Supporting information

Asymmetric organic carbonate catalyzed by Enzyme with dimethyl carbonate: a fruitful sustainable alliance

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More information about free Novozym 435 catalyst for asymmetric organic carbonate synthesis

Procedure for IMC synthesis from DMC and isoamyl alcohol by Novozym 435

Enzymatic synthesis of IMC has been performed in a solvent free system. Given amounts of isoamyl alcohol (1.0 g, 11.3 mmol) and DMC at different isoamyl alcohol / DMC molar ratios (1:2, 1:4, 1:6, 1:8, 1:10, 1:12, 1:14, 1:16, 1:18, 1:20, 1:25) were mixed together with the lipase catalyst (0.41, 0.82, 1.63, 3.26, 6.53, 8.16, 9.79, 13.05, 14.68‰, on the base of DMC) in a 25 mL flask. The mixtures were incubated for a maximum of 74 h under stirring at temperatures in the range 50–65 °C with agitation speed of 180rpm.. After the reaction was completed, the vessel was then cooled to room temperature. The products were analyzed by GC .The catalyst enzyme was recovered by cetrifugation of the resulted suspension and washed using acetone. The residue obtained was dried at room temperture under reduced pressure overnight (at 1 Torr for 24h) and was then used for the next generation.

The conversion ratio, the yield and the selectivity

The conversion ratio of alcohol, the yield in alcohol and the selectivity to un-symmetric carbonate was calculated using equations (S1-S3), via GC with methyl benzoate as intemal standard, in which the number of moles was determined by Internal Standard Method from the chromatographic analysis (IA- isoamyl alcohol, MB-methyl benzoate) (isoamyl alcohol's standard curve: $y=1.0502x+0.0440$ with $R^2=0.9993$, where $y=m_{IA}/M_{MB}$ and $x=A_{IA}/A_{MB}$ with A being the integral area of GC).

$$\text{isoamyl alcohol conversion}(\%) = [m_{IA0}-(A_{IA}/A_{MB}-0.0440)\times m_{MB}/1.0502]/\ m_{IA0}\times 100 \quad \text{(S1)}$$

$$\text{un-symmetric carbonate yield}(\%) = \text{isoamyl alcohol conversion}(\%)\times A_{IMC}/(A_{IMC}+A_{DIC})\times 100 \quad \text{(S2)}$$

$$\text{selectivity}(\%) = \text{sum of un-symmetric carbonate} / (\text{sum of un-symmetric carbonate} + \text{sum of symmetric carbonate})\times 100 \quad \text{(S3)}$$

The recyclability of lipase

Table S1 the stability and reusability of Novozym 435 in asymmetric organic carbonate synthesis. Conditions: 11.3 mmol isoamyl alcohol; isoamyl alcohol/DMC molar ratio = 1:12; 9.79‰ (w/w) lipase; temperature 60 °C; 72h incubation time.

Cycle	1	2	3	4	5	6	7	8	9	10
isoamyl alcohol conversion (%)	93.4	88.5	91.4	89.5	91.2	89.4	88.6	85.3	84.7	84.9
IMC yield (%)	93.4	88.5	91.4	89.5	91.2	89.4	88.6	85.3	84.7	84.9

Representative examples of GC chromatograms from reaction mixtures

GC chromatograms of flavour esters samples obtained from Novozym 435 catalyzed esterification between DMC with isoamyl alcohol. Influence of the incubation time on the IMC synthesis. Conditions: 11.3 mmol isoamyl alcohol; isoamyl alcohol : DMC molar ratio = 1:12; 9.79‰ (w/w) lipase; temperature 60 °C. (see Fig. S1)

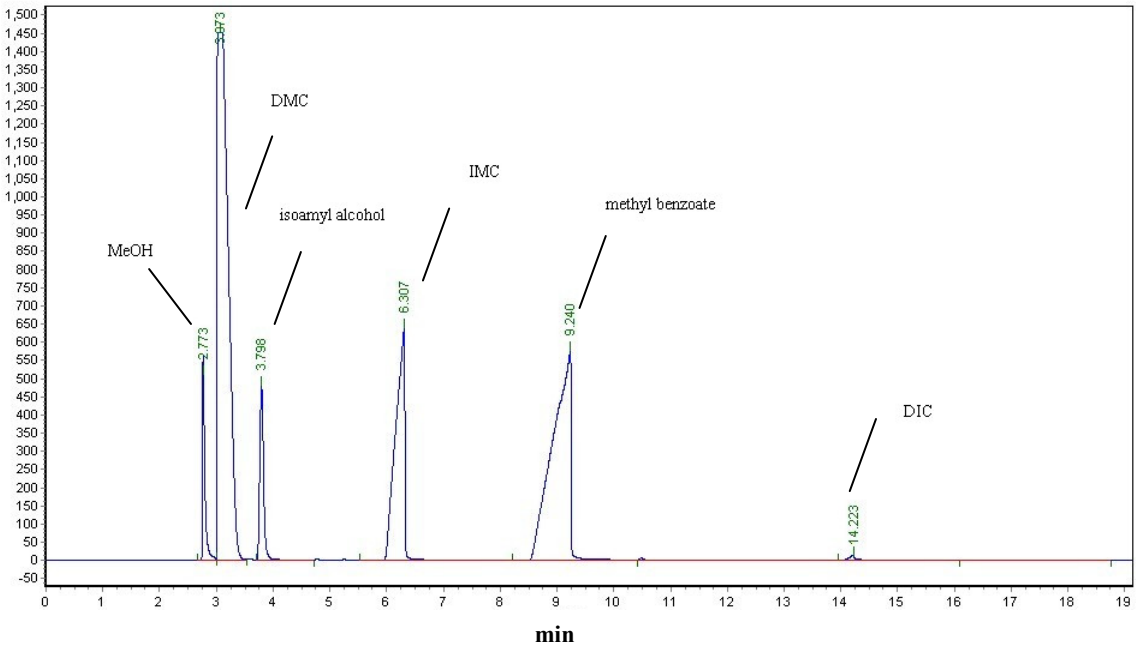


Fig. S1. Representative examples of GC chromatograms for reaction mixtures after reacting 6 hours.

GC chromatograms with integration for the synthesis of asymmetric carbonates in Table 2

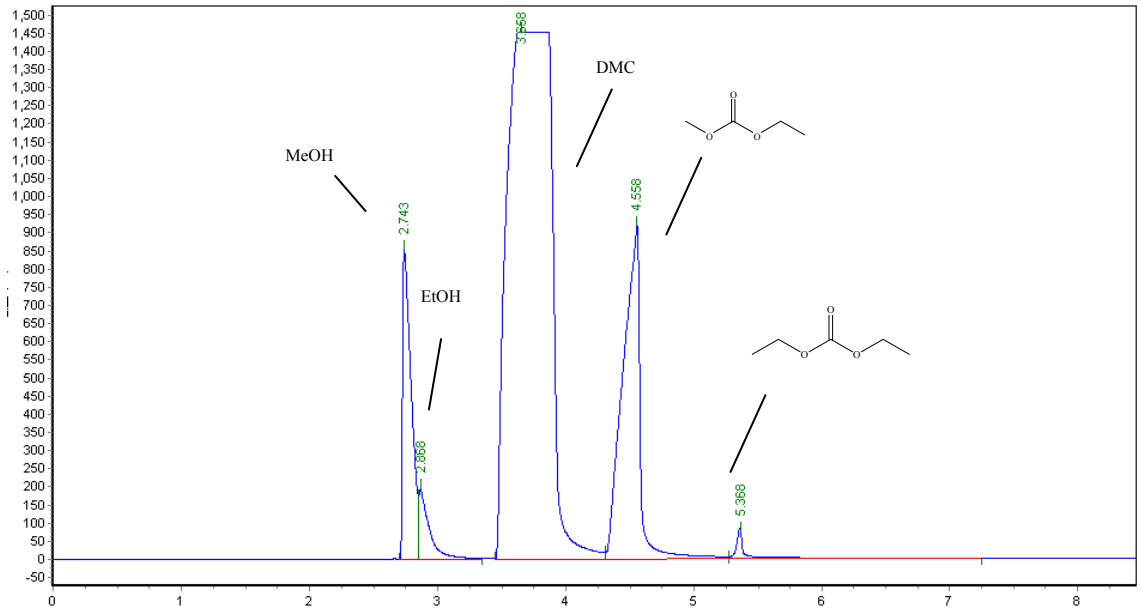


Fig. S2. GC chromatograms for reaction mixtures after reacting 24 hours (Table 2, 1)

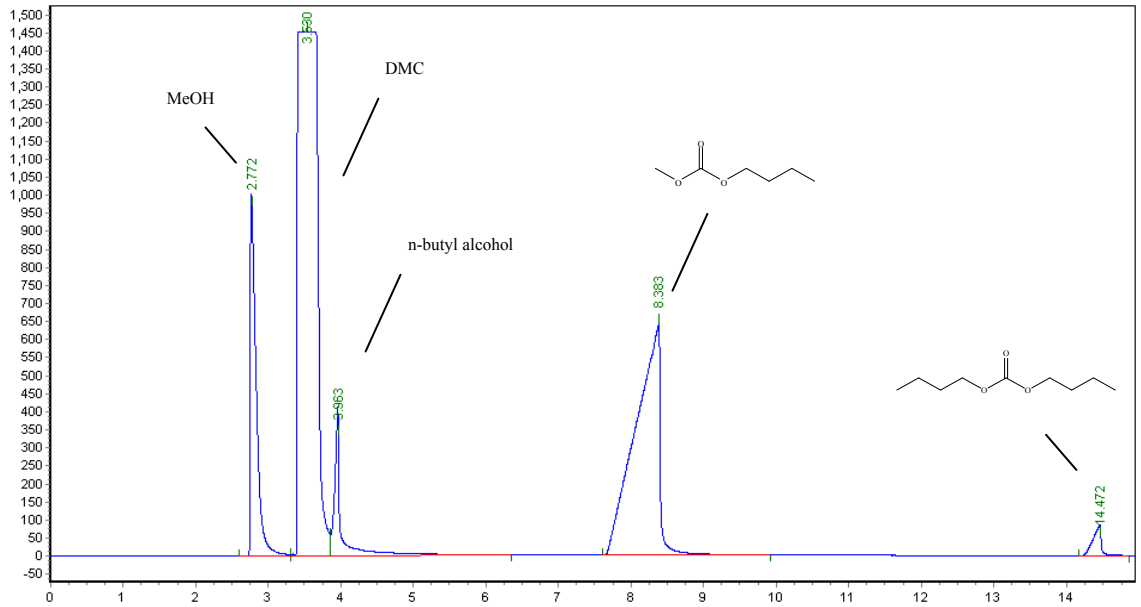


Fig. S3. GC chromatograms for reaction mixtures after reacting 24 hours (Table 2, 2)

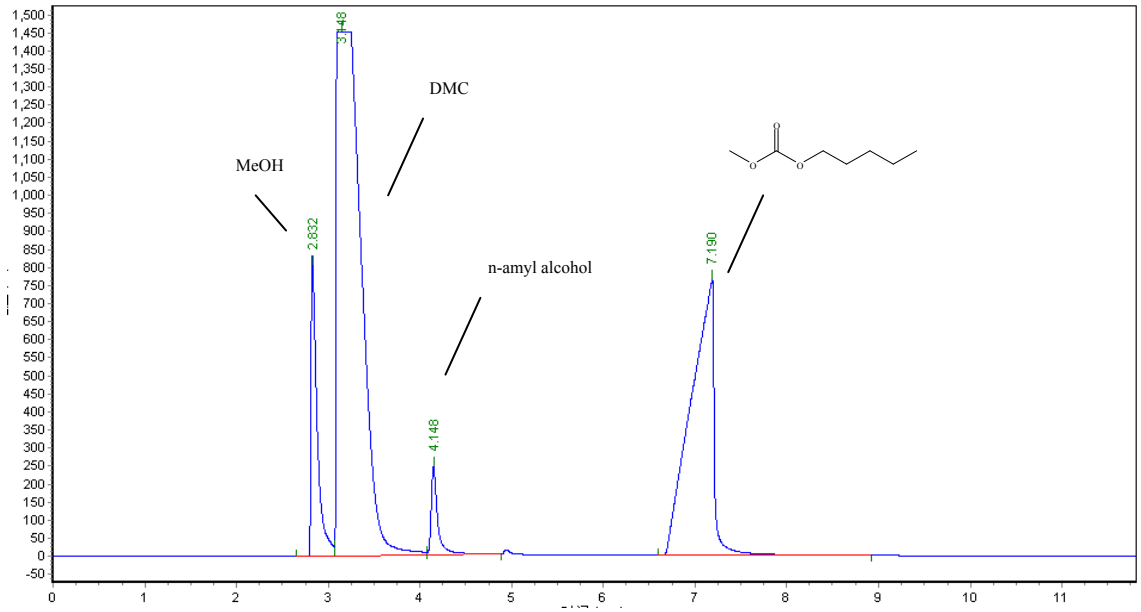


Fig. S4. GC chromatograms for reaction mixtures after reacting 36 hours (Table 2, 3)

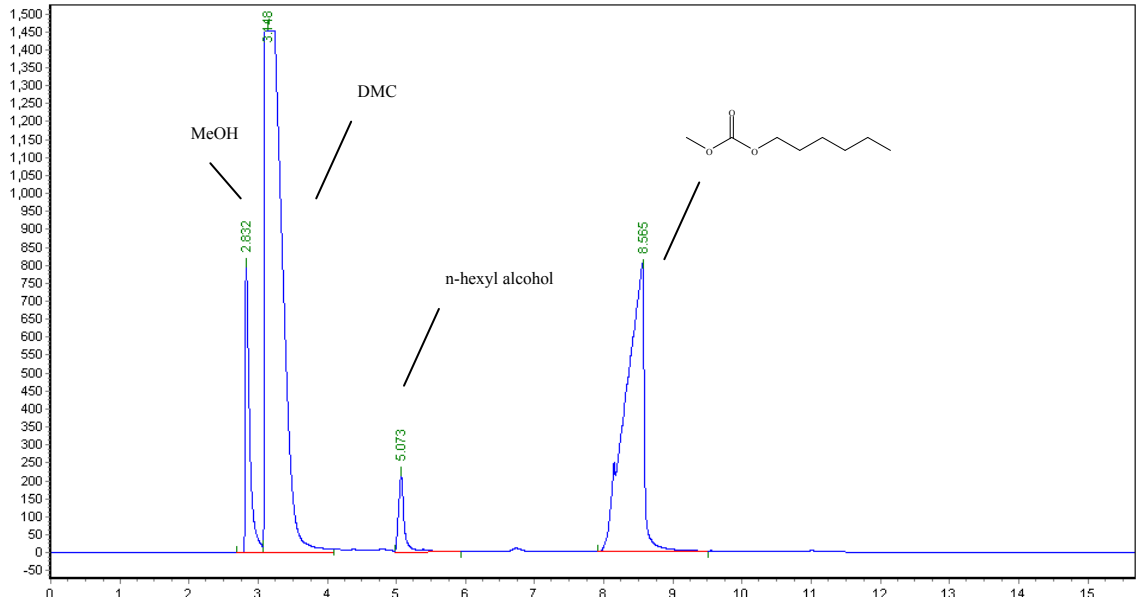


Fig. S5. GC chromatograms for reaction mixtures after reacting 48 hours (Table 2, 4)

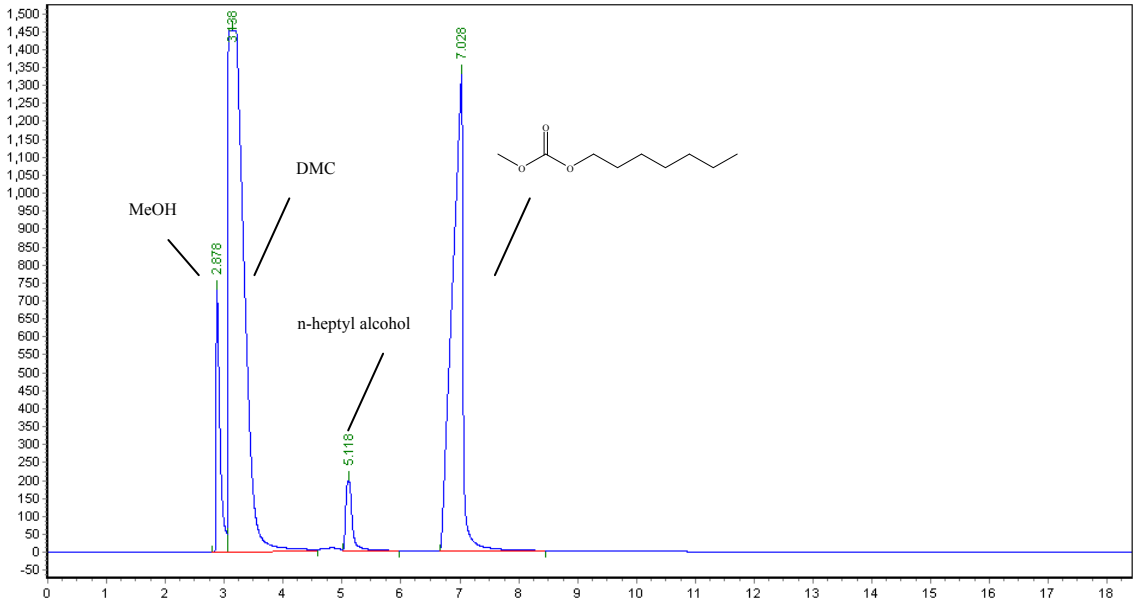


Fig. S6. GC chromatograms for reaction mixtures after reacting 48 hours (Table 2, 5)

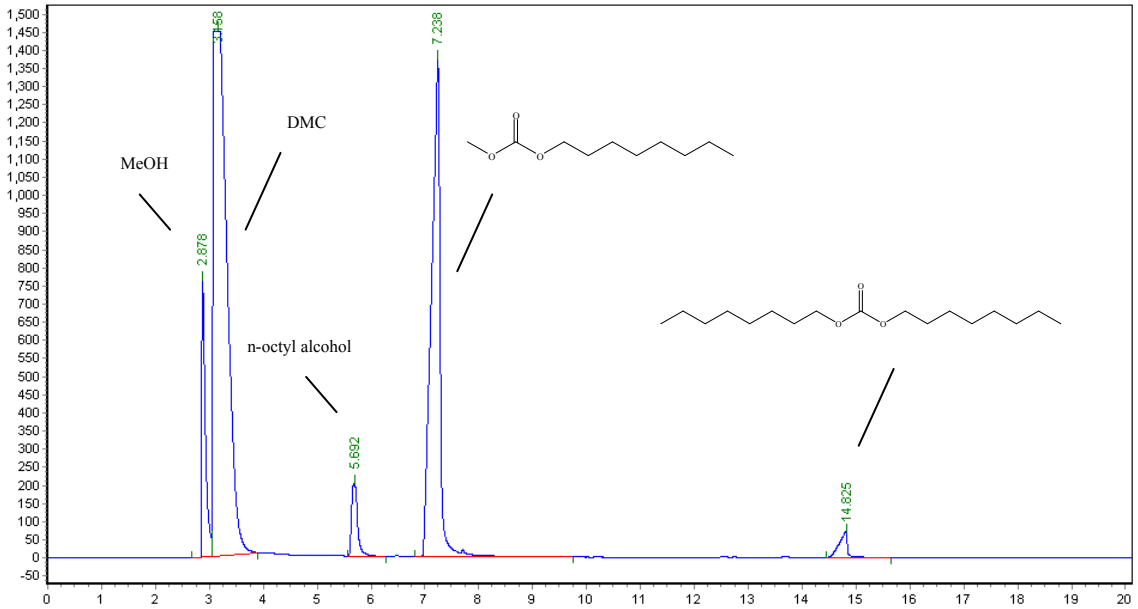


Fig. S7. GC chromatograms for reaction mixtures after reacting 48 hours (Table 2, 6)

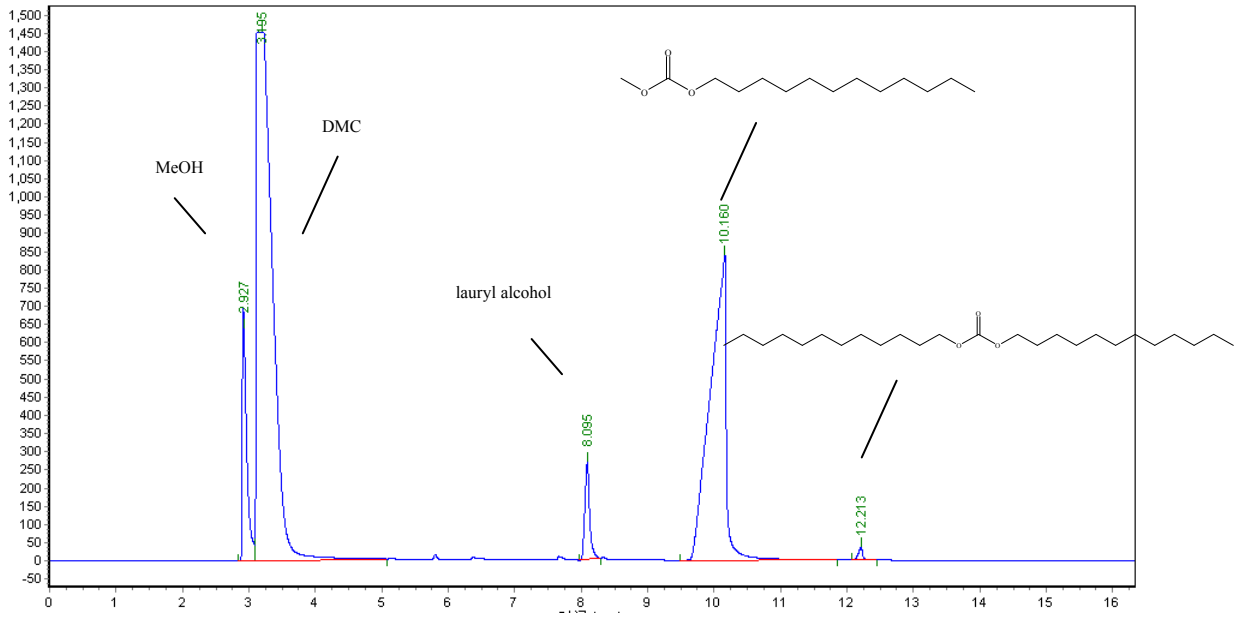


Fig. S8. GC chromatograms for reaction mixtures after reacting 30 hours (Table 2, 7)

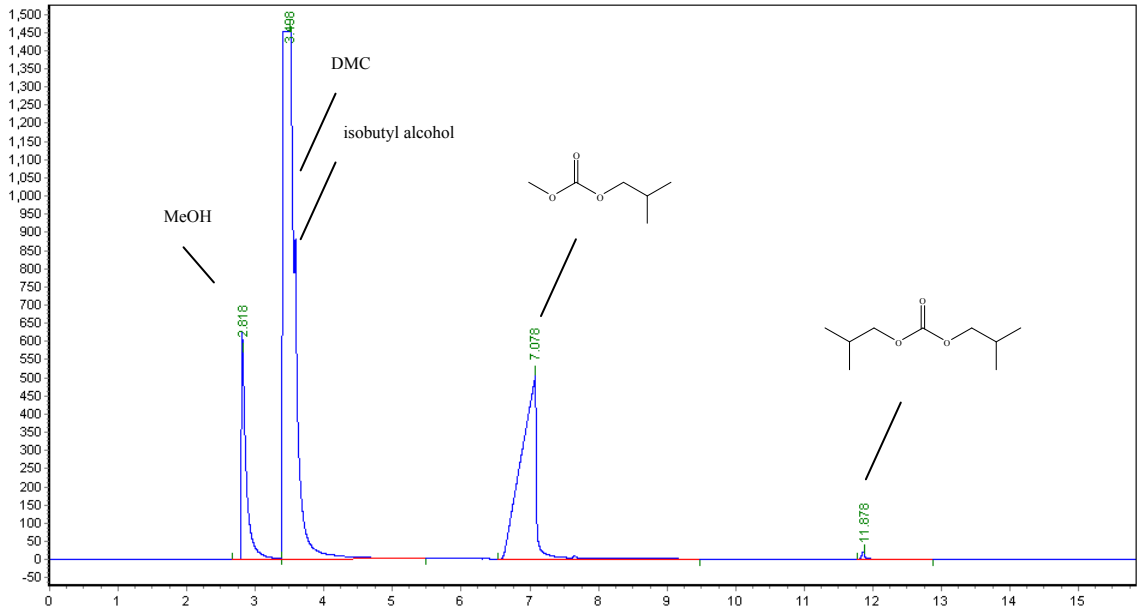


Fig. S9. GC chromatograms for reaction mixtures after reacting 24 hours (Table 2, 8)

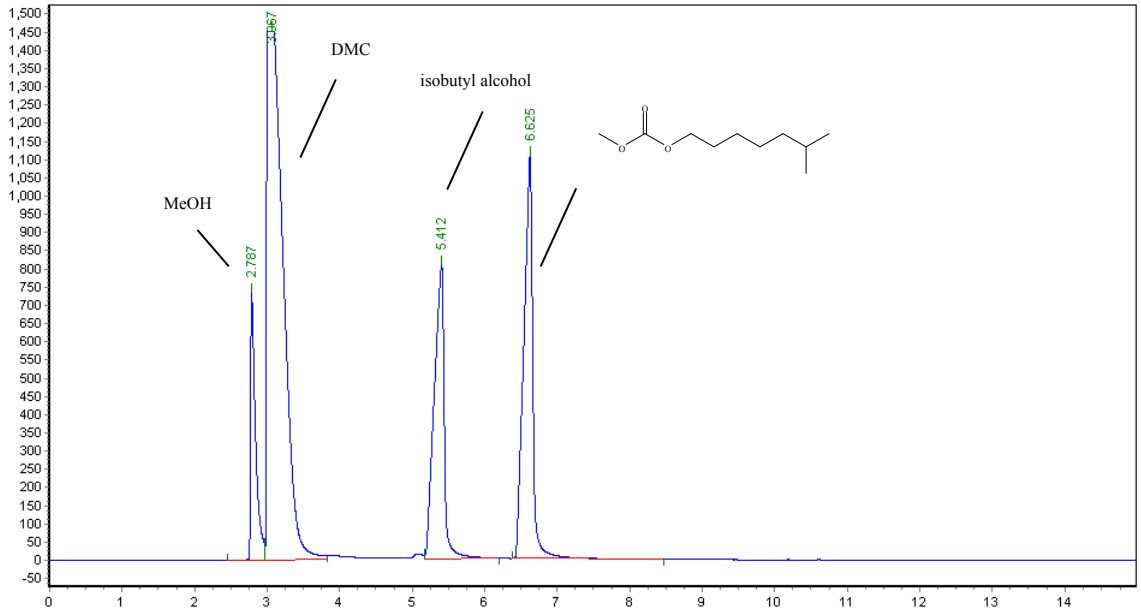


Fig. S9. GC chromatograms for reaction mixtures after reacting 48 hours (Table 2, 10)

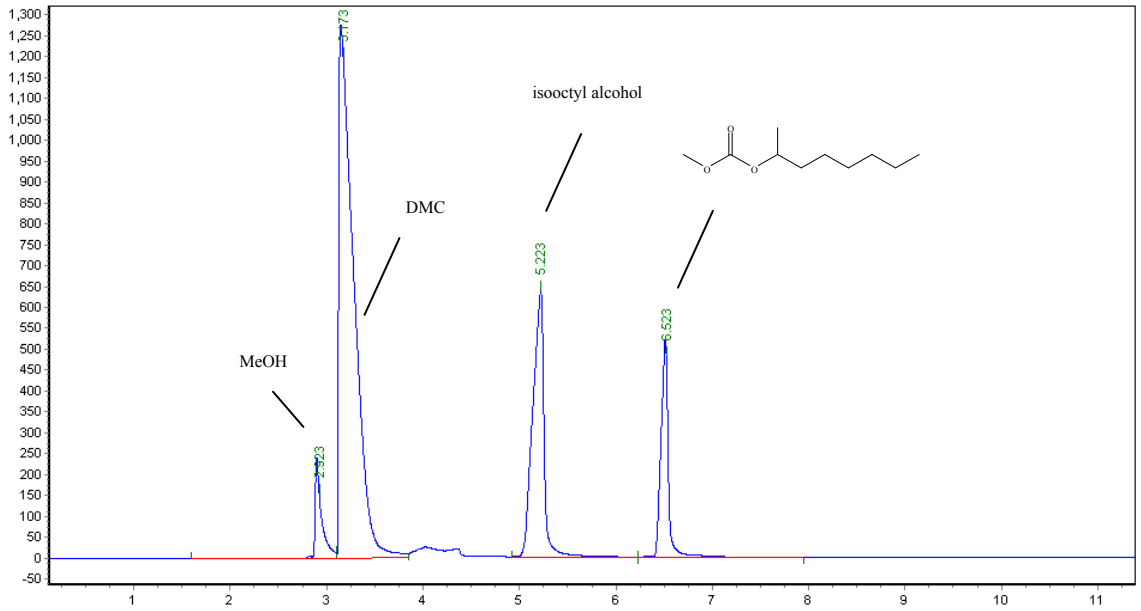


Fig. S10. GC chromatograms for reaction mixtures after reacting 48 hours (Table 2, 11)

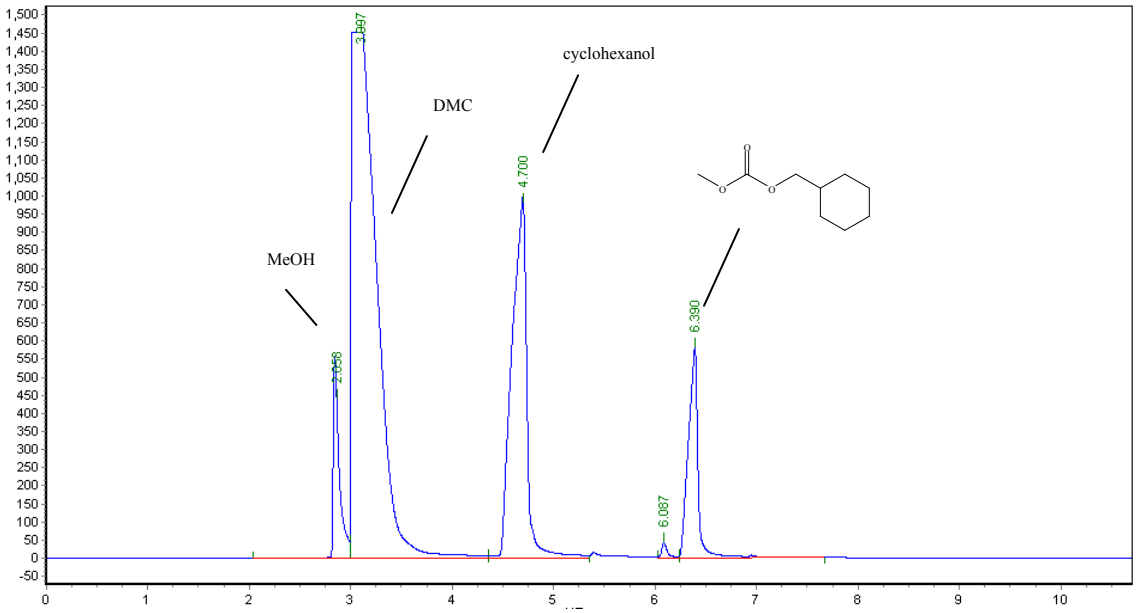


Fig. S11. GC chromatograms for reaction mixtures after reacting 48 hours (Table 2, 12)

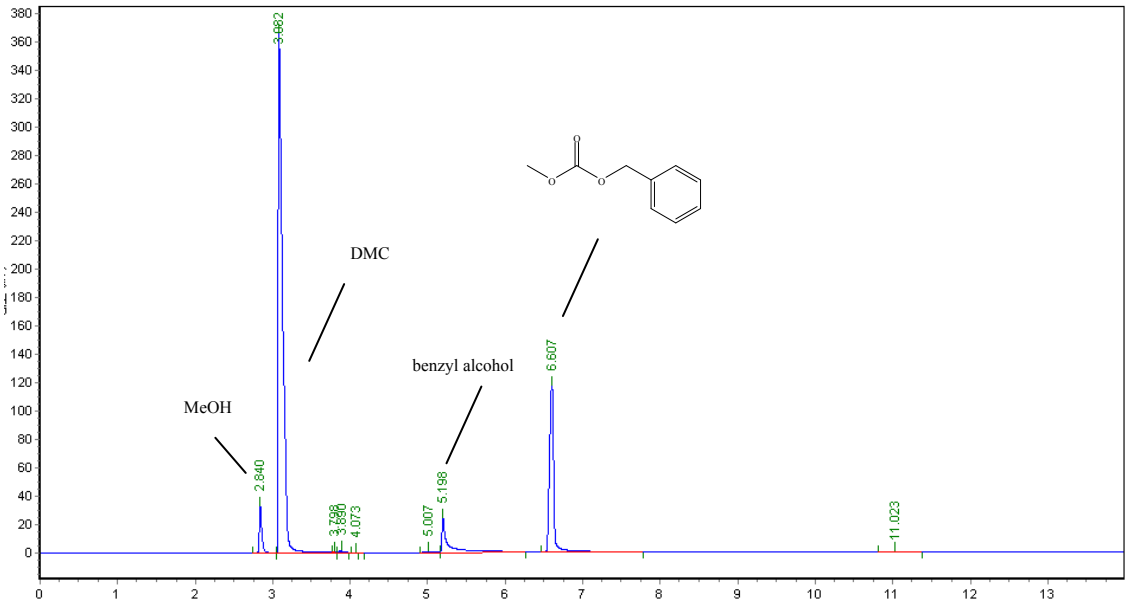
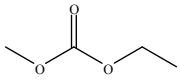


Fig. S12. GC chromatograms for reaction mixtures after reacting 48 hours (Table 2, 13)

The ^{1}H and ^{13}C NMR spectra of the products



(Table 2, 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.21 (q, 2H, -O-**CH_2**-), 3.78 (s, 3H, -O-**CH_3**), 1.31 (t, 3H, -O-CH_2-**CH_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):155.75 (s), 64.02 (s), 54.59 (s), 14.26 (s).

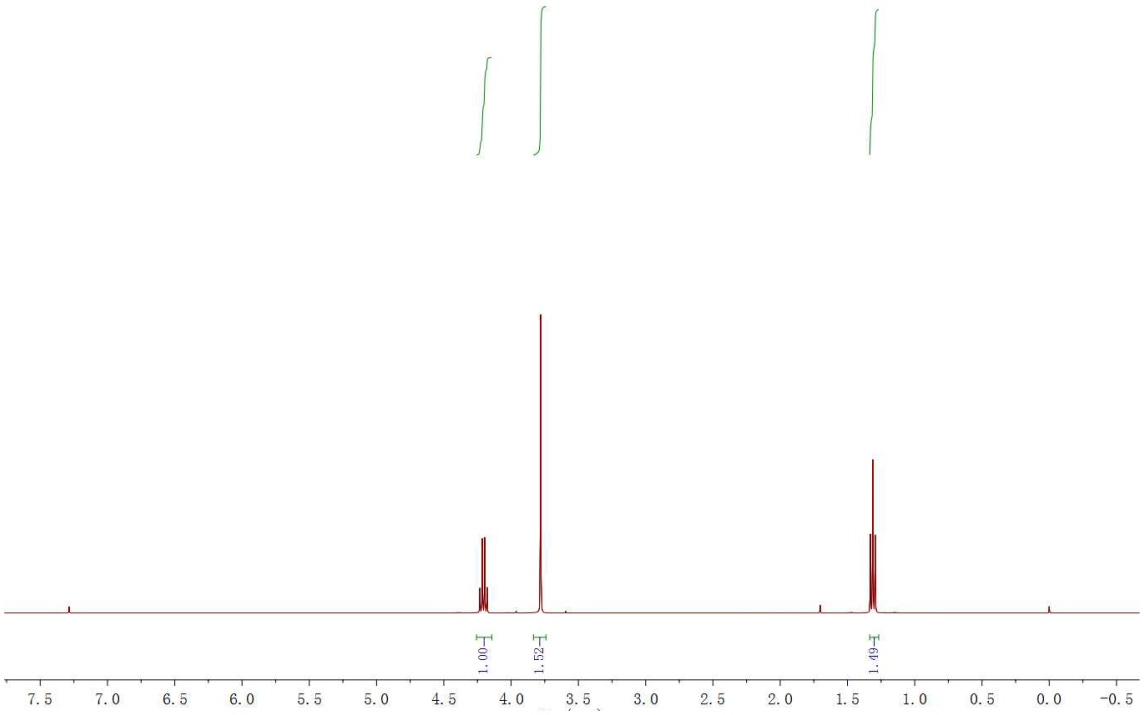


Table 2, 1

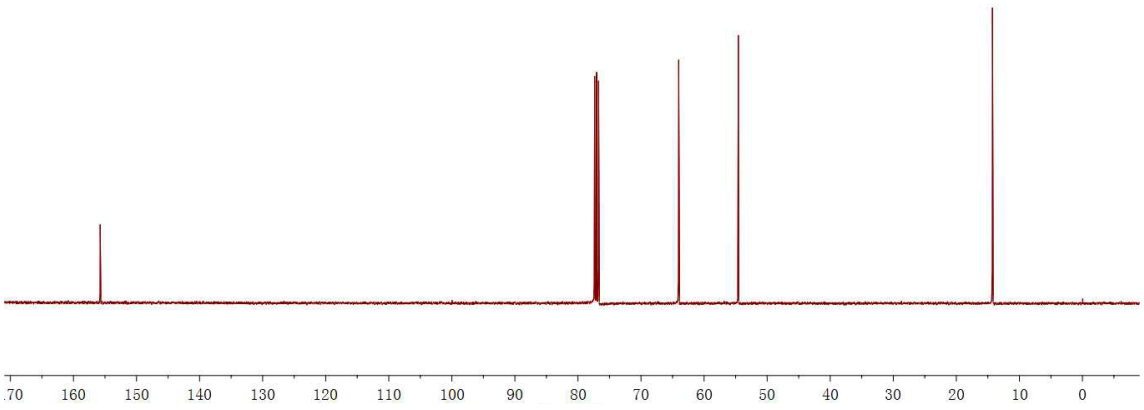
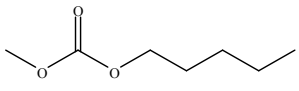


Table 2, 1



(Table 2, 3)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.13 (t, 2H, -O-**CH_2**-), 3.79 (s, 3H, -O-**CH_3**), 1.74 – 1.62 (m, 2H, -O-CH_2-**CH_2**-), 1.41 – 1.30 (m, 4H, -O-$(CH_2)_2$-**$(CH_2)_2$**-), 0.96 – 0.86 (t, 3H, -O-$(CH_2)_4$-**CH_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.89 (s), 68.24 (s), 54.64 (s), 28.35 (s), 27.80 (s), 22.30 (s), 13.94 (s).

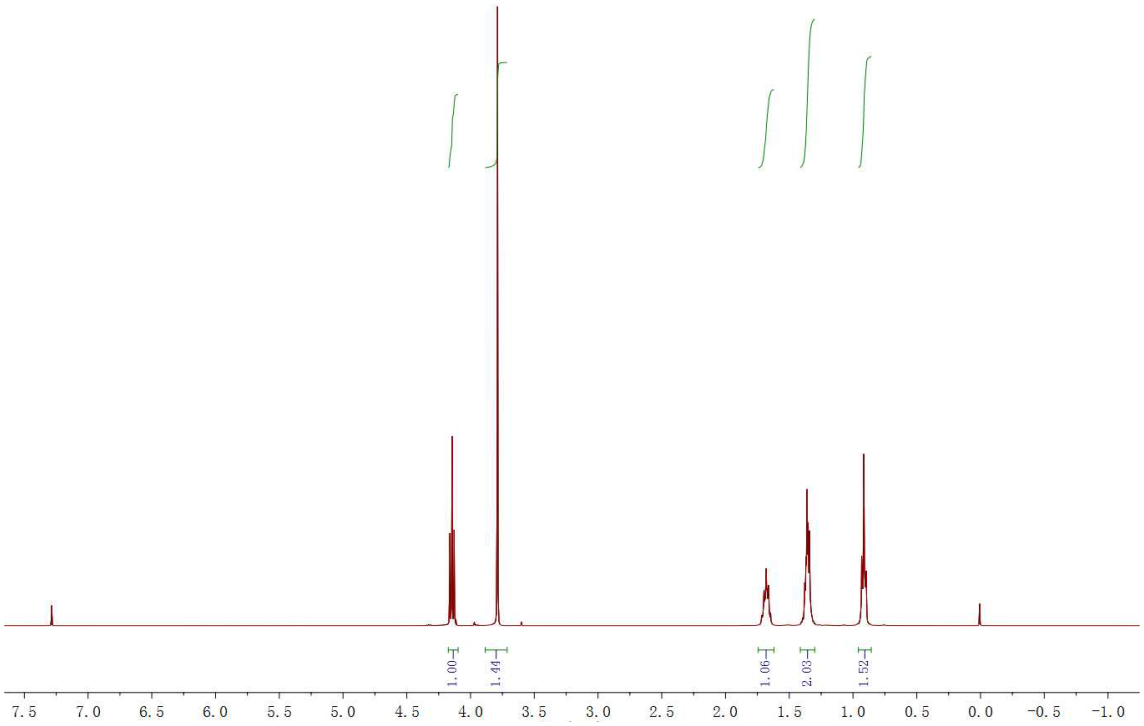


Table 2, 3

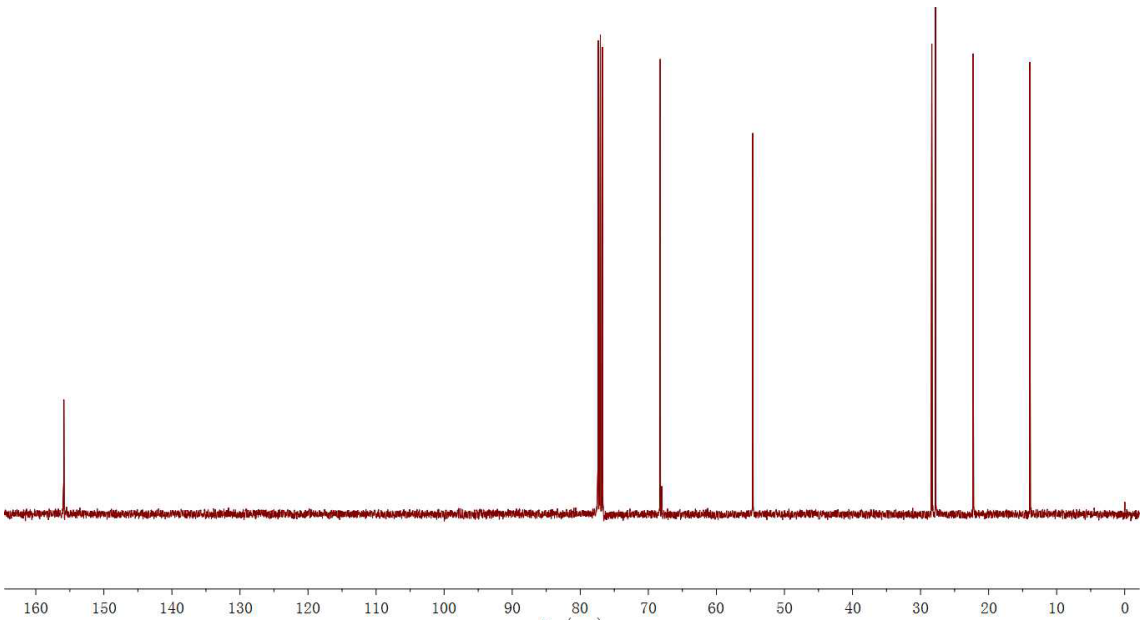
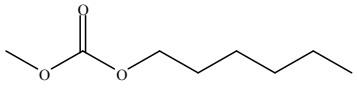


Table 2, 3



(Table 2, 4)

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 4.13 (t, 2H, -O-**CH_2**-), 3.78 (s, 3H, -O-**CH_3**), 1.71 – 1.61 (m, 2H, -O-CH_2-**CH_2**-), 1.41 – 1.23 (m, 6H, -O-$(CH_2)_2$-**$(CH_2)_3$**-), 0.89 (t, 3H, -O-$(CH_2)_5$-**CH_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 155.87 (s), 68.23 (s), 54.60 (s), 31.38 (s), 28.61 (s), 25.34 (s), 22.51 (s), 13.97 (s).

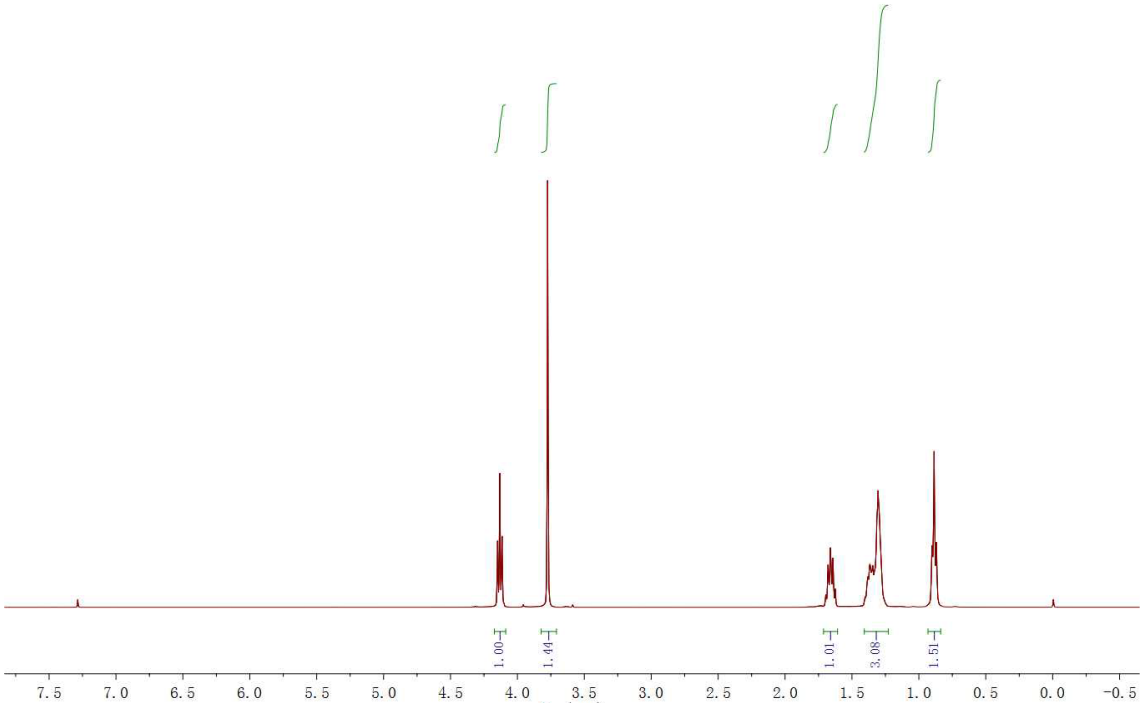


Table 2,4

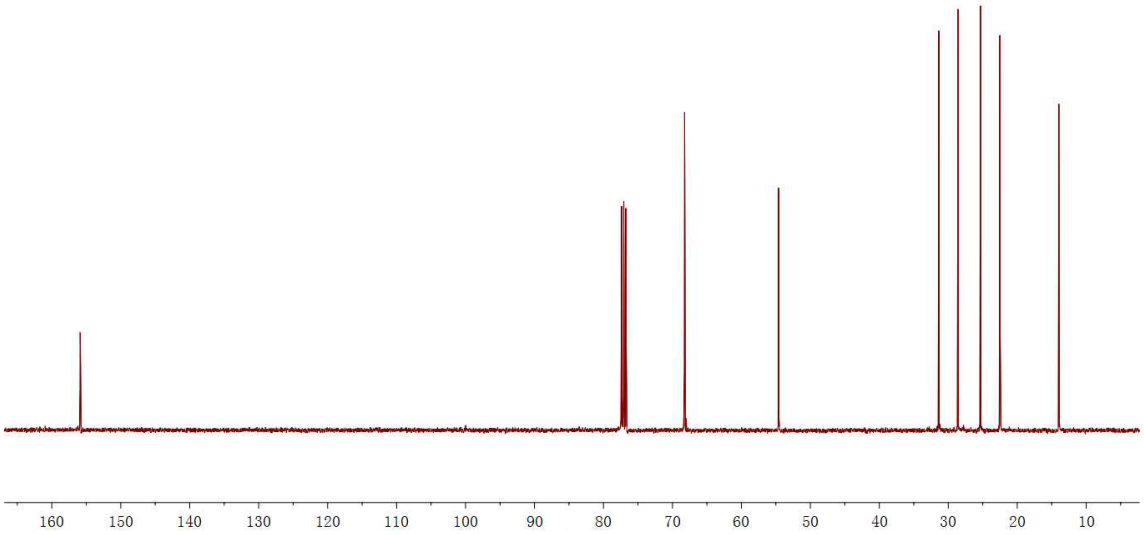
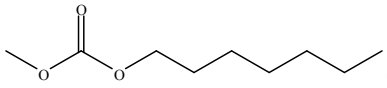


Table 2,4



(Table 2, 5)

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 4.14 (t, 2H, -O-**CH_2**-), 3.78 (s, 3H, -O-**CH_3**), 1.71 – 1.61 (m, 2H, -O-CH_2-**CH_2**-), 1.41 – 1.23 (m, 8H, -O-$(CH_2)_2$-**$(CH_2)_4$**-), 0.89 (t, 3H, -O-$(CH_2)_6$-**CH_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 155.90 (s), 68.27 (s), 54.64 (s), 31.69 (s), 28.89 (s), 28.66 (s), 25.64 (s), 22.57 (s), 14.07 (s).

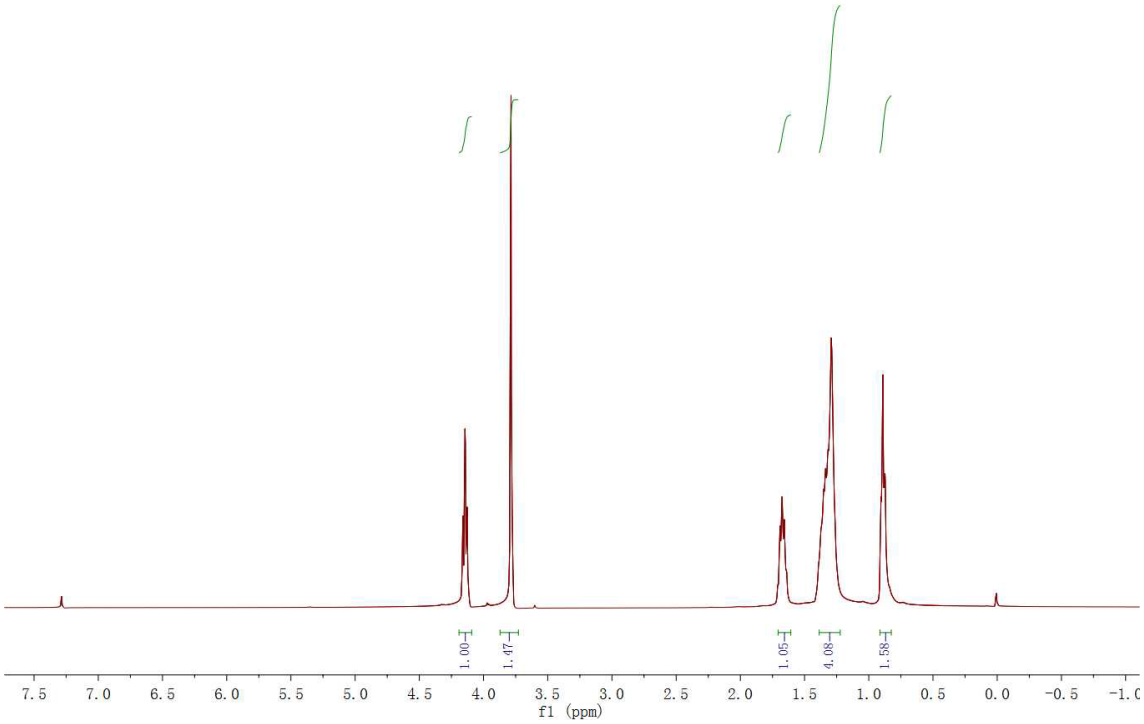


Table 2, 5

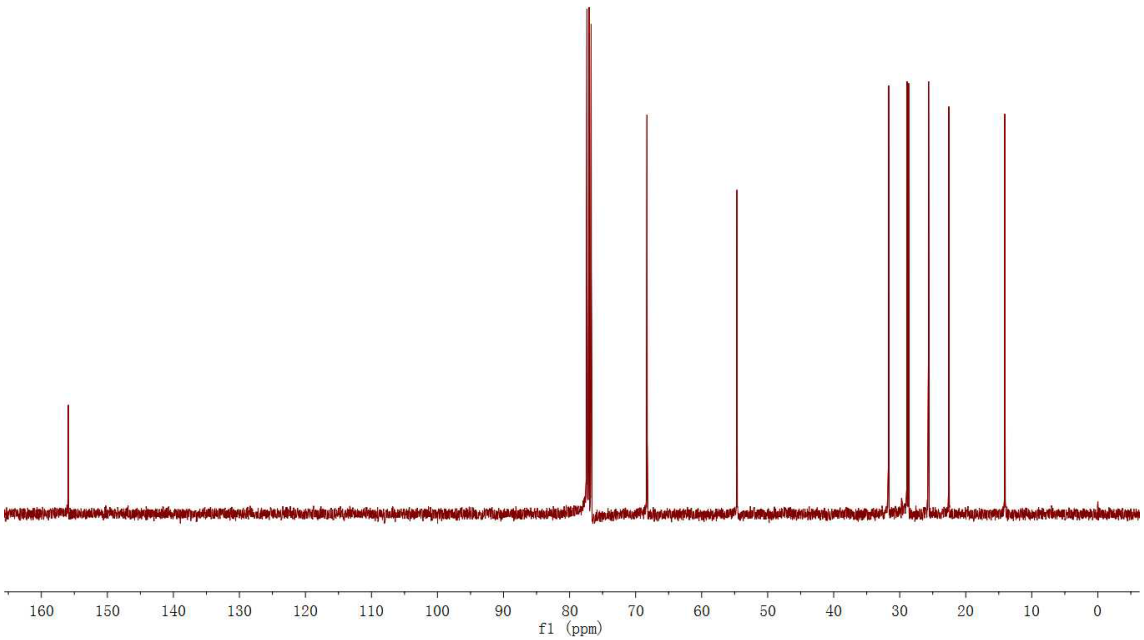
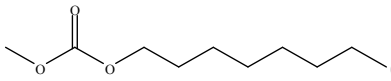


Table 2, 5



(Table 2, 6)

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 4.13 (t, 2H, -O-**CH_2**-), 3.78 (s, 3H, -O-**CH_3**), 1.71 – 1.59 (m, 2H, -O-CH_2-**CH_2**-), 1.39 – 1.19 (m, 10H, -O-$(CH_2)_2$-**$(CH_2)_5$**-), 0.88 (t, 3H, -O-$(CH_2)_7$-**CH_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 155.88 (s), 68.24 (s), 54.61 (s), 31.76 (s), 29.16 (d, J = 1.8 Hz), 28.65 (s), 25.67 (s), 22.63 (s), 14.08 (s).

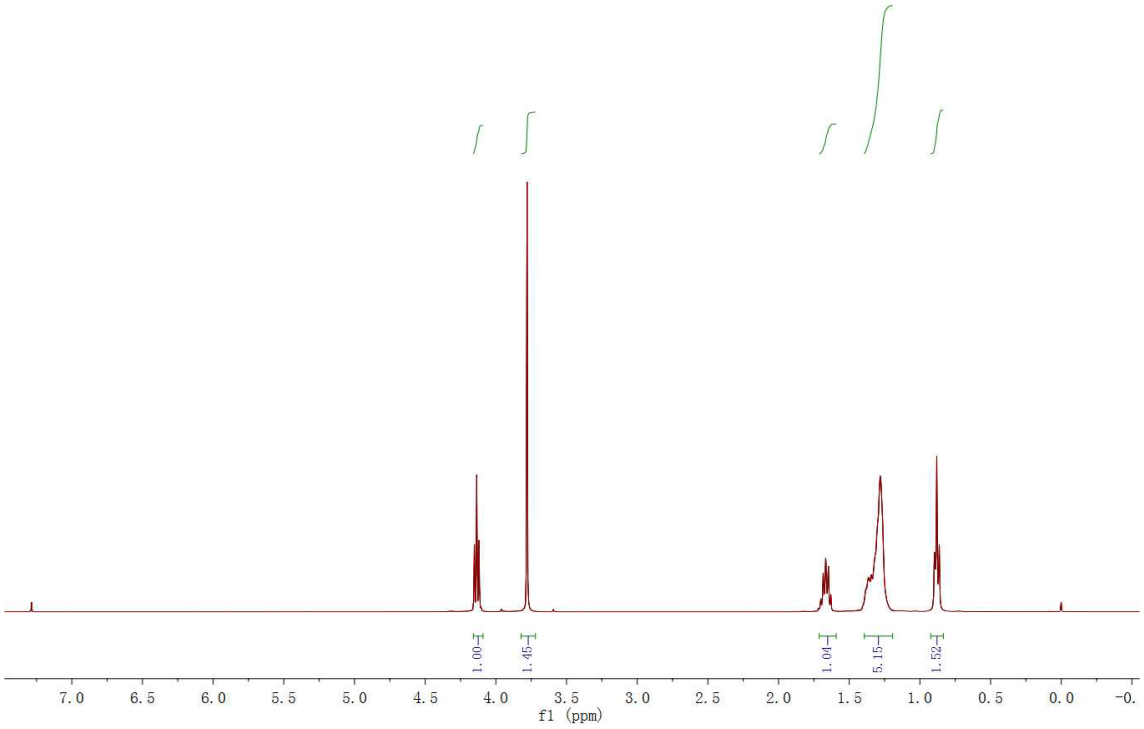


Table 2, 6

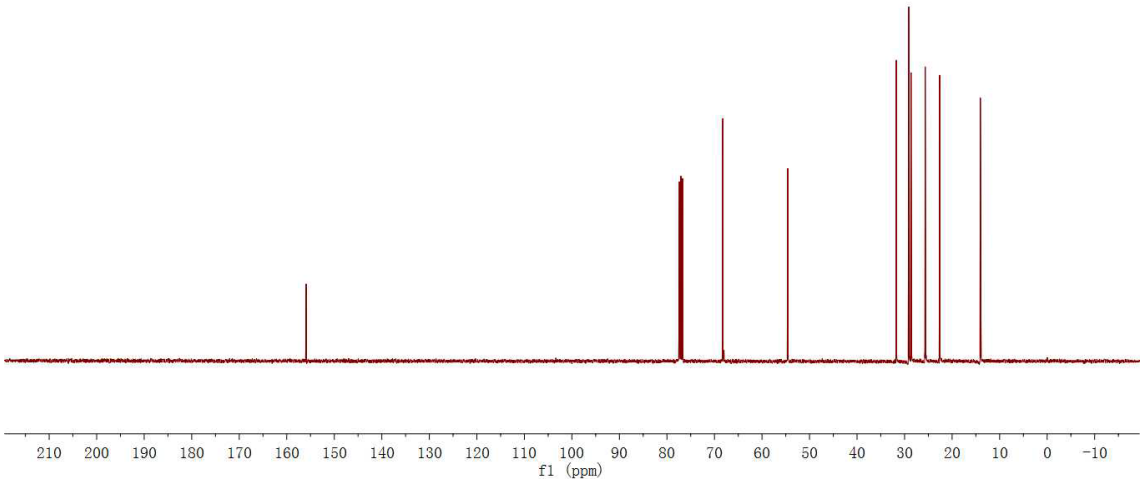
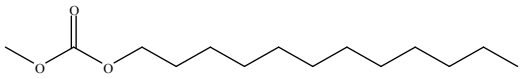


Table 2, 6


(Table 2, 7)

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 4.15 (t, 2H, -O-**CH_2**-), 3.79 (s, 3H, -O-**CH_3**), 1.73 – 1.61 (m, 2H, -O-CH_2-**CH_2**-), 1.38 – 1.24 (m, 18H, -O-$(CH_2)_2$-**$(CH_2)_6$**-), 0.89 (t, 3H, -O-$(CH_2)_8$-**CH_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 155.89 (s), 68.27 (s), 54.64 (s), 31.93 (s), 29.64(d), 29.57(s), 29.50(s), 29.36(s), 29.23(s), 28.67 (s), 25.69 (s), 22.71 (s), 14.14 (s).

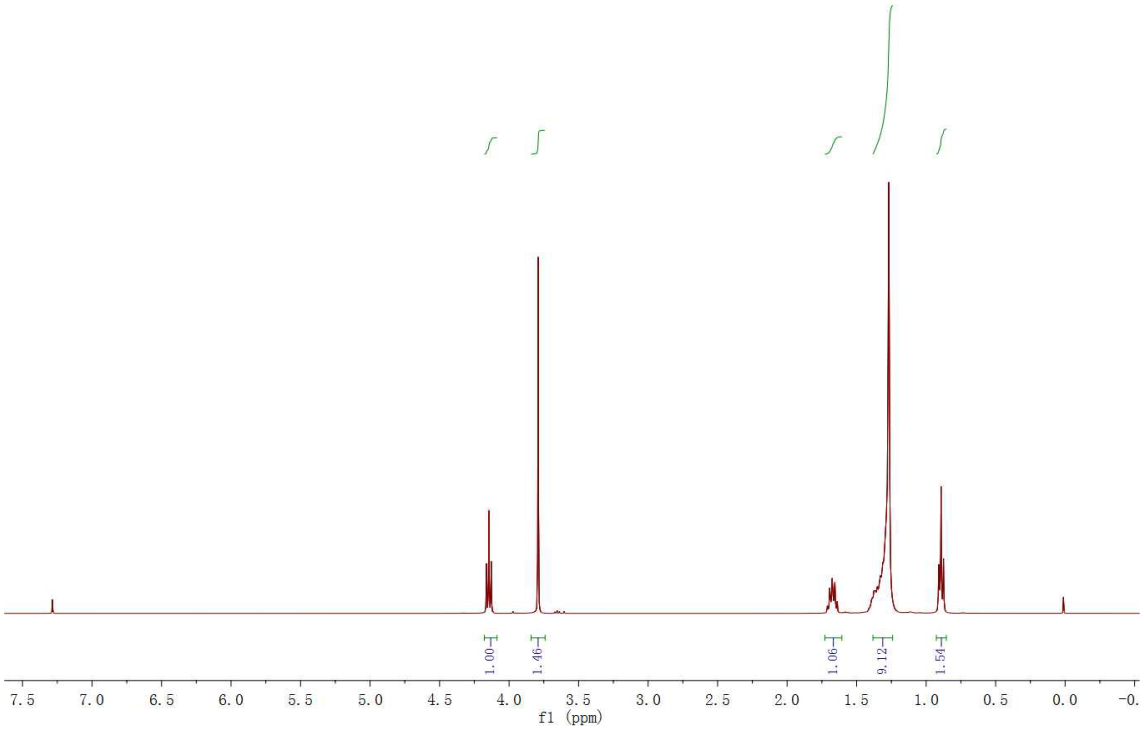


Table 2, 7

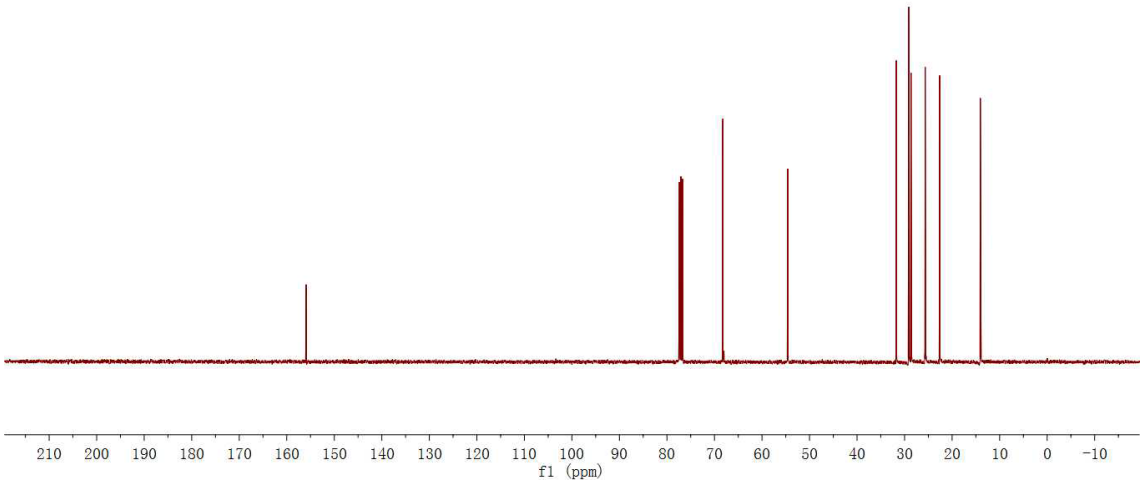
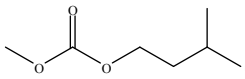


Table 2, 7



(Table 2, 9)

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 4.19 (t, 2H, -O-**CH_2**-), 3.79 (s, 3H, -O-**CH_3**), 1.72 (m, 1H, -**CH**-$(CH_3)_2$), 1.57 (q, 2H, -O-CH_2-**CH_2**-), 0.94 (d, 6H, -CH-**$(CH_3)_2$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 155.67 (s), 66.76 (s), 54.67 (s), 37.31 (s), 24.79 (s), 22.41 (s).

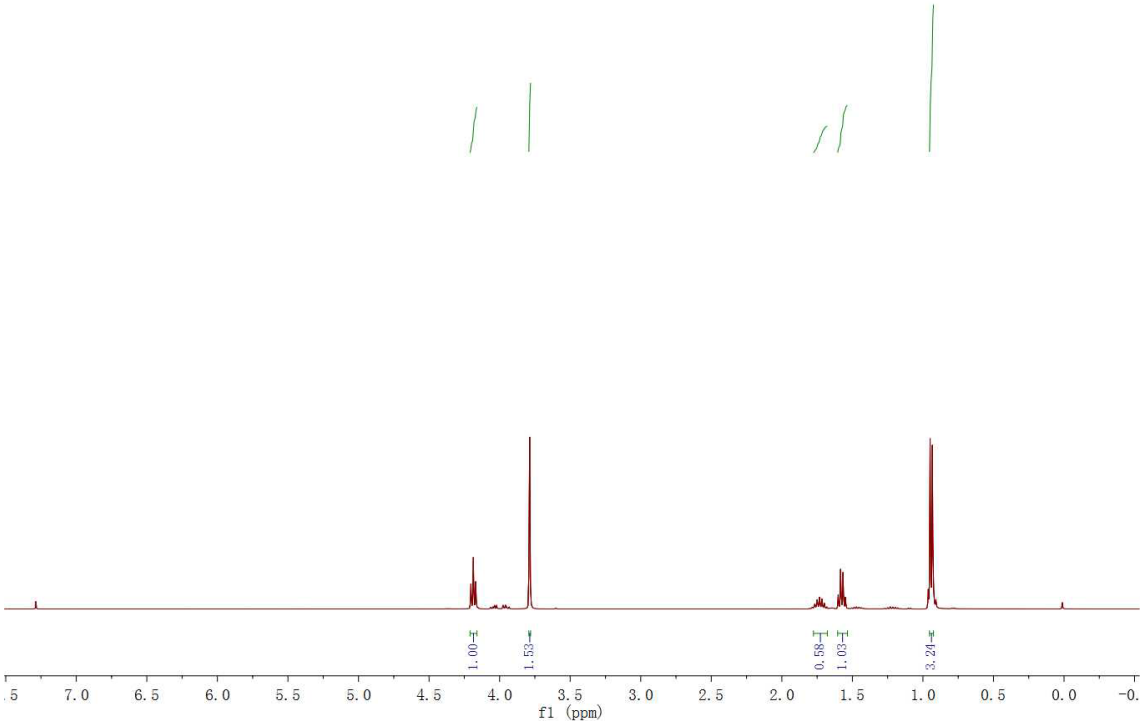


Table 2, 9

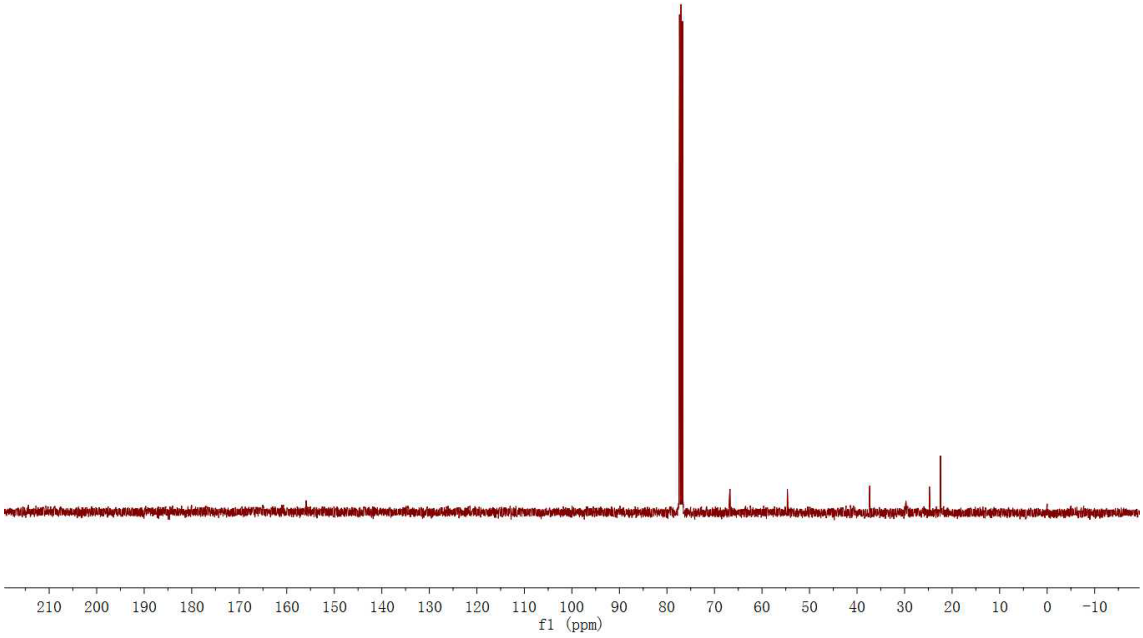
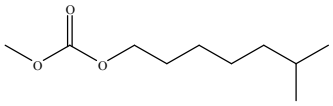


Table 2, 9



(Table 2, 10)

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 4.06 (t, 2H, -O-**CH_2**-), 3.79 (s, 3H, -O-**CH_3**), 1.68 – 1.54 (m, 1H, -**CH**-$(CH_3)_2$), 1.44 – 1.22 (m, 8H, -O-CH_2-**$(CH_2)_4$**-), 0.95 – 0.83 (m, 6H, -CH-**$(CH_3)_2$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 156.01 (s), 70.50 (s), 54.60 (s), 38.86 (s), 30.14 (s), 28.88 (s), 23.50 (s), 22.93 (s), 14.01 (s), 10.90 (s).

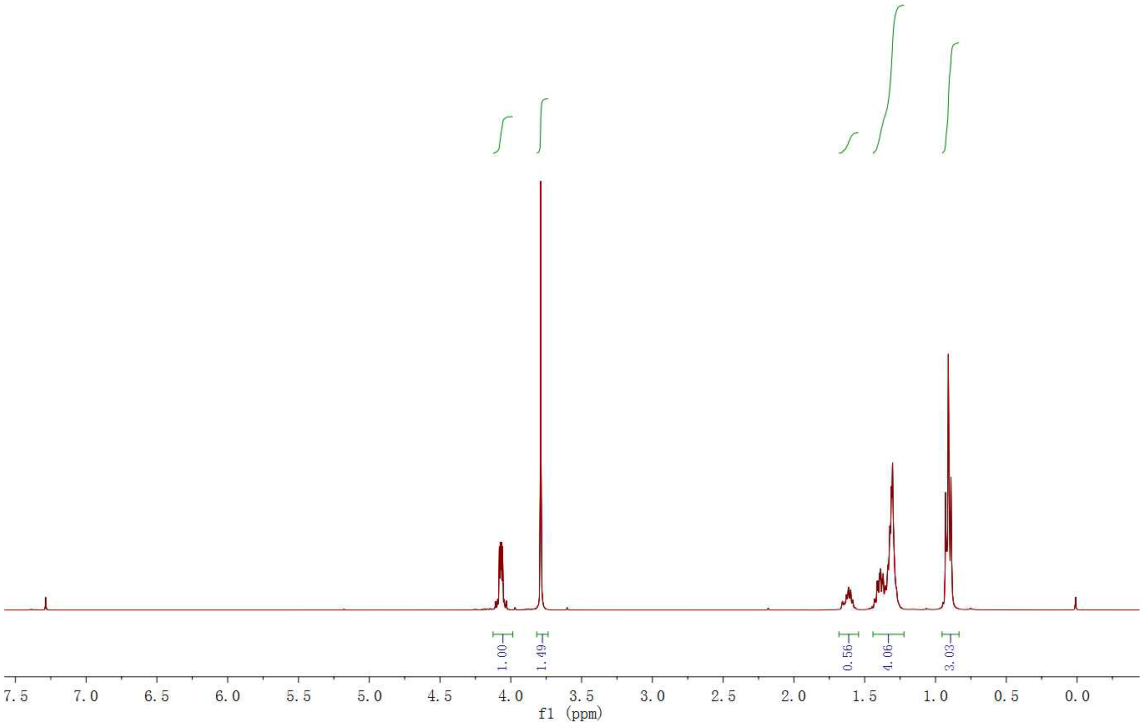


Table 2, 10

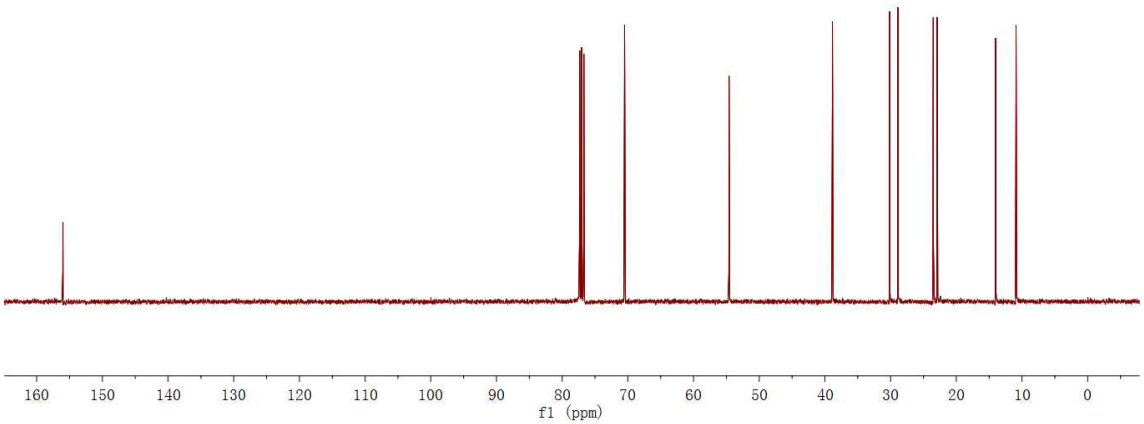
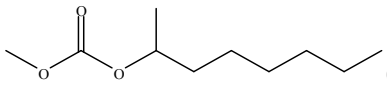


Table 2, 10



(Table 2, 11)

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 4.84 – 4.61 (m, 1H, -O-**CH**-), 3.77 (s, 3H, -O-**CH_3**), 1.36 – 1.22 (m, 10H, -O-CH-(**CH_2**)$_5$-), 1.20 (d, 3H, -O-CH-**CH_3**), 0.93 – 0.82 (m, 3H, -O-CH-(CH_2)$_5$- **CH_3**).

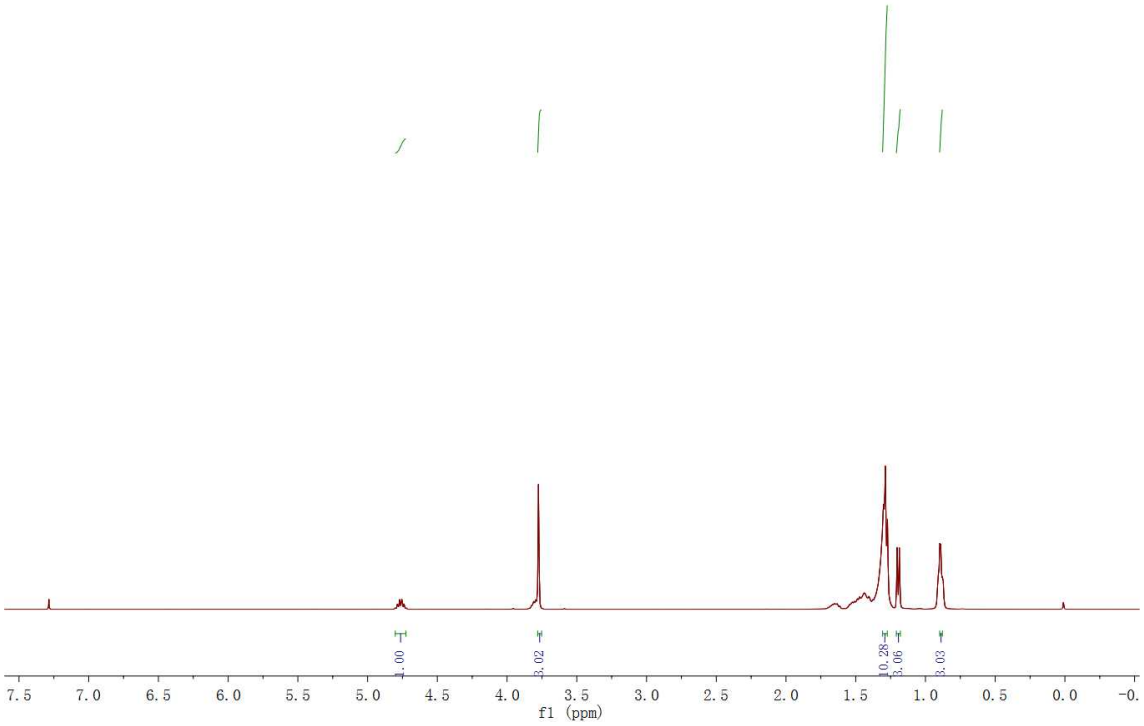
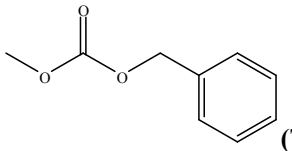


Table 2, 11



(Table 2, 13)

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.48 – 7.31 (m, 5H, -O-CH_2-**CH_5**), 5.20 (s, 2H, -O-**CH_2**-CH_5), 3.82 (s, 3H, -O-**CH_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 155.74 (s), 135.27 (s), 128.57 (d, J = 6.5 Hz), 128.30 (s), 69.65 (s), 54.87 (s).

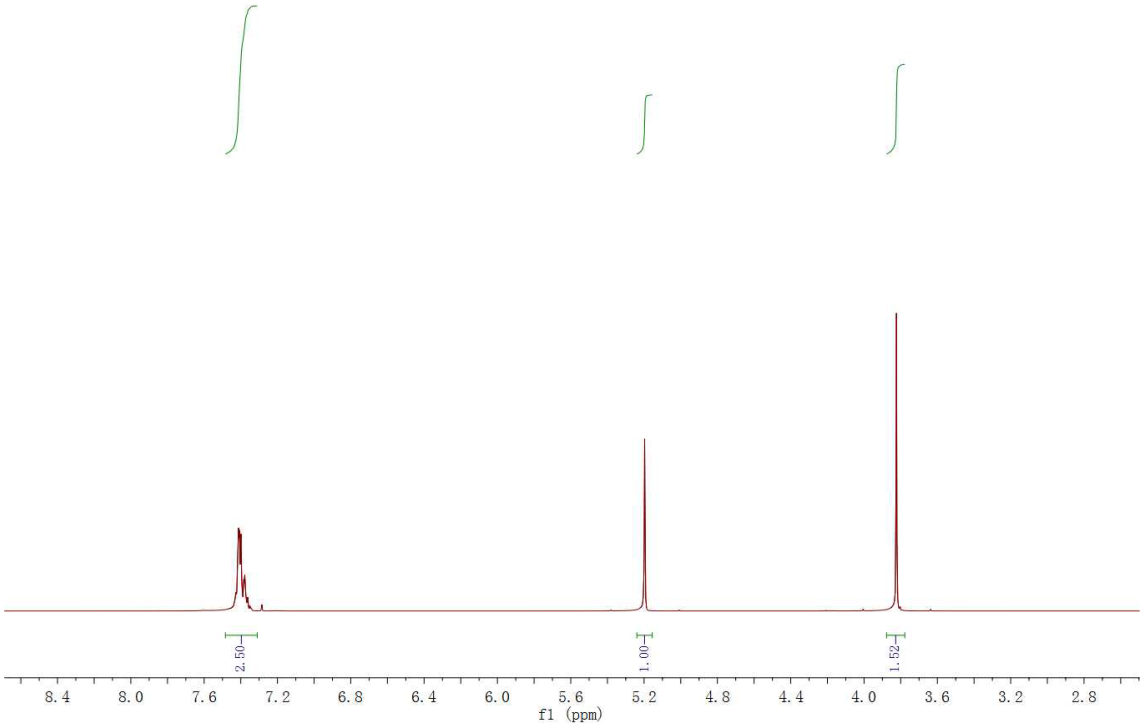


Table 2, 13

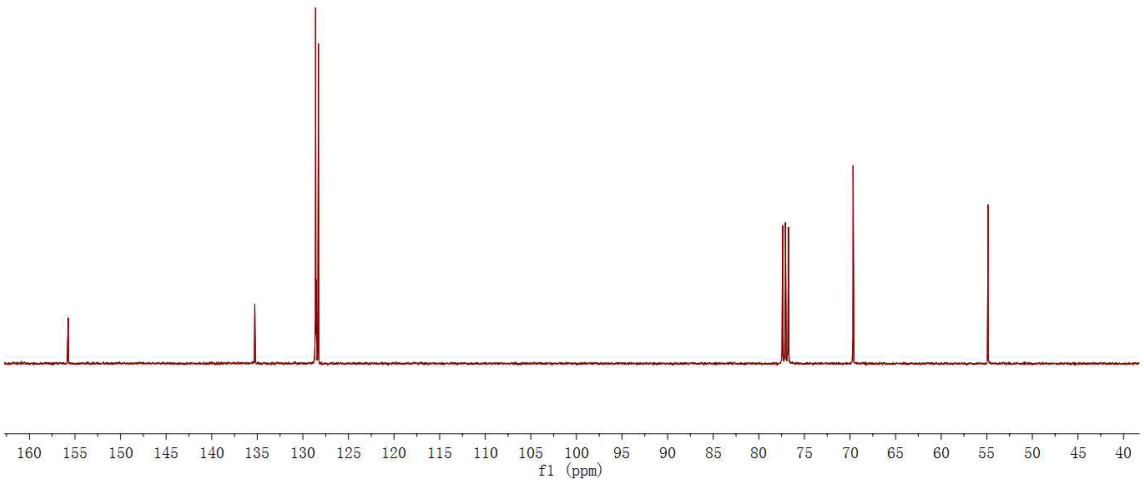
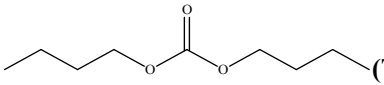


Table 2, 13

Example of The ^{1}H and ^{13}C NMR spectra for the by-product



(Table 2, 2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15(ppm): (t, 4H, -O-**CH_2**-), 1.66 (m, 4H, -O-CH_2-**CH_2**-), 1.41 (m, 4H, -O-$(CH_2)_2$-**CH_2**-), 0.95 (t, 6H, -O-$(CH_2)_3$-**CH_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.45 (s), 67.73 (s), 30.69 (s), 18.93 (s), 13.67 (s).

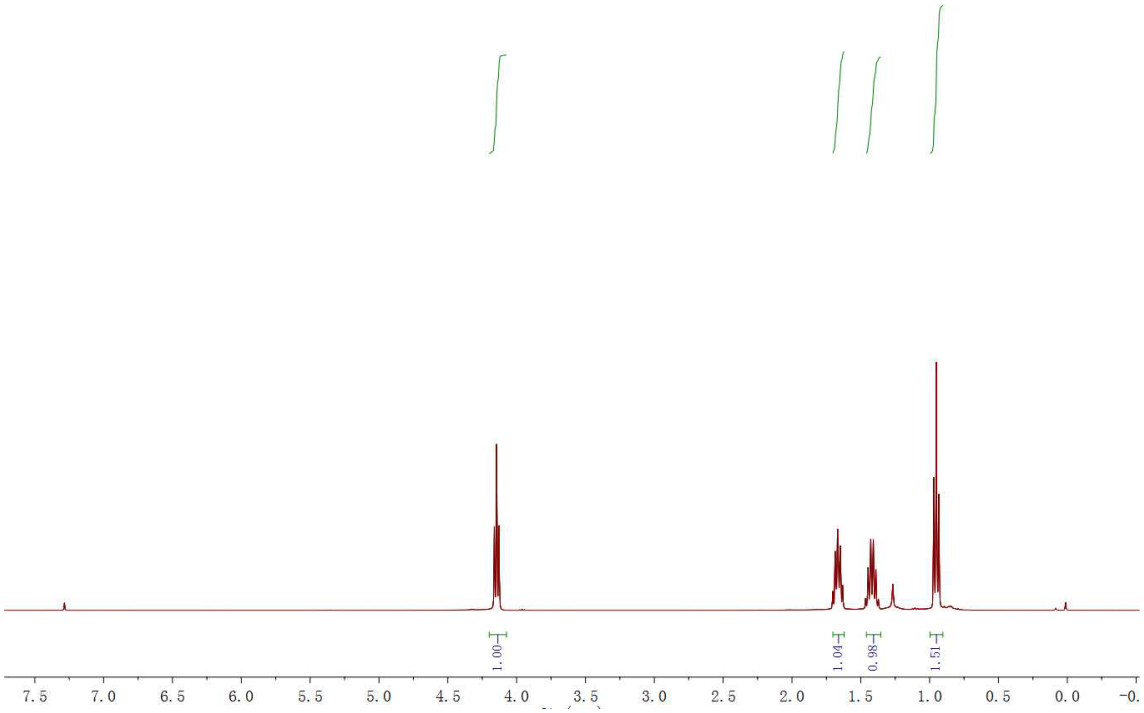


Table 2, 2

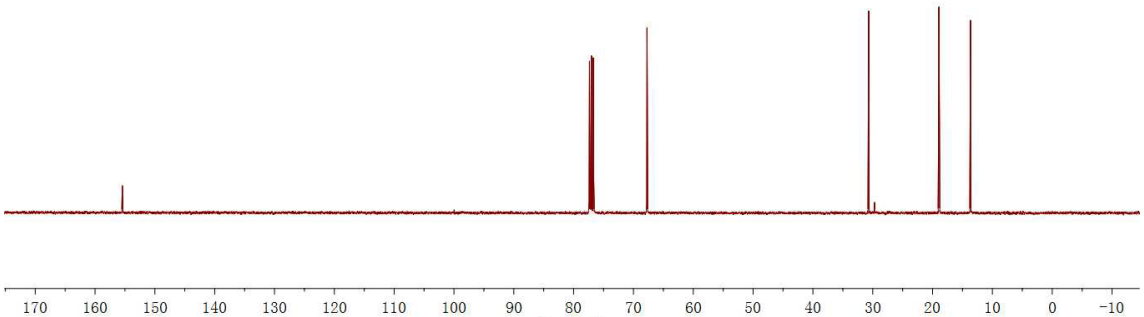


Table 2, 2