Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

SUPPLEMENTARY INFORMATION

Conversion of Organosolv and Kraft lignins into value-added compounds assisted by an acidic deep eutectic solvent

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S1 – 2D HSQC NMR characterization of initial Kraft and Organosolv lignins

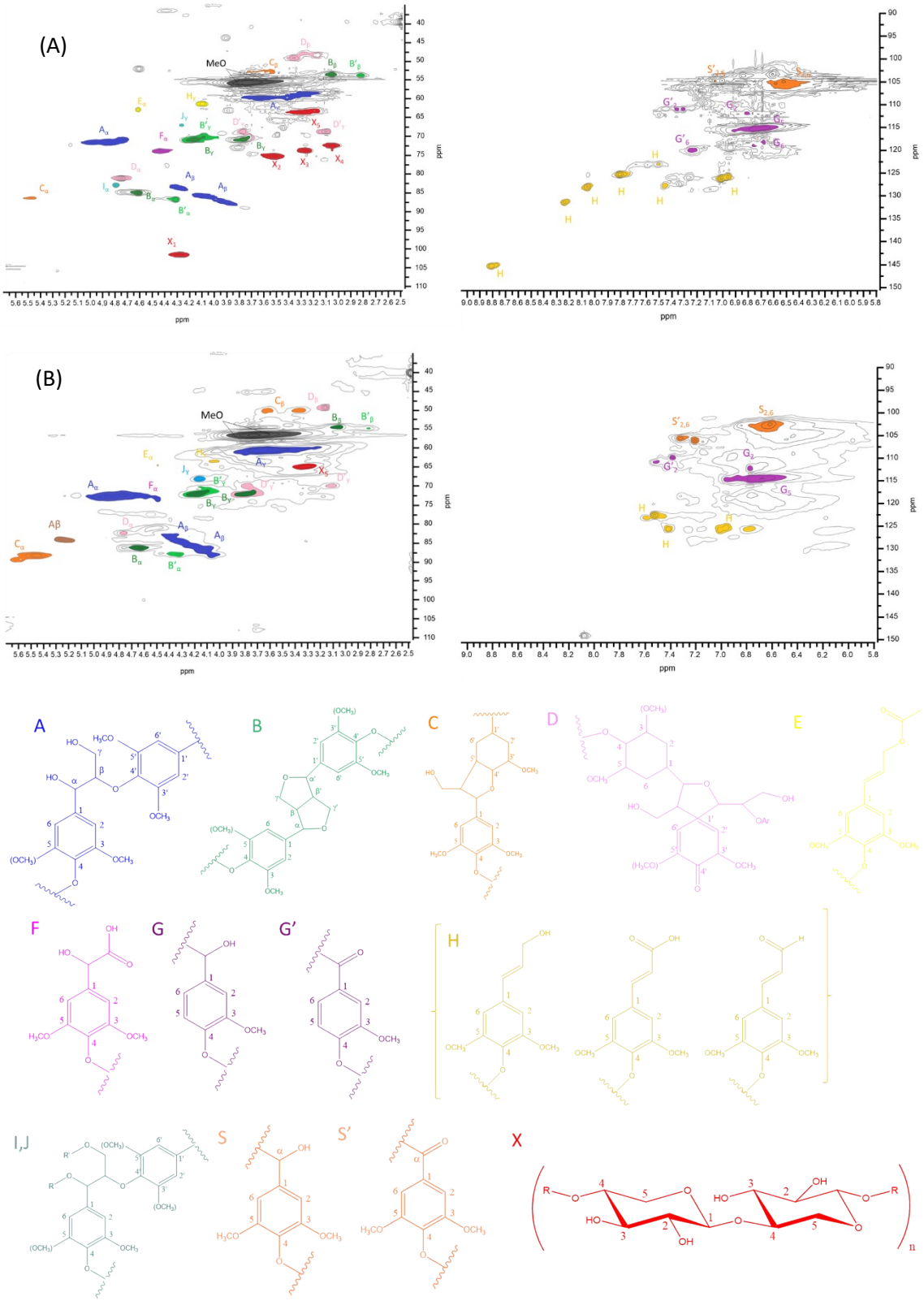


Figure S1. 2D HSQC NMR spectra of (A) Kraft lignin and (B) Organosolv Lignin with corresponding assignments of lignin substructures.

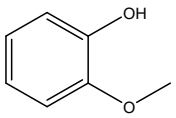
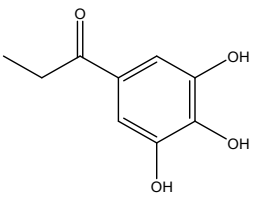
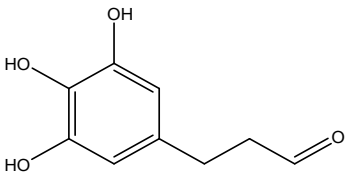
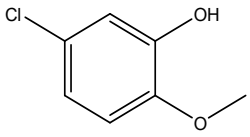
Table S1. Assignments of main lignin ^{1}H-^{13}C correlation signals found in the HSQC spectra.

Labels	δC	δH	Assignment
Dβ	49.61	3.39	C_β-H_β in β-1' spirodienone substructures (D)
Bβ	53.50	3.07	C_β-H_β in resinol substructures (B)
Cβ	53.71	3.46	C_β-H_β in β-5 phenylcoumaran
B'β	54.20	2.82	C_β-H_β in epiresinol substructures (B)
MeO	56.06	3.75	C-H in methoxyls
Aγ	59.00	3.2	C_γ-H_γ in β-O-4' substructures (A)
Aγ	59.87	3.71	C_γ-H_γ in β-O-4' substructures (A)
Hγ	61.59	4.11	C_γ-H_γ in p-hydroxycynnamyl alcohol
Eα	63.16	4.64	C_α-H_α in p-hydroxycinnamyl alcohol
Cγ	63.26	3.89	C_γ-H_γ in β-5 phenylcoumaran
X5	63.63	3.28	C_5-H_5 in xylan
Jγ	66.88	4.28	C_γ-H_γ in β-O-4' Cα- etherified with carbohydrate
Dγ'	68.89	3.79	C_γ-H_γ in β-1' spirodienone substructures (D)
Dγ'	68.92	3.13	C_γ-H_γ in β-1' spirodienone substructures (D)
B'β	70.56	4.09	C_β-H_β in epiresinol substructures (B)
Bγ	71.07	3.79	C_γ-H_γ in resinol substructures (B)
Bγ	71.14	4.2	C_γ-H_γ in resinol substructures (B)
Aα	71.62	4.91	C_α-H_α in β-O-4' substructures (A)
X4	72.85	3.06	C_4-H_4 in xylan
Fα	74.18	4.43	C_α-H_α in Ar-CHOH-COOH unit
X3	74.28	3.28	C_3-H_3 in xylan
X2	75.84	3.53	C_2-H_2 in xylan
B'α	81.36	4.78	C_α-H_α in epiresinol substructures (B)
Cα	82.92	5.51	Cα-Hα in β-5 phenylcoumaran
Iα	83.41	4.83	Cα-Hα in β-O-4' Cα- etherified with carbohydrate
Aβ	83.96	4.31	(G) CβHβ in β-O-4' linked to G units
Aβ	83	5.2	Cβ−Hβ in β-O-4′ substructures
Bα	85.3	4.67	C_α-H_α in resinol substructures (B)
Dβ'	86.89	4.44	C_β-H_β in β-1' spirodienone substructures (D)
B'α	87.22	4.33	C_α-H_α in epiresinol substructures (B)
Aβ	87.23	3.69	(S) C_β-H_β in β-O-4' linked to S units

X1	101.8	4.29	C_1-H_1 in xylan
S'2.6	104.88	7.07	$C_{2.6}$ - $H_{2.6}$ in oxidized Syringyl units (S')
S2.6	105.22	6.47	$C_{2.6}$ - $H_{2.6}$ in Syringyl units (S)
G2	111.00	6.95	C_2-H_2 in Guaiacyl units (G)
G2'	111.04	7.33	C_2-H_2 in oxidized Guaiacyl units (G)
G5	115.00	6.75	C_5-H_5 in Guaiacyl units (G)
G6	119.00	6.75	C_6-H_6 in Guaiacyl units (G)
G6'	120.14	7.24	C_6-H_6 in oxidized Guaiacyl units (G)
H	122.98	7.56	Cynnamyl alcohols. aldehydes or acids (aromatic and end groups)
H	125.53	7.79	Cynnamyl alcohols. aldehydes or acids (aromatic and end groups)
H	126.16	4.00	Cynnamyl alcohols. aldehydes or acids (aromatic and end groups)
H	127.01	7.35	Cynnamyl alcohols. aldehydes or acids (aromatic and end groups)
H	128.42	8.09	Cynnamyl alcohols. aldehydes or acids (aromatic and end groups)
H	131.29	8.23	Cynnamyl alcohols. aldehydes or acids (aromatic and end groups)
H	145.73	8.8	Cynnamyl alcohols. aldehydes or acids (aromatic and end groups)

S2 – Characterization of lignin depolymerized fraction

Table S2. Main compounds identified in the GC-MS.

Entry	Molecular structure	Entry	Molecular structure
1		**2**	
3		**4**	

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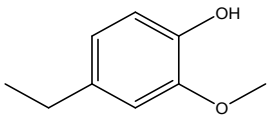

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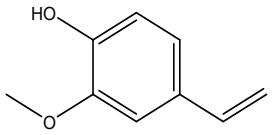

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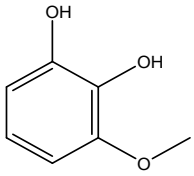

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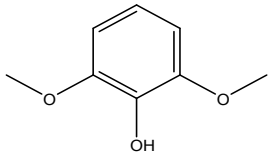

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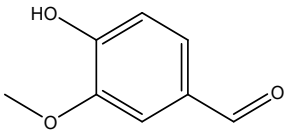

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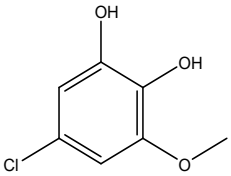

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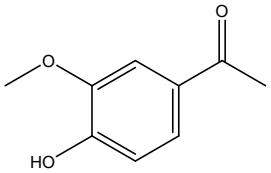

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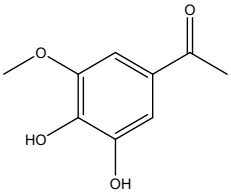

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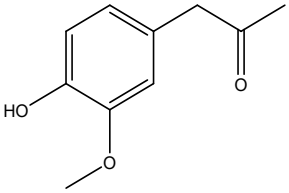

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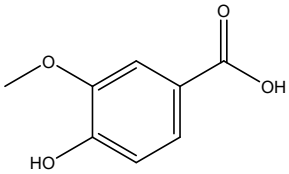

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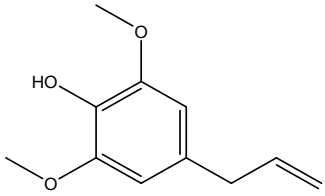

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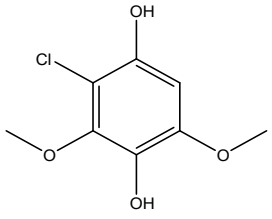

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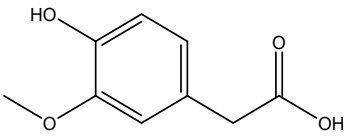

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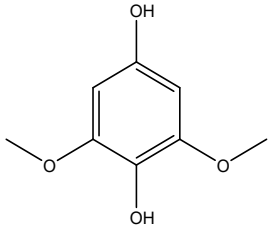

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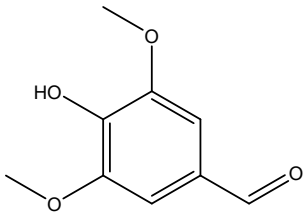

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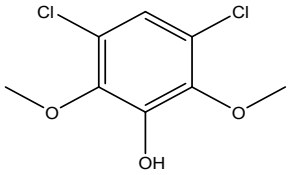

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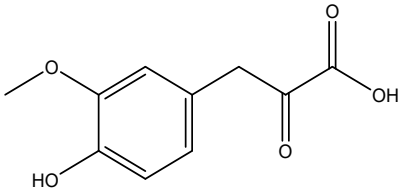

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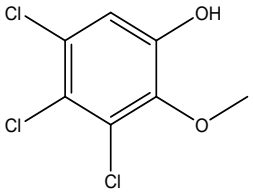

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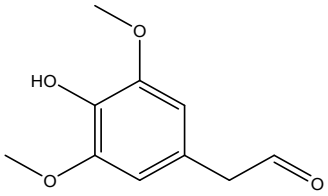

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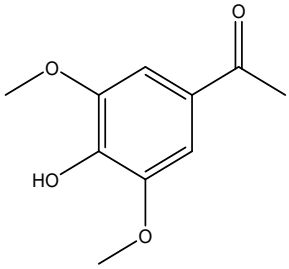

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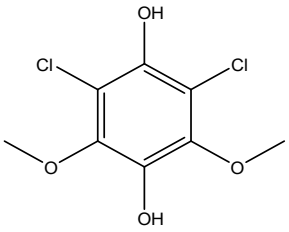

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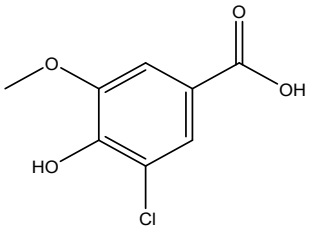

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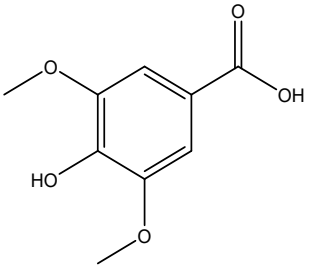

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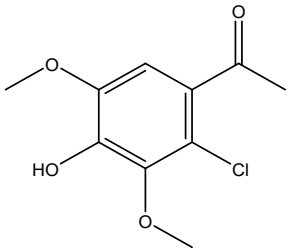

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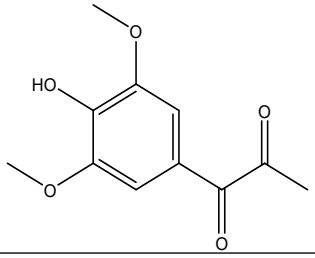

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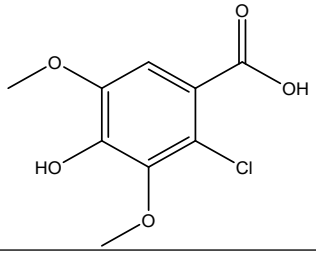

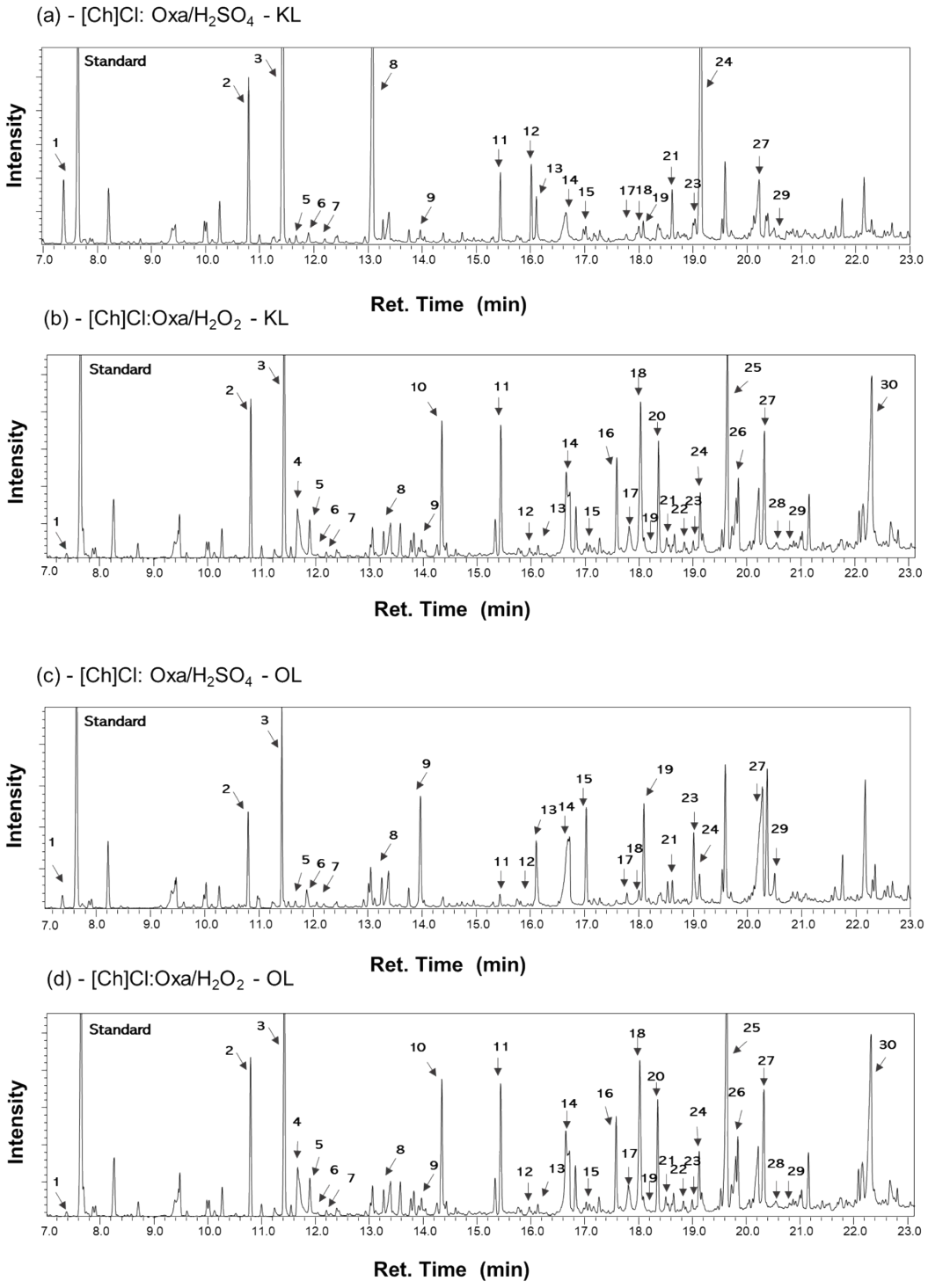

Figure S2. Gas chromatogram of lignin depolymerisation products obtained after treatment of Kraft lignin with (a) [Ch]Cl:Oxa/H_2SO_4 and (b) [Ch]Cl:Oxa/H_2O_2 and Organolsolv lignin with (c) [Ch]Cl:Oxa/H_2SO_4 and (d) [Ch]Cl:Oxa/H_2O_2. The reactions were performed at 80 ºC for 3 h. Methyl benzoate was used as a standard compound.

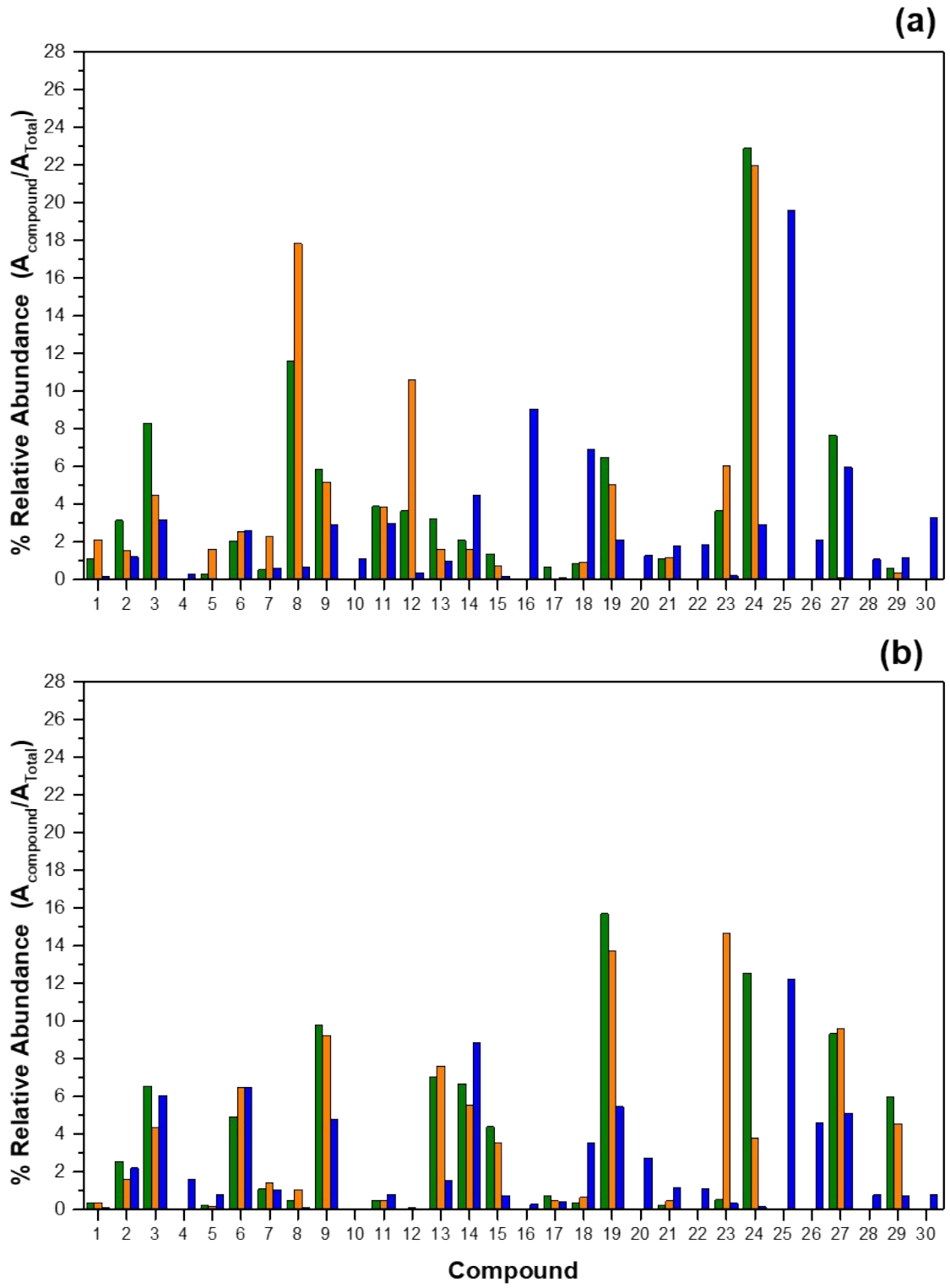

Figure S3. Relative abundance (%) of lignin depolymerisation products from (a) KL and (b) OL treatments at 80 °C for 1 hour with (■) [Ch]Cl:Oxa, (■) [Ch]Cl:Oxa/H_2SO_4 and (■) [Ch]Cl:Oxa/H_2O_2.

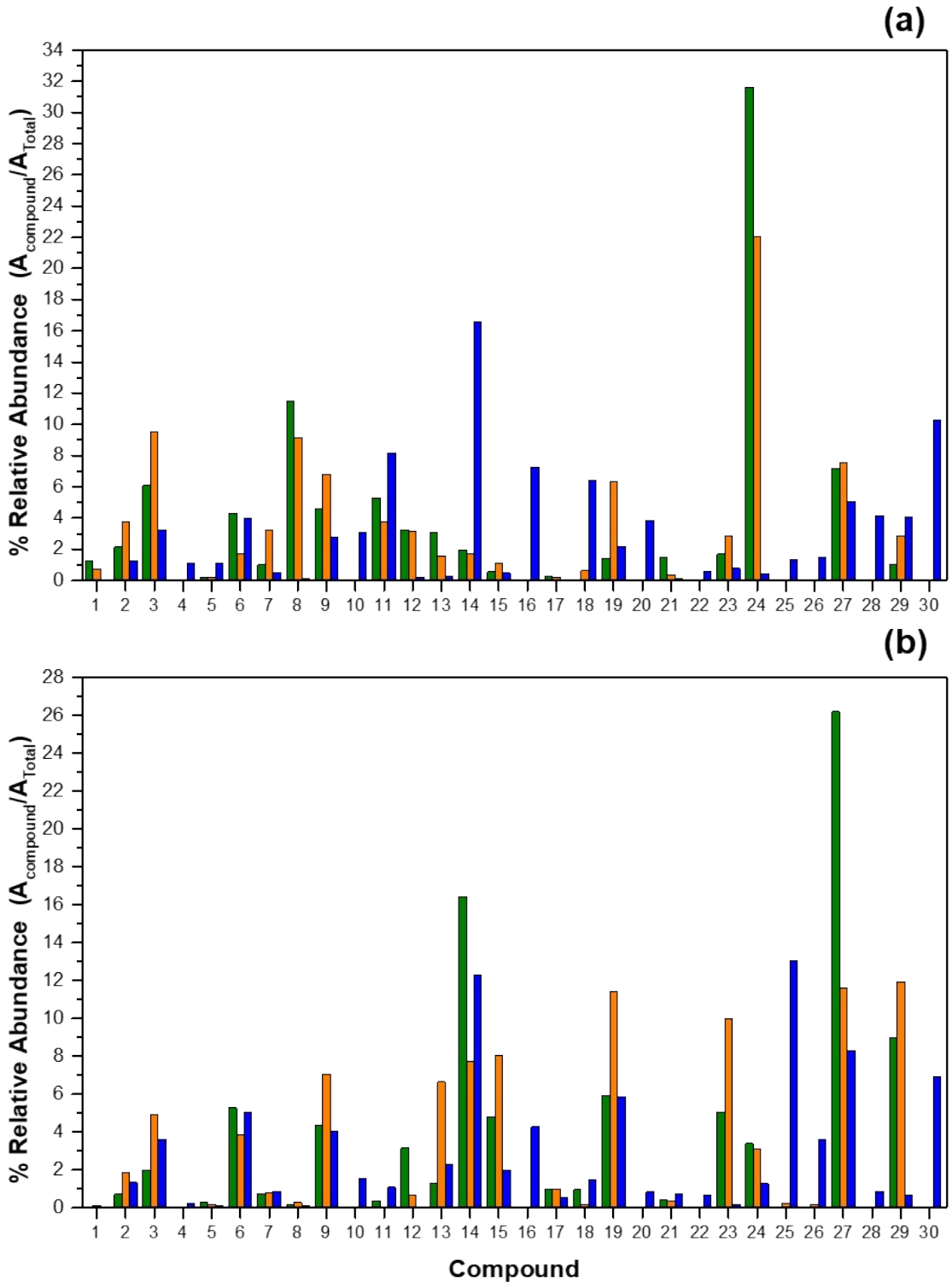

Figure S4. Relative abundance (%) of lignin depolymerisation products from (a) KL and (b) OL treatments at 80 °C for 6 hours with (■) [Ch]Cl:Oxa, (■) [Ch]Cl:Oxa/H_2SO_4 and (■) [Ch]Cl:Oxa/H_2O_2.

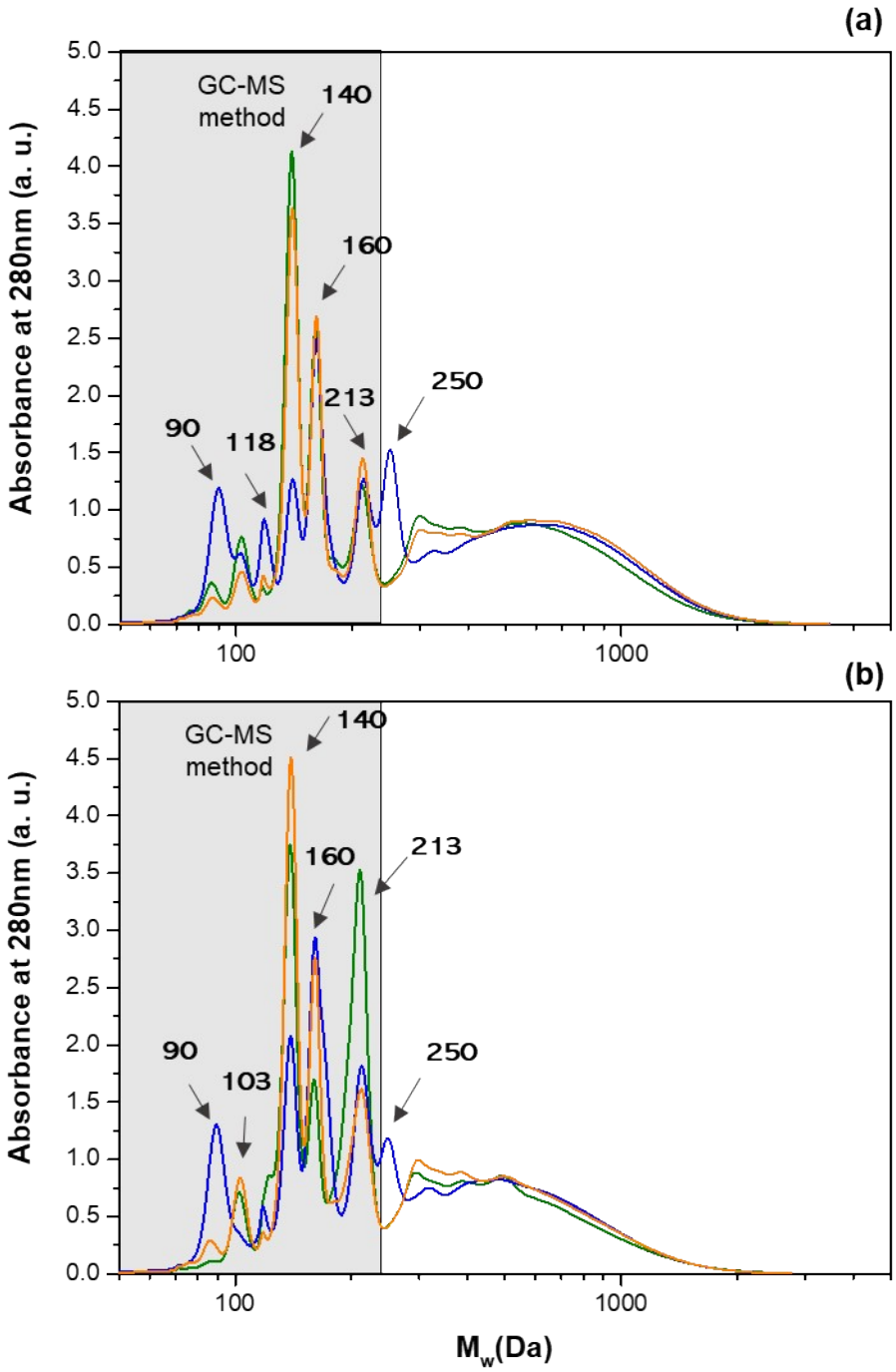

Figure S5. GPC analysis of lignin depolymerisation products from OL treatment at 80 °C during (a) 1 h and (b) 6 h with (■) [Ch]Cl:Oxa, (■) [Ch]Cl:Oxa/H_2SO_4 and (■) [Ch]Cl:Oxa/H_2O_2.

S3 – Kinetics of lignin depolymerisation

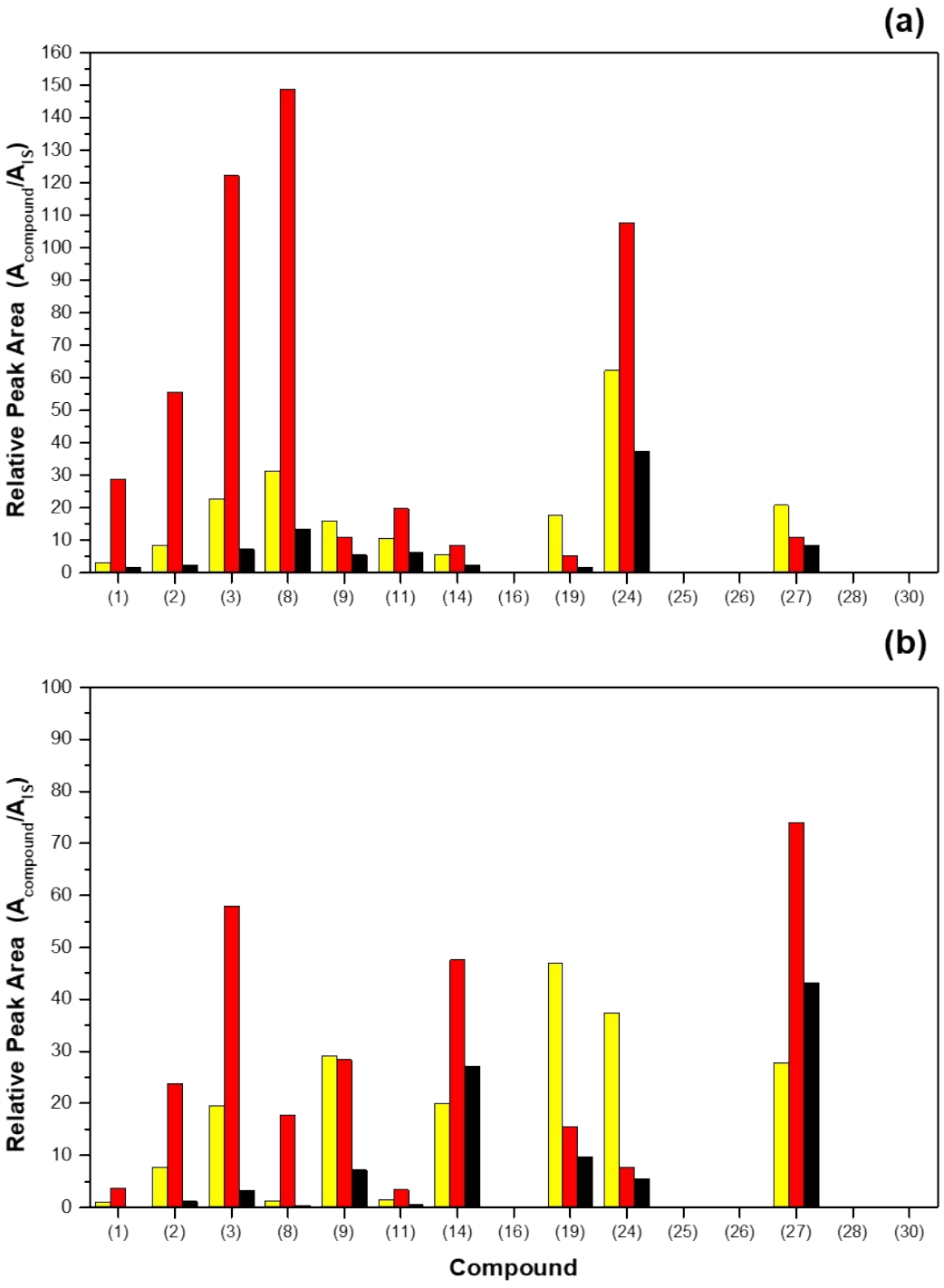

Figure S6. Relative peak area of identified compounds after (a) KL and (b) OL depolymerisation at 80 °C for (■) 1 h, (■) 3 h and (■) 6 h with [Ch]Cl:Oxa.

S4 - Structural characterization of regenerated lignin samples

Table S3. Molecular weight average (Mw), molecular number average (Mn) weights ($g.mol^{-1}$) and polydispersity (Mw/Mn) of lignin with corresponding deviations.

Sample	Kraft Lignin			Organosolv Lignin		
	Mw	**Mn**	**PDI**	**Mw**	**Mn**	**PDI**
Untreated	2500±90	1200±38	2.1±0.0	3300±111	1500±10	2.2±0.1
			1 hour			
[Ch]Cl:Oxa	2200±126	1100±14	2.0±0.1	2900±83	1300±20	2.2±0.0
[Ch]Cl:Oxa +H_2SO_4	2300±82	1150±29	2.0±0.0	3000±87	1400±28	2.1±0.0
[Ch]Cl:Oxa + H_2O_2	2400±149	1100±18	2.2±0.1	2800±69	1250±17	2.2±0.0
			3 hours			
[Ch]Cl:Oxa	2500±104	1250±14	2.0±0.1	3300±81	1400±37	2.4±0.0
[Ch]Cl:Oxa/H_2SO_4	2600±38	1250±24	2.1±0.0	3500±94	1400±42	2.5±0.0
[Ch]Cl:Oxa/H_2O_2	3600±131	1450±36	2.5±0.0	4100±118	1600±30	2.6±0.0
			6 hours			
[Ch]Cl:Oxa	1800±80	1050±23	1.7±0.1	2100±77	1100±22	1.9±0.1
[Ch]Cl:Oxa +H_2SO_4	2100±57	1050±14	2.0±0.0	2600±74	1100±17	2.4±0.1
[Ch]Cl:Oxa + H_2O_2	2000±100	1000±13	2.0±0.1	2600±64	1100±10	2.4±0.1

Table S4. FTIR vibrational bands/regions and corresponding assignments for lignin.

Vibrational band (cm^{-1})	Assignments
3200-3500	O-H vibrations[1]
2844-2980	Aliphatic C–H and CH2 stretching vibrations[1]
1775-1750	C=O of esters, ketones, aldehydes and acids. (C=O stretching, non conjugated[2]
1731	C=O stretching in xylan, C=O stretching of acetyl or carboxylic acid[3,4]
1700	Unconjugated C=O (ketone, carboxyl or ester stretching)[3,5]
1600 - 1690	Aromatic skeletal vibration[6–8]
1514	Aromatic skeletal vibration[6–8]
1456	Aromatic skeletal vibration and C-H deformations[6–8]
1425	Aromatic skeletal vibrations combined with C-H in-plane deformation[6–8]
1370-1365	Phenolic hydroxyl group[9,10]
1327 - 1365	Syringyl unit breathing with C=O stretching and condensed Guaiacyl rings[6–8]
1241	Guaiacyl ring breathing C–O stretch in lignin and for C–O linkage in guiacyl aromatic methoxyl groups[11]
1212	C-C plus C-O plus C=O stretch; Guaiacyl condensed > Guaiacyl etherified[6–8]
1152	C–O–C vibration (Cellulose and hemicellulose)[11]
1109	β-O-4 ether bond (Ether-O-)[12,13]
1040	Aromatic C H in-plane deformation (Guaiacyl > Syringyl) plus C-O deformation in primary alcohols plus C=O stretch (unconjugated) [6–8]
979	C–O valance vibration; aromatic C–H in plane deformation[14]
925	Aromatic C-H out-of-plane[6]
838	Aromatic C-H out-of-plane deformation in Guaiacyl and Syringyl units[15]

Table S5. Elemental characterization and ash content of Kraft lignin (KL), Organosolv lignin (OL) and recovered lignins from depolymerization reactions with [Ch]Cl:Oxa, [Ch]Cl:Oxa/H_2SO_4, and [Ch]Cl:Oxa/H_2O_2 at 80 °C for 1, 3 and 6 hours.

Samples	Reaction time	Elemental Analysis (wt%)					Ash (%)
		C	H	N	S	O	
KL		58.65±0.13	5.29±0.16	0.19±0.01	2.08±0.54	32.31±0.26	1.47±0.10
[Ch]Cl:Oxa (KL)	1h	58.69±0.35	5.83±0.01	0.56±0.01	1.89±0.28	32.82±0.03	0.22±0.02
	3h	58.78±0.91	5.73±0.02	0.54±0.01	1.68±0.07	32.85v0.50	0.42±0.03
	6h	58.07±0.61	6.34±0.49	0.72±0.04	1.16±0.17	33.03±0.45	0.68±0.03
[Ch]Cl:Oxa/H_2SO_4 (KL)	1h	59.57±0.26	5.27±0.1	0.37±0.01	1.79±0.27	32.63±0.04	0.38±0.03
	3h	59.33±0.03	5.43±0.01	0.47 ±0.02	1.75±0.07	32.16±0.04	0.86±0.04
	6h	58.76±0.41	5.43±0.17	0.59±0.05	0.97±0.02	33.57±0.32	0.68±0.03
[Ch]Cl:Oxa/H_2O_2 (KL)	1h	50.05±0.73	4.27±0.16	0.51±0.02	1.02±0.25	43.98±0.33	0.19±0.03
	3h	48.53±0.84	4.32±0.27	0.76±0.06	0.76±0.02	44.90±0.59	0.73±0.05
	6h	50.55±0.38	4.87±0.1	0.74±0.03	0.62±0.03	42.63±0.27	0.59±0.04
OL		61.88±0.16	5.35±0.03	0.23±0.01	0.00±0.00	32.13±0.10	0.42±0.06
[Ch]Cl:Oxa (OL)	1h	60.30±1.41	5.35±0.10	0.41±0.00	0.00±0.00	33.81±0.75	0.14±0.02
	3h	61.31±0.41	5.44±0.04	0.46±0.02	0.00±0.00	32.44±0.23	0.36±0.04
	6h	59.79±0.23	5.34±0.07	0.51±0.02	0.00±0.00	34.28±0.16	0.08±0.01
[Ch]Cl:Oxa/H_2SO_4 (OL)	1h	60.58±0.07	5.59±0.05	0.32±0.01	0.00±0.00	33.27±0.01	0.24±0.03
	3h	60.36±0.02	5.47±0.41	0.41±0.01	0.00±0.00	33.28±0.05	0.48±0.03
	6h	60.15±0.12	5.26±0.06	0.46±0.01	0.00±0.00	34.00±0.04	0.12±0.02
[Ch]Cl:Oxa/H_2O_2 (OL)	1h	53.52±0.32	4.30±0.02	0.38±0.02	0.00±0.00	41.60±0.16	0.20±0.02
	3h	56.20±0.04	4.49±0.02	0.47±0.01	0.00±0.00	38.49±0.01	0.35±0.01
	6h	53.53±0.49	4.55±0.04	0.65±0.01	0.00±0.00	40.89±0.22	0.39±0.03

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