Supplementary Materials

Immunomodulatory Polyketides from a *Phoma*-like Fungus Isolated from a Soft Coral

Yi-Zhe Sun,[†] Tibor Kurtán,[‡] Attila Mándi,[‡] Hua Tang,[†] Yalan Chou,[§] Keryea Soong,[§] Li Su,[†] Peng Sun,[†] Chun-Lin Zhuang,[†] and Wen Zhang[*,†]

[†]Research Center for Marine Drugs and Pharmaceutical Analysis Center, School of Pharmacy, Second Military Medical University, 325 Guo-He Rd., Shanghai 200433, P. R. China

[‡]Department of Organic Chemistry, University of Debrecen, POB 400, H-4002 Debrecen, Hungary

[§]Department of Oceanography, National Sun Yat-sen University, 70 Lien-Hai Rd., Kaohsiung 80424, Taiwan

Content

1. Supplementary Figures

2. Supplementary Table

D:\data\...\EI-GYW-17158_A20-c1 3/14/2017 10:46:34 AM

EI-GYW-17158_A20-c1#9 RT: 1.78
T: + c EI Full ms [49.50-1000.50]
m/z= 47.50-1002.50

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Compositic
163.1098	2923124.0	13.21	163.1117	-1.92	4.5	$C_{11}H_{15}O_1$
164.1178	3007200.0	13.59	164.1196	-1.78	4.0	$C_{11}H_{16}O_1$
165.0896	419175.0	1.89	165.0910	-1.39	4.5	$C_{10}H_{13}O_2$
165.1261	17093120.0	77.27	165.1274	-1.28	3.5	$C_{11}H_{17}O_1$
166.0977	321448.0	1.45	166.0988	-1.17	4.0	$C_{10}H_{14}O_2$
167.1059	607760.0	2.75	167.1067	-0.75	3.5	$C_{10}H_{15}O_2$
170.0934	239456.0	1.08	170.0937	-0.35	3.0	$C_9H_{14}O_3$
172.1241	491313.0	2.22	172.1247	-0.54	6.0	$C_{13}H_{16}$
173.0953	233377.0	1.05	173.0961	-0.83	6.5	$C_{12}H_{13}O_1$
173.1319	1056410.0	4.78	173.1325	-0.60	5.5	$C_{13}H_{17}$
174.1394	688260.0	3.11	174.1403	-0.89	5.0	$C_{13}H_{18}$
175.1119	652048.0	2.95	175.1117	0.15	5.5	$C_{12}H_{15}O_1$
175.1481	11233792.0	50.78	175.1481	-0.06	4.5	$C_{13}H_{19}$
176.1185	359810.0	1.63	176.1196	-1.08	5.0	$C_{12}H_{16}O_1$
176.1539	3428505.0	15.50	176.1560	-2.02	4.0	$C_{13}H_{20}$
177.1275	3010668.0	13.61	177.1274	0.08	4.5	$C_{12}H_{17}O_1$
177.1611	819806.0	3.71	177.1638	-2.71	3.5	$C_{13}H_{21}$
178.1341	2270197.0	10.26	178.1352	-1.07	4.0	$C_{12}H_{18}O_1$
179.1068	252361.0	1.14	179.1067	0.11	4.5	$C_{11}H_{15}O_2$
179.1428	1909926.0	8.63	179.1430	-0.24	3.5	$C_{12}H_{19}O_1$
182.1300	861065.0	3.89	182.1301	-0.13	3.0	$C_{11}H_{18}O_2$
187.1476	5729625.0	25.90	187.1481	-0.58	5.5	$C_{14}H_{19}$
189.1276	358669.0	1.62	189.1274	0.22	5.5	$C_{13}H_{17}O_1$
190.1346	2145476.0	9.70	190.1352	-0.60	5.0	$C_{13}H_{18}O_1$
191.1417	1123851.0	5.08	191.1430	-1.32	4.5	$C_{13}H_{19}O_1$
192.1481	285741.0	1.29	192.1509	-2.77	4.0	$C_{13}H_{20}O_1$
193.1217	302355.0	1.37	193.1223	-0.57	4.5	$C_{12}H_{17}O_2$
193.1582	2239648.0	10.12	193.1587	-0.46	3.5	$C_{13}H_{21}O_1$
195.1380	1460179.0	6.60	195.1380	0.09	3.5	$C_{12}H_{19}O_2$
196.1442	677045.0	3.06	196.1458	-1.62	3.0	$C_{12}H_{20}O_2$
202.1724	287694.0	1.30	202.1716	0.77	5.0	$C_{15}H_{22}$
203.1435	1333439.0	6.03	203.1430	0.43	5.5	$C_{14}H_{19}O_1$
204.1493	482337.0	2.18	204.1509	-1.55	5.0	$C_{14}H_{20}O_1$
205.1595	1537759.0	6.95	205.1587	0.86	4.5	$C_{14}H_{21}O_1$
206.1640	335142.0	1.52	206.1665	-2.52	4.0	$C_{14}H_{22}O_1$
207.1382	377279.0	1.71	207.1380	0.23	4.5	$C_{13}H_{19}O_2$
208.1463	926663.0	4.19	208.1458	0.55	4.0	$C_{13}H_{20}O_2$
209.1531	463309.0	2.09	209.1536	-0.54	3.5	$C_{13}H_{21}O_2$
215.1424	1173230.0	5.30	215.1430	-0.68	6.5	$C_{15}H_{19}O_1$
217.1584	570956.0	2.58	217.1587	-0.24	5.5	$C_{15}H_{21}O_1$
218.1647	355158.0	1.61	218.1665	-1.79	5.0	$C_{15}H_{22}O_1$
221.1530	633854.0	2.87	221.1536	-0.56	4.5	$C_{14}H_{21}O_2$
223.1679	229229.0	1.04	223.1693	-1.35	3.5	$C_{14}H_{23}O_2$
230.1659	548417.0	2.48	230.1665	-0.60	6.0	$C_{16}H_{22}O_1$
233.1529	1267709.0	5.73	233.1536	-0.71	5.5	$C_{15}H_{21}O_2$
236.1751	350461.0	1.58	236.1771	-1.96	4.0	$C_{15}H_{24}O_2$
248.1762	1389907.0	6.28	248.1771	-0.85	5.0	$C_{16}H_{24}O_2$
266.1870	977425.0	4.42	266.1876	-0.66	4.0	$C_{16}H_{26}O_3$

Figure S1. HREIMS spectrum of **1**

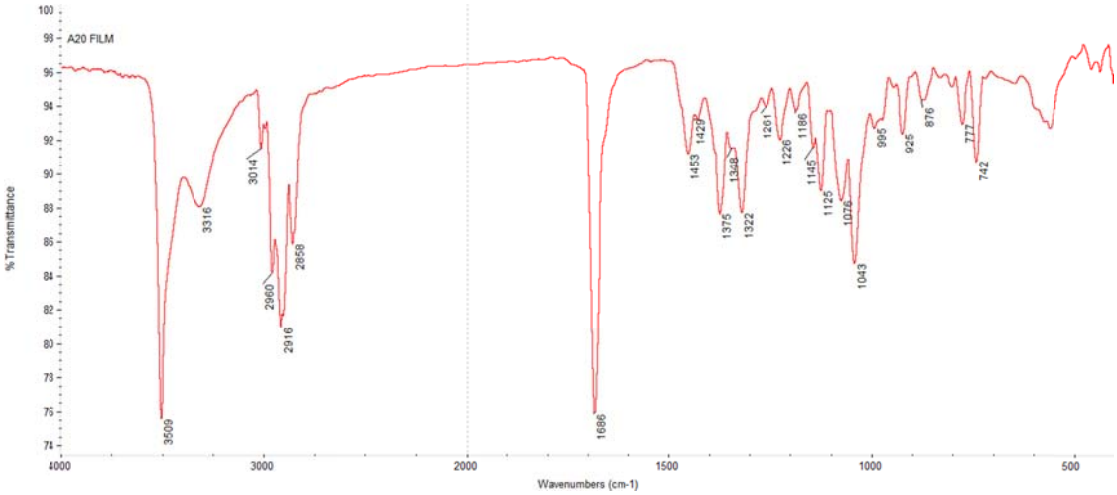


Figure S2. FTIR spectrum of **1**

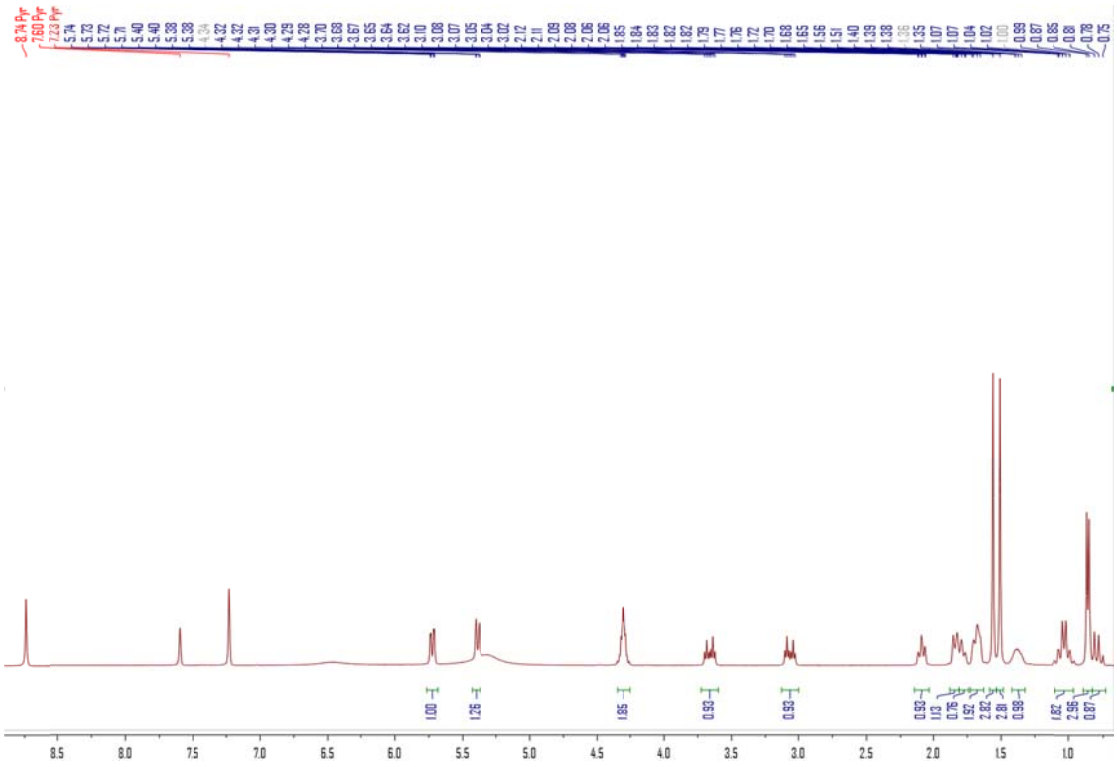


Figure S3. ^{1}H NMR spectrum of **1** in *Pyridine-d$_5$* at 400 MHz

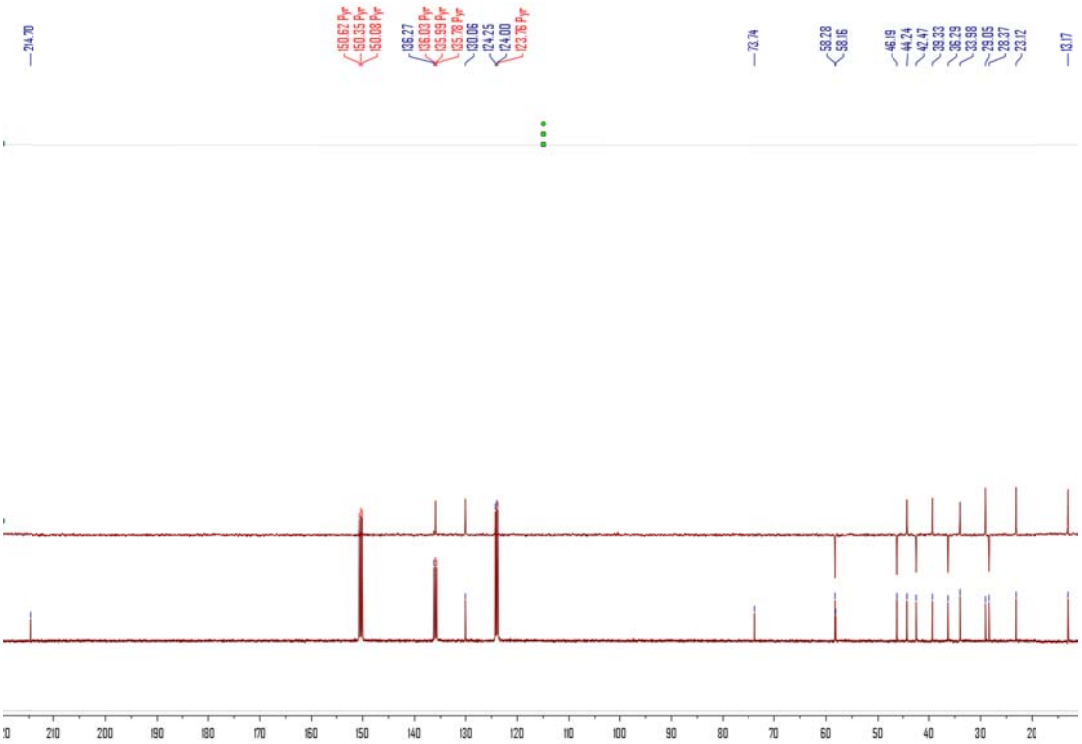


Figure S4. ^{13}C and NMR DEPT spectra of **1** in *Pyridine-d_5* at 100 MHz

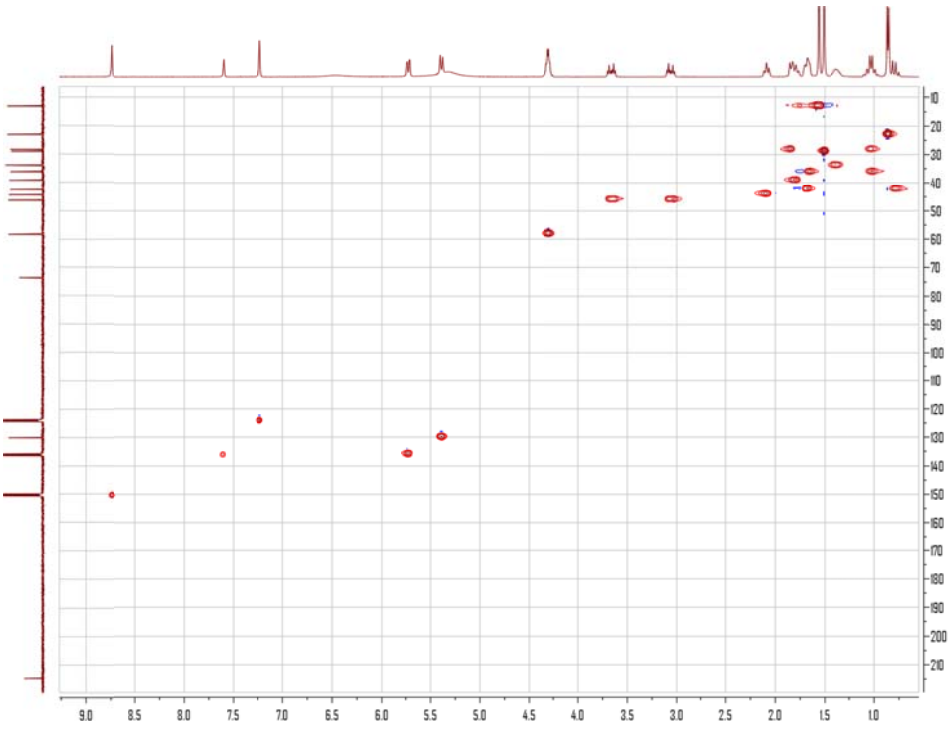


Figure S5. HSQC spectrum of **1** in *Pyridine-d_5*

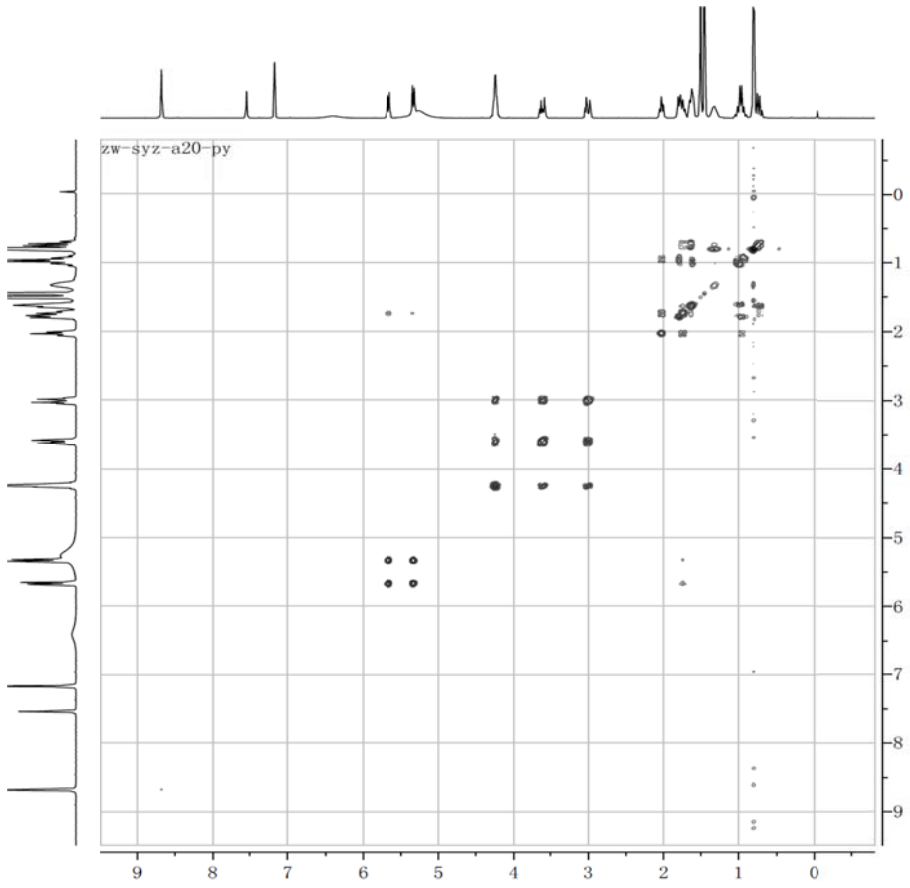


Figure S6. ^{1}H-^{1}H COSY spectrum of **1** in *Pyridine-d_5*

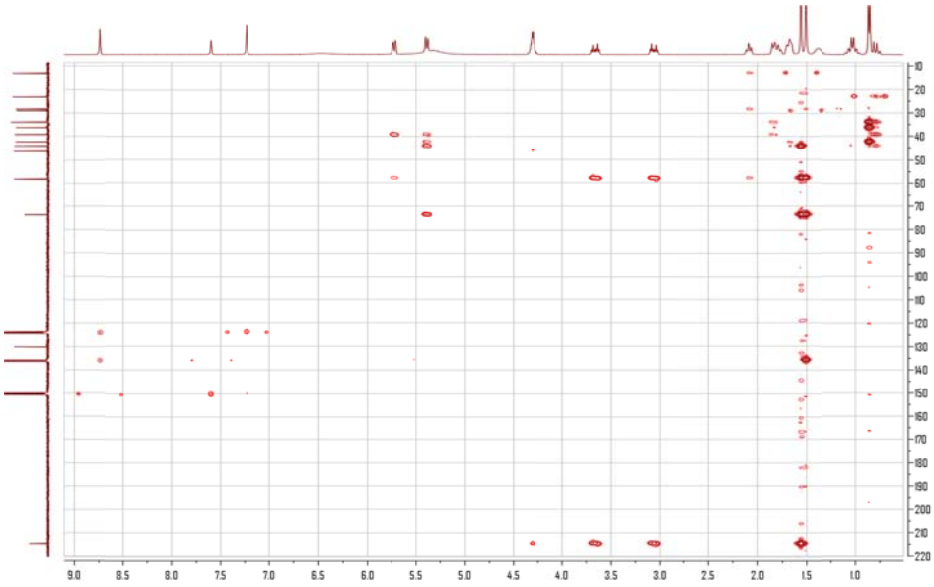


Figure S7. HMBC spectrum of **1** in *Pyridine-d_5*

Figure S8. NOESY spectrum of **1** in *Pyridine-d_5*

D:\data\...\EI-GYW-17160_A2-c1 3/14/2017 2:36:47 PM

EI-GYW-17160_A2-c1#17 RT: 3.56
T: + c EI Full ms [49.50-1000.50]
m/z= 47.50-1002.50

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
136.0877	1307410.0	8.09	136.0883	-0.57	4.0	$C_9H_{12}O_1$
137.0963	2277857.0	14.09	137.0961	0.19	3.5	$C_9H_{13}O_1$
138.1035	1262245.0	7.81	138.1039	-0.38	3.0	$C_9H_{14}O_1$
139.0761	1073287.0	6.64	139.0754	0.70	3.5	$C_8H_{11}O_2$
141.0915	1333922.0	8.25	141.0910	0.48	2.5	$C_8H_{13}O_2$
143.0858	504086.0	3.12	143.0855	0.31	6.5	$C_{11}H_{11}$
144.0790	877679.0	5.43	144.0781	0.88	2.0	$C_7H_{12}O_3$
145.1012	1705408.0	10.55	145.1012	0.02	5.5	$C_{11}H_{13}$
147.0802	882178.0	5.46	147.0804	-0.23	5.5	$C_{10}H_{11}O_1$
147.1168	2176245.0	13.47	147.1168	-0.02	4.5	$C_{11}H_{15}$
148.0881	700857.0	4.34	148.0883	-0.17	5.0	$C_{10}H_{12}O_1$
149.0961	3681020.0	22.78	149.0961	0.01	4.5	$C_{10}H_{13}O_1$
149.1328	3477182.0	21.52	149.1325	0.32	3.5	$C_{11}H_{17}$
151.1114	1620036.0	10.02	151.1117	-0.31	3.5	$C_{10}H_{15}O_1$
152.0834	1177466.0	7.29	152.0832	0.19	4.0	$C_9H_{12}O_2$
152.1199	4027641.0	24.92	152.1196	0.34	3.0	$C_{10}H_{16}O_1$
157.1013	421765.0	2.61	157.1012	0.13	6.5	$C_{12}H_{13}$
164.1187	3728994.0	23.07	164.1196	-0.87	4.0	$C_{11}H_{16}O_1$
165.1268	15808768.0	97.82	165.1274	-0.58	3.5	$C_{11}H_{17}O_1$
170.0947	552499.0	3.42	170.0937	0.94	3.0	$C_9H_{14}O_3$
172.1248	1121612.0	6.94	172.1247	0.12	6.0	$C_{13}H_{16}$
173.0963	448122.0	2.77	173.0961	0.17	6.5	$C_{12}H_{13}O_1$
173.1325	1604323.0	9.93	173.1325	0.01	5.5	$C_{13}H_{17}$
174.1394	850246.0	5.26	174.1403	-0.90	5.0	$C_{13}H_{18}$
175.1119	1094531.0	6.77	175.1117	0.20	5.5	$C_{12}H_{15}O_1$
175.1483	9457408.0	58.52	175.1481	0.19	4.5	$C_{13}H_{19}$
177.1274	7694308.0	47.61	177.1274	0.03	4.5	$C_{12}H_{17}O_1$
179.1425	936407.0	5.79	179.1430	-0.54	3.5	$C_{12}H_{19}O_1$
187.1482	8422400.0	52.11	187.1481	0.10	5.5	$C_{14}H_{19}$
189.1270	668618.0	4.14	189.1274	-0.41	5.5	$C_{13}H_{17}O_1$
190.1351	4152888.0	25.70	190.1352	-0.15	5.0	$C_{13}H_{18}O_1$
193.1584	2865493.0	17.73	193.1587	-0.32	3.5	$C_{13}H_{21}O_1$
202.1355	447793.0	2.77	202.1352	0.24	6.0	$C_{14}H_{18}O_1$
202.1722	734303.0	4.54	202.1716	0.56	5.0	$C_{15}H_{22}$
203.1433	835344.0	5.17	203.1430	0.21	5.5	$C_{14}H_{19}O_1$
205.1592	1393440.0	8.62	205.1587	0.49	4.5	$C_{14}H_{21}O_1$
221.1536	530443.0	3.28	221.1536	-0.06	4.5	$C_{14}H_{21}O_2$
230.1667	2290213.0	14.17	230.1665	0.18	6.0	$C_{16}H_{22}O_1$
233.1534	1894695.0	11.72	233.1536	-0.24	5.5	$C_{15}H_{21}O_2$
248.1769	2371656.0	14.67	248.1771	-0.21	5.0	$C_{16}H_{24}O_2$
308.1982	558864.0	3.46	308.1982	0.00	5.0	$C_{18}H_{28}O_4$

Figure S9. HREIMS spectrum of **2**

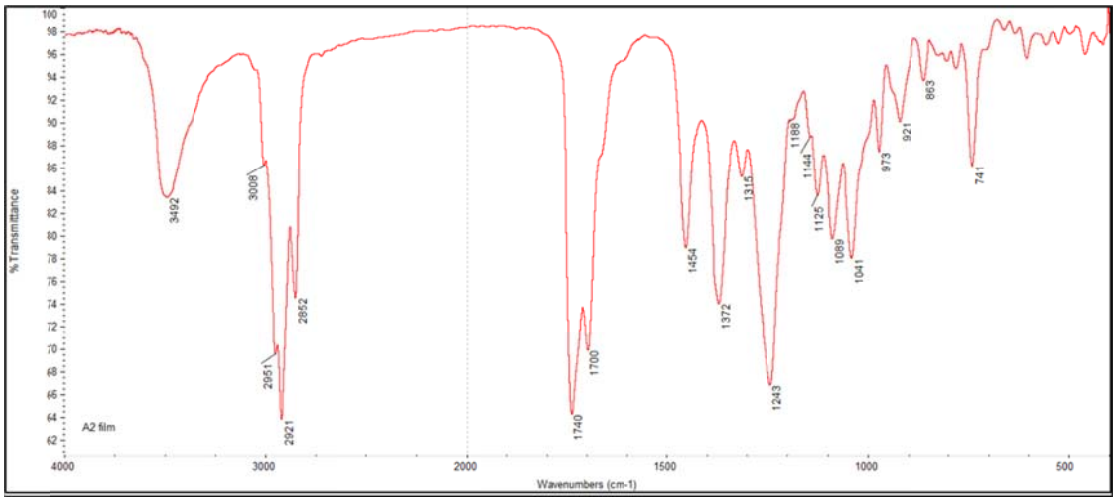


Figure S10. FTIR spectrum of **2**

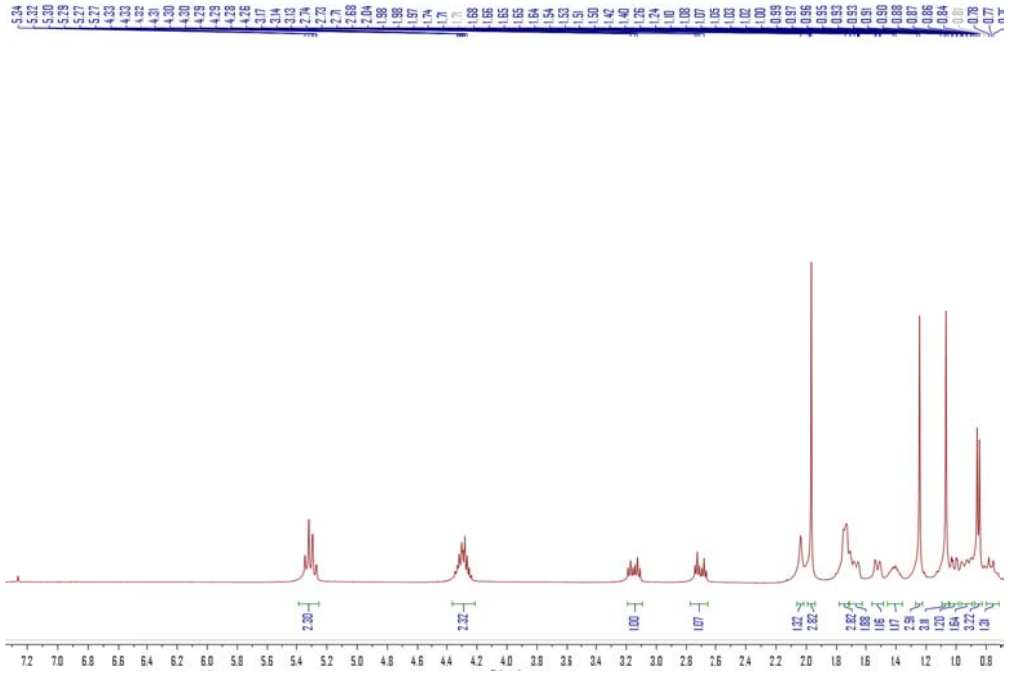


Figure S11. ^{1}H NMR spectrum of **2** in $CDCl_3$ at 400 MHz

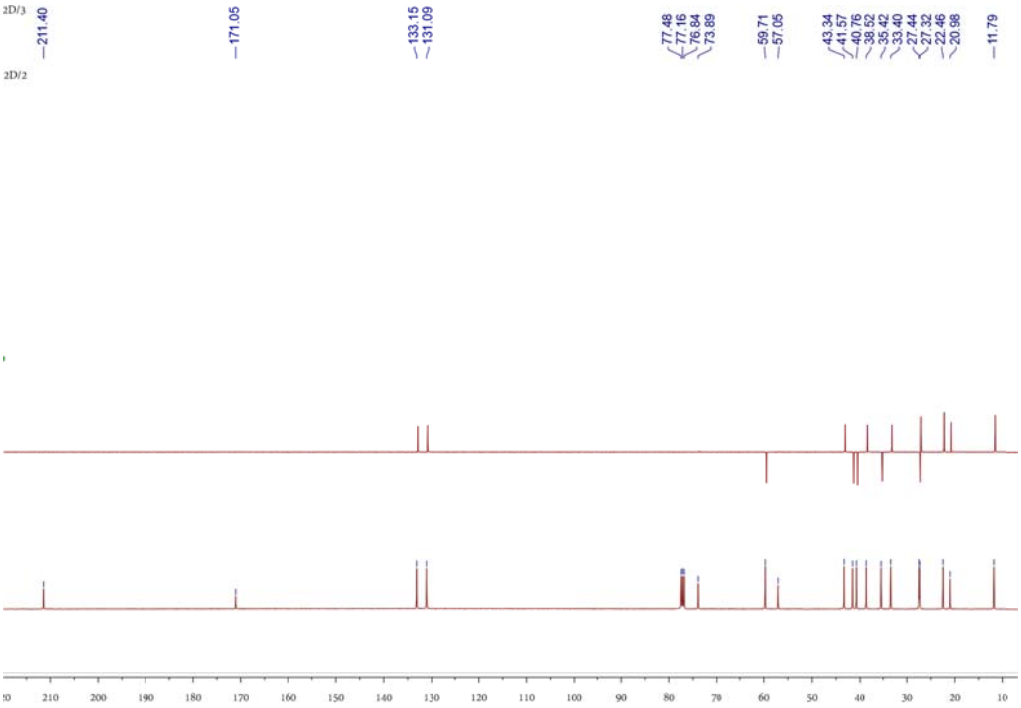


Figure S12. ^{13}C and NMR DEPT spectra of **2** in $CDCl_3$ at 100 MHz

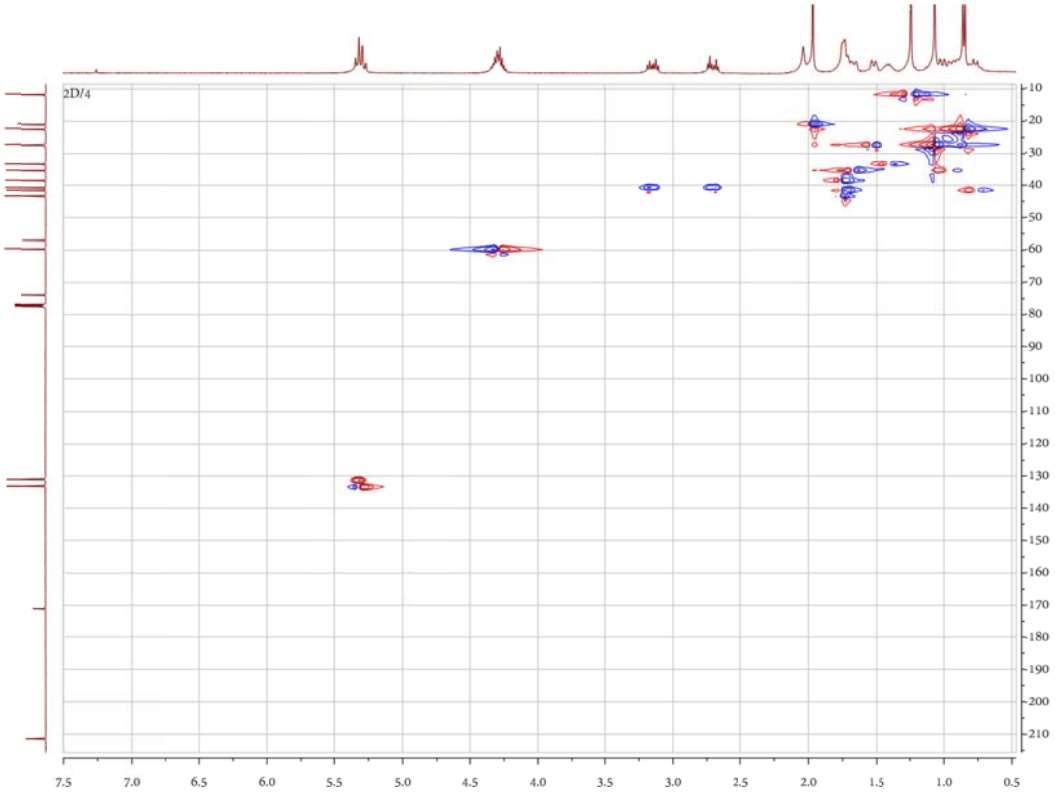


Figure S13. HSQC spectrum of **2** in $CDCl_3$

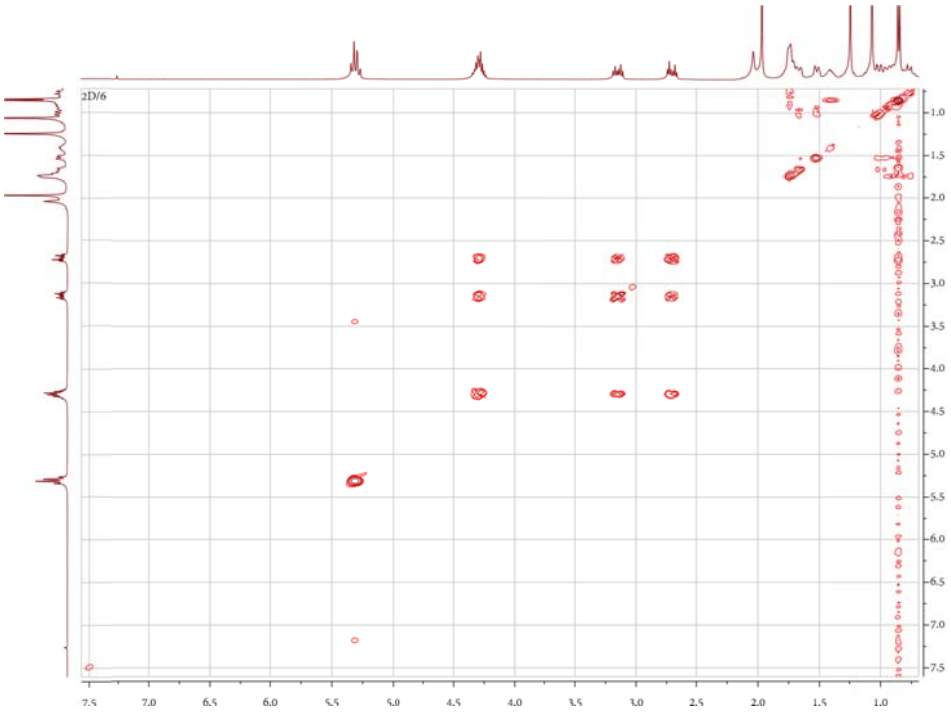


Figure S14. ^{1}H-^{1}H COSY spectrum of **2** in $CDCl_3$

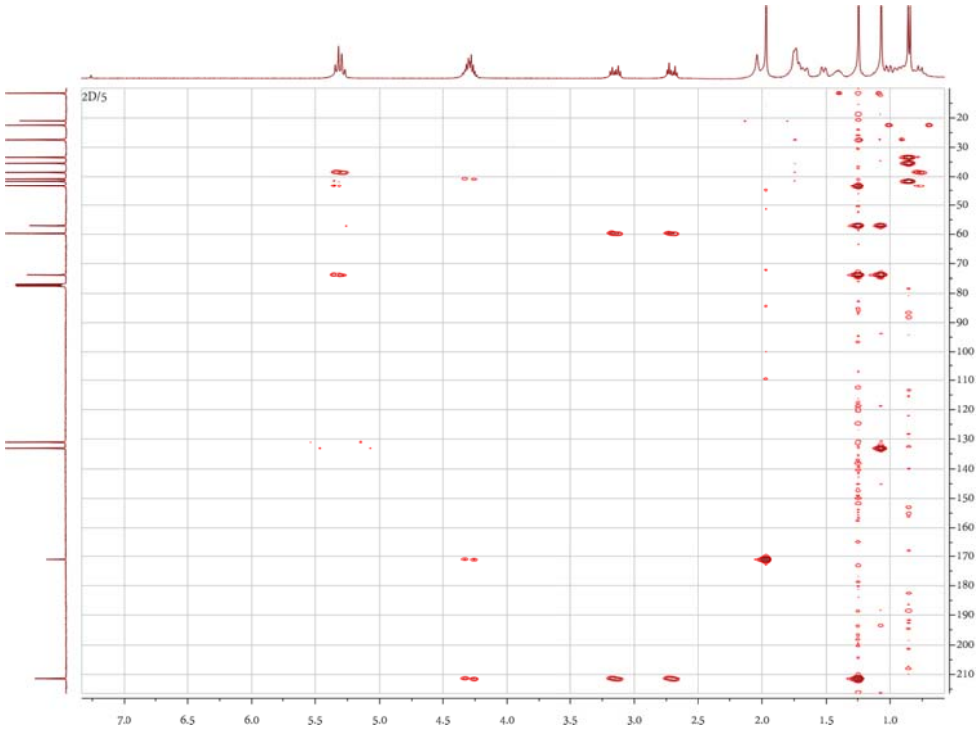


Figure S15. HMBC spectrum of **2** in $CDCl_3$

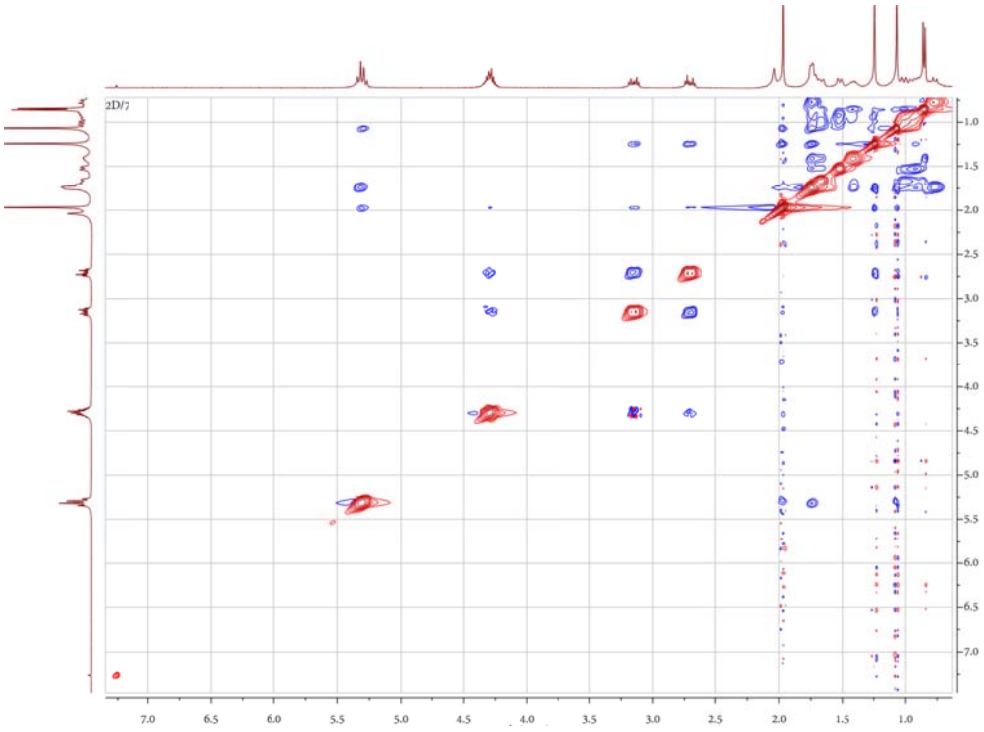


Figure S16. NOESY spectrum of **2** in $CDCl_3$

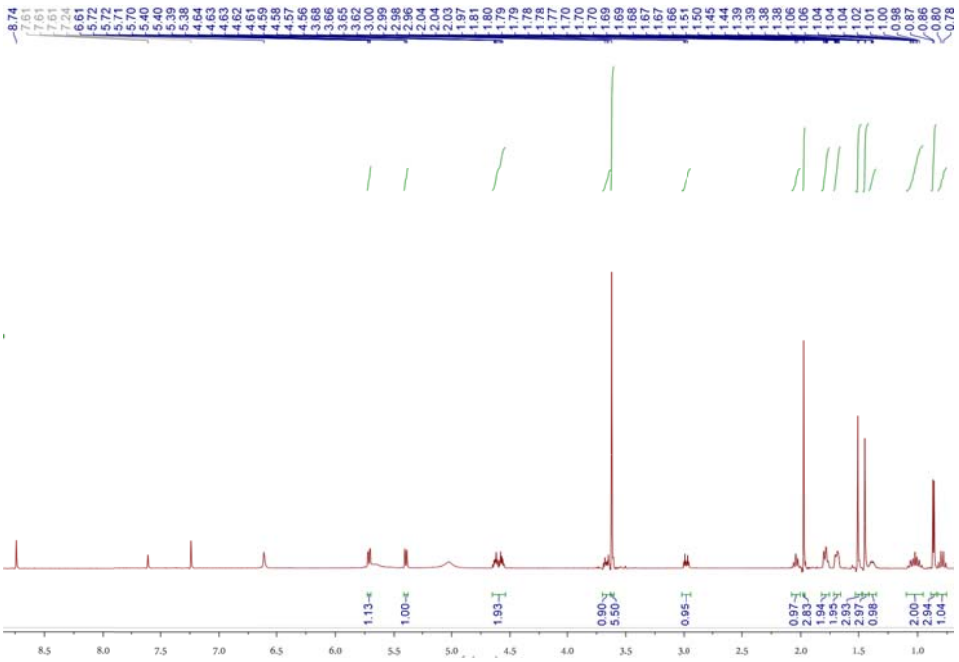


Figure S17. ^{1}H NMR spectrum of **2** in *Pyridine-d*$_5$ at 600 MHz

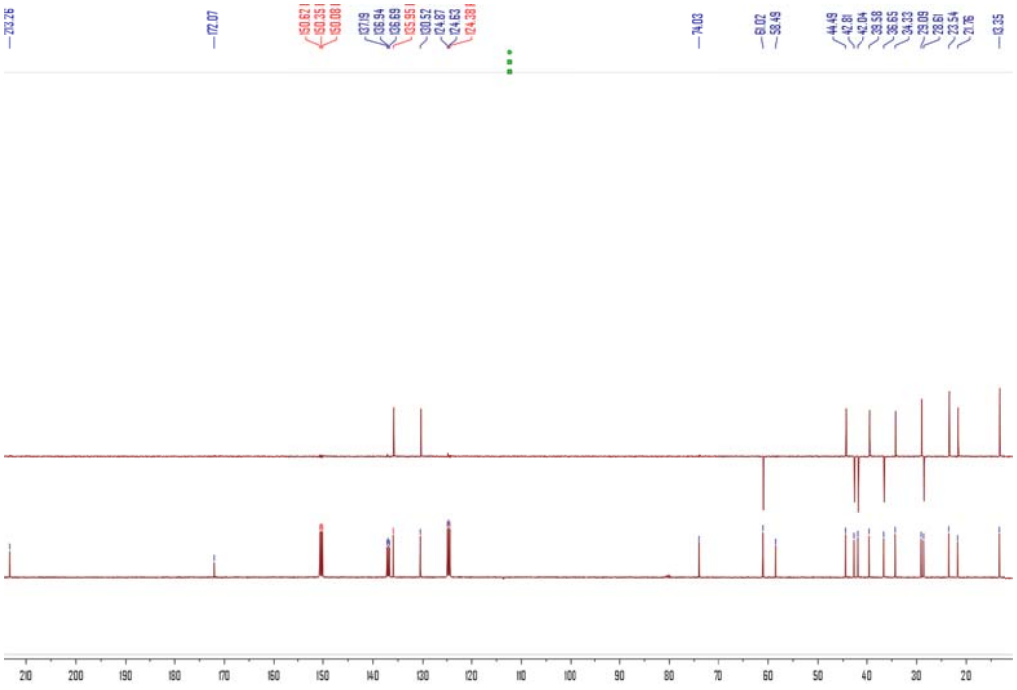


Figure S18. ^{13}C and NMR DEPT spectra of **2** in *Pyridine-d_5* at **1**00 MHz

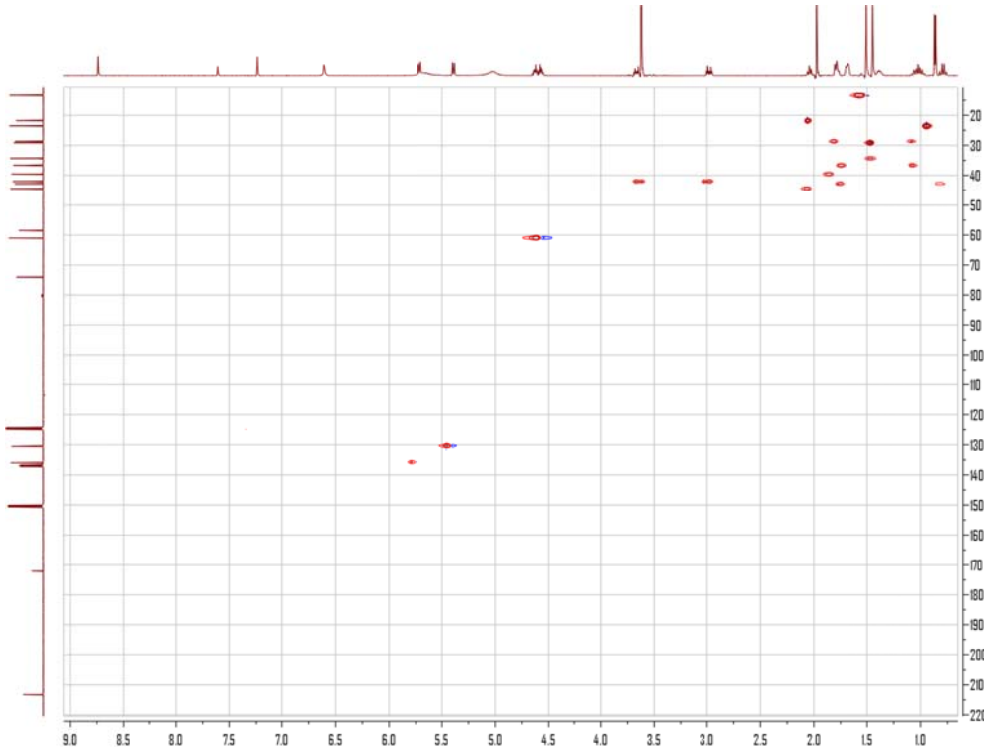


Figure S19. HSQC spectrum of **2** in *Pyridine-d_5*

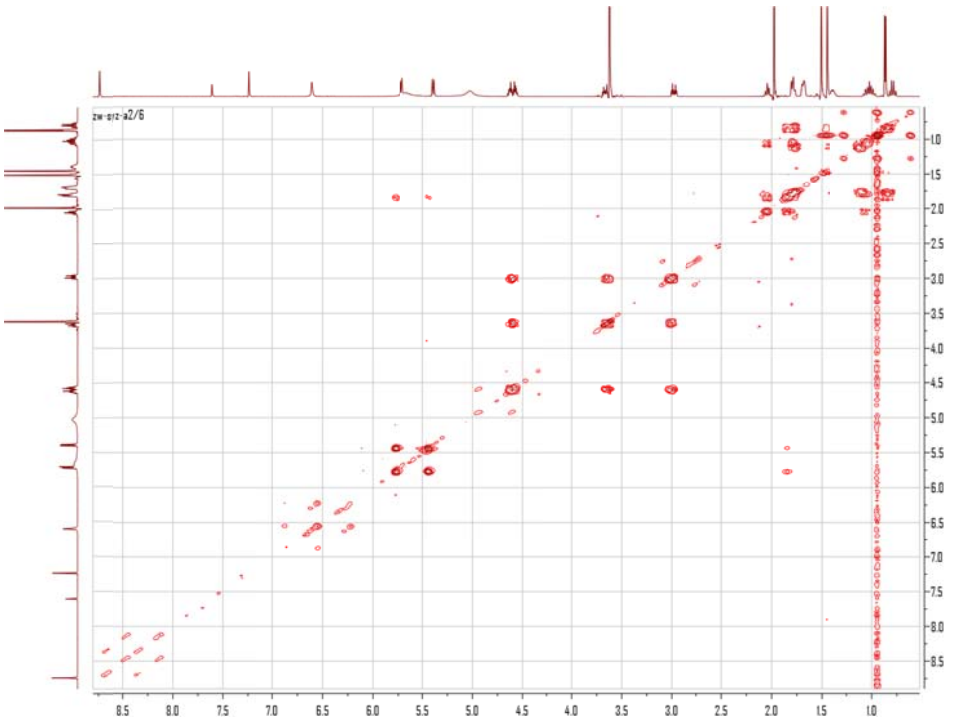


Figure S20. ^{1}H-^{1}H COSY spectrum of **2** in *Pyridine-d*$_5$

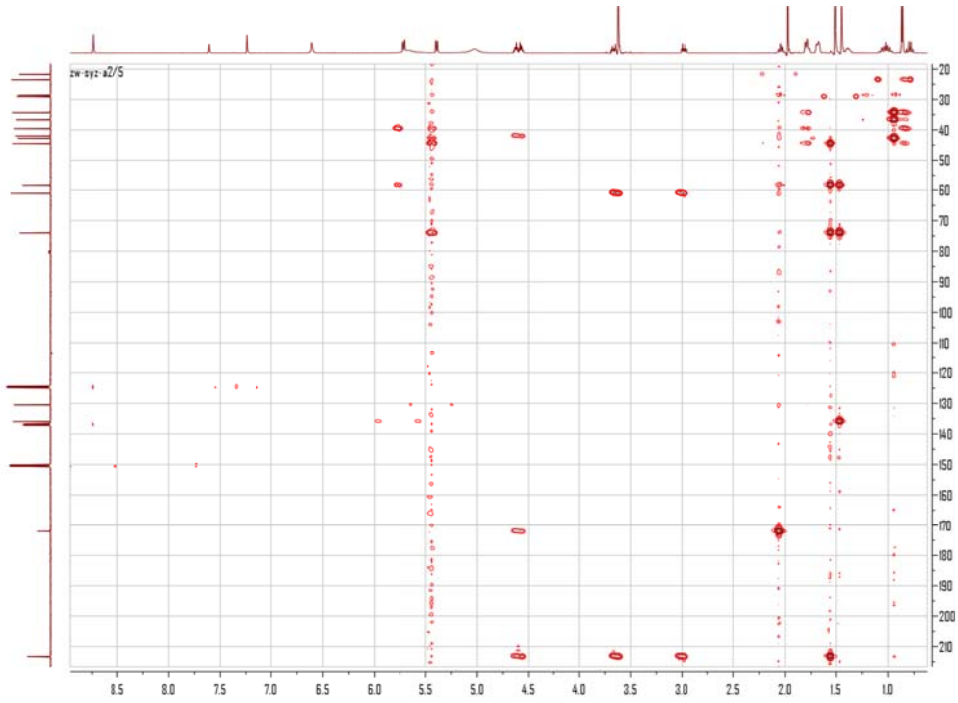


Figure S21. HMBC spectrum of **2** in *Pyridine-d*$_5$

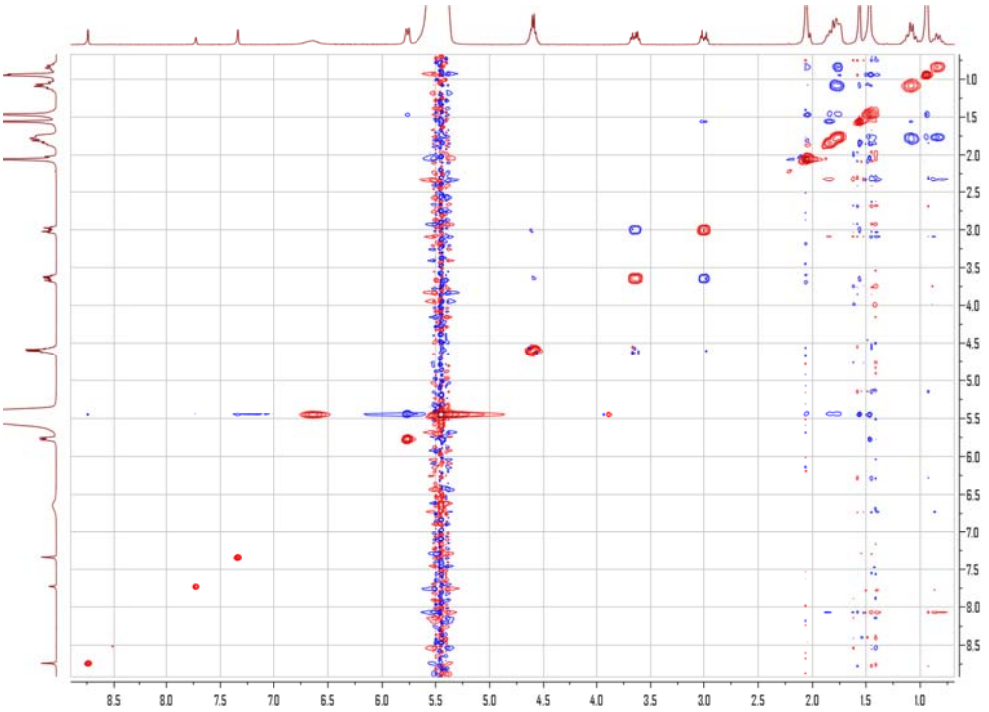


Figure S22. NOESY spectrum of **2** in *Pyridine-d_5*

D:\data\...\EI-GYW-17161_A6-c1 3/14/2017 2:51:23 PM

EI-GYW-17161_A6-c1#13-17 RT: 2.67-3.56 AV: 5
T: + c EI Full ms [49.50-1000.50]
m/z= 47.50-1002.50

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Compositic
60.0205	432127.0	5.71	60.0206	-0.05	1.0	$C_2H_4O_2$
93.0694	1544724.4	20.40	93.0699	-0.46	3.5	C_7H_9
98.0730	3187629.0	42.10	98.0726	0.39	2.0	$C_6H_{10}O_1$
103.0545	297438.2	3.93	103.0542	0.23	5.5	C_8H_7
105.0693	2099195.2	27.72	105.0699	-0.55	4.5	C_8H_9
110.0732	2500401.0	33.02	110.0726	0.56	3.0	$C_7H_{10}O_1$
117.0694	653039.8	8.62	117.0699	-0.51	5.5	C_9H_9
118.0769	317712.6	4.20	118.0777	-0.83	5.0	C_9H_{10}
123.0813	1245173.6	16.44	123.0804	0.87	3.5	$C_8H_{11}O_1$
129.0702	489965.2	6.47	129.0699	0.34	6.5	$C_{10}H_9$
136.0878	324532.0	4.29	136.0883	-0.45	4.0	$C_9H_{12}O_1$
143.0854	608642.2	8.04	143.0855	-0.14	6.5	$C_{11}H_{11}$
151.0956	208085.6	2.75	151.0965	-0.86	-0.5	$C_6H_{15}O_4$
152.0830	213075.6	2.81	152.0832	-0.13	4.0	$C_9H_{12}O_2$
156.0927	113225.0	1.50	156.0934	-0.60	7.0	$C_{12}H_{12}$
161.0966	801827.0	10.59	161.0961	0.46	5.5	$C_{11}H_{13}O_1$
167.1059	3817270.2	50.41	167.1067	-0.77	3.5	$C_{10}H_{15}O_2$
169.1018	114813.8	1.52	169.1012	0.66	7.5	$C_{13}H_{13}$
170.0938	473145.4	6.25	170.0937	0.06	3.0	$C_9H_{14}O_3$
188.1191	367556.8	4.85	188.1196	-0.43	6.0	$C_{13}H_{16}O_1$
205.1220	137400.2	1.81	205.1223	-0.34	5.5	$C_{13}H_{17}O_2$
219.1380	161551.0	2.13	219.1380	0.06	5.5	$C_{14}H_{19}O_2$
227.1277	224370.6	2.96	227.1278	-0.10	3.5	$C_{12}H_{19}O_4$
228.1505	377002.8	4.98	228.1509	-0.32	7.0	$C_{16}H_{20}O_1$
231.1382	296679.0	3.92	231.1380	0.21	6.5	$C_{15}H_{19}O_2$
306.1821	196542.6	2.60	306.1826	-0.42	6.0	$C_{18}H_{26}O_4$
324.1925	85932.8	1.13	324.1931	-0.63	5.0	$C_{18}H_{28}O_5$

Figure S23. HREIMS spectrum of **3**

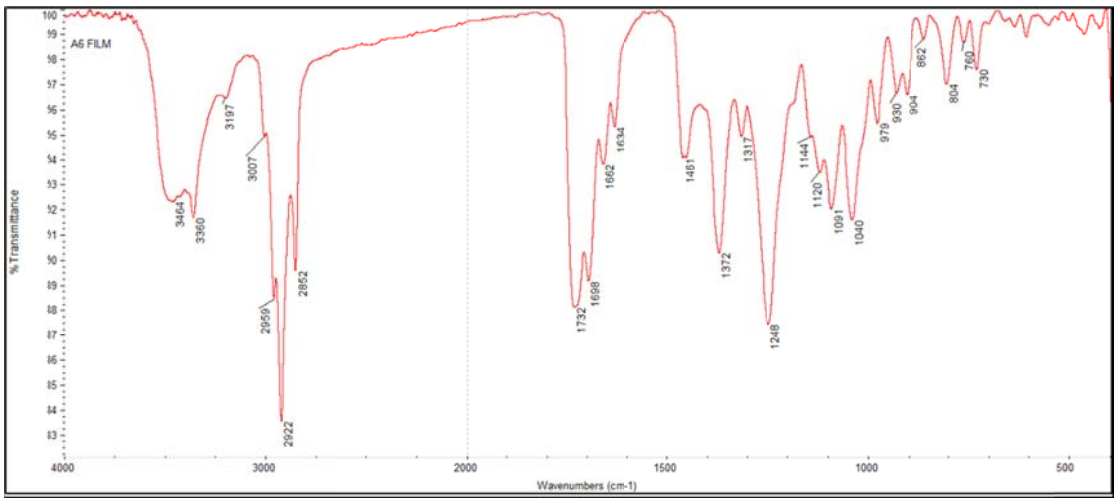


Figure S24. FTIR spectrum of **3**

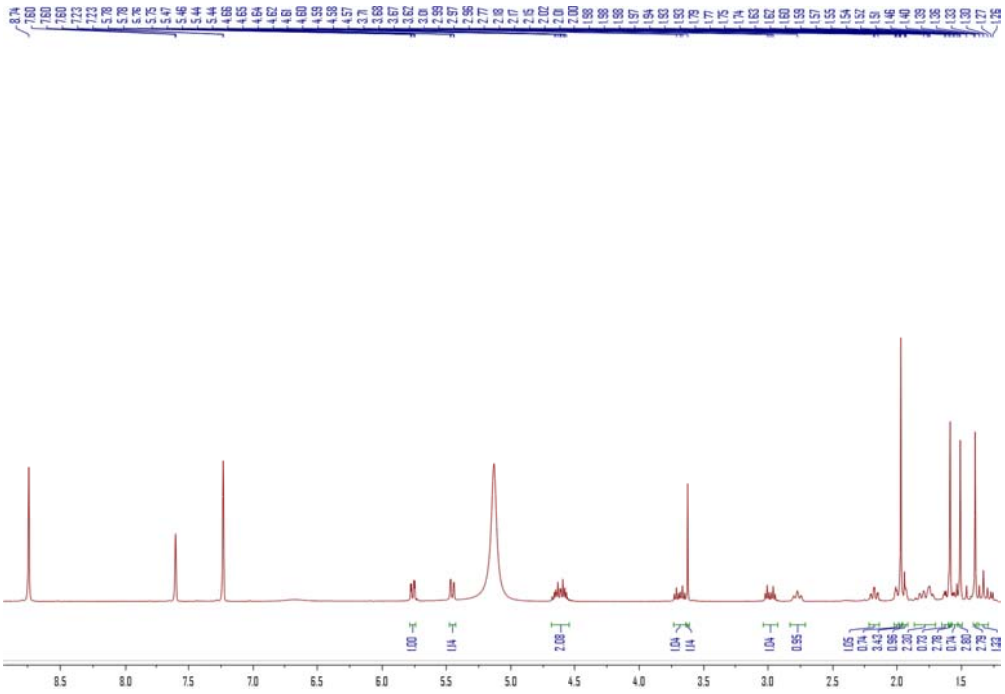


Figure S25. ^{1}H NMR spectrum of **3** in *Pyridine-d*$_5$ at 400 MHz

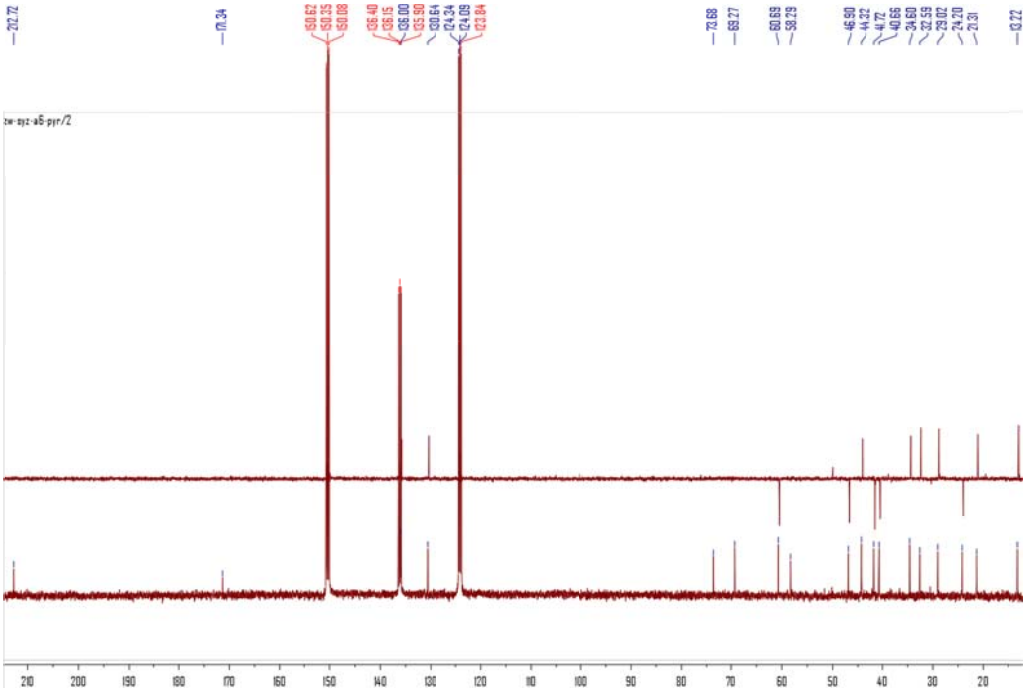


Figure S26. ^{13}C and NMR DEPT spectra of **3** in *Pyridine-d_5* at 100 MHz

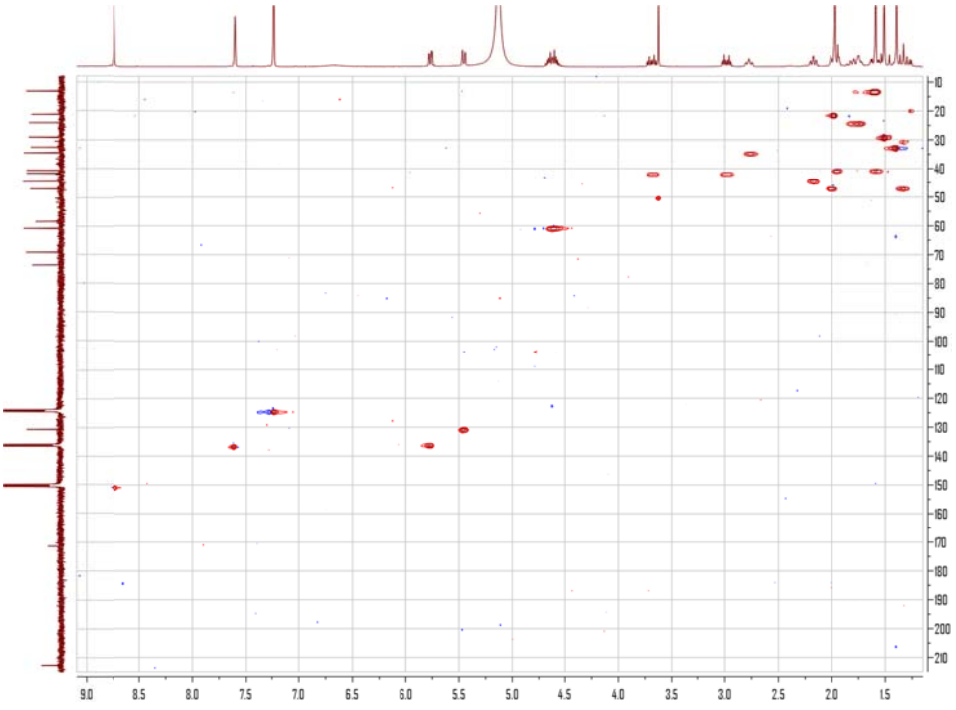


Figure S27. HSQC spectrum of **3** in *Pyridine-d_5*

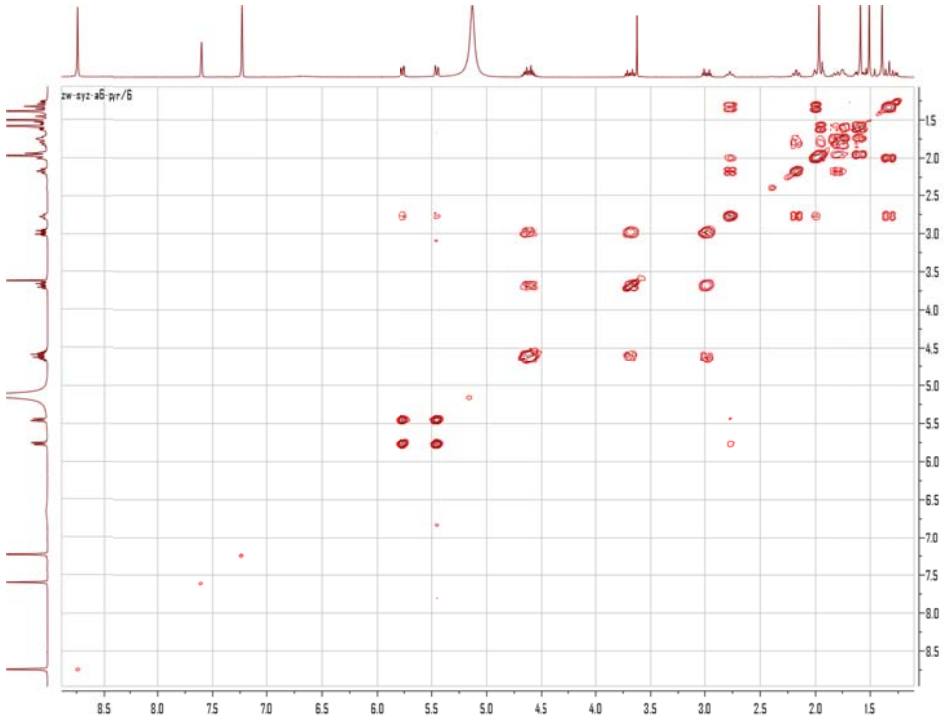


Figure S28. ^{1}H-^{1}H COSY spectrum of **3** in *Pyridine-d*$_5$

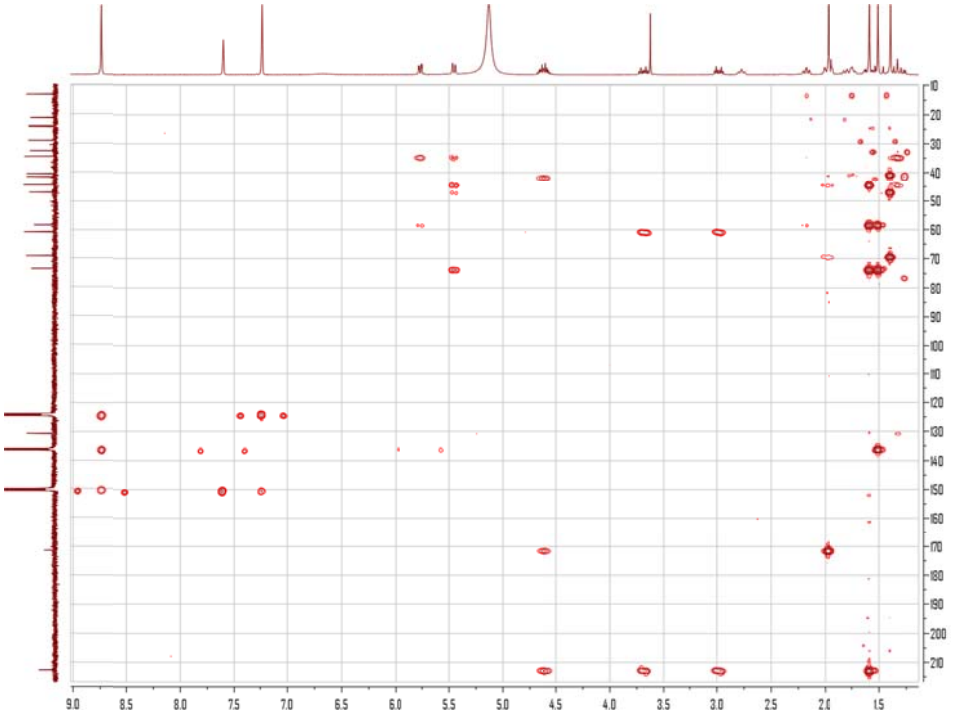


Figure S29. HMBC spectrum of **3** in *Pyridine-d*$_5$

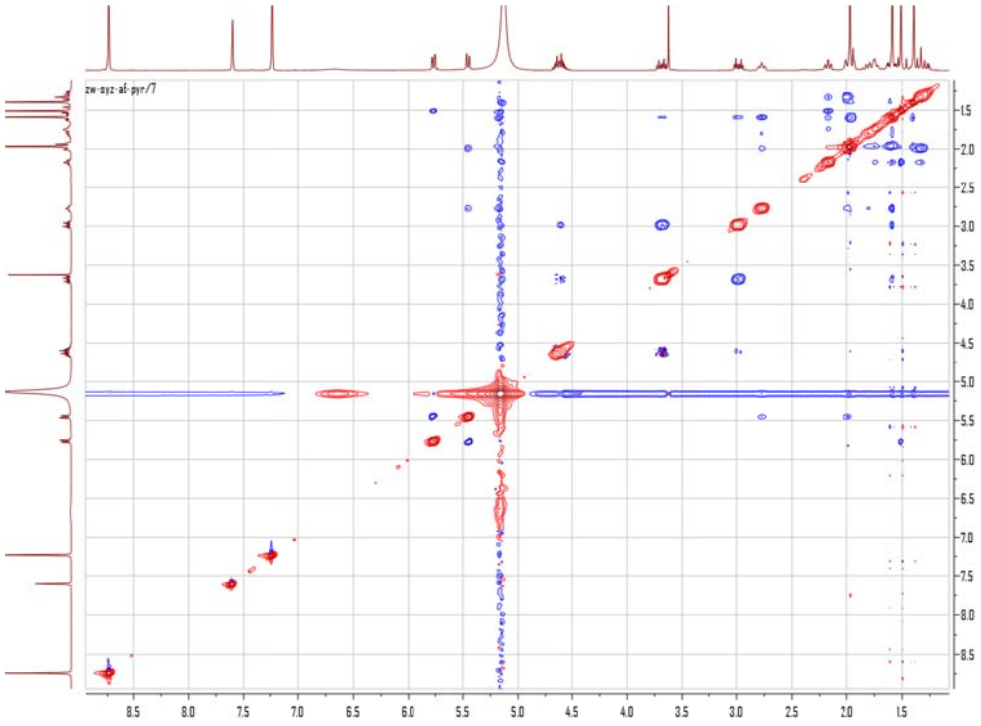


Figure S30 NOESY spectrum of **3** in *Pyridine-d_5*

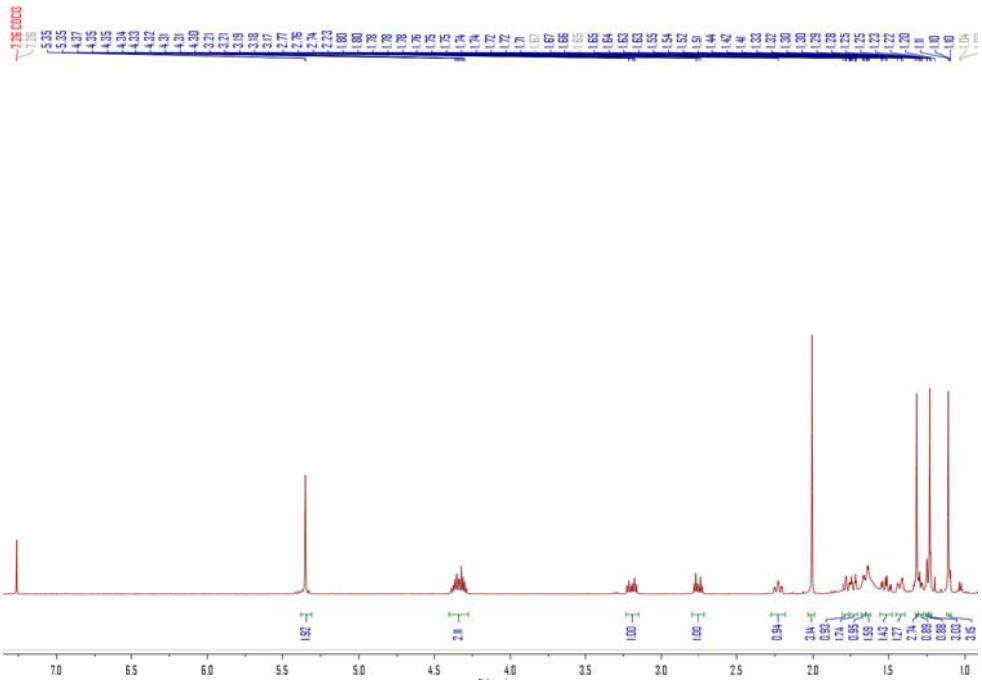


Figure S31. ^{1}H NMR spectrum of **3** in $CDCl_3$ at 500 MHz

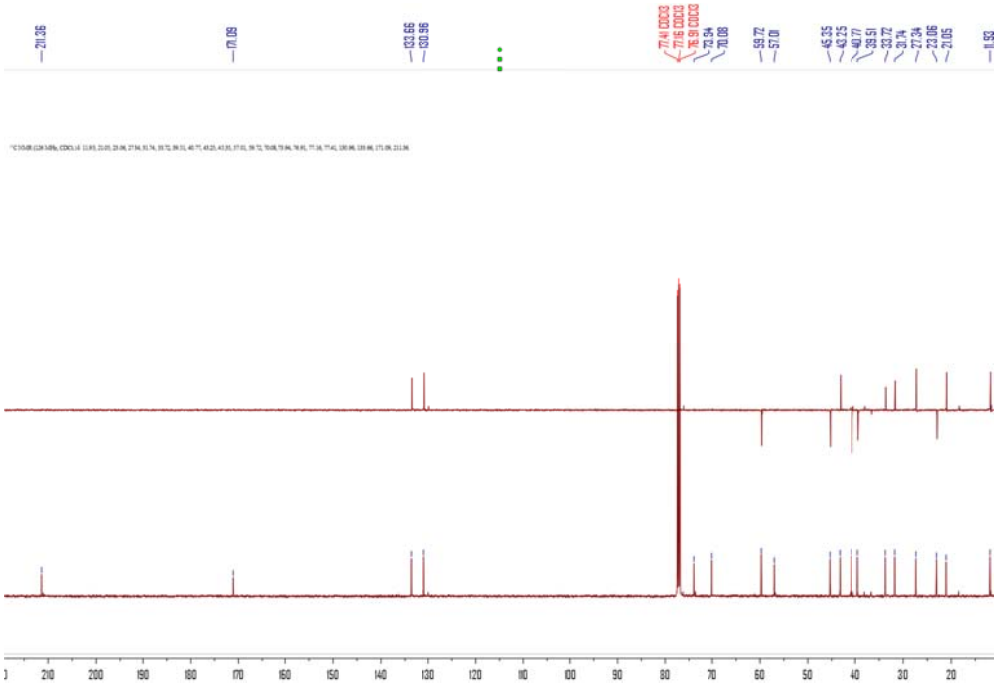


Figure S32. ^{13}C and NMR DEPT spectra of **3** in $CDCl_3$ at 125 MHz

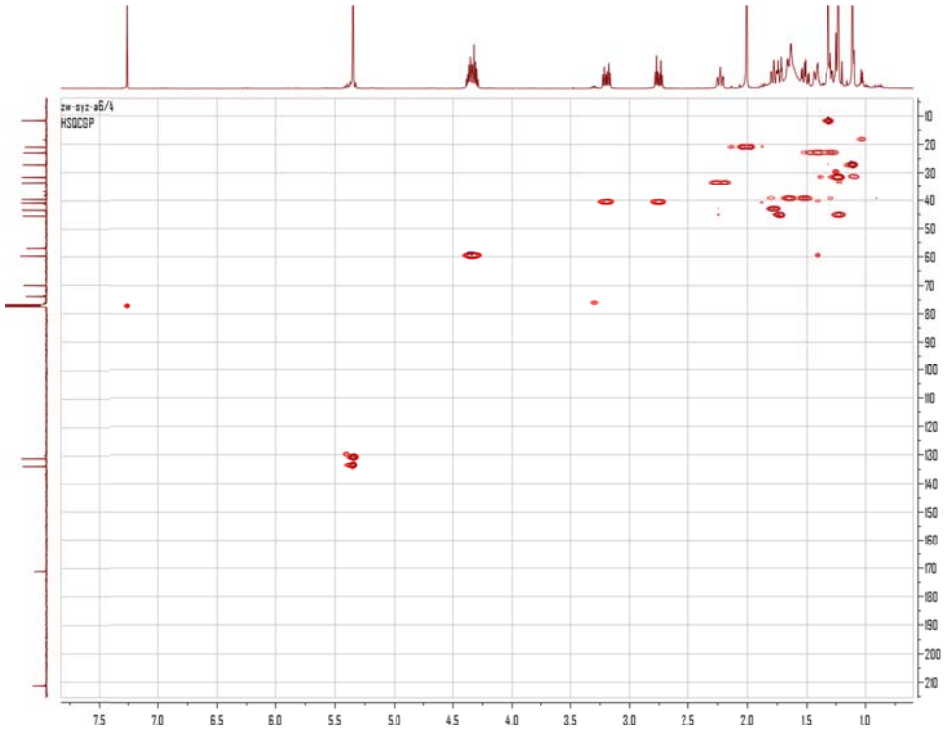


Figure S33. HSQC spectrum of **3** in $CDCl_3$

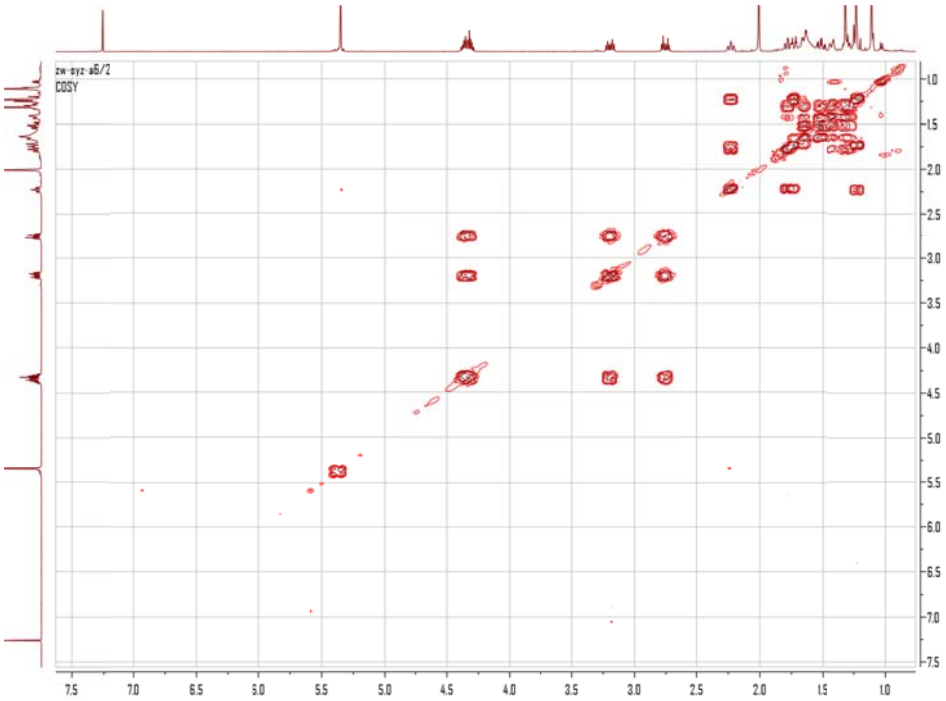


Figure S34. ^{1}H-^{1}H COSY spectrum of **3** in $CDCl_3$

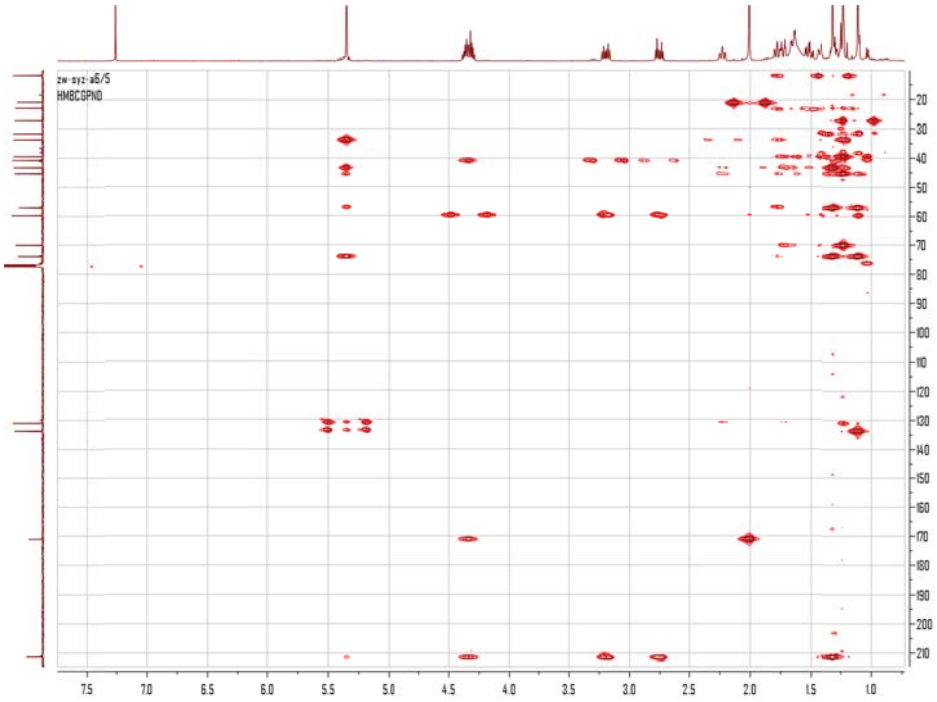


Figure S35. HMBC spectrum of **3** in $CDCl_3$

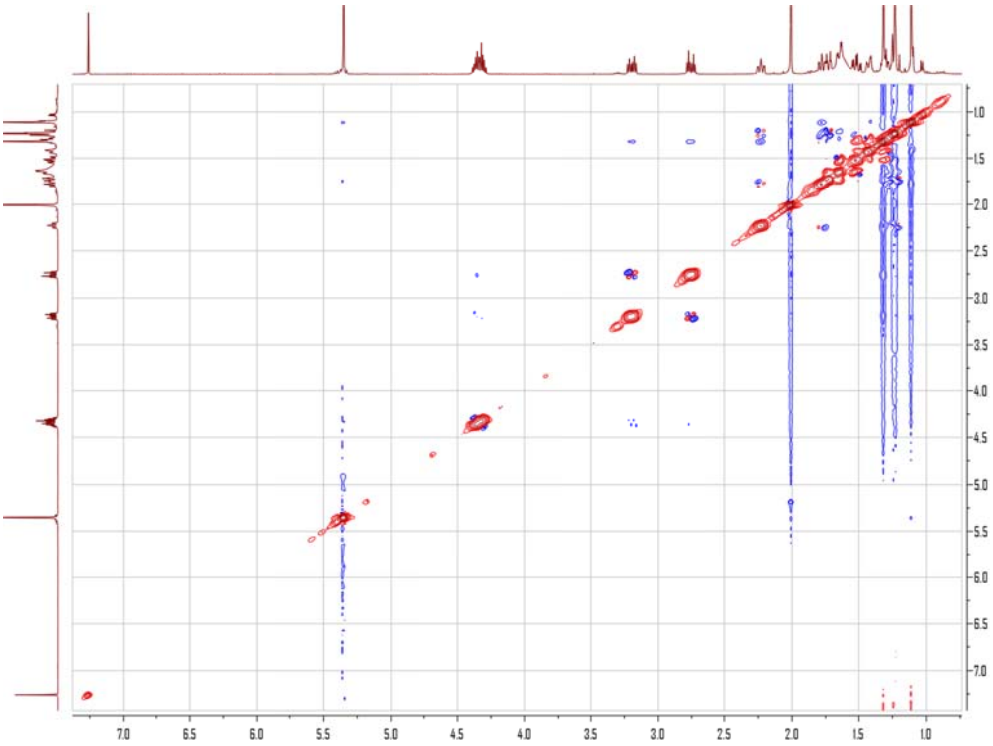


Figure S36. NOESY spectrum of **3** in $CDCl_3$

D:\data\...\20170313_EI_GYW_17155_A10-c1 3/14/2017 10:00:59 AM

20170313_EI_GYW_17155_A10-c1#14 RT: 2.93
T: + c EI Full ms [49.50-1000.50]
m/z= 48.97-305.15

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composit
53.8829	64807.0	2.56	54.0100	-127.10	3.0	$C_3H_2O_1$
65.0682	84032.0	3.32	65.0386	29.60	3.5	C_5H_5
77.0376	247335.0	9.78	77.0386	-1.00	4.5	C_6H_5
78.0450	73103.0	2.89	78.0464	-1.40	4.0	C_6H_6
79.0534	213582.0	8.44	79.0542	-0.78	3.5	C_6H_7
81.0689	94523.0	3.74	81.0699	-1.02	2.5	C_6H_9
91.0539	667827.0	26.40	91.0542	-0.35	4.5	C_7H_7
92.0598	82496.0	3.26	92.0621	-2.25	4.0	C_7H_8
93.0697	173903.0	6.87	93.0699	-0.18	3.5	C_7H_9
94.0772	66695.0	2.64	94.0777	-0.46	3.0	C_7H_{10}
95.0490	80060.0	3.16	95.0491	-0.12	3.5	$C_6H_7O_1$
95.0854	71369.0	2.82	95.0855	-0.10	2.5	C_7H_{11}
97.0641	164027.0	6.48	97.0648	-0.64	2.5	$C_6H_9O_1$
103.0542	119827.0	4.74	103.0542	-0.01	5.5	C_8H_7
104.0619	96871.0	3.83	104.0621	-0.19	5.0	C_8H_8
105.0700	1771137.0	70.01	105.0699	0.15	4.5	C_8H_9
106.0762	304681.0	12.04	106.0777	-1.52	4.0	C_8H_{10}
107.0858	172300.0	6.81	107.0855	0.32	3.5	C_8H_{11}
108.0932	63622.0	2.51	108.0934	-0.20	3.0	C_8H_{12}
115.0539	215930.0	8.54	115.0542	-0.28	6.5	C_9H_7
116.0608	78897.0	3.12	116.0621	-1.27	6.0	C_9H_8
117.0698	276041.0	10.91	117.0699	-0.11	5.5	C_9H_9
118.0771	133675.0	5.28	118.0777	-0.58	5.0	C_9H_{10}
119.0856	2529713.0	100.00	119.0855	0.09	4.5	C_9H_{11}
120.0924	1076952.0	42.57	120.0934	-0.95	4.0	C_9H_{12}
121.0641	97200.0	3.84	121.0648	-0.69	4.5	$C_8H_9O_1$
121.0990	208183.0	8.23	121.1012	-2.14	3.5	C_9H_{13}
128.0616	105057.0	4.15	128.0621	-0.48	7.0	$C_{10}H_8$
129.0693	111355.0	4.40	129.0699	-0.57	6.5	$C_{10}H_9$
131.0854	147325.0	5.82	131.0855	-0.15	5.5	$C_{10}H_{11}$
132.0926	168591.0	6.66	132.0934	-0.73	5.0	$C_{10}H_{12}$
133.1007	207634.0	8.21	133.1012	-0.52	4.5	$C_{10}H_{13}$
134.1072	118488.0	4.68	134.1090	-1.76	4.0	$C_{10}H_{14}$
145.0995	72444.0	2.86	145.1012	-1.68	5.5	$C_{11}H_{13}$
147.1144	93710.0	3.70	147.1168	-2.41	4.5	$C_{11}H_{15}$
149.1302	87127.0	3.44	149.1325	-2.26	3.5	$C_{11}H_{17}$
159.1152	302662.0	11.96	159.1168	-1.59	5.5	$C_{12}H_{15}$
161.1313	535074.0	21.15	161.1325	-1.15	4.5	$C_{12}H_{17}$
162.1359	70403.0	2.78	162.1403	-4.45	4.0	$C_{12}H_{18}$
174.1404	163544.0	6.46	174.1403	0.14	5.0	$C_{13}H_{18}$
175.1475	656547.0	25.95	175.1481	-0.60	4.5	$C_{13}H_{19}$
176.1554	939370.0	37.13	176.1560	-0.60	4.0	$C_{13}H_{20}$
177.1264	558096.0	22.06	177.1274	-1.04	4.5	$C_{12}H_{17}O_1$
177.1584	124918.0	4.94	177.1638	-5.36	3.5	$C_{13}H_{21}$
178.1325	148181.0	5.86	178.1352	-2.74	4.0	$C_{12}H_{18}O_1$
220.1467	133785.0	5.29	220.1458	0.92	5.0	$C_{14}H_{20}O_2$
238.1563	123536.0	4.88	238.1563	-0.09	4.0	$C_{14}H_{22}O_3$

Figure S37. HREIMS spectrum of **4**

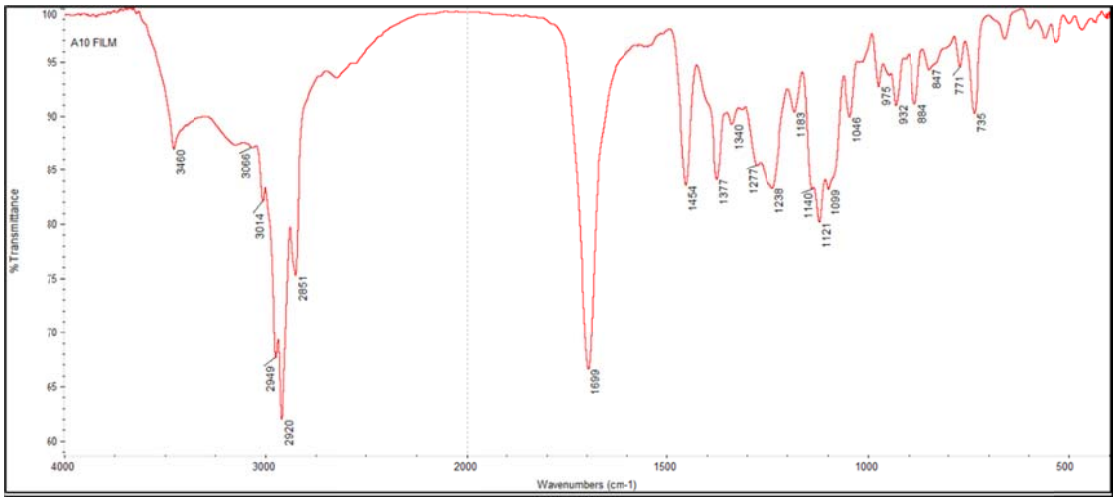


Figure S38. FTIR spectrum of **4**

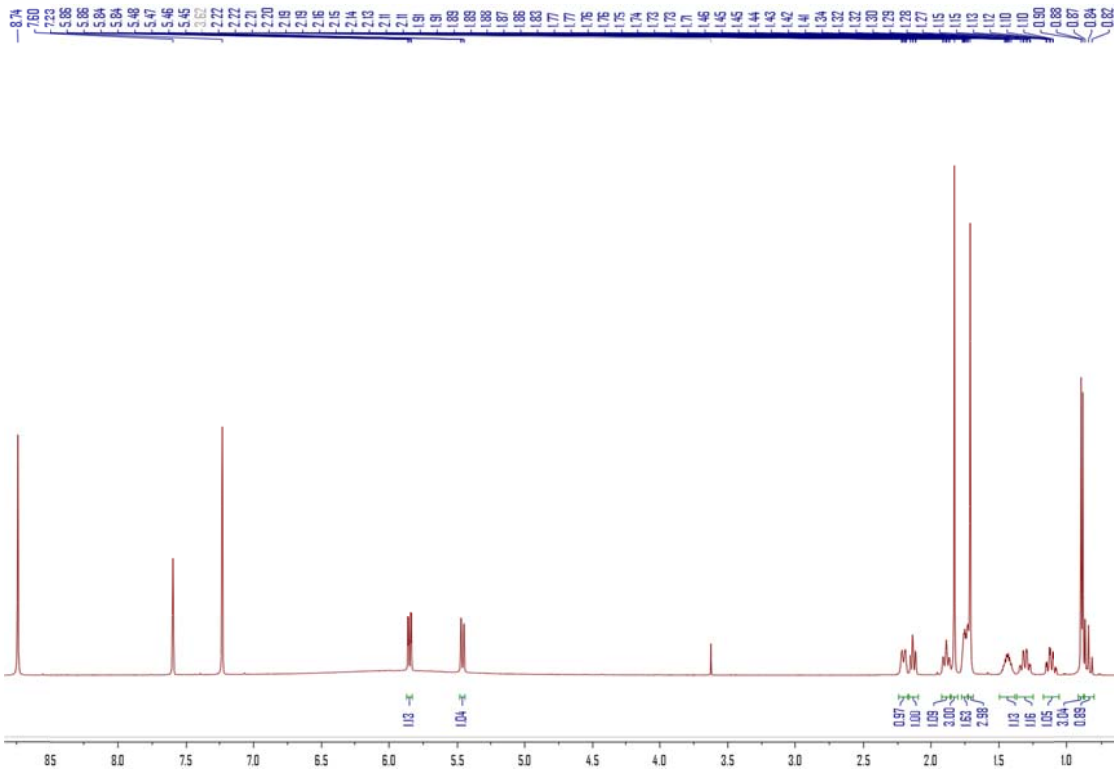


Figure S39. ^{1}H NMR spectrum of **4** in *Pyridine-d*$_5$ at 500 MHz

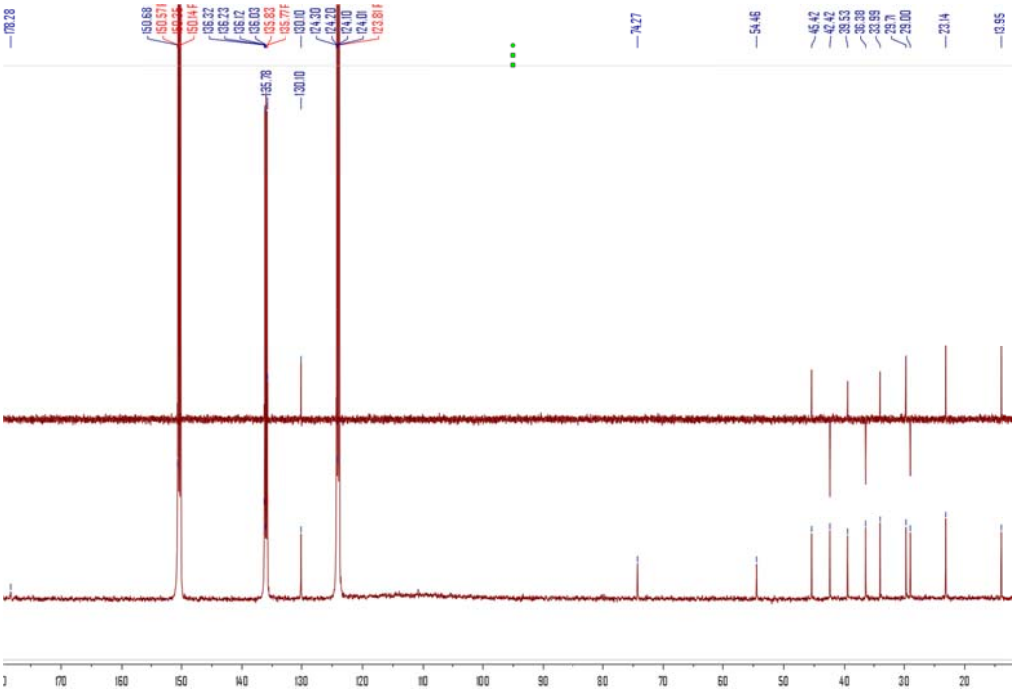


Figure S40. ^{13}C and NMR DEPT spectra of **4** in *Pyridine-d_5* at 125 MHz

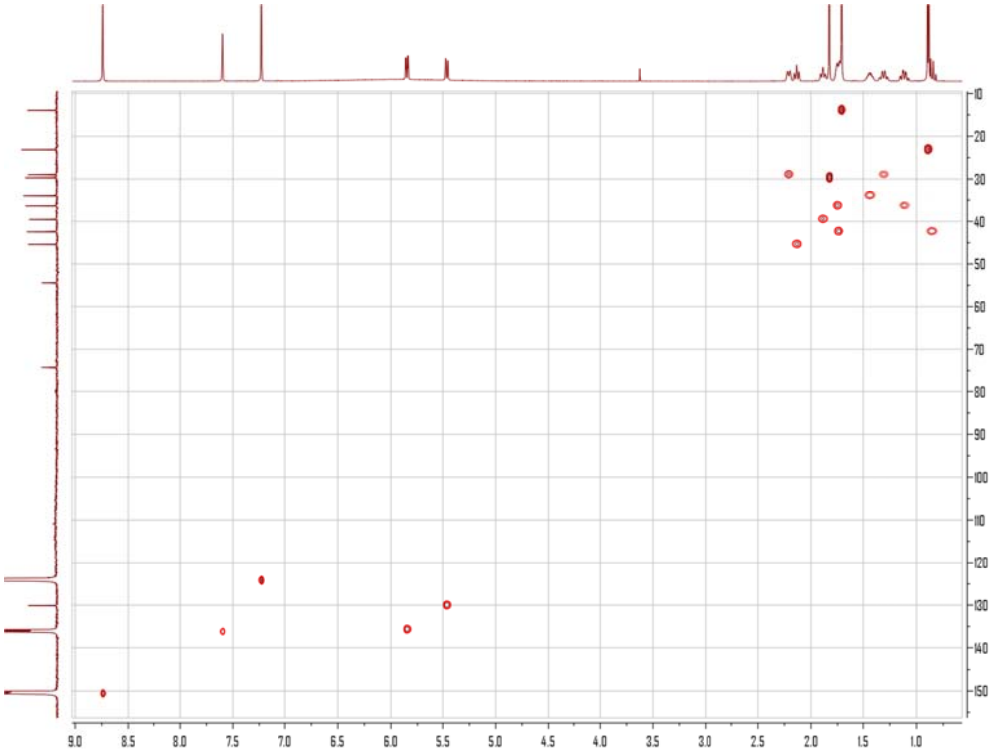


Figure S41. HSQC spectrum of **4** in *Pyridine-d_5*

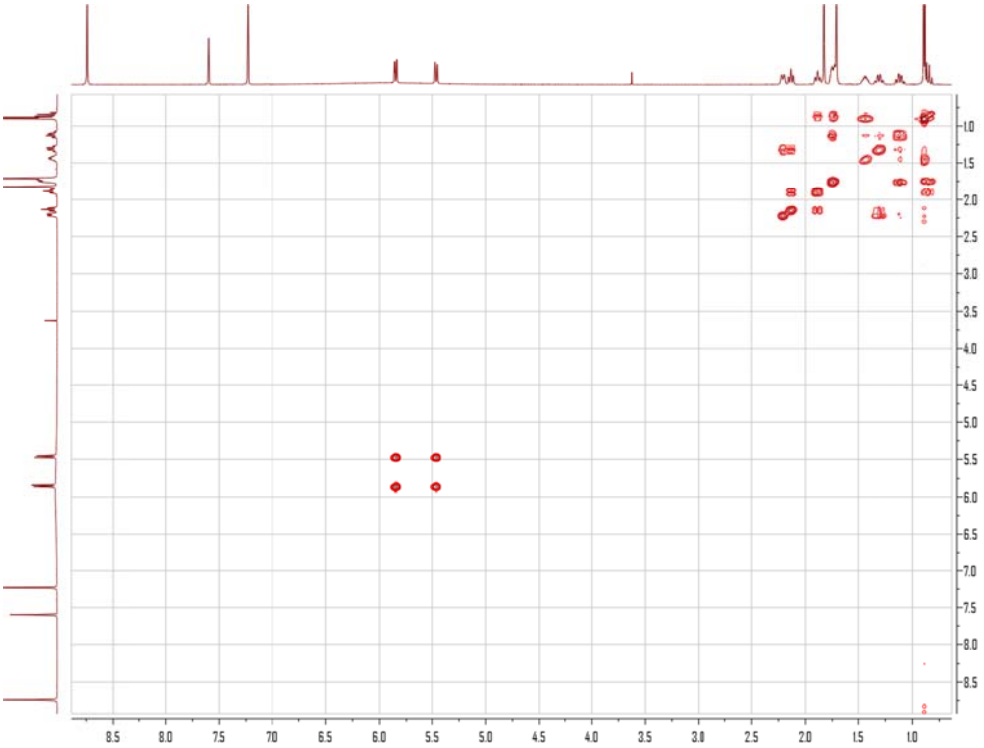


Figure S42. ^{1}H-^{1}H COSY spectrum of **4** in *Pyridine-d_5*

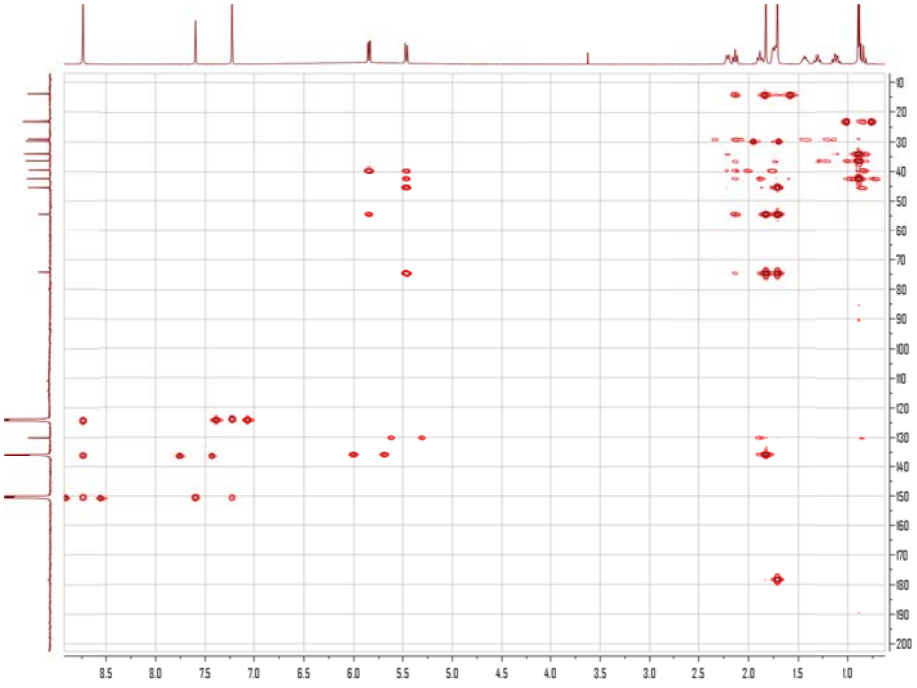


Figure S43. HMBC spectrum of **4** in *Pyridine-d_5*

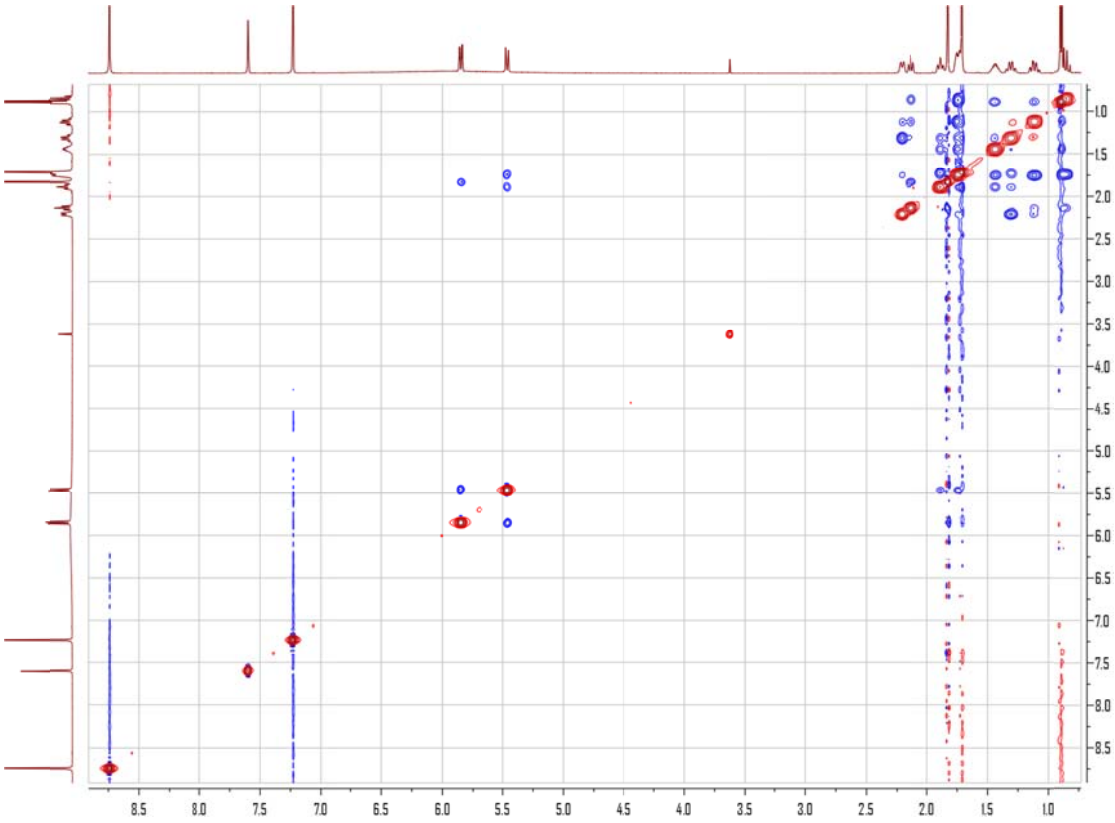


Figure S44. NOESY spectrum of **4** in *Pyridine-d_5*

D:\data\...\EI-GYW-17156_A13-c1 3/14/2017 10:15:59 AM

EI-GYW-17156_A13-c1#20 RT: 4.16
T: + c EI Full ms [49.50-1000.50]
m/z= 48.97-302.95

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
170.1097	33248.0	0.66	170.1090	0.65	7.0	$C_{13}H_{14}$
171.1163	123536.0	2.44	171.1168	-0.53	6.5	$C_{13}H_{15}$
172.1238	133719.0	2.64	172.1247	-0.83	6.0	$C_{13}H_{16}$
173.0957	82606.0	1.63	173.0961	-0.39	6.5	$C_{12}H_{13}O_1$
173.1323	4782749.0	94.50	173.1325	-0.17	5.5	$C_{13}H_{17}$
174.1035	54800.0	1.08	174.1039	-0.41	6.0	$C_{12}H_{14}O_1$
174.1373	1002071.0	19.80	174.1403	-2.97	5.0	$C_{13}H_{18}$
175.1114	486945.0	9.62	175.1117	-0.35	5.5	$C_{12}H_{15}O_1$
176.1187	470617.0	9.30	176.1196	-0.89	5.0	$C_{12}H_{16}O_1$
177.0928	28091.0	0.56	177.0910	1.83	5.5	$C_{11}H_{13}O_2$
177.1267	601659.0	11.89	177.1274	-0.68	4.5	$C_{12}H_{17}O_1$
178.0989	101216.0	2.00	178.0988	0.11	5.0	$C_{11}H_{14}O_2$
179.1053	101875.0	2.01	179.1067	-1.33	4.5	$C_{11}H_{15}O_2$
181.1211	120726.0	2.39	181.1223	-1.22	3.5	$C_{11}H_{17}O_2$
183.1156	42510.0	0.84	183.1168	-1.20	7.5	$C_{14}H_{15}$
187.1101	36101.0	0.71	187.1117	-1.60	6.5	$C_{13}H_{15}O_1$
189.1249	43014.0	0.85	189.1274	-2.44	5.5	$C_{13}H_{17}O_1$
190.1342	57192.0	1.13	190.1352	-1.05	5.0	$C_{13}H_{18}O_1$
191.1416	975472.0	19.27	191.1430	-1.41	4.5	$C_{13}H_{19}O_1$
192.1132	68670.0	1.36	192.1145	-1.33	5.0	$C_{12}H_{16}O_2$
193.1209	47799.0	0.94	193.1223	-1.44	4.5	$C_{12}H_{17}O_2$
194.1286	39810.0	0.79	194.1301	-1.56	4.0	$C_{12}H_{18}O_2$
195.1385	26511.0	0.52	195.1380	0.58	3.5	$C_{12}H_{19}O_2$
201.1271	290569.0	5.74	201.1274	-0.25	6.5	$C_{14}H_{17}O_1$
207.1370	57367.0	1.13	207.1380	-0.97	4.5	$C_{13}H_{19}O_2$
216.1498	325991.0	6.44	216.1509	-1.09	6.0	$C_{15}H_{20}O_1$
217.1559	80938.0	1.60	217.1587	-2.84	5.5	$C_{15}H_{21}O_1$
219.1372	228681.0	4.52	219.1380	-0.73	5.5	$C_{14}H_{19}O_2$
234.1612	646715.0	12.78	234.1614	-0.22	5.0	$C_{15}H_{22}O_2$
237.1487	137998.0	2.73	237.1485	0.14	4.5	$C_{14}H_{21}O_3$
252.1703	149937.0	2.96	252.1720	-1.70	4.0	$C_{15}H_{24}O_3$

Figure S45. HREIMS spectrum of **5**

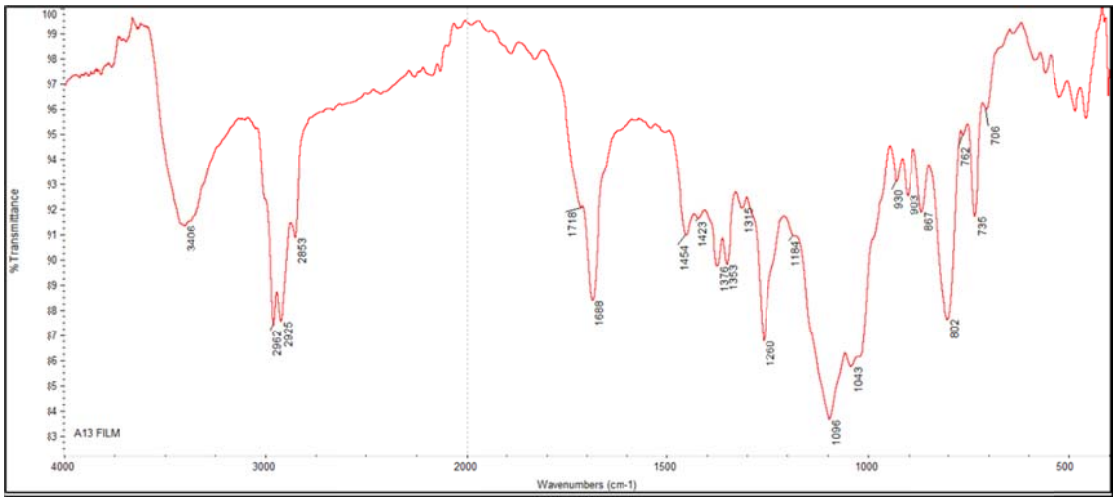


Figure S46. FTIR spectrum of **5**

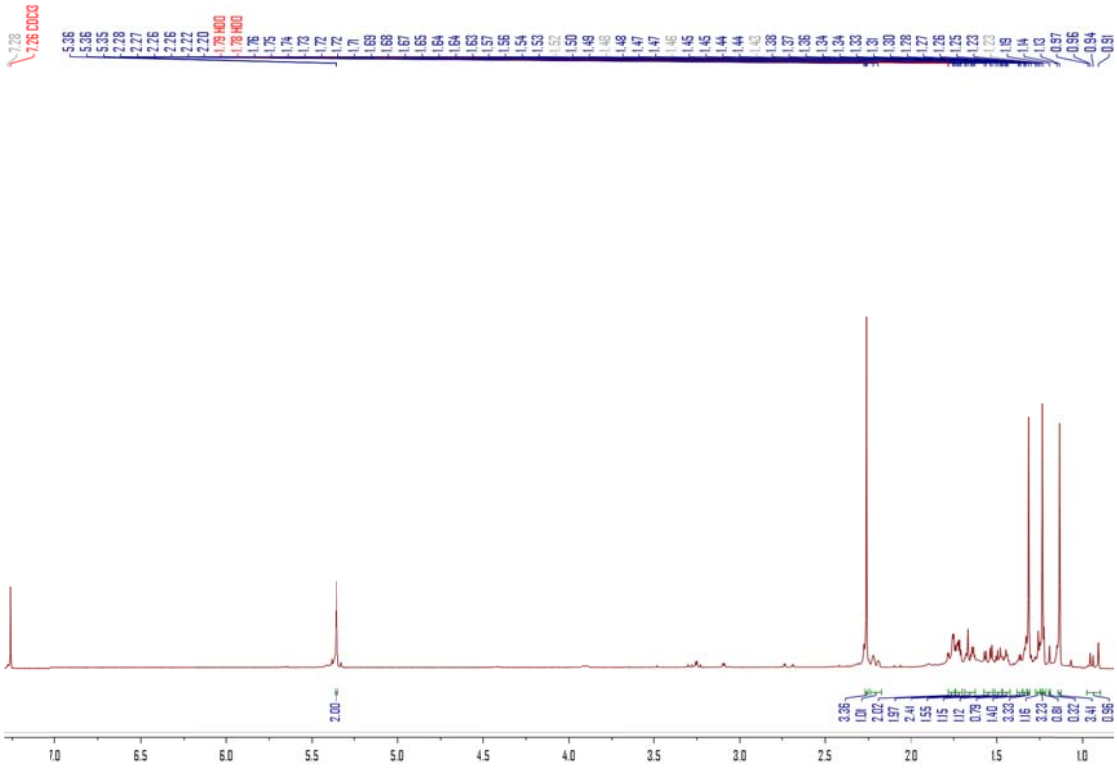


Figure S47. ^{1}H NMR spectrum of **5** in $CDCl_3$ at 400 MHz

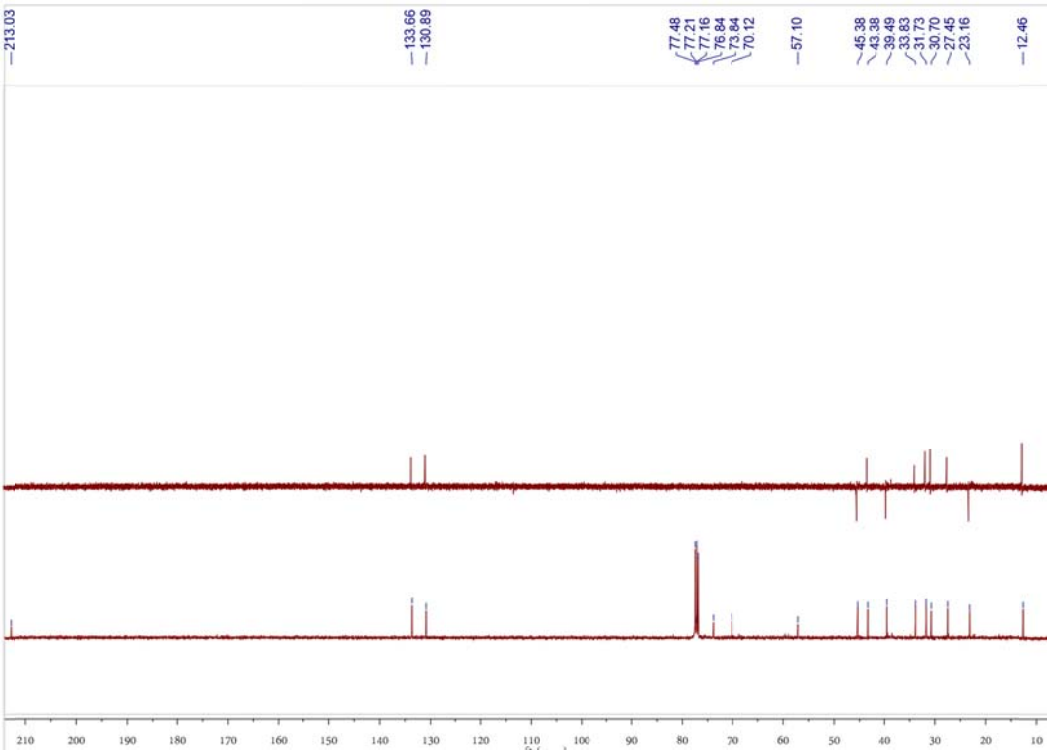


Figure S48. ^{13}C and NMR DEPT spectra of **5** in $CDCl_3$ at 100 MHz

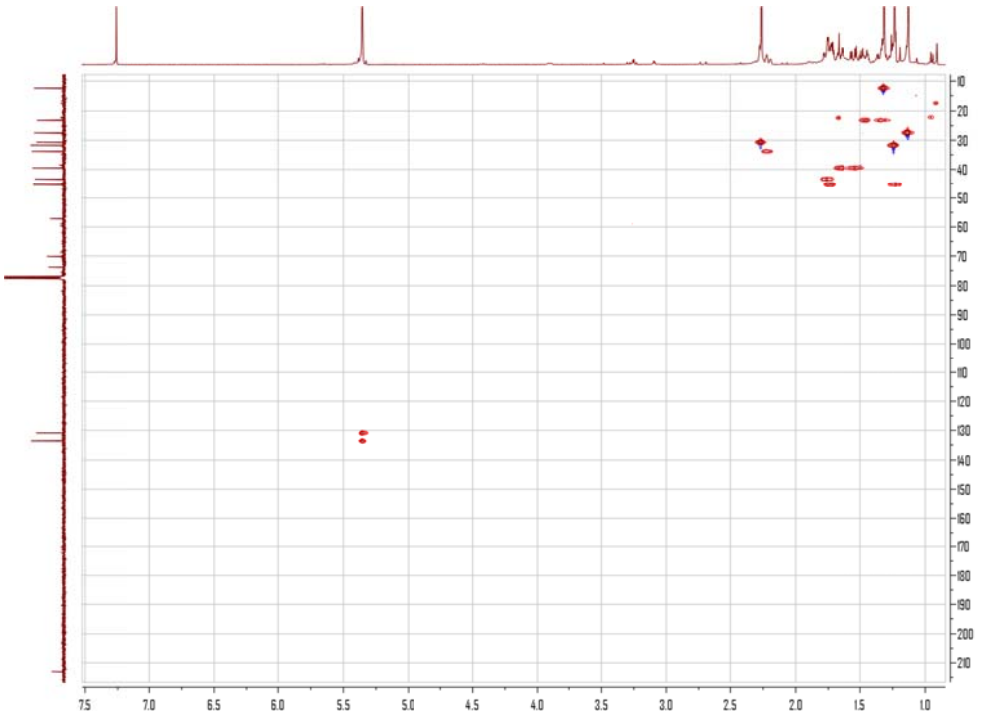


Figure S49. HSQC spectrum of **5** in $CDCl_3$

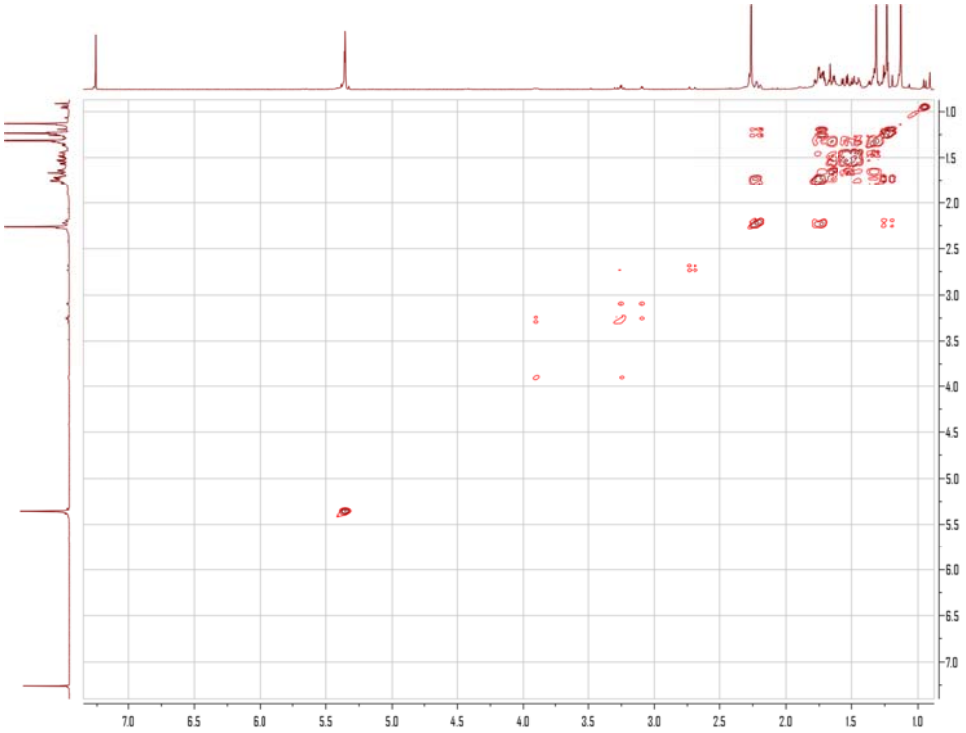


Figure S50. ^{1}H-^{1}H COSY spectrum of **5** in $CDCl_3$

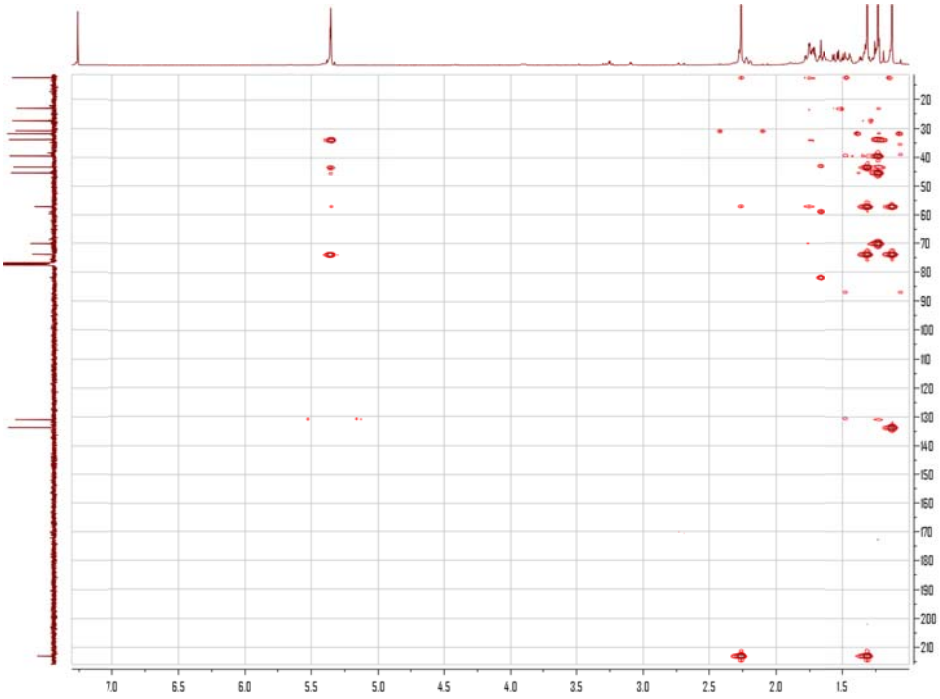


Figure S51. HMBC spectrum of **5** in $CDCl_3$

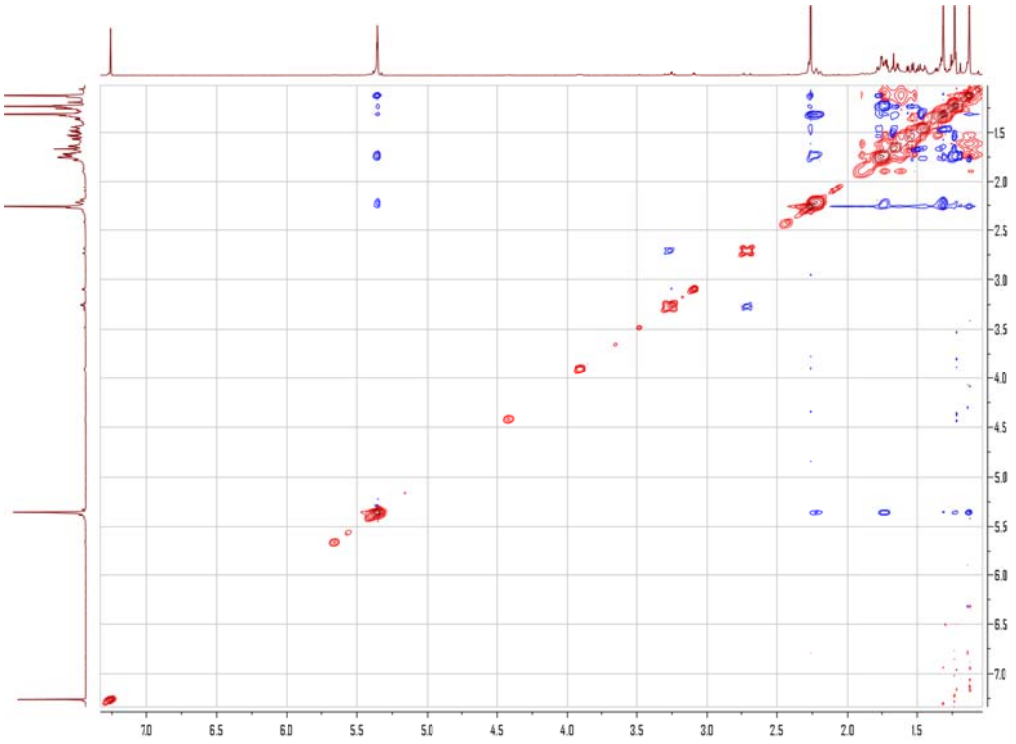


Figure S52. NOESY spectrum of **5** in $CDCl_3$

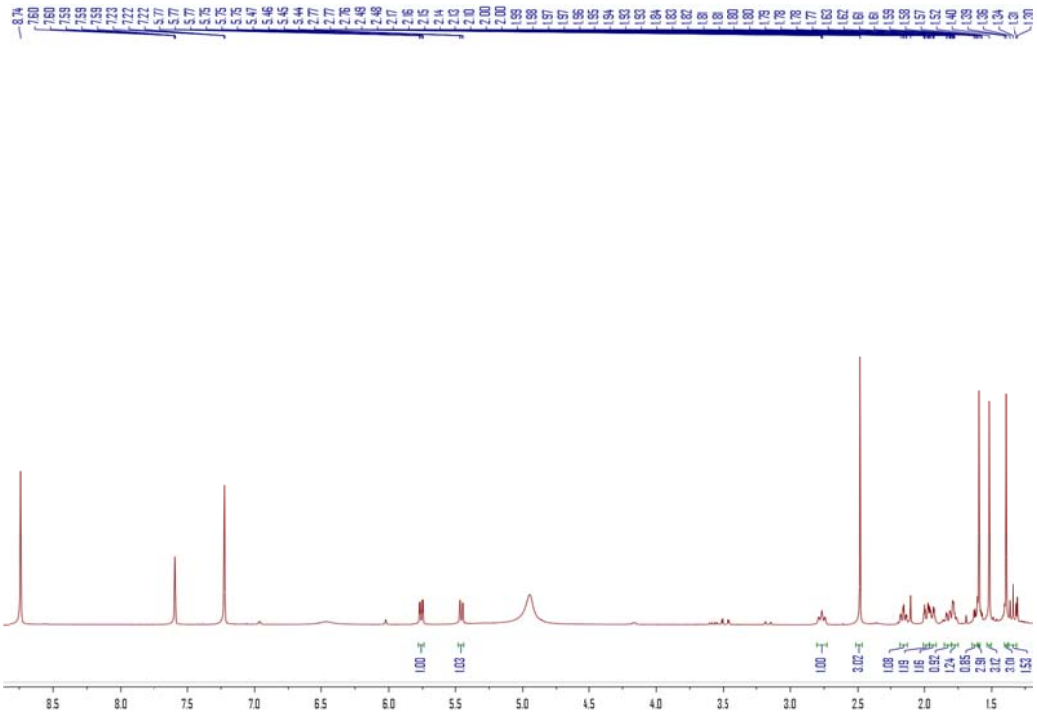


Figure S53. ^{1}H NMR spectrum of **5** in *Pyridine-d_5* at 500 MHz

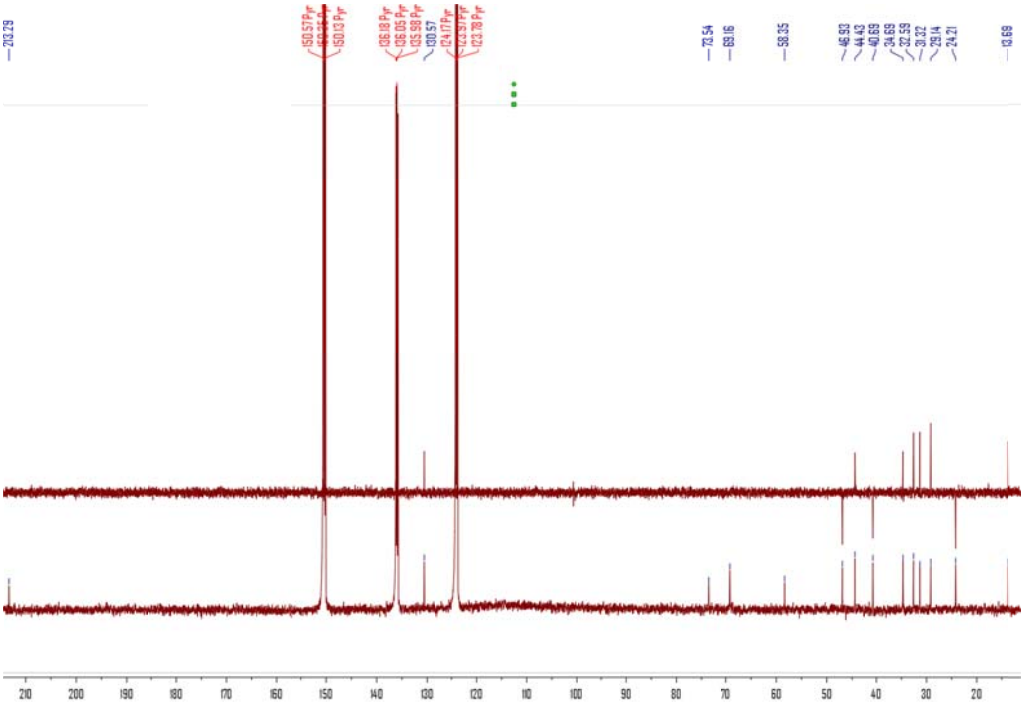


Figure S54. ^{13}C and NMR DEPT spectra of **5** in *Pyridine-d_5* at 125 MHz

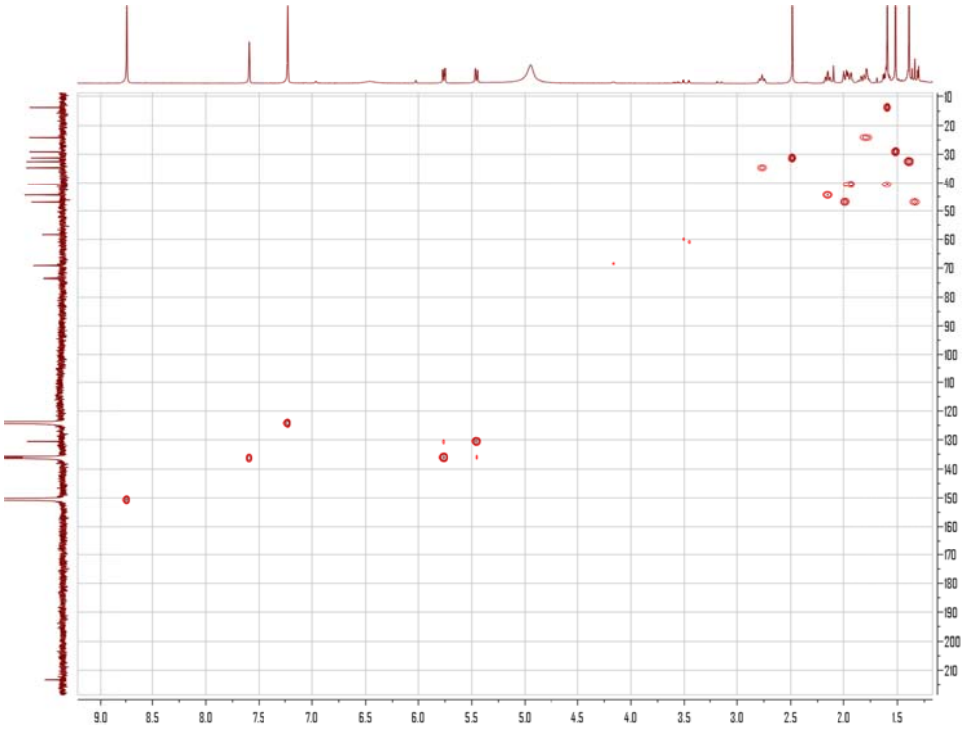


Figure S55. HSQC spectrum of **5** in *Pyridine-d_5*

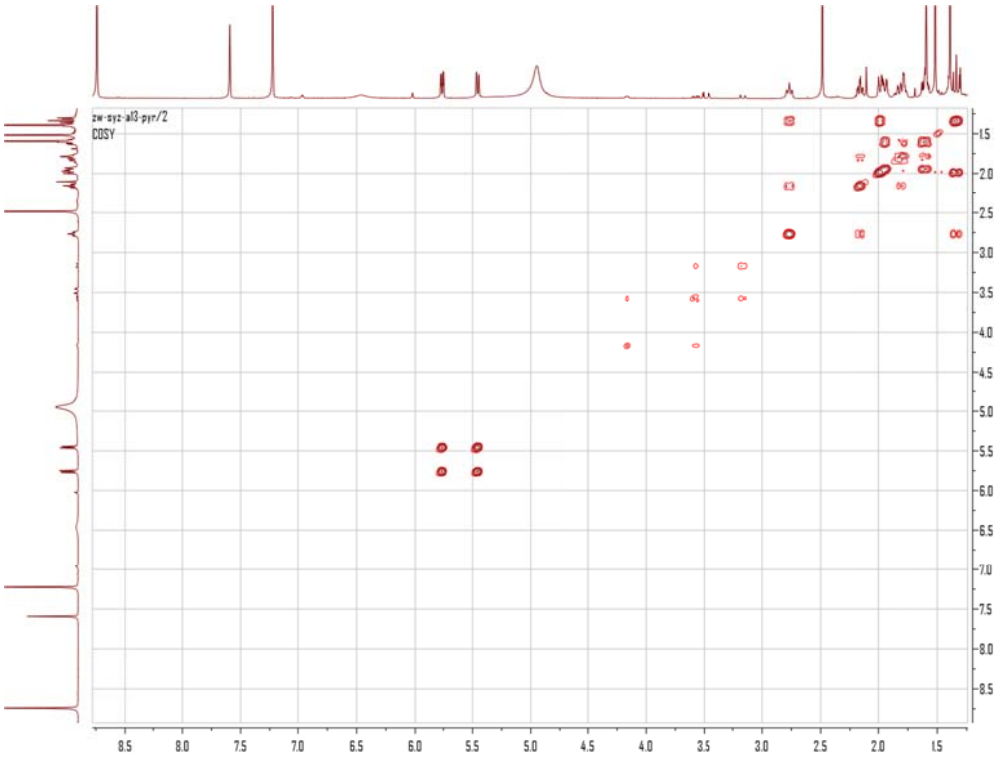


Figure S56. ^{1}H-^{1}H COSY spectrum of **5** in *Pyridine-d*$_5$

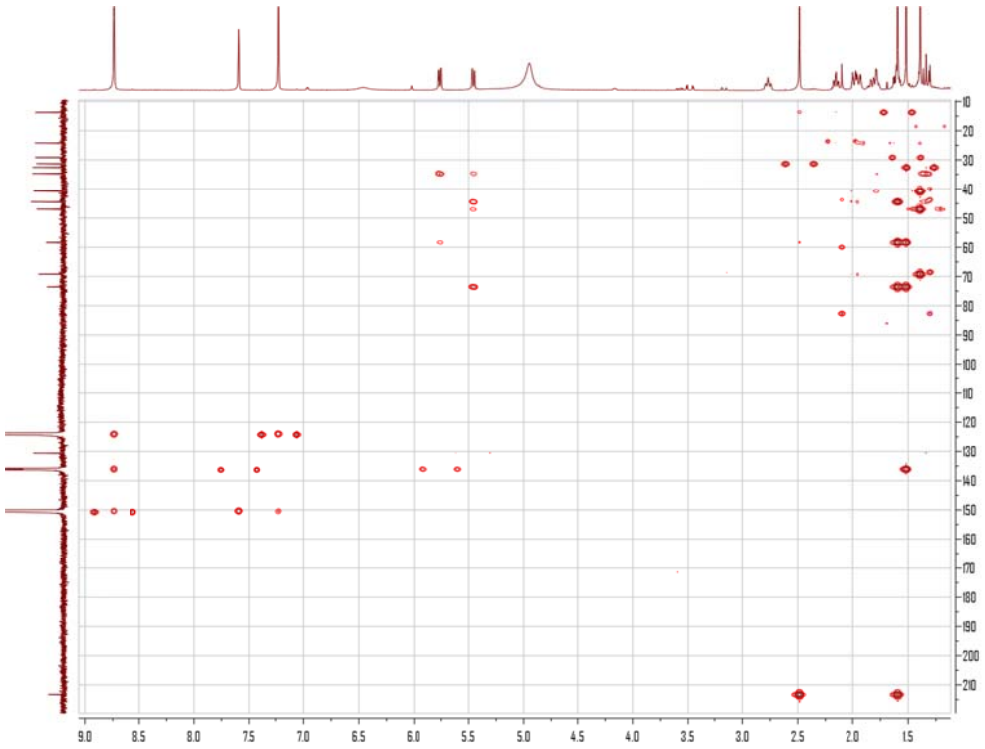


Figure S57. HMBC spectrum of **5** in *Pyridine-d*$_5$

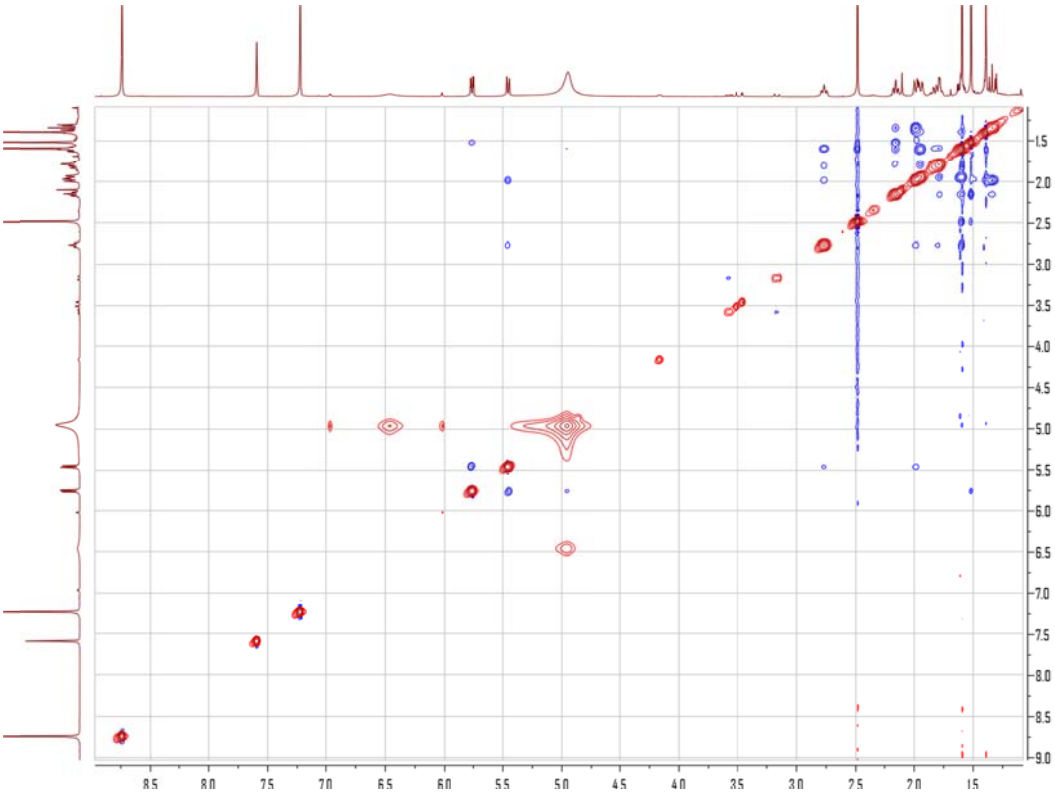


Figure S58. NOESY spectrum of **5** in *Pyridine-d_5*

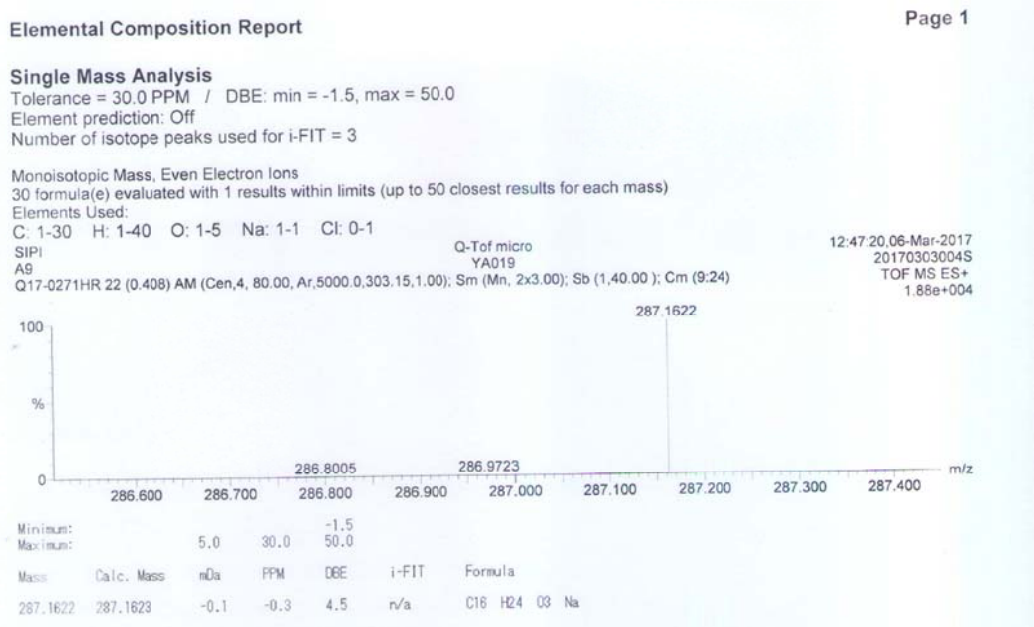


Figure S59. HRESIMS spectrum of **6**

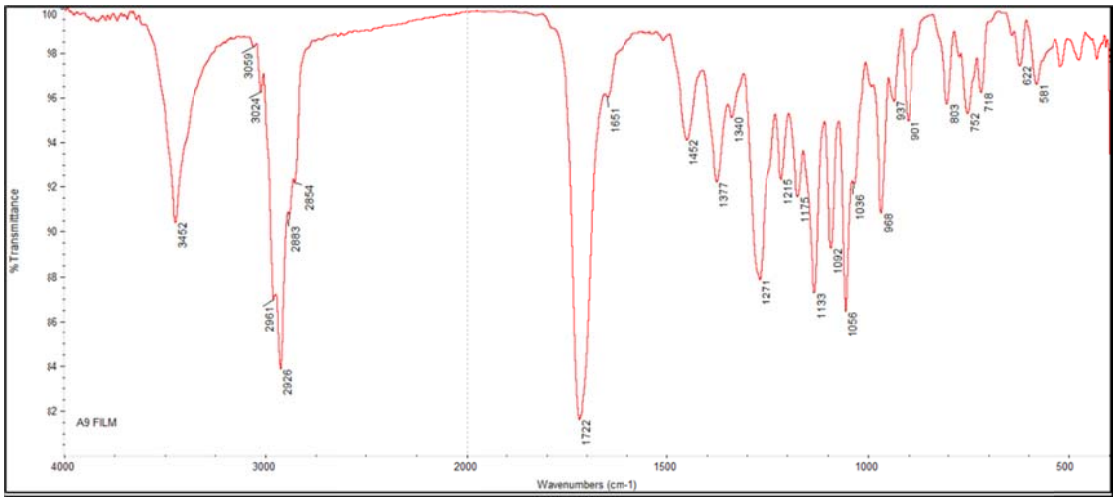


Figure S60. FTIR spectrum of **6**

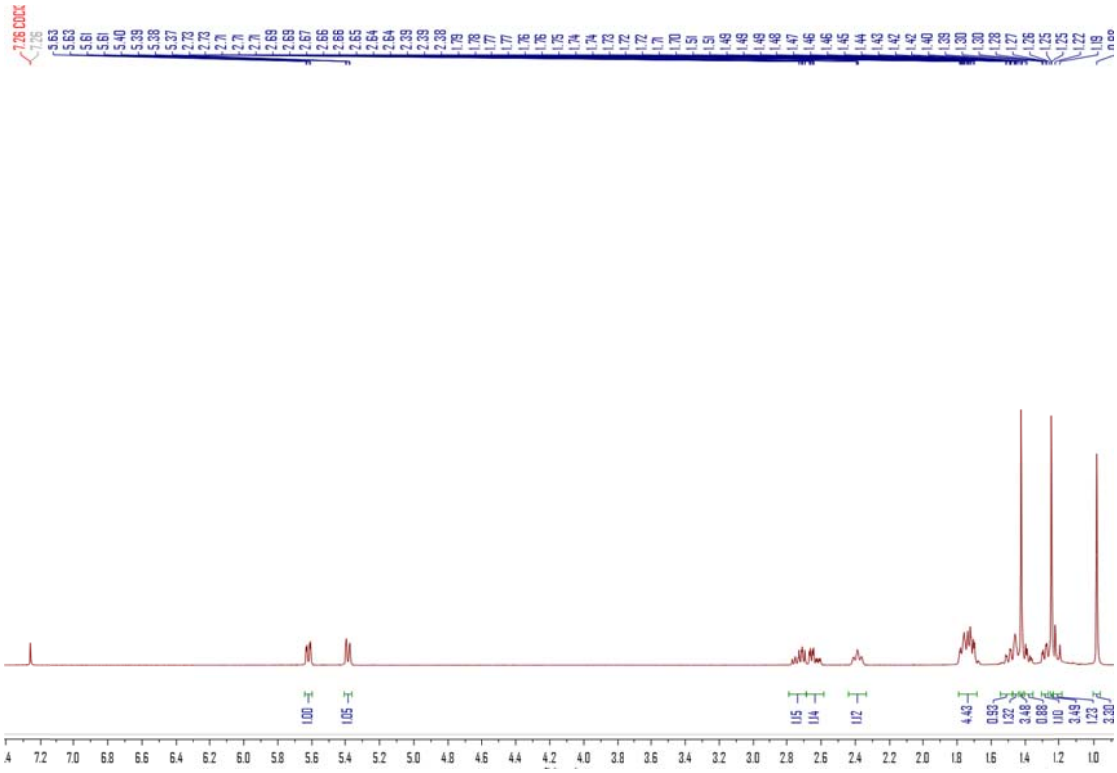


Figure S61. ^{1}H NMR spectrum of **6** in $CDCl_3$ at 500 MHz

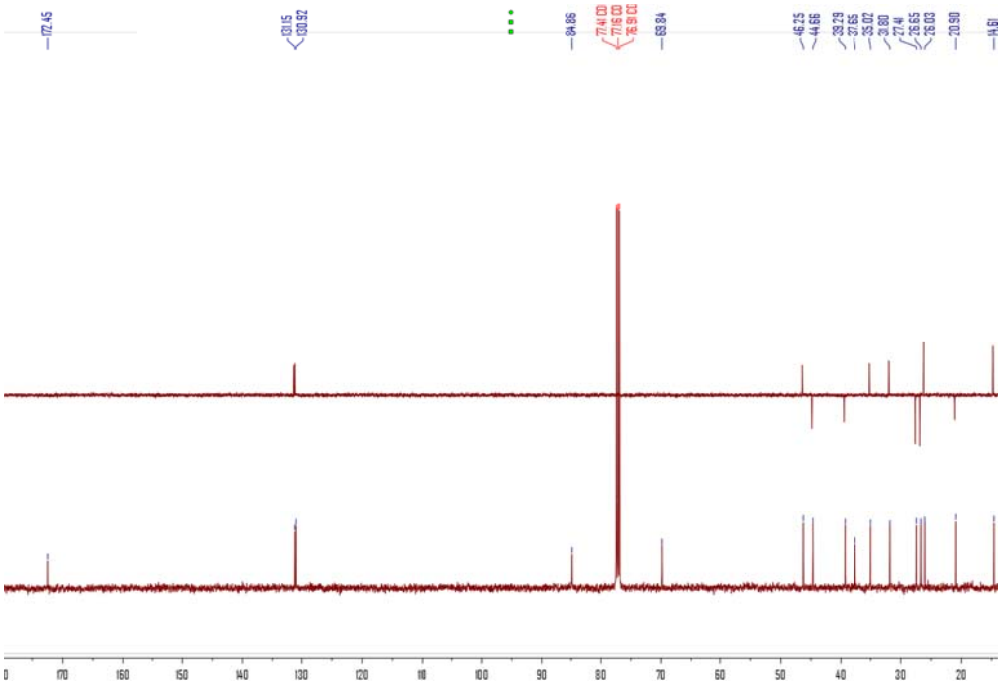


Figure S62. ^{13}C and NMR DEPT spectra of **6** in $CDCl_3$ at 125 MHz

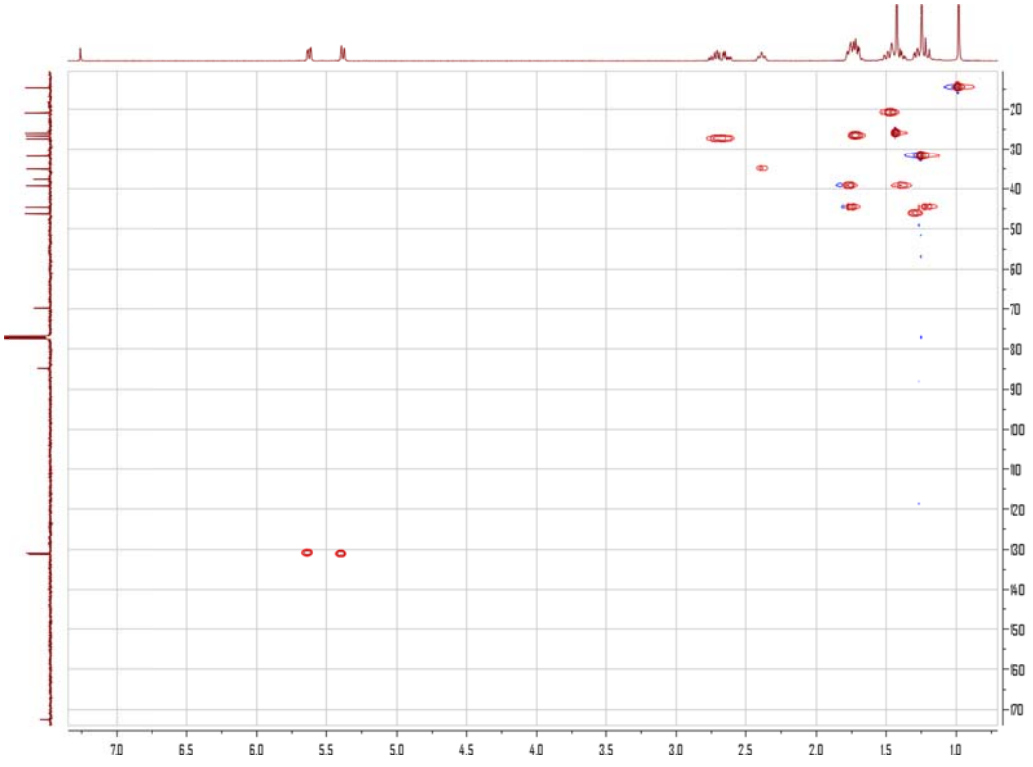


Figure S63. HSQC spectrum of **6** in $CDCl_3$

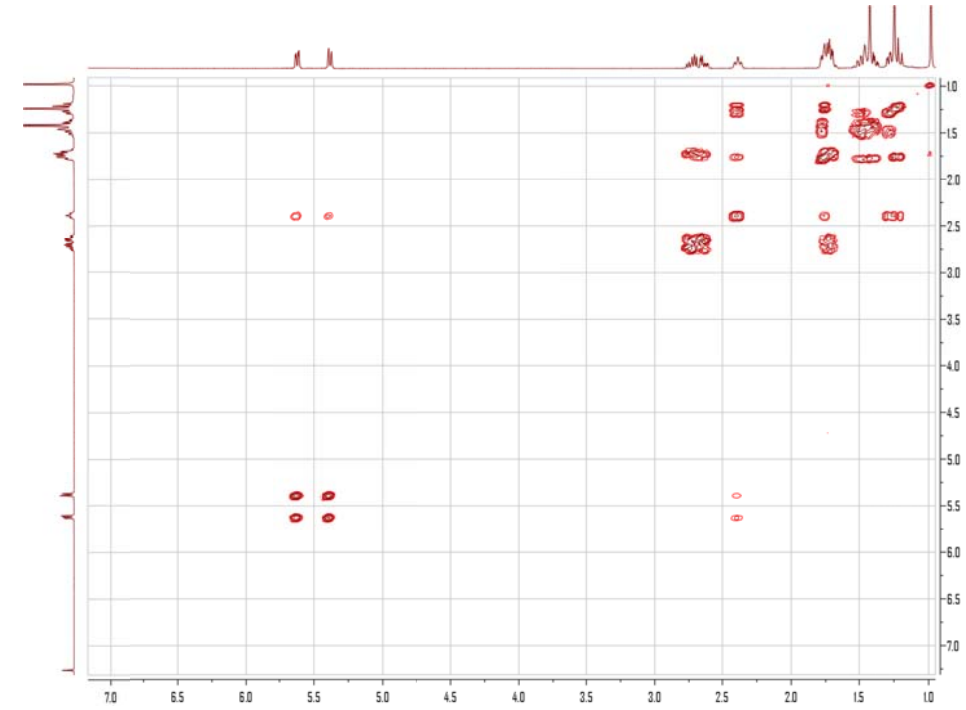


Figure S64. ^{1}H-^{1}H COSY spectrum of **6** in $CDCl_3$

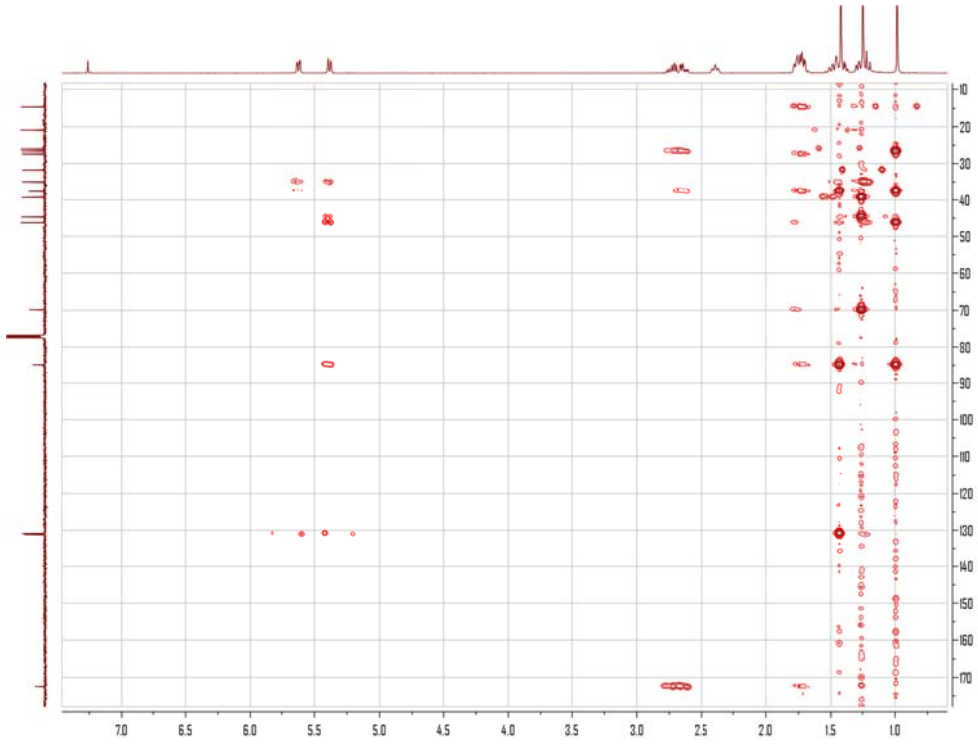


Figure S65. HMBC spectrum of **6** in $CDCl_3$

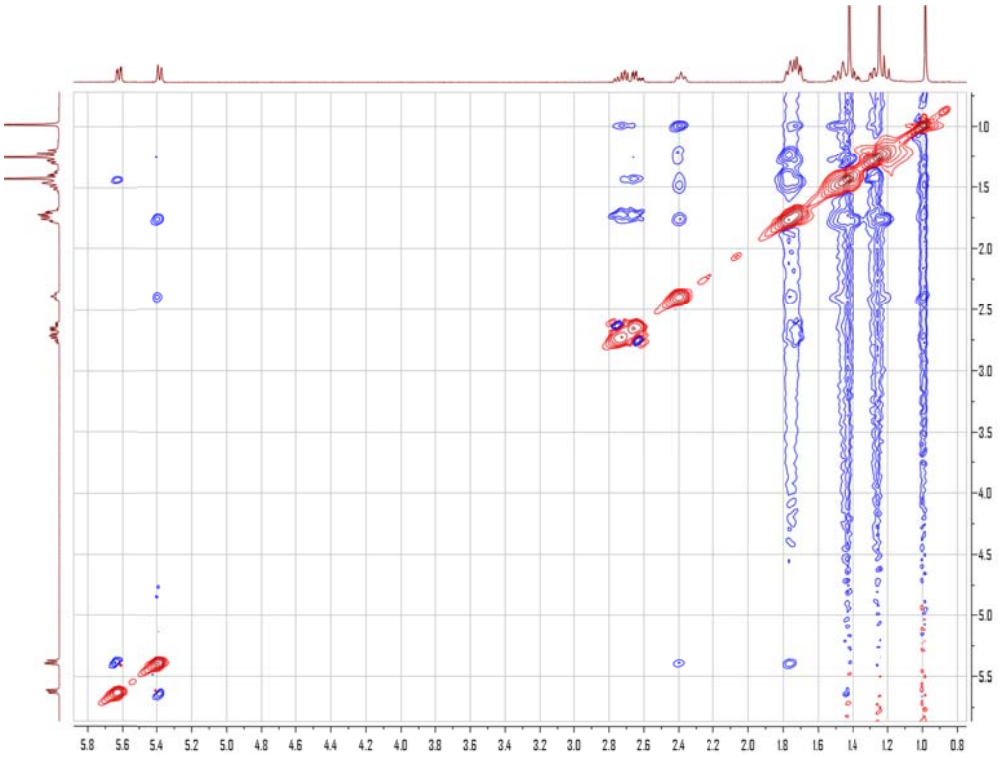


Figure S66. NOESY spectrum of **6** in $CDCl_3$

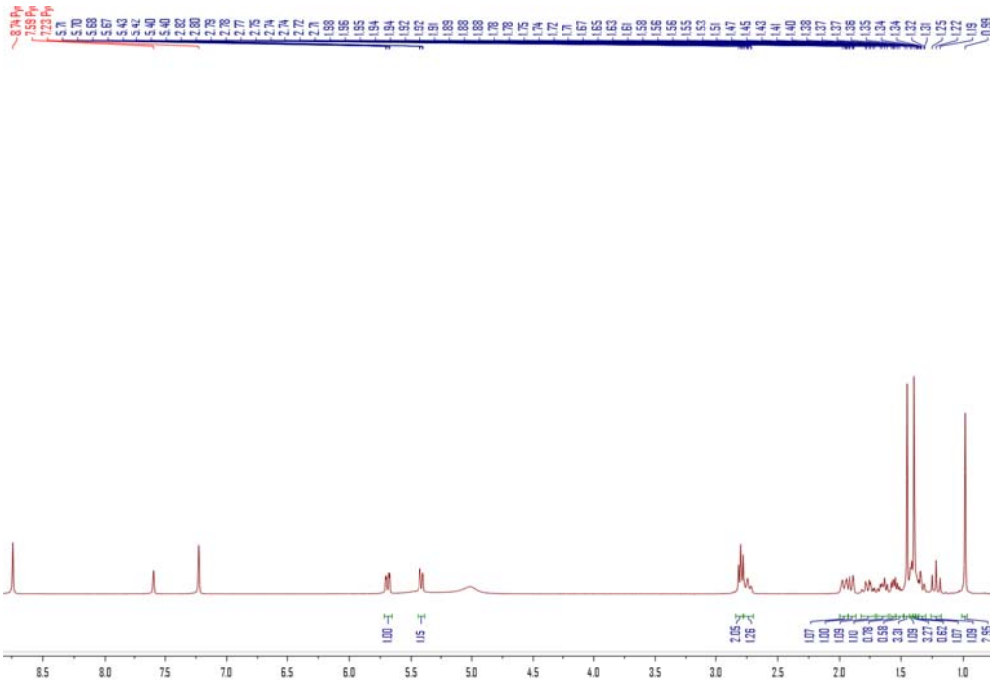


Figure S67. ^{1}H NMR spectrum of **6** in *Pyridine-d*$_5$ at 400 MHz

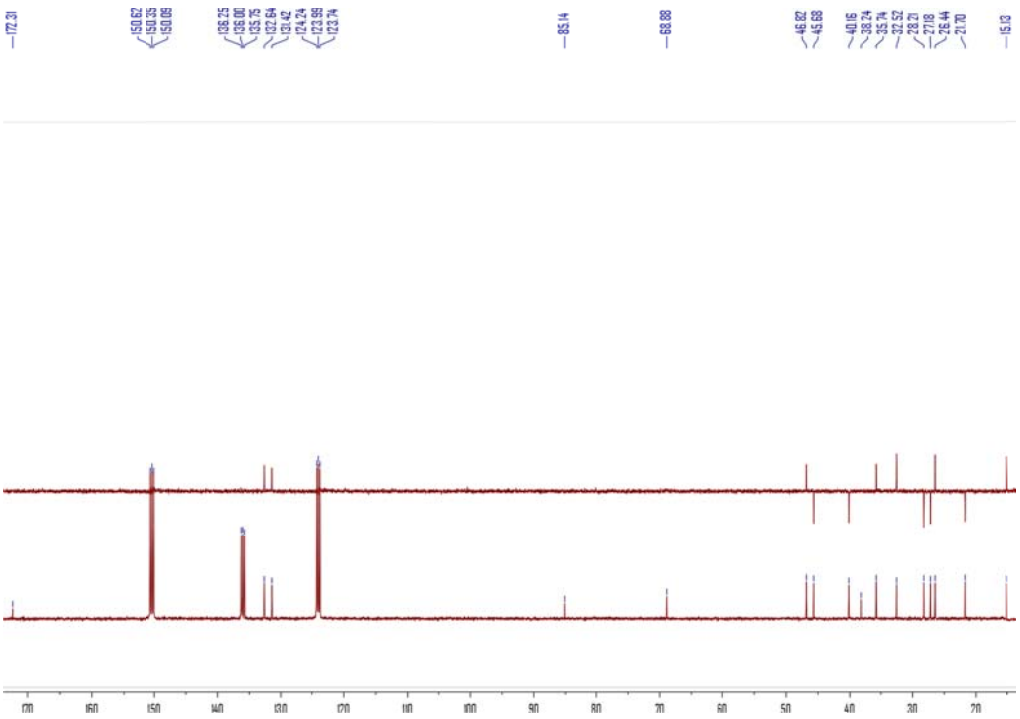


Figure S68. ^{13}C and NMR DEPT spectra of **6** in *Pyridine-d_5* at 100 MHz

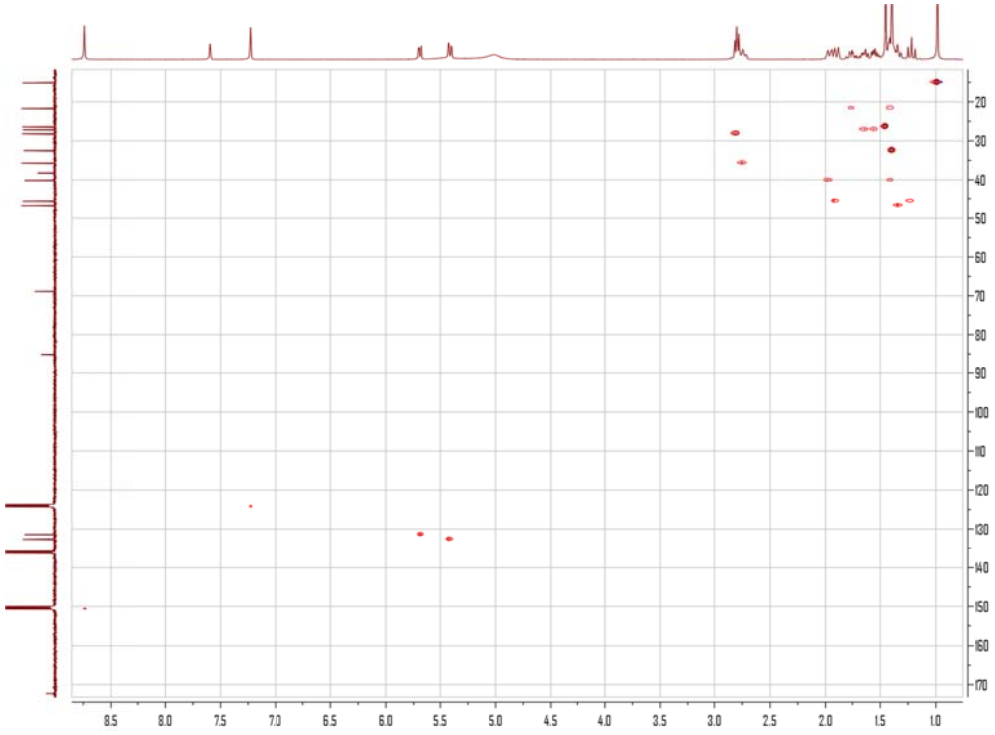


Figure S69. HSQC spectrum of **6** in *Pyridine-d_5*

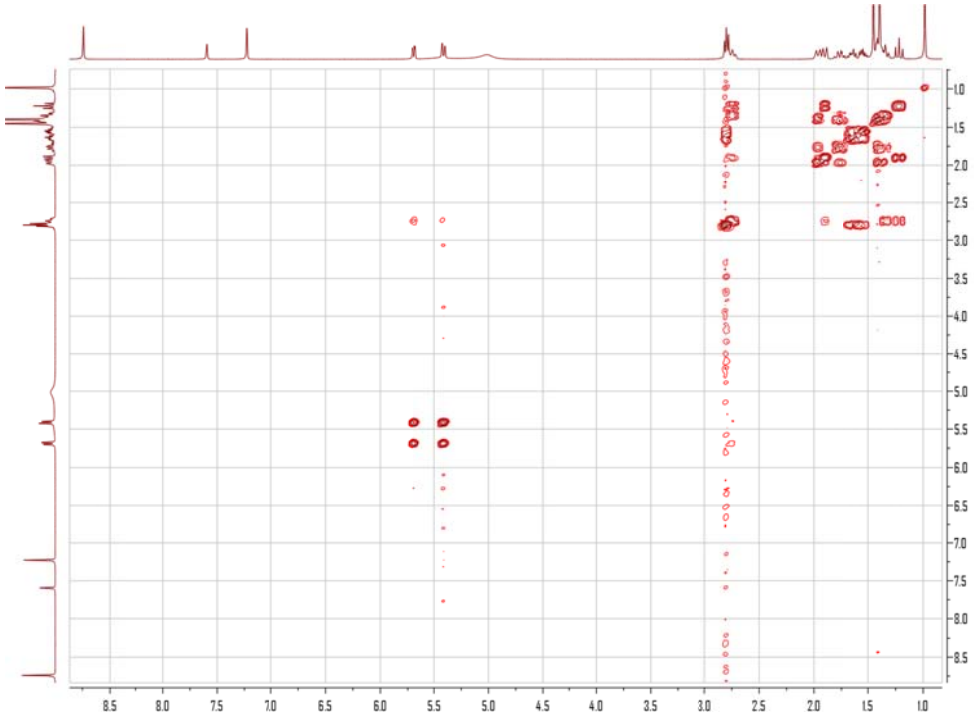


Figure S70. ^{1}H-^{1}H COSY spectrum of **6** in *Pyridine-d*$_5$

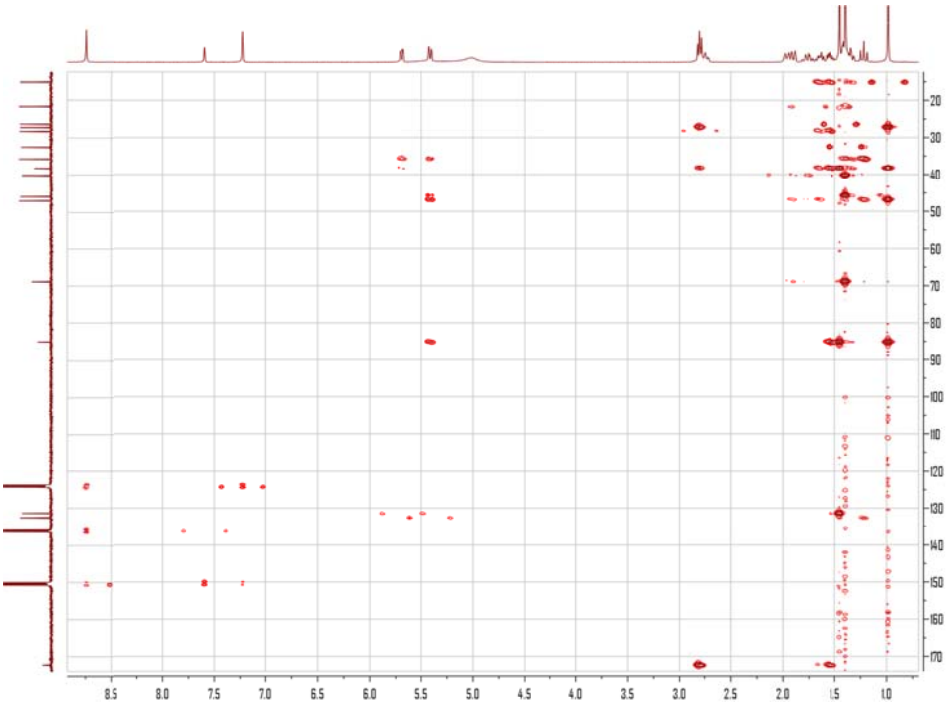


Figure S71. HMBC spectrum of **6** in *Pyridine-d*$_5$

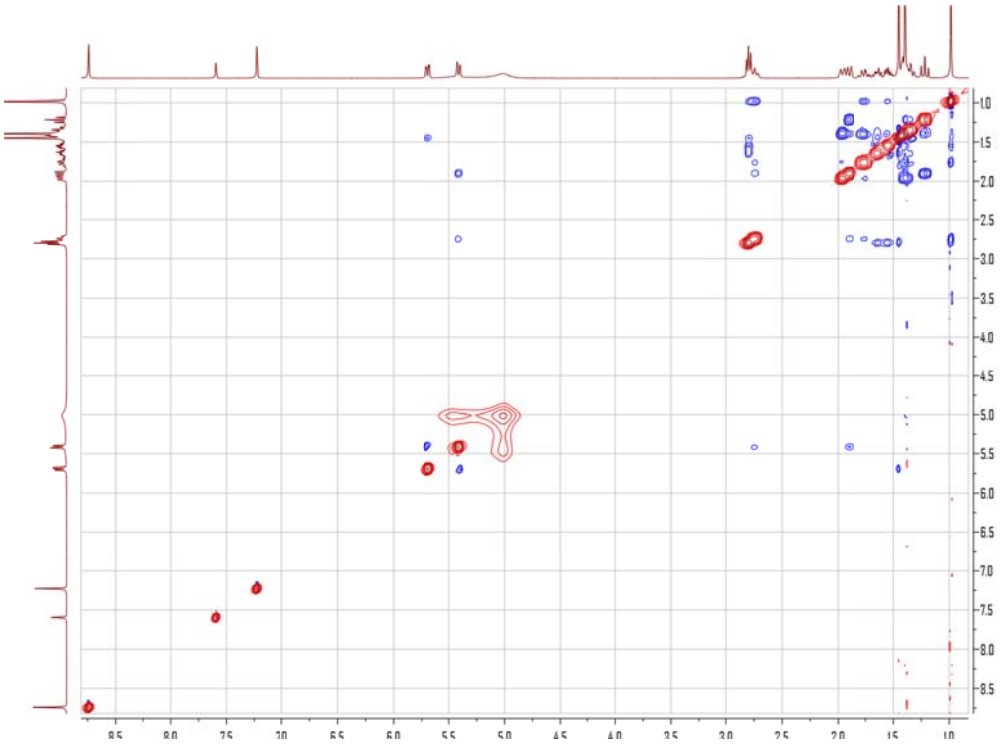


Figure S72. NOESY spectrum of **6** in *Pyridine-d_5*

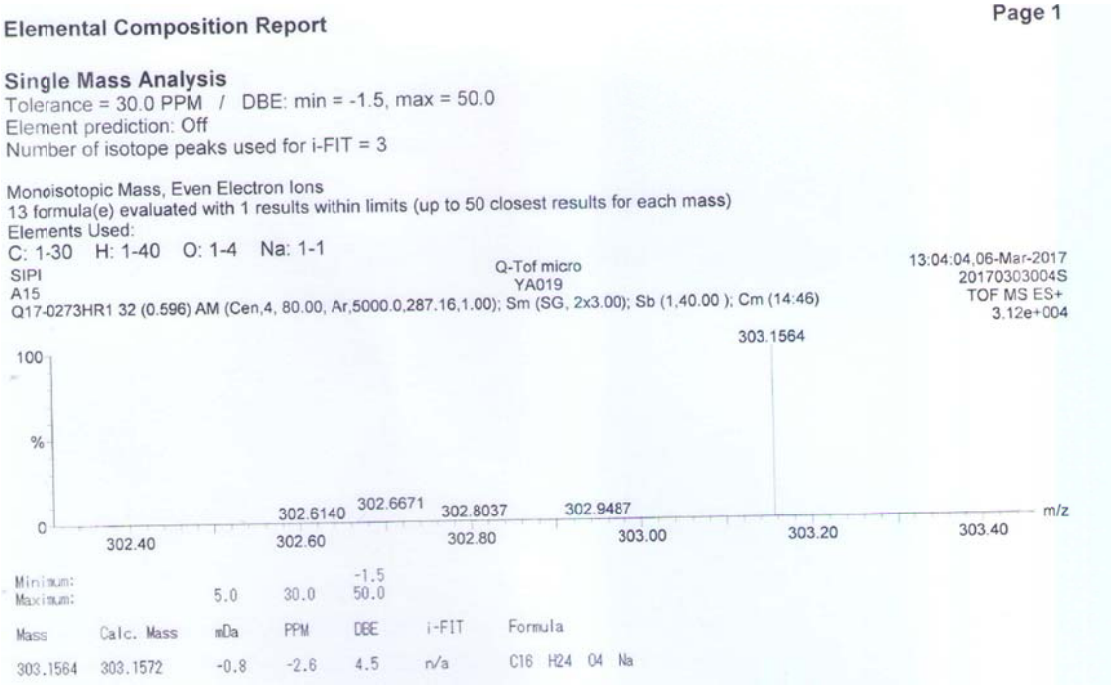


Figure S73. HRESIMS spectrum of **7**

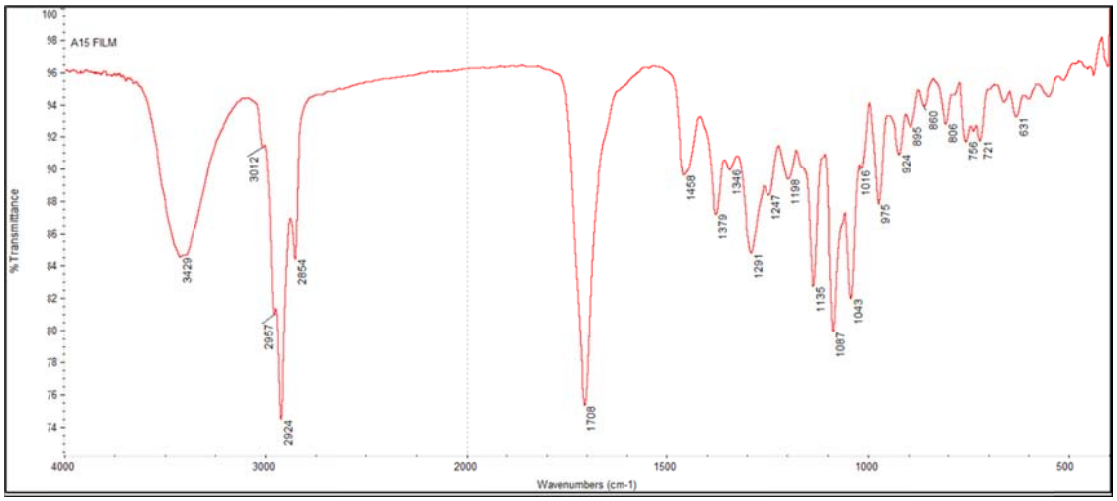


Figure S74. FTIR spectrum of **7**

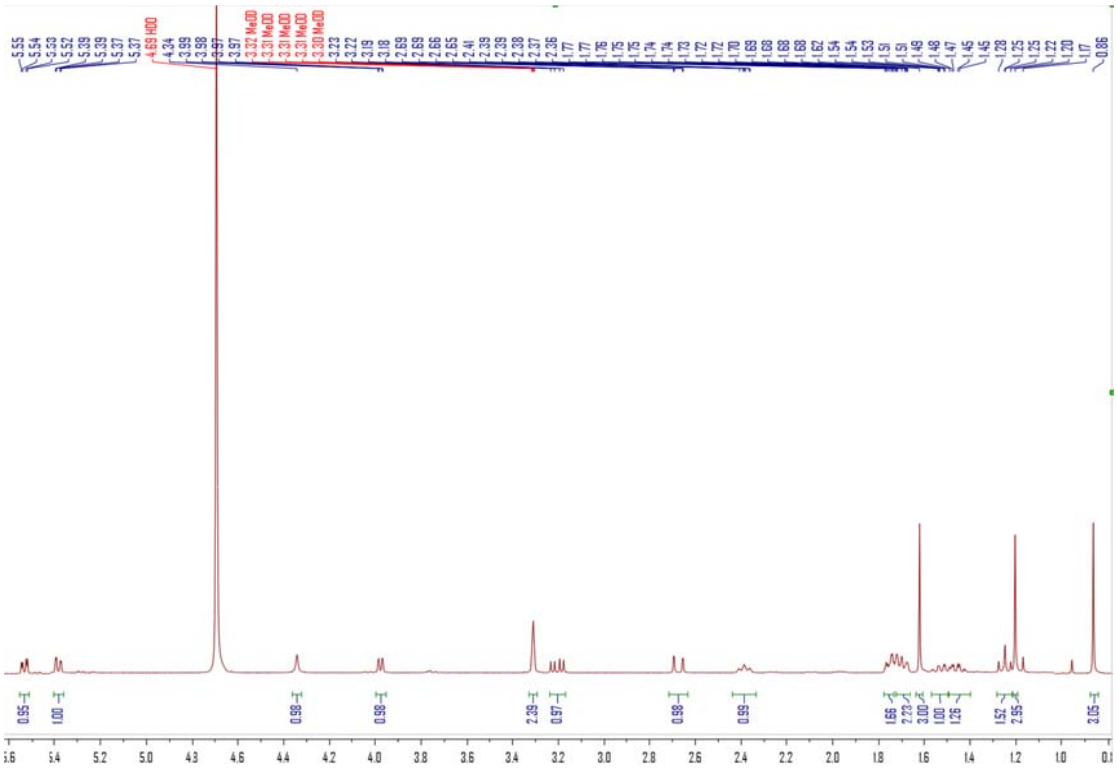


Figure S75. ^{1}H NMR spectrum of **7** in MeOD at 500 MHz

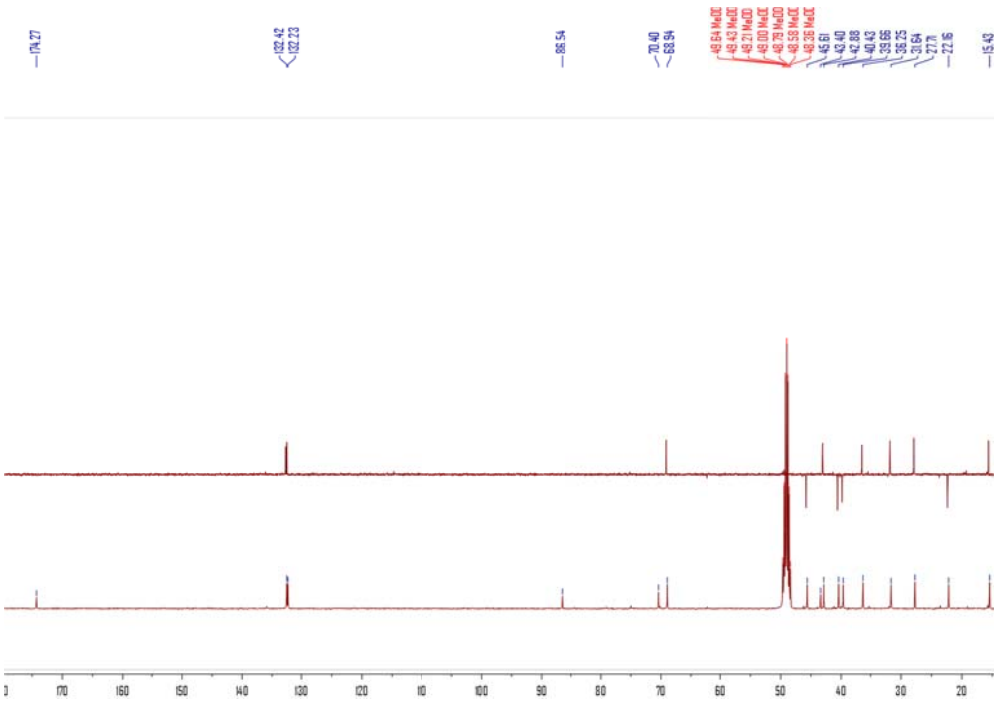


Figure S76. ^{13}C and NMR DEPT spectra of **7** in MeOD at 100 MHz

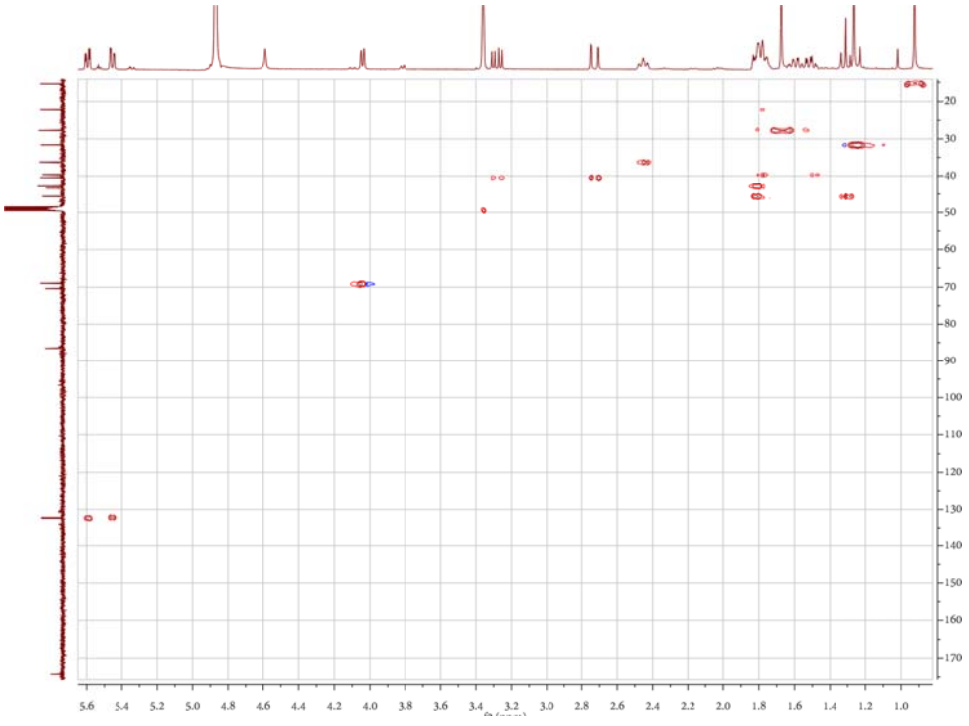


Figure S77. HSQC spectrum of **7** in MeOD

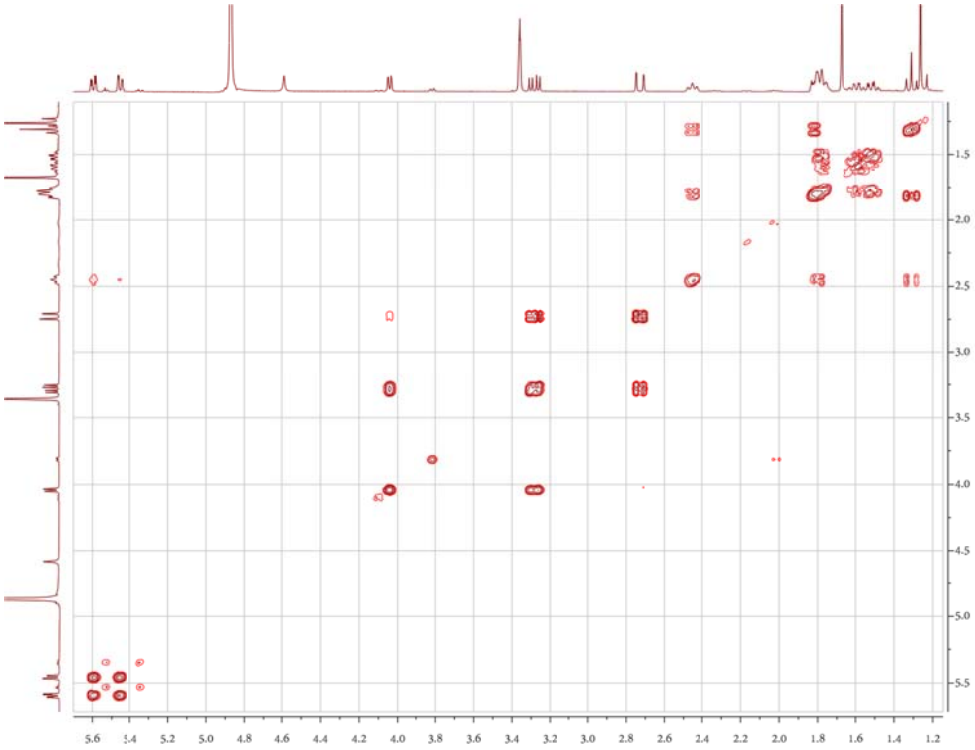


Figure S78. ^{1}H-^{1}H COSY spectrum of **7** in MeOD

Figure S79. HMBC spectrum of **7** in MeOD

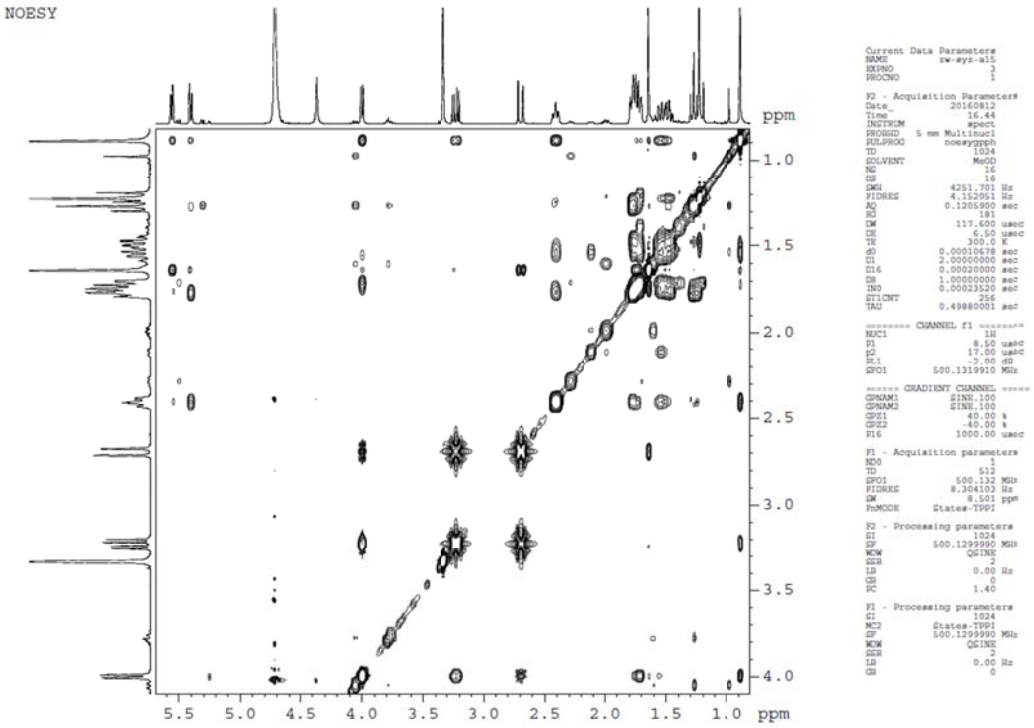


Figure S80. NOESY spectrum of **7** in MeOD

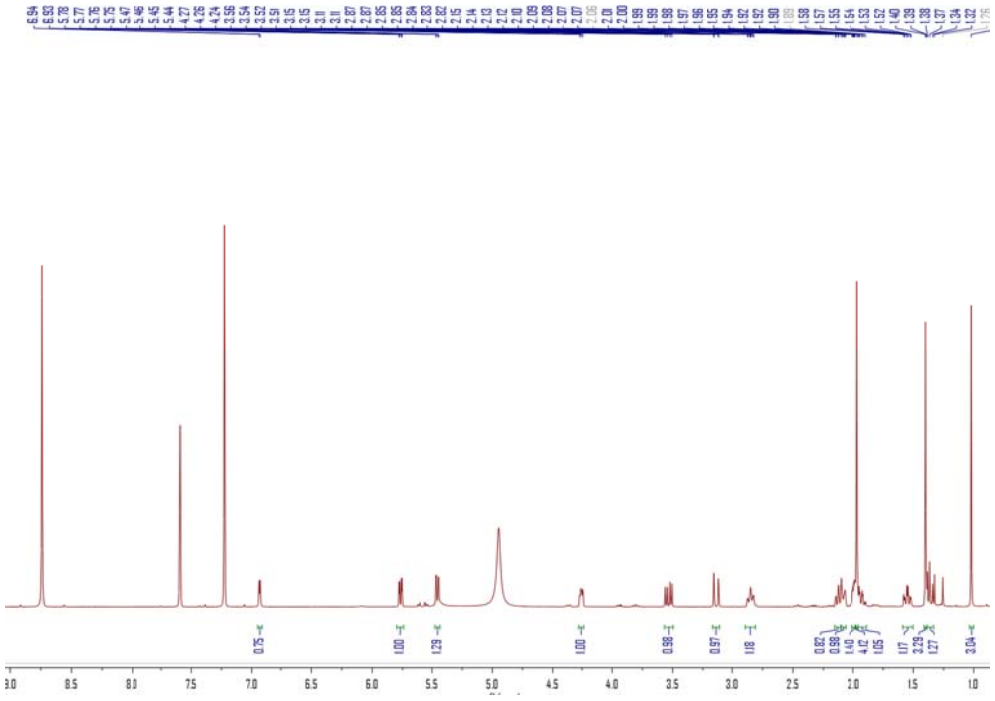


Figure S81. ^{1}H NMR spectrum of **7** in *Pyridine-d*$_5$ at 500 MHz

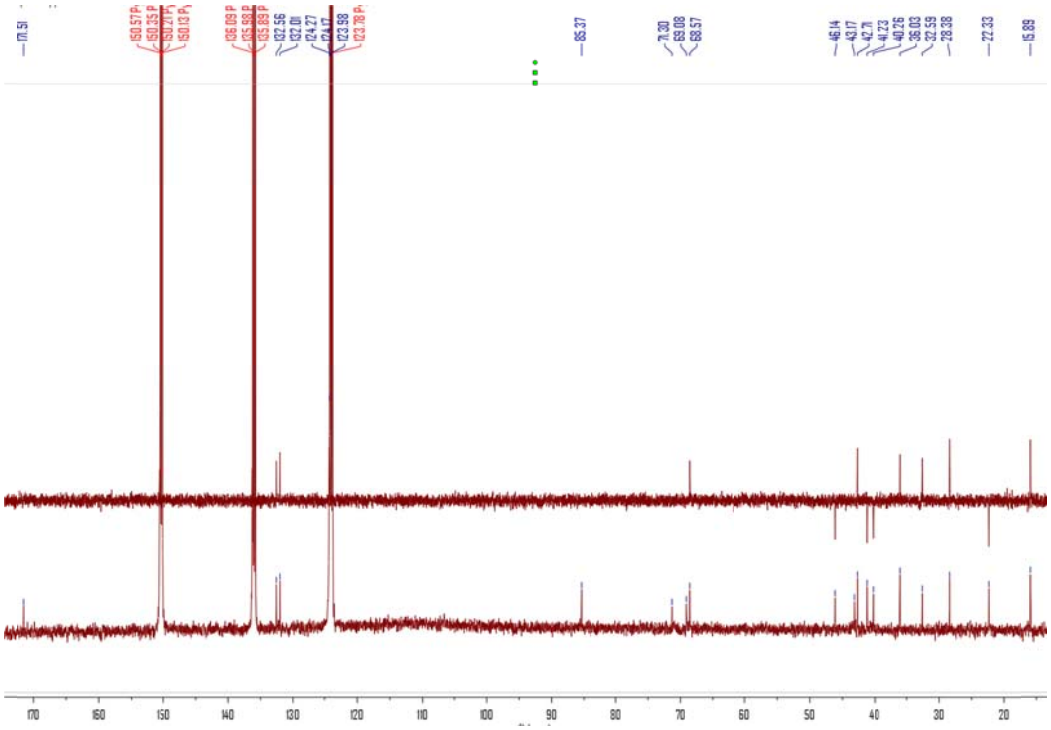


Figure S82. ^{13}C and NMR DEPT spectra of **7** in *Pyridine-d_5* at **1**25 MHz

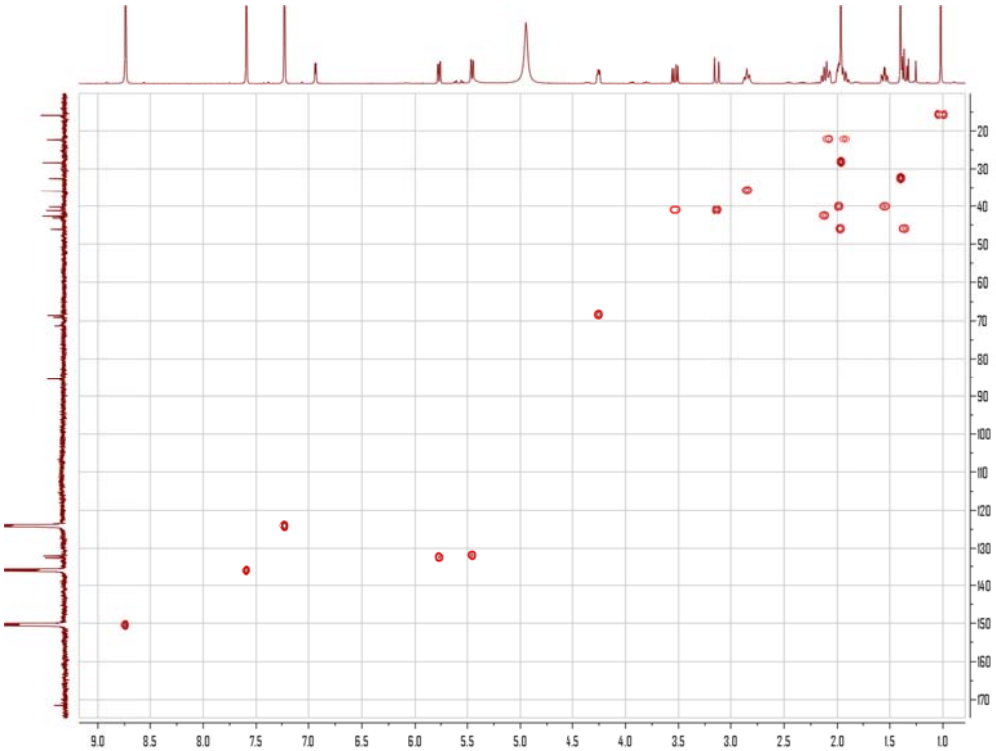


Figure S83. HSQC spectrum of 7 in *Pyridine-d_5*

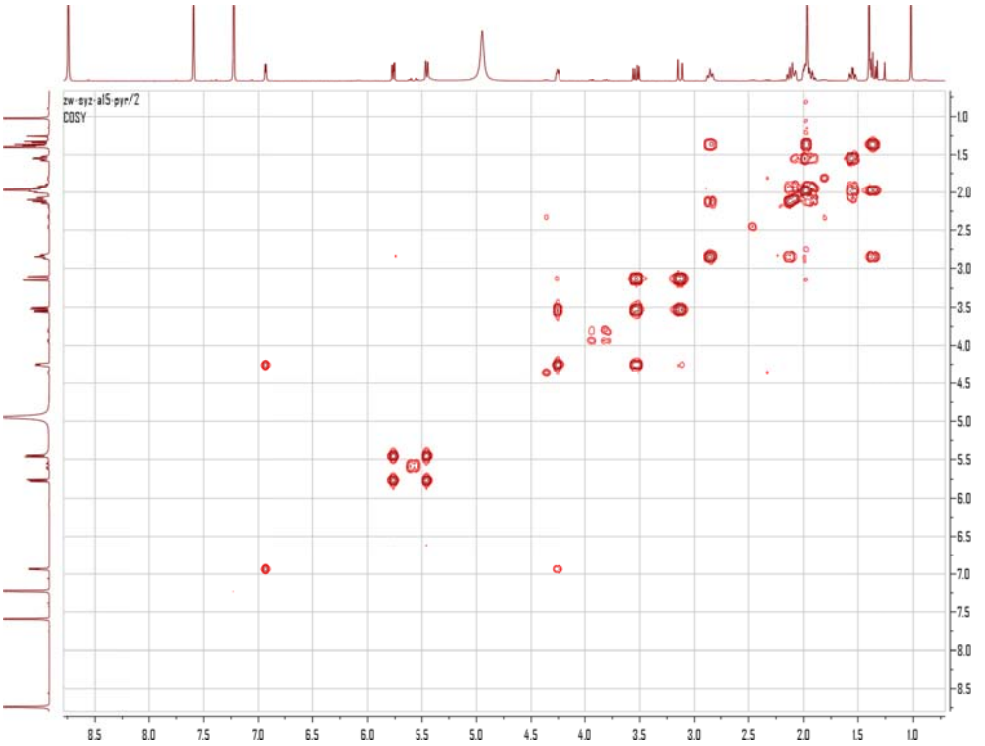


Figure S84. ^{1}H-^{1}H COSY spectrum of **7** in *Pyridine-d*$_5$

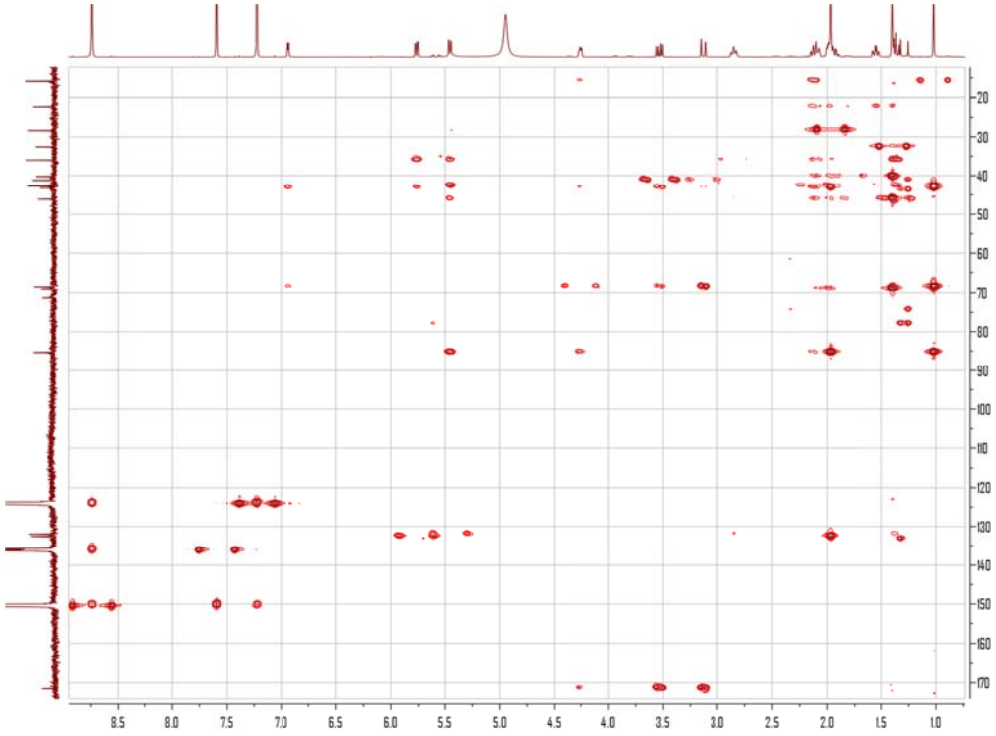


Figure S85. HMBC spectrum of **7** in *Pyridine-d*$_5$

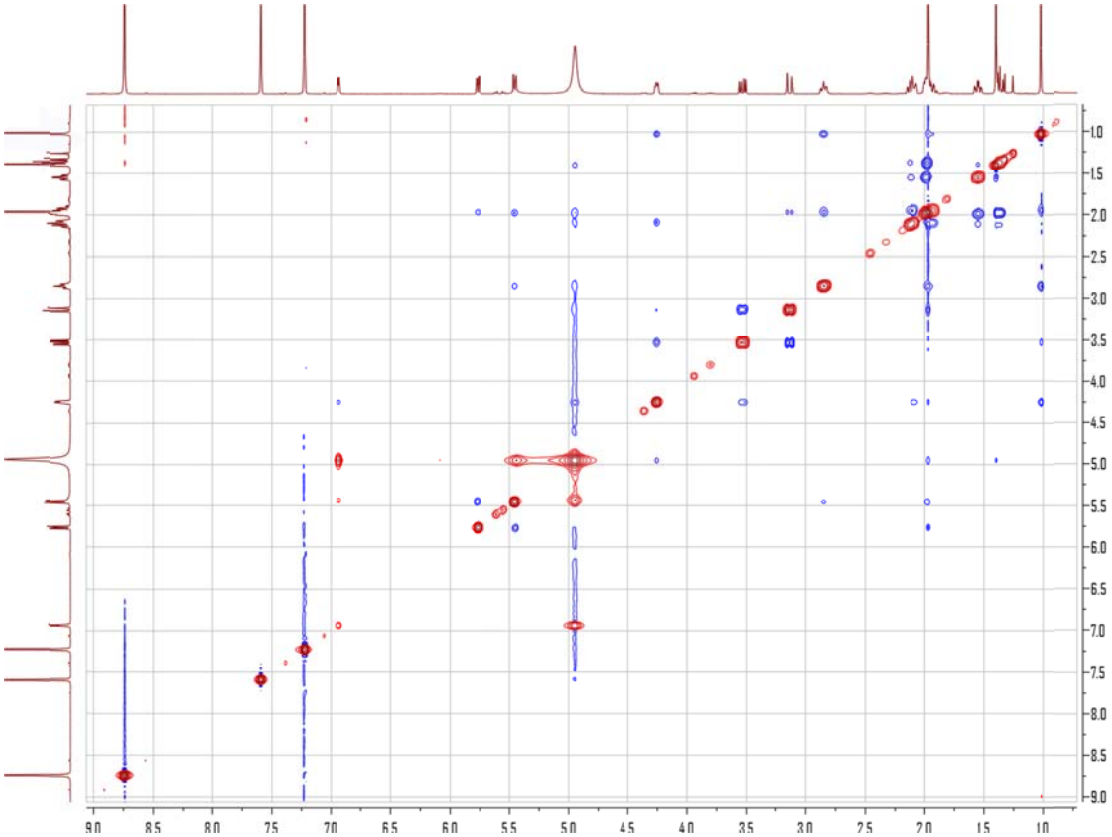


Figure S86. NOESY spectrum of **7** in *Pyridine-d_5*

D:\data\...\EI-GYW-17159_A21-c1 3/14/2017 2:29:29 PM

EI-GYW-17159_A21-c1#16-19 RT: 3.34-4.00 AV: 4
T: + c EI Full ms [49.50-1000.50]
m/z= 47.50-1002.50

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
55.0186	299687.5	27.20	55.0178	0.76	2.5	$C_3H_3O_1$
65.0378	83582.5	7.58	65.0386	-0.74	3.5	C_5H_5
67.0536	183751.0	16.67	67.0542	-0.58	2.5	C_5H_7
71.0516	168744.3	15.31	71.0491	2.48	1.5	$C_4H_7O_1$
77.0384	244998.0	22.23	77.0386	-0.19	4.5	C_6H_5
78.0458	60955.5	5.53	78.0464	-0.64	4.0	C_6H_6
79.0541	329118.3	29.87	79.0542	-0.12	3.5	C_6H_7
80.0611	64949.8	5.89	80.0621	-0.96	3.0	C_6H_8
84.0574	149448.3	13.56	84.0570	0.45	2.0	$C_5H_8O_1$
91.0540	517582.5	46.97	91.0542	-0.26	4.5	C_7H_7
92.0600	82940.3	7.53	92.0621	-2.01	4.0	C_7H_8
93.0693	344705.5	31.28	93.0699	-0.59	3.5	C_7H_9
94.0763	368566.3	33.45	94.0777	-1.43	3.0	C_7H_{10}
97.0657	285103.8	25.87	97.0648	0.92	2.5	$C_6H_9O_1$
98.0717	218277.0	19.81	98.0726	-0.92	2.0	$C_6H_{10}O_1$
101.0589	226617.5	20.56	101.0597	-0.85	1.5	$C_5H_9O_2$
103.0538	71879.3	6.52	103.0542	-0.43	5.5	C_8H_7
105.0692	438098.3	39.76	105.0699	-0.65	4.5	C_8H_9
106.0768	201406.8	18.28	106.0777	-0.90	4.0	C_8H_{10}
108.0795	84706.3	7.69	108.0781	1.38	-1.0	$C_4H_{12}O_3$
111.0787	115502.5	10.48	111.0804	-1.71	2.5	$C_7H_{11}O_1$
115.0537	119552.3	10.85	115.0542	-0.48	6.5	C_9H_7
117.0693	182236.8	16.54	117.0699	-0.57	5.5	C_9H_9
118.0766	85519.0	7.76	118.0777	-1.14	5.0	C_9H_{10}
119.0848	868817.3	78.84	119.0855	-0.73	4.5	C_9H_{11}
120.0908	181446.5	16.47	120.0934	-2.59	4.0	C_9H_{12}
121.0869	220873.0	20.04	121.0859	1.00	-0.5	$C_5H_{13}O_3$
129.0699	137131.3	12.44	129.0699	0.04	6.5	$C_{10}H_9$
130.0772	62217.5	5.65	130.0777	-0.53	6.0	$C_{10}H_{10}$
131.0834	247005.3	22.41	131.0855	-2.12	5.5	$C_{10}H_{11}$
132.0918	139128.3	12.63	132.0934	-1.57	5.0	$C_{10}H_{12}$
137.0936	83746.5	7.60	137.0961	-2.48	3.5	$C_9H_{13}O_1$
142.0768	72861.3	6.61	142.0777	-0.95	7.0	$C_{11}H_{10}$
143.0846	176541.5	16.02	143.0855	-0.93	6.5	$C_{11}H_{11}$
144.0919	107317.3	9.74	144.0934	-1.47	6.0	$C_{11}H_{12}$
147.1037	175131.3	15.89	147.1016	2.16	0.5	$C_7H_{15}O_3$
149.0586	196830.3	17.86	149.0597	-1.08	5.5	$C_9H_9O_2$
157.1010	166605.5	15.12	157.1012	-0.14	6.5	$C_{12}H_{13}$
171.1157	154222.0	14.00	171.1168	-1.09	6.5	$C_{13}H_{15}$
172.1222	83862.0	7.61	172.1247	-2.47	6.0	$C_{13}H_{16}$
173.1298	1101970.0	100.00	173.1325	-2.68	5.5	$C_{13}H_{17}$
174.1384	983931.3	89.29	174.1403	-1.94	5.0	$C_{13}H_{18}$
175.1340	276688.0	25.11	175.1329	1.16	0.5	$C_9H_{19}O_3$
215.1416	478638.8	43.43	215.1430	-1.41	6.5	$C_{15}H_{19}O_1$
230.1653	63155.8	5.73	230.1665	-1.20	6.0	$C_{16}H_{22}O_1$
233.1529	497370.0	45.13	233.1536	-0.75	5.5	$C_{15}H_{21}O_2$
248.1761	114285.3	10.37	248.1771	-0.95	5.0	$C_{16}H_{24}O_2$
251.1633	472938.3	42.92	251.1642	-0.91	4.5	$C_{15}H_{23}O_3$
266.1879	65196.8	5.92	266.1876	0.22	4.0	$C_{16}H_{26}O_3$

Figure S87. HREIMS spectrum of **8**

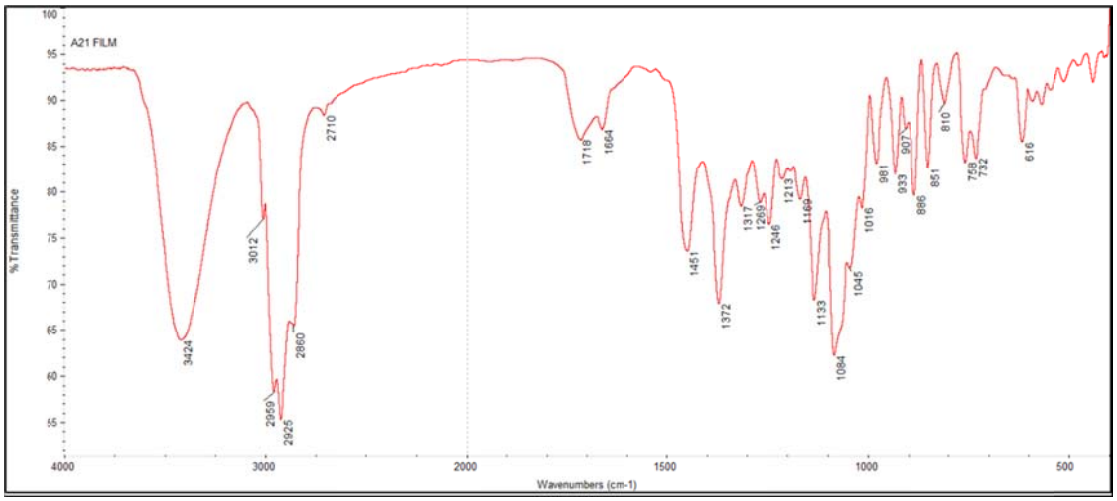


Figure S88. FTIR spectrum of **8**

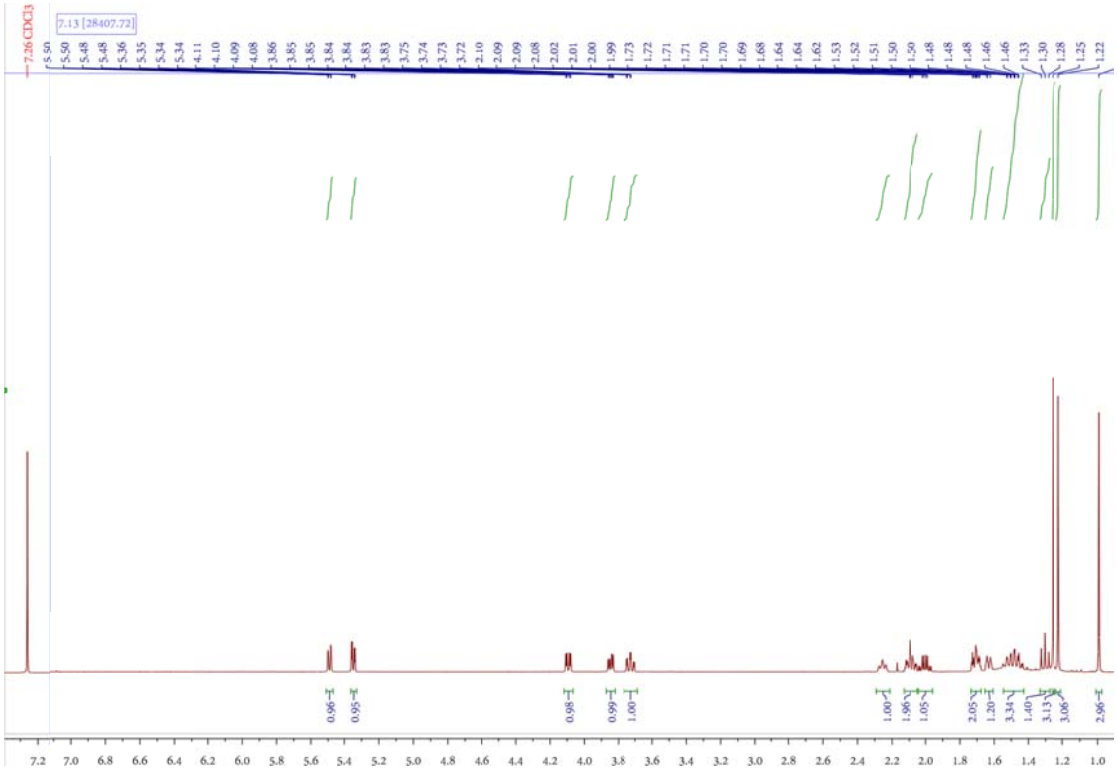


Figure S89. ^{1}H NMR spectrum of **8** in $CDCl_3$ at 600 MHz

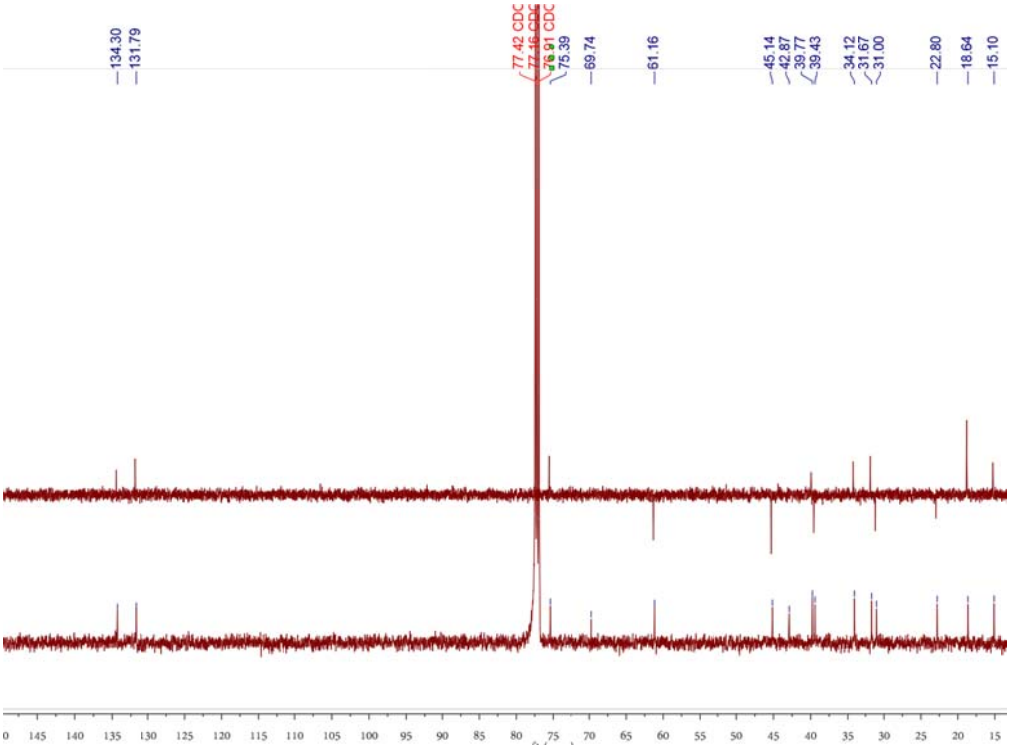


Figure S90. ^{13}C and NMR DEPT spectra of **8** in $CDCl_3$ at 125 MHz

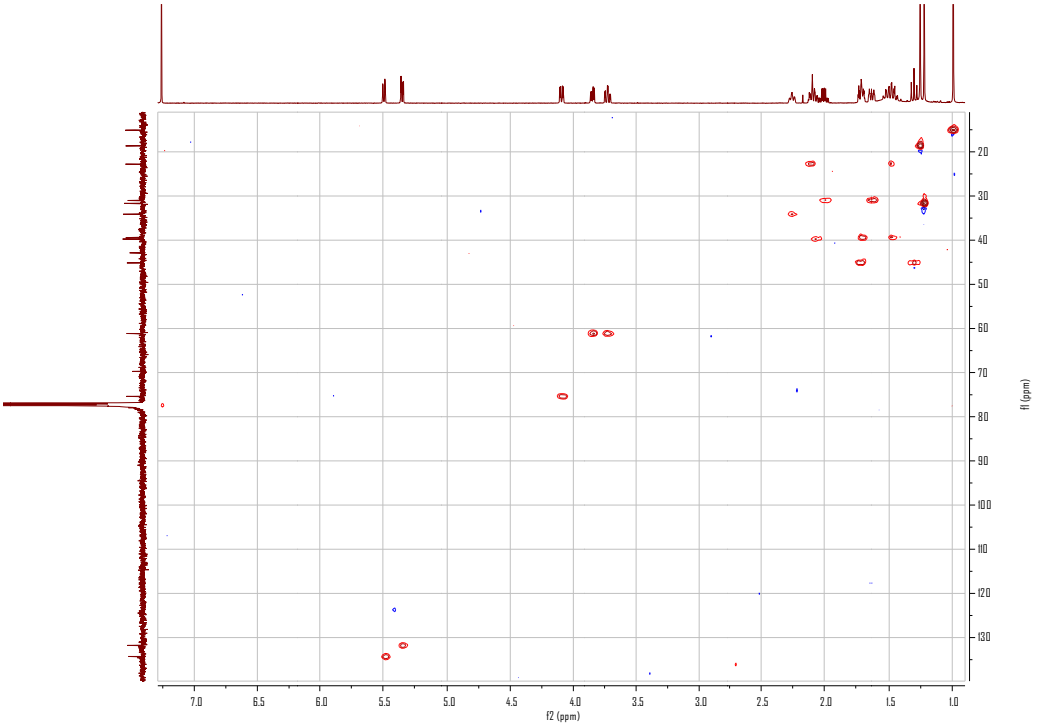


Figure S91. HSQC spectrum of **8** in $CDCl_3$

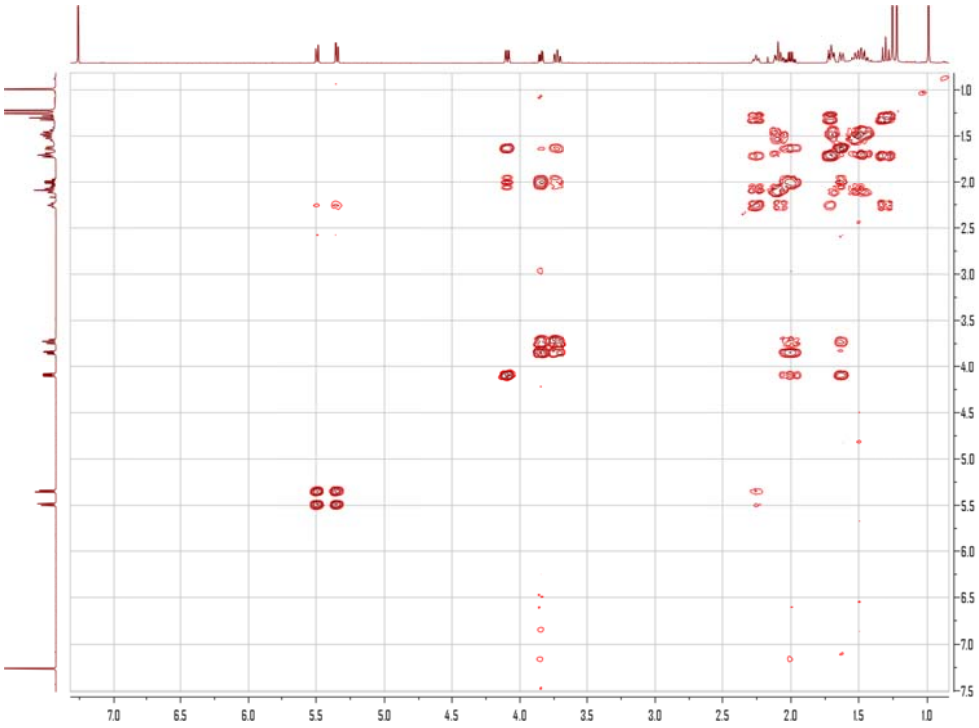


Figure S92. ^{1}H-^{1}H COSY spectrum of **8** in $CDCl_3$

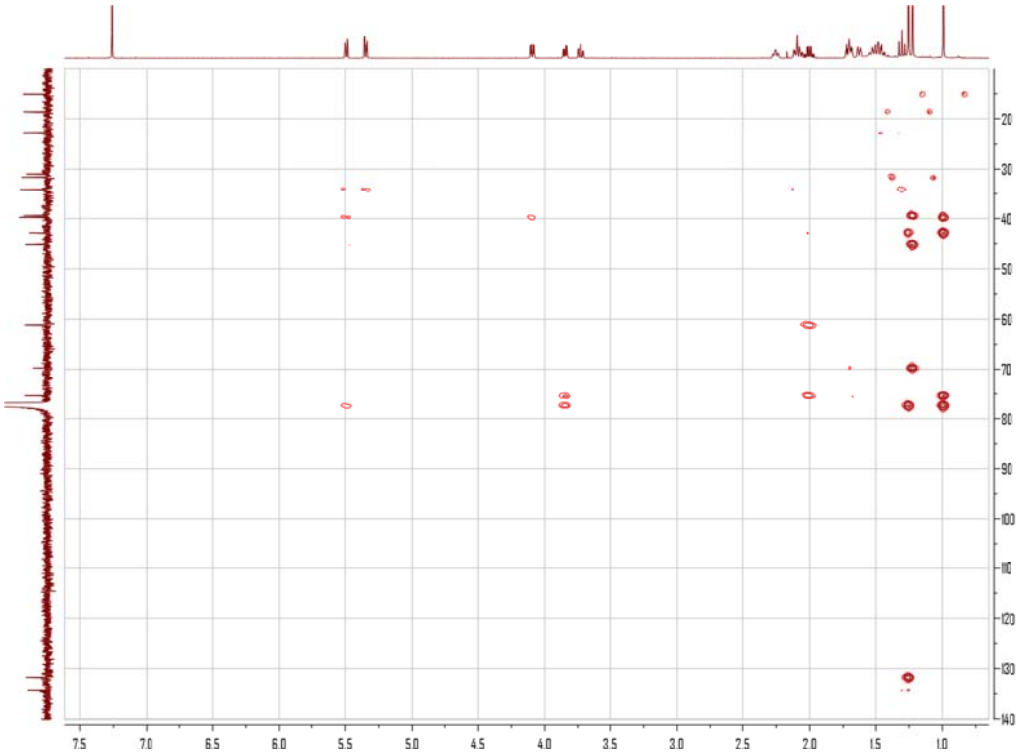


Figure S93. HMBC spectrum of **8** in $CDCl_3$

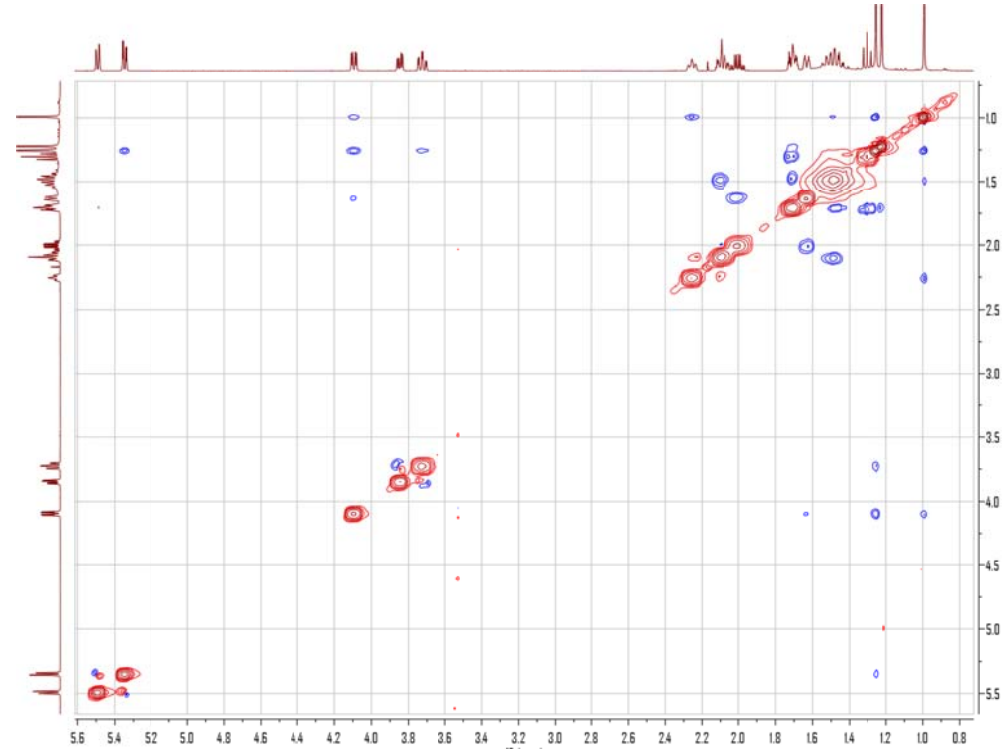


Figure S94. NOESY spectrum of **8** in $CDCl_3$

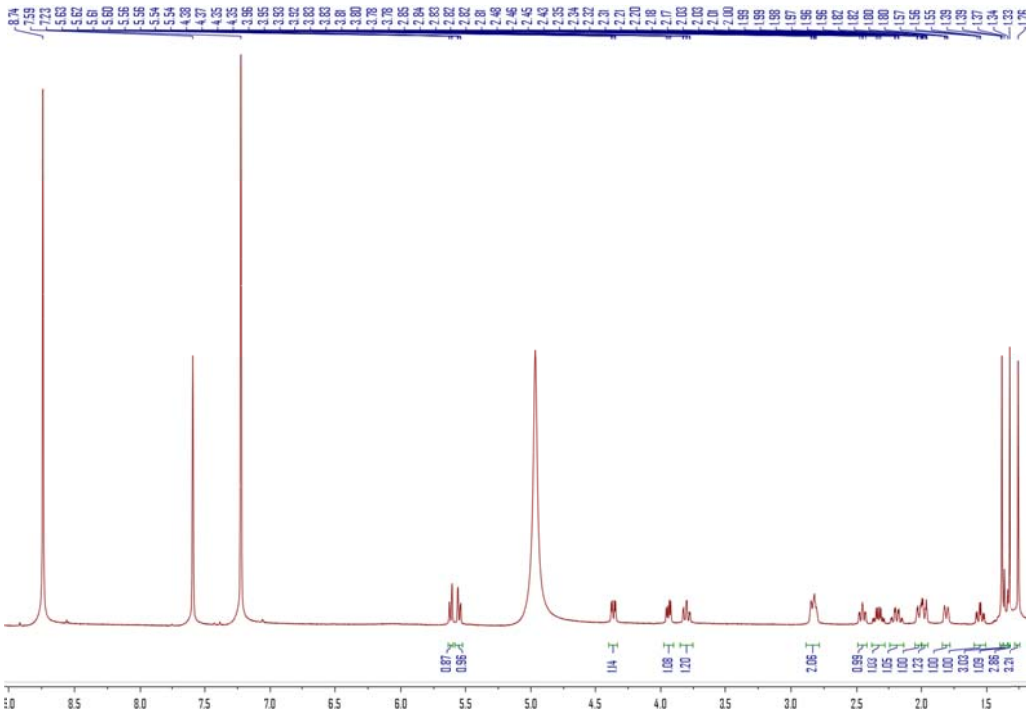


Figure S95. ^{1}H NMR spectrum of **8** in *Pyridine-d_5* at 500 MHz

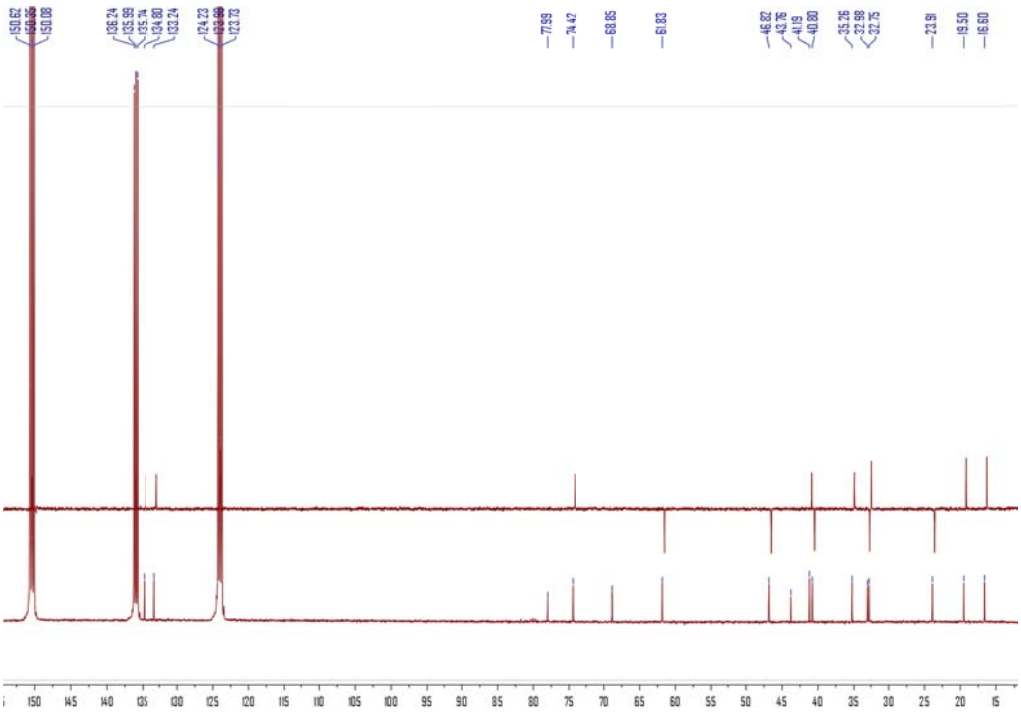


Figure S96. ^{13}C and NMR DEPT spectra of **8** in *Pyridine-d*$_5$ at **1**00 MHz

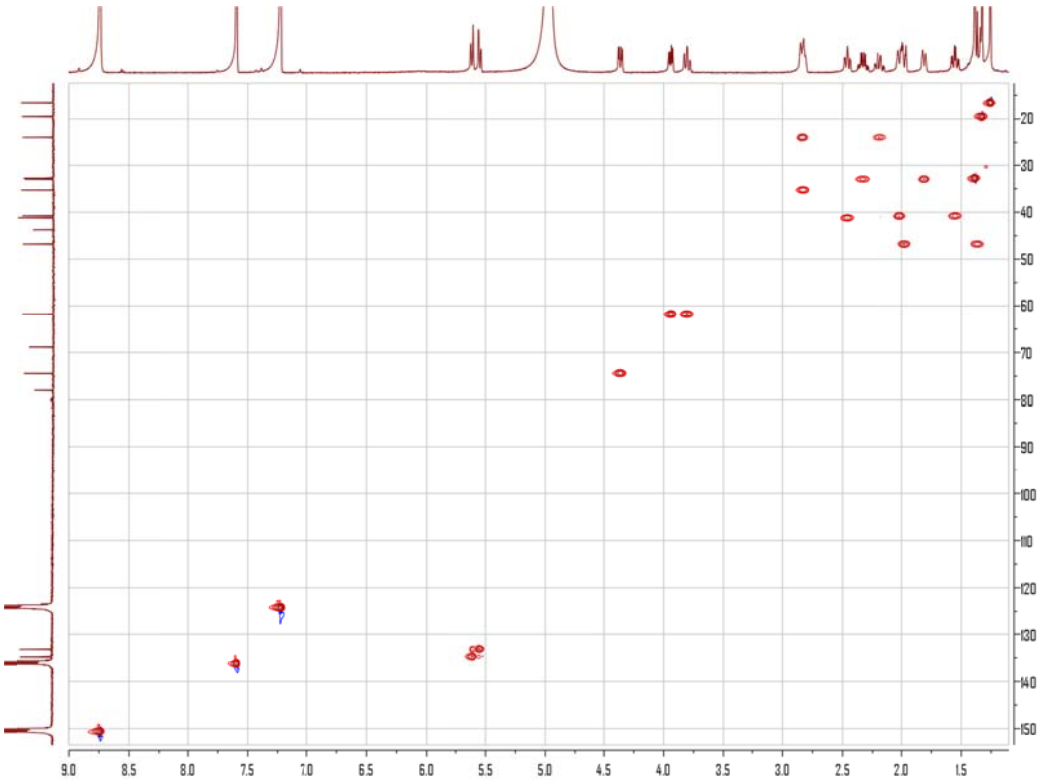


Figure S97. HSQC spectrum of **8** in *Pyridine-d*$_5$

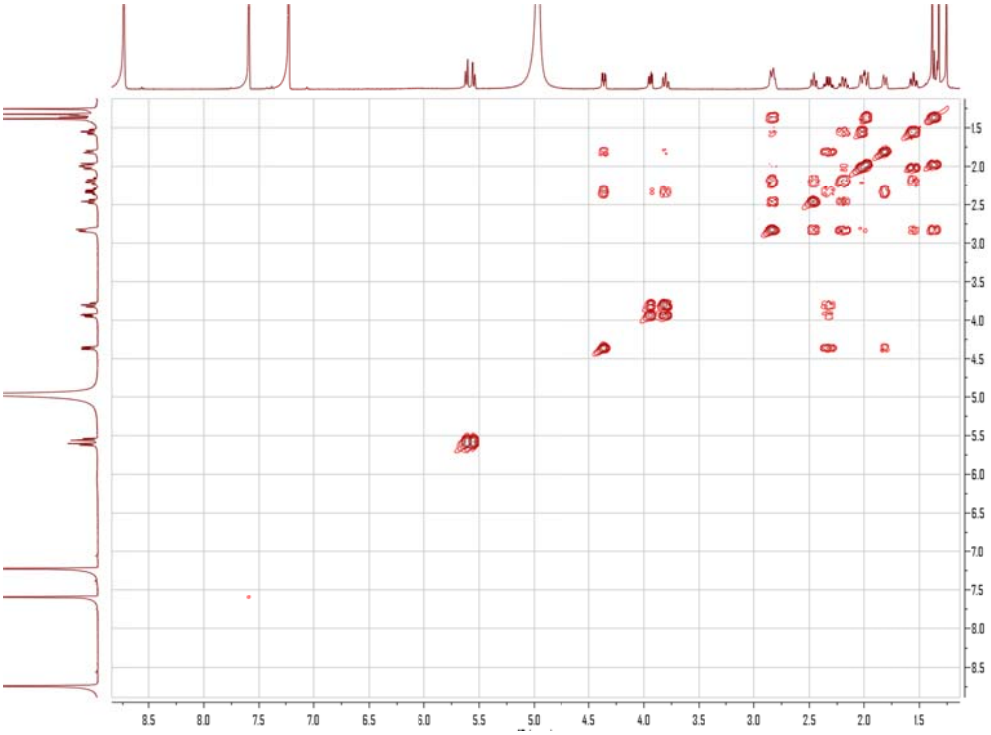


Figure S98. ^{1}H-^{1}H COSY spectrum of **8** in *Pyridine-d*$_5$

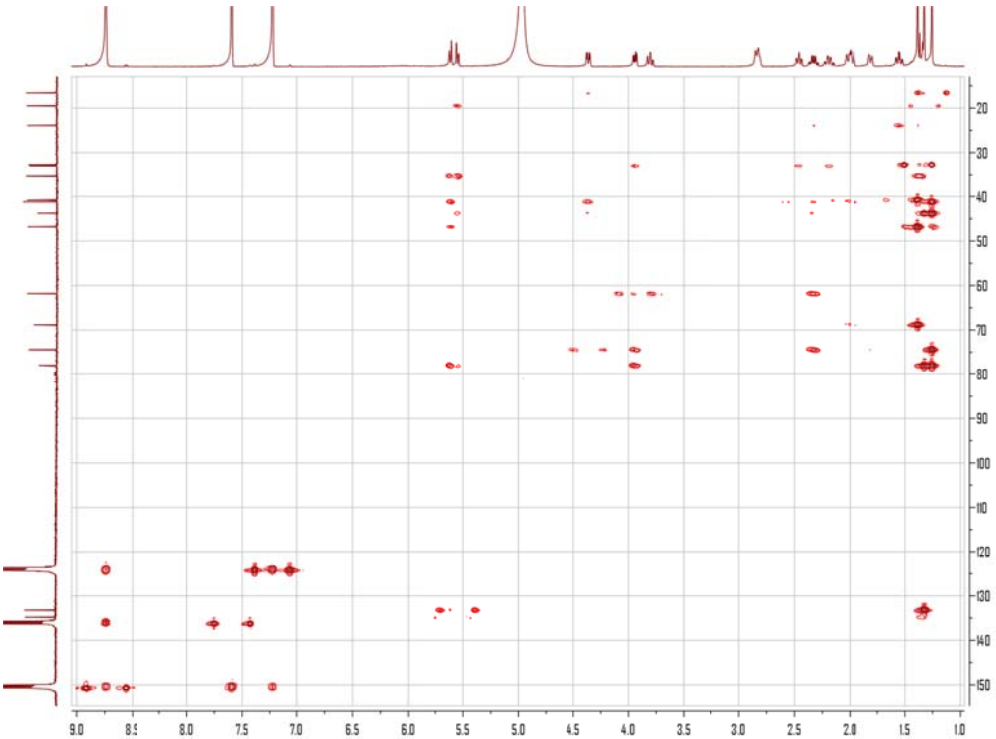


Figure S99. HMBC spectrum of **8** in *Pyridine-d*$_5$

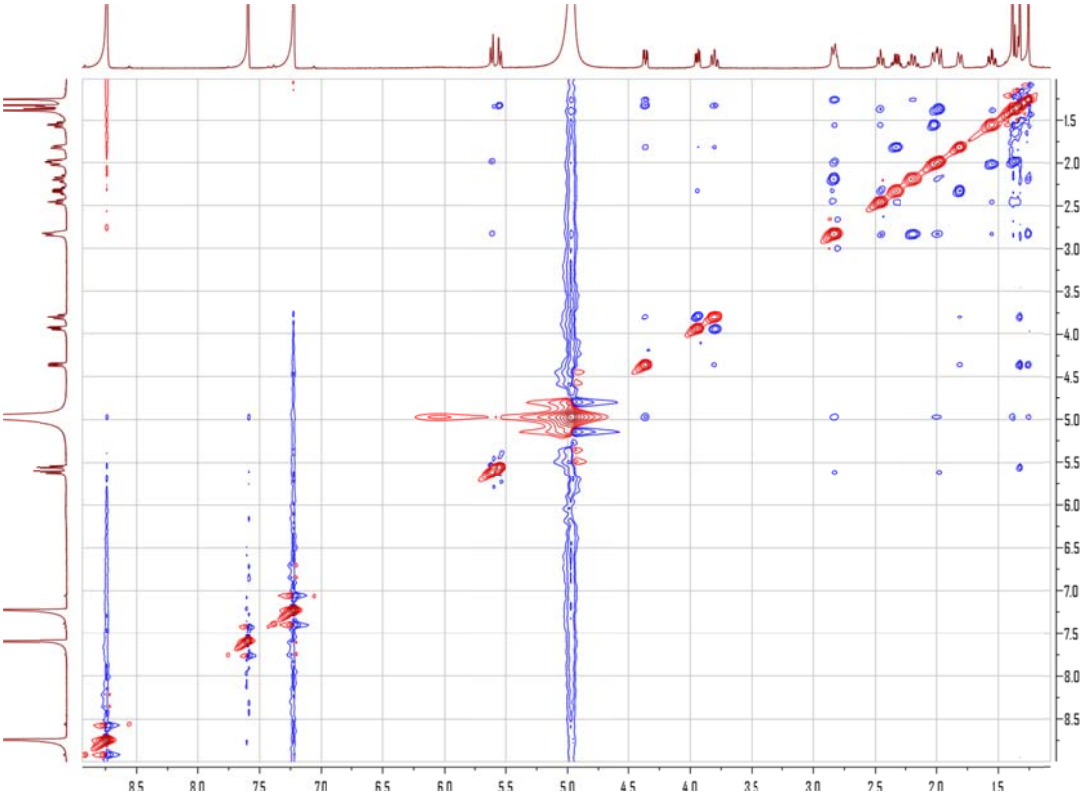


Figure S100. NOESY spectrum of **8** in *Pyridine-d_5*

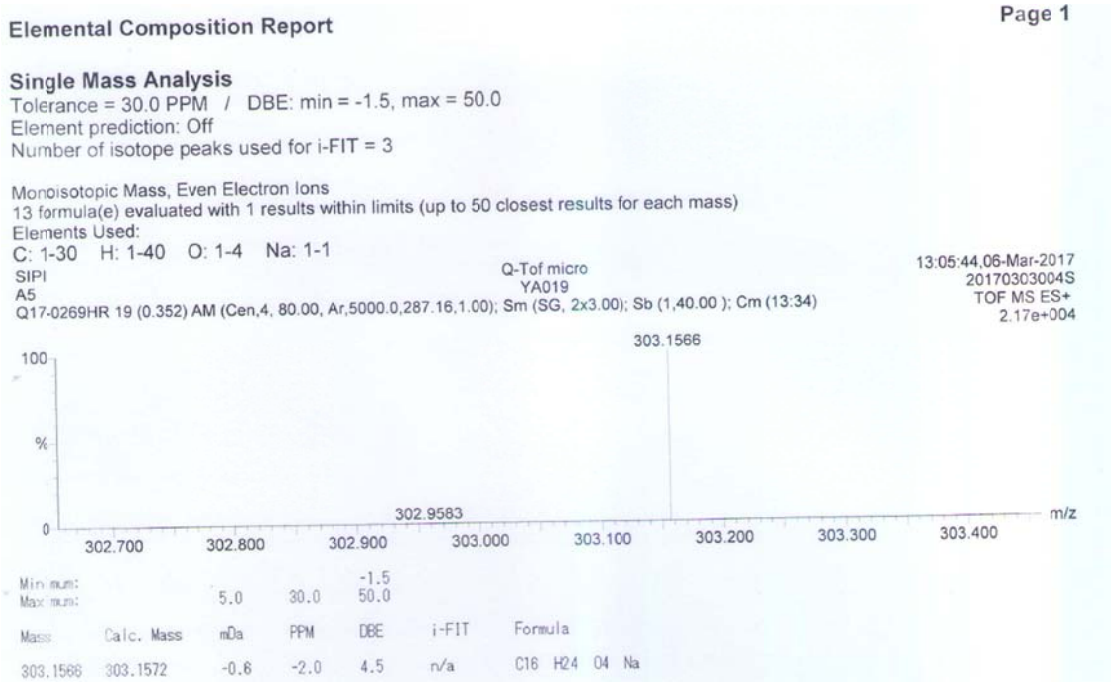


Figure S101. HRESIMS spectrum of **9**

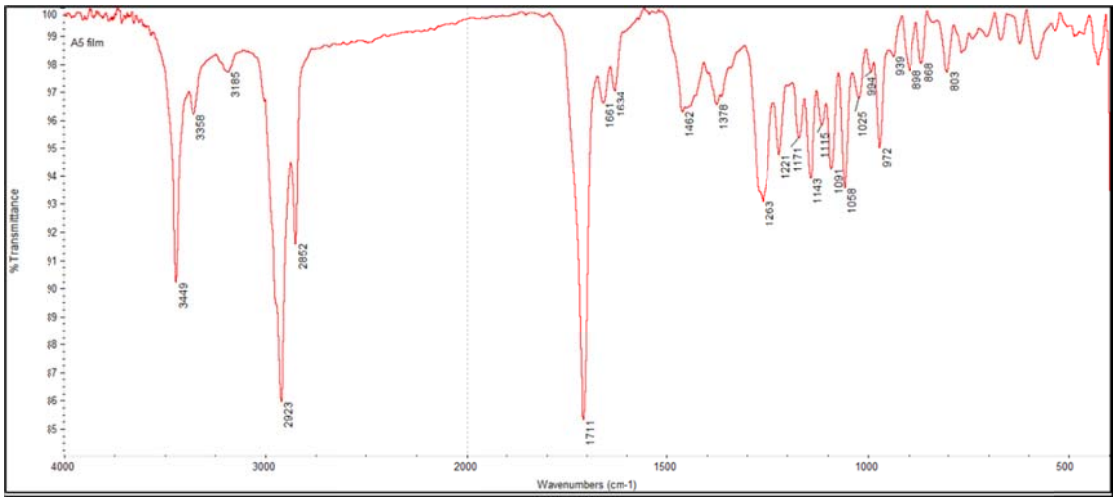


Figure S102. FTIR spectrum of **9**

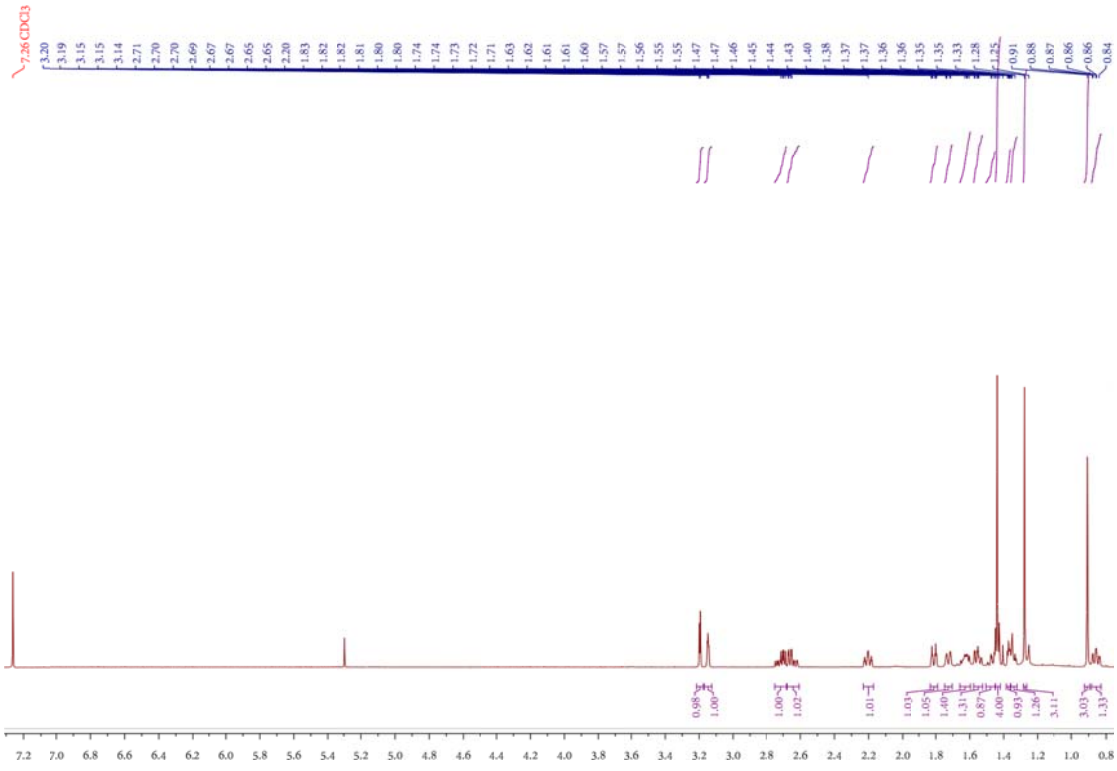


Figure S103. ^{1}H NMR spectrum of **9** in $CDCl_3$ at 600 MHz

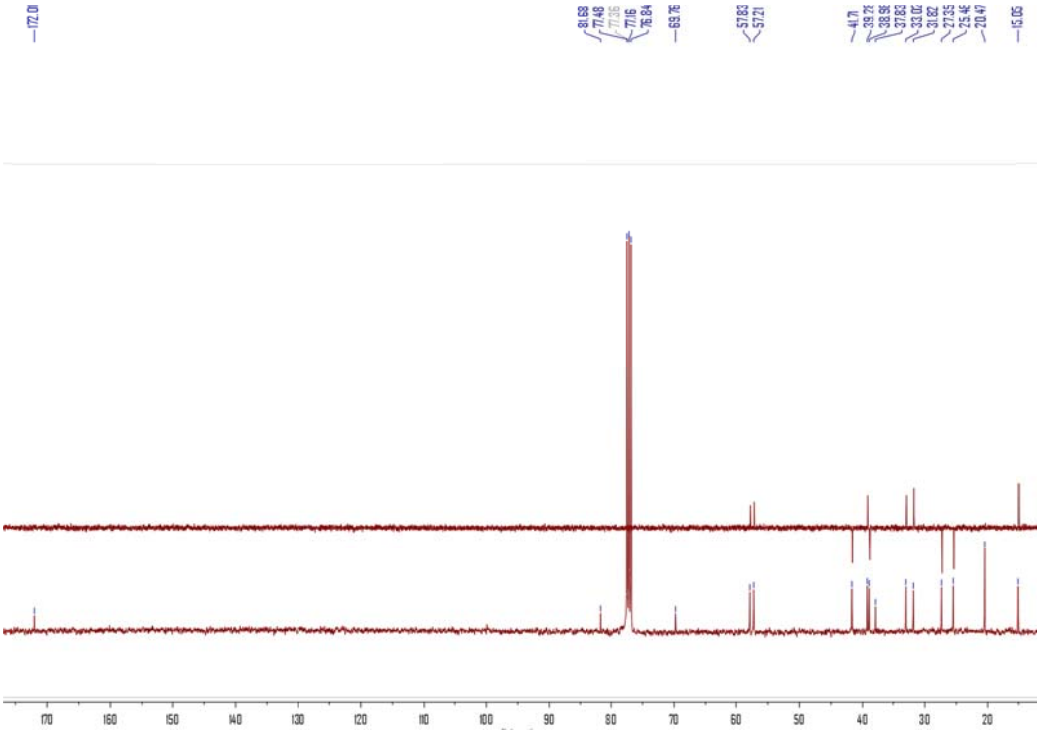


Figure S104. ^{13}C and NMR DEPT spectra of **9** in $CDCl_3$ at 100 MHz

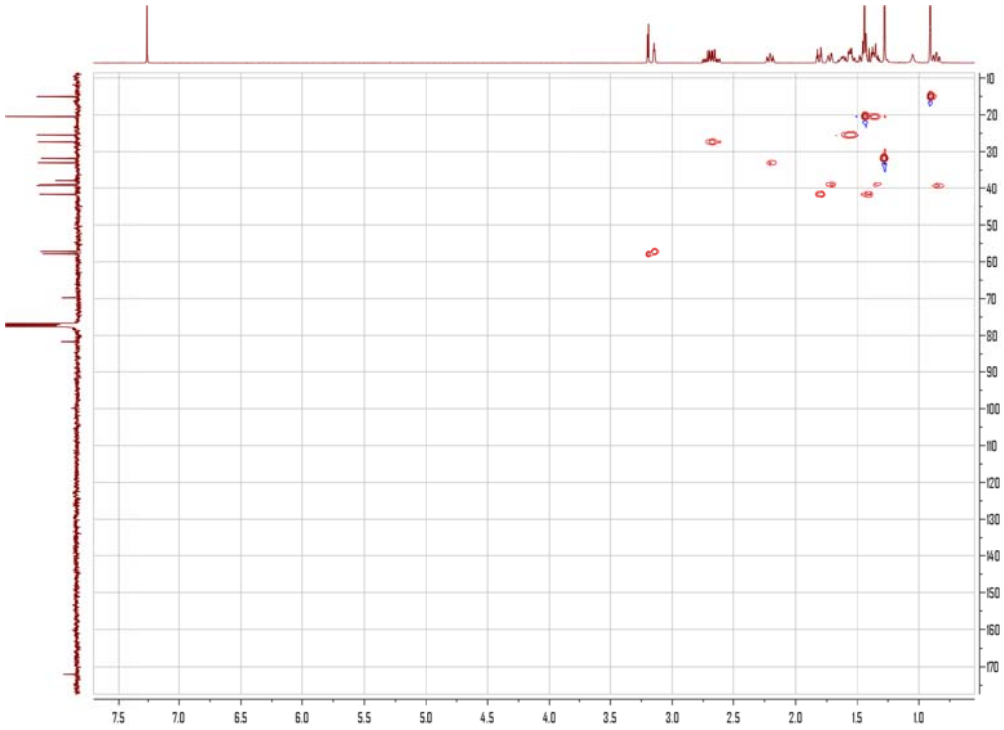


Figure S105. HSQC spectrum of **9** in $CDCl_3$

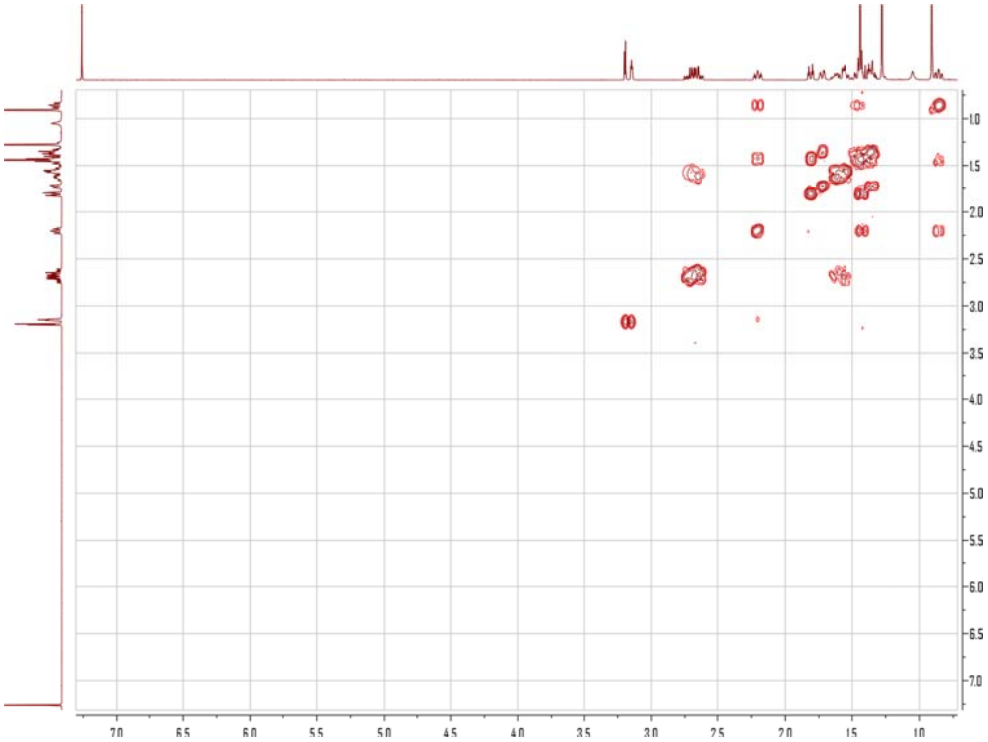


Figure S106. ^{1}H-^{1}H COSY spectrum of **9** in $CDCl_3$

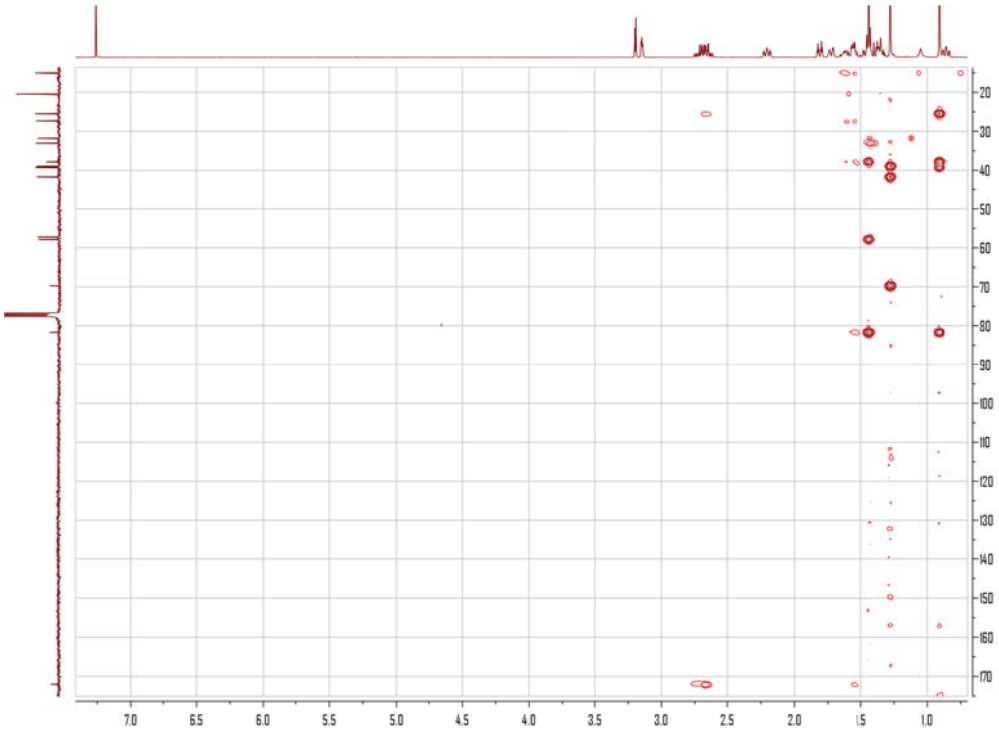


Figure S107. HMBC spectrum of **9** in $CDCl_3$

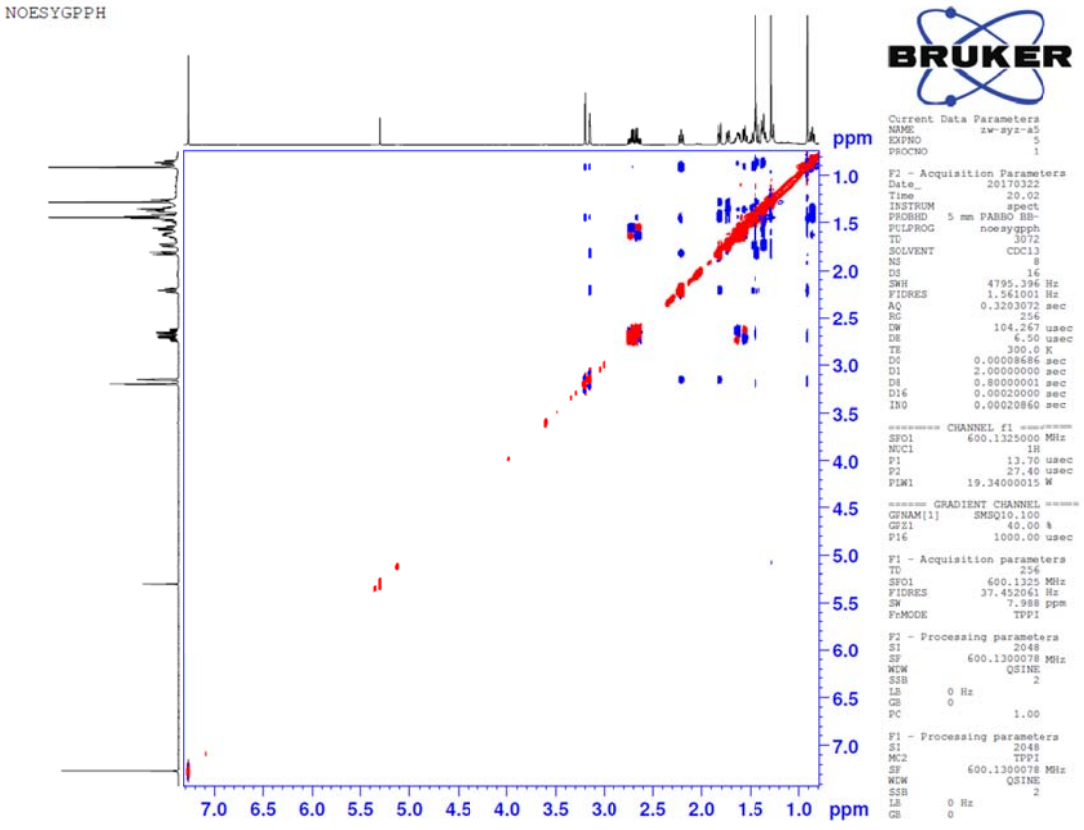


Figure S108. NOESY spectrum of **9** in $CDCl_3$

D:\data\2017-HR\EI-17178-GTW_A12-c1 3/24/2017 3:19:19 PM

EI-17178-GTW_A12-c1#10 RT: 4.13
T: + c EI Full ms [49.50-800.50]
m/z= 116.5837-310.8237

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Compositic
154.0625	134144.0	5.87	154.0624	0.03	4.0	$C_8H_{10}O_3$
155.0721	220747.0	9.66	155.0703	1.79	3.5	$C_8H_{11}O_3$
157.1021	730440.0	31.97	157.1012	0.94	6.5	$C_{12}H_{13}$
159.0793	332246.0	14.54	159.0804	-1.11	6.5	$C_{11}H_{11}O_1$
159.1166	631758.0	27.65	159.1168	-0.24	5.5	$C_{12}H_{15}$
160.0863	149692.0	6.55	160.0883	-1.95	6.0	$C_{11}H_{12}O_1$
161.0957	644832.0	28.22	161.0961	-0.43	5.5	$C_{11}H_{13}O_1$
161.1319	189106.0	8.28	161.1325	-0.63	4.5	$C_{12}H_{17}$
163.0761	282680.0	12.37	163.0754	0.72	5.5	$C_{10}H_{11}O_2$
163.1119	751384.0	32.88	163.1117	0.15	4.5	$C_{11}H_{15}O_1$
164.0833	123576.0	5.41	164.0832	0.16	5.0	$C_{10}H_{12}O_2$
164.1197	403301.0	17.65	164.1196	0.15	4.0	$C_{11}H_{16}O_1$
165.0917	391159.0	17.12	165.0910	0.72	4.5	$C_{10}H_{13}O_2$
165.1284	821283.0	35.94	165.1274	0.99	3.5	$C_{11}H_{17}O_1$
167.0709	266683.0	11.67	167.0703	0.59	4.5	$C_9H_{11}O_3$
168.0789	729187.0	31.91	168.0781	0.85	4.0	$C_9H_{12}O_3$
169.0854	163505.0	7.16	169.0859	-0.52	3.5	$C_9H_{13}O_3$
169.1010	128009.0	5.60	169.1012	-0.13	7.5	$C_{13}H_{13}$
171.1178	416761.0	18.24	171.1168	0.96	6.5	$C_{13}H_{15}$
173.0952	311815.0	13.65	173.0961	-0.93	6.5	$C_{12}H_{13}O_1$
174.1029	227108.0	9.94	174.1039	-1.03	6.0	$C_{12}H_{14}O_1$
175.1111	836541.0	36.61	175.1117	-0.67	5.5	$C_{12}H_{15}O_1$
177.0901	451293.0	19.75	177.0910	-0.90	5.5	$C_{11}H_{13}O_2$
177.1265	250686.0	10.97	177.1274	-0.89	4.5	$C_{12}H_{17}O_1$
178.0976	137517.0	6.02	178.0988	-1.23	5.0	$C_{11}H_{14}O_2$
179.1055	843640.0	36.92	179.1067	-1.15	4.5	$C_{11}H_{15}O_2$
181.0848	259134.0	11.34	181.0859	-1.14	4.5	$C_{10}H_{13}O_3$
181.1214	194246.0	8.50	181.1223	-0.95	3.5	$C_{11}H_{17}O_2$
185.0950	224409.0	9.82	185.0961	-1.08	7.5	$C_{13}H_{13}O_1$
186.1036	133181.0	5.83	186.1039	-0.27	7.0	$C_{13}H_{14}O_1$
187.1129	862786.0	37.76	187.1117	1.19	6.5	$C_{13}H_{15}O_1$
188.1176	193057.0	8.45	188.1196	-1.96	6.0	$C_{13}H_{16}O_1$
189.0917	117344.0	5.14	189.0910	0.65	6.5	$C_{12}H_{13}O_2$
189.1293	354860.0	15.53	189.1274	1.95	5.5	$C_{13}H_{17}O_1$
191.1082	273300.0	11.96	191.1067	1.59	5.5	$C_{12}H_{15}O_2$
193.0876	162477.0	7.11	193.0859	1.71	5.5	$C_{11}H_{13}O_3$
194.1311	219527.0	9.61	194.1301	0.99	4.0	$C_{12}H_{18}O_2$
195.1031	136778.0	5.99	195.1016	1.53	4.5	$C_{11}H_{15}O_3$
200.1195	137453.0	6.02	200.1196	-0.09	7.0	$C_{14}H_{16}O_1$
203.1067	315670.0	13.82	203.1067	0.06	6.5	$C_{13}H_{15}O_2$
205.1212	543742.0	23.80	205.1223	-1.09	5.5	$C_{13}H_{17}O_2$
207.1365	168837.0	7.39	207.1380	-1.47	4.5	$C_{13}H_{19}O_2$
217.1215	662082.0	28.98	217.1223	-0.83	6.5	$C_{14}H_{17}O_2$
221.1168	188111.0	8.23	221.1172	-0.43	5.5	$C_{13}H_{17}O_3$
221.1523	270666.0	11.85	221.1536	-1.26	4.5	$C_{14}H_{21}O_2$
235.1345	327716.0	14.34	235.1329	1.59	5.5	$C_{14}H_{19}O_3$
245.1173	380365.0	16.65	245.1172	0.08	7.5	$C_{15}H_{17}O_3$
249.1483	342300.0	14.98	249.1485	-0.19	5.5	$C_{15}H_{21}O_3$
261.1486	184738.0	8.09	261.1485	0.12	6.5	$C_{16}H_{21}O_3$
264.1347	218081.0	9.54	264.1356	-0.88	6.0	$C_{15}H_{20}O_4$
278.1532	2284894.0	100.00	278.1513	1.97	6.0	$C_{16}H_{22}O_4$
296.1623	124379.0	5.44	296.1618	0.45	5.0	$C_{16}H_{24}O_5$

Figure S109. HREIMS spectrum of **10**

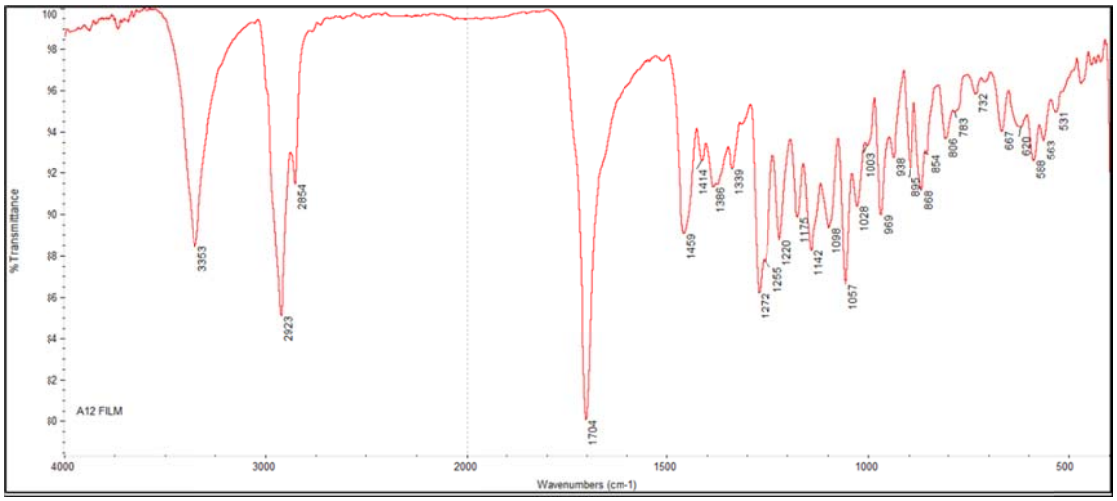


Figure S110. FTIR spectrum of **10**

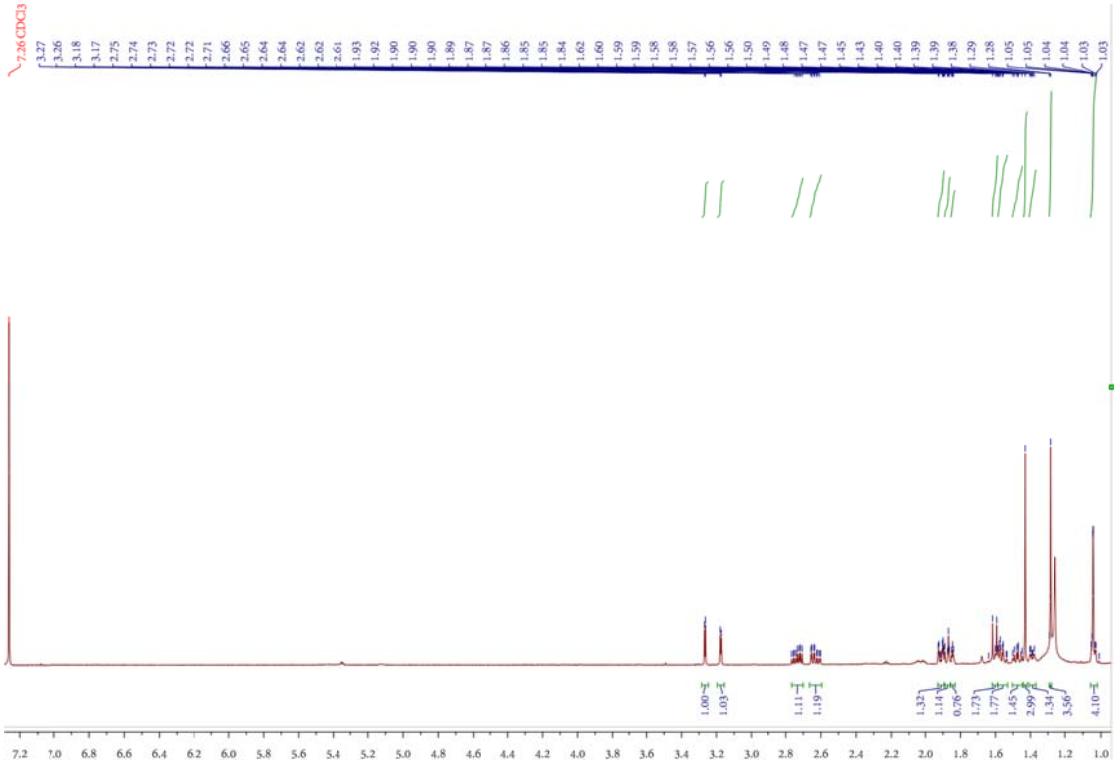


Figure S111. ^{1}H NMR spectrum of **10** in $CDCl_3$ at 600 MHz

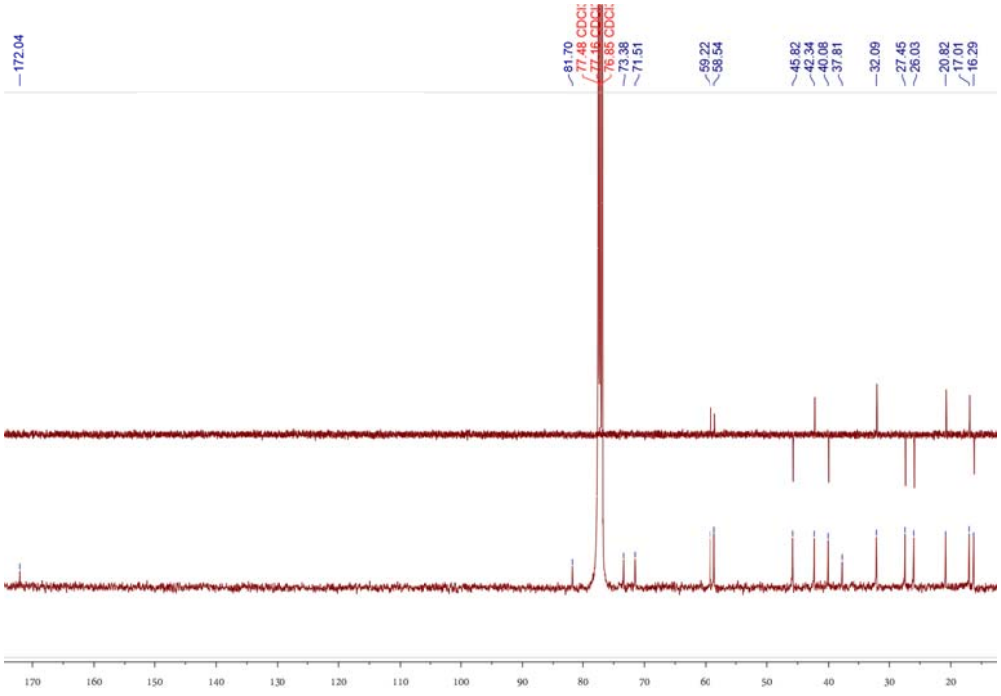


Figure S112. ^{13}C and NMR DEPT spectra of **10** in $CDCl_3$ at 100 MHz

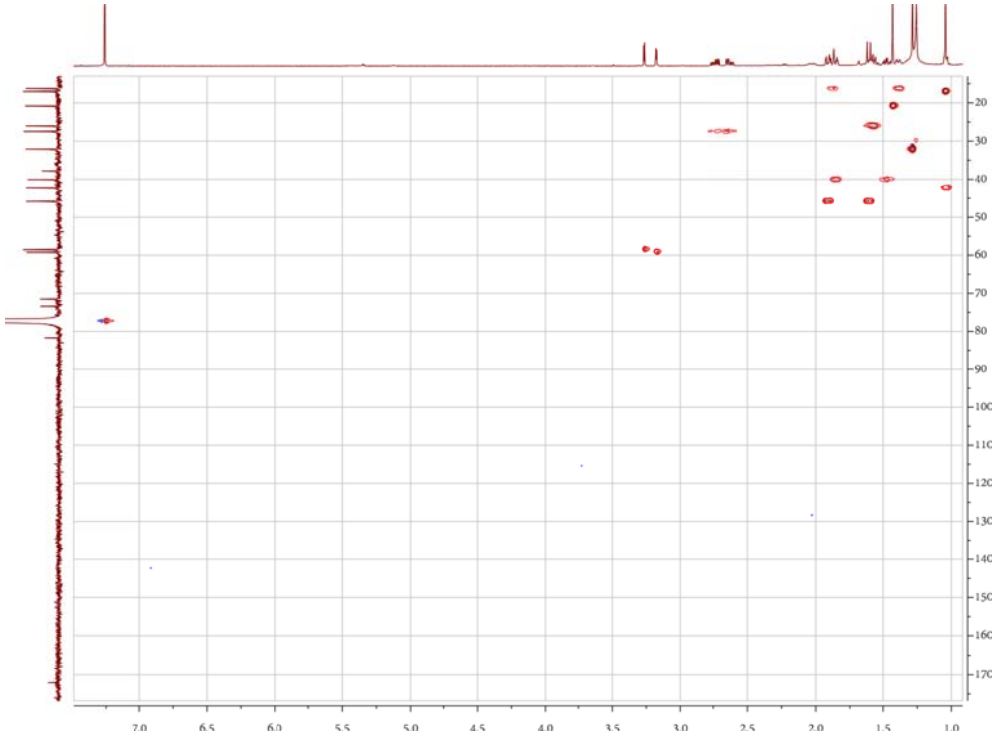


Figure S113. HSQC spectrum of **10** in $CDCl_3$

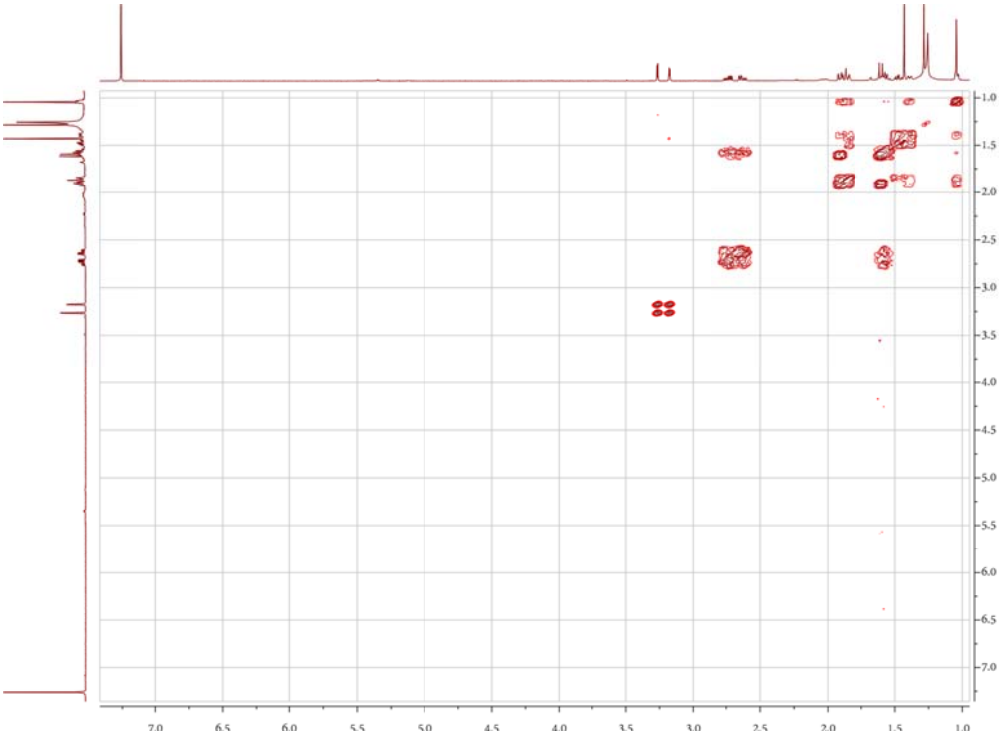


Figure S114. ^{1}H-^{1}H COSY spectrum of **10** in $CDCl_3$

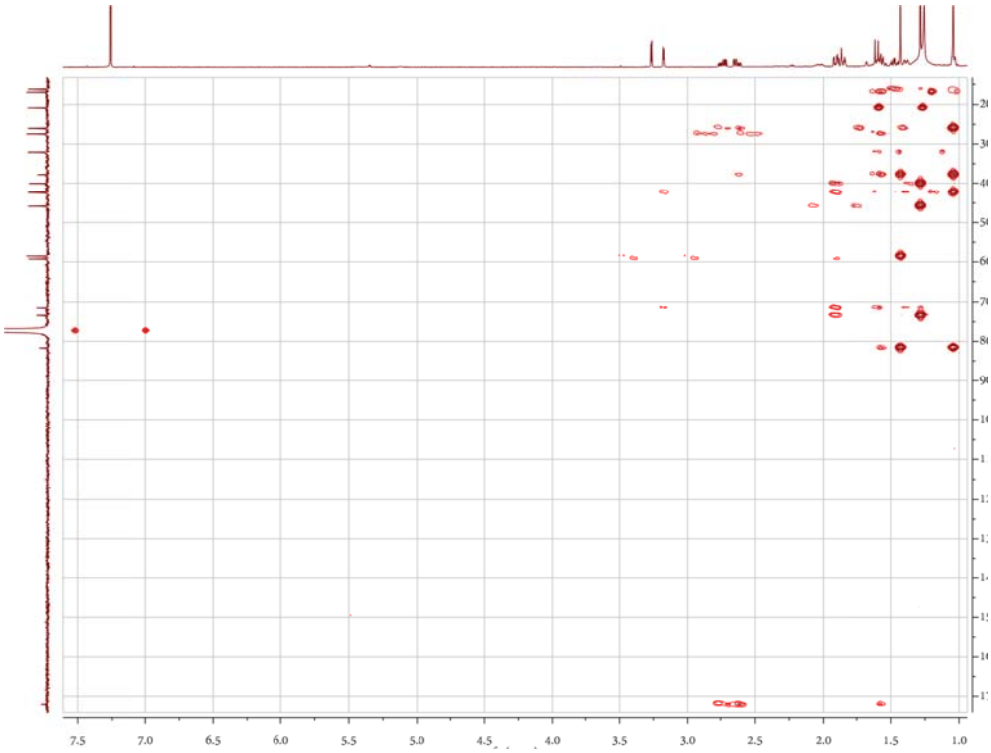


Figure S115. HMBC spectrum of **10** in $CDCl_3$

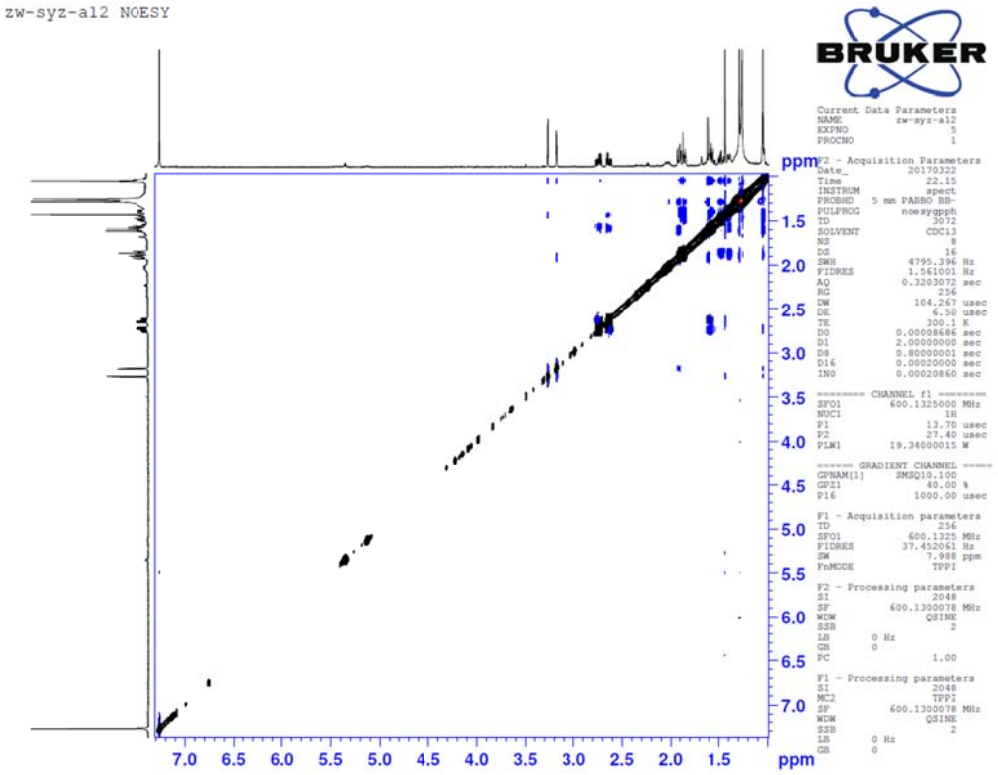


Figure S116. NOESY spectrum of **10** in $CDCl_3$

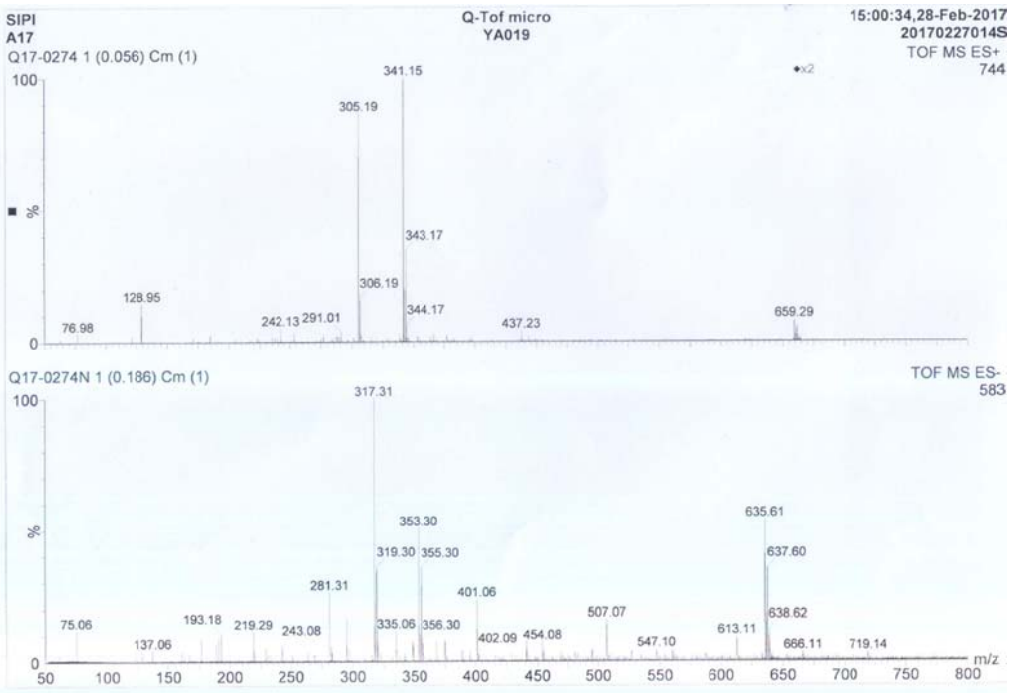


Figure S117. ESIMS spectrum of **11**

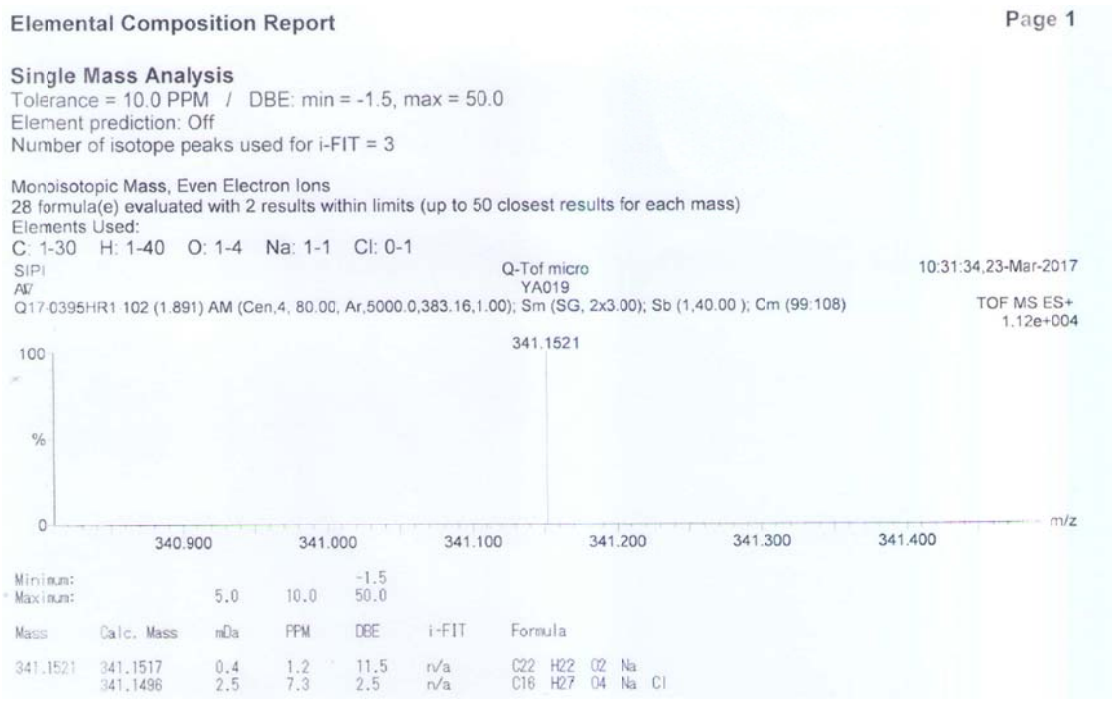


Figure S118. HRESIMS spectrum of **11**

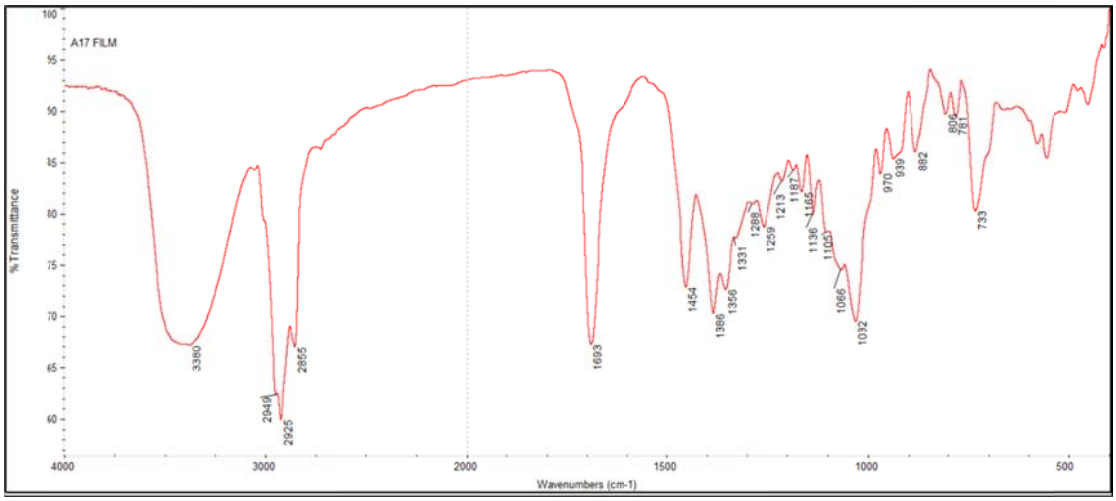


Figure S119. FTIR spectrum of **11**

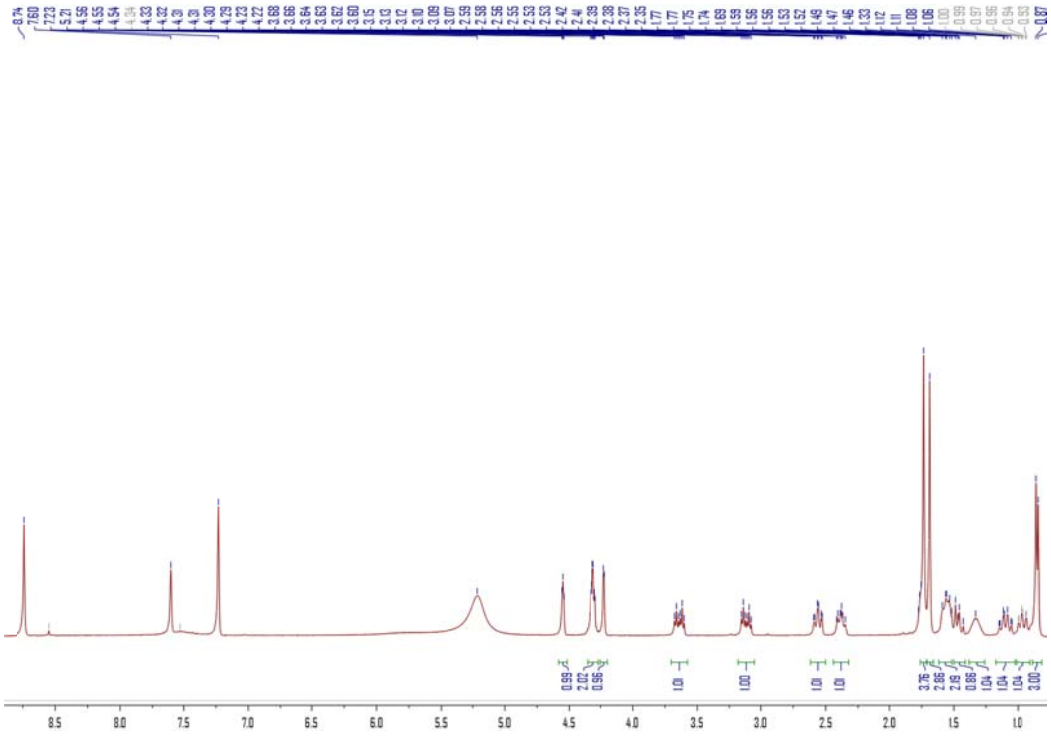


Figure S120. [1]H NMR spectrum of **11** in *Pyridine-d_5* at 400 MHz

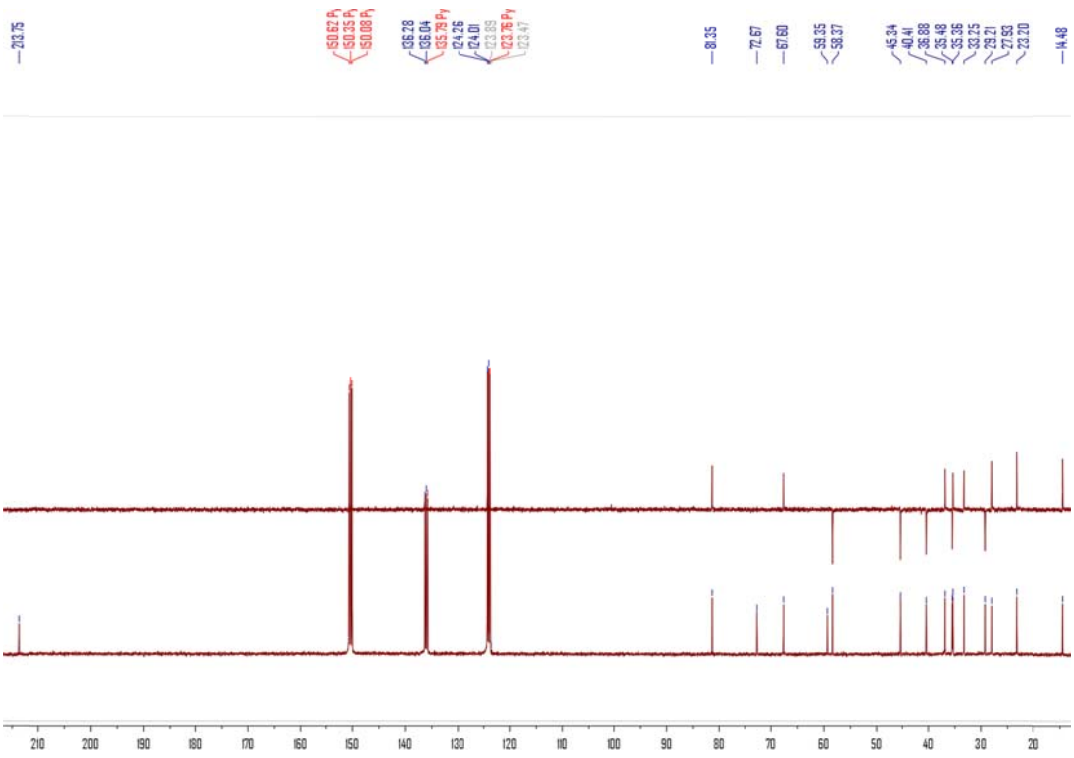


Figure S121. [13]C and NMR DEPT spectra of **11** in *Pyridine-d_5* at 100 MHz

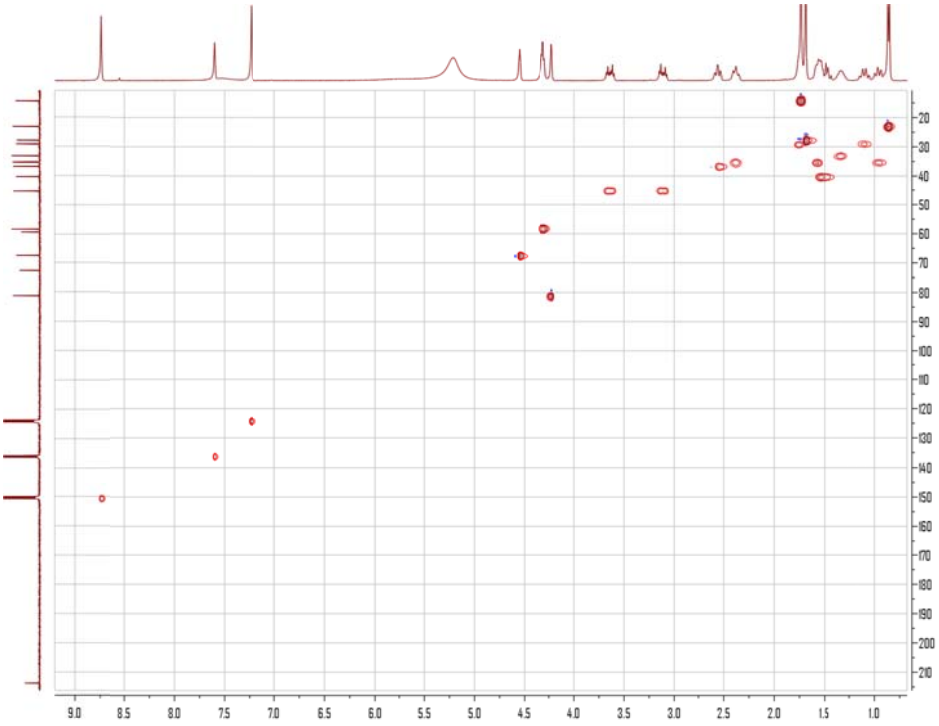


Figure S122. HSQC spectrum of **11** in *Pyridine-d_5*

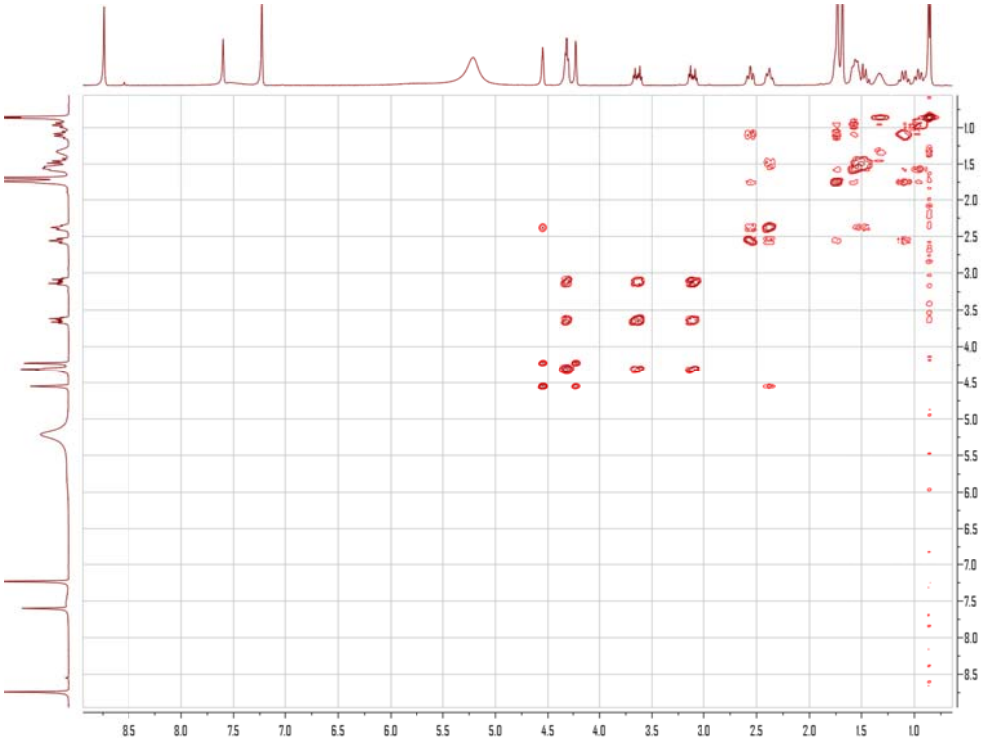


Figure S123. ^{1}H-^{1}H COSY spectrum of **11** in *Pyridine-d_5*

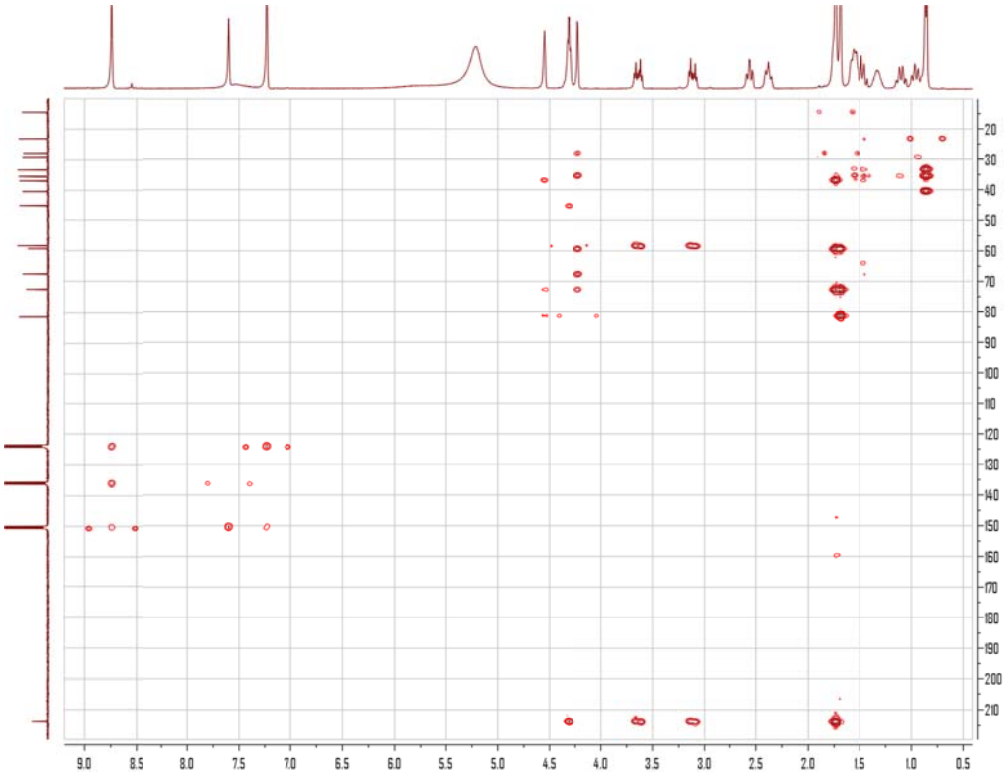


Figure S124. HMBC spectrum of **11** in *Pyridine-d_5*

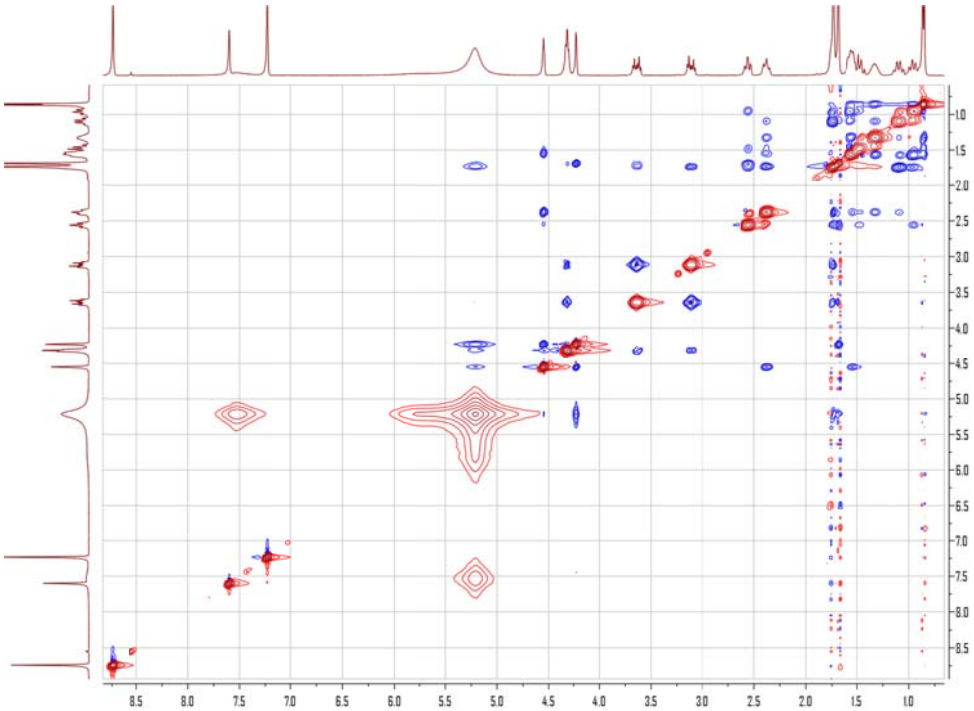


Figure S125. NOESY spectrum of **11** in *Pyridine-d_5*

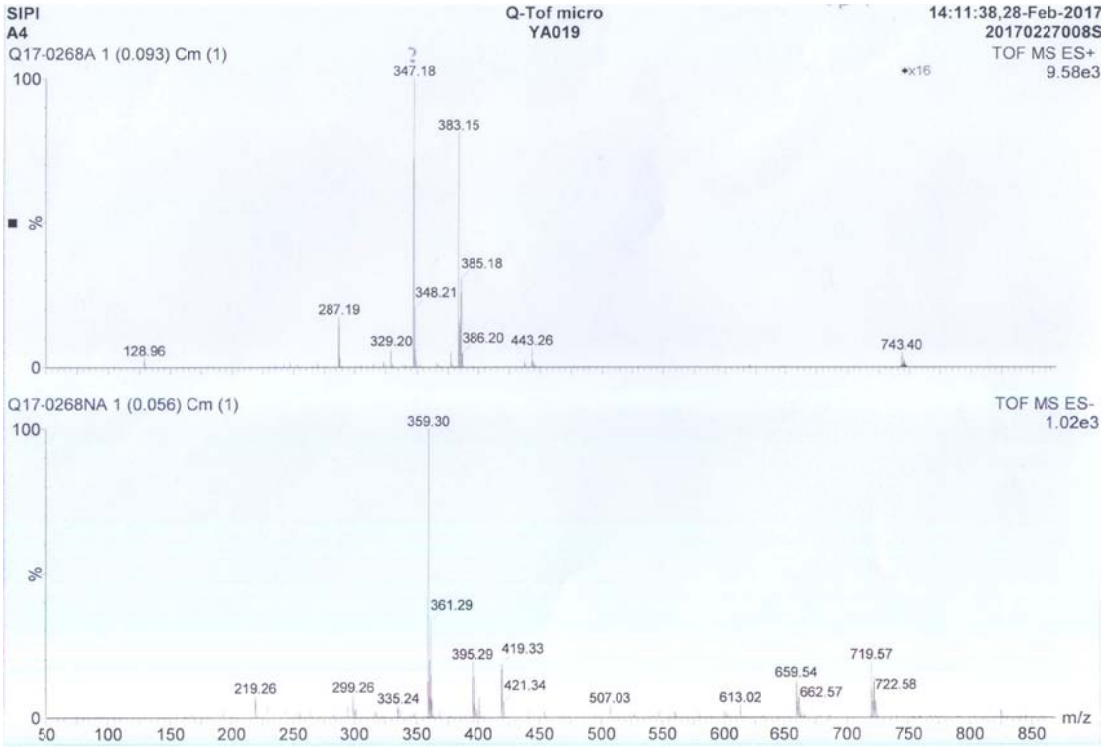


Figure S126. ESIMS spectrum of **12**

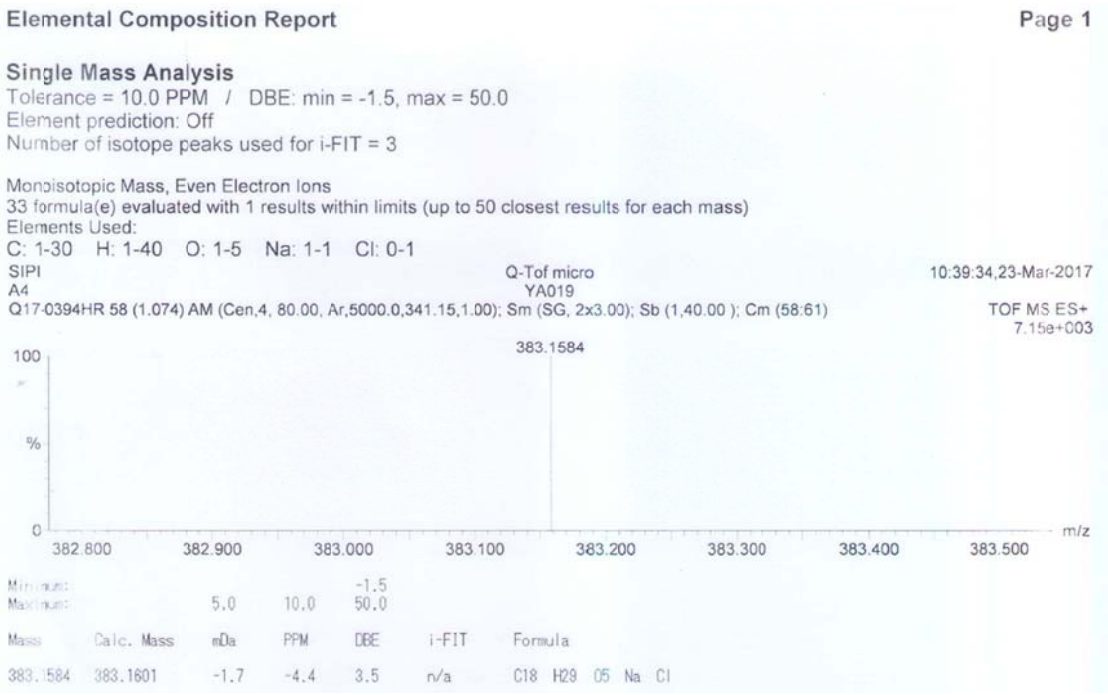


Figure S127. HRESIMS spectrum of **12**

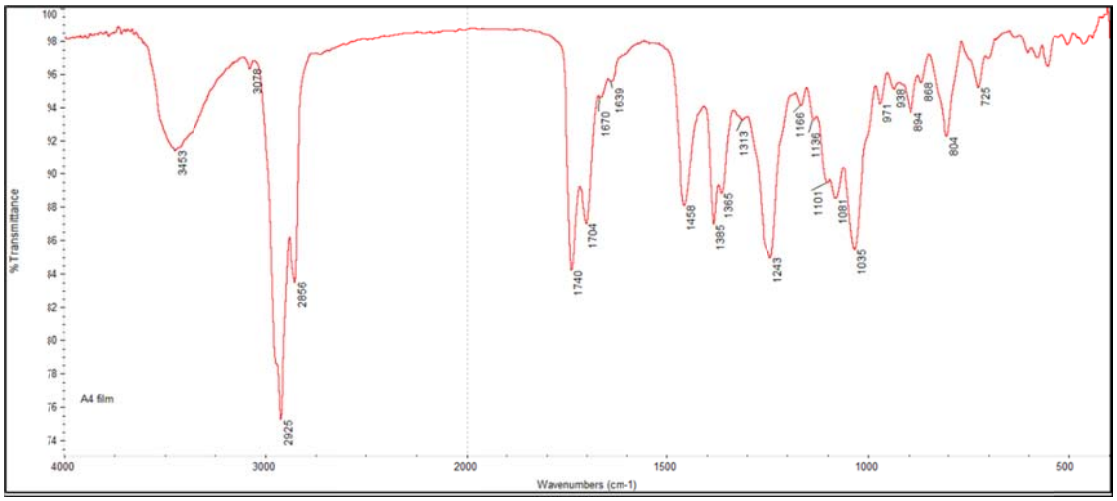


Figure S128. FTIR spectrum of **12**

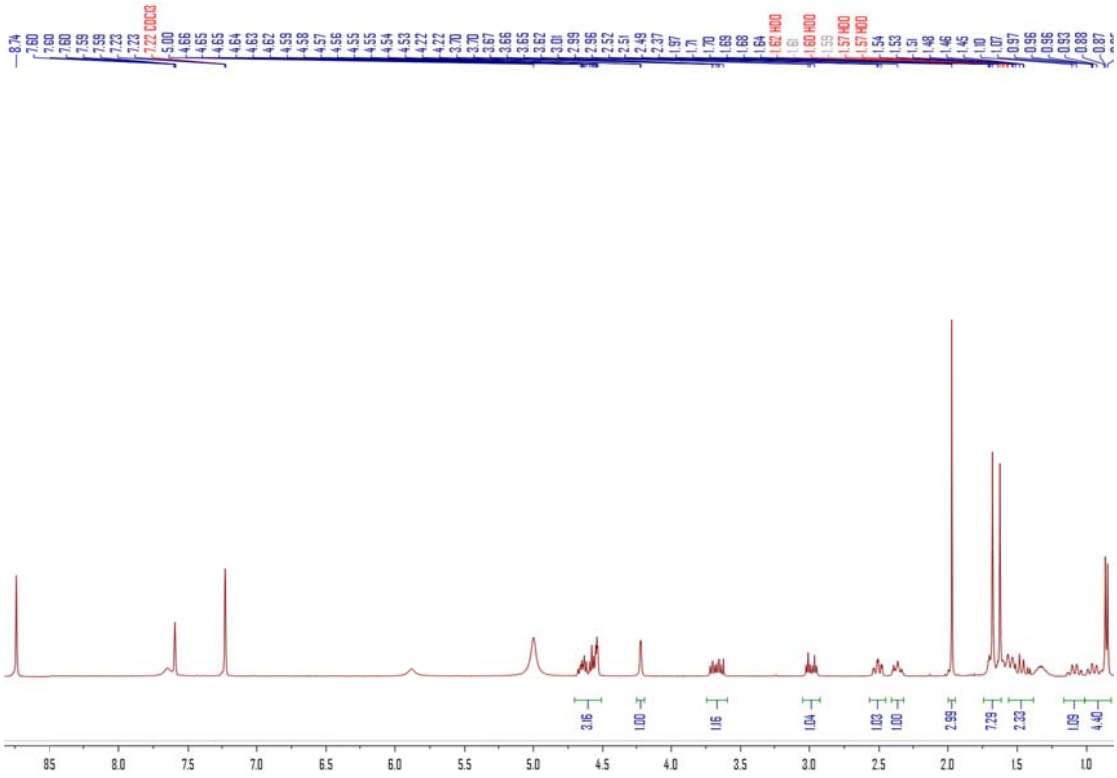


Figure S129. ^{1}H NMR spectrum of **12** in *Pyridine-d_5* at 400 MHz

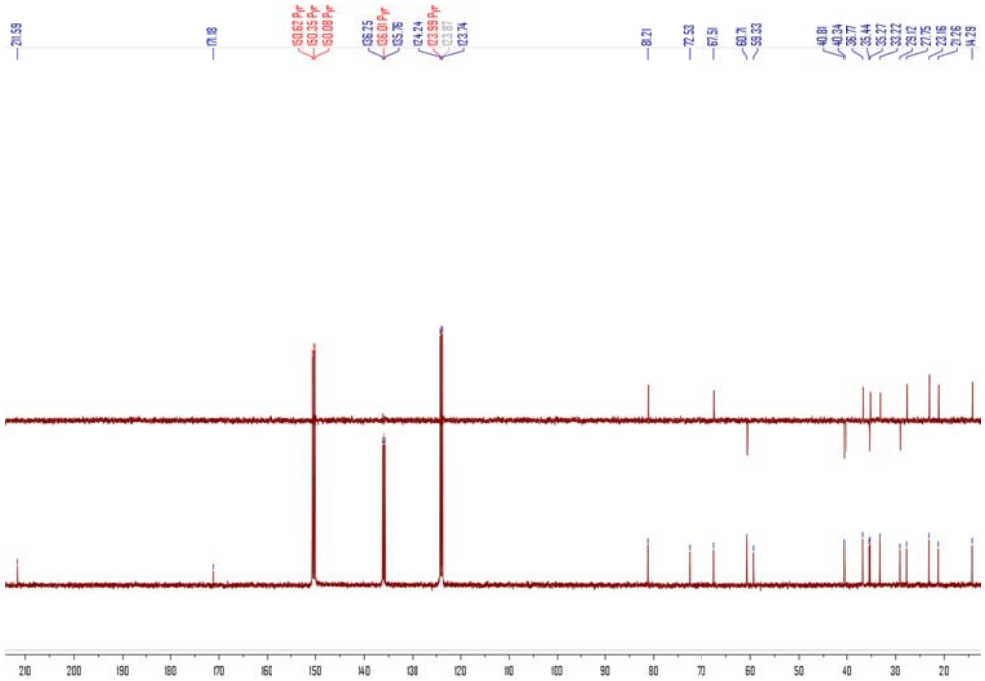


Figure S130. ^{13}C and NMR DEPT spectra of **12** in *Pyridine-d_5* at 100 MHz

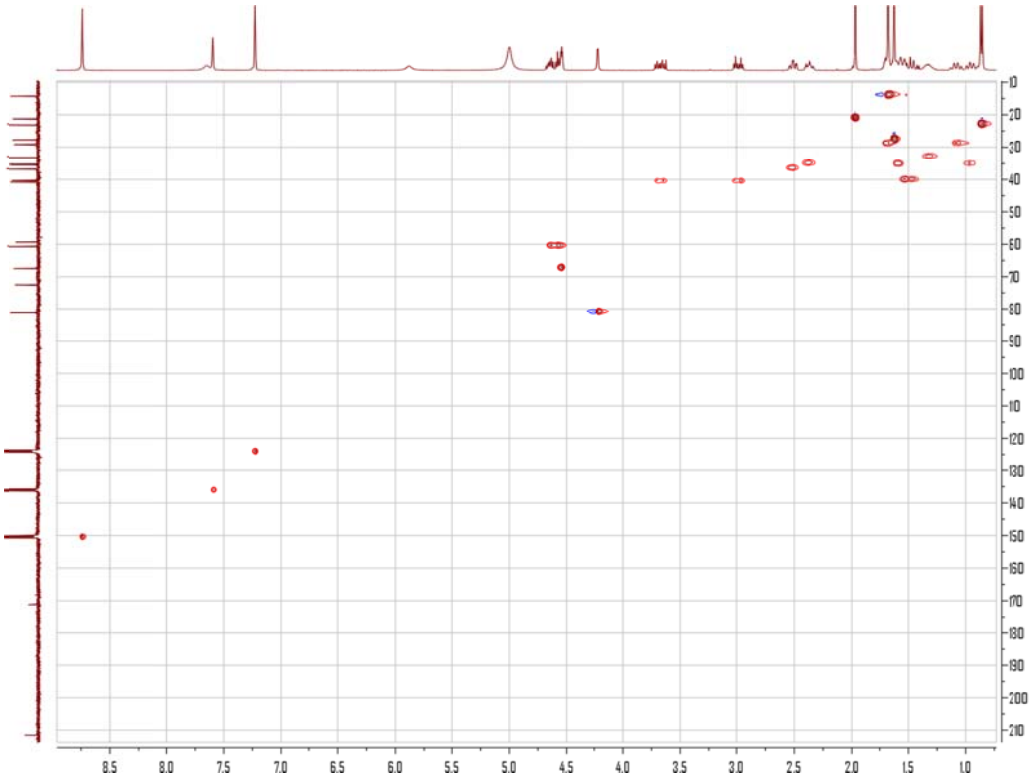


Figure S131. HSQC spectrum of **12** in *Pyridine-d_5*

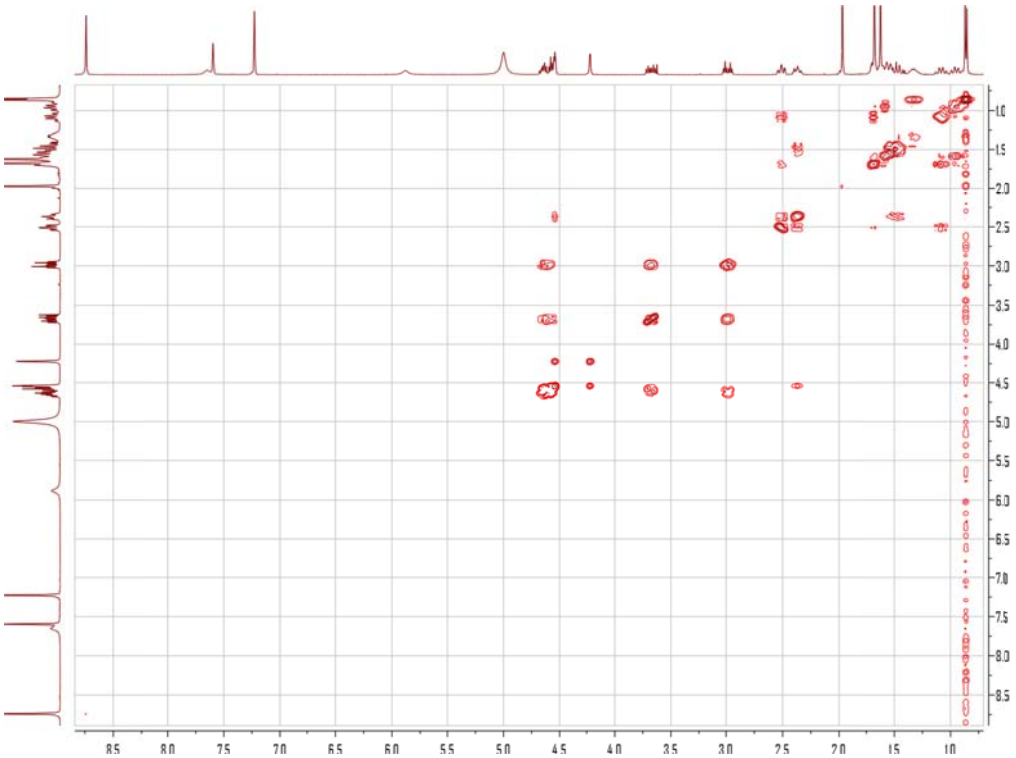


Figure S132. ^{1}H-^{1}H COSY spectrum of **12** in *Pyridine-d*$_5$

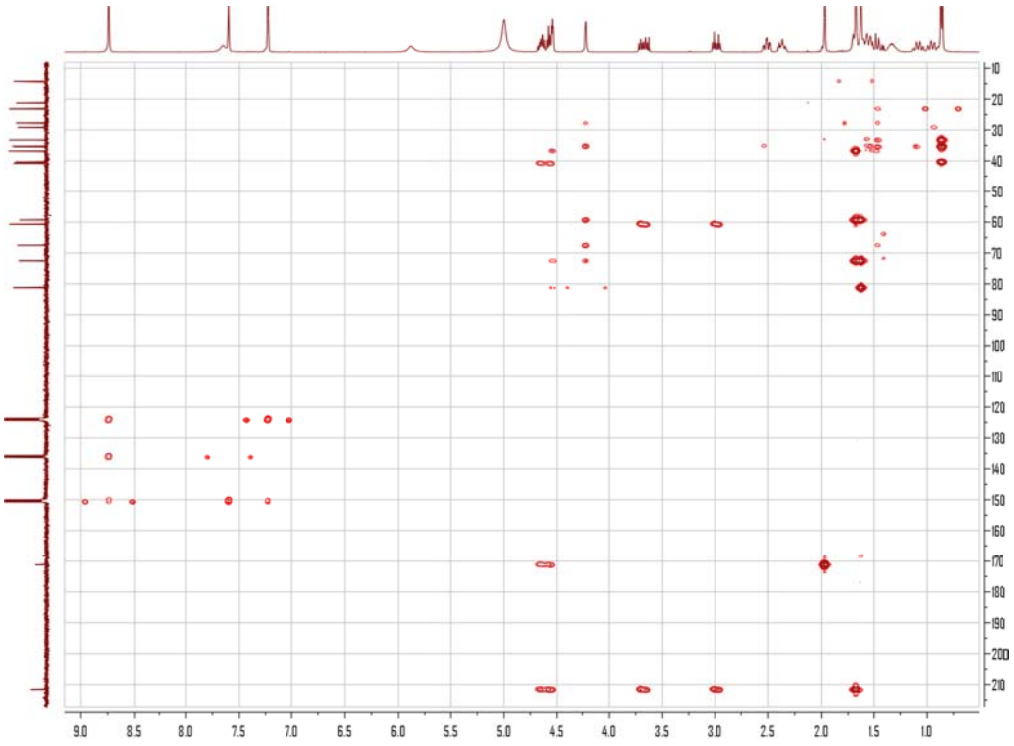


Figure S133. HMBC spectrum of **12** in *Pyridine-d*$_5$

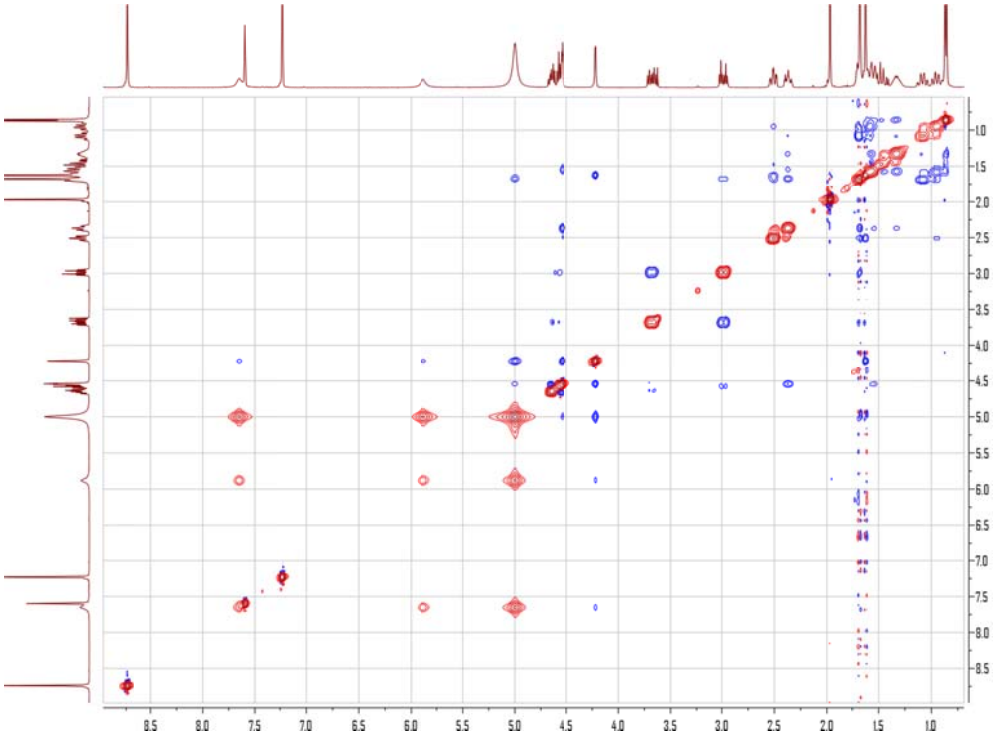


Figure S134. NOESY spectrum of **12** in *Pyridine-d_5*

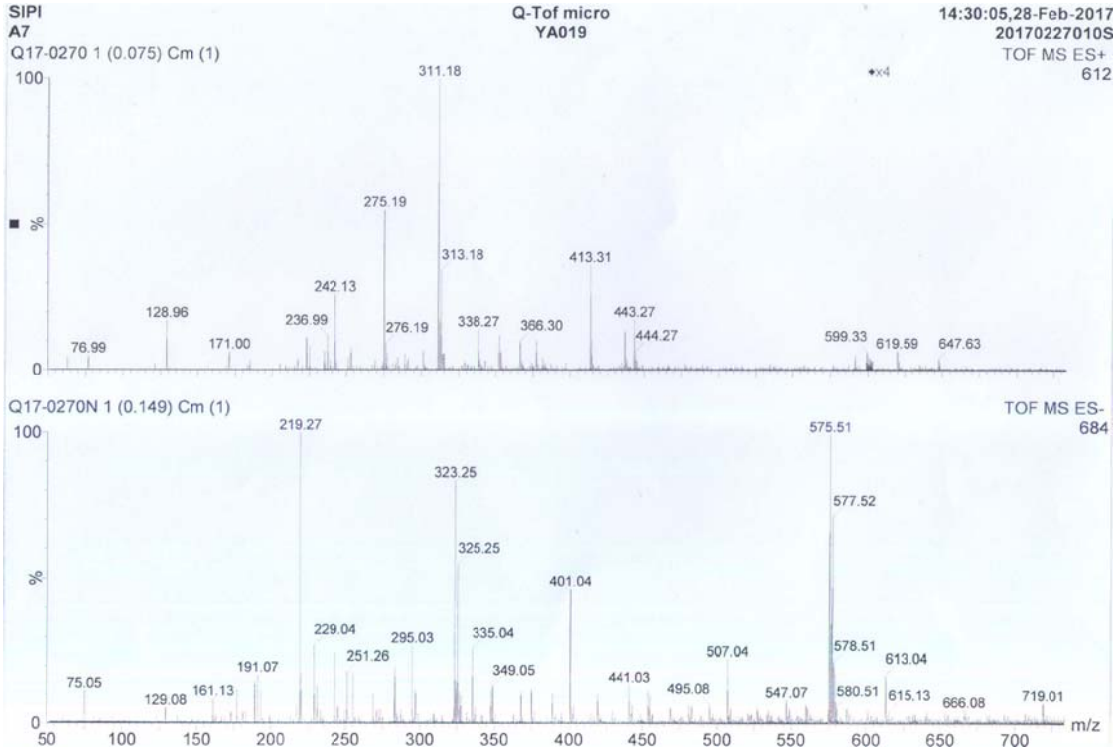


Figure S135. ESIMS spectrum of **13**

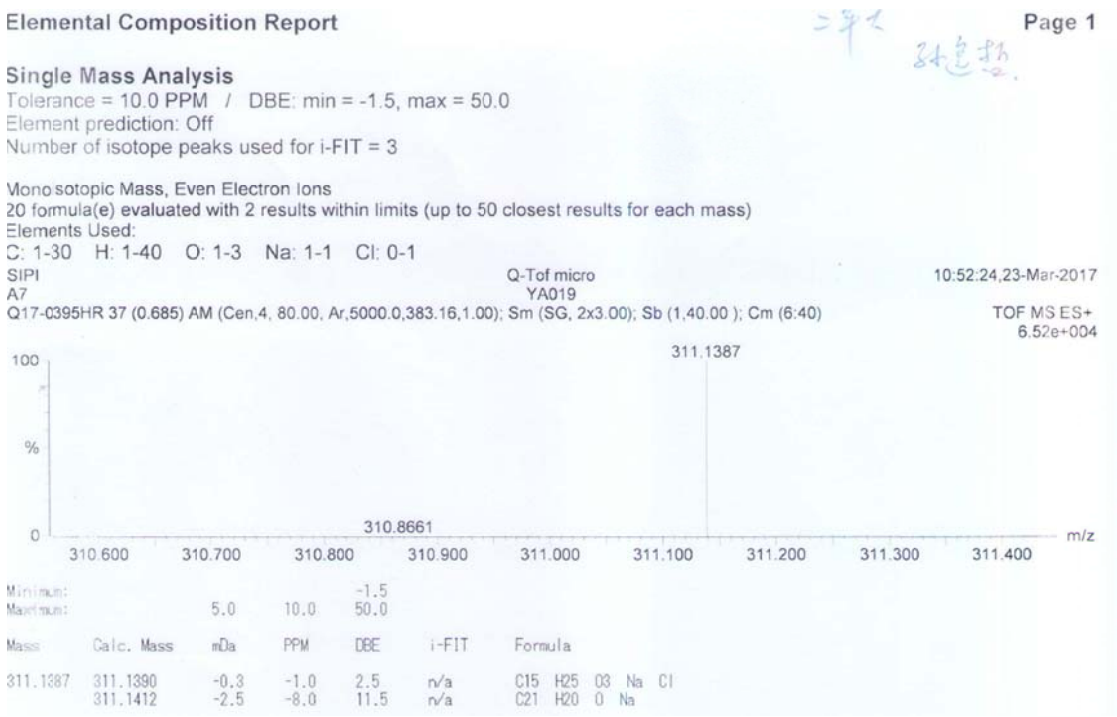


Figure S136. HRESIMS spectrum of **13**

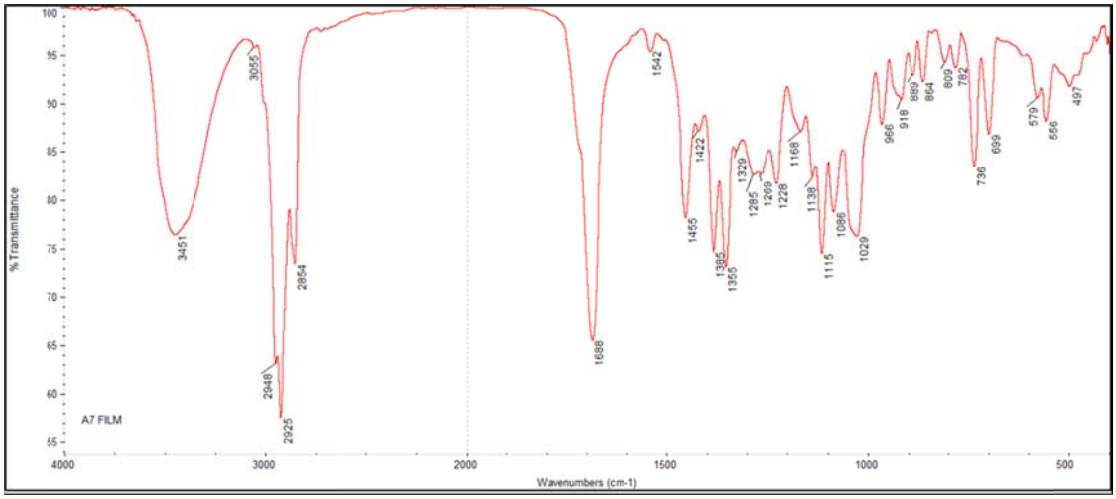


Figure S137. FTIR spectrum of **13**

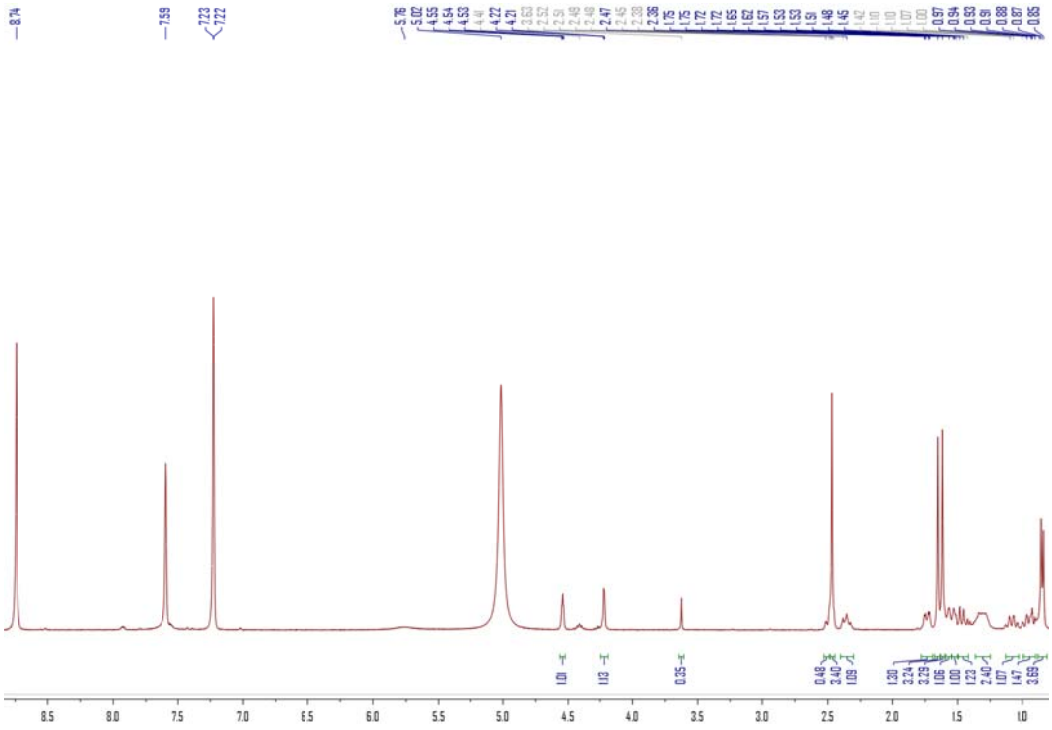


Figure S138. [1]H NMR spectrum of **13** in *Pyridine-d_5* at 400 MHz

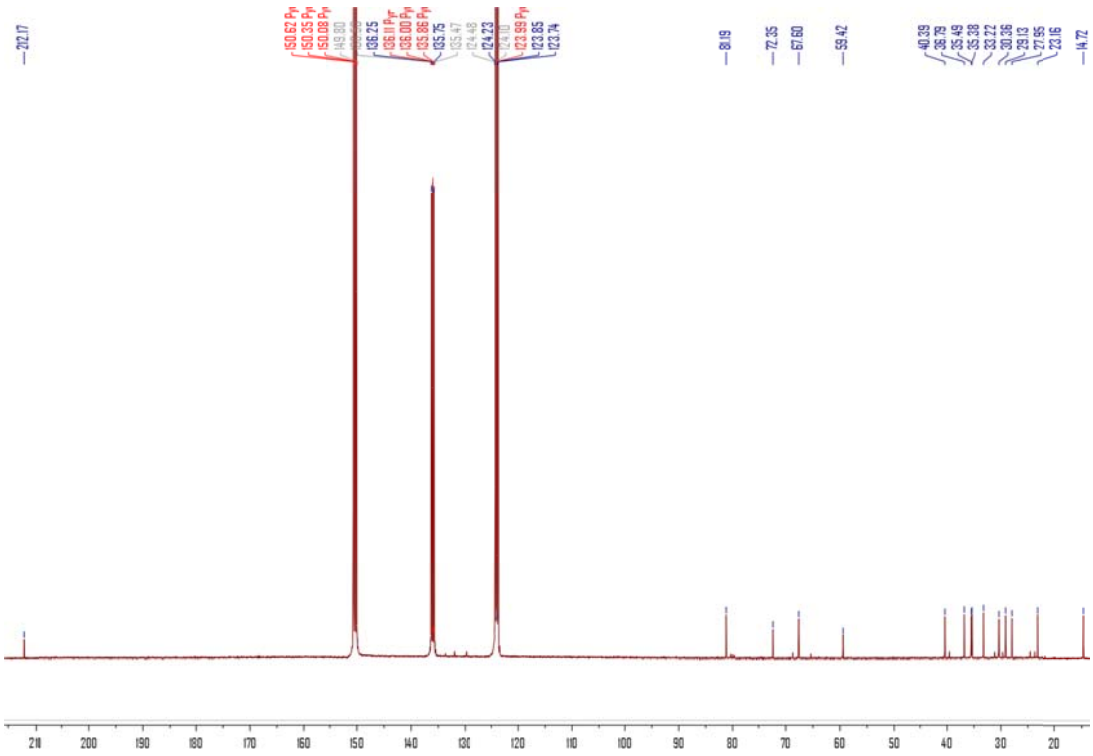


Figure S139. [13]C and NMR DEPT spectra of **13** in *Pyridine-d_5* at 100 MHz

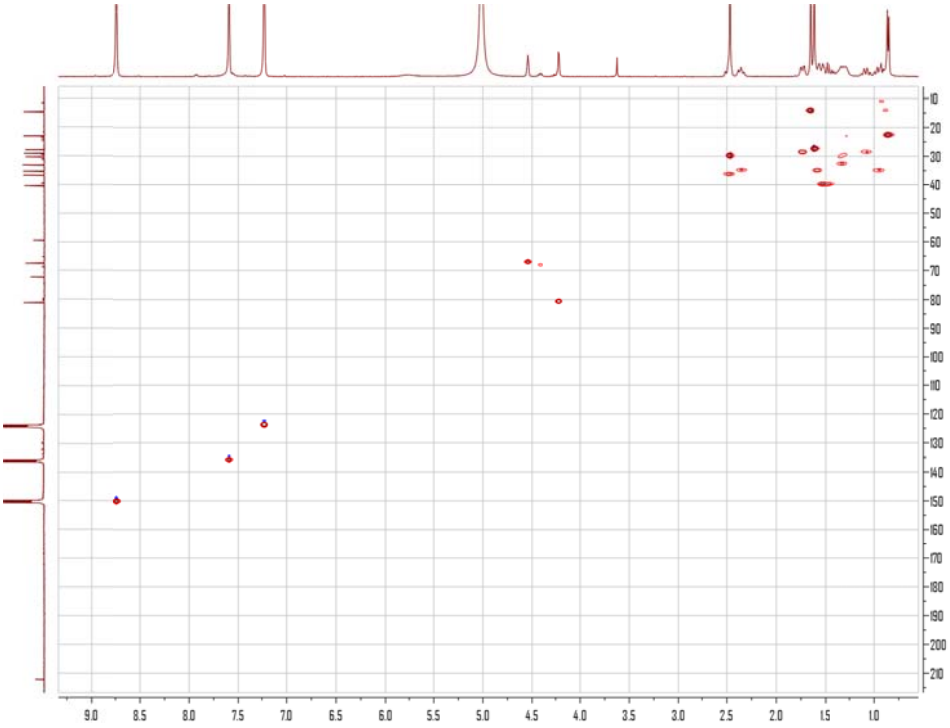


Figure S140. HSQC spectrum of **13** in *Pyridine-d_5*

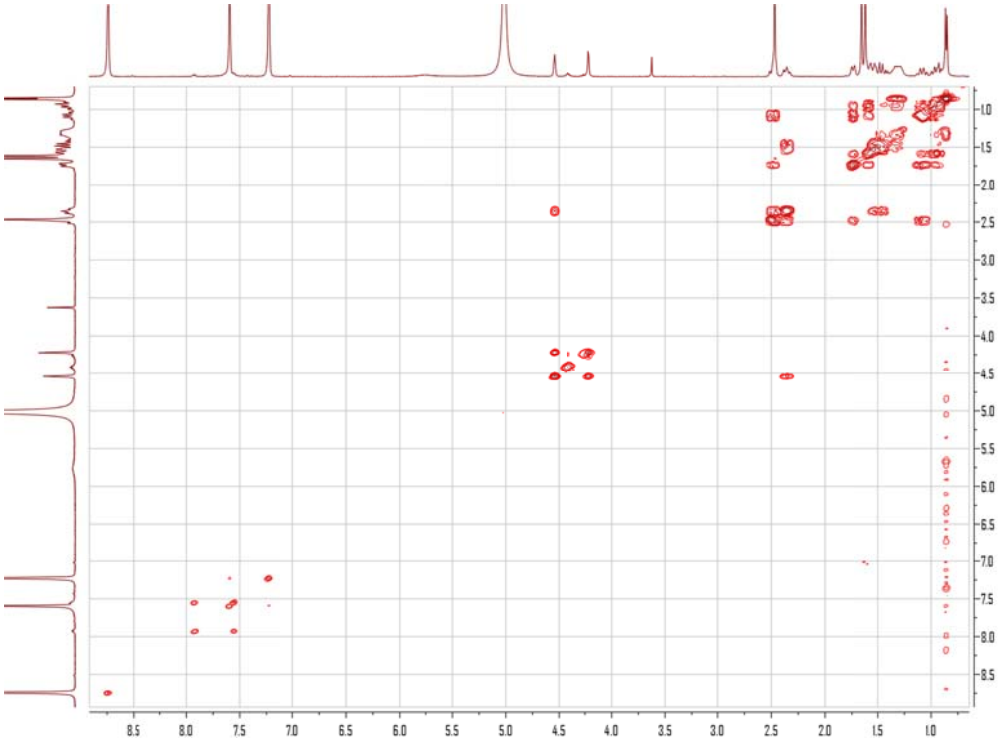


Figure S141. ^{1}H-^{1}H COSY spectrum of **13** in *Pyridine-d_5*

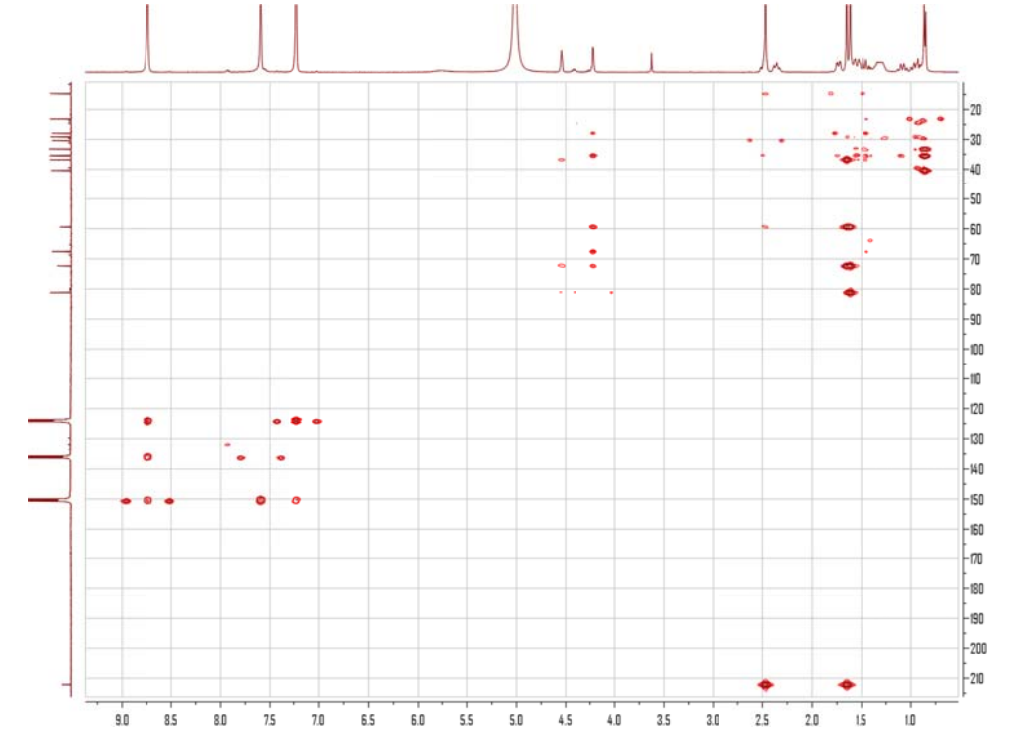


Figure S142. HMBC spectrum of **13** in *Pyridine-d_5*

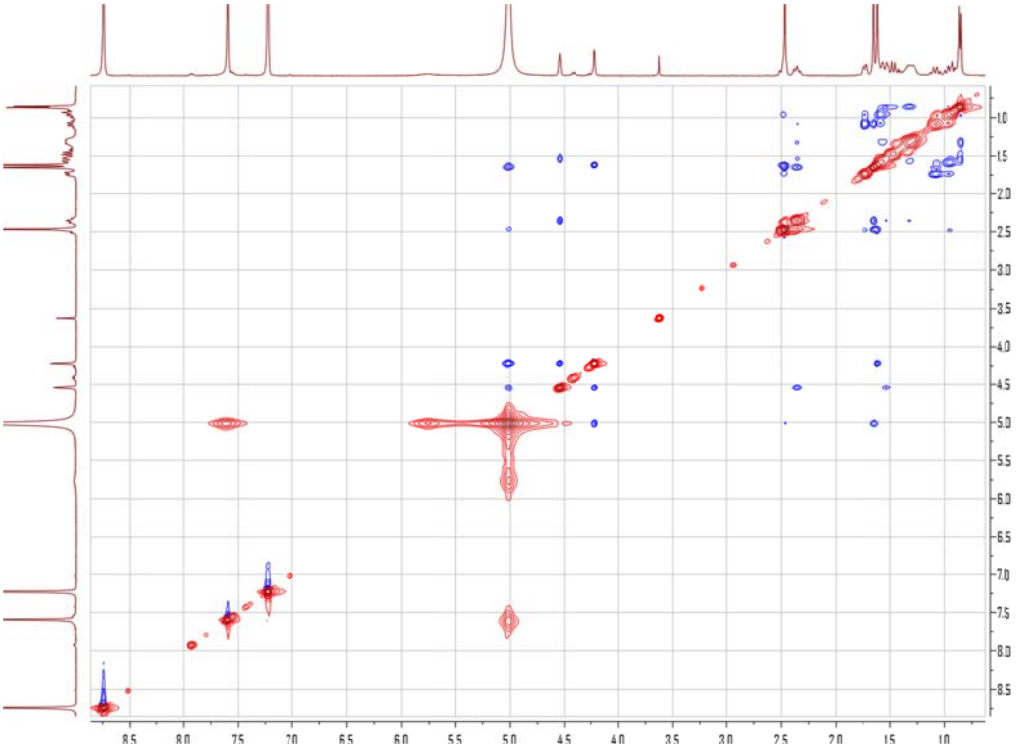


Figure S143. NOESY spectrum of **13** in *Pyridine-d_5*

D:\data\...\EI-GYW-17157_A14-c1

3/14/2017 10:32:46 AM

EI-GYW-17157_A14-c1#13 RT: 2.67
T: + c EI Full ms [49.50-1000.50]
m/z= 47.50-1002.50

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
191.1423	3337866.0	60.74	191.1430	-0.71	4.5	$C_{13}H_{19}O_1$
192.1134	8383.0	0.15	192.1145	-1.08	5.0	$C_{12}H_{16}O_2$
195.1143	5157.0	0.09	195.1168	-2.48	8.5	$C_{15}H_{15}$
199.1092	10797.0	0.20	199.1117	-2.58	7.5	$C_{14}H_{15}O_1$
201.1246	147677.0	2.69	201.1274	-2.76	6.5	$C_{14}H_{17}O_1$
208.1448	36957.0	0.67	208.1458	-0.96	4.0	$C_{13}H_{20}O_2$
215.1404	10622.0	0.19	215.1430	-2.65	6.5	$C_{15}H_{19}O_1$
216.1508	136155.0	2.48	216.1509	-0.11	6.0	$C_{15}H_{20}O_1$
218.1638	4235.0	0.08	218.1665	-2.75	5.0	$C_{15}H_{22}O_1$
219.1398	76900.0	1.40	219.1380	1.84	5.5	$C_{14}H_{19}O_2$
220.1470	8317.0	0.15	220.1458	1.18	5.0	$C_{14}H_{20}O_2$
233.1555	11126.0	0.20	233.1536	1.87	5.5	$C_{15}H_{21}O_2$
234.1599	99417.0	1.81	234.1614	-1.54	5.0	$C_{15}H_{22}O_2$
237.1486	39942.0	0.73	237.1485	0.09	4.5	$C_{14}H_{21}O_3$
252.1696	145175.0	2.64	252.1720	-2.45	4.0	$C_{15}H_{24}O_3$

Figure S144. HREIMS spectrum of **14**

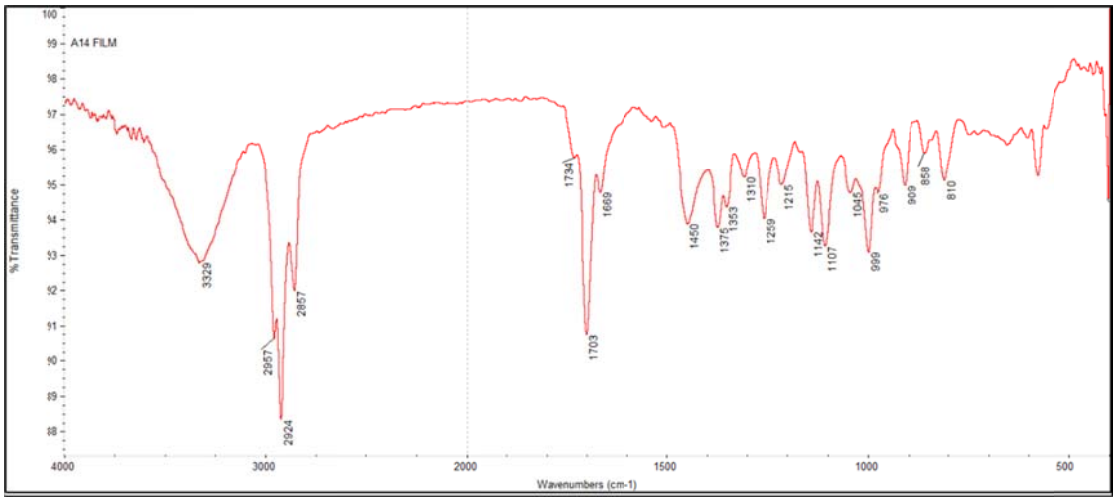


Figure S145. FTIR spectrum of **14**

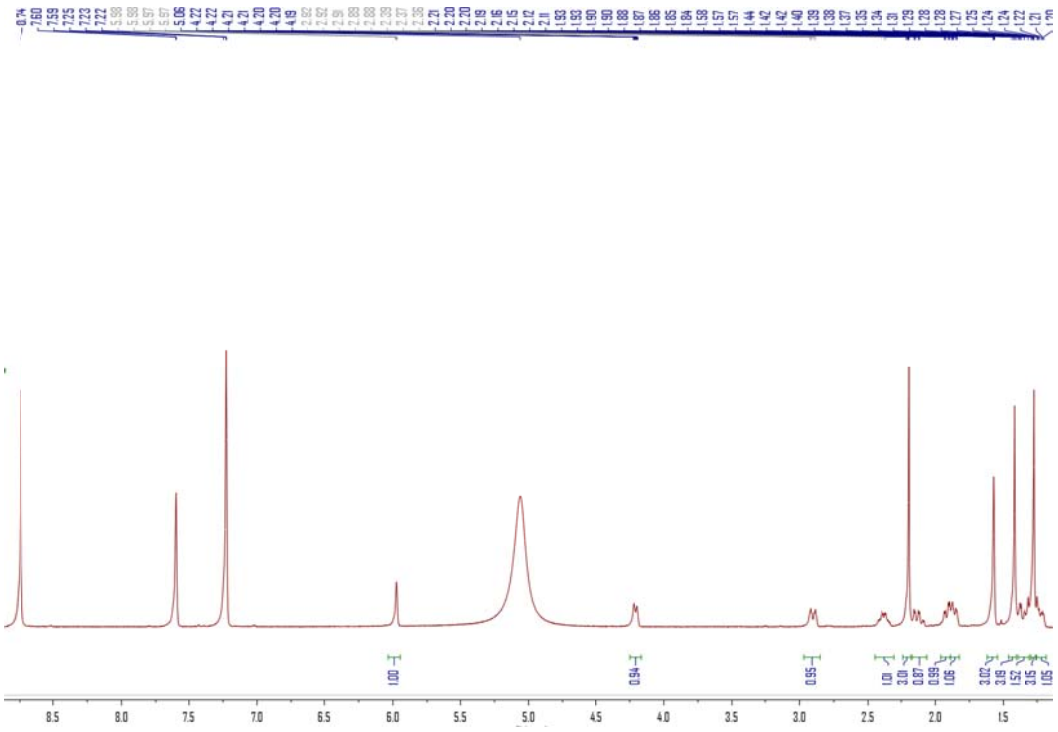


Figure S146. [1]H NMR spectrum of **14** in *Pyridine-d_5* at 400 MHz

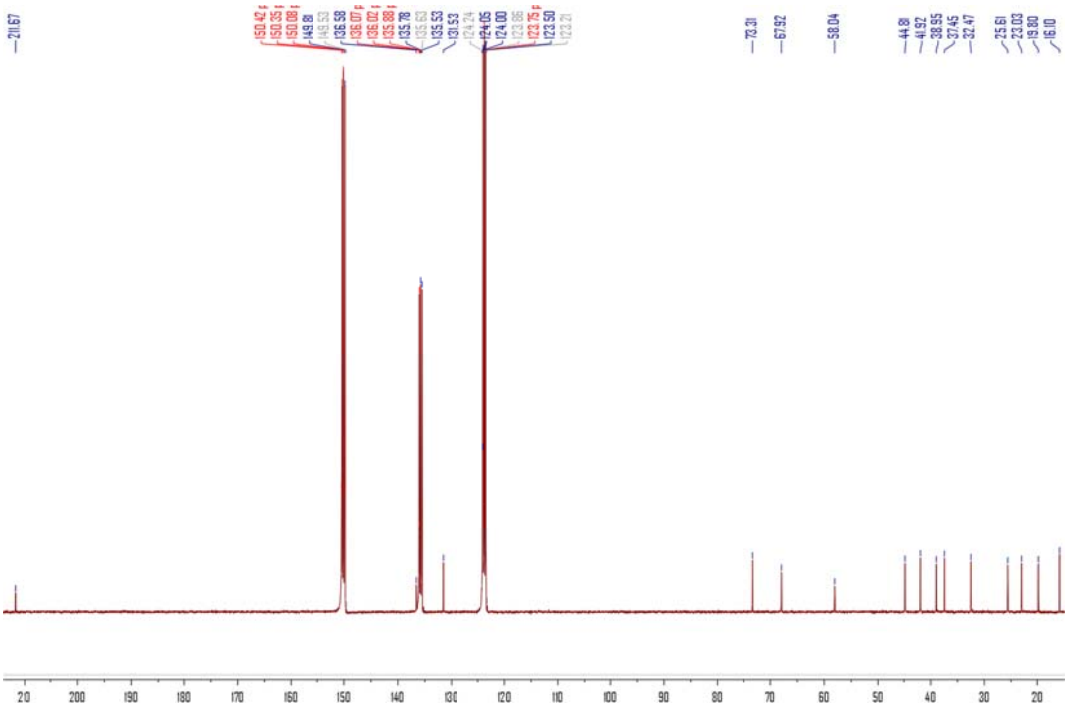


Figure S147. [13]C and NMR DEPT spectra of **14** in *Pyridine-d_5* at 100 MHz

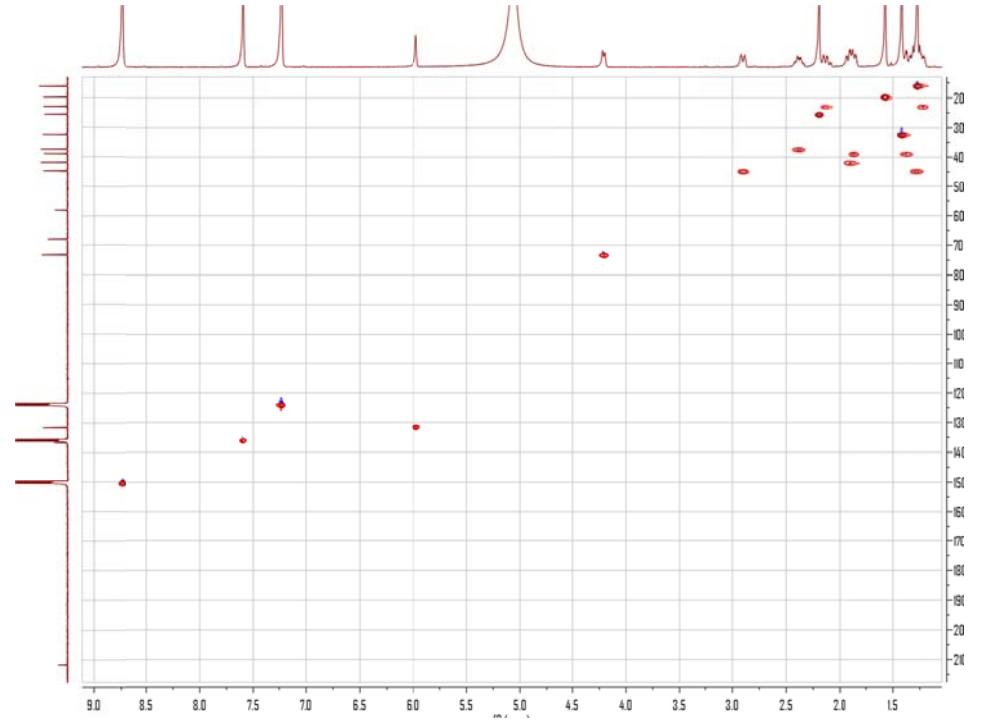


Figure S148. HSQC spectrum of **14** in *Pyridine-d_5*

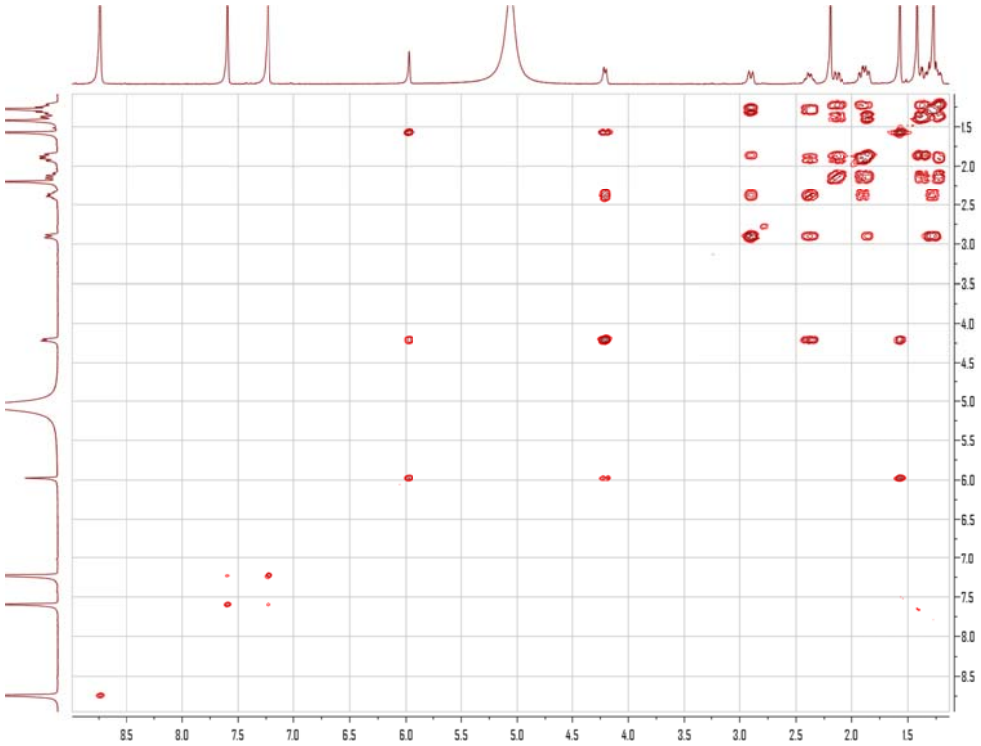


Figure S149. ^{1}H-^{1}H COSY spectrum of **14** in *Pyridine-d_5*

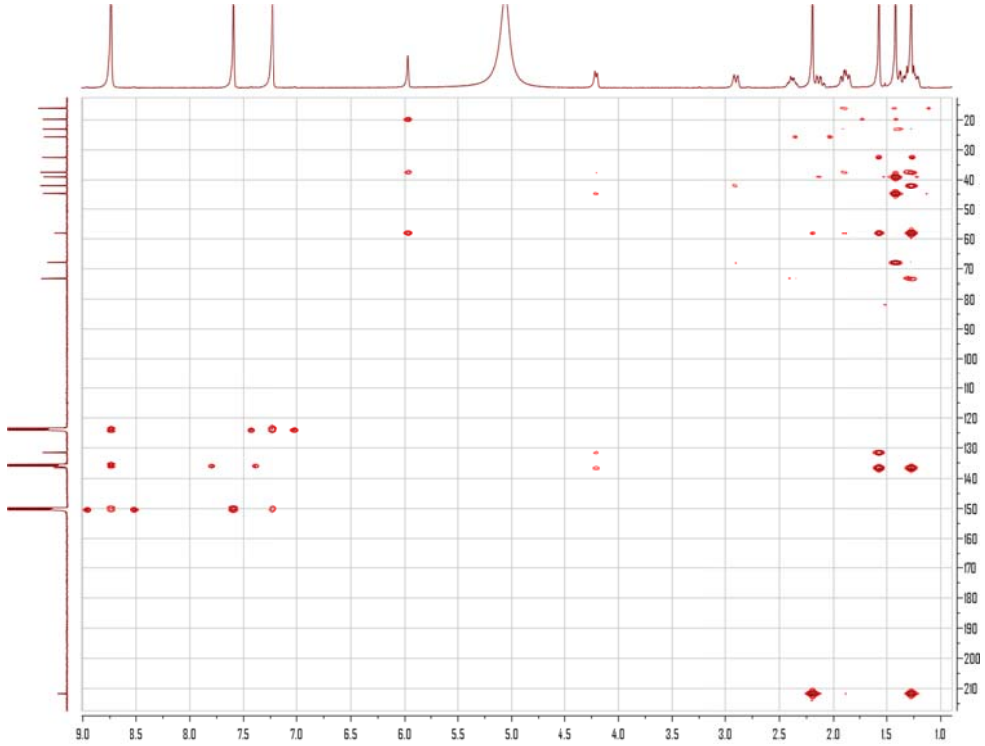


Figure S150. HMBC spectrum of 14 *Pyridine-d_5*

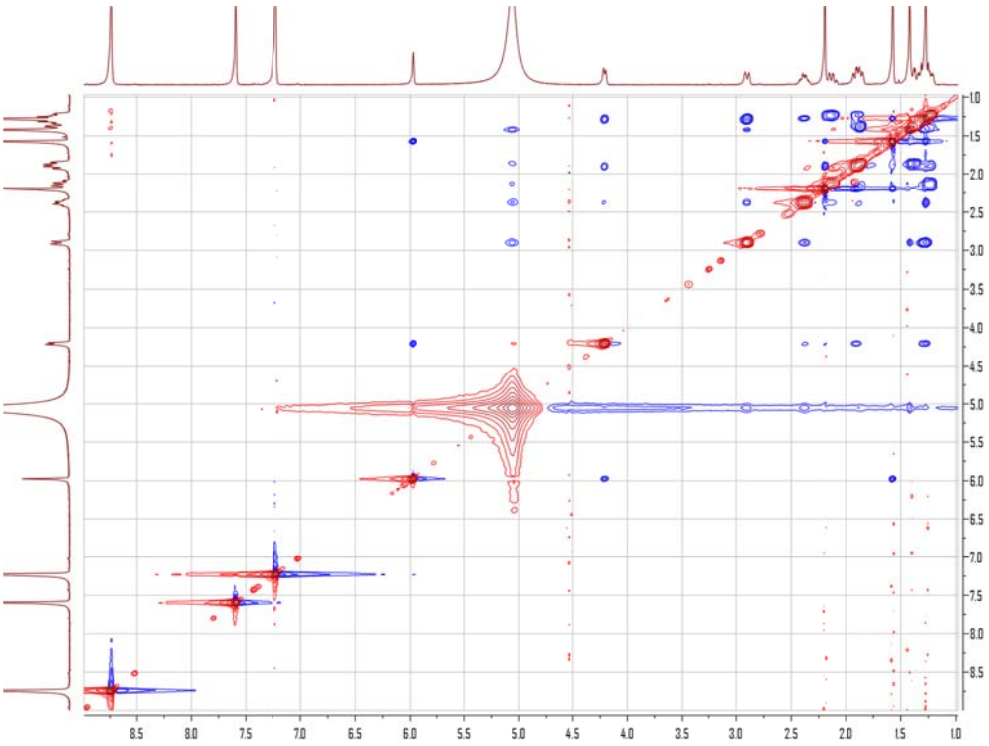


Figure S151. NOESY spectrum of 14 in *Pyridine-d_5*

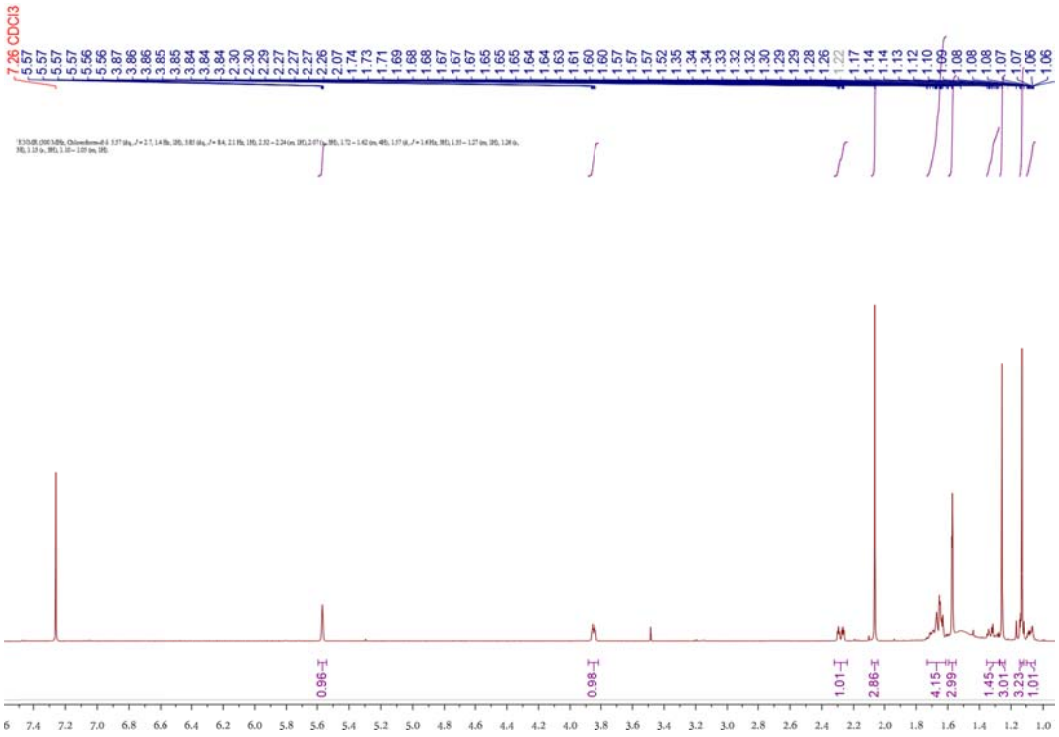


Figure S152. ^{1}H NMR spectrum of 14 in $CDCl_3$ at 500 MHz

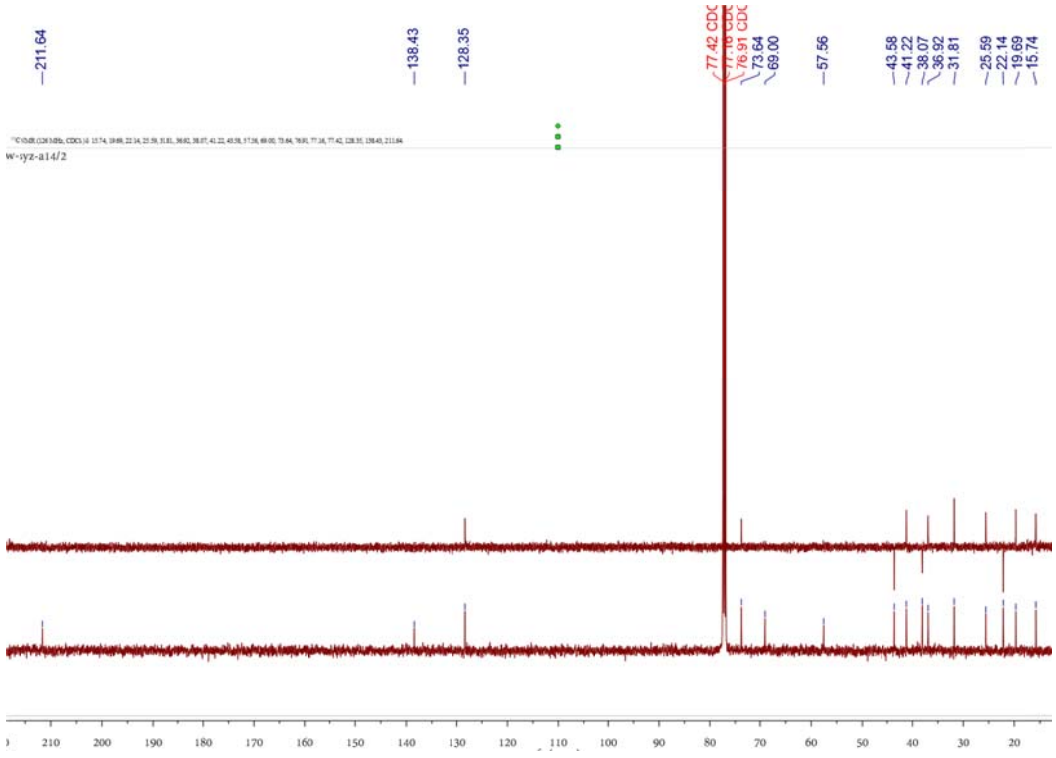


Figure S153. ^{13}C and NMR DEPT spectra of 14 in $CDCl_3$ at 125 MHz

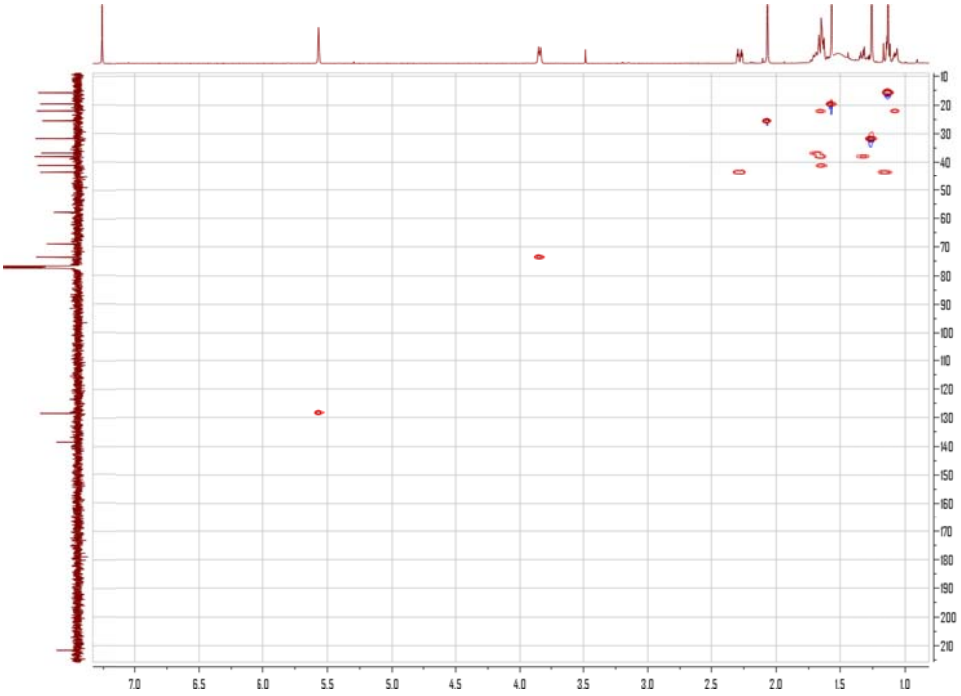


Figure S154. HSQC spectrum of 14 in $CDCl_3$

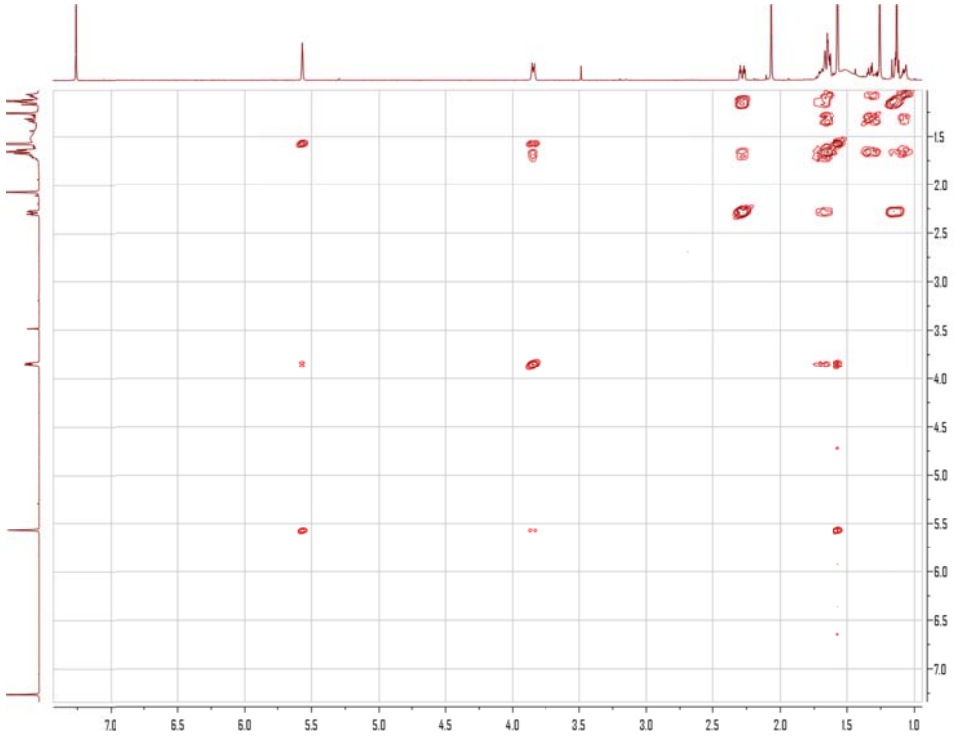


Figure S155. ^{1}H-^{1}H COSY spectrum of 14 in $CDCl_3$

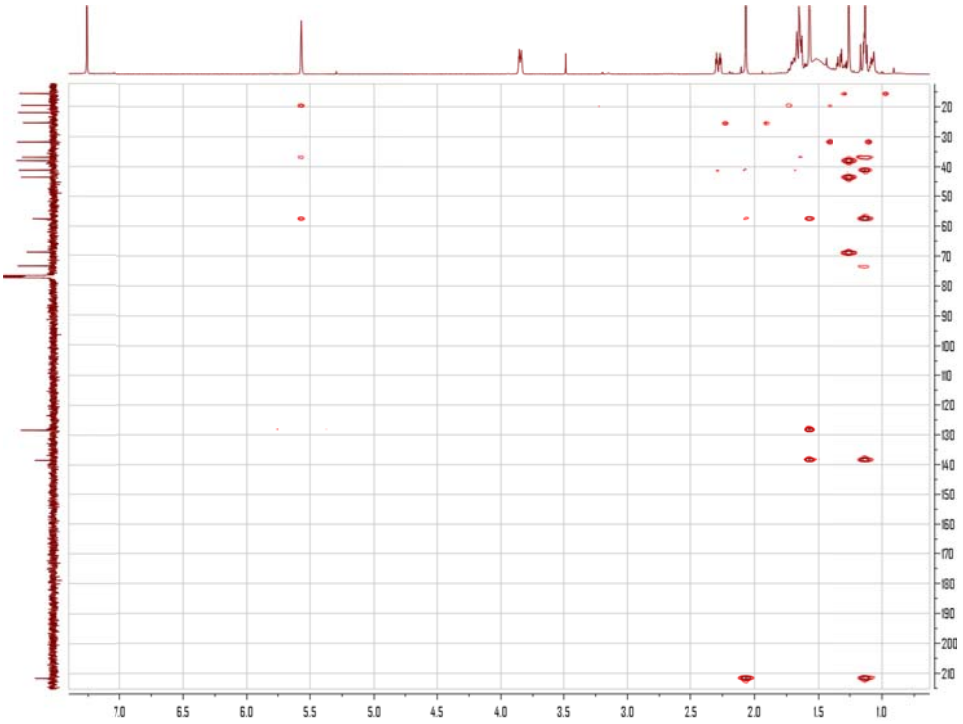


Figure S156. HMBC spectrum of 14 in $CDCl_3$

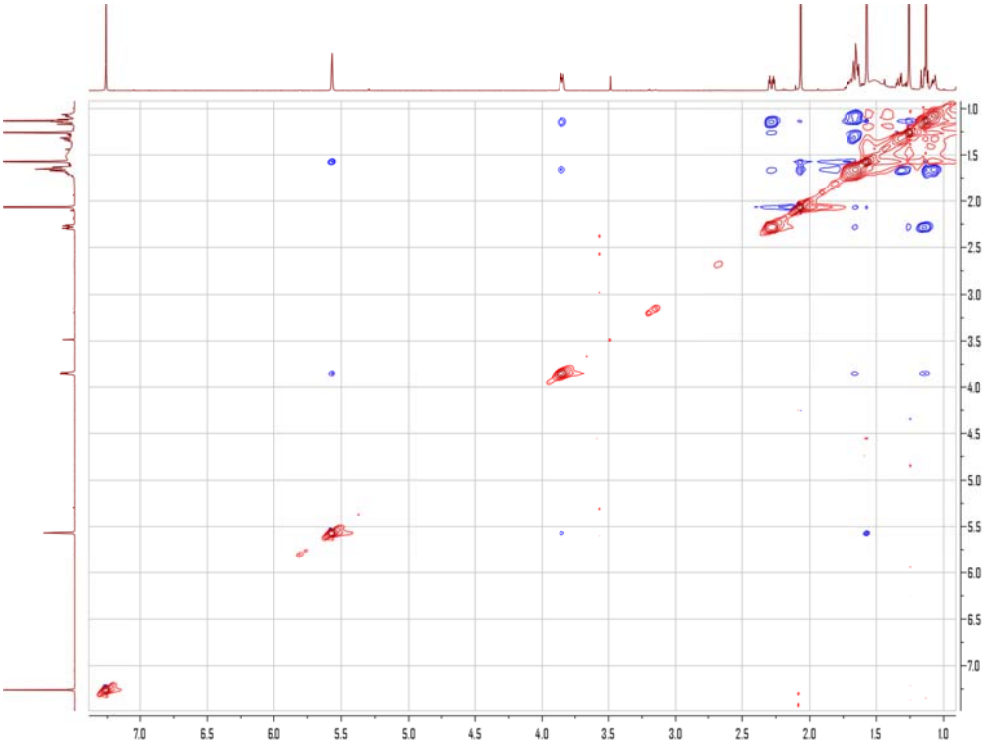
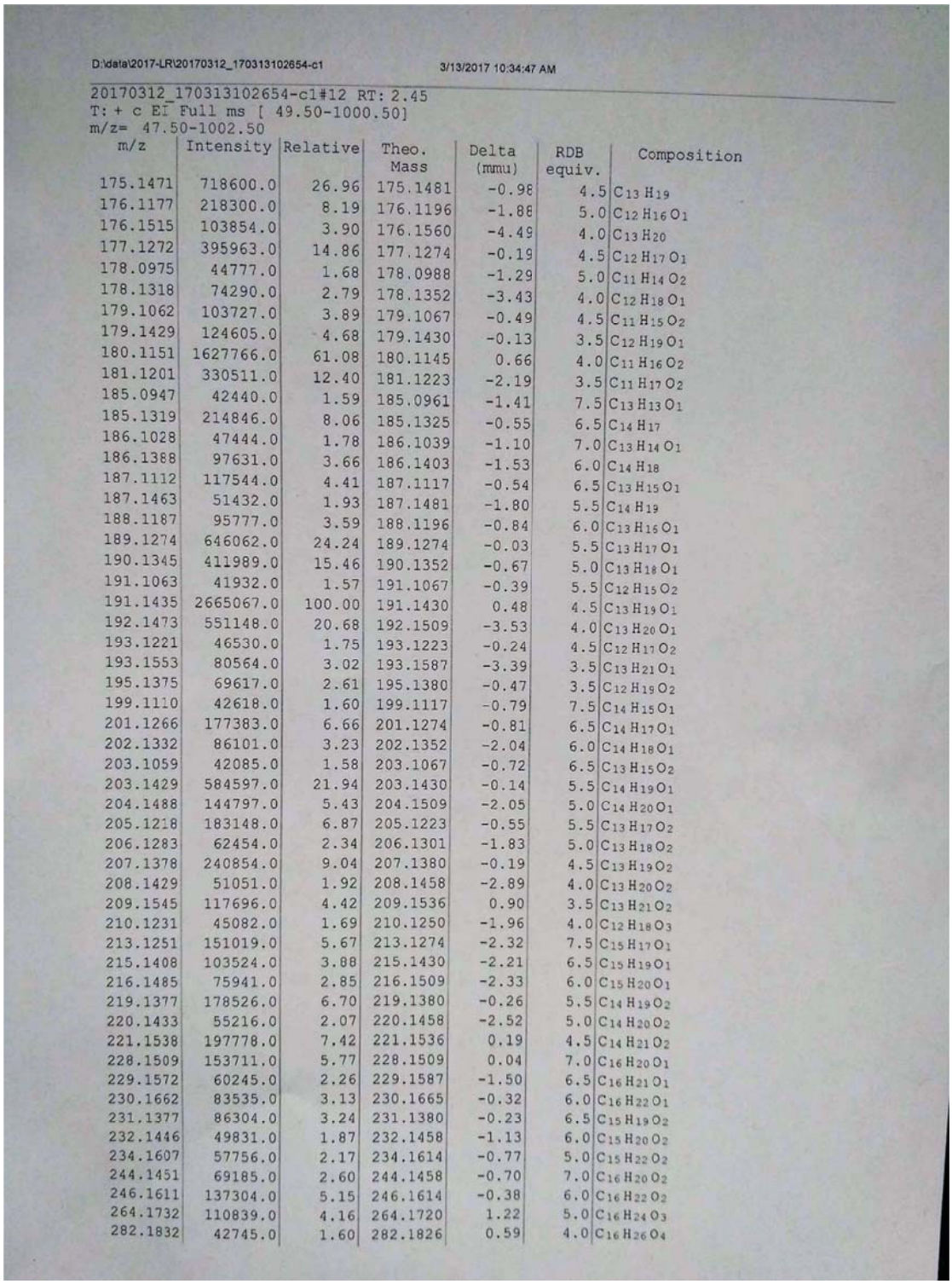


Figure S157. NOESY spectrum of 14 in $CDCl_3$



D:\data\2017-LR\20170312_170313102654-c1 3/13/2017 10:34:47 AM

20170312_170313102654-c1#12 RT: 2.45
T: + c EI Full ms [49.50-1000.50]
m/z= 47.50-1002.50

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
175.1471	718600.0	26.96	175.1481	-0.98	4.5	$C_{13}H_{19}$
176.1177	218300.0	8.19	176.1196	-1.88	5.0	$C_{12}H_{16}O_1$
176.1515	103854.0	3.90	176.1560	-4.49	4.0	$C_{13}H_{20}$
177.1272	395963.0	14.86	177.1274	-0.19	4.5	$C_{12}H_{17}O_1$
178.0975	44777.0	1.68	178.0988	-1.29	5.0	$C_{11}H_{14}O_2$
178.1318	74290.0	2.79	178.1352	-3.43	4.0	$C_{12}H_{18}O_1$
179.1062	103727.0	3.89	179.1067	-0.49	4.5	$C_{11}H_{15}O_2$
179.1429	124605.0	4.68	179.1430	-0.13	3.5	$C_{12}H_{19}O_1$
180.1151	1627766.0	61.08	180.1145	0.66	4.0	$C_{11}H_{16}O_2$
181.1201	330511.0	12.40	181.1223	-2.19	3.5	$C_{11}H_{17}O_2$
185.0947	42440.0	1.59	185.0961	-1.41	7.5	$C_{13}H_{13}O_1$
185.1319	214846.0	8.06	185.1325	-0.55	6.5	$C_{14}H_{17}$
186.1028	47444.0	1.78	186.1039	-1.10	7.0	$C_{13}H_{14}O_1$
186.1388	97631.0	3.66	186.1403	-1.53	6.0	$C_{14}H_{18}$
187.1112	117544.0	4.41	187.1117	-0.54	6.5	$C_{13}H_{15}O_1$
187.1463	51432.0	1.93	187.1481	-1.80	5.5	$C_{14}H_{19}$
188.1187	95777.0	3.59	188.1196	-0.84	6.0	$C_{13}H_{16}O_1$
189.1274	646062.0	24.24	189.1274	-0.03	5.5	$C_{13}H_{17}O_1$
190.1345	411989.0	15.46	190.1352	-0.67	5.0	$C_{13}H_{18}O_1$
191.1063	41932.0	1.57	191.1067	-0.39	5.5	$C_{12}H_{15}O_2$
191.1435	2665067.0	100.00	191.1430	0.48	4.5	$C_{13}H_{19}O_1$
192.1473	551148.0	20.68	192.1509	-3.53	4.0	$C_{13}H_{20}O_1$
193.1221	46530.0	1.75	193.1223	-0.24	4.5	$C_{12}H_{17}O_2$
193.1553	80564.0	3.02	193.1587	-3.39	3.5	$C_{13}H_{21}O_1$
195.1375	69617.0	2.61	195.1380	-0.47	3.5	$C_{12}H_{19}O_2$
199.1110	42618.0	1.60	199.1117	-0.79	7.5	$C_{14}H_{15}O_1$
201.1266	177383.0	6.66	201.1274	-0.81	6.5	$C_{14}H_{17}O_1$
202.1332	86101.0	3.23	202.1352	-2.04	6.0	$C_{14}H_{18}O_1$
203.1059	42085.0	1.58	203.1067	-0.72	6.5	$C_{13}H_{15}O_2$
203.1429	584597.0	21.94	203.1430	-0.14	5.5	$C_{14}H_{19}O_1$
204.1488	144797.0	5.43	204.1509	-2.05	5.0	$C_{14}H_{20}O_1$
205.1218	183148.0	6.87	205.1223	-0.55	5.5	$C_{13}H_{17}O_2$
206.1283	62454.0	2.34	206.1301	-1.83	5.0	$C_{13}H_{18}O_2$
207.1378	240854.0	9.04	207.1380	-0.19	4.5	$C_{13}H_{19}O_2$
208.1429	51051.0	1.92	208.1458	-2.89	4.0	$C_{13}H_{20}O_2$
209.1545	117696.0	4.42	209.1536	0.90	3.5	$C_{13}H_{21}O_2$
210.1231	45082.0	1.69	210.1250	-1.96	4.0	$C_{12}H_{18}O_3$
213.1251	151019.0	5.67	213.1274	-2.32	7.5	$C_{15}H_{17}O_1$
215.1408	103524.0	3.88	215.1430	-2.21	6.5	$C_{15}H_{19}O_1$
216.1485	75941.0	2.85	216.1509	-2.33	6.0	$C_{15}H_{20}O_1$
219.1377	178526.0	6.70	219.1380	-0.26	5.5	$C_{14}H_{19}O_2$
220.1433	55216.0	2.07	220.1458	-2.52	5.0	$C_{14}H_{20}O_2$
221.1538	197778.0	7.42	221.1536	0.19	4.5	$C_{14}H_{21}O_2$
228.1509	153711.0	5.77	228.1509	0.04	7.0	$C_{16}H_{20}O_1$
229.1572	60245.0	2.26	229.1587	-1.50	6.5	$C_{16}H_{21}O_1$
230.1662	83535.0	3.13	230.1665	-0.32	6.0	$C_{16}H_{22}O_1$
231.1377	86304.0	3.24	231.1380	-0.23	6.5	$C_{15}H_{19}O_2$
232.1446	49831.0	1.87	232.1458	-1.13	6.0	$C_{15}H_{20}O_2$
234.1607	57756.0	2.17	234.1614	-0.77	5.0	$C_{15}H_{22}O_2$
244.1451	69185.0	2.60	244.1458	-0.70	7.0	$C_{16}H_{20}O_2$
246.1611	137304.0	5.15	246.1614	-0.38	6.0	$C_{16}H_{22}O_2$
264.1732	110839.0	4.16	264.1720	1.22	5.0	$C_{16}H_{24}O_3$
282.1832	42745.0	1.60	282.1826	0.59	4.0	$C_{16}H_{26}O_4$

Figure S158. HREIMS spectrum of **15**

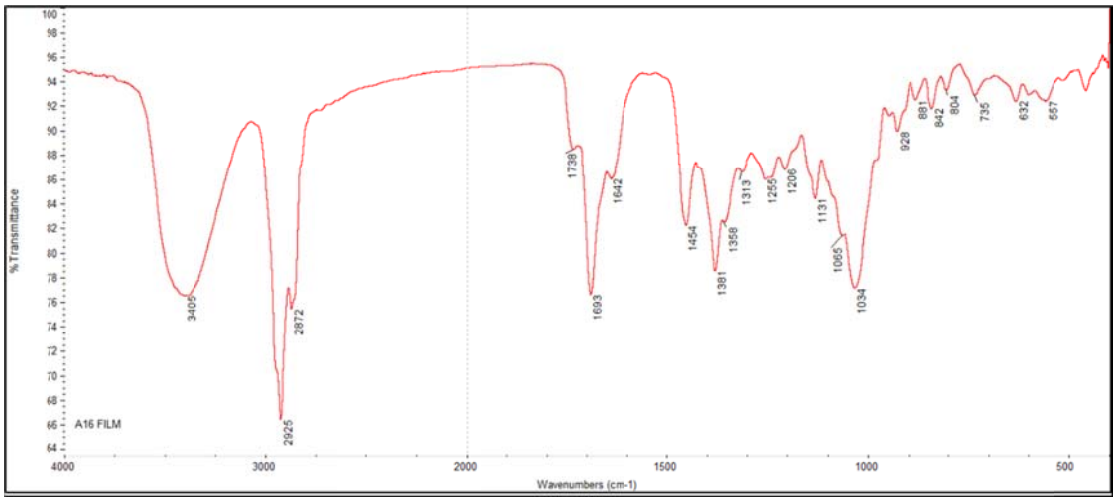


Figure S159. FTIR spectrum of **15**

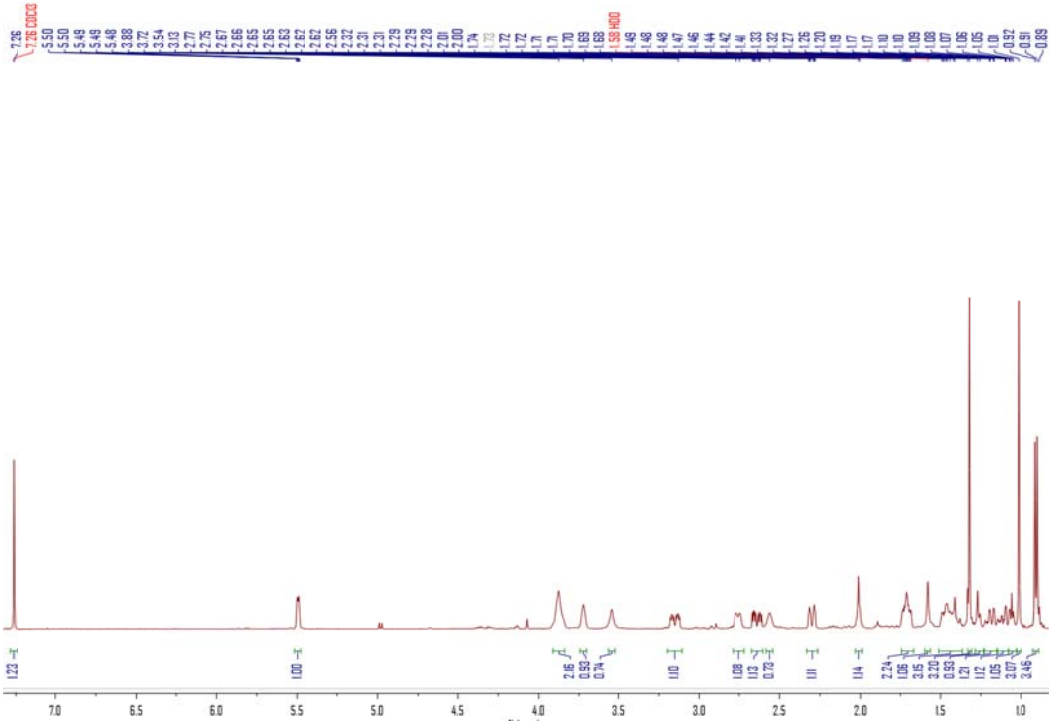


Figure S160. ^{1}**H NMR spectrum of 15 in** $CDCl_3$ **at 500 MHz**

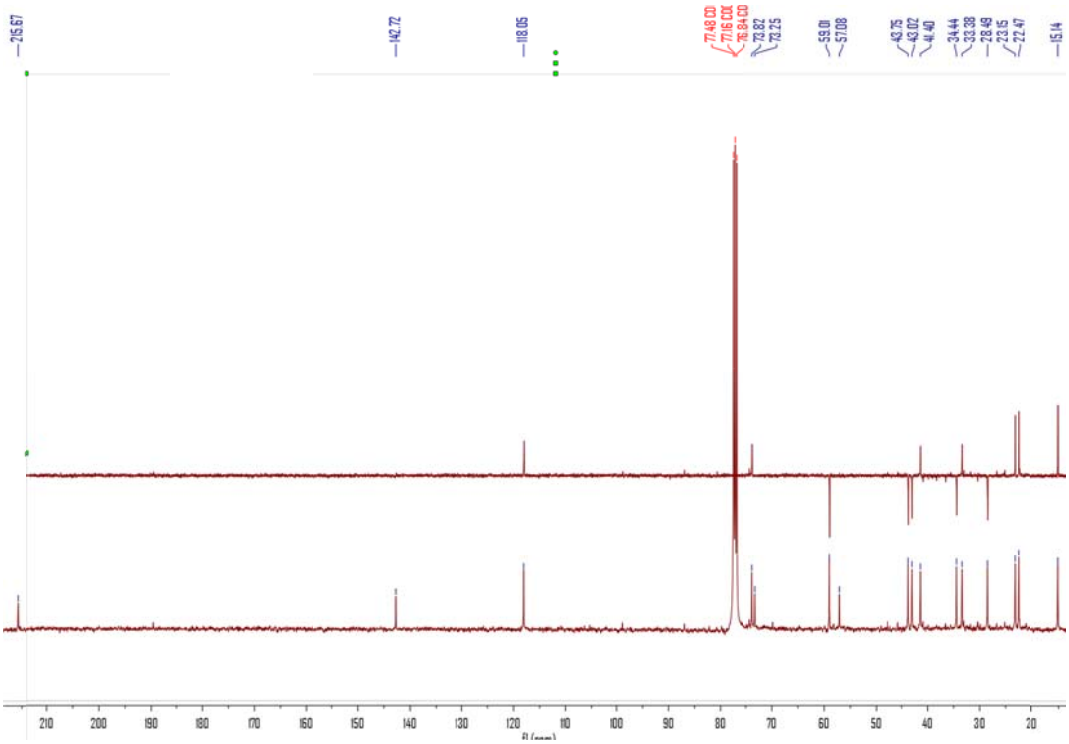


Figure S161. ^{13}C and NMR DEPT spectra of 15 in $CDCl_3$ at 100 MHz

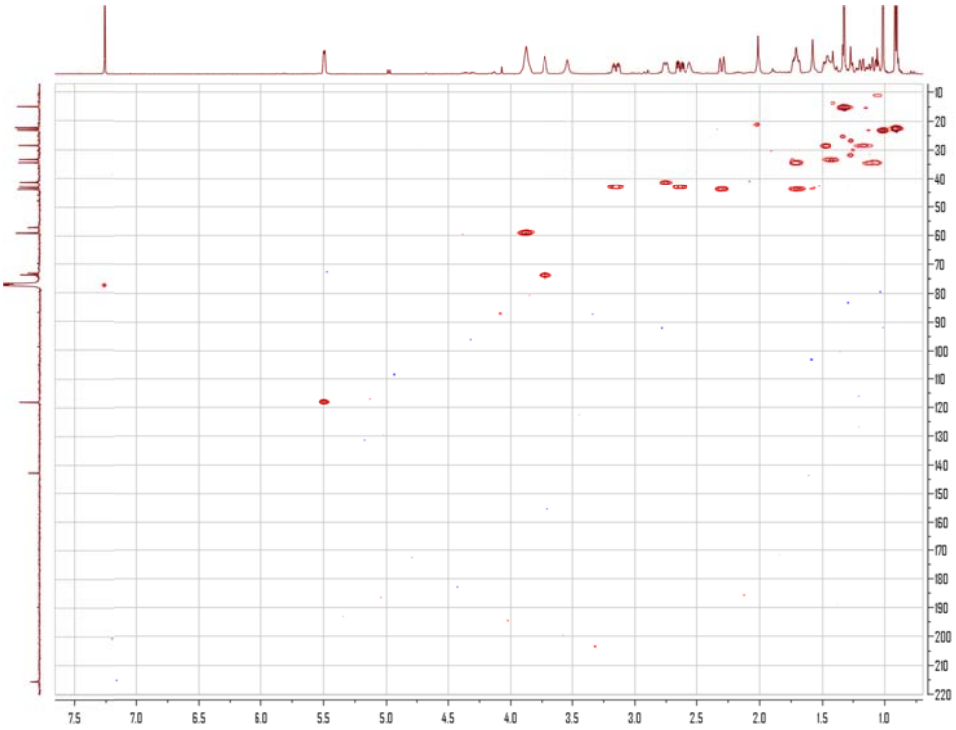


Figure S162. HSQC spectrum of **15** in $CDCl_3$

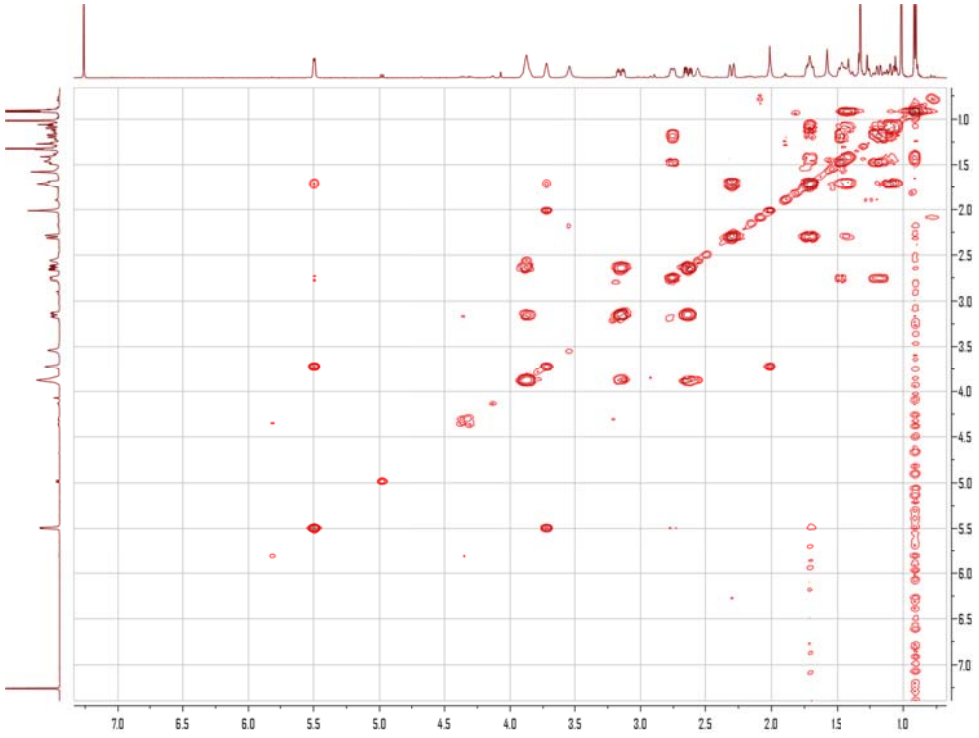


Figure S163. ^{1}H-^{1}H COSY spectrum of **15** in $CDCl_3$

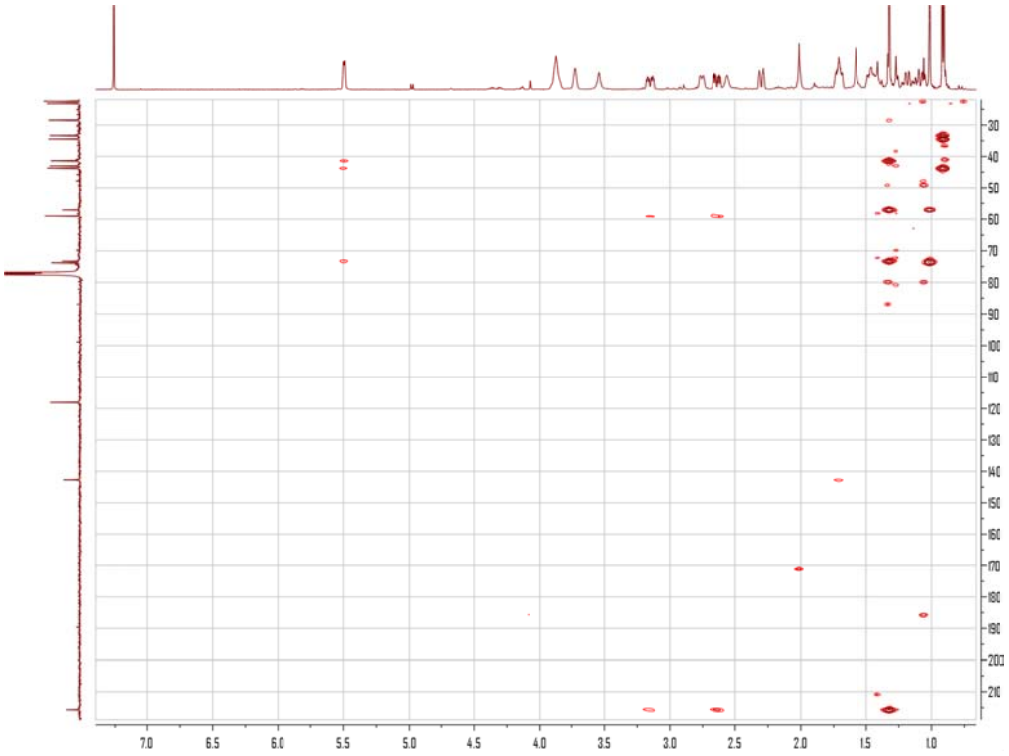


Figure S164. HMBC spectrum of **15** in $CDCl_3$

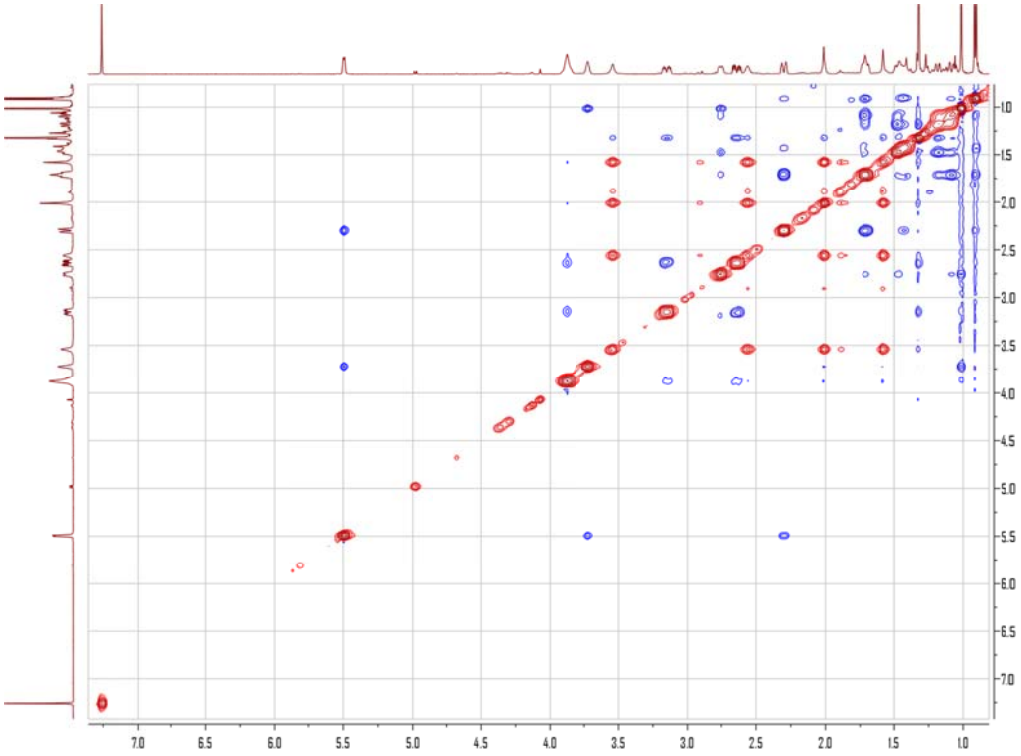


Figure S165. NOESY spectrum of **15** in $CDCl_3$

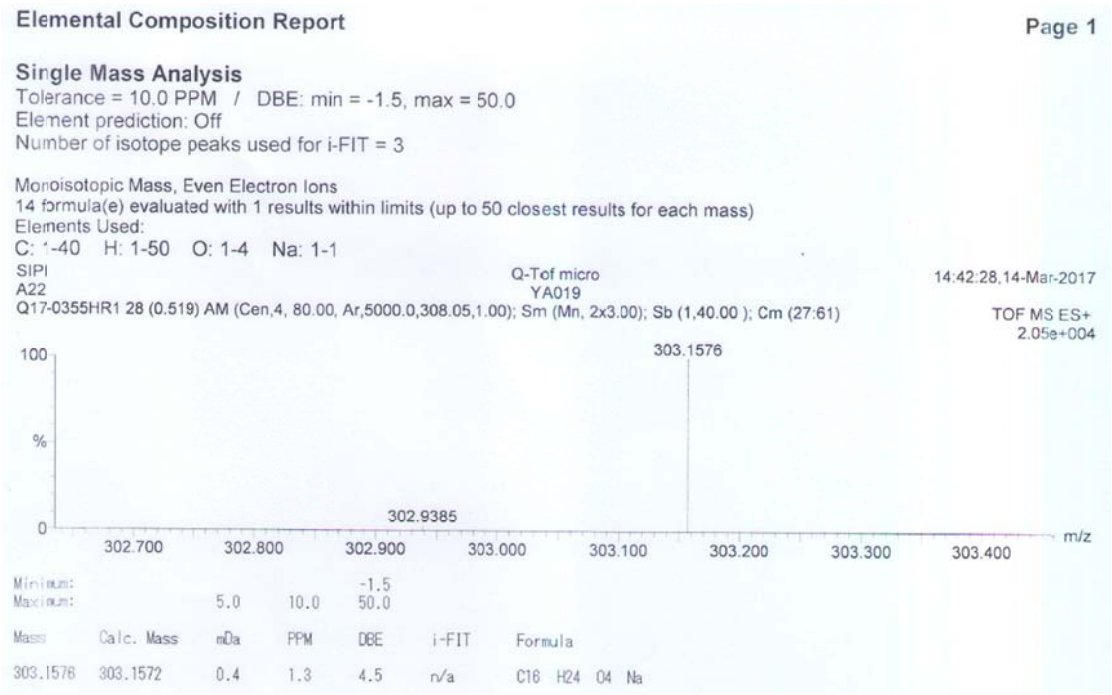


Figure S166. HRESIMS spectrum of **16**

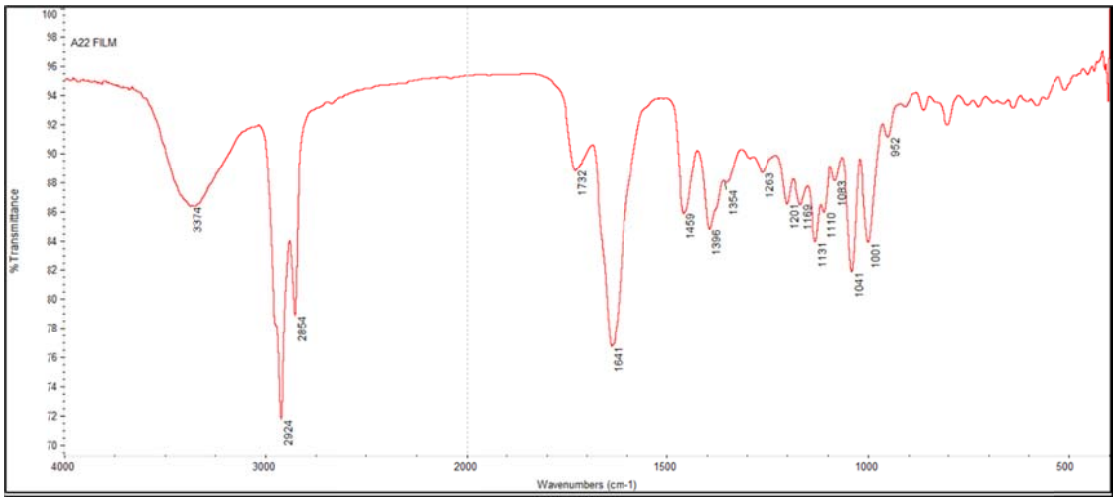


Figure S167. FTIR spectrum of **16**

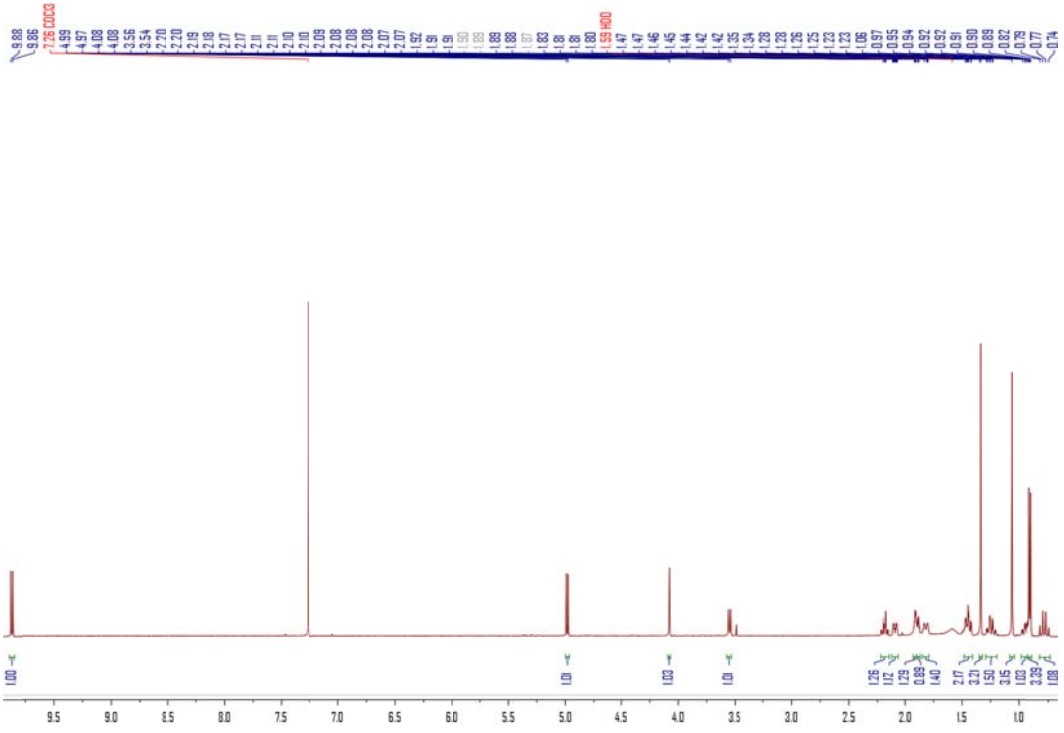


Figure S168. ^{1}H NMR spectrum of **16** in $CDCl_3$ at 500 MHz

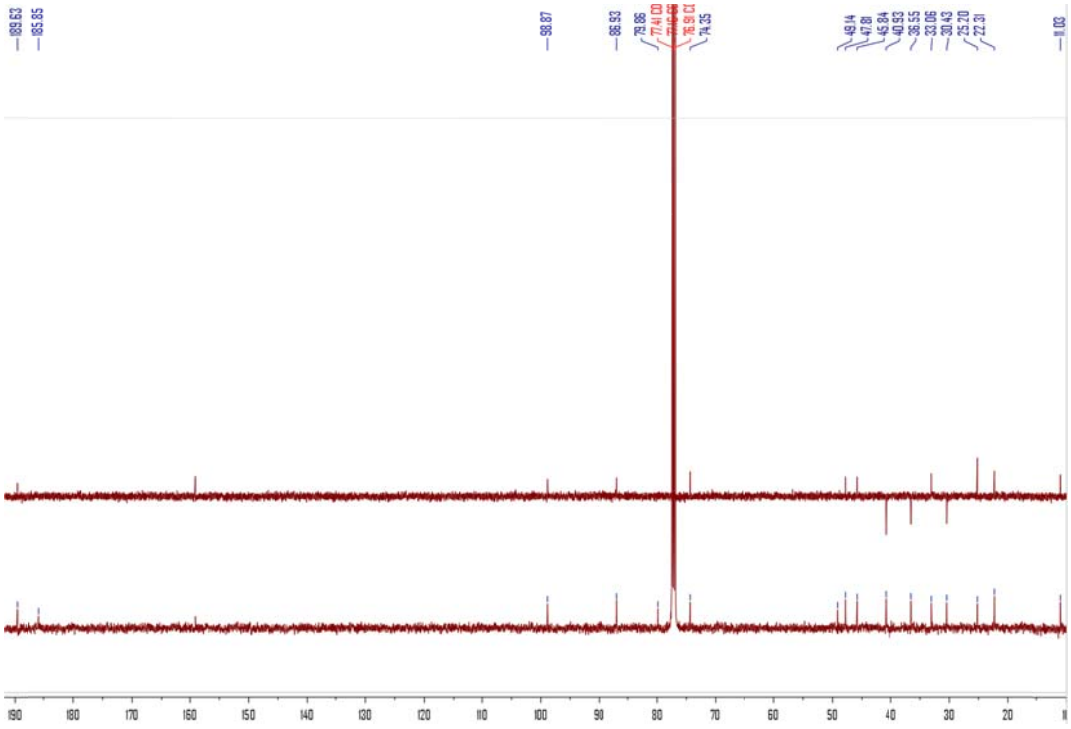


Figure S169. ^{13}C and NMR DEPT spectra of **16** in $CDCl_3$ at 125 MHz

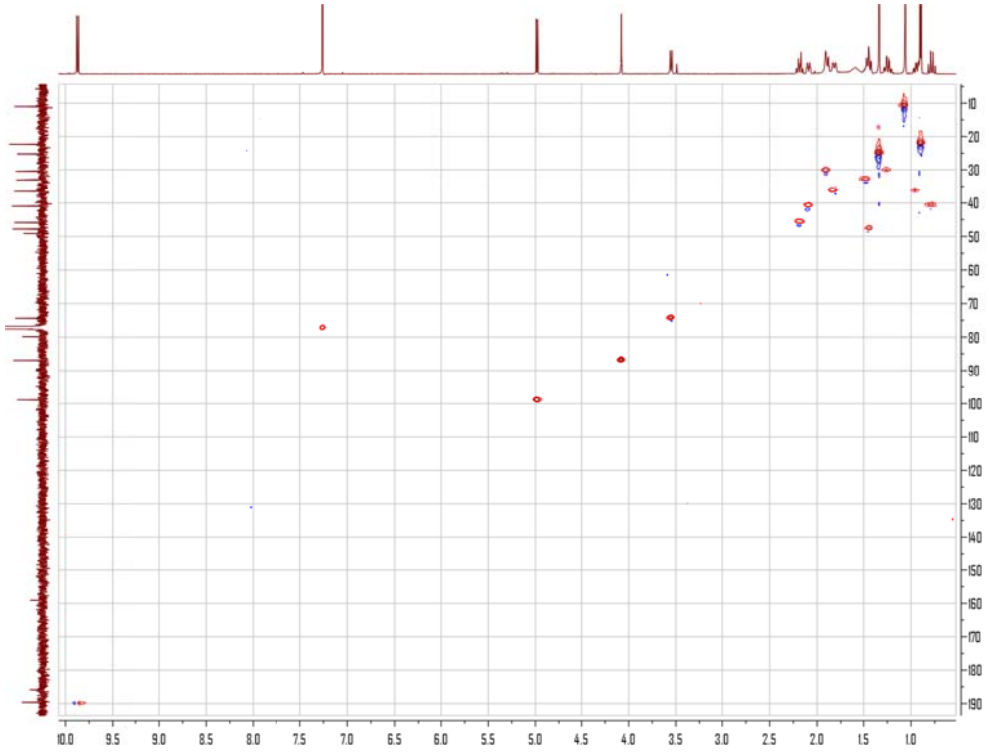


Figure S170. HSQC spectrum of **16** in $CDCl_3$

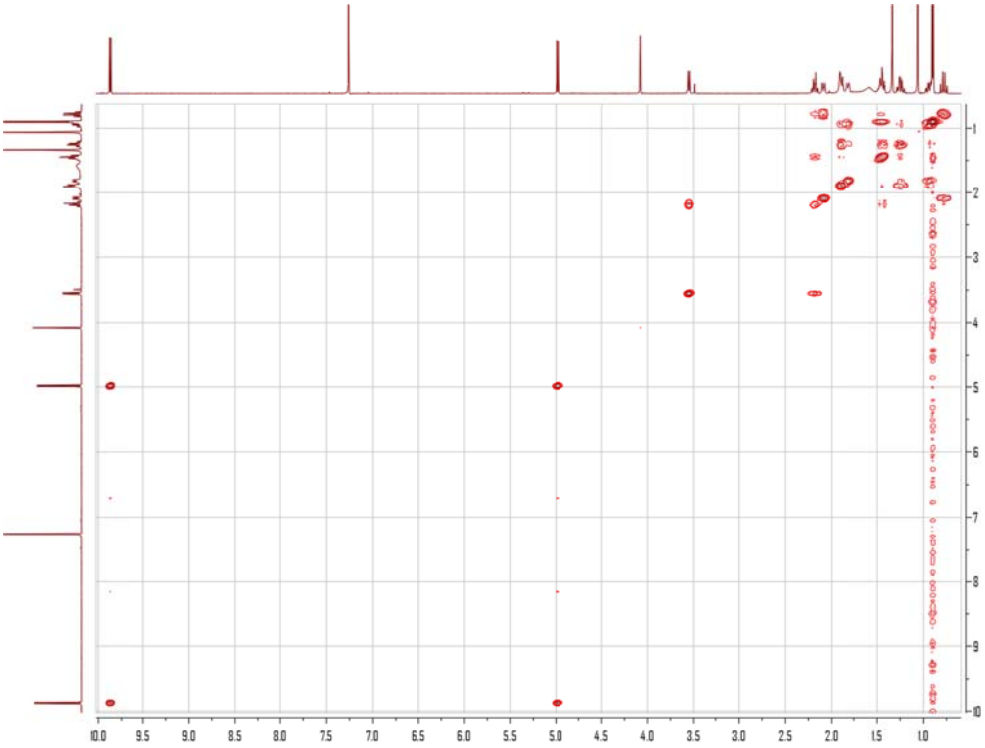


Figure S171. ^{1}H-^{1}H COSY spectrum of **16** in $CDCl_3$

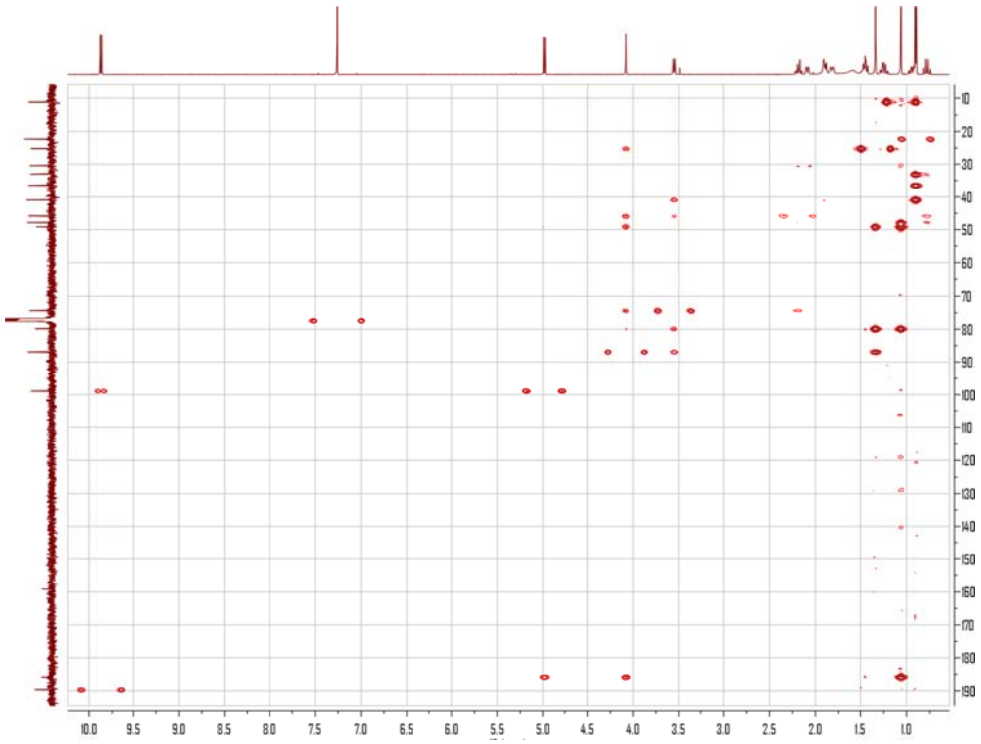


Figure S172. HMBC spectrum of **16** in $CDCl_3$

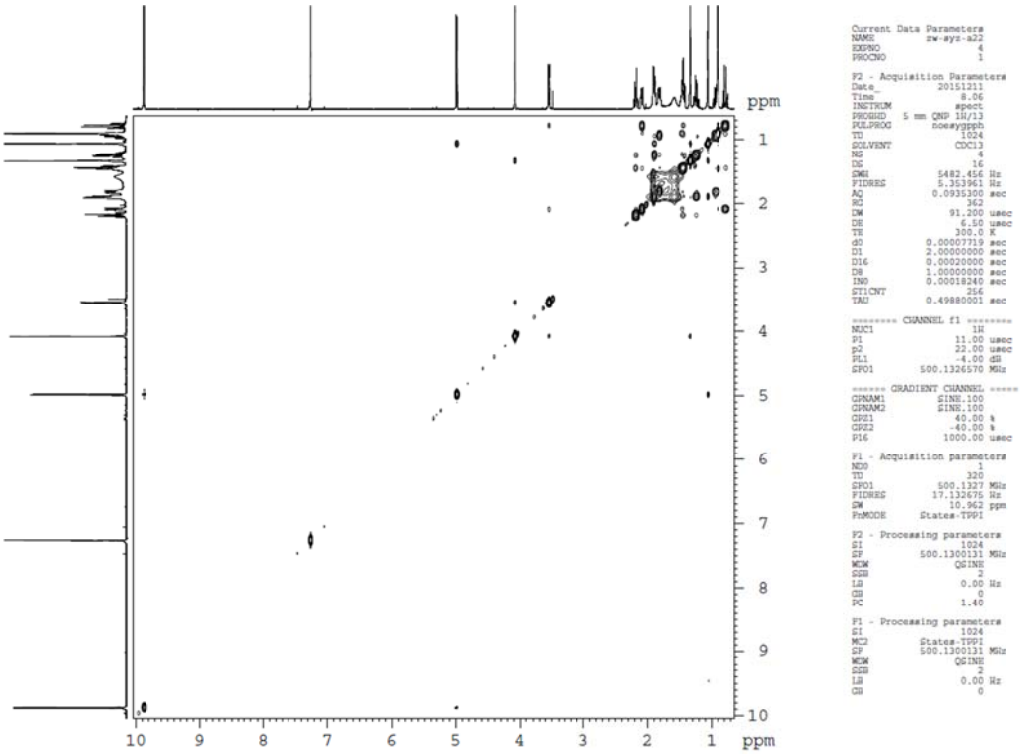


Figure S173. NOESY spectrum of **16** in $CDCl_3$

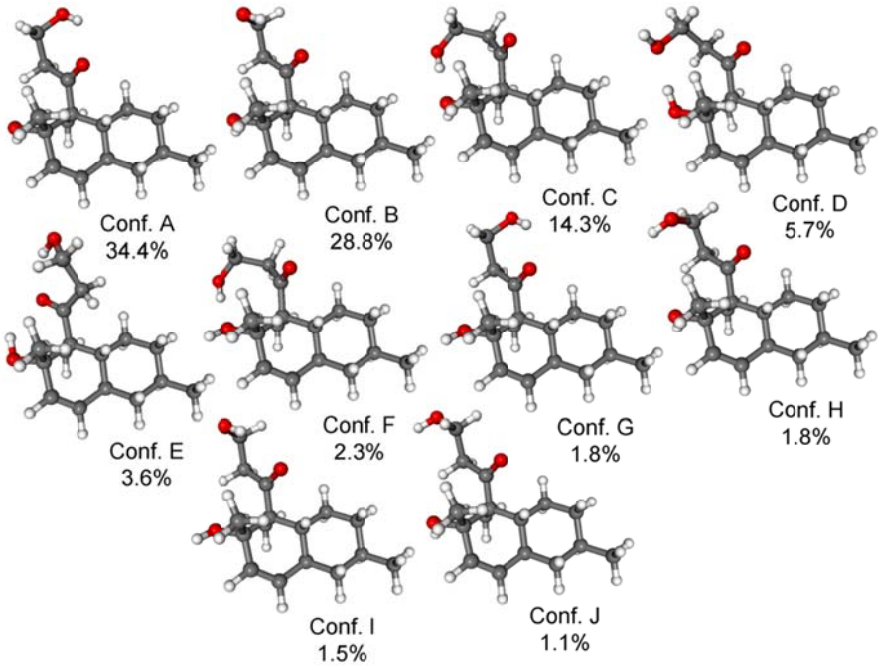


Figure S174. Structures and populations of the low-energy B97D/TZVP PCM/MeCN conformers (≥ 1%) of (1R,4R,6S,9S,10S)-**1**.

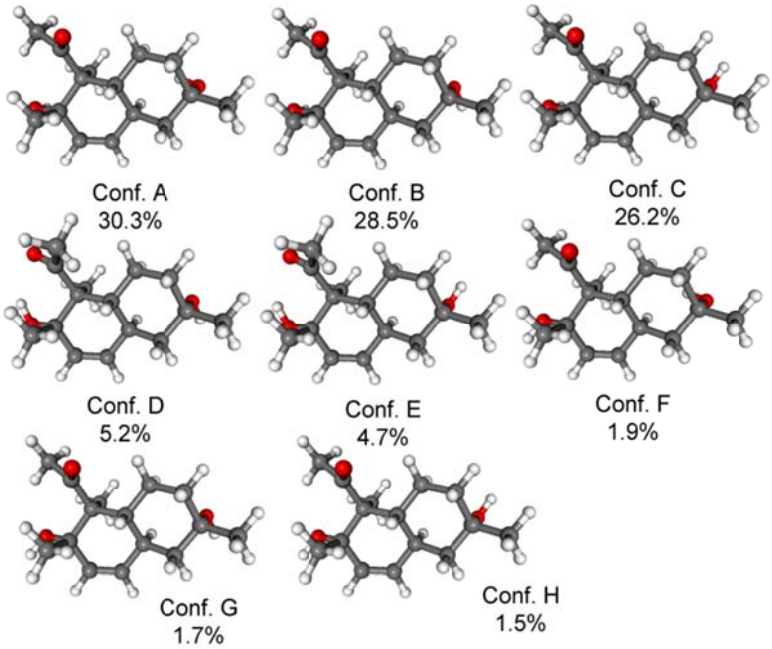


Figure S175. Structures and populations of the low-energy B97D/TZVP PCM/MeCN conformers (≥ 1%) of (1R,4S,6S,9S,10S)-**5**.

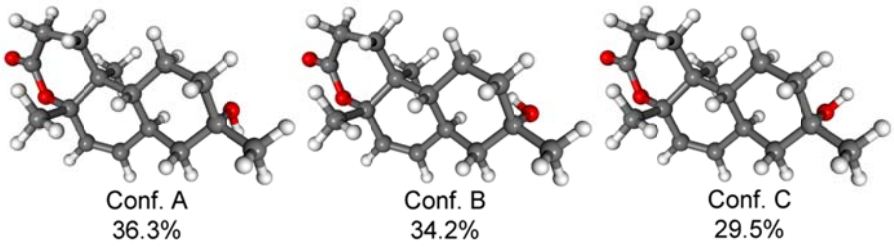


Figure S176. Structures and populations of the low-energy B97D/TZVP PCM/MeCN conformers (≥ 1%) of (1R,4S,6S,9S,10S)-**6**.

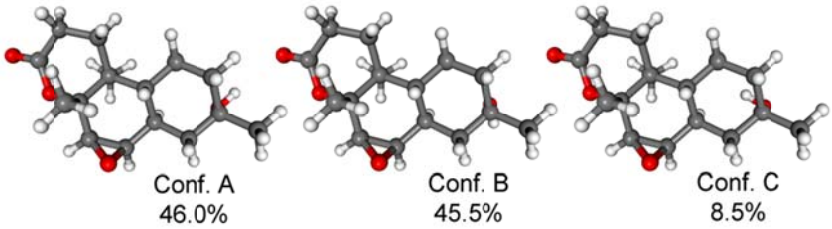


Figure S177. Structures and populations of the low-energy CAM-B3LYP/TZVP PCM/MeCN conformers (≥ 1%) of (1R,4S,6R,7R,8R,9R,10S)-**9**.

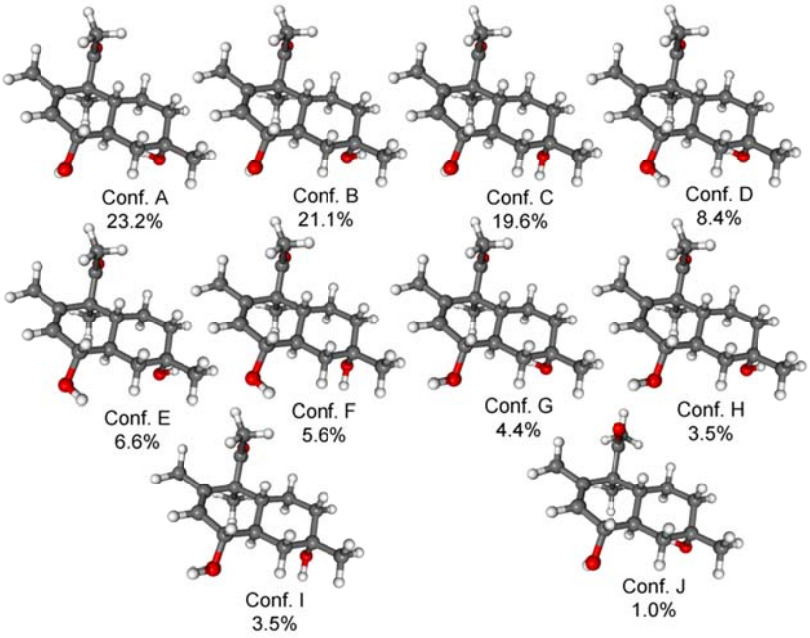


Figure S178. Structures and populations of the low-energy B97D/TZVP PCM/MeCN conformers (≥ 1%) of (1R,4S,6R,7S,10S)-**14**.

Analysis of splenocytes proliferation, apoptosis and T cell subtypes

Splenocytes (2×10^6 cell/ml) from C57BL/6 mice were incubated with compounds for 24 h. The cells were collected and washed with PBS, and then samples were immediately detected by a FACScan flow cytometer (BD, USA) for apoptosis.

To investigate the effects of compounds on the differentiation of T cell subtypes. The cells were collected and stained with PE-CD3, FITC-CD4 and Percp/cy5.5-CD8, respectively. The percentage of CD3+T, CD4+T, and CD8+T cells was analyzed by flow cytometry.

Supplementary Data

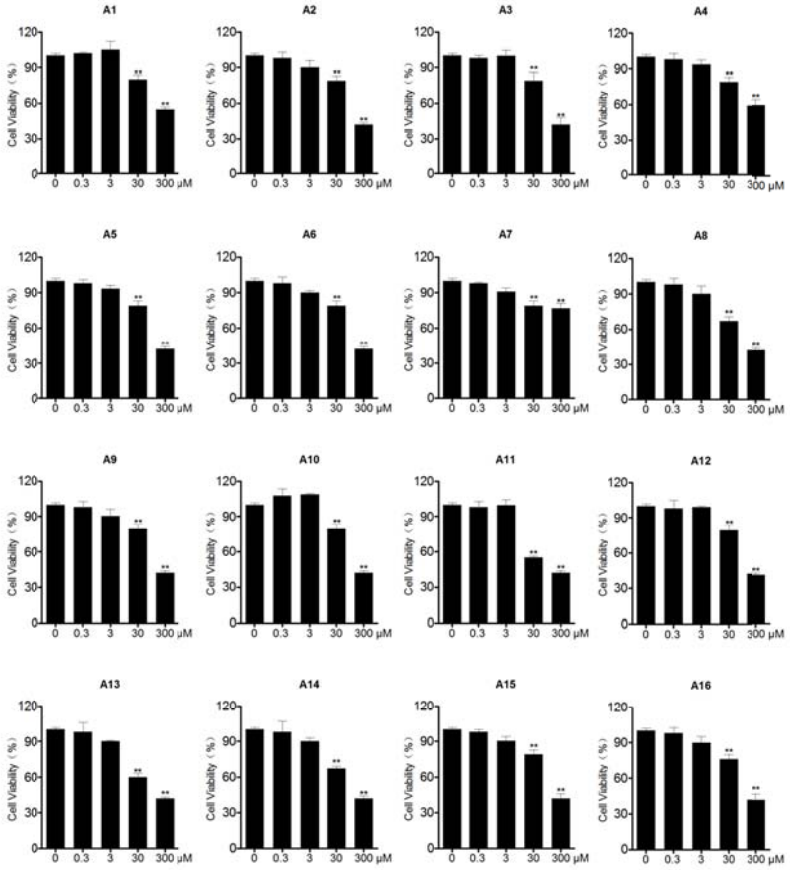


Figure S179. Effects of the compounds **1-16** on the Cell Viability by CCK-8 assay. Splenocytes were incubated with compounds for 24 h. The values are presented as means±S.D. (n=3). *P<0.05 and **P<0.01.

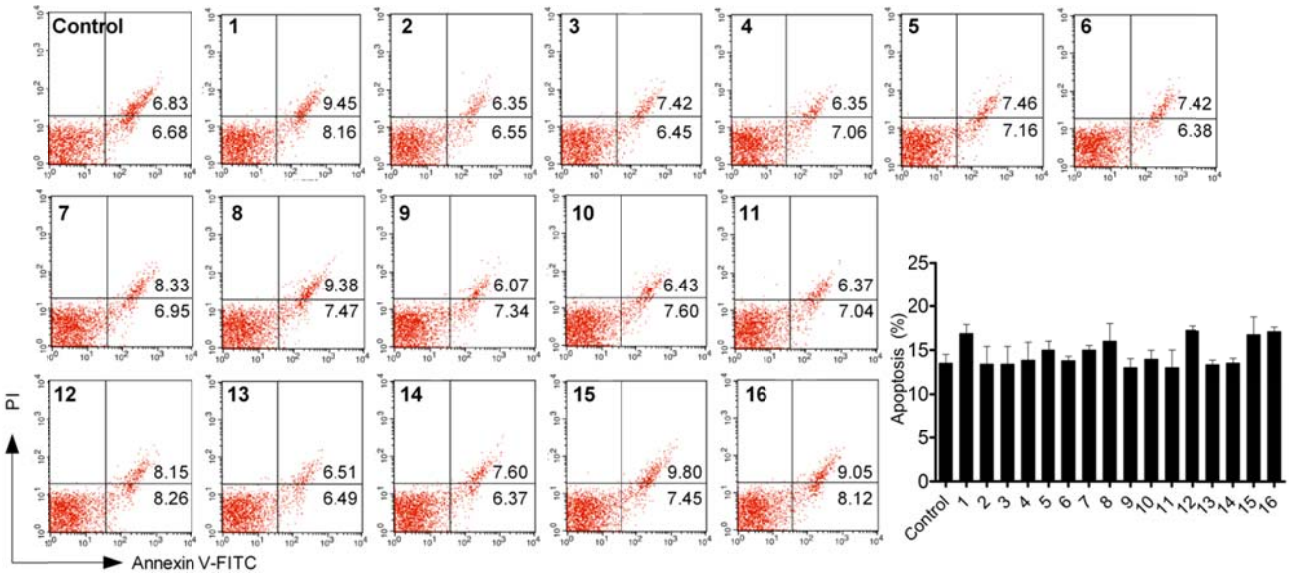


Figure S180. Effects of compounds **1-16** on the apoptosis of splenocytes by Annexin V-FITC/PI staining. Splenocytes were incubated with compounds (3μM) for 24 h. The apoptosis of splenocytes was analyzed by flow cytometry. The values are presented as means±S.D. (n=3). *P<0.05 and **P<0.01.

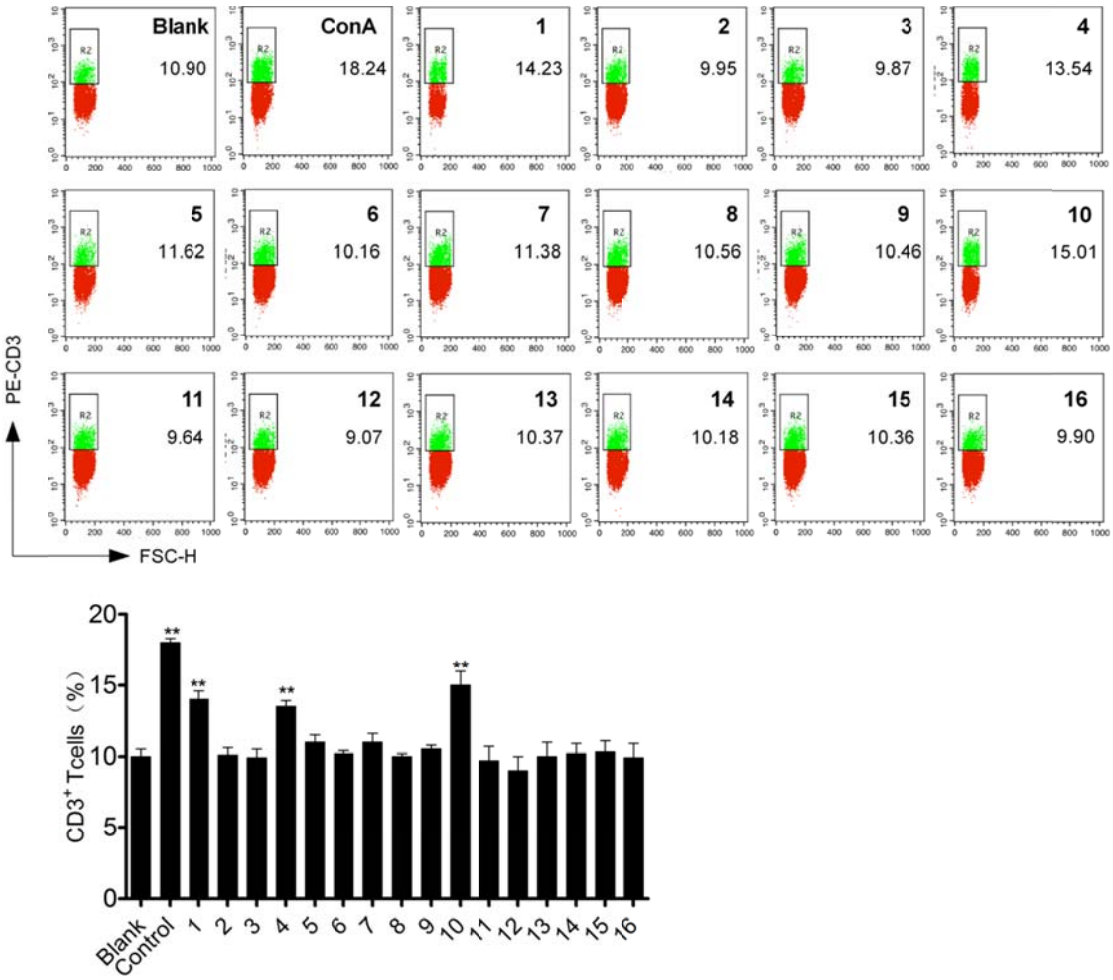


Figure S181. Effects of compounds **1-16** on the proliferation of CD3+T. Splenocytes

were incubated with compounds (3μM) for 24 h using Con A as a positive control (5μg/mL). The cells were collected and stained with PE-CD3. The percentage of CD3+T was analyzed by flow cytometry. The values are presented as means±S.D. (n=3). Significant differences with Con A group were designated as *P<0.05 and **P<0.01.

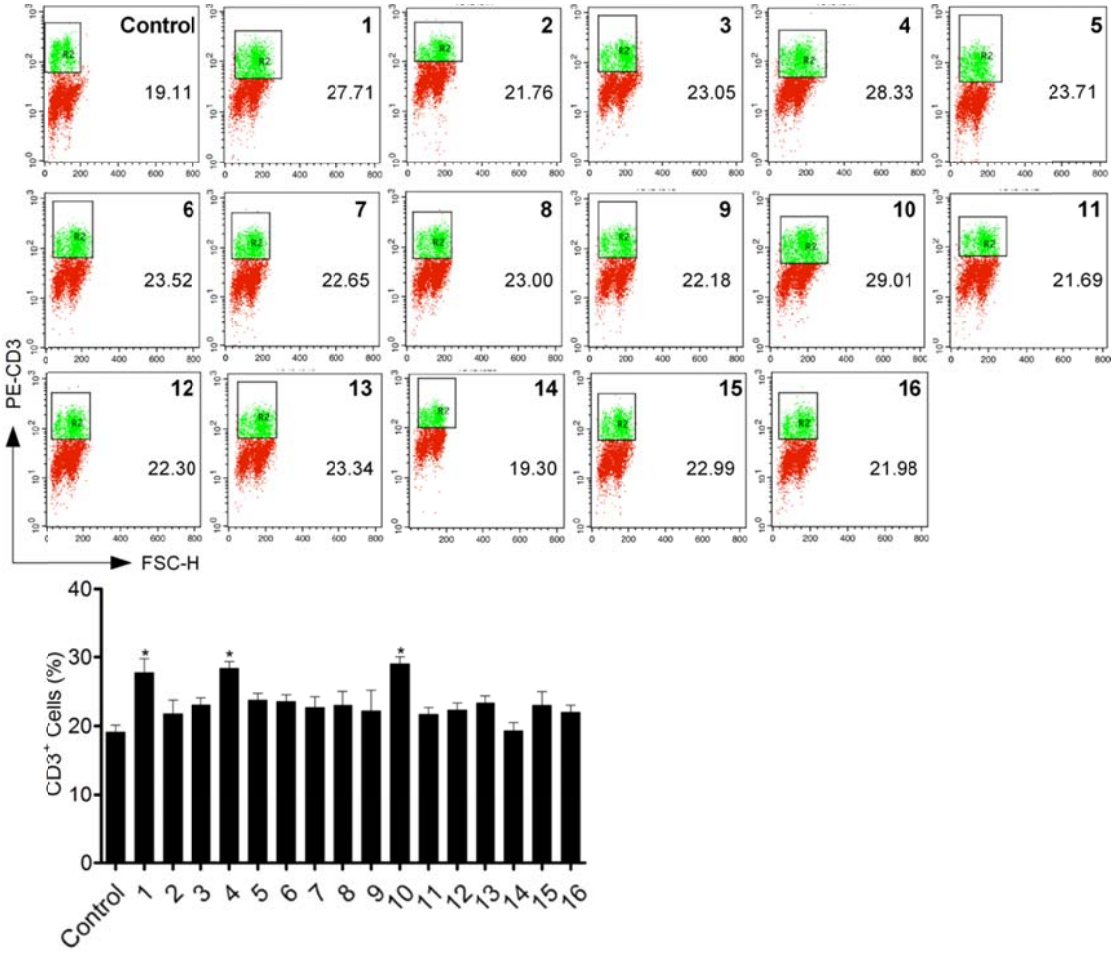


Figure S182. Effects of compounds **1-16** on the proliferation of CD3+T. Con A-stimulated (5μg/mL) splenocytes were incubated with compounds for 24 h. The cells were collected and stained with PE-CD3. The percentage of CD3+T was analyzed by flow cytometry. The values are presented as means±S.D. (n=3). Significant differences with Con A group were designated as *P<0.05 and **P<0.01.

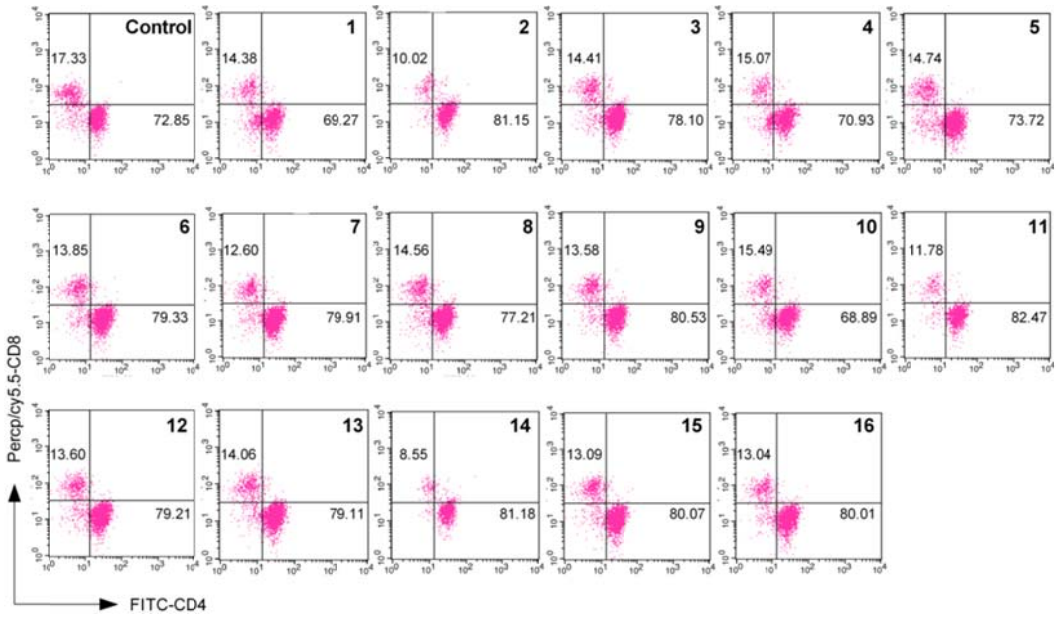


Figure S183. Effects of compounds **1-16** on the differentiation of T cell subtypes. Con A-stimulated splenocytes were incubated with compounds for 24 h. The cells were collected and stained with FITC-CD4 and Percp/cy5.5-CD8. The percentage of CD4+T and CD8+T cells was analyzed by flow cytometry. The values are presented as means±S.D. (n=3). Significant differences with Con A group were designated as *P<0.05 and **P<0.01.

Table S1. ^{1}H and ^{13}C NMR Data for compounds **3**, **5** and **6** (in $CDCl_3$, *J* in Hz)

	3		**5**		**6**	
	*δ*H (mult., *J* in Hz)	*δ*C	δH (mult., *J* in Hz)	*δ*C	δH (mult., *J* in Hz)	*δ*C
1	1.78 ddd 10.9, 10.7, 2.43	43.2	1.75 ov	43.4	1.29 ov	46.2
2	α 1.43 ov β 1.29 ov	23.1	α 1.46 ov β 1.34 ov	23.2	1.48 ov	20.9
3	α 1.52 ddd 13.8, 13.5, 4.2 β 1.65 ddd 13.8, 3.2, 3.1	39.5	α 1.55 ddd 13.5 13.2, 4.2 β 1.66 ov	39.5	α 1.38 ov β 1.79-1.68 ov	39.3
4	-	70.1	-	70.1	-	69.8
5	α 1.25 ov β 1.73 ddd 13.3, 3.0, 3.0	45.3	α 1.25 ov β 1.72 ov	45.4	α 1.79-1.68 ov β 1.21 ov	69.8
6	2.23 dddd 13.0, 11.7, 5.2, 3.0	33.7	2.21 ov	33.8	2.38 dddd 13.0, 11.5, 5.7, 2.5	35.0
7	5.35 ov	130.7	5.37-5.35 ov	130.9	5.38 dd 10.2, 2.5	131.1
8	5.35 ov	133.7	5.37-5.35 ov	133.7	5.62 dd 10.1, 2.9	130.9
9	-	73.9	-	73.8	-	84.9
10	-	57.0	-	57.1	-	37.65
11	1.23 s	31.7	1.23 s	31.7	1.25 s	31.8
12	1.11 s	27.3	1.13 s	27.4	1.42 s	26.0
13	1.32 s	11.9	1.31 s	12.5	0.98 s	14.6
14	-	211.4	-	213.0	1.79-1.68 ov	26.6
15	a 2.75 (dt, 18.5, 6.0) b 3.19 (dt,18.5, 6.0)	40.7	2.26 s	30.7	a 2.73 ddd 19.8, 9.5, 7.3 b 2.64 ddd 19.8, 9.2, 3.3	27.4
16	a 4.31 (dt, 11.1, 6.0) b 4.36 (dt, 11.1, 6.0)	59.7				172.4
17		171.1				
18	2.01 s	21.0				

500 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR

Table S2. ^{1}H and ^{13}C NMR Data for compounds **7**, **8** and **14** (in $CDCl_3$, *J* in Hz)

	7[a]		**8**[a]		**14**[b]	
	*δ*H (mult., *J* in Hz)	*δ*C	*δ*H (mult., *J* in Hz)	*δ*C	*δ*H (mult., *J* in Hz)	*δ*C
1	1.84-1.73 ov	42.9	2.09 ov	39.8	1.74-1.62 ov	41.2
2	α 1.84-1.73 ov β 1.58 ov	26.2	α 2.13 ov β 1.29 ov	22.8	α 1.08 m β 1.74-1.62 ov	22.1
3	α 1.51 ov β 1.84-1.73 ov	39.7	α 1.70 ov β 2.47 ov	39.4	α 1.31 m β 1.74-1.62 ov	38.0
4		70.4		69.7		69.0
5	α 1.51 dd 15.0, 10.0 β 1.84-1.73 ov	45.6	α 1.73 ov β 1.32 dd 13.2, 13.2	61.2	α 1.13 ov β 2.28 ddd 13.8, 3.6, 3.6	43.6
6	2.44 dddd 13.1, 10.4, 2.8, 2.5	36.2	2.24 m	34.1	1.74-1.62 ov	36.9

7	5.44 dd 10.2, 2.5	132.2	5.49 dd 9.8, 1.8	134.3	3.85 ddd 8.4, 2.1, 1.4	73.6
8	5.58 dd 10.1, 3.0	132.4	5.35 dd 9.8, 2.6	131.8	5.57 d 1.4	128.3
9		86.5		77.4		138.4
10		43.4		42.9		57.6
11	1.26 s	31.6	1.22 s	31.7	1.26 s	31.8
12	1.66 s	27.7	1.26 s	18.6	1.57 t 1.7	19.7
13	0.91 s	15.4	0.99 s	15.1	1.13 s	15.7
14	4.03 dd 8.6, 1.7	68.9	4.09 dd 12.7, 4.0	75.4		211.6
15	α 2.72 dd 19.4, 1.6 β 3.27 dd 19.4, 8.5	40.4	α 2.00 dddd 12.6, 12.6, 12.6, 5.6 β 1.70 dddd 12.4, 4.1, 2.8, 1.3	31.0	2.07 s	25.6
16		174.3	α 3.85 ddd 11.9, 5.5, 1.3 β 3.73 ddd 12.3, 12.1, 2.9	61.2		

[a]500 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR; [b]400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR

Table S3. ^{1}H and ^{13}C NMR Data for compounds **16** (in C_5D_5N, *J* in Hz)

	δ_H	δ_C
1	1.55, ov	48.8
2α	1.60, ov	29.6
2β	1.02, ov	
3α	1.03, ov	36.1
3β	1.66, ov	
4	1.36, m	33.2
5α	0.81, ov	40.3
5β	2.67, ov	
6	3.10, ov	44.8
7	3.97, dd (9.6, 1.0)	75.2
8	4.51, d (1.0)	90.1
9	-	79.5
10	-	50.0
11	0.89, d (6.5)	23.3
12	1.45, s	25.4
13	1.17, s	12.1
14	-	187.9
15	5.35, d (8.5)	99.6
16	10.43, d (8.5)	189.1

500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR

Table S4. Boltzmann populations and optical rotations of the low-energy conformers of (1*R*,4*R*,6*S*,9*S*,10*S*)-**1** computed at various levels for the B3LYP/6-31G(d) in vacuo optimized MMFF conformers.

Conformer	Boltzmann population	B3LYP/TZVP	BH&HLYP/TZVP	PBE0/TZVP

Conf. A	44.68 %	30.37	15.40	30.56
Conf. B	32.73 %	-57.02	-67.64	-57.03
Conf. C	8.50 %	-32.57	-41.80	-33.08
Conf. D	6.68 %	53.31	41.60	53.43
Conf. E	2.74 %	16.03	0.04	13.74
Conf. F	2.71 %	-75.04	-55.67	-73.31
Average	N/A	-6.01	-17.89	-5.98

Table S5. Boltzmann populations and optical rotations of the low-energy conformers of (1*R*,4*R*,6*S*,9*S*,10*S*)-**1** computed at various levels for the B97D/TZVP PCM/MeCN optimized MMFF conformers.

Conformer	Boltzmann population	B3LYP/TZVP	BH&HLYP/TZVP	CAM-B3LYP/TZVP	PBE0/TZVP
Conf. A	34.44 %	76.32	52.94	59.55	76.58
Conf. B	28.83 %	-32.86	-50.04	-45.43	-34.08
Conf. C	14.32 %	-93.46	-67.81	-79.93	-90.64
Conf. D	5.65 %	26.35	5.68	13.44	23.98
Conf. E	3.65 %	-140.44	-114.12	-129.99	-138.11
Conf. F	2.25 %	-76.04	-43.75	-56.34	-72.62
Conf. G	1.82 %	90.82	75.47	80.66	92.11
Conf. H	1.76 %	-27.77	-40.89	-38.21	-28.31
Conf I	1.50 %	-20.61	-30.88	-27.53	-21.25
Conf J	1.09 %	37.61	14.00	20.99	35.20
Average	N/A	-0.69	-10.90	-9.10	-0.53

Table S6. Boltzmann populations and optical rotations of the low-energy conformers of (1*R*,4*R*,6*S*,9*S*,10*S*)-**1** computed at various levels for the CAM-B3LYP/TZVP PCM/MeCN optimized MMFF conformers.

Conformer	Boltzmann population	B3LYP/TZVP	BH&HLYP/TZVP	CAM-B3LYP/TZVP	PBE0/TZVP
Conf. A	40.64 %	70.33	47.08	53.69	70.27
Conf. B	25.45 %	-44.11	-61.48	-56.57	-45.39
Conf. C	8.92 %	86.01	69.89	75.37	86.72
Conf. D	8.68 %	22.43	2.69	10.31	19.83
Conf. E	5.86 %	-24.94	-36.87	-32.64	-25.99
Conf. F	1.99 %	-85.30	-63.12	-73.18	-82.92
Conf. G	1.02 %	-34.53	-47.23	-44.60	-35.39

Conf. H	0.99 %	-70.96	-41.68	-52.90	-68.12
Conf I	0.97 %	14.56	-6.84	-0.51	13.14
Average	N/A	24.23	5.90	11.31	23.68

Table S7. Boltzmann populations and optical rotations of the low-energy conformers of (1*R*,4*S*,6*S*,9*S*,10*S*)-**5** computed at various levels for the B3LYP/6-31G(d) in vacuo optimized MMFF conformers.

Conformer	Boltzmann population	B3LYP/TZVP	BH&HLYP/TZVP	PBE0/TZVP
Conf. A	45.52 %	-26.25	-38.94	-26.28
Conf. B	32.60 %	-51.33	-59.16	-50.64
Conf. C	6.68 %	5.31	-5.83	4.77
Conf. D	6.15 %	-60.75	-65.38	-59.71
Conf. E	5.10 %	-15.46	-22.81	-15.52
Conf. F	1.48 %	-97.93	-82.33	-96.59
Conf G	1.29 %	-75.58	-63.60	-74.60
Conf H	1.18 %	-25.21	-29.56	-24.92
Average	N/A	-35.57	-44.97	-35.30

Table S8. Boltzmann populations and optical rotations of the low-energy conformers of (1*R*,4*S*,6*S*,9*S*,10*S*)-**5** computed at various levels for the B97D/TZVP PCM/MeCN optimized MMFF conformers.

Conformer	Boltzmann population	B3LYP/TZVP	BH&HLYP/TZVP	CAM-B3LYP/TZVP	PBE0/TZVP
Conf. A	30.27 %	-3.00	-17.24	-12.69	-2.86
Conf. B	28.51 %	-3.88	-18.96	-13.54	-3.33
Conf. C	26.23 %	20.35	-0.88	5.19	20.05
Conf. D	5.24 %	-92.37	-73.01	-85.62	-89.88
Conf. E	4.71 %	-68.77	-54.68	-66.78	-66.85
Conf. F	1.87 %	15.28	7.40	10.82	16.02
Conf. G	1.67 %	14.16	5.45	9.67	15.27
Conf. H	1.50 %	36.59	22.25	27.07	36.98
Average	N/A	-3.68	-16.69	-13.20	-3.30

Table S9 Boltzmann populations and optical rotations of the low-energy conformers of (1*R*,4*S*,6*S*,9*S*,10*S*)-**5** computed at various levels for the CAM-B3LYP/TZVP PCM/MeCN optimized MMFF conformers.

Conformer	Boltzmann population	B3LYP/TZVP	BH&HLYP/TZVP	CAM-B3LYP/TZVP	PBE0/TZVP
Conf. A	35.05 %	7.45	-12.94	-7.17	6.94
Conf. B	33.51 %	-18.61	-32.27	-27.40	-18.13
Conf. C	9.21 %	-19.13	-31.52	-27.80	-18.95
Conf. D	7.61 %	29.81	14.60	19.78	29.69
Conf. E	7.37 %	5.70	-3.34	0.99	6.42
Conf. F	2.56 %	-97.40	-77.80	-89.97	-95.74
Conf. G	2.52 %	-72.65	-58.96	-70.33	-71.70
Conf. H	2.17 %	5.13	-2.67	0.60	5.60
Average	N/A	-6.92	-20.93	-16.75	-6.80

Table S10 Boltzmann populations and optical rotations of the low-energy conformers of (1*R*,4*S*,6*R*,7*S*,10*S*)-**14** computed at various levels for the B3LYP/6-31G(d) in vacuo optimized MMFF conformers.

Conformer	Boltzmann population	B3LYP/TZVP	BH&HLYP/TZVP	PBE0/TZVP
Conf. A	42.06 %	-103.56	-66.97	-100.65
Conf. B	36.46 %	-125.02	-88.01	-122.65
Conf. C	4.20 %	-143.02	-106.64	-140.85
Conf. D	3.44 %	-127.68	-89.73	-124.95
Conf. E	3.05 %	-58.35	-31.21	-57.45
Conf. F	2.43 %	-83.47	-53.66	-82.97
Conf G	2.41 %	-122.41	-86.48	-119.67
Conf H	2.13 %	-160.04	-137.19	-161.84
Conf I	1.61 %	-151.48	-127.42	-152.55
Average	N/A	-114.68	-78.88	-112.30

Table S11 Boltzmann populations and optical rotations of the low-energy conformers of (1*R*,4*S*,6*R*,7*S*,10*S*)-**14** computed at various levels for the B97D/TZVP PCM/MeCN optimized MMFF conformers.

Conformer	Boltzmann population	B3LYP/TZVP	BH&HLYP/TZVP	CAM-B3LYP/TZVP	PBE0/TZVP
Conf. A	23.15 %	-137.81	-91.95	-98.75	-134.02

Conf. B	21.13 %	-117.30	-73.82	-80.32	-113.52
Conf. C	19.55 %	-135.13	-90.75	-96.65	-131.63
Conf. D	8.43 %	-107.35	-69.95	-74.52	-106.00
Conf. E	6.56 %	-86.49	-51.38	-55.66	-85.14
Conf. F	5.55 %	-107.95	-70.85	-74.99	-106.75
Conf. G	4.45 %	-157.15	-112.01	-119.32	-153.58
Conf. H	3.49 %	-137.49	-94.42	-101.54	-133.88
Conf I	3.46 %	-155.27	-110.99	-117.70	-151.87
Conf J	1.01 %	-133.73	-111.16	-115.32	-135.41
Average	N/A	-126.41	-83.76	-89.80	-123.29

Table S12 Boltzmann populations and optical rotations of the low-energy conformers of (1*R*,4*S*,6*R*,7*S*,10*S*)-**14** computed at various levels for the CAM-B3LYP/TZVP PCM/MeCN optimized MMFF conformers.

Conformer	Boltzmann population	B3LYP/TZVP	BH&HLYP/TZVP	CAM-B3LYP/TZVP	PBE0/TZVP
Conf. A	25.45 %	-125.73	-79.86	-87.63	-121.82
Conf. B	24.61 %	-145.44	-97.63	-105.22	-141.59
Conf. C	9.05 %	-165.77	-117.76	-126.41	-161.95
Conf. D	8.62 %	-145.66	-99.94	-108.58	-141.86
Conf. E	8.03 %	-95.98	-57.55	-63.62	-94.29
Conf. F	7.17 %	-119.19	-77.74	-84.15	-117.46
Conf. G	6.07 %	-146.26	-97.30	-105.64	-142.17
Conf. H	2.51 %	-165.14	-116.74	-125.77	-161.23
Conf I	2.30 %	-117.03	-75.55	-82.25	-115.22
Conf J	1.63 %	-131.94	-107.36	-112.74	-133.14
Conf K	1.60 %	-150.49	-123.46	-128.81	-151.74
Average	N/A	-135.90	-90.80	-98.41	-132.57