Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Eugenunilones A–H: Rearranged Sesquiterpenoids from *Eugenia uniflora*

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Contents

1. Chiral separation of 2–8

The racemic mixtures of (±)-**2**–(±)-**8** were subjected to a chiral HPLC column to afford the optical pure enantiomers (+)-**2**, (−)-**2**, (+)-**3**, (−)-**3**, (+)-**4,** (−)-**4,** (+)-**5,** (−)-**5,** (+)-**6,** (−)-**6**, (+)-**7**, (−)-**7**, (+)-**8**, and (−)-**8**, respectively.

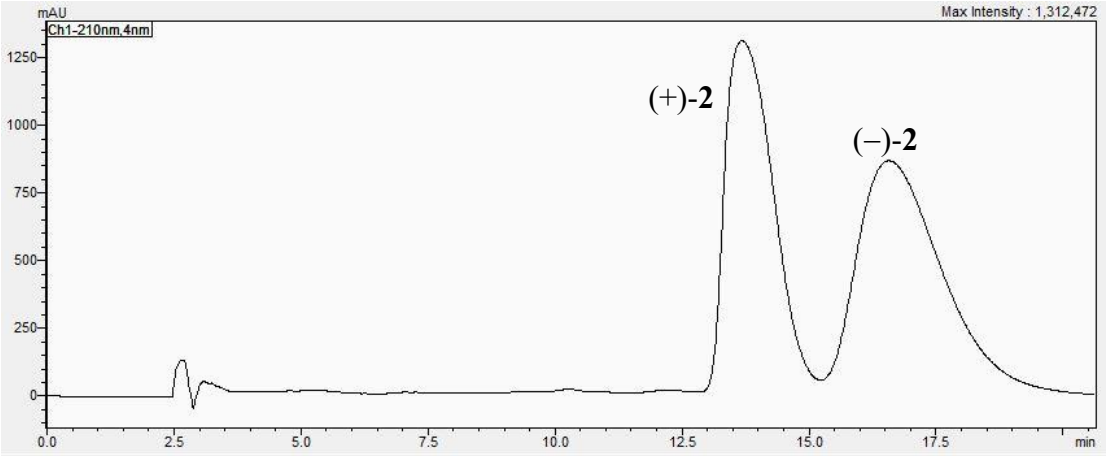


Figure S1. Chiral HPLC Chromatogram of **2** [column: Phenomenex Amylose-1 (4.6× 250 mm, 5 μm), mobile phase: CH_3CN/H_2O/HCOOH (68:32:0.1, V/V/V), flow rate: 1.0 mL/min, detection wavelength: 210 nm]

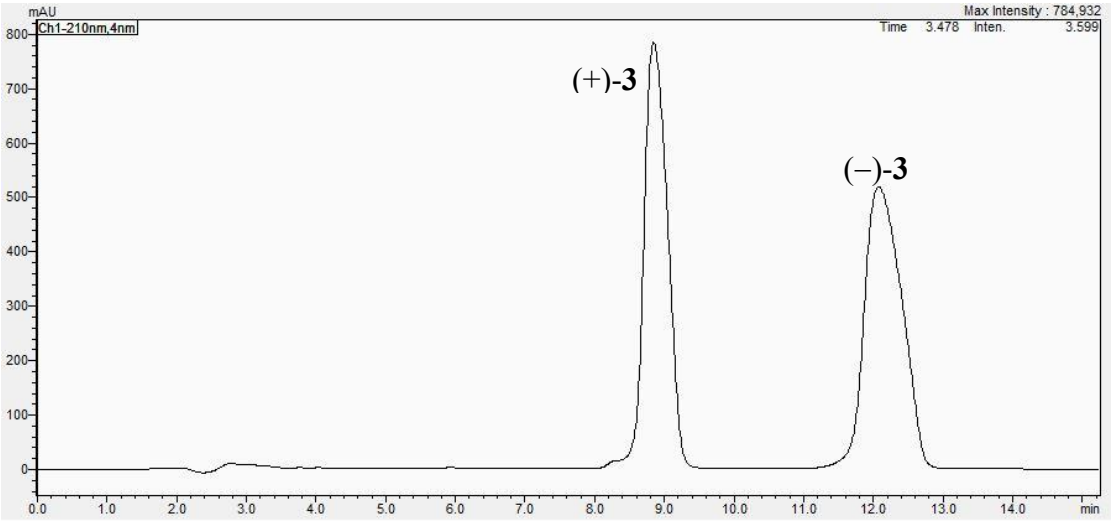


Figure S2. Chiral HPLC Chromatogram of **3** [column: Phenomenex Amylose-1 (4.6× 250 mm, 5 μm), mobile phase: CH_3CN/H_2O/HCOOH (40:60:0.1, V/V/V), flow rate: 1.0 mL/min, detection wavelength: 210 nm]

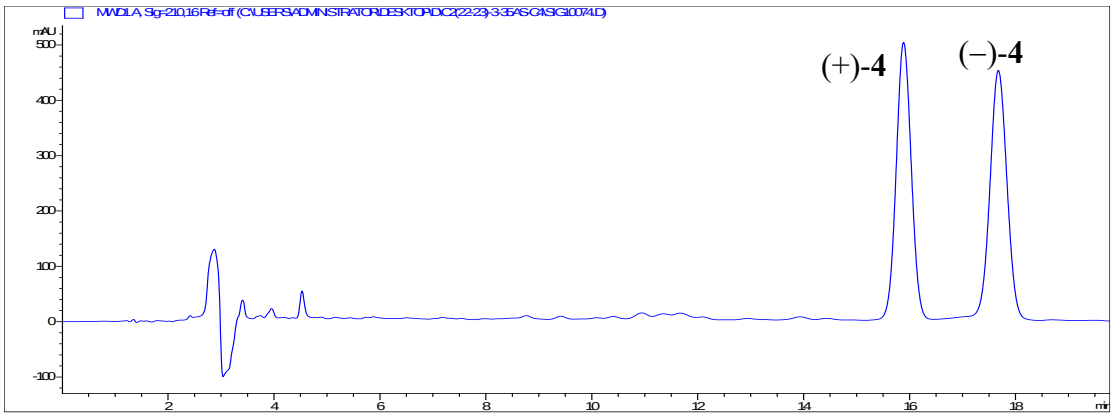


Figure S3. Chiral HPLC Chromatogram of **4** [column: Phenomenex Cellulose-4 (4.6 × 250 mm, 5 μm), mobile phase: CH_3CN/H_2O/HCOOH (35:65:0.1, V/V/V), flow rate: 1.0 mL/min, detection wavelength: 210 nm]

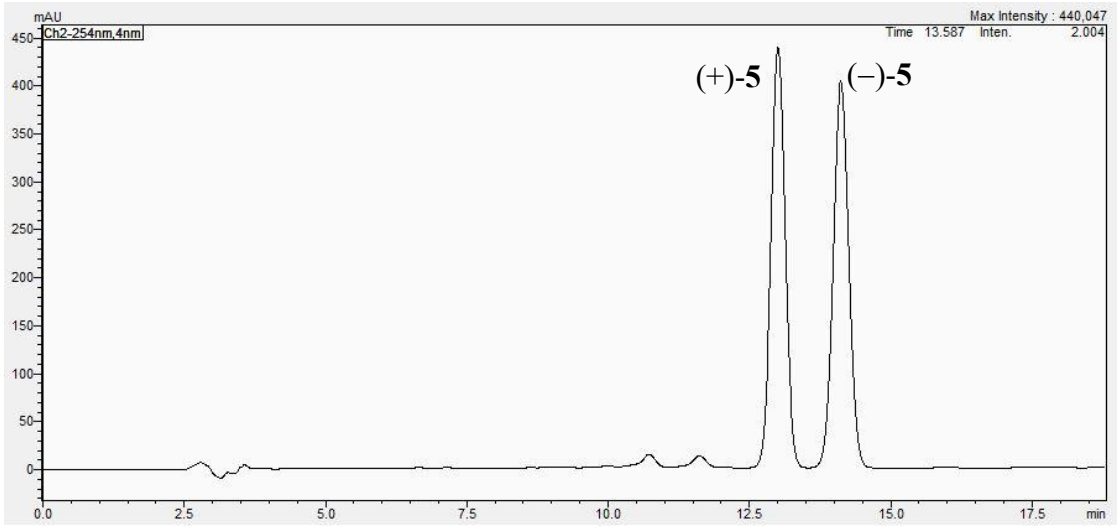


Figure S4. Chiral HPLC Chromatogram of **5** [column: Phenomenex Cellulose-4 (4.6 × 250 mm, 5 μm), mobile phase: CH_3CN/H_2O/HCOOH (40:60:0.1, V/V/V), flow rate: 1.0 mL/min, detection wavelength: 254 nm]

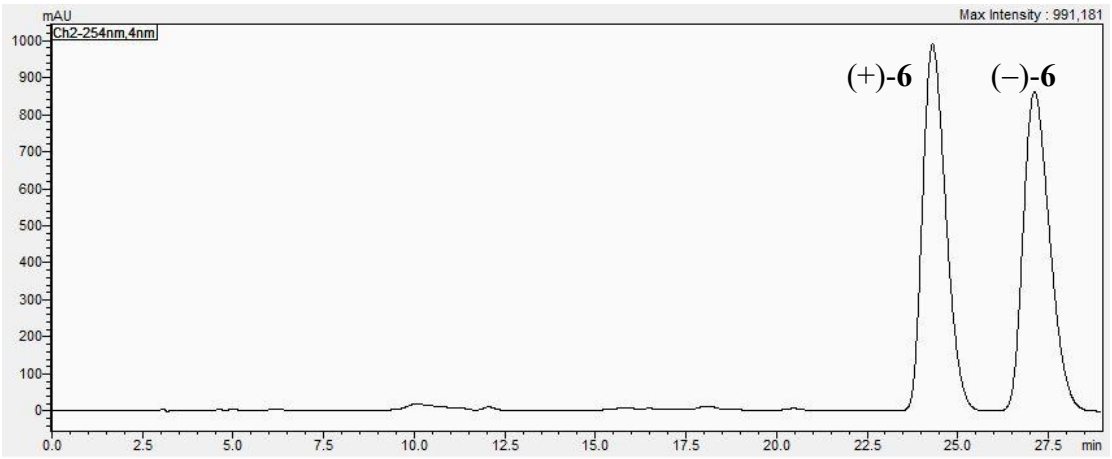


Figure S5. Chiral HPLC Chromatogram of **6** [column: Industries ChromegaChiral CC4 (4.6 × 250 mm, 5 μm), mobile phase: CH_3CN/H_2O/HCOOH (30:70:0.1, V/V/V), flow rate: 1.0 mL/min, detection wavelength: 254 nm]

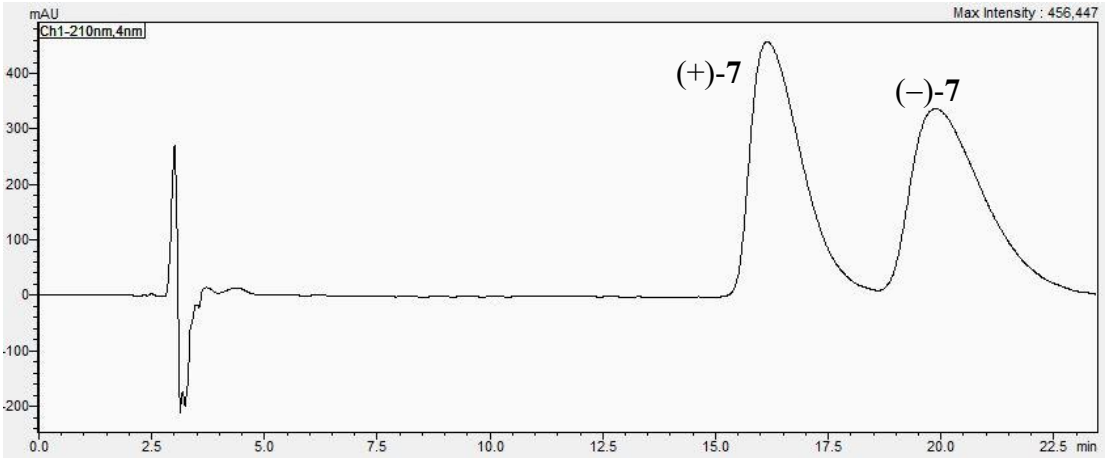


Figure S6. Chiral HPLC Chromatogram of **7** [column: Phenomenex Amylose-2 (4.6× 250 mm, 5 μm), mobile phase: CH_3CN/H_2O/HCOOH (23:77:0.1, V/V/V), flow rate: 1.0 mL/min, detection wavelength: 210 nm]

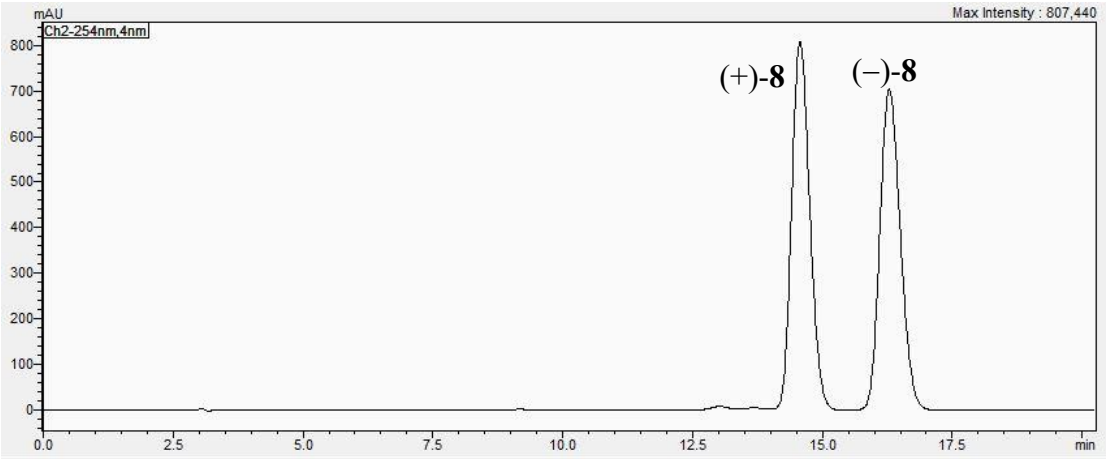
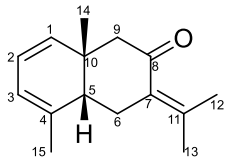


Figure S7. Chiral HPLC Chromatogram of **8** [column: Industries ChromegaChiral CC4 (4.6 × 250 mm, 5 μm), mobile phase: $CH_3CN/H_2O/HCOOH$ (32:68:0.1, V/V/V), flow rate: 1.0 mL/min, detection wavelength: 254 nm]

2. Structural elucidation of (±)-9



(+)/(−)-**9**

Figure S8. Chemical structure of compound **9**.

Compound **9** was obtained as yellow oil. The molecular formula of **9** was determined to be $C_{15}H_{20}O_2$ via its HR-ESI-MS data at *m/z* 217.1608 $[M + H]^+$ (calcd for $C_{15}H_{21}O$, 217.1587). A comprehensive analysis of the 1D NMR data (Table S1) revealed that **9** possessed the same structure as selina-1,3,7(11)-trien-8-one[1]. However, the absolute configuration of **9** has never been reported in previous studies. With the optical rotation value close to zero as well as the absence of a Cotton effect in its ECD spectrum, **9** was assumed to be a racemic mixture. Subsequently, **9** was successfully separated into two enantiomers (+)-**9** and (−)-**9**, in a ratio of 1:1, by an amylose chiral column using acetonitrile-water (60:40) as the mobile phase (Figure S9). The absolute configurations of (+)-**9** and (−)-**9** were further determined by electronic circular dichroism (ECD) calculation methods. The absolute configurations of (+)-**9** and (−)-**9** were deduced to

be 5*S*,10*R* and 5*R*,10*S*, respectively, by a comparison of the experimental ECD spectrum with the calculated ones (Figure S10).

Table S1. ^{1}H and ^{13}C NMR data of **9** (*J* in Hz)[a]

No.	δ_H	δ_C	No.	δ_H	δ_C
1	5.33 d (9.4)	131.9	8		204.0
2	5.77 dd (9.4, 5.3)	118.1	9	2.25 m	53.5
3	5.63 d (5.0)	123.1	10		38.6
4		138.4	11		139.7
5	2.00 dd (10.6, 4.7)	46.3	12	1.90 s	22.4
6a	2.46 d (14.5)	29.9	13	1.75 s	21.9
6b	2.66 dd (15.0, 4.7)		14	1.00 s	26.9
7		132.8	15	1.81 s	22.8

[a] Data were recorded in $CDCl_3$ at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR.

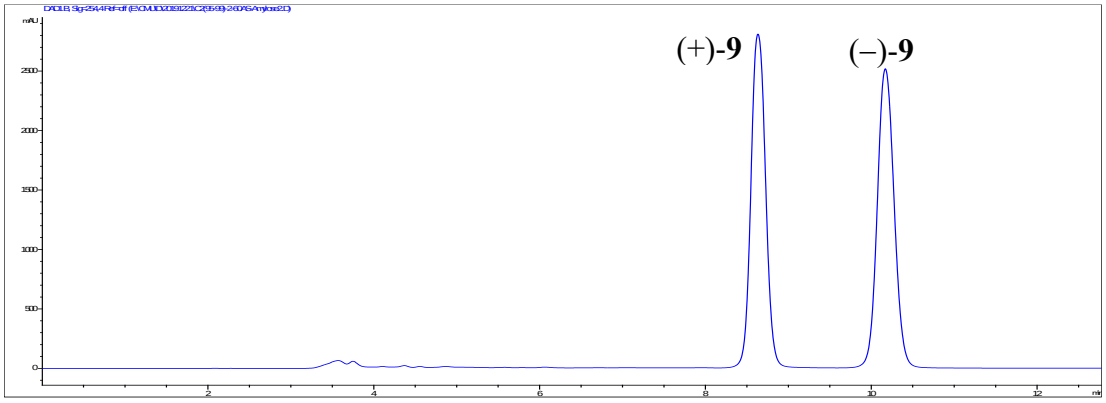


Figure S9. Chiral HPLC Chromatogram of **9** [column: Phenomenex Amylose-2 (4.6× 250 mm, 5 μm), mobile phase: CH_3CN/H_2O/HCOOH (60:40:0.1, V/V/V), flow rate: 1.0 mL/min, detection wavelength: 254 nm]

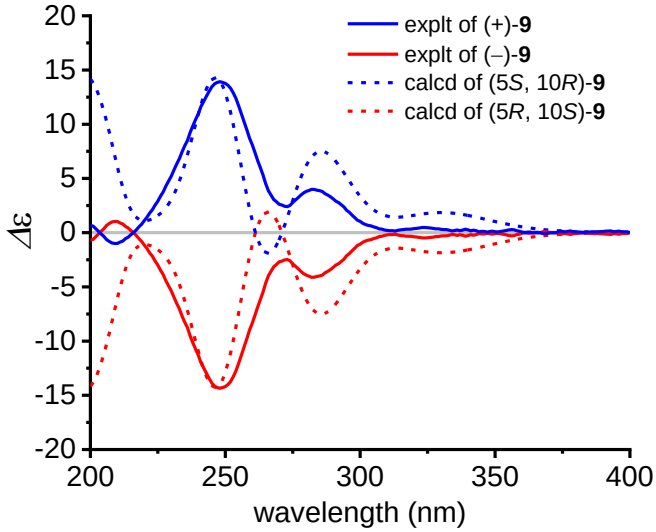


Figure S10. Experimental and calculated ECD spectra of **9**.

3. Quantum chemical ECD calculations of 2–9

3.1 Chemical calculation details for **2**, **3**, **4**, **6**, **7**, **8**, and **9**

The systematic random conformational analysis of **2**, **3**, **4**, **6**, **7**, **8**, and **9** were performed in the SYBYL-X 2.1.1 program by using MMFF94s molecular force field with an energy cutoff of 10 kcal/mol^{-1} to the global minima, which afforded 9, 7, 16, 4, 4, 3, and 7 conformers, respectively. All of the obtained conformers were further optimized using DFT at the CAM-B3LYP/6-31+G(d) level in gas phase using Gaussian09 software,[2] which afforded 9, 4, 9, 4, 3, 3, and 7 stable conformers, respectively. The optimized stable conformers were further subjected to ECD calculations at the CAM-B3LYP/6-31+G(d) level with the PCM solvation model of acetonitrile. The first 30 excitations for **2**, **3**, **4**, and **9**, as well as the first 50 excitations for **6**, **7**, and **8** were considered. The overall ECD curves of **2**, **3**, **4**, **6**, **7**, **8**, and **9** were all weighted by Boltzmann distribution, and were subsequently compared with the experimental one. The ECD spectra were produced by SpecDis 1.71 software.[3]

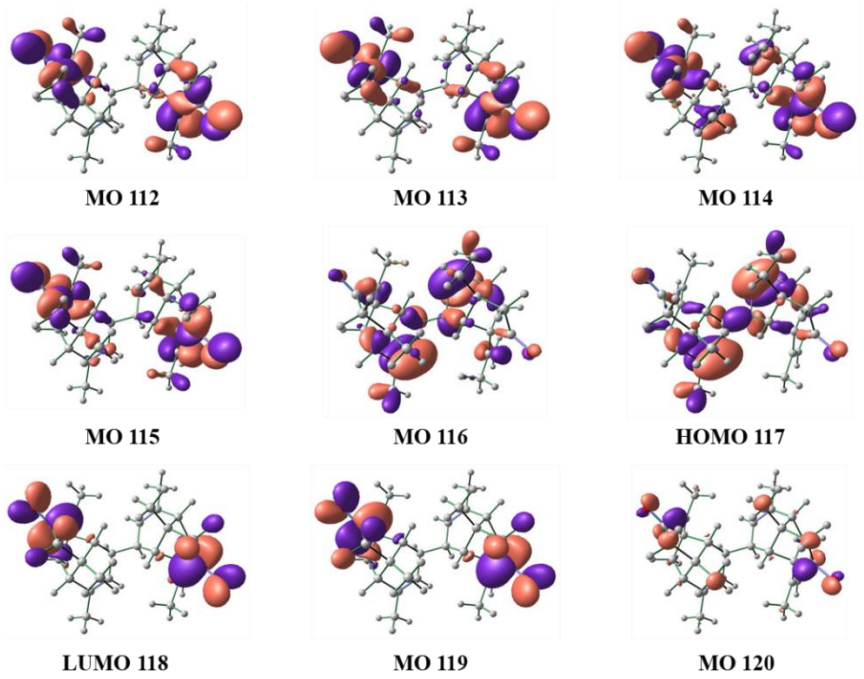


Figure S11. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **2**.

Table S2. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **2**

HOMO is 117					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	35495.09248	281.7290871	5.7412	0.0003	H-5->L+1 (11%), H-4->LUMO (10%), H-3->L+1 (24%), H-2->LUMO (23%)
2	35495.09248	281.7290871	0.2838	0.0003	H-5->LUMO (10%), H-4->L+1 (11%), H-3->LUMO (22%), H-2->L+1 (25%)
3	49529.23648	201.9009521	-7.4458	0.0034	H-1->L+1 (28%), HOMO->LUMO (46%), HOMO->L+3 (10%)
4	49627.6368	201.5006284	-11.7902	0.0028	H-1->LUMO (37%), HOMO->L+1 (44%)
5	50223.68464	199.1092464	-33.4028	0.0093	HOMO->L+2 (16%), HOMO->L+3 (42%)

6	50602.76784	197.6176487	15.3121	0.0808	H-1->L+2 (11%), H-1->L+3 (31%), HOMO->L+5 (14%)
7	51711.78784	193.3795063	97.4402	0.0683	H-5->L+1 (13%), H-4->LUMO (13%), H-1->L+1 (10%), HOMO->LUMO (11%), HOMO->L+2 (10%)
8	51866.64736	192.8021283	-124.7419	0.024	H-5->LUMO (14%), H-4->L+1 (17%), HOMO->L+1 (13%)
9	51943.27056	192.5177197	705.9842	0.476	H-1->L+2 (10%), HOMO->L+13 (14%)
10	52206.20912	191.5480968	67.7118	0.0611	H-5->L+1 (14%), H-4->LUMO (14%), H-3->L+4 (13%), HOMO->L+2 (17%)
11	52210.24192	191.5333014	-67.7673	0.0522	H-5->LUMO (12%), H-4->L+1 (12%), H-3->L+2 (11%), H-2->L+4 (18%)
12	52363.48832	190.9727621	-302.4767	0.2548	H-1->L+4 (12%), HOMO->L+2 (10%)
13	53849.9784	185.7010958	73.9707	0.0317	H-3->L+2 (12%), H-2->L+7 (14%), H-1->L+3 (16%)
14	54105.65792	184.8235542	-92.4528	0.1514	H-3->L+7 (14%), H-2->L+2 (12%), H-2->L+3 (20%), H-1->L+7 (12%)
15	54738.00096	182.6884399	3.8039	0	H-1->L+13 (10%), HOMO->L+3 (18%), HOMO->L+10 (10%), HOMO->L+12 (17%)
16	54779.94208	182.5485683	-39.851	0.0756	H-1->L+3 (13%), HOMO->L+5 (12%), HOMO->L+7 (19%), HOMO->L+13 (10%)
17	55134.02192	181.3762111	-5.5244	0.0604	H-1->LUMO (19%), HOMO->L+1 (17%), HOMO->L+4 (12%)

18	55344.53408	180.6863165	-14.6249	0.003	H-1->L+1 (32%), HOMO->LUMO (15%)
19	55497.78048	180.1873861	-19.1814	0.0922	H-1->LUMO (20%)
20	55556.65936	179.9964237	0.0934	0	H-1->L+5 (10%), HOMO->L+8 (12%)
21	56047.8544	178.4189619	26.8775	0.0397	H-1->L+8 (12%), HOMO->L+4 (10%), HOMO->L+7 (26%)
22	56124.4776	178.1753778	-43.6316	0.012	HOMO->L+6 (32%)
23	56418.872	177.2456564	-102.2654	0.0426	HOMO->L+4 (11%), HOMO->L+7 (19%)
24	56766.49936	176.1602373	0.8033	0.0021	H-1->L+7 (24%), HOMO->L+8 (16%)
25	57192.36304	174.8485194	-9.3255	0.0025	H-1->L+5 (10%), HOMO->L+2 (21%), HOMO->L+6 (12%), HOMO->L+10 (16%)
26	57655.32848	173.4445066	0.1064	0	H-1->L+2 (31%), H-1->L+10 (11%)
27	58085.22496	172.1608207	26.2049	0.0234	H-1->L+12 (22%), HOMO->L+9 (34%)
28	58199.75648	171.8220248	-4.0683	0.0031	H-1->L+7 (10%), H-1->L+9 (22%), HOMO->L+12 (13%)
29	58384.45872	171.278457	42.7012	0.0109	
30	58461.08192	171.0539674	1.304	0.0005	H-3->L+5 (18%), H-2->L+8 (17%)

Table S3. Cartesian coordinate of dominant conformer of **2**

Standard orientation:					
Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	8	0	4.722157	-1.12922	1.564083
2	1	0	4.356415	-2.40877	-2.71634
3	1	0	4.601459	-0.59656	-2.52101
4	8	0	-4.72181	1.129472	1.564366
5	1	0	0.049922	2.138143	-2.04483
6	1	0	-0.04984	-2.138	-2.04487
7	1	0	-4.35813	2.408438	-2.71564
8	1	0	-4.60345	0.596327	-2.51967
9	6	0	2.720316	2.044581	0.162266

10	1	0	3.290123	2.843754	0.648317
11	6	0	2.014476	1.116575	1.193603
12	6	0	3.763164	-0.44499	1.238363
13	6	0	3.137743	-0.33447	-0.15603
14	6	0	1.63748	-0.06756	0.252109
15	1	0	1.241171	-0.91312	0.812708
16	6	0	1.692586	2.599332	-0.80331
17	6	0	-0.7323	-0.28606	-0.97054
18	1	0	-1.19663	0.183823	-1.85079
19	6	0	3.644295	1.065797	-0.61623
20	1	0	4.69303	1.230515	-0.33701
21	1	0	3.570599	1.212174	-1.69985
22	6	0	-0.7654	-1.76784	-1.31448
23	6	0	-1.63744	0.067618	0.252124
24	1	0	-1.24117	0.913229	0.812678
25	6	0	0.732338	0.286173	-0.97054
26	1	0	1.196653	-0.18369	-1.8508
27	6	0	0.765486	1.76795	-1.31446
28	6	0	1.784771	4.049766	-1.15903
29	1	0	1.010304	4.346043	-1.87406
30	1	0	2.758413	4.269115	-1.60854
31	1	0	1.666755	4.667384	-0.263
32	6	0	-2.01432	-1.11655	1.193668
33	6	0	-3.13775	0.334415	-0.15594
34	6	0	3.042631	0.487133	2.171357
35	1	0	3.727257	1.229422	2.588946
36	1	0	2.559396	-0.09857	2.95889
37	6	0	-1.69244	-2.59927	-0.8033
38	6	0	0.924887	1.806619	2.004759
39	1	0	1.368983	2.545428	2.68239
40	1	0	0.376257	1.089228	2.621494
41	1	0	0.201223	2.347917	1.392234
42	6	0	-2.72013	-2.04461	0.162384
43	1	0	-3.28981	-2.84386	0.648464
44	6	0	3.42949	-1.54982	-1.01076
45	6	0	-3.763	0.445037	1.238526
46	6	0	-3.42988	1.54965	-1.0107
47	6	0	-0.92469	-1.80655	2.004803
48	1	0	-0.37592	-1.08909	2.621329
49	1	0	-0.20117	-2.34804	1.392281
50	1	0	-1.36875	-2.54519	2.682648
51	6	0	-3.64428	-1.06592	-0.616
52	1	0	-4.69295	-1.23071	-0.33659

53	1	0	-3.57074	-1.21232	-1.69963
54	6	0	-3.04248	-0.48715	2.171453
55	1	0	-3.72714	-1.22946	2.588983
56	1	0	-2.55925	0.098482	2.959041
57	6	0	2.880272	-2.8725	-0.5339
58	1	0	3.2671	-3.12158	0.458684
59	1	0	3.151809	-3.69641	-1.20305
60	1	0	1.789842	-2.84689	-0.48148
61	6	0	-1.78466	-4.04967	-1.15909
62	1	0	-1.01058	-4.34581	-1.87459
63	1	0	-2.75854	-4.26909	-1.60806
64	1	0	-1.66609	-4.66734	-0.26317
65	6	0	4.160874	-1.51	-2.13826
66	6	0	-2.88007	2.872328	-0.53453
67	1	0	-3.26538	3.12126	0.458681
68	1	0	-3.1527	3.696293	-1.20315
69	1	0	-1.78957	2.846781	-0.48377
70	6	0	-4.16226	1.509751	-2.13755

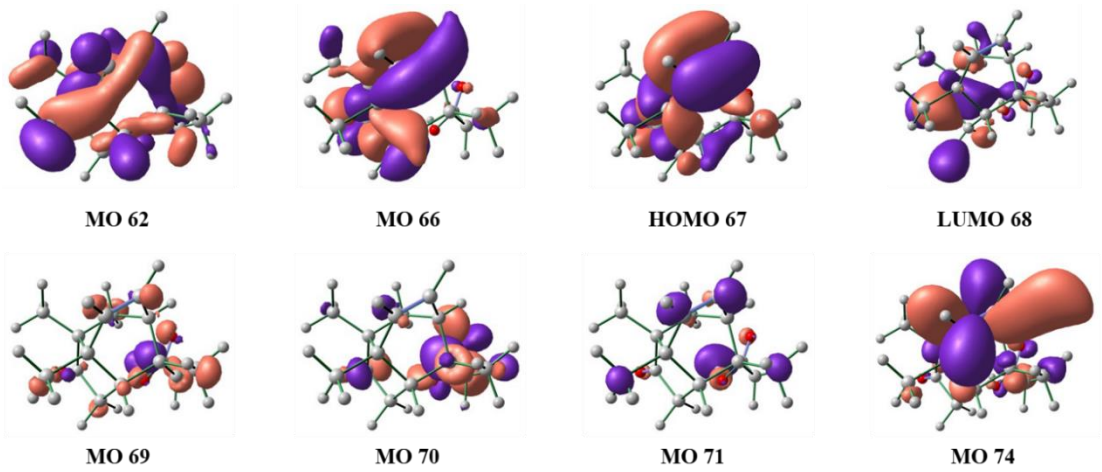


Figure S12. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **3**.

Table S4. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **3**

HOMO is 67					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	35070.84192	285.1371525	12.5274	0.0003	H-1->LUMO (44%), HOMO->LUMO (38%)
2	46521.57424	214.9540329	3.9265	0.0009	H-5->L+2 (17%), H-2->L+2 (36%)
3	51387.55072	194.599662	-25.3939	0.0335	H-1->LUMO (36%), HOMO->LUMO (49%)
4	52529.63968	190.3687149	-31.3053	0.0553	HOMO->L+1 (31%), HOMO->L+2 (12%), HOMO->L+3 (16%), HOMO->L+6 (11%)
5	53804.81104	185.8569858	67.2801	0.1019	HOMO->L+1 (11%), HOMO->L+4 (24%), HOMO->L+6 (32%)
6	54033.87408	185.0690918	-68.9496	0.0519	H-1->L+1 (15%), H-1->L+2 (10%), HOMO->L+2 (19%), HOMO->L+3 (22%)
7	55498.58704	180.1847675	-2.1243	0.0028	HOMO->L+1 (18%), HOMO->L+2 (45%), HOMO->L+6 (10%)
8	57104.448	175.1177071	20.1706	0.0129	H-4->L+6 (10%), H-1->L+4 (15%), H-1->L+6 (27%)
9	57964.24096	172.5201578	-0.1611	0.0141	HOMO->L+3 (11%), HOMO->L+5 (47%)
10	58459.4688	171.0586874	7.1008	0.016	H-1->L+1 (12%), H-1->L+2 (36%), HOMO->L+5 (17%)
11	58660.30224	170.4730391	-7.8848	0.0349	H-5->LUMO (25%), H-2->LUMO (35%), HOMO->L+4 (10%)
12	58975.6672	169.561456	15.725	0.0035	H-2->LUMO (15%), HOMO->L+4 (34%), HOMO->L+6 (12%)
13	59667.69568	167.594875	21.8128	0.0236	H-4->LUMO (19%), H-3->LUMO (56%)

14	59923.3752	166.8797855	-0.4797	0.02	H-1->L+1 (15%), H-1->L+3 (10%), HOMO->L+1 (12%), HOMO->L+9 (13%)
15	60150.01856	166.2509878	-5.3293	0.0049	H-1->L+5 (41%), HOMO->L+8 (10%)
16	60805.75184	164.458126	-11.9072	0.0134	H-1->L+4 (32%)
17	60926.73584	164.1315567	-18.6064	0.0095	H-4->LUMO (50%), H-3->LUMO (23%)
18	61274.3632	163.2003905	21.9111	0.0285	H-2->L+1 (18%)
19	62019.62464	161.2392861	-17.2785	0.0217	H-1->L+1 (23%), H-1->L+3 (10%)
20	62422.90464	160.1976079	-2.5154	0.0008	H-5->L+6 (10%), H-2->L+6 (29%)
21	63475.46544	157.5411843	5.9773	0.0346	H-4->L+6 (17%), H-1->L+6 (13%)
22	63975.53264	156.3097576	-15.4391	0.0225	H-1->L+3 (21%), HOMO->L+9 (13%)
23	64207.01536	155.7462209	-13.8069	0.0056	HOMO->L+7 (26%), HOMO->L+10 (37%)
24	64295.73696	155.5313069	18.1488	0.0081	H-4->L+1 (14%), H-4->L+2 (35%)
25	64468.3408	155.1148963	8.7532	0.0376	H-3->L+2 (37%)
26	64638.52496	154.7065006	-0.4703	0.0011	H-1->L+5 (10%), HOMO->L+8 (46%)
27	64843.3912	154.2177208	-12.7511	0.009	H-3->L+6 (24%)
28	65013.57536	153.8140295	0.8278	0.0009	H-8->LUMO (25%), H-5->LUMO (11%)
29	65038.57872	153.7548974	-7.9375	0.0169	H-1->L+4 (12%), HOMO->L+9 (13%), HOMO->L+10 (15%)
30	65492.672	152.6888382	5.2641	0.0017	HOMO->L+11 (37%)

Table S5. Cartesian coordinate of dominant conformer of **3**

Standard orientation:					
Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	0	1.694168	0.426139	-0.34119
2	6	0	0.388513	0.529384	-1.2282
3	6	0	-0.74587	1.244918	-0.41381
4	6	0	-0.33258	1.176772	1.09322
5	6	0	0.894785	2.031086	1.26574

6	6	0	1.922022	1.64676	0.511623
7	6	0	1.265197	-0.77198	0.579533
8	6	0	0.645526	-1.73736	-0.42425
9	6	0	0.130991	-0.93745	-1.6067
10	6	0	2.367133	-1.42549	1.399467
11	6	0	0.106241	-0.25582	1.492271
12	6	0	2.92868	0.121266	-1.19199
13	1	0	0.590947	1.122004	-2.12604
14	8	0	0.58313	-2.9407	-0.30326
15	6	0	-0.81795	2.711321	-0.88806
16	6	0	-2.1952	0.713384	-0.66634
17	6	0	-2.7414	-0.41742	0.17099
18	8	0	-3.18305	-0.29312	1.290823
19	8	0	-2.7391	-1.60712	-0.46353
20	1	0	-1.16067	1.502672	1.728363
21	1	0	0.918943	2.881063	1.941564
22	1	0	2.888105	2.145828	0.506178
23	1	0	-0.90199	-1.20428	-1.8285
24	1	0	0.718017	-1.22403	-2.48636
25	1	0	2.827301	-0.69605	2.07413
26	1	0	1.950919	-2.2386	2.001584
27	1	0	3.14652	-1.85853	0.765826
28	1	0	0.464558	-0.22451	2.525927
29	1	0	-0.73156	-0.95648	1.493951
30	1	0	3.086392	0.917674	-1.92809
31	1	0	3.825746	0.06651	-0.56748
32	1	0	2.853231	-0.82525	-1.73548
33	1	0	-1.43989	3.312446	-0.21438
34	1	0	0.168065	3.173828	-0.93933
35	1	0	-1.26246	2.759805	-1.88936
36	1	0	-2.87226	1.54422	-0.44981
37	1	0	-2.31212	0.468113	-1.72526
38	1	0	-3.10723	-2.27214	0.146443

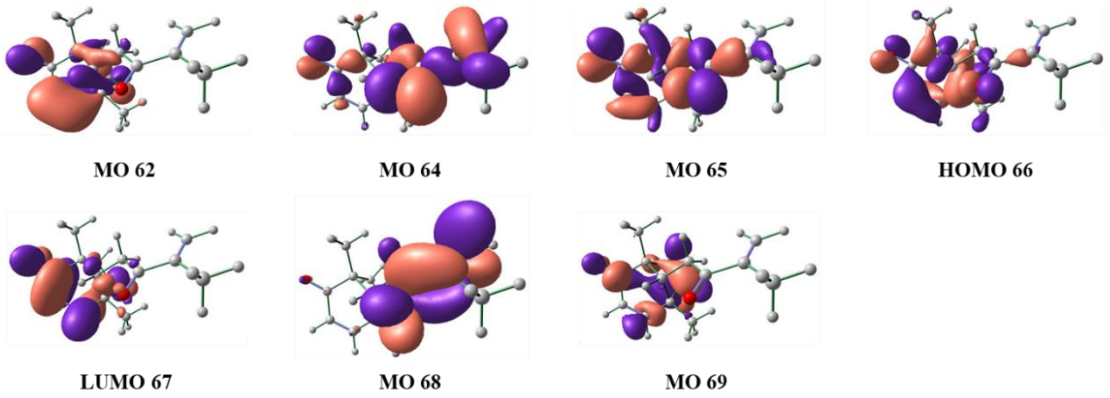


Figure S13. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **4**.

Table S6. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **4**

HOMO is 66					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	31830.08384	314.1681954	9.0587	0.0006	H-2->LUMO (16%), H-1->LUMO (49%), HOMO->LUMO (19%)
2	32975.39904	303.2563757	1.1243	0.0002	H-2->L+1 (51%), H-1->L+1 (23%)
3	34223.14736	292.1998931	-96.3558	0.0167	H-1->LUMO (12%), HOMO->LUMO (33%), HOMO->L+2 (36%)
4	43024.33008	232.4266289	21.0448	0.1302	H-1->LUMO (11%), HOMO->LUMO (39%), HOMO->L+2 (33%)
5	46358.64912	215.7094779	1.969	0.3233	H-3->L+1 (79%), H-2->L+1 (14%)
6	49000.13312	204.0810782	68.3997	0.1182	H-4->LUMO (72%)
7	50321.2784	198.7230913	-0.1672	0.0079	HOMO->L+1 (68%)
8	50463.23296	198.1640774	21.3841	0.0265	H-2->LUMO (49%), H-1->LUMO (14%), HOMO->L+1 (15%)
9	52343.32432	191.0463298	-57.0134	0.0453	H-5->LUMO (17%), H-1->L+2 (32%)

10	53130.52688	188.215713	-14.1452	0.0088	H-5->LUMO (33%), H-1->L+1 (28%)
11	53635.43344	186.4439114	3.7884	0.0041	H-5->LUMO (16%), H-2->L+1 (10%), H-1->L+1 (26%), H-1->L+2 (20%)
12	55068.69056	181.5913888	1.9818	0.0131	H-6->LUMO (53%), H-5->LUMO (15%)
13	55613.11856	179.8136889	4.153	0.0055	H-3->LUMO (70%), H-2->LUMO (10%)
14	56069.63152	178.349665	36.4652	0.0256	HOMO->L+3 (56%), HOMO->L+5 (10%), HOMO->L+6 (10%)
15	56494.68864	177.0077903	-4.356	0.0415	H-6->LUMO (11%), H-4->L+2 (57%)
16	57444.81632	174.080111	-17.3539	0.0303	H-1->L+3 (30%), H-1->L+4 (11%)
17	57894.8768	172.7268552	-5.8801	0.0015	H-10->L+1 (28%), H-5->L+1 (10%), H-4->L+1 (22%)
18	58249.7632	171.6745176	7.7051	0.0079	H-2->L+3 (27%)
19	58757.08944	170.1922286	8.5984	0.0156	H-7->LUMO (64%)
20	59268.44848	168.7238363	-14.0528	0.016	H-3->L+3 (42%), H-3->L+5 (21%)
21	59589.45936	167.814914	2.981	0.0003	H-4->L+1 (44%)
22	60028.228	166.5882924	-4.5393	0.0423	HOMO->L+5 (30%), HOMO->L+6 (20%)
23	60354.07824	165.6888862	-1.4692	0.0039	H-2->L+2 (30%), H-1->L+2 (14%)
24	61045.30016	163.8127747	23.5584	0.0094	H-2->L+2 (19%)
25	61534.07552	162.5115827	-8.8329	0.0117	HOMO->L+4 (57%)
26	61761.52544	161.9130993	-1.0745	0.031	H-8->L+1 (10%), H-7->L+1 (10%), H-5->L+1 (45%)
27	62743.10896	159.3800525	-0.6534	0.0095	H-11->L+1 (10%)
28	62820.53872	159.1836078	29.2041	0.0598	H-1->L+4 (11%), H-1->L+5 (18%)
29	62984.2704	158.7697998	-9.9481	0.0147	H-5->L+2 (27%), H-3->L+2 (17%)
30	63288.34352	158.0069795	-11.9784	0.0177	H-1->L+5 (11%), HOMO->L+6 (12%)

Table S7. Cartesian coordinate of dominant conformer of **4**

Standard orientation:					
Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	8	0	-1.28226	2.314432	1.833375
2	8	0	-3.52128	-1.73183	-0.82017
3	8	0	2.14786	-0.24152	-1.65699
4	6	0	-0.68831	1.195697	-0.26435
5	6	0	1.019908	-0.60914	0.417538
6	1	0	1.109925	-0.04032	1.349293
7	1	0	1.054298	-1.66569	0.706993
8	6	0	3.614432	-0.36857	0.172352
9	6	0	-1.29145	1.318362	1.151582
10	6	0	-2.79469	0.438104	-1.37538
11	1	0	-1.96123	2.353353	-1.68181
12	6	0	-0.29507	-0.30624	-0.30334
13	1	0	-0.18922	-0.63313	-1.34168
14	6	0	-1.85721	-0.03631	1.546693
15	1	0	-2.91891	0.034981	1.802515
16	1	0	-1.33712	-0.36917	2.452513
17	6	0	-1.54676	-0.97501	0.354167
18	6	0	-2.7024	-0.84677	-0.65217
19	6	0	-1.87186	1.387905	-1.18856
20	1	0	-3.6434	0.566393	-2.0398
21	6	0	-1.38751	-2.43249	0.765153
22	1	0	-0.68905	-2.53855	1.600051
23	1	0	-1.02947	-3.04365	-0.07008
24	1	0	-2.35131	-2.84268	1.074251
25	6	0	4.753795	-0.12379	-0.77637
26	1	0	4.639755	0.839631	-1.28274
27	1	0	4.776176	-0.88498	-1.56202
28	1	0	5.70958	-0.13318	-0.24667
29	6	0	3.791371	-0.58495	1.479392
30	6	0	0.392356	2.233657	-0.52926
31	1	0	1.226828	2.13634	0.170605
32	1	0	-0.02019	3.237455	-0.39321
33	1	0	0.782449	2.140156	-1.54574
34	6	0	2.251564	-0.37823	-0.45095
35	1	0	2.970649	-0.7682	2.164087
36	1	0	4.786671	-0.59076	1.914625

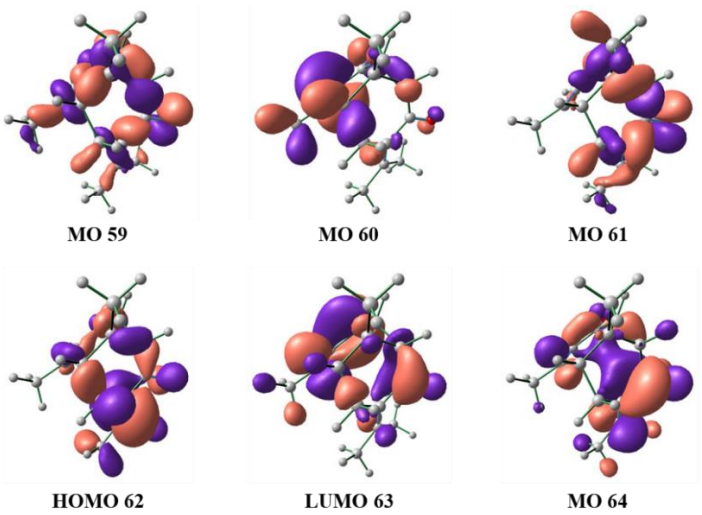


Figure S14. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **6**.

Table S8. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **6**

HOMO is 62					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	31560.6928	316.8498253	-0.6514	0.0004	H-3->L+1 (16%), H-1->LUMO (21%), H-1->L+1 (46%)
2	32910.06768	303.8583845	1.5736	0.0006	H-3->LUMO (46%), H-1->LUMO (18%), H-1->L+1 (10%)
3	40694.9848	245.7305255	104.6038	0.2748	HOMO->LUMO (23%), HOMO->L+1 (64%)
4	43652.64032	229.0812177	122.7842	0.1156	H-2->LUMO (33%), HOMO->LUMO (41%)
5	44380.964	225.3218294	-178.899	0.2066	H-2->LUMO (45%), HOMO->LUMO (21%), HOMO->L+1 (16%)
6	45501.27584	219.7740572	3.9006	0.0621	H-3->LUMO (22%), H-1->LUMO (47%), H-1->L+1 (15%)

7	47508.80368	210.4873039	-2.528	0.0256	H-3->L+1 (30%), H-2->L+1 (31%), H-1->L+1 (14%)
8	48970.2904	204.2054462	-18.7634	0.0102	H-3->L+1 (29%), H-2->L+1 (51%)
9	51840.83744	192.8981184	12.4294	0.1727	H-4->LUMO (84%)
10	52767.57488	189.51032	-18.1968	0.0257	H-5->LUMO (71%)
11	53620.1088	186.4971971	-19.0656	0.0684	H-4->L+1 (83%)
12	54552.49216	183.3096822	5.4701	0.002	H-1->L+2 (10%), HOMO->L+2 (52%)
13	54856.56528	182.293586	3.2565	0.004	H-5->L+1 (60%)
14	54979.1624	181.8870926	-5.6197	0.0175	H-5->L+1 (11%), H-1->L+2 (27%), H-1->L+4 (16%), HOMO->L+2 (10%)
15	56072.0512	178.3419687	-89.2173	0.0263	H-6->LUMO (47%)
16	57011.6936	175.4026125	57.7844	0.0393	H-3->L+2 (15%), H-3->L+4 (12%), H-1->L+5 (11%)
17	57398.03584	174.2219895	19.4142	0.0334	H-7->L+1 (18%)
18	58239.27792	171.7054256	-56.0037	0.0453	H-7->L+1 (12%), HOMO->L+3 (17%), HOMO->L+4 (28%)
19	58355.42256	171.3636807	4.9663	0.0463	H-2->L+2 (43%), H-2->L+5 (21%)
20	58709.5024	170.3301781	26.2937	0.0211	H-7->L+1 (15%), H-1->L+3 (12%), H-1->L+4 (15%)
21	59312.00272	168.5999383	45.4061	0.015	HOMO->L+3 (26%), HOMO->L+5 (10%)
22	59653.98416	167.6333968	-26.5586	0.0127	H-1->L+3 (16%)
23	60750.0992	164.6087847	-40.9044	0.0396	HOMO->L+3 (12%), HOMO->L+4 (10%)
24	60925.12272	164.1359025	-42.1525	0.0224	H-1->L+3 (21%), H-1->L+6 (10%)
25	61459.06544	162.7099262	4.3184	0.0206	H-1->L+4 (10%)
26	61624.41024	162.2733583	3.5165	0.0692	H-2->L+3 (32%), H-2->L+4 (19%), H-2->L+11 (11%)
27	62093.0216	161.0486934	-3.9474	0.0068	H-6->L+1 (23%), H-1->L+10 (13%)
28	62269.65824	160.5918562	14.849	0.009	H-1->L+5 (13%)
29	62785.05008	159.2735848	12.5731	0.0324	H-7->LUMO (20%)

30	63147.19552	158.3601602	2.6972	0.0491	H-1->L+5 (10%)
31	63459.33424	157.5812309	-7.8622	0.0328	
32	63594.83632	157.2454712	30.282	0.0066	H-2->L+3 (22%), H-2->L+4 (36%)
33	63965.04736	156.3353802	-11.5843	0.0254	HOMO->L+9 (25%)
34	64157.8152	155.8656567	-7.8661	0.002	H-8->L+1 (27%)
35	64327.1928	155.4552525	-4.3124	0.0116	H-8->L+1 (18%), H-3->L+2 (17%)
36	64595.77728	154.808881	-4.2368	0.0103	HOMO->L+6 (22%)
37	64841.77808	154.2215574	-13.5155	0.0044	HOMO->L+6 (15%), HOMO->L+7 (15%), HOMO->L+11 (17%)
38	65106.32976	153.5948968	3.4364	0.0014	H-2->L+2 (12%), H-2->L+5 (14%)
39	65508.8032	152.6512394	13.9712	0.005	H-1->L+6 (18%)
40	65756.41712	152.0764123	11.339	0.0091	H-1->L+6 (11%)
41	65975.80144	151.5707241	-5.4627	0.0087	H-1->L+9 (31%)
42	66192.76608	151.0739102	21.1108	0.014	
43	66274.22864	150.8882141	31.2293	0.0246	H-4->L+3 (11%)
44	66621.04944	150.102709	2.6501	0.0094	H-1->L+9 (13%), HOMO->L+8 (17%)
45	66793.65328	149.7148233	17.8397	0.0235	H-9->LUMO (18%), HOMO->L+8 (11%)
46	66889.63392	149.4999959	38.8431	0.0228	H-9->L+1 (13%)
47	67197.73984	148.8145289	-6.2406	0.0159	HOMO->L+8 (13%)
48	67374.37648	148.4243792	-7.2259	0.0066	H-2->L+6 (12%)
49	67615.53792	147.8950003	1.5549	0.0015	H-2->L+6 (12%)
50	68034.14256	146.9850229	-15.5205	0.0386	H-1->L+8 (19%)

Table S9. Cartesian coordinate of dominant conformer of **6**

Standard orientation:					
Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	8	0	1.912076	-0.83386	-2.66965
2	8	0	-1.02685	-2.59716	0.115579
3	6	0	1.620543	-0.28343	-1.61919
4	6	0	0.954031	-1.47346	0.680056
5	1	0	1.299904	-2.38503	1.160064
6	6	0	1.975367	-0.90224	-0.30799
7	1	0	2.884793	-1.49301	-0.37619
8	6	0	1.012955	1.054219	-1.59705
9	1	0	0.871265	1.512715	-2.57208

10	6	0	0.693125	1.702879	-0.46858
11	6	0	-0.58884	0.75234	1.468695
12	1	0	-0.4478	0.359448	2.484784
13	1	0	-1.1681	1.669138	1.573276
14	6	0	-0.52211	-1.52457	0.410056
15	6	0	0.817355	1.073411	0.902022
16	1	0	1.269097	1.823198	1.564339
17	6	0	-2.53496	-0.11662	0.07609
18	6	0	-1.30515	-0.27337	0.613448
19	6	0	1.681842	-0.1936	0.980676
20	6	0	2.727738	-0.18928	2.072695
21	1	0	2.269777	-0.02713	3.055829
22	1	0	3.463991	0.605382	1.906191
23	1	0	3.263885	-1.14291	2.107973
24	6	0	0.130689	3.095504	-0.50963
25	1	0	0.140498	3.499091	-1.52485
26	1	0	0.710265	3.766798	0.135707
27	1	0	-0.90338	3.120867	-0.14746
28	6	0	-3.19758	-1.12789	-0.82441
29	1	0	-3.91874	-0.6255	-1.47781
30	1	0	-3.74711	-1.86551	-0.22786
31	1	0	-2.48895	-1.69086	-1.43086
32	6	0	-3.40117	1.093265	0.312415
33	1	0	-3.03752	1.773381	1.082378
34	1	0	-4.40657	0.766854	0.604069
35	1	0	-3.52018	1.658252	-0.62082

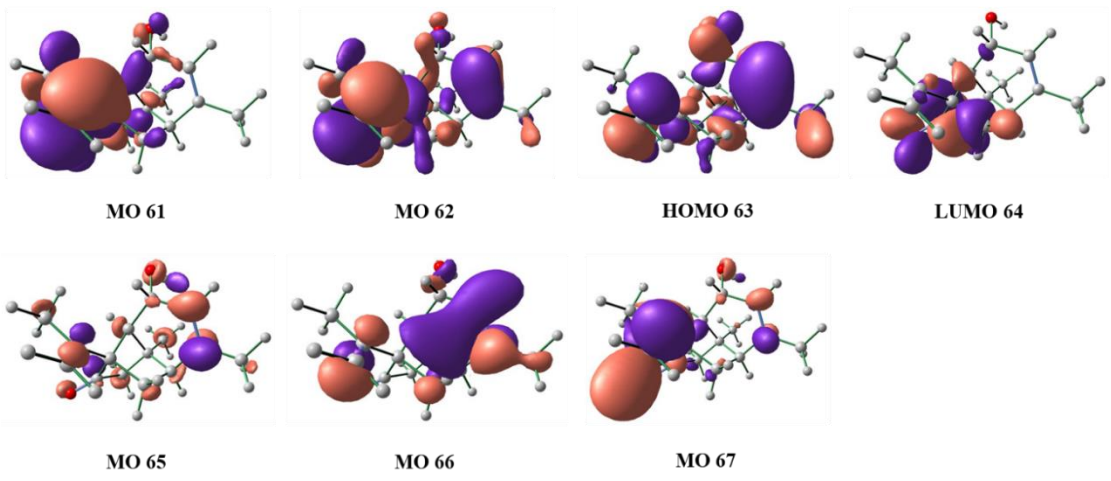


Figure S15. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **7**.

Table S10. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **7**

HOMO is 63					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	35866.11008	278.8147356	-0.3848	0.0002	H-2->LUMO (26%), H-1->LUMO (50%), HOMO->LUMO (11%)
2	51138.32368	195.5480602	83.7691	0.1854	HOMO->L+1 (38%), HOMO->L+2 (17%), HOMO->L+3 (11%)
3	51998.9232	192.3116746	-18.6854	0.0265	H-2->LUMO (50%), H-1->LUMO (12%), HOMO->LUMO (27%)
4	52231.21248	191.4564017	-120.2375	0.2076	H-1->L+1 (33%), H-1->L+3 (28%), HOMO->L+3 (10%)
5	52826.45376	189.2990971	-40.0667	0.0137	H-1->LUMO (20%), HOMO->LUMO (28%), HOMO->L+2 (18%)
6	53238.60592	187.8336186	22.0059	0.0228	H-1->LUMO (10%), HOMO->LUMO (21%), HOMO->L+1 (14%), HOMO->L+2 (13%)
7	54217.76976	184.4413749	89.2516	0.1235	H-1->L+1 (10%), H-1->L+2 (24%), HOMO->L+2 (11%)
8	55905.89984	178.8719979	16.0291	0.0351	H-3->L+1 (14%), H-1->L+2 (16%), H-1->L+3 (13%)
9	56205.1336	177.919691	1.5472	0.0557	H-2->L+1 (22%), H-1->L+5 (15%)
10	57210.10736	174.7942883	10.3839	0.0204	H-1->L+3 (13%), HOMO->L+3 (25%), HOMO->L+4 (23%)
11	58786.93216	170.1058319	50.6828	0.0235	HOMO->L+4 (16%)
12	58841.77824	169.9472772	-8.557	0.0088	H-1->L+4 (22%)
13	59067.61504	169.2975075	-84.6227	0.0387	H-2->L+3 (20%), H-1->L+6 (11%)

14	59262.80256	168.7399105	-0.3076	0.0219	HOMO->L+5 (11%), HOMO->L+6 (31%)
15	59585.42656	167.8262719	13.8611	0.0172	H-1->L+1 (15%), H-1->L+4 (13%)
16	59811.26336	167.1925895	1.7335	0.0211	H-3->LUMO (12%), H-1->L+5 (10%), H-1->L+6 (22%), HOMO->L+5 (14%)
17	60046.77888	166.5368266	-0.8883	0.0555	H-4->LUMO (12%), H-3->LUMO (23%)
18	60324.23552	165.7708534	-10.6952	0.0156	H-1->L+5 (23%), HOMO->L+5 (16%)
19	60996.1	163.944908	-15.3636	0.011	H-5->LUMO (19%), H-4->LUMO (53%)
20	61738.1352	161.974442	-13.3042	0.0179	
21	62100.28064	161.0298681	-3.6247	0.0045	H-1->L+9 (17%)
22	62447.10144	160.135535	-10.2558	0.004	H-1->L+10 (15%), H-1->L+11 (10%)
23	62801.98784	159.2306286	-1.8943	0.0277	H-2->L+1 (18%)
24	62986.69008	158.7637005	-15.6118	0.0179	HOMO->L+12 (10%)
25	63218.1728	158.1823637	51.4176	0.0258	H-4->L+1 (19%)
26	63274.632	158.0412194	-7.6405	0.0144	H-5->LUMO (38%), H-3->LUMO (12%)
27	63583.54448	157.2733965	20.0468	0.0134	HOMO->L+7 (21%), HOMO->L+11 (10%)
28	63651.29552	157.1059932	9.6455	0.0186	H-1->L+10 (11%), HOMO->L+10 (39%)
29	64084.41824	156.0441723	-2.2113	0.0379	H-1->L+8 (16%)
30	64398.97664	155.2819706	2.6376	0.0043	HOMO->L+8 (12%), HOMO->L+9 (21%), HOMO->L+13 (12%)
31	64940.1784	153.9878739	-28.8006	0.0101	H-1->L+10 (11%)
32	65034.54592	153.7644318	7.4633	0.0243	H-2->L+2 (16%)
33	65211.18256	153.3479322	8.6626	0.0147	H-6->LUMO (31%)
34	65545.0984	152.5667097	7.5822	0.0054	H-3->L+2 (13%), H-2->L+3 (13%)
35	65739.47936	152.1155947	-6.5638	0.0022	H-6->LUMO (33%)
36	65885.46672	151.7785408	-16.6649	0.0191	H-1->L+11 (12%)
37	66283.90736	150.8661815	-17.7378	0.0162	H-2->L+6 (17%)
38	66512.9704	150.3466157	-32.4641	0.0244	H-3->L+1 (11%), H-2->L+4 (10%), H-1->L+7 (15%)
39	66777.52208	149.7509894	57.903	0.0278	H-2->L+9 (10%)

40	66877.53552	149.5270411	7.5165	0.019	H-2->L+4 (13%)
41	67107.40512	149.0148514	1.1211	0.0085	
42	67363.8912	148.4474816	-5.7733	0.0101	
43	67611.50512	147.9038217	-7.0602	0.0113	H-8->LUMO (19%), H-7->LUMO (10%)
44	67649.41344	147.8209417	-0.7393	0.0039	HOMO->L+12 (14%)
45	68112.37888	146.8161906	-24.5363	0.0065	H-4->L+2 (12%)
46	68483.39648	146.020795	-4.1257	0.0047	H-3->L+4 (10%)
47	68725.36448	145.5066856	-17.0229	0.0108	H-4->L+1 (11%), H-3->L+1 (10%)
48	68946.36192	145.0402853	0.5726	0.0031	H-1->L+12 (13%)
49	69164.93968	144.5819232	-18.1466	0.0165	HOMO->L+7 (10%), HOMO->L+18 (10%)
50	69273.01872	144.356348	9.804	0.0052	H-1->L+14 (13%)

Table S11. Cartesian coordinate of dominant conformer of **7**

Standard orientation:					
Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	8	0	-1.16327	-1.64084	-2.28753
2	1	0	-1.89531	-1.04324	-2.49978
3	8	0	2.708323	1.882814	0.239481
4	6	0	-2.15219	-0.40213	0.858545
5	6	0	-0.73477	1.182008	-0.48732
6	6	0	0.373605	2.2444	-0.37727
7	1	0	0.592913	2.697458	-1.35166
8	1	0	0.147397	3.061816	0.316947
9	6	0	-0.73518	-1.38085	-0.9449
10	1	0	-0.07246	-2.22455	-0.72151
11	6	0	1.590079	1.45409	0.083005
12	6	0	0.07836	-0.07882	-0.87009
13	1	0	0.587436	0.040724	-1.83309
14	6	0	-1.91037	-1.3915	-0.00456
15	1	0	-2.56916	-2.25521	-0.07294
16	6	0	-1.85917	1.628585	-1.41104
17	1	0	-2.27891	2.581987	-1.06865
18	1	0	-2.68092	0.908318	-1.44977
19	1	0	-1.48666	1.781786	-2.43022
20	6	0	1.09467	0.024068	0.313656
21	6	0	-1.16698	0.747847	0.937326
22	1	0	-1.5901	1.580037	1.510698
23	6	0	0.164648	0.223225	1.552948

24	1	0	0.002266	-0.7229	2.071497
25	1	0	0.604921	0.918408	2.275559
26	6	0	-3.31344	-0.39463	1.807585
27	1	0	-3.93271	-1.28942	1.699344
28	1	0	-3.94672	0.48627	1.642669
29	1	0	-2.96712	-0.3416	2.847846
30	6	0	2.184677	-1.00897	0.397631
31	6	0	2.475407	-1.66787	1.52025
32	6	0	2.971337	-1.23618	-0.86807
33	1	0	2.334121	-1.61167	-1.6773
34	1	0	3.772161	-1.96209	-0.70592
35	1	0	3.425702	-0.30138	-1.21426
36	1	0	1.942543	-1.50961	2.451532
37	1	0	3.286049	-2.39056	1.547194

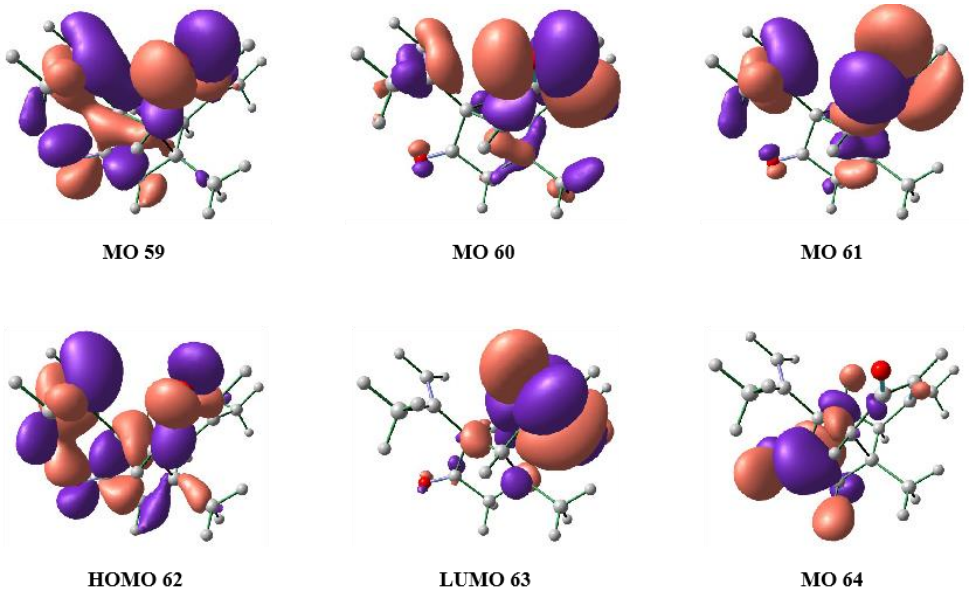


Figure S16. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **8**

Table S12. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **8**

HOMO is 62					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	32931.03824	303.6648868	13.136	0.0011	H-3->LUMO (14%), H-2->LUMO (23%), H-1->LUMO (38%), HOMO->LUMO (18%)
2	35938.70048	278.2515747	7.1872	0.0002	H-3->L+1 (32%), HOMO->L+1 (59%)
3	43994.62176	227.3005108	-44.1236	0.3088	H-2->LUMO (54%), H-1->LUMO (41%)
4	45654.52224	219.0363519	21.959	0.0393	H-2->LUMO (13%), HOMO->LUMO (77%)
5	51101.22192	195.6900368	0.5803	0.0024	H-3->LUMO (31%), H-3->L+1 (17%), H-1->L+1 (14%), HOMO->L+1 (22%)
6	52245.73056	191.4031997	-2.5906	0.0118	H-3->LUMO (43%), H-3->L+1 (11%), H-1->L+1 (14%)
7	52733.69936	189.6320592	43.5546	0.1856	H-4->LUMO (10%), HOMO->L+2 (44%), HOMO->L+3 (27%)
8	53049.87088	188.5018726	6.6987	0.0544	H-5->LUMO (13%), H-4->LUMO (58%)
9	55029.97568	181.7191426	-9.1979	0.0963	HOMO->L+2 (13%), HOMO->L+3 (23%), HOMO->L+4 (22%), HOMO->L+6 (11%)
10	55350.98656	180.6652532	-33.7496	0.033	H-5->LUMO (56%), H-4->LUMO (14%)
11	55875.25056	178.9701147	-18.9821	0.0428	H-3->L+1 (25%), H-1->L+1 (44%)
12	56518.07888	176.9345349	-18.9799	0.0051	H-2->L+2 (10%), H-1->L+2 (22%)
13	56751.98128	176.205302	-11.6453	0.0299	H-2->L+1 (65%), H-1->L+1 (12%)

14	56952.00816	175.5864336	1.6659	0.0778	H-3->L+2 (20%), H-1->L+3 (14%), HOMO->L+6 (19%)
15	57724.69264	173.2360891	-1.4753	0.0127	H-2->L+2 (31%), H-2->L+3 (21%), H-1->L+2 (11%)
16	58786.1256	170.1081658	43.997	0.0406	H-1->L+3 (22%), HOMO->L+6 (12%)
17	59024.0608	169.4224332	-15.7637	0.0103	
18	59812.87648	167.1880804	-6.0487	0.0078	HOMO->L+5 (49%), HOMO->L+7 (11%)
19	60308.10432	165.8151937	-9.296	0.0232	H-2->L+3 (10%), H-2->L+9 (11%), H-2->L+10 (13%)
20	60510.55088	165.2604357	-12.4292	0.0298	HOMO->L+2 (13%), HOMO->L+4 (15%), HOMO->L+9 (10%)
21	60537.16736	165.1877753	-5.5869	0.0456	H-7->LUMO (20%), H-6->LUMO (44%)
22	61518.75088	162.5520651	-15.6817	0.0627	H-4->L+1 (71%)
23	62075.27728	161.0947295	-7.1101	0.0142	H-7->LUMO (35%), H-6->LUMO (15%)
24	62224.49088	160.7084262	11.7918	0.0078	H-3->L+2 (11%), H-3->L+3 (20%)
25	62499.52784	160.0012087	-10.0028	0.0067	H-2->L+2 (12%), H-2->L+3 (15%), H-2->L+5 (12%), H-2->L+8 (11%), H-1->L+5 (11%)
26	62510.81968	159.9723064	0.9452	0.0202	HOMO->L+9 (13%), HOMO->L+11 (12%)
27	62719.71872	159.4394905	-5.9229	0.0445	H-8->LUMO (51%)
28	62952.008	158.851168	-13.2081	0.0166	
29	63405.29472	157.7155353	5.2035	0.0104	H-2->L+5 (14%)
30	63577.89856	157.2873628	38.6079	0.0298	HOMO->L+6 (15%)
31	63827.93216	156.67122	0.6978	0.0069	H-1->L+4 (12%), HOMO->L+8 (10%), HOMO->L+10 (11%)
32	64019.08688	156.2034151	-2.9762	0.0042	H-5->L+1 (72%)
33	64325.57968	155.4591509	-2.0997	0.0055	H-2->L+4 (11%), H-2->L+6 (27%)
34	64438.49808	155.1867331	10.24	0.045	HOMO->L+10 (11%), HOMO->L+11 (12%)

35	65157.14304	153.4751147	1.3584	0.0015	H-1->L+4 (11%), HOMO->L+12 (18%)
36	65433.79312	152.8262313	21.7156	0.0147	H-2->L+4 (10%), H-2->L+5 (14%)
37	65528.16064	152.6061452	-19.436	0.011	H-3->L+2 (10%)
38	65822.55504	151.9236072	-15.7652	0.0046	H-6->L+1 (15%), H-6->L+3 (11%)
39	66172.60208	151.1199452	19.5051	0.0198	H-6->L+1 (24%), HOMO->L+9 (14%)
40	66407.31104	150.5858292	20.8907	0.0105	H-6->L+1 (44%)
41	66554.91152	150.2518713	-0.5191	0.0064	HOMO->L+7 (34%)
42	66870.27648	149.5432728	-1.4429	0.0015	HOMO->L+8 (12%)
43	67273.55648	148.6468164	-1.2734	0.005	H-9->LUMO (12%), H-7->L+1 (27%)
44	67534.88192	148.0716293	-22.8142	0.0299	
45	67638.1216	147.8456197	0.3747	0.0181	H-3->L+5 (12%), HOMO->L+11 (13%)
46	67819.5976	147.4500049	3.4717	0.0091	H-2->L+6 (12%), H-2->L+11 (17%)
47	68106.73296	146.8283614	6.7372	0.0024	H-11->LUMO (11%), H-9->LUMO (24%), H-7->L+1 (25%)
48	68208.35952	146.6095955	-34.0626	0.014	H-2->L+7 (12%), H-1->L+7 (18%)
49	68530.98352	145.9194	-4.0725	0.0189	H-2->L+7 (13%)
50	68809.24672	145.329305	-4.3898	0.0112	H-4->L+2 (11%), HOMO->L+14 (12%)

Table S13. Cartesian coordinate of dominant conformer of **8**

Standard orientation:					
Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	8	0	2.532745	1.980311	-0.53733
2	8	0	-0.27845	-2.17521	1.83386
3	6	0	1.003325	0.063514	-0.32533
4	6	0	-0.67948	-1.29321	1.076031
5	6	0	-1.32094	0.686752	-0.80317
6	1	0	-1.75021	1.39711	-1.32476
7	6	0	-2.24095	-0.49899	-0.60247
8	6	0	2.114223	-0.94757	-0.41175
9	6	0	-0.01943	0.159336	-1.49804
10	1	0	-0.16761	-0.7094	-1.90314

11	1	0	0.287914	0.777969	-2.17888
12	6	0	1.451746	1.530953	-0.22831
13	6	0	-0.80083	1.204635	0.553025
14	6	0	0.084546	0.004907	0.943068
15	1	0	0.596406	0.19608	1.756297
16	6	0	0.254227	2.300717	0.295297
17	1	0	-0.06239	2.940597	-0.36152
18	1	0	0.474188	2.771366	1.114237
19	6	0	-1.89746	-1.43675	0.285325
20	1	0	-2.43751	-2.18516	0.399666
21	6	0	-1.85087	1.615682	1.576851
22	1	0	-2.35779	2.356234	1.235987
23	1	0	-1.41751	1.873592	2.393808
24	1	0	-2.43918	0.876251	1.746498
25	6	0	2.293938	-1.74343	-1.45755
26	1	0	1.716009	-1.59167	-2.01916
27	6	0	3.023565	-1.01854	0.784515
28	1	0	3.341007	-0.13805	0.997986
29	1	0	3.770236	-1.58827	0.585568
30	1	0	2.539867	-1.37458	1.533354
31	6	0	-3.43441	-0.59501	-1.49013
32	1	0	-3.99737	0.170362	-1.35291
33	1	0	-3.92422	-1.39401	-1.28198
34	1	0	-3.15004	-0.62331	-2.4063
35	1	0	3.056701	-2.39394	-1.49111

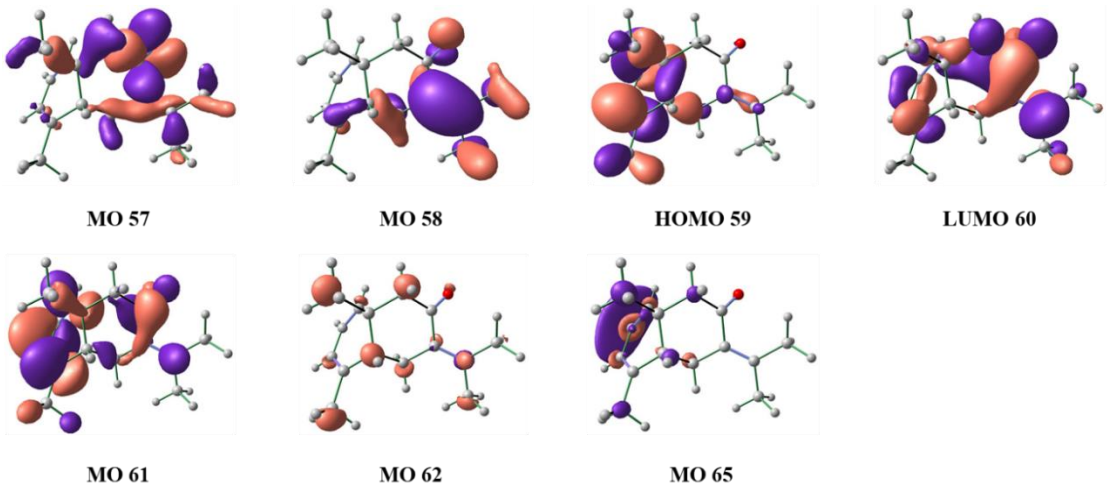


Figure S17. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **9**

Table S14. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **9**

HOMO is 59					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	32967.33344	303.3305687	-0.8798	0.0009	H-2->LUMO (70%), H-2->L+1 (12%)
2	37345.34112	267.7710178	-123.6907	0.159	HOMO->LUMO (63%), HOMO->L+1 (35%)
3	40649.81744	246.0035648	116.8801	0.108	H-1->LUMO (44%), HOMO->LUMO (14%), HOMO->L+1 (32%)
4	43546.1744	229.6412977	-78.1932	0.1647	H-1->LUMO (35%), HOMO->LUMO (20%), HOMO->L+1 (31%)
5	46223.14704	216.3418253	4.2576	0.0048	HOMO->L+2 (64%), HOMO->L+5 (18%)
6	50112.37936	199.5514906	0.6581	0.0043	HOMO->L+4 (31%), HOMO->L+5 (43%)
7	51004.43472	196.0613828	-2.4115	0.0252	HOMO->L+3 (61%), HOMO->L+5 (16%)
8	51360.12768	194.7035658	9.7298	0.0099	H-1->L+1 (36%), HOMO->L+4 (13%)
9	51844.06368	192.8861144	2.99	0.04	H-1->L+1 (30%), HOMO->L+2 (10%), HOMO->L+4 (16%), HOMO->L+6 (12%)
10	53106.33008	188.3014696	-23.5454	0.0114	H-2->LUMO (12%), H-2->L+1 (45%)
11	53655.59744	186.373845	-7.5124	0.0148	H-2->L+1 (12%), H-1->L+2 (30%)
12	54216.15664	184.4468627	-12.015	0.0028	H-4->LUMO (15%), H-3->LUMO (29%), H-3->L+1 (10%), H-1->L+1 (17%)
13	54938.02784	182.0232796	14.1234	0.0306	HOMO->L+7 (20%), HOMO->L+8 (37%), HOMO->L+9 (10%)

14	55280.00928	180.89722	37.8643	0.0451	H-5->LUMO (17%), H-5->L+1 (10%), H-4->LUMO (17%), H-3->L+1 (15%), H-2->L+2 (12%)
15	55928.48352	178.7997702	-8.2652	0.009	H-2->L+2 (20%), H-2->L+4 (11%), HOMO->L+10 (16%)
16	56143.83504	178.113946	-13.9279	0.0219	HOMO->L+8 (15%), HOMO->L+9 (13%), HOMO->L+10 (18%)
17	56388.22272	177.3419966	29.3286	0.0376	H-4->L+1 (19%), HOMO->L+10 (12%)
18	56663.25968	176.4811989	14.1006	0.0341	HOMO->L+9 (11%), HOMO->L+10 (20%)
19	56778.59776	176.1227011	-65.0286	0.1183	HOMO->L+9 (17%), HOMO->L+11 (13%)
20	57242.36976	174.6957724	31.7555	0.0395	
21	58009.40832	172.38583	-19.0005	0.0286	HOMO->L+12 (15%)
22	58187.65808	171.8577501	17.8626	0.0433	H-5->LUMO (10%), H-5->L+1 (22%), H-4->LUMO (12%), H-3->L+1 (14%)
23	58732.89264	170.2623445	-24.6078	0.0197	H-1->L+5 (18%)
24	59268.44848	168.7238363	-11.6766	0.0099	H-1->L+4 (26%), H-1->L+6 (11%), HOMO->L+11 (10%)
25	60154.85792	166.2376132	-3.8192	0.05	H-1->L+3 (18%), H-1->L+5 (17%), HOMO->L+13 (11%)
26	60227.44832	166.0372518	3.9066	0.0065	HOMO->L+13 (28%)
27	60574.26912	165.0865977	6.7609	0.0424	H-3->LUMO (10%), HOMO->L+13 (13%)
28	60958.19168	164.046861	32.8707	0.1048	HOMO->L+6 (13%)
29	61480.84256	162.6522927	-18.1323	0.1323	H-2->L+3 (10%), H-2->L+5 (30%)
30	61733.29584	161.9871394	2.244	0.025	H-2->L+3 (29%), H-2->L+5 (10%)

Table S15. Cartesian coordinate of dominant conformer of **9**

Standard orientation:					
Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	0	2.602051	-0.57228	-1.51631
2	6	0	2.906479	0.735064	-0.93131
3	6	0	2.151569	1.2412	0.056034
4	6	0	0.915323	0.472803	0.489255
5	6	0	1.149334	-1.05116	0.435846
6	6	0	1.75519	-1.41215	-0.90747
7	6	0	-0.25785	0.919152	-0.41672
8	6	0	-1.55452	0.17618	-0.17197
9	6	0	-1.38042	-1.30389	-0.09678
10	6	0	-0.17401	-1.79621	0.677854
11	6	0	2.41522	2.56694	0.703866
12	8	0	-2.17083	-2.09861	-0.57804
13	6	0	-2.77062	0.744491	-0.04439
14	6	0	-3.01312	2.229832	-0.13049
15	6	0	-4.04306	-0.02561	0.204373
16	6	0	2.140295	-1.48559	1.53404
17	1	0	3.090286	-0.85451	-2.4454
18	1	0	3.757425	1.293127	-1.3153
19	1	0	0.664539	0.738455	1.525926
20	1	0	1.543074	-2.39471	-1.32383
21	1	0	-0.39075	1.99489	-0.29549
22	1	0	0.049305	0.760367	-1.45841
23	1	0	-0.06064	-2.86743	0.484226
24	1	0	-0.44167	-1.68891	1.739817
25	1	0	3.258745	3.084783	0.238301
26	1	0	1.536926	3.222636	0.643067
27	1	0	2.638383	2.442013	1.771405
28	1	0	-2.14757	2.812288	-0.44454
29	1	0	-3.82287	2.425991	-0.84394
30	1	0	-3.35434	2.616366	0.83827
31	1	0	-3.87782	-1.03503	0.577304
32	1	0	-4.6756	0.523526	0.911861
33	1	0	-4.61206	-0.12039	-0.72869
34	1	0	3.115801	-1.01197	1.395673
35	1	0	1.760052	-1.21435	2.526749
36	1	0	2.284211	-2.571	1.512444

4.2 Chemical calculation details for 5

The systematic random conformational analysis of **5** were performed in the SYBYL-X 2.1.1 program by using MMFF94s molecular force field with an energy cutoff of 10 kcal/mol^{-1} to the global minima, which afforded 3 conformers, respectively. All of the obtained conformers were further optimized using DFT at the B3LYP/6-31+G(d) level in gas phase using Gaussian09 software,[2] which afforded 3 stable conformers. The optimized stable conformers were further subjected to ECD calculations at the B3LYP/6-31+G(d) level with the PCM solvation model of acetonitrile, with the consideration of the first 30 excitations. The overall ECD curves of **5** were weighted by Boltzmann distribution, and were subsequently compared with the experimental ones. The ECD spectra were produced by SpecDis 1.71 software.[3]

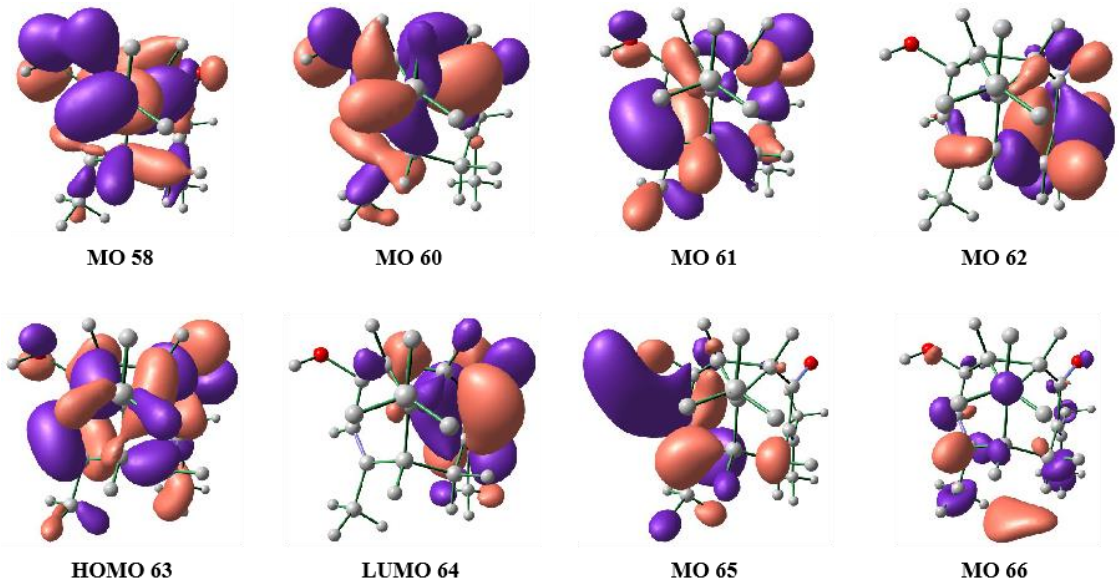


Figure S18. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **5**

Table S16. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **5**

HOMO is 63					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R(length)**	**Osc. Strength**	**Major contribs**
1	29821.74944	335.3257333	-2.6145	0.0004	H-2->LUMO (24%), HOMO->LUMO (72%)
2	36115.33712	276.890673	-1.0265	0.0134	H-2->LUMO (72%), HOMO->LUMO (26%)
3	37998.65472	263.1672114	67.4833	0.2653	H-1->LUMO (90%)
4	42508.13168	235.2491066	12.2345	0.0557	H-3->LUMO (89%)
5	44263.20624	225.9212752	0.6586	0.0241	H-4->LUMO (91%)
6	46187.6584	216.5080532	-22.9543	0.033	H-1->L+1 (11%), HOMO->L+1 (82%)
7	47104.71712	212.2929637	-7.6551	0.0043	H-1->L+1 (82%)
8	48371.82288	206.7319238	-56.7318	0.0786	H-5->LUMO (30%), H-2->L+1 (46%)
9	48638.79424	205.5972019	49.0976	0.0335	H-5->LUMO (64%), H-2->L+1 (18%)
10	49392.12128	202.46144	-75.8582	0.0304	H-1->L+2 (31%), HOMO->L+2 (54%)
11	49453.41984	202.2104848	13.7384	0.0365	H-1->L+2 (61%), HOMO->L+2 (21%)
12	50486.6232	198.0722688	20.3633	0.0062	H-2->L+2 (34%), HOMO->L+3 (37%)
13	50674.55168	197.3377103	26.7871	0.0049	H-2->L+2 (32%), HOMO->L+3 (40%)
14	51695.65664	193.4398487	14.2139	0.0547	H-3->L+1 (70%)
15	52009.40848	192.2729039	-4.386	0.0285	H-2->L+3 (14%), H-1->L+3 (10%), HOMO->L+4 (45%)
16	52159.42864	191.7198915	28.2423	0.0257	H-1->L+3 (79%)
17	52516.73472	190.4154943	-27.4594	0.0132	H-2->L+3 (48%), HOMO->L+4 (17%)
18	52728.05344	189.6523643	7.5066	0.0051	H-6->LUMO (84%)
19	52810.32256	189.3569195	-10.1566	0.0305	HOMO->L+5 (64%)
20	53070.03488	188.4302511	2.2335	0.0036	H-1->L+4 (82%)
21	53409.59664	187.2322697	32.953	0.0101	H-7->LUMO (66%)
22	53590.26608	186.6010515	-21.5805	0.0128	H-2->L+4 (73%)
23	53815.29632	185.8207737	-6.3	0.0121	H-1->L+5 (61%)

24	54007.2576	185.1602996	1.7233	0.0052	H-1->L+5 (10%), HOMO->L+6 (45%)
25	54892.86048	182.1730533	-38.4676	0.034	H-4->L+1 (10%), H-2->L+5 (66%)
26	55501.81328	180.1742936	0.8487	0.0139	H-4->L+1 (82%)
27	55889.76864	178.9236249	9.6528	0.0087	H-2->L+6 (19%), HOMO->L+6 (21%), HOMO->L+7 (33%)
28	56094.63488	178.2701683	-10.0182	0.0352	H-2->L+6 (29%), H-1->L+6 (18%), HOMO->L+7 (34%)
29	56366.4456	177.4105125	-40.6063	0.069	H-2->L+6 (15%), H-1->L+6 (66%)
30	56405.96704	177.2862079	21.446	0.0182	H-3->L+2 (69%)

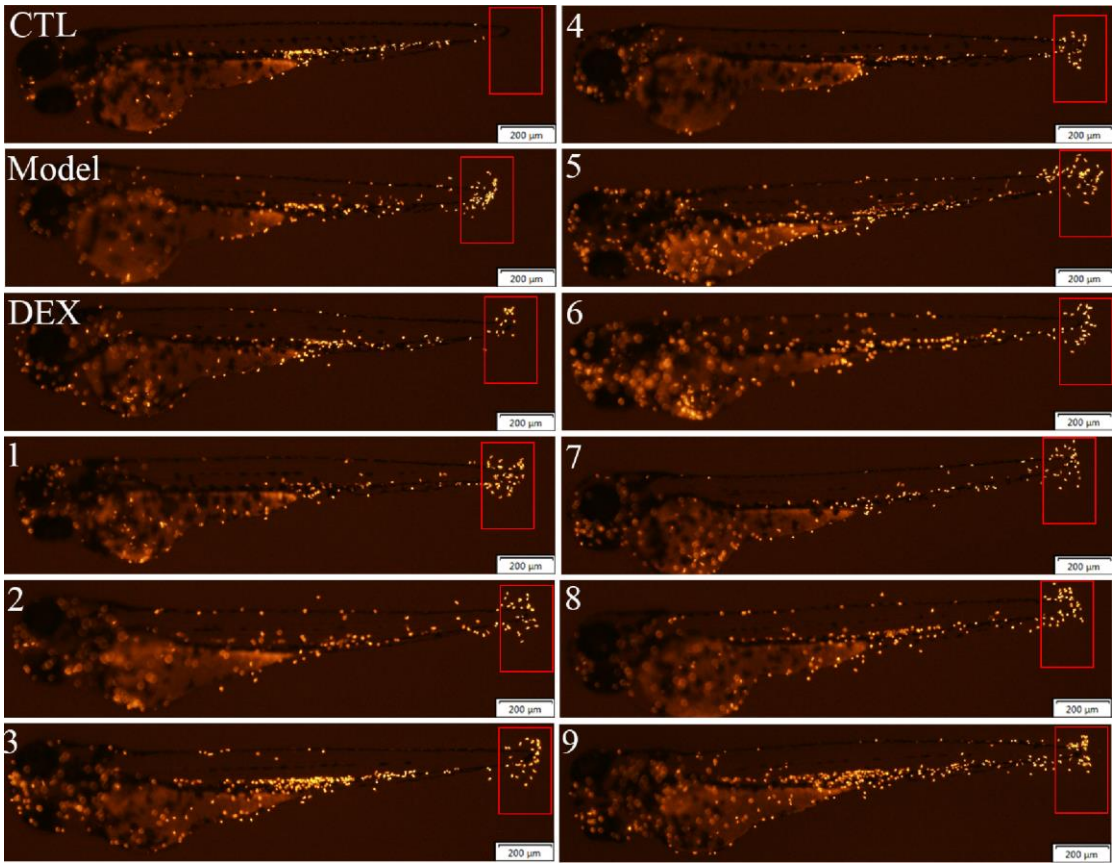
Table S17. Cartesian coordinate of dominant conformer of **5**

Standard orientation:					
Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	0	2.100775	-0.56281	-1.18261
2	6	0	1.586389	0.824278	-1.42171
3	6	0	0.928448	1.571641	-0.51609
4	6	0	0.614666	1.068348	0.890045
5	6	0	1.25814	-0.26487	1.266935
6	6	0	1.890709	-1.12417	0.191132
7	6	0	-0.91083	0.93427	1.13896
8	6	0	-1.59027	-0.14507	0.309139
9	6	0	-0.70109	-1.29688	-0.09118
10	6	0	0.52146	-1.47851	0.735351
11	6	0	1.838851	-0.33405	2.653056
12	8	0	-0.9094	-2.05604	-1.02575
13	6	0	-2.88541	-0.09408	-0.0916
14	6	0	0.494639	2.973908	-0.84833
15	6	0	-3.55523	-1.16961	-0.91642
16	6	0	-3.82983	1.030267	0.263624
17	1	0	0.999654	1.829502	1.582977
18	8	0	3.506773	-0.51812	-1.42512
19	1	0	2.684346	-1.81466	0.459965
20	1	0	0.479009	-2.36213	1.365563
21	1	0	1.672166	-1.2437	-1.92515
22	1	0	1.784547	1.226836	-2.41283
23	1	0	-1.36817	1.913223	0.968035

24	1	0	-1.07835	0.692892	2.197394
25	1	0	2.657371	0.385617	2.756626
26	1	0	1.075698	-0.0995	3.402044
27	1	0	2.236859	-1.32881	2.880712
28	1	0	0.880091	3.304308	-1.81894
29	1	0	-0.59637	3.044289	-0.88744
30	1	0	0.86501	3.675396	-0.09383
31	1	0	-3.30861	-2.17303	-0.55643
32	1	0	-4.64685	-1.09267	-0.85788
33	1	0	-3.27663	-1.07163	-1.97033
34	1	0	-3.42608	1.74029	0.987627
35	1	0	-4.10412	1.586353	-0.63882
36	1	0	-4.74474	0.626746	0.711948
37	1	0	3.867627	0.157868	-0.82618

4. *In vivo* anti-inflammatory effects of compounds 1–9

wound model



$CuSO_4$ model

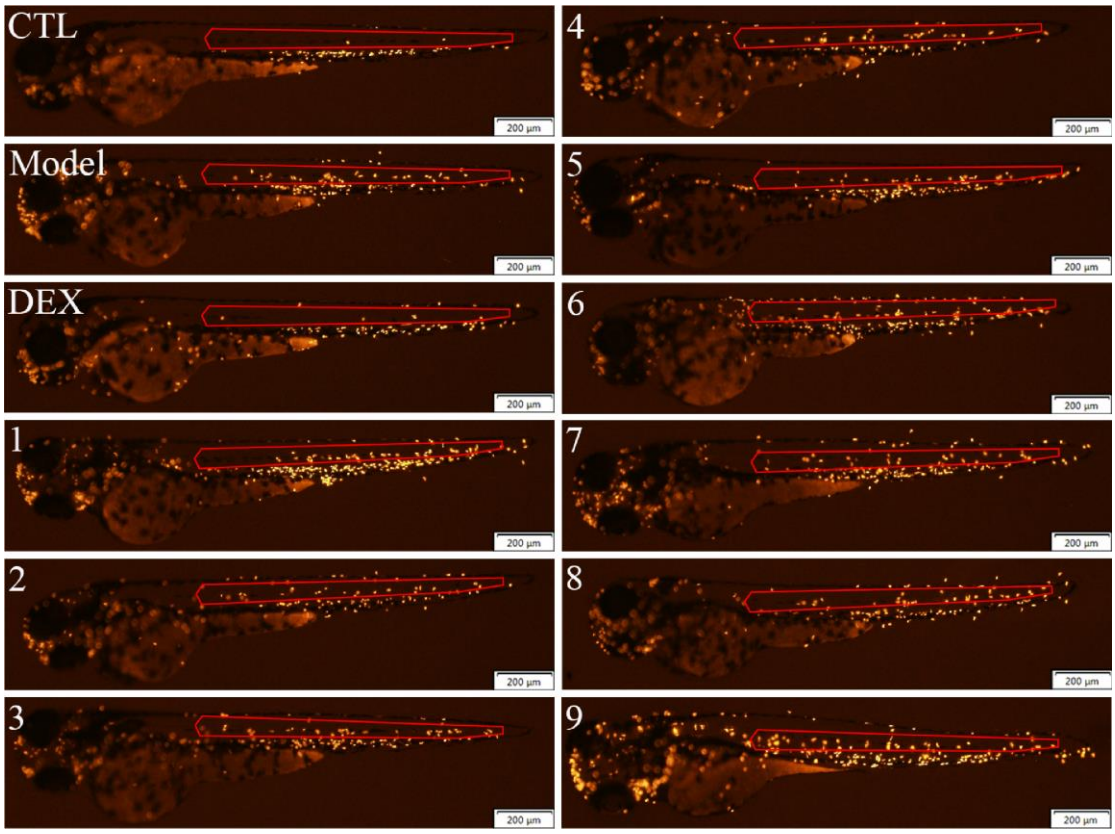


Figure S19. Anti-inflammatory effects of compounds **1**–**9**. The neutrophil number (red fluorescence) in inflammatory sites (red rectangle or ellipse marked) in wound (top panel) and $CuSO_4$ (down panel) models was observed by fluorescence microscopy (MVX10, Olympus, Japan).

5. HPLC-HR-MS analyses of the methanol extract of the fresh fruits of *Eugenia uniflora*

In order to verify that compounds **1**–**9** are indeed naturally occurring in plants, the identification of these compounds in the methanol extract of the fresh fruits of *E. uniflora* was conducted using HPLC-ESI-MS. Ion peaks with the identical retention times and exact mass data of compounds **1**–**9** were presented in the extracted-ion chromatogram (EIC) for the methanol extract, shown in Figures S106–121. The above results suggested that compounds **1**–**9** are presented in the plant itself.

Preparation of sample solution: The fresh fruits (20 g) of *E. uniflora* were smashed into crude powders and extracted using MeOH by ultrasonic extraction in dark for 60

minutes. Then the extract was concentrated in vacuo and filtered for further HPLC-HRESIMS analysis.

HPLC conditions: HPLC analyses were performed on an SCIEX Integrated System Shimadzu Nexera Prominence LC. All the separations were carried out at 35 ºC on an Agilent Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A gradient program with the mobile phase CH_3CN/H_2O was used as eluent.

MS conditions: ESI-MS analysis was performed using a SCIEX X500R Q-TOF mass spectrometer equipped with an ESI source. The mass range was set at *m*/*z* 50–1000. The Q-TOF MS data were acquired in positive mode and conditions of MS analysis were as follows: CAD gas flow-rate, 7 L/min; drying gas temperature, 550 ºC; Ion source gas pressure, 60 psi; Ion spray voltage, 5500 V; Declustering potential, 80 V. Software generated data file: SCIEX OS 1.0.

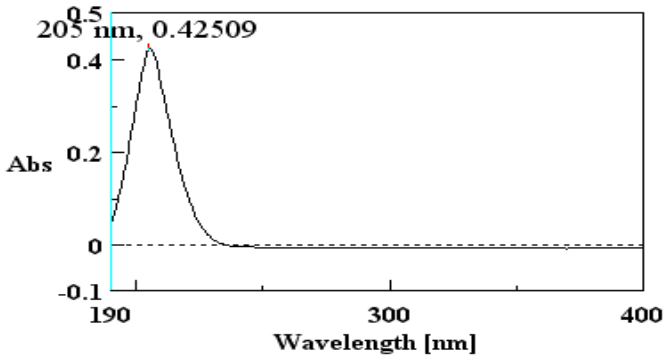


Figure S20. UV spectrum of **1** in MeOH

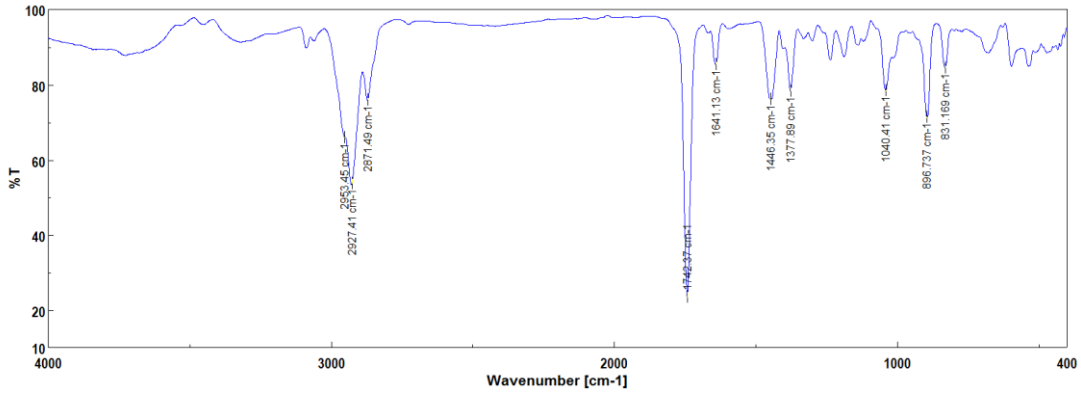


Figure S21. IR spectrum of **1** (KBr disc)

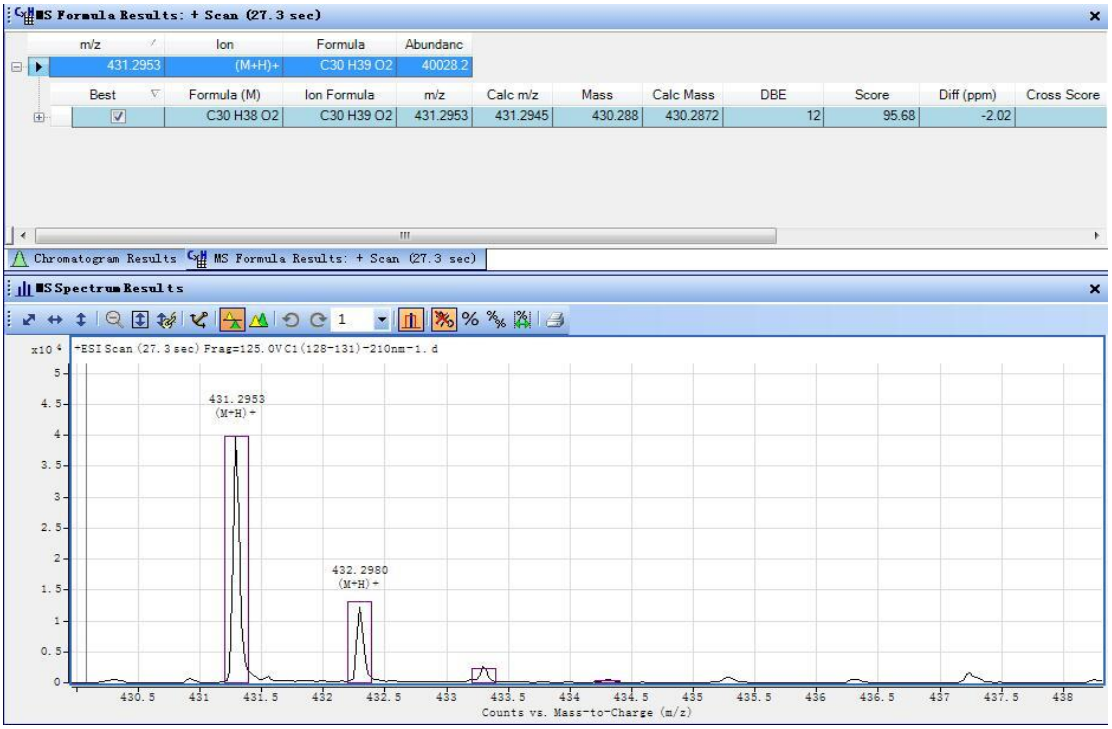


Figure S22. HR-ESI-MS spectrum of **1**

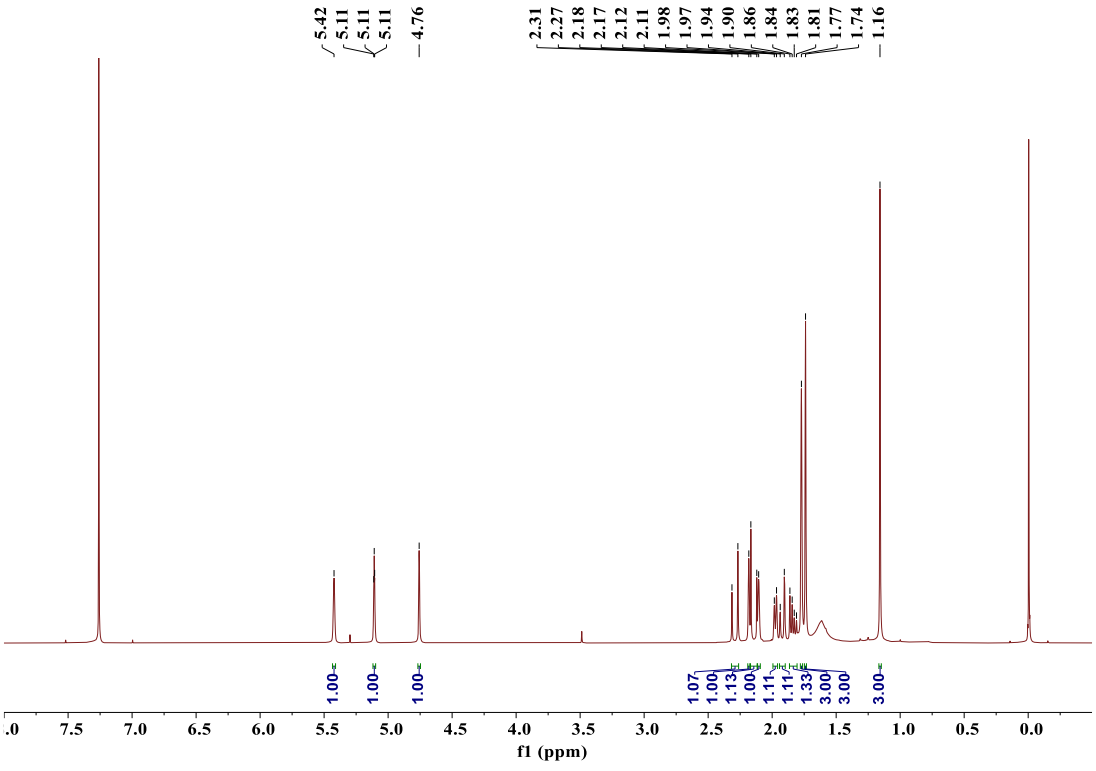


Figure S23. ^{1}H NMR spectrum of **1** in $CDCl_3$

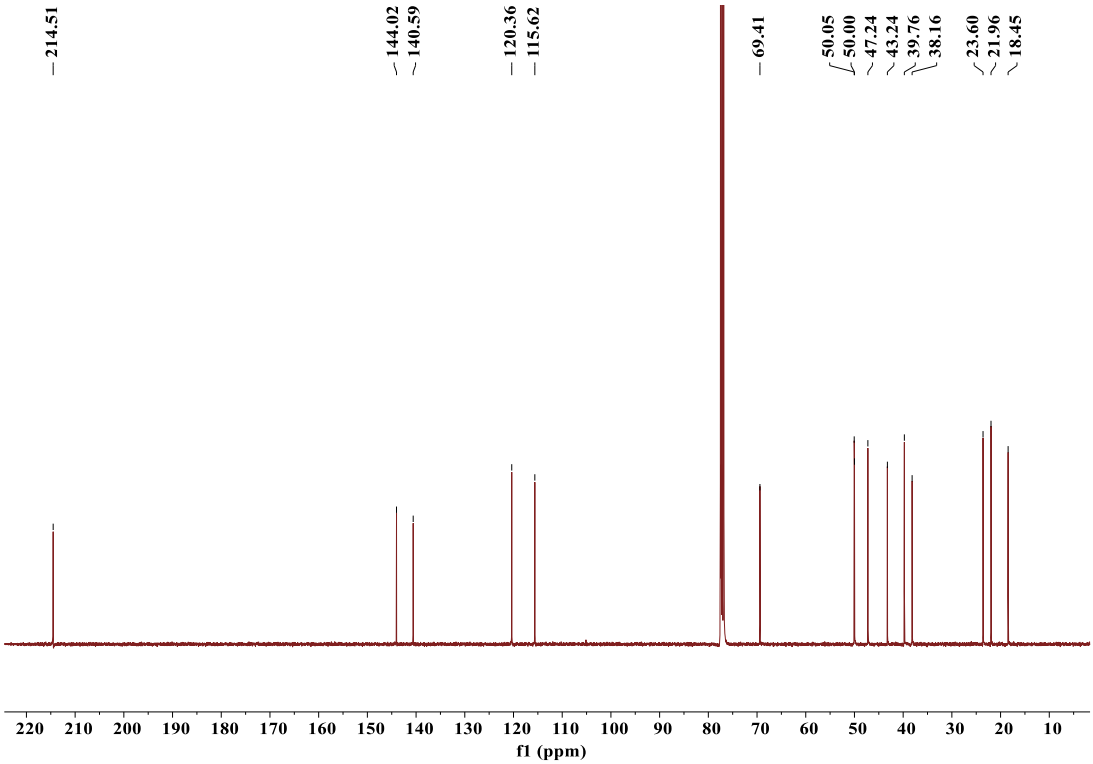


Figure S24. ^{13}C NMR spectrum of **1** in $CDCl_3$

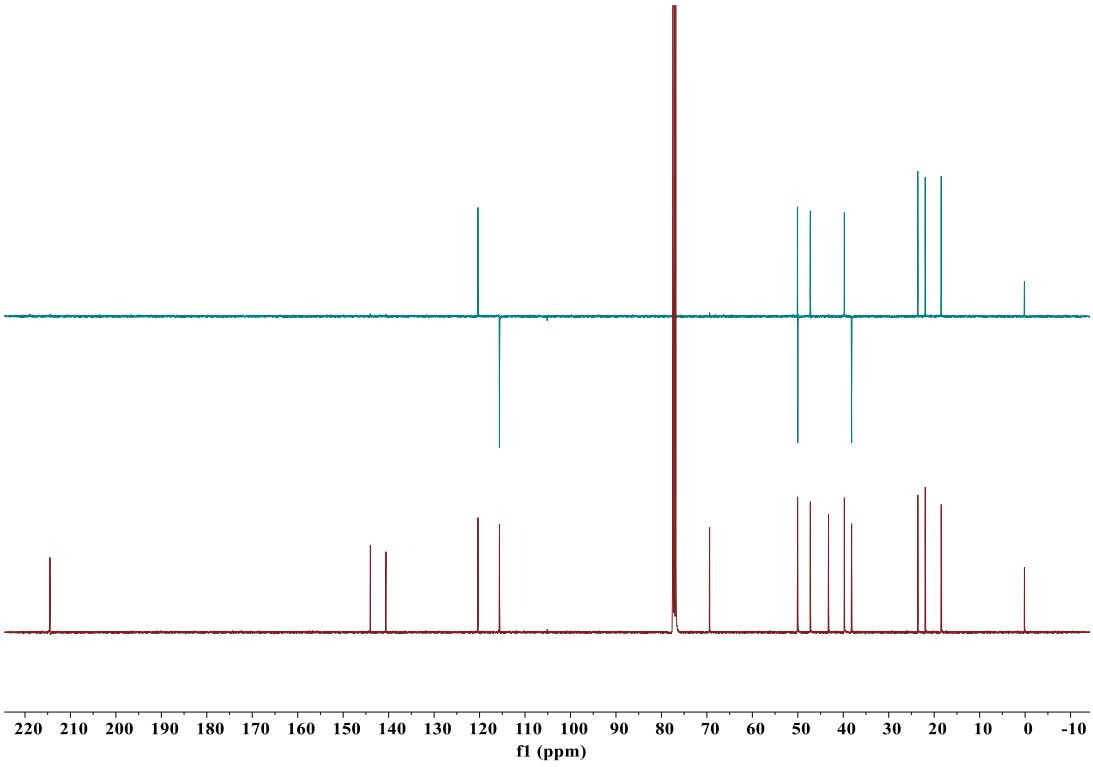


Figure S25. ^{13}C NMR and DEPT-135 Spectra of **1** in $CDCl_3$

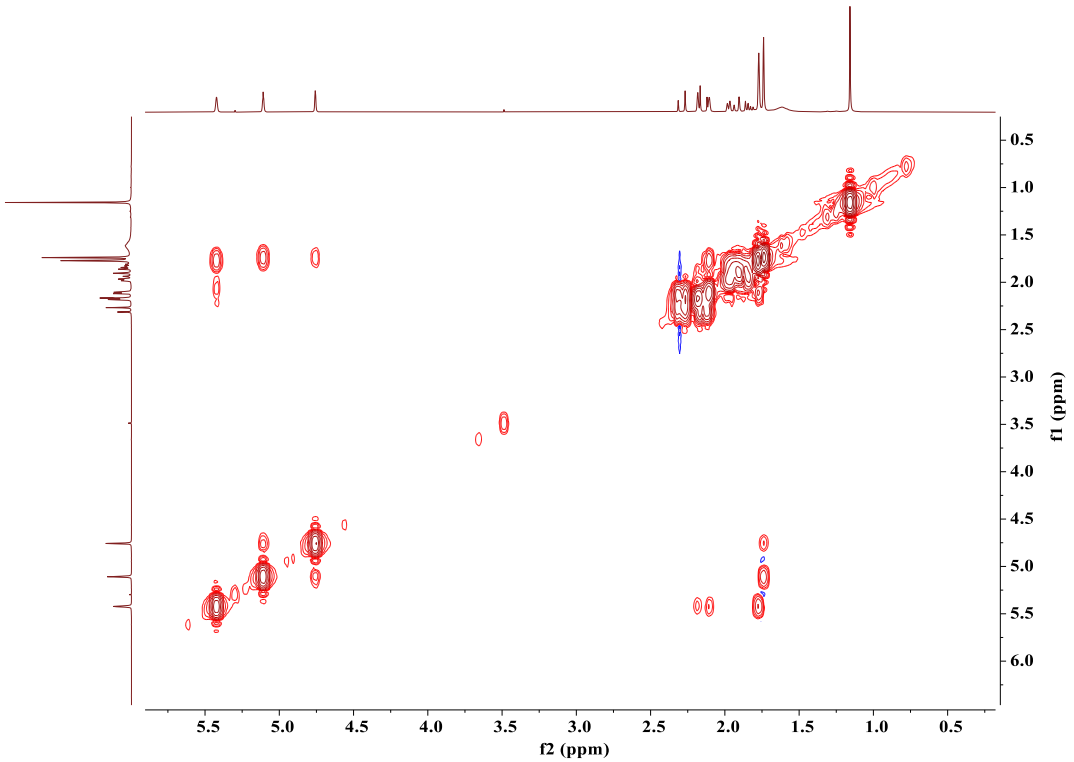


Figure S26. ^{1}H-^{1}H COSY spectrum of **1** in $CDCl_3$

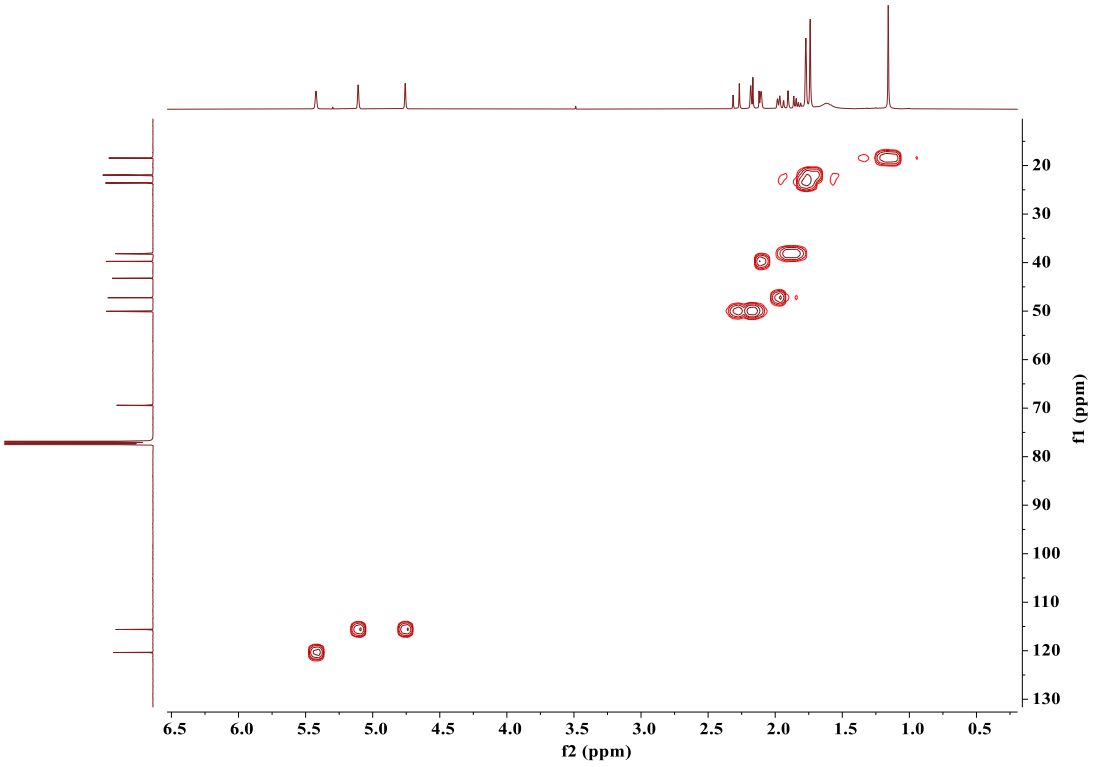


Figure S27. HSQC spectrum of **1** in $CDCl_3$

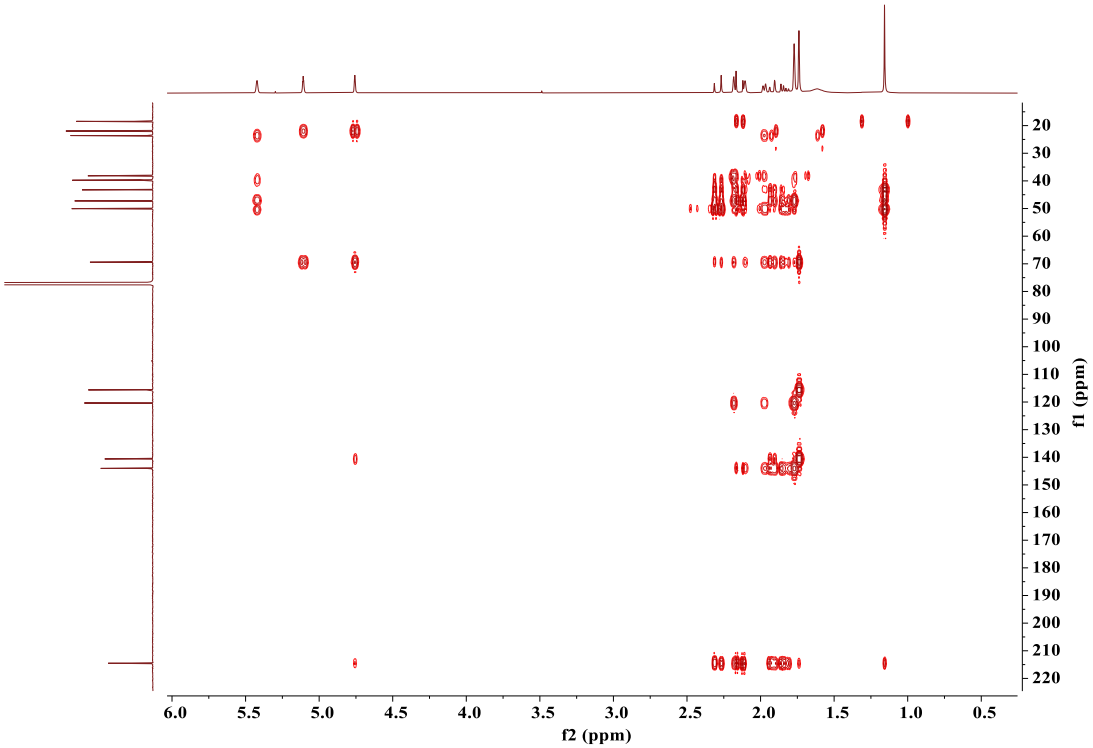


Figure S28. HMBC spectrum of **1** in $CDCl_3$

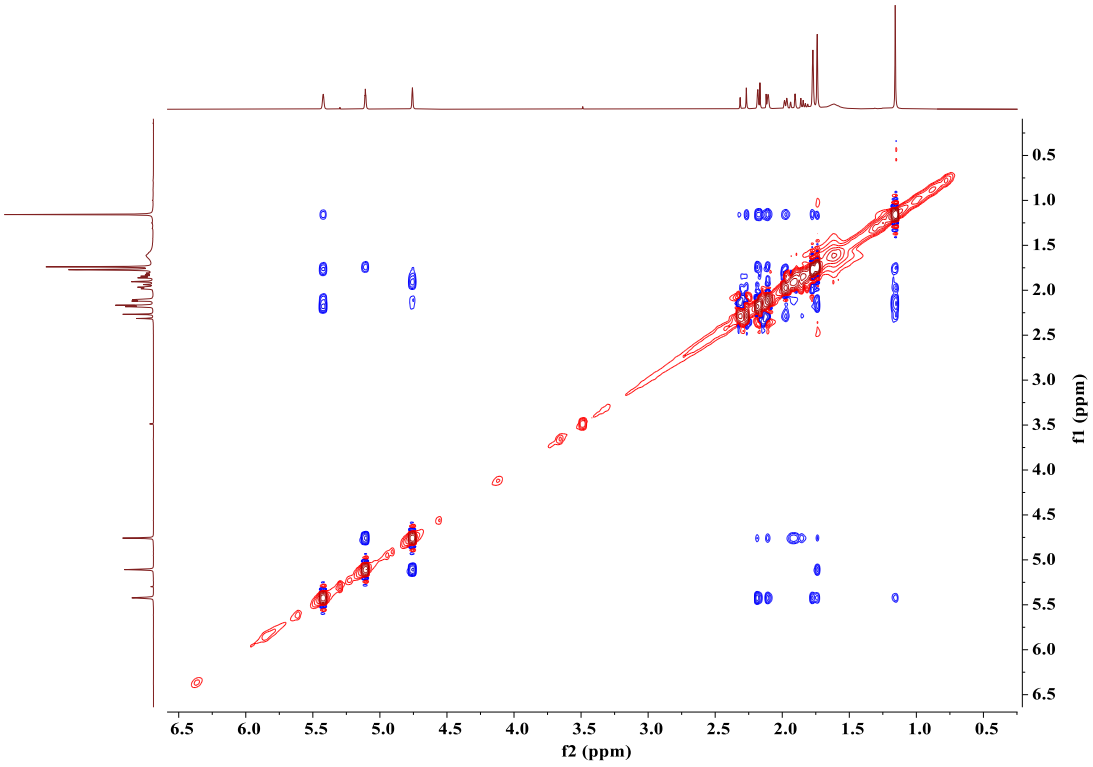


Figure S29. NOESY spectrum of **1** in $CDCl_3$

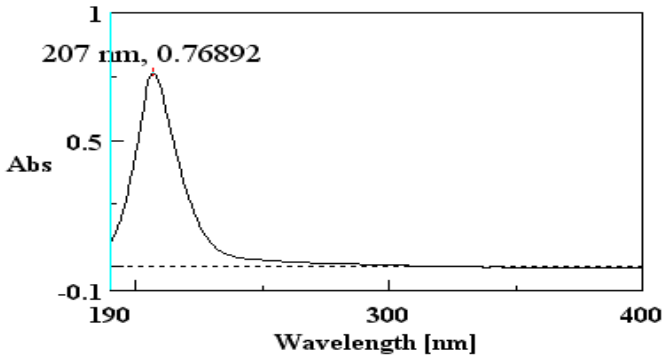


Figure S30. UV spectrum of **2** in MeOH

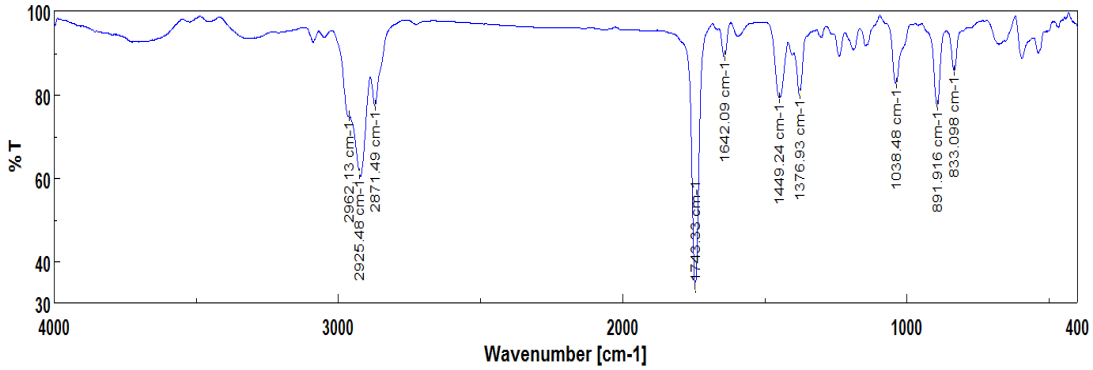


Figure S31. IR spectrum of **2** (KBr disc)

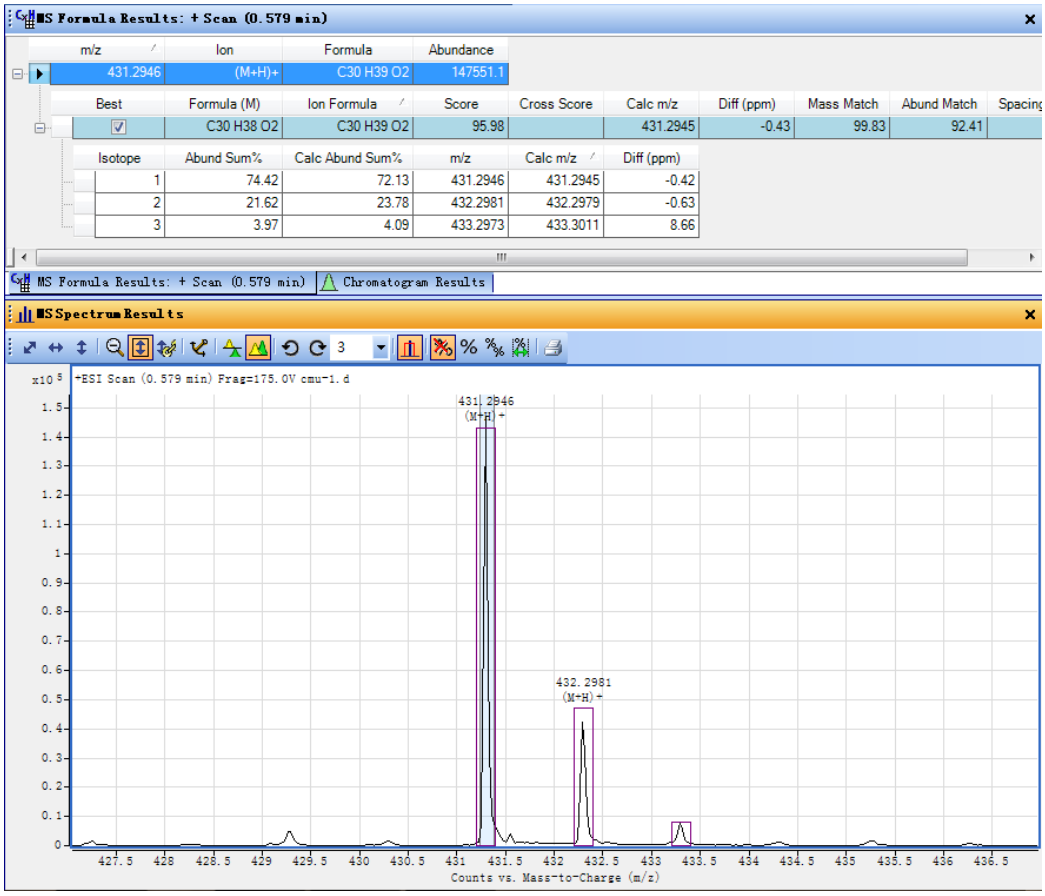


Figure S32. HR-ESI-MS spectrum of **2**

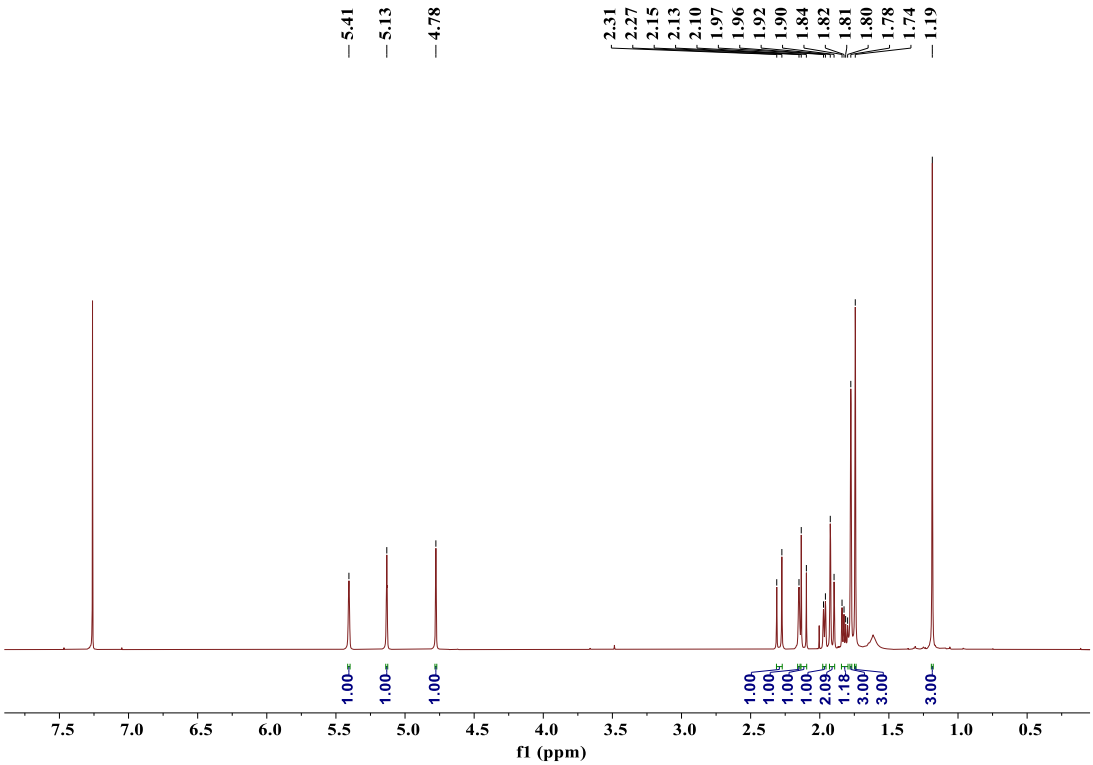


Figure S33. ^{1}H NMR spectrum of **2** in $CDCl_3$

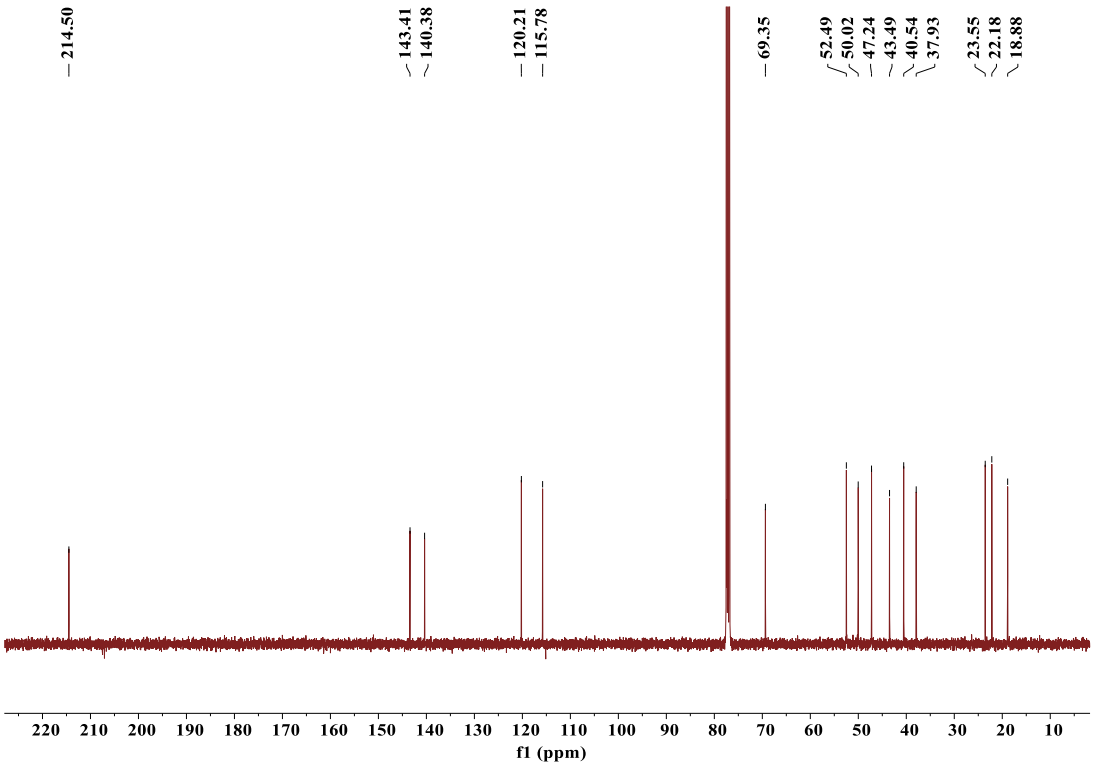


Figure S34. ^{13}C NMR spectrum of **2** in $CDCl_3$

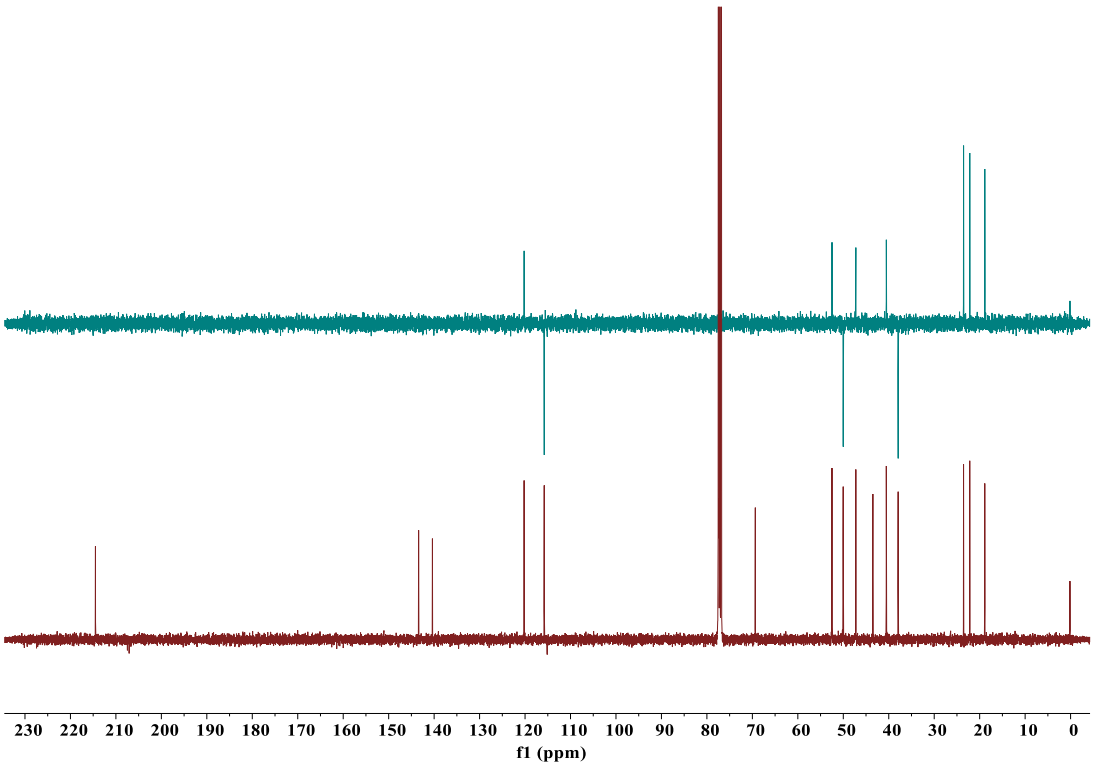


Figure S35. ^{13}C NMR and DEPT-135 Spectra of **2** in $CDCl_3$

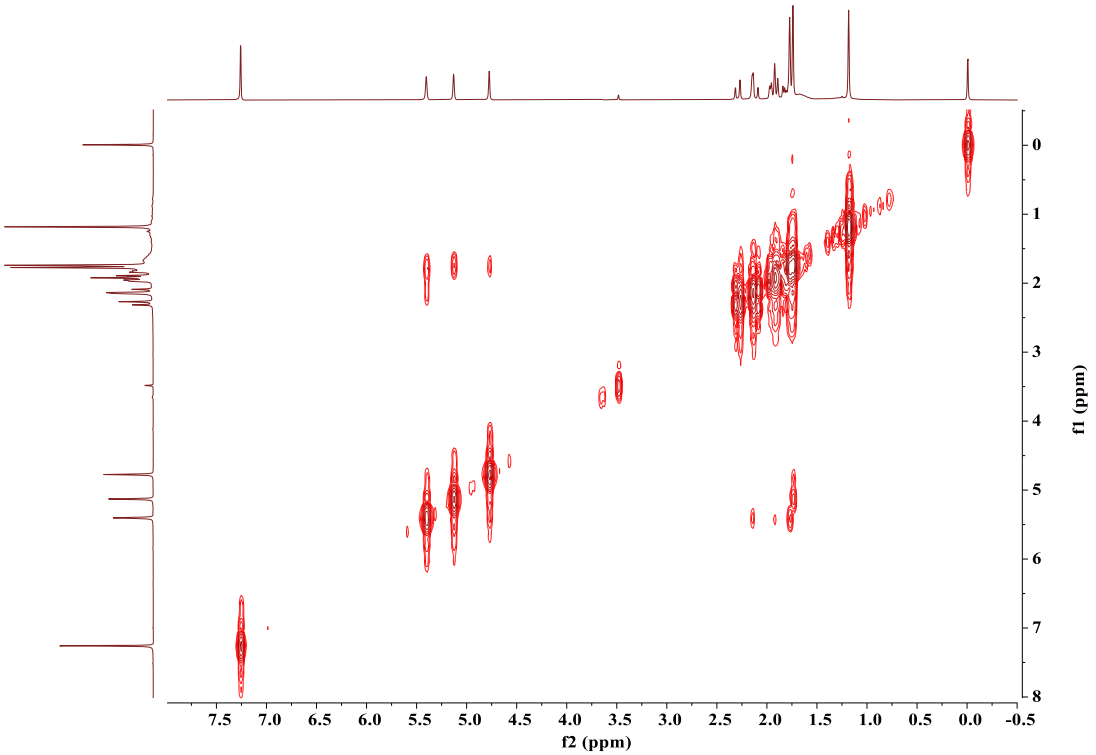


Figure S36. ^{1}H-^{1}H COSY spectrum of **2** in $CDCl_3$

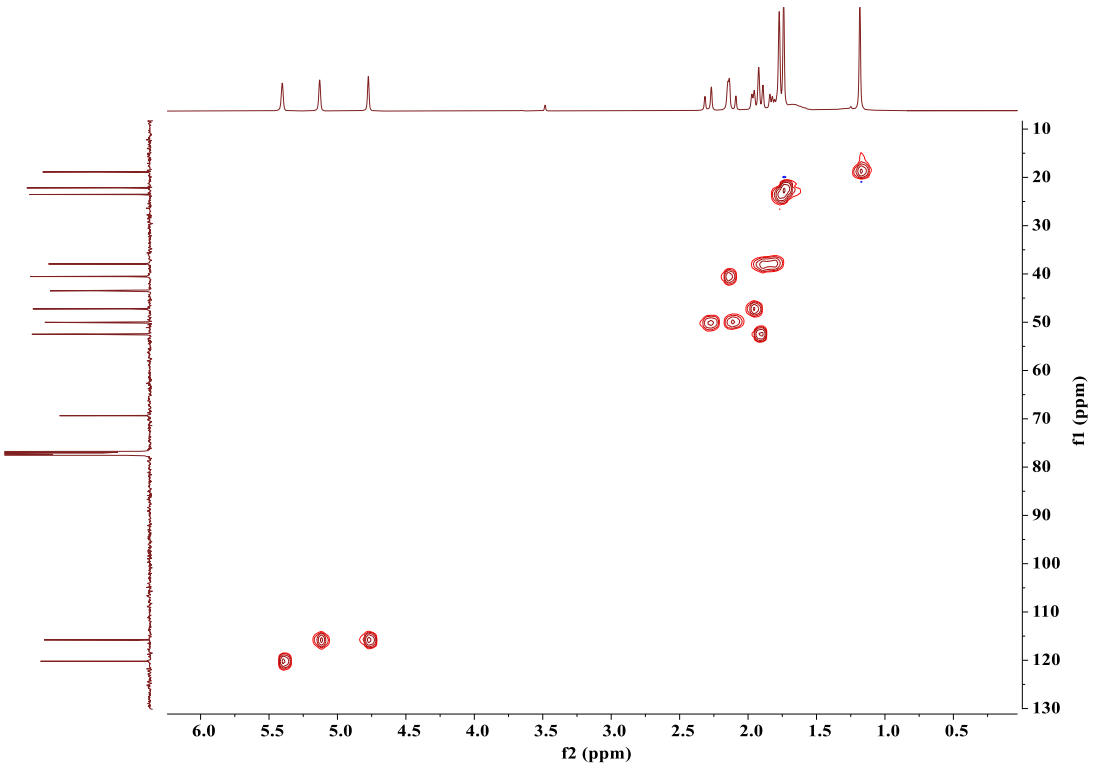


Figure S37. HSQC spectrum of **2** in $CDCl_3$

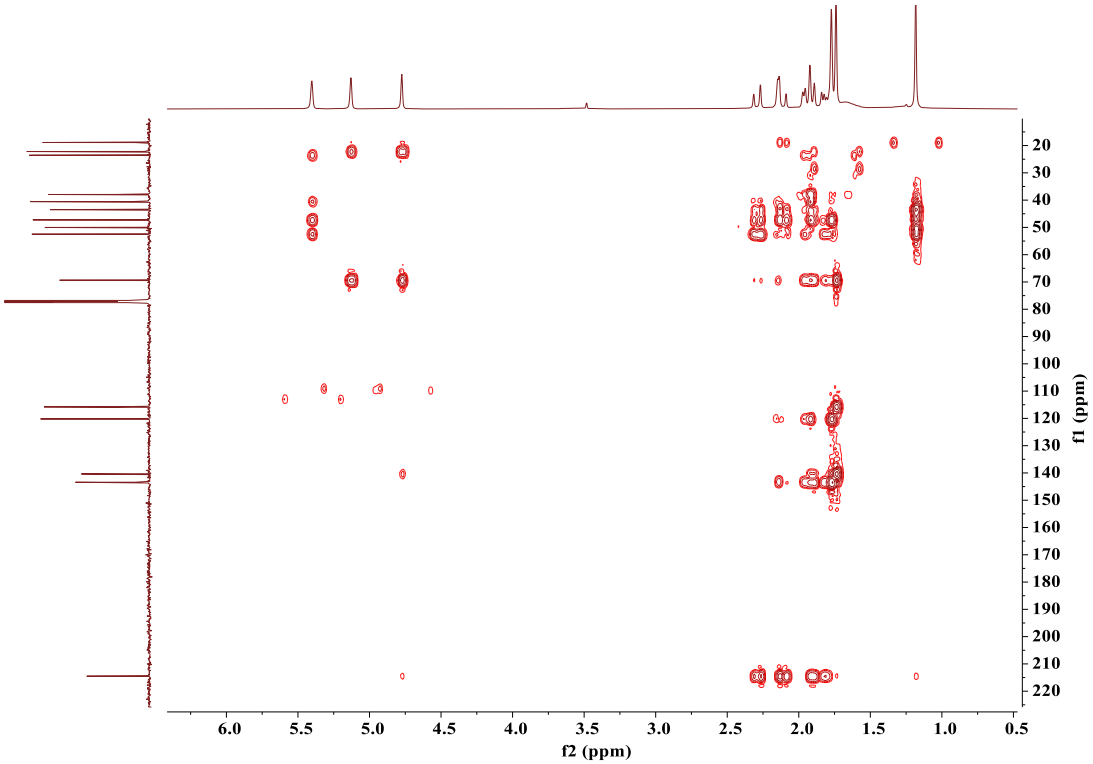


Figure S38. HMBC spectrum of **2** in $CDCl_3$

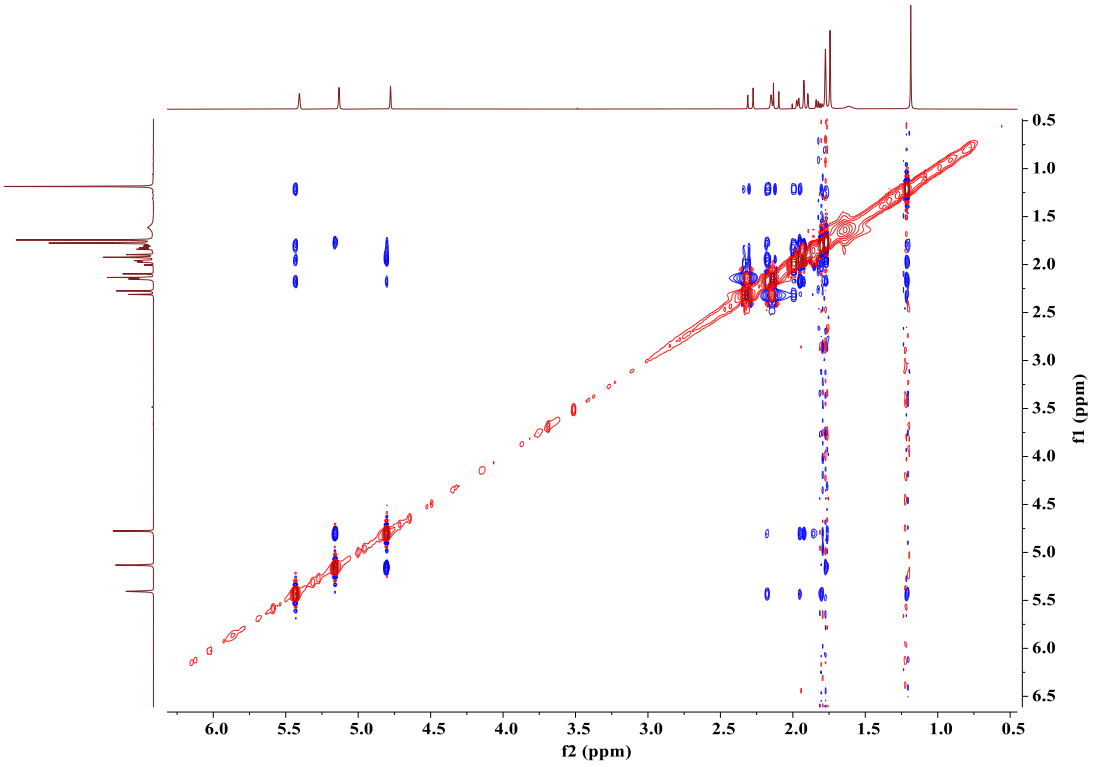


Figure S39. NOESY spectrum of **2** in $CDCl_3$

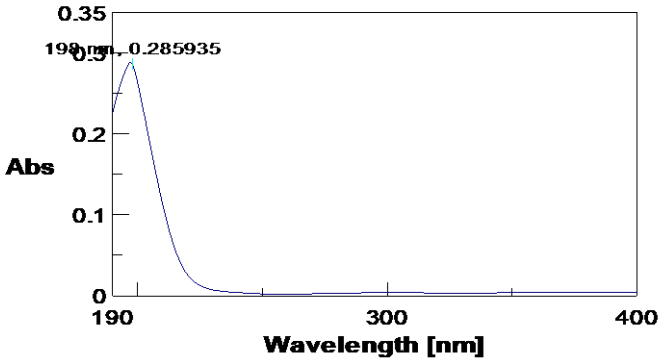


Figure S40. UV spectrum of **3** in MeOH

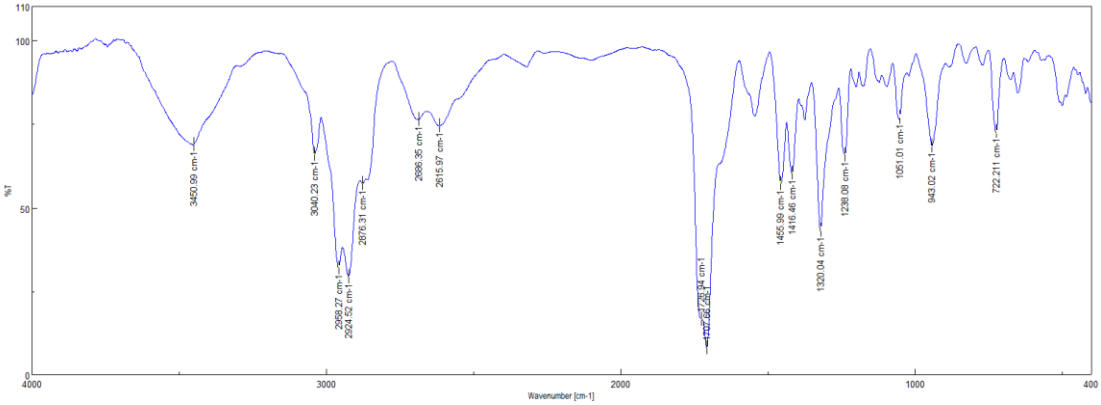


Figure S41. IR spectrum of **3** (KBr disc)

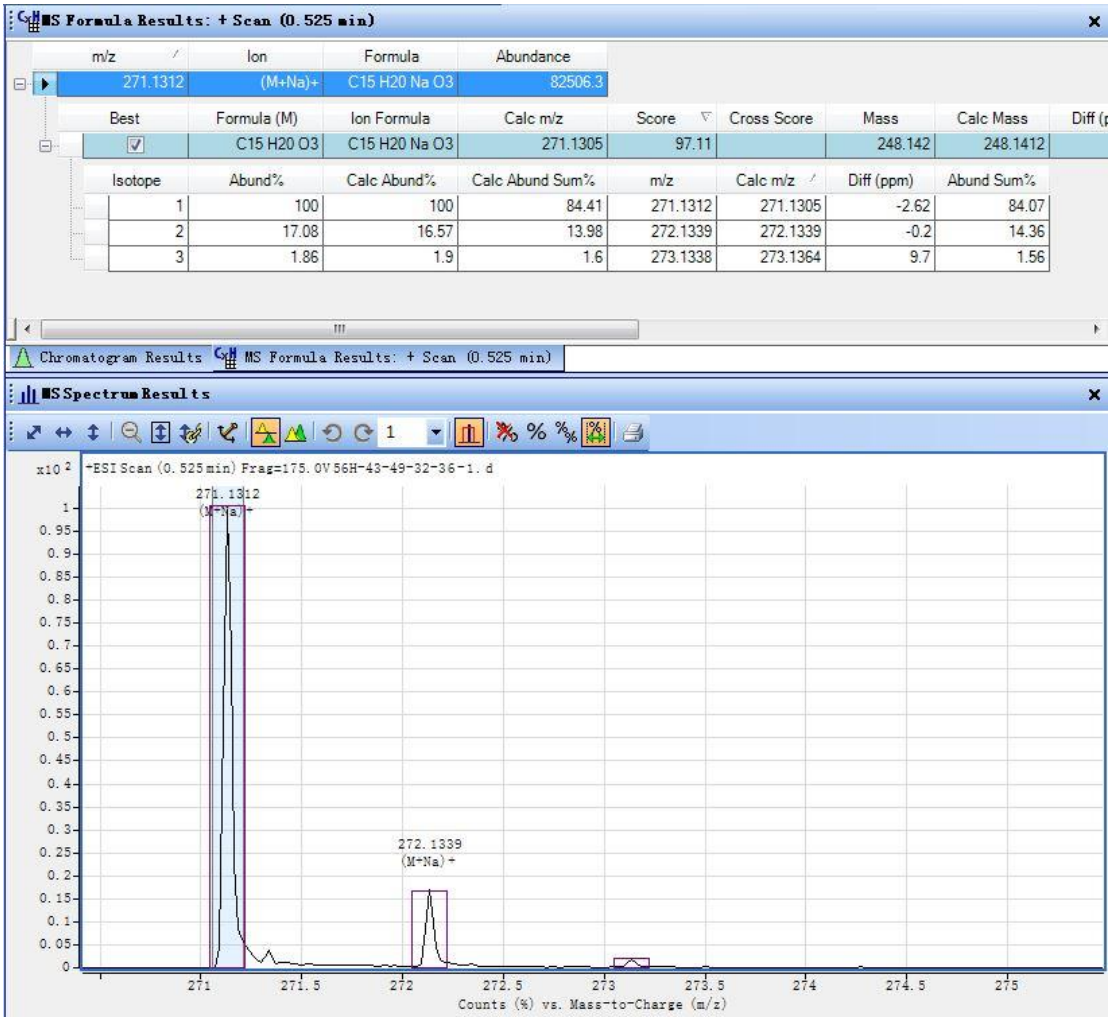


Figure S42. HR-ESI-MS spectrum of **3**

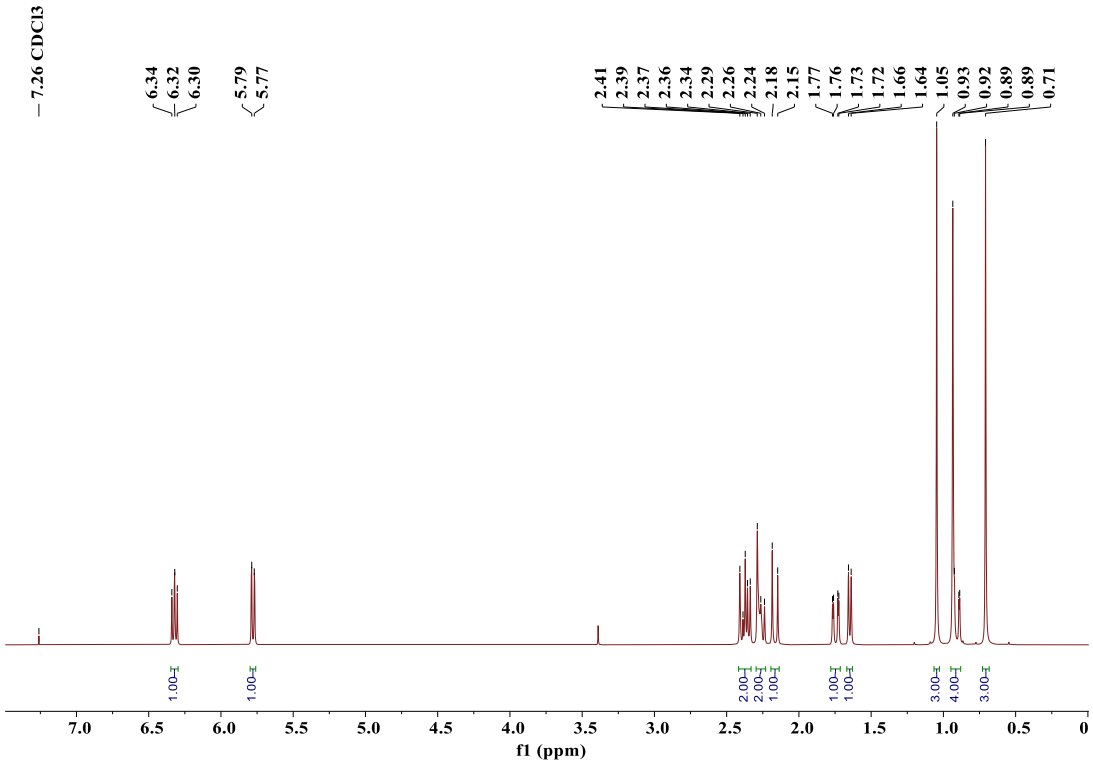


Figure S43. ^{1}H NMR spectrum of **3** in $CDCl_3$

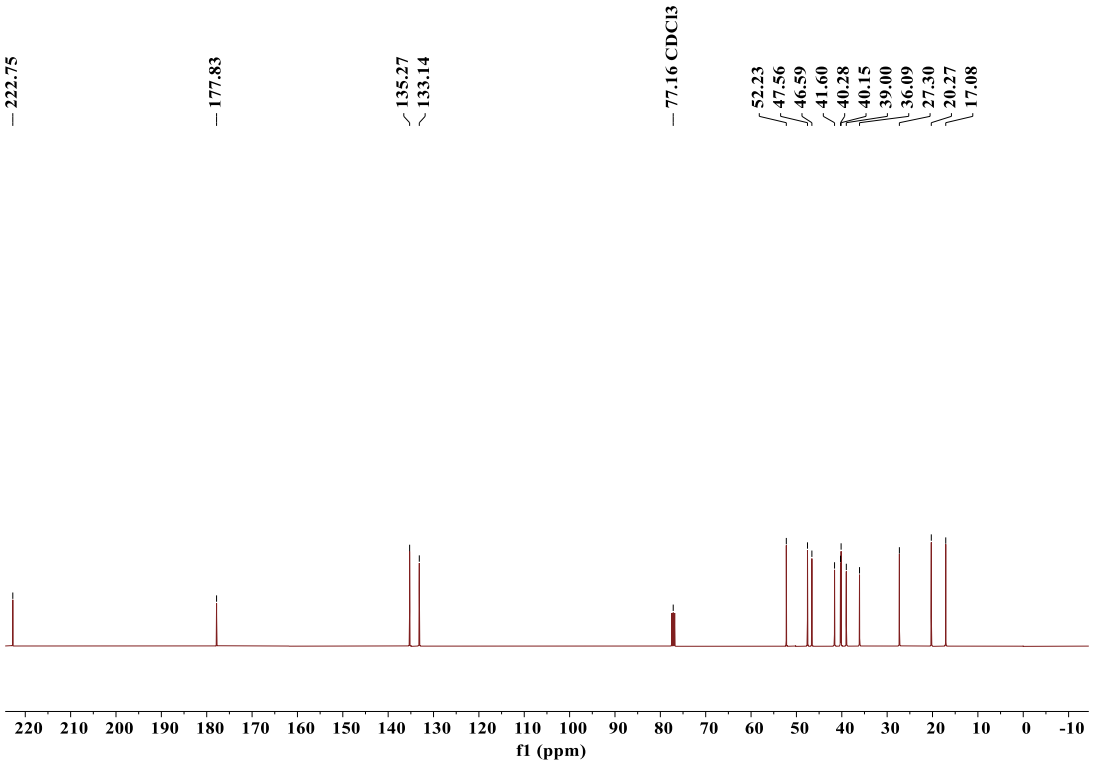


Figure S44. ^{13}C NMR spectrum of **3** in $CDCl_3$

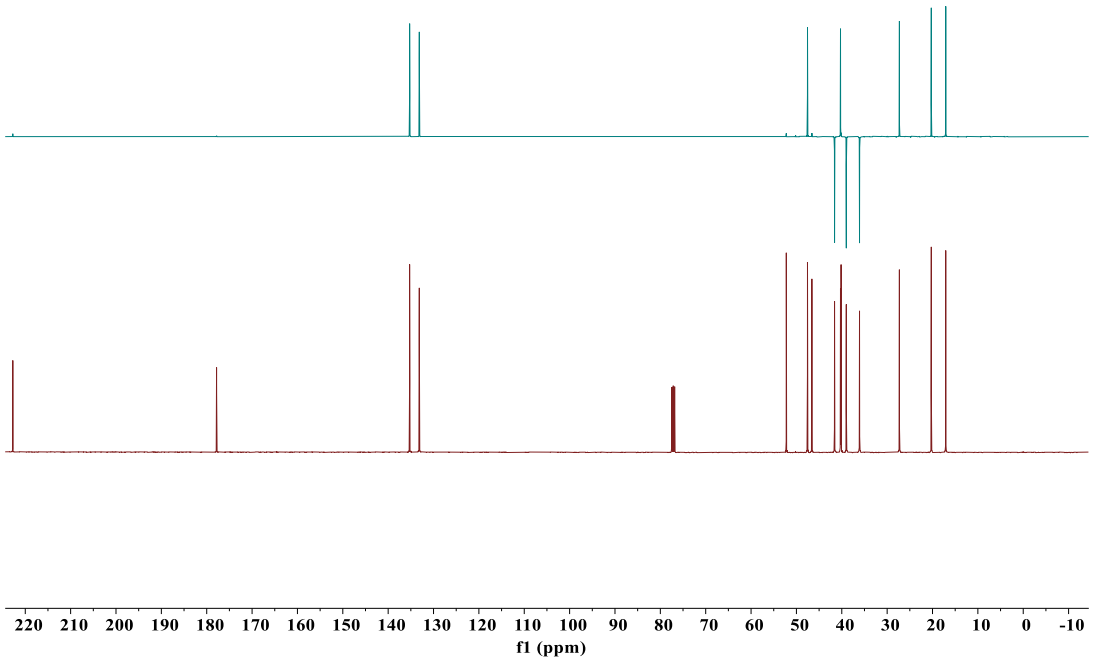


Figure S45. ^{13}C NMR and DEPT-135 Spectra of **3** in $CDCl_3$

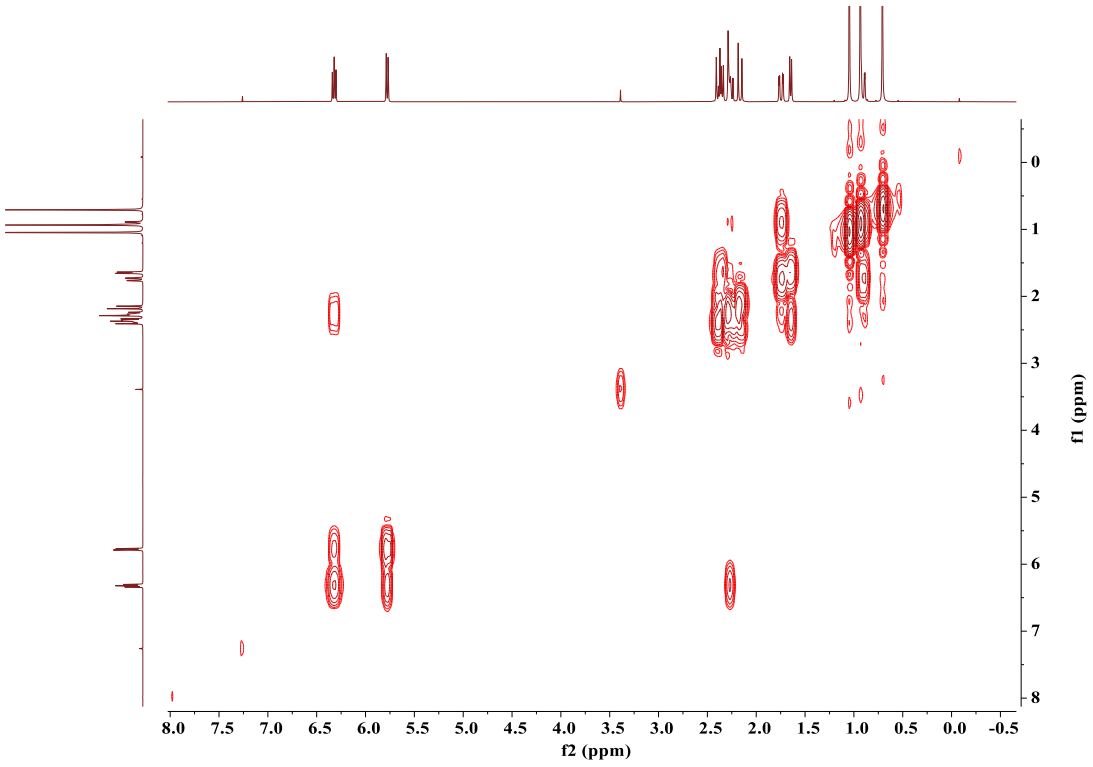


Figure S46. ^{1}H-^{1}H COSY spectrum of **3** in $CDCl_3$

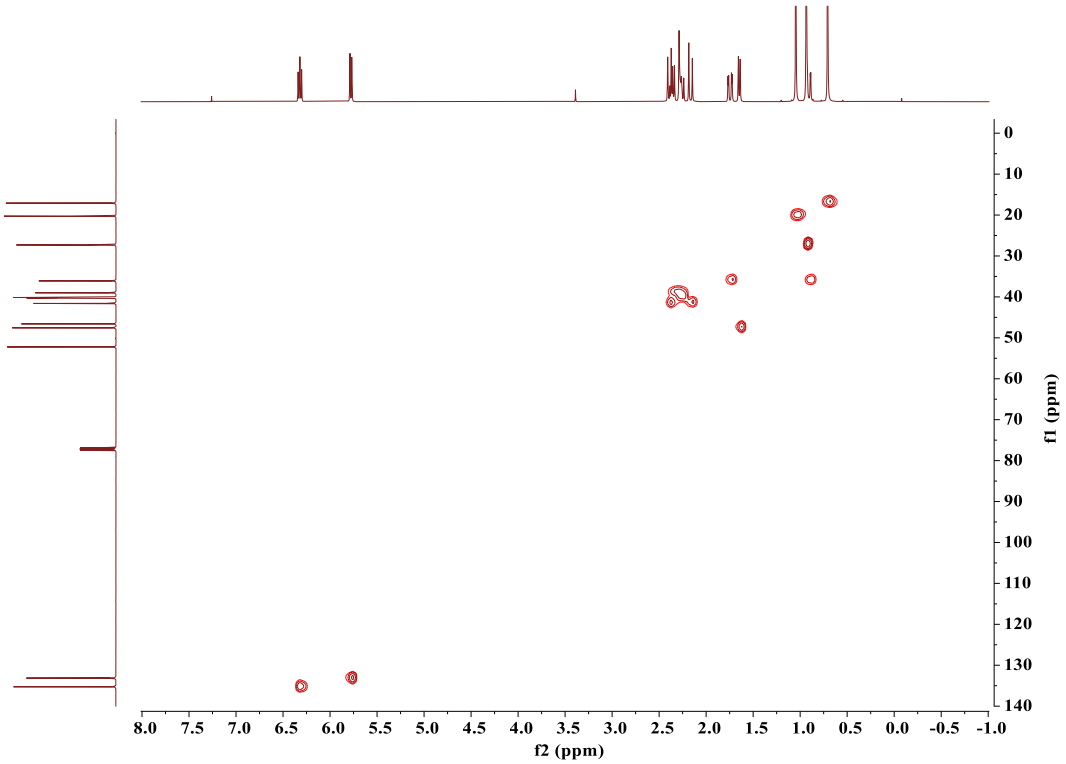


Figure S47. HSQC spectrum of **3** in $CDCl_3$

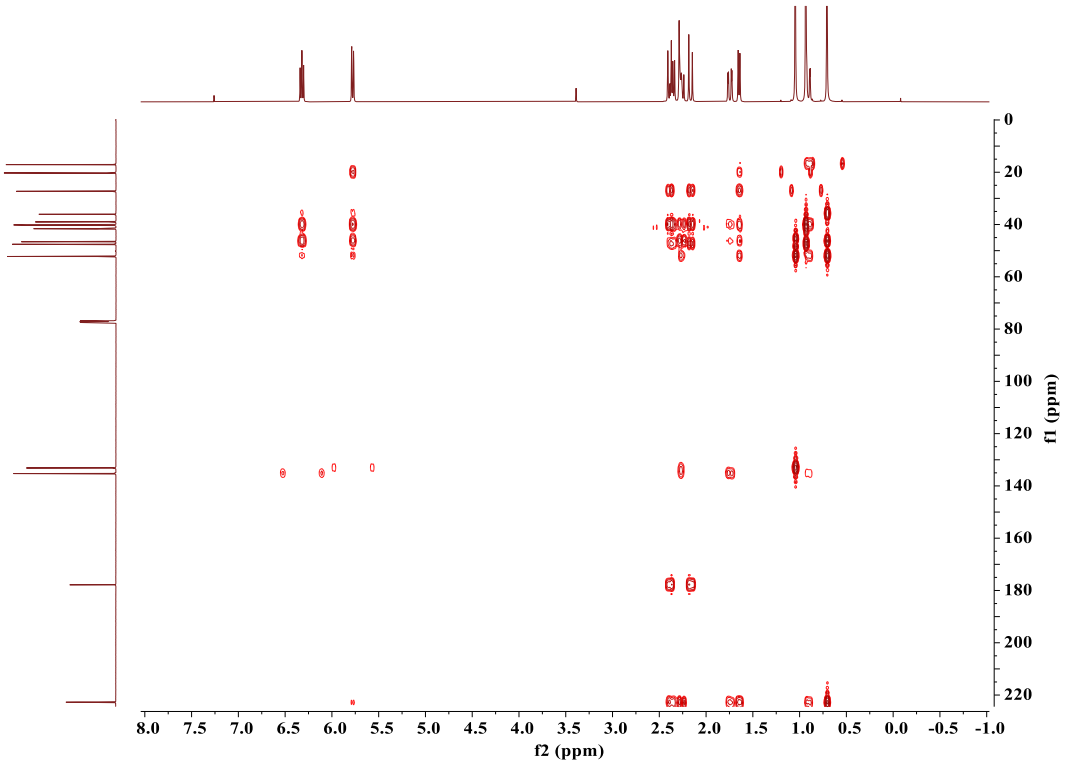


Figure S48. HMBC spectrum of **3** in $CDCl_3$

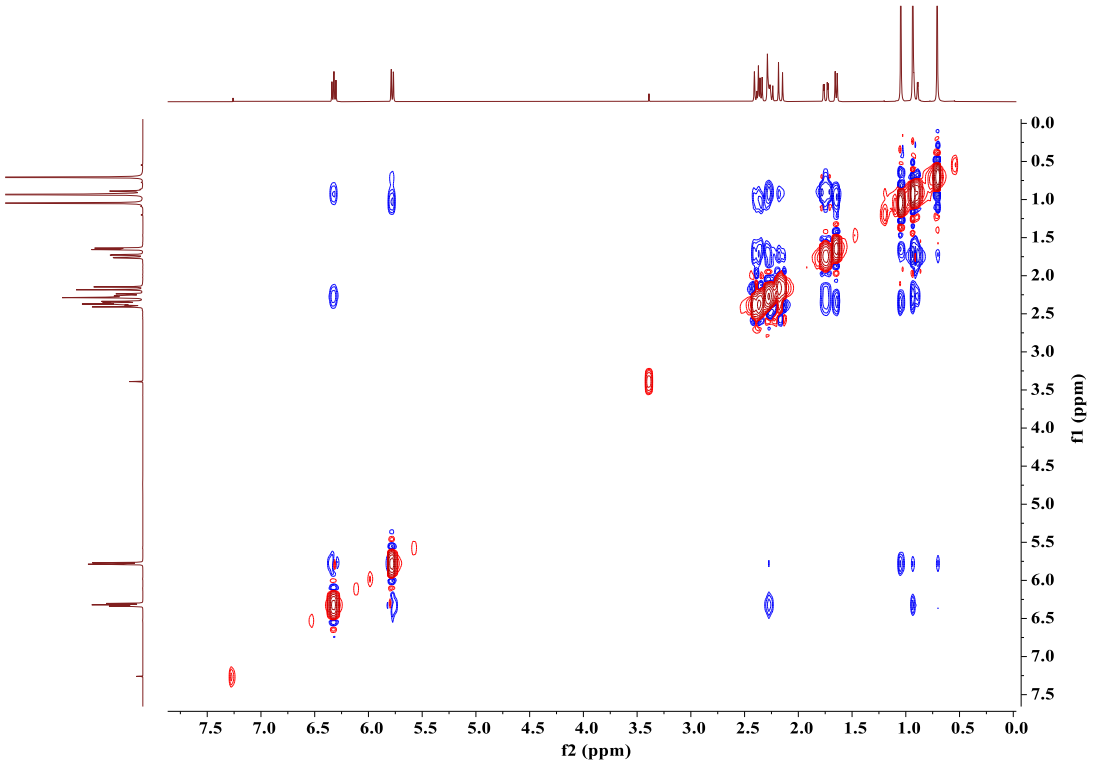


Figure S49. NOESY spectrum of **3** in $CDCl_3$

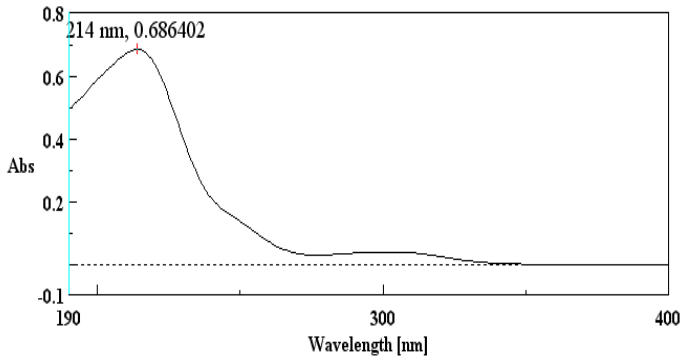


Figure S50. UV spectrum of **4** in MeOH

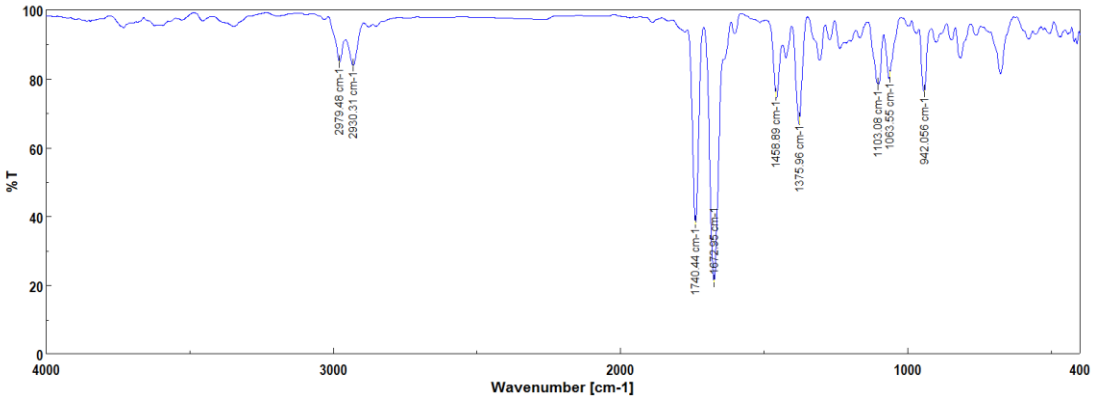


Figure S51. IR spectrum of **4** (KBr disc)

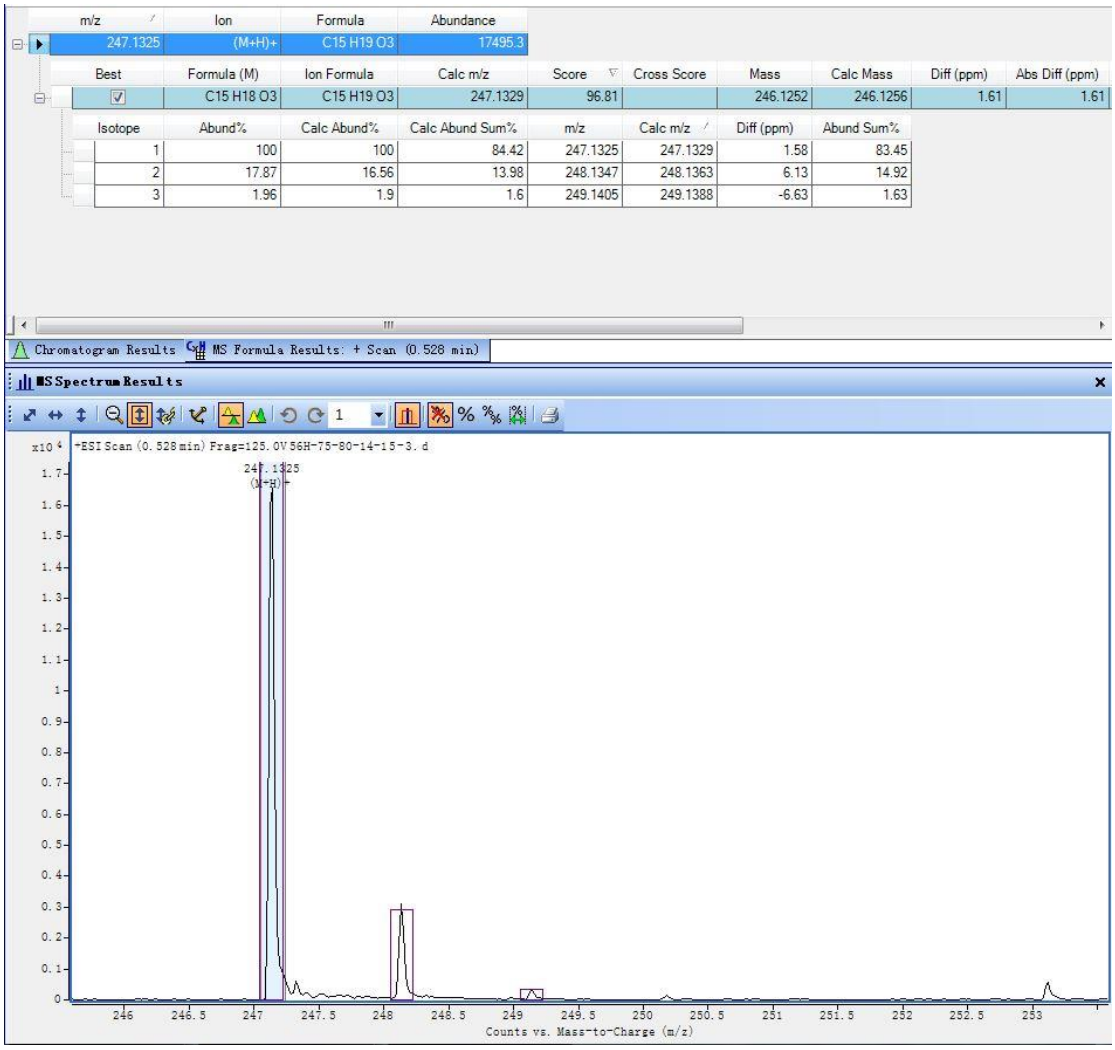


Figure S52. HR-ESI-MS spectrum of **4**

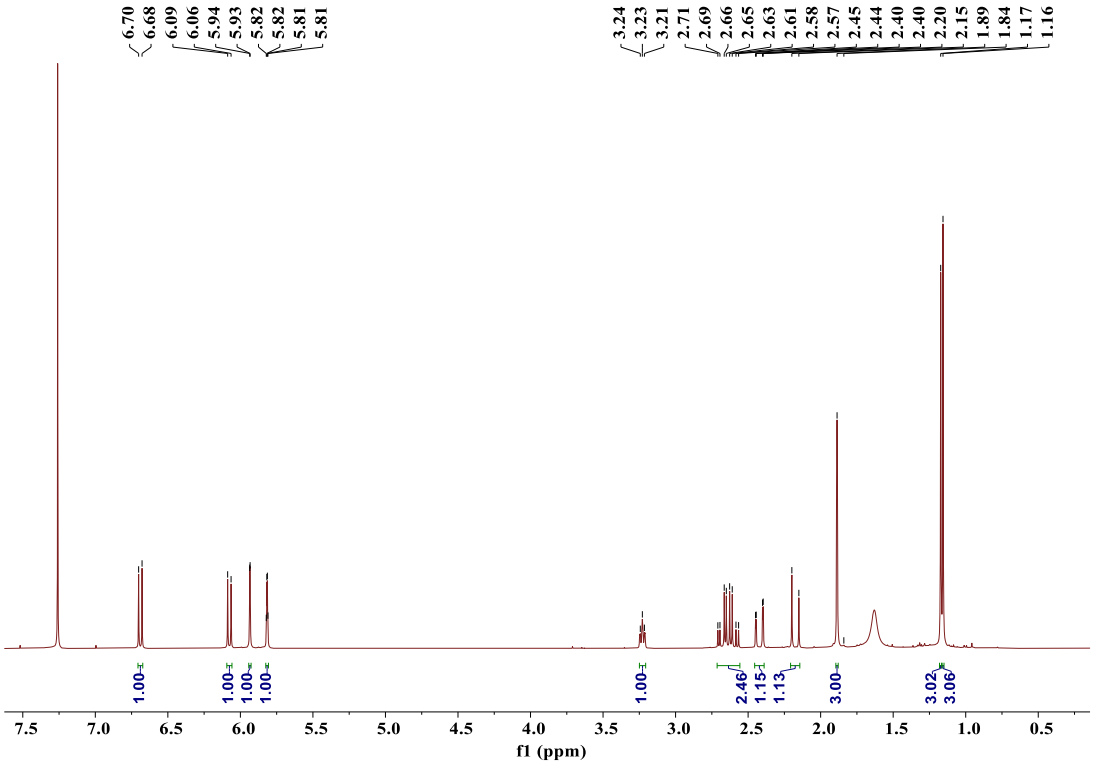


Figure S53. ^{1}H NMR spectrum of **4** in $CDCl_3$

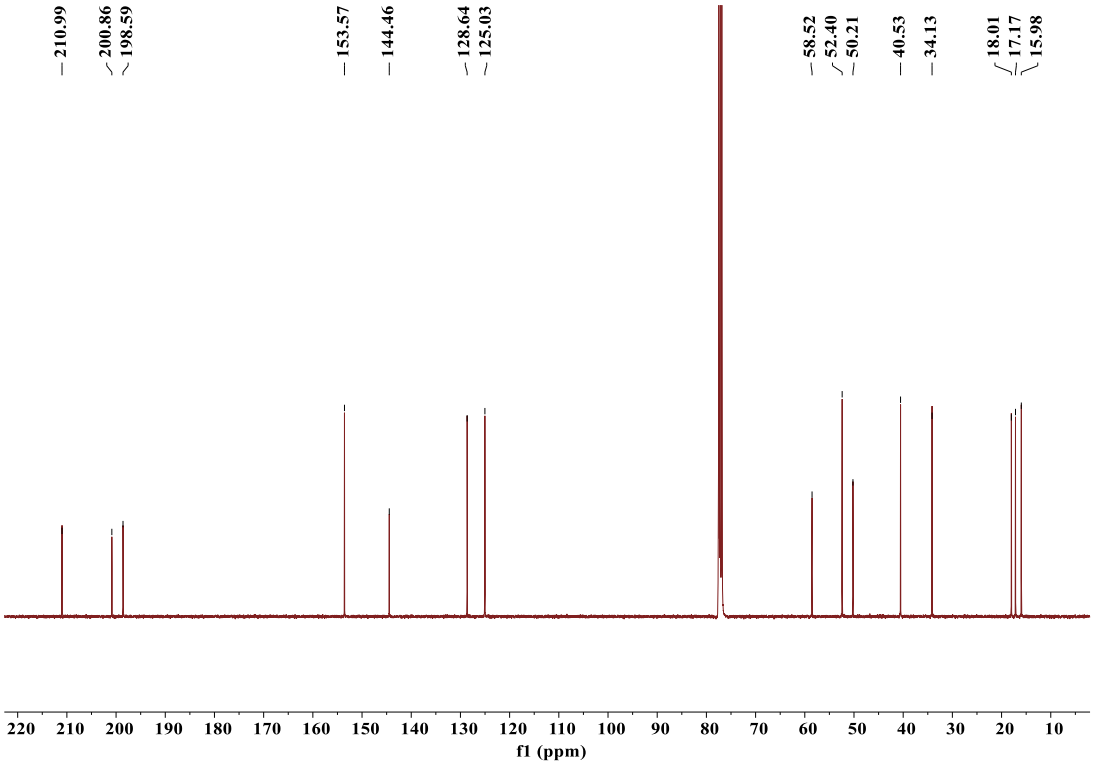


Figure S54. ^{13}C NMR spectrum of **4** in $CDCl_3$

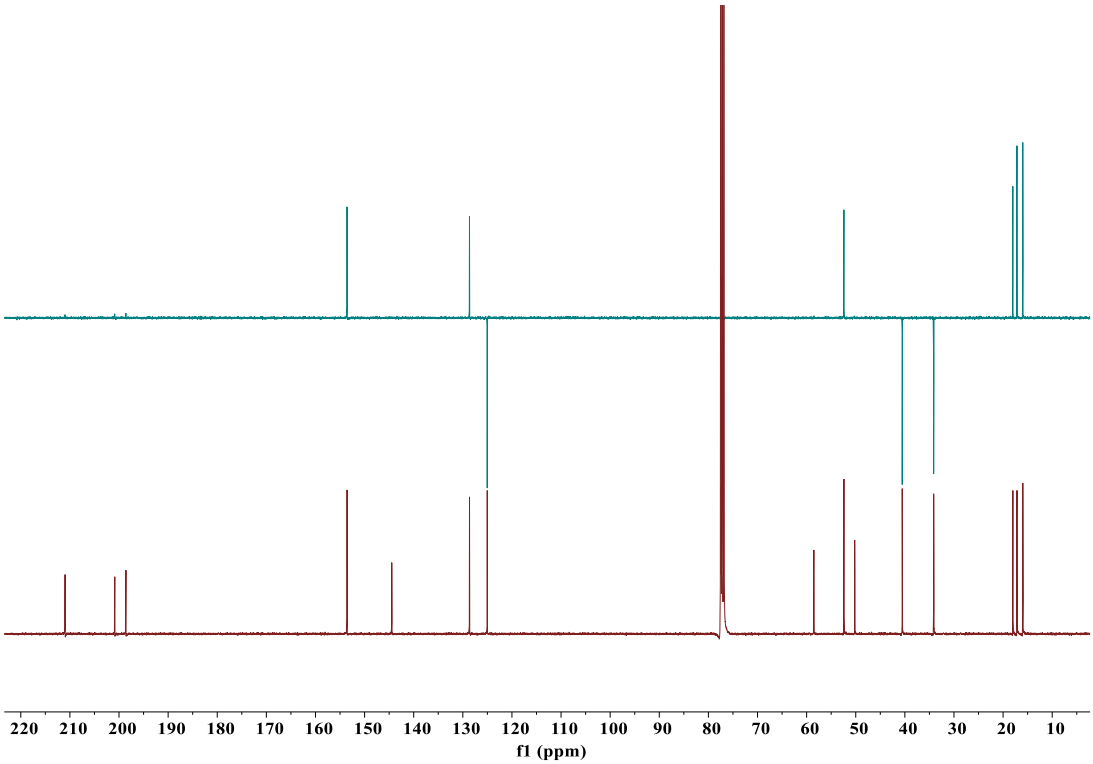


Figure S55. ^{13}C NMR and DEPT-135 Spectra of **4** in $CDCl_3$

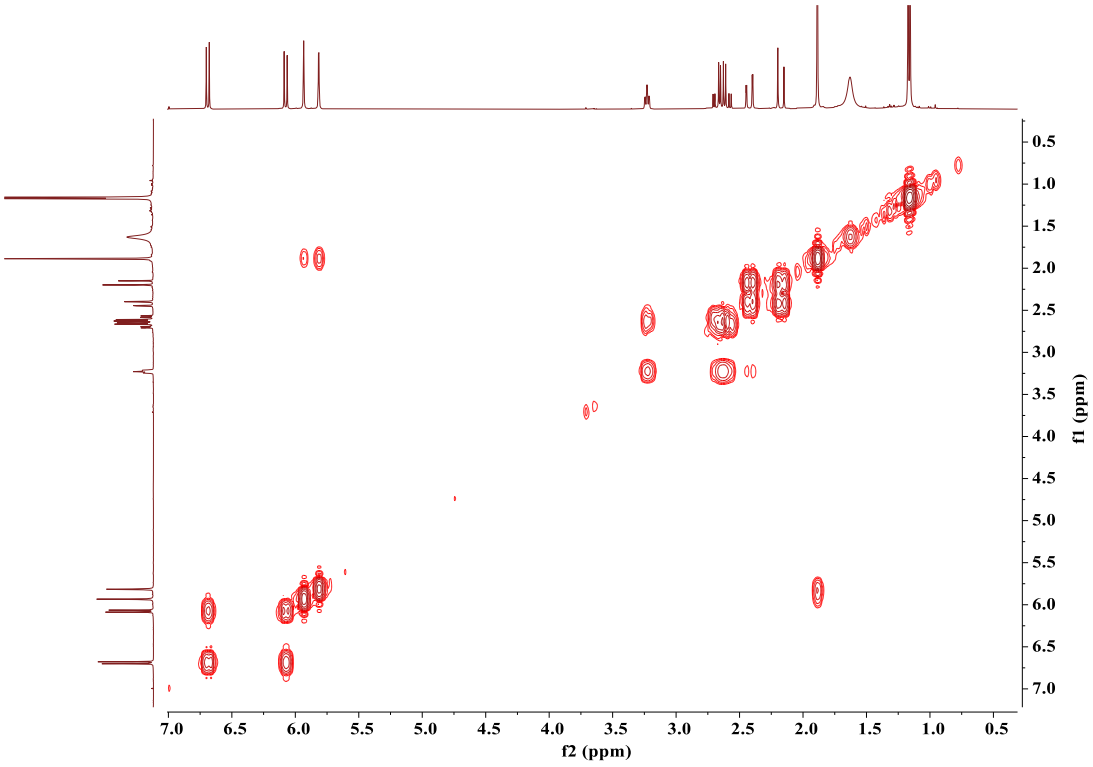


Figure S56. ^{1}H-^{1}H COSY spectrum of **4** in $CDCl_3$

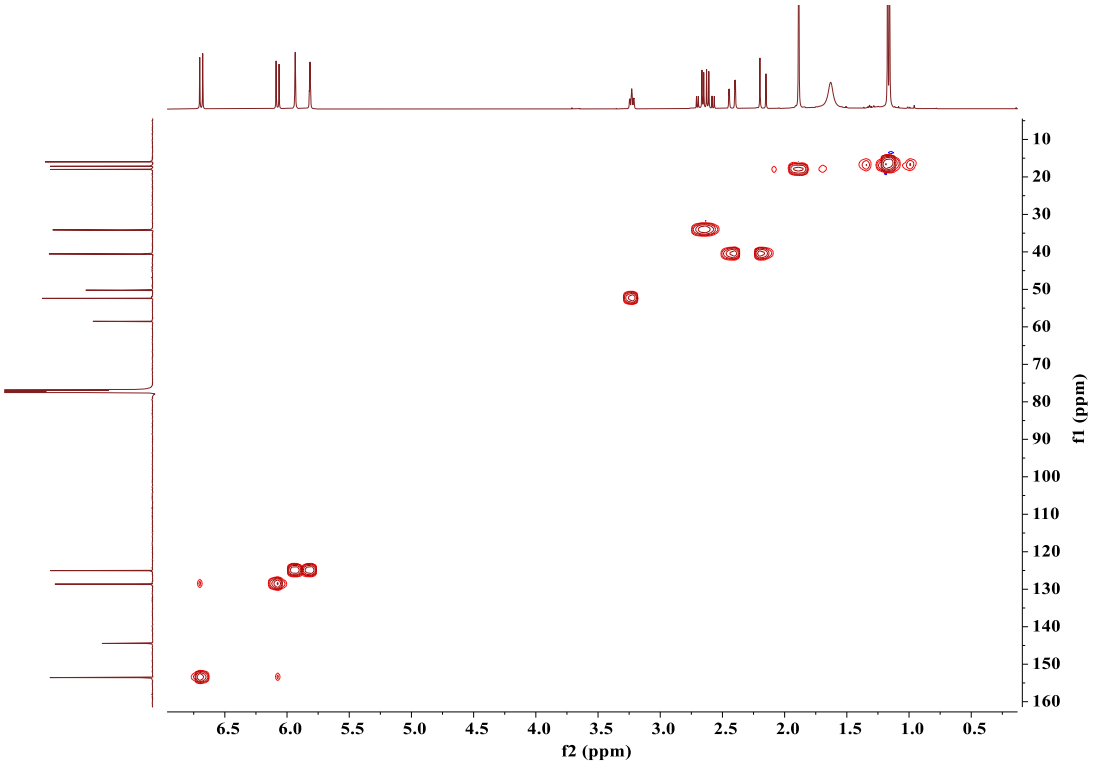


Figure S57. HSQC spectrum of **4** in $CDCl_3$

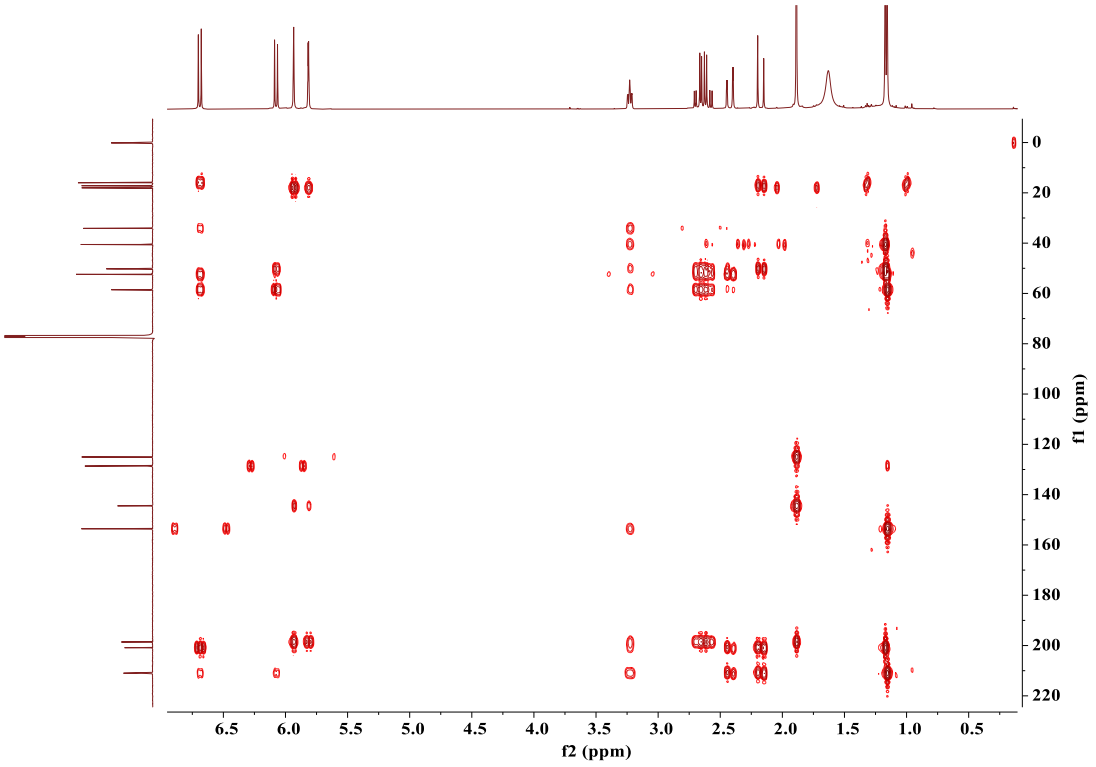


Figure S58. HMBC spectrum of **4** in $CDCl_3$

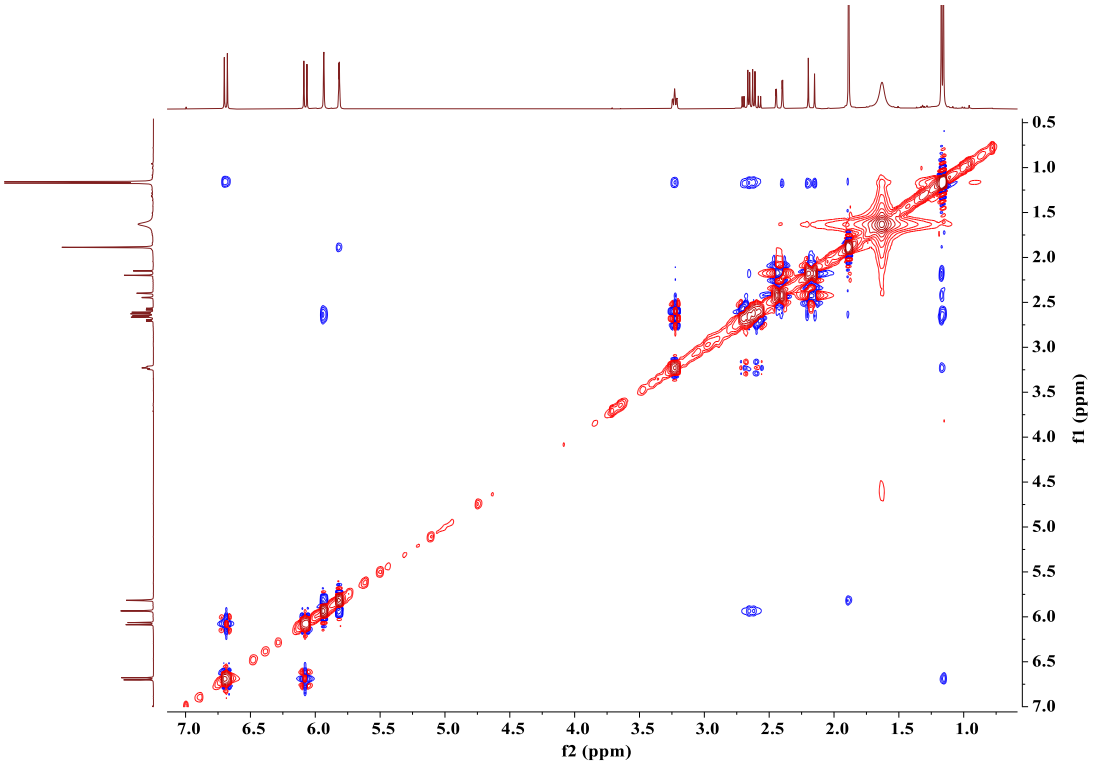


Figure S59. NOESY spectrum of **4** in $CDCl_3$

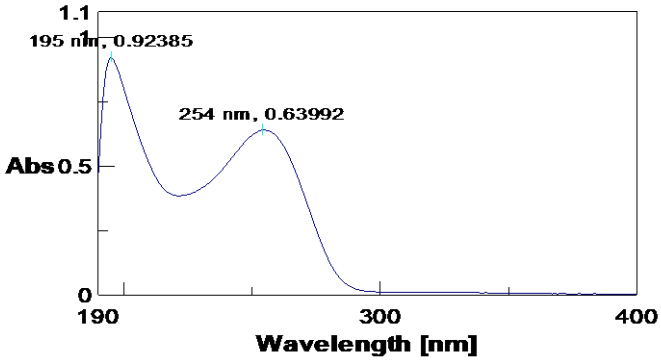


Figure S60. UV spectrum of **5** in MeOH

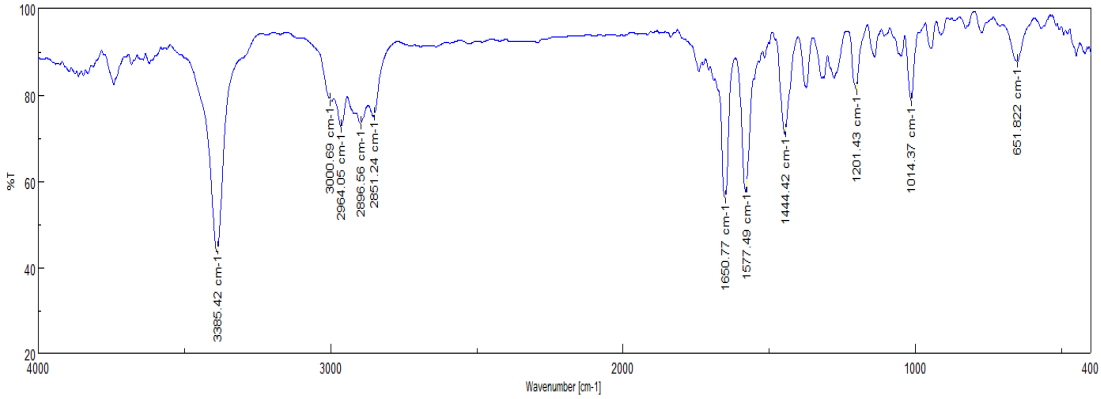


Figure S61. IR spectrum of **5** (KBr disc)

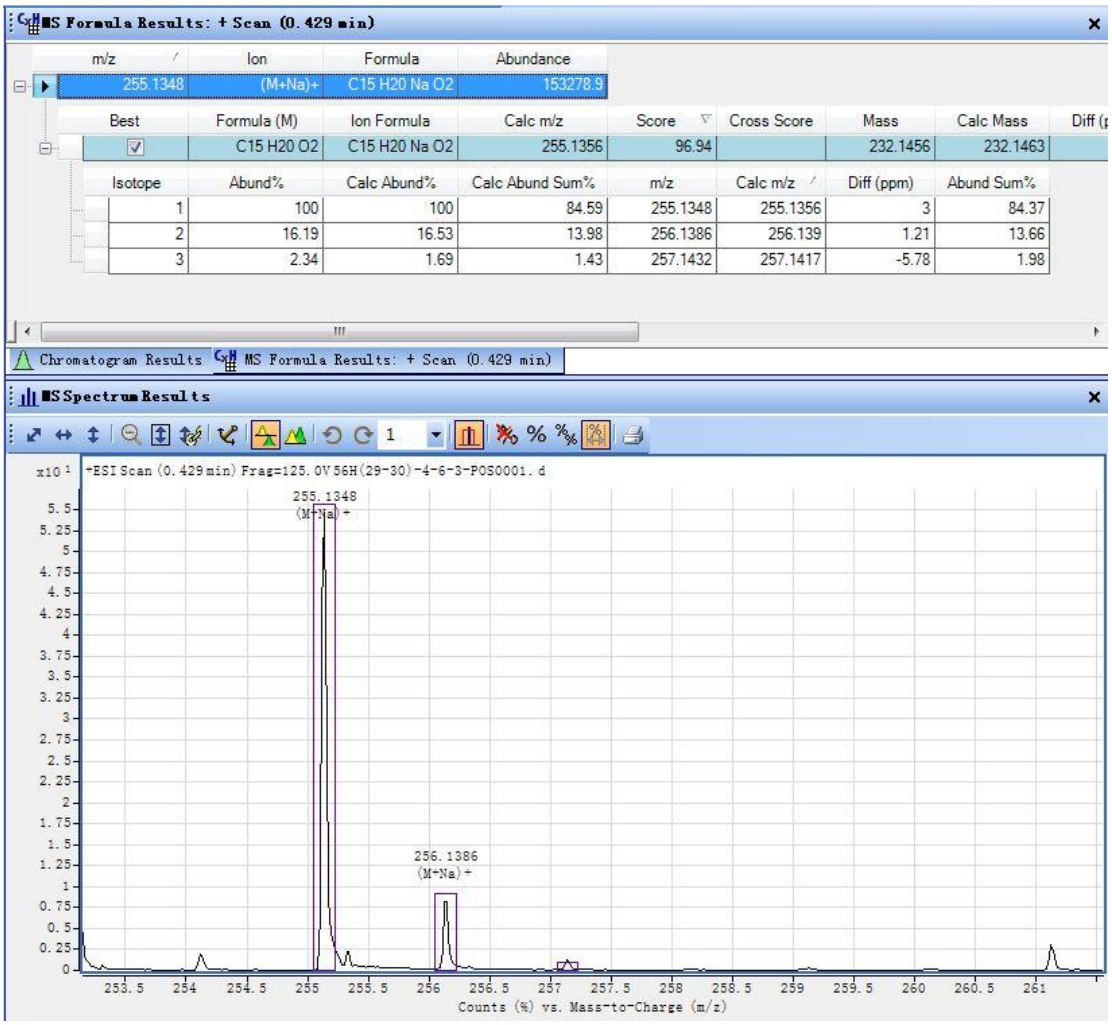


Figure S62. HR-ESI-MS spectrum of **5**

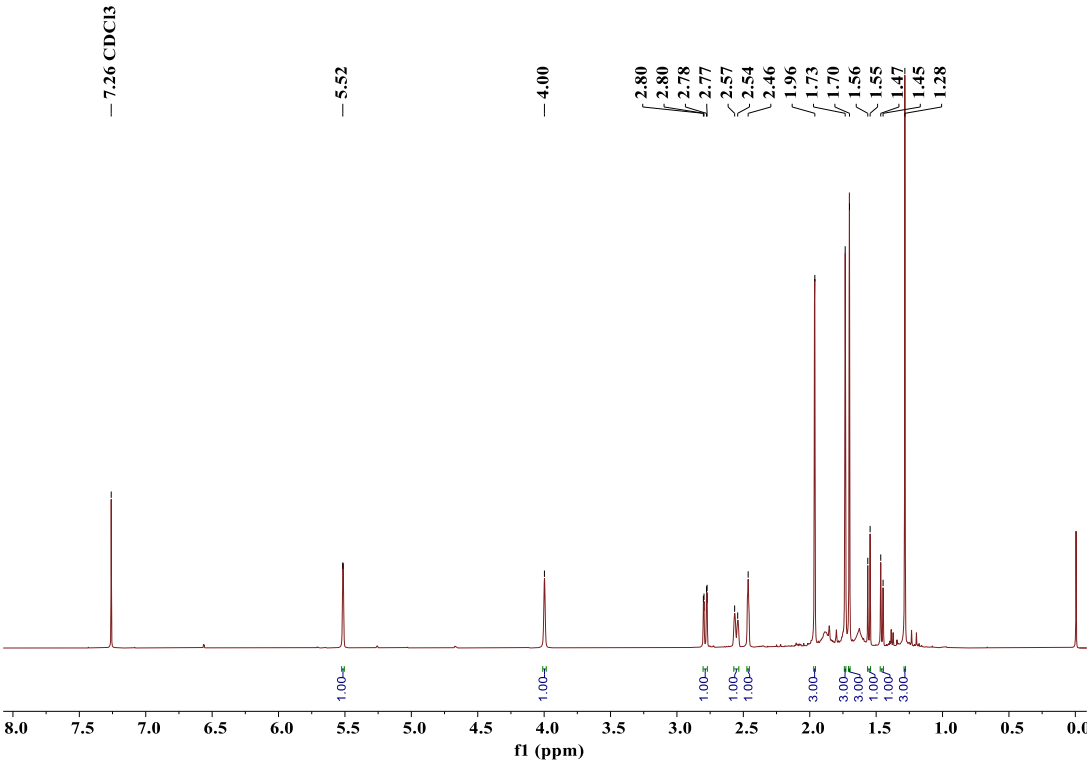


Figure S63. ^{1}H NMR spectrum of **5** in $CDCl_3$

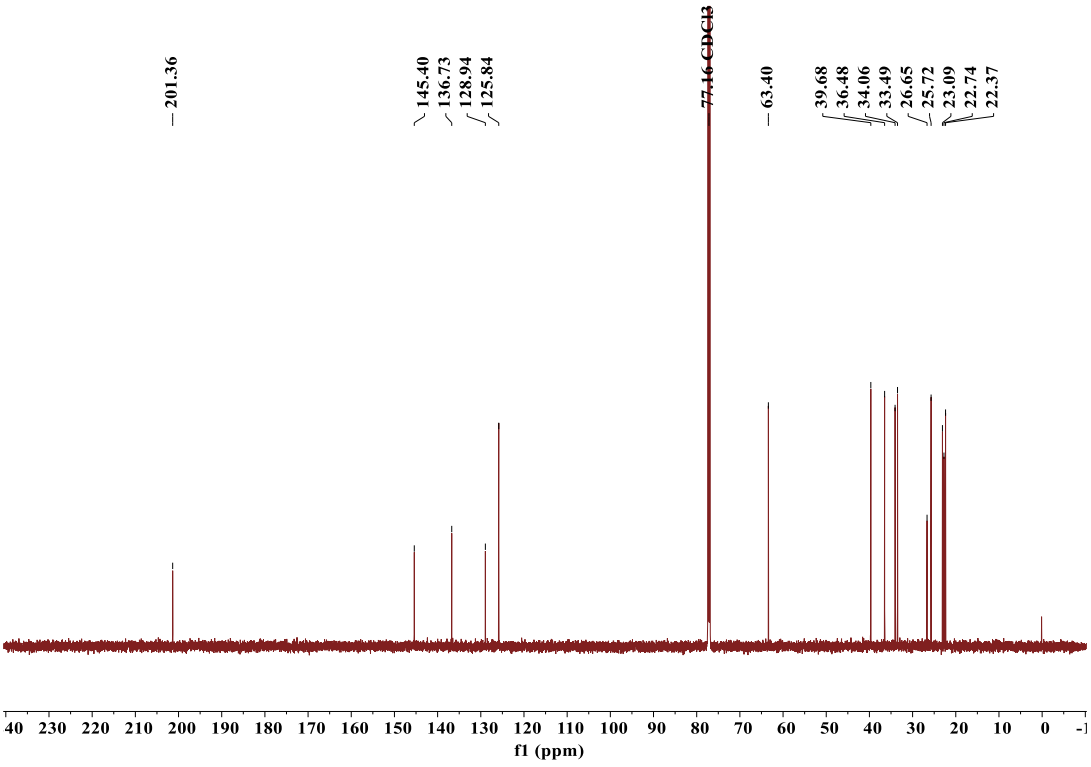


Figure S64. ^{13}C NMR spectrum of **5** in $CDCl_3$

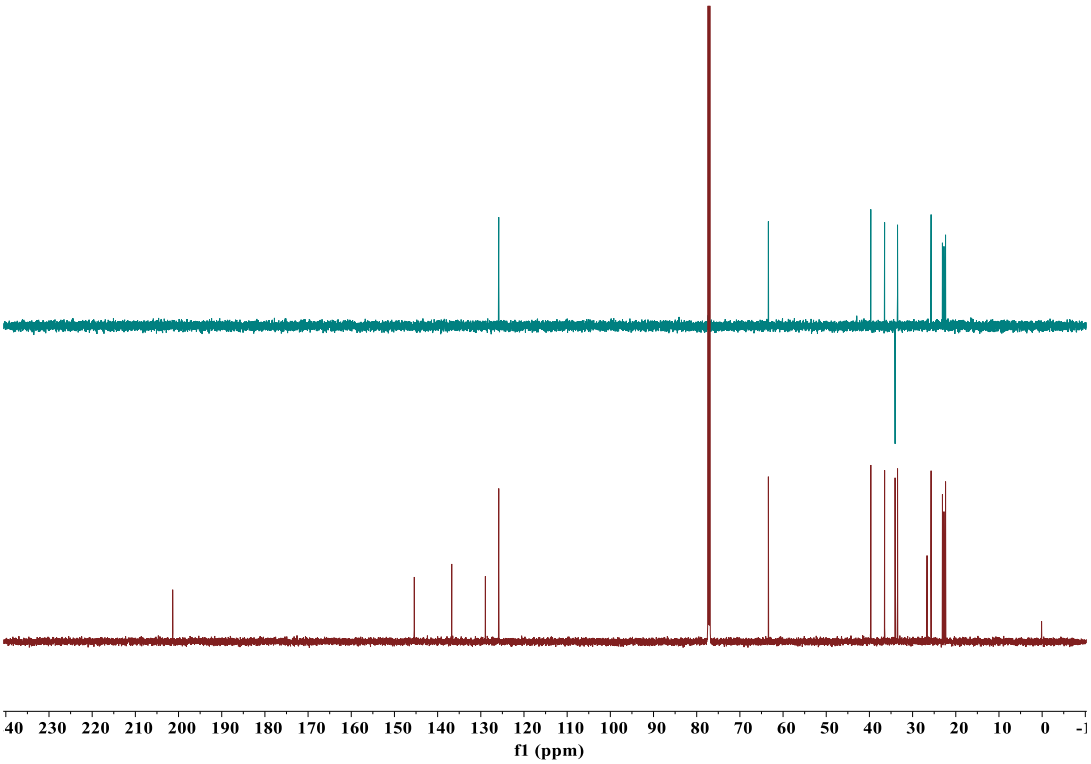


Figure S65. ^{13}C NMR and DEPT-135 Spectra of **5** in $CDCl_3$

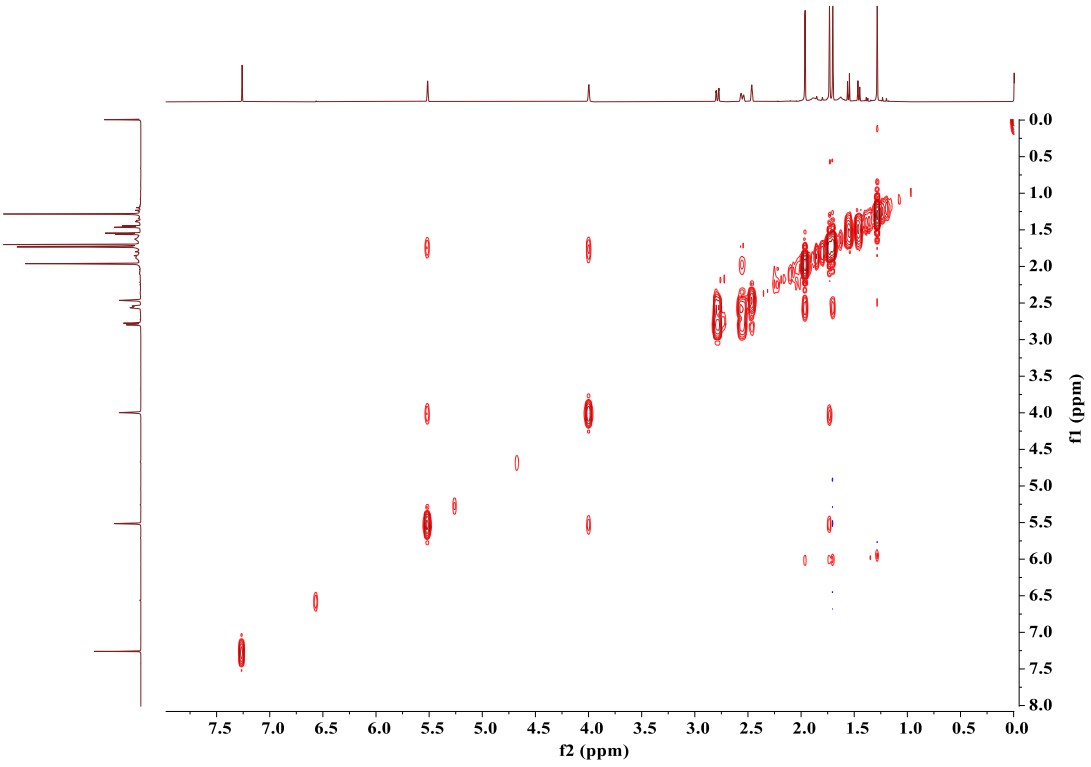


Figure S66. $^{1}H–^{1}H$ COSY spectrum of **5** in $CDCl_3$

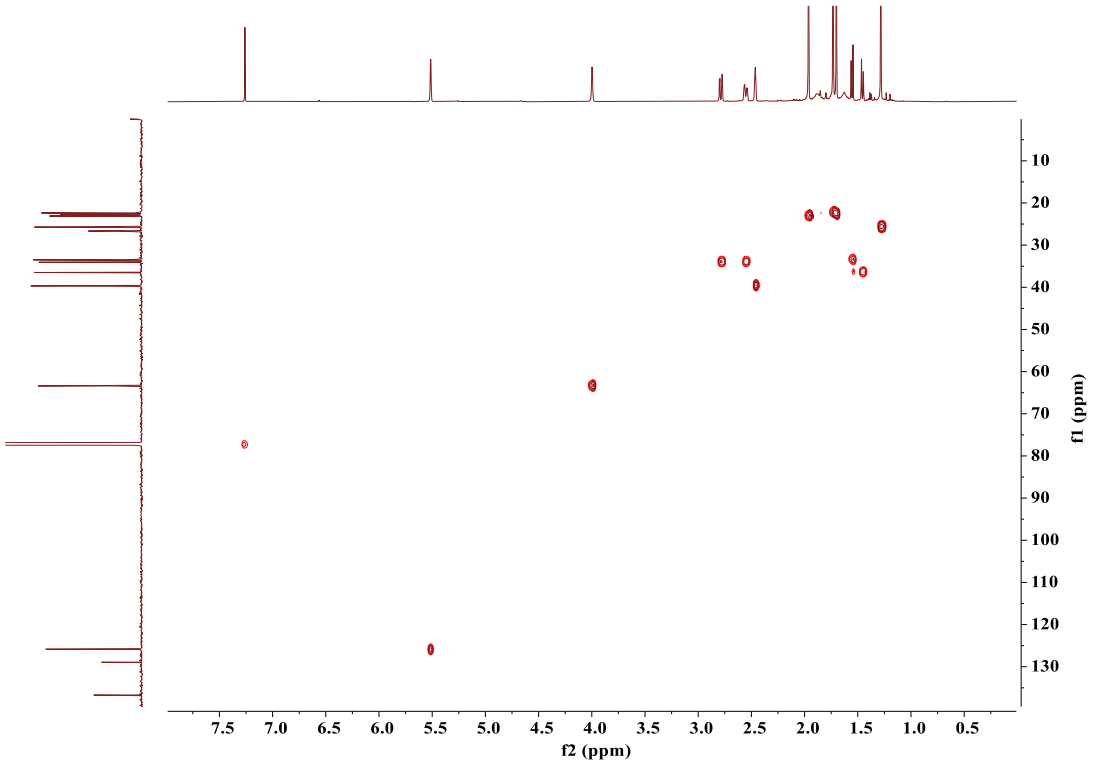


Figure S67. HSQC spectrum of **5** in $CDCl_3$

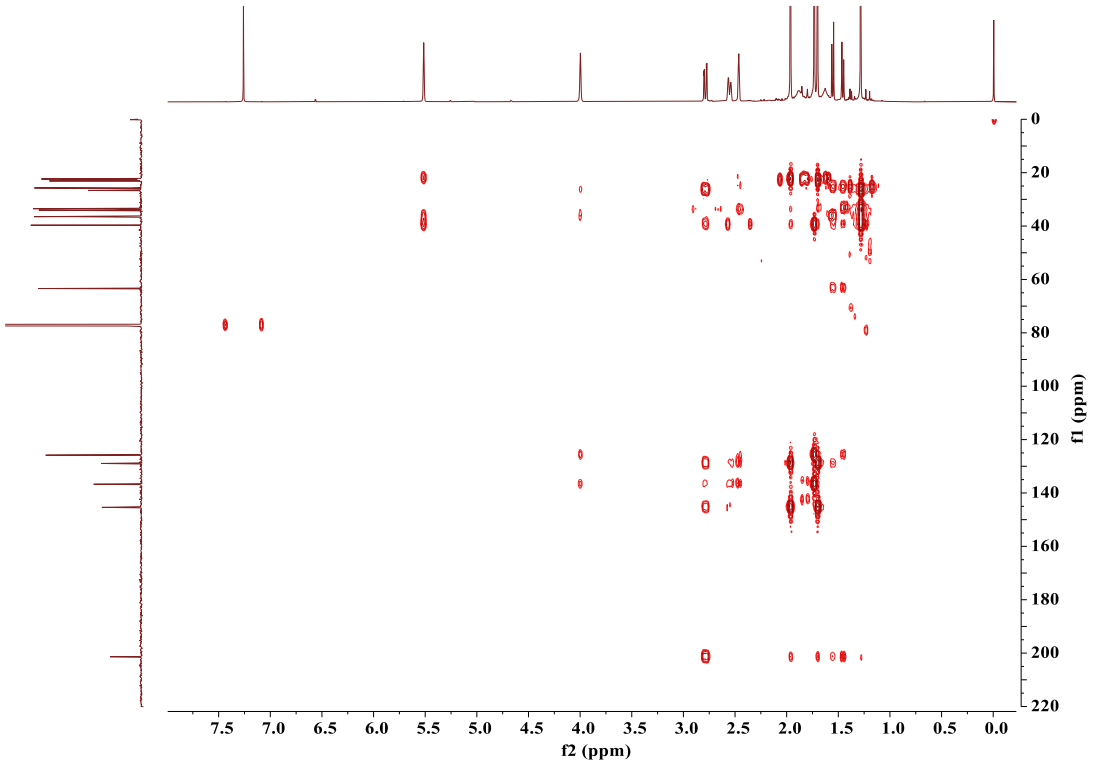


Figure S68. HMBC spectrum of **5** in $CDCl_3$

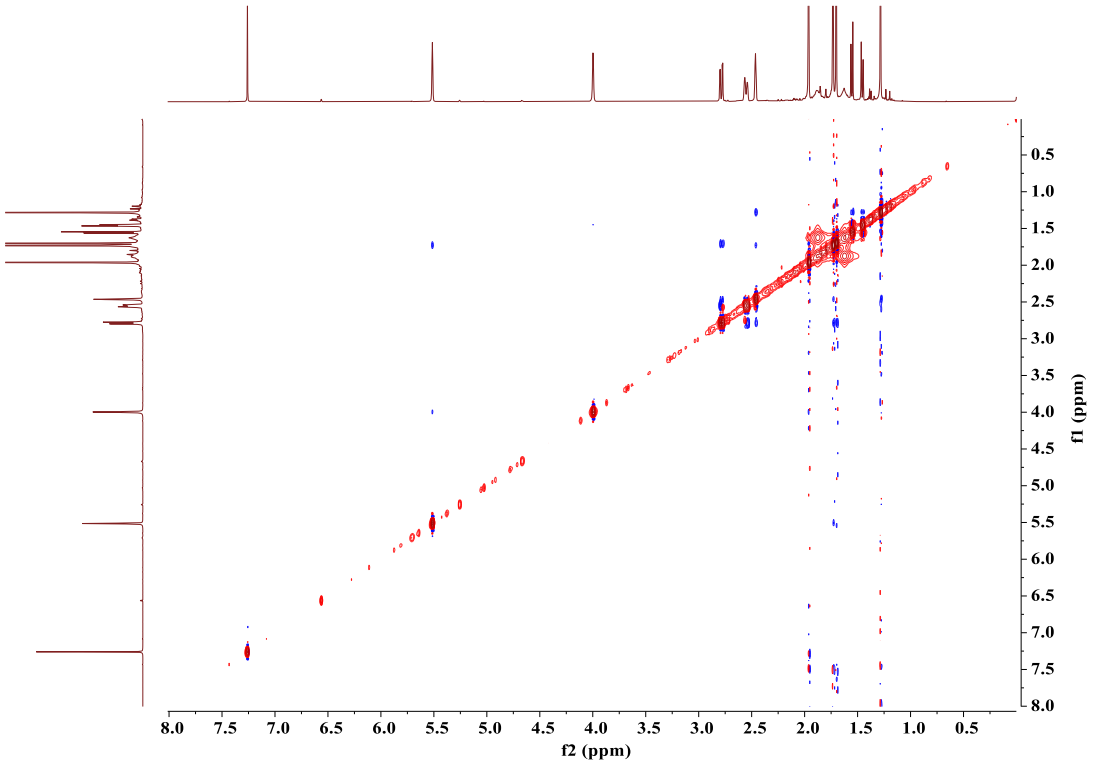


Figure S69. NOESY spectrum of **5** in $CDCl_3$

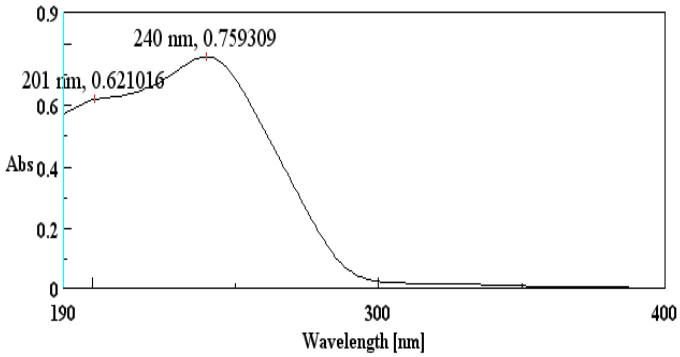


Figure S70. UV spectrum of **6** in MeOH

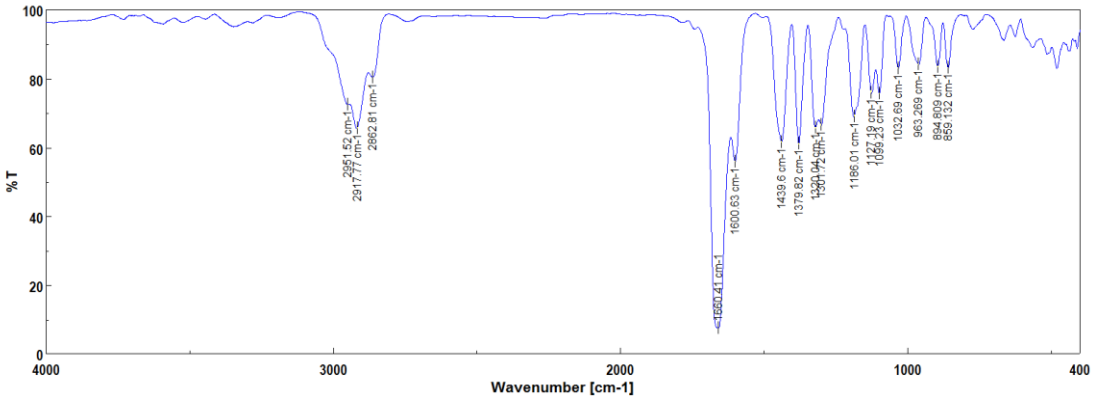


Figure S71. IR spectrum of **6** (KBr disc)

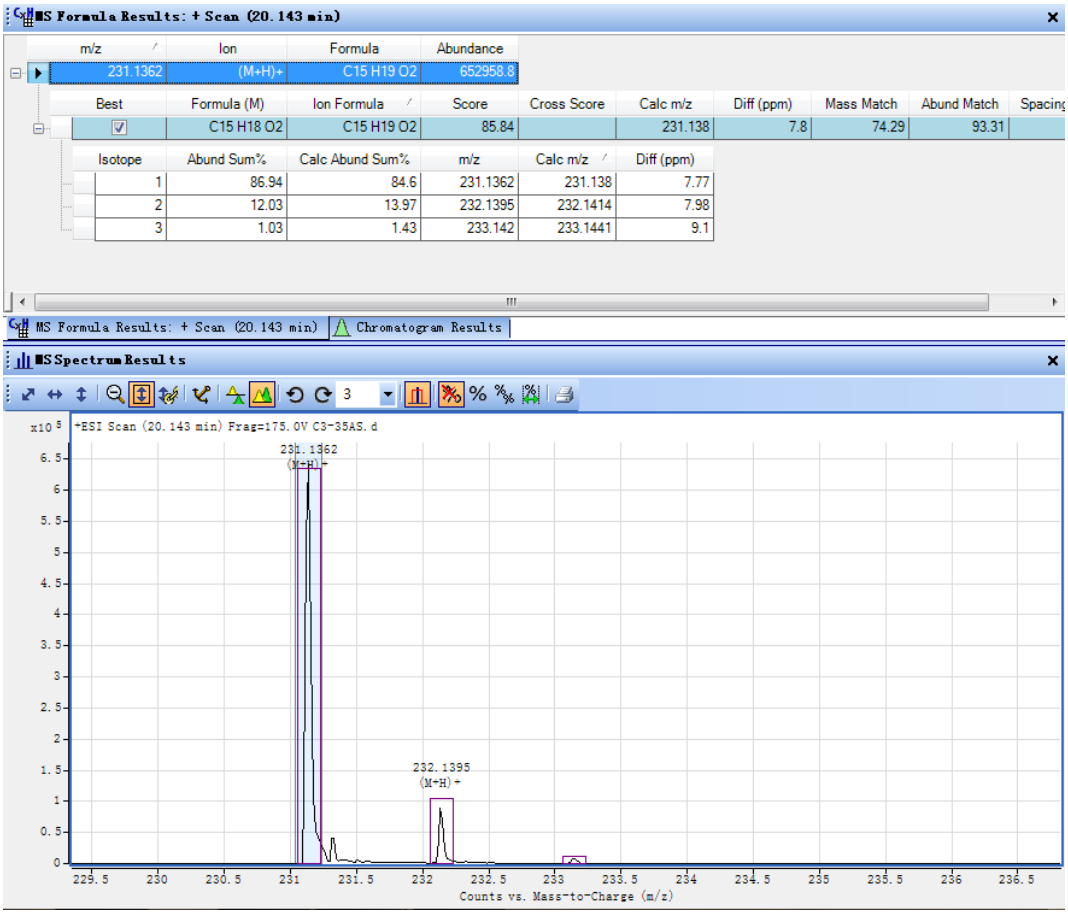


Figure S72. HR-ESI-MS spectrum of **6**

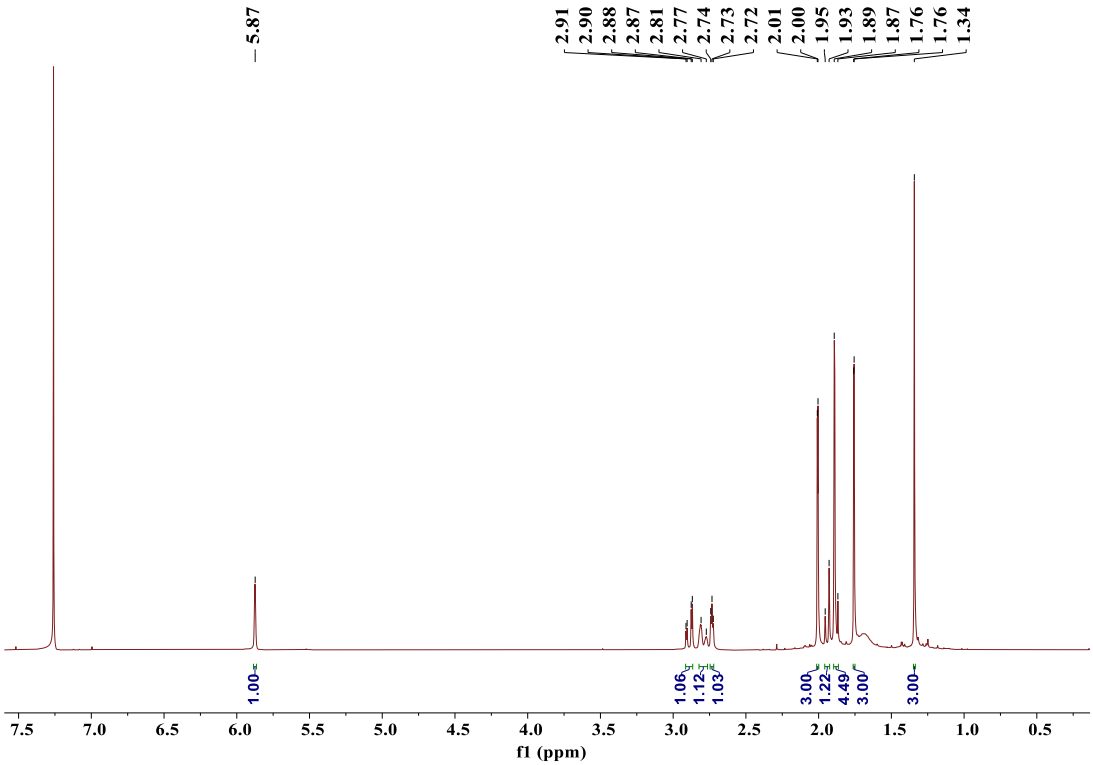


Figure S73. ^{1}H NMR spectrum of **6** in $CDCl_3$

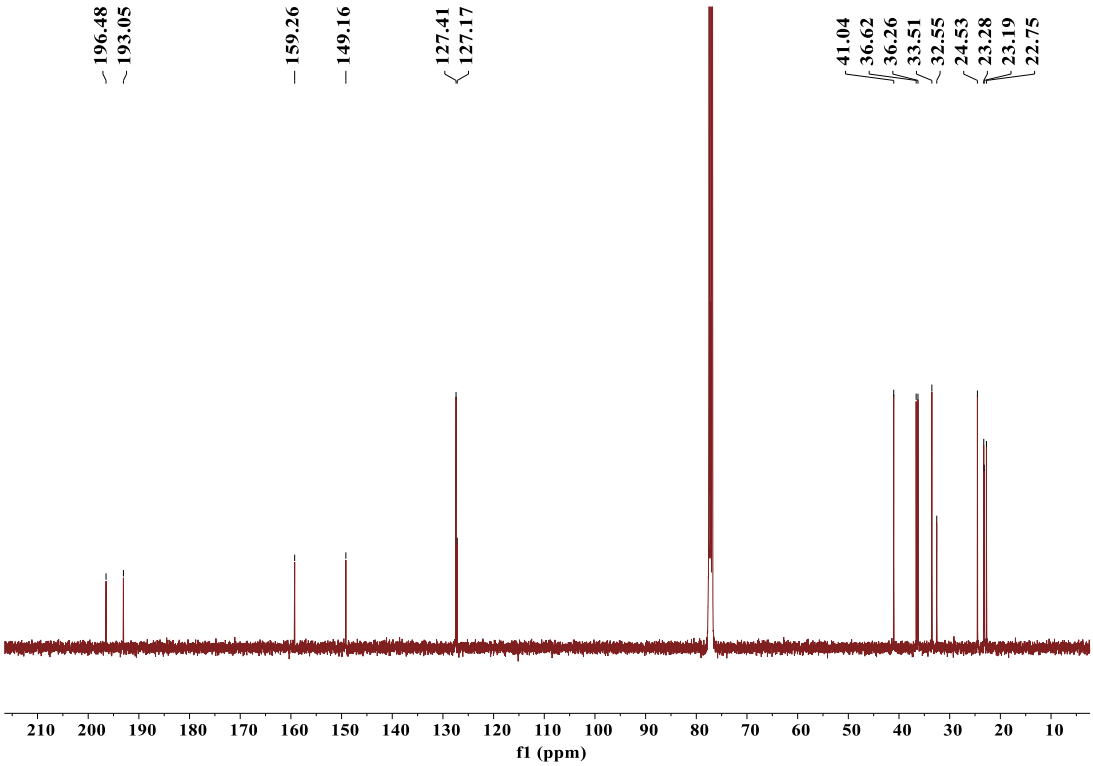


Figure S74. ^{13}C NMR spectrum of **6** in $CDCl_3$

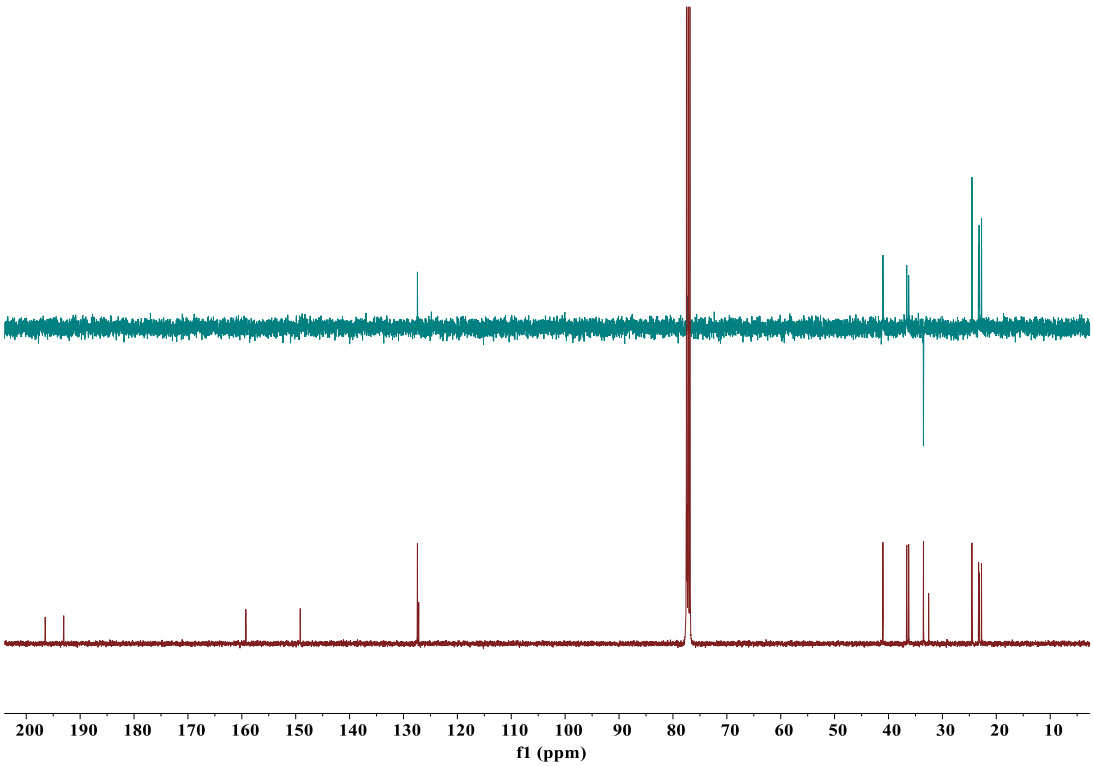


Figure S75. ^{13}C NMR and DEPT-135 Spectra of **6** in $CDCl_3$

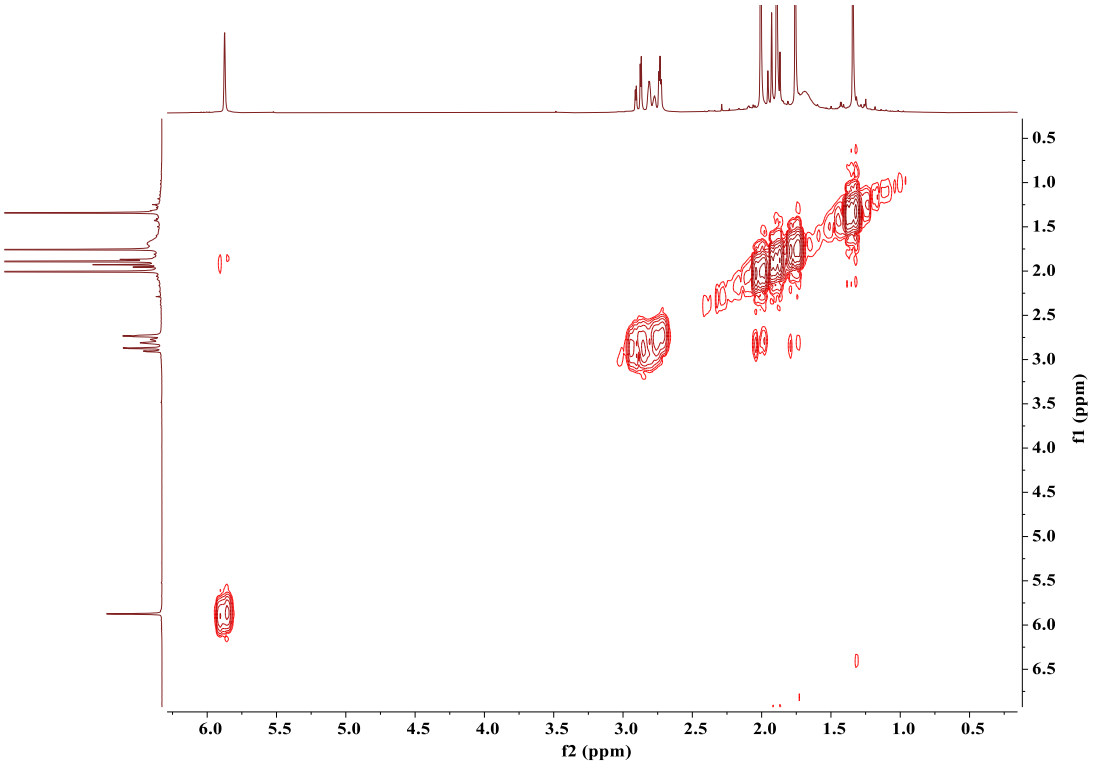


Figure S76. ^{1}H-^{1}H COSY spectrum of **6** in $CDCl_3$

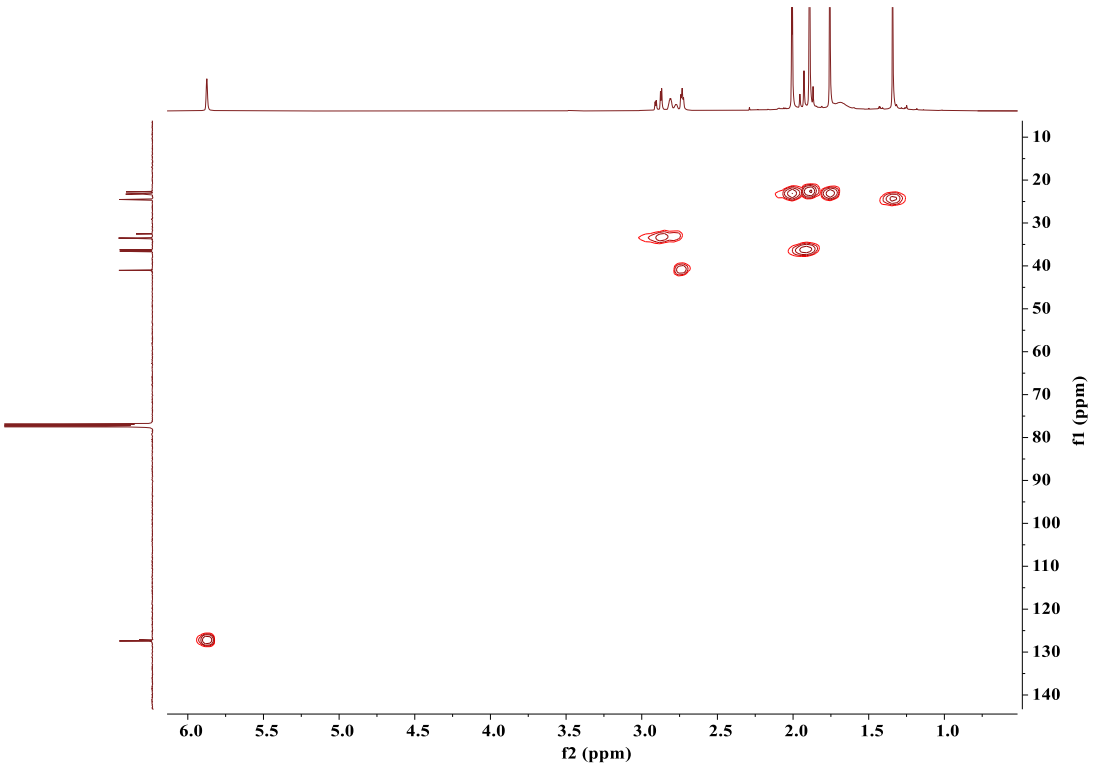


Figure S77. HSQC spectrum of **6** in $CDCl_3$

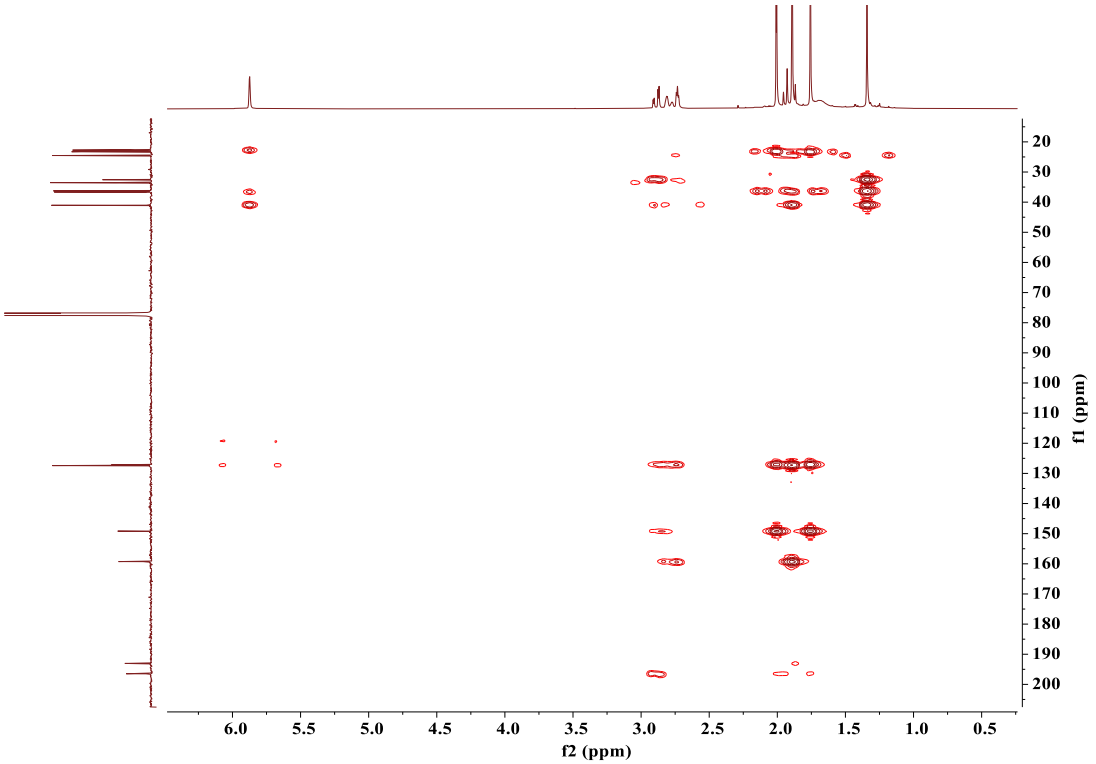


Figure S78. HMBC spectrum of **6** in $CDCl_3$

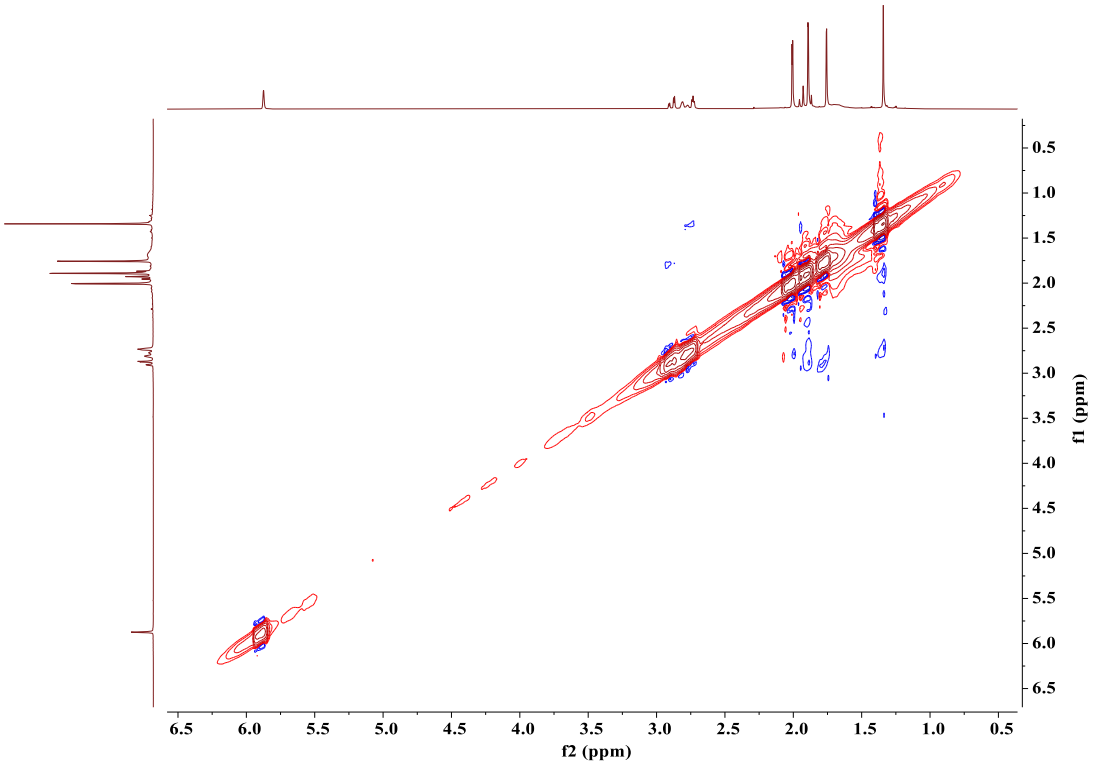


Figure S79. NOESY spectrum of **6** in $CDCl_3$

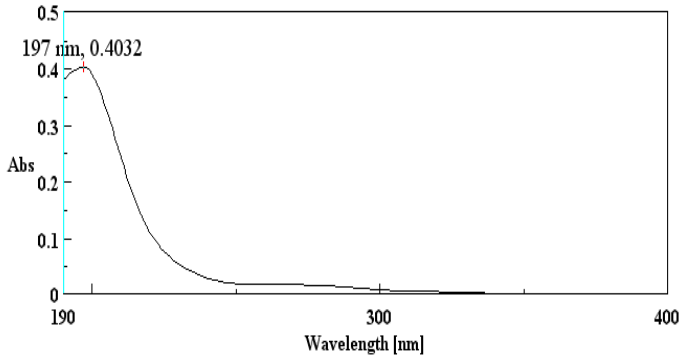


Figure S80. UV spectrum of **7** in MeOH

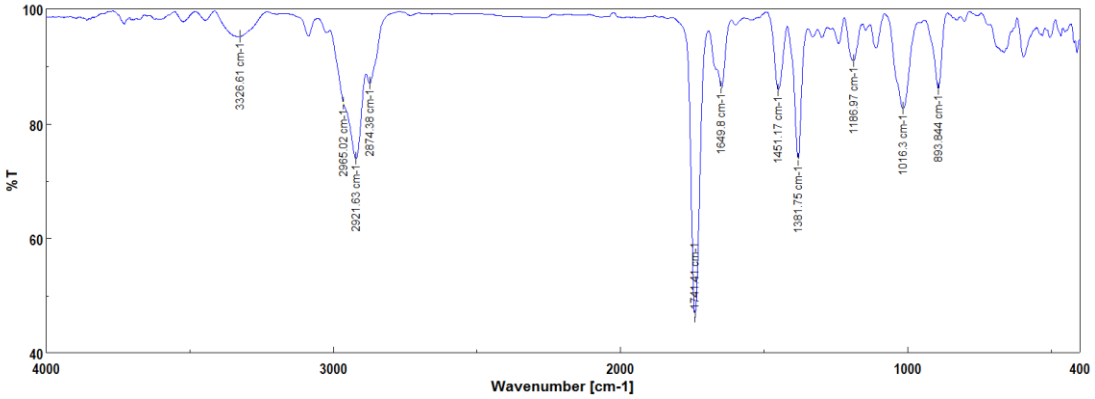


Figure S81. IR spectrum of **7** (KBr disc)

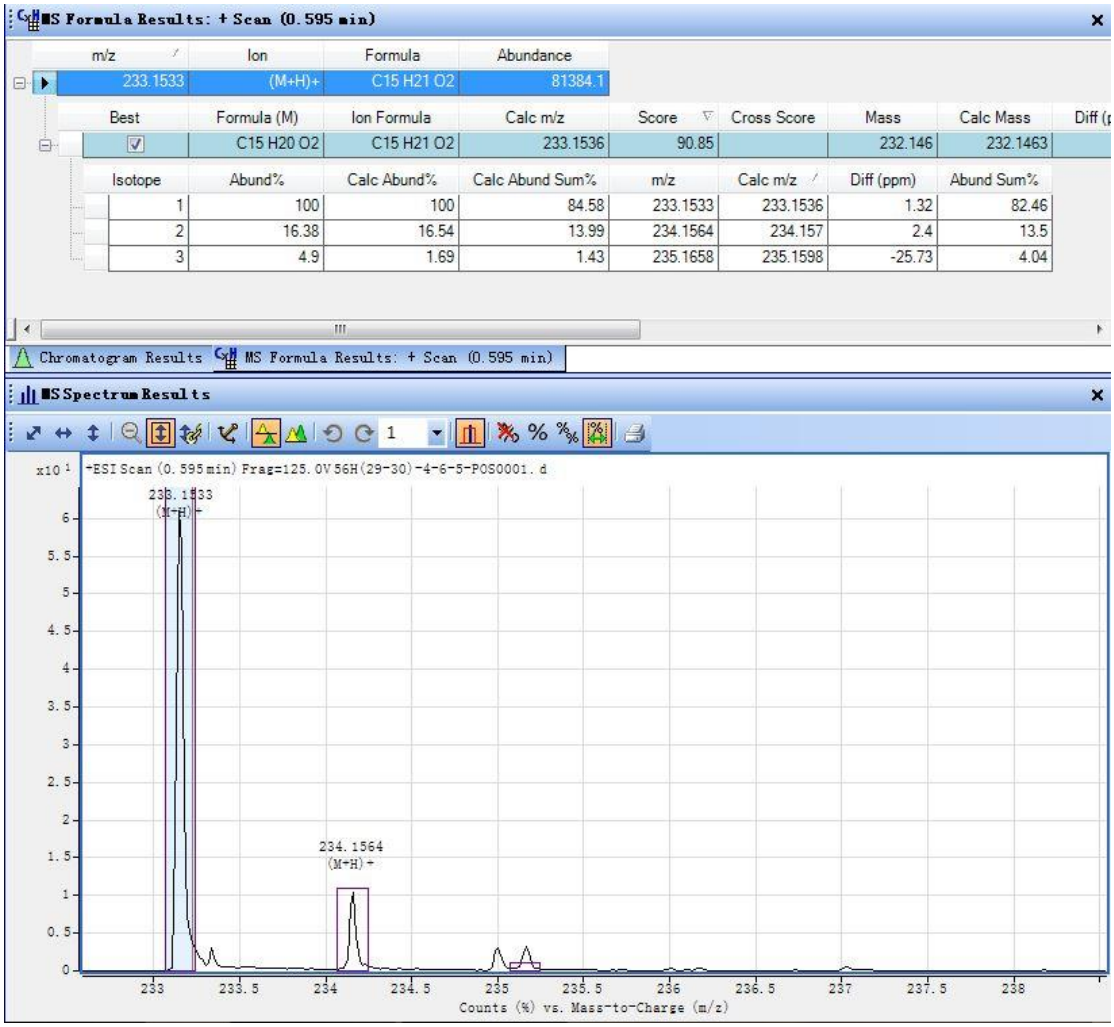


Figure S82. HR-ESI-MS spectrum of **7**

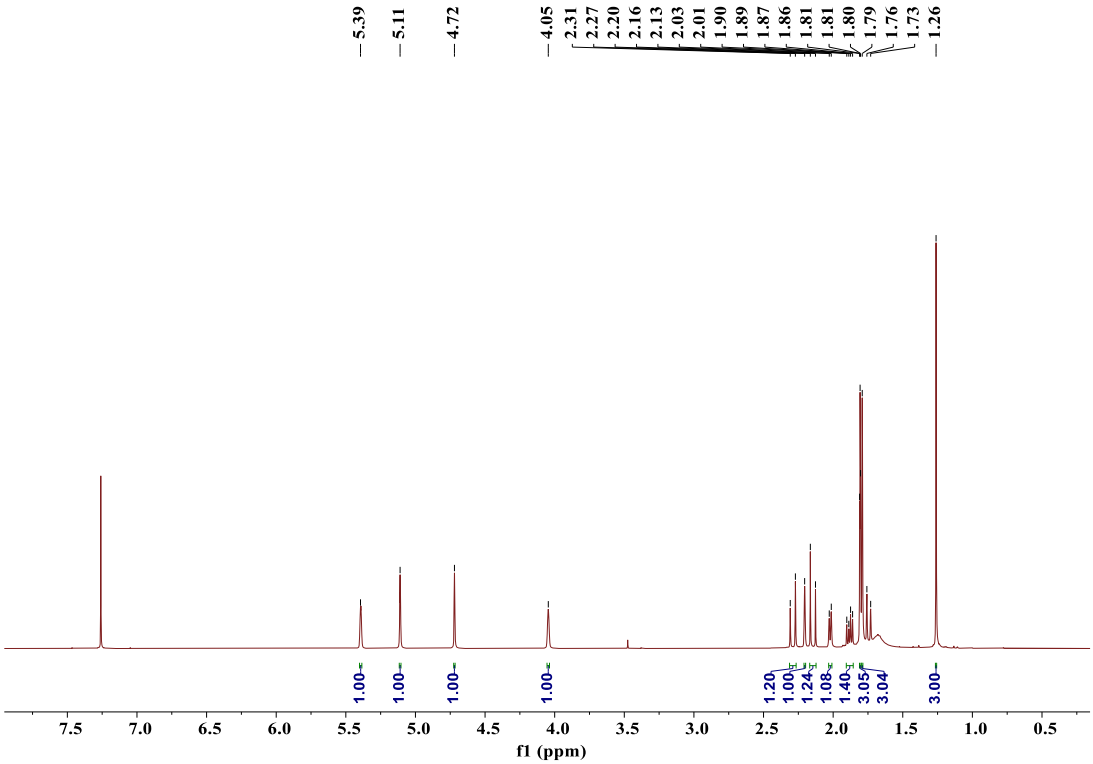


Figure S83. ^{1}H NMR spectrum of **7** in $CDCl_3$

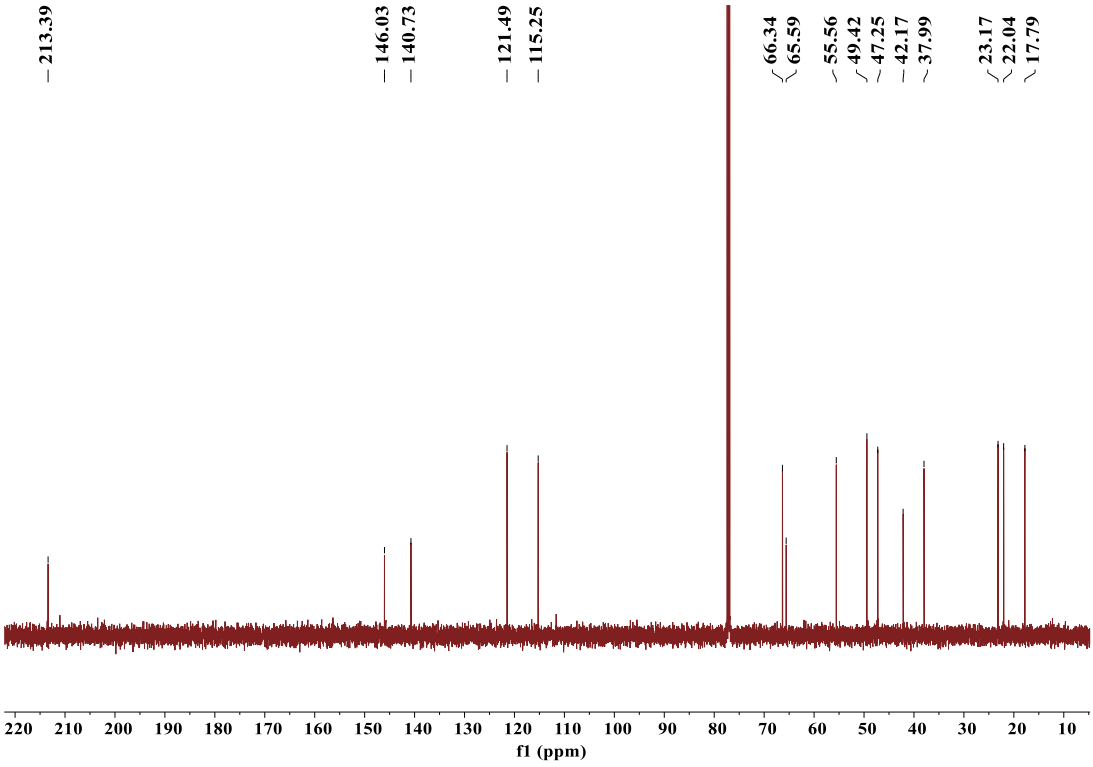


Figure S84. ^{13}C NMR spectrum of **7** in $CDCl_3$

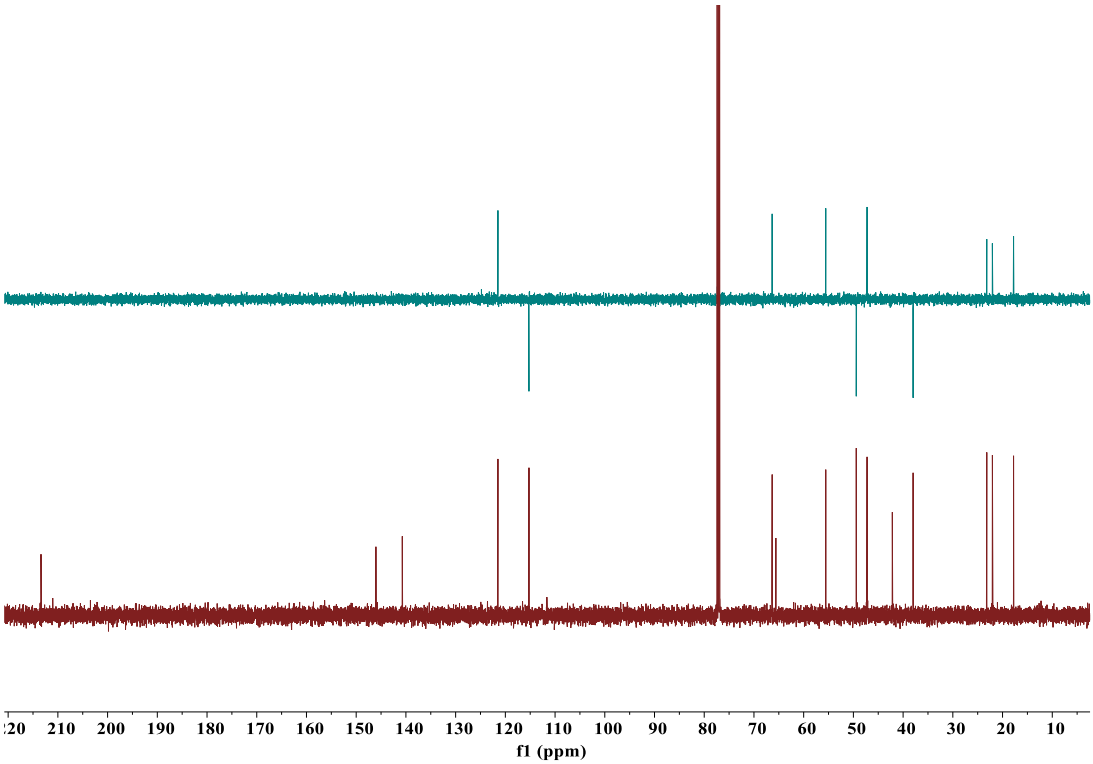


Figure S85. ^{13}C NMR and DEPT-135 Spectra of **7** in $CDCl_3$

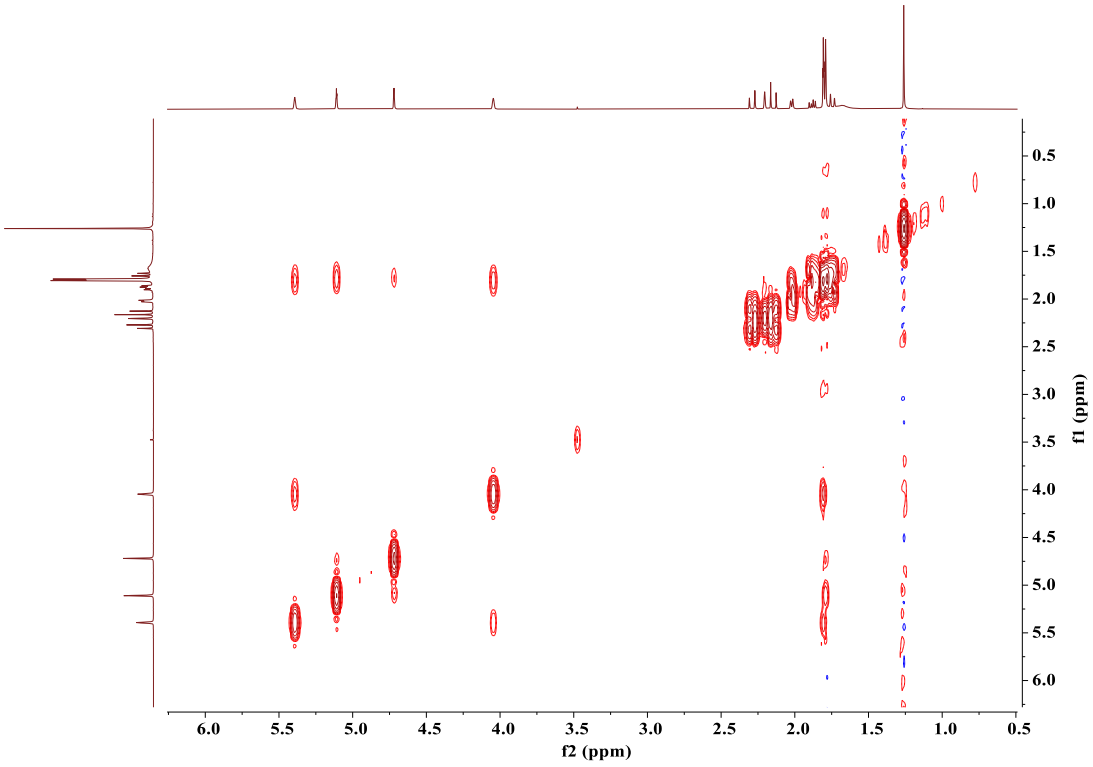


Figure S86. ^{1}H-^{1}H COSY spectrum of **7** in $CDCl_3$

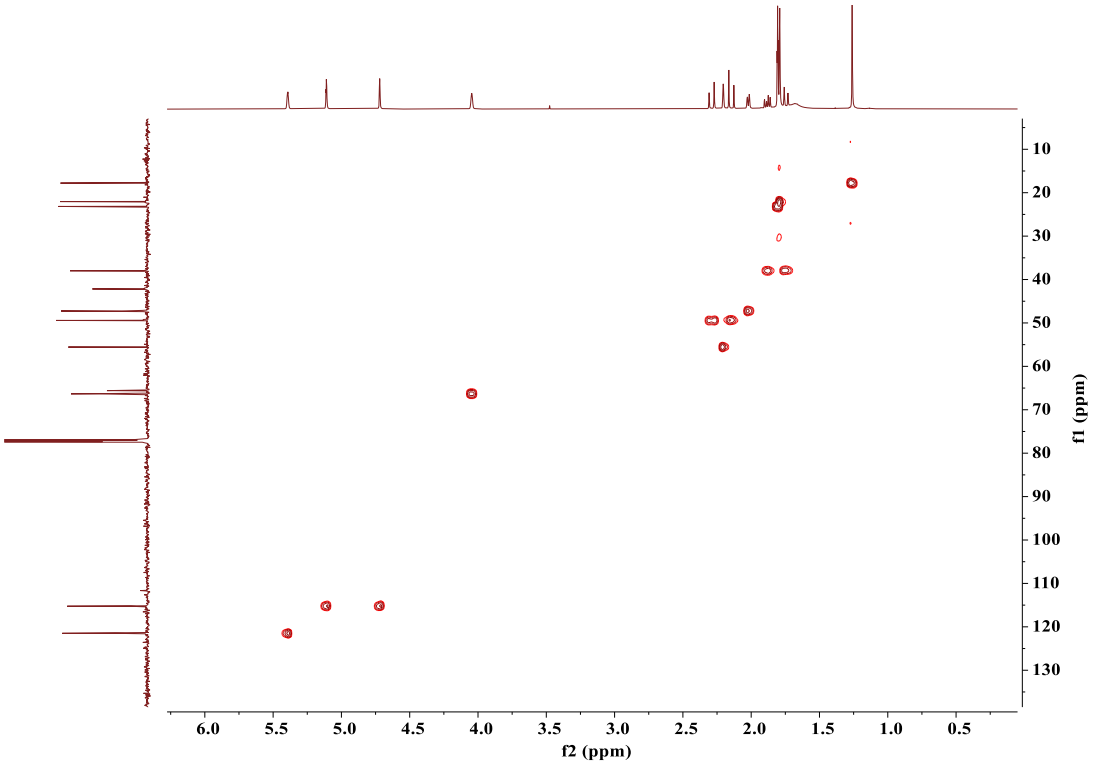


Figure S87. HSQC spectrum of **7** in $CDCl_3$

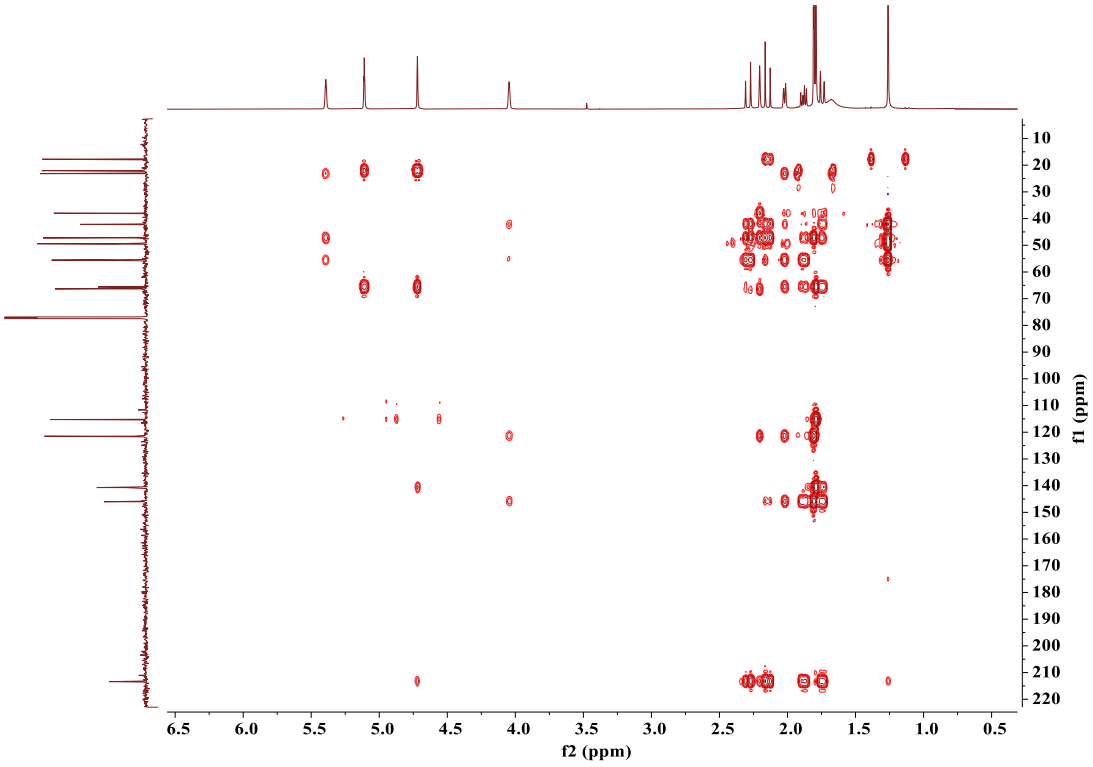


Figure S88. HMBC spectrum of **7** in $CDCl_3$

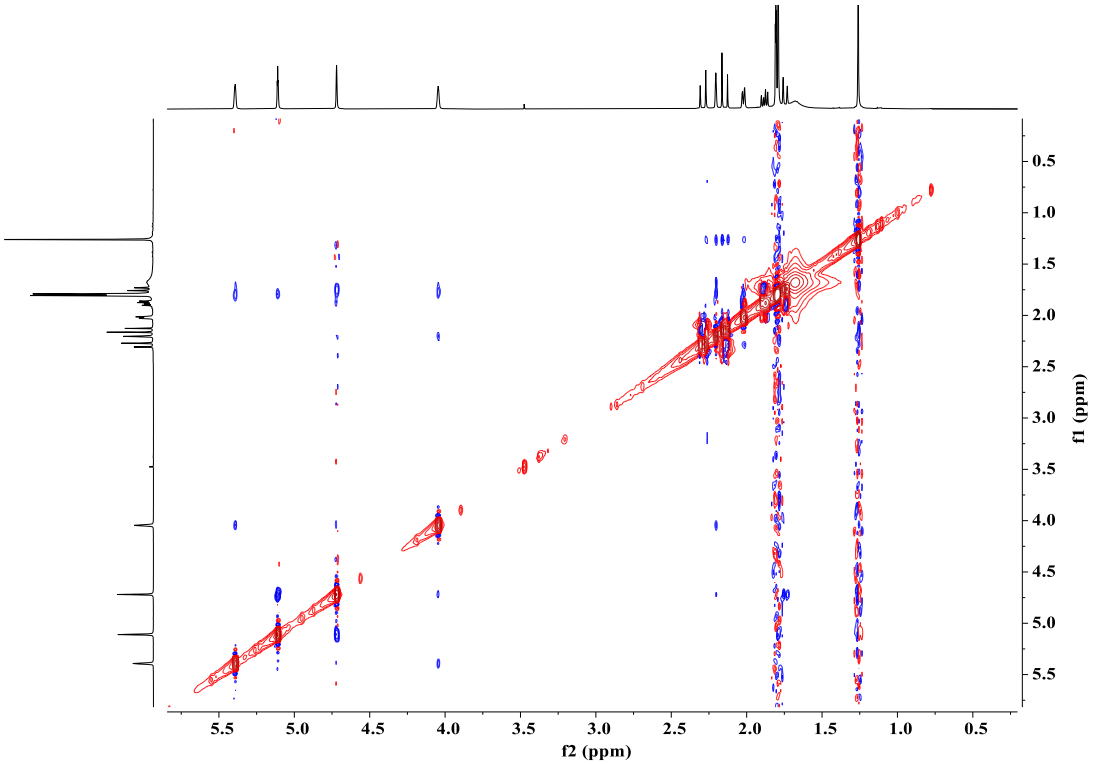


Figure S89. NOESY spectrum of **7** in $CDCl_3$

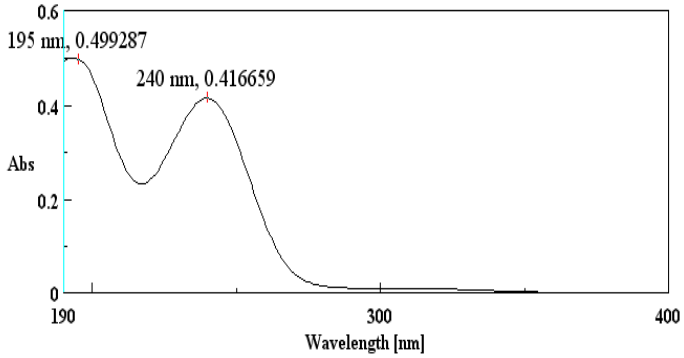


Figure S90. UV spectrum of **8** in MeOH

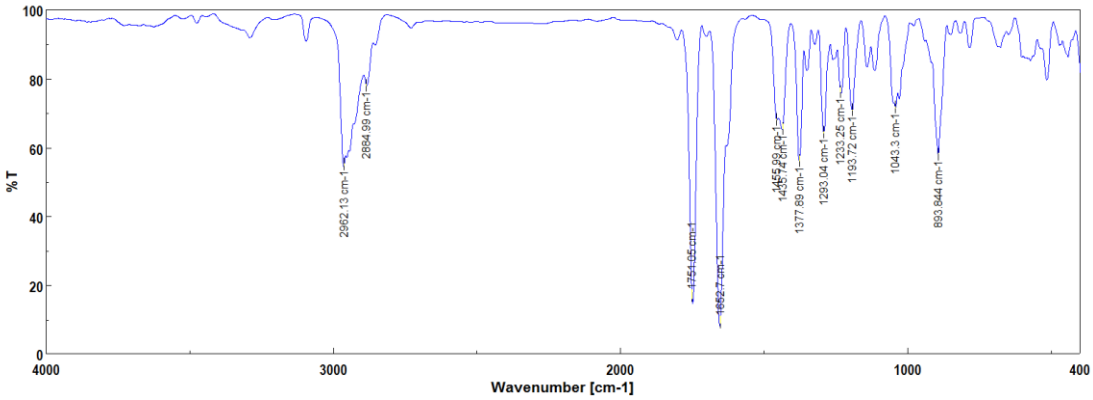


Figure S91. IR spectrum of **8** (KBr disc)

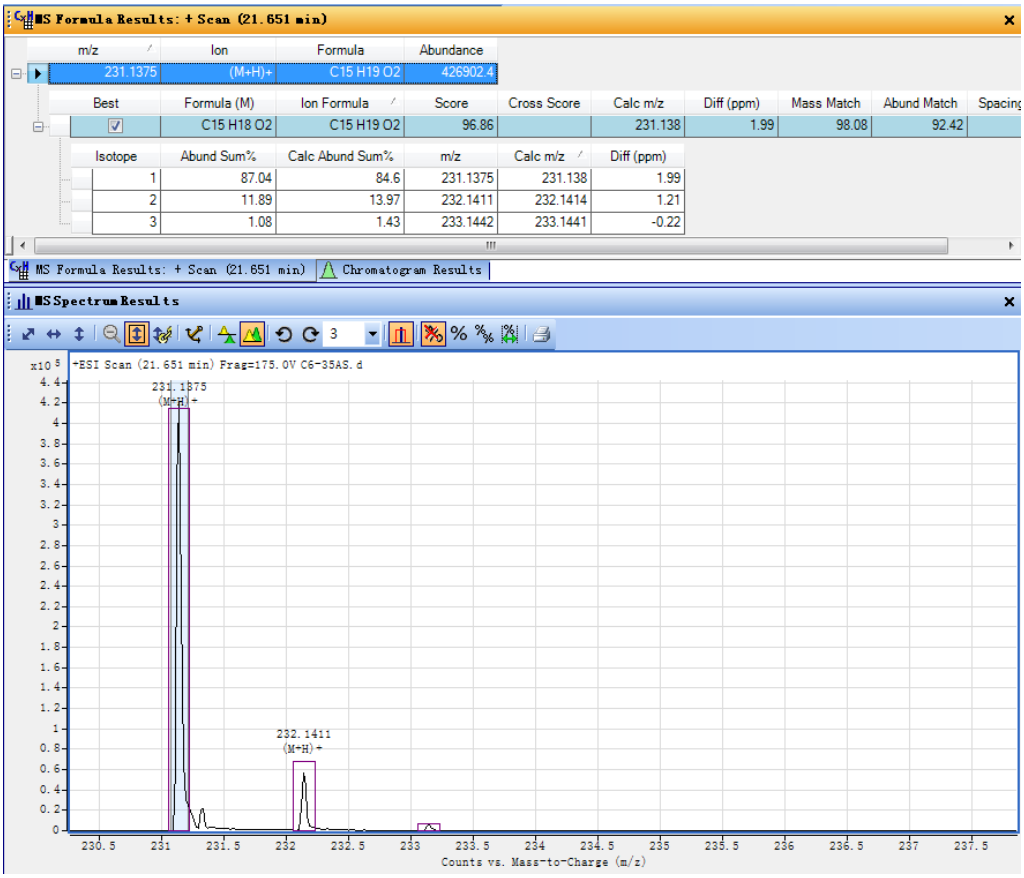


Figure S92. HR-ESI-MS spectrum of **8**

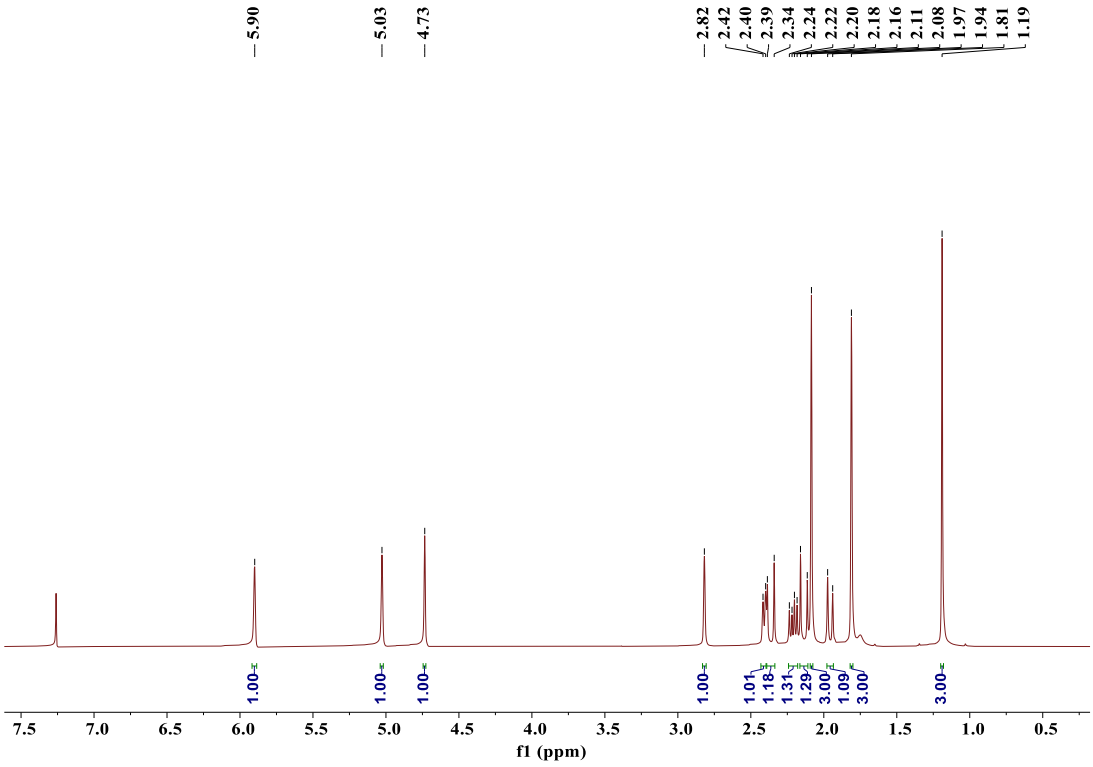


Figure S93. ^{1}H NMR spectrum of **8** in $CDCl_3$

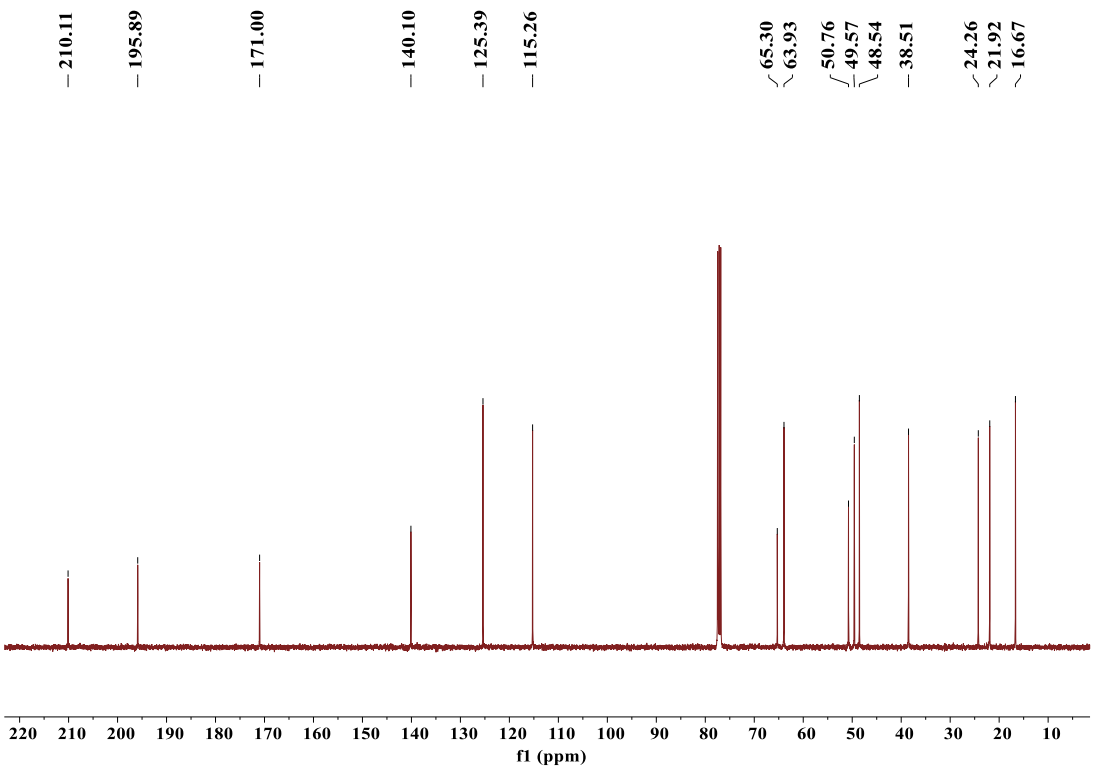


Figure S94. ^{13}C NMR spectrum of **8** in $CDCl_3$

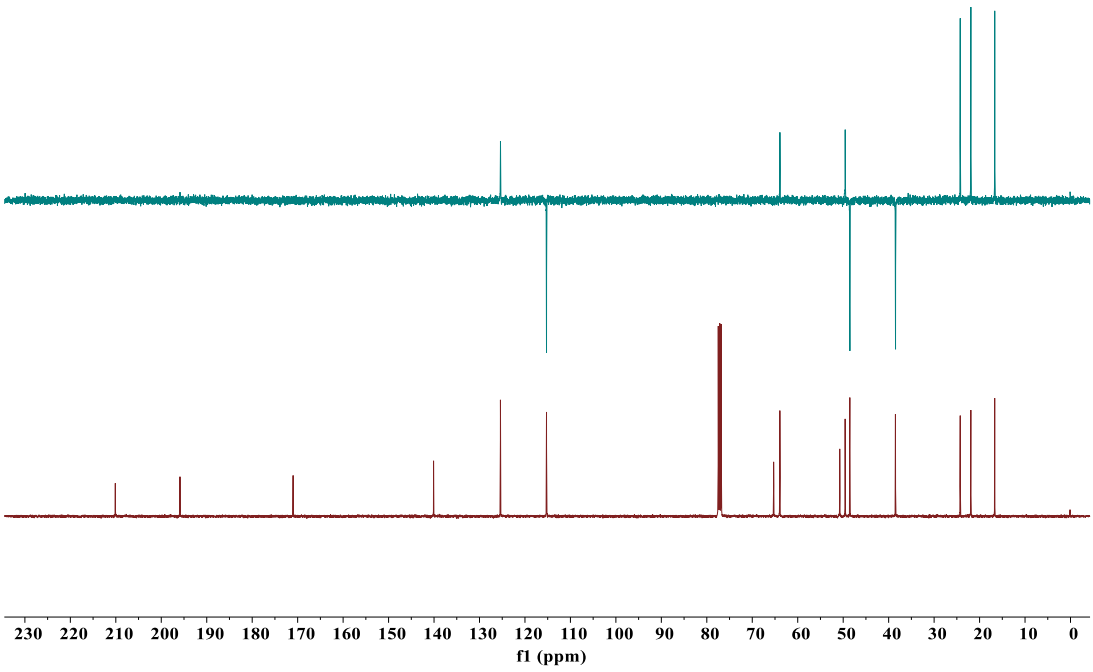


Figure S95. ^{13}C NMR and DEPT-135 Spectra of **8** in $CDCl_3$

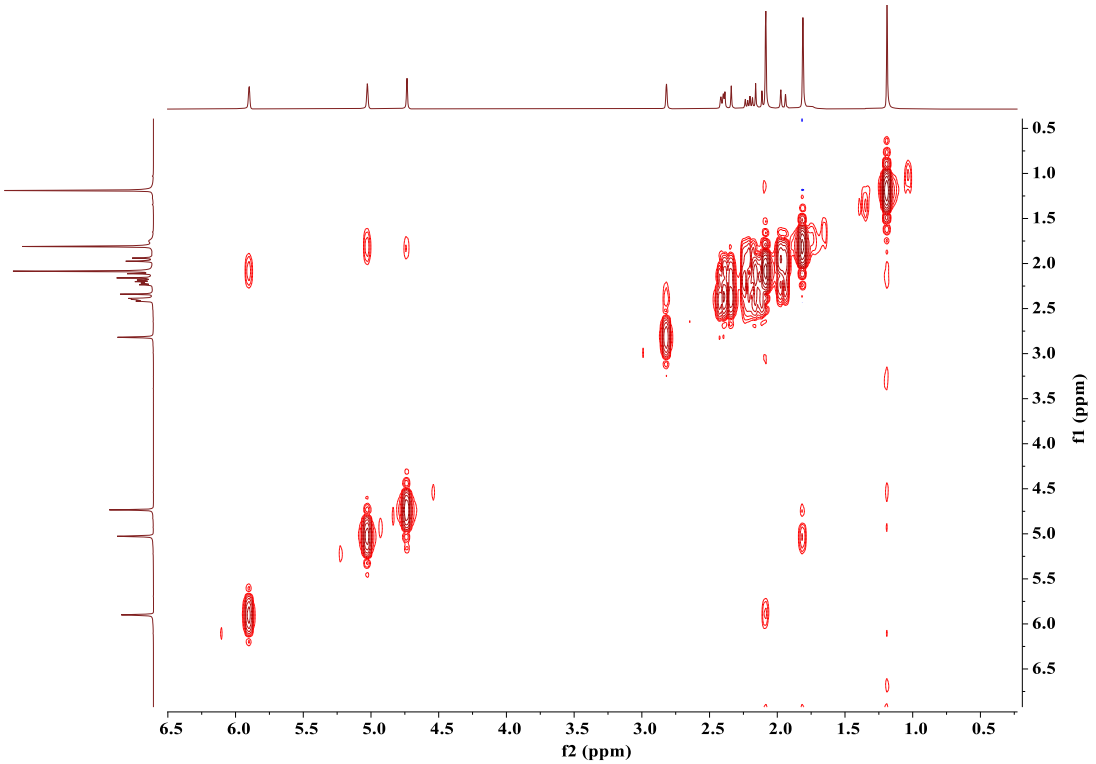


Figure S96. ^{1}H-^{1}H COSY spectrum of **8** in $CDCl_3$

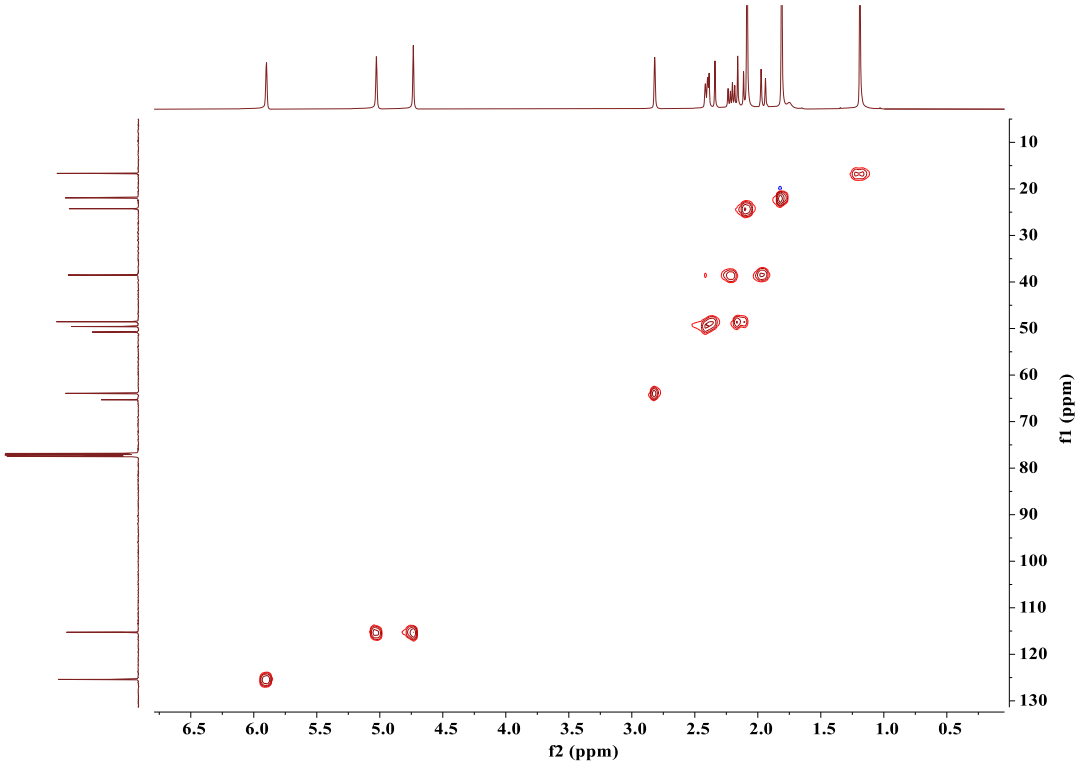


Figure S97. HSQC spectrum of **8** in $CDCl_3$

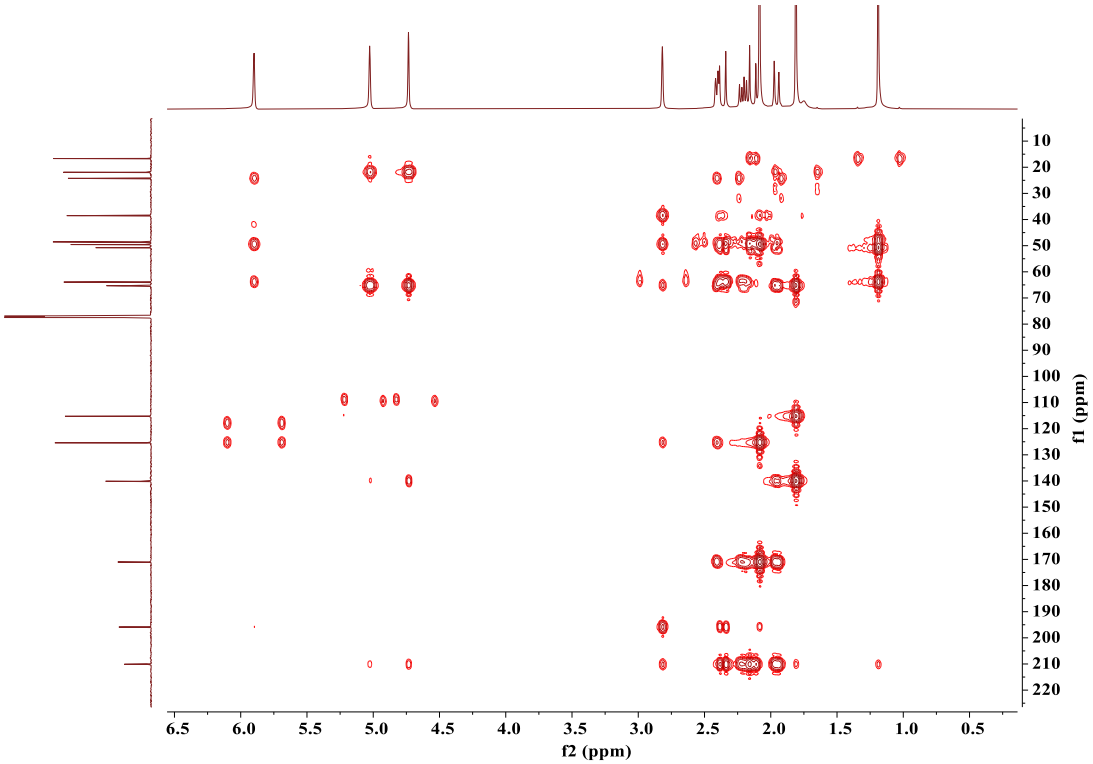


Figure S98. HMBC spectrum of **8** in $CDCl_3$

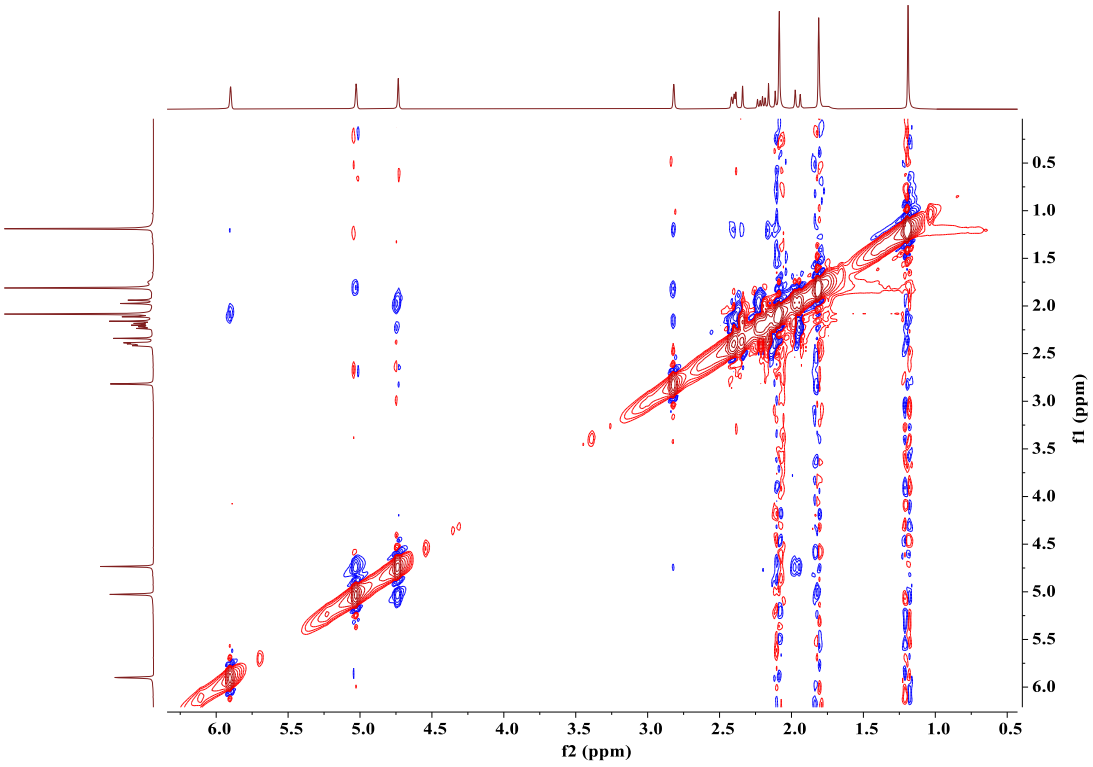


Figure S99. NOESY spectrum of **8** in $CDCl_3$

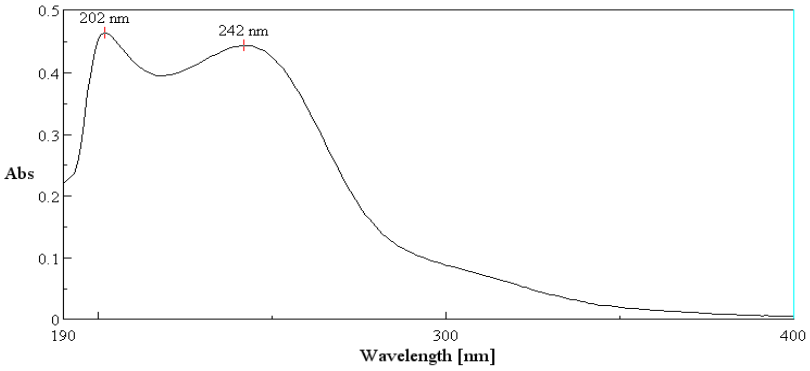


Figure S100. UV spectrum of **9** in MeOH

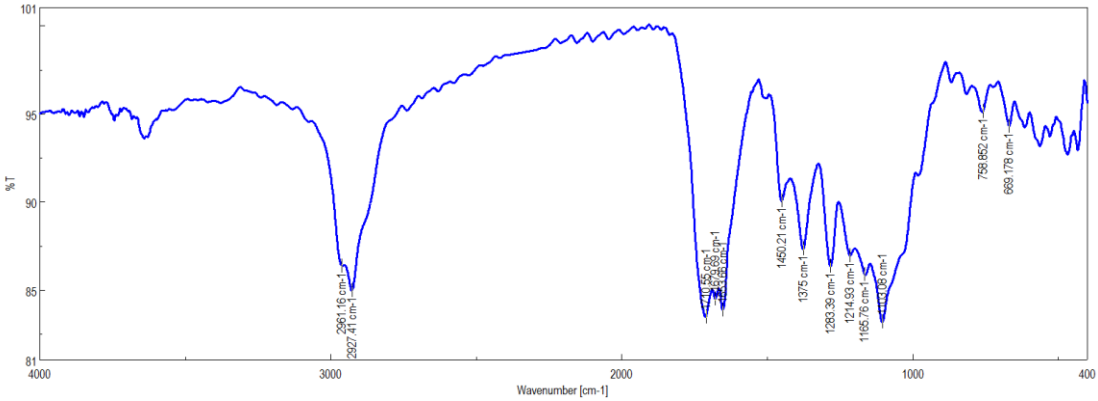


Fig.S101 IR spectrum of **9** (KBr disc)

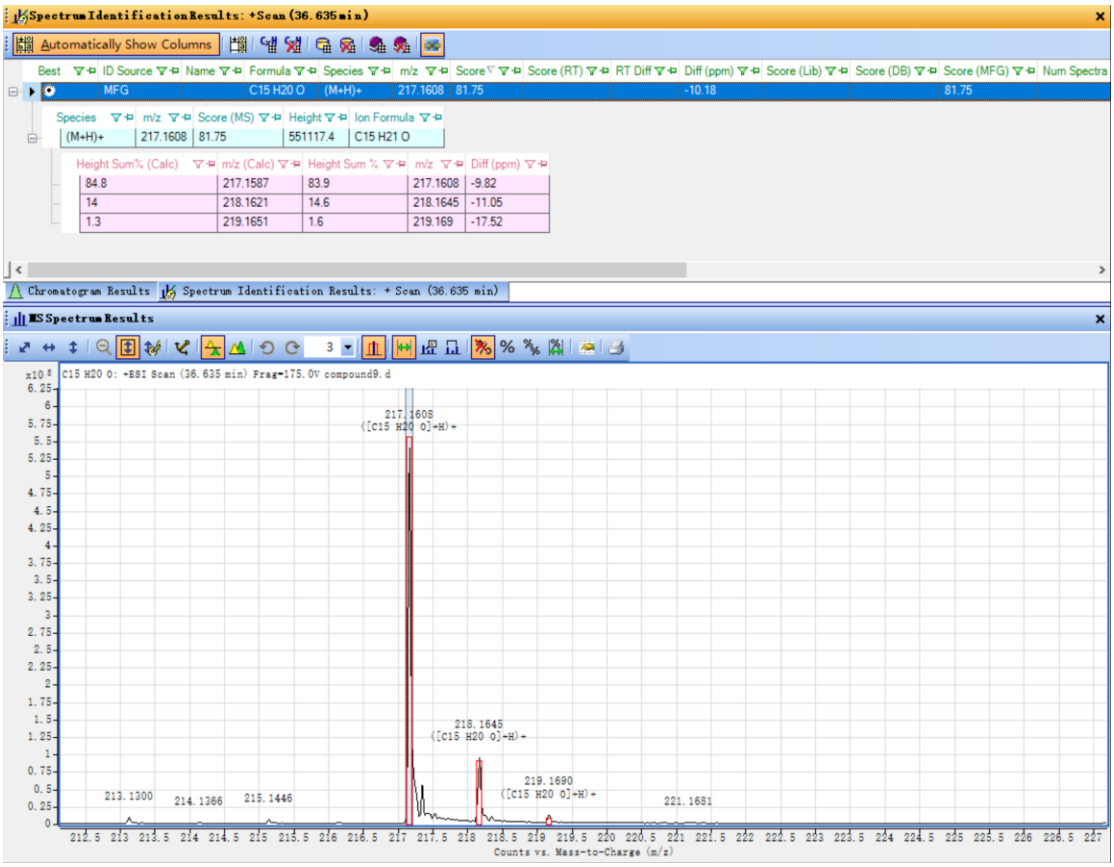


Figure S102. HR-ESI-MS spectrum of **9**

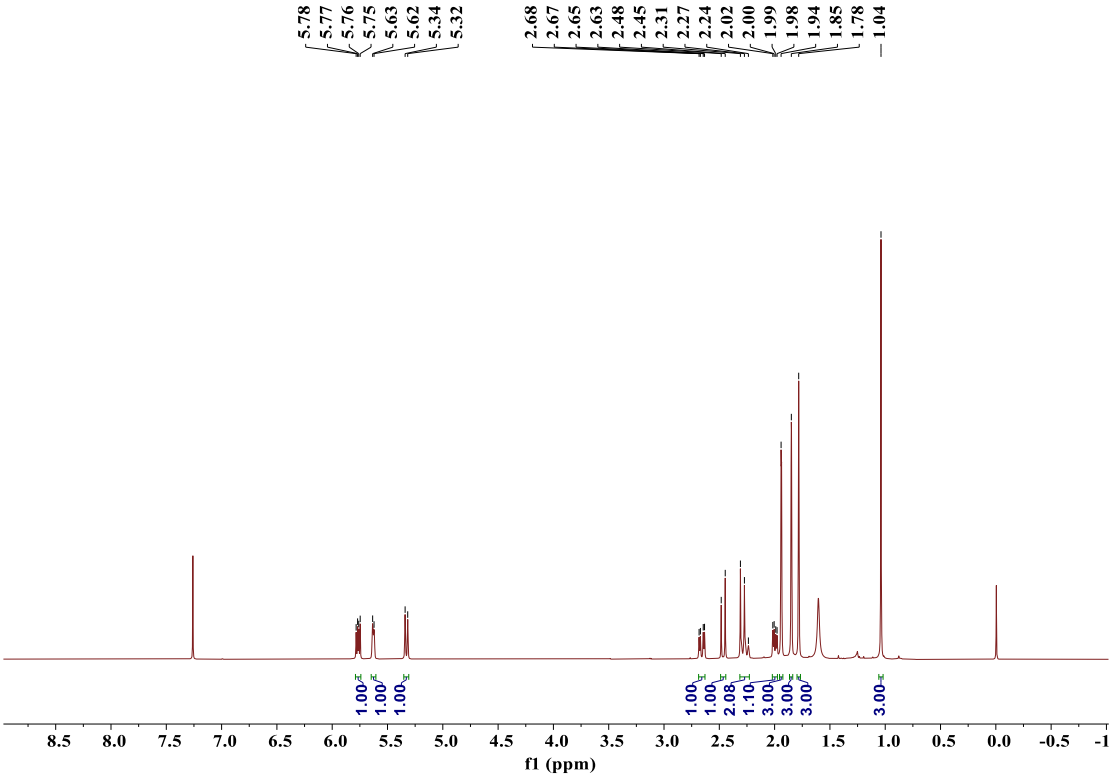


Figure S103. ^{1}H NMR spectrum of **9** in $CDCl_3$

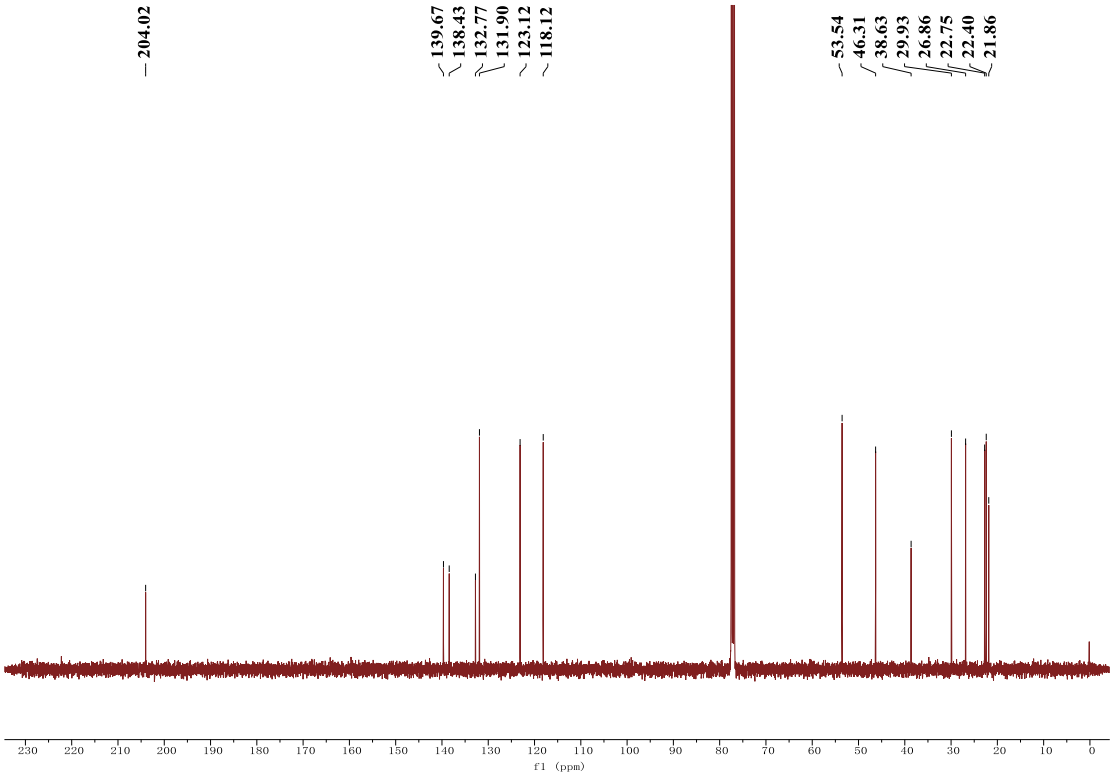


Figure S104. ^{13}C NMR spectrum of **9** in $CDCl_3$

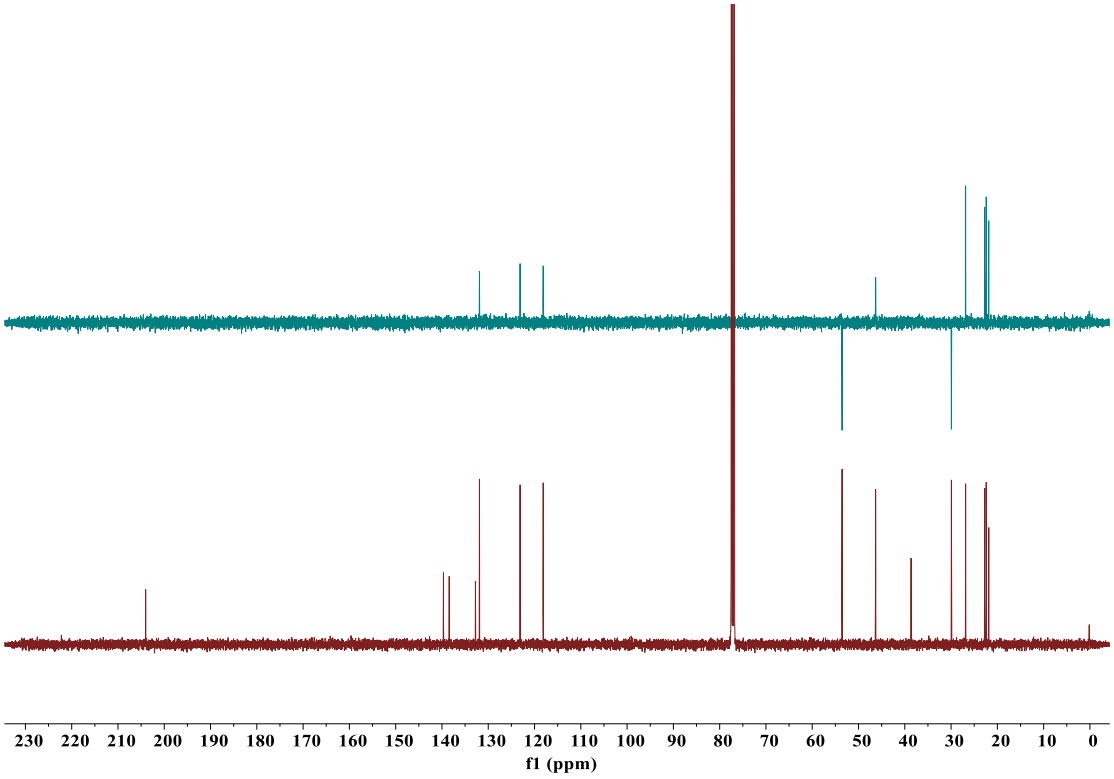
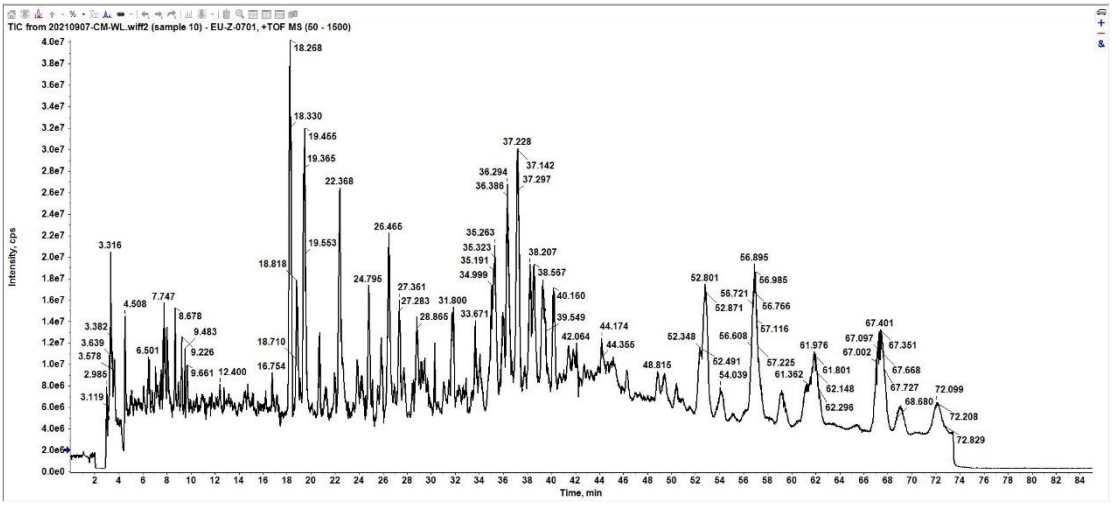


Figure S105. ^{13}C NMR and DEPT-135 Spectra of **9** in $CDCl_3$

Figure S106. The total ion chromatogram (TIC) for the methanol extract of the fresh fruits of *E. uniflora*.



The analysis was performed on SCIEX X500R Q-TOF mass spectrometer using a Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A linear gradient program with the mobile phase (20% to 80% CH_3CN at 0–40 min, 80% CH_3CN at 40–75 min, 100% CH_3CN at 75–85 min) was used as eluent at flow rate of 0.4 mL/min.

Figure S107. The extracted ion chromatogram (EIC) for 431.1900 to 431.3900 (calcd for $C_{30}H_{39}O_2$: 431.2945), Peak **A** and **B**: retention time: 56.911 min; *m/z* 431.2923 $[M+H]^+$.

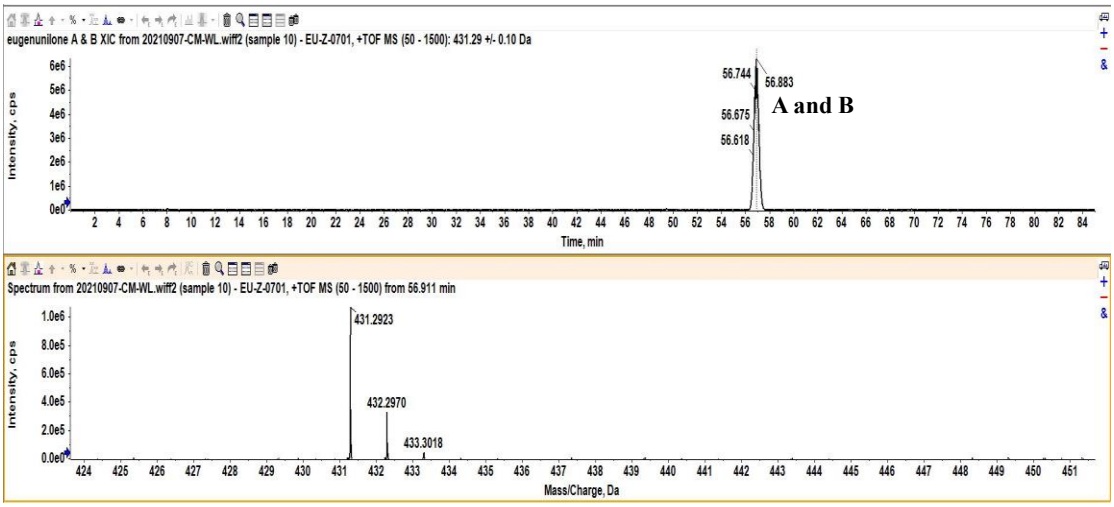
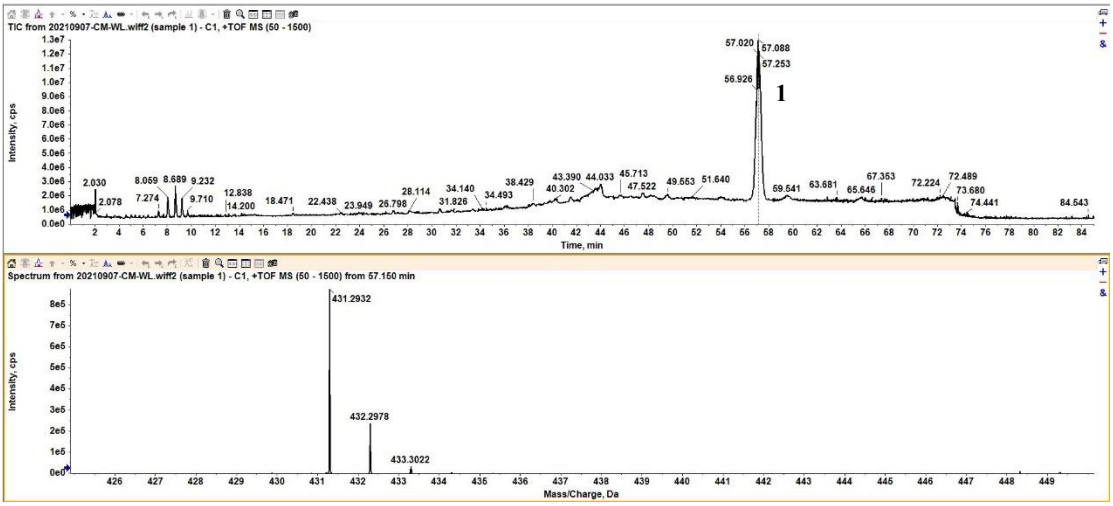
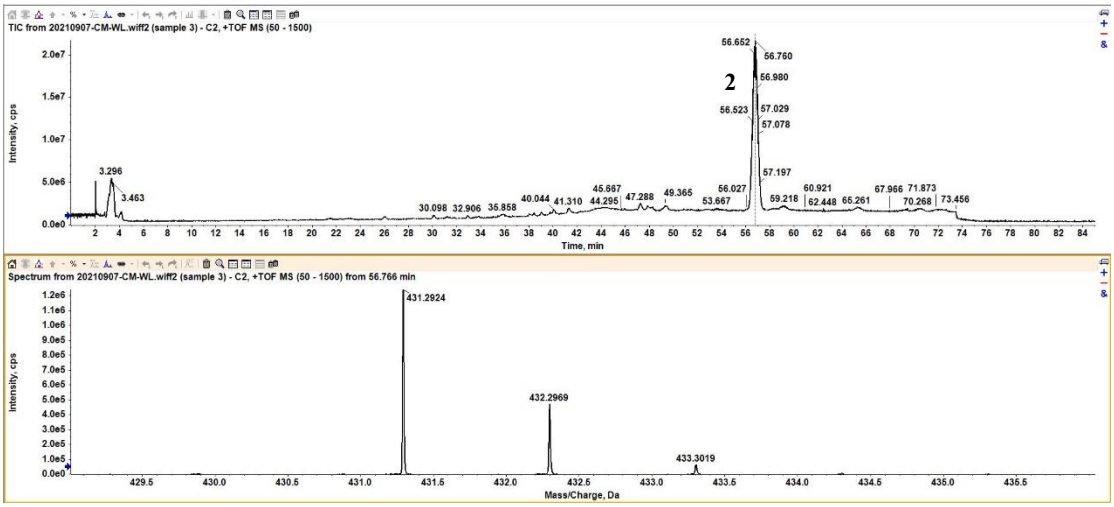


Figure S108. The total ion chromatogram (TIC) for eugenunilone A (**1**), Peak **1**: retention time: 57.150 min; *m*/*z* 431.2932 $[M+H]^+$.



The analysis was performed on SCIEX X500R Q-TOF mass spectrometer using a Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A linear gradient program with the mobile phase (20% to 80% CH_3CN at 0–40 min, 80% CH_3CN at 40–75 min, 100% CH_3CN at 75–85 min) was used as eluent at flow rate of 0.4 mL/min.

Figure S109. The total ion chromatogram (TIC) for eugenunilone B (**2**), Peak **2**: retention time: 56.766 min; *m*/*z* 431.2924 $[M+H]^+$.



The analysis was performed on SCIEX X500R Q-TOF mass spectrometer using a Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A linear gradient program with the mobile phase (20% to 80% CH_3CN at 0–40 min, 80% CH_3CN at 40–75 min, 100% CH_3CN at 75–85 min) was used as eluent at flow rate of 0.4 mL/min.

Figure S110. The extracted ion chromatogram (XIC) for 249.0500 to 249.2500 (calcd for $C_{15}H_{21}O_3$: 249.1485), Peak **C**: retention time: 22.367 min; *m/z* 249.1472 $[M+H]^+$.

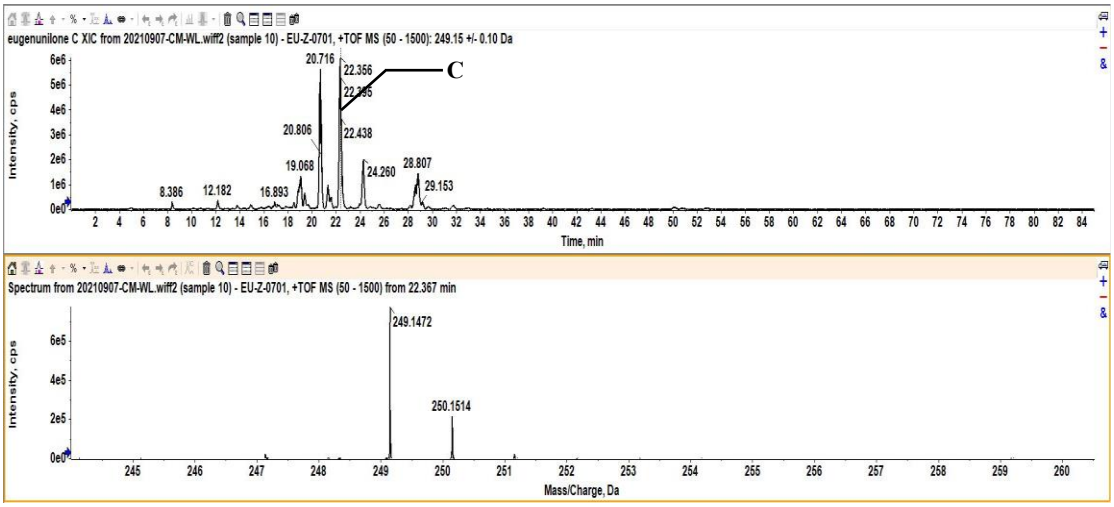
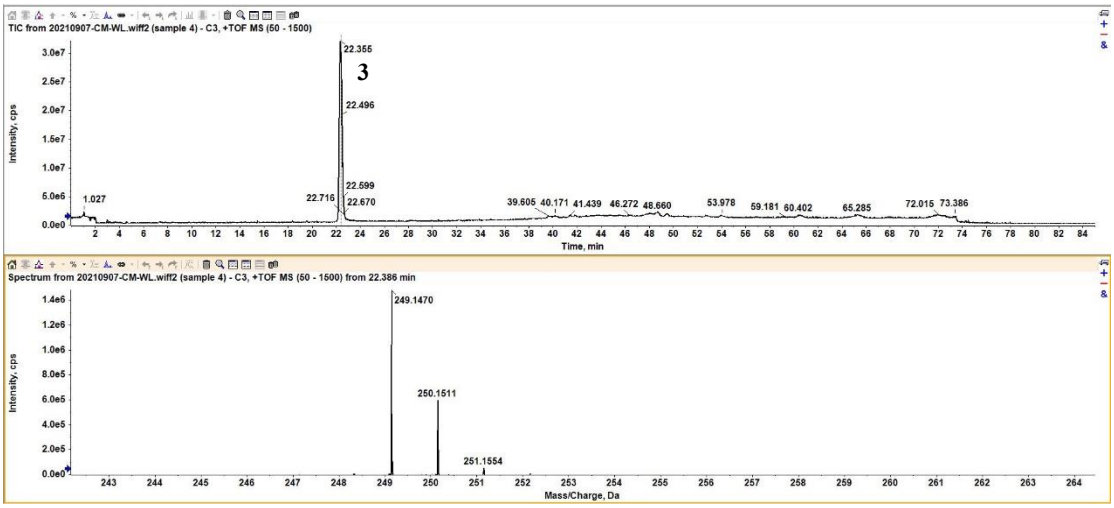


Figure S111. The total ion chromatogram (TIC) for eugenunilone C (**3**), Peak **3**: retention time: 22.386 min; *m/z* 249.1470 $[M+H]^+$.



The analysis was performed on SCIEX X500R Q-TOF mass spectrometer using a Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A linear gradient program with the mobile phase (20% to 80% CH_3CN at 0–40 min, 80% CH_3CN at 40–75 min, 100% CH_3CN at 75–85 min) was used as eluent at flow rate of 0.4 mL/min.

Figure S112. The extracted ion chromatogram (XIC) for 247.0300 to 247.2300 (calcd for $C_{15}H_{19}O_3$: 247.1329), Peak **D**: retention time: 31.756 min; *m/z* 247.1318 $[M+H]^+$.

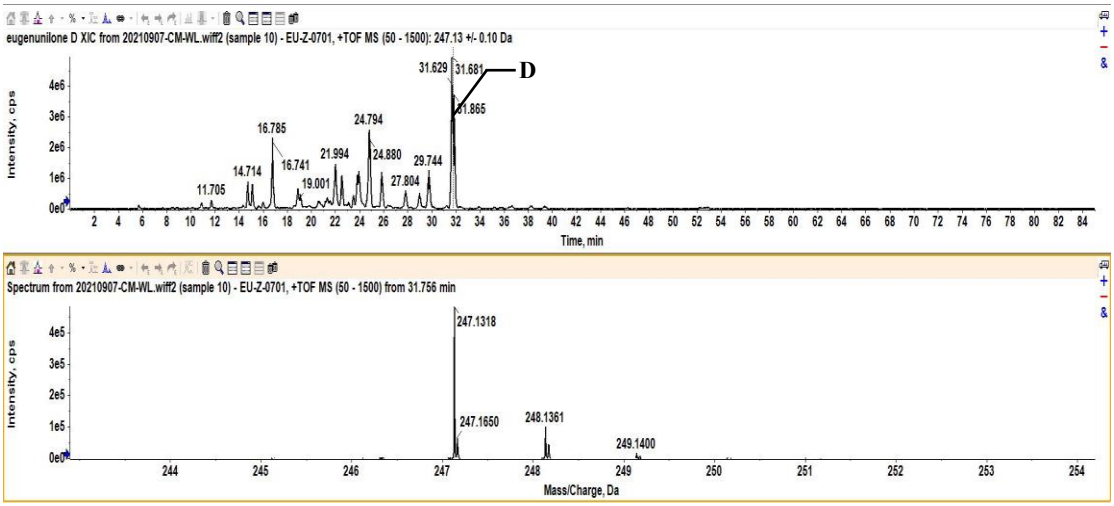
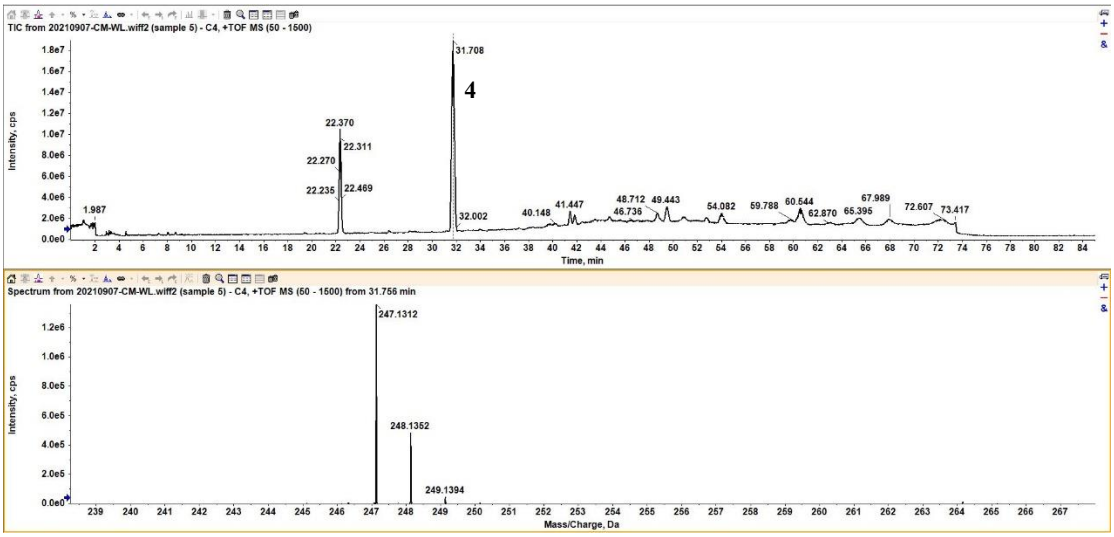


Figure S113. The total ion chromatogram (TIC) for eugenunilone D (**4**), Peak **4**: retention time: 31.756 min; *m/z* 247.1312 $[M+H]^+$.



The analysis was performed on SCIEX X500R Q-TOF mass spectrometer using a Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A linear gradient program with the mobile phase (20% to 80% CH_3CN at 0–40 min, 80% CH_3CN at 40–75 min, 100% CH_3CN at 75–85 min) was used as eluent at flow rate of 0.4 mL/min.

Figure S114. The extracted ion chromatogram (XIC) for 233.0500 to 233.2500 (calcd for $C_{15}H_{21}O_2$: 233.1536), Peak **E**: retention time: 18.343 min; *m/z* 233.1527 $[M+H]^+$.

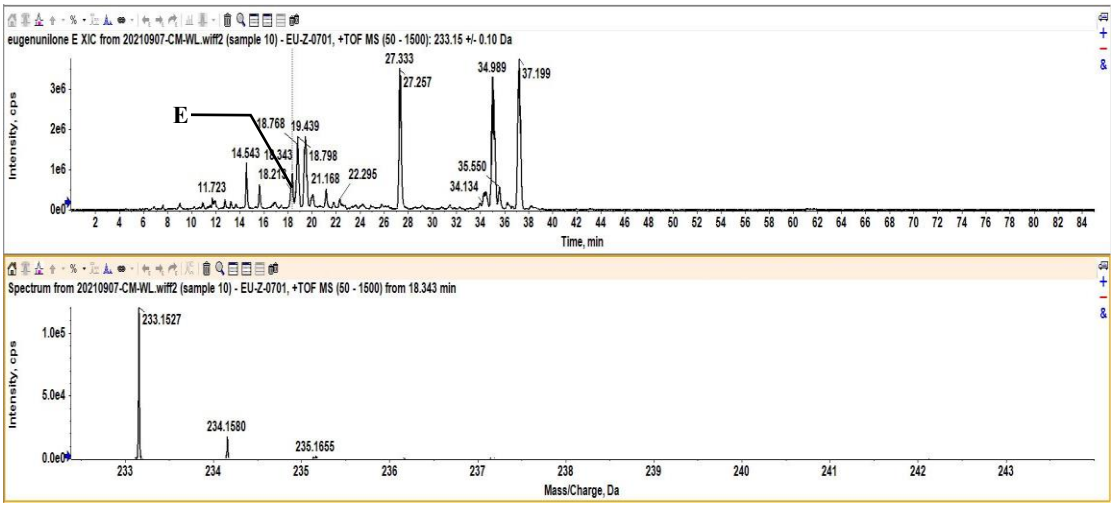
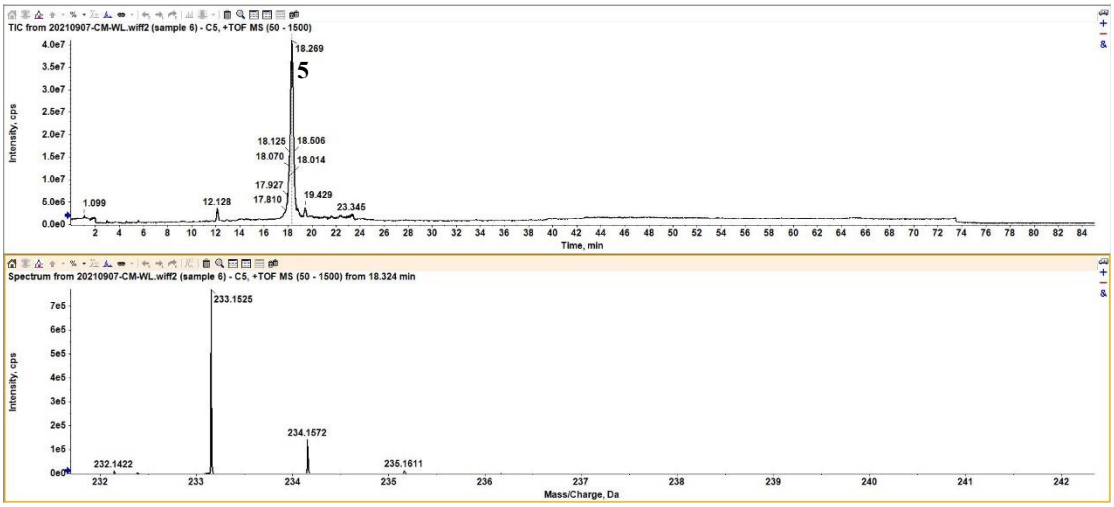


Figure S115. The total ion chromatogram (TIC) for eugenunilone E (**5**), Peak **5**: retention time: 18.324 min; *m/z* 233.1525 $[M+H]^+$.



The analysis was performed on SCIEX X500R Q-TOF mass spectrometer using a Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A linear gradient program with the mobile phase (20% to 80% CH_3CN at 0–40 min, 80% CH_3CN at 40–75 min, 100% CH_3CN at 75–85 min) was used as eluent at flow rate of 0.4 mL/min.

Figure S116. The extracted ion chromatogram (XIC) for 231.0400 to 231.2400 (calcd for $C_{15}H_{19}O_2$: 231.1380), Peak **F**: retention time: 18.249 min; *m/z* 231.1364 $[M+H]^+$.

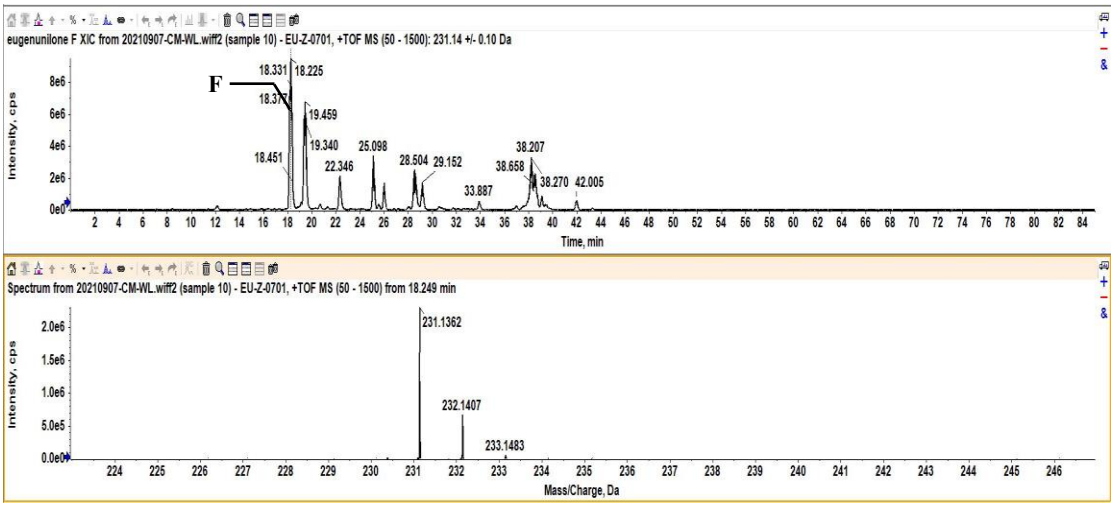
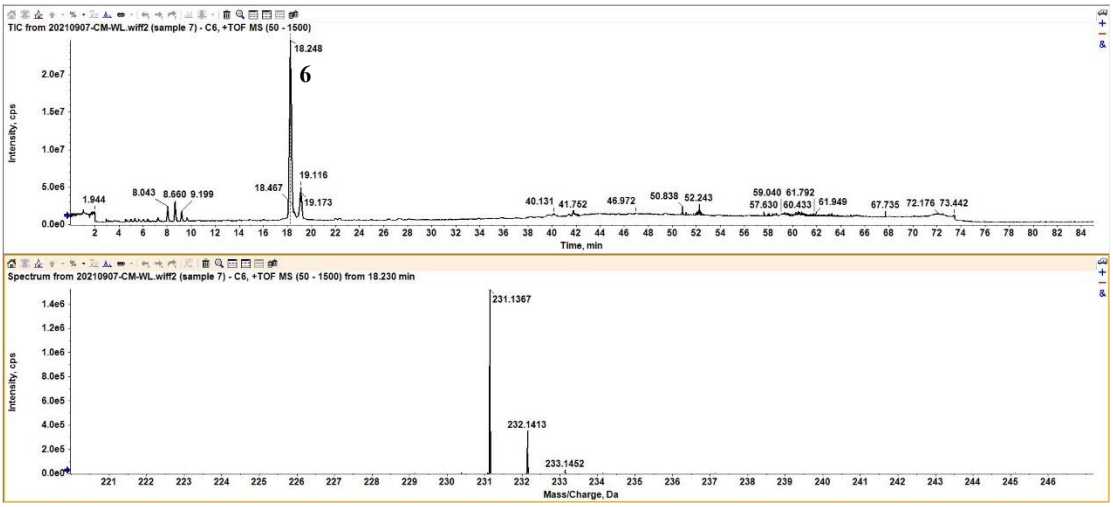


Figure S117. The total ion chromatogram (TIC) for eugenunilone F (**6**), Peak **6**: retention time: 18.230 min; *m/z* 231.1367 $[M+H]^+$.



The analysis was performed on SCIEX X500R Q-TOF mass spectrometer using a Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A linear gradient program with the mobile phase (20% to 80% CH_3CN at 0–40 min, 80% CH_3CN at 40–75 min, 100% CH_3CN at 75–85 min) was used as eluent at flow rate of 0.4 mL/min.

Figure S118. The extracted ion chromatogram (XIC) for 233.0500 to 233.2500 (calcd for $C_{15}H_{21}O_2$: 233.1536), Peak **G**: retention time: 19.460 min; *m*/*z* 233.1526 $[M+H]^+$.

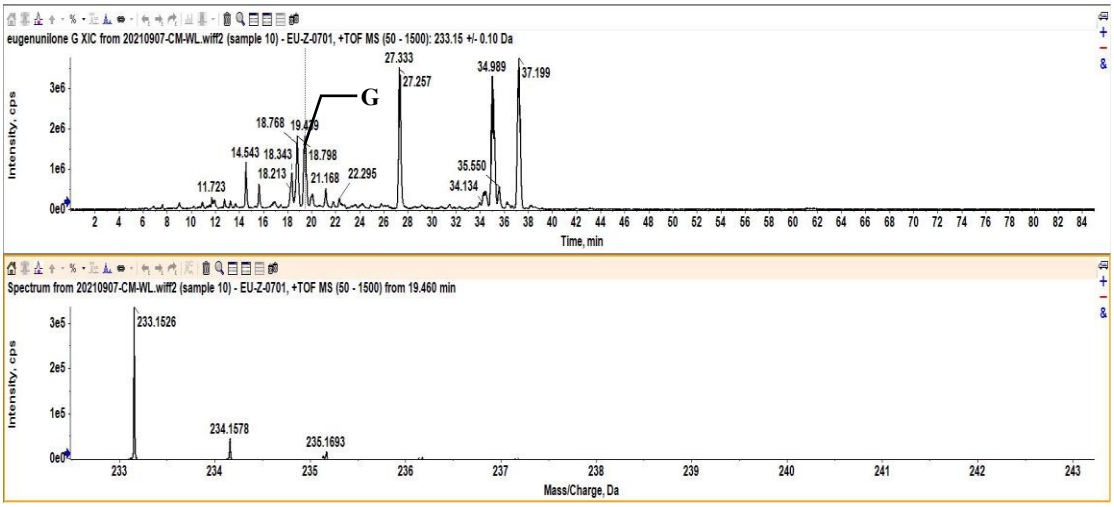
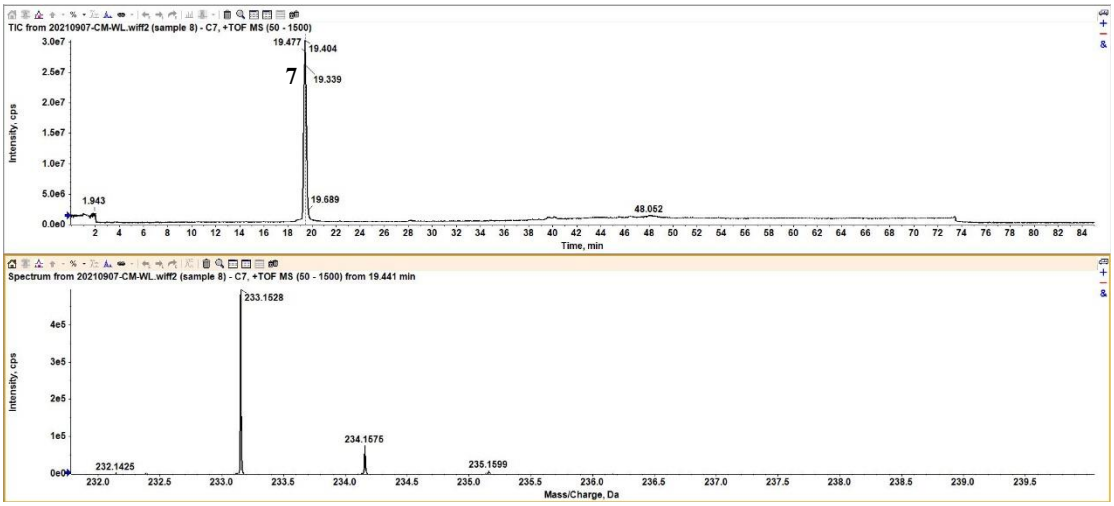


Figure S119. The total ion chromatogram (TIC) for eugenunilone G (**7**), Peak 7: retention time: 19.441 min; *m*/*z* 233.1528 $[M+H]^+$.



The analysis was performed on SCIEX X500R Q-TOF mass spectrometer using a Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A linear gradient program with the mobile phase (20% to 80% CH_3CN at 0–40 min, 80% CH_3CN at 40–75 min, 100% CH_3CN at 75–85 min) was used as eluent at flow rate of 0.4 mL/min.

Figure S120. The extracted ion chromatogram (XIC) for 231.0400 to 231.2400 (calcd for $C_{15}H_{19}O_2$: 231.1380), Peak **H**: retention time: 19.460 min; *m/z* 231.1364 $[M+H]^+$.

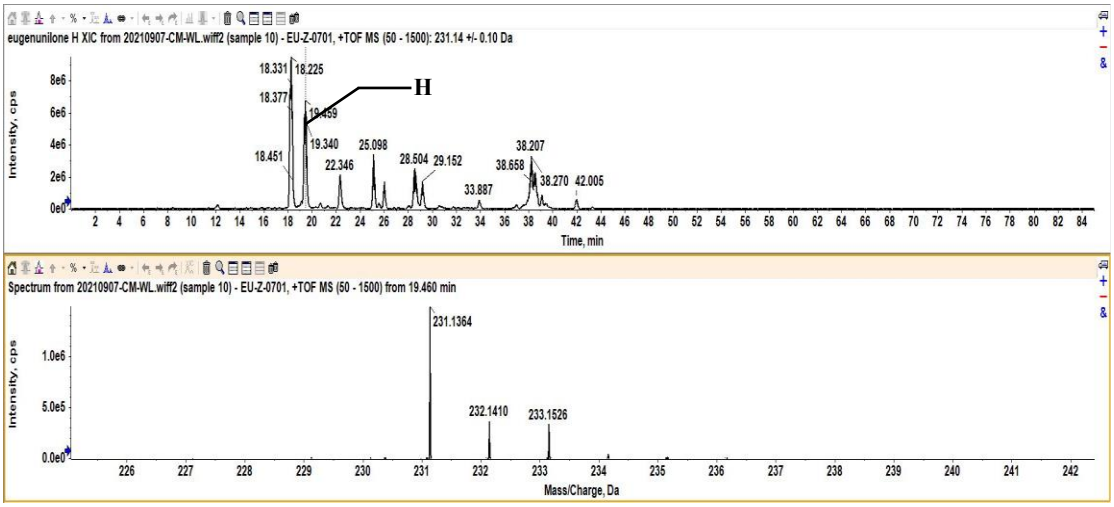
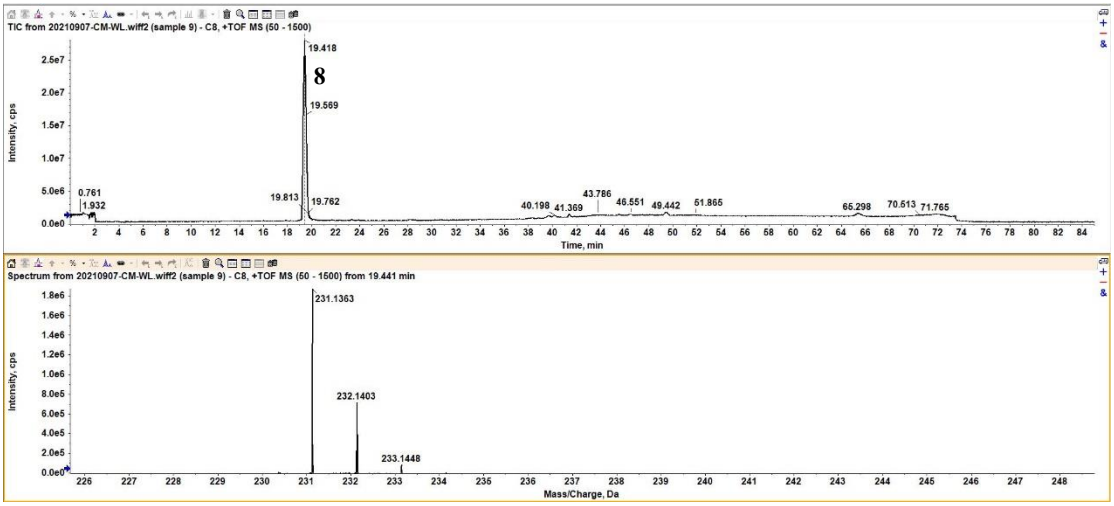


Figure S121. The total ion chromatogram (TIC) for eugenunilone H (**8**), Peak **8**: retention time: 19.441 min; *m/z* 231.1363 $[M+H]^+$.



The analysis was performed on SCIEX X500R Q-TOF mass spectrometer using a Poroshell 120 EC-C18 column (4.6 mm × 150 mm, 4 μm). A linear gradient program with the mobile phase (20% to 80% CH_3CN at 0–40 min, 80% CH_3CN at 40–75 min, 100% CH_3CN at 75–85 min) was used as eluent at flow rate of 0.4 mL/min.

Notes and references

1 Weyerstahl P.; Marschall-Weyerstahl H.; Christiansen C.; Oguntimein B.; Adeoye A.; Volatile Constituents of *Eugenia uniflora* Leaf Oil. *Planta medica,* **1988**, 54, 546−549.

2 Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

3 Bruhn, T.; Schaumloffel, A.; Hemberger, Y.; Pescitelli, G. SpecDis version 1.71, Berlin, Germany, **2017**, http://specdis-software.jimdo.com.