SUPPLEMENTARY MATERIAL

Two new epimers of C_{15}-acetogenin, 4-*epi*-isolaurallene and 4-*epi*-itomanallene as diastereomeric model

Chin-Soon Phan[1], Takashi Kamada[2] & Charles S. Vairappan[1]*

[1]*Laboratory of Natural Products Chemistry, Institute for Tropical Biology and Conservation, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia*

[2]*Laboratory of Natural Products Chemistry, Department of Materials and Life Science, Faculty of Science and Technology, Shizuoka Institute of Science and Technology, 2200-2 Toyosawa, Fukuroi, Shizuoka 437-8555, Japan*

*****Author to whom correspondence should be addressed; *****E-Mail: csv@ums.edu.my

Tel.: +60-88-320-000 ext. 2384; Fax: +60-88-320-291.

Two new C_{15}-acetogenins, 4-*epi*-isolaurallene (**1**) and 4-*epi*-itomanallene A (**2**) were isolated from a population of marine red alga *Laurencia nangii* Masuda from Carrington Reef. The structures of these compounds were determined intensively by NMR and HRESIMS data. Their configurations were elucidated by detailed comparison of chemical shifts, germinal protons splitting and nOe correlations with known and synthesized analogues. In addition, antibacterial activities of these compounds were evaluated. These compounds would serve as diastereomeric models for future reference. Since the isolaurallene, neolaurallene, 9-acetoxy-1,10,12-tribromo-4,7:6,13-bisepoxypentadeca-1,2-diene, itomanallene A and laurendecumallene A were isolated, compounds **1** and **2** were the sixth example of C_{15}-acetogenin with dioxabicyclo[7.3.0]dodecene skeleton.

Keywords: *Laurencia nangii*; red alga; Borneo; C_{15}-acetogenin; antibacterial

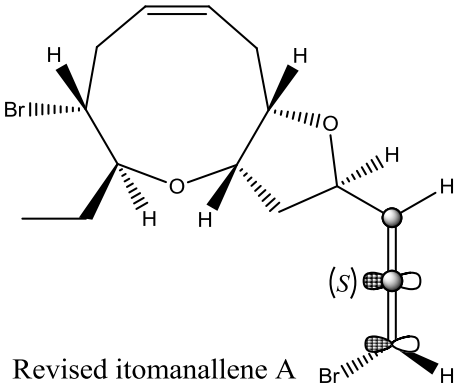
Supplementary Information

Table S1. ^{13}C (150 MHz) and ^{1}H NMR (600 MHz) of 1 and 2 ($CDCl_3$, δ in ppm, J in Hz).

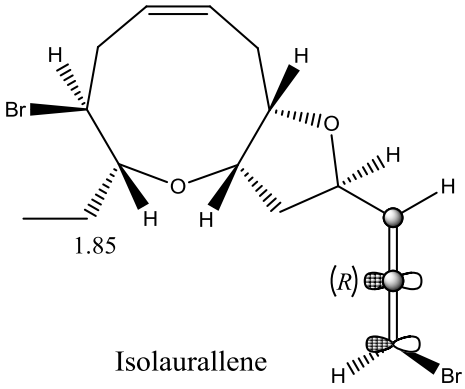
	1		2	
No.	**^{13}C**	**^{1}H**	**^{13}C**	**^{1}H**
1	73.8	6.04 dd (5.9, 1.8)	73.3	6.07 dd (5.6, 1.1)
2	201.5		201.6	
3	101.9	5.54 t (5.9)	102.1	5.61 dd (7.6, 5.6)
4	73.6	4.36 tdd (6.9, 5.9, 1.8)	75.1	4.53 td (7.6, 6.2)
5	40.7	2.44 dt (13.1, 6.9)	39.3	2.29-2.31 m
		1.84-1.85 m		2.03-2.04 m
6	82.9	3.92-3.94 m	73.3	4.04 br
7	82.1	3.94-3.96 m	80.9	3.76-3.77 m
8	29.4	2.81 q (11.0)	27.1	2.78-2.80 m
		2.27 dt (11.0, 5.5)		2.31-2.33 m
9	128.5	5.68 td (11.0, 5.5)	127.6	5.59 q (10.0)
10	126.8	5.78 td (11.0, 5.5)	129.0	5.76 q (9.6)
11	32.2	3.44 ddd (14.4, 11.0, 4.1)	34.5	3.13 br
		2.37 ddd (14.4, 5.5, 2.1)		2.74-2.76 m
12	52.5	4.14 m	53.0	3.79-3.78 m
13	84.9	3.34 dt (9.6, 4.1)	83.8	3.74-3.75 m
14	23.9	1.79-1.81 m	23.5	2.03-2.04 m
				1.64 septet (6.9)
15	7.6	0.92 t (6.9)	11.2	1.08 t (6.9)

Table S2. Key positions different in chemical shifts ($CDCl_3$, δ in ppm).

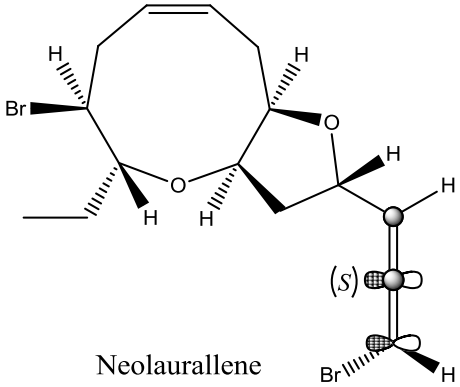
No.	1	2	Isolaurallene	Revised itomanallene A	Neolaurallene
3	δ_H 5.54	δ_H 5.61	δ_H 5.39	δ_H 5.48	δ_H 5.46
4	δ_H 4.36	δ_H 4.53	δ_H 4.75	δ_H 4.86	δ_H 4.86
6	δ_C 82.9	δ_C 73.3	δ_C 82.3	δ_C 72.6	δ_C 72.8
14	δ_H 1.79-1.81	δ_H 2.04	δ_H 1.85	δ_H 2.07	δ_H 2.06
		δ_H 1.62		δ_H 1.56-1.68	δ_H 1.63
15	δ_C 7.6	δ_C 11.2	δ_C 7.7	δ_C 11.4	δ_C 11.4



Revised itomanallene A

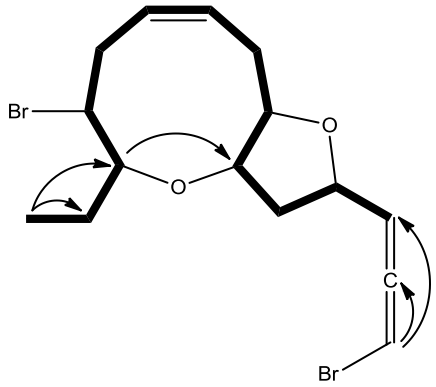


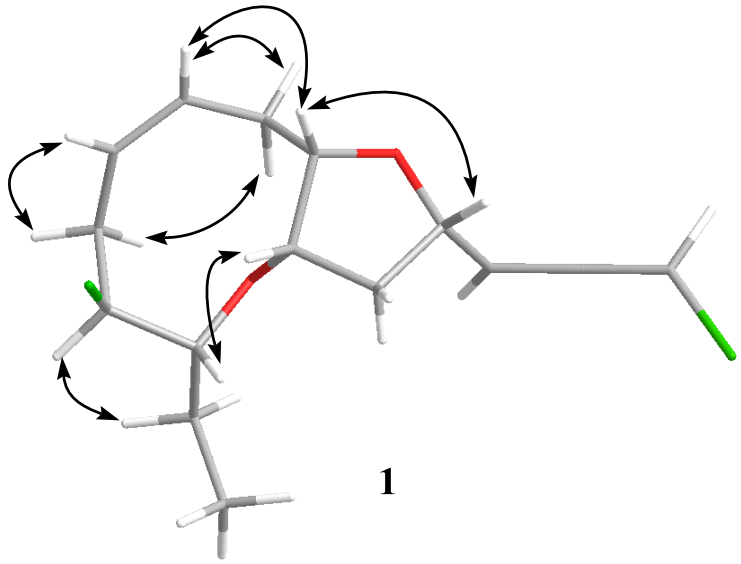
Isolaurallene



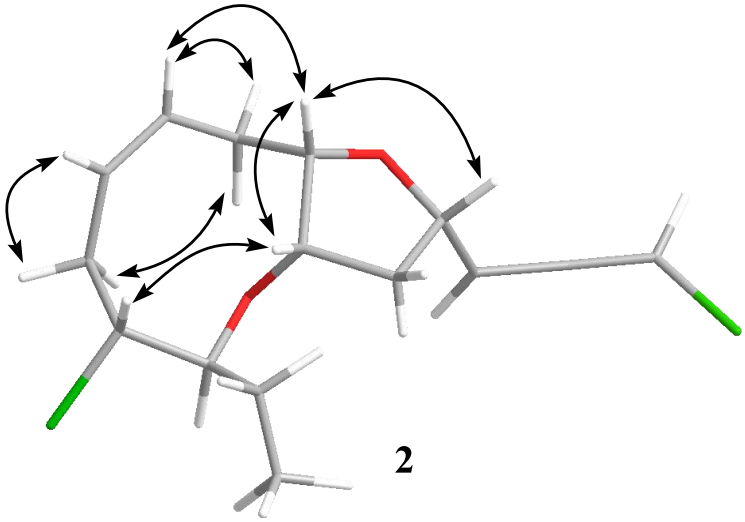
Neolaurallene

Figure S2. The ^{1}H-^{1}H COSY, key HMBC and NOE correlations of **1** and **2**.





1



2

Figure S3. ^{1}H NMR spectrum of **1** in $CDCl_3$ (600 MHz).

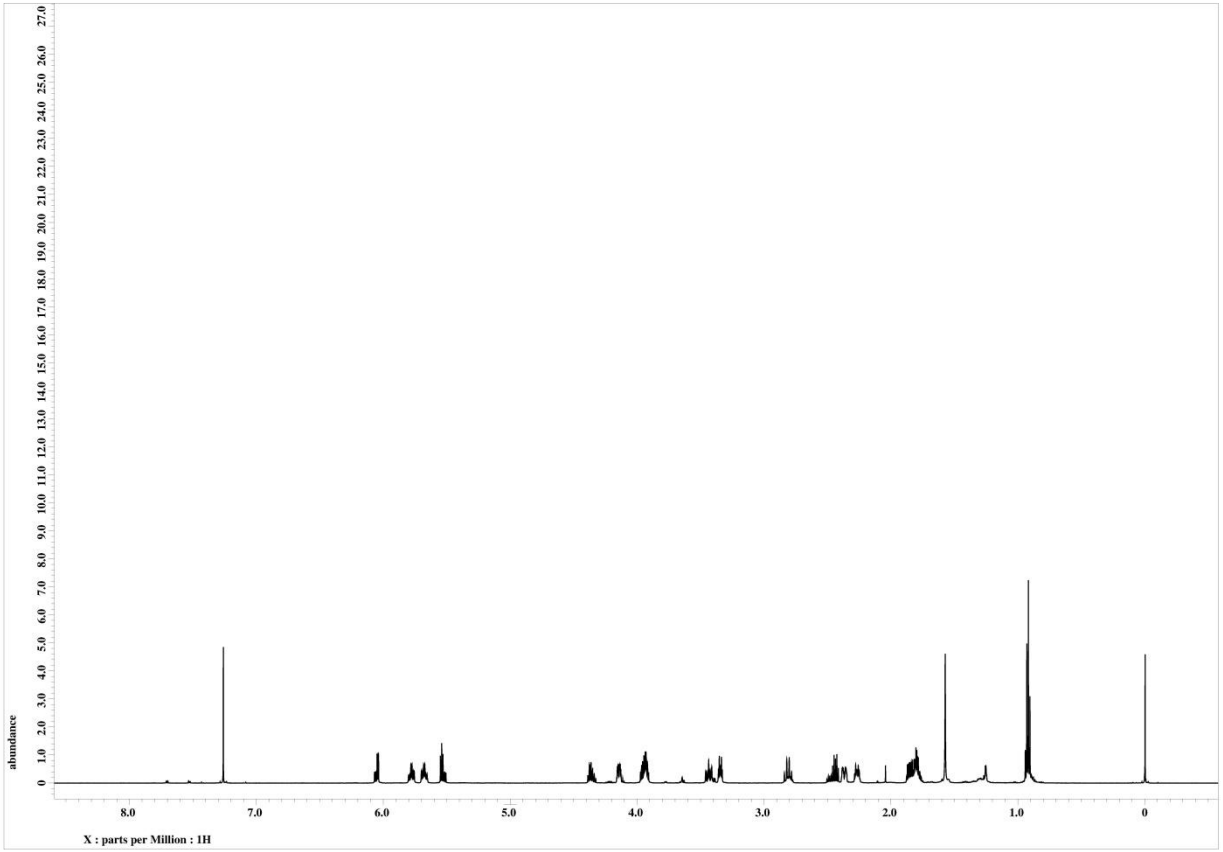


Figure S4. ^{13}C NMR spectrum of **1** in $CDCl_3$ (150 MHz).

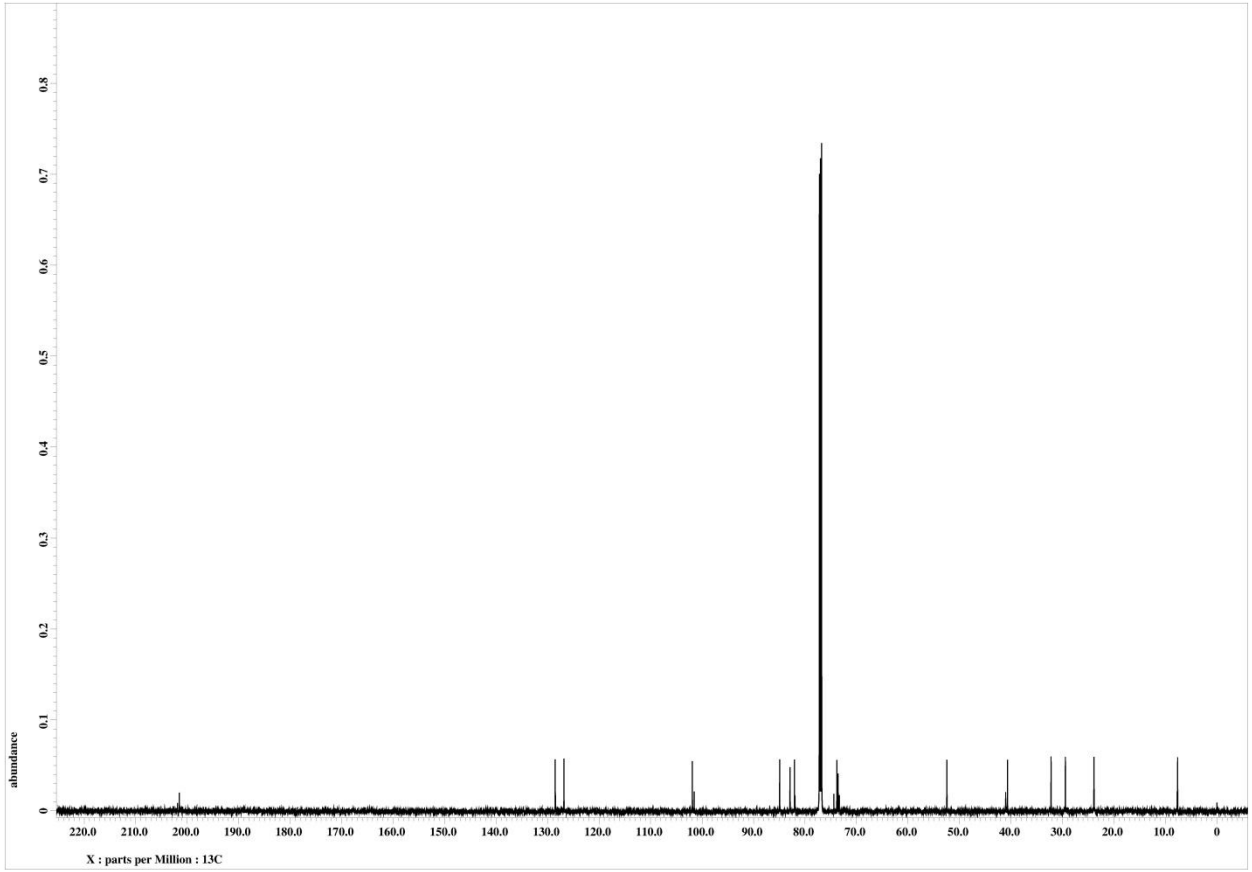


Figure S5. HSQC spectrum of **1** in $CDCl_3$.

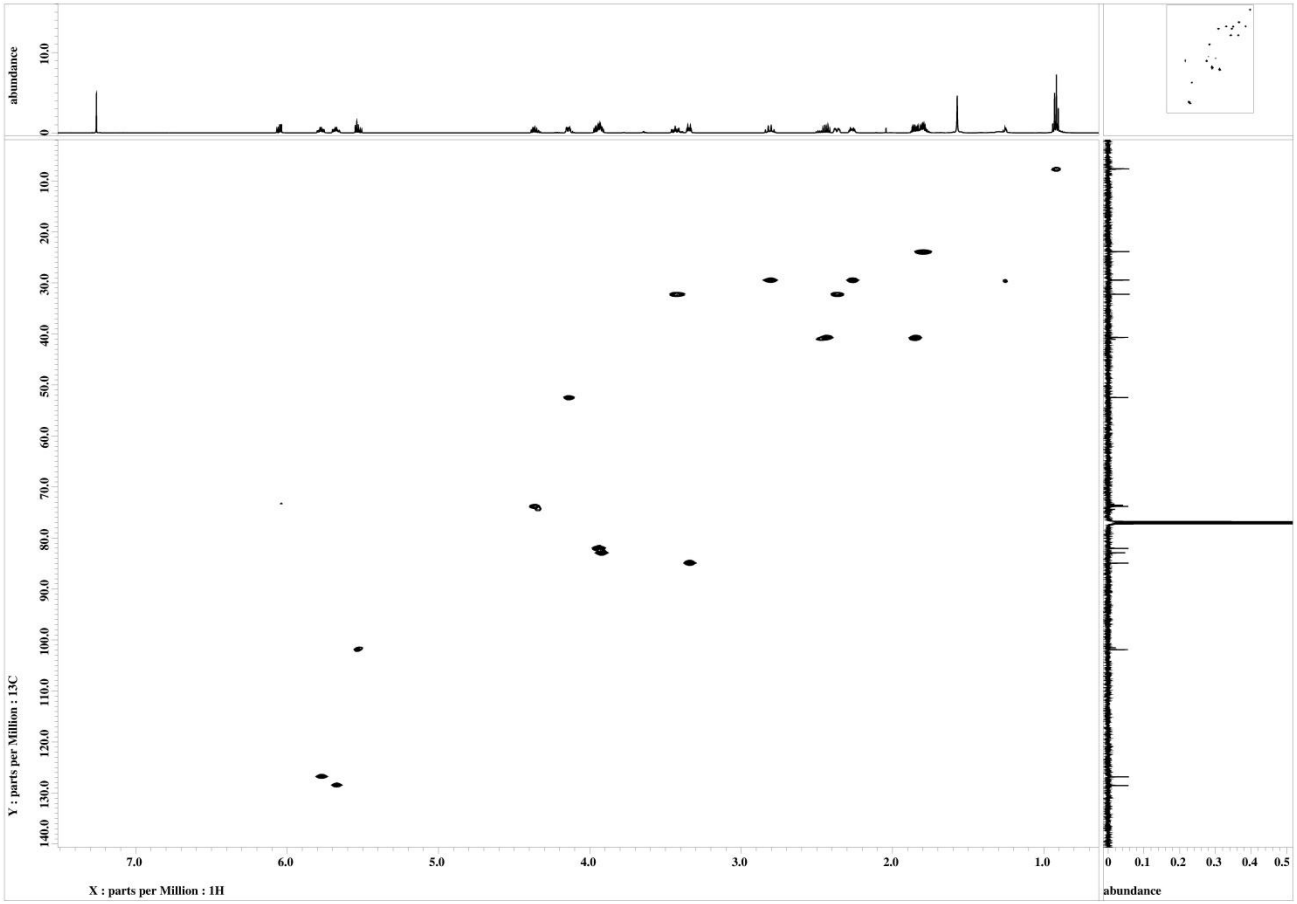


Figure S6. ^{1}H-^{1}H COSY spectrum of **1** in $CDCl_3$.

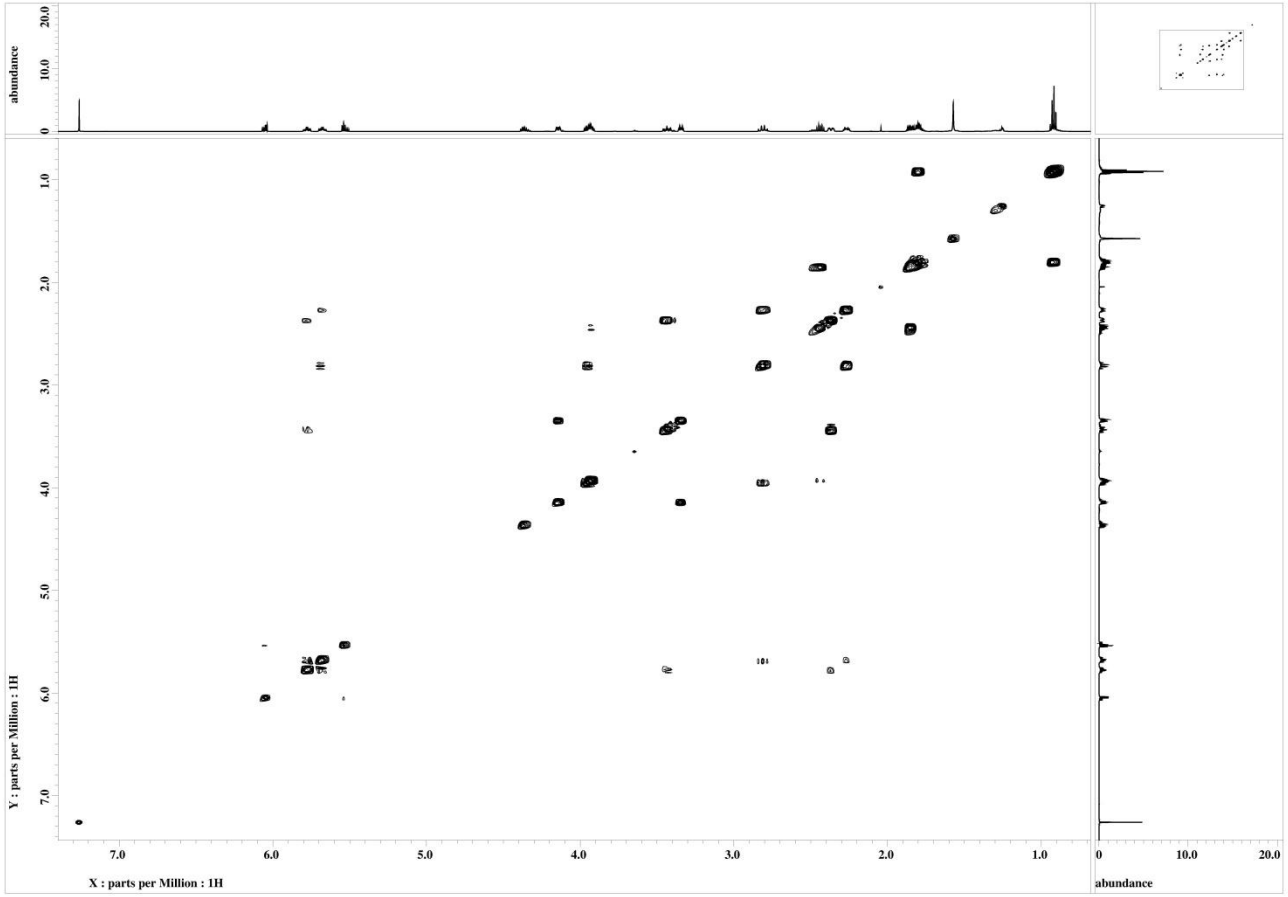


Figure S7. HMBC spectrum of **1** in $CDCl_3$.

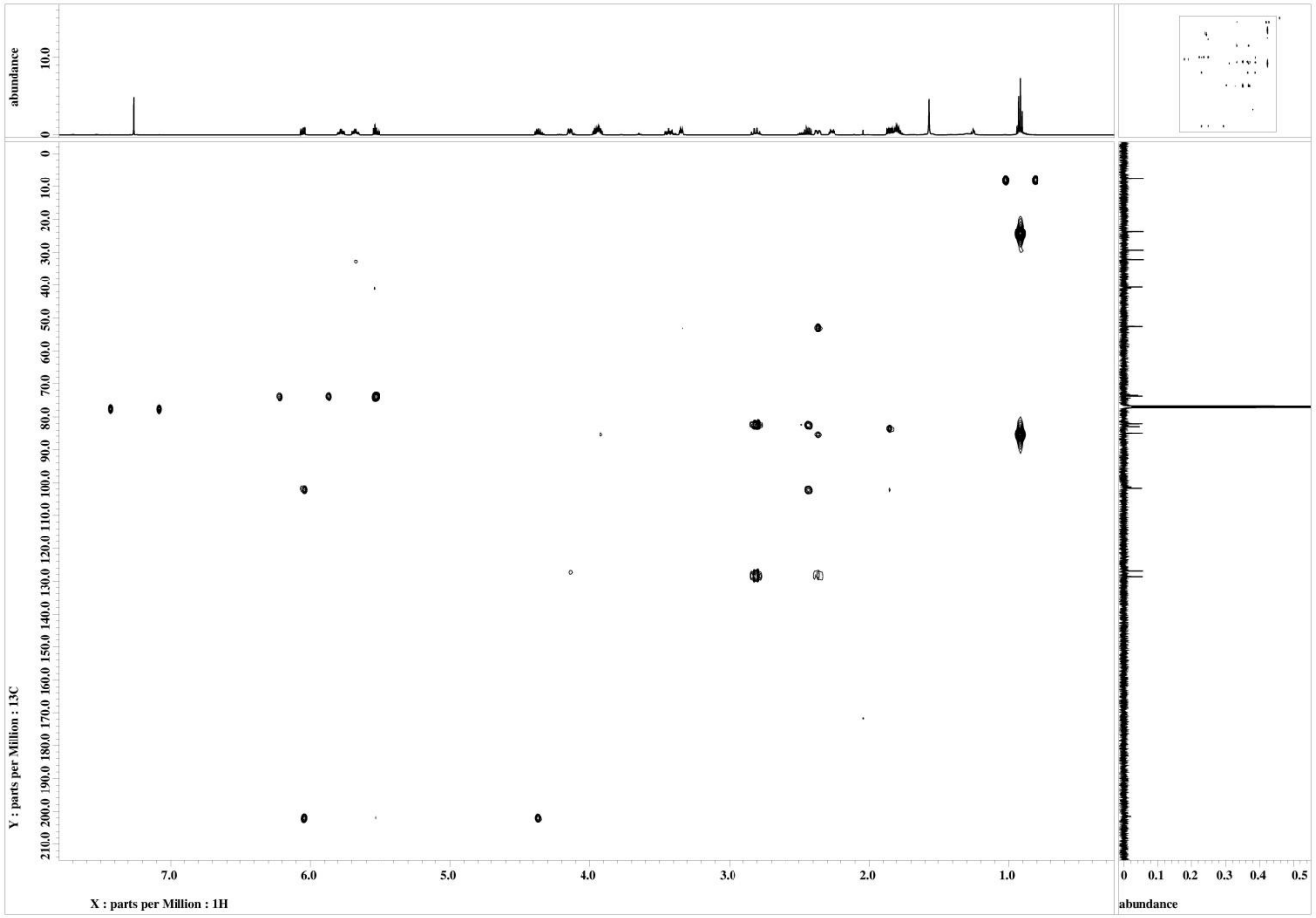


Figure S8. NOESY spectrum of **1** in $CDCl_3$.

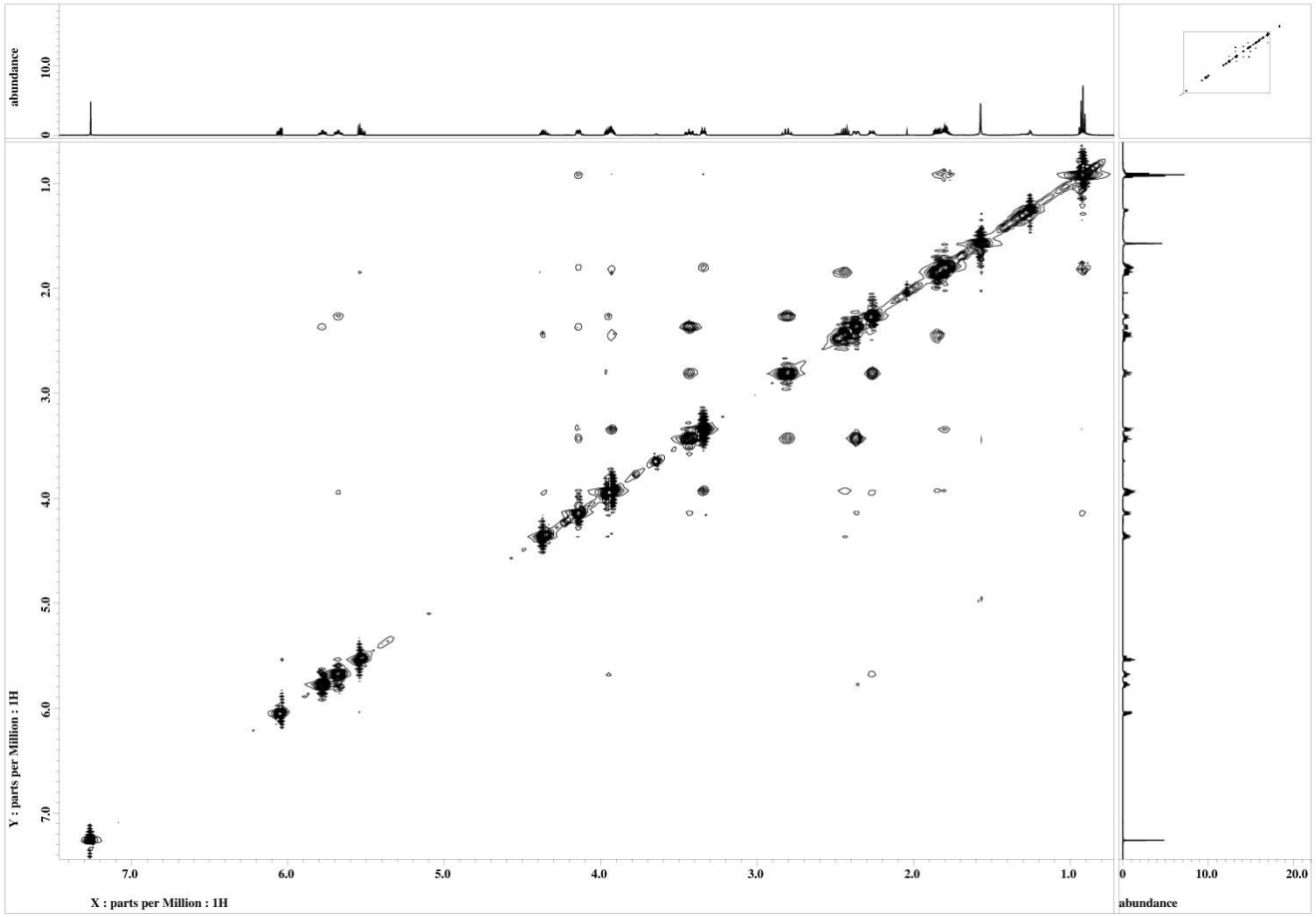
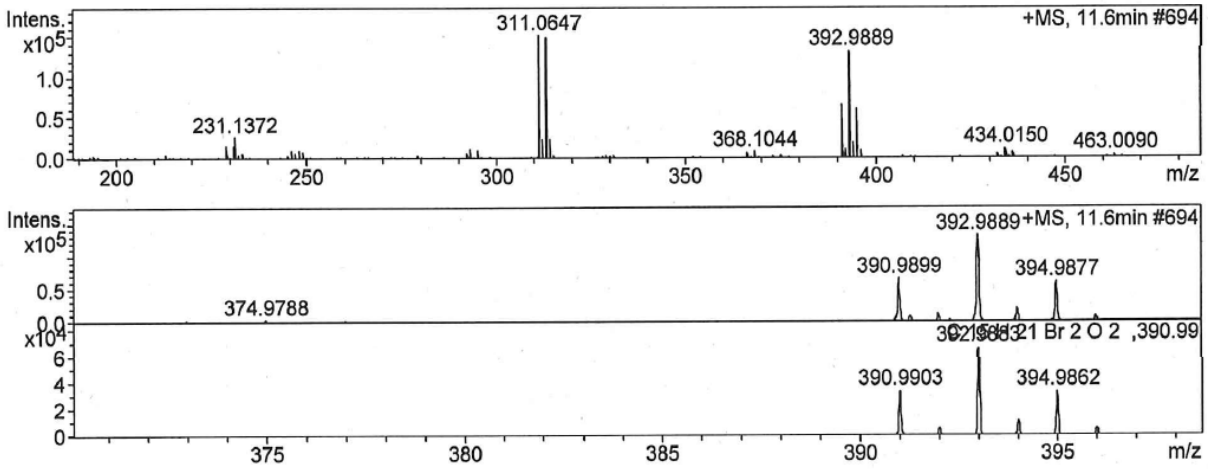


Figure S9. HRESIMS spectrum of **1**.



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
390.9899	1	C 15 H 21 Br 2 O 2	100.00	390.9903	0.4	1.1	14.2	4.5	even	ok
	2	C 10 H 16 Br O 11	0.00	390.9871	-2.8	-7.2	298.0	2.5	even	ok
	3	C 17 H 12 Br O 6	0.00	390.9812	-8.7	-22.2	300.8	11.5	even	ok
	4	C 21 H 12 Br O 3	0.00	390.9964	6.6	16.8	304.1	15.5	even	ok
	5	C 16 H 7 O 12	0.00	390.9932	3.3	8.6	548.2	13.5	even	ok
	6	C 23 H 3 O 7	0.00	390.9873	-2.5	-6.5	550.3	22.5	even	ok

Figure S10. ^{1}H NMR spectrum of **2** in $CDCl_3$ (600 MHz).

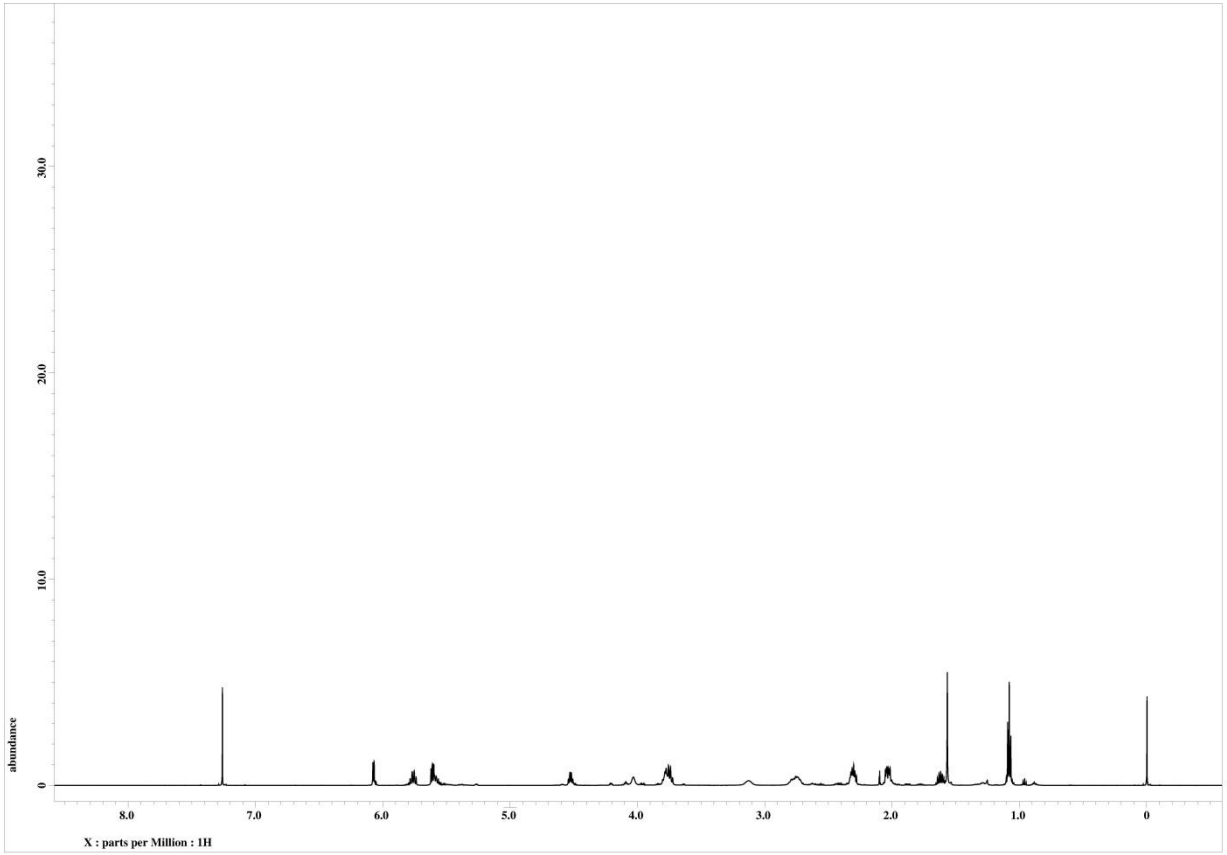


Figure S11. ^{13}C NMR spectrum of **2** in $CDCl_3$ (150 MHz).

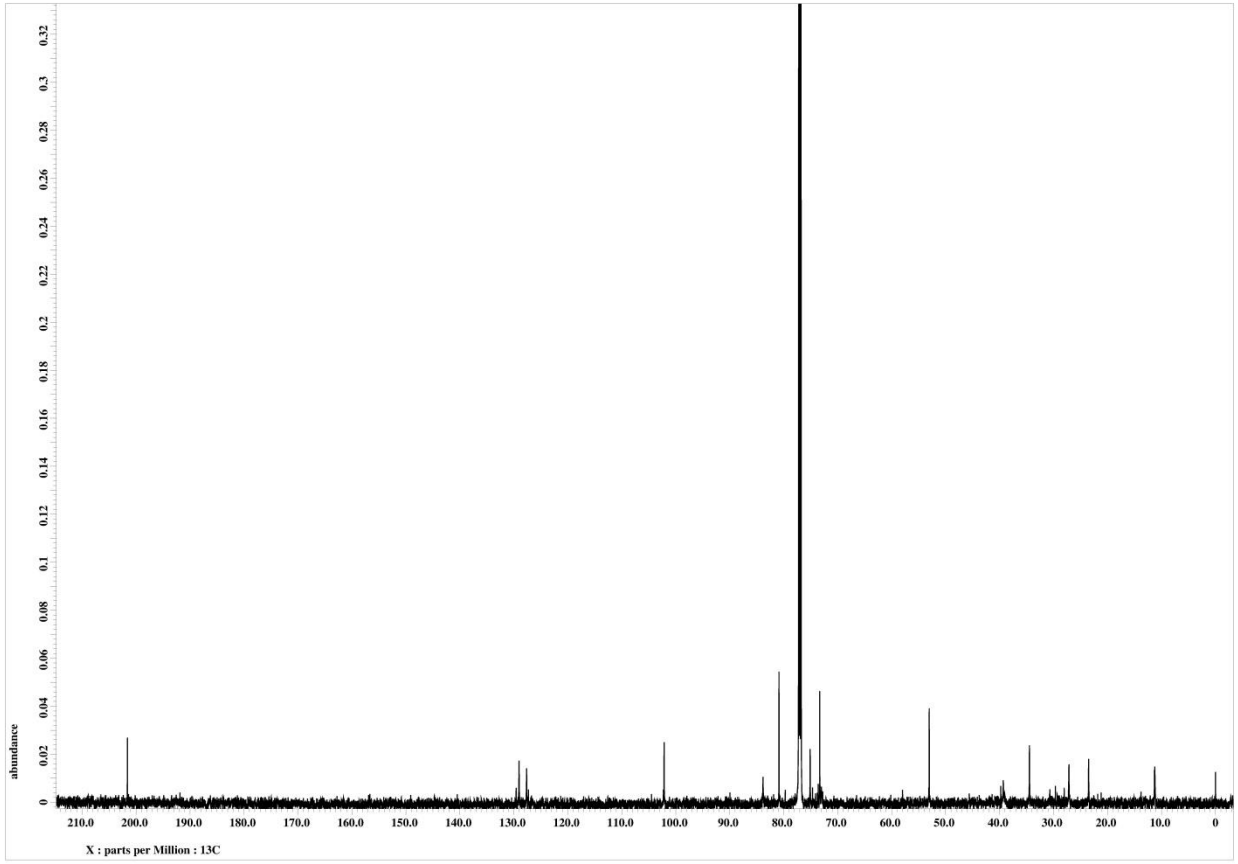


Figure S12. HSQC spectrum of **2** in $CDCl_3$.

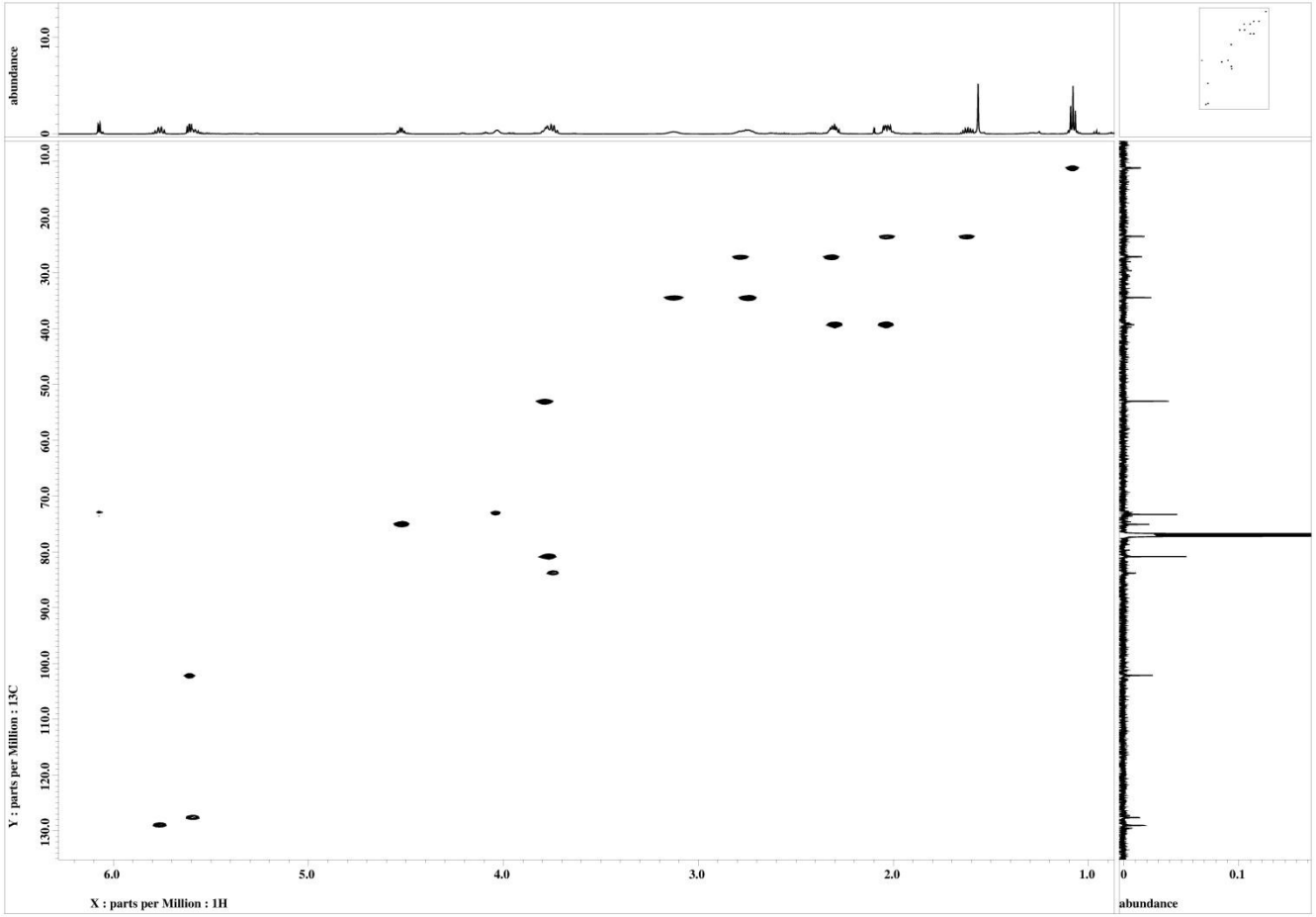


Figure S13. ^{1}H-^{1}H COSY spectrum of **2** in $CDCl_3$.

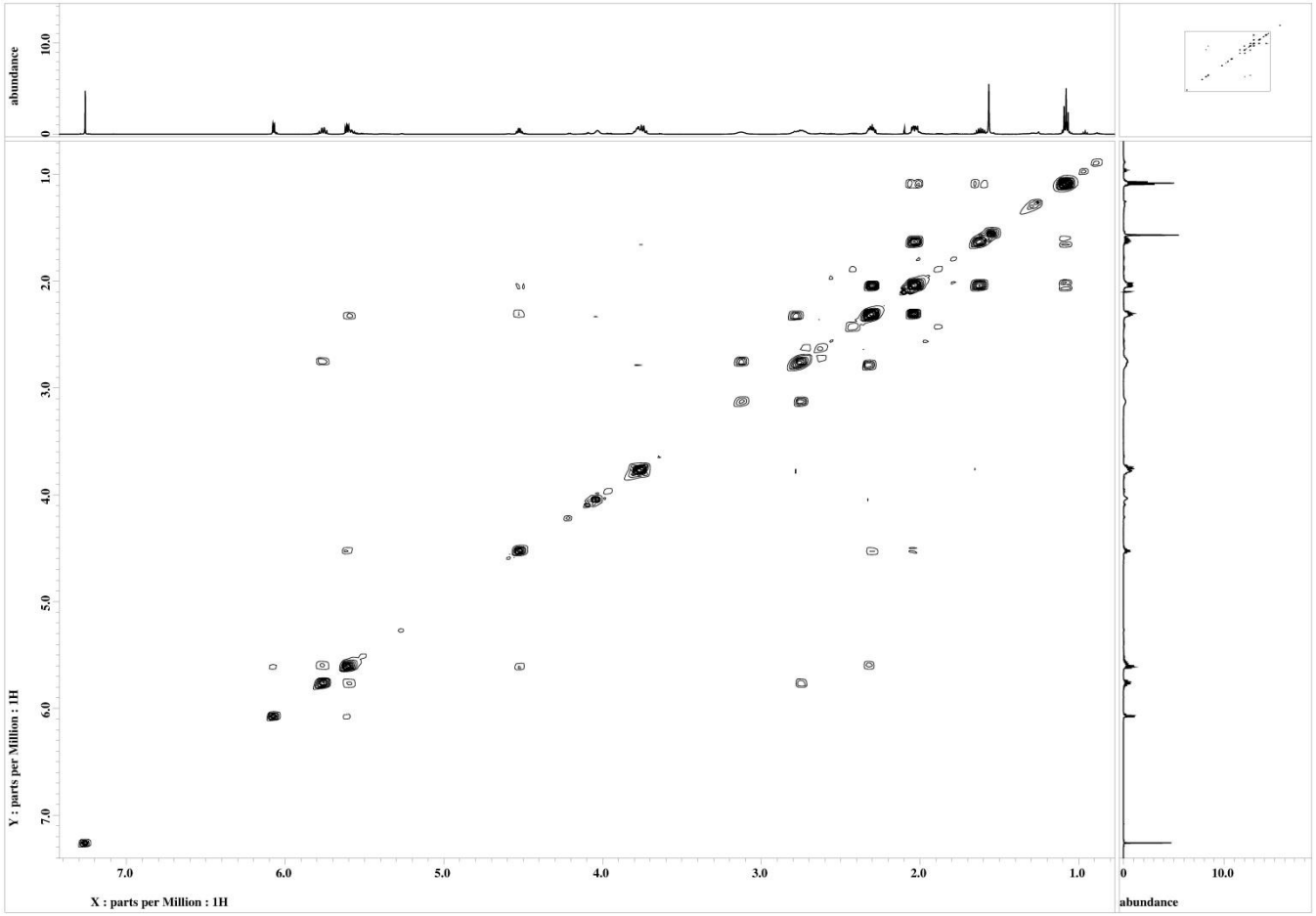


Figure S14. HMBC spectrum of **2** in $CDCl_3$.

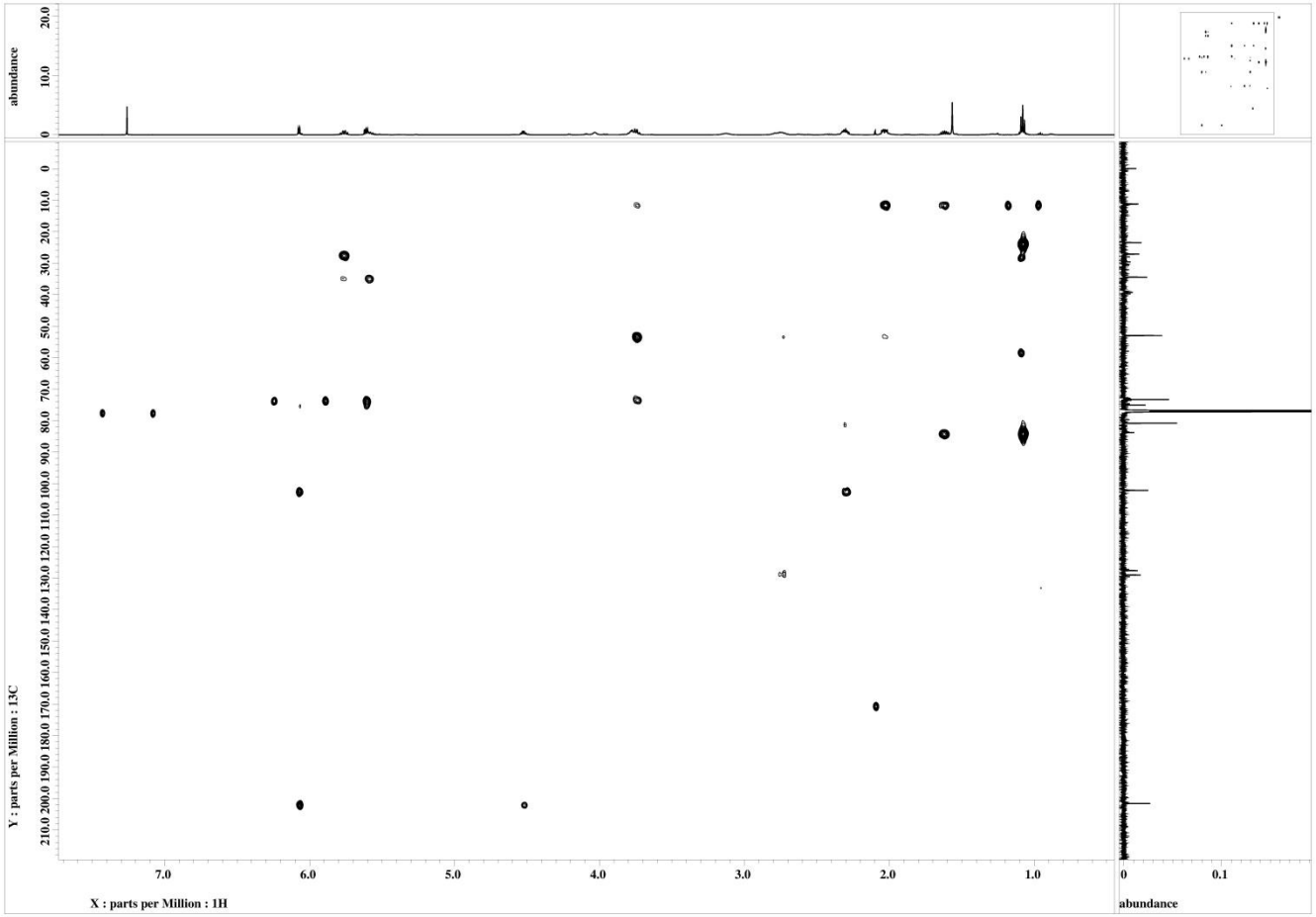


Figure S15. NOESY spectrum of **2** in $CDCl_3$.

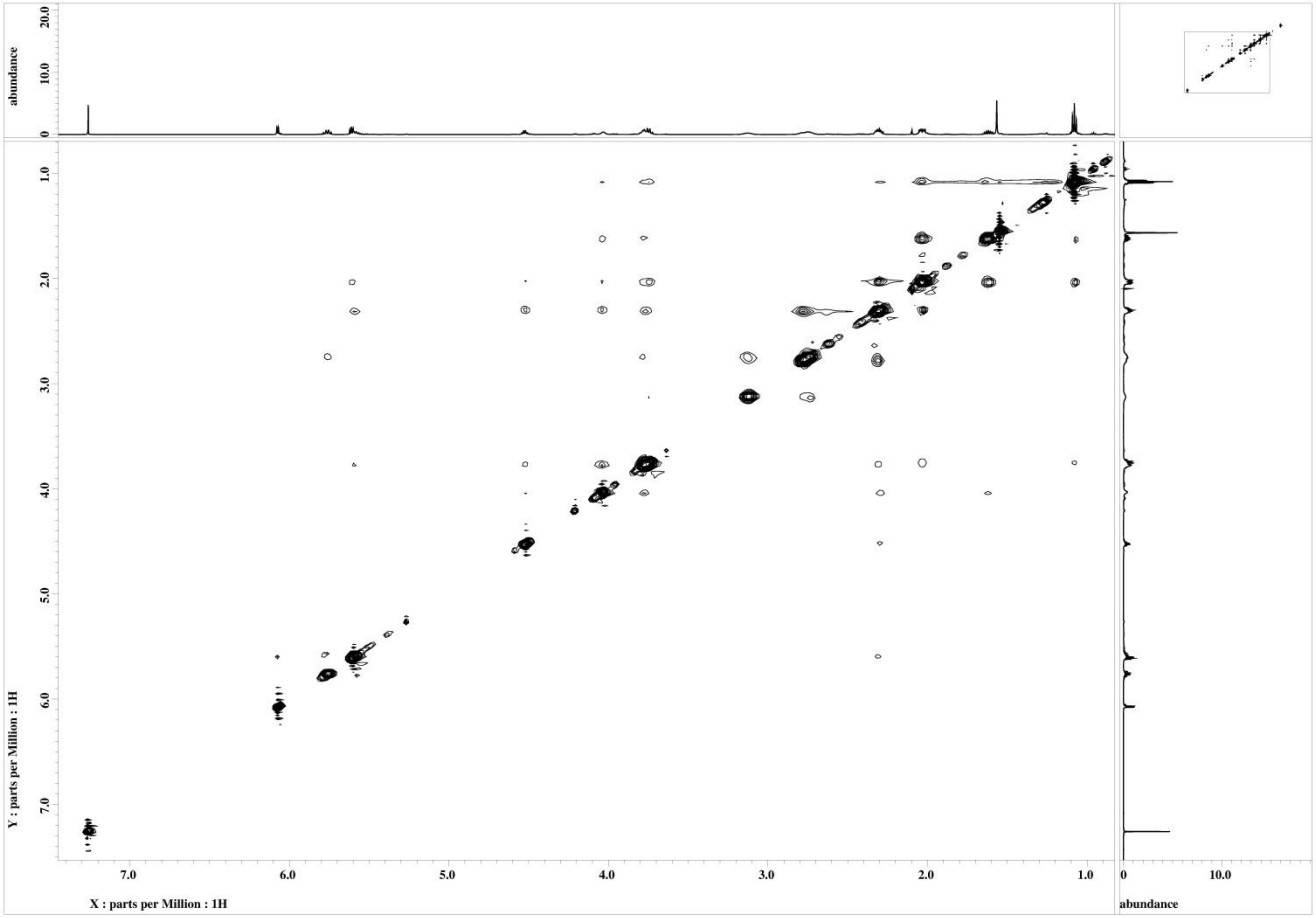
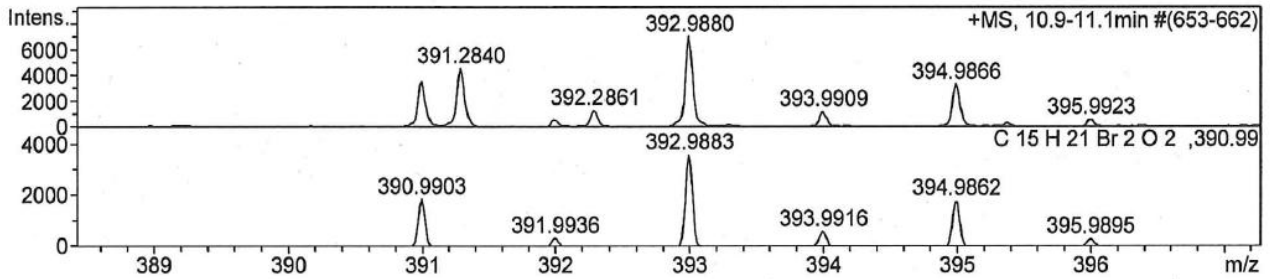


Figure S16. HRESIMS spectrum of **2**.



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
390.9893	1	C 15 H 21 Br 2 O 2	100.00	390.9903	1.0	2.6	10.9	4.5	even	ok
	2	C 10 H 16 Br O 11	0.00	390.9871	-2.2	-5.7	297.8	2.5	even	ok
	3	C 17 H 12 Br O 6	0.00	390.9812	-8.1	-20.7	299.9	11.5	even	ok
	4	C 21 H 12 Br O 3	0.00	390.9964	7.2	18.3	302.8	15.5	even	ok
	5	C 16 H 7 O 12	0.00	390.9932	3.9	10.1	548.0	13.5	even	ok
	6	C 23 H 3 O 7	0.00	390.9873	-1.9	-5.0	550.3	22.5	even	ok