

## Supporting Information

### BREVISULCENAL-G, -H, and -I, POLYCYCLIC ETHER MARINE TOXINS FROM THE DINOFLAGELLATE *KARENIA BREVISULCATA*

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Table S1 NMR spectroscopic data (800 MHz, pyridine-*d*<sub>5</sub>) for brevisulcenal-H (**3**)

Table S2 NMR spectroscopic data (900 MHz, pyridine-*d*<sub>5</sub>) for brevisulcenal-I (**4**)

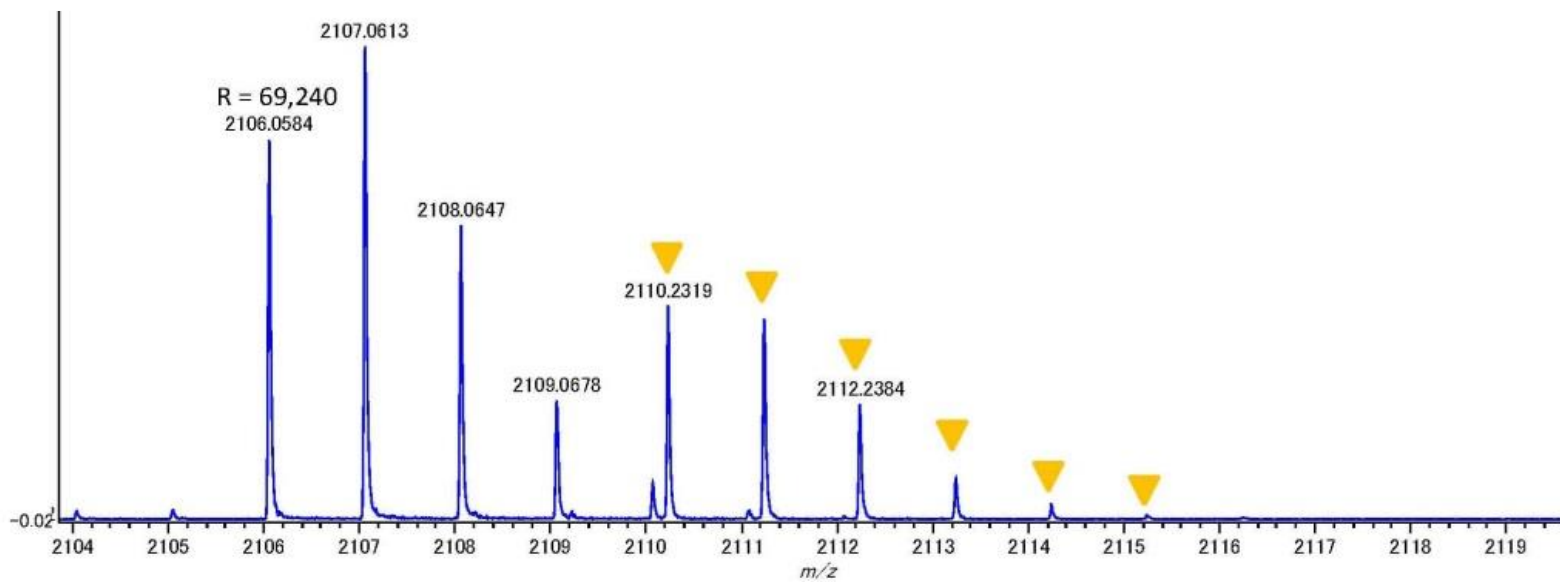


Figure S1. MALDI-TOF mass of KBT-G

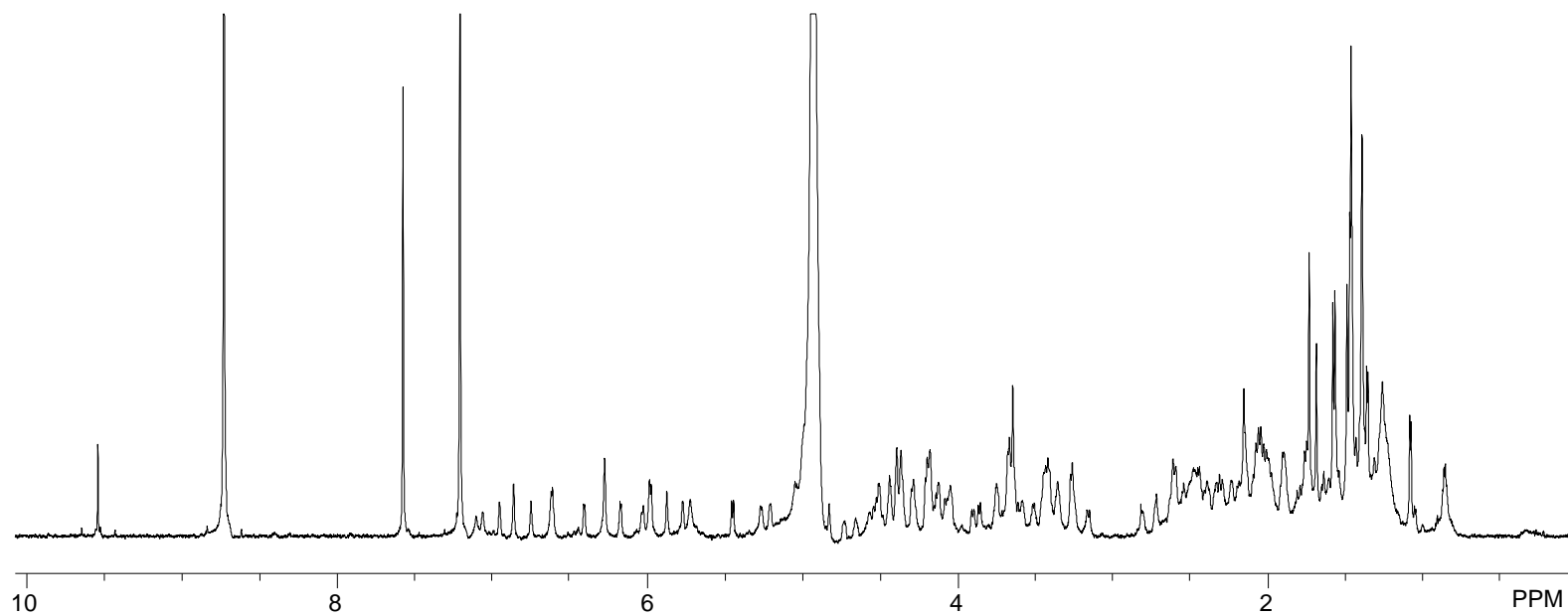


Figure S2.  $^1\text{H}$  NMR spectrum of KBT-G in  $\text{pyridine-}d_5$  (800 MHz)

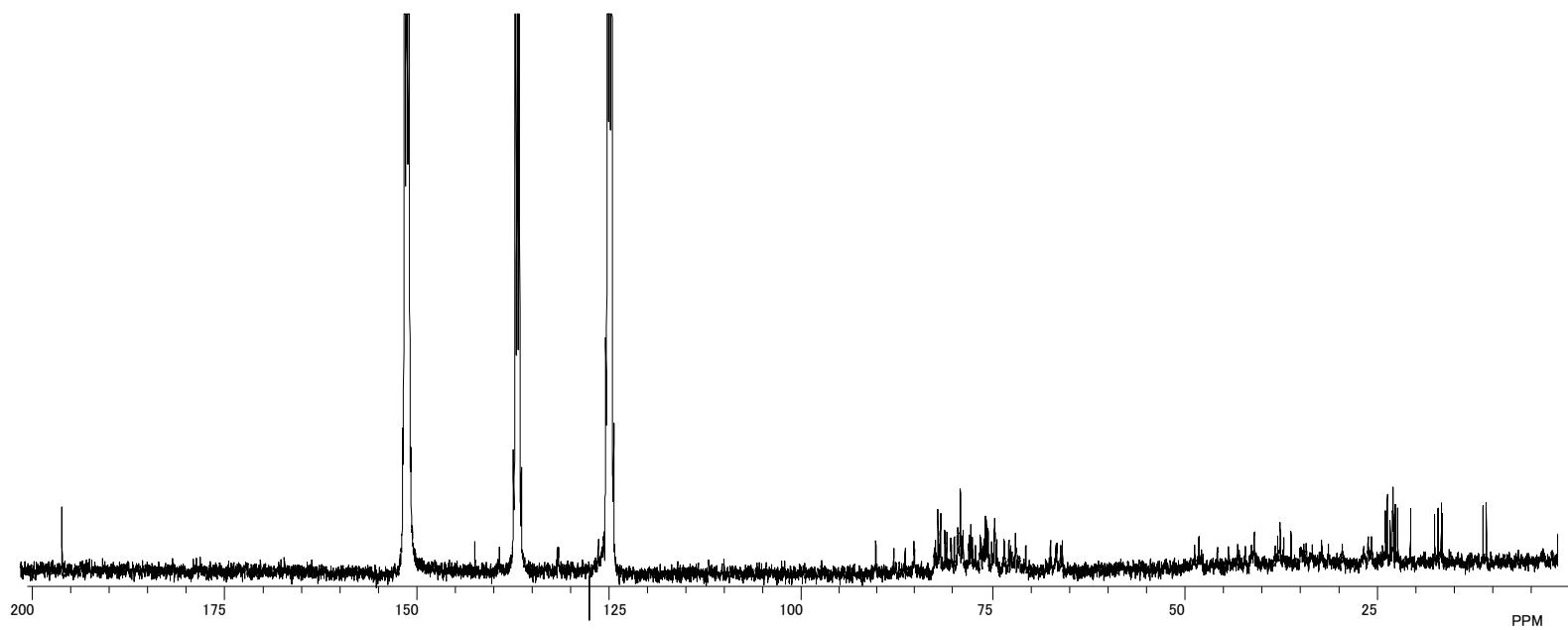


Figure S3.  $^{13}\text{C}$  NMR spectrum of KBT-G in  $\text{pyridine-}d_5$  (100 MHz).

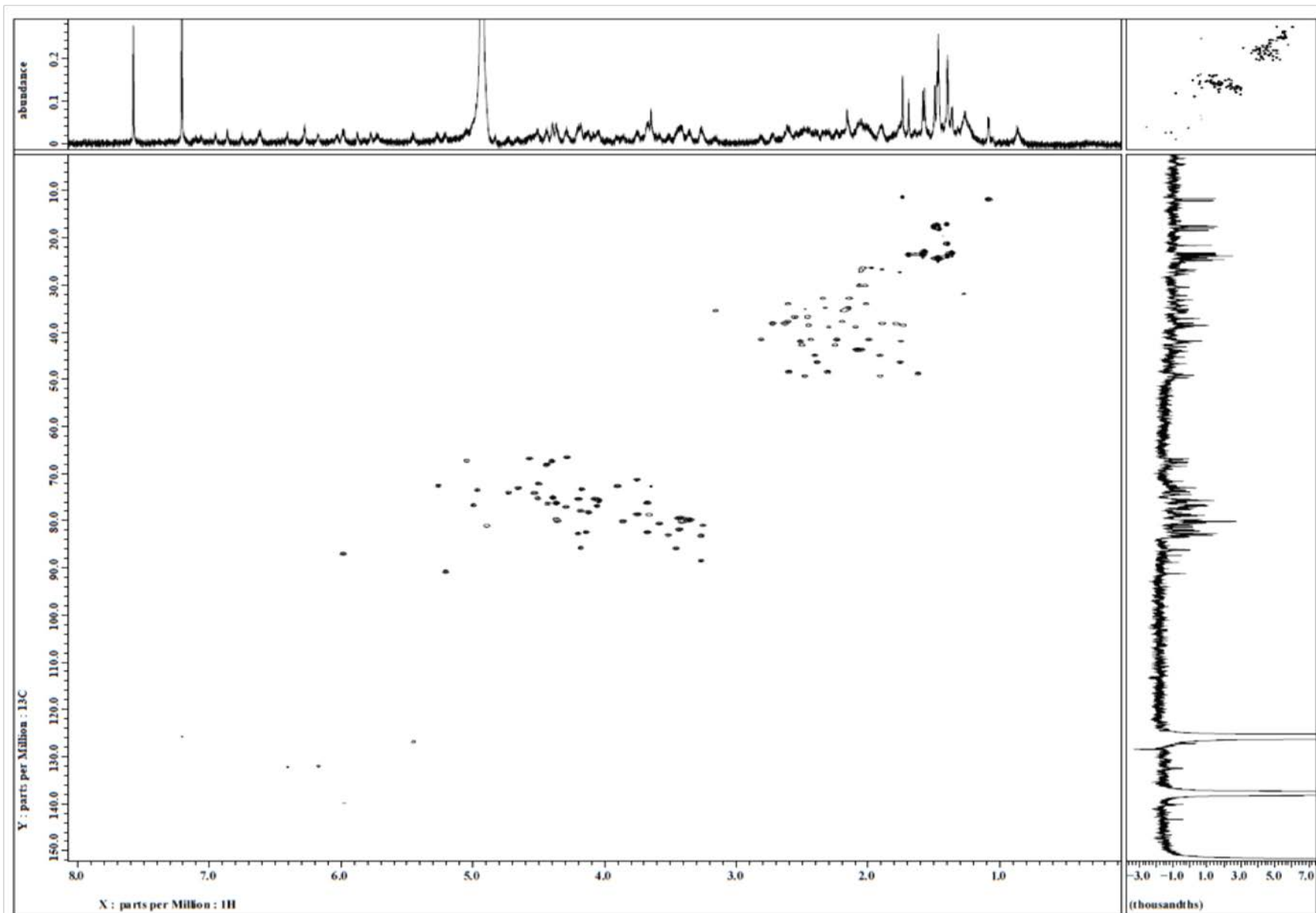


Figure S4. HSQC spectrum of KBT-G in pyridine- $d_5$  (800 MHz)

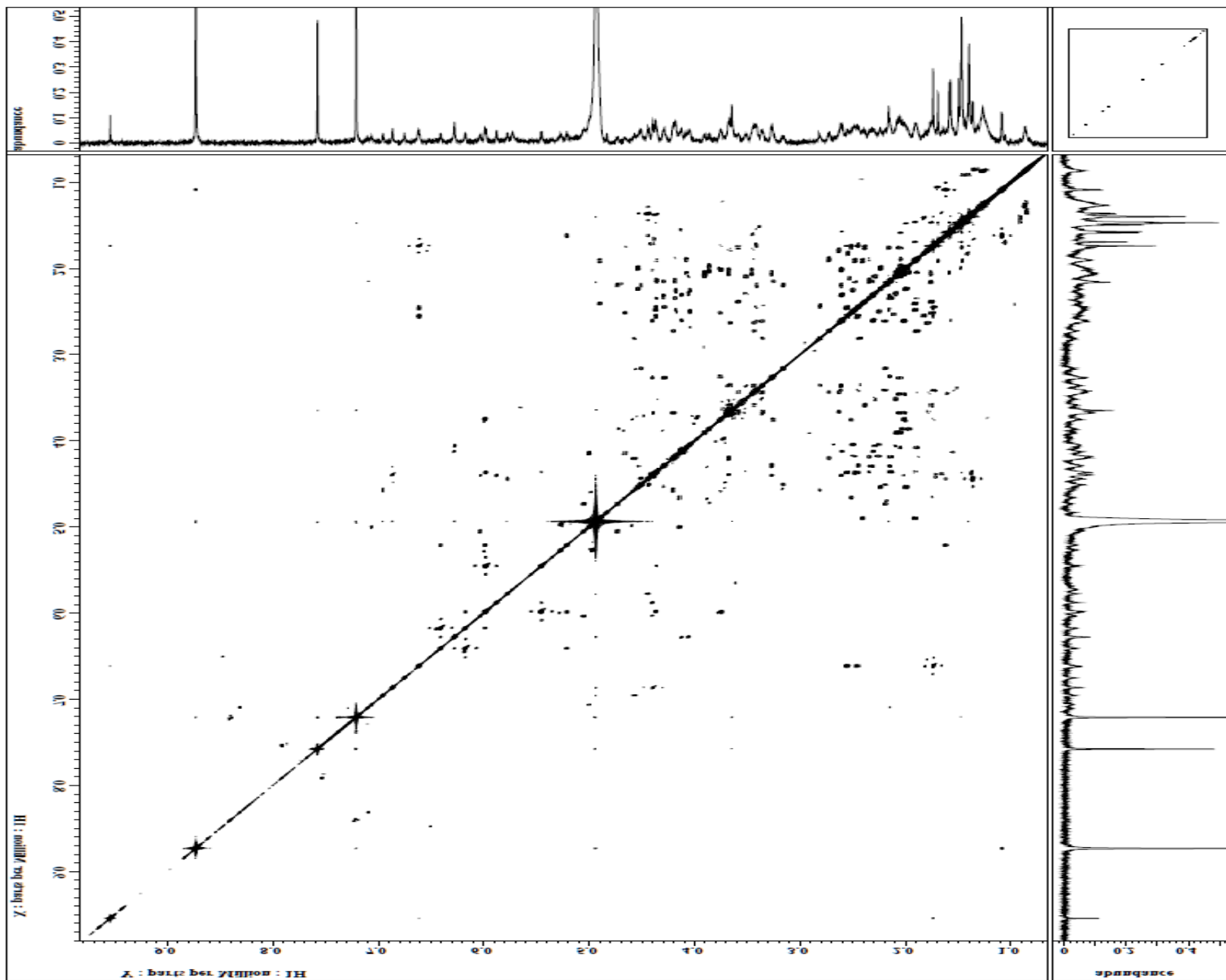


Figure S5.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of KBT-G in pyridine- $d_5$  (800 MHz)

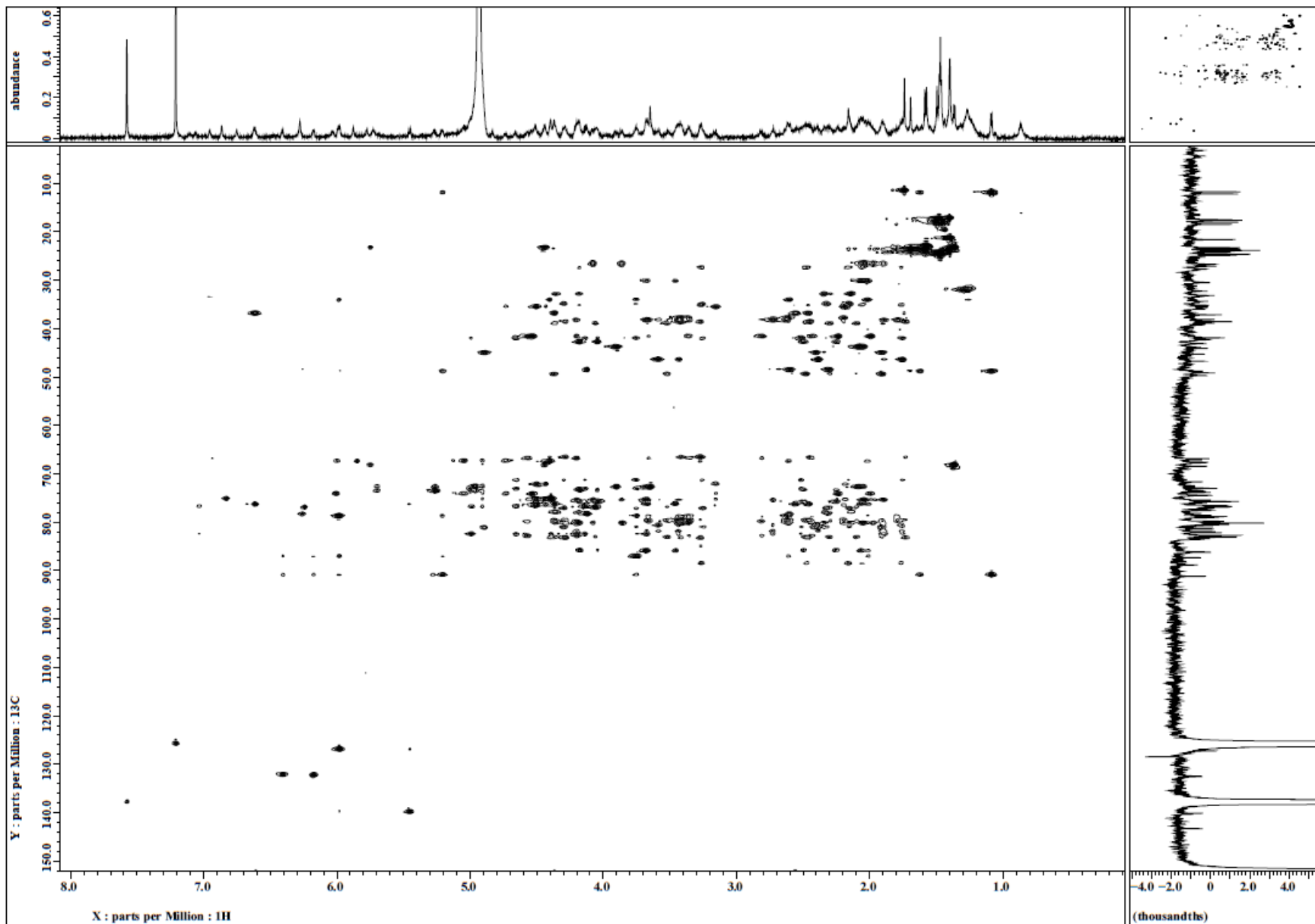


Figure S6. HSQC-TOCSY spectrum of KBT-G in pyridine- $d_5$  (800 MHz).

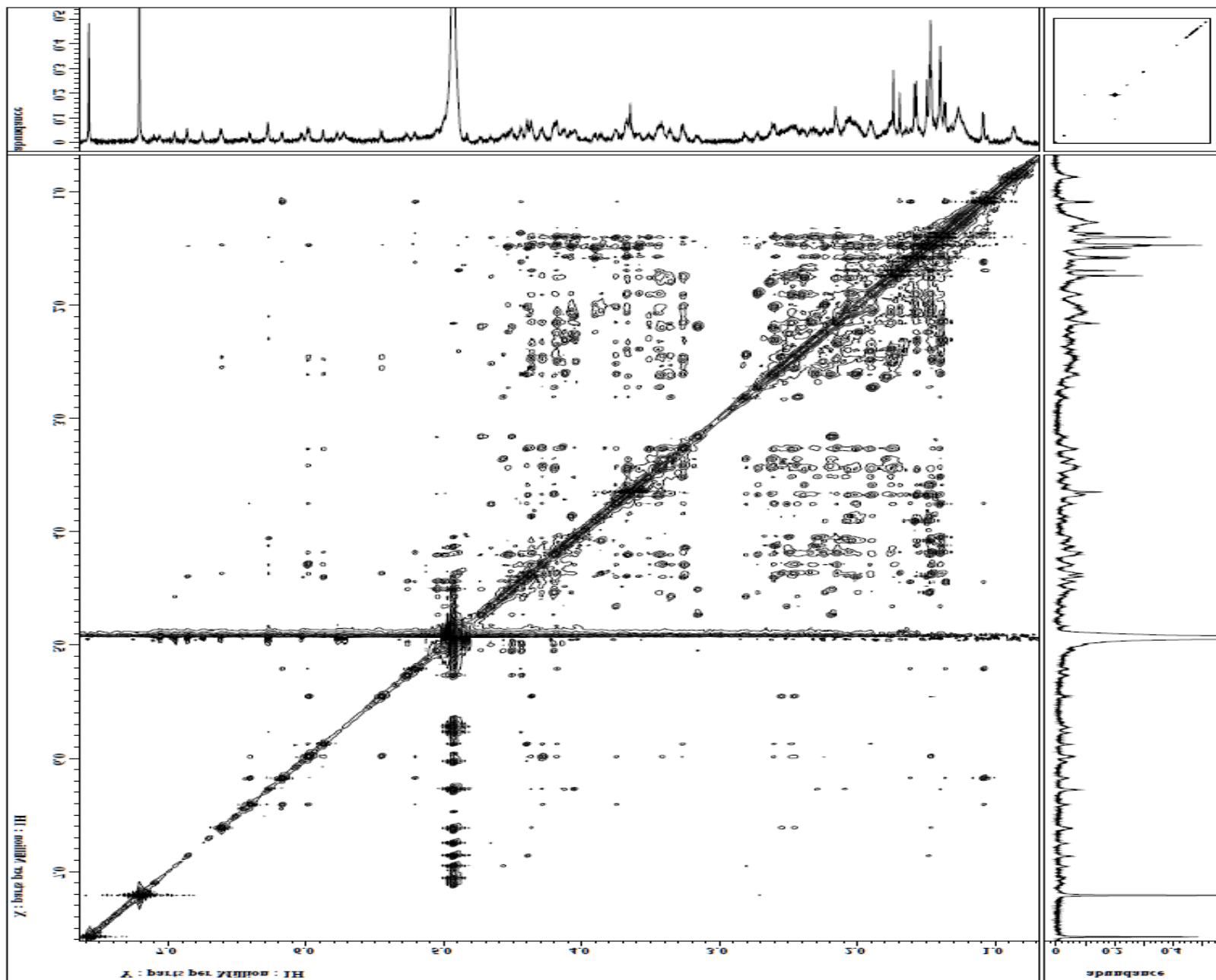


Figure S7. NOESY spectrum of KBT-G in pyridine-*d*<sub>5</sub> (800 MHz).

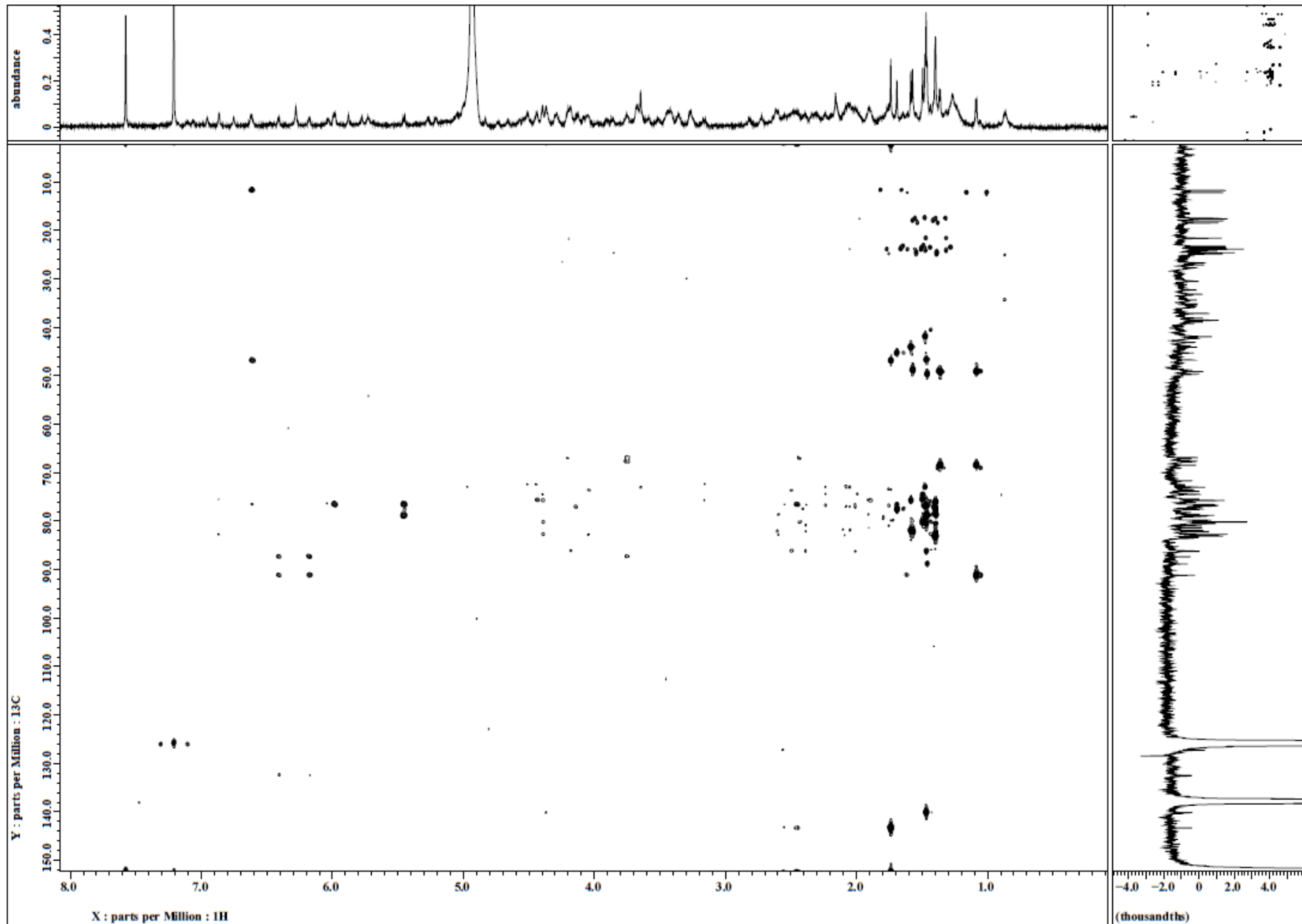


Figure S8. HMBC spectrum of KBT-G in pyridine- $d_5$  (800 MHz).

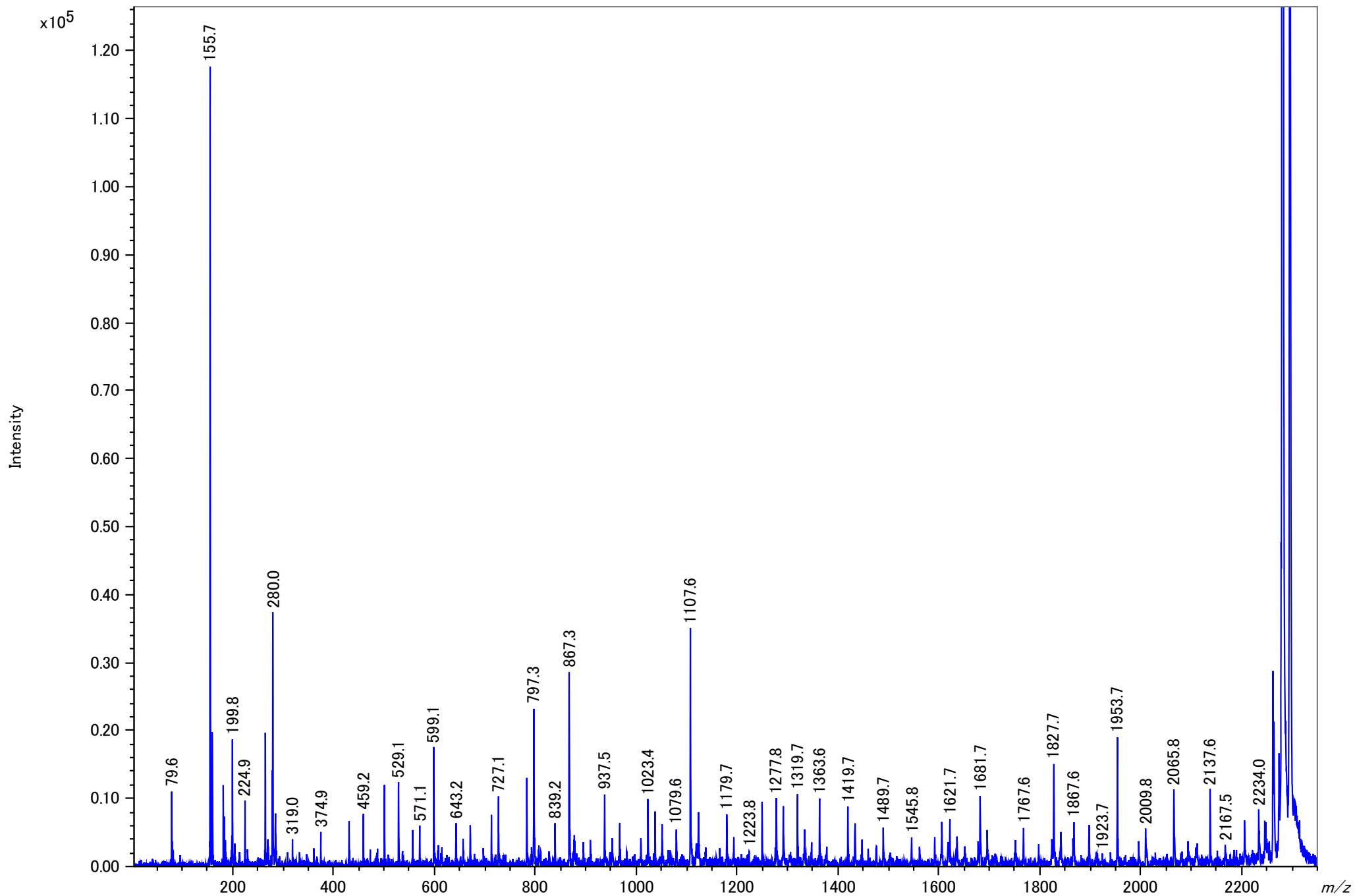


Figure S9. MS/MS of KBT-G hydrazine ( $m/z$  2280)

# $m/z$ 2092 (KBT-H)

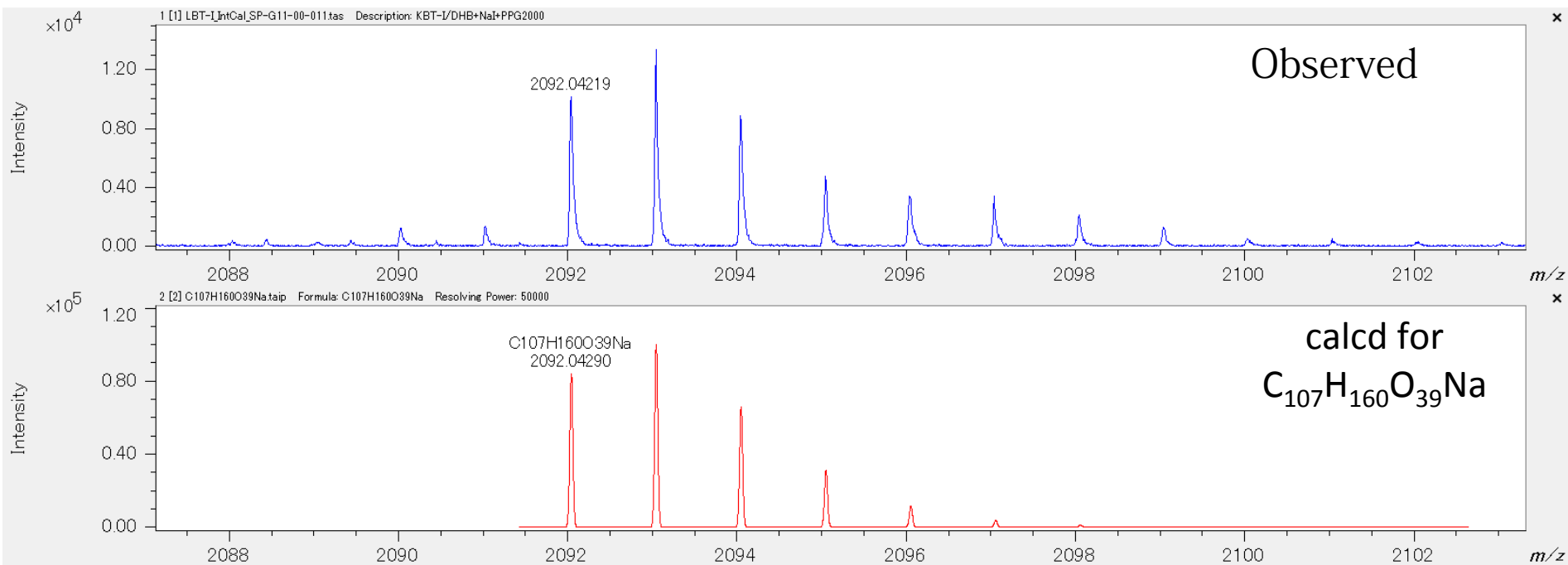


Figure S10. MALDI-TOF mass of KBT-H

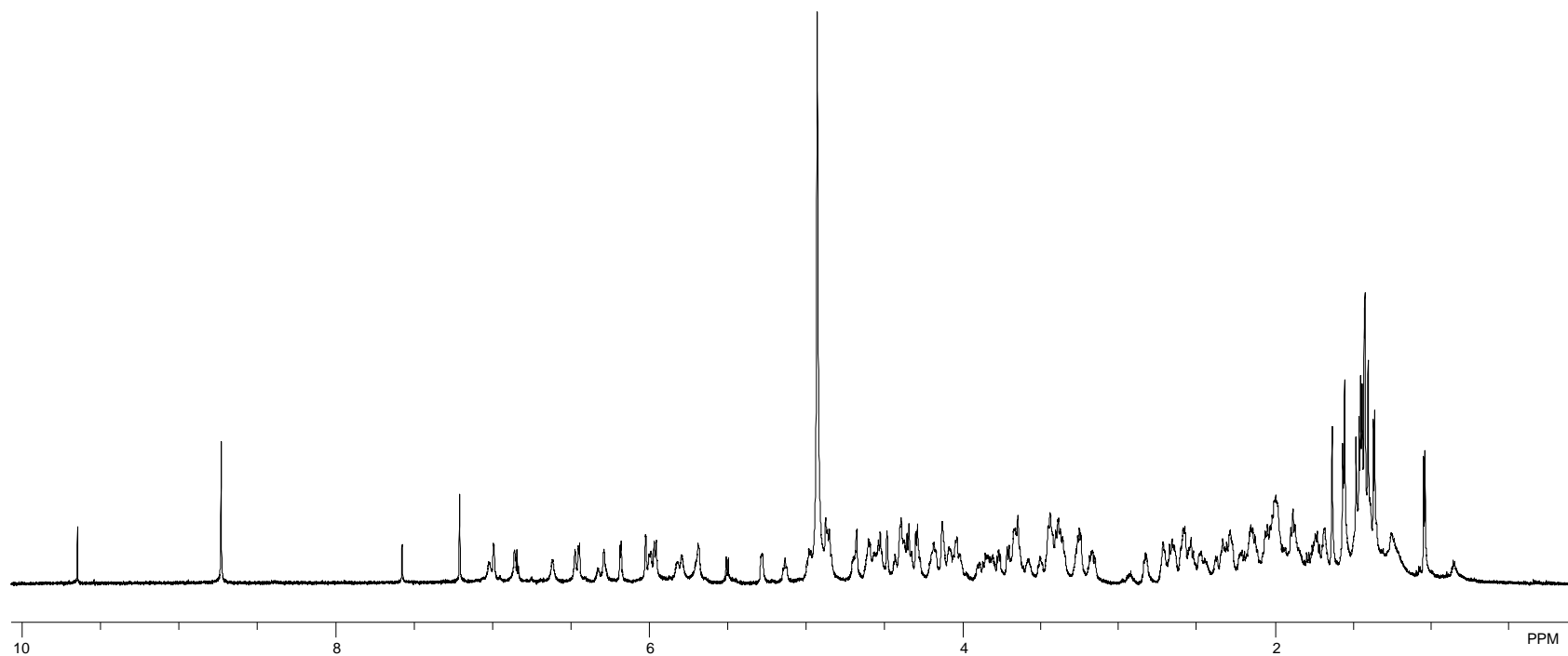


Figure S11.  $^1\text{H}$  NMR spectrum of KBT-H in pyridine- $d_5$  (800 MHz).

# $m/z$ 2122 (KBT-I)

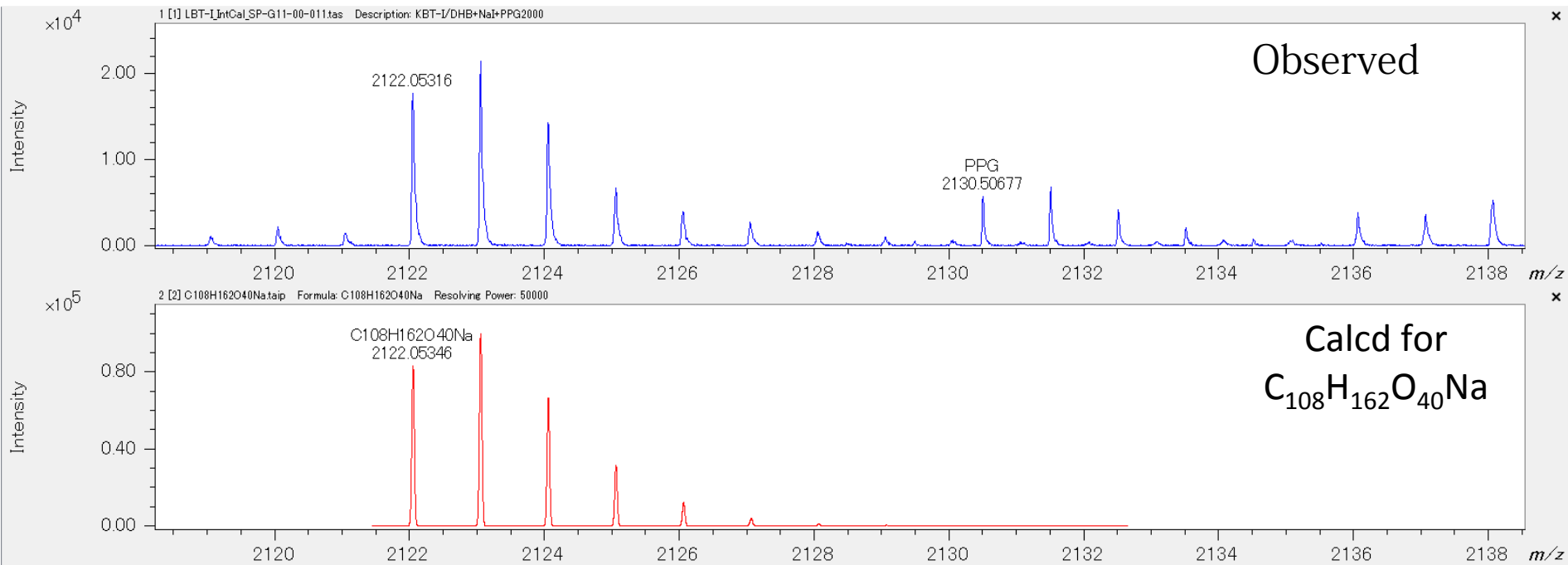


Figure S12. MALDI-TOF mass of KBT-I

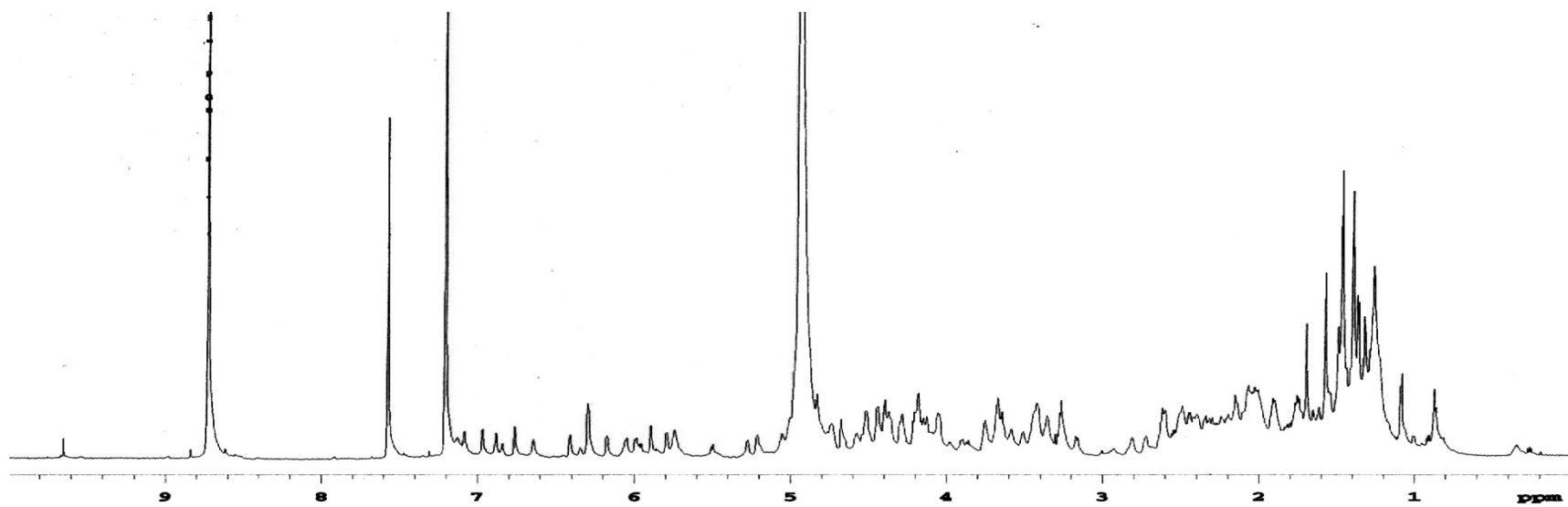


Figure S13.  $^1\text{H}$  NMR spectrum of KBT-I in  $\text{pyridine-}d_5$  (800 MHz).

**Table S1** NMR spectroscopic data (800 MHz, pyridine-*d*<sub>5</sub>) for brevisulcinal-H (**3**)

Pos.	$\delta_{\text{H}}$ (J in Hz)	$\delta_{\text{C}}$	Pos.	$\delta_{\text{H}}$ (J in Hz)	$\delta_{\text{C}}$	Pos.	$\delta_{\text{H}}$ (J in Hz)	$\delta_{\text{C}}$
1	9.64, s	196.6	36	4.13, m	78.6	71	5.13, m	67.6
2		147.4	37		82.9	72	4.35, m	82.3
3	6.61, dd (6,6)	152.0	38	4.33, m	80.5	73	4.61, m	67.3
4a	2.84, m	37.2	39a	2.14, m	33.1	74a	2.53, m	41.7
4b	2.94, m		39b	2.29, m		74b	2.83, m	
5	4.43, m	76.6	40	4.17, m	78.4	75	3.38, m	80.4
6	5.49, d (10)	127.3	41		82.7	76	3.81, m	78.8
7	5.96, dd (2,10)	140.1	42	4.04, m	75.9	77a	1.80, m	38.6
8		78.8	43a	2.29, m	42.2	77b	2.65, m	
9	3.85, d (10)	80.5	43b	2.68, m		78	3.50, m	79.6
10a	1.98, m	26.6	44	3.84, m	84.4	79	3.37, m	80.1
10b	2.04, m		45	4.09, m	86.4	80a	2.20, m	37.9
11a	1.88, m	27.1	46a	2.13, m	33.3	80b	2.58, m	
11b	2.04, m		46b	2.45, m		81	3.38, m	80.2
12	4.06, m	75.7	47a	1.95, m	30.4	82	3.45, m	79.7
13		81.9	47b	2.01, m		83a	1.73, m	39.0
14a	2.05, m	44.1	48	3.27, m	85.4	83b	2.49, m	
14b	2.08, m		49	3.26, m	85.2	84	4.28, m	66.9
15	3.90, d (10)	73.0	50a	1.89, m	42.6	85	3.25, m	83.5
16		76.9	50b	2.55, m		86	4.40, m	67.6
17a	1.99, m	41.9	51	3.44, m	82.2	87a	2.00, m	34.4
17b	2.24, m		52	3.18, m	82.7	87b	2.60, m	
18	4.52	74.5	53a	1.69, m	31.2	88	3.77, m	79.0
19		80.1	53b	1.86, m		89	5.99, m	87.4
20	4.39, m	75.5	54a	1.76, m	40.6	90	6.18, d (10)	132.3
21	3.68, m	82.7	54b	2.01, m		91	6.45, d (10)	132.9
22	4.20, m	75.7	55		80.2	92	5.28, m	91.2
23a	1.89, m	38.5	56	3.40, m	86.0	93	1.70, m	49.0
23b	2.73, m		57a	2.17, m	35.9	94	4.37, m	69.1
24	3.43, m	82.1	57b	2.34, m		95	1.37, d (7)	23.8
25	3.59, m	80.9	58	4.02, m	73.2	96	4.67, s	56.2
26a	1.75, m	46.7	59	3.72, m	75.8	97	1.46, s	24.7
26b	2.38, m		60	4.48, m	72.7	98	1.57, s	23.8
27		76.8	61	4.12, m	75.4	99	1.47, s	17.6
28	3.45, m	86.2	62	4.85, m	76.3	100	1.49, s	18.0
29a	2.01, m	30.5	63a	2.65, m	38.6	101	1.45, s	24.8
29b	2.06, m		63b	2.72, m		102	1.64, s	23.9
30	3.66, m	76.5	64	4.98, m	70.9	103	1.56, s	23.3
31		77.5	65	4.59, m	77.5	104	1.41, s	21.5
32a	1.89, m	45.3	66	4.29, m	77.0	105	1.44, s	24.6
32b	2.34, m		67	4.52, m	75.5	106	1.43, s	19.9
33	4.85, m	81.4	68	4.56, m	72.4	107	1.06, d (6)	12.4
34		82.1	69a	2.17, m	35.9			

35a	2.30, m	48.8	69b	3.16, m	
35b	2.60, m		70	4.69, m	74.5

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**Table S2** NMR spectroscopic data (800 MHz, pyridine-*d*<sub>5</sub>) for brevisulcinal-I (**4**)

Pos.	$\delta_{\text{H}}$ ( <i>J</i> in Hz)	$\delta_{\text{C}}^{\text{a}}$	Pos.	$\delta_{\text{H}}$ ( <i>J</i> in Hz)	$\delta_{\text{C}}^{\text{a}}$	Pos.	$\delta_{\text{H}}$ ( <i>J</i> in Hz)	$\delta_{\text{C}}^{\text{a}}$
1	9.64, s	196.6	36	4.12, m	78.3	71	5.05, m	67.1
2		147.4	37		82.7	72	4.21, m	82.6
3	6.61, dd (5,5)	152.0	38	4.35, m	80.0	73	4.57, m	66.8
4a	2.84, m	37.2	39a	2.14, m	32.8	74a	2.44, m	41.6
4b	2.94, m		39b	2.35, m		74b	2.83, m	
5	4.43, m	76.6	40	4.18, m	78.0	75	3.36, m	79.7
6	5.49, d (10)	127.3	41		82.7	76	3.66, m	78.6
7	5.96, dd (2,10)	140.1	42	4.05, m	75.6	77a	1.79, m	38.1
8		78.8	43a	2.25, m	42.8	77b	2.63, m	
9	3.85, d (10)	80.5	43b	2.50, m		78	3.42, m	79.5
10a	1.97, m	26.4	44	4.18, m	73.3	79	3.41, m	80.0
10b	2.04, m		45	4.18, m	85.6	80a	2.20, m	37.8
11a	1.90, m	26.7	46a	2.16, m	35.2	80b	2.61, m	
11b	2.05, m		46b	2.48, m		81	3.36, m	79.7
12	4.07, m	75.4	47a	1.76, m	27.2	82	3.42, m	79.5
13		81.4	47b	2.06, m		83a	1.74, m	38.4
14a	2.05, m	43.7	48	3.27, m	88.5	83b	2.46, m	
14b	2.08, m		49		78.3	84	4.28, m	66.6
15	3.90, d (10)	72.7	50a	1.91, m	49.3	85	3.27, m	83.3
16		76.4	50b	2.48, m		86	4.40, m	67.4
17a	2.00, m	41.6	51	4.37, m	79.7	87a	2.02, m	34.0
17b	2.24, m		52	3.52, m	83.0	87b	2.61, m	
18	4.53, m	74.2	53a	2.10, m	39.0	88	3.75, m	78.6
19		79.6	53b	2.30, m		89	5.98, m	87.1
20	4.39, m	75.1	54	4.06, m	76.8	90	6.17, d (5)	132.0
21	3.67, m	82.4	55		82.0	91	6.41, d (5)	132.3
22	4.20, m	75.4	56	4.29, m	77.1	92	5.21, m	90.9
23a	1.90, m	38.1	57a	2.16, m	34.9	93	1.62, m	48.7
23b	2.73, m		57b	2.33, m		94	4.44, m	68.0
24	3.43, m	81.8	58	3.25, m	80.9	95	1.37, d (7)	23.1
25	3.59, m	80.6	59	3.76, m	71.2	96	4.67, s	56.2
26a	1.76, m	46.3	60a	1.75, m	41.9	97	1.47, s	24.3
26b	2.39, m		60b	2.52, m		98	1.59, s	23.4
27		76.3	61	4.66, m	73.0	99	1.48, s	17.3
28	3.46, m	85.9	62	4.14, m	82.4	100	1.50, s	17.6
29a	2.02, m	30.2	63	4.99, m	76.8	101	1.47, s	24.3
29b	2.07, m		64	5.26, m	72.7	102	1.69, s	23.4
30	3.67, m	76.2	65	4.97, m	73.6	103	1.58, s	22.8
31		77.2	66	4.44, m	76.5	104	1.40, s	21.4
32a	1.91, m	44.8	67	4.50, m	75.4	105	1.40, s	23.7
32b	2.41, m		68	4.50, m	72.1	106	1.46, s	18.2

33	4.89, m	80.9	69a	2.19, m	35.5	107	1.41, d (6)	17.0
34		81.7	69b	3.16, m		108	1.09, s	11.7
35a	2.31, m	48.4	70	4.73, m	74.2			
35b	2.60, m							

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<sup>a</sup> <sup>13</sup>C chemical shifts were assigned using HSQC and HMBC spectra.