

## Aryloxy ionic liquids-catalyzed homogenous esterification of cellulose with low-reactive acyl donors

Akina Yoshizawa,<sup>a</sup> Chie Maruyama,<sup>a</sup> Samuel Budi Wardhana Kusuma,<sup>a,b</sup> Naoki Wada,<sup>a</sup>  
Kosuke Kuroda,<sup>a</sup> Daisuke Hirose,<sup>a,\*</sup> and Kenji Takahashi<sup>a,\*</sup>

<sup>a</sup>*Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.*

<sup>b</sup>*Department of Chemistry, Faculty of mathematics and Natural Sciences, Universitas Negeri Semarang, Semarang City, Central Java 50229, Indonesia.*

\*To whom correspondence should be addressed. E-mail: dhirose@se.kanazawa-u.ac.jp, ktkenji@staff.kanazawa-u.ac.jp.

## Preparation of ILs from EmimCl

Potassium hydroxide (85%, 4.94 g, 68.2 mmol)/2-propanol (120 mL) and EmimCl (10 g, 68.2 mmol)/2-propanol (20 mL) solutions were prepared. Both potassium hydroxide and EmimCl solution were cooled to  $-60^{\circ}\text{C}$ . The cooled potassium hydroxide and EmimCl solution were mixed and followed by filtration twice to remove the precipitated potassium chloride. 1-Ethyl-3-methylimidazolium hydroxide (EmimOH) was obtained as a 2-propanol solution, and the EmimOH solution was neutralized by an equal amount of corresponding hydroxy aryls or theophyllin in 2-propanol (10 mL) solution. The reaction mixture was filtrated by a glass fiber filter (Advantec, GA-55, 21 mm), evaporation of 2-propanol, and drying in vacuo at room temperature. EmimOPys were quantitatively obtained as a yellow, brown sticky oil or white solid.

### *1-Ethyl-3-methylimidazolium 4,6-dimethyl-2-hydroxypyrimidinolate (Emim2OPm(diMe)) (3)*

Prepared from potassium hydroxide (85%, 4.94 g, 68.2 mmol), EmimCl (10.0 g, 68.2 mmol), 4,6-dimethyl-2-hydroxypyrimidine (8.40 g, 68.2 mmol) and 2-propanol (150 mL). Yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.95 (s, 1H), 7.84 (s, 1H), 7.75 (s, 1H), 5.78 (s, 1H), 4.24 (q,  $J = 7.2$  Hz, 2H), 3.89 (s, 3H), 1.98 (s, 6H), 1.41 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 166.85, 166.49, 137.93, 124.00, 122.41, 102.79, 44.52, 36.08, 23.60, 15.76. IR (ATR,  $\text{cm}^{-1}$ ) 2964, 1556, 1378, 1334. HRMS FAB ( $m/z$ ) calcd. for  $\text{C}_6\text{H}_{11}\text{N}_2$  ( $[\text{M}]^+$ ) 111.0917, found: 111.0924 (cation), and  $\text{C}_6\text{H}_7\text{N}_2\text{O}$  ( $[\text{M}]^-$ ) 123.0564, found: 123.0555 (anion).

### *1-Ethyl-3-methylimidazolium theophyllinate (EmimTEO) (4)*

Prepared from potassium hydroxide (85%, 4.94 g, 68.2 mmol), EmimCl (10.0 g, 68.2 mmol), theophylline (12.3g, 68.2 mmol) and 2-propanol (150 mL). Yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.26 (s, 1H), 7.75 (s, 1H), 7.66 (s, 1H), 7.11 (s, 1H), 4.15 (q,  $J = 7.2$  Hz, 2H), 3.81 (s, 3H), 3.35 (s, 3H), 3.15 (s, 3H), 1.36 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 158.19, 152.33, 150.23, 147.12, 136.94, 124.04, 122.42, 115.59, 44.63, 36.15, 30.41, 27.89, 15.60. IR (ATR,  $\text{cm}^{-1}$ ) 3076, 1689, 1637, 1473. HRMS FAB ( $m/z$ ) calcd. for  $\text{C}_6\text{H}_{11}\text{N}_2$  ( $[\text{M}]^+$ ) 111.0917, found: 111.0926 (cation), and  $\text{C}_7\text{H}_7\text{N}_4\text{O}_2$  ( $[\text{M}]^-$ ) 179.0574, found: 179.0570 (anion).

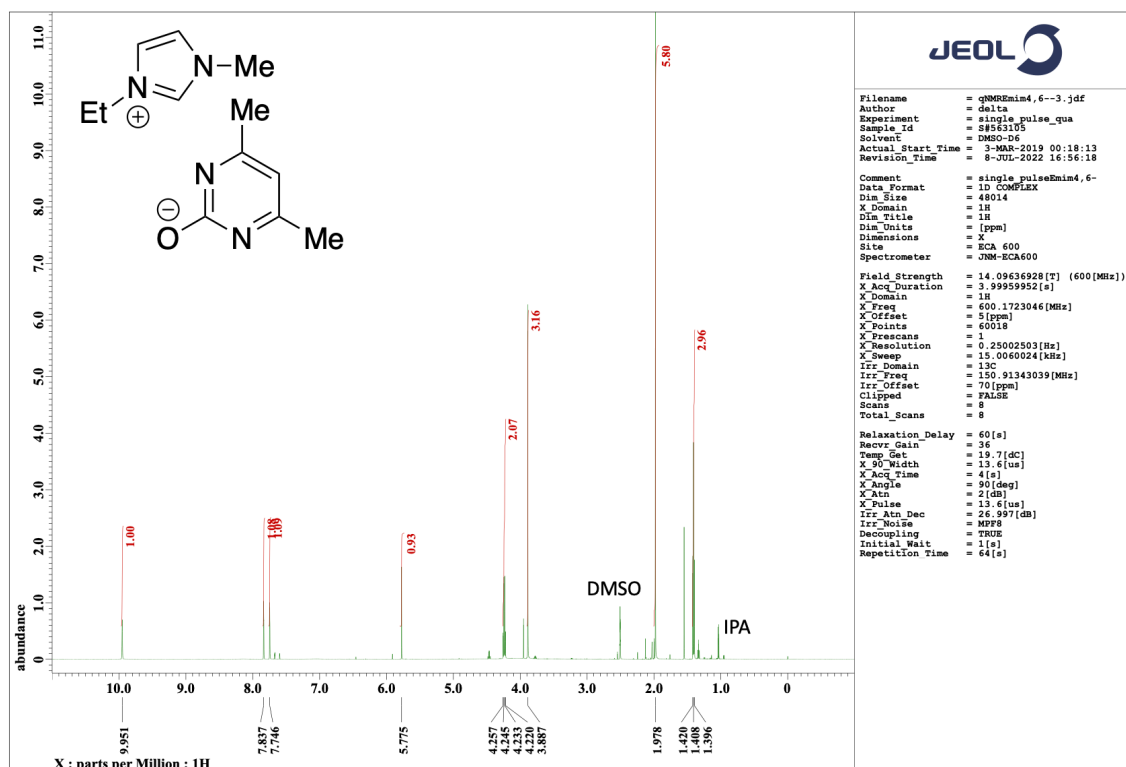
### *1-Ethyl-3-methylimidazolium 3-pyridinolate (Emim3OPy) (7)*

Prepared from potassium hydroxide (85%, 4.94 g, 68.2 mmol), EmimCl (10.0 g, 68.2 mmol), 3-hydroxypyridine (6.49g, 68.2 mmol) and 2-propanol (150 mL). Brown oil.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.48 (s, 1H), 7.79 (d,  $J = 2.4$  Hz, 1H), 7.70 (d,  $J = 1.8$  Hz, 1H), 7.41 (d,  $J = 2.4$  Hz, 1H), 7.06 (d,  $J = 3.6$  Hz, 1H), 6.62 (dd,  $J = 8.4, 4.2$  Hz, 1H), 6.24 (d,  $J = 7.8$  Hz, 1H), 4.13 (q,  $J = 7.2$  Hz, 2H), 3.80 (s, 3H), 1.35 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 166.87, 143.02, 137.41, 129.41, 124.08, 124.05, 123.14, 122.50, 44.61, 36.14, 15.66. IR (ATR,  $\text{cm}^{-1}$ ) 2991, 1556, 1470.

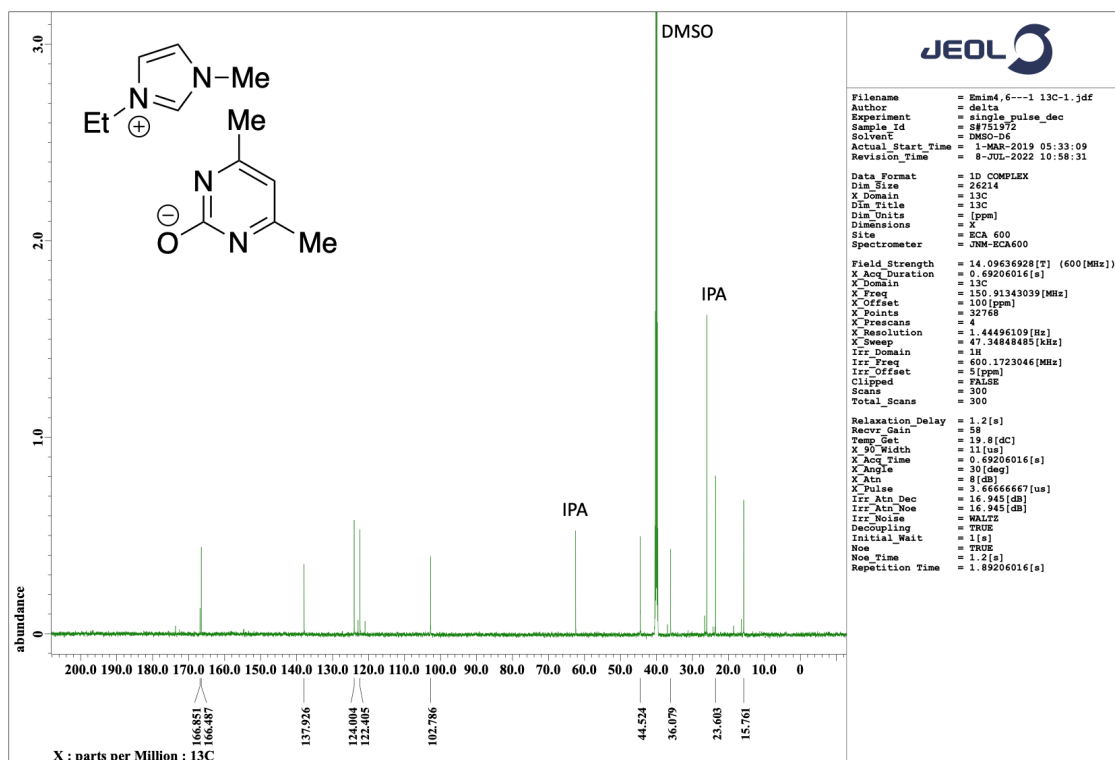
HRMS (FAB) calcd for  $C_6H_{11}N_2$  ( $[M]^+$ ) 111.0917, found: 111.0919 (cation), and  $C_5H_4NO$  ( $[M]^-$ ) 94.0298, found: 94.0292 (anion).

***1-Ethyl-3-methylimidazolium 4-pyridinolate (Emim4OPy) (8)***

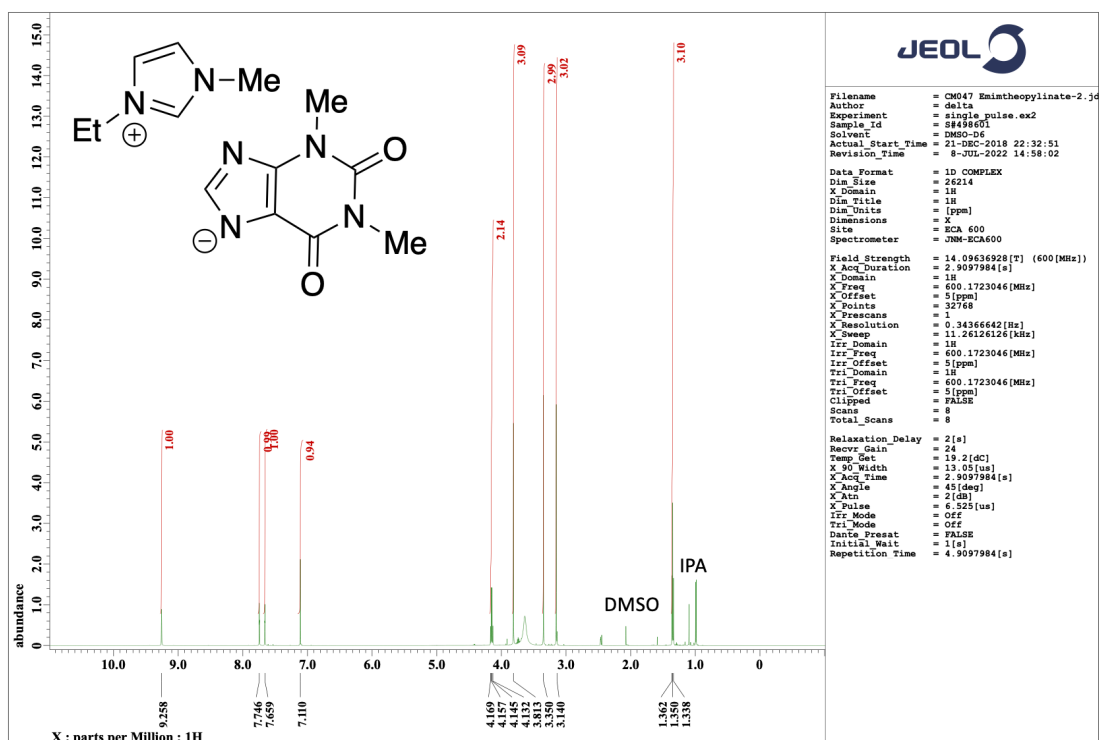
Prepared from potassium hydroxide (85%, 4.94 g, 68.2 mmol), EmimCl (10.0 g, 68.2 mmol), 4-hydroxypyridine (6.49g, 68.2 mmol) and 2-propanol (150 mL). Off-white solid (hygroscopic).  $^1H$  NMR (600 MHz, DMSO- $d_6$ )  $\delta$ : 9.27 (s, 1H), 7.80 (s, 1H), 7.71 (s, 1H), 7.52 (d,  $J = 6.6$  Hz, 2H), 5.84 (d,  $J = 6.0$  Hz, 2H), 4.18 (q,  $J = 7.2$  Hz, 2H), 3.84 (s, 3H), 1.41 (t,  $J = 7.2$  Hz, 3H).  $^{13}C$  NMR (150 MHz, DMSO- $d_6$ )  $\delta$ : 175.49, 149.26, 137.12, 124.10, 122.53, 116.70, 44.62, 36.18, 15.66. IR (ATR,  $cm^{-1}$ ) 2973, 1583, 1489. HRMS (FAB) calcd for  $C_6H_{11}N_2$  ( $[M]^+$ ) 111.0917, found: 111.0921 (cation), and  $C_5H_4NO$  ( $[M]^-$ ) 94.0298, found: 94.0295 (anion).



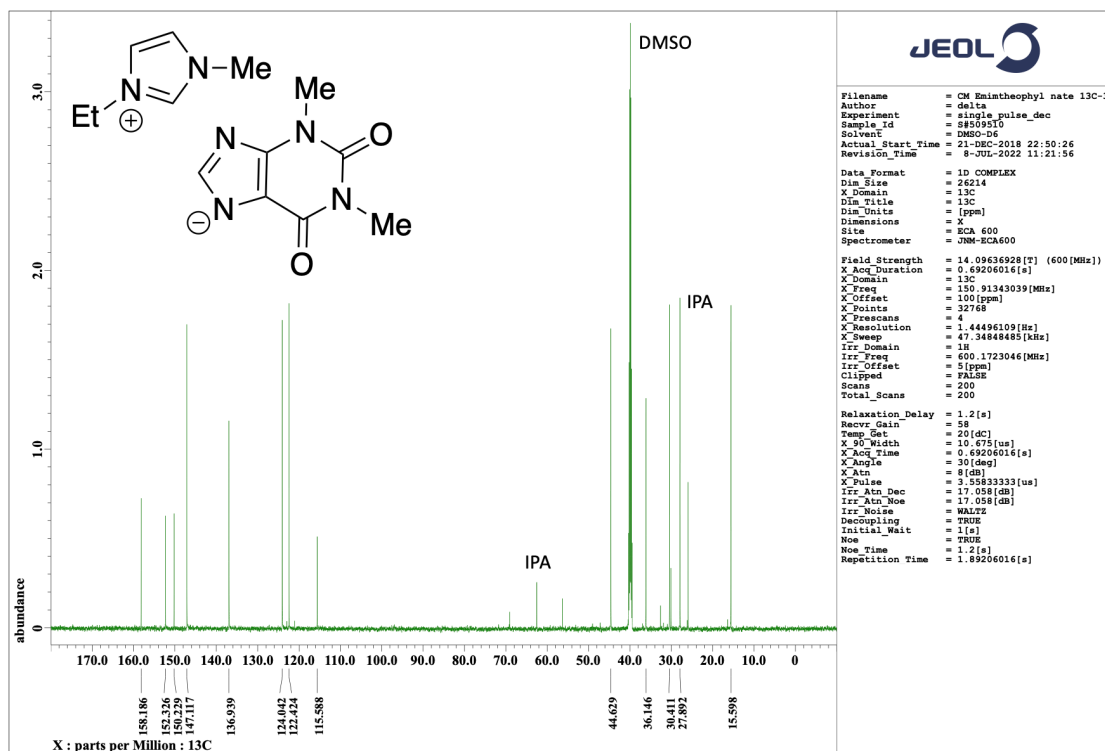
**Figure S1.** <sup>1</sup>H NMR spectrum of 1-ethyl-3-methylimidazolium 4,6-dimethyl-2-hydroxypyrimidinolate (Emim2OPm(diMe)) (3) in DMSO-*d*<sub>6</sub> at rt.



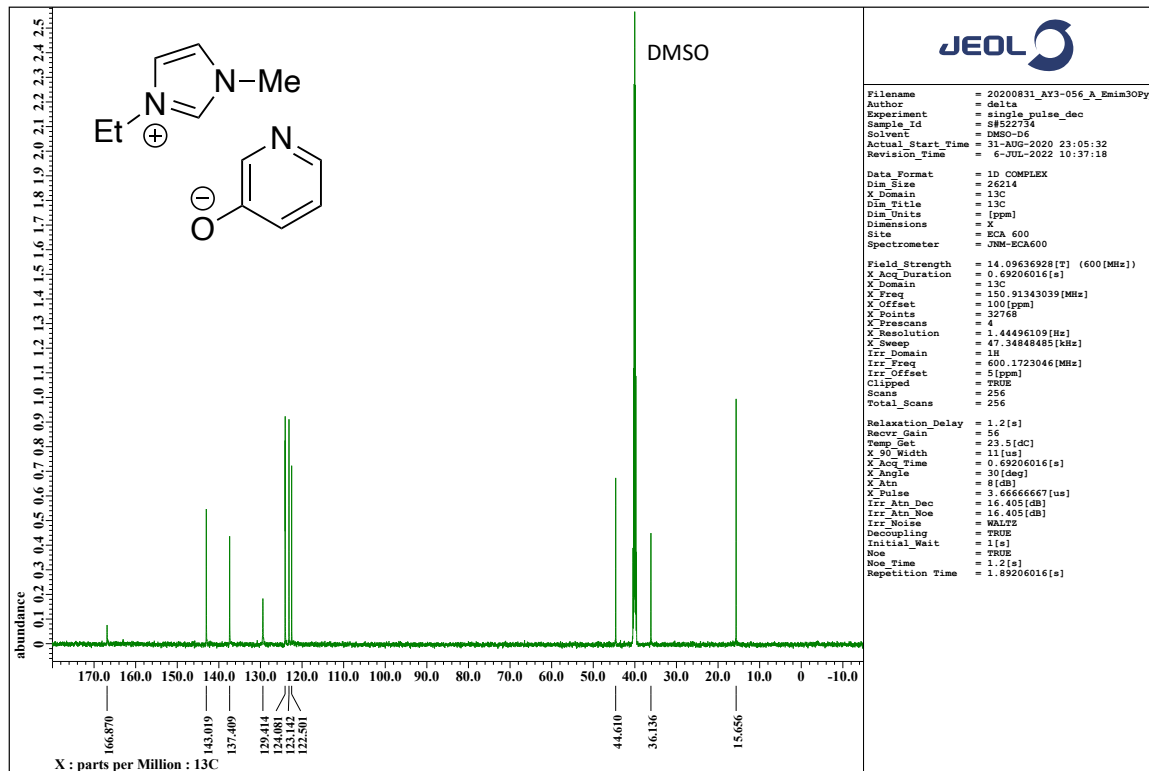
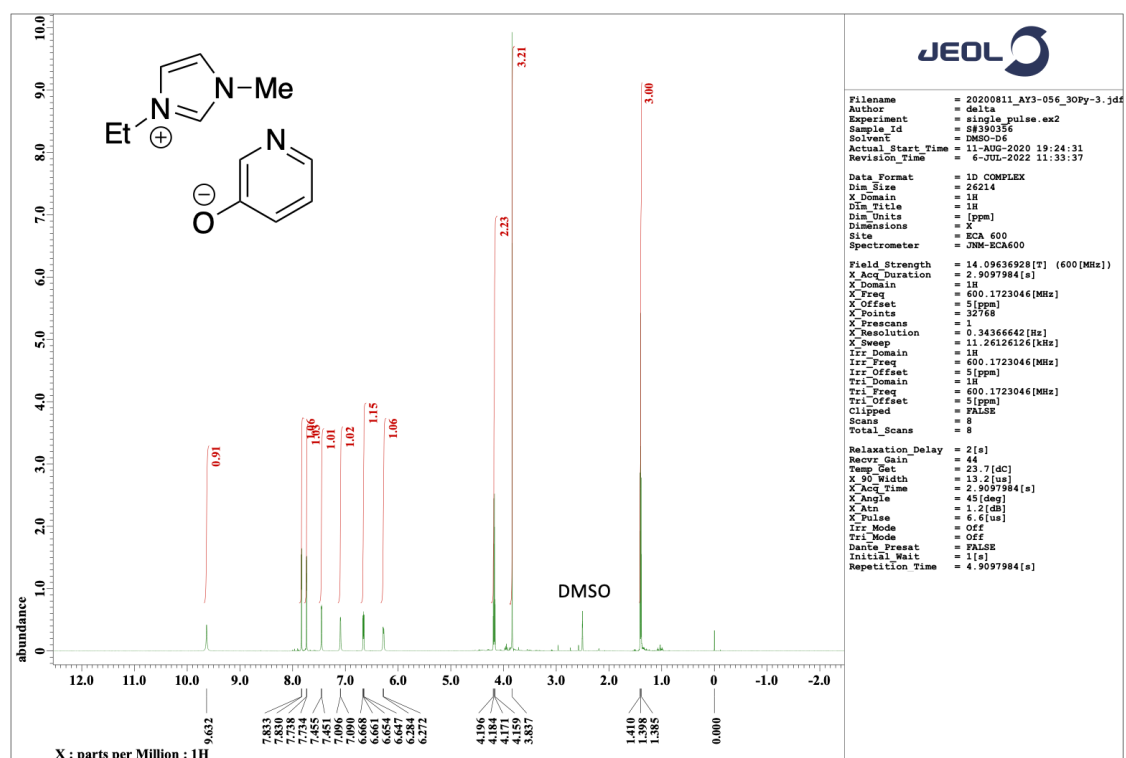
**Figure S2.** <sup>13</sup>C NMR spectrum of 1-ethyl-3-methylimidazolium 4,6-dimethyl-2-hydroxypyrimidinolate (Emim2OPm(diMe)) (3) in DMSO-*d*<sub>6</sub> at rt.

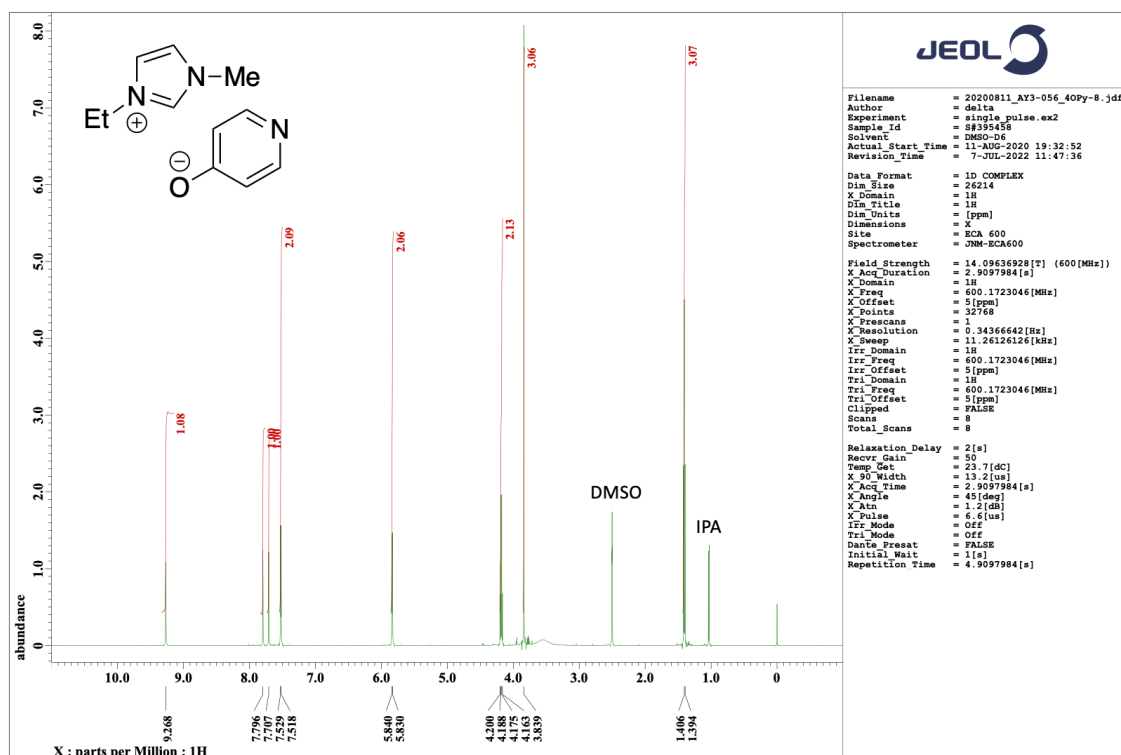


**Figure S3.** <sup>1</sup>H NMR spectrum of 1-ethyl-3-methylimidazolium theophyllinate (EmimTEO) (4) in DMSO-*d*<sub>6</sub> at rt.

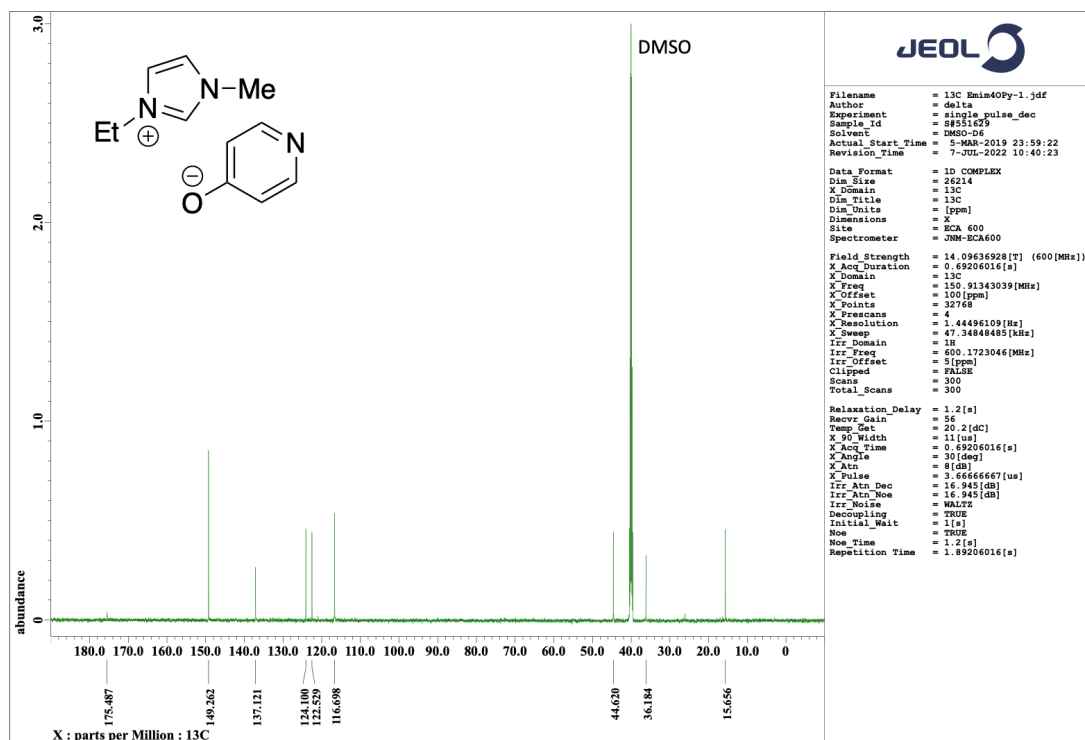


**Figure S4.** <sup>13</sup>C NMR spectrum of 1-ethyl-3-methylimidazolium theophyllinate (EmimTEO) (4) in DMSO-*d*<sub>6</sub> at rt.

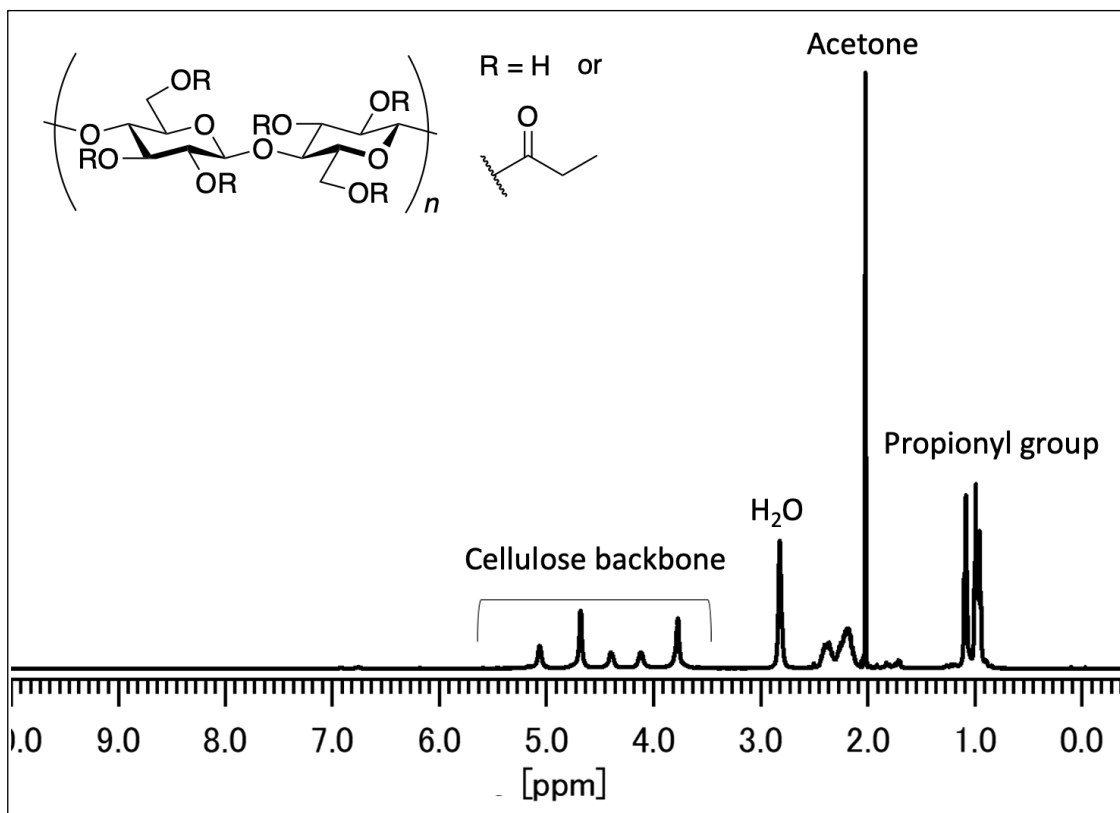




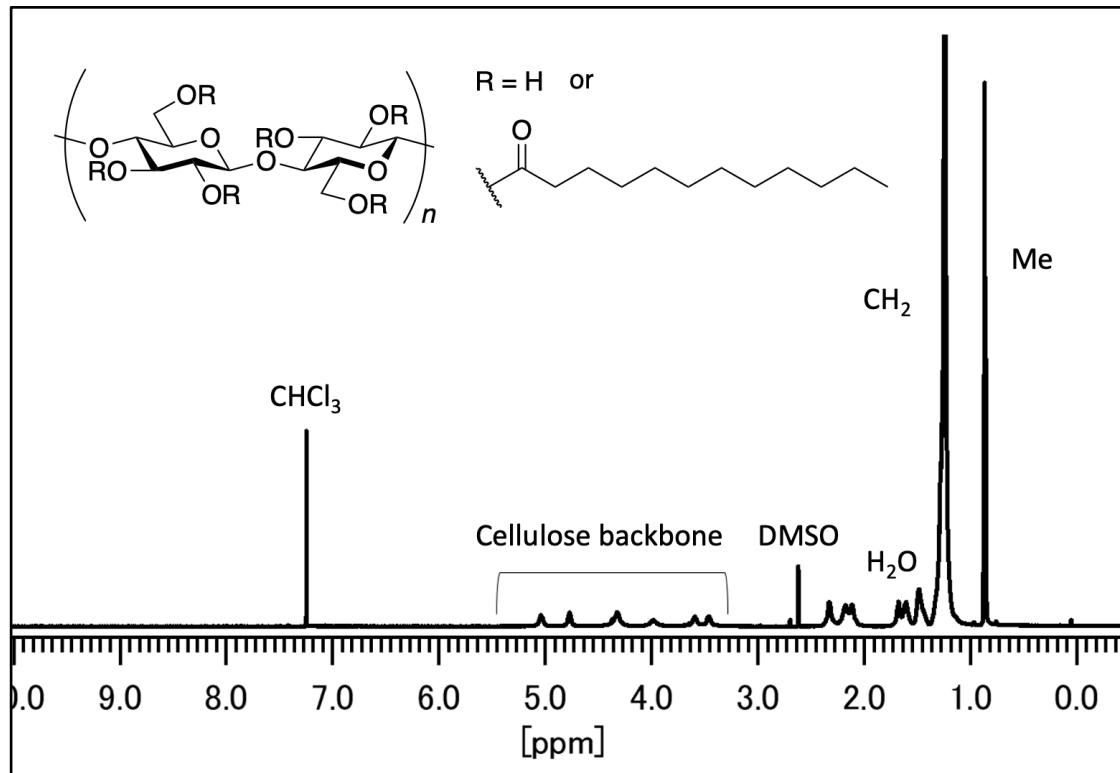
**Figure S7.** <sup>1</sup>H NMR spectrum of 1-ethyl-3-methylimidazolium 4-pyridinolates (Emim4OPy) (8) in DMSO-*d*<sub>6</sub> at rt.



**Figure S8.** <sup>13</sup>C NMR spectrum of 1-ethyl-3-methylimidazolium 4-pyridinolates (Emim4OPy) (8) in DMSO-*d*<sub>6</sub> at rt.

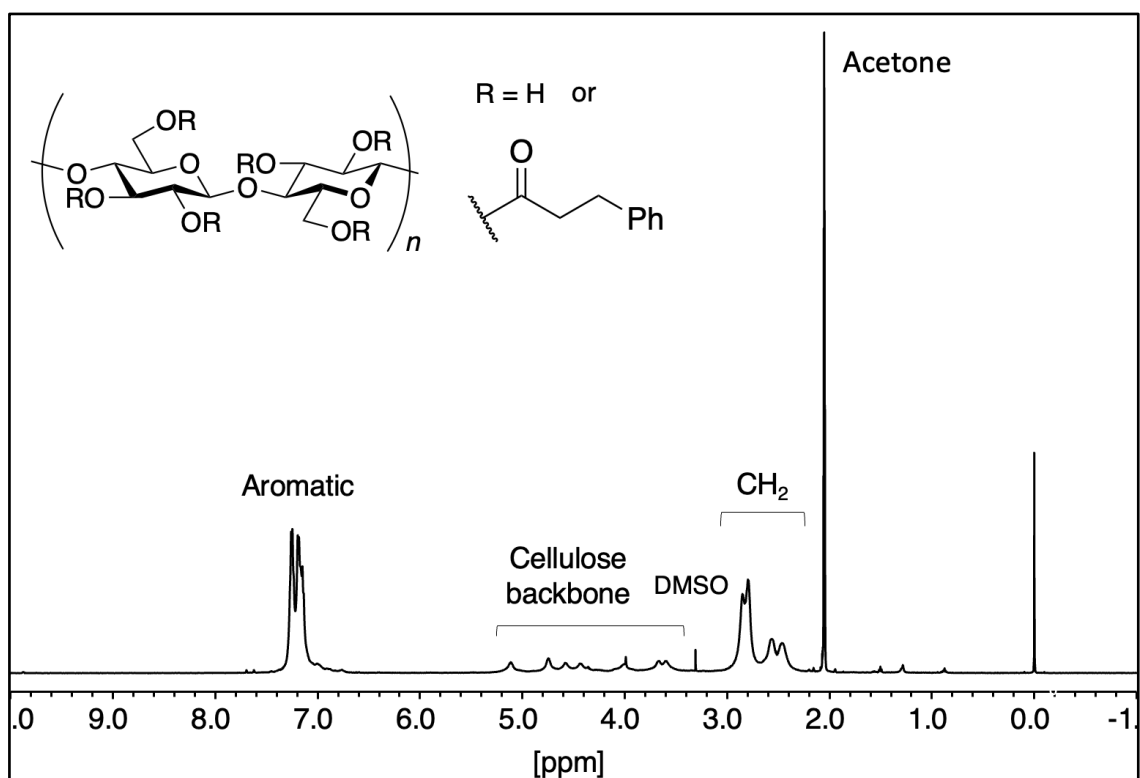


**Figure S9.**  $^1H$  NMR spectrum of cellulose propionate (DS = 2.85) in  $CDCl_3$  at rt (Table 3, entry 3).

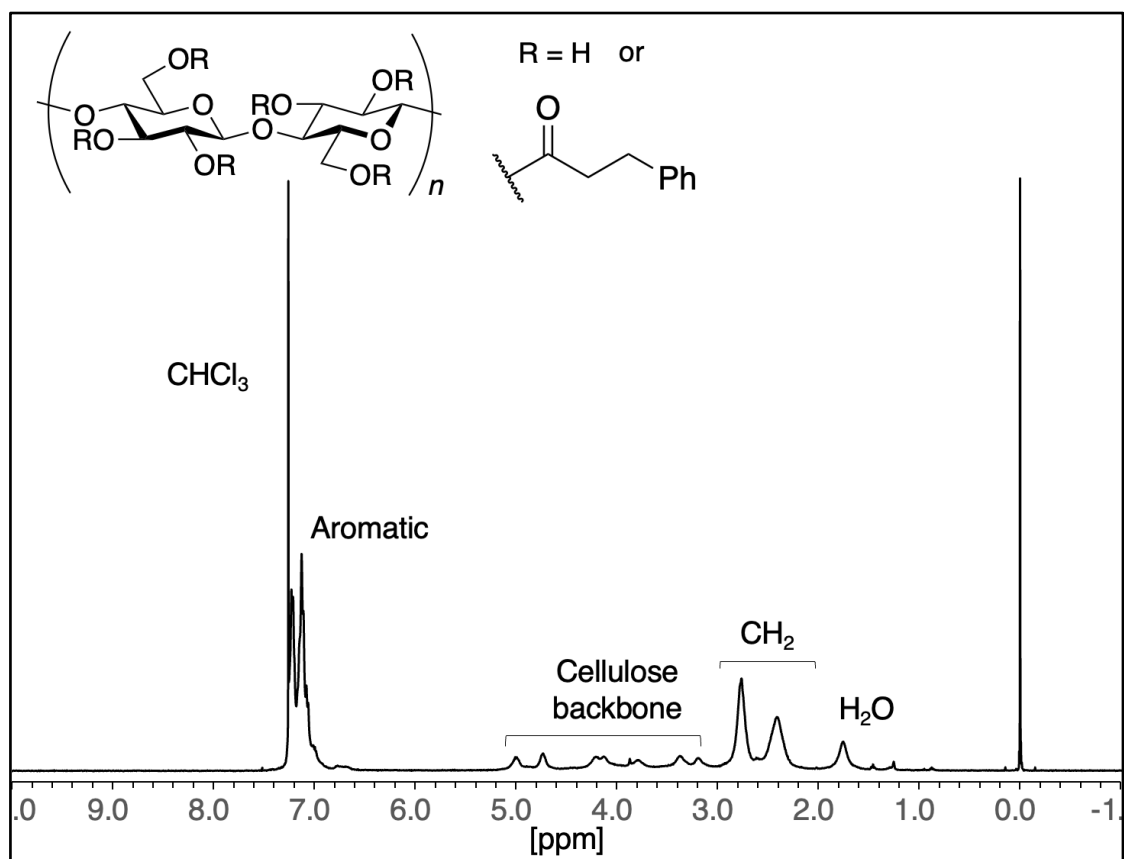


**Figure S10.**  $^1H$  NMR spectrum of cellulose laurate (DS = 2.96) in  $CDCl_3$  at rt (Table 3, entry 4).

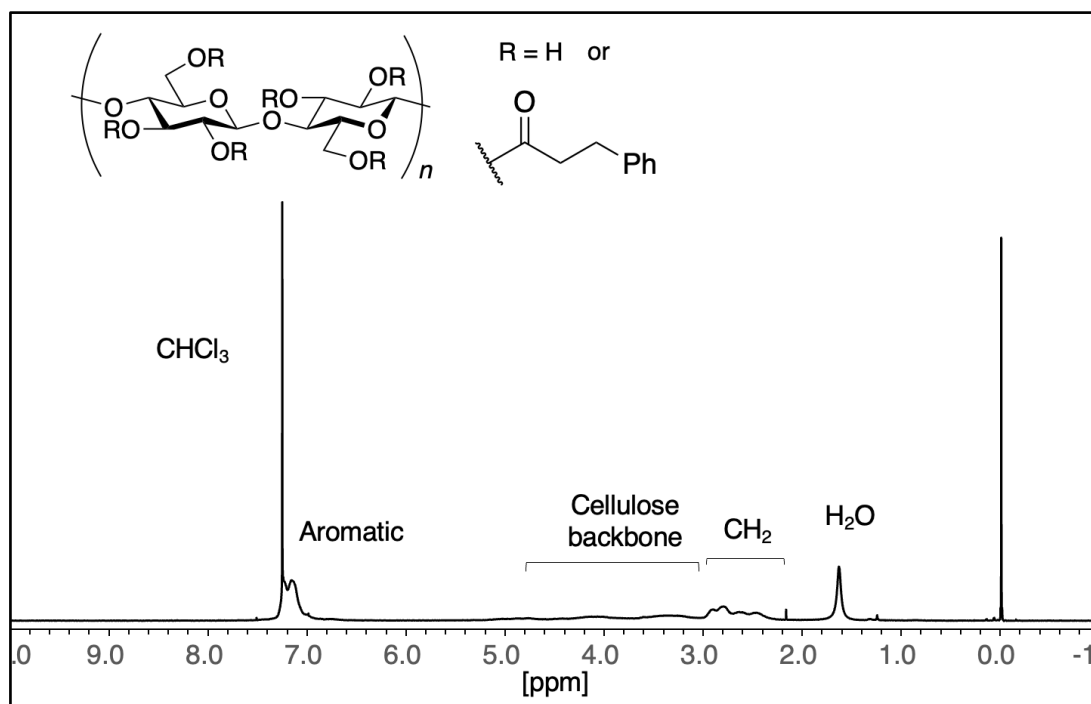




**Figure S11.**  $^1\text{H}$  NMR spectrum of cellulose phenylpropionate (DS = 2.78) synthesized from Emim2OPy **6** in acetone- $d_6$  at rt (Figure 5, blue, 24h).



**Figure S12.**  $^1\text{H}$  NMR spectrum of cellulose phenylpropionate (DS = 2.78) synthesized from Emim3OPy **7** in CDCl<sub>3</sub> at rt (Figure 5, orange, 24h).



**Figure S13.**  $^1\text{H}$  NMR spectrum of cellulose phenylpropionate (DS = 2.60) synthesized from Emim4OPy **8** in CDCl<sub>3</sub> at rt (Figure 5, gray, 24h).

**Table S1.** Solubility test (1.0 mg/mL) of resulting cellulose esters (Table 3) at room temperature.

	Toluene	CHCl <sub>3</sub>	THF	Acetone	DMF	DMSO	MeOH	H <sub>2</sub> O
Entry 1	○	○	○	○	○	○	X	X
Entry 3	X	○	○	○	○	○	X	X
Entry 4	○	○	○	○	○	○	X	X

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