Supplementary Material

Six new tigliane diterpenoids with anti-inflammatory activity from *Euphorbia kansuensis*

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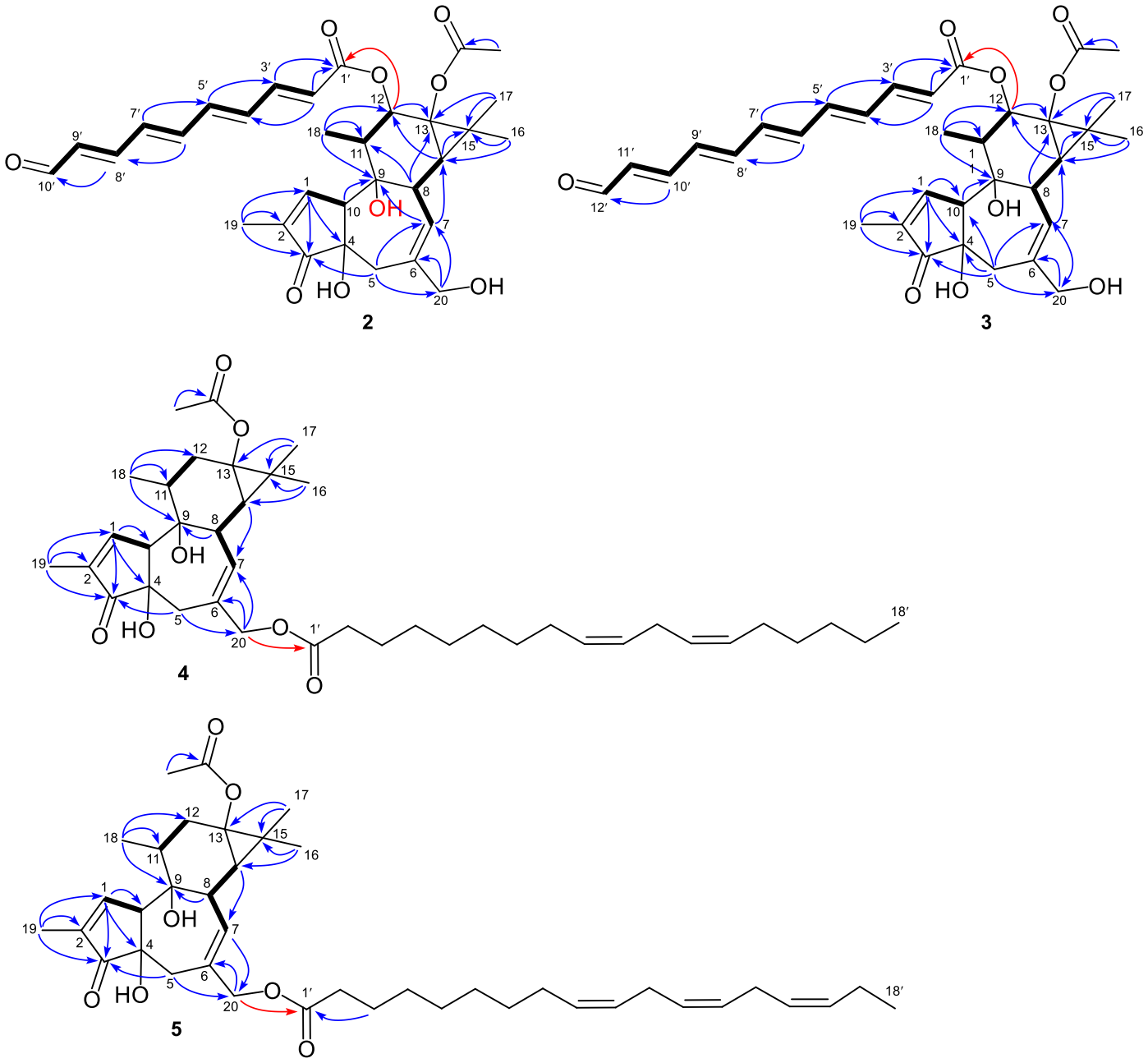


Fig. S1. The key ^{1}H-^{1}H COSY (—) and HMBC (arrows) correlations of **2–5**.

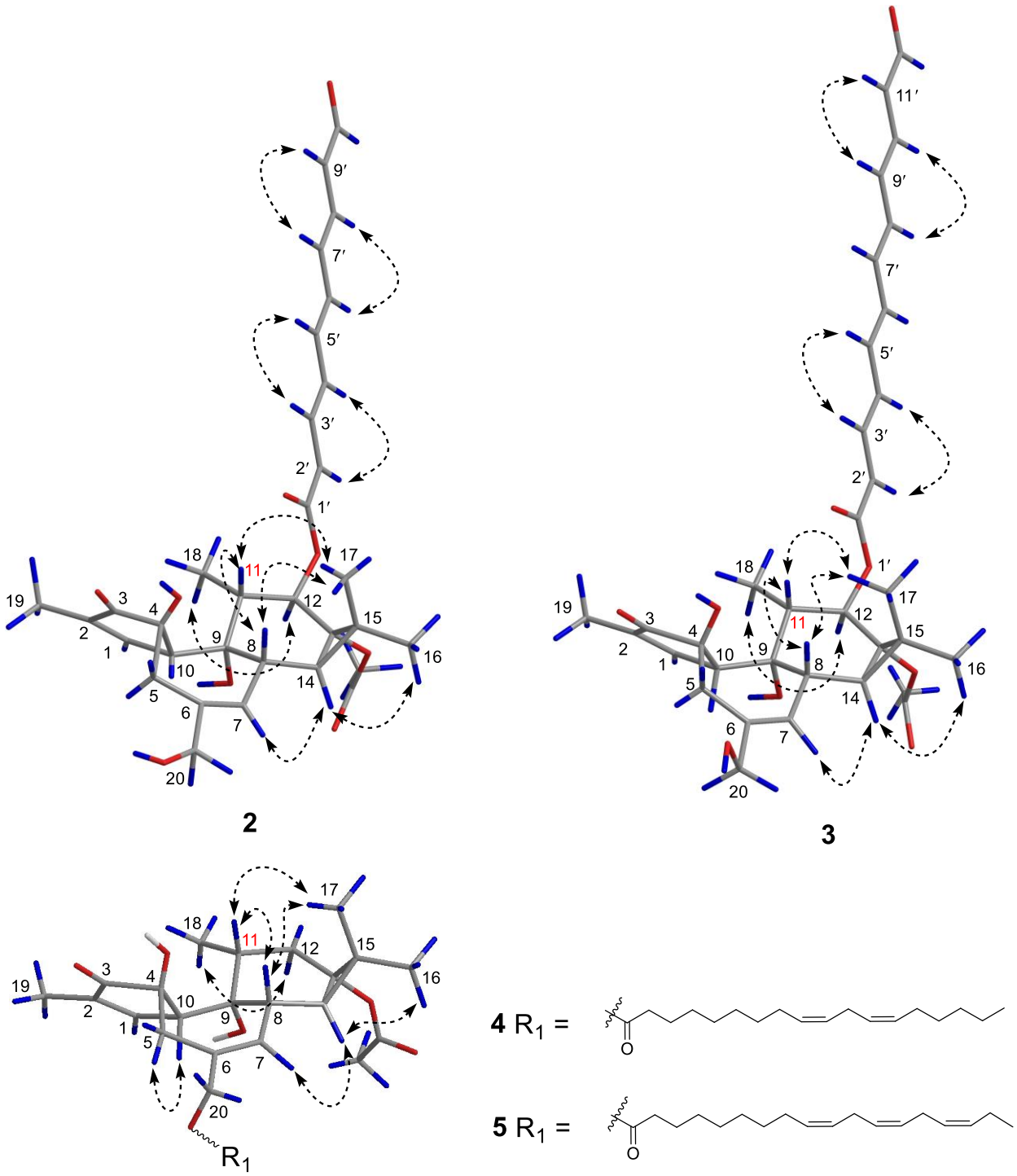


Fig. S2. The key NOE correlations (⇢) of compounds **2–5**.

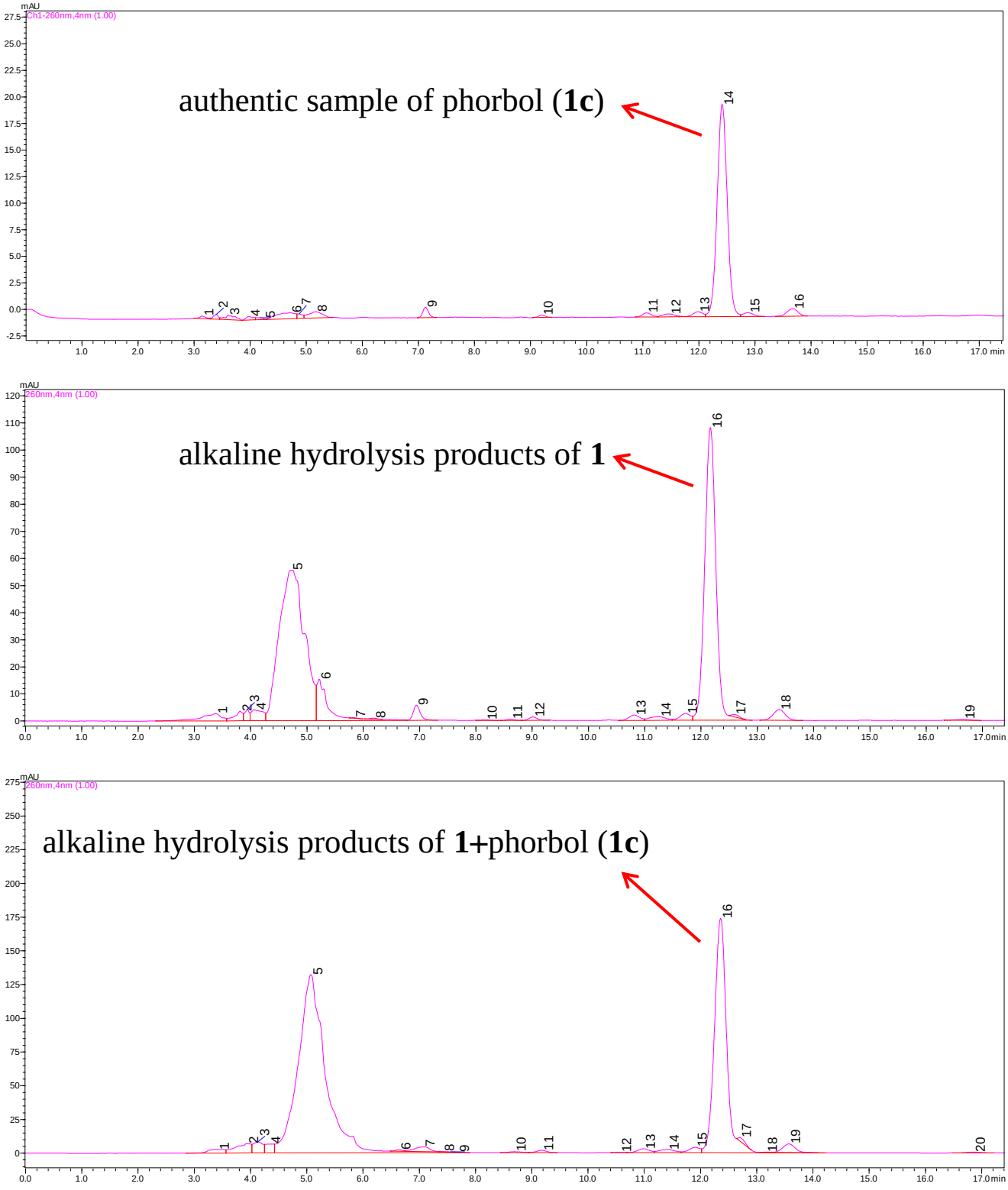


Fig. S3. HPLC analysis of the hydrolyzed products of **1**.

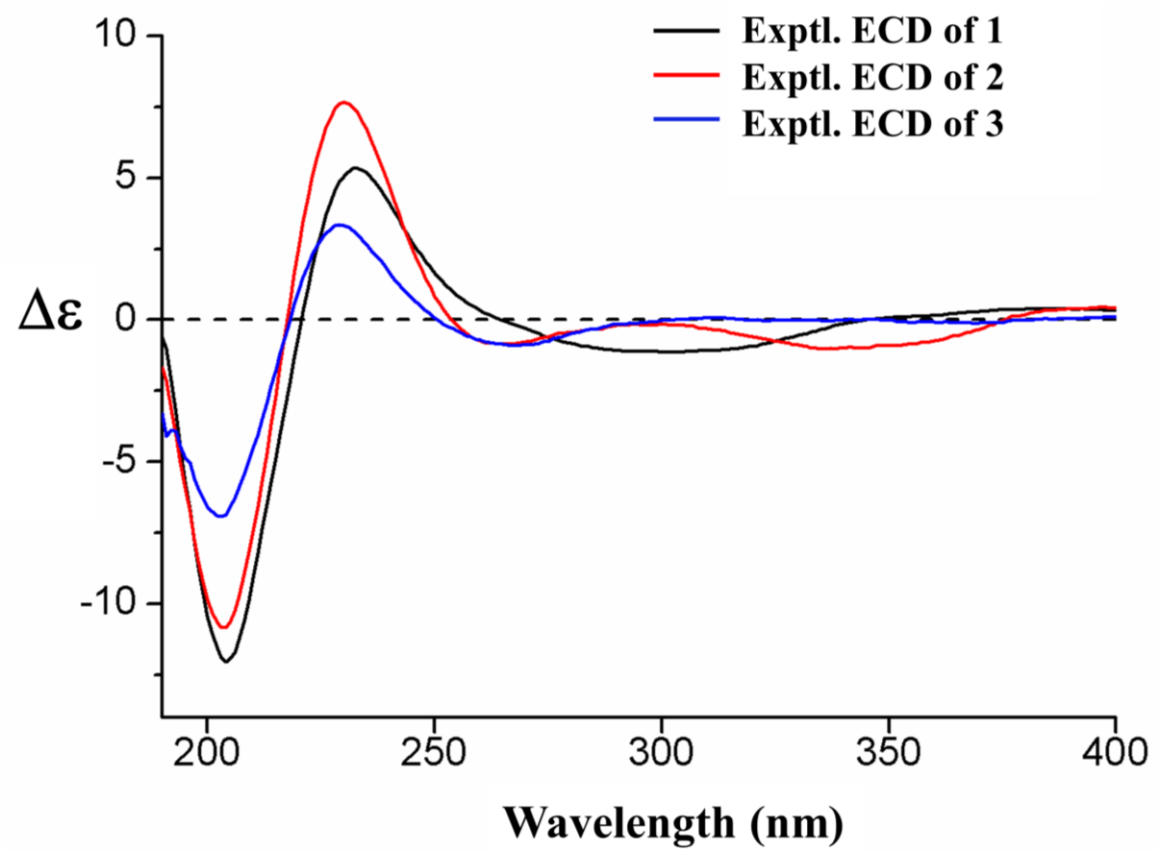


Fig. S4. Experimental ECD curves of compounds **1–3**.

Table S1. Viability of RAW 264.7 cells under the treatment of compounds **1–6**.

compounds	Viability (%) at 20 μM	Viability (%) at 50 μM
1	86.4	80.7
2	90.5	86.3
3	89.4	78.7
4	85.3	80.2
5	85.7	86.4
6	86.0	82.1

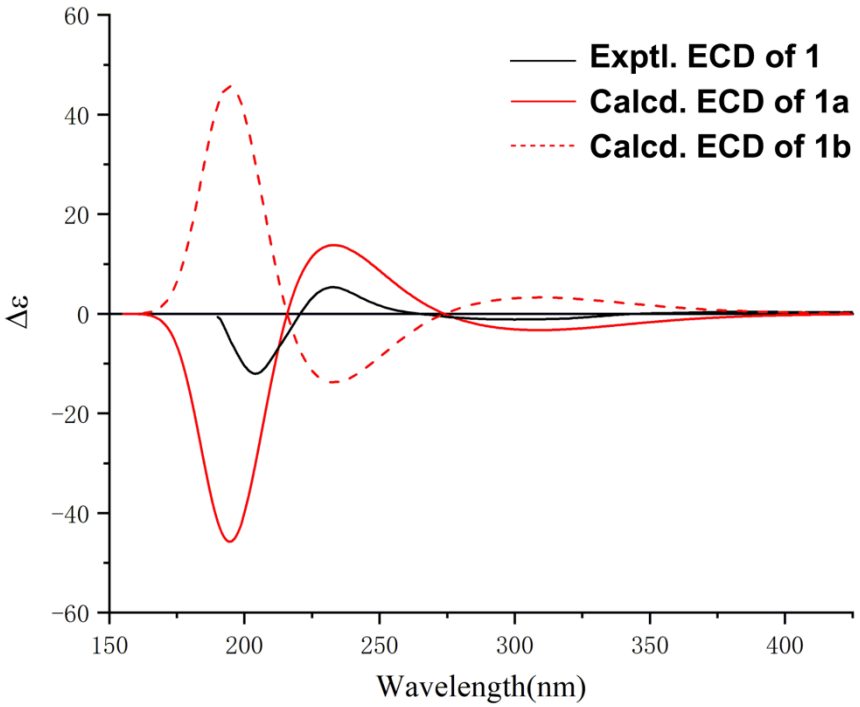


Fig.S5. Experimental and calculated ECD spectra of **1.**

The absolute configuration of **1** was studied by comparison of its experimental and simulated electronic circular dichroism (ECD) spectra using the quantum chemical time-dependent density functional theory (TDDFT) method. As shown in Fig.S5, the experimental ECD spectrum of **1** showed three Cotton effects around 205 (–), 229 (+), and 300 (–) nm, respectively, which matched well with those calculated for the (4*R*,8*S*,9*S*,10*S*,11*R*,12*R*,13*S*,14*R*)-**1a**, indicating that **1** possessed the same corresponding absolute configuration. Details of ECD calculations were provided as following:

ECD calculation method of compound 1

Conformational analyses were first carried out via Monte Carlo searching using molecular mechanism with MMFF force field in the *Spartan 18* program.[1] The results showed eight lowest energy conformers for **1** within an energy window of 2.0 Kcal/mol. These conformers were reoptimized using DFT at the B3LYP/6-31G(d) level in gas phase using the Gaussian 09 program.[2] Six conformers of **1** whose relative Gibbs free energies in the range of 0–1.5 Kcal/mol were refined and considered for next step (**Fig. S6, Table S2**).

The absolute configuration of **1** was determined by quantum chemical calculations of their theoretical ECD spectra. One of the two enantiomers for **1**, (4*R*,8*S*,9*S*,10*S*,11*R*,12*R*,13*S*,14*R*)-**1a** was arbitrary chosen for theoretical studies. The theoretical ECD were calculated and compared with the corresponding experimental data. All the reoptimized conformers mentioned above for **1** were applied for theoretical ECD calculation. The energies, oscillator strengths, and rotational strengths of the first 60 electronic excitations

were calculated using the TD-DFT methodology at the M062X/TZVP level in gas phase (**Table S3**). The ECD spectrum was simulated by the overlapping Gaussian function (σ = 0.55 eV, +5 nm in horizontal axis for **1a**),[3] in which velocity rotatory strengths of the first 20 exited states for **1a** were adopted. To get the final ECD spectrum of **1**, the simulated spectra of the lowest energy conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy (ΔG). The theoretical ECD curve of (4*S*,8*R*,9*R*,10*R*,11*S*,12*S*,13*R*,14*S*)-**1b** was obtained by directly reverse that of (4*R*,8*S*,9*S*,10*S*,11*R*,12*R*,13*S*,14*R*)-**1a**.

Reference

(1) *Spartan 18*; Wavefunction Inc.:Irvine, CA.

(2) *Gaussian 09*, Revision A.1, 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, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; 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, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(3) Grimblat, N.; Zanardi, M. M.; Sarotti, A. M. *J. Org. Chem.* **2015**, *80*, 12526−12534.

Conformers and energy analysis

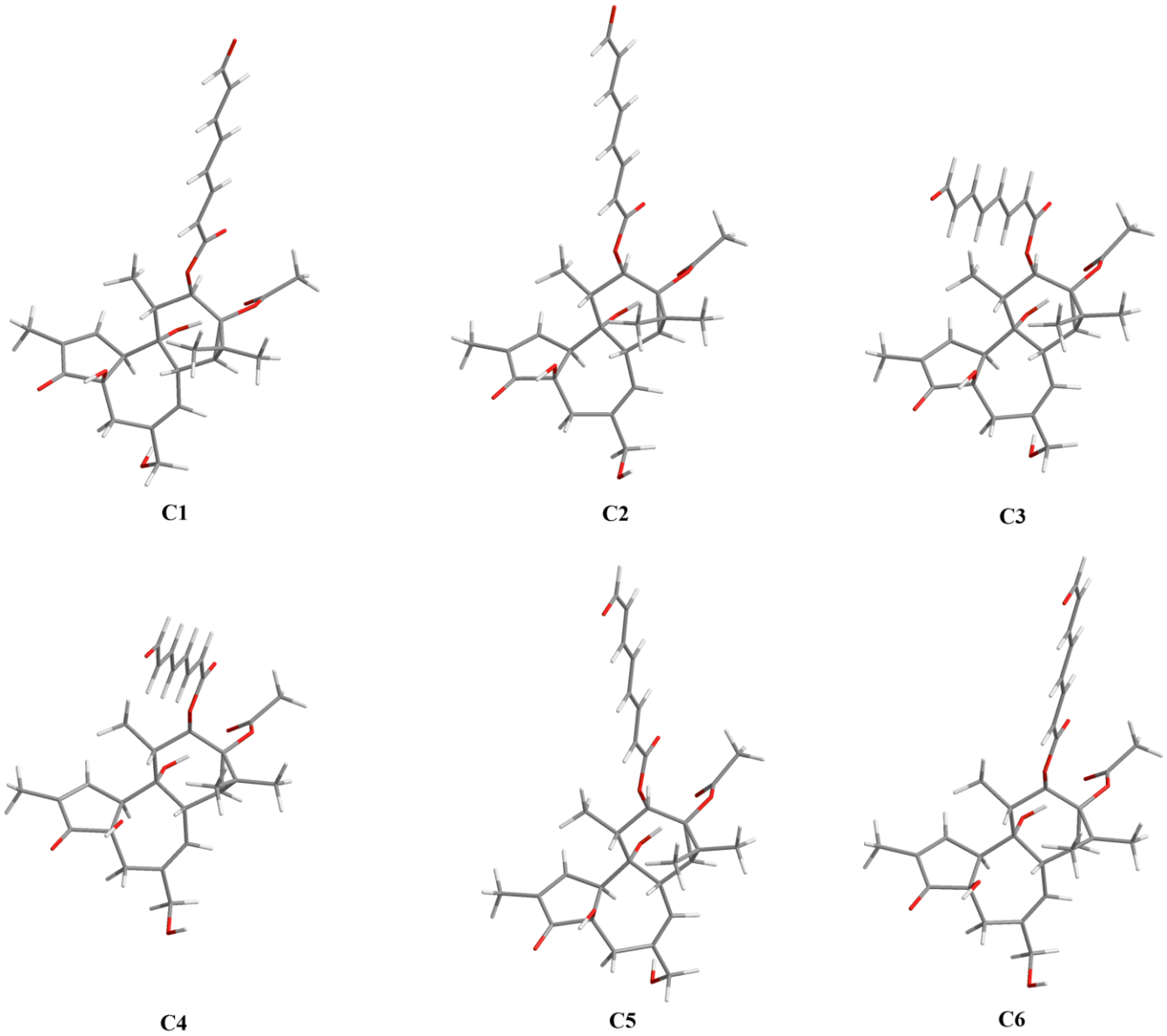


Fig. S6. B3LYP/6-31G(d) optimized lowest energy conformers for **1**.

Table S2. Energy (298.15 K) analysis for **1**.

Conf.	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
C1	-1841.231085	0	0.492786307
C2	-1841.230269	0.51204816	0.207555005
C3	-1841.229492	0.99962343	0.091107828
C4	-1841.228709	1.49096376	0.039739003
C5	-1841.229758	0.83270577	0.120772935
C6	-1841.228888	1.37863947	0.048038922

ECD data

ECD spectrum of each conformation is simulated according to the overlapping Gaussian functions expressed as:

$$\Delta\varepsilon(E)=\frac{1}{2.296\times10^{-39}\sqrt{\pi}\sigma}\sum_{i}^{A}\Delta E_i R_i e^{[-(E-\Delta Ei)^2/\sigma^2]}$$

Where σ is half the bandwidth at 1/e peak height and expressed in energy units. The parameters ΔE_i and R_i are the excitation energies and rotational strengths for the transition *i*, respectively. The above function is converted to Δε, λ (wavelength) correlations as:

$$\Delta\varepsilon(\lambda)=\frac{1}{2.296\times10^{-39}\sqrt{\pi}\sigma}\sum_{i}^{A}\Delta E_i R_i e^{[-(1240/\lambda-\Delta Ei)^2/\sigma^2]}$$

and then simulation was accomplished by using the Excel 2003 and the Origin 9.1 software. To get the final spectra, all the simulated spectra of conformations of each compound were averaged according to their energy and the Boltzmann distribution theory expressed as:

$$\frac{N_i^*}{N}=\frac{g_i e^{-\varepsilon_i/k_B T}}{\sum g_i e^{-\varepsilon_i/k_B T}}$$

Table S3. Calculated ECD data for **1** in gas phase.

state	C1		C2		C3		C4		C5		C6	
	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*	Excitation energies(eV)	Rotatory Strengths*
1	3.3485	0.0651	3.3484	0.0687	3.3499	-0.0434	3.3497	-0.0406	3.2587	0.0178	3.2586	0.031
2	3.7334	-3.1735	3.7362	-2.7167	3.7334	0.2678	3.7364	0.7378	3.733	-3.5224	3.7356	-2.9932
3	4.1158	-22.739	4.1159	-22.0171	4.1371	29.8658	4.1372	23.2779	3.9851	-18.2027	3.9853	-18.8706
4	4.6885	-3.5367	4.6884	-3.5574	4.6294	-12.12	4.6292	-12.2055	4.6877	-3.4614	4.6877	-3.4751
5	4.9151	0.7035	4.9185	0.6677	4.8671	2.7246	4.8699	2.5492	4.8997	0.7111	4.9034	0.6658
6	5.3203	42.4687	5.3182	49.8011	5.3198	34.2156	5.3176	41.9847	5.3209	30.8271	5.3186	38.6076
7	5.451	-0.0196	5.4588	0.003	5.394	-0.0495	5.4024	-0.0627	5.4342	-0.0884	5.4424	-0.0577
8	5.6012	0.3772	5.5934	0.8946	5.5356	0.1463	5.5306	0.6778	5.582	0.2636	5.5748	0.6694
9	5.629	1.9251	5.6428	1.295	5.5798	3.2665	5.5905	2.8048	5.5989	2.0977	5.5998	2.8502
10	5.685	-2.3439	5.6915	-2.7348	5.6473	0.1198	5.6535	0.502	5.6161	3.9827	5.6292	2.5439
11	5.7453	5.5004	5.7441	6.0903	5.7467	1.7582	5.7456	1.7489	5.673	-0.8341	5.6803	-0.9639
12	5.7703	-1.6301	5.7703	-1.7235	5.7842	-0.5821	5.7844	-0.6915	5.7449	1.7281	5.744	2.0105
13	5.8642	31.0752	5.8506	25.068	5.8655	29.5813	5.8515	22.9162	5.8578	-44.4455	5.8481	-22.6864
14	6.0649	0.7946	6.0657	0.073	6.1158	4.3764	6.1173	4.6481	5.8696	82.9505	5.8659	55.6515
15	6.1919	6.314	6.194	6.5459	6.1632	-0.6403	6.1628	-0.6939	6.1699	4.7481	6.1725	5.2175
16	6.2592	-1.3064	6.2586	-0.9397	6.2655	0.5279	6.2652	0.5584	6.2868	0.7087	6.2864	0.9604
17	6.3615	7.0702	6.3719	4.3912	6.3663	7.5379	6.3762	4.7076	6.3608	7.0686	6.3708	4.3724
18	6.4833	-152.687	6.4847	-146.462	6.4844	-156.604	6.4861	-148.948	6.4825	-153.859	6.4838	-149.091
19	6.5612	-2.8655	6.5605	-3.699	6.5321	3.1376	6.5309	2.866	6.4896	1.1525	6.4896	2.3982
20	6.632	-28.9962	6.6062	-24.5394	6.6256	-20.5984	6.6028	-22.4583	6.5443	0.6659	6.5438	-0.3418
21	6.6448	0.4988	6.6439	0.4225	6.6367	0.0478	6.6156	0.149	6.6264	-21.4542	6.603	-20.8004
22	6.7394	-0.2291	6.6809	0.1644	6.6685	-13.8532	6.65	0.0026	6.6764	-10.3397	6.6619	-2.4377

23	6.7438	-3.2759	6.7315	-1.2175	6.6954	-0.0679	6.6537	-6.5717	6.7225	-0.1414	6.6631	-2.8743
24	6.8544	19.7672	6.8144	24.5289	6.8106	-0.11	6.811	15.9379	6.8167	0.5404	6.8125	23.405
25	6.8627	8.8601	6.8697	1.8194	6.8549	28.4059	6.8169	9.9783	6.8507	2.4489	6.8177	0.8258
26	6.8928	-1.7527	6.8758	-2.6582	6.8807	-2.2021	6.8658	-1.1379	6.8573	25.2667	6.8583	1.7848
27	6.9363	37.2817	6.9285	36.7548	6.9359	36.7642	6.928	36.9471	6.8796	-3.2153	6.8677	-2.8166
28	6.9851	1.3202	6.9877	1.3478	6.9449	-0.3	6.9472	-1.1945	6.9048	-1.2116	6.9074	-1.1104
29	7.0033	-3.4471	7.0063	-3.6137	6.9929	-0.1311	6.9981	-0.5709	6.9328	38.9105	6.925	36.9957
30	7.0928	4.158	7.0922	2.8985	7.0317	-1.0926	7.0367	-0.7396	6.995	0.2078	6.9943	-0.1528
31	7.1145	-3.6073	7.1236	-1.9199	7.0915	-0.0333	7.0909	0.3928	7.0749	0.9818	7.0831	1.1738
32	7.1544	16.8016	7.1724	80.2289	7.1567	12.6519	7.1743	79.9635	7.1291	-11.9888	7.1316	-10.5425
33	7.1878	-3.1142	7.1853	-5.5536	7.1922	11.2	7.1929	-15.63	7.1494	21.548	7.1697	71.6414
34	7.1907	7.3097	7.1875	-3.9933	7.2102	24.0475	7.2111	-4.0609	7.1894	7.8785	7.1818	8.3601
35	7.2041	27.2589	7.2501	17.711	7.2123	-0.1754	7.2396	0.9563	7.2003	27.9468	7.2497	21.3694
36	7.2843	-0.1022	7.2841	-0.1919	7.242	-0.8107	7.2481	27.9891	7.2732	1.2951	7.269	-4.0014
37	7.3228	1.4729	7.3181	0.2545	7.2625	0.448	7.2603	0.1437	7.3174	3.7853	7.3175	12.1969
38	7.3557	7.5472	7.3372	2.7572	7.3527	7.4714	7.3355	1.5153	7.3219	-5.4652	7.3215	-5.3674
39	7.387	0.4543	7.3766	46.8806	7.3908	3.8913	7.3775	42.8592	7.3545	0.8303	7.3373	-6.2105
40	7.3902	3.3804	7.3872	-14.8007	7.3962	4.9017	7.391	-2.5609	7.358	-1.0486	7.3576	-11.3528
41	7.4133	96.2248	7.4287	-8.9127	7.4125	101.5263	7.4301	3.8209	7.3886	3.4917	7.3763	43.5706
42	7.4348	3.6134	7.4358	15.5772	7.4532	6.6588	7.46	4.702	7.4099	102.575	7.4273	13.4587
43	7.4847	18.2746	7.4751	33.3725	7.4865	14.1052	7.4756	29.6958	7.4475	-7.878	7.4451	-1.9105
44	7.5094	16.1221	7.5018	1.6822	7.4888	-0.8361	7.4911	0.1336	7.4644	29.2099	7.4668	-3.1856
45	7.5246	0.937	7.5233	6.4501	7.5092	21.3232	7.5021	2.0508	7.4851	12.977	7.4732	29.3683
46	7.5359	-4.4671	7.5376	-31.9835	7.5168	-13.0367	7.5166	-3.1557	7.5063	5.5544	7.5011	3.9127
47	7.5484	18.3068	7.5474	1.6092	7.5546	-10.5852	7.5437	-23.8971	7.5286	0.3176	7.5335	-1.2832
48	7.5558	-21.1133	7.5578	17.583	7.562	8.3868	7.569	-18.7491	7.5444	17.5013	7.5414	-18.6286
49	7.5664	8.535	7.5683	-25.1275	7.5783	0.589	7.5783	14.2153	7.5533	-23.8293	7.5581	3.9288

50	7.5797	3.2591	7.5774	22.1438	7.5885	-20.5159	7.6101	3.328	7.5791	-0.2826	7.5689	-3.1467
51	7.5896	-11.4354	7.6387	11.8156	7.6129	8.576	7.6364	4.5231	7.5859	-13.6802	7.5928	0.8351
52	7.6517	-7.885	7.6683	-12.1253	7.6355	1.2425	7.6431	10.8954	7.6003	0.2919	7.6354	2.5243
53	7.684	7.4393	7.6872	-1.2684	7.6438	6.5246	7.649	-0.9703	7.6289	8.3577	7.64	20.3907
54	7.6981	6.2804	7.6957	13.1846	7.6543	-9.5894	7.6674	-10.9346	7.6384	9.5908	7.6541	8.57
55	7.7092	-3.4504	7.7204	6.3835	7.698	9.1035	7.7058	12.4802	7.6534	4.005	7.6692	-7.0193
56	7.7313	0.5943	7.7454	1.1069	7.709	-6.8185	7.7204	2.6222	7.7057	-0.4641	7.7168	4.0238
57	7.7614	4.0742	7.7656	0.8473	7.7576	3.4696	7.7654	-1.0066	7.7477	-10.2925	7.7541	-1.1878
58	7.8111	11.8847	7.8173	-1.3771	7.7846	-0.3179	7.7871	-0.1359	7.7501	1.3362	7.756	-1.0226
59	7.82	-12.5226	7.8238	-2.177	7.8087	-0.302	7.8151	1.2759	7.7652	7.6938	7.7667	1.5884
60	7.8313	3.7788	7.8396	1.5863	7.8164	2.6799	7.8359	6.4072	7.8147	1.3747	7.8164	-4.0562

NMR, ESIMS, HRESIMS, and IR spectra of compounds

Fig. S7. ^{1}H NMR spectrum of **1** in $CDCl_3$

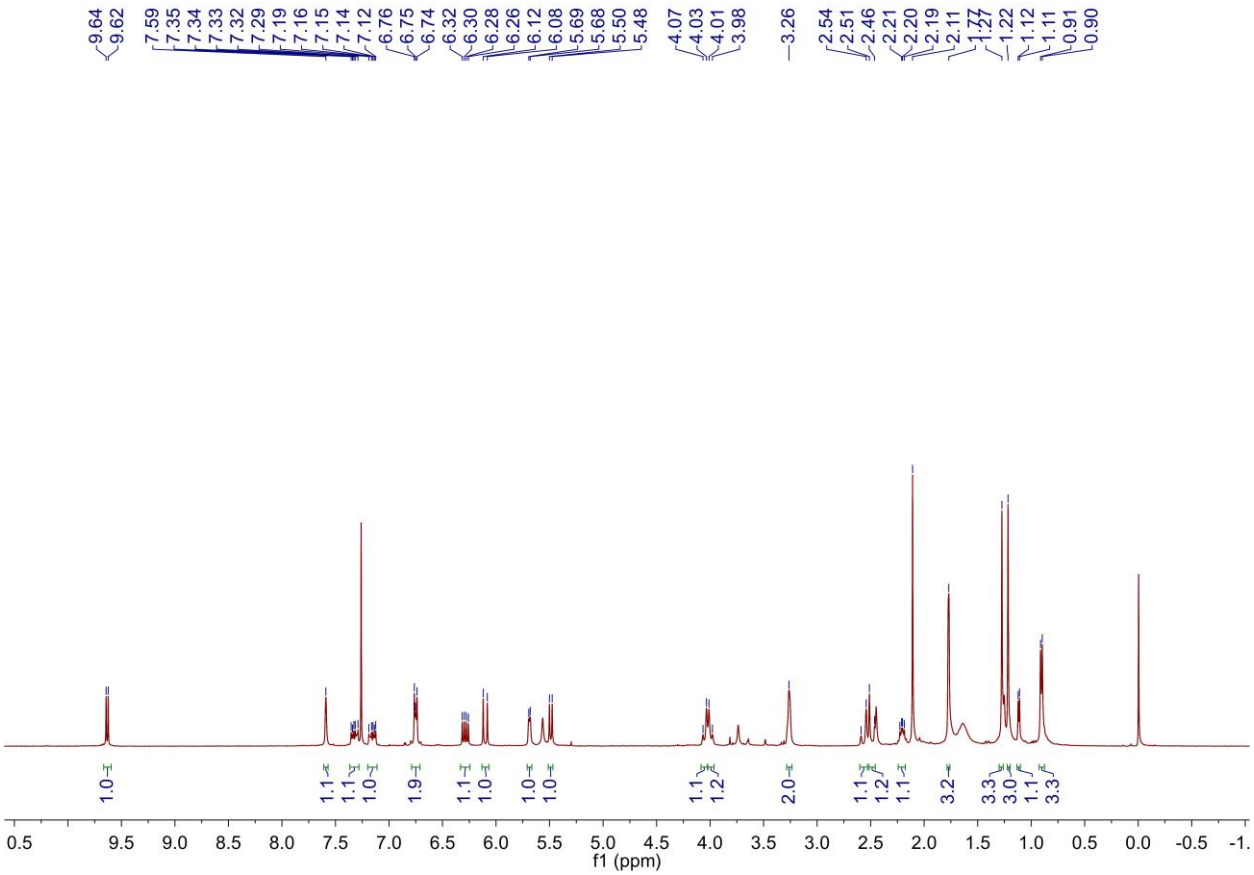


Fig. S8. ^{13}C NMR spectrum of **1** in $CDCl_3$

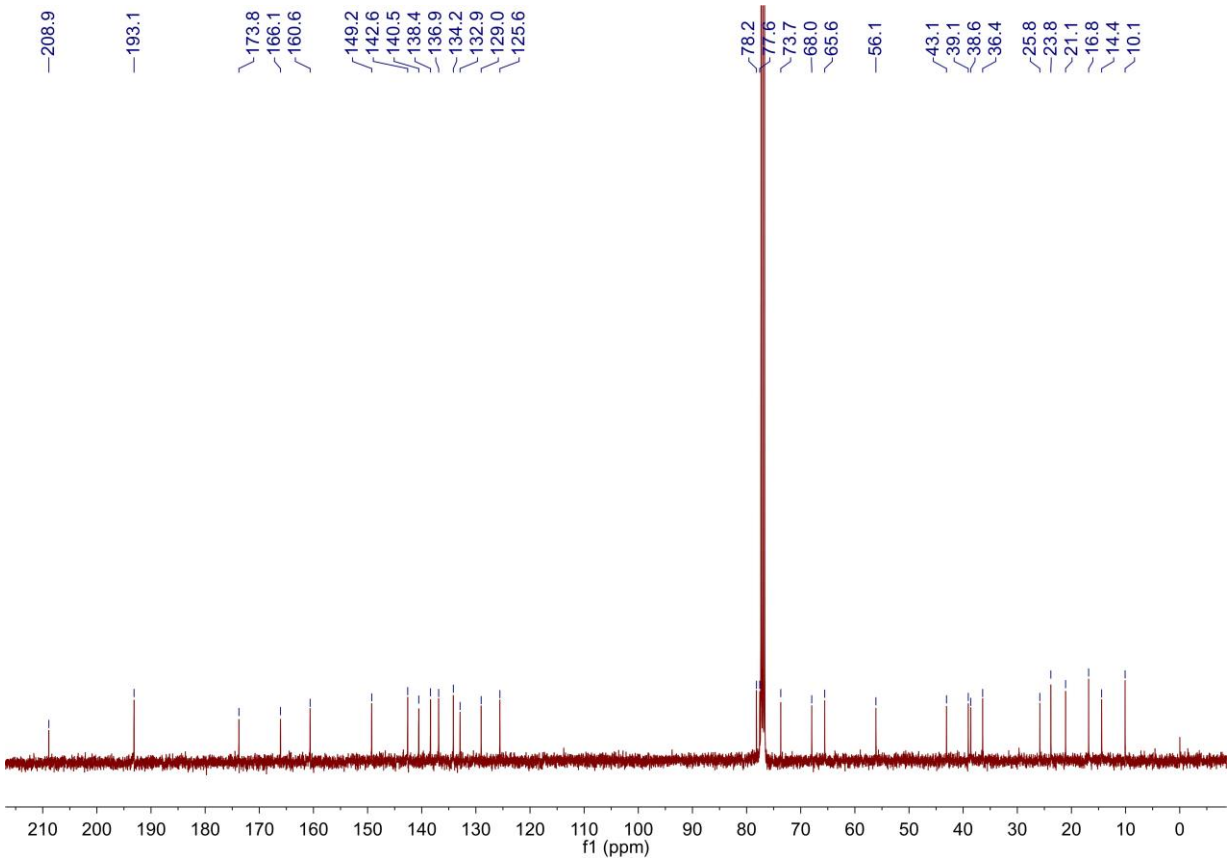


Fig. S9. HSQC spectrum of **1** in $CDCl_3$

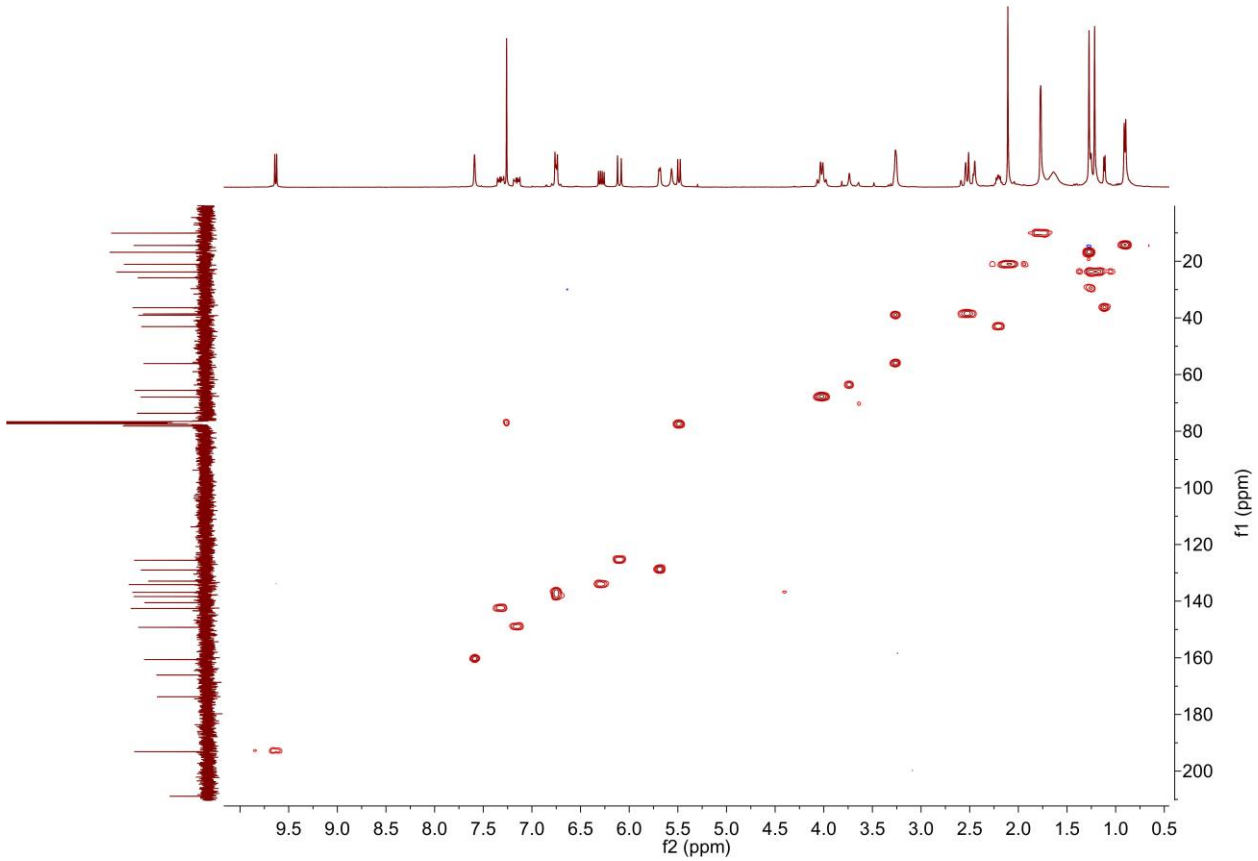


Fig. S10. HMBC spectrum of **1** in $CDCl_3$

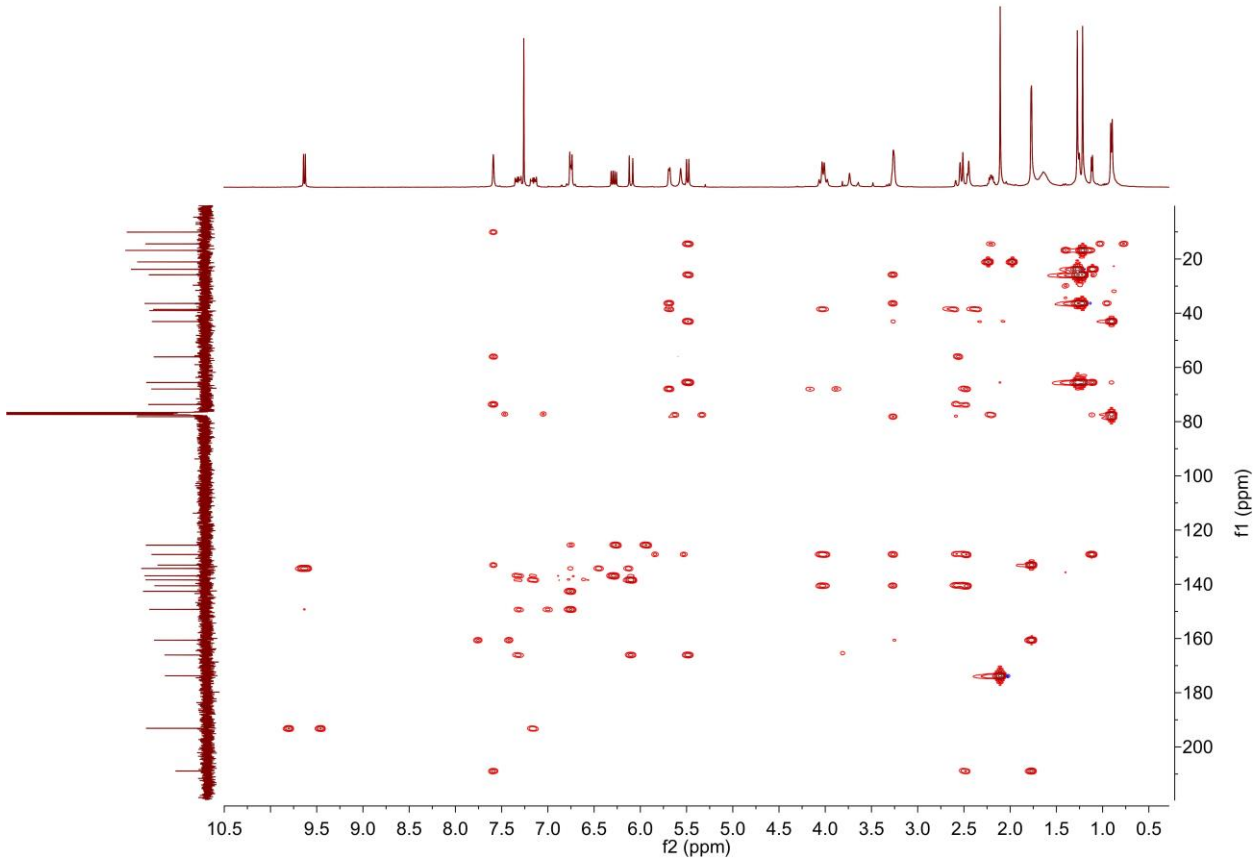


Fig. S11. $^{1}H–^{1}H$ COSY spectrum of **1** in $CDCl_3$

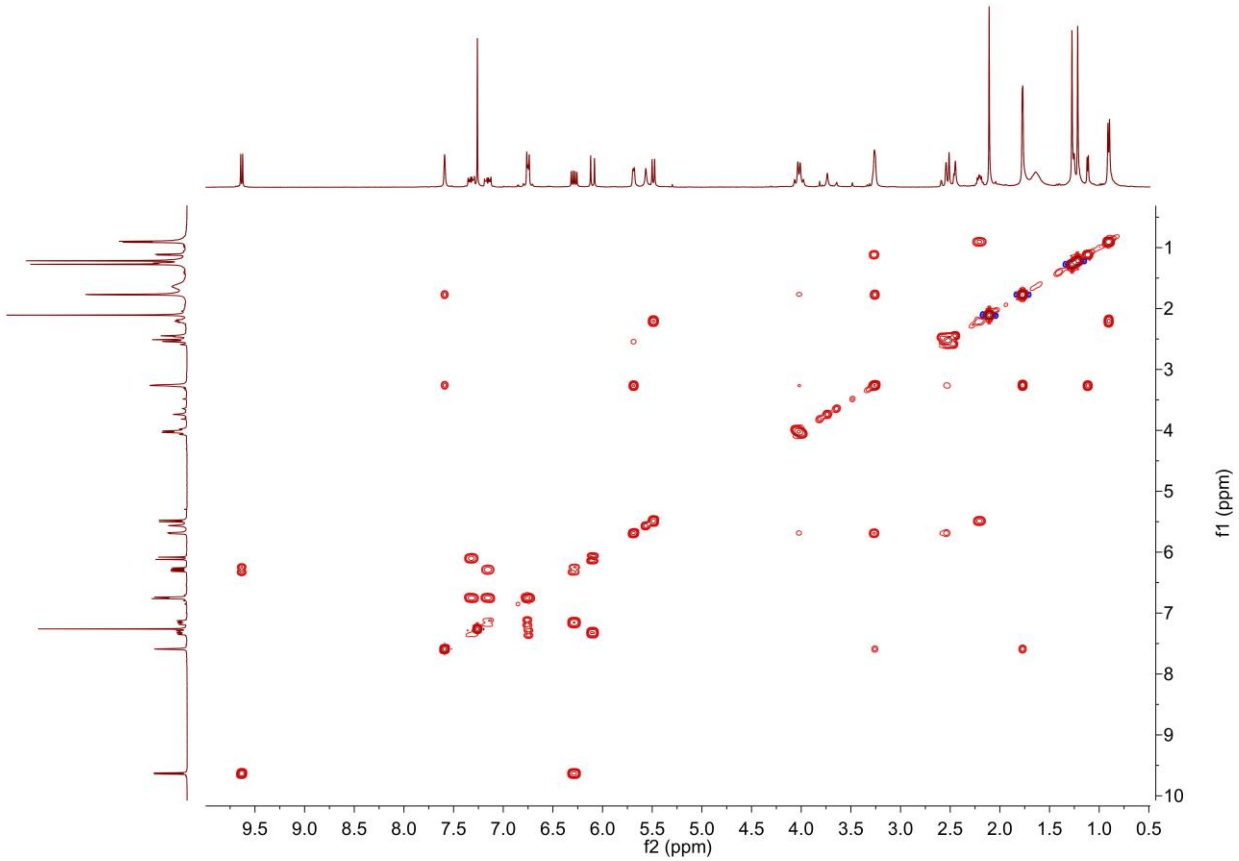


Fig. S12. NOESY spectrum of **1** in $CDCl_3$

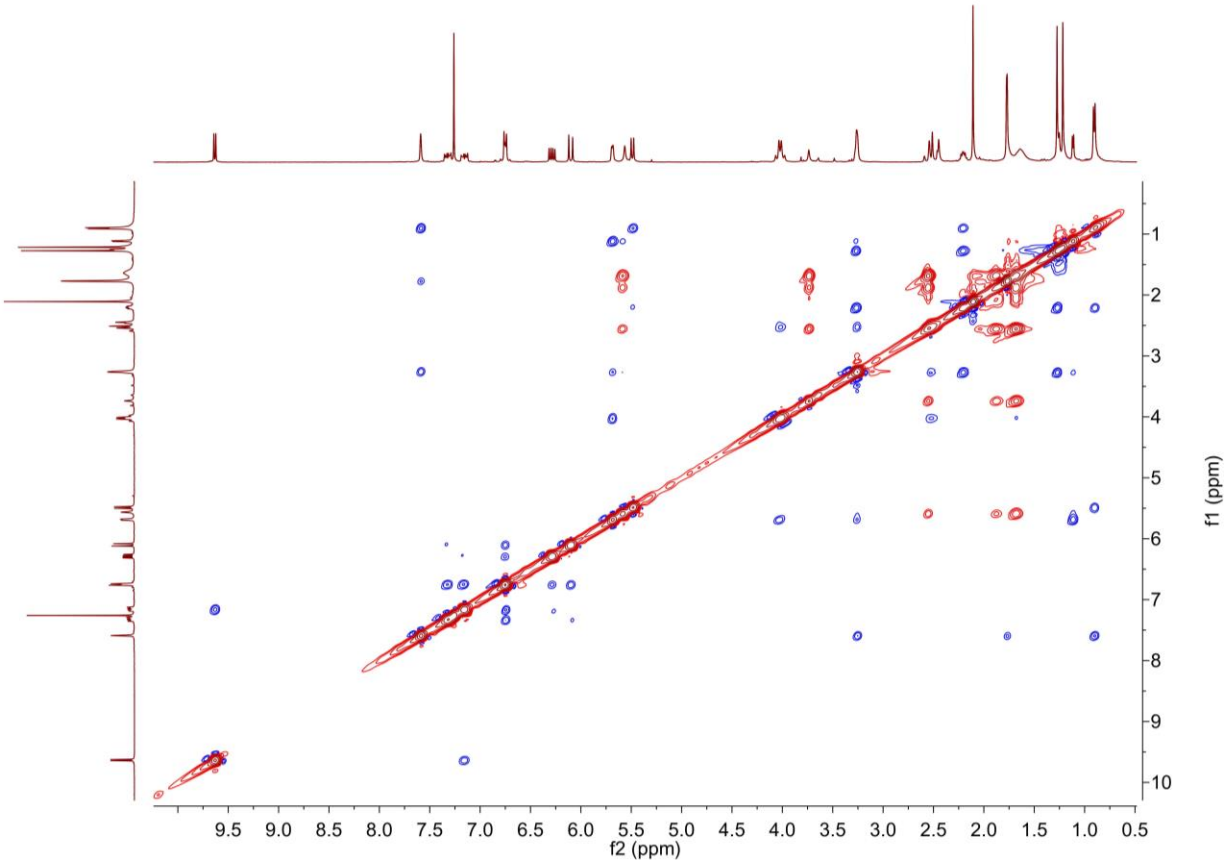
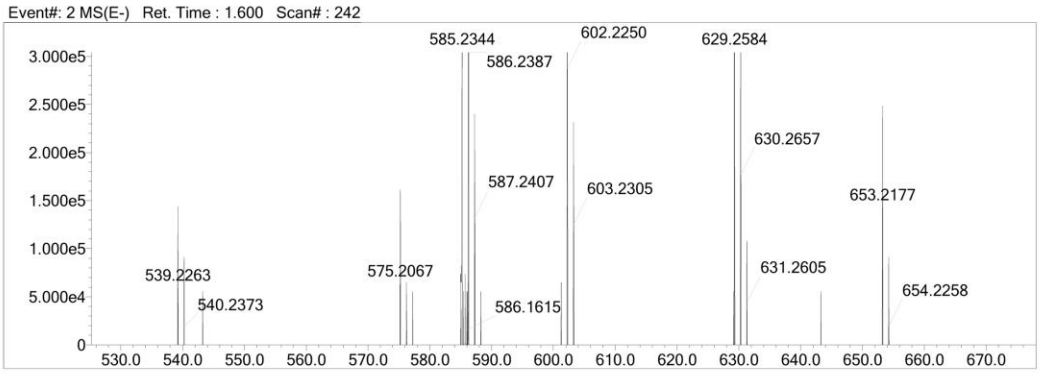
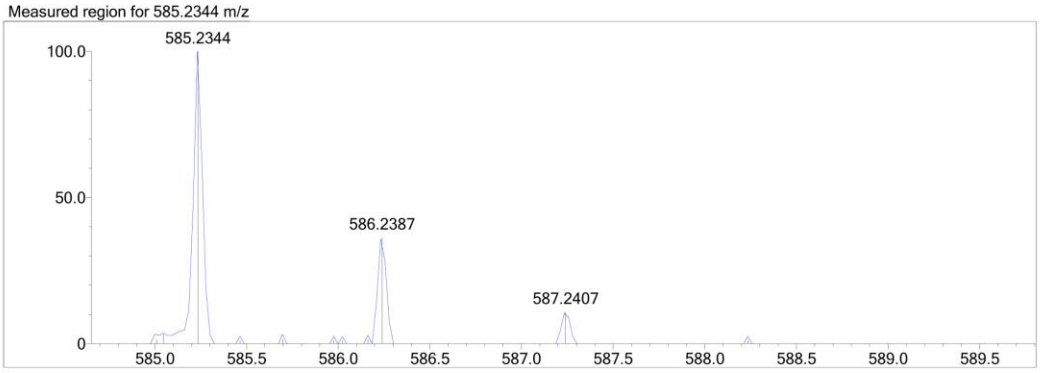
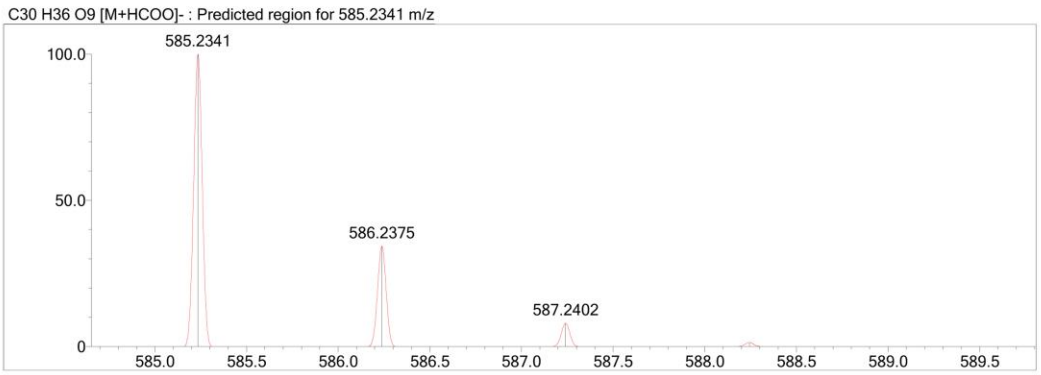


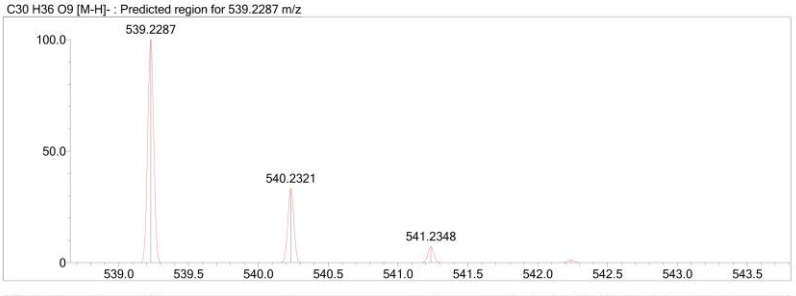
Fig. S13. HRESIMS spectrum of **1**







Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
2	84.54	C30 H36 O9	[M+HCOO]-	585.2344	585.2341	0.3	0.51	84.54	13.0



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	0.00	C30 H36 O9	[M-H]-	539.2263	539.2287	-2.4	-4.45	0.00	13.0

Fig. S14. IR (KBr disc) spectrum of **1**

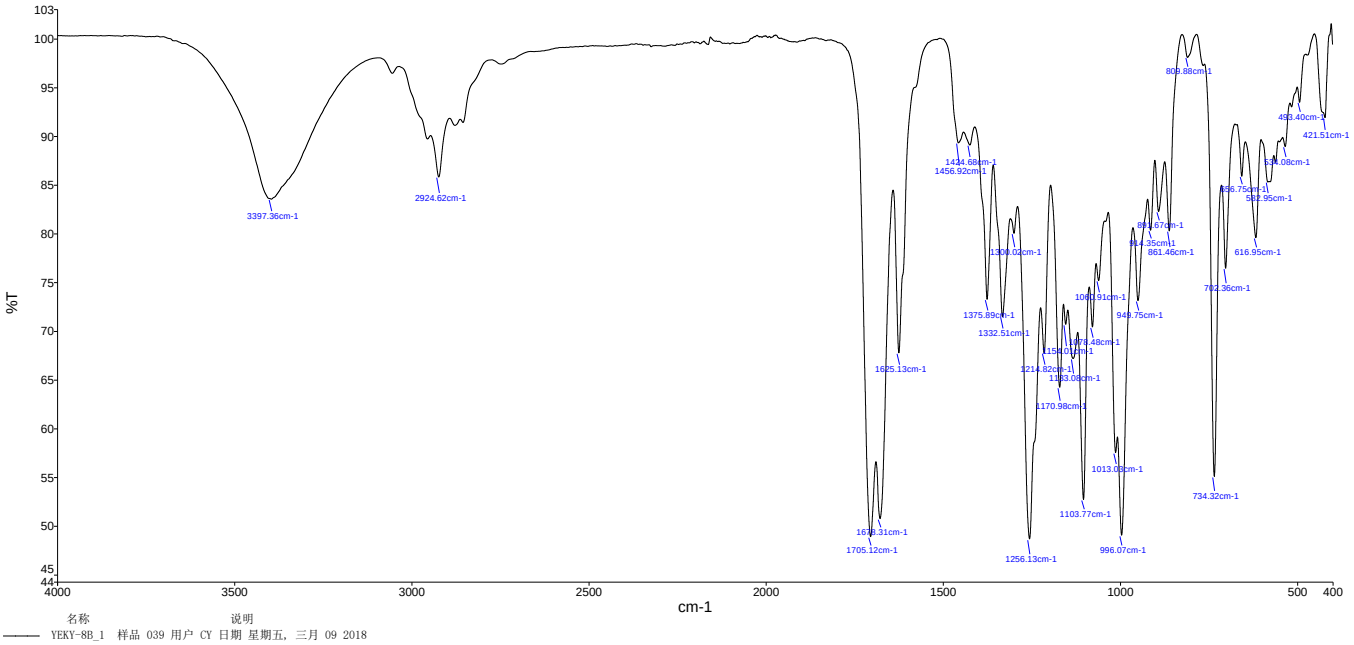


Fig. S15. ^{1}H NMR spectrum of **2** in $CDCl_3$

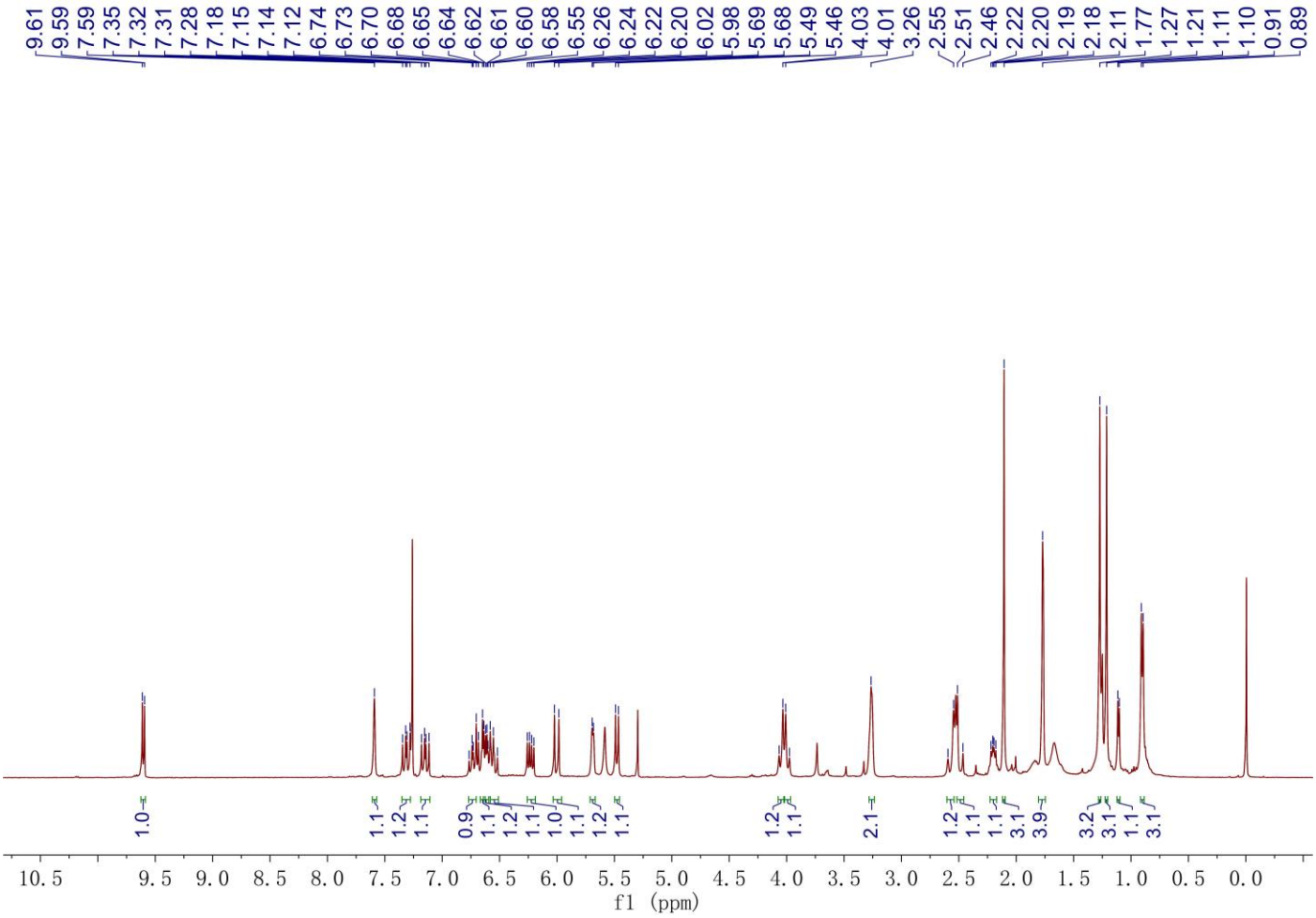


Fig. S16. ^{13}C NMR and DEPT135 spectra of **2** in $CDCl_3$

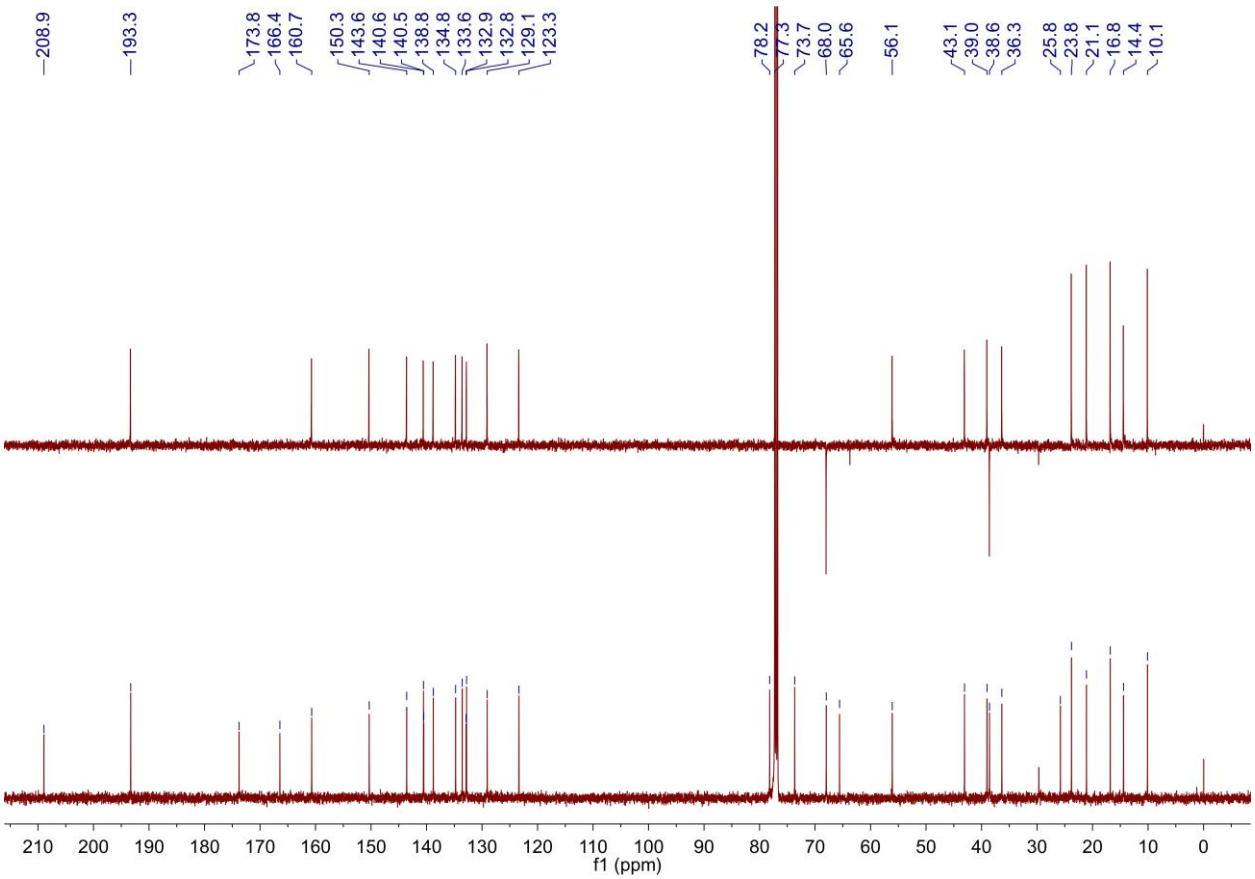


Fig. S17. HSQC spectrum of **2** in $CDCl_3$

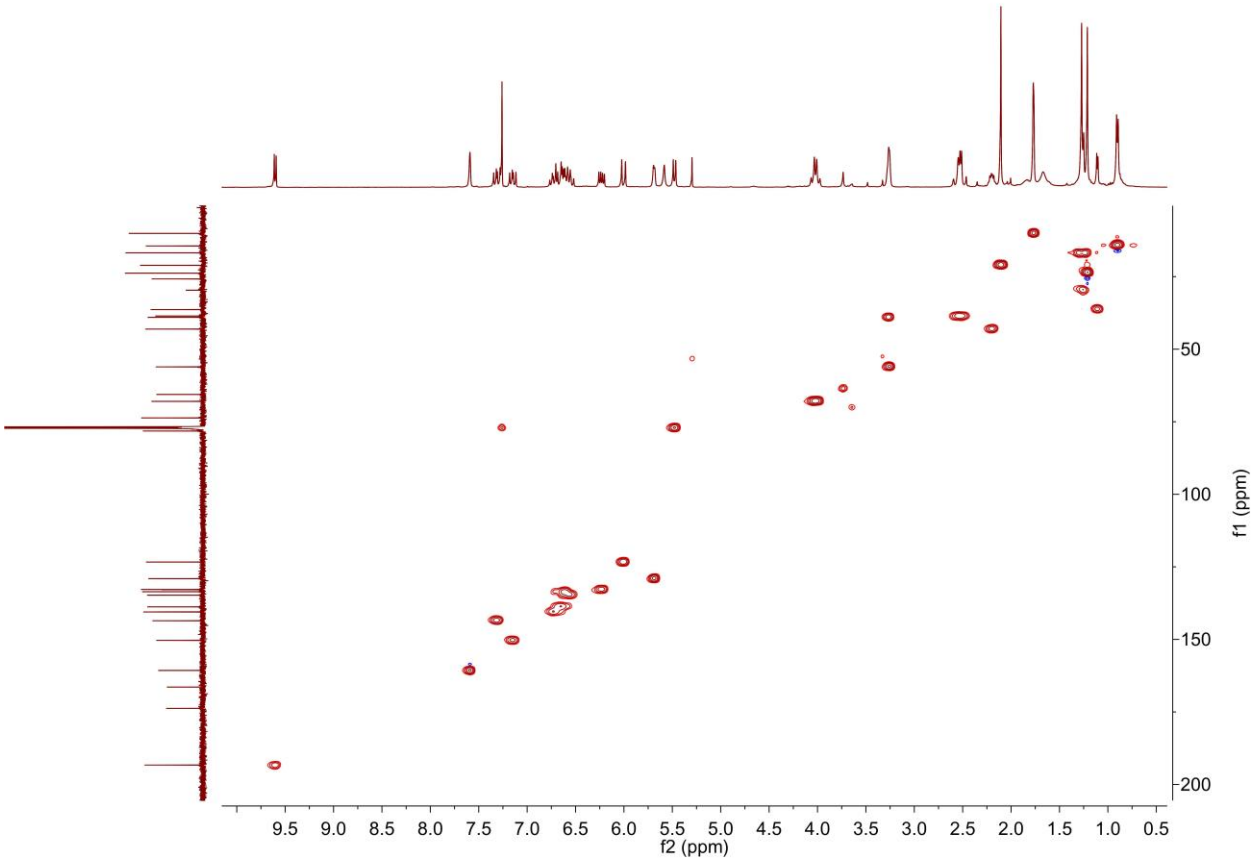


Fig. S18. HMBC spectrum of **2** in $CDCl_3$

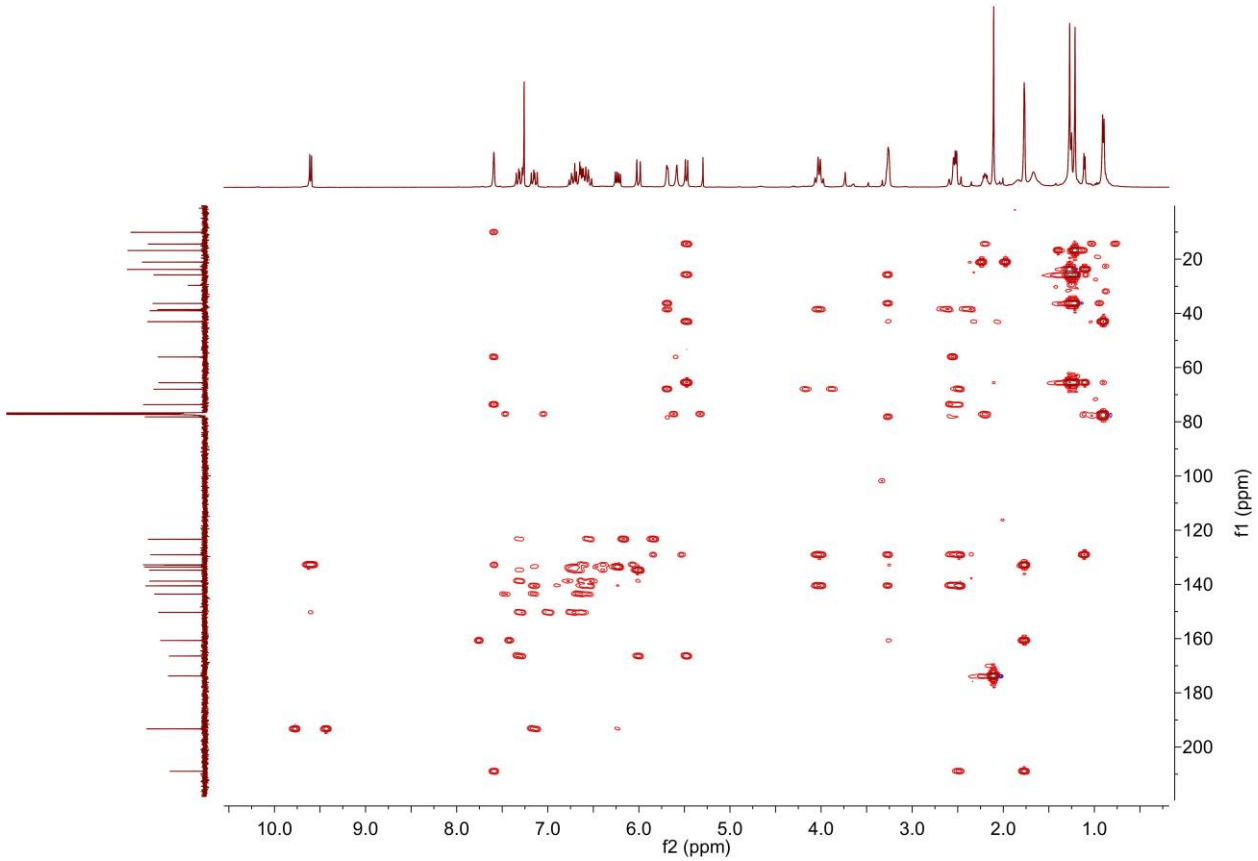


Fig. S19. $^{1}H–^{1}H$ COSY spectrum of **2** in $CDCl_3$

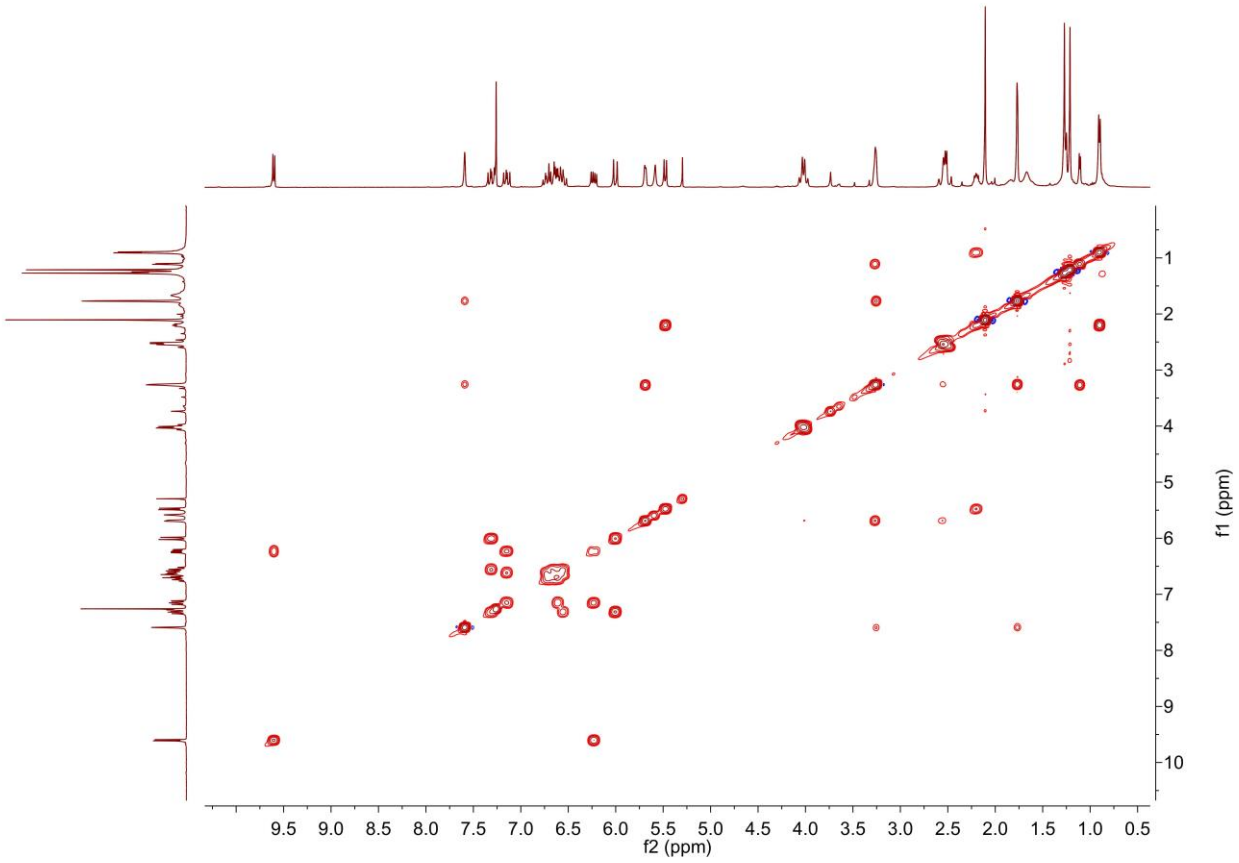


Fig. S20. NOESY spectrum of **2** in $CDCl_3$

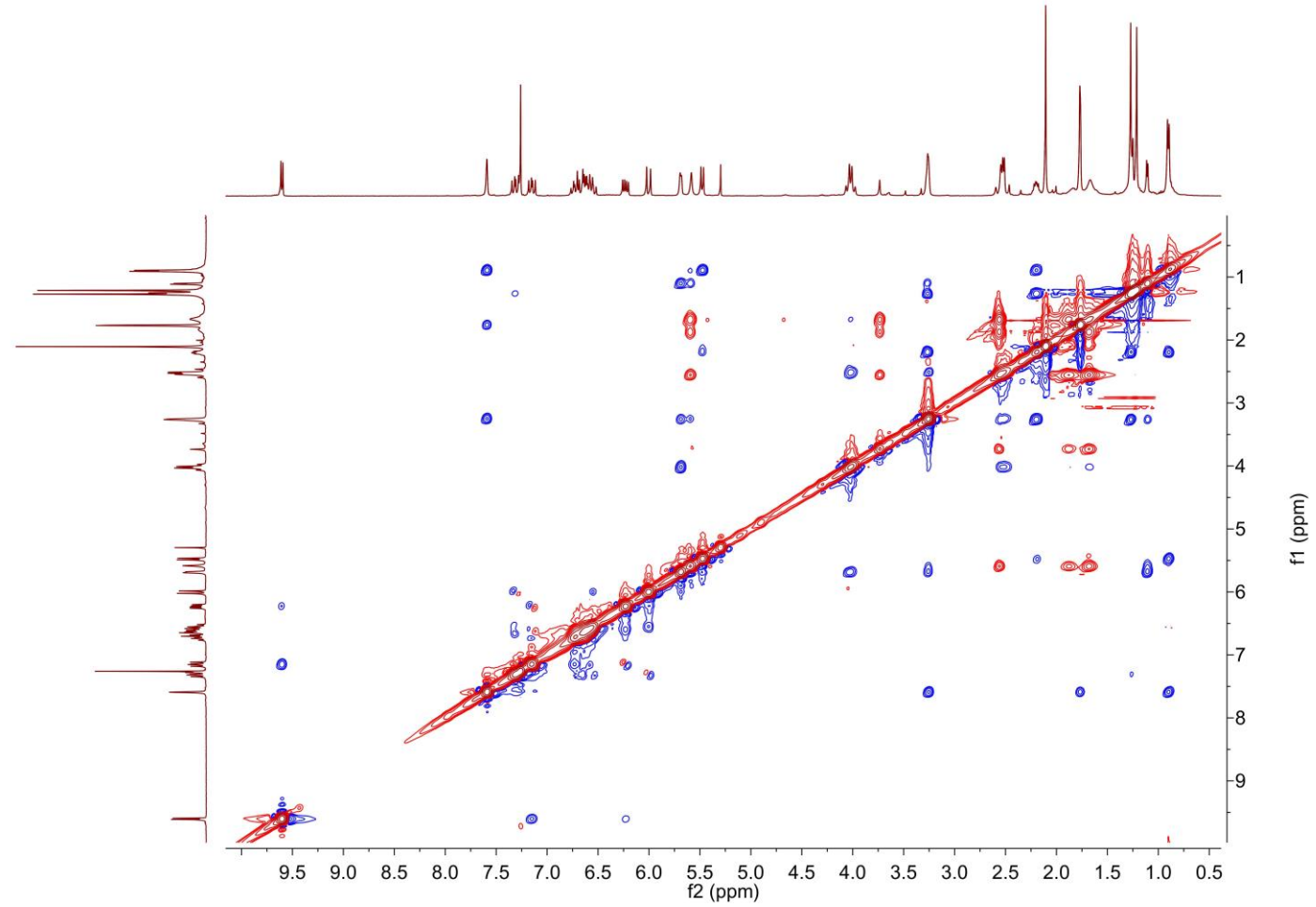


Fig. S21. IR (KBr disc) spectrum of **2**

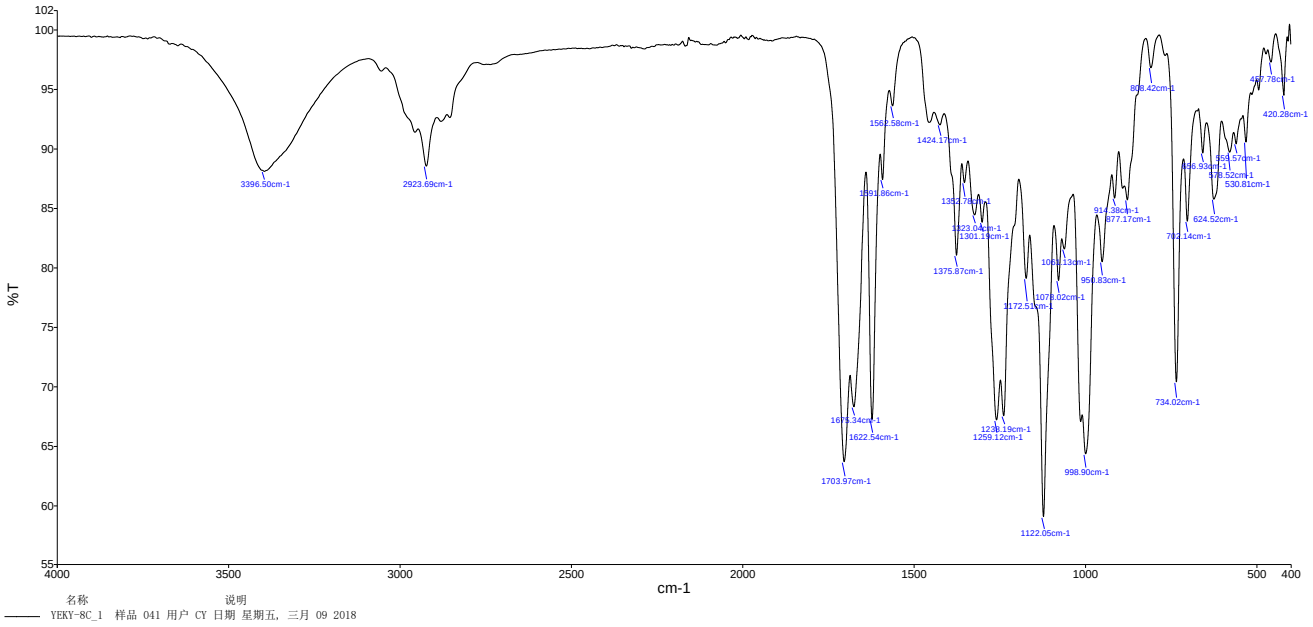
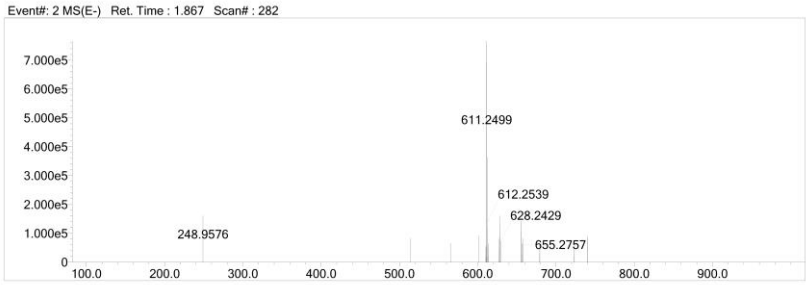
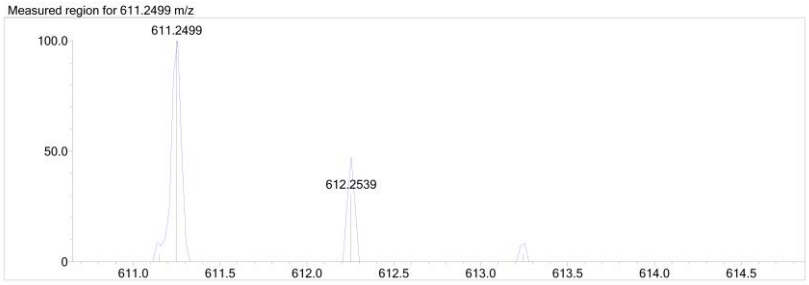
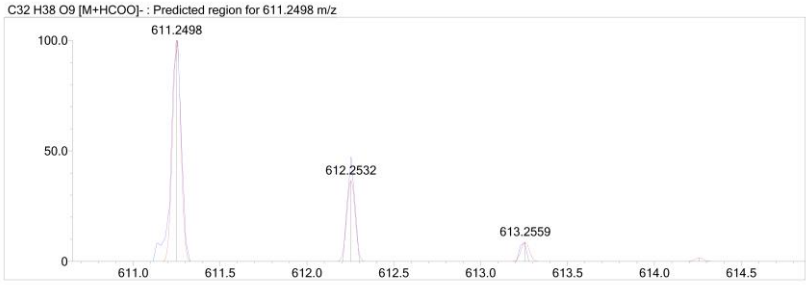


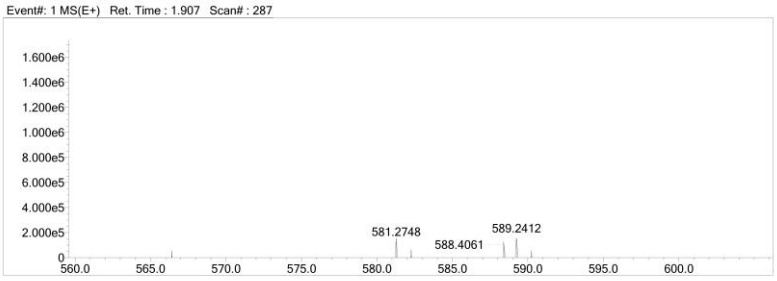
Fig. S22. HRESIMS spectrum of **2**

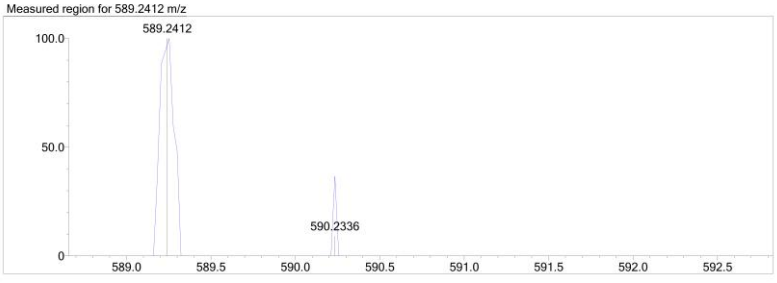


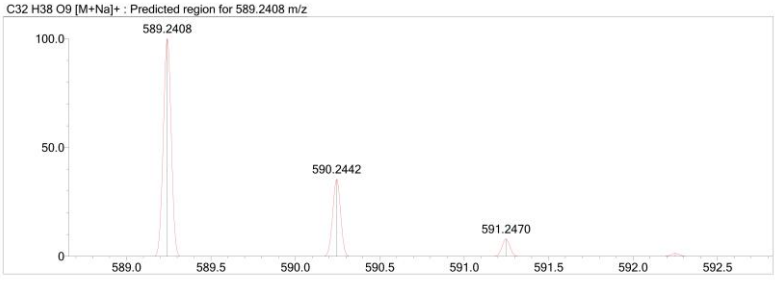




Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
2	49.18	C32 H38 O9	[M+HCOO]-	611.2499	611.2498	0.1	0.16	49.18	14.0







Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	0.00	C32 H38 O9	[M+Na]+	589.2412	589.2408	0.4	0.68	0.00	14.0

Fig. S23. ^{1}H NMR spectrum of **3** in $CDCl_3$

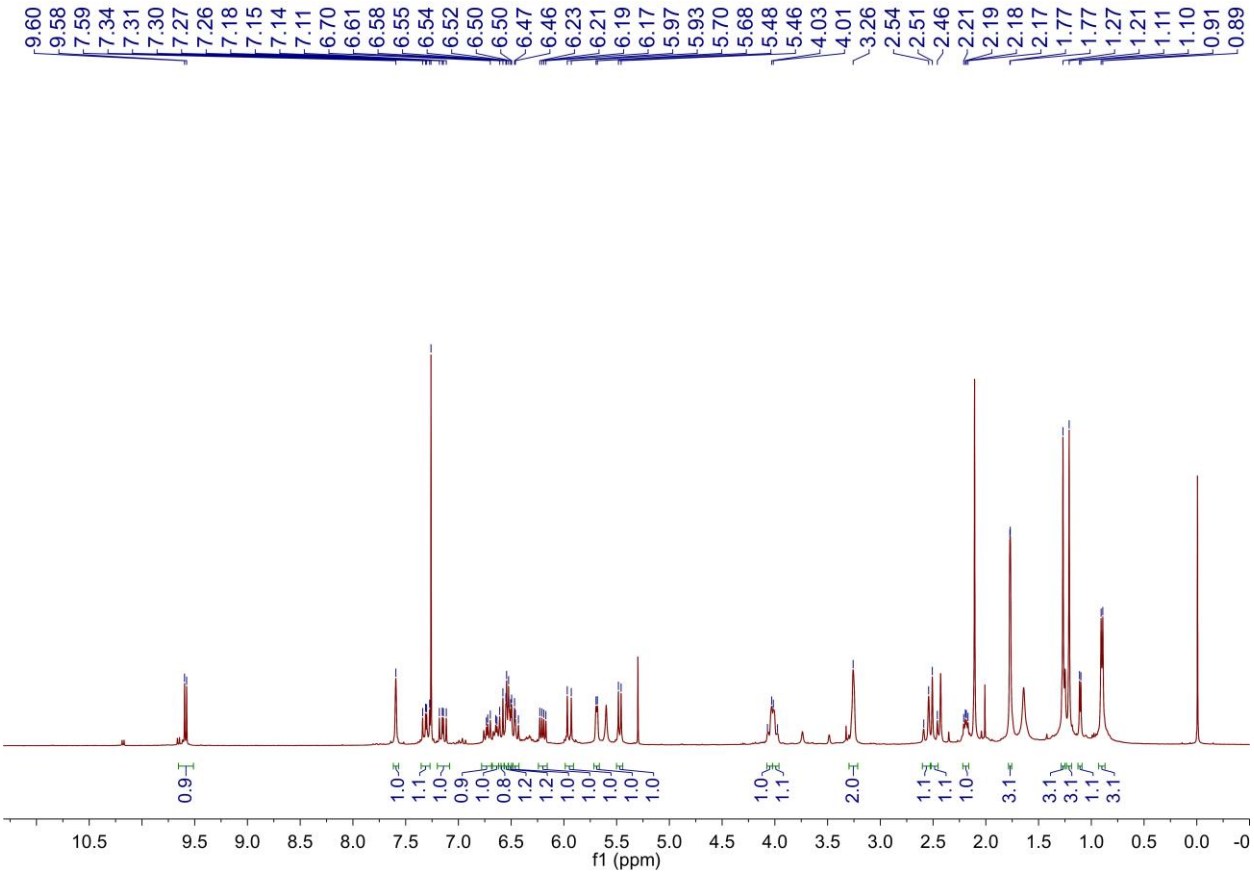


Fig. S24. ^{13}C NMR and DEPT135 spectra of **3** in $CDCl_3$

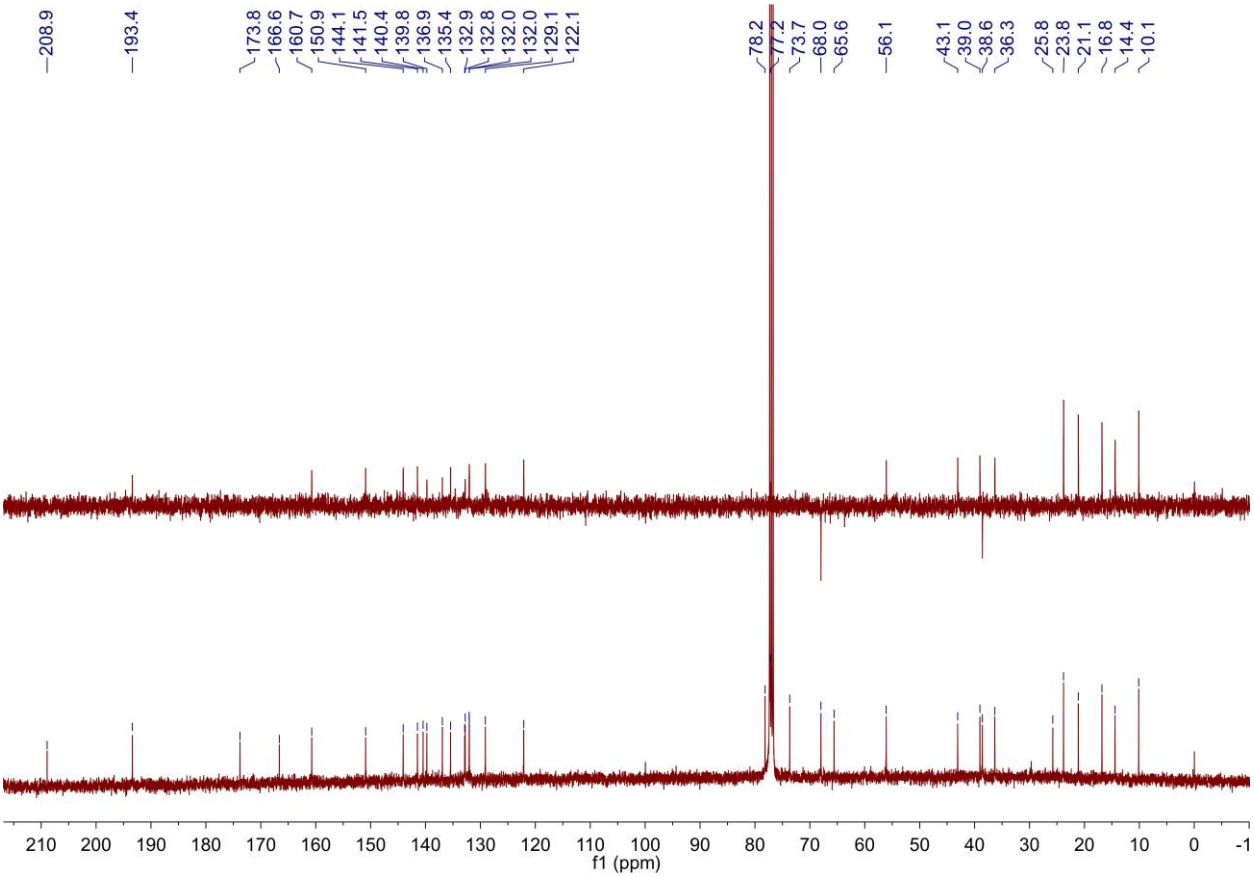


Fig. S25. HSQC spectrum of **3** in $CDCl_3$

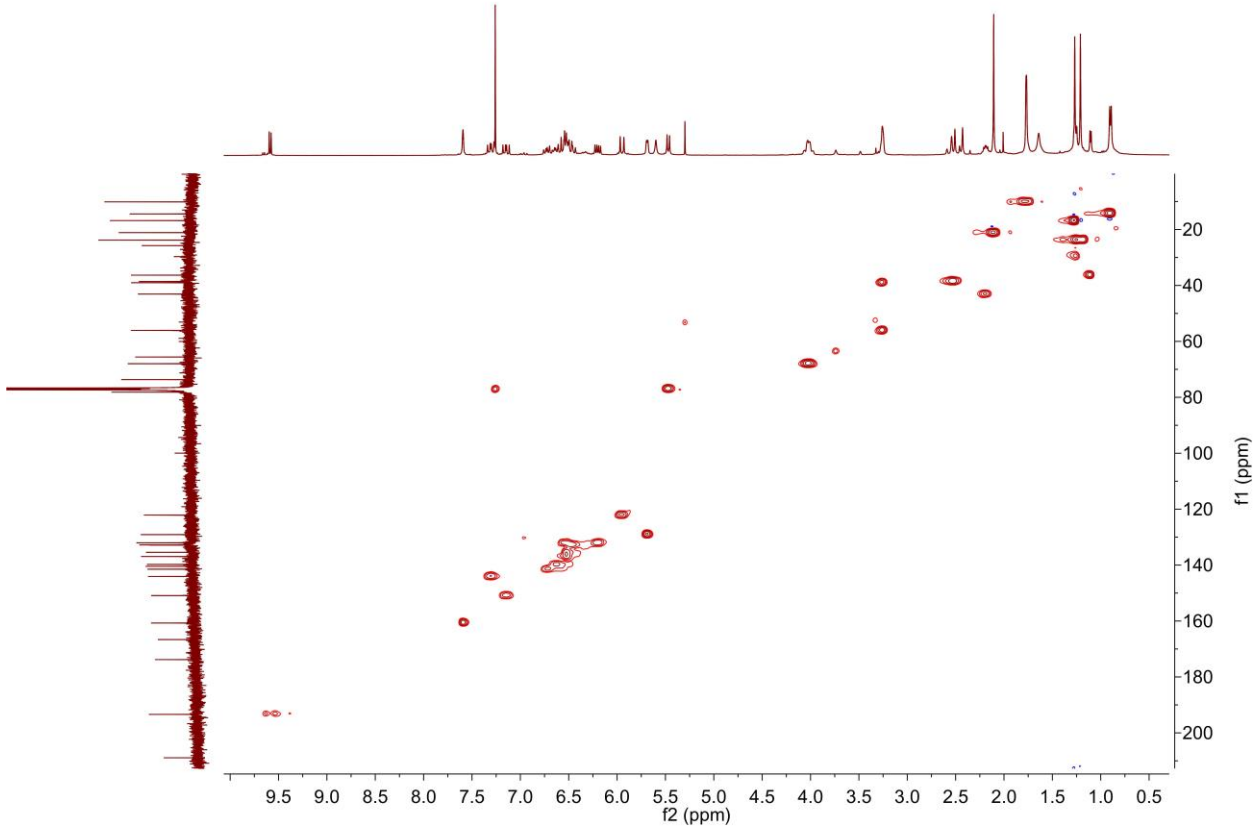


Fig. S26. HMBC spectrum of **3** in $CDCl_3$

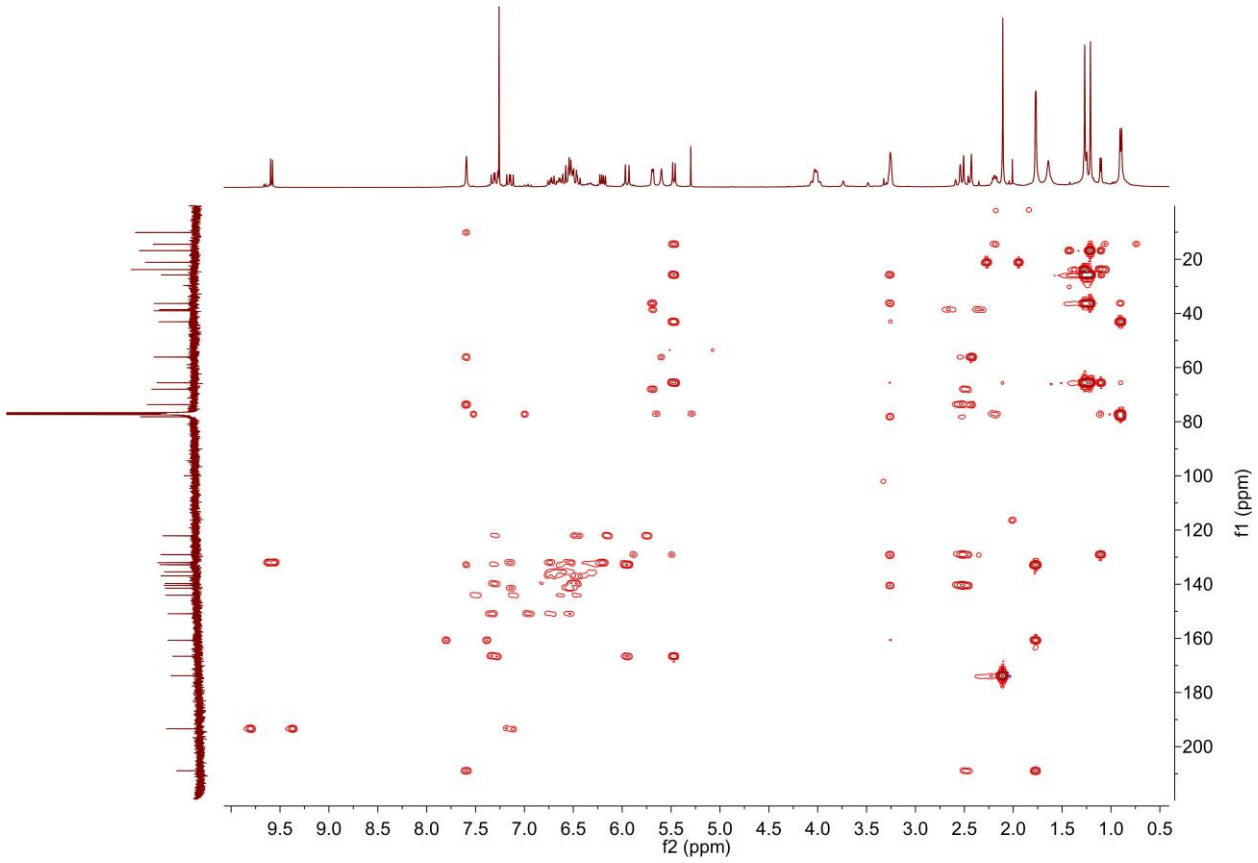


Fig. S27. $^{1}H–^{1}H$ COSY spectrum of **3** in $CDCl_3$

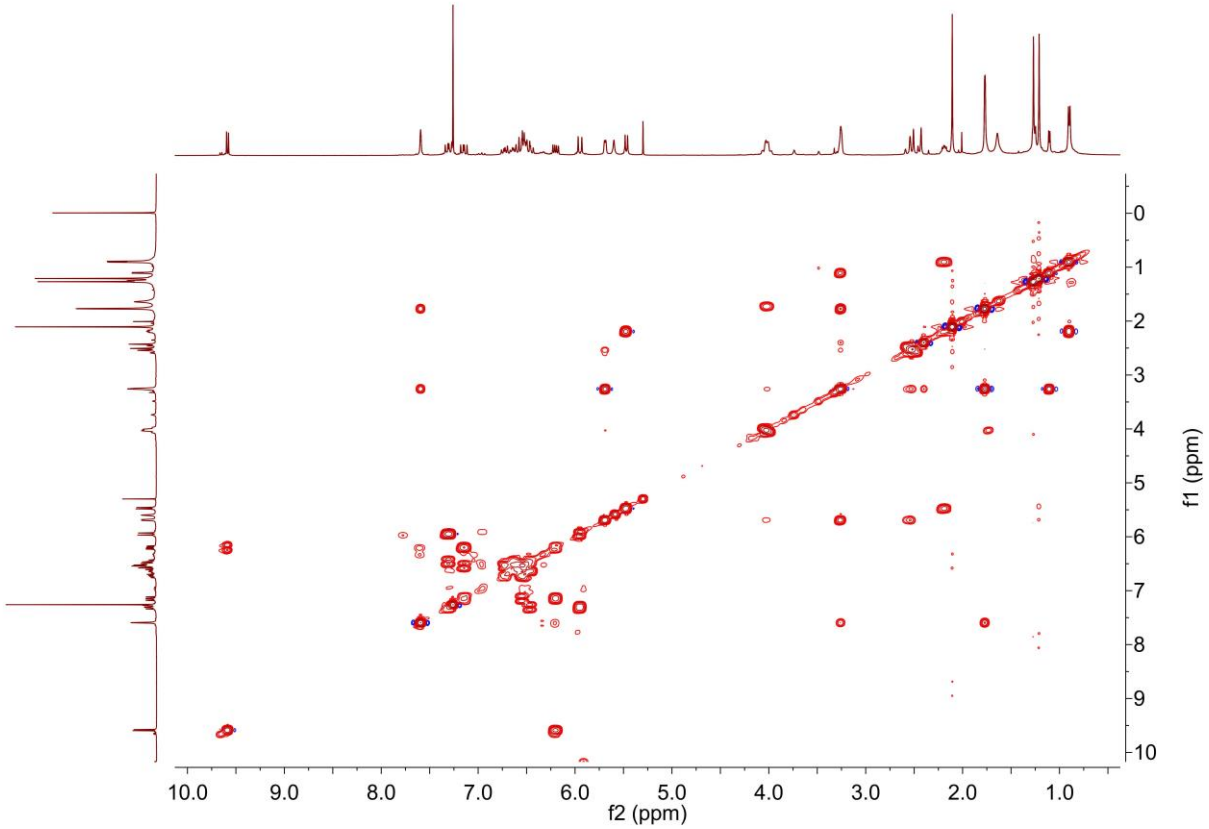


Fig. S28. NOESY spectrum of **3** in $CDCl_3$

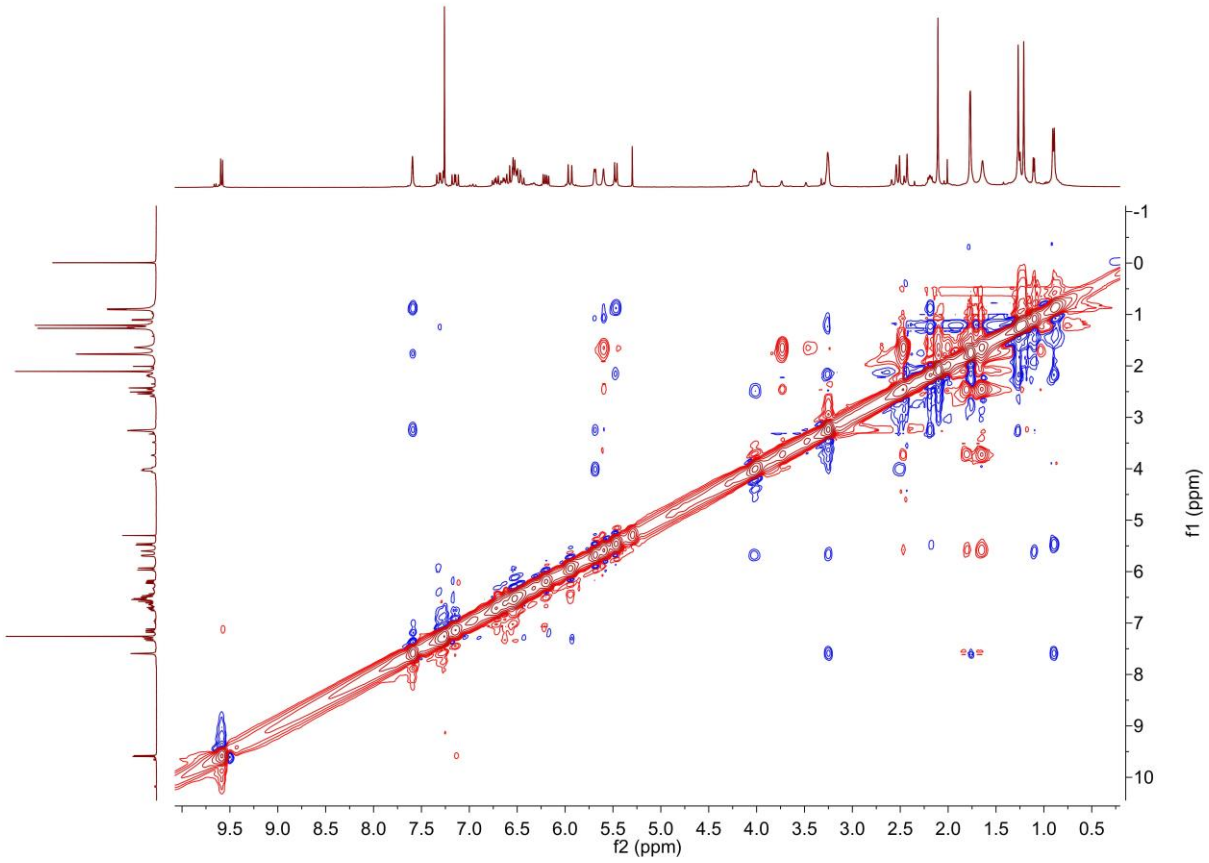
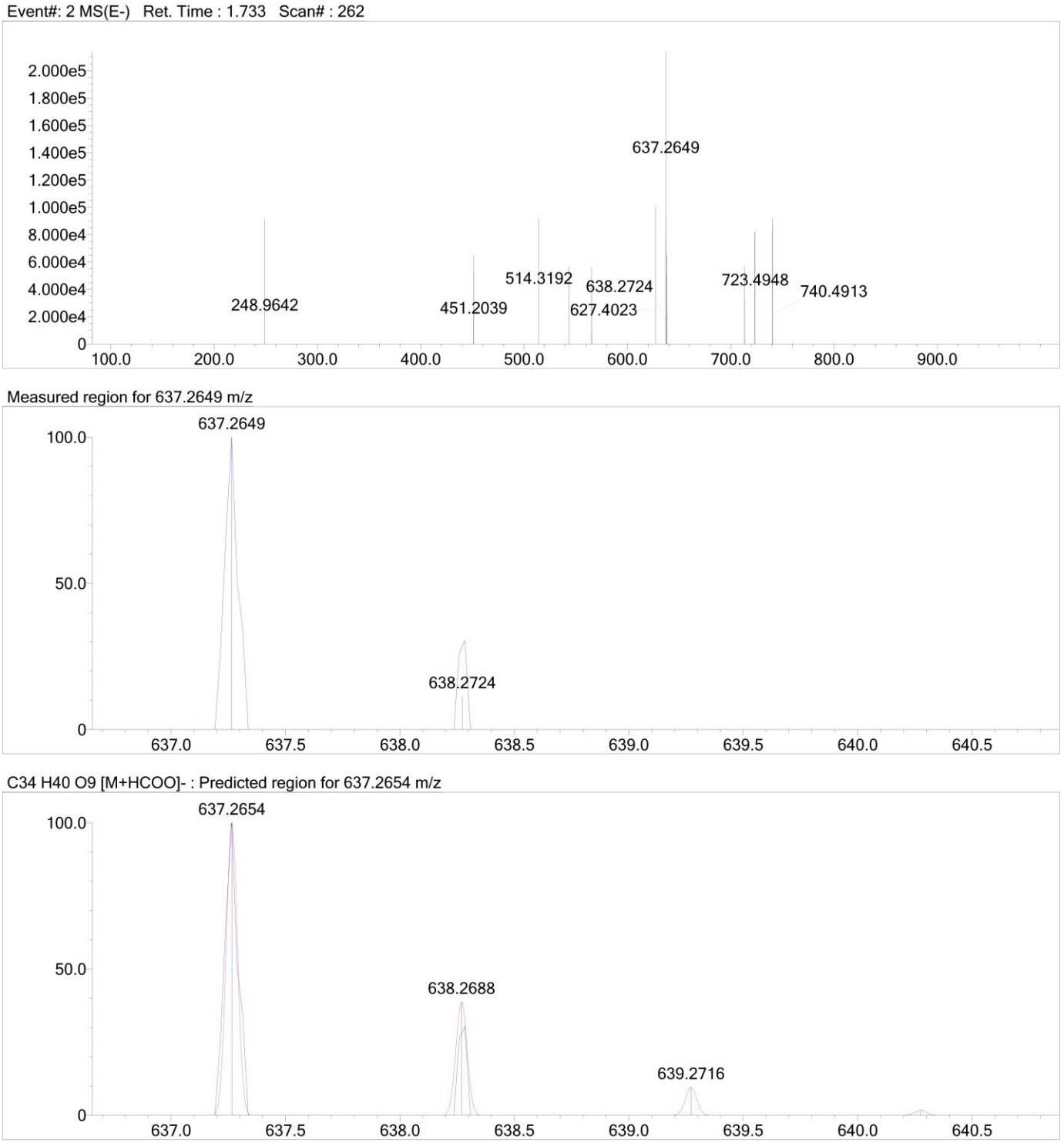


Fig. S29. HRESIMS spectrum of **3**



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	0.00	C34 H40 O9	[M+HCOO]-	637.2649	637.2654	-0.5	-0.78	0.00	15.0

Fig. S30. IR (KBr disc) spectrum of **3**

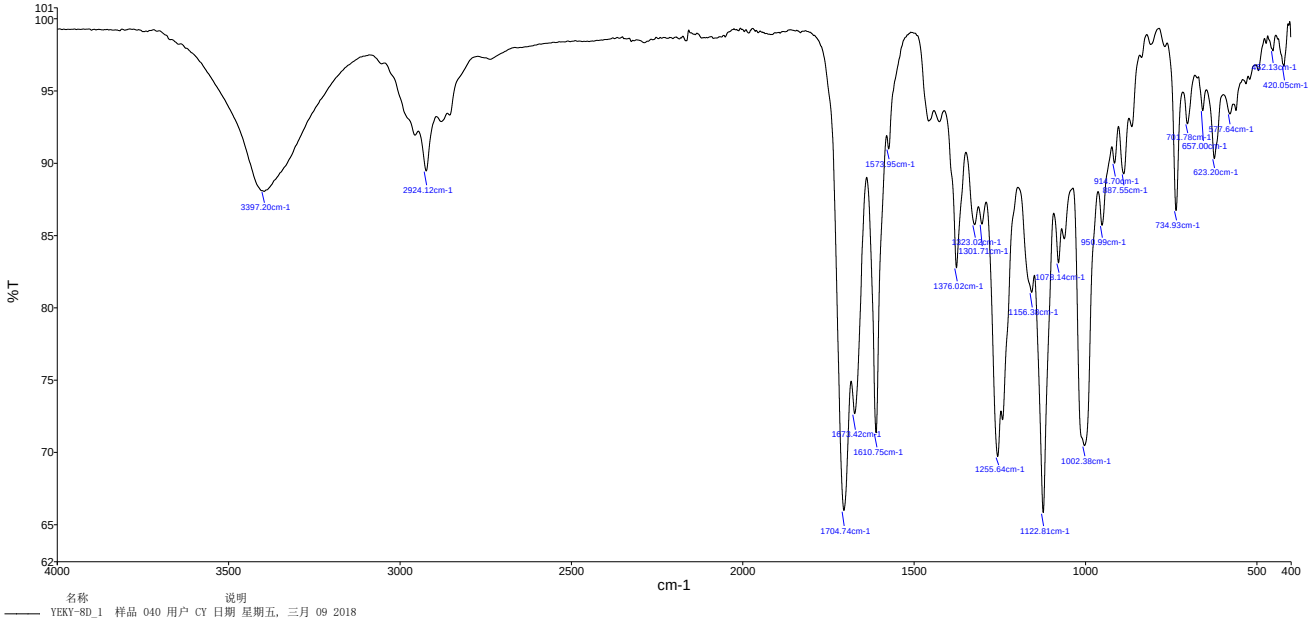


Fig. S31. ^{1}H NMR spectrum of **4** in $CDCl_3$

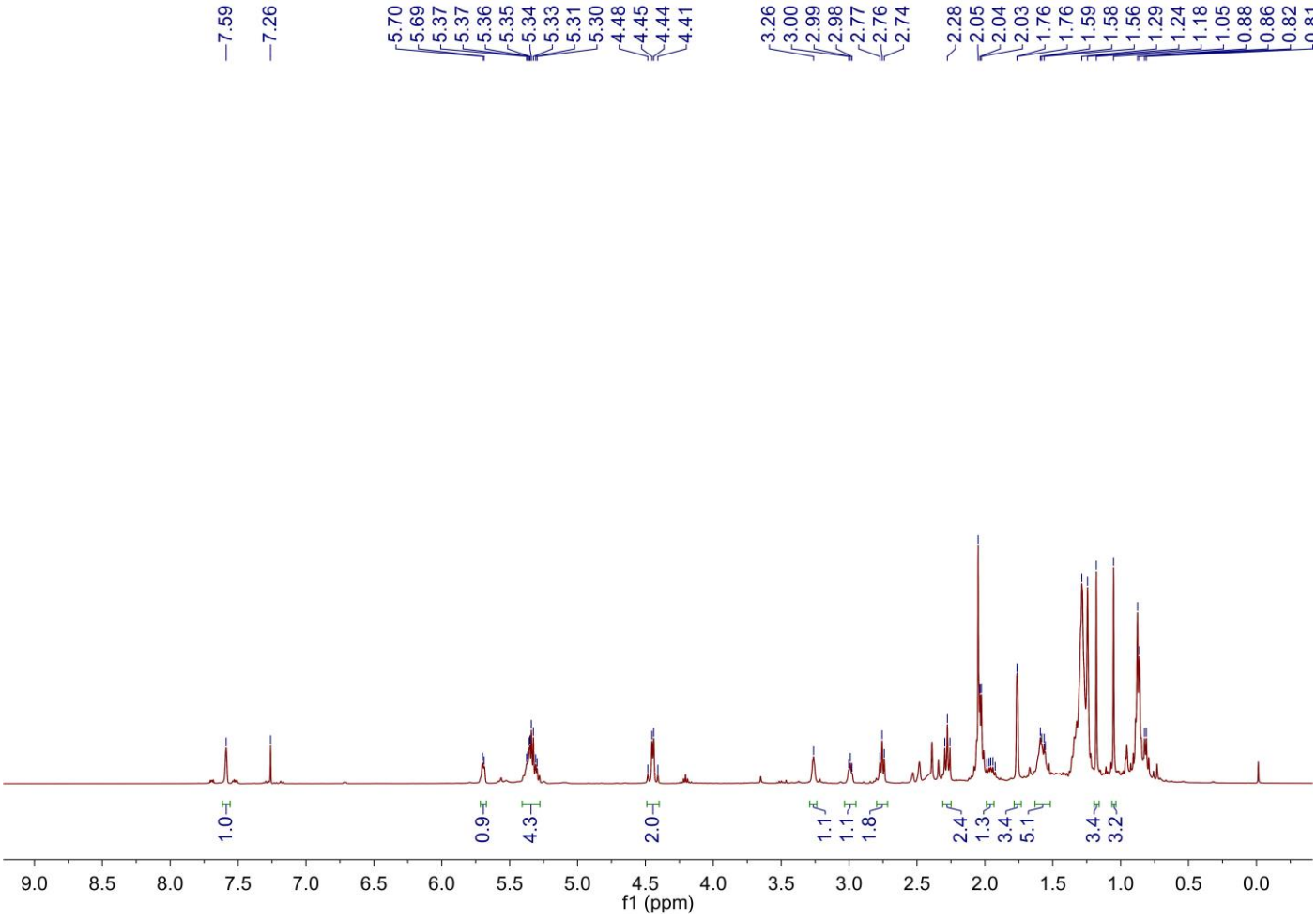


Fig. S32. ^{13}C NMR and DEPT spectra of **4** in $CDCl_3$

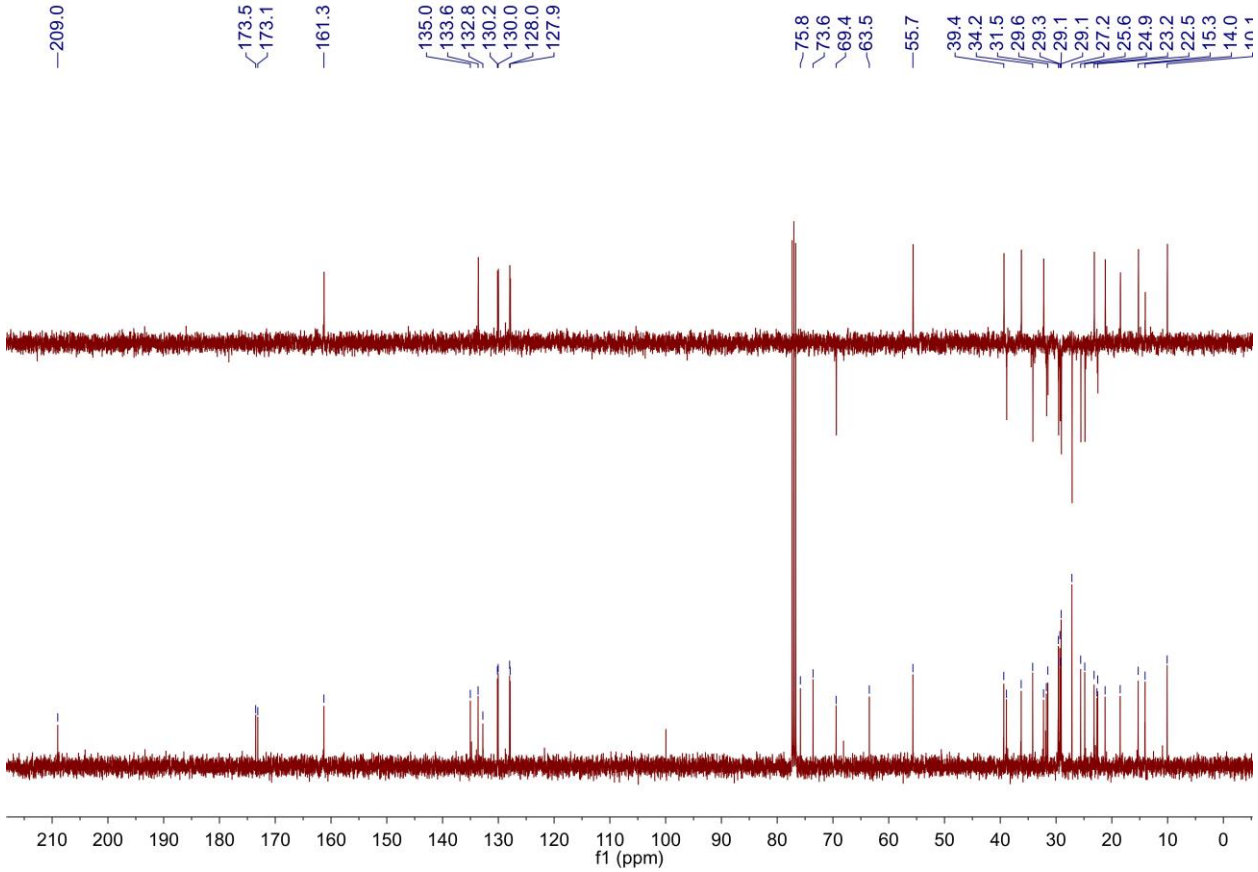


Fig. S33. HSQC spectrum of **4** in $CDCl_3$

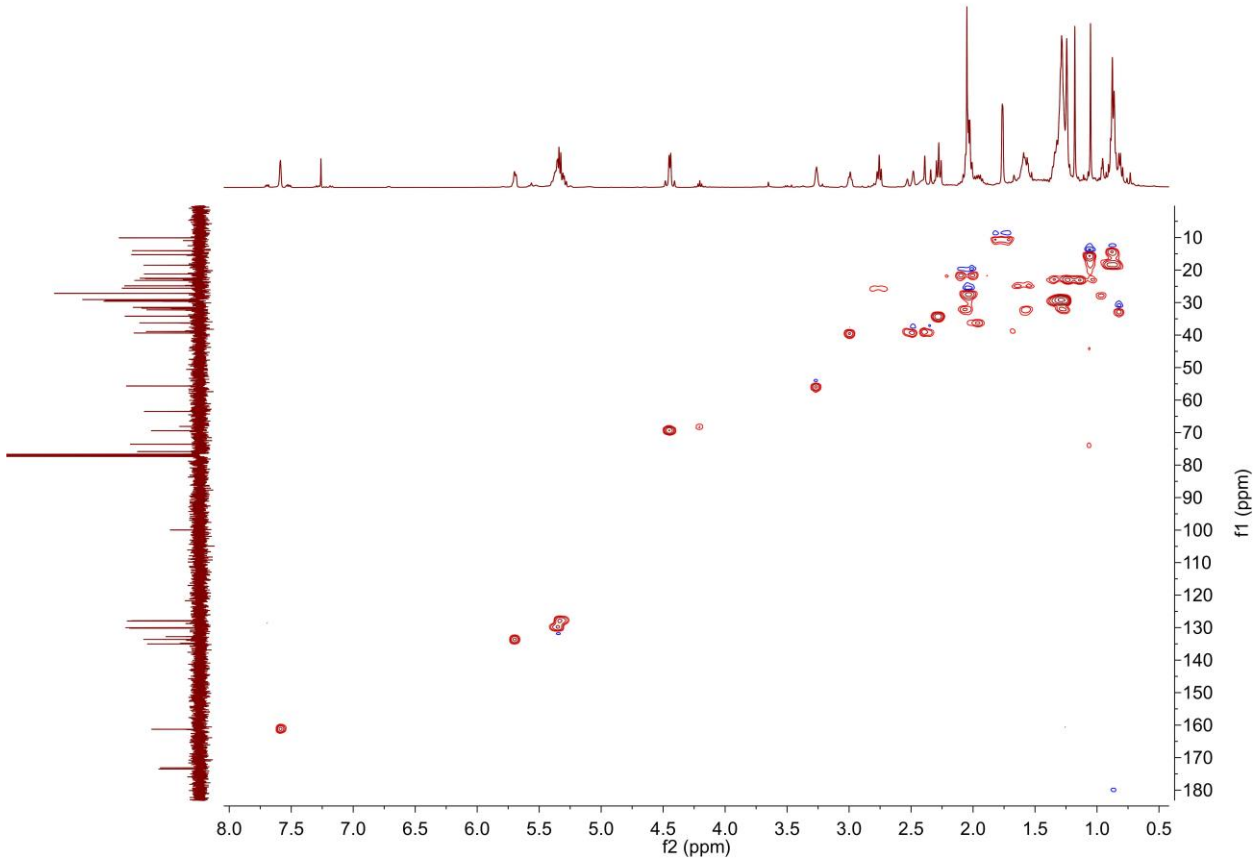


Fig. S34. HMBC spectrum of **4** in $CDCl_3$

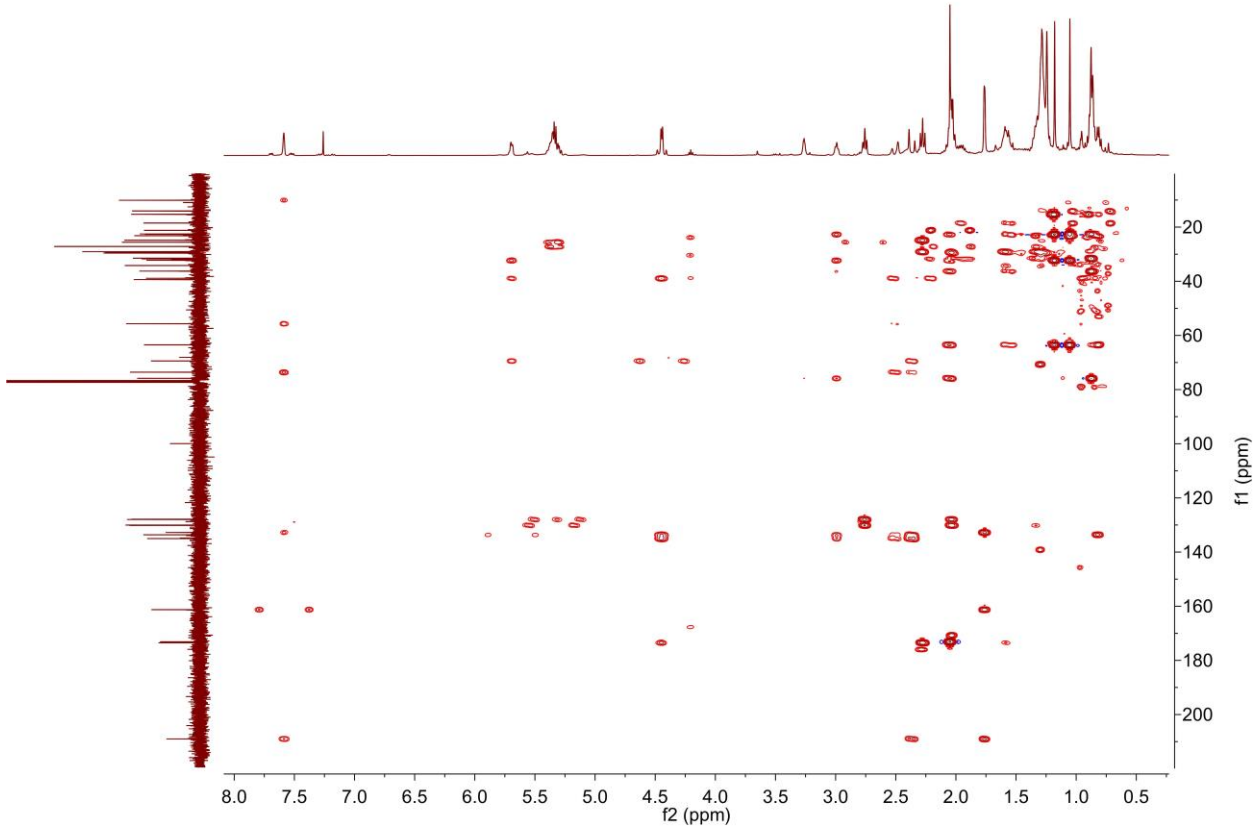


Fig. S35. $^{1}H–^{1}H$ COSY spectrum of **4** in $CDCl_3$

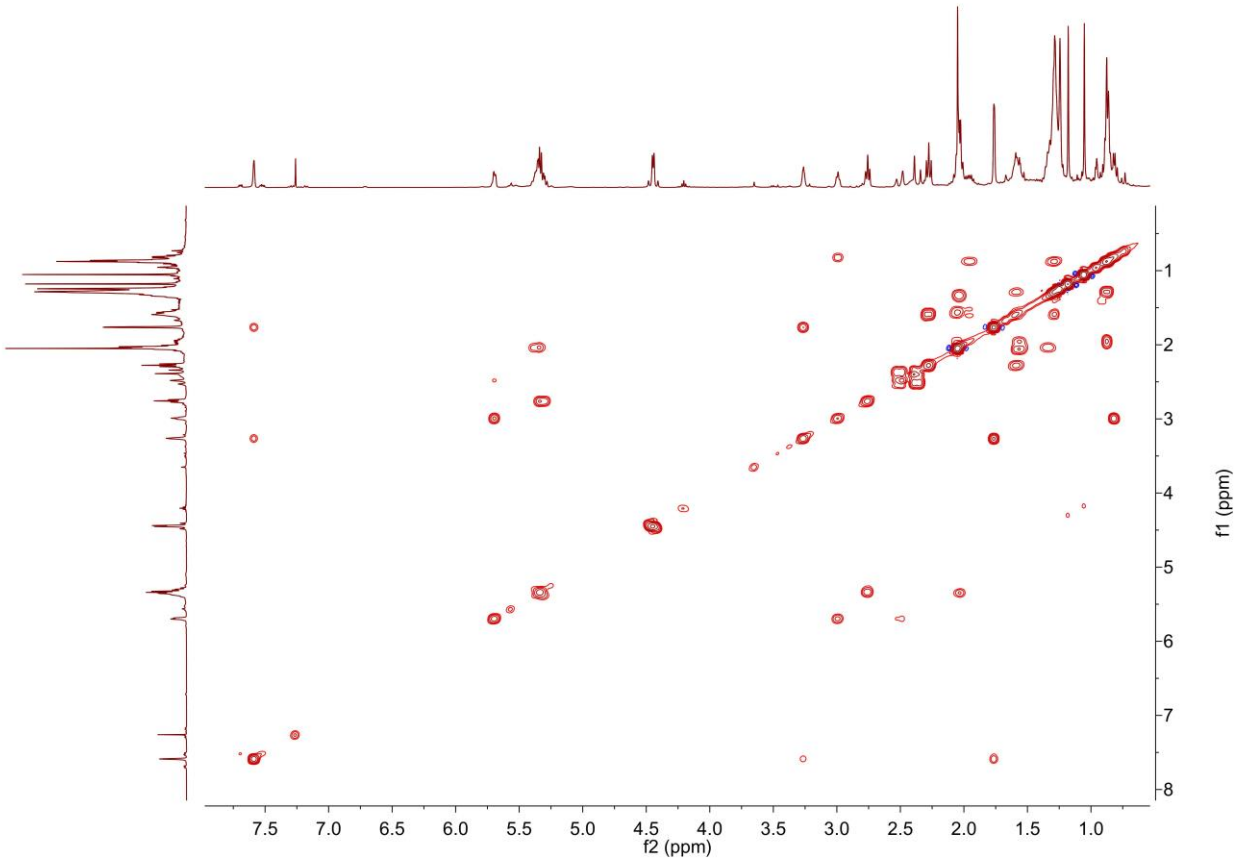


Fig. S36. NOESY spectrum of **4** in $CDCl_3$

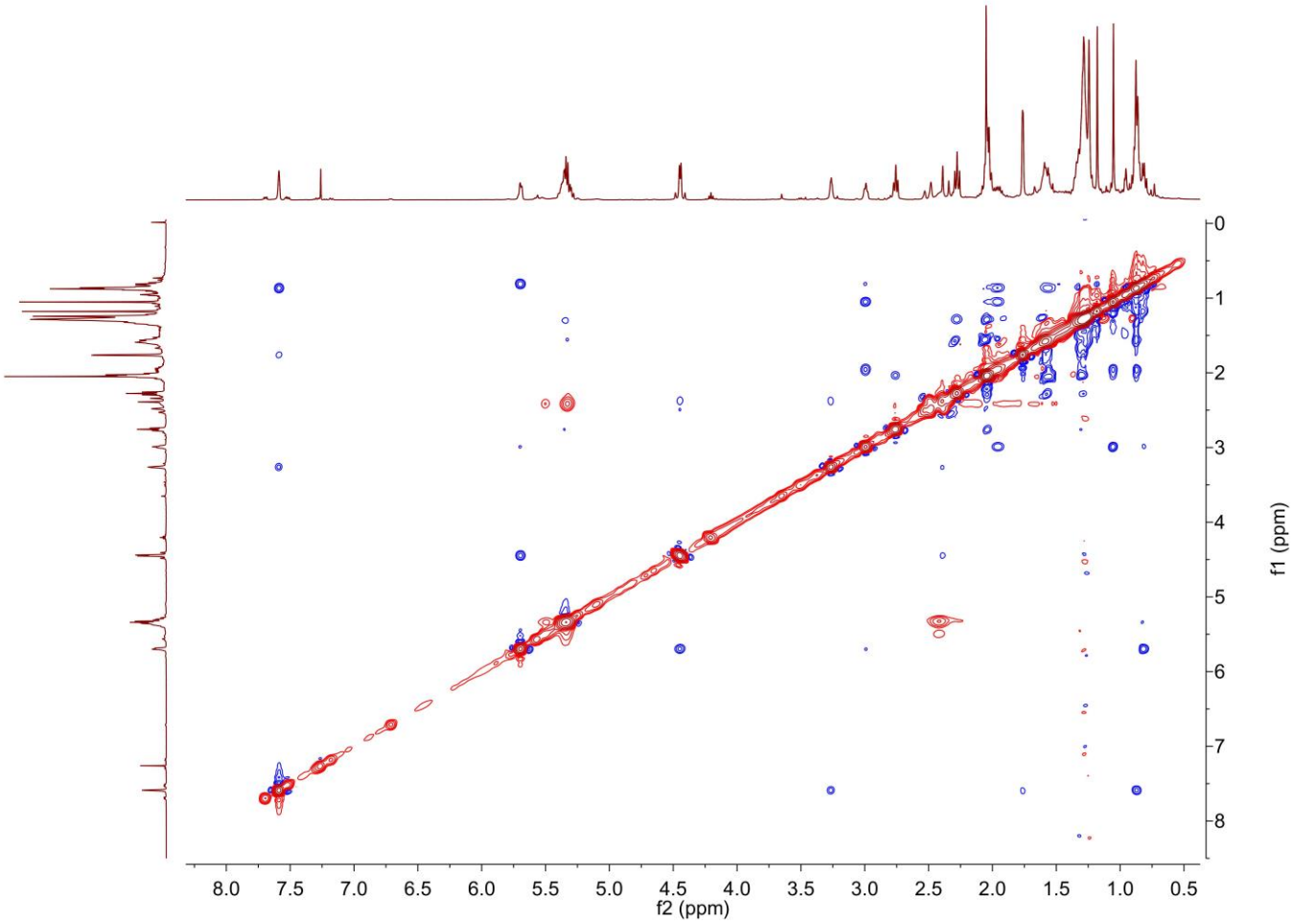


Fig. S37. IR (KBr disc) spectrum of **4**

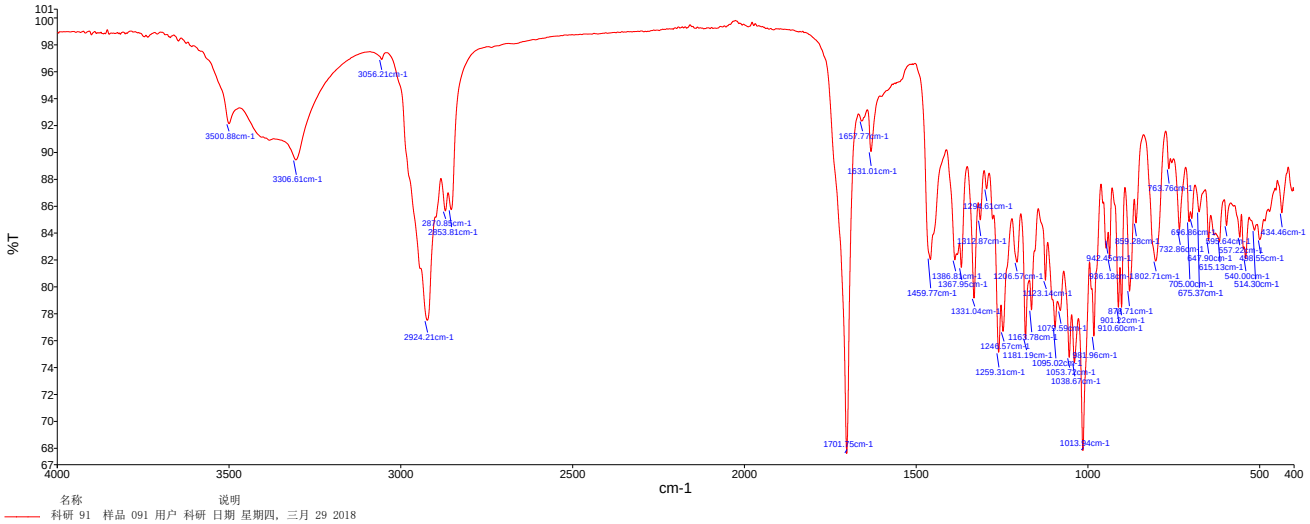
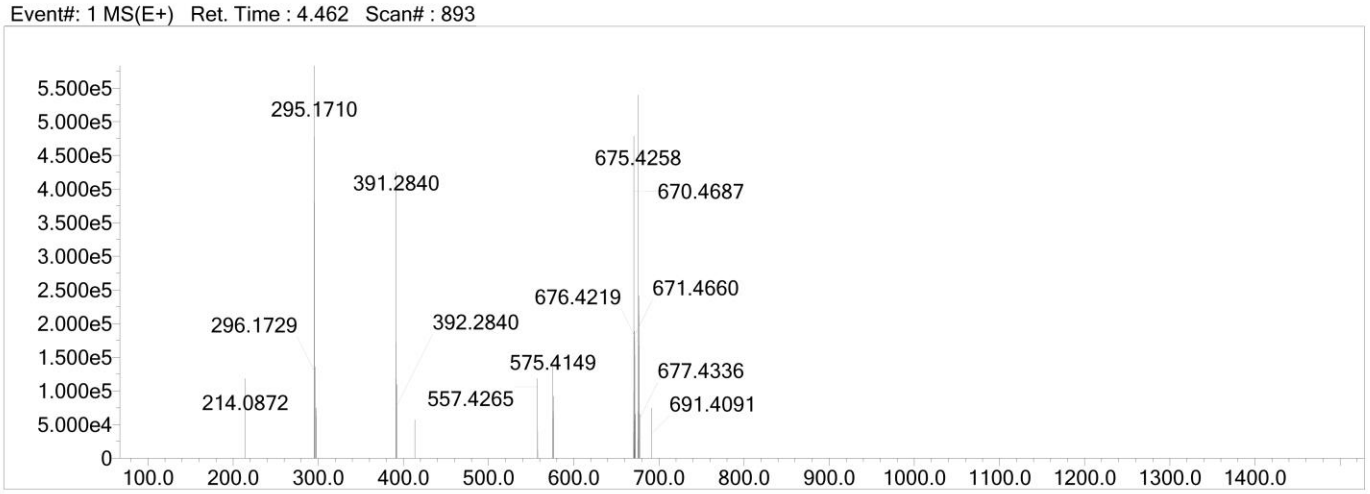
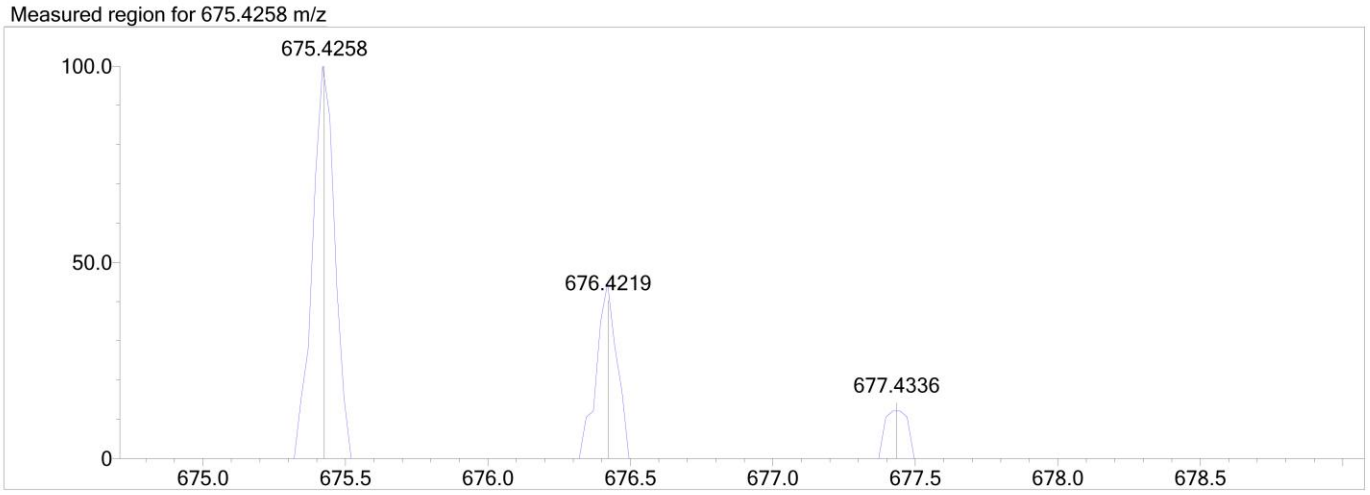
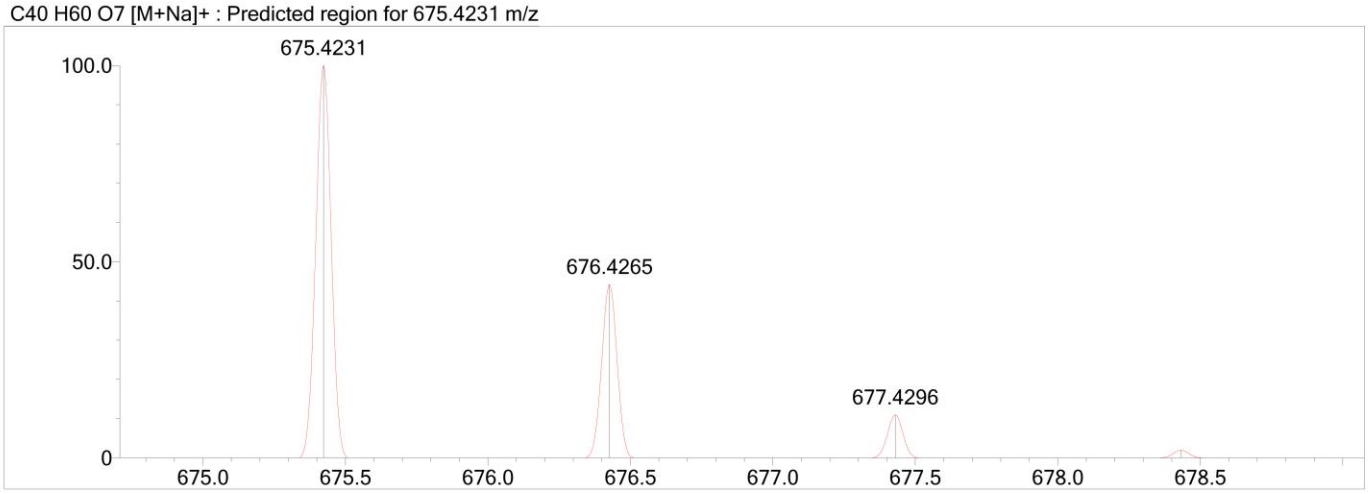


Fig. S38. HRESIMS spectrum of **4**







Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	73.52	C40 H60 O7	[M+Na]+	675.4258	675.4231	2.7	4.00	79.48	11.0

Fig. S39. ^{1}H NMR spectrum of **5** in $CDCl_3$

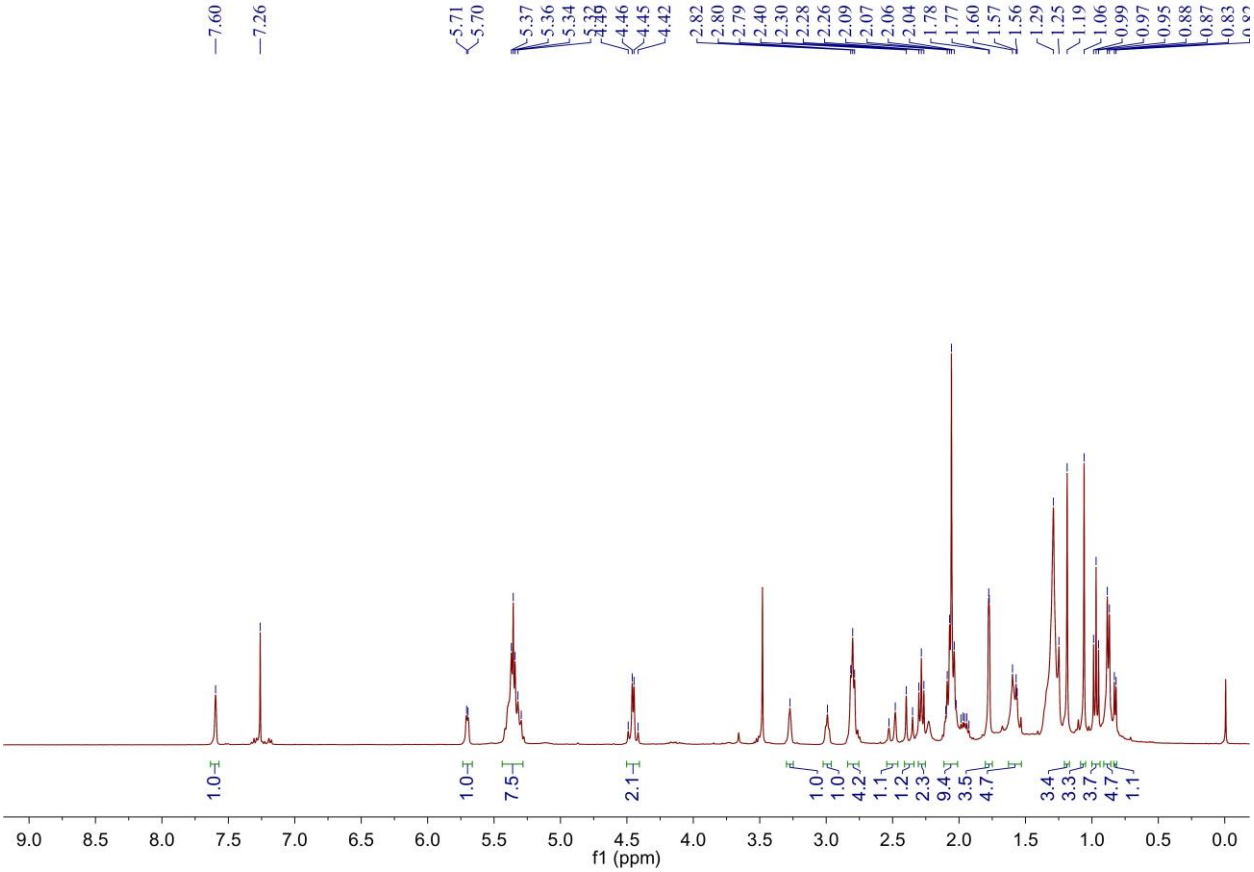


Fig. S40. ^{13}C NMR and DEPT spectra of **5** in $CDCl_3$

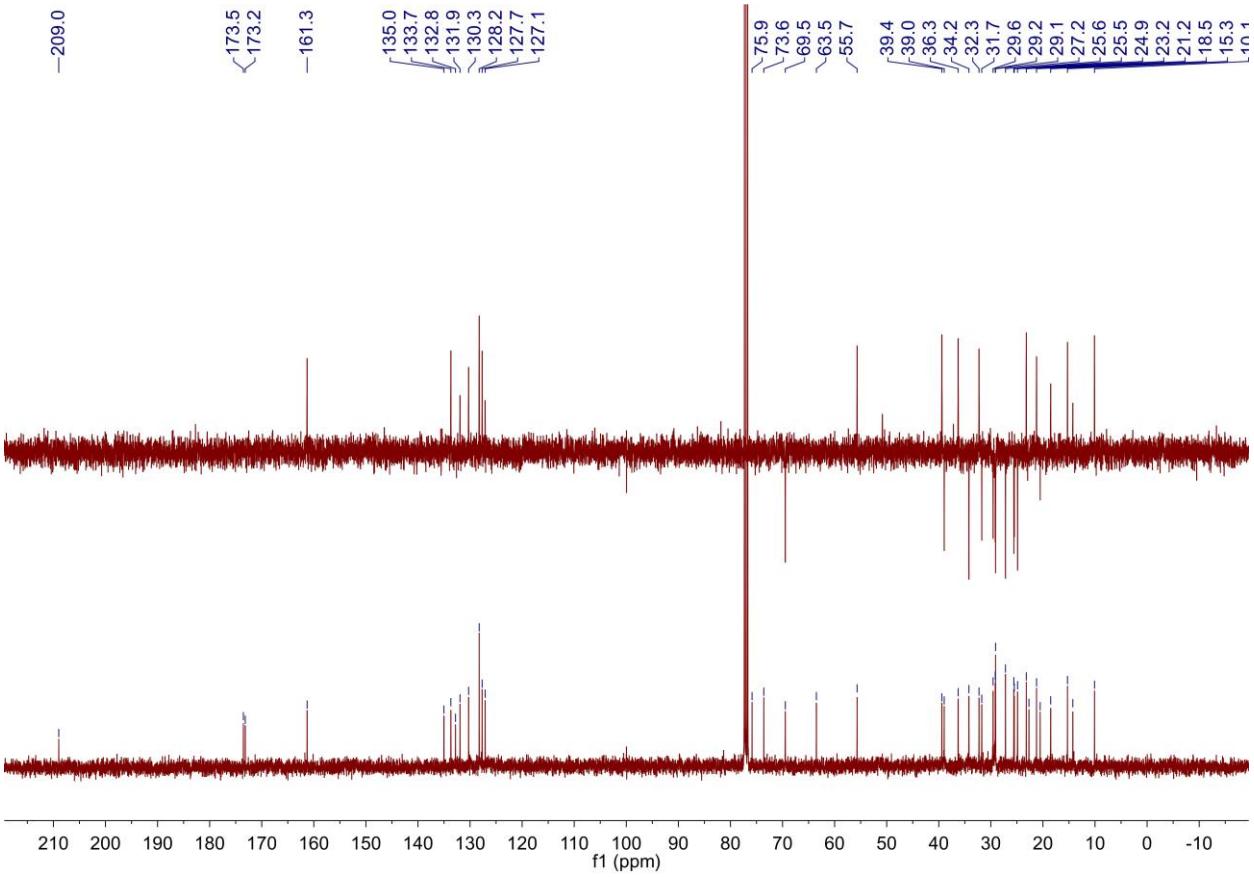


Fig. S41. HSQC spectrum of **5** in $CDCl_3$

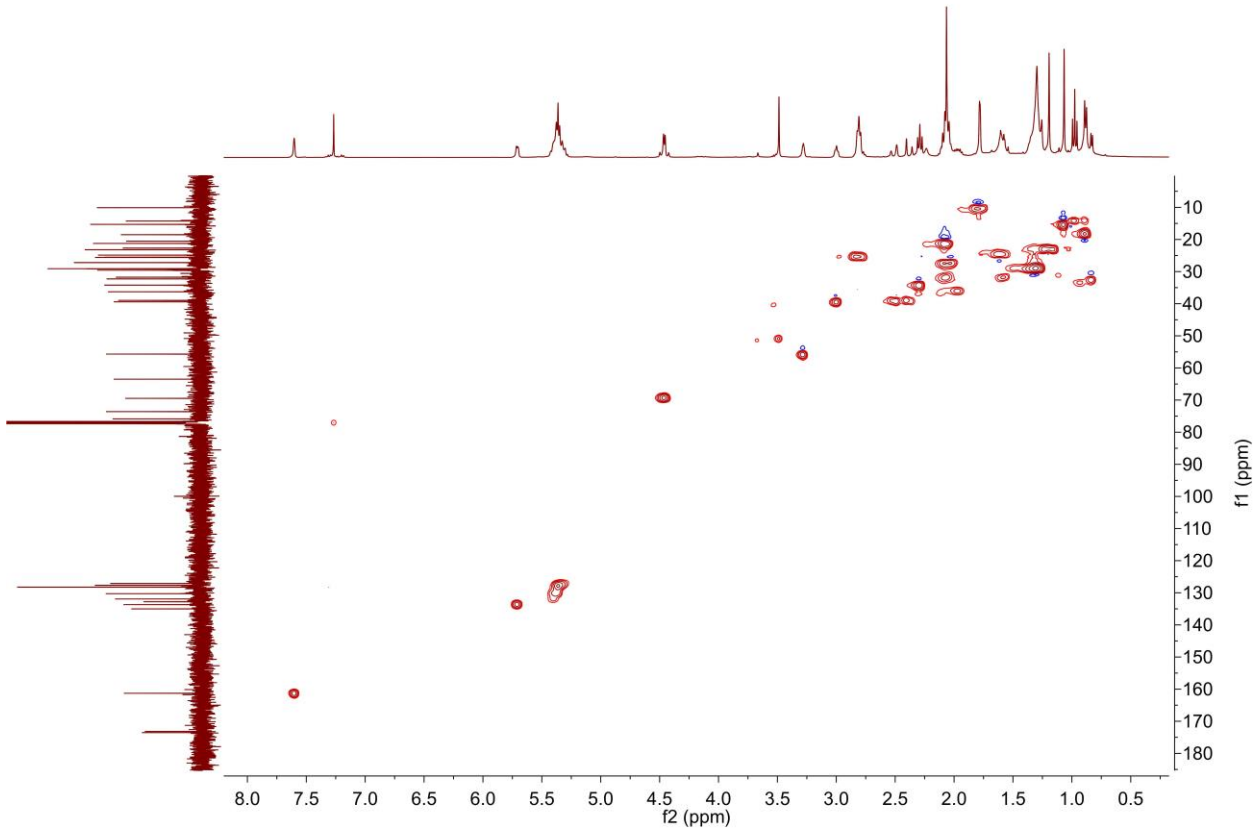


Fig. S42. HMBC spectrum of **5** in $CDCl_3$

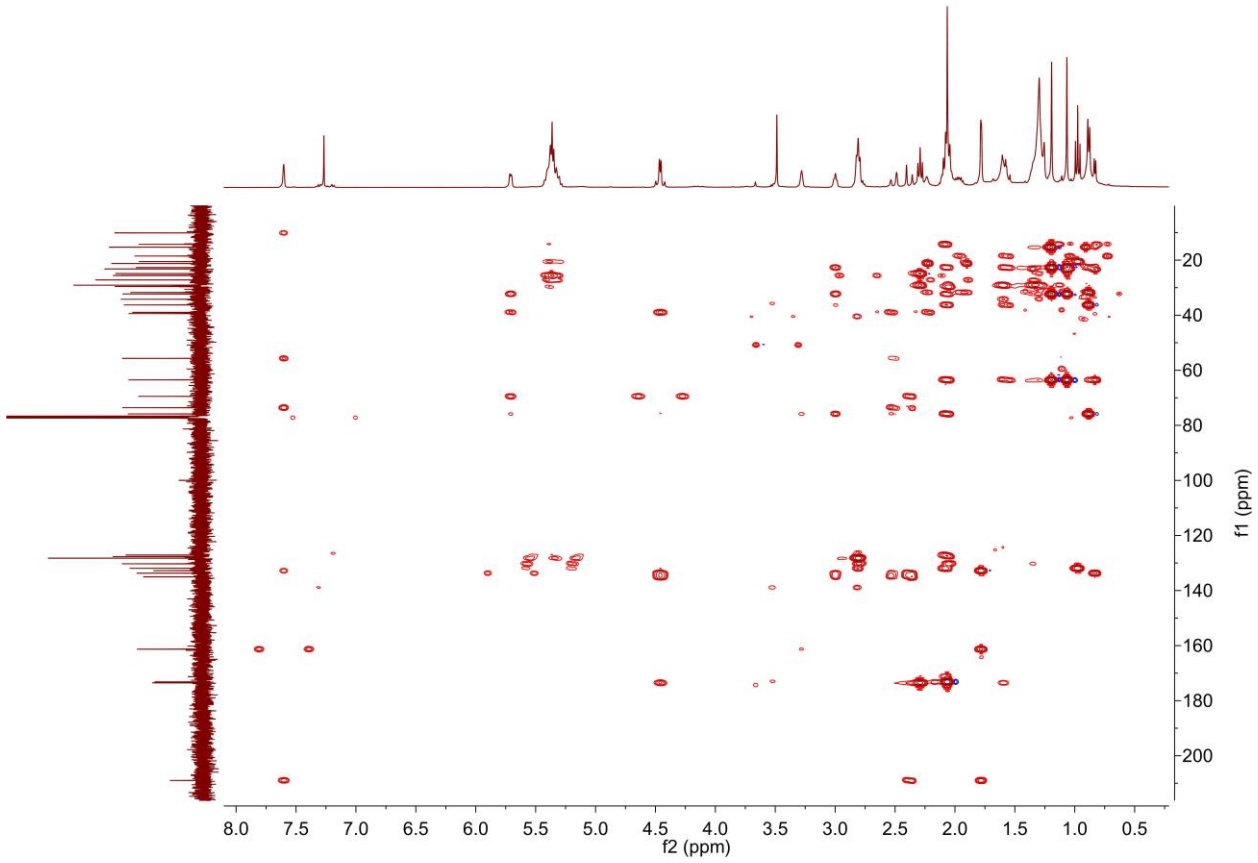


Fig. S43. $^{1}H–^{1}H$ COSY spectrum of **5** in $CDCl_3$

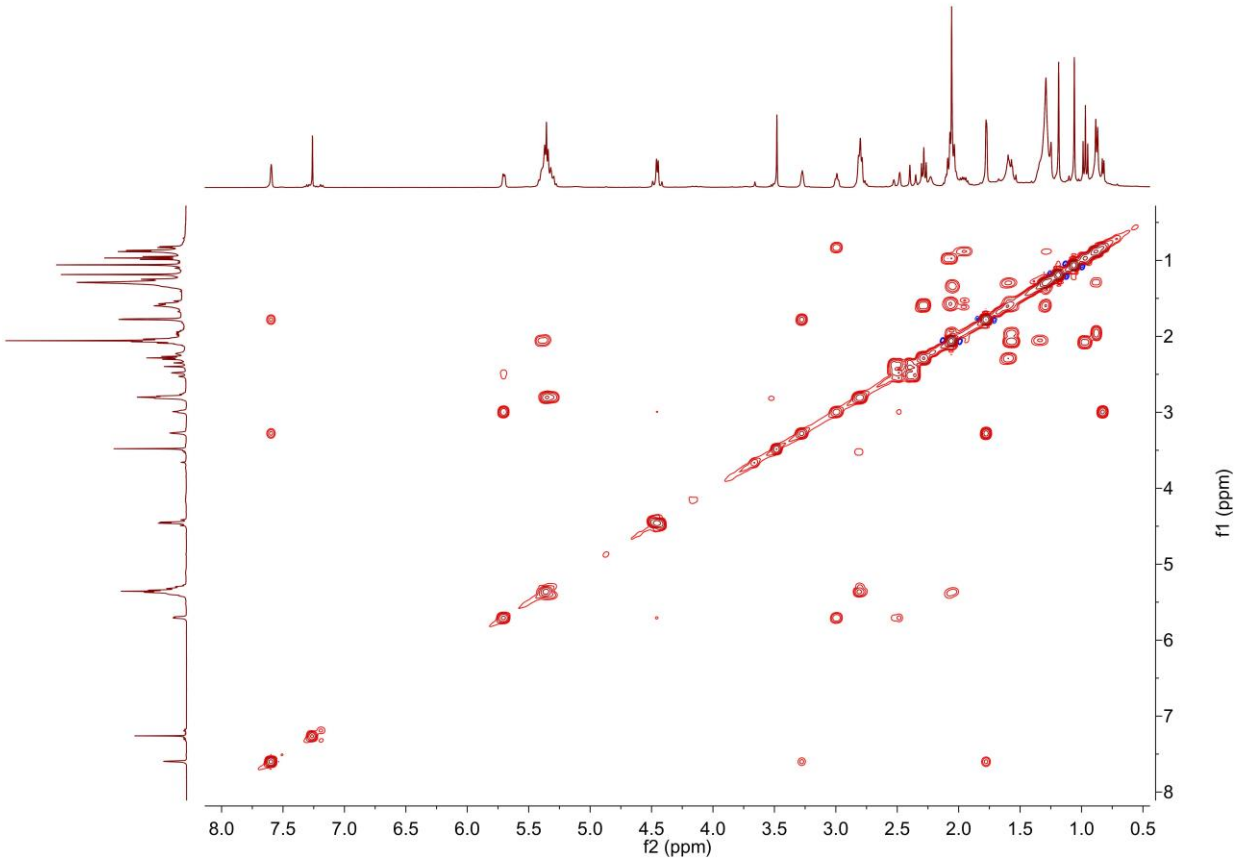


Fig. S44. NOESY spectrum of **5** in $CDCl_3$

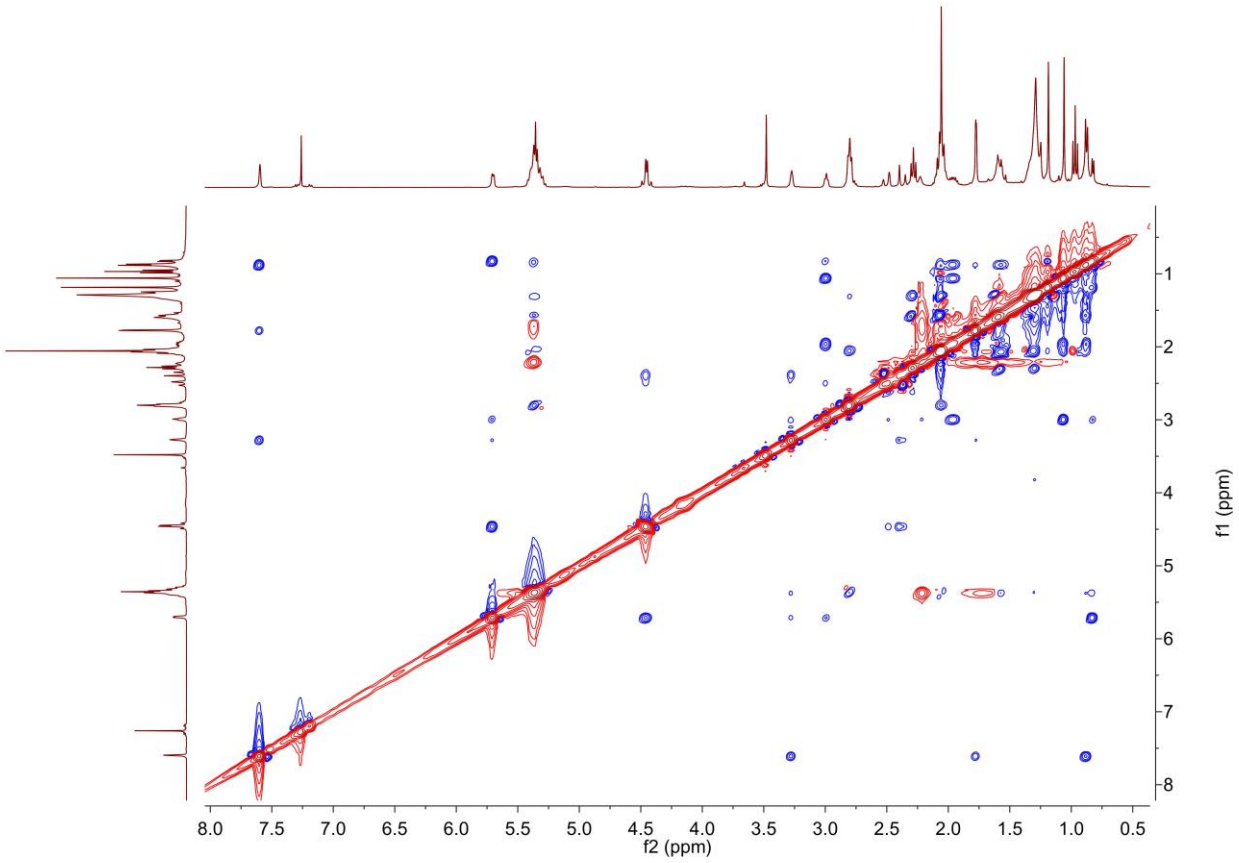
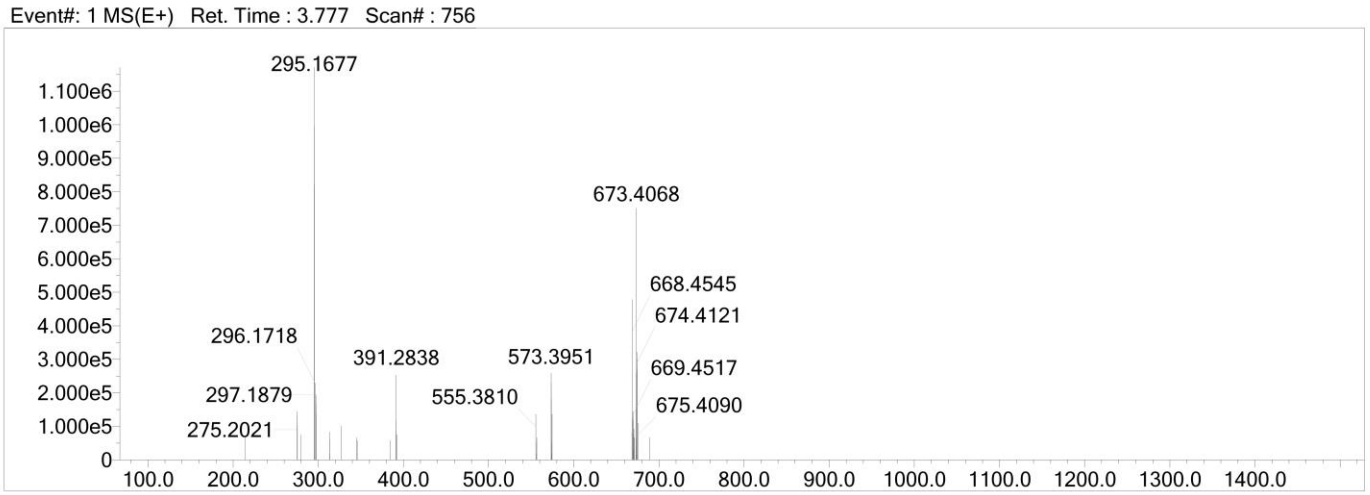
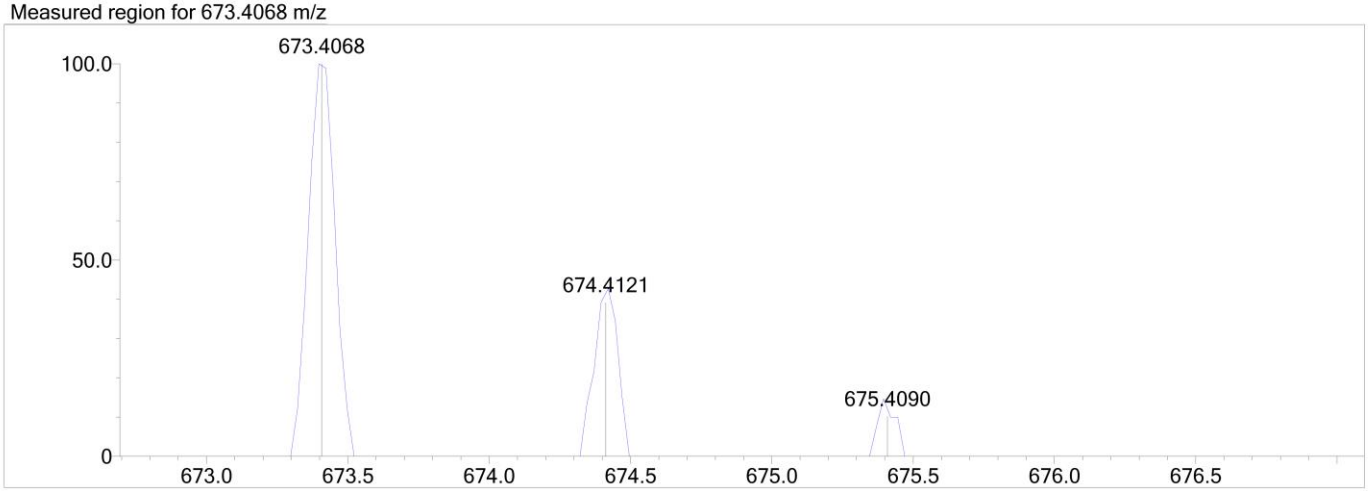
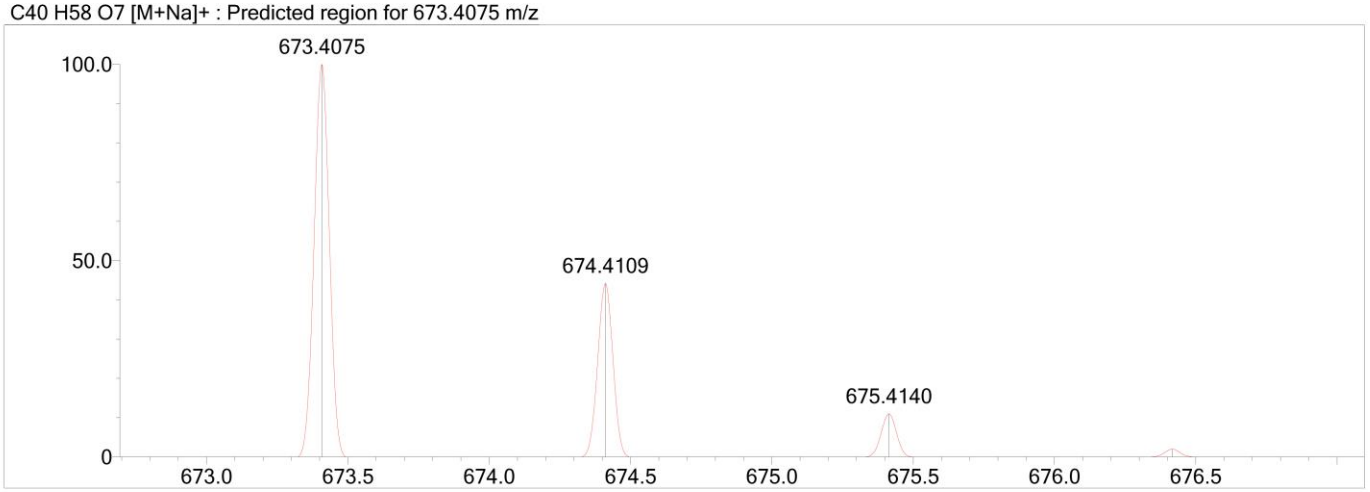


Fig. S45. HRESIMS spectrum of **5**







Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	82.74	C40 H58 O7	[M+Na]+	673.4068	673.4075	-0.7	-1.04	82.82	12.0

Fig. S46. IR (KBr disc) spectrum of **5**

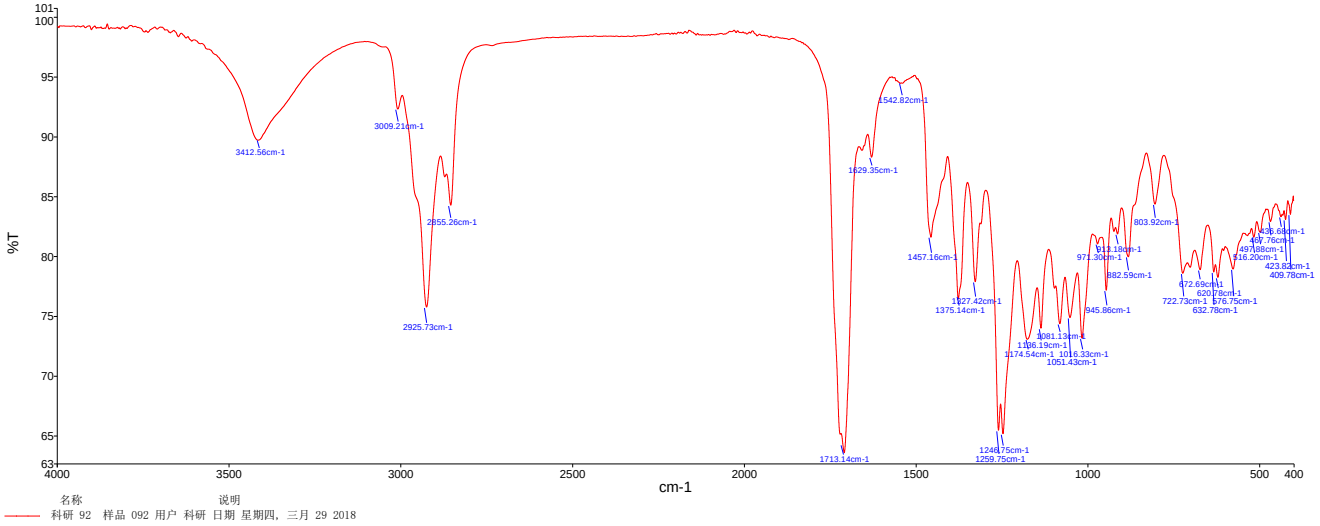


Fig. S47. ^{1}H NMR spectrum of **6** in CD_3OD

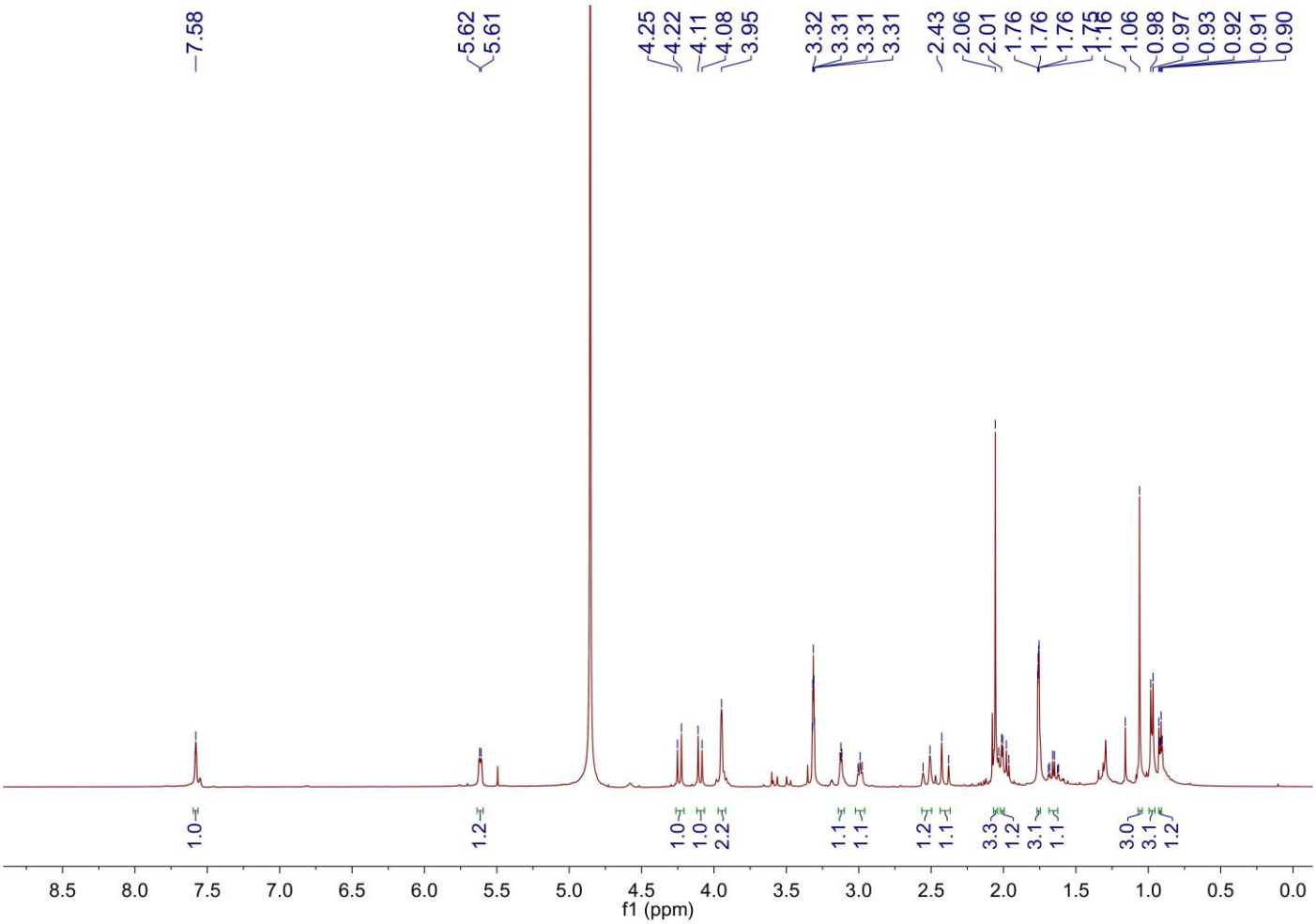


Fig. S48. ^{13}C NMR and DEPT spectra of **6** in CD_3OD

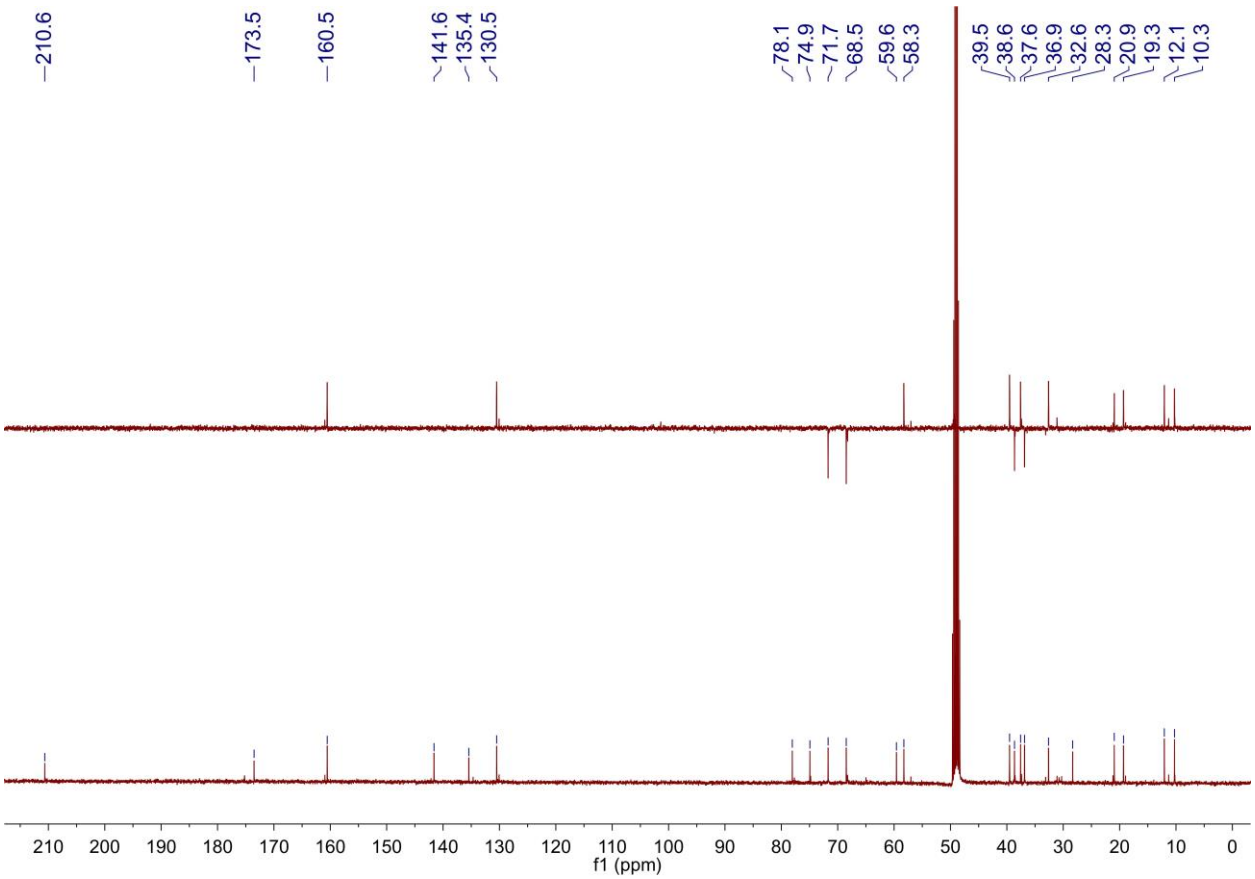


Fig. S49. HSQC spectrum of **6** in CD_3OD

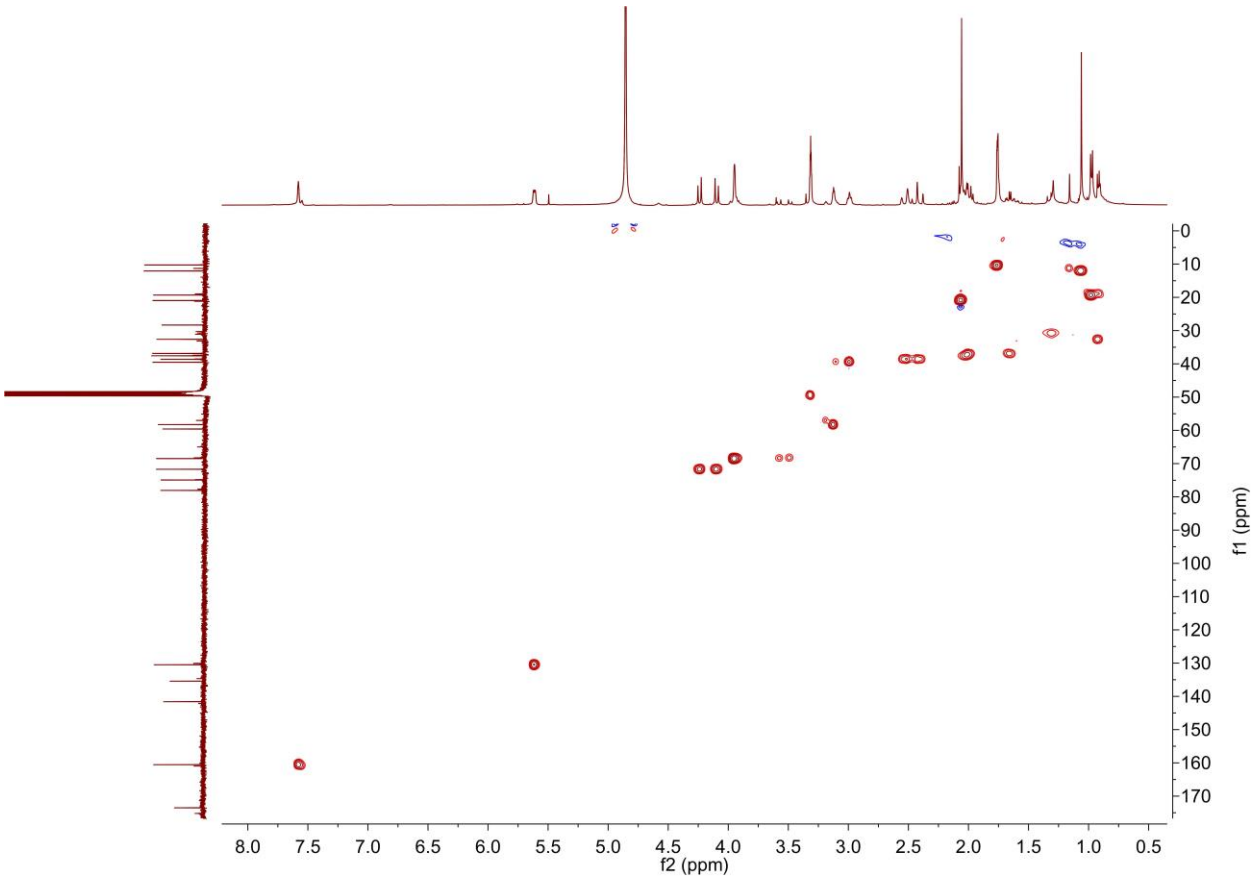


Fig. S50. HMBC spectrum of **6** in CD_3OD

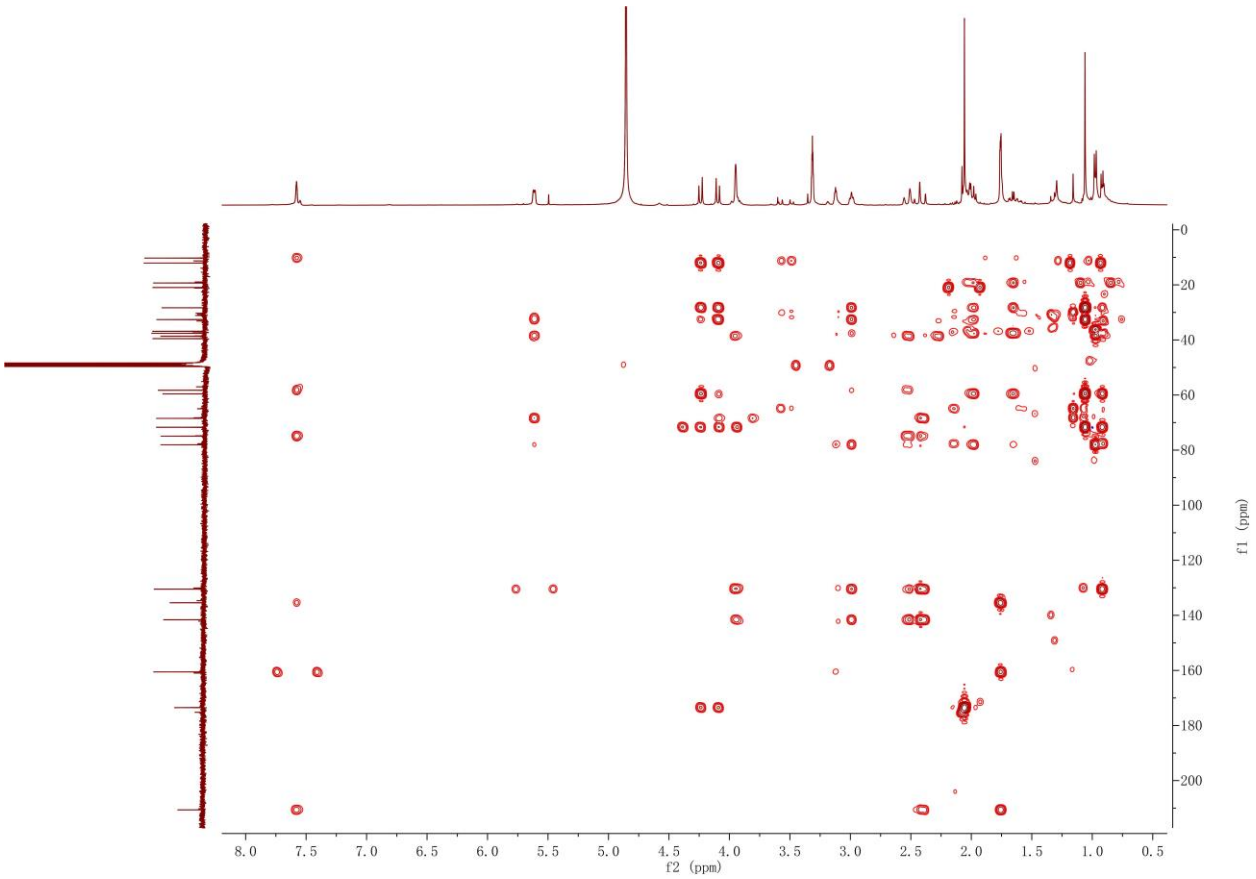


Fig. S51. ^{1}H–^{1}H COSY spectrum of **6** in CD_3OD

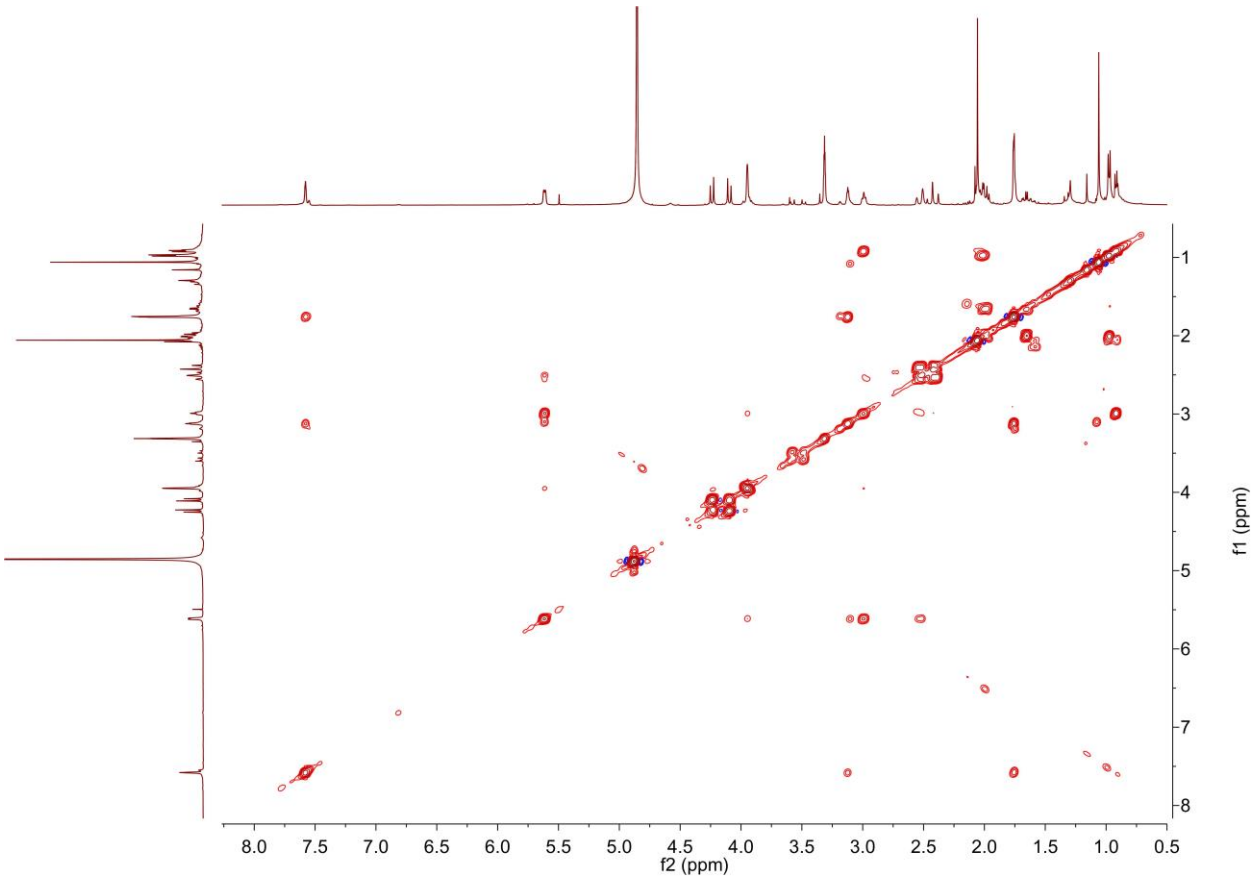


Fig. S52. NOESY spectrum of **6** in CD_3OD

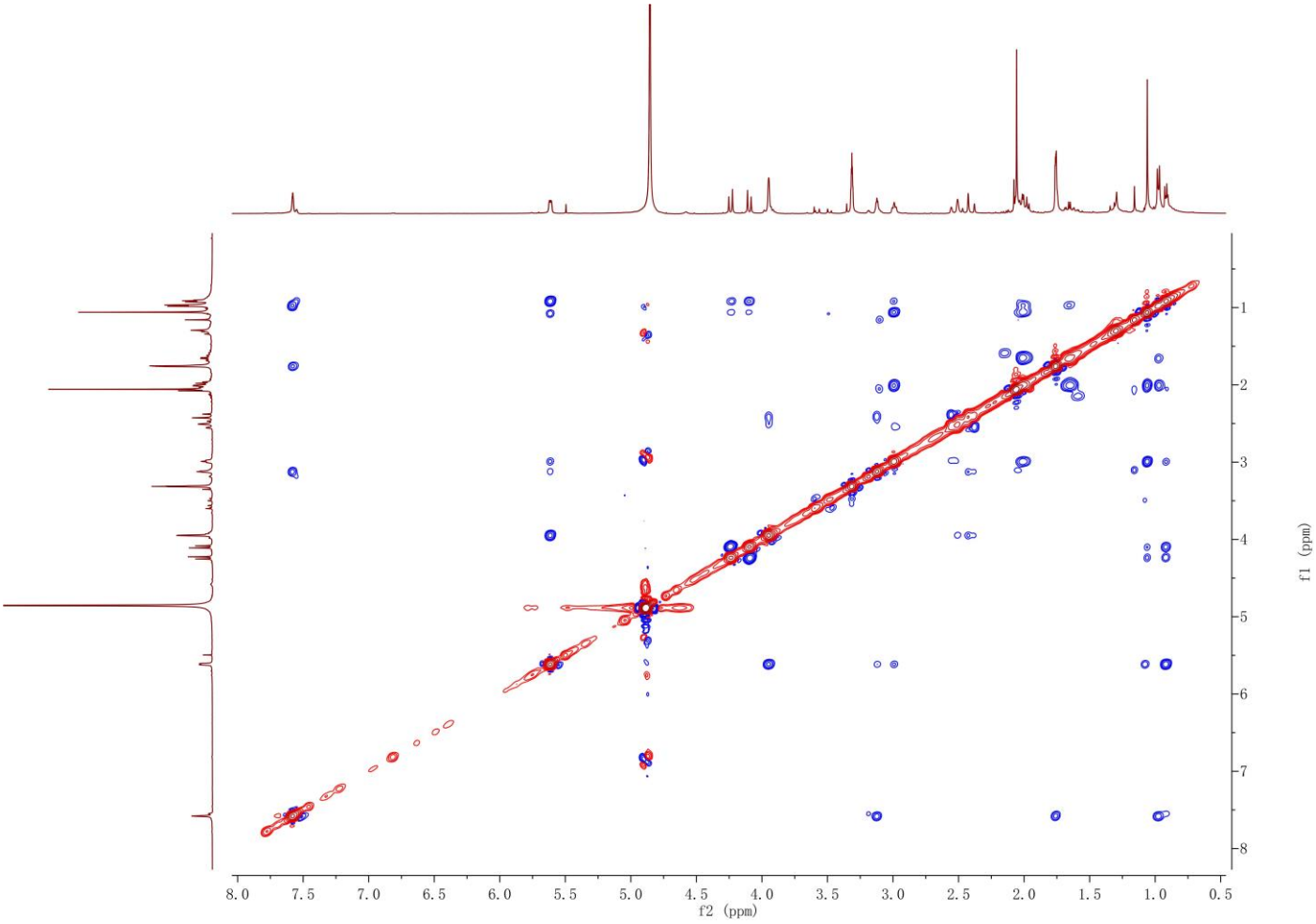


Fig. S53. IR (KBr disc) spectrum of **6**

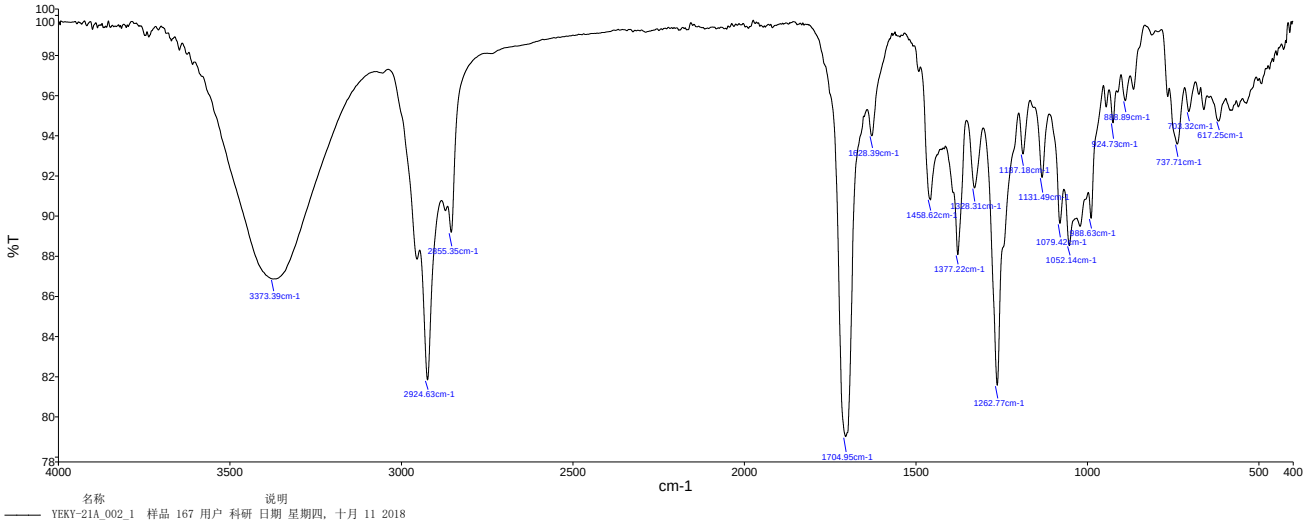
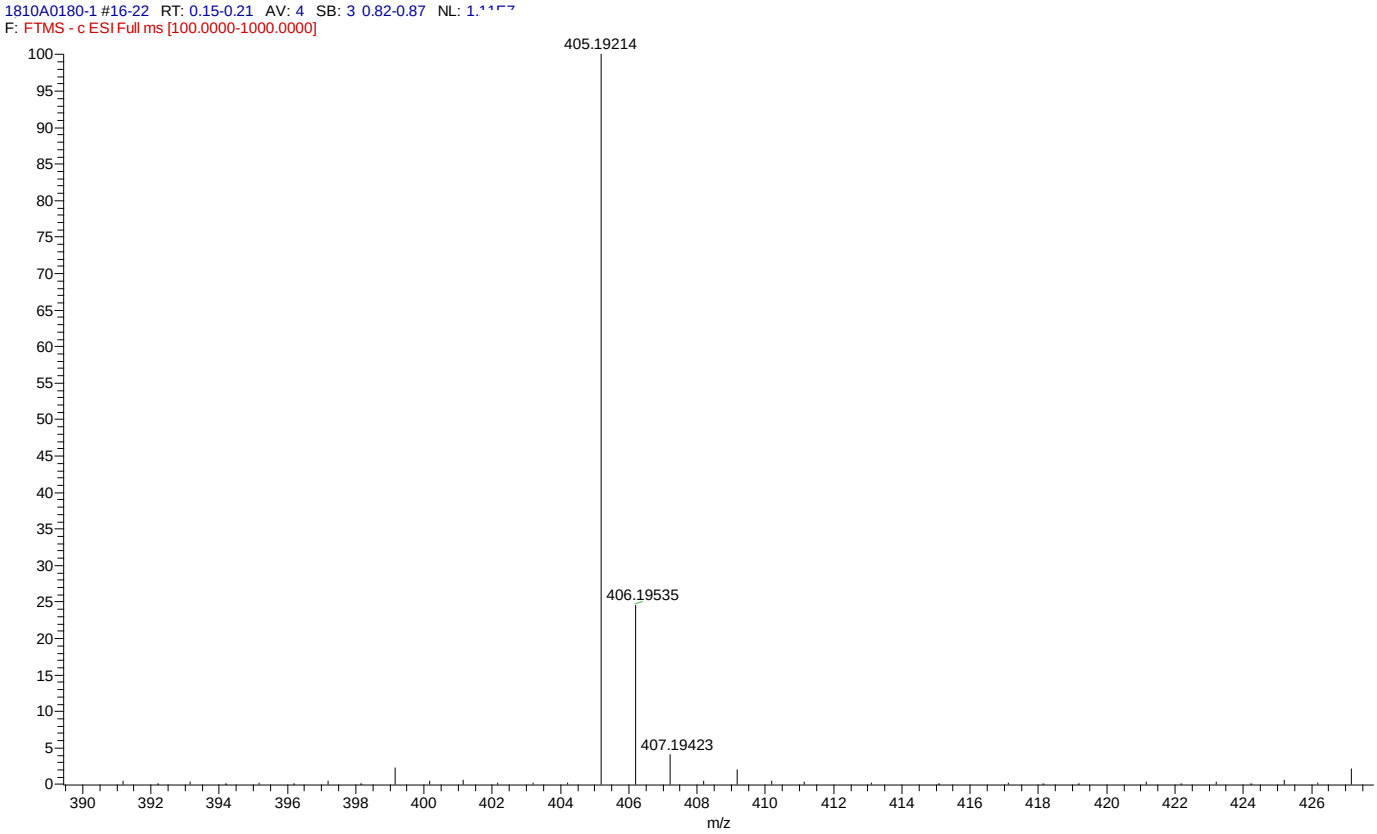


Fig. S54. HRESIMS spectrum of **6**



SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
405.19214	405.19188	0.65	8.5	C22 H29 O7

Fig. S55. ^{1}H NMR spectrum of **1c** in $CDCl_3$

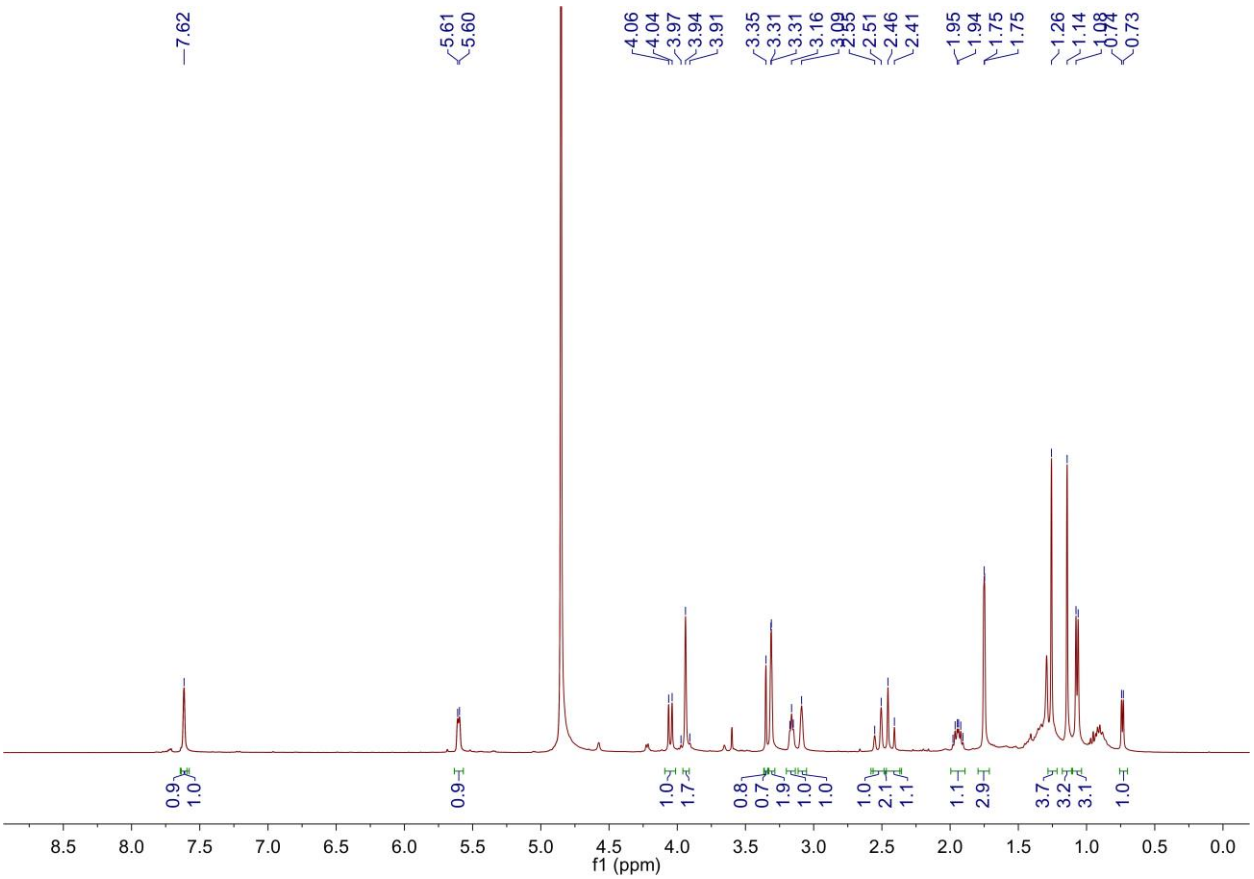


Fig. S56. ^{13}C NMR and DEPT135 spectra of **1c** in $CDCl_3$

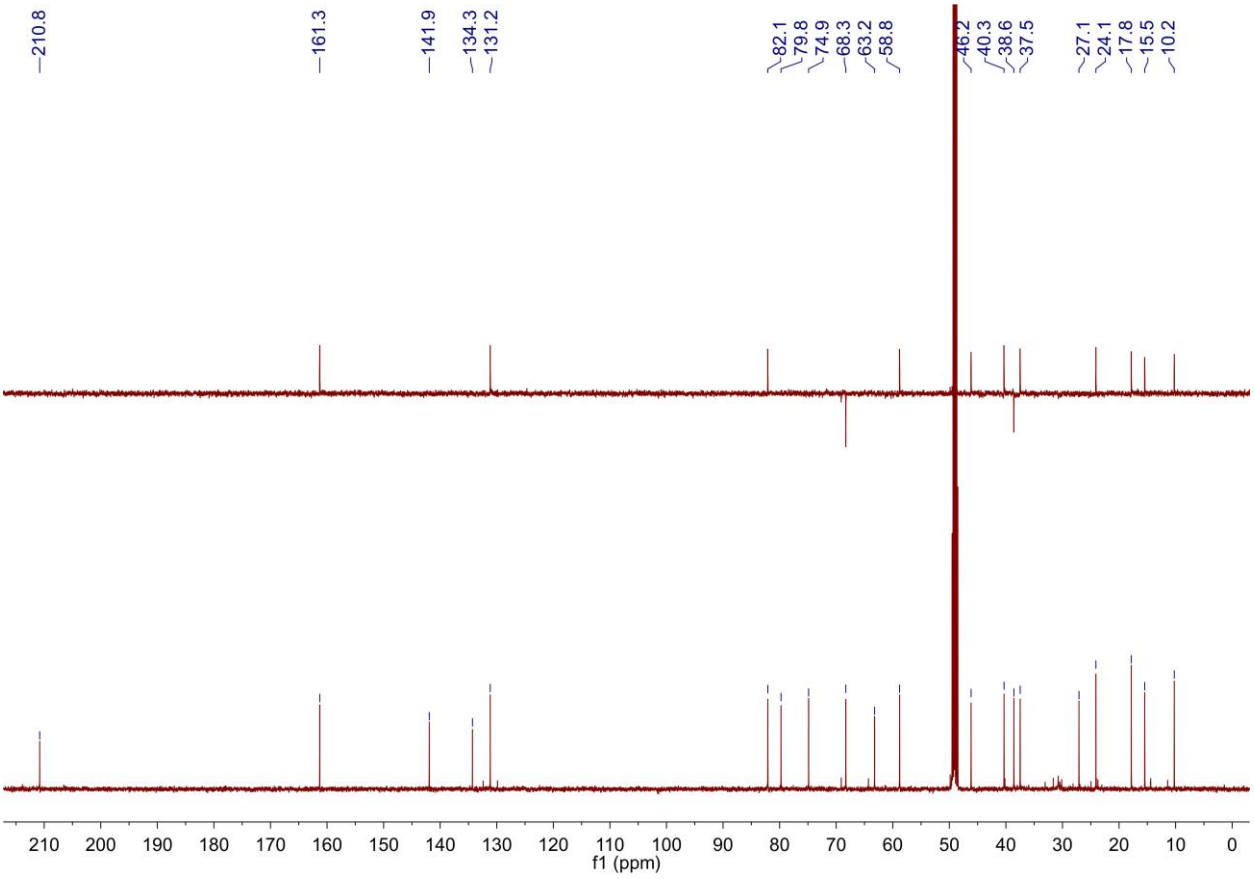


Fig. S57. ESIMS spectrum of **1c**

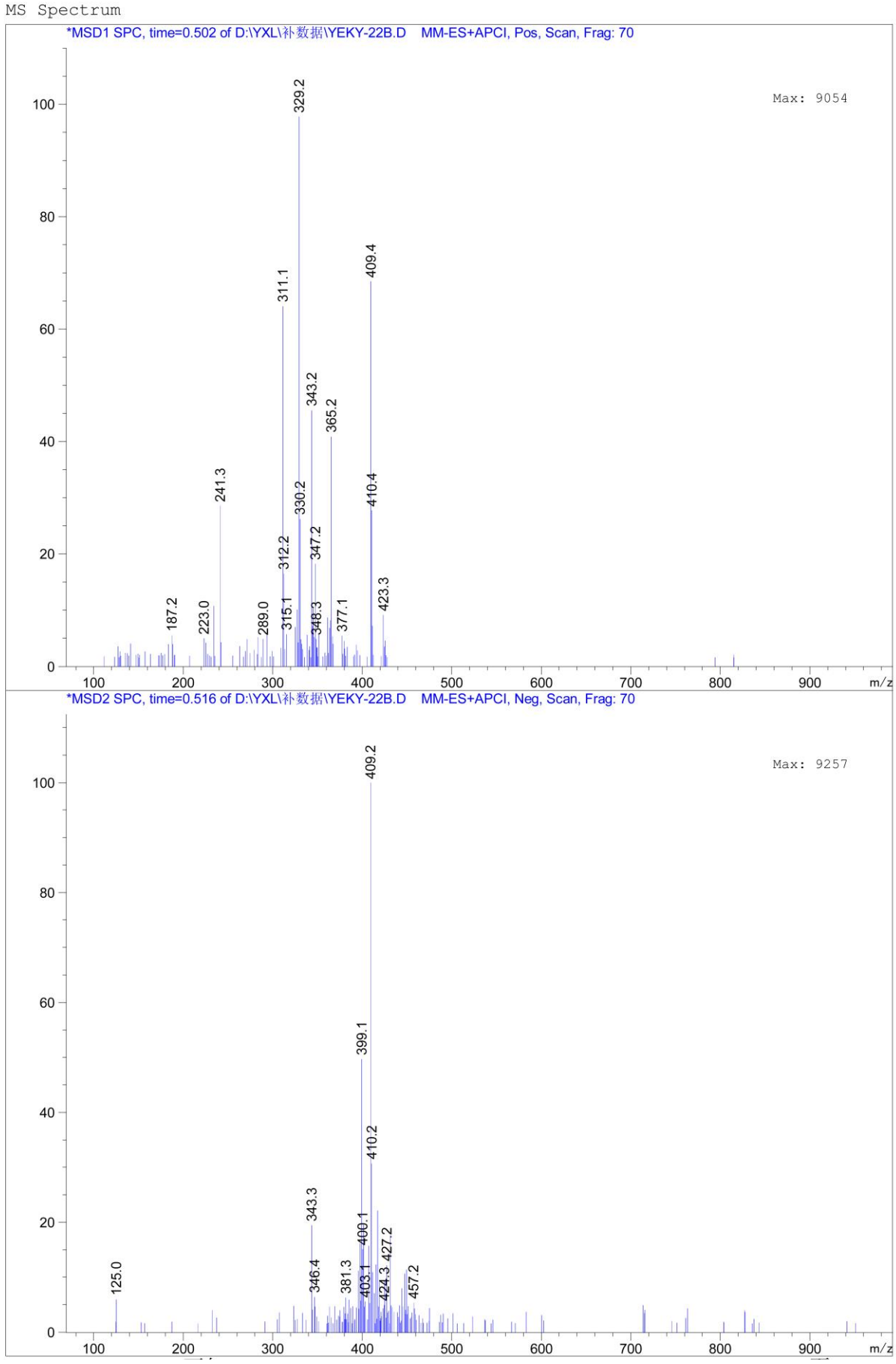


Fig. S58. ^{1}H NMR spectrum of **4a** in $CDCl_3$

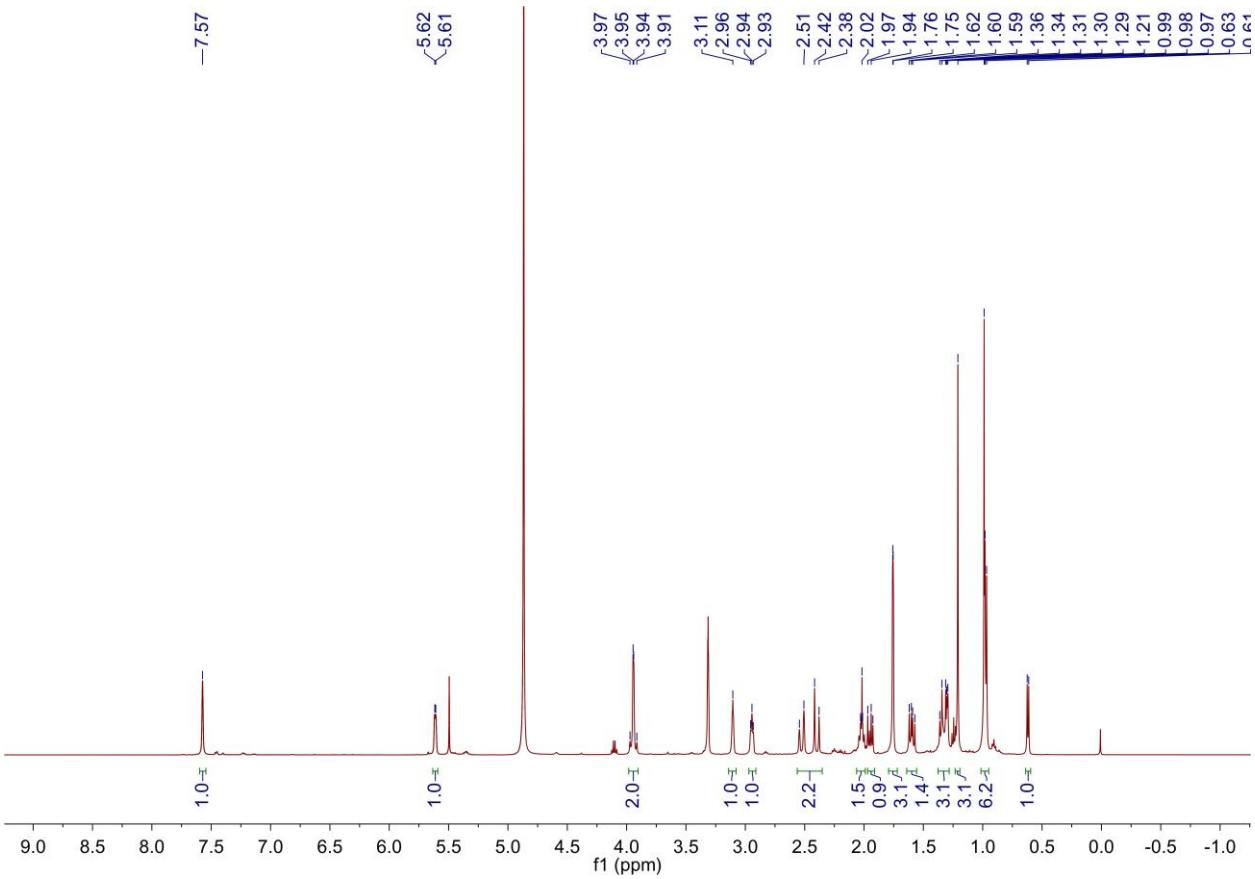


Fig. S59. ^{13}C NMR and DEPT135 spectra of **4a** in $CDCl_3$

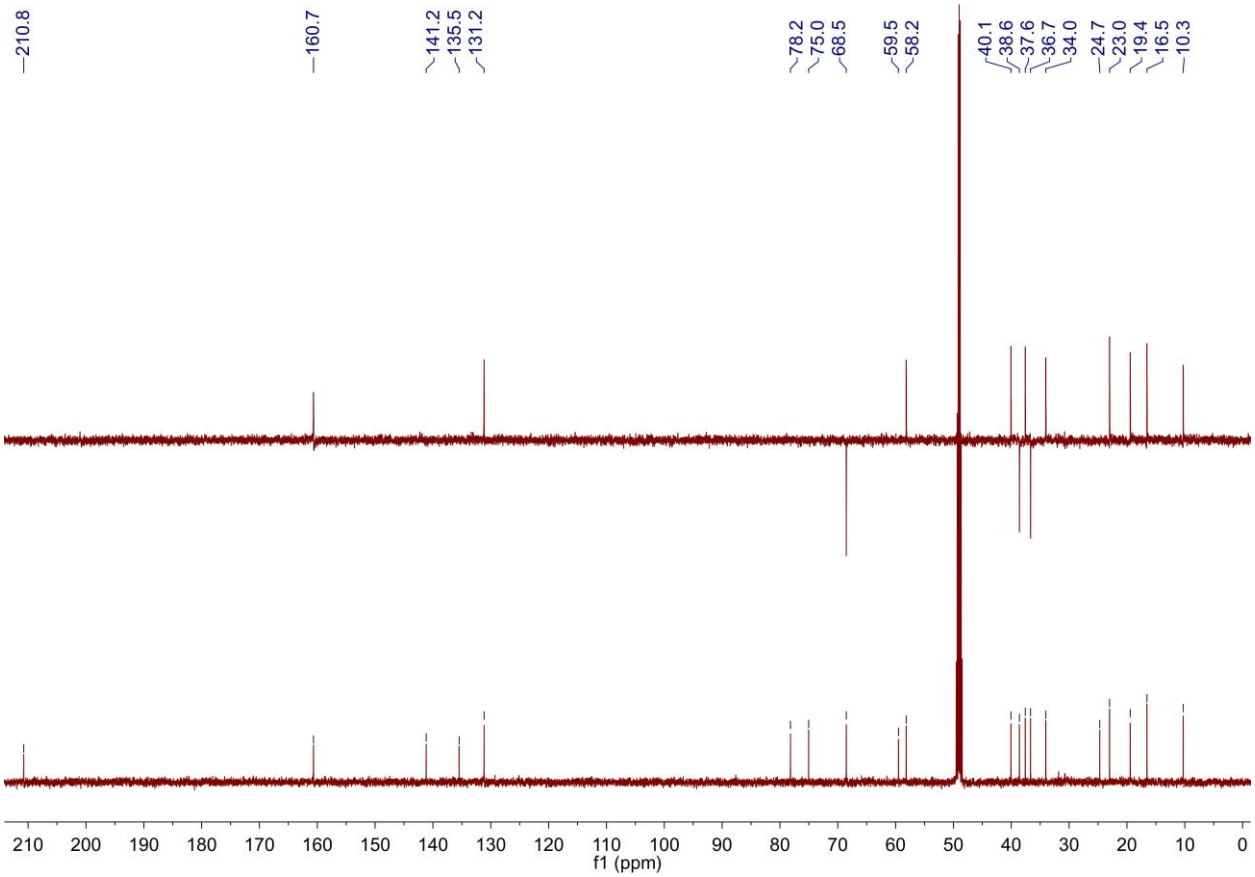


Fig. S60. HSQC spectrum of **4a** in $CDCl_3$

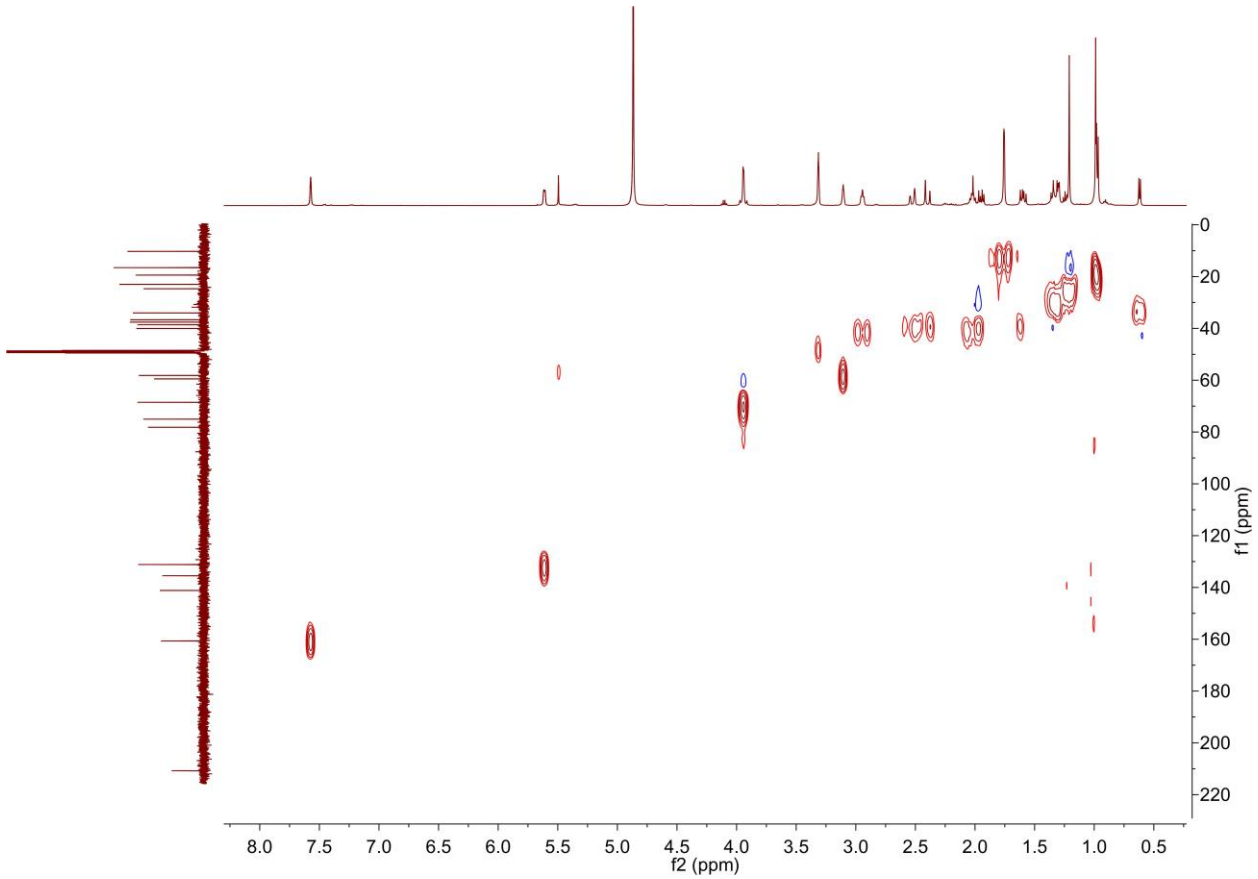


Fig. S61. HMBC spectrum of **4a** in $CDCl_3$

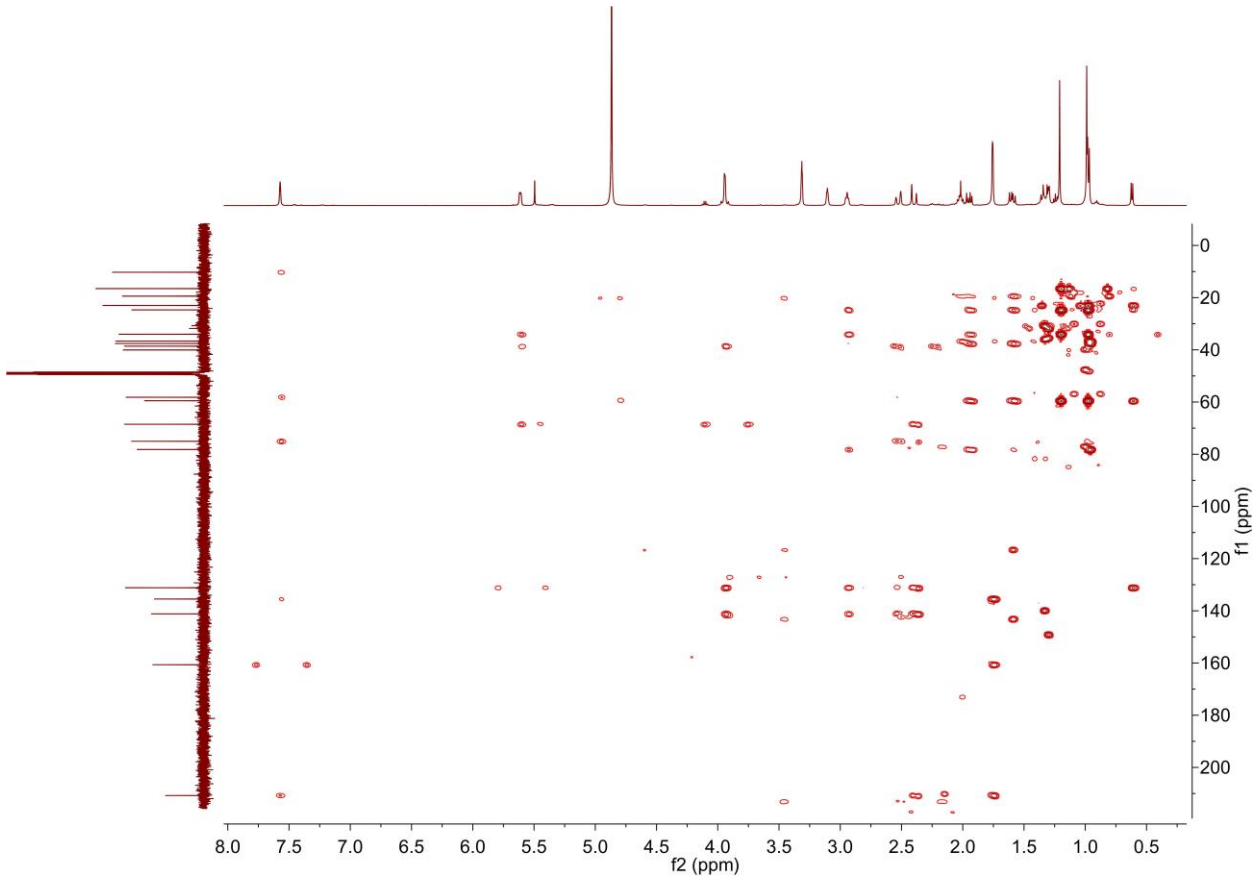


Fig. S62. $^{1}H–^{1}H$ COSY spectrum of **4a** in $CDCl_3$

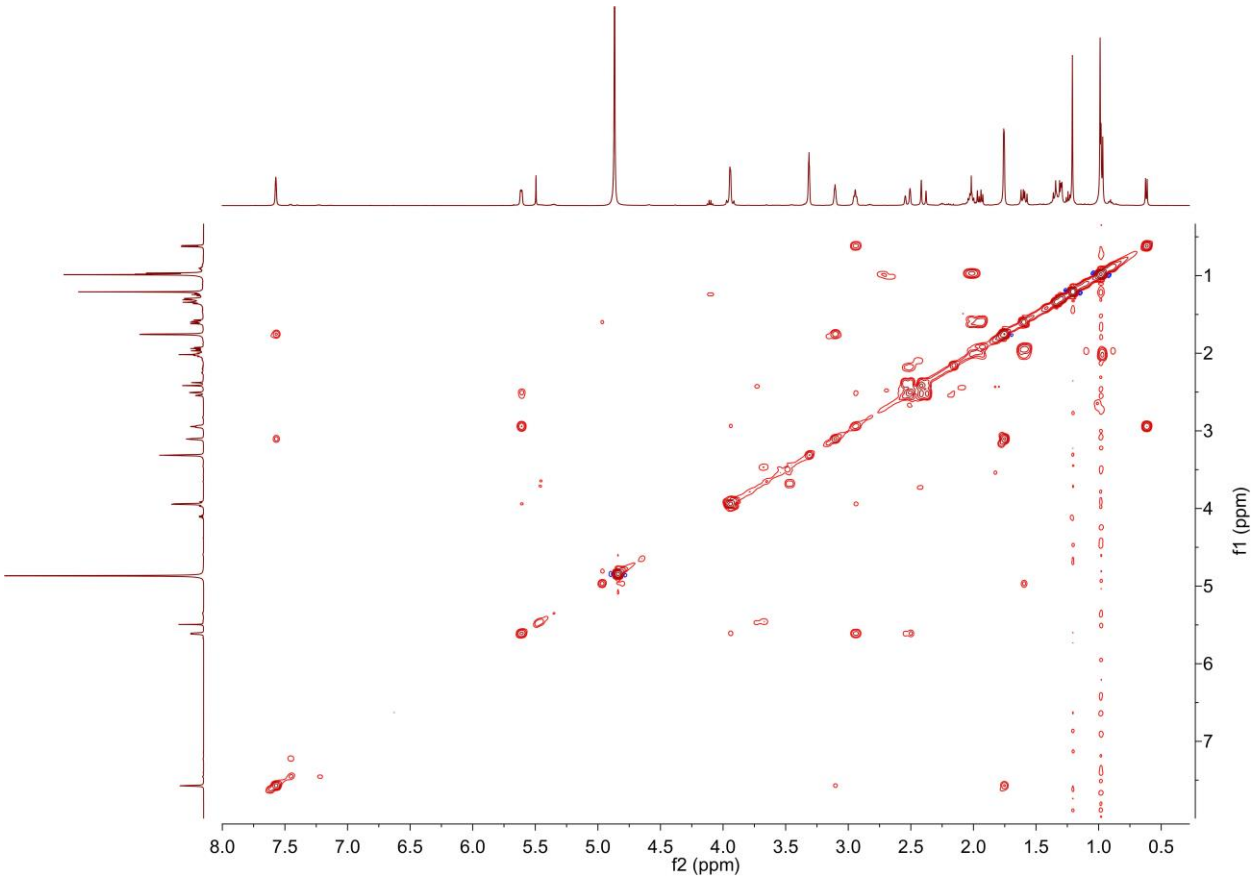


Fig. S63. ^{1}H NMR spectrum of methyl linoleate in $CDCl_3$

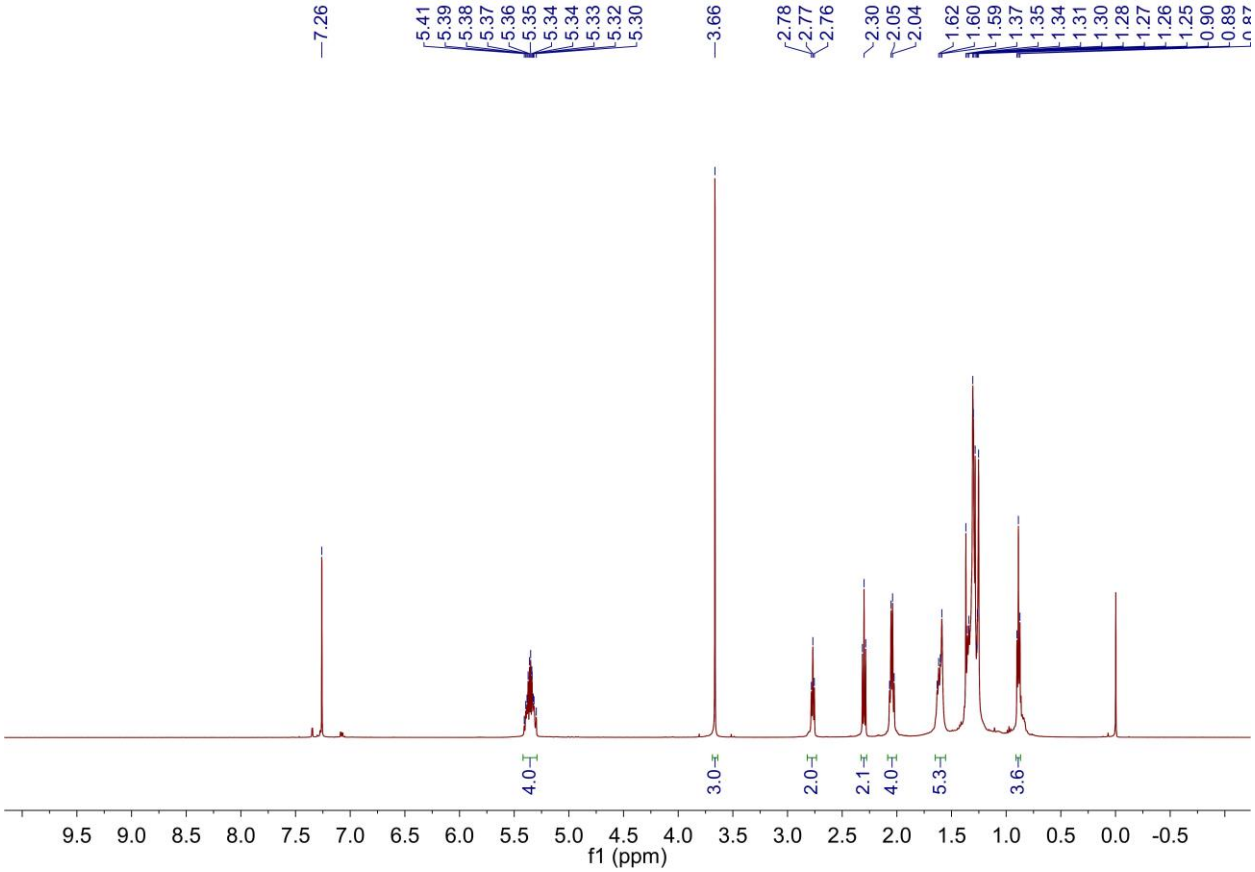


Fig. S64. ^{13}C NMR and DEPT135 spectra of methyl linoleate in $CDCl_3$

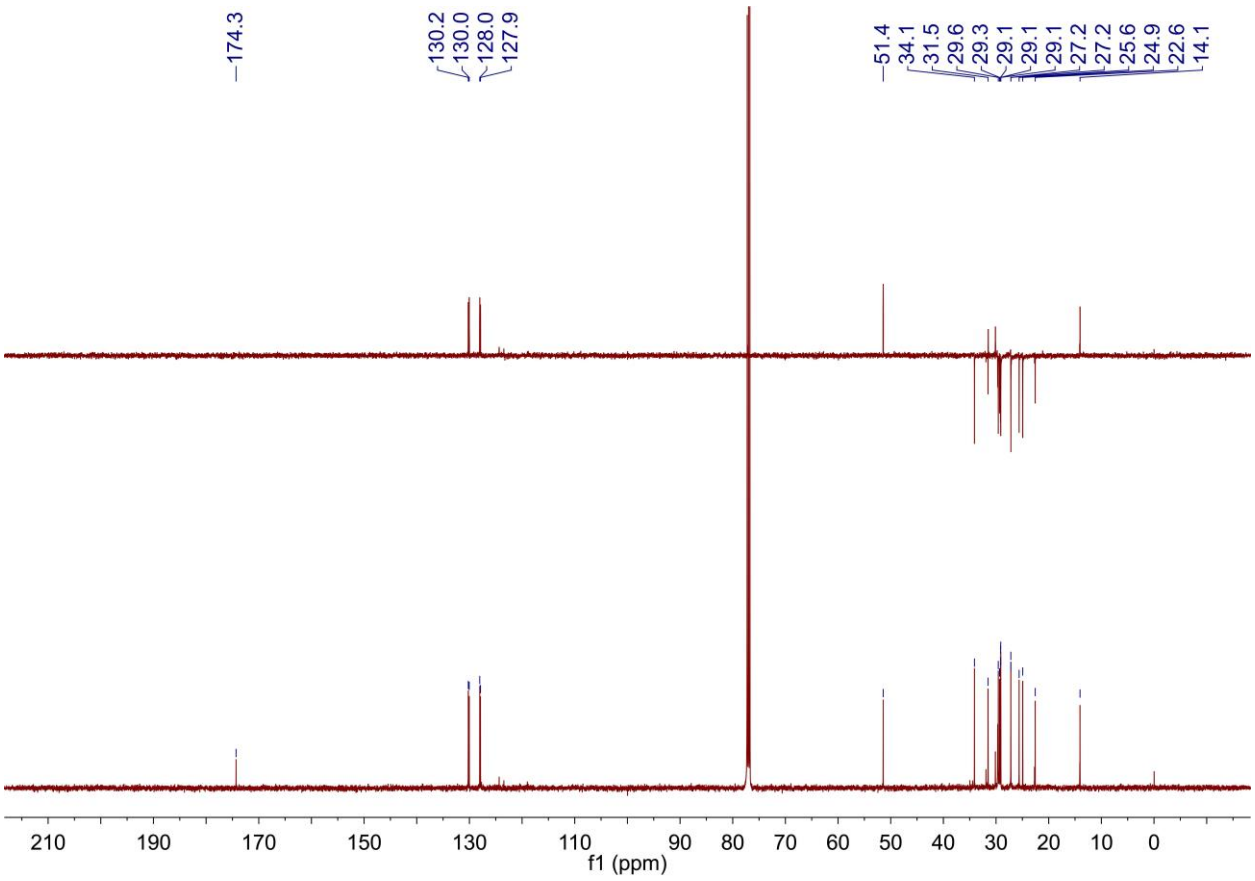


Fig. S65. GC-MS spectrum of methyl linoleate

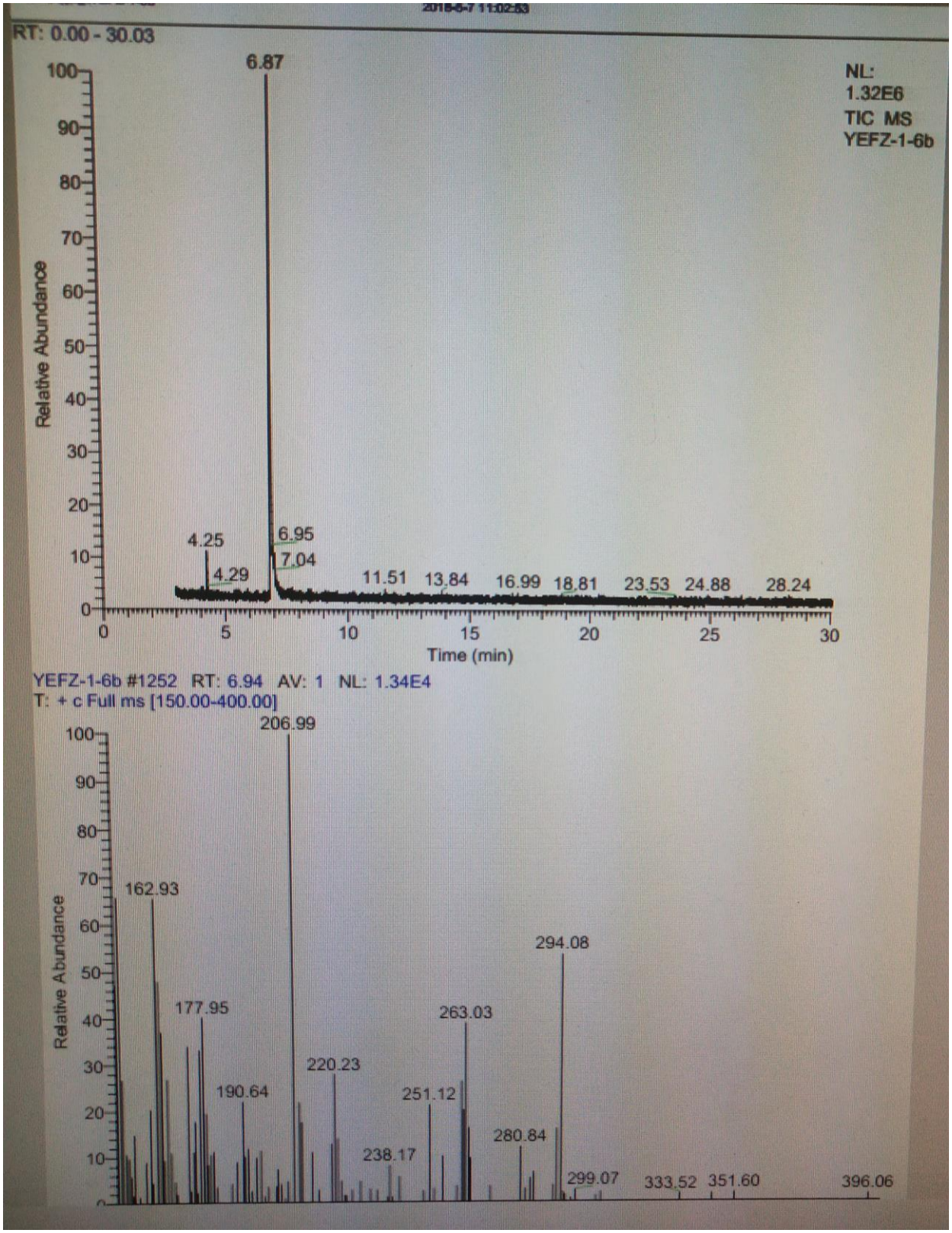


Fig. S66. ^{1}H NMR spectrum of methyl linolenate in $CDCl_3$

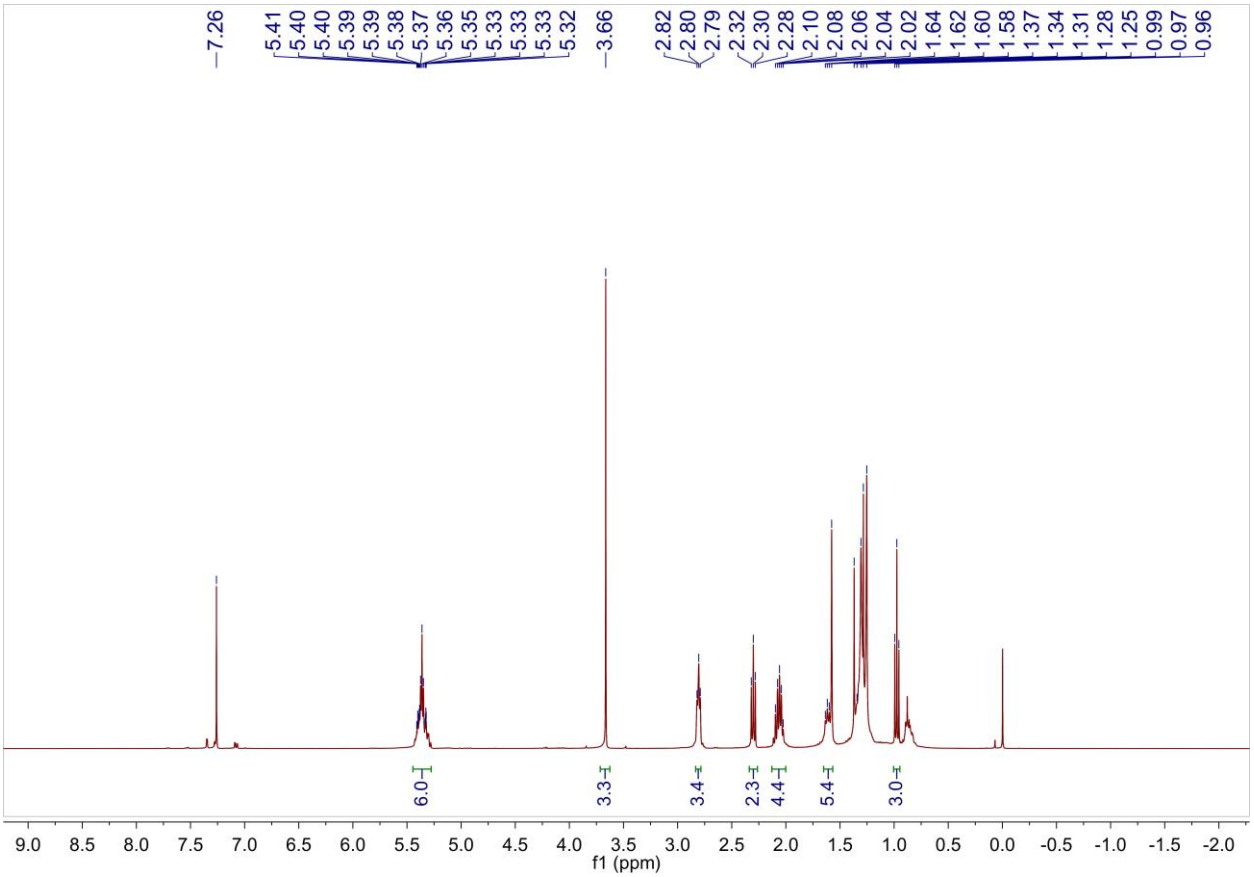


Fig. S67. ^{13}C NMR and DEPT135 spectra of methyl linolenate in $CDCl_3$

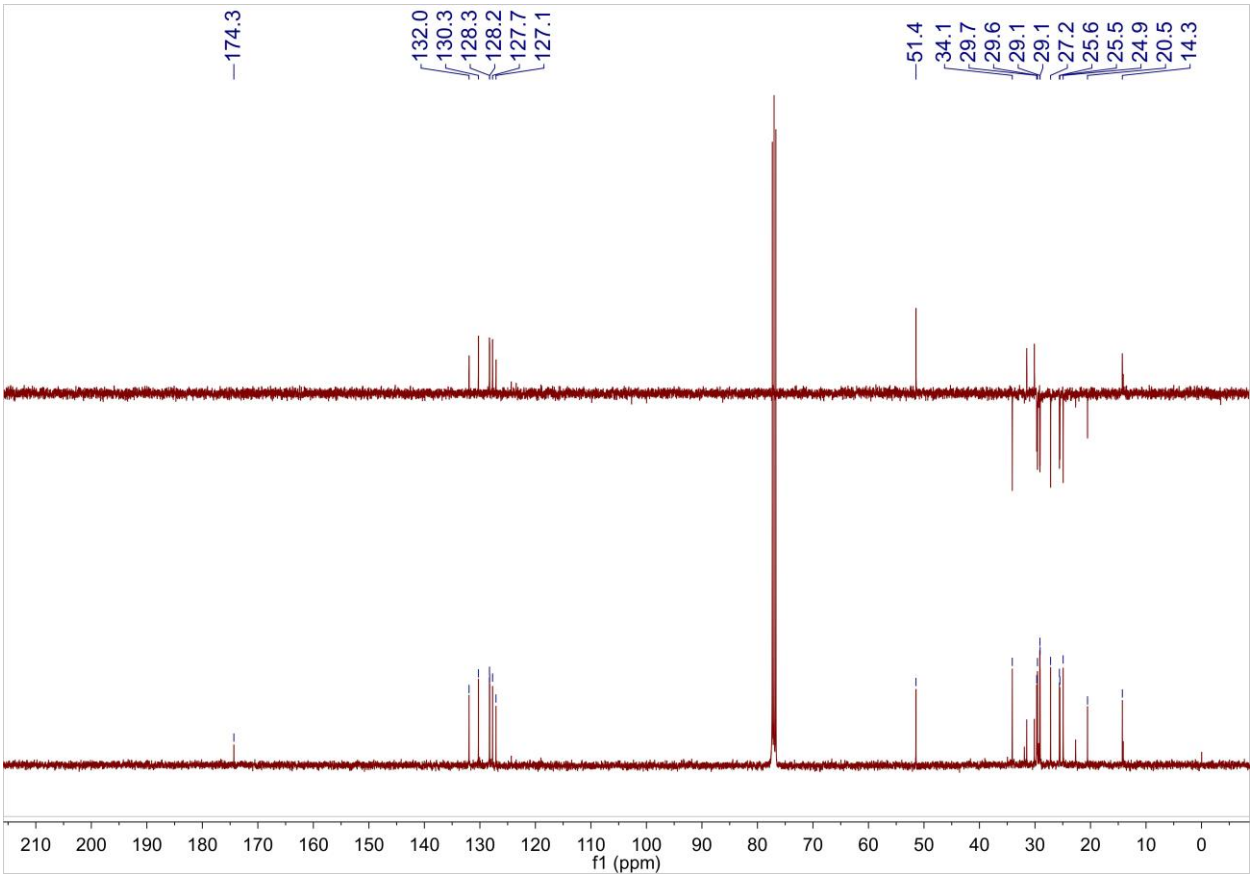


Fig. S68. GC-MS spectrum of methyl linolenate

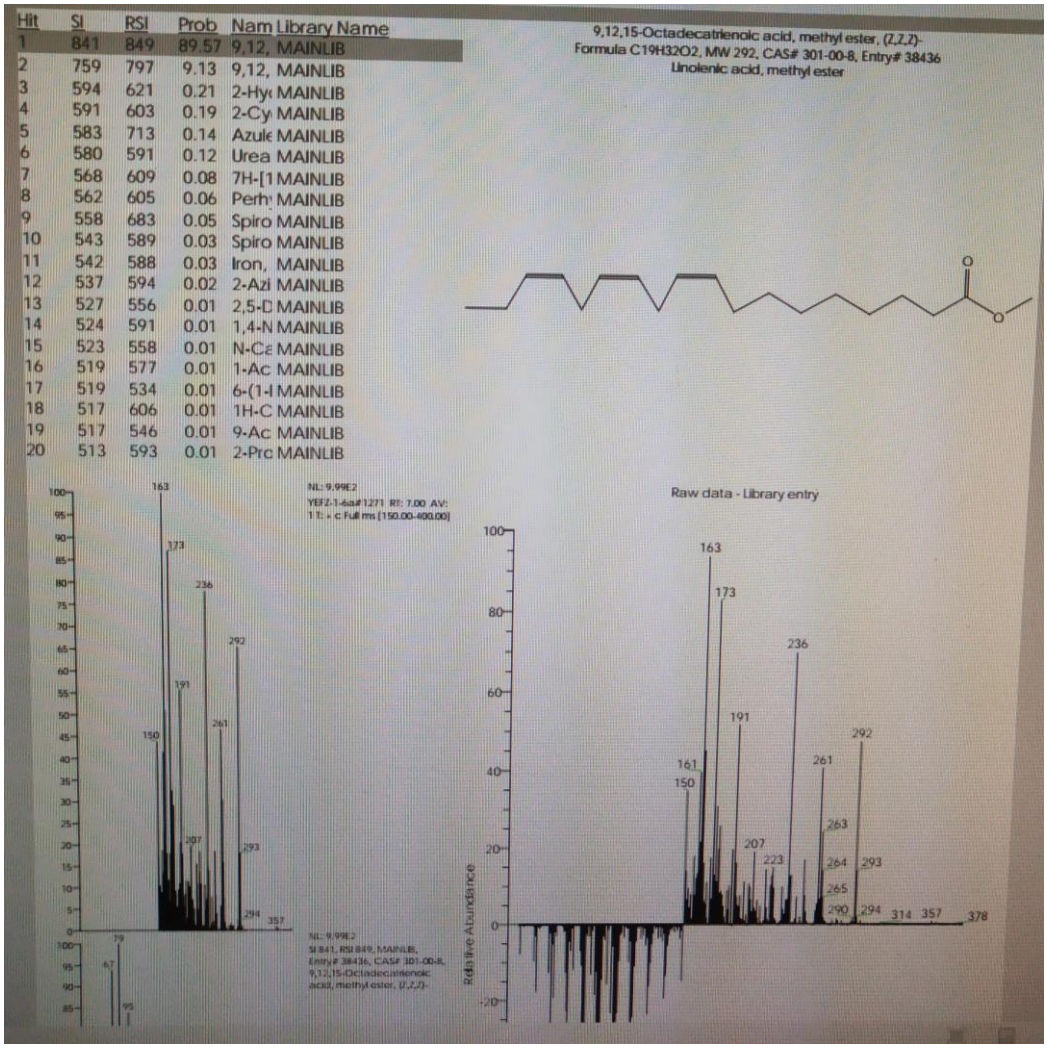


Fig. S69. ECD curves of **6** and **7**