

## Supplementary Information

### 1, 3-Dimethylimidazolium-2-carboxylate: A zwitterionic salt for the efficient synthesis of vicinal diols from cyclic carbonates

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#### Catalysts preparation and characterization

1-Alkyl-3-methylimidazolium trifluoroacetate ([AMIm]TA) ionic liquids were prepared according to following procedures. A typical synthesis route to [EMIm]TFA is as follows: The mixture of 1-ethylimidazole (50 mmol) and methyl trifluoroacetate (52.5 mmol) was placed in a 25 mL Teflon-lined, stainless steel autoclave and then was heated in an oven at 100 °C for 24 h. The resulting [EMIm]TFA was decanted and washed with 1,1,1-trichloroethane for three times and then dried under vacuum at 70 °C for 24 h to give product [EMIm]TFA. [MMIm]TFA, [PMIm]TFA and [VMIm]TFA were prepared similarly, but 1-ethylimidazole was replaced by 1-methylimidazole, 1-propylimidazole and 1-vinylimidazole, respectively.

[MMIm]TFA: Yellow liquid; <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO): δ=3.86 (s, 6H), 7.72 (s, 2H), 9.15 ppm (s, 1H); Anal. calcd for C<sub>7</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>: C, 39.81; H, 4.74; N, 13.27; Found: C, 39.62; H, 4.76; N, 12.90.

[EMIm]TFA: Yellow liquid; <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO): δ=1.37 (t, 3H), 3.81 (s, 3H), 4.16 (m, 2H) 7.69 (s, 1H), 7.78 (s, 1H), 9.20 ppm (s, 1H); Anal. calcd for C<sub>8</sub>H<sub>12</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>: C, 42.67; H, 5.33; N, 10.66; Found: C, 42.62; H, 5.34; N, 10.71.

[VMIm]TFA: Yellow liquid; <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO): δ=3.89 (s, 3H), 5.40 (s, 1H), 5.95 (s, 1H), 7.33 (s, 1H), 7.86 (s, 1H), 8.21 (s, 1H), 9.51 ppm (s, 1H); Anal. calcd for C<sub>8</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>: C, 43.05; H, 4.48; N, 12.56; Found: C, 42.98; H, 4.50; N, 12.60.

[PMIm]TFA: Yellow liquid; <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO): δ=0.85 (t, 3H), 1.80 (m, 2H), 3.86 (s, 3H), 4.14 (t, 2H) 7.74 (s, 1H), 7.81 (s, 1H), 9.22 ppm (s, 1H); Anal. calcd for C<sub>9</sub>H<sub>14</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>: C, 45.19; H, 5.86; N, 11.72; Found: C, 45.23; H, 5.81; N, 11.78.

[MMIm]OAc: Firstly, in a 250 mL three-necked flask, ethylamine solution (78 mL, 0.9 mol) was added into a formaldehyde solution (25 mL, 0.42 mol) dropwise at around 4 °C cooled by an ice bath. After addition, the mixture was stirred at 70 °C for 30 min, and then cooled down. Secondly, acetic

acid (25 mL, 0.51 mol) was added dropwise at 4 °C. After that, the mixture was stirred at 70 °C for 1 h, and then cooled down. Thirdly, glyoxal (36 mL, 0.40 mol) solution was added into the mixture dropwise at 4 °C, and then stirred at 75 °C for 10 h to afford a dark-brown liquid; <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO): δ=1.85 (s, 3H), 3.59 (s, 3H), 3.80 (s, 3H), 6.87 (d, 1H, *J*=12), 7.05 (d, 1H, *J*=12), 7.63 ppm (s, 1H); Anal. calcd for C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 53.83; H, 7.74; N, 17.94; Found: C, 53.60; H, 7.84; N, 18.02.

**[EEIm]OAc**: According to the synthetic procedure of [MMIm]OAc, [EEIm]OAc was obtained as a yellow liquid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ=1.42 (t, 6H, *J*=12 Hz), 1.70 (s, 3H), 4.22-4.24 (m, 4H), 7.88 (s, 4H), 9.87 (s, 1H). Anal. calcd for C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 58.67; H, 8.75; N, 15.21; Found: C, 58.59; H, 8.72; N, 15.30.

**[EMIm]OAc**: Yellow liquid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ=1.33 (t, 3H, *J*=7.56 Hz), 1.66 (s, 3H), 3.82 (s, 3H), 4.12-4.13 (m, 2H), 7.26 (d, 1H, *J*=6.0 Hz), 7.31 ppm (d, 1H, *J*=6.0 Hz). Anal. calcd for C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 56.45; H, 8.29; N, 16.46; Found: C, 56.37; H, 8.37; N, 16.50.

**[BMIm]OAc**: Yellow liquid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ=0.97 (t, 3H, *J*=14.4 Hz), 1.38-1.39 (m, 2H), 1.90-1.92 (m, 2H), 1.92 (s, 3H), 4.10 (s, 3H), 4.34 (d, 2H, *J*=12 Hz), 7.64 (d, 2H, *J*=6.0 Hz), 7.70 (d, 2H, *J*=6.6 Hz), 10.24 ppm (s, 1H). Anal. calcd for C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 60.58; H, 9.15; N, 14.13; Found: C, 60.51; H, 9.20; N, 14.20.

**DMImC**: A mixture of DMC (4.5 mL, 53 mmol) and 1-methylimidazole (4.1 mL, 52 mmol) was heated in a 25 mL stainless-steel reactor equipped with a magnetic stirrer and automatic temperature control system for 36 h at 110 °C in a nitrogen atmosphere. After removing the solvent under reduced pressure, a yellow solid was obtained, then a white solid was further obtained by recrystallized from methanol, yield: 87%; <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O): δ=5.76 (s, 6H), 10.86 ppm (s, 2H). Anal. calcd for C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 51.42; H, 5.75; N, 19.99; Found: C, 51.80; H, 6.06; N, 20.11.

**[HDBU]OAc**: In a 25 mL flask, acetic acid (0.72 g, 12 mmol) was added dropwise into 1,5-diazabicyclo[4.3.0]non-5-ene (DBU) (1.8 g, 12 mmol) and acetone (1 mL) in an ice bath. After addition, the ice bath was removed and the reaction mixture was stirred at 30 °C for 24 h. The obtained residue was dried at 60 °C under vacuum for 24 h to afford 1,8-diazabicyclo [5.4.0] undec-7-enium acetate as a yellow, viscous liquid. <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO): δ=1.51-1.58 (m, 4H), 1.59-1.65 (m, 6H), 1.80-1.86 (m, 2H), 2.73 (t, 2H, *J*=4.9 Hz), 3.22 (t, 2H, *J*=5.5 Hz), 3.43 (t, 2H, *J*=5.7 Hz), 3.49 ppm (t, 2H, *J*=4.3 Hz). Anal. calcd for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 62.24; H, 9.50; N, 13.20; Found: C, 60.41; H, 9.67; N, 13.63.

**[HDBU]HSO<sub>4</sub>**: Yellow solid; <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO): 1.53-1.66 (m, 6H), 1.84-1.91 (m, 2H), 2.61 (t, 2H, *J*=3.6 Hz), 3.21 (t, 2H, *J*=6.0 Hz), 3.44 (t, 2H, *J*=5.4 Hz), 3.51 (t, 2H, *J*=2.9 Hz), 9.51 ppm (s, 1H). Anal. calcd for C<sub>9</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S: C, 43.18; H, 7.25; N, 11.19; Found: C, 43.09; H, 6.769; N, 11.14.

**[HDBU]HCOO**: Yellow solid; <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO): δ=1.53-1.65 (m, 6H), 1.83-1.87 (m, 2H), 2.71 (t, 2H, *J*=5.6 Hz), 3.20 (t, 2H, *J*=5.7 Hz), 3.41 (t, 2H, *J*=5.8 Hz), 3.48 (t, 2H, *J*=4.8 Hz), 8.46

ppm (s, 1H). Anal. calcd for  $C_{10}H_{18}N_2O_2$ : C, 60.58; H, 9.15; N, 14.13; Found: C, 58.58; H, 9.70; N, 14.0.

**[HDBU]Cl**: Synthesized according to the procedure in Ref. 30c. Yellow solid;  $^1H$  NMR (600 MHz,  $[D_6]$ DMSO):  $\delta$ =1.54-1.67 (m, 6H), 1.84-1.90 (m, 2H), 2.71 (t, 2H,  $J$ =3.6 Hz), 3.19 (t, 2H,  $J$ =7.3 Hz), 3.43 (t, 2H,  $J$ =4.9 Hz), 3.51 ppm (t, 2H,  $J$ =2.8 Hz). Anal. calcd for  $C_9H_{18}ClN_2$ : C, 56.98; H, 9.56; N, 14.77; Found: C, 56.86; H, 9.51; N, 14.68.

**[HDBU]C<sub>2</sub>H<sub>5</sub>COO**: Yellow solid;  $^1H$  NMR (600 MHz,  $[D_6]$ DMSO):  $\delta$ =0.90 (t, 3H,  $J$ =7.6 Hz), 1.58-1.59 (m, 4H), 1.65-1.66 (m, 2H), 1.82 (q, 2H,  $J$ =8.5 Hz), 1.87 (t, 2H,  $J$ =7.6 Hz), 2.72 (t, 2H,  $J$ =5.2 Hz), 3.19 (t, 2H,  $J$ =5.6 Hz), 3.39 (t, 2H,  $J$ =5.8 Hz), 3.45 ppm (t, 2H,  $J$ =4.7 Hz). Anal. calcd for  $C_{12}H_{22}N_2O_2$ : C, 63.68; H, 9.80; N, 12.38; Found: C, 62.24; H, 10.31; N, 13.54.

**[HDBU]PhCOO**: Yellow solid;  $^1H$  NMR (600 MHz,  $[D_6]$ DMSO):  $\delta$ =1.54-1.65 (m, 6H), 1.84-1.88 (m, 2H), 2.78 (t, 2H,  $J$ =5.8 Hz), 3.25 (t, 2H,  $J$ =5.7 Hz), 3.42 (t, 2H,  $J$ =5.8 Hz), 3.42 (t, 2H,  $J$ =5.8 Hz), 7.22 (d, 2H,  $J$ =6.7 Hz), 7.24 (d, 1H,  $J$ =5.8 Hz), 7.79 (d, 1H,  $J$ =2.0 Hz), 7.81 ppm (d, 1H,  $J$ =2.0 Hz). Anal. calcd for  $C_{16}H_{22}N_2O_2$ : C, 70.04; H, 8.08; N, 10.21; Found: C, 70.23; H, 8.43; N, 10.12.

## NMR detections on hydrolysis process

The hydrolysis reaction of ethylene carbonate (EC) and water catalyzed by DMIMC was carried out using *in-situ* NMR spectroscopy (600 MHz). At the beginning, EC, water and DMIMC was added into a glass-tube using D<sub>2</sub>O as an inner standard. The detection was operated at 50 °C for about 30 min, and the results were list in Figures 1S and 2S.

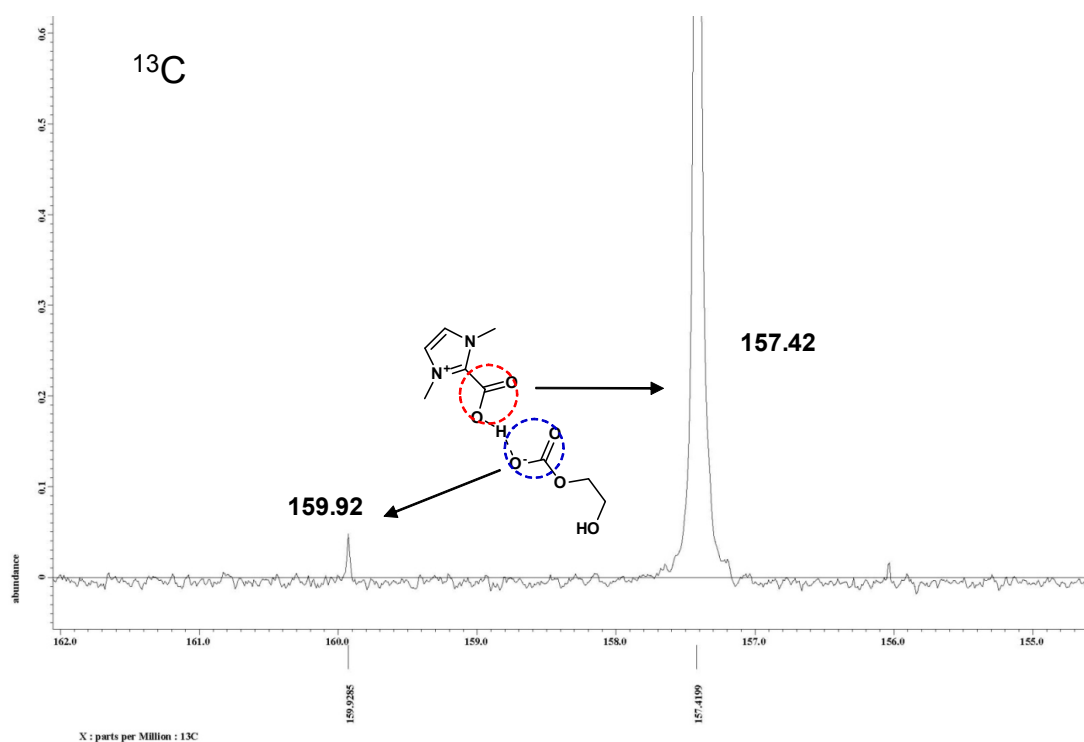


Figure 1S. <sup>13</sup>CNMR of hydrolysis reaction of EC operated at 50 °C with 600 MHz (Zoom).

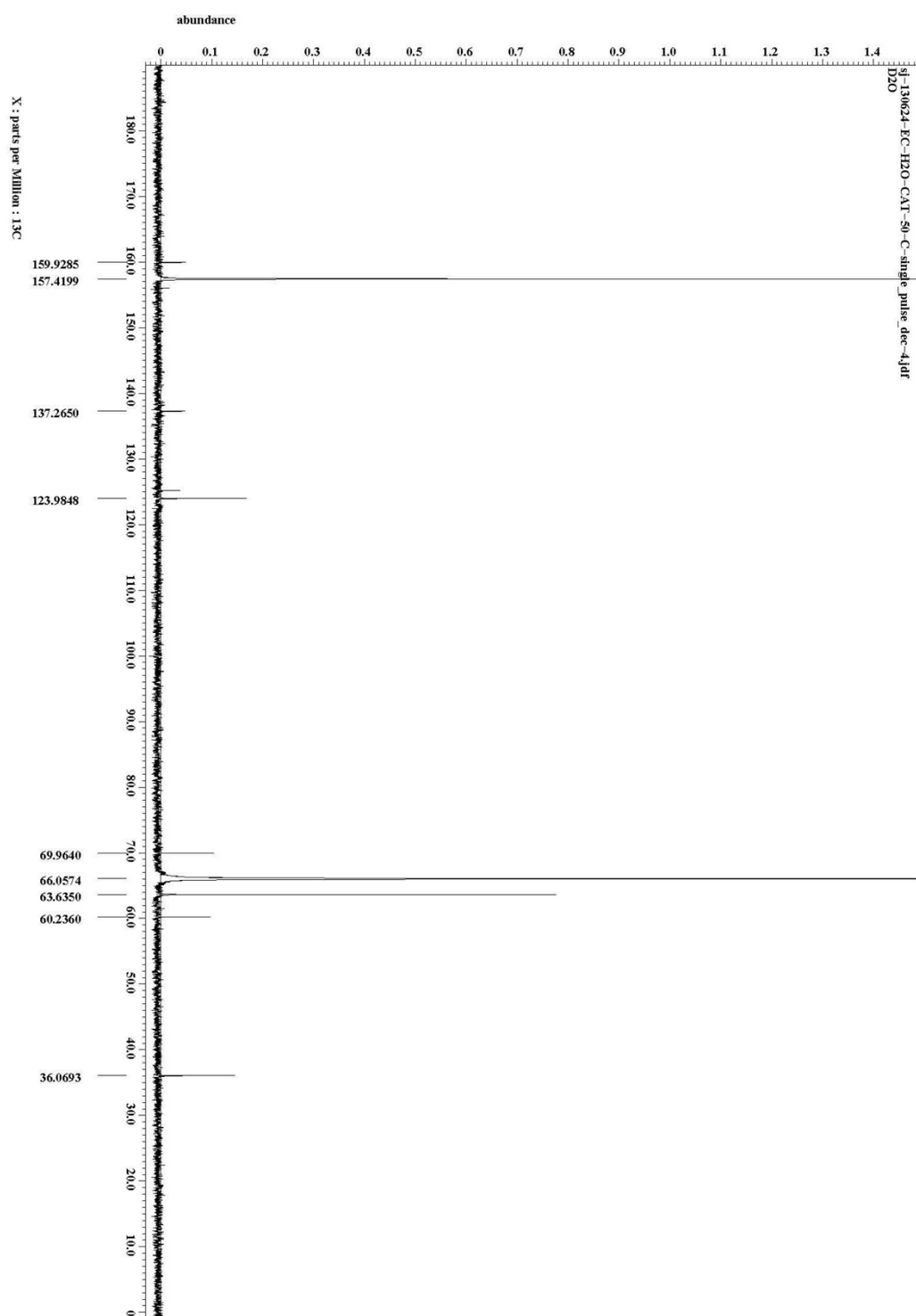


Figure 1S.  $^{13}\text{C}$ NMR of hydrolysis reaction of EC operated at 50 °C with 600 MHz.

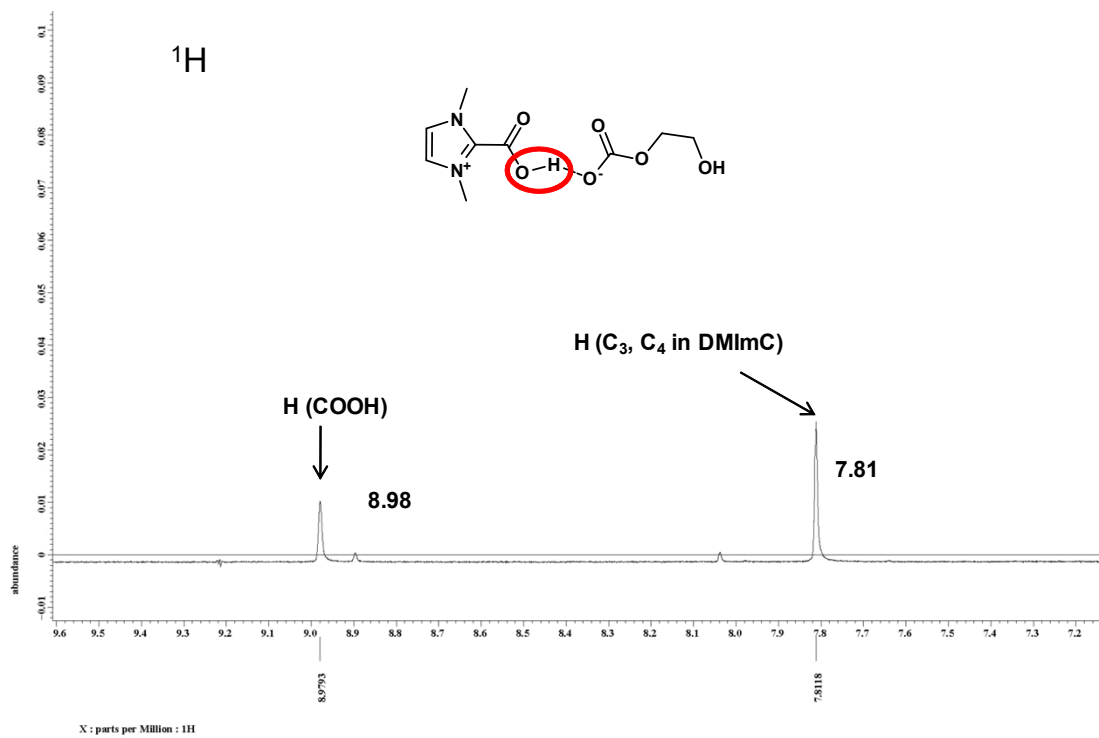


Figure 2S. <sup>1</sup>HNMR of hydrolysis reaction of EC operated at 50 °C with 600 MHz (Zoom).

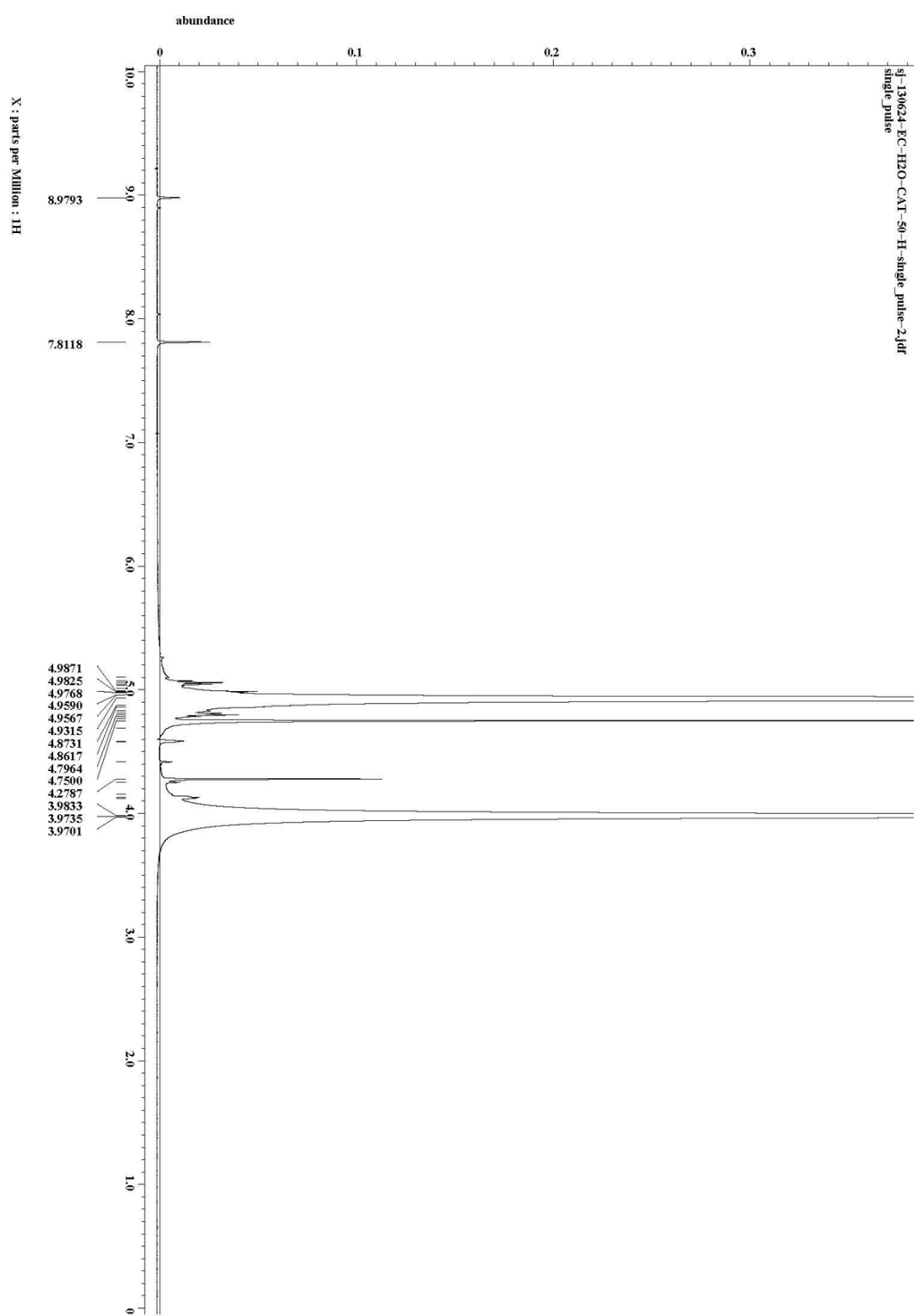


Figure 2S. <sup>1</sup>H NMR of hydrolysis reaction of EC operated at 50 °C with 600 MHz.

## Density functional theory calculation

Density functional theory calculation were carried out with the DMol program package in the Materials Studio 6.0 of Accelrys Inc. Structure optimizations and energy calculations were carried out with B3LYP method in the package. The meshsize in medium quality for the numerical integration was used, and the tolerances of energy, gradient and displacement convergence were  $2 \times 10^{-5}$  au,  $4 \times 10^{-3}$  au/Å and  $5 \times 10^{-3}$  Å, and the real space cut off of atomic orbital was set at 3.3 Å. Complete linear synchronous transit and quadratic synchronous transit (LST/QST) calculations were performed to determine the structures of transition states, confirmed by additional calculations of the intrinsic reaction path. The corresponding frequencies were computed at the same level in order to check the obtained stationary points to be ground states (minimum structures) with only real frequencies, or to be transition states (maximum structures or saddle points) with only one imaginary frequency. The ZPE corrections have been taken into account for all the cited energies.