Supporting Information

Chitin Hydrolysis in Acidified Molten Salt Hydrates

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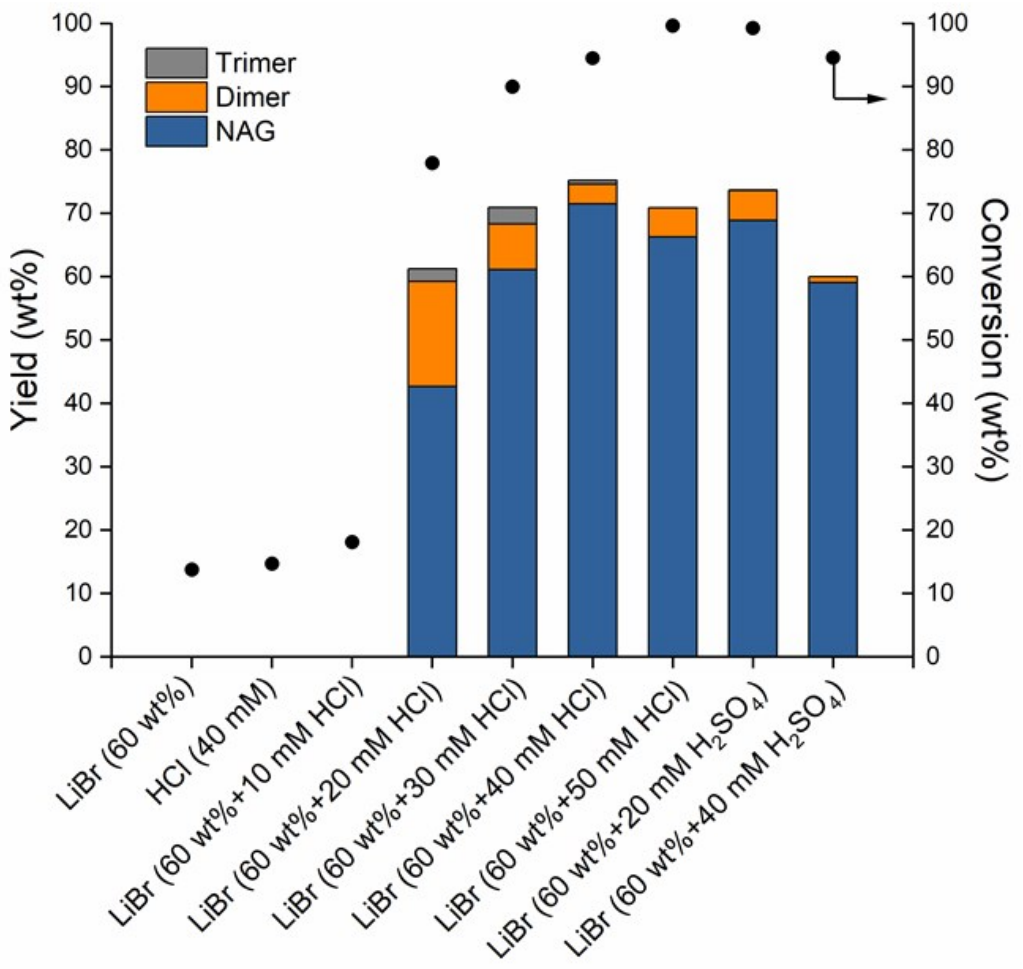

Fig. S1 Conversion and monomers/oligomers' yields from chitin with different concentrations of HCl and H_2SO_4. Reaction conditions: 0.2 g chitin and 4 mL LiBr AMSH at 120 ℃ for 30 min.

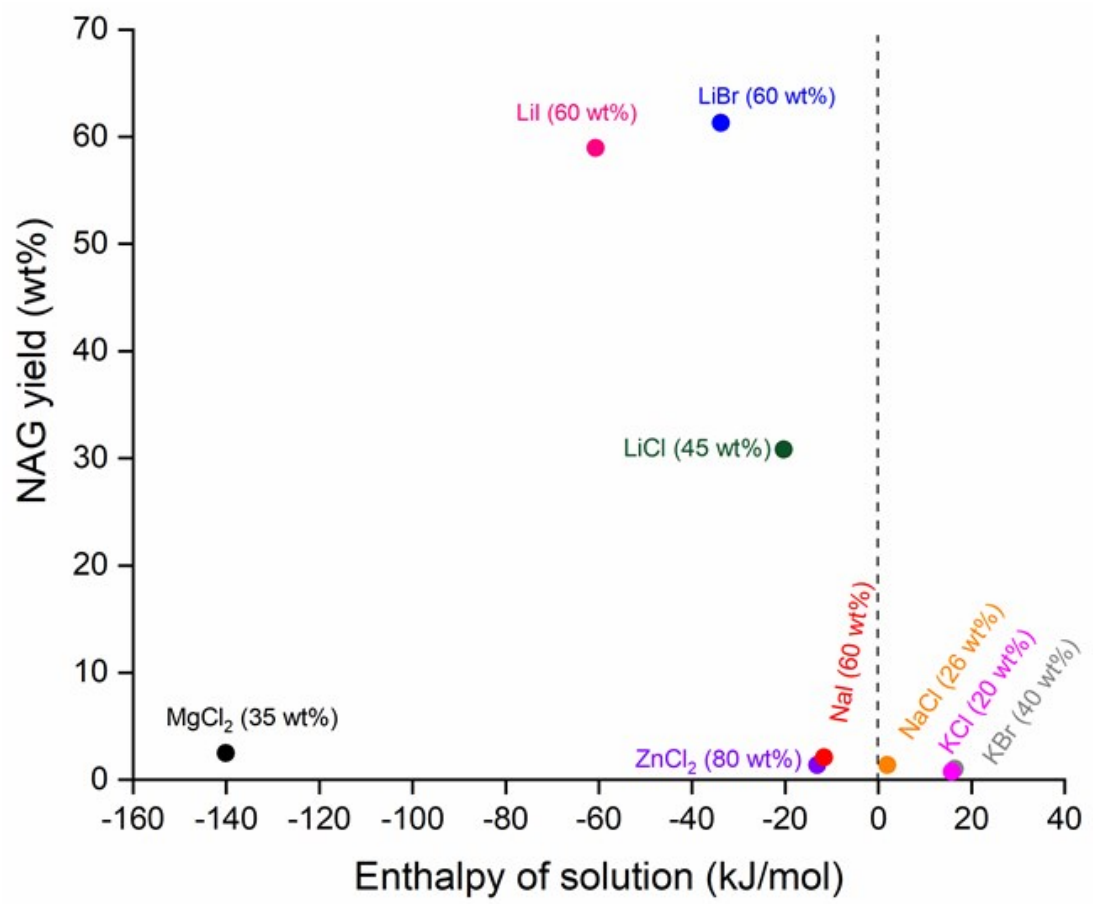

Fig. S2 The correlation between the formation of NAG and the different salts' enthalpy of solution in AMSH systems. The enthalpy of solution of salt molten hydrates were calculated by using thermodynamic properties of salts.[1]

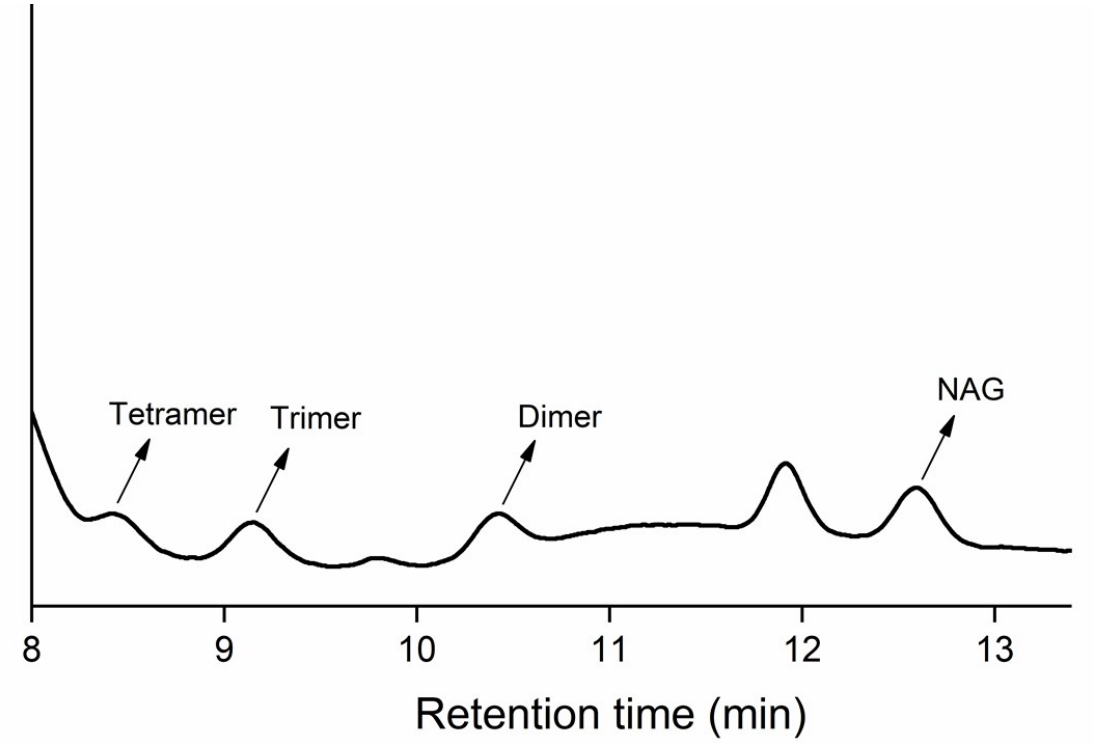

Fig. S3 HPLC chromatogram of chitin depolymerization. At low temperatures and short reaction time, tetramer formation was also observed. Reaction conditions: 0.2 g chitin and 4 mL AMSH (60 wt% LiBr containing 40 mM HCl) at 80 °C for 15 min.

Table S1 The detailed results of NAG concentration with respect to time at various temperatures for the Arrhenius plot (chitin conversion is lower than 30 wt%).

Temperature (^{0}C)	Time (min)	NAG concentration (M)	slope	ln(slope)
50	45	2.49×10^{-5}	9.00×10^{-7}	-13.921
	50	2.75×10^{-5}		
	55	3.17×10^{-5}		
	60	3.83×10^{-5}		
55	30	2.32×10^{-5}	2.25×10^{-6}	-13.004
	40	3.79×10^{-5}		
	50	5.75×10^{-5}		
	60	9.17×10^{-5}		
60	25	3.22×10^{-5}	6.00×10^{-6}	-12.024
	30	5.36×10^{-5}		
	40	8.56×10^{-5}		
	50	1.89×10^{-4}		
65	20	2.71×10^{-5}	7.46×10^{-6}	-11.806
	25	3.46×10^{-5}		
	30	7.20×10^{-5}		
	35	1.39×10^{-4}		
70	20	4.33×10^{-5}	2.10×10^{-5}	-10.773
	25	1.53×10^{-4}		
	30	2.91×10^{-4}		
	35	3.47×10^{-4}		

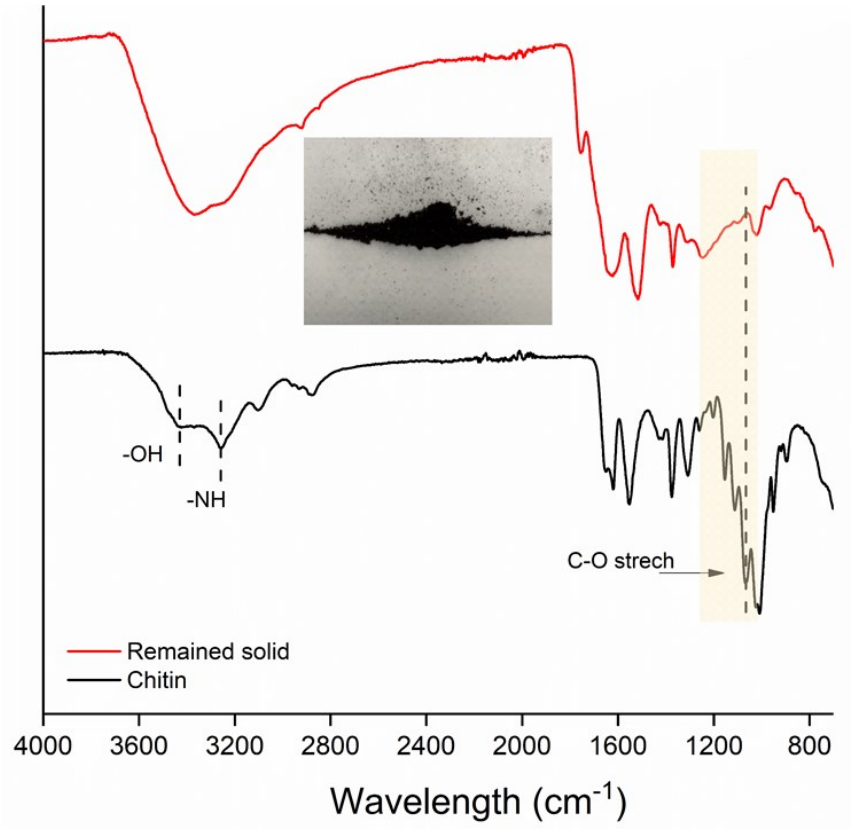

Fig. S4 ATR-FTIR spectra of pure chitin and the remained solid after reaction. Reaction conditions: 0.2 g chitin and 4 mL AMSH (60 wt% of LiBr containing 40 mM HCl) at 140 °C for 180 min. The broader and combined bands of O-H (3430 cm^{-1}) and N-H (3260 cm^{-1}) in remained solid was observed, specifically disappearing sharpness of latter peak. Amide I band was broaden and C-O stretching band asymmetric in-phase ring modes were altered after the depolymerization of chitin.

Table S2 The chemical shift, area and height to width ratios (H/W) of the peaks with and without salt after ball milling. Ball-milling conditions: 0.5 g chitin, 0.5 g salt at 500 rpm and 4 cycles (10 min grinding and 5 min rest).

	Carbon numbers	ppm	Area (x10^6)	H/W (x10^4)
BM chitin	C8	23.81	8.94	19.38
	C2	56.34	5.30	17.17
	C6	61.96	8.25	21.56
	C5,3 (merged)	75.45	18.40	23.14
	C4	81.46	4.23	8.19
	C1	103.35	8.86	5.91
	C7	174.41	6.54	8.83
BM chitin-LiBr	C8	26.14	2.99	10.03
	C2	56.61	3.49	10.49
	C6	61.74	1.02	5.07
	C5,3 (merged)	74.63	6.74	13.43
	C4	79.15	1.57	3.87
	C1	101.89	3.56	3.26
	C7	177.39	2.58	3.33
BM chitin-LiCl	C8	25.14	2.62	4.85
	C2	56.79	2.80	4.86
	C6	62.39	0.19	67.91
	C5,3 (merged)	75.07	1.35	6.13
	C4	89.09	6.69	4.64
	C1	102.28	2.99	2.28
	C7	176.63	1.90	2.35
BM chitin-KBr	C8	24.25	5.22	14.83
	C2	56.46	4.10	15.16
	C6	62.29	5.09	11.39
	C5,3 (merged)	75.24	12.06	17.69
	C4	82.08	2.79	5.88
	C1	102.53	5.64	4.68
	C7	174.56	4.64	6.63
BM chitin-KCl	C8	24.01	4.89	14.93
	C2	56.42	4.20	10.40
	C6	62.26	4.58	11.55
	C5,3 (merged)	75.36	11.63	14.67
	C4	82.12	2.38	5.18
	C1	102.94	5.64	4.53
	C7	174.66	4.08	6.42

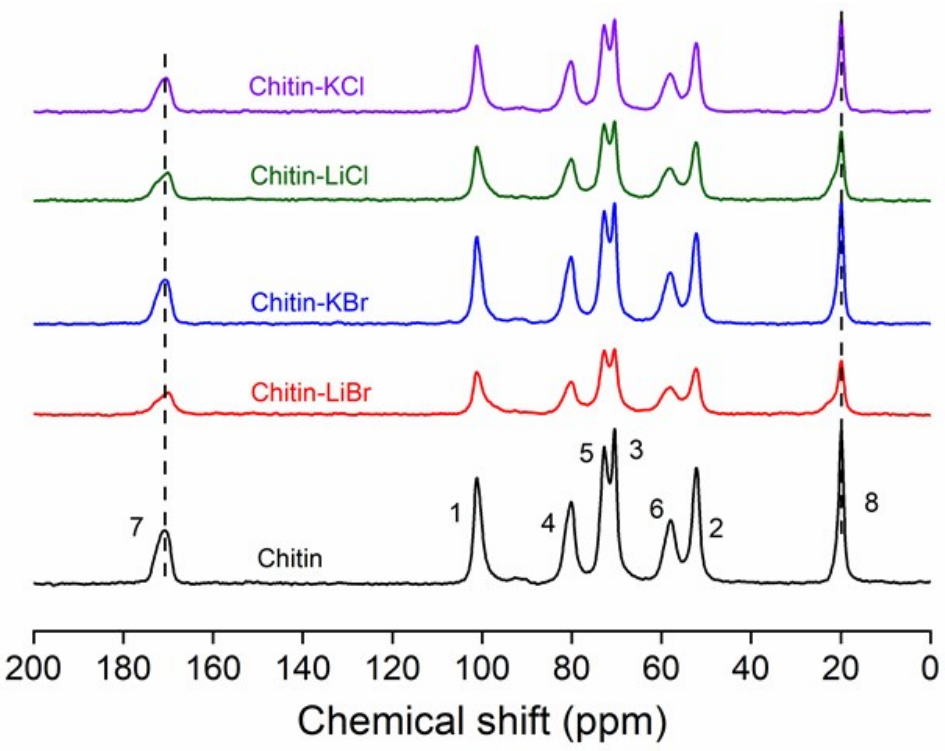

Fig. S5 Solid-state ^{13}C NMR spectra of raw chitin and physically-mixed chitin-salt composites.

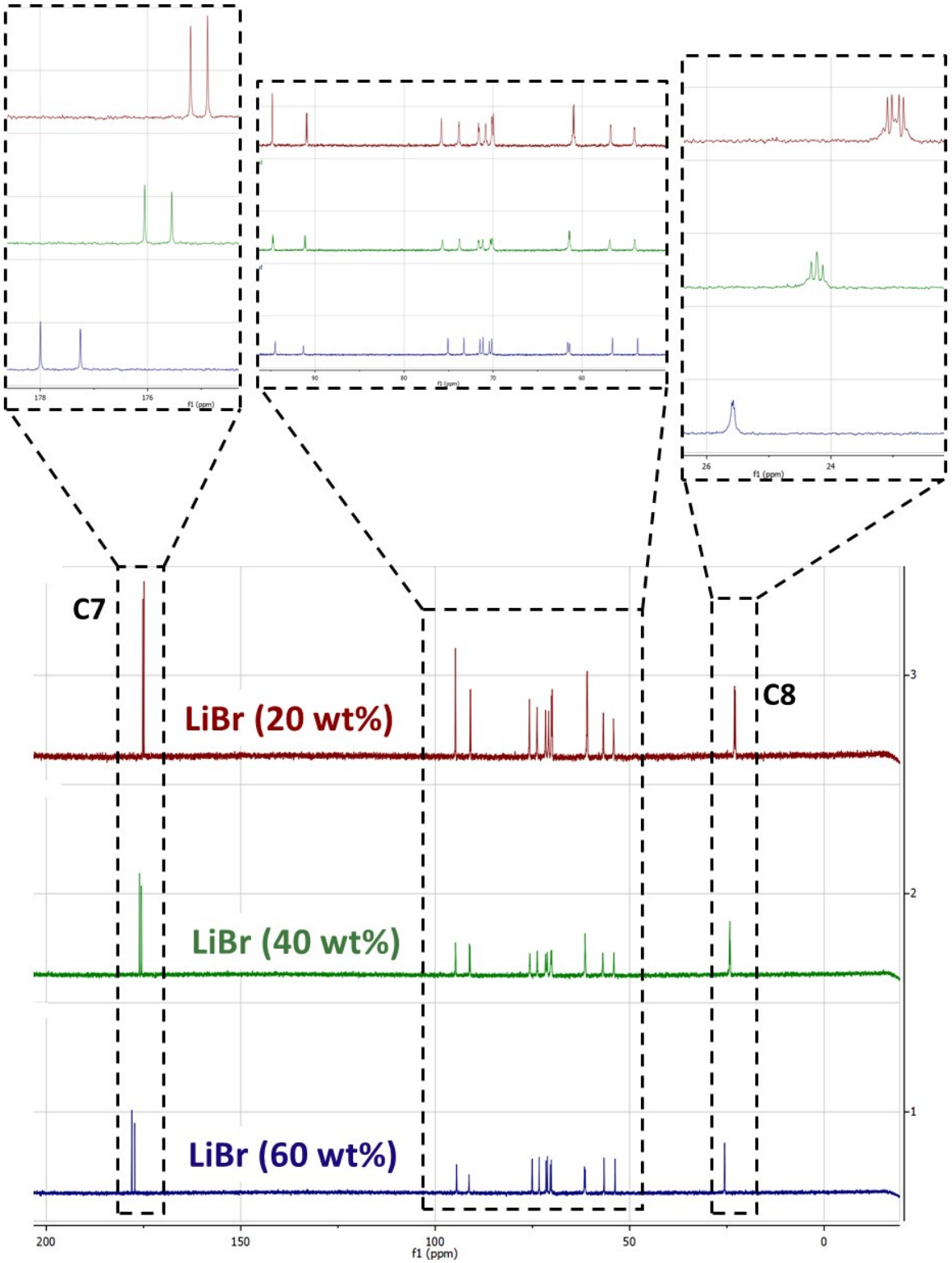

Fig. S6 ^{13}C NMR spectrum of NAG in different concentration of LiBr MSH. Reaction conditions: 0.1 g NAG and 2 mL LiBr MSH stirring at room temperature for 1 h.

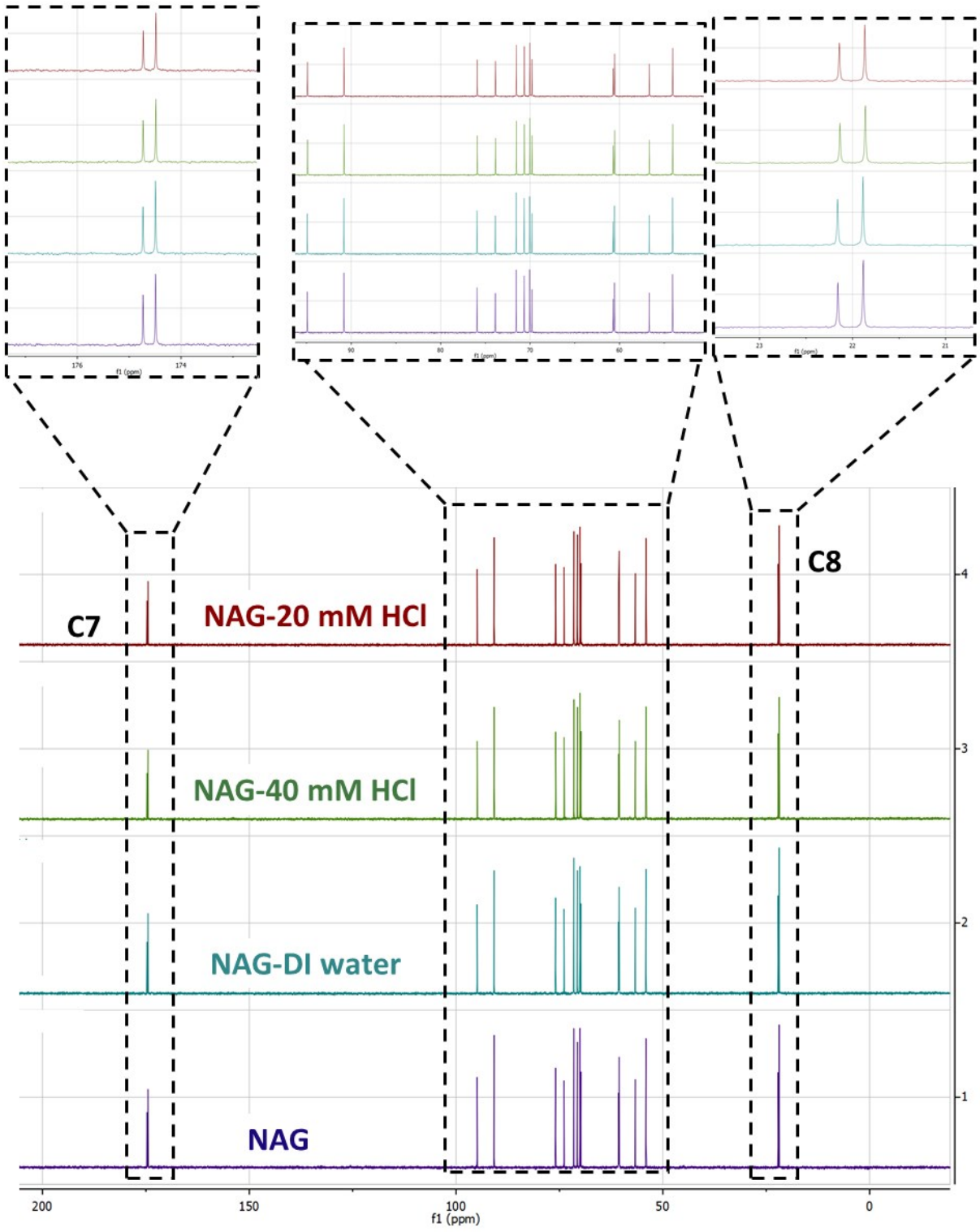

Fig. S7 ^{13}C NMR spectrum of NAG in the presence of D_2O with the addition of 20 mM, 40 mM HCl and DI water (the same amount as the amount of water contained in 32% HCl).

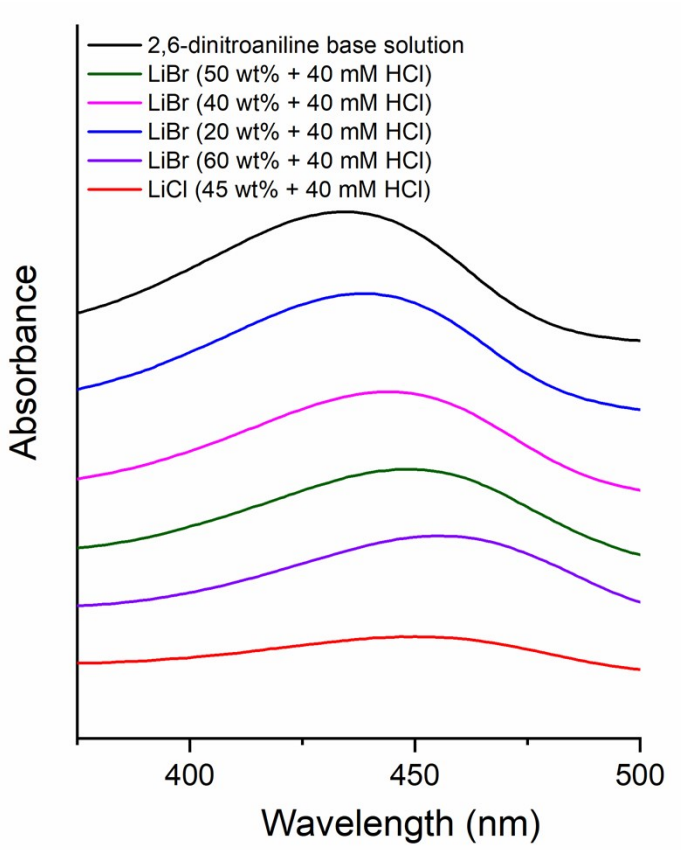

Fig. S8 Absorption spectra of 2,6-dinitroaniline base solution with a varied LiBr amount (20 wt%, 40 wt%, 50 wt% and 60 wt% containing 40 mM HCl) and LiCl (45 wt% containing 40 mM HCl).

Table S3 Hammett function of AMSH with varied amount of LiBr and LiCl AMSH (45 wt% containing 40 mM HCl).

Solvent system	Hammett function
LiBr AMSH (20 wt% including 40 mM HCl)	-4.53
LiBr AMSH (40 wt% including 40 mM HCl)	-4.84
LiBr AMSH (50 wt% including 40 mM HCl)	-4.99
LiBr AMSH (60 wt% including 40 mM HCl)	-5.09
LiCl AMSH (45 wt% including 40 mM HCl)	-5.39

References

1. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *Journal of Physical and Chemical Reference Data*, 1982, **11**.