

Supporting information

Synthesis of fully biobased cellulose-3-(2-hydroxyphenyl) propionate ester with antioxidant activity and UV-resistant properties by the DBU/CO₂/DMSO solvent system

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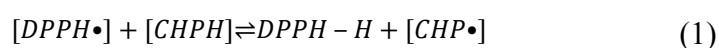
Table S1 Comparison of antioxidant activity of bio-based materials

code	Raw materials, system	Reaction conditions	DPPH Radical scavenging
1 ¹	Cellulose with 3,5-di-tert-butyl-4-hydroxybenzoic acid in ionic liquid	50-80°C, 0.5-5h to reaction	The products with DS of 0.83 and a concentration of 60mM took 30min to reach a radical scavenging of 90%

2 ²	Chitosan with anthocyanin films with casting method	30 °C with 50% relative humidity for 2 days to get anthocyanin <i>films</i>	The films with concentration of 5mg/ml took 60min to reach a radical scavenging of about 70-80%.
3 ³	Chitosan with Essential oil extraction from <i>E. globulus</i> films with casting method	at room temperature during four days	The films with concentration of 40mg/g reach a max radical scavenging of 43.62%.
4 ⁴	Cellulose acetate with thymol films	at room temperature with vacuum drying for 45min	The films with 20ug/ml concentration of Thymol reach a max radical scavenging of 65.16%.
5 ⁵	a-D(+)-fructose in HCl solution	The solutions were incubated at 75, 85, or 95°C	The systems to reach 90% free radical scavenging activity ranged from about 48 to 536 h. The activation energy was 77 kJ/mol.
6 ⁶	Chitosan grafted lignin monomers by ester activation through a carbodiimide-mediated coupling reaction	At 60°C for 12h	The sinapic acid grafted films with 1cm ² /ml reach a max radical scavenging of 90% at 9h.

The principle of radical scavenging of CHP

The radical scavenging assay is based on the following principle⁷:



[DPPH•] on accepting a hydrogen (H) atom from CHP resulting into reduction of DPPH₂, the purple colour changed to yellow with concomitant decrease in absorbance at 517 nm. The secondary reactions may be of limited occurrence. According to Eq. (2) and (3), the less reactive [CHP•] could reaction with another [DPPH•] as well as [CHP•].

Table S2 The kinetic parameters for CHP-2 to DPPH

Concentration of 2(mM)	Reaction CHP- temperature	Pseudo-first order reaction kinetic equation		Pseudo-second order kinetics equation	
	T (°C)	k_1 (min ⁻¹)	R ²	k_2 ((mMol/L) ⁻¹ min ⁻¹)	R ²
1	25	0.00702	0.98441	0.11091	0.98502
5	25	0.01129	0.98685	0.21417	0.93977
10	25	0.01663	0.98862	0.43161	0.94712
20	25	0.01881	0.99056	0.59584	0.95201
40	25	0.09424	0.821	14.01969	0.51497
5	35	0.01212	0.96451	0.31091	0.85457
5	45	0.02021	0.96174	0.66794	0.8285
5	55	0.02577	0.98732	0.92160	0.92722

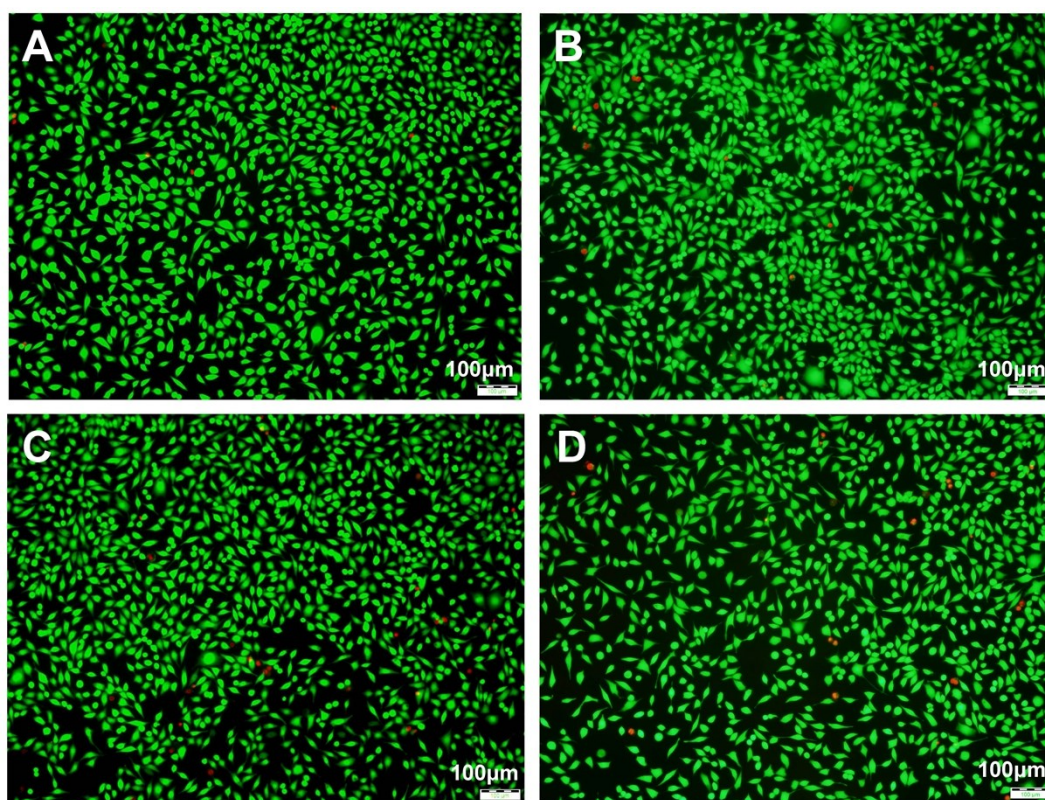


Fig. S1 Fluorescent images of L929 cells stained by Calcein-AM (green) and PI (red) treated with 10 µM CHP-7 (A); treated with 30 µM CHP-7 (B); treated with 60 µM CHP-7 (C); treated with 100 µM CHP-7 (D).

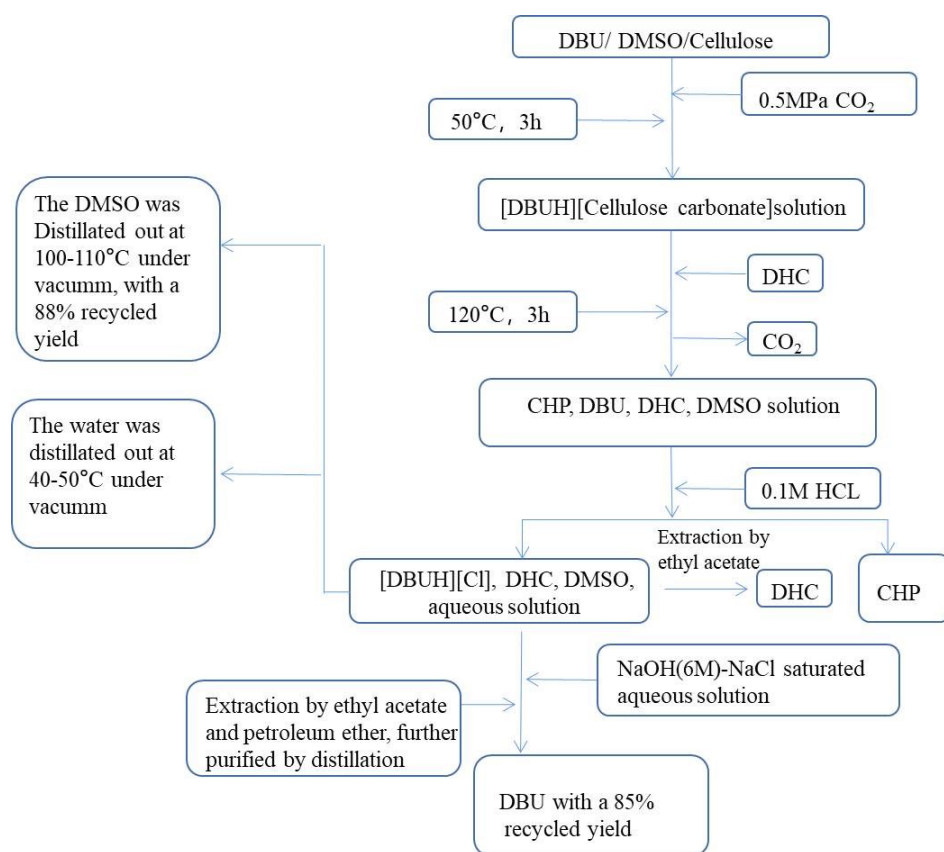


Fig. S2 A flowchart for the primary recycling of DBU and DMSO

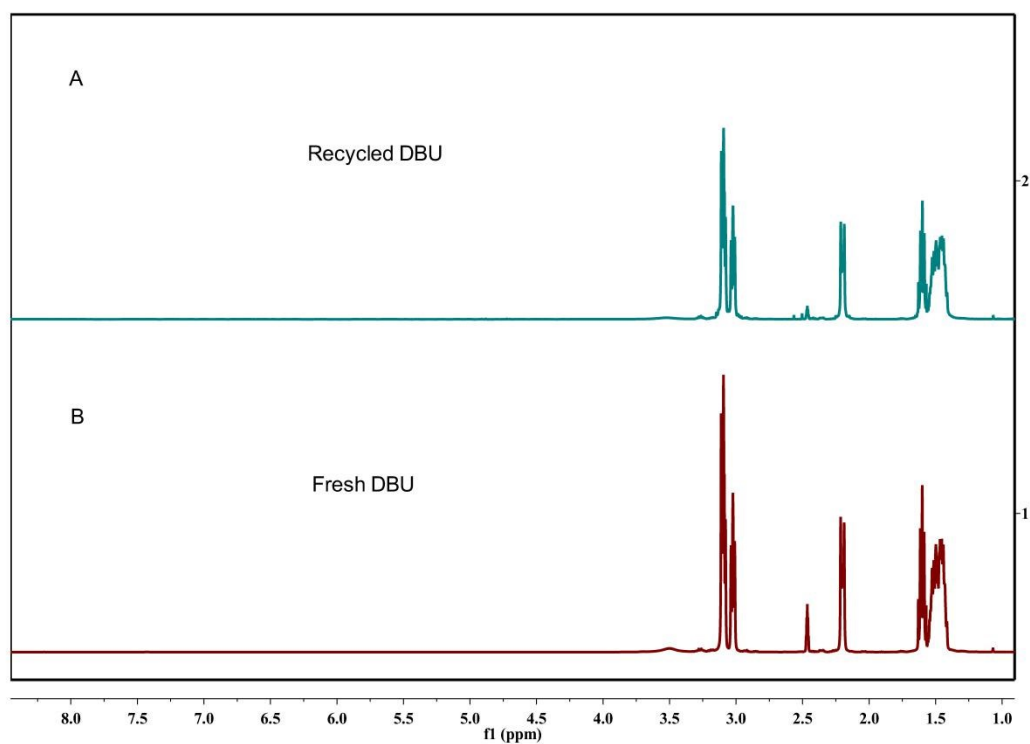


Fig.S3 Comparative ^1H NMR spectra of fresh DBU and recycled DBU.

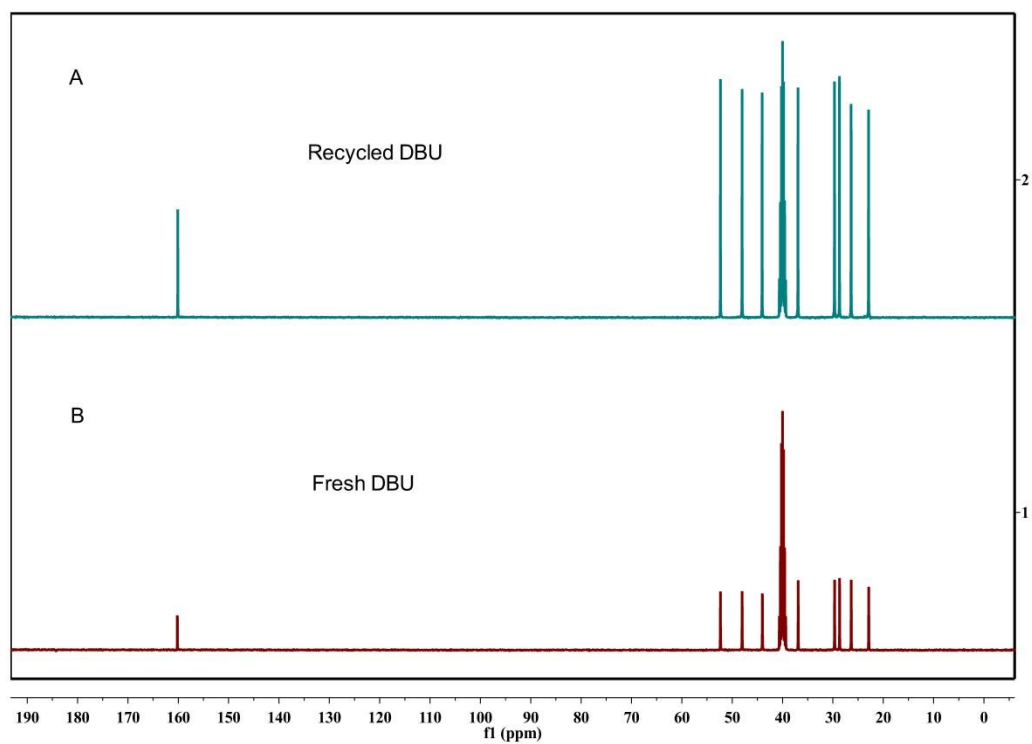


Fig.S4 Comparative ^{13}C NMR spectra of fresh DBU and recycled DBU.

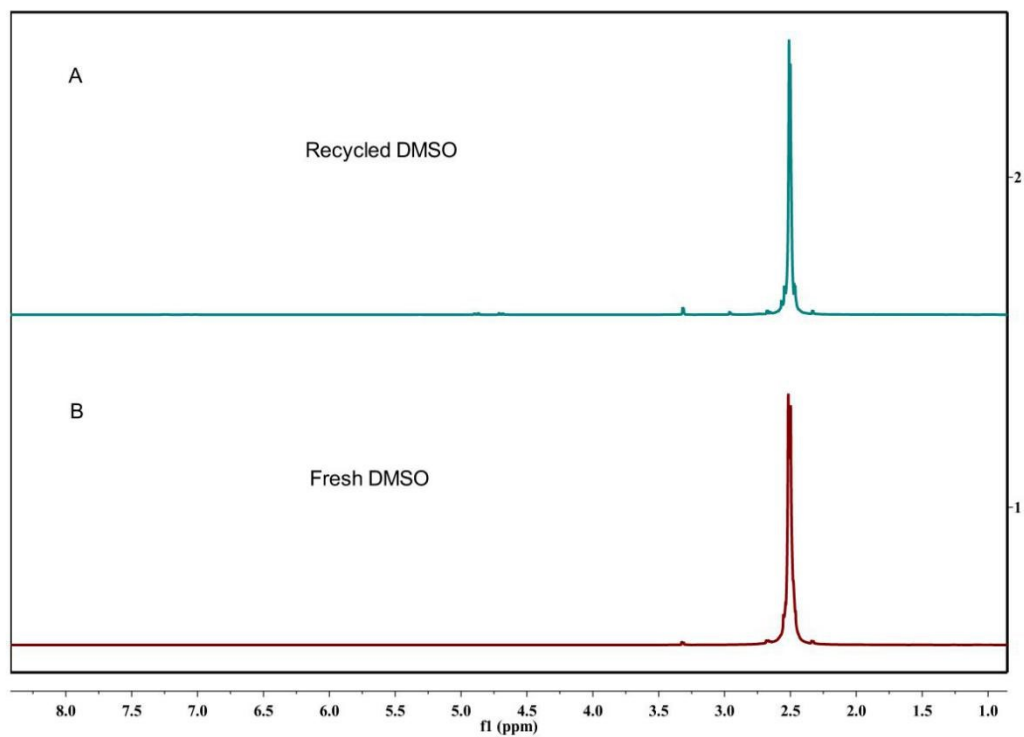


Fig. S5 Comparative ^1H NMR spectra of fresh DMSO and recycled DMSO

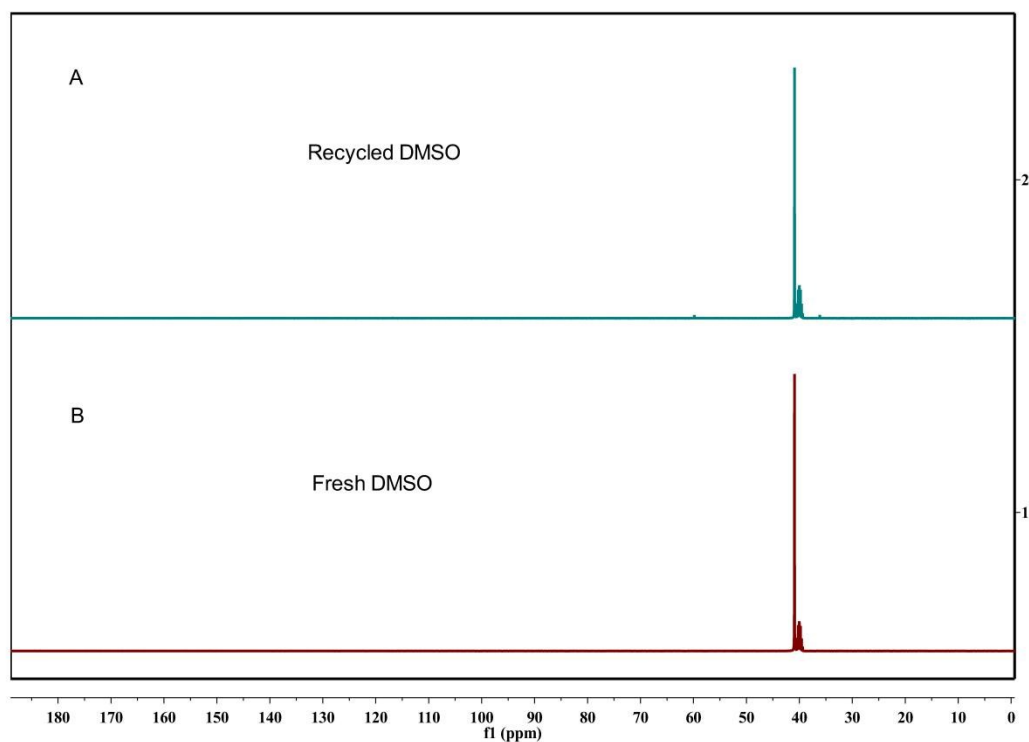


Fig. S6 Comparative ^{13}C NMR spectra of fresh DMSO and recycled DMSO.

References

1. T. Yang, P. Xiao, J. Zhang, R. Jia, H. Nawaz, Z. Chen and J. Zhang, *ACS Applied Materials & Interfaces*, 2019, **11**, 4302-4310.
2. H. Yong, X. Wang, R. Bai, Z. Miao, X. Zhang and J. Liu, *Food Hydrocolloids*, 2019, **90**, 216-224.
3. J. Hafsa, M. A. Smach, M. R. B. Khedher, B. Charfeddine, K. Limem, H. Majdoub and S. Rouatbi, *LWT - Food Science and Technology*, 2016, **68**, 356-364.
4. K. Harini and M. Sukumar, *Carbohydrate Polymers*, 2019, **204**, 202-213.
5. S.-L. Chen, D.-J. Yang, H.-Y. Chen and S.-C. Liu, *Food Chemistry*, 2009, **114**, 582-588.

6. K. Crouvisier-Urien, F. Regina da Silva Farias, S. Arunatat, D. Griffin, M. Gerometta, J. R. Rocca-Smith, G. Weber, N. Sok and T. Karbowiak, *Green Chemistry*, 2019, **21**, 4633-4641.
7. K. Mishra, H. Ojha and N. K. J. F. C. Chaudhury, 2012, **130**, p.1036-1043.