Grassypeptolides F and G, Cyanobacterial Peptides from *Lyngbya majuscula*

Wendy L. Popplewell,[†] *Ranjala Ratnayake,*[†] *Jennifer A. Wilson,*[†] *John A. Beutler,*[†] *Nancy H. Colburn,*[‡] *Curtis J. Henrich,*[†§] *James B. McMahon,*[†] *Tawnya C. McKee*[*,†]

[†]Molecular Targets Laboratory, Center for Cancer Research, NCI-Frederick, Frederick, Maryland 21702-1124

[‡]Laboratory of Cancer Prevention, Center for Cancer Research, NCI-Frederick, Frederick, Maryland 21702-1124

[§]SAIC-Frederick, Inc, NCI-Frederick, Frederick, Maryland 21702-1124

Contents		Page

Table S1. ^{15}N (60 MHz), ^{13}C (150 MHz) and ^{1}H (600 MHz) NMR data ($CDCl_3$) for grassypeptolide F (**1**).

Amino acids	pos.	δ_C or δ_N, mult.	$^1J_{CH}$ (Hz)	δ_H (J in Hz)	COSY	HMBC[a]	NOE
Maba	1	172.0, C					
	2	44.6, CH	132	2.49, qd (7.1, 3.3)	3, 5	1, 3, 4, 5, 53,[b] N-1	3
	3	48.6, CH	143	4.03, m	2, 4, N-1	1, 2, 4, 5, 6	2, 4, 5, N-1
	4	19.8, CH_3	127	1.06, d (6.7)	3	2, 3, N-1	3
	5	14.6, CH_3	129	0.96, d (6.9)	2	1, 2, 3	3
	N-1	117.7, NH		7.15, d (8.2)	3	2, 3, 6	3,7,8
Val	6	171.9, C					
	7	60.6, CH	141	4.36, dd (8.6, 6.4)	8, N-2	6, 8, 9, 10, 11, N-2	8, 9,10, N-1, N-2
	8	30.7, CH	130	2.25, m	7, 9, 10	6, 7, 9, 10, N-2	7, N-1, N-2
	9	19.6, CH_3	126	0.98, d (6.8)	8	7, 8, 10	7, 20, N-2
	10	18.7, CH_3	125	0.98, d (6.8)	8	7, 8, 9	7, 20, N-2
	N-2	115.8, NH		7.16, d (8.2)	7	7, 8, 11	7, 8, 9, 10
N-Me-Phe	11	169.7, C					
	12	58.5, CH	139	5.50, t (7.2)	13a, 13b	11, 13, 14, 20, 21, N-3	13a, 13b, 15/19, 20
	13	34.7, CH_2	129	3.44, m	12, 13b	11, 12, 14, 15/19, N-3	12, 13b, 15/19, 20
			126	2.94, m	12, 13a	11, 12, 14, 15/19	12, 13a, 15/19, 20
	14	137.6, C					
	15/19	129.5, CH	156	7.24, m	16/18	13, 15/19, 17	12, 13a, 13b, 20
	16/18	128.5, CH	154	7.13, t (6.6)	15/19, 17	14, 16/18	
	17	126.6, CH	159	7.13, t (6.6)	16/18	15/19	
	N-3	113.5,[c] N					
	20	31.6, CH_3	140	3.12, s		12, 21, N-3	9, 10, 12, 13a, 13b, 15/19, 22, 23a
Aba-thn-ca	21	169.9, C					
	22	77.6, CH	141	5.40, t (8.8)	23a, 23b, 25[d]	21, 23, 24	20, 23a, 23b
	23	33.4, CH_2	146	3.45, m	22, 23b	21, 22, 24	20, 22, 23b
			147	3.17, t (10.4)	22, 23a	21, 22, 24	22, 23a
	N-4	N[e]					
	24	178.5, C					
	25	54.1, CH	140	4.68, m	22,[d] 26a, 26b, N-5	24, 26, 27, 28	26, 27
	26	25.6, CH_2	126	2.17, m	25, 26b, 27	24, 25, 27, N-5	N-5
			127	1.98, m	25, 26a, 27	24, 25, 27, N-5	N-5
	27	10.8, CH_3	127	0.97, t (7.6)	26a, 26b	25, 26	25
	N-5	124.7, NH		7.64, d (8.0)	25	25, 26, 28	26a, 26b, 29, 30b
N-Me-Phe-thn-ca	28	171.2, C					
	29	79.4, CH	151	5.31, dd (7.3, 5.0)	30, 32[d]	28, 30, 31, N-5, N-6	30, N-5
	30	37.8, CH_2	146	3.70, m	29	28, 29, 31	29, N-5
	N-6	294.8,[c] N					
	31	177.3, C					
	32	69.0, CH	135	3.82, dd (10.6, 1.9)	29,[d] 33a, 33b	31, 33, 34, 40, 41	33b, 35/39, 40

	33	35.3, CH_2	127	3.59, dd (13.7, 10.8)	32, 33b	31, 32, 34, 35/39	33b, 35/39
			129	3.41, m	32, 33a	31, 32, 34, 35/39, N-7	32, 33a, 35/39
	34	138.2, C					
	35/39	129.9, CH	158	7.33, d (7.1)	36/38	33, 35/39, 37	32, 33a, 33b, 40
	36/38	128.9, CH	153	7.36, t (7.5)	35/39, 37	34, 36/38	
	37	126.9, CH	158	7.25, m	36/38	35/39	
	N-7	110.2,[c] N					
	40	39.4, CH_3	138	2.70, s		32, 41, N-7	32, 35/39, 42, 43
Pro	41	172.6, C					
	42	57.5, CH	146	4.75, dd (8.1, 5.4)	43	41, 43, 44, 45, 46	40, 43, 51
	43	27.2, CH_2	133	2.02, m	42, 44a, 44b	41, 42, 44, 45, N-8	40, 42, 45a, 45b
	44	25.3, CH_2	137	2.21, m	43, 44b, 45a, 45b	42, 43, 45, N-8	44b, 45a, 45b
			131	1.81, dquin (12.9, 7.1)	43, 44a, 45a, 45b	42, 43, 45, N-8	44a, 45b
	45	47.2, CH_2	147	3.50, dt (10.9, 7.3)	44a, 44b, 45b	42, 43, 44, 46	43, 44a, 45b, 47
			145	3.28, m	44a, 44b, 45a	42, 43, 44, 46	43, 44a, 44b, 45a, 47, 51
	N-8	137.2,[c] N					
N-Me-Val	46	166.9, C					
	47	61.4, CH	136	4.79, d (10.6)	48	46, 48, 49, 50, 51, 52, N-9	45a, 45b, 49, 50, 51
	48	26.6, CH	131	2.44, dsept (10.8, 6.4)	47, 49, 50	46, 47, 49, 50	51
	49	20.1, CH_3	126	0.91, d (6.3)	48	47, 48, 50	47, 51
	50	18.1, CH_3	125	0.72, d (6.9)	48	47, 48, 49	47, 51
	N-9	114.0,[c] N					
	51	30.8, CH_3	139	2.92, s		47, 52, N-9	42, 45b, 47, 48, 49, 50
Pla	52	171.2, C					
	53	70.4, CH	152	5.72, dd (8.6, 5.4)	54a, 54b	1, 52, 54, 55	54a, 54b, 56/60
	54	38.3, CH_2	129	3.03, dd (14.4, 8.7)	53, 54b	52, 53, 55, 56/60	53, 56/60
			126	2.93, m	53, 54a	52, 53, 55, 56/60	53, 56/60
	55	135.2, C					
	56/60	129.4, CH	155	7.20, d (7.1)	57/59	54, 56/60, 58	53, 54a, 54b
	57/59	128.8, CH	159	7.29, t (7.5)	56/60, 58	55, 57/59	
	58	127.5, CH	161	7.26, m	57/59	56/60	

[a]HMBC correlations, optimized for 8 Hz, are from proton(s) stated to the indicated carbon or nitrogen.
[b]Four bond HMBC correlation.
[c]Assigned from HMBC data.
[d]Homoallylic cosy correlation.
[e]Not observed.

Table S2. ^{13}C (150 MHz) and ^{1}H (600 MHz) NMR data (CD_3OD) for grassypeptolide F (**1**).

Amino acids	pos.	δ_C, mult.	δ_H (*J* in Hz)	COSY	HMBC[a]
Maba	1	172.8, C			
	2	45.5, CH	2.55, qd (7.0, 3.2)	3, 5	1, 3, 4, 5, 53[b]
	3	50.2, CH	4.02, m	2, 4, N-1	1, 2, 4, 5, 6
	4	20.1, CH_3	1.08, d (6.8)	3	2, 3
	5	15.0, CH_3	0.99, d (7.2)	2	1, 2, 3
	N-1	NH	7.72, d (7.3)	3	2, 3, 6
Val	6	174.3, C			
	7	62.1, CH	4.21, dd (8.3, 6.9)	8, N-2	6, 8, 9, 10, 11
	8	31.9, CH	2.23, oct (6.6)	7, 9, 10	6, 7, 9, 10
	9	20.2, CH_3	1.00, d (6.5)	8	7, 8, 10
	10	19.4, CH_3	1.05, d (6.8)	8	7, 8, 9
	N-2	NH	7.59, d (8.2)	7	7, 8, 11
N-Me-Phe	11	172.2, C			
	12	58.9, CH	5.55, m	13a, 13b	11, 13, 14, 20, 21
	13	34.8, CH_2	3.32, m	12, 13b	11, 12, 14, 15/19
			3.11, m	12, 13a	11, 12, 14, 15/19
	14	138.6, C			
	15/19	130.0, CH	7.22, d (7.8)	16/18	13, 15/19, 17
	16/18	129.7, CH	7.19, t (7.3)	15/19, 17	14, 16/18
	17	127.8, CH	7.17, t (6.9)	16/18	15/19
	N-3	N			
	20	31.7, CH_3	3.13, s		12, 21
Aba-thn-ca	21	172.2, C			
	22	77.9, CH	5.55, m	23a, 23b, 25[c]	21, 23, 24
	23	34.8, CH_2	3.29, m	22, 23b	21, 22, 24
			3.23, dd (10.7, 7.2)	22, 23a	21, 22, 24
	N-4	N			
	24	180.7, C			
	25	55.6, CH	4.57, m	22,[c] 26a, 26b, N-5	24, 26, 27, 28
	26	26.7, CH_2	2.19, m	25, 26b, 27	24, 25, 27
			2.10, m	25, 26a, 27	24, 25, 27
	27	11.4, CH_3	1.00, t (7.3)	26a, 26b	25, 26
	N-5	NH	7.92, d (7.9)	25	25, 26, 28
N-Me-Phe-thn-ca	28	173.4, C			
	29	80.2, CH	5.24, dt (10.4, 1.8)	30a, 30b, 32[c]	28, 30, 31
	30	37.9, CH_2	3.79, dd (11.6, 10.5)	29, 30b	28, 29
			3.61, dd (11.5, 2.1)	29, 30a	28, 29, 31
	N-6	N			
	31	180.5, C			

	32	69.5, CH	4.15, brd (10.5)	29,[c] 33a, 33b	31, 33, 34, 40
	33	36.3, CH_2	3.53, dd (13.5, 10.9)	32, 33b	31, 32, 34, 35
			3.39, dd (13.7, 3.6)	32, 33a	31, 32, 34, 35
	34	139.5, C			
	35/39	131.1, CH	7.40, d (7.7)	36/38	33, 35/39, 37
	36/38	129.7, CH	7.36, t (7.7)	35/39, 37	34, 36/38
	37	127.7, CH	7.26, m	36/38	35/39
	N-7	N			
	40	39.7, CH_3	2.73, s		32, 41
Pro	41	174.1, C			
	42	59.1, CH	4.79, dd (8.9, 4.6)	43a, 43b	41, 43, 44, 45, 46
	43	28.4, CH_2	2.18, m	42, 43b, 44a, 44b	41, 42, 44, 45
			2.02, m	42, 43a, 44a, 44b	41, 42, 44, 45
	44	26.2, CH_2	2.10, m	43a, 43b, 44b, 45a, 45b	42, 43, 45
			1.79, dquin (12.1, 7.1)	43a, 43b, 44a, 45a, 45b	42, 43, 45
	45	48.6, CH_2	3.64, dt (10.9, 6.9)	44a, 44b, 45b	42, 43, 44, 46
			3.46, m	44a, 44b, 45a	42, 43, 44, 46
	N-8	N			
N-Me-Val	46	168.5, C			
	47	62.7, CH	4.95, d (10.9)	48	46, 48, 49, 50, 51, 52
	48	27.9, CH	2.47, dsept (10.8, 6.6)	47, 49, 50	46, 47, 49, 50
	49	20.9, CH_3	1.00, d (7.1)	48	47, 48, 50
	50	18.8, CH_3	0.81, d (6.8)	48	47, 48, 49
	N-9	N			
	51	31.1, CH_3	3.07, s		47, 52
Pla	52	173.1, C			
	53	72.4, CH	5.77, dd (9.9, 4.1)	54a, 54b	1, 52, 54, 55
	54	38.8, CH_2	3.13, dd (14.4, 4.2)	53, 54b	52, 53, 55, 56
			3.04, dd (14.3, 10.0)	53, 54a	52, 53, 55, 56
	55	136.9, C			
	56/60	130.5, CH	7.25, m	57/59	54, 56/60, 58
	57/59	129.7, CH	7.31, t (7.2)	56/60, 58	55, 57/59
	58	128.4, CH	7.27, m	57/59	56/60

[a]HMBC correlations, optimized for 8 Hz, are from proton(s) stated to the indicated carbon.
[b]Four bond HMBC correlation.
[c]Homoallylic cosy correlation.

Table S3. ^{15}N (60 MHz), ^{13}C (150 MHz) and ^{1}H (600 MHz) NMR data ($CDCl_3$) for grassypeptolide G (**2**).

Amino acids	pos.	δ_C or δ_N, mult.	$^{1}J_{CH}$ (Hz)	δ_H (J in Hz)	COSY	HMBC[a]	NOE
Maba	1	172.1, C					
	2	44.6, CH	132	2.50, qd (7.0, 3.4)	3, 5	1, 3, 4, 5, N-1	3
	3	48.5, CH	142	4.03, m	2, 4, N-1	1, 2, 4, 5, 6	2, 5, N-1
	4	19.9, CH_3	126	1.05, d (6.7)	3	2, 3, N-1	
	5	14.6, CH_3	128	0.96, d (7.0)	2	1, 2, 3	3
	N-1	117.6, NH		7.14, m	3	2, 3, 6	3,7,8
Val	6	171.9, C					
	7	60.6, CH	142	4.36, dd (8.8, 6.2)	8, N-2	6, 8, 9, 10, 11, N-2	9,10, N-1, N-2
	8	30.8, CH	129	2.23, sept (6.8)	7, 9, 10	6, 7, 9, 10, N-2	N-1, N-2
	9	19.7, CH_3	127	0.99, d (6.3)	8	7, 8, 10	7, 20
	10	18.8, CH_3	125	0.98, d (6.0)	8	7, 8, 9	7, 20
	N-2	115.9, NH		7.13, m	7	7, 8, 11	7, 8
N-Me-Phe	11	169.7, C					
	12	58.6, CH	139	5.51, t (7.4)	13a, 13b	11, 13, 14, 20, 21, N-3	13a, 13b, 15/19, 20
	13	34.7, CH_2	130	3.45, dd (14.0, 8.4)	12, 13b	11, 12, 14, 15/19, N-3	12, 13b, 15/19, 20
			126	2.91, dd (13.9, 7.5)	12, 13a	11, 12, 14, 15/19	12, 13a, 15/19, 20
	14	137.7, C					
	15/19	129.6, CH	158	7.25, m	16/18	13, 15/19, 17	12, 13a, 13b, 20
	16/18	128.6, CH	158	7.13, m	15/19, 17	14, 16/18	
	17	126.6, CH	169	7.13, m	16/18	15/19	
	N-3	113.9,[b] N					
	20	31.6, CH_3	140	3.14, s		12, 21, N-3	9, 10, 12, 13a, 13b, 15/19, 22
Ala-thn-ca	21	169.9, C					
	22	77.5, CH	143	5.39, t (8.1)	23a, 23b, 25[c]	21, 23, 24	20, 23a, 23b
	23	33.7, CH_2	144	3.49, m	22, 23b	21, 22, 24	22, 23b,
			143	3.18, t (10.4)	22, 23a	21, 22, 24	22, 23a
	N-4	N[d]					
	24	179.0, C					
	25	48.3, CH	142	4.87, quin (7.1)	22,[c] 26, N-5	24, 26, 28	26, N-5
	26	18.5, CH_3	129	1.59, d (7.3)	25	24, 25, N-5	25, N-5
	N-5	128.6, NH		7.77, d (7.7)	25	25, 26, 28	25, 26, 29, 30
N-Me-Phe-thn-ca	28	170.7, C					
	29	79.1, CH	151	5.30, t (6.0)	30, 32[c]	28, 30, 31, N-5, N-6	30, N-5
	30	38.0, CH_2	146	3.71, d (6.7)	29	28, 29, 31	29, N-5
	N-6	293.4,[b] N					
	31	177.6, C					
	32	69.0, CH	134	3.83, m	29,[c] 33a, 33b	31, 33, 34, 40, 41	33b, 35/39, 40
	33	35.3, CH_2	130	3.62, dd (13.6, 10.9)	32, 33b	31, 32, 34, 35/39	33b, 35/39
			127	3.39, dd (14.1, 3.8)	32, 33a	31, 32, 34, 35/39, N-7	32, 33a, 35/39

	34	138.3, C					
	35/39	129.9, CH	159	7.33, d (7.0)	36/38	33, 35/39, 37	32, 33a, 33b, 40
	36/38	128.9, CH	160	7.37, t (7.4)	35/39, 37	34, 36/38	
	37	126.9, CH	157	7.26, m	36/38	35/39	
	N-7	109.8,[b] N					
	40	39.4, CH_3	139	2.69, s		32, 41, N-7	32, 35/39, 42, 43
Pro	41	172.4, C					
	42	57.7, CH	148	4.74, t (6.7)	43	41, 43, 44, 45, 46	40, 43, 51
	43	27.3, CH_2	135	2.02, q (6.9)	42, 44a, 44b	41, 42, 44, 45, N-8	40, 42, 45a, 45b
	44	25.3, CH_2	136	2.20, m	43, 44b, 45a, 45b	42, 43, 45, N-8	44b, 45a
			135	1.83, dquin (13.1, 7.1)	43, 44a, 45a, 45b	42, 43, 45, N-8	44a, 45b
	45	47.3, CH_2	148	3.50, m	44a, 44b, 45b	42, 43, 44	43, 44a, 45b, 47
			148	3.29, m	44a, 44b, 45a	42, 43, 44	43, 44b, 45a, 47, 51
	N-8	136.8,[b] N					
N-Me-Val	46	167.0, C					
	47	61.3, CH	140	4.80, d (10.6)	48	46, 48, 49, 50, 51, 52, N-9	45a, 45b, 49, 50, 51
	48	26.6, CH	130	2.43, dsept (10.9, 6.5)	47, 49, 50	46, 47, 49, 50	49, 50, 51
	49	20.0, CH_3	125	0.88, d (6.3)	48	47, 48, 50	47, 48
	50	18.1, CH_3	125	0.71, d (6.9)	48	47, 48, 49	47, 48
	N-9	114.0,[b] N					
	51	30.8, CH_3	140	2.93, s		47, 52, N-9	42, 45b, 47, 48
Pla	52	171.2, C					
	53	70.4, CH	150	5.72, dd (8.4, 5.5)	54a, 54b	1, 52, 54, 55	54a, 54b, 56/60
	54	38.3, CH_2	129	3.02, dd (14.4, 8.7)	53, 54b	52, 53, 55, 56/60	53, 56/60
			126	2.91, dd (13.9, 6.4)	53, 54a	52, 53, 55, 56/60	53, 56/60
	55	135.3, C					
	56/60	129.5, CH	156	7.21, d (7.1)	57/59	54, 56/60, 58	53, 54a, 54b
	57/59	128.8, CH	160	7.30, t (7.3)	56/60, 58	55, 57/59	
	58	127.5, CH	161	7.26, m	57/59	56/60	

[a]HMBC correlations, optimized for 8 Hz, are from proton(s) stated to the indicated carbon or nitrogen.
[b]Assigned from HMBC data.
[c]Homoallylic cosy correlation.
[d]Not observed.

Table S4. ^{13}C (150 MHz) and ^{1}H (600 MHz) NMR data (CD_3OD) for grassypeptolide G (**2**).

Amino acids	pos.	δ_C, mult.	δ_H (*J* in Hz)	COSY	HMBC[a]
Maba	1	172.8, C			
	2	45.5, CH	2.54, qd (6.9, 3.2)	3, 5	1, 3, 4, 5
	3	50.2, CH	4.02, m	2, 4, N-1	1, 5, 6
	4	20.1, CH_3	1.07, d (6.8)	3	2, 3
	5	15.0, CH3	0.98, d (6.8)	2	1, 2, 3
	N-1	NH	7.75, d (8.0)	3	
Val	6	174.3, C			
	7	62.1, CH	4.20, dd (8.1, 7.0)	8, N-2	6, 8, 9, 10, 11
	8	31.9, CH	2.21, sept (6.8)	7, 9, 10	6, 7, 9, 10
	9	20.2, CH_3	0.99, d (6.6)	8	7, 8, 10
	10	19.5, CH_3	1.05, d (6.7)	8	7, 8, 9
	N-2	NH	7.61, d (7.9)	7	
N-Me-Phe	11	172.2, C			
	12	59.0, CH	5.55, dd (9.4, 6.5)	13a, 13b	11, 13, 14, 20, 21
	13	34.8, CH_2	3.31, m	12, 13b	11, 12, 14, 15/19
			3.10, m	12, 13a	11, 12, 14, 15/19
	14	138.6, C			
	15/19	130.0, CH	7.22, d (7.9)	16/18	13, 15/19, 17
	16/18	129.7, CH	7.18, t (7.8)	15/19, 17	14, 16/18
	17	127.8, CH	7.16, m	16/18	15/19
	N-3	N			
	20	31.7, CH_3	3.13, s		12, 21
Ala-thn-ca	21	172.3, C			
	22	77.8, CH	5.51, t (8.5)	23a, 23b, 25[b]	21, 24
	23	35.1, CH_2	3.30, m	22, 23b	21, 22, 24
			3.26, m	22, 23a	21, 22, 24
	N-4	N			
	24	181.1, C			
	25	49.6, CH	4.77, m	22,[b] 26, N-5	24, 26
	26	19.4, CH_3	1.63, d (7.2)	25	24, 25
	N-5	NH	8.03, d (7.8)	25	28
N-Me-Phe-thn-ca	28	172.9, C			
	29	79.9, CH	5.20, dt (11.6, 10.5)	30a, 30b, 32[b]	28, 31
	30	38.0, CH_2	3.78, dd (11.6, 1.9)	29, 30b	28 29
			3.60, dd (11.5, 2.0)	29, 30a	28, 29, 31
	N-6	N			
	31	180.6, C			
	32	69.5, CH	4.14, m	29,[b] 33a, 33b	40, 41
	33	36.2, CH_2	3.52, dd (13.7, 11.0)	32, 33b	31, 32, 34, 35/39

			3.36, dd (13.6, 3.6)	32, 33a	32, 34, 35/39
	34	139.6, C			
	35/39	131.1, CH	7.40, d (8.2)	36/38	33, 35/39, 37
	36/38	129.7, CH	7.35, t (7.7)	35/39, 37	34, 36/38
	37	127.7, CH	7.25, m	36/38	35/39
	N-7	N			
Pro	40	39.7, CH_3	2.72, s		32, 41
	41	174.0, C			
	42	59.3, CH	4.78, dd (9.0, 4.5)	43a, 43b	41, 43, 44, 45, 46
	43	28.4, CH_2	2.17, m	42, 43b, 44a, 44b	41, 42, 44, 45
			1.99, m	41, 43a, 44a, 44b	41, 42, 44, 46
	44	26.1, CH_2	2.06, dquin (12.3, 6.3)	43a, 43b, 44b, 45a, 45b	42, 43, 45
			1.78, dquin (12.1, 7.0)	43a, 43b, 44a, 45a, 45b	42, 43, 45
	45	48.9, CH_2	3.65, dt (10.8, 7.1)	44a, 44b, 45b	43, 44
N-Me-Val			3.47, m	44a, 44b, 45a	42
	N-8	N			
	46	168.7, C			
	47	62.7, CH	4.95, d (10.8)	48	46, 48, 49, 50, 51, 52
	48	27.9, CH	2.45, dsept (10.8, 6.8)	47, 49, 50	46, 47, 49, 50
	49	20.6, CH_3	0.95, d (6.3)	48	47, 48, 50
	50	18.8, CH_3	0.80, d (6.7)	48	47, 48, 49
Pla	N-9	N			
	51	31.1, CH_3	3.07, s		47, 52
	52	173.0, C			
	53	72.5, CH	5.75, dd (9.9, 4.2)	54a, 54b	1, 52, 54, 55
	54	38.8, CH2	3.11, dd (14.3, 10.0)	53, 54b	52, 55, 56/60
			3.05, dd (14.1, 4.2)	53, 54a	52, 53, 55, 56/60
	55	136.9, C			
	56/60	130.5, CH	7.25, m	57/59	54, 56/60, 58
	57/59	129.7, CH	7.30, t (7.3)	56/60, 58	55, 57/59
	58	128.7, CH	7.26, m	57/59	56/60

[a]HMBC correlations, optimized for 8 Hz, are from proton(s) stated to the indicated carbon.
[b]Homoallylic cosy correlation.

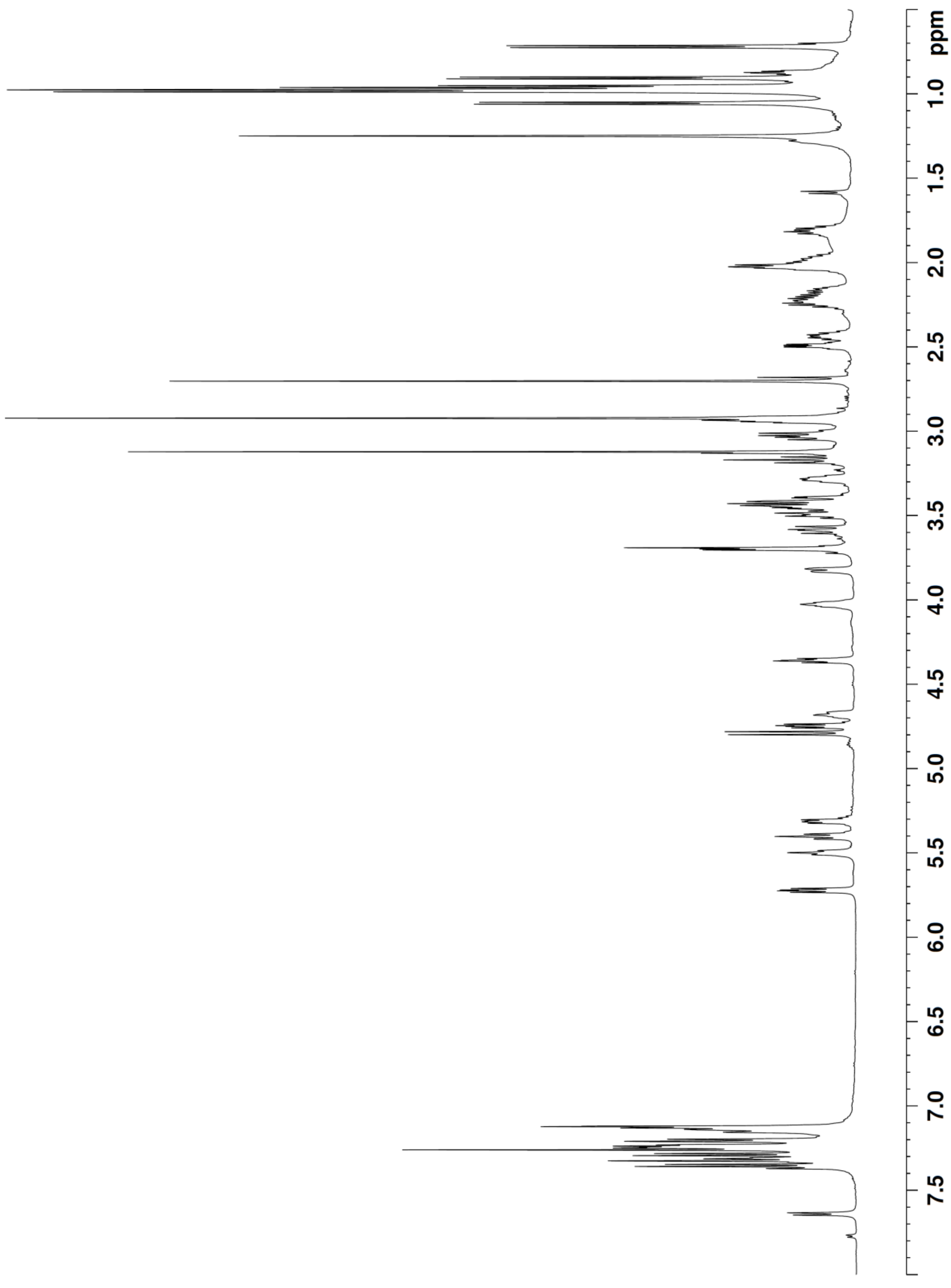

Figure S1. ^{1}H NMR spectrum of grassypeptolide F (**1**) (600 MHz, $CDCl_3$)

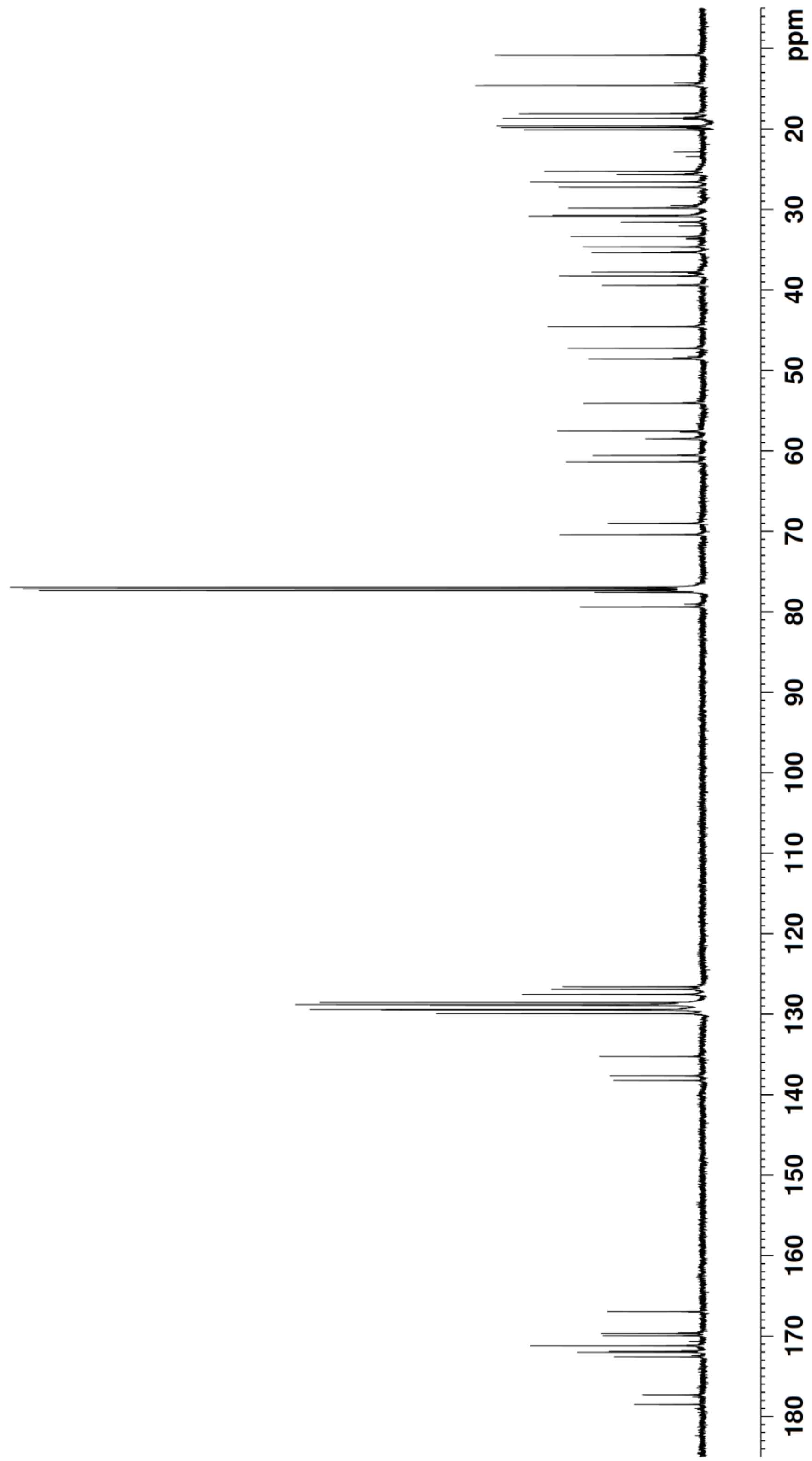

Figure S2. ^{13}C NMR spectrum of grassypeptolide F (**1**) (150 MHz, $CDCl_3$)

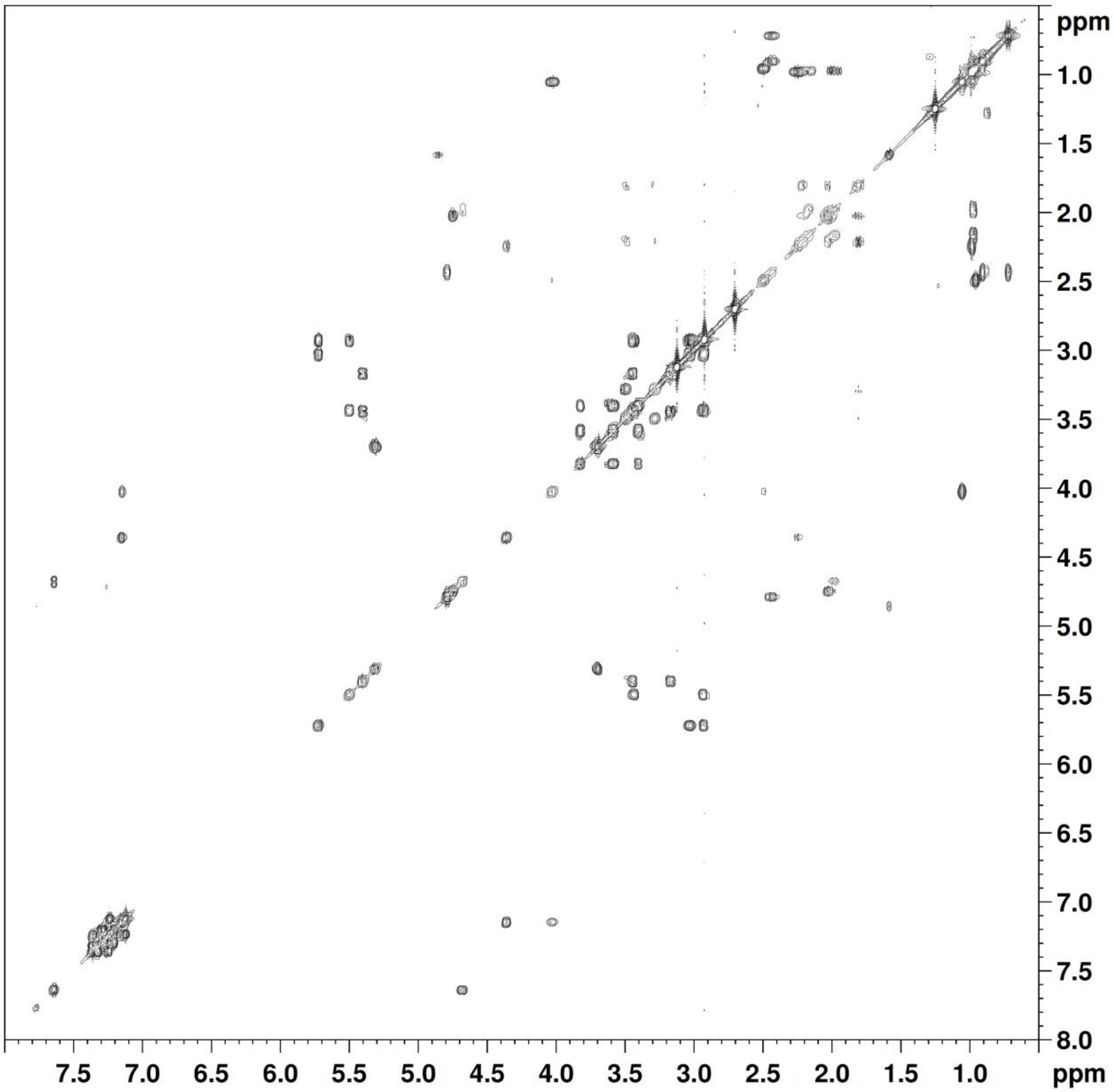

Figure S3. COSY NMR spectrum of grassypeptolide F (**1**) (600 MHz, $CDCl_3$)

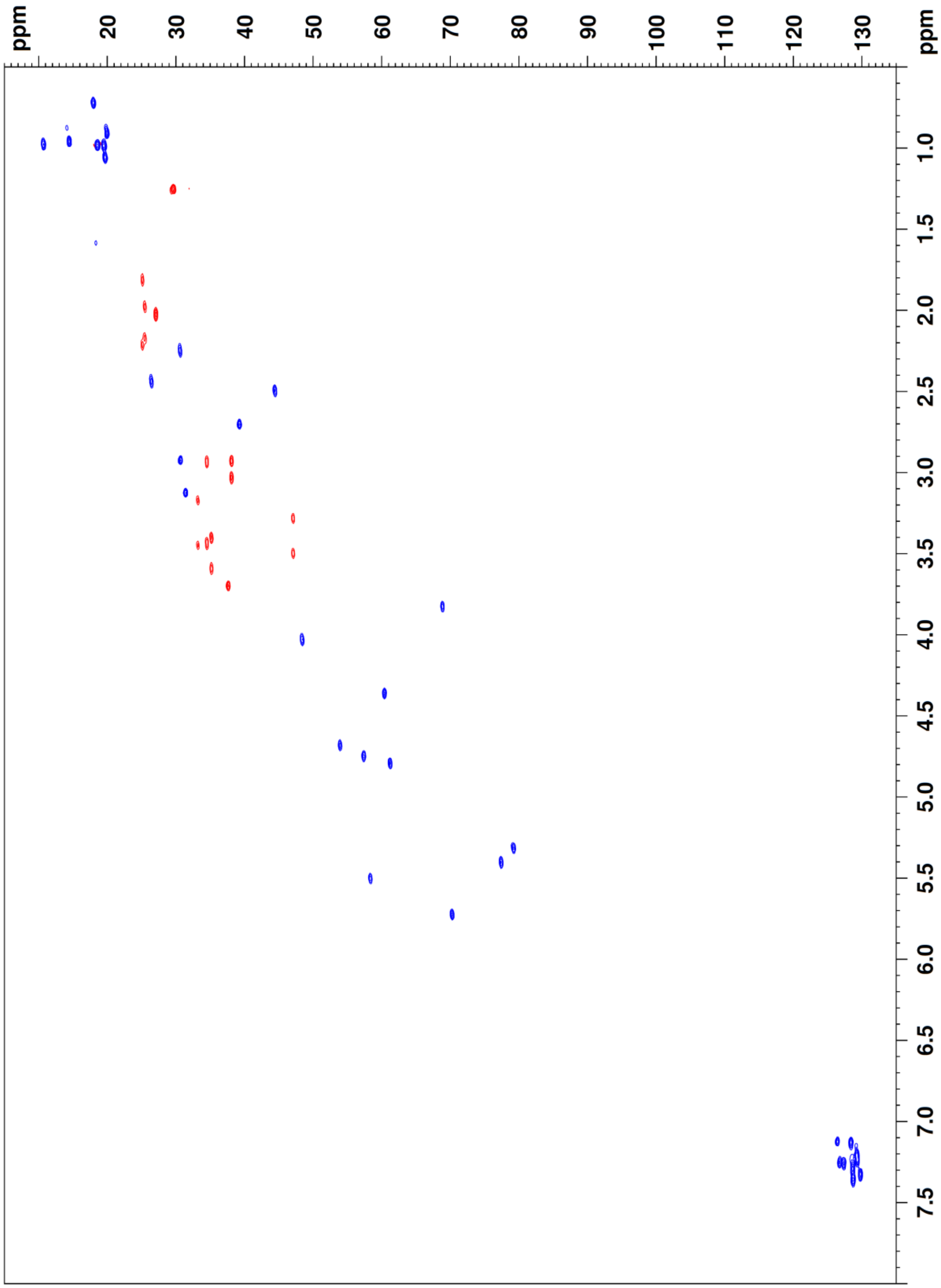

Figure S4. HSQC NMR spectrum of grassypeptolide F (**1**) (600 MHz, $CDCl_3$)

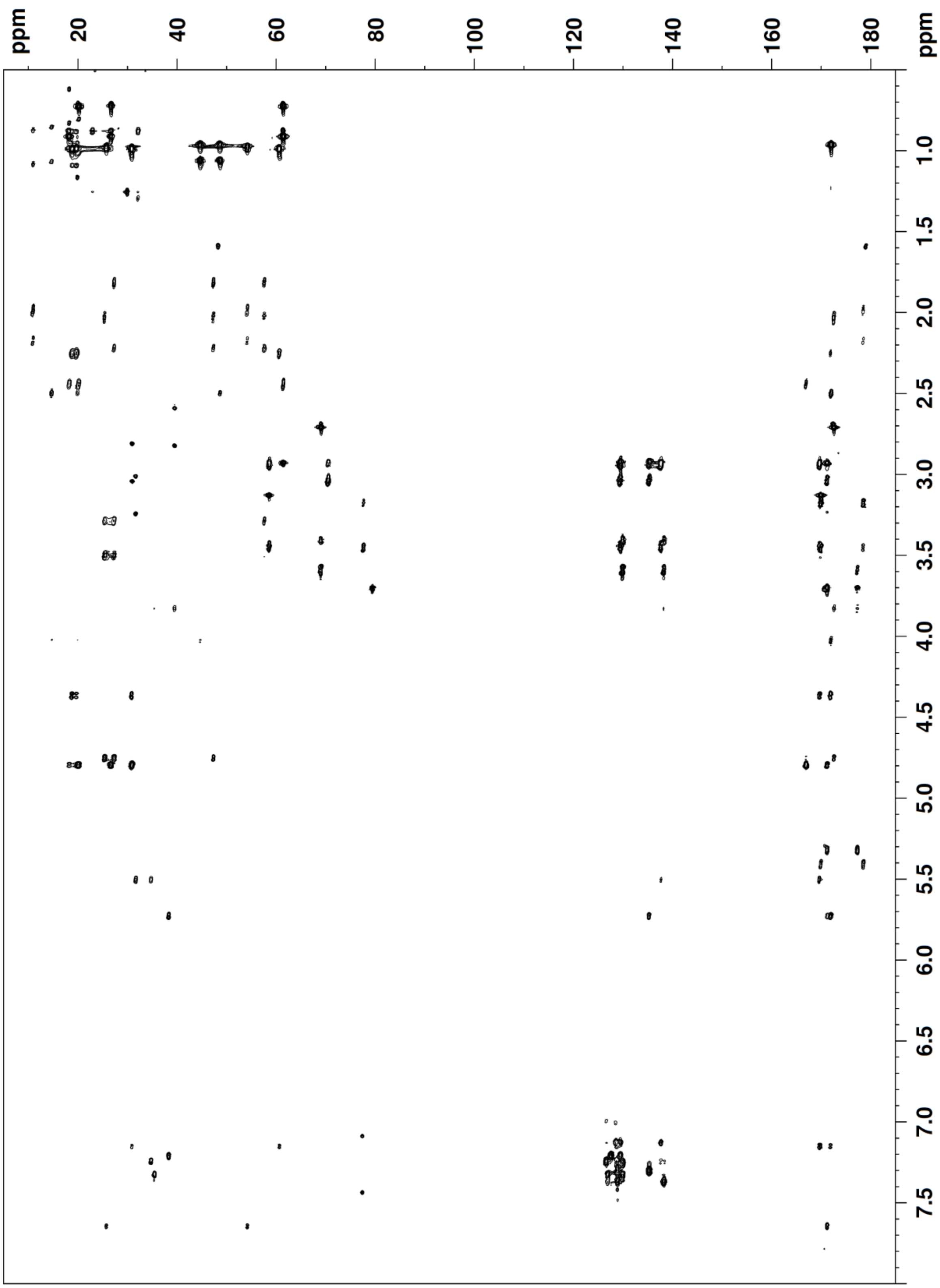

Figure S5. HMBC NMR spectrum of grassypeptolide F (**1**) (600 MHz, $CDCl_3$)

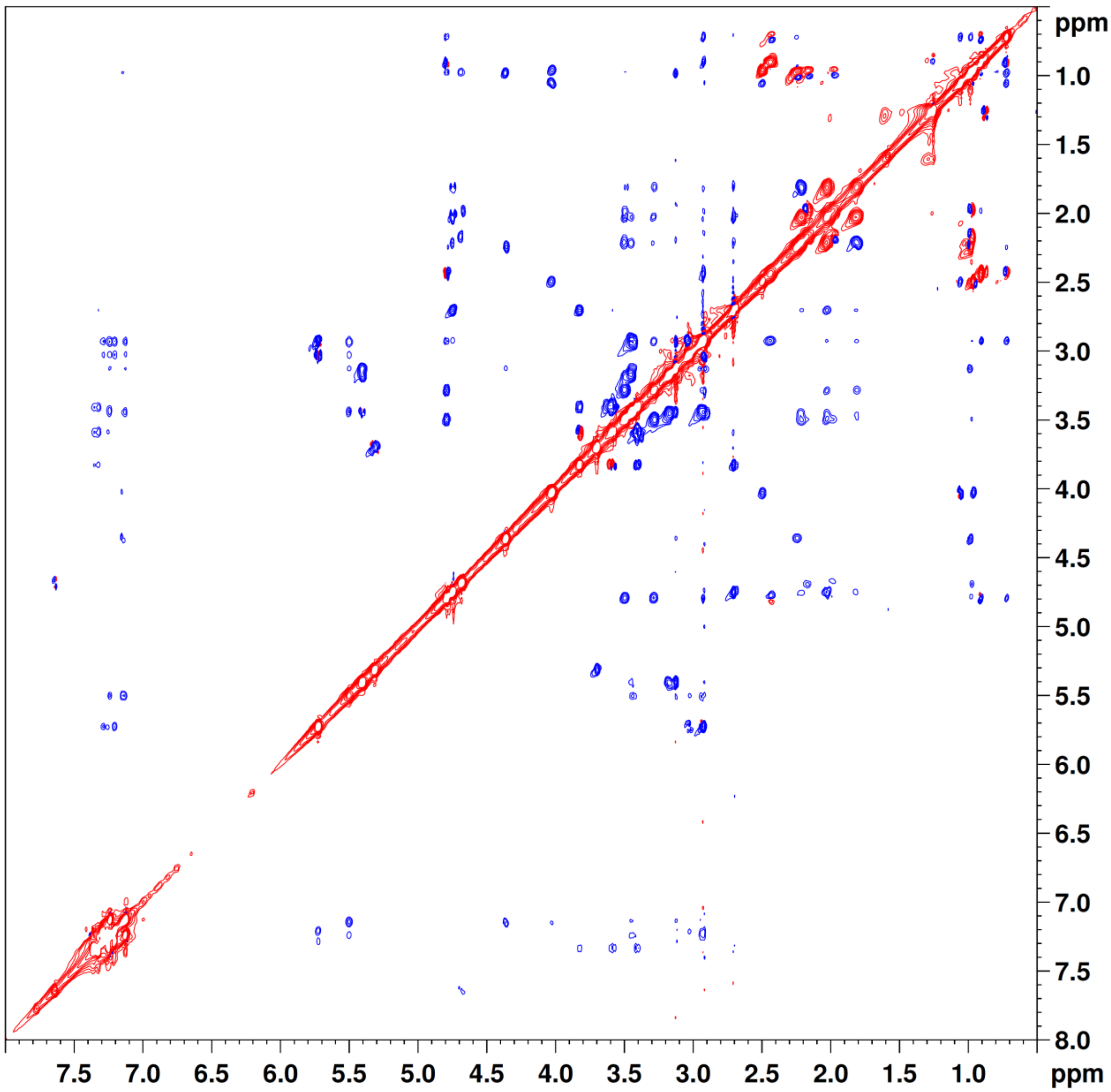

Figure S6. ROESY NMR spectrum of grassypeptolide F (**1**) (600 MHz, $CDCl_3$)

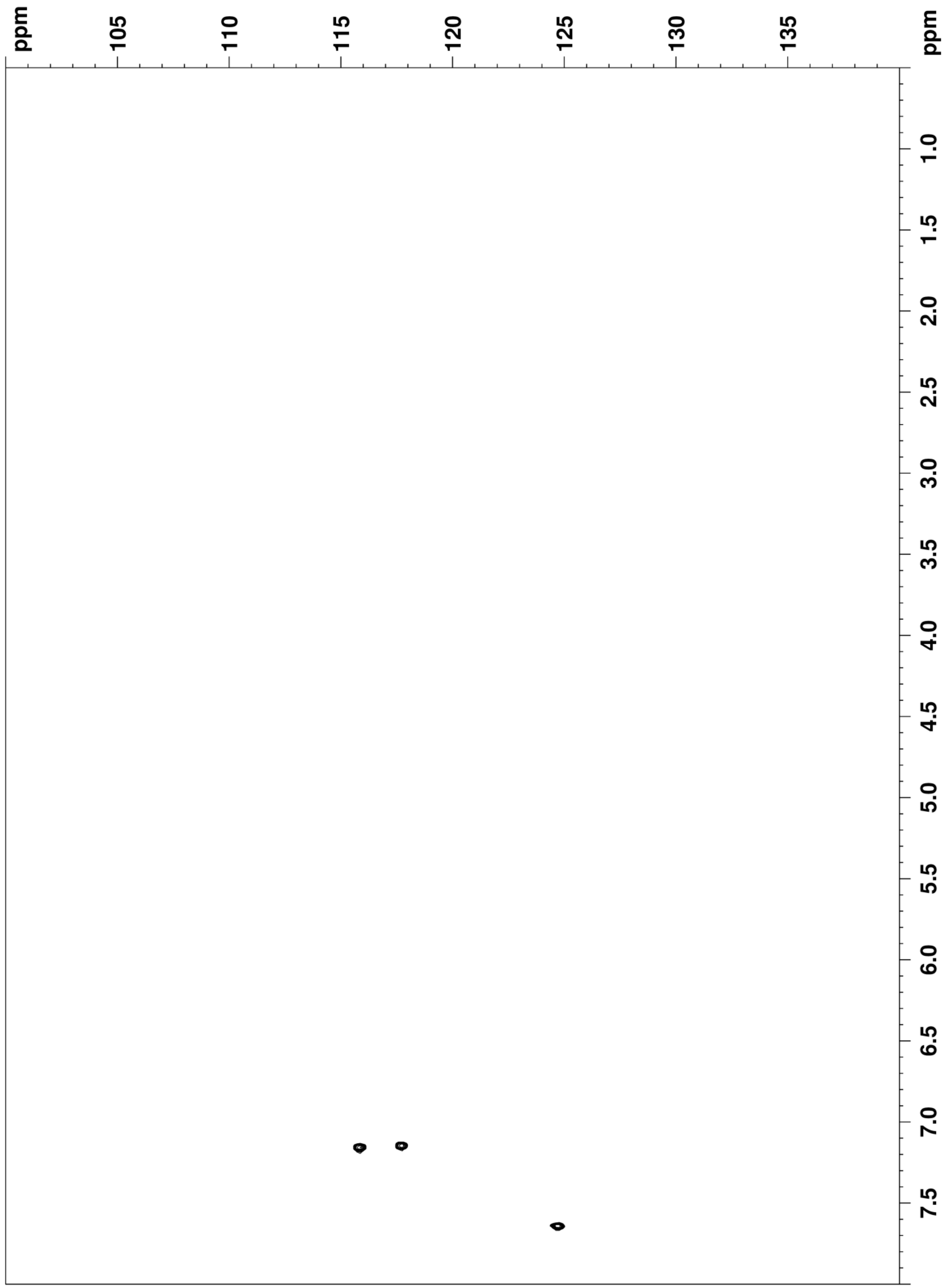

Figure S7. ^{15}N HSQC NMR spectrum of grassypeptolide F (**1**) (600 MHz, $CDCl_3$)

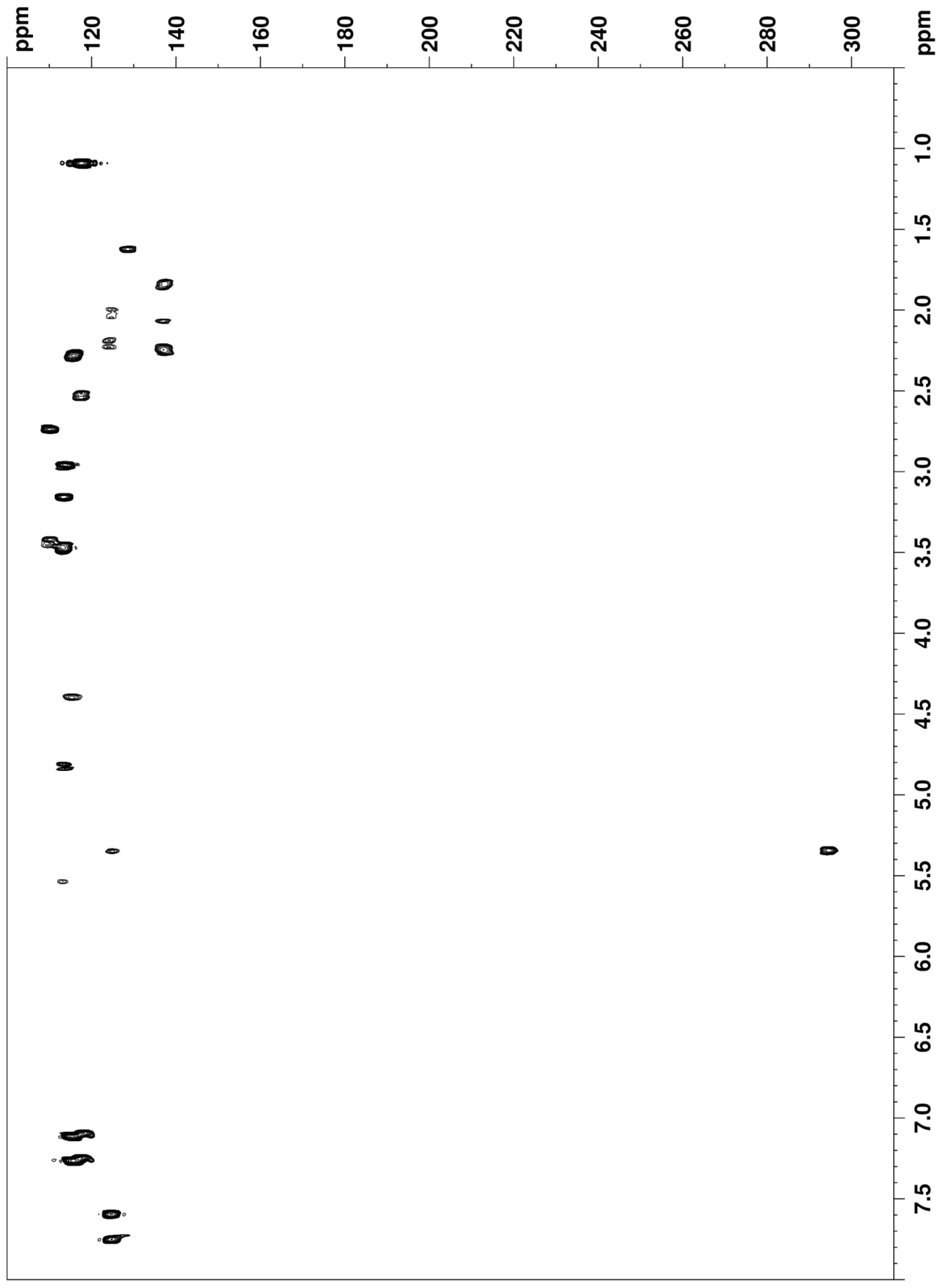

Figure S8. ^{15}N HMBC NMR spectrum of grassypeptolide F (**1**) (600 MHz, $CDCl_3$)

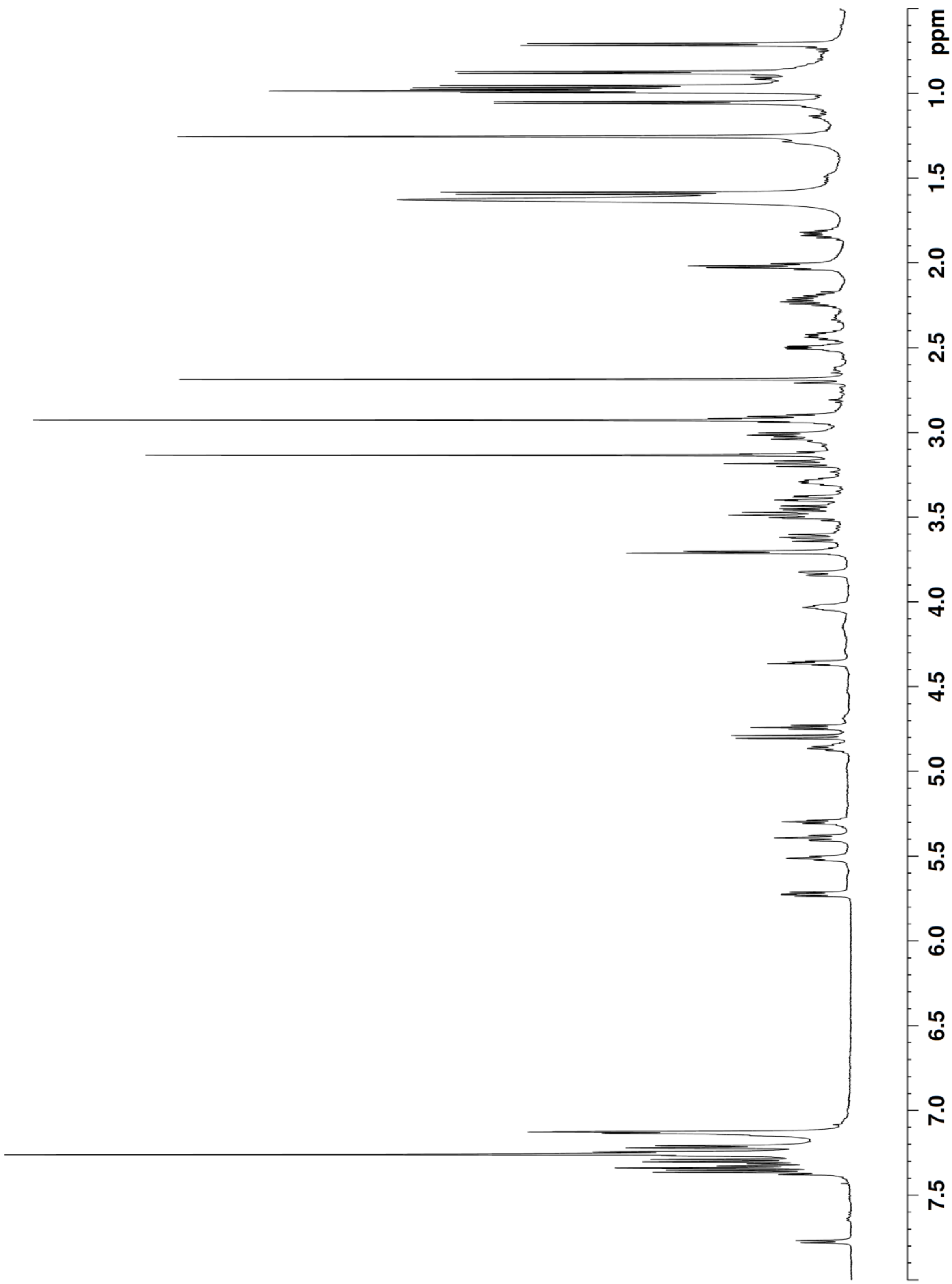

Figure S9. ^{1}H NMR spectrum of grassypeptolide G (**2**) (600 MHz, $CDCl_3$)

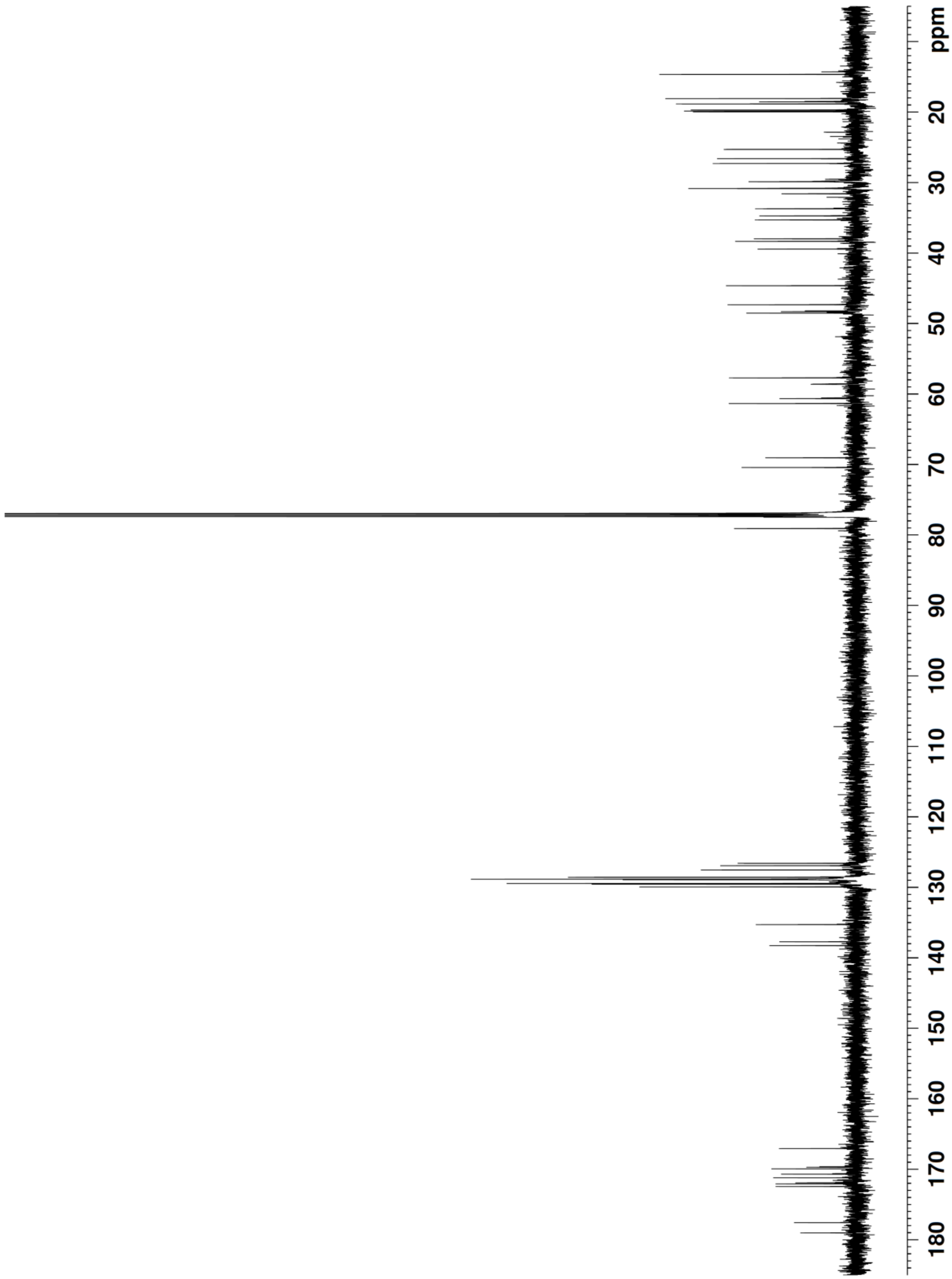

Figure S10. ^{13}C NMR spectrum of grassypeptolide G (**2**) (150 MHz, $CDCl_3$)

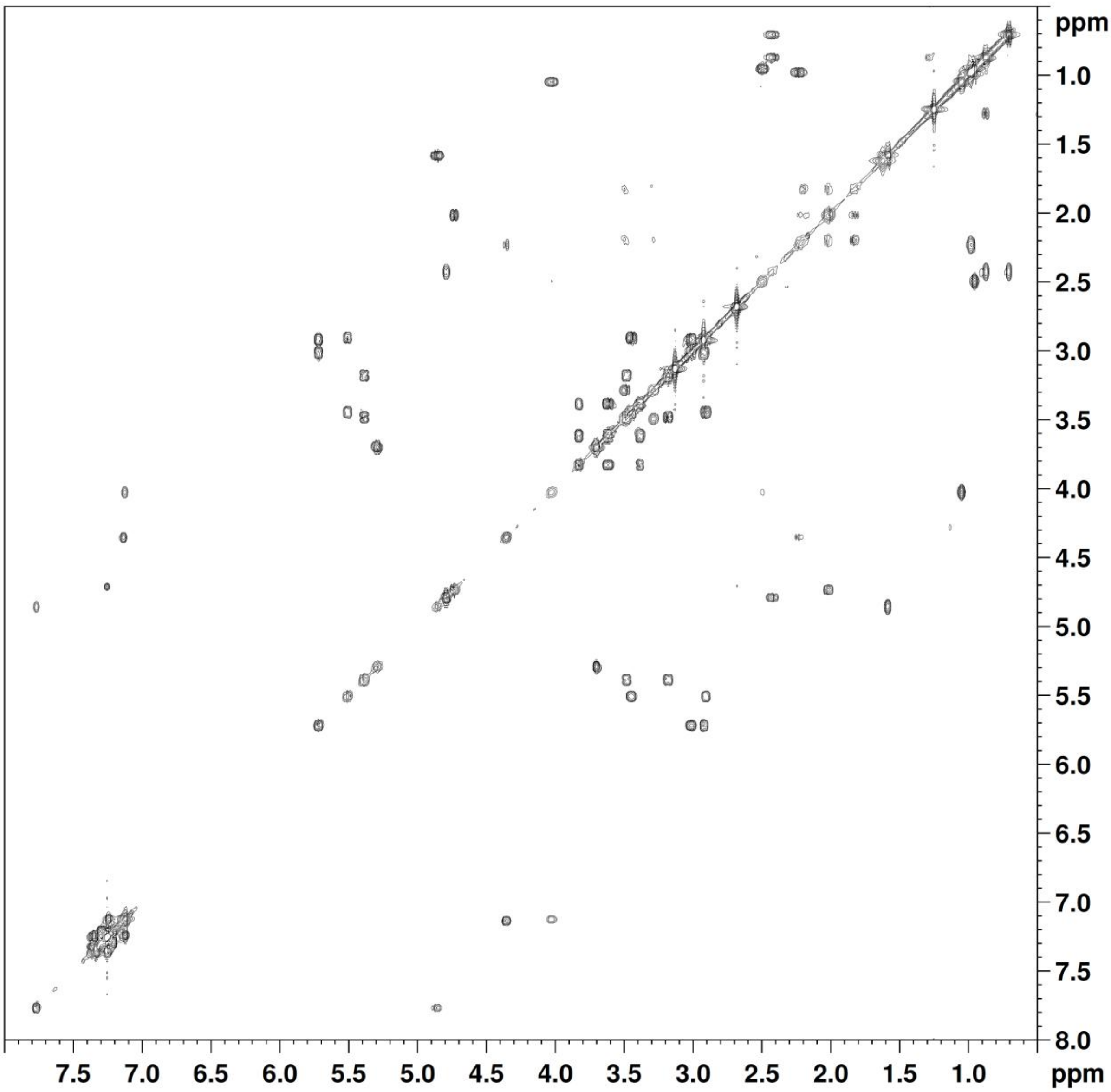

Figure S11. COSY NMR spectrum of grassypeptolide G (**2**) (600 MHz, $CDCl_3$)

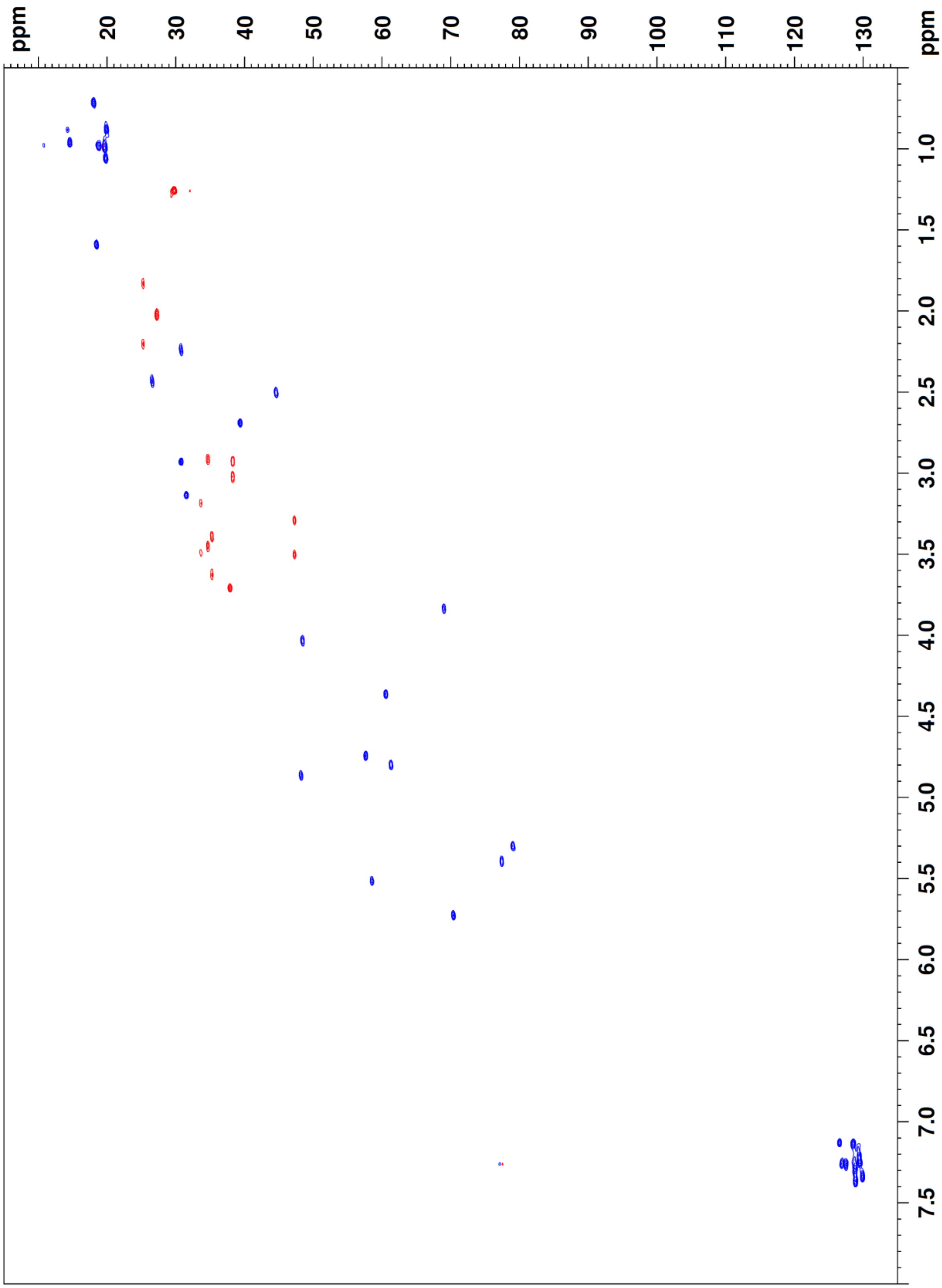

Figure S12. HSQC NMR spectrum of grassypeptolide G (**2**) (600 MHz, $CDCl_3$)

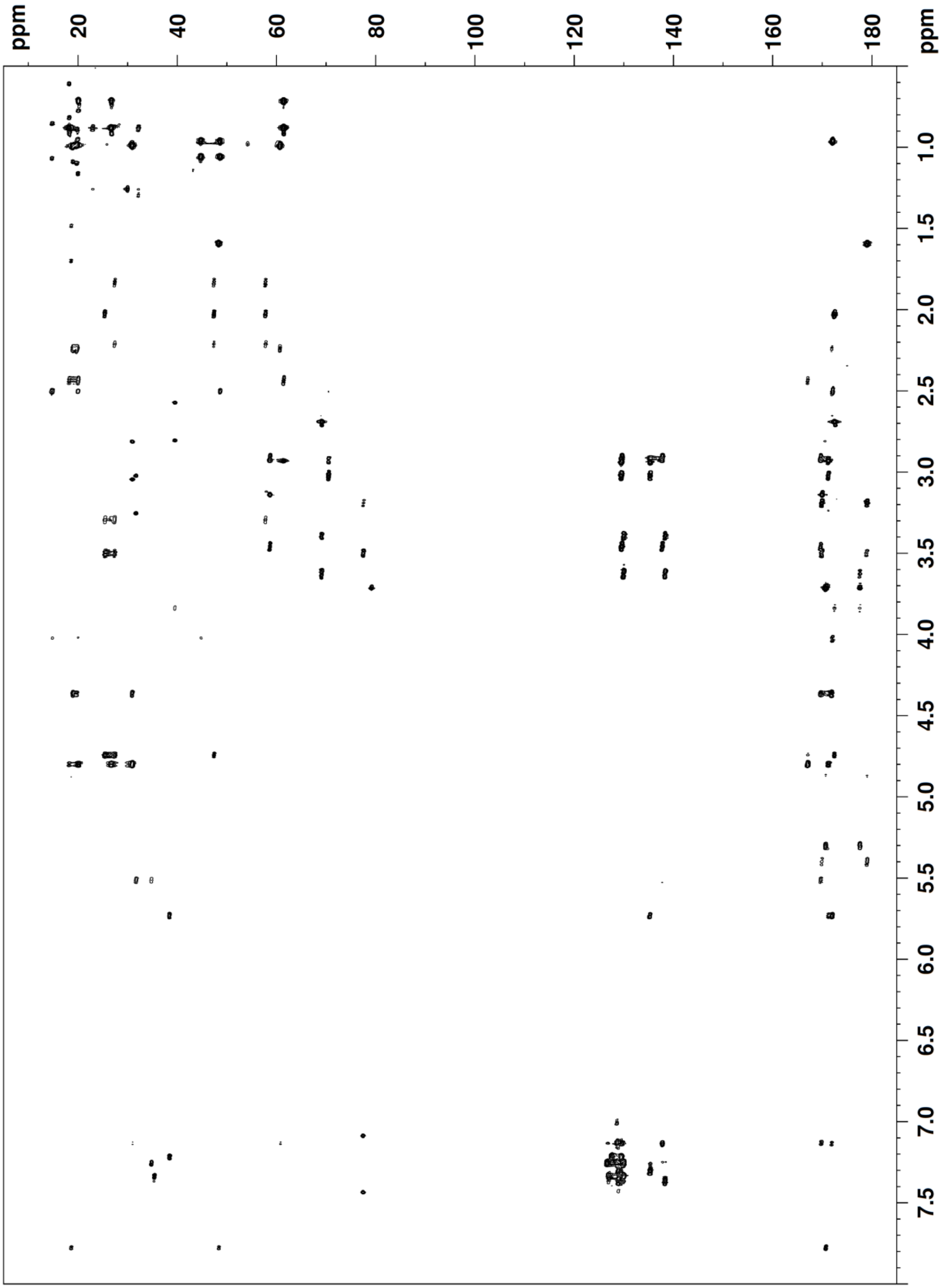

Figure S13. HMBC NMR spectrum of grassypeptolide G (**2**) (600 MHz, $CDCl_3$)

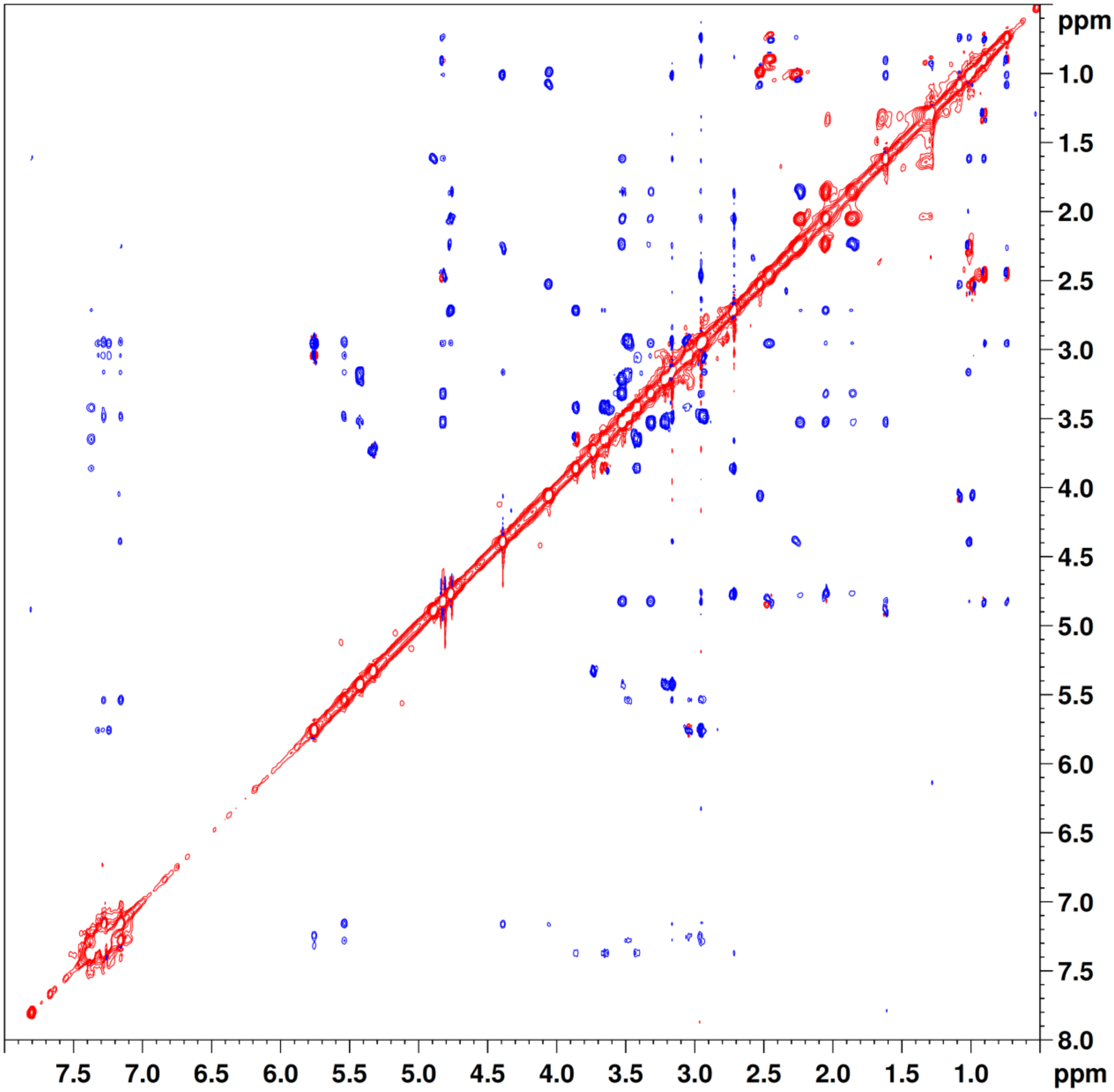

Figure S14. ROESY NMR spectrum of grassypeptolide G (**2**) (600 MHz, $CDCl_3$)

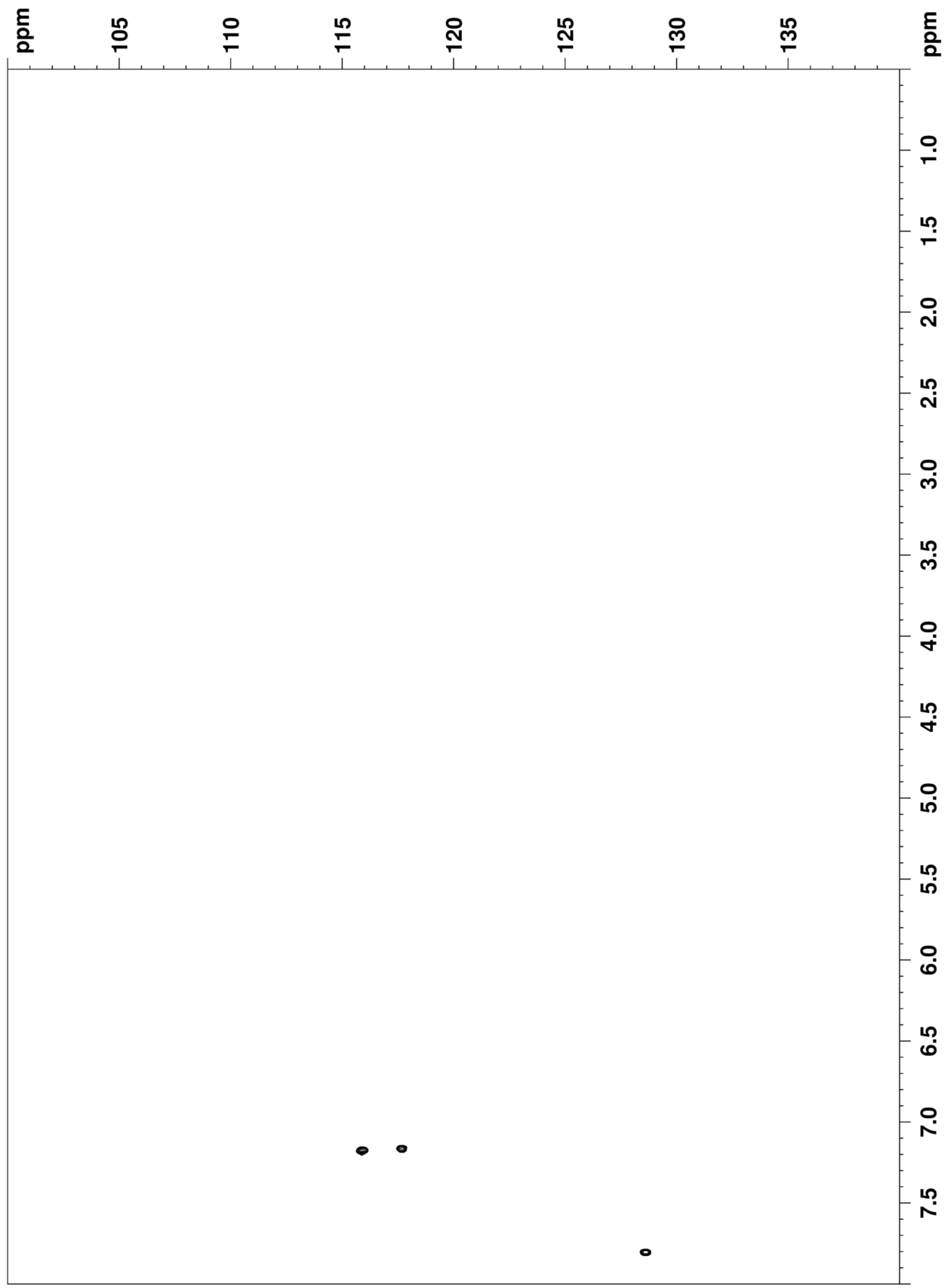

Figure S15. ^{15}N HSQC NMR spectrum of grassypeptolide G (**2**) (600 MHz, $CDCl_3$)

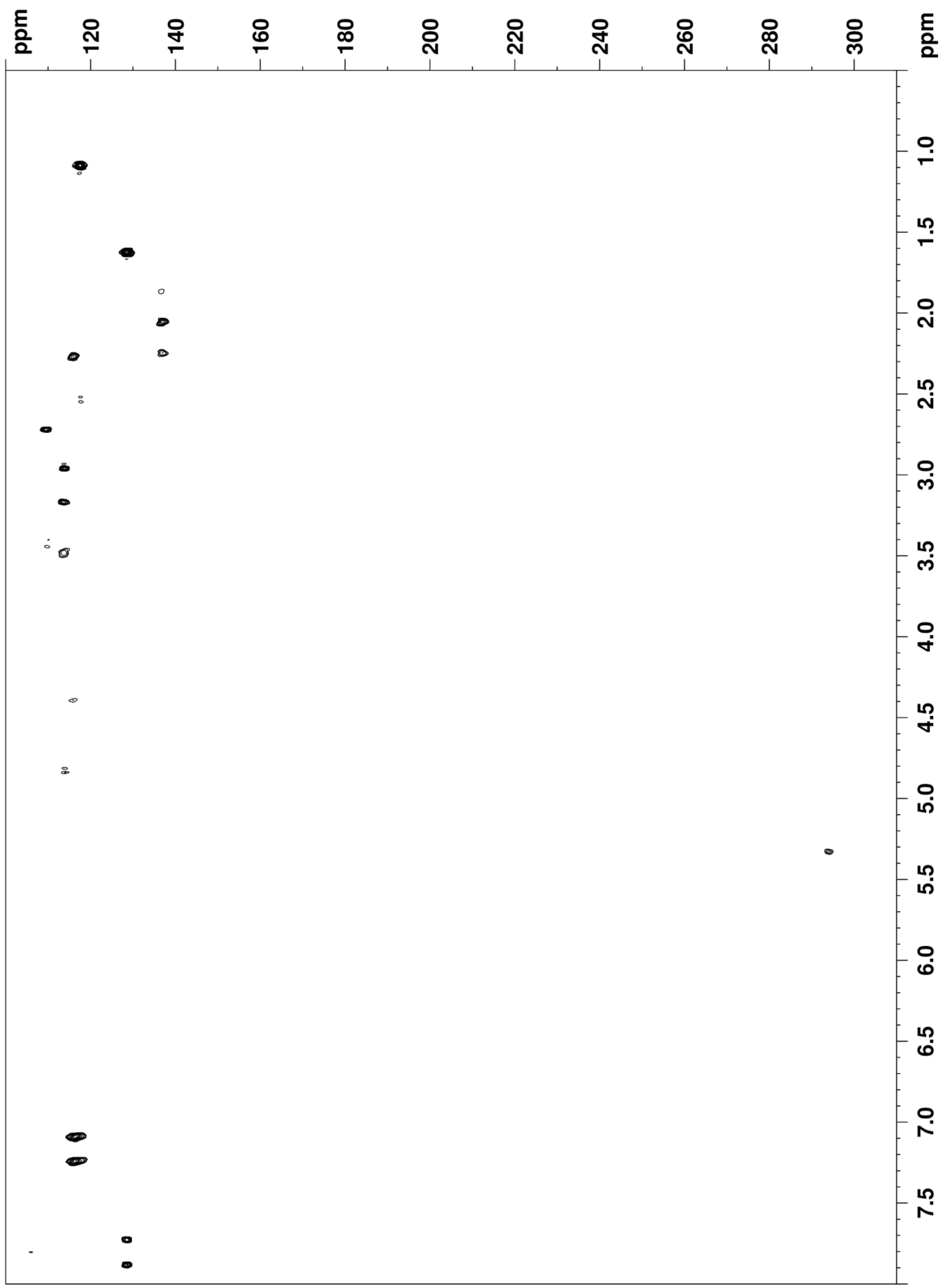

Figure S16. ^{15}N HMBC NMR spectrum of grassypeptolide G (**2**) (600 MHz, $CDCl_3$)