Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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SUPPLEMENTARY INFORMATION

Low-molecular-weight gelators consisting of hybrid cyclobutane-based peptides

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Appearance of the gels from compounds 1-4

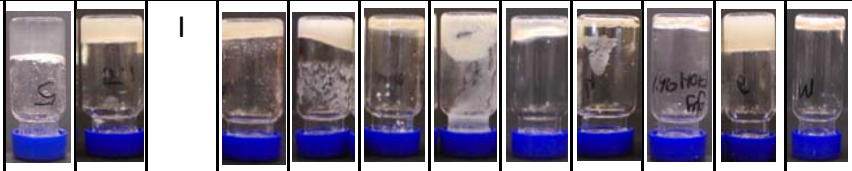
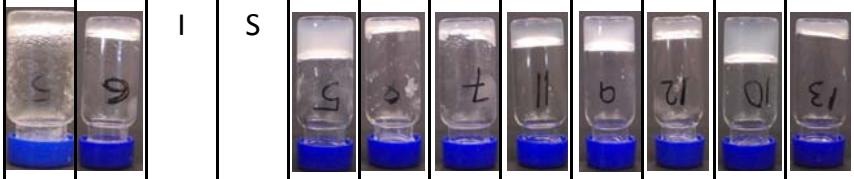
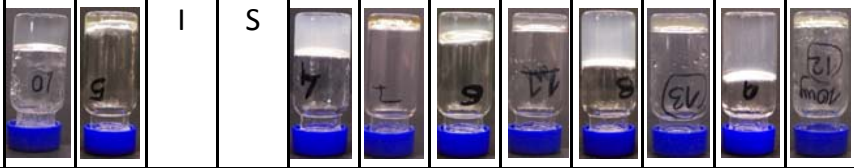
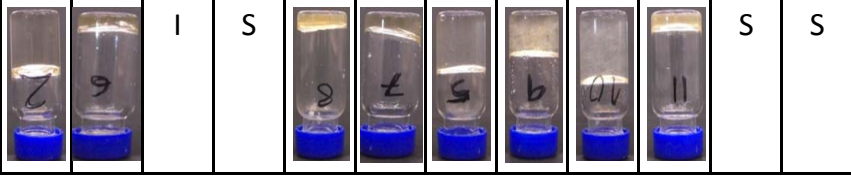
	ε												
	Pentane	Toluene		Et_2O	$CHCl_3$	EtOAc	CH_2Cl_2	THF	iPrOH	Acetone	EtOH	ACN	MeOH	H_2O
1	I			I										I
2	I			I	S									I
3	I			I	S									I
4	I			I	S							S	S	I

Fig. S1 Appearance of the gels formed from compounds **1** - **4** in the different solvents tested. I = insoluble; S = soluble.

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SEM micrographs of xerogels from compound 1 in toluene at different concentrations

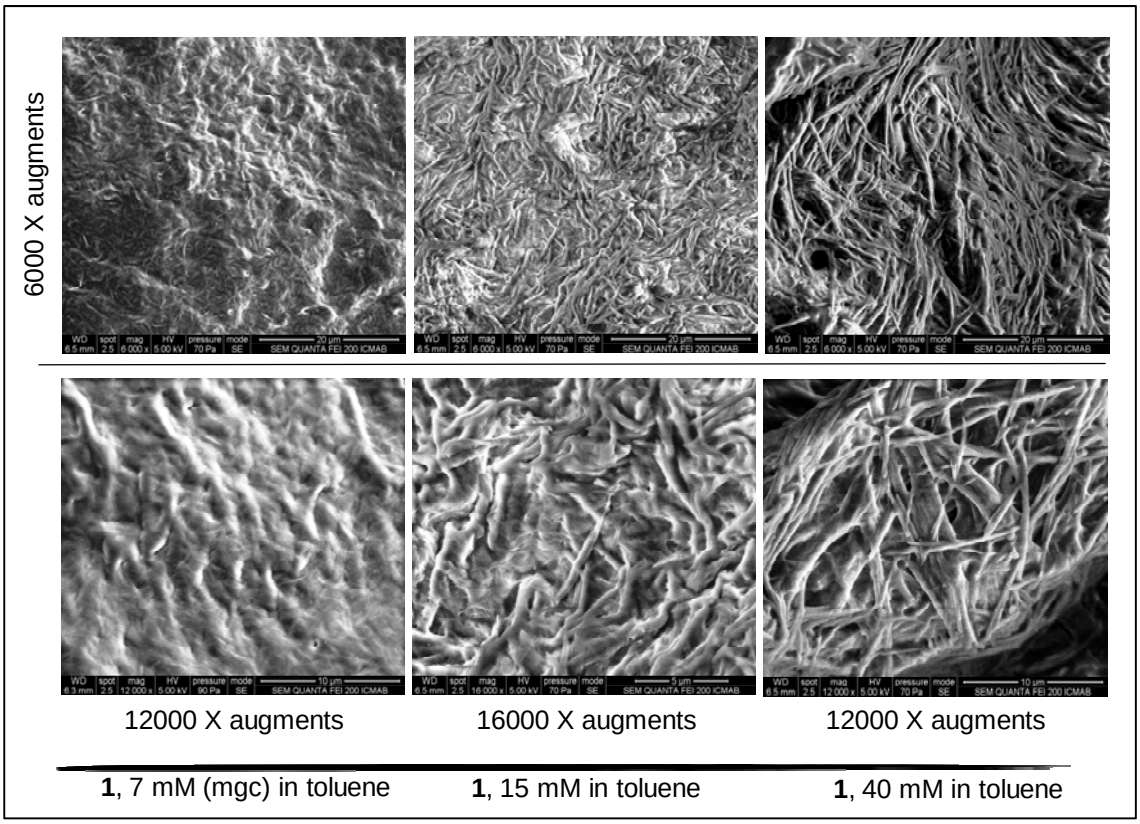

Fig. S2 SEM micrographs of xerogels from 7 mM (mgc), 15 mM,and 40mM peptide **1** in toluene at two different magnifications each.

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IR data

Table S1. N-H and C=O bands[a] in the IR spectra of peptides **1** - **4** as solids, as xerogels from toluene, and in solution.

Compound	NH			CO		
	Crystalline solid[b]	Xerogel[c]	Solution[d]	Crystalline solid[b]	Xerogel[c]	Solution[d]
1	3307	3305	3423	1703 1650	1759 1729 1686 1638	1739 1706 1662
2	3308	3305	3438	1734 1689 1642	1734 1689 1642	1712 1652
3	3308	3307	3439	1735 1688 1639	1733 1688 1640	1719 1656
4	3307	3307	3441 3310	1688 1639	1690 1641	1703 1653

[a] In cm^{-1}. [b] ATR. [c] Xerogel from toluene gel at 30 mM in KBr. [d] 5 mM solution in $CDCl_3$

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Computational calculations: an alternative gelation pattern for 1

An alternative interaction pattern has also been explored for dimeric (**D'**) and tetrameric (**T'**) aggregates of tetrapeptide **1**. The resultant structures are shown in Figure S2. They are clearly unfavoured with respect to those shown in Figure 6 of the main text as can be deduced from comparison between data for D and T with data for D' and T' in Table S2.

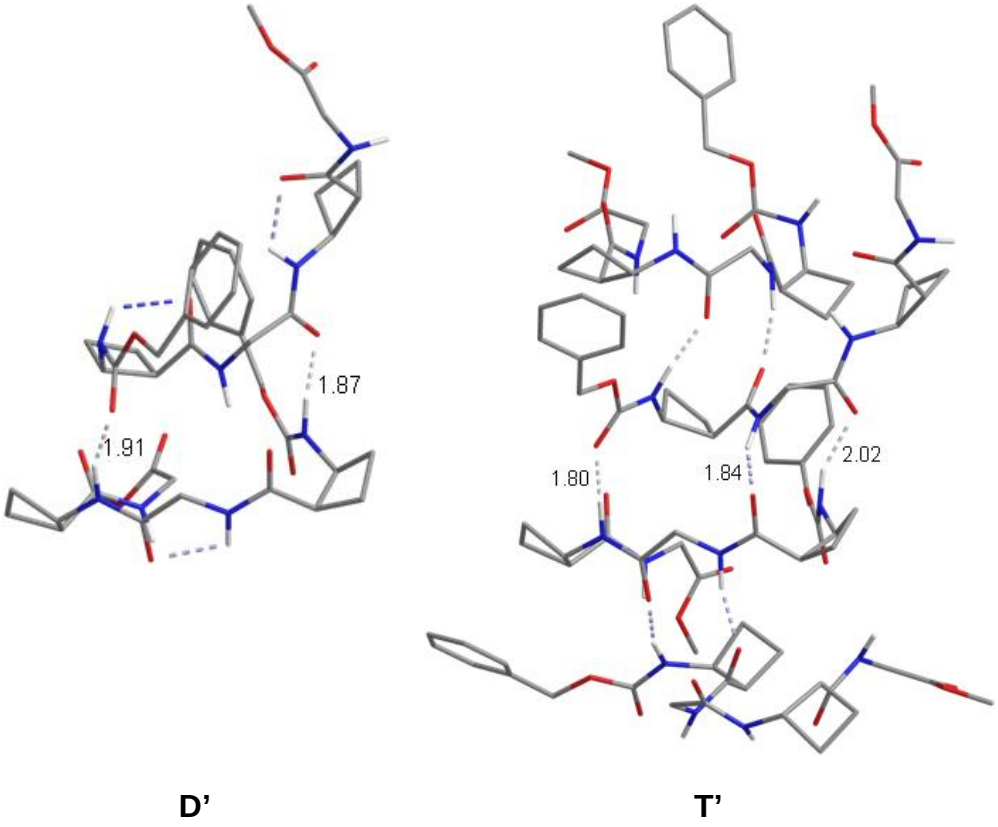

Fig. S2 Structures of dimeric (**D'**) and tetrameric (**T'**) aggregates of peptide **1** optimized at the M06-2X/6-31G(d) level of calculation. Selected interatomic distances are in Å.

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Table S2. Aggregation energies[a] computed for tetrapeptide **1**

	In *vacuo*[b]		In toluene[c]	
	ΔE	ΔE/n	ΔE	ΔE/n
D (n=2)	–22.1	–11.0	–15.8	–7.9
D' (n=2)	–11.1	–5.6		
T (n=4)	–76.9	–19.2	–50.6	–12.6
T' (n=4)	–35.4	–8.8		

[a] All values in kcal mol^{-1}. ΔE corresponds to the n **X** → (**X**)$_n$ process. [b] M06-2X/6-31G(d) level of calculation. [c] SMD-M06-2X/6-311+G(d,p)// M06-2X/6-31G(d) level of calculation.

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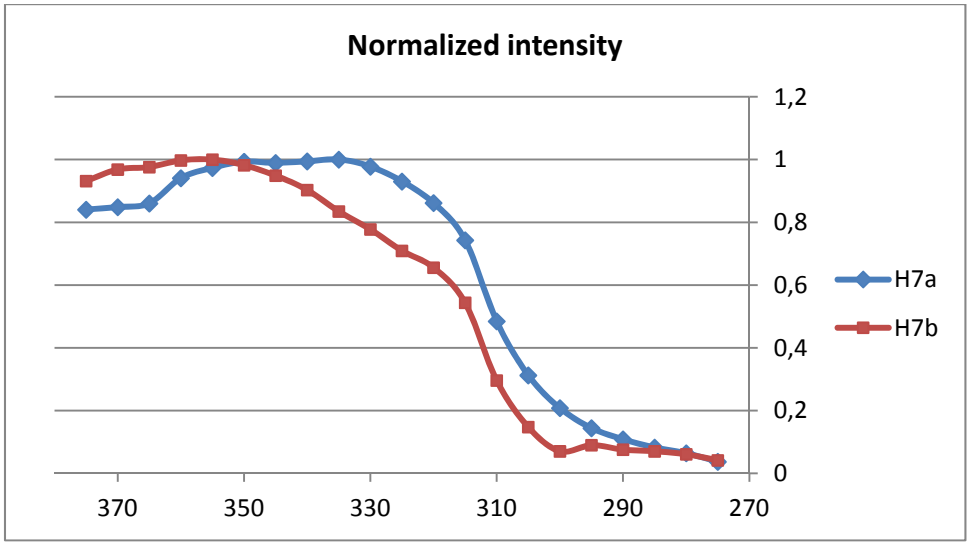
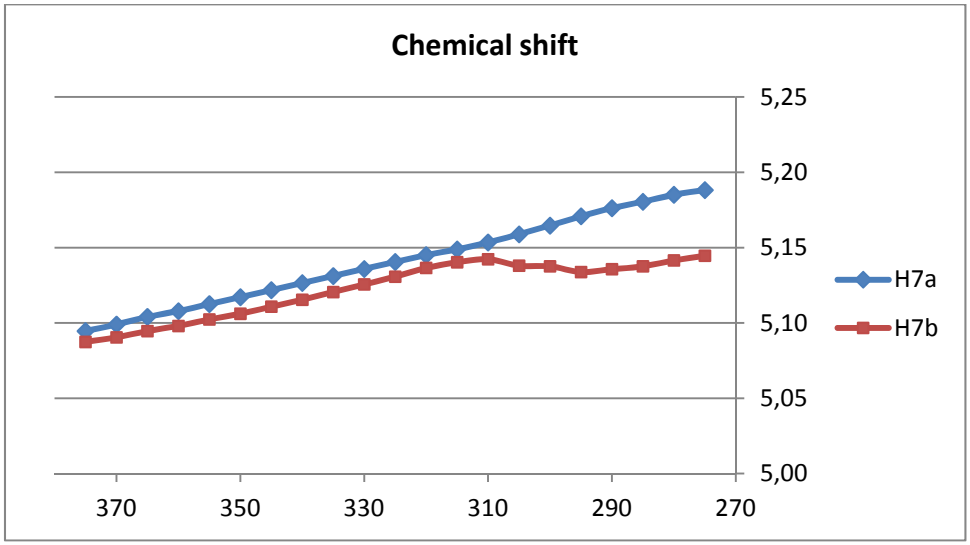
NMR studies on gelation of tetrapeptide 1:

Graphical representation of intensity and chemical-shift variations with temperature

H7a/H7b pair:





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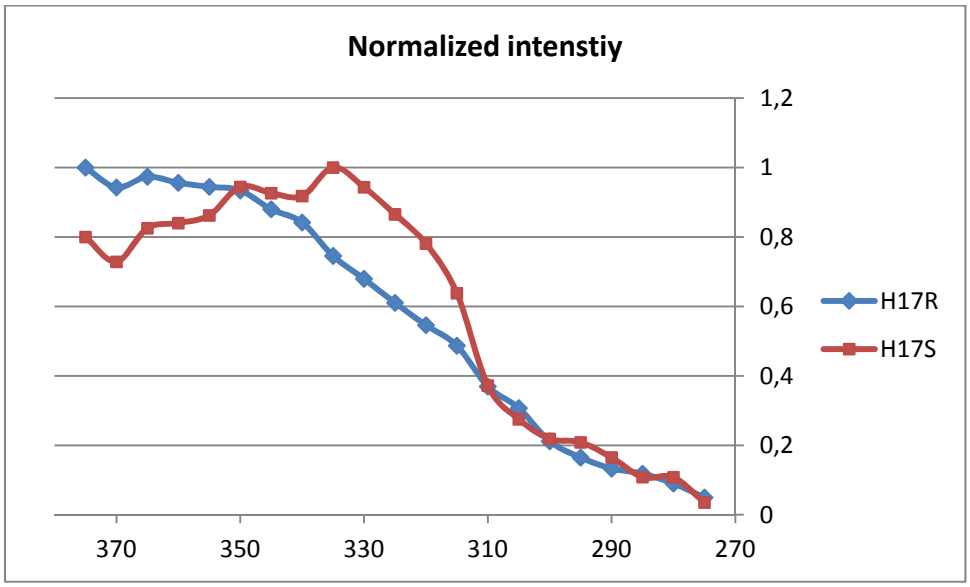
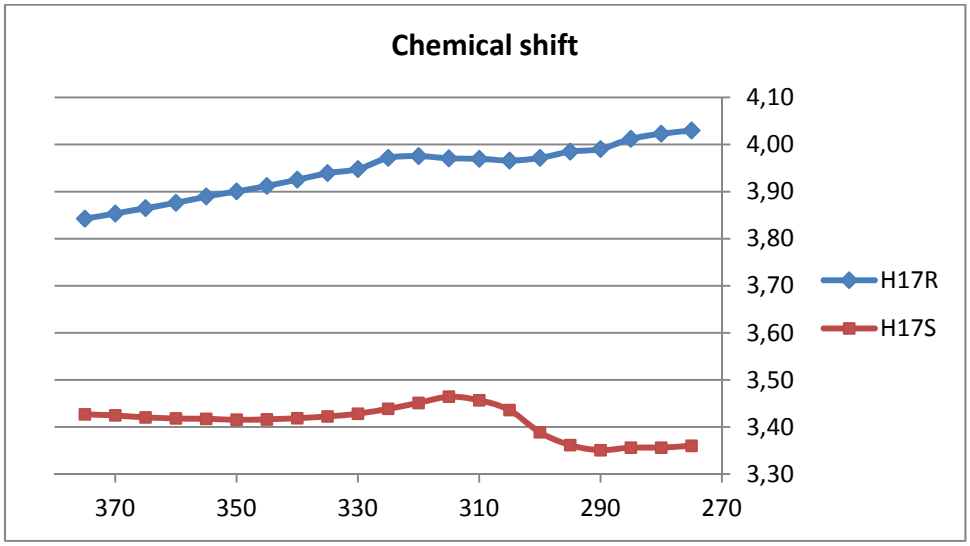
$H17_R$/$H17_S$ pair:





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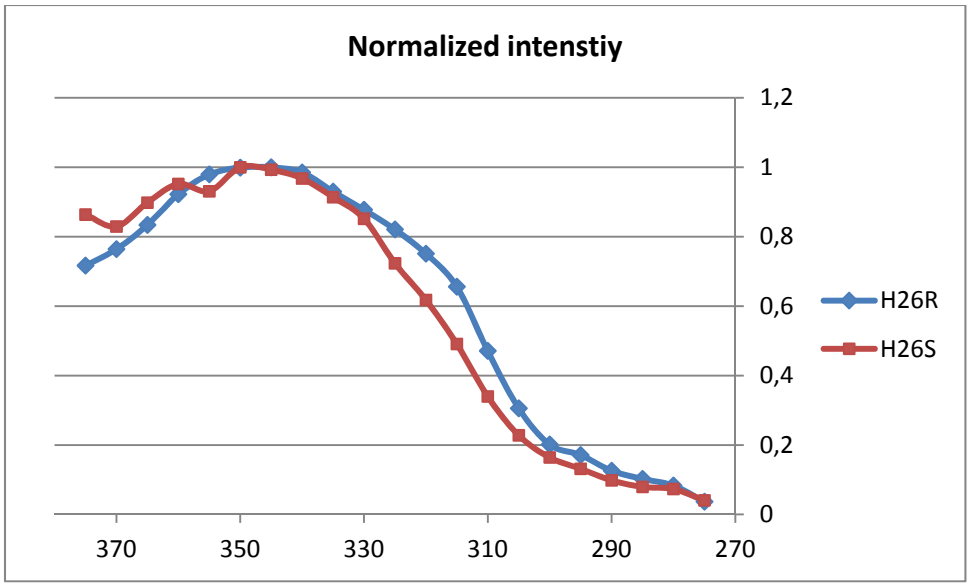
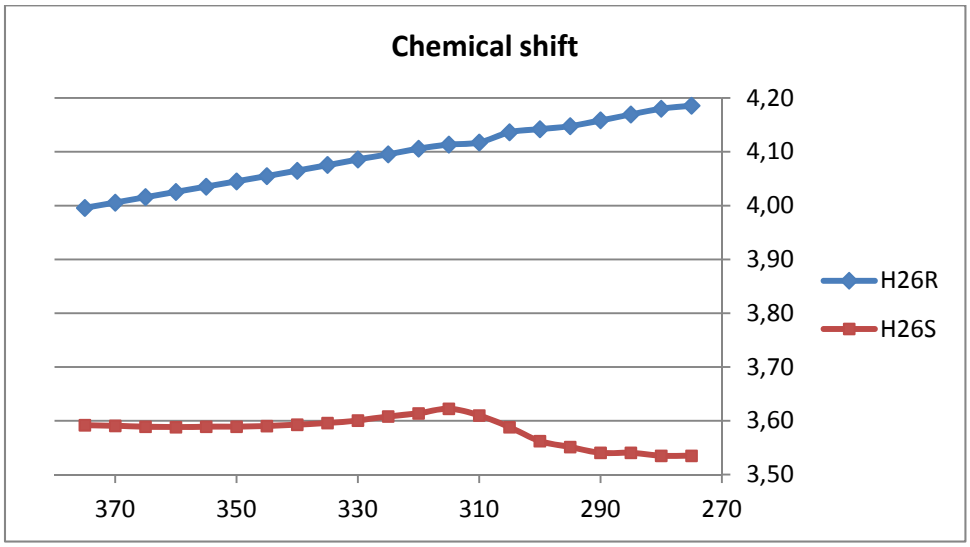
$H26_R$/$H26_S$ pair:





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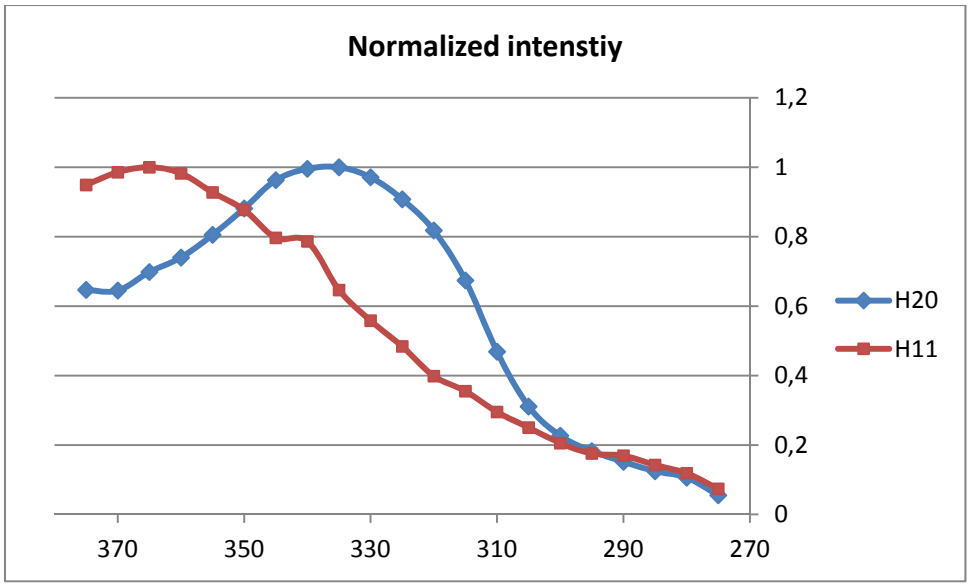
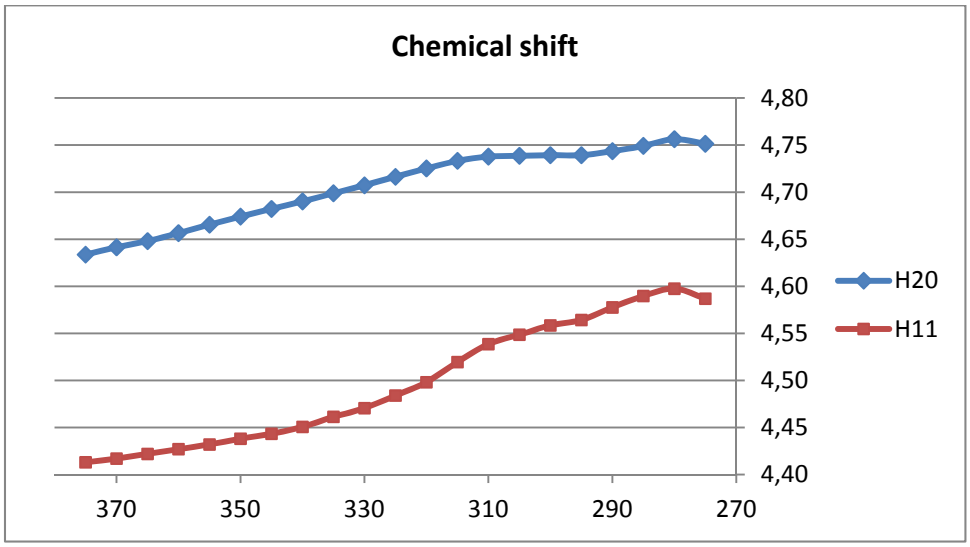
H20 and H11:





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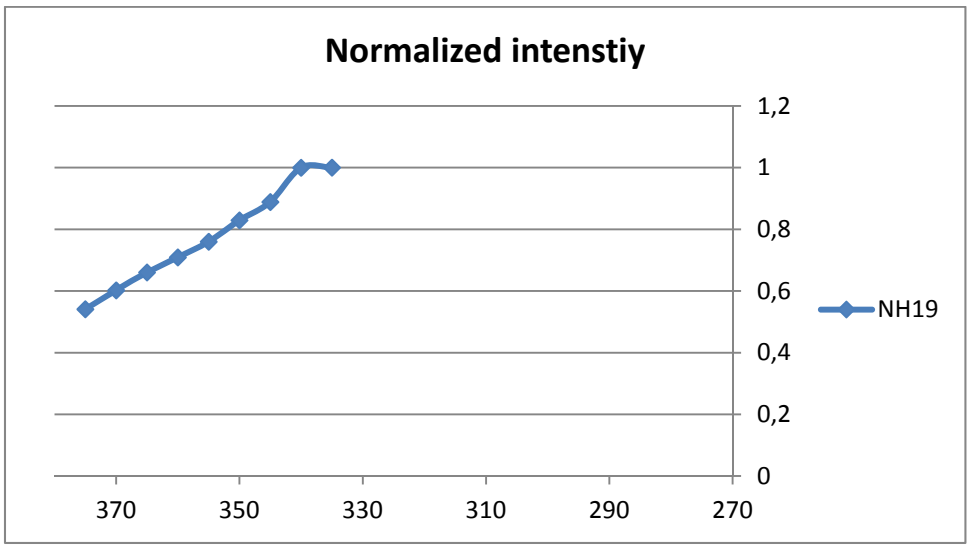
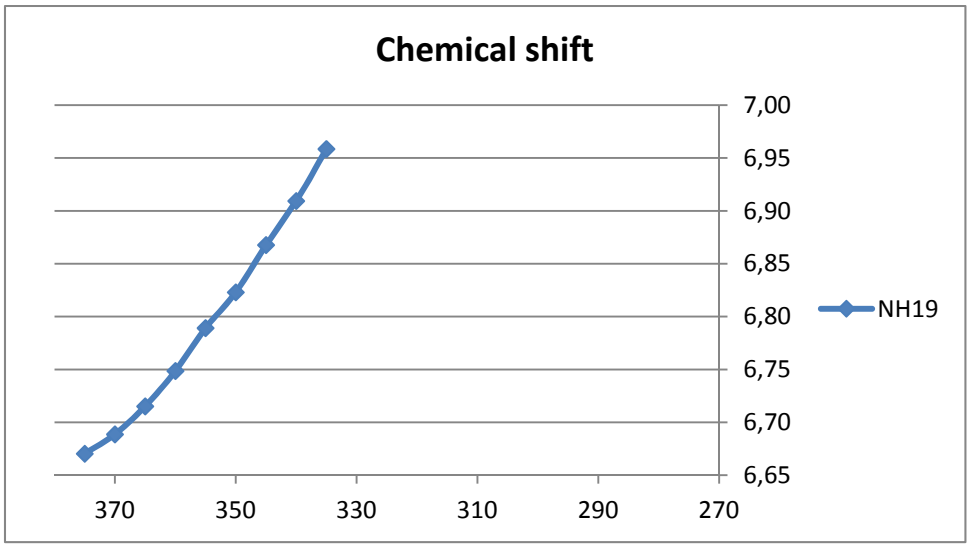
NH_{19}:





Unfortunately, in this case, curve is “broken” due to overlapping with toluene signals

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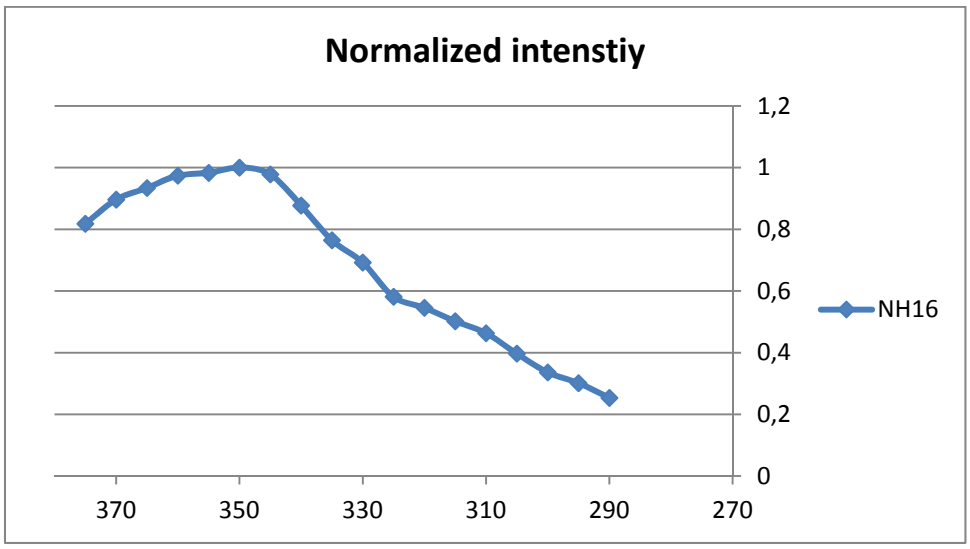
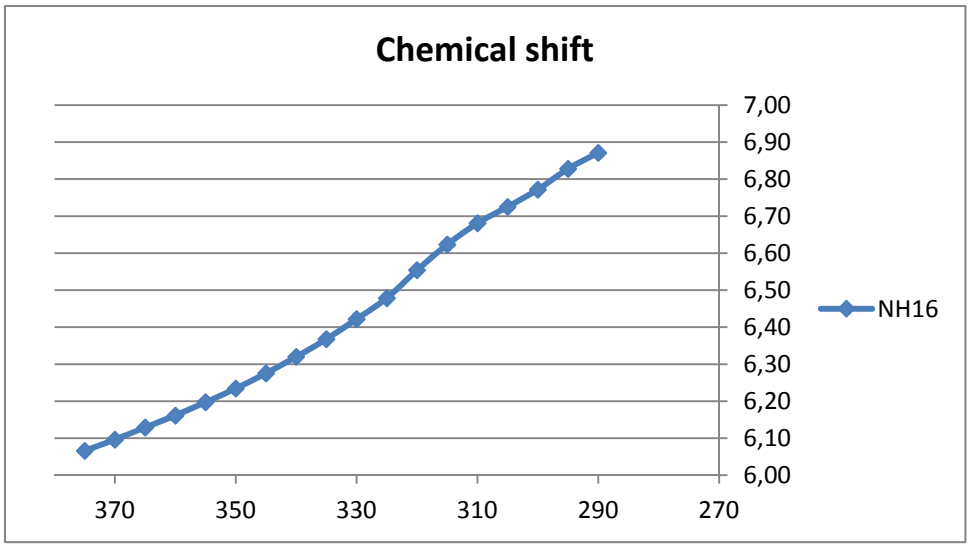
NH_{16}:





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NH_{10} and NH_{25}: