Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Transfer Hydrogenation of Cyclic Carbonates and Polycarbonate to Methanol and Diols by Iron Pincer Catalysts

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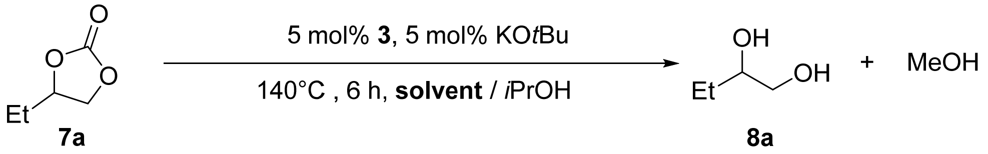
1. General Information

All experiments were performed under inert argon atmosphere by using standard Schlenk technic or glove box, if not stated otherwise. THF, 1,4-dioxane, toluene, CH_3CN, CH_2Cl_2 and heptane were obtained from a solvents purification system. Dry EtOH and Dry *i*PrOH was purchased from Across Organics, degassed and purged with argon prior to use. Chemicals were purchased from Sigma, Alfa, Strem, abcr, Acros and TCI. $HN(CH_2CH_2P(i\text{Pr})_2)_2$ (10%wt in THF) was purchased from Strem and used without further purification. All cyclic carbonates **7a**–**7j** were synthesized according to literature procedures in our lab.[1] The products were degassed and purged with argon prior to use. Poly(propylene carbonate), 4-Methyl-1, 3-dioxolan-2-one (**7c**) and 1, 3-dioxan-2-one (**7k**) was purchased from Sigma-Aldrich and abcr GmbH. Deuterated solvents were ordered from *Deutero GmbH* and stored over molecular sieves. NMR spectra were received using *Bruker* 300 Fourier, *Bruker* AV 300 and *Bruker* AV 400 spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s= singlet, d= doublet, t= triplet and m= multiplet. The molar masses were analyzed employing size exclusion chromatography (SEC) 1100 GPC from Agilent Technologies with a refraction index detector at 40 °C. GC analyses were performed on a Trace 1310 chromatograph with a 29m HP5 column. Starting temperature was 35 °C which was kept for 5 min and then raised with a rate 10°C min^{-1} to 180 °C, and keeping this temperature for another 0.5 min. The reported gas chromatography (GC) yields and conversions are based on a calibrated area of mesitylene as internal standard.

2. Parameter screening for the transfer hydrogenation of cyclic carbonate

2.1 Solvent screening

Table S1. Solvent effect on the Fe-catalyzed transfer hydrogenation of 4-ethyl-1, 3-dioxolan-2-one (**7a**).[a]

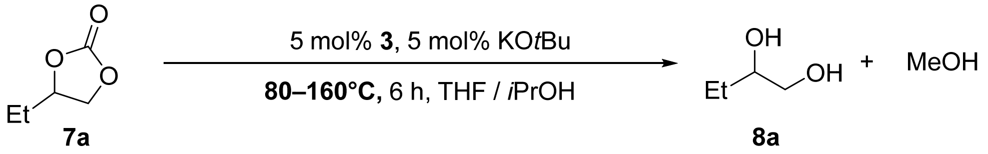


Entry	solvent	Conv/ %[b]	Yield of MeOH/ %[b]	Yield of **8a**/ %[b]
1	-	81	60	80
2	dioxane	65	37	54
3	THF	99	91	95
4	Toluene	77	45	61
5	Heptane	21	4	14
6	CH_3CN	7	trace	trace
7	DCM	13	trace	trace

[a] Reaction conditions: Catalyst **3** (5 mol%), KO*t*Bu (5 mol%), **7a** (1.0 mmol), solvent (1 mL), *i*PrOH (4 mL), 140 °C, 6 h. [b] Determined by GC using mesitylene as the internal standard.

2.2 Reaction temperature screening

Table S2. Effect of different reaction temperatures on the Fe-catalyzed transfer hydrogenation of 4-ethyl-1, 3-dioxolan-2-one(**7a**).[a]

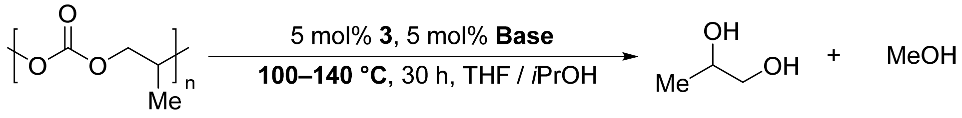


Entry	T/ °C	Conv./ %[b]	Yield of MeOH/ %[b]	Yield of diol/ %[b]
1	80	10	trace	7
2	100	41	28	34
3	120	70	56	63
4	140	99	91	95
5	160	38	21	29

[a] Reaction conditions: Catalyst **3** (5 mol%), KO*t*Bu (5 mol%), **7a** (1.0 mmol), THF (1 mL), *i*PrOH (4 mL), 80–160 °C, 6 h. [b] Determined by GC using mesitylene as the internal standard.

3. Parameter screening for the transfer hydrogenation of poly(propylene carbonate)

Table S3 Effect of differen reaction conditions on the transfer hydrogenation of poly(propylene carbonate)[a]

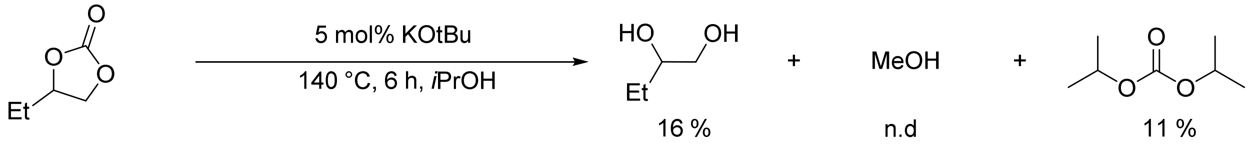


Entry	T/°C	Base/ mol%	Yield of MeOH/ %[b]	Yield of diol/ %[b]
1	100	KO*t*Bu/5.0	24	53
2	120	KO*t*Bu/5.0	32	47
3	140	KO*t*Bu/5.0	58	65
4	150	KO*t*Bu/5.0	8	34
5	140	K_2CO_3/5.0	traces	traces
6	140	$KHCO_3$/5.0	traces	traces
7	140	Na_2CO_3/5.0	traces	traces

[a] Reaction conditions: Catalyst **3** (5 mol%), Base (5 mol%), poly(propylene carbonate) (1.0 mmol), THF (1 mL), *i*PrOH (4 mL), 100–150 °C, 6 h. [b] Determined by GC using mesitylene as the internal standard.

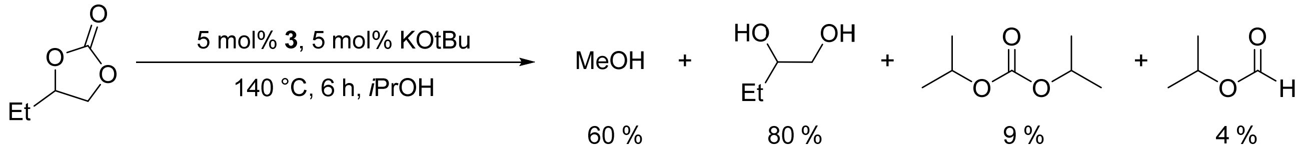
4. Complementary and cross experiments for the cyclic carbonate reduction

In the absence of the catalyst and catalytic amounts of KO*t*Bu (5 mol%) only small amounts of the diol **8a** (16%) were obtained (Scheme S1). In addition the transesterification product diisopropyl carbonates was observed in 11% yield. Notably, the formation of MeOH was not detected.



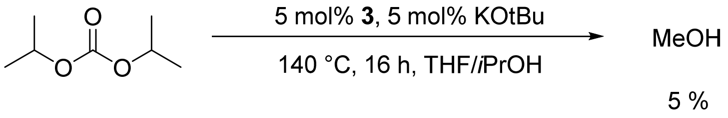
Scheme S1. Transfer hydrogenation of cyclic carbonate without complex **3**.

In the absence of THF small amounts of the diisopropyl carbonates was observed in 9% yield. In addition the diol **8a** (80%) and methanol (60%) was obtained (Scheme S2). Notably, the isopropyl formate **11** was detected (4%).



Scheme S2. Transfer hydrogenation of cyclic carbonate without THF.

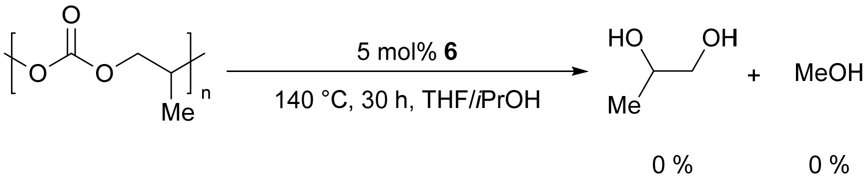
It was attempted to convert the byproduct diisopropyl carbonate under the reaction condtions shown in Scheme S3. However, only 5% yield of methanol was observed indicating that diisopropyl carbonate is unlikely an intermediate of the transfer hydrogenation process.



Scheme S3. Transfer hydrogenation of diisopropy carbonate to methanol.

5. Complementary and cross experiments for the poly(propylene carbonate) reduction

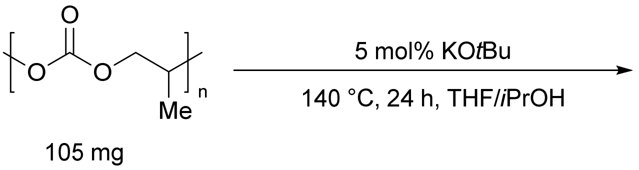
The well-known base free iron pincer complex **6** was tested as transfer hydrogenation catalyst for the reduction of poly(propylene carbonate). Under the previously optimized condtions no methanol and diol was detected after 30 h reaction time.



Scheme S4. Transfer hydrogenation of poly(propylene carbonate) by complex **6**

To investigate if KO*t*Bu will cause poly(propylene carbonate) depolymerization or the formation of the respective cyclic carbonate a blind experiment with 5 mol% KO*t*Bu was performed. The molecular weight of the poly(propylene carbonate) drops significantly in the presence of a KO*t*Bu.

Table.S4 KO*t*Bu catalyzed depolymerization of poly(propylene carbonate) under the reaction conditions.



	Poly(propylene carbonate)	
	Before the reaction[a]	After the reaction KO*t*Bu[a]
M_w	33.000 g·mol^{-1}	<1000 g·mol^{-1}
M_n	120.000 g·mol^{-1}	<1000 g·mol^{-1}

[a] Determined by GPC

Moreover the formation the cyclic carbonate **7c** as well as the diol **8c** could be observed by ^{1}H NMR. The latter might be formed by transesterification of **7c** with *i*PrOH.

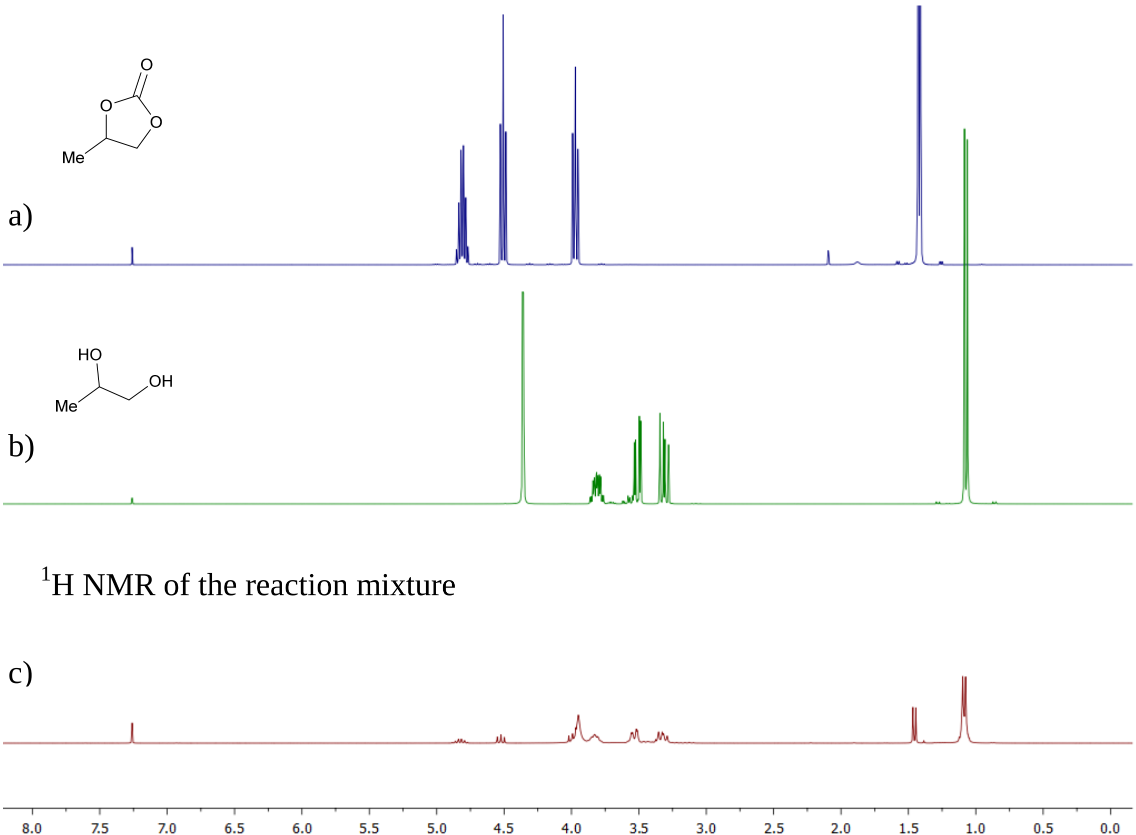
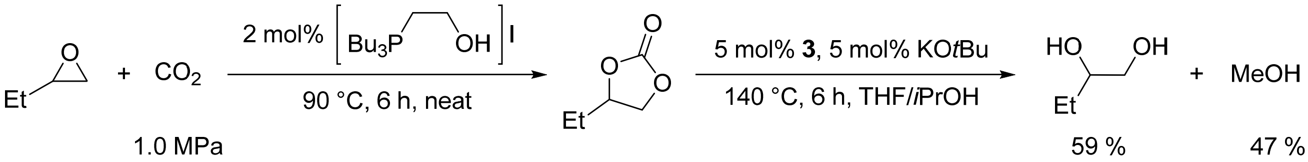


Figure S1. a) Segment of the ^{1}H NMR of neat cyclic carbonate **7c**. b) Segment of the ^{1}H NMR of neat diol **8c**. c) Segment of the ^{1}H NMR of the reaction mixture of poly(propylene carbonate) and KO*t*Bu (5 mol%) after 24 h at 140°C in THF/*i*PrOH.

6. One-pot and two steps reaction

Conversion of butylene oxide and CO_2 to diol **8a** and methanol in a one-pot and two steps:



Scheme S5. One-pot and two steps reaction for transfer hydrogenation.

In a 45 cm^3 stainless-steel autoclave was charged with bifunctional phosphorus-based organocatalyst (24.7 mg, 2 mol%) and butylene oxide (460 mg, 5.0 mmol). The reactor was purged once with CO_2 and an initial pressure of 1.0 MPa was set. The reaction mixture was stirred for 6 h at 90 °C while the CO_2 pressure was kept constant at 1.0 MPa. Subsequently, the reactor was cooled to room temperature and CO_2 was released slowly. Simultaneously, complex **3** (120 mg, 5 mol %) and KO*t*Bu (28.0 mg, 5 mol%) were dissolved in THF (3.0 mL) under argon. The mixture was stirred for 5 min at 23 °C. Then, add the complex mixture and *i*PrOH (8.0 mL) into the reactor under argon. After 6 h at 140 °C, the reaction mixture was cooled to 23°C and the residual H_2 was released carefully. The mixture was analyzed by GC with mesitylene as the internal standard to determine the MeOH and diol yield. The MeOH (47 %) and diol (59 %) were detected.

7. Catalyst recycling

In a Schlenk vessel, complex **3** (24 mg, 5 mol%) and KO*t*Bu (5.6 mg, 5 mol%) were dissolved in THF (1.0 mL) under argon. The mixture was stirred for 5 min at 23 °C. Subsequently, the cyclic carbonate **7a** (1.0 mmol) and *i*PrOH (4.0 mL) were added in one portion. The Schlenk vessel was placed in a pre-heated oil bath (140 °C) and the mixture was stirred for 6 h. The reaction mixture was cooled to 23°C and subsequently cooled to 0°C in an ice bath for 1 h. The residual H_2 was released carefully and the mixture was analyzed by GC with mesitylene as the internal standard to determine the yield on **8a** and MeOH. All volatiles were removed from the reaction mixture in vaccuo at 100°C for 2 h. Subsequently, the catalyst was redesolved in THF (1.0 mL) under argon and fresh cyclic carbonate **7a** (1.0 mmol) and *i*PrOH (4.0 mL) were added in one portion. The reaction was repeated as described above. The results of the recycling experiments can be found below (Figure S1).

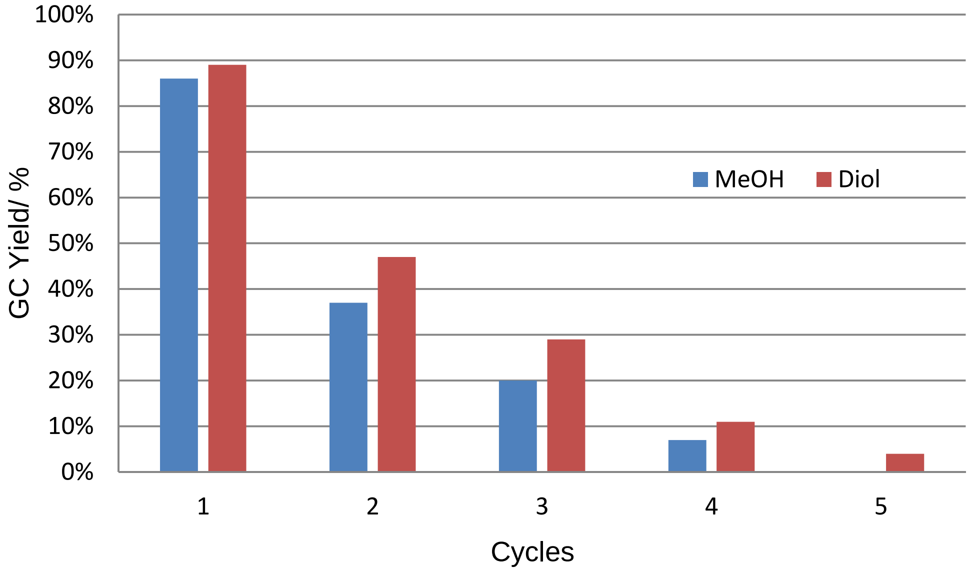


Figure S2. Results of 4 recycling experiments for catalyst **3** under standard reaction conditons.

8. Determination of the quantatie of substrate 7a and reaction products in the transfer hydrogenation reaction

8.1 Calibration curve data for different compounds

Table.S5 Calibration curve data for MeOH.

Entry	MeOH/ mmol	Relative Area[a]		
		A(MeOH)/ %	A(Mes)/ %	A(MeOH)/A(Mes)
1	0.50	10.19	89.81	0.1135
2	0.75	15.02	84.98	0.1767
3	1.00	19.84	80.16	0.2475
4	1.25	24.60	75.40	0.3262

[a] Determined by GC using mesitylene as the internal standard. Mes: Mesetylene.

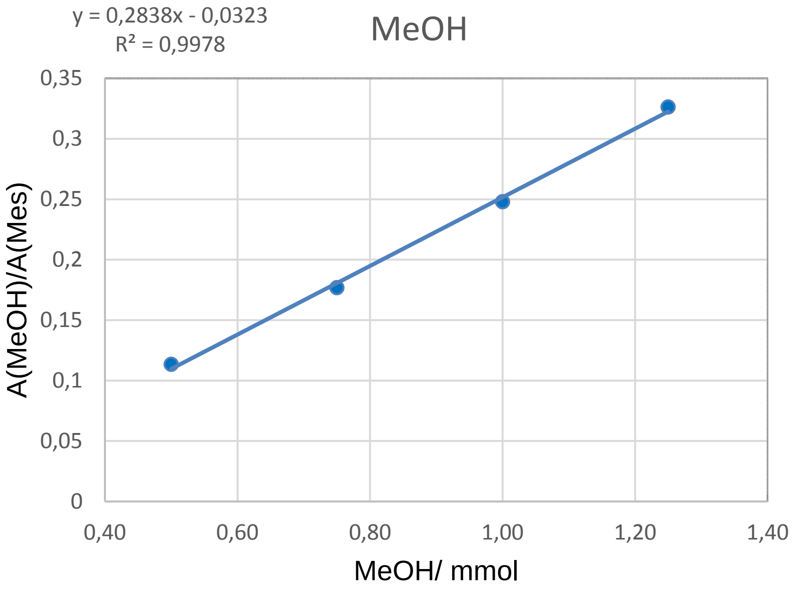


Figure S3. Calibration curve for MeOH.

Table S6. Calibration curve data for 2-butylene carbonate.

Entry	2-butylene carbonate / mmol	Relative Area[a]		
		A(Carbonate)/ %	A(Mes)/ %	A(Carbonate)/ A(Mes)
1	0.40	12.46	87.54	0.1423
2	0.60	21.89	78.11	0.2802
3	0.80	30.86	69.14	0.4463
4	1.00	35.75	64.25	0.5564

[a] Determined by GC using mesitylene as the internal standard. Carbonate: 2-butylene carbonate, Mes: Mesetylene

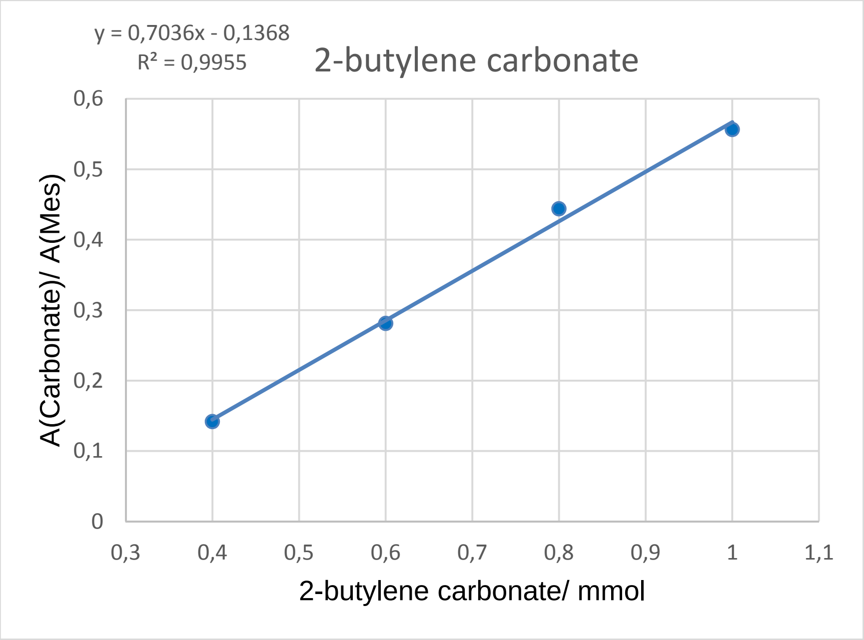


Figure S4. Calibration curve for 2-butylene carbonate.

Table.S7 Calibration curve data for 1,2-butanediol.

Entry	1,2-butanediol / mmol	Relative Area[a]		
		A(Diol)/ %	A(Mes)/ %	A(diol)/ A(Mes)
1	0.60	18.79	81.21	0.2313
2	0.80	34.70	65.30	0.5313
3	1.00	43.33	56.67	0.7646
4	1.20	50.92	49.08	1.0374

[a] Determined by GC using mesitylene as the internal standard. Diol: 1,2-butanediol, Mes: Mesetylene

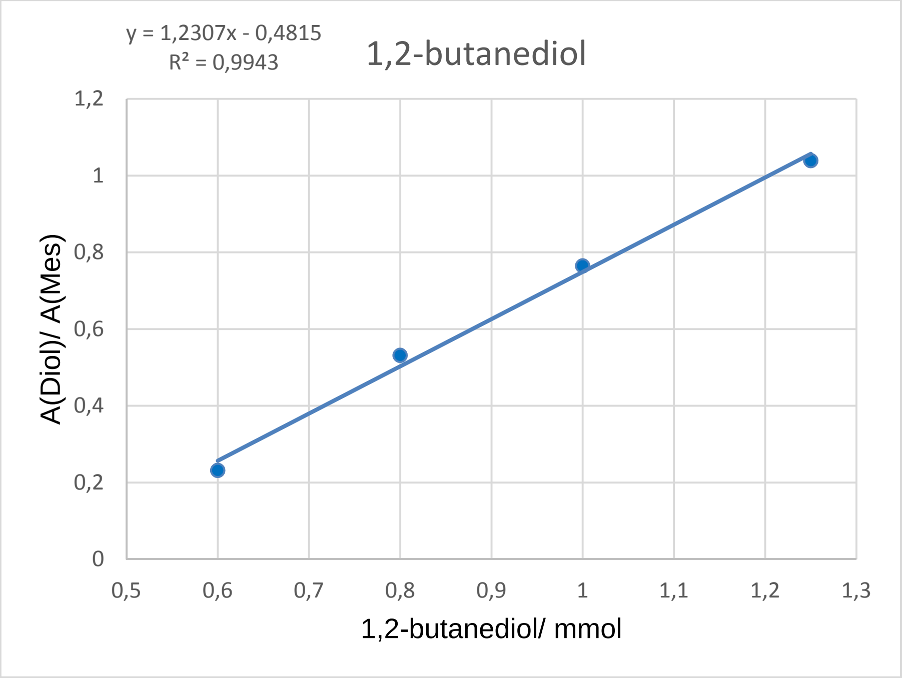


Figure S5. Calibration curve for 1,2-butanediol.

Table S8. Calibration curve data for isopropyl formate.

Entry	Isopropyl formate / mmol	Relative Area[a]		
		A(Iso)/ %	A(Mes)/ %	A(Iso)/ A(Mes)
1	0.40	8.23	91.77	0.0897
2	0.60	15.64	84.36	0.1854
3	0.80	22.97	77.03	0.2982
4	1.00	30.70	69.30	0.4430

[a] Determined by GC using mesitylene as the internal standard. Iso: Isopropyl formate, Mes: Mesitylene

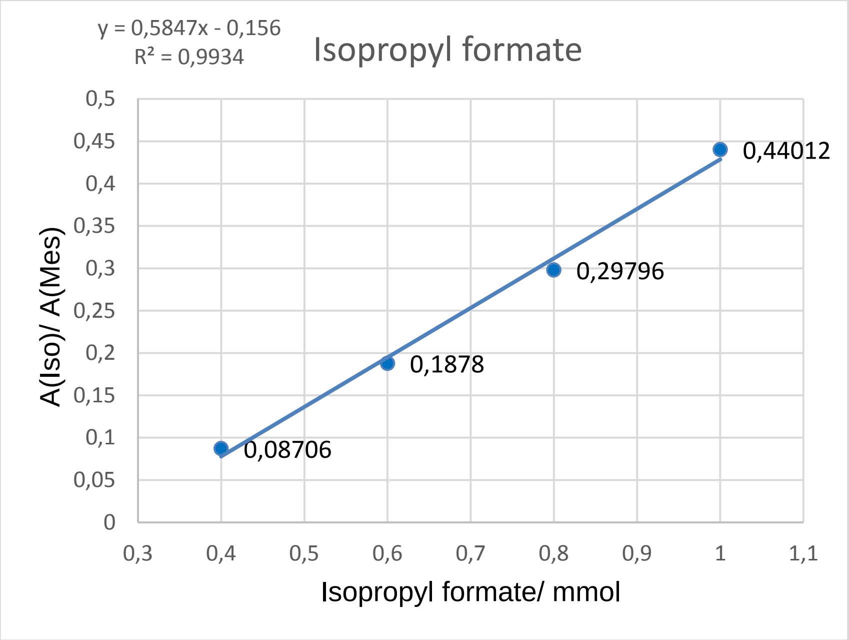


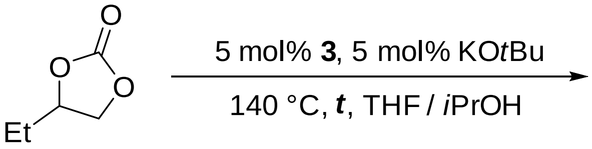
Figure S6. Calibration curve for isopropyl formate.

Table S9. Different concentrations of samples for verification.

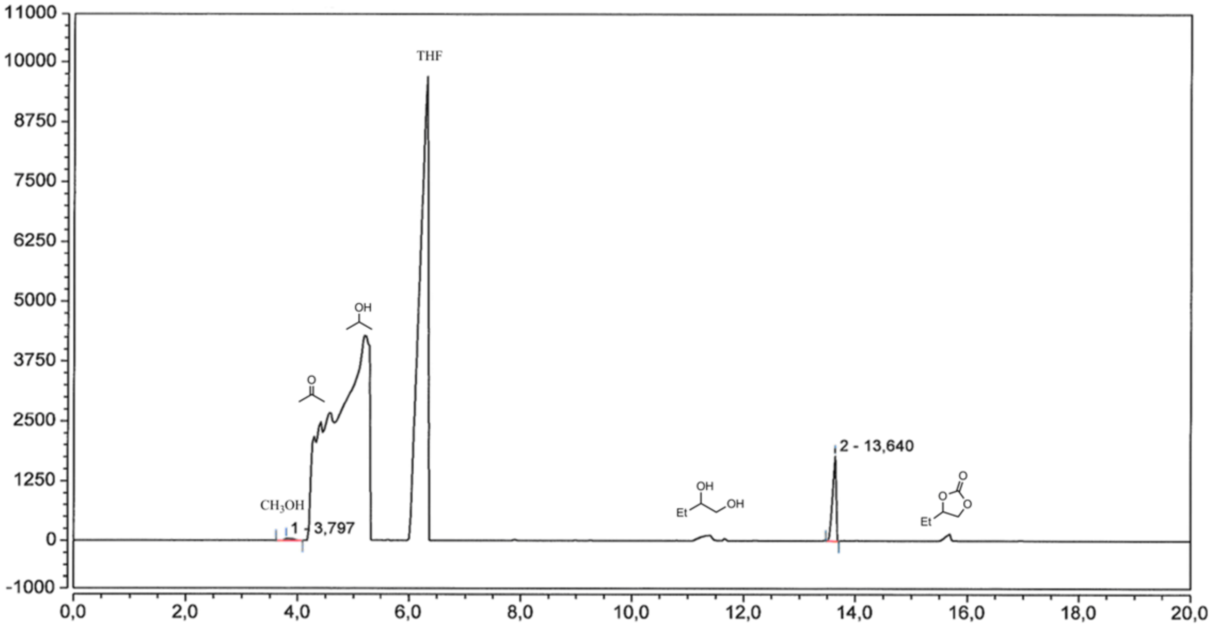
Entry	Substrate	Actual amount/ mmol	GC/ mmol[a]
1	MeOH	0.38	0.40
2	MeOH	0.48	0.46
3	MeOH	1.43	1.47
4	2-butylene carbonate	0.51	0.48
5	2-butylene carbonate	0.73	0.70
6	2-butylene carbonate	0.81	0.77
7	1,2-butanediol	0.42	0.44
8	1,2-butanediol	0.57	0.58
9	1,2-butanediol	0.63	0.65
10	Isopropyl formate	0.38	0.34
11	Isopropyl formate	0.66	0.61
12	Isopropyl formate	1.03	0.99

[a] Determined by GC using mesitylene as the internal standard.

8.2 GC charts for transfer hydrogenation of cyclic carbonate 7a.



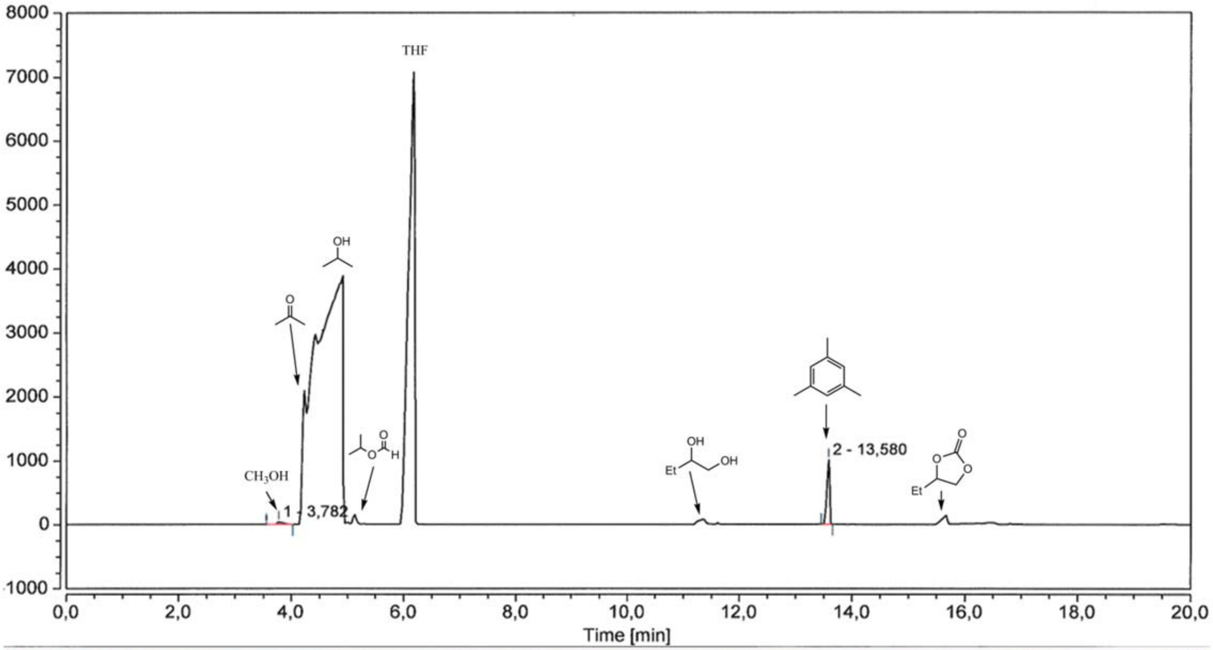
5 min



Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		3,797	6,295	33,741	4,76	1,87	n.a.
2		13,640	125,841	1772,695	95,24	98,13	n.a.
Total:			**132,135**	**1806,436**	**100,00**	**100,00**	

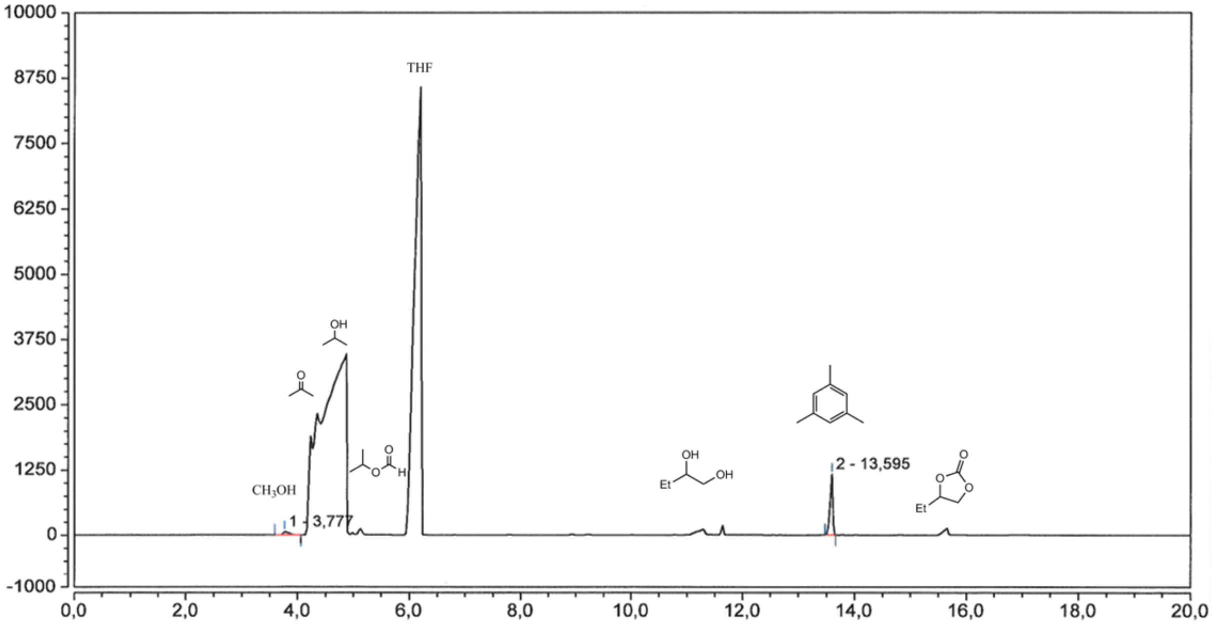
15 min



Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		3,782	4,601	34,845	7,63	3,35	n.a.
2		13,580	55,739	1005,561	92,37	96,65	n.a.
Total:			**60,340**	**1040,406**	**100,00**	**100,00**	

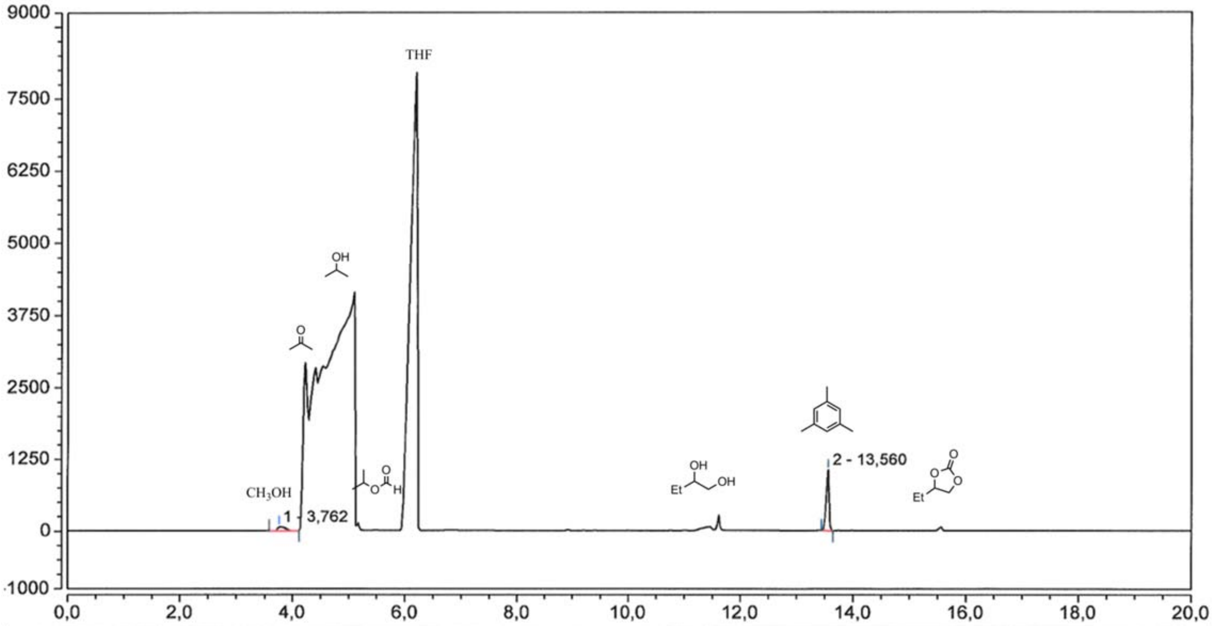
30 min



Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		3,777	6,700	60,189	9,29	4,92	n.a.
2		13,595	65,438	1163,400	90,71	95,08	n.a.
Total:			**72,138**	**1223,589**	**100,00**	**100,00**	

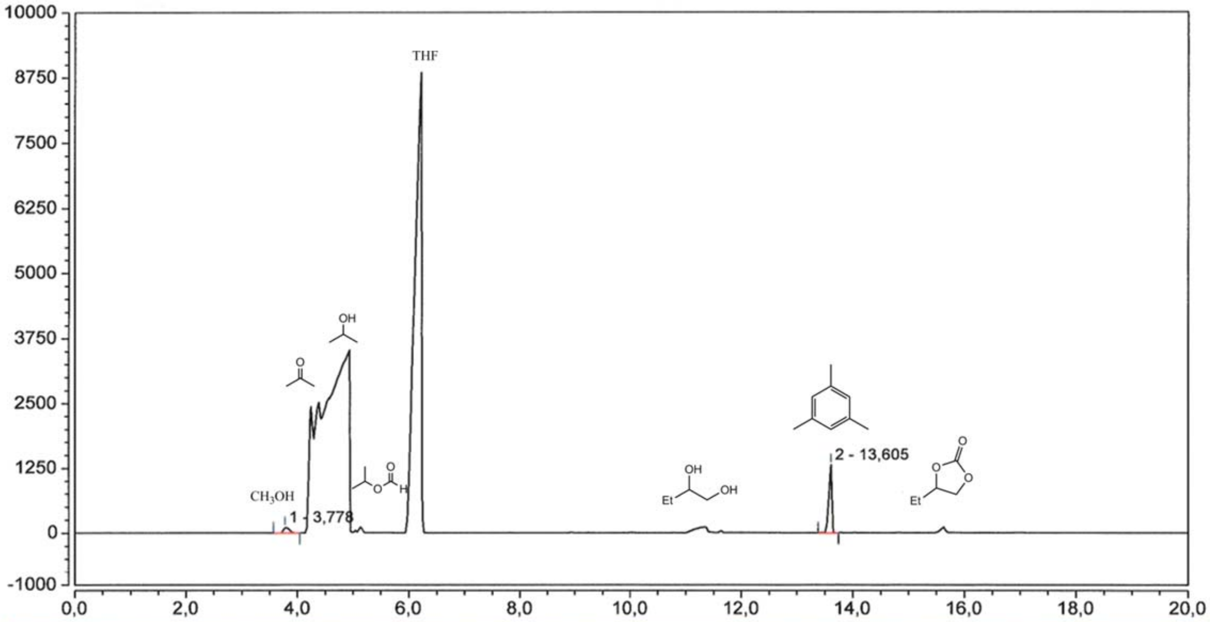
60 min



Integration Results

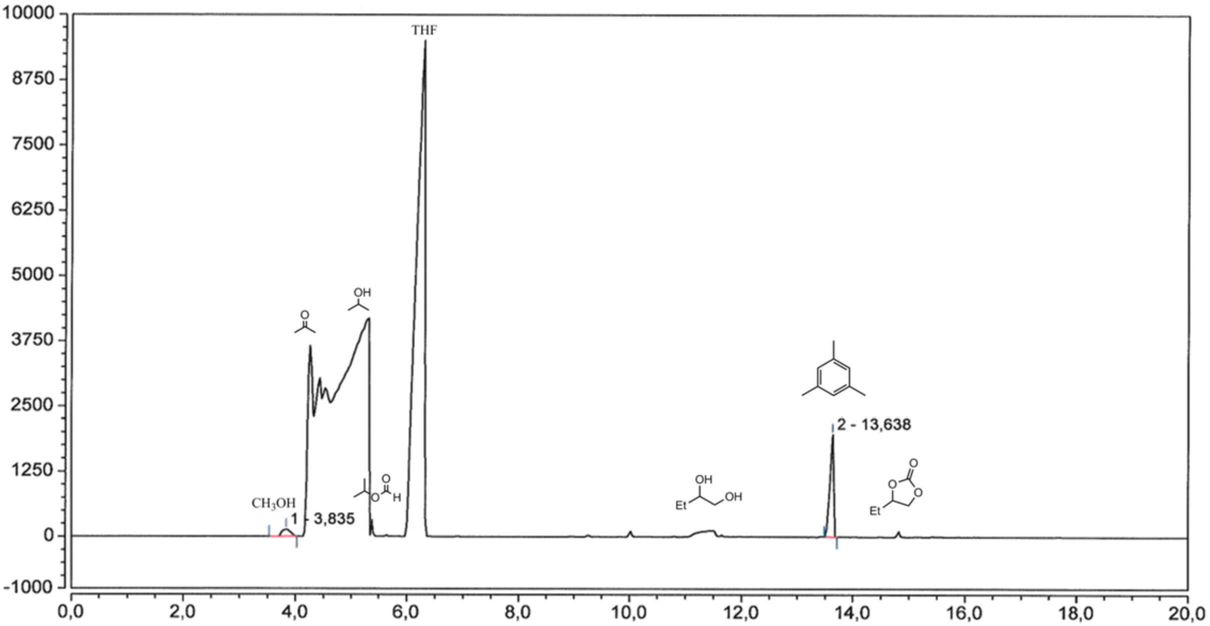
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		3,762	10,484	65,194	14,79	5,85	n.a.
2		13,560	60,396	1049,419	85,21	94,15	n.a.
Total:			**70,881**	**1114,613**	**100,00**	**100,00**	

120 min



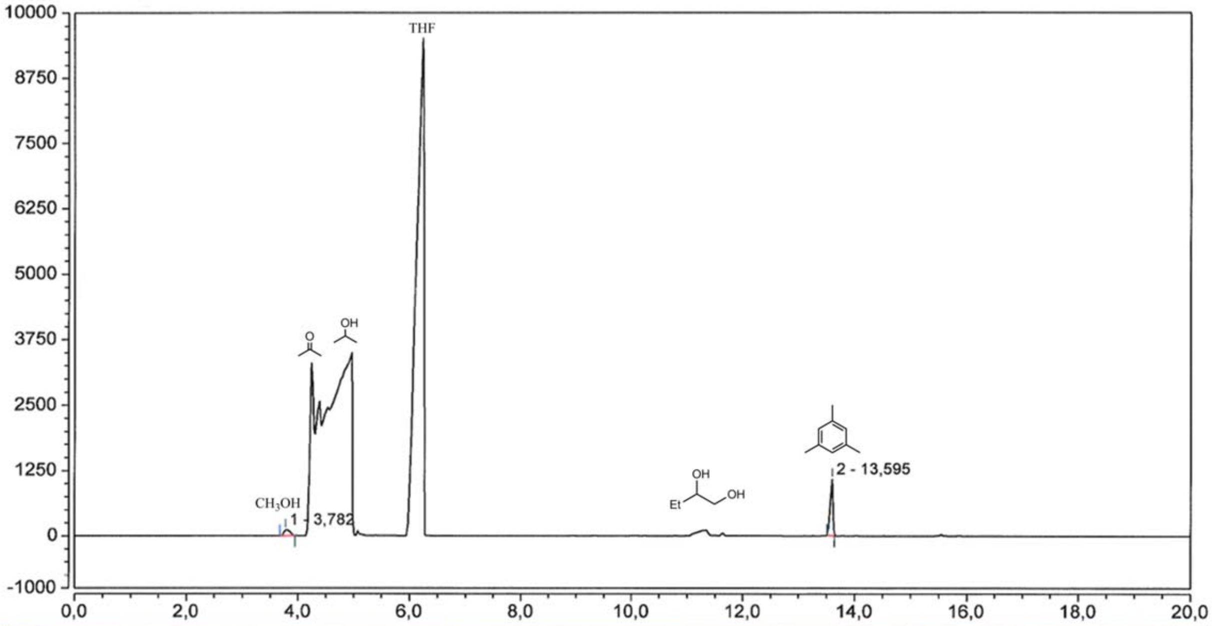
Integration Results							
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		3,778	12,050	98,405	13,08	7,02	n.a.
2		13,605	80,046	1304,237	86,92	92,98	n.a.
Total:			**92,096**	**1402,642**	**100,00**	**100,00**	

180 min



Integration Results							
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		3,783	13,033	88,831	16,94	7,33	n.a.
2		13,590	63,896	1122,813	83,06	92,67	n.a.
Total:			**76,929**	**1211,645**	**100,00**	**100,00**	

360 min



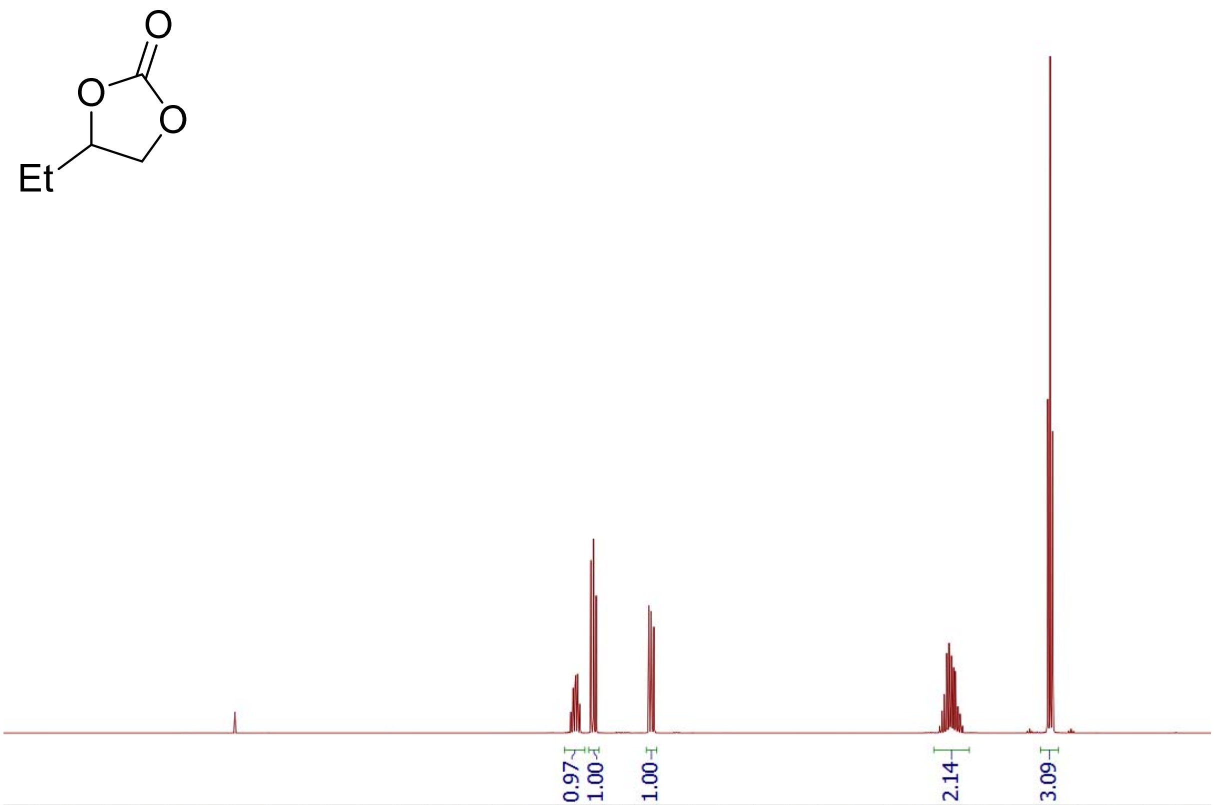
Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		3,782	13,787	108,353	18,63	9,19	n.a.
2		13,595	60,224	1070,837	81,37	90,81	n.a.
Total:			**74,010**	**1179,190**	**100,00**	**100,00**	

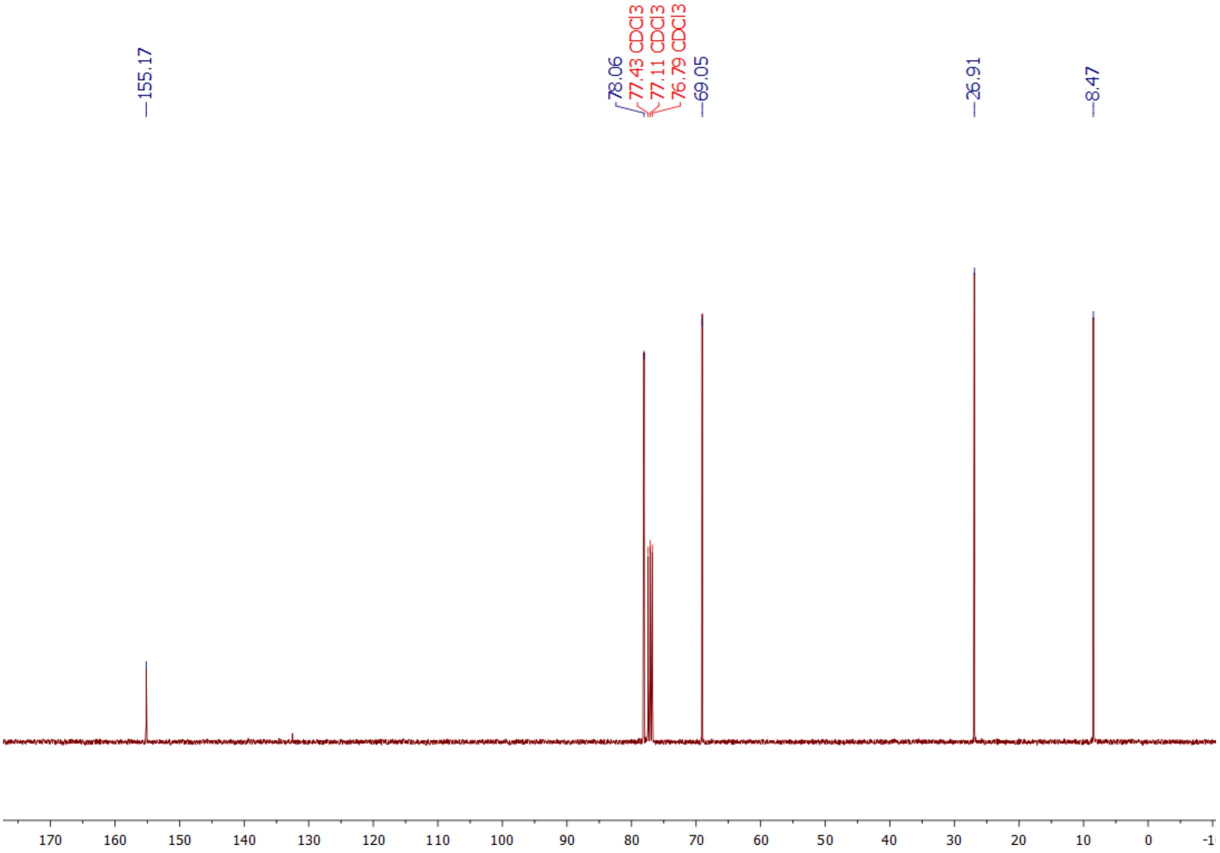
9. NMR spectra of the substrates 7 and products 8

9.1 NMR spectra of the substrates 7

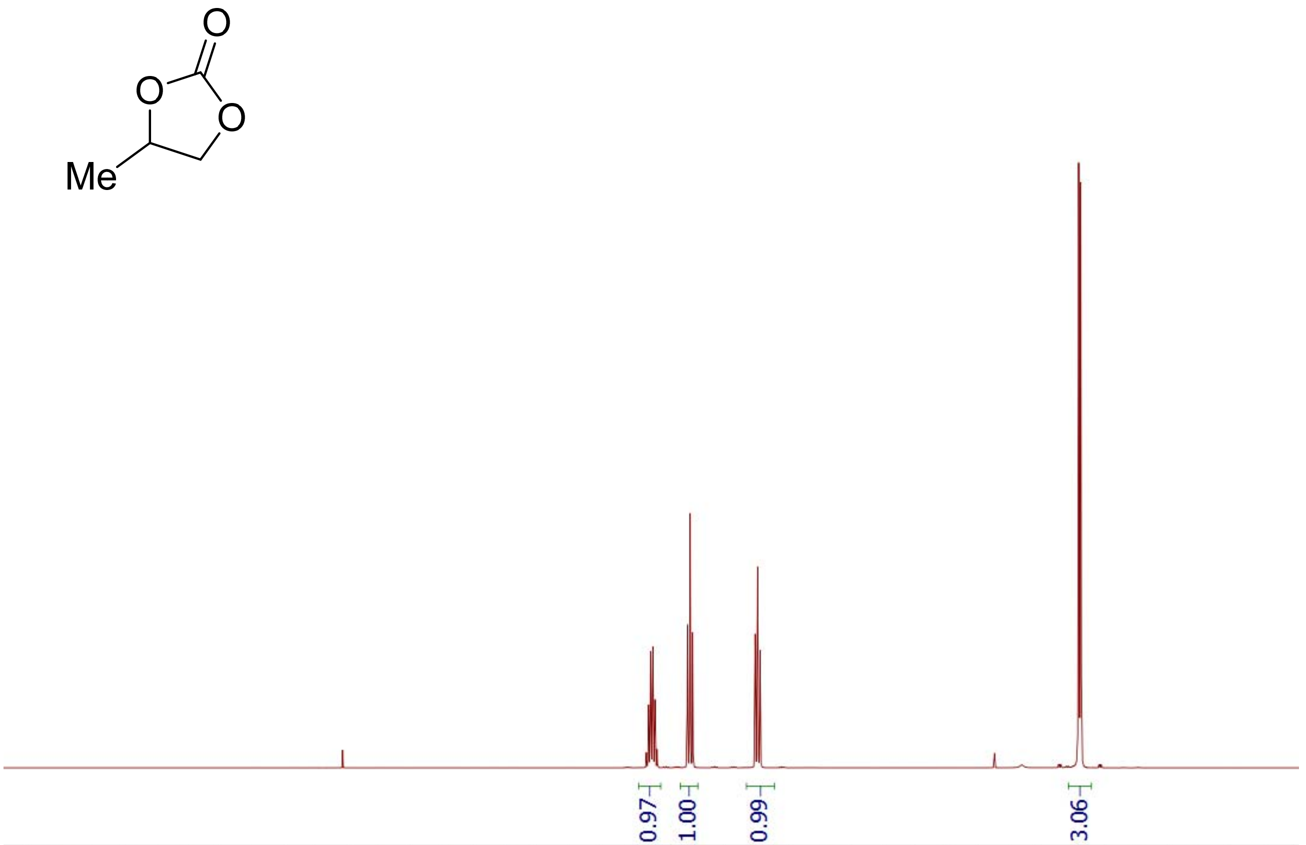
4-ethyl-1, 3-dioxolan-2-one (**7a**) ^{1}**H-NMR** spectrum in $CDCl_3$



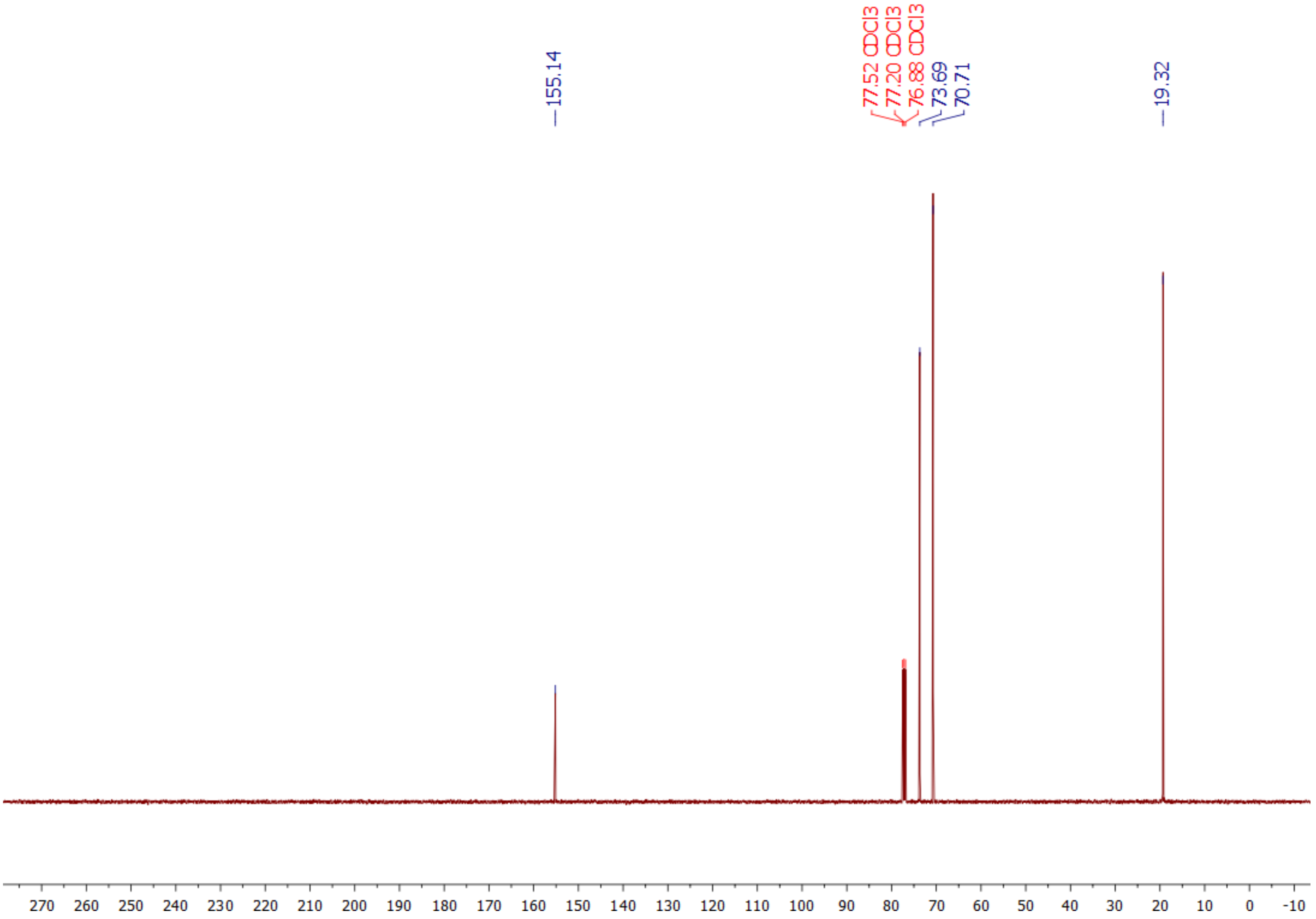
4-Ethyl-1, 3-dioxolan-2-one (**7a**) ^{13}**C-NMR** spectrum in $CDCl_3$



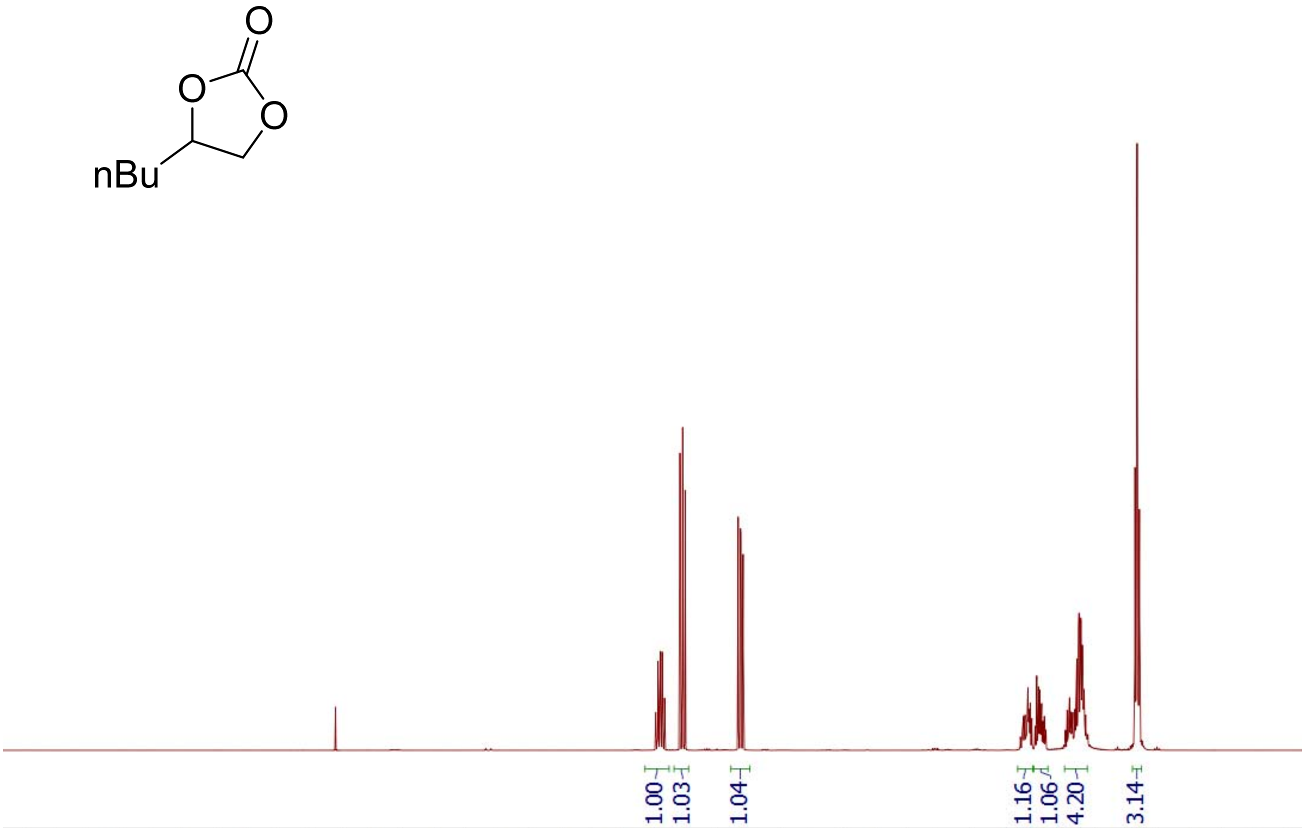
4-Methyl-1, 3-dioxolan-2-one (**7c**) ^{1}**H-NMR** spectrum in $CDCl_3$



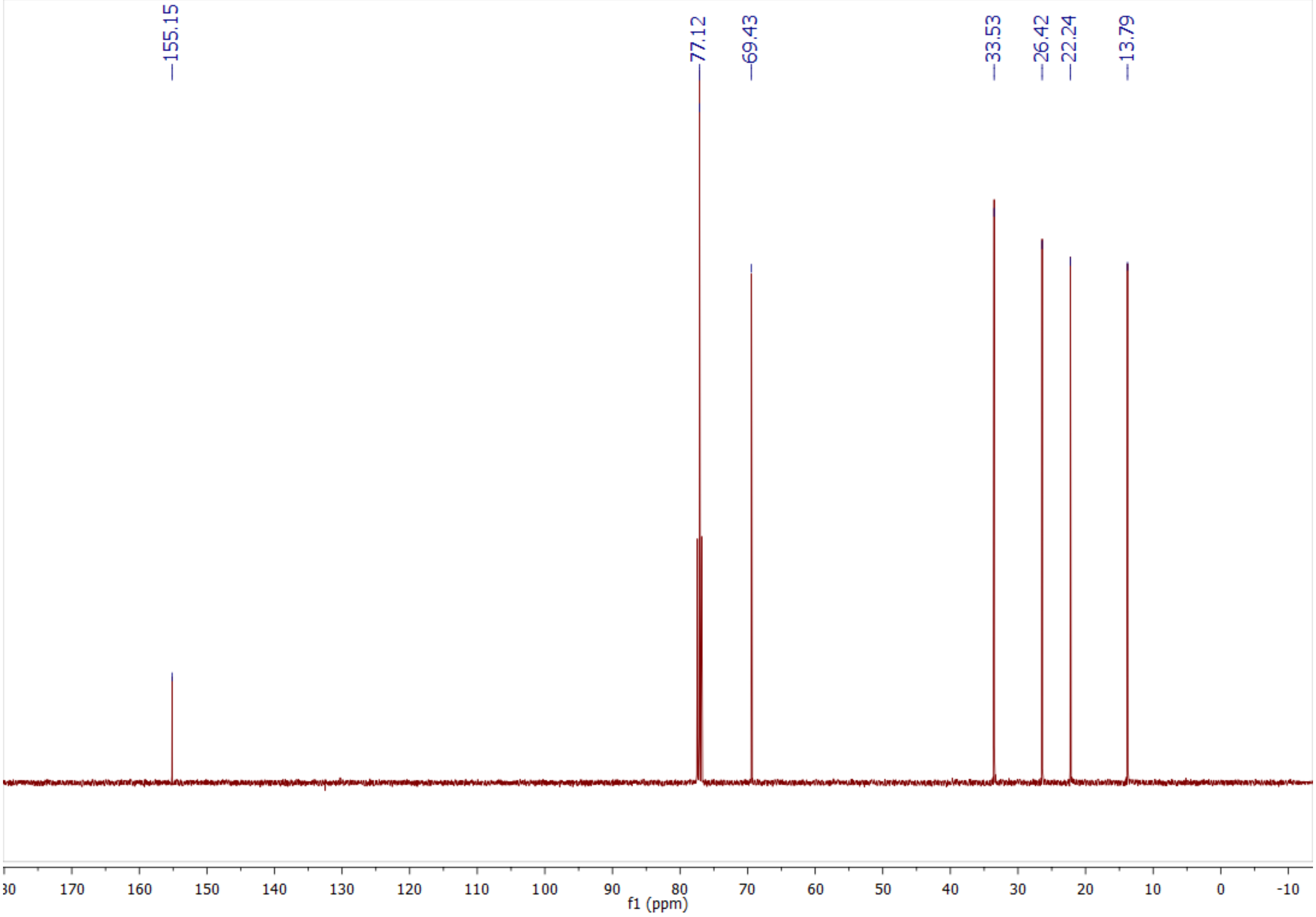
4-Methyl-1, 3-dioxolan-2-one (**7c**) ^{13}**C-NMR** spectrum in $CDCl_3$



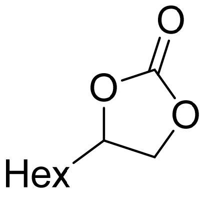
4-butyl-1, 3-dioxolan-2-one (**7d**) **^{1}H-NMR** spectrum in CDCl$_3$

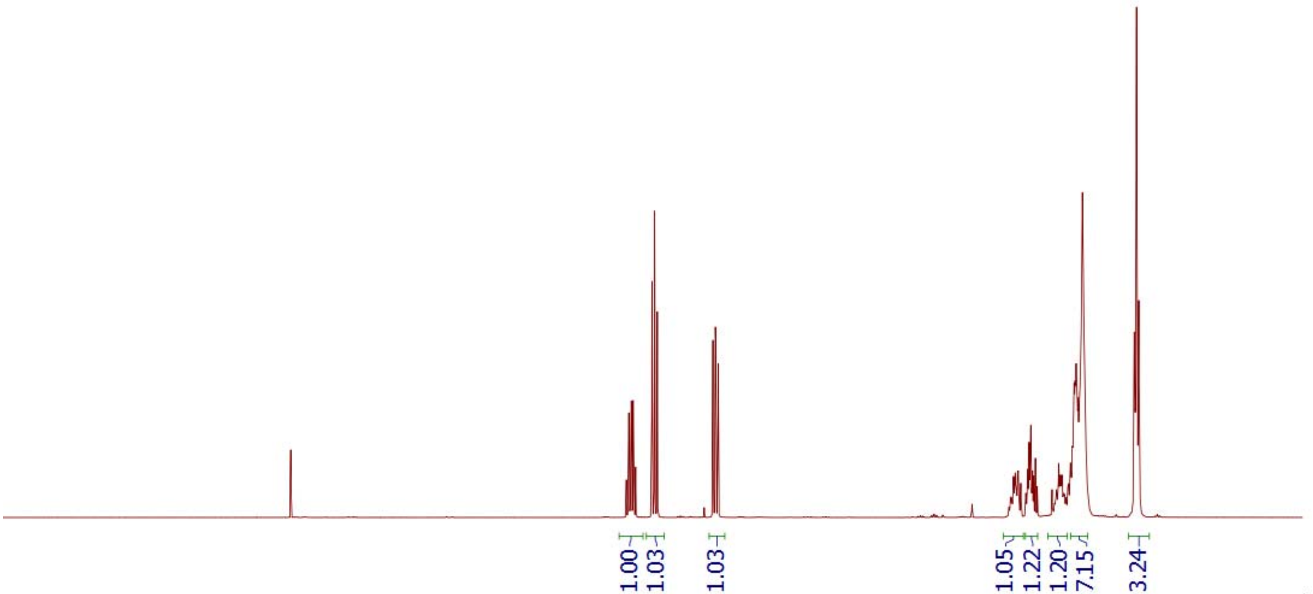


4-butyl-1, 3-dioxolan-2-one (**7d**) **^{13}C-NMR** spectrum in CDCl$_3$

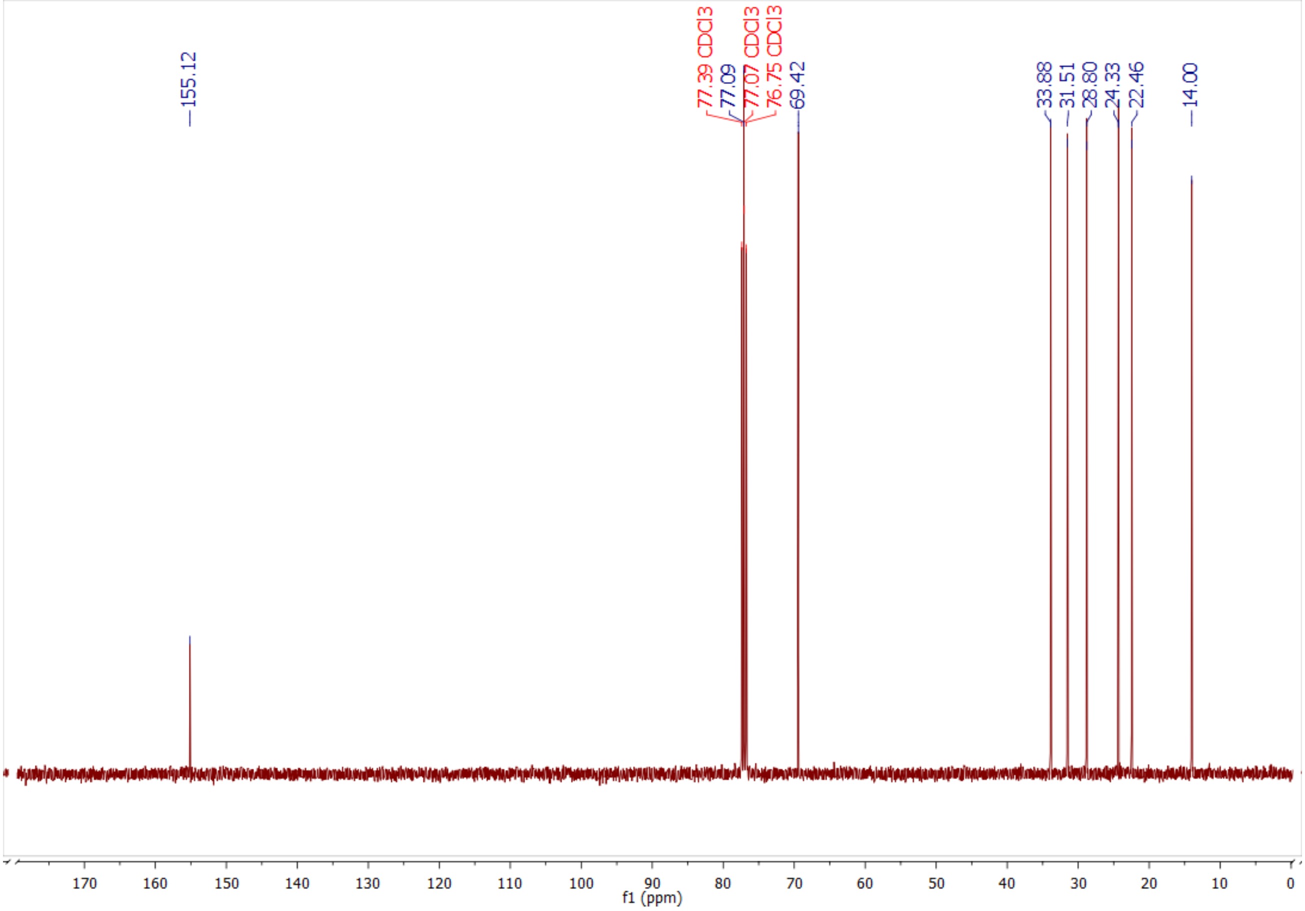


4-hexyl-1, 3-dioxolan-2-one (**7e**) **^{1}H-NMR** spectrum in $CDCl_3$

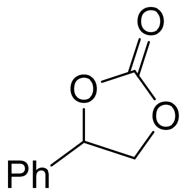


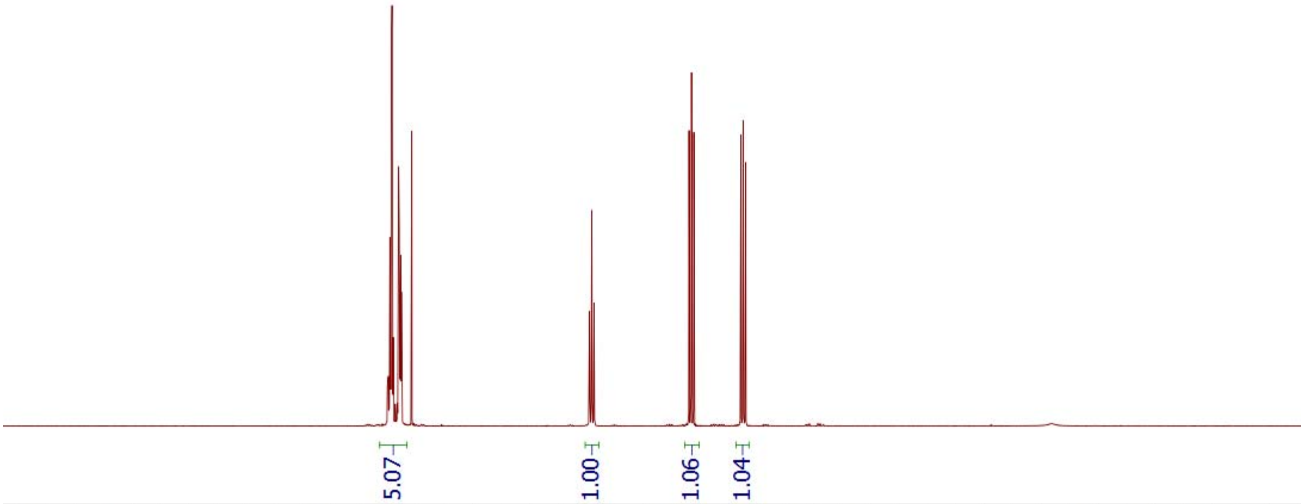


4-hexyl-1, 3-dioxolan-2-one (**7e**) **^{13}C-NMR** spectrum in $CDCl_3$

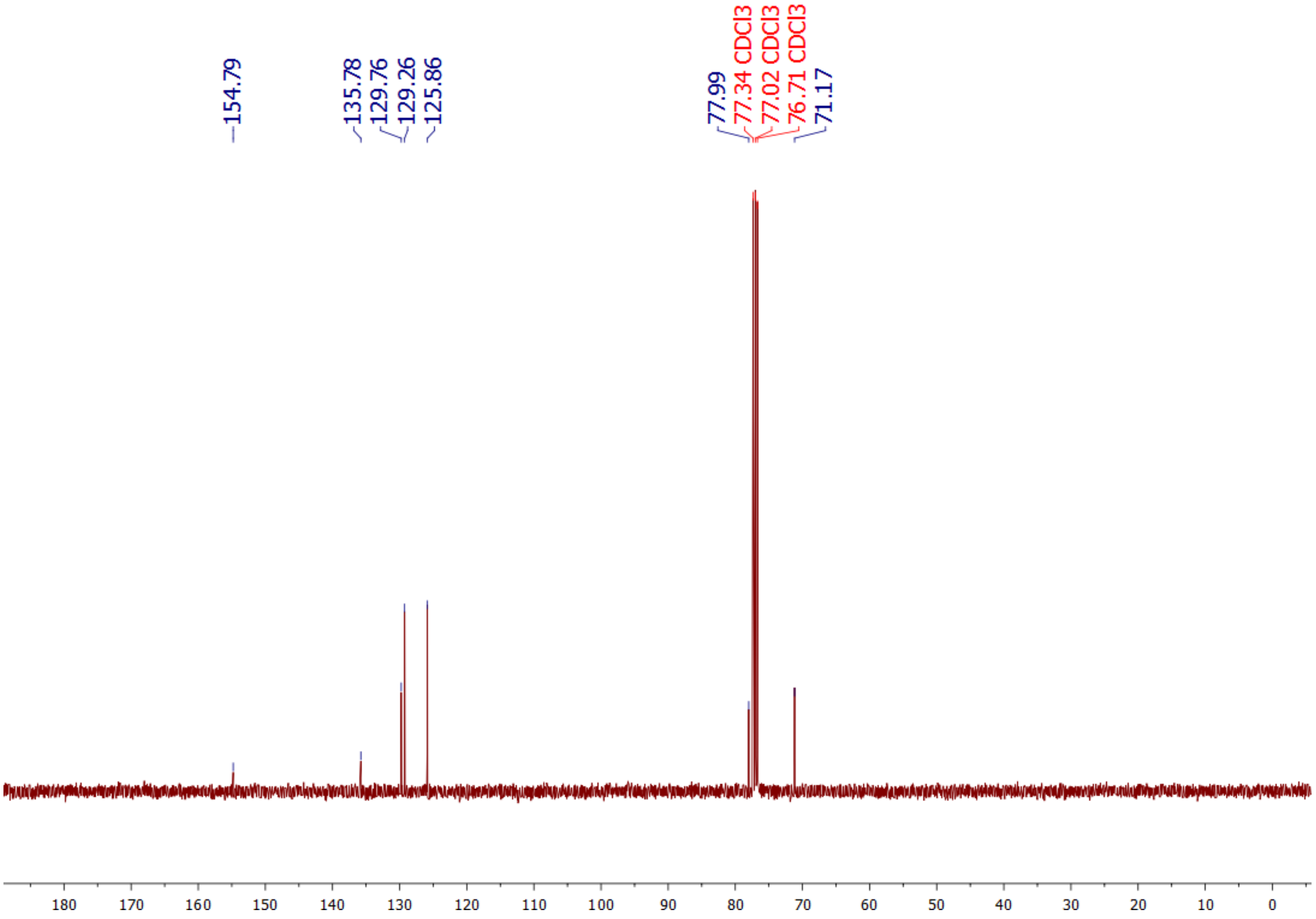


4-Phenyl-1, 3-dioxolan-2-one (**7f**) ^{1}**H-NMR** spectrum in $CDCl_3$

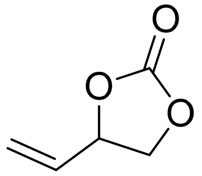


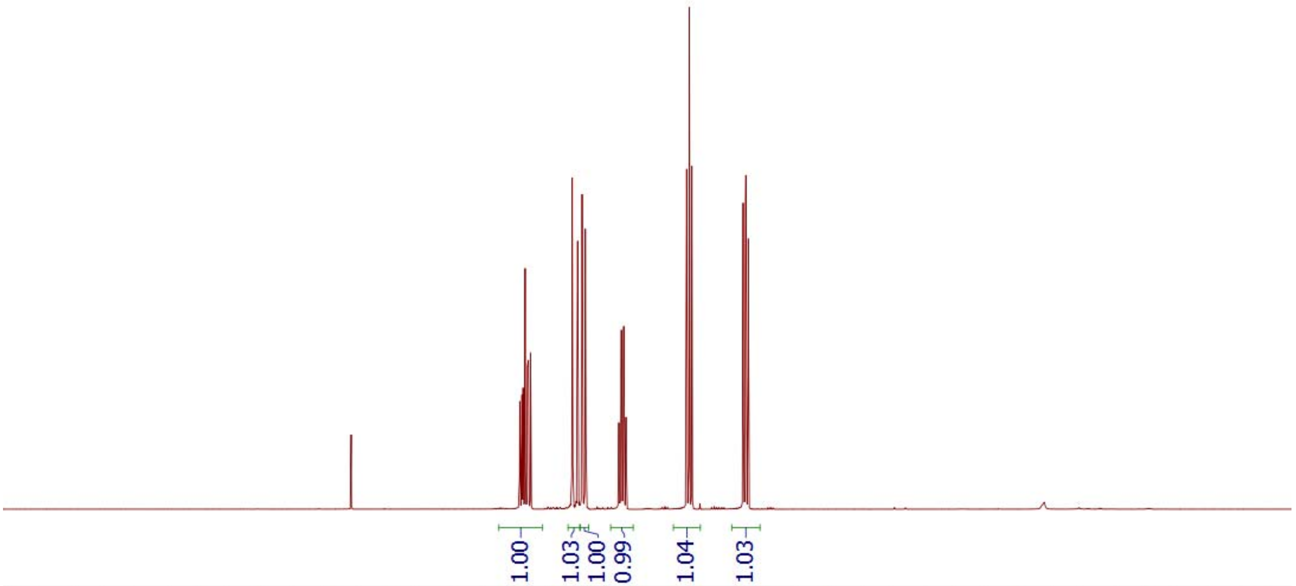


4-Phenyl-1, 3-dioxolan-2-one (**7f**) ^{13}**C-NMR** spectrum in $CDCl_3$

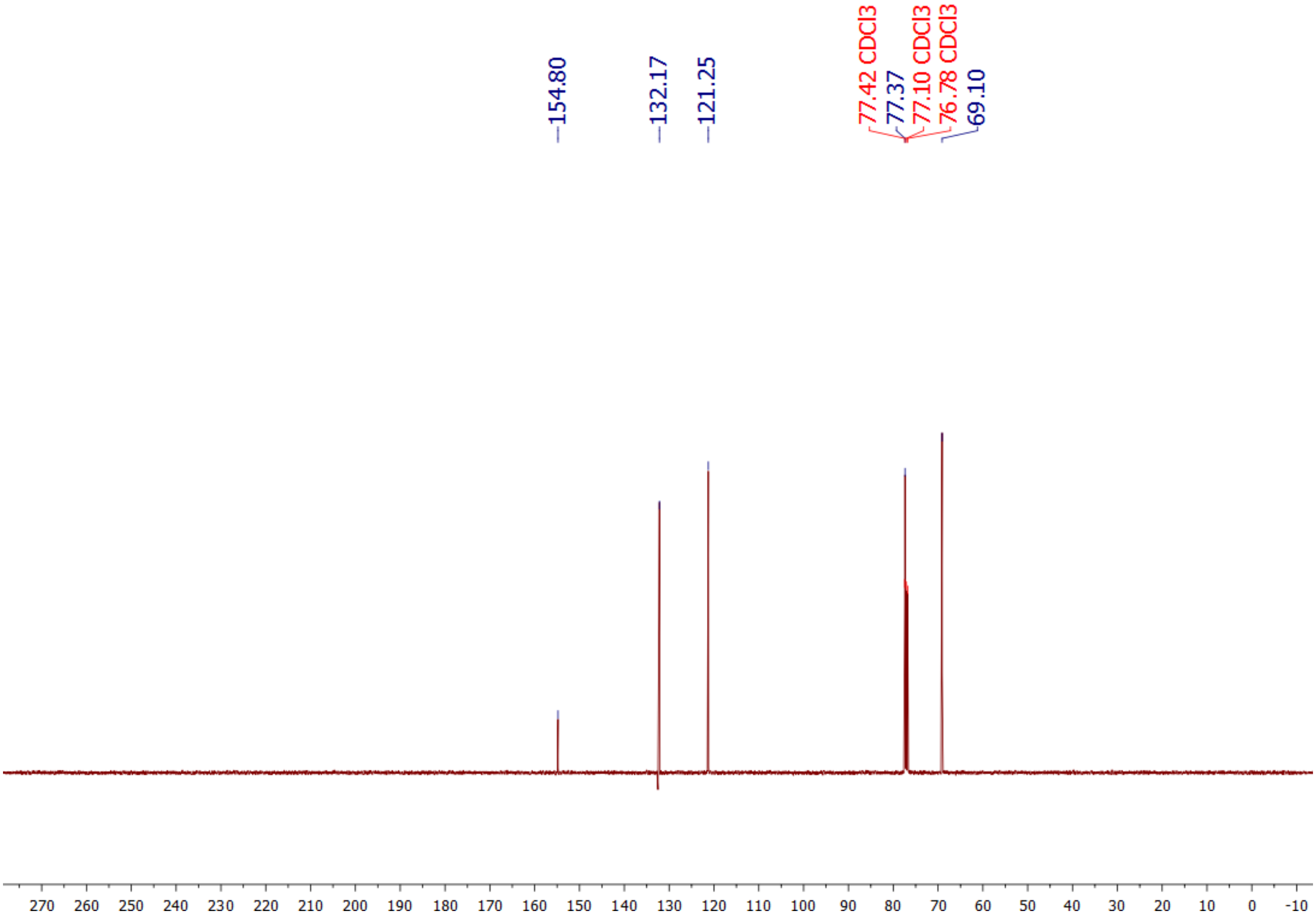


4-Vinyl-1,3-dioxolan-2-one (**7g**) ^{1}**H-NMR** spectrum in $CDCl_3$

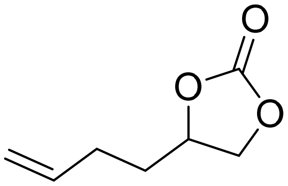


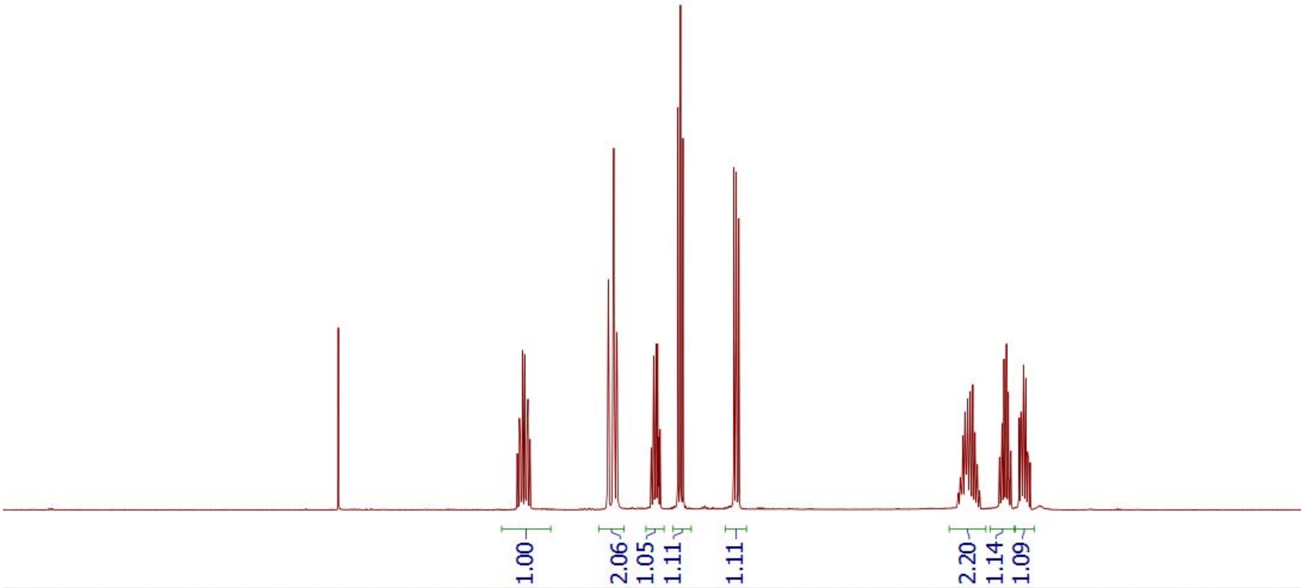


4-Vinyl-1,3-dioxolan-2-one (**7g**) ^{13}**C-NMR** spectrum in $CDCl_3$

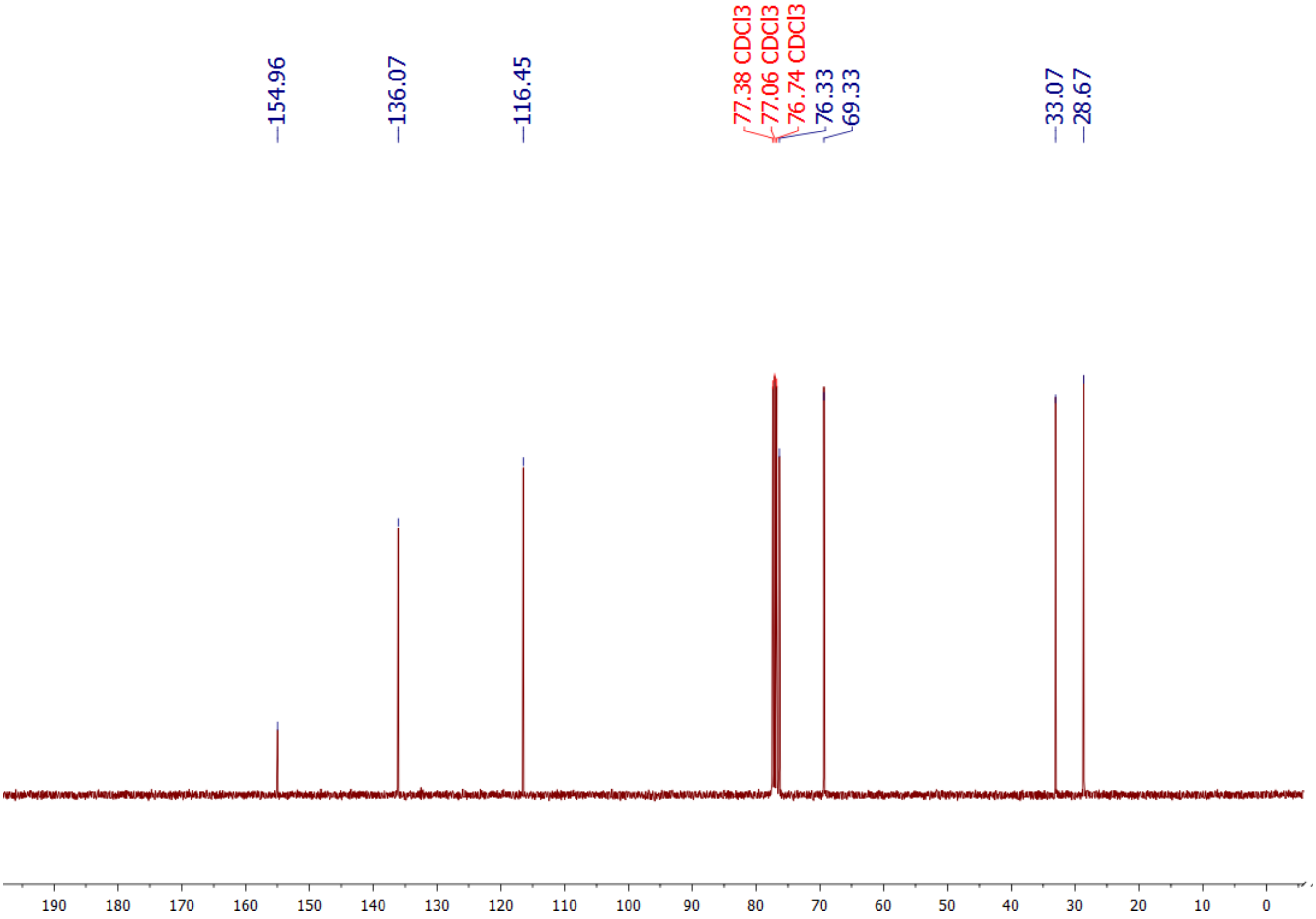


4-(3-butenyl)-1,3-dioxolan-2-one (**7h**) ^{1}**H-NMR** spectrum in CDCl$_3$

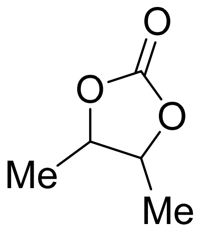


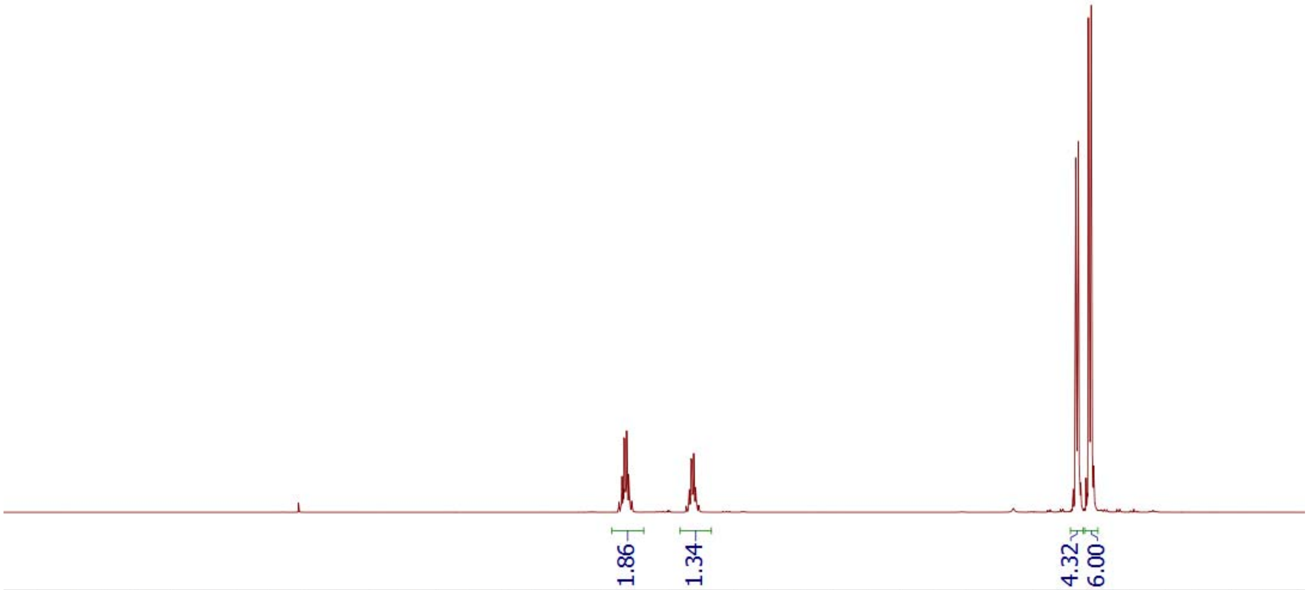


4-(3-butenyl)-1,3-dioxolan-2-one (**7h**) ^{13}**C-NMR** spectrum in CDCl$_3$

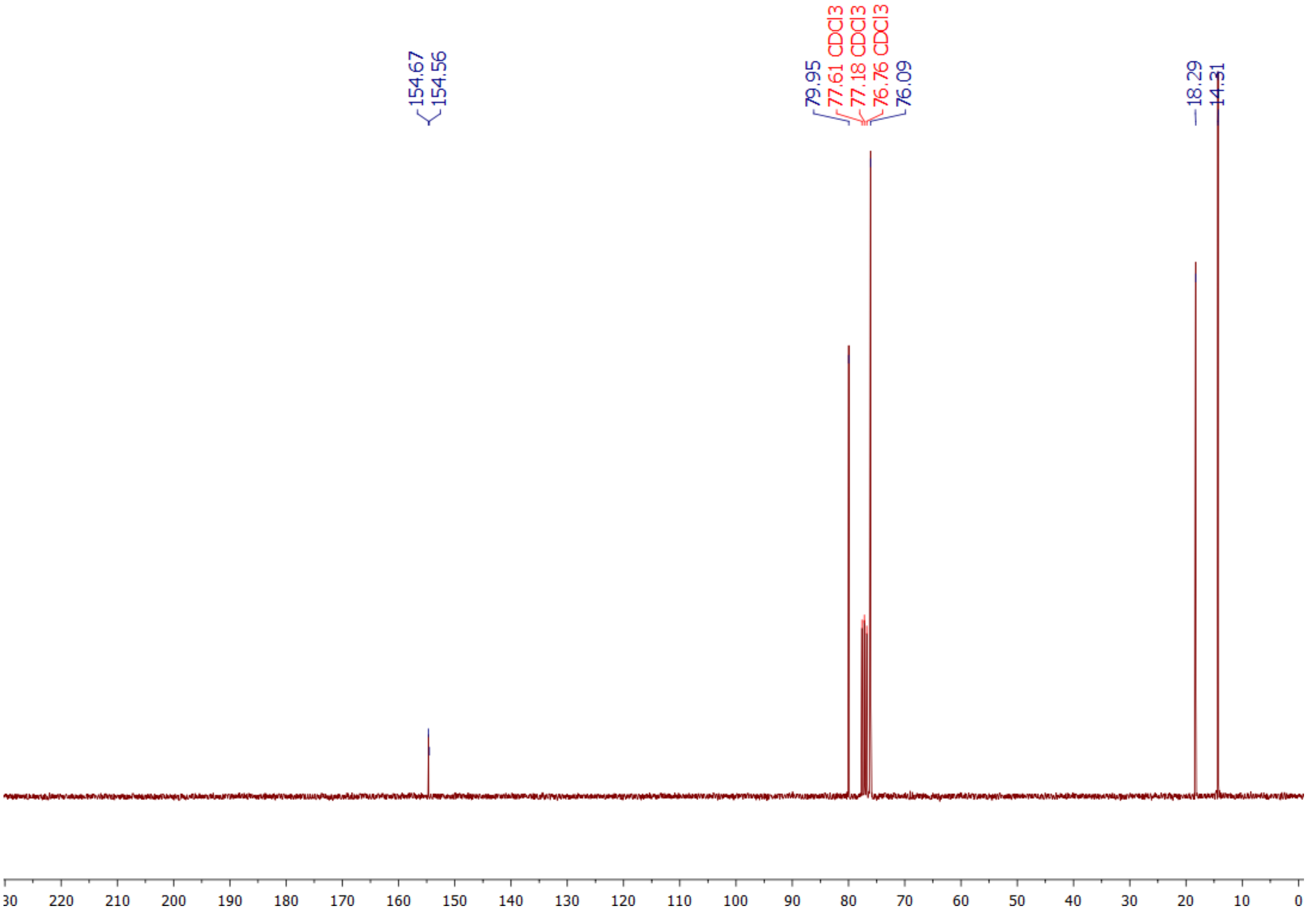


4, 5-dimethyl-1, 3-dioxolan-2-one (**7i**) ^{1}**H-NMR** spectrum in $CDCl_3$

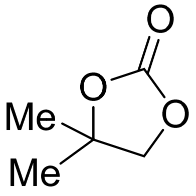




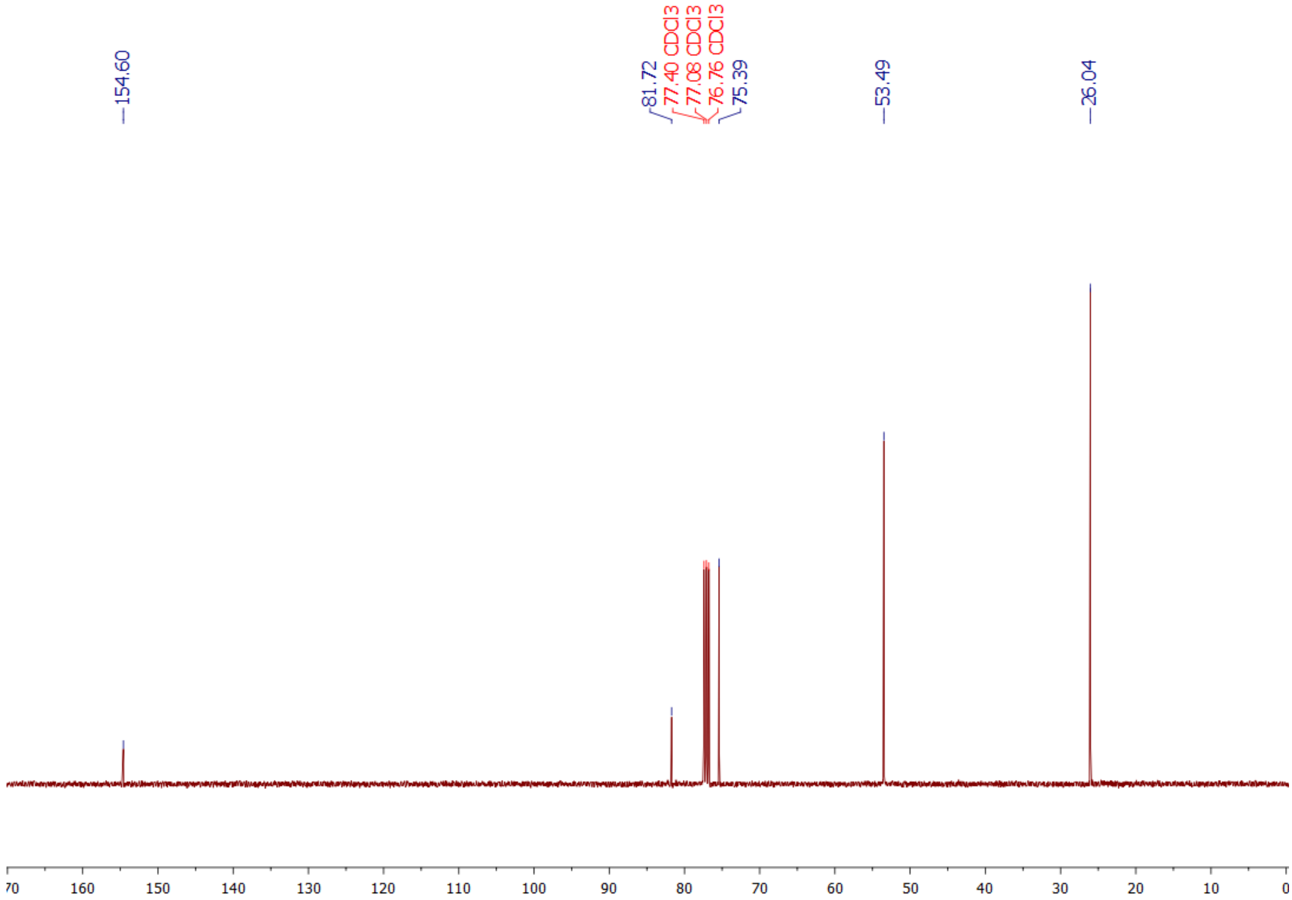
4, 5-dimethyl-1, 3-dioxolan-2-one (**7i**) ^{13}**C-NMR** spectrum in $CDCl_3$



4, 4-dimethyl-1, 3-dioxolan-2-one (**7j**) ^{1}**H-NMR** spectrum in CDCl$_3$

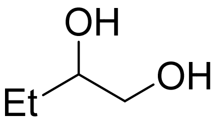


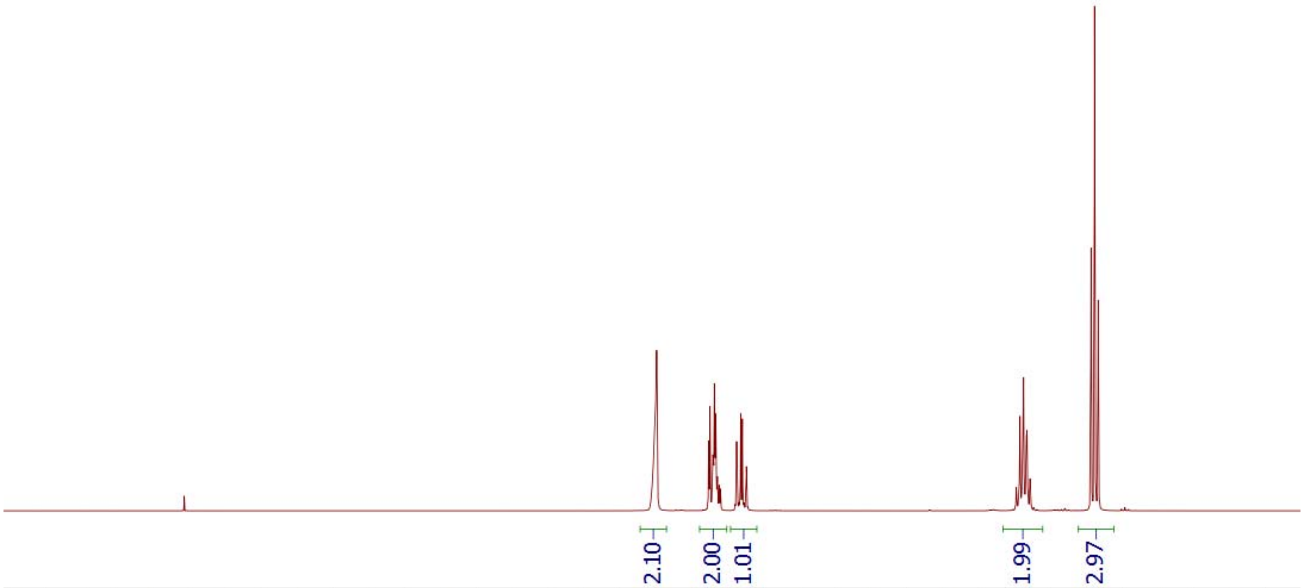
4, 4-dimethyl-1, 3-dioxolan-2-one (**7j**) ^{13}**C-NMR** spectrum in CDCl$_3$



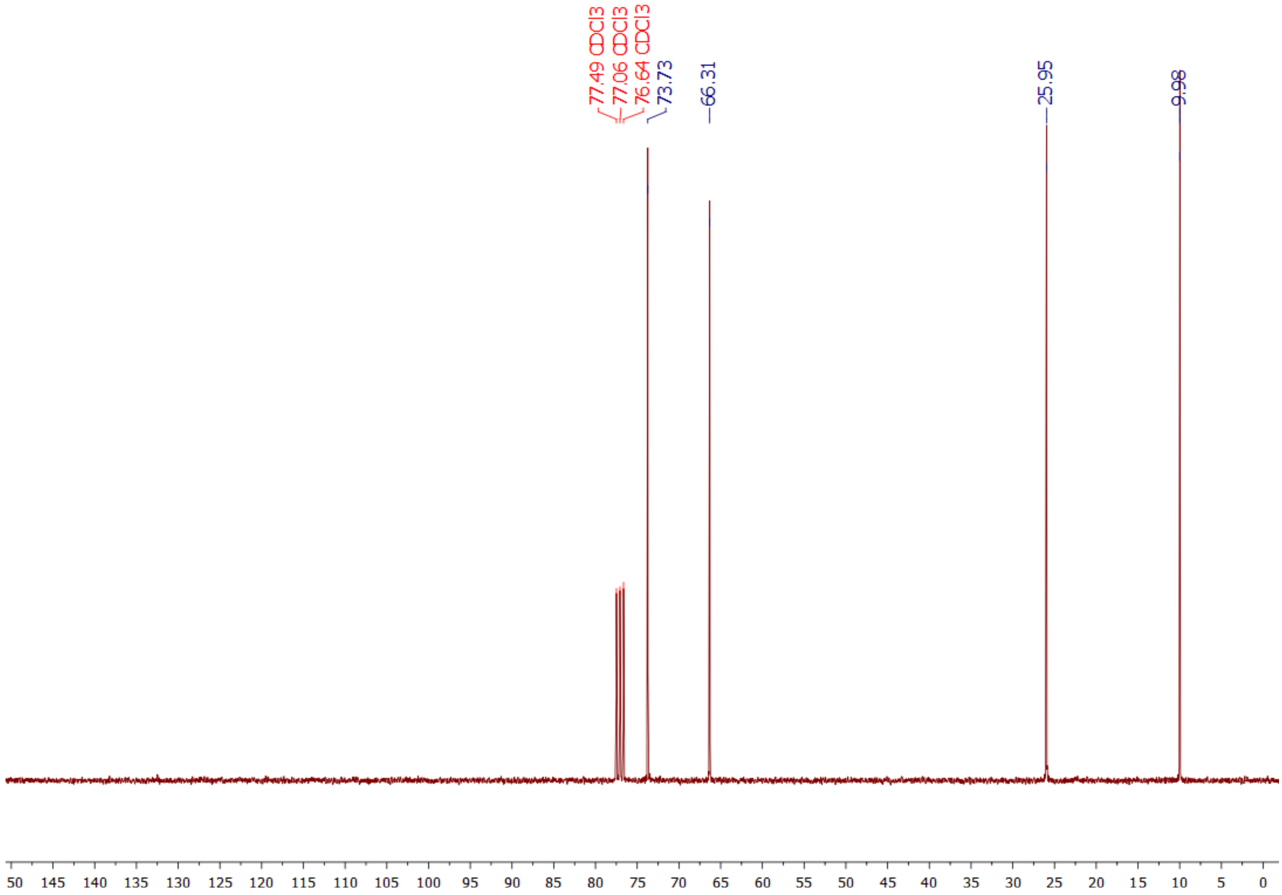
9.2 NMR spectra of the products 8

1, 2-butanediol (**8a**) ^{1}**H-NMR** spectrum in $CDCl_3$

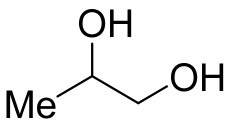


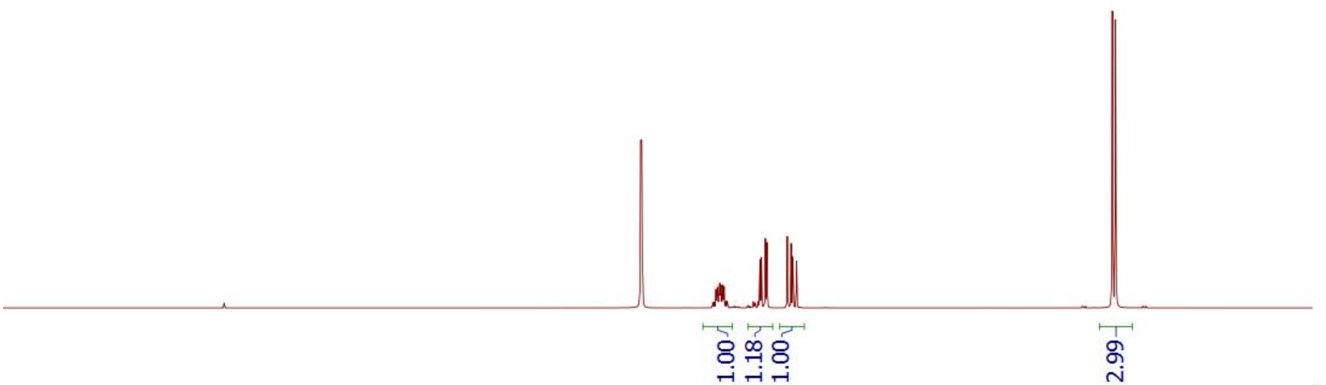


1, 2-butanediol (**8a**) (**8a**) ^{13}**C-NMR** spectrum in $CDCl_3$

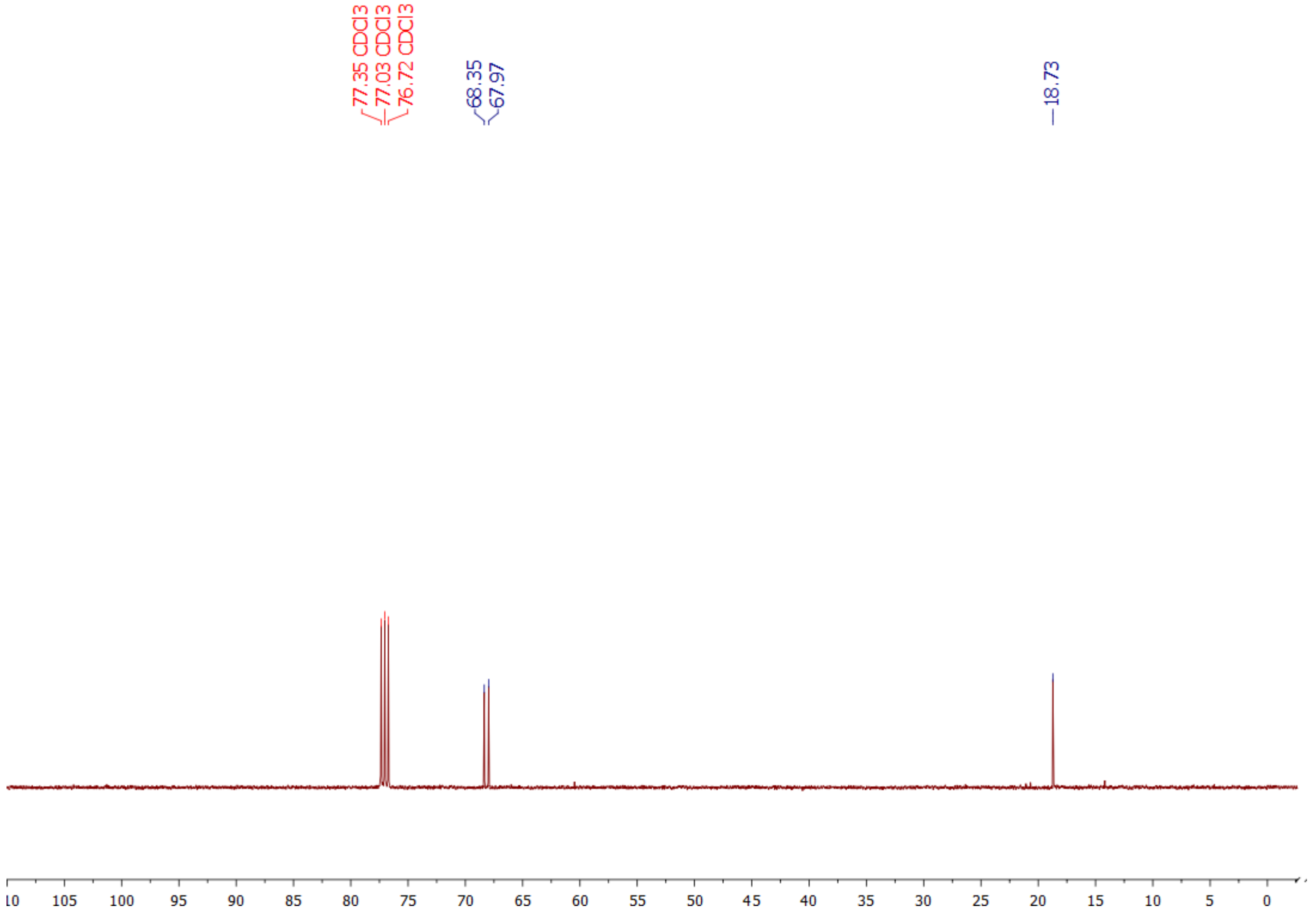


1, 2-propanediol (**8c**) ^{1}**H-NMR** spectrum in $CDCl_3$

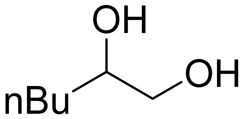


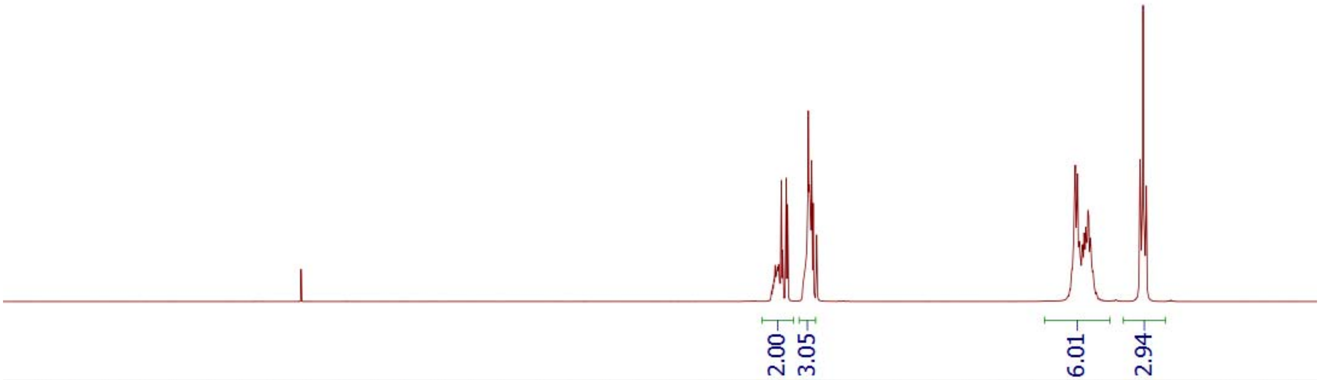


1, 2-propanediol (**8c**) ^{13}**C-NMR** spectrum in $CDCl_3$

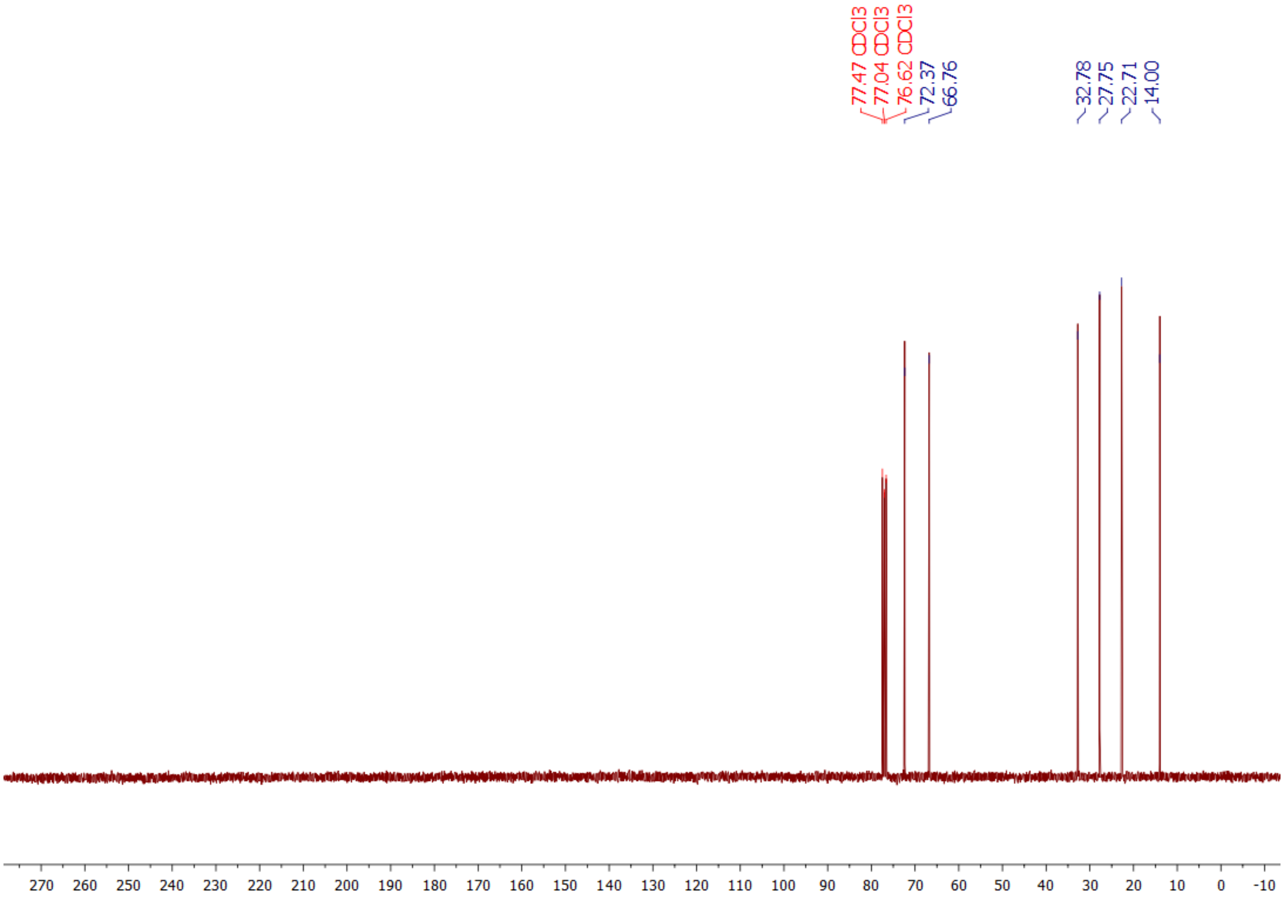


1, 2-Hexanediol (**8d**) ^{1}**H-NMR** spectrum in $CDCl_3$

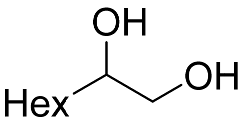




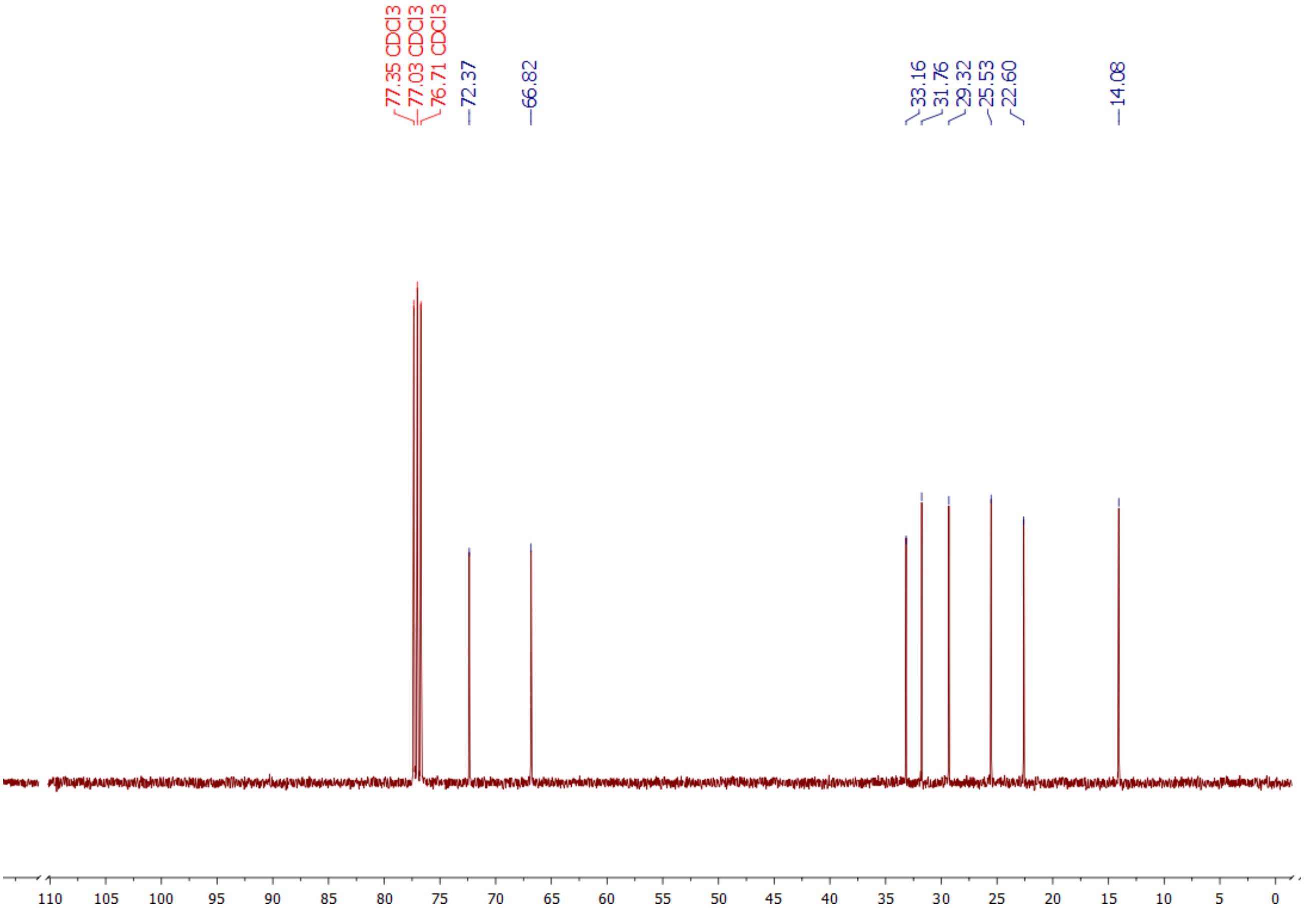
1, 2-Hexanediol (**8d**) ^{13}**C-NMR** spectrum in $CDCl_3$



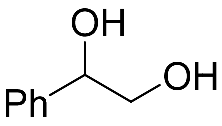
1, 2-Octanediol (**8e**) ^{1}**H-NMR** spectrum in $CDCl_3$

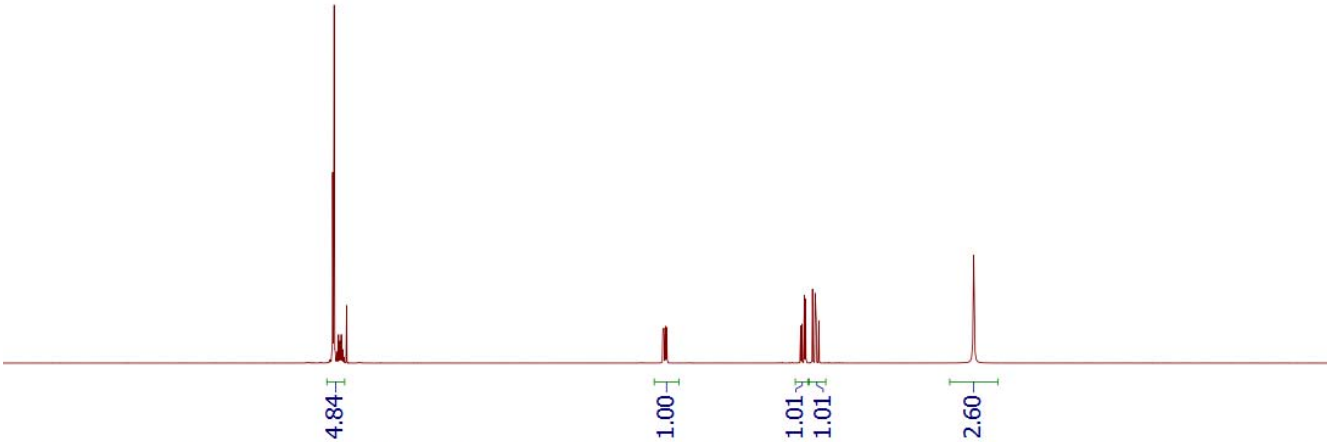


1, 2-Octanediol (**8e**) ^{13}**C-NMR** spectrum in $CDCl_3$

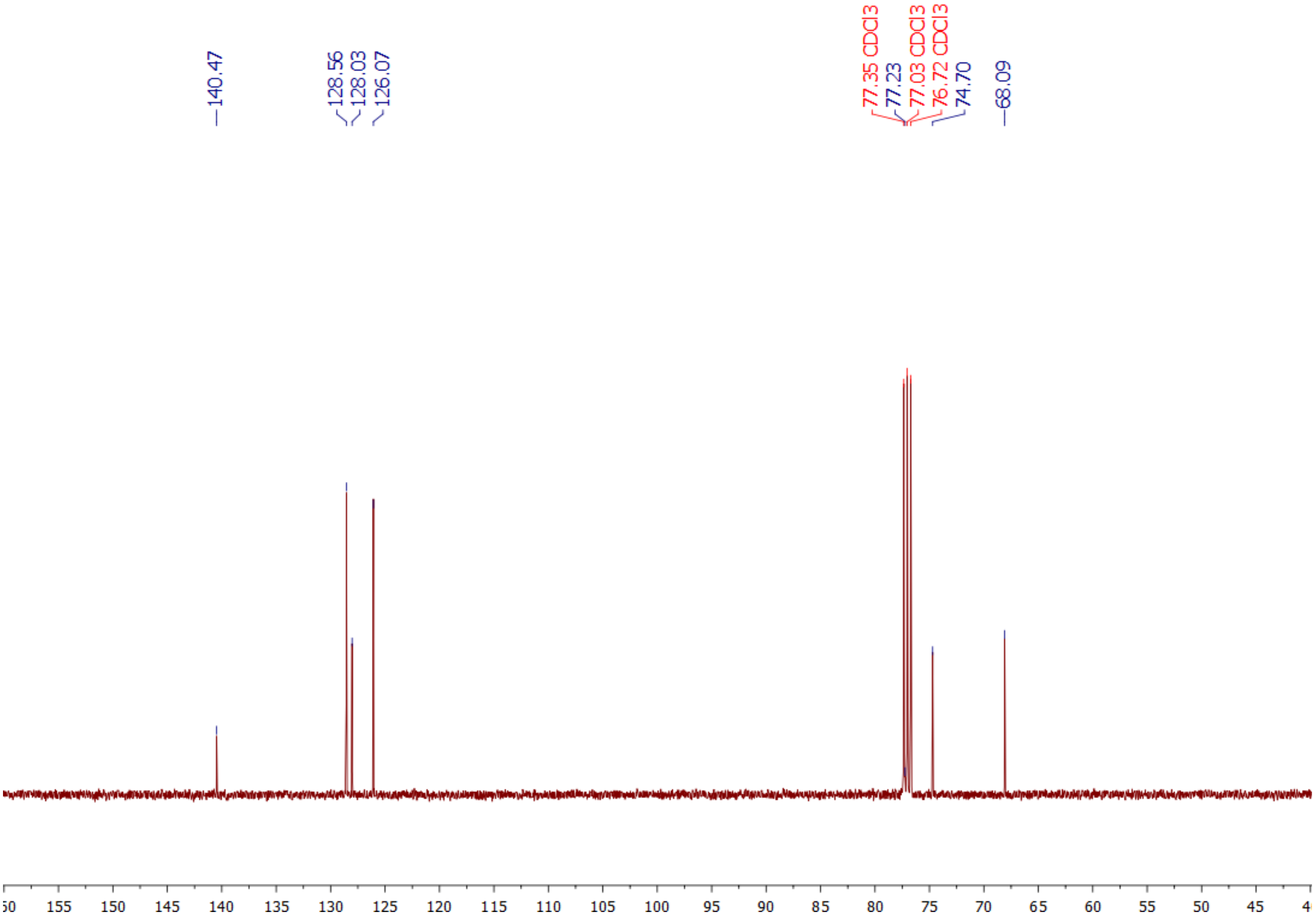


1-phenyl-1, 2-ethanediol (**8f**) ^{1}**H-NMR** spectrum in CDCl$_3$

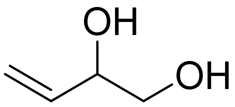


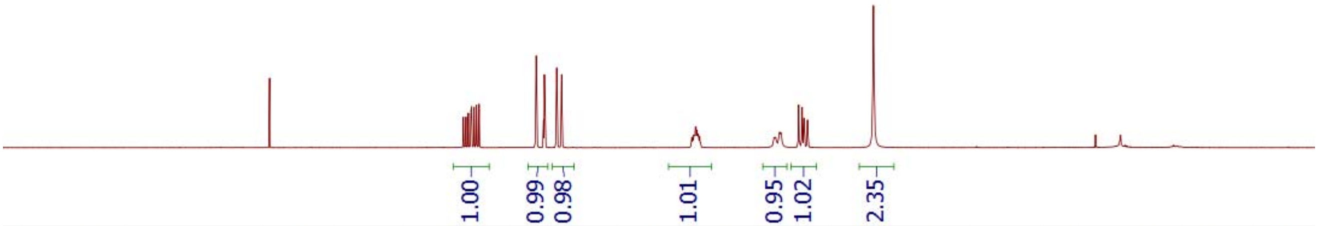


1-phenyl-1, 2-ethanediol (**8f**) ^{13}**C-NMR** spectrum in CDCl$_3$

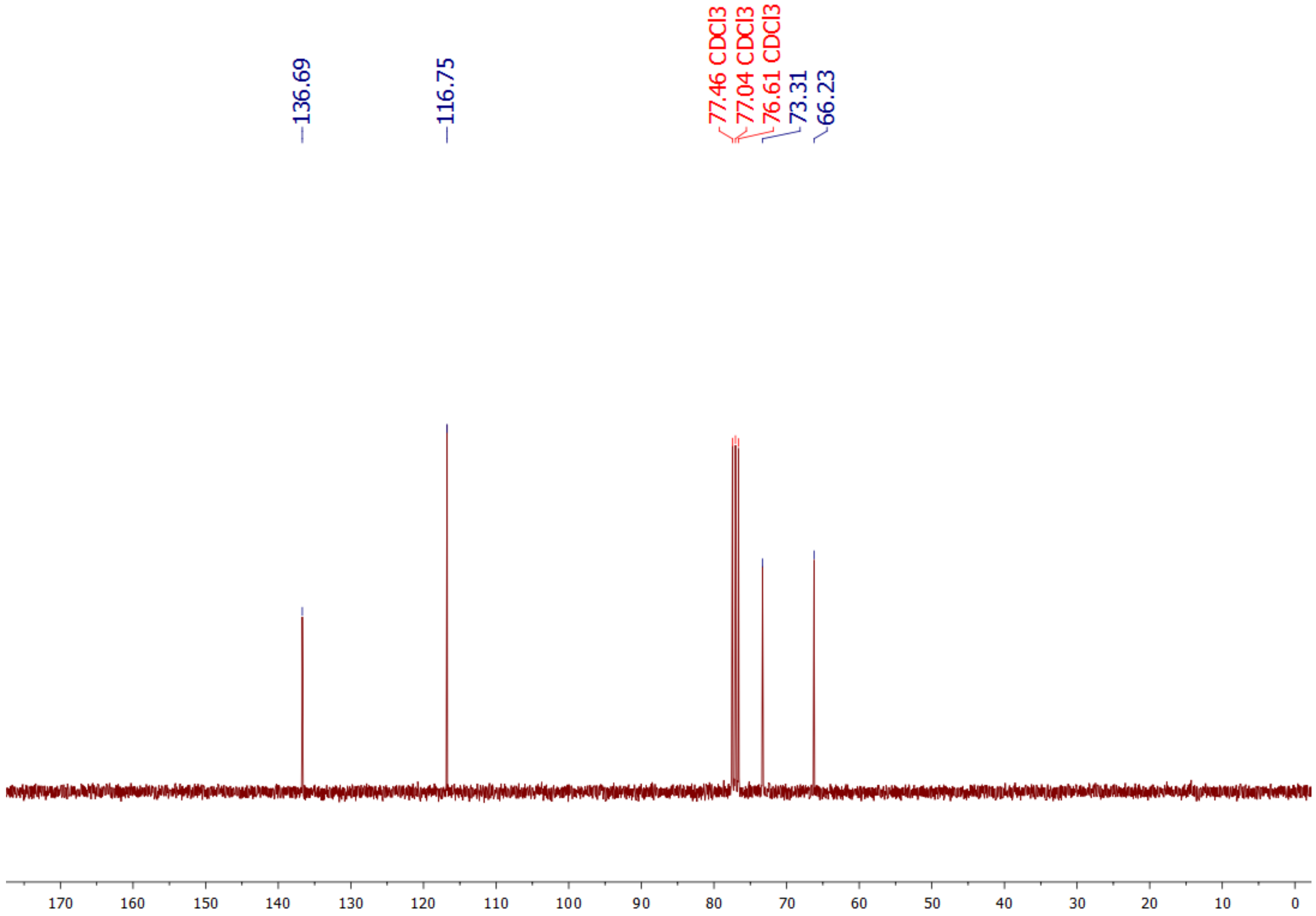


3,4-butenediol (**8g**) ^{1}**H-NMR** spectrum in $CDCl_3$

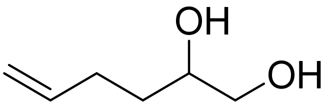


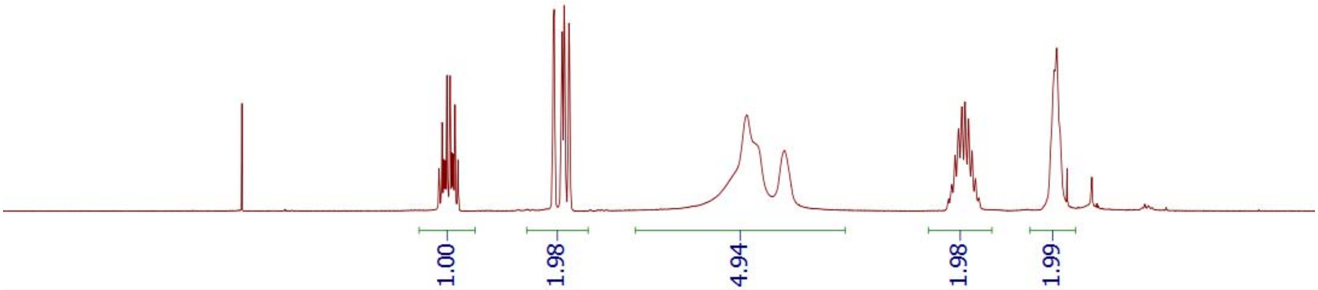


3,4-butenediol (**8g**) ^{13}**C-NMR** spectrum in $CDCl_3$

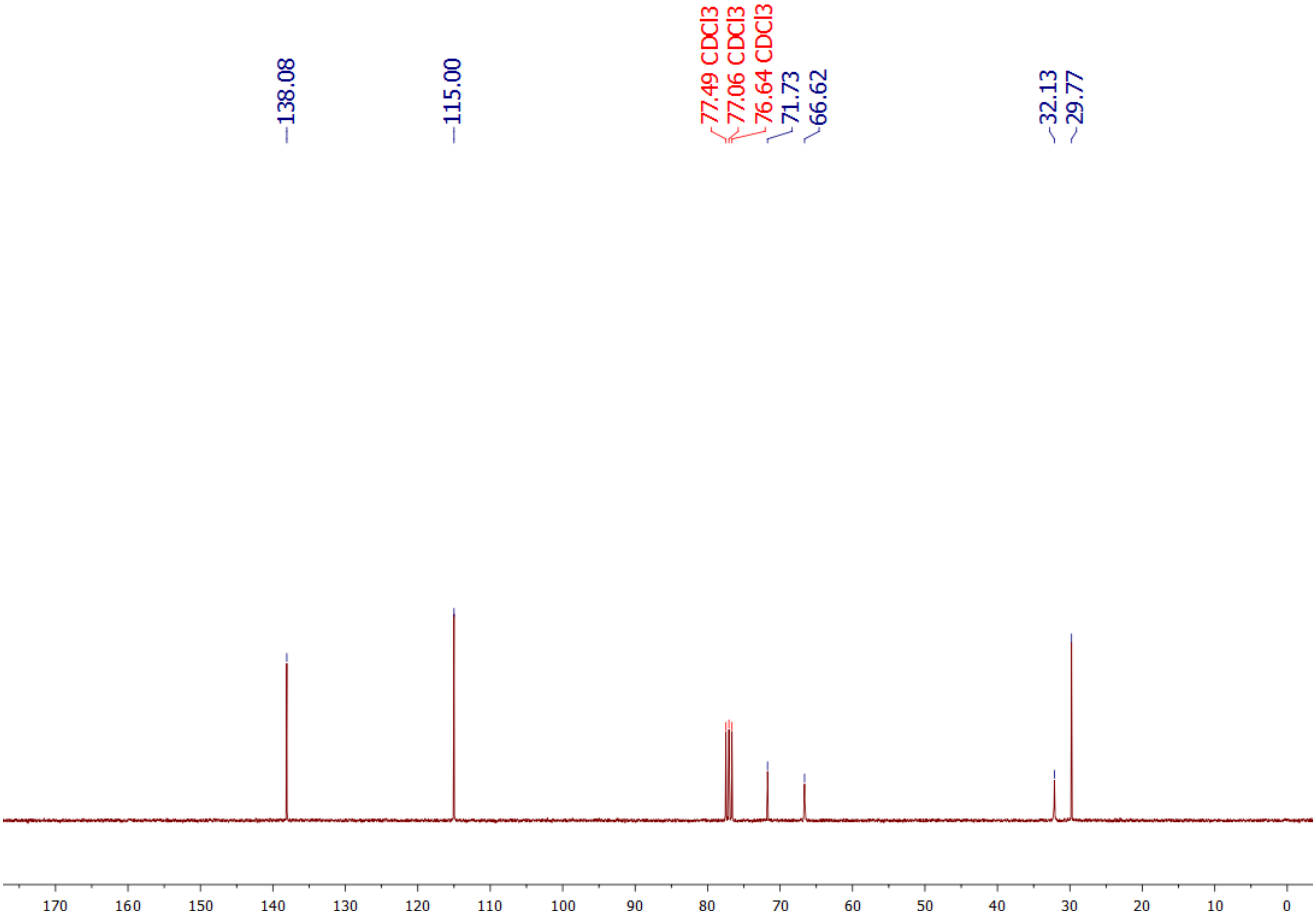


5-hexene-1, 2-diol **(8h)** ^{1}**H-NMR** spectrum in $CDCl_3$

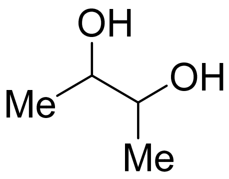


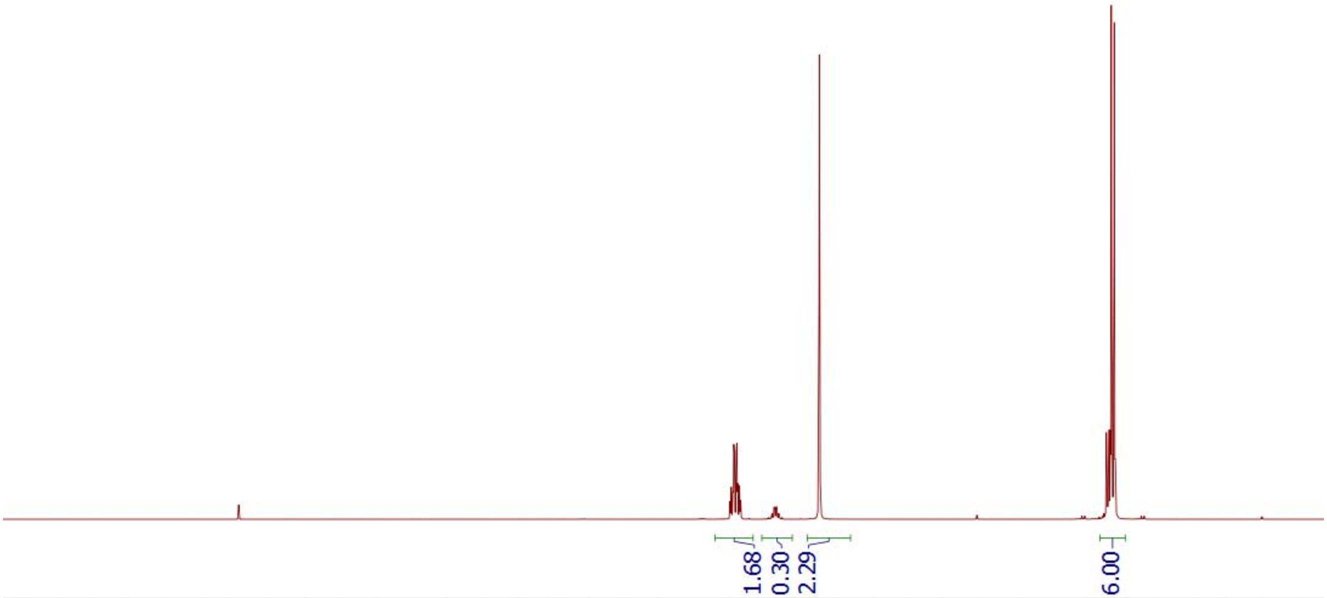


5-hexene-1, 2-diol **(8h)** ^{13}**C-NMR** spectrum in $CDCl_3$

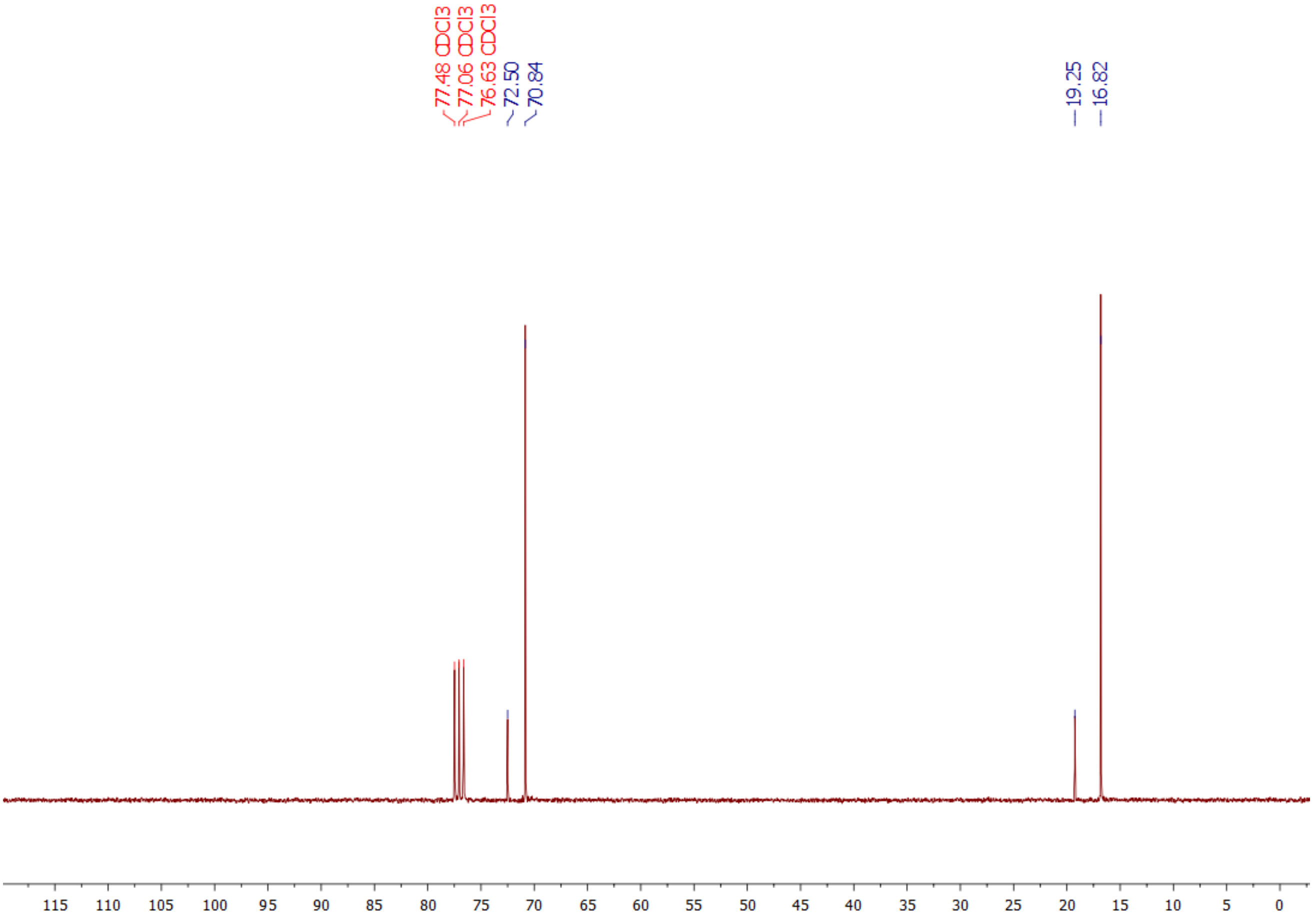


2, 3-butanediol **(8i)** ^{1}**H-NMR** spectrum in $CDCl_3$

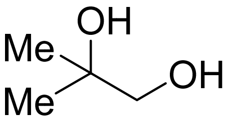


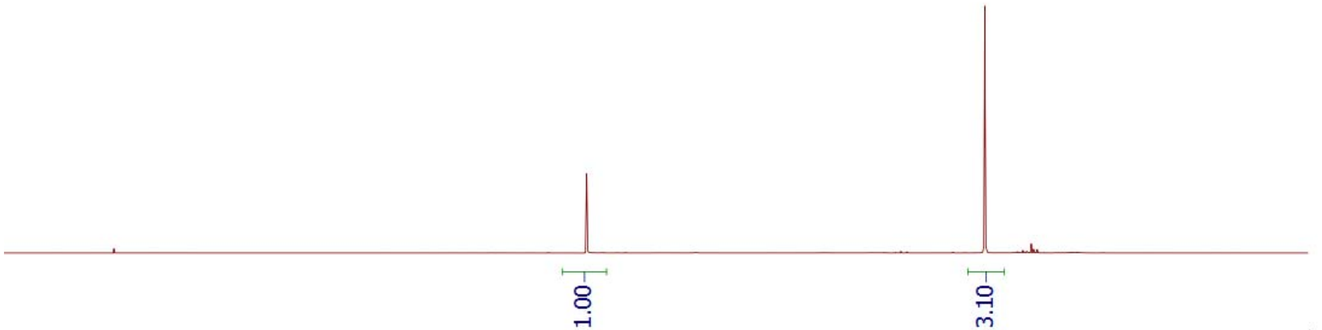


2, 3-butanediol **(8i)** ^{1}**H-NMR** spectrum in $CDCl_3$



2-Methyl-1, 2-propanediol **(8j)** ^{1}**H-NMR** spectrum in CDCl$_3$





2-Methyl-1, 2-propanediol **(8j)** ^{1}**H-NMR** spectrum in CDCl$_3$