(Supporting Information)

Direct one-step synthesis of a formally fully bio-based polymer from cellulose and cinnamon flavor

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Chemicals

1-Ethyl-3-methylimidazolium acetate (EmimOAc) was obtained from Kanto Chemical Co., Inc. (Tokyo, Japan) and used without further purification. 1-Ethyl-3-methylimidazolium chloride (EmimCl) was purchased from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA) and was used after being recrystallized twice from acetonitrile. Cellulose (Avicel®PH-101, particle size < 50 μm) and 2-mesityl-2,5,6,7-tetrahydropyrolo[2,1-*c*][1,2,4]triazol-4-ium chloride (TMesCl) were obtained from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA). The number-average degree of polymerization of Avicel was calculated to be 105.[1] EmimPPA was synthesized according to conventional protocols. Cinnamaldehyde was purchased from Tokyo Chemical Industry (TCI, Tokyo, Japan). Other chemicals were obtained from commercial sources and were used as received unless otherwise stated.

Instruments

^{1}H and ^{13}C NMR spectra were recorded using JNM-ECA 400 and 600 spectrometers (JEOL Ltd., Tokyo, Japan) in deuterated solvents, and the chemical shifts (δ, ppm) were referenced to either the residual solvent peak or tetramethylsilane [TMS, $\delta = 0$ (ppm)] as the internal standard. Fourier transform-infrared (FT-IR) spectra were recorded using a Thermo Fisher Scientific Nicolet IS10 (Thermo Fisher Scientific Inc., Tokyo, Japan) spectrometer equipped with an attenuated total reflection (ATR) unit. Mass spectra were recorded in fast atom bombardment (FAB) mode on a JMS-700 (JEOL Ltd., Tokyo, Japan). The size exclusion chromatography (SEC) measurements were performed with a JASCO PU-4180 liquid chromatograph equipped with a photo diode array (MD-4010) detector. All SEC measurements were carried out at 40 °C using Shodex (Tokyo, Japan) KF-805L, and tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curves were obtained with polystyrene standards (Tosoh)

Synthesis of 1-ethyl-3-methylimidazolium 3-phenylpropionate

1-Ethyl-3-methylimidazolium chloride (EmimCl; 10 g, 68.2 mmol) and KOH (4.94 g, 75.0 mmol, [KOH]/[EmimCl] = 1.1, molar ratio) were reacted in 2-propanol (340 mL) at −60 °C and then filtered twice at −60 °C to remove the precipitated KCl and the residual KOH. 1-Ethyl-3-methylimidazolium hydroxide (EmimOH) was obtained as a 2-propanol solution. The concentration of the EmimOH solution was calculated by titration using benzoic acid using a phenolphthalein solution as the indicator. 1-Ethyl-3-methylimidazolium propionate (EmimPPA) was prepared by neutralization of the EmimOH in 2-propanol solution (50 mL) with an equal amount of 3-phenylpropionic acid (1.64 g, 11 mmol), followed by filtration using a glass fiber filter (Advantec, GA-55, 21 mm), evaporation of the 2-propanol, and drying *in vacuo* at room temperature. Finally, EmimPPA was obtained as a pale-yellow liquid.

^{1}H NMR (600 MHz, DMSO-d_6) δ; 9.93 (s, 1H), 7.89 (dd, J = 1.8 Hz, 1.8 Hz, 1H), 7.80 (dd, J = 1.8 Hz, 1.8 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.91 (s, 3H), 1.89 (q, J = 7.8 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ; 176.5, 137.3, 123.5, 121.9, 44.0, 35.5, 31.1, 15.1, 11.3. IR (ATR, cm^{-1}) 3024, 2946, 1561, 1375, 1173. HRMS (FAB) calcd for $C_6H_{11}N_2$ ([M]$^+$) 111.0917, found: 111.0919 (cation), and $C_8H_7O_2$ ([M]$^-$) 149.0608, found: 149.0600 (anion).

General procedure for the oxidative esterification of cellulose.

Cellulose (120 mg, [OH] = 2.22 mmol) in EmimOAc (2.22 mmol) was dried for 3 h *in vacuo* at 80 °C. After the drying process was completed, dimethylsulfoxide (DMSO) (3.15 mL) was added and the mixture was stirred under Ar atmosphere. After 1 h, cinnamaldehyde (2.22

mmol) was added and the reaction mixture was stirred for 24 h at 60 °C. The resulting solution was poured into a large amount of MeOH. The polymer was washed with excess methanol to give a pale brown fiber.

Per-acetylation of resulting polymer using acetic acid.

The cellulose ester sample (50 mg) was mixed with 1.0 mL *N,N*-dimethylacetamide and sonicated at room temperature. After the sample was dissolved, acetic acid (108 μL), *N,N*-dimethylaminopyridine (23 mg) and EDC (108 mg) were added, and the mixture was stirred at room temperature for 24 h under an Ar atmosphere. The resulting solution was poured into a large amount of MeOH. The polymer was purified by washing with excess methanol to give a pale brown fiber.

Synthesis of cellulose phenylpropionate using acid chloride.

Cellulose (300 mg, [OH] = 5.5 mmol) in 6.0 mL (74.5 mmol) pyridine was stirred under an Ar atmosphere at 100 °C for 30 min. After 1 h, 3-phenylpropionylchloride (11.1 mmol) was slowly added, and the reaction mixture was stirred for 12 h at 100 °C. The resulting solution was poured into a large amount of MeOH. The polymer was purified by reprecipitation (from dichloromethane solution to methanol) to give a pale brown fiber.

Per-phenylpropionylation of resulting polymer using acid chloride.

The cellulose phenylpropionate sample (DS = 2.04, 100 mg) was mixed with 2.0 mL pyridine and sonicated at room temperature. After the sample was dissolved, 3-phenylpropionylchloride (550 μL) was slowly added dropwise, and the mixture was stirred at 100 °C for 12 h under an Ar atmosphere. The resulting solution was poured into a large amount of a 1:1 mixture of MeOH/water. The polymer was purified by washing with excess methanol to give a pale brown fiber.

Evaluation of the degree of substitution values of the cellulose esters.

The degree of substitution (DS) values of the cellulose esters were determined using ^{1}H NMR measurements in $CDCl_3$, DMSO-d_6, or acetone-d_6 depending on the solubility of the product and overlap between the target and solvent peaks.

Generally, the DS_{main} values were calculated using the following equation (1):

$$\mathbf{DS_{main} = (I_{main}/X)/(I_{AGU}/7)} \qquad (1)$$

The DS_{main} values of the phenylpropionate group on the cellulose ester were calculated from the integrals of the peaks (I_{main}) at 6.7−7.7 ppm (X = 5) corresponding to aromatic ring and the anhydroglucose unit (AGU) peaks (I_{AGU}) at 3.0−5.8 ppm.

Generally, the DS_{side} values were calculated using following equation (2):

$$\mathrm{DS_{side} = (I_{side}/X)/(I_{AGU}/7)} \qquad (2)$$

The DS_{side} values of the cellulose ester derived from Emim acetate were calculated from the integrals of the peaks (I_{side}) at 1.7−2.1 ppm (X = 3) corresponding to the methyl group and the peaks of AGU (I_{AGU}) at 3.0−5.8 ppm.

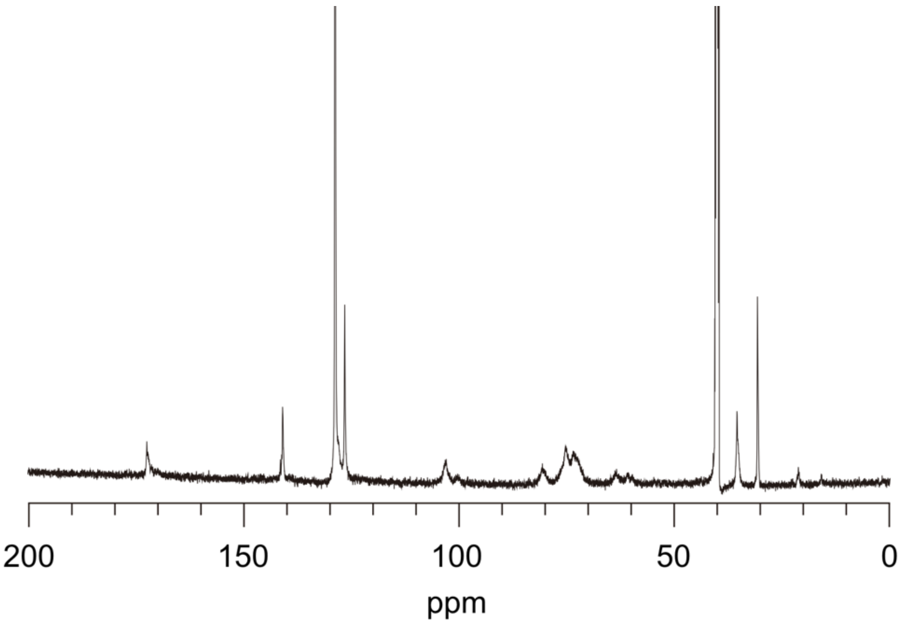


Figure S1. ^{13}C NMR spectrum of cellulose phenylpropionate shown in Scheme 2 in DMSO-d_6 at rt.

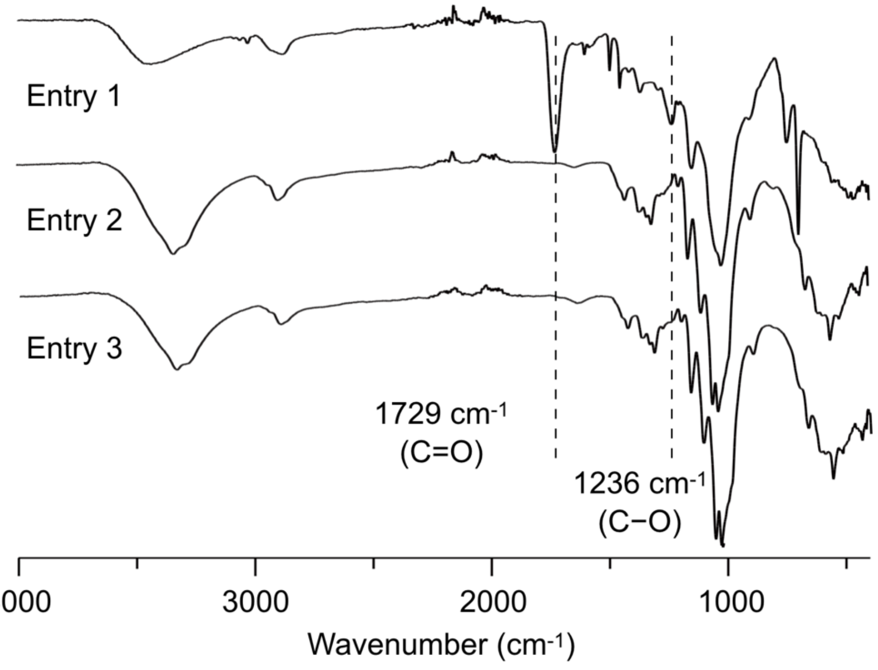


Figure S2. ATR-mode FT-IR of resulting cellulose derivatives after reaction in Table 1.

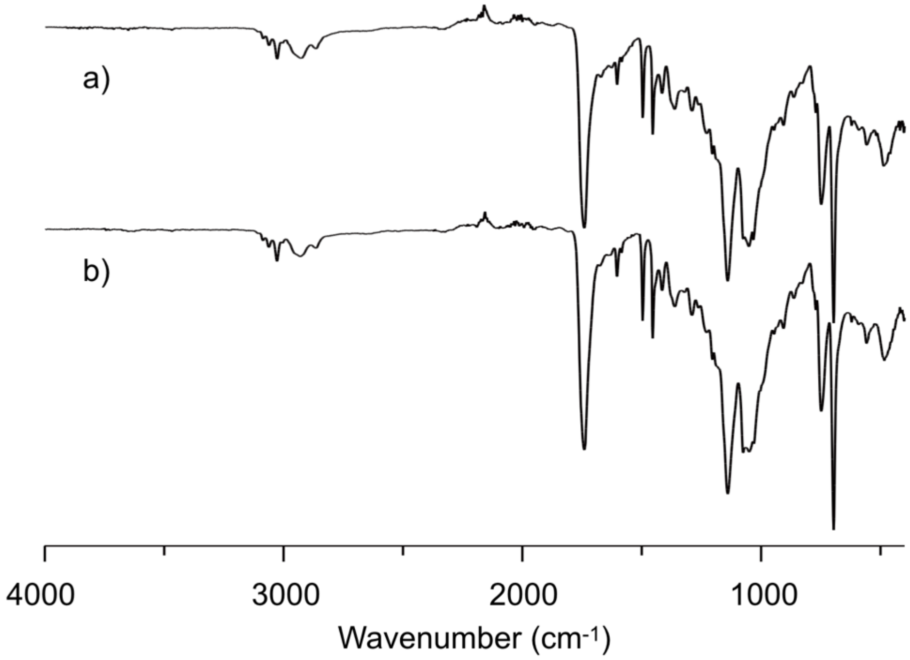


Figure S3. ATR-mode FT-IR of cellulose phenylpropionate synthesized by oxidative esterification using EmimPPA and additional per-phenylpropionylation using acid chloride (a) and conventional method (b) from Avicel.

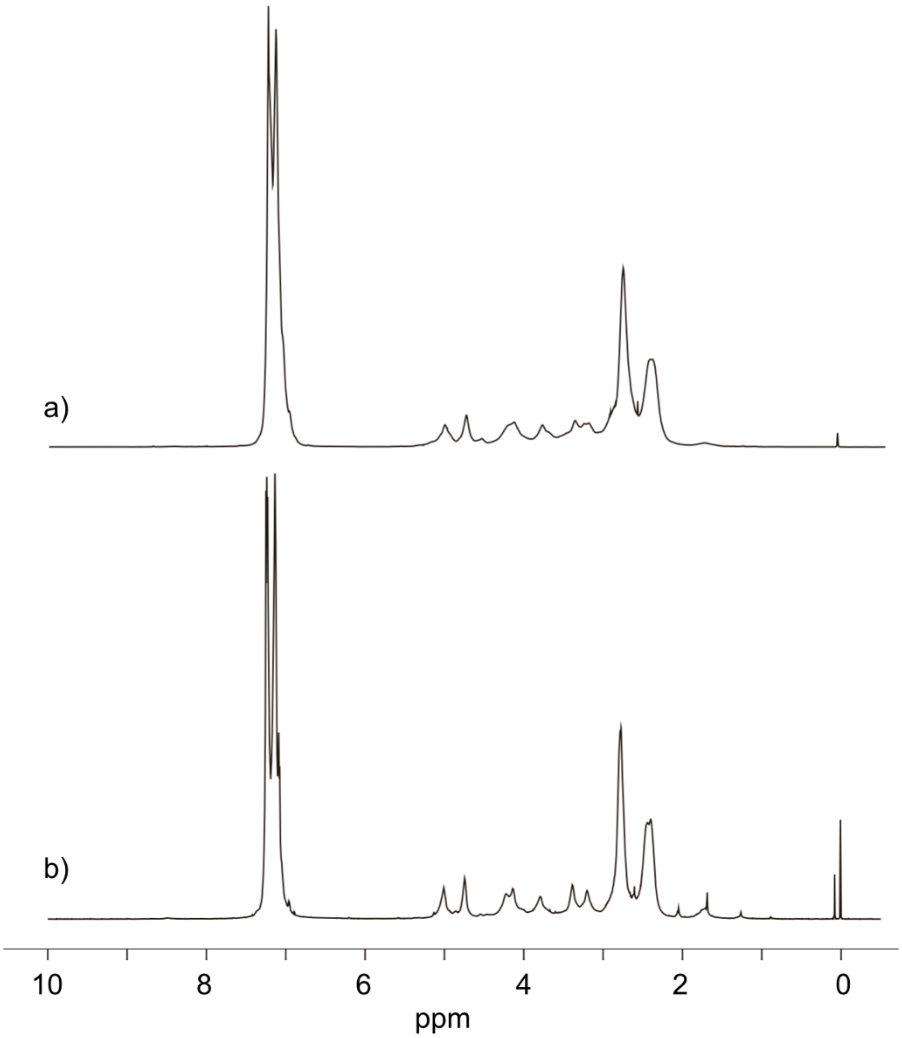


Figure S4. ^{1}H NMR spectra of cellulose phenylpropionate synthesized by oxidative esterification using EmimPPA and additional per-phenylpropionylation using acid chloride (a) and conventional method (b) from Avicel, measured at 25 °C in $CDCl_3$.

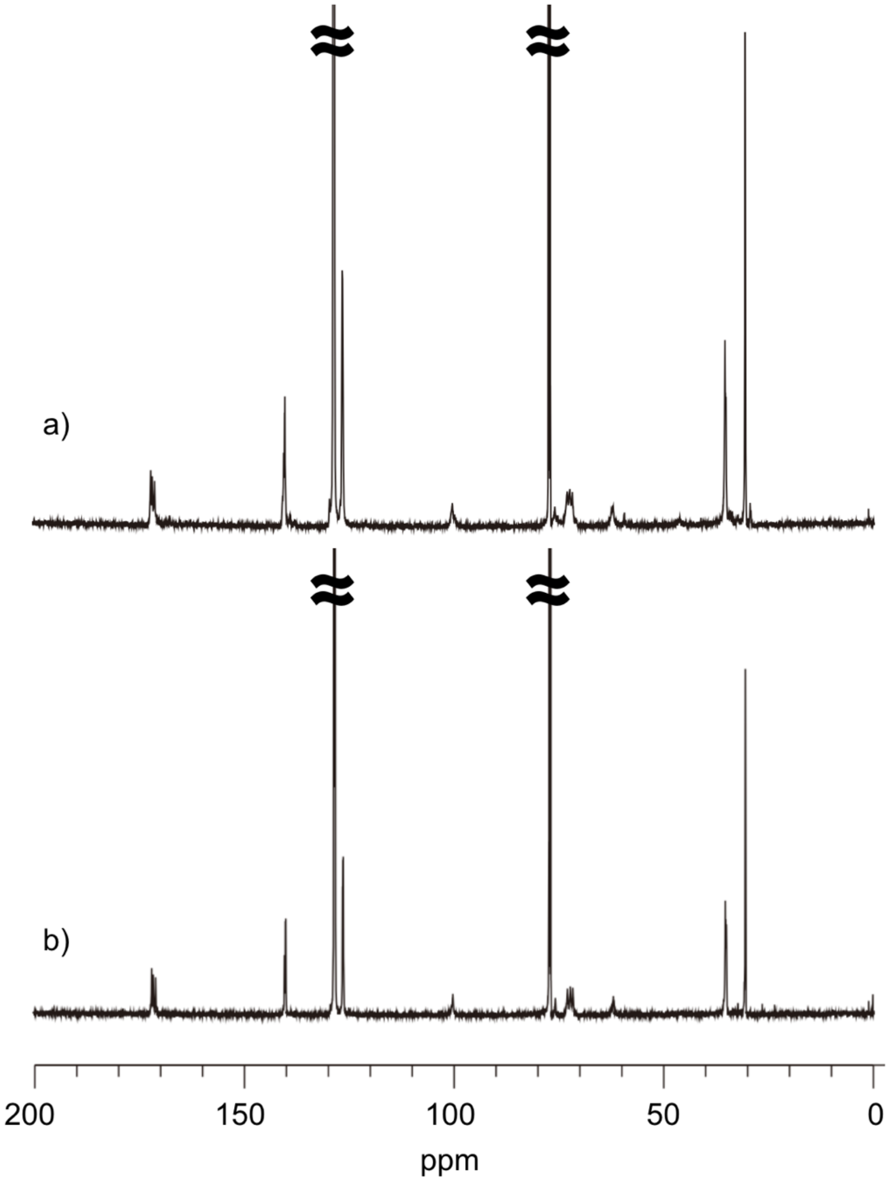
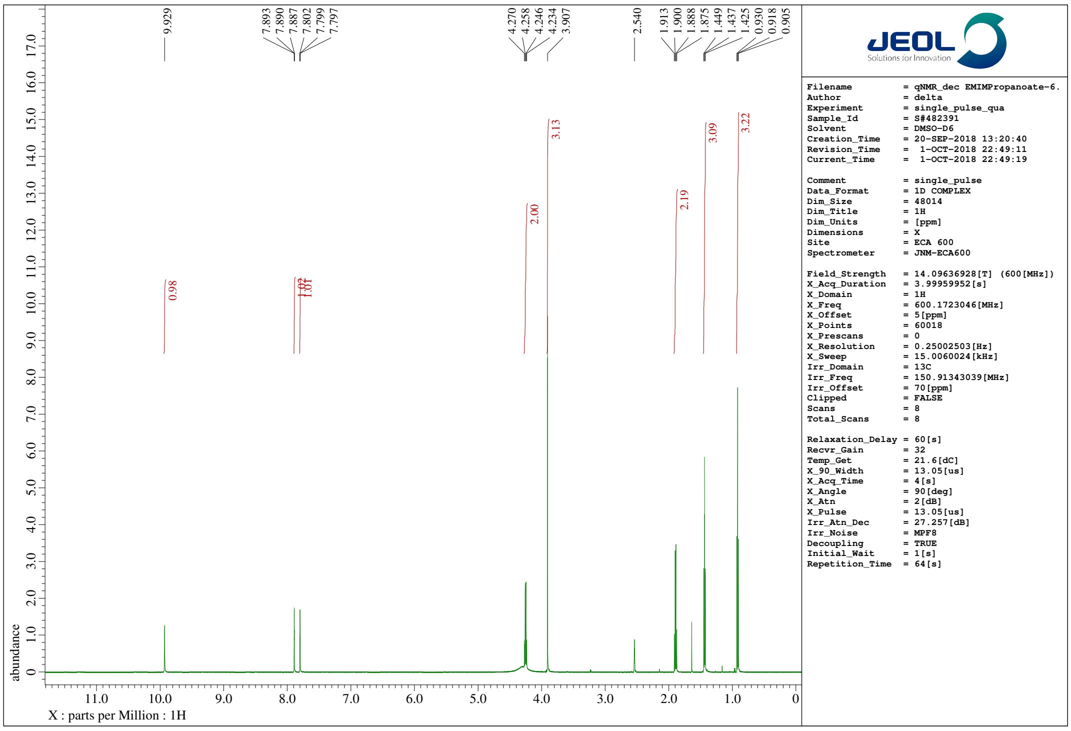


Figure S5. ^{13}C NMR spectra of cellulose phenylpropionate synthesized by oxidative esterification using EmimPPA and additional per-phenylpropionylation using acid chloride (a) and conventional method (b) from Avicel, measured at 25 °C in $CDCl_3$.

Table S1. Solubility test (1.0 mg/mL) of resulting cellulose esters (Table 1, entry 6) at room temperature.

Toluene	$CHCl_3$	THF	Acetone	DMF	DMSO	MeOH	H_2O
X	○	○	○	○	○	X	X

○: Soluble, X: Insoluble (lower than 1.0 mg/mL).



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Revision_Time    =  1-OCT-2018 22:49:11
Current_Time     =  1-OCT-2018 22:49:19

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Dimensions       = X
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Spectrometer     = JNM-ECA600

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X_Points         = 60018
X_Prescans       = 0
X_Resolution     = 0.25002503[Hz]
X_Sweep          = 15.0060024[kHz]
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Irr_Freq         = 150.91343039[MHz]
Irr_Offset       = 70[ppm]
Clipped          = FALSE
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X_Atn            = 2[dB]
X_Pulse          = 13.05[us]
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Decoupling       = TRUE
Initial_Wait     = 1[s]
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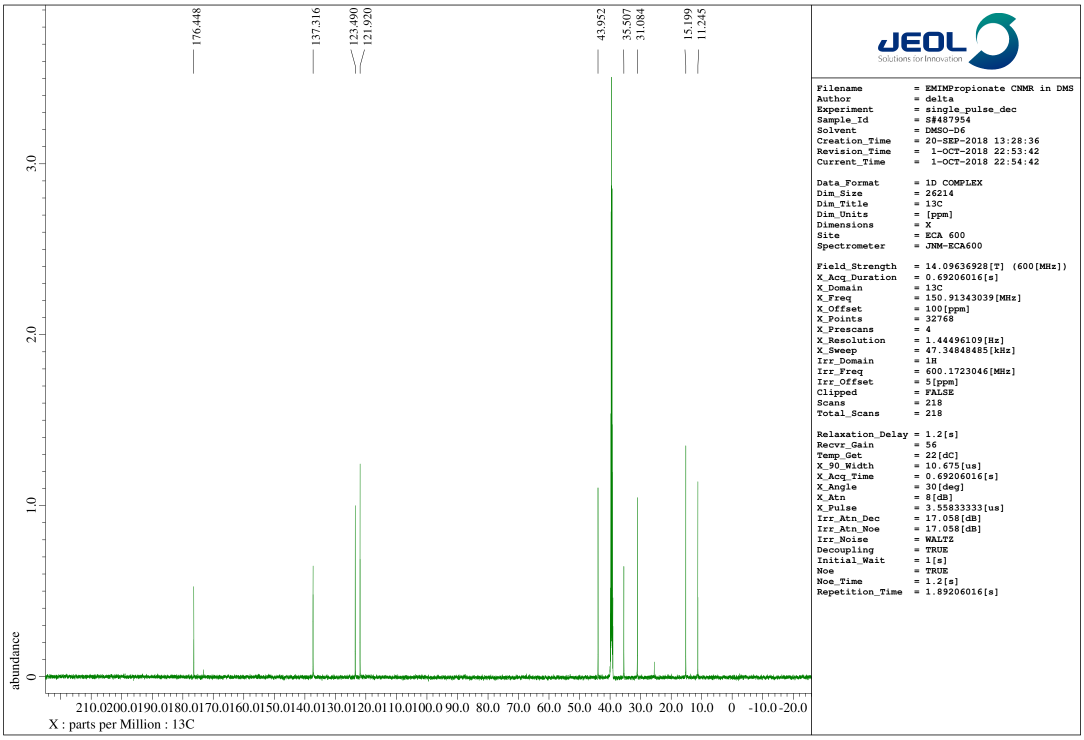
Figure S6. ^{1}H NMR spectrum of 1-ethyl-3-methylimidazolium 3-phenylpropionate (EmimPPA) in DMSO-d_6 at rt.



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Revision_Time    =  1-OCT-2018 22:53:42
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Dim_Units        = [ppm]
Dimensions       = X
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Spectrometer     = JNM-ECA600

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X_Offset         = 100[ppm]
X_Points         = 32768
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X_Resolution     = 1.44496109[Hz]
X_Sweep          = 47.34848485[kHz]
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Irr_Freq         = 600.1723046[MHz]
Irr_Offset       = 5[ppm]
Clipped          = FALSE
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Total_Scans      = 218

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Recvr_Gain       = 56
Temp_Get         = 22[dC]
X_90_Width       = 10.675[us]
X_Acq_Time       = 0.69206016[s]
X_Angle          = 30[deg]
X_Atn            = 8[dB]
X_Pulse          = 3.55833333[us]
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Irr_Atn_Noe      = 17.058[dB]
Irr_Noise        = WALTZ
Decoupling       = TRUE
Initial_Wait     = 1[s]
Noe              = TRUE
Noe_Time         = 1.2[s]
Repetition_Time  = 1.89206016[s]
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Figure S7. ^{13}C NMR spectrum of 1-ethyl-3-methylimidazolium 3-phenylpropionate (EmimPPA) in DMSO-d_6 at rt.

Reference

1. R. Kakuchi, R. Ito, S. Nomura, H. Abroshan, K. Ninomiya, T. Ikai, K. Maeda, H. J. Kim and K. Takahashi, *RSC Adv.*, 2017, **7**, 9423-9430.