Electronic Supplementary Information

Hydrolytic hydrogenation of chitin to amino sugar alcohol

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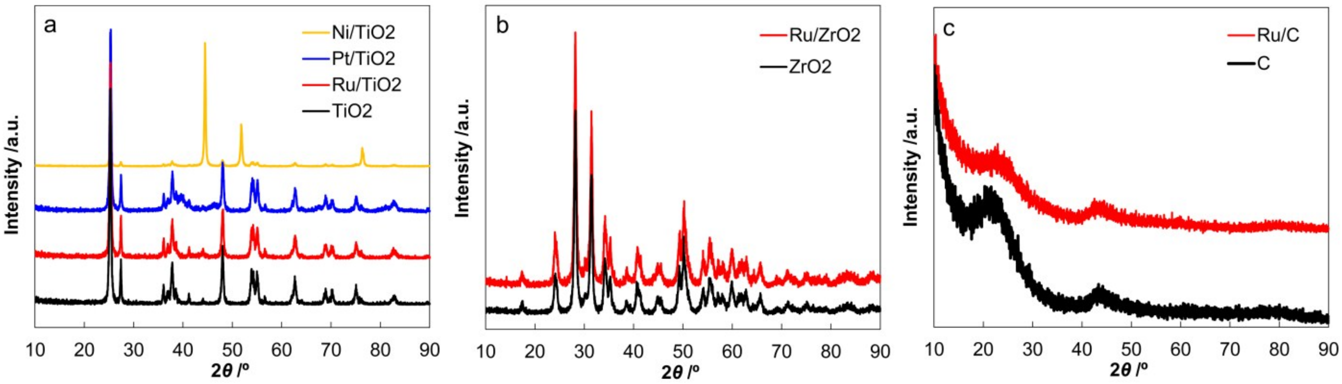


Fig. S1. XRD patterns of catalysts.

No peak of Ru can be seen for all the Ru catalysts due to formation of amorphous Ru oxide. The intensity for Ni/TiO_2 was reduced to be 20%. Crystallite size of Ni on Ni/TiO_2 was 43 nm, determined from (111) peak at 44.5°.

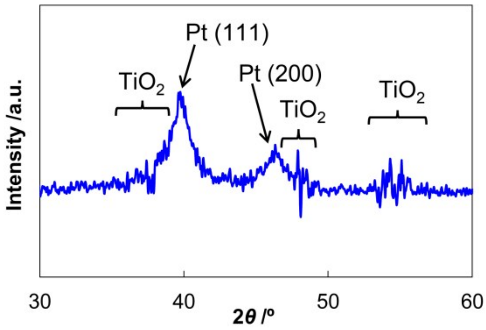


Fig. S2. Difference XRD pattern of Pt/TiO_2 – TiO_2.

Crystallite size of Pt is 6 nm, determined from (111) peak at 39.7°.

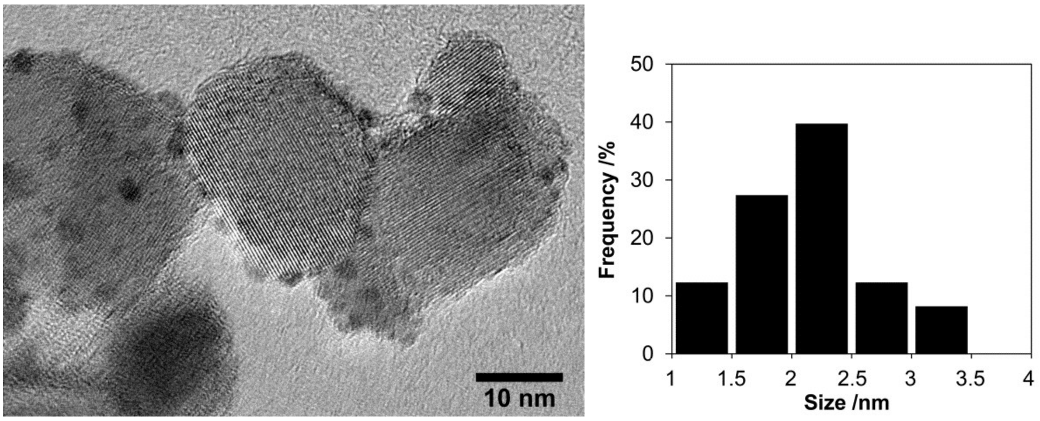


Fig. S3. TEM image of 5 wt% Ru/TiO_2.

A mean diameter to give the same surface area/volume ratio was 2.4 nm, corresponding to the dispersion of 46%.

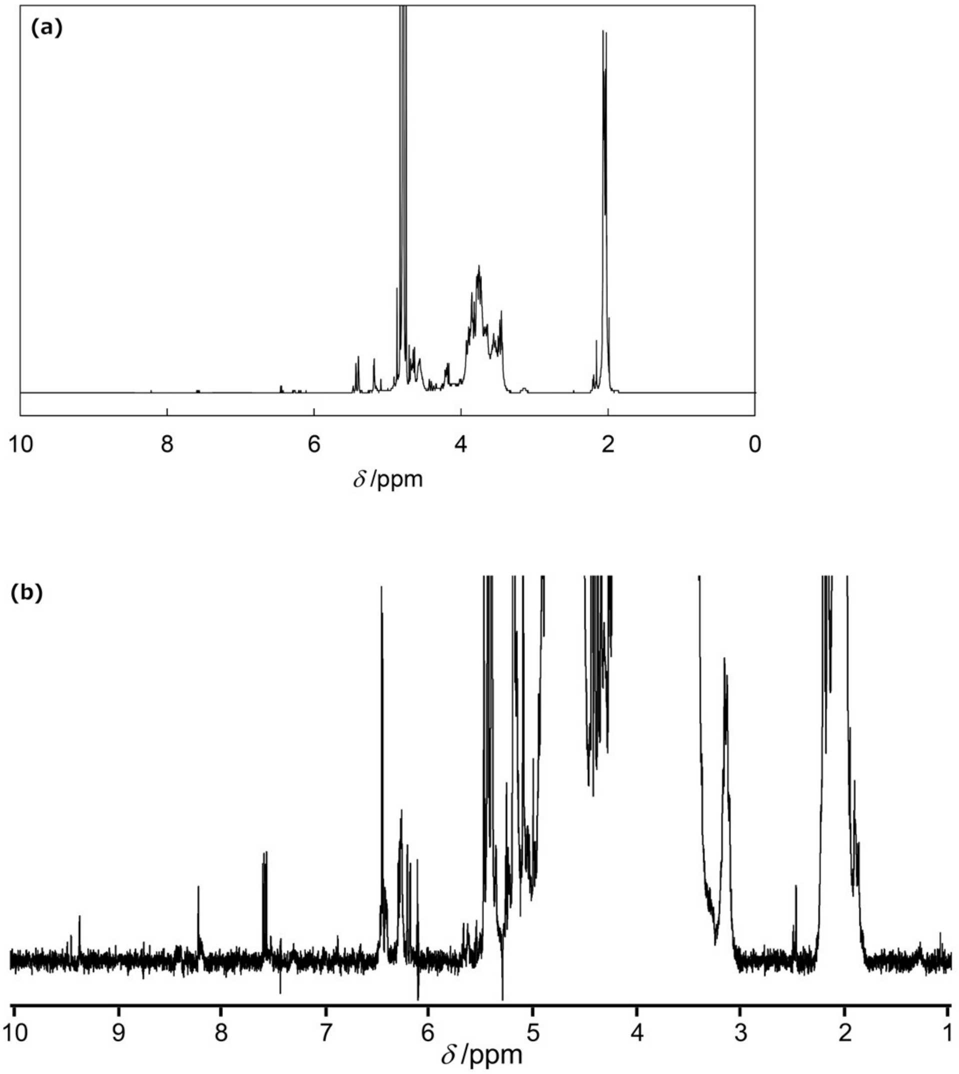


Fig. S4. ^{1}H NMR spectrum of *Oligomer-*H_2SO_4 in D_2O (a) and its enlarged image (b).

Peaks at 2–6 ppm are mainly due to oligomers of NAG and HDO, those at 6–8 ppm are ascribed to aromatic C-H and those at 9–10 ppm are attributed to aldehyde.

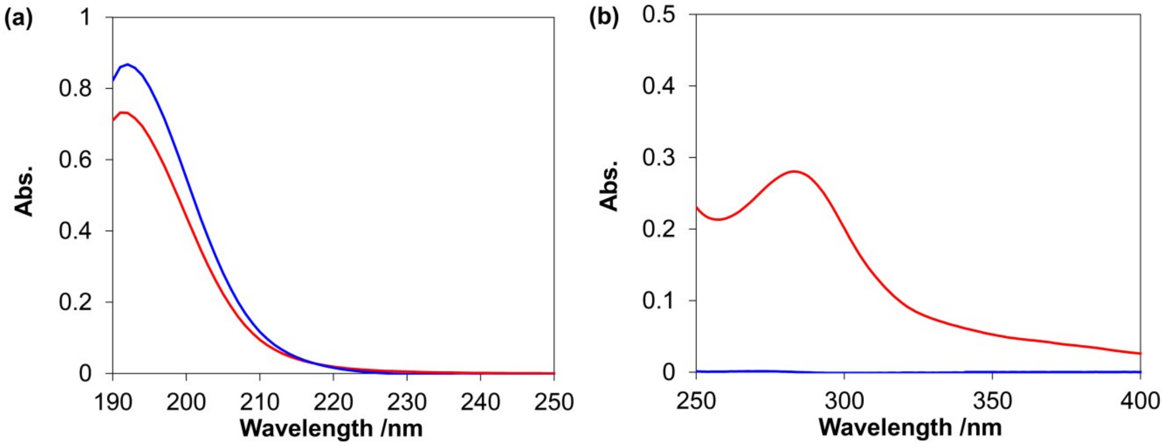


Fig. S5. UV-vis spectrum of NAG in H_2SO_4 *aq*. (blue) and *Oligomer-*H_2SO_4 *aq*. (red) at 0.1 mM (a) and 10 mM (b).

The peak at 192 nm is attributed to $\pi\text{–}\pi^*$ transition of amide group in NAG unit, while that at 283 nm is typical absorption of $\pi\text{–}\pi^*$ transition of furfural derivatives.[S1]

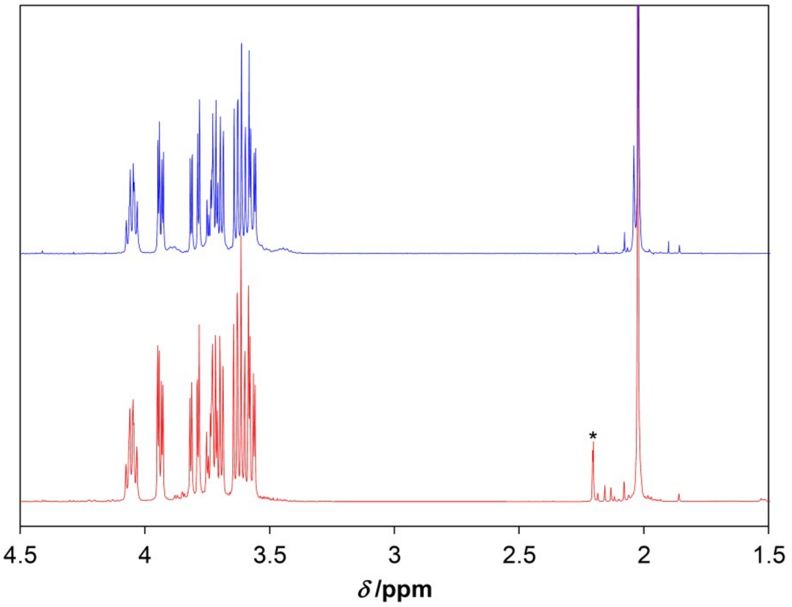


Fig. S6. ^{1}H NMR spectra of standard ADS (blue) and our product accumulated by fraction collector (red) in D_2O. *Contamination of the NMR tube with acetone. Assignment is available below.

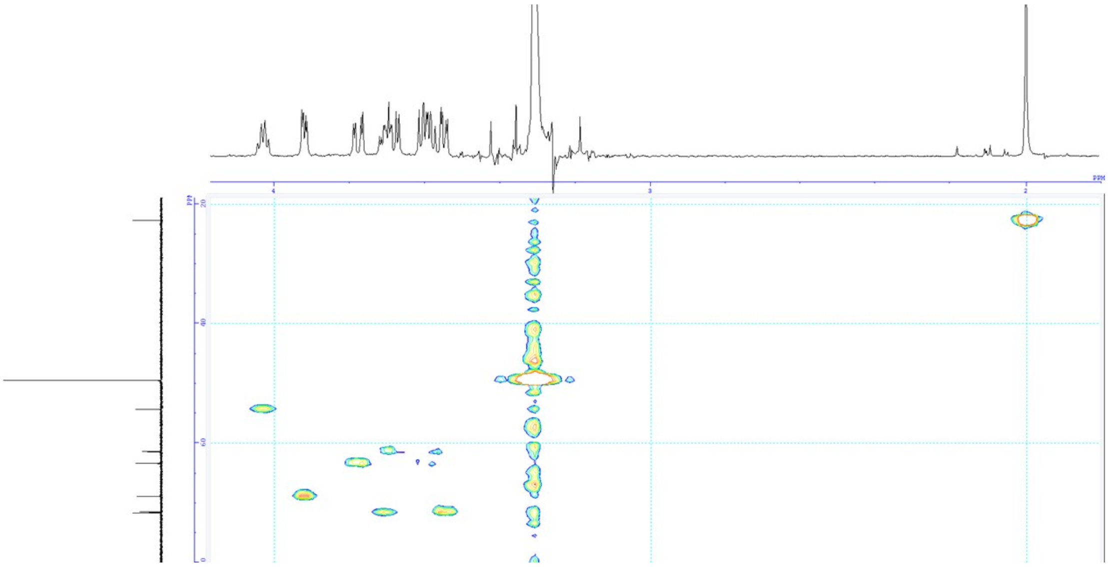
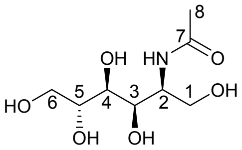


Fig. S7. ^{13}C–^{1}H HMQC spectrum of ADS produced in our experiments. ^{13}C signal at 50 ppm and ^{1}H signal at 3.3 ppm are derived from internal standard (MeOH). Assignment is available below.

NMR assignment for ADS from Fig. S6, Fig. S7, ^{13}C–^{1}H HMBC and ^{13}C DEPT.



Assignment (^{1}H, 400 MHz, D_2O): δ 4.05 (ddd, J = 6.4, 6.4, 4.8 Hz, 1H, *H*-C2), 3.94 (dd, J = 6.4, 2.4 Hz, 1H, *H*-C3), 3.80 (dd, J = 12, 2.8 Hz, 1H, *H*-C6), 3.73 (m, 1H, *H*-C5), 3.70 (dd, J = 12, 4.4 Hz, 1H, *H*-C1), 3.63 (dd, J = 6.0, 5.6 Hz, 1H, *H*-C6), 3.62 (dd, J = 6.0, 5.6 Hz, 1H, *H*-C1), 3.57 (dd, J = 8.0, 2.4 Hz, 1H, *H*-C4), 2.02 (s, 3H, *H*-C8)

Assignment (^{13}C, 100 MHz, D_2O): δ 175.0 (C, C7), 71.7 (CH, C5), 71.5 (CH, C4), 68.9 (CH, C3), 63.4 (CH_2, C6), 61.4 (CH_2, C1), 54.4 (CH, C2), 22.7 (CH_3, C8)

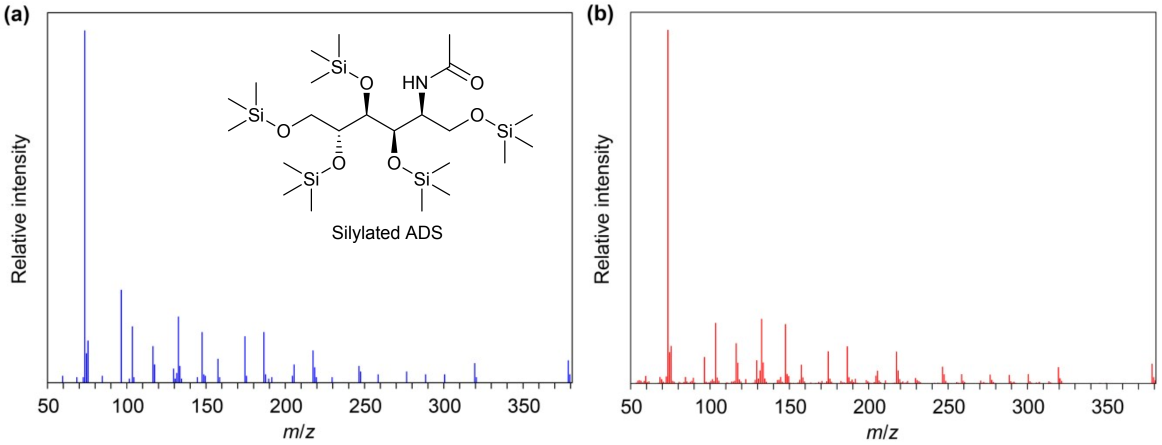


Fig. S8. GC/MS standard data of silylated ADS (a) and analytical data of our major product after silylation of reaction mixture (b).

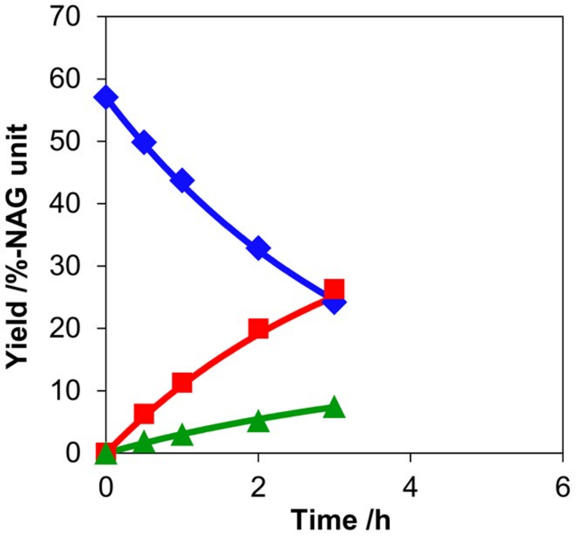


Fig. S9. Time course of hydrogenation of chitin hydrolysate at pH 3.0 by used Ru/TiO_2 after the experiment shown in Fig. 3b.

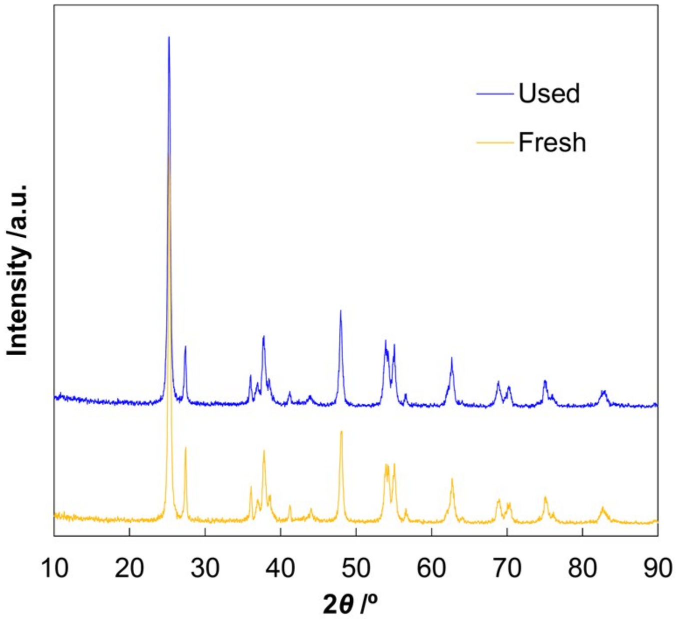
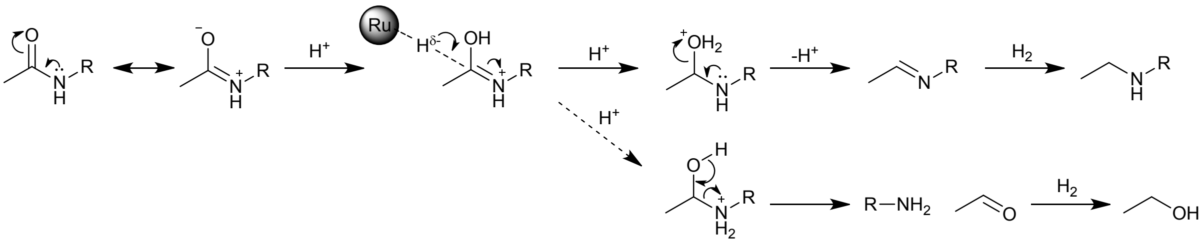


Fig. S10. XRD patter of used Ru/TiO$_2$ after the experiment shown in Fig. 3b. Normalised by the peak at 25°.



Scheme S1. Speculated mechanism for the decomposition of amide by acid and Ru under H$_2$ pressure.

Table S1. Effect of milling time in the mechanocatalytic hydrolysis.[a]

Time /h	Yield of product /%-NAG unit		Solubility /%
	NAG	Oligomers (DP = 2–5)	
3	4.2	28	>99
6	5.3	42	>99
12	6.3	45	>99

[a] Milling conditions: S/C = 8.2, 500 rpm, water content *ca.* 1.5 wt%

Table S2. Effect of milling revolution rate in the mechanocatalytic hydrolysis.[a]

Rate /rpm	Yield of product /%-NAG unit		Solubility /%
	NAG	Oligomers (DP = 2–5)	
300	1.9	18	68
400	3.8	31	>99
500	5.3	42	>99

[a] Milling conditions: S/C = 8.2, 6 h, water content *ca.* 1.5 wt%.

Table S3. Effect of amount of H_2SO_4 in the mechanocatalytic hydrolysis.[a]

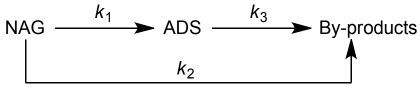
S/C	Yield of product /%-NAG unit		Solubility /%
	NAG	Oligomers (DP = 2–5)	
16.6	1.6	20	81
8.2	5.3	42	>99
4.1	10	38	>99
2.0	18	27	>99

[a] Milling conditions: 500 rpm, 6 h, water content *ca.* 1.5 wt%.

Table S4. BET specific surface area of catalysts.

Catalyst	BET surface area /m^2 g^{-1}
TiO_2	51
Ru/TiO_2	48
Pt/TiO_2	44
Ni/TiO_2	19
ZrO_2	27
Ru/ZrO_2	30
C	1362
Ru/C	1300

Differential equations of kinetics



$$\frac{\mathrm{d[NAG]}}{\mathrm{d}t} = -(k_1 + k_2)[\mathrm{NAG}] \qquad \text{(S1)}$$

$$\frac{\mathrm{d[ADS]}}{\mathrm{d}t} = k_1[\mathrm{NAG}] - k_3[\mathrm{ADS}] \qquad \text{(S2)}$$

$$\frac{\mathrm{d[By\text{-}products]}}{\mathrm{d}t} = k_2[\mathrm{NAG}] + k_3[\mathrm{ADS}] \qquad \text{(S3)}$$

$$\text{(S1)} \Leftrightarrow [\mathrm{NAG}] = [\mathrm{NAG}]_0 e^{-(k_1+k_2)t} \qquad \text{(S4)}$$

Thus, eq. S2 can be descried as $\frac{\mathrm{d[ADS]}}{\mathrm{d}t} = k_1[\mathrm{NAG}]_0 e^{-(k_1+k_2)t} - k_3[\mathrm{ADS}]$ (S5)

When $k_1 + k_2 \neq k_3$,

$$\Leftrightarrow [\mathrm{ADS}] = \frac{k_1[\mathrm{NAG}]_0}{-(k_1+k_2)+k_3}\left\{e^{-(k_1+k_2)t} - e^{-k_3 t}\right\} \qquad \text{(S6)}$$

Differentiating eq. S6, at the local maximum of [ADS],

$$\frac{\mathrm{d[ADS]}}{\mathrm{d}t} = \frac{k_1[\mathrm{NAG}]_0}{-(k_1+k_2)+k_3}\left\{-(k_1+k_2)e^{-(k_1+k_2)t} + k_3 e^{-k_3 t}\right\} = 0 \qquad \text{(S7)}$$

$$\Leftrightarrow t = \frac{1}{-(k_1+k_2)+k_3}\ln\frac{k_3}{k_1+k_2} \qquad \text{(S8)}$$

Combining eqs. S6 and S8,

$$[\mathrm{ADS}]_{\max} = \frac{k_1[\mathrm{NAG}]_0}{-(k_1+k_2)+k_3}\left\{ e^{\frac{k_1+k_2}{k_1+k_2-k_3}\ln\frac{k_3}{k_1+k_2}} - e^{\frac{k_3}{k_1+k_2-k_3}\ln\frac{k_3}{k_1+k_2}} \right\} \qquad \text{(S9)}$$

$$\Leftrightarrow [\mathrm{ADS}]_{\max} = \frac{\frac{k_1}{k_1+k_2}[\mathrm{NAG}]_0}{-1+\frac{k_3}{k_1+k_2}}\left\{ \left(\frac{k_3}{k_1+k_2}\right)^{\frac{1}{1-\frac{k_3}{k_1+k_2}}} - \left(\frac{k_3}{k_1+k_2}\right)^{\frac{\frac{k_3}{k_1+k_2}}{1-\frac{k_3}{k_1+k_2}}} \right\} \qquad \text{(S10)}$$

$$\Leftrightarrow [\mathrm{ADS}]_{\max} = [\mathrm{NAG}]_0 \frac{k_1}{k_1+k_2}\frac{1}{R-1}\left\{ R^{\frac{1}{1-R}} - R^{\frac{R}{1-R}} \right\}, \text{ where } R = \frac{k_3}{k_1+k_2} \qquad \text{(S11)}$$

When $k_1 + k_2 = k_3$, $[\mathrm{ADS}]_{\max} = [\mathrm{NAG}]_0 \frac{k_1}{k_1+k_2} e^{-1}$ (S12)

$[\mathrm{NAG}]_0$ can be changed to M_{NAG}, where M_{NAG} is the initial amount of NAG (%), and then $[\mathrm{ADS}]_{\max}$ is converted to the maximum ADS yield.

References

S1 (a) R. Boopathy, H. Bokang and L. Daniels, *J. Ind. Microbiol.*, 1993, **11**, 147-150; (b) X. Chen, S. L. Chew, F. M. Kerton and N. Yan, *Green Chem.*, 2014, **16**, 2204-2212.