Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information (ESI)

Synthesis of Tosylated Starch in Eco-Friendly Media

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1. Dissolution of starch in aqueous solutions

Fig. S1 Homogeneous dissolution of starch in water facilitated by the addition of NaOH-urea and a surfactant (Brij® 30)

2. ATR-FTIR spectra of starch synthesised from aqueous solution containing surfactants

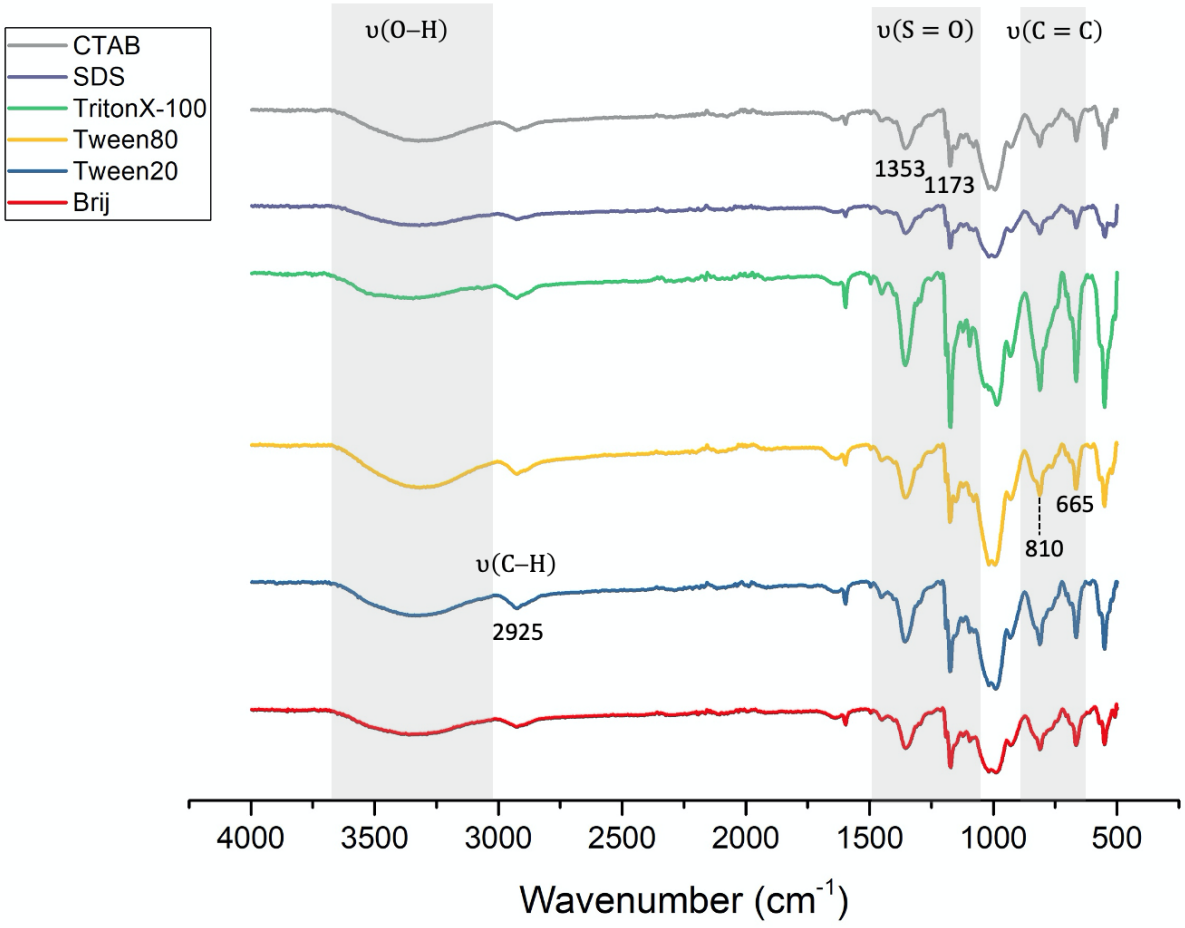

Fig. S2 FTIR spectra of tosyl starch samples obtained under aqueous NaOH-urea with the addition of different surfactants.

Table S1 FTIR peak assignments of tosyl starch samples.

ῡ(cm^{-1})	Vibrational Mode
3600-3000	O–H stretching
2925	CH_2, CH_3 stretching
1597	Aromatic C=C stretching
1353	Symmetric S=O stretching
1173	Asymmetric S=O stretching
810, 665	Aromatic C=C bending

3. ^{1}H-NMR spectra of starch samples

3.1 Native cassava starch sample

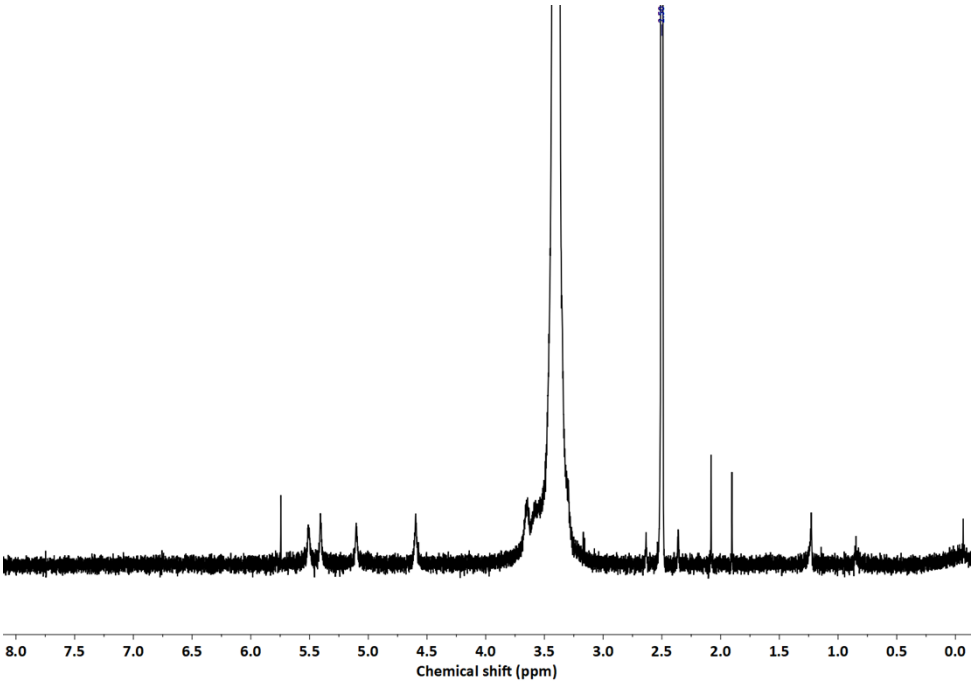

Fig. S3 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of native cassava starch

3.2 Tosyl starch prepared in pyridine

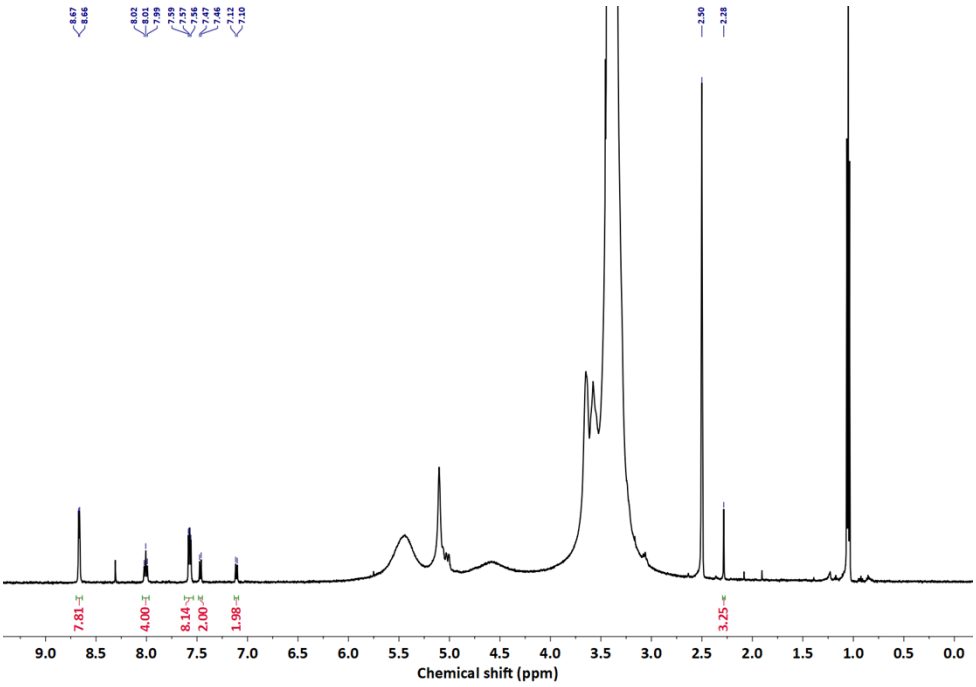

Fig. S4 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch (pyridine system)

3.3 Tosyl starch prepared in DMA/LiCl system

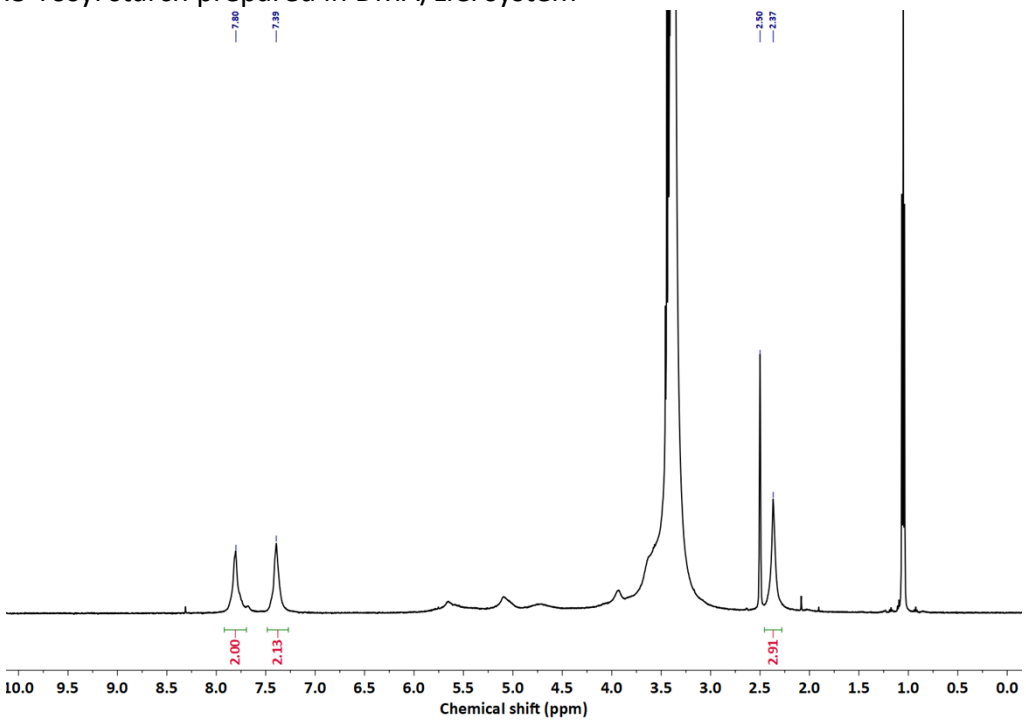

Fig. S5 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch (DMA/LiCl system)

4. ^{1}H-NMR spectra of tosyl starch samples prepared in NaOH-urea systems

4.1 Brij® 30

4.1.1 Brij® 30 (2.62 mmol) and TsCl (4 equiv. per AGU)

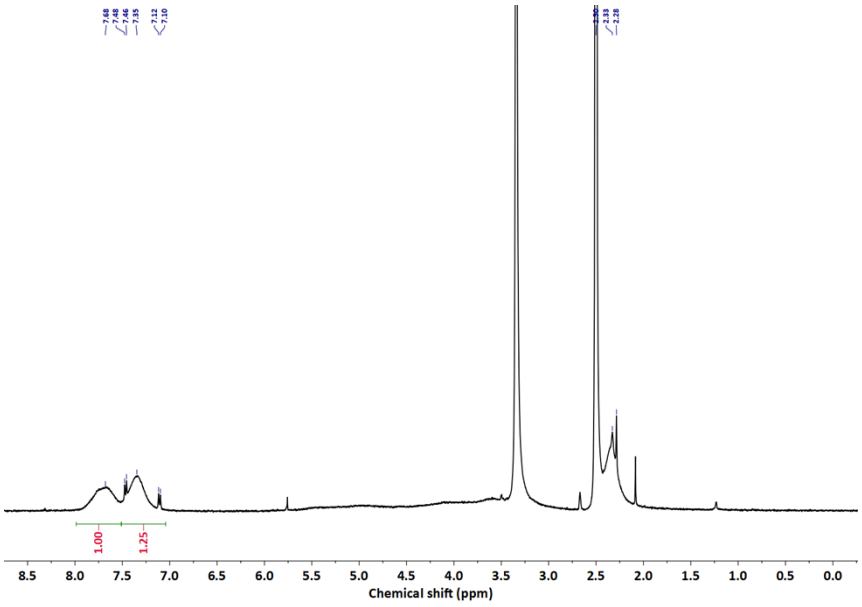

Fig. S6 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in Brij® 30 (2.62 mmol) in the presence of TsCl (4 equiv. per AGU)

4.1.2 Brij® 30 (1.57 mmol) and TsCl (4 equiv. per AGU)

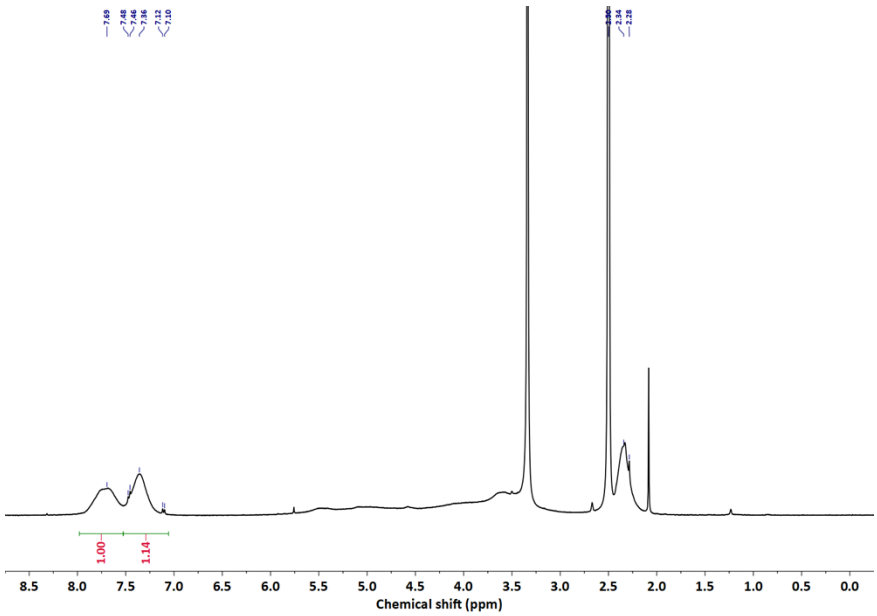

Fig. S7 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in Brij® 30 (1.57 mmol) in the presence of TsCl (4 equiv. per AGU)

4.1.3 Brij® 30 (1.05 mmol) and TsCl (4 equiv. per AGU)

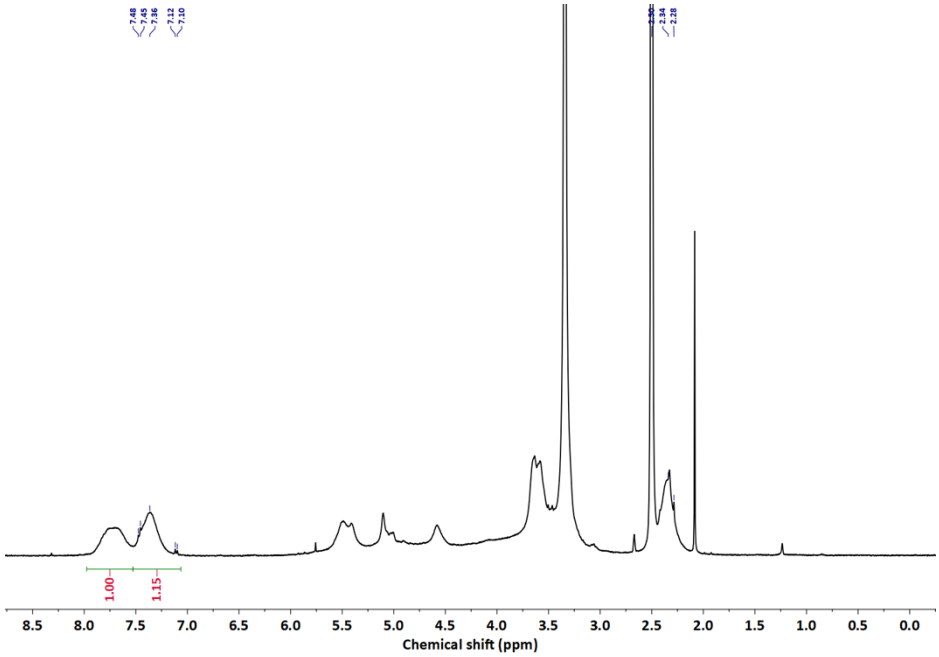

Fig. S8 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in Brij® 30 (1.05 mmol) in the presence of TsCl (4 equiv. per AGU)

4.1.4 Brij® 30 (0.52 mmol) and TsCl (4 equiv. per AGU)

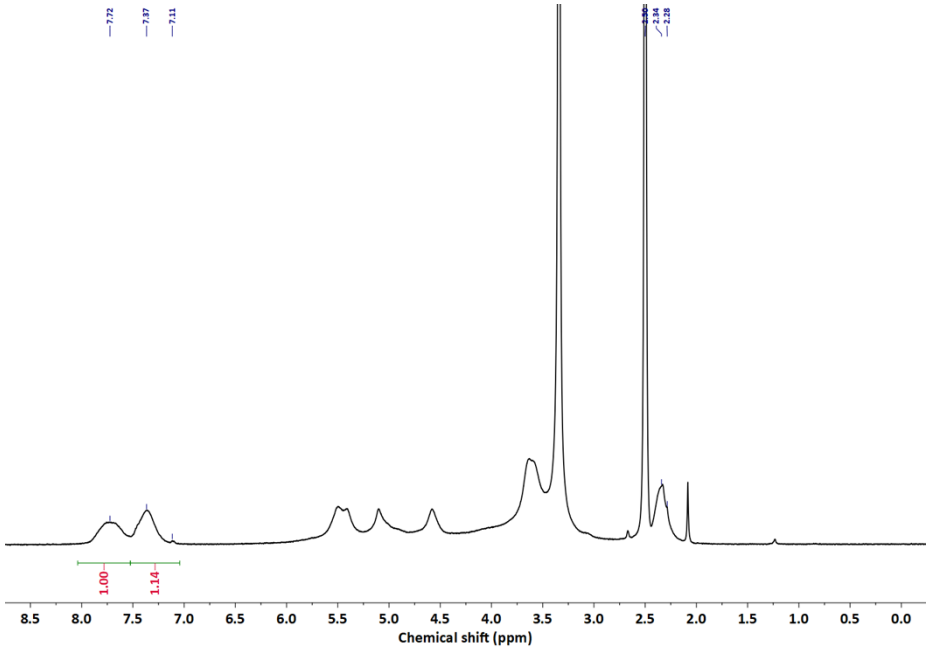

Fig. S9 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in Brij® 30 (0.52 mmol) in the presence of TsCl (4 equiv. per AGU)

4.1.5 Brij® 30 (2.62 mmol) and TsCl (3 equiv. per AGU)

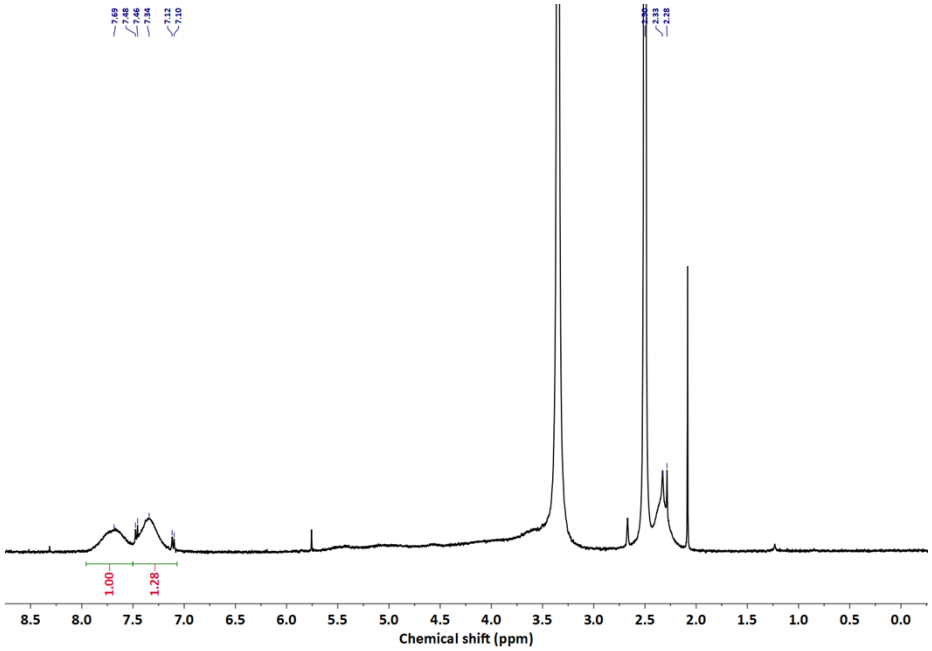

Fig. S10 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in Brij® 30 (2.62 mmol) in the presence of TsCl (3 equiv. per AGU)

4.1.6 Brij® 30 (2.62 mmol) and TsCl (2 equiv. per AGU)

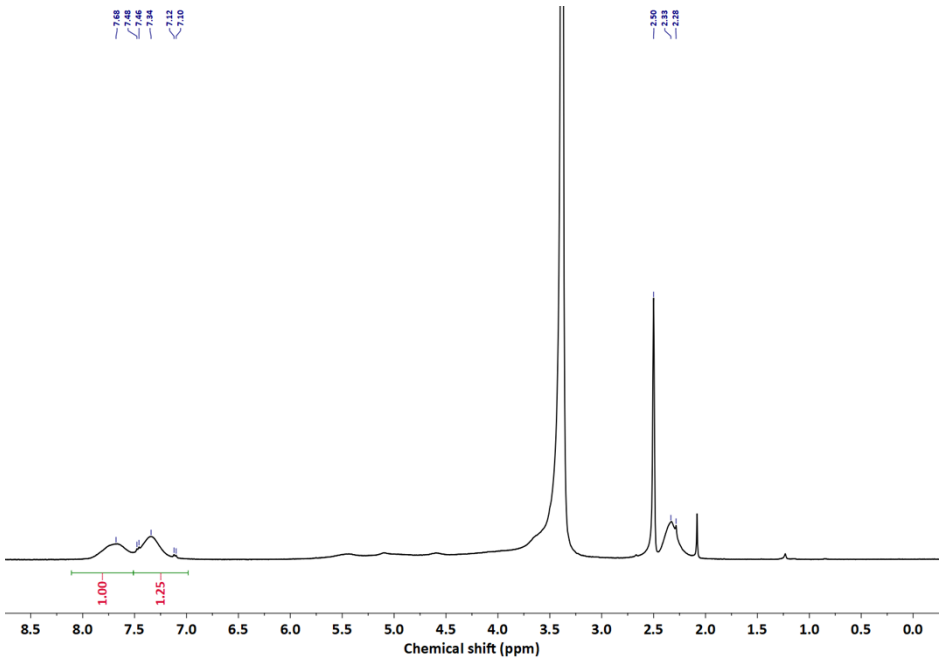

Fig. S11 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in Brij® 30 (2.62 mmol) in the presence of TsCl (2 equiv. per AGU)

4.1.7 Brij® 30 (2.62 mmol) and TsCl (1 equiv. per AGU)

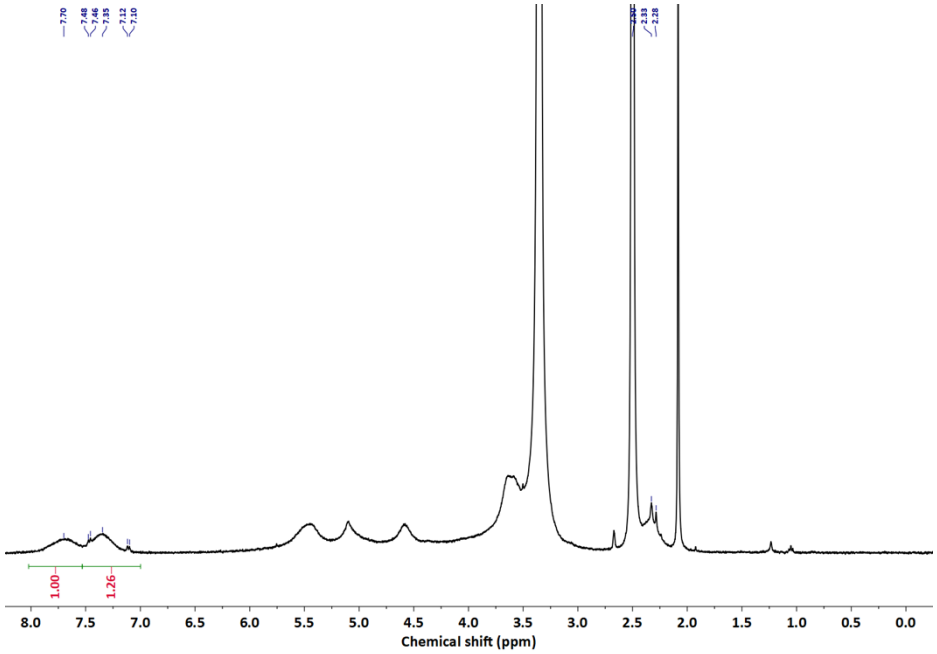

Fig. S12 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in Brij® 30 (2.62 mmol) in the presence of TsCl (1 equiv. per AGU)

4.2 Tween®20

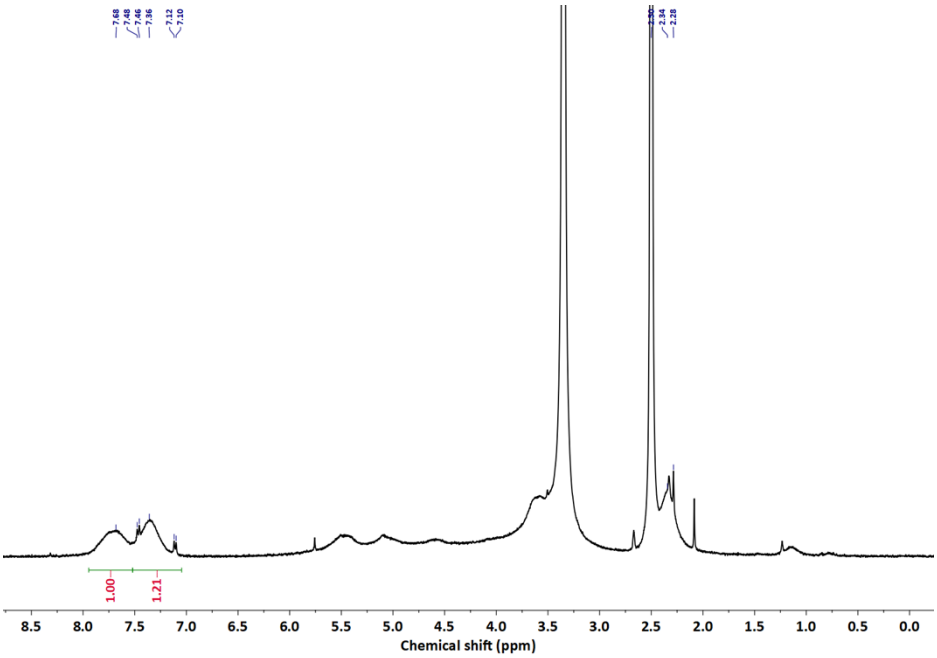

Fig. S13 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in Tween®20 (2.62 mmol) in the presence of TsCl (equiv. per AGU)

4.3 Tween®80

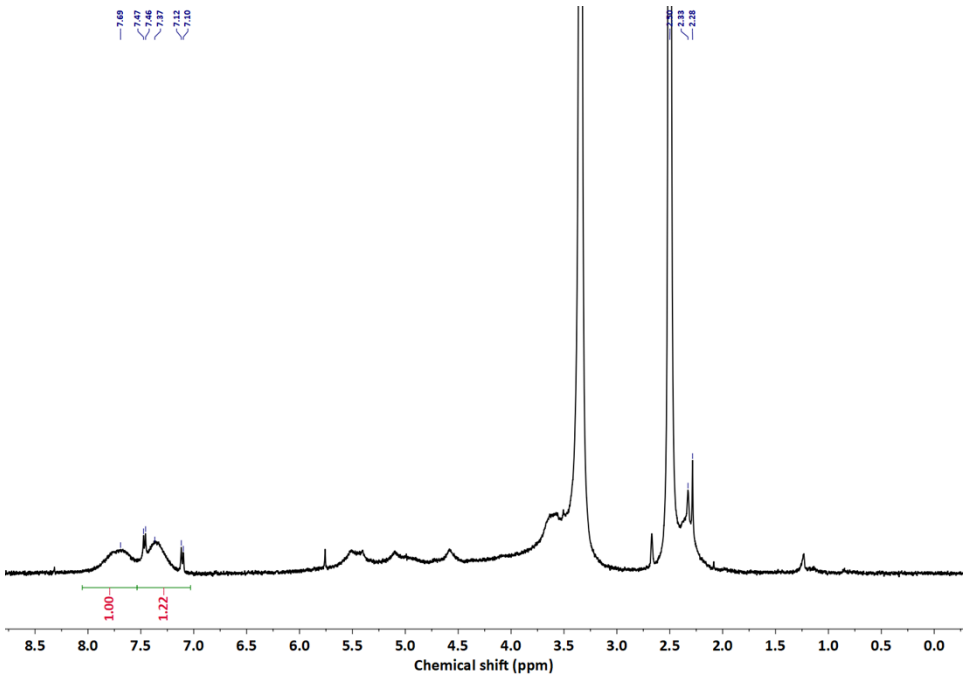

Fig. S14 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in Tween®80 (2.62 mmol) in the presence of TsCl (equiv. per AGU)

4.4 Triton™X-100

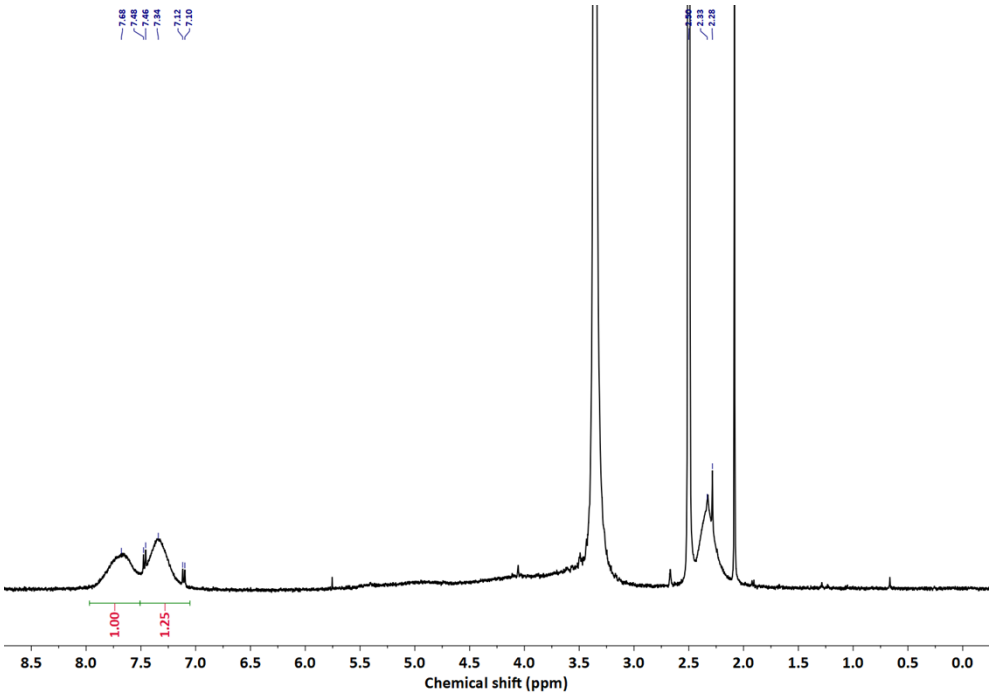

Fig. S15 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of of tosyl starch prepared inTriton™X-100 (2.62 mmol) in the presence of TsCl (equiv. per AGU)

4.5 Sodium dodecyl sulfate (SDS)

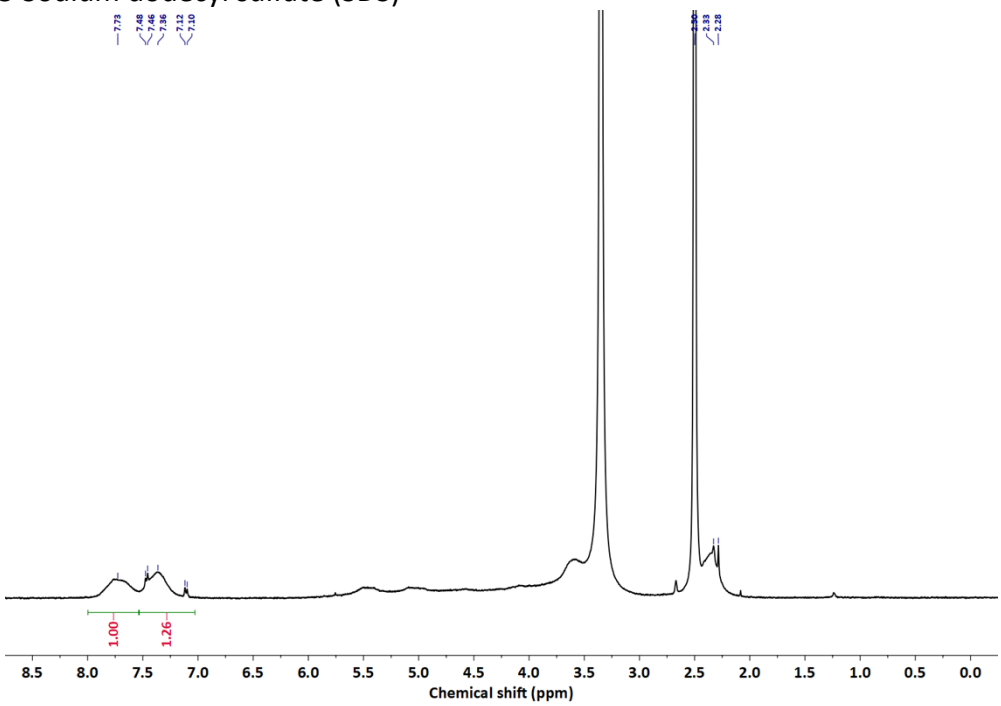

Fig. S16 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in SDS (2.62 mmol) in the presence of TsCl (equiv. per AGU)

4.6 Hexadecyltrimethylammonium bromide (CTAB)

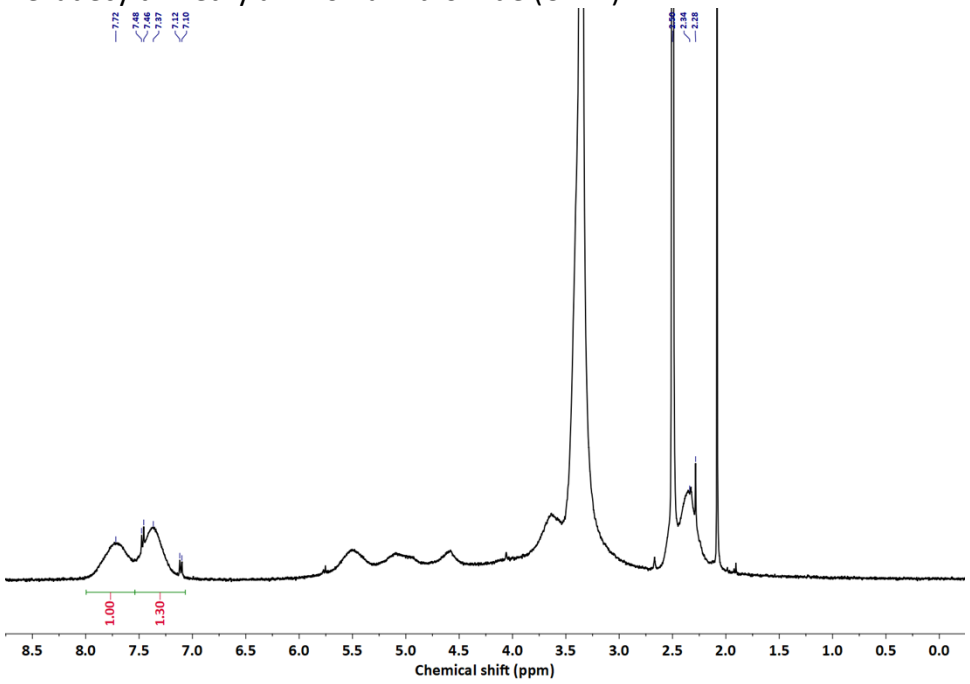

Fig. S17 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of tosyl starch prepared in CTAB (2.62 mmol) in the presence of TsCl (equiv. per AGU)

5. ^{1}H-NMR spectra of substituted tosyl starch samples

5.1 Azide-substituted tosyl starch prepared in DMSO

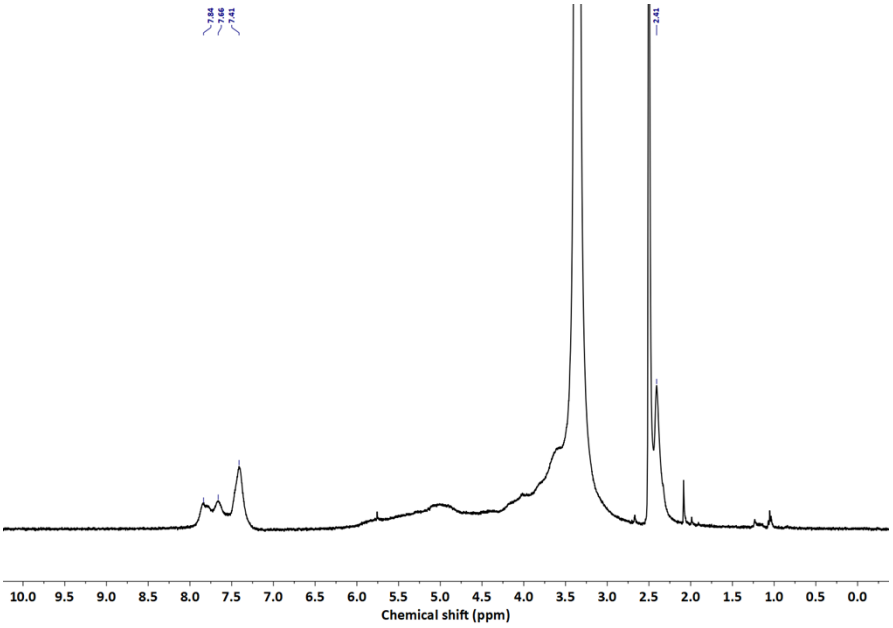

Fig. S18 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of azide-substituted tosyl starch prepared in DMSO

5.2 Phthalimide-substituted tosyl starch prepared in DMSO

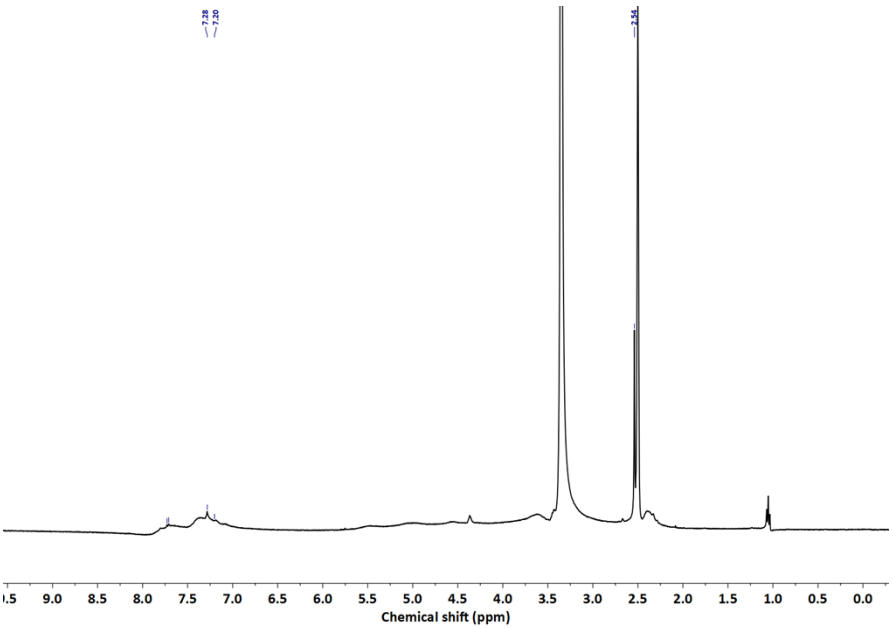

Fig. S19 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of phthalimide-substituted tosyl starch prepared in DMSO

5.3 Azide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

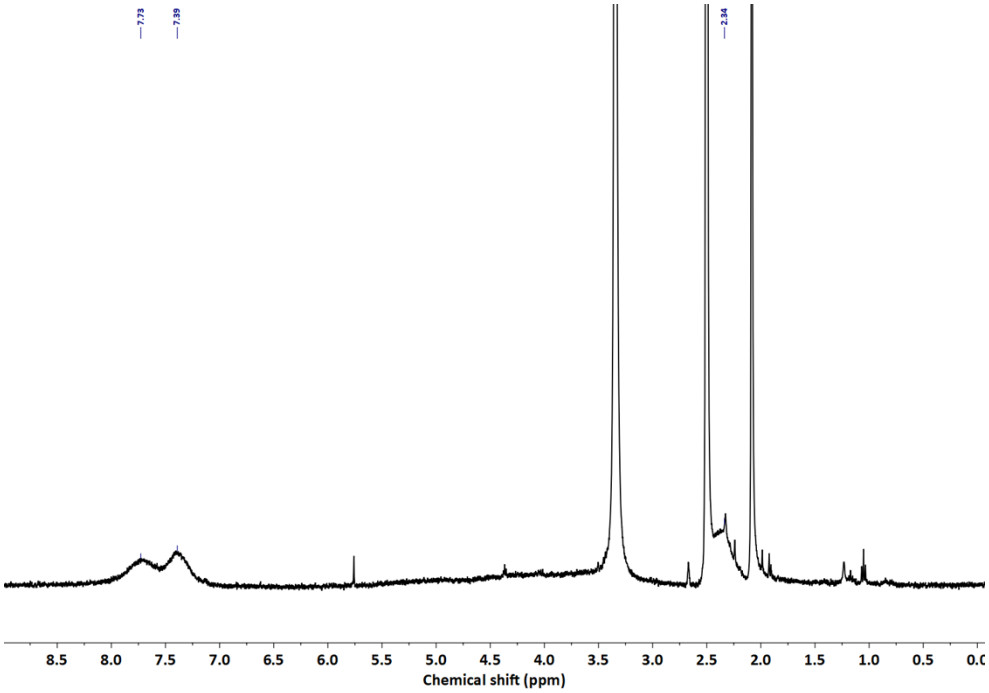

Fig. S20 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of azide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

5.4 Phthalimide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

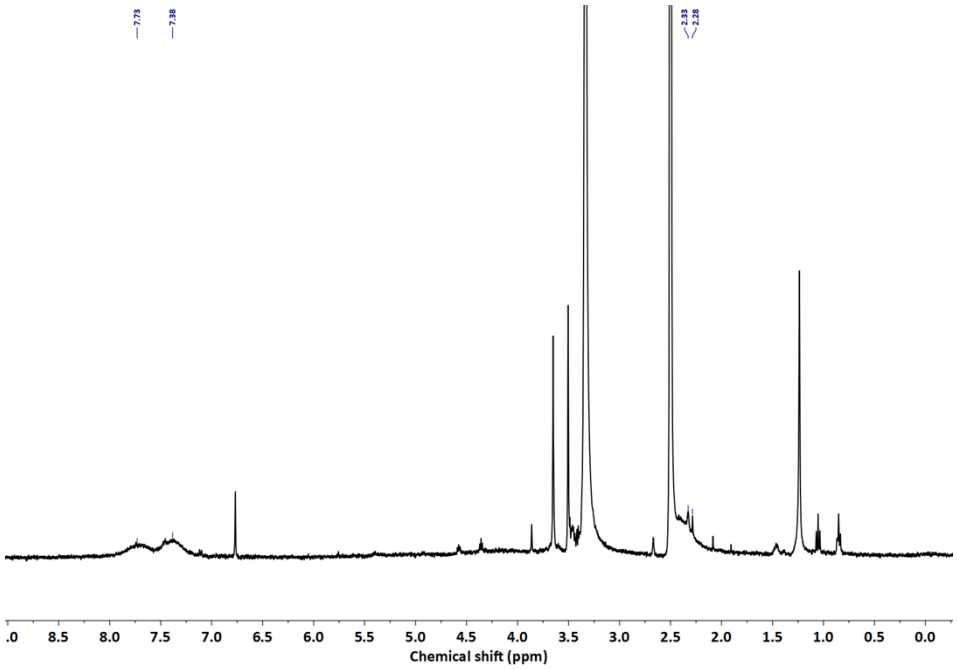

Fig. S21 ^{1}H NMR spectrum (400 MHz, DMSO-d6, 298 K) of phthalimide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

6 ATR-FTIR spectra of substituted tosyl starch samples

6.1 Azide-substituted tosyl starch prepared in DMSO

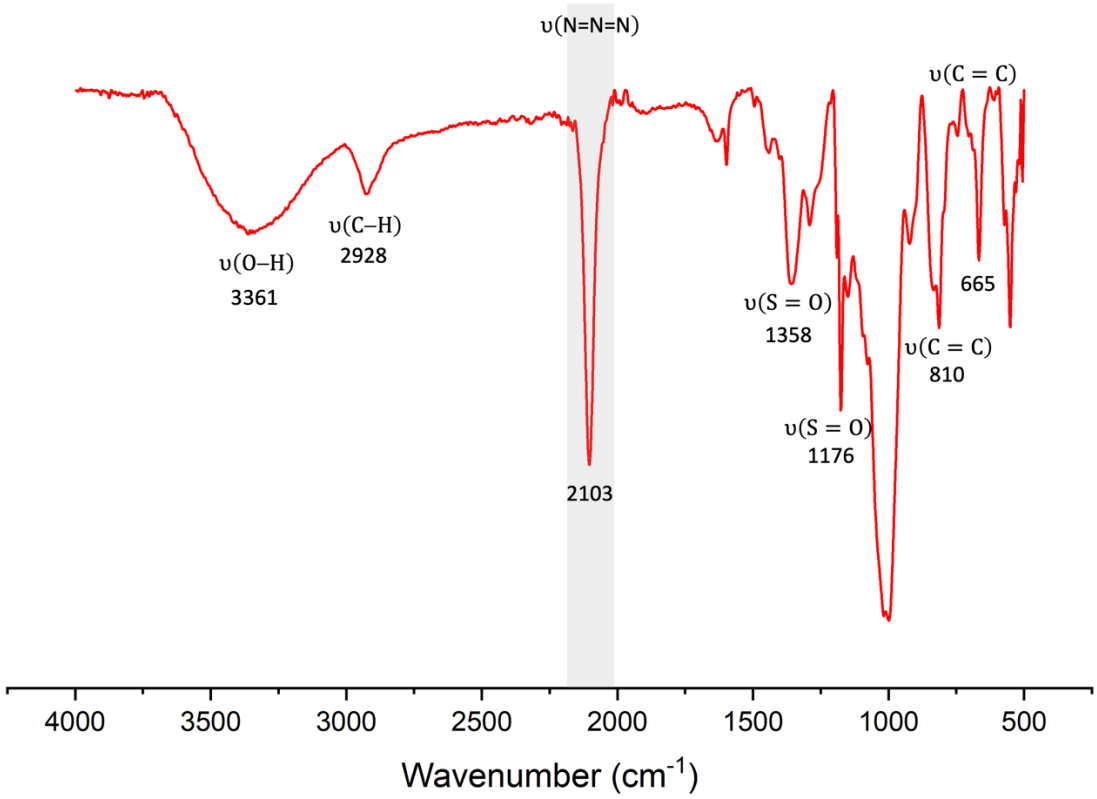

Fig. S22 FTIR spectra of azide-substituted tosyl starch prepared in DMSO

Table S2 FTIR peak assignments of azide-substituted tosyl starch prepared in DMSO

$\bar{\upsilon}$(cm^{-1})	Vibrational Mode
3600-3000	O–H stretching
2928	CH_2, CH_3 stretching
2103	Azide N=N=N stretching
1358	Symmetric S=O stretching
1176	Asymmetric S=O stretching
810, 665	Aromatic C=C bending

6.2 Phthalimide-substituted tosyl starch prepared in DMSO

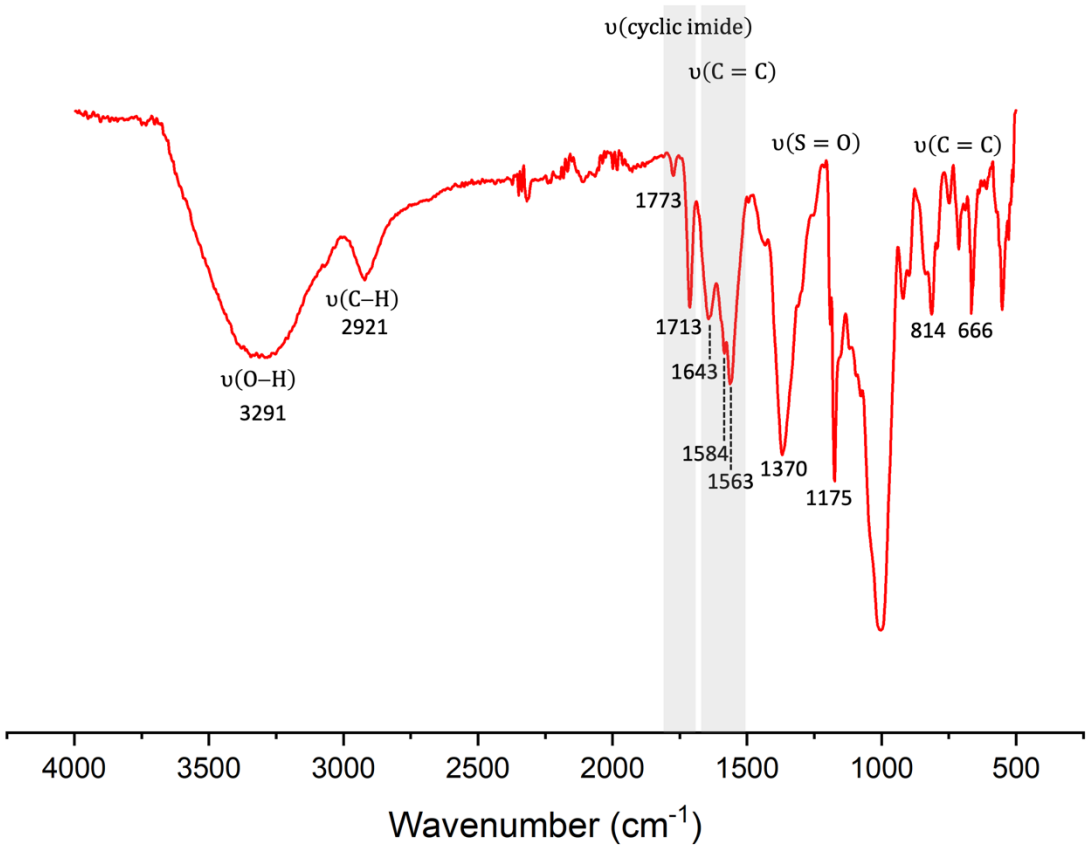

Fig. S23 FTIR spectra of phthalimide-substituted tosyl starch prepared in DMSO

Table S3 FTIR peak assignments of phthalimide-substituted tosyl starch prepared in DMSO

$\bar{\upsilon}$(cm^{-1})	Vibrational Mode
3600-3000	O–H stretching
2921	CH_2, CH_3 stretching
1773, 1713	Cyclic imide stretching
1643	Aromatic C=C bending
1584, 1563	α,β-unsaturated C=O stretching
1370	Symmetric S=O stretching
1175	Asymmetric S=O stretching
814, 666	Aromatic C=C bending

6.3 Azide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

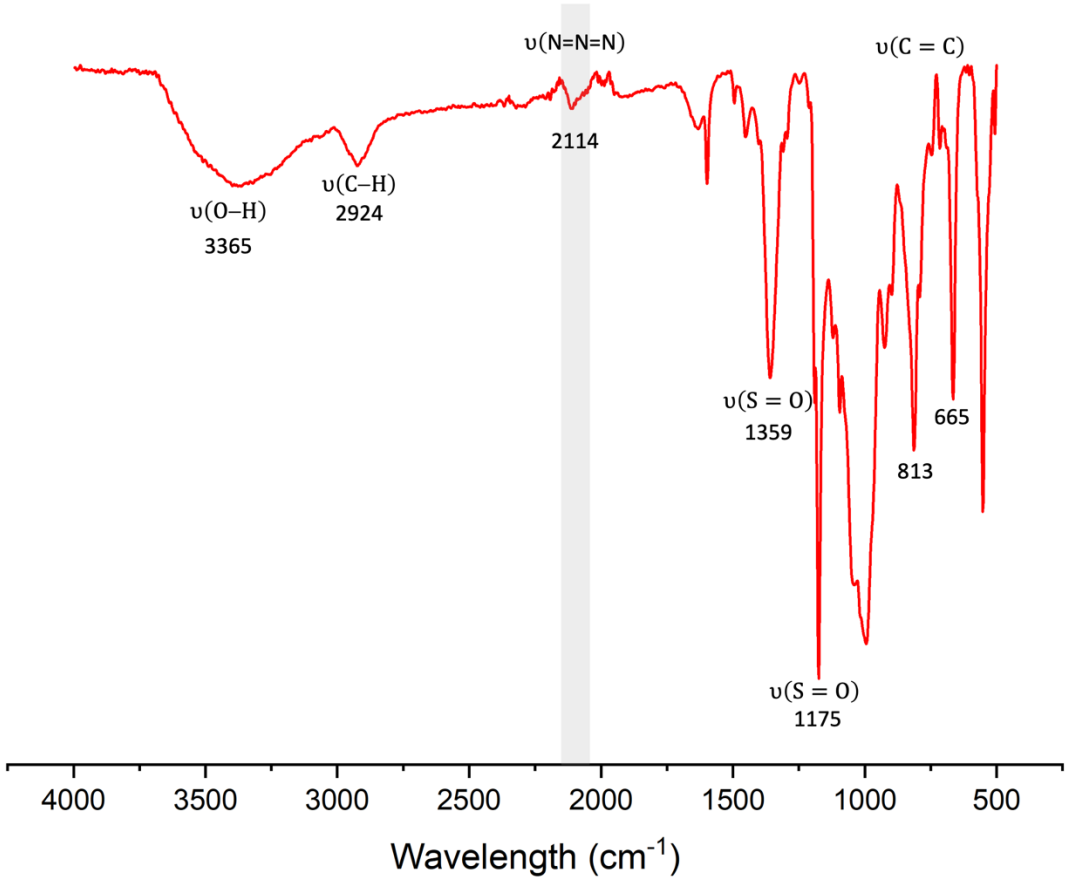

Fig. S24 FTIR spectra of azide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

Table S4 FTIR peak assignments of azide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

$\bar{\upsilon}$(cm^{-1})	Vibrational Mode
3600-3000	O–H stretching
2924	CH_2, CH_3 stretching
2114	Azide N=N=N stretching
1359	Symmetric S=O stretching
1175	Asymmetric S=O stretching
813, 665	Aromatic C=C bending

6.4 Phthalimide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

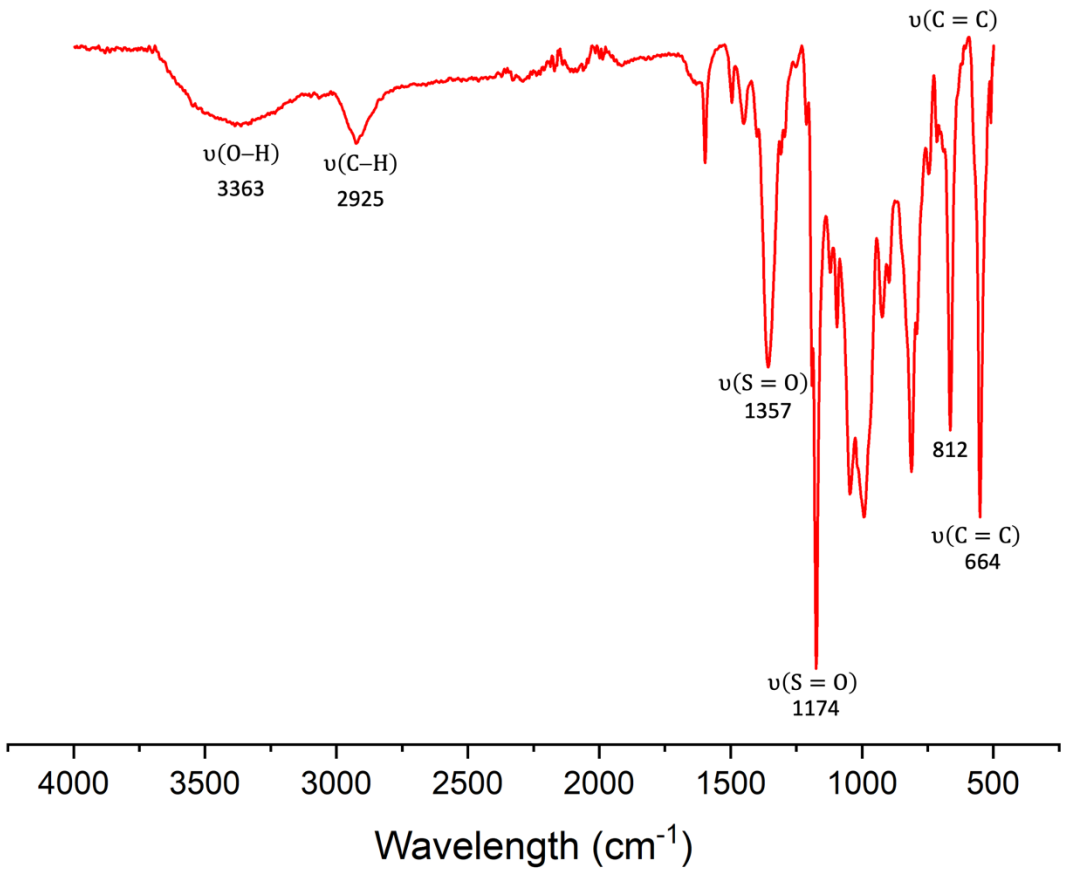

Fig. S25 FTIR spectra of phthalimide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

Table S5 FTIR peak assignments of phthalimide-substituted tosyl starch prepared in NaOH-urea-Brij® 30

ῡ(cm^{-1})	**Vibrational Mode**
3600-3000	O–H stretching
2925	CH_2, CH_3 stretching
1357	Symmetric S=O stretching
1174	Asymmetric S=O stretching
812, 664	Aromatic C=C bending

7 Thermogravimetric analysis curves of starch samples

7.1 Native starch

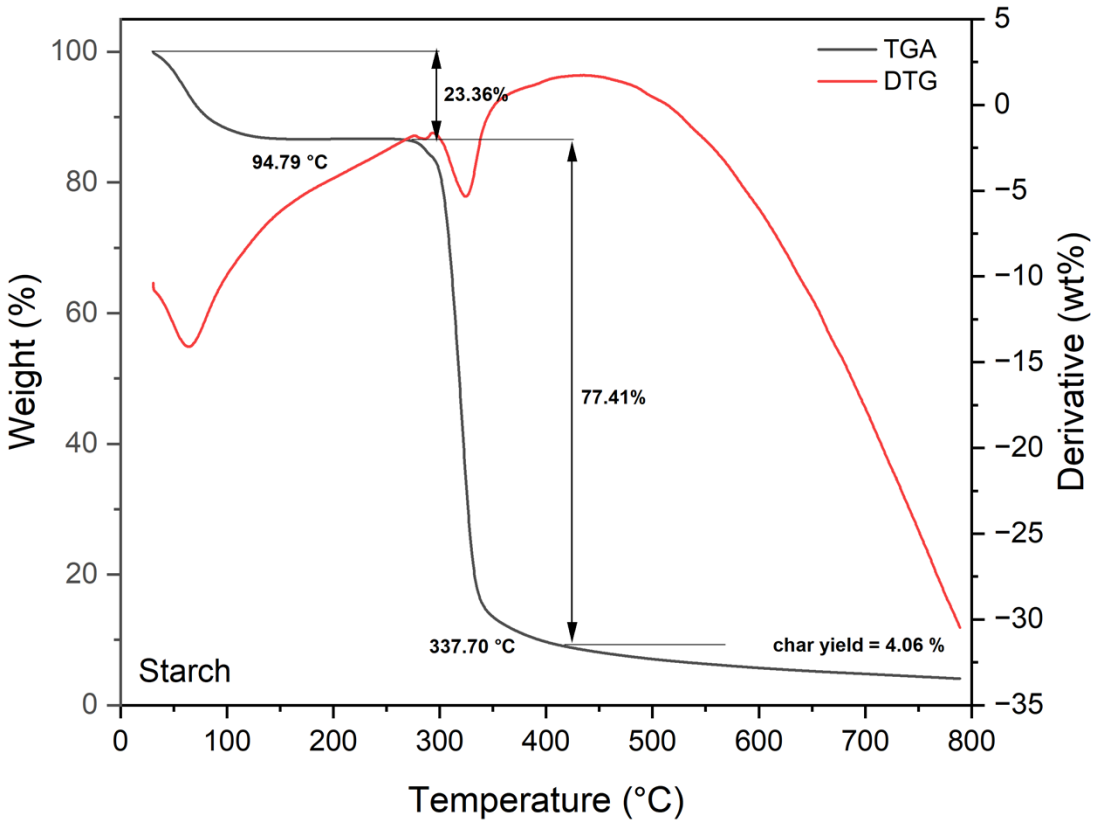

Fig. S26 TGA curve of native starch recorded under a N_2 flow with a heating rate of 10 °C min^{-1}

7.2 Tosyl starch (DS_{Tos} = 0.33)

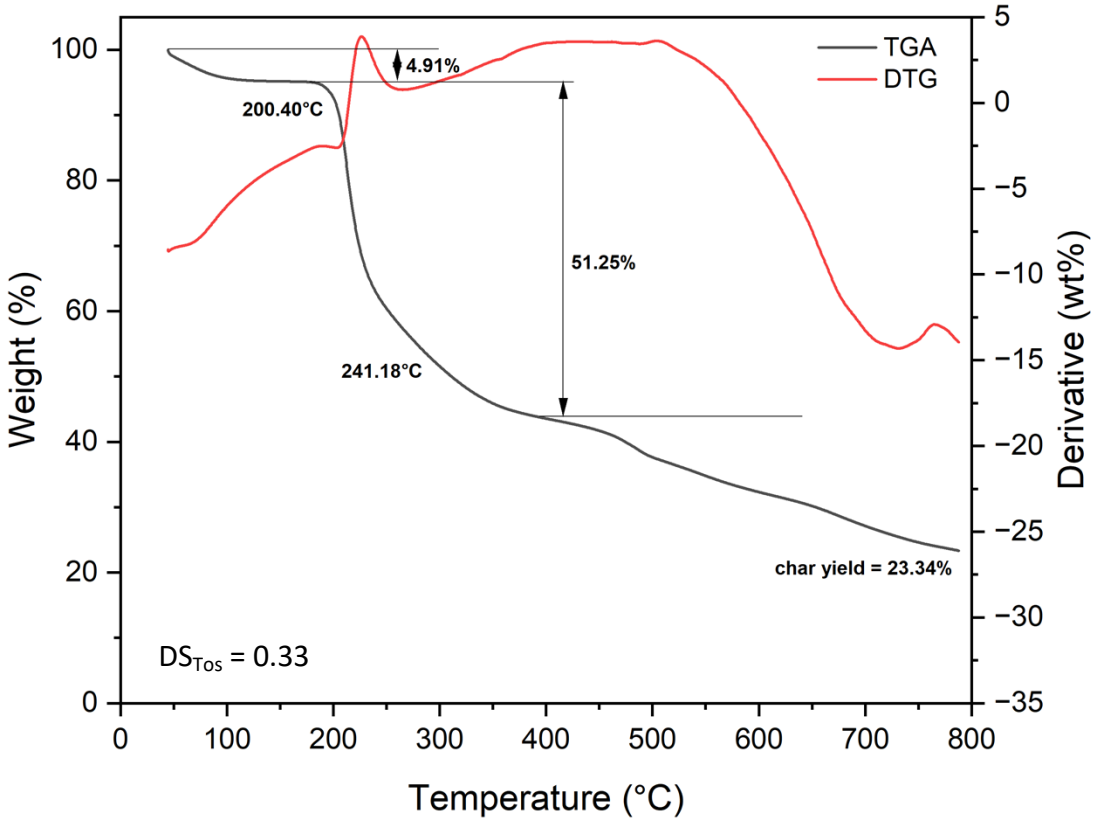

Fig. S27 TGA curve of tosyl starch (DS_{Tos} = 0.33) recorded under a N_2 flow with a heating rate of 10 °C min^{-1}

7.3 Tosyl starch (DS_{Tos} = 0.54)

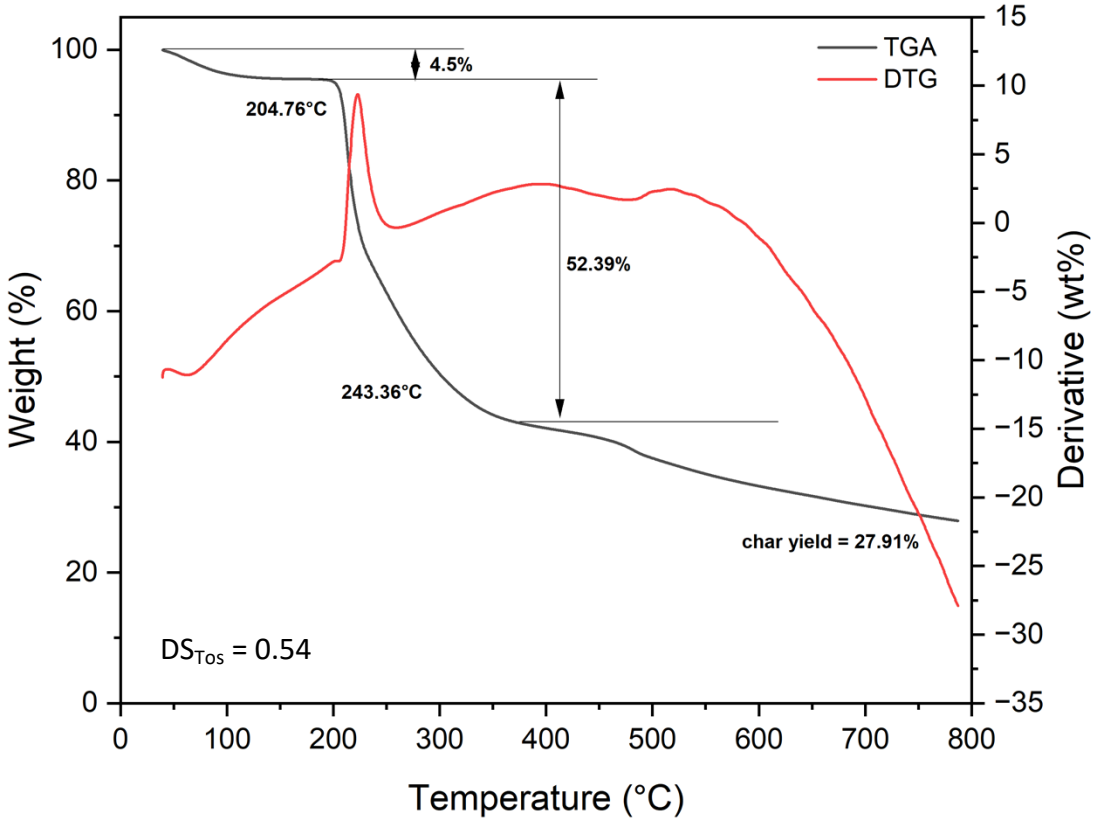

Fig. S28 TGA curve of tosyl starch (DS_{Tos} = 0.54) recorded under a N_2 flow with a heating rate of 10 °C min^{-1}

7.4 Tosyl starch (DS_{Tos} = 0.62)

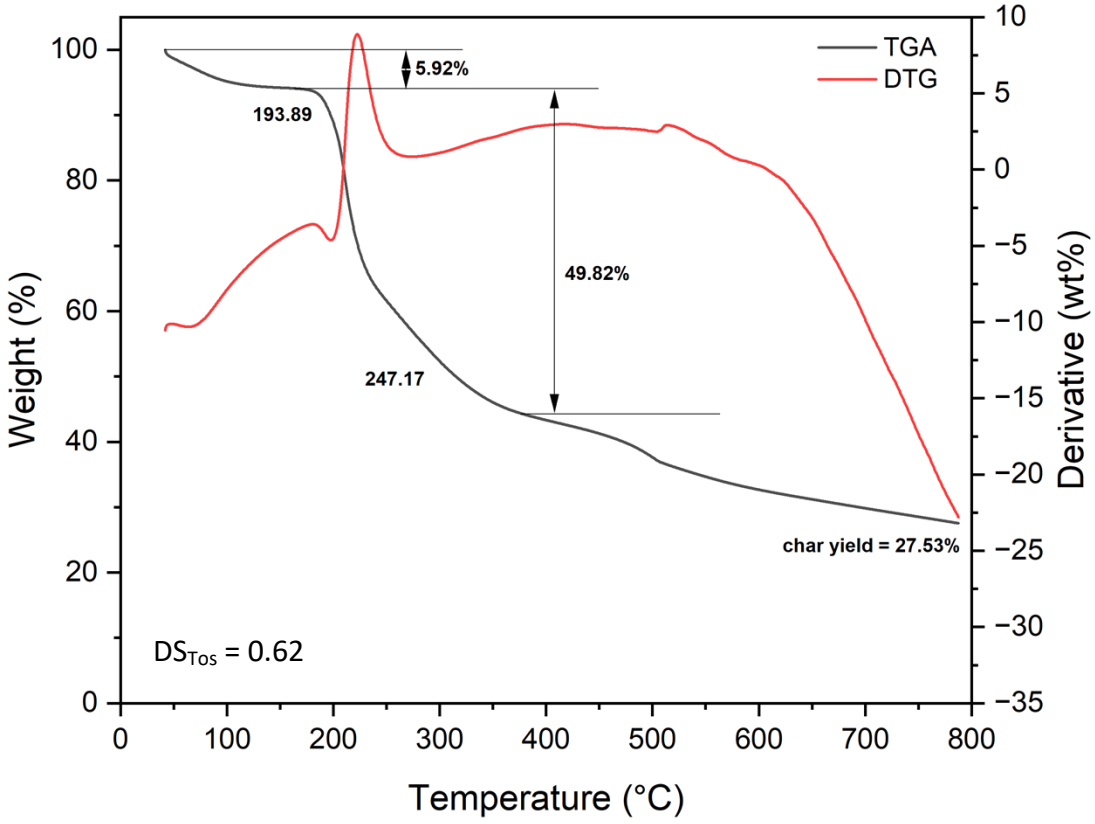

Fig. S29 TGA curve of tosyl starch (DS_{Tos} = 0.62) recorded under a N_2 flow with a heating rate of 10 °C min^{-1}

7.5 Tosyl starch (DS_{Tos} = 0.65)

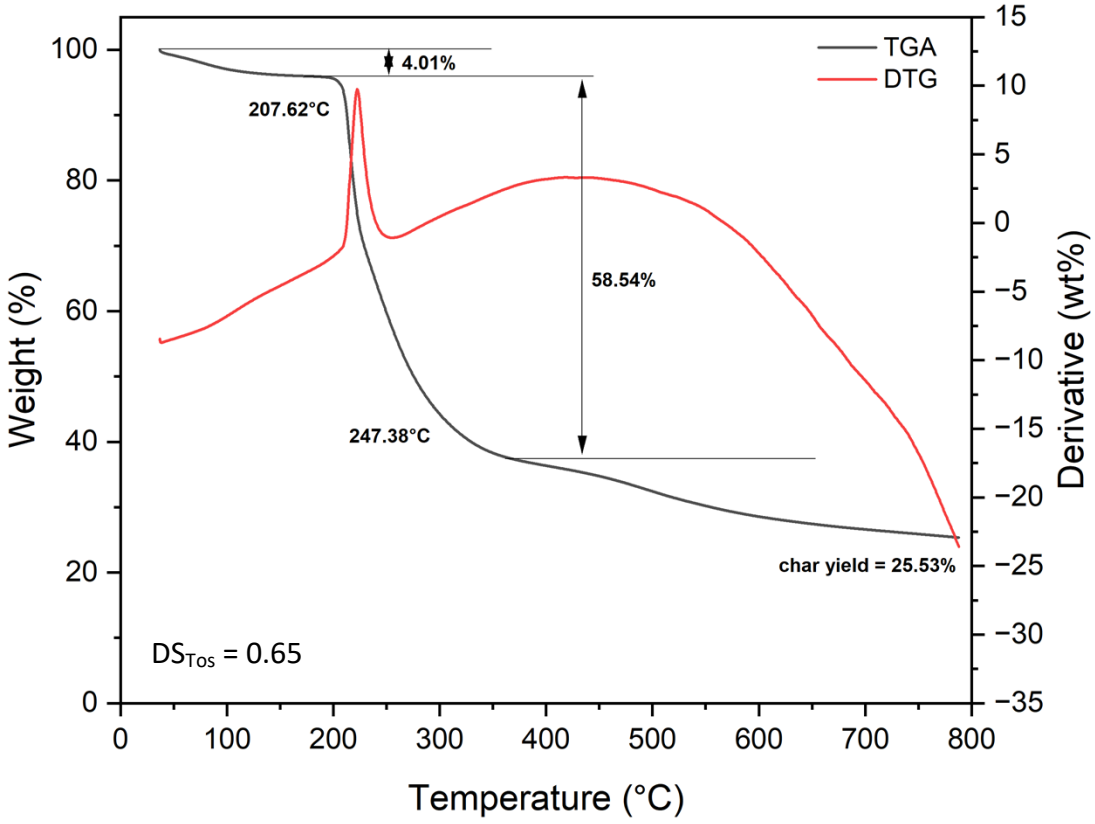

Fig. S30 TGA curve of tosyl starch (DS_{Tos} = 0.65) recorded under a N_2 flow with a heating rate of 10 °C min^{-1}