

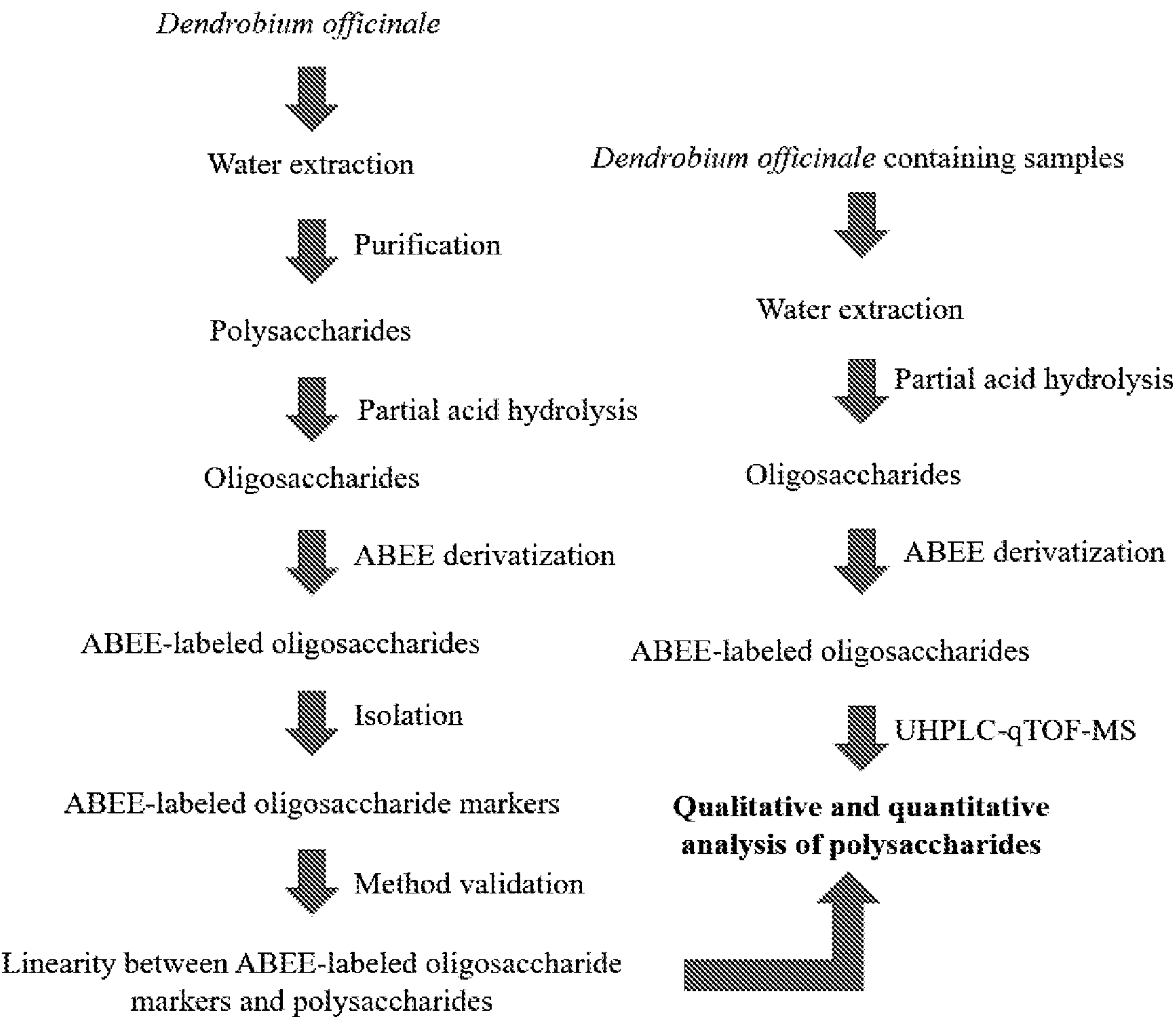


FIG. 1

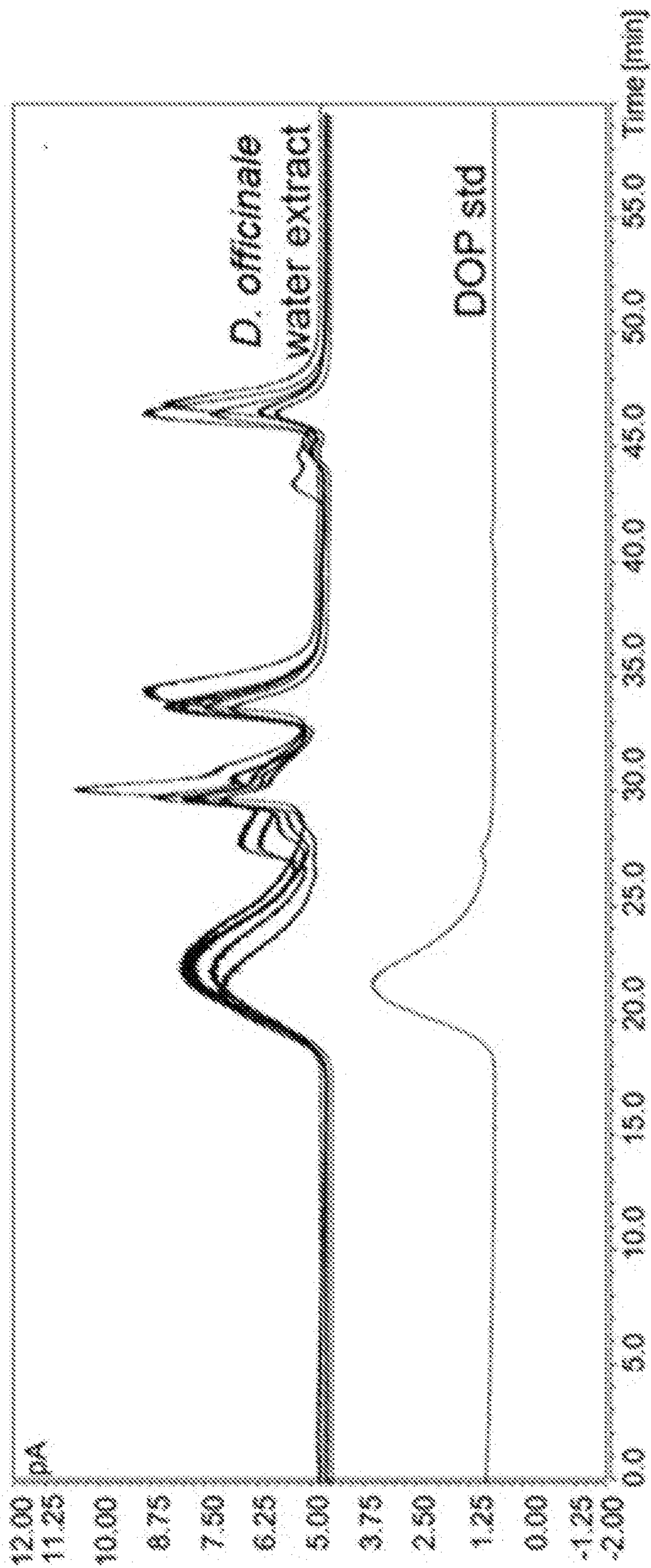


FIG. 2A

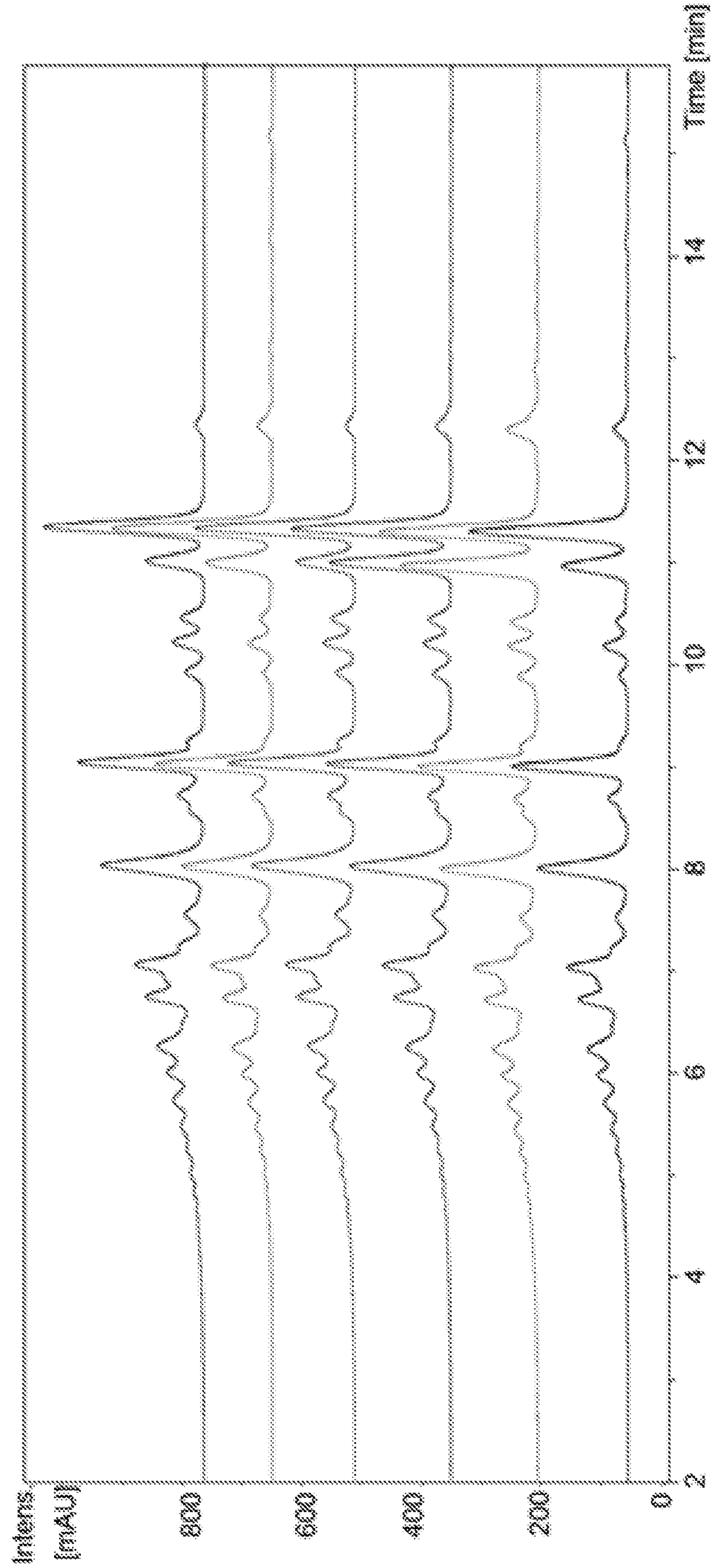


FIG. 2B

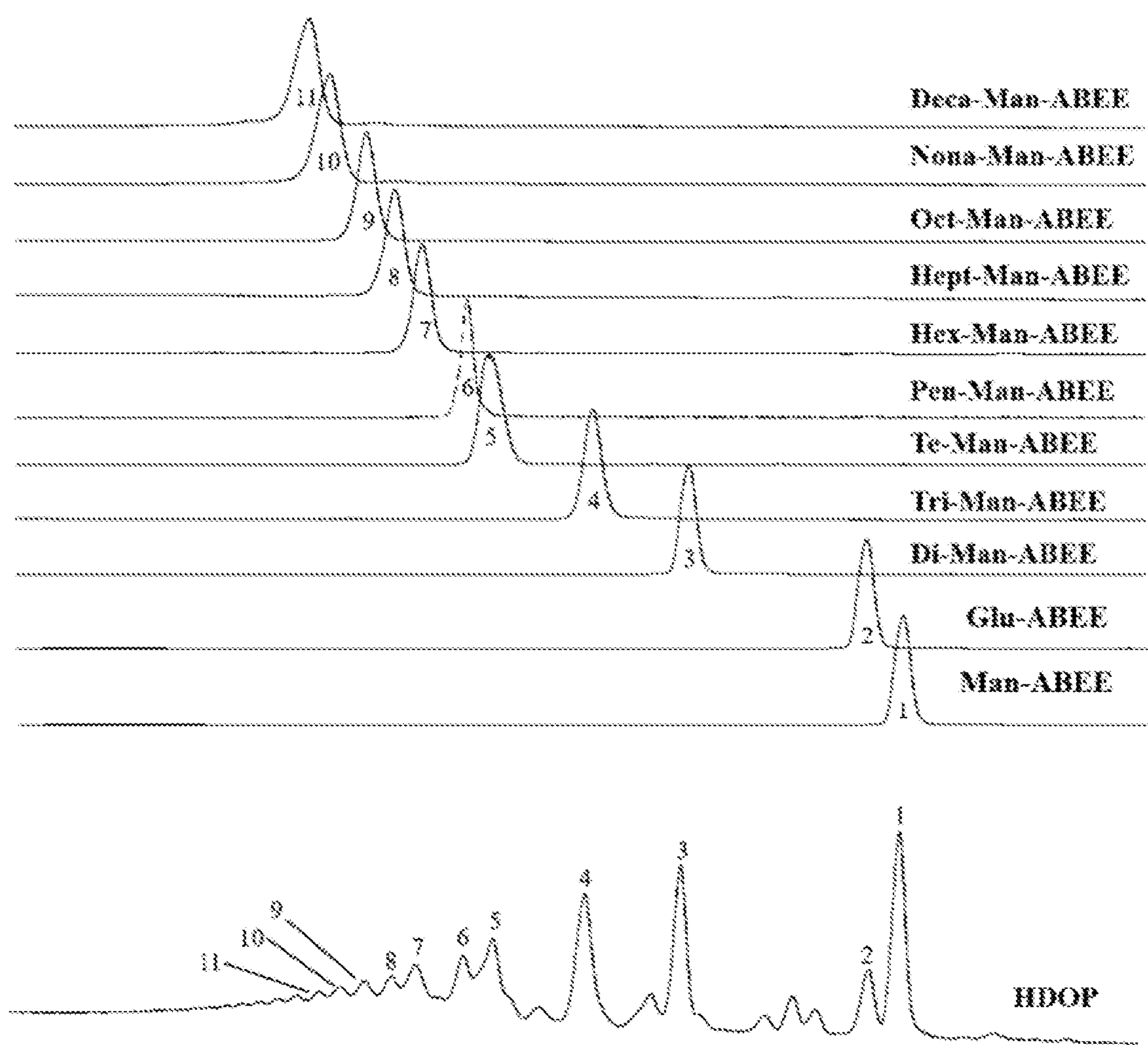


FIG. 3

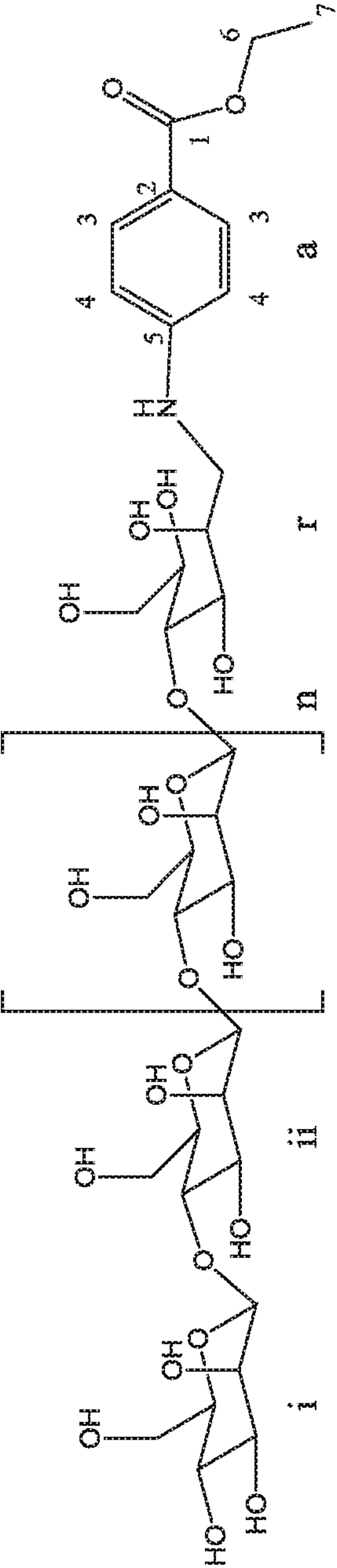


FIG. 4

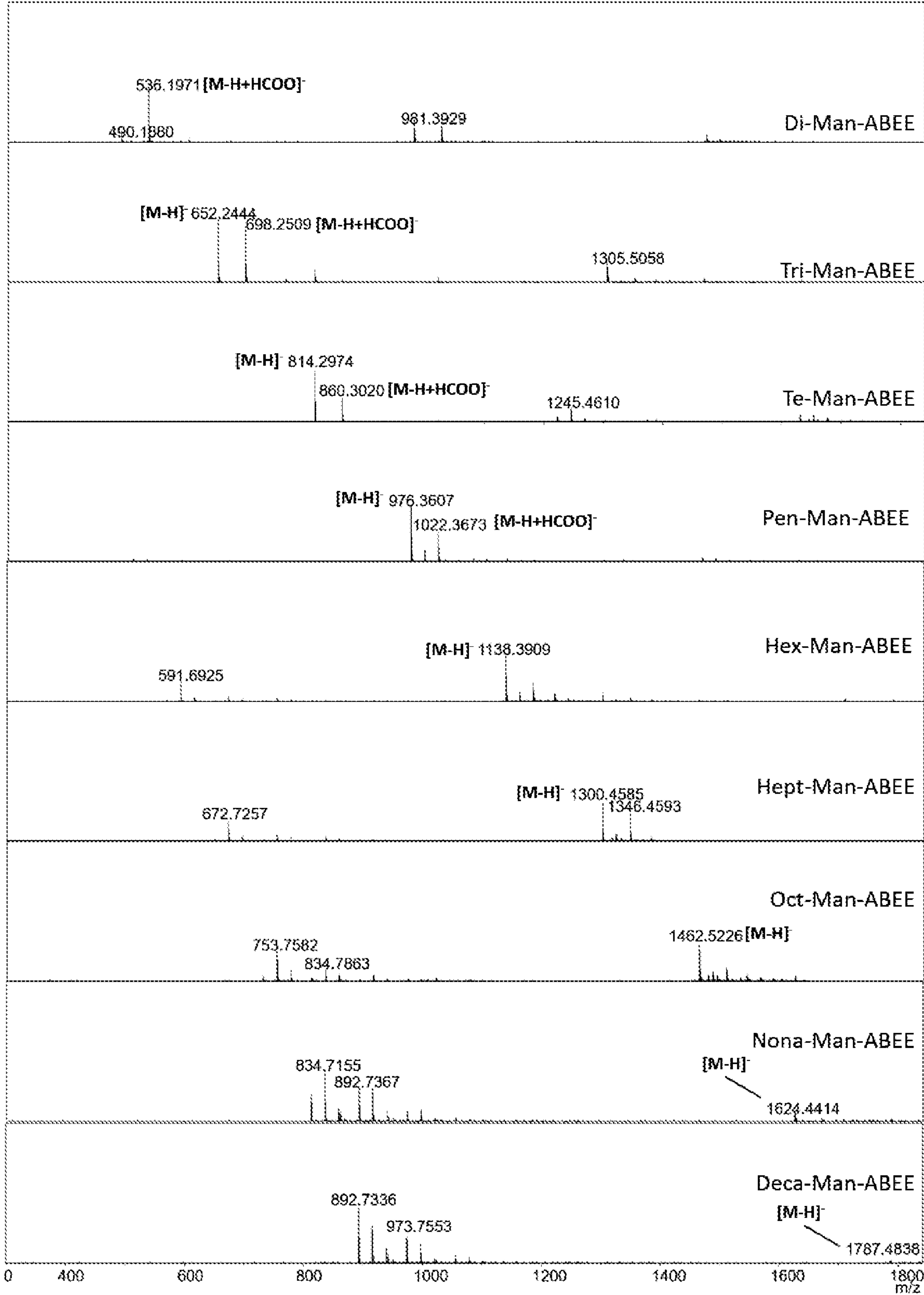


FIG. 5

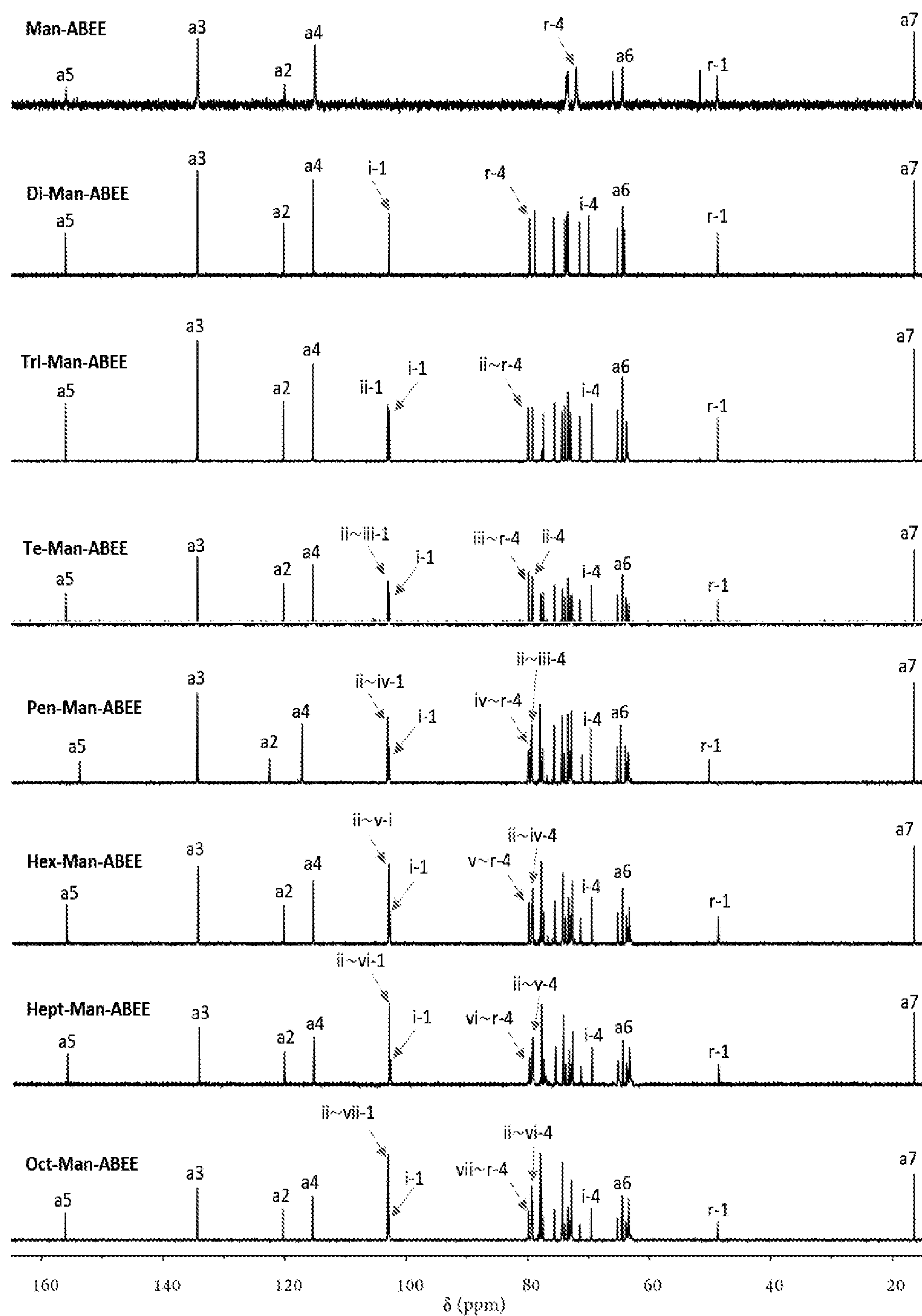


FIG. 6

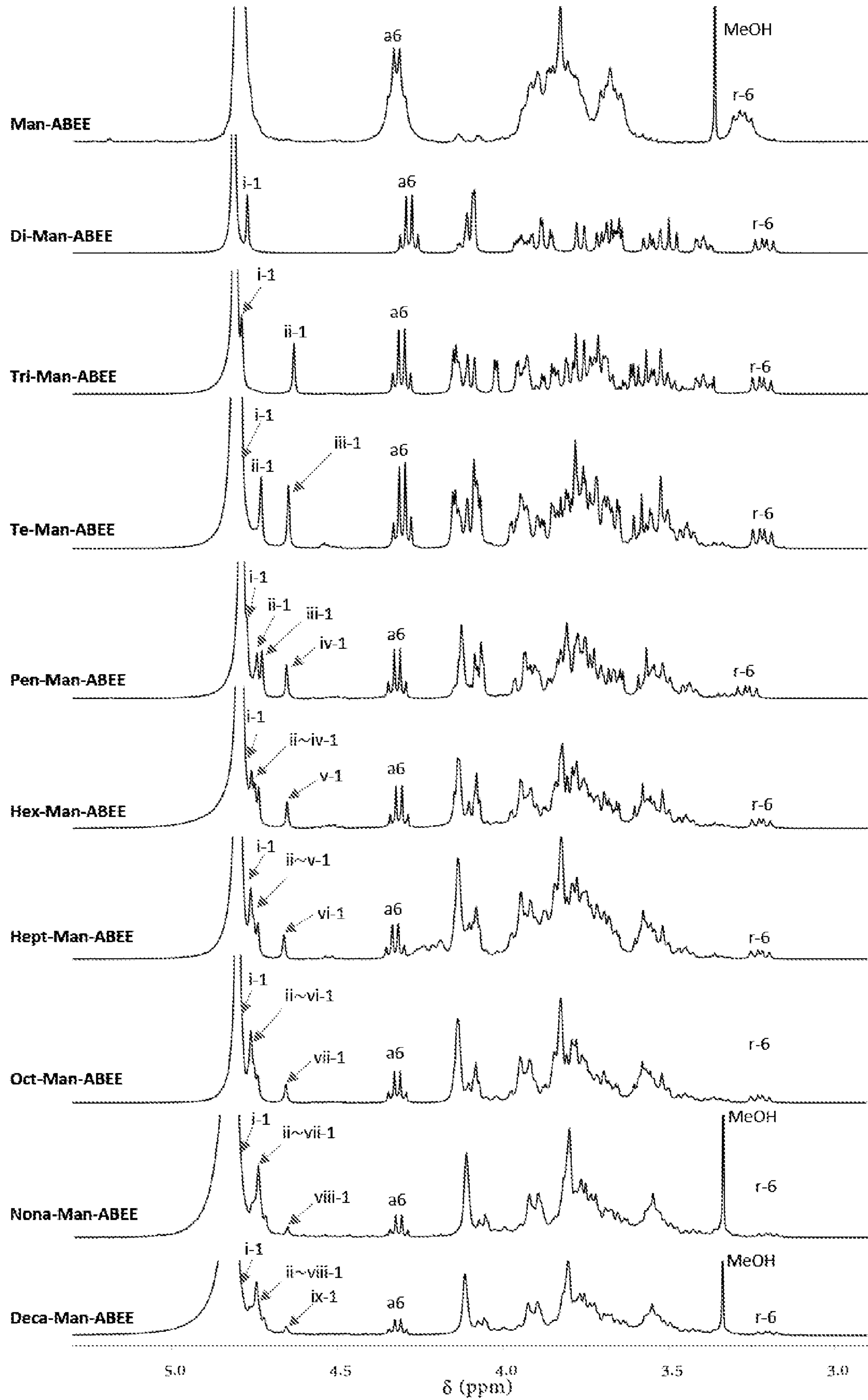


FIG. 7

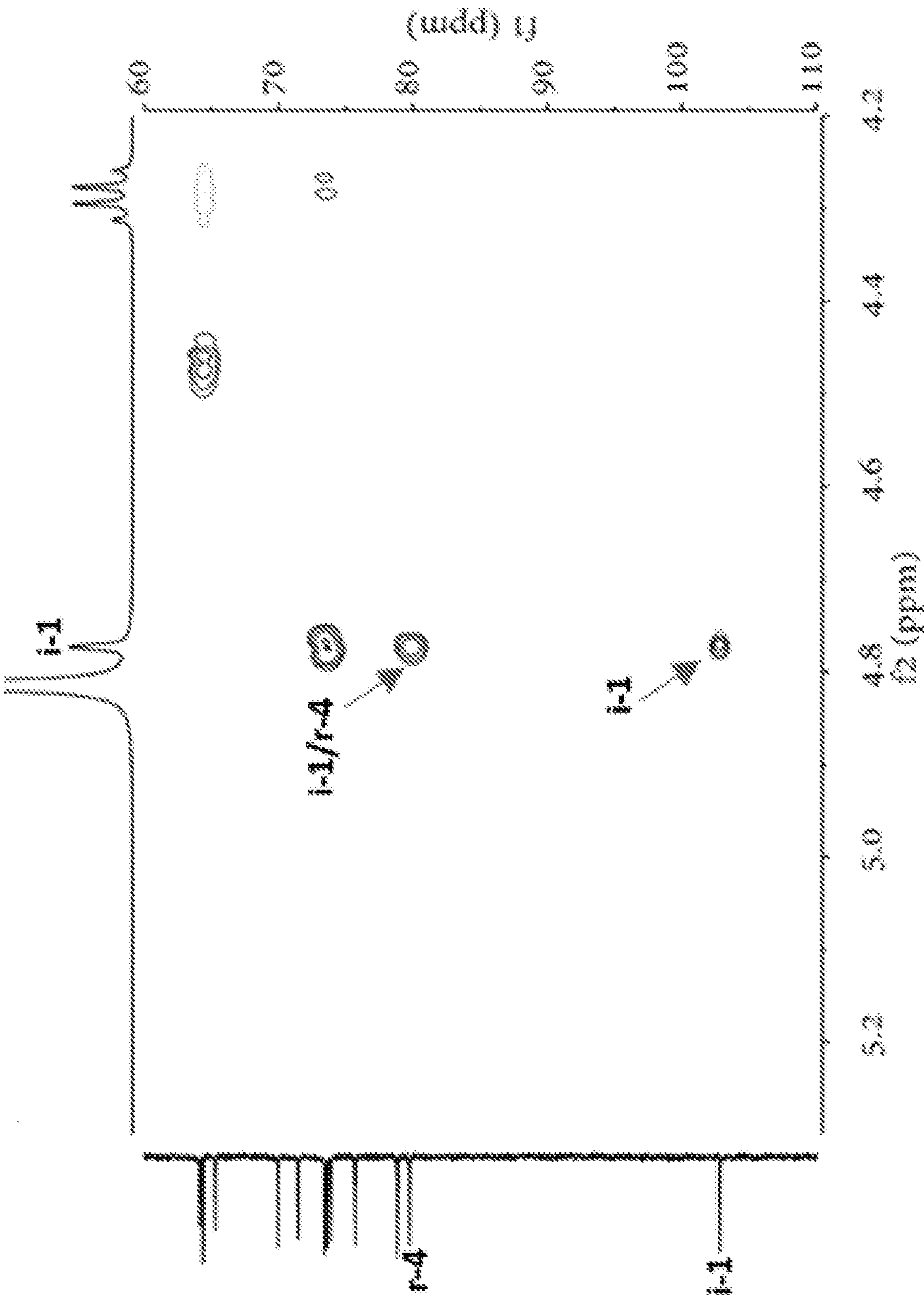


FIG. 8A

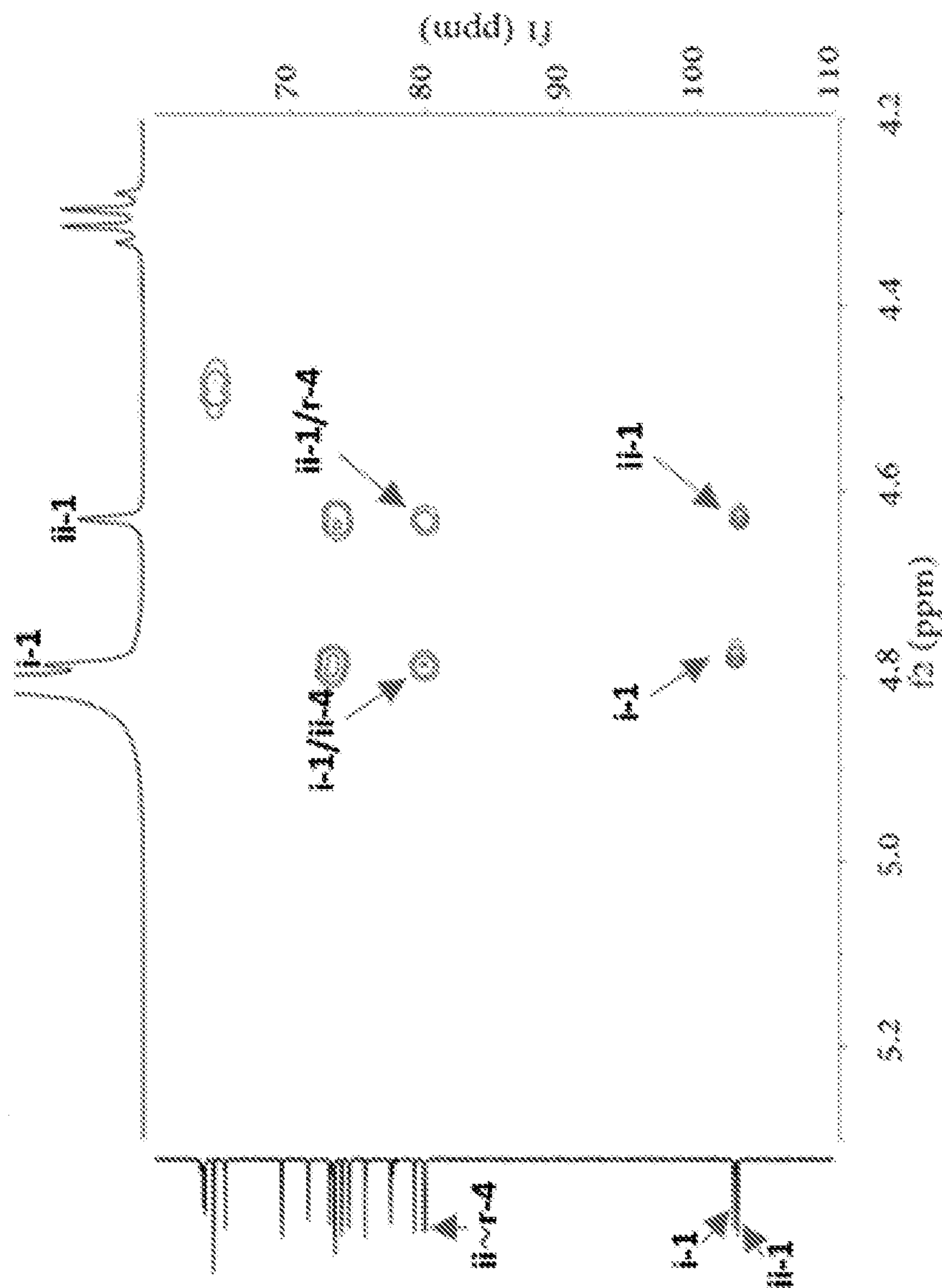


FIG. 8B

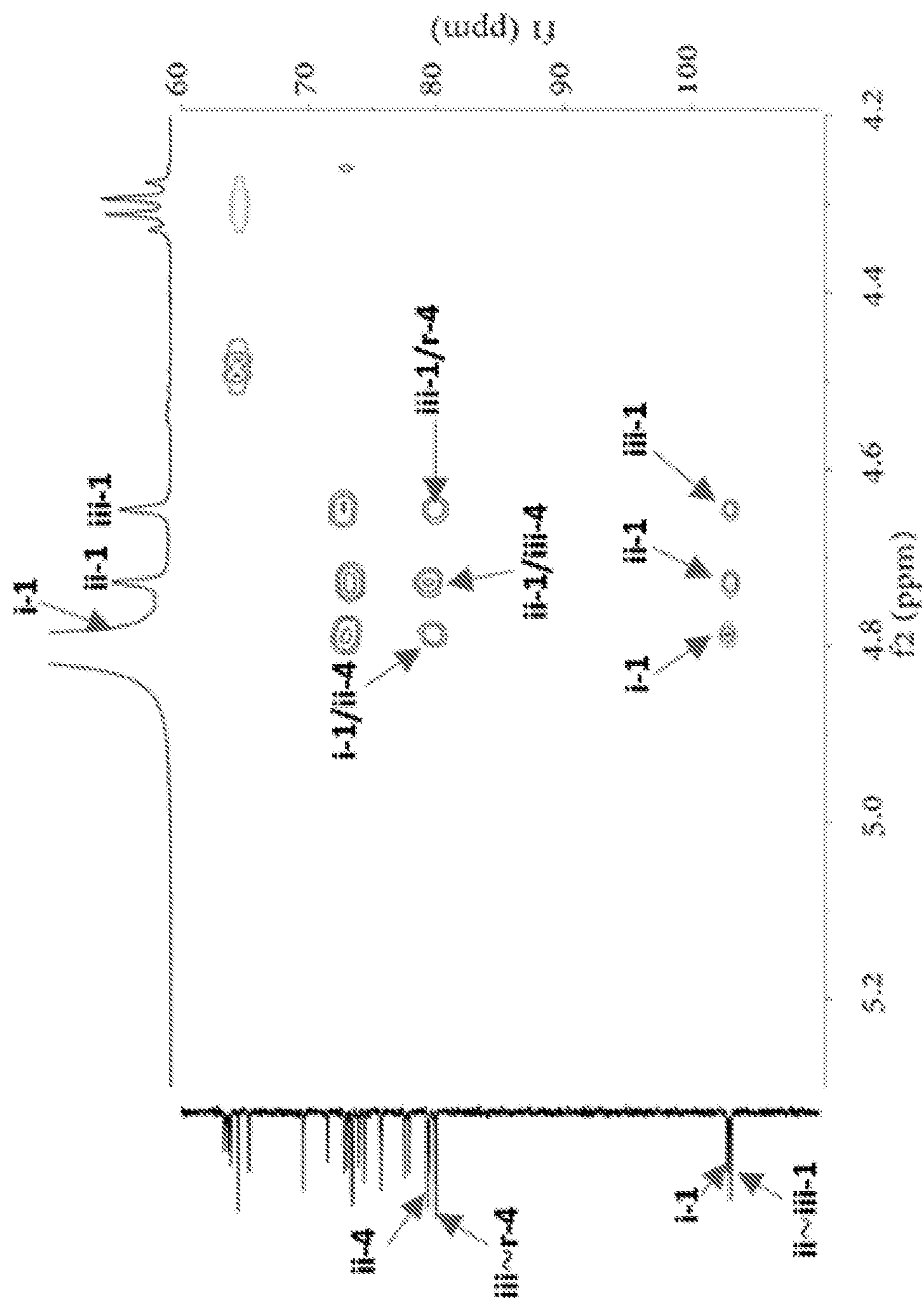


FIG. 8C

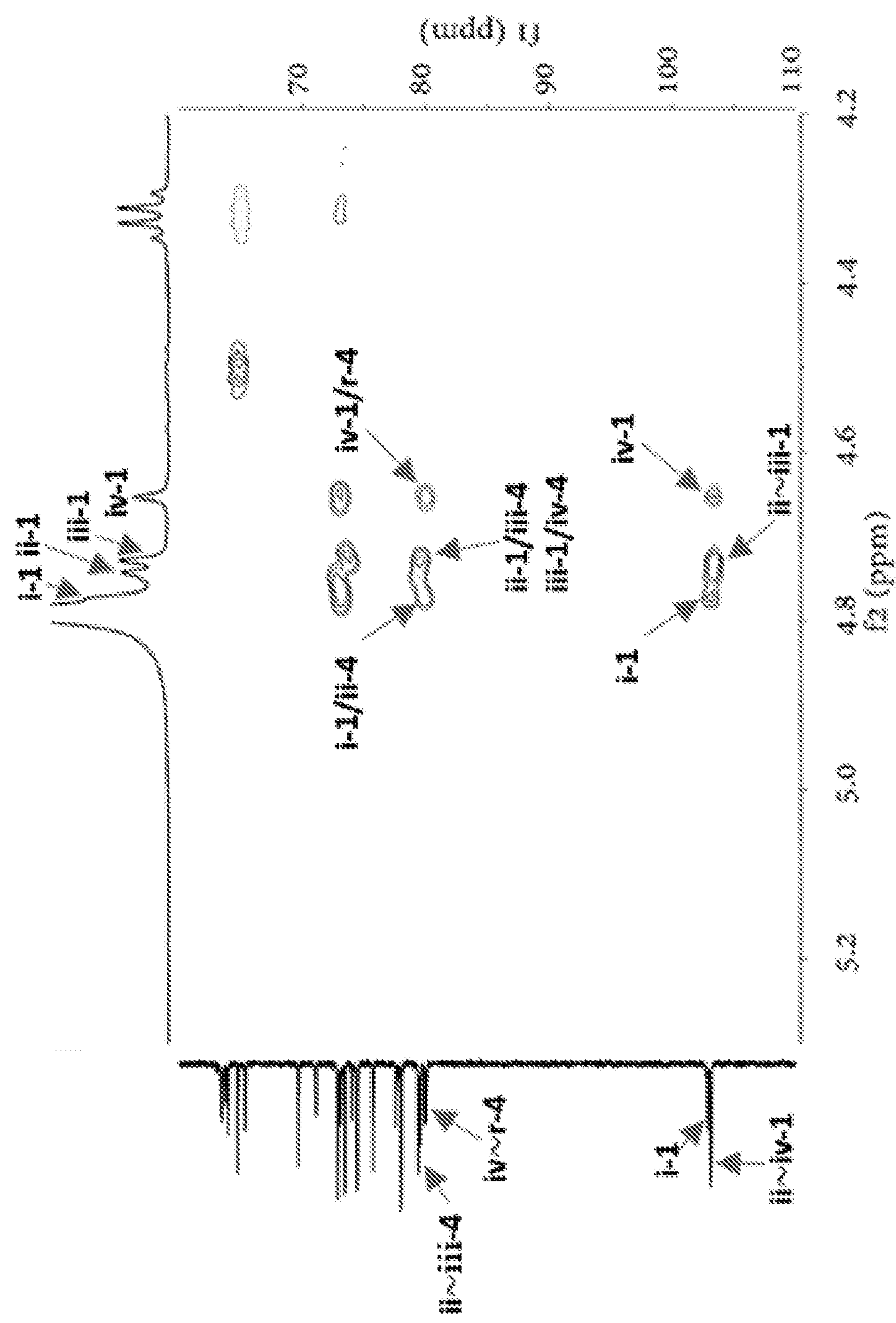


FIG. 8D

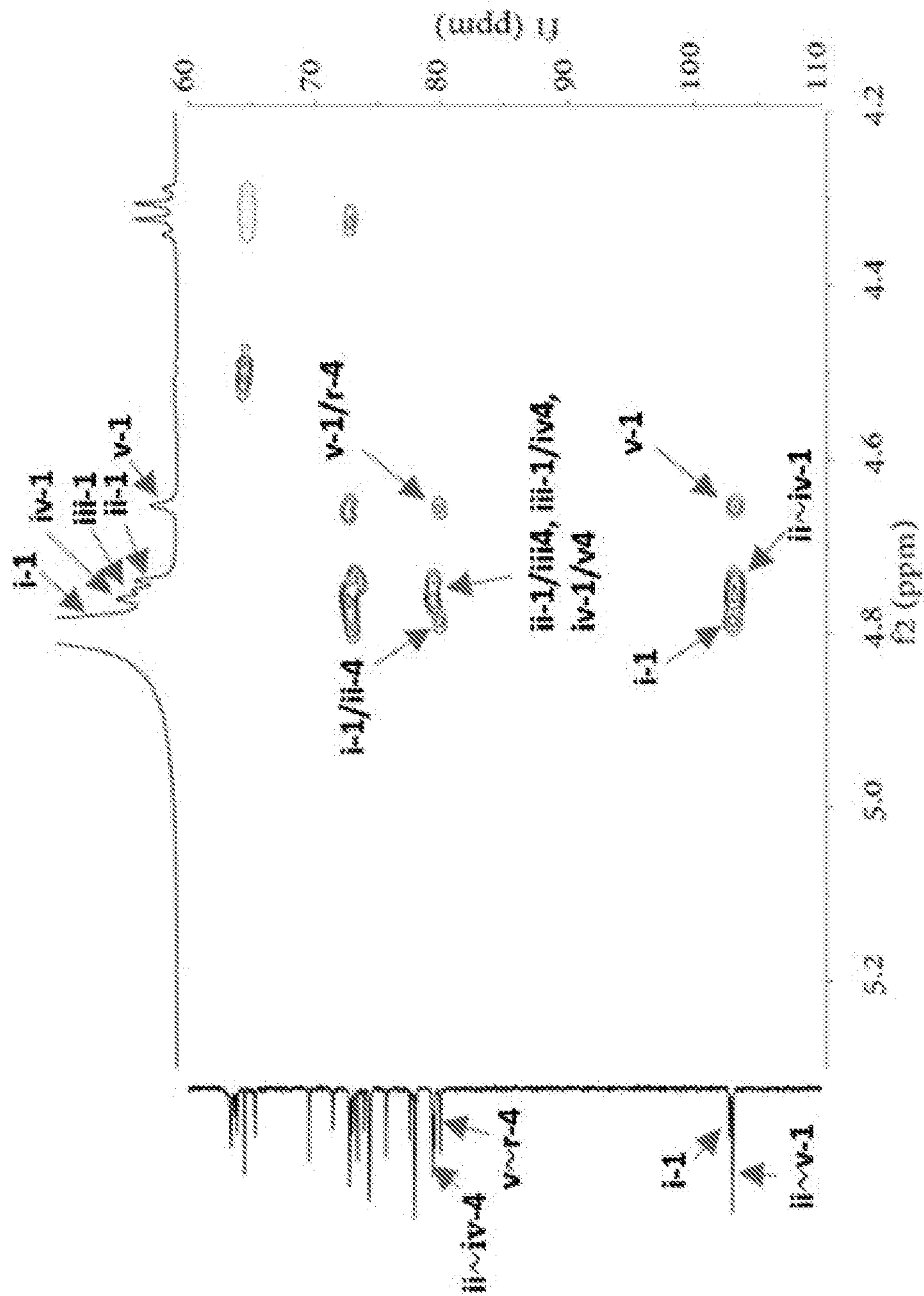


FIG. 8E

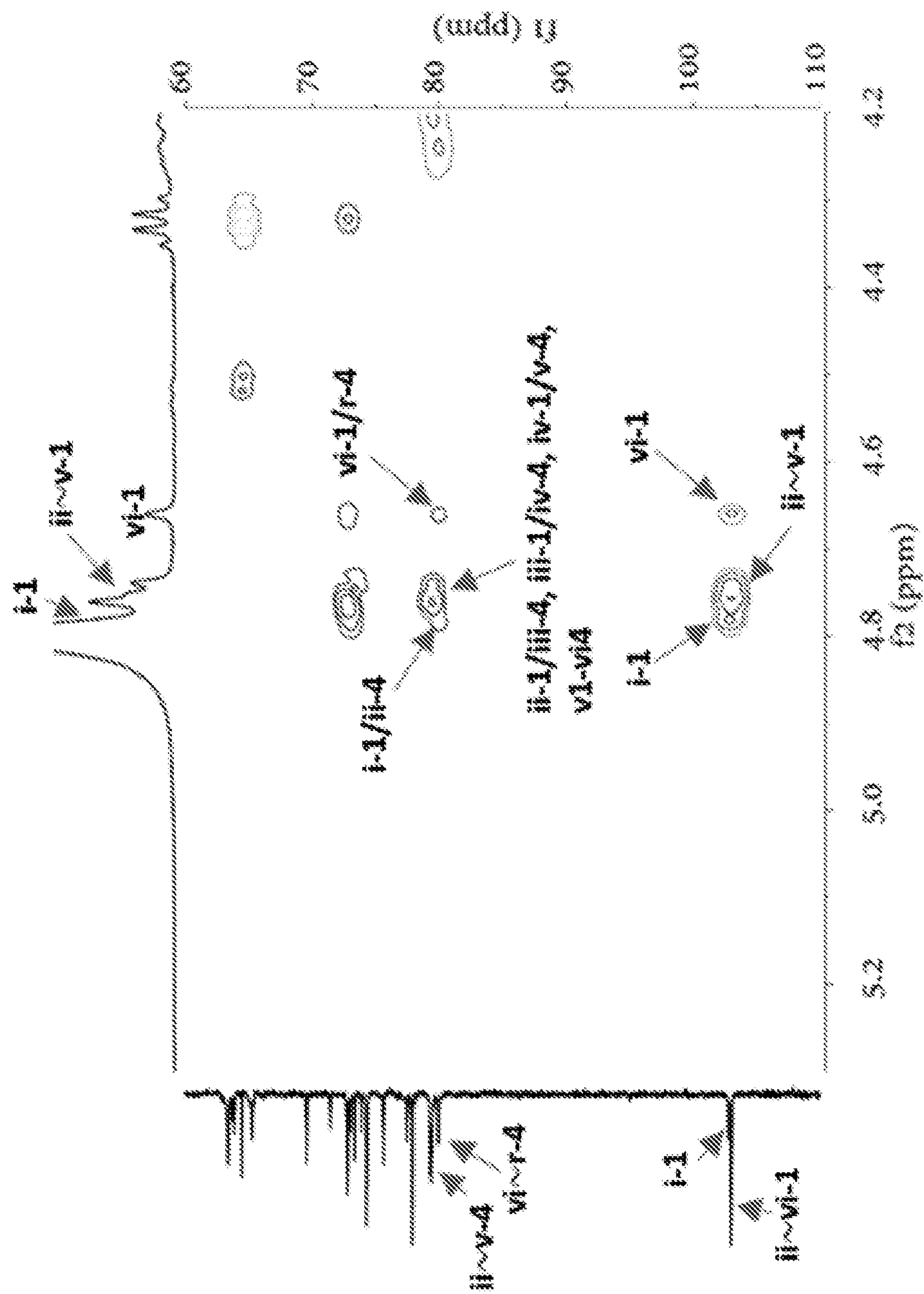


FIG. 8F

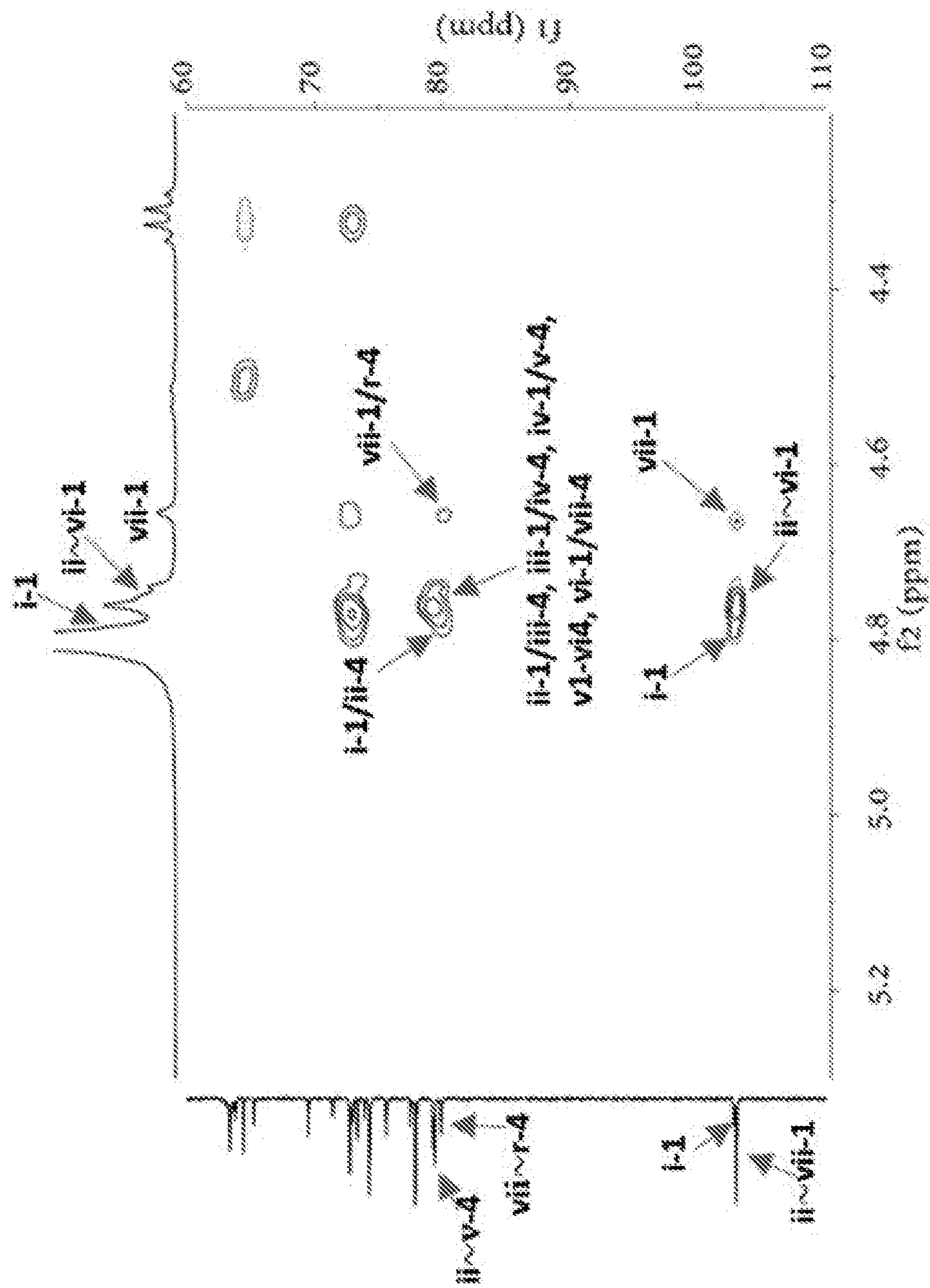


FIG. 8G

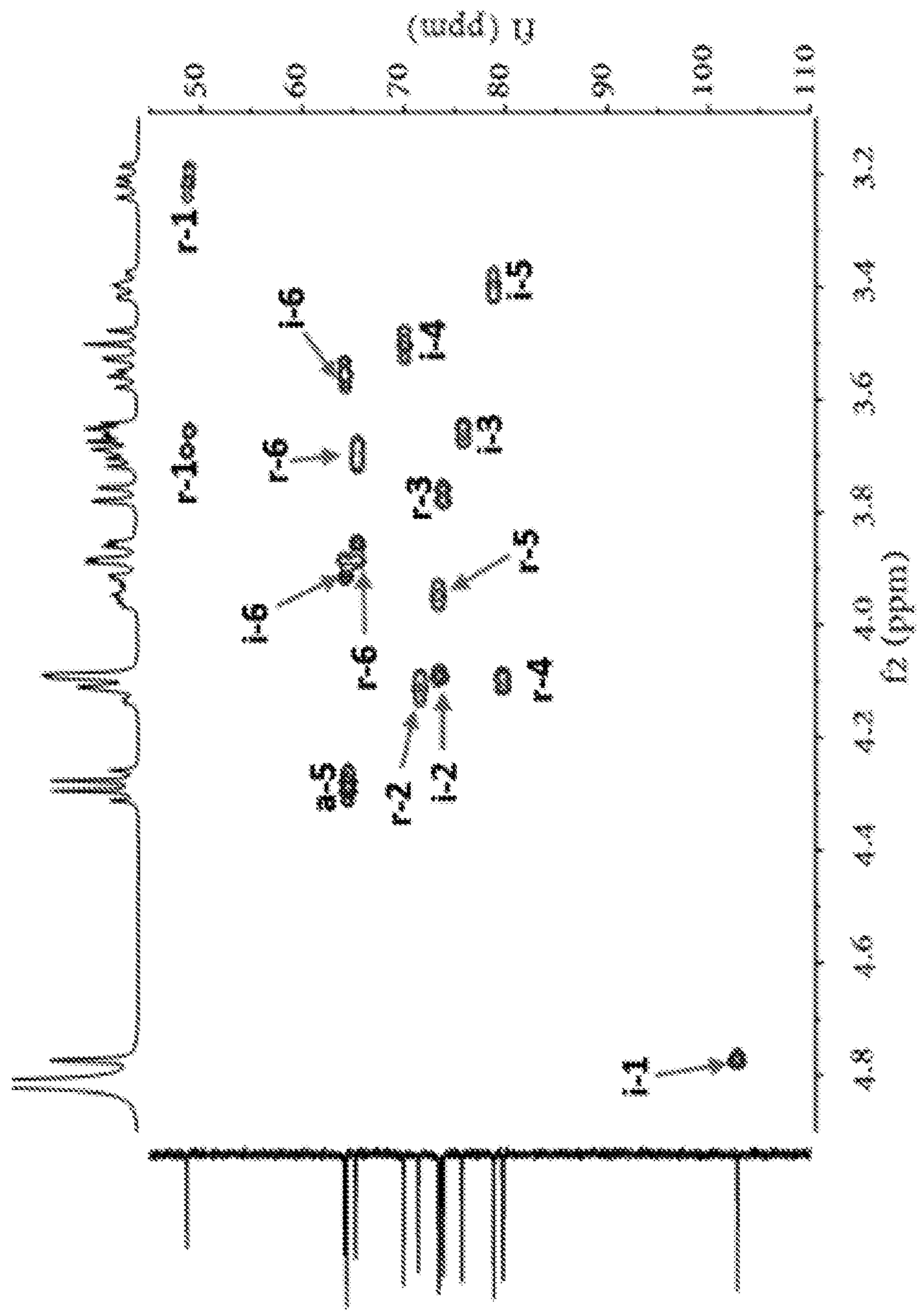


FIG. 9A

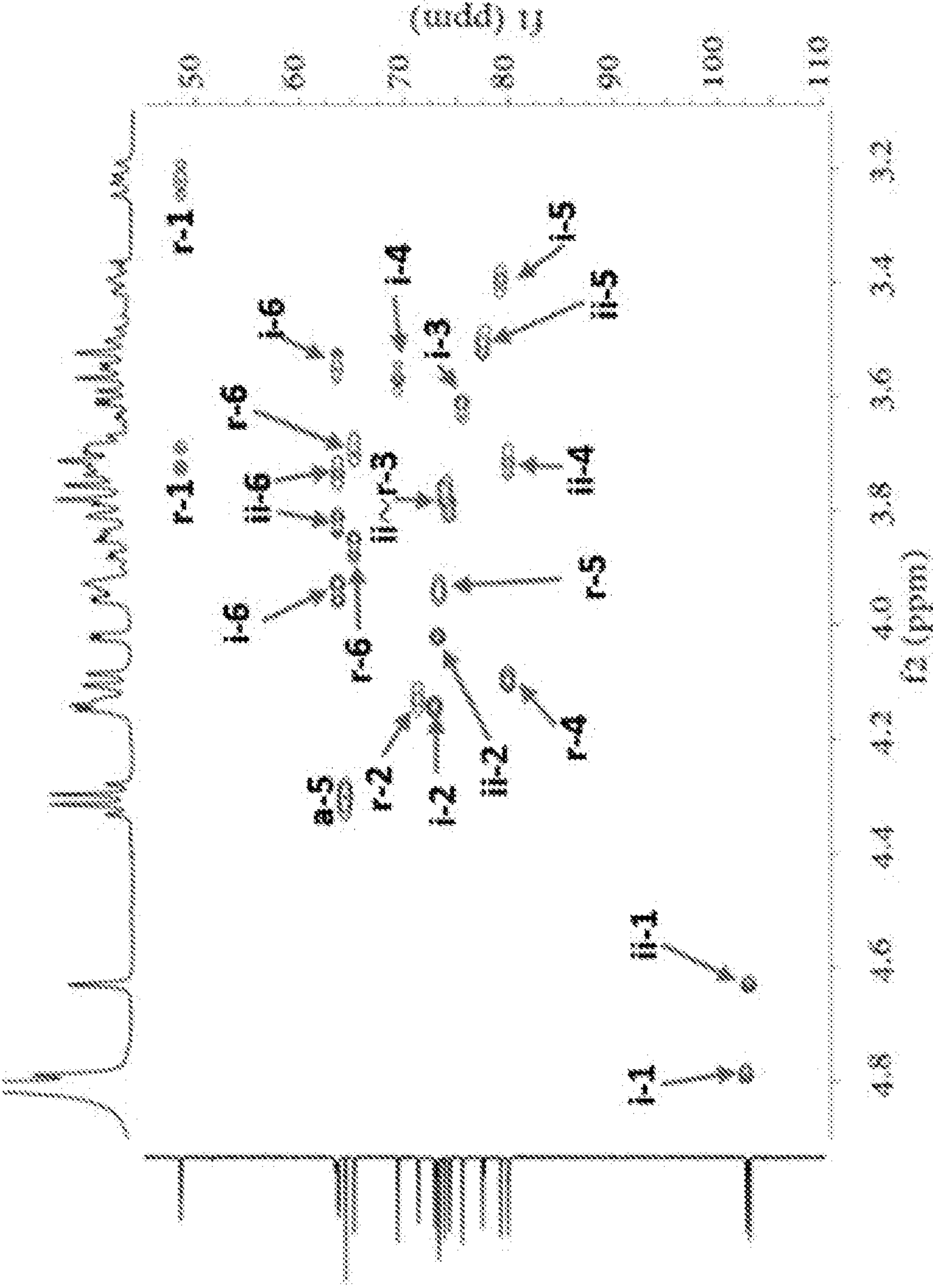


FIG. 9B

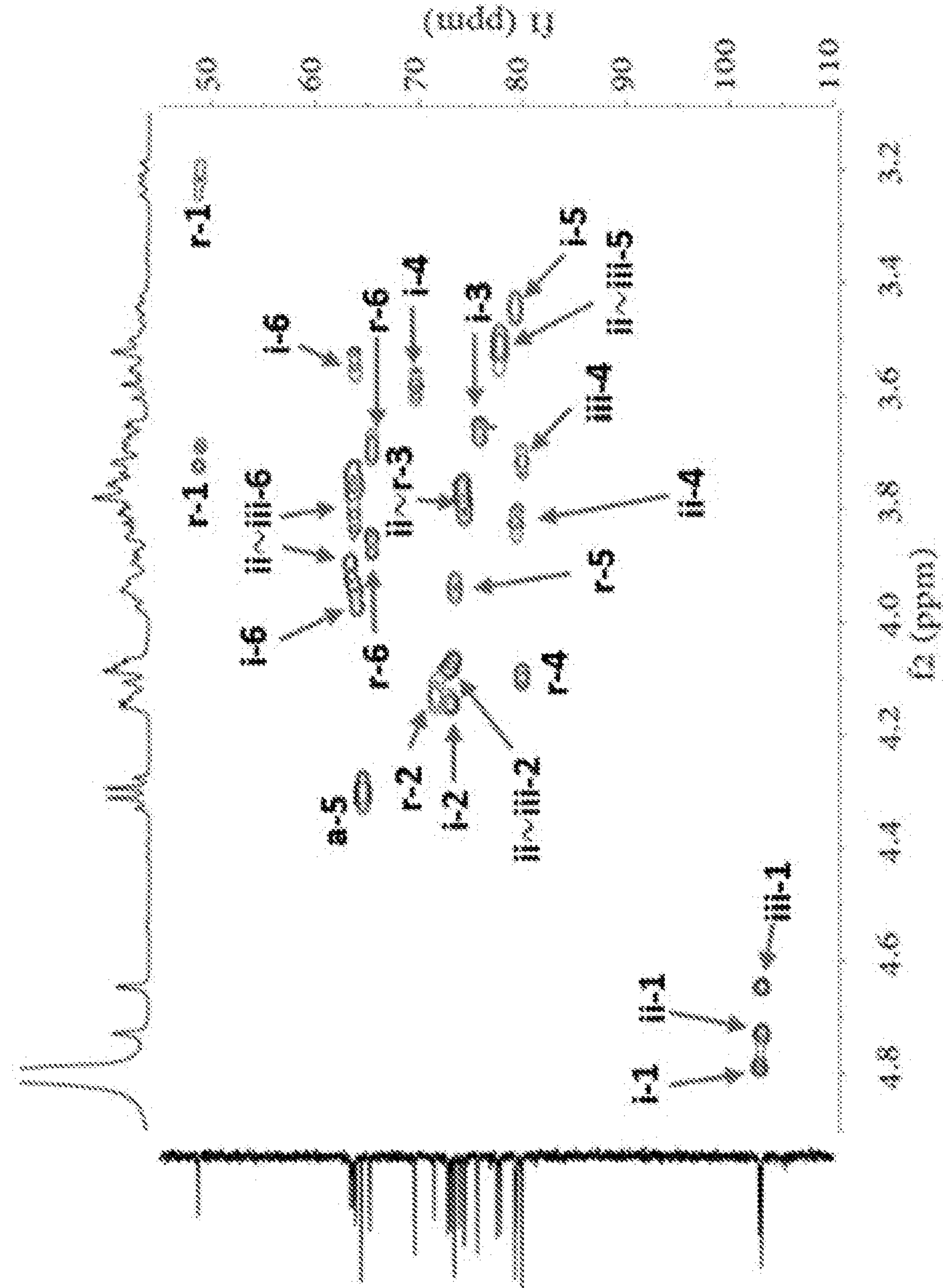


FIG. 9C

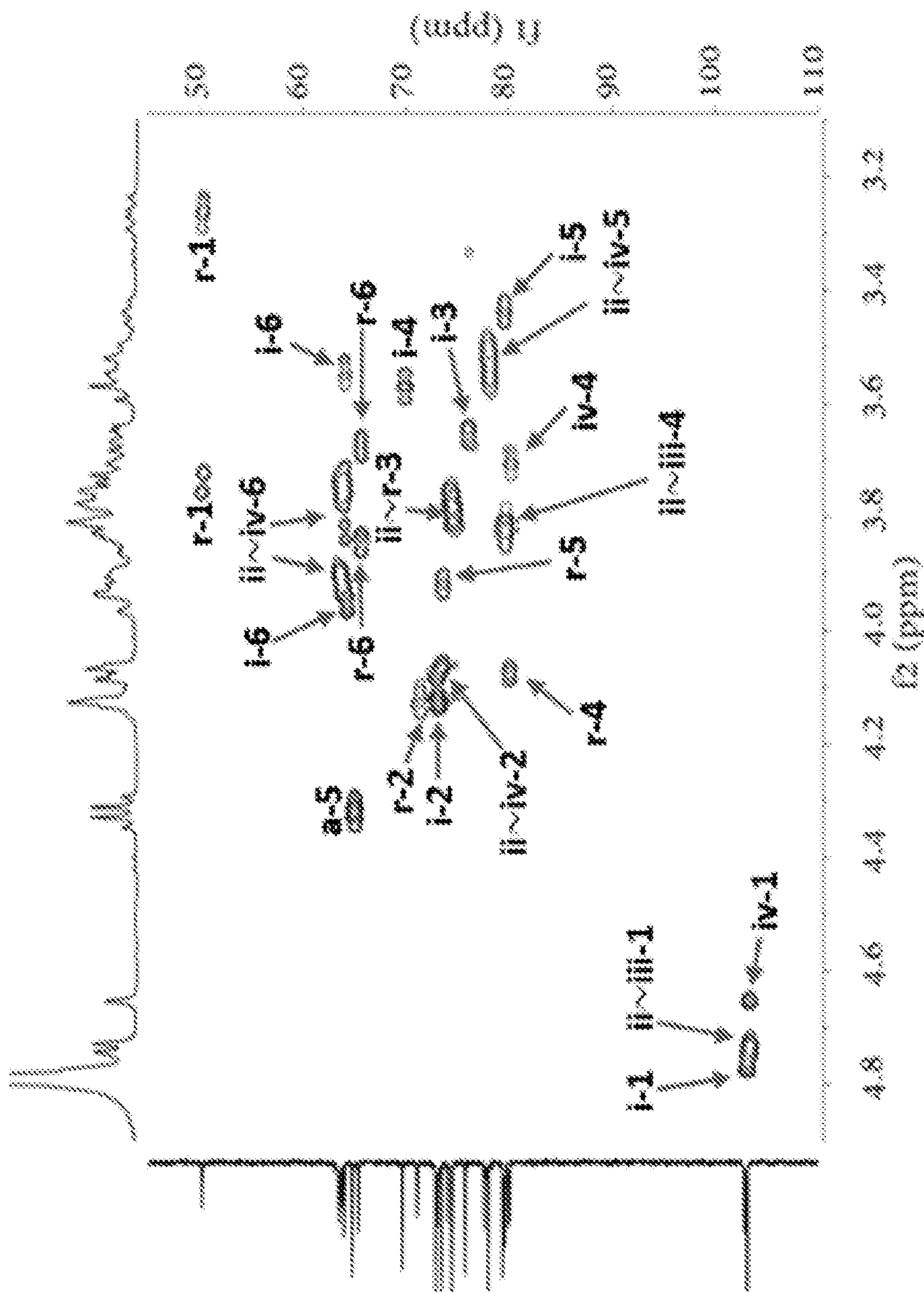


FIG. 9D

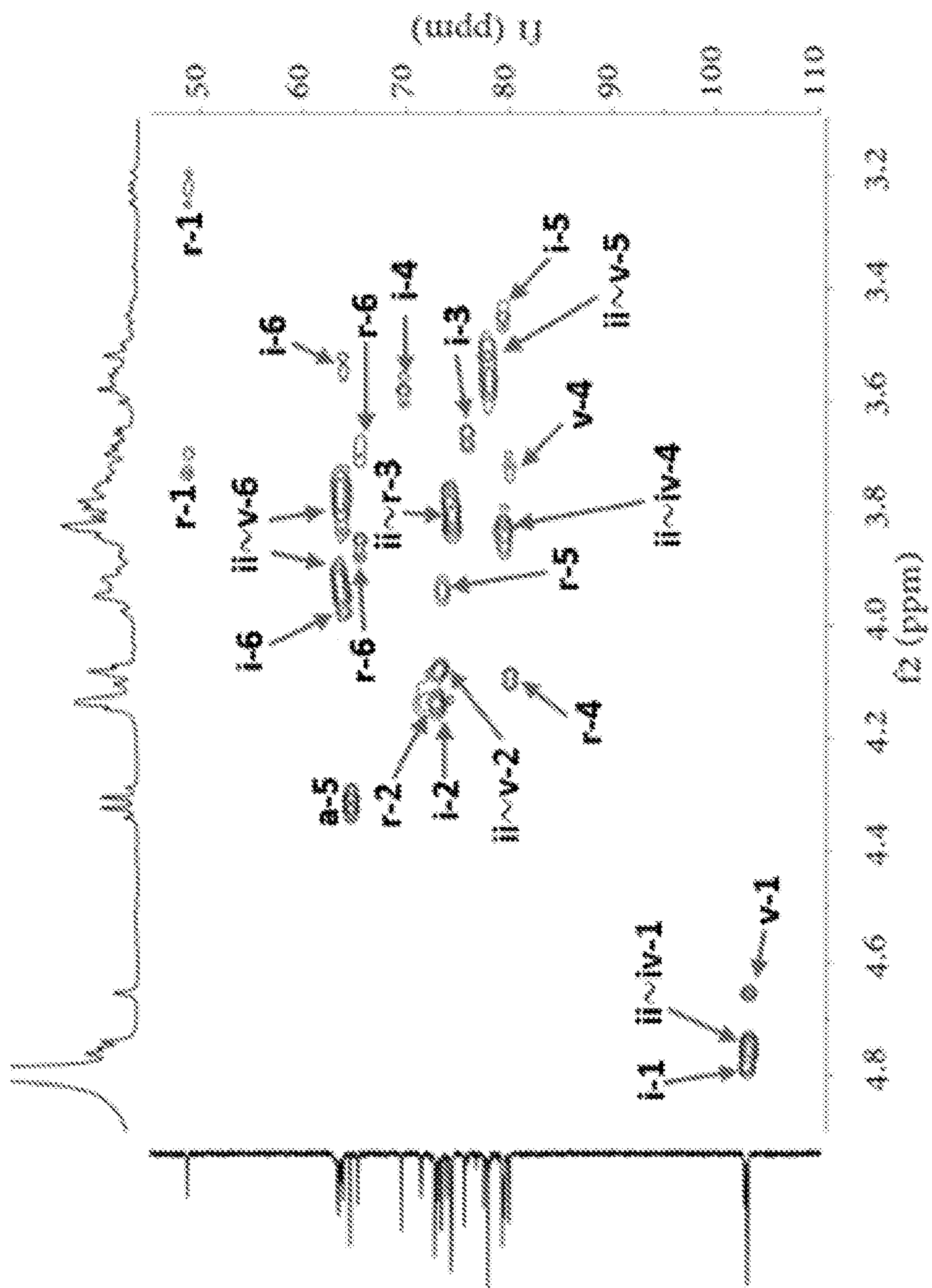


FIG. 9*

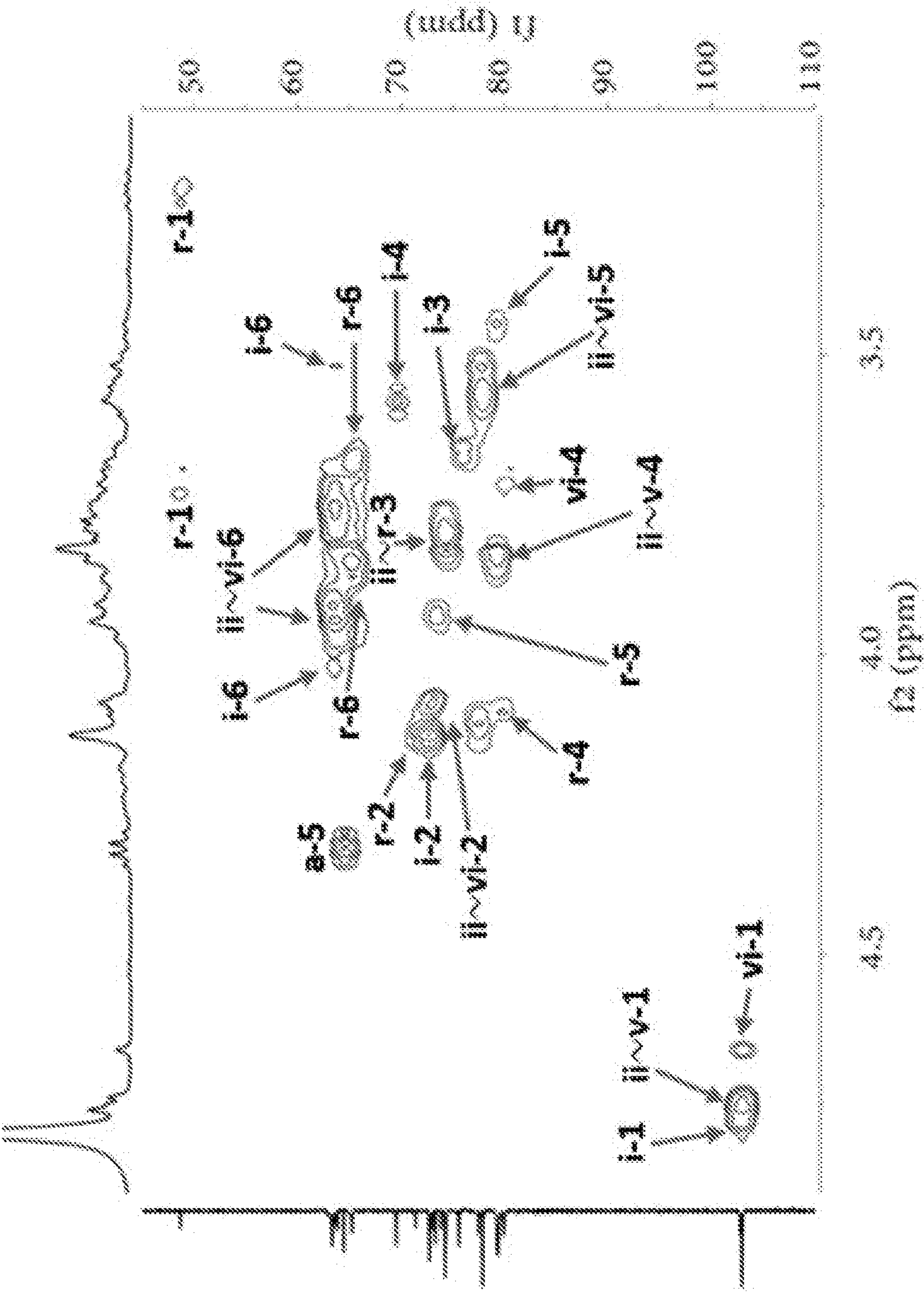


FIG. 9F

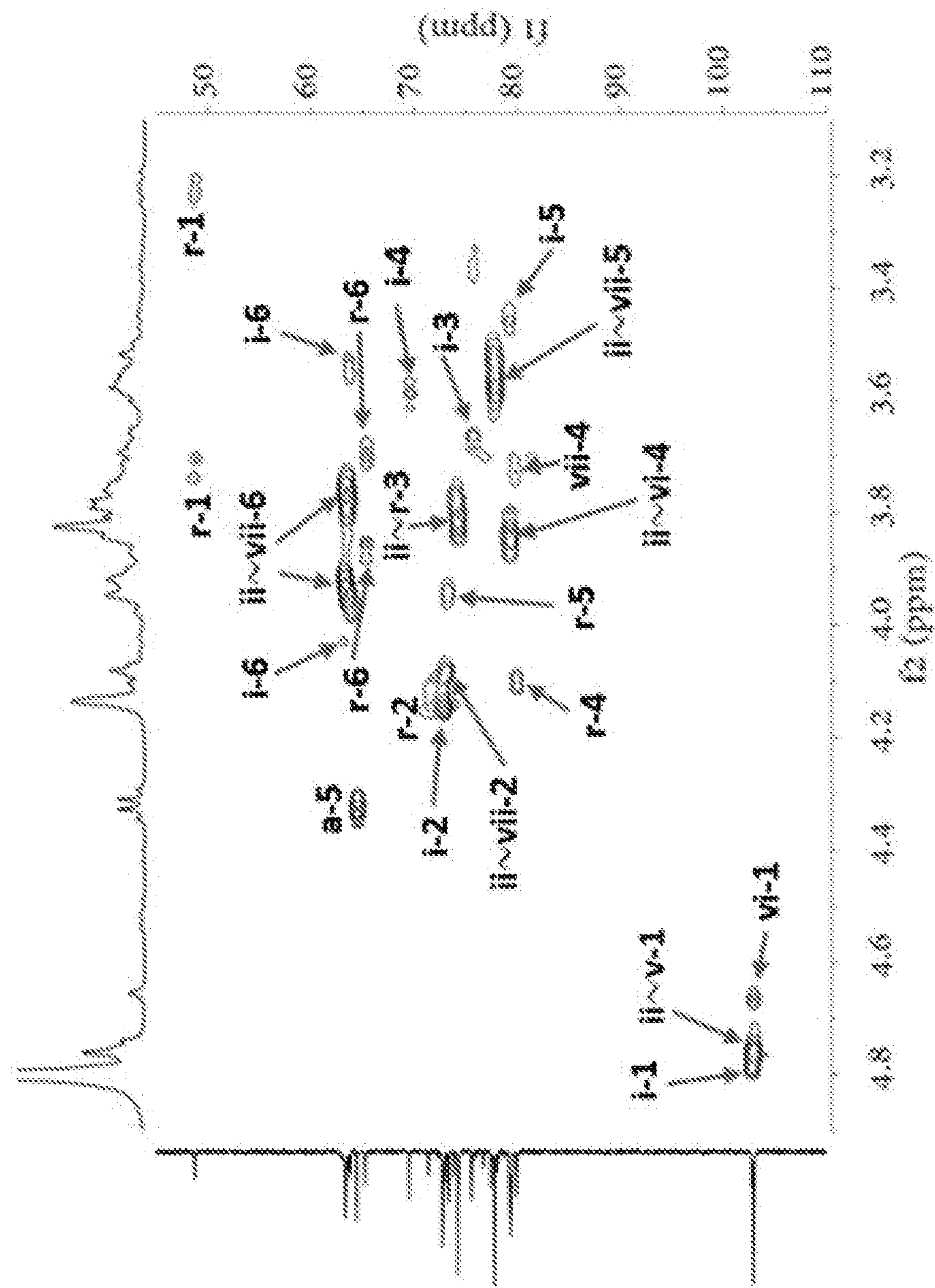


FIG. 9G

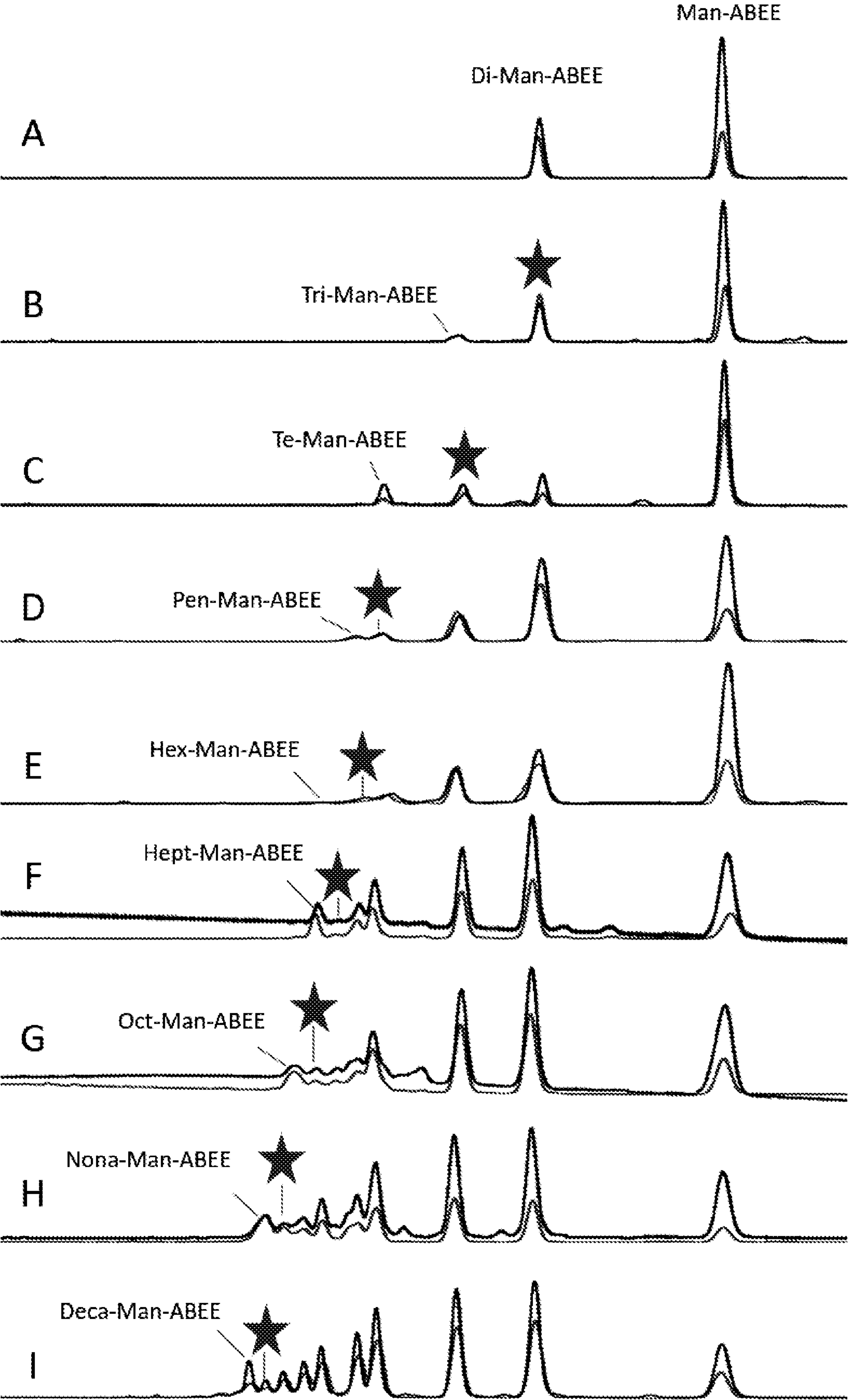


FIG. 10

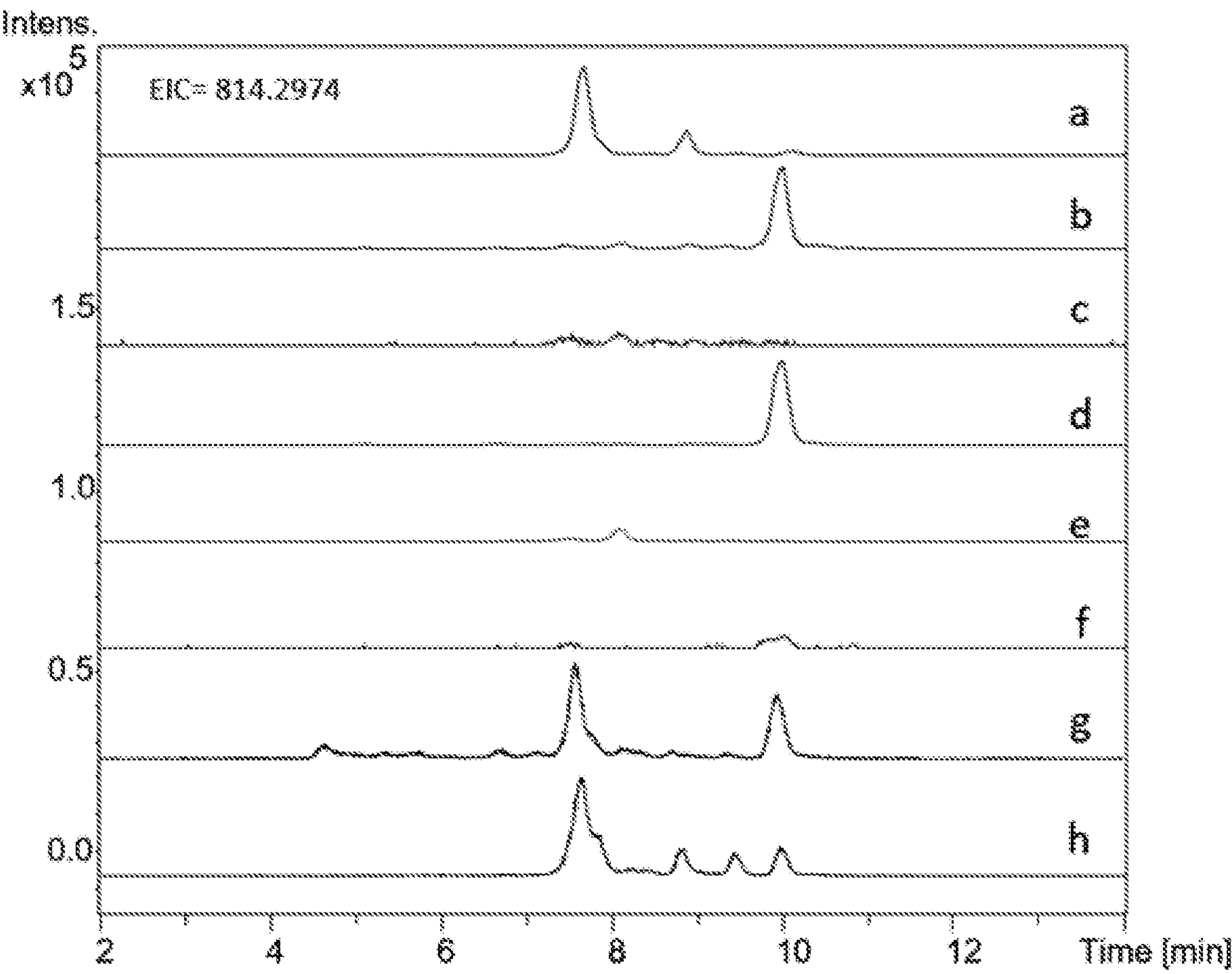


FIG. 11A

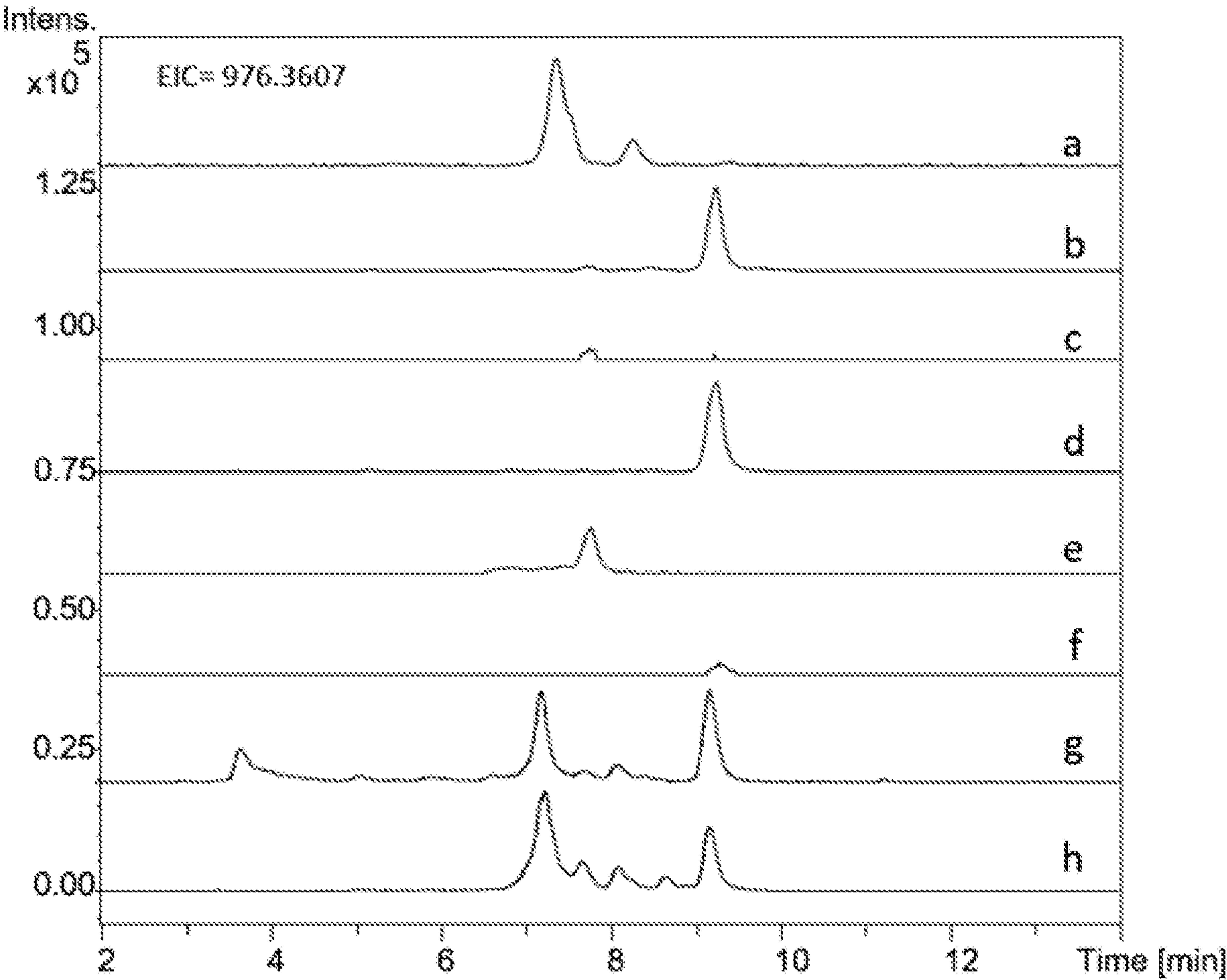


FIG. 11B

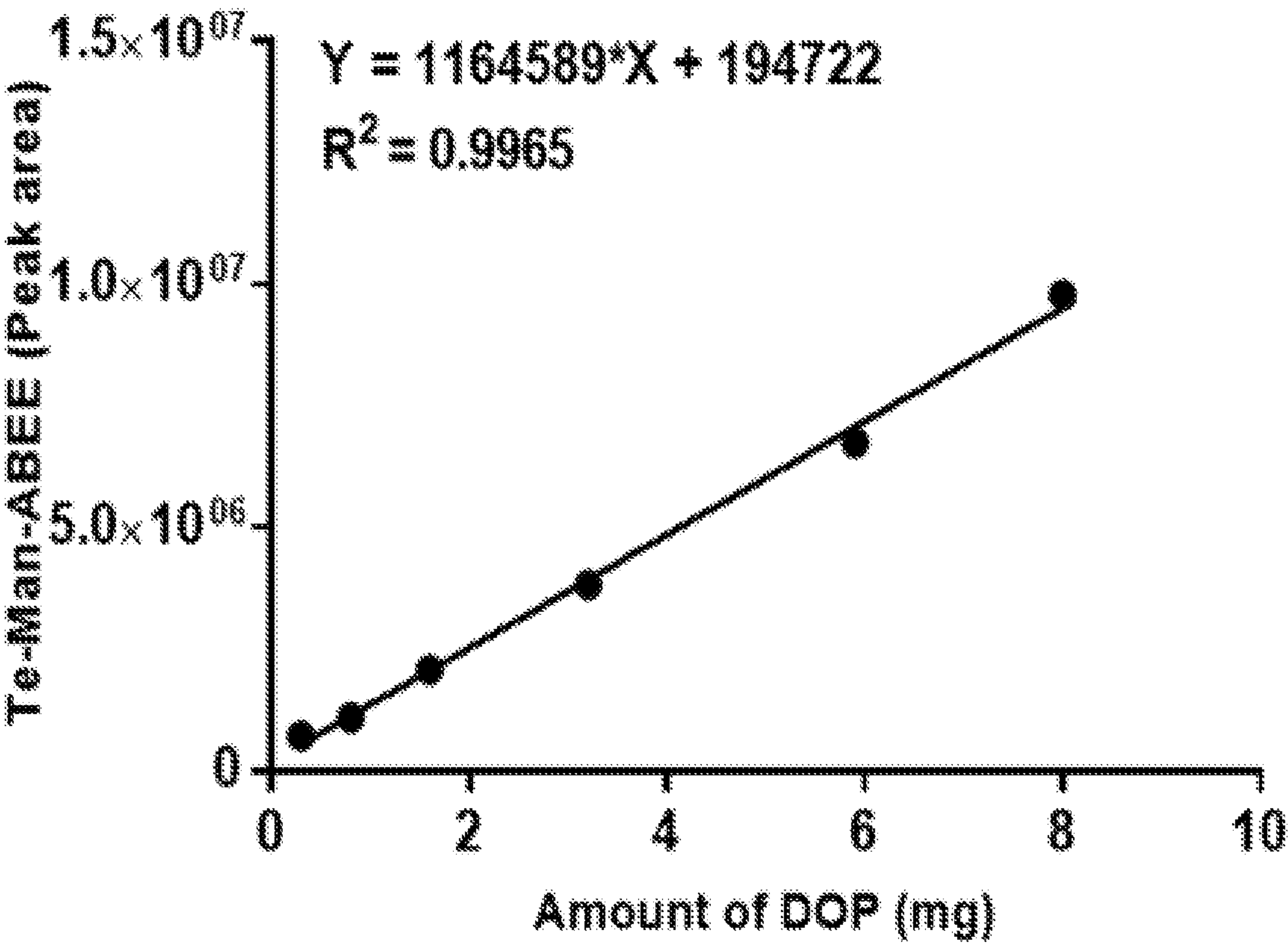


FIG. 12A

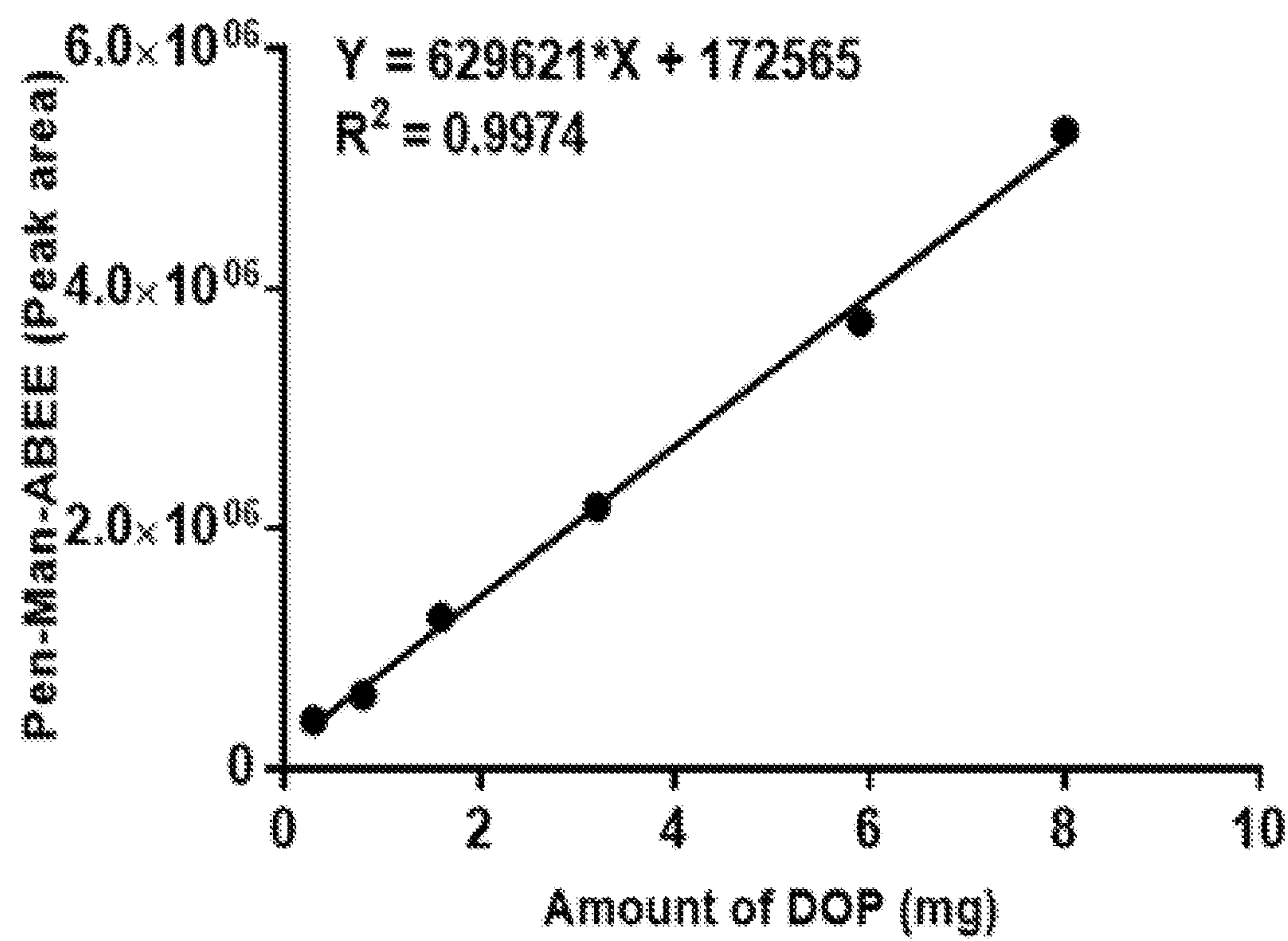


FIG. 12B

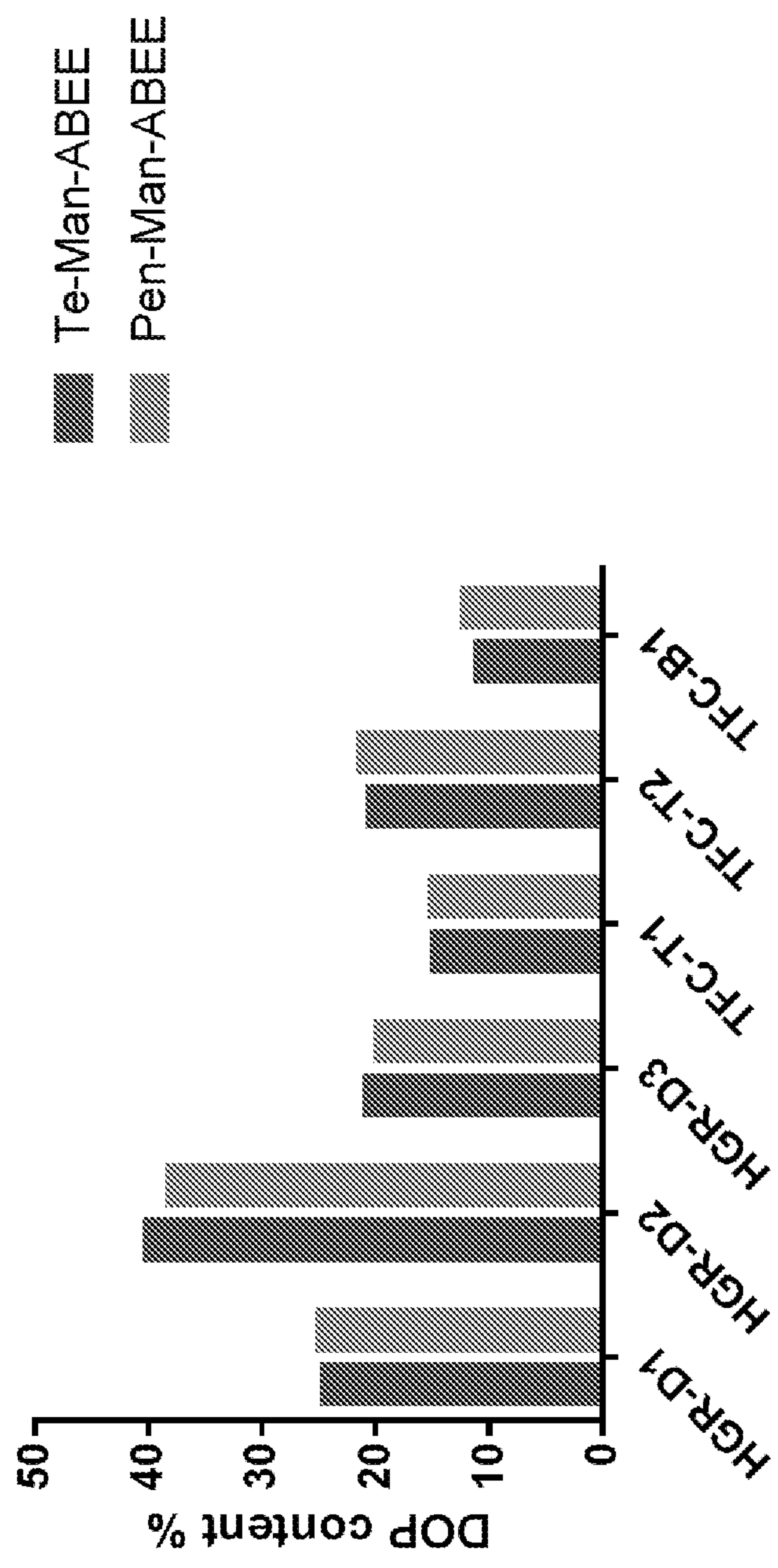


FIG. 13A

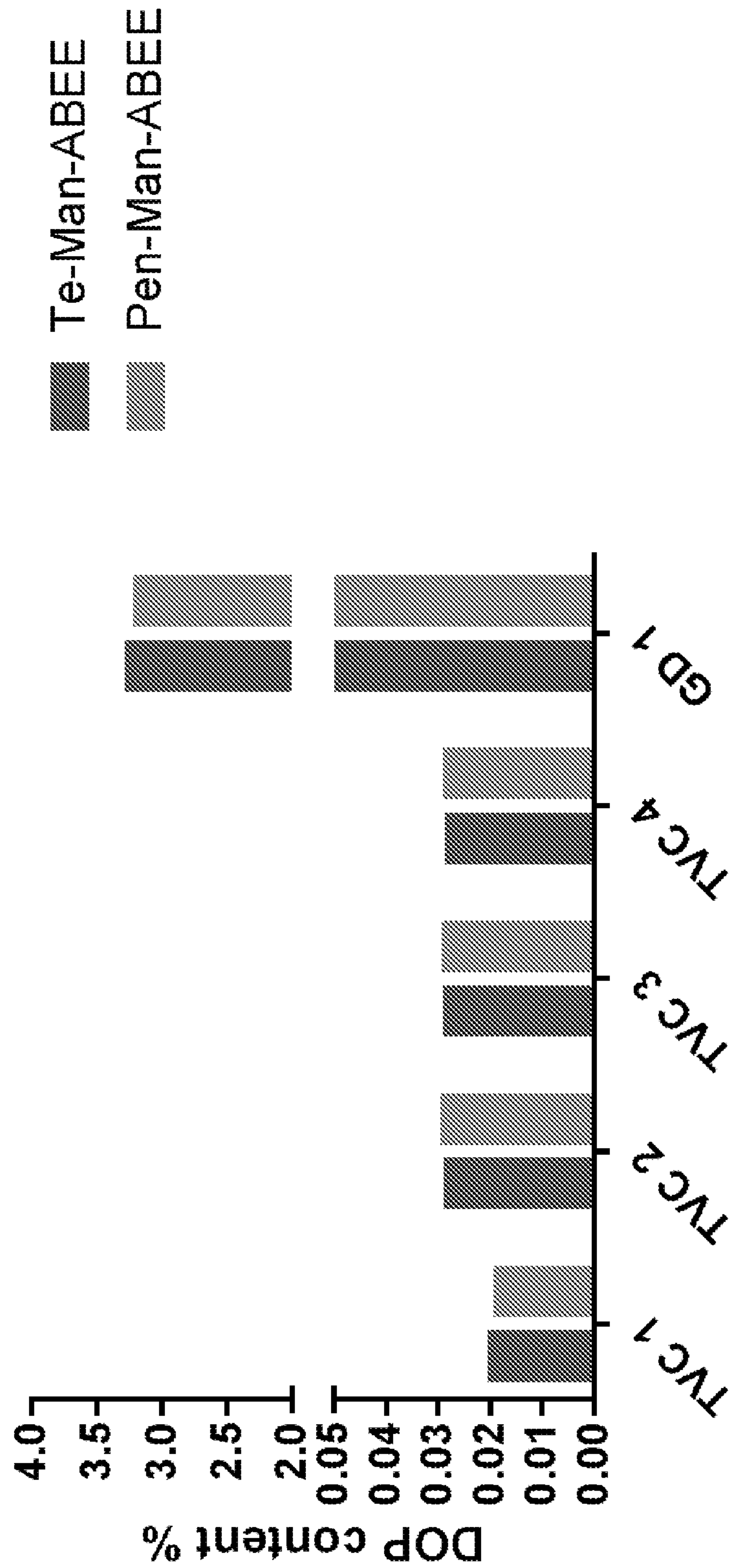


FIG. 13B

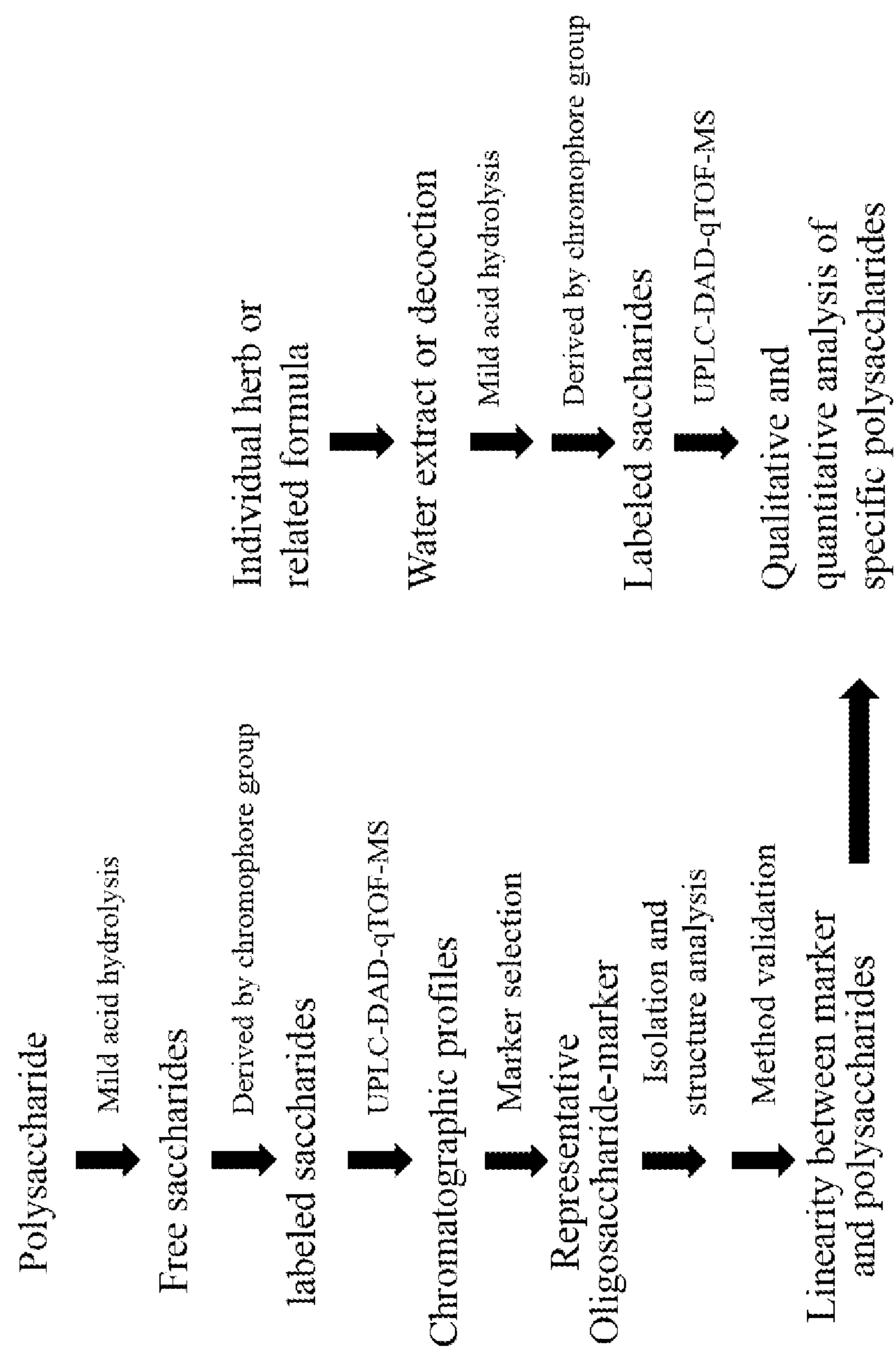


FIG. 14

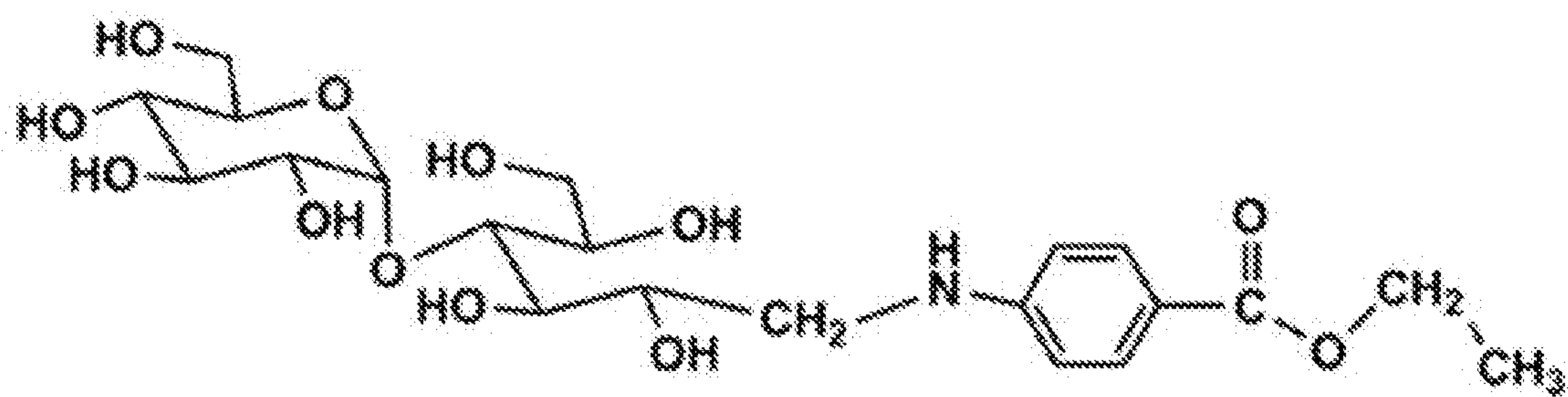
**Rm-1**

FIG. 15A

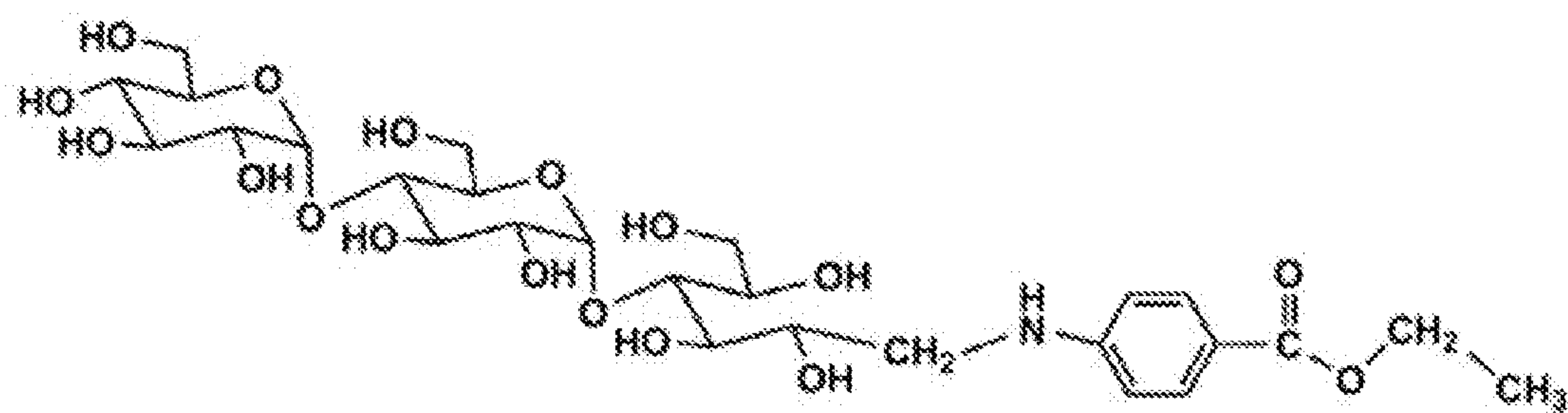
**Rm-2**

FIG. 15B

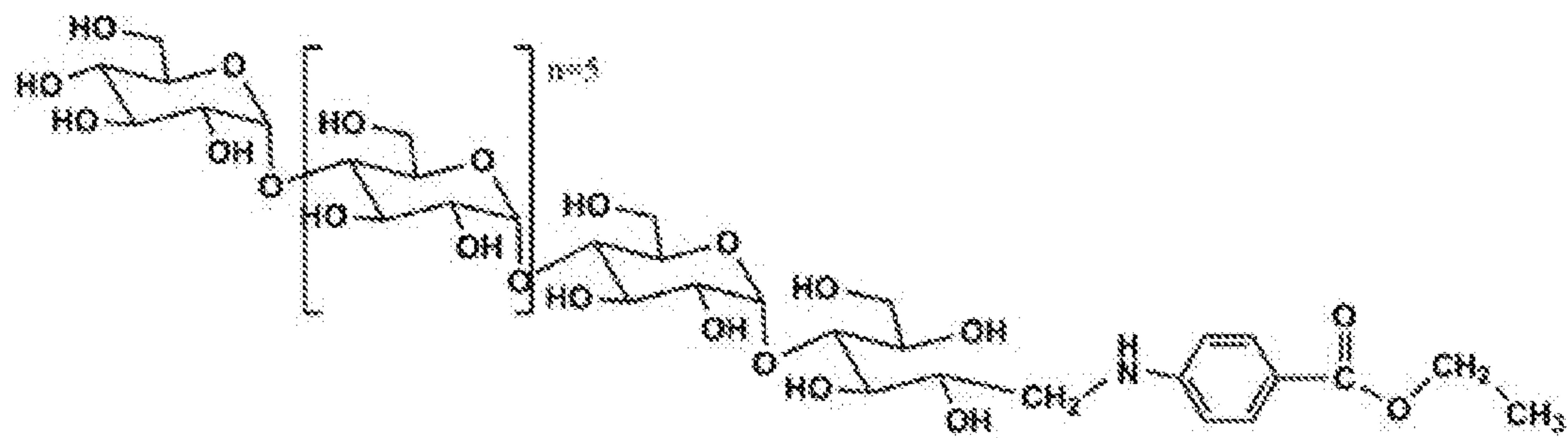
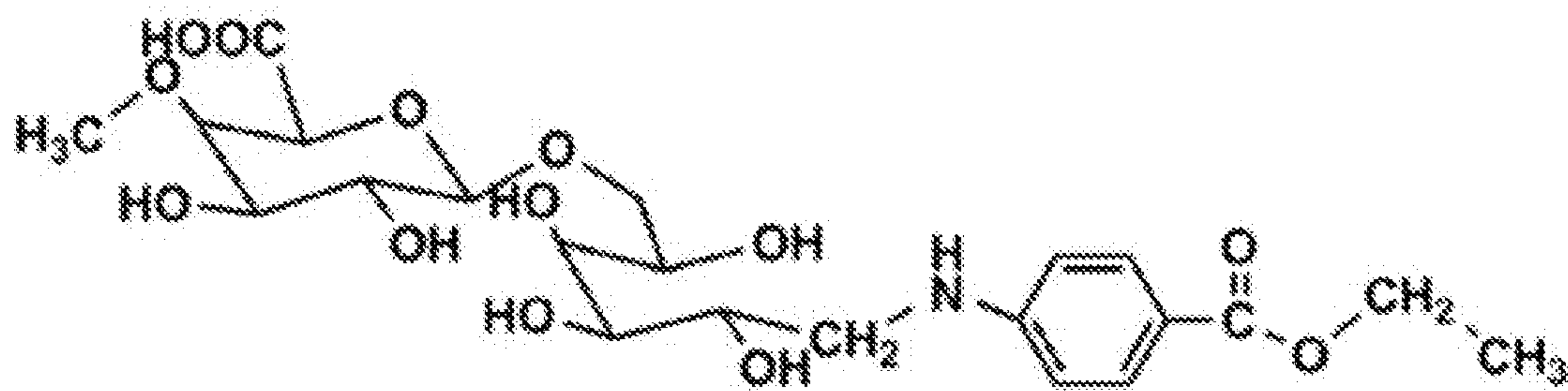
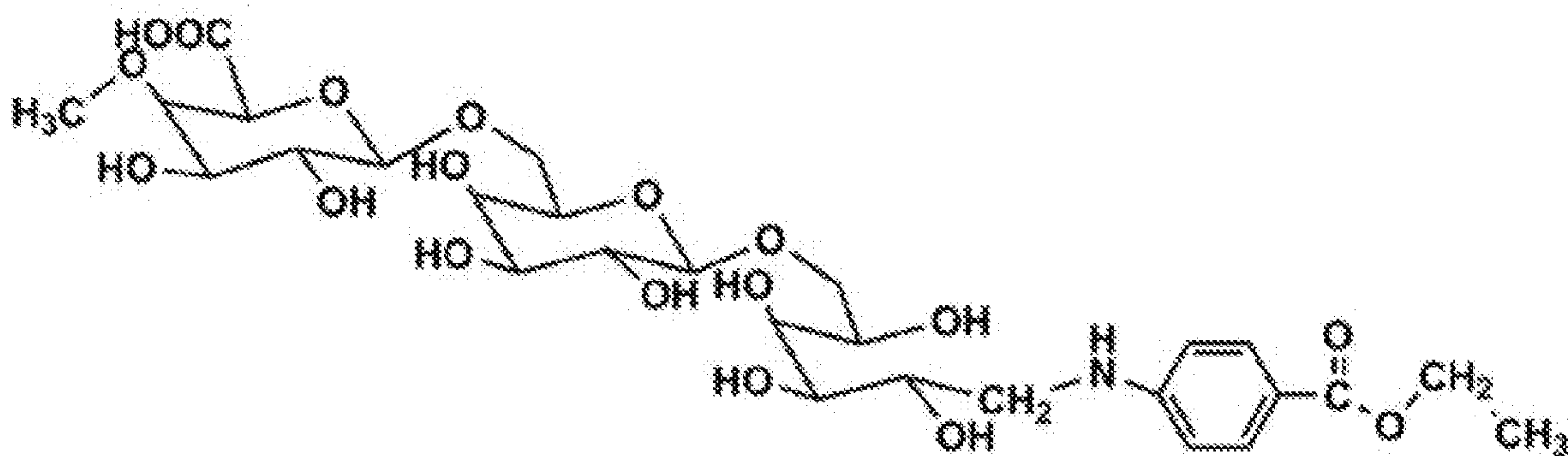
**Rm-3**

FIG. 15C



Am-1

FIG. 15D



Am-2

FIG. 15E

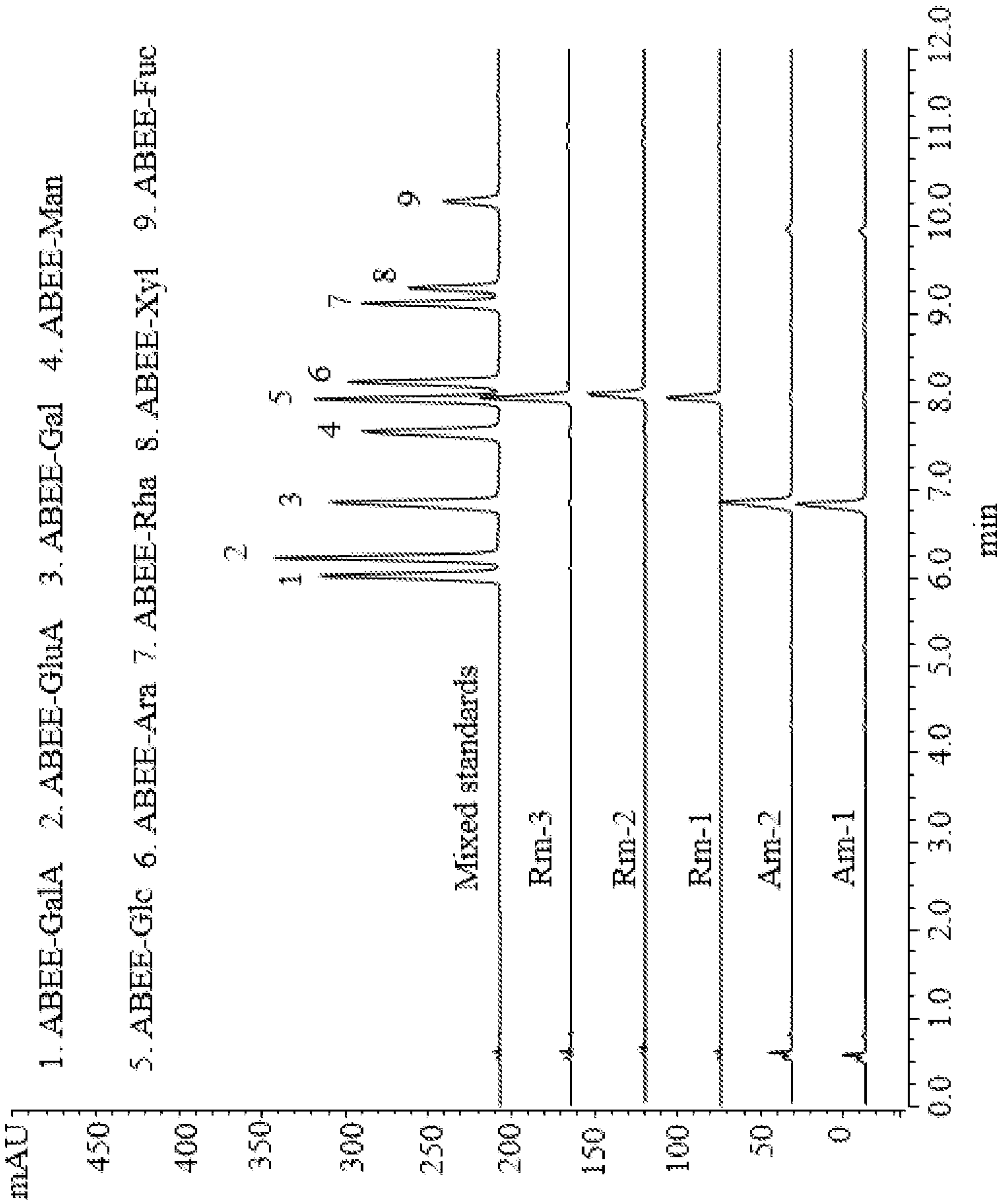


FIG. 16

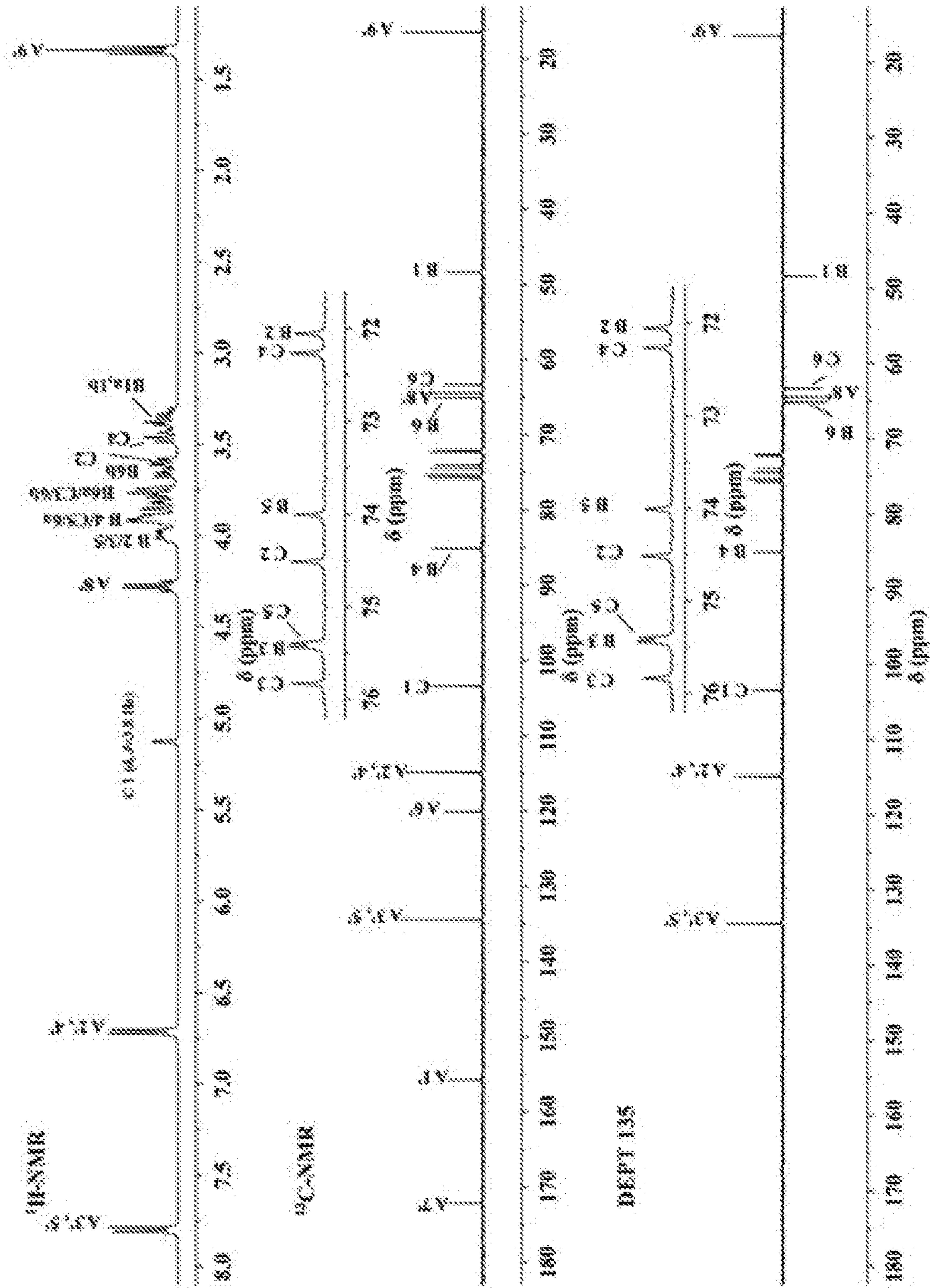


FIG. 17A

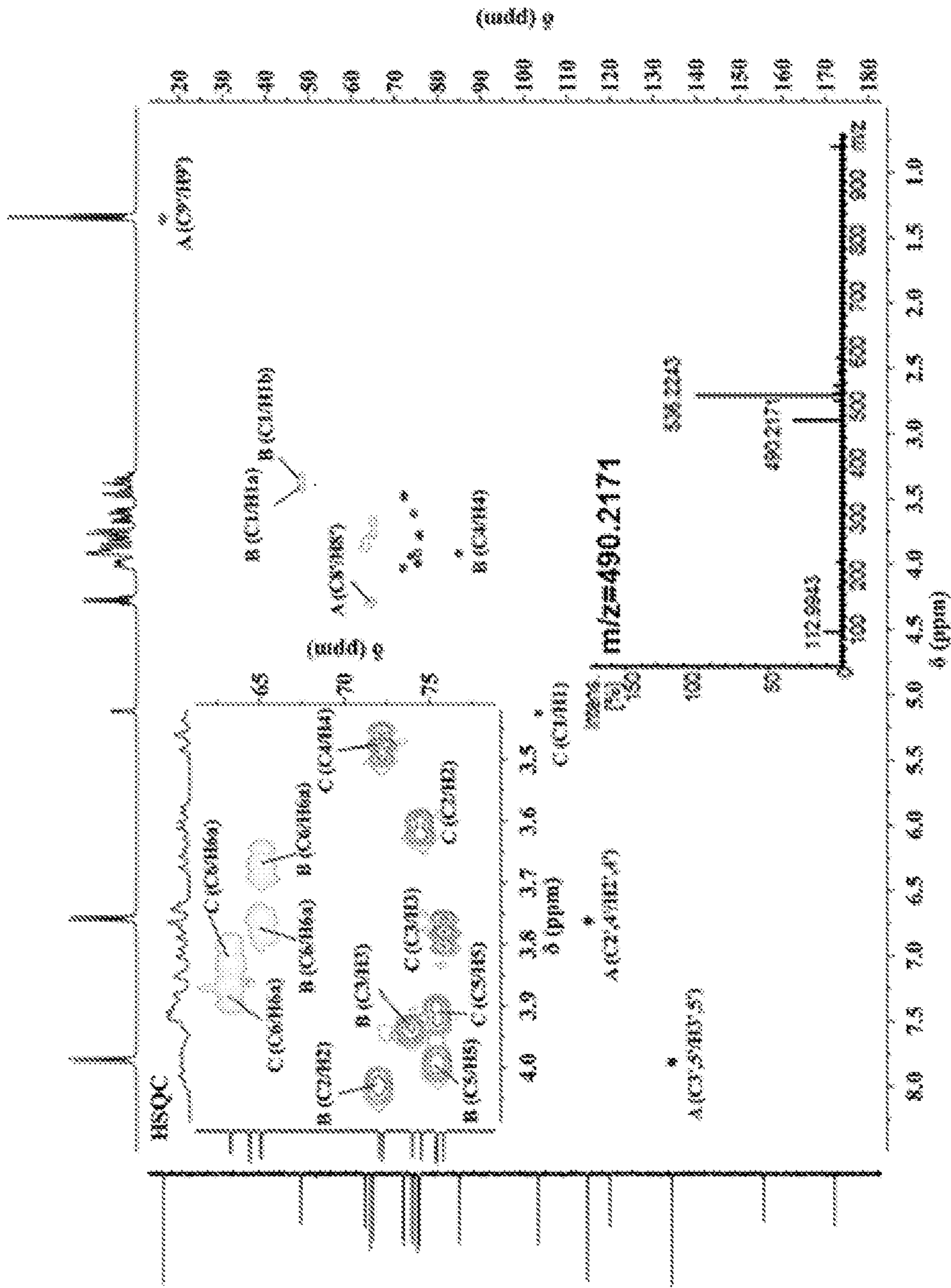


FIG. 17B

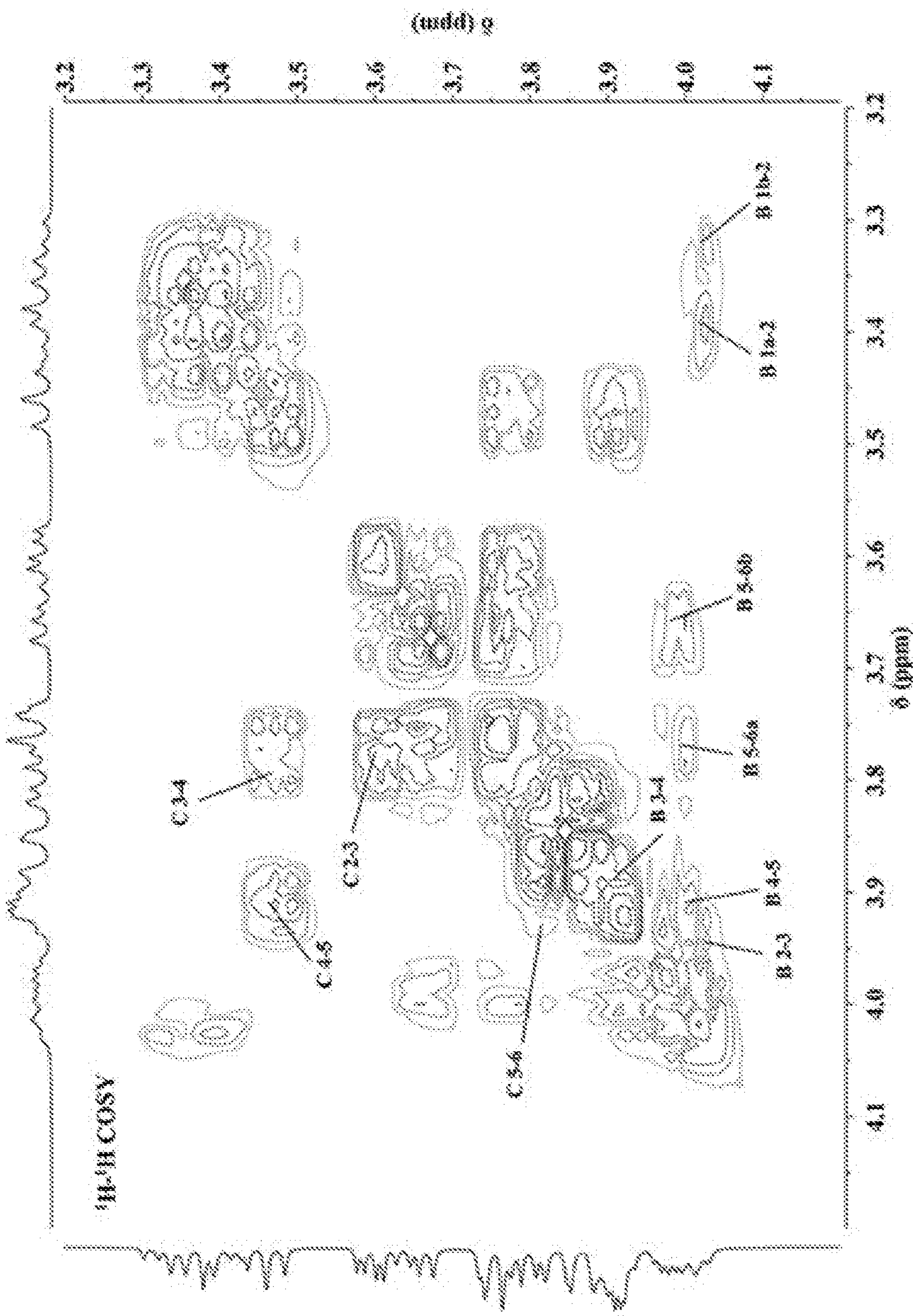


FIG. 17C

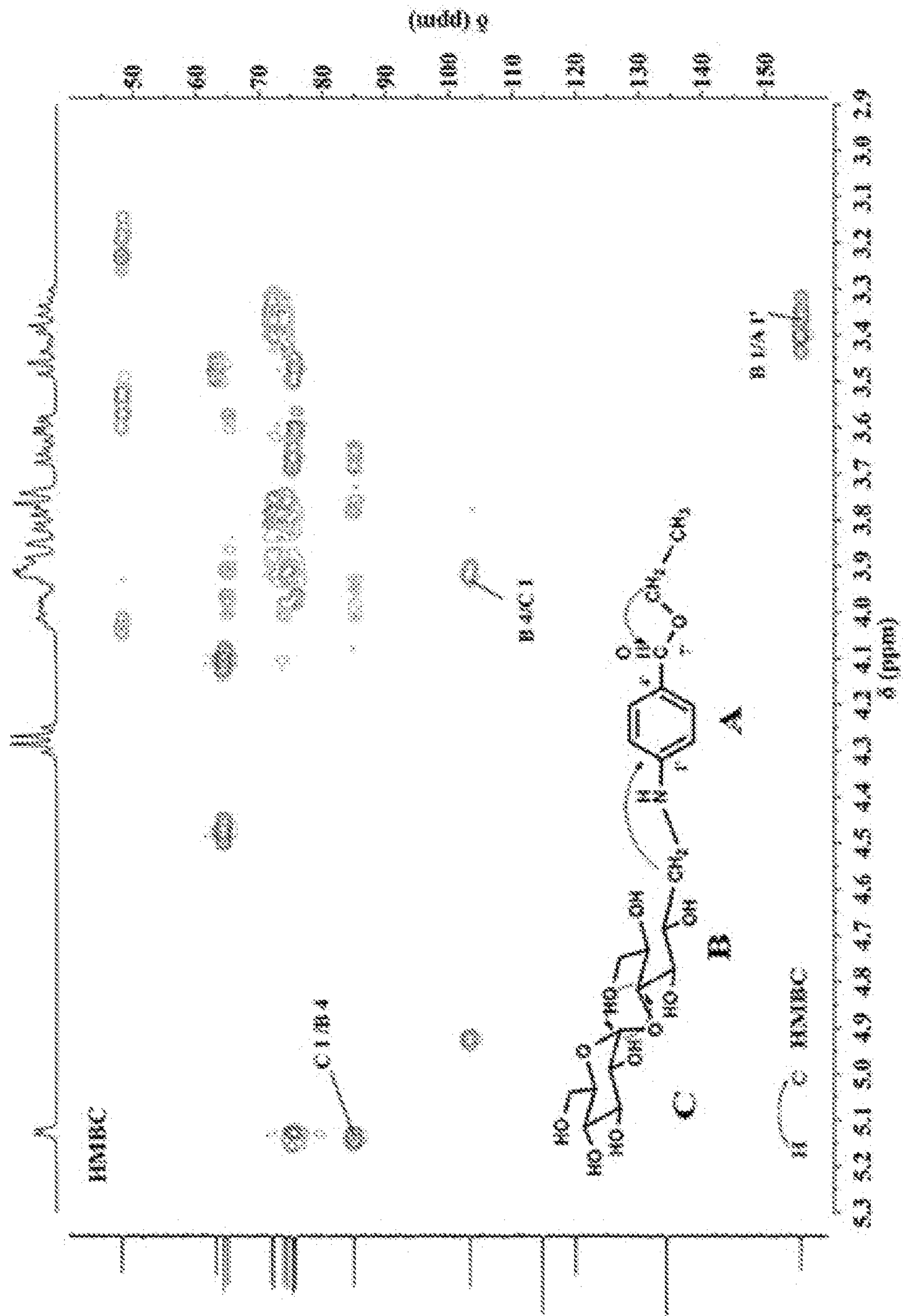


FIG. 17D

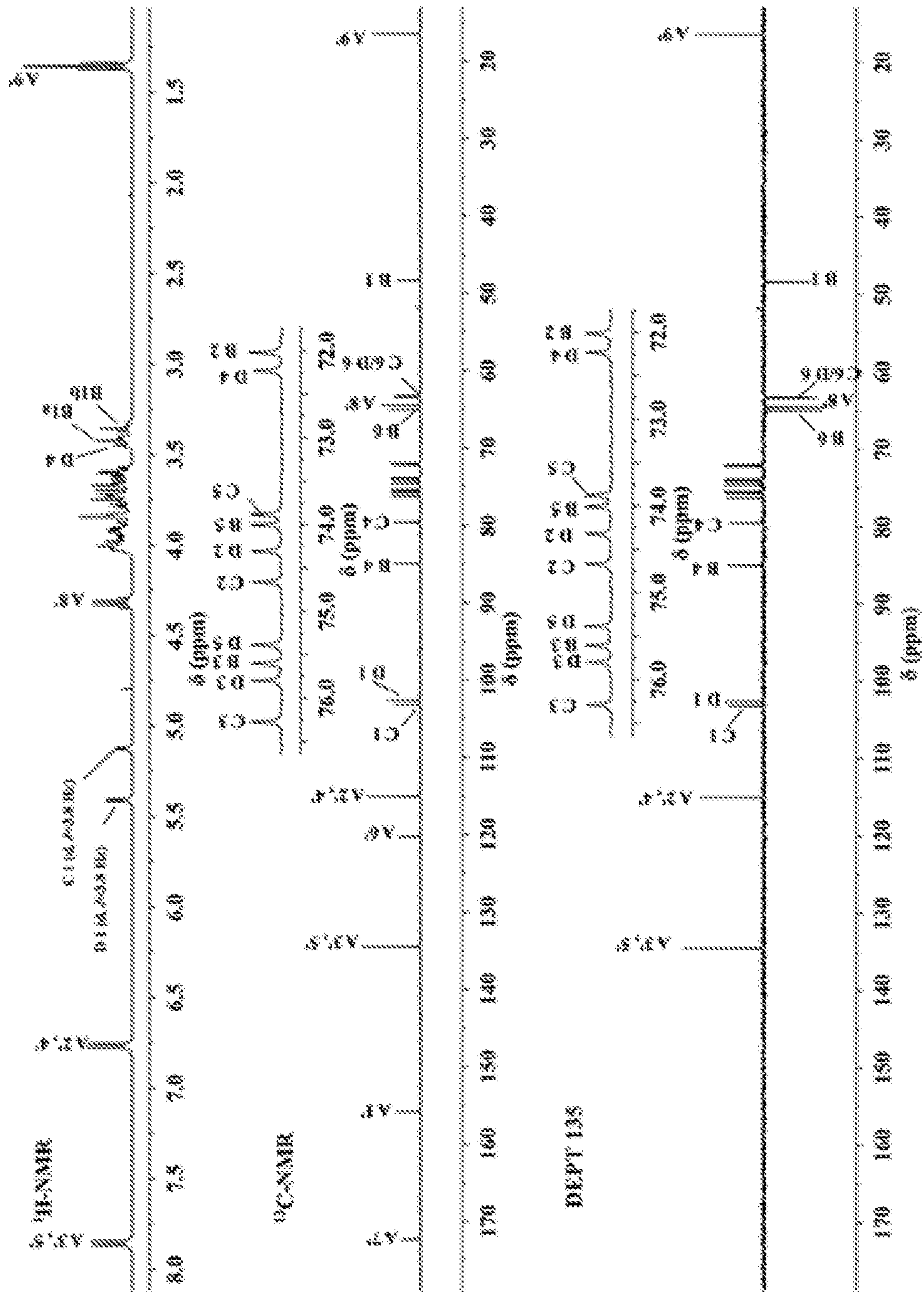


FIG. 17E

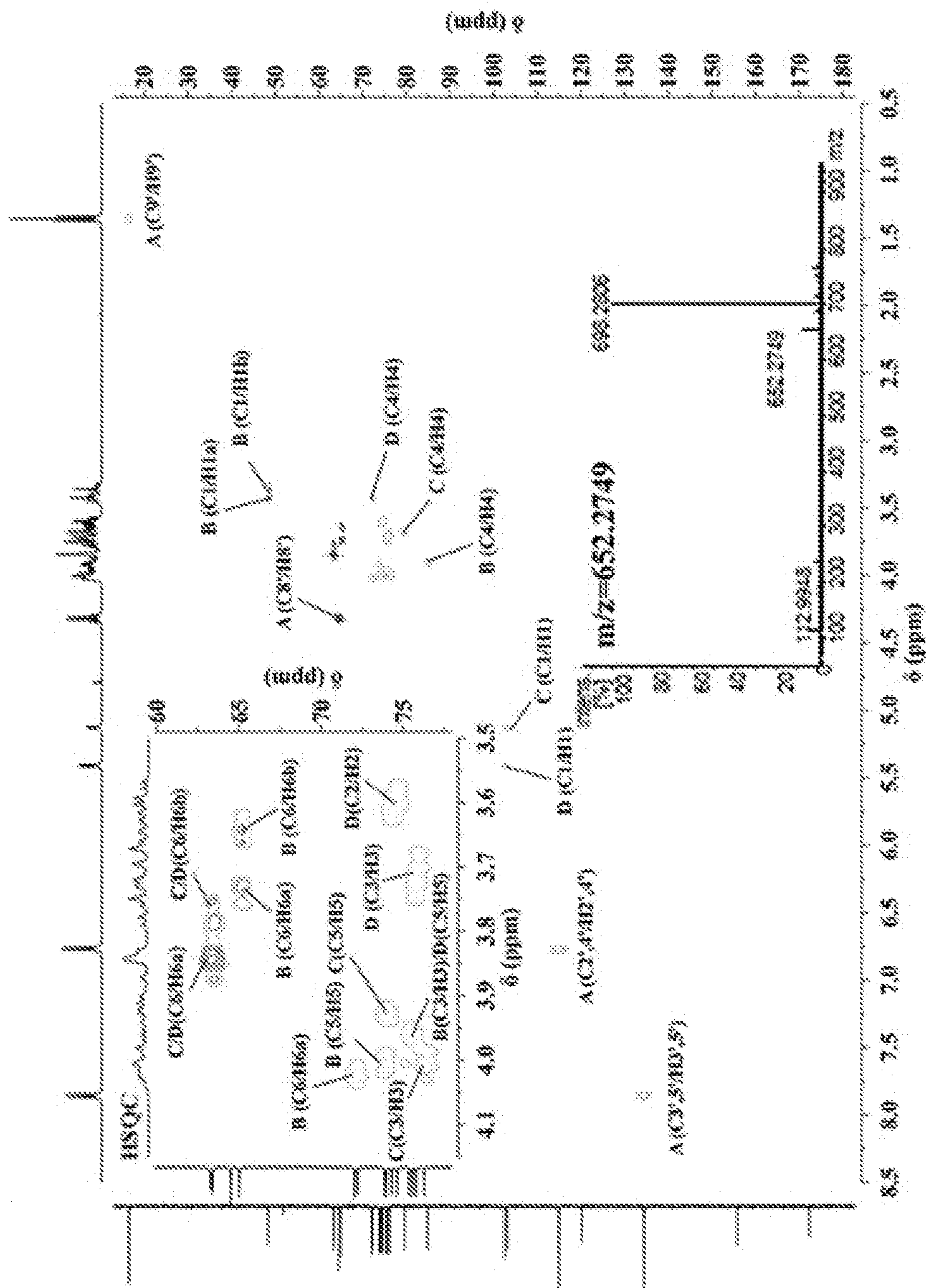


FIG. 17F

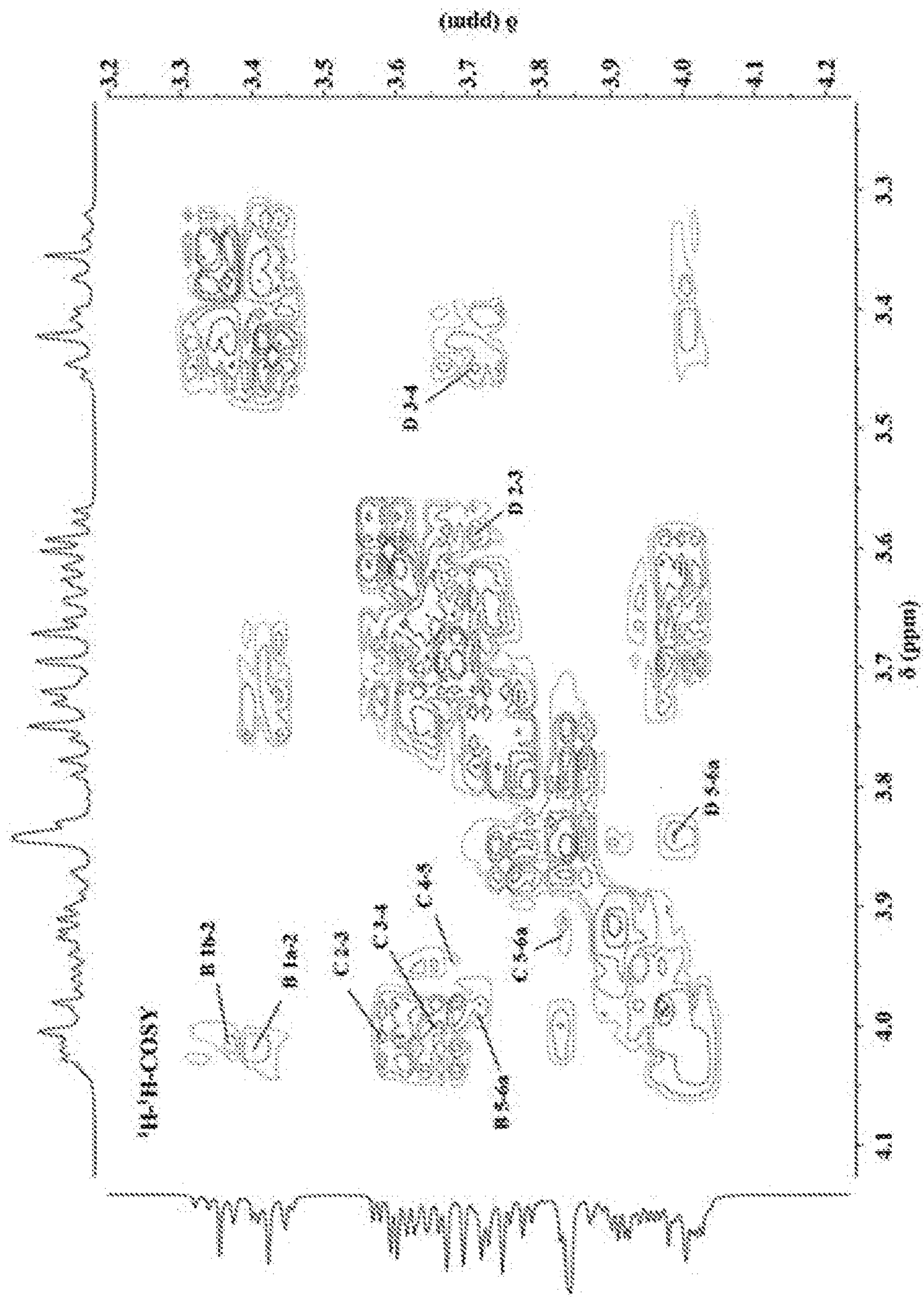


FIG. 17G

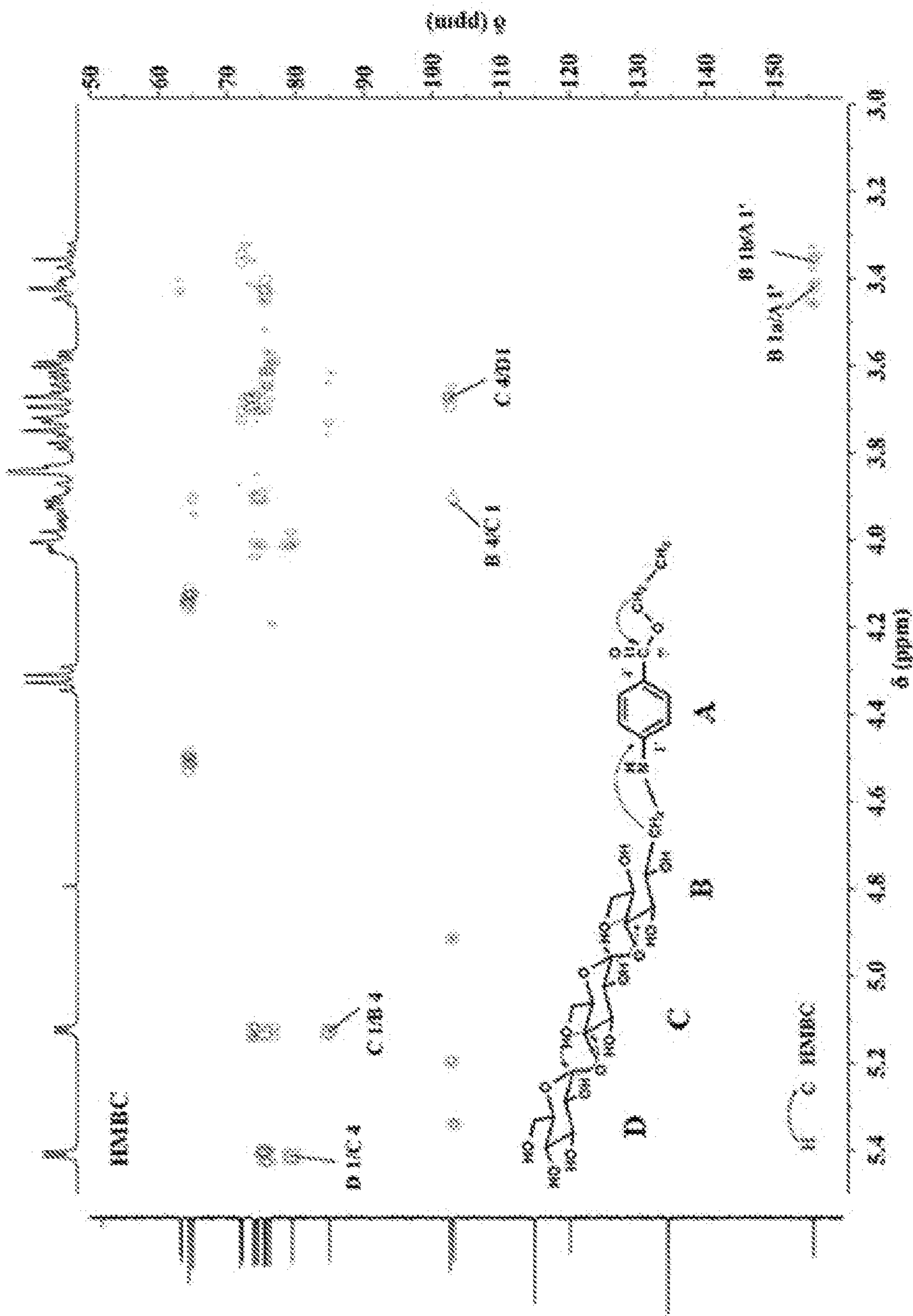


FIG. 17H

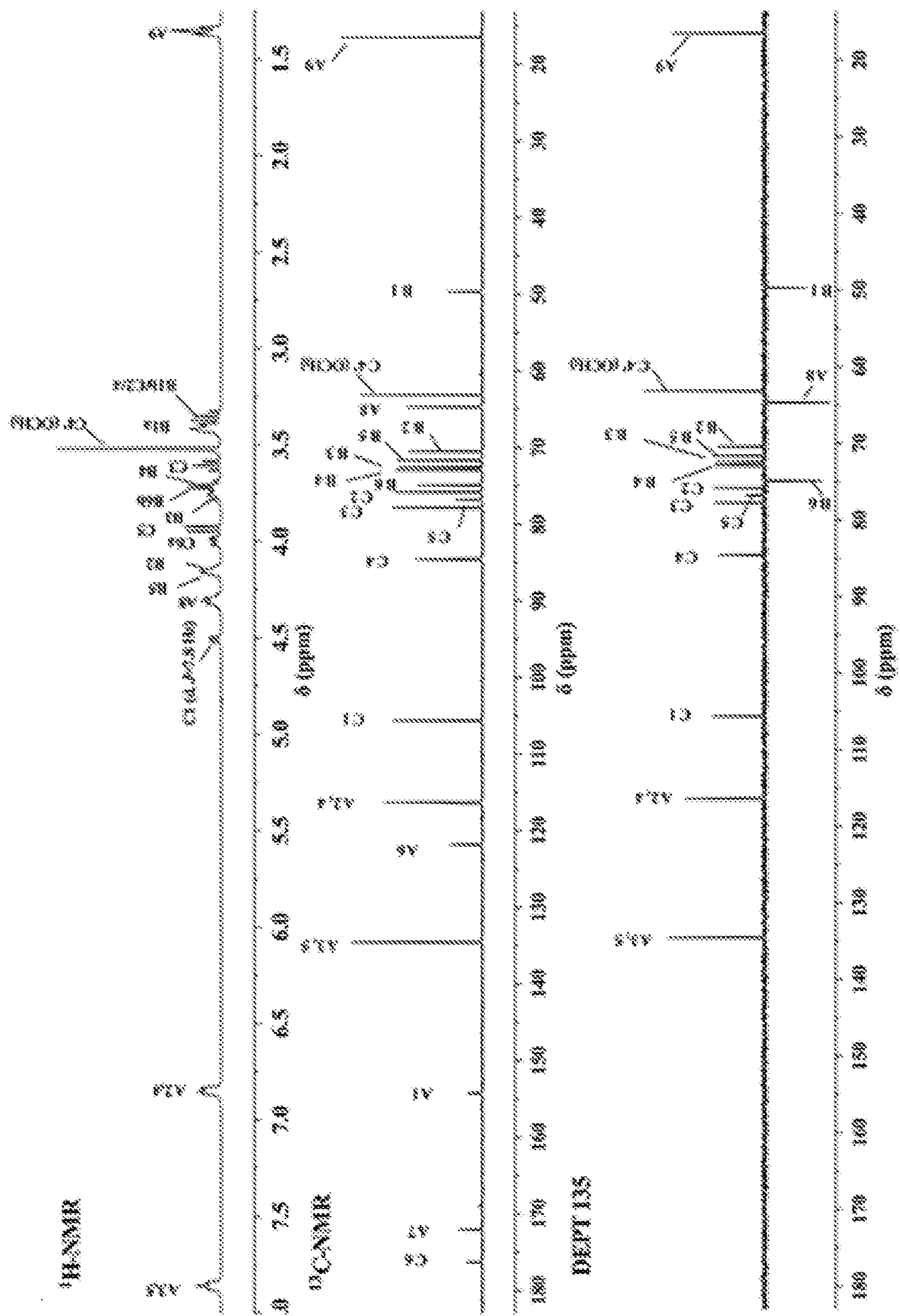


FIG. 17I

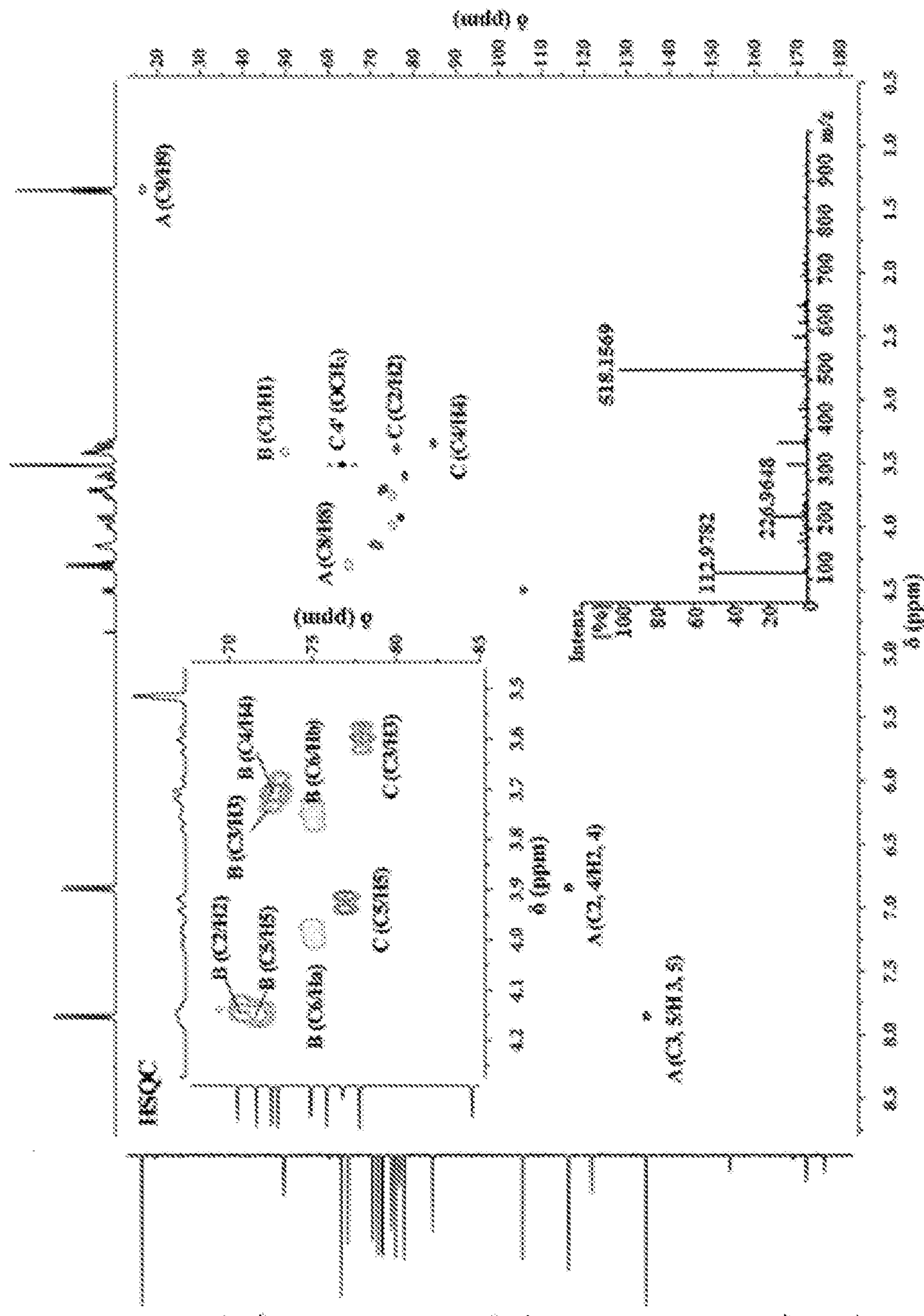


FIG. 17J

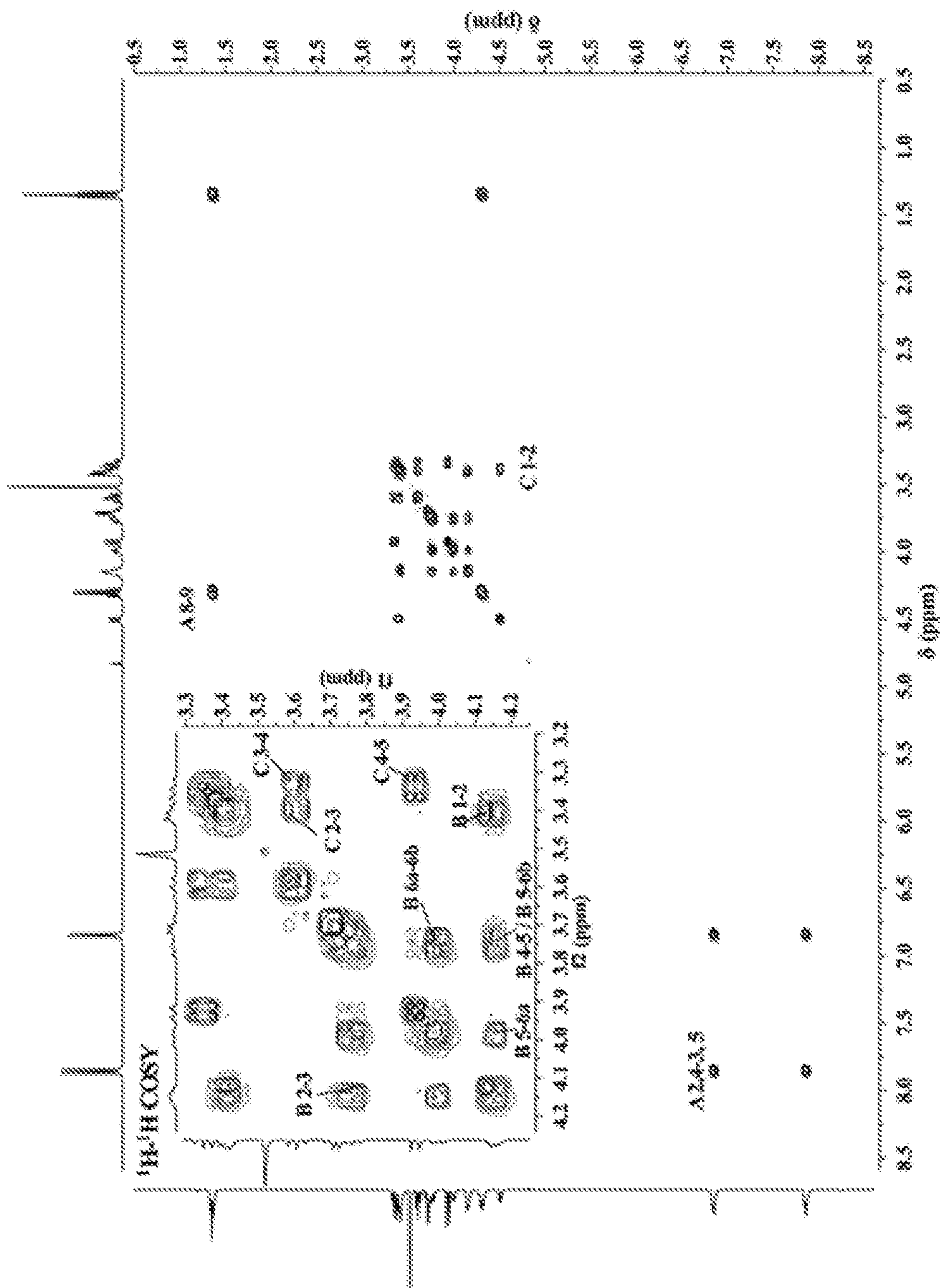


FIG.17K

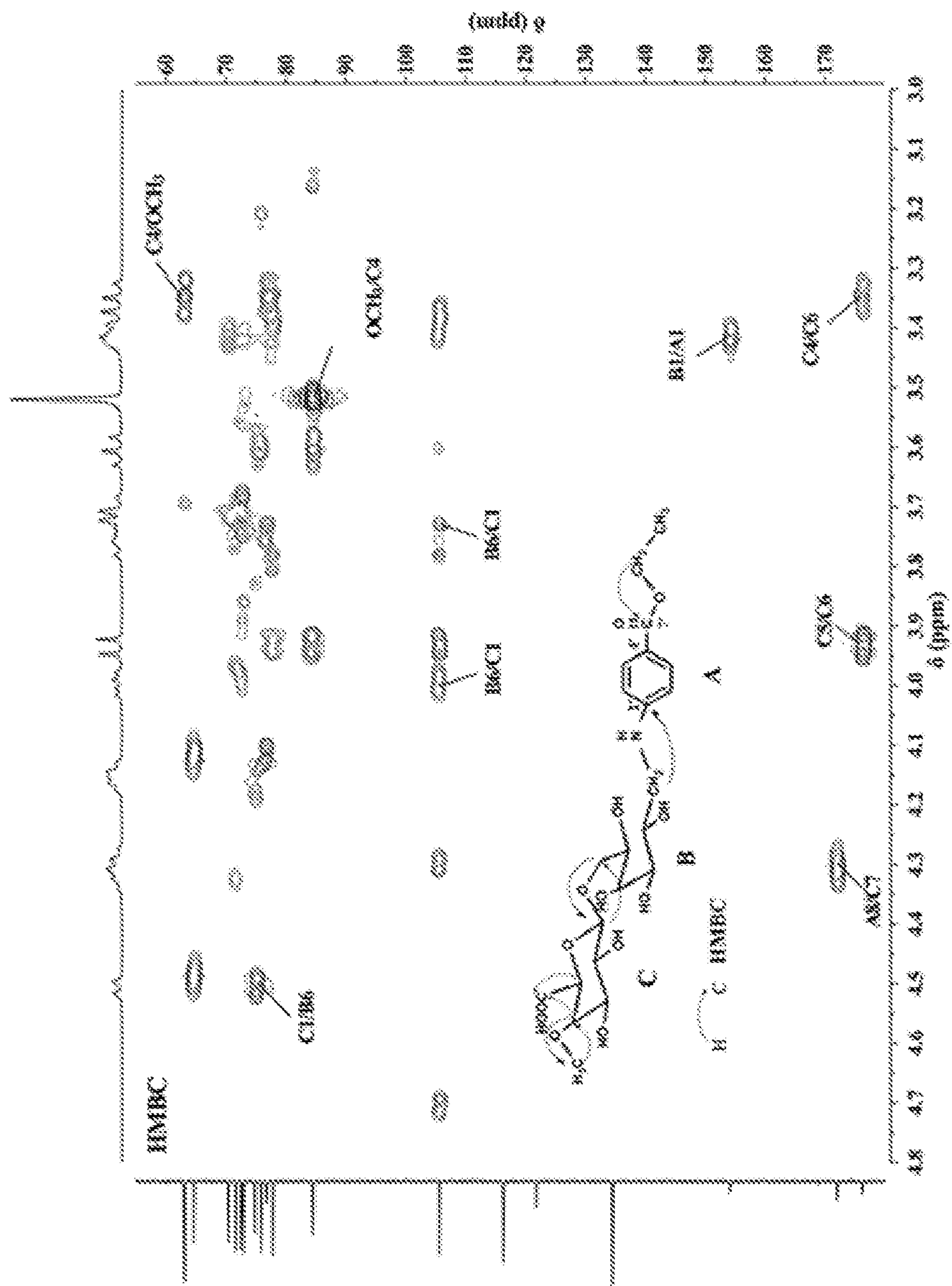


FIG. 17L

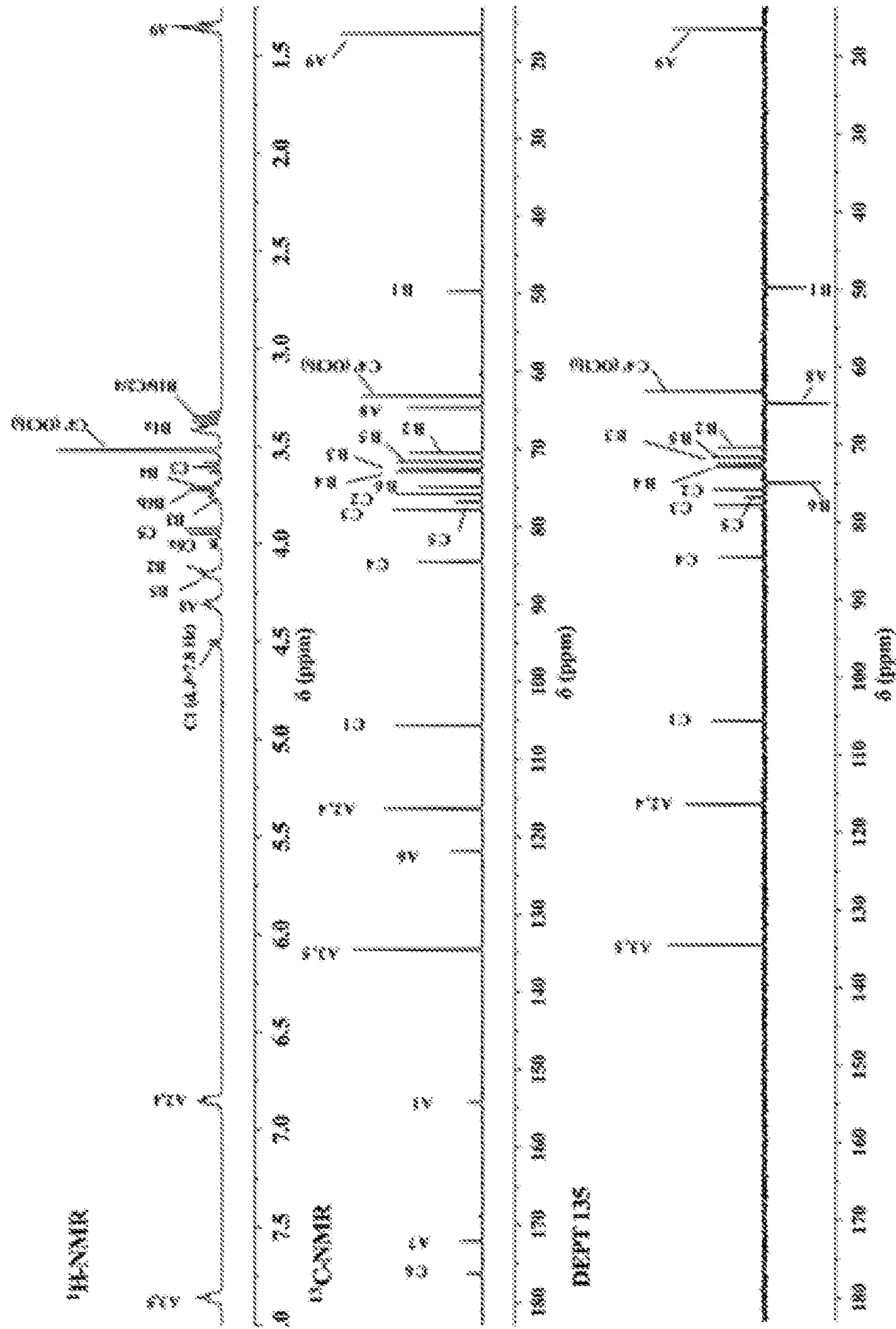


FIG. 17M

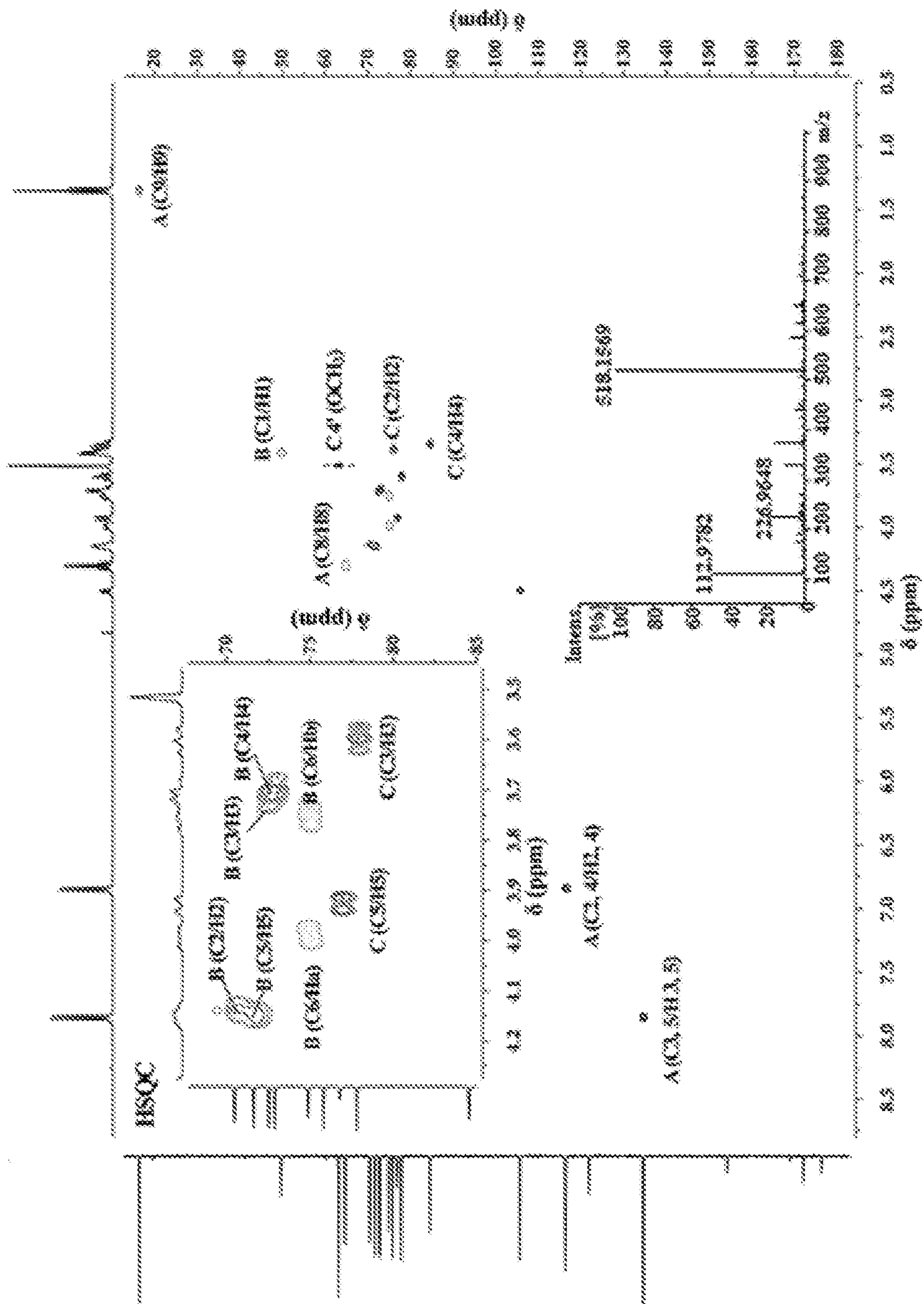


FIG. 17N

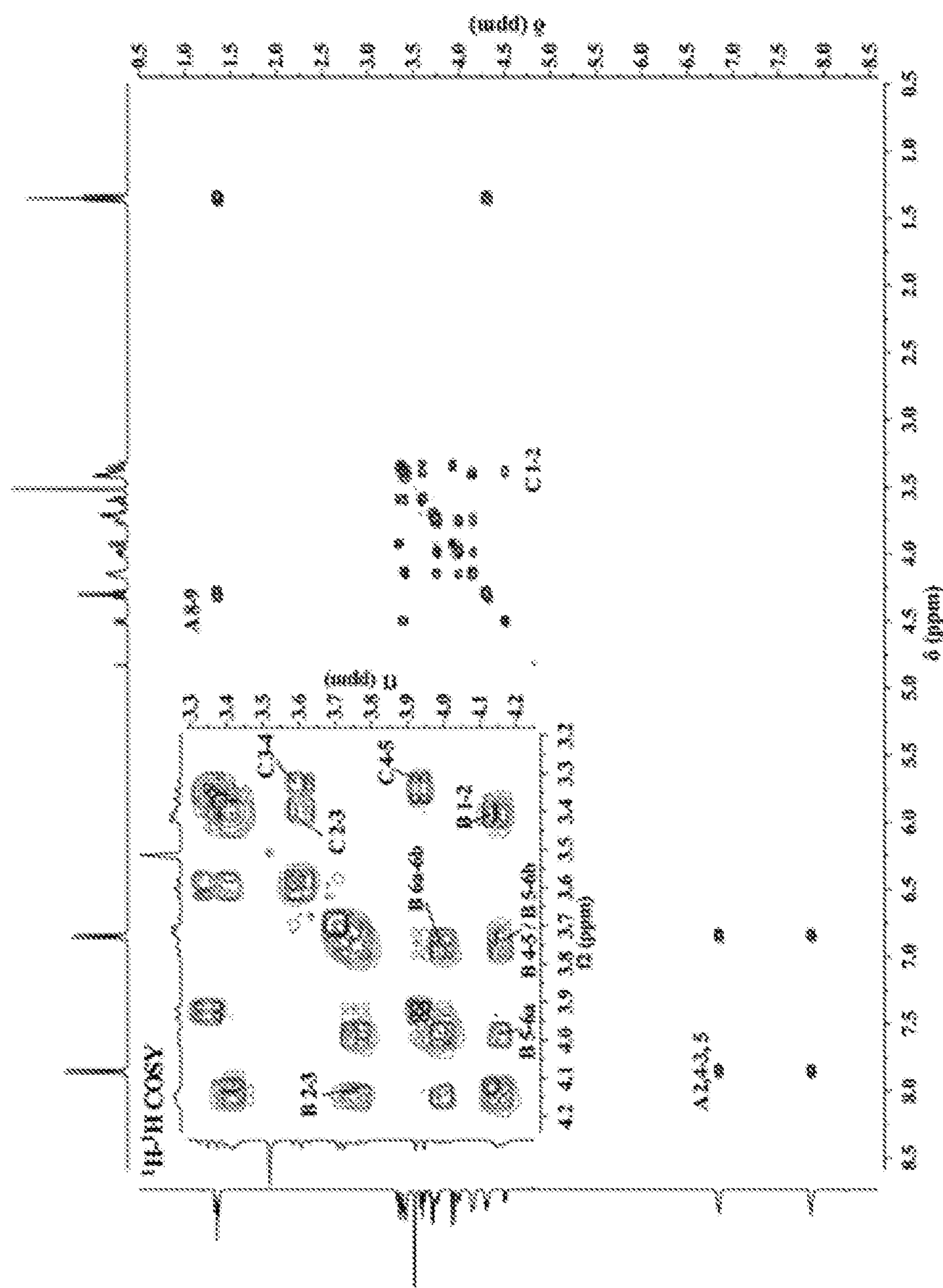


FIG. 170

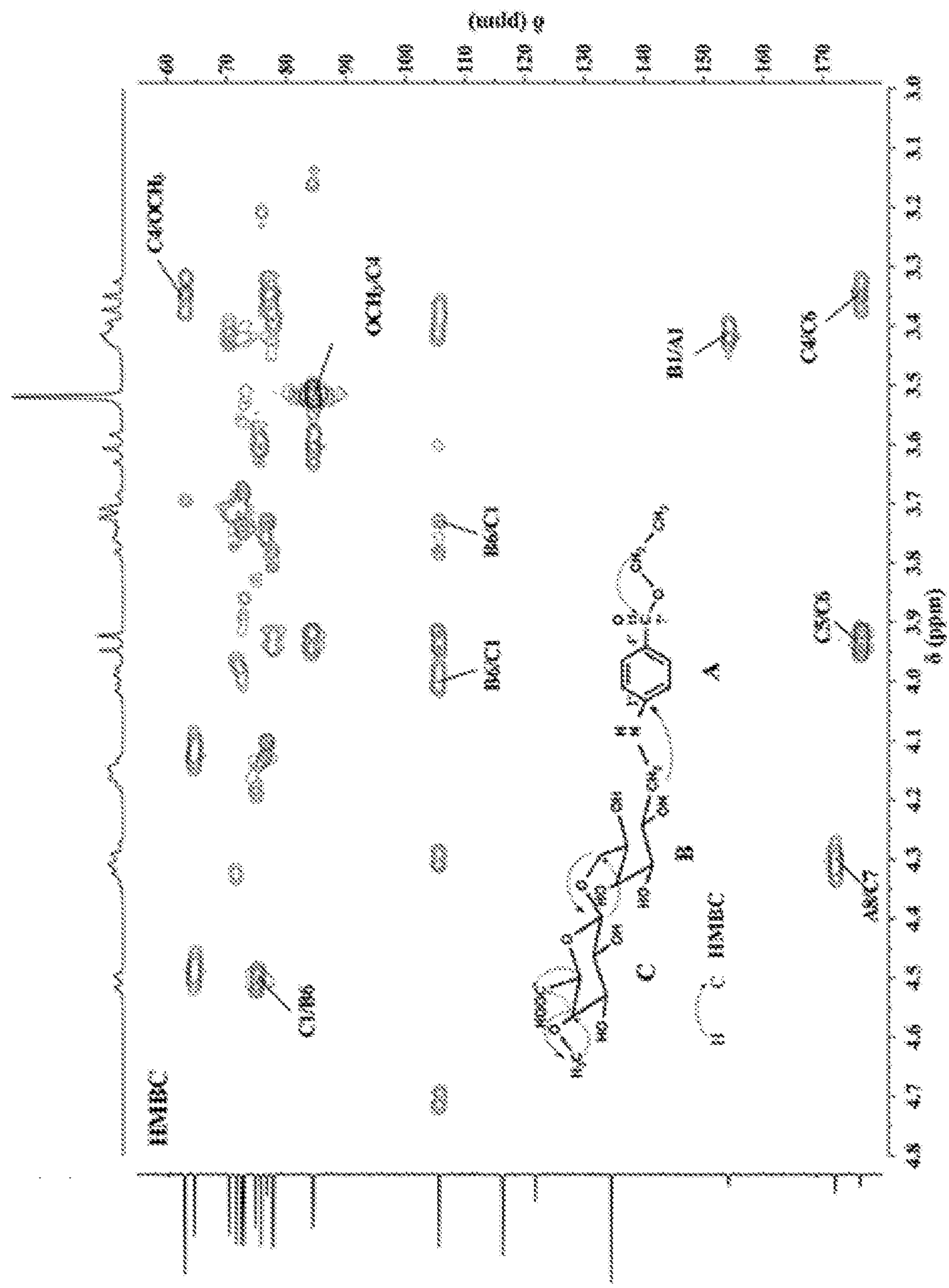


FIG. 17P

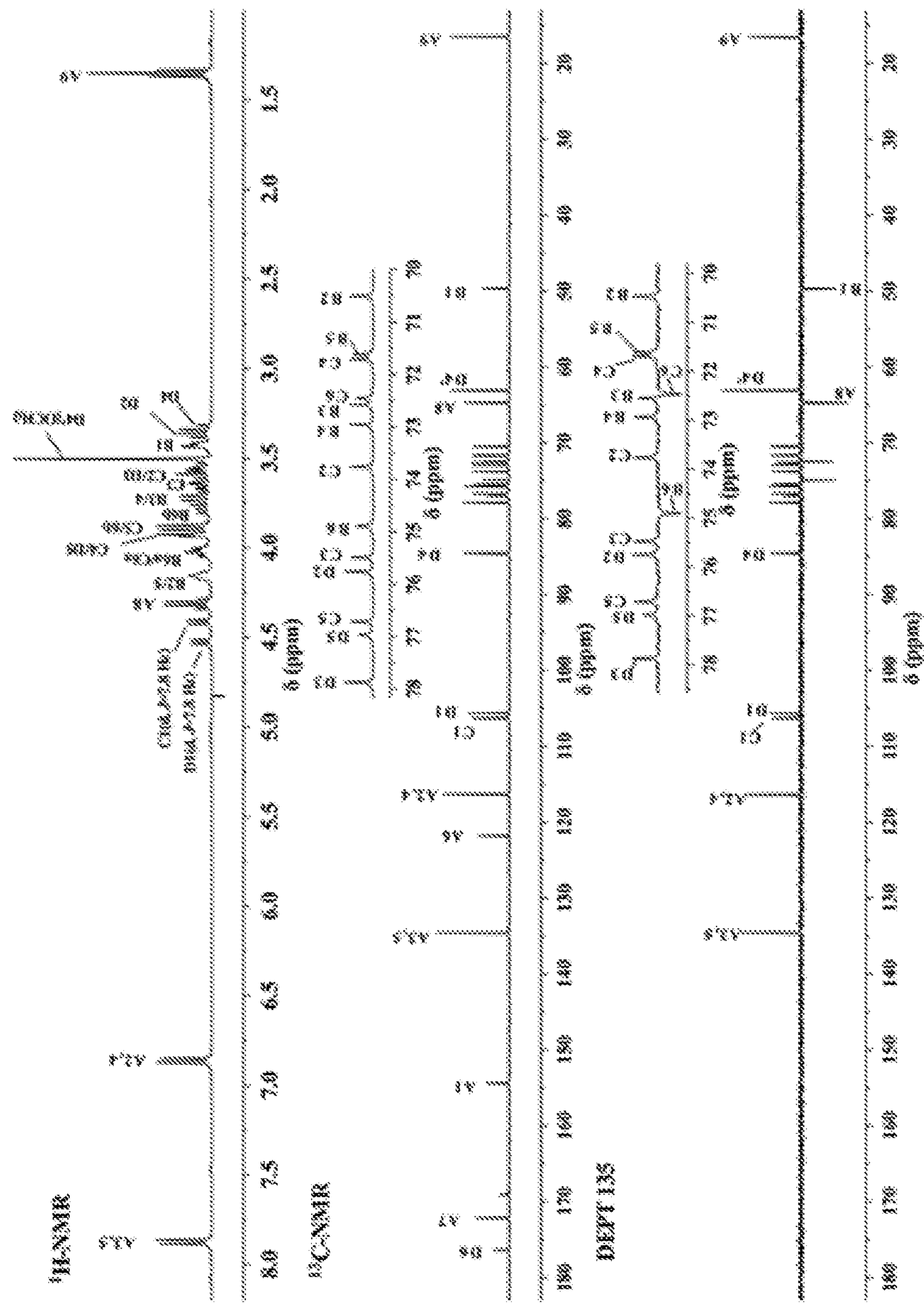


FIG. 17Q

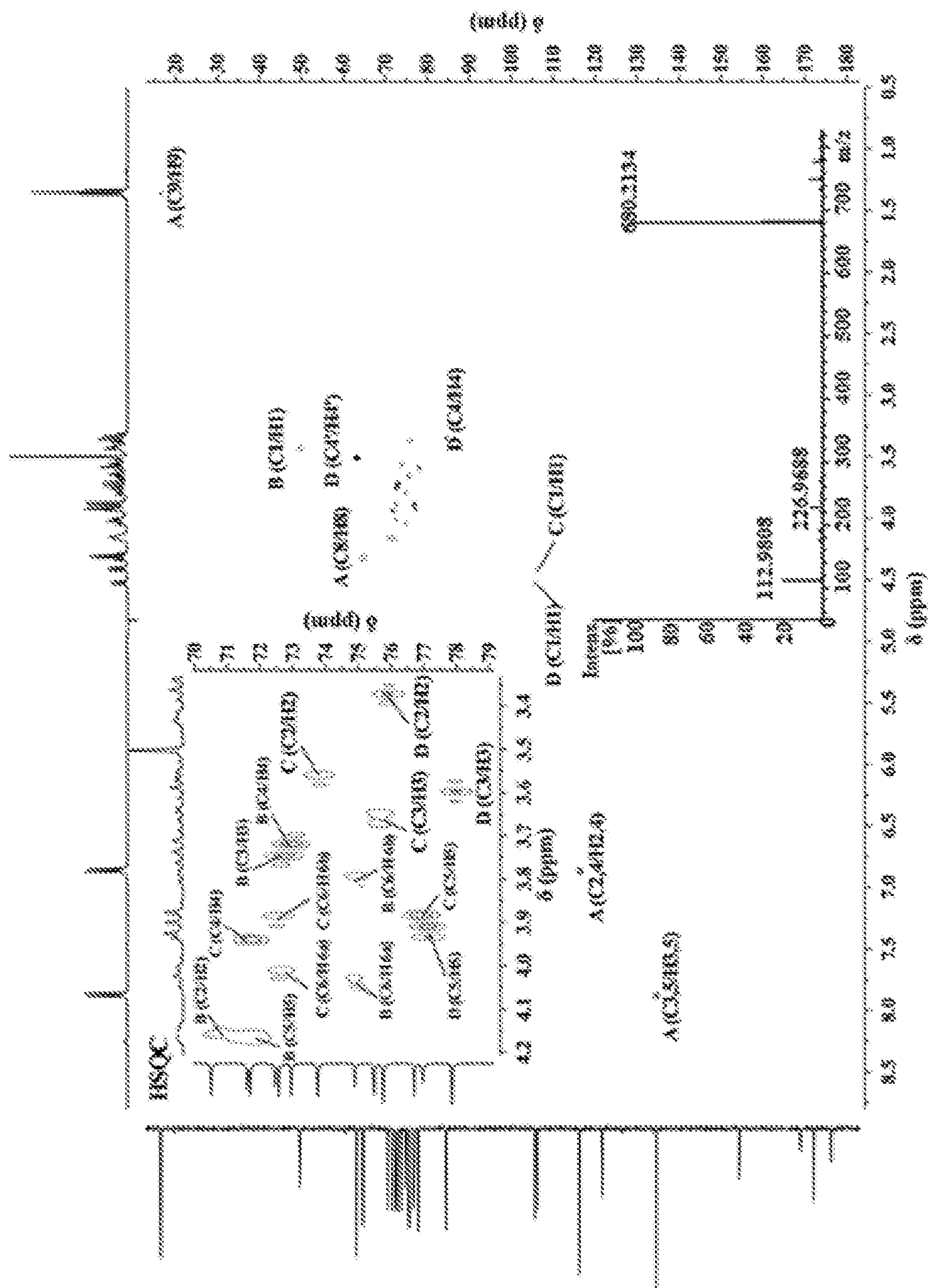


FIG. 17R

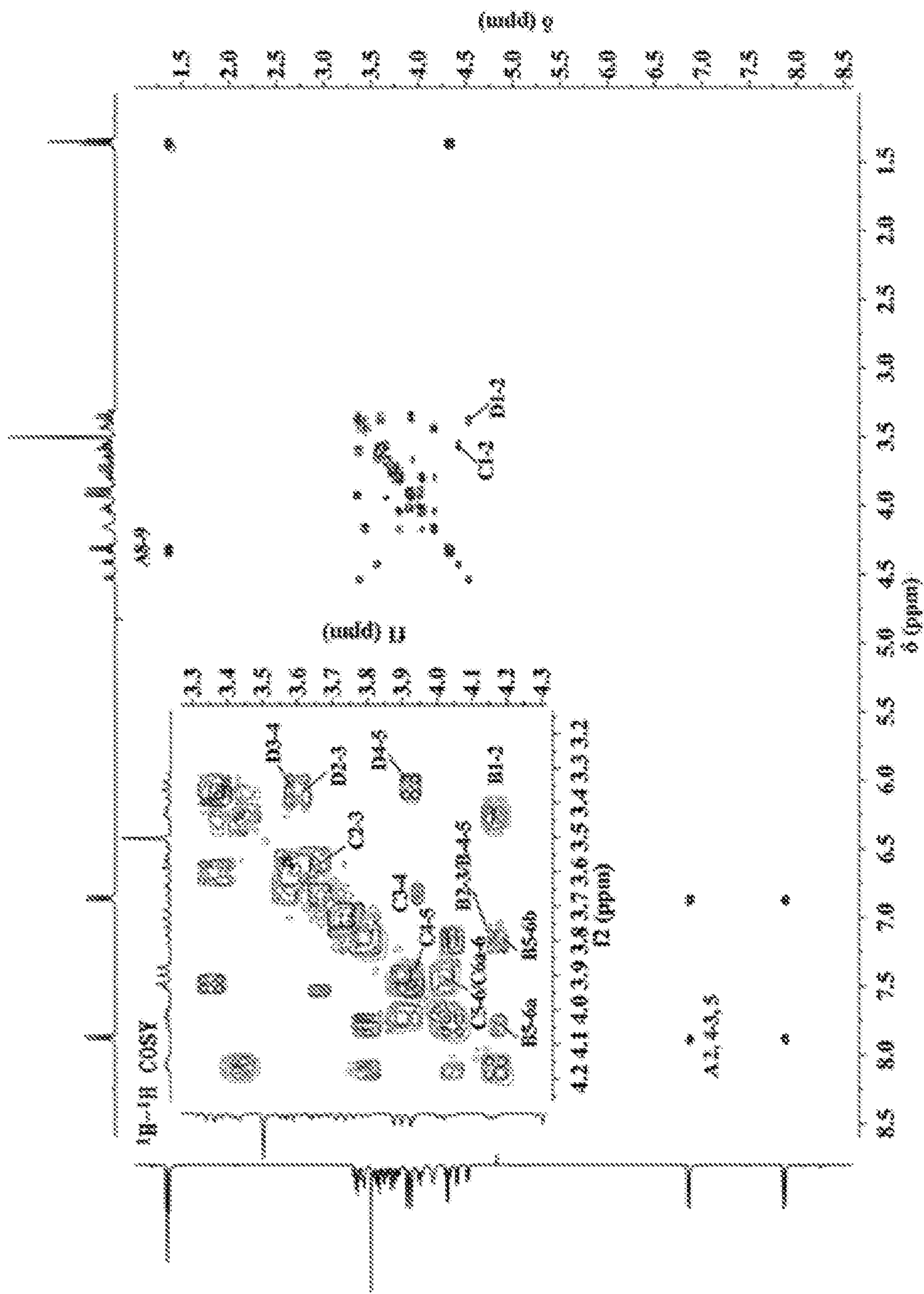


FIG. 17S

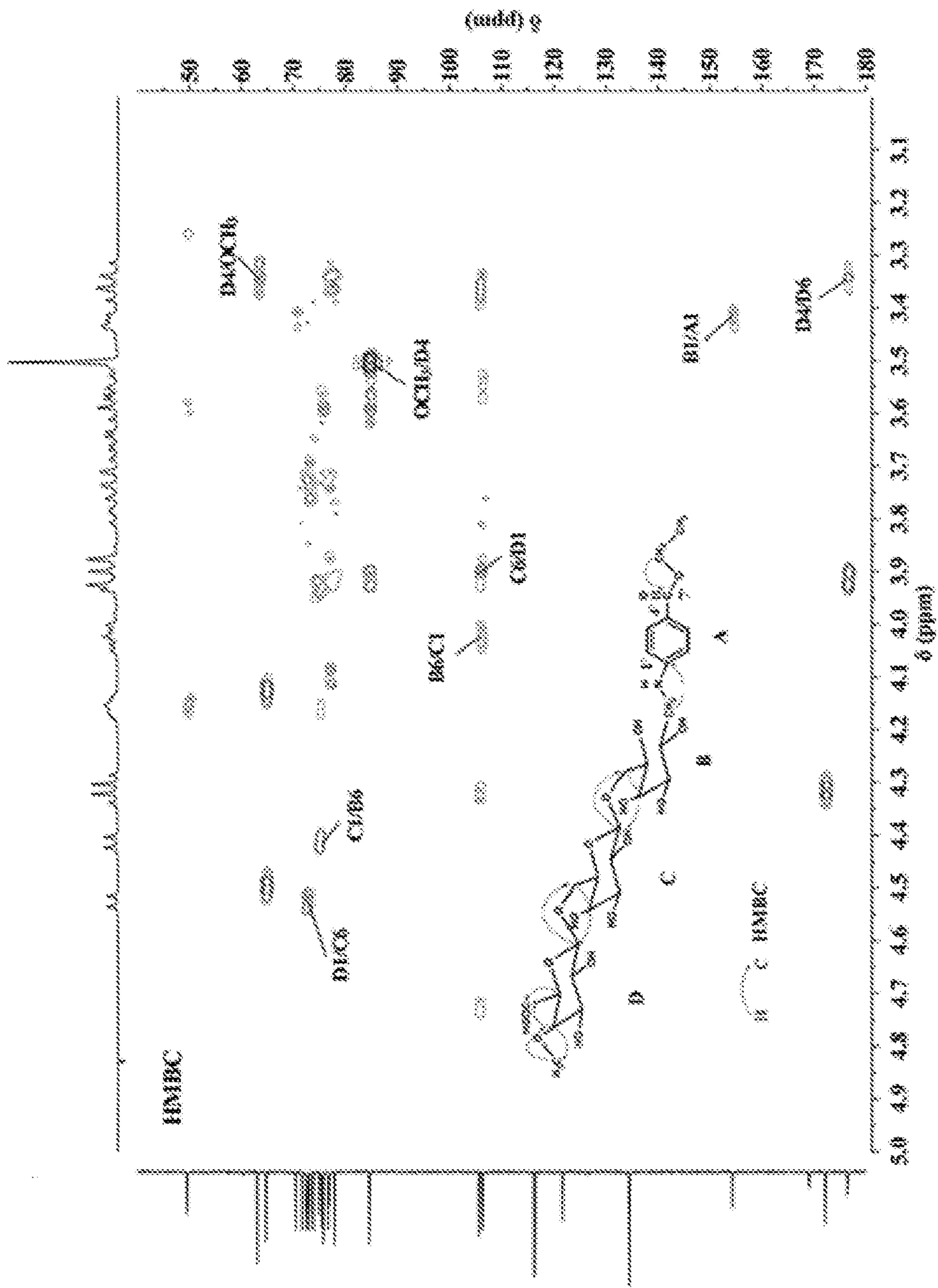


FIG. 17T

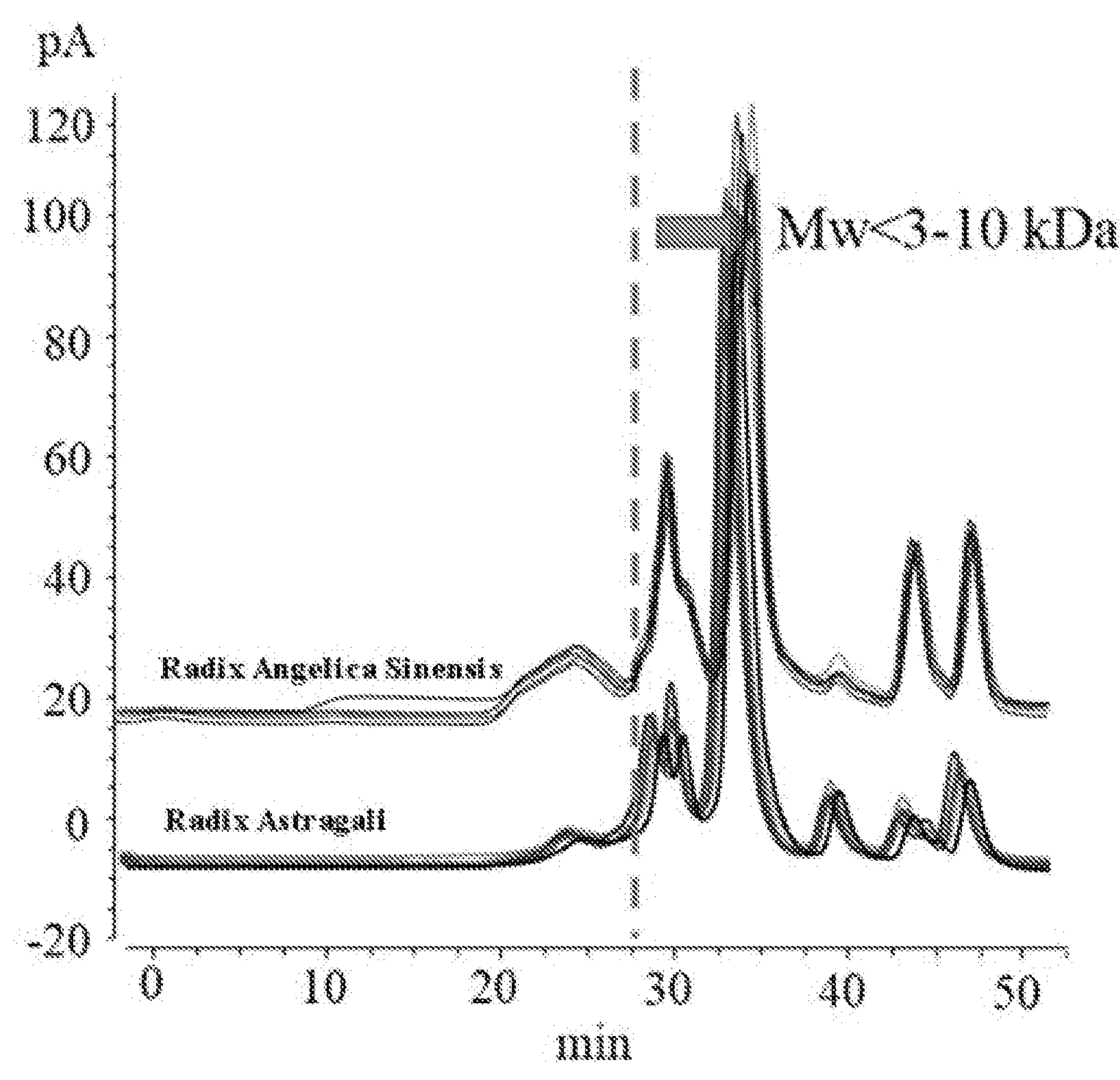


FIG. 18A

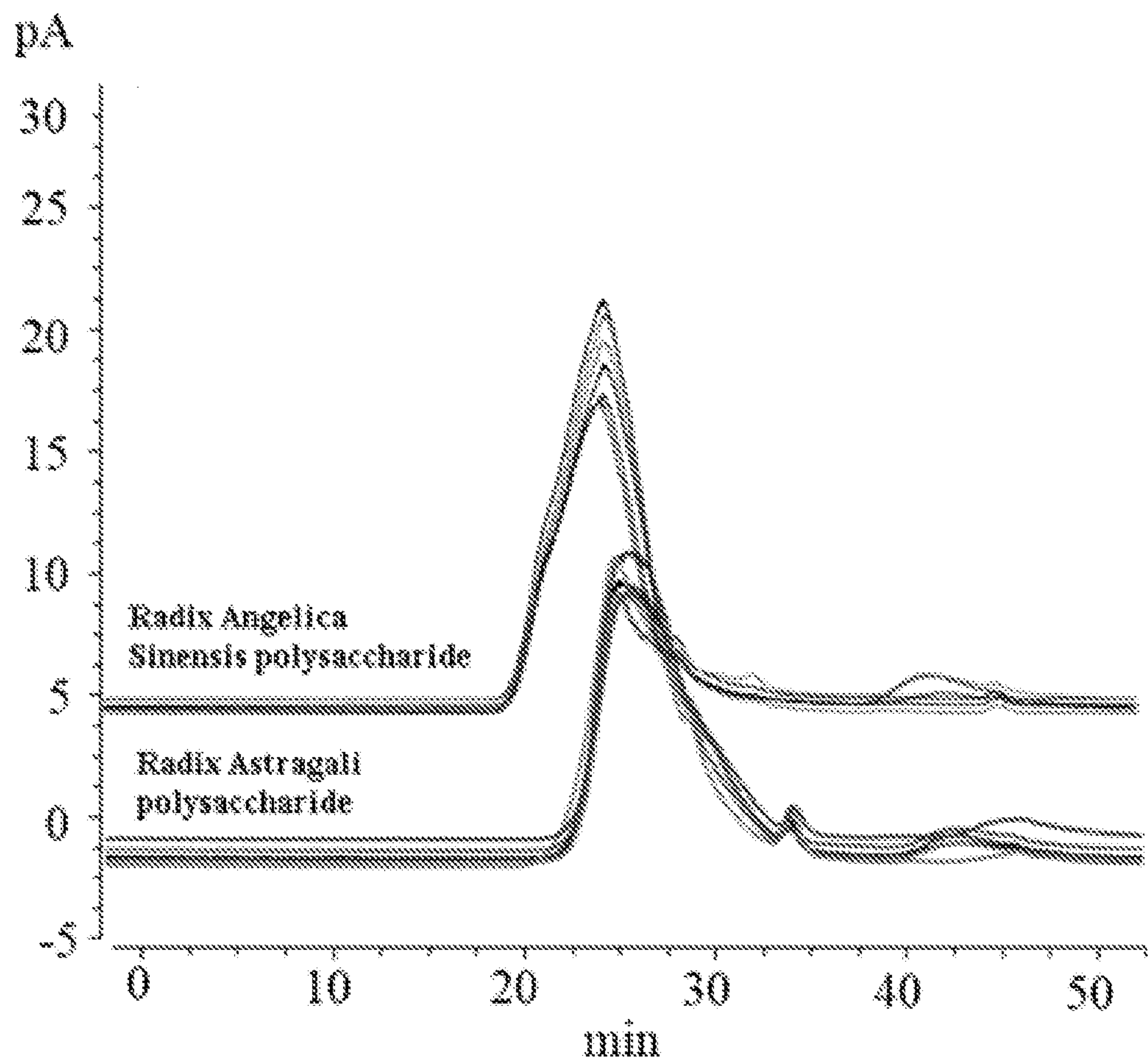


FIG. 18B

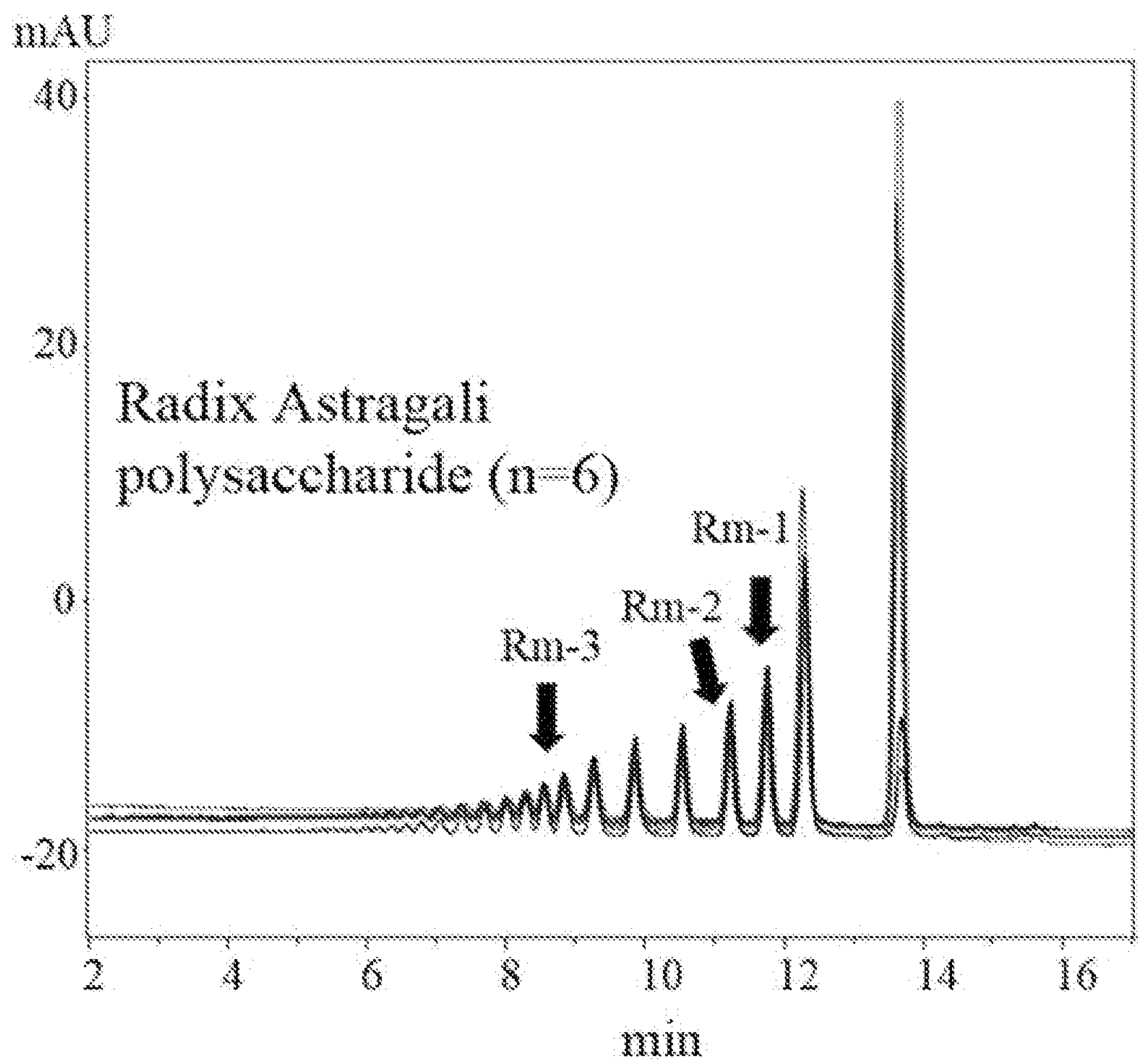


FIG. 19A

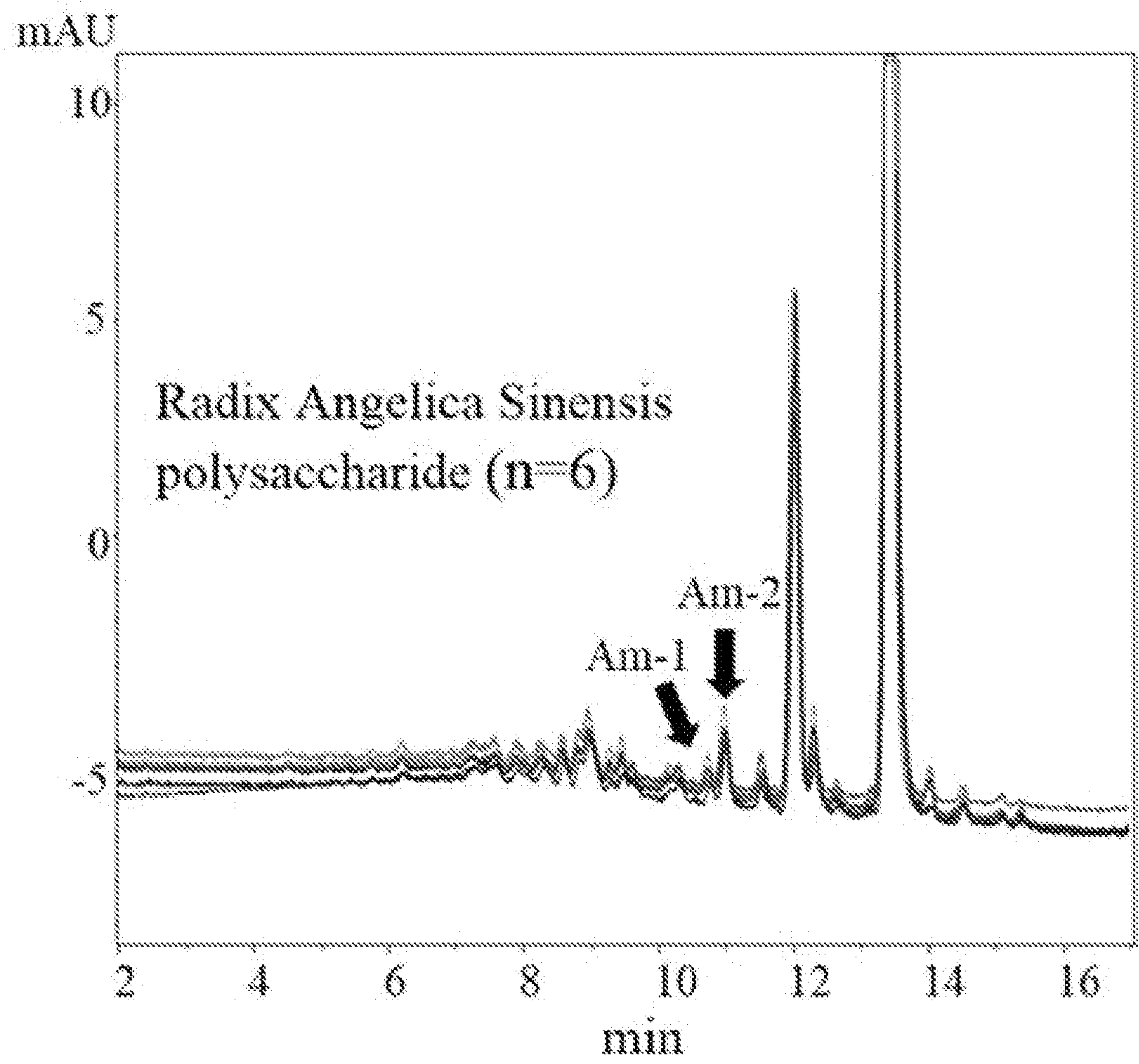


FIG. 19B

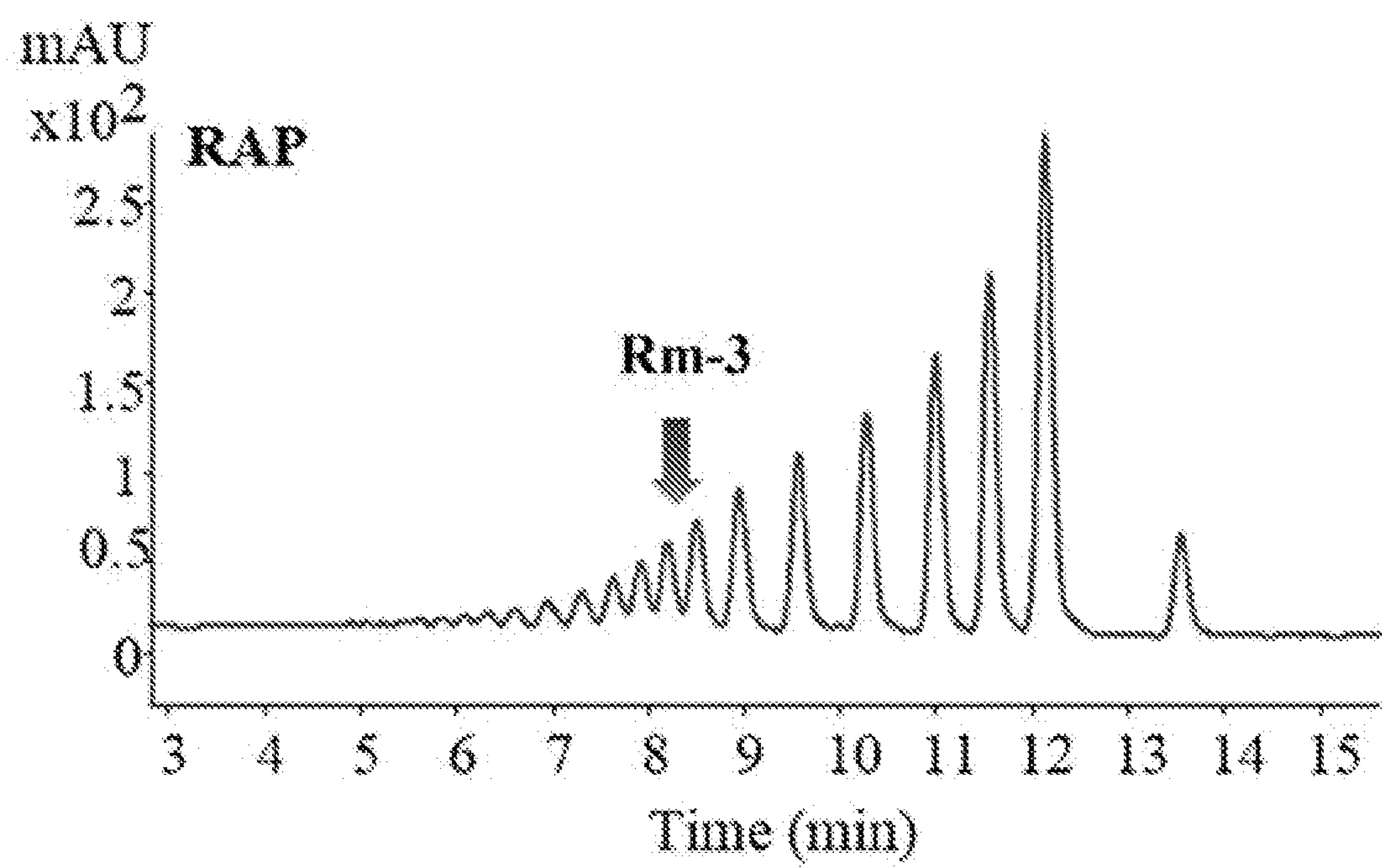


FIG. 20A

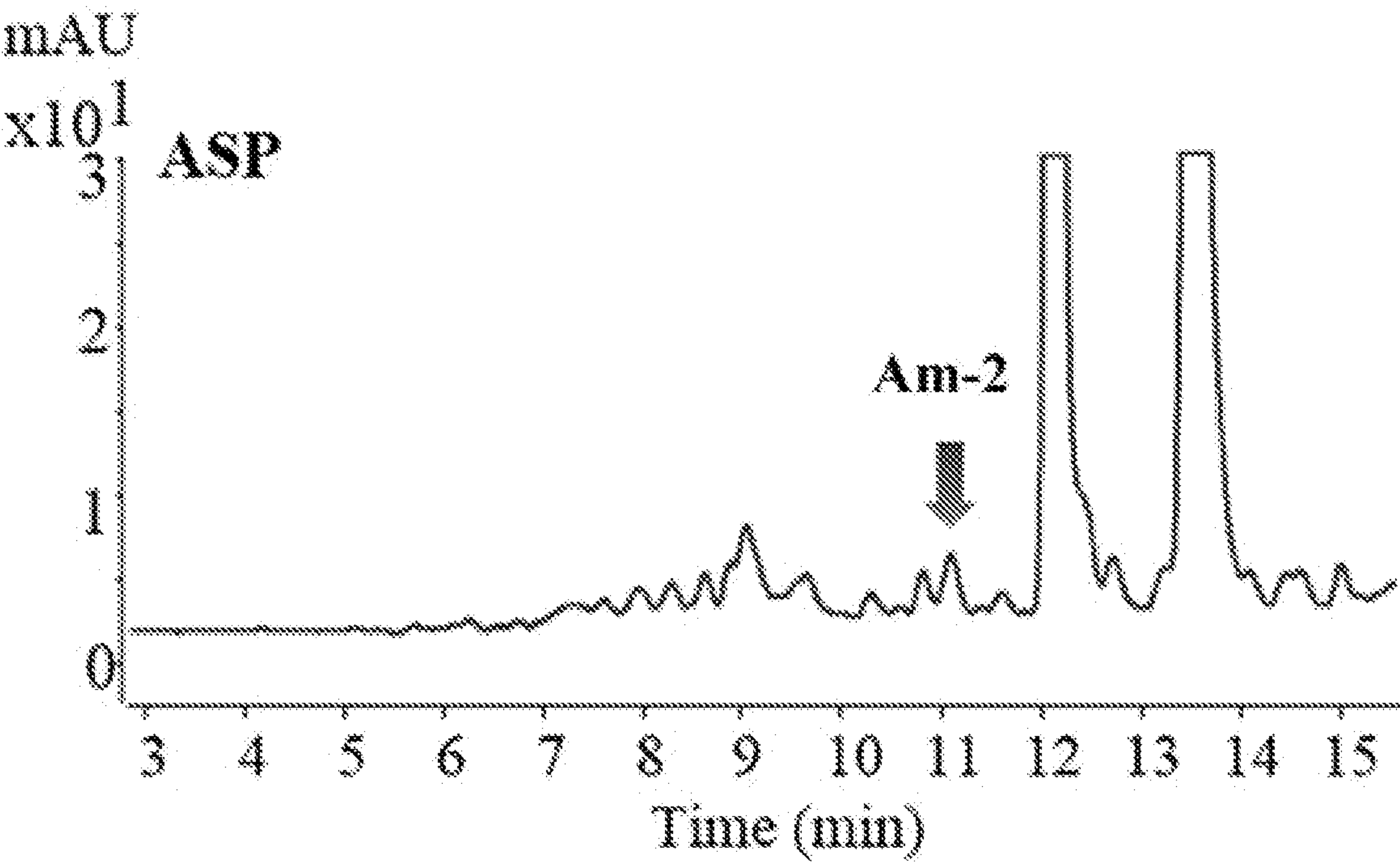


FIG. 20B

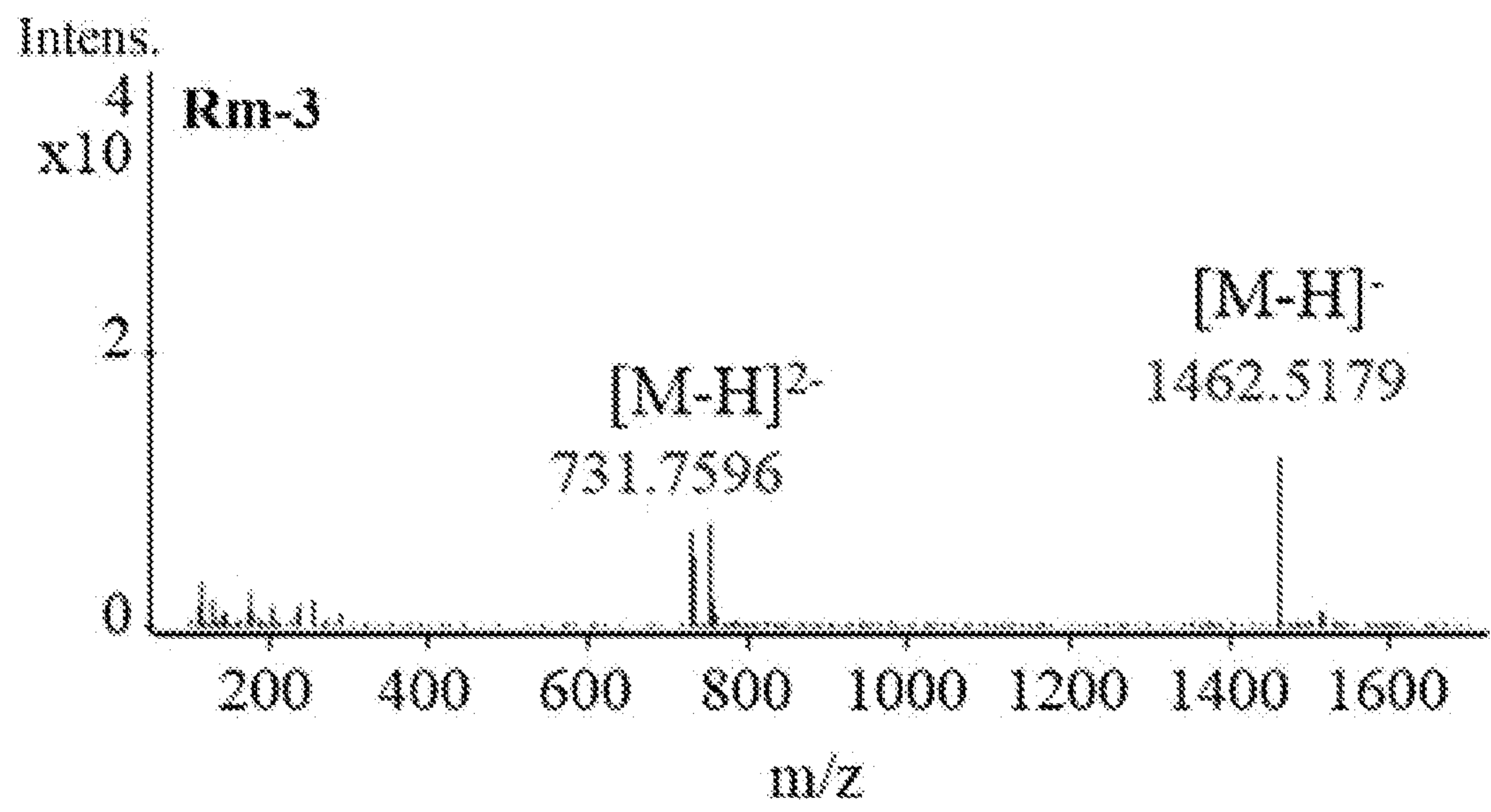


FIG. 20C

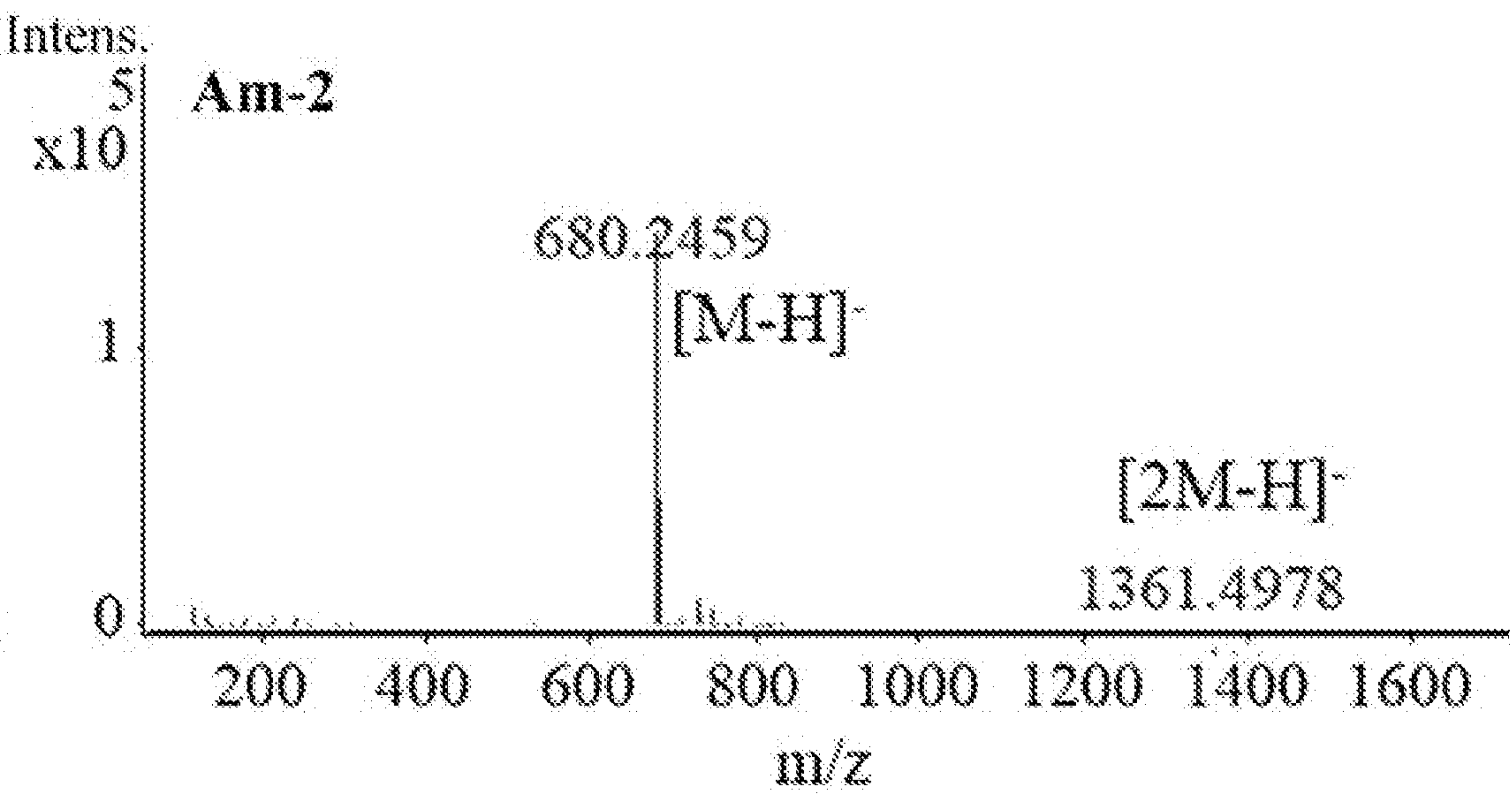


FIG. 20D

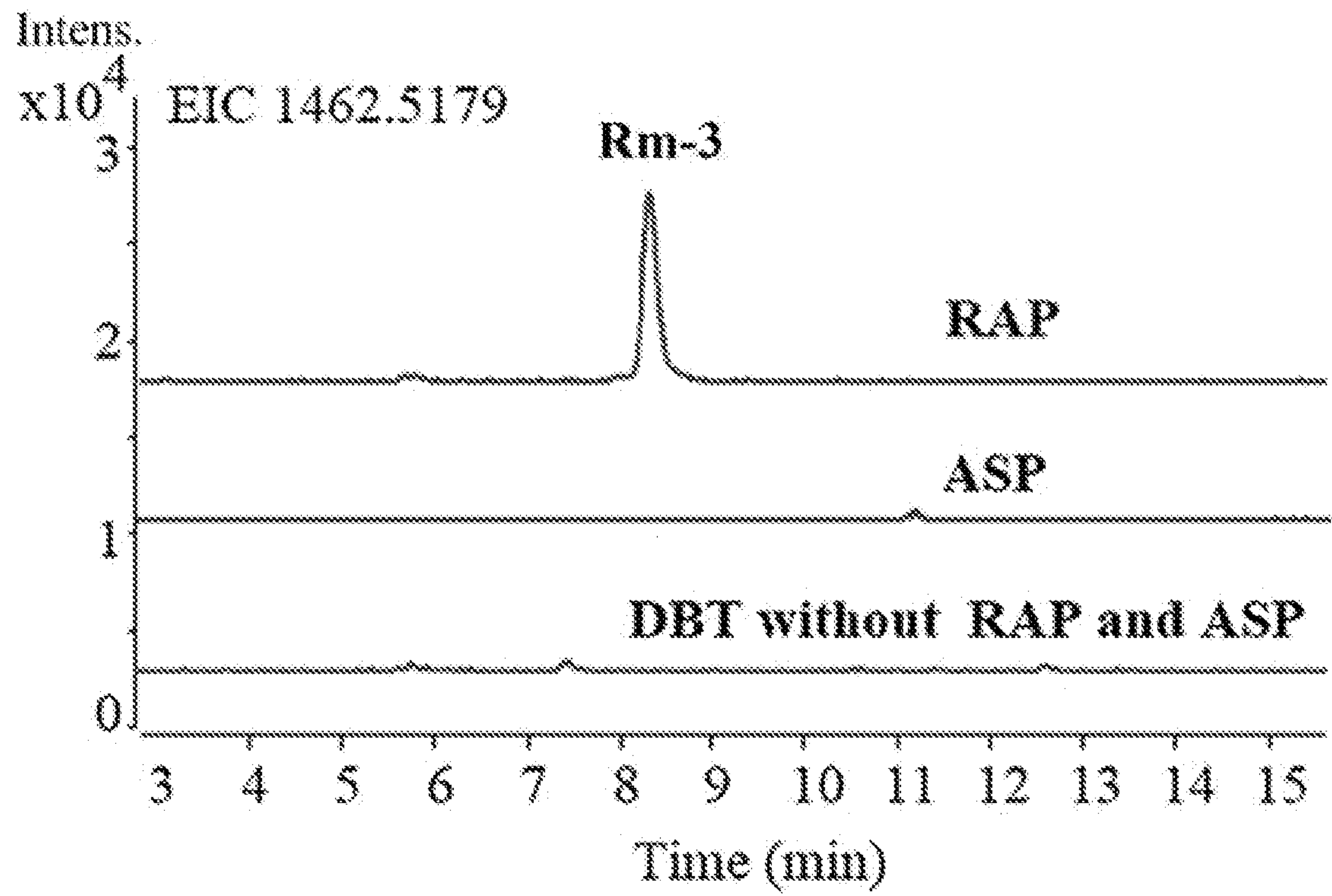


FIG. 20E

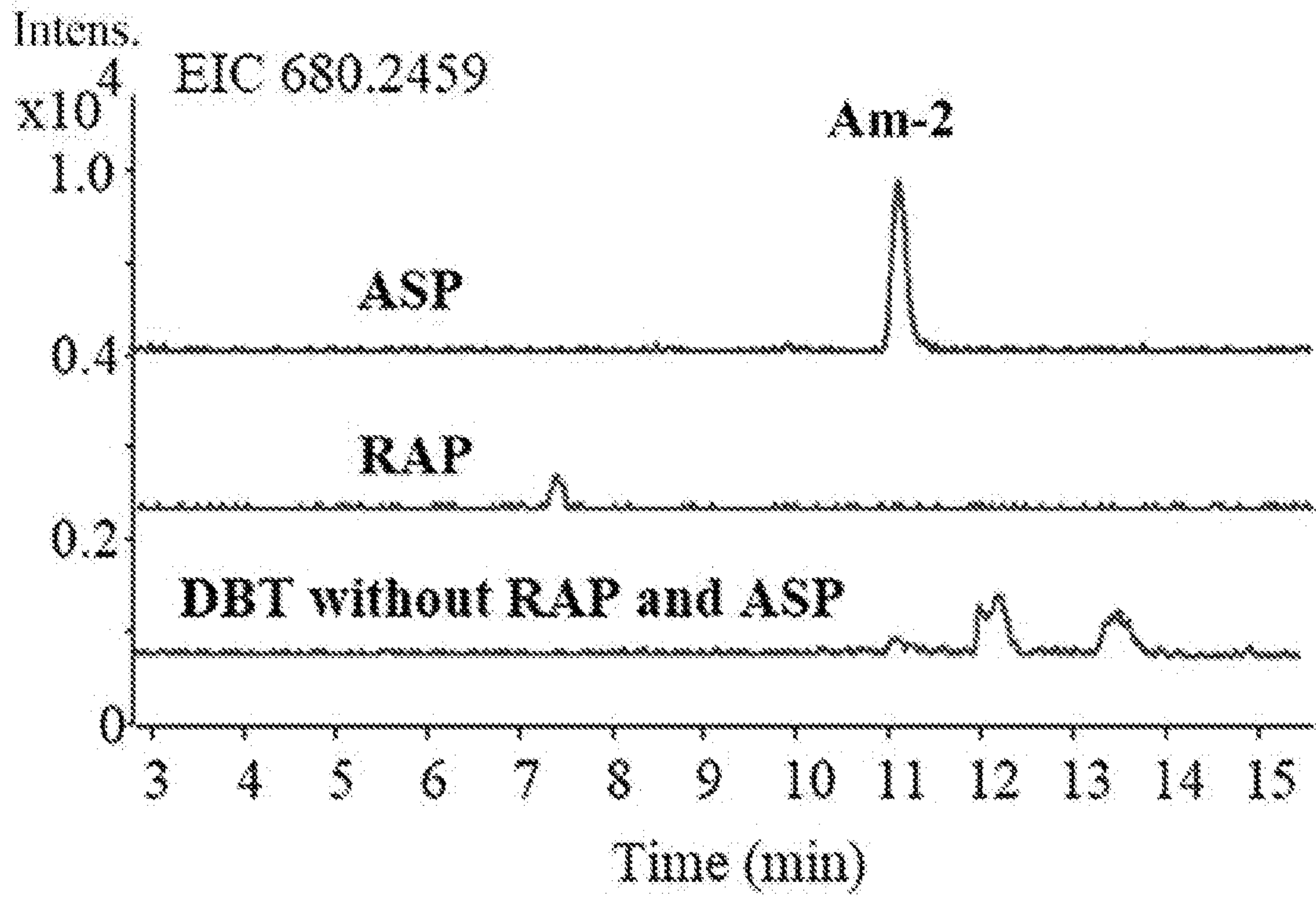


FIG. 20F

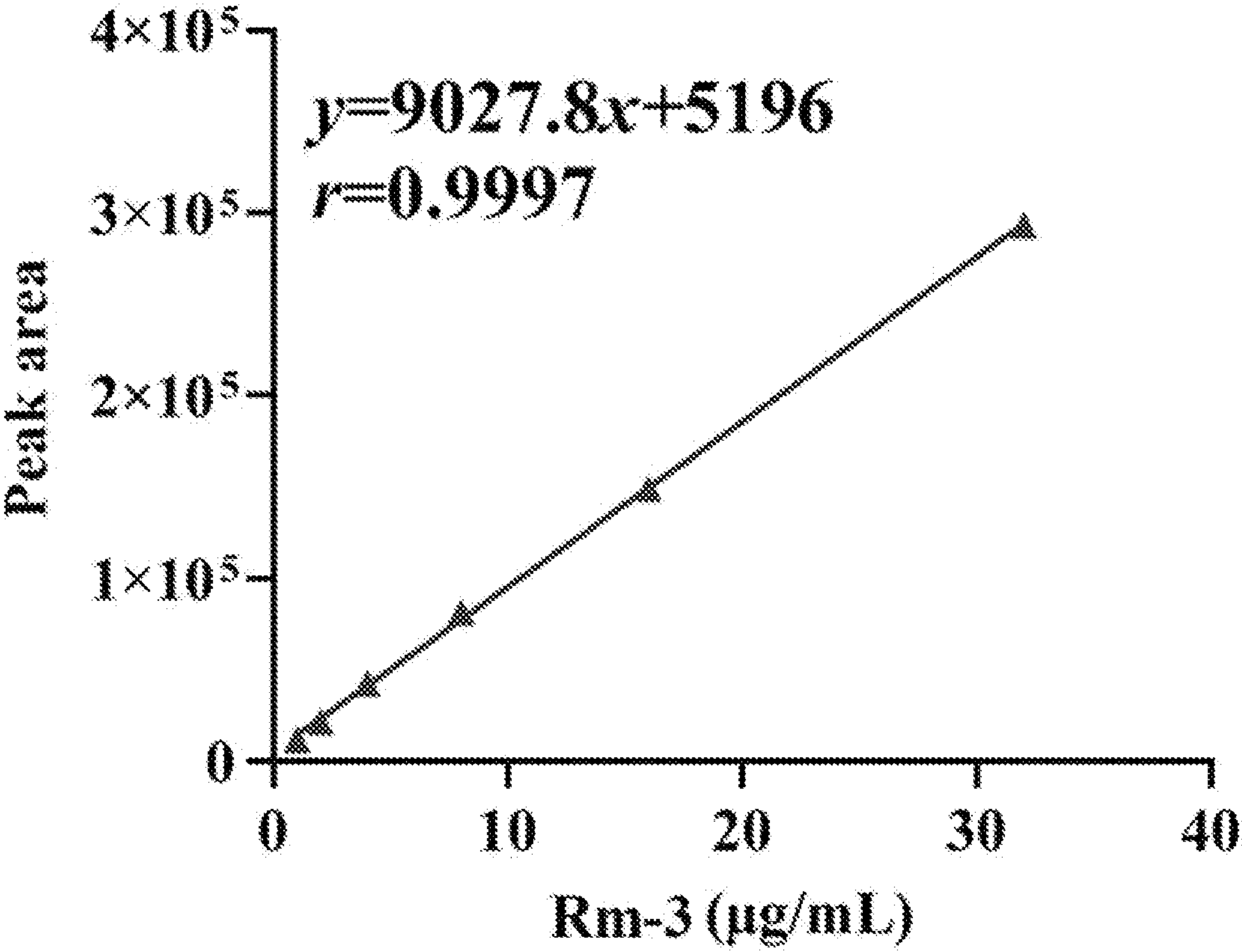


FIG. 21A

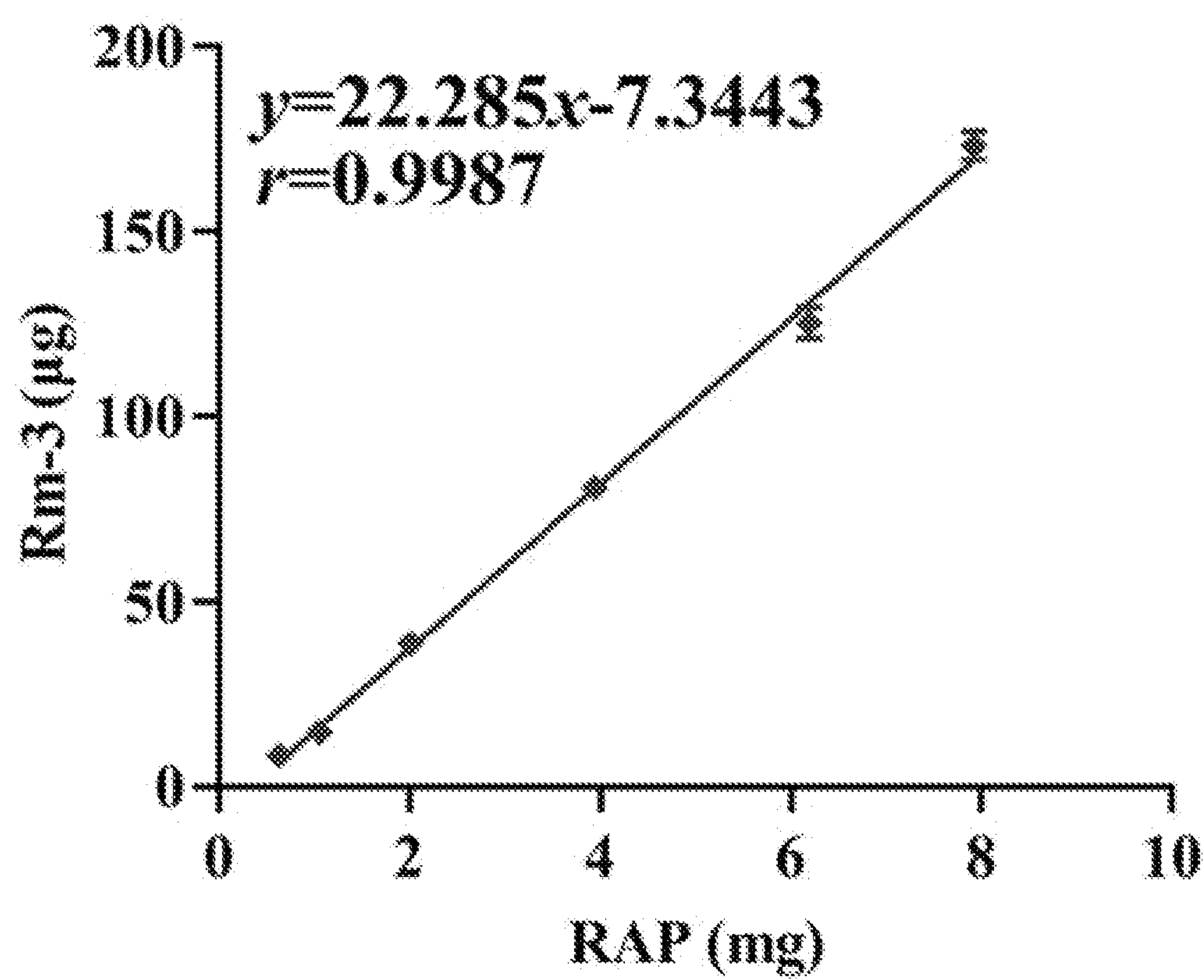


FIG. 21B

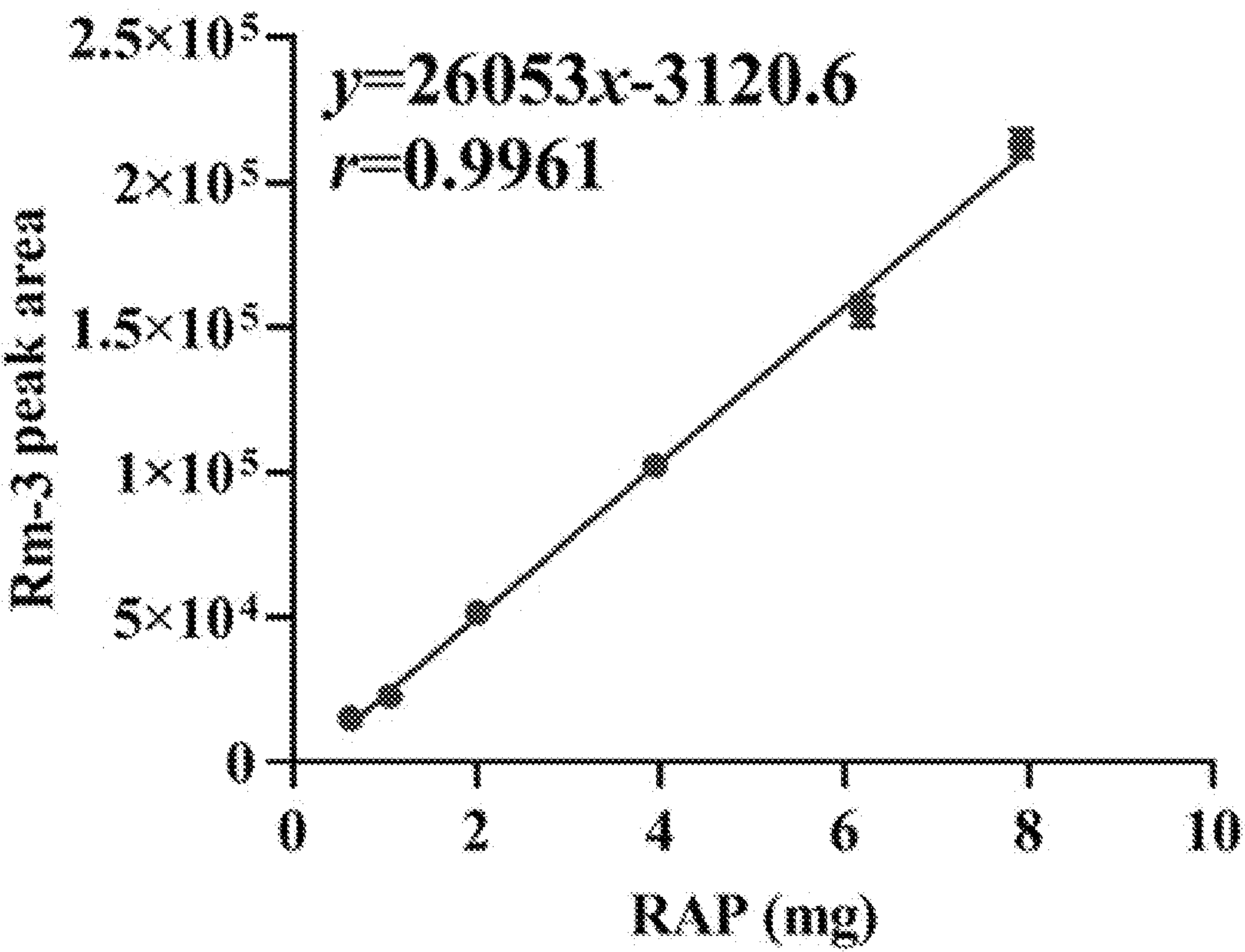


FIG. 21C

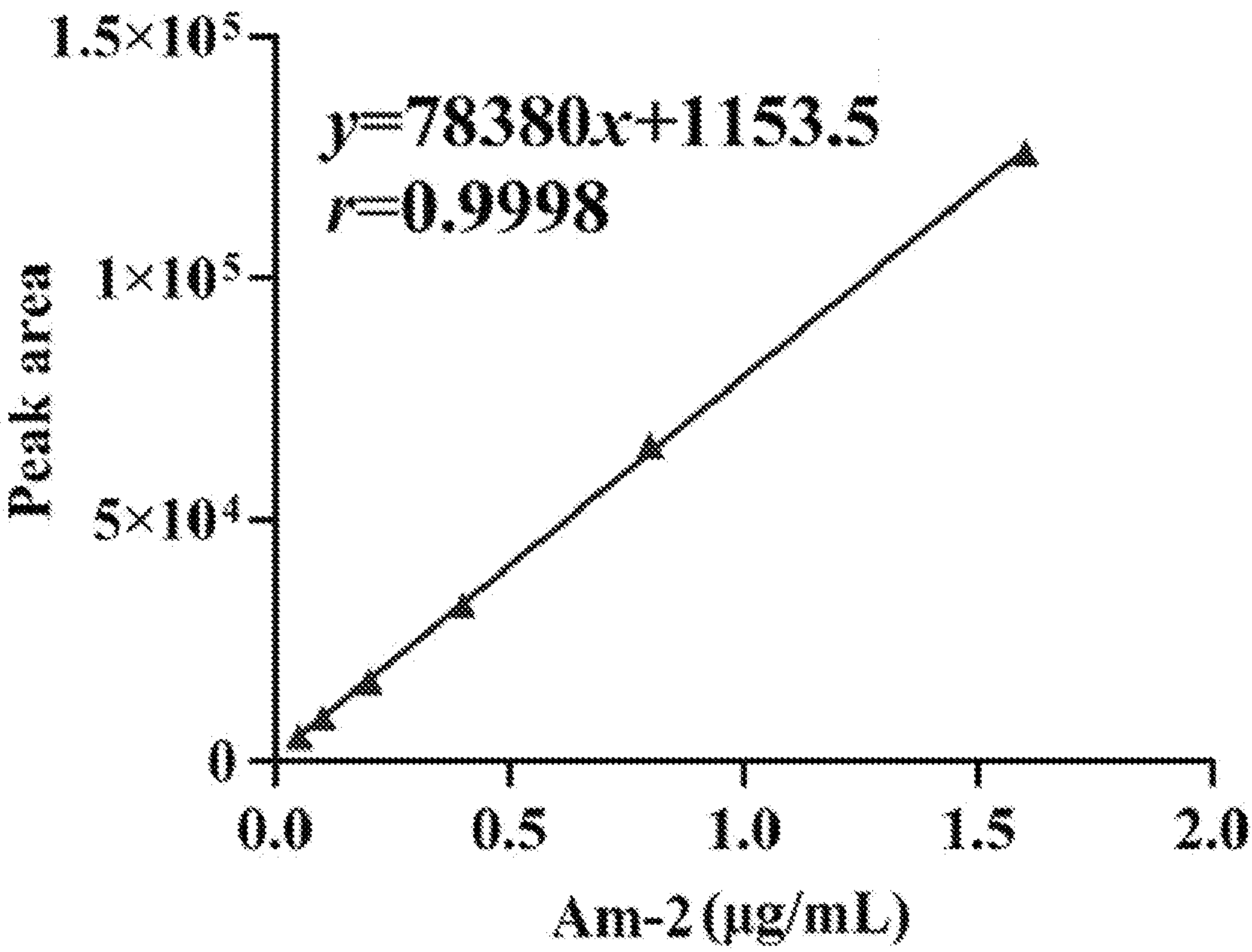


FIG. 21D

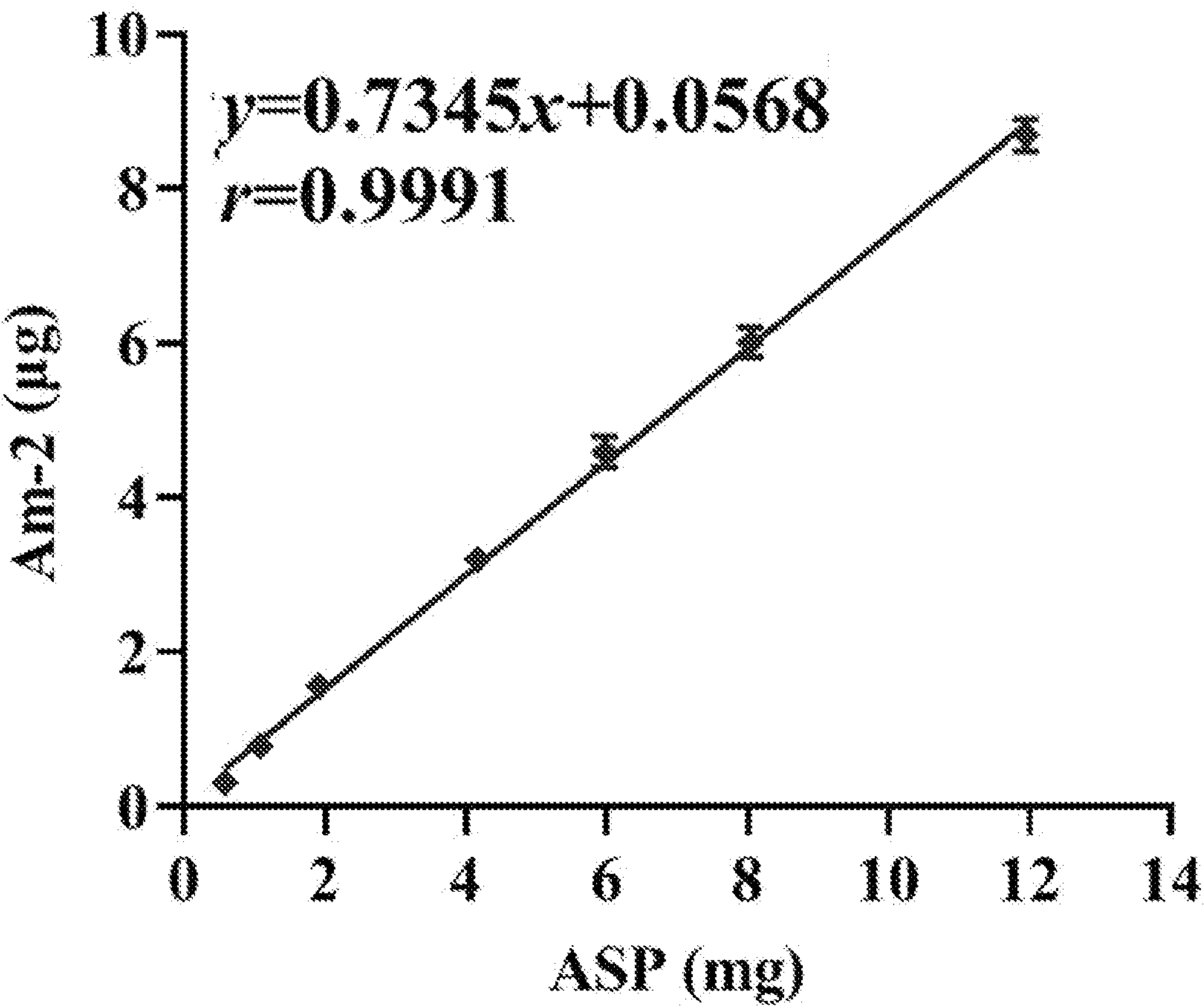


FIG. 21E

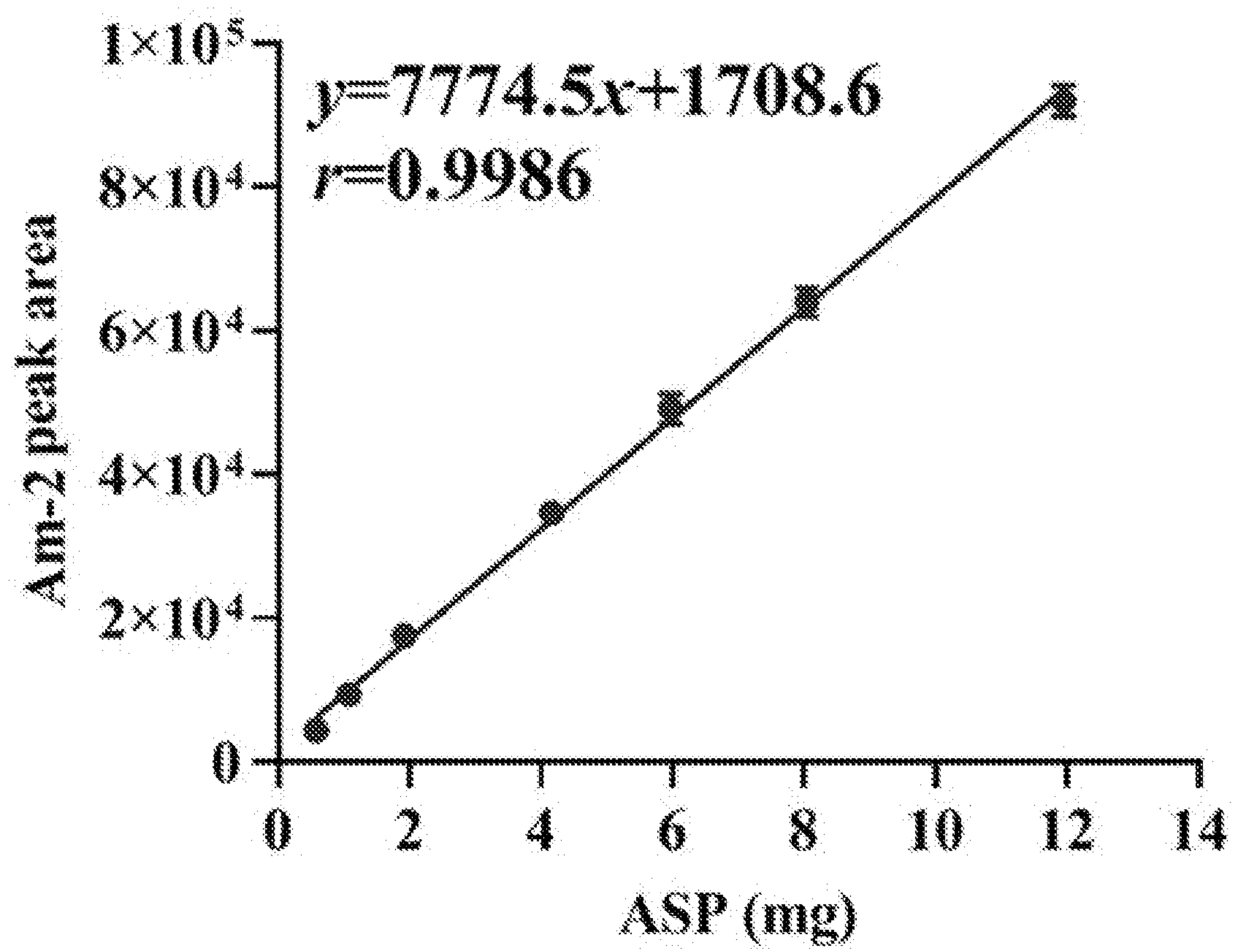


FIG. 21F

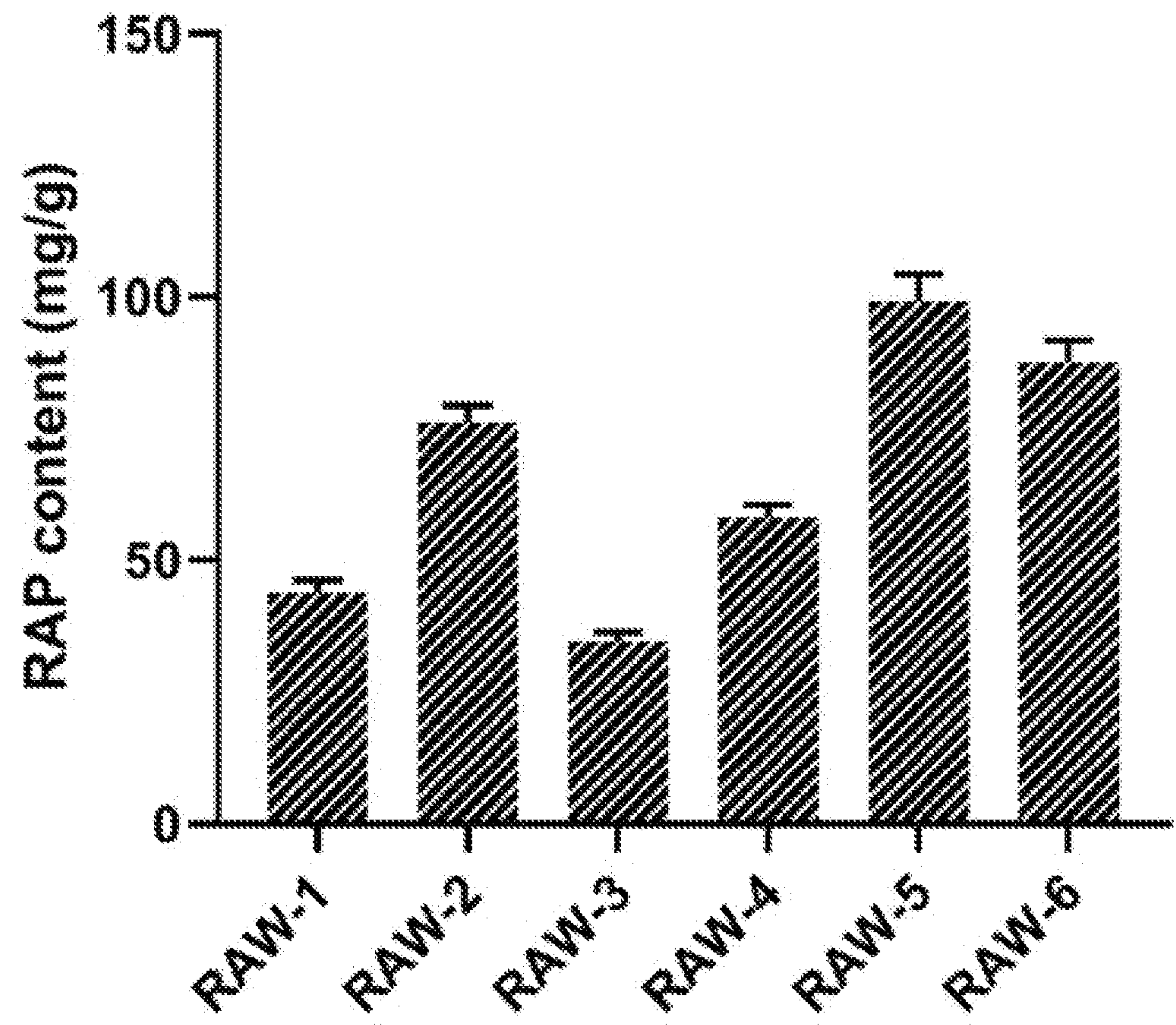


FIG. 22A

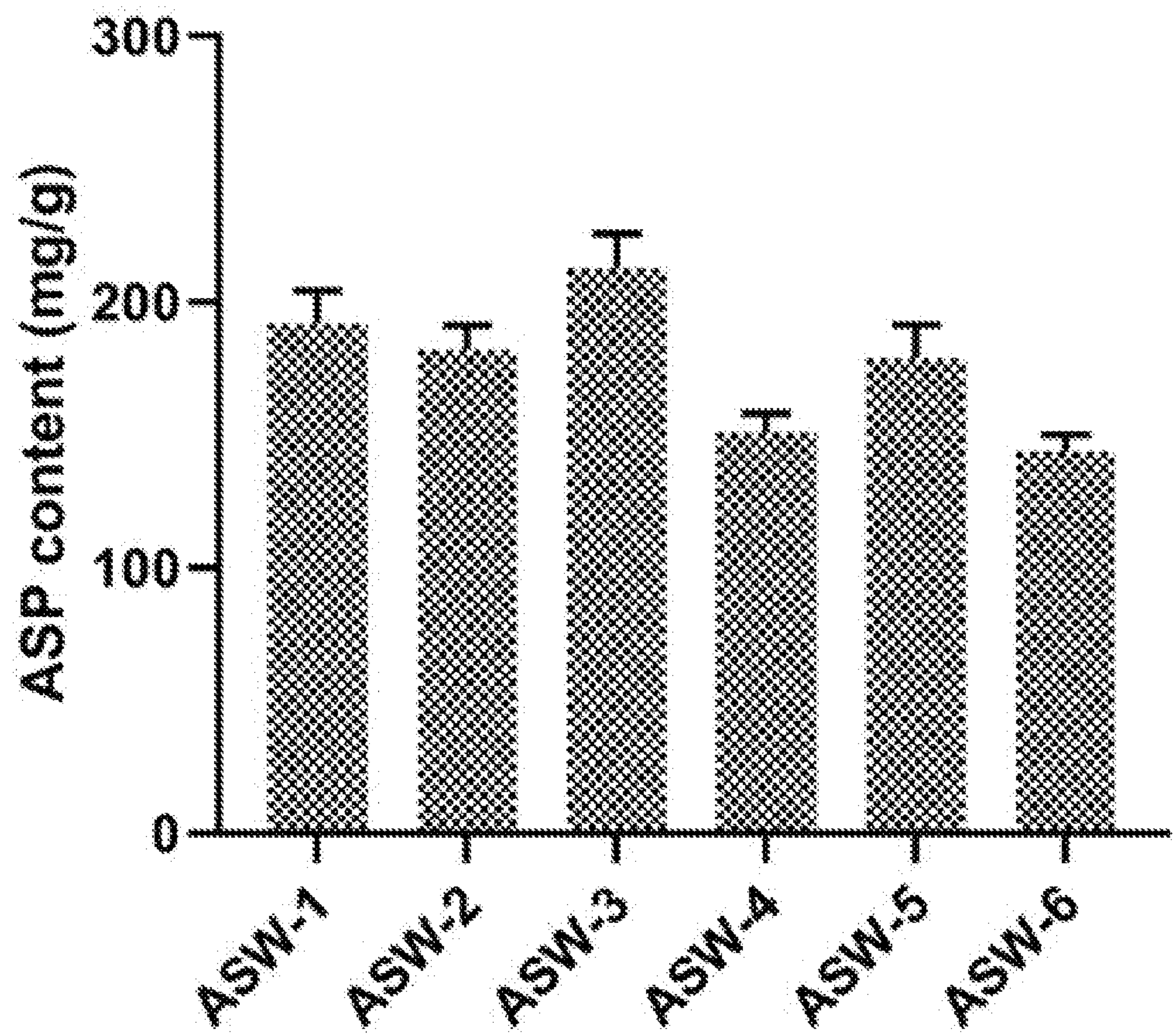


FIG. 22B

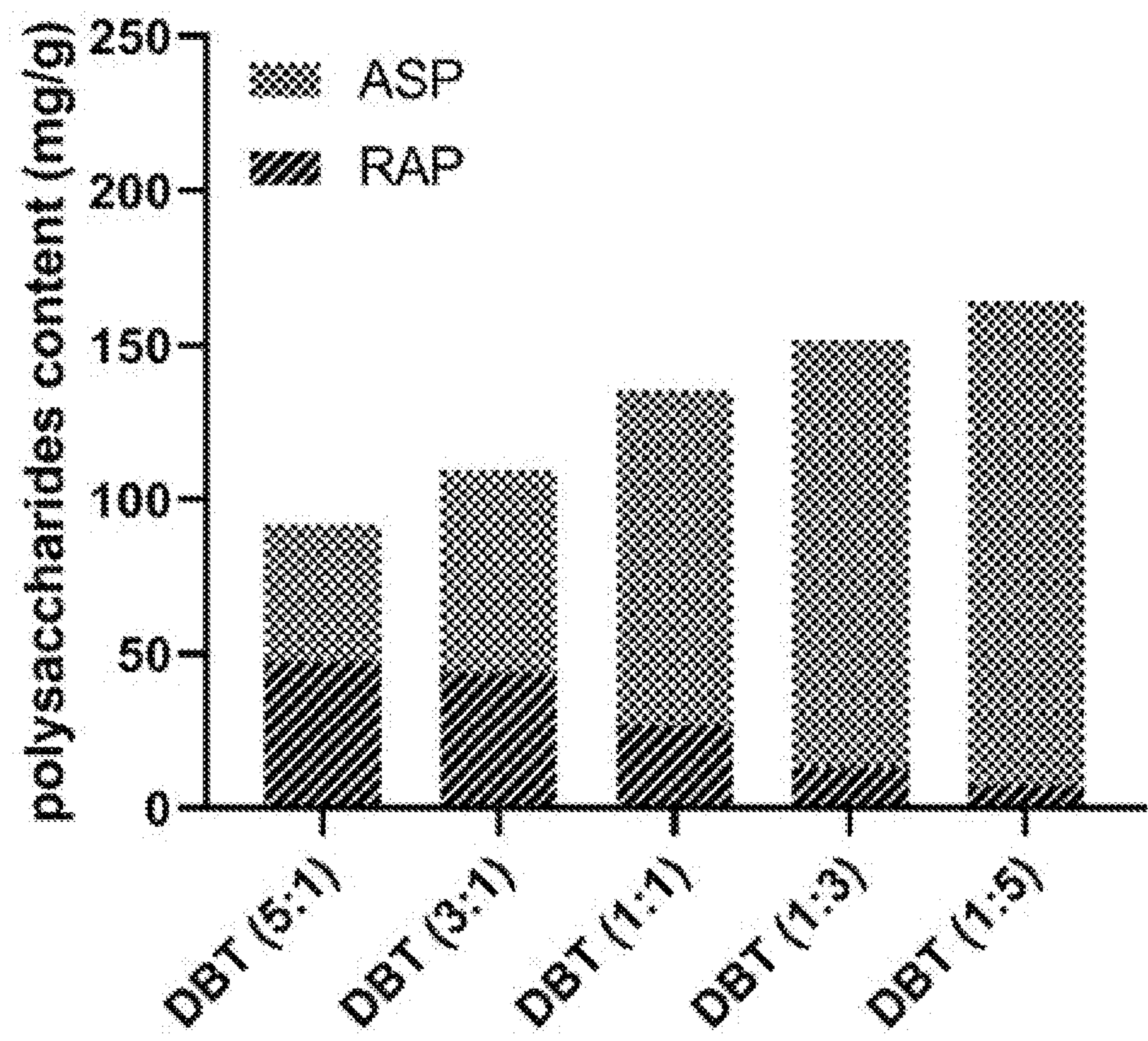


FIG. 22C

Table 1

Sample code	Locality	Type	Molecular weight ^a	Sugar content ^b	DOP
HGR-D1	Yunna, China	Dry powdered	750kDa	72.05%	261.29
HGR-D2	Yunna, China	Dry powdered	770kDa	72.94%	459.51
HGR-D3	Yunna, China	Dry powdered	790kDa	72.79%	220.11
TFC-T1	Guangdong, China	Fresh pulp	800kDa	67.91%	161.47
TFC-T2	Guangdong, China	Fresh pulp	770kDa	71.10%	236.61
TFC-B1	Zhejiang, China	Fresh pulp	770kDa	75.44%	120.99
DOP standard	NA	NA	770kDa	92.65%	NA

FIG. 23

Table 2

Oligosaccharide	Mass		Error	DP	Monosaccharides composition		Residue linkage Peak area percentage	
	Observed	Calculated	(ppm)		Man	Glu	T-Manp	1,4-linked-Manp
Di-Man-ABEE	490.1880	490.193	-10.2	2	96.76	3.24	NA	NA
Tri-Man-ABEE	652.2444	652.2458	-2.15	3	95.23	4.77	43.36	56.64
Te-Man-ABEE	814.2974	814.2986	-1.47	4	96.91	3.09	29.39	70.61
Pen-Man-ABEE	976.3520	976.3515	0.51	5	96.71	3.29	26.57	73.43
Hex-Man-ABEE	1138.3909	1138.4043	-11.77	6	96.4	3.6	20.54	79.46
Hept-Man-ABEE	1300.4585	1300.4571	1.08	7	97.15	2.85	16.91	83.09
Oct-Man-ABEE	1462.5226	1462.5099	8.68	8	97.83	2.17	13.69	86.31
Nona-Man-ABEE	1624.4835	1624.4628	12.7	9	96.89	3.11	NA	NA
Deca-Man-ABEE	1787.6407	1787.6156	14.0	10	97.60	2.40	NA	NA

FIG. 24

Table 3

Saccharide	Chemical shift (¹ H/ ¹³ C, in ppm)						
	1	2	3	4	5	6	7
Man	5.18/96.88	3.94/74.06	3.66/75.89	3.52/69.45	3.58/79.01	3.75,3.82/63.82	
Man-ABEE							
a (ABEE)	172.3	120.13	7.84/134.45	6.81/115.41	156.16	4.32/64.85	1.35/16.65
r Man	3.27,3.67/48.83	3.82/73.49	3.79/73.72	3.92/72.01	3.84/72.13	3.68,3.89/66.09	
Di-Man-ABEE							
a (ABEE)	172.16	120.19	7.80/134.27	6.76/115.27	156.06	4.28/64.45	1.34/16.36
i Man	4.77/102.81	4.11/71.59	3.67/75.82	3.50/70.04	3.40/78.82	3.56,3.89/64.39	
r Man	3.22,3.66/48.69	4.12/73.42	3.78/73.89	4.11/79.74	3.94/73.50	3.71,3.86/65.28	
Tri-Man-ABEE							
a (ABEE)	172.2	120.26	7.83/134.35	6.80/115.39	156.07	4.30/64.48	1.35/16.47
i Man	4.79/102.82	4.14/73.05	3.65/75.68	3.57/69.55	3.39/79.30	3.55,3.93/63.71	
ii Man	4.63/103.08	4.02/73.36	3.61/75.68	3.72/80.03	3.51/77.60	3.74/3.81/63.78	
r Man	3.22,3.69/48.68	4.13/71.46	3.78/74.18	4.11/80.05	3.94/73.48	3.68,3.85/65.35	

FIG. 25

Table 3 (Continued)

Saccharide	Chemical shift (¹ H/ ¹³ C, in ppm)						
	1	2	3	4	5	6	7
Man	5.18/96.88	3.94/74.06	3.66/75.89	3.52/69.45	3.58/79.01	3.75,3.82/63.82	
Man-ABEE							
a (ABEE)	172.3	120.13	7.84/134.45	6.81/115.41	156.16	4.32/64.85	1.35/16.65
r Man	3.27,3.67/48.83	3.82/73.49	3.79/73.72	3.92/72.01	3.84/72.13	3.68,3.89/66.09	
Di-Man-ABEE							
a (ABEE)	172.16	120.19	7.80/134.27	6.76/115.27	156.06	4.28/64.45	1.34/16.36
i Man	4.77/102.81	4.11/71.59	3.67/75.82	3.50/70.04	3.40/78.82	3.56,3.89/64.39	
r Man	3.22,3.66/48.69	4.12/73.42	3.78/73.89	4.11/79.74	3.94/73.50	3.71,3.86/65.28	
Tri-Man-ABEE							
a (ABEE)	172.2	120.26	7.83/134.35	6.80/115.39	156.07	4.30/64.48	1.35/16.47
i Man	4.79/102.82	4.14/73.05	3.65/75.68	3.57/69.55	3.39/79.30	3.55,3.93/63.71	
ii Man	4.63/103.08	4.02/73.36	3.61/75.68	3.72/80.03	3.51/77.60	3.74/3.81/63.78	
r Man	3.22,3.69/48.68	4.13/71.46	3.78/74.18	4.11/80.05	3.94/73.48	3.68,3.85/65.35	

FIG. 25 (Continued)

Table 3 (Continued)

Saccharide	Chemical shift (¹ H/ ¹³ C, in ppm)						
	1	2	3	4	5	6	7
Te-Man-AB EE							
a (ABEE)	172.18	120.23	7.83/134. 36	6.79/115. 38	156.06	4.31/64.51	1.35/16. 40
i Man	4.79/102.82	4.15/73. 02	3.65/75.7 4	3.58/69.6 3	3.45/79. 26	3.52,3.94/63 .69	
ii Man	4.73/103.05	4.08/72. 86	3.81/74.2 9	3.83/79.4 0	3.52/77. 71	3.75,3.90/63 .36	
iii Man	4.64/103.03	4.07/73. 21	3.78/74.1 3	3.72/79.9 1	3.50/77. 75	3.81,3.93/63 .42	
r Man	3.22,3.69/4 8.85	4.13/71. 53	3.78/74.1 3	4.09/79.9 3	3.94/73. 43	3.69,3.85/65 .39	
Pen-Man-A BEE							
a (ABEE)	172.01	122.52	7.89/134. 72	6.80/117. 19	153.98	4.31/65.00	1.35/16. 50
i Man	4.88/103.11	4.13/73. 08	3.64/76.0 4	3.57/69.9 3	3.44/79. 56	3.52,3.97/64 .06	
ii Man	4.74/103.34	4.06/73. 53	3.81/74.6 0	3.82/79.6 7	3.64/76. 04	~ 3.76/63.92	
iii Man	4.73/103.40	4.08/73. 53	3.76/74.3 9	3.81/79.7 1	3.52/78. 03	~ 3.76/63.92	
iv-Man	3.65/103.37	4.08/73. 06	3.76/74.4 7	3.71/80.1 7	3.50/78. 03	~ 3.76/63.92	
r Man	3.26,3.72/5 0.36	4.13/71. 44	3.78/74.4 4	4.07/80.0 4	3.92/73. 65	3.67,3.83/65 .64	

FIG. 25 (Continued)

Table 3 (Continued)

Saccharide	Chemical shift (¹ H/ ¹³ C, in ppm)						
	1	2	3	4	5	6	7
a (ABEE)	172.21	120.27	7.85/134.33	6.80/115.41	156.08	4.31/64.63	1.34/16.43
i Man	4.78/102.80	4.14/72.74	3.65/75.66	3.58/69.54	3.45/79.21	3.52,3.97/6~3.60	
ii Man	4.76/102.95	4.08/72.95	3.79/74.16	3.82/79.34	3.57/77.78	~3.76/63.92	
iii Man	4.74/103.00	4.08/72.95	3.79/74.16	3.82/79.34	3.57/77.78	~3.76/63.92	
iv Man	4.76/102.96	4.08/72.95	3.79/74.16	3.82/79.34	3.57/77.78	~3.76/63.92	
v Man	4.65/102.99	4.08/72.95	3.79/74.16	3.72/79.84	3.57/77.78	3.76/63.92	
r Man	3.22,3.69/48.59	4.13/71.47	3.79/74.16	4.08/79.91	3.94/73.34	3.68,3.85/65.27	
Hept-Man-ABEE							
a (ABEE)	172.22	120.27	7.86/134.35	6.82/115.41	156.08	4.32/64.55	1.37/16.36
i Man	4.78/102.78	4.13/72.72	3.65/75.88	3.58/69.67	3.45/79.26	3.52,4.02/63.43	
ii Man	4.76/103.01	4.08/73.09	3.80/74.34	3.83/79.33	3.56/77.92	~3.75/63.64	
iii Man	4.76/103.01	4.08/73.09	3.80/74.34	3.83/79.33	3.56/77.92	~3.75/63.64	
iv Man	4.76/103.01	4.08/73.09	3.80/74.34	3.83/79.33	3.56/77.92	~3.75/63.64	
v Man	4.76/103.01	4.08/73.09	3.80/74.34	3.83/79.33	3.56/77.92	~3.75/63.64	
vi Man	4.66/103.05	4.08/73.09	3.80/74.34	3.72/80.05	3.56/77.92	~3.75/63.64	
r Man	3.22,3.69/48.91	4.13/72.72	3.80/74.34	4.10/79.88	3.94/73.52	3.67,3.84/65.32	

FIG. 25 (Continued)

Table 3 (Continued)

Saccharide	Chemical shift (¹ H/ ¹³ C, in ppm)						
	1	2	3	4	5	6	7
a (ABEE)	172.2	120.26	7.83/134.35	6.80/115.39	156.07	4.30/64.48	1.35/16.47
i Man	4.79/102.83	4.15/72.86	3.66/75.76	3.59/69.61	3.46/79.25	3.53,4.06/63.14	
ii Man	4.75/103.00	4.08/73.19	3.80/74.28	3.83/79.39	3.58/77.91	~ 3.77/63.46	
iii Man	4.75/103.00	4.08/73.19	3.80/74.28	3.83/79.39	3.58/77.91	~ 3.77/63.46	
iv Man	4.75/103.00	4.08/73.19	3.80/74.28	3.83/79.39	3.58/77.91	~ 3.77/63.46	
v Man	4.75/103.00	4.08/73.19	3.80/74.28	3.83/79.39	3.58/77.91	~ 3.77/63.46	
vi Man	4.75/103.00	4.08/73.19	3.80/74.28	3.83/79.39	3.58/77.91	~ 3.77/63.46	
vii Man	4.66/103.03	4.08/73.19	3.80/74.28	3.73/79.84	3.58/77.91	~ 3.77/63.46	
r Man	3.23,3.70/48.83	4.15/71.56	3.80/74.28	4.09/79.95	3.94/73.32	3.70,3.86/65.34	

FIG. 25 (Continued)

Table 4

Oligosaccharide markers	Linearity	Equation	R ²
	Range (mg/mL)		
Te-Man-ABEE	0.34-8.01	y = 1164589x + 194721.9	0.997
Pen-Man-ABEE	0.34-8.01	y = 629621x + 172565	0.997

FIG. 26

Table 5

Analyte	Oligosaccharide markers	Repeatability (RSD, %)		Spike recovery % (RSD, n=3)		
		Intra-day (n=6)	Inter-day (n=3)	Low	Middle	High
<i>Dendrobium officinale</i> water extract	Te-Man-ABEE	2.31	4.49	93.30 (4.05)	117.86 (1.41)	104.79 (0.74)
	Pen-Man-ABEE	3.04	5.50	98.19 (0.83)	118.30 (2.80)	107.75 (0.87)
TVC	Te-Man-ABEE	4.76	6.67	102.24 (6.88)	100.05 (8.09)	91.41 (7.38)
	Pen-Man-ABEE	3.66	5.23	103.62 (7.94)	117.04 (4.40)	96.47 (5.39)
GD	Te-Man-ABEE	2.11	5.30	112.91 (5.16)	99.50 (5.19)	100.05 (3.79)
	Pen-Man-ABEE	2.14	6.91	109.20 (2.80)	97.71 (7.37)	98.99 (6.01)

FIG. 27

Table 6

Type	Conc. of <i>Dendrobium officinale</i> water extract (mg/g)						Conc. of TVC (mg/g)				Conc. Of GD (mg/g)
Analyte	HGR-D1	HGR-D2	HGR-D3	TFC-T1	TFC-T2	TFC-B1	1	2	3	4	1
Tc-Man-ABEE	245.12(1.32)	401.38(0.13)	208.00(0.28)	148.48(0.97)	205.78(0.30)	110.77(0.20)	0.20 (6.50)	0.28 (1.13)	0.28 (1.10)	0.28 (2.87)	32.55 (2.37)
Pen-Man-ABEE	248.98(0.78)	382.02(0.89)	198.13(0.61)	150.14(1.02)	213.63(1.92)	122.32(0.99)	0.19 (5.53)	0.29 (3.04)	0.29 (3.02)	0.28 (3.48)	31.88 (2.57)
RSD between two markers	1.11	3.5	3.44	0.79	2.65	7.01	3.72	1.36	0.55	1.47	1.48

FIG. 28

Table 7

Marker	Sugar Residues	Chemical shift						
		H-1/C-1	H-2/C-2	H-3/C-3	H-4/C-4	H-5/C-5	H-6/C-6	OCH ₃
Rm-1	B:4)- α -D-Glcp-(1-ABEE	3.41,3.36/	4.03/	3.99/	3.92/	3.94/	3.67,3.78/	/
		48.3	72.1	75.4	85.1	74	65.1	
	C: α -D-Glcp-(1	5.14/	3.62/	3.78/	3.46/	3.90/	3.81,3.88/	/
		103.4	74.5	75.8	72.3	75.4	63.3	
Rm-2	B:4)- α -D-Glcp-(1-ABEE	3.36,3.42/	4.02/	3.96/	3.90/	3.99/	3.64,3.73/	/
		48.4	72	75.6	85	74	65	
	C: 4)- α -D-Glcp-(1	5.13/	3.59/	4.01/	3.67/	3.93/	3.78,3.88/	/
		103.2	74.7	76.3	79.6	73.9	63.4	
Rm-3	D: α -D-Glcp-(1	5.41/	3.58/	3.72/	3.43/	3.96/	3.75,3.84/	/
		102.6	74.3	75.8	72.2	75.4	63.3	
	B:4)- α -D-Glcp-(1-ABEE	3.35,3.43/	4.04/	3.94/	3.90/	4.00/	3.65,3.73/	/
		48.4	72.1	75.6	85.1	73.9	65	
	C: 4)- α -D-Glcp-(1	5.13/	3.63/	3.94/	3.65/	3.92/	3.83/	/
		103.2	74.4	76.8	79.8	74.2	63.3	
	D: 4)- α -D-Glcp-(1	5.36/	3.63/	3.94/	3.65/	3.82/	3.83/	/
		102.7	74.4	76.8	80.1	74	63.3	
	E: α -D-Glcp-(1	5.36/	3.57/	3.69/	3.43/	3.94/	3.83/	/
		102.6	74.6	75.8	72.1	75.3	63.3	

FIG. 29

Table 7 (Continued)

Marker	Sugar Residues	Chemical shift							
		H-1/C-1	H-2/C-2	H-3/C-3	H-4/C-4	H-5/C-5	H-6/C-6	OCH ₃	
Am-1	B:6)-β-D-Galp-(1-ABEE	3.41/	4.14/	3.76/	3.70/	4.16/	3.73,3.98/	/	
		49.7	70.5	72.5	72.9	70.5	74.9		
	C:β-4-O-Me-D-GalAp-(1	4.51/	3.38/	3.60/	3.34/	3.92/	176.3	3.51/63.1	
		105.6	75.8	77.8	84.6	76.8			
	B:6)-β-D-Galp-(1-ABEE	3.44/	4.16/	3.75/	3.72/	4.17/	3.79,4.03/	/	
		49.6	70.5	72.5	72.9	71.6	74.9		
Am-2	C: 6)-β-D-Galp-(1	4.41/	3.57/	3.65/	3.95/	3.88/	3.88,4.01/	/	
		106.3	73.8	75.5	71.7	76.7	72.5		
	D: β-4-O-Me-D-	4.52/	3.38/	3.60/	3.35/	3.92/	176.3	3.51/	
	GalAp-(1	105.7	75.8	77.9	84.5	77			
	ABEE Residues	C-1'	H-2',6'	H-3',5'	C-4'	C-7'	H-8'/C-8'	H-9'/C-9'	
			/C-2',6'	/C-3',5'					
Rm-1,	A: ABEE	155.8	6.76/	7.85/	120.1	172.1	4.31/	1.35/	
Rm-2,			114.9	134.5			64.5	16.5	
Rm-3									
Am-1,	A: ABEE	154.2	6.83/	7.85/	121.8	172.1	4.30/	1.35/	
Am-2			116.3	134.5			64.7	16.5	

FIG. 29 (Continued)

Table 8

PMAA	Linkage pattern	Molar ratio ^a	Ion fragmentation (m/z)
2,3,4,6-Me4-Glcp	1-linked Glcp	1	43,71,87, 101, 117, 129, 145, 161, 205
2,3,6-Me3-Glcp	1,4-linked Glcp	6	43, 71, 101, 113, 117,131, 143, 173, 233

FIG. 30

Table 9

Polysaccharide	Molecular weight ^a	Sugar content ^b	Uronic acid content ^c	Protein content ^d	Monosaccharide composition ^e
RAP	113±3 kDa	88.03±3.51%	4.21±0.21%	2.90±0.16%	Glc: GalA: Gal: Ara=94:2.8:2.5:1.0
ASP	136±5 kDa	66.3±1.46%	37.1±0.88%	4.65±0.28%	GalA: Gal: Glc: Ara=1.9:1.2:1.2:1.0

FIG. 31

Table 10

Polysaccharides	Analytes	Repeatability (RSD%)		LOQ ^d (μg/mL)	LOD ^d (μg/mL)	Spike recovery % (RSD% n=3)					
		Intra-day (n=6)	Inter-day (n=3)			Low	RSD	Middle	RSD	High	RSD
RAP	RAW ^a	4.81%	5.79%	0.5	0.25	96.2	3.62	86.7	6.36	84.9	5.21
	DBT ^b	4.21%	4.74%			87.2	5.44	83.3	4.98	86.2	3.24
ASP	ASW ^c	5.24%	7.39%	0.05	0.02	85.9	7.12	83.2	5.49	79.8	6.72
	DBT ^b	5.65%	8.31%			86.3	6.41	84.5	6.23	81.2	5.98

FIG. 32

Table 11

H-RAP	Peak No.	Rt (min)	m/z	H-ASP	H-DBTS
	1	11.63	490.1959	+	+
	2	11.07	652.249	+	+
	3	10.35	814.3058	+	+
	4	9.63	976.3611	+	+
	5	9.04	1138.411	-	+
	6	8.56	1300.463	-	+
	7*	8.23	1462.518	-	-
	8	7.99	1624.553	-	-
	9	7.26	892.8162 (²⁻)	-	-
H-ASP	Peak No.	Rt (min)	m/z	H-RAP	H-DBTS
	1	11.65	490.1959	+	+
	2#	11.03	680.2459	-	-
	3	10.73	518.1491	-	-
	4	10.26	814.3058	+	+
	5	9.48	976.3611	+	+
	6	8.95	652.249	-	+
	7	8.29	814.3027	-	-
	8	7.81	1138.421	-	-
	9	7.51	1300.475	-	-

FIG. 33