Supplementary Material

Choline-based eutectic mixtures as catalysts for effective synthesis of cyclic carbonates from epoxides and CO_2

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Contents

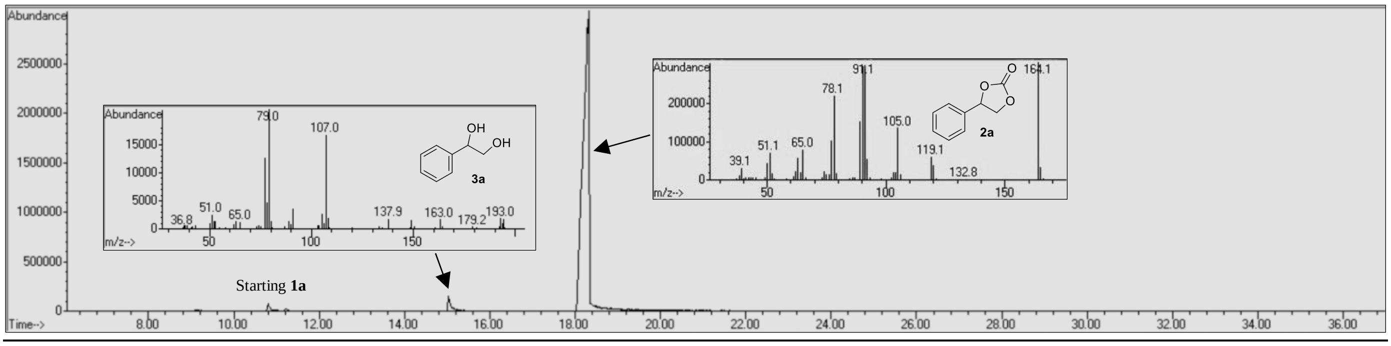
1. TABLE S1. Table of reagents

The water content shown in the table is that provided by the technical specifications. Particularly hygroscopic reagents (Choline chloride, choline iodide, Glycerol, Ethylene Glycol and carboxylic acids) were used after vacuum drying and kept in dryer.

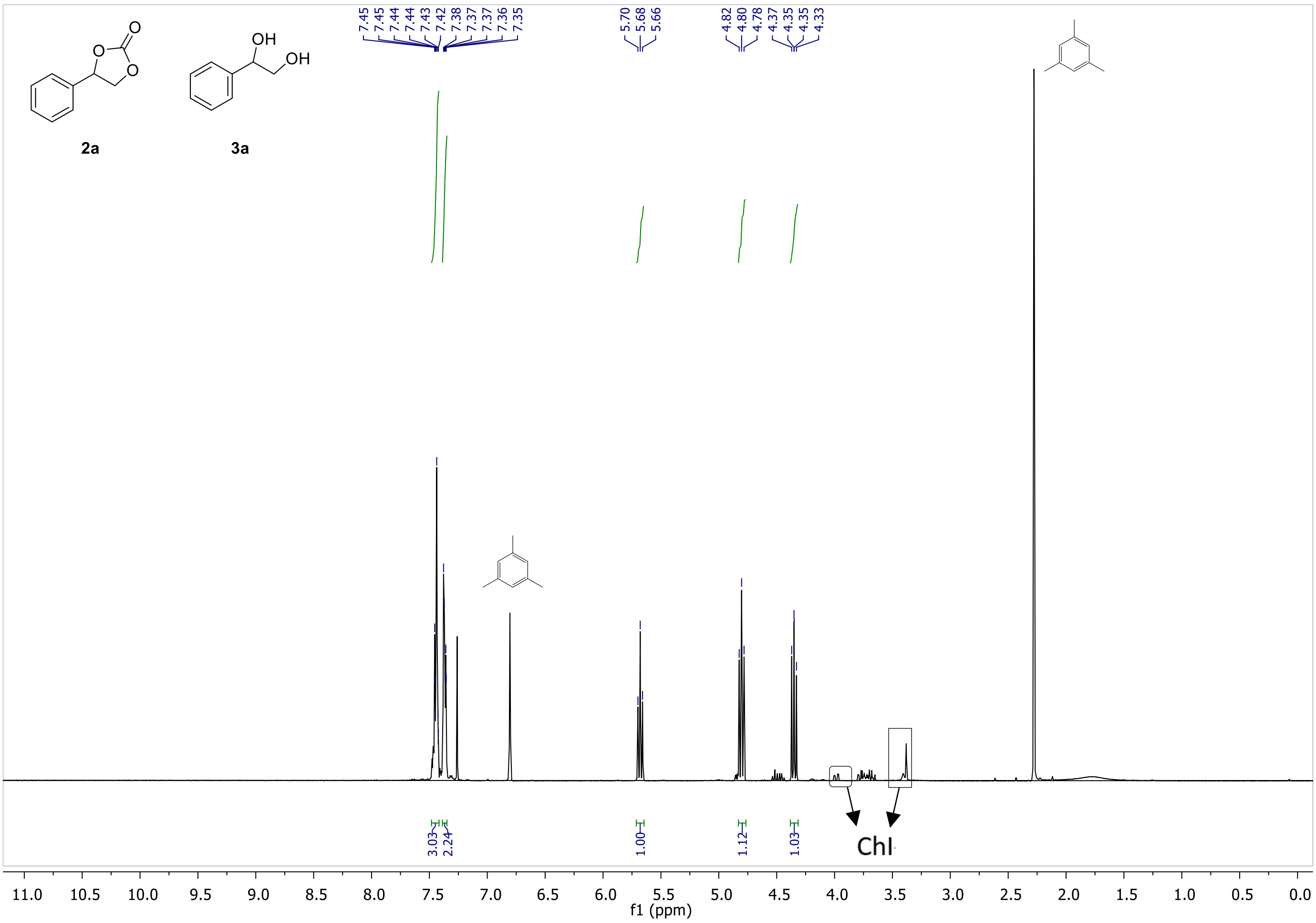
REAGENT (abbreviation in the text)	CAS number	PRODUCER	PURITY	WATER CONTENT
Choline Chloride (ChCl)	67-48-1	Sigma-Aldrich	≥98%	<1%
Choline Iodide (ChI)	17773-10-3	Alfa Aesar	98%	<0.5%
Styrene Oxide	96-09-3	Sigma-Aldrich	97%	Not given
Benzyl Glycidyl Ether	2930-05-4	Sigma-Aldrich	99%	Not given
Epichlorohydrine	106-89-8	Alfa Aesar	99%	Not given
Allyl glycidyl ether	106-92-3	Alfa Aesar	97%	Not given
2-Ethylhexyl glycidyl ether	2461-15-6	Sigma Aldrich	98%	Not given
Cyclohexene oxide	286-20-4	Alfa Aesar	98+%	Not given
Urea	57-13-6	Sigma Aldrich	99-100.5%	Not given
Ethylene Glycol	107-21-1	Sigma Aldrich	99.8%	<0.003%
Glycerol	56-81-5	Sigma-Aldrich	>99.5%	<0.1%
Oxalic Acid	144-62-7	Sigma-Aldrich	98%	<0.7%
Citric Acid	77-92-9	Sigma-Aldrich	>99.5%	Not given
Maleic Acid	110-16-7	Sigma-Aldrich	99%	<2%
Malonic Acid	141-82-2	Sigma-Aldrich	99%	Not given
L-(+)-Tartaric Acid	87-69-4	Sigma-Aldrich	99+%	Not given
DL-Malic Acid	6915-15-7	Sigma-Aldrich	99%	Not given
Fumaric Acid	110-17-8	Sigma-Aldrich	99+%	Not given
alpha-Hydroxyisobutyric Acid	594-61-6	Sigma-Aldrich	98%	Not given
3-Hydroxybutyric acid	300-85-6	Sigma-Aldrich	95%	Not given
Crotonic acid	107-93-7	Sigma-Aldrich	98%	Not given
Benzoic acid	65-85-0	Sigma-Aldrich	>99.5%	Not given
Octanoic Acid	124-07-2	Sigma-Aldrich	>98%	Not given
Butyric Acid	107-92-6	Sigma-Aldrich	>99%	Not given
Acetic Acid	64-19-7	Sigma-Aldrich	99-100%	Not given
Tetrabutylammonium Iodide	311-28-4	Sigma Aldrich	98%	Not given

2. PRODUCT **2a**

2.1 GC-MS chromatogram of reaction crude for conversion of 1a into 2a (Table 3, entry 1[a])

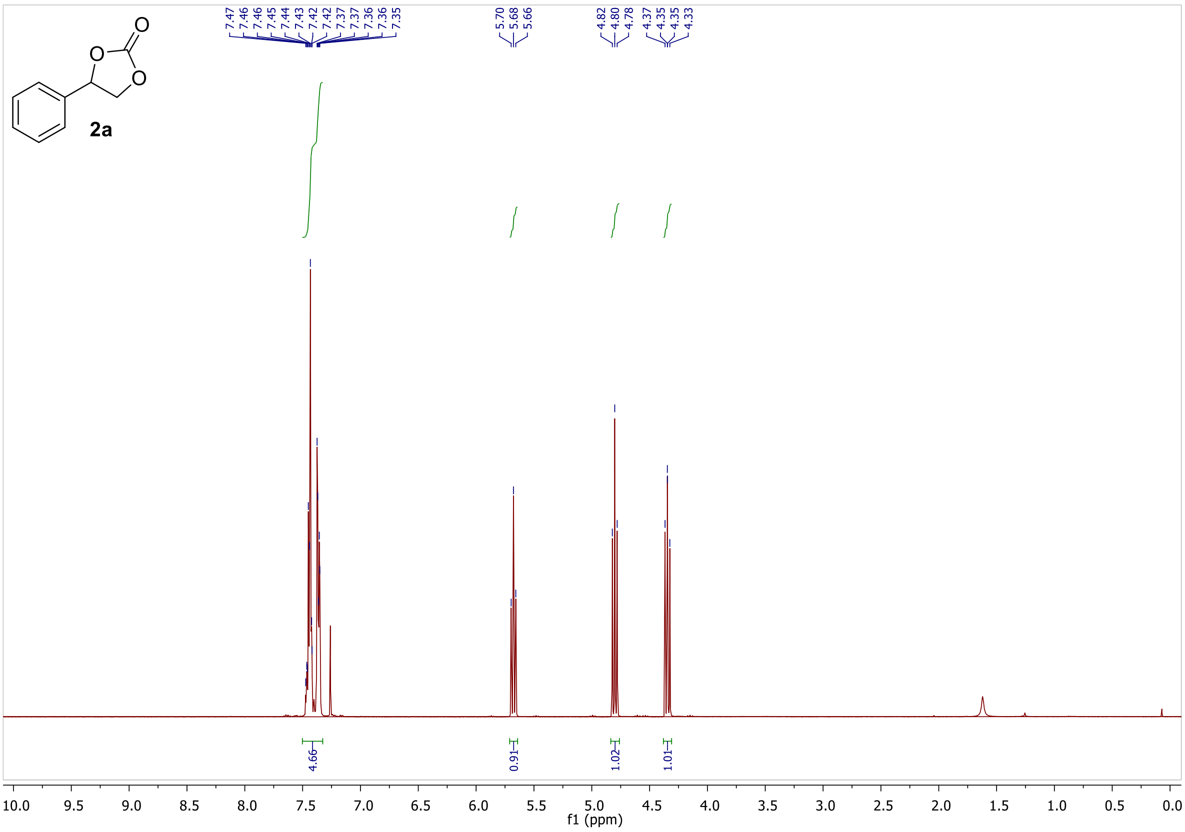


2.2 [1]H NMR spectrum of reaction crude for conversion of 1a into 2a (Table 3, entry 1[a])

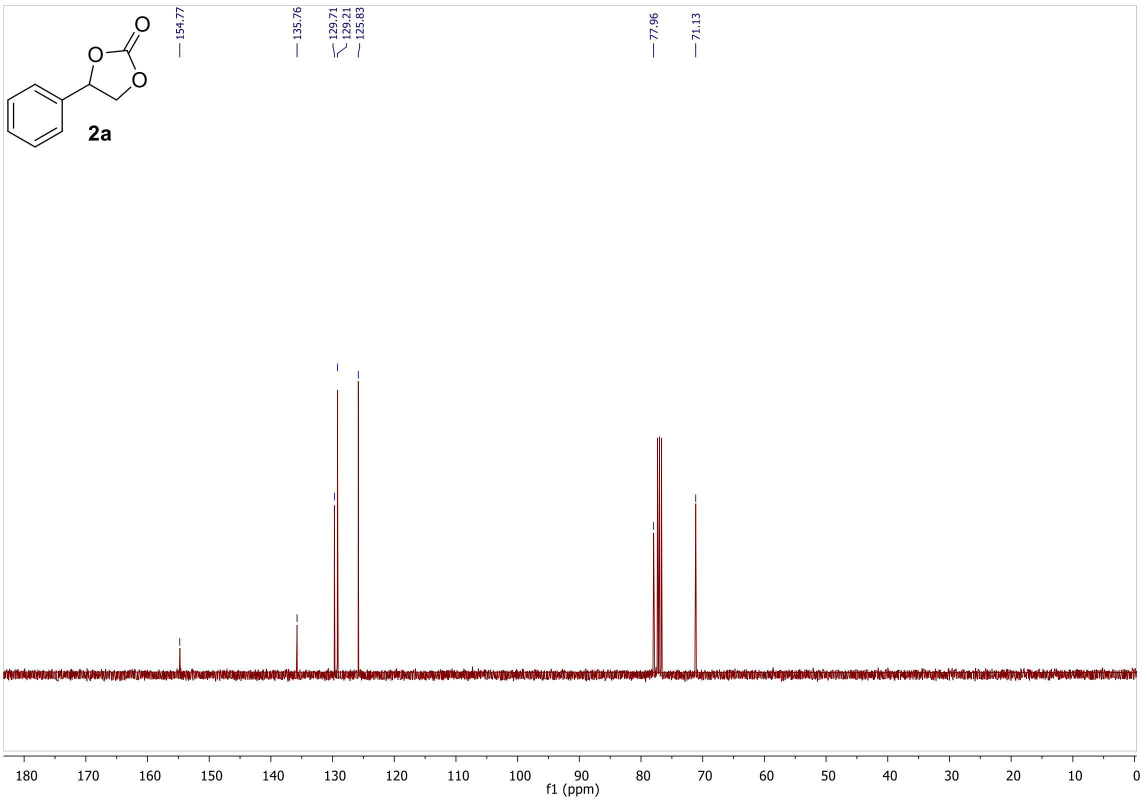


2a. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.42 (m, 3H), 7.39 – 7.35 (m, 2H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.80 (dd, *J* = 8.4, 7.7 Hz, 1H), 4.35 (dd, *J* = 8.6, 7.9 Hz, 1H).
3a. (diagnostic signals) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.42 (m, 3H), 7.39 – 7.35 (m, 2H), δ 4.49 (m, 1H), 3.81 – 3.73 (m, 1H), 3.73 – 3.64 (m, 1H).

2.3 ^{1}H and ^{13}C NMR spectra of isolated product **2a** (Table 3, entry 1[a])



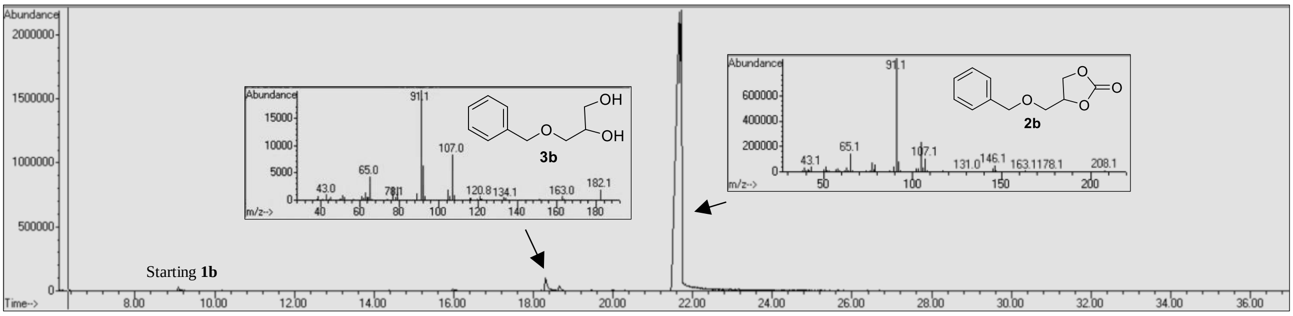
2a. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.33 (m, 5H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.35 (dd, *J* = 8.5, 8.0 Hz, 1H).



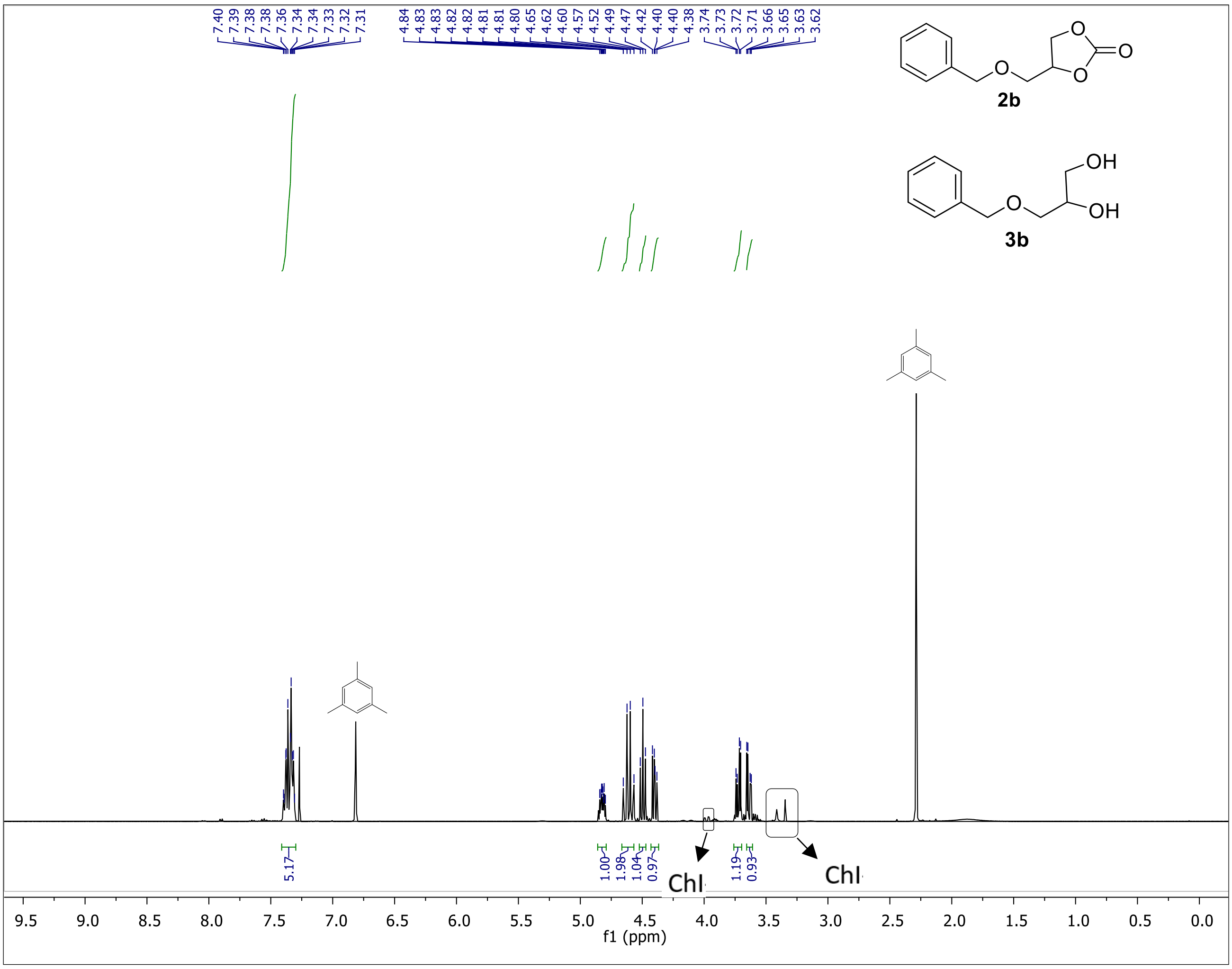
2a. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.77, 135.76, 129.71, 129.21, 125.83, 77.96, 71.1

3. PRODUCT **2b**

3.1 GC-MS chromatogram and of reaction crude for conversion of 1b into 2b (Table 3, entry 2[a])

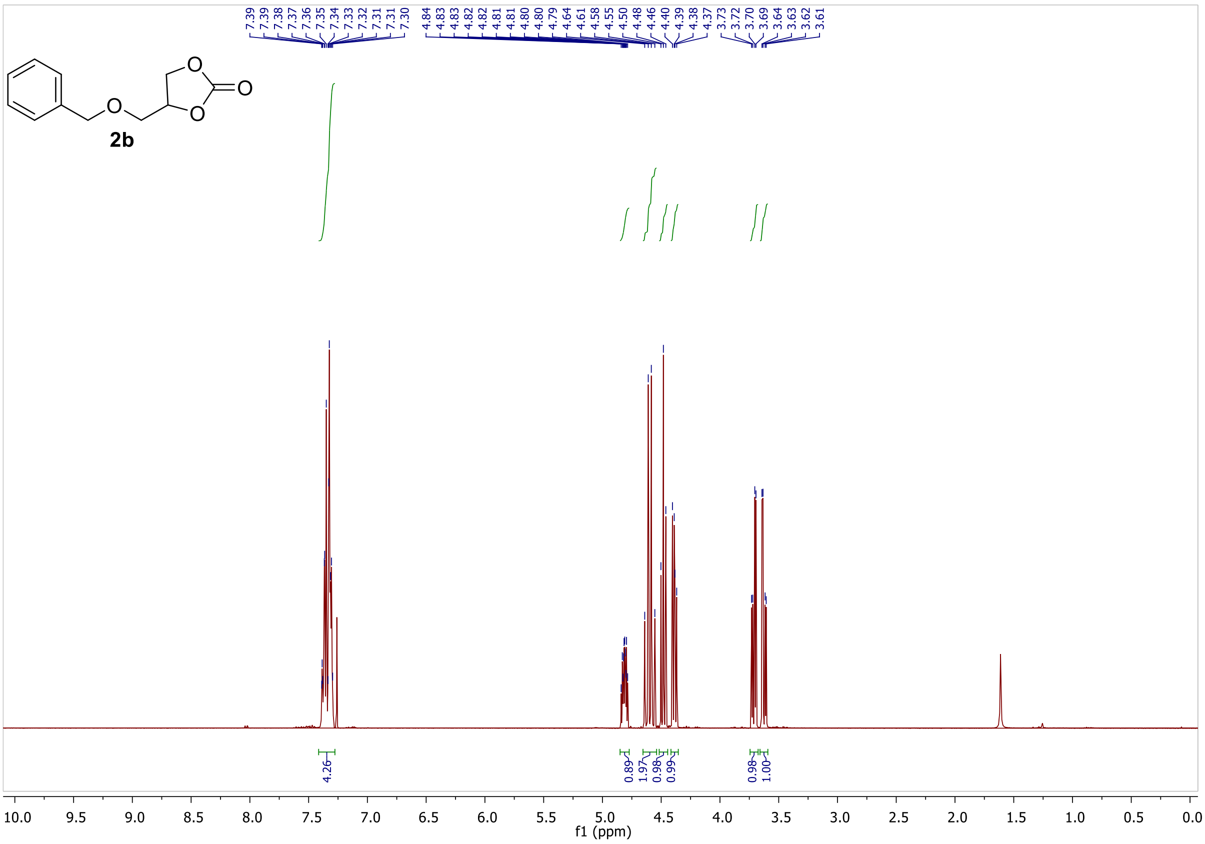


3.2 ^{1}H NMR spectrum of reaction crude for conversion of 1b into 2b (Table 3, entry 2[a])

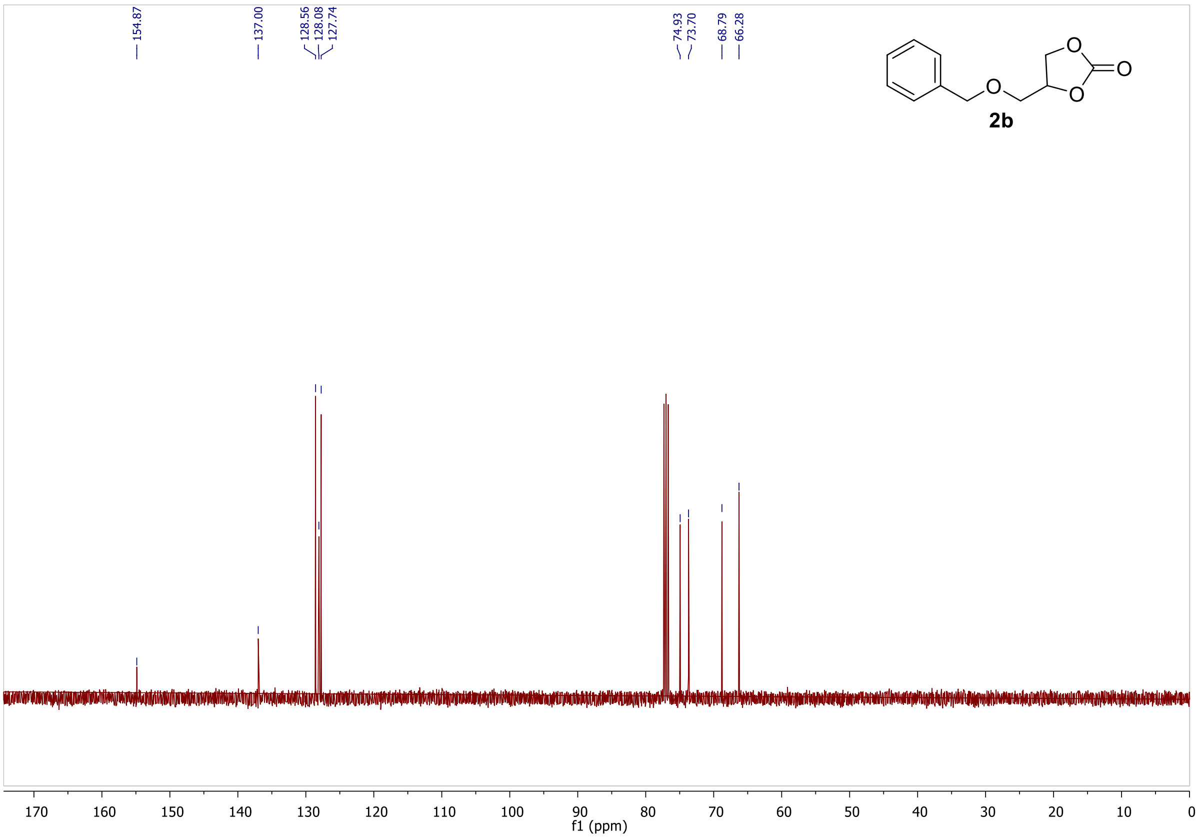


2b. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 5H), 4.82 (ddt, *J* = 8.1, 6.0, 4.1 Hz, 1H), 4.66 – 4.57 (m, 2H), 4.49 (t, *J* = 8.4 Hz, 1H), 4.40 (dd, *J* = 8.4, 6.1 Hz, 1H), 3.72 (dd, *J* = 10.9, 4.1 Hz, 1H), 3.64 (dd, *J* = 10.9, 3.7 Hz, 1H).
3b. (diagnostic signals) ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 – 3.89 (m, 1H), 3.61 – 3.55 (m, 2H).

3.3 ^{1}H and ^{13}C NMR spectra of isolated product **2b** (Table 3, entry 2[a])



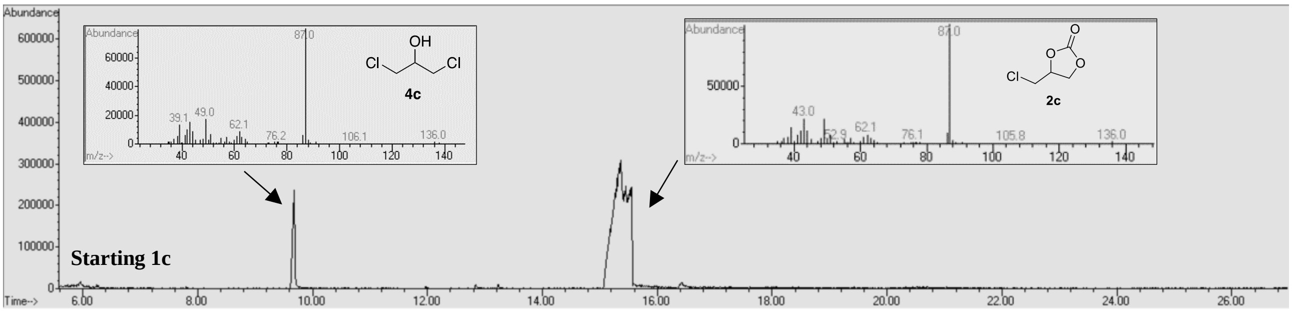
2b. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 4.81 (ddt, *J* = 7.9, 6.1, 3.9 Hz, 1H), 4.60 (m, 2H), 4.48 (t, *J* = 8.4 Hz, 1H), 4.39 (dd, *J* = 8.4, 6.1 Hz, 1H), 3.71 (dd, *J* = 10.9, 4.0 Hz, 1H), 3.62 (dd, *J* = 10.9, 3.8 Hz, 1H).



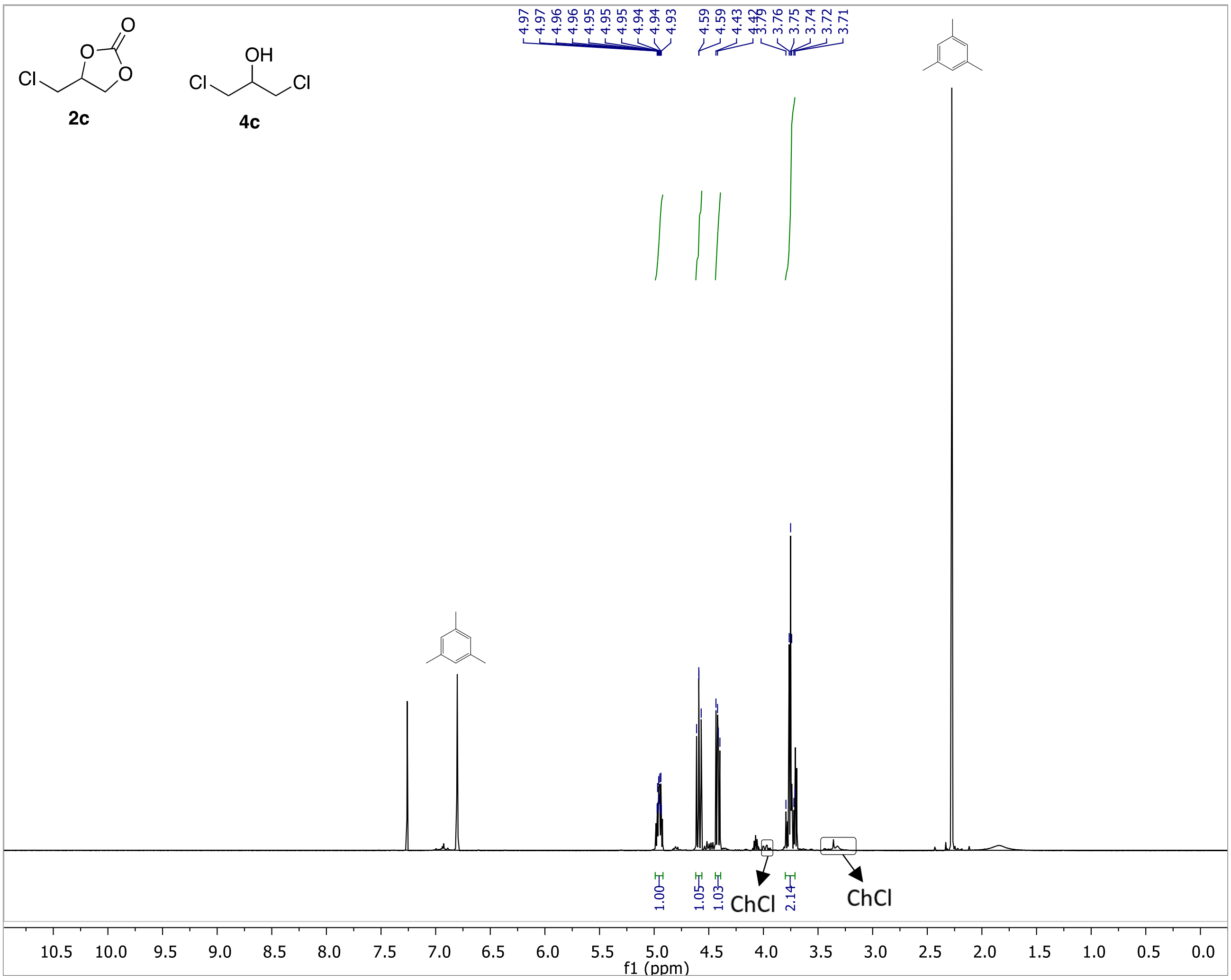
2b. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.87, 137.00, 128.56, 128.08, 127.74, 74.93, 73.70, 68.79, 66.2

4. PRODUCT **2c**

4.1 GC-MS chromatogram and of reaction crude for conversion of 1c into 2c (Table 3, entry 3[b])

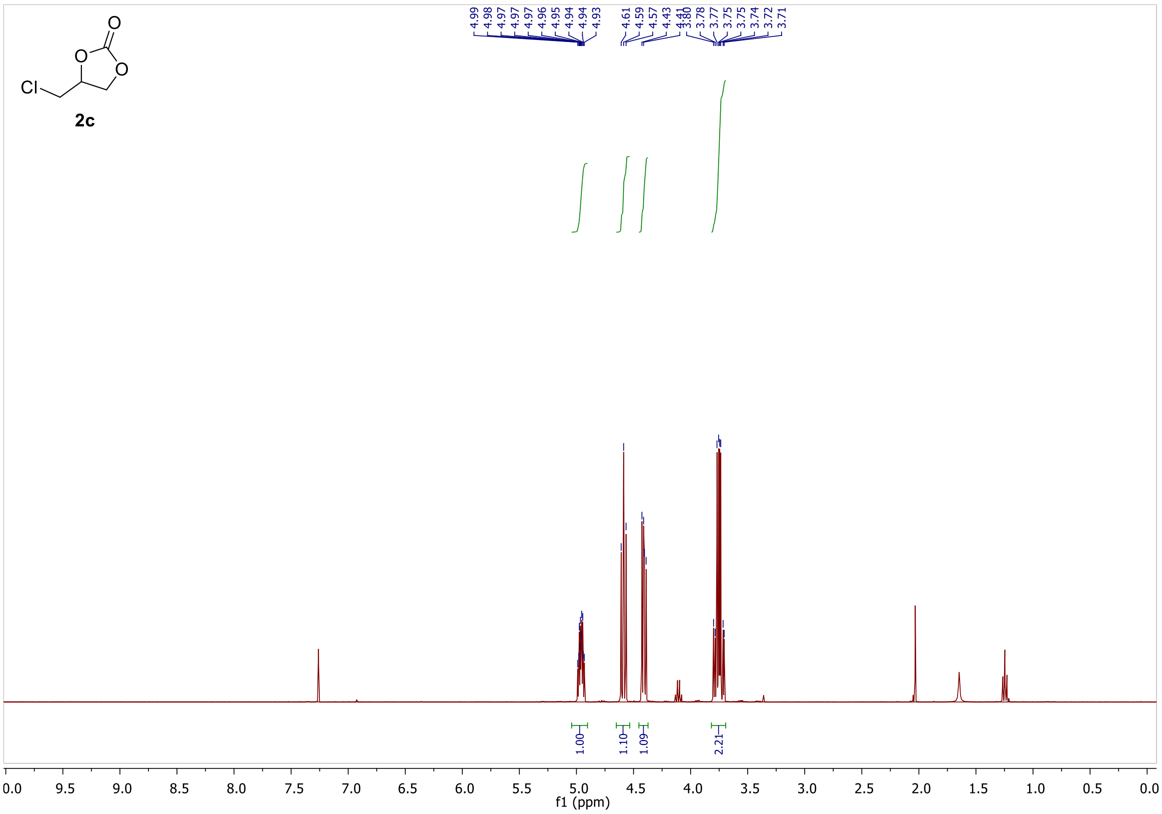


4.2 ^{1}H NMR spectrum and of reaction crude for conversion of 1c into 2c (Table 3, entry 3[b])

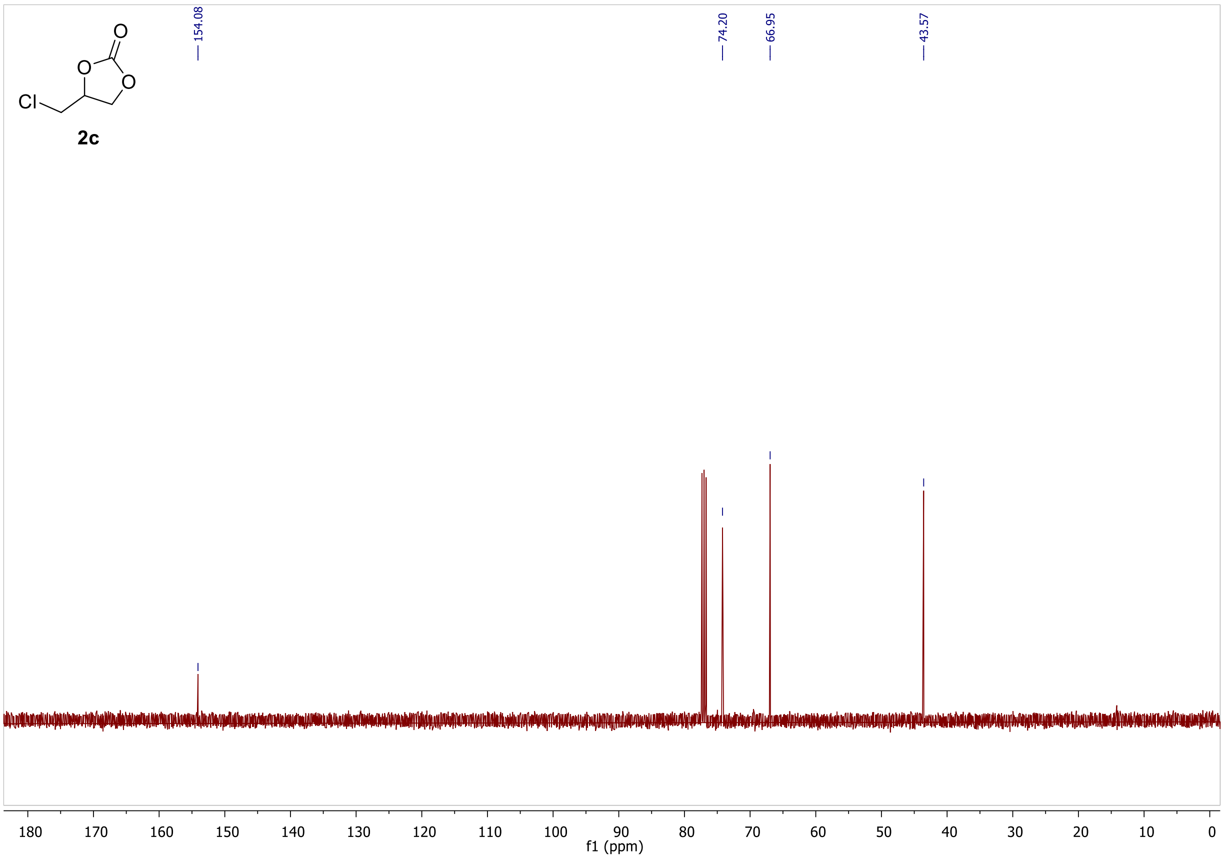


2c. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 – 4.93 (m, 1H), 4.59 (dd, J = 8.8, 8.3 Hz, 1H), 4.42 (dd, J = 8.9, 5.7 Hz, 1H), 3.80 – 3.71 (m, 2H).
4c. (diagnostic signals) ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (m, 1H).

4.3 ^{1}H and ^{13}C NMR spectra of isolated product **2c** (Table 3, entry 3[b])



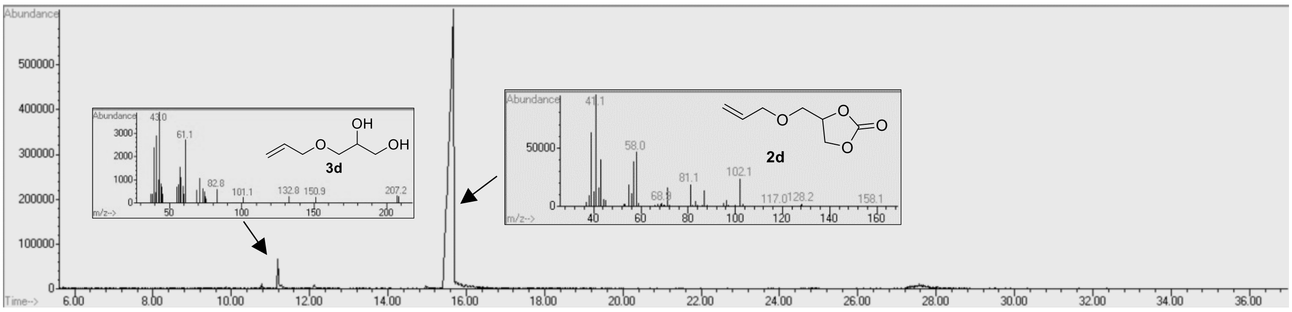
2c. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96 (m, 1H), 4.59 (t, *J* = 8.6 Hz, 1H), 4.41 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.75 (m, 2H).



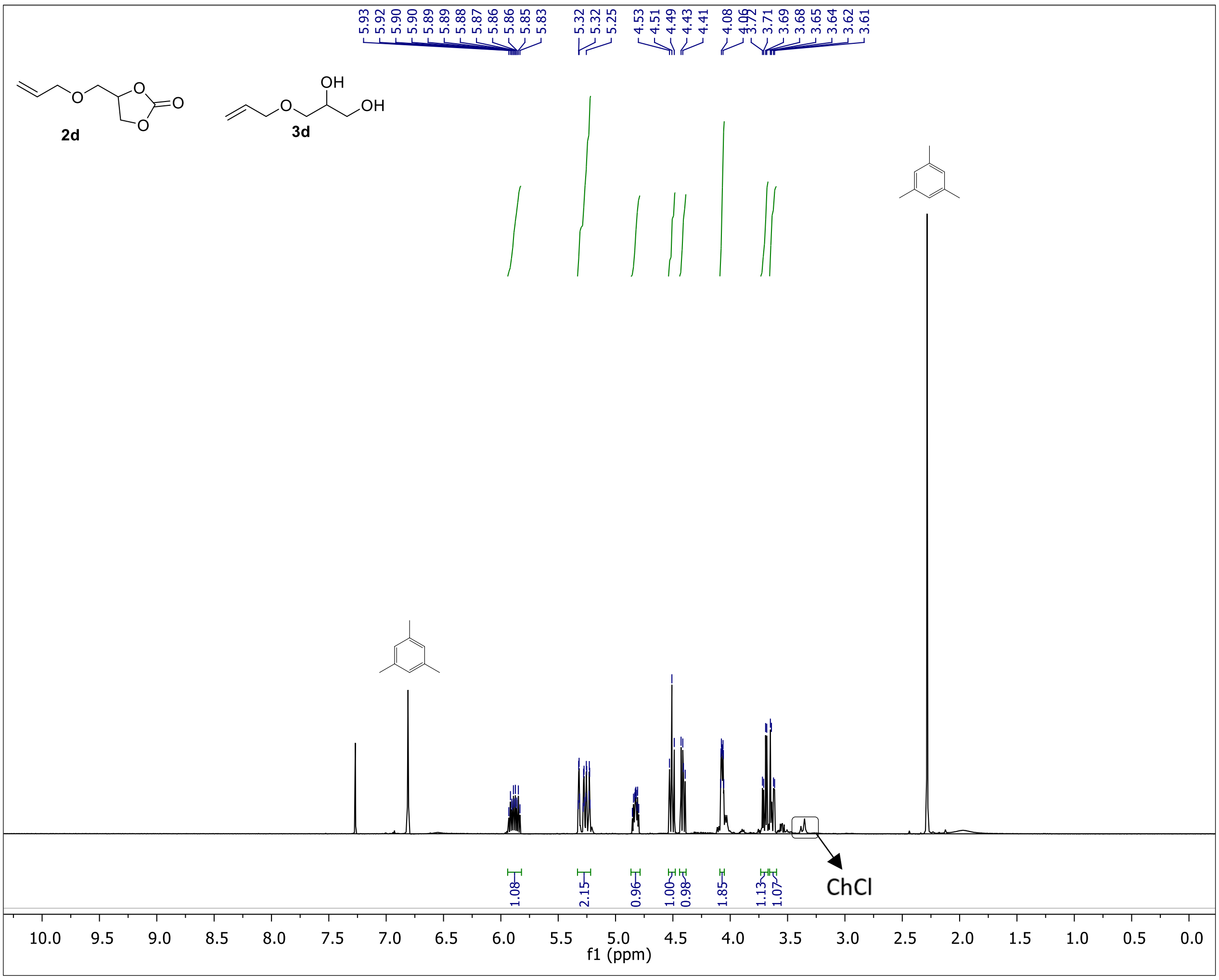
2c. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.08, 74.20, 66.95, 43.57.

5. <u>PRODUCT **2d**</u>

5.1 GC-MS chromatogram of reaction crude for conversion of 1d into 2d (Table 3, entry 4[b])



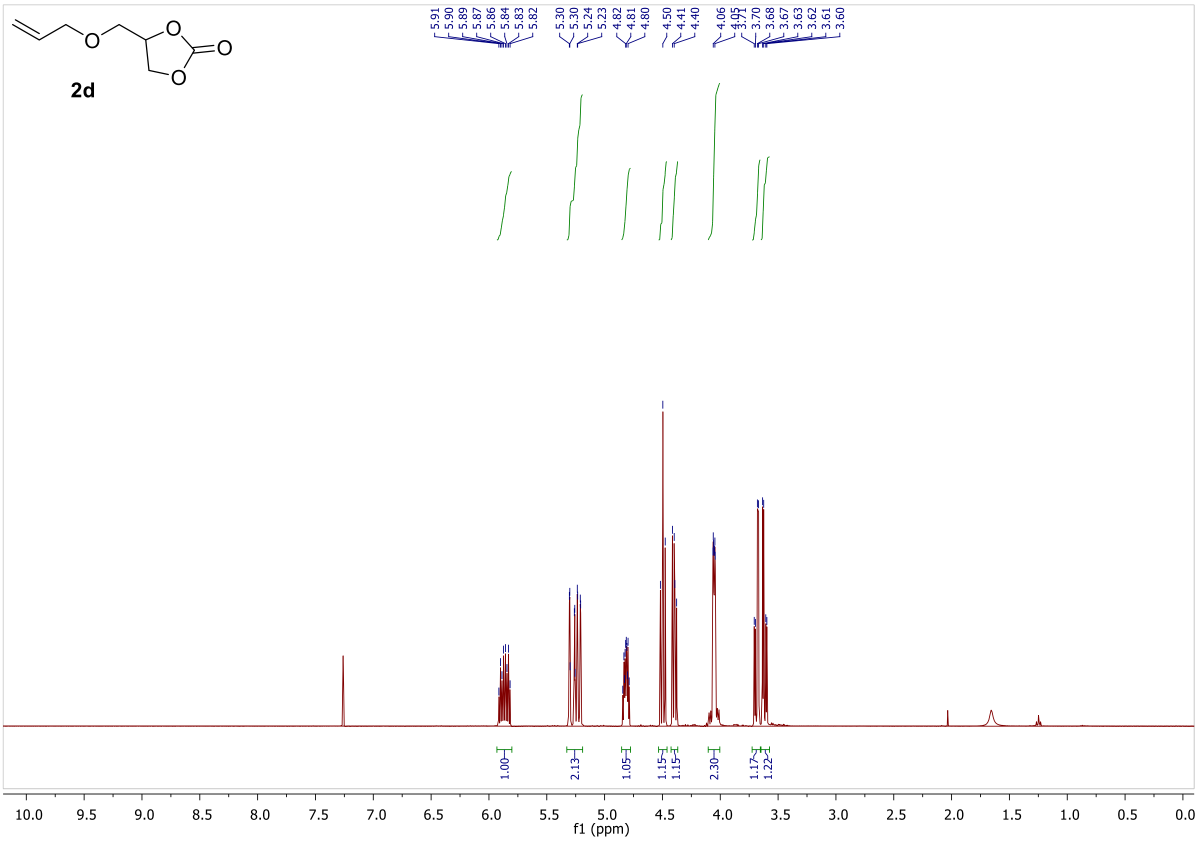
5.2 ^{1}H NMR spectrum of reaction crude for conversion of 1d into 2d (Table 3, entry 4[b])



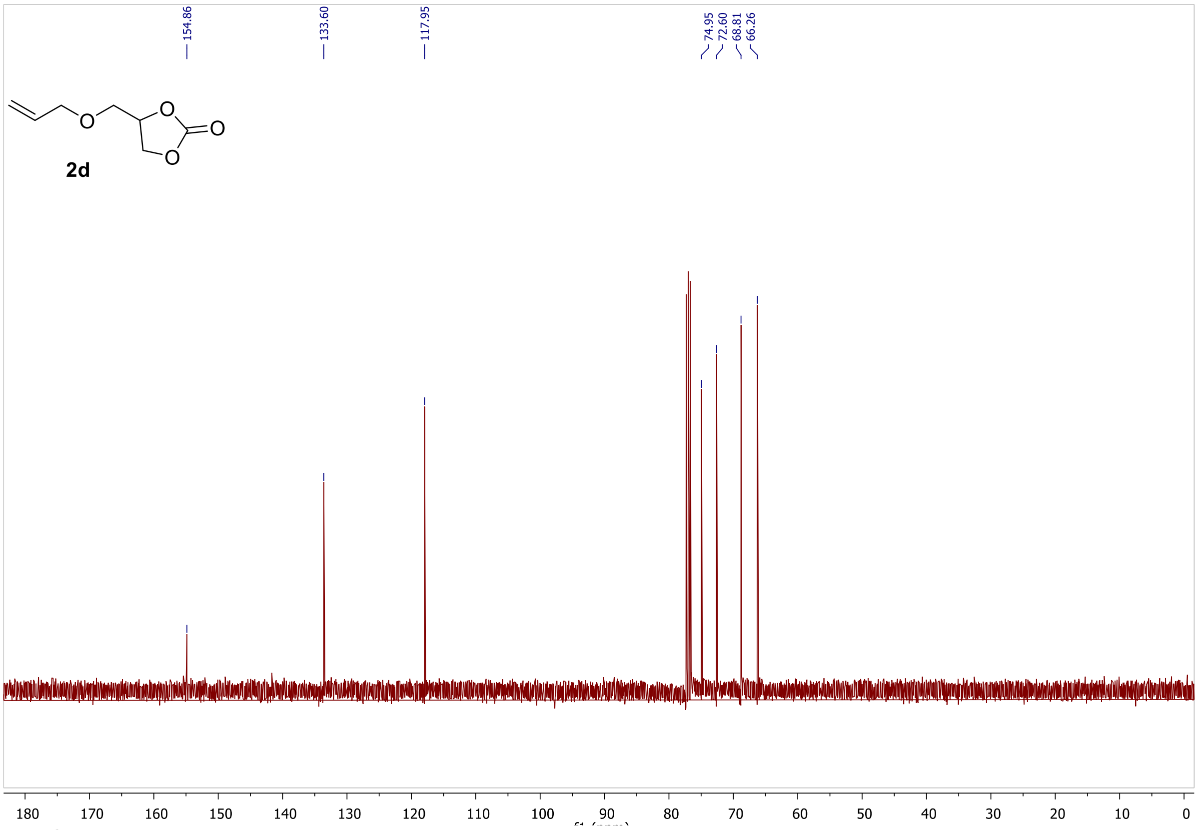
2d. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddt, J = 17.1, 10.5, 5.7 Hz, 1H), 5.33 – 5.22 (m, 2H), 4.87 – 4.79 (m, 1H), 4.51 (t, J = 8.3 Hz, 1H), 4.41 (dd, J = 8.4, 6.1 Hz, 1H), 4.07 (m, 2H), 3.70 (dd, J = 11.0, 4.1 Hz, 1H), 3.63 (dd, J = 11.0, 3.8 Hz, 1H).

3d. (diagnostic signals) ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (m, 1H), 3.59 – 3.51 (m, 2H).

5.3 ^{1}H and ^{13}C NMR spectra of isolated product **2d** (Table 3, entry 4[b])



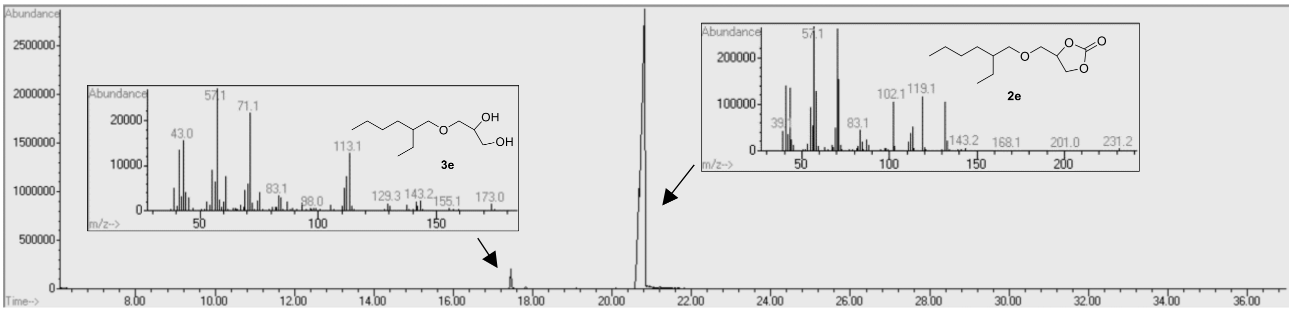
2d. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 22.8, 10.8, 5.6 Hz, 1H), 5.33 – 5.19 (m, 2H), 4.82 (ddt, *J* = 8.1, 6.1, 3.9 Hz, 1H), 4.50 (t, *J* = 8.4 Hz, 1H), 4.40 (dd, *J* = 8.3, 6.1 Hz, 1H), 4.10 – 4.00 (m, 2H), 3.69 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.62 (dd, *J* = 11.0, 3.8 Hz, 1H).



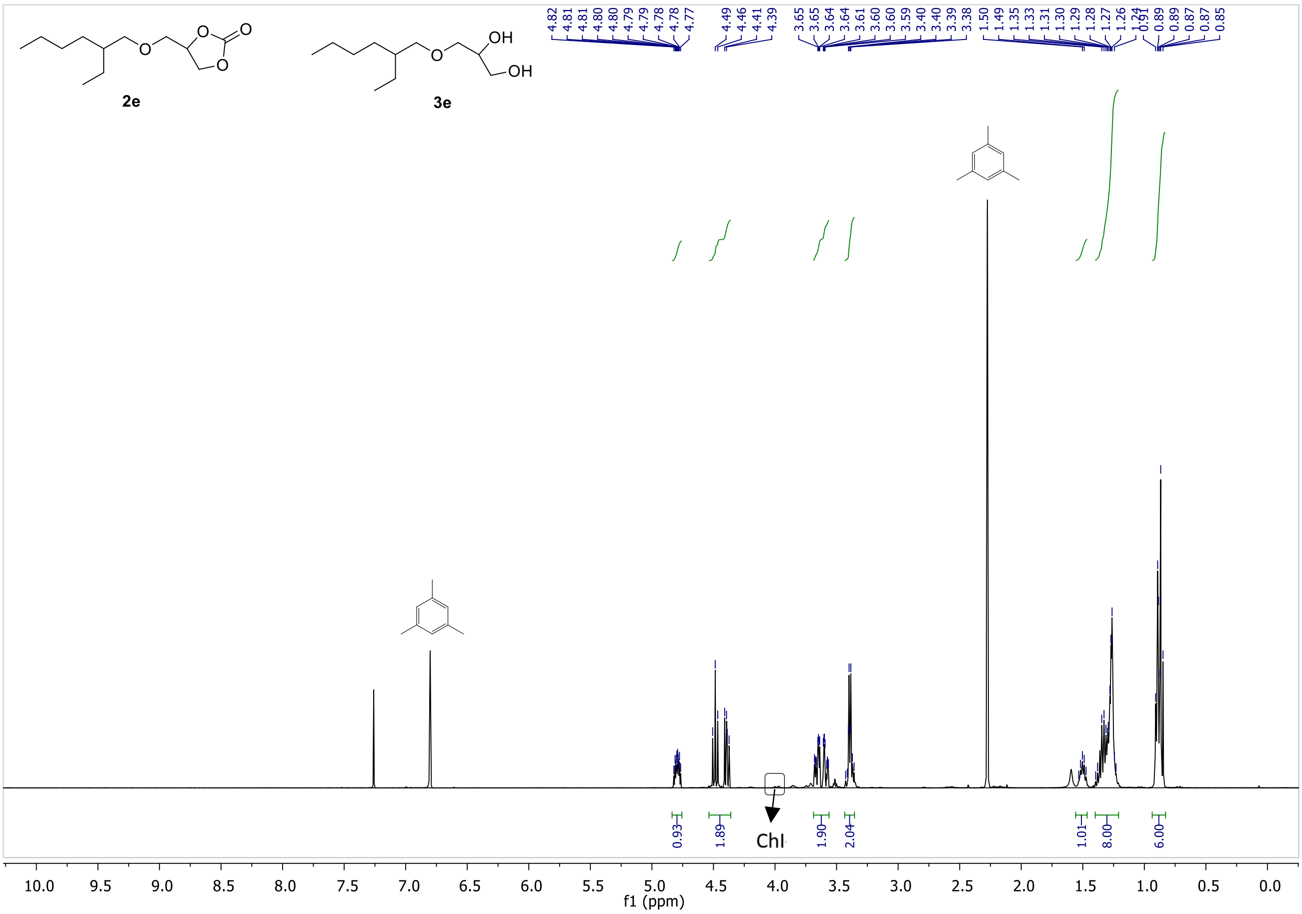
2d. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.86, 133.60, 117.95, 74.95, 72.60, 68.81, 66.26

6. <u>PRODUCT **2e**</u>

6.1 GC-MS chromatogram of reaction crude for conversion of 1e into 2e (Table 3, entry 5[a])

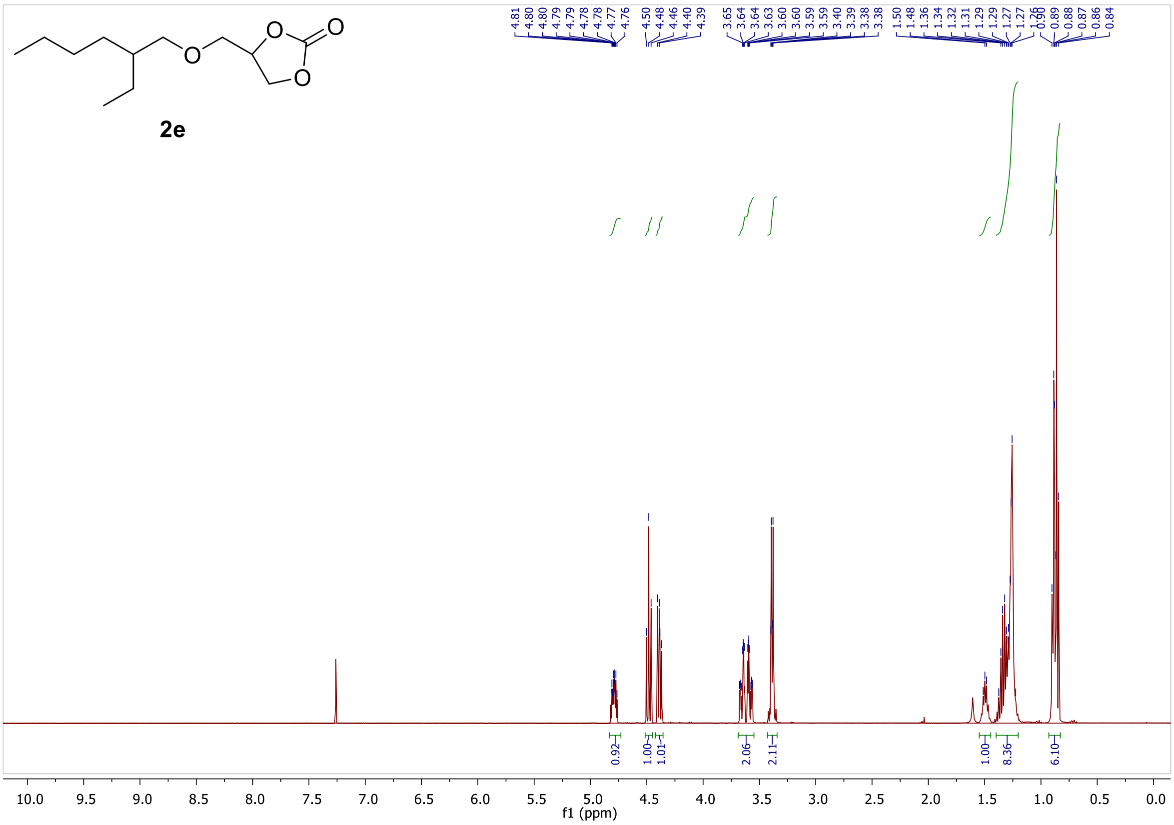


6.2 ^{1}H NMR spectrum of reaction crude for conversion of 1e into 2e (Table 3, entry 5[a])

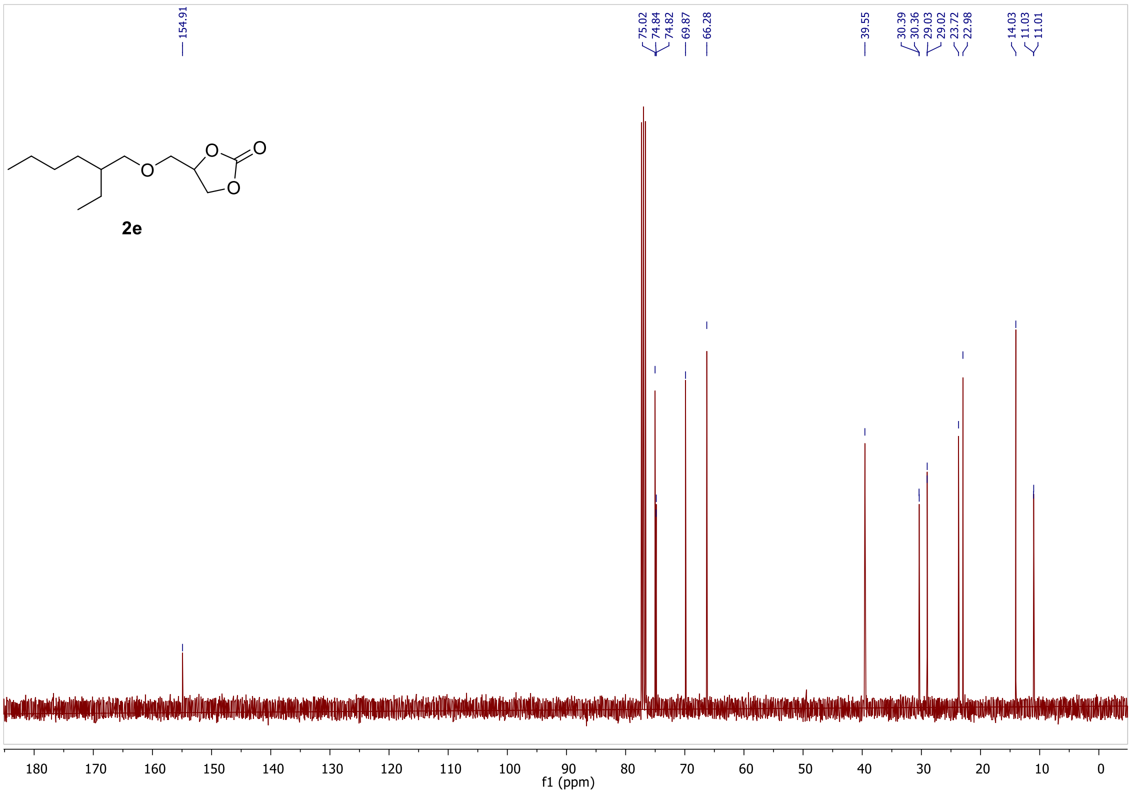


2e. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 – 4.76 (m, 1H), 4.51 – 4.36 (m, 2H), 3.62 (m, 2H), 3.39 (dd, *J* = 5.7, 1.9 Hz, 2H), 1.55 – 1.45 (m, 1H), 1.40 – 1.20 (m, 8H), 0.88 (dt, *J* = 10.6, 7.0 Hz, 6H).
3e. (diagnostic signals)^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 – 3.49 (m, 2H), 1.50 (dt, *J* = 12.0, 6.0 Hz, 14H).

6.3 ^{1}H and ^{13}C NMR spectra of isolated product **2e** (Table 3, entry 5[a])

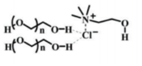
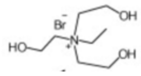
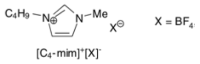
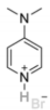
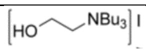
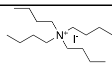
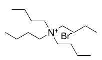
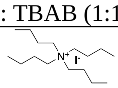
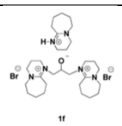
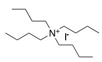
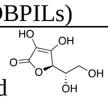
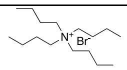
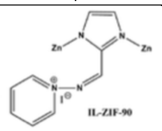


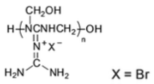
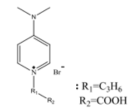
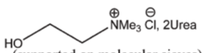
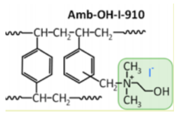
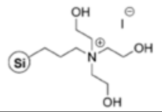
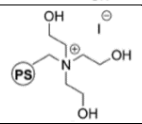
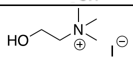
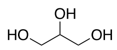
2e. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 – 4.73 (m, 1H), 4.48 (t, *J* = 8.3 Hz, 1H), 4.39 (dd, *J* = 8.3, 6.0 Hz, 1H), 3.62 (m, 2H), 3.39 (dd, *J* = 5.7, 2.0 Hz, 2H), 1.55 – 1.45 (m, 1H), 1.40 – 1.26 (m, 8H), 0.87 (dt, *J* = 10.2, 7.0 Hz, 6H).



2e. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.91, 75.02, 74.83, 69.87, 66.28, 39.55, 30.37, 29.02, 23.72, 22.98, 14.03, 11.02

7. TABLE S2. Comparison of various homogeneous/heterogeneous IL-type, DES-type or ammonium-based catalysts, for the synthesis of styrene carbonate from CO_2 and styrene oxide.

Substrate	Homogeneous/ Heterogeneous	Active site	Catalyst Loading (mol%)	Pressure (MPa)	T (°C)	Time (h)	Yield[a] (%)	Reference
SO	Homogeneous	 ChCl/PEG200	2	0.8	150	5	82.3	[1]
SO	Homogeneous	L-Proline/Propanedioic Acid $ZnBr_2$	2 0.3	1.2	150	5	55.6	[2]
SO	Homogeneous	 PEG6000-supported hexaalkylguanidinium bromide	0.5	4	110	4	97 (Selectivity 99)	[3]
SO	Homogeneous	 NEt(HE)3Br	1	1.5	130	2	97 (Selectivity 99)	[4]
SO	Heterogeneous	 [C4-mim]+[BF4]/SiO2 1-butyl-3-methylimidazolium ionic liquids supported on silica gel	1.8	8	160	4	96 (Selectivity 98)	[5]
SO	Homogeneous	 [DMAPH]Br 4-(dimethylamino)pyridine hydrobromide	1	0.1	120	4	96[b] (Selectivity 99)	[6]
SO	Homogeneous	 Tri-n-butyl-(2-hydroxyethyl) ammonium iodide	2	0.5	90	2	95	[7]
			5	1.0	45	18	89	
SO	Homogeneous	 and  TBAI: TBAB (1:1 w/w)	250 (w/w)	0.1	120	4	83[c] (purity >95%) [a,b]	[8]
		 TBAI	10 (w/w)		60	22	80[c] (purity >95%) [a,b]	
SO	Homogeneous	 DBU based protic ionic liquids (DBPILs)	6	0.1	50	6	87[b]	[9]
SO	Homogeneous	 and  TBAI and Ascorbic Acid	4 / 2	0.1	60	23	96[c]	[10]
SO	Homogeneous	 Bu_4NBr	1	2	100	4	59	[11]
SO	Heterogeneous		0.49 (Zn)	1	120	3	81 (Selectivity 98)	[12]

SO	Heterogeneous		1.5	2	130	5	99	[13]
SO	Homogeneous	 [CBDMAPy]Br	1	2	130	0.33	85[c]	[14]
SO	Homogeneous	$Et_3\overset{\oplus}{N}{-}H\ I^{\ominus}$	10	0.1	40	24	97[c]	[15]
SO	Heterogeneous	 (supported on molecular sieves)	1	molar ratio of CO_2: epoxide = 1.5–1.87	110	5	95	[16]
SO	Homogeneous	$BrBu_3N$–PEG_{6000}–NBu_3Br	0.5	8	120	6	94 (Selectivity 98)	[17]
SO	Homogeneous	Cholie Iodide (+ EtOH as solvent)	6	1	85	6	99[c]	[18]
SO	Heterogeneous	 H_2O	1 0.02 ml (20 mmol of epoxide)	1	80	18	66[b]	[19]
SO	Heterogeneous		2	1	90	6	85[c]	[20]
						4	93[c]	
SO	Homogeneous	  Choline Iodide/Glycerol	5	0.1	80	7	90[b] 88[c]	This work

[a] Determined by GC
[b] Determined by ^1H NMR
[c] Isolated Yield

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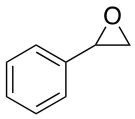
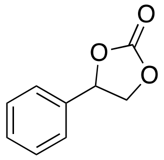
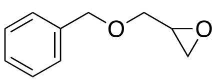
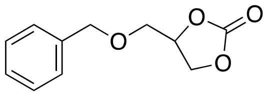
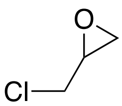
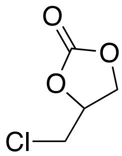
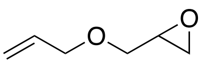
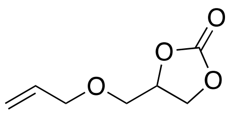
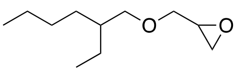
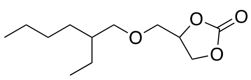
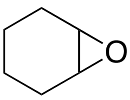
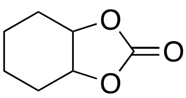
8. TABLE S3. TON/TOF values calculated for substrates **1a-1f**

Entry	Substrate	Product	Time (h)	Yield **2** [%][c]	TON[d]	TOF[e]

1[a]	 **1a**	 **2a**	7	90 (88)	18.1 (17.6)	2.6 (2.5)
2[a]	 **1b**	 **2b**	7	94 (87)	18.8 (17.4)	2.7 (2.5)
3[b]	 **1c**	 **2c**	7	80 (80)	16 (16)	2.3 (2.3)
4[b]	 **1d**	 **2d**	5	91 (80)	18.1 (16)	3.6 (3.2)
5[a]	 **1e**	 **2e**	22	95 (83)	19 16.6	0.9 0.7
6[a,b]	 **1f**	 **2f**	23	0	-	-

[a] Reaction conditions: 2.6 mmol of substrate, ChI: Glycerol (1: 1) 5%, 80°C (5[a] 100°C), p(CO2) =0.1 MPa (balloon)
[b] Reaction conditions: 1.3 mmol of substrate, ChCl: Malic Acid (1:1) 5%, 80°C, p(CO2) =0.4 MPa (autoclave)
[c] Calculated by ^{1}H-NMR (see experimental part), isolated yields in parentheses
[d] Turnover number, defined as $mol_{cyclic\ carbonate\ (\mathbf{2})}/mol_{choline}$
[e] TOF = TON/h