Electronic Supporting Information For:

Pathway to fully-renewable biobased polyesters derived from HMF and phenols

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Thermodynamic calculations:

DFT calculations were performed using Gaussian 16 (Gaussian Inc.) at b3lyp/6-31++g(d,p) level of theory. Frequency calculations were performed on all optimized structures to determine electronic energies (EE), thermal energies and thermal free energies. These values were used to obtain enthalpies:

$$H = EE + \text{thermal energies} \quad (1)$$

and free energies:

$$G = EE + \text{thermal free energies} \quad (2)$$

Figure S1 shows the Gibbs free energy differences between the substrate (FCA) and possible products. These values were then used to calculate prospective rate constants. Our results show very large rate constants ($K_1=1.1\times10^{29}$, $K_2=5.9\times10^{53}$ and $K_3=5.7\times10^{37}$) which leads to 100% theoretical equilibrium conversion.

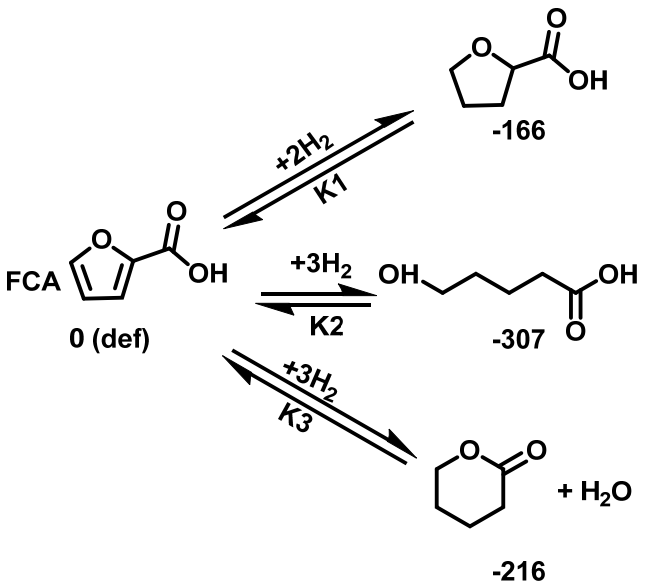

Figure S1. Energetics of FCA reduction to possible products calculated by DFT. The values are Gibbs free energy difference (ΔG) in kJ/mol between FCA and products on the right hand of reactions.

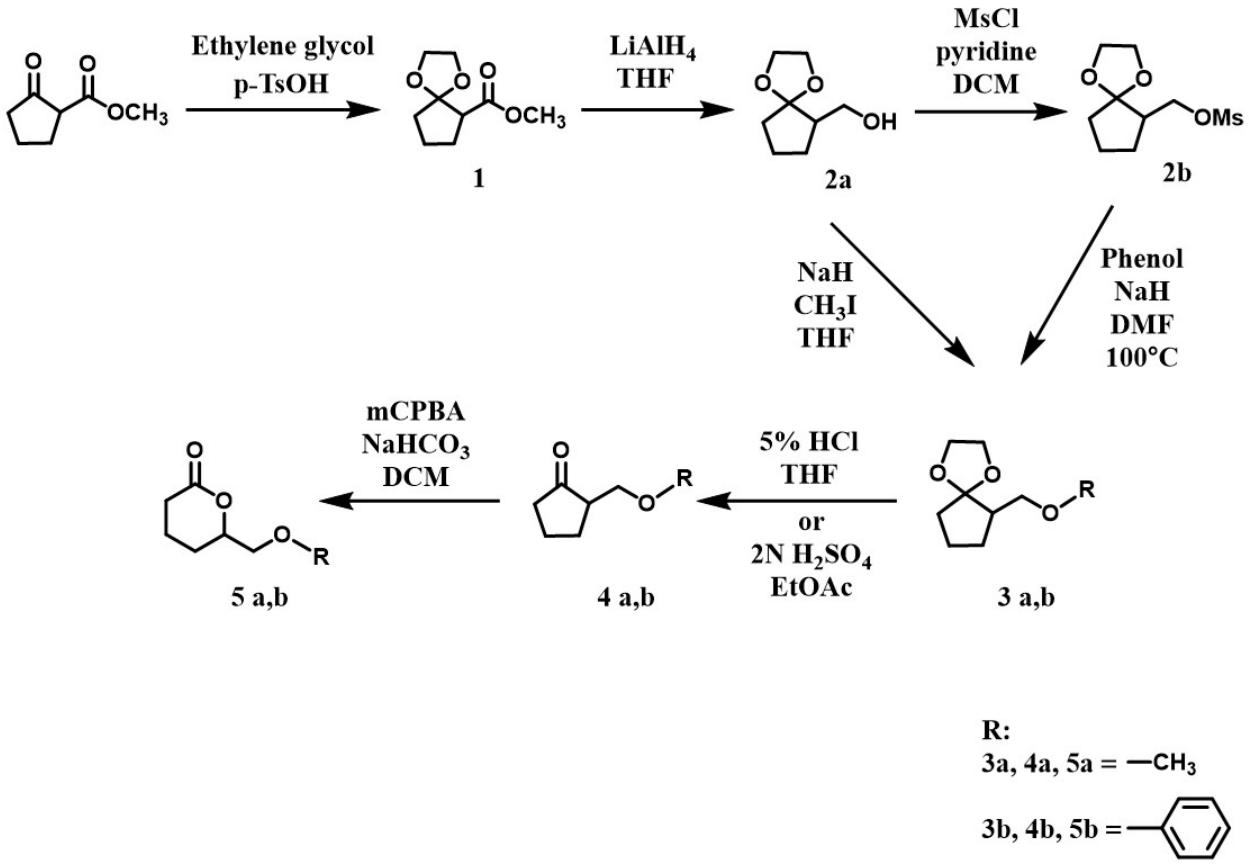

Figure S2. Overall synthesis scheme for MDHL and PDHL monomers

Monomer Synthesis:

Synthesis of methyl 1,4-dioxaspiro[4.4]nonane-6-carboxylate (1)[1]

First, *p*-toluene sulfonic acid (37 g, 0.22 mol) was dissolved in ethylene glycol (120 mL) and stirred at 30 °C for 30 minutes. After 30 minutes, molecular sieves (3Å, 4 to 8 mesh) (40 g) were added to the mixture and the ethylene glycol solution was separated from the sieves. The methyl cyclopentanone-2-carboxylate (25 mL, 0.2 mol) was added into the solution and stirred for 3 hours at room temperature. After the reaction time, the mixture was poured into 1 M potassium hydroxide solution (100 mL) saturated with sodium chloride (NaCl) and extracted with diethyl ether (3 x 100 mL). After collecting the organic layer, the solution was washed with brine solution (100 mL) and dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator to give **1** as a colorless product (24.2 g, 65% yield).

^{1}H NMR (Chloroform-*d*) δ (ppm): 3.9 - 4.0 (m, 4H), 3.70 (s, 3H), 2.92 (t, 1H), 1.6 - 2.2 (m, 6H).

Synthesis of 1,4-dioxaspiro[4.4]non-6-ylmethanol (2a)[1]

Lithium aluminum hydride ($LiAlH_4$) (4 g, 0.11 mol) was added to tetrahydrofuran (THF) solvent (150 mL) and stirred at 0 °C. After 30 minutes, synthesized **1** (24.2 g, 0.13 mol) was added dropwise into the $LiAlH_4$ suspension and stirred overnight at room temperature. Ethyl acetate (200 mL) was added very slowly to quench excess $LiAlH_4$ in an ice bath and then the reaction mixture was poured into ice-cold saturated sodium potassium tartrate solution (100 mL). The organic layer

[1] Wang, S.; Chen, G.; Kayser, M. M.; Iwaki, H.; Lau, P. C. K.; Hasegawa, Y. Baeyer-Villiger oxidations catalyzed by engineered microorganisms: Enantioselective synthesis of δ-valerolactones with functionalized chains. Canadian Journal of Chemistry. 2002, 80(6): 613-621.

was separated and dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator to obtain the desired product **2a** (14.8 g, 72% yield).

^{1}H NMR (Chloroform-*d*) δ (ppm): 3.92 (m, 4H), 3.62 (m, 2H), 2.65 (t, 1H), 2.11 (m, 1H), 1.5-1.95 (m, 7H).

Synthesis of 6-(methoxymethyl)-1,4-dioxaspiro[4.4]nonane (3a)[1]

NaH (22 g, 60% dispersion in mineral oil) was washed with tetrahydrofuran (3 x 30 mL) to remove the mineral oil. After washing, THF (100 mL) was added to the NaH and stirred for 5 mins. Then the starting material **2a** (10.5 g, 0.066 mol) was added into the suspended solution. Iodomethane (4.1 mL, 0.066 mol) was added dropwise into the mixture and stirred overnight. The next morning, the mixture was poured onto ice cubes to quench the excess NaH and extracted with ethyl acetate (3 × 50 mL). The organic layer was washed with 0.2 M KOH (100 mL), 0.5 M HCl (100 mL) and brine solution (100 mL). The extracted organic layer was washed with saturated K_2CO_3 solution in water and the solvent was removed on a rotary evaporator to obtain **3a** (8.5 g, 75% yield).

^{1}H NMR (Chloroform-*d*) δ (ppm): 3.86 (m, 4H), 3.44 (m, 1H), 3.32 (s, 3H), 3.25-3.3 (m, 1H) 2.21 (m, 1H), 1.4 - 1.96 (m, 6H)

Synthesis of 1,4-dioxaspiro[4.4]non-6-ylmethyl methanesulfonate (2b)[2]

Pyridine (14.5 mL, 0.18 mol) and methanesulfonyl chloride (5.1 mL, 0.07 mol) were added into the solution of **2a** (9.4 g, 0.06 mol) in dichloromethane (50 mL). The mixture was stirred for 24 h

[2]Boeykens, M.; Kimpe, N. D.; Tehrani, K. A. Synthesis of 1-Amino-2,2-dialkylcyclopropanecarboxylic Acids via Base-Induced Cyclization of γ-Chloro-α-imino Esters. *The Journal of Organic Chemistry,* **1994,** *59* (23), 6973-6985.

at room temperature forming a white precipitate. The mixture was filtered, then washed with NaCl saturated 1N HCl (15 mL, 0.03 mol) and extracted with dichloromethane (2 x 50 mL). The organic layer was separated and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give **2b** (9.21 g, 65% yield).

^{1}H NMR (Chloroform-*d*) δ (ppm): 4.30 (dd, *J* = 9.8, 6.2 Hz, 1H), 4.14 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.90 (m, 4H), 3.00 (s, 3H), 2.37 (m, 1H), 1.4 - 2.02 (m, 5H).

Synthesis of 6-(phenoxymethyl)-1,4-dioxaspiro[4.4]nonane (3b)

NaH (4.68 g, 60% dispersion in mineral oil) was washed with THF (3 x 10 mL) in 500 mL round-bottom flask to remove mineral oil and then the NaH was suspended in DMF (50 mL) solvent. Phenol (5.5 g or 0.058 mol in 20 mL DMF) solution was added dropwise into the NaH suspension under an ice bath and stirred for 30 min at room temperature to deprotonate the phenol. After deprotonation, the round-bottom flask was sealed with a septa, flushed with N_2, and connected to a bubbler. **2b** (9.21 g, 0.039 mol) was added into the mixture using a plastic syringe and placed in a 100 °C preheated oil bath and stirred for 18 h. After the reaction time, the round-bottom flask was removed from the oil bath and excess NaH was quenched by adding deionized water (100 mL). The mixture was extracted with ethyl acetate (3 x 50 mL) and washed with 5 M KOH solution (100 mL). The organic layer was dried over Na_2SO_4 and removed on a rotary evaporator to give **3b** (7.5 g, 55% yield).

^{1}H NMR (Chloroform-*d*) δ (ppm): 7.27 (m, 2H), 6.91 (m, 3H), 3.84-4.1 (m, 6H), 2.46 (m, 1H), 2.04 (m, 1H), 1.52 - 1.9 (m,, 6H).

Synthesis of 2-(methoxymethyl)cyclopentanone (4a) Error! Bookmark not defined.

In this synthesis, a 5% (w/w) HCl (36 mL, 1.18 mol) solution in water was added into a solution of **3a** (8.5 g**,** 0.05 mol) in tetrahydrofuran (50 mL) solvent and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate (3 x 50 mL) and the organic layer was washed with brine solution (50 mL). The extracted organic layer was dried over anhydrous Na_2SO_4 and rotary evaporated to yield **4a** (3.4 g, 53% yield).

^{1}H NMR (Chloroform-*d*) δ (ppm): 3.55 (m, 2H), 3.32 (s, 3H), 1.72 - 2.36 (m, 7H).

Synthesis of 2-(phenoxymethyl)cyclopentanone (4b)

In this synthesis, a 2N H_2SO_4 (19 mL, 0.35 mol) solution was added into a mixture of **3b** (7.5 g**,** 0.032 mol) in ethyl acetate (30 mL) solvent and stirred overnight at room temperature. Brine solution (50 mL) was poured into the mixture the next morning and extracted with ethyl acetate (3 x 50 mL). The extracted organic layer was dried over Na_2SO_4 and removed on a rotary evaporator to give **4b** (3.1 g, 51% yield).

^{1}H NMR (Chloroform-*d*) δ (ppm): 7.26 (m, 3H), 6.92 (m3H), 4.19 (dd, J = 9.3, 3.7 Hz, 1H), 4.10 (dd, J = 9.3, 6.3 Hz, 1H), 2.56 (m, 1H), 2.4 – 1.8 (m, 7H).

Synthesis of 6-(methoxymethyl)oxan-2-one (5a)

In this synthesis, 3-chloroperoxybenzoic acid (mCPBA, 70%) (8.3 g, 0.034 mol) and sodium bicarbonate (3.4 g, 0.04 mol) were added to dichloromethane (50 mL) and stirred for 15 mins at room temperature. **4a** (3.4 g, 0.027 mol) was added into the mixture and stirred for 3h. After the reaction time, extra dichloromethane (50 mL) solvent was added into the reaction mixture. The organic layer was washed with saturated Na_2SO_3 (20 mL), saturated $NaHCO_3$ (50 mL), then brine

solution (20 mL) and separated. The organic layer was dried over anhydrous Na_2SO_4 and removed on a rotary evaporator to get the crude product (δ-substituted 85% major and α-substituted 15% minor product). The resulting crude product was purified via silica gel flash column chromatography using 67:33 hexane:ethyl acetate mobile phase. After running flash column chromatography, 1.83 g of pure MDHL (**5a**) was collected with a 47% yield.

^{1}H NMR (Chloroform-*d*) δ (ppm): 4.45 (m, 1H), 3.52 (m, 2H), 3.39 (s, 3H), 2.56 (m, 1H), 2.47 (m, 1H), 1.98 – 1.64 (m, 5H) and ^{13}C NMR (Chloroform-*d*) δ (ppm): 171.41, 79.25, 77.27, 74.58, 59.71, 24.68, 18.53.

Synthesis of 6-(phenoxymethyl)oxan-2-one (5b)

In this synthesis, 3-chloroperoxybenzoic acid (mCPBA, 70%) (7.9 g, 0.032 mol) and sodium bicarbonate (3.4 g, 0.04 mol) were added to dichloromethane (50 mL) and stirred for 15 mins at room temperature. **4b** (3.1 g, 0.016 mol) was added into the mixture and stirred for 9h. After the reaction time, extra dichloromethane (50 mL) solvent was added into the reaction mixture. The organic layer was washed with saturated Na_2SO_3 (20 mL), saturated $NaHCO_3$ (50 mL), then brine solution (20 mL) and separated. The organic layer was dried over anhydrous Na_2SO_4 and removed on a rotary evaporator to get the crude product (δ-substituted 81% major and α-substituted 19% minor product). The resulting solid was purified via silica gel flash column chromatography using 72:28 hexane:ethyl acetate mobile phase. After running flash column chromatography, 1.3 g of pure PDHL (**5b**) was collected at a 40% yield.

^{1}H NMR (Chloroform-*d*) δ (ppm): 7.27 (m, 2H), 7.0 – 6.87 (m 3H), 4.68 (m, 1H), 4.14 (dd, J = 10, 4.6 Hz, 1H), 4.08 (dd, J = 10, 5.3 Hz, 1H), 2.7 – 2.48 (m, 2H), 2.15 – 1.77 (m, 4H) and ^{13}C NMR (Chloroform-*d*) δ (ppm): 129.83, 121.56, 114.77, 77.26, 69.61, 29.93, 24.98.

Table S1: Results for ROP of FDHL monomers without any initiator in the presence of DPP catalyst

Run	Monomer	$[M]_0/[C]$	Time (d)	Conversion	$M_{n,\ SEC}$ (kg/ mol)
1	MDHL	40/1	5	0.90	10.0
2	MDHL	80/1	10	0.90	12.0
3	PDHL	50/1	6	0.57	3.5

Here, [C] = concentration of catalyst which was taken based on the monomer mol%

Table S2: Results for acid and base catalyzed ROP of functionalized δ-hexalactones (FDHLs)

Monomer	Catalyst	Entry	$[M]_0/[I]/[C]$	Time (days)	Conv. [c]	$M_{n,\ expected}$ [d] (kg/ mol)	$M_{n,\ SEC}$ [e] (kg/ mol)	Đ [e]
PDHL	DPP	1[a]	50/1/0.15	12	0.04	-	-	-
		2[a]	50/1/1.5	9	0.73	7.5	2.2	1.2
		3[a]	50/1/3	9	0.75	7.7	1.2	2.14
		4[a]	100/1/6	9	0.69	14.2	1.3	1.5
MDHL	TBD	5[a]	50/1/0.15	3	0.0	-	-	-
		6[b]	50/1/0.15	7	0.0	-	-	-

[a]1,4-dioxane as solvent, $[M]_0 = 1.1$ M; [b]Bulk polymerization, $[M]_0 = 5.5$ M; where $[M]_0$ = Initial monomer concentration. [c]Fractional conversion measured by ^{1}H NMR spectroscopy. [d]Calculated from $[M]_0/[I]$ × monomer conversion × MW of MDHL or PDHL. [e]Measured by SEC in THF as the mobile phase when DPP used as catalyst and DMF with 0.5 wt% LiBr as the mobile phase when TBD used as catalyst, using linear polystyrene standards with a refractive index detector.

Table S3: Results for ROP of PDHL monomer with different TBD catalyst loading after 48 hours

Run	**$[M]_0/[I]$**	**Catalyst (mole%)**	**% Conversion**	**Đ**
1	50/1	9%	50%	2.08
2	100/1	3%	48%	1.9
3	50/1	2%	49%	2.1
4	50/1	1.5%	48%	2.1
5	100/1	0.7%	47%	1.6
6	100/1	0.5%	48%	1.6
7	100/1	0.3%	45%	1.4
8	100/1	0.1%	5%	1.2

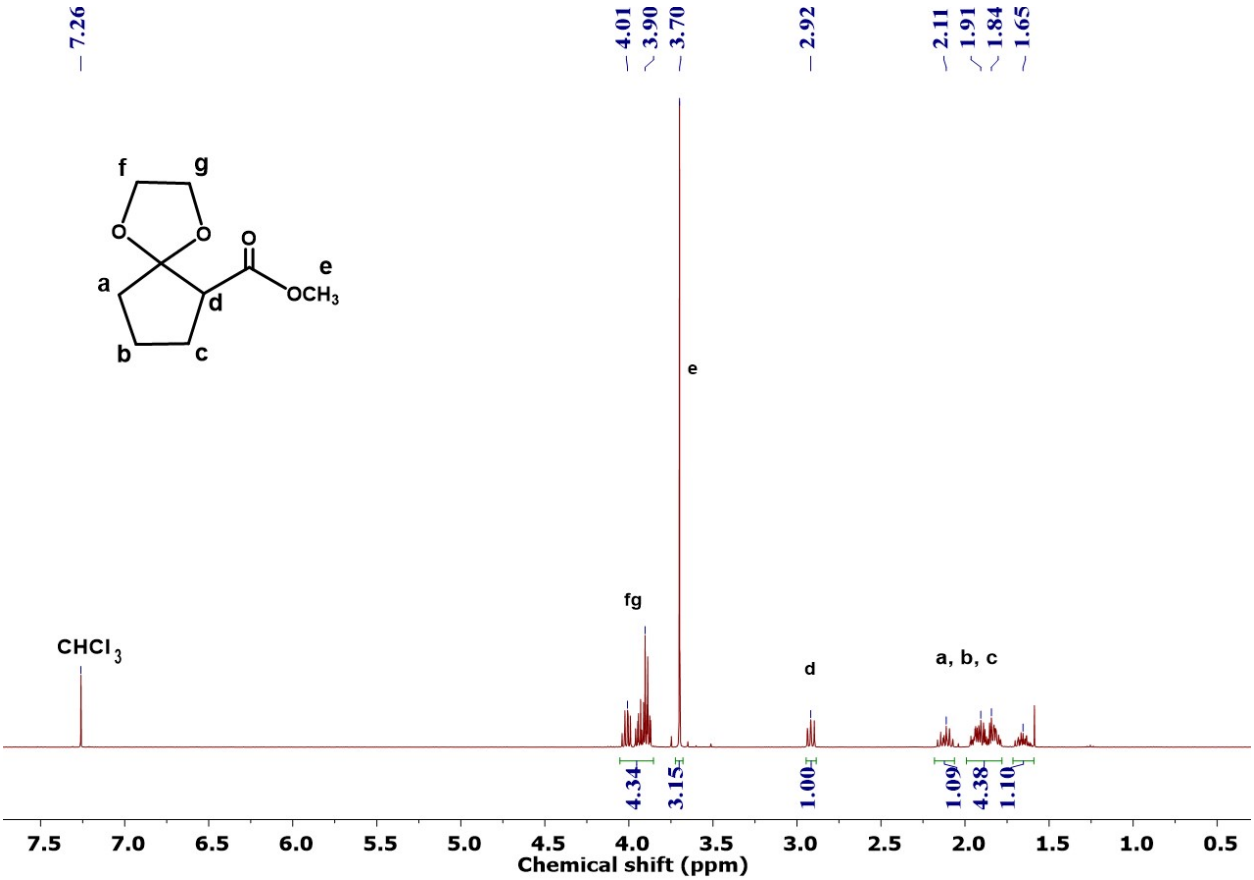

Figure S3. ^{1}H NMR spectrum of methyl 1,4-dioxaspiro[4.4]nonane-6-carboxylate (1)

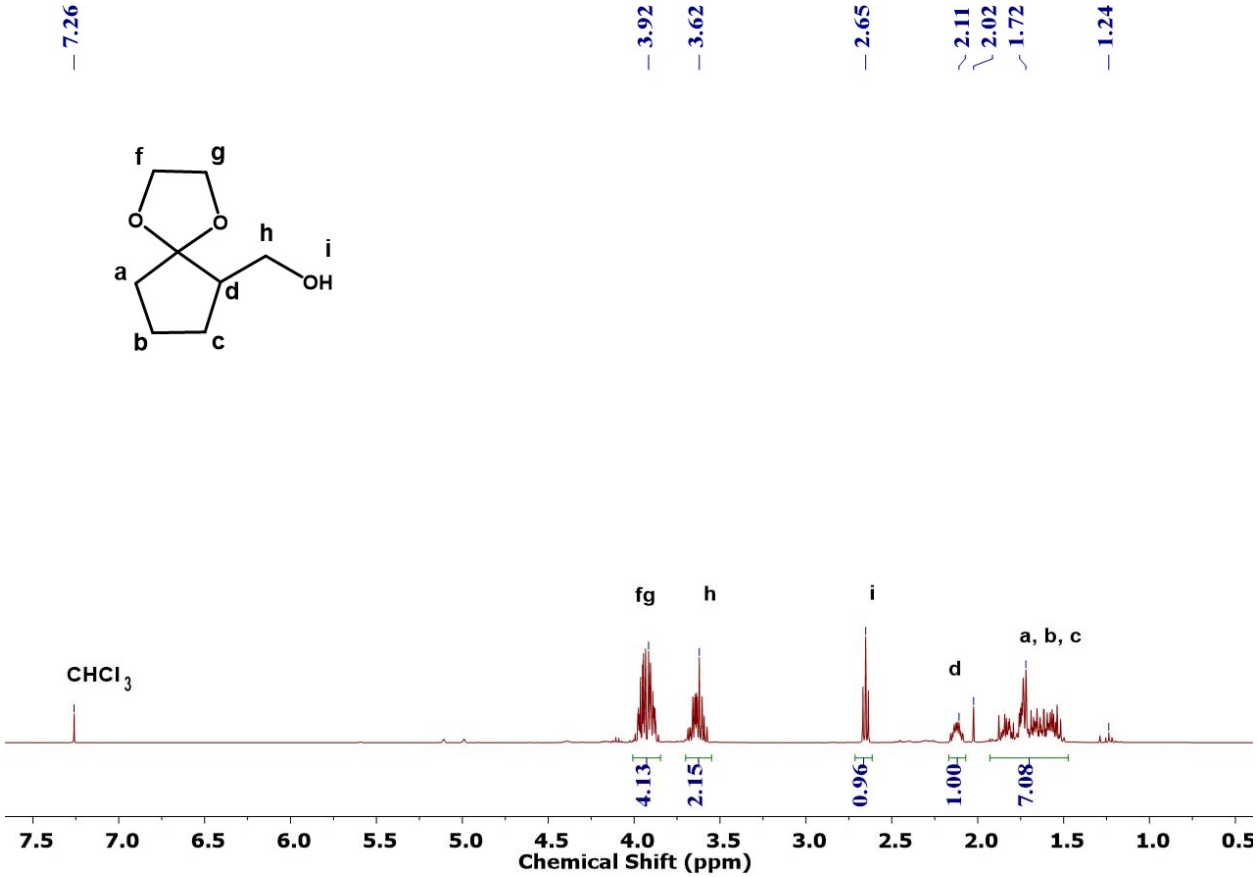

Figure S4. ^{1}H NMR spectrum of 1,4-dioxaspiro[4.4]non-6-ylmethanol (2a).

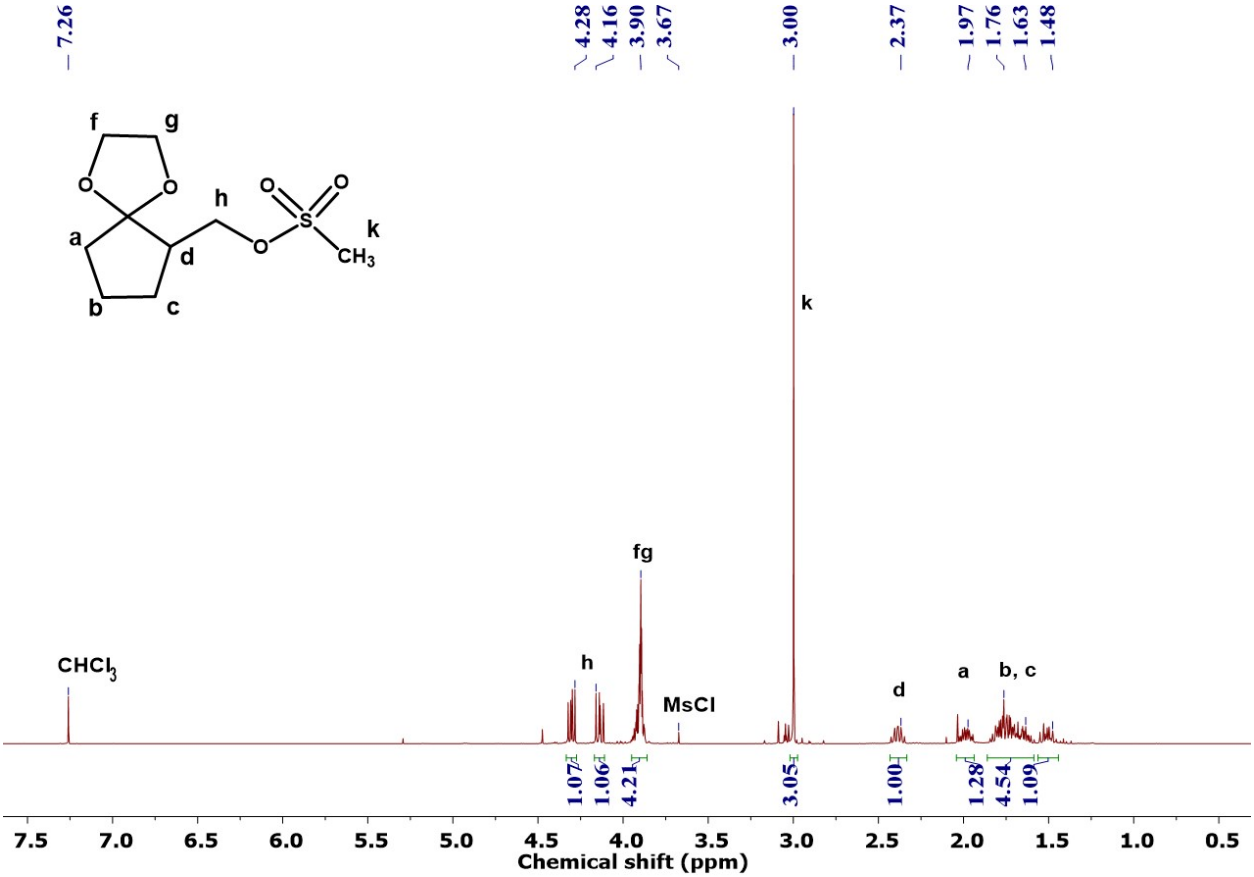

Figure S5. ^{1}H NMR spectrum of 1,4-dioxaspiro[4.4]non-6-ylmethyl methanesulfonate (2b)

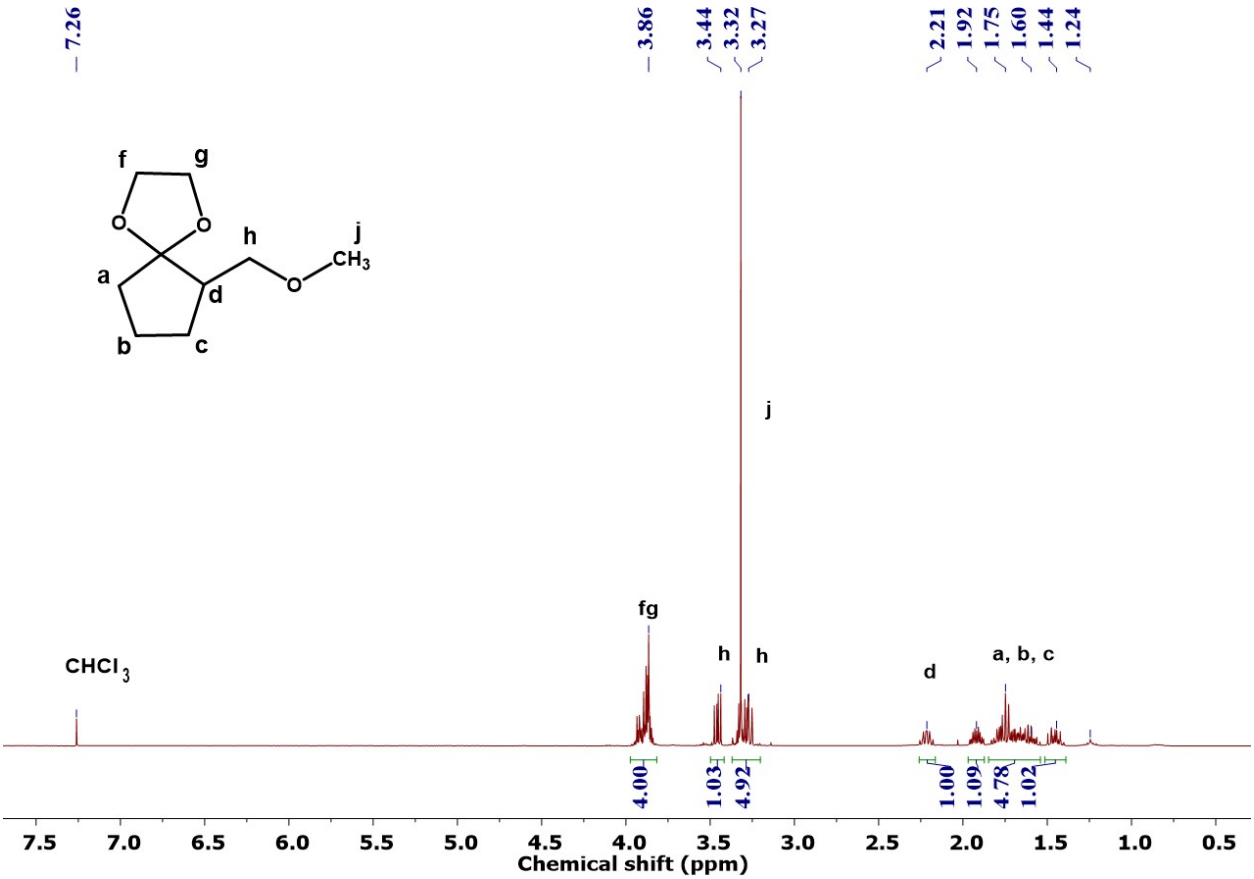

Figure S6. ^{1}H NMR spectrum of 6-(methoxymethyl)-1,4-dioxaspiro[4.4]nonane (3a)

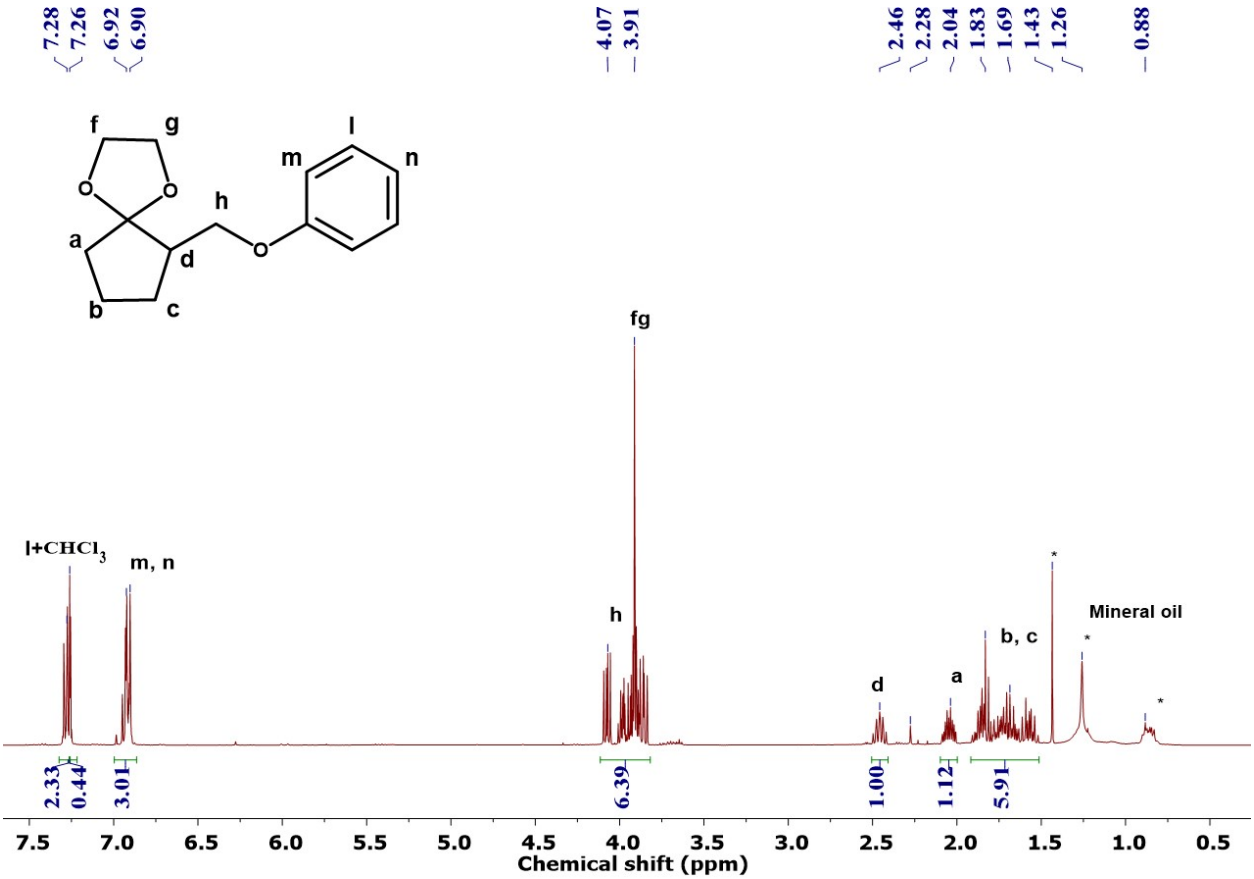

Figure S7. ^{1}H NMR spectrum of 6-(phenoxymethyl)-1,4-dioxaspiro[4.4]nonane (3b). *Mineral oil from NaH washing step

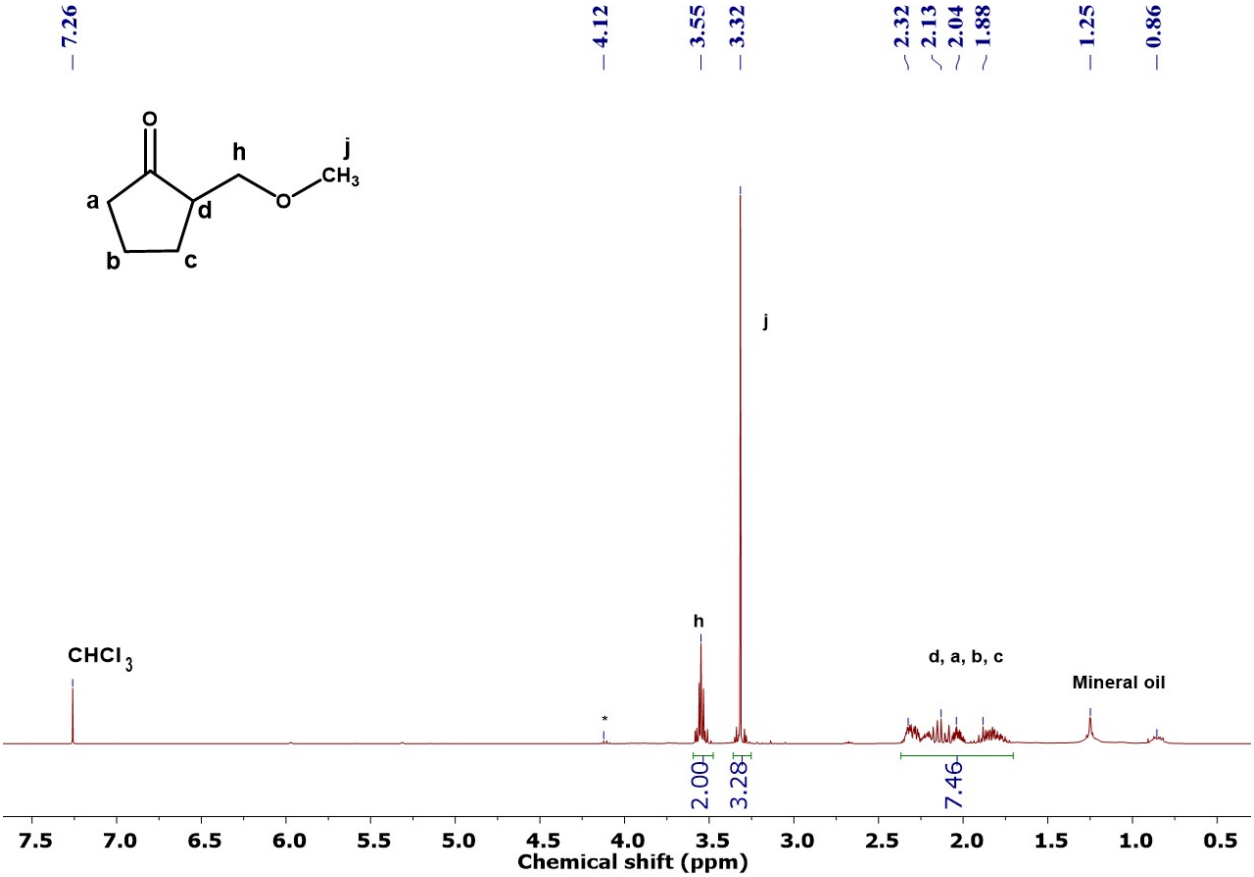

Figure S8. ^{1}H NMR spectrum of 2-(methoxymethyl)cyclopentanone (4a). *Ethyl acetate solvent

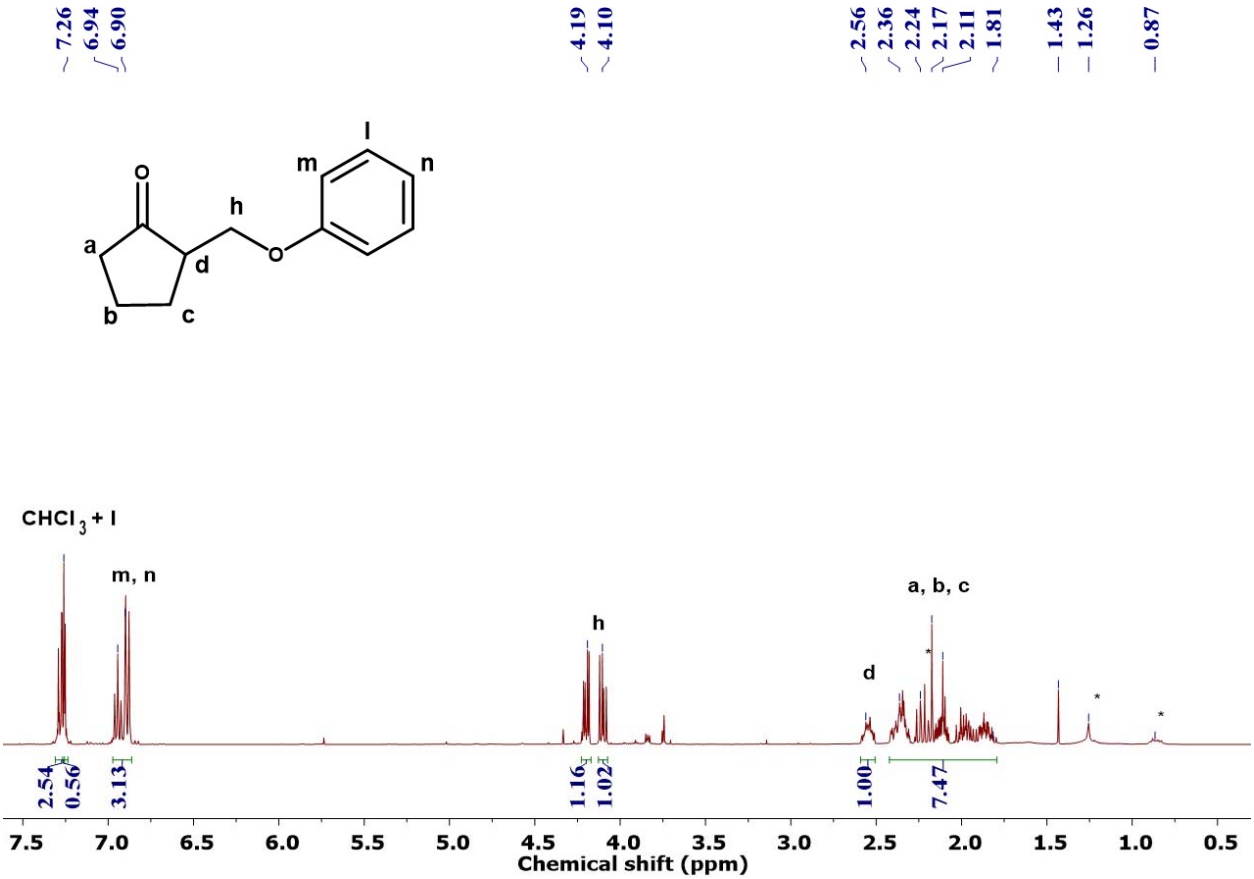

Figure S9. ^{1}H NMR spectrum of 2-(phenoxymethyl)cyclopentanone (4b). *Acetone solvent and mineral oil

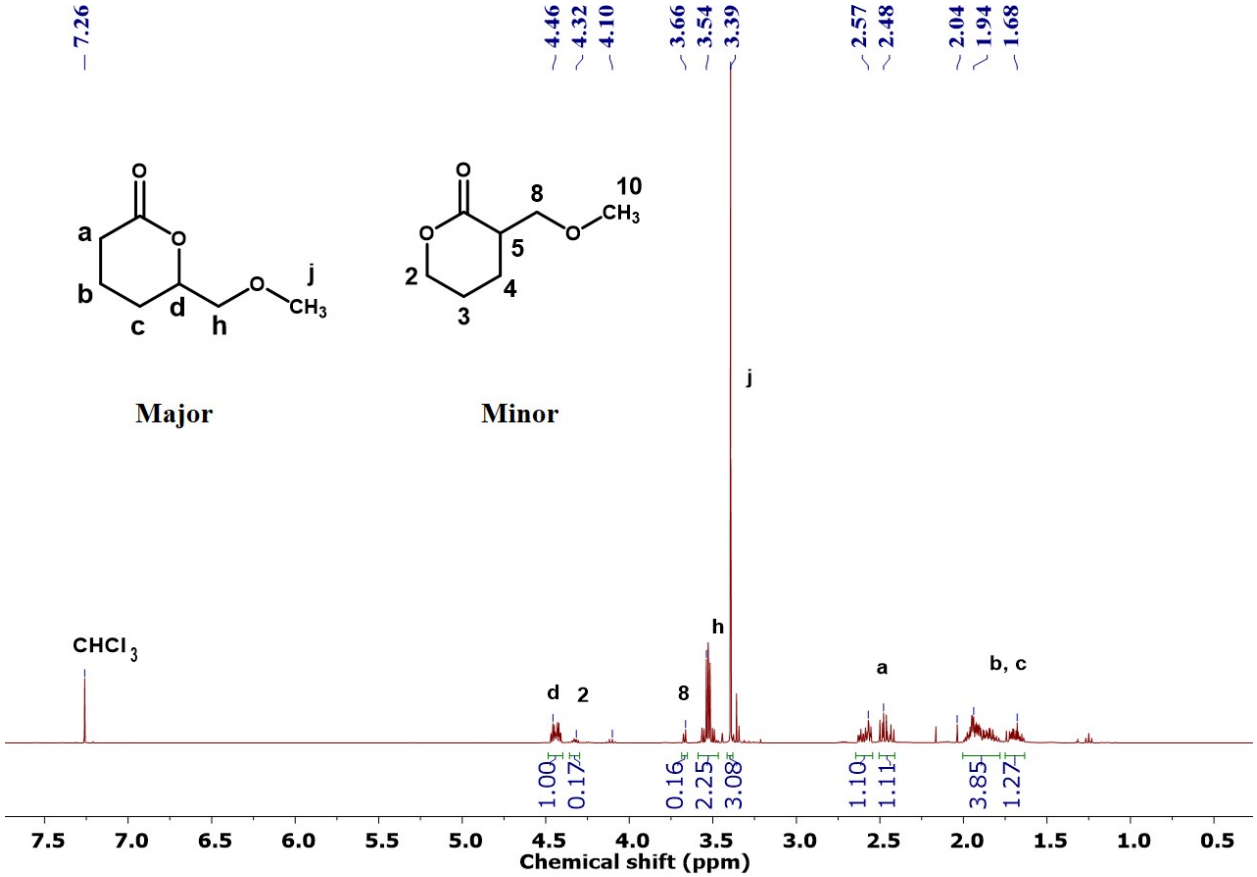

Figure S10. ^{1}H NMR spectrum of a crude mixture of 6-(methoxymethyl)oxan-2-one (5a)

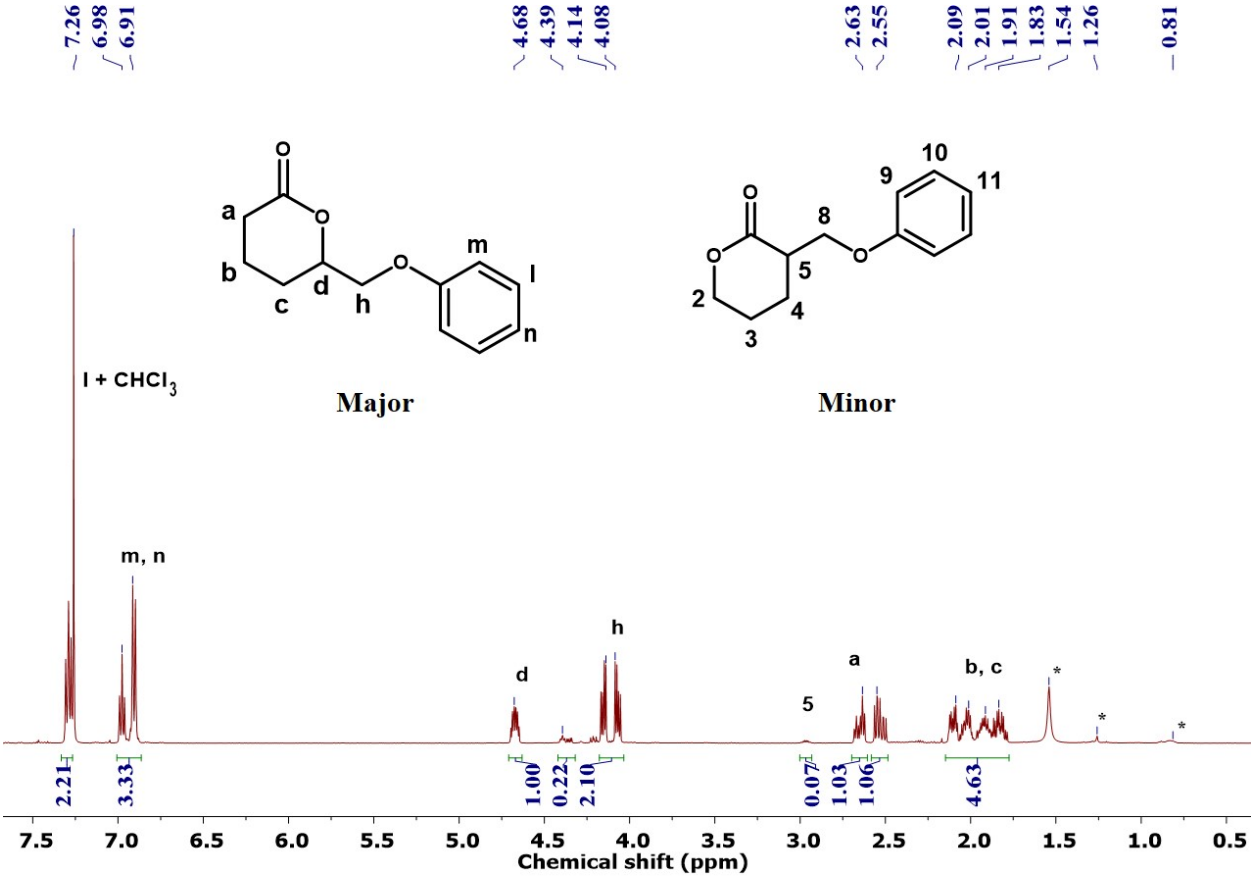

Figure S11. ^{1}H NMR spectrum of a crude mixture of 6-(phenoxymethyl)oxan-2-one (5b)

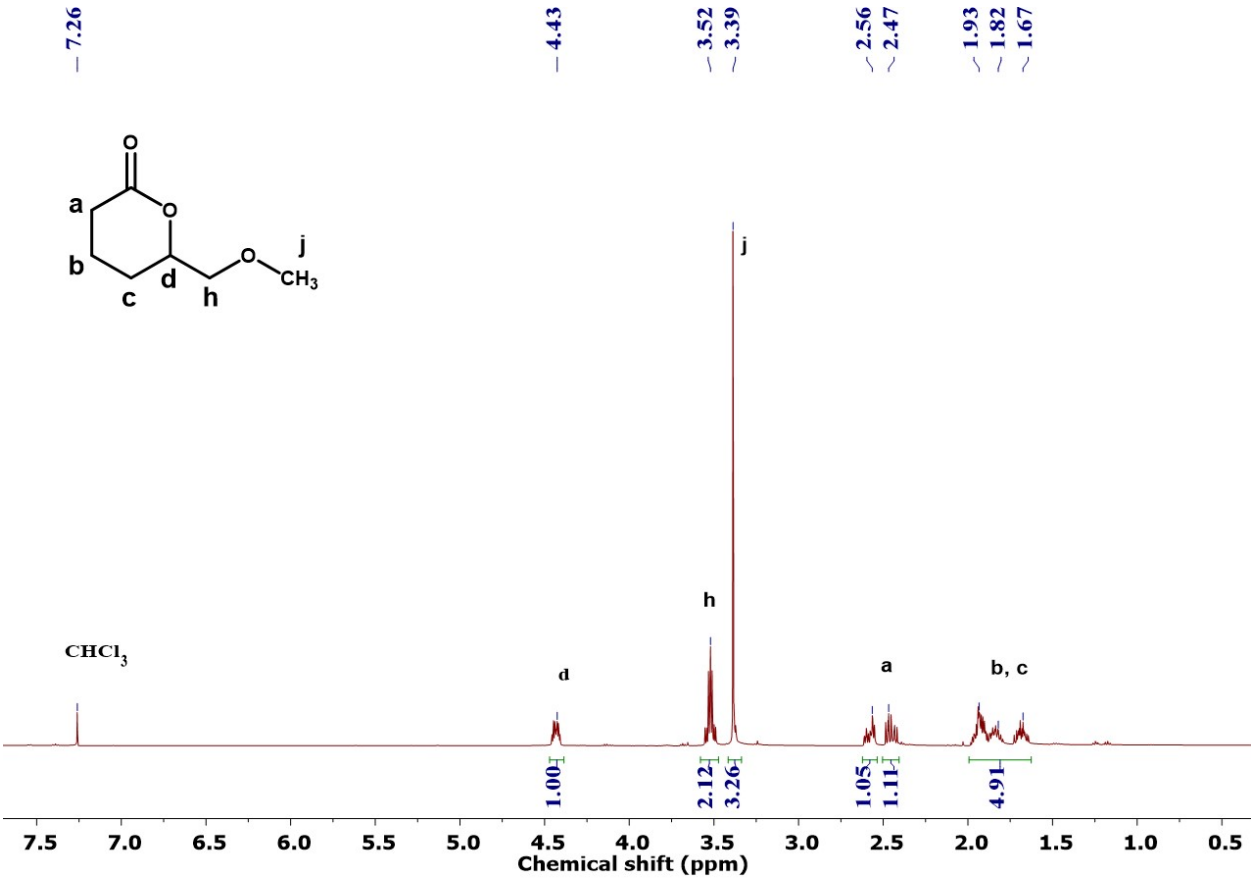

Figure S12. ^{1}H NMR spectrum of pure MDHL monomer (5a), collected after flash column chromatography

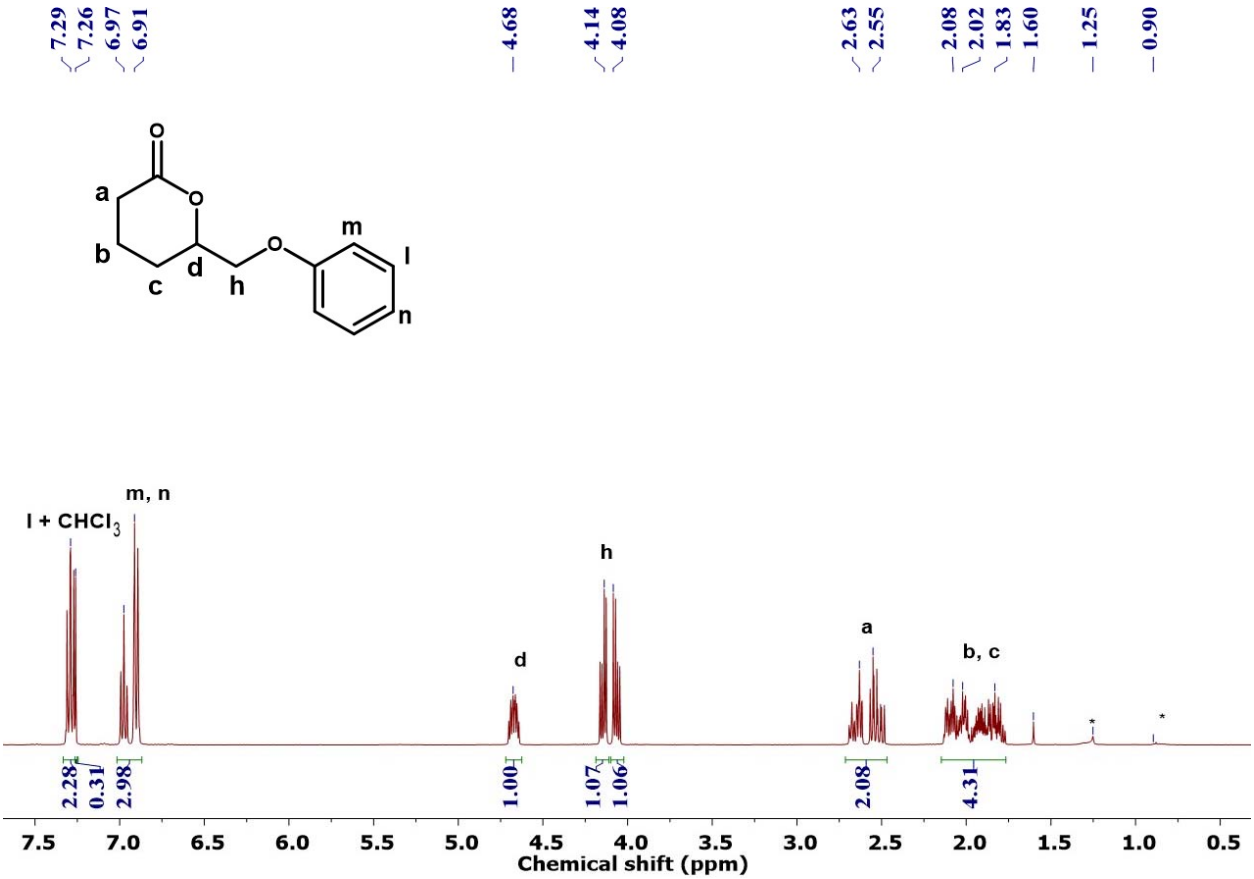

Figure S13. ^{1}H NMR spectrum of pure PDHL monomer (5b), collected after flash column chromatography

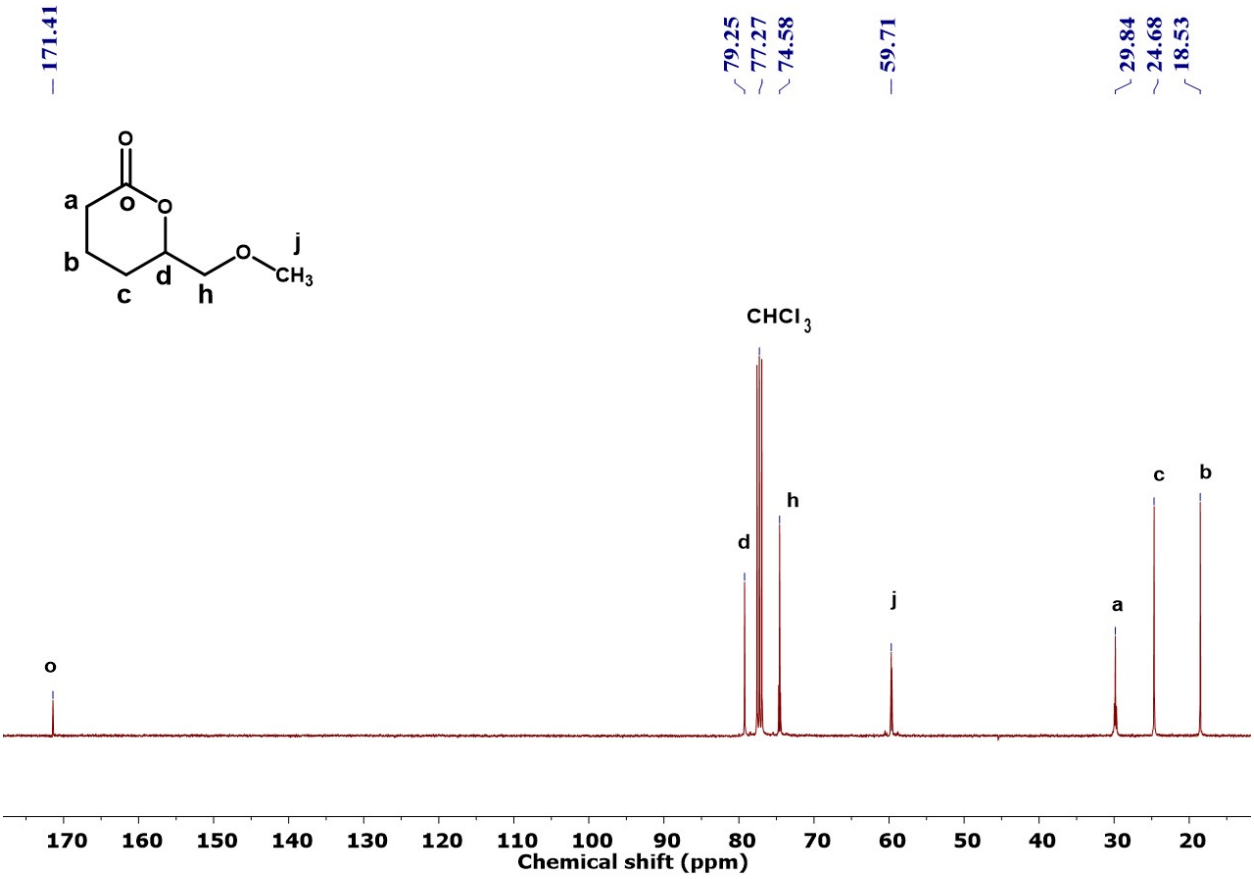

Figure 14. ^{13}C NMR spectrum of pure MDHL monomer (5a)

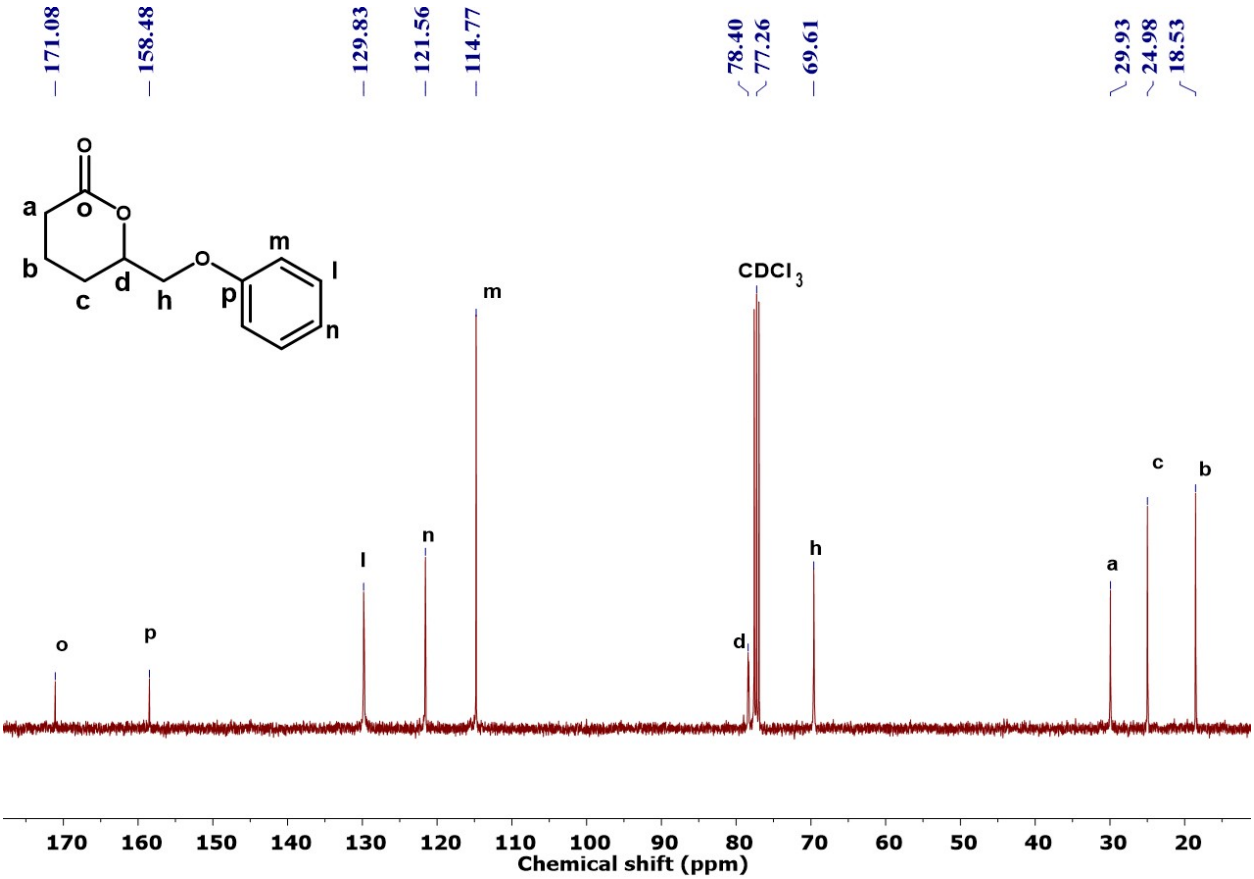

Figure S15. ^{13}C NMR spectrum of pure PDHL monomer (5b)

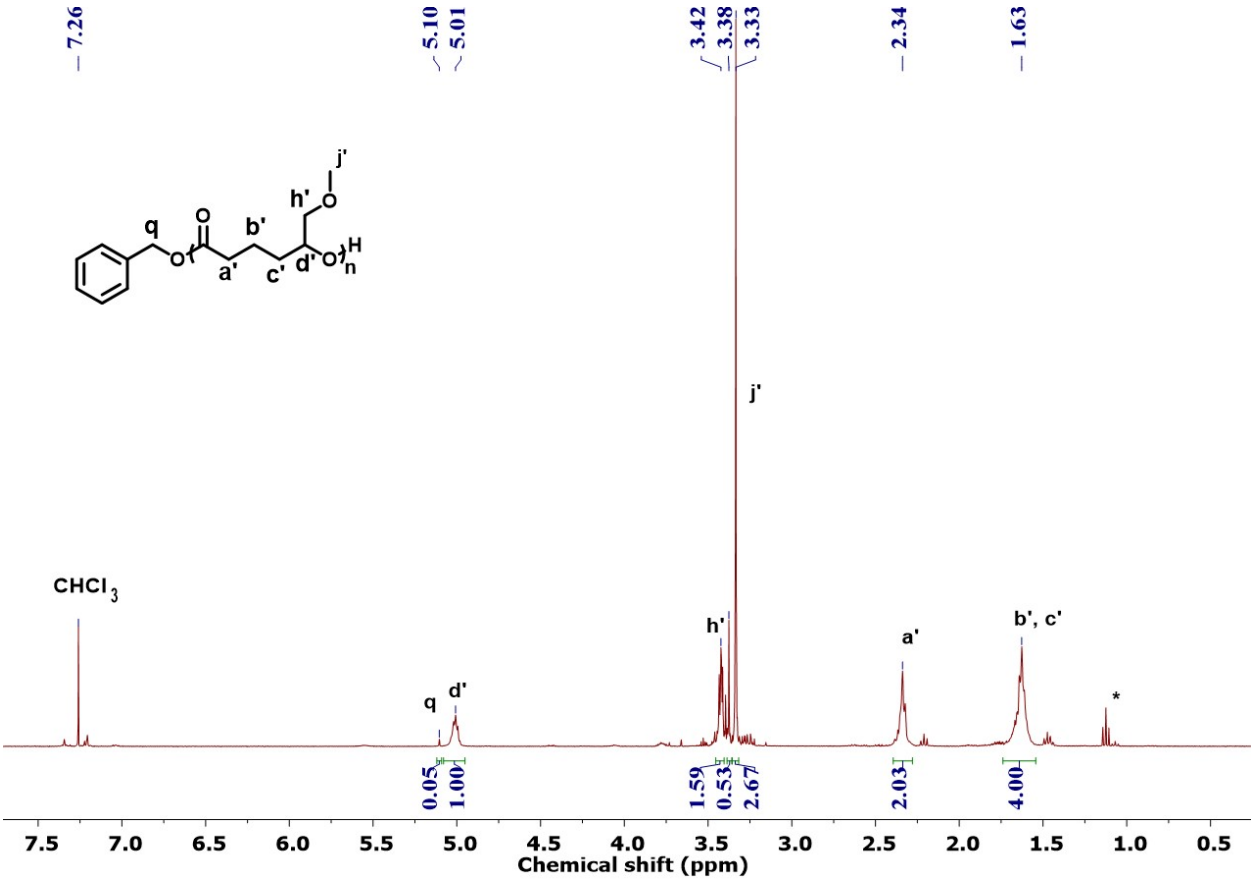

Figure S16. ^{1}H NMR spectrum of crude poly(MDHL). ^{1}H NMR spectrum was collected after the polymerization reached equilibrium on day three.

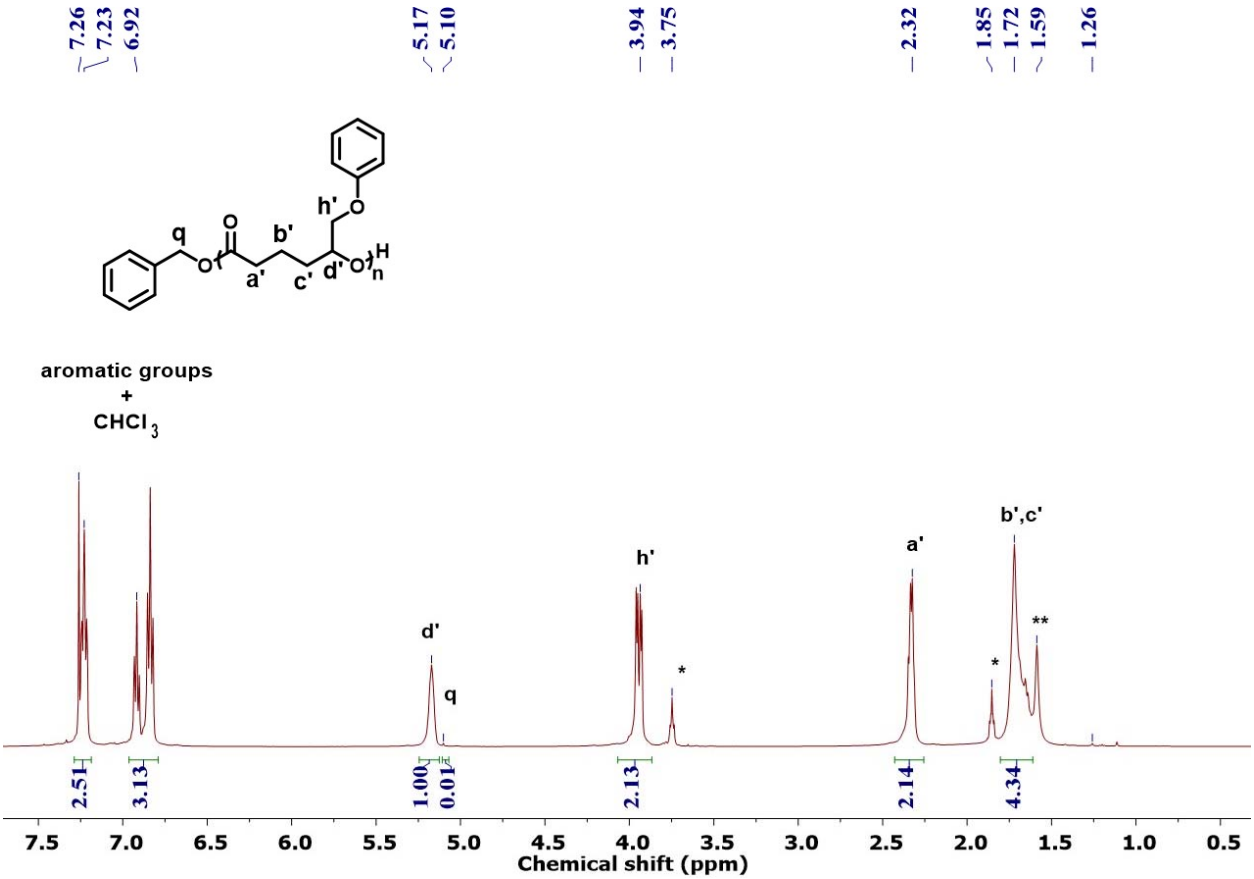

Figure S17. ^{1}H NMR spectrum of crude poly(PDHL). ^{1}H NMR spectrum was collected after the polymerization reached equilibrium on day seven. (*THF solvent,**H_2O)

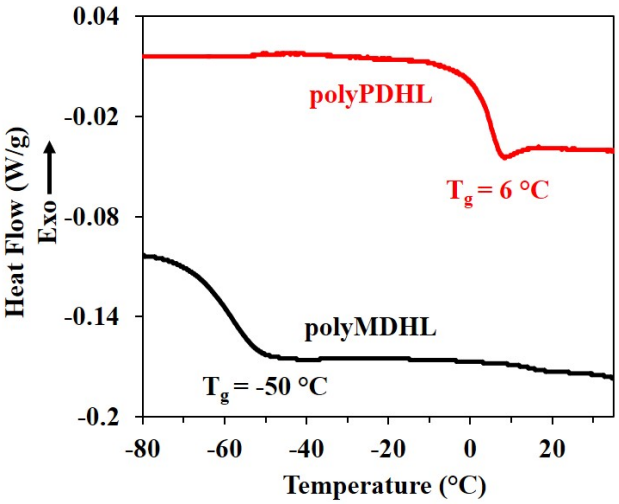

Figure S18. DSC thermograms of polyMDHL and polyPDHL. Curves are shifted vertically to provide clarity. Here, M_n = 3.7 kg/mol for polyMDHL and M_n = 7 kg/mol for polyPDHL

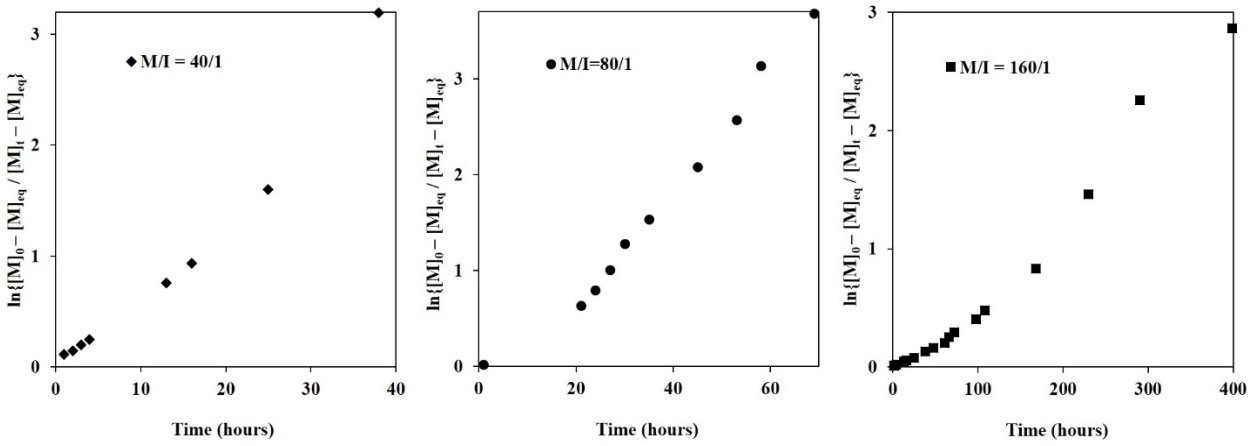

Figure S19. Kinetic plots for ROP of MDHL at different $[M]_0/[I]$ ratios which shows the deviation from first order kinetics behavior.

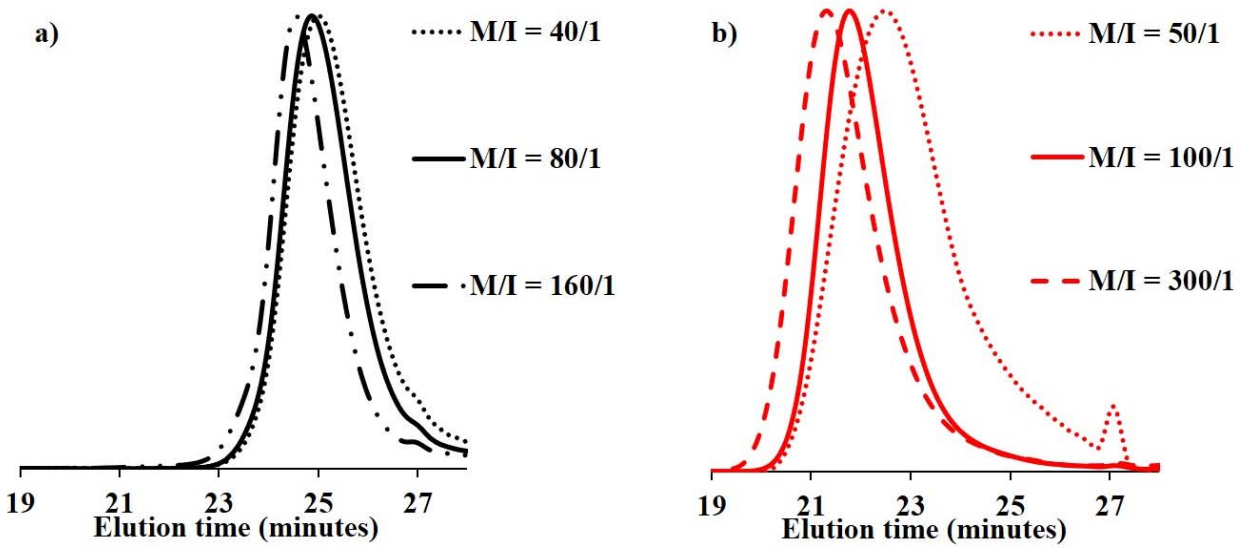

Figure S20. SEC elution curves for ROP of a) MDHL and b) PDHL after reaching equilibrium conversion at different $[M]_0/[I]$ ratios. Molecular weights ($M_{n,\,SEC}$) and dispersity are in the Table1.

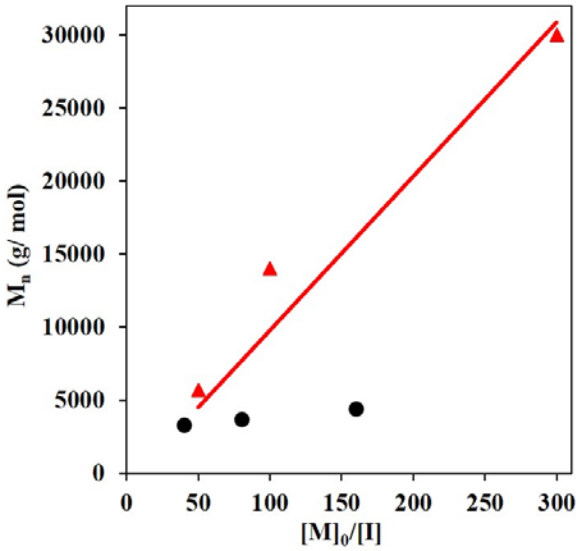

Figure S21. Evolution of molecular weight for varying $[M]_0$/ [I] ratios. Molecular weights (M_n) for both poly(MDHL) (black circle) and poly(PDHL) (red triangle) measured by SEC. Solid lines used to show expected molecular weight of poly(PDHL) (red) measured by ^{1}H NMR conversion. Calculated from ($[M]_0$/[I] x conversion x MW of MDHL or PDHL).

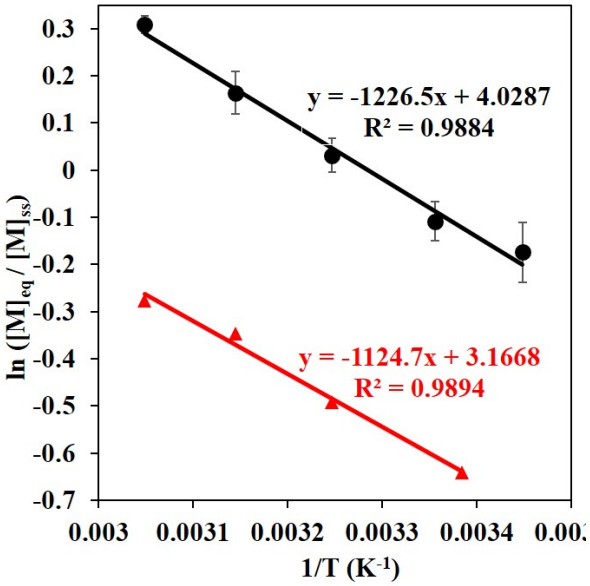

Figure S22. Van't Hoff analysis for poly(MDHL) (black circle) and poly(PDHL) (red triangle). Both polymerizations were carried out at a different temperature until equilibrium was reached as confirmed by ^{1}H NMR spectroscopy. $[M]_{eq}$ was calculated from monomer conversion by ^{1}H NMR spectroscopy. Here, T is the polymerization temperature and $[M]_{ss}$ is standard state monomer concentration and we assume $[M]_{ss}$ = 1 M.