Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Effect of the L-DOPA hydroxyl groups in the formation of supramolecular hydrogels

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Table S1. Physical properties of hydrogels obtained under selected conditions.

Hydrogel	Gelator	Trigger (equiv.)	Gelation time	Gel	Final pH	T_{gel} (°C)	Gel properties
1	**A**	GdL (1.1)	16 h	✓	4.0	60 [a]	-
2	**B**	GdL (1.1)	16 h	✓	4.5	66 [a]	-
3	**C**	GdL (1.1)	16 h	✓	4.5	85 [b]	thixotropic
4	**A**	$CaCl_2$ (0.3)	30 min	✓	6.5	78 [b]	-
5	**B**	$CaCl_2$ (0.3)	30 min	✓	7.0	75 [b]	-
6	**C**	$CaCl_2$ (0.3)	30 min	✓	7.0	57 [b]	thixotropic
7	**A**	$ZnCl_2$ (0.3)	30 min	✓	7.0	89 [b]	-
8	**B**	$ZnCl_2$ (0.3)	5 h	✓	7.0	90 [b]	thixotropic
9	**C**	$ZnCl_2$ (0.3)	30 min	✓	7.0	98 [c]	thixotropic
10	**A**	$BaCl_2$ (0.3)	3 h	✓	7.0	65 [b]	thixotropic
11	**B**	$BaCl_2$ (0.3)	3 h	✓	7.0	73 [b]	thixotropic
12	**C**	$BaCl_2$ (0.3)	-	×	-	-	-
13	**A**	histidine (1)	1 h	✓	6.5	76 [a]	thixotropic
14	**B**	histidine (1)	1 h	✓	6.5	70 [b]	-
15	**C**	histidine (1)	-	×	-	-	-
16	**A**	$MgCl_2$ (0.3)	-	×	-	-	-
17	**B**	$MgCl_2$ (0.3)	3 h	✓	7.0	62 [a]	thixotropic
18	**C**	$MgCl_2$ (0.3)	3 h	✓	7.5	52 [c]	thixotropic
19	**A**	$CuCl_2$ (0.3)	3 h	✓	7.5	40 [b]	-
20	**B**	$CuCl_2$ (0.3)	-	×	-	-	-
21	**C**	$CuCl_2$ (0.3)	16 h	✓	7.0	89 [c]	-
22	**A**	$Al_2(SO_4)_3$ (0.15)	-	×	-	-	-
23	**B**	$Al_2(SO_4)_3$ (0.15)	-	×	-	-	-
24	**C**	$Al_2(SO_4)_3$ (0.15)	30 min	×	-	-	-
25	**A**	$Fe(NO_3)_3$ (0.3)	-	×	-	-	-
26	**B**	$Fe(NO_3)_3$ (0.3)	-	×	-	-	-
27	**C**	$Fe(NO_3)_3$ (0.3)	16 h	×	-	-	-
28	**A**	arginine (1)	-	×	-	-	-
29	**B**	arginine (1)	-	×	-	-	-
30	**C**	arginine (1)	1 h	✓	7.5	64 [a]	-

[a]Thermoreversible. [b]Not thermoreversible gel, syneresis occurs after heating. [c]Not thermoreversible gel, the gelator melts then precipitate on cooling.

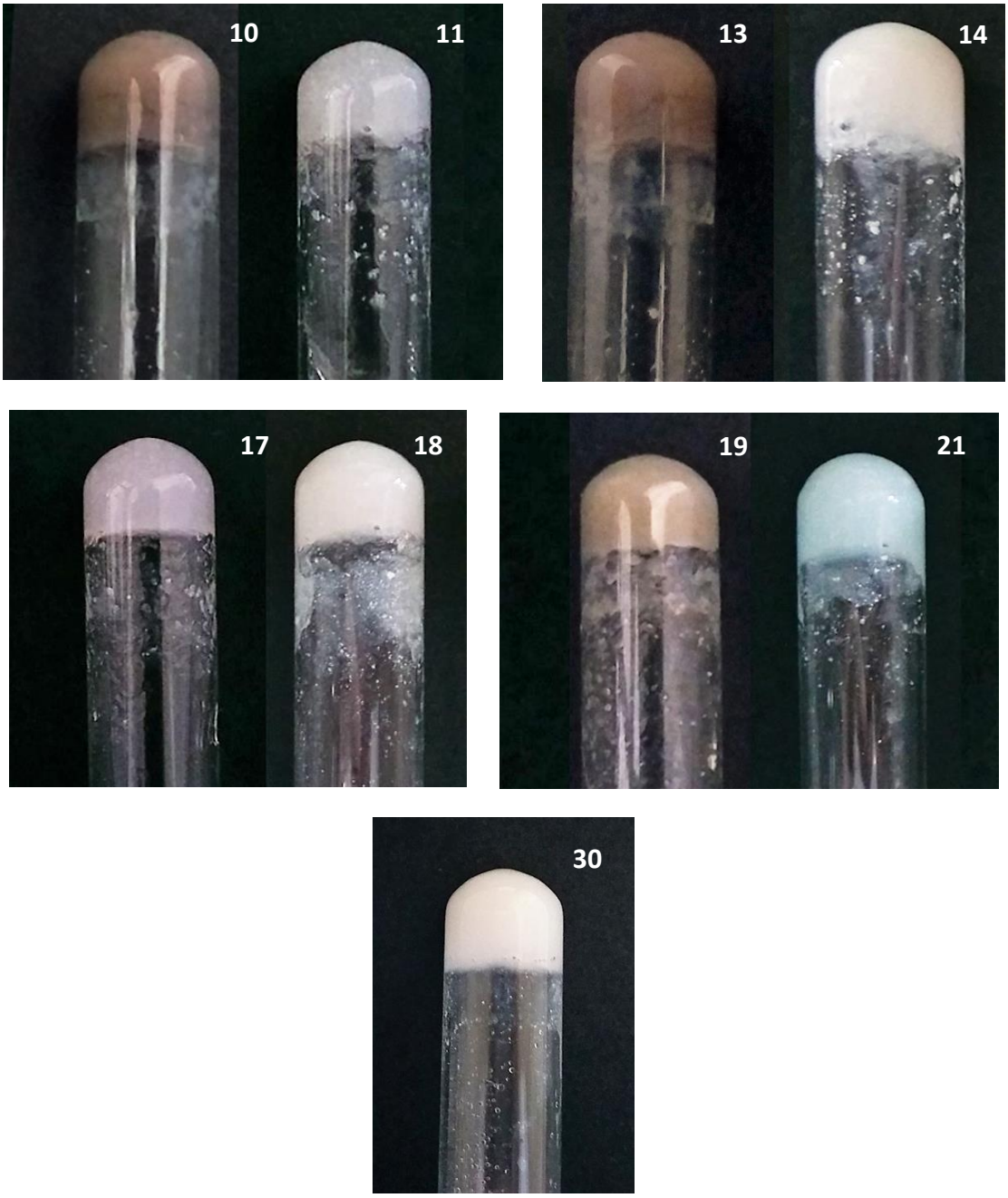


Figure S1. Photographs of hydrogels **10**, **11**, **13**, **14**, **17**, **18**, **19**, **21**, **30**.

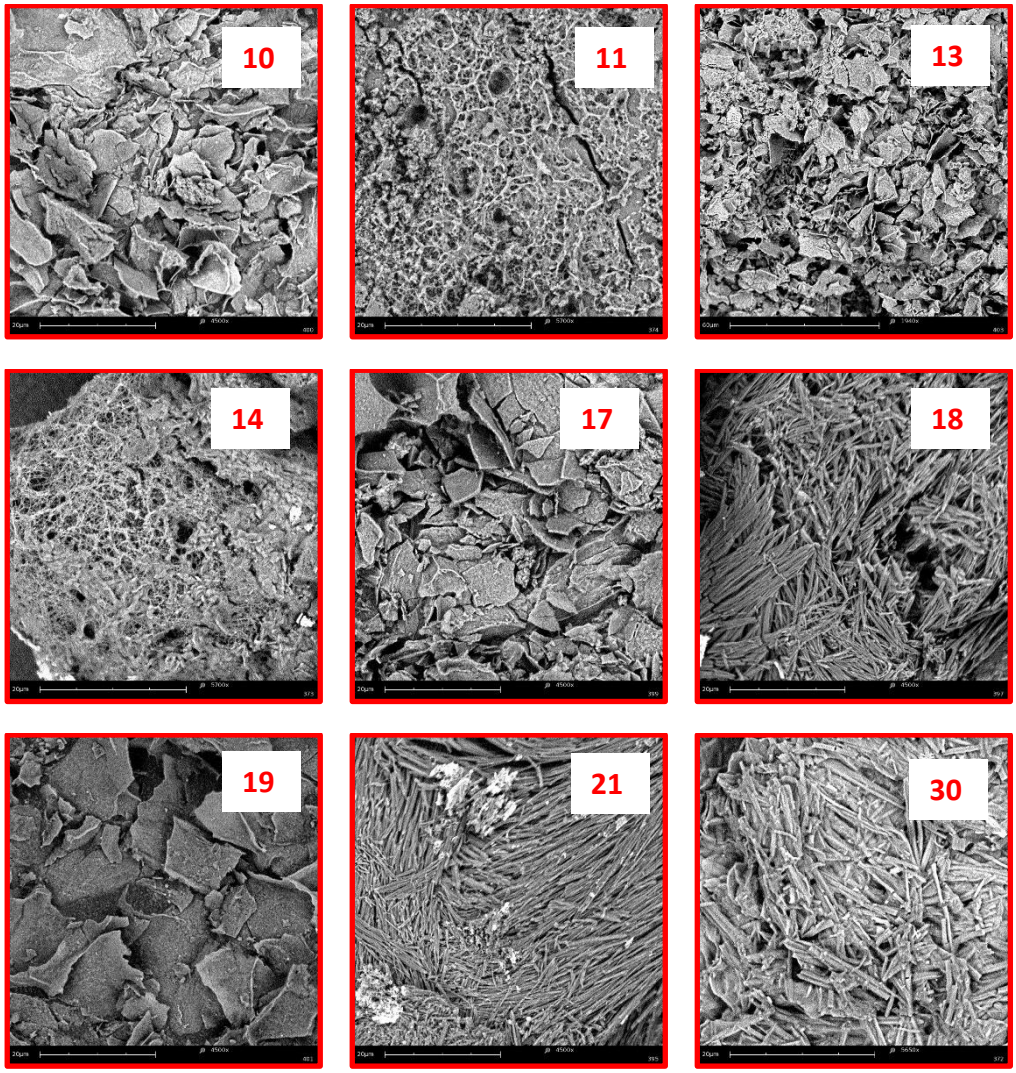
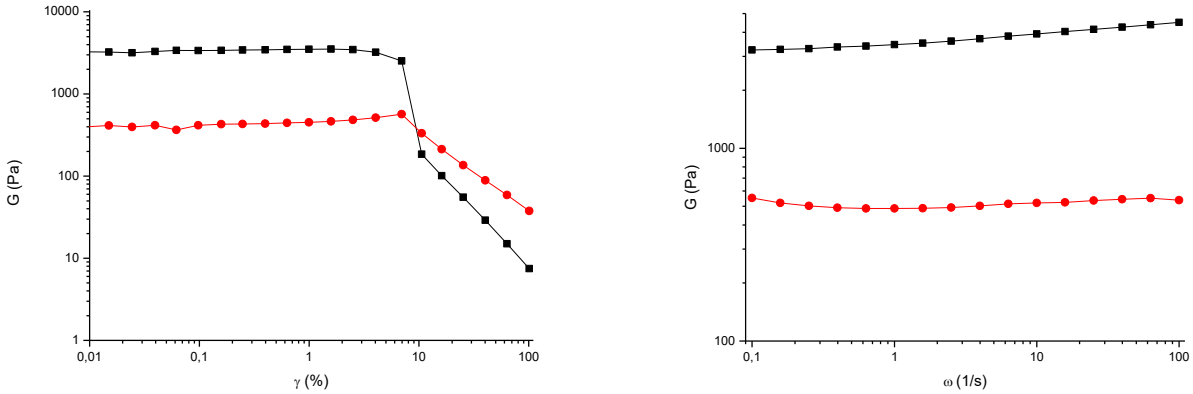
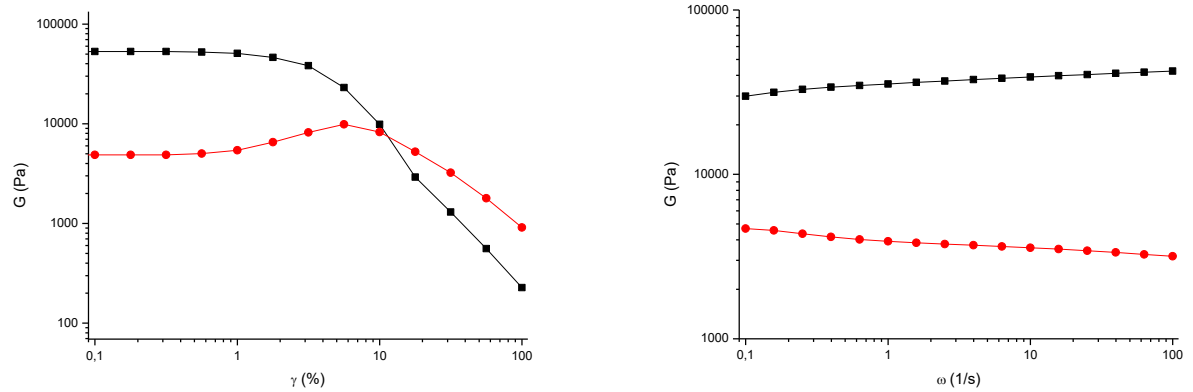


Figure S2. SEM images of samples of xerogel obtained by freeze drying samples of hydrogel **10**, **11**, **13**, **14**, **17**, **18**, **19**, **21** and **30**. Bar = 20 µm.

Hydrogel **1**



Hydrogel **2**



Hydrogel **3**

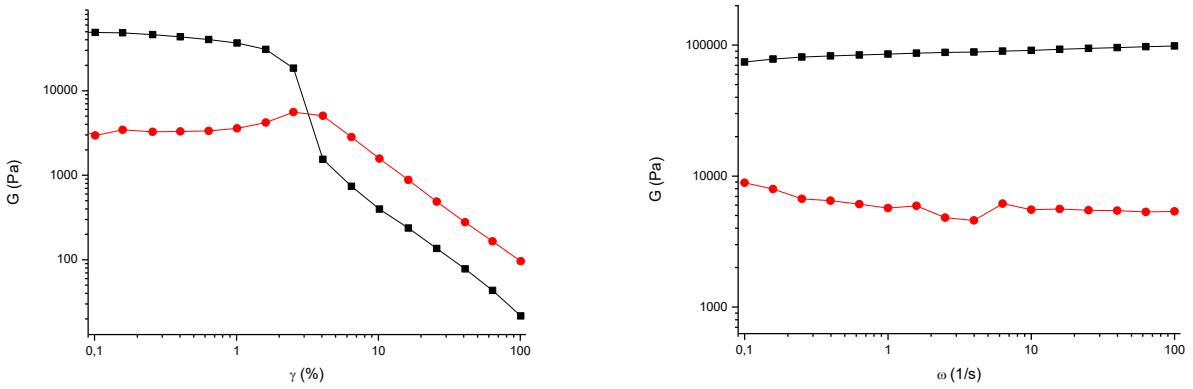
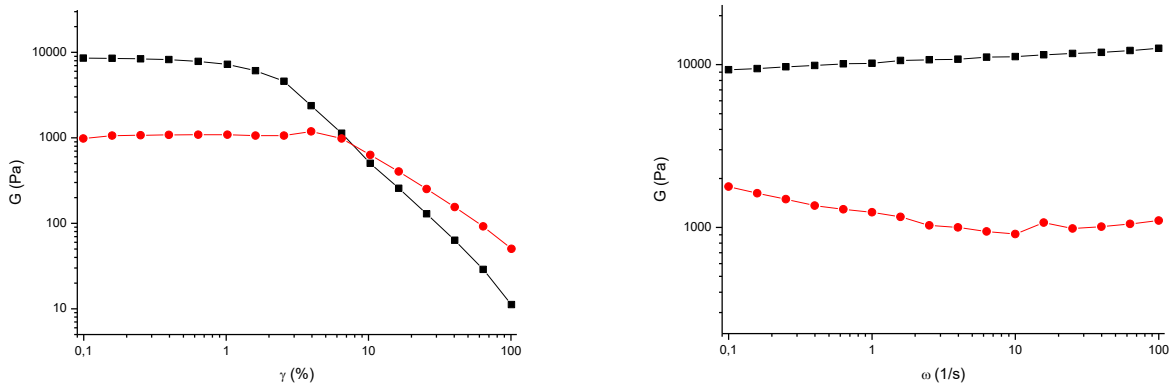
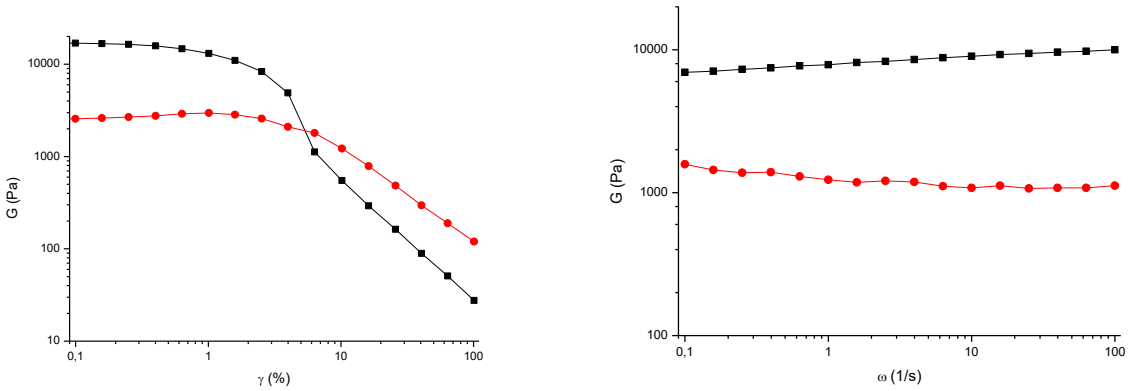


Figure S3. Strain dependence (left) and frequency dependence (right) of storage modulus (square) and loss modulus (triangle) for hydrogels **1**, **2** and **3**. The analyses were performed on the hydrogel about 20 hours after the gelation begun.

Hydrogel **4**



Hydrogel **5**



Hydrogel **6**

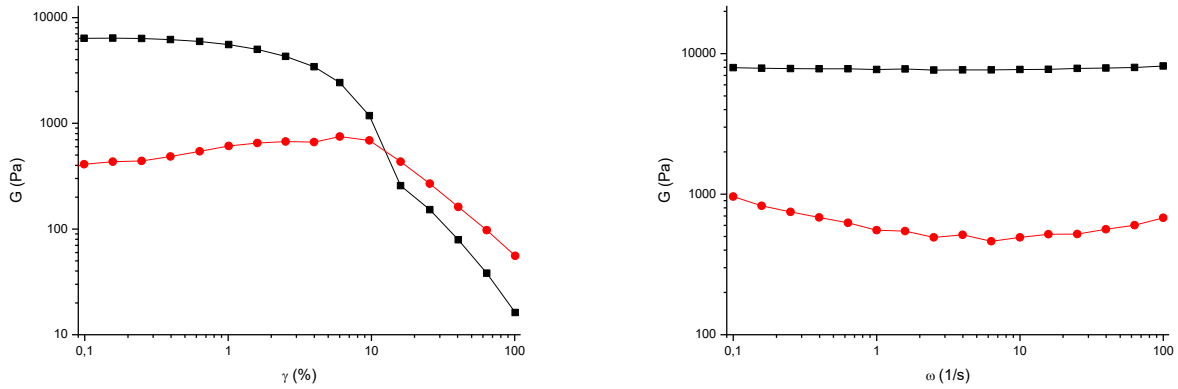
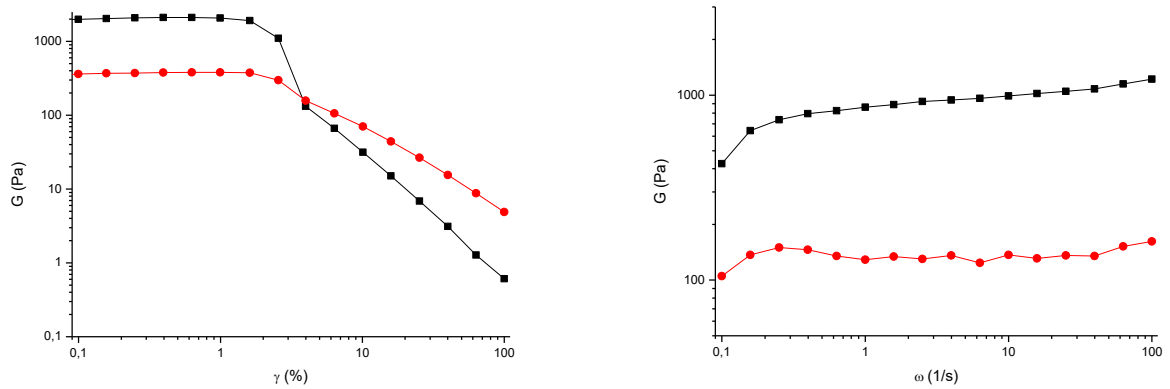
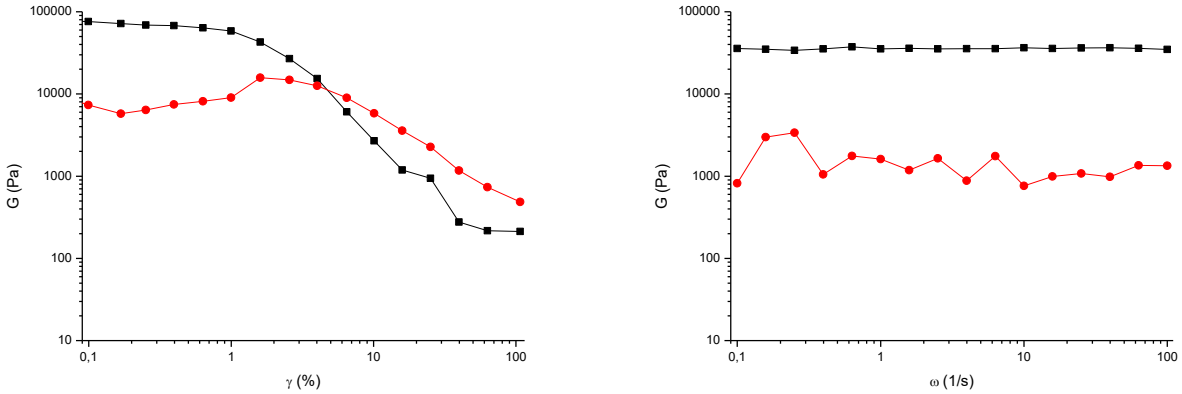


Figure S4. Strain dependence (left) and frequency dependence (right) of storage modulus (square) and loss modulus (triangle) for hydrogels **4**, **5** and **6**. The analyses were performed on the hydrogel about 20 hours after the gelation begun.

Hydrogel **7**



Hydrogel **8**



Hydrogel **9**

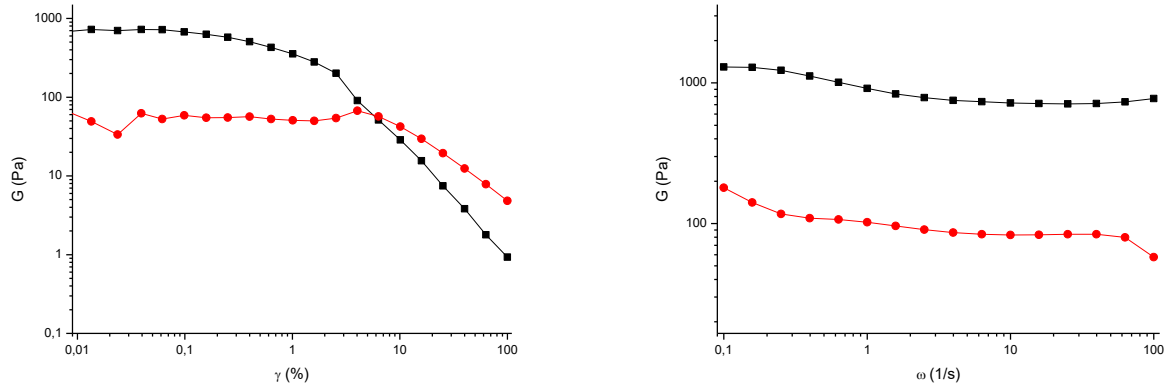


Figure S5. Strain dependence (left) and frequency dependence (right) of storage modulus (square) and loss modulus (triangle) for hydrogels **7**, **8** and **9**. The analyses were performed on the hydrogel about 20 hours after the gelation begun.

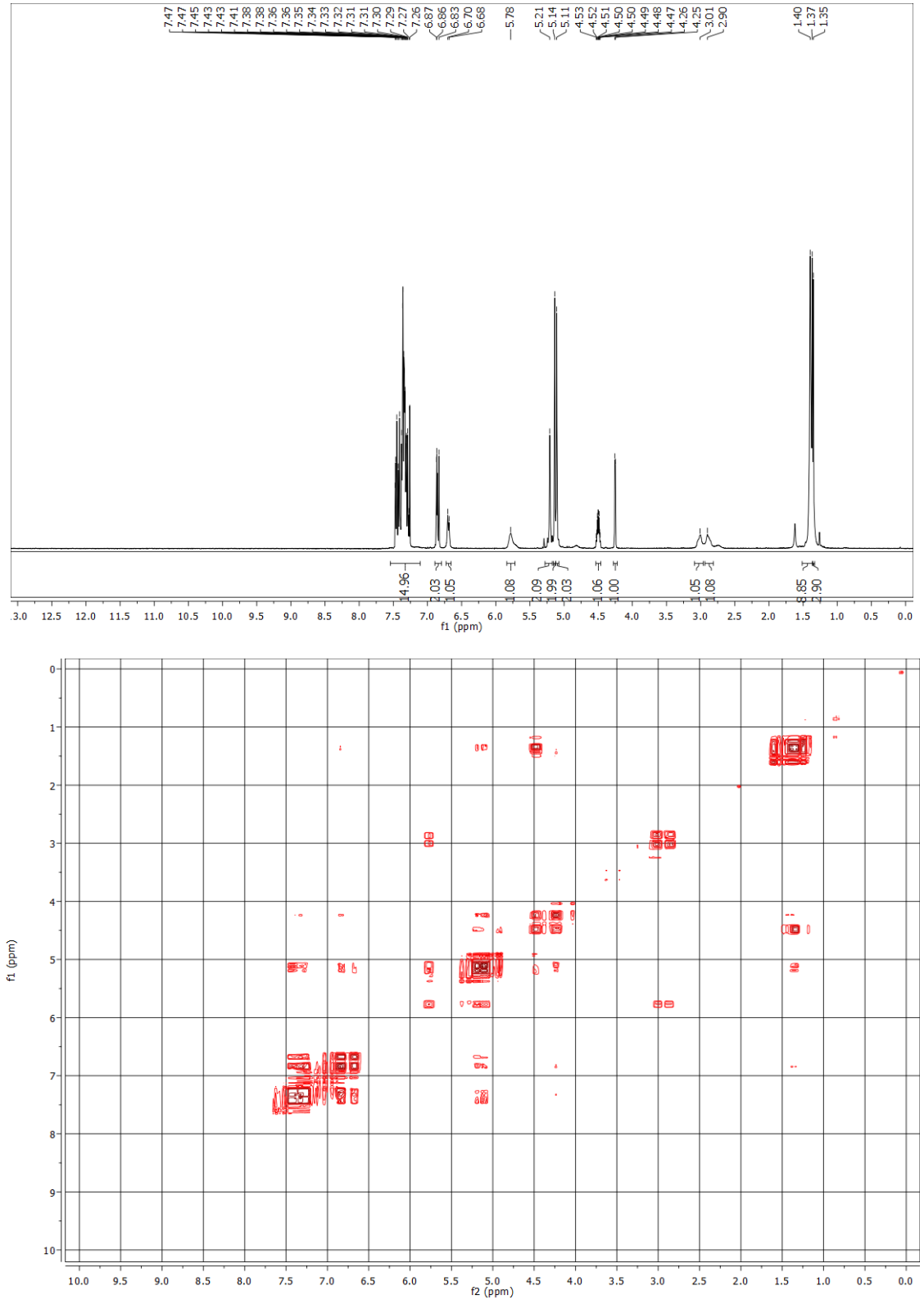
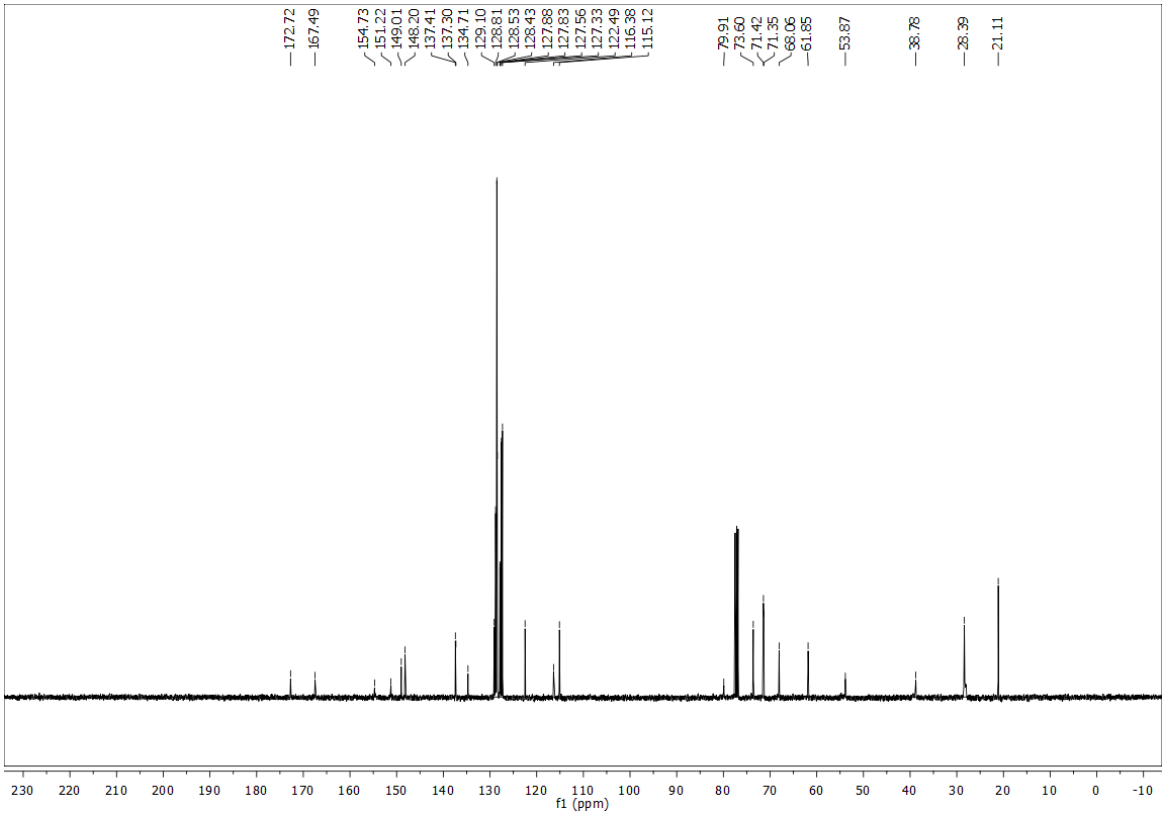


Figure S6. ^{1}H NMR and COSY spectra of Boc-L-DOPA[OBn]$_2$-D-Oxd-OBn.



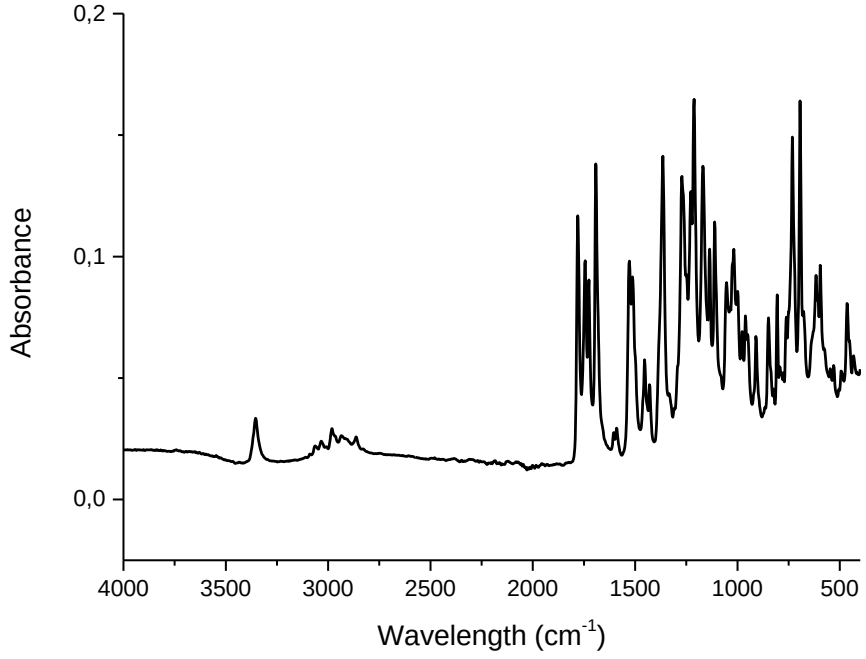


Figure S7. ^{13}C NMR (top) and FT-IR (bottom) spectra of Boc-L-DOPA[OBn]$_2$-D-Oxd-OBn.

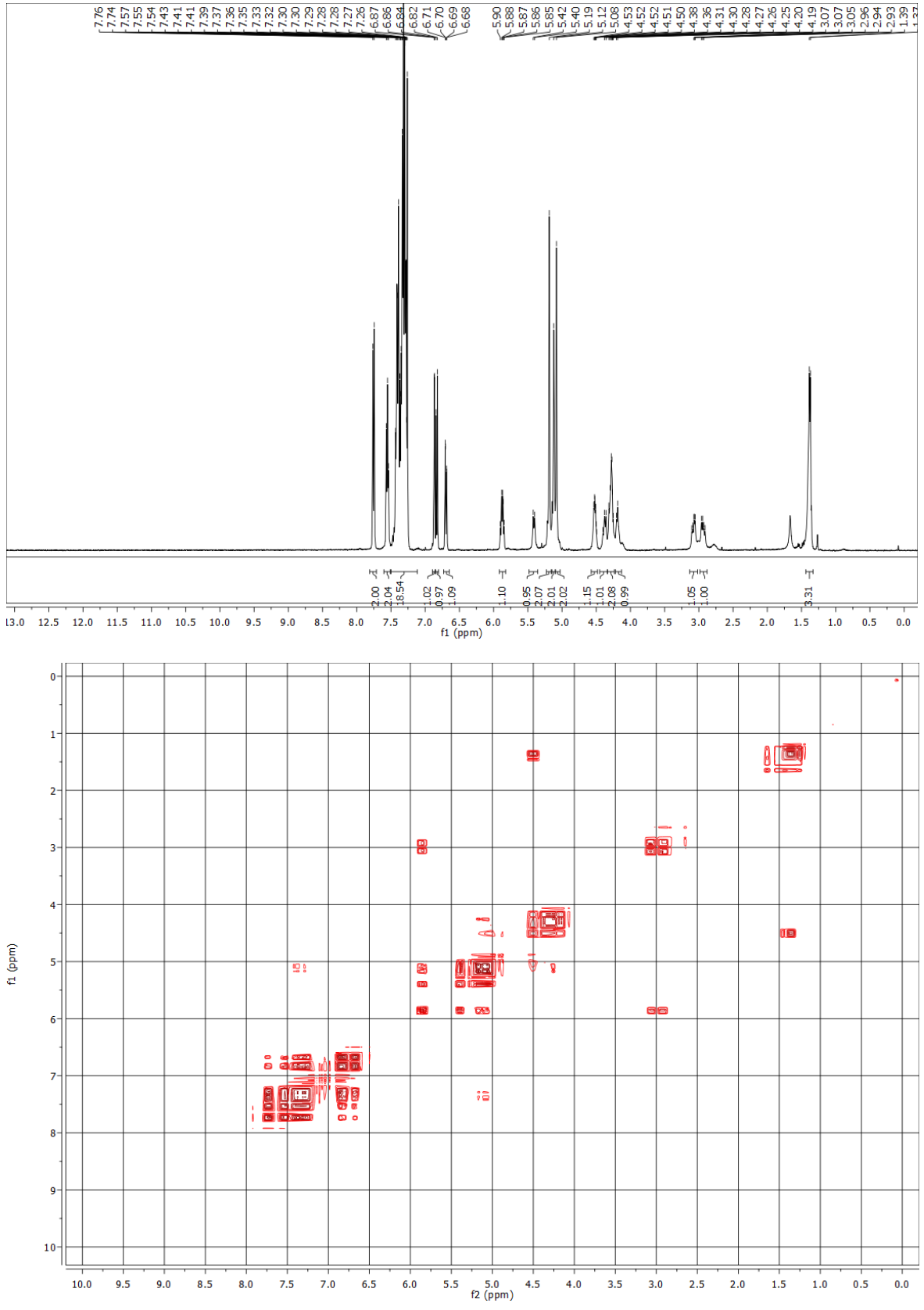
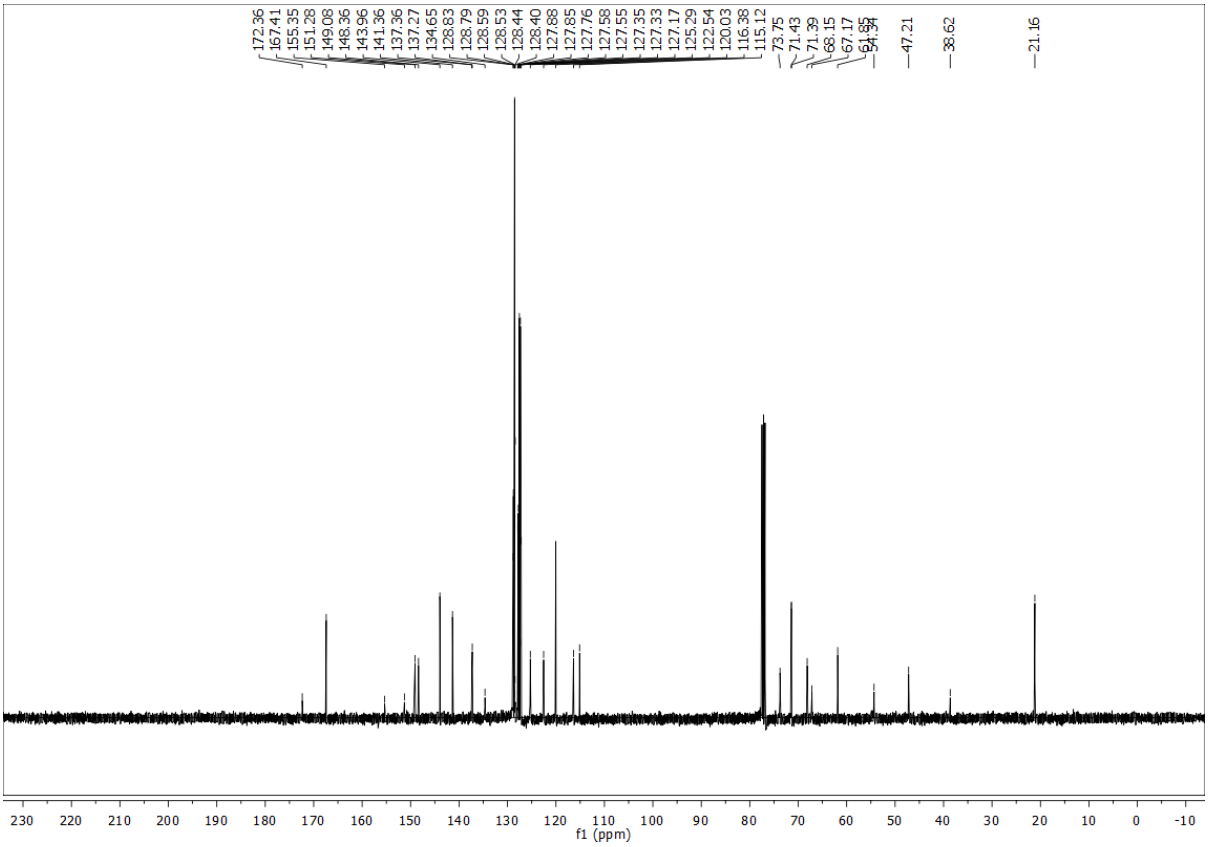


Figure S8. ^{1}H NMR and COSY spectra of Fmoc-L-DOPA[OBn]$_2$-D-Oxd-OBn.



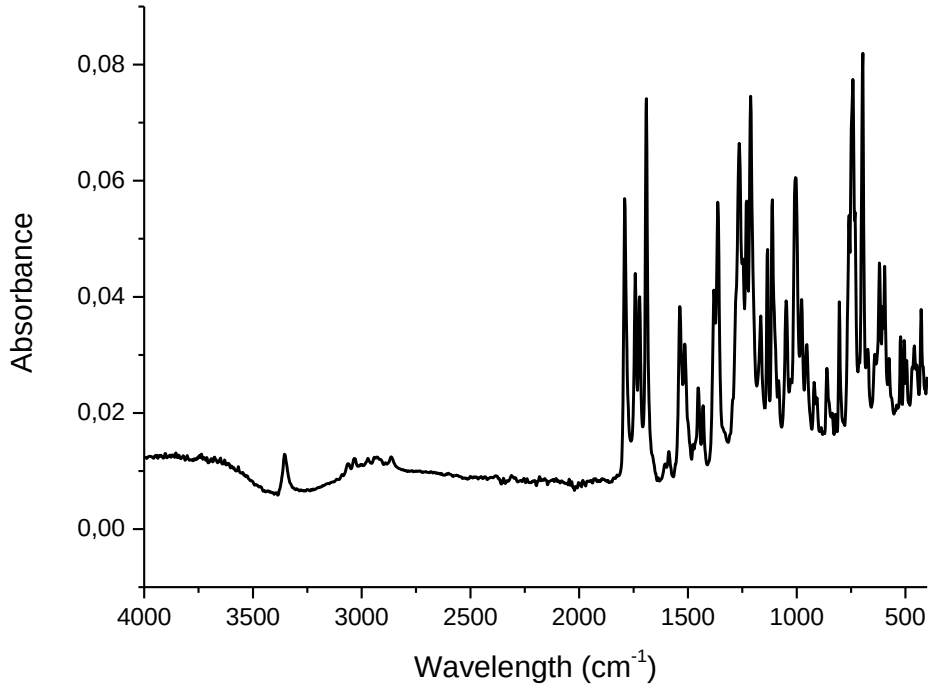


Figure S9. ^{13}C NMR (top) and FT-IR (bottom) spectra of Fmoc-L-DOPA[OBn]$_2$-D-Oxd-OBn.

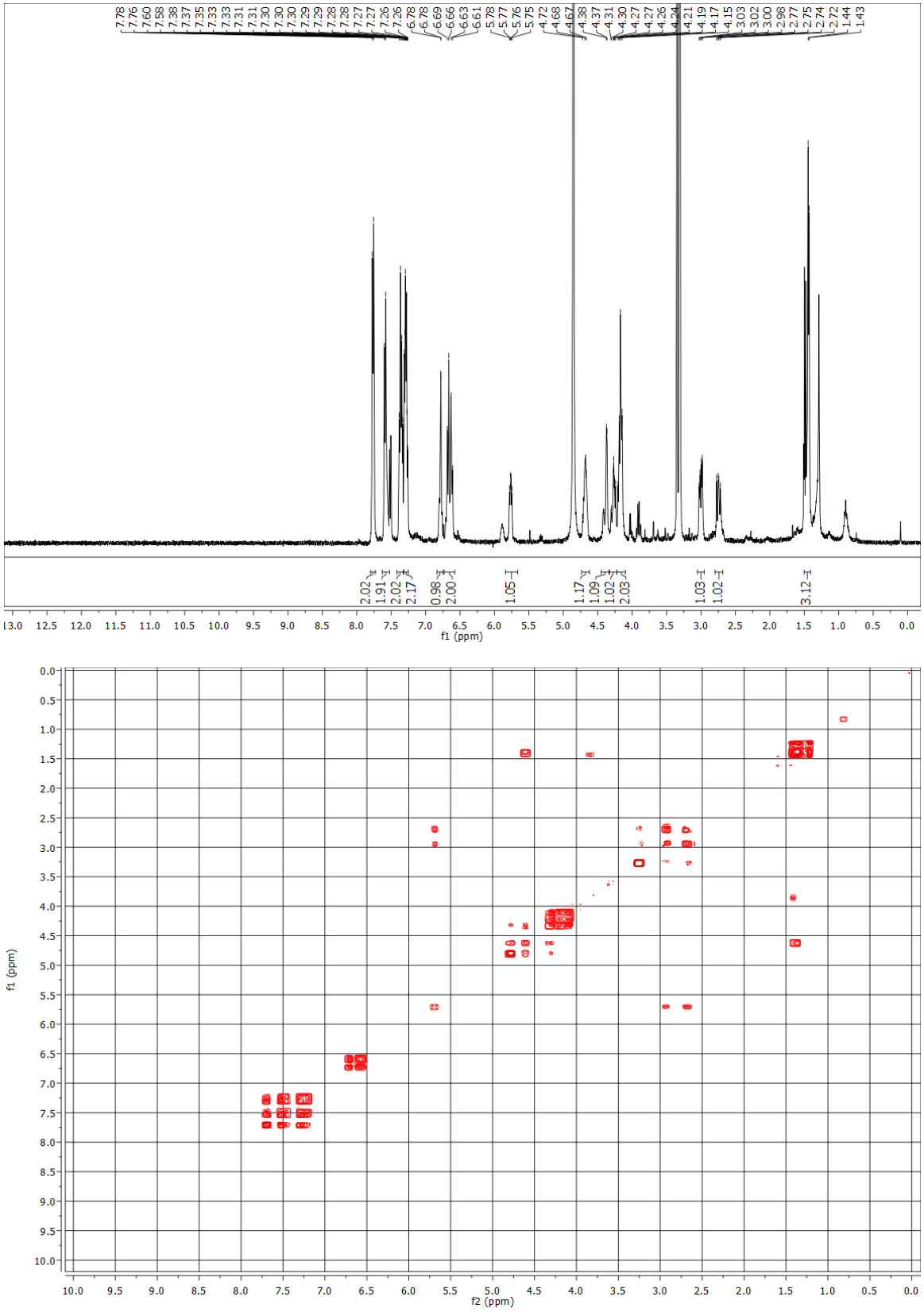
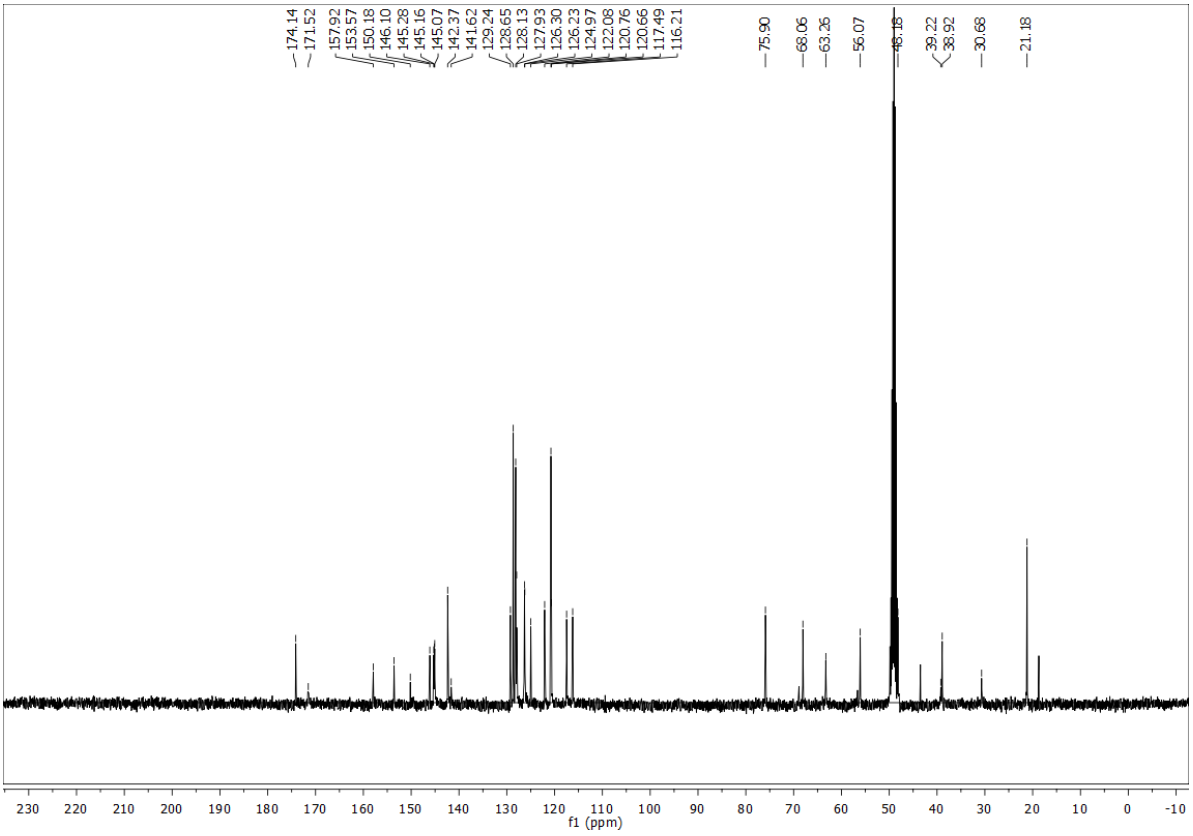


Figure S10. ^{1}H NMR and COSY spectra of Fmoc-L-DOPA-D-Oxd-OH.



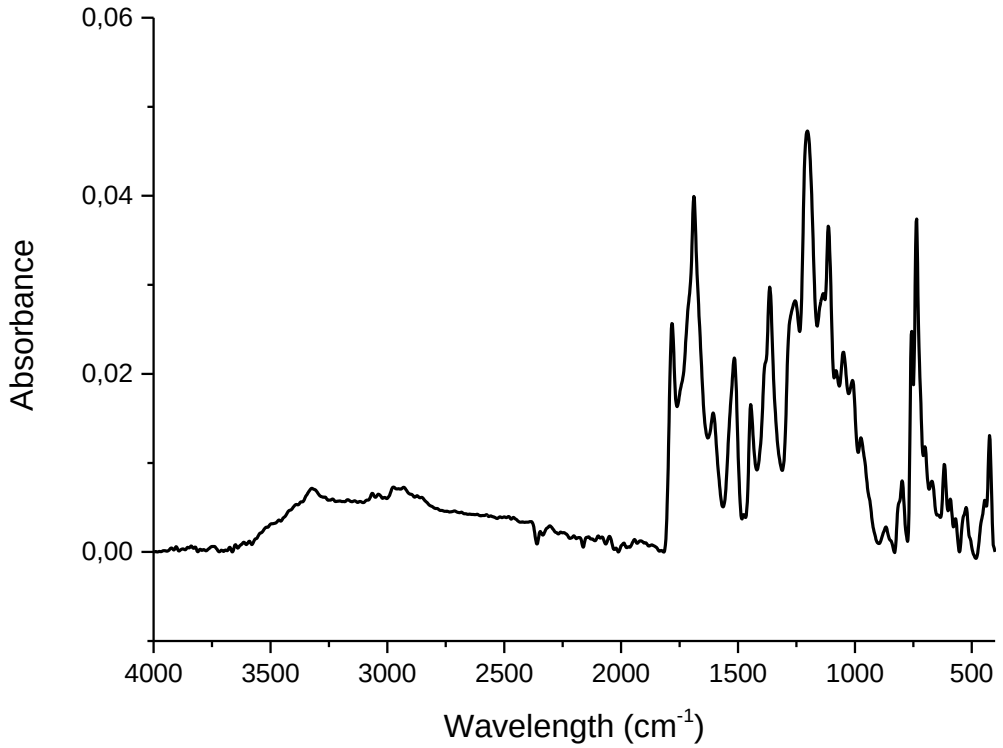


Figure S11. ^{13}C NMR (top) and FT-IR (bottom) spectra of Fmoc-L-DOPA-D-Oxd-OH.

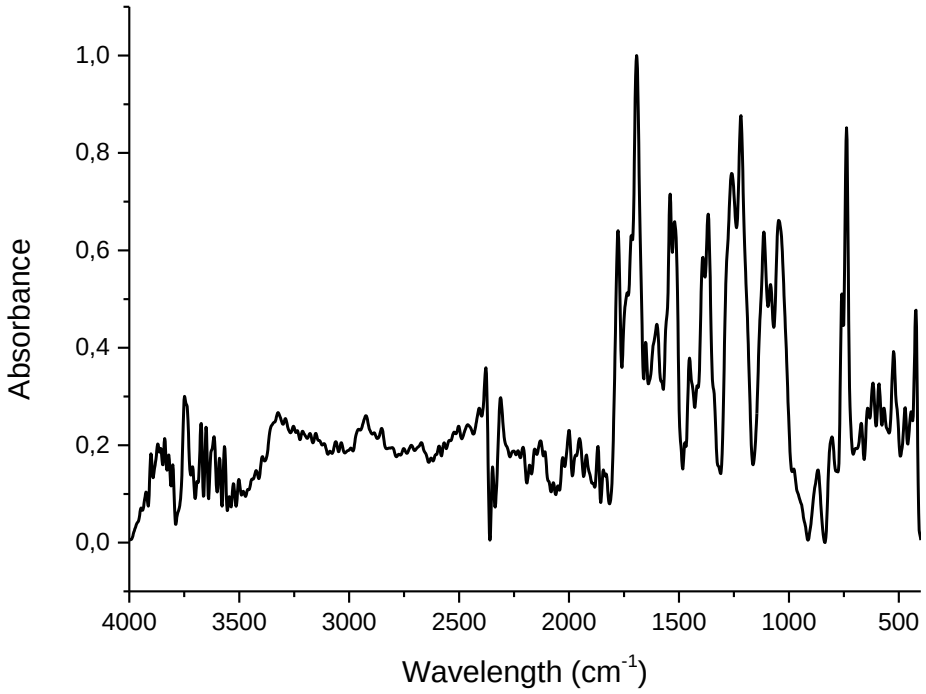


Figure S12. FT-IR spectrum of aerogel **1**.

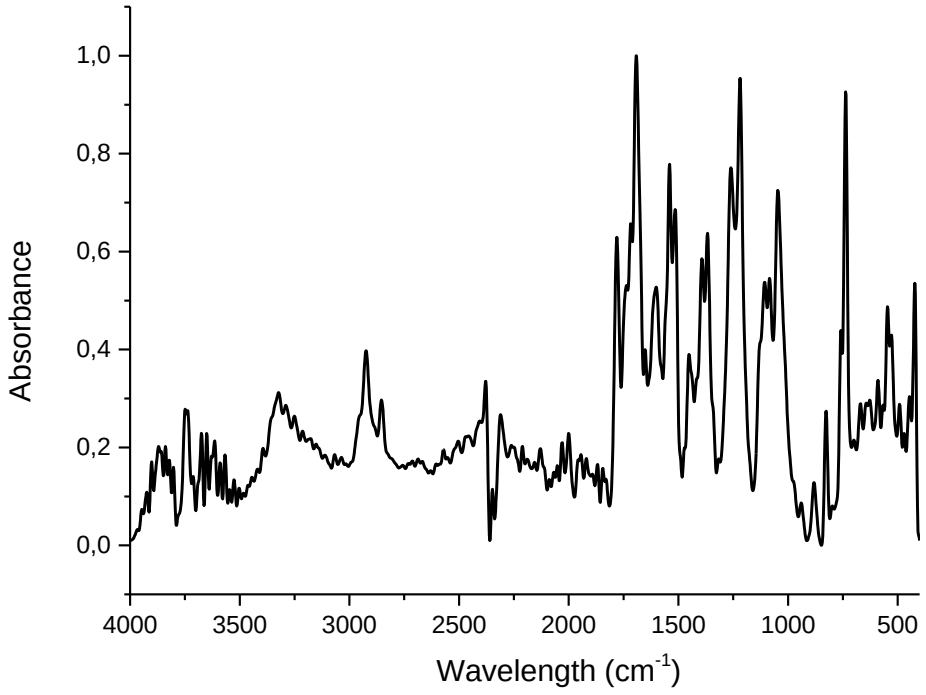


Figure S13. FT-IR spectrum of aerogel **2**.

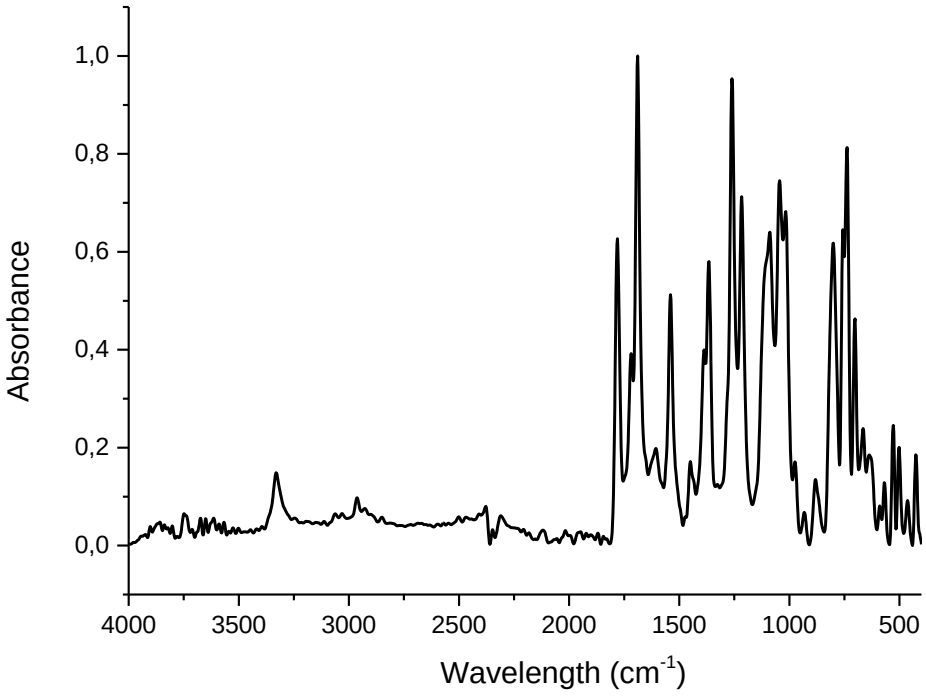


Figure S14. FT-IR spectrum of aerogel **3**.

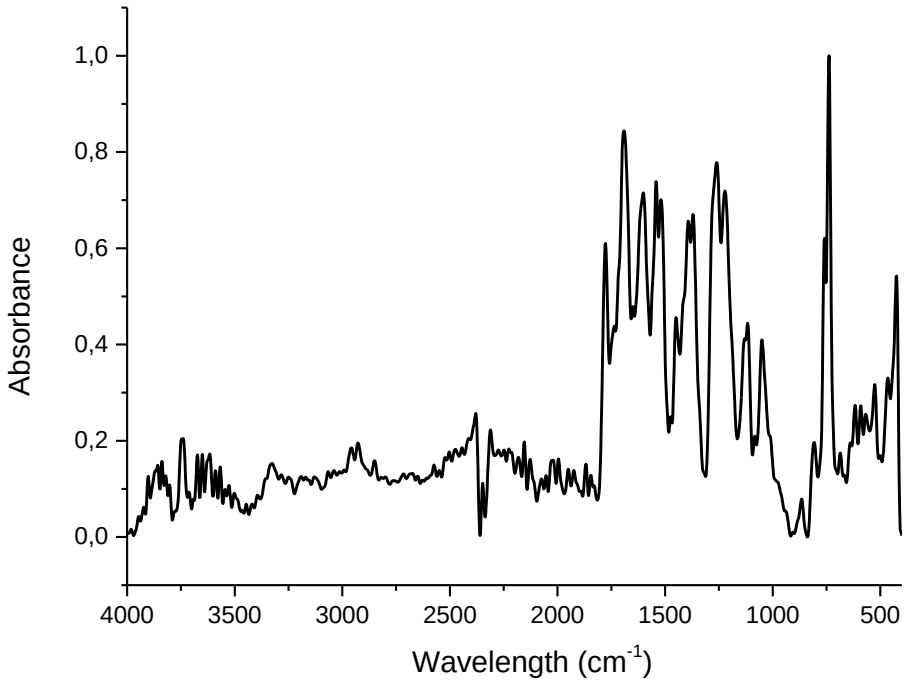


Figure S15. FT-IR spectrum of aerogel **4**.

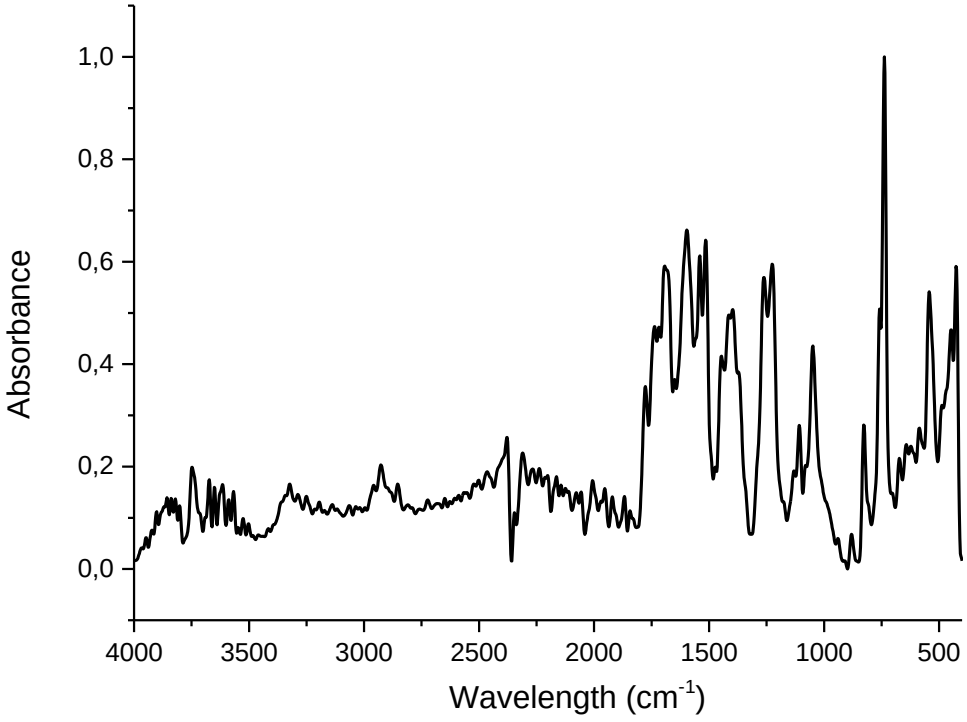


Figure S16. FT-IR spectrum of aerogel **5**.

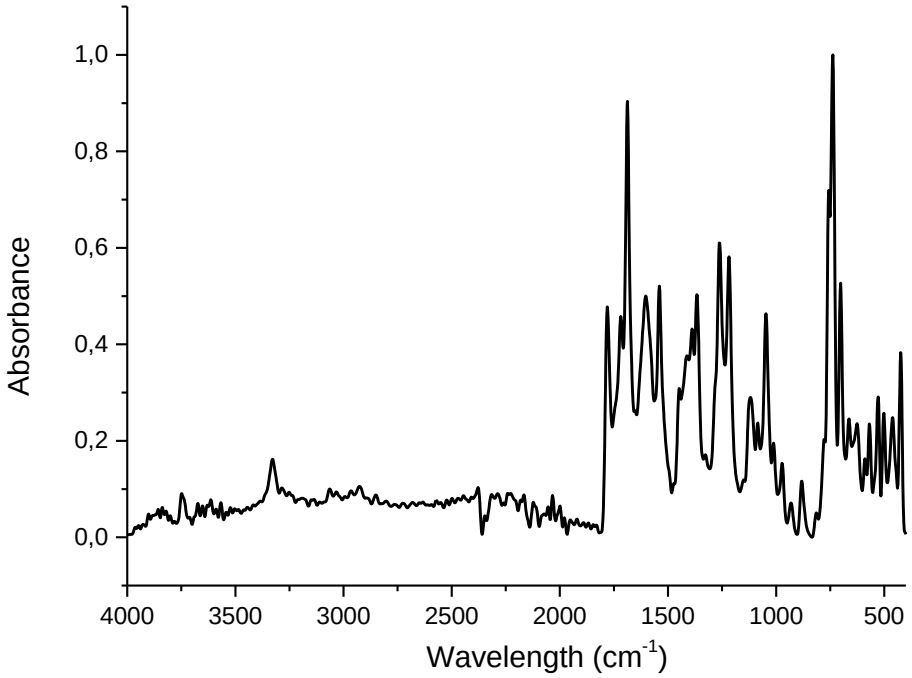


Figure S17. FT-IR spectrum of aerogel **6**.

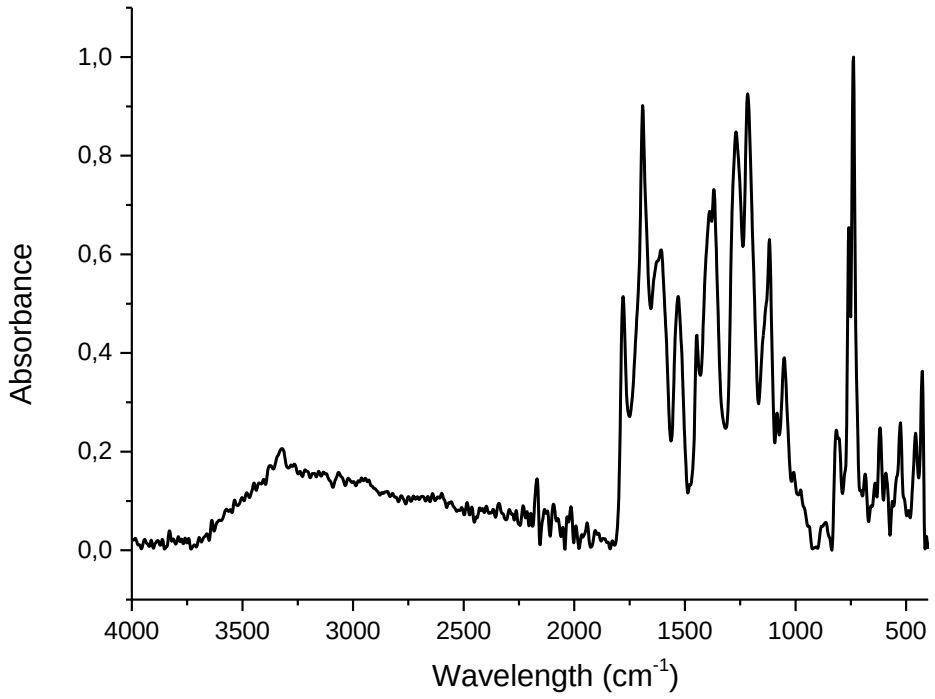


Figure S18. FT-IR spectrum of aerogel **7**.

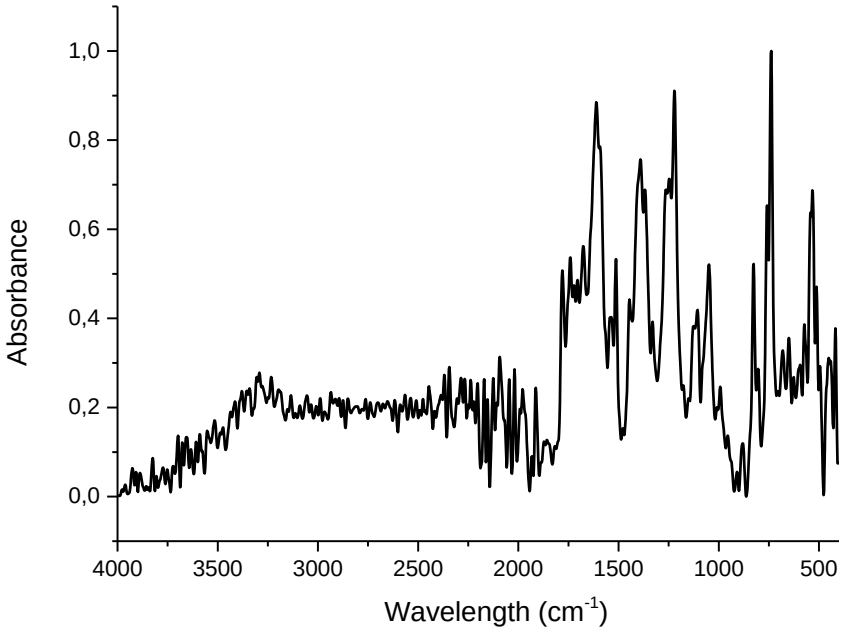


Figure S19. FT-IR spectrum of aerogel **8**.

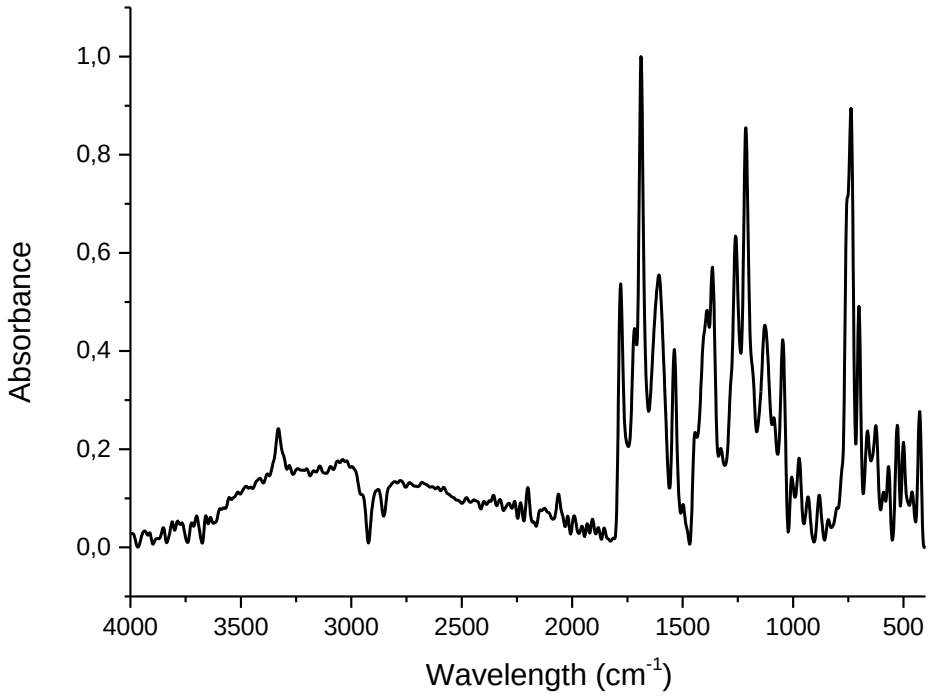


Figure S20. FT-IR spectrum of aerogel **9**.

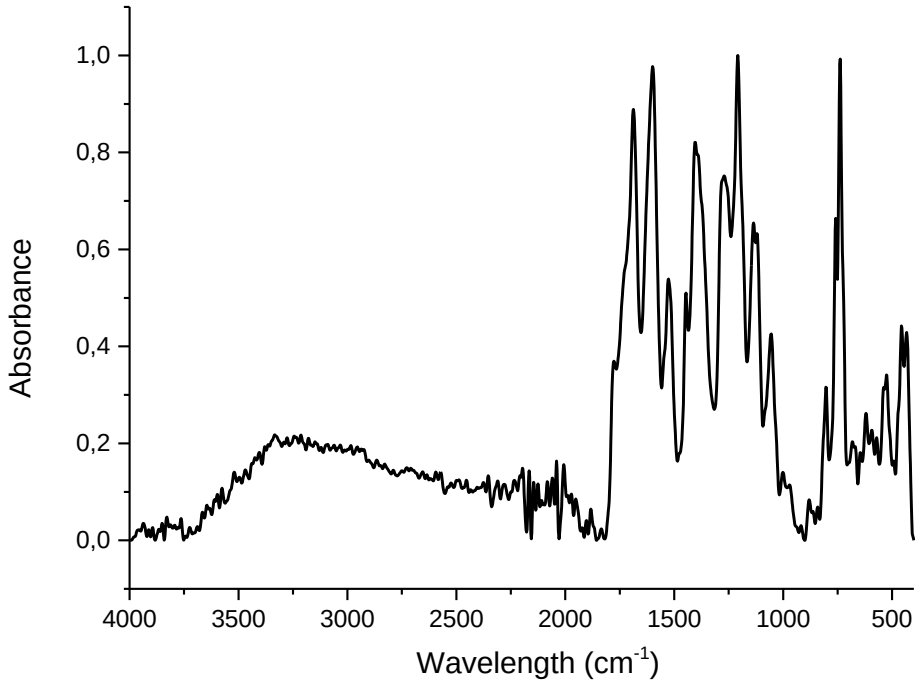


Figure S21. FT-IR spectrum of aerogel **10**.

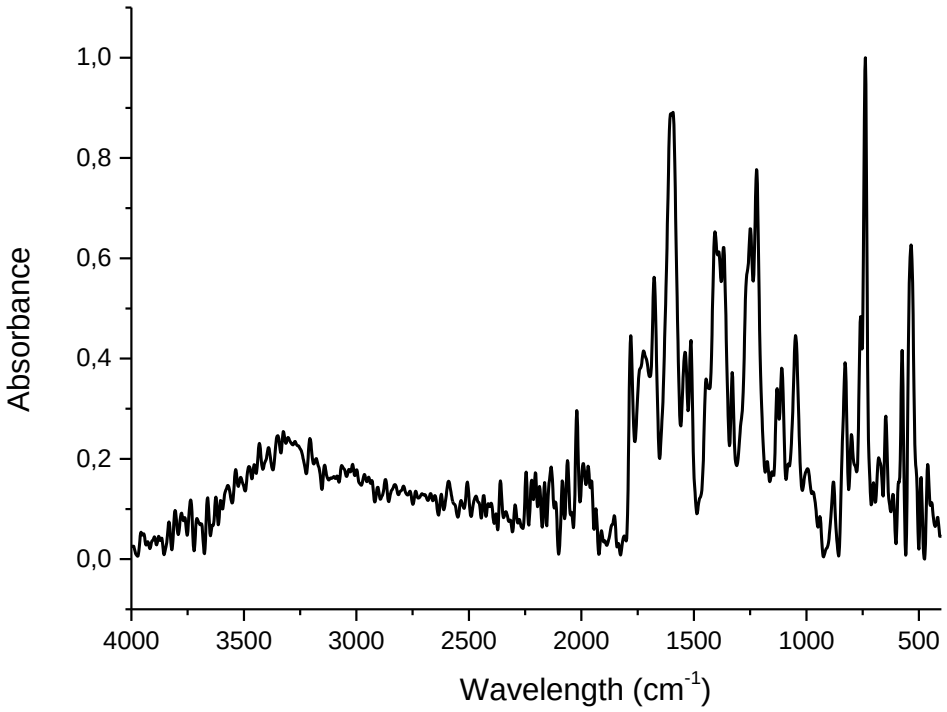


Figure S22. FT-IR spectrum of aerogel **11**.

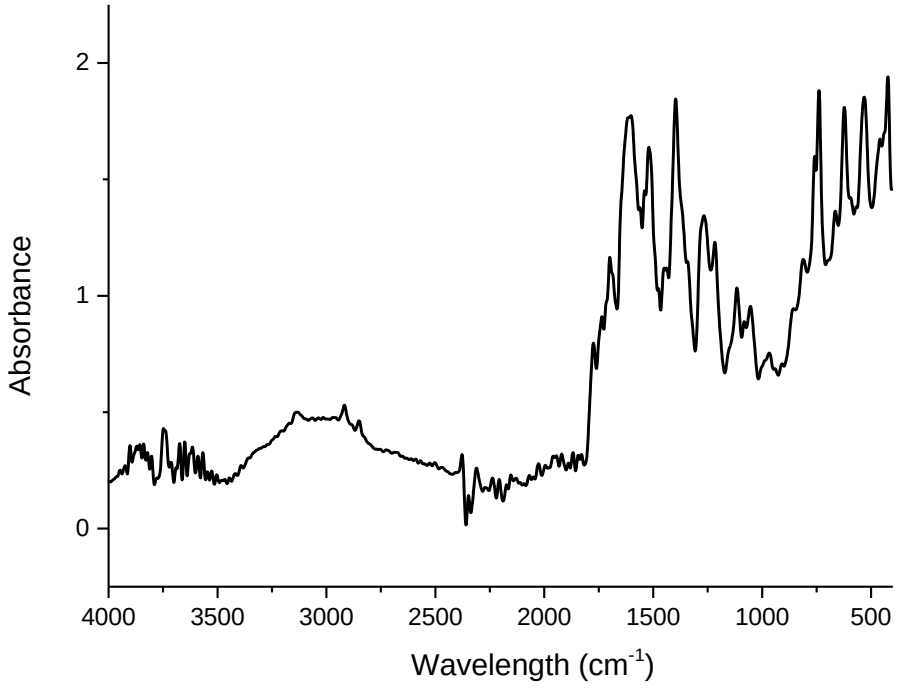


Figure S23. FT-IR spectrum of aerogel **13**.

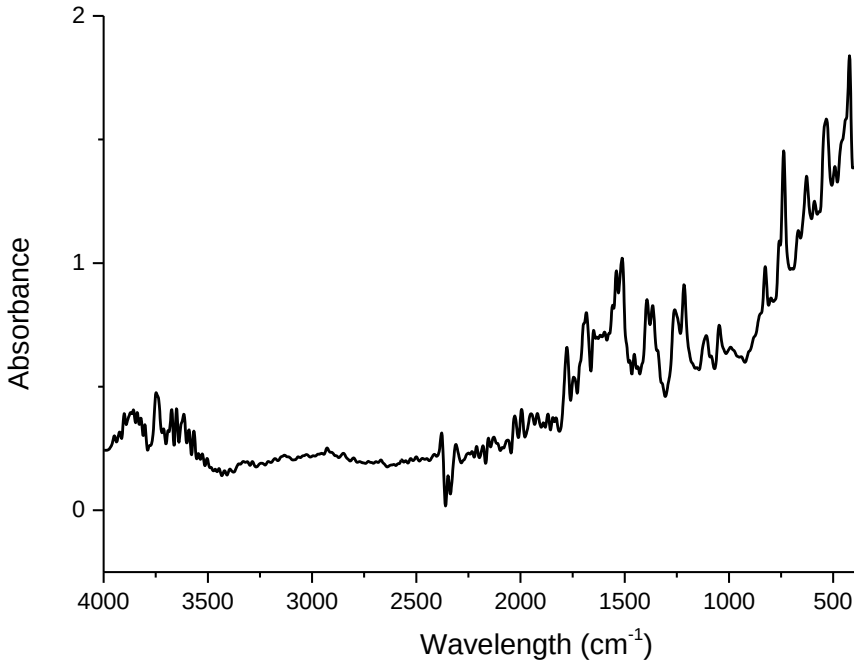


Figure S24. FT-IR spectrum of aerogel **14**.

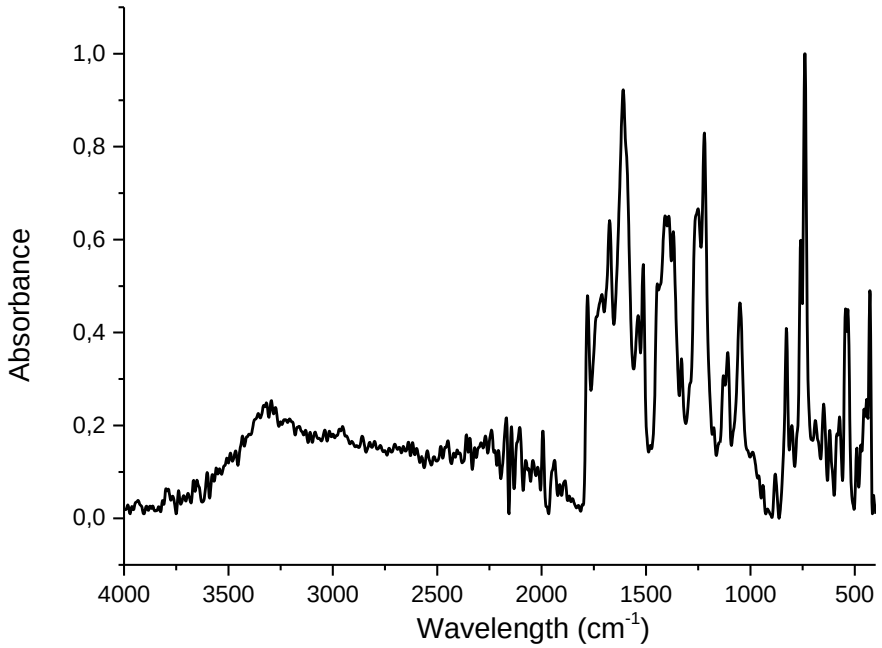


Figure S25. FT-IR spectrum of aerogel **17**.

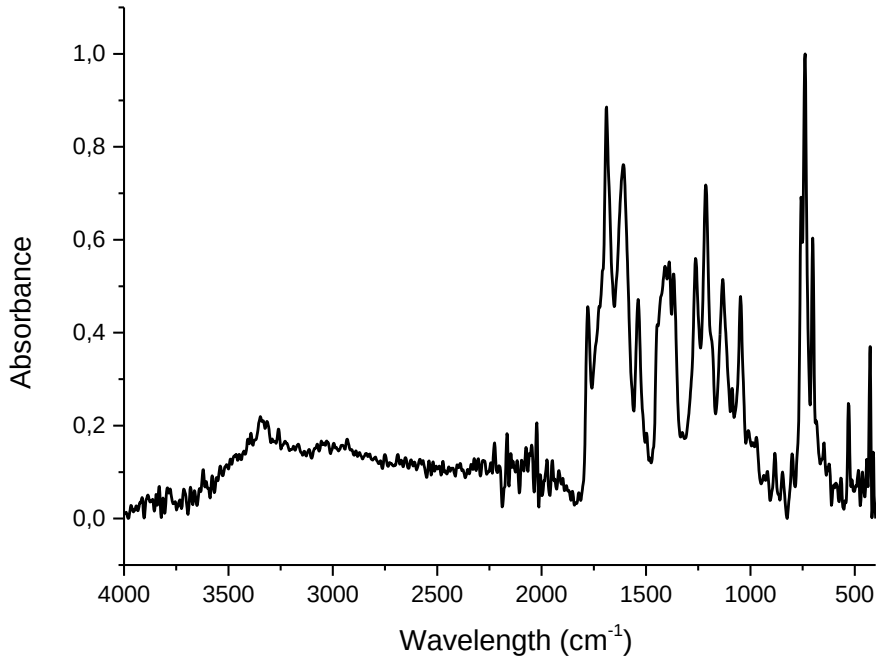


Figure S26. FT-IR spectrum of aerogel **18**.

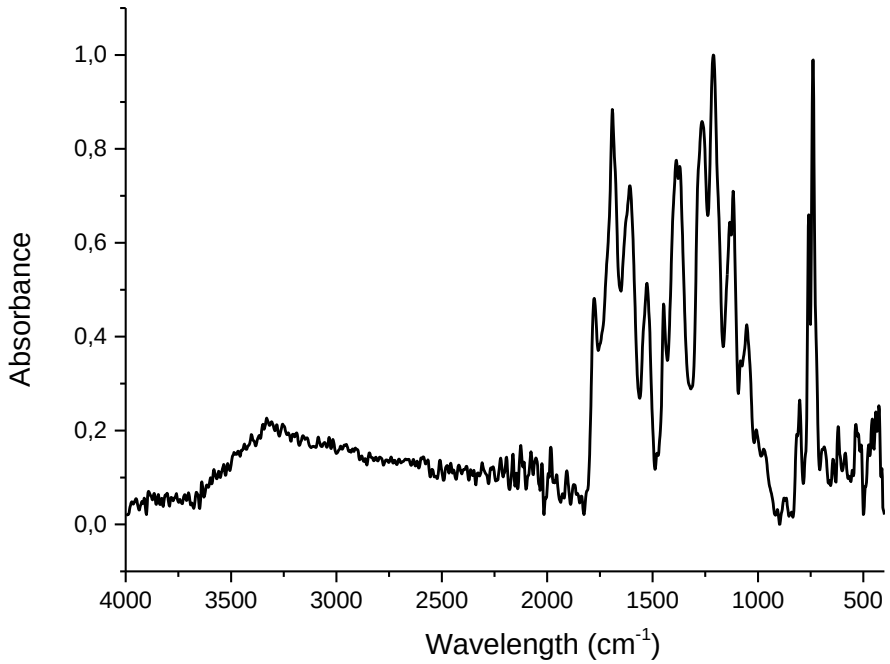


Figure S27. FT-IR spectrum of aerogel **19**.

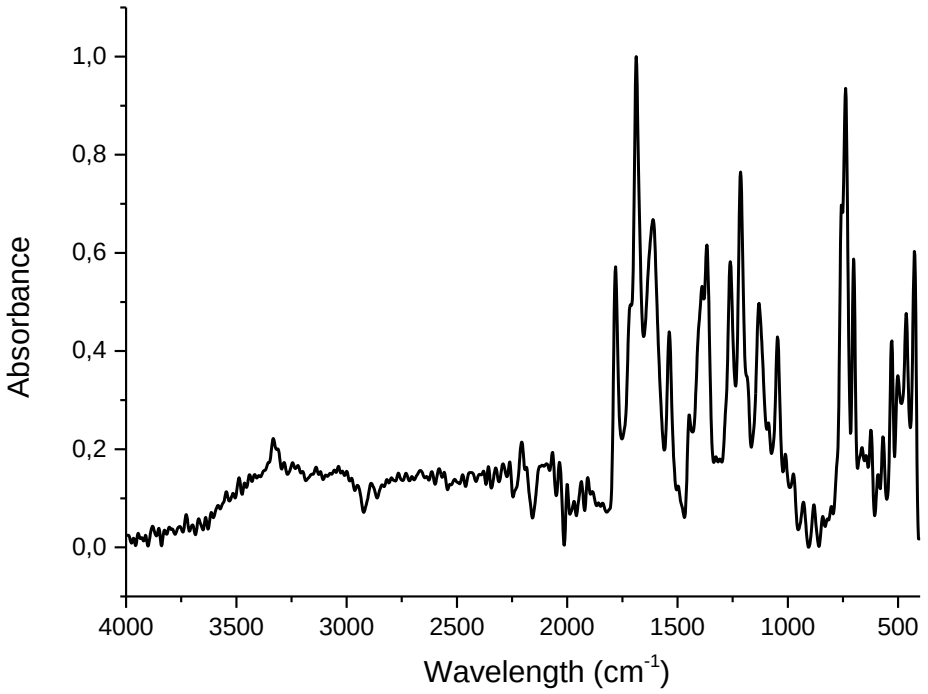


Figure S28. FT-IR spectrum of aerogel **21**.

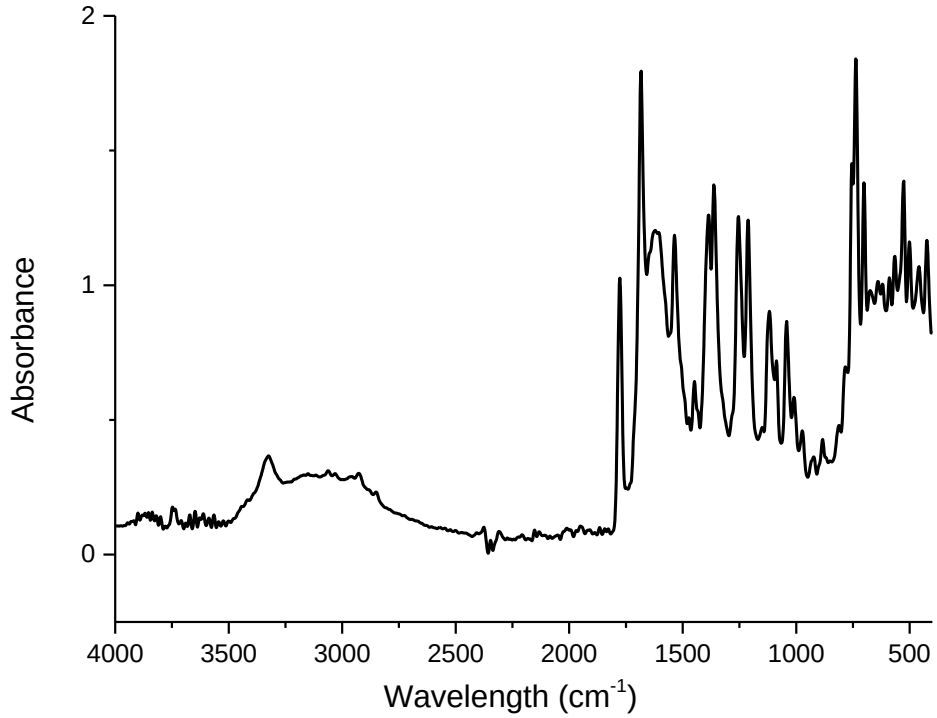


Figure S29. FT-IR spectrum of aerogel **30**.