Electronic Supplementary Information

Characteristic activity of phosphorous acid in the dehydration condensation of a chitin-derived nitrogen-containing sugar alcohol

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Table S1 Optimisation of reaction conditions for the dehydration of ADS by H_3PO_3.[a]

Entry	S/C	Temp. /°C	Conv. /%	Yield of product /%					
				ADI	1,4-AHADS	3,6-AHADS	1,5-AHADS	ADIAc	Others
S1	2.0	150	100	24	1.8	1.3	7.0	3.5	63
S2	2.0	130	100	24	2.3	1.5	8.0	3.4	61
S3	2.0	110	100	18	5.4	5.5	23	3.0	46
S4	4.0	130	100	25	3.1	1.6	14	3.1	53
S5	8.0	130	100	10	16	4.8	30	2.0	38

[a]3 h, pressure <0.1 kPa, no solvent.

Table S2 Dehydration of ADS by various catalysts under the optimised condition for H_3PO_3.[a]

Entry	Catalyst	Conv. /%	Yield of product /%					
			ADI	1,4-AHADS	3,6-AHADS	1,5-AHADS	ADIAc	Others
S6	None	42	<0.1	10	2.3	7.1	<0.1	23
S7	CF_3SO_3H	100	28	<0.1	<0.1	2.0	2.9	67
S8	Oxalic acid	100	13	11	21	33	7.8	14
S4	H_3PO_3	100	25	3.1	1.6	14	3.1	53
S9	2,4-DNBA	100	12	17	6.8	19	2.7	43
S10	H_3PO_4	100	8.9	20	5.0	21	3.9	41

[a]S/C = 4.0, 130 °C, 3 h, pressure <0.1 kPa, no solvent. 2,4-DNBA: 2,4-dinitrobenzoic acid.

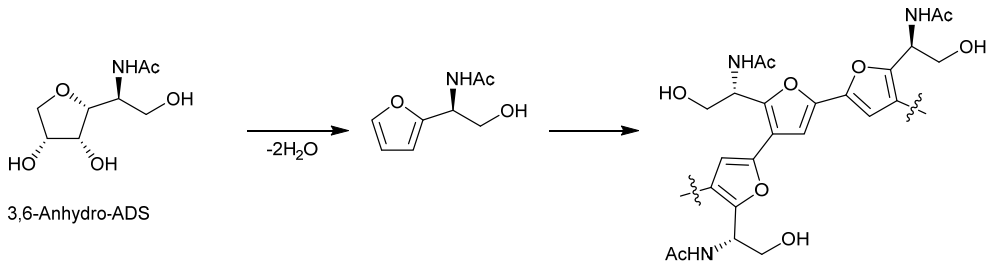

Fig. S1 A possible formation route of a furan derivative, and structure of a humin compound. Speculated based on the literature (ChemSusChem, 2013, 6, 1745).

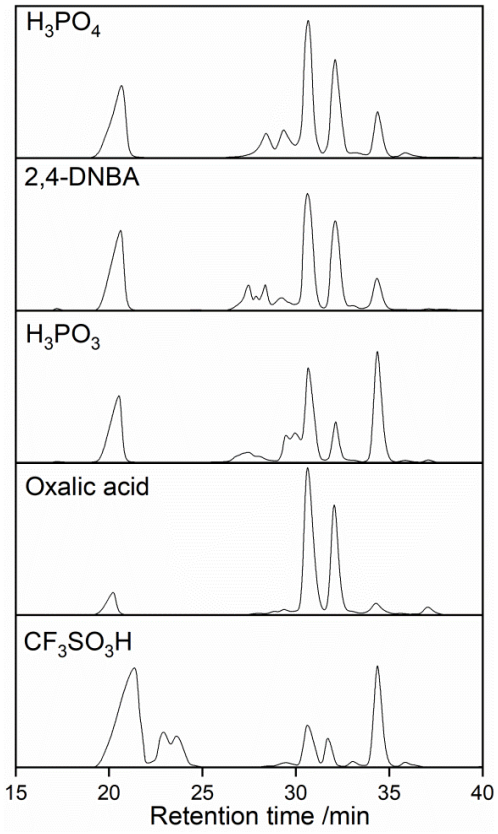

Fig. S2 GPC charts of ADS dehydration product using various acid catalysts. 2,4-DNBA: 2,4-dinitrobenzoic acid.

Table S3 GPC analysis of the product in the dehydration of ADS

Catalyst	Ratio of peak area /%	
	$M_w > 300$	$300 \geq M_w$
None	0	100
CF_3SO_3H	62	38
$H_2C_2O_4$	10	90
H_3PO_3	37	63
2,4-DNBA	60	40
H_3PO_4	53	47

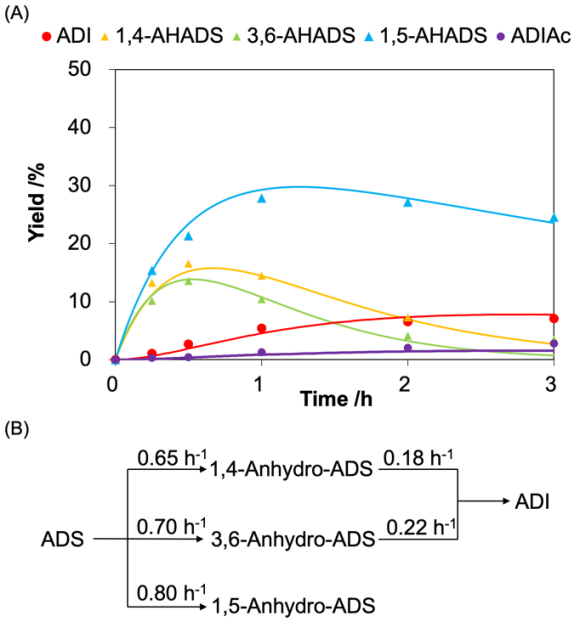

Fig. S3 Time course of ADS dehydration by H_3PO_4. The plots indicate actual experimental results, and the lines show theoretical yield curves based on the kinetic analysis.

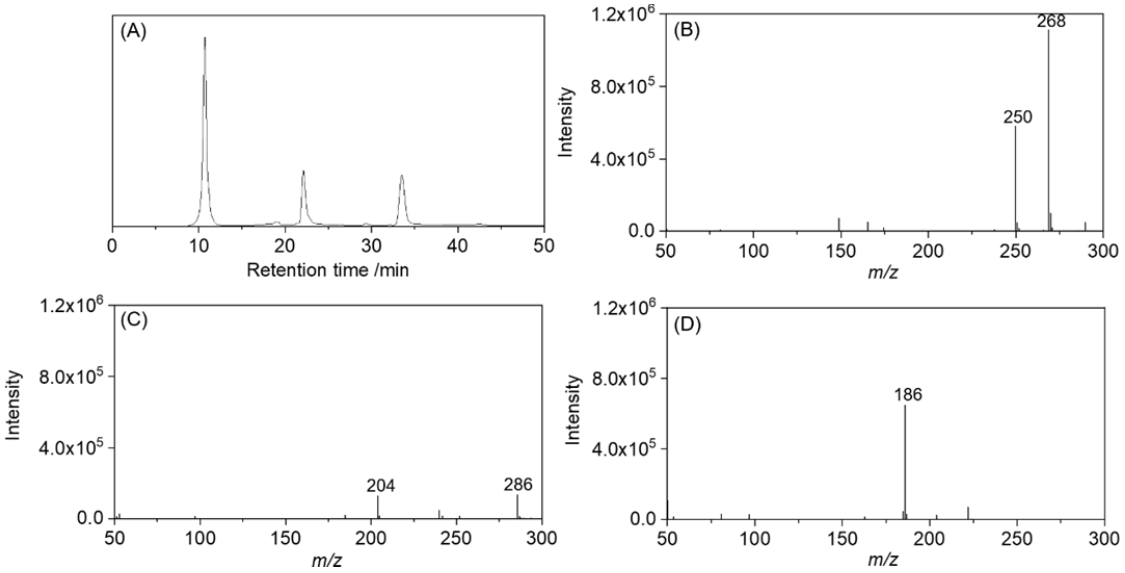

Fig. S4 (A) LC chart of the product solution after the dehydration of ADS by H_3PO_3 (S/C = 4.0) at 130 °C under < 0.1 kPa of pressure for 1 h. The mass spectra with a negative ion mode at (B) 10 min, (C) 22 min and (D) 34 min.

Assignment of peaks observed in the mass spectra in Fig. S4

In (B), the peaks of *m*/*z* = 250 and *m*/*z* = 268 are ascribed to phosphorous acid esters of anhydro-ADS ($[M-H_2O-H]^-$, *m*/*z* = 250; $[M-H]^-$, *m*/*z* = 268). In (C), the peaks of *m*/*z* = 204 and *m*/*z* = 286 are ascribed to anhydro-ADS ($[M-H]^-$, *m*/*z* = 204) and phosphorous acid esters of ADS ($[M-H]^-$, *m*/*z* = 286). In (D), *m*/*z* = 186 is ascribed to ADI ($[M-H]^-$, *m*/*z* = 186).

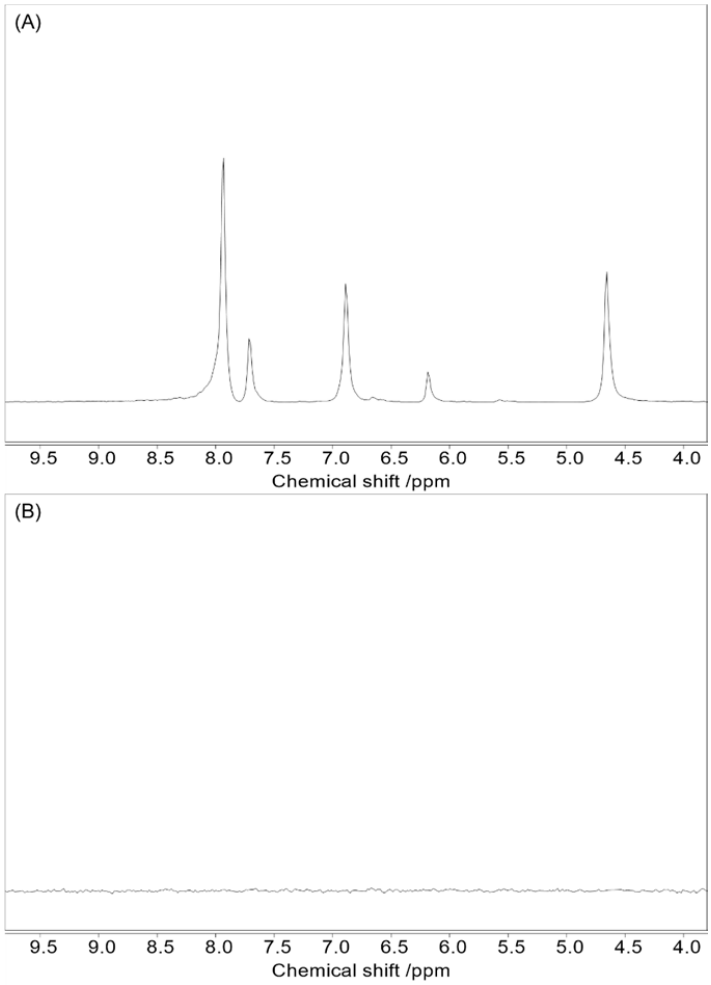

Fig. S5 ^{31}P NMR spectra of HPLC fractions for LC-MS analysis shown in Fig. S4. (A) Retention time: 10 min. (B) Retention time: 22 min.

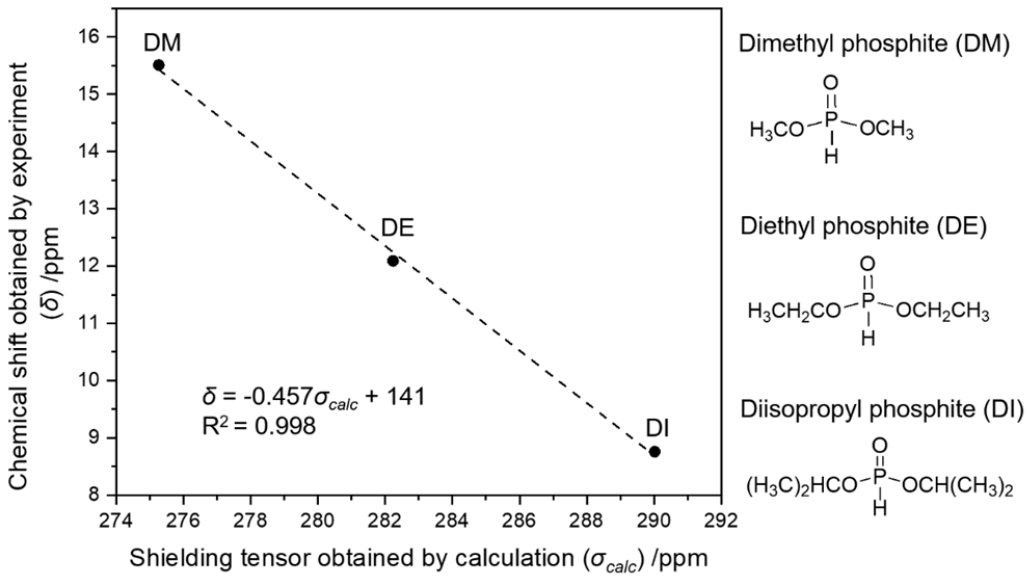

Fig. S6 Determination of the coefficients *a* and *b* using the least-squares method using standard compounds

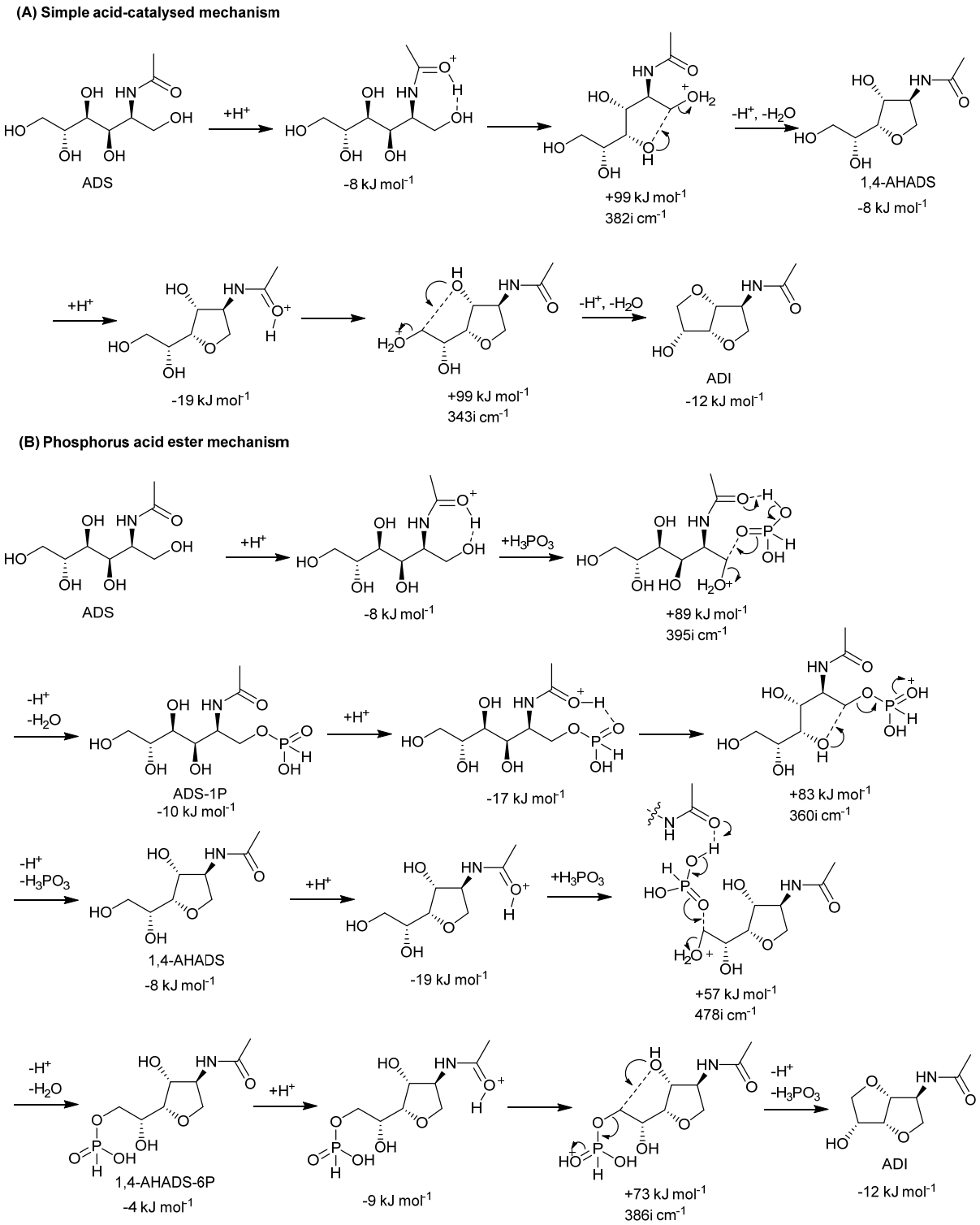

Fig. S7 Proposed reaction mechanisms for (A) typical acid catalysts and (B) H_3PO_3. Proton formation assumes $2H_3PO_3 \rightarrow H^+ + [H_2PO_3 \cdots H_3PO_3]^-$.