

SUPPLEMENTARY MATERIAL

Effect of four novel bio-based DES (Deep Eutectic Solvents) on hardwood fractionation

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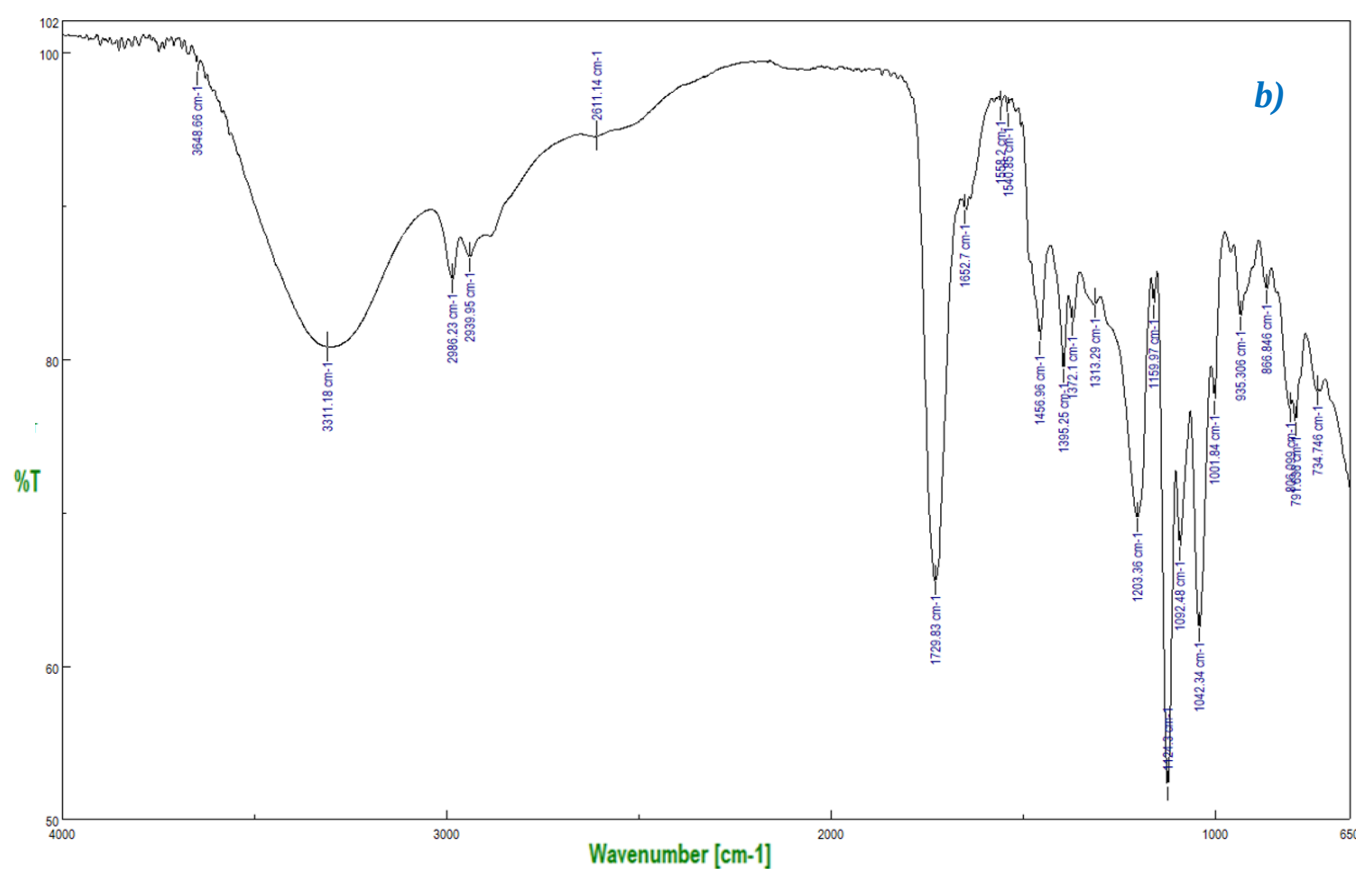
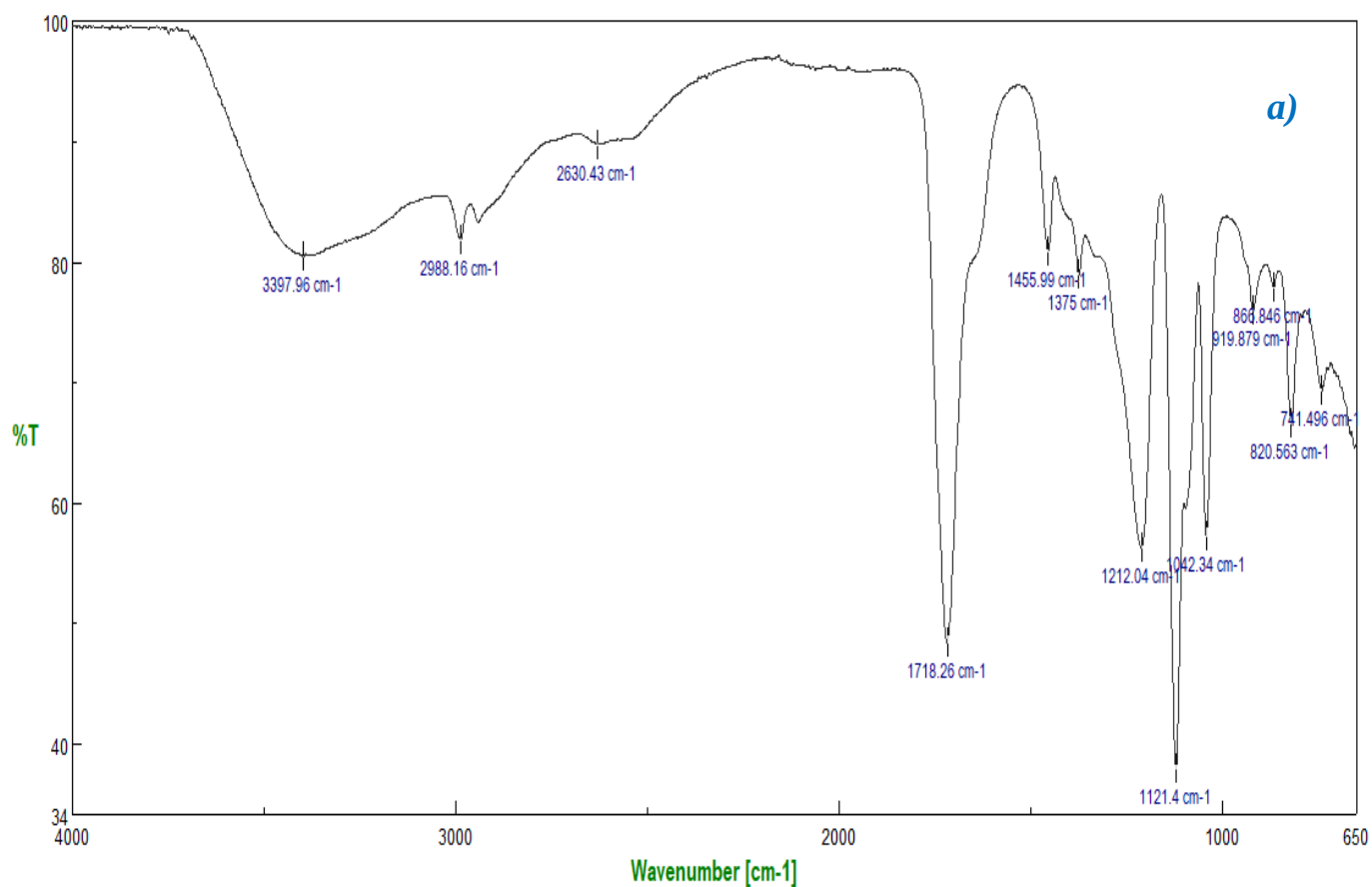


Figure S3: a) FT-IR spectra of lactic acid. b) FT-IR spectra of [DPTAC][LA].

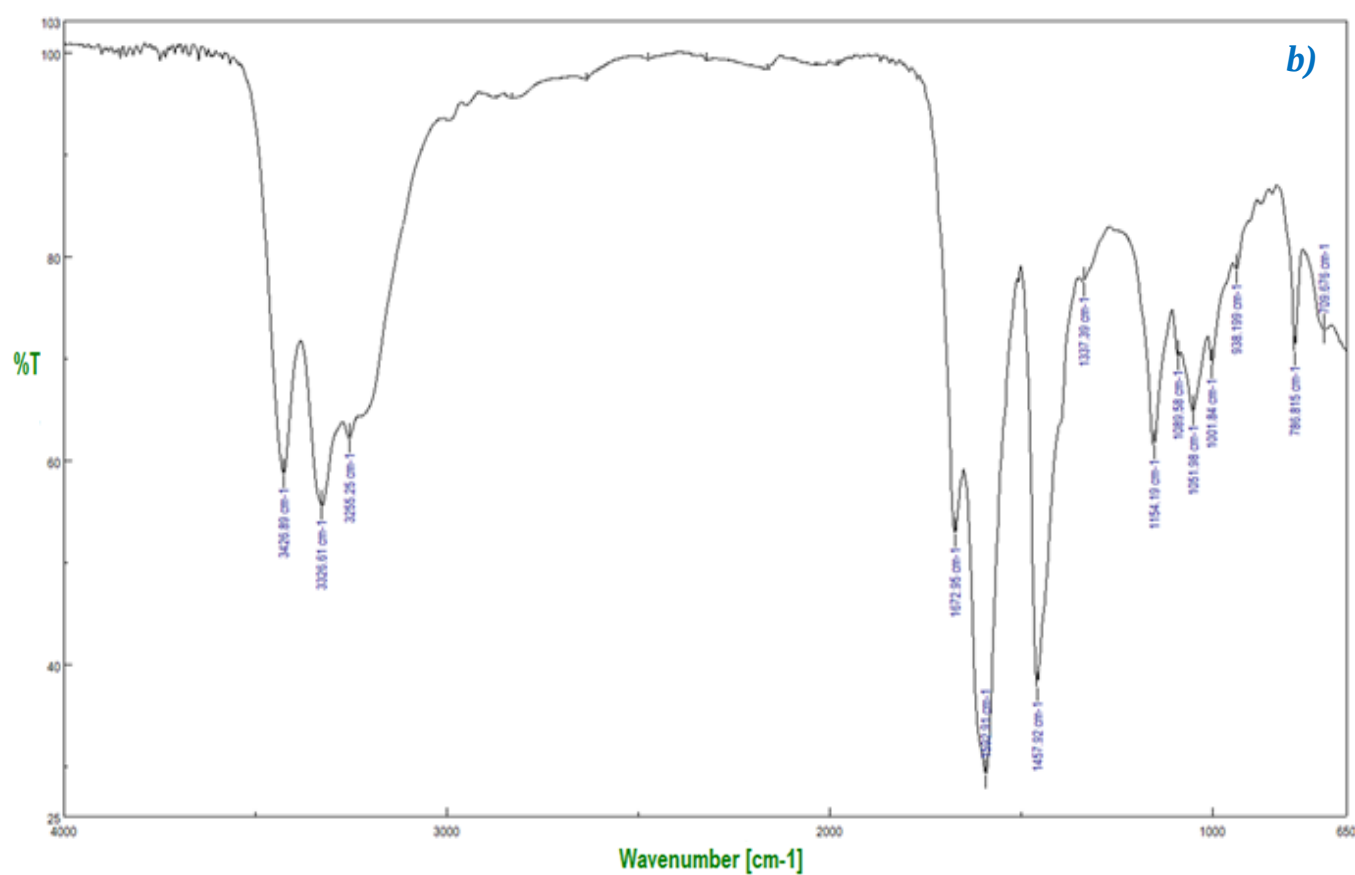
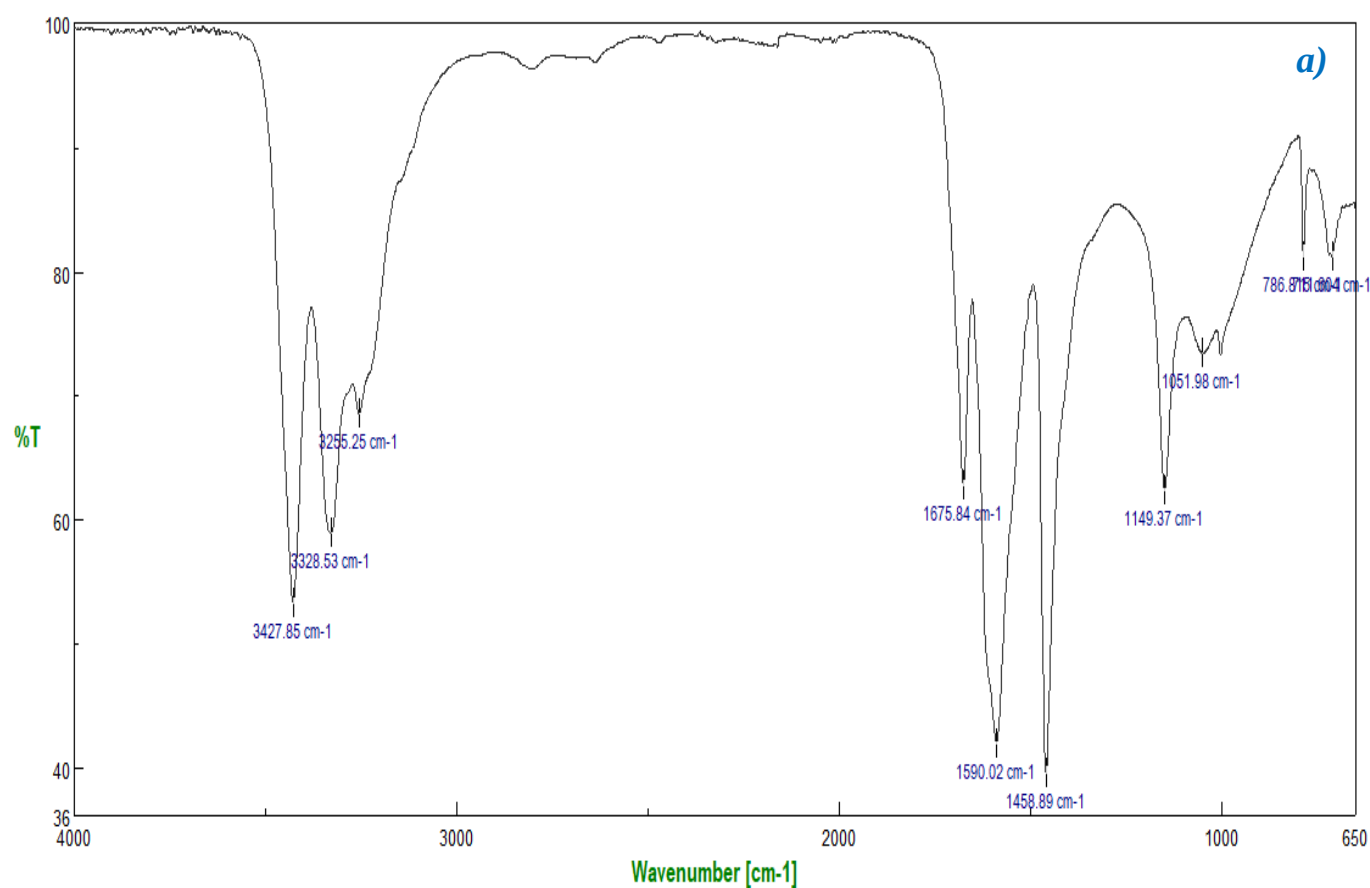


Figure S4: a) FT-IR spectra of urea. **b)** FT-IR spectra of [DPTAC][UREA].

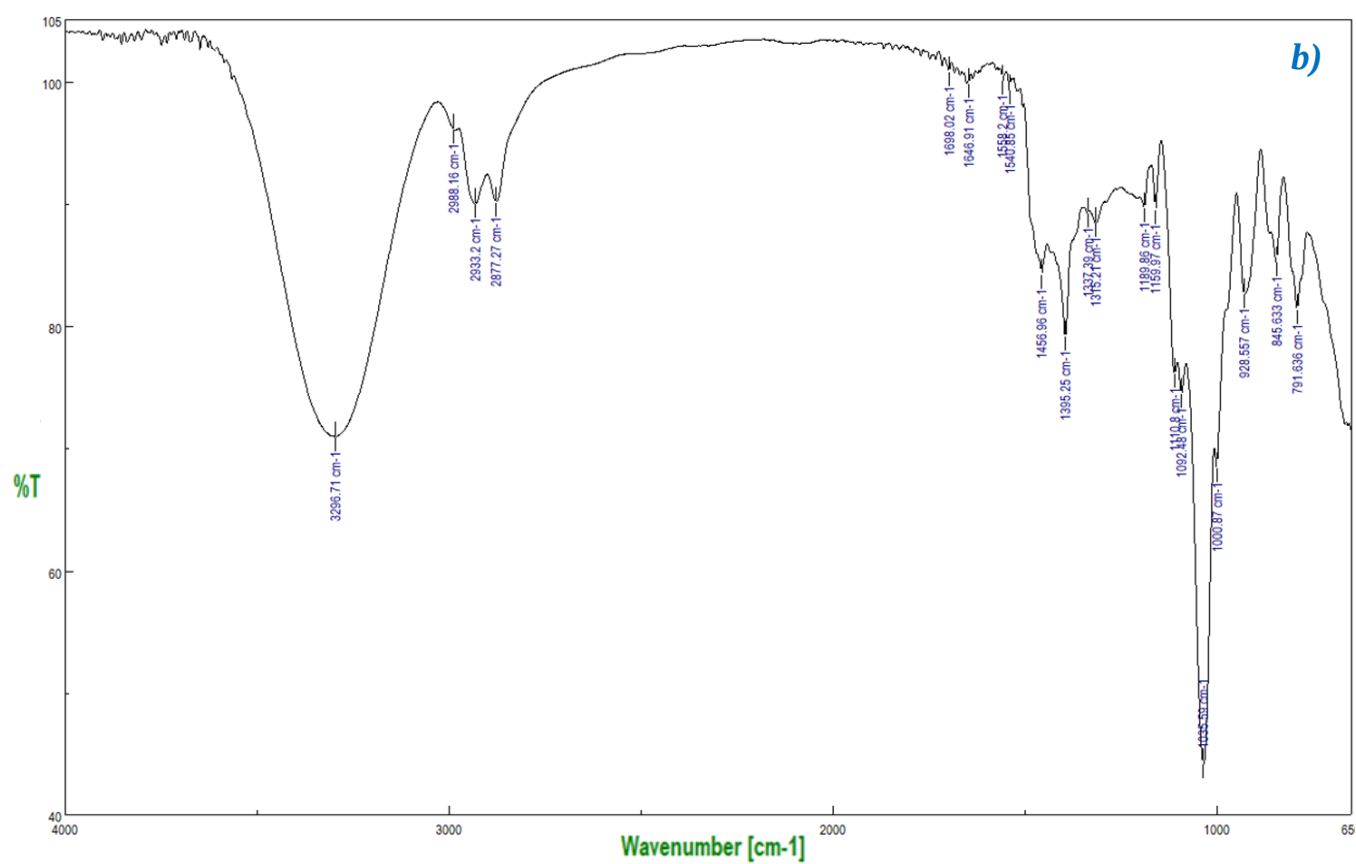
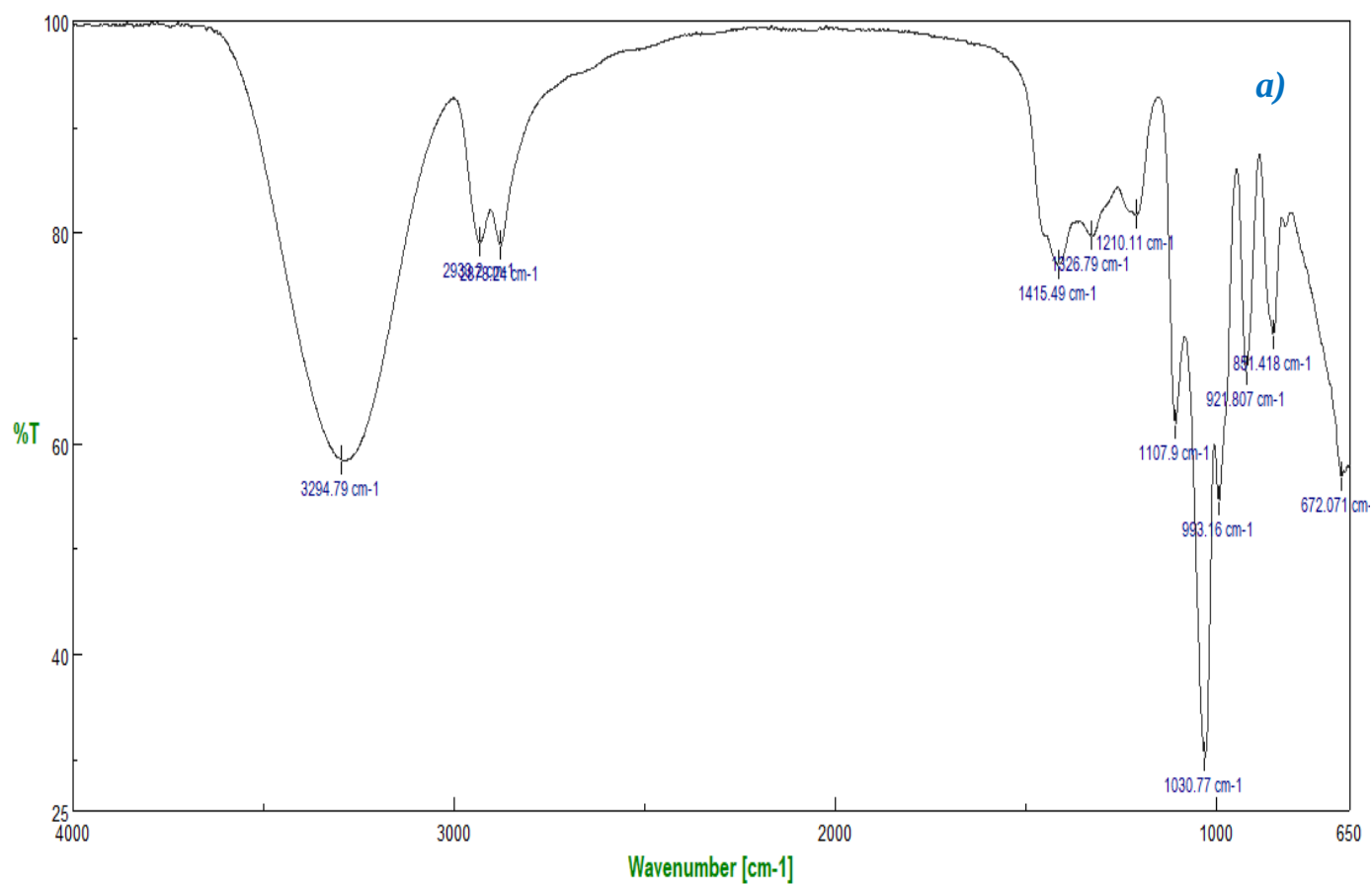


Figure S5: a) FT-IR spectra of glycerol. b) FT-IR spectra of [DPTAC][GLY].

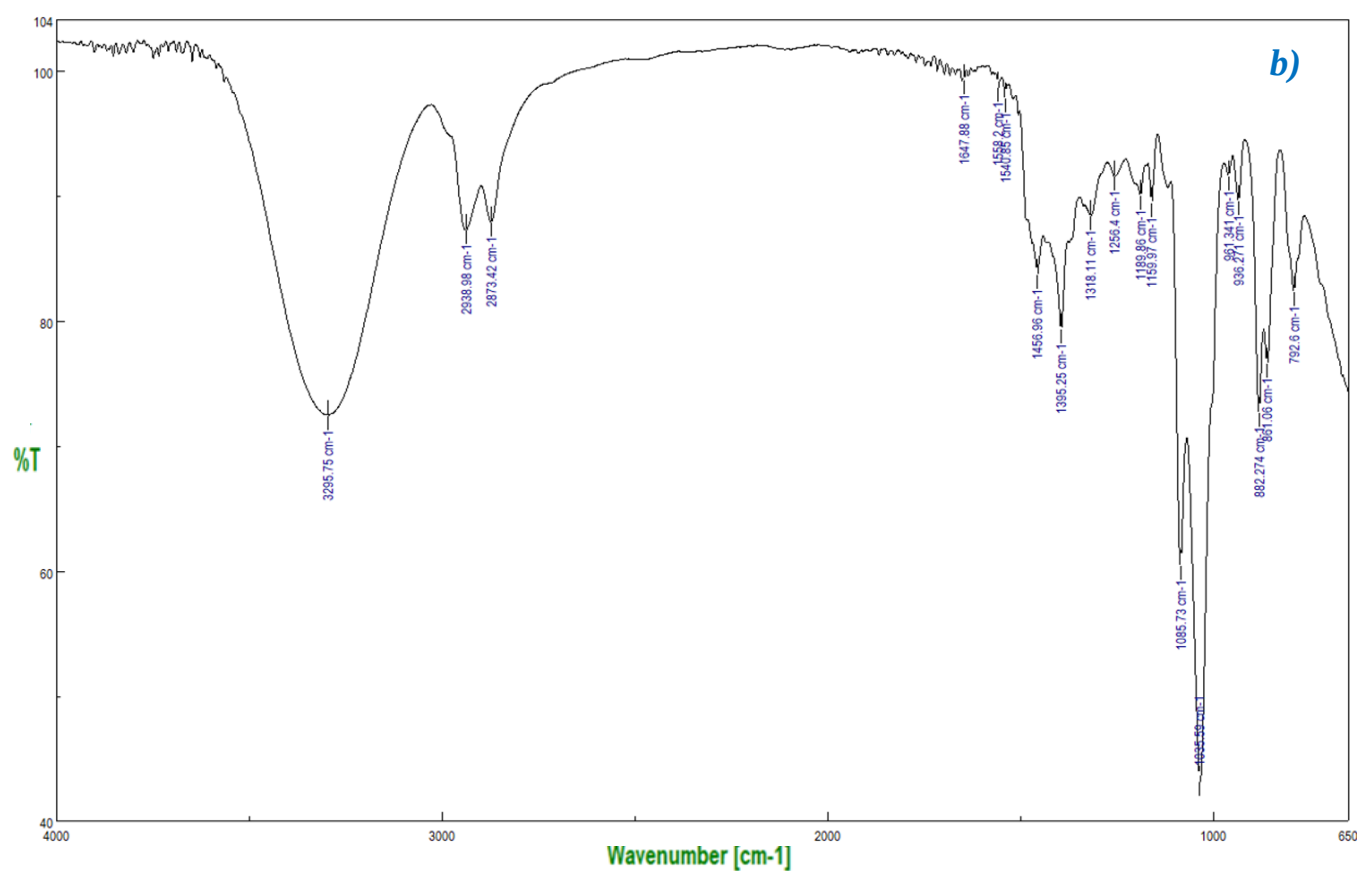
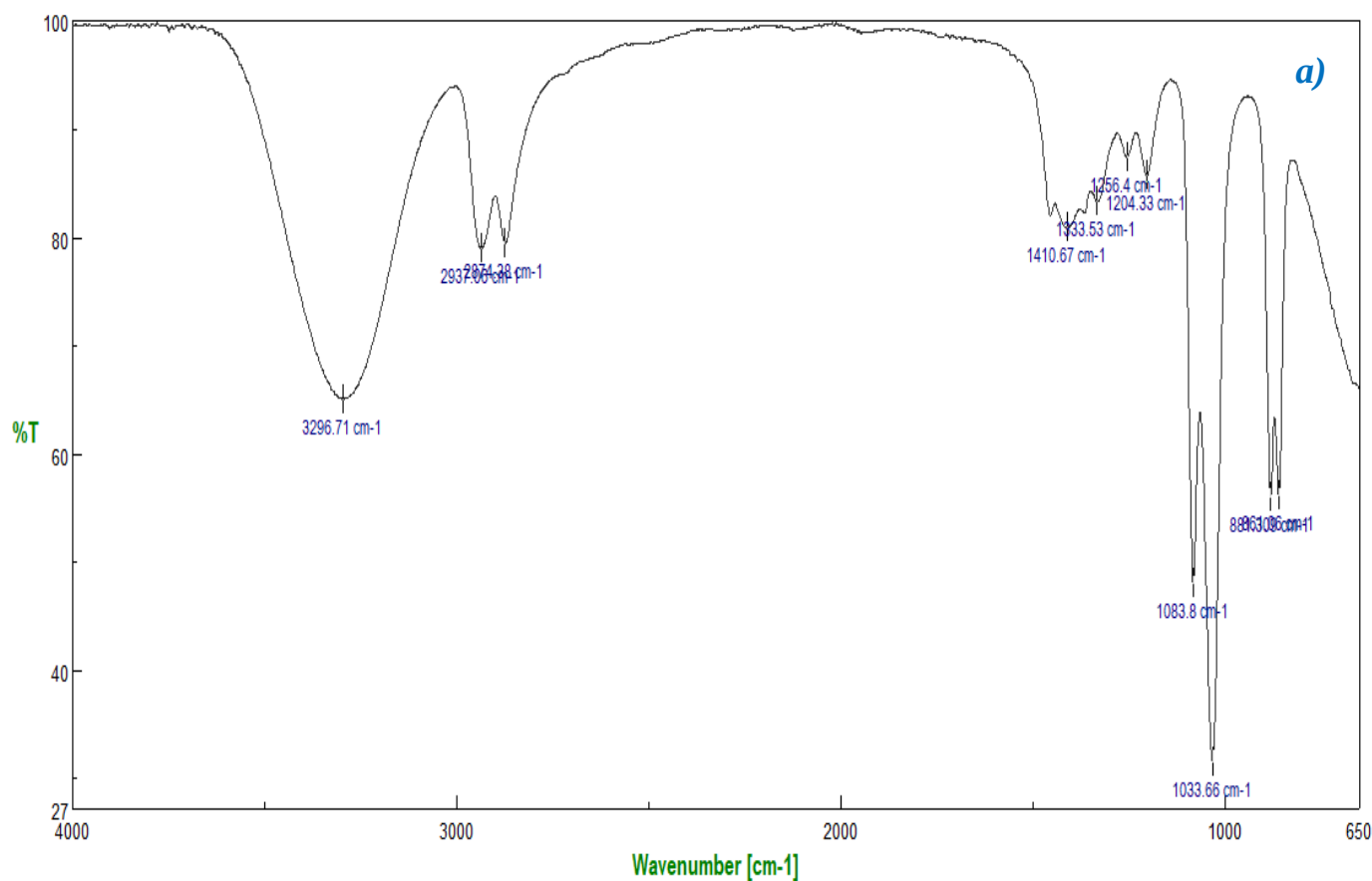


Figure S6: a) FT-IR spectra of ethylene glycol. **b)** FT-IR spectra of [DPTAC][EG]

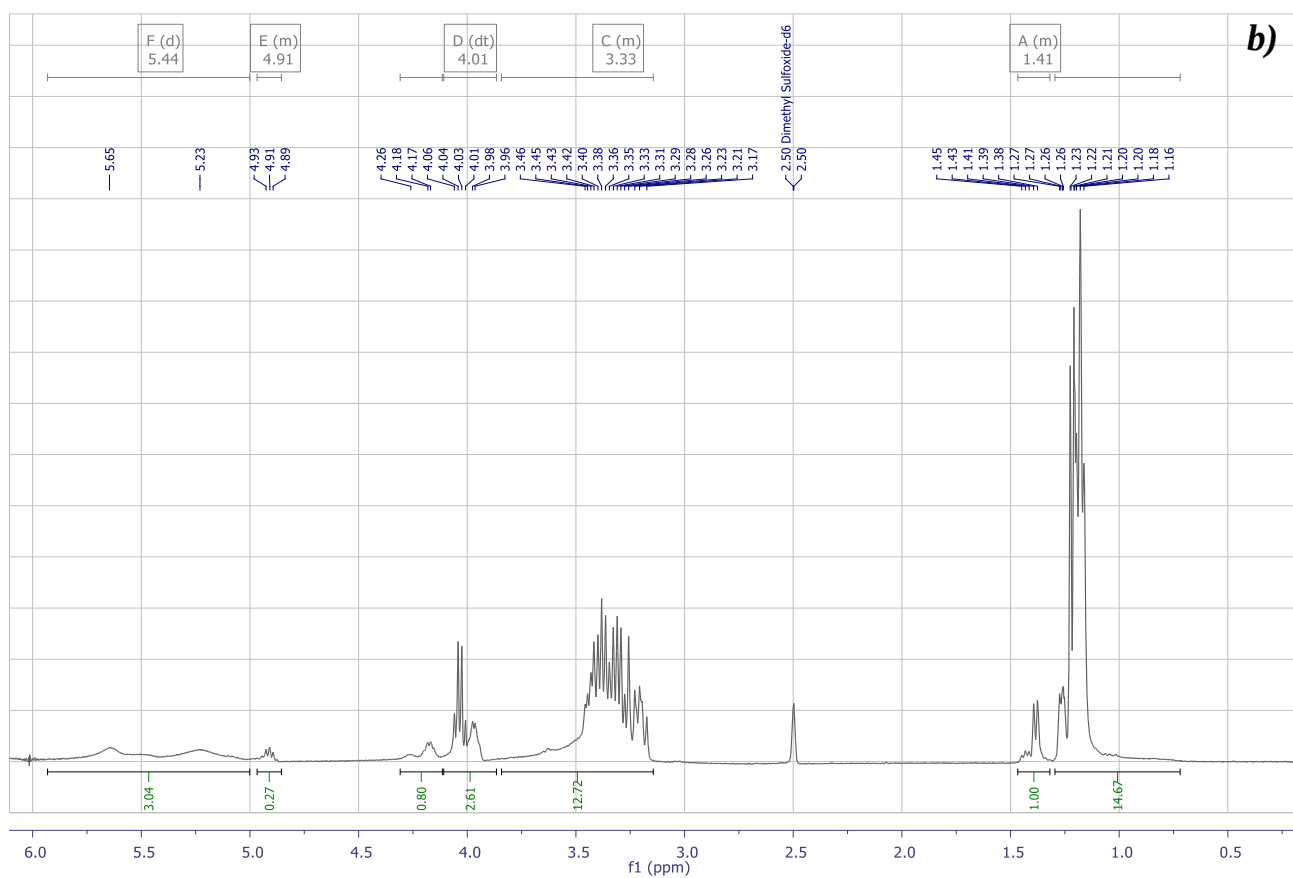
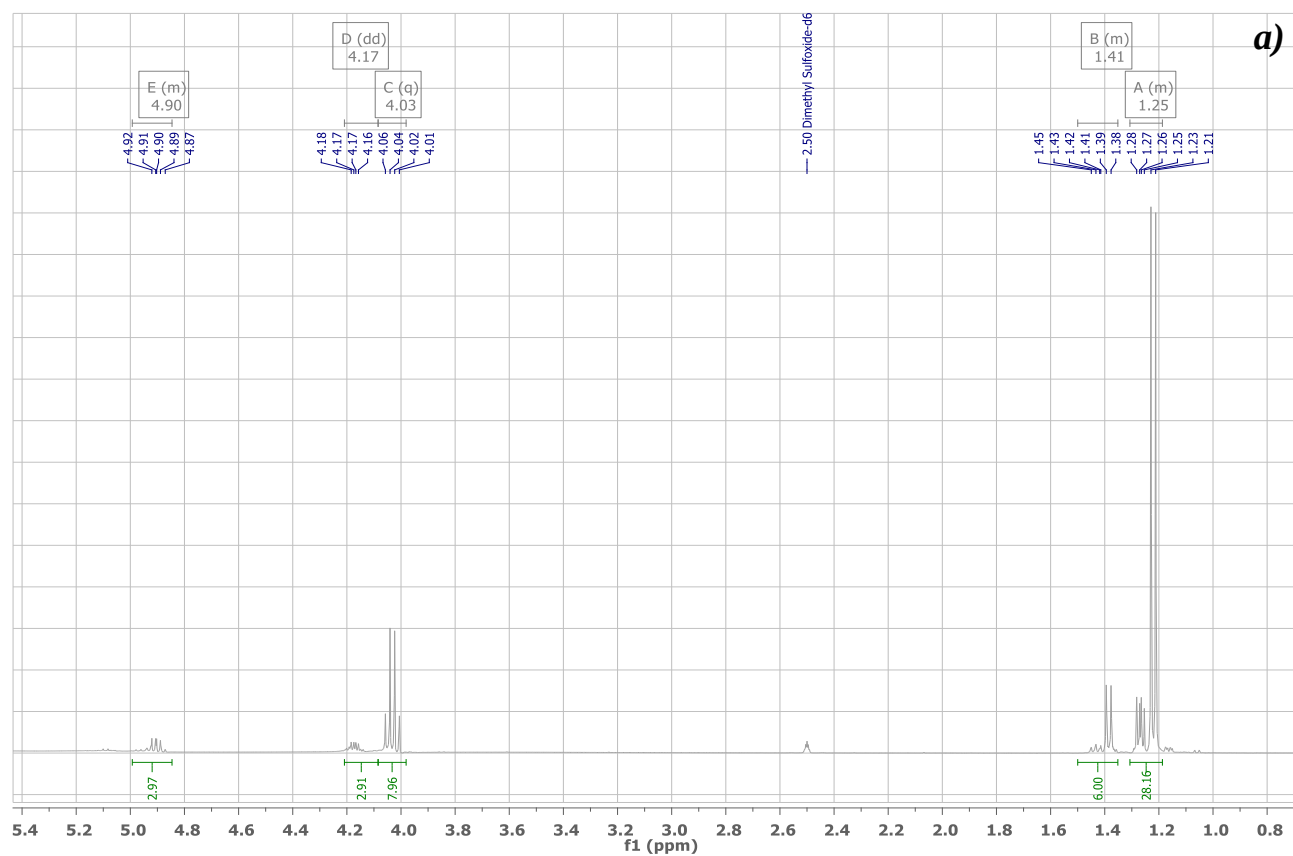


Figure S7: a) ^1H NMR (DMSO d_6 , 400 MHz) spectra of lactic acid. **b)** ^1H NMR (DMSO d_6 , 400 MHz) spectra of [DPTAC][LA].

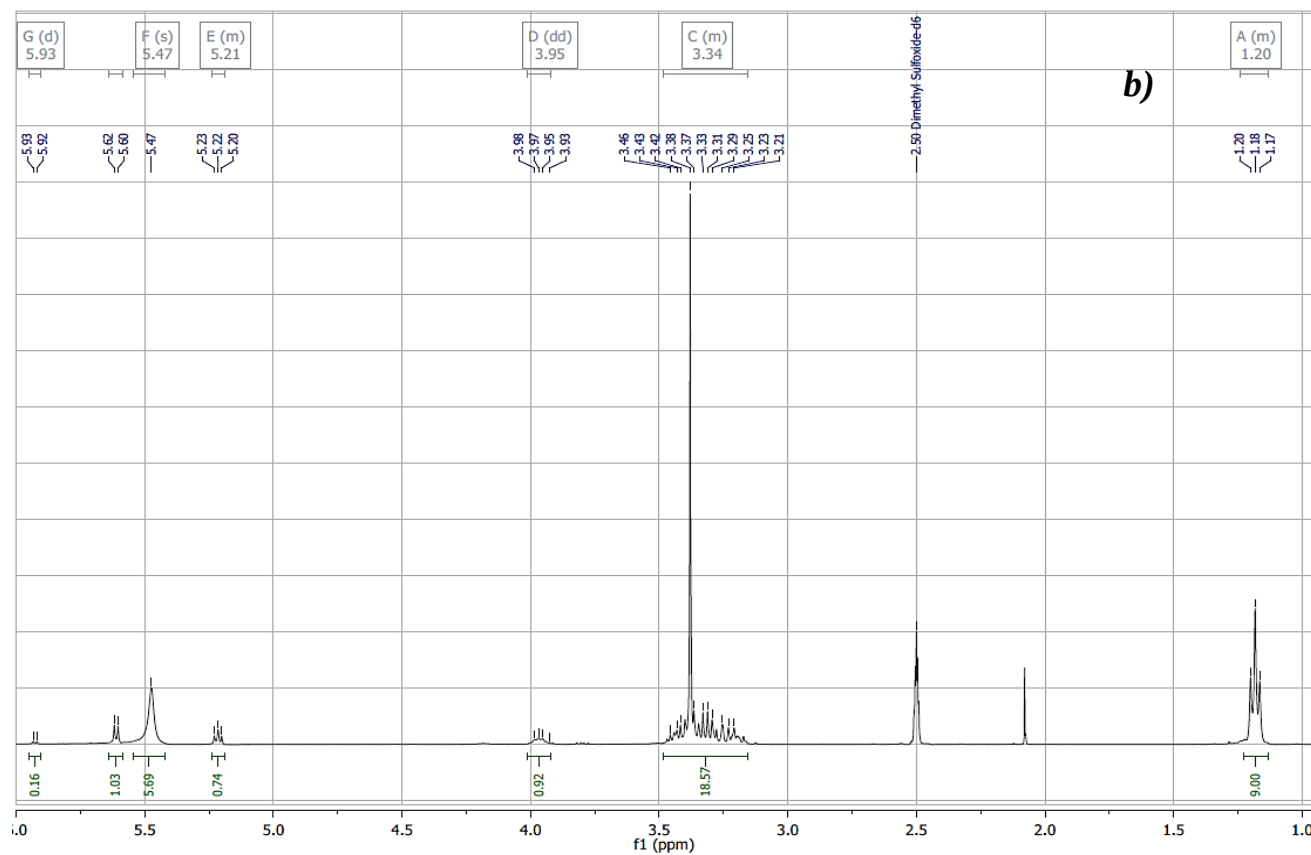
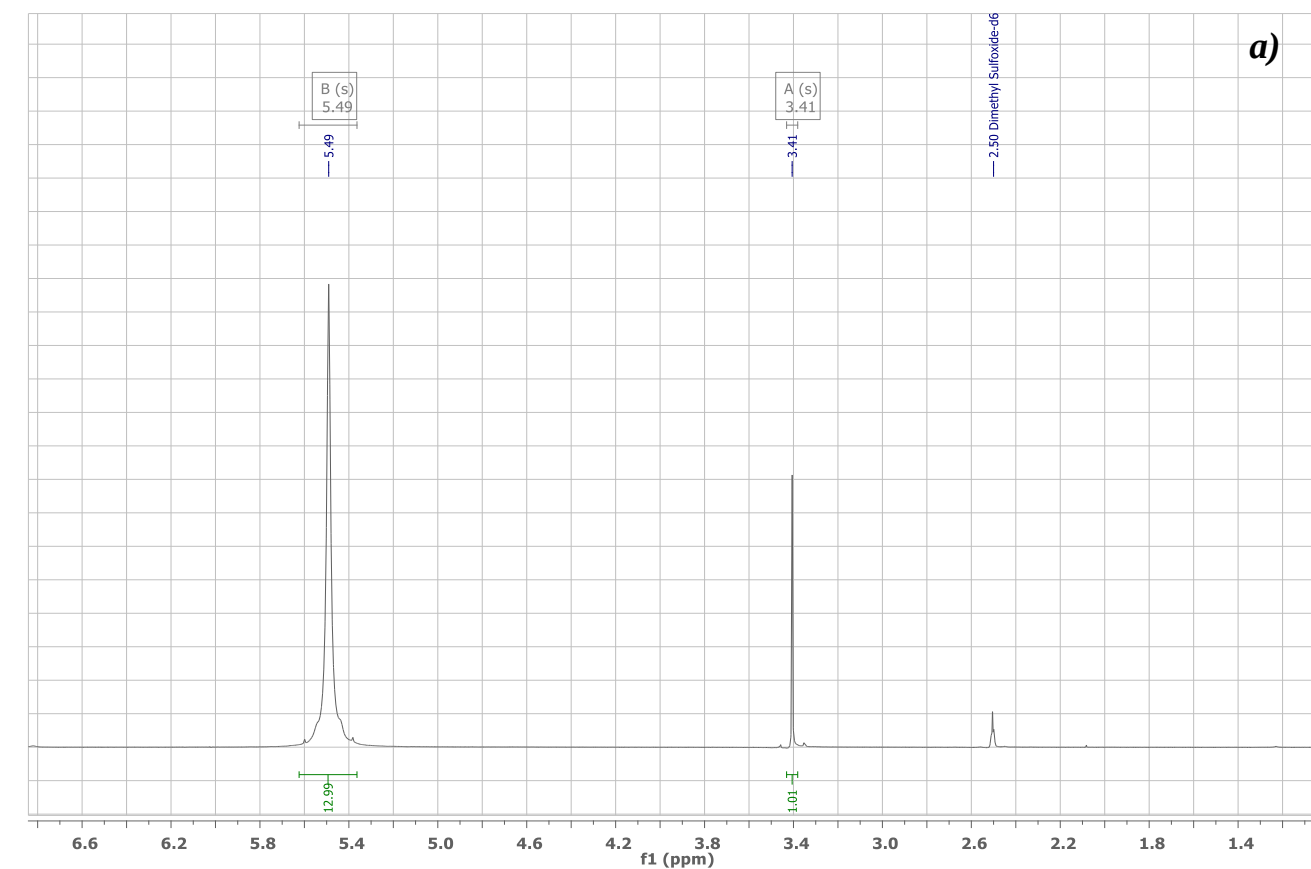


Figure S8: a) ^1H NMR (Dms o d_6 , 400 MHz) spectra of urea. **b)** ^1H NMR (Dms o d_6 , 400 MHz) spectra of [DPTAC][UREA].

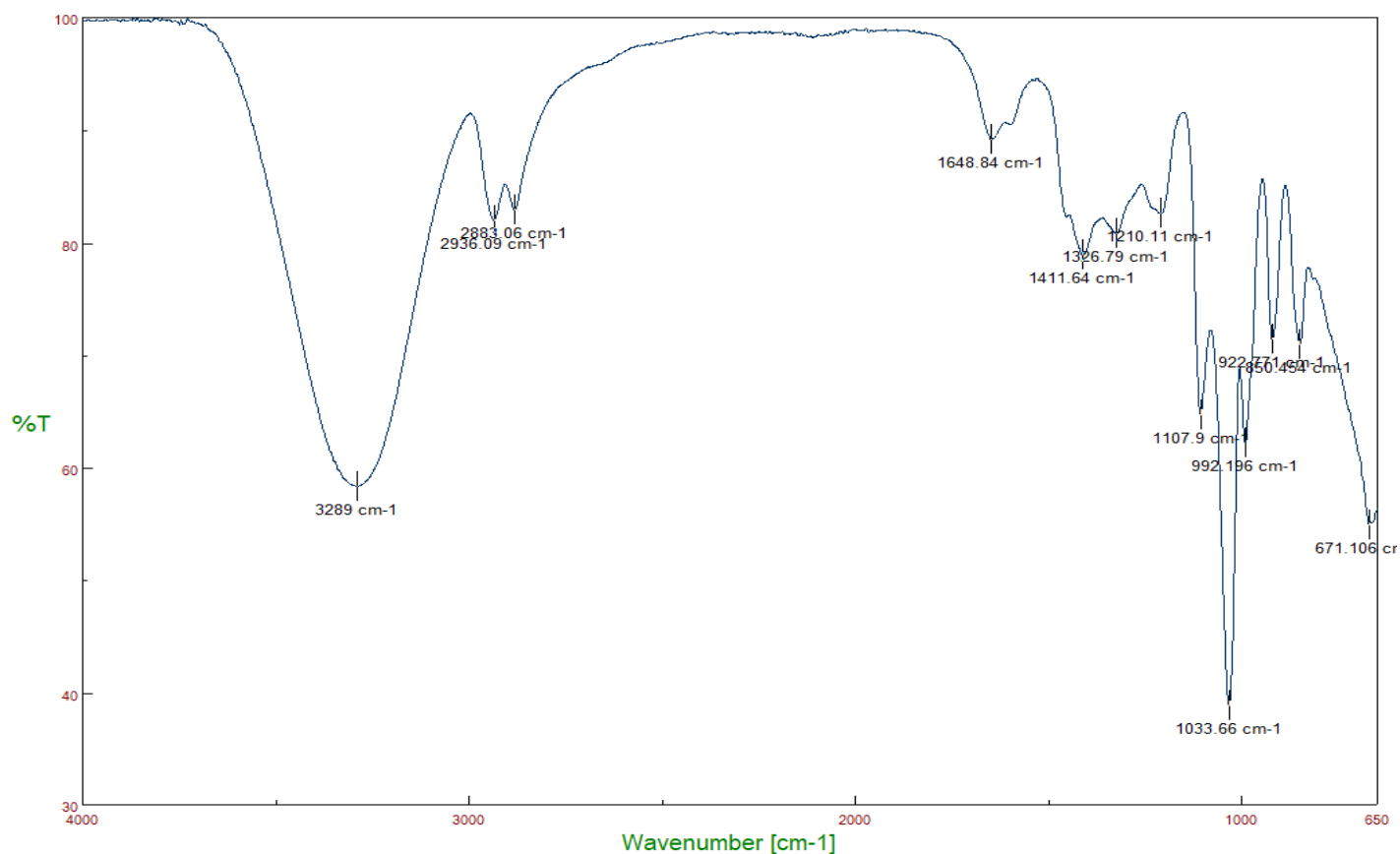
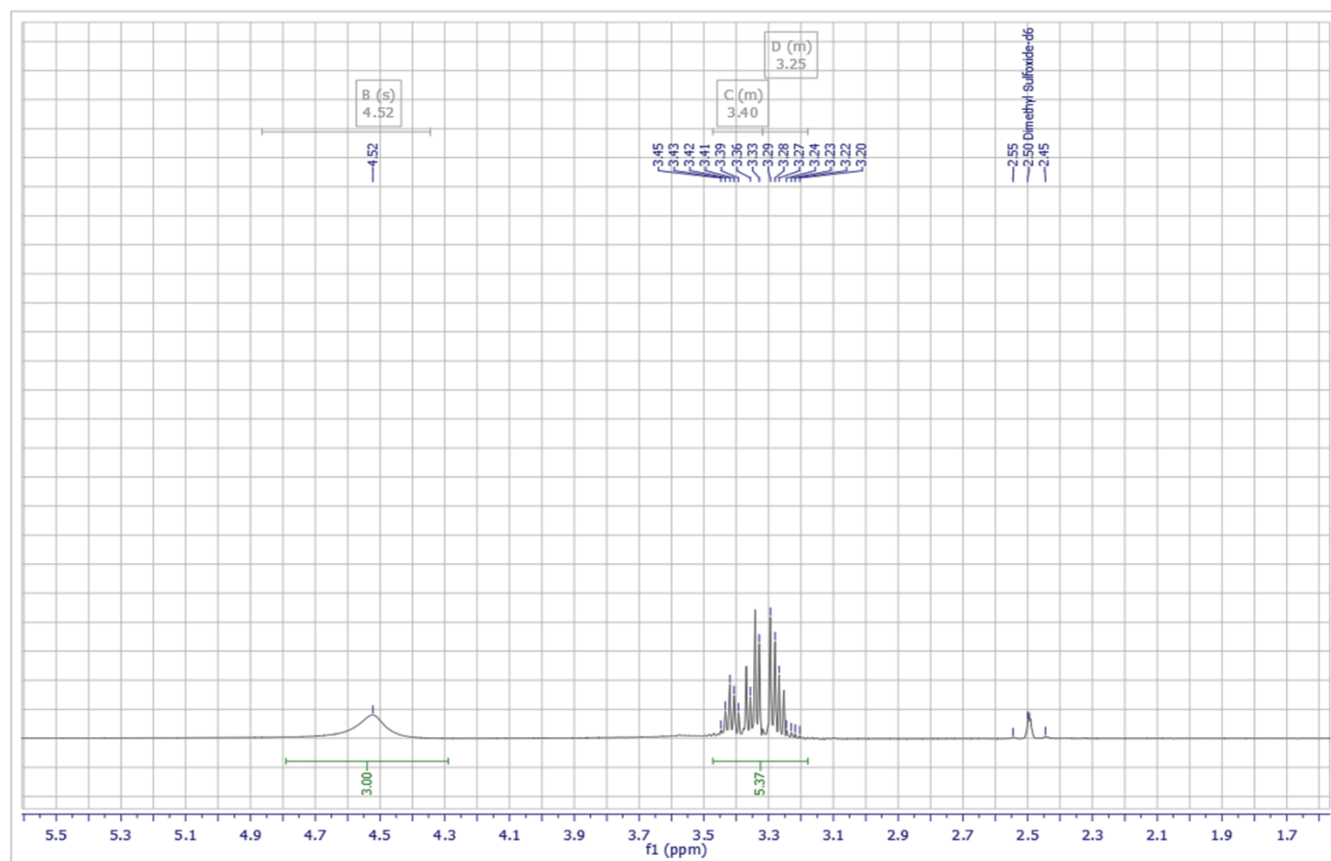


Figure S9: ¹H NMR (DMSO d₆, 400 MHz) spectra of glycerol obtained from fat and FT-IR spectra of glycerol obtained from fat.

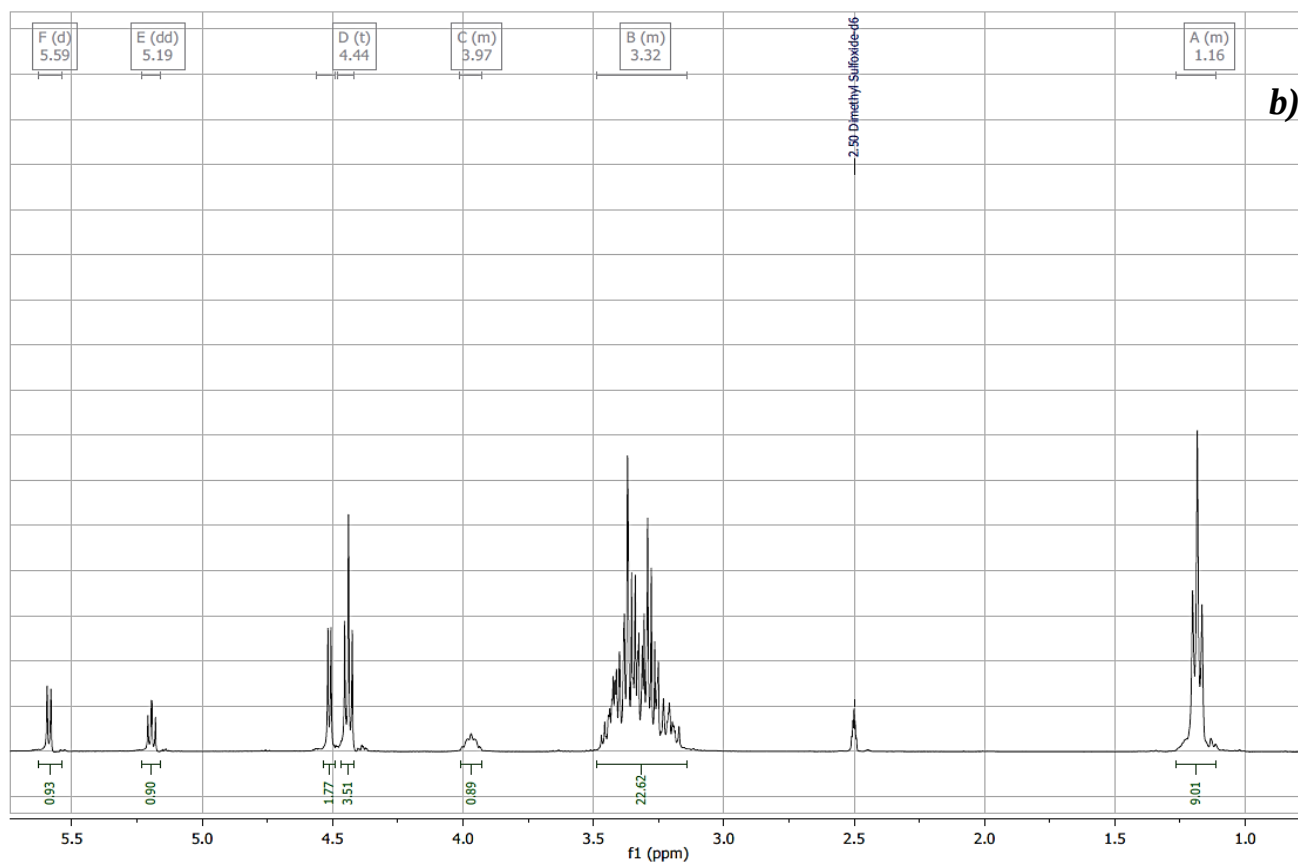
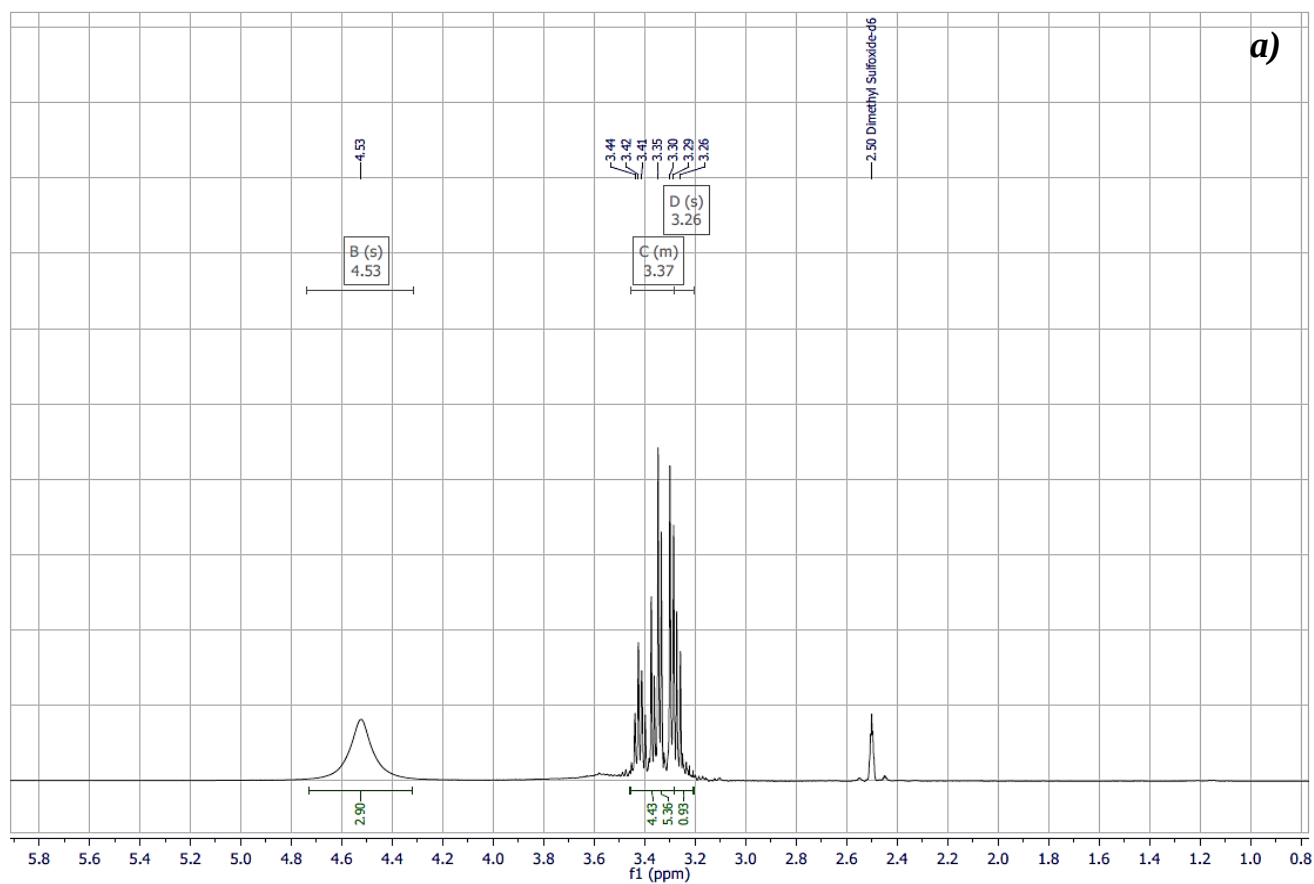


Figure S10: a) ^1H NMR (DmsO d_6 , 400 MHz) spectra of commercial glycerol. **b)** ^1H NMR (DmsO d_6 , 400 MHz) spectra of [DPTAC][GLY].

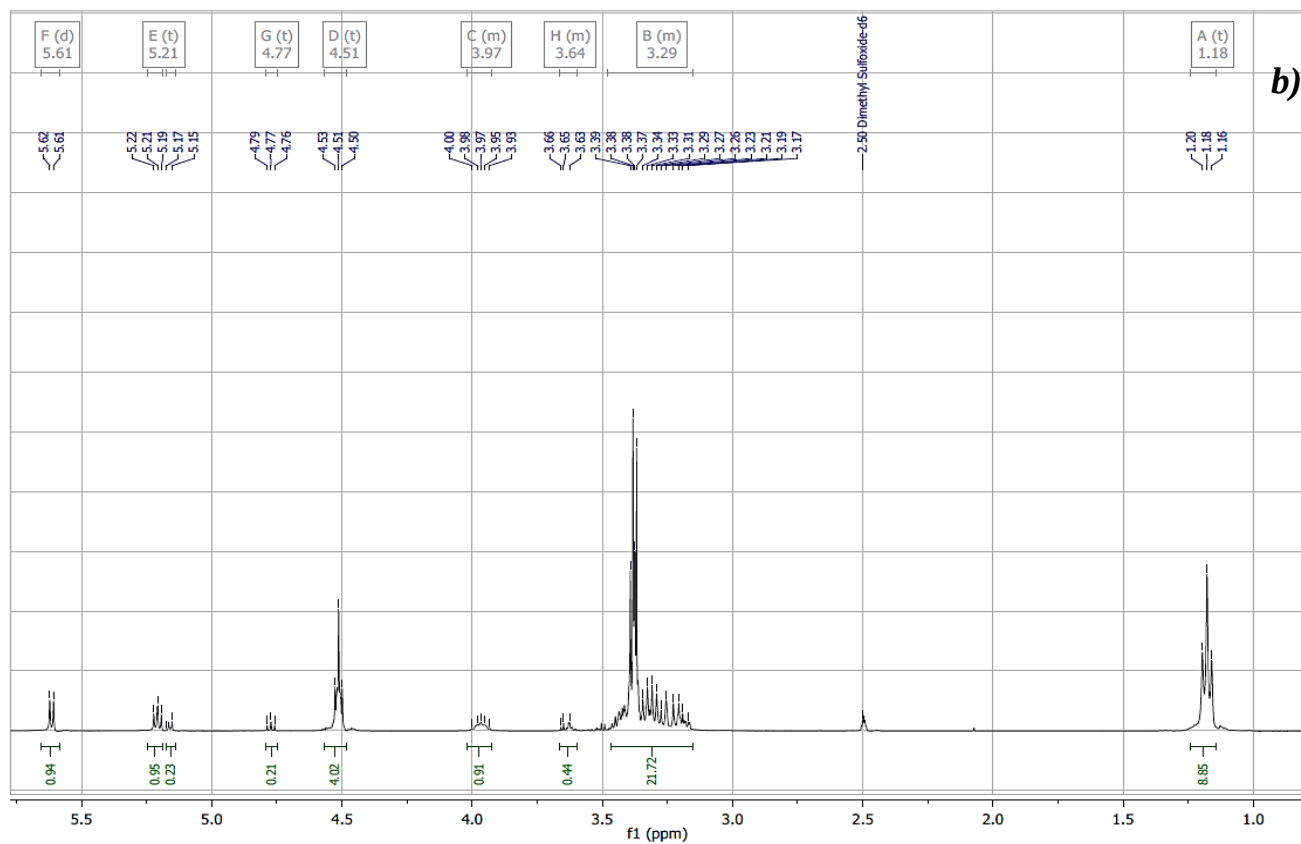
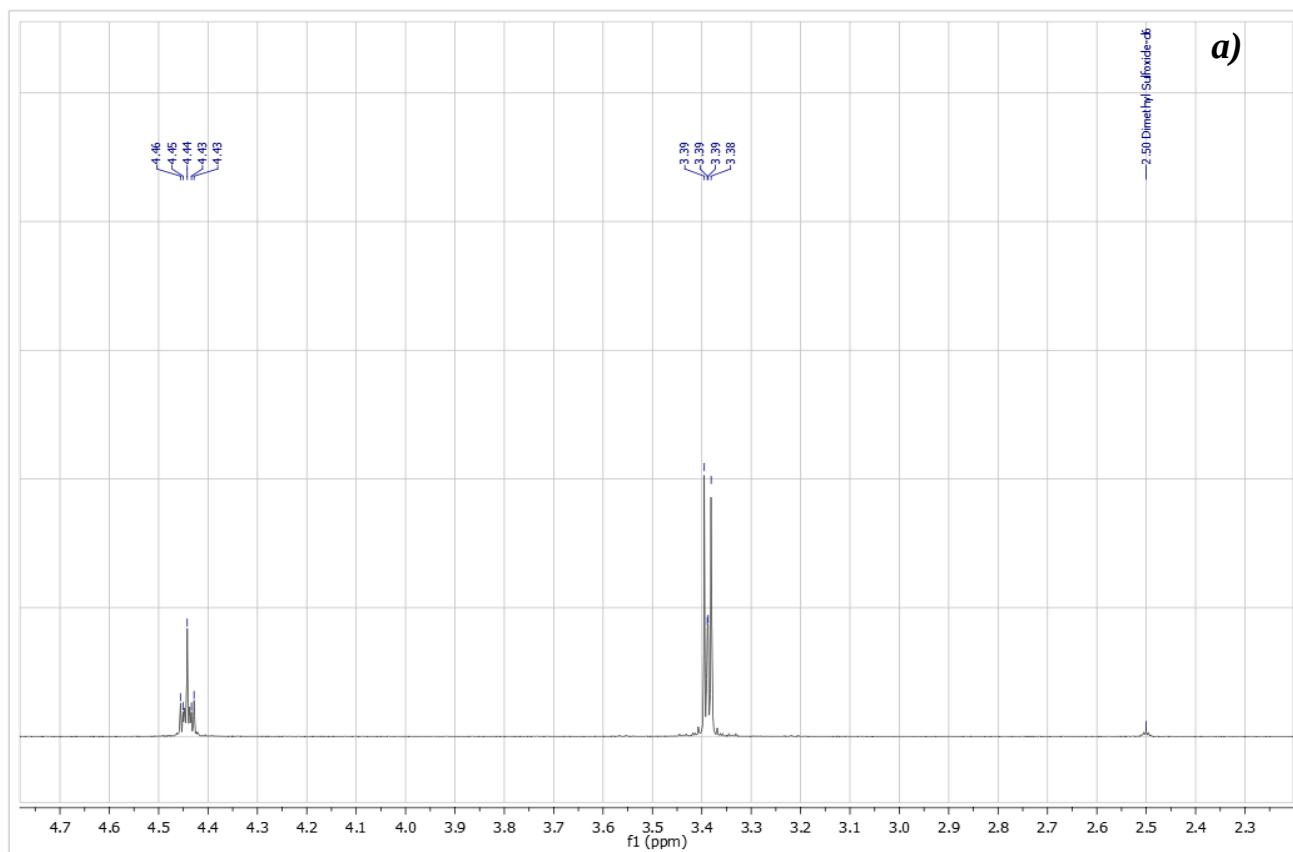


Figure S11: **a)** ^1H NMR (DMSO d_6 , 400 MHz) spectra of ethylene glycol. **b)** ^1H NMR (DMSO d_6 , 400 MHz) spectra of [DPTAC][EG].

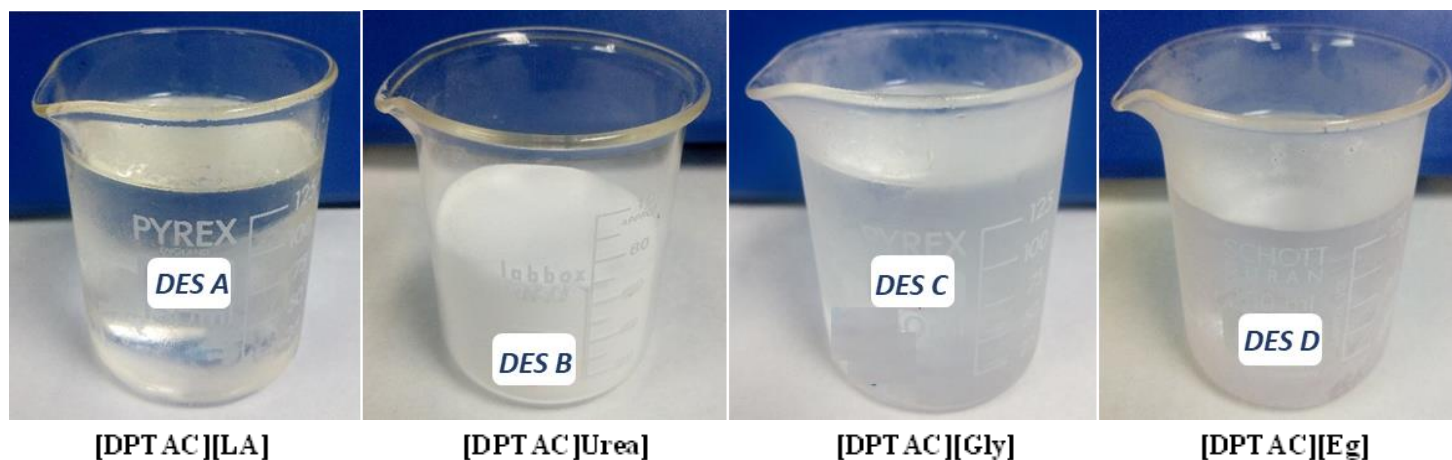


Figure S12: DESs obtained between different hydrogen bond donors with the HBA [1].

Table S1: Peak assignments of the ^1H -NMR spectrum of 2 before and after the formation of each of the eutectic mixtures.

Before eutectic mixture			After eutectic mixture											
2			[DPTAC][LA]			[DPTAC][Urea]			[DPTAC][Gly]			[DPTAC][Eg]		
δ (ppm)	shape	assignments	δ (ppm)	shape	assignments	δ (ppm)	shape	assignments	δ (ppm)	shape	assignments	δ (ppm)	shape	assignments
1.18	t	9H	1.26	m	12H	1.20	t	9H	1.16	t	9H	1.18	T	9H
3.03	q	1H	3.34	m	10H	3.34,	m	18H	3.32	m	22H	3.29	m	22H
3.25	dd	1H	4.02	m	2H	3.95	dd	1H	3.97	m	1H	3.64	m	1H
3.39	m	3H	4.18	m	1H	5.21	t	1H	4.44	t	3H	3.97	m	1H
3.48	dd	3H	4.91	m	1H	5.51	bs	4H	4.51	d	1H	4.51	t	4H
3.56	m	1H										4.77	t	1H
3.63	q	1H												
3.96	m	1H												
5.28	t	OH	5.23	bs	OH	5.61	d	OH	5.19	dd	OH	5.21	t	OH
5.74	d	OH	5.65	bs	OH	5.93	d	OH	5.59	d	OH	5.61	d	OH

Table S2: Band assignments of the FT-IR of 2 before and after the formation of each of the eutectic mixtures.

Before eutectic mixture				After eutectic mixture					
2		[DPTAC][LA]		[DPTAC][Urea]		[DPTAC][Gly]		[DPTAC][Eg]	
cm ⁻¹	group	cm ⁻¹	group	cm ⁻¹	group	cm ⁻¹	group	cm ⁻¹	group
3284.18	(OH)	3331.18	(OH)	3426.89	(N-H)	3296.71	(OH)	3295.75	(OH)
3216.68	(OH)	2986.23	(CH ₃)	3326.61	(N-H)	2933.20	(CH ₂)	2938.98	(CH)
2986.23	(C-H alkyl)	1456.96	(CH ₃)	3255.25	(N-H ₂)	2877.21	(N ⁺ -CH)	2873.42	(CH)
2924.52	(C-H alkyl)	1372.10	(CH ₃)	1154.19	(N-H ₂)	1456.96	(CH ₂)	1456.96	(CH ₂)
2885.92	(N ⁺ CH)	1729.83	(C=O)	1672.95	(C=O)	1395.25	(N-CH ₃)	1395.25	(N-CH ₃)
2817.49	(N ⁺ CH)	1203.36	(C-O)	1457.92	(C-N)	1337.39	(CH ₂)	1256.40	(CH ₂)
1489.74	((CH ₂) ³ -N ⁺)	1124.30	(C-O)	1089.58	(C-N)	1159.97	(C-N)	1159.97	(C-N)
1398.14	(CH ₂ -N)	1042.34	(C-O)	1001.84	(C-N)	1092.48	(C-N)	1085.73	(-C-O)
1373.07	(C-N)			786.81	(H ₂ N-CO)	1110.80	(C-O)	1035.59	(O-C-C-O)
1292.07	(C-N)					1035.59	(C-O)	882.27	(CH ₂)
1163.83	(C-N)					1000.87	((CH ₂) ₃ -N ⁺)	861.06	(C-C)
1087.66	(C-N)					928.55	(C-OH)		
1150.83	(C-O-C)					845.63	(-O-C ₂ H ₄)		
1040.00	(CO)								
1002.8	((CH ₂) ₃ -N ⁺)								
961.34	(C-C)								
937.23	(C-C)								
847.56	(CH)								
793.56	(γ CH ₂)								
703.89	(CH ₂)								

Table S3: Total content of lignocellulosic material in dry samples.

Sample	% hemicellulose	% cellulose	% lignin
Apricot	27	37	14
Plum	10	41	26
Peach	10	40	18
Nectarine	10	41	16
Flat Peach	11	36	28
Olive Pomace	3,4	16	37

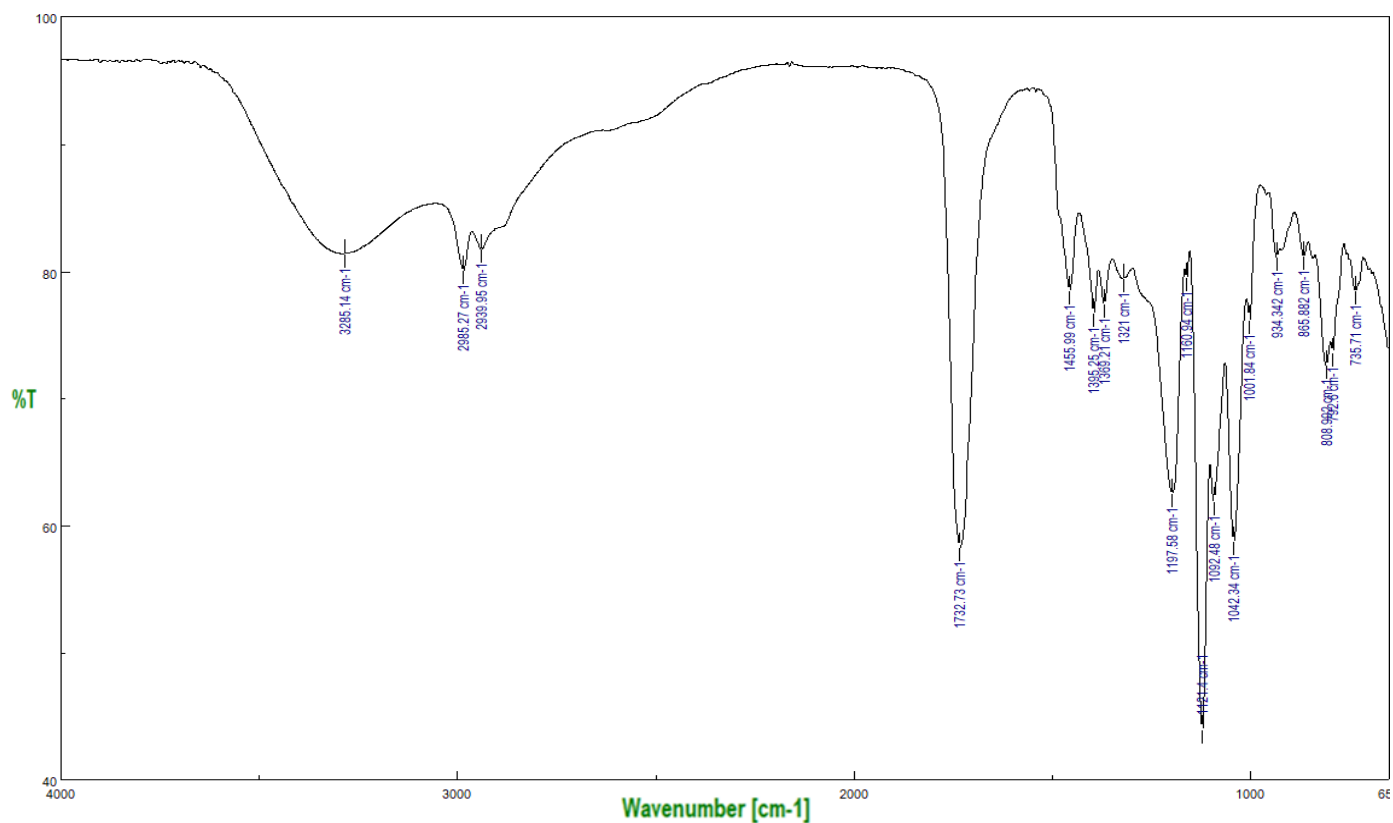


Figure S13: FT-IR spectra of "filtrate 2" fraction from olive pomace using [DPTAC][LA].

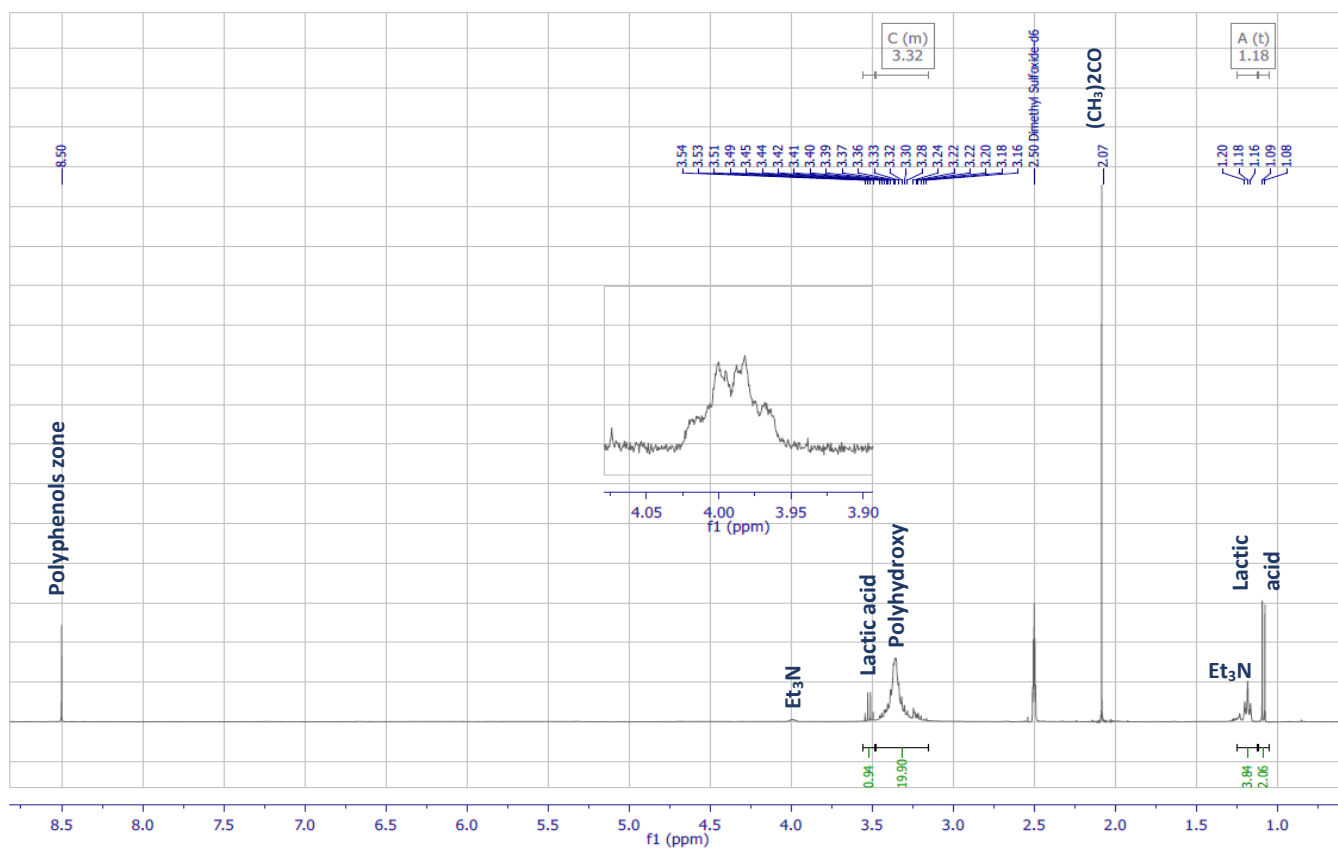


Figure S14: ¹H NMR (DMSO d₆, 400 MHz) spectra of "filtrate 3" fraction from olive pomace using [DPTAC][LA].

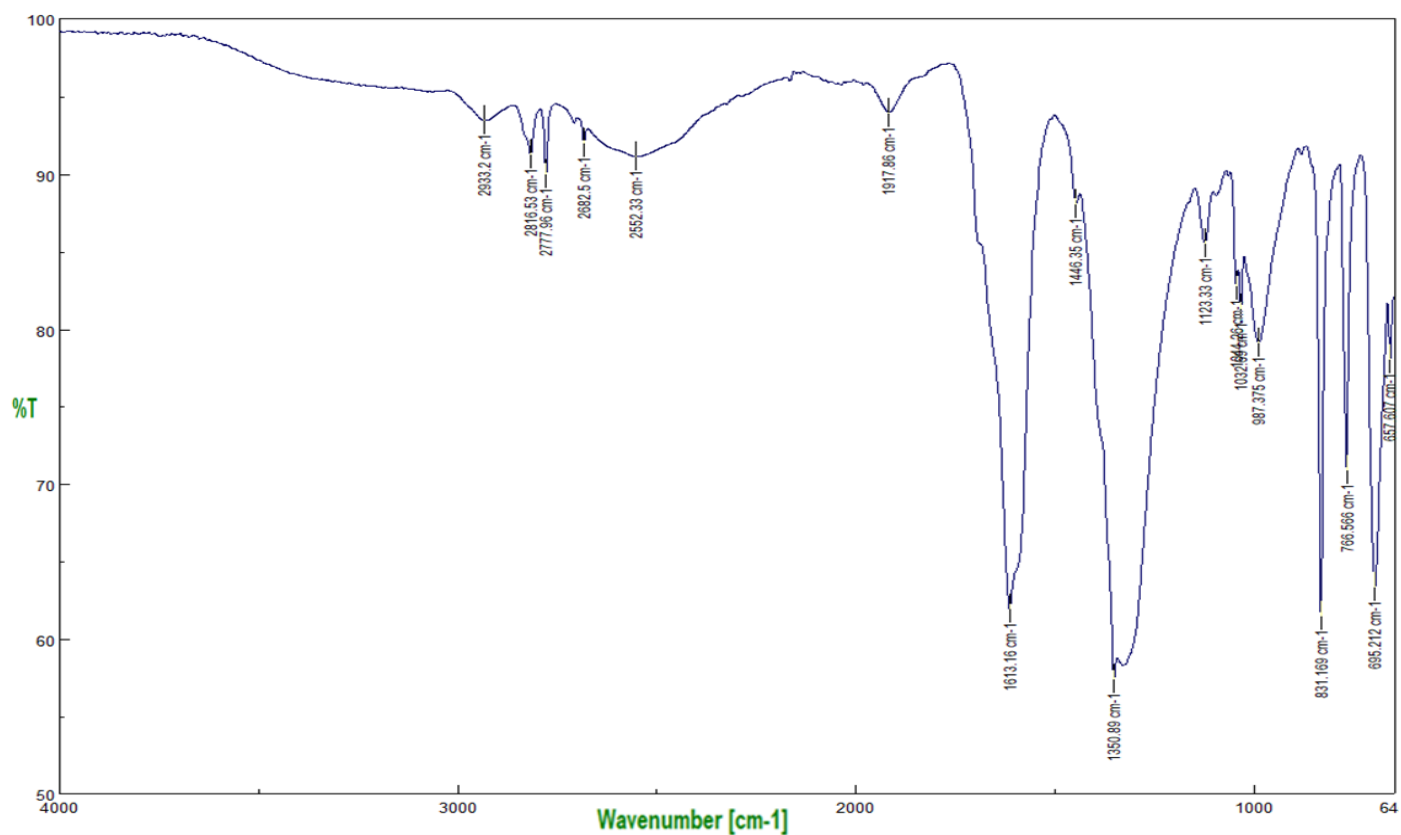


Figure S15: FT-IR spectra of "filtrate 3" fraction from olive pomace using [DPTAC][LA].

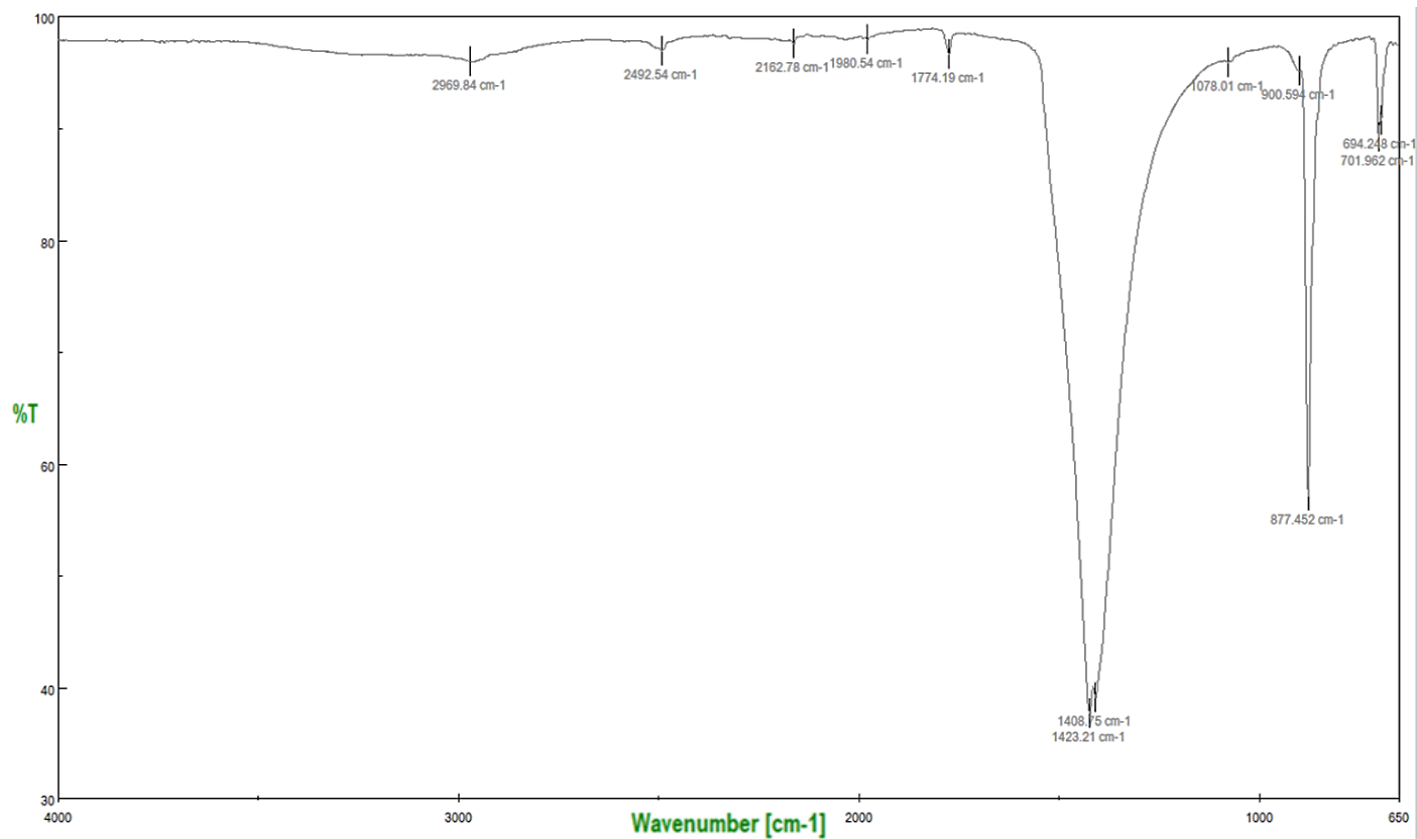


Figure S16: FT-IR spectra of ashes obtained from "filtrate 3" fraction in olive pomace using [DPTAC][LA].

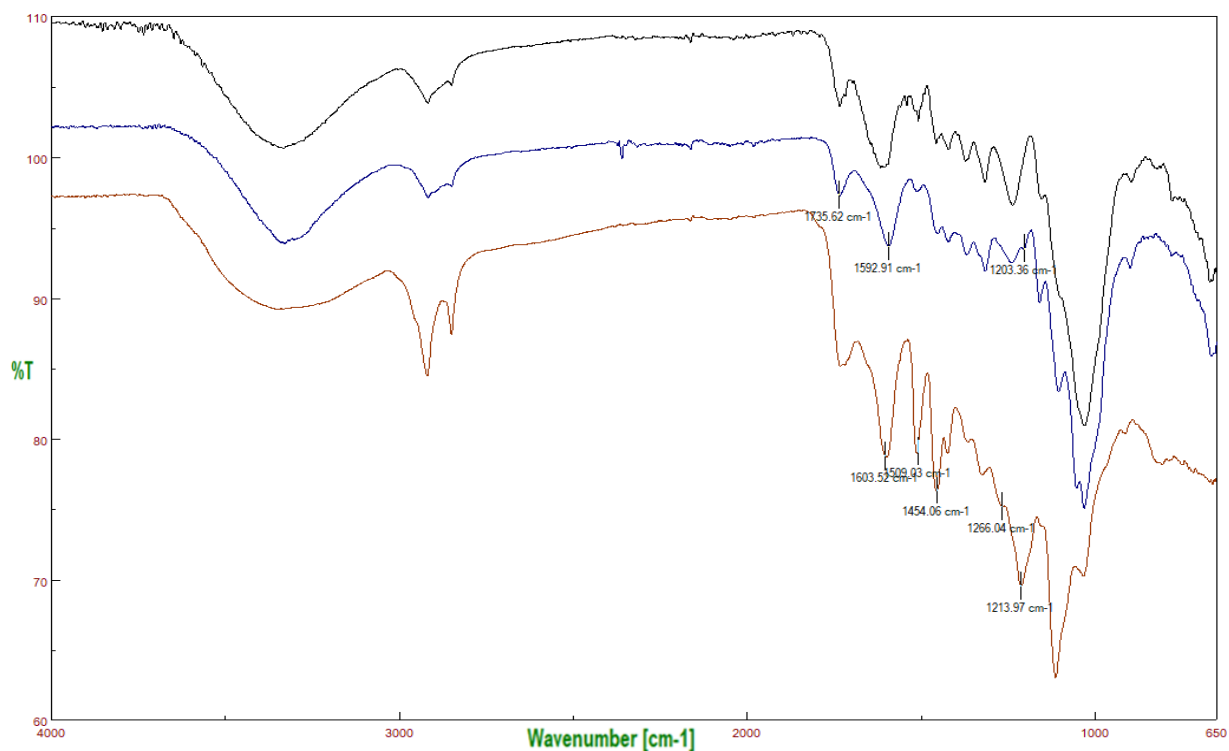


Figure S17: FT-IR spectra of pruning waste of apricot branches tree before treatment (black line), holocellulose-rich fraction (blue line) and extracted lignin (red line) using [DPTAC][LA].

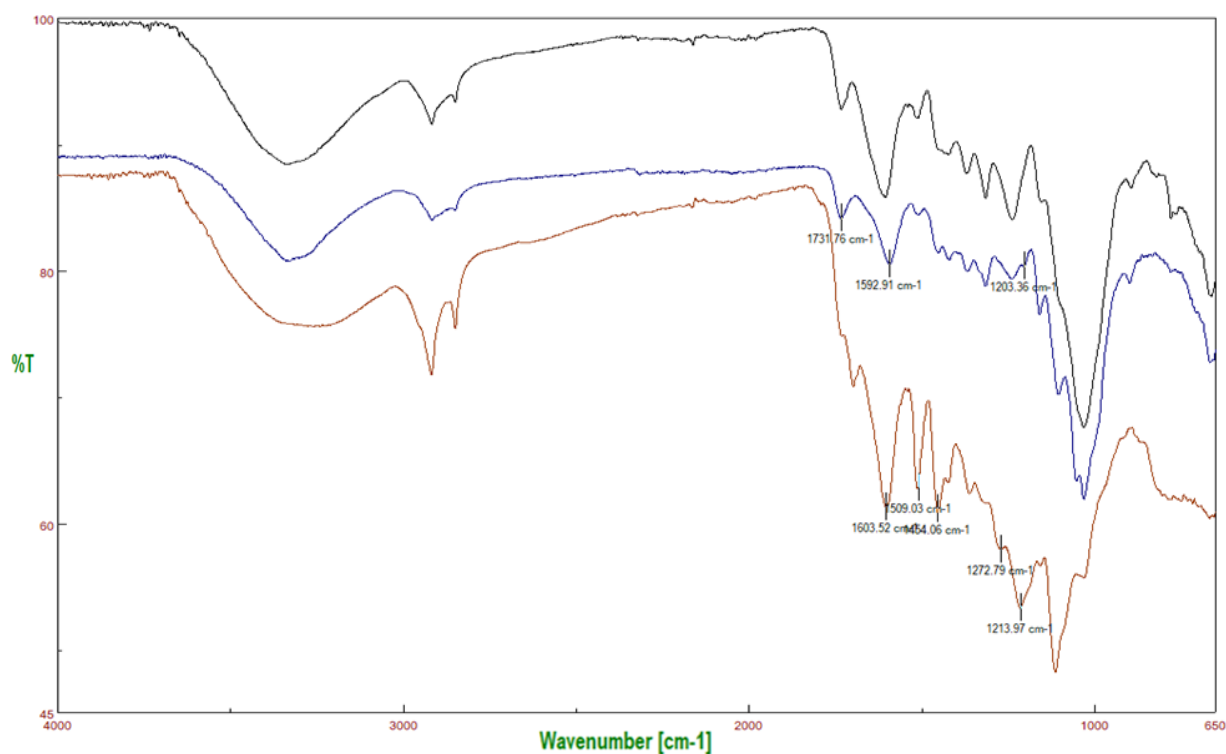


Figure S18: FT-IR spectra of pruning waste of plum branches tree before treatment (black line), holocellulose-rich fraction (blue line) and extracted lignin (red line) using [DPTAC][LA].

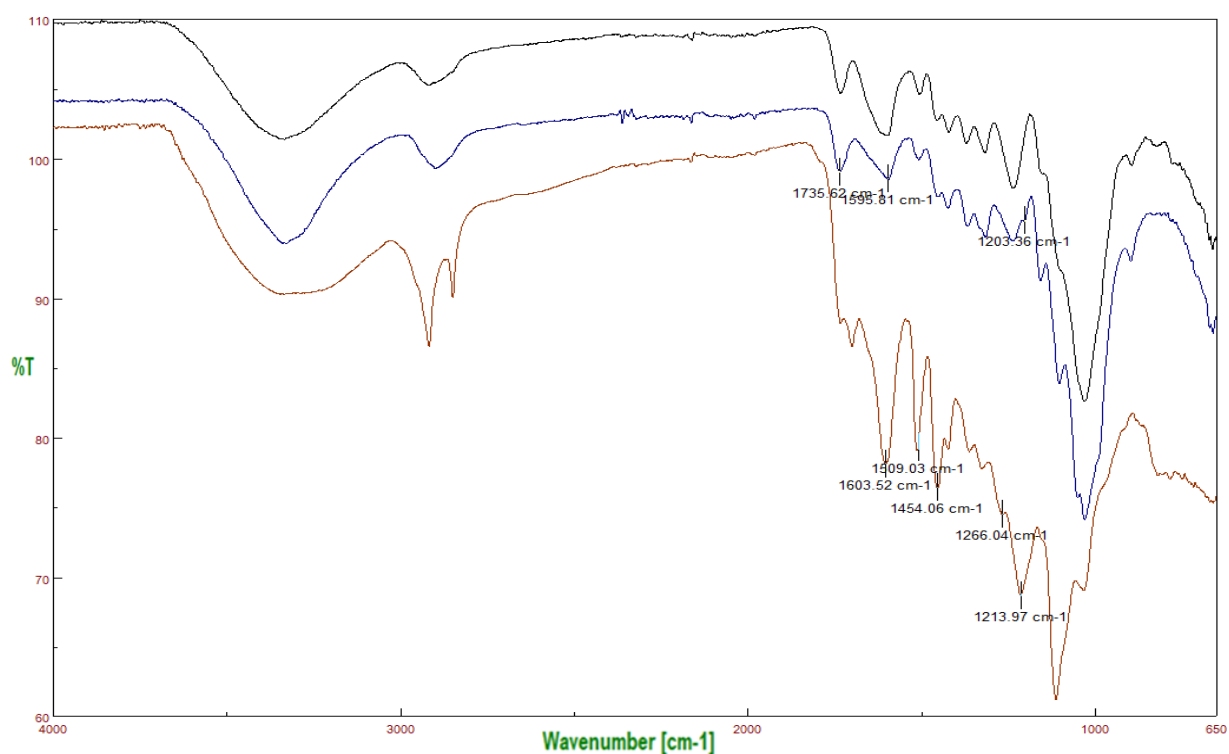


Figure S19: FT-IR spectra of pruning waste of peach branches tree before treatment (black line), holocellulose-rich fraction (blue line) and extracted lignin (red line) using [DPTAC][LA].

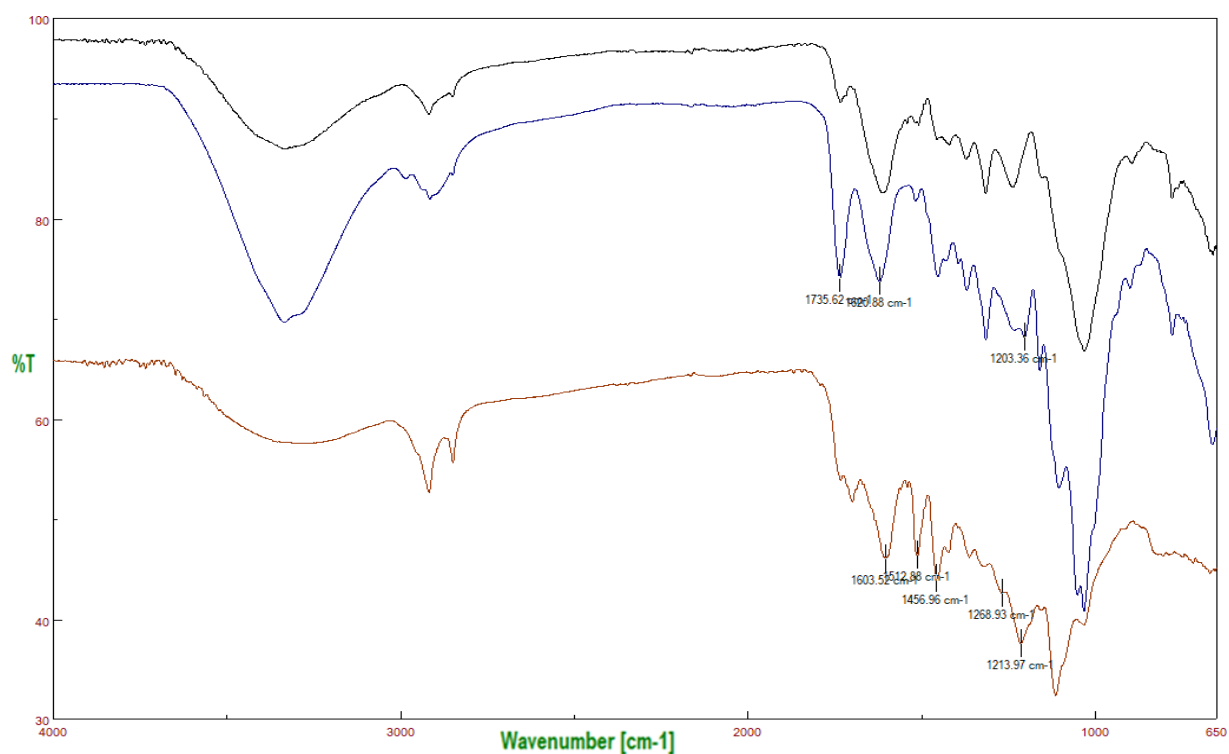


Figure S20: FT-IR spectra of pruning waste of nectarine branches tree before treatment (black line), holocellulose-rich fraction (blue line) and extracted lignin (red line) using [DPTAC][LA].

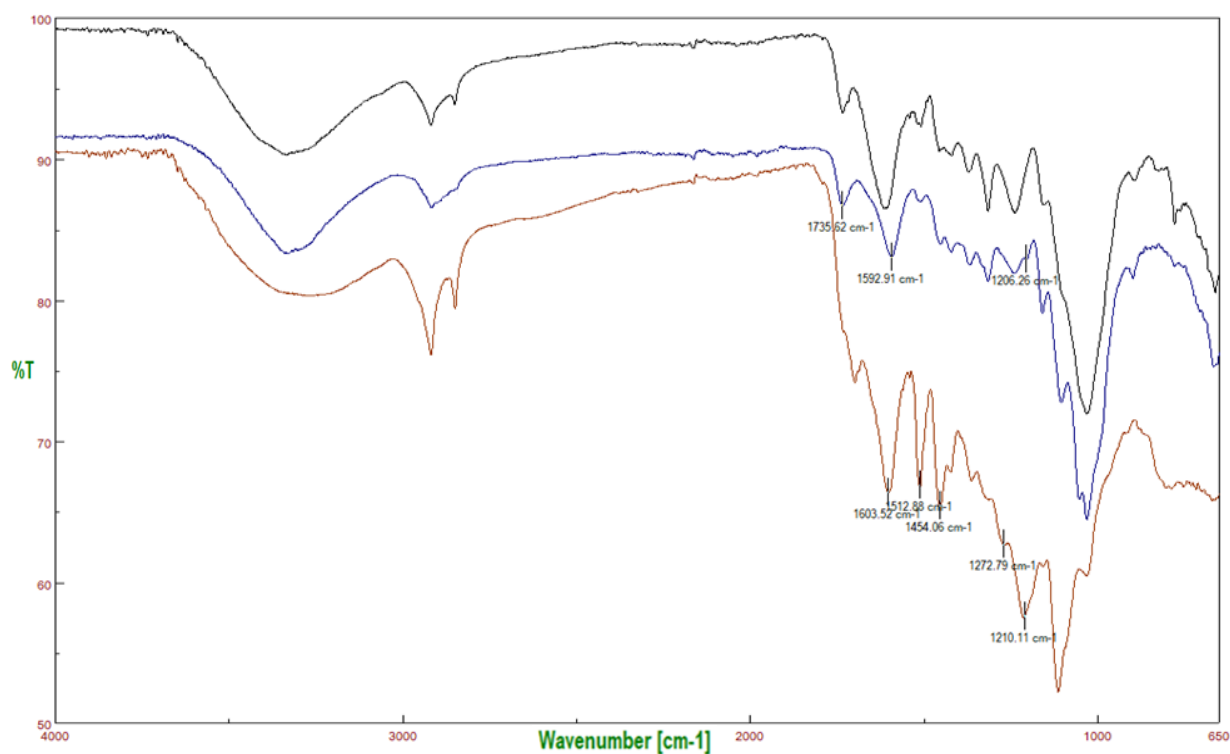


Figure S21: FT-IR spectra of pruning waste of flat peach branches tree before treatment (black line), holocellulose-rich fraction (blue line) and extracted lignin (red line) using [DPTAC][LA].

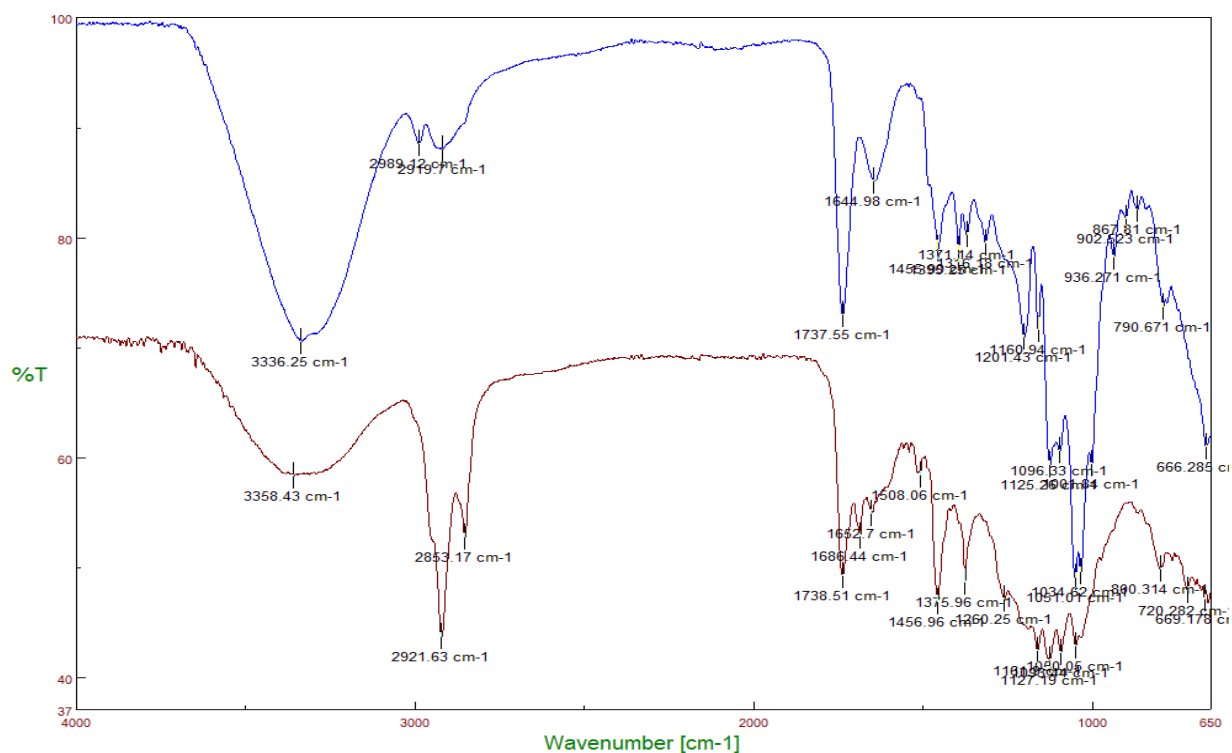


Figure S22: FT-IR spectra of holocellulose-rich fraction (blue line) and lignin (red line) obtained from olive pomace using [DPTAC][LA] extracted at 150°C.

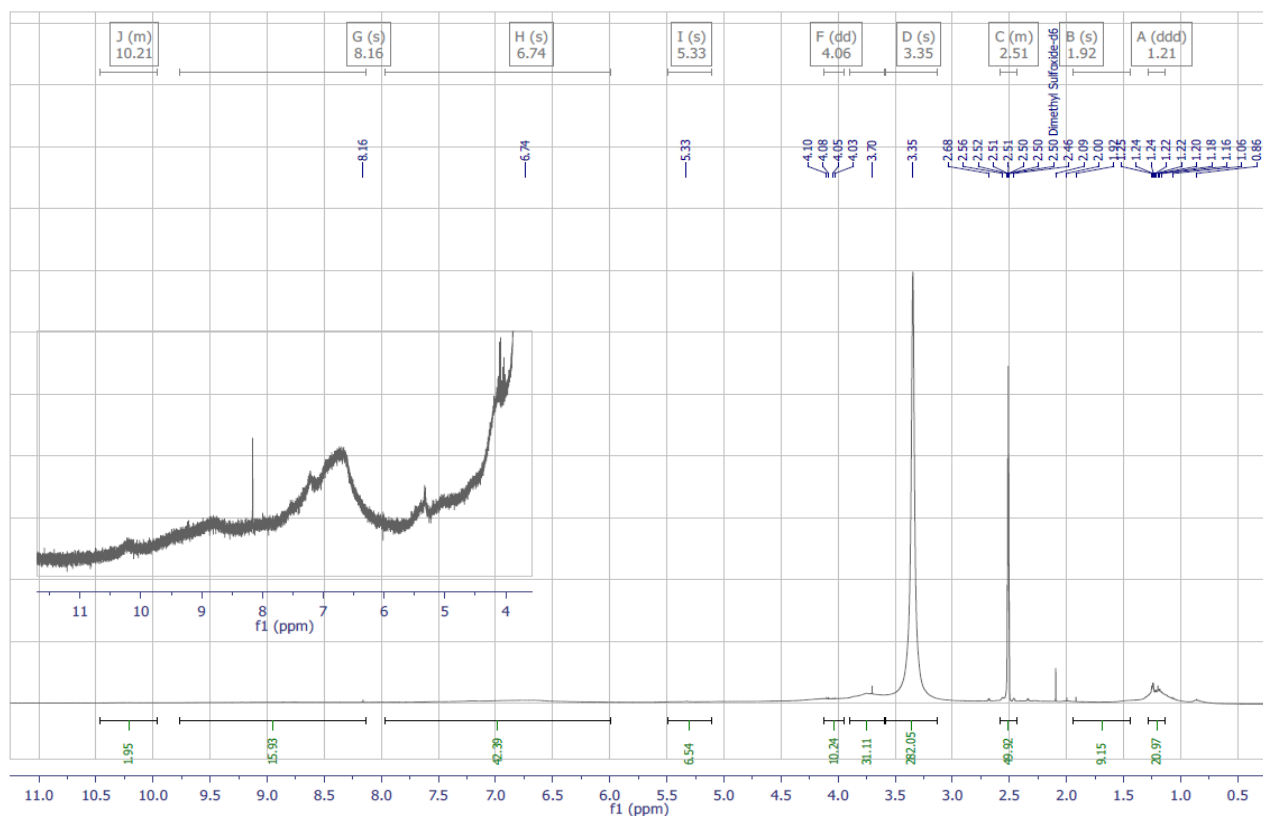


Figure S23. ^1H NMR (DMSO d_6 , 400 MHz) spectra of lignin fraction obtained from olive pomace using [DPTAC][LA].

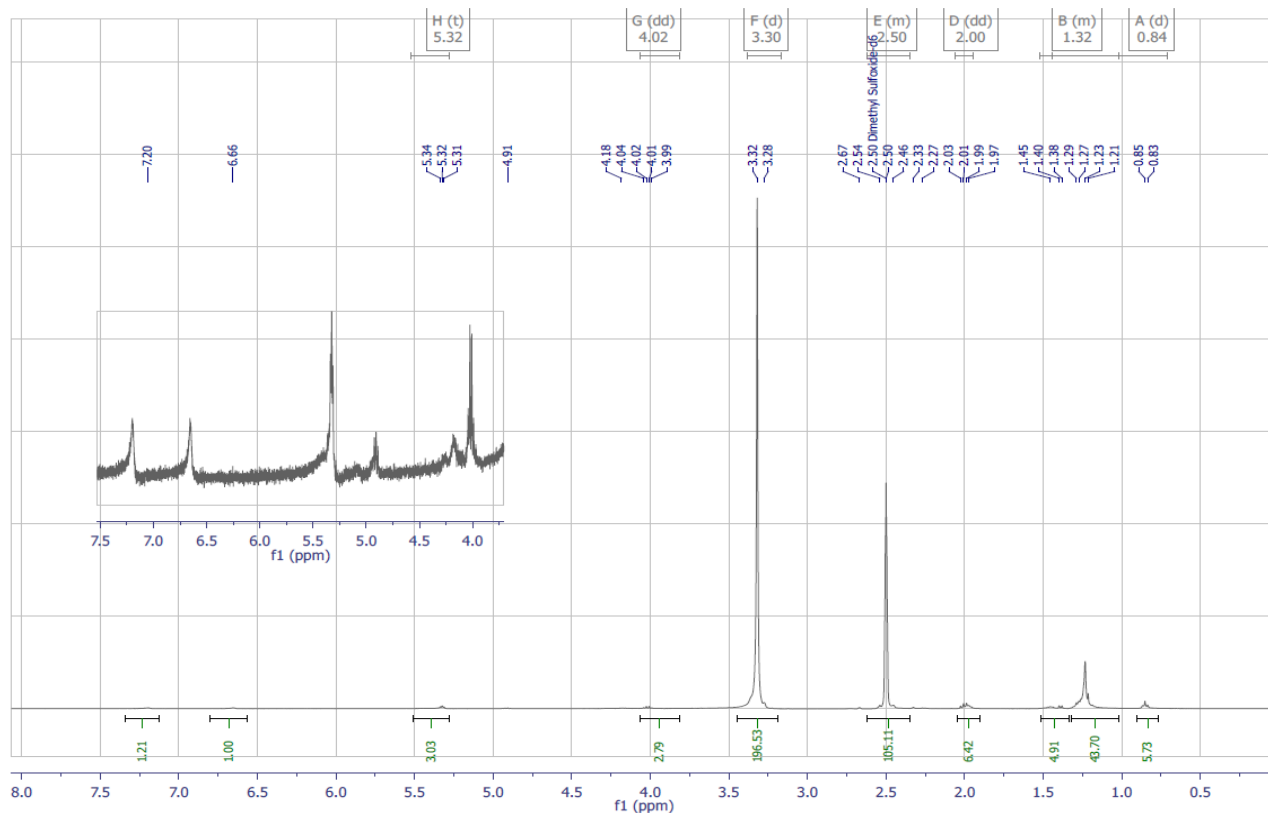


Figure S24. ^1H NMR (DMSO d_6 , 400 MHz) spectra of lignin fraction obtained from olive pomace using [DPTAC][UREA].

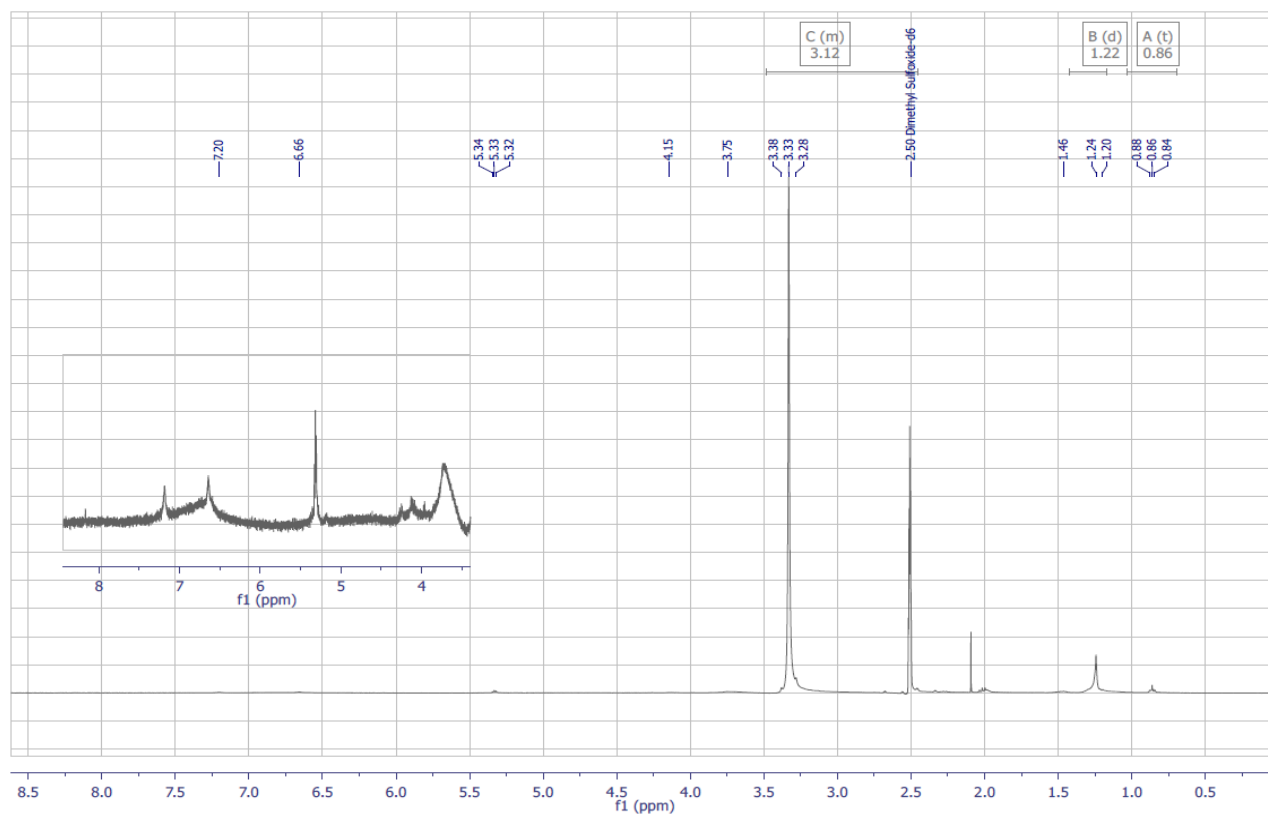


Figure S25: ^1H NMR (DMSO d_6 , 400 MHz) spectra of lignin fraction obtained from olive pomace using [DPTAC][GLY].

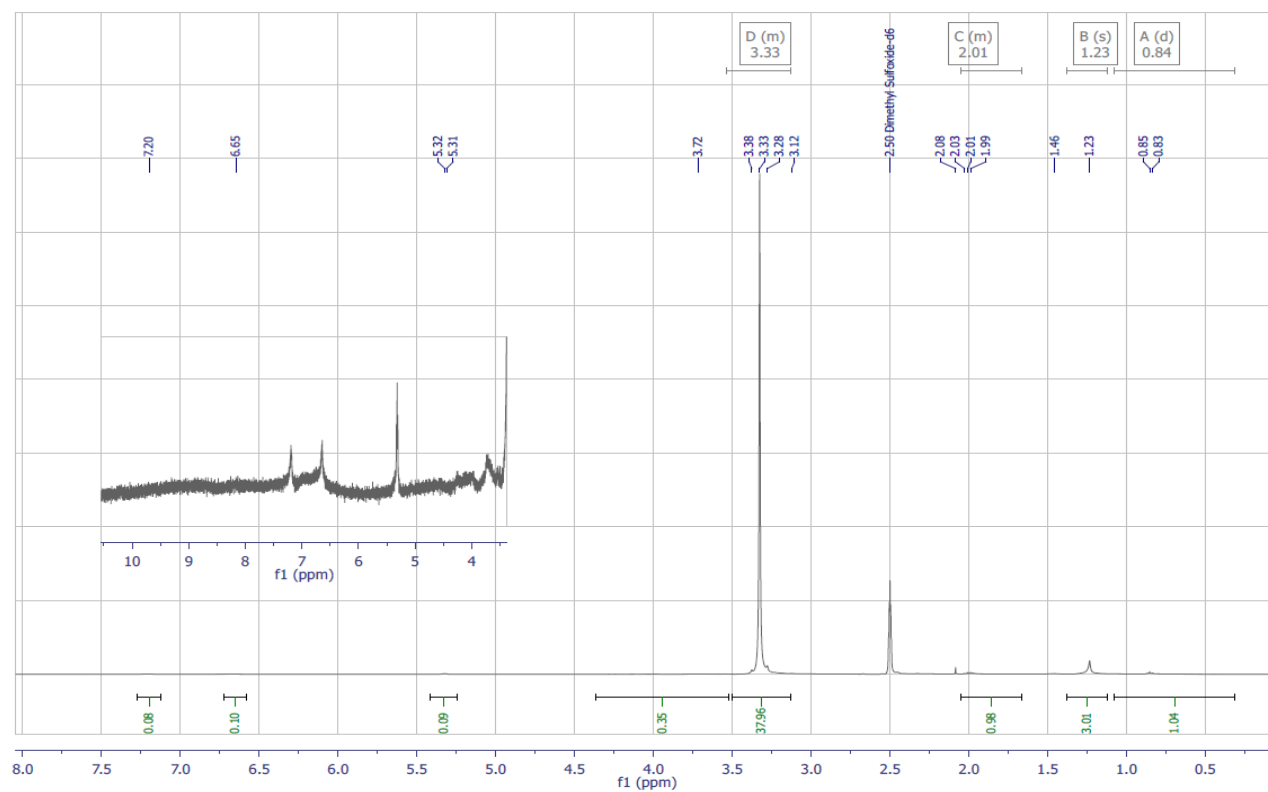


Figure S26: ^1H NMR (DMSO d_6 , 400 MHz) spectra of lignin fraction obtained from olive pomace using [DPTAC][EG].

Table S4: Molecular weight (Mw) and polydispersity index (PDI) of lignin determined by GPC (Gel permeation chromatography) in hardwood samples

Sample	DES/IL	Mw	PDI
Apricot	[DPTAC][LA].	30986	2,4
Plum	[DPTAC][LA].	45192	2,5
Peach	[DPTAC][LA].	57771	2,6
Nectarine	[DPTAC][LA].	39955	2,3
Flat Peach	[DPTAC][LA].	41979	2,3
Olive Pomace	[DPTAC][LA].	20486	2,4
Olive Pomace	IL	113677	6,3