CHEMISTRY

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Supporting Information

Discovery of New Natural Products by Intact-cell Mass Spectrometry and LC-SPE-NMR--Malbranpyrroles, Novel Polyketides from Thermophilic Fungus *Malbranchea sulfurea*

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Figures

Tables

NMR spectra

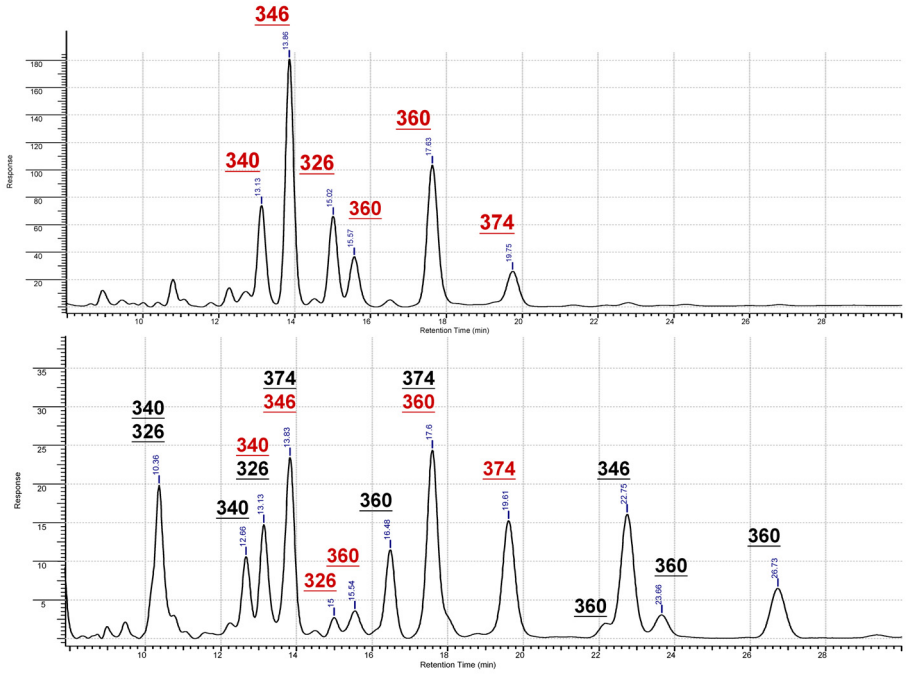


Figure S1. LC-DAD-MS profiles (70% MeCN, 30% H_2O, C-30, 225 nm) of the crude extract of *M. sulfurea* without (up) and with (down) UV irradiation

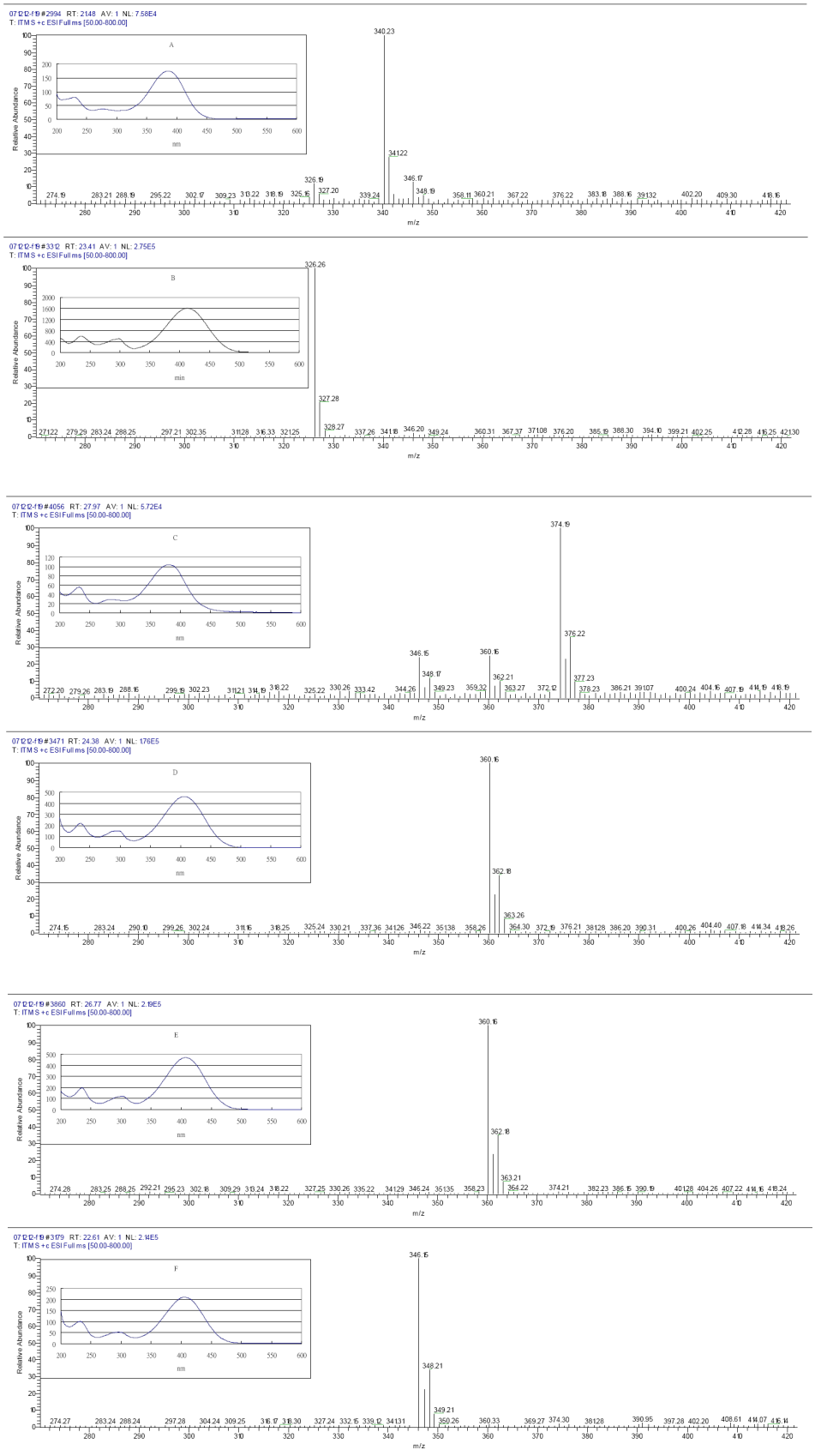


Figure S2. ESI MS and UV spectra of malbranpyrroles A-F (**1**-**6**)

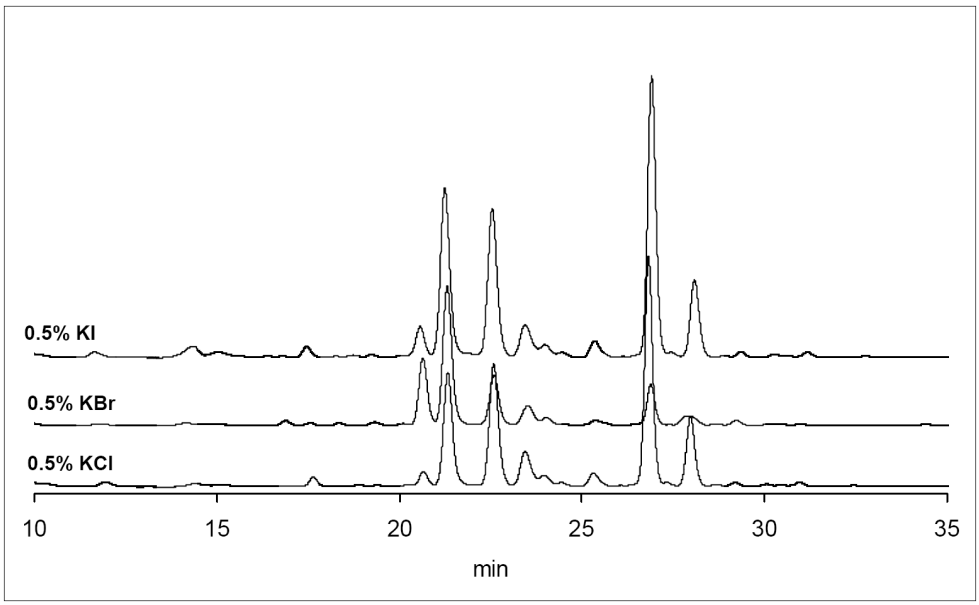


Figure S3. HPLC profiles of the crude extracts of *M. sulfurea* cultured in PDA containing 0.5% KCl, KBr, and KI, respectively

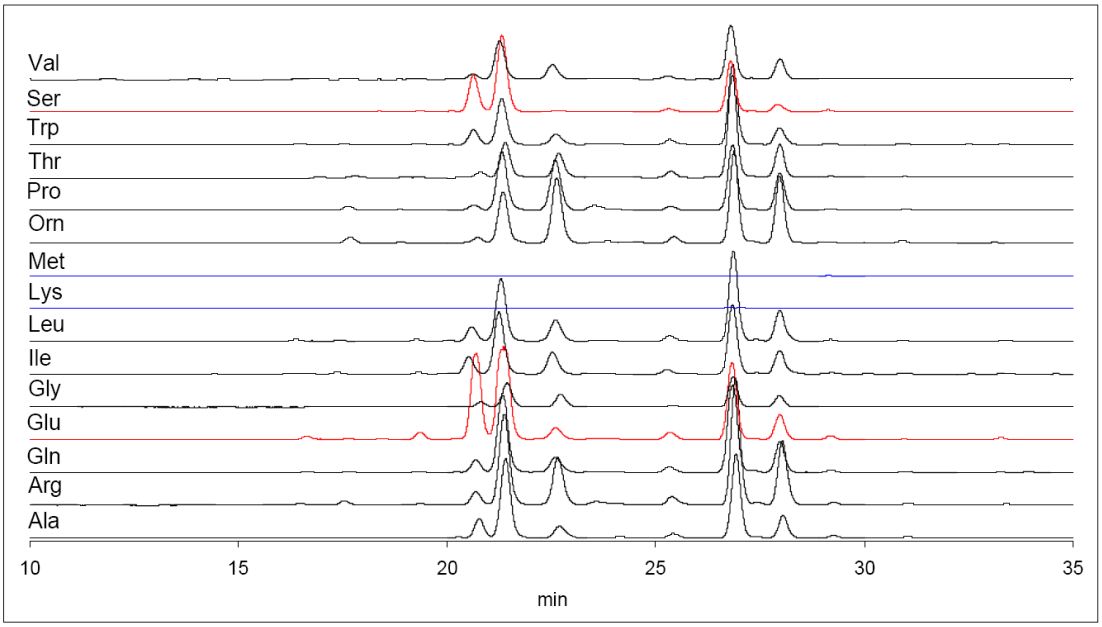


Figure S4. The HPLC profiles of malbranpyrroles from *M. sulfurea* incubated in PDA containing 1% amino acids

Table S1. ^{13}C NMR chemical shifts (125 MHz, in d_6-acetone) and enrichment ratios of malbranpyrrole F (**6**), isolated after feeding of [1-^{13}C]acetate, [2-^{13}C]acetate, [$^{13}C_2$]acetate, and [2-^{13}C]glycerol

		[1-^{13}C]acetate	[2-^{13}C]acetate	[$^{13}C_2$]acetate	[2-^{13}C]glycerol
carbon	ppm	enrichment (%)	enrichment (%)	^{2}J to C (Hz)	enrichment (%)
2	121.5	4.7	0.5	32.4	0.3
3	110.7	-1.0	14.1	32.4	-1.0
4	114.8	-3.0	6.8	[b] -	-1.0
5	127.6	-2.0	6.9	34.4	-2.0
6	124.9	13.3	2.5	34.4	9.0
7	121.2	0.4	11.7	29.8	-1.0
8	133.3	19.6	[a] 0	29.8	10.3
9	126.2	0.3	8.4	32.8	-1.0
10	164.6	8.8	-1.0	32.8	11.1
11	93.9	[a] 0	5.4	33.5	-2.0
12	170.2	9.8	-3.0	33.5	12.3
13	109.5	1.2	13.6	42.9	4.4
14	160.4	13.6	0.6	42.9	3.9
15	12.8	-2.0	-2.0	[b] -	3.2
18	14.9	16.9	-1.0	19.9	11.7
17	92.6	0.5	4.4	19.9	0.2
16	43.7	15.6	-2.0	18.0	9.7
20	20.5	0.9	10.1	18.0	[a] 0.5
19	25.8	-3.0	11.2	[c] 18.0	[a] 0.2

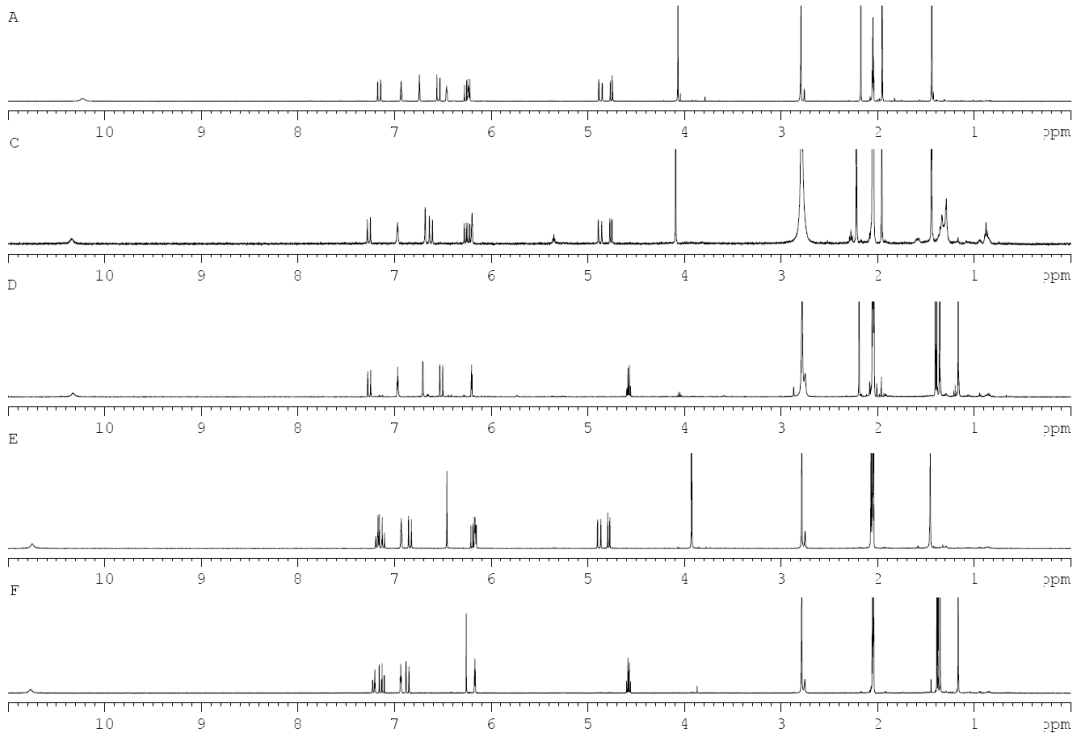
[a] standard carbon for enrichment ratio calculation; [b] singlet signal; [c] the enrichment ratio is much smaller than the other signals.

Table S2. Cytotoxicity (μM) of malbarnpyrroles C-F (**3**-**6**) without[a]/with[b] UV irradiation

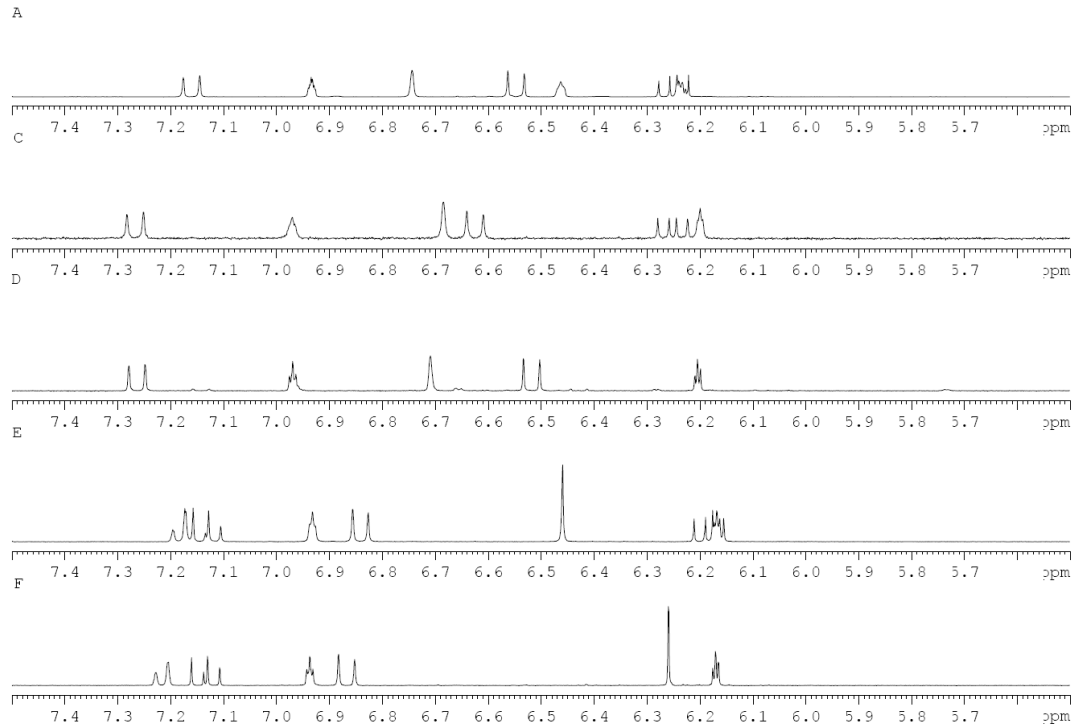
	PANC-1[a]	PANC-1[b]	HepG2[a]	HepG2[b]	MCF-7[a]	MCF-7[b]
C	11	7.0	4.6	2.8	7.1	6.3
D	6.3	7.2	7.7	7.3	8.9	5.8
E	4.5	7.4	5.3	0.7	8.4	5.6
F	3.3	7.8	7.1	7.3	7.7	4.8
Doxorubicin	4.0	-	1.6	-	2.8	-

Table S3. Cell cycle analysis of malbranpyrroles C-F (**3**-**6**) in MCF-7 and HepG2

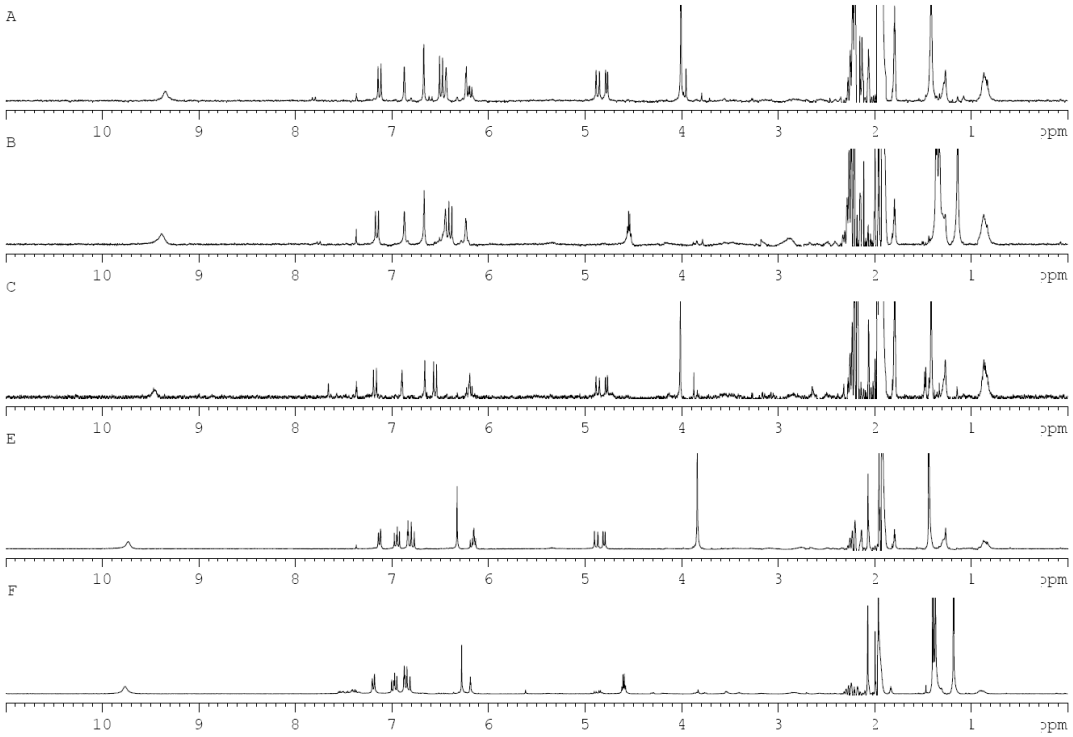
		MCF-7			HepG2		
	Conc. (μM)	G0/G1	S	G2/M	G0/G1	S	G2/M
Control		47.2	34.6	17.3	63.4	12.0	24.6
F	1	53.7	29.3	17.0	65.0	14.4	20.7
	10	62.8	20.9	16.3	72.0	7.0	21.1
	25	60.5	20.5	19.0	69.4	8.3	22.3
D	1	53.7	33.3	13.1	62.6	16.1	21.4
	10	61.8	22.2	16.0	77.2	0.3	22.6
	25	62.1	20.1	17.8	70.9	6.0	23.1
E	1	55.9	28.7	15.4	65.9	12.0	22.1
	10	70.7	16.4	13.0	69.7	9.0	21.3
	25	62.5	20.0	17.5	67.8	2.6	29.6
C	1	56.5	29.3	14.2	66.3	12.0	21.7
	10	65.1	17.5	17.5	68.9	7.9	31.1
	25	61.4	19.9	18.7	71.5	0	28.5



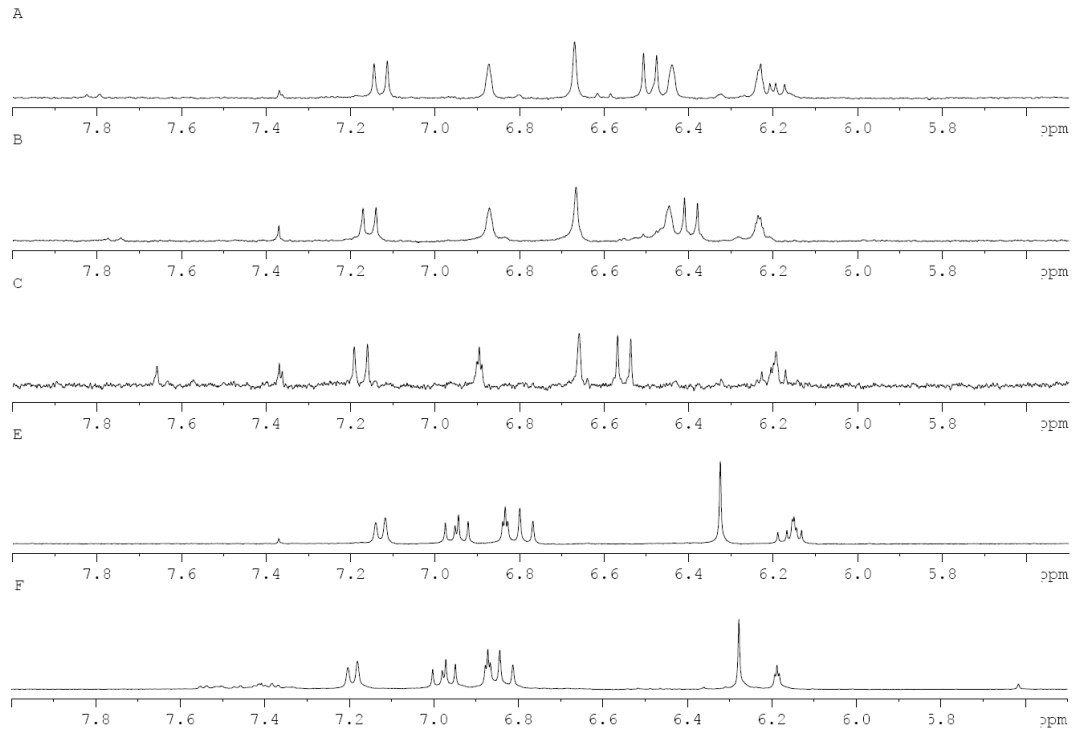
SS1. ^{1}H NMR (500 MHz, d_6-acetone) spectra of malbranpyrroles A (**1**) and C-F (**3**-**6**)



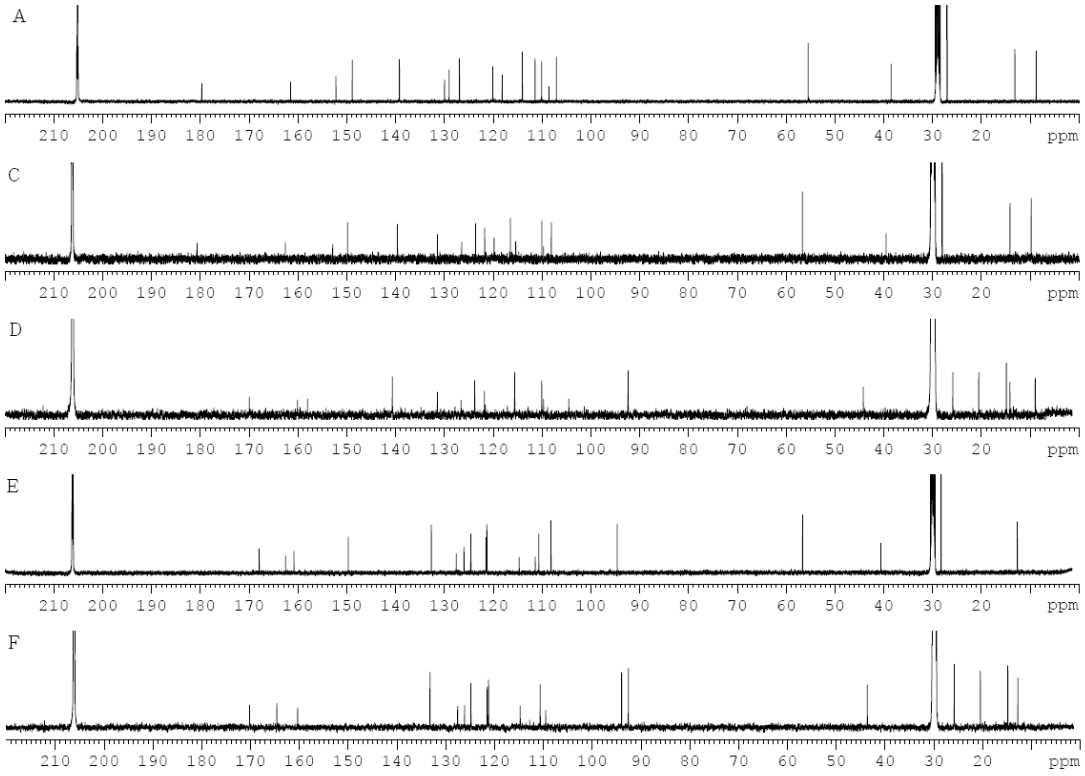
SS2. ^{1}H NMR (500 MHz, d_6-acetone) expanded spectra of malbranpyrroles A (**1**) and C-F (**3**-**6**)



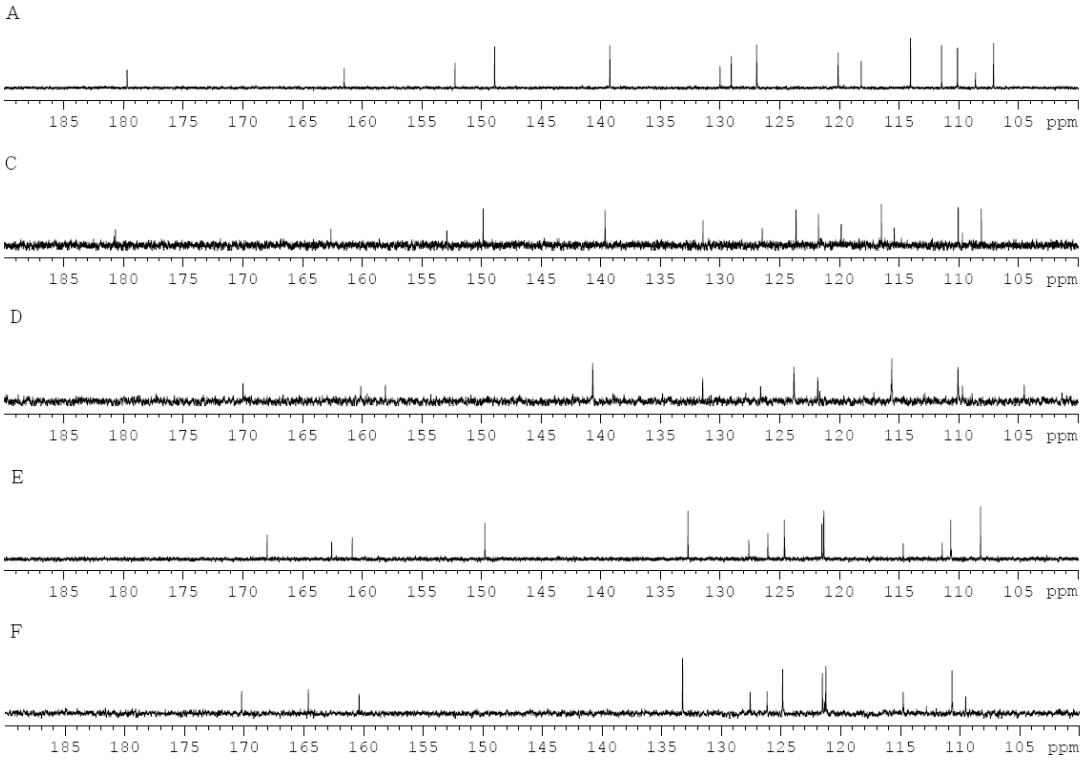
SS3. ^{1}H NMR (500 MHz, CD_3CN, LC-SPE-NMR) spectra of malbranpyrroles A-C (**1**-**3**) and E-F (**5**-**6**)



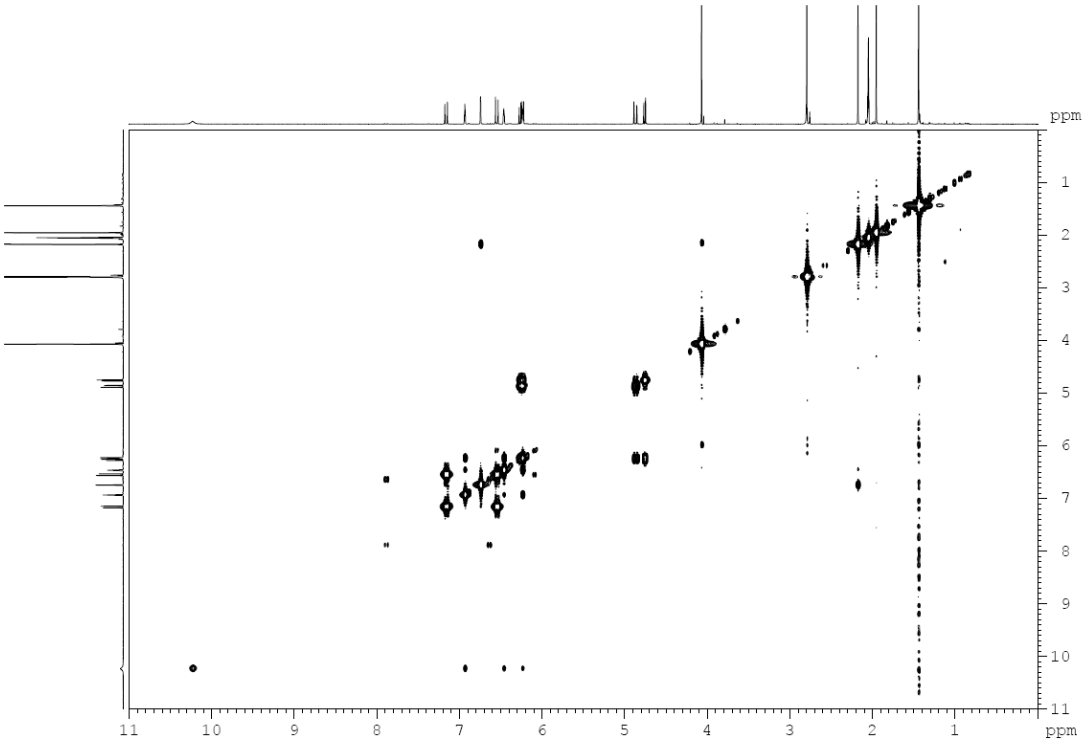
SS4. ^{1}H NMR (500 MHz, CD_3CN, LC-SPE-NMR) expanded spectra of malbranpyrroles A-C (**1**-**3**) and E-F (**5**-**6**)



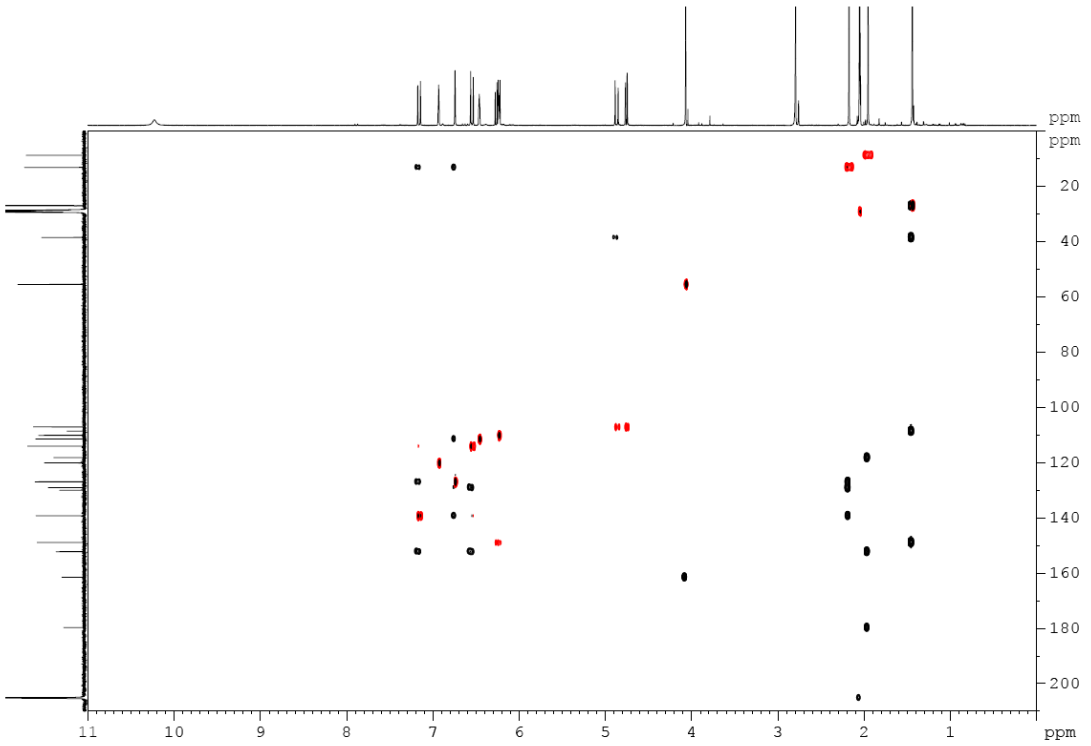
SS5. ^{13}C NMR (125 MHz, d_6-acetone) spectra of malbranpyrroles A (**1**) and C-F (**3**-**6**)



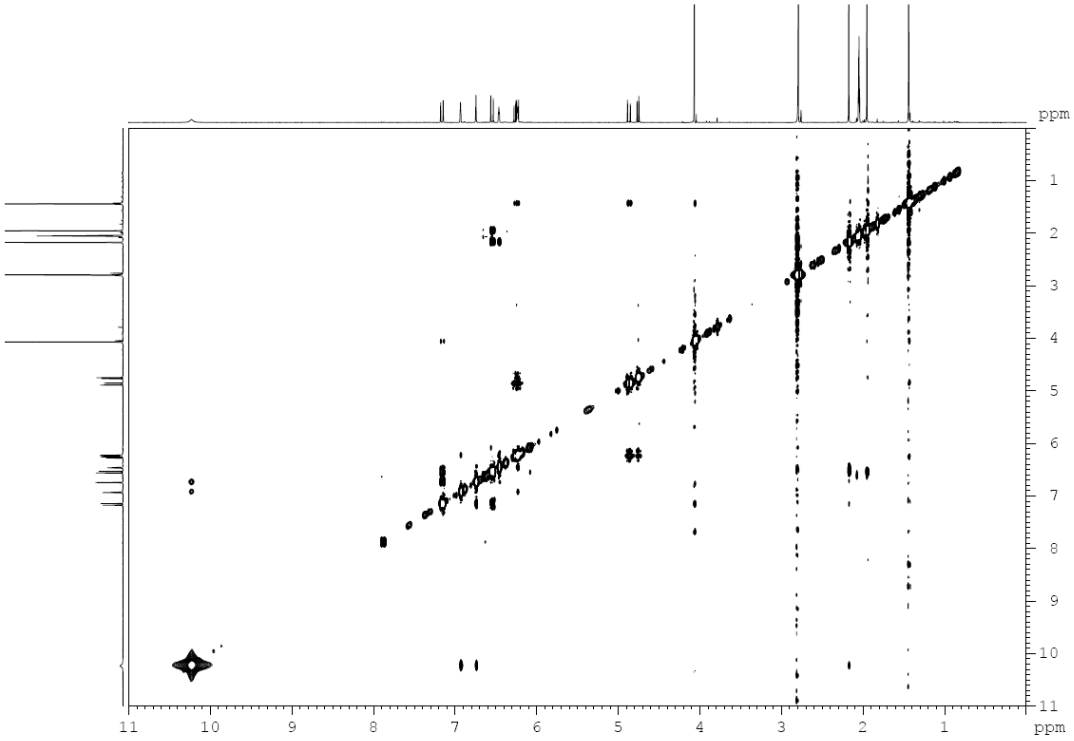
SS6. ^{13}C NMR (125 MHz, d_6-acetone) expanded spectra of malbranpyrroles A (**1**) and C-F (**3**-**6**)



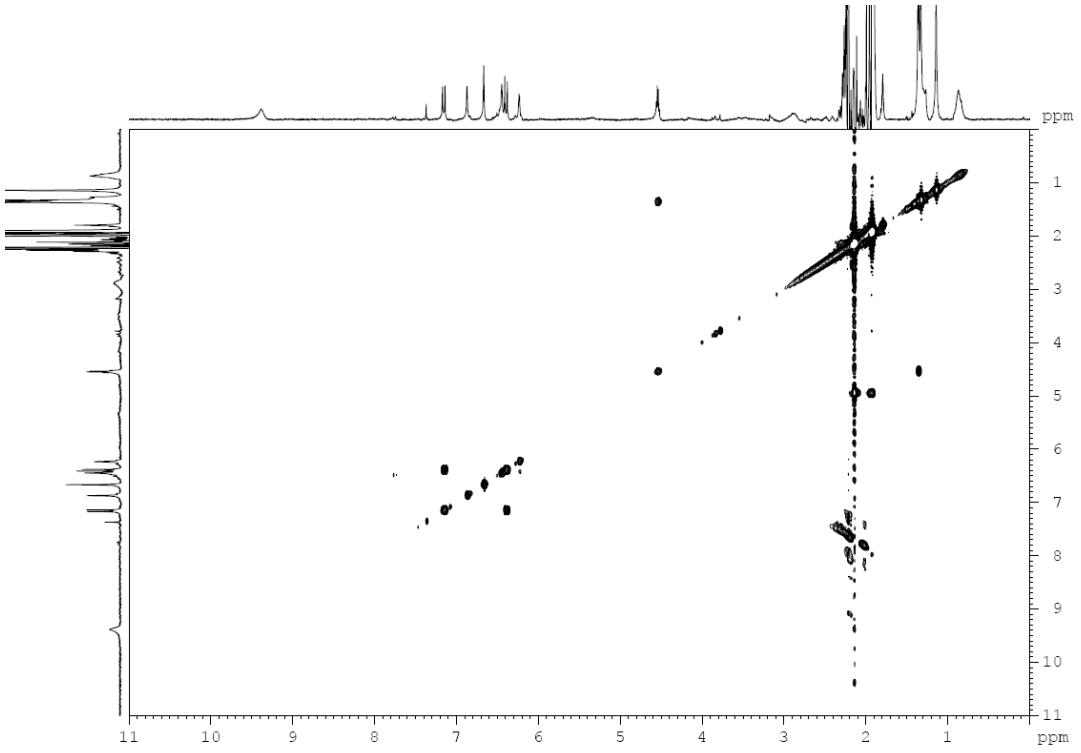
SS7. ^{1}H-^{1}H COSY spectrum of malbranpyrrole A (**1**)



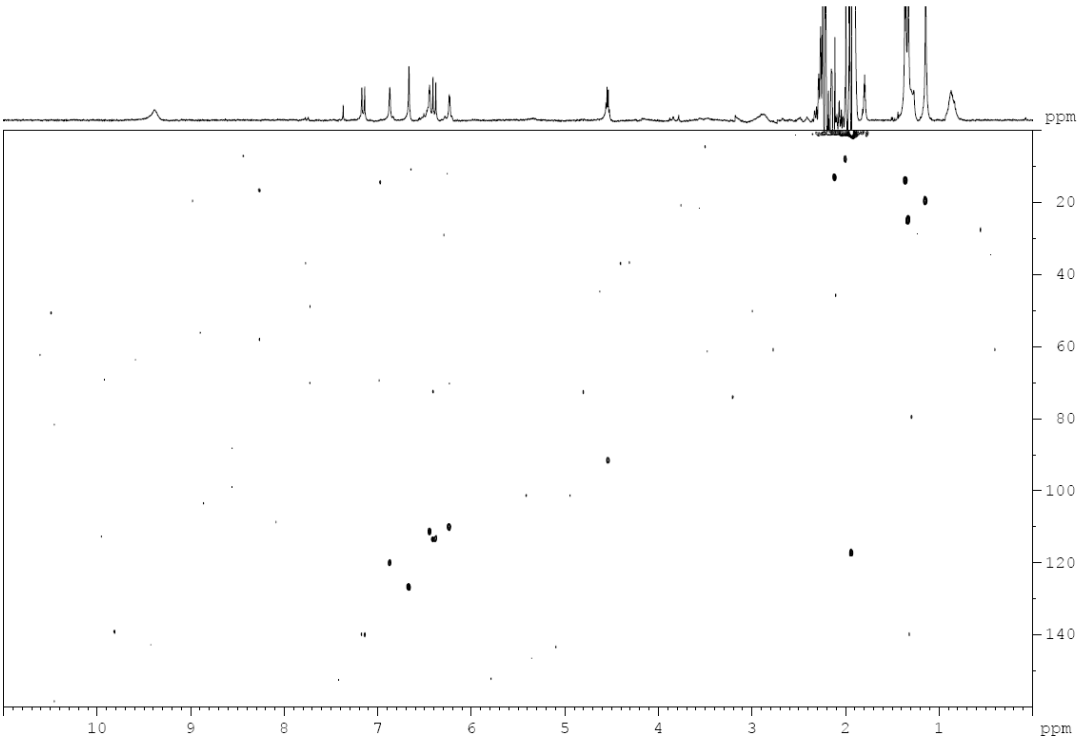
SS8. Superposition of HSQC (red) and HMBC (black) spectra of malbranpyrrole A (**1**)



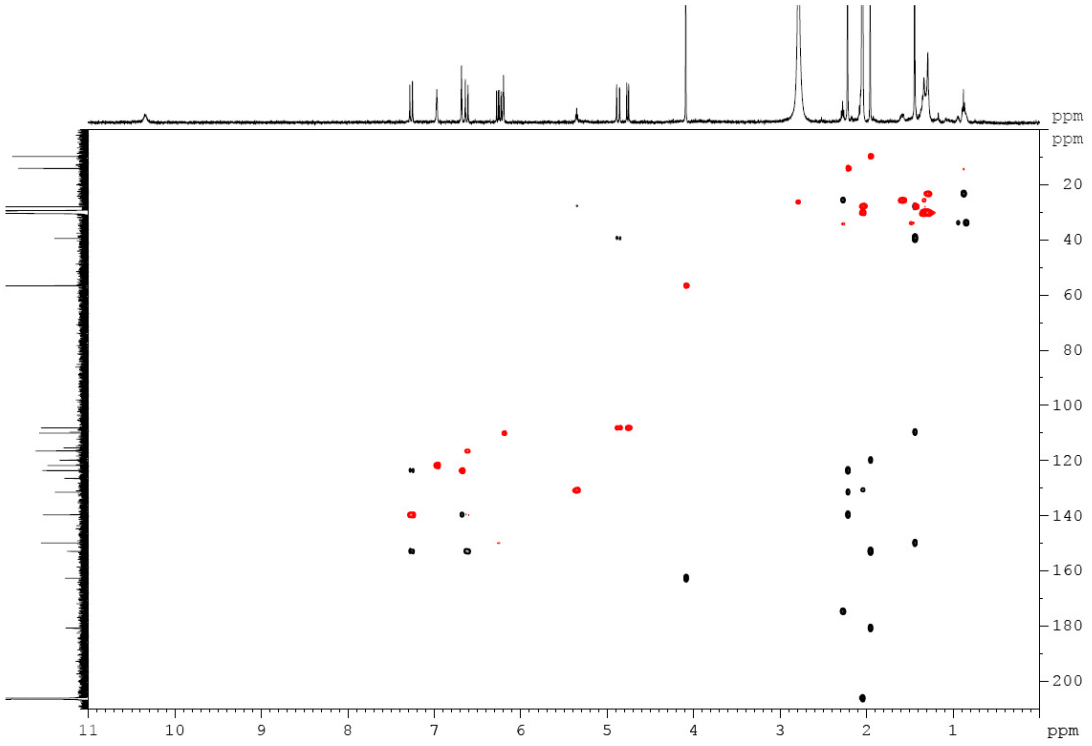
SS9. NOESY spectrum of malbranpyrrole A (**1**)



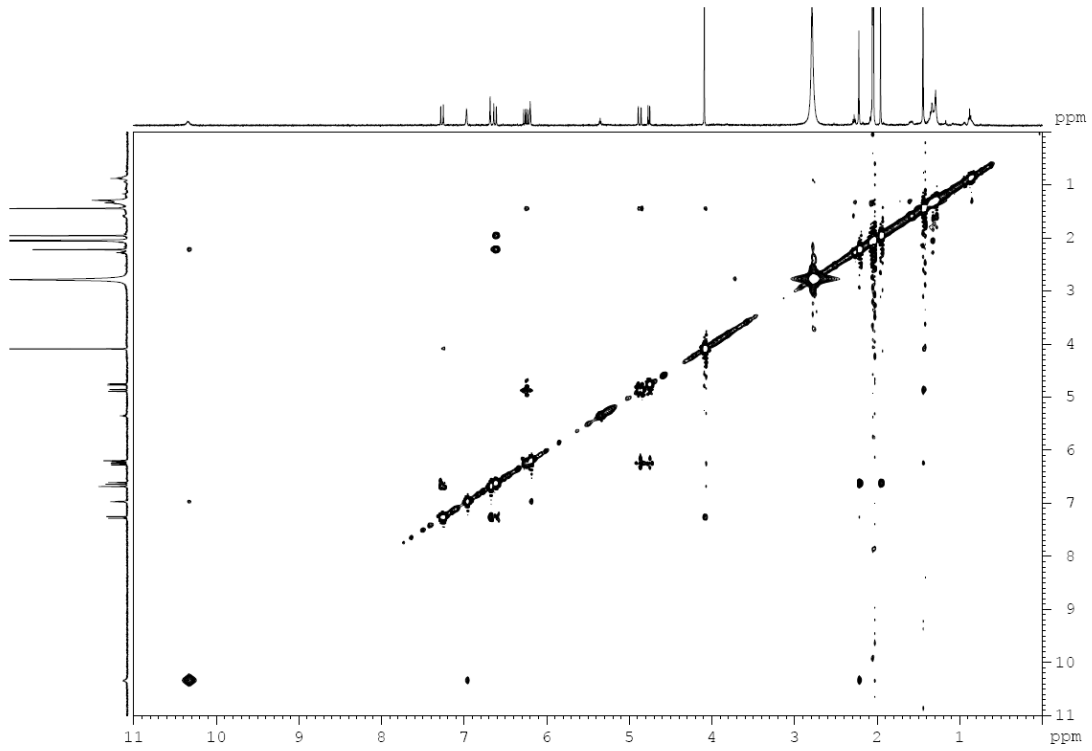
SS10. ^{1}H-^{1}H COSY spectrum (deduced from LC-SPE-NMR) of malbranpyrrole B (**2**)



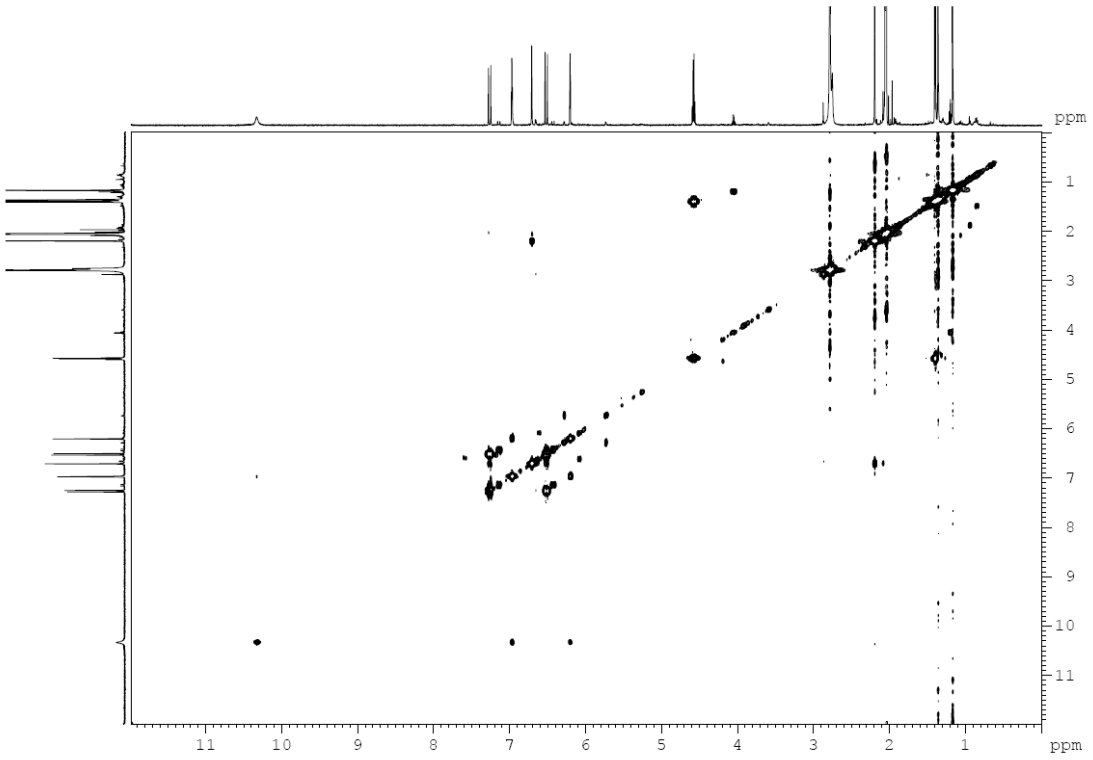
SS11. HSQC spectrum (deduced from LC-SPE-NMR) of malbranpyrrole B (**2**)



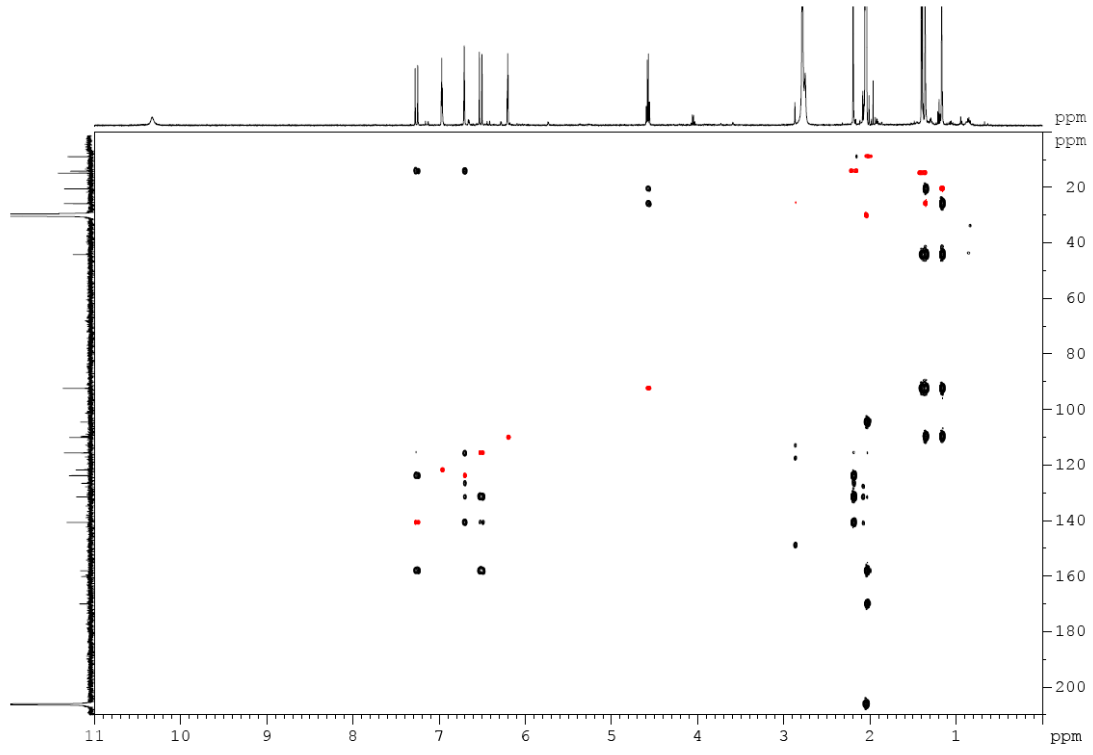
SS12. Superposition of HSQC (red) and HMBC (black) spectra of malbranpyrrole C (**3**)



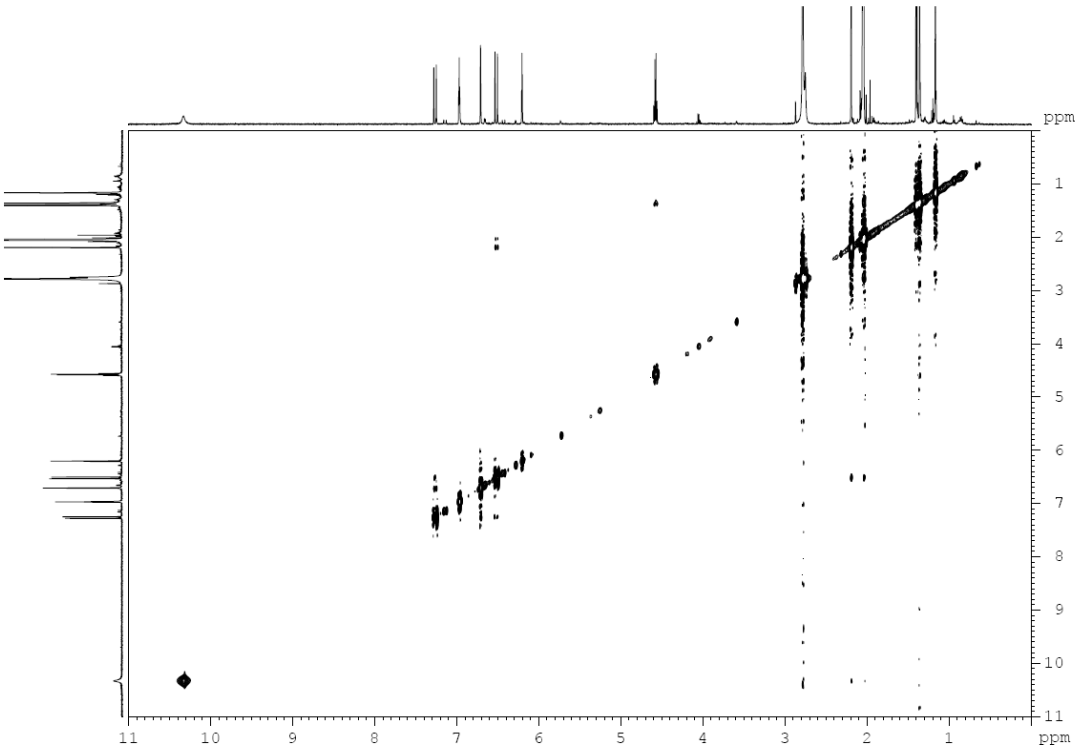
SS13. NOESY spectrum of malbranpyrrole C (**3**)



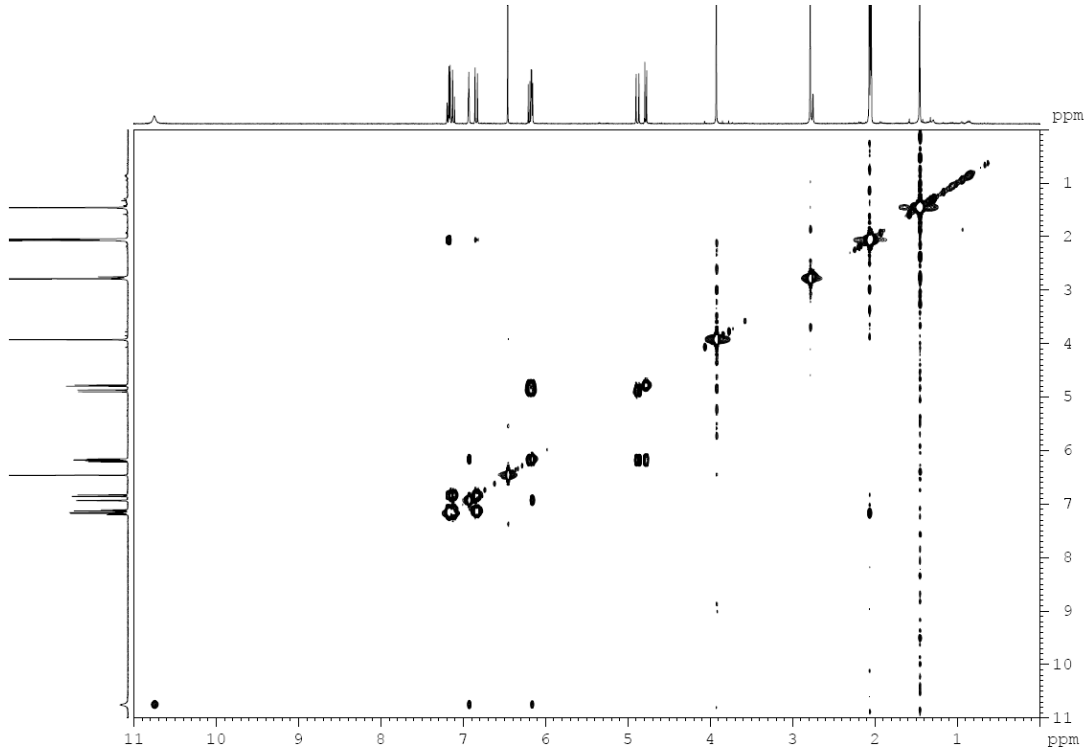
SS14. ^{1}H-^{1}H COSY spectrum of malbranpyrrole D (**4**)



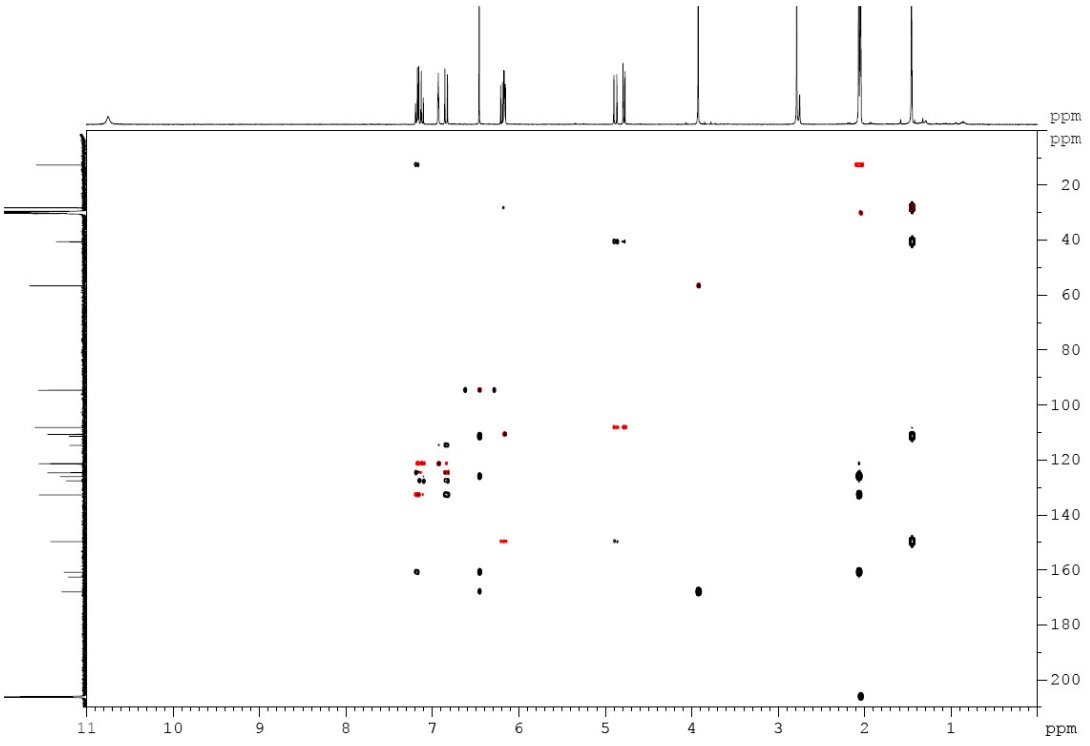
SS15. Superposition of HSQC (red) and HMBC (black) spectra of malbranpyrrole D (**4**)



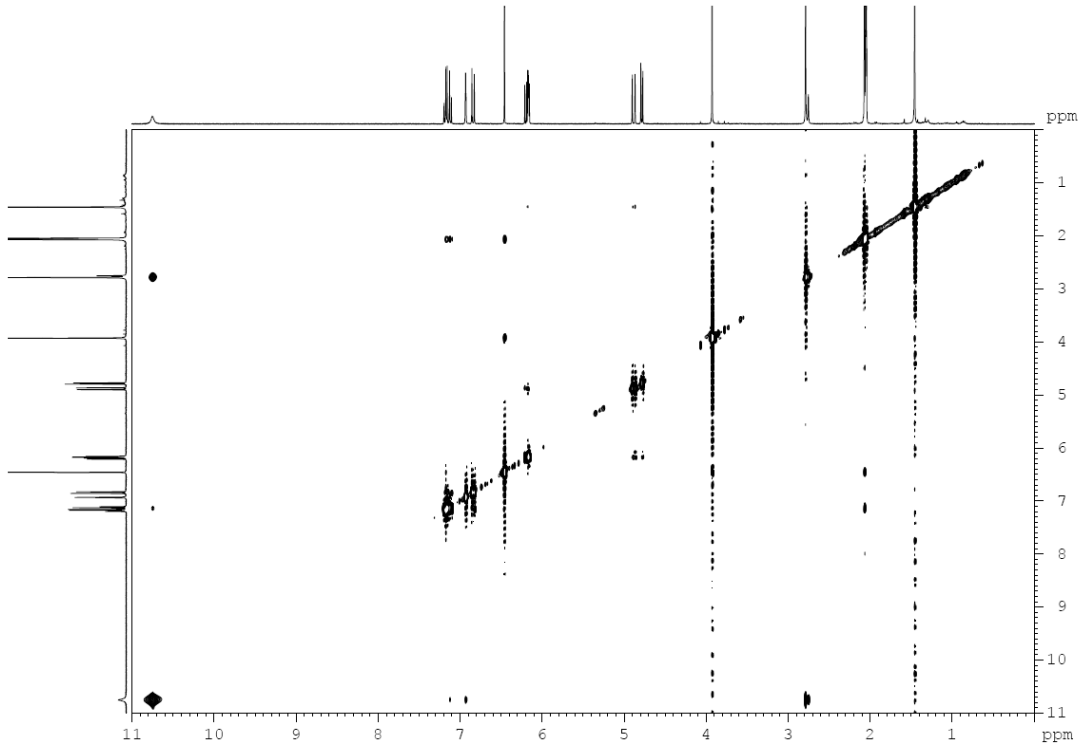
SS16. NOESY spectrum of malbranpyrrole D (**4**)



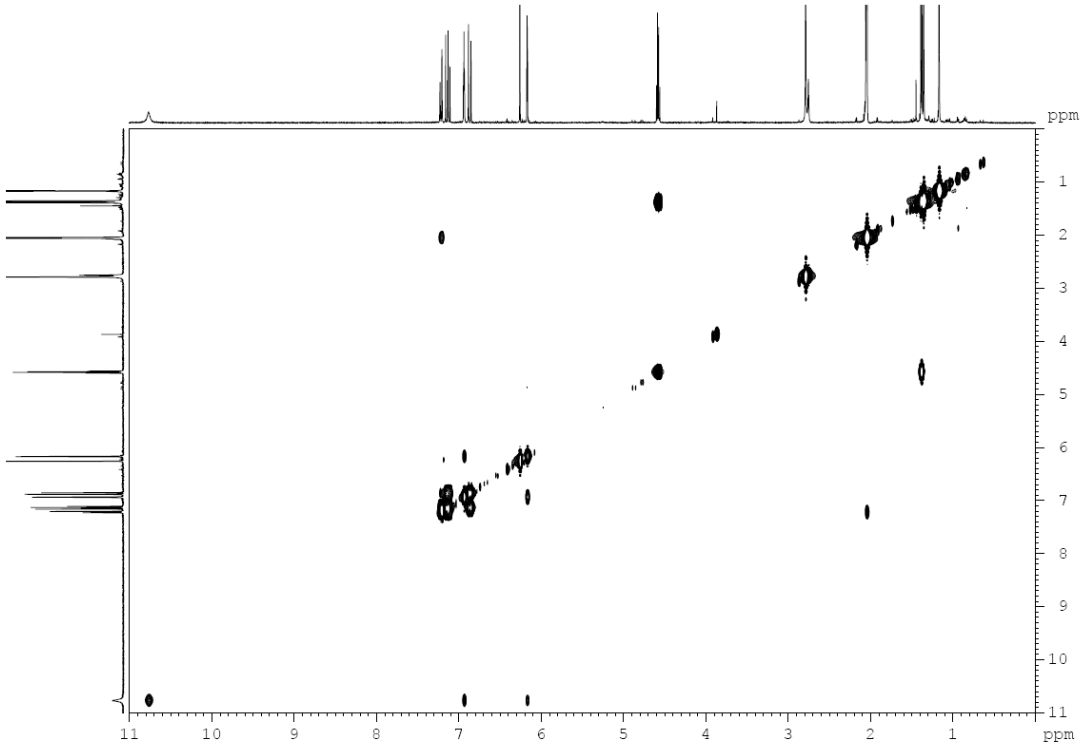
SS17. ^{1}H-^{1}H COSY spectrum of malbranpyrrole E (**5**)



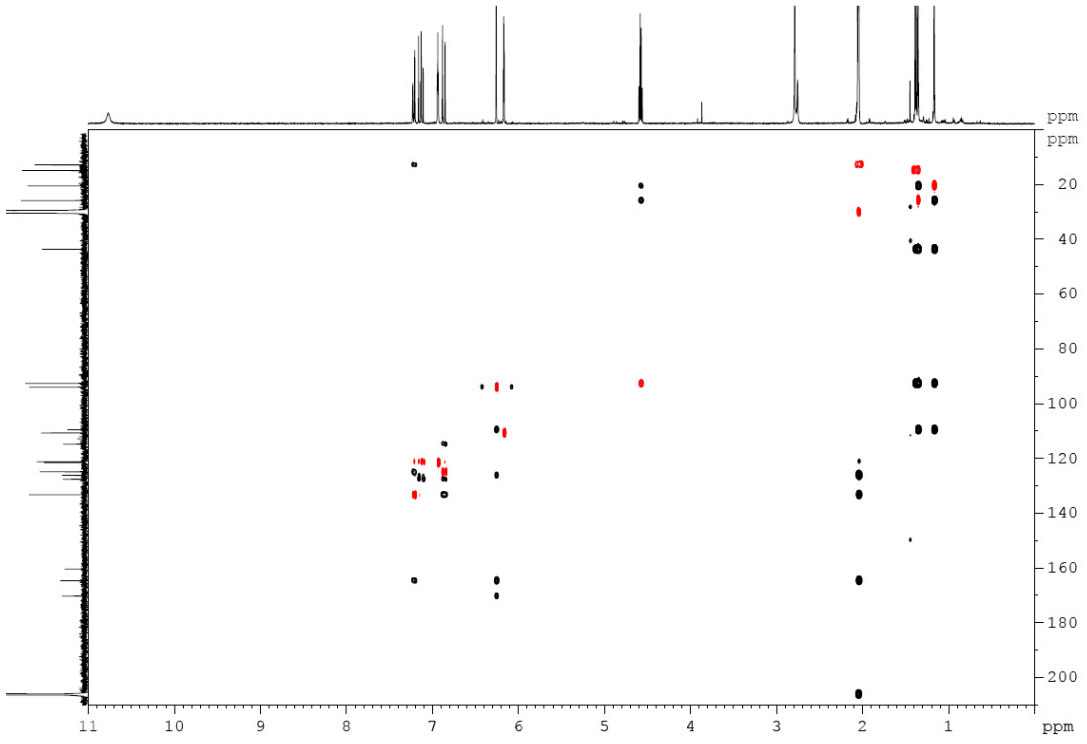
SS18. Superposition of HSQC (red) and HMBC (black) spectra of malbranpyrrole E (**5**)



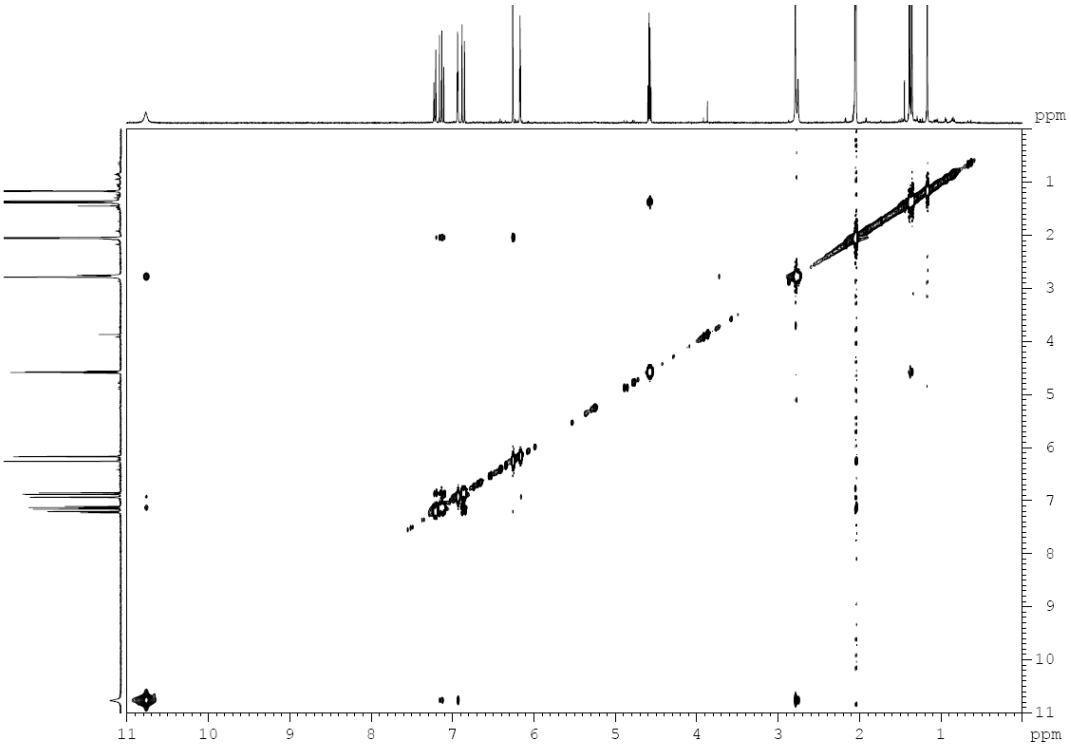
SS19. NOESY spectrum of malbranpyrrole E (**6**)



SS20. ^{1}H-^{1}H COSY spectrum of malbranpyrrole F (**6**)



SS21. Superposition of HSQC (red) and HMBC (black) spectra of malbranpyrrole F (**6**)



SS22. NOESY spectrum of malbranpyrrole F (**6**)