Supplementary information

Furan distribution as severity indicator upon organosolv fractionation of hardwood sawdust through novel ternary solvent system

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A. Number of pages: 14 (S1-S14)

B. Number of figures: 2

C. Number of Tables: 15

S1 Lignin characterization

Table S1.1: Compositional data for the lignins isolated without additional of mineral acid.

Treatment	Klason lignin content [%g/g] Primary (wash)	Hemicellulosic sugar content [%g/g] Primary (wash)	Cellulosic sugar content [%g/g] Primary (wash)
A0-1	0.85 (0.91)	2.01 (1.17)	0.29 (0.01)
A0-2	0.87 (0.89)	2.15 (1.17)	0.00 (0.01)
A0-3	0.90 (0.76)	2.03 (1.45)	0.24 (0.34)
A0-4	0.86 (0.89)	2.33 (1.03)	0.45 (0.11)
A0-5	0.89 (0.89)	1.68 (1.08)	0.44 (0.20)
A0-6	0.89 (0.90)	1.81 (0.00)	0.26 (0.00)
A0-7	0.87 (0.89)	2.68 (1.64)	0.43 (0.68)
A0-8	0.83 (0.89)	3.47 (1.53)	0.46 (0.54)
A0-9	0.88 (0.90)	2.32 (1.66)	0.37 (0.87)
A0-10	0.87 (0.88)	1.96 (1.30)	0.58 (1.08)
A0-11	0.90 (0.91)	1.42 (1.06)	0.36 (0.62)
A0-12	0.88 (0.90)	1.54 (1.18)	0.34 (0.48)

Table S1.2: Compositional data for the lignins isolated with additional of mineral acid.

Treatment	Klason lignin content [%g/g] Primary (wash)	Hemicellulosic sugar content [%g/g] Primary (wash)	Cellulosic sugar content [%g/g] Primary (wash)
A20-1	0.92 (0.89)	0.40 (0.38)	0.84 (0.71)
A20-2	0.92 (0.93)	0.24 (0.23)	0.53 (0.51)
A20-3	0.92 (0.91)	0.13 (0.22)	0.61 (0.63)
A20-4	0.92 (0.90)	0.19 (1.01)	0.57 (3.60)
A20-5	0.92 (0.91)	0.28 (0.77)	0.81 (1.65)
A20-6	0.91 (0.91)	0.22 (0.19)	0.59 (0.52)
A20-7	0.89 (0.86)	0.44 (1.37)	0.98 (2.64)
A20-8	0.91 (0.89)	0.24 (0.22)	0.57 (0.71)
A20-9	0.91 (0.90)	0.51 (0.12)	1.24 (2.84)
A20-10	0.82 (0.89)	0.50 (0.94)	1.58 (2.05)
A20-11	0.92 (0.86)	0.21 (0.50)	0.51 (7.94)
A20-12	0.92 (0.91)	0.27 (0.70)	0.90 (2.41)

S2 Mass balances

S2.1 Lignin mass balance

Table S2.1.1: Mass balance data for the lignins (Klason lignin content) isolated without addition of mineral acid.

Treatment	Lignin recovered in pulp [%g/g in raw]	Primary lignin recovered [%g/g in raw]	Wash lignin recovered [%g/g in raw]	Lignin recovered in primary liquid [%g/g in raw]	Lignin recovered in wash liquid [%g/g in raw]	Sum [%]
A0-1	59.26	37.08	4.50	6.64	2.01	109.49
A0-2	53.29	35.21	6.22	7.29	2.09	104.10
A0-3	50.30	44.09	5.52	7.91	11.61	119.43
A0-4	39.29	51.01	6.81	7.70	1.91	106.72
A0-5	35.37	51.29	7.34	6.56	2.09	102.65
A0-6	42.40	55.80	7.16	6.02	1.72	113.11
A0-7	44.80	44.40	6.46	3.71	0.79	100.16
A0-8	42.59	55.72	6.27	6.57	5.83	116.99
A0-9	42.03	49.28	4.96	5.02	0.59	101.87
A0-10	57.29	31.91	6.01	3.55	2.19	100.95
A0-11	60.40	39.71	3.08	4.45	0.74	108.39
A0-12	58.41	43.04	3.13	7.88	0.55	113.02

Table S2.1.2: Mass balance data for the lignins (Klason lignin content) isolated with addition of mineral acid.

Treatment	Lignin recovered in pulp [%g/g in raw]	Primary lignin recovered [%g/g in raw]	Wash lignin recovered [%g/g in raw]	Lignin recovered in primary liquid [%g/g in raw]	Lignin recovered in wash liquid [%g/g in raw]	Sum [%]
A20-1	38.38	44.07	6.64	6.34	0.64	96.07
A20-2	36.18	47.14	6.79	7.39	0.88	98.38
A20-3	37.38	52.97	7.64	7.92	0.35	106.26
A20-4	19.38	68.77	9.06	7.52	0.41	105.14
A20-5	15.10	67.38	9.30	7.62	0.37	99.76
A20-6	12.68	76.28	11.21	9.98	0.25	110.40
A20-7	7.44	76.43	10.07	7.18	0.42	101.54
A20-8	5.77	89.35	9.33	9.01	0.56	114.01
A20-9	5.88	98.56	11.04	12.05	0.58	128.11
A20-10	6.86	70.02	5.13	9.73	0.58	92.32
A20-11	5.53	81.59	9.60	10.60	0.35	107.66
A20-12	5.23	100.71	5.56	14.91	0.50	126.90

S2.2 Cellulose mass balance

Table S2.2.1: Mass balance data for the cellulose isolated without addition of mineral acid.

Treatment	Cellulose recovered in pulp [%g/g in raw]	Cellulose recovered in primary lignin [%g/g in raw]	Cellulose recovered in wash lignin [%g/g in raw]	Cellulose recovered in prim. Liq. as mono. [%g/g in raw]	Cellulose recovered in prim liq. as polym. [%g/g in raw]	Cellulose recovered in wash Liq. as mono. [%g/g in raw]	Cellulose recovered in wash liq. as polym. [%g/g in raw]	Sum [%g/g in raw]
A0-1	95.22	0.08	0.00	1.99	0.00	0.03	0.17	97.50
A0-2	83.90	0.00	0.00	0.56	0.58	0.00	0.22	85.26
A0-3	101.15	0.07	0.01	0.38	0.97	0.07	0.20	102.86
A0-4	92.89	0.16	0.01	0.47	0.44	0.00	0.22	94.19
A0-5	92.21	0.16	0.01	0.42	0.66	0.00	0.29	93.74
A0-6	98.52	0.10	0.00	0.33	0.78	0.00	0.21	99.94
A0-7	102.07	0.13	0.03	1.46	0.00	0.00	0.14	103.84
A0-8	95.43	0.18	0.02	0.29	0.26	0.00	0.13	96.31
A0-9	99.41	0.12	0.03	0.00	0.51	0.00	0.13	100.20
A0-10	103.91	0.13	0.04	0.19	0.02	0.07	0.00	104.35
A0-11	110.02	0.10	0.01	0.03	0.22	0.27	0.00	110.65
A0-12	107.16	0.10	0.01	0.22	0.11	0.00	0.06	107.67

Table S2.2.2: Mass balance data for the cellulose isolated with addition of mineral acid.

Treatment	Cellulose recovered in pulp [%g/g in raw]	Cellulose recovered in primary lignin [%g/g in raw]	Cellulose recovered in wash lignin [%g/g in raw]	Cellulose recovered in prim. Liq. as mono. [%g/g in raw]	Cellulose recovered in prim liq. as polym. [%g/g in raw]	Cellulose recovered in wash Liq. as mono. [%g/g in raw]	Cellulose recovered in wash liq. as polym. [%g/g in raw]	Sum [%g/g in raw]
A20-1	81.46	0.24	0.03	9.34	2.70	1.77	0.56	96.11
A20-2	75.86	0.16	0.02	10.99	1.47	2.20	0.37	91.08
A20-3	75.77	0.21	0.03	12.21	2.03	1.56	0.00	91.80
A20-4	83.31	0.26	0.22	9.06	4.30	1.61	0.79	99.50
A20-5	74.61	0.36	0.10	9.23	2.52	1.68	0.37	88.86
A20-6	72.62	0.30	0.04	11.07	0.00	2.09	14.06	100.19
A20-7	73.17	0.51	0.19	7.87	5.05	0.07	2.49	89.35
A20-8	66.04	0.34	0.05	0.91	13.45	0.12	2.27	83.18
A20-9	59.76	0.81	0.21	1.52	0.73	0.56	0.21	63.79
A20-10	68.17	0.82	0.07	1.83	0.00	0.29	2.70	73.89
A20-11	62.49	0.27	0.53	5.52	0.00	1.60	0.00	70.42
A20-12	51.92	0.60	0.09	11.12	0.00	1.99	0.00	65.72

S2.3 Hemicellulose mass balance

Table S2.3.1: Mass balance data for the hemicellulose isolated without addition of mineral acid.

Treatment	Hemicell. recovered in pulp [%g/g in raw]	Hemicell. recovered in primary lignin [%g/g in raw]	Hemicell. recovered in wash lignin [%g/g in raw]	Hemicell. recovered in prim. Liq. as mono. [%g/g in raw]	Hemicell. recovered in prim liq. as polym. [%g/g in raw]	Hemicell. recovered in wash Liq. as mono. [%g/g in raw]	Hemicell. recovered in wash liq. as polym. [%g/g in raw]	Sum [%g/g in raw]
A0-1	30.51	0.84	0.06	7.03	29.75	1.01	4.30	73.49
A0-2	35.46	0.83	0.08	7.54	24.96	5.85	0.00	74.72
A0-3	30.43	0.96	0.12	5.99	32.30	1.16	5.30	76.26
A0-4	48.02	1.32	0.08	4.43	20.18	1.20	3.55	78.78
A0-5	47.31	1.09	0.10	4.35	21.45	0.99	4.34	79.63
A0-6	58.80	1.30	0.00	4.32	21.93	0.68	3.17	90.21
A0-7	67.59	1.56	0.13	2.98	10.32	0.70	2.74	86.03
A0-8	66.86	2.55	0.12	2.85	13.19	0.54	2.44	88.55
A0-9	65.64	1.45	0.09	3.00	12.66	0.52	2.20	85.55
A0-10	89.23	0.82	0.11	1.93	5.44	1.63	0.00	99.15
A0-11	95.82	0.84	0.04	2.58	4.71	2.11	0.00	106.12
A0-12	86.22	0.96	0.05	2.93	7.33	0.00	1.21	98.71

Table S2.3.2: Mass balance data for the hemicellulose isolated with addition of mineral acid.

Treatment	Hemicell. recovered in pulp [%g/g in raw]	Hemicell. recovered in primary lignin [%g/g in raw]	Hemicell. recovered in wash lignin [%g/g in raw]	Hemicell. recovered in prim. Liq. as mono. [%g/g in raw]	Hemicell. recovered in prim liq. as polym. [%g/g in raw]	Hemicell. recovered in wash Liq. as mono. [%g/g in raw]	Hemicell. recovered in wash liq. as polym. [%g/g in raw]	Sum [%g/g in raw]
A20-1	0.00	0.26	0.04	22.79	0.10	6.51	0.00	29.69
A20-2	0.00	0.16	0.02	21.92	0.04	5.96	21.74	49.84
A20-3	0.00	0.07	0.02	15.98	0.12	3.62	0.00	19.81
A20-4	0.00	0.13	0.10	21.94	0.00	5.75	0.00	27.92
A20-5	0.00	0.32	0.10	20.69	0.26	5.61	0.00	26.98
A20-6	0.00	0.32	0.02	20.29	0.00	5.50	16.65	42.78
A20-7	0.00	0.36	0.21	23.54	0.60	1.10	4.15	29.96
A20-8	0.00	0.39	0.02	2.42	18.38	0.41	2.50	24.12
A20-9	0.00	0.52	0.18	2.06	0.15	1.33	0.00	4.25
A20-10	0.00	0.61	0.07	4.49	0.12	1.32	3.37	9.98
A20-11	0.00	0.21	0.07	11.09	0.57	5.68	0.00	17.63
A20-12	0.00	0.28	0.06	16.62	0.32	6.21	0.00	23.49

S3 Quaternary carbon content

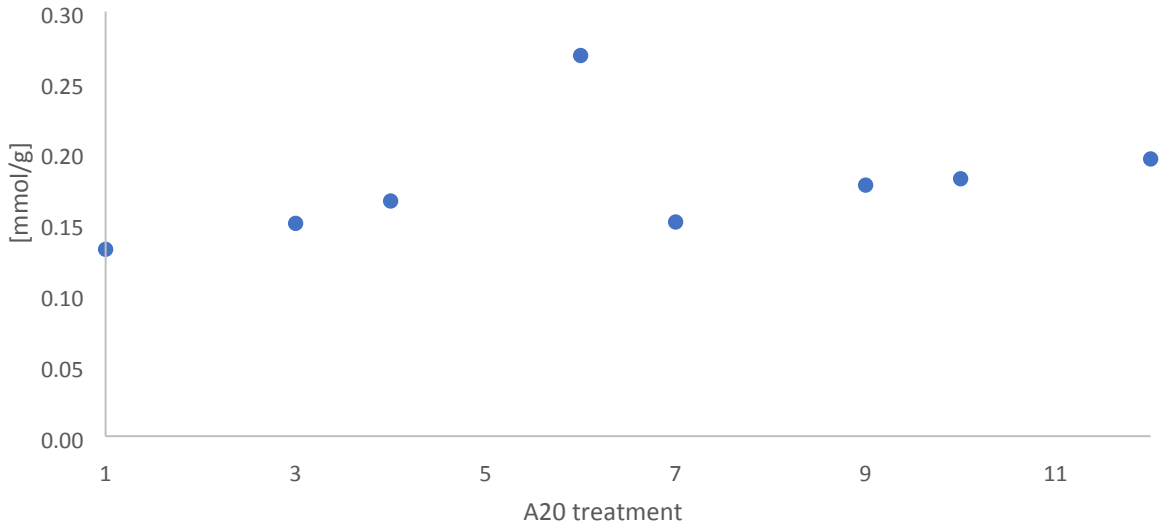

Figure S1. *Content of quaternary carbon linker (48.5-50.25 ppm) for the various A20 treatments.*

S4 Prominent Figures and Tables discussed in manuscript

Table S4.1: Pyr-GC/MS data for selected lignins isolated subsequent acid-free organosolv processing. *N.B.*: names as listed in the NIST database have been used.

Identified compound	**Content in samples [% area]**							
	A0-1	A0-3	A0-4	A0-6	A0-7	A0-9	A0-10	A0-12
Furfural	ND	ND	ND	ND	ND	ND	ND	ND
5-HMF	ND	ND	ND	ND	ND	ND	ND	ND
Furan, 2-(2-propenyl)-	ND	ND	ND	ND	ND	ND	ND	ND
2-Furancarboxaldehyde, 5-methyl-	ND	ND	ND	ND	ND	ND	ND	ND
3-Buten-2-one, 4-(2-furanyl)-	ND	0.20	ND	0.21	ND	0.19	ND	0.20
1-Heptanone, 1-(2-furanyl)-	ND	ND	ND	ND	ND	ND	ND	ND
Benzene, 1,2,3,4-tetramethoxy-5-(2-propenyl)-	1.31	0.84	0.51	0.25	0.59	ND	0.82	ND
alpha-*D*-Glucopyranose, 1,6-anhydro	ND	ND	ND	ND	ND	ND	ND	ND
Eugenol (G)	0.96	0.80	0.71	0.77	1.00	0.80	0.97	0.98
trans-Isoeugenol (G)	2.13	2.14	1.54	2.26	2.02	2.00	2.29	2.47
Vanillin (G)	2.42	2.53	3.97	3.19	2.70	2.94	3.78	3.42
Apocynin (G)	1.65	1.89	1.49	1.90	1.37	1.63	1.77	1.86
Benzenepropanol, 4-hydroxy-3-methoxy- (G)	0.69	0.64	0.76	0.63	ND	ND	0.55	ND
Butyrovanillone (G)	ND	ND	ND	ND	ND	ND	ND	ND
Phenol, 2-methoxy-4-(1-propenyl)- (G)	ND	ND	ND	ND	ND	ND	ND	ND
Phenol, 2,6-dimethoxy- (G)	4.77	4.87	4.00	4.82	3.38	3.88	4.45	4.66
2-Methoxy-4-vinylphenol (G)	3.94	3.48	2.81	3.41	3.36	3.50	3.42	3.71
Phenol, 4-ethyl-2-methoxy-	1.69	1.63	1.60	1.93	1.59	1.64	1.81	1.78

(G)								
Phenol, 2-methoxy- (G)	2.11	2.08	1.83	2.37	2.09	2.07	2.32	2.45
trans-Sinapyl alcohol (S)	3.12	3.44	2.49	0.99	1.49	1.30	2.01	1.79
(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol (S)	1.64	1.60	0.95	1.47	1.19	0.95	1.10	1.16
Butylsyringone (S)	ND	0.63	ND	0.57	ND	ND	0.60	0.52
Phenol, 4-ethenyl-2,6-dimethoxy- (S)	4.32	5.23	4.40	4.54	3.30	3.96	4.18	4.19
3,5-Dimethoxy-4-hydroxytoluene (S)	4.16	4.32	2.91	4.22	3.05	2.80	3.01	3.30
Phenol, 2,6-dimethoxy-4-(2-propenyl)- (S)	2.57	2.76	2.01	2.50	1.87	1.72	2.07	2.07
(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol (S)	5.70	5.88	4.79	5.45	3.89	3.87	4.46	4.58
Benzaldehyde, 4-hydroxy-3,5-dimethoxy- (S)	5.93	6.85	8.20	6.81	4.27	4.47	6.42	5.76
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- (S)	3.44	3.57	2.82	3.19	2.21	2.27	2.80	2.70
Syringylacetone (S)	0.88	0.94	0.92	0.93	0.73	2.97	1.09	0.98
1-Propanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- (S)	1.11	1.29	0.74	1.13	0.83	0.78	0.89	0.85
Creosol	3.17	3.01	2.37	3.25	2.68	2.85	2.55	3.01
Methylated (2/3) phenol	1.54	1.48	1.54	1.93	1.65	1.66	1.61	1.84
Phenol, 4-propyl-	ND	ND	ND	ND	ND	ND	ND	ND
Formic acid, 2,3-dimethylphenyl ester	0.54	0.51	ND	0.68	ND	0.93	0.69	ND
(G:S:H)	(35:62:3)	(33:65:3)	(35:62:3)	(37:60:4)	(41:55:4)	(39:57:4)	(39:58:3)	(40:57:4)

ND: indicates that a compound is below detection limit of %area = 0.5.

%area: Corresponding area for a compound relative to the sum of all the signal areas in the chromatogram.

Table S4.2: Pyr-GC/MS data for selected lignins isolated from acid-catalyzed organosolv processing. *N.B.*: names as listed in the NIST database have been used.

Identified compound	**Content in samples [%A]**							
	A20-1	A20-3	A20-4	A20-6	A20-7	A20-9	A20-10	A20-12
Furfural	2.29	2.98	2.91	4.97	4.43	4.91	5.36	3.71
5-HMF	0.79	1.09	1.66	2.01	4.35	4.08	7.30	4.31
Furan, 2-(2-propenyl)-	ND	1.26	ND	1.10	ND	1.62	ND	1.27
2-Furancarboxaldehyde, 5-methyl-	ND	0.76	0.57	0.79	1.16	1.48	1.68	0.94
3-Buten-2-one, 4-(2-furanyl)-	ND	3.99	ND	4.09	ND	5.46	ND	3.80
1-Heptanone, 1-(2-furanyl)-	ND	ND	ND	ND	ND	ND	0.27	ND
4,5,6-Trimethoxy-7-methyl-3H-2-benzofuran-1-one; Benzene, 1,2,3,4-tetramethoxy-5-(2-propenyl)-	ND	ND	ND	ND	ND	ND	ND	ND
alpha-D-Glucopyranose, 1,6-anhydro	0.63	ND	ND	ND	0.77	ND	0.74	0.98
Eugenol (G)	0.76	0.54	0.74	0.64	0.65	ND	ND	ND
trans-Isoeugenol (G)	ND	ND	ND	ND	ND	ND	ND	ND
Vanillin (G)	2.47	2.27	2.56	3.06	2.11	1.62	2.09	1.74
Apocynin (G)	1.94	1.94	1.73	2.27	1.56	1.43	1.45	1.30
Benzenepropanol, 4-hydroxy-3-methoxy- (G)	0.82	0.56	0.51	0.56	0.54	0.51	ND	1.12
Butyrovanillone (G)	1.64	1.44	2.08	2.04	2.28	1.09	2.46	1.51
Phenol, 2-methoxy-4-(1-propenyl)- (G)	0.66	0.58	0.58	0.54	0.78	0.53	0.74	0.53
Phenol, 2,6-dimethoxy- (G)	5.86	4.59	5.85	4.27	5.05	3.29	4.71	3.19
2-Methoxy-4-vinylphenol (G)	3.04	1.69	3.09	1.87	2.52	1.40	2.26	1.34
Phenol, 4-ethyl-2-methoxy- (G)	1.77	1.57	1.92	1.44	1.88	1.07	1.72	0.94
Phenol, 2-methoxy- (G)	3.58	2.81	3.37	2.73	3.73	2.53	3.29	2.21
***trans*-Sinapyl alcohol (S)**	ND	ND	ND	ND	ND	ND	ND	ND
(*E*)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol (S)	ND	ND	ND	ND	ND	ND	ND	ND
Butylsyringone (S)	1.30	1.24	1.52	1.40	1.44	0.93	1.46	1.24
Phenol, 4-ethenyl-2,6-dimethoxy- (S)	2.11	1.84	1.74	1.79	1.53	1.19	1.34	1.18
3,5-Dimethoxy-4-hydroxytoluene (S)	4.79	3.97	4.19	4.07	4.36	3.13	4.35	2.75
Phenol, 2,6-dimethoxy-4-(2-propenyl)- (S)	0.71	0.73	0.85	0.81	0.74	0.61	0.78	0.61
(*E*)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol (S)	1.98	1.27	1.21	1.21	1.50	0.99	1.38	1.24
Benzaldehyde, 4-hydroxy-3,5-dimethoxy- (S)	2.51	2.57	2.94	2.86	2.15	1.70	1.98	2.45
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- (S)	3.40	2.39	3.27	2.35	2.05	2.11	1.65	2.42
Syringylacetone (S)	1.35	1.29	1.48	1.31	2.01	1.76	2.10	1.98

1-Propanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- (S)	0.88	0.72	0.57	0.75	0.64	0.57	0.58	0.82
Creosol	4.52	3.39	4.32	3.82	5.15	0.37	4.86	2.58
Methylated (2/3) phenol	2.30	2.55	2.40	1.34	2.68	2.26	2.68	1.23
Phenol, 4-propyl-	ND	ND	ND	1.18	ND	1.43	ND	0.97
Formic acid, 2,3-dimethylphenyl ester	ND	0.59	ND	ND	0.57	0.38	ND	ND
(G:S:H)	(45:50:5)	(43:51:6)	(45:50:5)	(47:50:3)	(48:46:6)	(37:55:8)	(46:47:7)	(41:55:4)

ND: indicates that a compound is below detection limit of %area = 0.5.
%area: Corresponding area for a compound relative to the sum of all the signal areas in the chromatogram.

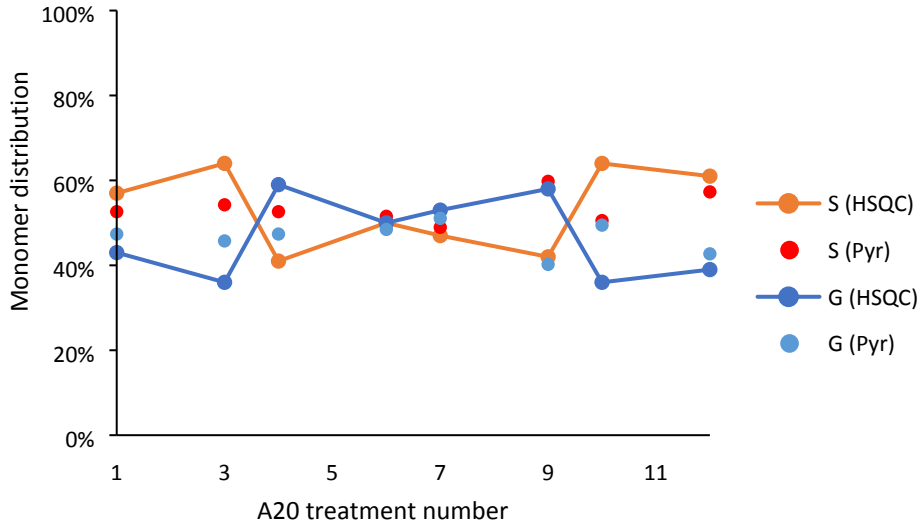

Figure S2. Lignin monomer ratios obtained through HSQC analyses and pyr-GC/MS.

Table S4.3: Dehydration products measured in the liquors isolated from non-acid catalyzed treatments.

Treatment	Furfural [g/100$g_{biomass}$]	HMF [g/100$g_{biomass}$]	Formic acid [g/100$g_{biomass}$]	Acetic acid [g/100$g_{biomass}$]	Tot. Phenolics [g/100$g_{biomass}$]
A0-1	0.10	0.06	0.00	1.89	0.09
A0-2	0.07	0.05	0.23	1.62	0.09
A0-3	0.07	0.05	0.39	1.65	0.08
A0-4	0.04	0.04	0.08	1.42	0.07
A0-5	0.05	0.04	0.12	1.71	0.08
A0-6	0.05	0.03	0.21	1.61	0.09
A0-7	0.03	0.02	0.14	1.18	0.06
A0-8	0.02	0.02	0.28	1.19	0.06
A0-9	0.03	0.02	0.41	1.33	0.08
A0-10	0.02	0.02	0.15	1.03	0.07
A0-11	0.02	0.02	0.18	0.17	0.08
A0-12	0.02	0.02	0.28	2.20	0.11

[a]Levulinic acid was not detected.

Table S4.4: Dehydration products measured in the liquors isolated from acid catalyzed treatments.

Treatment	Furfural [g/100$g_{biomass}$]	HMF [g/100$g_{biomass}$]	Formic acid [g/100$g_{biomass}$]	Acetic acid [g/100$g_{biomass}$]	Tot. Phenolics [g/100$g_{biomass}$]
A20-1	0.76	0.70	0.47	2.73	0.13
A20-2	1.02	0.69	0.91	3.14	0.13
A20-3	1.13	1.03	1.72	3.69	0.13
A20-4	0.65	0.66	0.71	2.40	0.10
A20-5	0.93	0.83	1.18	2.64	0.13
A20-6	0.72	0.89	1.41	3.09	0.12
A20-7	0.69	0.57	0.85	1.80	0.09
A20-8	0.94	0.93	0.35	0.16	0.12
A20-9	1.17	1.56	0.68	0.36	0.13
A20-10	0.20	1.10	0.00	0.28	0.04
A20-11	0.88	0.88	0.46	0.58	0.10
A20-12	0.93	1.25	0.33	1.34	0.11

[a]Levulinic acid was not detected.

S5 Assigned NMR shifts

Table S5.1: Shifts assigned for NMR analysis.

Motif	^{13}C	^{1}H
G_2[1]	110.15	6.93
G_6[1]	119.05-120.76	6.53-6.78
$S_{2,6}$	103.42	6.62
-OMe	56.5-55.0	-
Quat. Phe C-OMe	148.5-145.0	-
	151.0-153.5	-
β-O-4' to G		
(C_α)	71.29	4.91
(C_β)	83.21	4.34
(C_γ)	59.91	3.24
β-O-4' to S		
(C_α)	72.06	4.89
(C_β)	85.92	4.13
(C_γ)	59.43	3.41
β-β'		
(C_α)	87.03	5.44
(C_β)	53.05	3.48
(C_γ)	62.97	3.63
β-5'		
(C_α)	85.16	4.63
(C_β)	53.52	3.07
(C_γ)	70.88/71.05	4.19/3.81
β-D-Xylopyr.		
(C_1)	101.83	4.29
(C_2)	72.51	3.06
(C_3)	73.95	3.27
(C_4)	75.42	3.53
(C_5)	64.52	3.45
BE	80.87	4.59
Furan C_4 type 1	106.38	7.28
Furan C_4 type 2	122.86	7.53
Furan C_3 type 2[1]	112.75	6.77
Furan C_3 type 1	106.07	6.51
Ketone	207.2-206.5	-
Ester	170.5-169.0	-
Furan aldehyde	178.5-177.9	-

[1]A20 lignins show expanded guaiacyl shifts. Full range given for G_6 whereas G_2 overlaps with Furan C_3 type 2.

Spectroscopic data

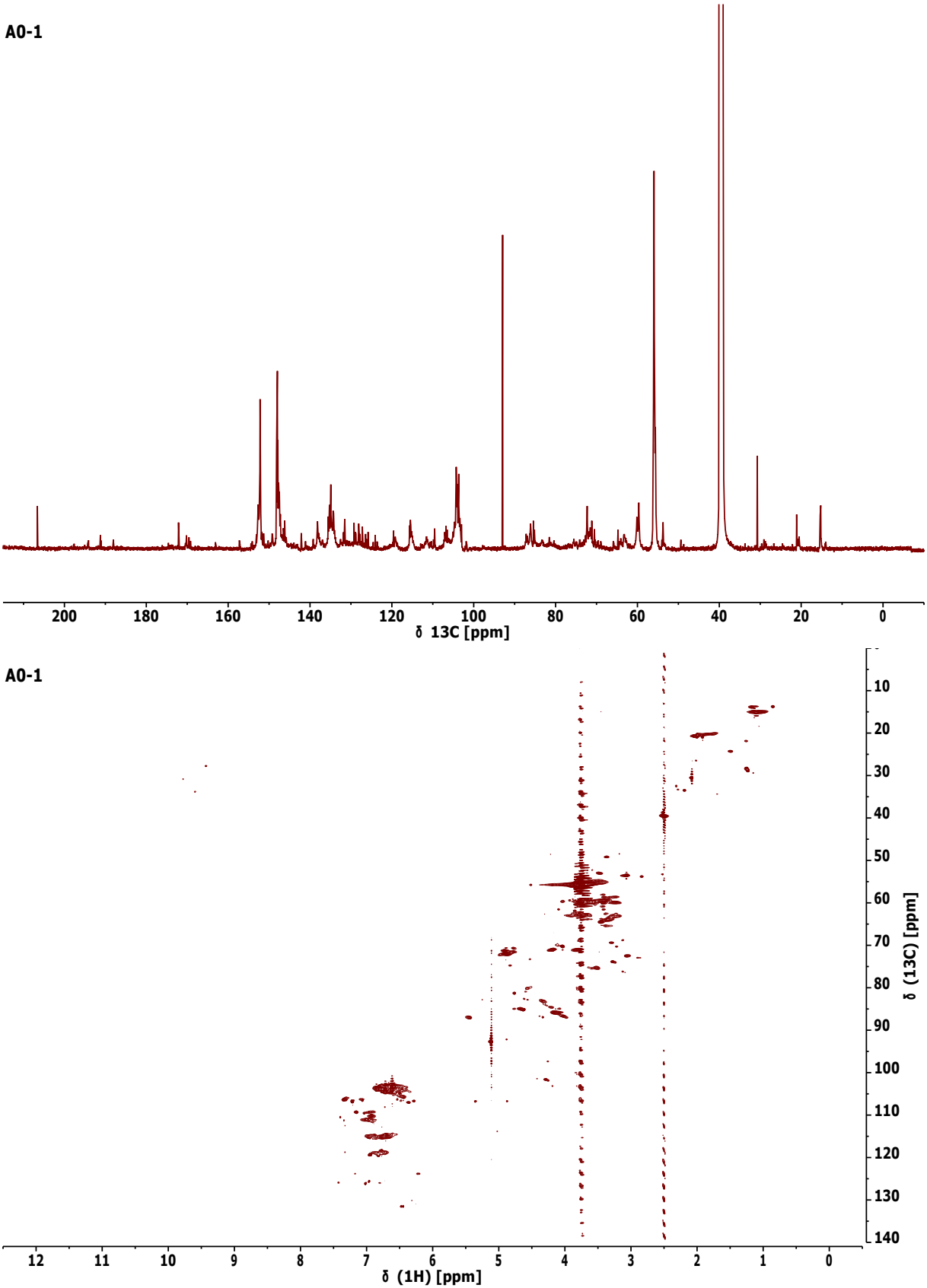

Figure S3. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A0-1**.

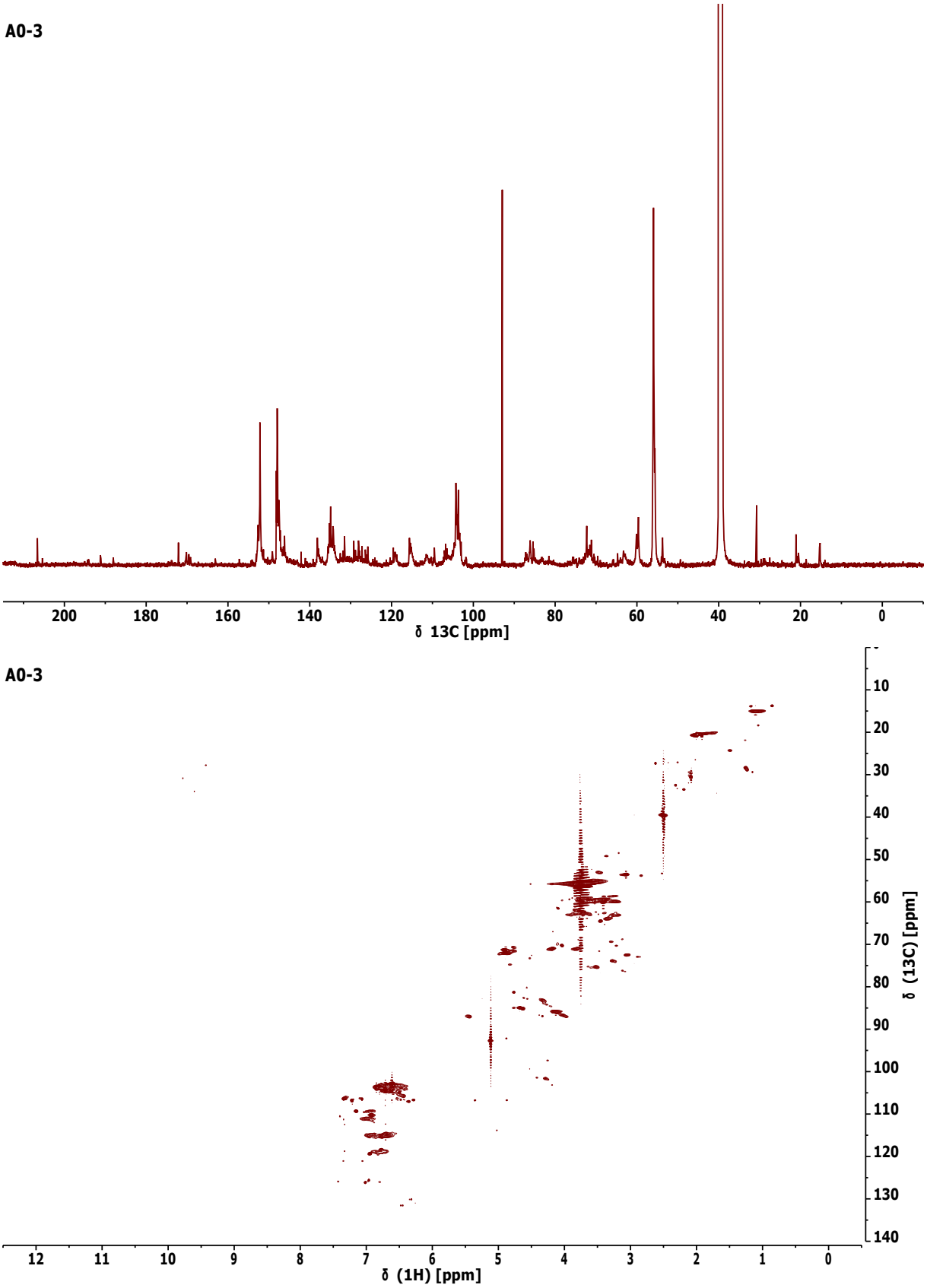

Figure S4. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A0-3**.

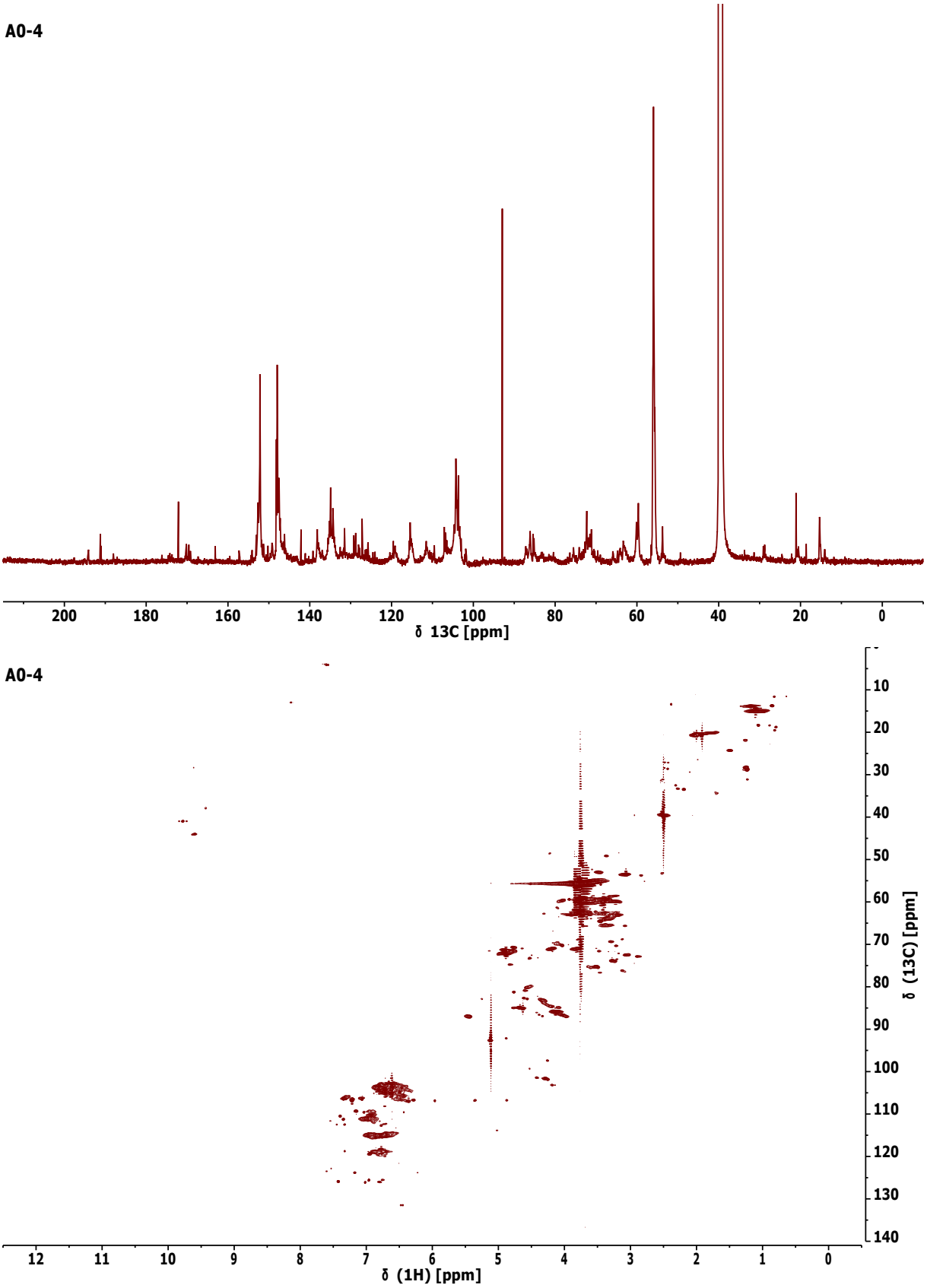

Figure S5. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A0-4**.

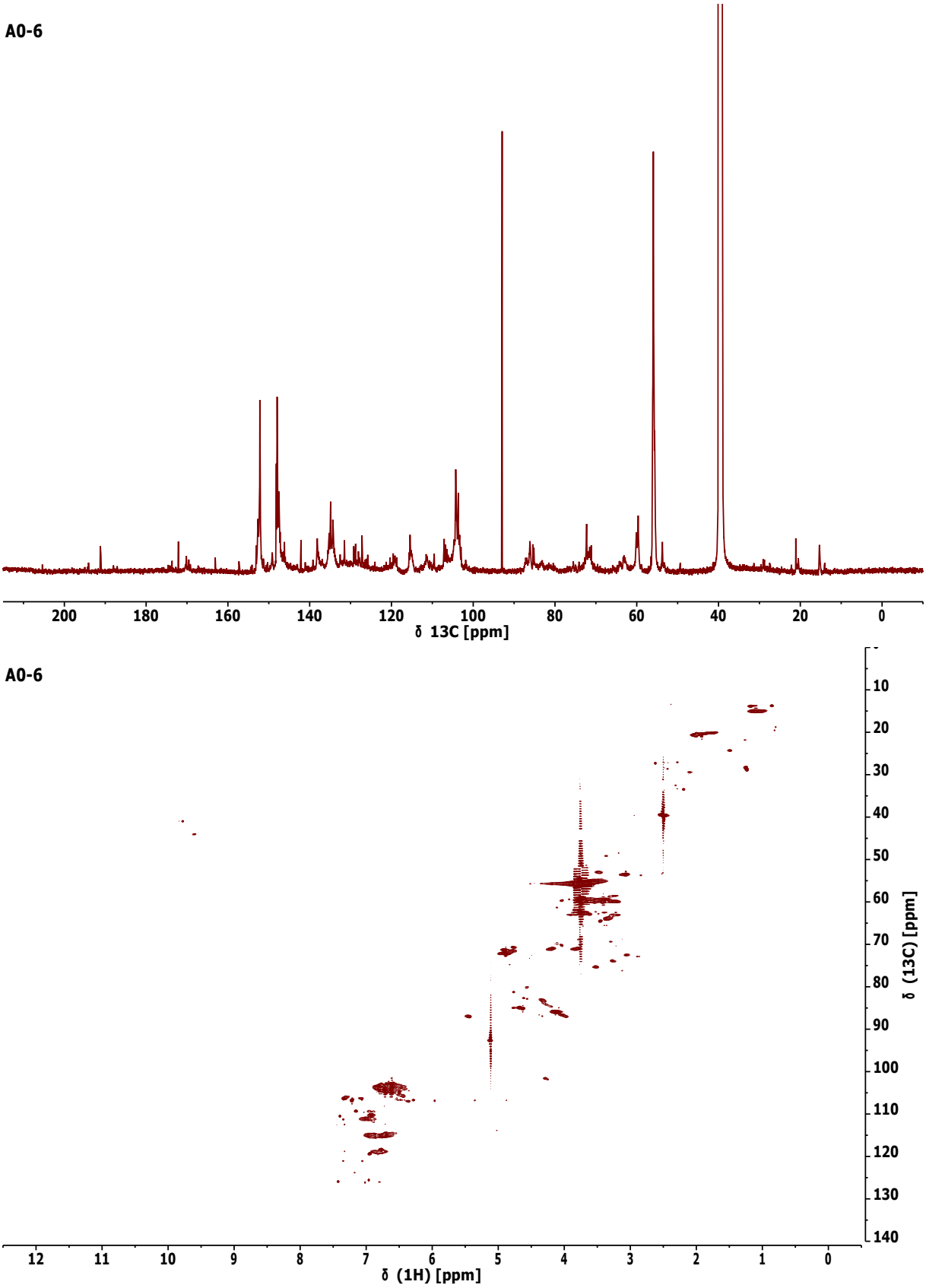

Figure S6. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A0-6**.

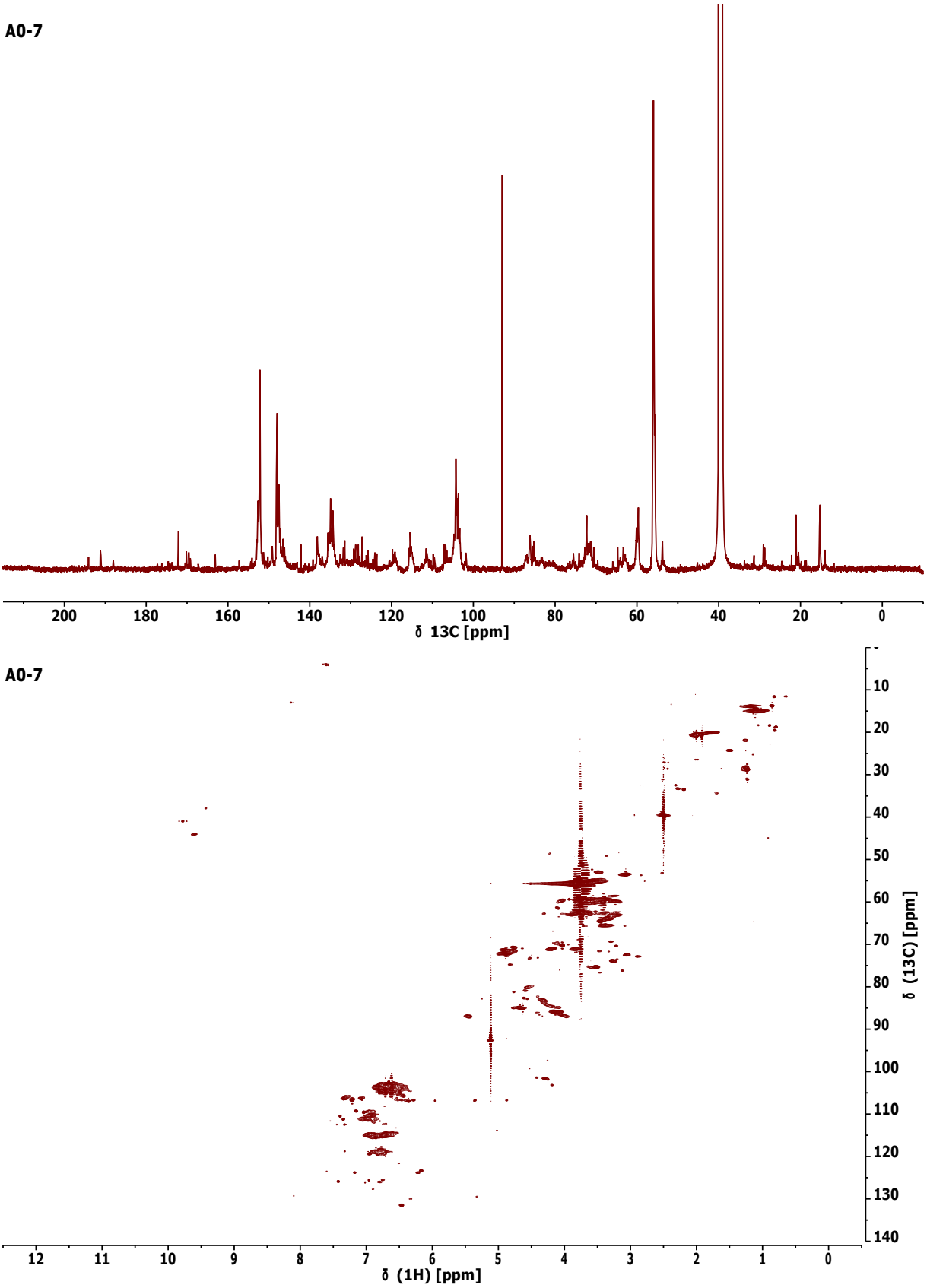

Figure S7. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A0-7**.

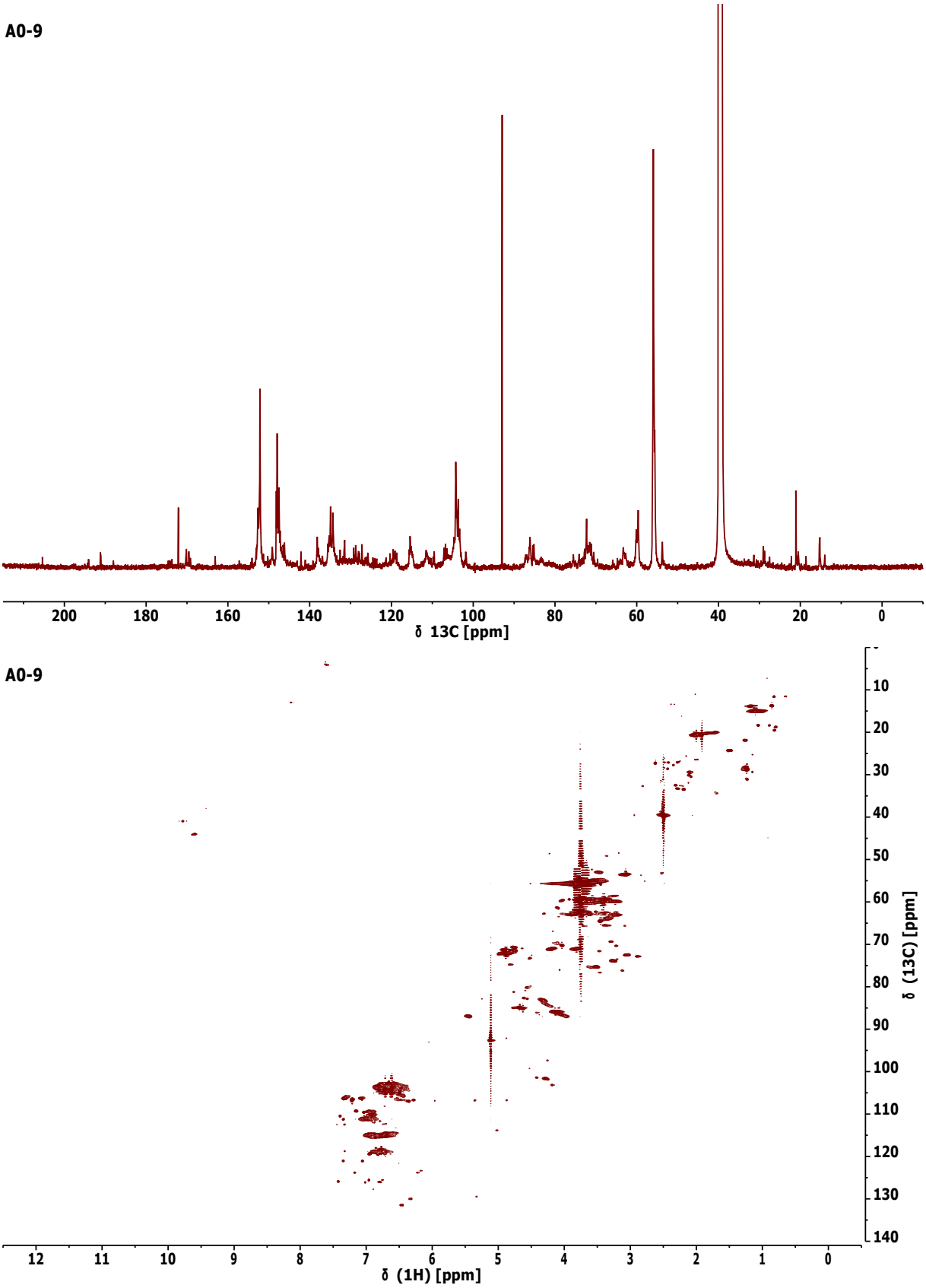

Figure S8. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A0-9**.

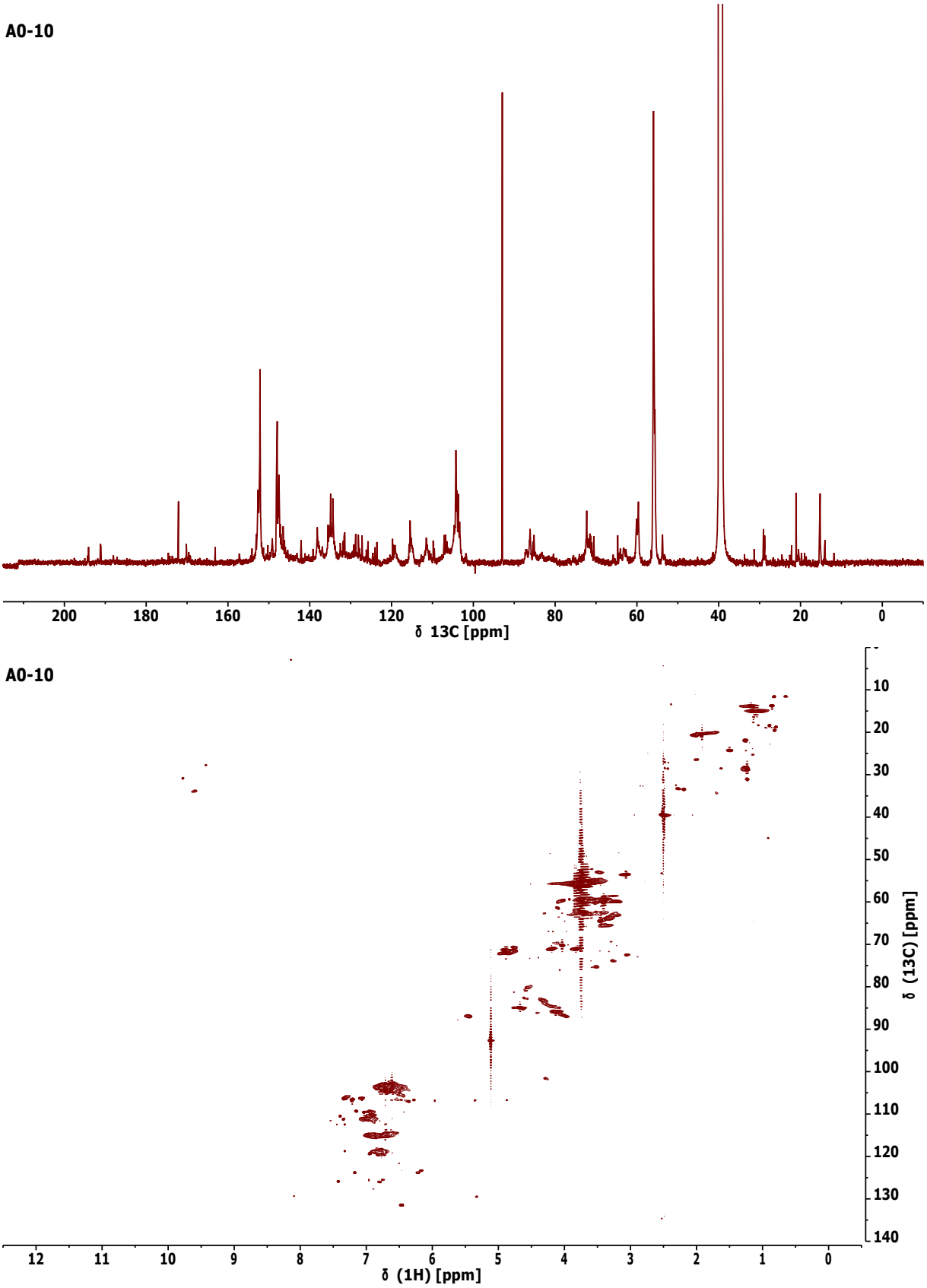

Figure S9. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A0-10**.

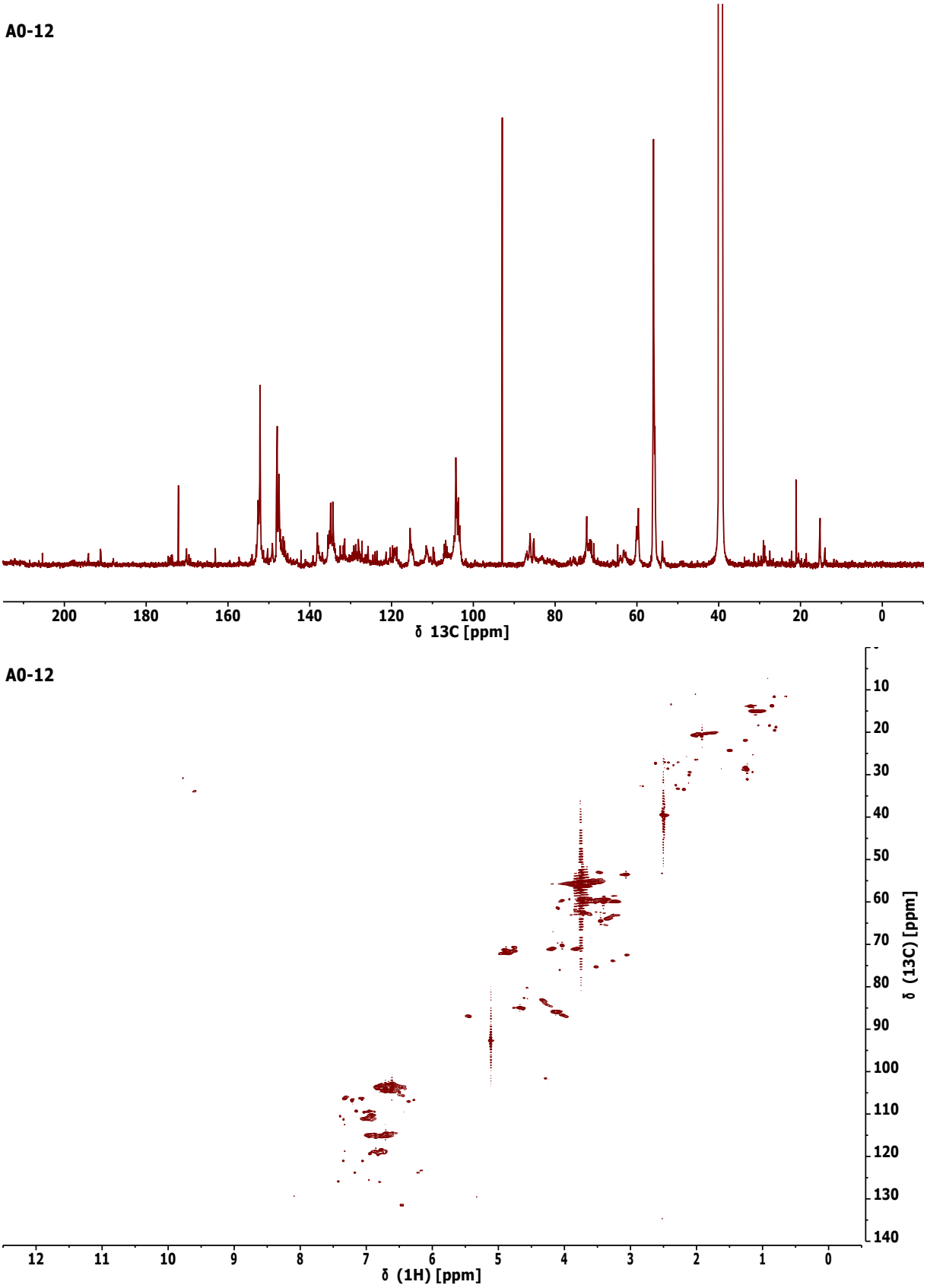

Figure S10. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A0-12**.

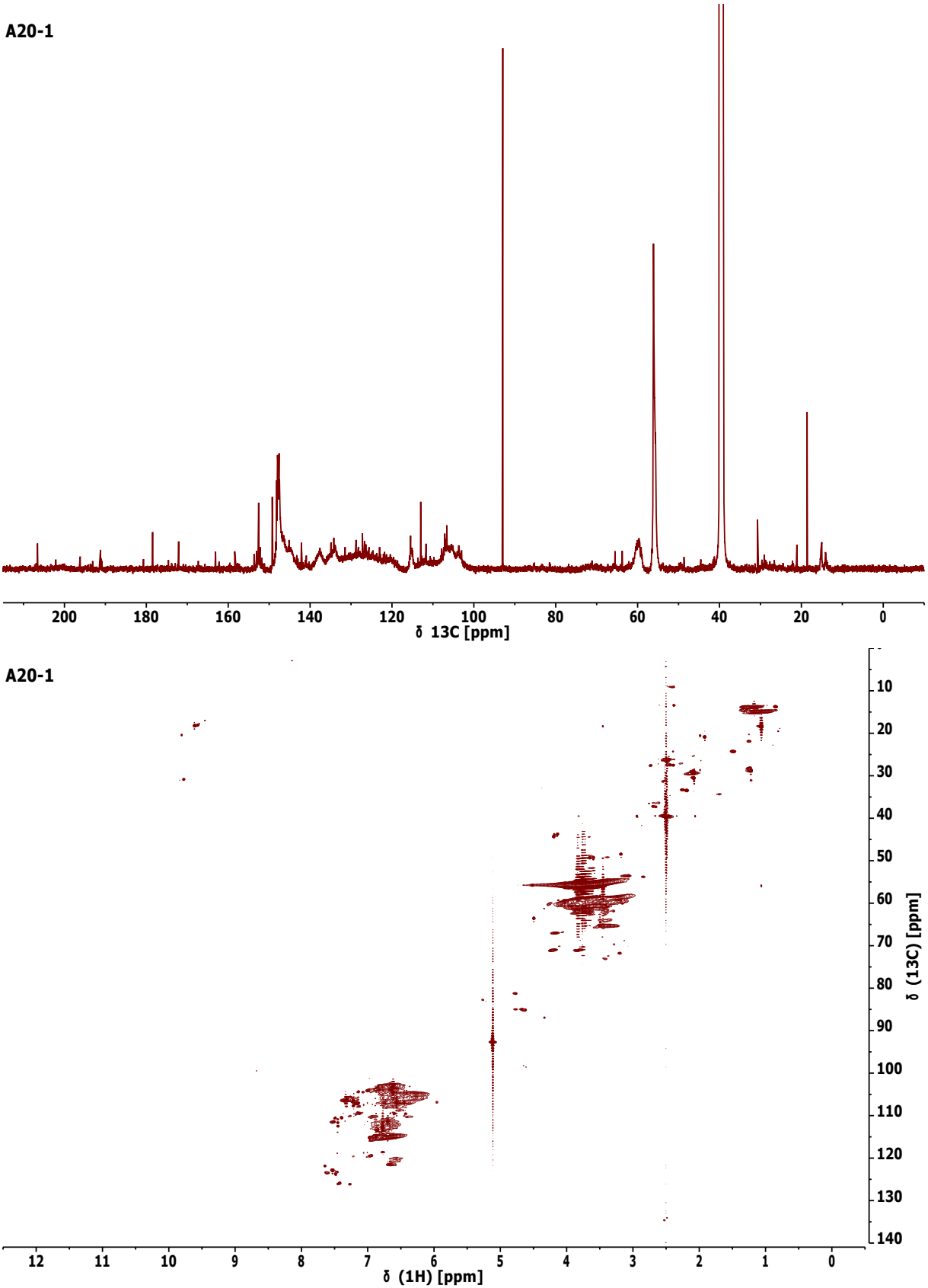

Figure S11. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A20-1**.

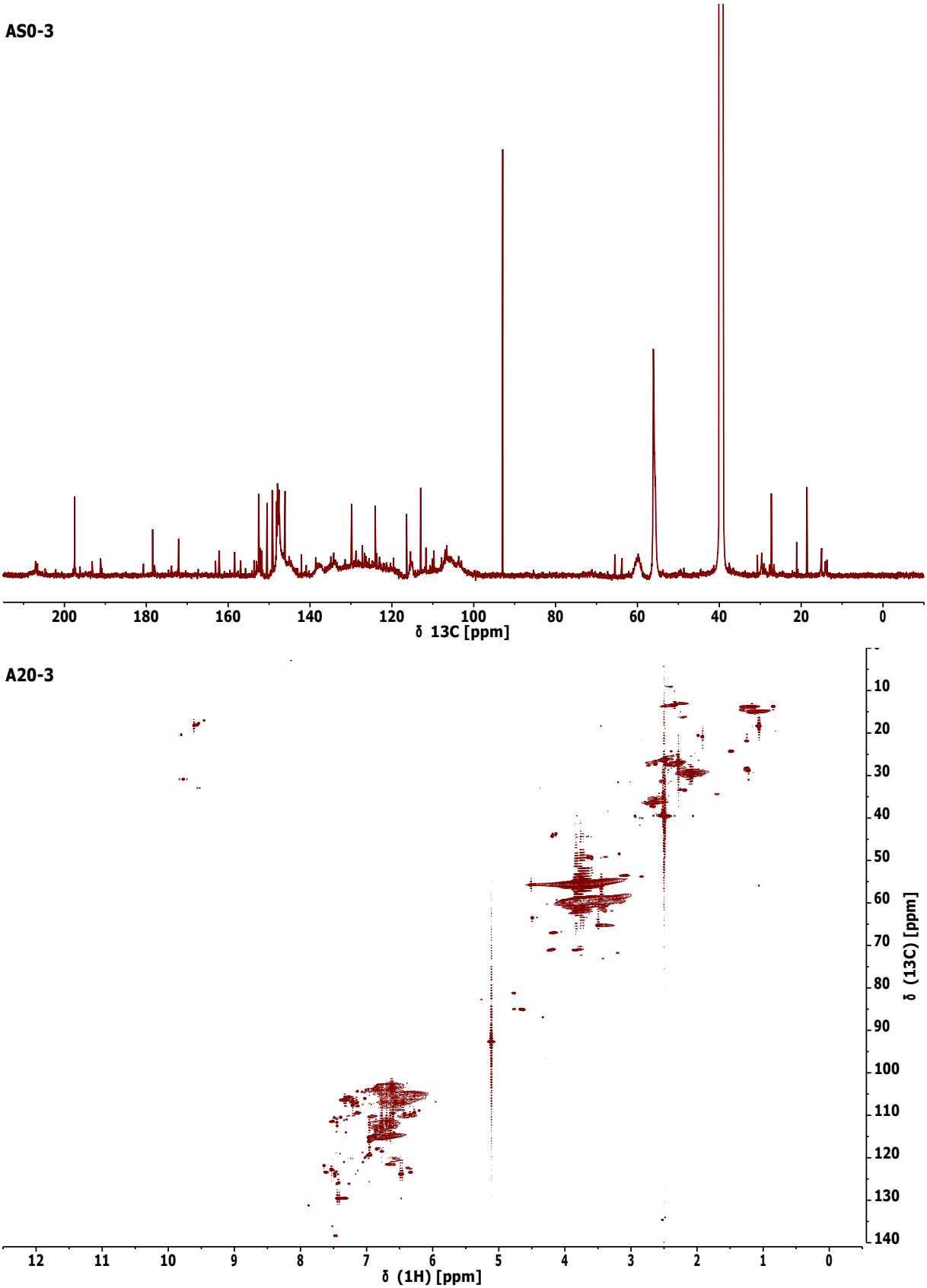

Figure S12. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A20-3**.

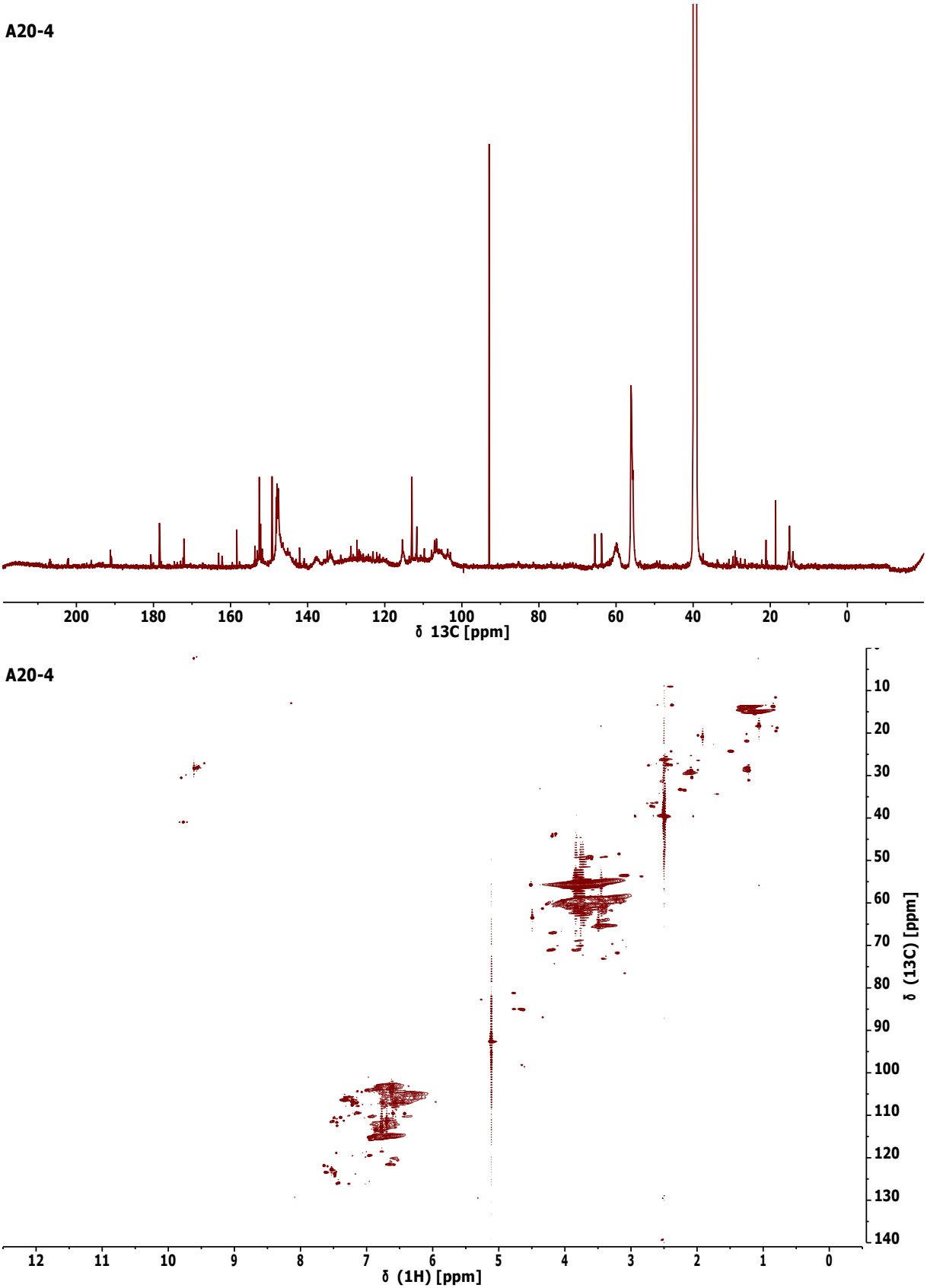

Figure S13. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A20-4**.

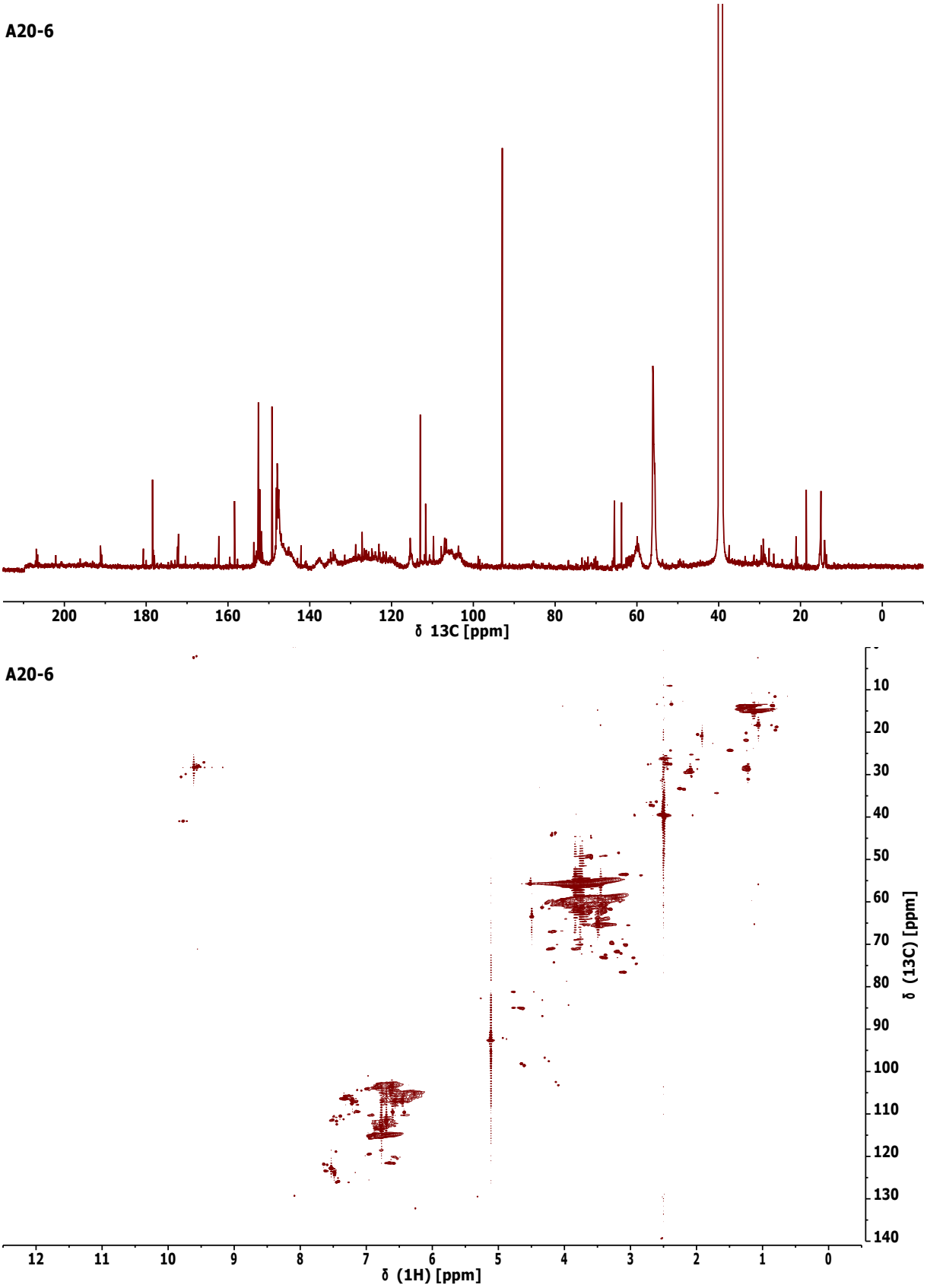

Figure S14. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A20-6**.

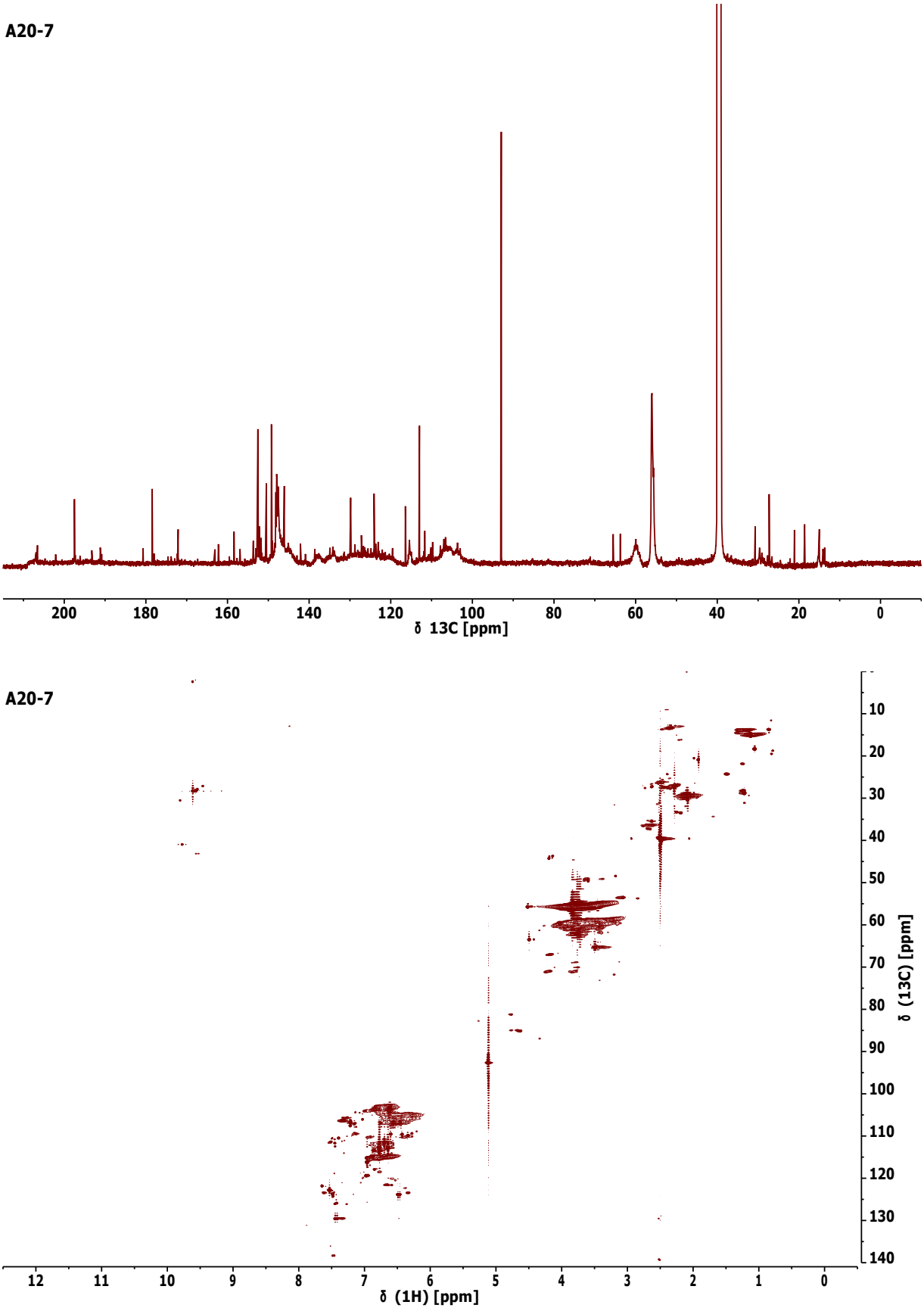

Figure S15. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A20-7**.

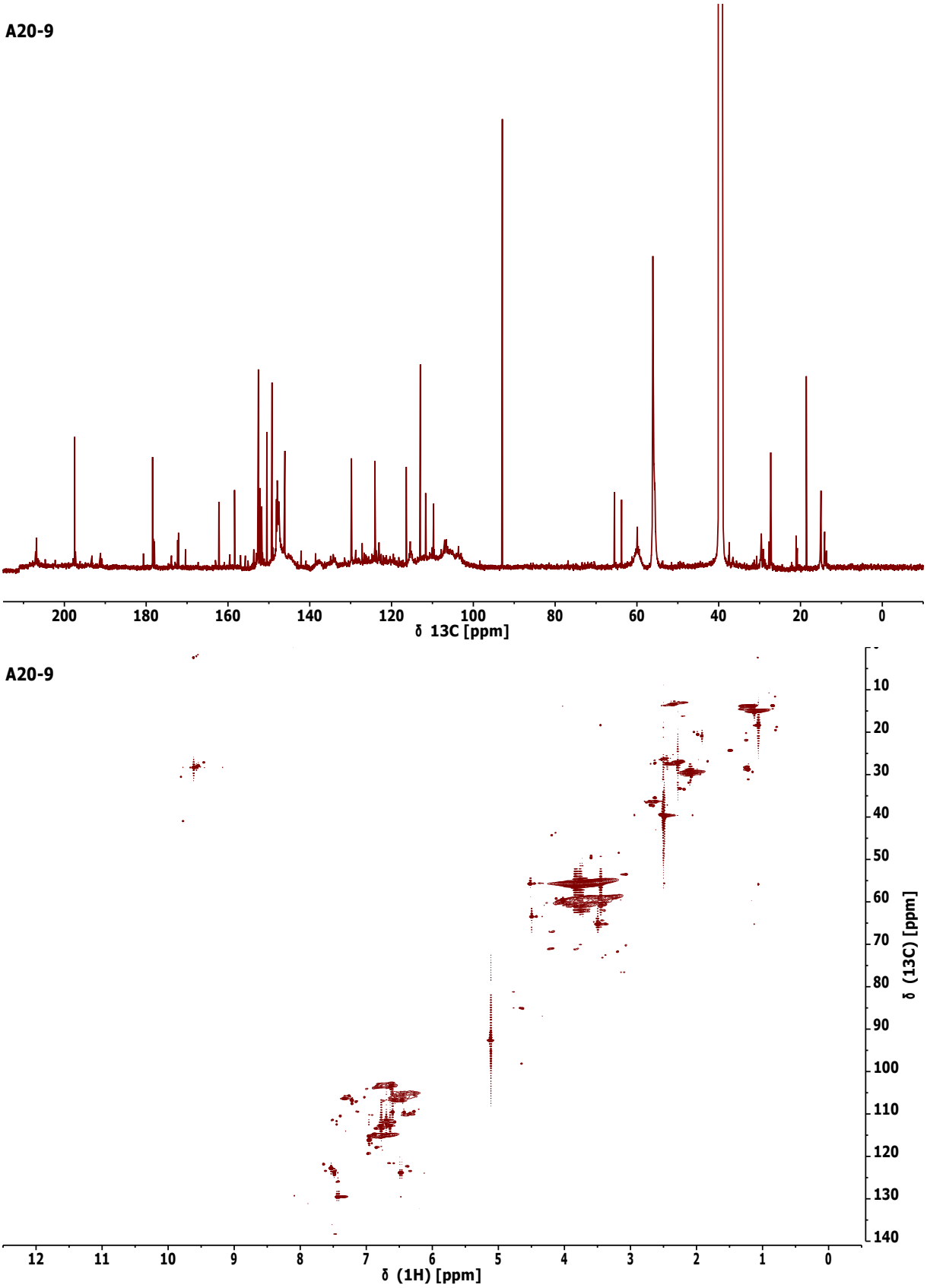

Figure S16. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A20-9**.

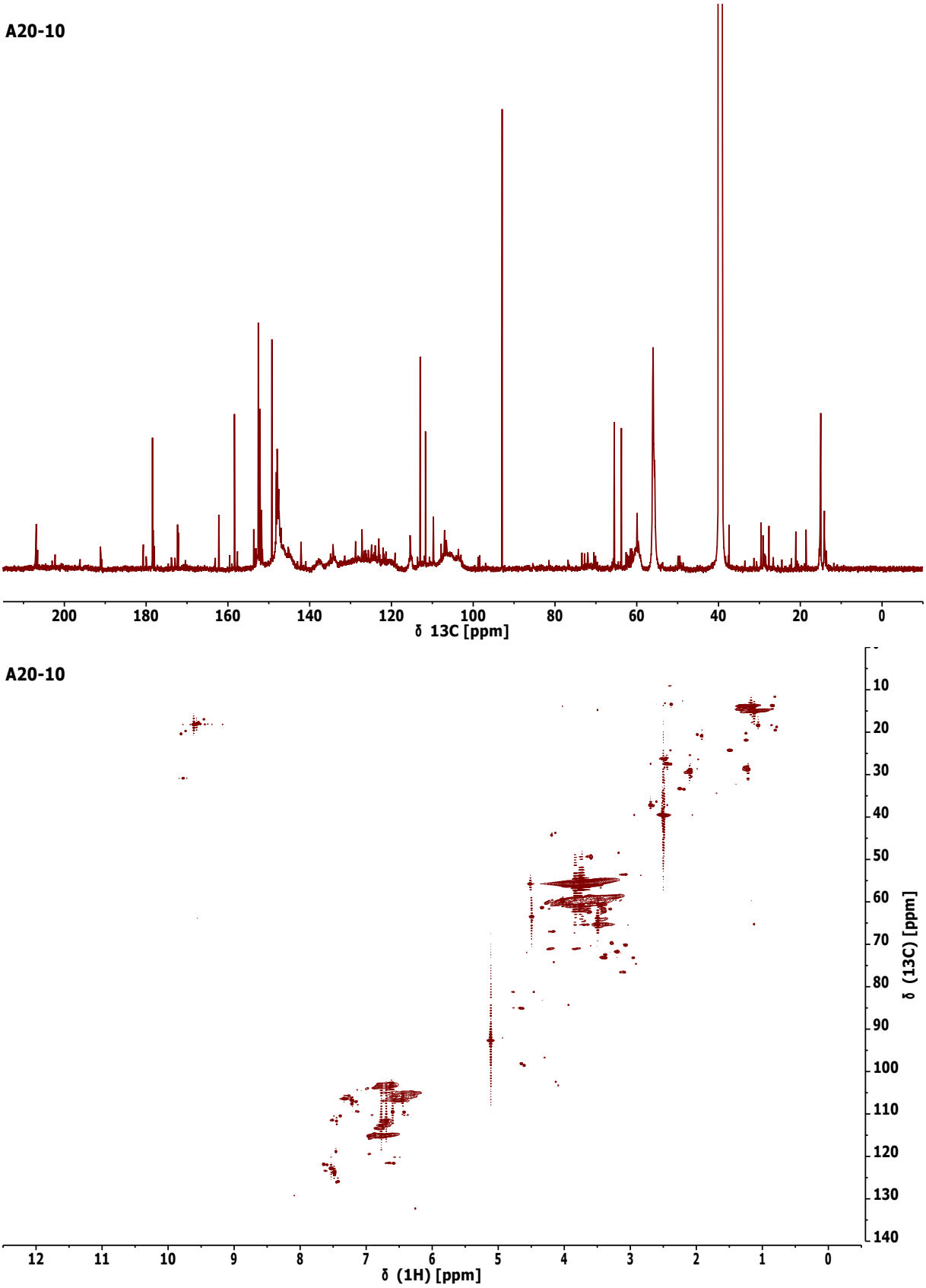

Figure S17. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A20-10**.

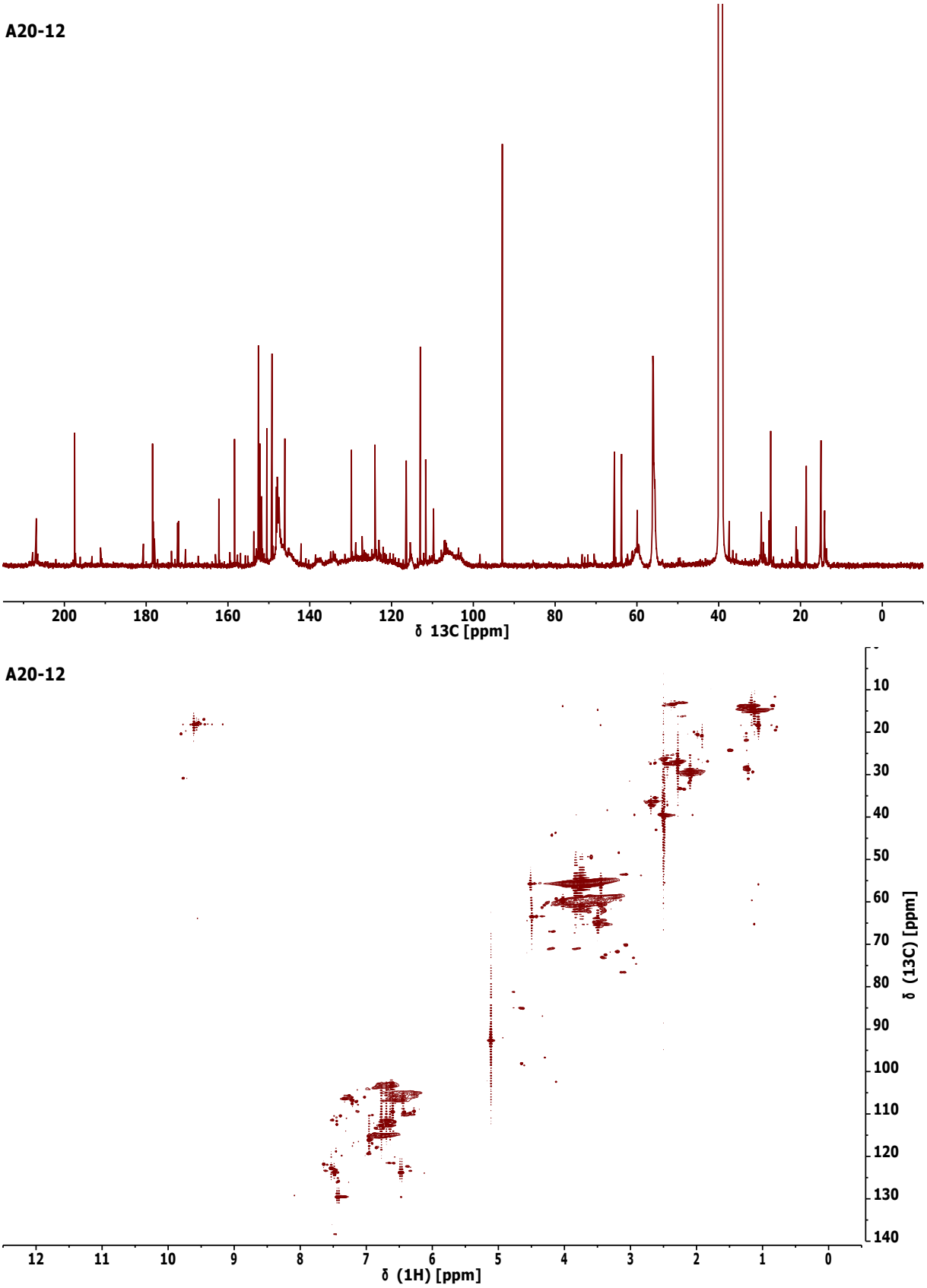

Figure S18. The ^{13}C (top) and HSQC (bottom) spectra for lignin sample **A20-12**.