Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Acylation of cellulose in reversible ionic liquids

Yunlong Yang,[a,b] *Haibo Xie*[b,c,*] *Enhui Liu,*[a, *]

[a]Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan, China, 411105

[b]Division of Biotechnology, Dalian Institute of Chemical Physicals, Chinese Academy of Sciences, Dalian, 116023

[c]Bioenergy Research Division, Dalian National Laboratory for Clean Energy, Dalian, 116023

1. Experimental Details

1.1 Materials

Microcrystalline cellulose (MCC) with a degree of polymerization (DP) of 240 was obtained from Aladdin Commerce Reagent Co., Ltd. and dried at 60 °C for 24 h in vacuum oven before use. CO_2 with a purity of >99.999% was supplied from Beijing Bei Temperature Gas Factory. DMSO was purchased from Beijing Chemcial Reagent Co., Ltd. Methanol was purchased from Tianjing Damao Chemcial Reagent Factory. Acetic anhydride (Ac_2O) was purchased from Sinopharm Chemcial Reagent Co., Ltd. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), propionic anhydride (Pr_2O) and butyric anhydride (Bu_2O) were purchased from Aladdin Commerce Reagent Co., Ltd. and used as received. All chemical reagents were analytical reagents and used without further purification.

1.2 Measurements

The IR spectra of the samples were recorded with a Fourier transform IR spectrometer (FTIR PE-2000, the United States). The test specimens were prepared by the KBr-disk method.

^1H NMR spectrum were recorded on a Bruker AV 500 spectrometer with 16 scans in DMSO-d_6 or $CDCl_3$. The DS of cellulose ester was calculated by Eq. (1):

$$DS = \frac{7 * (I_{\text{-CH3}})}{3 * I_{H,AGU}}$$

Where I_{CH3} is the peak integral of methyl protons and I_{AGU} is the peak integral of anhydroglucose unit.

The ^{13}C NMR spectra of cellulose ester in DMSO-d_6 were recorded at 100 ^oC on a Bruker AV-500 instrument. Each spectrum was obtained with an accumulation of 1000 scans. Wide-angle X-ray powder diffraction (WAXD) was performed by X'pert Pro-1 X-ray diffractometer using Ni-filtered Cu KR radiation (40 kV, 30 mA) with 5°/min scanning rate at room temperature. Diffraction intensity was measured in a range of 2θ=5-60°.

1.3 Dissolution of cellulose in *in situ* formed [DBUH][O_2COCH_3]/DMSO (X_{RILs}=0.2)

A mixture of MCC (1.3 g) , DMSO (14.4 g, 184 mmol) , methanol (1.5 g, 46 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (7.0 g, 46 mmol) was added into a high pressure reactor, and then 0.5 MPa of CO_2 was introduced into the system to stabilize for 5 min till the pressure of CO_2 stabilize. Then the solution was heated to 60 ^oC for 3 h with vigorous magnetic stirring. When the temperature was decrease to room temperature, the CO_2 was released slowly, and a 5 wt% of cellulose [DBUH] [O_2COCH_3]/DMSO (X_{RILs}=0.2) solution was obtained, and was ready for subsequent reactions. The dissolved cellulose can be regenerated by adding methanol in to the solution, and then washed by methanol (100 mL X 3) to remove the solvents and dried in a vacuum oven at 60 °C for about 24 h for WXRD analysis.

1.4 Esterification Procedure

A typical esterification procedure was used as follows: Acetic anhydride (2.86 g, 28 mmol) was dropped with a pipet into 10 g of 5 wt% of cellulose [DBUH][O_2COCH_3] (X_{RILs}=0.2) solution in a flask equipped with a mechanical stirrer under N_2 atmosphere at room temperature, and then the reaction temperature was increased to 80 °C for 5 h with vigorous mechanical stirring. After the reaction, the cellulose acetate was precipitated by adding 5-fold amount of methanol, and separated by filtration. Cellulose acetate (0.63 g, 90% yield, DS=2.25) was obtained after subsequent wash with water (100 mL x 3) with distilled water, and dried in a vacuum oven at 60 °C for about 24 h.

1.5 Supplemental Tables and Figures

Table S1 Primary evaluation of the distribution trend of acetyl moiety among the three OH groups of AGU in CAs

Code	Total DS	Distribution of substituents[a]		
		C_6	C_2	C_3
CA-9	0.98	0.71	0.16	0.11
CA-10	2.25	0.91	0.87	0.47
CA-6	2.51	0.99	0.89	0.63
CA-7	2.71	1.0	0.91	0.80

[a] The results were primary calculated from the quantitative integration of acetyl methyl protons area of the ^1H NMR spectra.

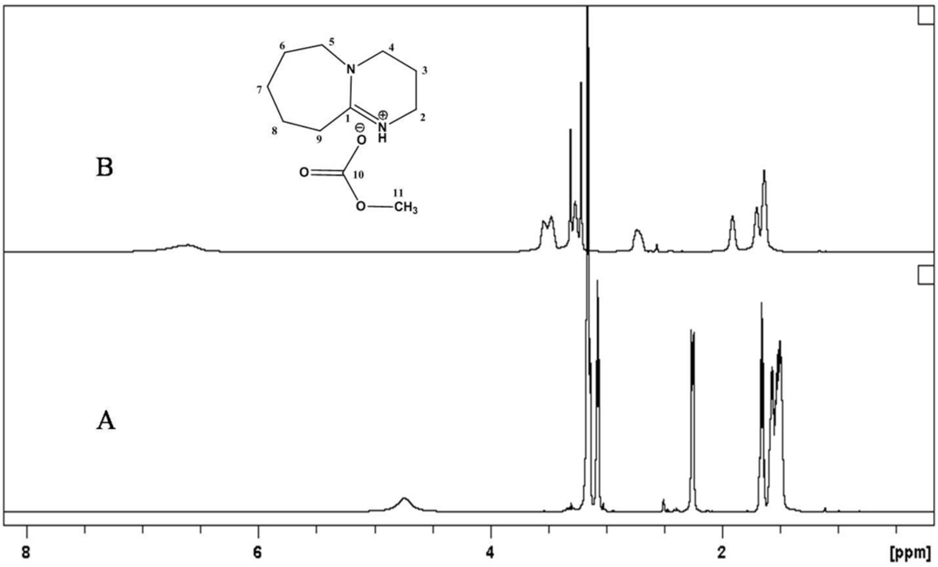

Figure S1 Comparative ^1H NMR spectra of A: DBU+Methanol (1:1, molar ratio) and B: the formed [DBUH][O_2COCH_3] in DMSO-d6 after CO_2 capture

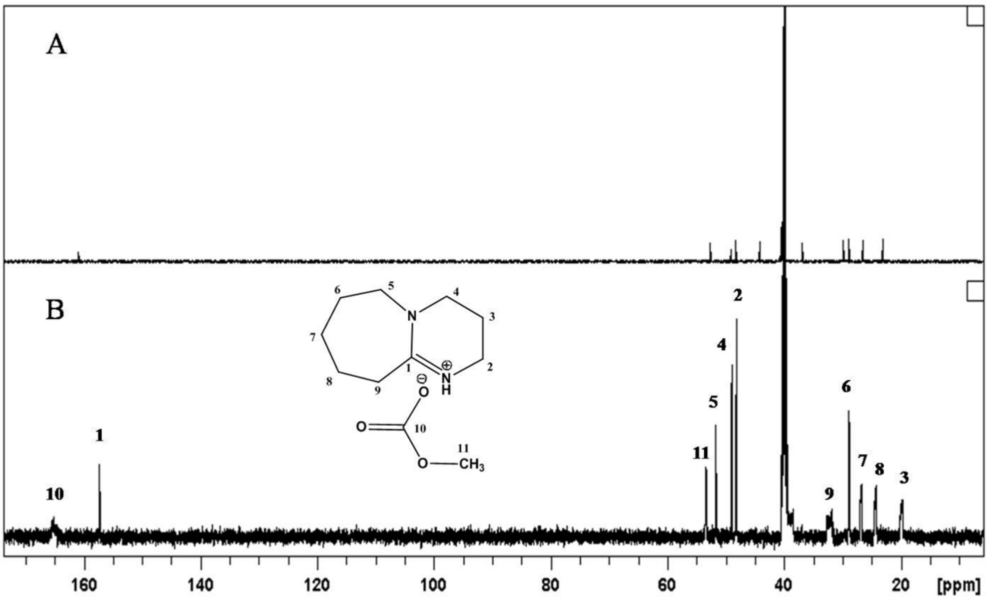

Figure S2 Comparative ^{13}C NMR spectra of A: DBU+Methanol (1:1, molar ratio) and B: the formed [DBUH] [O_2COCH_3] in DMSO-d6 after CO_2 capture

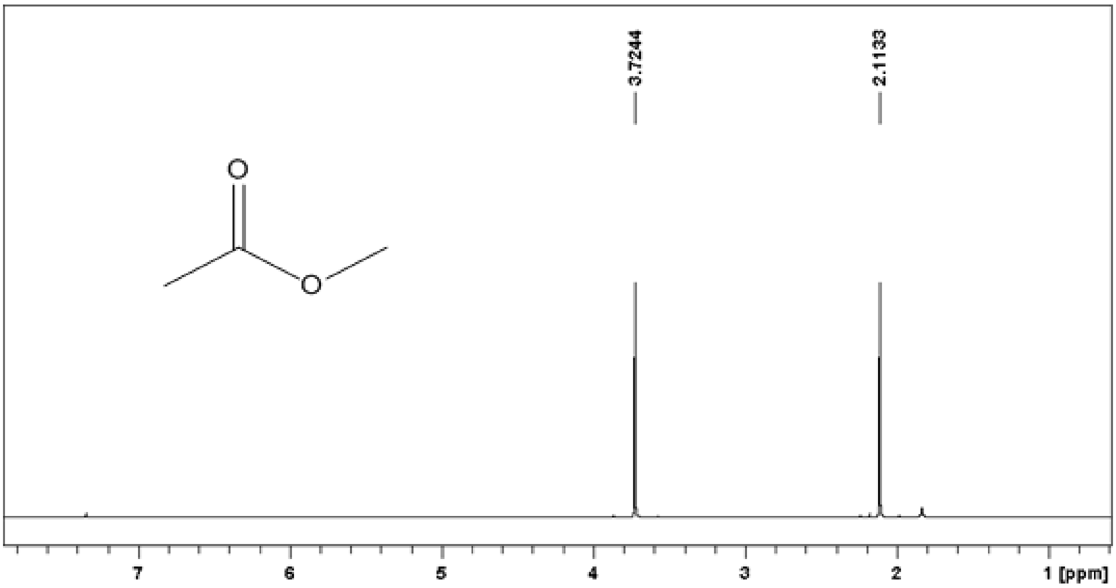

Figure S3 ^{1}H NMR spectrum of methyl acetate in $CDCl_3$

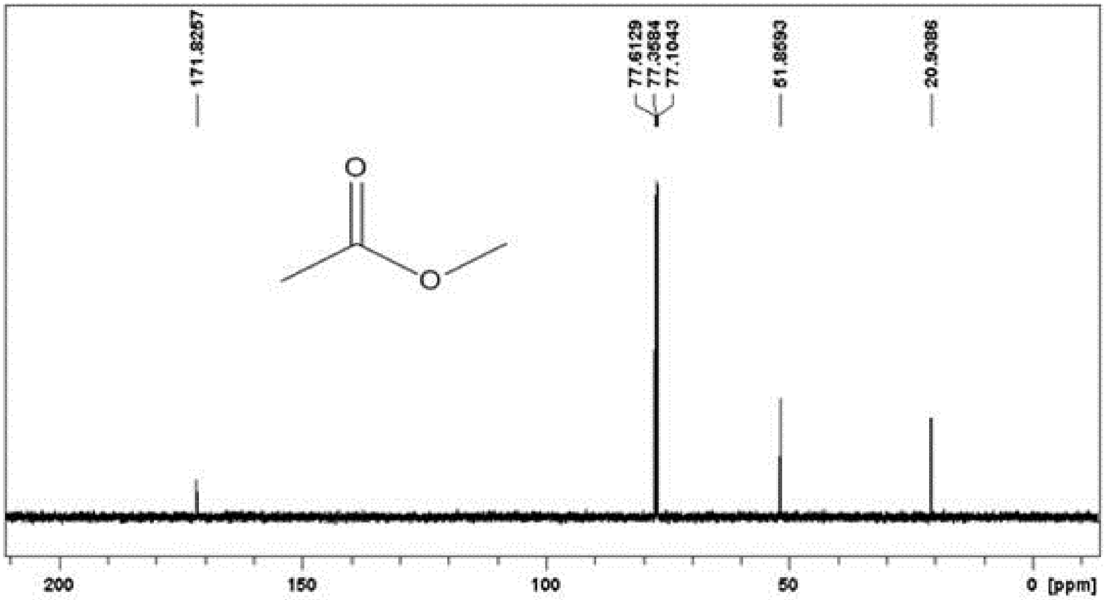

Figure S4 ^{13}C NMR spectrum of methyl acetate in $CDCl_3$

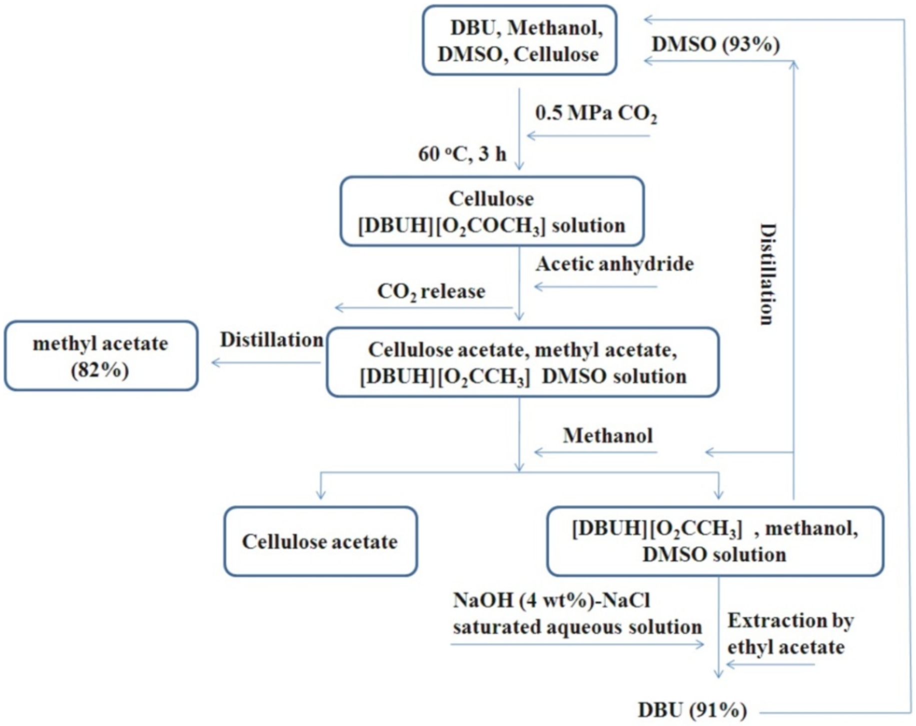

Figure S5 The flowchart of the whole procedure used in this study

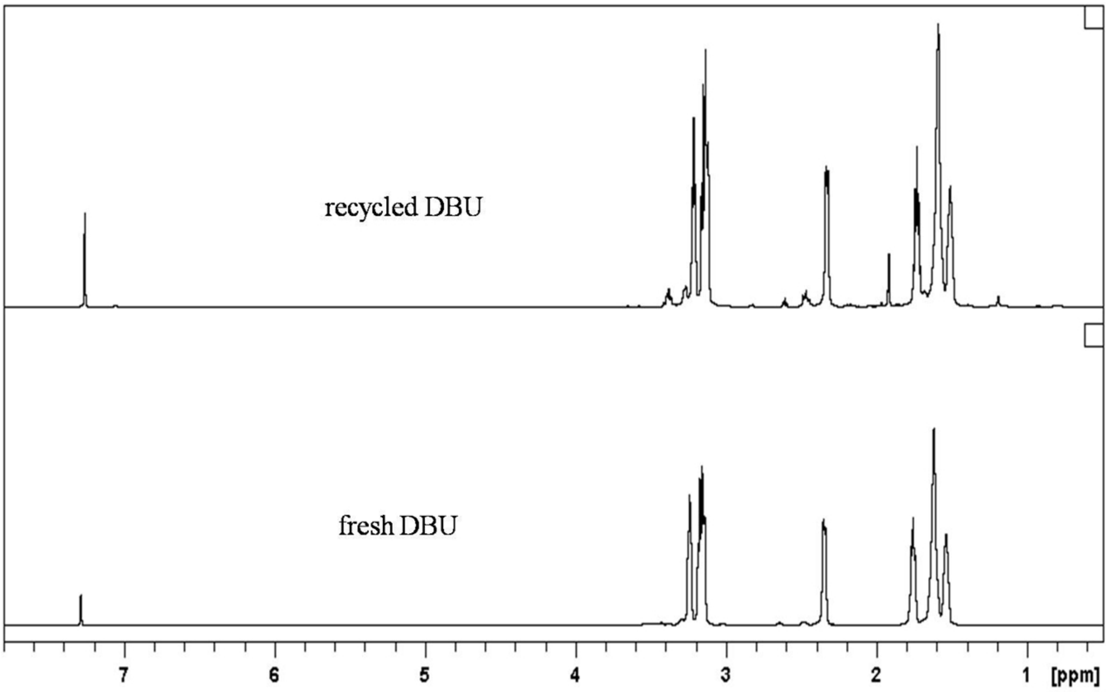

Figure S6 Comparative ^{1}H NMR spectra of fresh DBU and recycled DBU.

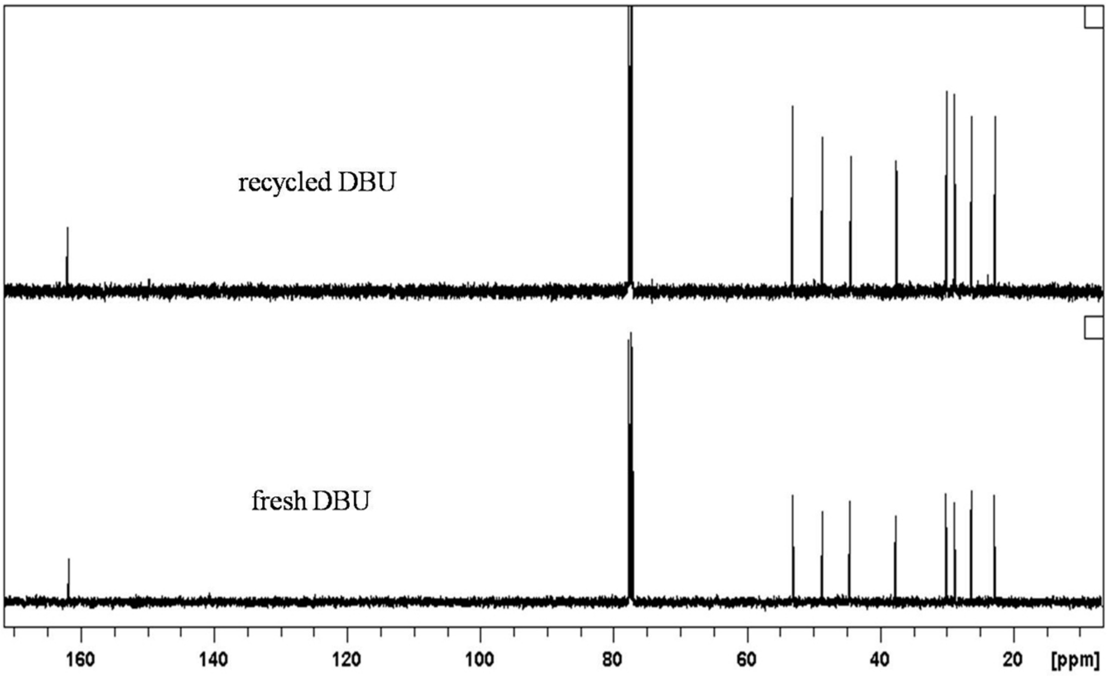

Figure S7 Comparative ^{13}C NMR spectra of fresh DBU and recycled DBU.

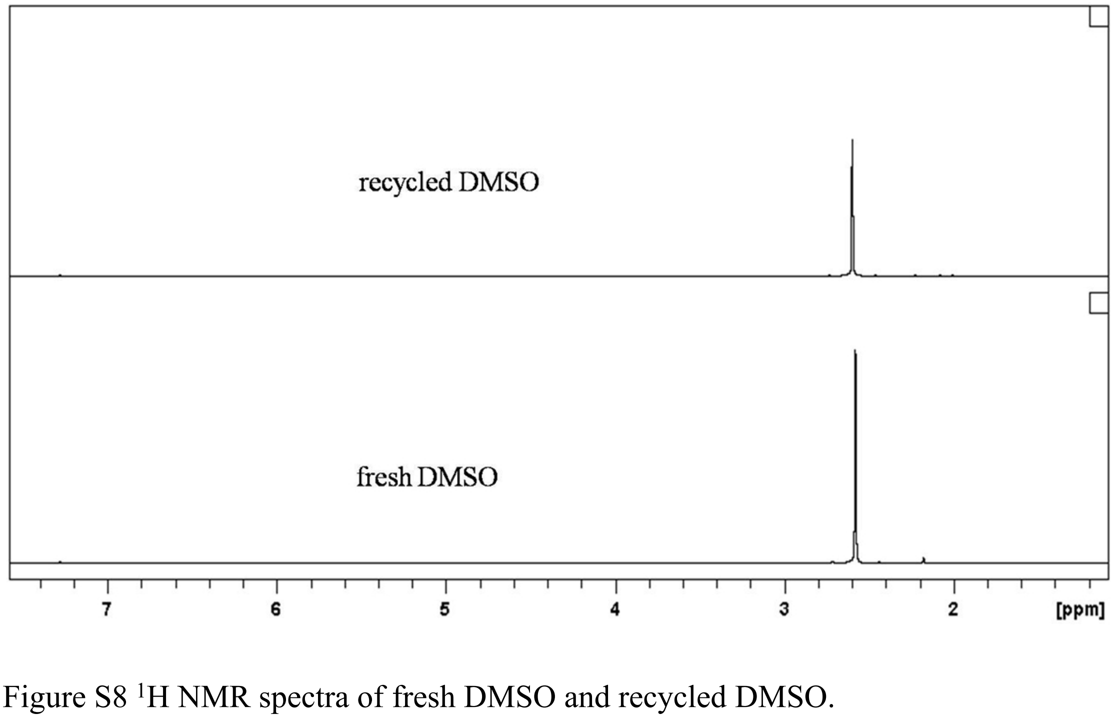

Figure S8 ^{1}H NMR spectra of fresh DMSO and recycled DMSO.

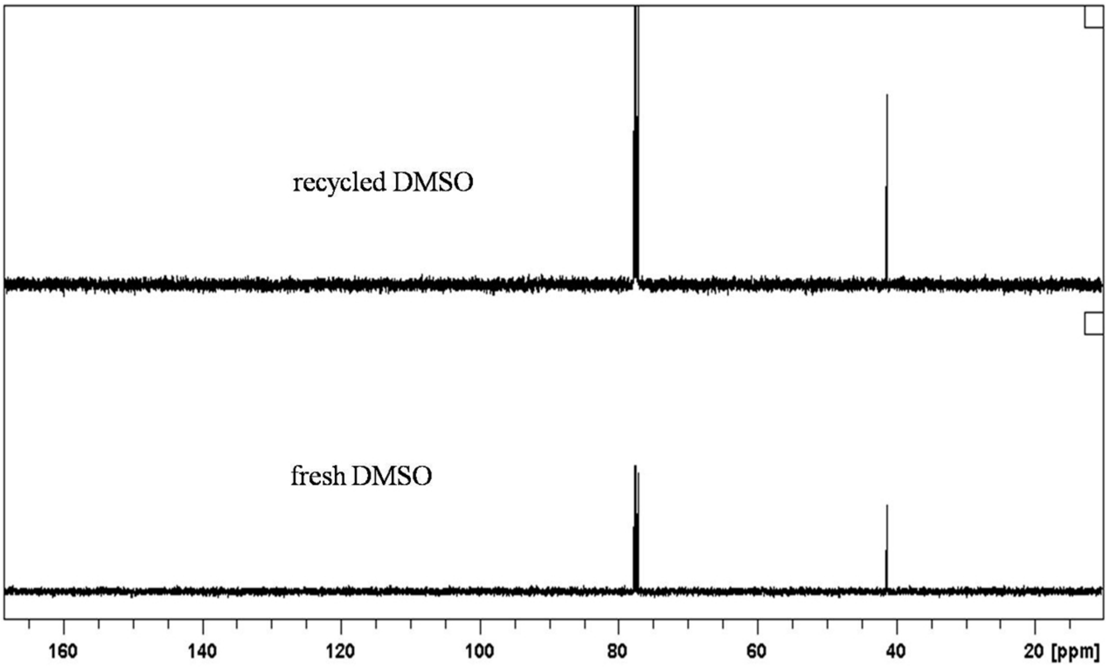

Figure S9 ^{13}C NMR spectra of fresh DMSO and recycled DMSO.