

Electronic supplementary information

The Design of Efficient Carbonate-Interchange-Reactions with Catechol Carbonate

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Materials

Commercial grade reagents and solvents were used without further purification.

Pyrocatechol carbonate (PCC) was synthesized according to the following procedure:

Catechol (2.5 g), DMC (19 ml) and the basic catalyst (NaOCH_3 , 41 mg) were charged in a two-necked round bottom flask in a molar ratio catechol:DMC: $\text{NaOCH}_3=1:10:0.033$. Afterwards the flask is equipped with an “implemented” reactive distillation system in which between the vertical column and the flask a porous glass support was added in order to hold up about ten grams of $4\text{\AA}$ molecular sieve (Sigma Aldrich, $\text{Na}_{12}[(\text{AlO}_2)_2(\text{SiO}_2)_{12}]\cdot x\text{H}_2\text{O}$); on the second neck, another condenser was needed both for liquid sampling and in order to avoid a possible over-pressure inside the flask (Fig.1).

The mixture is then heated in order to obtain the reflux of the mixture ($\approx 90^\circ\text{C}$) for 24 hours.

In this way, the sieves placed over the support get wet by the distilled mixture of the co-product methanol and DMC and, taking advantage of the different molecular size of these compounds, the former is preferentially held by the zeolites, the latter can fall again into the reaction batch, shifting the reaction equilibrium toward the desired product.

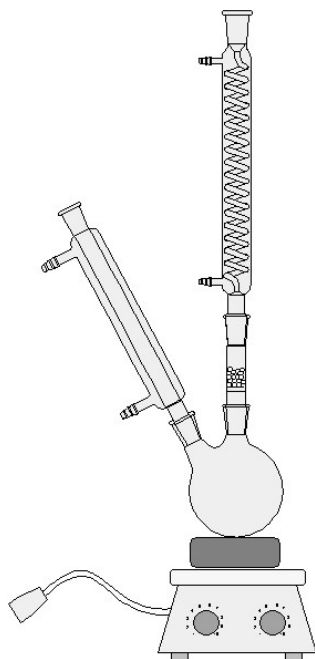


Fig.1: Schematically representation of the “implemented” reactive distillation system (RDS) with the selective adsorption of methanol inside molecular sieves.

The title compound was purified firstly by means of distillation in mild vacuum conditions (rotary evaporator) in order to remove the excess of DMC, that can be recovered from the 40% to the 60% and can be recycled in order to synthesize other PCC.

Thereafter, the solid obtained was washed with mildly acidic water ($\text{pH}=4$) in order to remove the catalyst and traces of unreacted catechol.

In this simple way, we were able to obtain 90% of isolated PCC yield (purity $>99\%$).

Instrumental analyses

GC-FID

The mixtures recovered from the transcarbonation reactions were analysed by a gas-chromatograph Thermo Focus equipped with a capillary column HP-5 (25m x 320µm x 1.05µm). The following conditions were used. Carrier gas: N₂ (1.2 mL/min); split ratio: 30:1; initial T: 50 °C (2 min), ramp rate: 20 °C min⁻¹; final T: 280 °C (5 min); T_{inj.}=280°C. The volume of solution injected for each analysis was 0.5 µL.

Each compounds was calibrated in an appropriate range of concentrations, by using decane or octane as an internal standard. The corresponding response factor was evaluated according to the following equation:

$$\frac{A}{A_{std}} = f * \frac{mol}{mol\ std}$$

GC-MS

The products isolated from the transcarbonation reactions were analysed by electrospray ionization mass spectroscopy (ESI-MS) and GC-MS.

The GC-MS (EI, 70eV) was a 6890 GC coupled with a mass spectrometer 5973 (both from Agilent) equipped with a HP5 column (5% Phenyl - 95% methylsiloxane; 30m x 250µm x 1.05µm).

The following conditions were used. Carrier gas: He (1.0 mL/min); split ratio: 50:1; initial T: 50 °C (2 min), ramp rate: 20 °C min⁻¹; final T: 280 °C (5 min); T_{inj.}=250°C.

¹H-NMR and ¹³C-NMR

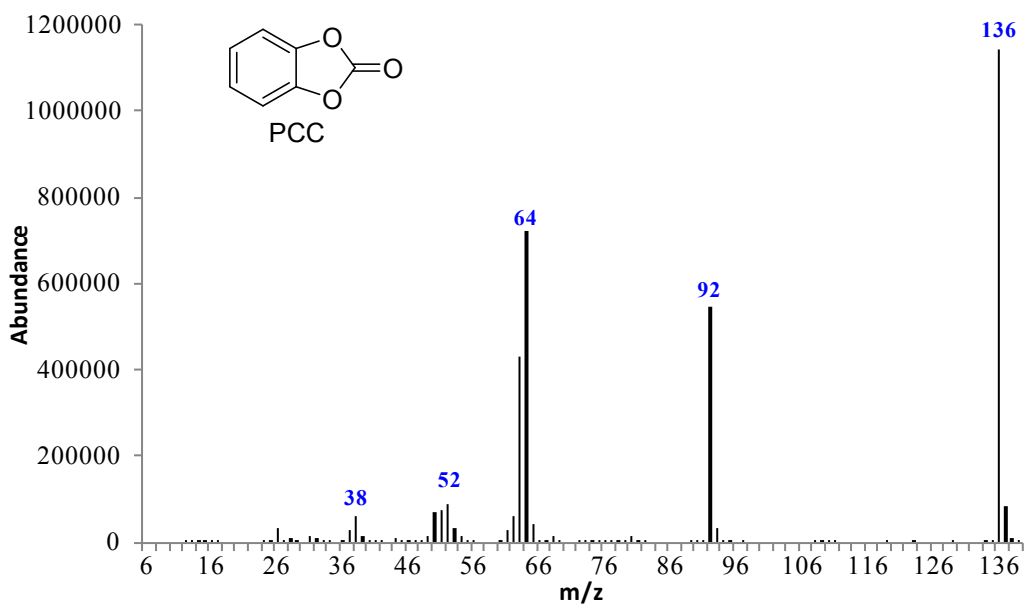
The ¹H and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz, respectively.

The chemical shifts (δ) for ¹H and ¹³C are given in δ values downfield from TMS; CDCl₃ or CD₃OD were used as solvent.

Characterisation of products

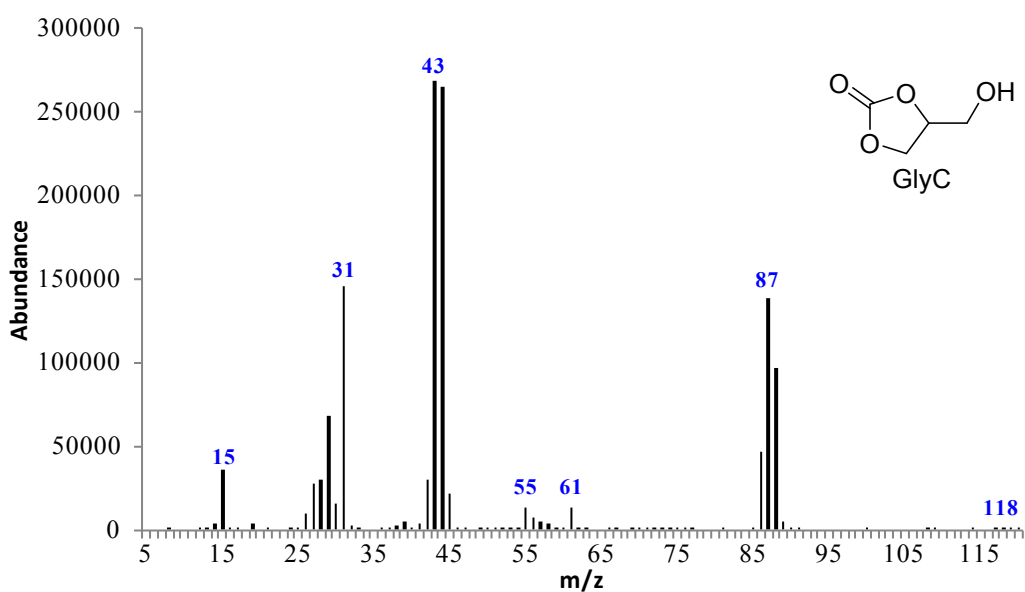
Mass Spectra

Pyrocatechol carbonate (PCC)



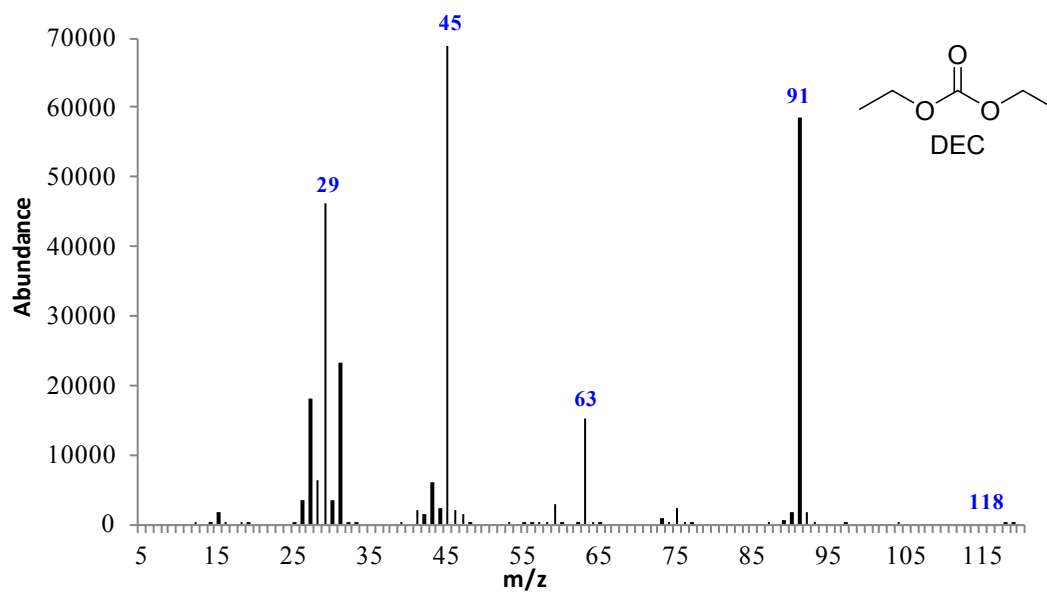
GC-MS (relative intensity, 70eV) m/z : 136 (M^+ , 100), 92 (48), 64 (63), 63 (38), 52 (8), 38 (5), 26 (3).

Glycerol carbonate (GlyC)



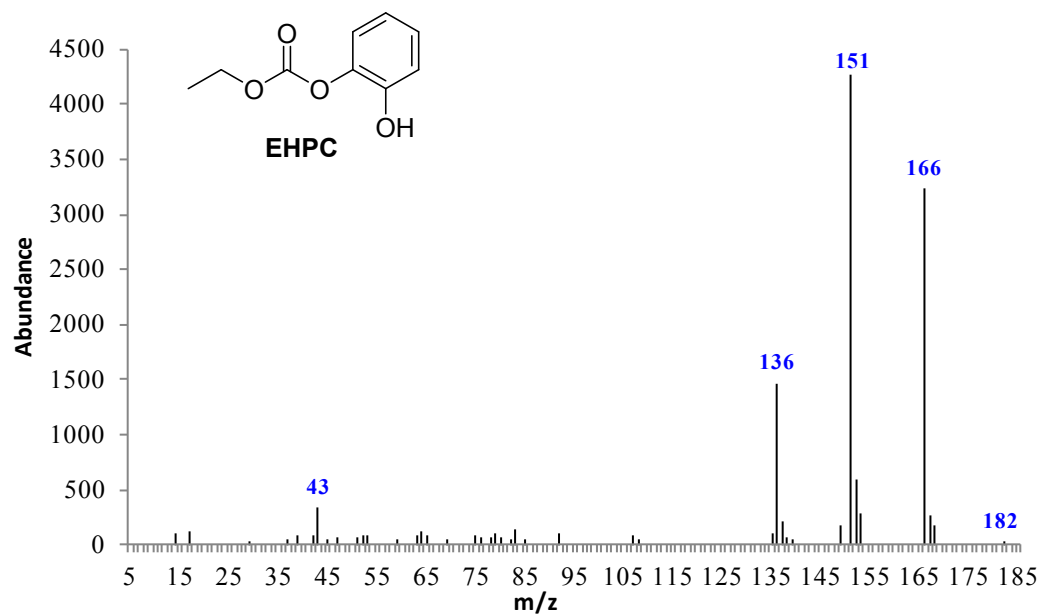
GC-MS (relative intensity, 70eV) m/z : 118 (M^+ , <1%), 88 (36), 87 (52), 61 (5), 55 (5), 44 (99), 43 (100), 31 (54), 29 (25), 15 (14).

Diethyl carbonate (DEC)



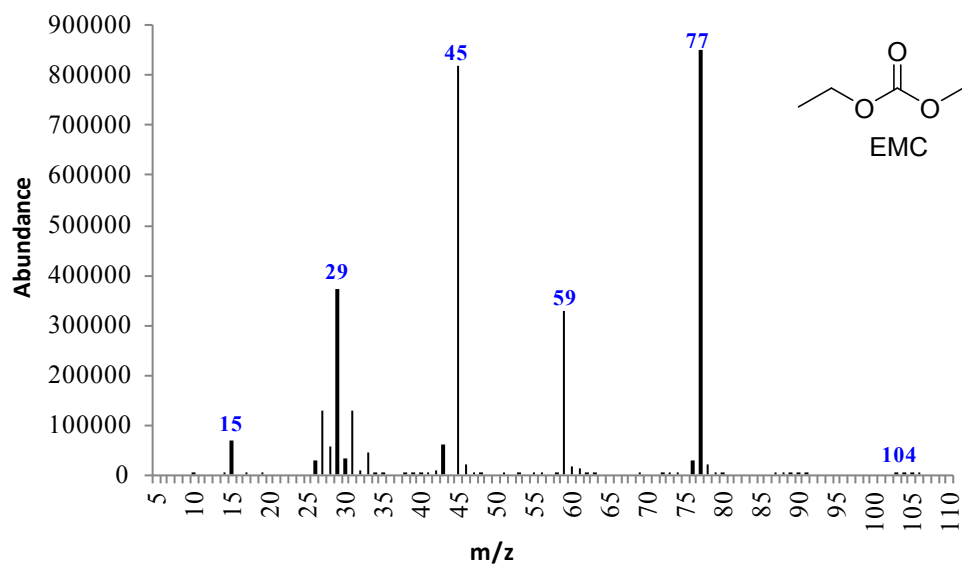
GC-MS (relative intensity, 70eV) m/z : 118 (M^+ , <1%), 91 (85), 75 (4), 63 (22), 59 (4), 45 (100), 43 (9), 31 (34), 29 (67), 27 (26).

Ethyl (2-hydroxyphenyl) carbonate (EHPC)



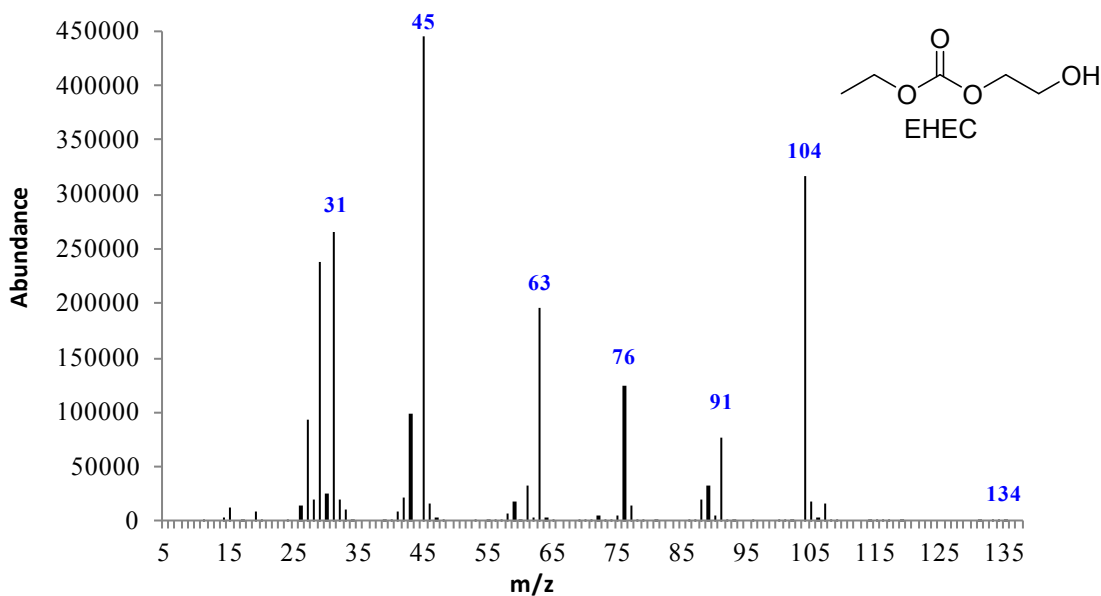
GC-MS (relative intensity, 70eV) m/z : 182 (M^+ , <1%), 166 (76), 151 (100), 136 (34), 107 (2), 83 (3), 64 (3), 43 (8).

Ethyl methyl carbonate (EMC)



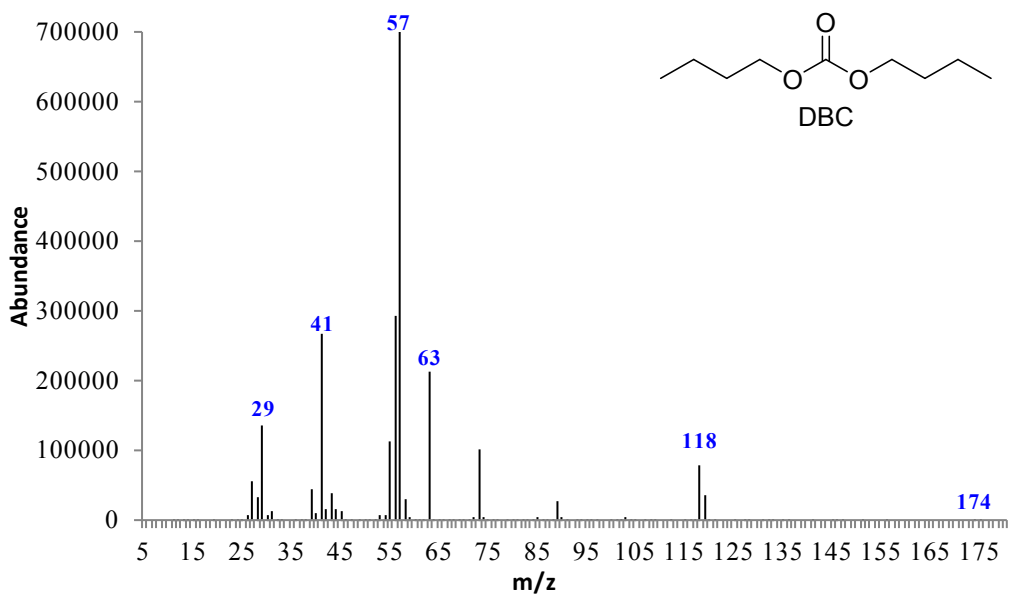
GC-MS (relative intensity, 70eV) m/z : 104 (M^+ , <1%), 77 (100), 59 (39), 45 (96), 31 (15), 29 (44), 27 (15), 15 (8).

Ethyl (2-hydroxyethyl) carbonate (EHEC)



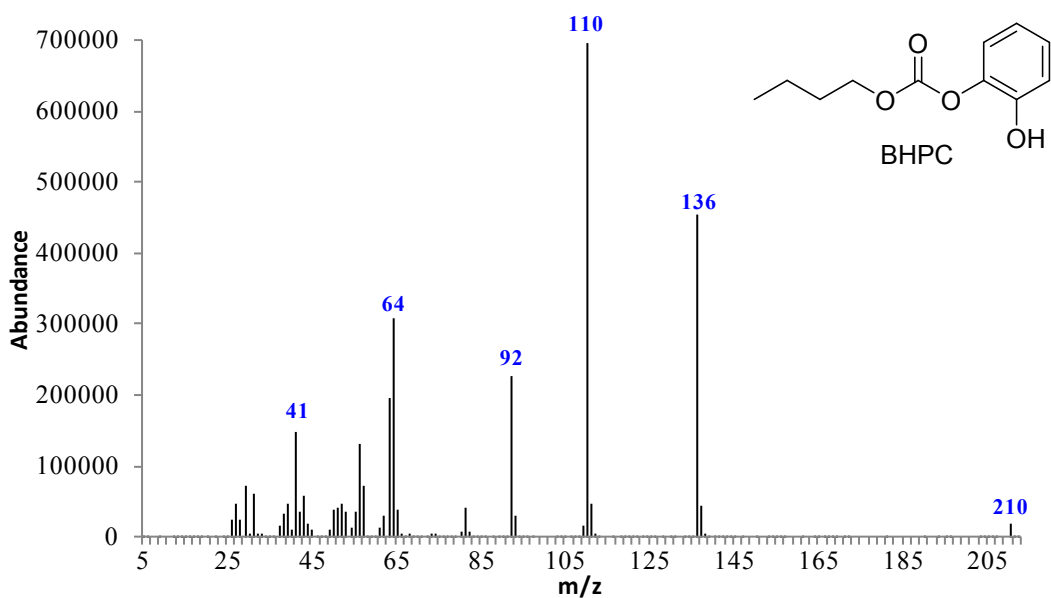
GC-MS (relative intensity, 70eV) m/z : 134 (M^+ , <0.1%), 133 (<1%), 104 (71), 91 (17), 76 (28), 63 (44), 45 (100), 43 (22), 31 (60), 29 (53), 27 (21).

Dibutyl carbonate (DBC)



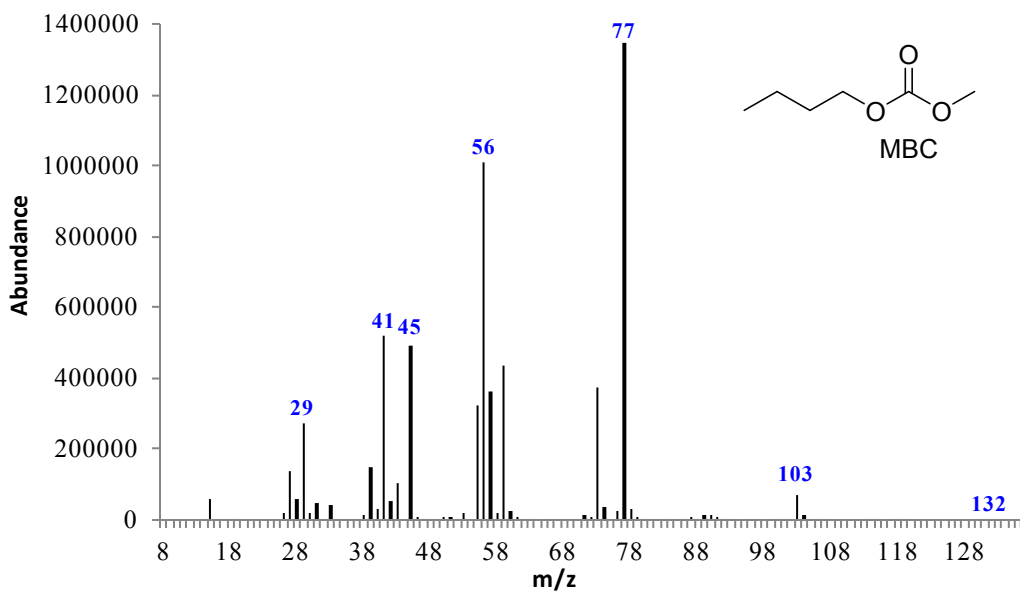
GC-MS (relative intensity, 70eV) m/z : 174 (M^+ , <1%), 118 (11), 89 (4), 73 (14), 63 (30), 57 (100), 56 (42), 41 (38), 29 (19).

Butyl (2-hydroxyphenyl) carbonate (BHPC)



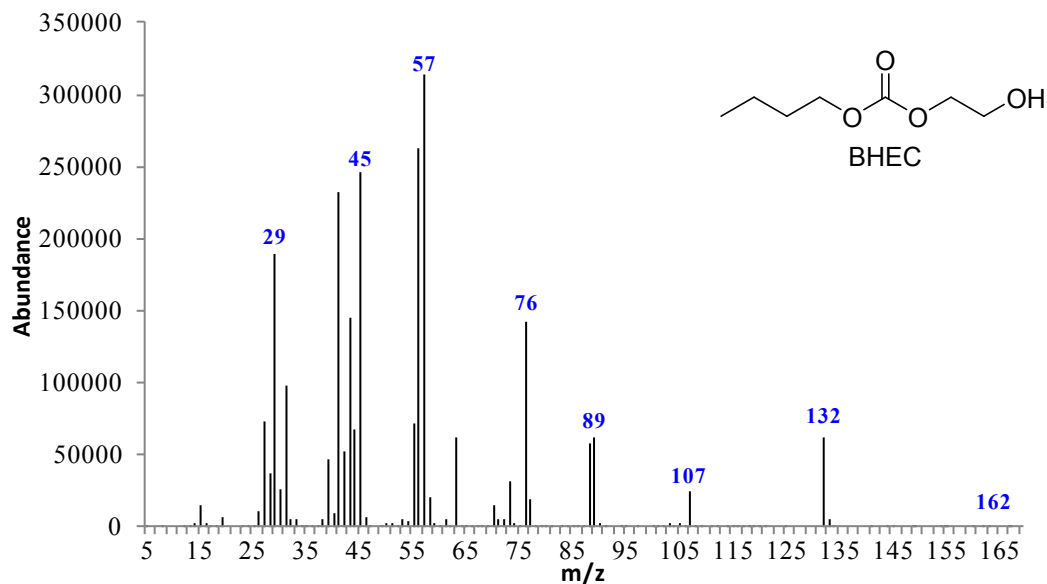
GC-MS (relative intensity, 70eV) m/z : 210 (M^+ , 3%), 136 (65), 110 (100), 92 (32), 64 (44), 56 (19), 41 (21), 29 (10).

Methyl butyl carbonate (MBC)



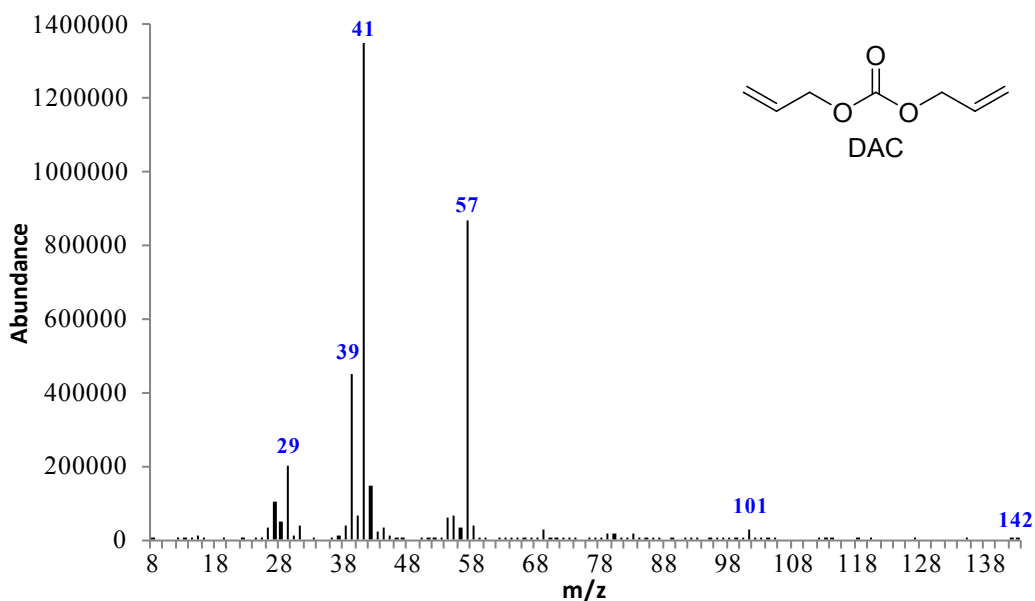
GC-MS (relative intensity, 70eV) m/z : 132 (M^+ , <1%), 103 (5), 77 (100), 73 (28), 59 (32), 56 (75), 45 (36), 41 (39), 29 (20).

Butyl (2-hydroxyethyl) carbonate (BHEC)



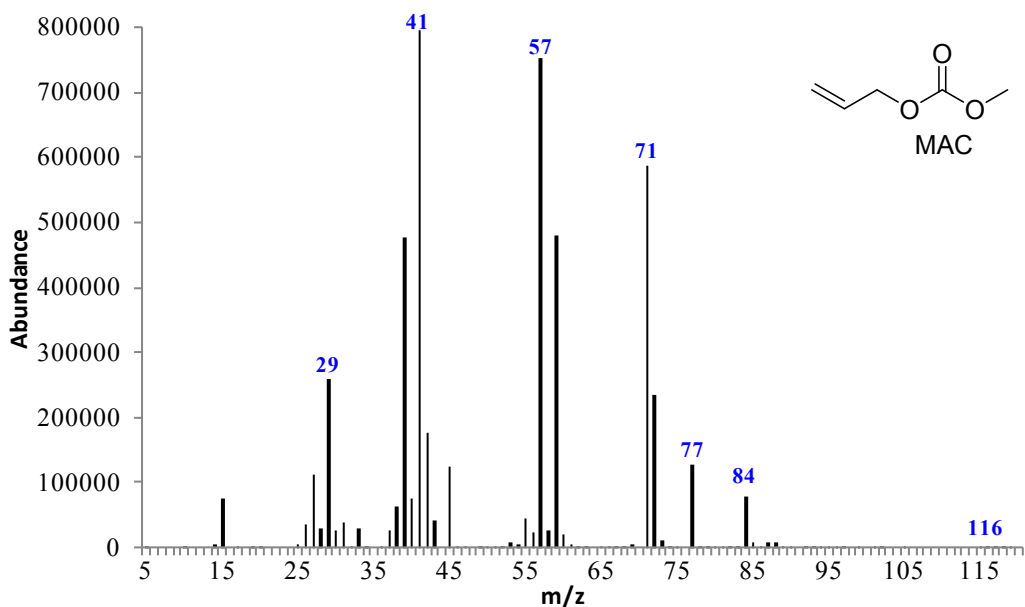
GC-MS (relative intensity, 70eV) m/z : 162 (M^+ , <1%), 132 (20), 107 (8), 89 (20), 88 (19), 76 (46), 63 (20), 57 (100), 56 (84), 45 (79), 41 (74), 29 (60).

Diallyl carbonate (DAC)



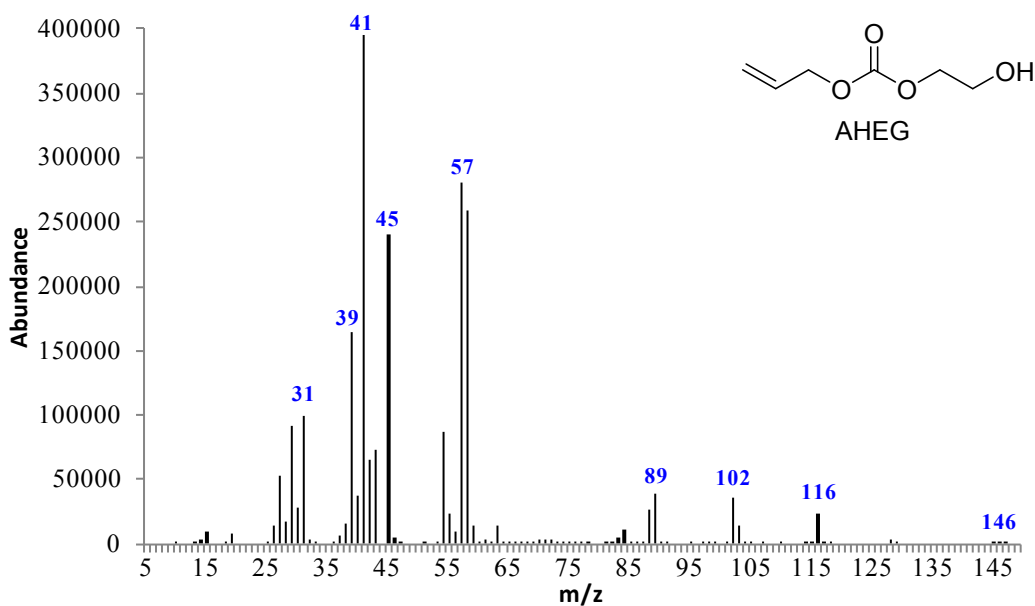
GC-MS (relative intensity, 70eV) m/z : 142 (M^+ , <1%), 101 (2), 69 (2), 57 (64), 41 (100), 39 (33), 29 (15), 27 (8).

Methyl allyl carbonate (MAC)



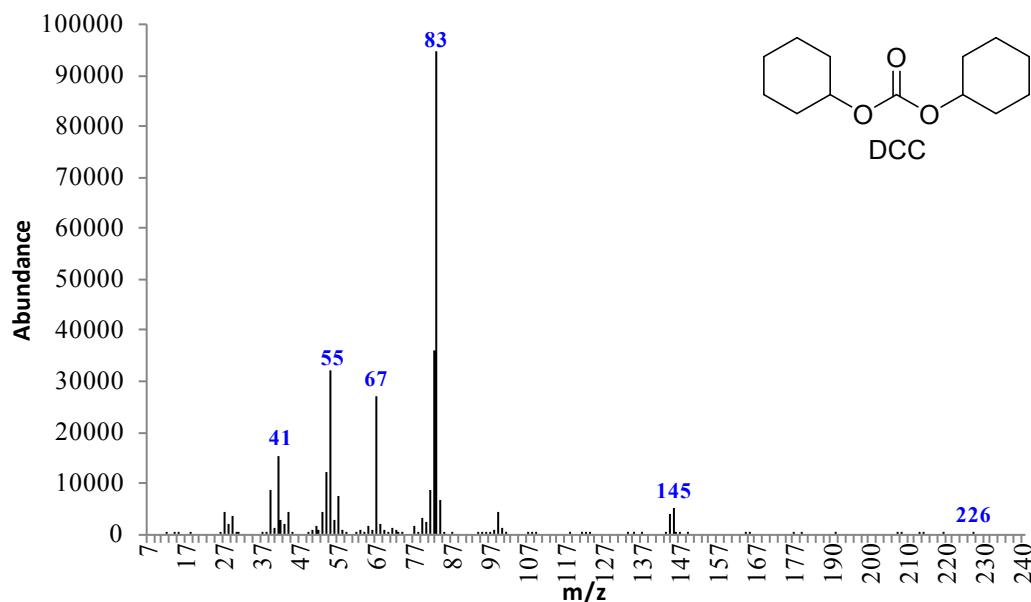
GC-MS (relative intensity, 70eV) m/z : 116 (M^+ , <1%), 84 (10), 77 (16), 74 (74), 59 (60), 57 (95), 41 (100), 39 (60), 29 (32), 15 (9).

Allyl (2-hydroxyethyl) carbonate (AHEC)



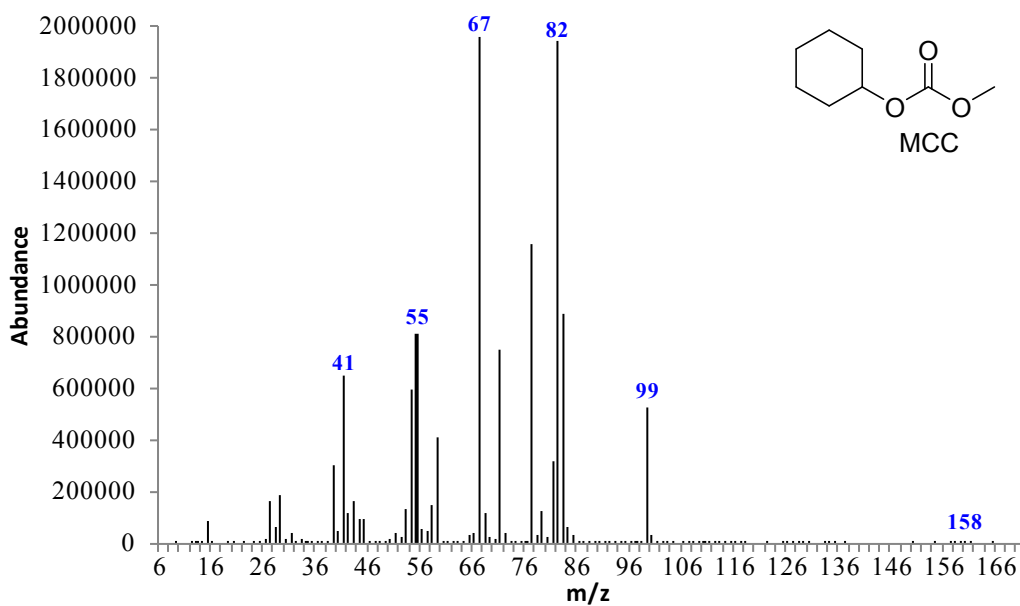
GC-MS (relative intensity, 70eV) m/z : 146 (M^+ , <1%), 116 (6), 102 (9), 89 (10), 58 (66), 57 (71), 54 (22), 45 (61), 41 (100), 39 (42), 31 (25), 29 (23), 27 (13).

Dicyclohexyl carbonate (DCC)



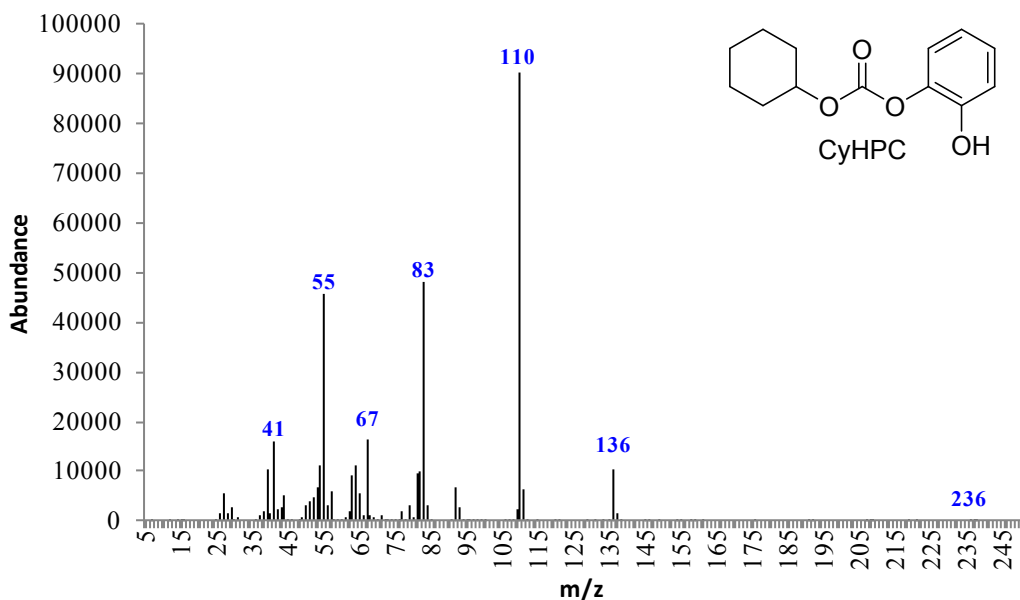
GC-MS (relative intensity, 70eV) m/z : 226 (M^+ , <0.1%), 145 (6), 99 (5), 83 (100), 82 (38), 67 (28), 55 (34), 54 (13), 41 (16), 29 (4), 27 (4).

Methyl cyclohexyl carbonate (MCC)



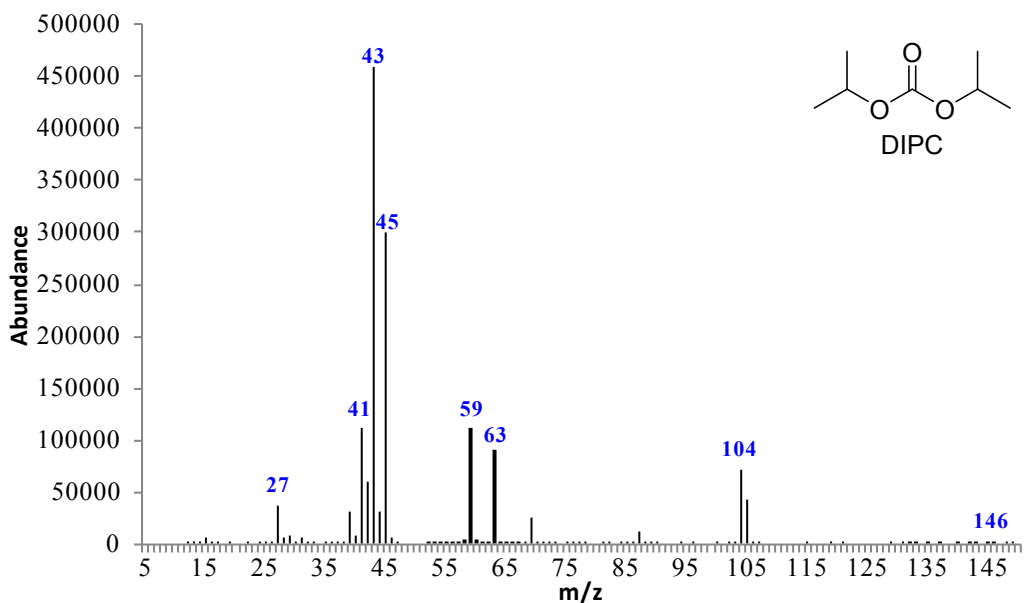
GC-MS (relative intensity, 70eV) m/z : 158 (M^+ , <1%), 99 (27), 83 (45), 82 (99), 77 (59), 71 (38), 67 (100), 59 (21), 55 (41), 54 (30), 41 (33), 29 (9), 27 (8).

Cyclohexyl (2-hydroxyphenyl) carbonate (CyHPC)



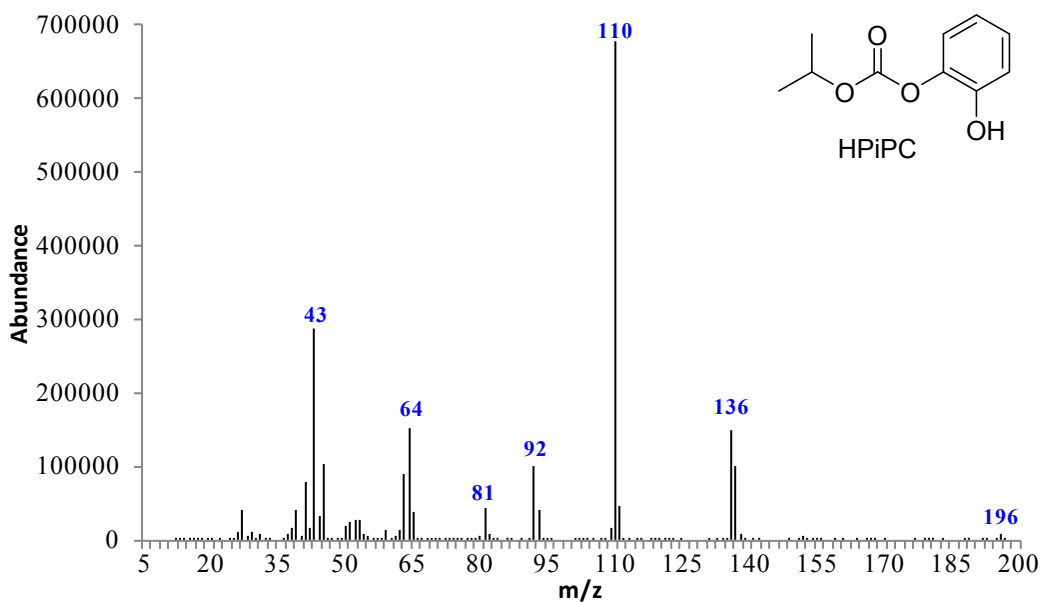
GC-MS (relative intensity, 70eV) m/z : 236 (M^+ , <1%), 136 (12), 110 (100), 92 (8), 83 (53), 67 (18), 64 (13), 55 (51), 41 (18), 39 (11), 27 (6).

Diisopropyl carbonate (DIPC)



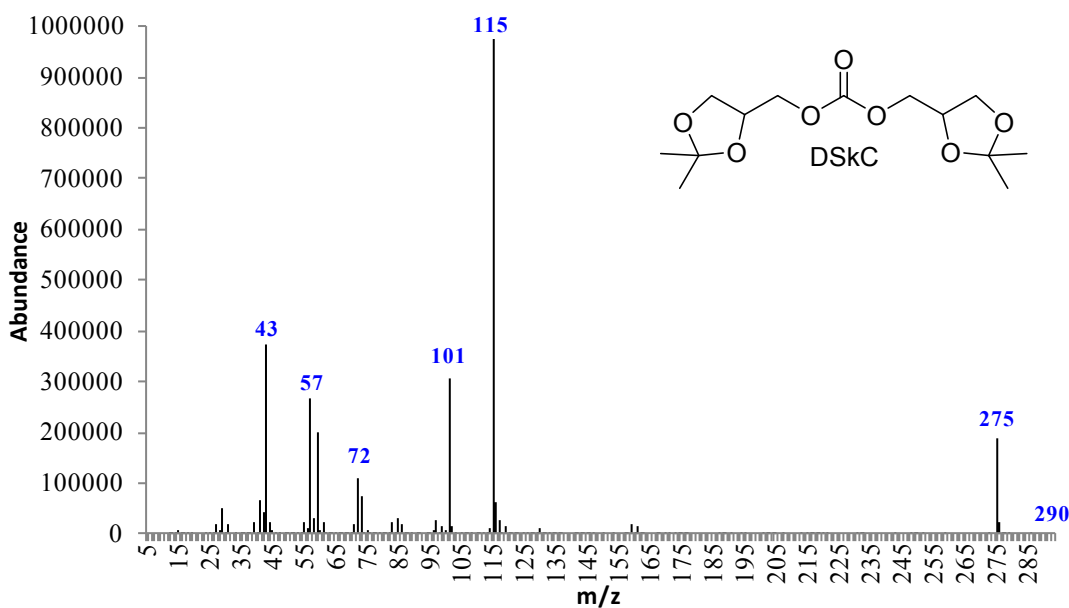
GC-MS (relative intensity, 70eV) m/z: 146 (M⁺, <1%), 104 (15), 87 (3), 69 (6), 63 (20), 59 (25), 45 (65), 43 (100), 41 (25), 27 (8).

2-Hydroxyphenyl isopropyl carbonate (HPiPC)



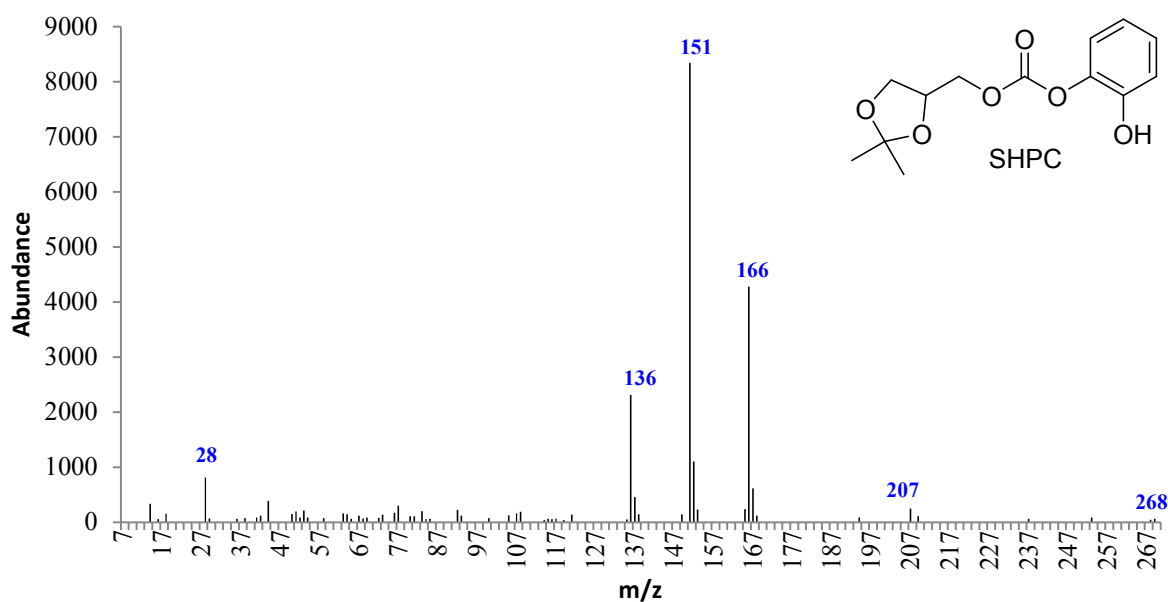
GC-MS (relative intensity, 70eV) m/z: 196 (M⁺, 1.5%), 137 (15), 136 (22), 110 (100), 92 (15), 81 (7), 64 (22), 43 (42), 27 (6).

Disolketal carbonate (DSkC)



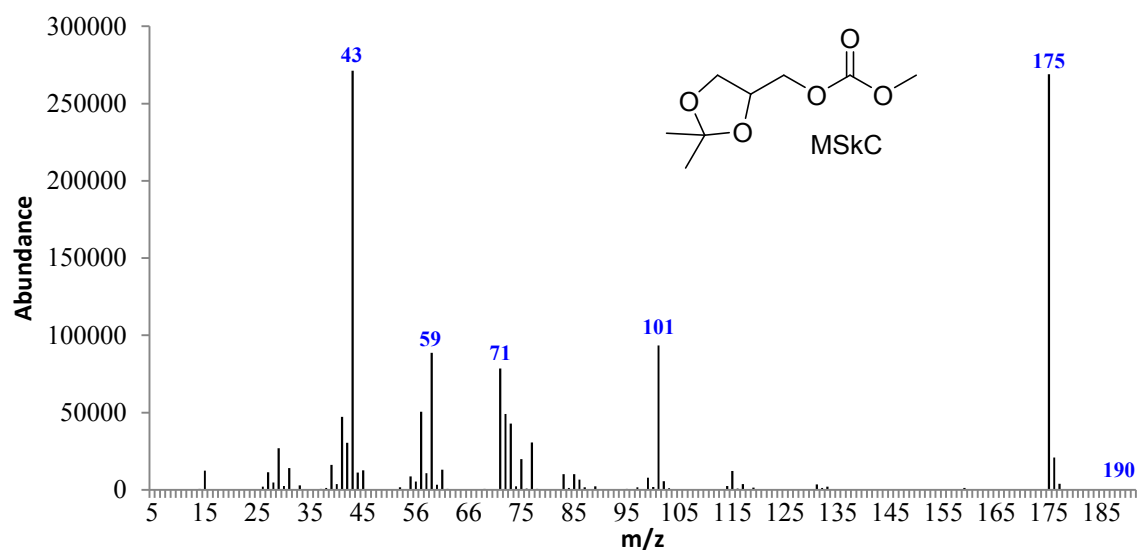
GC-MS (relative intensity, 70eV) m/z : 290 (M^+ , <1%), 275 (20), 159 (2), 115 (100), 101 (32), 85 (3), 72 (11), 57 (27), 43 (38), 27 (2).

Solketal (2-hydroxy)phenyl carbonate (SHPC) [(2,2-dimethyl-1,3-dioxolan-4-yl)methyl (2-hydroxy phenyl) carbonate]



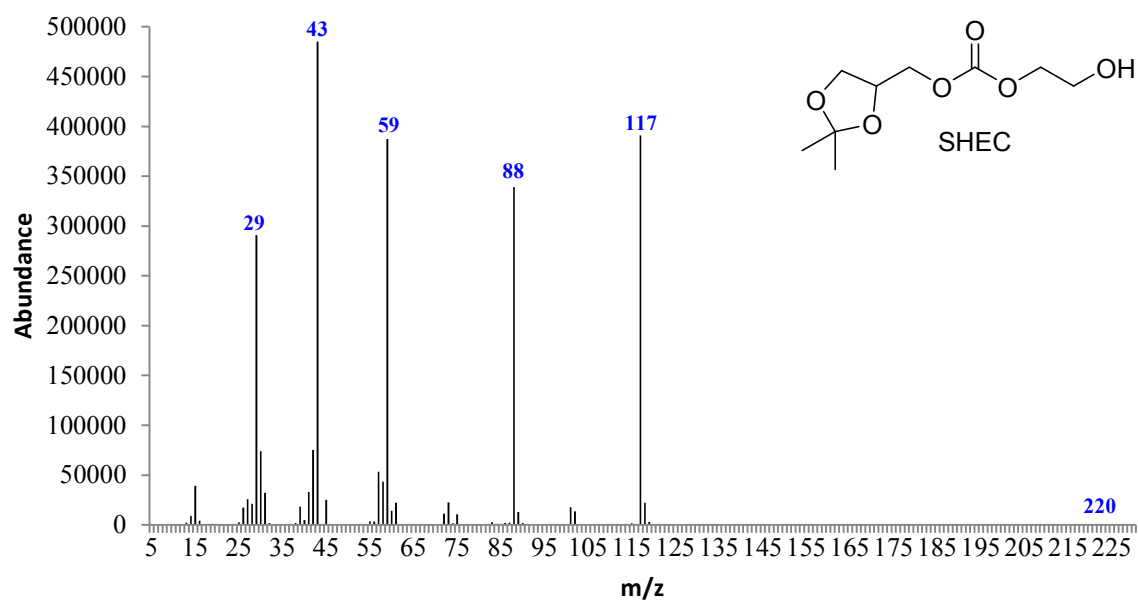
GC-MS (relative intensity, 70eV) m/z : 268 (M^+ , <1%), 207 (3), 166 (51), 151 (100), 136 (28), 121 (2), 108 (2), 92 (3), 77 (4), 44 (5), 28 (10).

Methyl solketal carbonate (MSkC)



GC-MS (relative intensity, 70eV) m/z : 190 (M^+ , <0.1%), 189 (<1%), 175 (99), 115 (4), 101 (34), 71 (29), 59 (33), 43 (100), 29 (10), 15 (5).

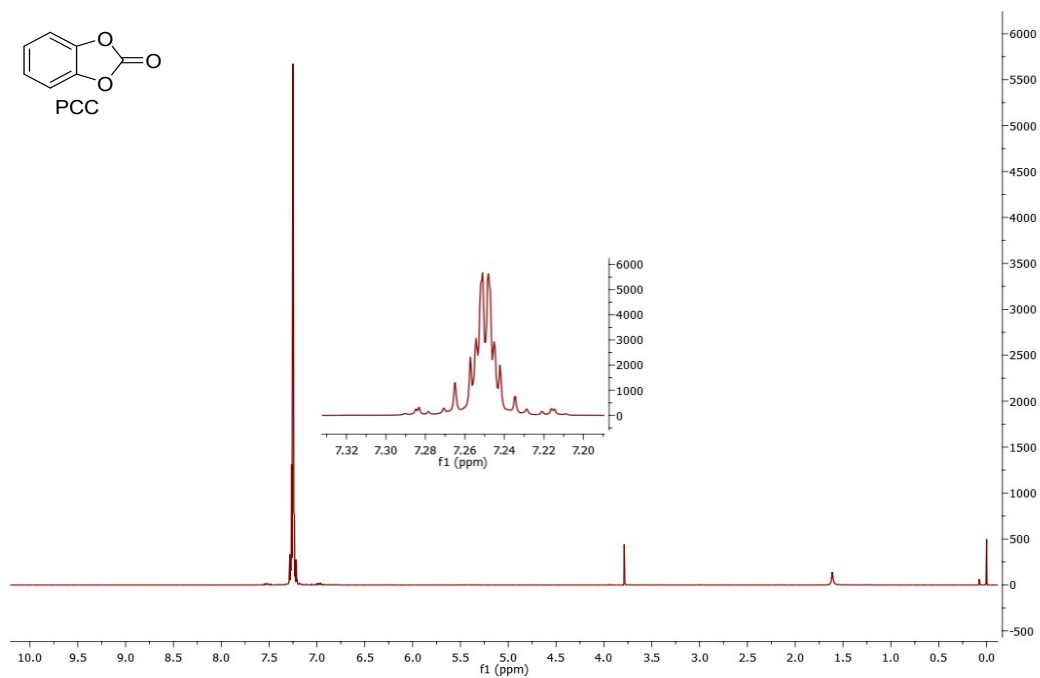
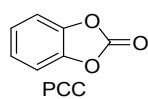
Solketal (2-hydroxyethyl) carbonate (SHEC) [(2,2-dimethyl-1,3-dioxolan-4-yl)methyl (2-hydroxyethyl) carbonate]



GC-MS (relative intensity, 70eV) m/z : 220 (M^+ , <0.1%), 117 (81), 101 (4), 88 (70), 73 (5), 59 (29), 59 (80), 43 (100), 29 (60), 15 (8).

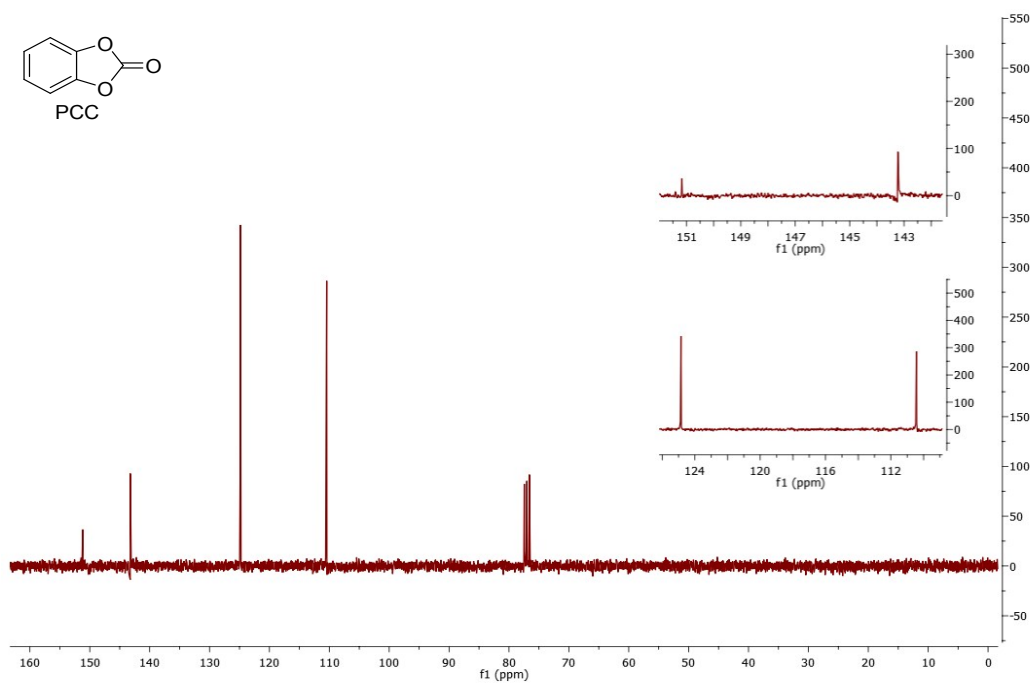
NMR spectra

Pyrocatechol carbonate (PCC)



^1H NMR spectrum of PCC

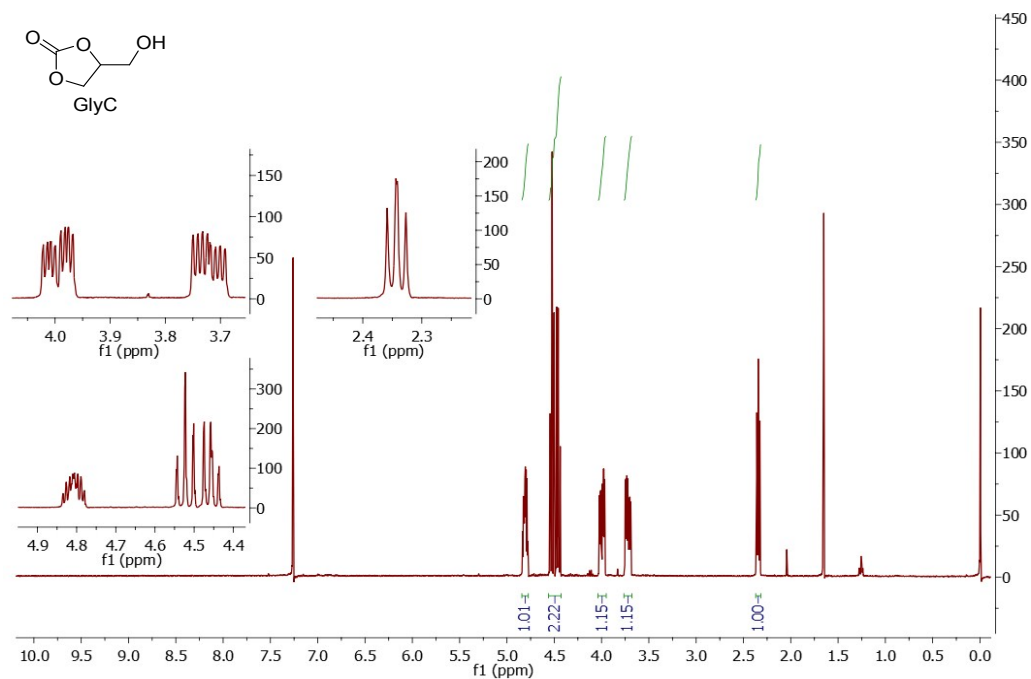
^1H NMR (CDCl_3 , 400MHz) δ (ppm): 7.25 (m, 4H).



^{13}C NMR spectrum of PCC

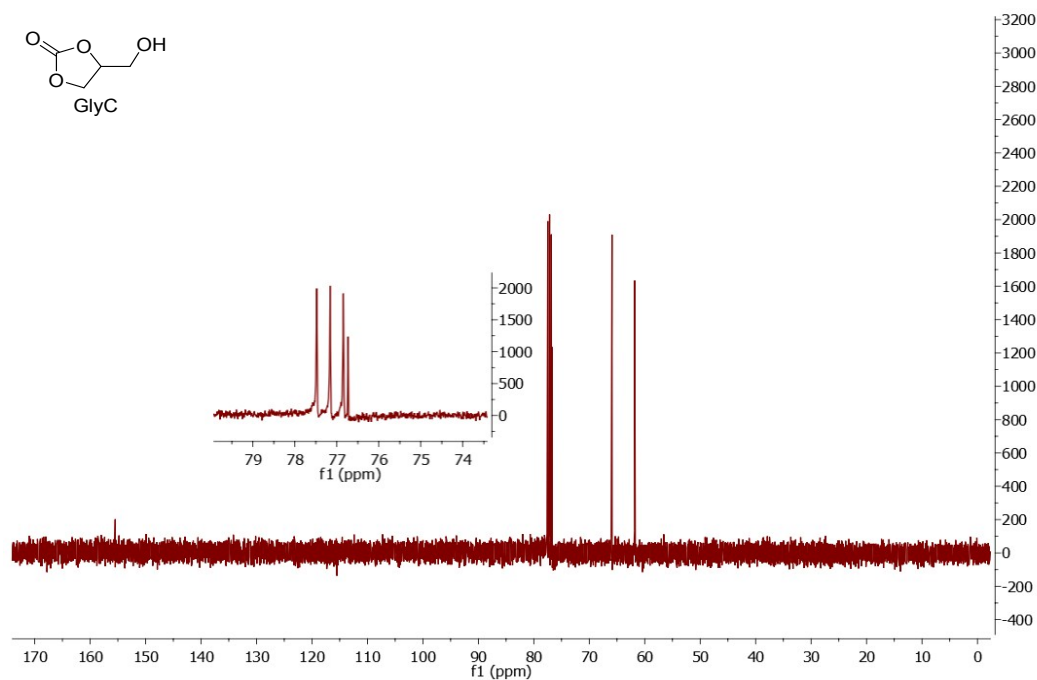
^{13}C NMR (CDCl_3 , 100MHz) δ (ppm): 151.1, 143.2, 124.8, 110.4.

Glycerol carbonate (GlyC)



^1H NMR spectrum of GlyC (traces of residual water, ethyl acetate and *n*-hexane derived from the FCC used for the purification of the product)

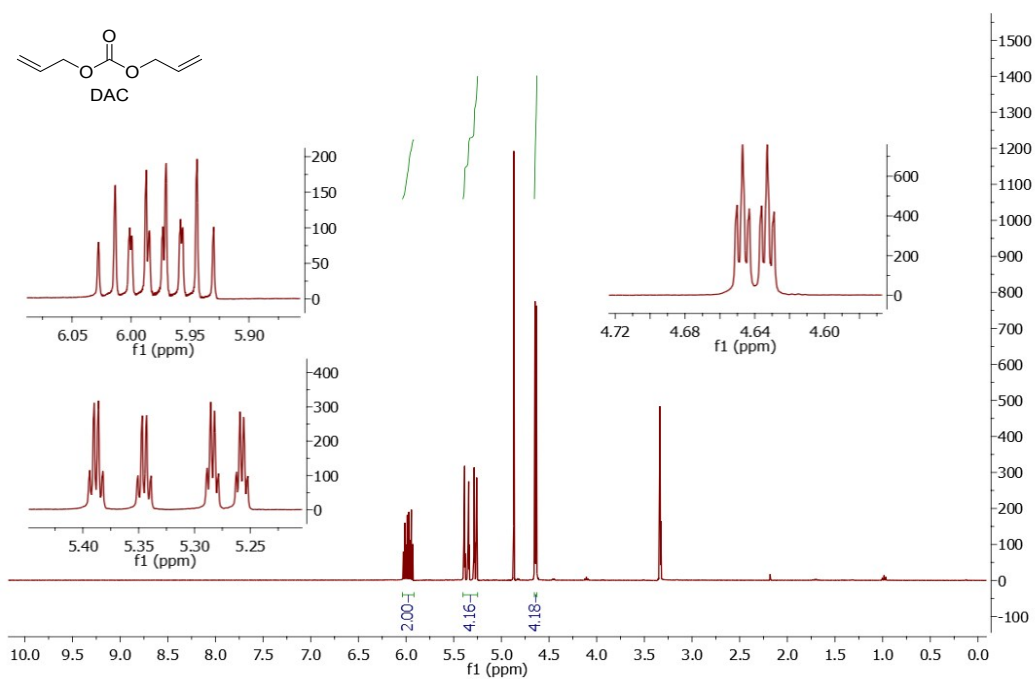
^1H NMR (CDCl_3 , 400MHz) δ (ppm): 2.34 (dd, $J = 6.8, 5.9$ Hz, 1H), 3.68-4.04 (m, 2H), 4.43-4.55 (m, 2H), 4.77-4.84 (m, 1H).



^{13}C NMR spectrum of GlyC

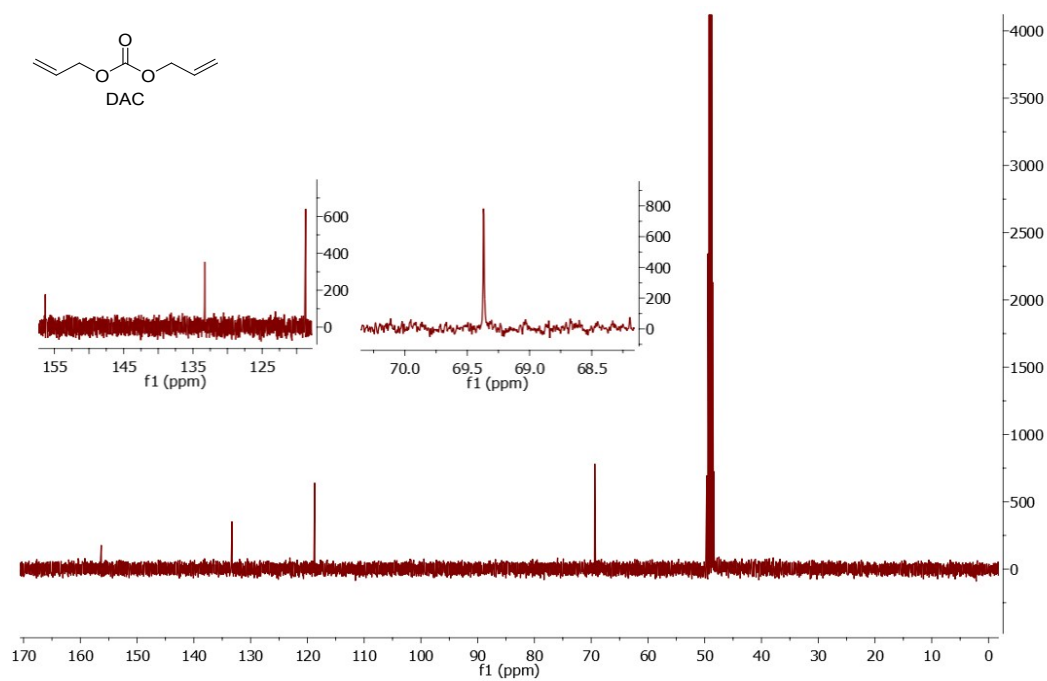
^{13}C NMR (CDCl_3 , 100MHz) δ (ppm): 155.4, 76.7, 65.9, 61.8.

Diallyl carbonate (DAC)



^1H NMR spectrum of DAC

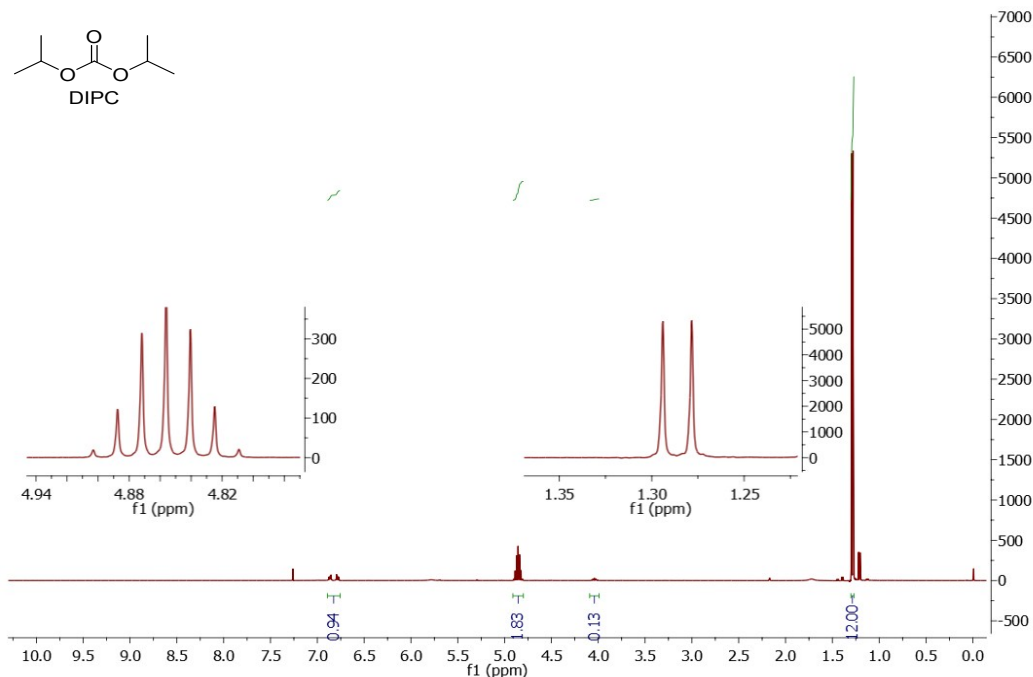
^1H NMR (CD_3OH , 400MHz) δ (ppm): 4.64 (m, 4H), 5.25-5.40 (ddq, $J=10.5, 4.0, 1.5$ Hz, 4H), 5.92-6.03 (m, 2H).



^{13}C NMR spectrum of DAC

^{13}C NMR (CD_3OH , 100MHz) δ (ppm): 156.3, 133.3, 118.7, 66.4.

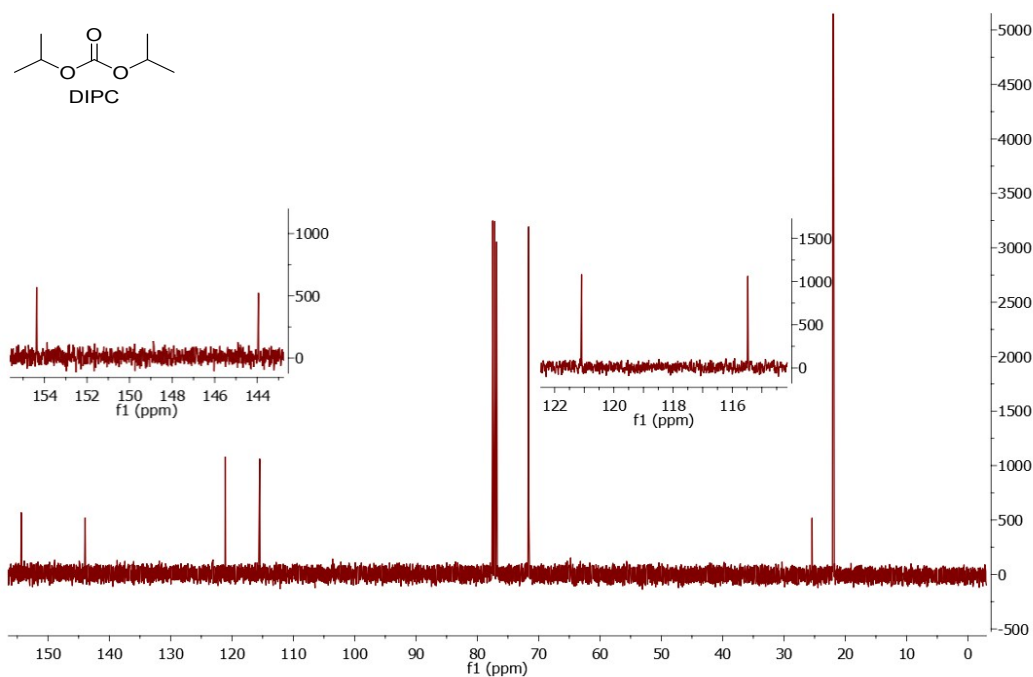
Diisopropyl carbonate (DIPC)



^1H NMR spectrum of DIPC

(residues of *i*-PrOH and catechol could not be completely removed from the product with solvent extractions, moreover the separation through a chromatographic column is tricky because of the important quantity of isopropanol involved in the synthesis and because of the impossibility to concentrate the solution due to the formation of an azeotrope between DIPC and *i*-PrOH)

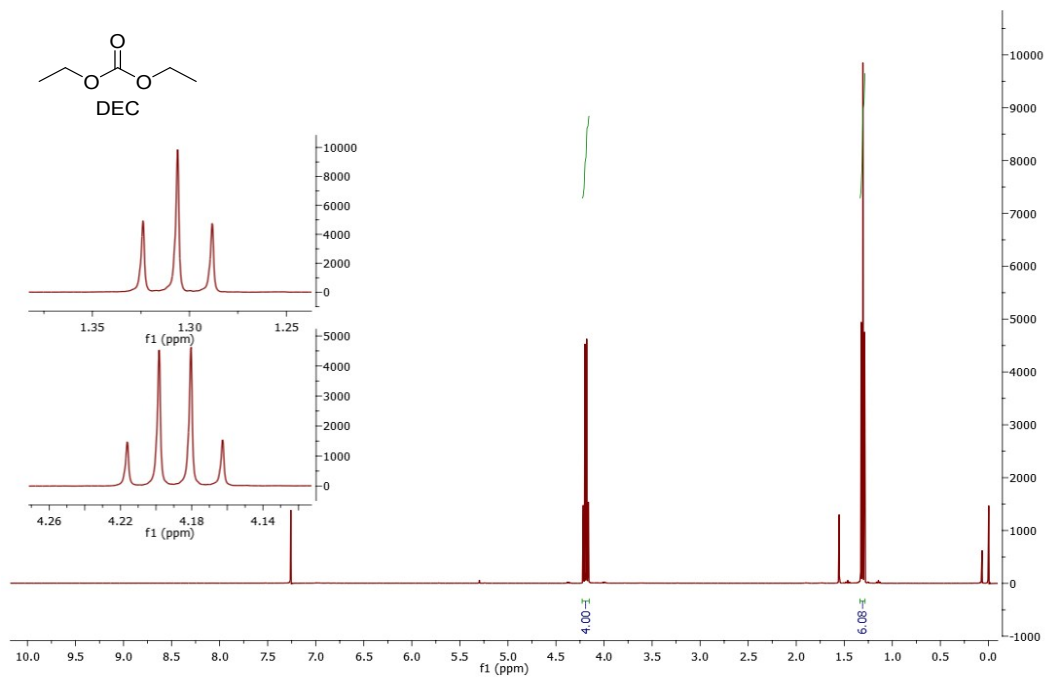
^1H NMR (CDCl_3 , 400MHz) δ (ppm): 1.29 (d, $J = 6.3$ Hz. 12H), 4.86 (hept, $J = 6.3$ Hz. 2H).



^{13}C NMR spectra of DIPC containing *i*-PrOH and catechol

^{13}C NMR (CDCl_3 , 100MHz) δ (ppm): 154.4, 71.6, 21.9. Signals at 144, 121.1, 115.5 are referred to catechol and signal at 25.4 is due to the CH_3 of *i*-PrOH.

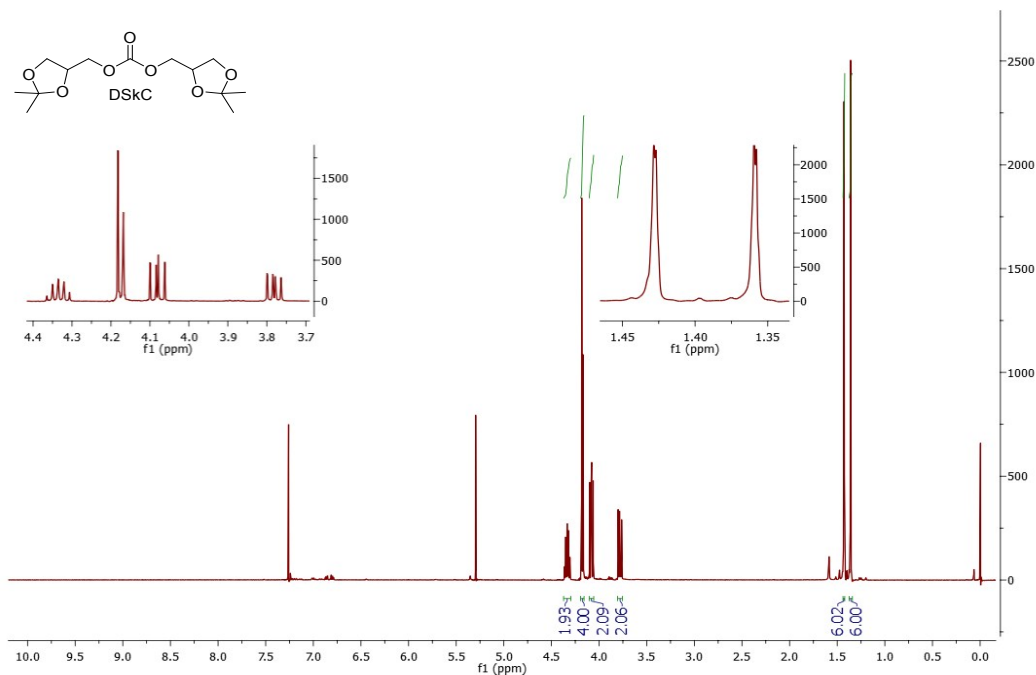
Diethyl carbonate (DEC)



^1H NMR spectrum of DEC

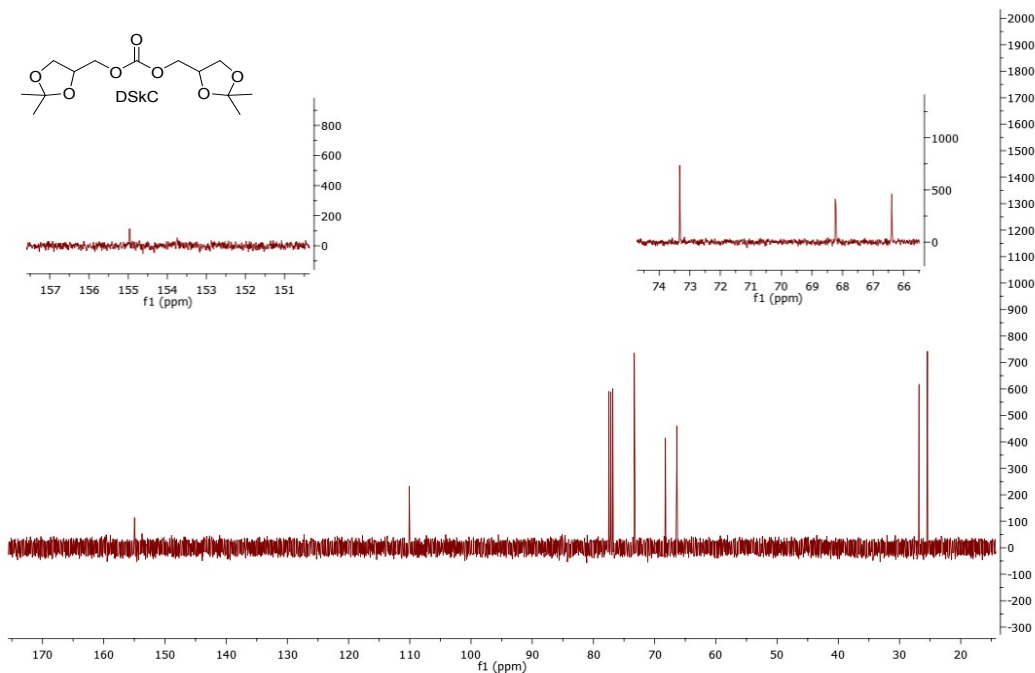
^1H NMR (CDCl_3 , 400MHz) δ (ppm): 1.31 (t, J = 7.1 Hz. 6H), 4.19 (q, J =7.1 Hz. 2H).

Disolketal carbonate (DSkC)



¹H NMR spectrum of DSkC

¹H NMR (CDCl₃, 400MHz) δ (ppm): 1.35 (s, 6H), 1.42 (s, 6H), 3.78 (ddd, J= 8.6, 5.8, 0.4 Hz. 2H), 4.08 (dd, J= 8.6, 6.4 Hz. 2H), 4.17 (m, 4H), 4.34 (m, 2H).



¹³C NMR spectra of DSkC

¹³C NMR (CDCl₃, 100MHz) δ (ppm): 155, 110, 73.3, 68.27 (splitted 68.24), 66.42 (splitted 66.41), 26.8, 25.4.

Reactivity tests of CC with phenol

Phenol and CC carbonate interchange reaction								
PhOH:CC ratio	CC:NaOCH ₃ ratio	Solvent	T (°C)	Reaction t(h)	X (CC)	Y (DPC)	Y(catechol)	Y intermediate
4	15	none	80	6	8	0	8	0
10	15	none	80	6	24	0	24	0
10	15	toluene	100	6	99	0	99	0

Polymerisation tests

Polymerization tests: CC and 1,4 butanediol (BD)							
BD:CC ratio	BD:NaOCH ₃ ratio	Solvent	T (°C)	Reaction t(h)	Reaction conditions	Mn (g/mol)	PD
1	40	anhydrous THF	65	24	THF reflux	410	1.306
0.66	10	anhydrous THF	65	6	THF reflux*	750	1.608
1	10	none	120	48	**	15200	2.312

* CC was added dropwise as a 1M solution in anhydrous THF during the first two hours of reaction

** Reaction system: round bottom Pyrex cylinder equipped with an internal cooling circuit (5°C); catechol (co-product of the reaction) sublimates during the reaction and is collected as solid crystals on the cooling circuit

A comparison of routes for glycerol carbonate synthesis

Oxidative Carbonylation of Alcohols/Phenols

Many organic carbonates (e.g glycerol carbonate) can be synthesized through the reaction of alcohols or diols with carbon monoxide and oxygen in the presence of catalyst (especially Cu(I) and Pd based catalysts).

Unfortunately, these syntheses lead to the formation of a large amount of byproducts.ⁱ Moreover, this synthetic route had limited uses because of the toxicity of carbon monoxide and the difficulty to handle it.ⁱⁱ

Alcohols and carbon dioxide condensation

Organic carbonates can also be obtained by reacting alcohols and diols with carbon dioxide in presence of catalysts (e.g Sn catalyst was the first reported for the carbonation of glycerol and CO₂)ⁱⁱⁱ.

However, these reaction are thermodynamically limited, this explains both the low yield achieved and the harsh reaction conditions (high pressure and temperature) reported in the literature.^{iv}

Carbon dioxide cycloaddition to oxiranes

Cyclic carbonates can be synthesized by cycloaddition of carbon dioxide and epoxide in the presence of a catalyst such as quaternary ammonium or phosphonium salts.

This synthetic route has the advantage of providing a chemical fixation of carbon dioxide; on the other hand oxiranes are very reactive and dangerous starting material.

Phosgenation^v

With this method, hydroxy compounds (aliphatic, aromatic) are dissolved in a mixture of inert components, anhydrous solvent (dichloromethane, chloroform, benzene, toluene) with excess pyridine and phosgenated at or below room

temperature. Pyridine acts as an acid acceptor and reacts with phosgene, and an ionic adduct is formed. Pyridine is the only one among the acid acceptors that may be used. Nearly all the organic carbonates (except few like ortho- and pyrocarbonate) can be prepared by this method.

Aromatic hydroxy compounds are much slower to react with phosgene than aliphatic hydroxyl compounds. Substitution in the ortho position also decreases the reactivity (e.g. catechol).

The main drawbacks of this reaction are:

- (a) the process involves the use of toxic and hazardous chemicals like pyridine and phosgene,
- (b) excess of pyridine has to be neutralized, and
- (c) the salt co-produced has to be completely removed and disposed, this involves additional purification steps.

Urea alcoholysis

The synthesis of organic carbonates (e.g glycerol carbonate) by urea alcoholys in the presence of a suitable catalyst (e.g ZnO)^{vi} is an attractive method.^{vii}

Noteworthy, the reaction leads to the production of high quantity of ammonia as a co-product, which is limiting its industrial implementation.

Moreover, these are equilibrium-limited reactions and both high temperature and low pressure are needed in order to remove ammonia.

Transcarbonation or "carbonate interchange reaction (CIR)"

It is the reaction between alcohols and a carbonate sources.

Conversion from one carbonate into another one results from a nucleophile attack of the carbon atom of the carbonate group by the oxygen atom of the hydroxyl group of the alcohol.

These are equilibrium-limited reactions and follows two main rules:

- a) the more nucleophilic reagent replaces the less nucleophilic one in the carbonate moiety;
- b) the heavier reagent replaces the more volatile alcohol (often removed by distillation in order to improve yield and selectivity).

The more investigated reagents for these reactions are the simplest cyclic and linear organic carbonates: ethylene carbonate (EC) and dimethyl carbonate (DMC) respectively.

However, EC leads to the production of ethylene glycol (EG), recently added to the suspected carcinogenic substances list. Furthermore, due to the high boiling point of EG, reduced pressure is often applied to remove this co-product and, therefore, chemical equilibrium is displaced toward the desired carbonate formation.

On the other hand, DMC, as an environmental benign chemical, is widely studied as a carbonate source in these reactions. The co-product methanol is often distilled away from the reaction mixture in order to shift the reaction equilibrium.

Then main catalysts exploited are homogeneous and heterogeneous basic catalysts or tin and titanium complex.

Tin complexes were found to be superior for both phenols and alcohols in the carbonate interchange reaction with DMC. However, these systems are completely inactive with *o*-hydroxy phenol (catechol) presumably due to the formation of a stable cyclic tin ester which is inert for further reaction.^{viii}

In conclusion, the more attractive synthetic routes for organic carbonates are the urea alcoholysis and the carbonate interchange reaction of DMC.

Unfortunately these reactions are often thermodynamically limited equilibrium reactions, that needs complex reaction system (in vacuum for the removal of NH_3 , or reactive distillation systems for the removal of CH_3OH , respectively) and frequently lead to a mixture of **asymmetric** and **symmetric carbonates**.

Table S1 compares our results with best literature results for the synthesis of glycerol carbonate.

Table S1. A comparison of best literature results for the synthesis of glycerol carbonate.

Reactants (mol ratio)	Solvent	Catalyst	T (°C)	P (MPa)	Reaction time (h)	Y GlyC (%)	Ref.
EC : glycerol (2:1)	Free	Amberlyst A26 HCO_3^-	80	0.1	1	88	ix
EC : glycerol (2:1)	Free	RNX-MCM-41	80	0.1	1.5	92	x
DMC : glycerol (3:1)	Free	K_2CO_3	75	0.1	3	97	xi
DMC : glycerol (2:1)	Free	3wt% KF/hydroxyapatite	78	0.1	1	99	xii
DMC : glycerol (1:1)	THF	Lipase (Novozyme 435)	60	0.1	30	99	xiii
DEC : glycerol (5:1)	Free	0.5wt% 1,3-dichlorodistannoxanes	100	0.1	2	99	xiv
DEC : glycerol (17:1)	Free	Mg/Al hydrotalcite-like	130	0.1	60	97	xv
Urea : glycerol (1:1)	Free	Zinc sulfate	140	3.0×10^{-3}	2	86	xvi
Urea : glycerol (1:3)	Free	0.5wt% calcined La_2O_3	140	3.0×10^{-3}	1	91	xvii
PCC : glycerol (1:1)	Free	3%mol NaOCH_3	40	0.1	1	92	Present work
PCC : glycerol (1:1)	Free	3%mol NaOCH_3	60	0.1	0.5	95	Present work
PCC : glycerol (1:1)	Free	3%mol NaOCH_3	60	0.1	1	98	Present work
PCC : glycerol (1:1)	Anhydrous THF	5wt% MgO	60	0.1	1	96	Present work

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