Supporting Information

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Monoester-Type C_{19}-Diterpenoid Alkaloids from *Aconitum carmichaelii* and Their Cardiotoxicity

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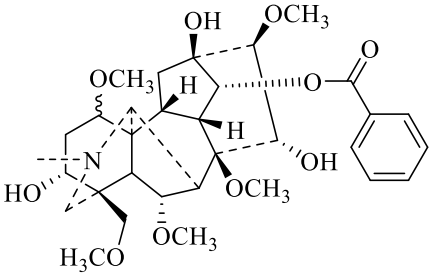
S1: NMR data calculation of compound 1

Conformational analyses of **1a** and **1b** (Figure S1) were carried out via Monte Carlo searching with the MMFF94s molecular mechanics force field using the MOE 2008 software[1]. 9 of **1a** (Figure S2) and 9 of **1b** (Figure S4) conformers having relative energies within 2 kcal/mol were optimized using DFT at the B3LYP/6-31G (d) level in vacuum with the Gaussian 16 program (Table S1 and S4)[2].

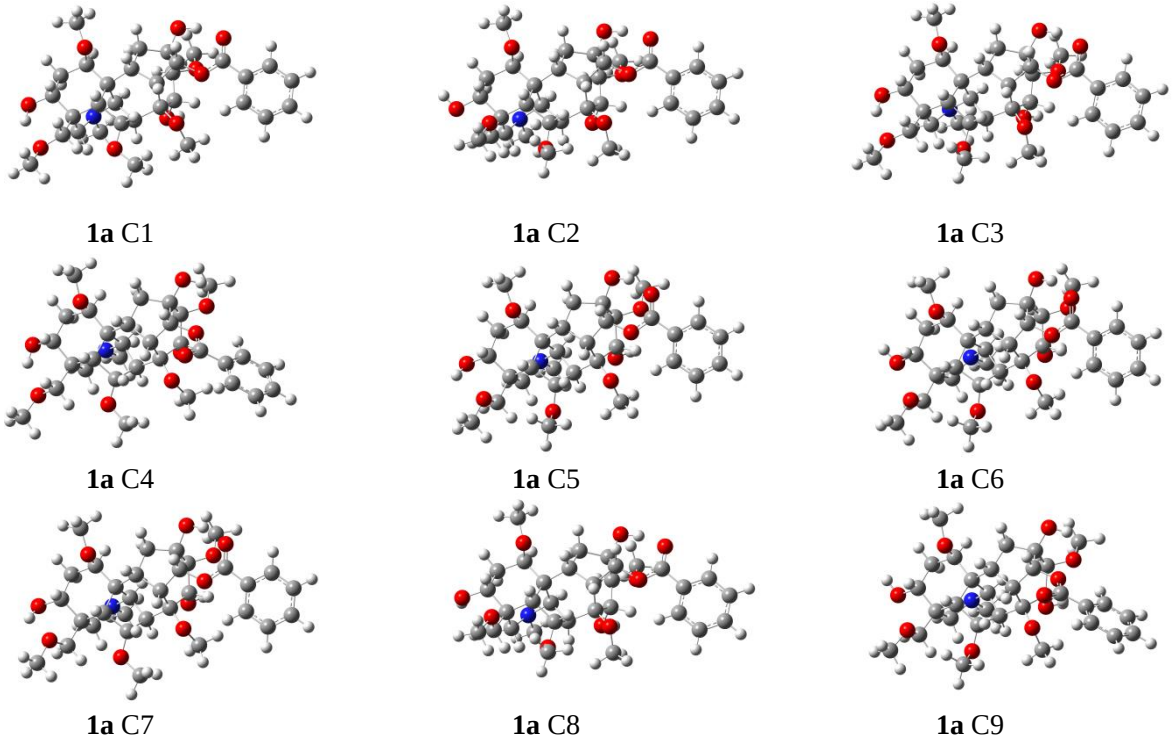


1a 1β-OCH_3
1b 1a-OCH_3

Figure S1: Proposed configurations of C-1 in **1a** and **1b**

S2: NMR data calculation of 1a

NMR chemical shifts calculation for the ωB97XD/DGDZVP-optimized 9 conformers of **1a** (Boltzmann distribution ≥ 1%, Figure S2) were carried out at PCM/mPW1PW91/6-311+G (d, p) level in acetone with GIAO method[3]. The calculated ^{13}C- and ^{1}H-NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy (Tables S2 and S3). Linear correlation coefficients (R^2) were calculated for evaluation of the comparative results of the experimental data and the calculated data (Figure S3). The isotropic values of TMS were calculated in the same level and used as references. The DP4+ parameters were calculated using the excel file, which was provided by Ariel M. Sarotti[4].



1a C1 **1a** C2 **1a** C3

1a C4 **1a** C5 **1a** C6

1a C7 **1a** C8 **1a** C9

Figure S2: ω B97XD/DGDZVP optimized 9 conformers of **1a** (Boltzmann distribution ⩾ 1%).

Table S1: Energy analysis for the conformers of **1a**.

Conf.	MMFF energy	B3LYP/6-31+G(d, p) Gibbs free energy (298.15 K)			*ω*B97XD/DGDZVP Gibbs free energy (298.15 K)		
	ΔE (Kcal/mol)	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
1a-C1	0.0000	-2052.684745	0.0000	0.181	-2052.367131	0.0000	0.006
1a-C2	0.3185	-2052.682819	1.2090	0.024	-2052.368584	-0.9120	0.027
1a-C3	0.6815	-2052.68557	-0.5180	0.434	-2052.370133	-1.8840	0.140
1a-C4	1.1779	-2052.684447	0.1870	0.132	-2052.369804	-1.6770	0.099
1a-C5	1.1929	-2052.684445	0.1880	0.132	-2052.368834	-1.0690	0.035
1a-C6	1.2006	-2052.682815	1.2110	0.023	-2052.368584	-0.9120	0.027
1a-C7	1.5680	-2052.683009	1.0890	0.029	-2052.367206	-0.0470	0.006
1a-C8	1.7893	-2052.683195	0.9730	0.035	-2052.368901	-1.1110	0.038
1a-C9	1.9724	-2052.682074	1.6760	0.011	-2052.371542	-2.7680	0.622

Table S2: Experimental ^{13}C-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of **1a**.

No.	Exptl.	1a-C1	1a-C2	1a-C3	1a-C4	1a-C5	1a-C6	1a-C7	1a-C8	1a-C9	Averaged[a]	Unscaled shifts(δ_U)[b]	Scaled shifts(δ_S)[c]
2	30.3	155.2747	153.0484	154.9160	155.4376	155.8898	153.0485	156.7860	153.3445	153.0701	153.7064	35.2	30.8
3	70.2	109.8665	118.6983	110.7725	110.3337	117.6464	118.6982	117.4115	117.8027	118.6888	116.6231	72.2	66.1
4	44.2	141.8558	141.8752	141.8123	141.7225	141.3065	141.8753	141.4583	141.3195	141.7645	141.7388	47.1	42.2
5	42.5	139.0281	143.9322	141.5139	138.7136	144.0982	143.9321	140.4471	143.9707	143.3729	142.6860	46.2	41.3
11	51.7	134.2883	133.7522	133.7882	134.5238	133.3719	133.7522	133.8195	133.9199	133.6583	133.7719	55.1	49.8
1	80.8	107.2995	107.0556	107.3001	107.1125	106.8456	107.0555	106.6514	107.1199	106.9056	106.9963	81.9	75.3
6	82.8	102.2111	102.2596	102.3876	102.2704	102.2405	102.2596	101.7404	102.5017	102.2099	102.2528	86.6	79.8
7	43.4	146.9519	145.1008	144.3920	147.0997	145.2343	145.1009	147.2223	144.8543	145.7124	145.5990	43.3	38.5
8	83.5	102.4964	102.2365	102.4296	102.7685	102.2242	102.2364	102.6243	102.2355	102.4980	102.4823	86.4	79.6
9	45.0	136.9260	135.6128	135.9130	142.2612	135.6061	135.6129	136.9015	135.6898	140.8962	139.6176	49.2	44.2
10	40.9	148.3066	148.3606	148.5634	148.6098	148.3887	148.3607	148.1804	148.4263	148.6064	148.5686	40.3	35.7
14	80.0	100.0252	100.7230	100.6385	104.433	100.7428	100.7231	100.1642	100.7545	104.4281	103.3774	85.5	78.7
13	75.4	106.7380	106.3648	106.2869	109.6677	106.3561	106.3647	106.8103	106.3834	109.2905	108.5060	80.4	73.8
12	36.6	144.7728	144.7136	144.3974	148.86	144.9078	144.7137	145.3853	144.5669	148.8231	147.6415	41.2	36.6
15	76.8	110.3111	105.6306	105.5988	111.3051	105.6599	105.6308	110.3269	105.6243	107.1712	107.2032	81.7	75.1
16	94.5	92.1226	91.8543	91.7111	91.9518	91.8719	91.8542	92.4508	91.8354	91.4258	91.5825	97.3	90.0
19	52.2	138.2852	138.6987	138.3694	138.18	139.0345	138.6987	137.7973	139.0518	138.5952	138.5542	50.3	45.2
18	77.4	103.9384	115.7502	104.6598	104.2245	115.2133	115.7502	112.7193	115.5844	115.563	112.8259	76.0	69.7

20	42.0	145.3078	145.1627	145.2639	145.3471	145.253	145.1627	145.5693	145.1413	145.1507	145.1933	43.7	38.9
7′	166.3	12.0704	12.0635	12.082	13.8301	12.0712	12.0636	12.1135	12.0734	14.5769	13.8053	175.1	164.1
1′	131.1	53.4316	53.079	53.2289	52.0435	53.0738	53.0789	53.4317	53.0862	52.4635	52.6190	136.2	127.1
2′	130.4	49.942	49.665	49.7103	51.6912	49.6807	49.6649	49.831	49.6799	51.4459	50.9834	137.9	128.6
3′	129.3	53.4156	53.2945	53.4357	53.1793	53.3135	53.2946	53.4752	53.3042	53.1921	53.2420	135.6	126.5
4′	133.9	46.9255	46.9614	47.0046	47.7827	46.9656	46.9614	46.8931	46.957	47.607	47.4497	141.4	132.0
5′	129.3	53.3883	53.535	53.4982	52.8977	53.5305	53.535	53.4307	53.533	53.3063	53.3228	135.5	126.4
6′	130.4	51.5115	51.5276	51.5325	51.3501	51.5135	51.5276	51.4647	51.5156	51.5195	51.5043	137.4	128.1
17	67.9	121.8278	122.2904	122.9076	121.2841	122.2181	122.2903	121.7566	122.2537	121.7652	121.9406	66.9	61.0
1-OCH_3	55.5	130.8992	130.7421	130.7852	131.0527	130.7227	130.7421	130.8743	130.6728	130.7769	130.7990	58.1	52.6
6-OCH_3	59.1	129.3904	129.105	128.9262	129.7876	128.7948	129.105	129.5692	129.1962	129.1781	129.1901	59.7	54.1
18-OCH_3	59.3	128.1407	128.8178	128.02	128.1737	128.4537	128.8177	128.3719	128.8261	128.8467	128.6411	60.2	54.7
8-OCH_3	50.3	135.5217	135.999	136.0096	136.6363	136.0356	135.9991	135.5827	136.0102	136.8219	136.5718	52.3	47.1
16-OCH_3	62.5	124.9736	124.8746	124.8466	123.9145	124.8617	124.8746	124.9681	124.8595	123.7732	124.0907	64.8	59.0

[a]Averaged according to the Boltzmann-calculated contribution at B3LYP/6-31+G(d, p) level. [b]δ_U = Calculated Shielding Value (TMS) – Calculated Shielding value (Averaged). $\delta_S = (\delta_U + 0.2478)/1.044$

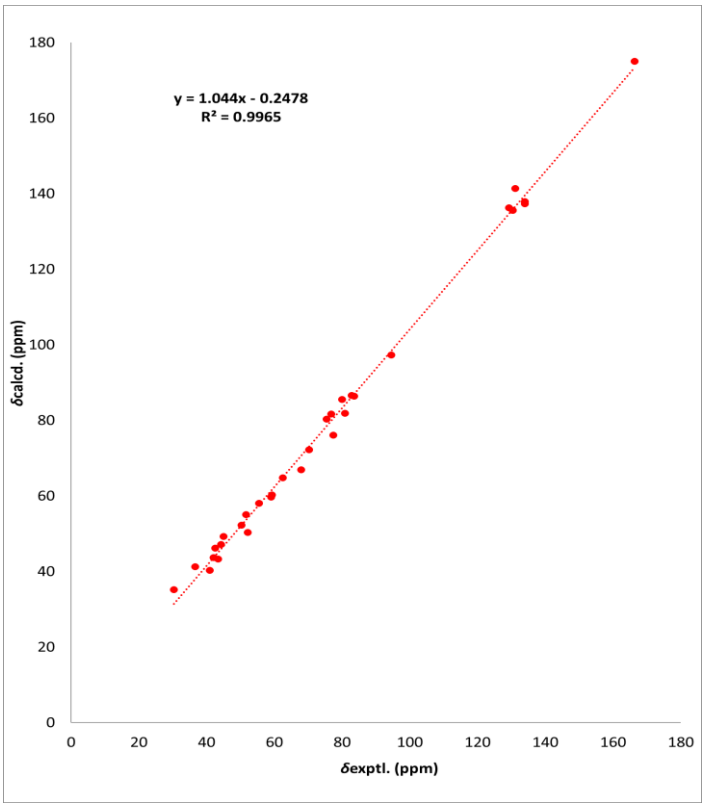


Figure S3: Correlation plots of experimental ^{13}C-NMR chemical shifts of **1**versus corresponding calculated ^{13}C-NMR chemical shifts of **1a**.

Table S3: Experimental ^{1}H-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of **1a**.

No.	Exptl.	1a-C1	1a-C2	1a-C3	1a-C4	1a-C5	1a-C6	1a-C7	1a-C8	1a-C9	Averaged[a]
9	2.63	29.4048	29.4053	29.4293	29.1762	29.4214	29.4053	29.3987	29.4164	29.1976	29.25773
10	2.56	29.0595	29.0663	29.0273	29.1819	29.0745	29.0663	29.1141	29.0484	29.1223	29.10697
2a	1.64	29.7490	29.8196	29.7633	29.7647	29.7337	29.8196	29.7737	29.5659	29.8254	29.79654
2b	2.38	29.4300	29.3385	29.4314	29.4815	29.4188	29.3385	29.4124	29.5686	29.3596	29.39133
3	4.29	27.8130	27.6349	27.7726	27.8775	27.6446	27.6349	27.6780	27.8554	27.6611	27.70454
5	2.60	29.8678	29.2335	29.8290	29.9028	29.3353	29.2335	29.4187	29.1941	29.2796	29.41879
1	3.71	28.4766	28.5539	28.5404	28.4178	28.5115	28.5539	28.4372	28.5587	28.4980	28.50130
6	4.26	27.7327	27.8296	27.9330	27.8862	27.8429	27.8296	27.6546	27.8416	27.9860	27.94625
7	3.12	28.8611	28.7857	28.7418	29.0695	28.8020	28.7857	28.9446	28.7816	28.9871	28.93474
14	4.87	26.9433	26.9050	26.9014	27.1058	26.9118	26.9050	26.9419	26.9092	27.1599	27.08377
12a	1.93	29.6938	29.7122	29.6942	29.7312	29.6995	29.7123	29.6941	29.7097	29.7765	29.75080
12b	2.33	30.0939	30.1245	30.1442	30.2372	30.1216	30.1245	30.1182	30.1359	30.2579	30.22150
15	4.70	27.4462	27.4197	27.4256	27.1628	27.4214	27.4198	27.4459	27.4234	27.2483	27.28900
16	3.42	28.8058	28.8362	28.8784	28.5935	28.8395	28.8362	28.8080	28.8472	28.6725	28.71644
19a	3.45	28.9679	29.4220	29.0281	29.0471	29.6460	29.4220	29.6206	29.3688	29.5327	29.40288
19b	3.65	28.7641	29.0579	28.6414	28.8404	29.1898	29.0579	29.1608	29.5382	29.0949	29.02279
18a	3.43	28.6694	28.1774	28.5368	28.7100	28.0014	28.1774	27.0872	28.2536	28.2246	28.30295
18b	3.59	26.7657	28.1926	27.3094	26.8240	28.6894	28.1926	28.9553	28.1809	28.2334	27.97180
20	3.15	29.4630	29.4629	29.4595	29.5231	29.4735	29.4629	29.5009	29.4636	29.5137	29.50061
	3.15	29.4924	29.5087	29.5186	29.5059	29.4917	29.5087	29.5054	29.5102	29.4935	29.49970
	3.15	29.4893	29.5132	29.5057	29.5299	29.4899	29.5132	29.4831	29.5435	29.4987	29.50480
2′	8.06	22.9287	22.8646	22.8123	23.0978	22.8677	22.8646	22.9189	22.8727	23.1963	23.08781
3′	7.53	23.8942	23.8554	23.8892	23.9296	23.8598	23.8554	23.8906	23.8607	23.8639	23.87356
4′	7.65	23.7318	23.7064	23.7260	23.8246	23.7078	23.7064	23.7111	23.7082	23.7676	23.75921
5′	7.53	23.8890	23.8831	23.8904	23.9171	23.8836	23.8831	23.8772	23.8841	23.8940	23.89432
6′	8.06	23.2524	23.2136	23.2211	23.2847	23.2150	23.2136	23.2387	23.2167	23.2218	23.22734
17	3.47	29.2056	29.3458	29.3219	29.2088	29.3879	29.3458	29.2988	29.3643	29.4063	29.36758
1-OCH_3	3.41	28.3912	28.4231	28.3937	28.4080	28.4101	28.4231	28.4111	28.3897	28.3796	28.38844
	3.41	28.9377	28.9224	28.9257	28.9339	28.9261	28.9224	28.9577	28.9106	28.9211	28.92318
	3.41	28.2820	28.3180	28.2987	28.2468	28.2894	28.3180	28.2861	28.2882	28.2961	28.29209

6-OCH_3	3.37	28.2267	28.4486	28.4763	28.4070	28.4141	28.4486	28.2765	28.4601	28.6340	28.56054
	3.37	28.1991	28.3275	28.3964	28.5447	28.4907	28.3275	28.2503	28.3328	28.4226	28.42248
	3.37	28.6715	28.4015	28.5669	28.9497	28.4239	28.4015	28.7035	28.4085	28.5350	28.56645
18-OCH_3	3.32	28.2150	28.2660	28.1873	28.2478	28.2219	28.2660	28.2147	28.2551	28.2815	28.26025
	3.32	28.7126	28.6632	28.6857	28.7707	28.6446	28.6632	28.6935	28.6679	28.6693	28.68079
	3.32	28.6039	28.5674	28.5686	28.6308	28.5196	28.5674	28.5857	28.5831	28.5986	28.59250
8-OCH_3	3.18	28.0909	28.2949	28.2731	29.4623	28.3116	28.2949	28.4469	28.3104	29.3707	29.07743
	3.18	28.2576	28.0115	28.0118	28.6136	28.0345	28.0116	28.1205	28.0215	28.5657	28.41918
	3.18	28.4458	28.1239	28.0875	29.3181	28.1418	28.1240	28.2780	28.1384	28.7967	28.65955
16-OCH_3	3.70	28.3724	28.4148	28.4153	27.9779	28.5778	28.4149	28.3654	28.5826	27.9600	28.10026
	3.70	28.5662	28.5770	28.5865	28.2427	27.7811	28.5770	28.5629	27.7838	28.2442	28.28009
	3.70	27.7742	27.7804	27.8009	28.0628	28.4113	27.7804	27.7475	28.4137	28.0615	28.03198

[a]Averaged according to the Boltzmann-calculated contribution at B3LYP/6-31+G (d, p) level.

S3: NMR Data Calculation of 1b

NMR chemical shifts calculation for the ωB97XD/DGDZVP-optimized 9 conformers of **1b** (Boltzmann distribution ≥ 1%, Figure S4) were carried out at PCM/mPW1PW91/6-311+G (d, p) level in acetone with GIAO method[3]. The calculated ^{13}C- and ^{1}H-NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy (Tables S5 and S6). Linear correlation coefficients (R^2) was calculated for evaluation of the comparative results of the experimental data and the calculated data (Figure S5). The isotropic values of TMS was calculated in the same level and used as references. The DP4+ parameters were calculated using the excel file, which was provided by Ariel M. Sarotti[4].

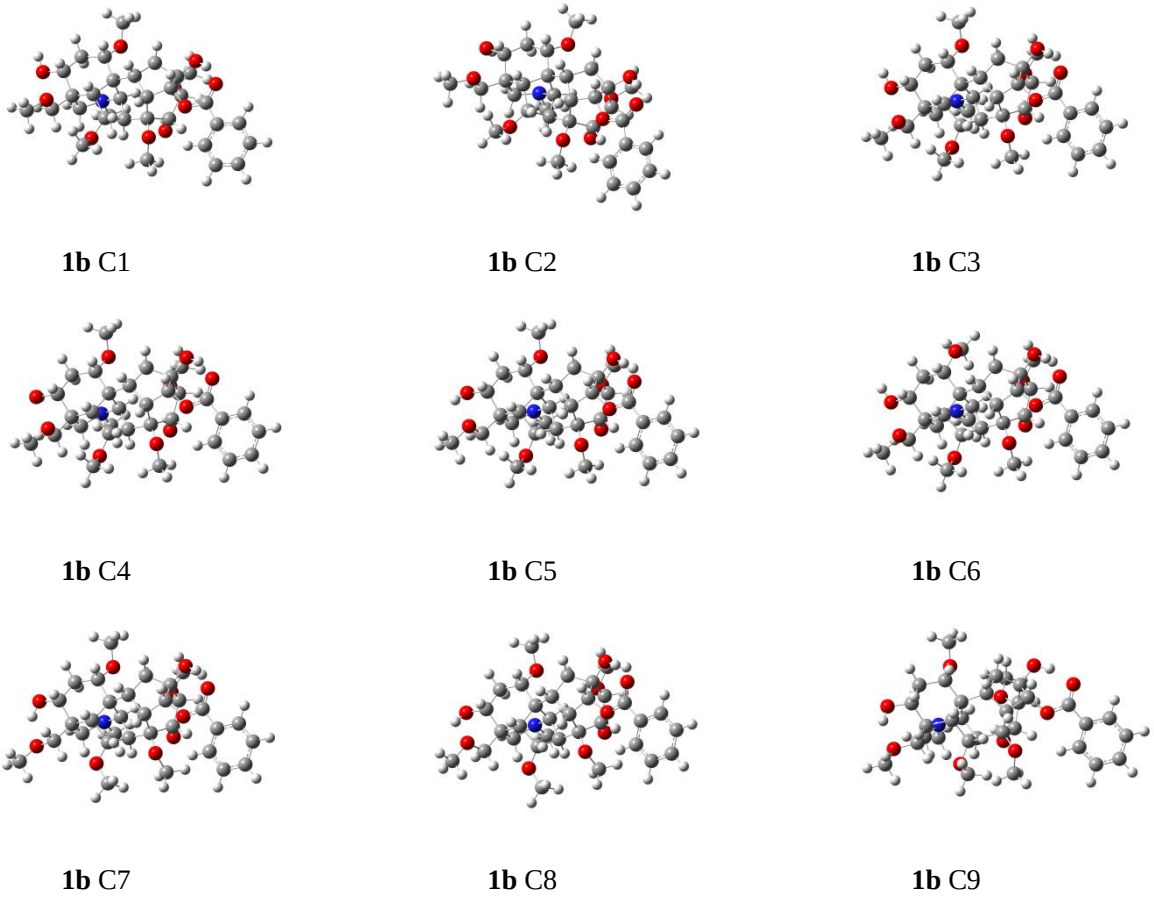


Figure S4: ωB97XD/DGDZVP optimized 9 conformers of **1b** (Boltzmann distribution ≥ 1%).

Table S4: Energy analysis for the conformers of **1b**.

Conf.	MMFF energy	B3LYP/6-31+G(d, p) Gibbs free energy (298.15 K)			ωB97XD/DGDZVP Gibbs free energy (298.15 K)		
	ΔG (Kcal/mol)	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
1b-C1	0.0000	-2052.679714	0.0000	0.056	-2052.363320	0.0000	0.082
1b-C2	0.0521	-2052.680394	-0.4270	0.115	-2052.363919	-0.3760	0.155
1b-C3	0.8300	-2052.679715	-0.0010	0.056	-2052.363321	-0.0010	0.082
1b-C4	1.0819	-2052.680386	-0.4220	0.114	-2052.363920	-0.3770	0.155
1b-C5	1.1697	-2052.680967	-0.7860	0.211	-2052.363925	-0.3800	0.156
1b-C6	1.2358	-2052.674069	3.5420	0	-2052.360673	1.6610	0.005
1b-C7	1.2892	-2052.680385	-0.4210	0.114	-2052.361889	0.8980	0.018
1b-C8	1.4575	-2052.679092	0.3900	0.029	-2052.361764	0.9760	0.016
1b-C9	1.9476	-2052.68131	-1.0020	0.304	-2052.364632	-0.8230	0.330

Table S5: Experimental ^{13}C-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of **1b**.

No.	Exptl.	1b-C1	1b-C2	1b-C3	1b-C4	1b-C5	1b-C6	1b-C7	1b-C8	1b-C9	Averaged[a]	Unscaled shifts(δ_U)[b]	Scaled shifts(δ_S)[c]
2	30.3	149.6742	149.7957	149.6741	149.7954	152.0775	150.1080	150.3659	152.3248	150.9882	150.4277	38.4	36.4
3	70.2	118.0570	117.0665	118.0570	117.0669	116.7244	116.5671	108.3552	116.2311	109.5499	114.4054	74.5	71.2
4	44.2	141.7182	140.9279	141.7184	140.9279	141.0040	141.1065	141.9620	141.1120	141.6580	141.1919	47.7	45.3
5	42.5	140.7492	140.7123	140.7493	140.7123	140.9669	139.3528	136.4502	137.9305	138.0858	139.6226	49.2	46.8
11	51.7	134.4858	134.6067	134.4859	134.6067	134.1409	132.7961	135.3934	134.8344	134.2080	134.2568	54.6	52.0
1	80.8	103.1637	103.1851	103.1638	103.1855	103.3789	107.0921	104.5313	104.2428	102.9666	103.0973	85.8	82.1
6	82.8	101.9693	102.0171	101.9692	102.0167	101.5293	103.4845	101.6504	101.0565	102.7205	102.0486	86.8	83.1
7	43.4	143.1815	143.2078	143.1814	143.2080	143.7818	141.9944	147.0833	147.2464	143.1517	143.2596	45.6	43.3
8	83.5	100.0152	100.0266	100.0152	100.0265	99.9640	100.1439	100.4745	100.6053	100.0870	99.9528	88.9	85.1
9	45.0	134.6604	134.7206	134.6603	134.7208	134.8993	134.5347	136.1513	136.3711	134.5664	134.6043	54.3	51.7
10	40.9	142.6925	142.6920	142.6926	142.6919	142.6359	143.0751	142.2945	142.3600	142.6614	142.5200	46.3	44.1
14	80.0	101.5430	101.5922	101.5431	101.5923	101.6615	101.2281	101.5935	101.2899	101.7073	101.5247	87.3	83.6
13	75.4	104.4030	104.4039	104.4030	104.4037	104.2451	105.0521	104.7966	104.4956	104.8886	104.4463	84.4	80.8
12	36.6	154.1822	154.2793	154.1823	154.2797	155.0471	149.5517	156.1113	156.2670	153.7999	154.1119	34.7	32.9
15	76.8	113.3904	113.4135	113.3905	113.4135	113.3852	113.3367	118.1170	117.9914	113.8822	113.6041	75.3	71.9
16	94.5	102.5155	102.4996	102.5152	102.4995	102.4220	102.6212	102.0798	101.9908	102.5509	102.3894	86.5	82.8
19	52.2	138.0916	138.4056	138.0916	138.4055	138.2101	137.9476	138.4352	137.4496	138.1529	138.0847	50.8	48.3
18	77.4	115.7226	115.5347	115.7226	115.5347	115.1511	115.6727	104.1965	112.7351	104.7369	111.5787	77.3	73.9
20	42.0	145.9337	145.9318	145.9337	145.9318	146.0913	145.8201	146.0169	146.1919	145.9275	145.8148	43.0	40.9
7′	166.3	11.5562	11.5644	11.5563	11.5643	11.5775	11.6057	11.4512	11.4577	11.6382	11.5743	177.3	170.4
1′	131.1	53.7940	53.8104	53.7940	53.8105	53.8162	53.7950	53.9814	53.9427	53.8244	53.7646	135.1	129.7
2′	130.4	49.5634	49.5698	49.5634	49.5699	49.5715	49.5559	49.7664	49.7928	49.6071	49.5388	139.3	133.8
3′	129.3	53.2382	53.2355	53.2382	53.2355	53.2326	53.2600	53.3111	53.2512	53.1990	53.1719	135.7	130.2
4′	133.9	46.5738	46.5726	46.5738	46.5725	46.5824	46.5785	46.5053	46.5031	46.5438	46.5159	142.3	136.7
5′	129.3	53.4639	53.4612	53.4640	53.4611	53.4557	53.4436	53.4100	53.3938	53.4492	53.4013	135.5	130.0
6′	130.4	51.3817	51.4044	51.3819	51.4044	51.4178	51.3523	51.2169	51.2902	51.4262	51.3531	137.5	132.0
17	67.9	124.4884	124.5484	124.4885	124.5485	124.8529	123.0018	124.077	124.5693	124.6417	124.4764	64.4	61.5
1-OCH_3	55.5	130.7860	130.7921	130.7860	130.7922	131.0443	135.3997	131.521	131.5274	130.6577	130.7032	58.2	55.5
6-OCH_3	59.1	129.0309	129.0514	129.0309	129.0513	128.5521	129.1755	129.6508	129.7143	128.9438	128.8276	60.0	57.3
18-OCH_3	59.3	128.8290	128.8603	128.8291	128.8603	128.5003	128.8947	128.1818	128.4731	127.992	128.3654	60.5	57.7
8-OCH_3	50.3	136.1206	136.1130	136.1205	136.1131	136.1471	136.1102	135.995	136.0274	136.2905	136.0385	52.8	50.3
16-OCH_3	62.5	127.3180	127.3263	127.3180	127.3264	127.3477	127.1604	127.6205	127.6226	127.3207	127.2083	61.7	58.8

[a]Averaged according to the Boltzmann-calculated contribution at B3LYP/6-31+G(d, p) level. [b]δ_U = Calculated Shielding Value (TMS) – Calculated Shielding value (Averaged). $\delta_S = (\delta_U – 0.6717)/1.0366$.

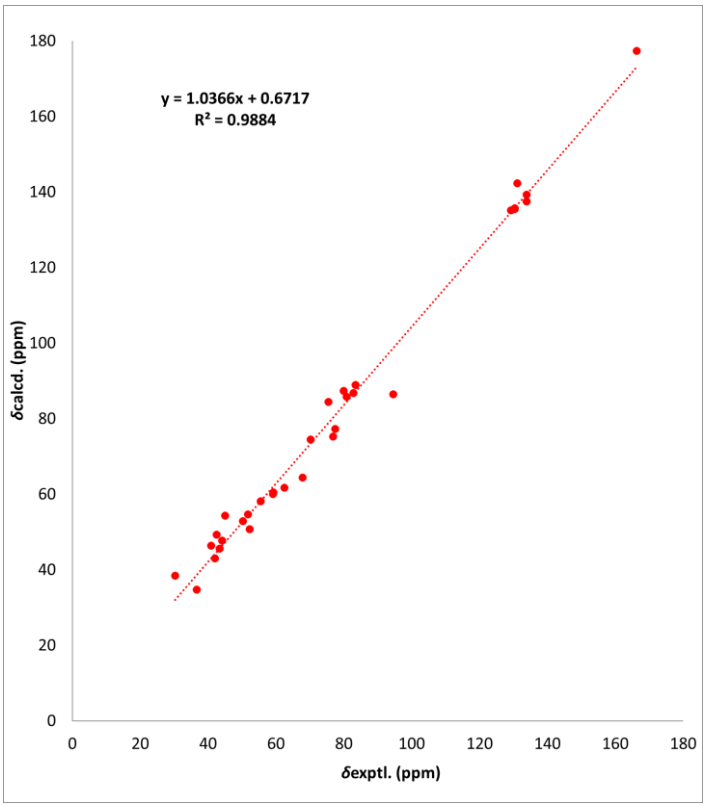


Figure S5: Correlation plots of experimental ^{13}C-NMR chemical shifts of **1** versus corresponding calculated ^{13}C-NMR chemical shifts of **1b**.

Table S6: Experimental ^{1}H-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of **1b**.

No.	Exptl.	1b-C1	1b-C2	1b-C3	1b-C4	1b-C5	1b-C6	1b-C7	1b-C8	1b-C9	Averaged[a]
9	2.63	29.4227	29.4206	29.4227	29.4206	29.4391	29.3976	29.4285	29.4256	29.4378	36.42620
10	2.56	29.7667	29.7547	29.7667	29.7547	29.74	29.7091	29.8229	29.7251	29.8048	71.17661
2a	1.64	29.4577	29.7137	29.4577	29.7138	29.6734	28.5842	29.7810	29.7537	29.5729	45.33595
2b	2.38	29.5523	29.2732	29.5523	29.2731	29.3974	30.1264	29.4292	29.4143	29.5561	46.84980
3	4.29	27.9751	28.1955	27.9751	28.1956	28.0442	27.8119	28.1716	28.0912	28.0643	52.02615
5	2.60	29.7035	29.6969	29.7035	29.6969	29.803	29.6403	30.2563	29.8217	30.2002	82.08548
1	3.71	28.8328	28.8028	28.8328	28.8029	28.8201	28.2537	28.8296	28.8287	28.7940	83.09718
6	4.26	27.8058	27.7994	27.8058	27.7994	27.8274	27.8523	27.7796	27.7218	27.9450	43.34117
7	3.12	28.8139	28.8194	28.8139	28.8194	28.8559	28.7251	28.995	29.0027	28.7912	85.11898
14	4.87	26.8365	26.8344	26.8365	26.8344	26.8279	26.8291	26.8493	26.8249	26.8516	51.69096
12a	1.93	30.0793	30.0791	30.0793	30.0791	30.0960	29.8627	30.1645	30.1672	30.0541	44.05472
12b	2.33	27.9098	27.9032	27.9098	27.9031	27.8375	29.1716	27.7160	27.7574	27.9294	83.60252
15	4.70	27.2608	27.2631	27.2608	27.2631	27.2682	27.2391	27.1716	27.1864	27.2685	80.78413
16	3.42	28.2469	28.2472	28.2469	28.2472	28.2445	28.2384	28.2243	28.2304	28.2547	32.87210
19a	3.45	29.3699	29.2941	29.3699	29.2941	29.5401	29.3312	28.9688	29.5464	29.0372	71.94965
19b	3.65	29.0884	29.5818	29.0884	29.5818	29.2553	28.9883	28.8643	29.2026	28.7302	82.76838
18a	3.43	28.0377	28.0994	28.0377	28.0994	27.8337	28.0207	28.7003	26.9857	28.6116	48.33336
18b	3.59	28.1818	28.1812	28.1818	28.1813	28.7352	28.1938	26.5428	28.9407	27.1020	73.90356
20	3.15	29.5459	29.5846	29.5866	29.5846	29.5316	29.5239	29.4825	29.4847	29.5113	40.87625
	3.15	29.4800	29.4904	29.5459	29.4904	29.4719	29.4969	29.4305	29.4263	29.4680	170.37696
	3.15	29.5866	29.5962	29.4800	29.5962	29.5930	29.5828	29.5825	29.5848	29.5655	129.67639
2′	8.06	22.8574	22.8596	22.8574	22.8596	22.8568	22.8340	22.9759	22.9764	22.9047	133.75293
3′	7.53	23.8855	23.8852	23.8855	23.8852	23.8874	23.8791	23.8623	23.8681	23.8598	130.24808
4′	7.65	23.7127	23.7117	23.7127	23.7117	23.7138	23.7053	23.6853	23.6999	23.6991	136.66907
5′	7.53	23.8634	23.8612	23.8634	23.8612	23.8605	23.8623	23.8809	23.8746	23.8664	130.02685
6′	8.06	23.1904	23.1876	23.1904	23.1876	23.1864	23.1920	23.2060	23.2028	23.1919	132.00269
17	3.47	28.5995	28.5901	28.5995	28.5900	28.6197	28.4646	28.4361	28.4639	28.5796	61.46118
1-OCH_3	3.41	28.4653	28.4601	28.3314	28.4601	28.4536	28.5712	28.4320	28.4376	28.4542	55.45424
	3.41	28.3315	28.2922	28.8561	28.2921	28.2593	28.4982	28.2666	28.2500	28.2996	57.26366
	3.41	28.8561	28.8378	28.4653	28.8379	28.8124	28.3762	28.8247	28.8049	28.8591	57.70955
6-OCH_3	3.37	28.4057	28.4071	28.4057	28.4071	28.4445	28.4114	28.2097	28.2159	28.4987	50.30732

	3.37	28.4282	28.4247	28.4282	28.4247	28.3847	28.4432	28.1999	28.2419	28.3616	58.82575
	3.37	28.3412	28.3347	28.3412	28.3346	28.5303	28.3501	28.7507	28.7190	28.6115	36.42620
18-OCH_3	3.32	28.2937	28.3011	28.2937	28.3011	28.2274	28.2922	28.2261	28.2443	28.1948	71.17661
	3.32	28.6345	28.6419	28.6345	28.6419	28.6545	28.6686	28.7227	28.6954	28.6880	45.33595
	3.32	28.5454	28.5577	28.5455	28.5577	28.5259	28.5784	28.6214	28.6151	28.5904	46.84980
8-OCH_3	3.18	28.1606	28.1629	28.1606	28.1629	28.1669	28.1715	28.2171	28.2335	28.1610	52.02615
	3.18	28.2879	28.2806	28.2879	28.2806	28.2849	28.3057	28.4454	28.4391	28.2852	82.08548
	3.18	27.9981	27.9971	27.9981	27.9971	28.0249	28.0009	28.1479	28.1431	28.0309	83.09718
16-OCH_3	3.70	28.1092	28.1133	28.1092	28.1133	28.1002	28.0956	28.1064	28.0986	28.1201	43.34117
	3.70	27.9896	27.9926	27.9896	27.9926	27.9912	27.9097	28.0506	28.0298	28.0158	85.11898
	3.70	28.7033	28.7034	28.7033	28.7034	28.7008	28.6590	28.7002	28.6875	28.7141	51.69096

[a]Averaged according to the Boltzmann-calculated contribution at B3LYP/6-31+G (d, p) level.

Table S7: Experimental chemical shifts, the calculated shielding tensors for **1a** (isomer 1) and **1b** (isomer 2), and the DP4+ probability of **1a** and **1b**.

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
12			DP4+	100.00%	0.00%	–	–	–
14	Nuclei	sp2?	xperiment	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
15	C		30.3	153.7	150.4			
16	C		70.2	116.6	114.4			
17	C		44.2	141.7	141.2			
18	C		42.5	142.7	139.6			
19	C		51.7	133.8	134.3			
20	C		80.8	107.0	103.1			
21	C		82.8	102.3	102.0			
22	C		43.4	145.6	143.3			
23	C		83.5	102.5	100.0			
24	C		45.0	139.6	134.6			
25	C		40.9	148.6	142.5			
26	C		80.0	103.38	101.52			
27	C		75.4	108.51	104.45			
28	C		36.6	147.64	154.11			
29	C		76.8	107.20	113.60			
30	C		94.5	91.58	102.39			
31	C		52.2	138.55	138.08			
32	C		77.4	112.83	111.58			
33	C		42.0	145.19	145.81			
34	C	x	166.3	13.81	11.57			
35	C	x	131.1	52.62	53.76			
36	C	x	130.4	50.98	49.54			
37	C	x	129.3	53.24	53.17			
38	C	x	133.9	47.45	46.52			
39	C	x	129.3	53.32	53.40			
40	C	x	130.4	51.5042518	51.3531109			
41	C		67.9	121.940604	124.476443			
42	C		55.5	130.798952	130.703237			
43	C		59.1	129.19012	128.827588			
44	C		59.3	128.641149	128.36538			
45	C		50.3	136.571768	136.038528			
46	C		62.5	124.090689	127.208325			
47								
48	H		2.63	29.2577324	29.400193			
49	H		2.56	29.1069692	29.7416791			
50	H		1.64	29.7965444	29.5854709			
51	H		2.38	29.3913339	29.4117475			
52	H		4.29	27.7045375	28.0602586			
53	H		2.60	29.4187877	29.8627091			
54	H		3.71	28.5013007	28.7768788			
55	H		4.26	27.9462503	27.8237327			
56	H		3.12	28.9347415	28.7916887			
57	H		4.87	27.0837718	26.8126617			
58	H		1.93	29.7507998	30.0453049			
59	H		2.33	30.2215004	27.8754001			
60	H		4.70	27.2890011	27.2350431			
61	H		3.42	28.7164412	28.2202324			
62	H		3.45	29.4028797	29.229203			
63	H		3.65	29.022794	29.1173889			
64	H		3.43	28.3029482	28.1813621			
65	H		3.59	27.9717964	27.8661445			
66	H		3.15	29.5006076	29.5158093			
67	H		3.15	29.4996988	29.4522585			
68	H		3.15	29.5047962	29.545162			
69	H	x	8.06	23.0878089	22.85466			
70	H	x	7.53	23.8735642	23.8526089			
71	H	x	7.65	23.7592102	23.6836259			
72	H	x	7.53	23.8943233	23.8398809			
73	H	x	8.06	23.2273395	23.1666998			
74	H		3.47	29.3675753	28.5587699			
75	H		3.41	28.3884445	28.4182416			
76	H		3.41	28.9231766	28.3105583			
77	H		3.41	28.2920866	28.7799297			
78	H		3.37	28.5605439	28.4079348			
79	H		3.37	28.4224808	28.3629076			
80	H		3.37	28.5664468	28.4429872			
81	H		3.32	28.2602497	28.2227058			
82	H		3.32	28.6807925	28.631667			
83	H		3.32	28.5925034	28.535132			
84	H		3.18	29.0774297	28.1365051			
85	H		3.18	28.4191806	28.2613333			
86	H		3.18	28.6595476	27.9898271			
87	H		3.70	28.1002646	28.0842668			
88	H		3.70	28.2800852	27.9727777			
89	H		3.70	28.0319841	28.6772716			

Table S8: DP4+ probabilities (%) details for **1a** and **1b**.

		Level of Theory: mPW1PW91/6-311+G (d, p) (Acetone, PCM)	
		1a	**1b**
DP4+	^{1}***H*-data**	100	0
	^{13}***C*-data**	100	0
	***All*-data**	100	0

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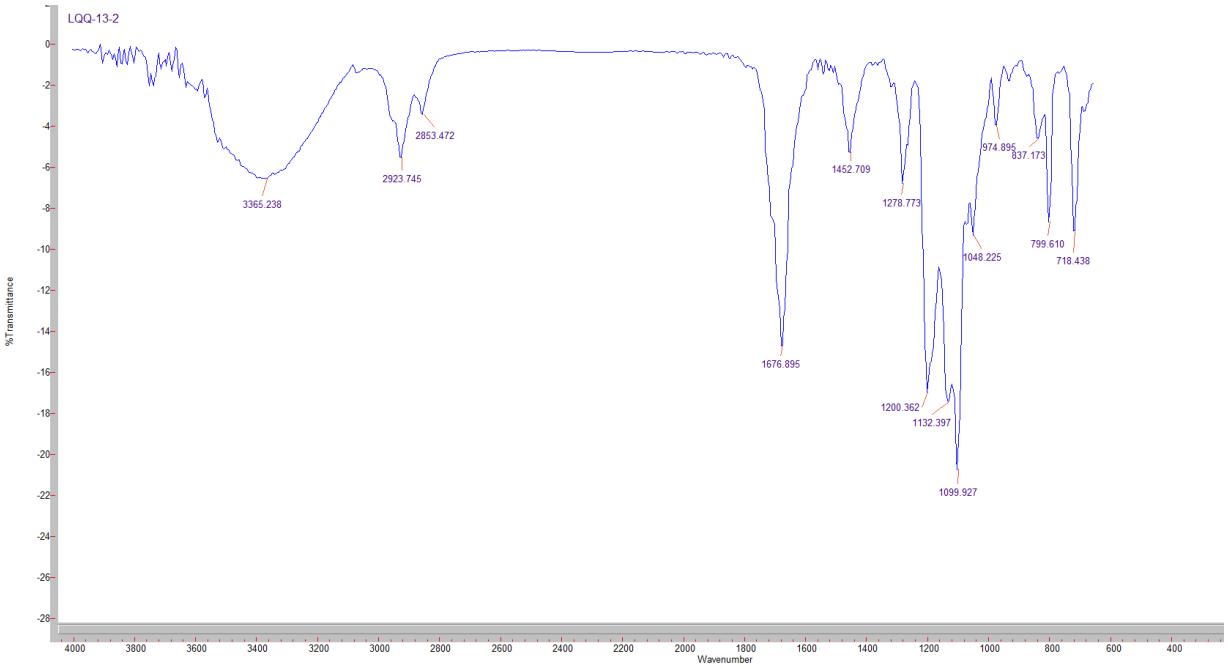

Figure S6: The IR Spectrum of **1** (1-*epi*-hokbusine A)

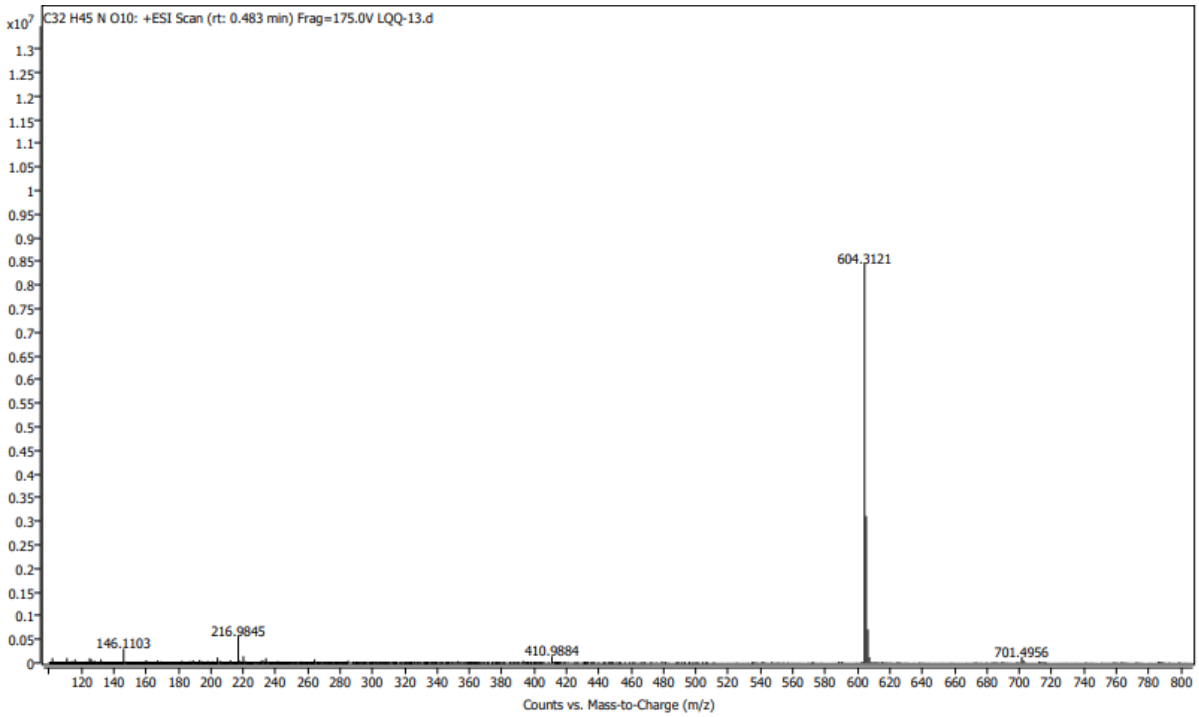

Figure S7: The (+)-HR-ESI-MS Spectrum of **1** (1-*epi*-hokbusine A)

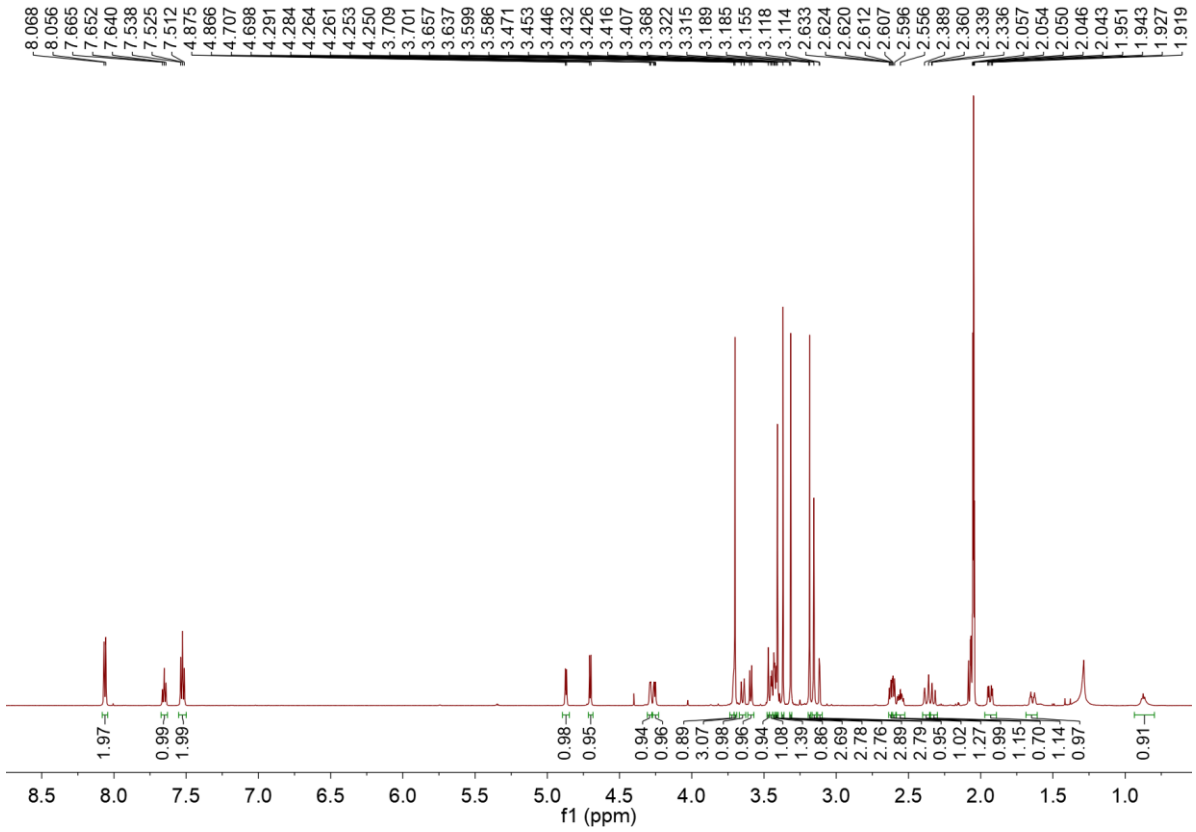

Figure S8: The ^{1}H NMR (600 MHz, Acetone-d_6) Spectrum of **1** (1-*epi*-hokbusine A)

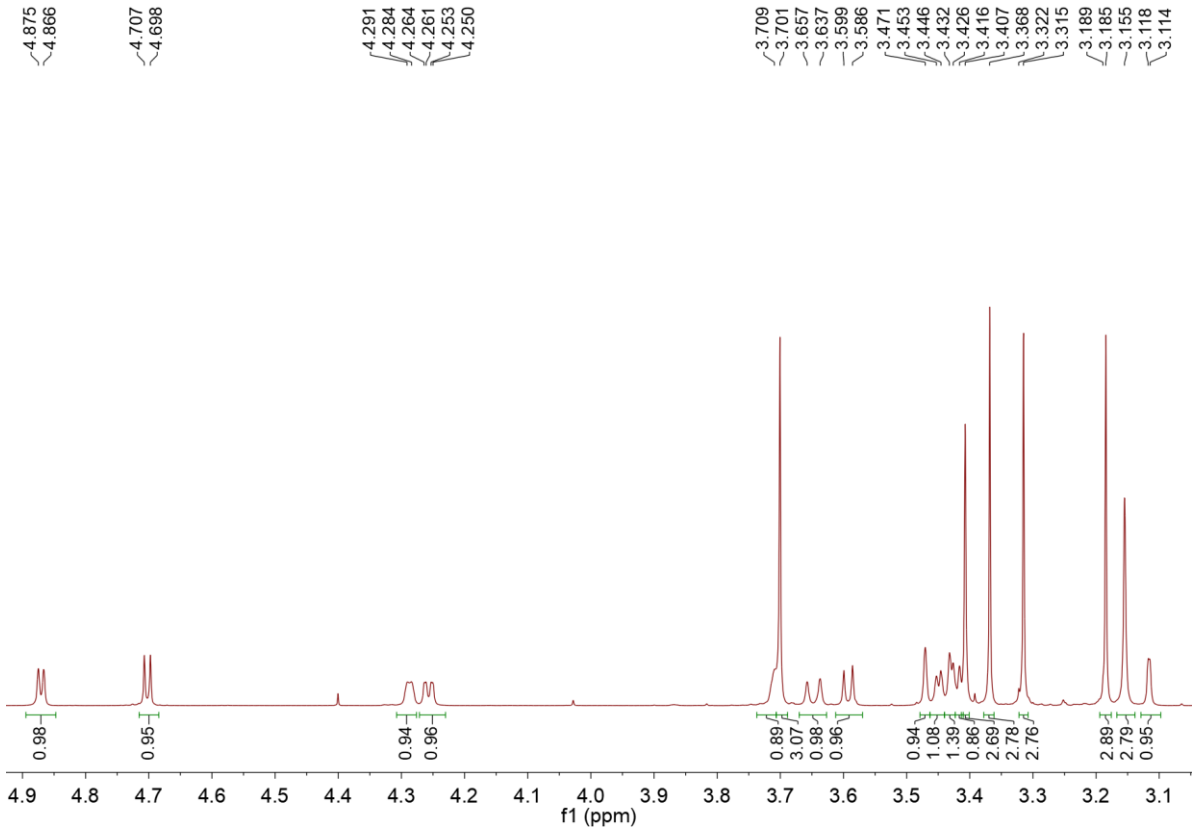

Figure S9: Expansion of ^{1}H NMR Spectrum of **1** (1-*epi*-hokbusine A) (From δ_H 3.1 ppm to 4.9 ppm)

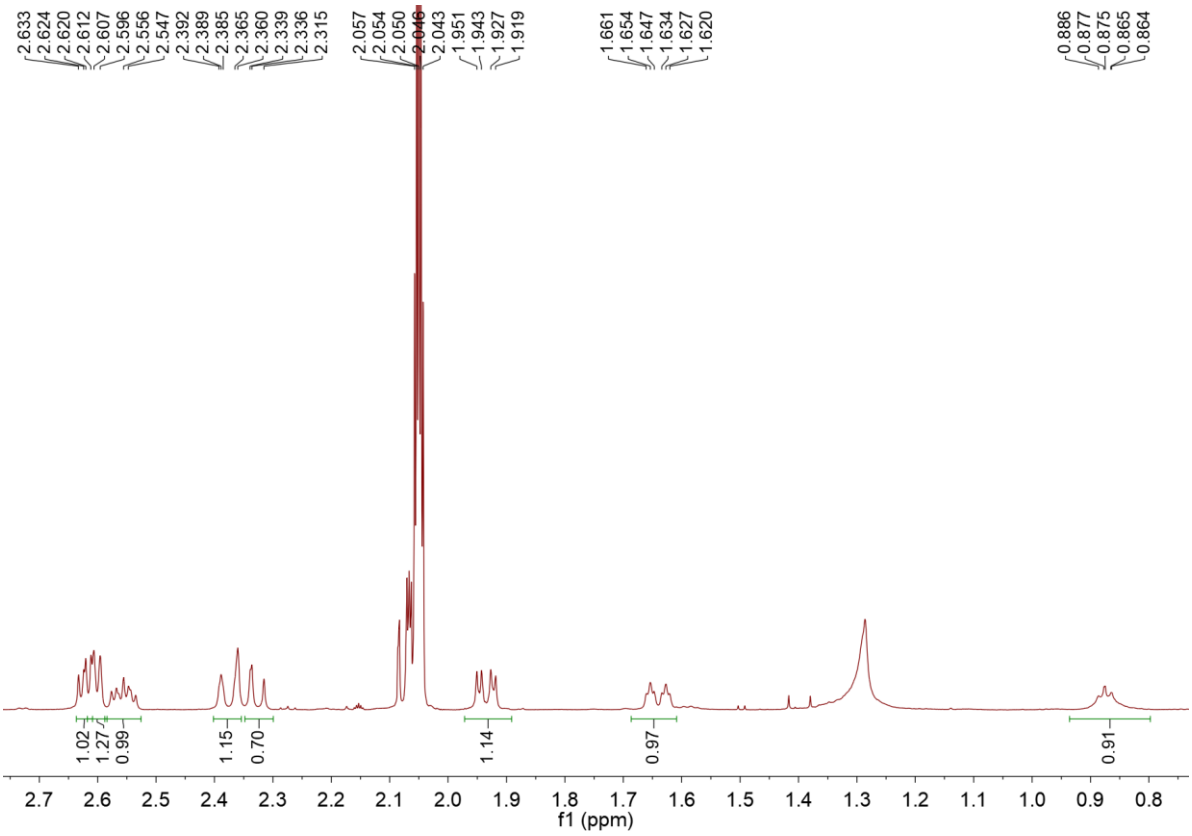

Figure S10: Expansion of ^{1}H NMR Spectrum of **1** (1-*epi*-hokbusine A) (From δ_H 0.8 ppm to 2.7 ppm)

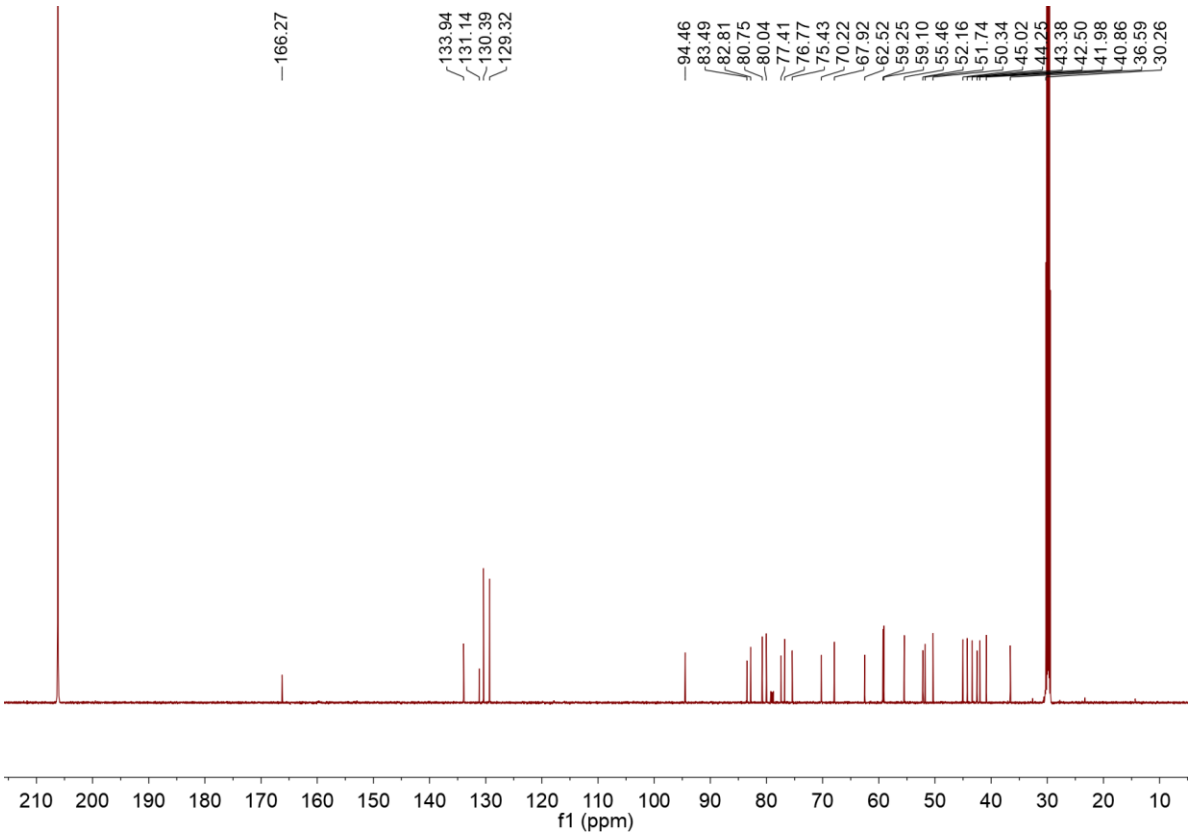

Figure S11: The ^{13}C NMR (150 MHz, Acetone-d_6) Spectrum of **1** (1-*epi*-hokbusine A)

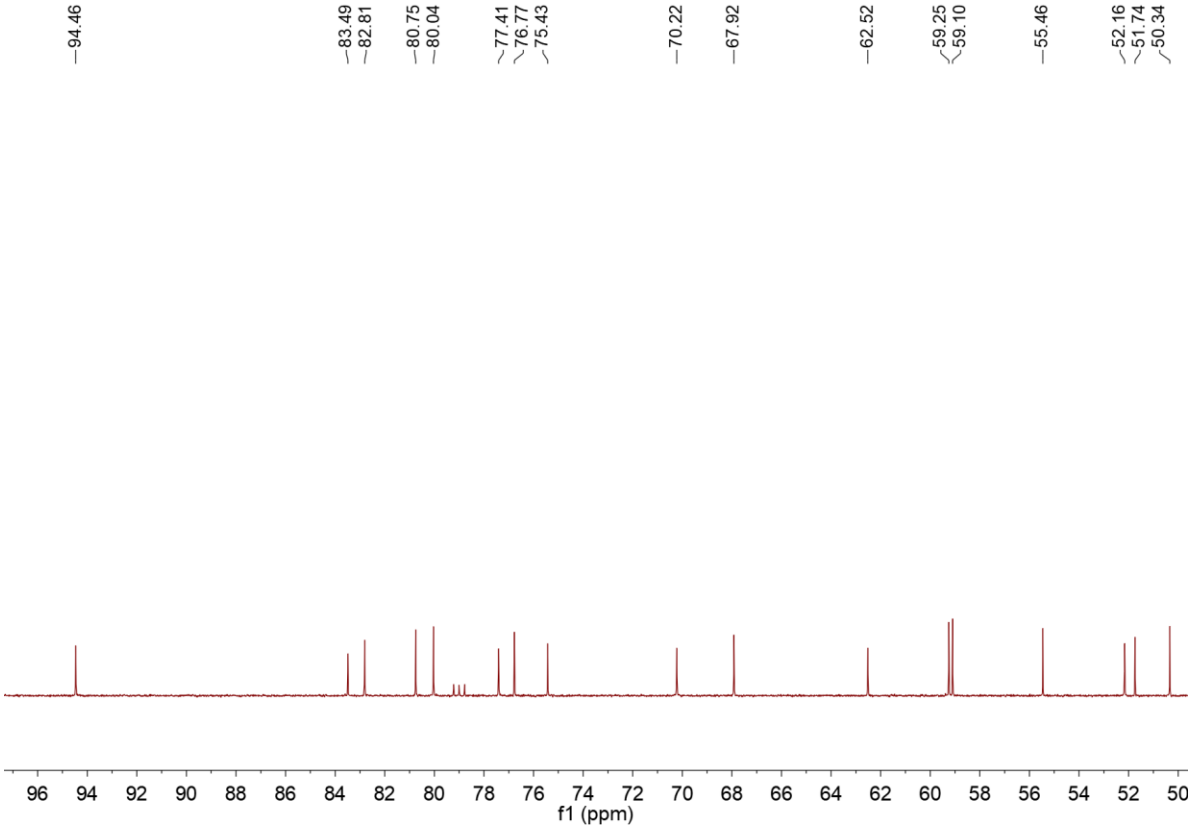

Figure S12: Expansion of ^{13}C NMR Spectrum of **1** (1-*epi*-hokbusine A) (From δ_C 50 ppm to 96 ppm)

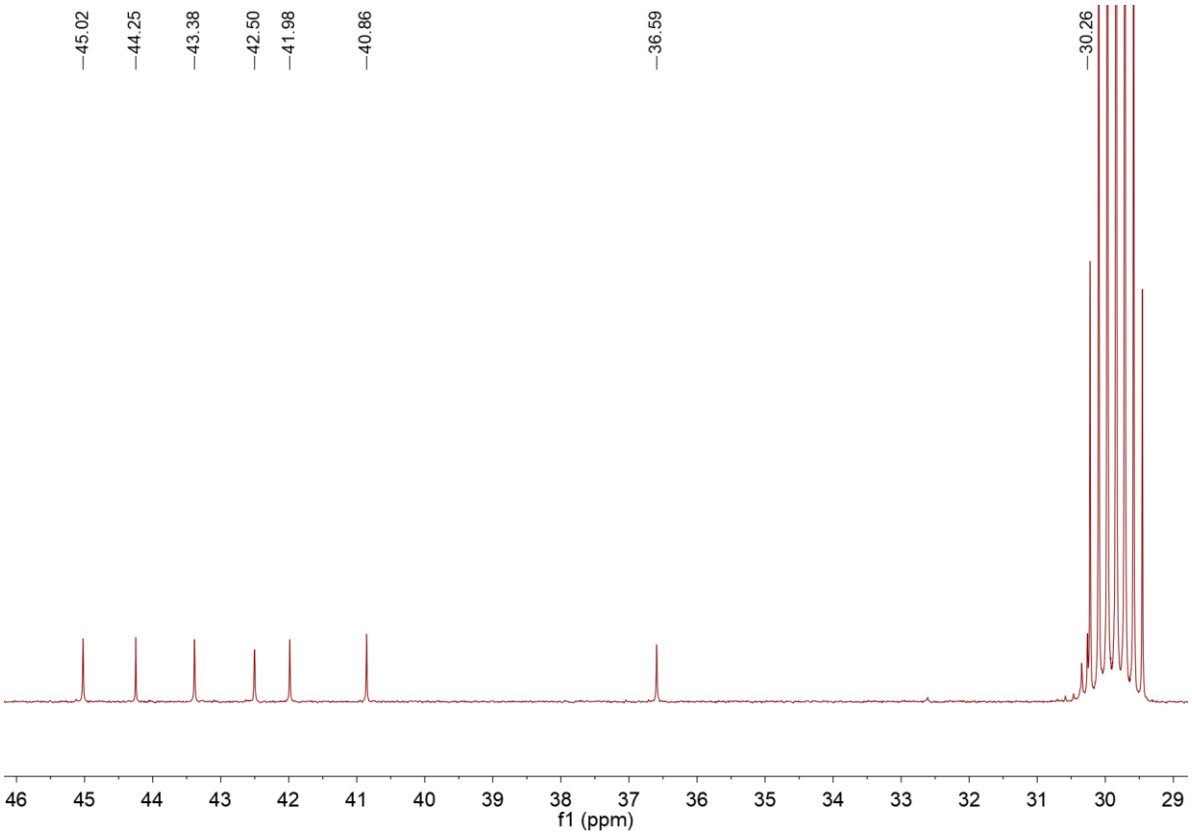

Figure S13: Expansion of ^{13}C NMR Spectrum of **1** (1-*epi*-hokbusine A) (From δ_C 29 ppm to 46 ppm)

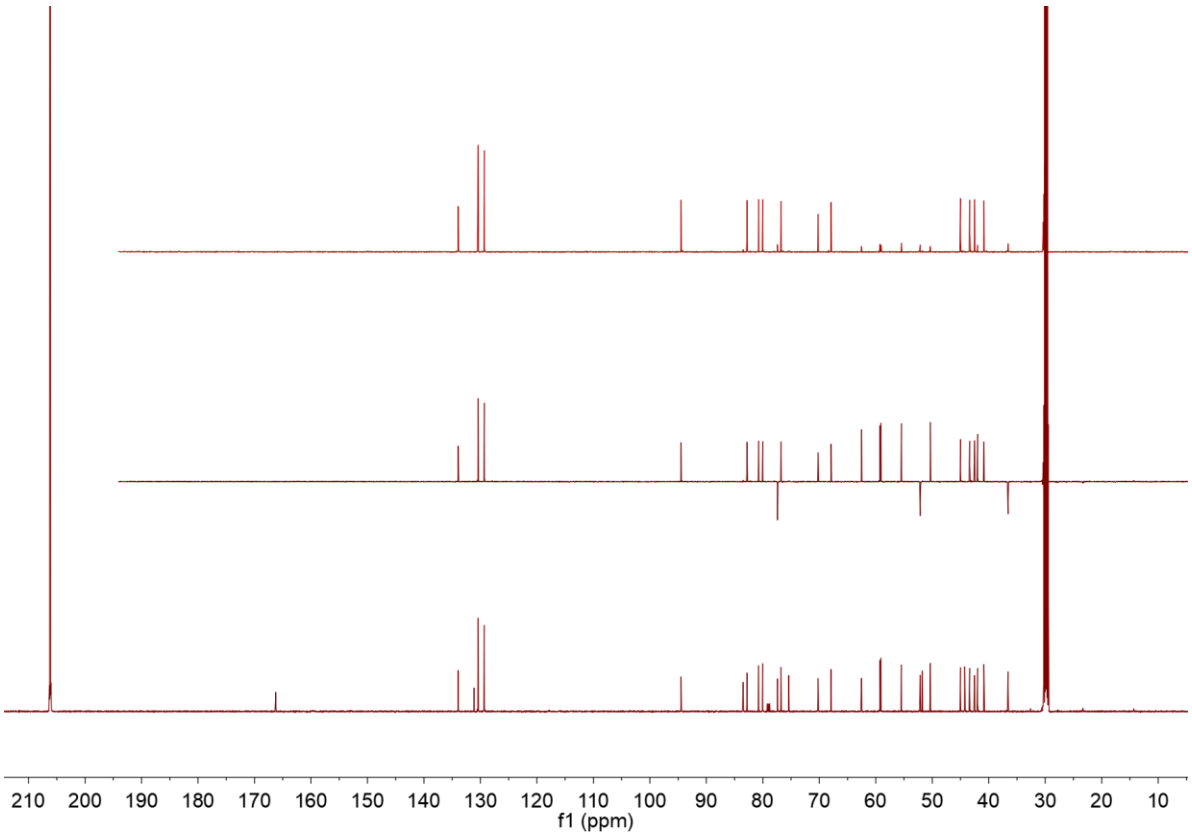

Figure S14: The DEPT (150 MHz, Acetone-d_6) Spectrum of **1** (1-*epi*-hokbusine A)

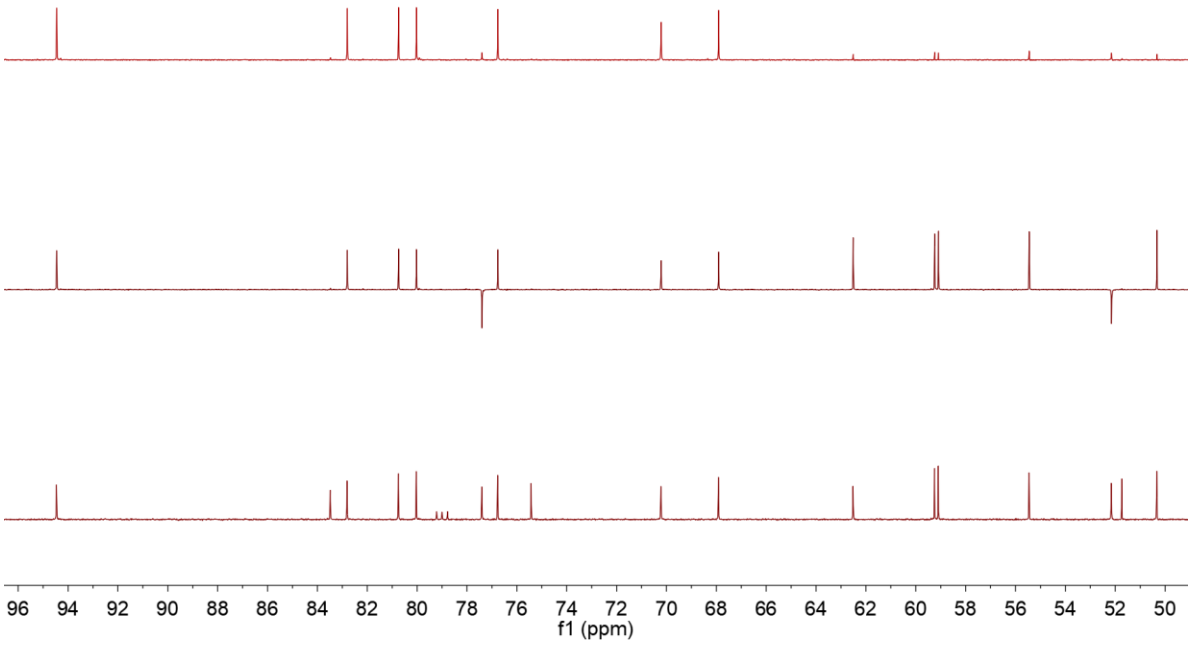

Figure S15: Expansion of DEPT Spectrum of **1** (1-*epi*-hokbusine A) (From δ_C 50 ppm to 96 ppm)

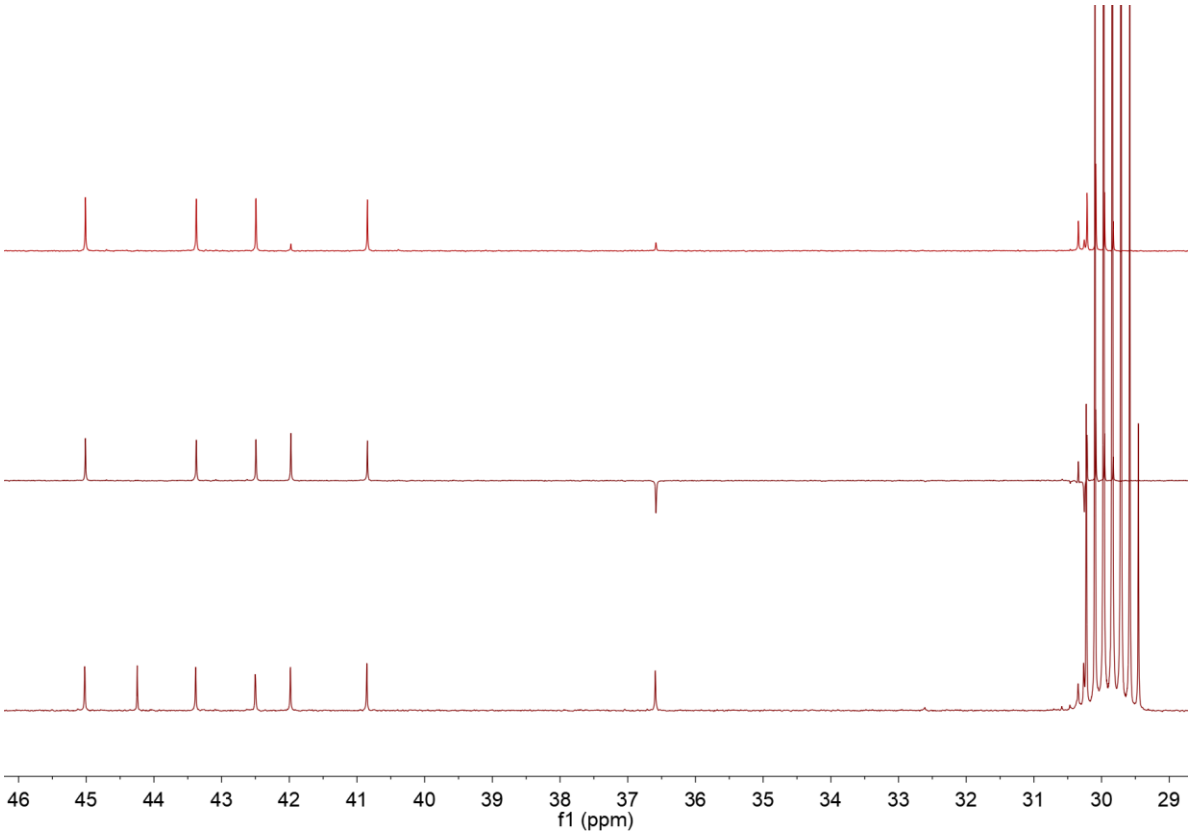

Figure S16: Expansion of DEPT Spectrum of **1** (1-*epi*-hokbusine A) (From δ_C 29 ppm to 46 ppm)

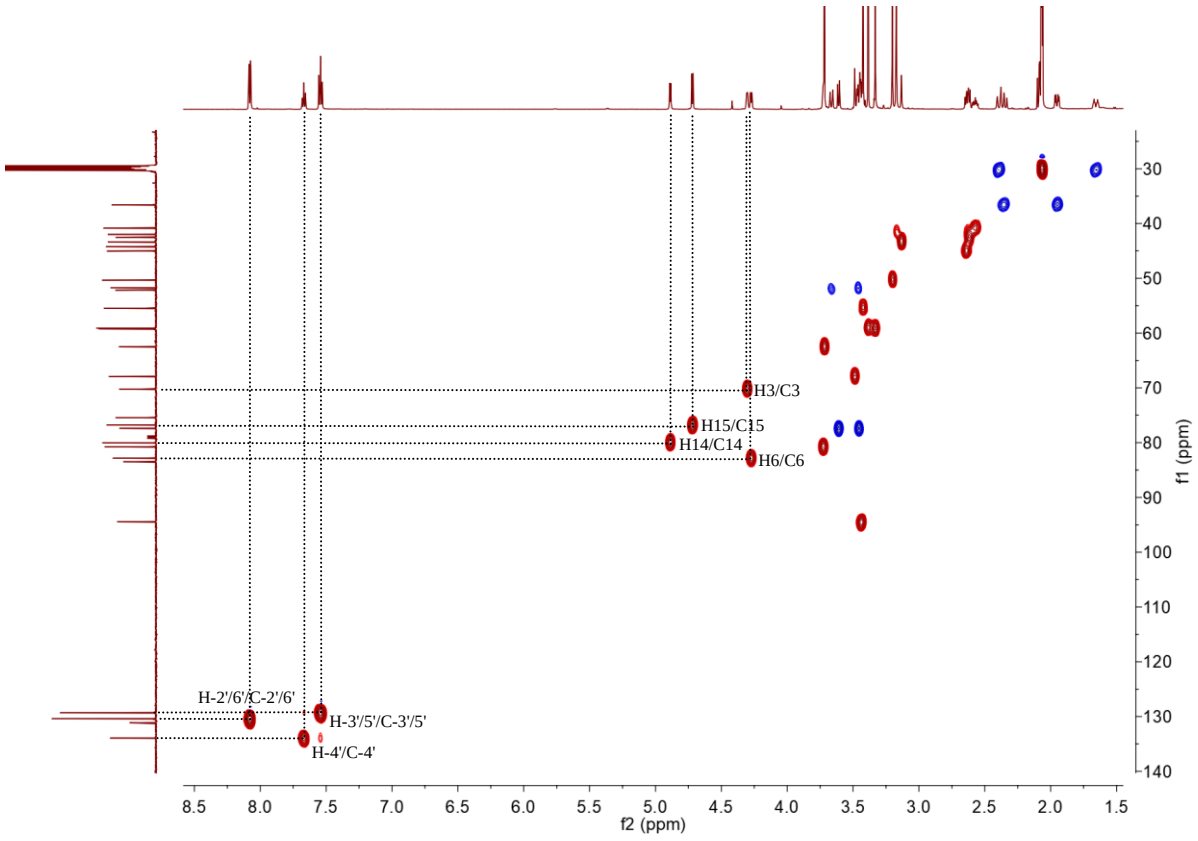

Figure S17: The HSQC Spectrum of **1** (1-*epi*-hokbusine A)

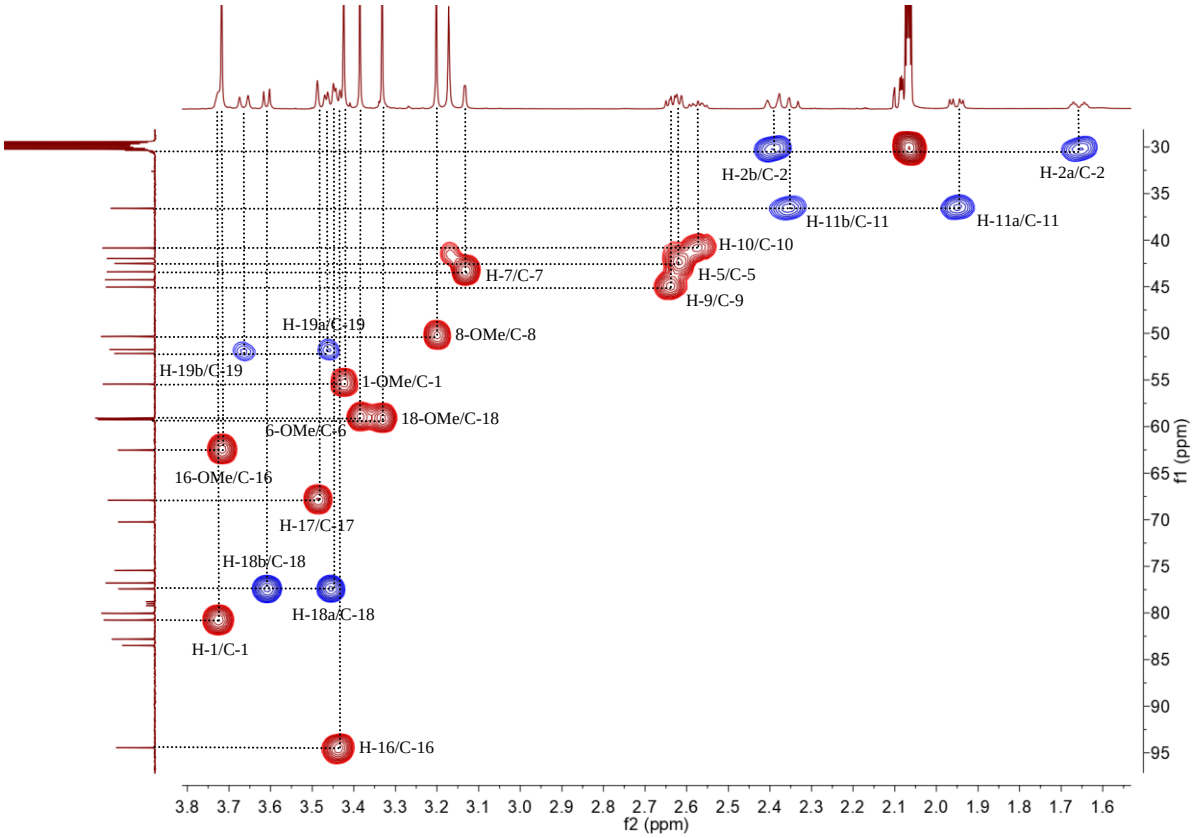

Figure S18: The HSQC Spectrum of **1** (1-*epi*-hokbusine A) (From δ_C 30 ppm to 95 ppm)

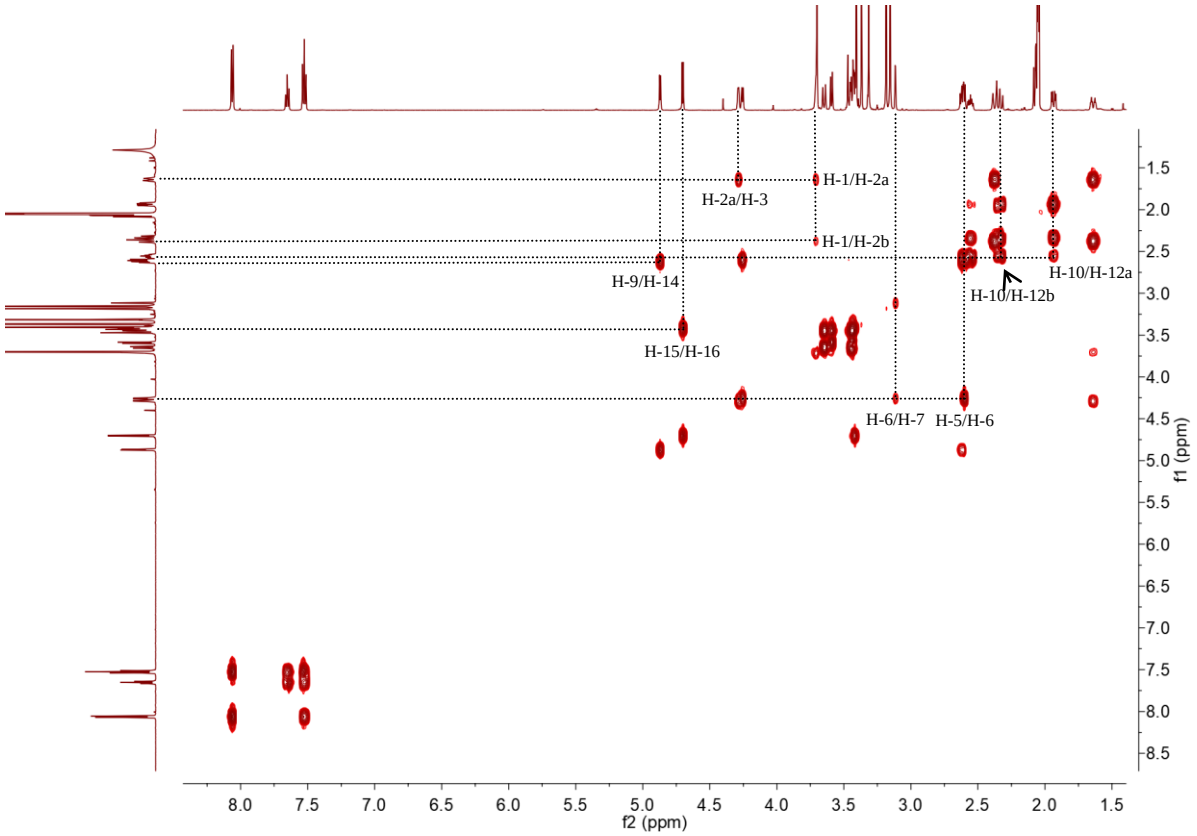

Figure S19: The ^{1}H-^{1}H COSY Spectrum of **1** (1-*epi*-hokbusine A)

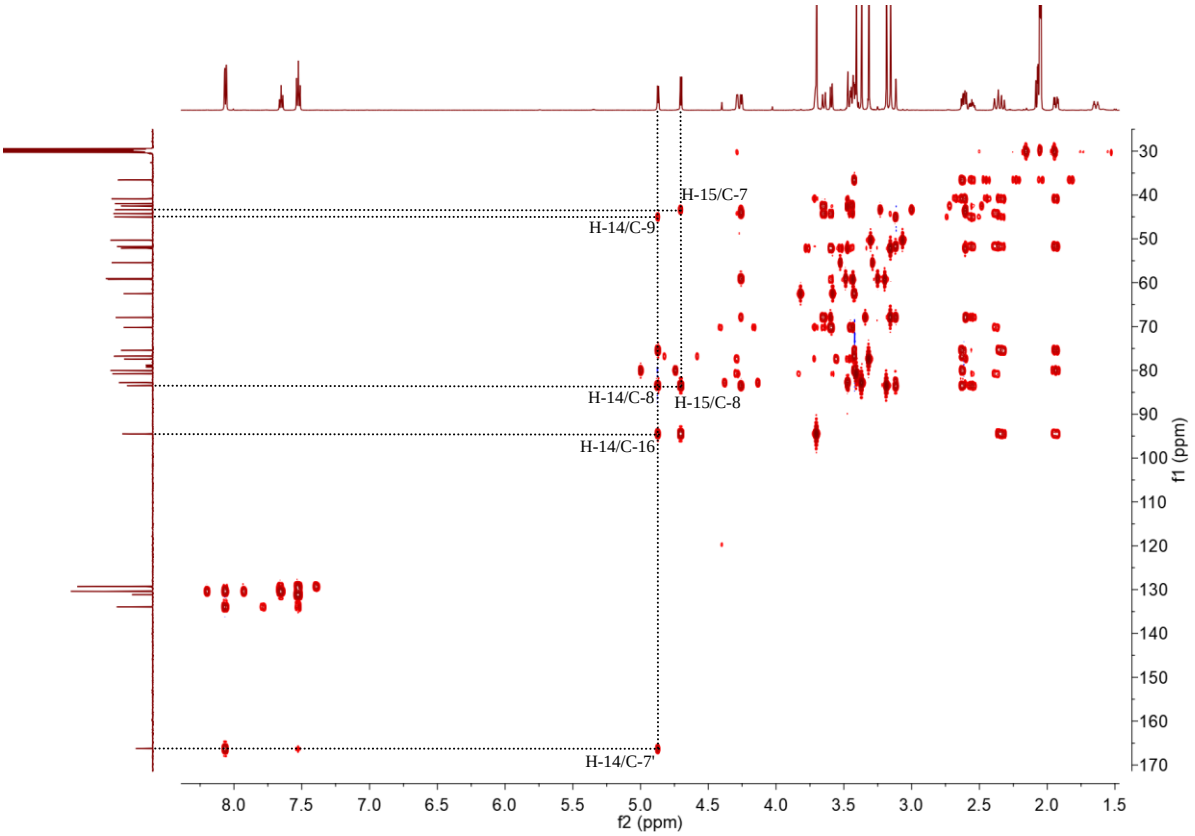

Figure S20: The HMBC Spectrum of **1** (1-*epi*-hokbusine A)

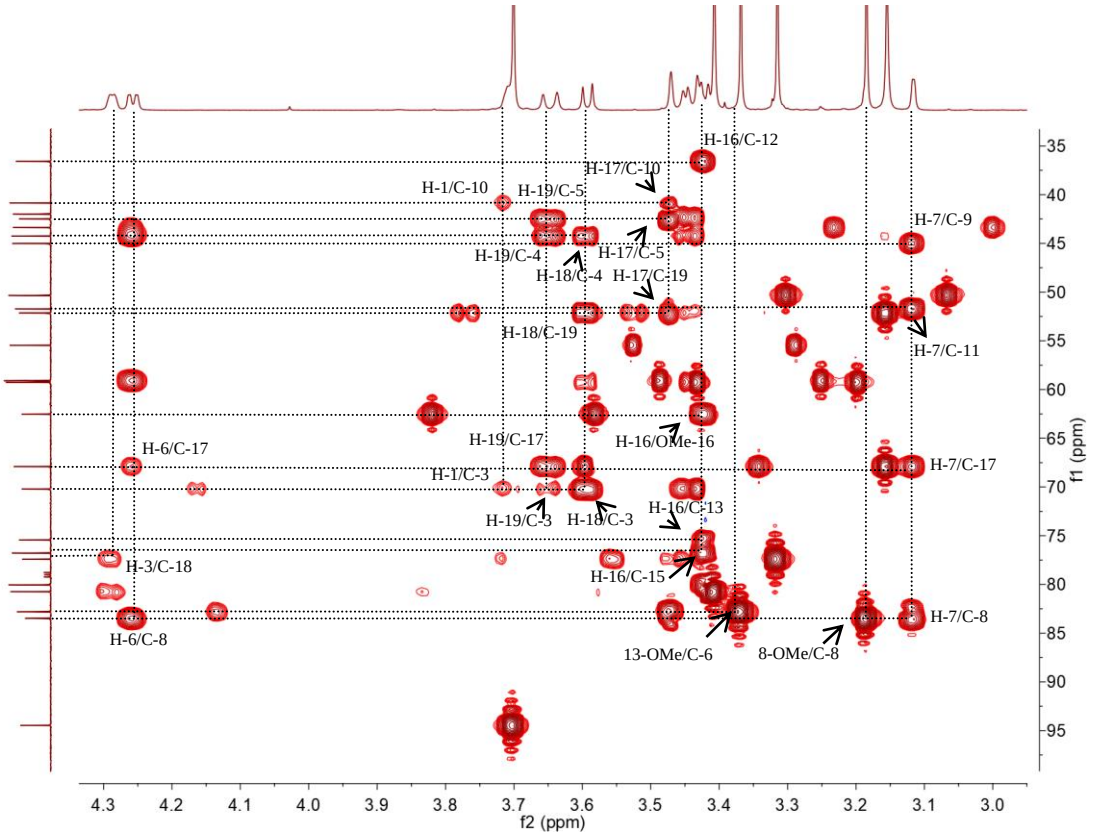

Figure S21: The HMBC Spectrum of **1** (1-*epi*-hokbusine A) (From δ_H 3.0 ppm to 4.3 ppm)

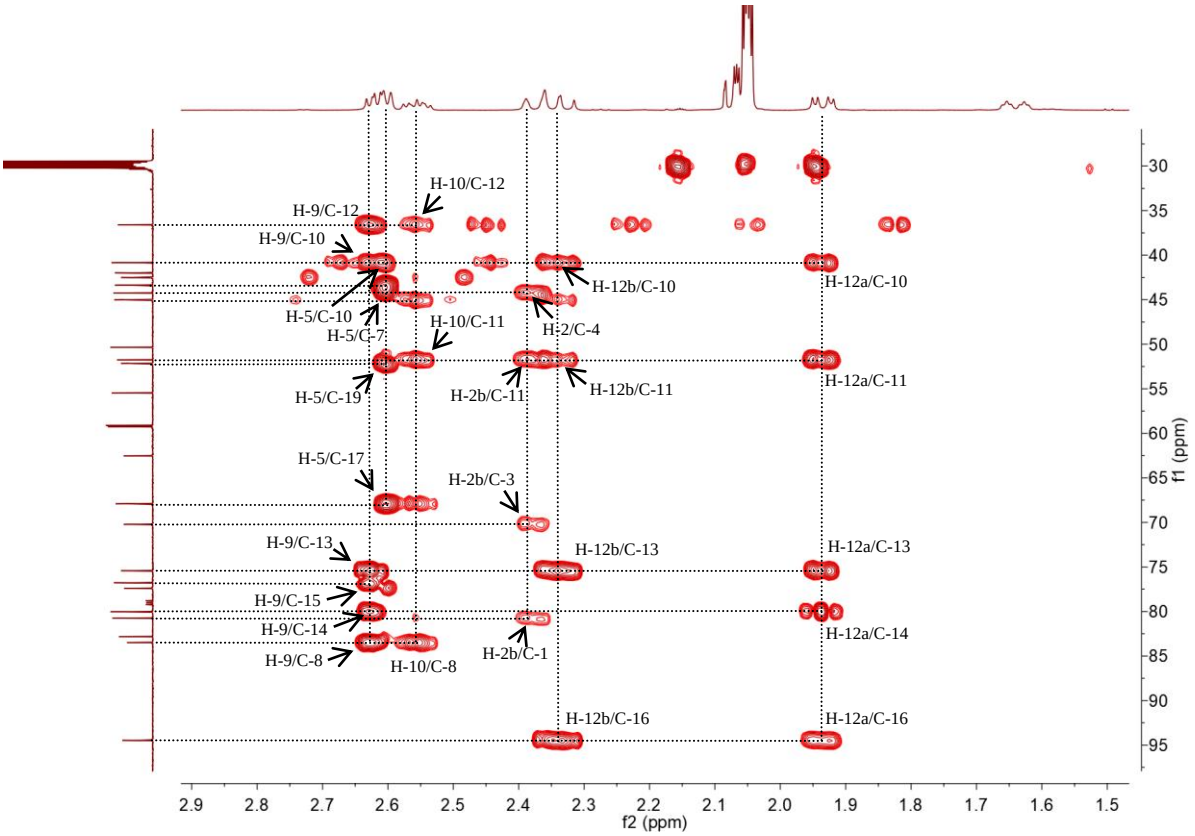

Figure S22: The HMBC Spectrum of **1** (1-*epi*-hokbusine A) (From δ_H 1.5 ppm to 2.9 ppm)

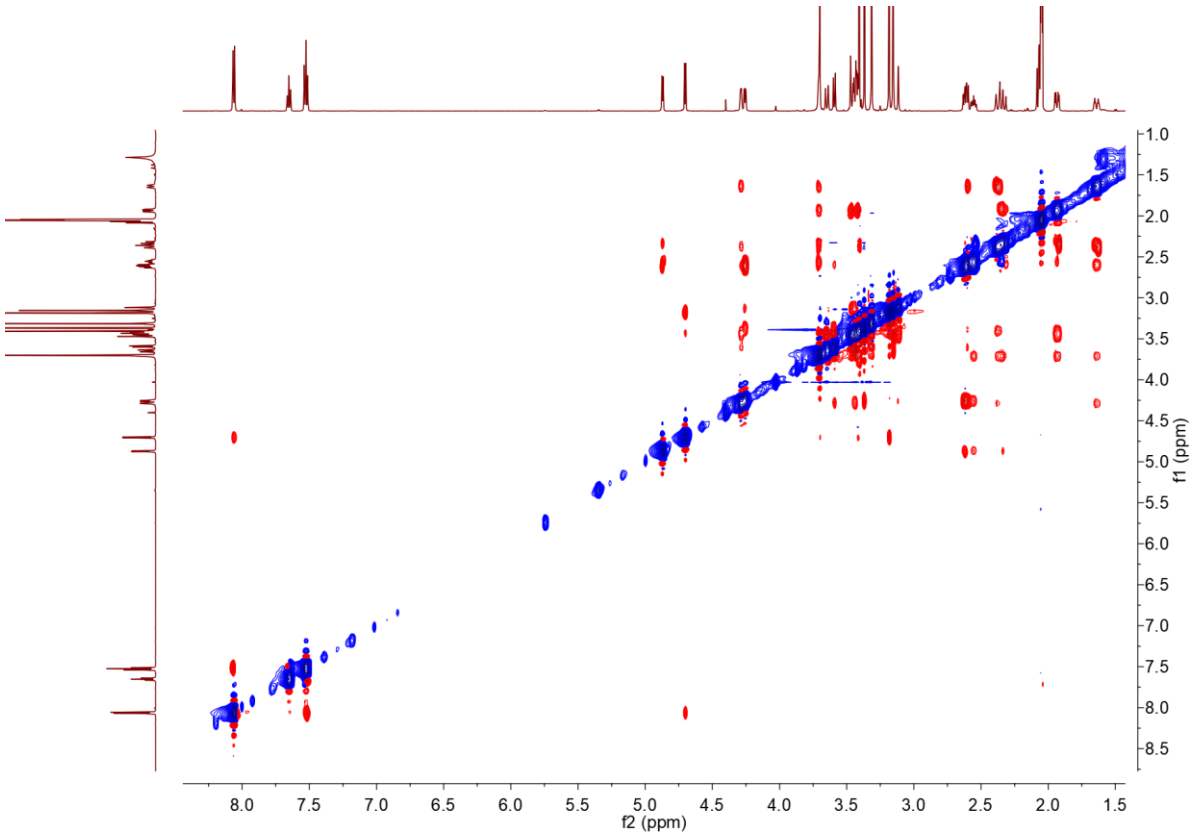

Figure S23: The ROESY Spectrum of **1** (1-*epi*-hokbusine A)

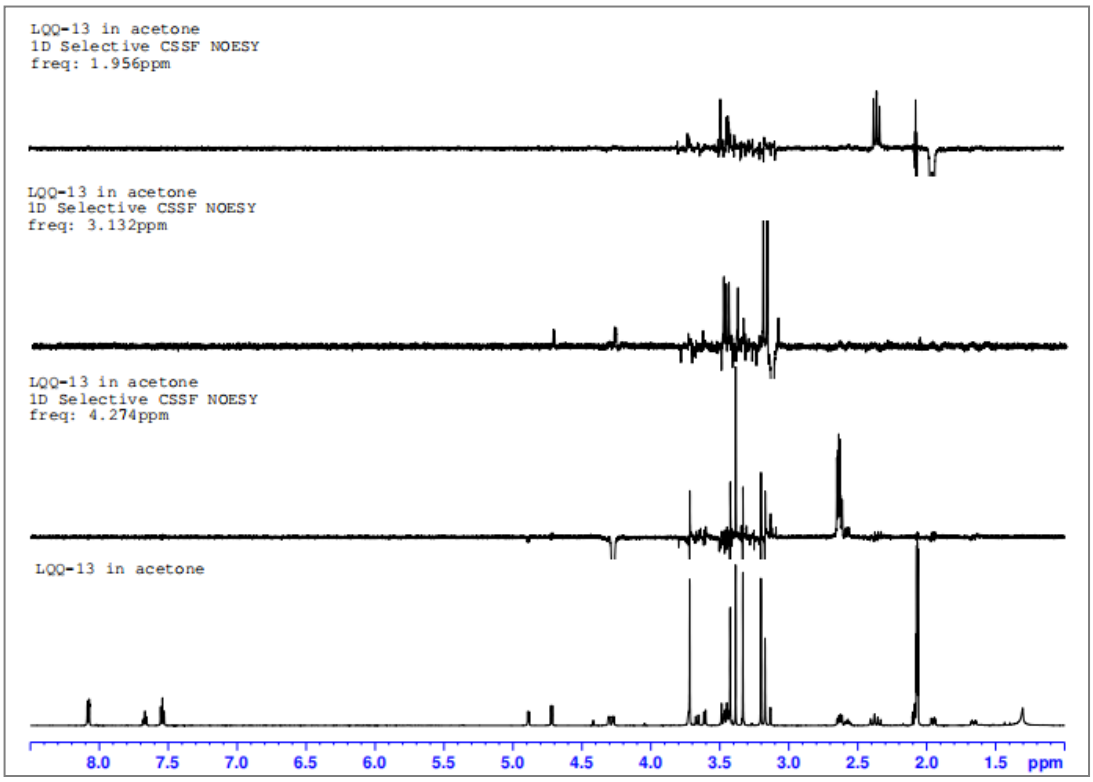

Figure S24: The 1D NOE Spectrum of **1** (1-*epi*-hokbusine A)