Electronic Supplementary Material (ESI) for Polymer Chemistry.

Study of cyclic carbonate aminolysis at room temperature: effect of cyclic carbonates structure and solvent on polyhydroxyurethane synthesis

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1. General information

Materials

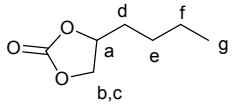
2,2'-(ethane-1,2-diylbis(oxy))bis(ethan-1-amine) noted JEFFAMINE® EDR-148 was obtained from Huntsman. 1,2-epoxyhexane, ethyl glycidyl ether, 1,2-epoxy-3-phenoxypropane, ethyl 2,3-epoxypropionate, 4-(hydroxymethyl)-1,3-dioxolan-2-one (Glycerin Carbonate noted GC), acetic anhydride, benzoyl chloride, 1,1,1-tris(hydroxymethyl)propane (TMP), *p*-toluene sulfonic acid (APTS), 3,5,5-trimethylhexanoyl chloride, ethyl chloroformate, trimethylolpropane allyl ether (TMPAE), 2,2-bis(hydroxymethyl)propionic acid (Bis-MPA), amberlyst® 15, carbon disulfide (CS_2), 1,4-butanediol diglycidyl ether, 1,3-dibutylurea, N-methylacetamide lithium bromide (LiBr), anhydrous magnesium sulfate ($MgSO_4$), pyridine, trimethylamine (Et_3N), sodium bicarbonate ($NaHCO_3$), calcium oxide (CaO), benzophenone, potassium carbonate (K_2CO_3), hydrochloric acid (HCl 1M), dimethylformamide (DMF), ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2), acetone, methanol, ethanol, tetrahydrofuran (THF) and chloroform were purchased from Sigma Aldrich. Deuterated solvents ($CDCl_3$, Methanol-d_4, DMSO-d_6, DMF-d_7, THF-d_8) were purchased from Euriso-top (Saint-Aubin, France).

2. Nuclear Magnetic Resonance

Chemical structures of the molecules were determined by ^1H, Chemical structures of the molecules were determined by ^1H, ^{13}C, COSY, HSQC, HMBC NMR spectroscopy using a Bruker Advance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. External reference was tetramethylsilane (TMS). Shifts were given in ppm. NMR samples were prepared as follows: around 10 mg of product for ^1H, ^{13}C, COSY, HSQC, and HMBC experiment in around 0.5 mL of $CDCl_3$ or DMSO-d_6.

1. Synthesis of cyclic carbonate and gudroxyurethane

Synthesis of 4-butyl-1,3-dioxolan-2-one: C_5-Butane and a general procedure for epoxy carbonation

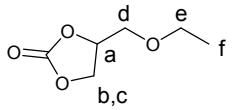


In a round-bottom flask (100 mL), 1,2-epoxyhexane (5.00 g, 49.92 mmol) and LiBr (0.22 g, 0.25 mmol) were dissolved in DMF (30 mL). The solution was introduced into a reactor and the atmosphere was replaced with CO2 (P=15 bar). The solution was then allowed to stand at 80°C with continuous stirring for 12 h. DMF was removed by distillation under vacuum (70°C, P= 10 mbar). The crude product was dissolved in ethyl acetate (50 mL) and washed three times with brine. Organic layers were collected, dried over anhydrous magnesium sulphate and concentrated under vacuum. The pure product C_5-Butane was obtained quantitatively as an orange liquid with 91% yield (^1H and ^{13}C NMR spectra, SI-Figure 1 and SI-Figure 2).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.61 (*m*, 1H, H_a), 4.43 (*dd*, 1H, *J* = 8.2, 8.2 Hz, H_b), 3.96 (*dd*, 1H, *J* = 8.4, 7.2 Hz, H_c), 1.78 – 1.49 (*m*, 2H, H_d), 1.41 – 1.15 (*m*, 4H, H_{ef}), 0.80 (*t*, 3H, *J* = 7.0 Hz, H_g)

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 155.0, 77.0, 69.3, 33.2, 26.2, 22.0, 13.5.

Synthesis of 4-ethoxy-1,3-dioxolan-2-one: C_5-Ethyl-Ether

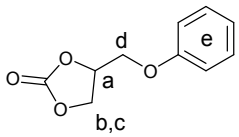


C5-Ethyl-Ether was synthesized from ethyl glycidyl ether (5.00 g, 48.96 mmol) and LiBr (0.21 g, 2.45 mmol). The pure product C5-Ethyl-Ether was obtained quantitatively as an orange liquid with 93% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 3 and SI Figure 4).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.76 (*m*, 1H, H_a), 4.44 (*m*, 1H, H_b), 4.29 (*m*, 1H, H_c), 3.73 – 3.36 (*m*, 4H, H_{de}), 1.12 (*t*, 3H, *J* = 7.0 Hz, H_f).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 155.1, 75.2, 69.2, 67.2, 66.2, 14.8.

Synthesis of 4-phenoxy-1,3-dioxolan-2-one: C_5-Phenyl-Ether

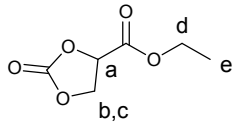


C5-Phenyl-Ether was synthesized from 1,2-epoxy-3-phenoxypropane (7.00 g, 46.61 mmol) and LiBr (0.20 g, 2.33 mmol). The pure product C5-Phenyl-Ether was obtained quantitatively as an orange liquid with 92% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 5 and SI-Figure 6).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.31 (*m*, 2H, H_e), 7.01 (*m*, 1H, H_e), 6.91 (*m*, 1H, H_e), 5.02 (*m*, 1H, H_a), 4.61 (*dd*, 1H *J* = 8.4, 8.4 Hz, H_b), 4.53 (*dd*, 1H, *J* = 8.5, 5.9 Hz, H_c), 4.18 (*m*, 1H, H_d).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 158.0, 155.0, 129.9, 122.2, 114.8, 74.4, 67.1, 66.4.

Synthesis of ethyl 2-oxo-1,3-dioxolane-4-carboxylate: C_5-Ethyl-Ester

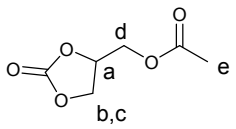


C5-Ethyl-Ester was synthesized from ethyl 2,3-epoxypropionate (5.00 g, 43.06 mmol) and LiBr (0.19 g, 2.15 mmol). The pure product C5-Ethyl-Ester was obtained quantitatively as a brown liquid with 91% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 7 and SI-Figure 8).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.08 (*dd*, 1H, *J* = 9.0, 5.4 Hz, H_a), 4.67 (*dd*, 1H *J* = 9.0, 9.0 Hz, H_b), 4.49 (*dd*, 1H *J* = 8.9, 5.4 Hz, H_c), 4.28 (*q*, 2H, *J* = 7.2 Hz, H_d), 1.29 (*t*, 4H *J* = 7.1 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 167.43, 153.98, 72.46, 66.95, 62.90, 13.99.

Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl acetate: C_5-Acetate

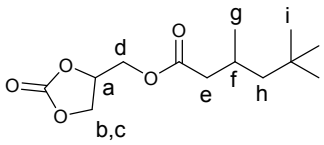


In a two-neck bottom-flask (50 mL), 4-(hydroxymethyl)-1,3-dioxolan-2-one (3 g, 25.40 mmol) and pyridine (2.21 g, 27.94 mmol) were dissolved in dry dichloromethane (15 mL). Acetic anhydride (2.85 g, 27.94 mmol) dissolved in dichloromethane (15 mL) were added dropwise to the mixture. The reaction was then allowed to stand at room temperature with continuous stirring for 12h. The crude mixture was washed twice with brine, dry over anhydrous magnesium sulfate and concentrated under vacuum. The pure product C5-Acetate was obtained quantitatively as a transparent liquid with 93% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 9 and SI-Figure 10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.87 (*m*, 1H, H_a), 4.48 (*dd*, 1H, *J* = 8.7, 8.7 Hz, H_b), 4.18 (*m*, 3H, H_{cd}), 1.98 (*s*, 3H, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 170.2, 154.5, 73.8, 65.8, 62.8, 20.2.

Synthesis of (2-oxo-1,3-dioxoloan-4-yl)methyl 3,5,5-tremethylhexanoate: C_5-Trimethylhexanoate

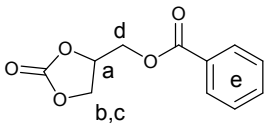


In a two-neck round-bottom flask (50 mL), 4-(hydroxymethyl)-1,3-dioxolan-2-one (3.00 g, 25.40 mmol) and triethylamine (3.34 g, 33.02 mmol) were dissolved in dry dichloromethane (15mL). 3,5,5-Trimethylhexanoyle (4.94 g, 27.94 mmol) dissolved in dry dichloromethane (15mL) was added dropwise to the stirring solution under 20 minutes at 0°C under nitrogen. The reaction was allowed to go back to room temperature then stirred during 12h. The ammonium salt was filtered off and the filtrate was washed twice with saturated NaHCO3 aqueous solution then three times with deionized water, dried over anhydrous magnesium sulfate and concentrated under vacuum. The pure product C_5-Trimethylhexanoate was obtained quantitatively as a colorless liquid with 89% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 11 and SI-Figure 12).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.86 (m, 1H, H_a), 4.50 (t, 1H, H_c), 4.28-4.14 (m, 3H, H_b, H_d), 2.31-2.25 (m, 2H, H_e), 2.13 – 1.94 (m, 1H, H_f), 1.16-1.03 (dd, 2H, H_h), 0.89-0.76 (m, 13H, H_g, H_i).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 172.3, 154.5, 73.8, 62.7, 50.3, 43.3, 30.9, 29.8, 26.8, 22.4.

Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl benzoate: C_5-Benzoate

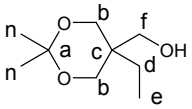


In a two-neck round-bottom flask (50 mL), 4-(hydroxymethyl)-1,3-dioxolan-2-one (3.00 g, 25.40 mmol) and triethylamine (3.34 g, 33.02 mmol) were dissolved in dry dichloromethane (15mL). Benzoyl chloride (3.93 g, 27.94 mmol) dissolved in dry dichloromethane (15mL) was added dropwise to the stirring solution under 20 minutes at 0°C under nitrogen. The reaction was allowed to go back to room temperature then stirred during 12h. The ammonium salt was filtered off and the filtrate was washed twice with saturated NaHCO3 aqueous solution then three times with deionized water, dried over anhydrous magnesium sulfate and concentrated under vacuum. The pure product C_5-Benzoate was obtained quantitatively as a white solid with 93% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 13 and SI-Figure 14).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.01 (m, 2H, H_e), 7.59 (m, 1H, H_e), 7.45 (m, 2H, H_e), 5.06 (m, 1H, H_a), 4.72 – 4.46 (m, 3H, H_{bd}), 4.42 (dd, 1H, J = 8.8, 5.7 Hz, H_c).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.0, 154.6, 133.8, 129.8, 128.8, 128.7, 74.0, 66.2, 63.8.

Synthesis of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol: Protected TMP

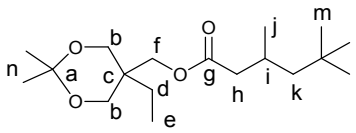


1,1,1-Tris(hydroxymethyl)propane (TMP) (100.00 g, 745.32 mmol) were dissolved in 700 mL of acetone in a round bottom-flask equipped with a condenser. When the mixture became homogeneous, paratoluene sulfonic acid (1.42 g, 7.45 mmol), was added. The medium was stirred at room temperature for 16 h. Potassium carbonate (1.03 g, 7.45 mmol) was subsequently added and left stirring at room temperature for 1h. After evaporation of acetone, the product was dissolved with 1000 mL of ethyl acetate and washed twice with deionized water. Organic layers were collected, dried over anhydrous magnesium sulfate and evaporated under vacuum. The pure product Protected TMP was obtained quantitatively as colorless liquid with 98% of yield (^{1}H and ^{13}C NMR spectra, SI-Figure 15 and SI-Figure 16).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.68 – 3.41 (*m*, 6H, H_{bf}), 3.22 (*s*, 1H, OH), 1.32 (*m*, 6H, H_g), 1.22 (*q*, 2H, J = 7.6 Hz, H_d), 0.75 (*t*, 3H, J = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 98.1, 65.0, 62.1, 36.9, 27.1, 23.6, 20.3, 7.0.

Synthesis of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methyl 3,5,5-trimethylhexanoate: Esterified Protected TMP 1 and a general procedure for esterified TMP-Protected

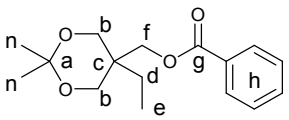


In a three-neck round-bottom flask (250 mL), Protected TMP (10.00 g, 57.39 mmol) and triethylamine (6.39 g, 63.13 mmol) were dissolved in 90 mL of dry dichloromethane. The mixture was immersed in an ice bath under nitrogen atmosphere. 3,5,5-Trimethylhexanoyl chloride (11.15 g, 63.13 mmol) was added dropwise to the solution, with continuous stirring for 20 minutes. The reaction was then placed at room temperature for 12 hours. At the end of reaction, the solution was filtered and the filtrate was washed twice with saturated NaHCO3 aqueous solution then three times with deionized water, dried over anhydrous magnesium sulfate and concentrated under vacuum. The pure product Esterified Protected TMP 1 was obtained quantitatively as colorless liquid with 71% of yield (^{1}H and 13C spectra, SI-Figure 17 and SI-Figure 18).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.10 (*m*, 2H, H_f), 3.57 (*m*, 4H, H_b), 2.25 (*m*, 1H, H_h), 2.06 (*dd*, 1H, *J* = 14.4, 8.2 Hz, H_h), 1.96 (*m*, 1H, H_i), 1.32 (*d*, 6H, *J* = 12.0 Hz, H_n), 1.25 (*m*, 2H, H_d), 1.10 (*m*, 2H, H_k), 0.90 (*d*, 3H, *J* = 6.6 Hz, H_j), 0.82 (*s*, 9H, H_m), 0.75 (*t*, 2H, *J* = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 172.87, 98.08, 64.97, 63.62, 50.43, 43.90, 35.70, 30.93, 29.85, 27.00, 26.45, 23.89, 22.60, 20.76, 6.89.

Synthesis of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methyl benzoate: Esterified Protected TMP 2

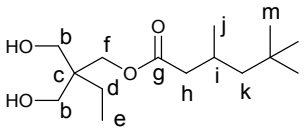


Esterified Protected TMP 2 was synthesized from Protected TMP (15.00 g, 86.09 mmol) and benzoyl chloride (18.15 g, 129.13 mmol). The crude Esterified Protected TMP 2 was obtained as yellow liquid with 98% yield. Remaining benzoyl chloride is visible on the 1H and 13C NMR spectra (^{1}H and ^{13}C NMR spectra, SI-Figure 19 and SI-Figure 20).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.01 (*m*, 2H, H_h), 7.51 (*m*, 1H, H_h), 7.40 (*m*, 2H, H_h), 4.44 (*s*, 2H, H_f), 3.73 (*m*, 4H, H_b), 1.52 – 1.27 (*m*, 8H, H_{dn}), 0.86 (*t*, 3H, *J* = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.4, 133.2, 129.8, 128.4, 98.3, 65.2, 64.5, 36.2, 26.9, 24.2, 20.6, 7.1.

Synthesis of 2,2-bis(hydroxymethyl)butyl 3,5,5-trimethylhexanoate: Esterified TMP 1 and a general procedure for deproctection of Esterified Protected TMP

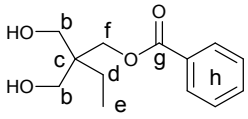


In a round-bottom flask (100 mL) equipped with a refrigerating apparatus, Esterified Protected TMP 1 (8 g, 35.04 mmol), methanol (20 mL) and aqueous hydrochloric acid (1M) (4 mL) were introduced. The reaction proceeds at 40°C for 24h with continuous stirring. The methanol was removed under vacuum and the crude product was dissolved in ethyl acetate (100 mL) and washed with deionized water until pH=7. Organic layers were collected, dried over magnesium sulfate, and evaporated under vacuum. The pure product Esterified TMP 1 was obtained quantitatively as colorless liquid with 74% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 21 and SI-Figure 22).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.06 (*m*, 2H, H_f), 3.50 (*s*, 4H, H_b), 2.30 (*dd*, 1H, *J* = 14.6, 5.7 Hz, H_h), 2.11 (*dd*, 1H, *J* = 14.6, 8.3 Hz, H_h), 1.98 (*m*, 1H, H_i), 1.27 (*q*, 2H, *J* = 7.6 Hz, H_d), 1.13 (*m*, 2H, H_k), 1.00 – 0.71 (*m*, 15H, H_{ejm}).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 174.1, 65.1, 63.9, 50.5, 43.9, 42.7, 31.0, 29.9, 29.9, 27.0, 22.6, 22.3, 7.3.

Synthesis of 2,2-bis(hydroxymethyl)butyl benzoate: Esterified TMP 2

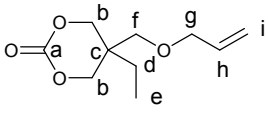


Esterified TMP 2 was synthesized from Esterified Protected TMP 2 (15.00 g, 54.08 mmol), 7.5 mL of HCl 1M and 37.5 mL of methanol. The pure product Esterified Protected TMP 2 was obtained quantitatively as yellow liquid with 88% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 23 and SI-Figure 24).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.99 (*dd*, 2H *J* = 8.2, 1.1 Hz, H_h), 7.53 (*m*, 1H, H_h), 7.39 (*m*, 2H, H_h), 4.35 (*s*, 2H, H_f), 4.12 (*brs*, 2H, OH), 3.34 (*m*, 4H, H_b), 1.40 (*q*, 2H, *J* = 7.6 Hz, H_d), 0.89 (*t*, 3H, *J* = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 167.2, 1332, 129.8, 129.6, 128.4, 65.0, 64.5, 43.0, 22.5, 7.4.

Synthesis of 5-((allyloxy)methyl)-5-ethyl-1,3-dioxan-2-one: C_6-Allyl-Ether and general procedure for carbonate ring formation

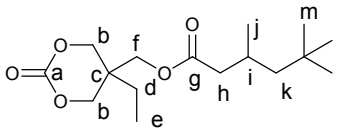


Ethyl chloroformate (6.22 g, 57.39 mmol) was added dropwise to a solution of trimethylolpropane allyl ether (TMPAE) (5.00 g, 28.70 mmol) and triethylamine (6.39 g, 63.13 mmol) in 200 mL of dried THF at 0°C over a period of 30 min. The reaction mixture was then stirred at room temperature for 2 h. The precipitated triethylamine hydrochloride was filtrated off, and the filtrate was concentrated under vacuum. Then, the crude was diluted with ethyl acetate (300 mL) and washed two times with aqueous hydrochloric acid (1M) and two times with deionized water. Organic phase was dried over anhydrous magnesium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography (eluent 20/80 ethyl acetate/cyclohexane). The pure product C6-Allyl-Ether was obtained quantitatively as colorless liquid with 74% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 25 and SI-Figure 26).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.76 (*m*, 1H, H_h), 5.13 (*m*, 2H, H_i), 4.14 (*m*, 4H, H_b), 3.88 (*m*, 2H, H_g), 3.31 (*s*, 2H, H_f), 1.44 (*q*, 2H, J = 7.6 Hz, H_d), 0.82 (*t*, 3H, J = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 148.4, 133.9, 117.1, 72.6, 72.1, 68.0, 35.2, 23.0, 7.1.

Synthesis of (5-ethyl-2-oxo-1,3-dioxan-5-yl)methyl 3,5,5-trimethylhexanoate: C_6-Trimethylhexanoate

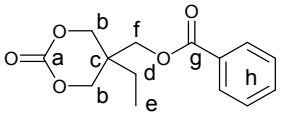


C6-Trimethylhexanoate was synthesized from Esterified TMP 1 (5.00 g, 18.22 mmol), triethylamine (4.05 g, 40.08 mmol) and ethyl chloroformate (3.95 g, 36.44 mmol). The pure product C6-Trimethylhexanoate was obtained quantitatively as yellow liquid with 76% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 27 and SI-Figure 28).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.19 (*m*, 4H, H_b), 4.04 (*m*, 2H, H_f), 2.28 (*dd*, 1H, J = 14.8, 5.9 Hz, H_h), 2.10 (*dd*, 1H, J = 14.8, 8.2 Hz, H_h), 1.95 (*m*, 1H, H_i), 1.47 (*q*, 2H, J = 7.6 Hz, H_d), 1.11 (*m*, 2H, H_k), 0.95 – 0.74 (*m*, 15H, H_{ejm}).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 172.4, 147.9, 72.4, 72.39, 62.3, 50.3, 43.4, 34.4, 30.9, 29.8, 26.8, 23.2, 22.5, 7.1.

Synthesis of (5-ethyl-2-oxo-1,3-dioxan-5-yl)methyl benzoate: C_6-Benzoate

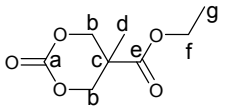


C6-Benzoate was synthesized from Esterified TMP 2 (5.00 g, 20.98 mmol), triethylamine (4.67 g, 46.16 mmol) and ethyl chloroformate (4.55 g, 41.97 mmol). The pure product C6-Benzoate was obtained quantitatively as yellowish solid after recrystallization in cyclohexane with 33% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 29 and SI-Figure 30).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.01 (*m*, 2H, H_h), 7.59 (*m*, 1H, H_h), 7.47 (*m*, 2H, H_h), 4.37 (*s*, 2H, H_f), 4.35 (*m*, 4H, H_b), 1.64 (*q*, 2H, *J* = 7.6 Hz, H_d), 1.00 (*t*, 3H, *J* = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.0, 148.1, 133.6, 129.7, 129.2, 128.7, 72.6, 63.2, 35.1, 23.7, 7.5.

Synthesis of ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate:C_6-Ethyl-Ester

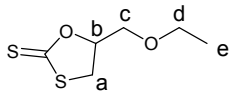


2,2-bis(hydroxymethyl)propionic acid (Bis-MPA) (10.00 g, 74.55 mmol) was added at solution of ethanol (70 mL) and Amberlyst-15 (3 g). After 12 hours of reaction at 80°C, the solution was filtered and the filtrate was evaporated. Dichloromethane (200 mL) was added to the resulting viscous liquid and the solution was washed 3 times with brine to remove the unreacted reagents and byproducts. The solution was then dried over anhydrous magnesium sulfate and concentrated under vacuum The crude was added at solution of dried THF (80 mL) and trimethylamine (2.2 equivalent) at 0°C. Ethyl chloroformate (2.0 equivalents) dissolved in dried THF was added dropwise. After 4 hours of reaction at 0°C, the mixture was filtered and the filtrate was concentrated under reduced pressure. Then, the crude was diluted with ethyl acetate and washed two times with aqueous hydrochloric acid (1M) and two times with deionized water. Organic phase was dried over anhydrous magnesium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography (eluent 20/80 ethyl acetate/cyclohexane). The pure product C6-Ethyl-Ester was obtained quantitatively as colorless liquid with 69% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 31 and SI-Figure 32).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.66-4.19 (*m*, 4H, H_b), 4.21 (*q*, 2H, H_f), 2.28 (*dd*, 1H, *J* = 14.8, 5.9 Hz, H_h), 2.10 (*dd*, 1H, *J* = 14.8, 8.2 Hz, H_h), 1.95 (*m*, 1H, H_i), 1.27 (s, 3H, H_d), 1.25 (*t*, 3H, H_g).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 171.3, 147.8, 73.2, 62.4, 40.2, 17.6, 14.1.

Synthesis of 5-(ethoxymethyl)-1,3-oxathiolane-2-thione: C_s-Ethyl-Ether

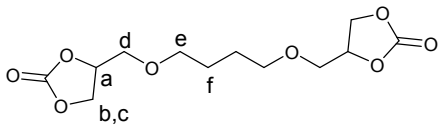


In a two-neck round-bottom flask (50 mL), ethyl glycidyl ether (5.00 g, 48.96 mmol) and carbon disulfide (4.1 g, 53.85 mmol) were introduced at 0°C with a catalytic amount of LiBr (0.21 g, 2.45 mmol) in THF (9 mL). After 20 min, the reaction was allowed to proceed at room temperature for 24 h. The mixture was then poured in ethyl acetate and washed three times with deionized water. The organic phase was dried over magnesium sulfate prior to the evaporation of the solvent under vacuum to obtain the pure product as yellowish liquid with 85% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 33 and SI-Figure 34).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.14 (*m*, 1H, H_b), 3.77 – 3.31 (*m*, 6H, H_{acd}), 1.08 (*t*, 3H, *J* = 8.4, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 212.0, 89.4, 68.7, 66.8, 35.6, 14.6.

Synthesis of 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one): Bis-C_5-Ether

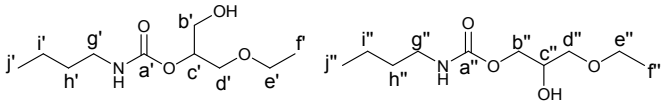


Bis-C_5-Ether was synthesized according to the general procedure for epoxy carbonation, 1,4-butanediol diglycidyl ether (20.00 g, 98.89 mmol) and LiBr (0.43 g, 4.94 mmol). The pure product Bis-C_5-Ether was obtained quantitatively as a white waxy solid with 95% yield (^{1}H and ^{13}C NMR spectra, SI-Figure 35 and SI-Figure 36).

^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) = 4.91 (*m*, 2H, H_a), 4.52(*t*, 2H, *J*=8.4 Hz, H_b), 4.25 (*dd,* 2H, *J*=8.3 Hz, *J*=5.9 Hz, H_c), 3.59 (*m*, 4H, H_d), 3.46 (*m*, 4H, H_e), 1.54 (*m*, 4H, H_f)

^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) = 155.0, 75.5, 70.5, 69.5, 66.11, 25.6.

Synthesis of hydroxyurethane compound models

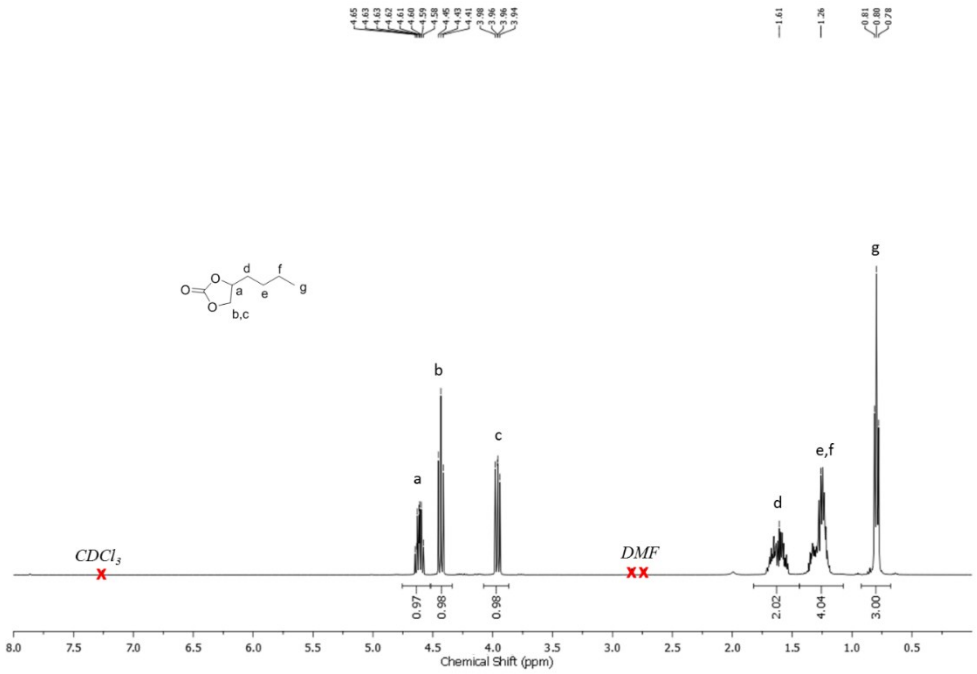


In a round-bottom flask (10 mL), C_5-Ethyl-Ether (0.300 g, 2.00 mmol, 1.00 eq), benzophenone (0.010 g) and butylamine (0.146 g, 2.00 mmol, 1.00 eq) were stirred in 2 mL of chloroform or methanol during 24 hours at room temperature (25°C) (^{1}H and ^{13}C NMR spectra, Figure 28 and Figure 29).

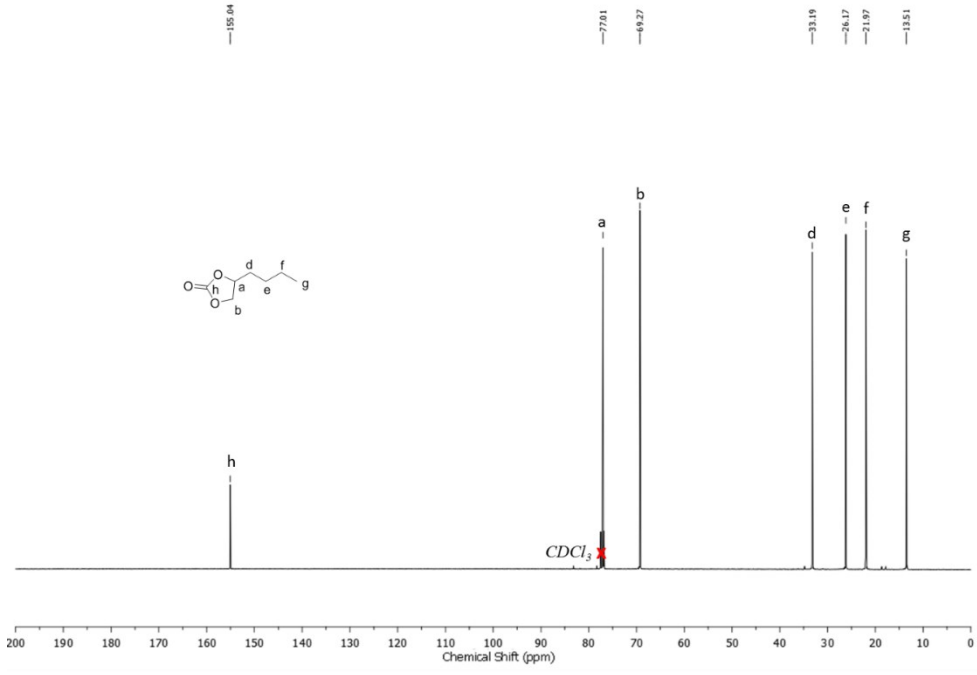
^{1}H NMR (400 MHz, *CDCl*$_3$) δ (ppm) = 4.73 (*m*, 1H, $H_{b'}$), 4-10 – 3.90 (*m*, 2H, $H_{b''}$), 3.84 (*m*, 1H, $H_{c''}$), 3.62 (*m*, 2H, $H_{b''}$), 3.57 – 3.22 (*m*, 8H, $H_{e',e'',d',d''}$), 3.02 (td, 4H, $H_{g',g''}$), 1.43 – 1.14 (*m,* 8H, $H_{h', h'', i',}$), 1.06 (*m*, 6H, $H_{f', f''}$), 0.78 (*t*, 6H, $H_{j', j''}$).

^{13}C NMR (100 MHz, *CDCl*$_3$) δ (ppm) = 156.4, 156.0, 73.3, 70.9, 68.9, 68.5, 66.3, 65.7, 61.6, 40.2, 31.4, 19.3, 14.5, 13.3.

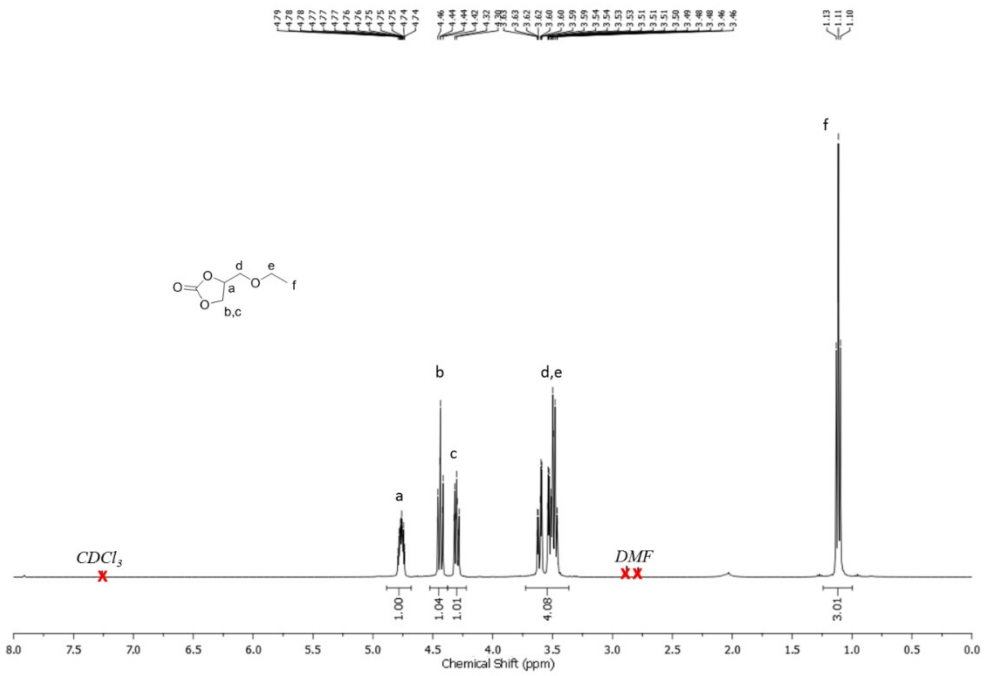
3. Graphical data of mono-cyclic carbonates and bis-cyclic carbonates



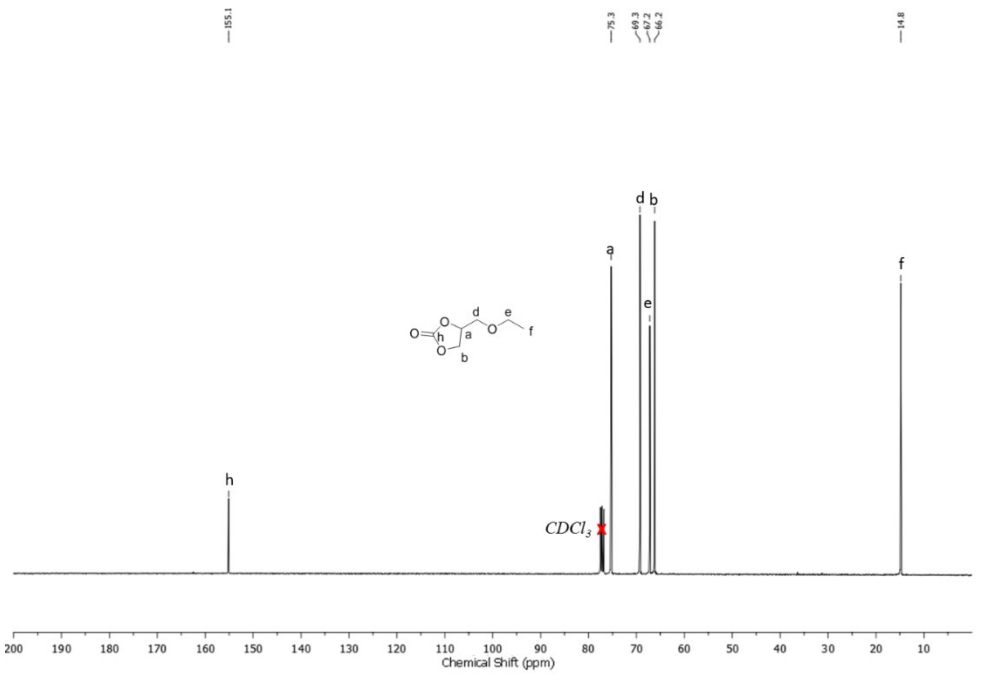
SI-Figure 1: ^{1}H NMR spectrum of C_5-Butane in CDCl3



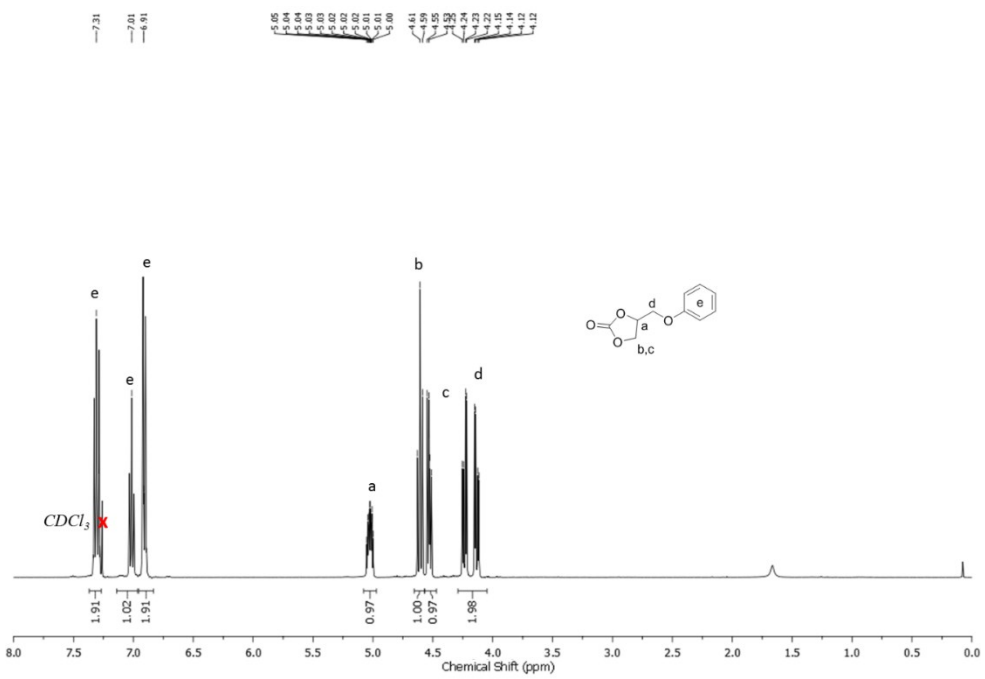
SI-Figure 2 : ^{13}C NMR spectrum of C5-Butane in CDCl3



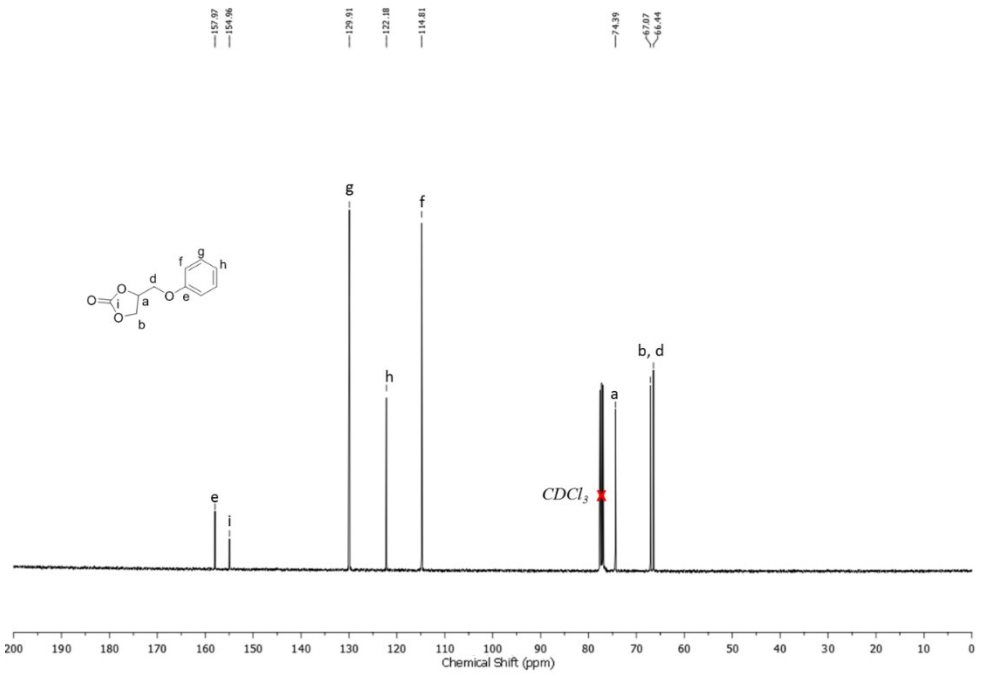
SI-Figure 3 : ^{1}H NMR spectrum of C_5-Ethyl-Ether in $CDCl_3$



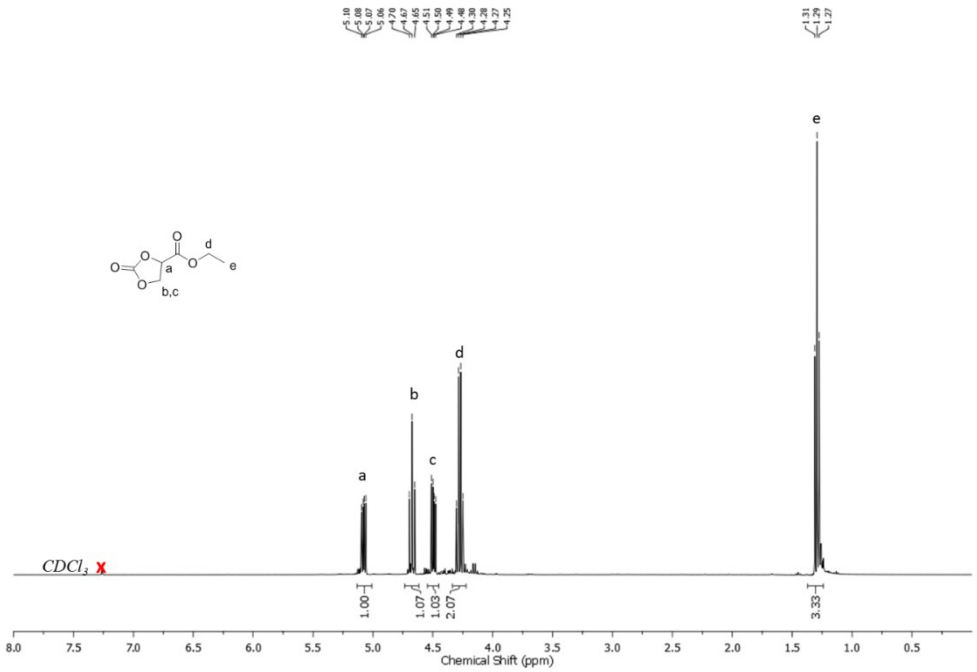
SI-Figure 4 : ^{13}C NMR spectrum of C_5-Ethyl-Ether in $CDCl_3$



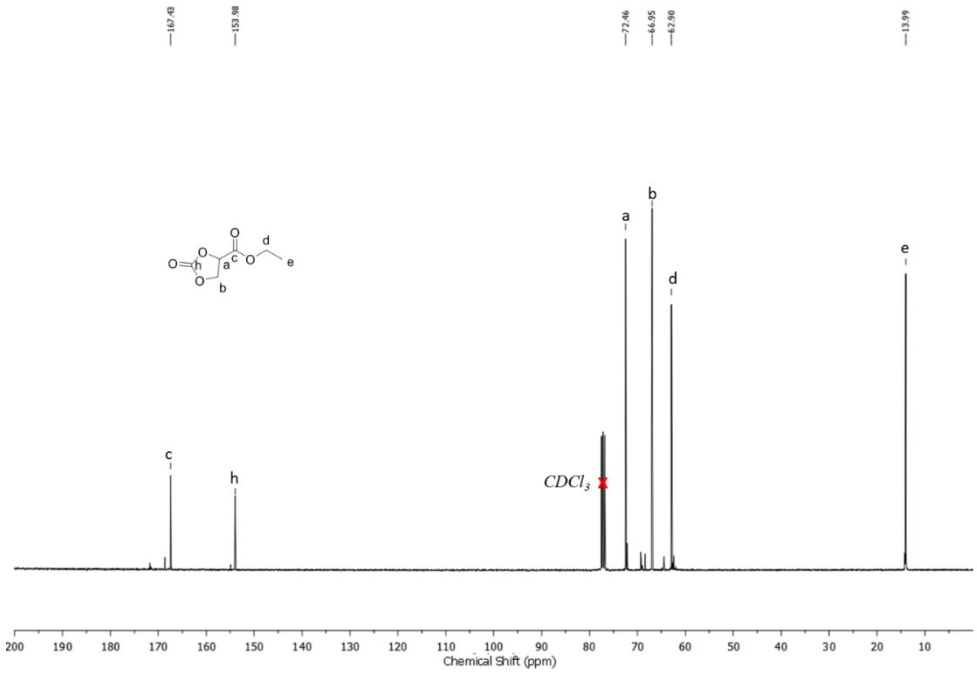
SI-Figure 5 : ^{1}H NMR spectrum of C_5-Phenyl-Ether



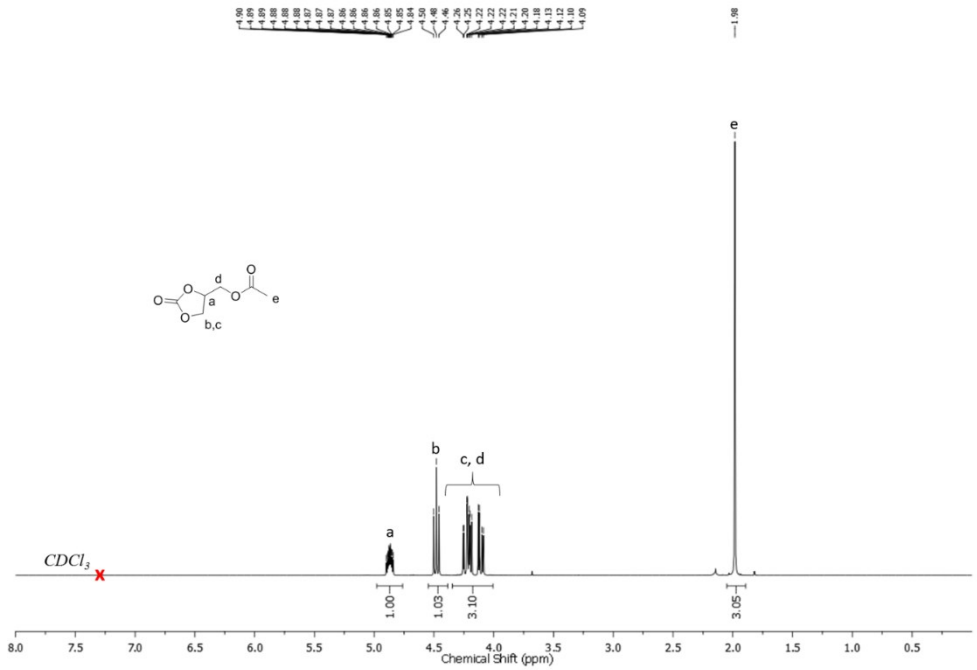
SI-Figure 6: ^{13}C NMR spectrum of C_5-Phenyl-Ether in $CDCl_3$



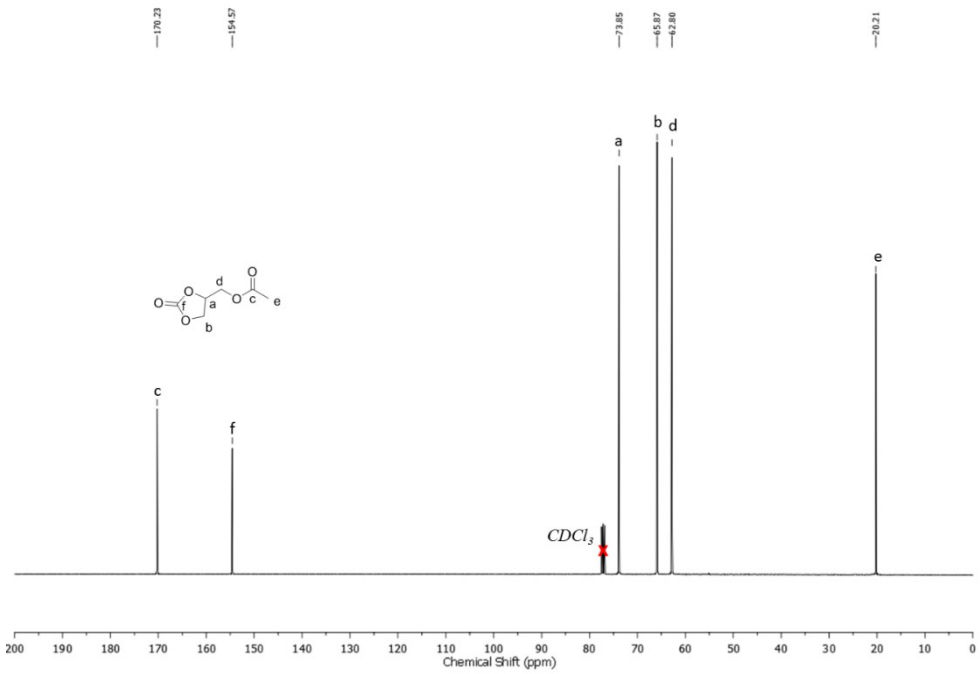
SI-Figure 7: ^{1}H NMR spectrum of C5-Ethyl-Ester in CDCl3



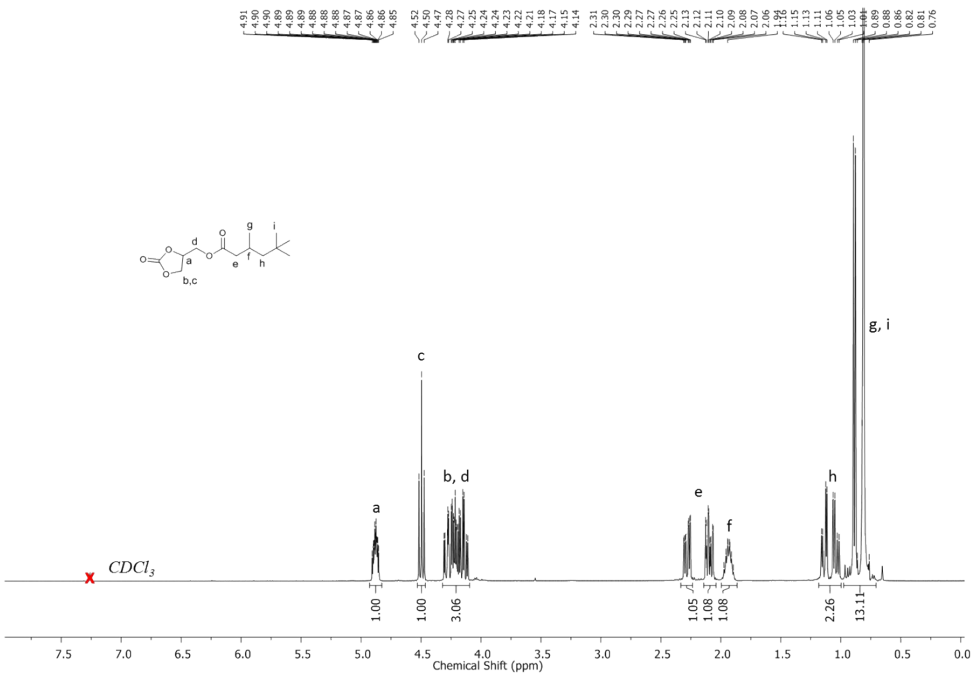
SI-Figure 8: ^{13}C NMR spectrum of C_5-Ethyl-Ester in $CDCl_3$



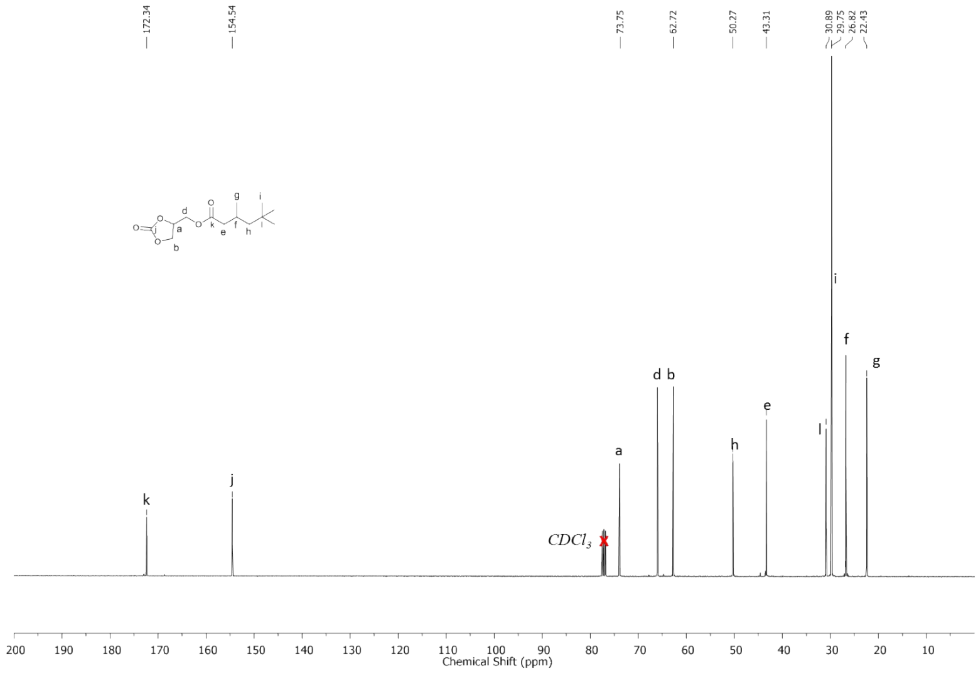
SI-Figure 9: ^{1}H NMR spectrum of C_5-Acetate in $CDCl_3$



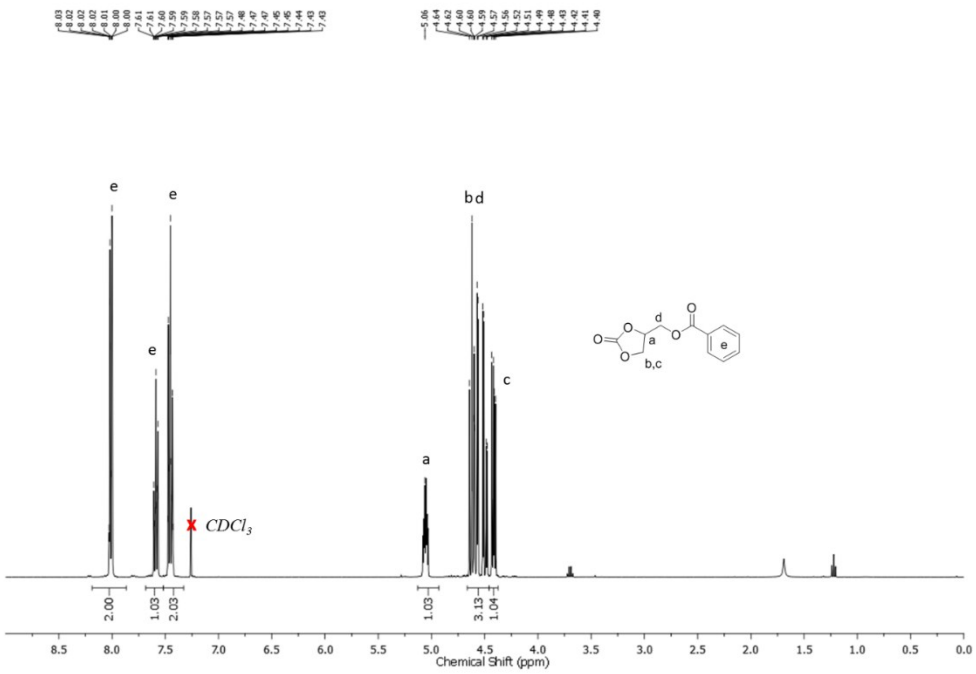
SI-Figure 10: ^{13}C NMR spectrum of C_5-Acetate in $CDCl_3$



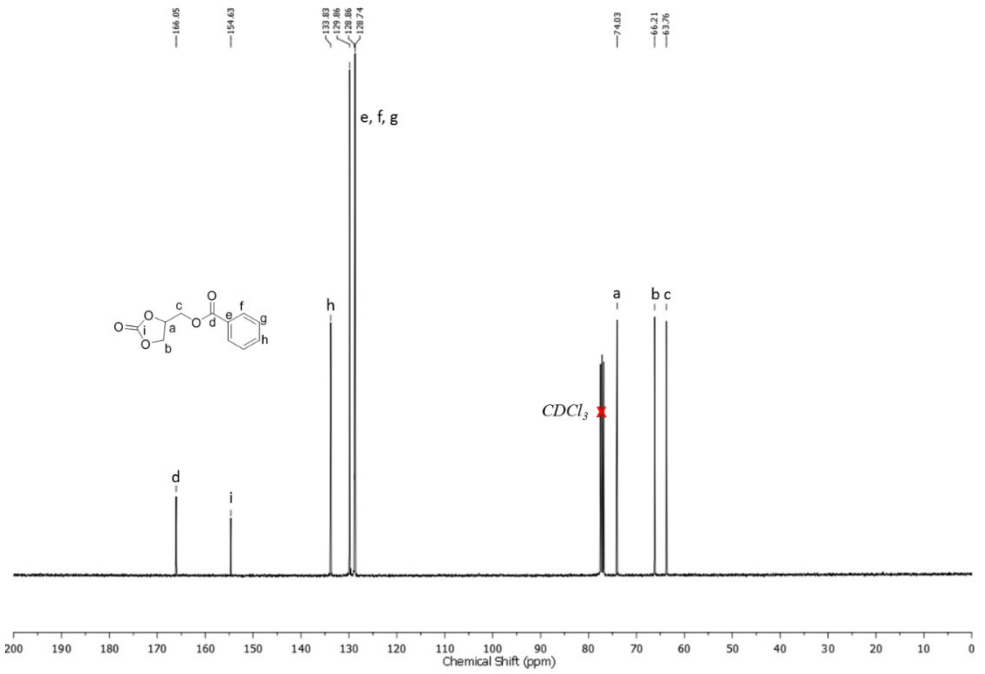
SI-Figure 11: ^{1}H NMR spectrum of C_5-Trimethylhexanoate



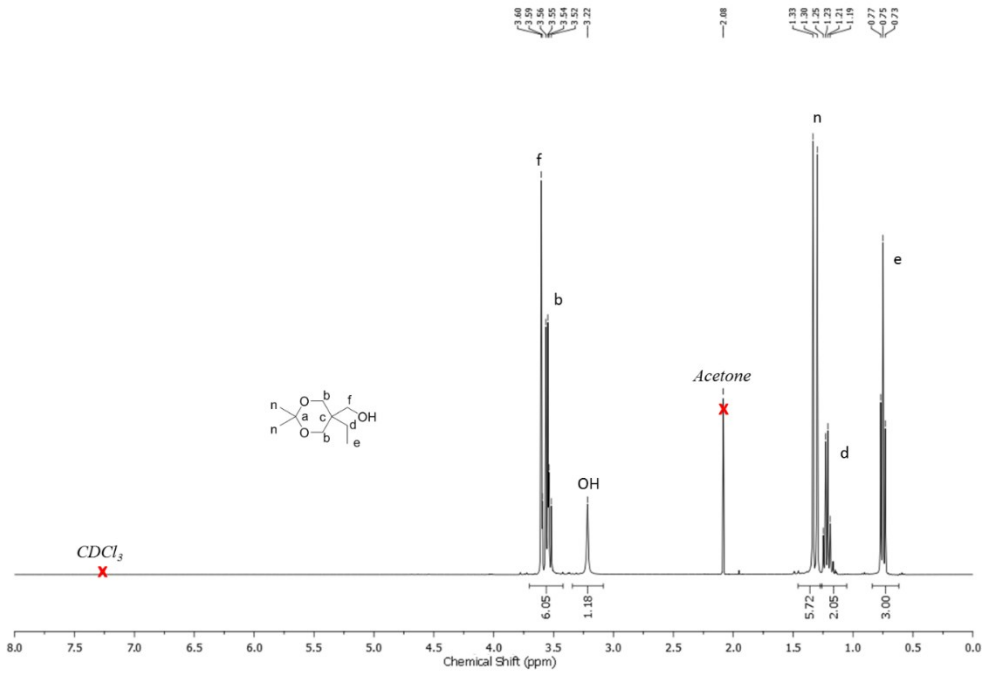
SI-Figure 12: ^{13}C NMR spectrum of C_5-Trimethylhexanoate



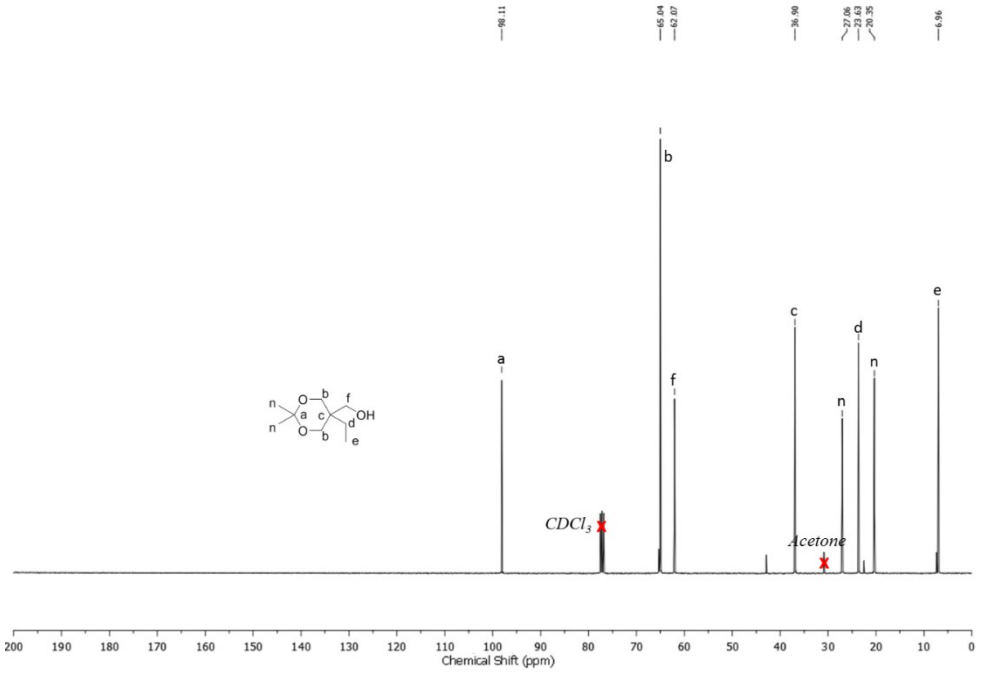
SI-Figure 13: ^{1}H NMR spectrum of C_5-Benzoate in $CDCl_3$



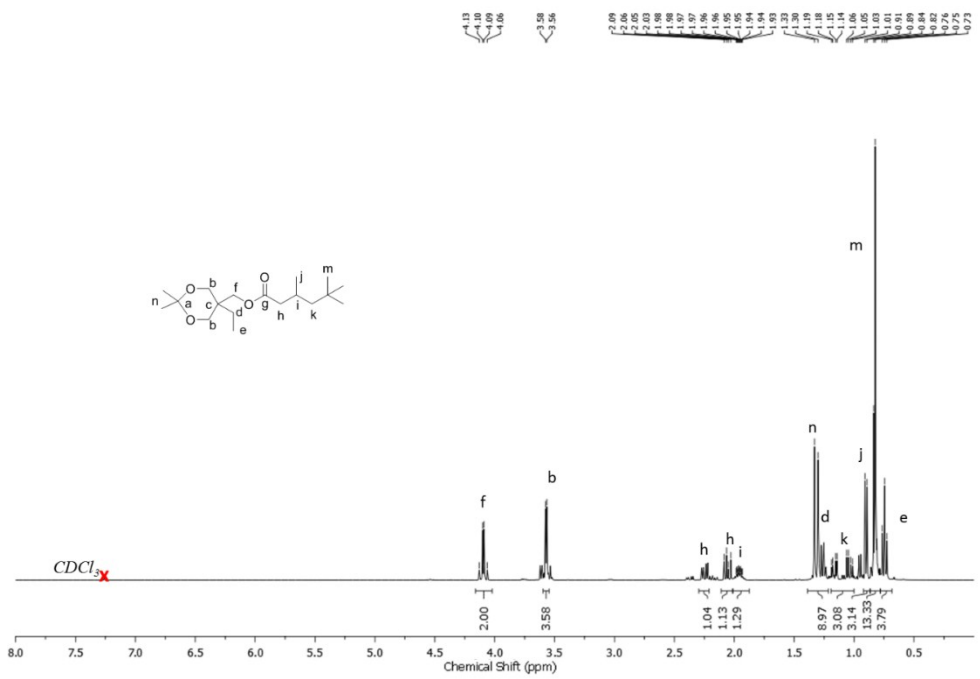
SI-Figure 14: ^{13}C NMR spectrum of C_5-Benzoate in $CDCl_3$



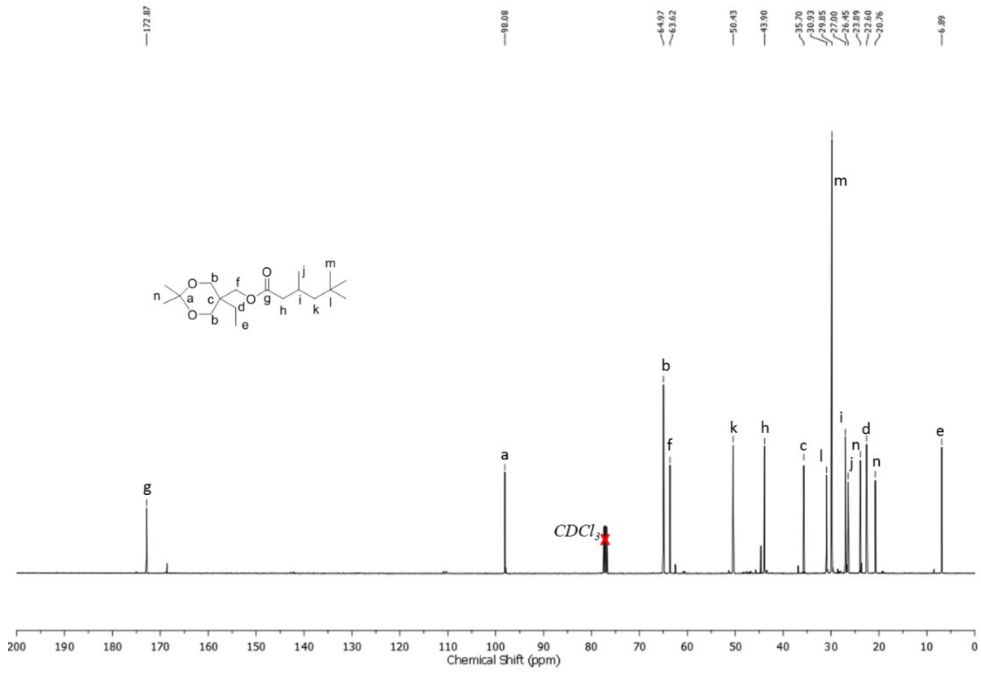
SI-Figure 15: ^{1}NMR spectrum of Protected TMP in $CDCl_3$



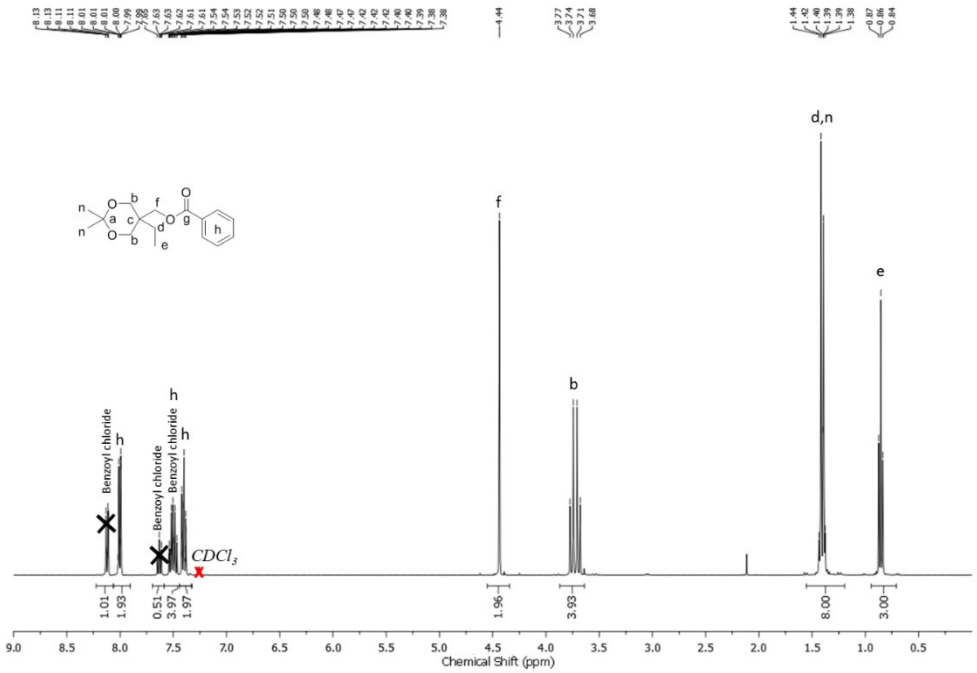
SI-Figure 16: ^{13}C NMR spectrum of Protected TMP in $CDCl_3$



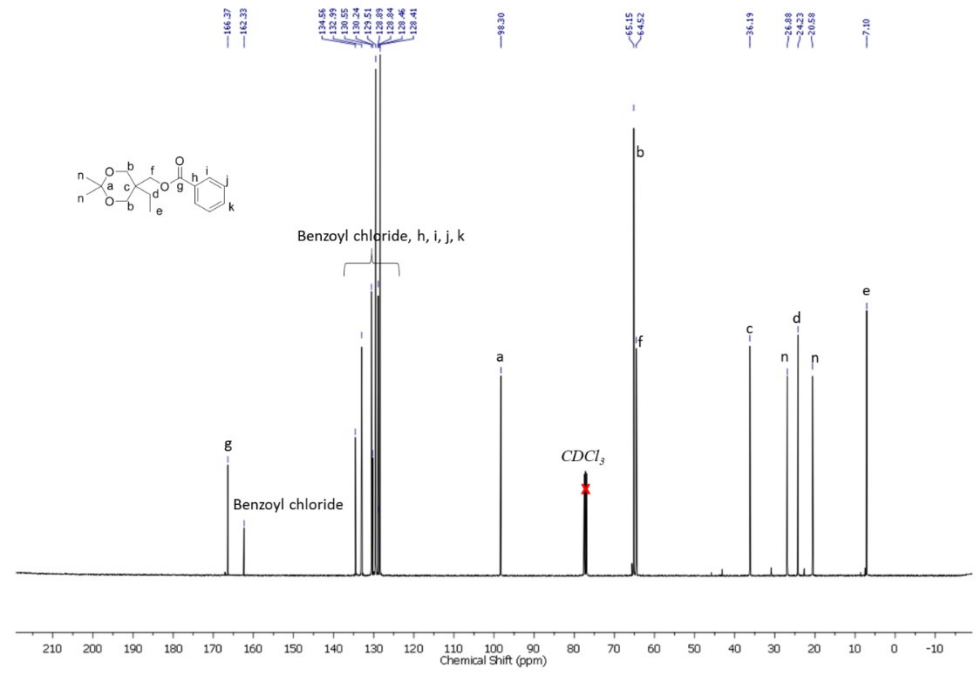
SI-Figure 17: ^{1}H NMR spectrum of Esterified Protected TMP 1 in $CDCl_3$



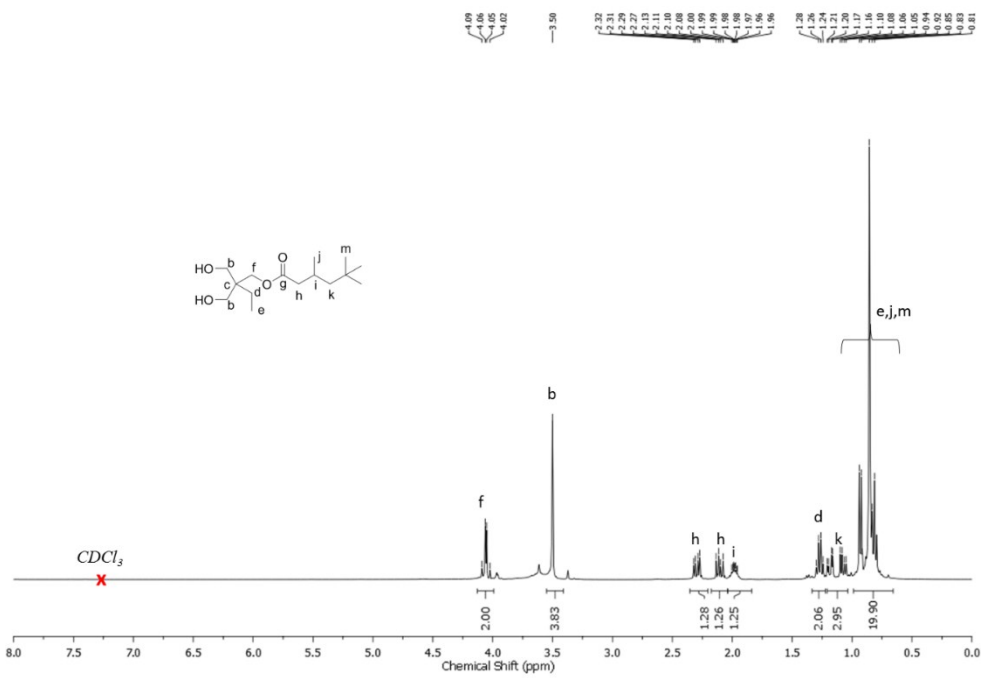
SI-Figure 18: ^{13}C NMR spectrum of Esterified Protected TMP 1 in $CDCl_3$



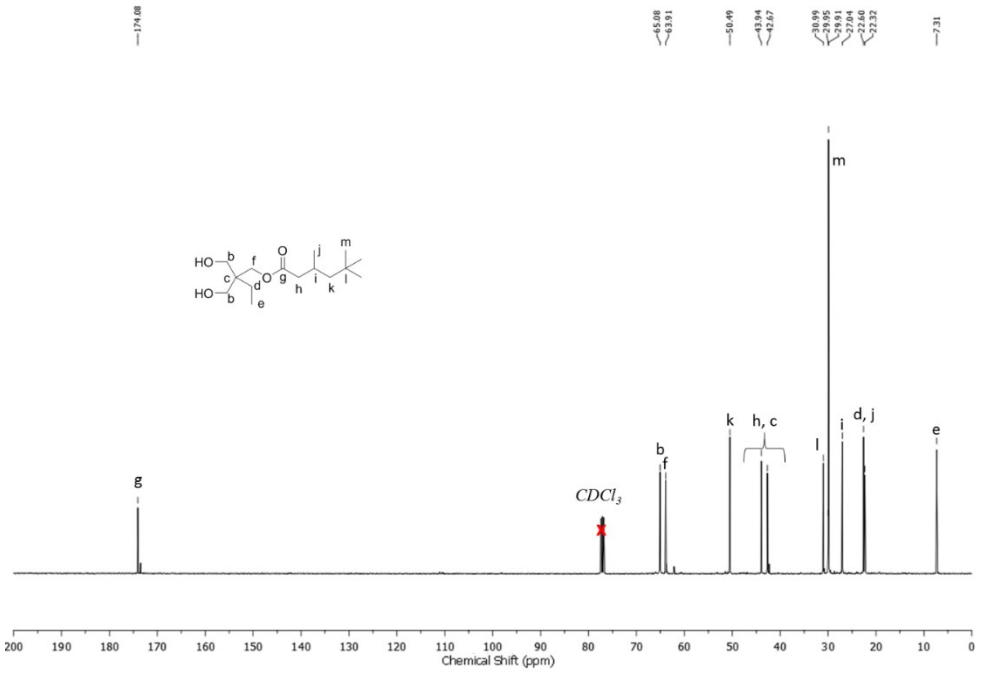
SI-Figure 19: ^{1}H NMR spectrum of Esterified Protected TMP 2 in $CDCl_3$



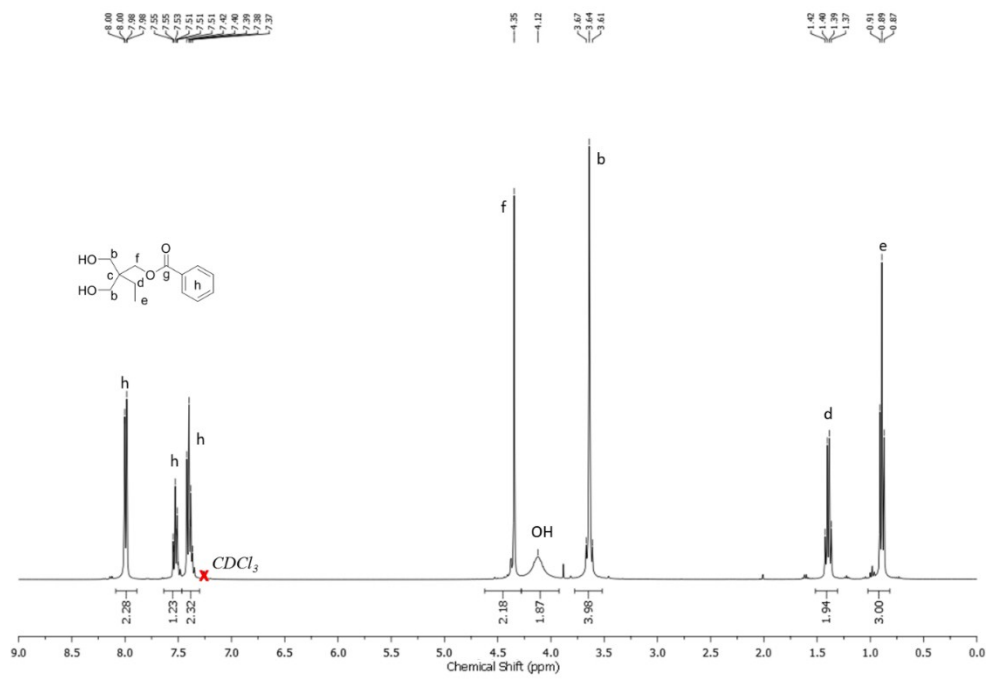
SI-Figure 20: ^{13}C NMR spectrum of Esterified Protected TMP 2 in $CDCl_3$



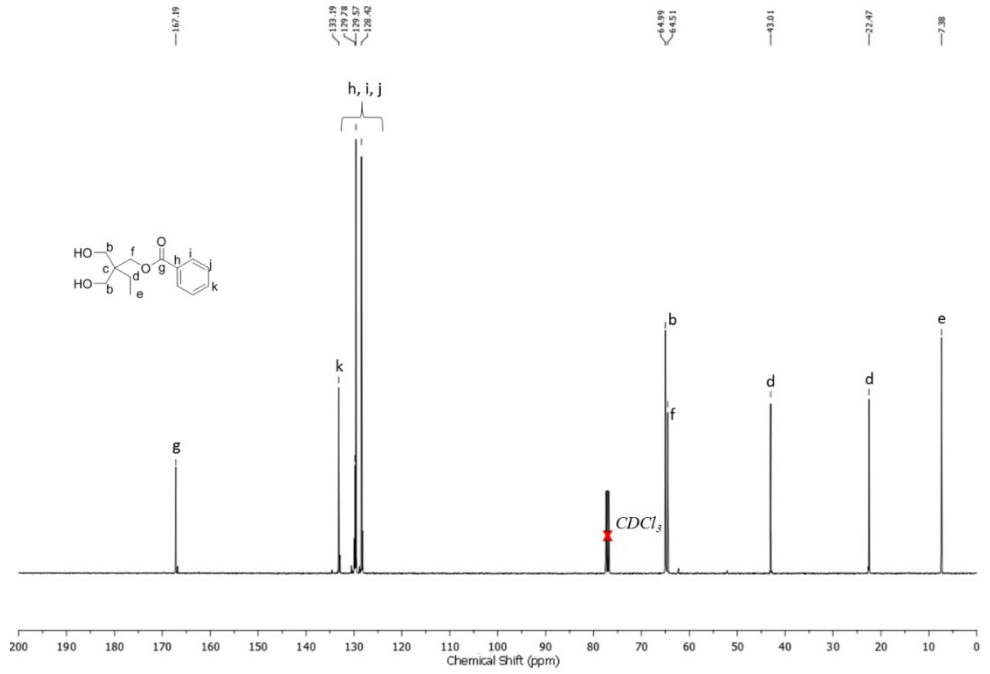
SI-Figure 21: ^{1}H NMR spectrum of Esterified TMP 1 in $CDCl_3$



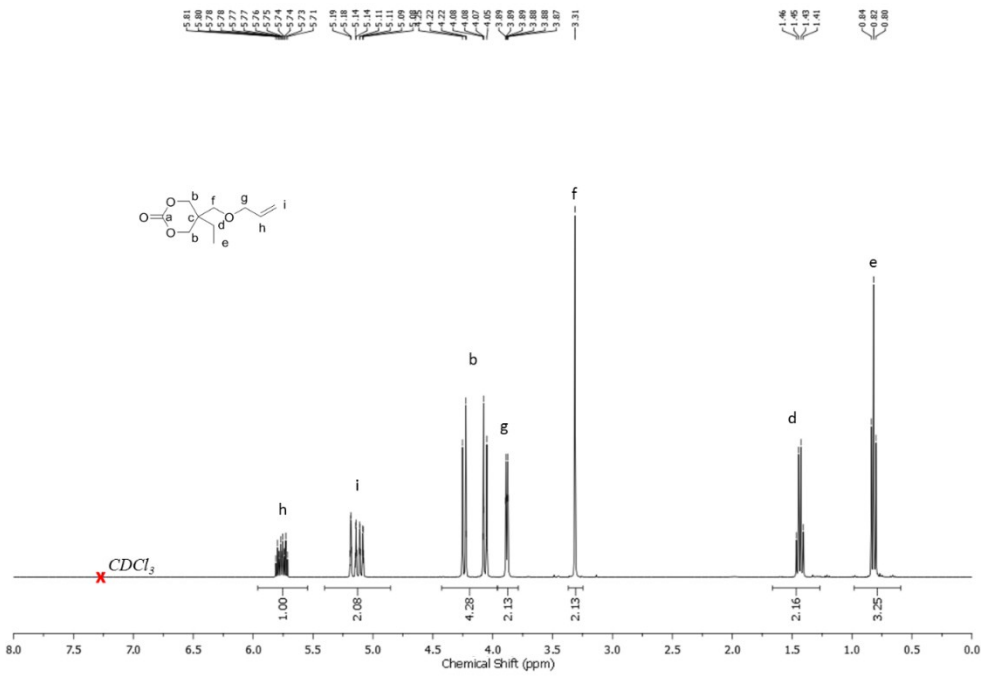
SI-Figure 22: ^{13}C NMR spectrum of Esterified TMP 1 in $CDCl_3$



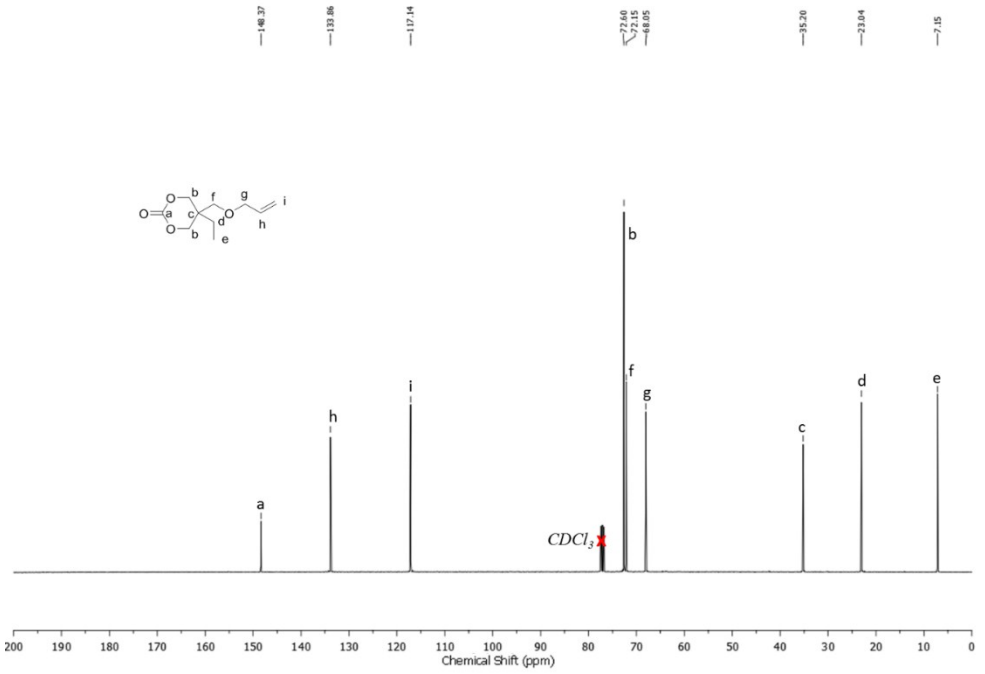
SI-Figure 23: ^{1}H NMR spectrum of Esterified TMP 2 in $CDCl_3$



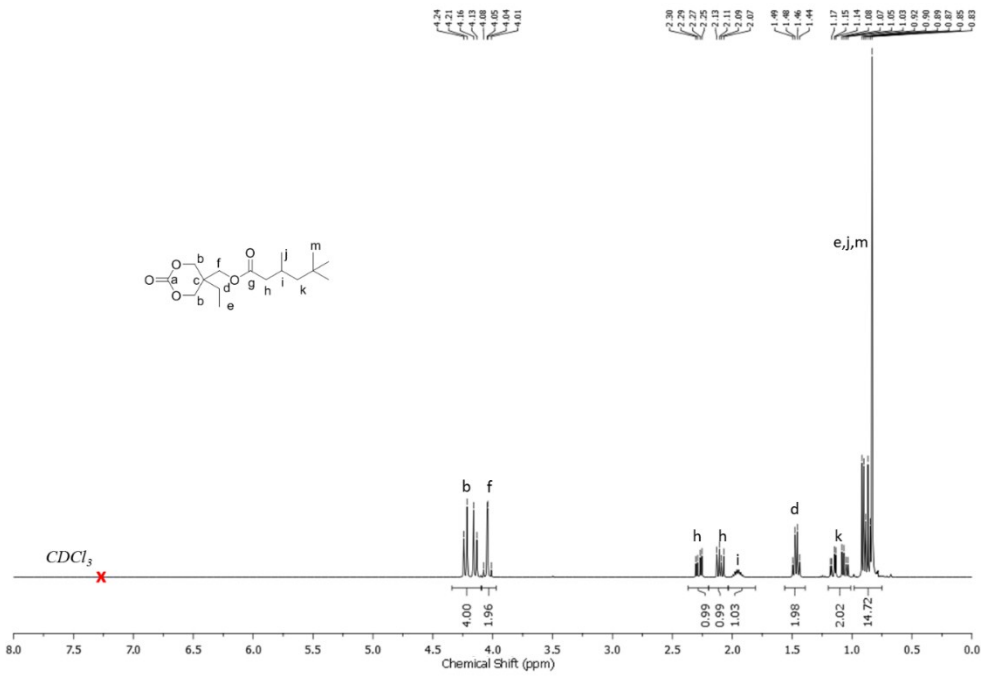
SI-Figure 24: ^{13}C NMR spectrum of Esterified TMP 2 in $CDCl_3$



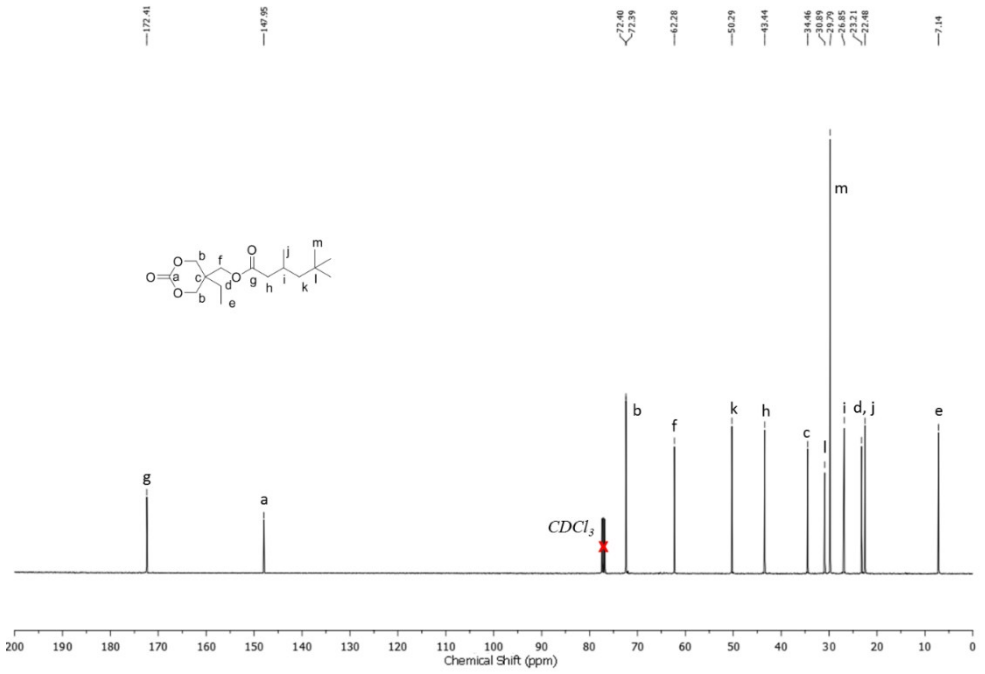
SI-Figure 25: ^{1}H NMR spectrum of C_6-Allyl-Ether in $CDCl_3$



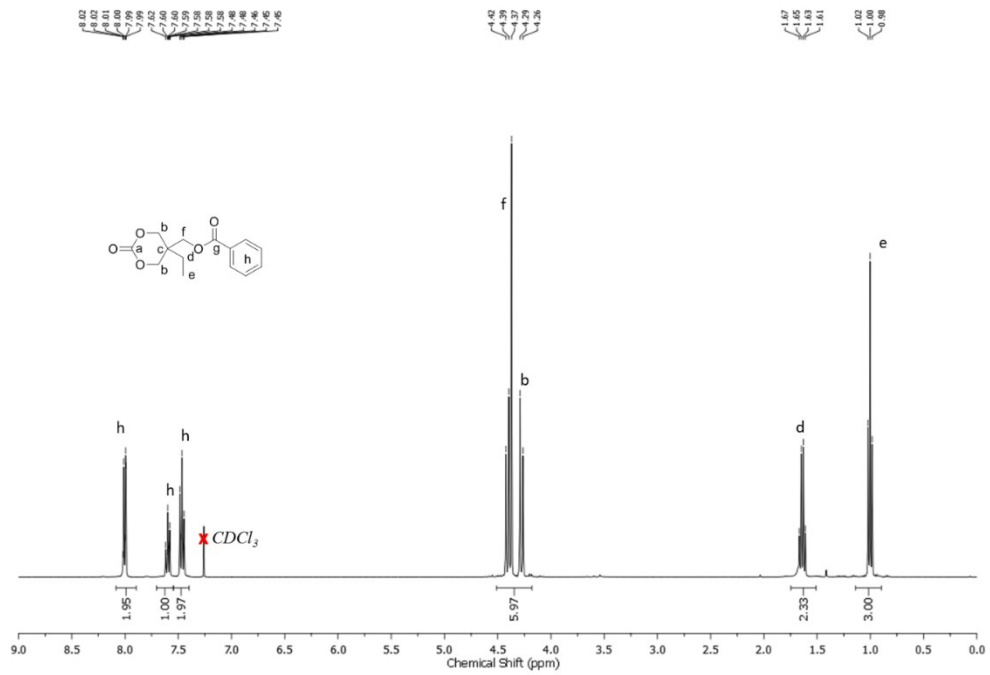
SI-Figure 26: ^{13}C NMR spectrum of C_6-Allyl-Ether in $CDCl_3$



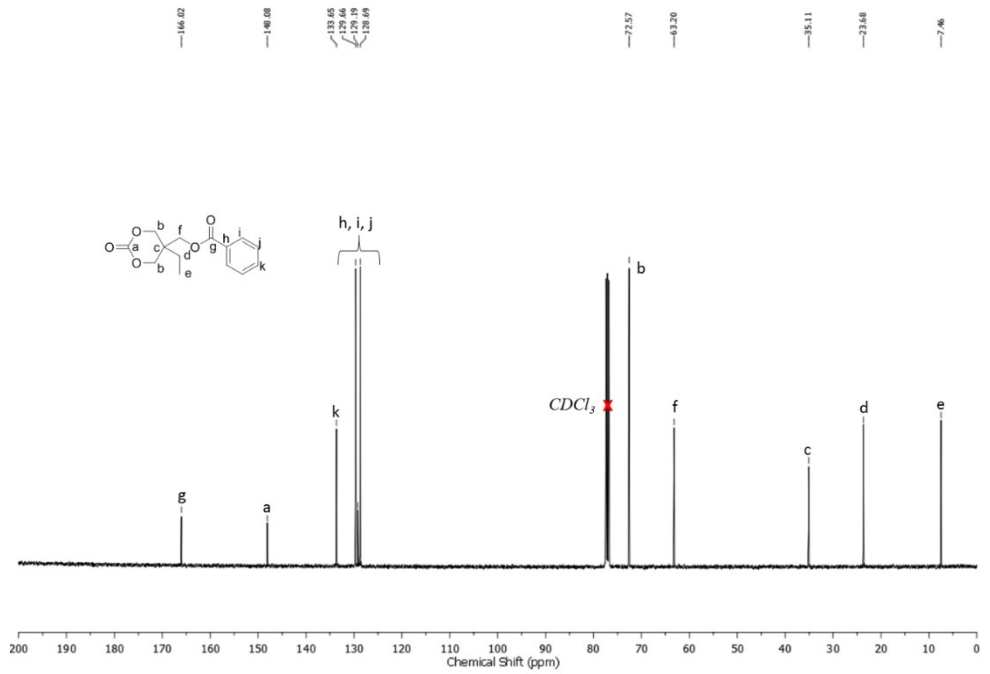
SI-Figure 27: 1H NMR spectrum of C6-Trimethylhexanoate in CDCl3



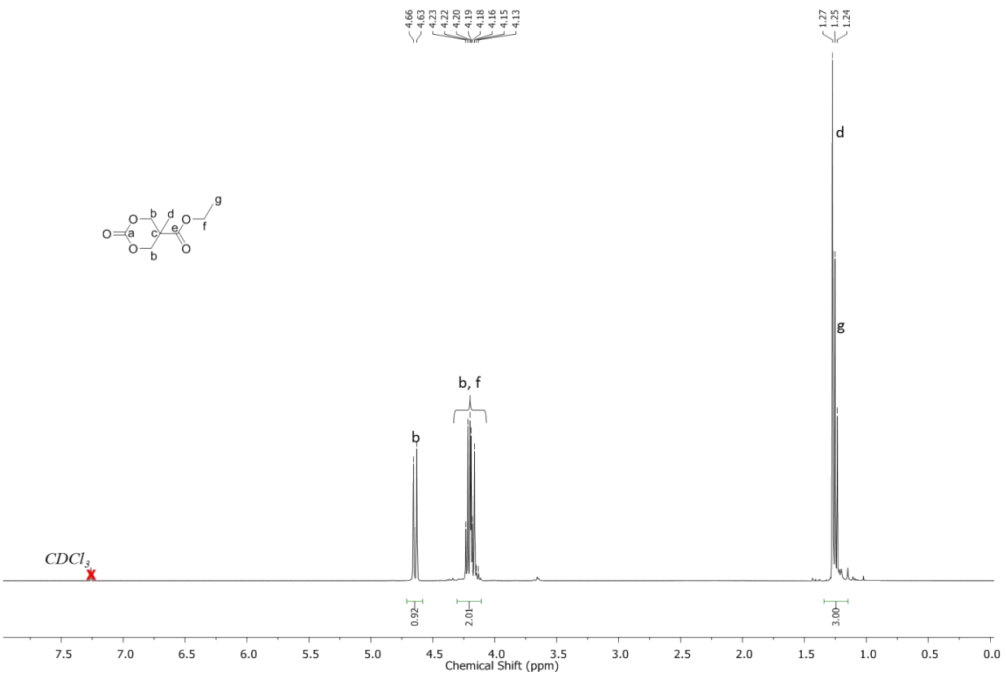
SI-Figure 28: ^{13}C NMR spectrum of C_6-Trimethylhexanoate in $CDCl_3$



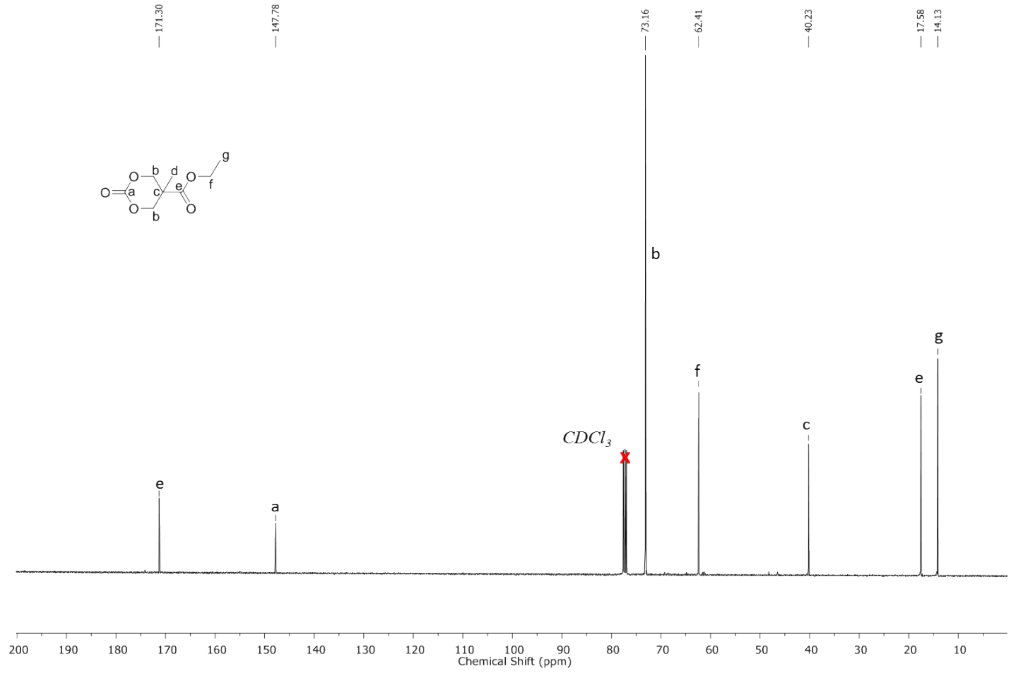
SI-Figure 29: ^{1}H NMR spectrum of C_6-Benzoate in $CDCl_3$



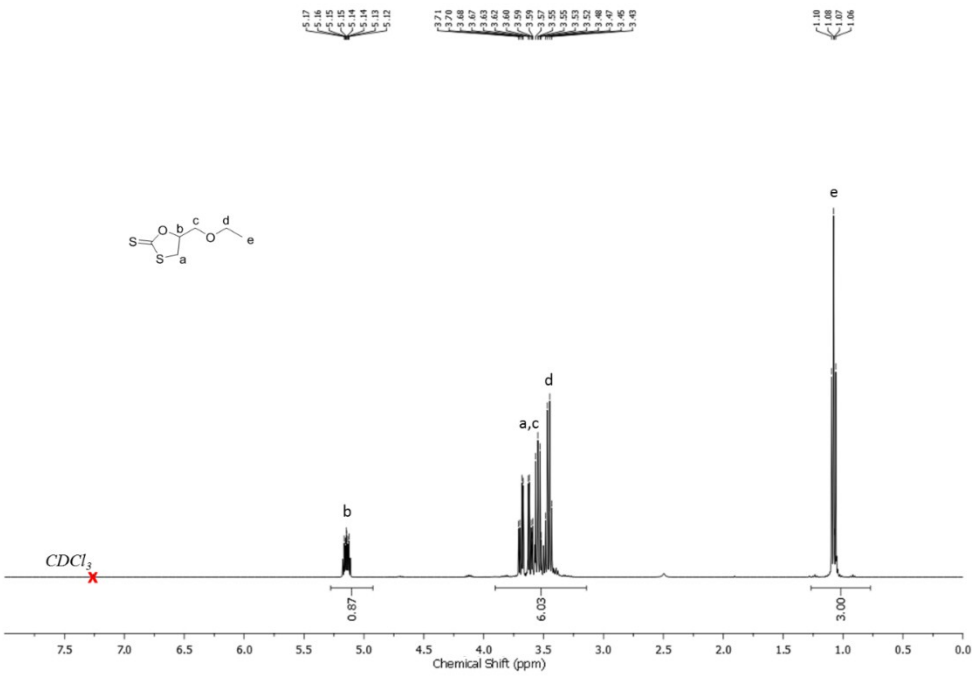
SI-Figure 30: ^{13}C NMR spectrum of C_6-Benzoate in $CDCl_3$



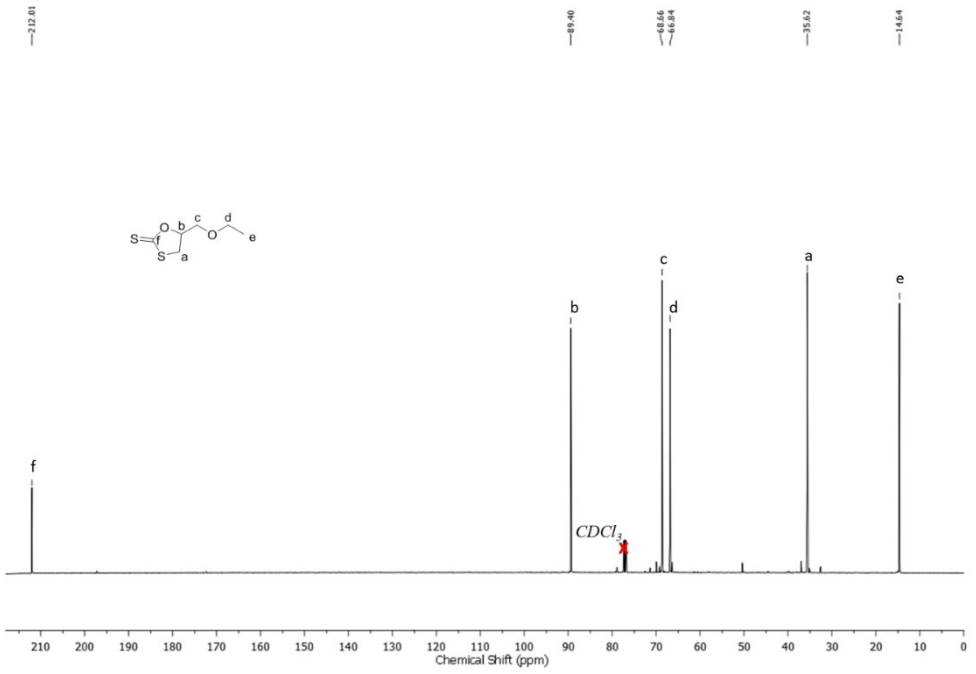
SI-Figure 31: ^{1}NMR spectrum of C_6-Ethyl-Ester in $CDCl_3$



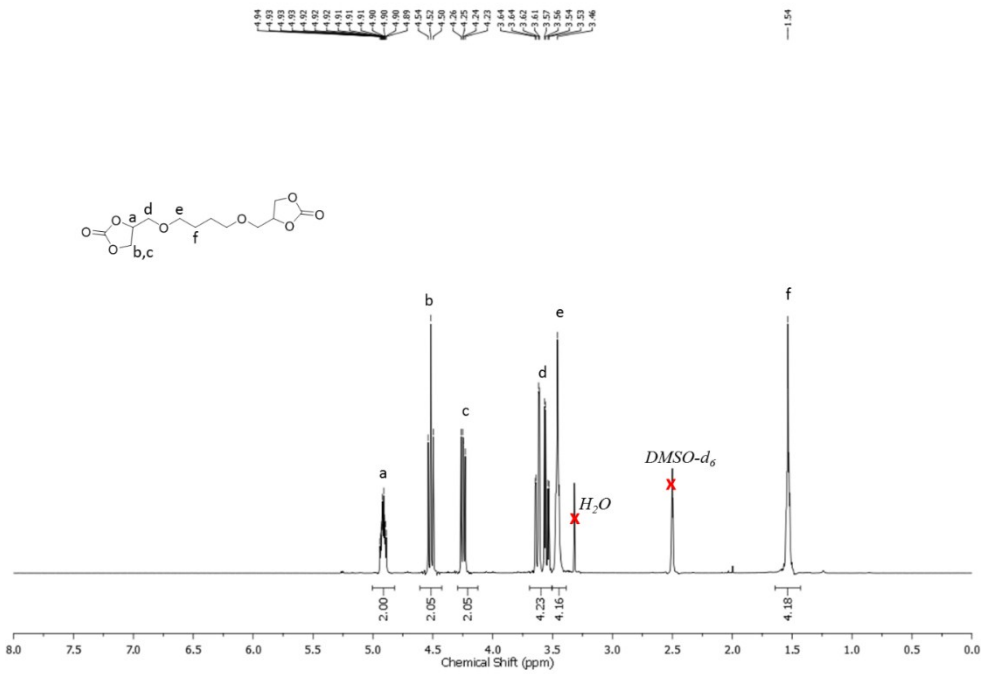
SI-Figure 32: ^{13}C NMR spectrum of C_6-Ethyl-Ester in $CDCl_3$



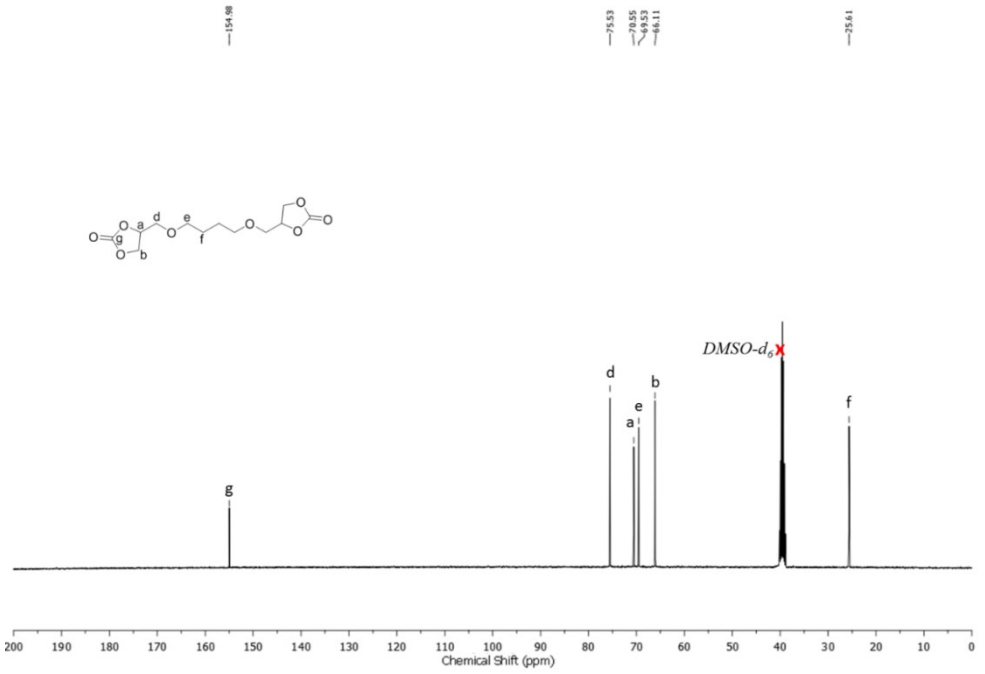
SI-Figure 33: ^{1}H NMR spectrum of C_s-Ethyl-Ether in $CDCl_3$



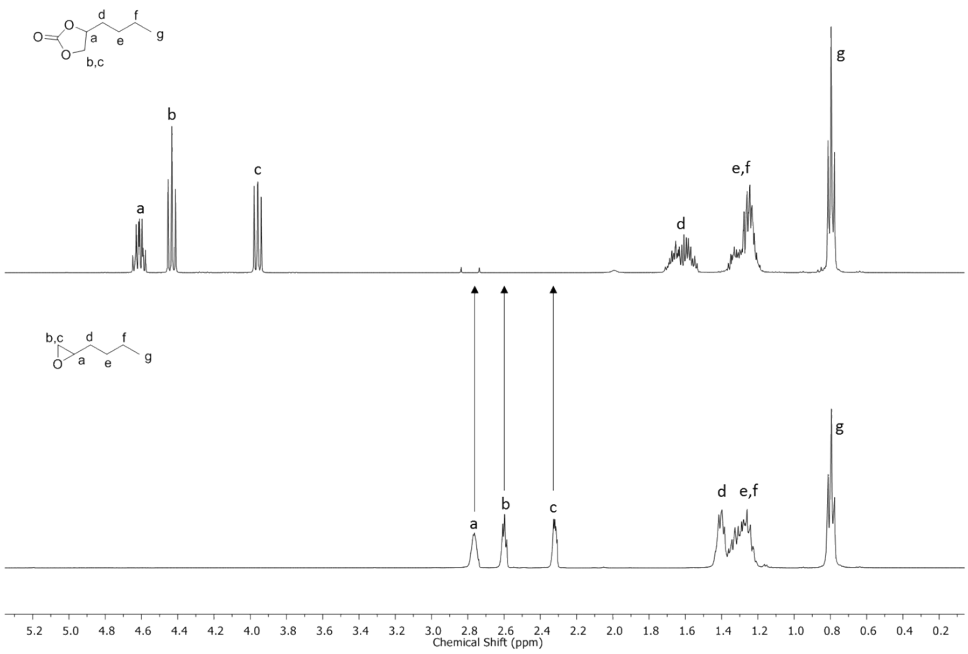
SI-Figure 34: ^{13}C NMR spectrum of C_s-Ethyl-Ether in $CDCl_3$



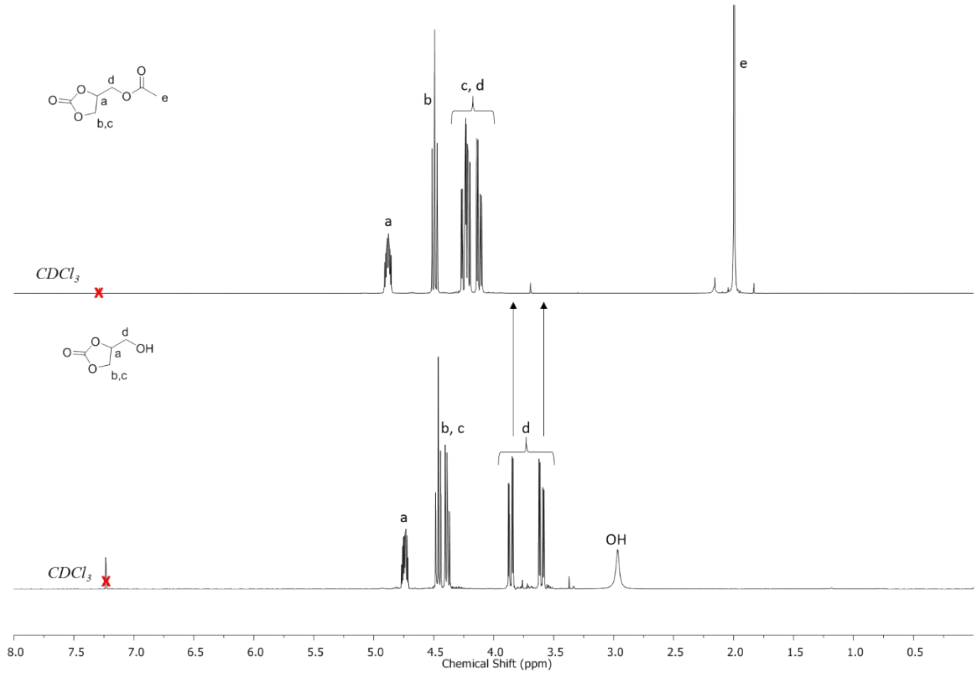
SI-Figure 35: ^{1}H NMR spectrum of Bis-C_5-Ether in DMSO-d_6



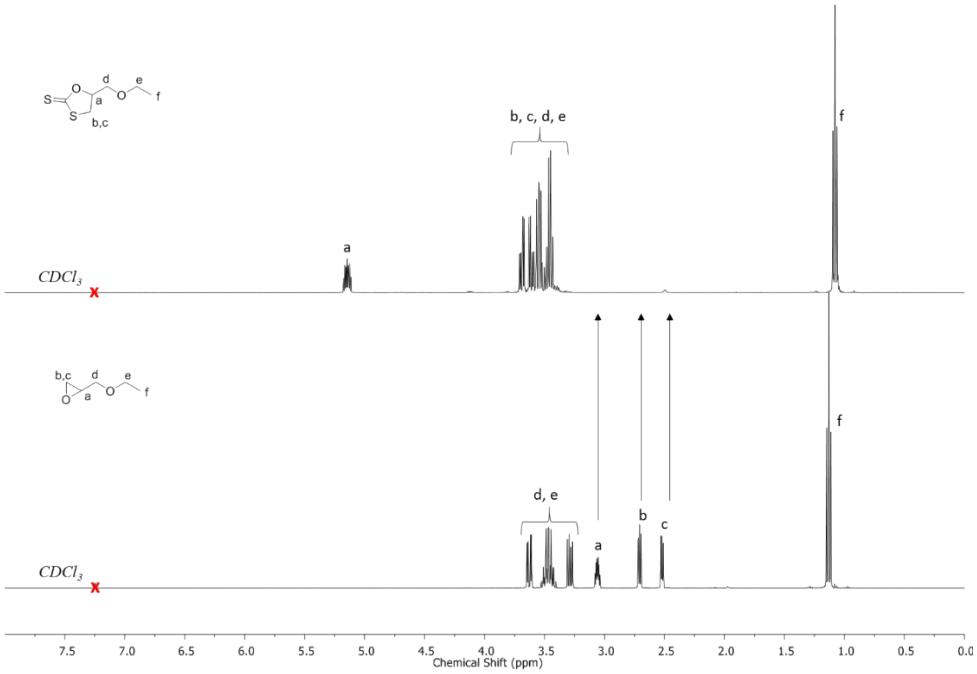
SI-Figure 36: ^{13}C NMR spectrum of Bis-C_5-Ether in $CDCl_3$



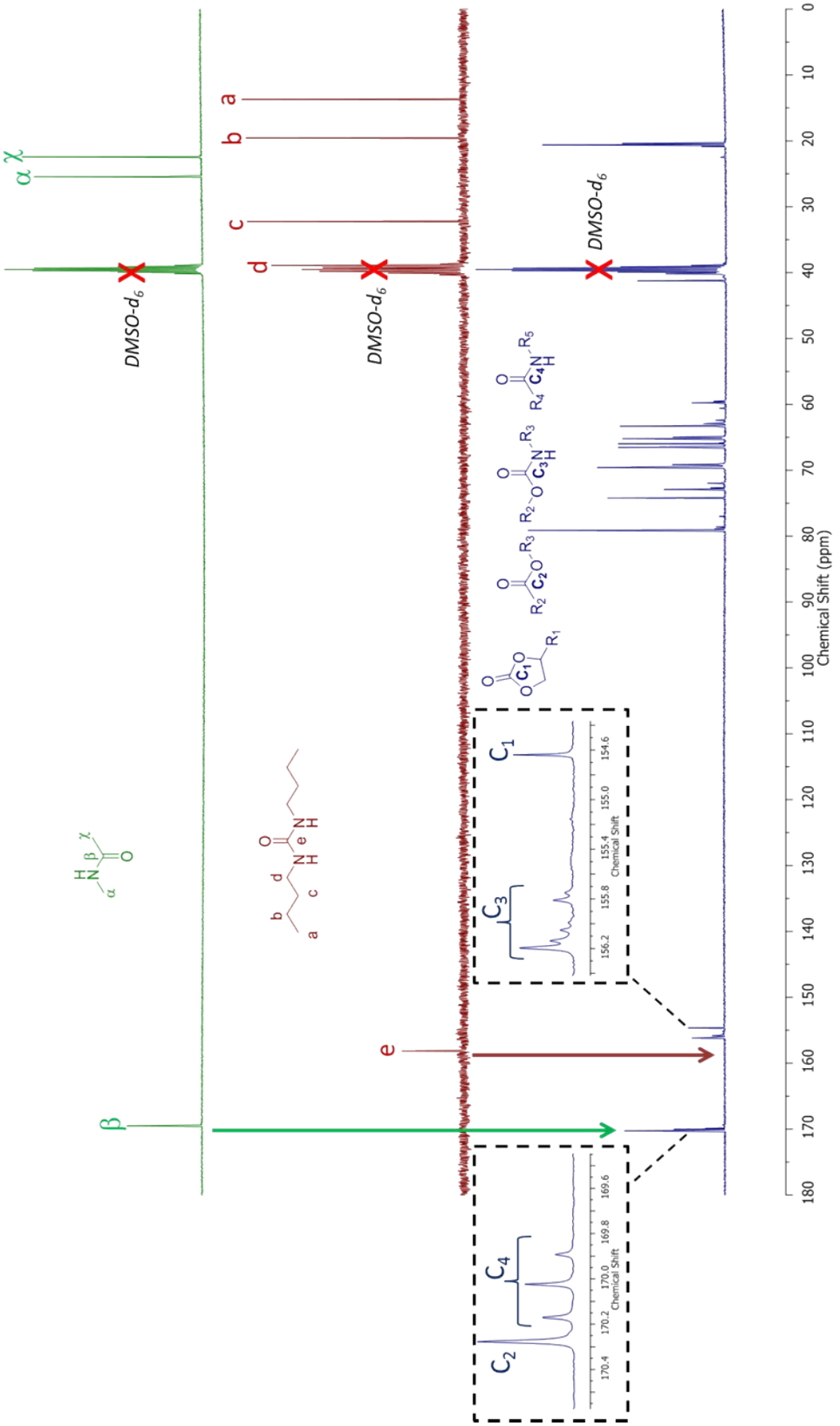
SI-Figure 37: Stacked ^{1}H NMR spectra of 1,2-epoxyhexane and C_5-Butane in $CDCl_3$



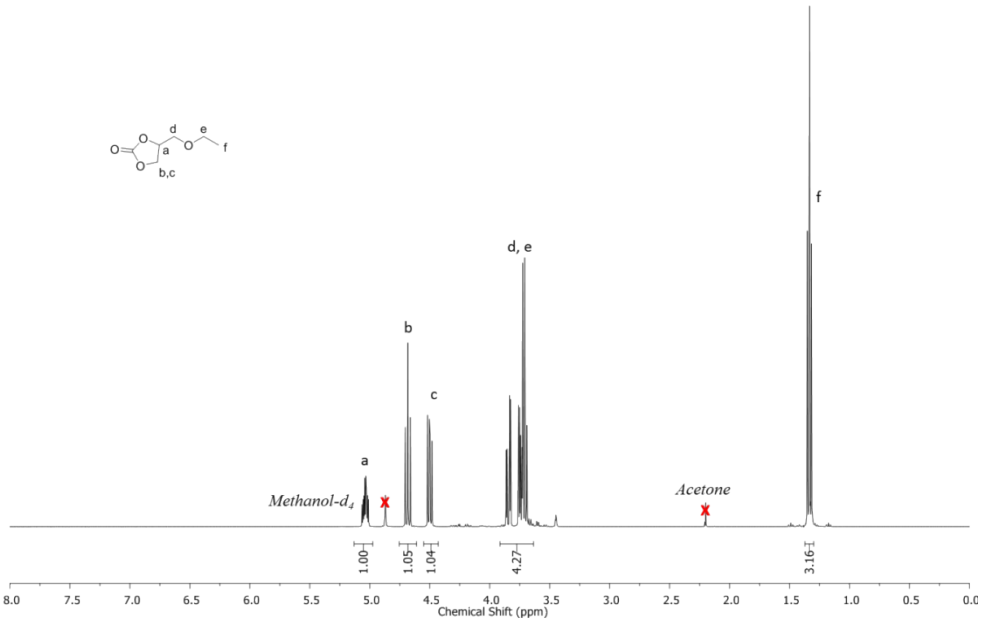
SI-Figure 38: Stacked 1H NMR spectra of glycerin carbonate and C_5-Acetate in CDCl3



SI-Figure 39: Stacked ^{1}NMR spectra of ethyl glycidyl ether and C_s-Ethyl-Ether in $CDCl_3$

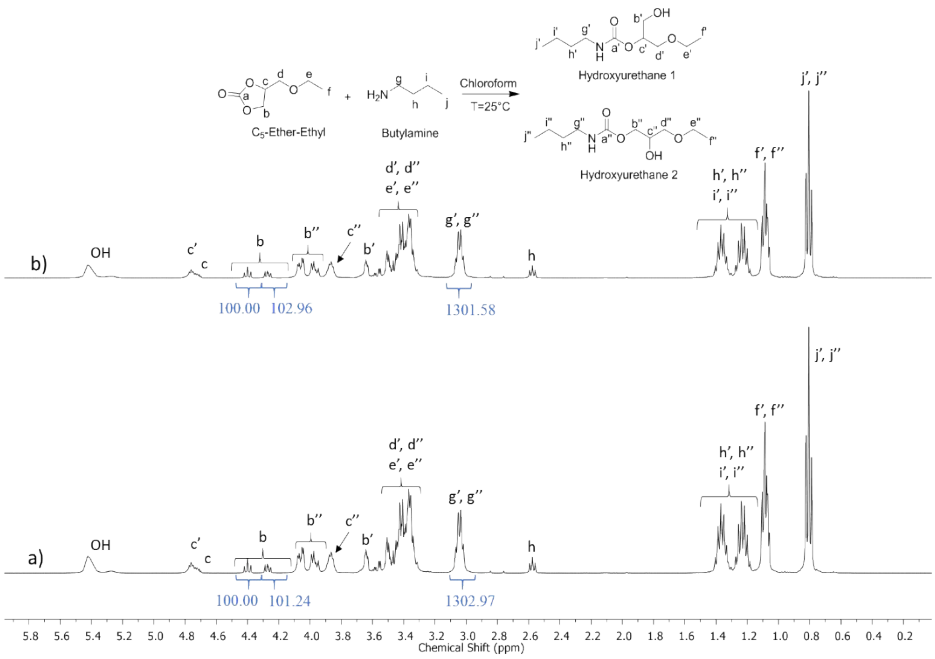


SI-Figure 40: Stacked ^{13}C NMR spectra of N-dimethylacetamide (green spectrum), 1,3-dibutylurea (red spectrum) and hydroxyurethane compounds synthesized from reaction between C_5-Acetate and EDR-148 (blue spectrum)

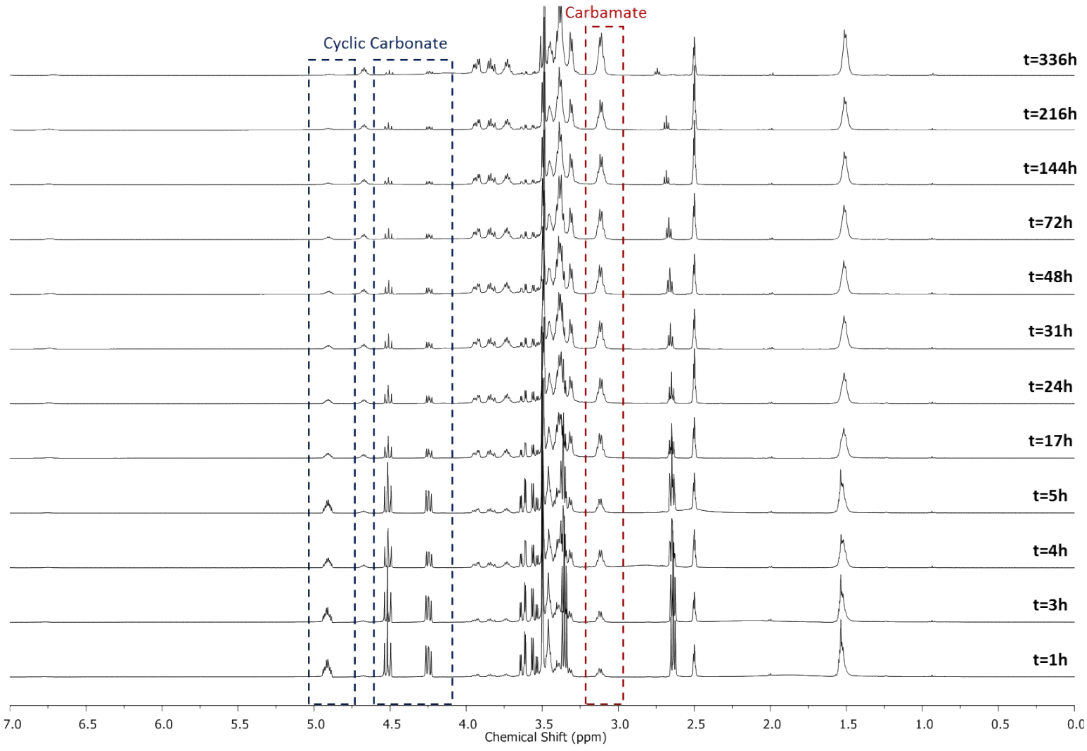


SI-Figure 41: ^{1}H NMR spectrum of C_5-Ethyl-Ether in Methanol-d_4 after 48 h

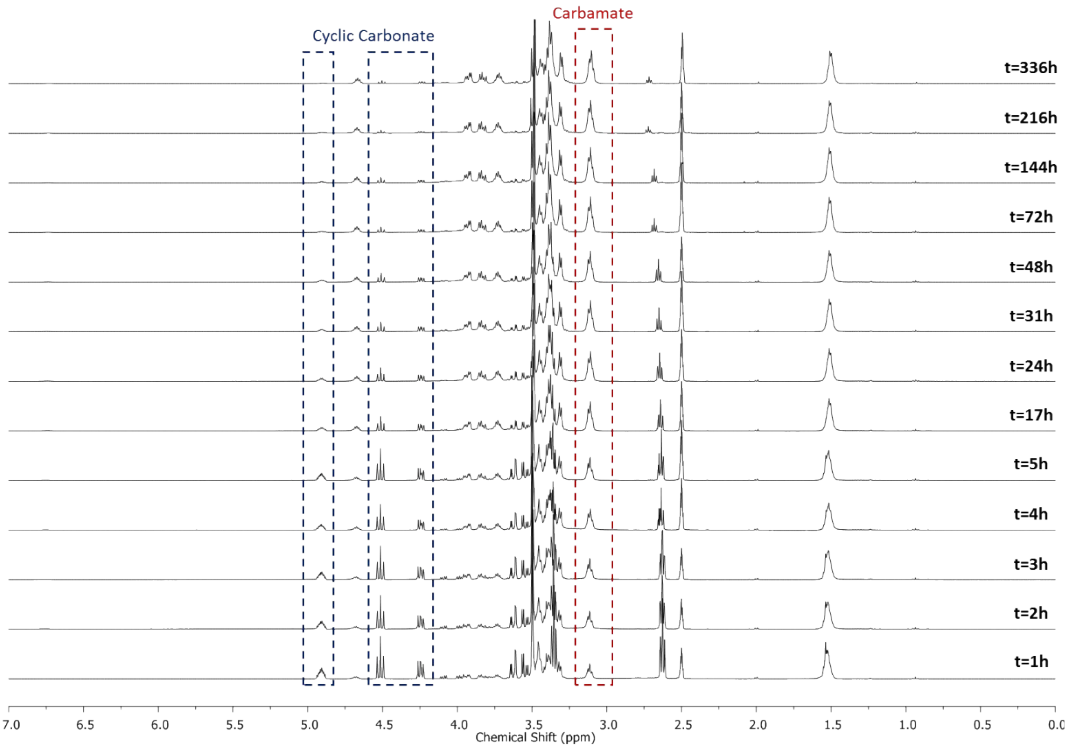
4. Graphical data of kinectic measurements



SI-Figure 42: Stacked ^{1}H NMR spectra of hydroxyurethane compounds in $CDCl_3$ synthesized in chloroform from C_5-Ethyl-Ether and butylamine at a) 24h and b) 7 days of reaction

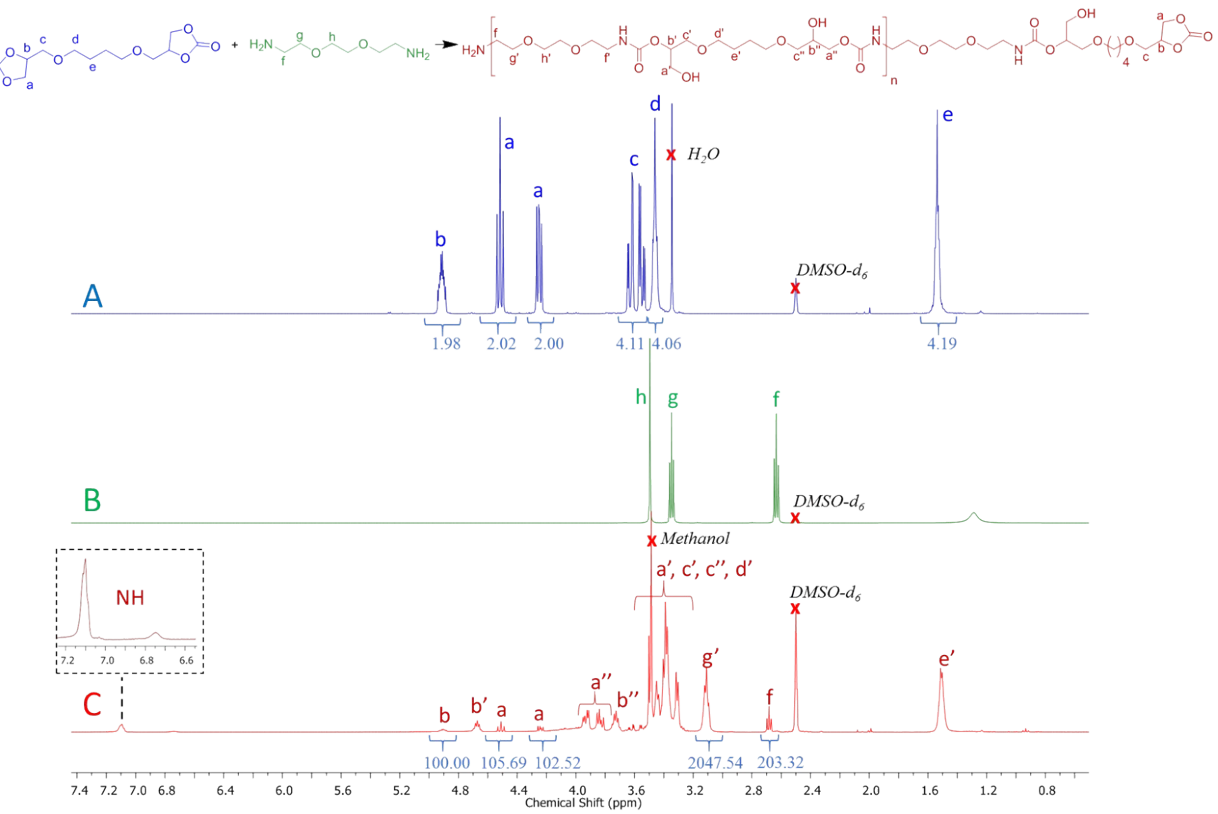


SI-Figure 43: Stacked ^{1}NMR spectra in DMSO-d_6 monitoring of the reaction between Bis-C_5-Ether and EDR-148 with a ratio 1:1, at 25°C in chloroform

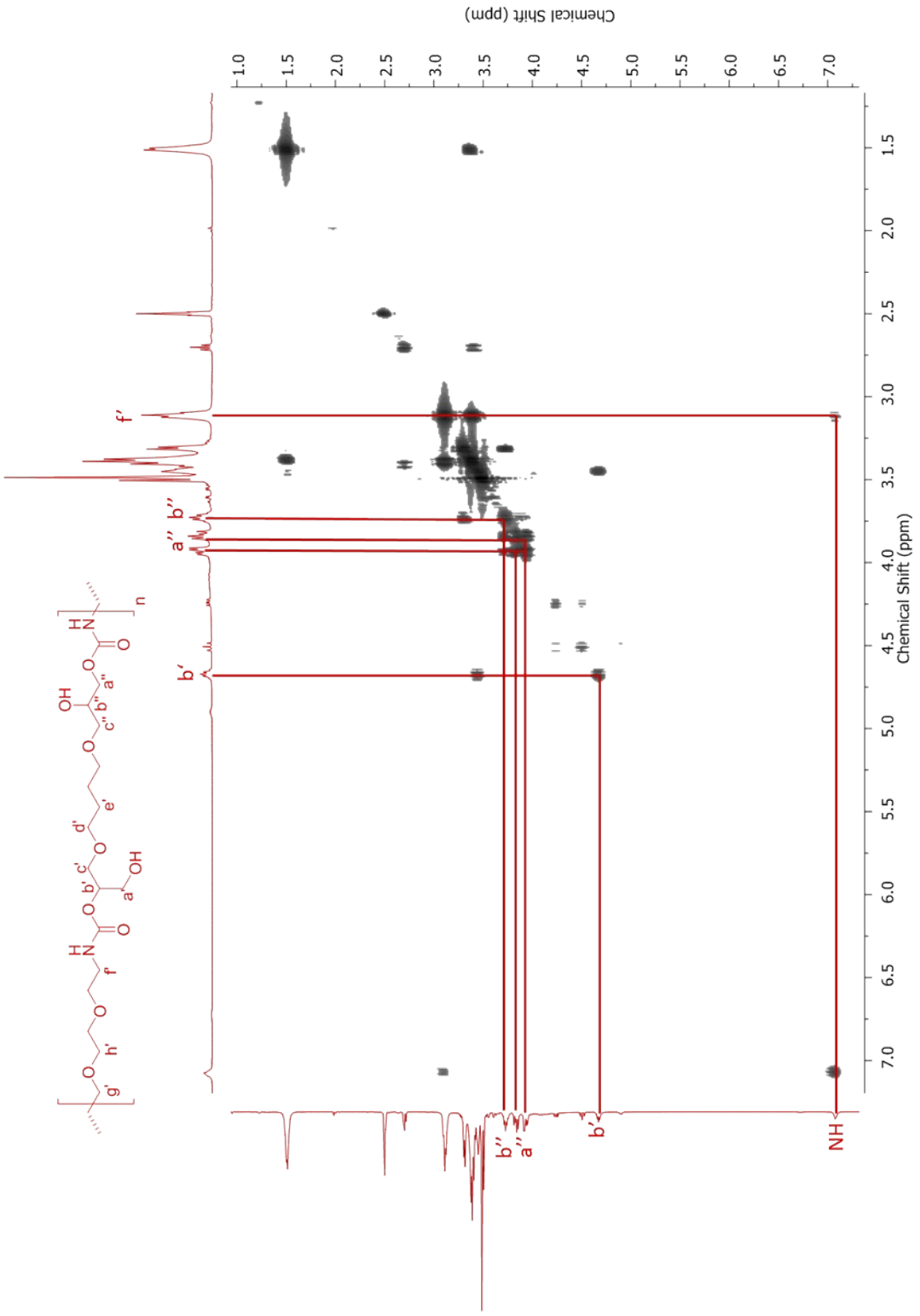


SI-Figure 44: Stacked ^{1}H NMR spectra in DMSO-d_6 monitoring of the reaction between Bis-C_5-Ether and EDR-148 with a ratio 1:1, at 25°C in methanol

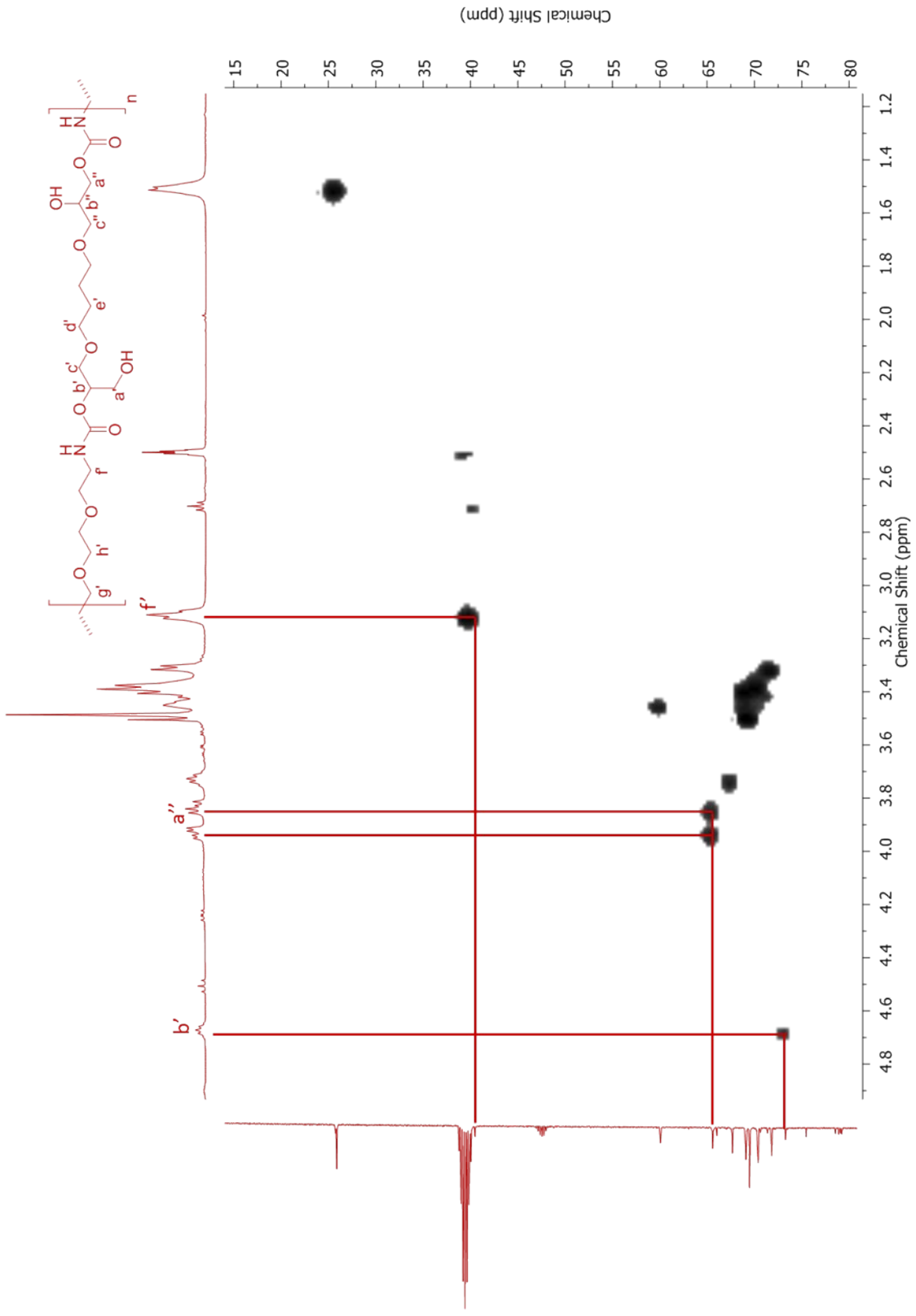
5. Graphical data of polyhydroxyurethane



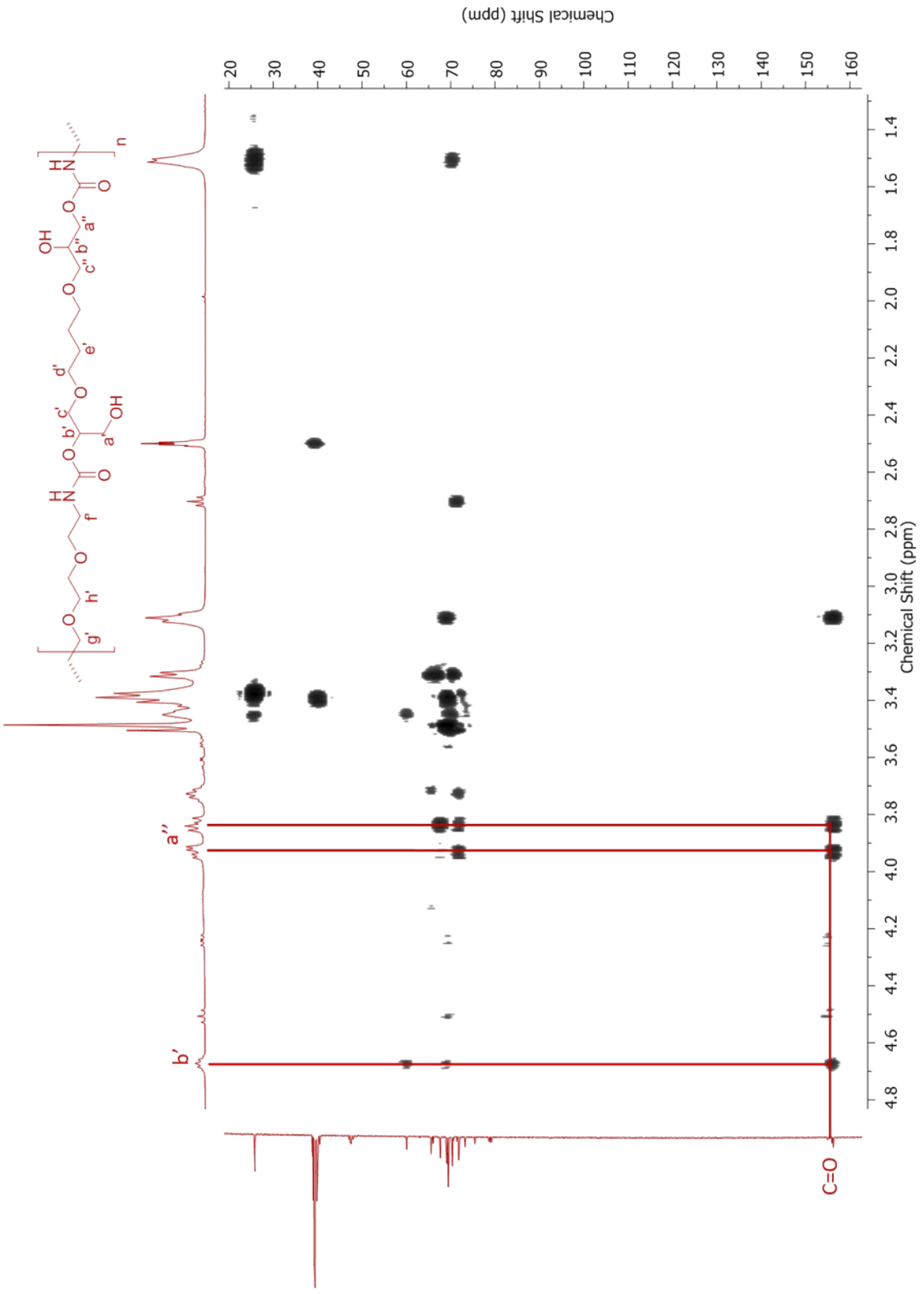
SI-Figure 45: Stacked of ^{1}H NMR of Bis-C_5-Ether (A), EDR-148 (B) and PHU (C) obtained at room temperature in mixture Chloroform/Methanol at t=144h



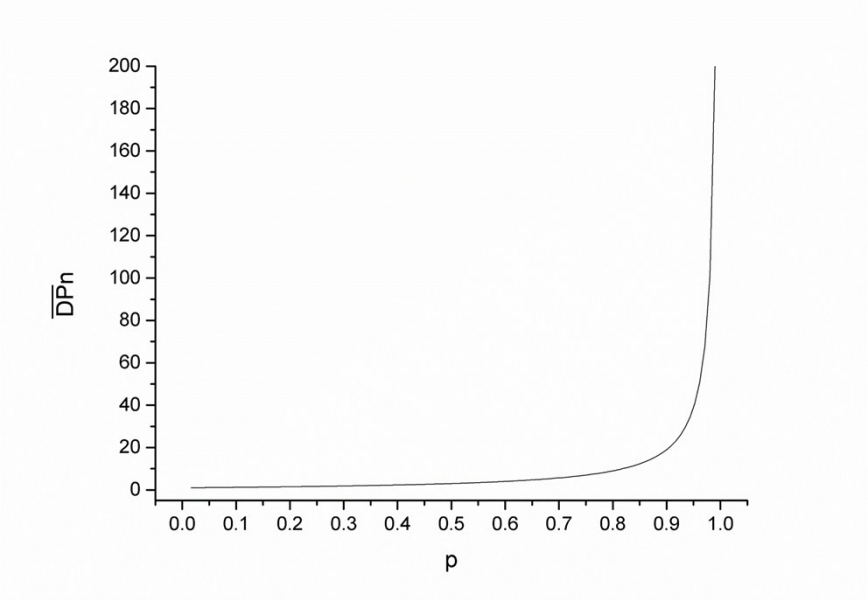
SI-Figure 46: 2D COSY NMR spectra in DMSO-d_6 of PHU obtained from the reaction of Bis-C_5-Ether with EDR-148 in mixture chloroform/methanol



SI-Figure 47: 2D HSQC NMR spectra in DMSO-d_6 of PHU obtained from the reaction of Bis-C_5-Ether with EDR-148 in mixture chloroform/methanol



SI-Figure 48: 2D HMBC NMR spectra in DMSO-d_6 of PHU obtained from the reaction of Bis-C_5-Ether with EDR-148 in mixture chloroform/methanol



SI-Figure 49: Theoretical evolution of the degree of polymerization ($\overline{DPn}$) according to advancement of reaction (p) during polyaddition of monomers in stoichiometric proportion