Electronic Supplementary Information

Control of phase separation behaviour of ionic liquid catalysts with reactants/products toward synthesis of long-chain wax esters at moderate temperatures

Yuki Kohno,[a*] Takashi Makino[a] and Mitsuhiro Kanakubo[a]

[a]National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1, Nigatake, Miyagino-ku, Sendai 983-8551, Japan.

1. Determination of conversion (*X*) value

Method 1

First, the *X* value to produce cetyl palmitate from cetyl alcohol and palmitic acid was determined using IL**1** by ^{1}H NMR measurements.[1] The mixture containing cetyl alcohol, palmitic acid, and IL**1** with a molar ratio of 1/1/0.3 was stirred for 6h at 60 °C. After the reaction, the mixture was settled to obtain clear liquid-liquid phase separation between the ester product (upper) phase and ILC (bottom) phase. ^{1}H NMR spectroscopic measurements for both phases were carried out. From the ^{1}H NMR spectra, IL**1** was found to be selectively partitioned in the ILC phase (Fig. S16).

The amounts of unreacted cetyl alcohol and cetyl palmitate in the ILC phase ($n_{\mathrm{alc,IL}}$ and $n_{\mathrm{est,IL}}$) were then calculated from eqns. S1 and S2, where $I_{\mathrm{alc,IL}}$, $I_{\mathrm{est,IL}}$, and I_{IL} were the integrated intensity of protons on α-carbon of cetyl alcohol in the ILC phase (A in Fig. S16, left), that of the corresponding protons of cetyl palmitate (C in Fig. S16, left), and that of IL**1** (IL**1** in Fig. S16, left), respectively.

$$n_{alc,\ IL} = \frac{I_{alc,IL}}{I_{IL}} \times n_{IL} \#(S1)$$

$$n_{est,\ IL} = \frac{I_{est,IL}}{I_{IL}} \times n_{IL} \#(S2)$$

The molar ratio of unreacted cetyl alcohol and cetyl palmitate in the product phase ($n_{\mathrm{alc,prod}}/n_{\mathrm{est,prod}}$) was calculated from eqn. S3, where $I_{\mathrm{alc,prod}}$ and $I_{\mathrm{est,prod}}$ respectively denote the integrated intensity of protons on α-carbon of cetyl alcohol in the product phase (A in Fig. S16, right) and that of the corresponding protons of cetyl palmitate (C in Fig. S16, right).

$$\frac{n_{est,prod}}{n_{alc,prod}}=\frac{I_{est,prod}}{I_{alc,prod}}\#(S3)$$

The initial amount of cetyl alcohol ($n_{\mathrm{alc,0}}$) is equal to the total amount of cetyl palmitate and unreacted cetyl alcohol in both phases. Then, we can derive eqn. S4. By substituting eqns. S1, S2, and S3 into eqn. S4, both $n_{\mathrm{est,prod}}$ and $n_{\mathrm{est,IL}}$ were calculated. The conversion (X) value was calculated by eqn. S5 to be 91.6 ± 0.4.

$$n_{alc,0}=n_{est,prod}+n_{est,IL}+n_{alc,prod}+n_{alc,IL}\#(S4)$$

$$X\ (\%)=\frac{n_{est,prod}+n_{est,IL}}{n_{alc,0}}\times 100\#(S5)$$

Method 2

The above method requires two NMR measurements for both separated phases (*i.e.*, product phase and ILC phase) to determine the X value quantitatively. When we can make a homogeneous solution by adding a suitable cosolvent in the reaction mixture, it is possible to determine the X value from a single NMR measurement of the homogeneous solution. Toluene was used to obtain the homogeneous solution, which was analysed by ^{1}H NMR spectroscopy.

In the case of the homogeneous solution, eqn. S5 can be simplified as eqn. S6. Then, the X value was obtained to be 92.5±1.6 for cetyl palmitate from the integrated intensity (I_{alc}) of protons on α-carbon of unreacted cetyl alcohol and that (I_{est}) of the corresponding protons of cetyl palmitate.

$$X\ (\%)=\frac{n_{est}}{n_{alc,0}}\times 100=\frac{I_{est}}{I_{est}+I_{alc}}\times 100\#(S6)$$

Both X values calculated by the method 1 and 2 were consistent within the experimental errors. In the present study, the method 2 was applied for all other experiments. For quantitative NMR measurements, the T_1 values were measured for all components used for calculating X values (Table S1). The delay time for ^{1}H NMR measurements was set as 40 seconds, longer than $5T_1$. The pulse width, number of scan time, spectral width, digital resolution, and temperature were 90° (~14.8 μs), 16, ~20 ppm (~8000 Hz), 0.12 Hz, and 25 °C, respectively. The average *X* value with the standard deviation was obtained by the multiple experiments, at least three times.

2. Solubilities of cetyl alcohol and palmitic acid with IL2

In order to analyse the solubilities of the reactants in IL**2**, each of cetyl alcohol or palmitic acid was mixed with IL**2** with a molar ratio of 1/0.3. The resulting mixture was heated up to melt the reactant, and stirred for 30 minutes. As for cetyl alcohol, the clear liquid-liquid phase separation was seen at 60 °C. On the other hand, palmitic acid remained solid state at 60 °C, and the temperature was then raised at 70 °C to obtain the clear liquid-liquid biphase. The separated phases were analysed by ^{1}H NMR. The ^{1}H NMR spectra were shown in Figs. S16 to S21. It was confirmed that both reactants were not dissolved in the IL**2** phase.

3. Partition of water between ester and ILC phases

To quantify the partition of water between ester and ILC phases, equimolar amounts of cetyl palmitate (10 mmol) and water (10 mmol) were added to IL**1** or IL**2** (3 mmol). After stirring and settling the mixture at 60 °C, both ILC and cetyl palmitate phases were analysed by ^{1}H NMR. The ^{1}H NMR spectra of cetyl palmitate phase did not clearly show the presence of ILCs (Figs. S24 and S25), whereas water peak could not be distinguished and possibly overlapped with the cetyl palmitate peaks. Instead, water peak was separately observed in ILCs phases, where methanol-d4 was used as solvent (Fig. S22 and S23). After subtracting the blank water existing in methanol-d4 and ILC, the amount of water in the ILC phase ($n_{\mathrm{water,IL}}$) to the total amount of added water ($n_{\mathrm{water,total}}$) was then calculated in % from the integral ratio per molecule ($I_{\mathrm{water,IL}}/I_{\mathrm{IL}}$) between water and ILC as eqn. S7. The amounts of water in IL**1** and IL**2** phases were calculated as 94.4±1.4 and 99.8±5.2%, respectively.

$$Amount\ of\ water\ in\ ILC\ phase\ (\%) = \frac{n_{water,IL}}{n_{water,total}} \times 100 = \frac{3I_{water,IL}}{10I_{IL}} \times 100\#(S7)$$

Supporting Figures and Tables

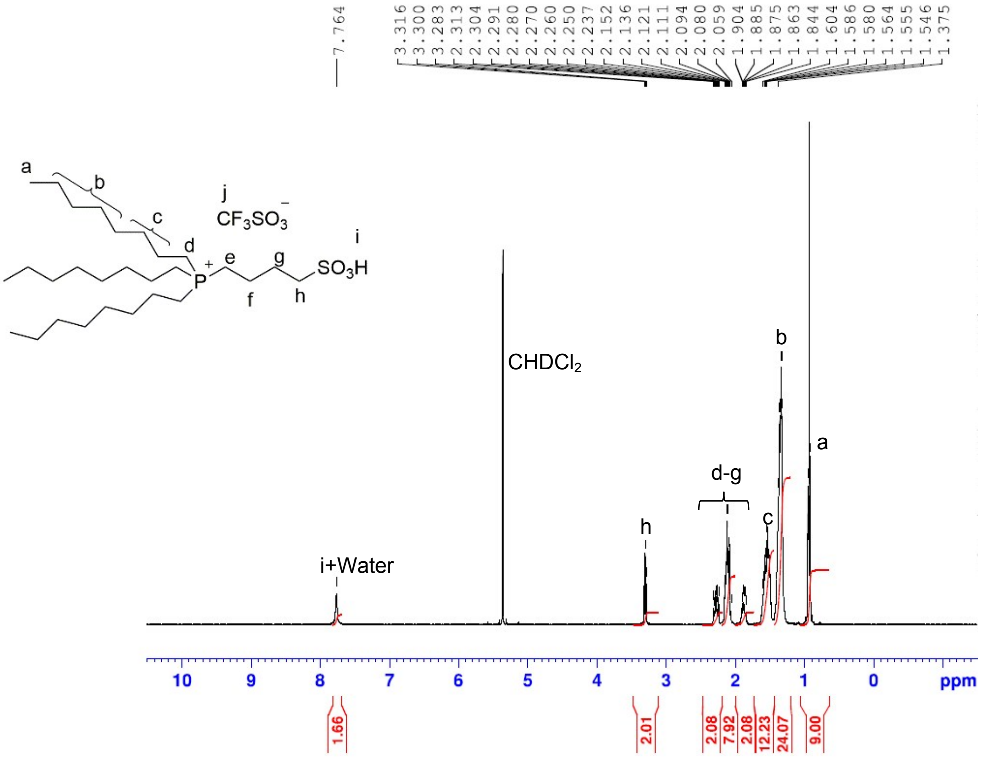

Fig. S1 ^1H NMR spectrum of IL**1** in CD_2Cl_2.

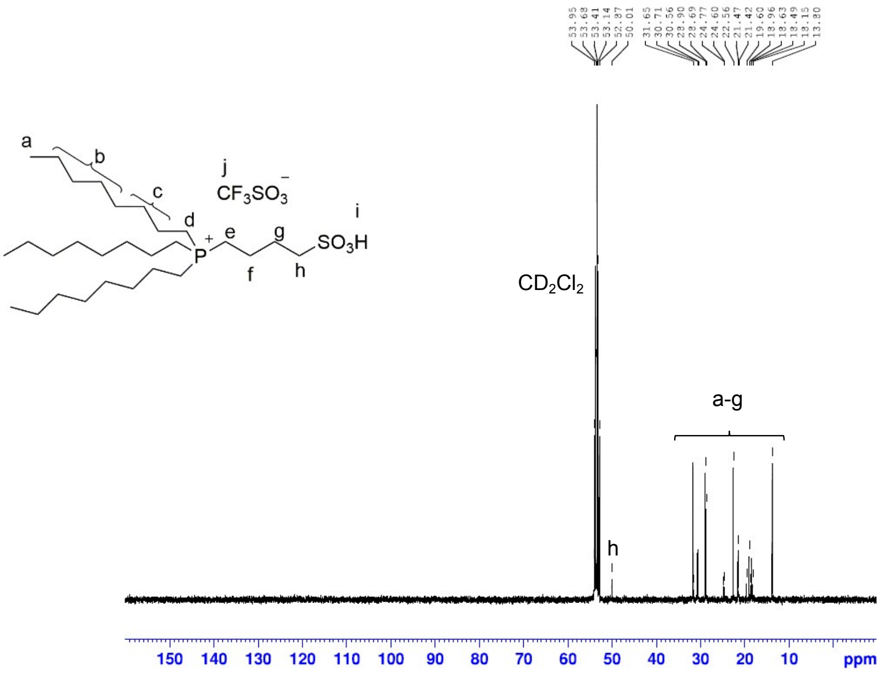

Fig. S2 ^{13}C NMR spectrum of IL**1** in CD_2Cl_2.

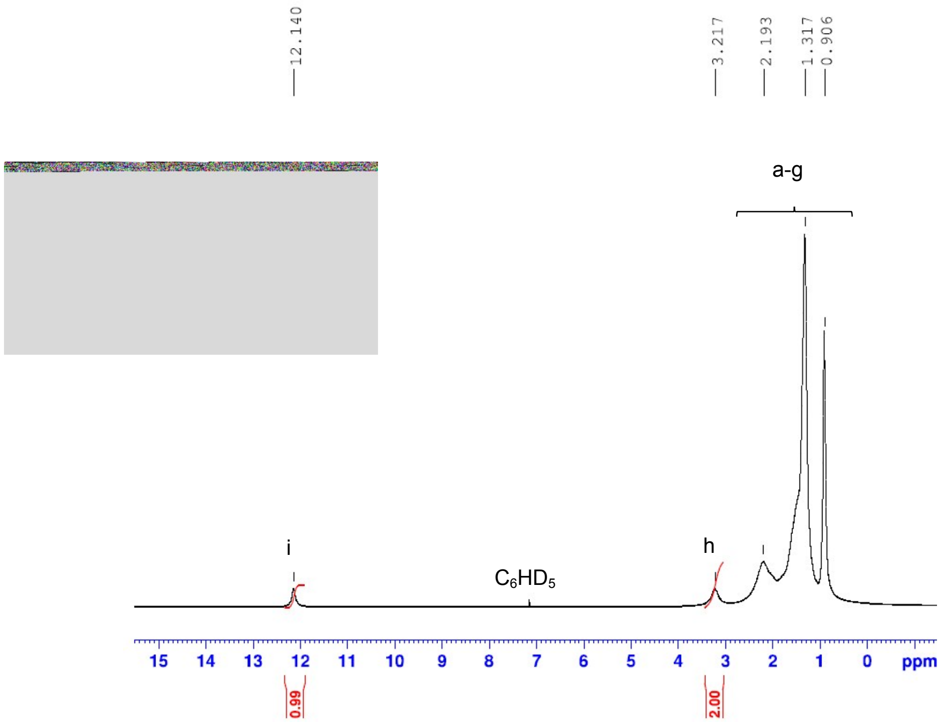

Fig. S3 ^{1}H NMR spectrum of neat IL**1** (C_6D_6 in capillary as an external standard).

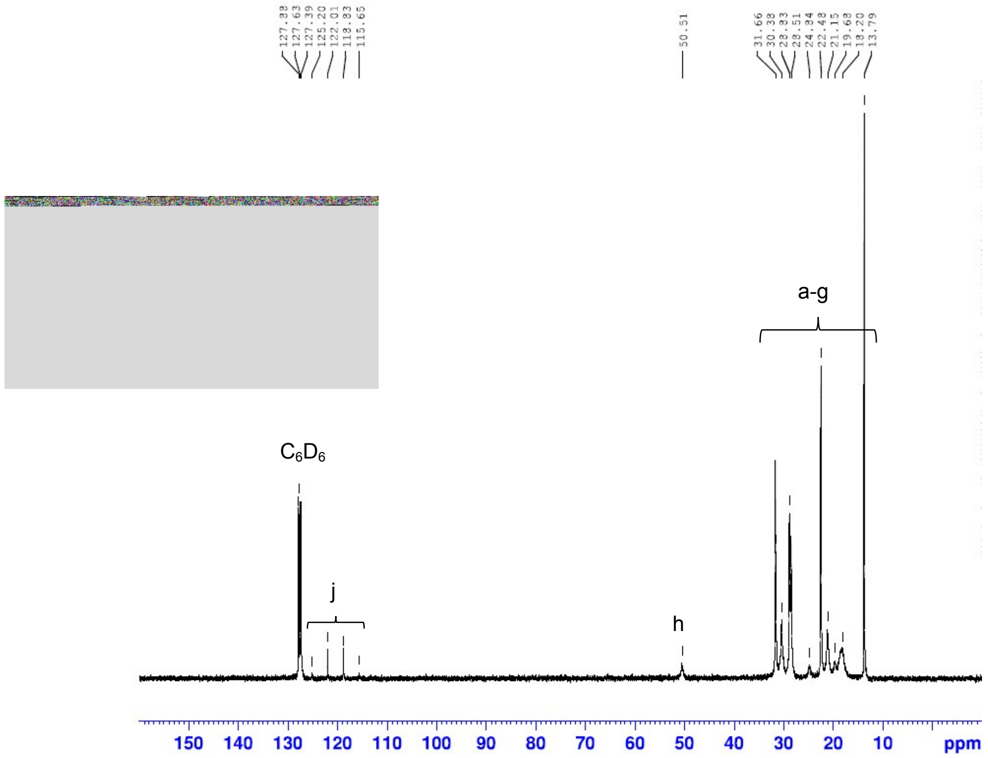

Fig. S4 ^{13}C NMR spectrum of neat IL**1** (C_6D_6 in capillary as an external standard).

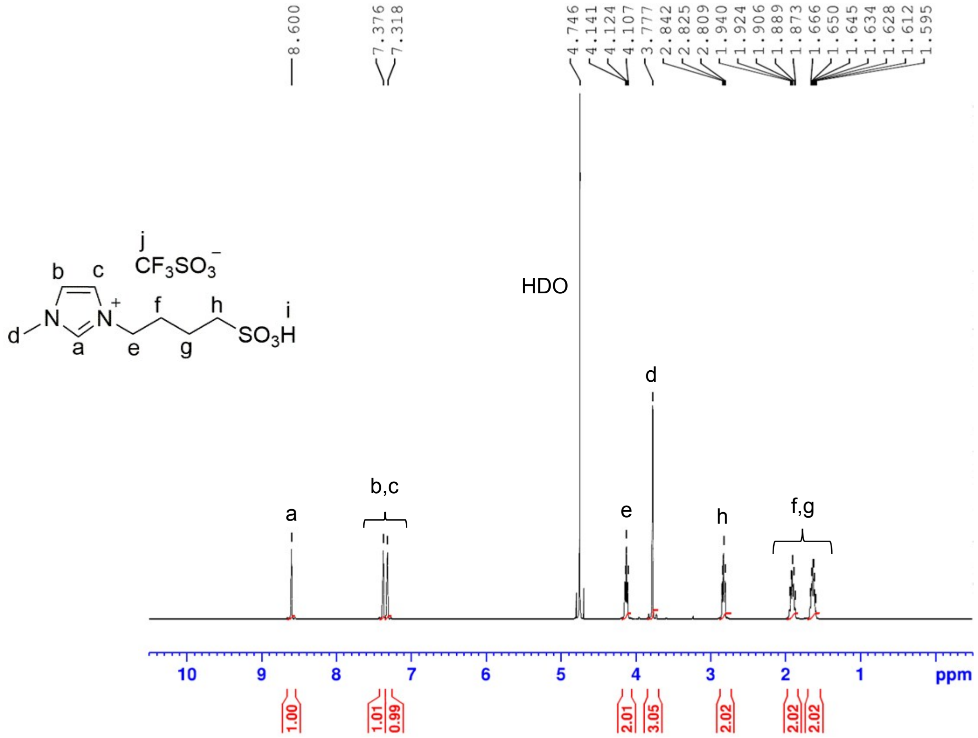

Fig. S5 ^1H NMR spectrum of IL**2** in D_2O.

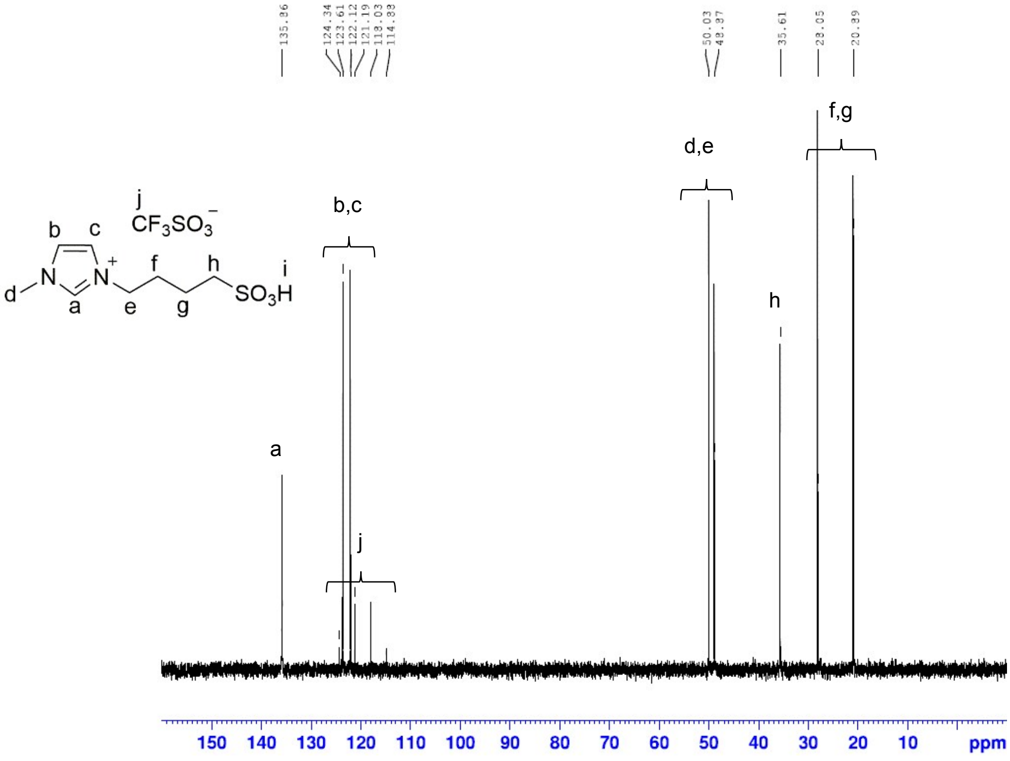

Fig. S6 ^{13}C NMR spectrum of IL**2** in D_2O.

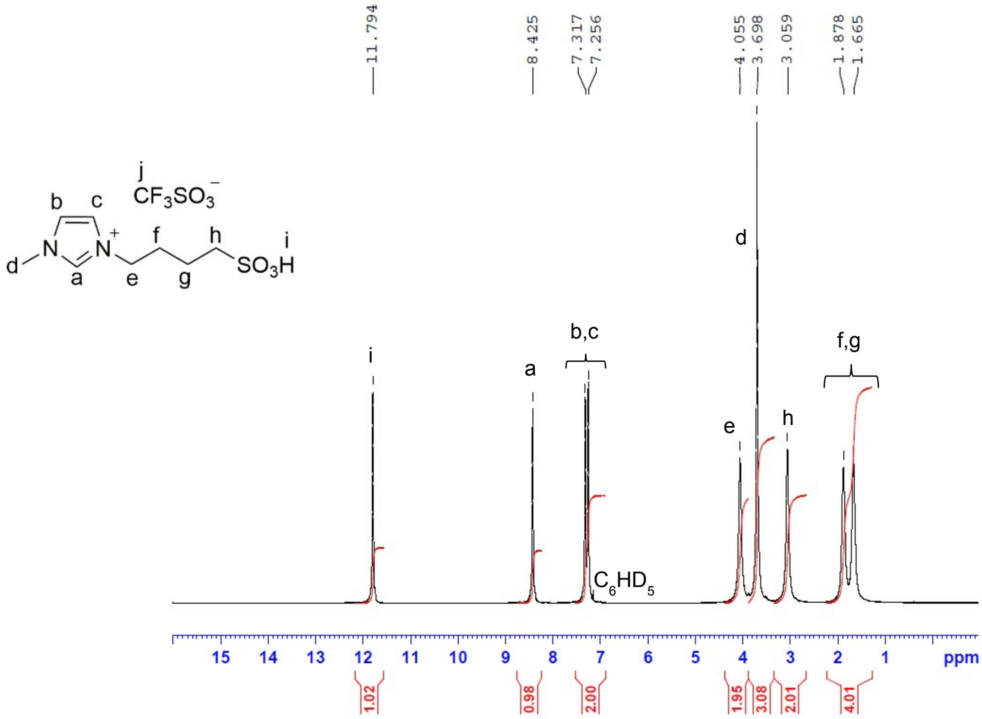

Fig. S7 ^1H NMR spectrum of neat IL**2** (C_6D_6 in capillary as an external standard).

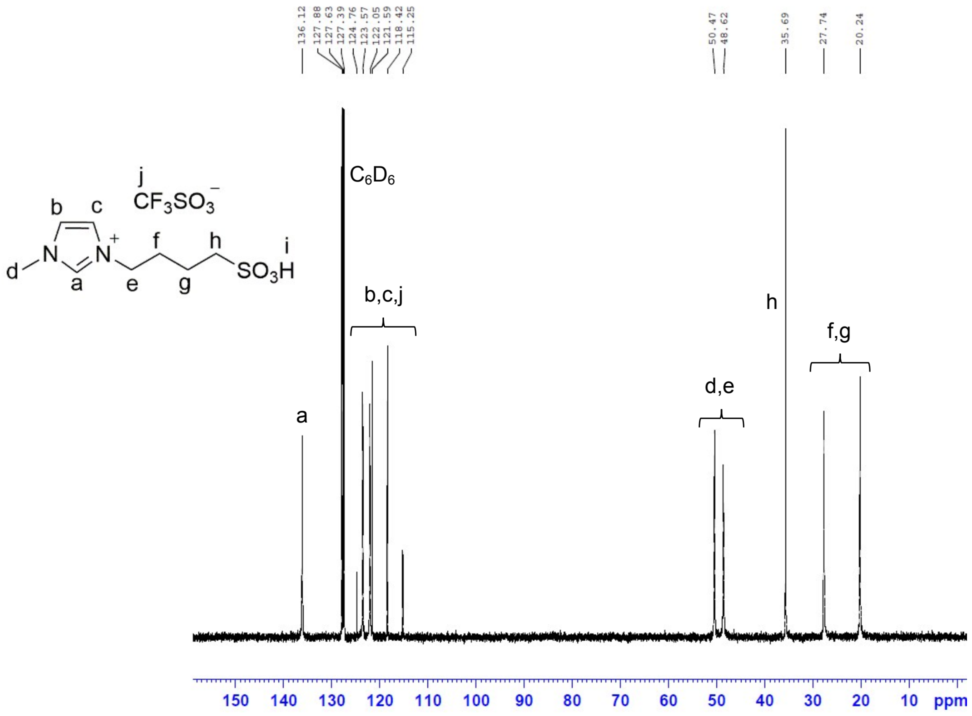

Fig. S8 ^1H NMR spectrum of neat IL**2** (C_6D_6 in capillary as an external standard).

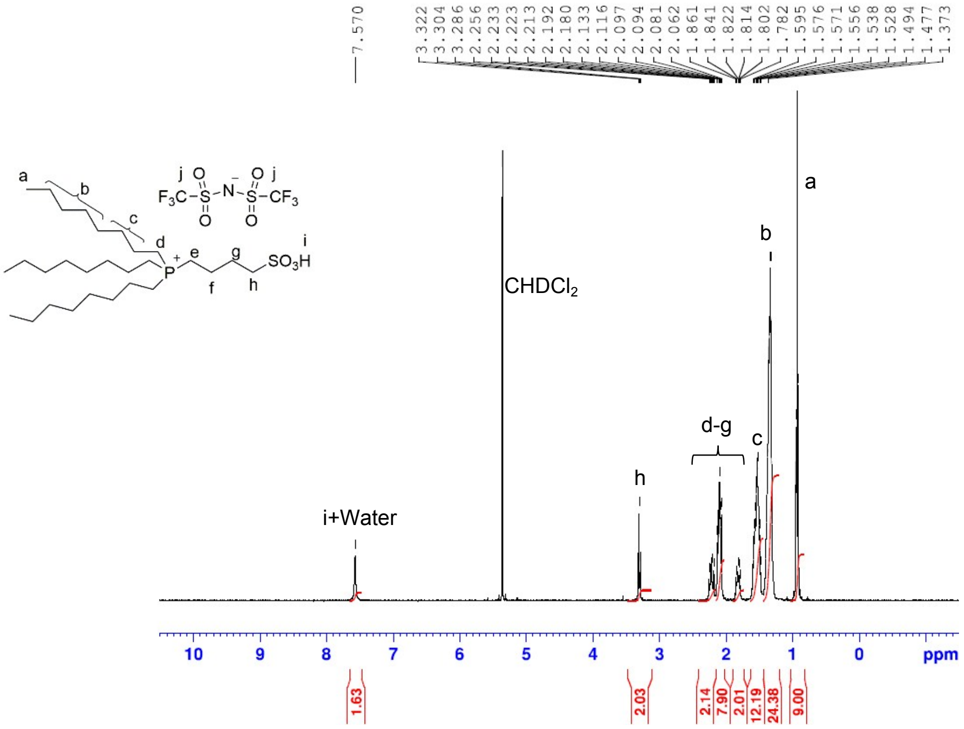

Fig. S9 ^{1}H NMR spectrum of IL**3** in CD_2Cl_2.

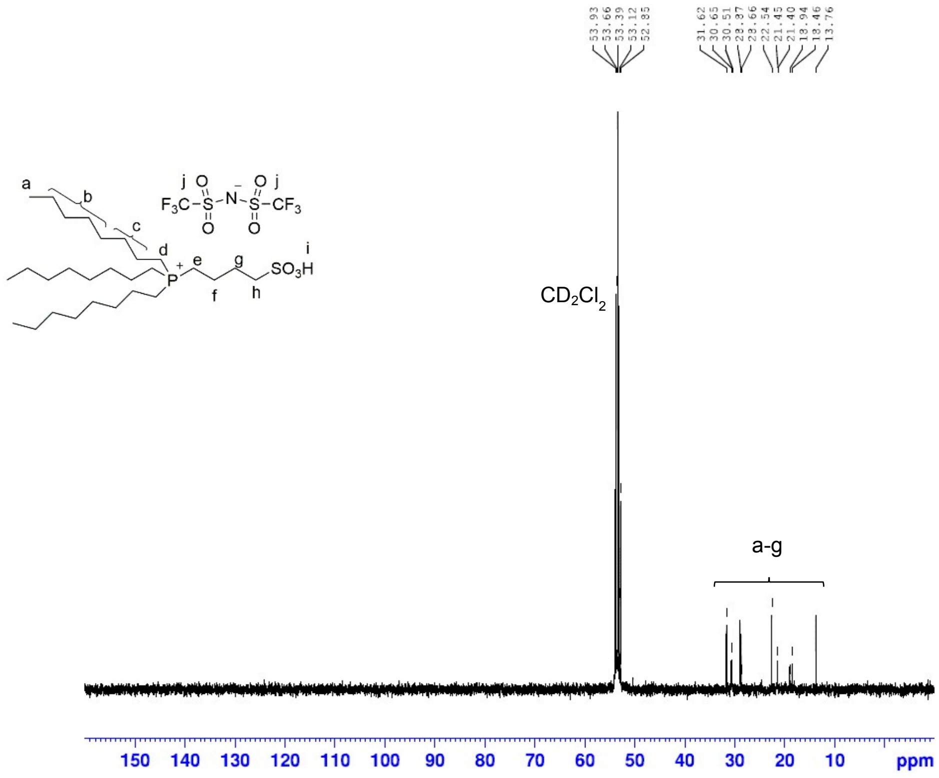

Fig. S10 ^{1}H NMR spectrum of IL**3** in CD_2Cl_2.

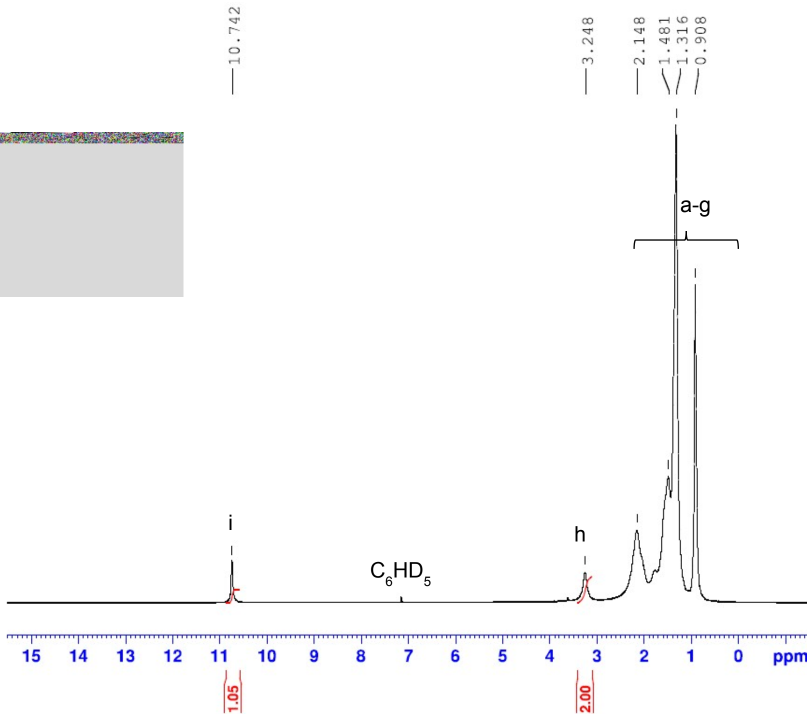

Fig. S11 ^{1}H NMR spectrum of neat IL**3** (C_6D_6 in capillary as an external standard).

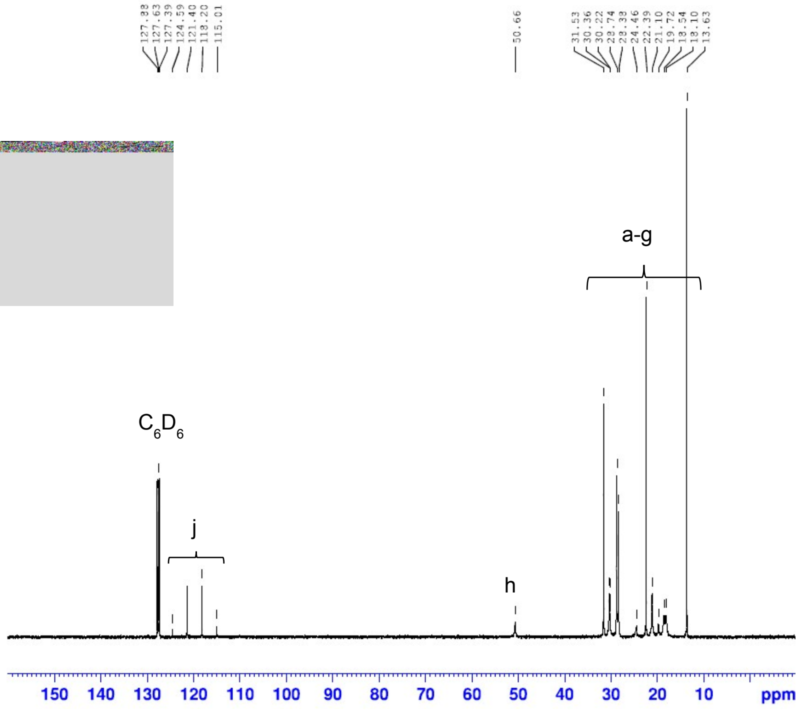

Fig. S12 ^{1}H NMR spectrum of neat IL**3** (C_6D_6 in capillary as an external standard).

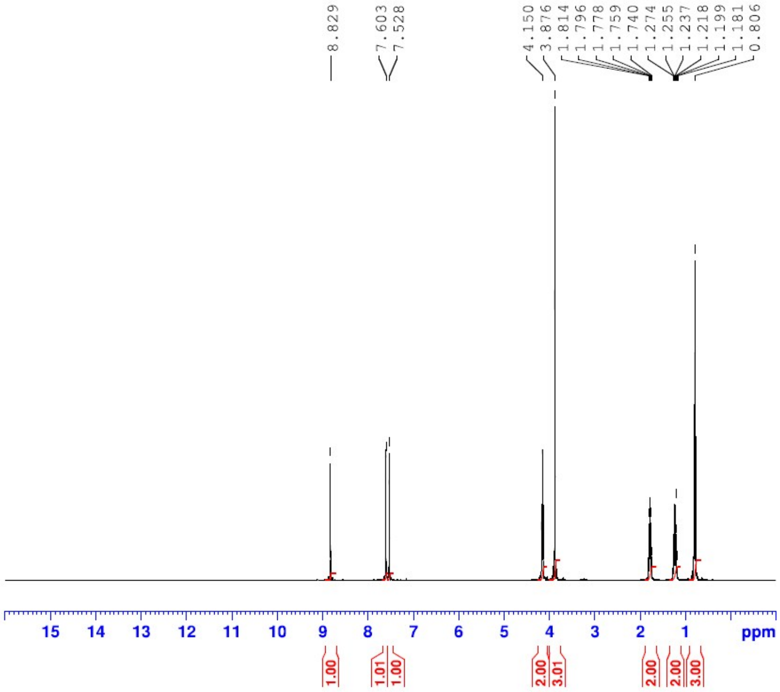

Fig. S13 ^{1}H NMR spectrum of neat [C_4mim][CF_3SO_3] (C_6D_6 in capillary as an external standard).

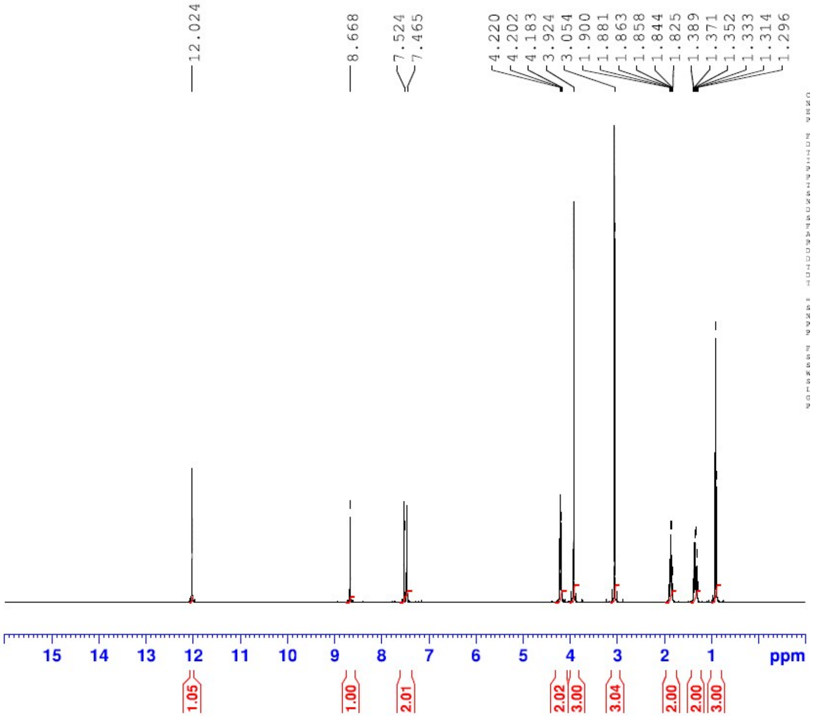

Fig. S14 ^{1}H NMR spectrum of equimolar mixture of CH_3SO_3H and [C_4mim][CF_3SO_3] (C_6D_6 in capillary as an external standard).

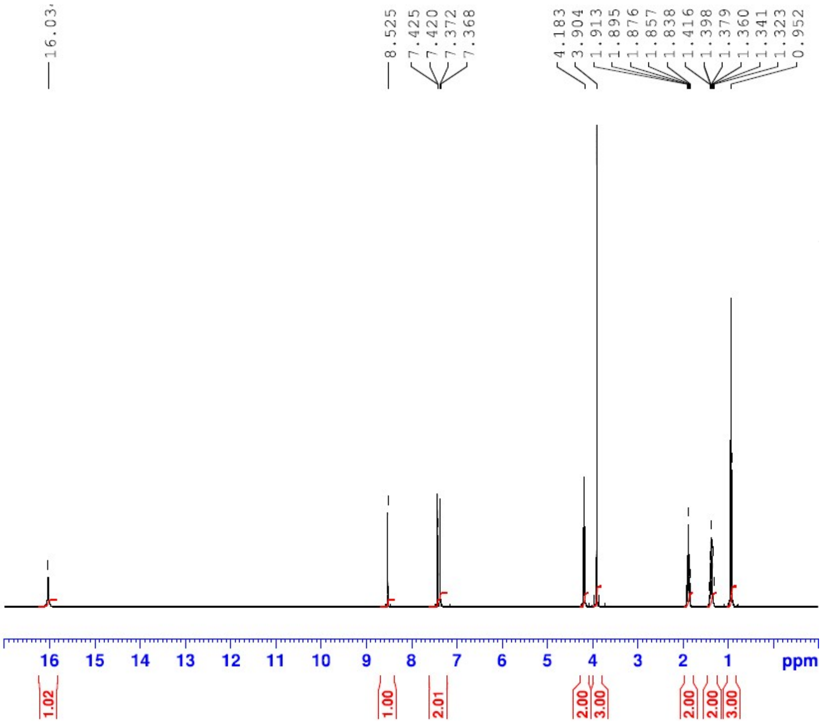

Fig. S15 ^{1}H NMR spectrum of equimolar mixture of CF_3SO_3H and $[C_4mim][CF_3SO_3]$ (C_6D_6 in capillary as an external standard).

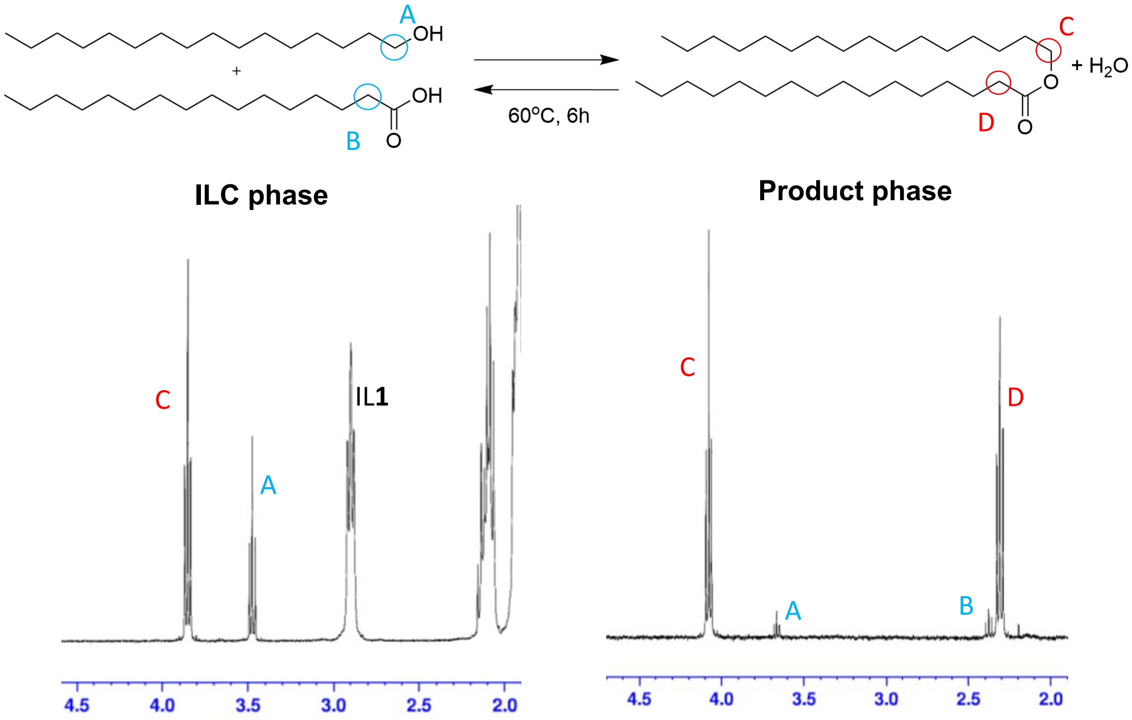

Fig. S16 ^{1}H NMR spectra of bottom (ILC) phase (left) and upper (ester product) phase (right) after the reaction of cetyl alcohol and palmitic acid using IL**1**.

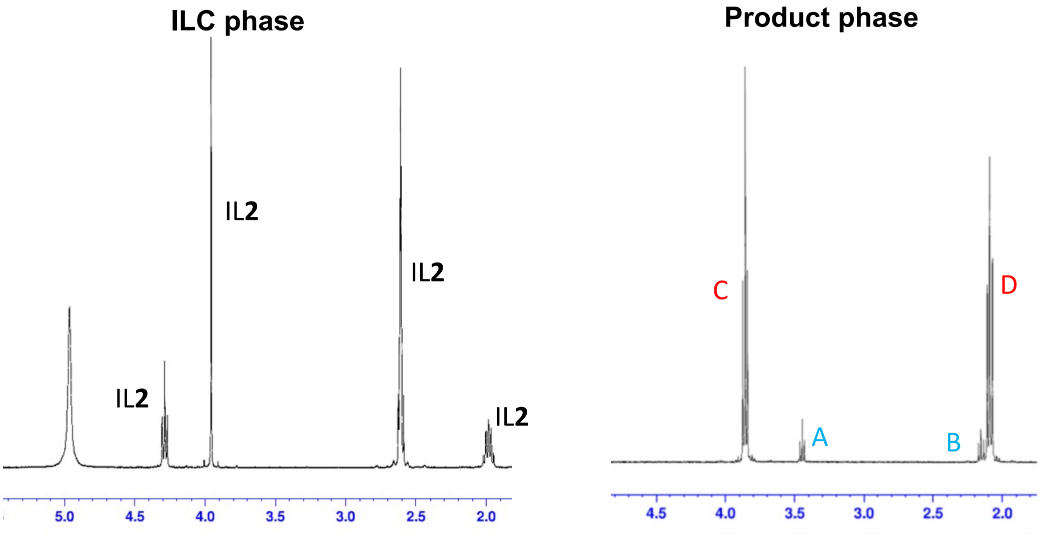

Fig. S17 ^{1}H NMR spectra of bottom (ILC) phase (left) and upper (ester product) phase (right) after the reaction of cetyl alcohol and palmitic acid using IL**2**.

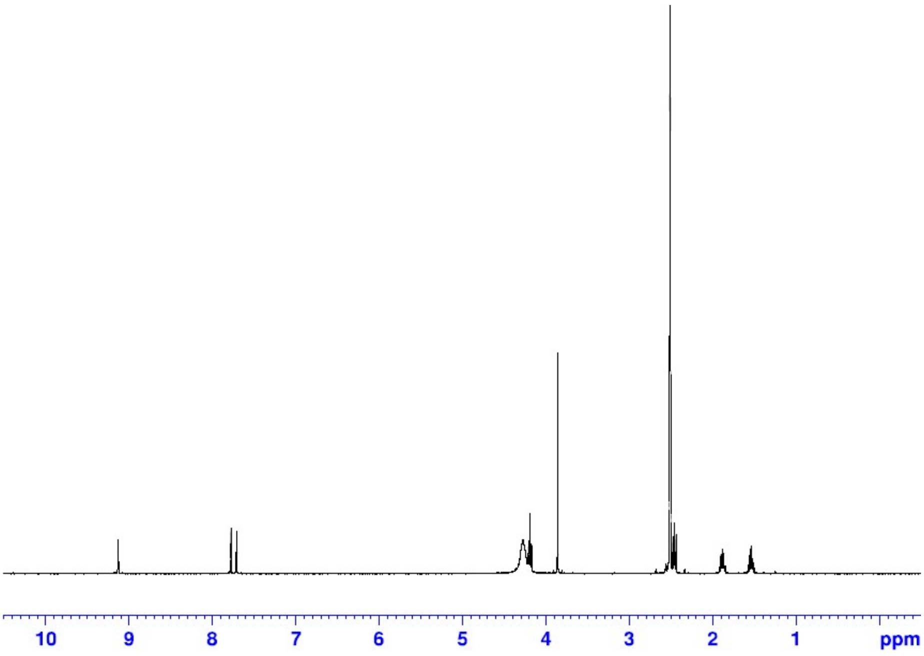

Fig. S18 ^{1}H NMR spectrum of bottom (ILC) phase for IL**2**/cetyl alcohol mixture. Cetyl alcohol was not observed in the bottom phase.

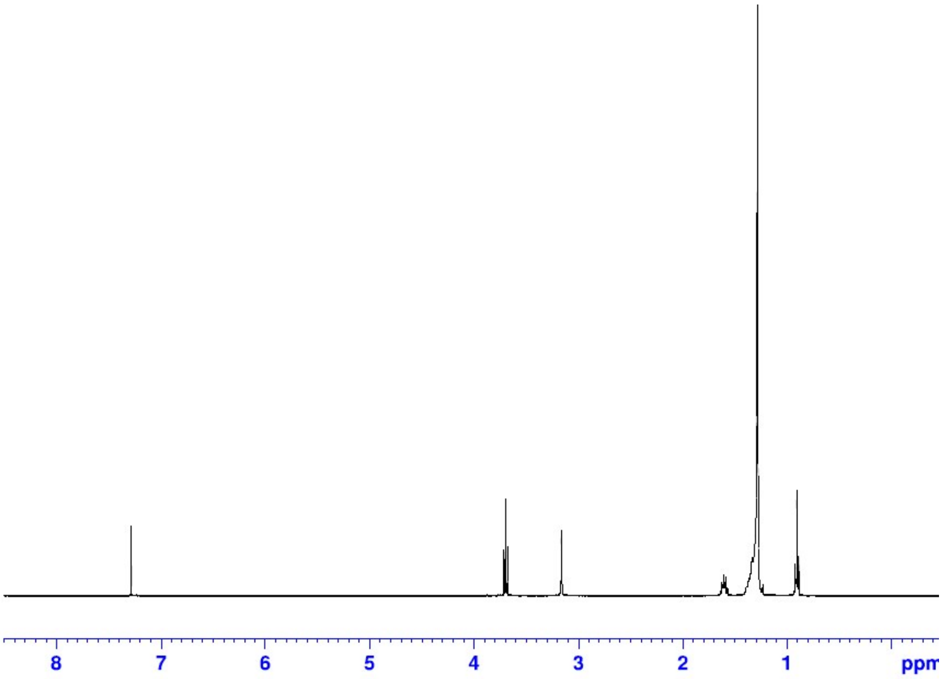

Fig. S19 ^{1}H NMR spectrum upper (ester product) phase for IL**2**/cetyl alcohol mixture. Cetyl alcohol was selectively observed in the upper phase.

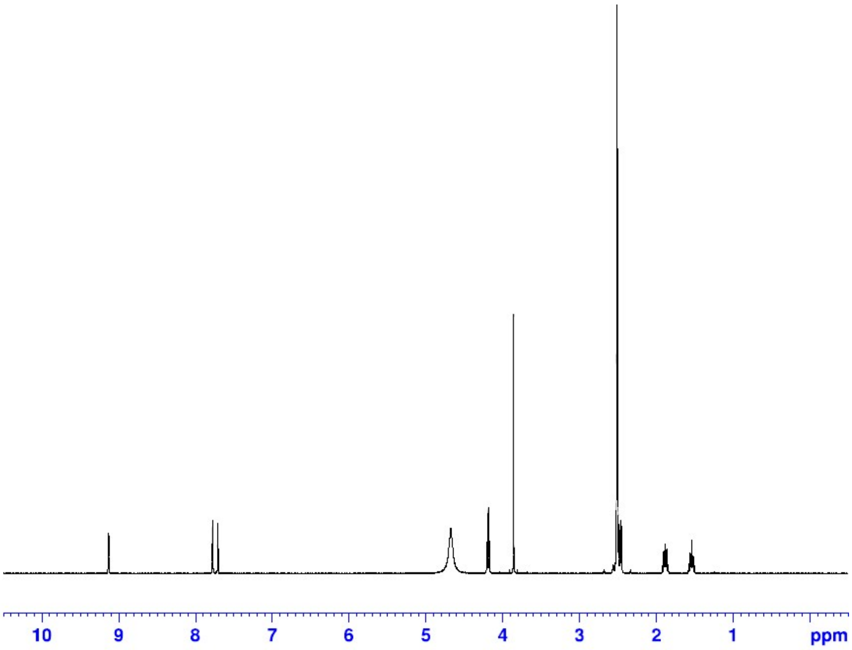

Fig. S20 ^{1}H NMR spectra of bottom (ILC) phase IL**2**/palmitic acid mixture. Palmitic acid was not observed in the bottom phase.

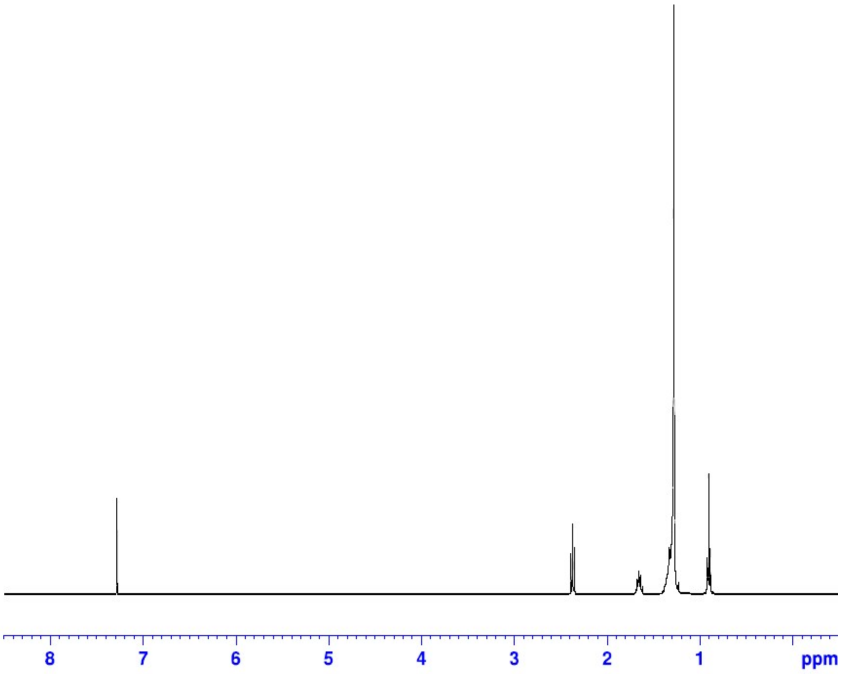

Fig. S21 ^{1}H NMR spectra of upper (ester product) phase for IL**2**/palmitic acid mixture. Palmitic acid was selectively observed in the upper phase.

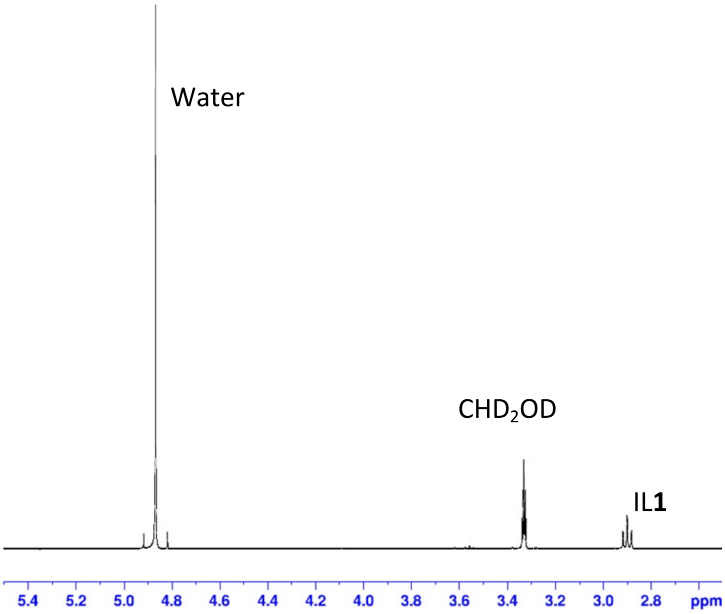

Fig. S22 ^{1}H NMR spectrum of IL**1** phase for cetyl palmitate/water/ILC mixtures (1/1/0.3 by mol).

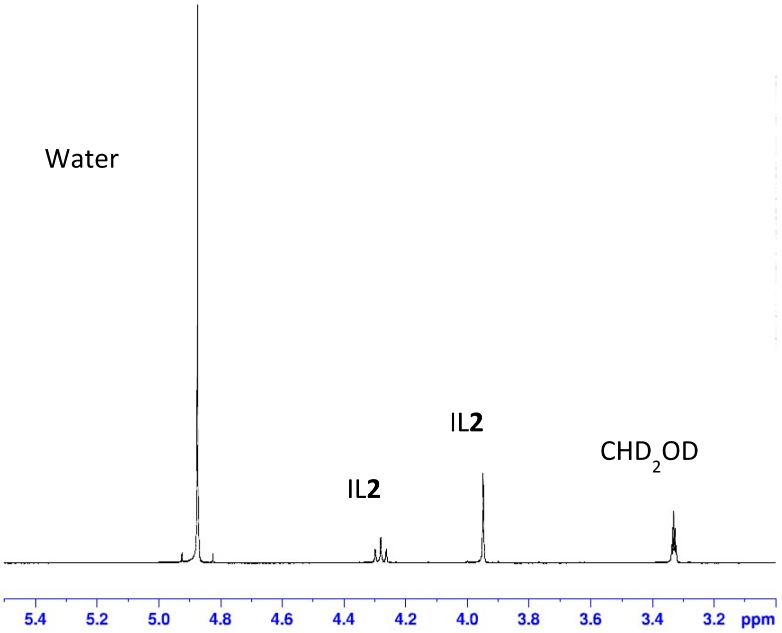

Fig. S23 ^{1}H NMR spectra of IL**2** phase for cetyl palmitate/water/ILC mixtures (1/1/0.3 by mol).

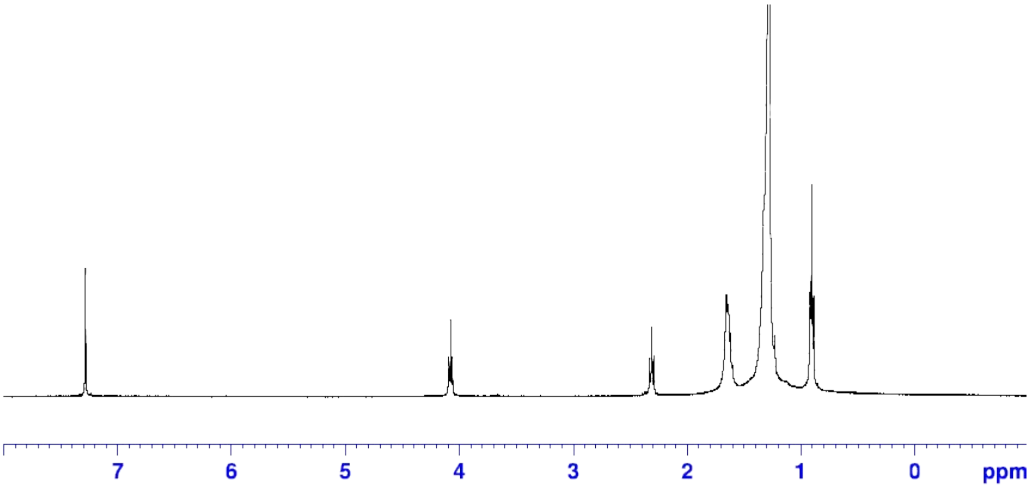

Fig. S24 ^{1}H NMR spectra of cetyl palmitate phase for cetyl palmitate/water/IL**1** mixture (1/1/0.3 by mol).

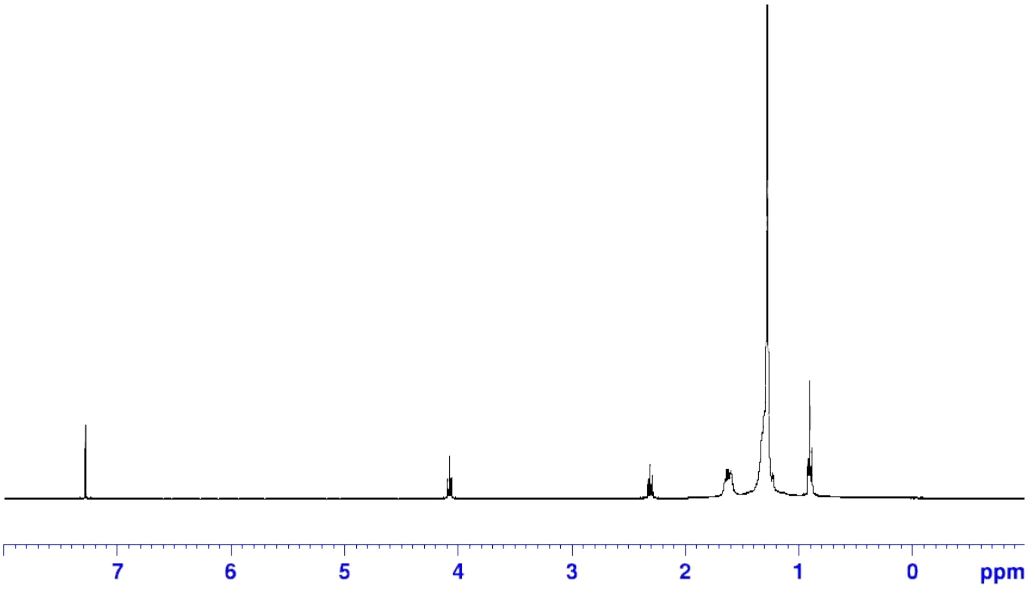

Fig. S25 ^{1}H NMR spectra of cetyl palmitate phase for cetyl palmitate/water/IL**2** mixture (1/1/0.3 by mol).

Fig. S26 Photographs of IL**1**/reactant/product mixture (left) and IL**2**/reactant/product mixture (right), both of which contain 50 wt% water.

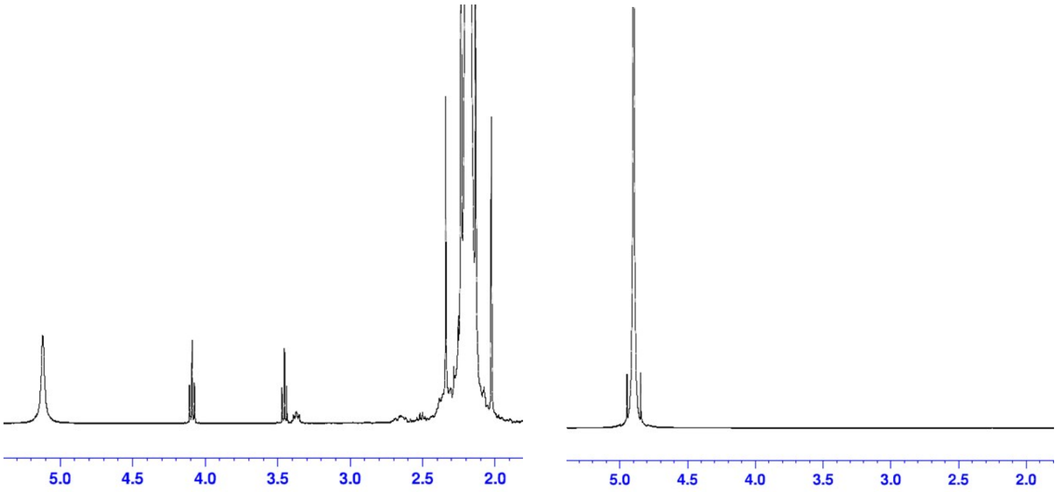

Fig. S27 ^{1}H NMR spectra of upper phase (left) and aqueous bottom phase (right) for IL**1**/reactant/product mixture containing 50 wt% water. The upper phase consists of reactants, products, and IL**1**, while no typical peak other than water was observed in the aqueous bottom phase.

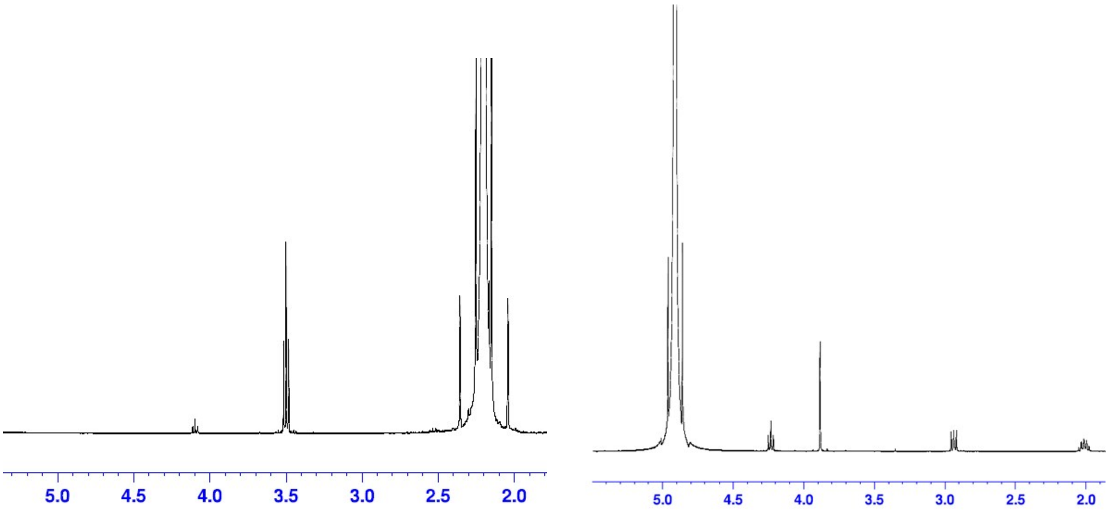

Fig. S28 ^{1}H NMR spectra of upper phase (left) and aqueous bottom phase (right) for IL**2**/reactant/product mixture containing 50 wt% water. The upper phase consists of reactants and products, while the aqueous bottom phase contains IL**2**.

Table S1 Relaxation time (T_1) of protons on α-carbon of alcohols and the corresponding esters, and Integrals of the protons after reacting alcohols and carboxylic acids in the presence of IL**1** for 6h at 60 °C (composition of reaction mixtures; alcohols (1 mmol), carboxylic acids (1 mmol), and IL**1** (0.3 mmol).

Compounds	T_1 value	Integrals
Ethanol	6.89	0.94±0.39
Octanol	3.51	0.31±0.05
Lauryl alcohol	2.57	0.17±0.03
Cetyl alcohol	2.11	0.16±0.04
Stearyl alcohol	2.58	0.16±0.02
Behenyl alcohol	2.34	0.10±0.04
Ethyl acetate	5.49	2.00
Octyl octanoate	1.44	2.00
Lauryl laurate	1.11	2.00
Cetyl palmitate	0.88	2.00
Stearyl stearate	0.91	2.00
Behenyl behenate	0.91	2.00

Reference

[1] E. Esveld, F. Chemat and J. van Haveren, *Chem. Eng. Technol.*, 2000, **23**, 429–435.