Supporting Information

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The First Example of Di-π-Methane Rearrangement in Nature: Cephalotanols A and B, Two Novel Rearranged Norlignan Glycosides from *Cephalotaxus fortunei* Hook

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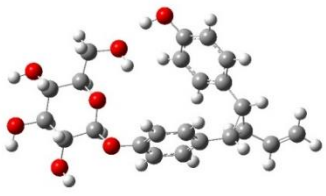
1. Quantum Chemical Calculations of 1 and 2

Conformation search for compounds were performed by Spartan's 14 using Merk Molecular Force Field (MMFF) level. The low energy conformations of compounds were submitted to the density functional theory (DFT) optimization at the level of b3lyp/6-31g (d,p), using the pcm solvation model with the dielectric constant representing Methanol. The optimized structures were subject to the frequency calculations at b3lyp/6-31g(d,p) level to confirm the true energy minimal located and generate the thermodynamic data. The optimized structures were further submitted to the Time-dependent density functional theory calculations at b3lyp/6-31g(d,p). Rotatory strengths for a total 80 excited states were calculated. ECD spectra was generated using the SpecDis 1.53 and GraphPad Prism 5 from dipole-length rotational strengths by applying Gaussian band shapes with = 0.16-0.22 ev.

Table S1: Energy analysis for **1**

conformer	Gibbs free energy (298.15 K)		
	G (Hartree)	ΔE (kcal/mol)	Population (%)
1-1	-1418.6350	0.2909	17.43
1-2	-1418.6355	0.0000	28.49
1-3	-1418.6355	0.0151	27.78
1-4	-1418.6354	0.0474	26.3



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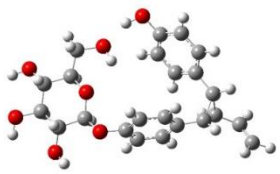

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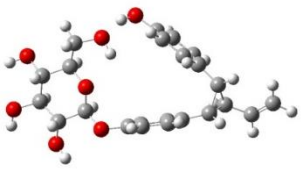

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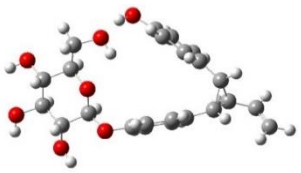


1-4

Figure Q1. B3LYP (PCM, methanol)/6-31G(d,p) optimized lowest energy conformers for **1**

Table S2: Calculated ECD Data for **1**

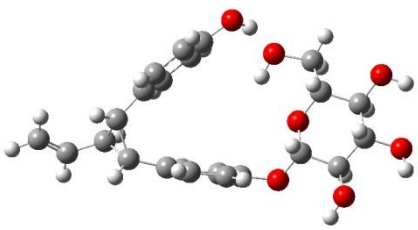
State	1-1		1-2		1-3		1-4	
	Excitation energies(ev)	**Rotatory Strengths***	**Excitation energies(ev)**	**Rotatory Strengths***	**Excitation energies(ev)**	**Rotatory Strengths***	**Excitation energies(ev)**	**Rotatory Strengths***
1	4.6037	-49.3989	4.5615	-49.1661	4.6887	23.4803	4.683	7.7343
2	4.7598	-7.9581	4.7076	-2.8372	4.8769	12.5165	4.922	18.875
3	4.958	54.6922	4.9206	58.5811	4.984	-0.9841	5.0079	8.3998
4	5.178	7.8879	5.1798	-2.3402	5.0676	-43.2469	5.1003	-34.0358
5	5.4343	-4.7627	5.2178	46.5942	5.4025	-5.0324	5.4592	47.7148
6	5.4934	54.8361	5.5092	35.5698	5.4639	7.6817	5.5043	1.1686
7	5.5548	2.5802	5.6808	3.8801	5.5795	47.8979	5.5796	-8.5604
8	5.7493	1.3008	5.779	27.4915	5.6676	10.2715	5.6718	58.5296
9	5.7816	39.7761	5.8697	-16.8154	5.775	-24.9171	5.7655	-32.8928
10	5.8567	-33.7272	5.8855	1.2464	5.8712	13.3419	5.8153	-1.3397
11	5.9093	14.4679	5.9229	-21.936	5.8803	-22.4658	5.8725	2.9404
12	5.9875	6.5686	5.9993	-38.7396	5.9718	-37.8177	5.9932	-46.7462
13	6.0893	-20.0956	6.036	16.7204	6.0447	-0.4319	6.0282	-5.9878
14	6.2008	0.4142	6.2666	4.3869	6.0942	-12.7014	6.0538	-0.3788
15	6.2259	-3.1797	6.307	6.716	6.1988	9.0598	6.1654	-1.6502
16	6.2817	10.958	6.3213	-1.1103	6.2907	-43.5959	6.2583	-9.9739
17	6.3695	-3.5664	6.3812	-23.994	6.4013	-15.8476	6.3736	-31.8764
18	6.3817	-6.6893	6.4069	-30.2587	6.4143	-9.0917	6.4065	-48.1238
19	6.4362	2.5495	6.4292	-10.2365	6.4866	-75.1041	6.4243	12.0445
20	6.5075	35.4598	6.4805	61.742	6.5141	-74.11	6.4995	-77.3192
21	6.5395	0.1793	6.5138	21.8089	6.5457	17.2079	6.5515	21.22
22	6.6099	-224.716	6.5349	-21.156	6.5993	90.4053	6.6133	64.8638
23	6.6825	180.7567	6.5922	-87.4257	6.6529	165.2918	6.6211	-70.1726
24	6.6833	-8.8874	6.6659	204.0279	6.6854	63.7147	6.6797	331.3787
25	6.7612	290.0352	6.7226	-235.388	6.7591	-26.5398	6.7599	-105.29
26	6.7661	50.8426	6.8117	57.2213	6.774	-159.431	6.7838	-183.613
27	6.8003	-92.8064	6.828	33.7071	6.8331	55.1553	6.8007	-119.869
28	6.8221	2.9872	6.8481	-1.6878	6.8365	10.7762	6.8154	-69.3134
29	6.883	-14.8117	6.9354	1.3317	6.8545	238.1684	6.8806	17.7765
30	6.9206	60.7315	6.9365	20.8641	6.9106	-26.0574	6.9257	-0.3645
31	6.9329	-31.1278	6.9672	24.4491	6.9222	-30.4184	6.9308	-12.2715
32	6.9446	-55.6853	6.9789	2.4366	6.9756	-68.9902	6.9544	18.0044
33	6.9673	-7.8736	6.9864	43.1367	6.9946	-3.6547	6.971	5.9702
34	6.9864	-11.6188	7.0085	-40.1098	7.0036	20.0113	7.0004	48.8832
35	7.0238	36.4052	7.0211	-2.5737	7.0176	-11.5038	7.0104	21.3841
36	7.0402	-1.045	7.0329	14.078	7.044	-0.007	7.0395	-6.5904
37	7.0422	-16.9221	7.0637	-1.4855	7.092	-85.1396	7.0686	8.2165
38	7.0833	6.6075	7.0694	11.0926	7.1123	-0.4105	7.1447	-1.0559
39	7.1185	-4.1886	7.0877	0.768	7.1604	-11.1517	7.1631	-51.0636

40	7.1459	-16.9444	7.0966	-78.7967	7.1757	-0.3162	7.1736	-49.6577
41	7.1746	8.8394	7.123	-1.909	7.1988	3.6314	7.196	1.9651
42	7.2003	4.1671	7.1421	-41.2878	7.215	28.1523	7.1987	15.3263
43	7.2104	-56.9831	7.1714	20.6526	7.2219	-16.0946	7.2195	54.3916
44	7.2407	-0.548	7.1972	-34.8109	7.2637	-0.5294	7.2748	-31.9717
45	7.2576	-2.8596	7.2245	8.4171	7.2658	-0.1451	7.2894	0.267
46	7.2673	-6.1361	7.2643	11.0754	7.3141	18.599	7.3182	10.1802
47	7.3233	-23.6636	7.2847	69.3055	7.329	-19.4116	7.3516	27.7729
48	7.3624	-4.0516	7.3405	16.5848	7.359	-5.3878	7.4028	-9.2098
49	7.3753	-1.796	7.353	-9.8032	7.3868	-0.0088	7.4126	5.9006
50	7.3986	-5.1105	7.3975	-1.7874	7.4141	-13.29	7.433	32.8582
51	7.4258	5.5152	7.4033	1.9325	7.426	9.4358	7.4487	12.1533
52	7.4432	-13.1206	7.4195	-0.964	7.4554	55.3181	7.4591	25.5399
53	7.4681	1.4729	7.4448	-5.2627	7.4669	2.8698	7.4802	-1.7616
54	7.4747	0.5976	7.4534	7.4335	7.4689	0.2427	7.4877	-0.4601
55	7.5006	-5.0039	7.4643	-7.2425	7.4887	5.1437	7.4951	14.5716
56	7.5041	0.1179	7.4764	-9.5167	7.5117	-0.7917	7.4995	6.7656
57	7.5079	-32.7585	7.5007	-1.1895	7.5227	-11.6794	7.503	23.2663
58	7.5109	-6.114	7.5123	-0.2714	7.5267	-6.1692	7.5172	-2.7665
59	7.5283	-2.8	7.5396	-8.097	7.5429	-56.1531	7.5244	1.1952
60	7.5532	-6.2607	7.5563	-6.1705	7.5455	-29.0681	7.5313	8.4048

* R(velocity) 10**-40 erg-esu-cm

Table S3: Energy analysis for **2**

conformer	Gibbs free energy (298.15 K)		
	G (Hartree)	ΔE (kcal/mol)	Population (%)
2-1	-1418.6356	0.1232	29.08
2-2	-1418.6358	0.0000	35.81
2-3	-1418.6353	0.2949	21.76
2-4	-1418.6349	0.5834	13.36



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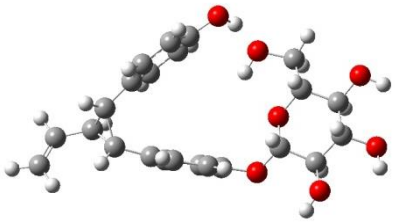

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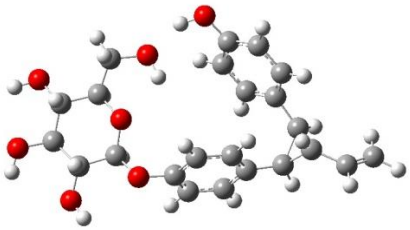

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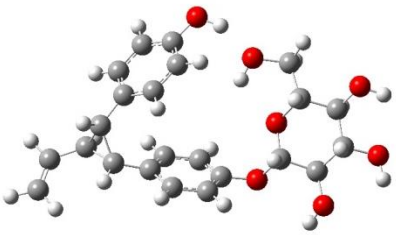


2-4

Figure Q2. B3LYP (PCM, methanol)/6-31G(d,p) optimized lowest energy conformers for **2**

Table S4. Calculated ECD Data for **2**

	2-1		2-2		2-3		2-4	
State	**Excitation energies(ev)**	**Rotatory Strengths***	**Excitation energies(ev)**	**Rotatory Strengths***	**Excitation energies(ev)**	**Rotatory Strengths***	**Excitation energies(ev)**	**Rotatory Strengths***
1	4.5662	32.5598	4.5489	34.9734	4.7649	-57.4752	4.8339	-60.9389
2	4.781	6.0251	4.7699	1.3539	4.8773	-13.0671	4.9302	-8.2337
3	4.9917	-12.5959	4.9667	-16.5594	5.0152	76.1326	5.0782	57.5384
4	5.1063	-3.091	5.1134	-9.1026	5.0913	25.9114	5.1128	25.7353
5	5.4157	-14.0891	5.2601	-33.6268	5.3192	78.2629	5.3916	40.5107
6	5.4692	27.2704	5.5343	38.0226	5.4614	39.6257	5.5465	50.0926
7	5.5485	9.033	5.5928	10.4269	5.5848	-88.3533	5.6293	-9.0992
8	5.707	27.6771	5.758	-25.1225	5.7578	-6.5289	5.7419	-30.3919
9	5.7946	8.1234	5.8081	29.9172	5.8295	-14.9102	5.8157	8.3163
10	5.8319	-15.4199	5.8755	-5.9324	5.8678	12.4207	5.8509	15.373
11	5.9537	-37.0035	5.8898	12.5066	5.9338	11.0309	5.8847	-14.8965
12	5.9684	14.0058	5.99	-24.5072	5.9764	-7.2904	5.9373	0.9326
13	6.0159	-3.3108	6.0559	-8.2839	6.0485	-6.6963	5.9819	-10.8956
14	6.1559	23.7489	6.1862	48.3248	6.1656	-0.6779	6.0114	-0.1804
15	6.2206	-7.4552	6.2824	-7.6919	6.2363	-9.7113	6.1463	2.245
16	6.3055	-10.2476	6.3034	-14.0424	6.3119	33.3116	6.2289	-8.1437
17	6.3421	-9.8644	6.3256	-2.5271	6.3912	9.7556	6.3849	2.2657
18	6.3793	-3.0953	6.3849	-17.3373	6.4516	1.0686	6.3939	-5.5236
19	6.4677	-11.5455	6.4068	-26.9844	6.4831	84.1229	6.4679	11.7779
20	6.5	-43.6064	6.4649	-117.563	6.4941	34.0811	6.5175	52.4212
21	6.5177	-49.8967	6.5175	22.2157	6.5453	30.9182	6.5215	-2.2949
22	6.6078	35.7944	6.5675	47.5922	6.6193	-241.703	6.6166	-257.038
23	6.6375	-50.3764	6.6528	122.4728	6.6587	94.5998	6.6462	174.5652
24	6.6985	170.786	6.7099	52.5194	6.6879	-3.0998	6.7087	58.5478
25	6.7483	-65.0616	6.7599	-117.197	6.7377	7.9733	6.729	236.3154
26	6.8019	-27.3282	6.781	55.8973	6.7959	116.076	6.7617	-53.5722
27	6.8088	-100.63	6.8131	14.5619	6.8405	8.9023	6.8066	62.9628
28	6.8304	-19.5129	6.8387	-105.106	6.8531	34.3992	6.8466	-5.4614
29	6.9122	-3.1928	6.8794	165.4626	6.8628	-12.718	6.8616	0.6099
30	6.938	7.6186	6.9305	18.2088	6.8889	-1.4375	6.8897	-0.8272
31	6.951	-4.6754	6.9644	3.764	6.893	31.1452	6.9029	-0.0827
32	6.9609	6.602	6.9697	3.41	6.9457	-161.467	6.9144	-3.6879
33	6.9701	-9.7284	6.9879	-61.0644	6.9551	-111.141	6.9845	-32.3794
34	6.9814	-12.4475	7.0118	-3.1569	6.978	8.152	6.9856	-93.7978
35	6.9914	-6.3106	7.0278	-1.9261	6.9846	16.3424	7.0156	2.8097
36	7.0046	15.5519	7.0388	-10.2647	7.0106	14.7323	7.0735	35.3159
37	7.0529	-47.2798	7.0437	23.5191	7.0594	-1.4461	7.1033	5.086

38	7.0547	-0.316	7.0815	-49.4818	7.0864	22.3564	7.1192	87.769
39	7.1456	0.7164	7.1083	1.7279	7.1133	35.7163	7.1599	-2.5011
40	7.1631	-15.2059	7.1582	0.1824	7.144	-2.6461	7.2018	-15.5253
41	7.1924	-15.6013	7.1877	9.4814	7.192	-9.1407	7.2317	-3.5749
42	7.1973	4.2443	7.2002	-44.6941	7.2132	-10.462	7.2362	4.3029
43	7.2067	15.5246	7.2228	-14.4802	7.2173	18.957	7.2383	-0.5504
44	7.2581	-2.4317	7.246	-61.4744	7.2271	-8.8443	7.2649	-26.1113
45	7.2854	-8.4512	7.2622	-3.1632	7.2357	42.2996	7.2754	16.9159
46	7.2894	0.8895	7.2731	0.5557	7.2466	-30.0285	7.2988	-30.0441
47	7.3169	10.2486	7.3137	36.1596	7.2909	0.5527	7.3312	-2.6706
48	7.34	-35.7972	7.3178	-21.1941	7.3259	-18.0933	7.3748	-11.0276
49	7.3778	-0.6685	7.3641	17.452	7.3608	39.308	7.4232	-9.531
50	7.398	12.8018	7.3835	-0.9398	7.3726	-59.5226	7.4631	1.6137
51	7.416	-9.7236	7.4059	-31.6753	7.4192	4.2834	7.4751	-31.4419
52	7.4392	58.5329	7.4285	31.1815	7.4513	-11.7866	7.4844	-0.9465
53	7.4473	4.6951	7.4372	-0.7477	7.494	-4.4804	7.4882	-26.9139
54	7.4623	1.8938	7.4394	-5.7397	7.4962	-31.1145	7.4969	-31.8539
55	7.4846	3.2798	7.4578	0.259	7.5332	-2.1667	7.5078	-5.249
56	7.4957	-1.1784	7.4707	2.781	7.547	-7.1648	7.5474	-1.8534
57	7.5012	7.7565	7.4976	-4.9855	7.5711	-13.9856	7.5575	-17.301
58	7.5142	12.3238	7.5061	0.0315	7.5807	-0.0768	7.5675	-1.6001
59	7.5209	17.2531	7.5297	-0.2269	7.597	11.3057	7.5863	-16.0466
60	7.5266	8.9443	7.5424	-5.9924	7.5999	2.3058	7.6247	-12.4602

* R(velocity) 10**-40 erg-esu-cm

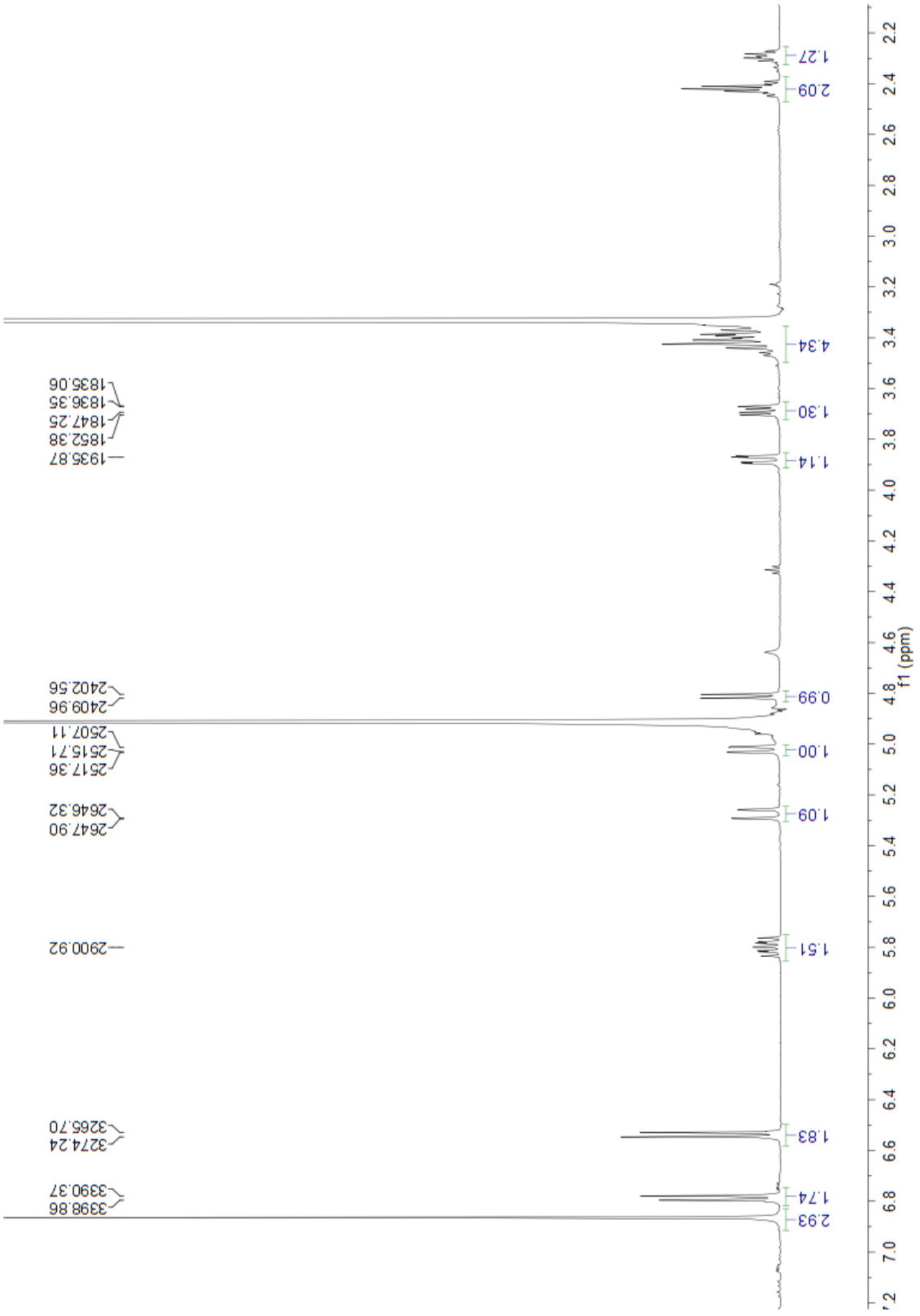


Figure S1: ^{1}H NMR spectrum of **1** in methanol-d_4

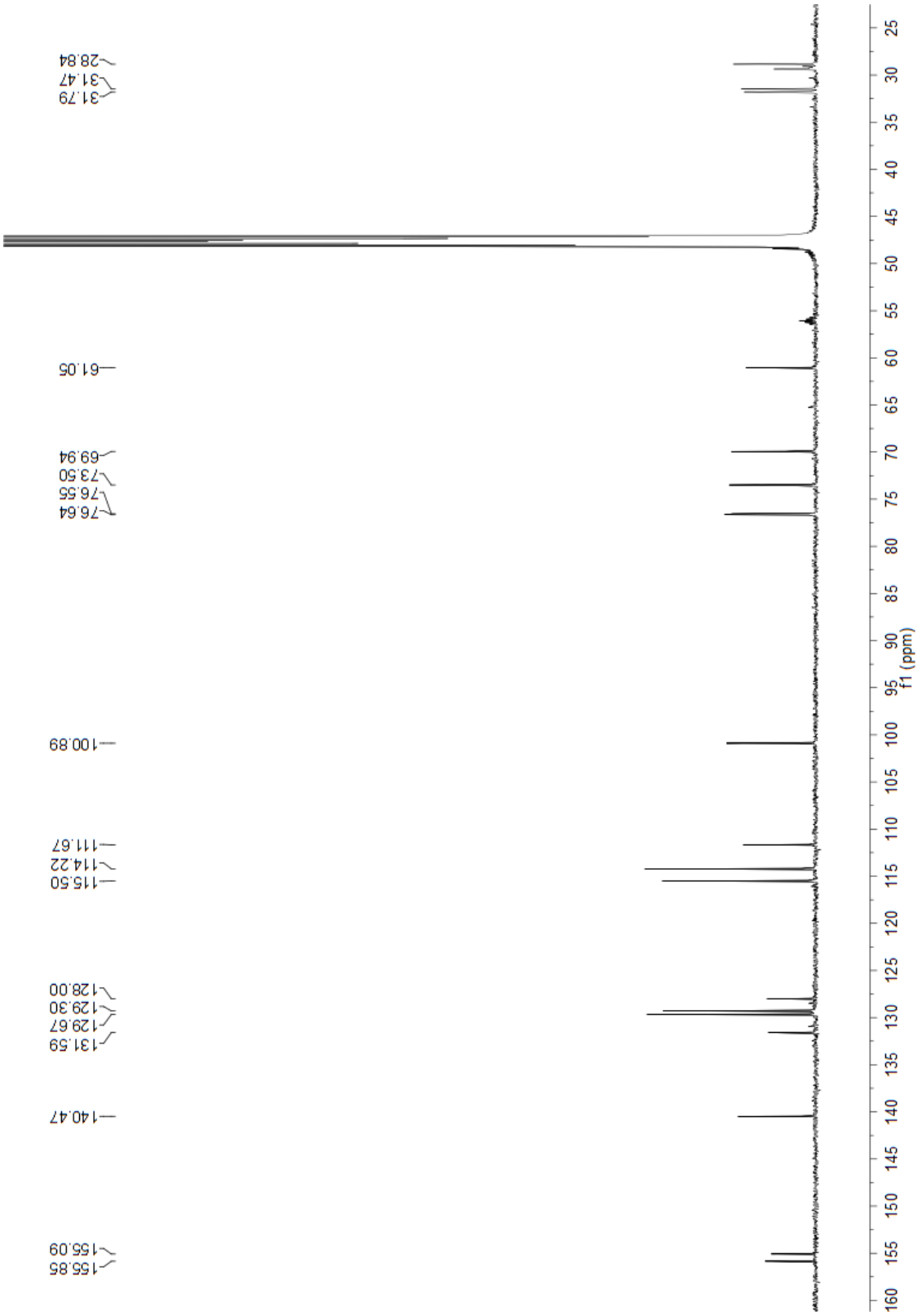


Figure S2: ^{13}C NMR spectrum of **1** in methanol-d_4

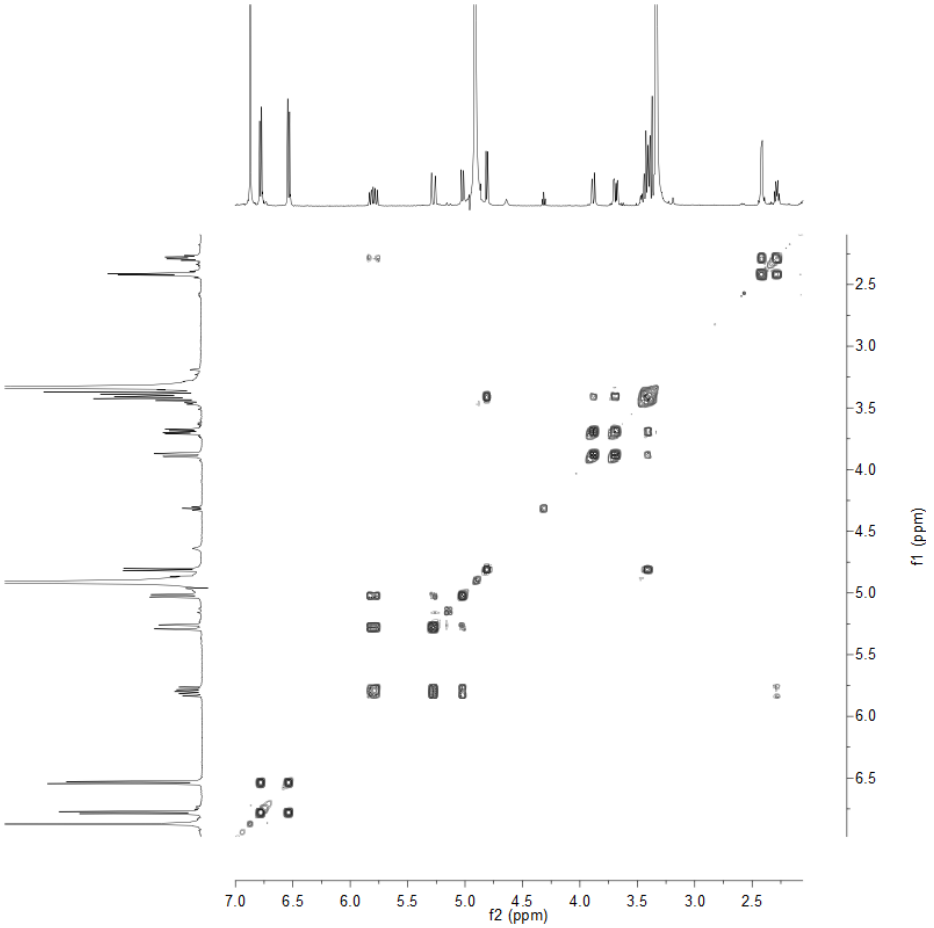


Figure S3: ^{1}H-^{1}H COSY spectrum of **1** in methanol-d_4

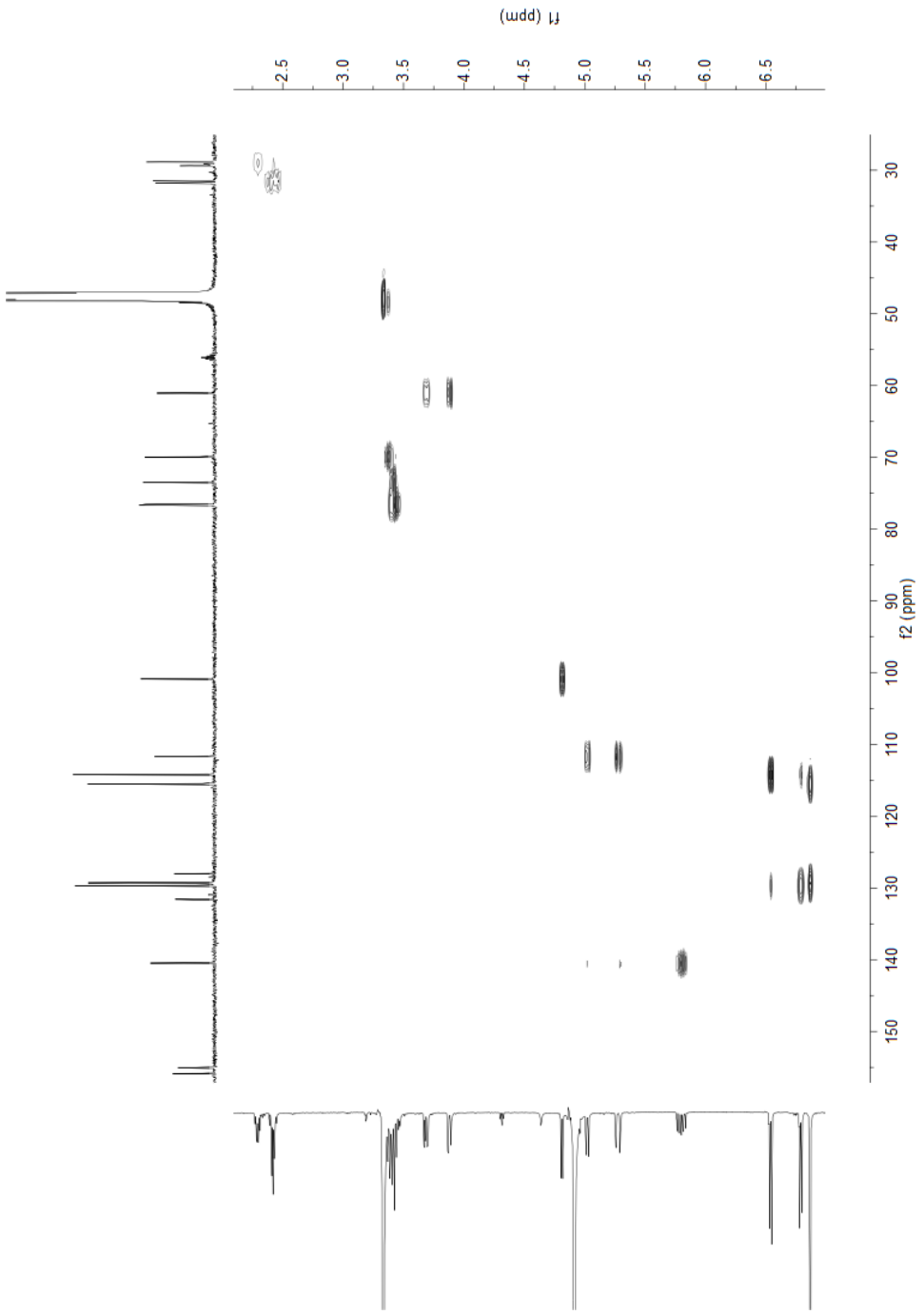


Figure S4: HSQC spectrum of **1** in methanol-d_4

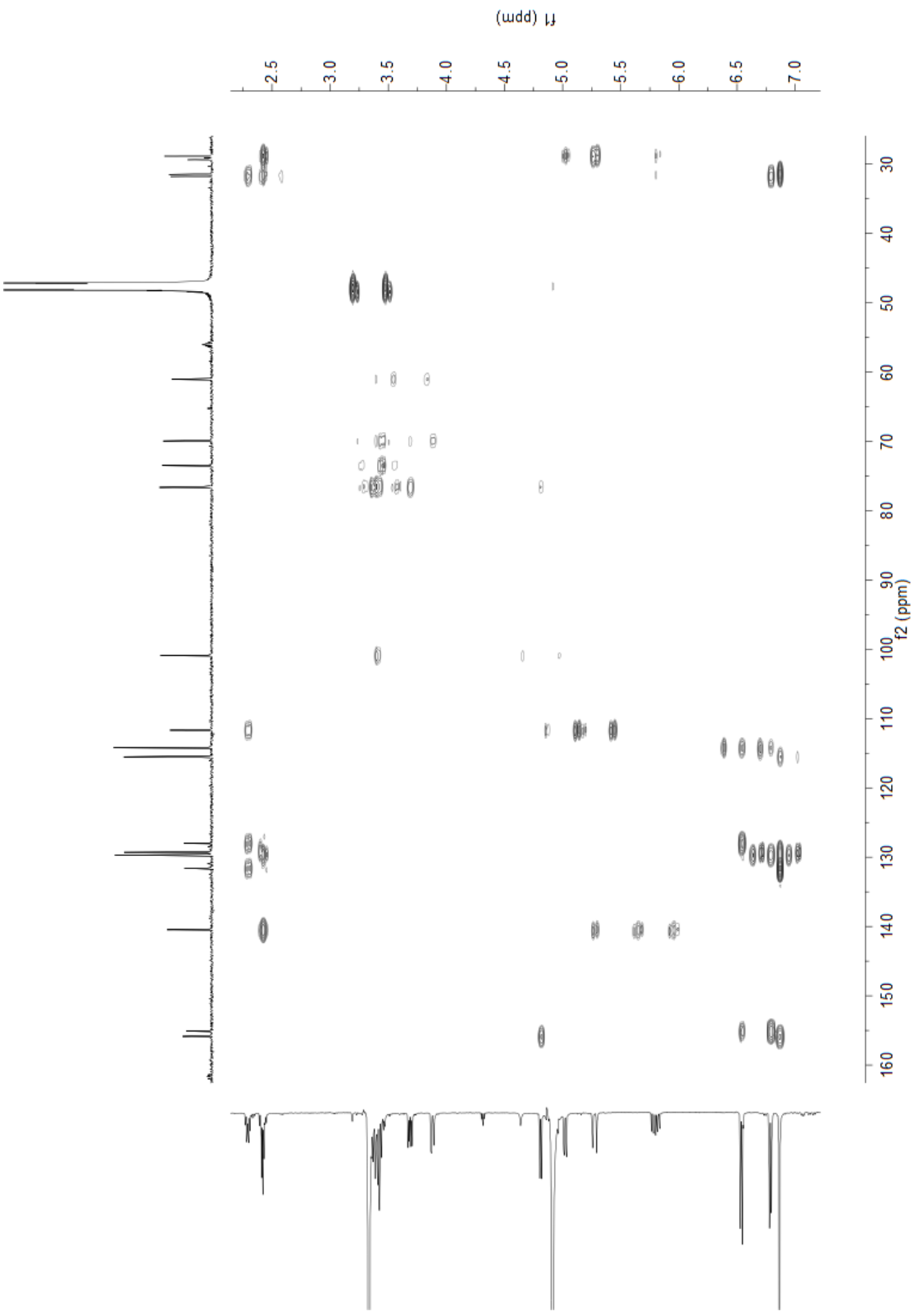


Figure S5: HMBC spectrum of **1** in methanol-d_4

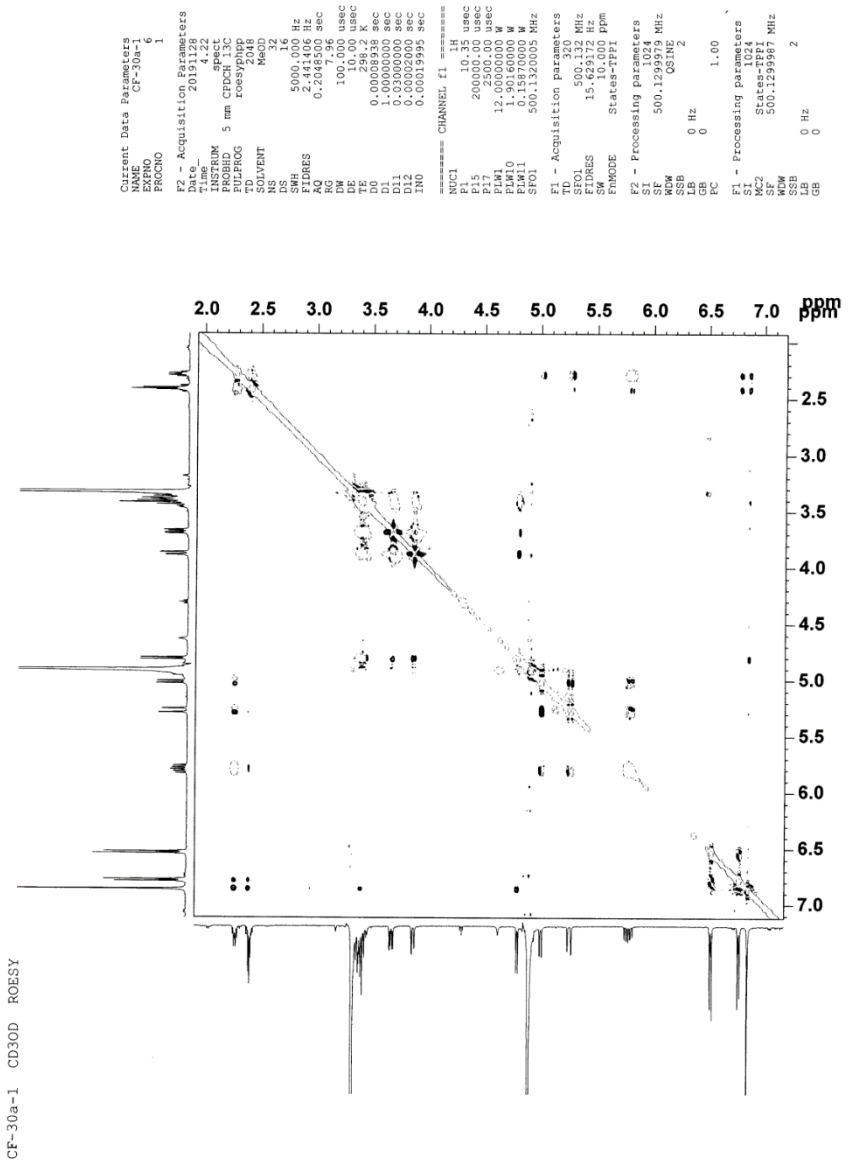


Figure S6: ROESY spectrum of **1** in methanol-d_4

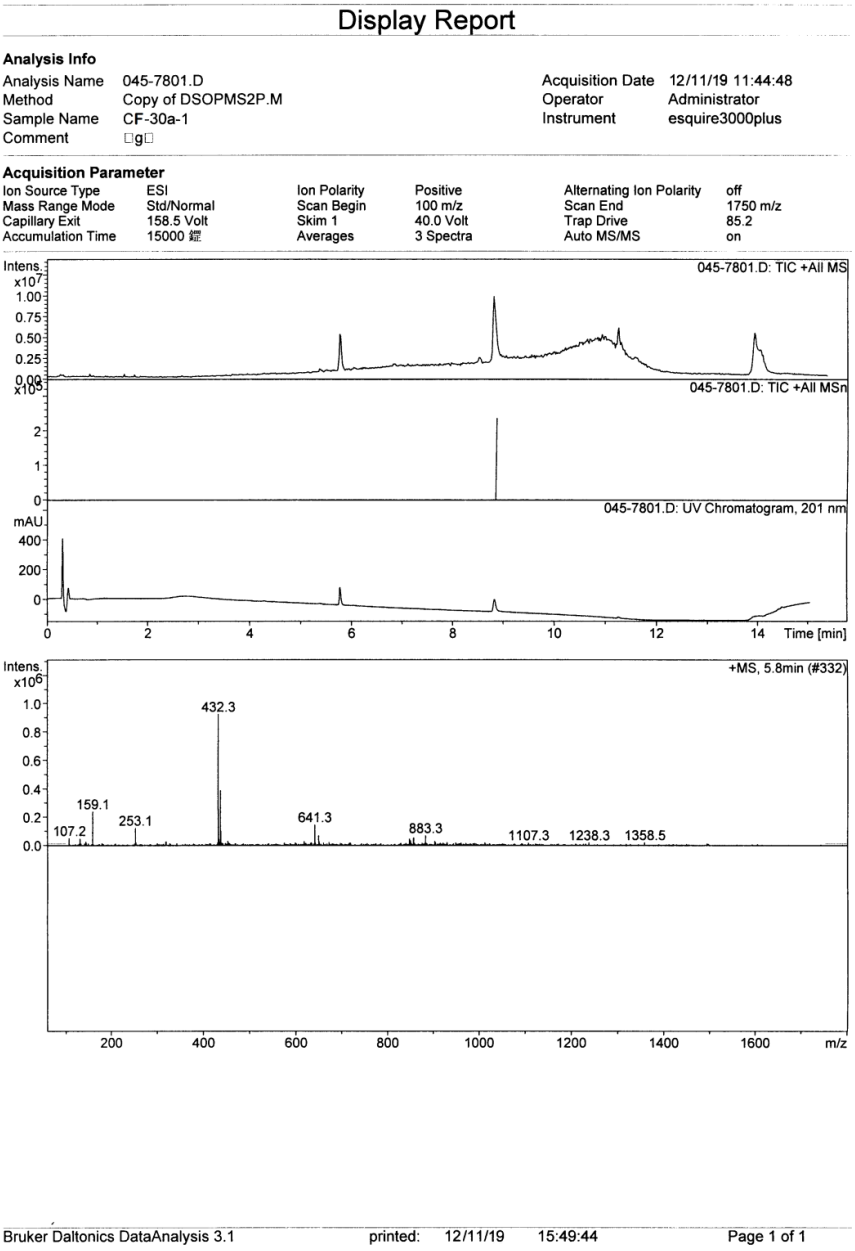


Figure S7: ESI(+)MS spectrum of **1**

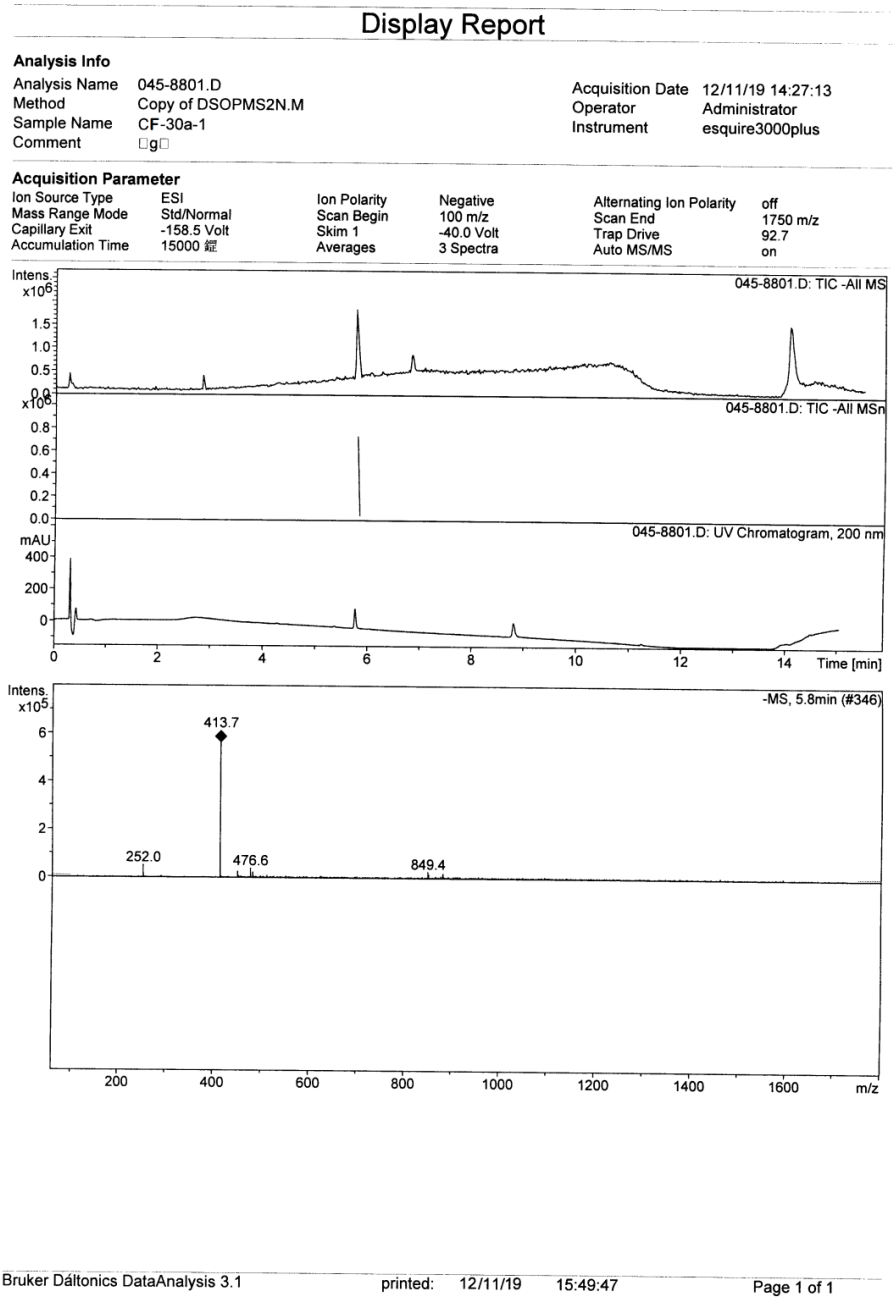


Figure S8: ESI(−)MS spectrum of **1**

Elemental Composition Report

Page 1

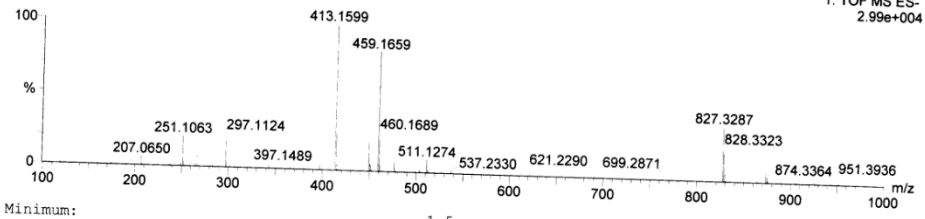
Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
81 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 6-60 H: 2-110 O: 0-30
CF-30a

LCT PXE KE324

CF-30a_20191102 28 (0.599) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (27:49)

02-Nov-2019
14:01:32
1: TOF MS ES-
2.99e+004



Minimum:		3.0	3.0	-1.5			
Maximum:				50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
413.1599	413.1600	-0.1	-0.2	11.5	169.1	0.0	C23 H25 O7

Figure S9: HRESIMS spectrum of **1**

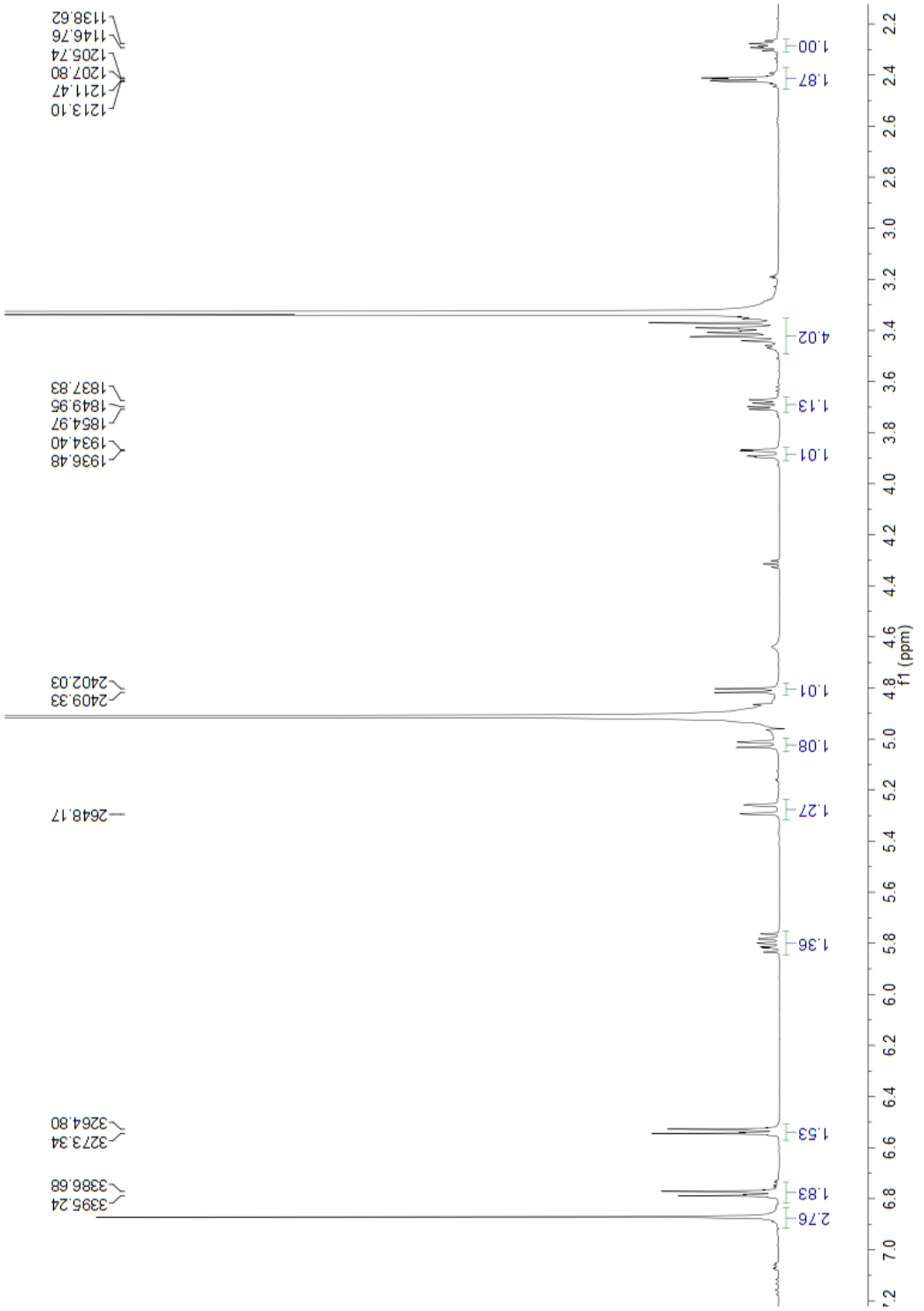


Figure S10: ^{1}H NMR spectrum of **2** in methanol-d_4

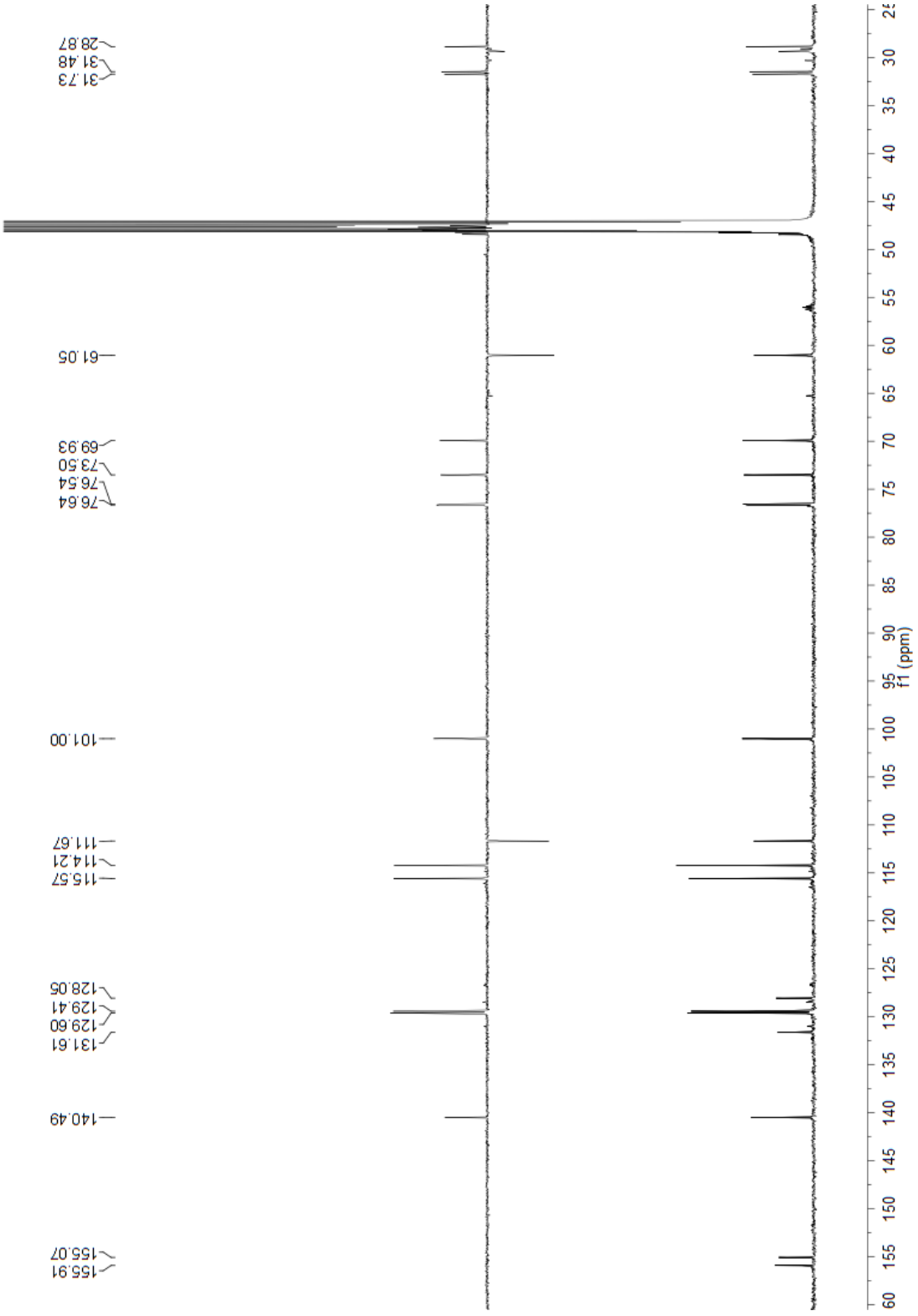


Figure S11: ^{13}C NMR spectrum of **2** in methanol-d_4

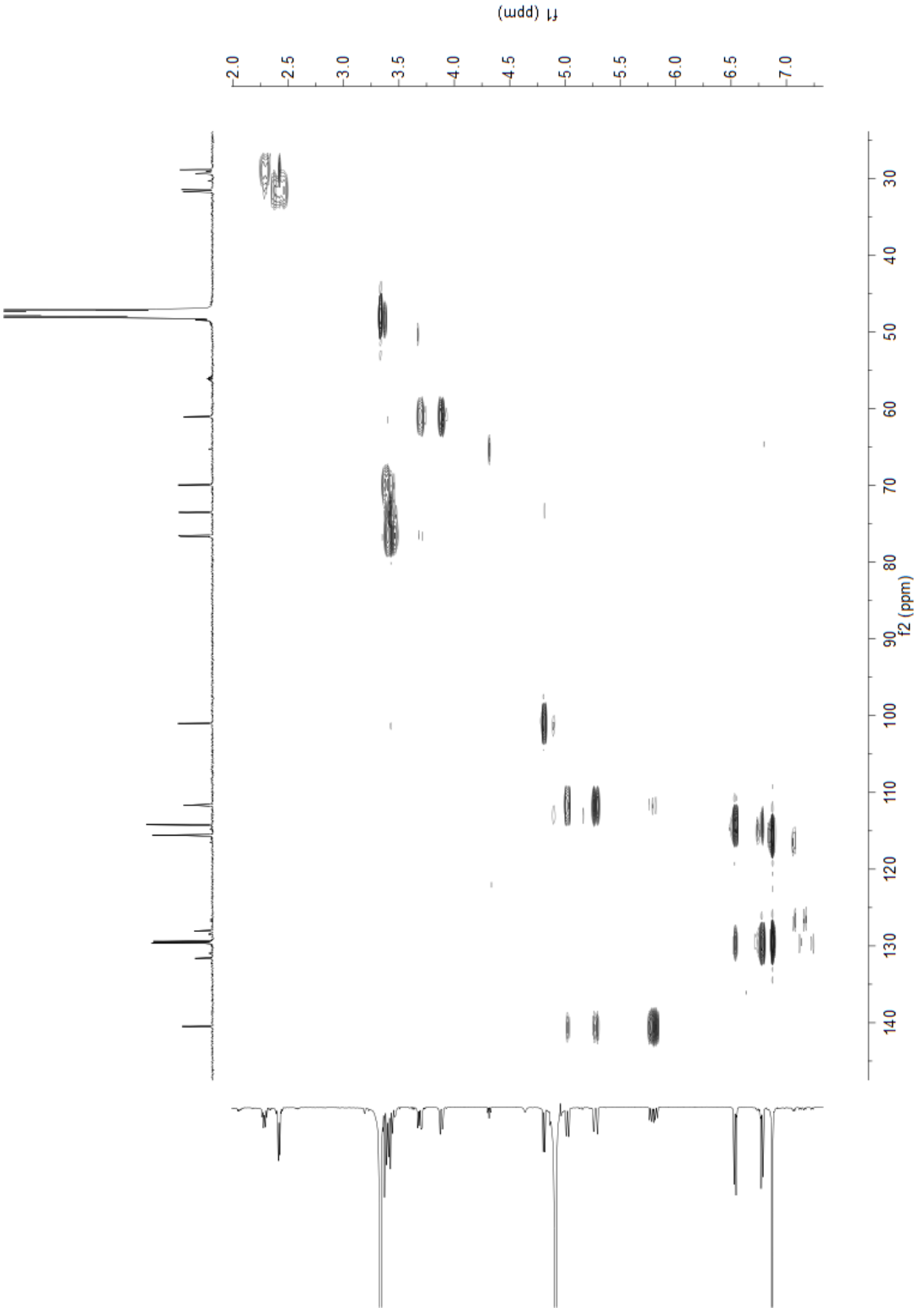


Figure S12: HSQC spectrum of **2** in methanol-d_4

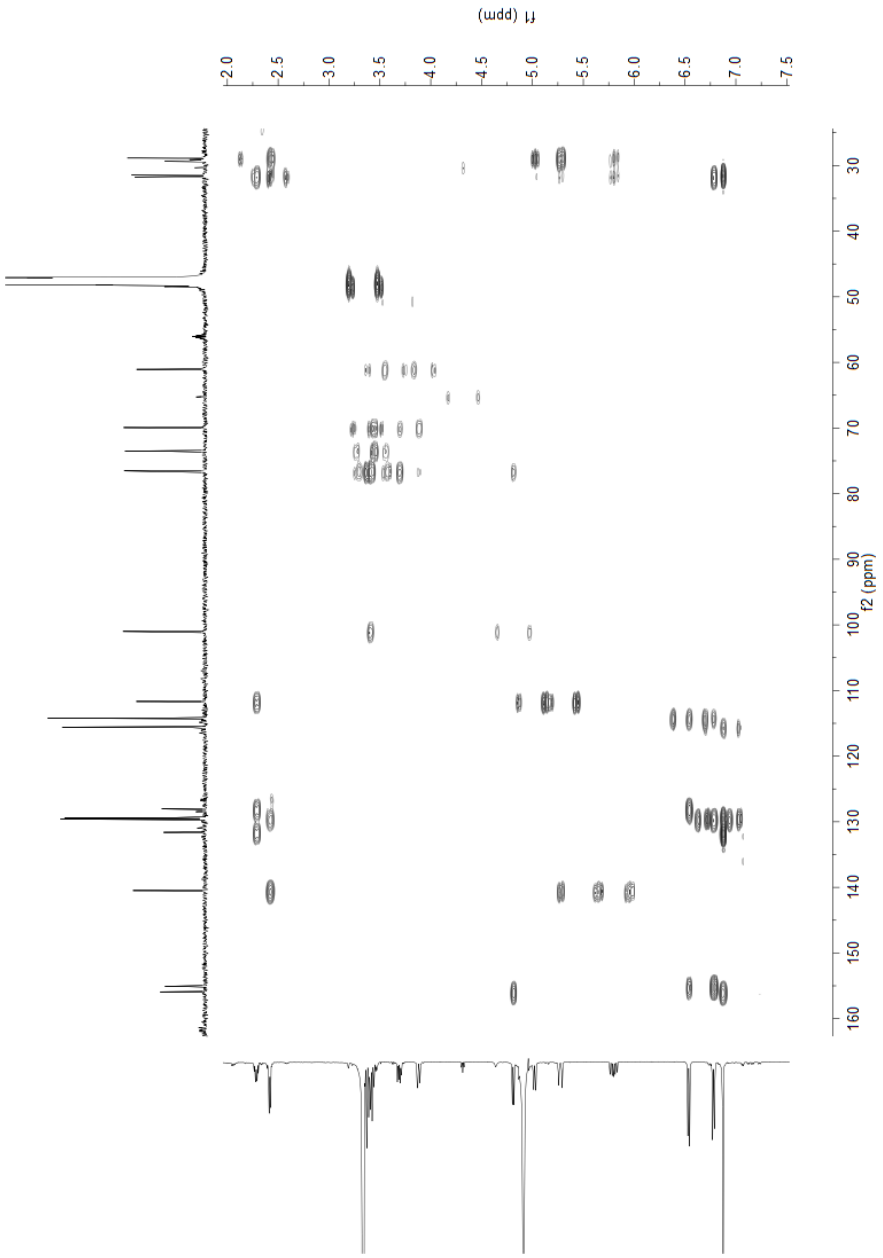


Figure S13: HMBC spectrum of **2** in methanol-d_4

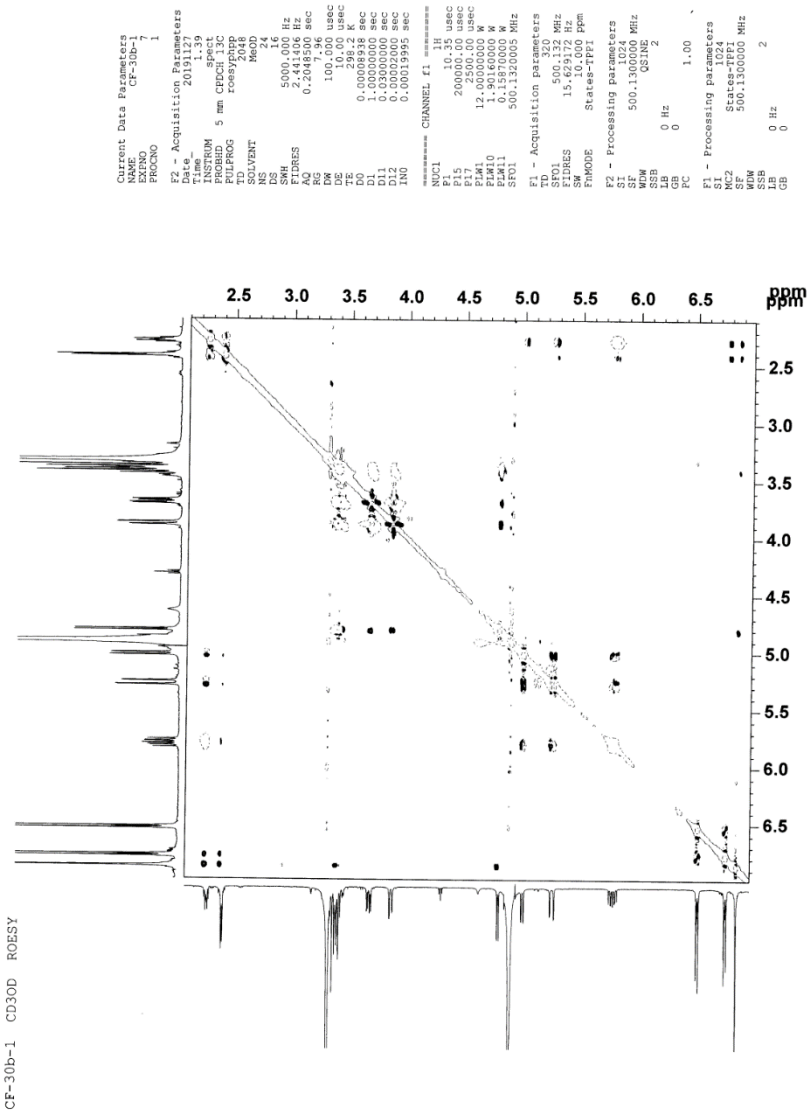


Figure S14: ROESY spectrum of **2** in methanol-d_4

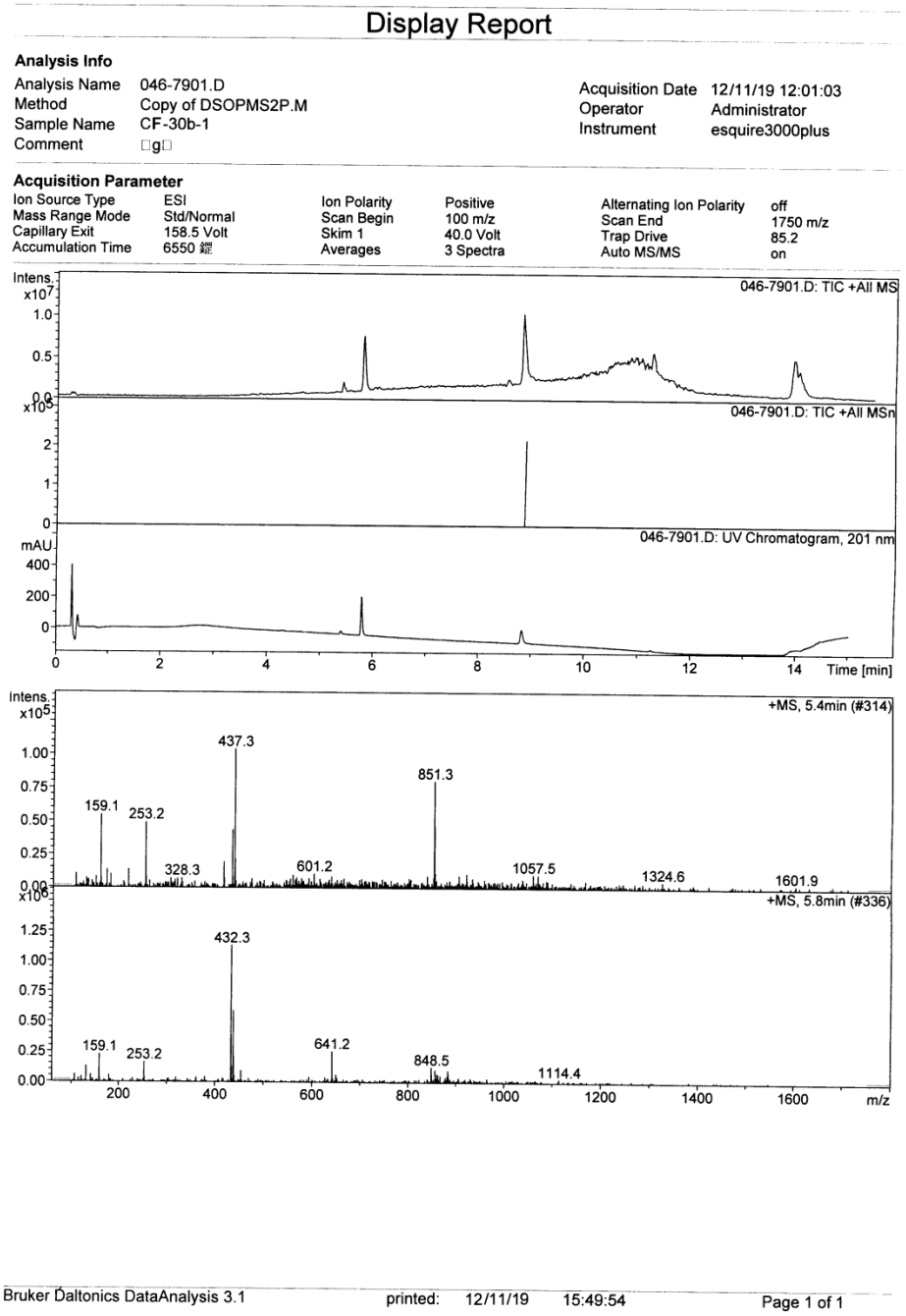


Figure S15: ESI(+)MS spectrum of **2**

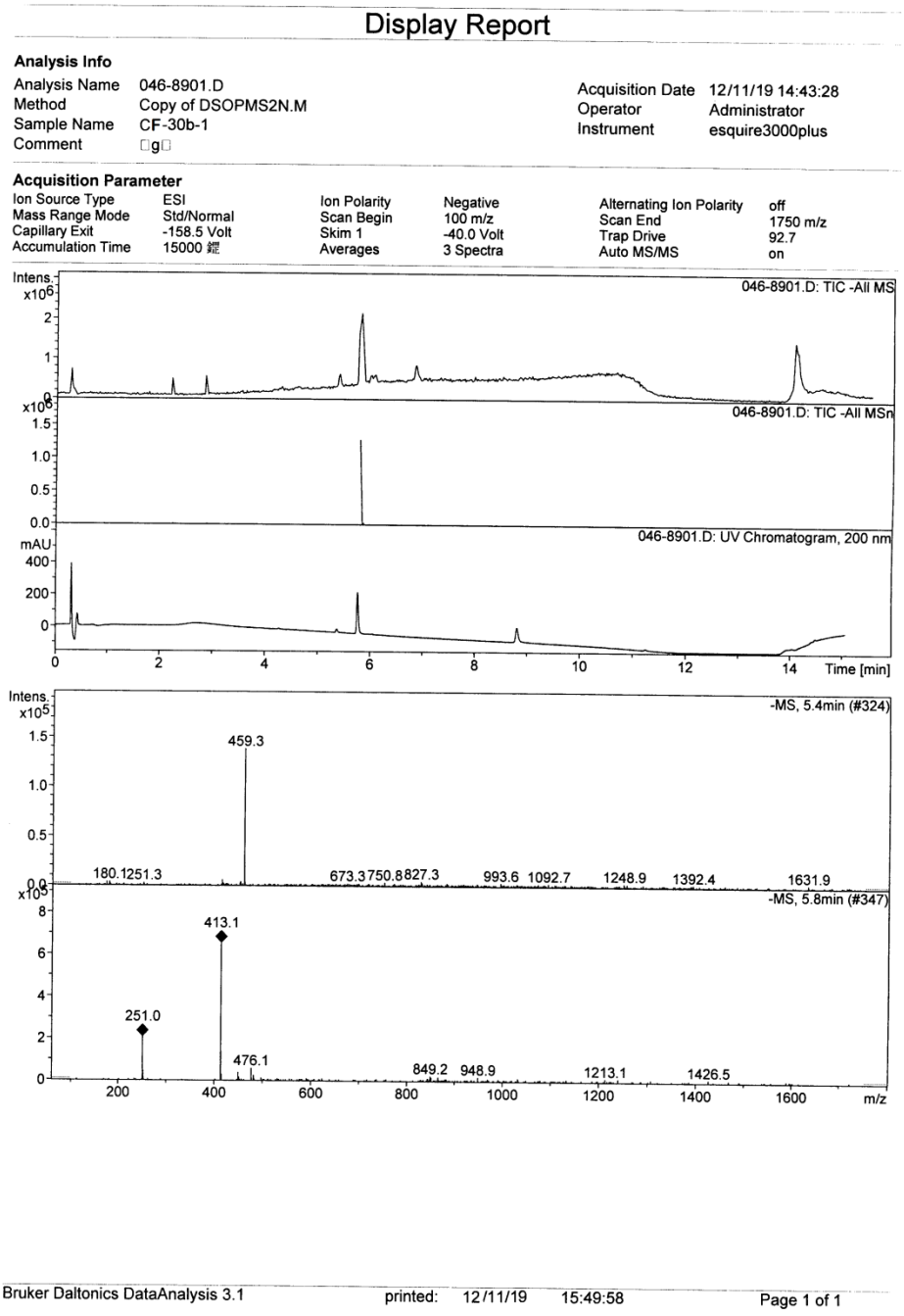


Figure S16:. ESI(–)MS spectrum of **2**