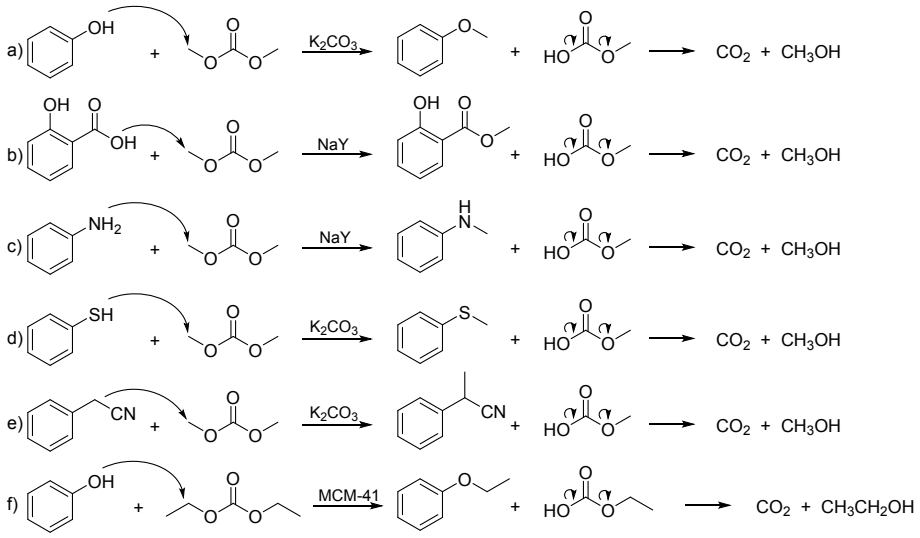
Electronic Supplementary Material (ESI) for Green Chemistry.

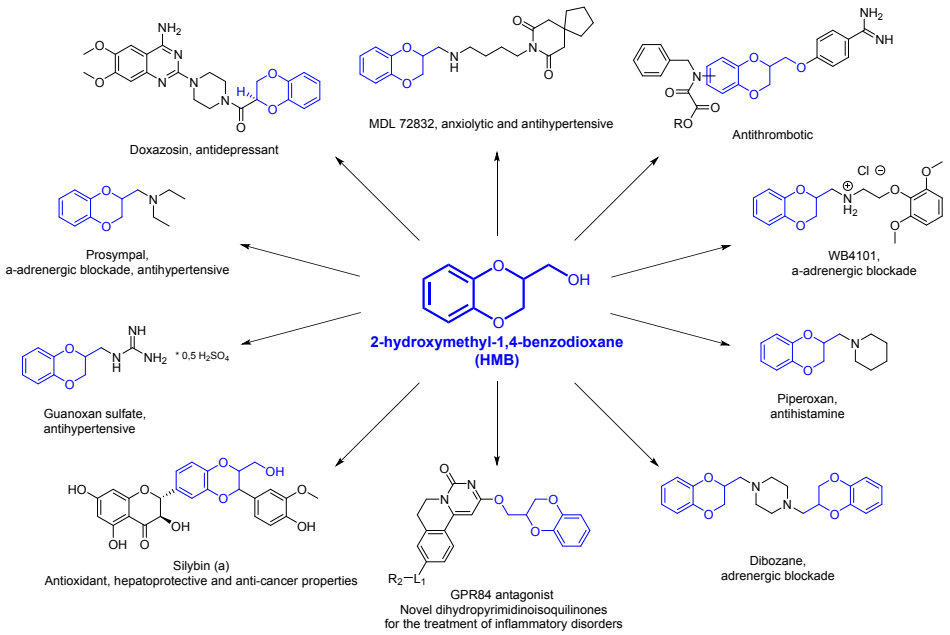
Electronic supplementary information

An innovative synthetic pathway to benzodioxanes: the peculiar reactivity of glycerol carbonate and catechol

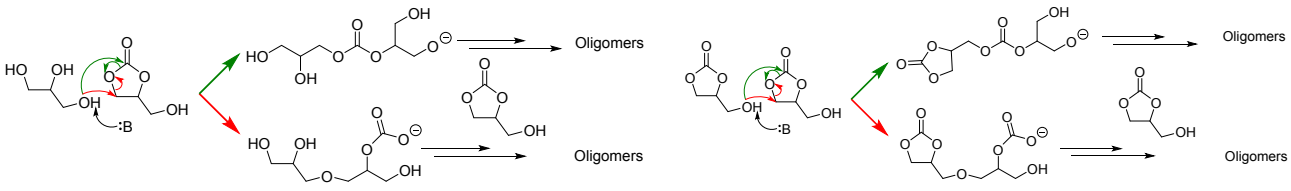
T. Tabanelli,*[,a] C. Giliberti,[a] Rita Mazzoni[a,] R. Cucciniello[b] and F. Cavani[a].



Scheme S1: Alkylation of different substrates with linear carbonates: DMC and DEC



Scheme S2: Main active principles derived from HMB



Scheme S3: possible mechanism for the formation of heavy by-products, mainly polyols-polycarbonates readily soluble in water

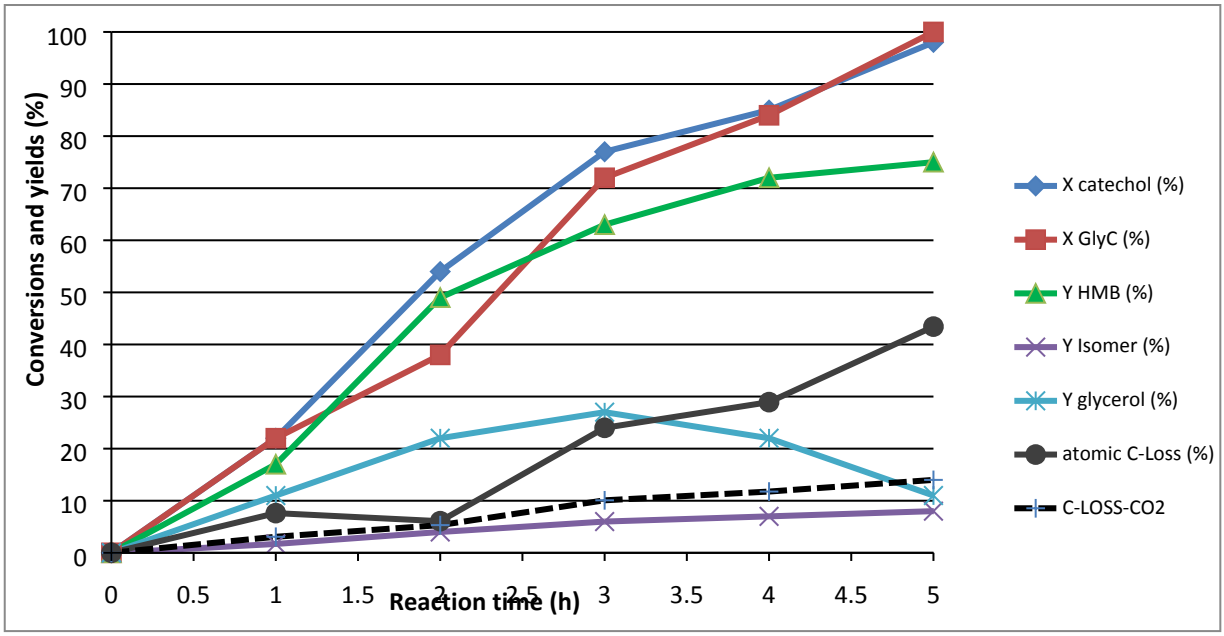


Fig.S1: Catalytic results obtained at 140°C with a catechol:GlyC:$NaOCH_3$ molar ratio of 1:2:0.066, N_2 atmosphere. Products yield are referred to catechol. The dotted line represents the part of C-loss related to the CO_2 released. The results showed was obtained performing feeding new reagents for each reaction time, to collect the mixture after the reaction and correctly calculate the C-loss.

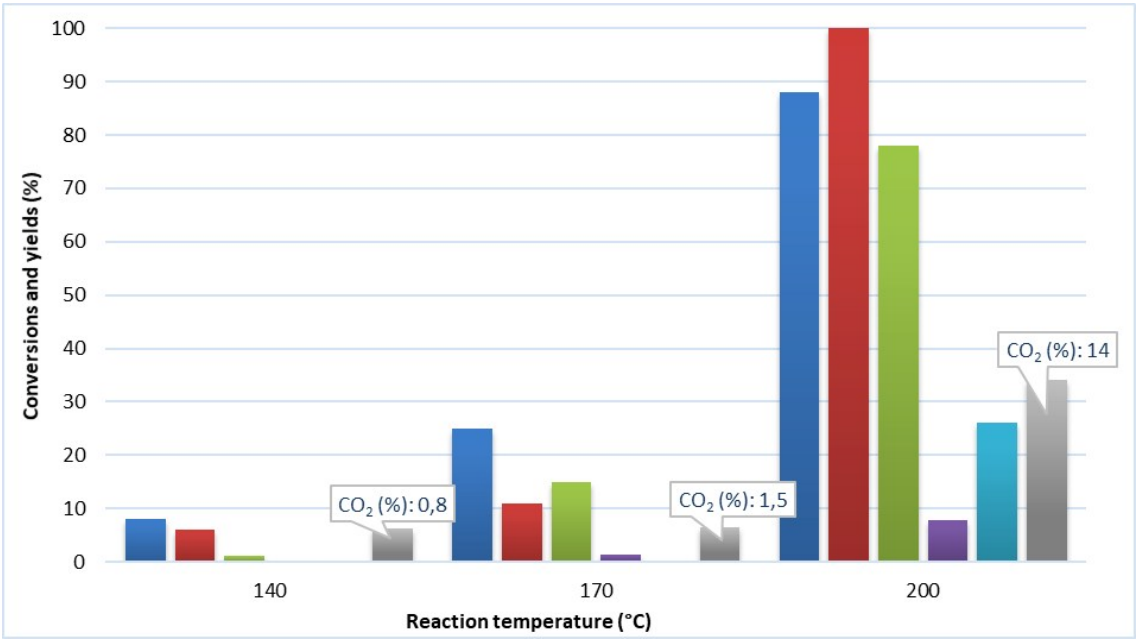
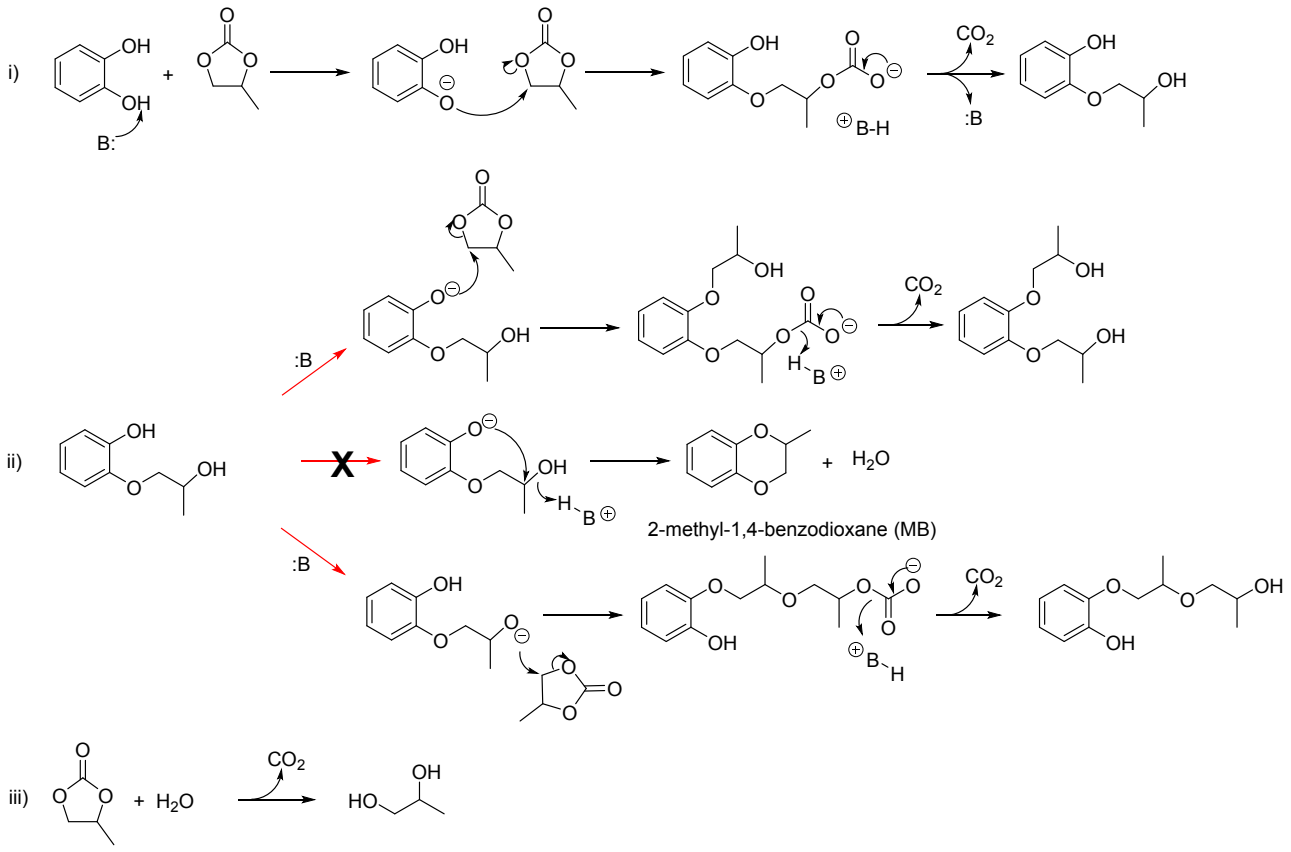


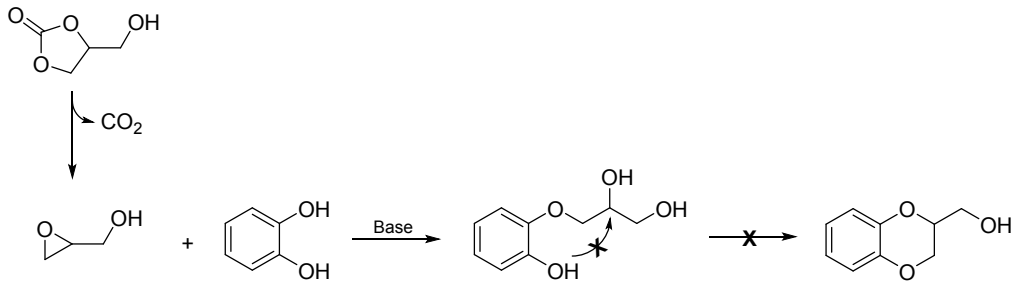
Fig. S2: Catalytic results obtained with a catechol:GlyC molar ratio of 1:2, Na-Mordenite 5%w/w respect to catechol, N_2 atmosphere, 6 hours at different reaction temperatures. Products yield are referred to catechol. C-loss is comprehensive of the CO_2 released (specified in the caption). Catechol conversion (blue bar), GlyC conversion (red bar), HMB yield (green), HMB isomer (purple), glycerol (light blue), atomic C-loss (grey).

Catalyst	X catechol	X GlyC	Y HMB	Y isomer	Y glycerol	Overall C-loss
Na-Mord	88	100	78	7	26	35
MgO	84	86	56	8	21	40

Table S1. Catalytic results obtained after 6 hours at 200°C with a catechol:GlyC molar ratio of 1:2, heterogeneous catalyst 5%w/w respect to catechol, N_2 atmosphere. Products yield are referred to catechol.



Scheme S4: Proposed reaction mechanism for the reaction of catechol and PC: (i) formation of the mono-alkylated compound, ii) formation of the dialkylated compounds, iii) PC hydrolysis to yield 1,2-propanediol.



Scheme S5: Proposed reaction mechanism for the reaction of catechol and glycidol with the formation of the monoarylglicidylethers. Glycidol may be formed by GlyC decarboxylation.

Sample	Mg (ppm)	Leaching Mg %
Blank test	**0**	**0**
Reaction with MgO	**0.23**	**0.3**

Table S2: Leaching test results for Mg from the microwave plasma atomic emission spectroscopy using a Agilent Technologies MP-EAS 4210. Reaction performed for 2 hours at 200°C: 0,2 g catechol, 0,429 g GlyC, 0,013 g MgO (or 0 g in the blank test).

NMR Spectra of the reactivity between glycidol and catechol

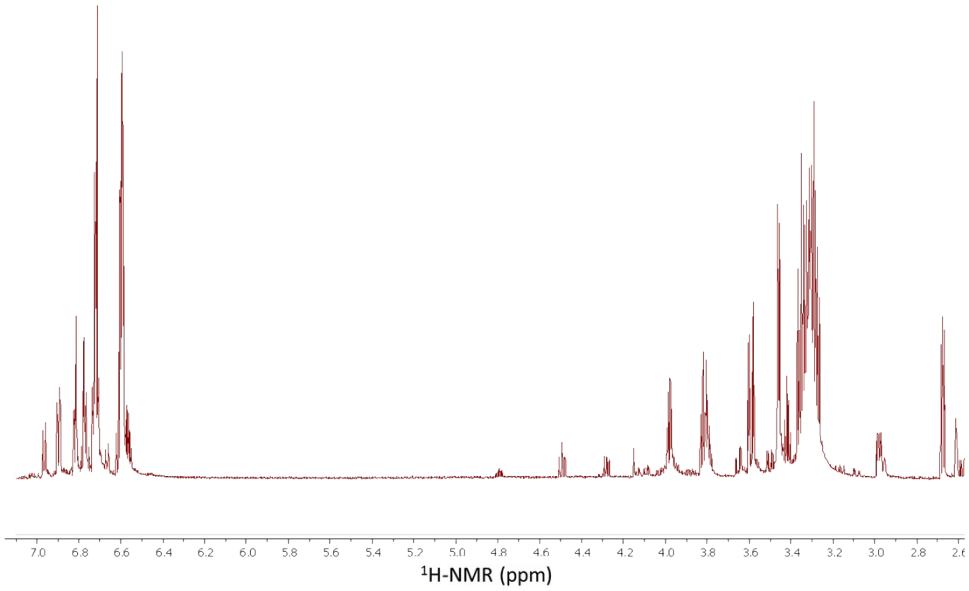


Fig. S3. ^{1}H-NMR (600 MHz, DMSO-d_6) of the reaction at T: 170°C and t: 2.5 hours.

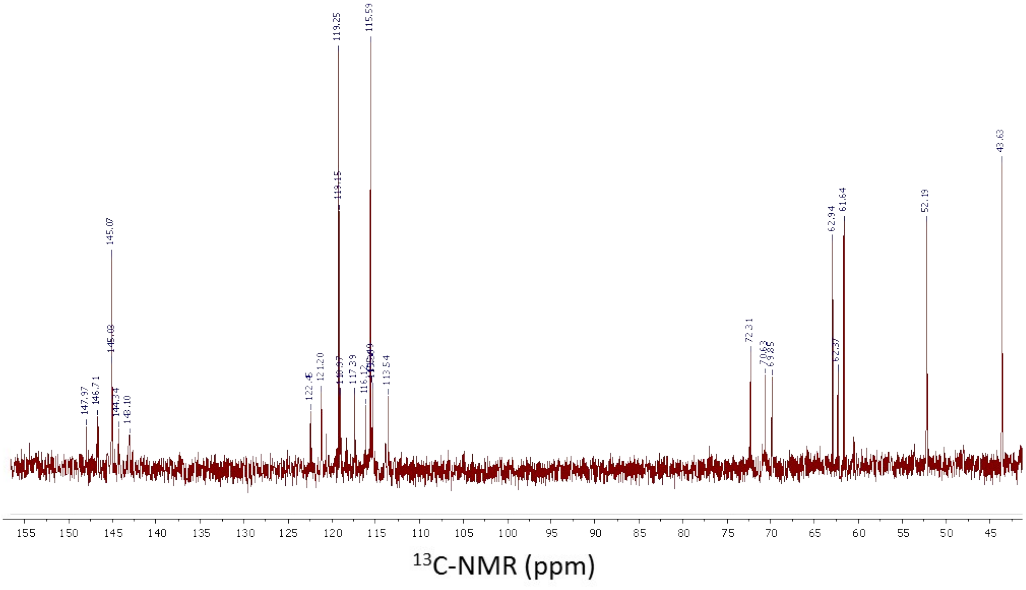
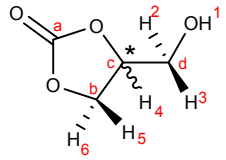
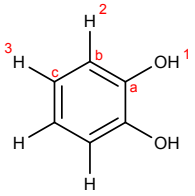
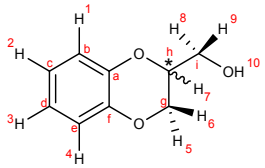
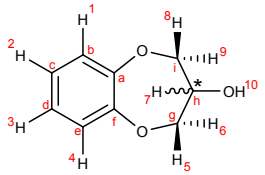
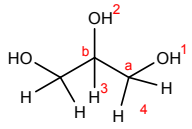
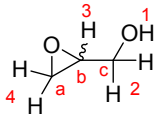


Fig. S4. ^{13}C-NMR (600 MHz, DMSO-d_6) of the reaction at T: 170°C and t: 2.5 hours.

Table S3. NMR chemical shifts assignment for known compounds.

NMR signals (DMSO-d^6)					
Compound	**^{1}H-NMR**			**^{13}C-NMR**	
	hydrogen	**multiplicity**	**ppm**	**carbon**	**ppm**
Glycerol carbonate (GlyC)	1	t	5.25	a	155.16
	2	dddd	3.64-3.68	d	60.60
	3	dddd	3.49-3.52	b	65.87
	4	m	4.78-4.81	c	77.02
	5	dd	4.27-4.29		
	6	dd	4.48-4.50		
Catechol	**^{1}H-NMR**			**^{13}C-NMR**	
	hydrogen	**multiplicity**	**ppm**	**carbon**	**ppm**
	1	s	8.78	a	145.25
	2	m	6.70-6.73	b	119.24
	3	m	6.55-6.61	c	115.65
HMB	**^{1}H-NMR**			**^{13}C-NMR**	
	hydrogen	**multiplicity**	**ppm**	**carbon**	**ppm**
	1,4	m	6.82-6.86	a,f	143.02-143.12
	2,3	m	6.78-6.82	b,e	120.97-121.30
	5	dd	4.30-4.32	c,d	116.84-117.00
	6	dd	3.97-4.00	i	59.86
	7	m	4.12-4.15	g	65.10
	8,9	m	3.57-3.66	h	73.58
	10	t	5.04		
HMB isomer (symmetric)	**^{1}H-NMR**			**^{13}C-NMR**	
	hydrogen	**multiplicity**	**ppm**	**carbon**	**ppm**
	1,4	m	6.90-6.92	a,f	150.16
	2,3	m	6.84-6.86	b,e	122.98
	5,8	dd	4.22-4.25	c,d	120.84
	9,6	dd	3.92-3.95	g,i	67.87
	10	d	5.31-5.32	h	74.46
Glycerol	**^{1}H-NMR**			**^{13}C-NMR**	
	hydrogen	**multiplicity**	**ppm**	**carbon**	**ppm**
	1	t	4.48	a	62.96
	2	d	4.48	b	72.37
	3	m	3.31-3.45		
	4	dd	3.31-3.45		
Glycidol	**^{1}H-NMR**			**^{13}C-NMR**	
	hydrogen	**multiplicity**	**ppm**	**carbon**	**ppm**
	1	-	variable	a	43.65
	2	m	3.51-4.08	b	52.21
	3	m	3.02-3.24	c	61.65
	4	m	2.61-2.92		

Control NMR spectra of commercially available products

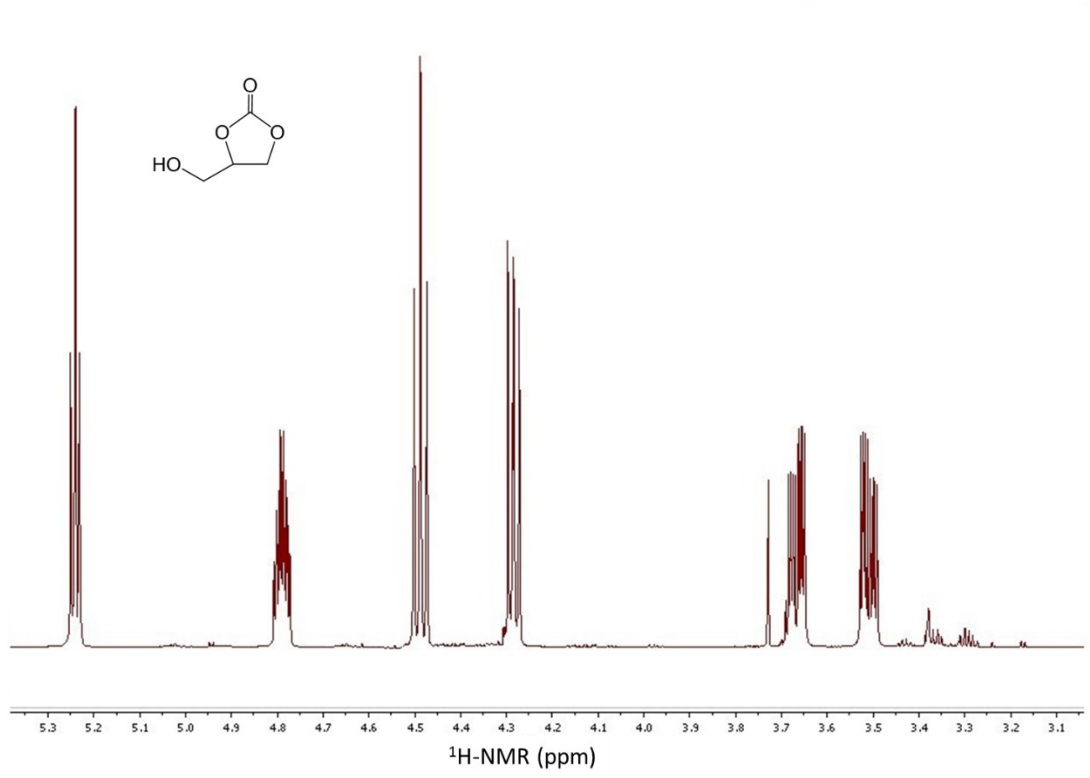


Figure S5. ^{1}H-NMR (600 MHz, DMSO-d_6) of glycerol carbonate.

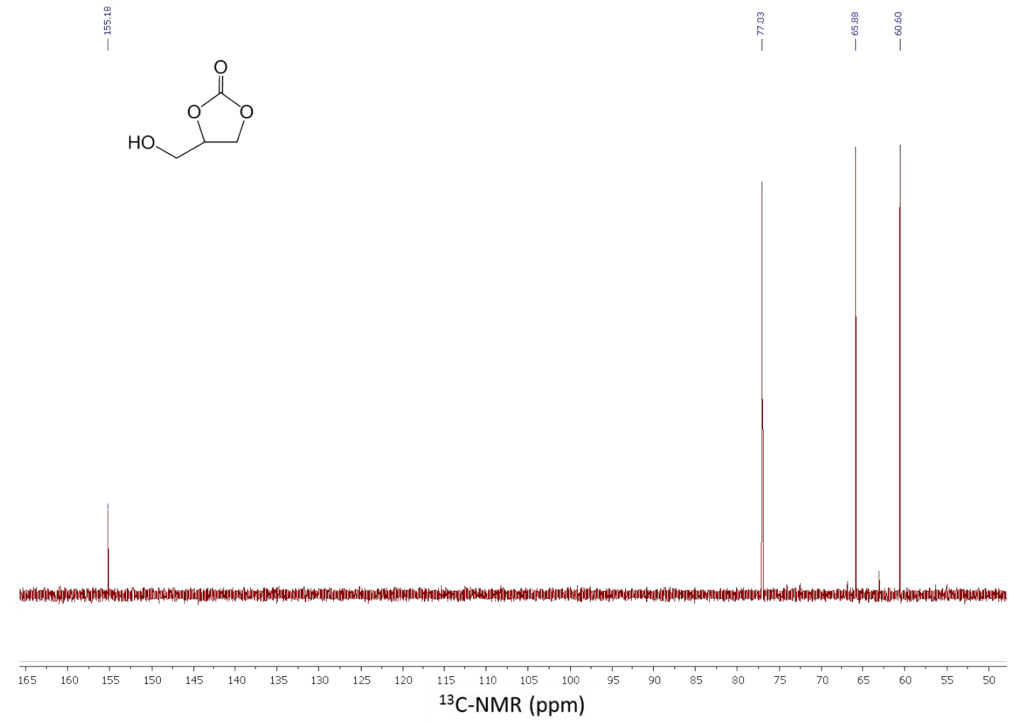


Figure S6. ^{13}C-NMR (600 MHz, DMSO-d_6) of glycerol carbonate

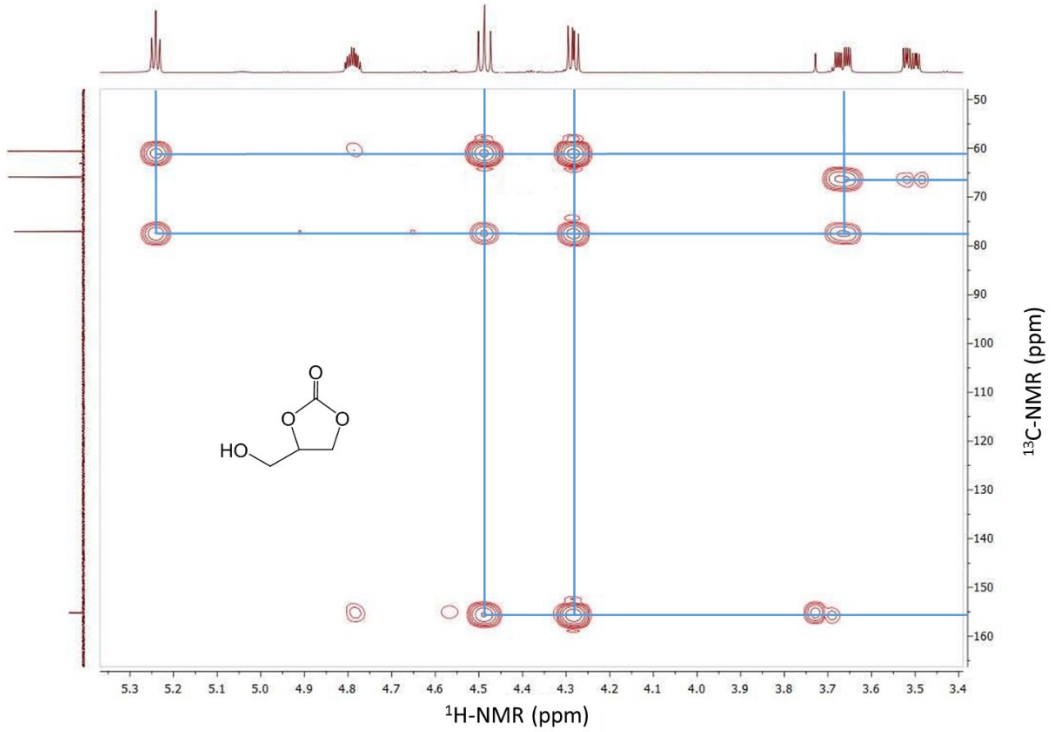


Figure S7. HMBC-NMR (600 MHz, DMSO-d_6) of glycerol carbonate

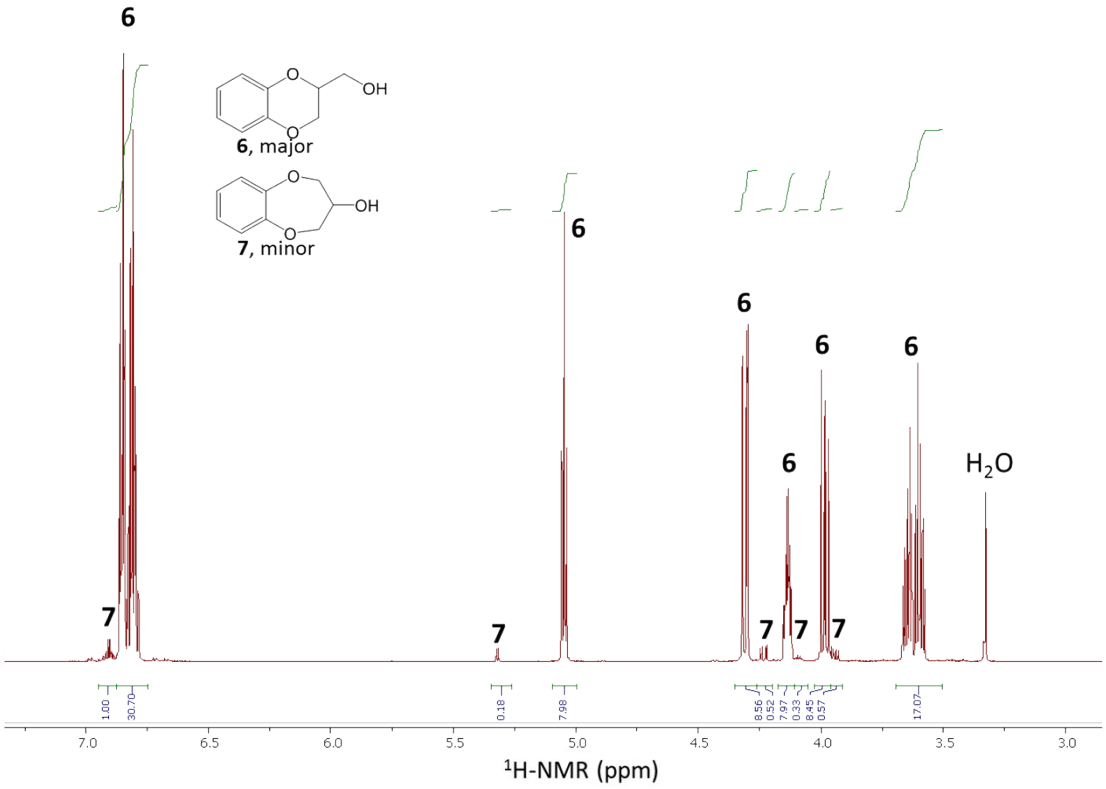


Figure S8. ^{1}H-NMR (600 MHz, DMSO-d_6) of a commercial mixture of HMB (**6**, major product) and its isomer (**7**, minor product).

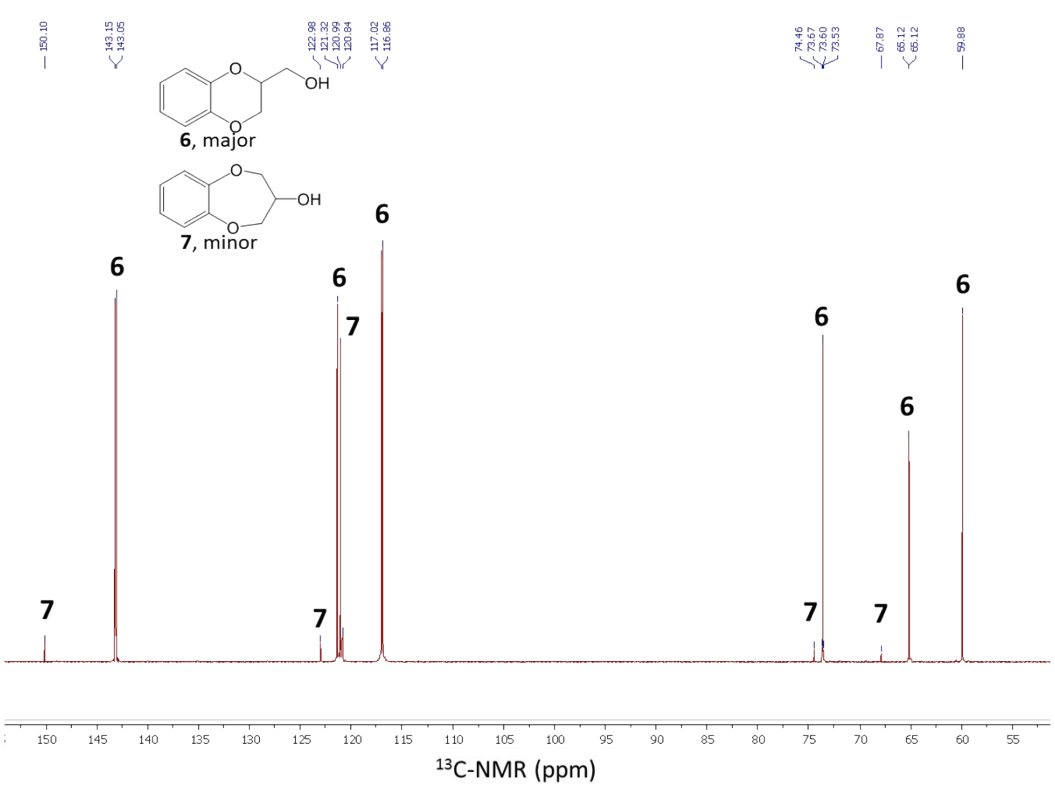


Figure S9. ^{13}C-NMR (600 MHz, DMSO-d_6) of a commercial mixture of HMB (**6**, major product) and its isomer (**7**, minor product).

NMR spectra of the mixture obtained from the reaction between phenol and glycerol carbonate

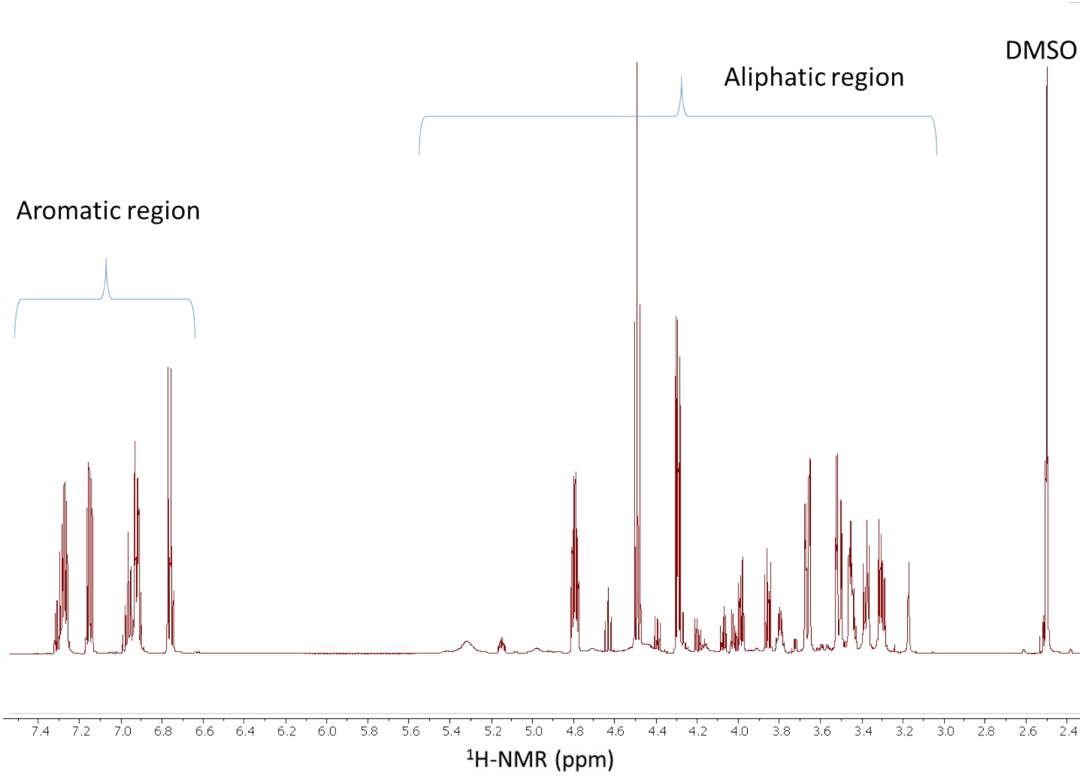


Figure S10. ^{1}H-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of phenol with glycerol carbonate.

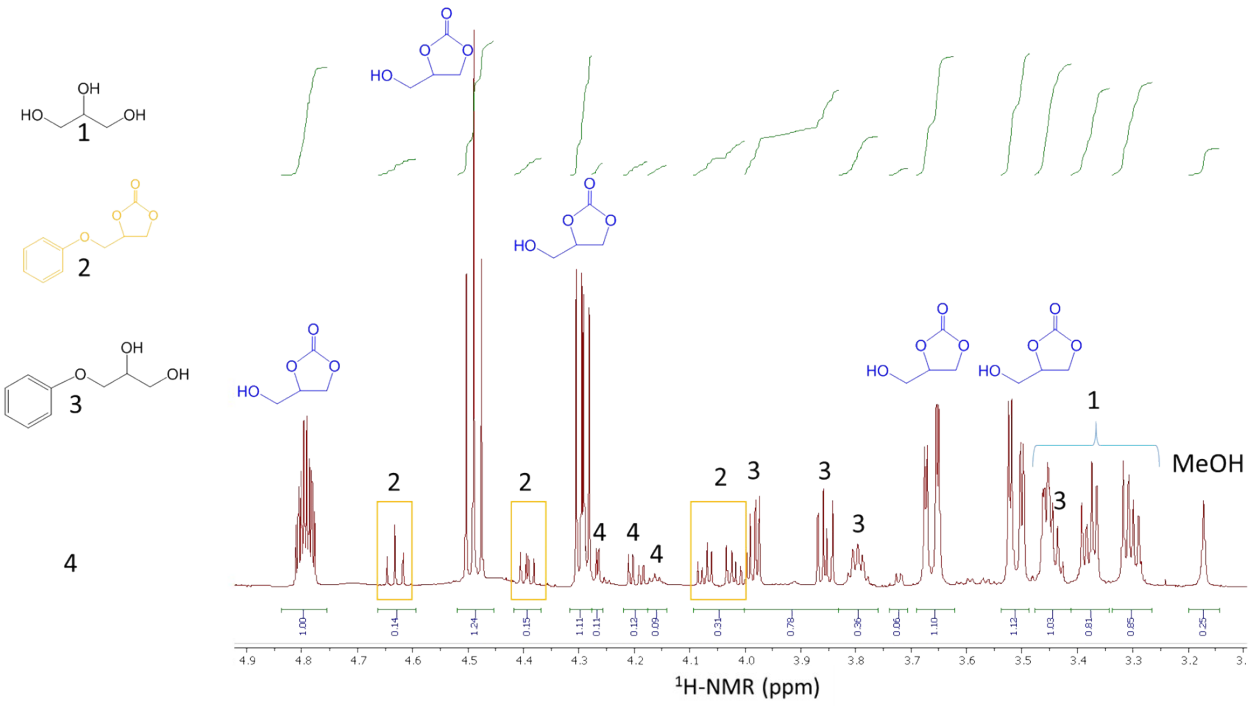


Figure S11. ^{1}H-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of phenol with glycerol carbonate, detail of the aliphatic region with integration and assignments defined with bidimensional HMBC characterization. The signal highlighted in orange are ascribable to **2**, the only product for which no characterization is available from control experiments or literature.

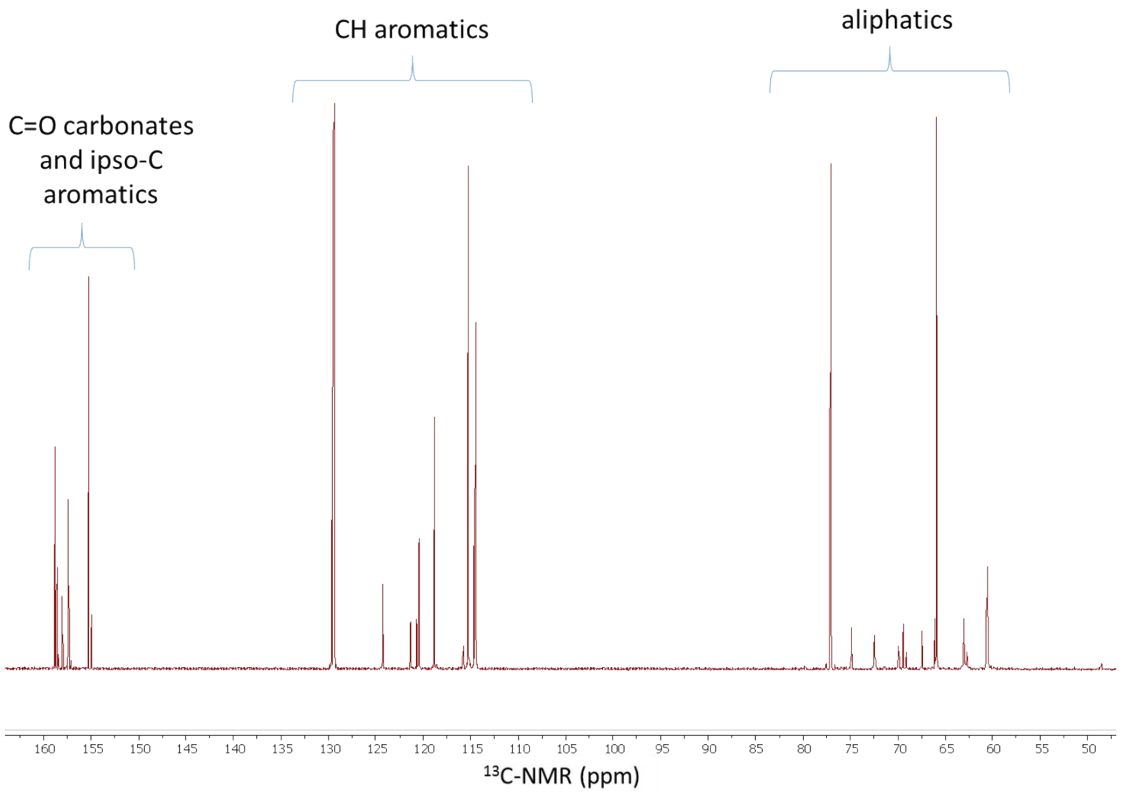


Figure S12. ^{13}C-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of phenol with glycerol carbonate.

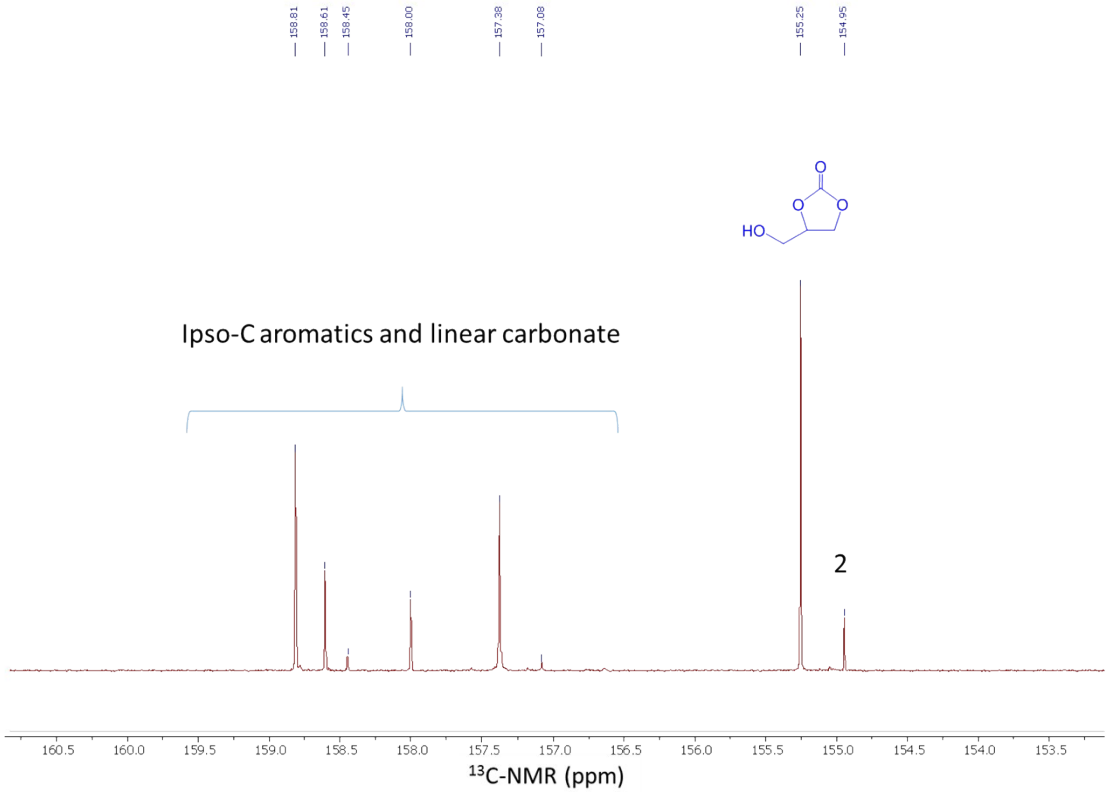


Figure S13. ^{13}C-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of phenol with glycerol carbonate, detail of the quaternary carbons (ipso-C and carbonates) region.

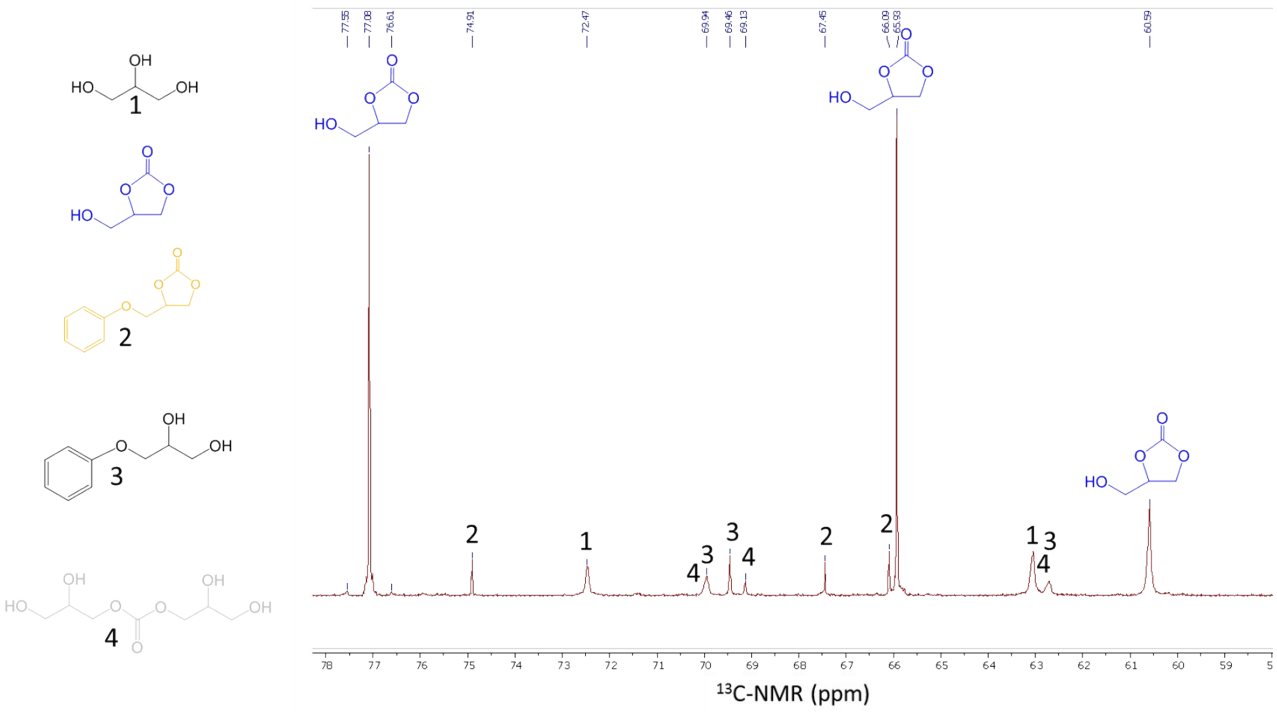


Figure S14. ^{13}C-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of phenol with glycerol carbonate, detail of the aliphatic region. Assignments defined with bidimensional HMBC characterization.

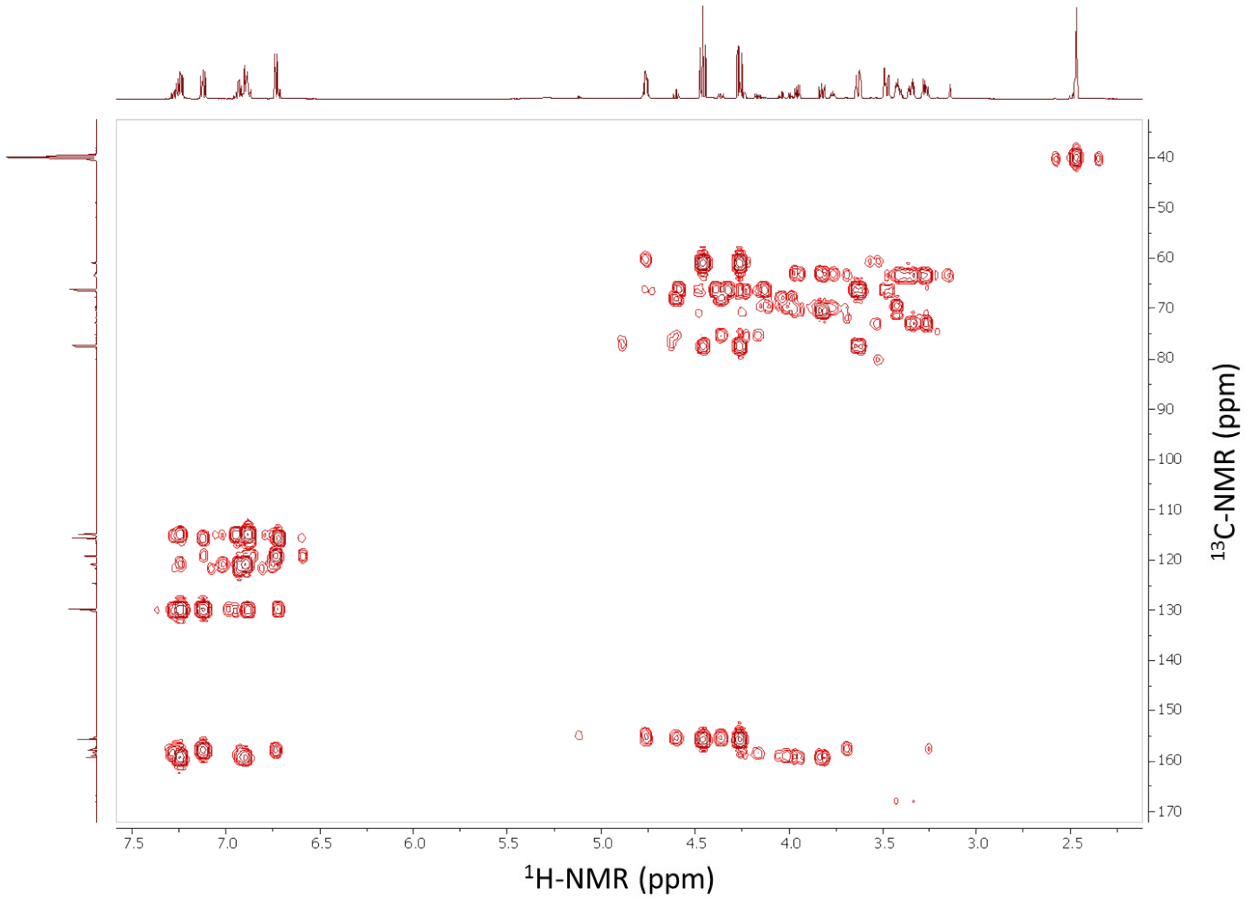


Figure S15. Whole HMBC-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of phenol with glycerol carbonate, details of the assignments are available in the main text.

NMR spectra of the mixture obtained from the reaction between catechol and glycerol carbonate

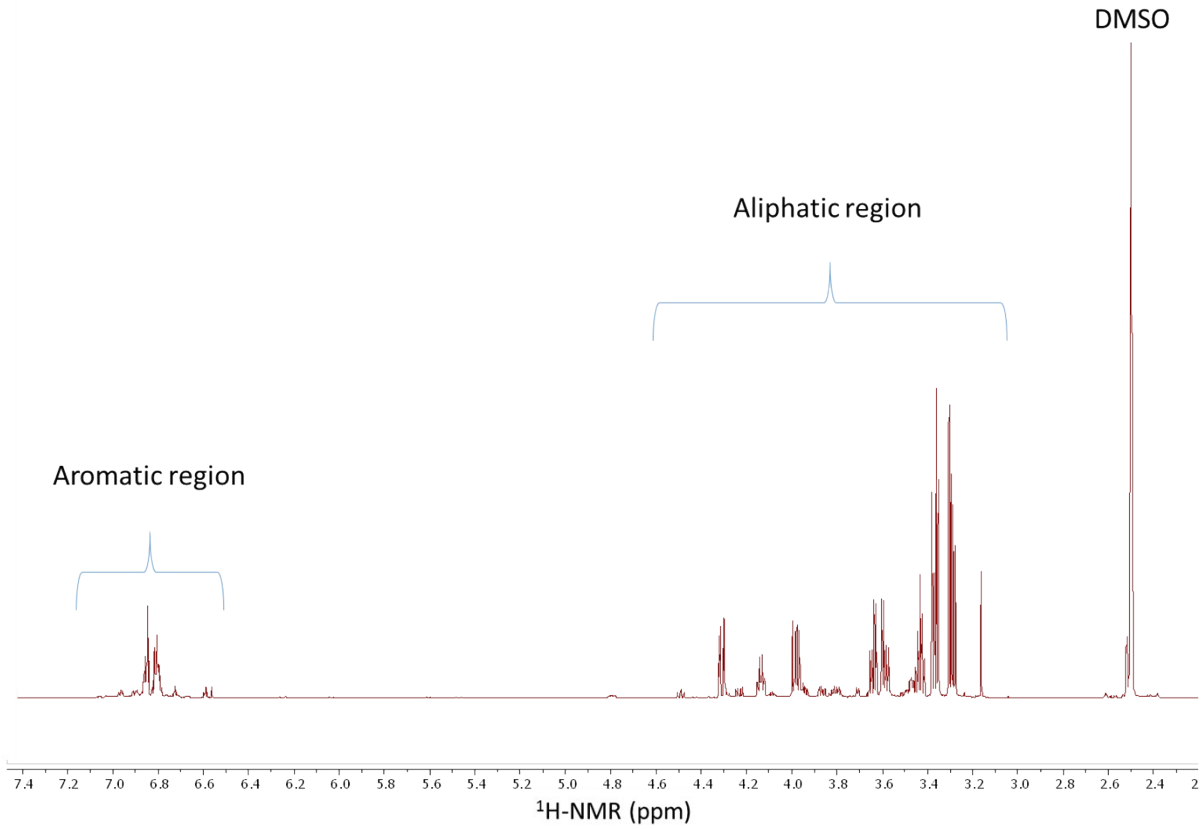


Figure S16. ^{1}H-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of catechol with glycerol carbonate.

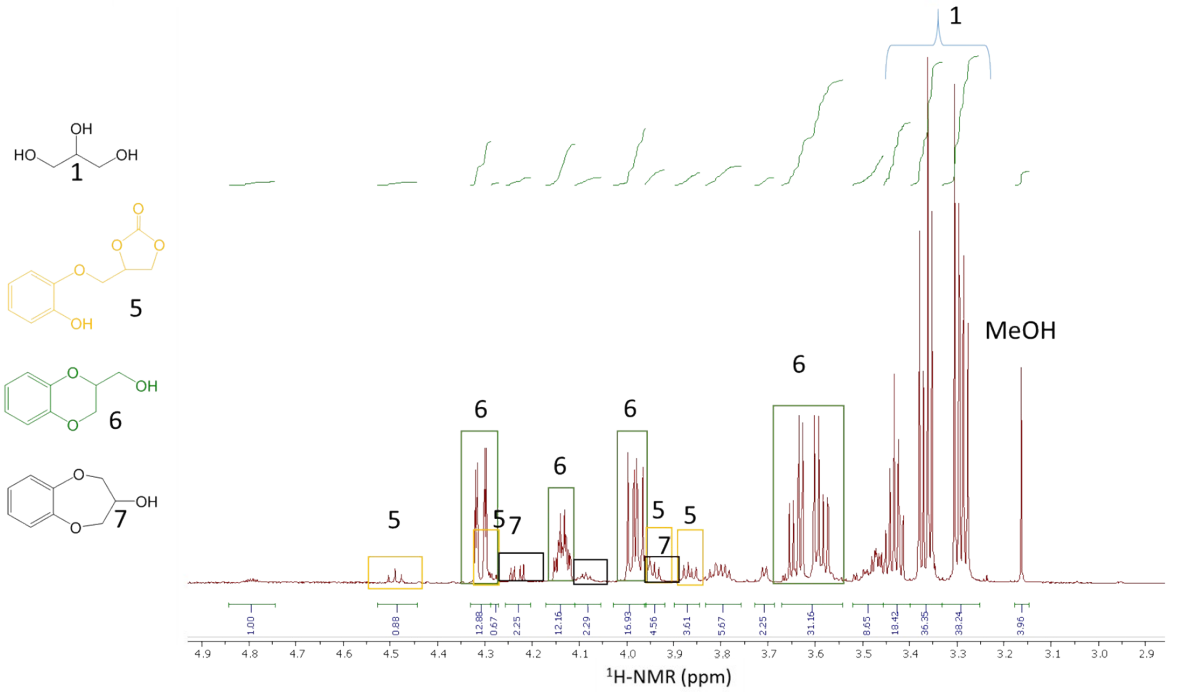


Figure S17. ^{1}H-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of catechol with glycerol carbonate, detail of the aliphatic region with integration and assignments defined with bidimensional HMBC characterization.

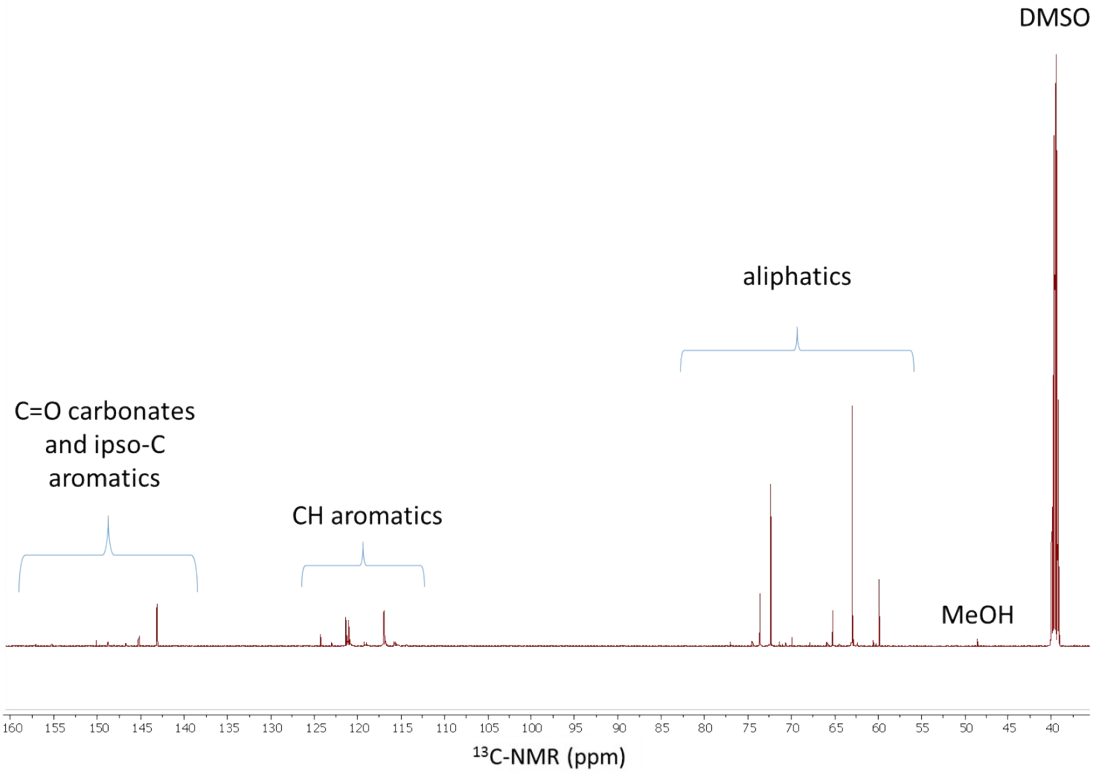


Figure S18. ^{13}C-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of catechol with glycerol carbonate.

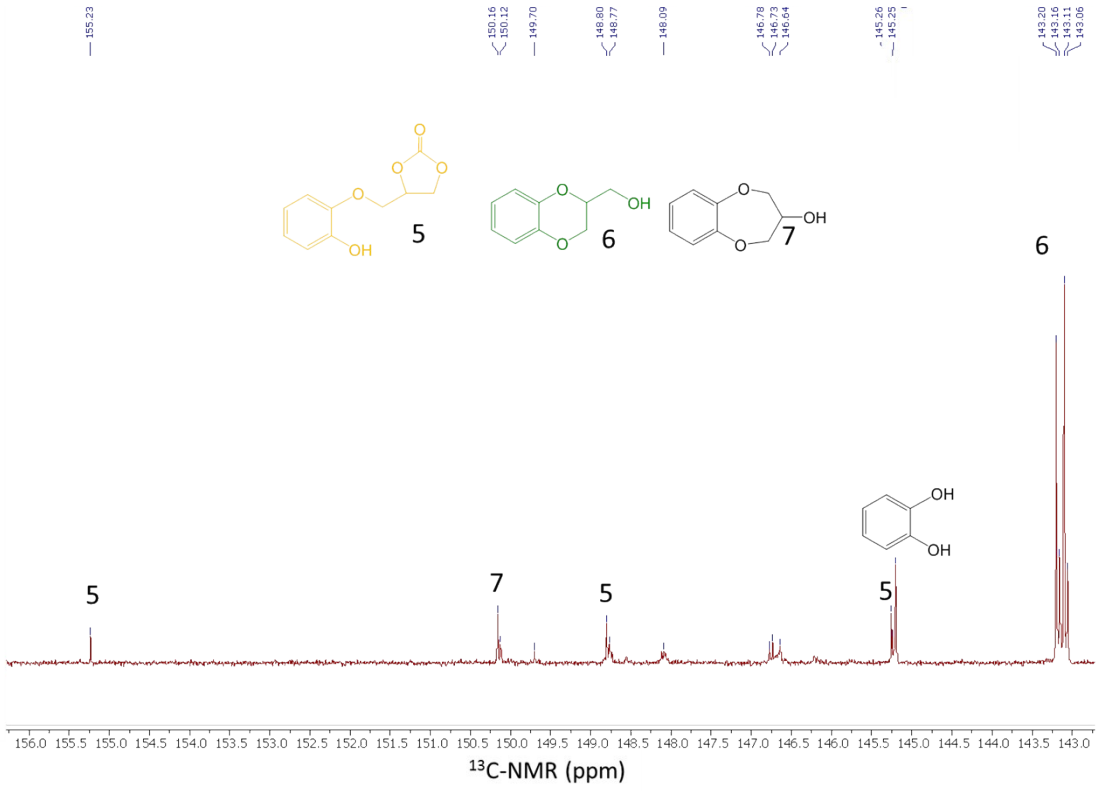


Figure S19. ^{13}C-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of catechol with glycerol carbonate, detail of the quaternary carbons (ipso-C and carbonates) region.

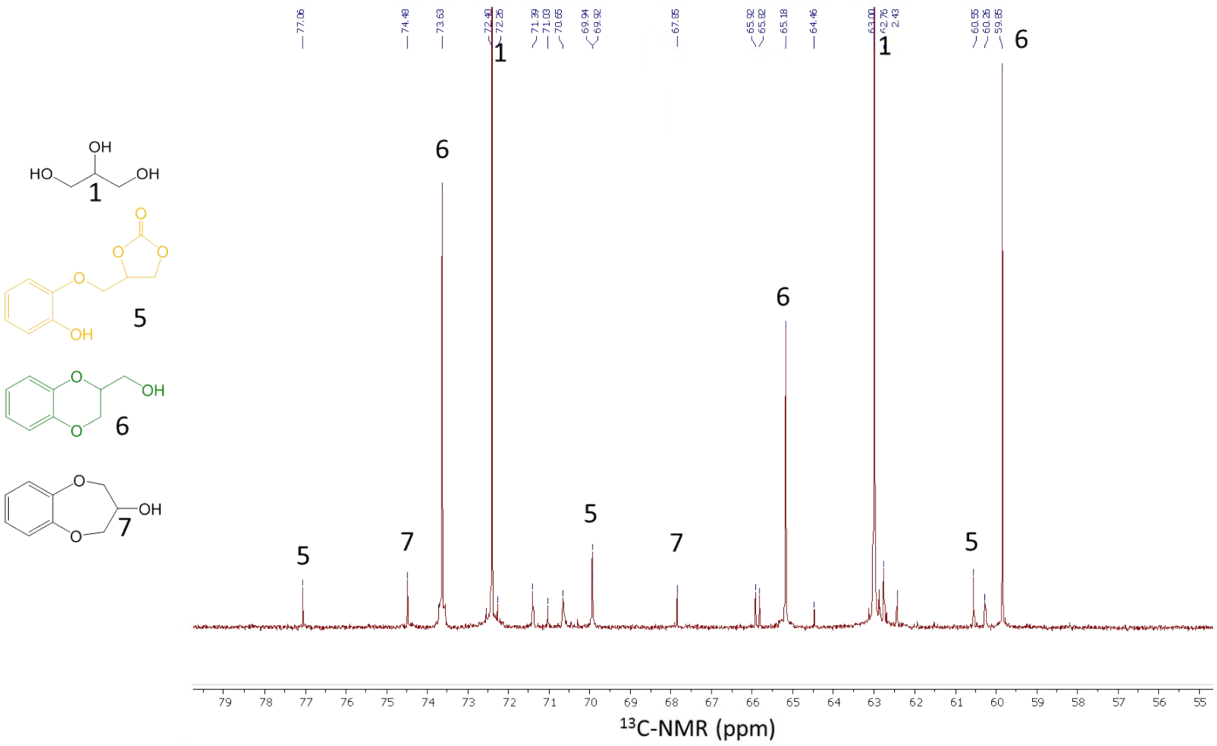


Figure S20. ^{13}C-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of catechol with glycerol carbonate, detail of the aliphatic region. Assignments defined with bidimensional HMBC characterization.

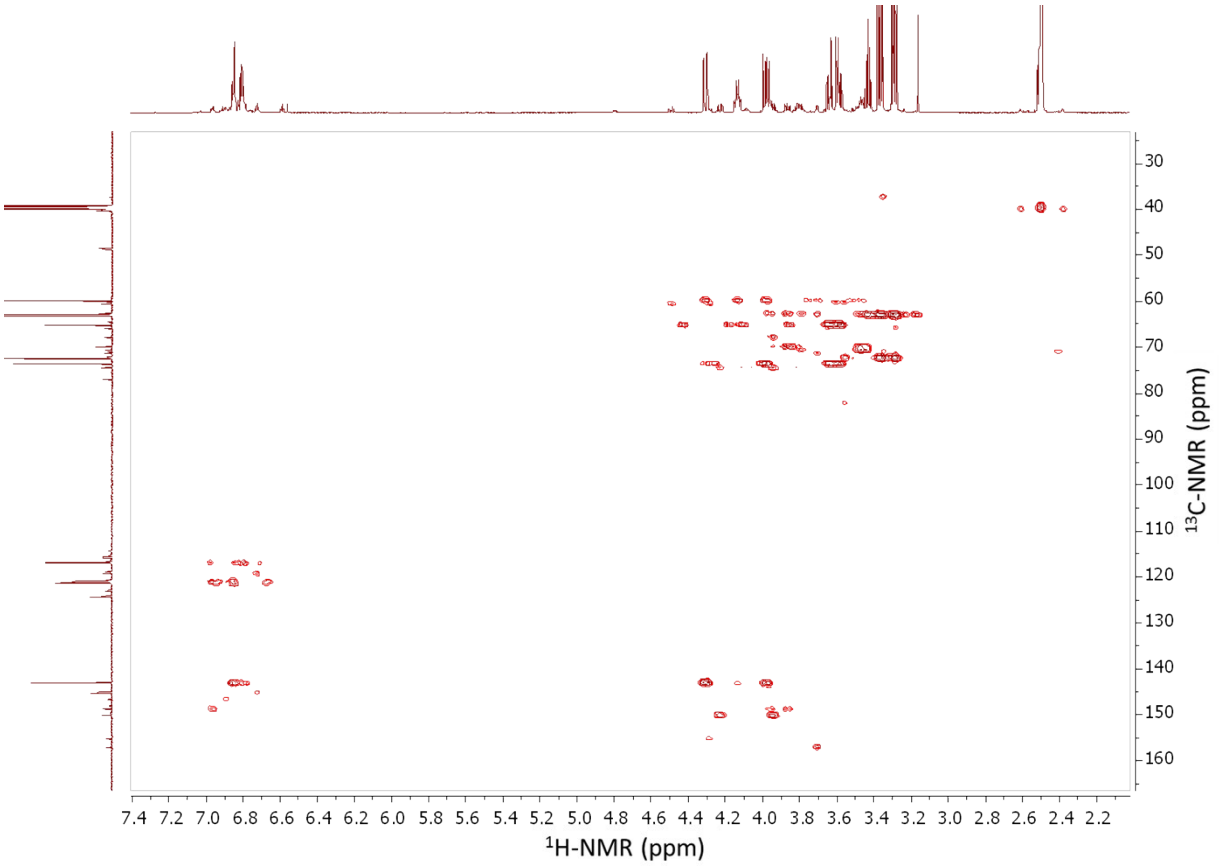


Figure S21. Whole HMBC-NMR (600 MHz, DMSO-d_6) of the mixture obtained from the reaction of catechol with glycerol carbonate, details of the assignments are available in the main text.

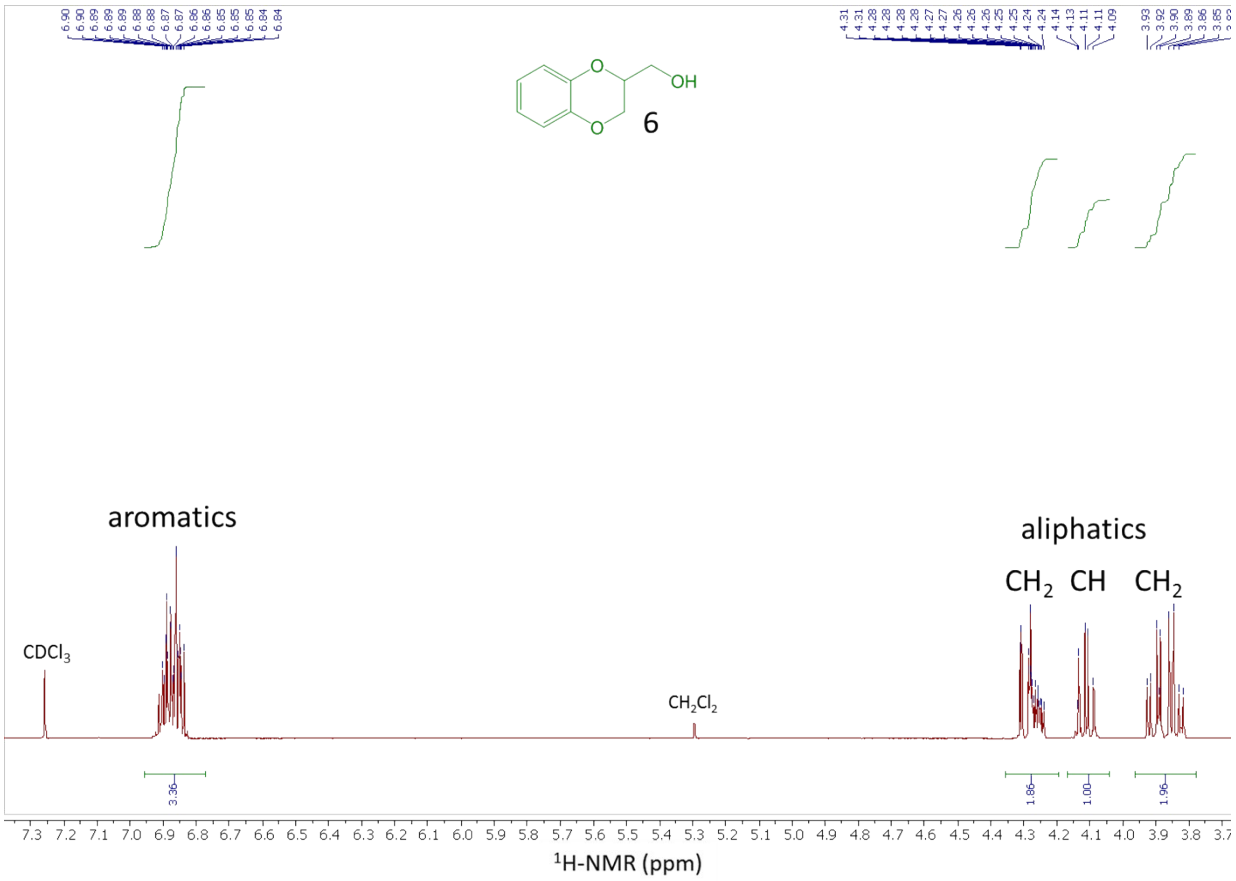
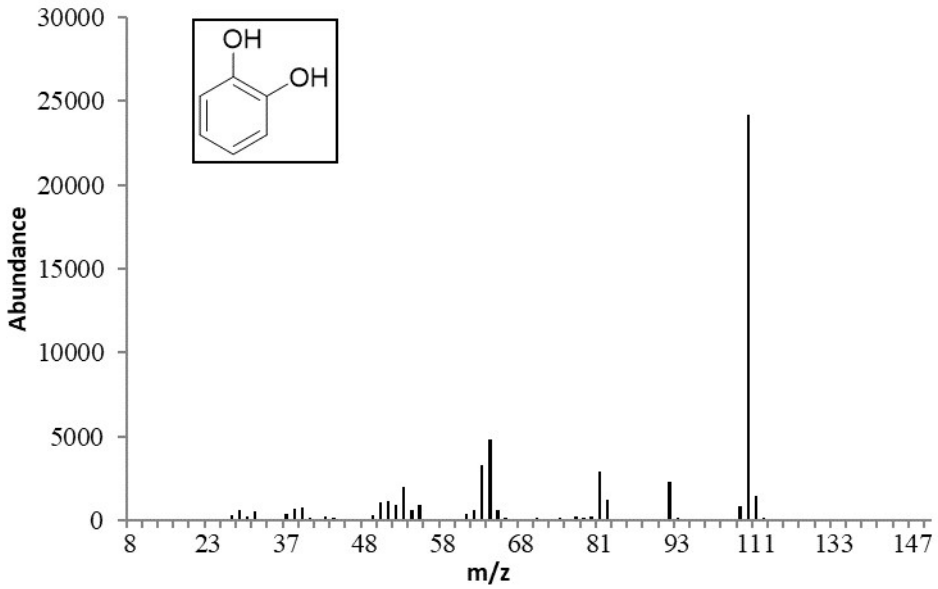


Figure S22. ^{1}H-NMR (400 MHz, $CDCl_3$) of the purified HMB.

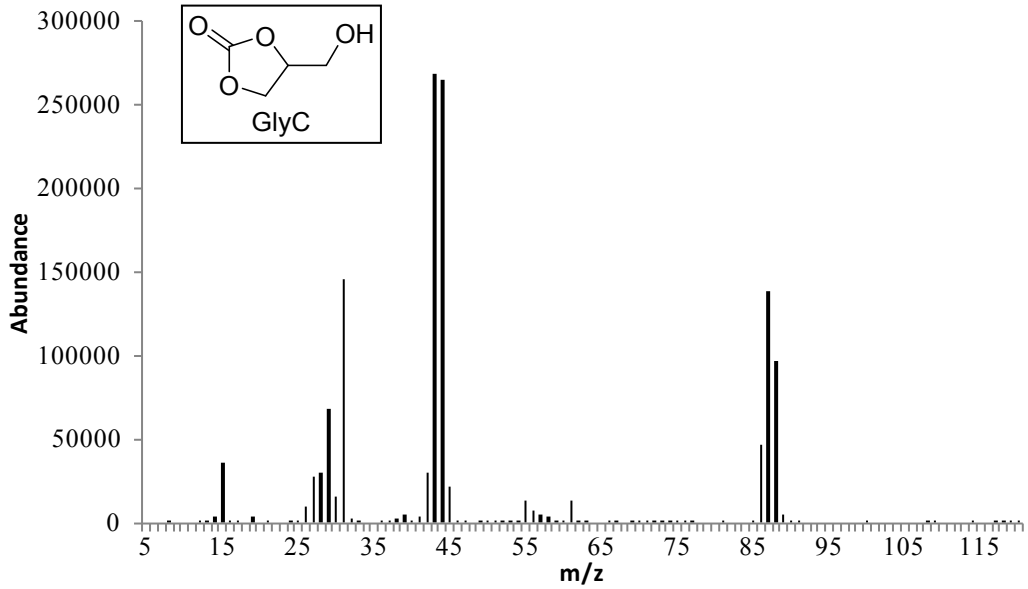
Characterisation of products: MS spectra

Catechol



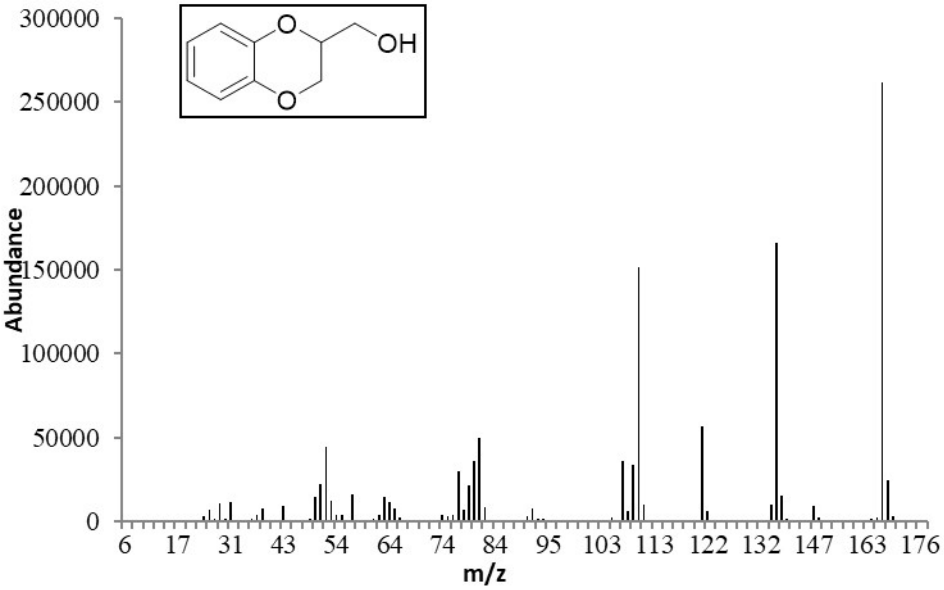
GC-MS (relative intensity, 70eV) *m/z*: 110 (M^+, 100), 92 (9), 81 (12), 64 (20), 63 (13), 53 (8), 39 (3).

Glycerol carbonate (GlyC)



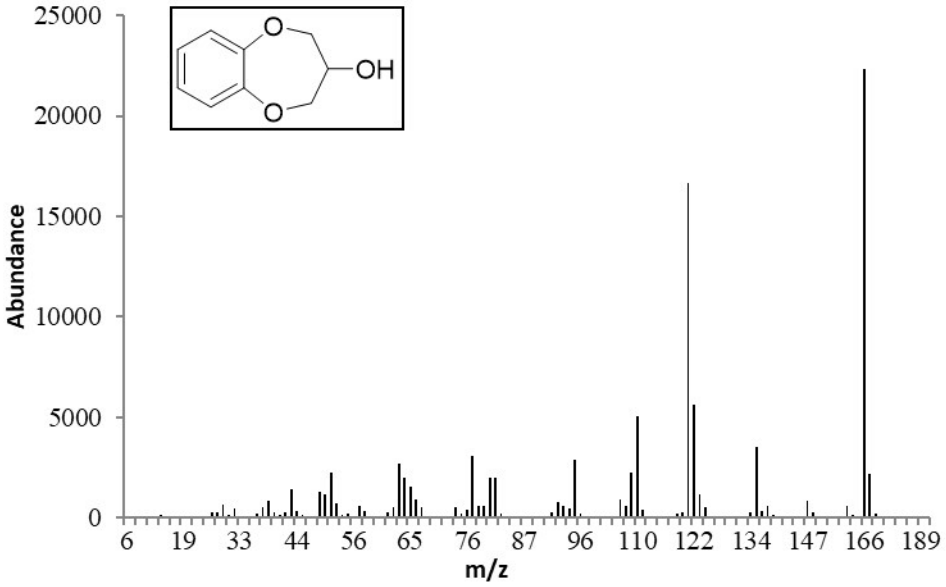
GC-MS (relative intensity, 70eV) *m/z*: 118 (M^+, <1%), 88 (36), 87 (52), 61 (5), 55 (5), 44 (99), 43 (100), 31 (54), 29 (25), 15 (14).

2-hydroxymethyl-1,4-benzodioxane (HMB)



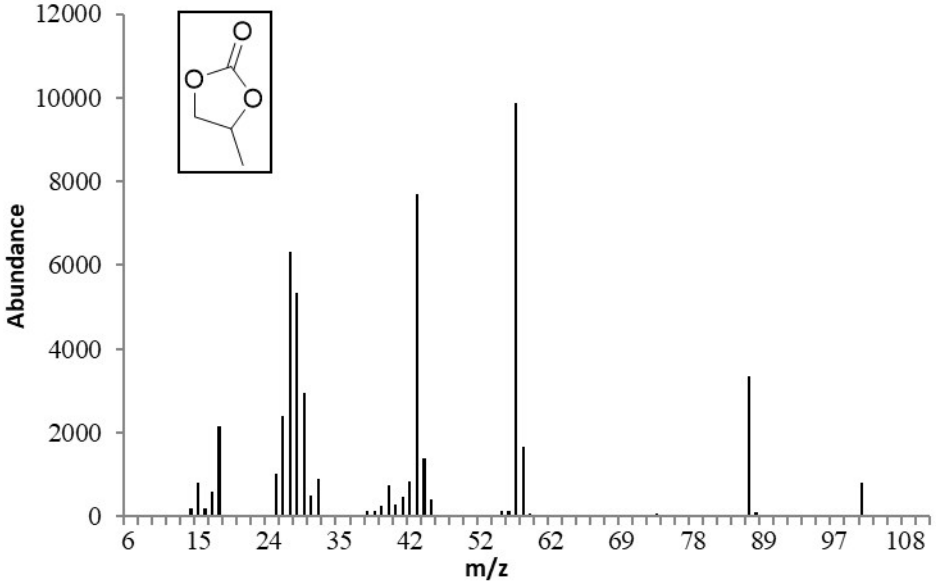
GC-MS (relative intensity, 70eV) *m/z*: 166 (M^+, 100), 135 (63), 121 (21), 110 (58), 107 (14), 92 (3), 81 (19), 63 (6), 51 (8).

3,4-dihydro-2H-benzo[b][1,4]dioxepin-3-ol



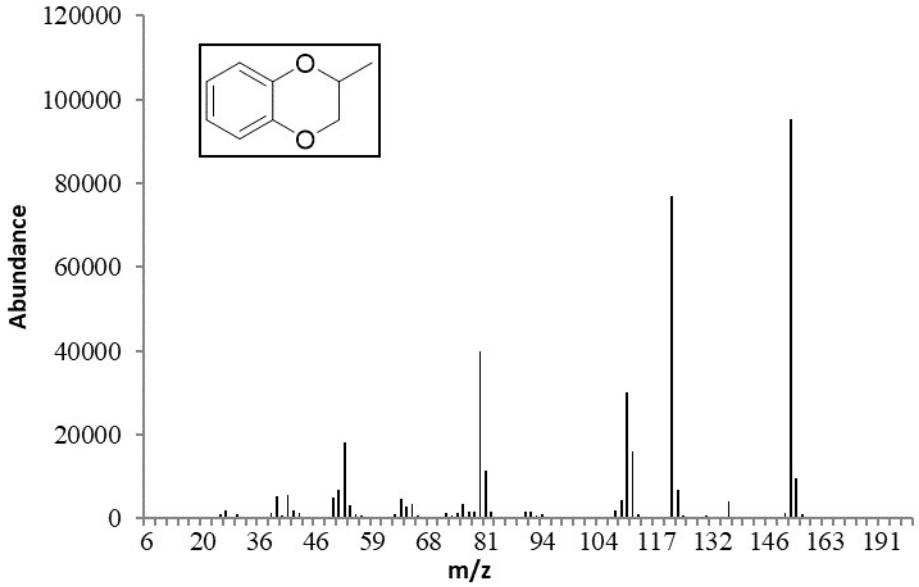
GC-MS (relative intensity, 70eV) *m/z*: 166 (M^+, 100), 135 (16), 121 (75), 110 (23), 95 (13), 81 (9), 77 (14), 63 (12), 52 (10), 43 (6).

Propylene carbonate



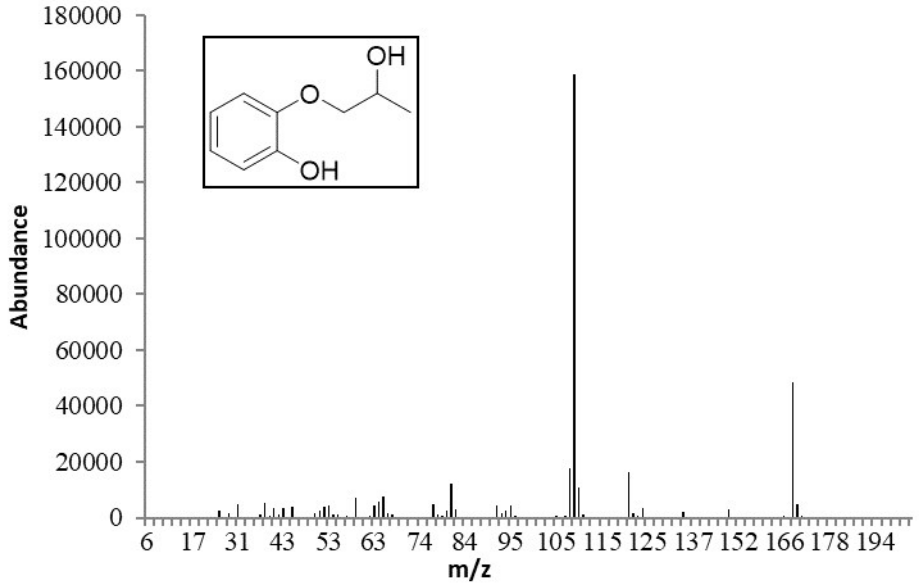
GC-MS (relative intensity, 70eV) *m/z*: 102 (M^+, 8), 87 (34), 57 (100), 43 (78), 30 (30), 29 (54), 28 (64), 18 (22).

2-methyl-1,4-benzodioxane (MB)



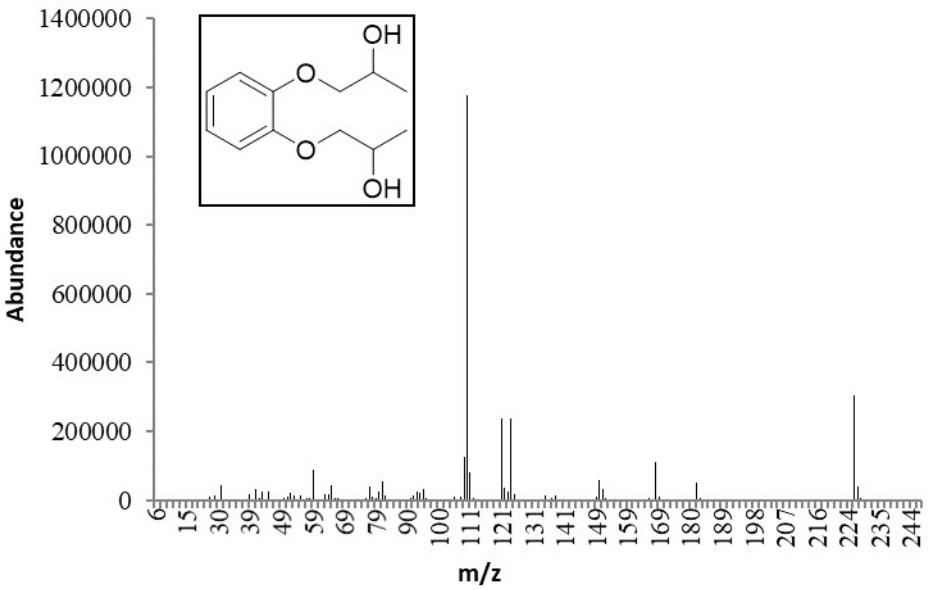
GC-MS (relative intensity, 70eV) *m/z*: 150 (M^+, 100), 135 (4), 121 (80), 110 (17), 80 (42), 65 (4), 52 (19), 41 (6), 39 (5).

2-(2-hydroxypropoxy)phenol



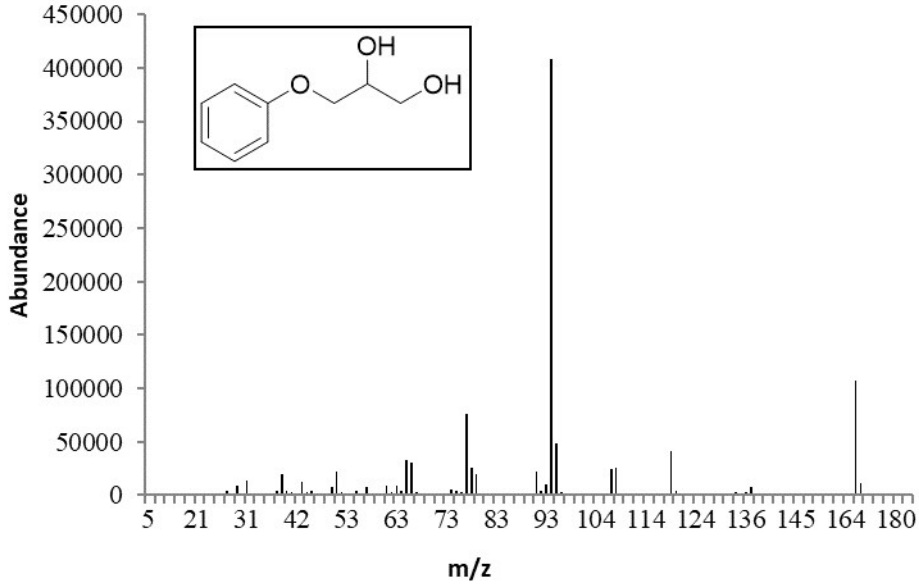
GC-MS (relative intensity, 70eV) *m/z*: 168 (M^+, 31), 150 (2), 121 (10), 110 (100), 92 (3), 81 (8), 65 (5), 59 (5).

1,1'-(1,2-phenylenebis(oxy))bis(propan-2-ol)



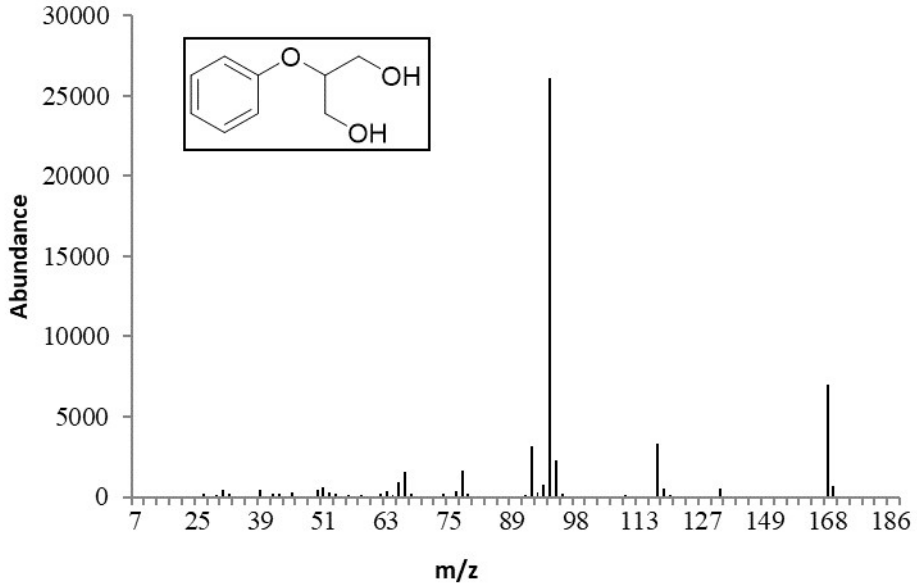
GC-MS (relative intensity, 70eV) *m/z*: 226 (M^+, 26), 182 (4), 168 (9), 150 (5), 124 (20), 121 (20), 110 (100), 81 (5), 59 (7).

3-phenoxy-1,2-propandiol



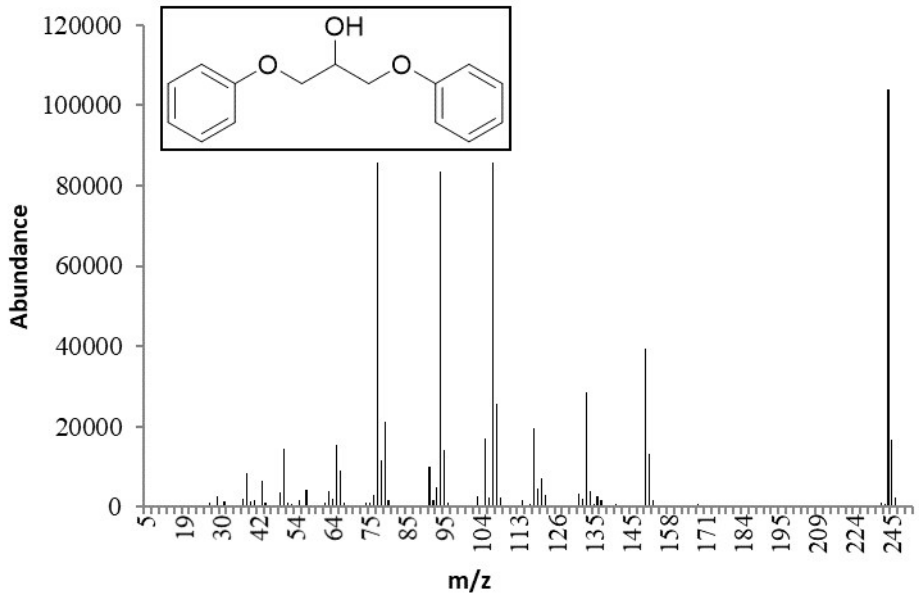
GC-MS (relative intensity, 70eV) *m/z*: 168 (M^+, 26), 119 (10), 108 (6), 94 (100), 77 (19), 65 (8), 51 (5), 39 (5).

2-phenoxy-1,3-propandiol



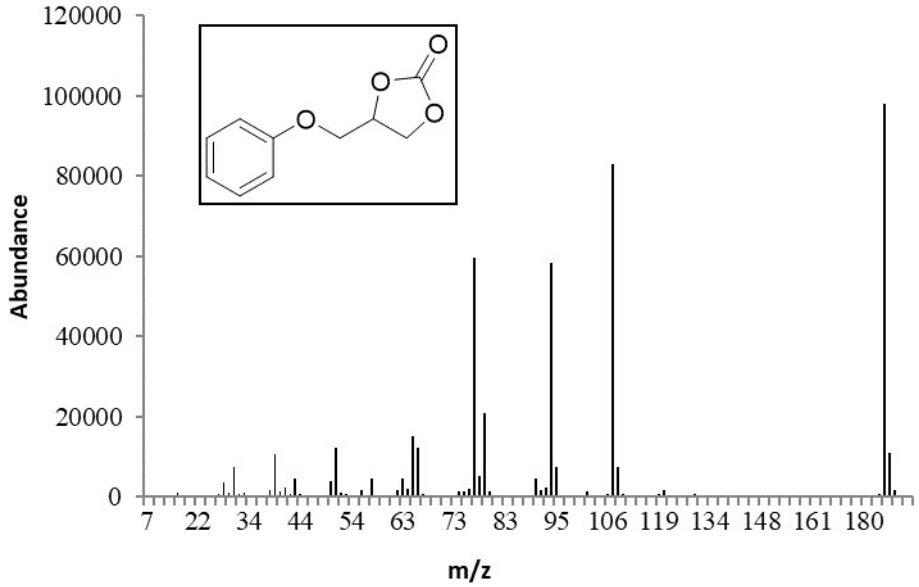
GC-MS (relative intensity, 70eV) *m/z*: 168 (M^+, 27), 119 (13), 94 (100), 91 (12), 77 (6), 66 (6), 51 (2), 39 (2).

1,3-diphenoxypropan-2-ol



GC-MS (relative intensity, 70eV) *m/z*: 244 (M^+, 100), 150 (38), 133 (27), 119 (19), 107 (82), 94 (80), 91 (10), 79 (20), 77 (82), 66 (9), 57 (4), 51 (14), 43 (6), 39 (8).

4-(phenoxymethyl)-1,3-dioxolan-2-one



GC-MS (relative intensity, 70eV) *m/z*: 194 (M^+, 100), 120 (2), 107 (85), 94 (60), 77 (61), 65 (15), 57 (5), 51 (12), 43 (5), 39 (11), 29 (8).