Electronic Supplementary Material (ESI) for RSC Advances.

Electronic supplementary information

Stimuli-responsive gelators from carbamoyl sugar derivatives and their responses to metal ions and tetrabutylammonium salts

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Part I.

1. Stability of the gels in basic solutions

The gel stability in alkaline conditions was analyzed and the results are summarized in Figure S1. The gels formed by compounds **13** (hexyl) and **17** (benzyl) in EtOH:H_2O (v/v 1:1) were used for the analysis, 0.4 mL of the gels were prepared then 0.4 mL of pH 10 and pH 12 solutions were added to the top of the gel carefully. The gel stability was checked by tilting the vials at certain time intervals (14 h, 36 h, 144 h). The gel formed by gelator **17** with pH 12 solution started to fall apart at 14 h while the other gels were stable for a much longer time (6 days).

A 12 mg sample of compound **13** was added to two vials and 0.4 mL EtOH/H_2O (v/v, 1/1) was added to make the gel. After heating and sonicating each vial, they were left standing at room temperature for 30 minutes undisturbed. Stable gels were formed. The gels for compound **17** were prepared the same way, using 3.0 mg of compound **17** and 0.4 mL EtOH/H_2O (v/v, 1/1); then 0.4 mL pH 10 or pH 12 solution was added to all gels respectively. The ^{1}H NMR spectra of compound **17** recovered from the gel vials (Figure S1-4 d) after the addition of pH 12 solution for 144 h are shown in Figure S1-5.

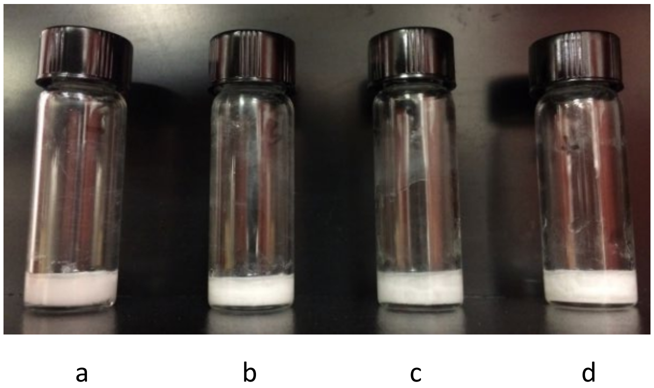


Figure S1-1. a, b) Gels formed by compound **13** in EtOH/H_2O (v/v, 1/1), 30.0 mg/mL; c, d) gels formed by compound **17** in EtOH/H_2O (v/v, 1/1) at 7.5 mg/mL.

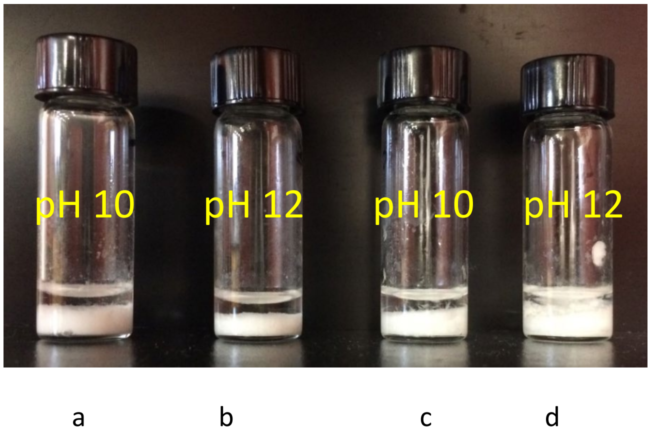


Figure S1-2. The gels in Figure S1-1 with equal volumes (0.4 mL) of basic aqueous solutions after 14 hours.

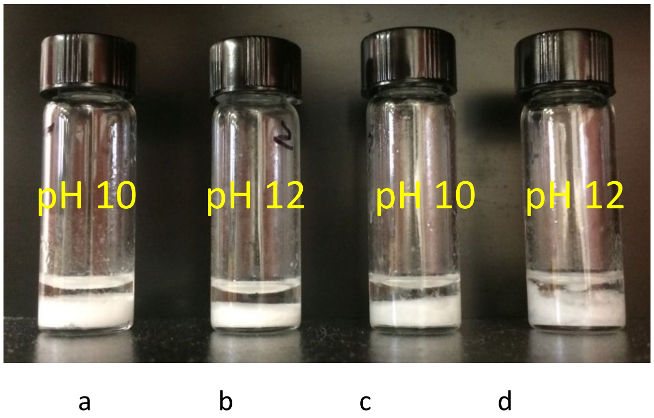


Figure S1-3. The gels in Figure S1-1 with equal volumes (0.4 mL) of basic aqueous solutions after 36 hours.

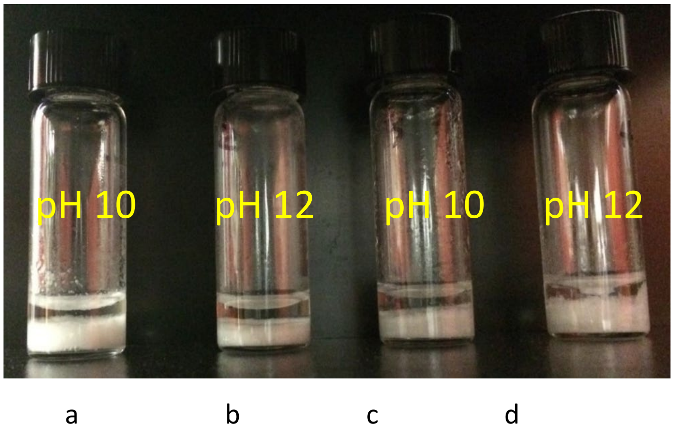


Figure S1-4. The gels in Figure S1-1 with equal volumes (0.4 mL) of basic aqueous solutions after 144 hours (6 days).

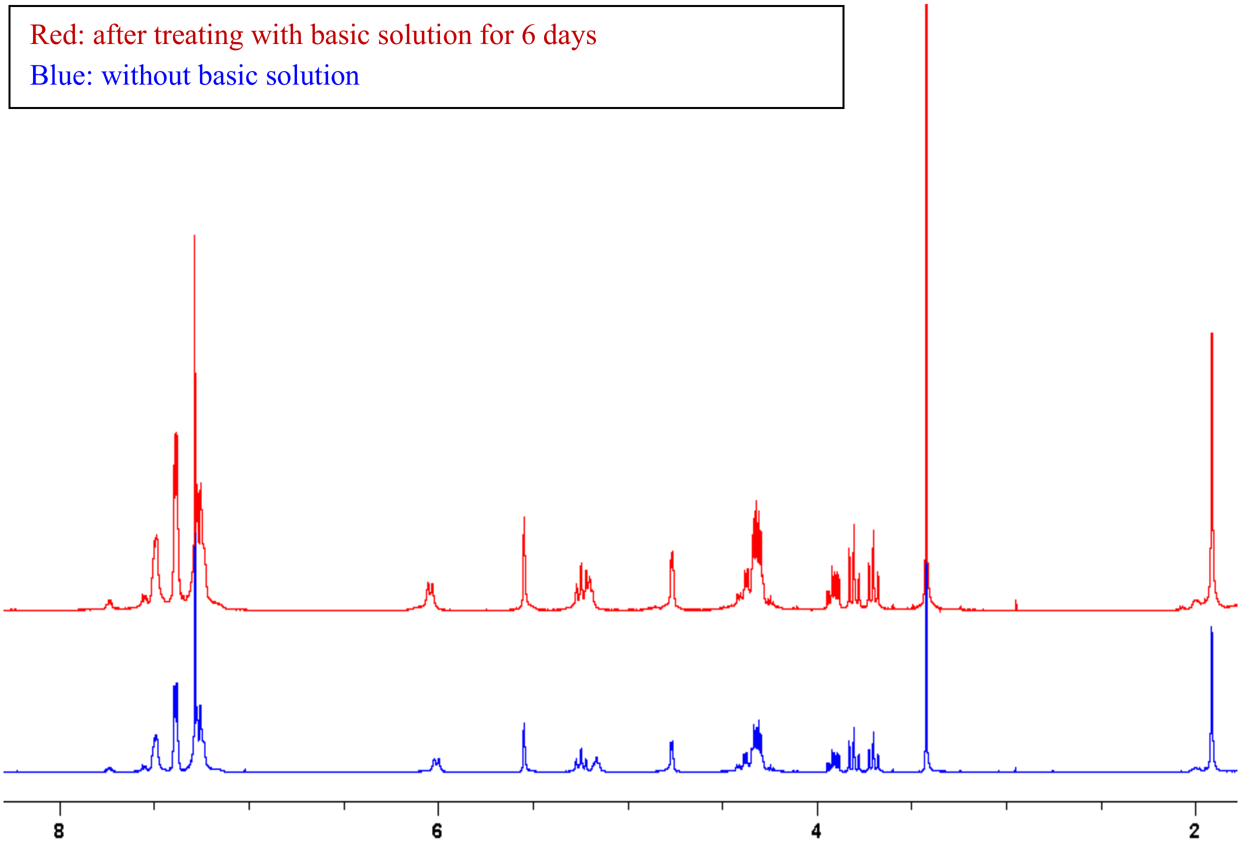


Figure S1-5. ^{1}H NMR spectra of compound **17** before (blue) and after addition of pH 12 solution (red), the NMR spectrum in red shows the compound extracted from the mixture in pH 12 solution for 6 days.

2. Stability of compound 18 in an organic base

The properties of the compound **18** under basic conditions were also analyzed by treating with DBU. A gel was prepared with compound **18** in DMSO:H_2O (v/v 1:1), then 5 equiv. of DBU was added to the vial. The mixture was reheated and then left standing at rt for 1 h, the gel didn’t reform. The mixture was analyzed using TLC and NMR, the results indicate that **18** was stable in the presence of 5 equiv. of DBU. The sample was prepared using compound **18** (2 mg, 4.11×10^{-3} mmol, 1 equiv.) in 0.8 mL of DMSO/H_2O (v/v 1:1) and 1,8-diazabicyclo(5.4.0) undec-7-ene (DBU) (3.1 mg, 2.055×10^{-2} mmol, 5 equiv.).

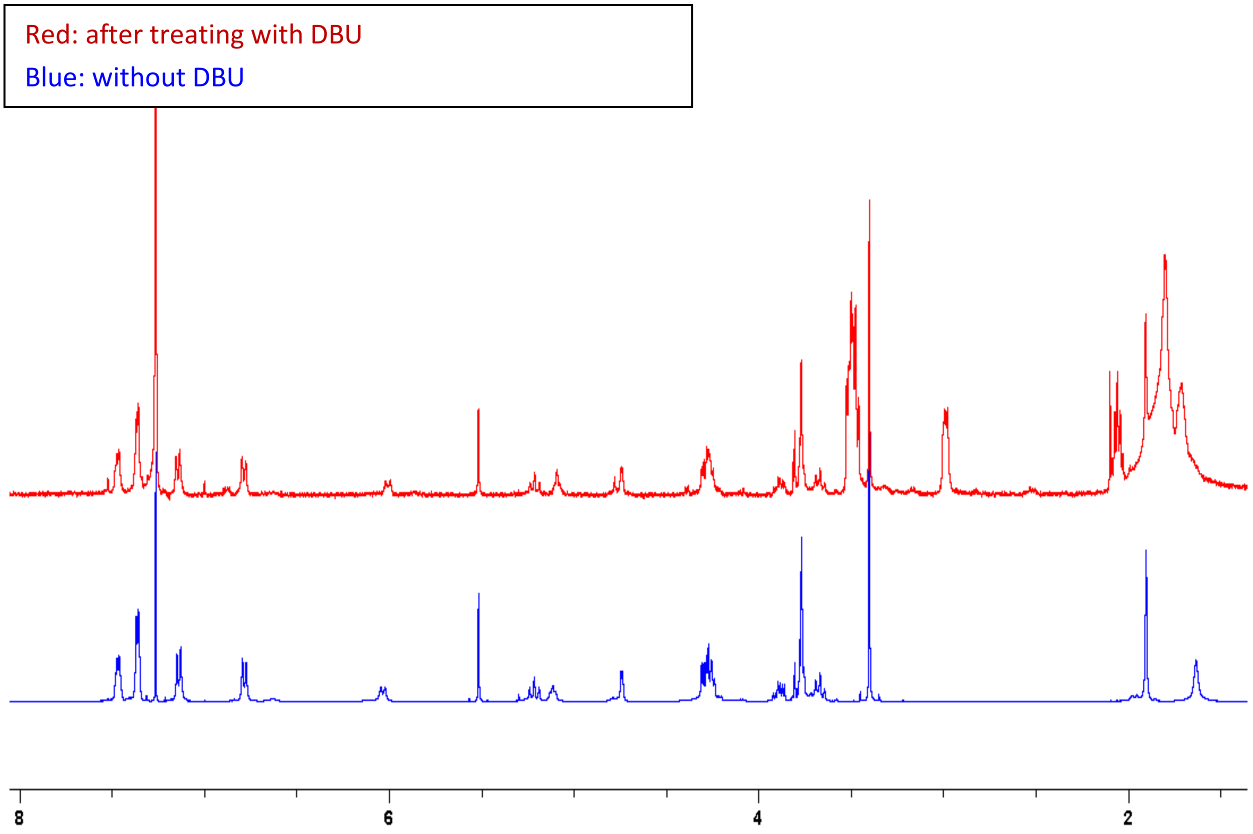
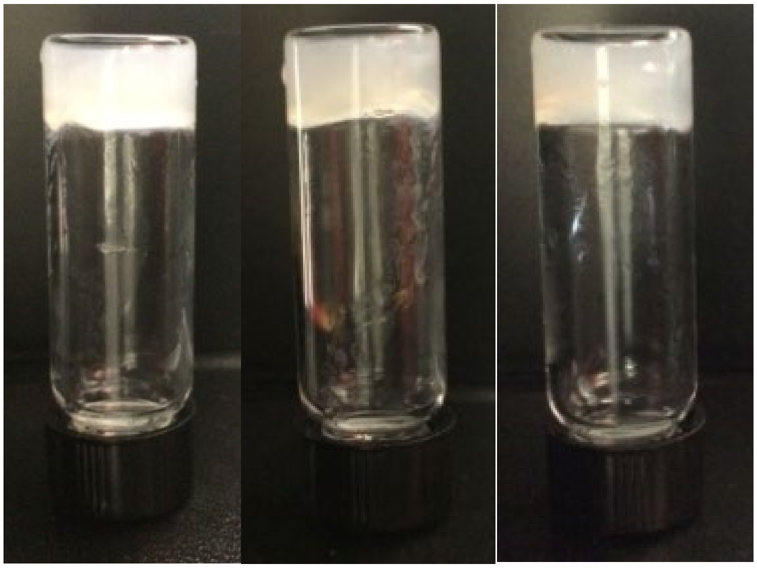


Figure S2. ^{1}H NMR spectra of compound **18** before (blue) and after addition of DBU (red).

3. Gelation of tetramethylammonium bromide electrolytes

Compound **18** (2.0 mg, 4.11×10^{-3} mmol, 1.0 equiv.) formed a stable gel (Figure S3-a) in 0.8 mL of DMSO:H_2O (v/v 1:1) in the presence of 0.5 equiv. of tetramethylammonium bromide (0.32 mg, 2.05×10^{-3} mmol). To the same gel in Fig S3-a, another 4.5 equiv. of the TMABr (2.85 mg, 1.85×10^{-2} mmol) was added, the mixture was heated to dissolve the salt and allowed to cool down to rt for 30 minutes, a stable gel reformed and is depicted in Figure S3-b. To the gel in Figure 3-b, an additional 5 equiv. of TMABr (3.2 mg, 2.06×10^{-2} mmol) was added and the mixture was heated again to a clear solution, upon cooling a stable gel reformed, this is shown in Figure S3-c.



a b c

Figure S3. The gels formed by compound **18** in the presence of different amounts of TMABr. All samples contain compound **18** (2.0 mg, 4.11×10^{-3} mmol, 1.0 equiv.) in 0.8 mL of DMSO:H_2O (v/v 1:1) and the TMABr for a) 0.32 mg, 2.05×10^{-3} mmol, 0.5 equiv.; b) 0.32+2.85=3.17 mg, 2.06×10^{-2} mmol, 5.0 equiv.; c) 0.32+2.85+3.2 =6.4 mg, 4.11×10^{-2} mmol, 10.0 equiv.

4. Gelation of tetrabutylammonium salts and response to chemical stimuli

Compound **18** (2.0 mg, 4.11×10^{-3} mmol, 1.0 equiv.) was added in 0.8 mL of DMSO:H_2O (v/v 1:1) followed by the addition of 0.5 equiv. of tetrabutylammonium salts of iodide, bromide, bisulfate and fluoride (0.8 mg, 0.7 mg, 0.7 mg, 0.7 µL, 2.06×10^{-3} mmol, 0.5 equiv. to compound **18**). Gels were formed after heating and sonicating the mixtures in the vial. Upon further addition of 4.5 equiv. of the tetrabutylammonium salts of iodide, bromide, bisulfate and fluoride (7.2 mg, 6.3 mg, 6.3 mg and 6.3 µL, 1.85×10^{-2} mmol, 4.5 equiv.) to compound **18** the gels reformed after heating and sonicating the mixtures in the vial. After adding another 5 equiv. of the tetrabutylammonium salts of iodide, bromide, bisulfate and fluoride (8.0 mg, 7.0 mg, 7.0 mg and 7.0 µL, 2.06×10^{-2} mmol, 5.0 equiv.) to the same vials, followed by reheating and sonicating, the gels containing TBA salts of bromide and bisulfate became unstable. After adding 10 equiv. of acetic acid (2.3 µL, 4.11×10^{-2} mmol) to all vials, the gel properties containing TBABr salts were restored.

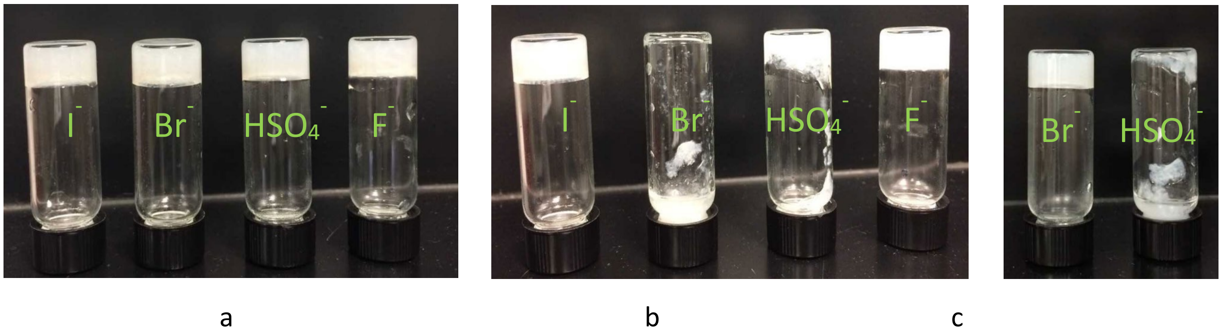
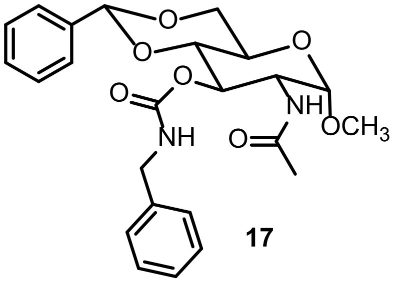


Figure S4. a) Gel pictures of compound **18** (2 mg) in 8 mL of DMSO:H_2O (v/v 1:1) with 5 equiv. of TBA salts of iodide, bromide, bisulfate and fluoride; b) Gel pictures after adding up to 10 equiv. of TBA salts; c) Pictures of gel containing 10 equiv. of TBA salts after adding 10 equiv. of acetic acid.

5. Rheological data and amplitude experiments of compounds 17 and 20

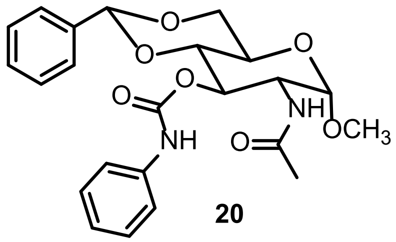


17

EtOH:H$_2$O=1:2
2.5 mg/mL opaque

Compound **17** 2.5 mg/mL, EtOH/H$_2$O, 1:2			
Angular frequency	**Storage modulus (*G′*)**	**Loss modulus (*G″*)**	***G′*/*G″***
rad/s	**Pa**	**Pa**	
0.1	1333.1	438.395	3.040865
0.15849	1530.59	436.608	3.505639
0.251189	1686.17	418.224	4.031739
0.398107	1801.42	414.081	4.350405
0.630957	1899.84	401.489	4.731985
1.0	1982.24	391.607	5.061809
1.5849	2082.31	373.351	5.577352
2.51189	2157.96	362.271	5.956756
3.98105	2235.16	347.212	6.43745
6.30957	2307.65	350.14	6.590649
10.0001	2375.95	338.832	7.012177
15.849	2452.18	337.418	7.267484
25.1188	2531.67	335.825	7.538659
39.8105	2600.78	339.322	7.664637
63.0957	2689.22	352.276	7.633844
100.0	2806.4	347.122	8.084766

Table S1. Storage modulus (*G′*), loss modulus (*G″*) and *G′*/*G″* values for the gel formed by compound **17** in EtOH:H$_2$O (v/v 1/2) at different angular frequencies.

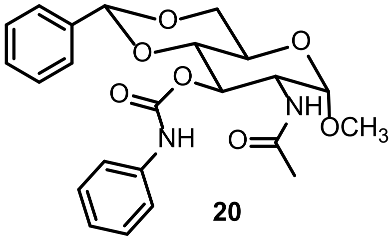


20

EtOH:H_2O=1:1
3.3 mg/mL opaque

Compound **20** 3.3 mg/mL, EtOH/H_2O, 1:1			
Angular frequency	**Storage modulus (*G′*)**	**Loss modulus (*G″*)**	***G′/G″***
rad/s	**Pa**	**Pa**	
0.1	10557.8	2475.75	4.264486
0.15849	11818.2	2346.79	5.0359
0.251189	12616.0	2293.77	5.500116
0.398107	13364.7	2285.43	5.847784
0.630957	13981.7	2284.54	6.120138
1.0	14507.8	2238.46	6.481152
1.5849	15078.1	2236.24	6.742613
2.51189	15618.6	2304.5	6.777435
3.98105	16176.3	2302.41	7.025812
6.30957	16719.1	2363.85	7.072826
10.0001	17263.0	2412.86	7.15458
15.849	17866.9	2463.27	7.253326
25.1188	18443.8	2595.99	7.104727
39.8105	19151.6	2693.74	7.109669
63.0957	19800.1	2851.01	6.944942
100.0	20621.3	2755.38	7.484013

Table S2. Storage modulus (*G′*), loss modulus (*G″*) and *G′/G″* values for the gel formed by compound **20** in EtOH:H_2O (v/v 1/1) at different angular frequencies.

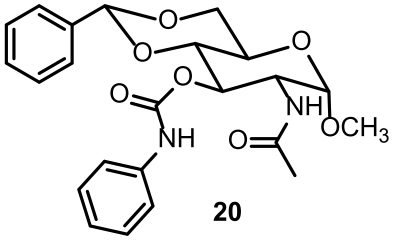


20

EtOH:H_2O=1:2
2.5 mg/mL opaque

Compound **20** 2.5 mg/mL, EtOH/H_2O, 1:2			
Angular frequency	**Storage modulus (*G′*)**	**Loss modulus (*G″*)**	***G′*/*G″***
rad/s	**Pa**	**Pa**	
0.1	21201.9	4744.87	4.264486
0.15849	23210.7	4322.71	5.0359
0.251189	24573.6	4107.44	5.500116
0.398107	25860.4	4019.82	5.847784
0.630957	26976.3	3976.89	6.120138
1.0	28049.6	4041.99	6.481152
1.5849	29143.1	4029.59	6.742613
2.51189	30199.0	4087.21	6.777435
3.98105	31318.0	4160.08	7.025812
6.30957	32481.4	4133.09	7.072826
10.0001	33641.1	4231.85	7.15458
15.849	34847.6	4250.01	7.253326
25.1188	36097.0	4285.21	7.104727
39.8105	37341.3	4381.39	7.109669
63.0957	38353.0	4484.01	6.944942
100.0	40213.0	3601.81	7.484013

Table S3. Storage modulus (*G′*), loss modulus (*G″*) and *G′*/*G″* values for the gel formed by compound **20** in EtOH:H_2O (v/v 1/2) at different angular frequencies.

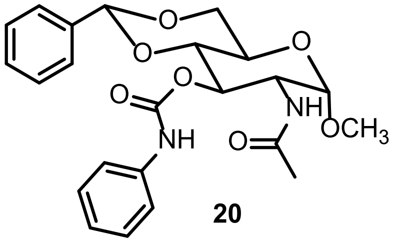


20

DMSO:H_2O=1:1
4.0 mg/mL opaque

Compound **20** 4.0 mg/mL, DMSO/H_2O, 1:1			
Angular frequency	**Storage modulus (*G′*)**	**Loss modulus (*G″*)**	***G′*/*G″***
rad/s	**Pa**	**Pa**	
0.1	5092.46	1682.21	3.027244
0.15849	5511.36	1625.87	3.389791
0.251189	5697.19	1544.32	3.689125
0.398107	5973.17	1404.64	4.252456
0.630957	6241.91	1307.95	4.772285
1.0	6357.21	1230.38	5.166867
1.5849	6537.37	1191.55	5.486442
2.51189	6679.0	1147.93	5.818299
3.98105	6808.81	1039.82	6.548066
6.30957	6843.25	1067.1	6.412942
10.0001	7039.21	1027.74	6.849213
15.849	7199.56	979.784	7.348109
25.1188	7309.85	970.764	7.529997
39.8105	7428.82	958.687	7.748952
63.0957	7492.72	976.236	7.675111
100.0	7685.26	975.933	7.874782

Table S4. Storage modulus (*G′*), loss modulus (*G″*) and *G′*/*G″* values for the gel formed by compound **20** in DMSO:H_2O (v/v 1/1) at different angular frequencies.



20

Toluene
2.8 mg/mL opaque

Compound **20** 2.8 mg/mL, Toluene			
Angular frequency	**Storage modulus (*G′*)**	**Loss modulus (*G″*)**	***G′*/*G″***
rad/s	**Pa**	**Pa**	
0.1	652.469	61.6158	10.58931
0.15849	686.316	55.8585	12.28669
0.251189	716.804	51.8025	13.83725
0.398107	749.154	49.9245	15.00574
0.630957	762.787	47.874	15.93322
1.0	778.765	43.6425	17.84419
1.5849	793.429	41.049	19.32883
2.51189	806.645	42.1127	19.15444
3.98105	816.782	41.825	19.52856
6.30957	830.491	41.9019	19.81989
10.0001	841.69	41.0918	20.48316
15.849	858.033	45.7647	18.7488
25.1188	870.971	48.3439	18.01615
39.8105	887.049	54.2949	16.33761
63.0957	912.425	63.218	14.43299
100.0	958.208	71.2342	13.45152

Table S5. Storage modulus (*G′*), loss modulus (*G″*) and *G′*/*G″* values for the gel formed by compound **20** in toluene at different angular frequencies.

Amplitude sweep experiments for rheology study

Amplitude sweep experiments were performed by the HR-2 Discovery Hybrid Rheometer from TA Instruments. All gels at their minimum gelation concentration were prepared in a 1-dram vial in different solvents (or solvent mixtures) and they were left undisturbed on the bench for 2 hours. The sample (approximately 1 mL) was placed on the steel plate of the rheometer. The experimental temperature was 25 °C. The samples were subjected to an amplitude sweep between 25-mm peltier plate and steel plate with a gap of 100 µm. The angular frequency was set as 10.0 rad/s. The operating and processing software used was TRIOS. The results for the storage moduli (*G′*) and loss moduli (*G″*) were as a function of oscillation strain in a range from 0.125% to 125%.

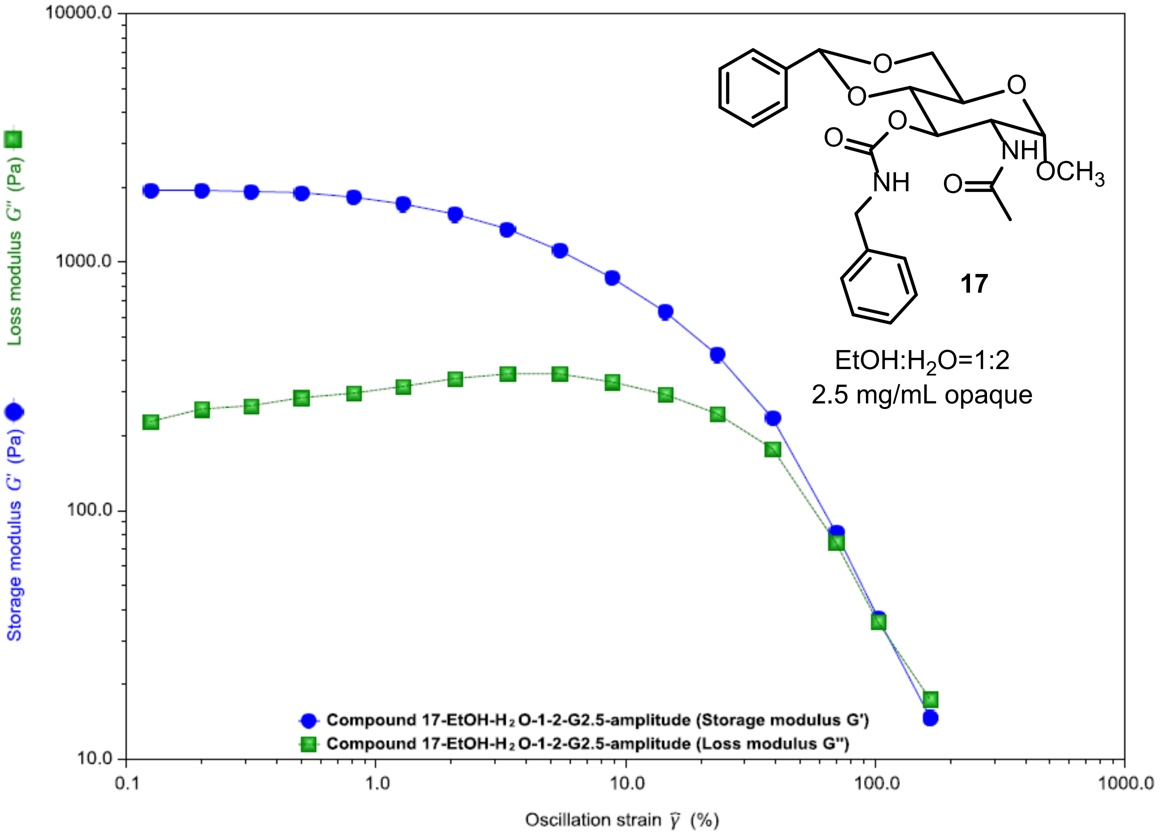
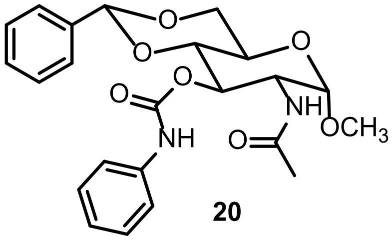


Figure S5-1. Rheological properties of the amplitude sweep experiment for the gel formed by compound **17** in EtOH:H_2O (v/v 1/2).



20

$EtOH:H_2O=1:1$
3.3 mg/mL opaque

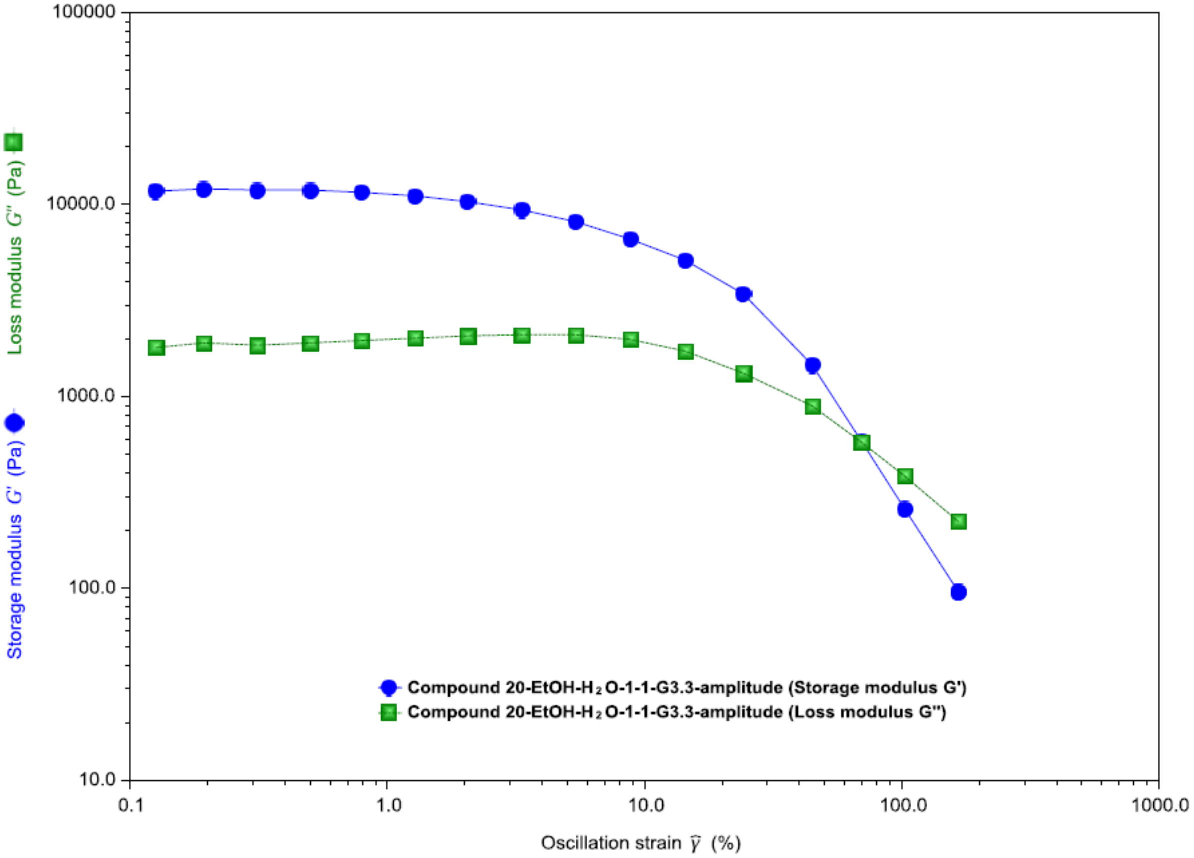
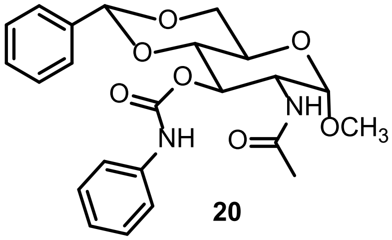


Figure S5-2. Rheological properties of the amplitude sweep experiment for the gel formed by compound **20** in $EtOH:H_2O$ (v/v 1/1).



20

EtOH:H$_2$O=1:2
2.5 mg/mL opaque

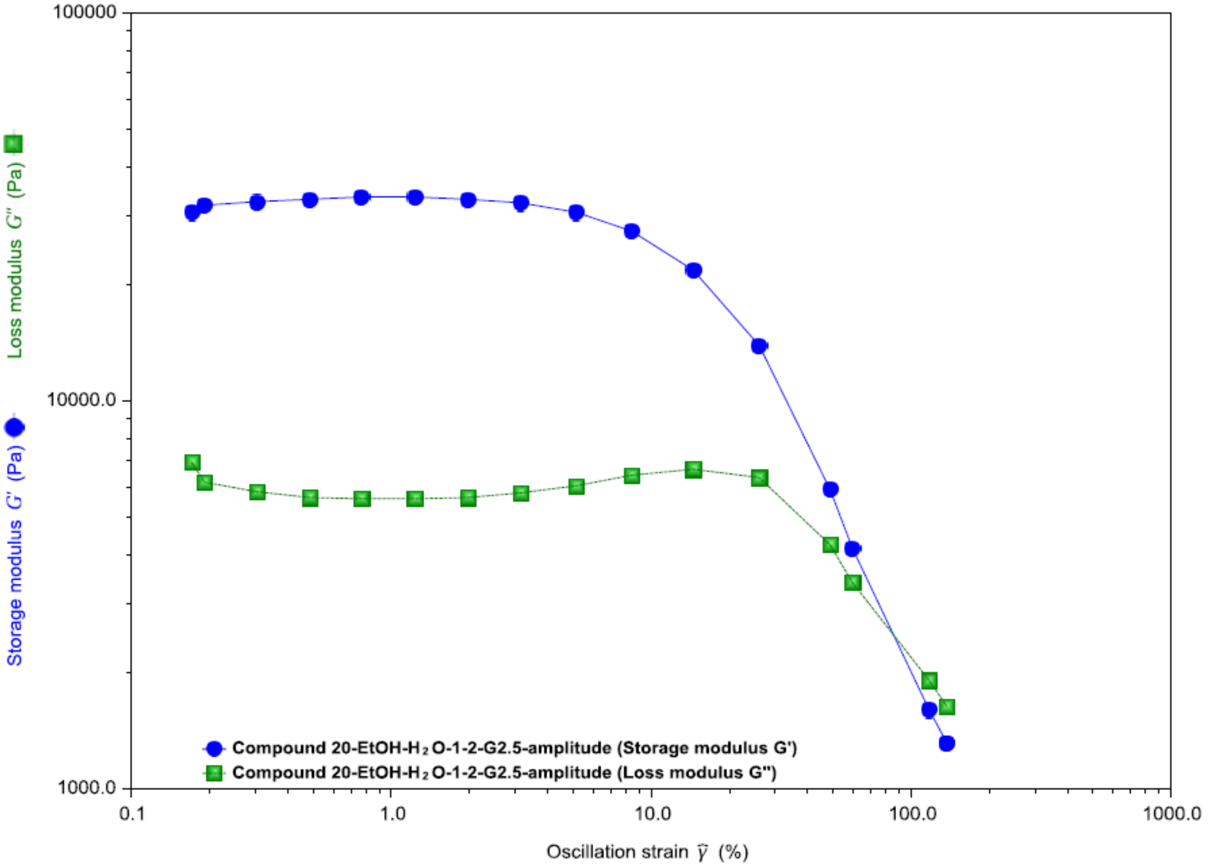
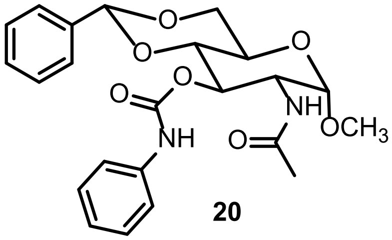


Figure S5-3. Rheological properties of the amplitude sweep experiment for the gel formed by compound **20** in EtOH:H$_2$O (v/v 1/2).



20

DMSO:H_2O=1:1
4.0 mg/mL opaque

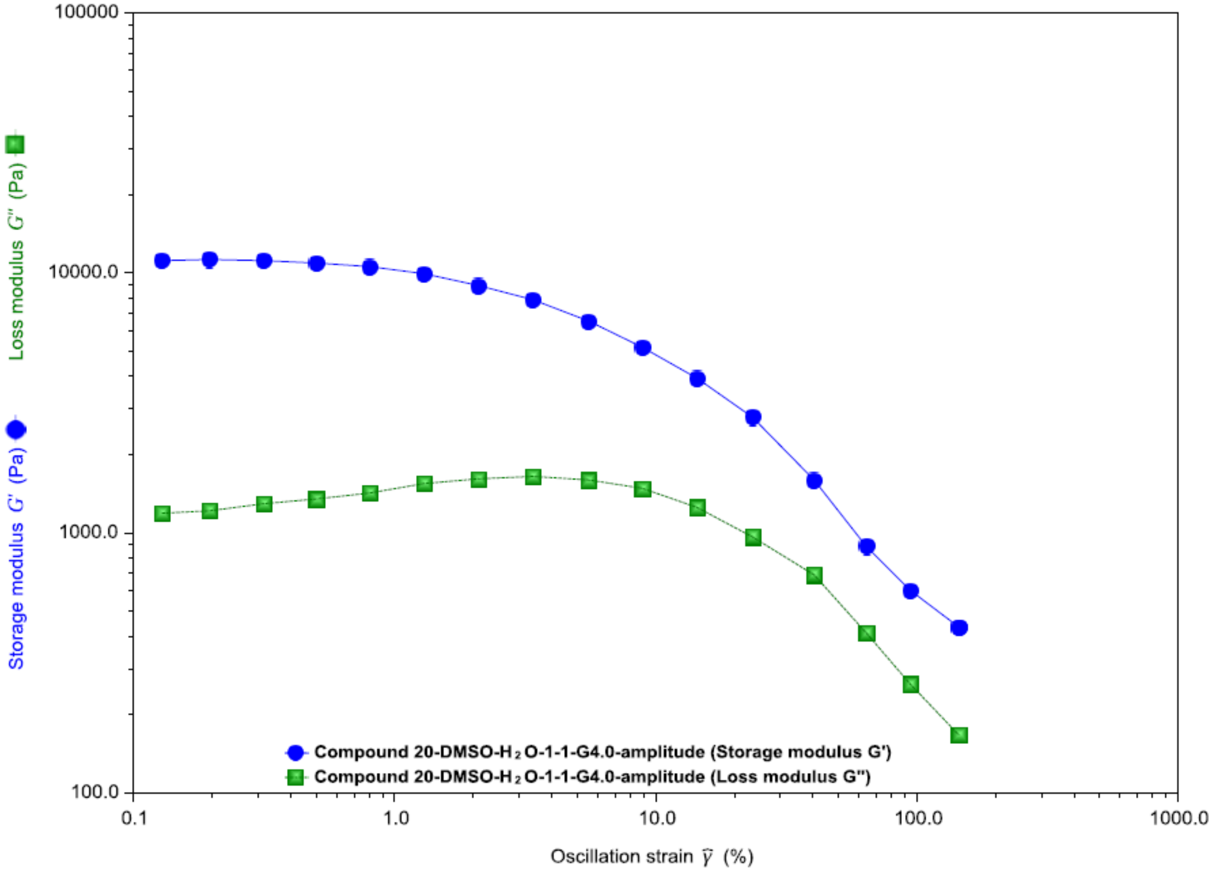
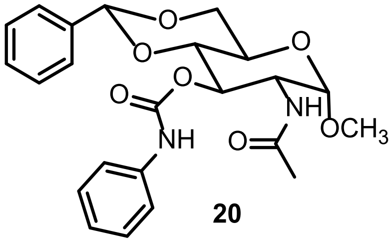


Figure S5-4. Rheological properties of the amplitude sweep experiment for the gel formed by compound **20** in DMSO:H_2O (v/v 1/1).



20

Toluene
2.8 mg/mL opaque

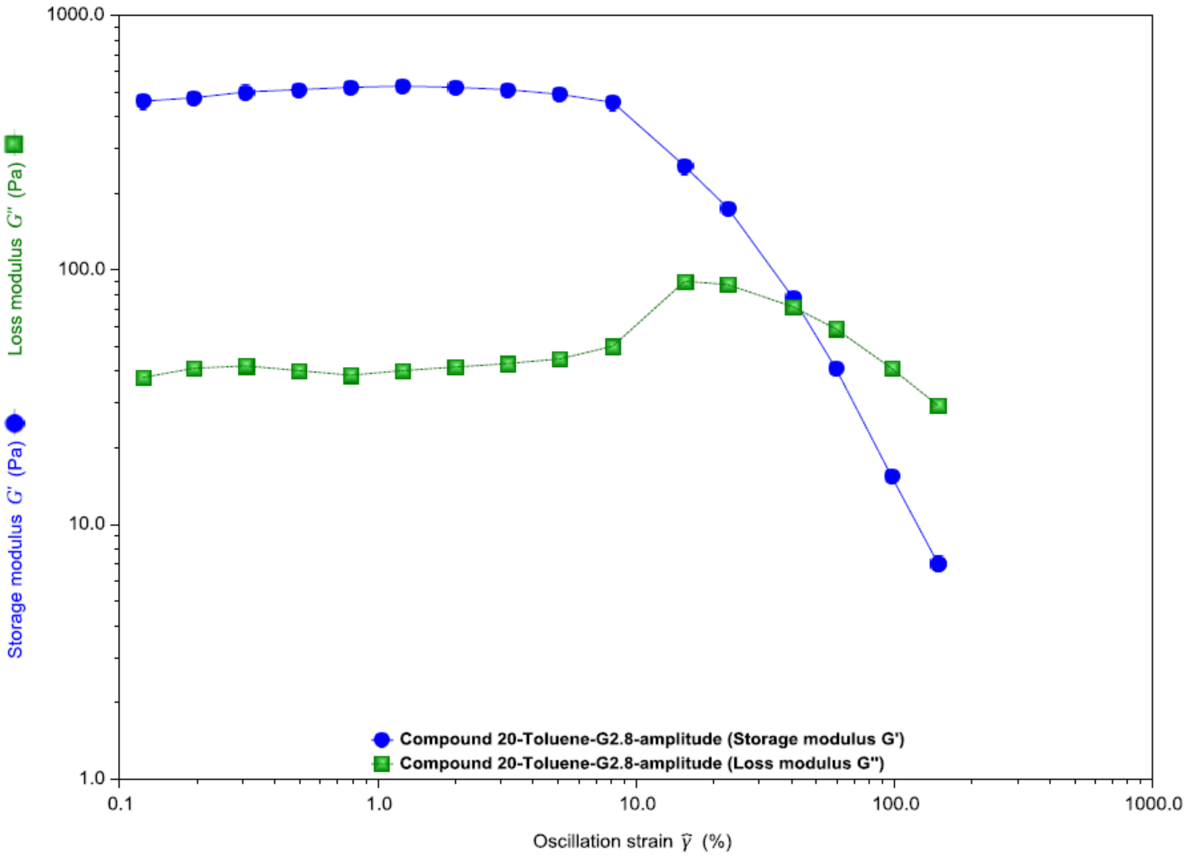
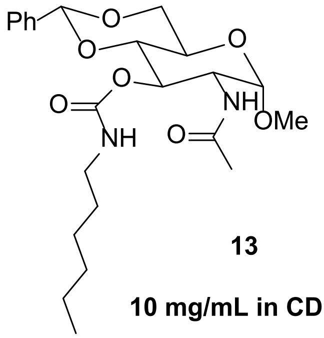


Figure S5-5. Rheological properties of the amplitude sweep experiment for the gel formed by compound **20** in Toluene.

6. ^{1}H NMR spectra of compounds 13 and 20 at different temperatures



13

10 mg/mL in $CDCl_3$

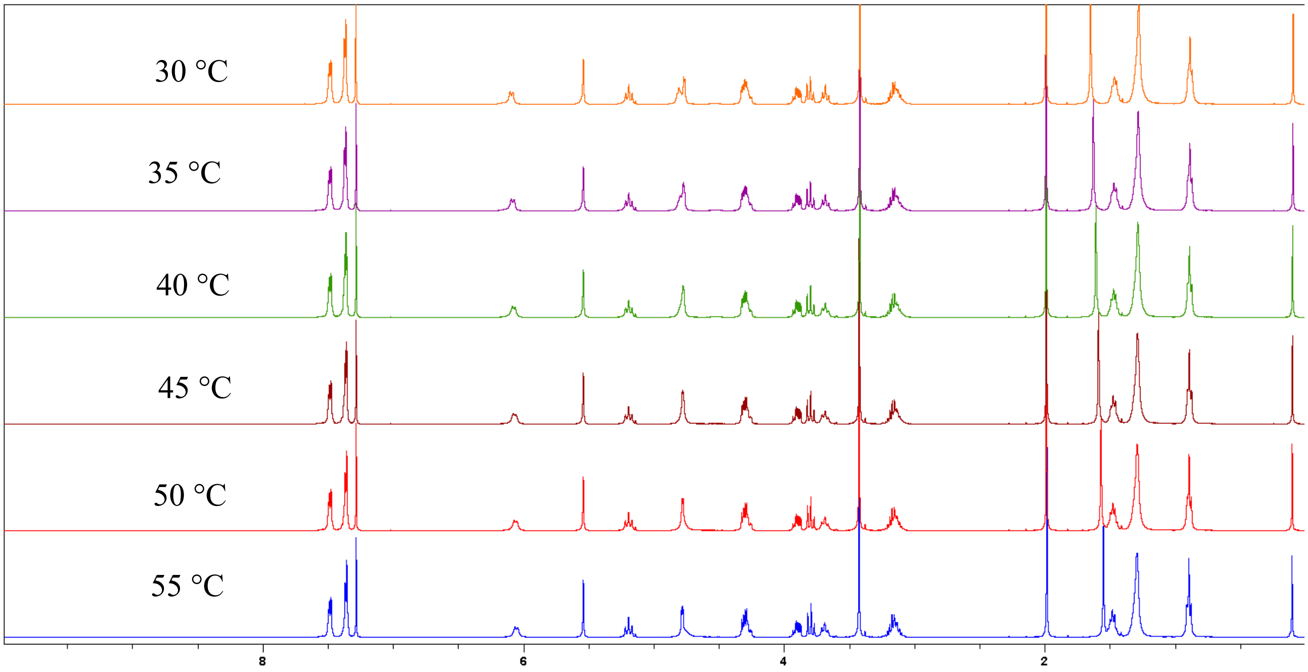


Figure S6. The ^{1}H NMR spectra (0 to 10.0 ppm) of compound **13** from 30 °C to 55 °C in $CDCl_3$ (10.0 mg/mL).

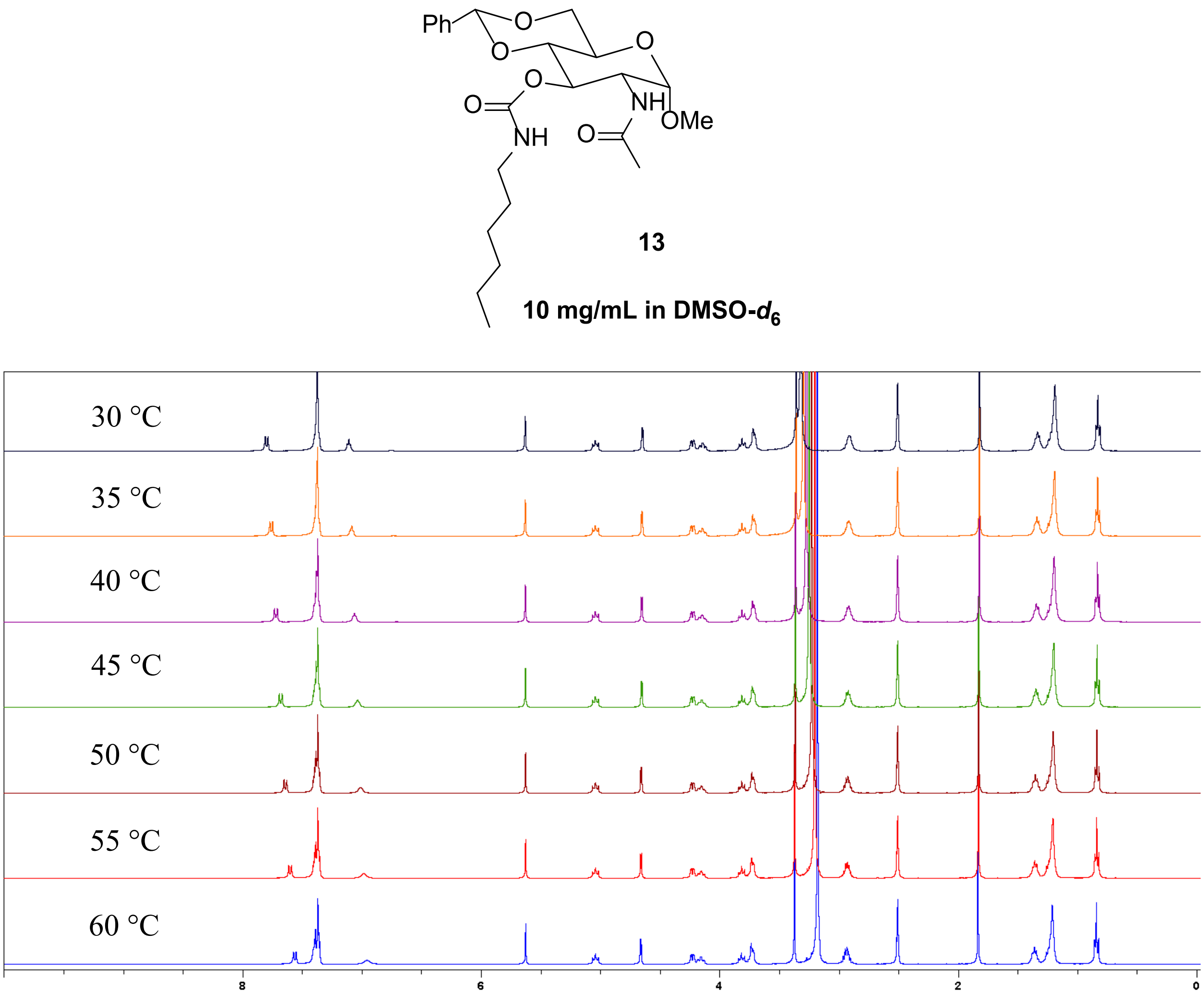
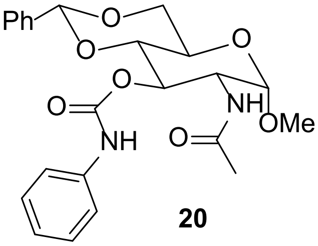


Figure S7. The ^{1}H NMR spectra (0 to 10.0 ppm) of compound **13** from 30 °C to 60 °C in DMSO-d_6 (10.0 mg/mL).



20

10 mg/mL $CDCl_3$

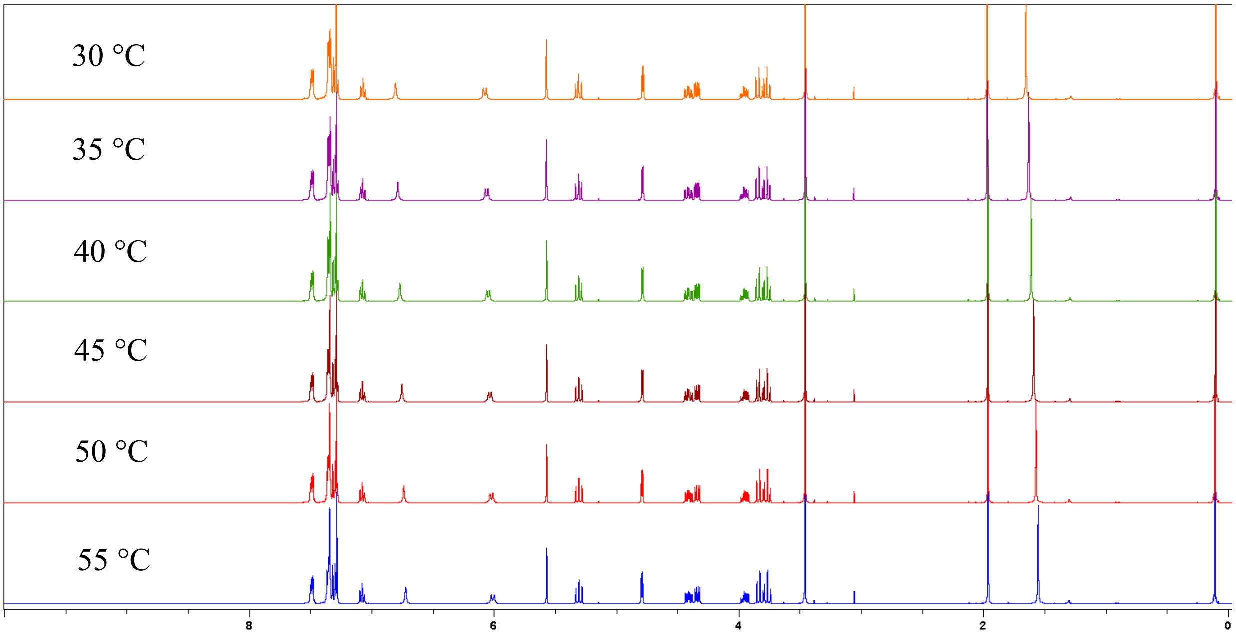
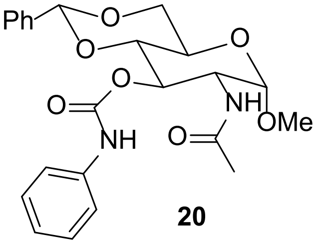


Figure S8. The ^{1}H NMR spectra (0 to 10.0 ppm) of compound **20** from 30 °C to 55 °C in $CDCl_3$ (10.0 mg/mL).



20

10 mg/mL DMSO-d_6

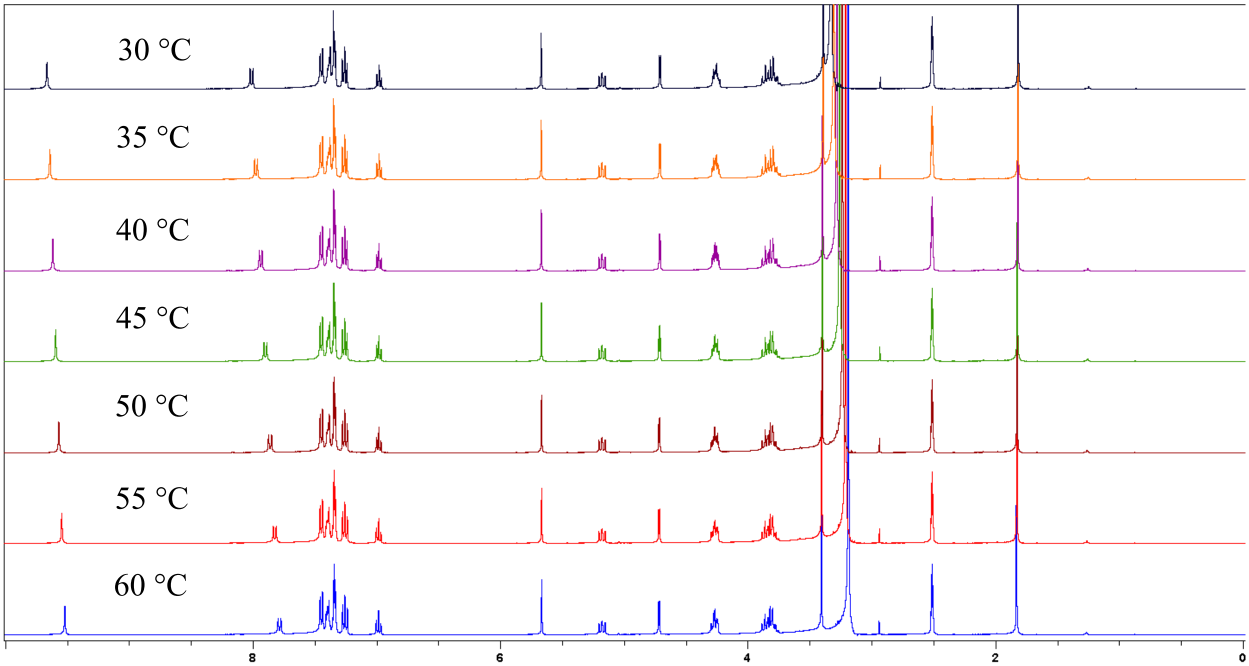


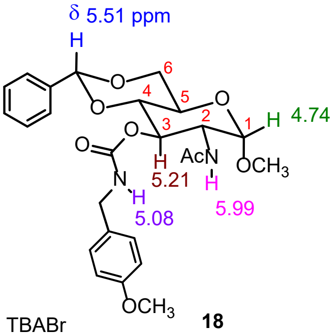
Figure S9. The ^{1}H NMR spectra (0 to 10.0 ppm) of compound **20** from 30 °C to 60 °C in DMSO–d_6 (10.0 mg/mL).

7. NMR studies of compound 18 with tetrabutylammonium bromide

The NMR spectra of gelator **18** with different amounts of TBABr were obtained in two different solvents, $CDCl_3$ and acetone-d_6.

Sample preparation: Compound **18** (3.8 mg, 0.0079 mmol, 1 eq.) was dissolved in 0.45 mL $CDCl_3$ or 0.8 mL acetone-d_6 in a standard NMR tube. Different amounts of TBABr salt was added to the NMR tube, it was sonicated to ensure that all of the salt was dissolved and the ^1H NMR spectrum was analyzed after each addition.

	Amount of TBABr
1	0 eq.
2	2.5 mg, 0.0079 mmol, 1 eq.
3	5.1 mg, 0.0158 mmol, 2 eq.
4	7.6 mg, 0.0237 mmol, 3 eq.
5	12.7 mg, 0.0395 mmol, 5 eq.
6	25.5 mg, 0.0790 mmol, 10 eq.
7	38.2 mg, 0.1185 mmol, 15 eq.



No TBABr **18**

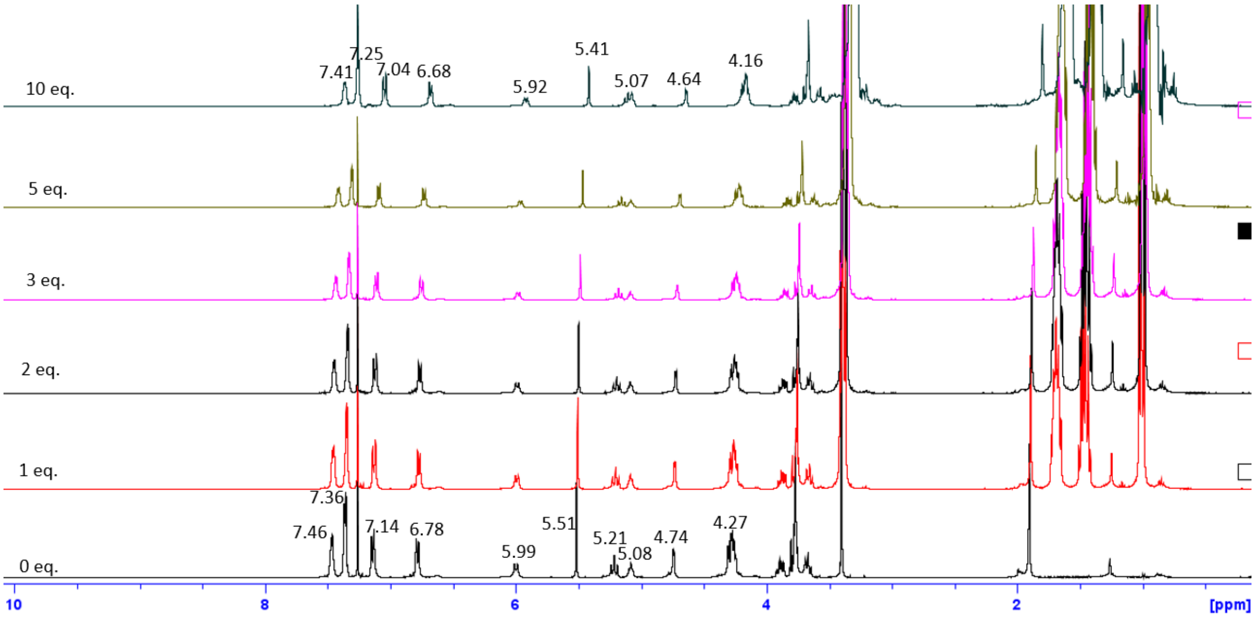


Figure S10a. ^{1}H NMR spectra (0-10.0 ppm) of gelator **18** in $CDCl_3$ with different amounts (0-10 eq.) of TBABr.

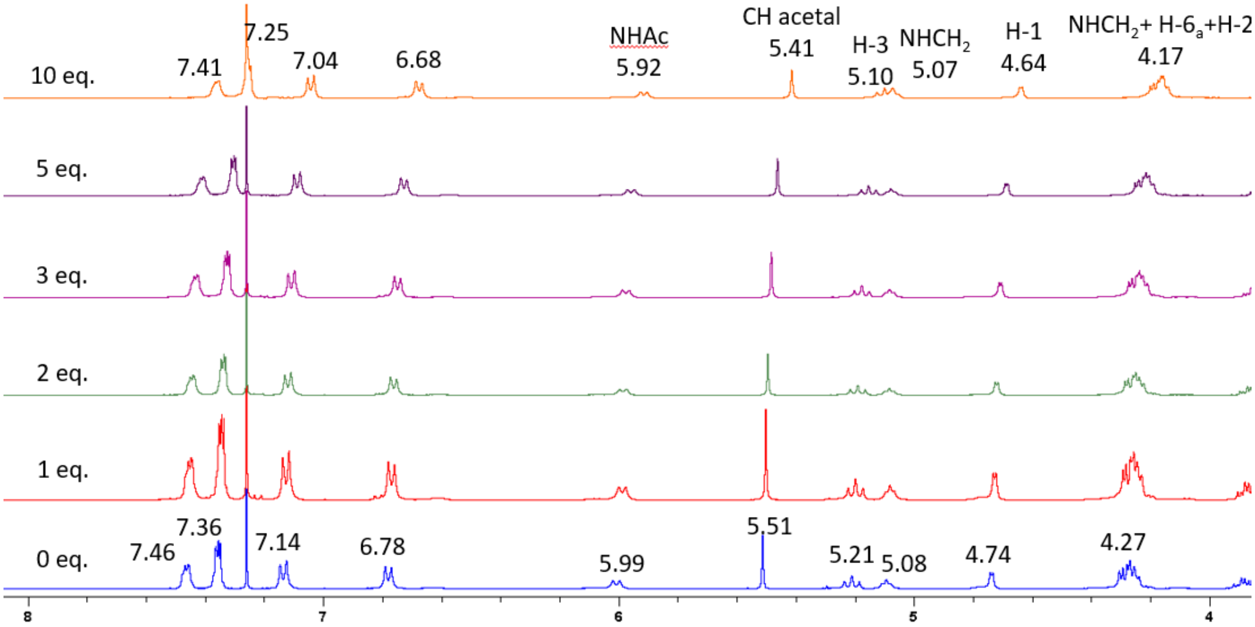


Figure S10b. ^{1}H NMR spectra 4.0-8.0 ppm of gelator **18** in CDCl$_3$ with different amounts (0-10 eq.) of TBABr.

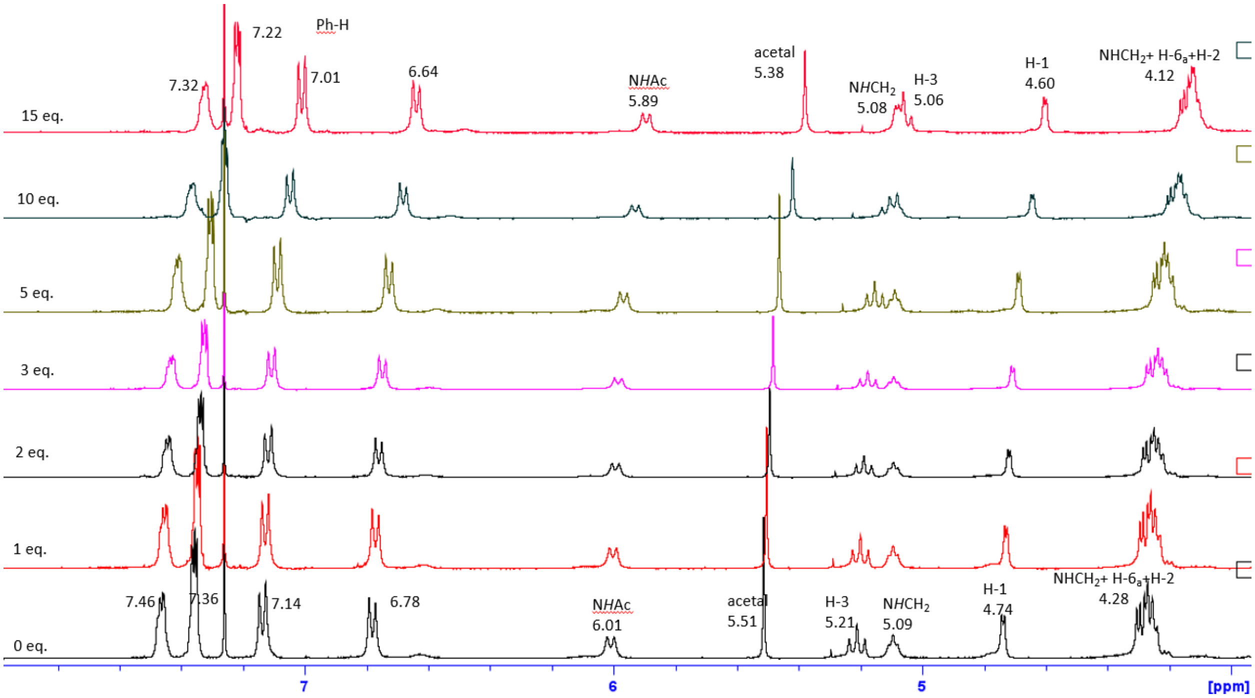


Figure S11. ^{1}H NMR spectra of gelator **18** in $CDCl_3$ with different amounts (0-15 eq.) of TBABr.

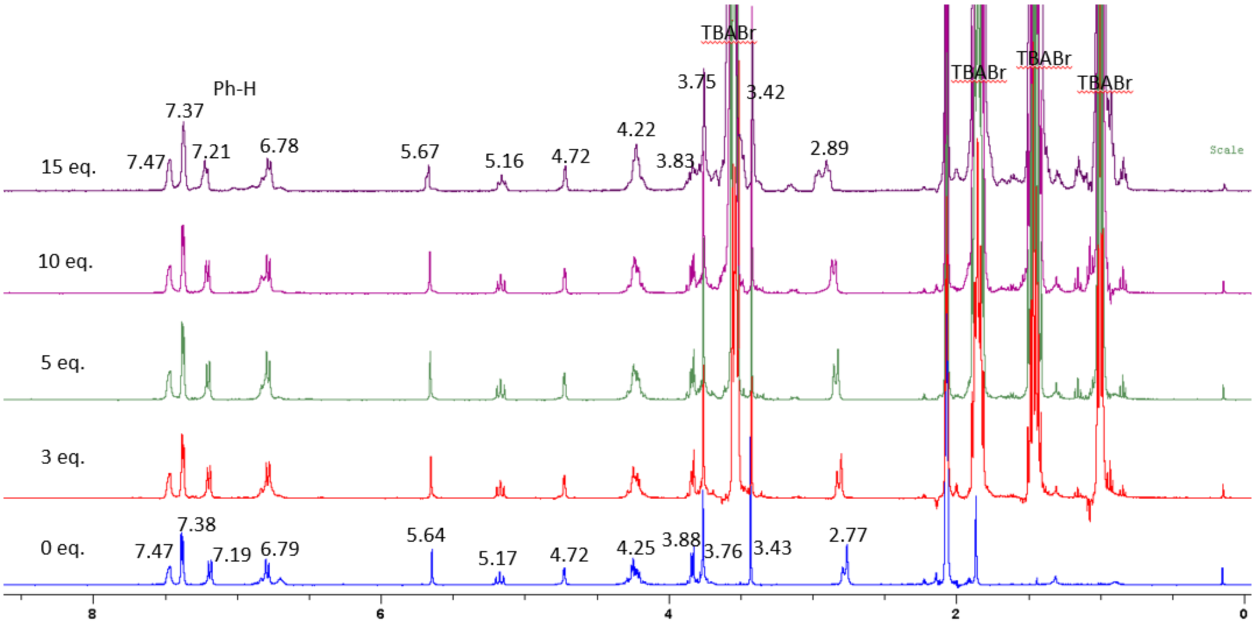
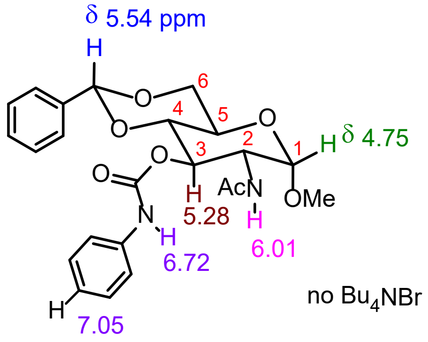


Figure S12. ^{1}H NMR spectra of gelator **18** in acetone-d_6 with different amounts (0-15 eq.) of TBABr.

8. NMR studies of compound 20 with tetrabutylammonium bromide

Compound **20** (3.5 mg, 0.0079mmol, 1 eq.) was dissolved in 0.45 mL of $CDCl_3$ or DMSO-d_6 in a NMR tube. Different amounts of the TBABr salt was added to the NMR tube, it was sonicated to ensure that all of the salt was dissolved and the ^{1}H NMR spectrum was analyzed after each addition.

	TBABr
1	0 eq.
2	2.5 mg, 0.0079 mmol, 1 eq.
3	5.1 mg, 0.0158 mmol, 2 eq.
4	7.6 mg, 0.0237 mmol, 3 eq.
5	12.7 mg, 0.0395 mmol, 5 eq.
6	25.5 mg, 0.0790 mmol, 10 eq.



20

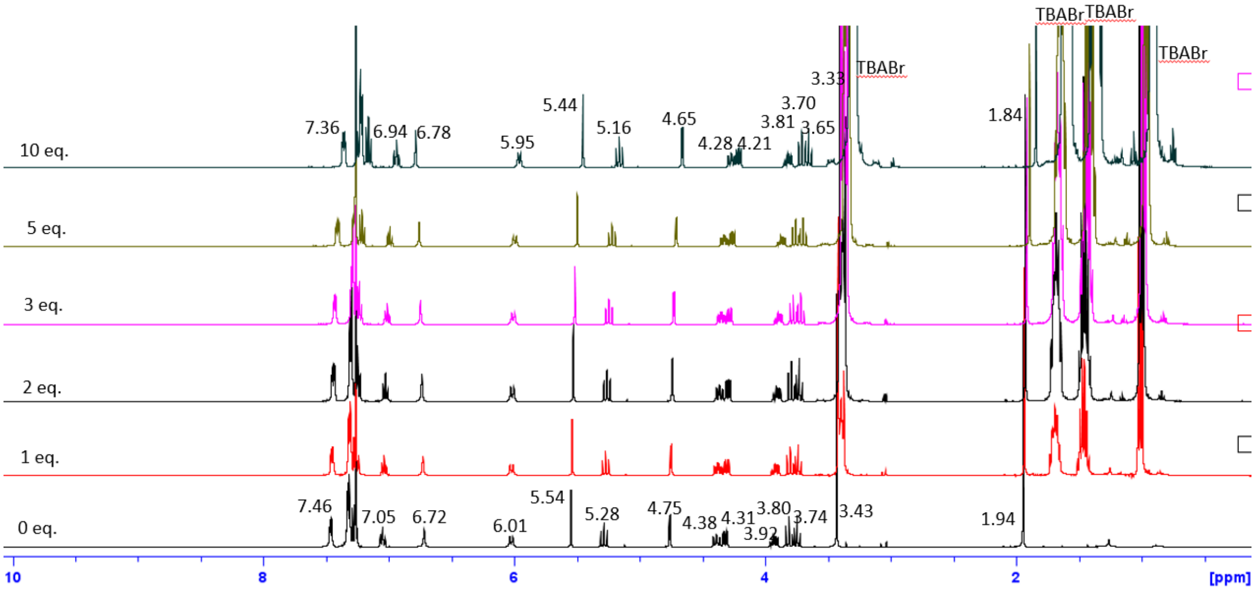


Figure S13a. ^{1}H NMR spectra of gelator **20** in CDCl$_3$ with different amounts of TBABr.

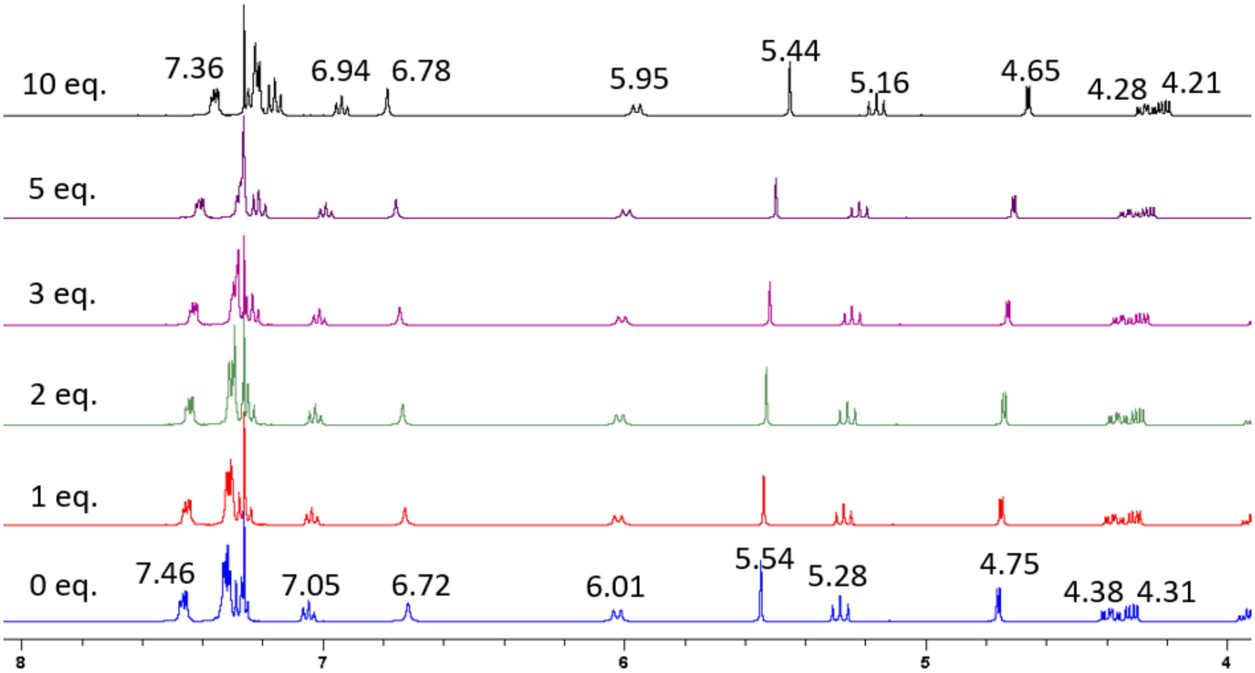


Figure S13b. ^{1}H NMR spectra (4.0-8.0 ppm) of gelator **20** in CDCl$_3$ with different amounts of TBABr.

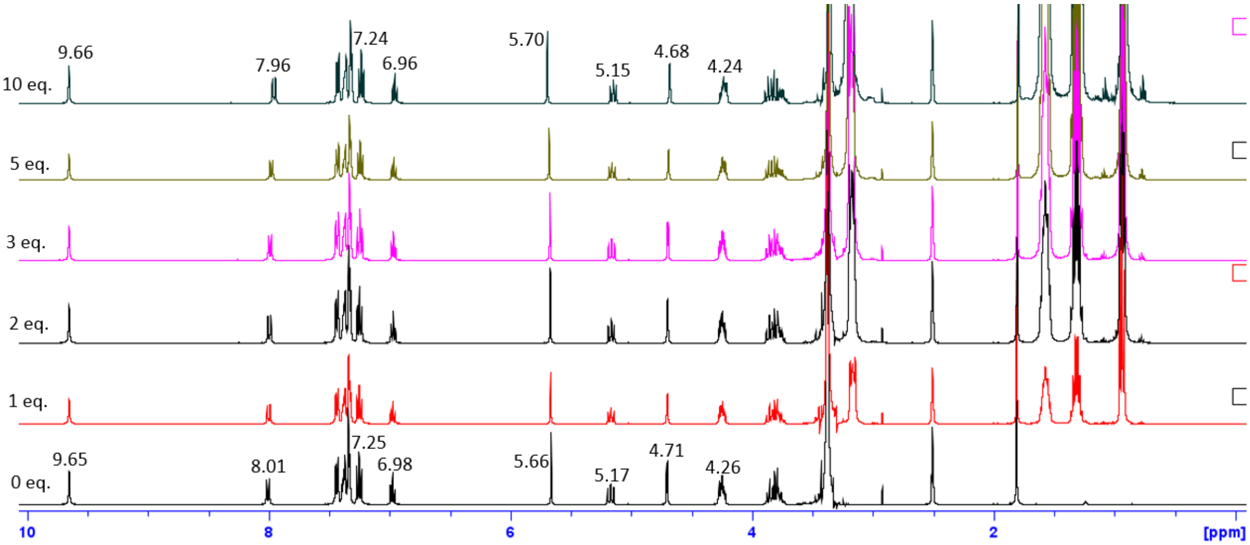


Figure S14a. ^{1}H NMR spectra of gelator **20** in DMSO-d_6 with different amounts (0-10 eq.) of TBABr.

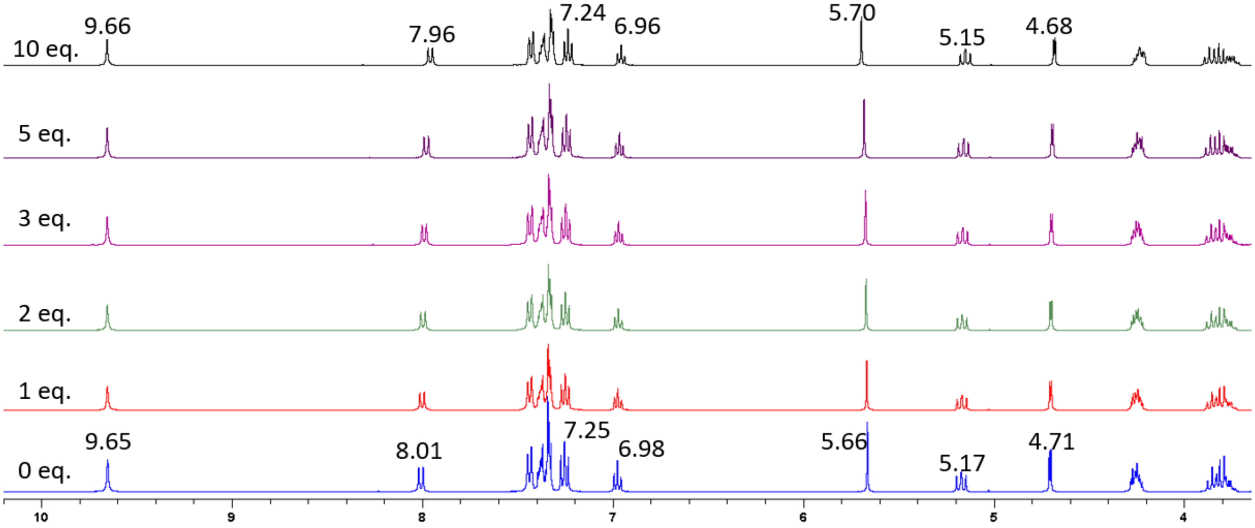
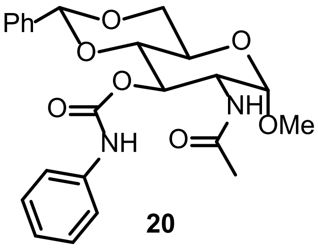


Figure S14b. ^{1}H NMR spectra (4.0-10.0 ppm) of **20** in DMSO-d_6 with different amounts (0-10 eq.) of TBABr.

9. Gel photos of naproxen release studies

Figure S15. Gel pictures from the release study of naproxen from the gel formed by compound **20** (5.6 mg) in 2.0 mL of DMSO:H_2O (v/v 1:7) with naproxen (0.25 mg) in the presence of phosphate buffered saline (1X concentrated) at pH 7.47 (2.0 mL) on top of the gel at different time points.



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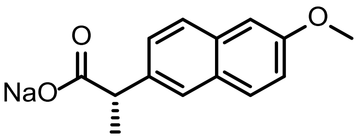
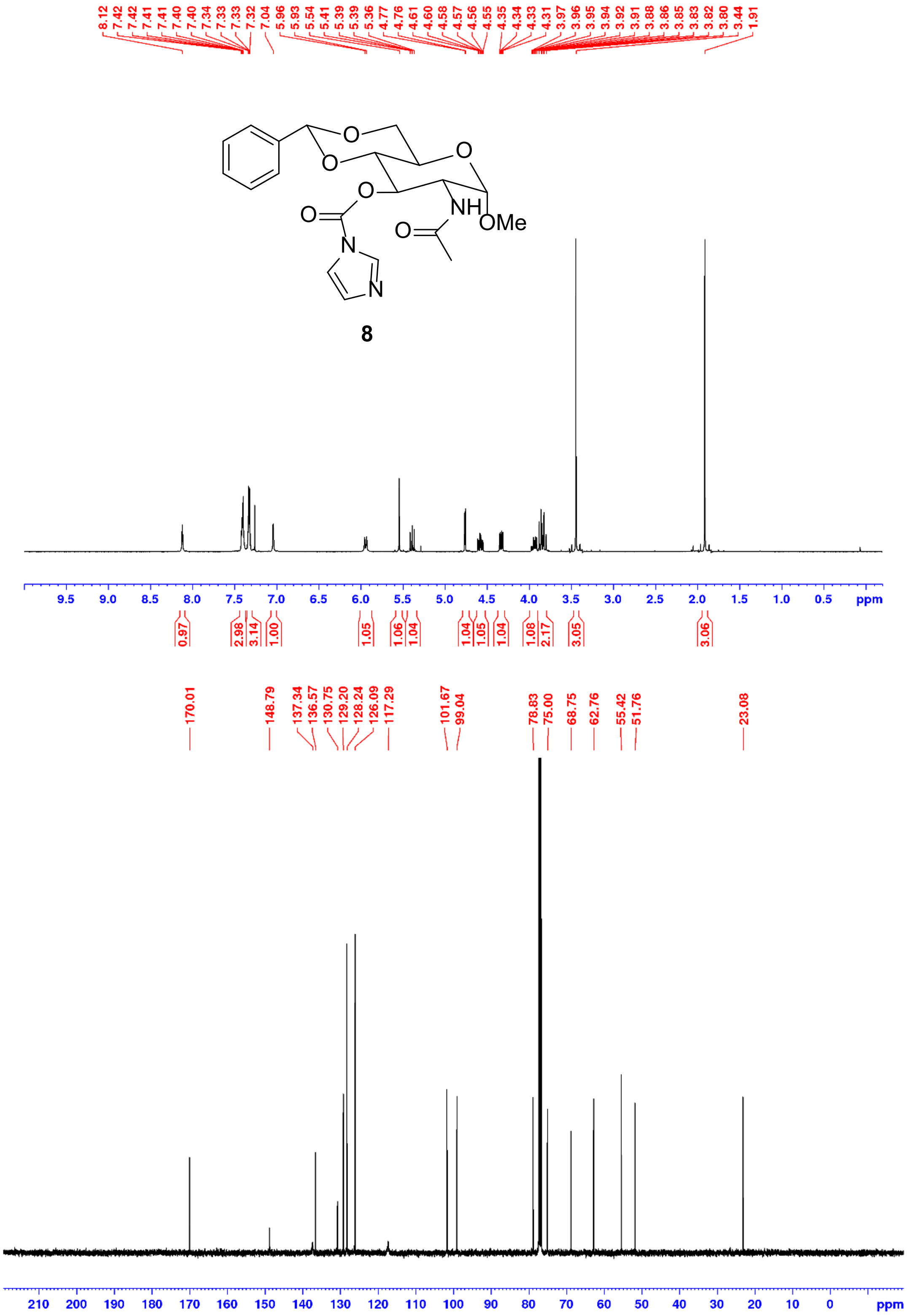


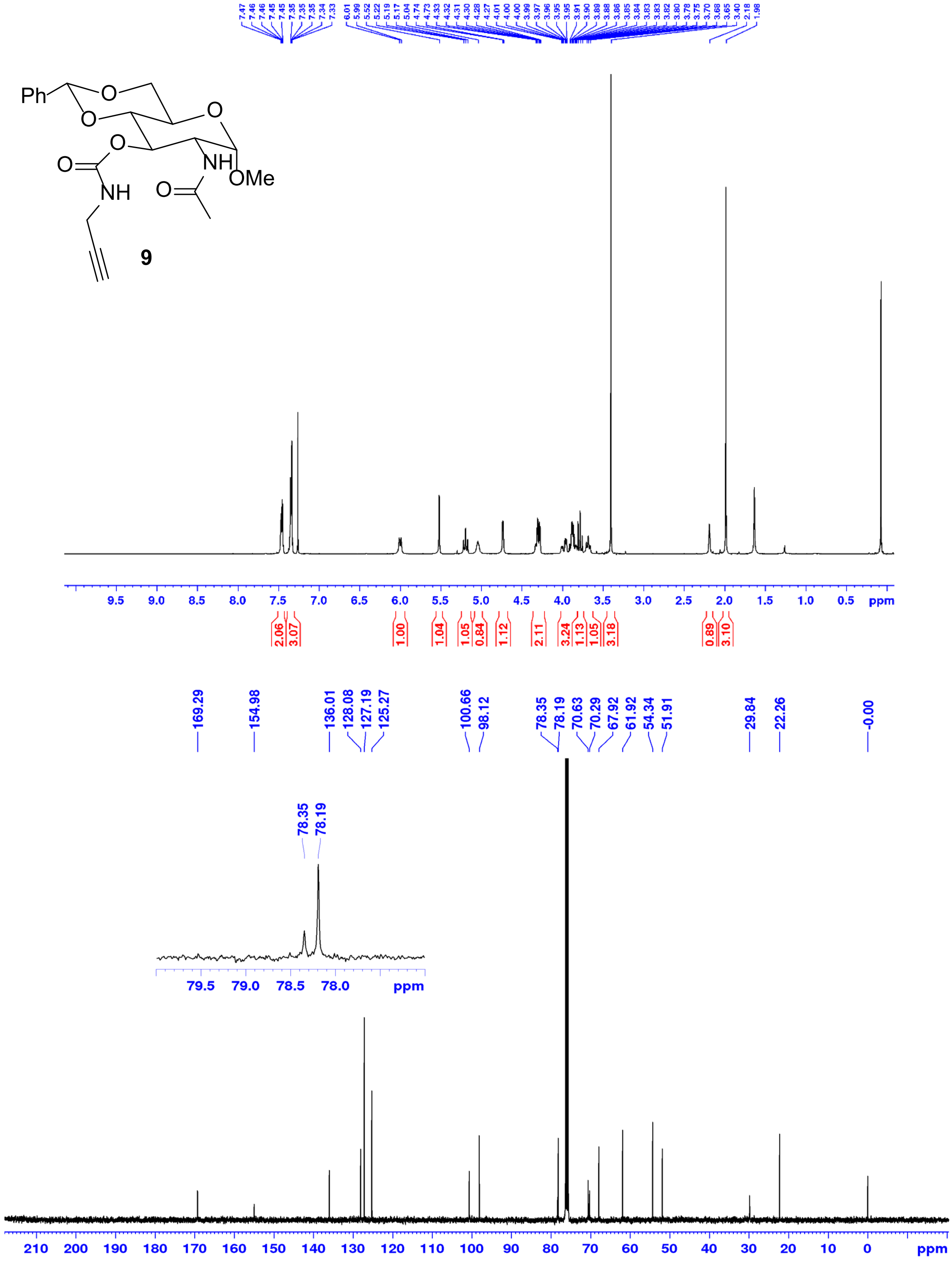
Naproxen sodium

Part II. ^{1}H and ^{13}C NMR spectra of synthesized carbamate derivatives

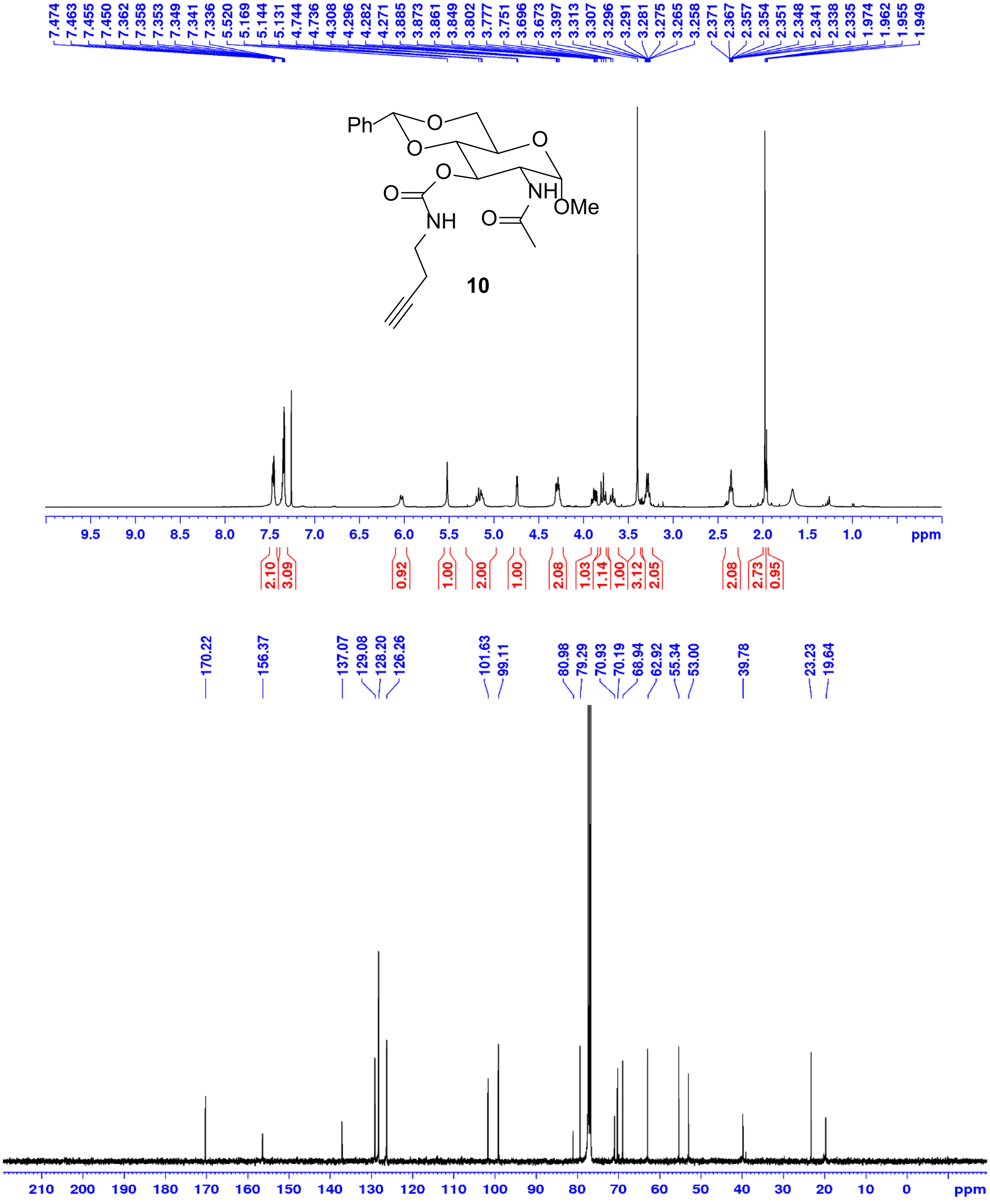


8

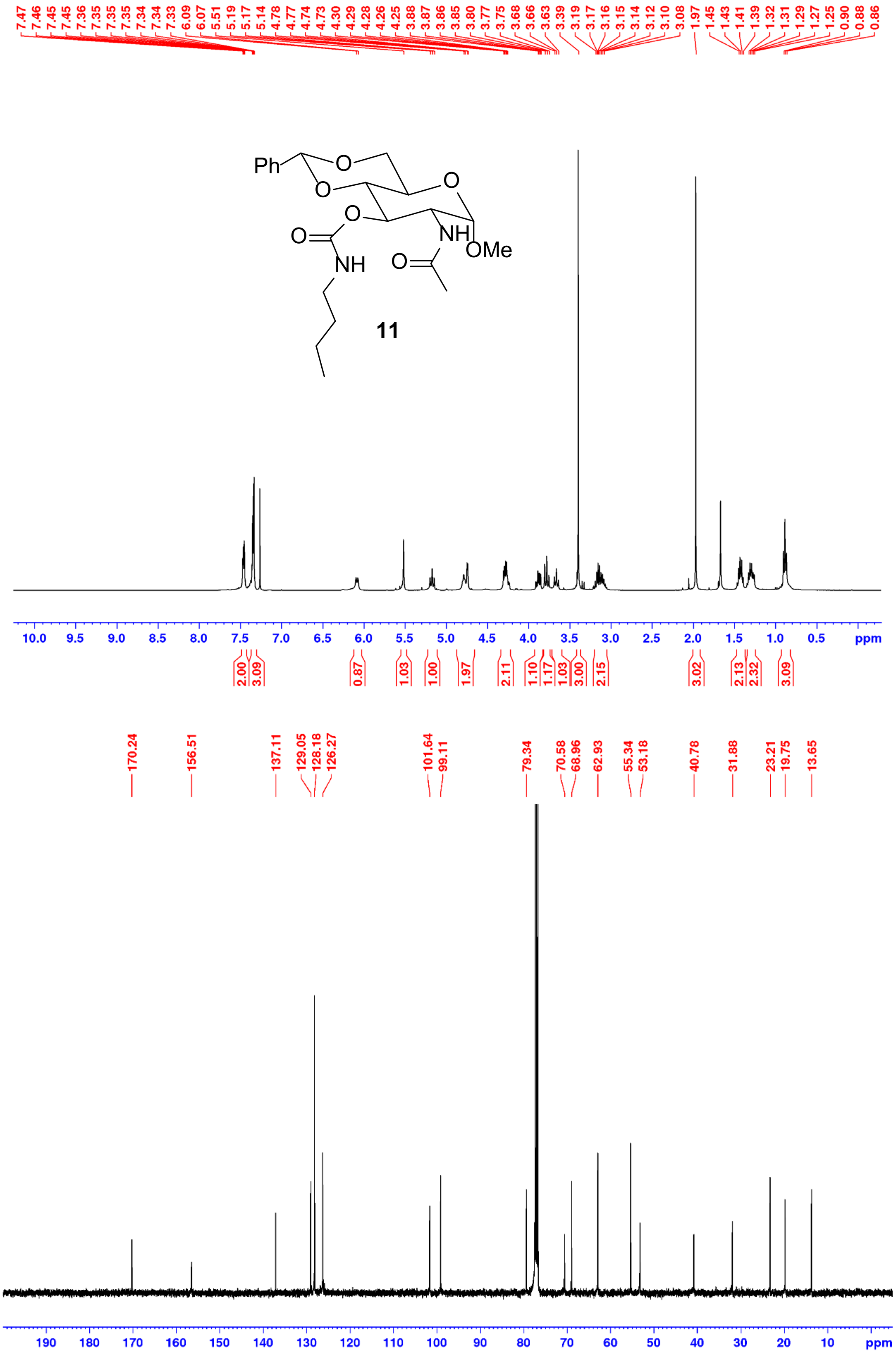
^{1}H NMR and ^{13}C NMR spectra of compound **8** in $CDCl_3$



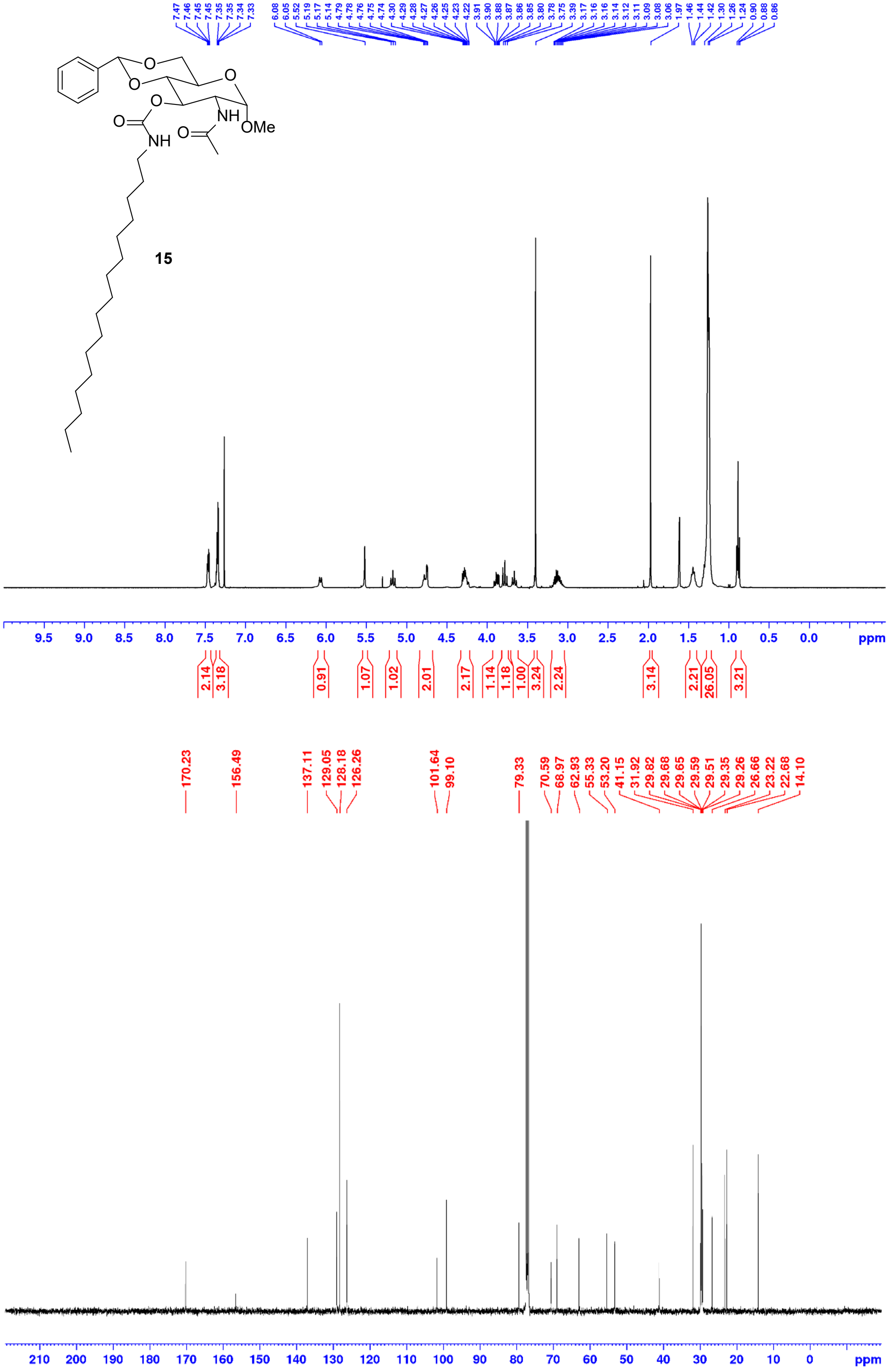
^{1}H NMR and ^{13}C NMR spectra of compound **9** in $CDCl_3$



^{1}H NMR and ^{13}C NMR spectra of compound **10** in $CDCl_3$

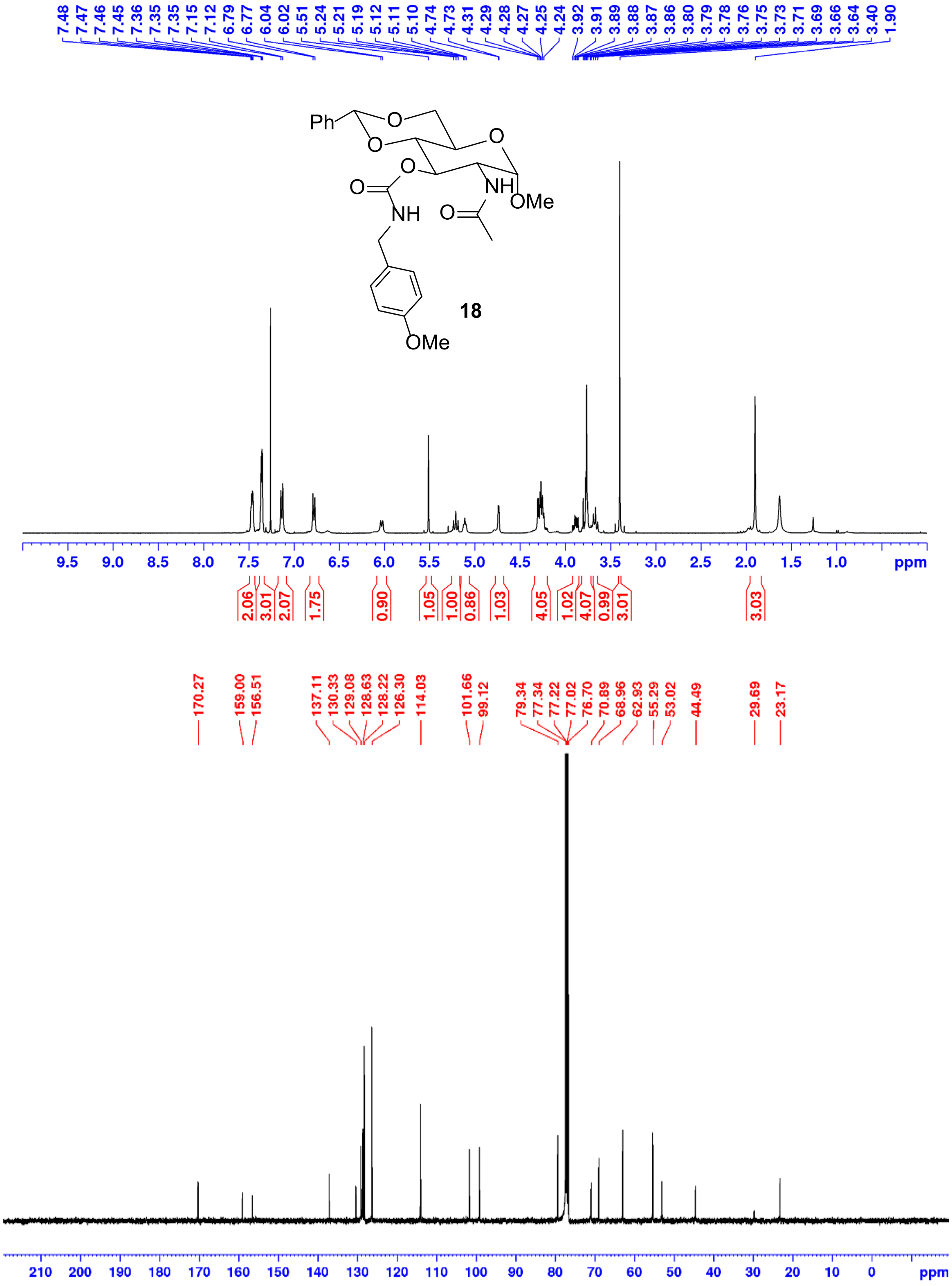


^{1}H NMR and ^{13}C NMR spectra of compound **11** in $CDCl_3$

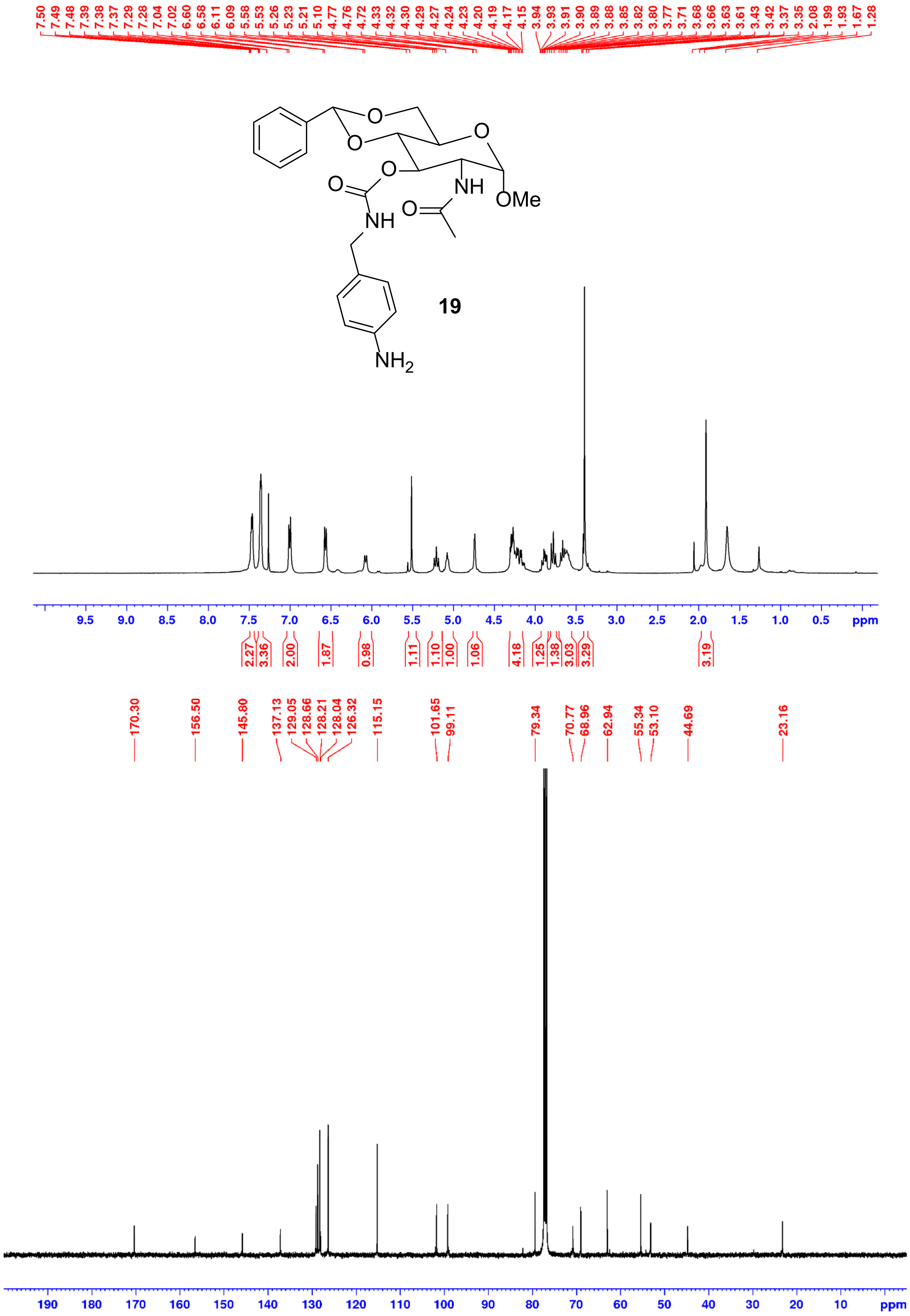


15

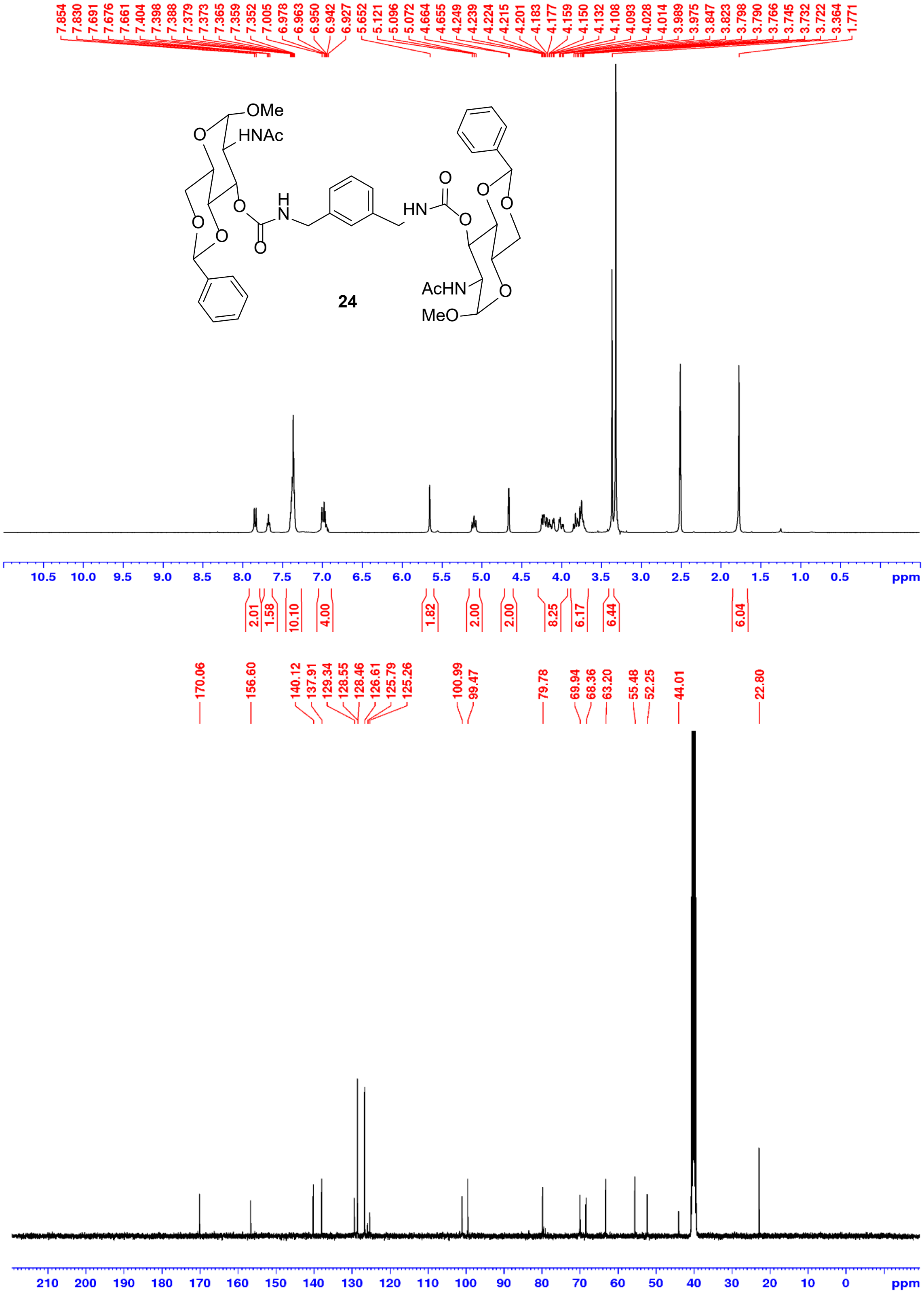
^{1}H NMR and ^{13}C NMR spectra of compound **15** in $CDCl_3$



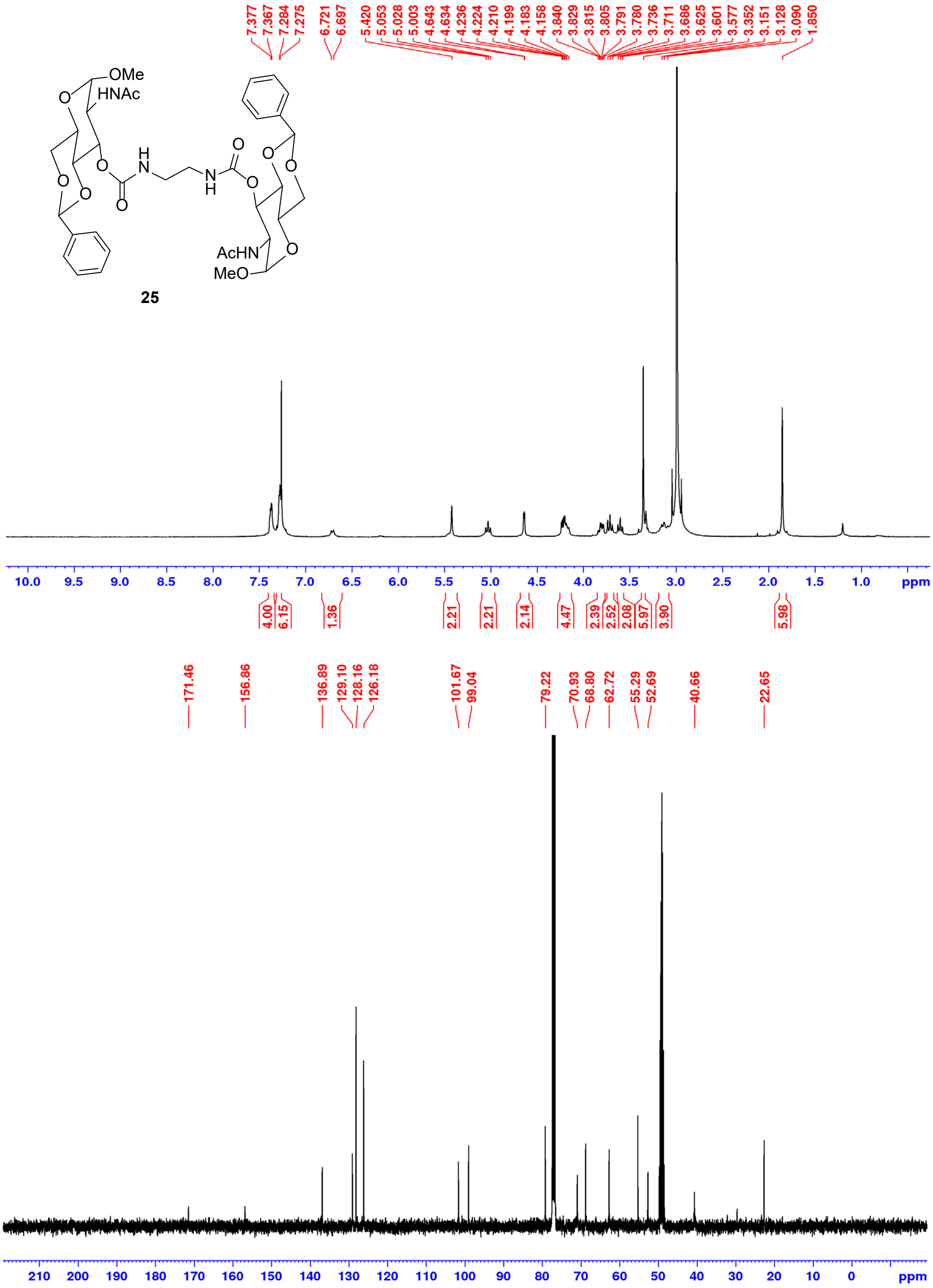
^{1}H NMR and ^{13}C NMR spectra of compound **18** in $CDCl_3$



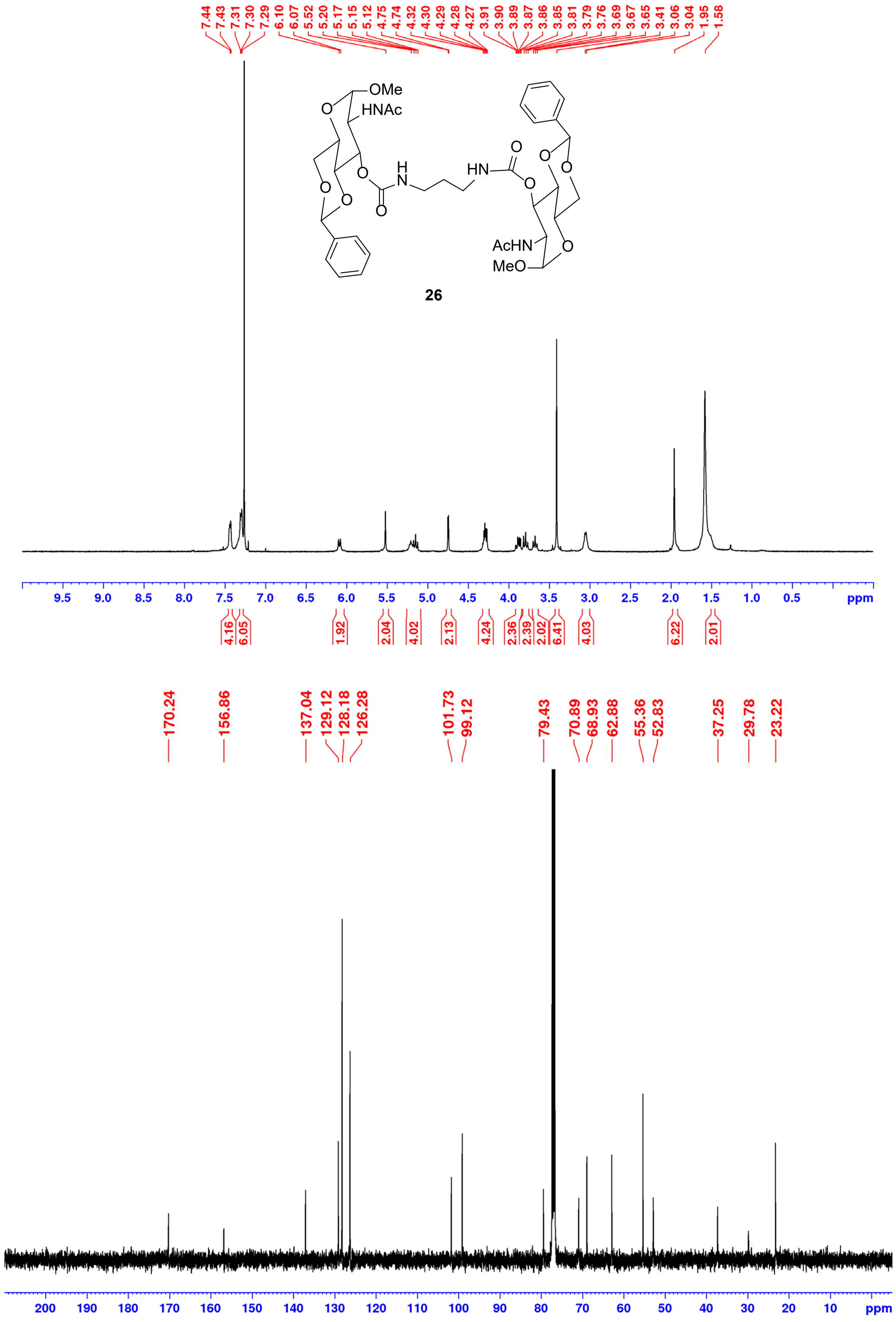
^{1}H NMR and ^{13}C NMR spectra of compound **19** in $CDCl_3$



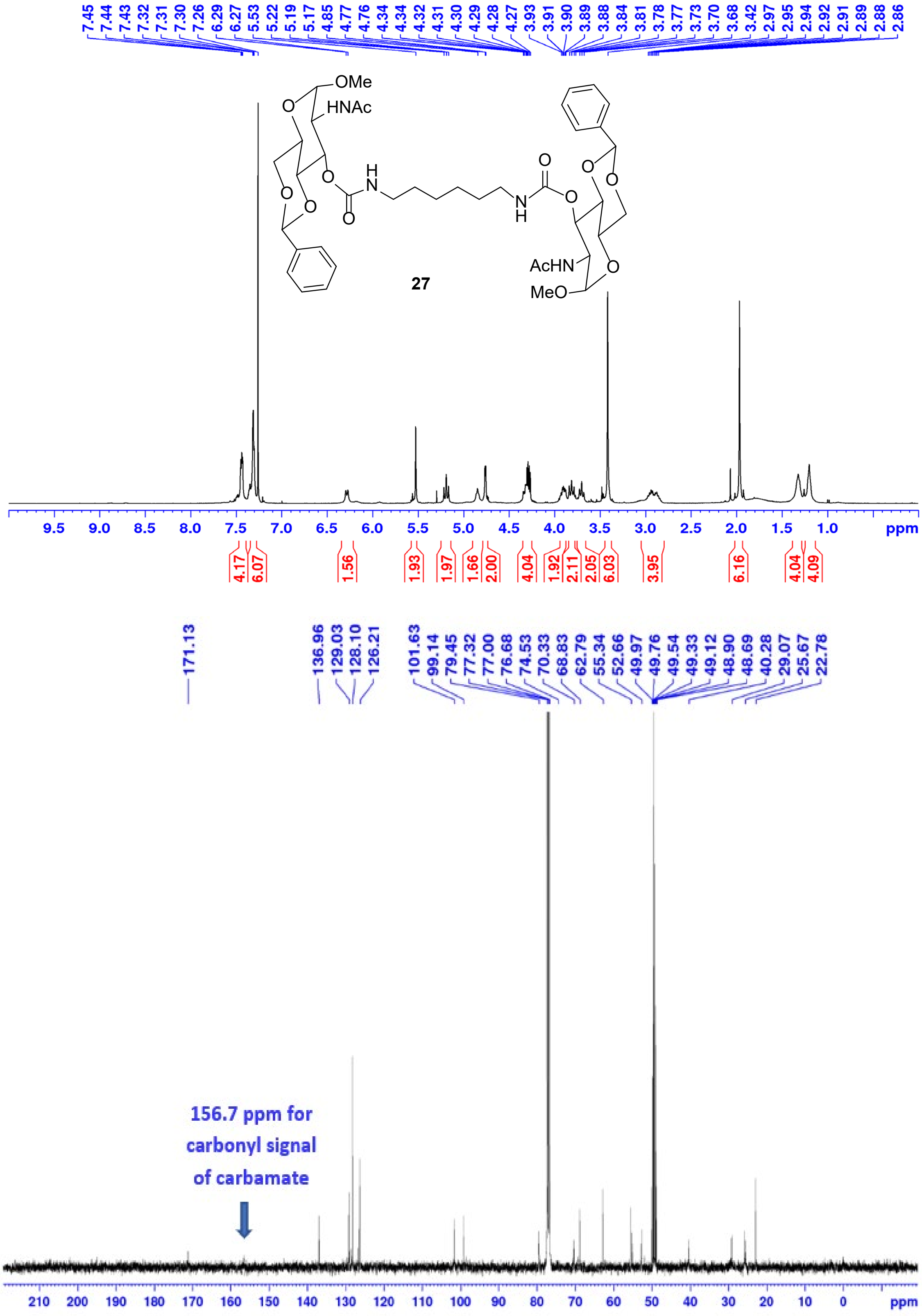
^{1}H NMR and ^{13}C NMR spectra of compound **24** in DMSO-d_6



^{1}H NMR and ^{13}C NMR spectra of compound **25** in $CDCl_3$ + *d*$_4$-MeOH



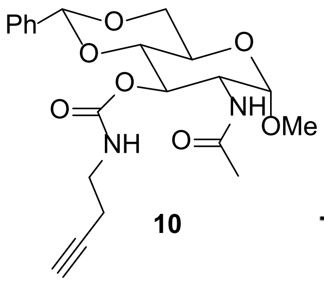
^{1}H NMR and ^{13}C NMR spectra of compound **26** in $CDCl_3$



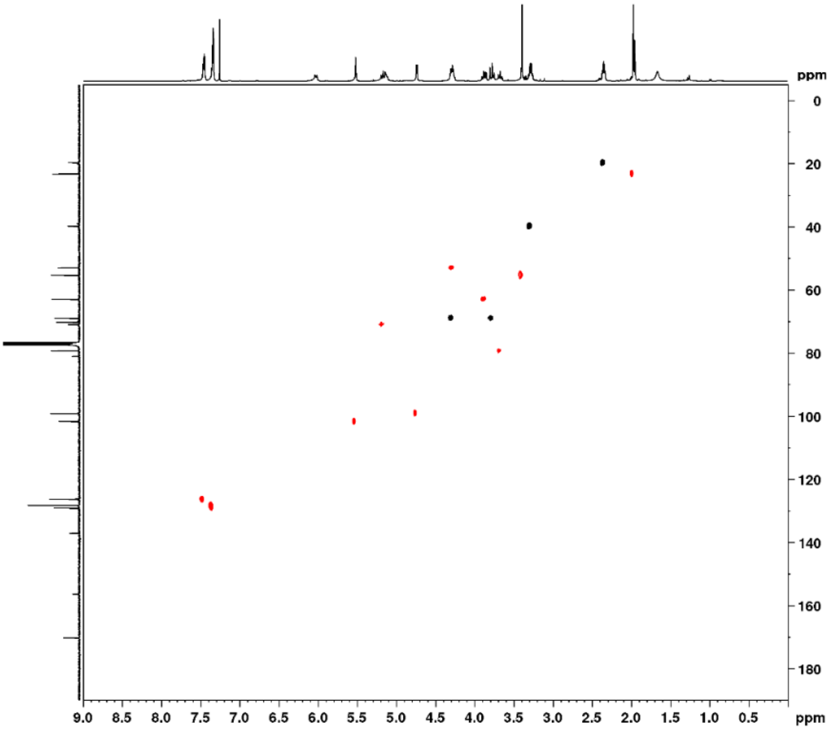
156.7 ppm for carbonyl signal of carbamate

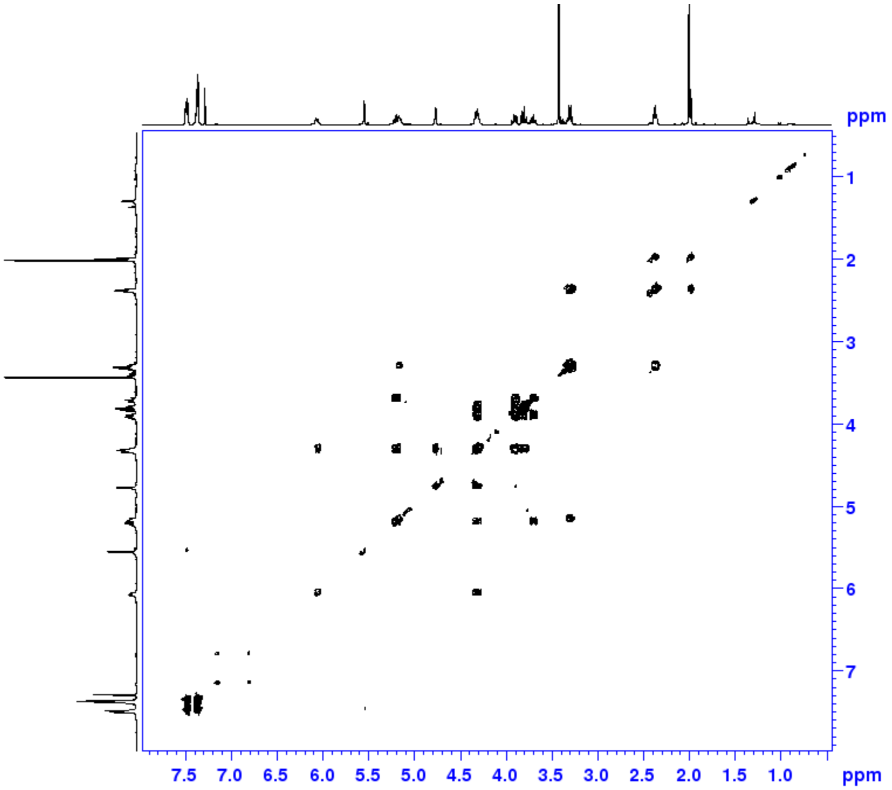
^{1}H NMR and ^{13}C NMR spectra of compound **27** in $CDCl_3$ + d_4-MeOH (low solubility in $CDCl_3$)

2D NMR spectra for compounds, HSQC and COSY spectra

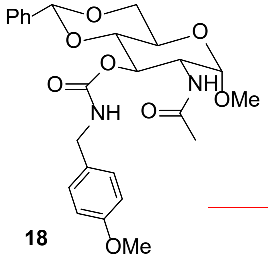


10



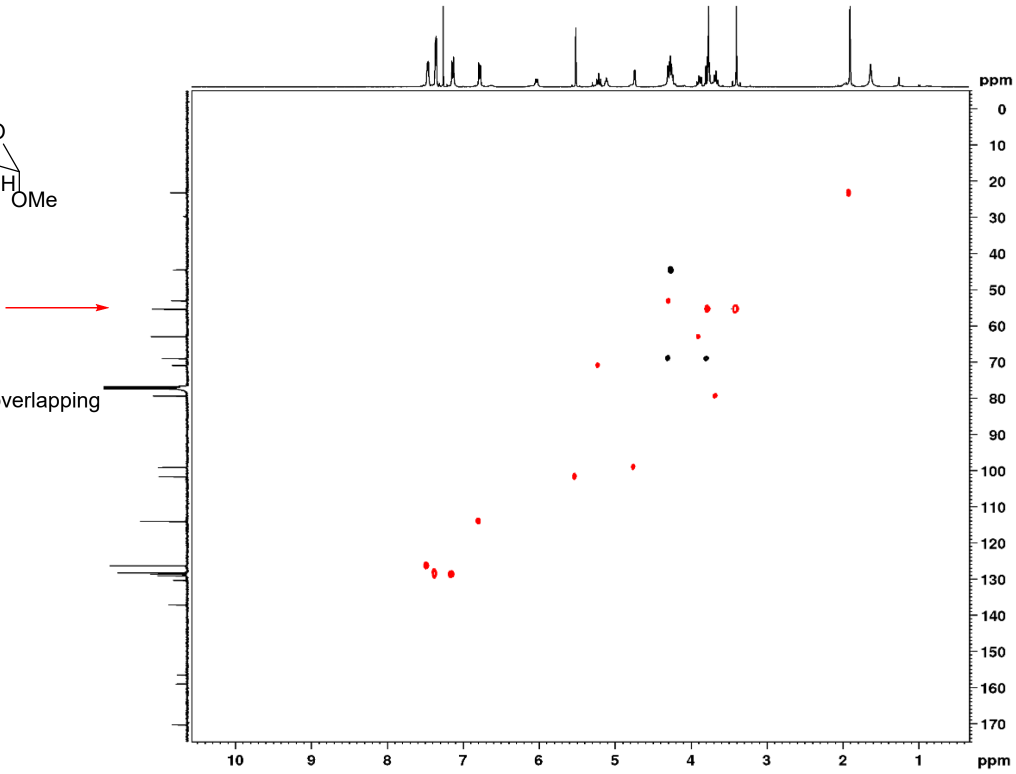


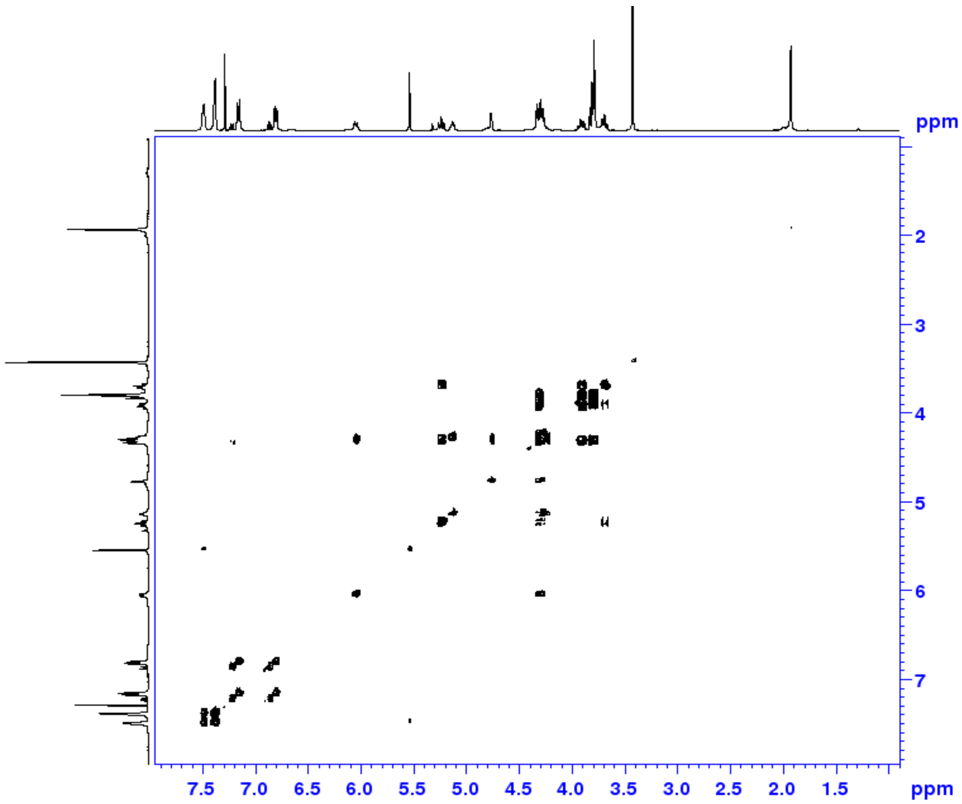
HSQC and COSY NMR spectra of compound 10 in $CDCl_3$



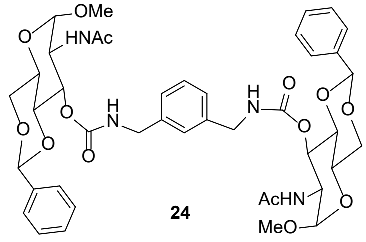
18

note the two OMe overlapping at δ 55.3 ppm

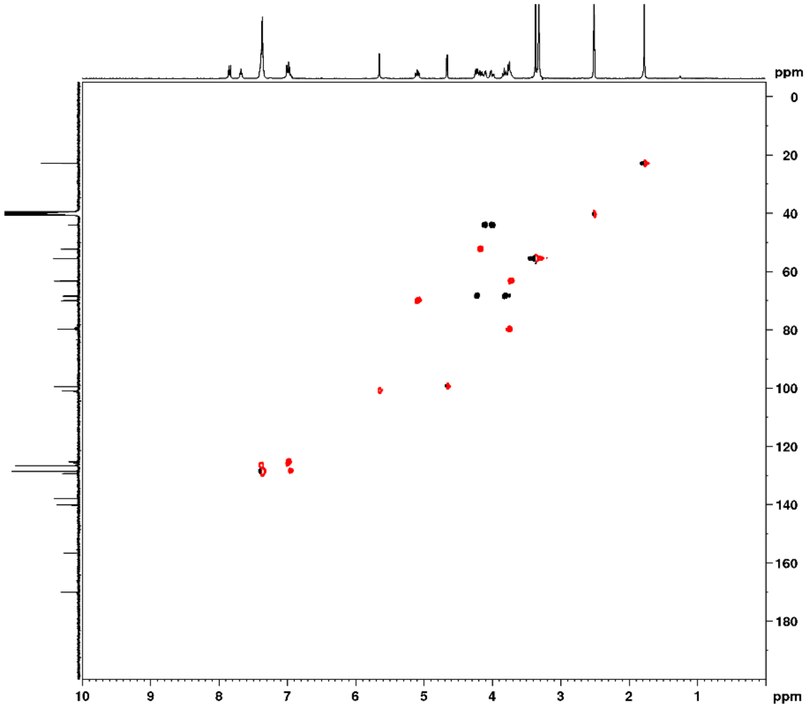


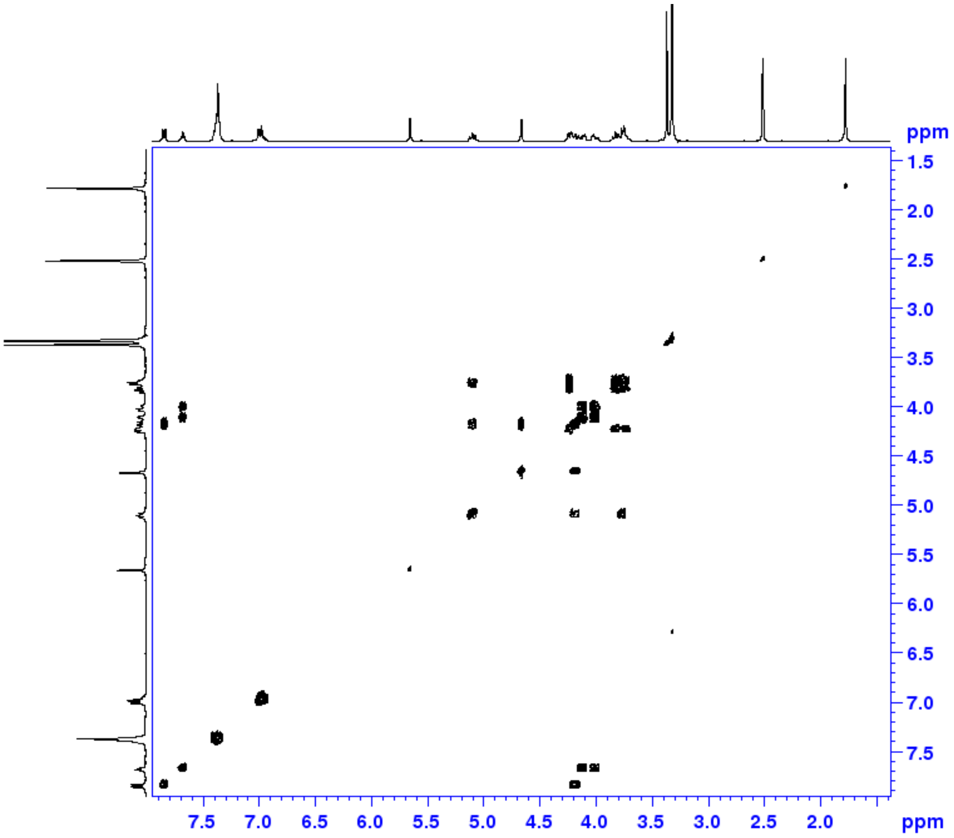


HSQC and COSY NMR spectra of compound **18** in $CDCl_3$



24





HSQC and COSY NMR spectra of compound **24** in DMSO-d_6