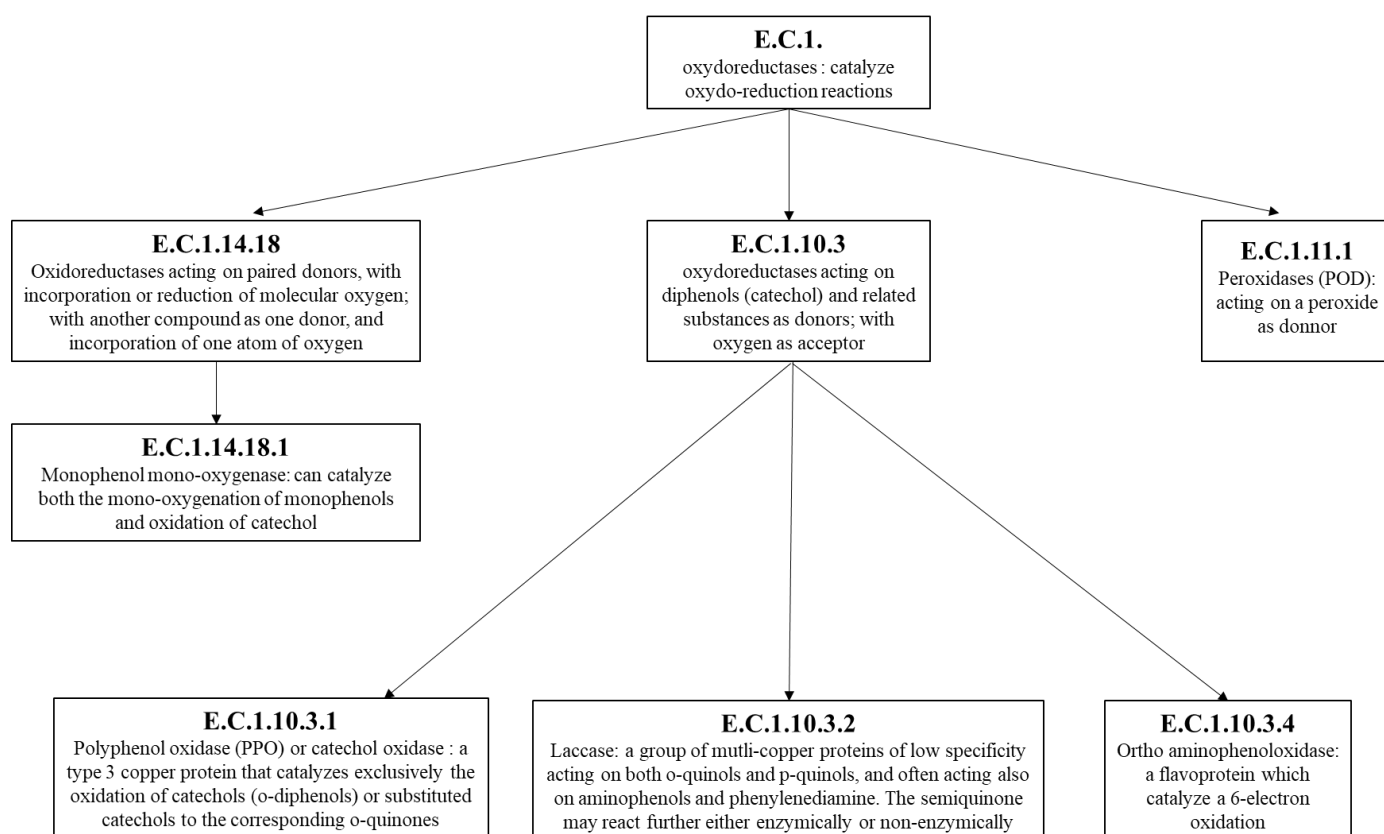


Supplementary Materials for

# Unambiguous NMR Structural Determination of (+)- Catechin-Laccase Dimeric Reaction Products as Potential Markers of Grape and Wine Oxidation.

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**Figure S1.** Classification of enzymes responsible for enzymatic browning

**Table S1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments of compounds N2, N3, N4, N6 and N8. The analyses were carried out in the solvent acetone- $d_6$

Compound	ring	H/C position	Chemical shift/ppm ( $\delta\text{H}$ )	Multiplicity pattern	J-coupling/Hz	Chemical shift/ppm ( $\delta\text{C}$ )
N2	A-u	4a	-	-	-	100.08
		5 (OH)	8.17	s	-	156.76
		6	5.96	d	2.29 ( $^4\text{J}$ )	95.53
		7 (OH)	8.02	s	-	157.24

		8	5.79	d	2.29 ( <sup>4</sup> J)	95.13
		8a	-	-	-	157.03
	<b>C-u</b>	2	4.54	d	2.17 ( <sup>3</sup> J)	67.92
		3	4.03	m	-	67.95
		3 (OH)	4.33	s		
		4α	2.89	dd	15.08 ( <sup>2</sup> J) / 5.41 ( <sup>3</sup> J)	28.93
		4β	2.38	dd	15.85 ( <sup>2</sup> J) / 8.79 ( <sup>3</sup> J)	
	<b>B-u</b>	1'	-	-	-	130.94
		2'	-	-	-	122.17
		3' (OH)	7.04	s	-	143.53
		4' (OH)	7.79	s	-	144.96
		5'	6.76	d	8.34 ( <sup>3</sup> J)	115.00
		6'	6.81	d	8.36 ( <sup>3</sup> J)	118.63
	<b>A-l</b>	4a	-	-	-	100.93
		5 (OH)	8.35	s	-	156.49
		6	6.13	s	-	96.71
		7 (OH)	7.47	s	-	155.05
		8	-	-	-	101.96
		8a	-	-	-	153.78
	<b>C-l</b>	2	4.52	d	1.89 ( <sup>3</sup> J)	67.96
		3	3.92	m	-	67.91
		3 (OH)	4.08	s	-	
		4α	2.93	dd	15.08 ( <sup>2</sup> J) / 5.22 ( <sup>3</sup> J)	28.37
		4β	2.54	dd	16.53 ( <sup>2</sup> J) / 8.77 ( <sup>3</sup> J)	
	<b>B-l</b>	1'	-	-	-	131.97
		2'	6.89	d	1.78 ( <sup>4</sup> J)	114.57
		3' (OH)	7.86	s	-	145.07
		4' (OH)	7.74	s	-	145.07
		5'	6.70	d	8.09 ( <sup>3</sup> J)	115.09
		6'	6.73	dd	8.79 ( <sup>3</sup> J) / 1.79 ( <sup>4</sup> J)	119.79
<b>N3</b>	<b>A-u</b>	4a	-	-	-	100.67
		5 (OH)	8.32	s	-	157.18
		6	6.01	d	2.26 ( <sup>4</sup> J)	96.22
		7 (OH)	8.08	s	-	157.79
		8	5.82	d	2.22 ( <sup>4</sup> J)	96.42
		8a	-	-	-	196.92
	<b>C-u</b>	2	4.53	d	8.38 ( <sup>3</sup> J)	82.80
		3	3.99	m	-	68.47
		3 (OH)	4.33	s	-	
		4α	2.98	dd	16.24 ( <sup>2</sup> J) / 5.89 ( <sup>3</sup> J)	29.42
		4β	2.52	dd	15.81 ( <sup>2</sup> J) / 9.36 ( <sup>3</sup> J)	
	<b>B-u</b>	1'	-	-	-	131.57
		2'	7.00	d	1.92 ( <sup>4</sup> J)	116.45

		3'	-	-	-	147.32
		4' (OH)	7.90	s	-	147.34
		5'	6.805	d	8.14 ( <sup>3</sup> J)	116.45
		6'	6.94	dd	8.06 ( <sup>3</sup> J) / 1.9 ( <sup>4</sup> J)	122.43
	<b>A-l</b>	4a	-	-	-	101.69
		5 (OH)	8.32	s	-	153.27
		6	6.15	s	-	96.18
		7 (OH)	8.2	s	-	149.62
		8	-	-	-	124.97
		8a	-	-	-	149.00
	<b>C-l</b>	2	4.62	d	7.57 ( <sup>3</sup> J)	82.71
		3	3.96	m	-	68.20
		3 (OH)	4.08	s	-	
		4α	2.90	dd	16.42 ( <sup>2</sup> J) / 5.18 ( <sup>3</sup> J)	28.6
		4β	2.58	dd	16.38 ( <sup>2</sup> J) / 8.23 ( <sup>3</sup> J)	
	<b>B-l</b>	1'	-	-	-	131.63
		2'	6.75	d	1.85 ( <sup>4</sup> J)	114.81
		3' (OH)	7.95	s	-	145.44
		4' (OH)	7.74	s	-	145.78
		5'	6.67	d	8.12 ( <sup>3</sup> J)	115.58
		6'	6.63	dd	8.15 ( <sup>3</sup> J) / 1.85 ( <sup>4</sup> J)	120.23
<b>N4-A</b>	<b>A-u</b>	4a	-	-	-	100.71
		5 (OH)	8.30	s	-	157.26
		6	6.02	d	2.33 ( <sup>4</sup> J)	96.16
		7 (OH)	8.08	s	-	157.76
		8	5.9	d	2.29 ( <sup>4</sup> J)	95.5
	<b>C-u</b>	8a	-	-	-	154.05
		2	4.57	d	6.13 ( <sup>3</sup> J)	83.15
		3	4.09	m	-	
		3 (OH)	4.34 or under H3C	s	-	68.83
		4α	2.96	dd	16.39 ( <sup>2</sup> J) / 7.12 ( <sup>3</sup> J)	28.91
		4β	2.55	dd	15.53 ( <sup>2</sup> J) / 8.95 ( <sup>3</sup> J)	
	<b>B-u</b>	1'	-	-	-	123.79
		2'	6.80	d	2.21 ( <sup>4</sup> J)	114.25
		3' (OH)	7.65	s	-	146.36
		4' (OH)	7.30	s	-	143.94
		5'	-	-	-	121.33
	<b>A-l</b>	6'	6.85	d	2.24 ( <sup>4</sup> J)	157.08
		4a	-	-	-	100.89
		5 (OH)	8.41	s	-	156.79
		6	6.15	s	-	96.55
		7 (OH)	7.43	s	-	155.05
		8	-	-	-	104.99
		8a	-	-	-	153.84

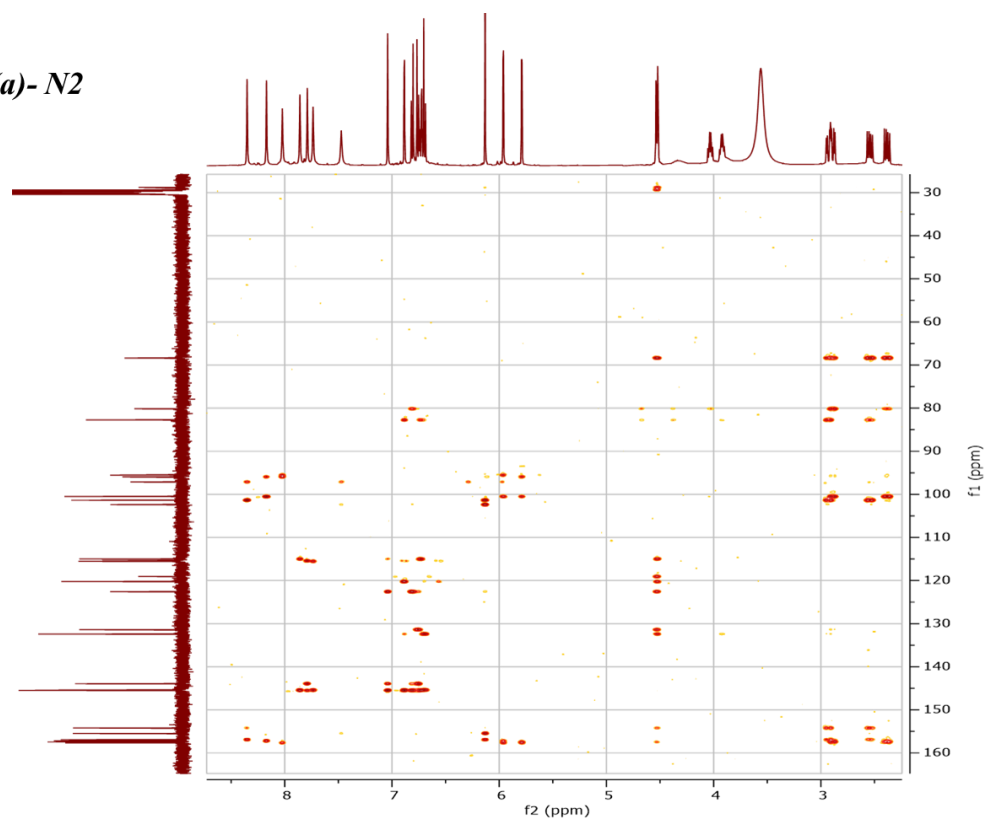
<b>N4-B</b>	<b>C-l</b>	2	4.73	d	6.21 ( <sup>3</sup> J)	81.93
		3	4.06	m	-	
		3 (OH)	4.34 or under H3C	s	-	67.66
		4 $\alpha$	2.84	dd	16.63 ( <sup>2</sup> J) / 5.1 ( <sup>3</sup> J)	
		4 $\beta$	2.62	dd	10.47 ( <sup>2</sup> J) / 6.94 ( <sup>3</sup> J)	28.02
	<b>B-l</b>	1'	-	-	-	131.84
		2'	6.84	d	1.83 ( <sup>4</sup> J)	114.82
		3' (OH)	8.08	s	-	145.45
		4' (OH)	7.70	s	-	145.59
		5'	6.72	d	8.48 ( <sup>3</sup> J)	115.67
		6'	6.69	dd	8.04 ( <sup>3</sup> J) / 1.92 ( <sup>4</sup> J)	119.31
	<b>A-u</b>	4a	-	-	-	100.78
		5 (OH)	8.26	s	-	157.17
		6	6.00	d	2.37 ( <sup>4</sup> J)	96.13
		7 (OH)	8.08	s	-	157.71
		8	5.82	d	2.34 ( <sup>4</sup> J)	95.51
		8a	-	-	-	157.71
	<b>C-u</b>	2	4.42	d	8.26 ( <sup>3</sup> J)	83.07
		3	3.82	m	-	
		3 (OH)	4.34 or under H3C	s	-	68.86
		4 $\alpha$	2.96	dd	16.52 ( <sup>2</sup> J) / 8.63( <sup>3</sup> J)	28.98
		4 $\beta$	2.46	dd	16.29 ( <sup>2</sup> J) / 9.1 ( <sup>3</sup> J)	
	<b>B-u</b>	1'	-	-	-	124.51
		2'	6.82	d	2.08 ( <sup>4</sup> J)	113.30
		3' (OH)	7.83	s	-	146.65
		4' (OH)	7.29	s	-	144.45
		5'	-	-	-	122.01
		6'	6.71	d	2.58 ( <sup>4</sup> J)	157.02
	<b>A-l</b>	4a	-	-	-	101.03
		5 (OH)	8.42	s	-	156.69
		6	6.15	s	-	96.31
		7 (OH)	7.23	s	-	155.06
		8	-	-	-	104.55
		8a	-	-	-	153.84
	<b>C-l</b>	2	4.55	d	5.71 ( <sup>3</sup> J)	82.93
		3	3.99	m	-	
		3 (OH)	4.34 or under H3C	s	-	68.25
		4 $\alpha$	2.93	dd	15.77 ( <sup>2</sup> J) / 6.55( <sup>3</sup> J)	28.91
		4 $\beta$	2.59	dd	9.48 ( <sup>2</sup> J) / 6.32 ( <sup>3</sup> J)	
	<b>B-l</b>	1'	-	-	-	132.10
		2'	6.94	d	2.00 ( <sup>4</sup> J)	115.08
		3' (OH)	8.00	s	-	145.38
		4' (OH)	7.79	s	-	145.61

		5'	6.69	d	8.23 ( <sup>3</sup> J)	115.60
		6'	6.77	dd	8.16 ( <sup>3</sup> J) / 2.04 ( <sup>4</sup> J)	120.05
N6	A-u	4a	-	-	-	100.66
		5 (OH)	8.23	s	-	157.23
		6	6.03	d	2.04 ( <sup>4</sup> J)	96.25
		7 (OH)	8.03	s	-	157.80
		8	5.89	d	2.04 ( <sup>4</sup> J)	95.49
		8a	-	-	-	156.86
	C-u	2	4.60	d	8.05 ( <sup>3</sup> J)	82.63
		3	4.01	m	-	68.36
		3 (OH)	4.14	s	-	
		4 $\alpha$	2.96	dd	9.57 ( <sup>2</sup> J) / 5.62( <sup>3</sup> J)	
		4 $\beta$	2.55	dd	15.85 ( <sup>2</sup> J) / 8.64 ( <sup>3</sup> J)	29.16
	B-u	1'	-	-	-	134.69
		2'	6.92	d	1.71 ( <sup>4</sup> J)	115.72
		3' (OH)	7.80	s	-	147.25
		4'	-	-	-	147.45
		5'	6.22	d	8.38 ( <sup>3</sup> J)	115.96
		6'	6.78	dd	8.38 ( <sup>3</sup> J) / 1.8 ( <sup>4</sup> J)	119.72
	A-l	4a	-	-	-	101.79
		5 (OH)	8.27	s	-	153.33
		6	6.19	s	-	96.17
		7 (OH)	8.17	s	-	149.67
		8	-	-	-	125.03
		8a	-	-	-	149.05
	C-l	2	4.66	d	7.32 ( <sup>3</sup> J)	82.68
		3	3.98	m	-	67.97
		3 (OH)	4.05	s	-	
		4 $\alpha$	2.93	dd	10.17 ( <sup>2</sup> J) / 5.02 ( <sup>3</sup> J)	
		4 $\beta$	2.62	dd	16.34 ( <sup>2</sup> J) / 7.86 ( <sup>3</sup> J)	28.60
	B-l	1'	-	-	-	131.63
		2'	6.71	d	1.71 ( <sup>4</sup> J)	114.88
		3' (OH)	7.83	s	-	146.72
		4'	-	-	-	145.90
		5'	6.73	d	8.11 ( <sup>3</sup> J)	115.69
		6'	6.64	dd	7.93 ( <sup>3</sup> J) / 1.59 ( <sup>4</sup> J)	119.92
N8	A-u	4a	-	-	-	100.24
		5 (OH)	8.36	s	-	157.41
		6	6.01	d	2.1 ( <sup>4</sup> J)	95.90
		7 (OH)	7.88	s	-	157.92
		8	5.61	d	2.34 ( <sup>4</sup> J)	96.98
		8a	-	-	-	155.97
	C-u	2	4.06	d	9.58 ( <sup>3</sup> J)	79.04
		3	4.01	m	-	66.22
		4 $\alpha$	2.95	dd	10.12 ( <sup>2</sup> J) / 5.40 ( <sup>3</sup> J)	27.95

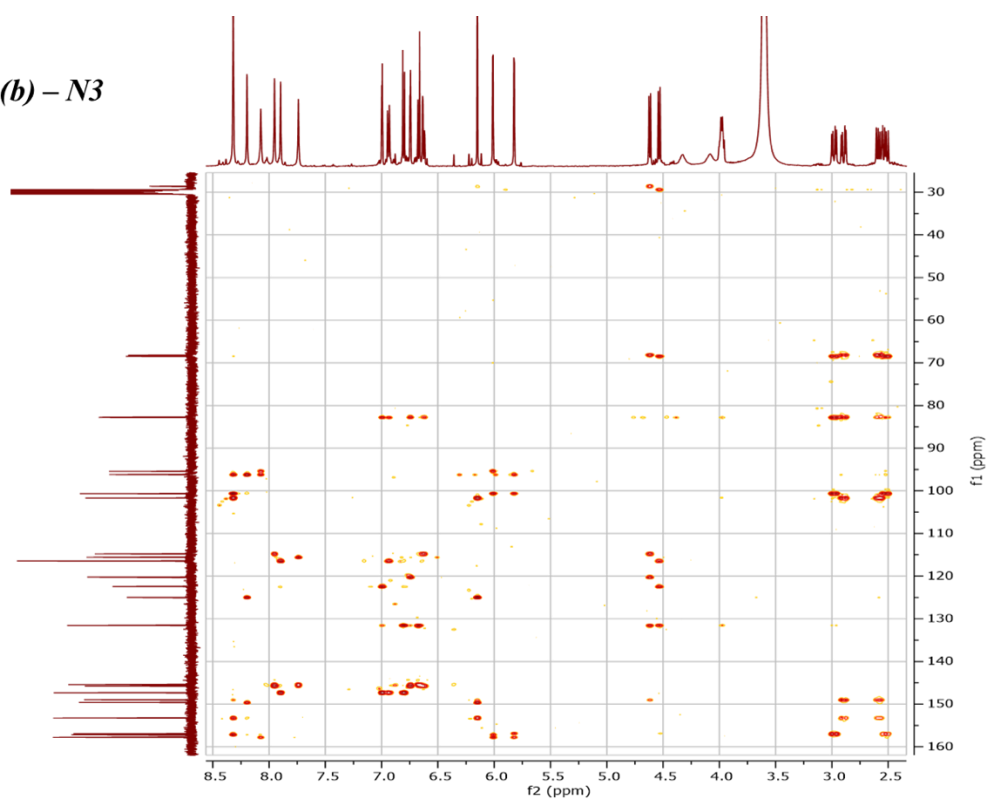
	4 $\beta$	2.53	dd	14.29 ( $^2J$ ) / 11.08 ( $^3J$ )	
<b>B-u</b>	1'	-	-	-	89.61
	2' $\alpha$	2.71	d	12.03 ( $^2J$ )	45.20
	2' $\beta$	2.49	d	12.03 ( $^2J$ )	
	3' (OH)	5.78	s	-	94.80
	4'	-	-	-	192.69
	5'	6.38	s	-	112.91
	6'	-	-	-	162.57
<b>A-l</b>	4a	-	-	-	103.96
	5 (OH)	9.72	s	-	164.46
	6	6.22	s	-	90.84
	7	-	-	-	167.13
	8	-	-	-	105.43
	8a	-	-	-	154.73
<b>C-l</b>	2	4.86	d	7.84 ( $^3J$ )	83.46
	3	4.12	m	-	67.70
	3 (OH)	4.23	s	-	
	4 $\alpha$	2.98	dd	11.16 ( $^2J$ ) / 5.40 ( $^3J$ )	
	4 $\beta$	2.95	dd	16.18 ( $^2J$ ) / 8.41 ( $^3J$ )	28.55
<b>B-l</b>	1'	-	-	-	131.16
	2'	6.94	d	1.51 ( $^4J$ )	115.04
	3' (OH)	7.97	s	-	145.88
	4' (OH)	7.92	s	-	146.06
	5'	6.83	d	7.97 ( $^3J$ )	116.02
	6'	6.80	dd	7.97 ( $^3J$ ) / 1.69 ( $^4J$ )	119.98

**Figure S2** - 2D  $^1\text{H}/^{13}\text{C}$  HMBC, top 1D  $^1\text{H}$ , side 1D  $^{13}\text{C}$  spectrum (a) N2; (b) N3; (c) N4; (d) N6 and (e) N8

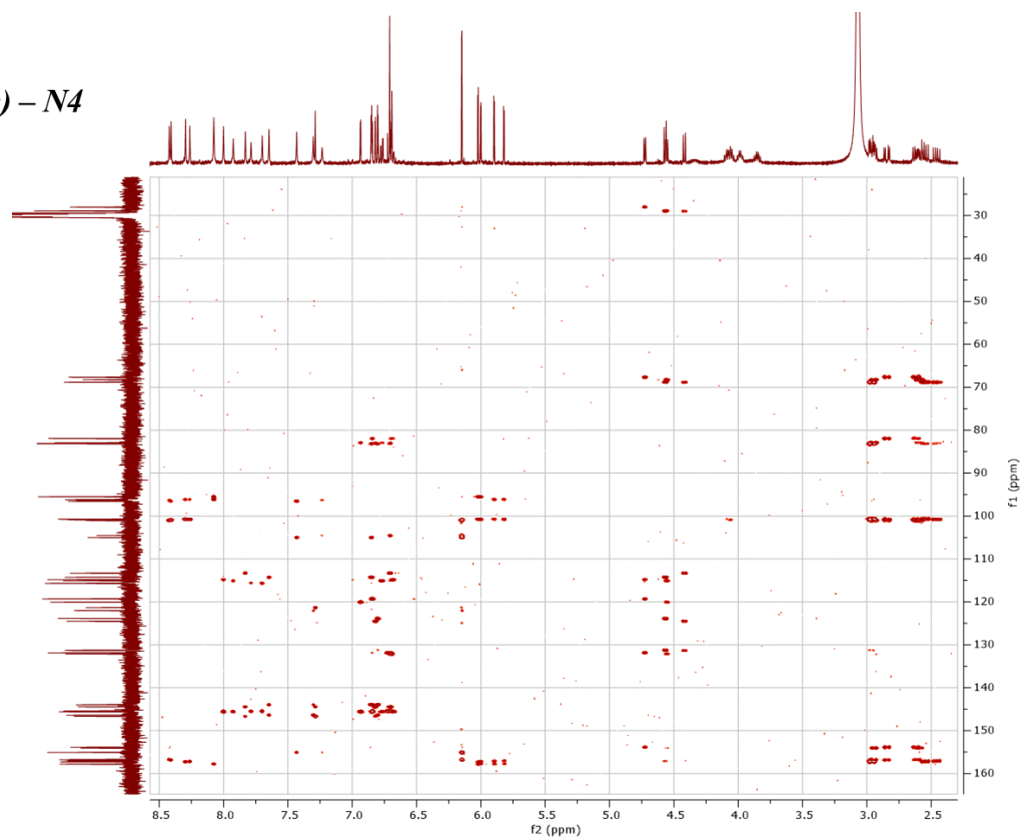
**(a)- N2**



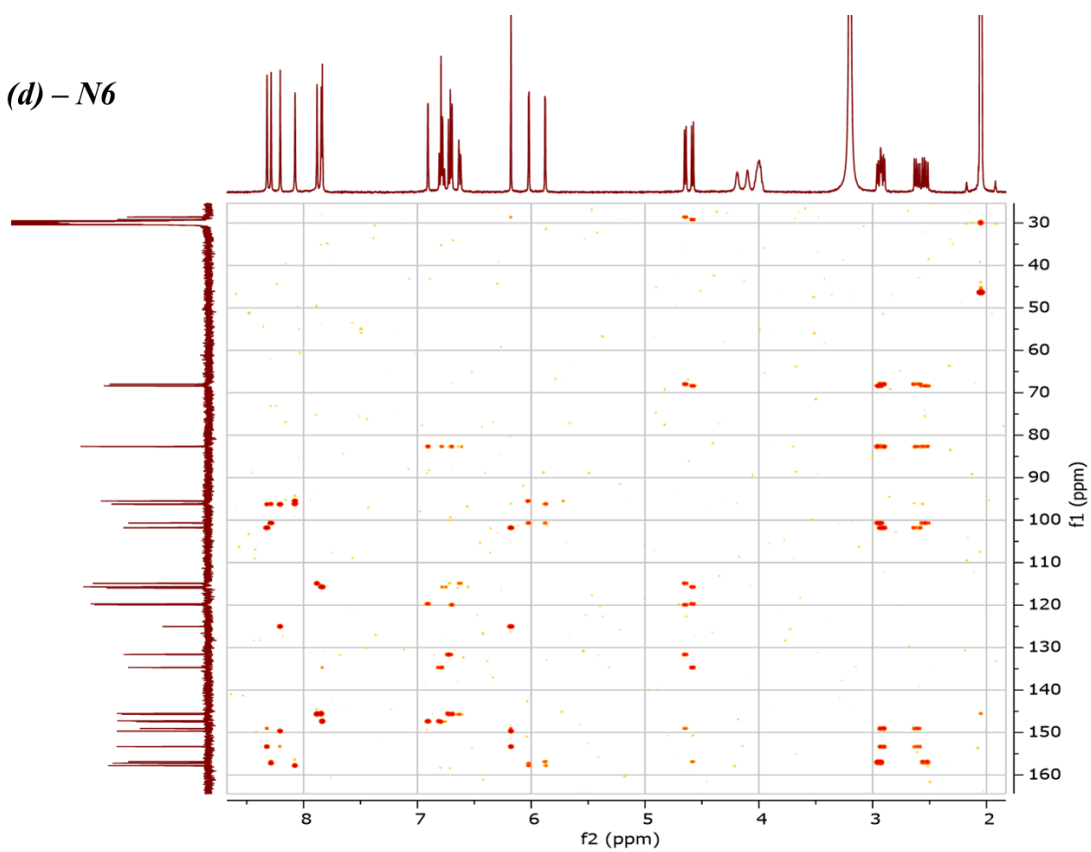
**(b) - N3**



(c) – N4

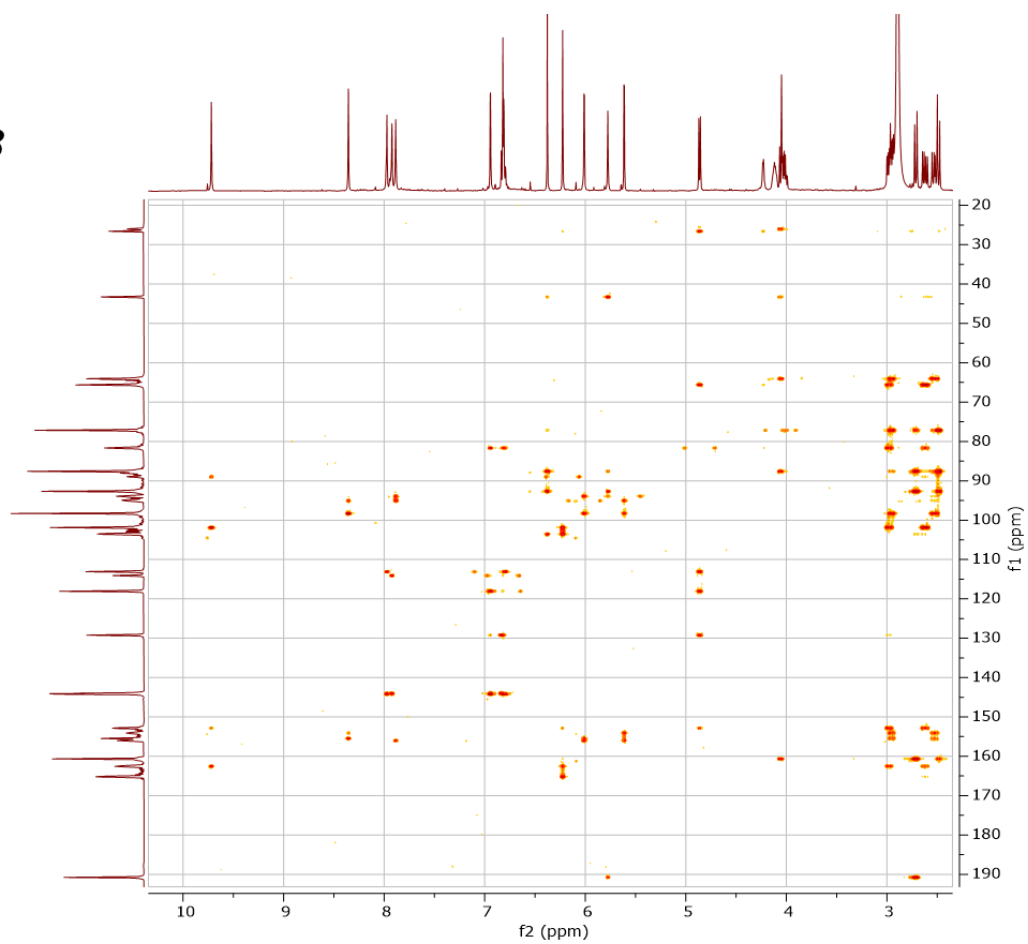


(d) – N6

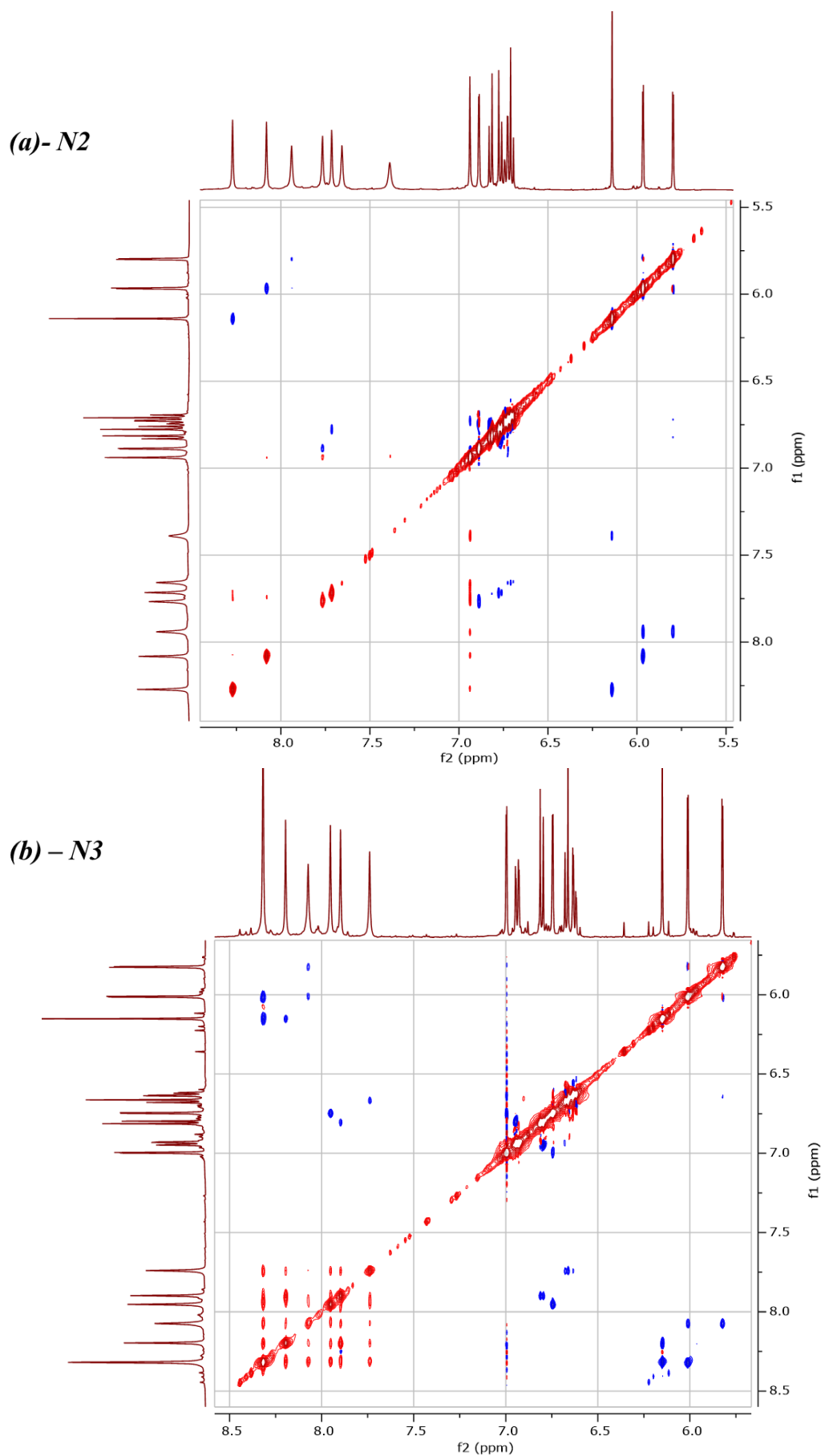




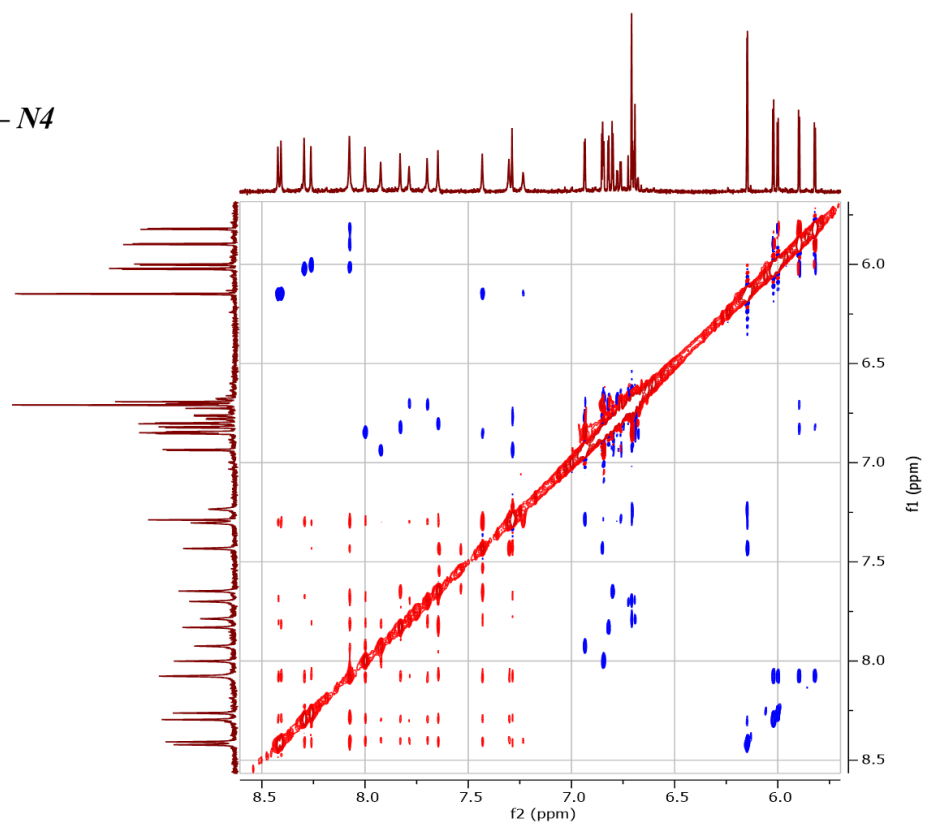
*(e)* - N8



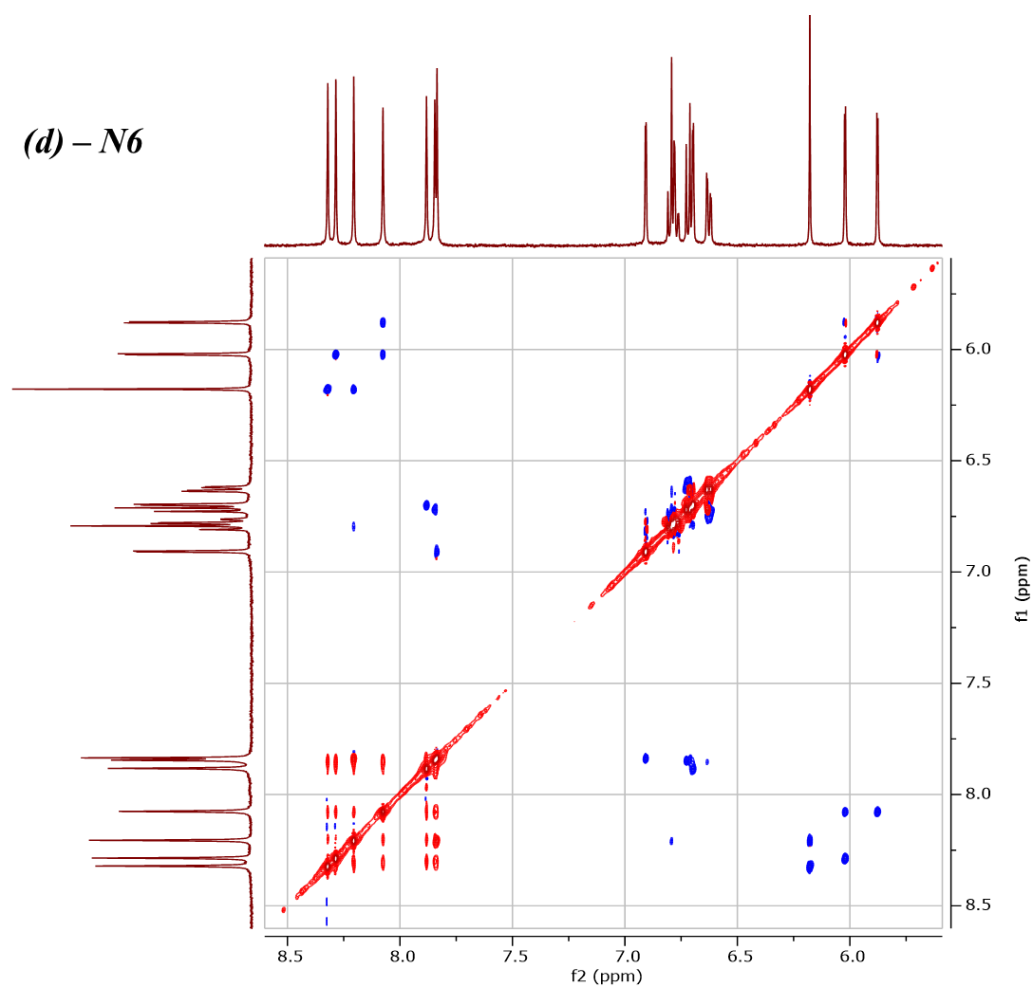
**Figure S3** -  $^1\text{H}$  2D ROESY spectrum showing correlations (in blue) between phenolic and aromatic protons, ROE correlations between phenolic protons due to chemical exchange appear in red (a) N2; (b) N3; (c) N4; (d) N6 and (e) N8



*(c) – N4*



*(d) – N6*



*(e) - N8*

