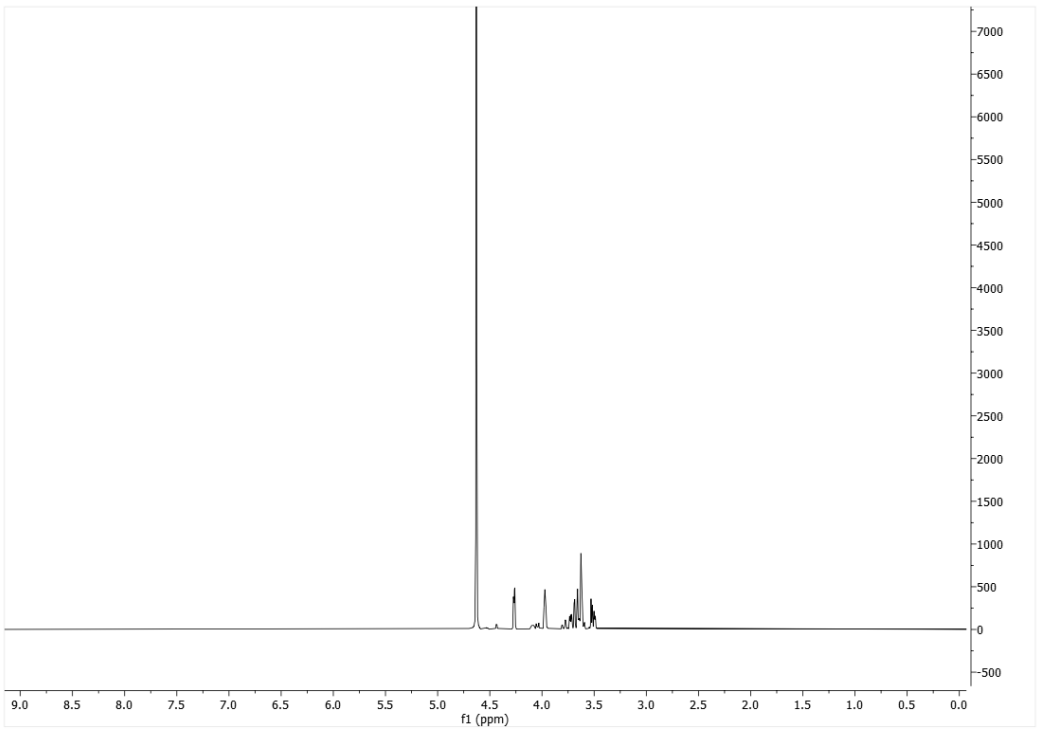
-200
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


7000
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1000
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0
-500
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

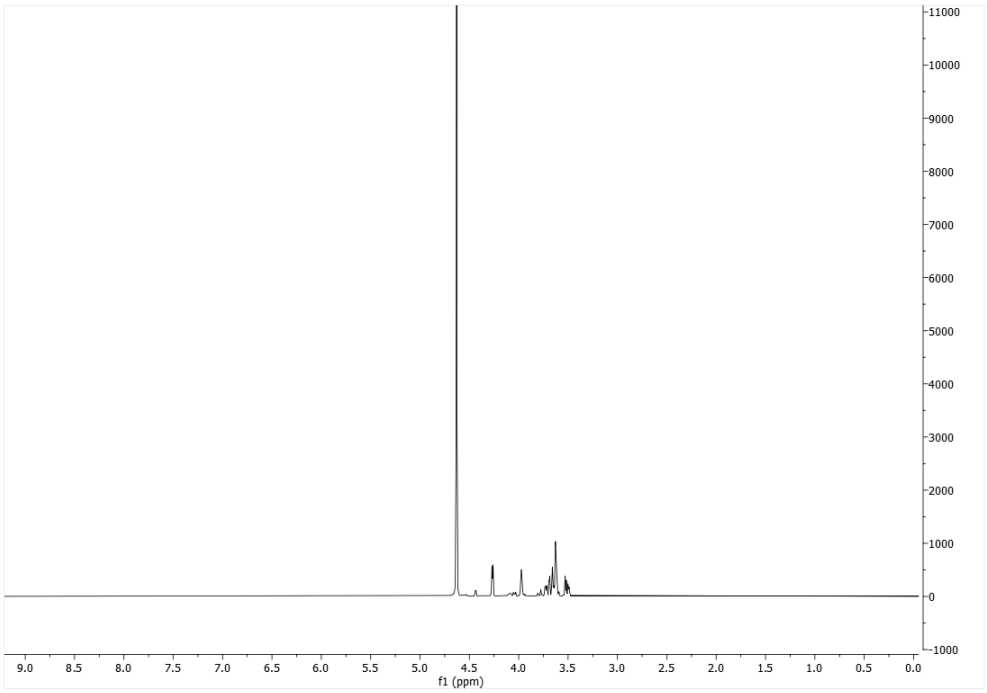


Figure S3. ^{1}H NMR spectra of hydrogels obtained from **A, B** and **C** in D_2O, NaOD and GdL.

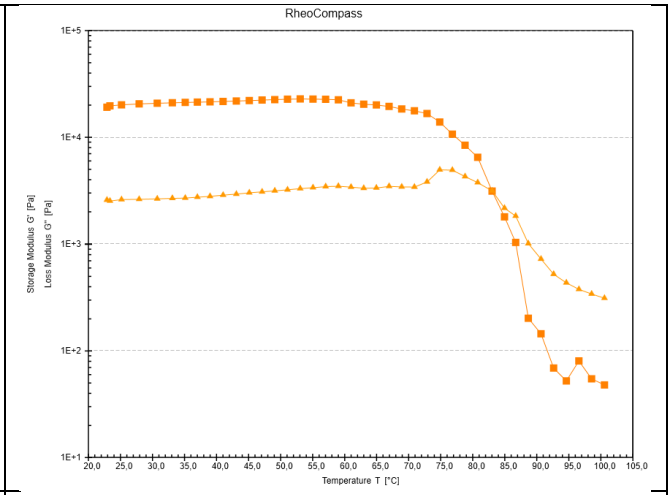
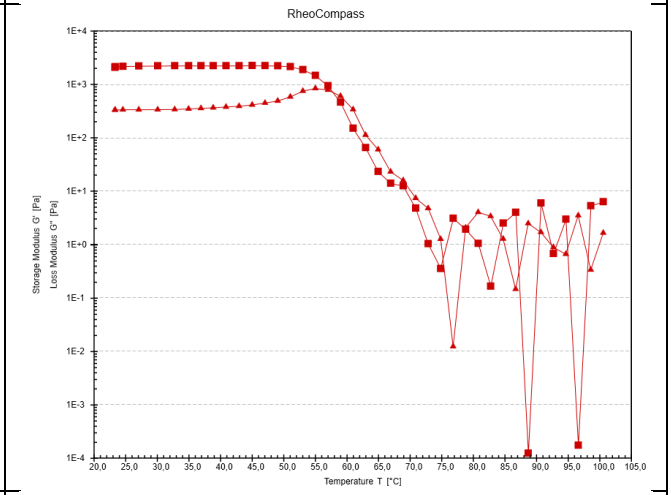
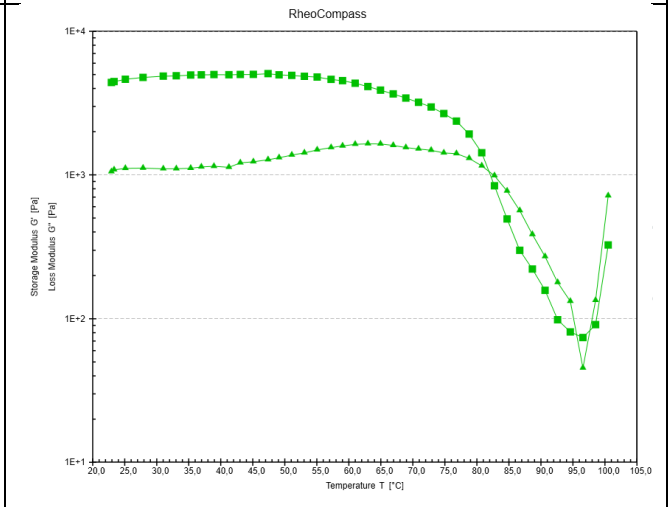
Lau-Dopa **A**	
Pal-Dopa **B**	
Az-Dopa **C**	

Figure S4. Temperature sweep test of the hydrogels at the 0.5% w/V. From top to bottom: Lau-Dopa **A**, Pal-Dopa **B** and Az-Dopa **C**.

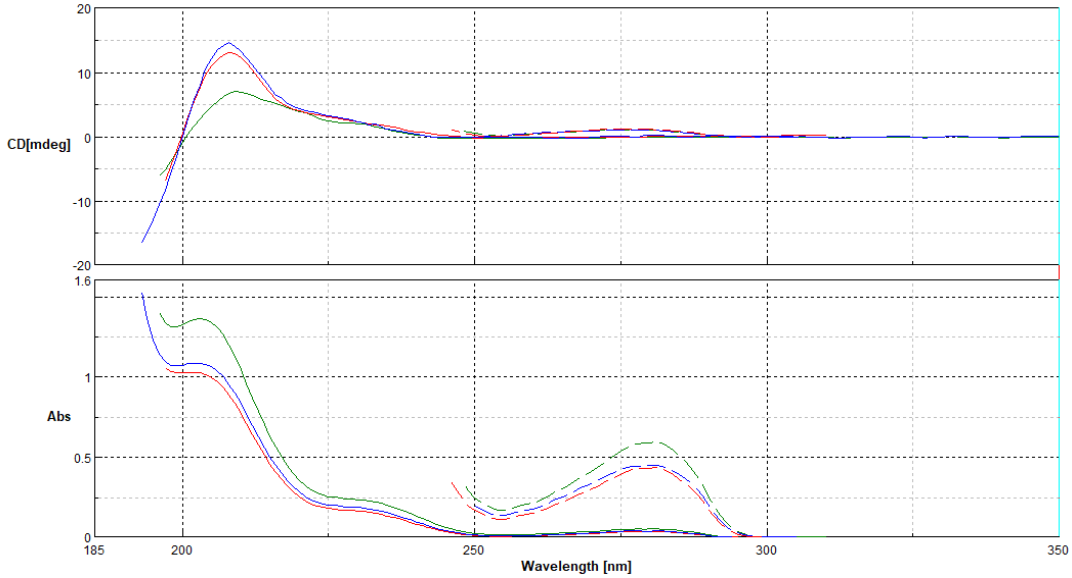


Figure S5. ECD/UV spectra recorded on 0.1 % w/V MeOH solutions of Lau-Dopa **A** (1.8 mM, blue lines), Pal-Dopa **B** (1.6 mM, red lines) and Az-Dopa **C** (1.1 mM, green lines). Measurements were performed by using a 0.01 cm (full lines) and 0.1 cm (dashed lines) path length cell. Ellipticity is expressed in millidegrees.

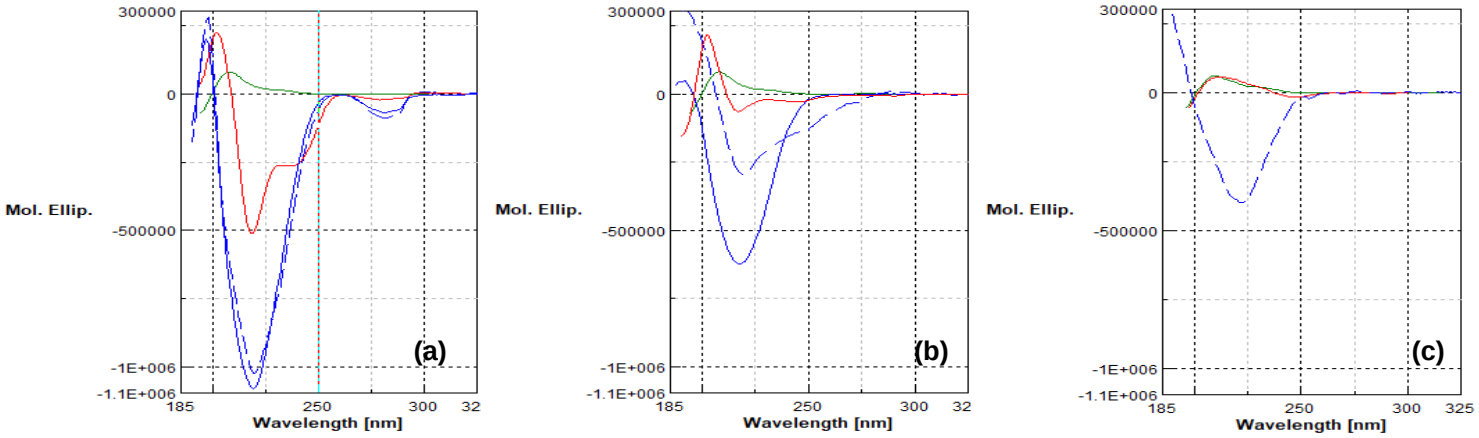


Figure S6. For the sake of comparison, ECD spectra recorded in different conditions on the three gelators Lau-Dopa **A**, Pal-Dopa **B** and Az-Dopa **C** are shown in frames (a), (b) and (c), respectively. MeOH solutions are depicted with green lines, aqueous alkaline solutions with red lines, hydrogel phases 3 hours after trigger addition with dashed blue lines and hydrogel phases 18 hours after trigger addition with full blue lines. Ellipticities are expressed in molar ellipticity (deg cm^2 $dmol^{-1}$). In the case of the Az-Dopa **C** hydrogel (frame c), 18 hours after trigger addition it was difficult to fill the sandwich cuvette and only noisy ECD traces could be recorded (not shown, see the text).

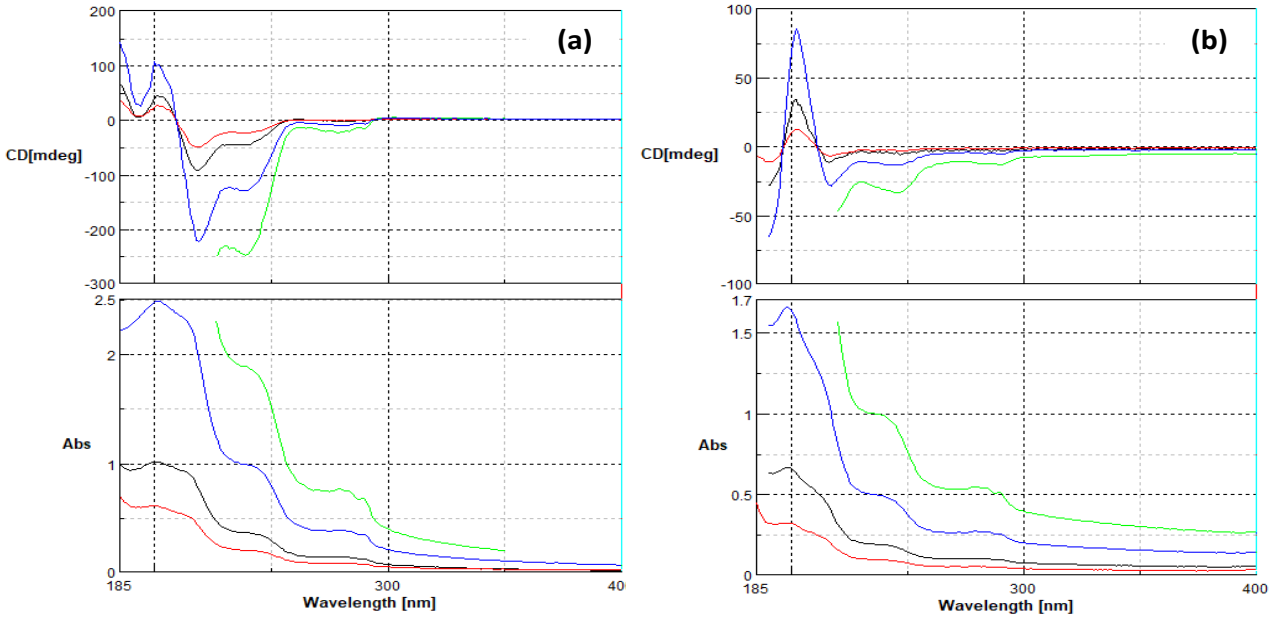


Figure S7. ECD/UV spectra recorded on the 0.5 % w/V aqueous alkaline solution of Lau-Dopa **A** ((a), 8.9 mM) and Pal-Dopa **B** ((b), 8.1 mM) before (green lines) and after 2-fold dilution (blue lines), 5-fold dilution (black lines) and 10-fold dilution with water (red lines). A 0.01 cm path length cell was used. Ellipticity is expressed in millidegrees.

Dissolution of the three gelators in basic water led to opalescent liquid phases. A moderate amount of light scattering impaired UV absorptions and may have affected ECD intensities to some extent. Nevertheless, reproducible ECD traces, always well aligned on the zero line, were collected in repeated experiments. ECD artifacts were ruled out by shaking the cell and recording spectra at different cell orientations. By positioning the cell closer to the detector the scattering of light was not reduced.