Supporting Information

Primary Aminomethyl Derivatives of Kaempferol: hydrogen-bond assisted synthesis, anticancer activity and spectral properties

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Content

Figure S1-S5

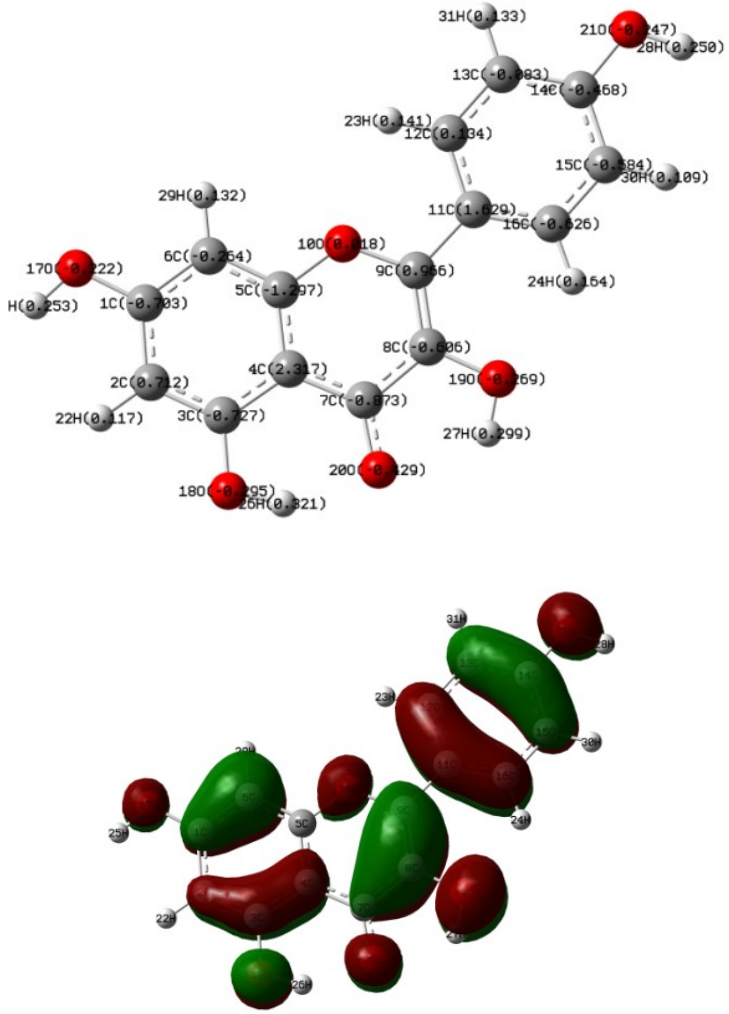


Figure S1. Computing result showing the Mulliken charge distribution (upper) and HOMO (down) for kaempferol based on B3LYP/6-311+G(d,p) level using Gaussian 09 package.

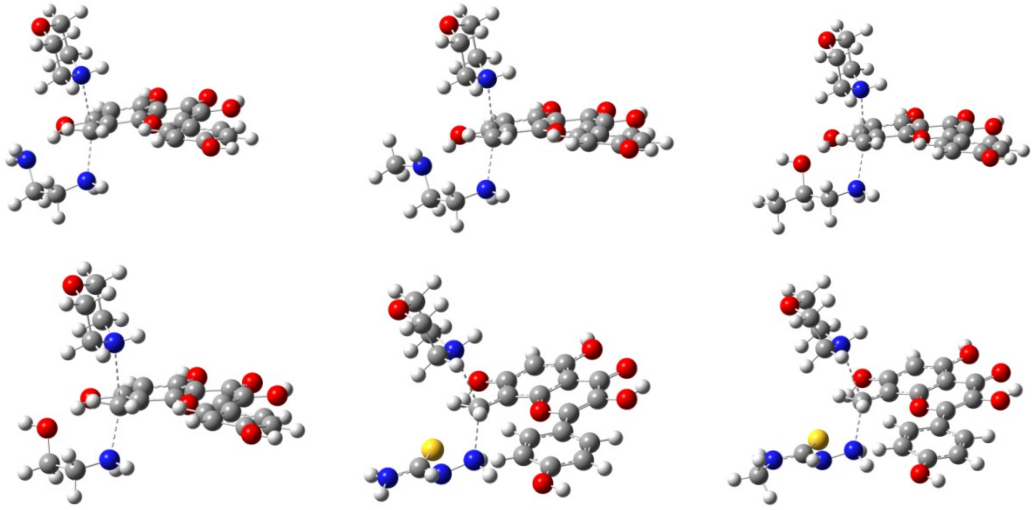
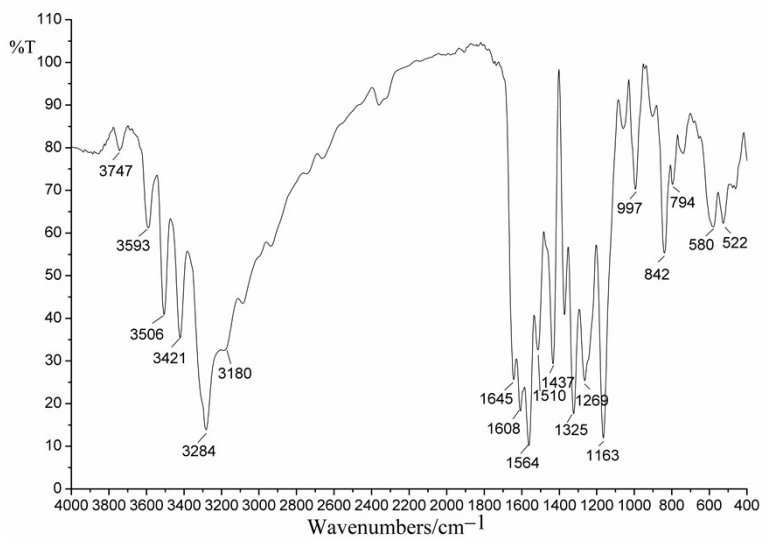
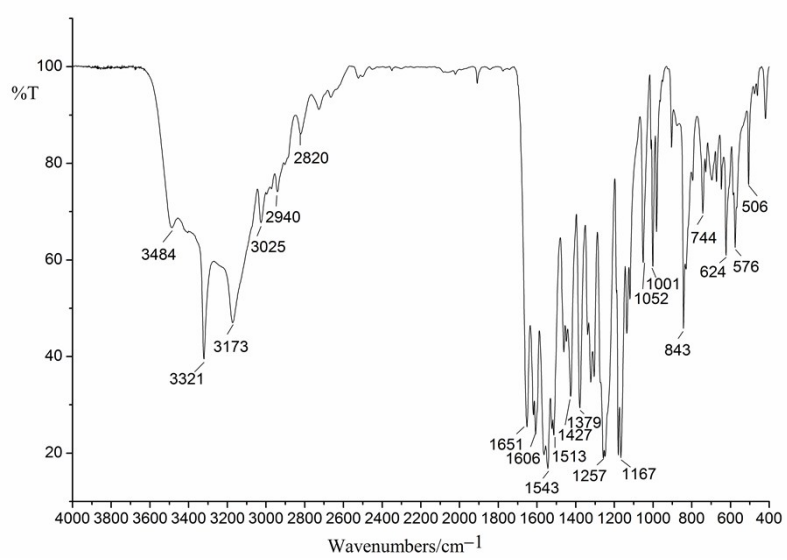


Figure S2. The optimized structures of the amine exchange transition states for morpholine···kaempferol···amines.

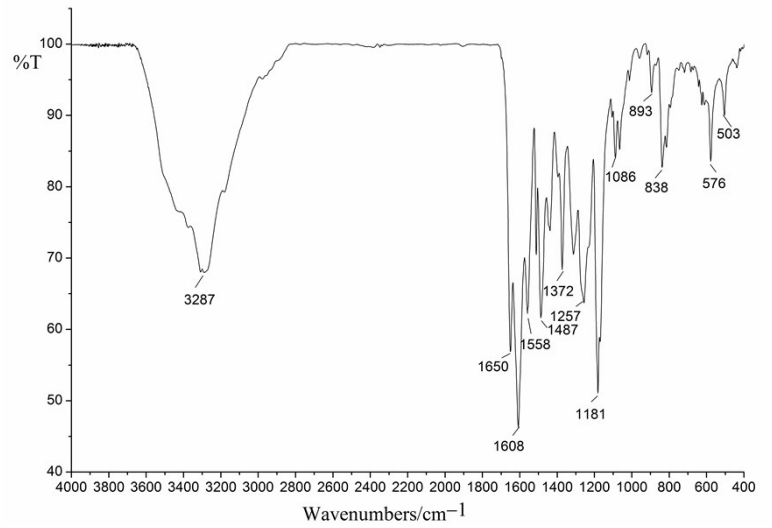
IR, NMR and MS of compounds 5a-h



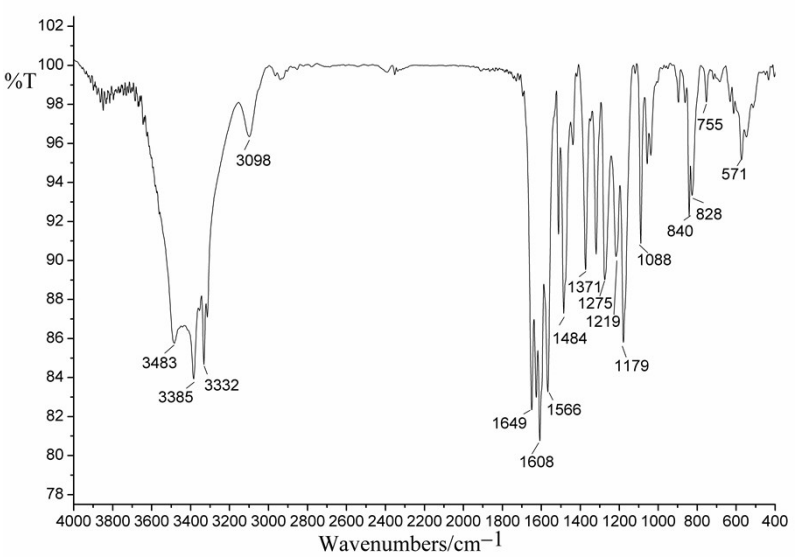
IR of 5a



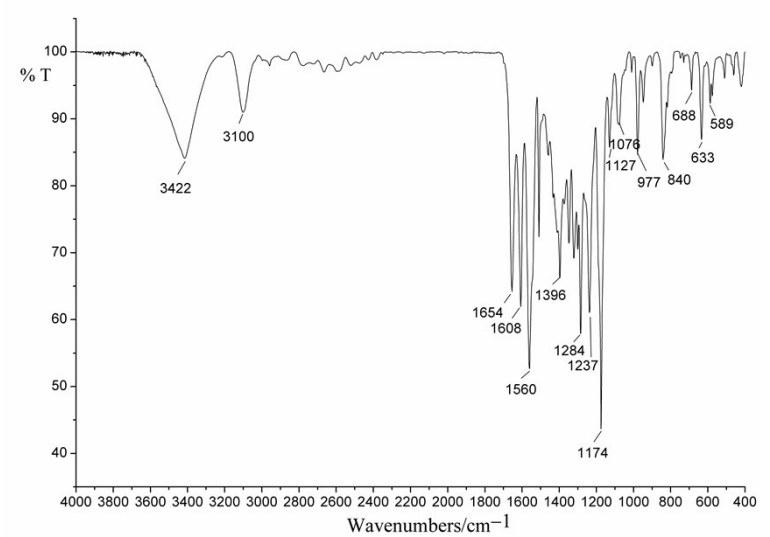
IR of 5b



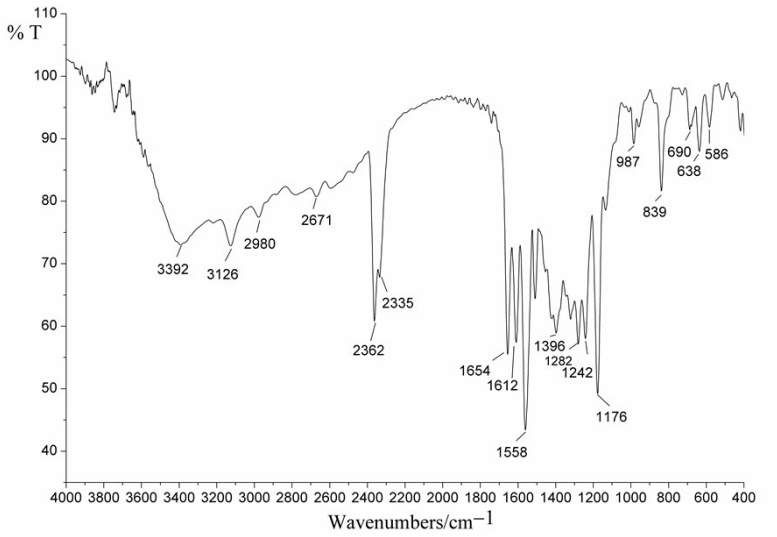
IR of 5c



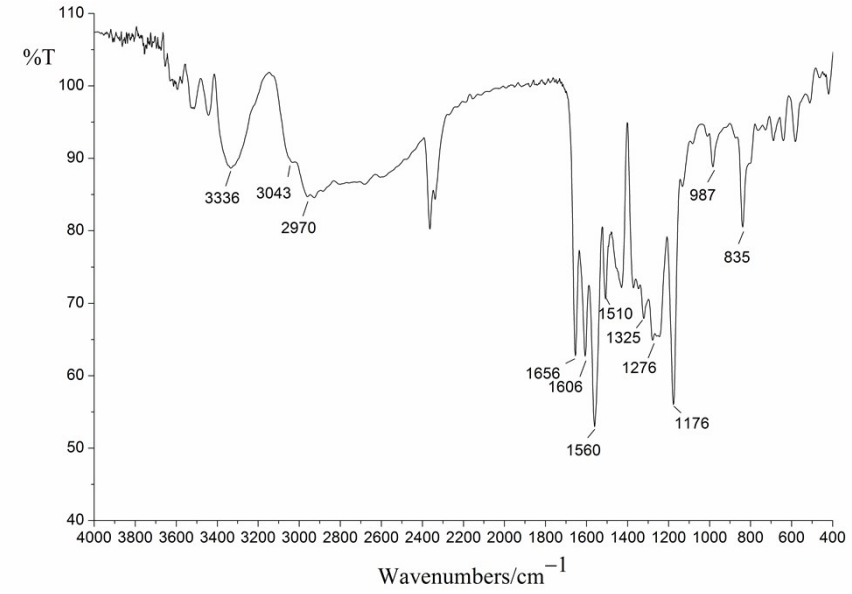
IR of 5d



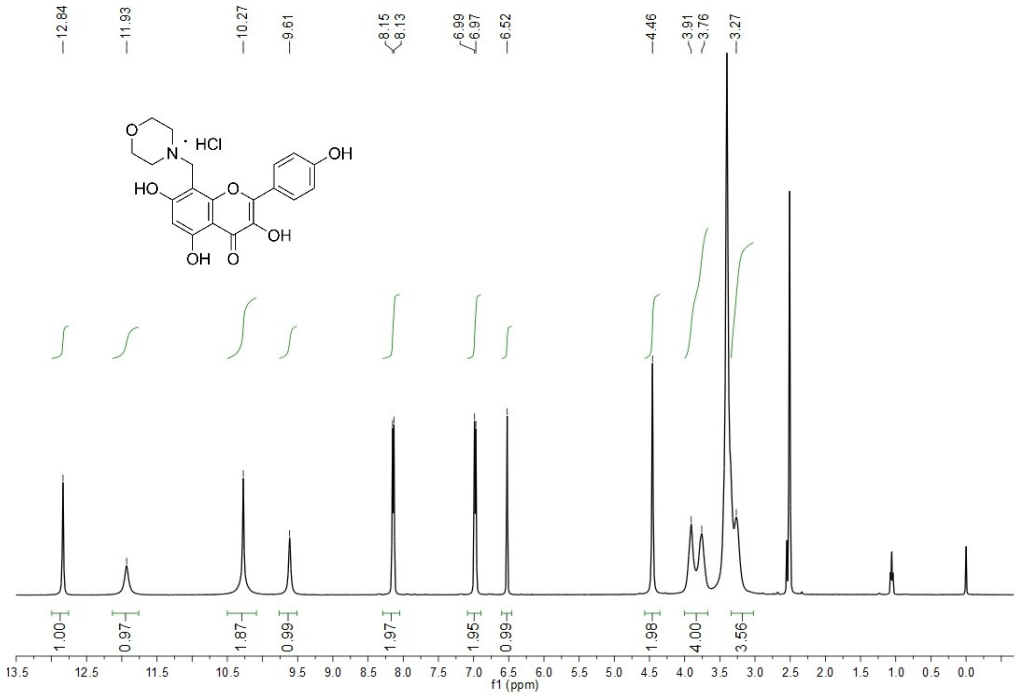
IR of 5e



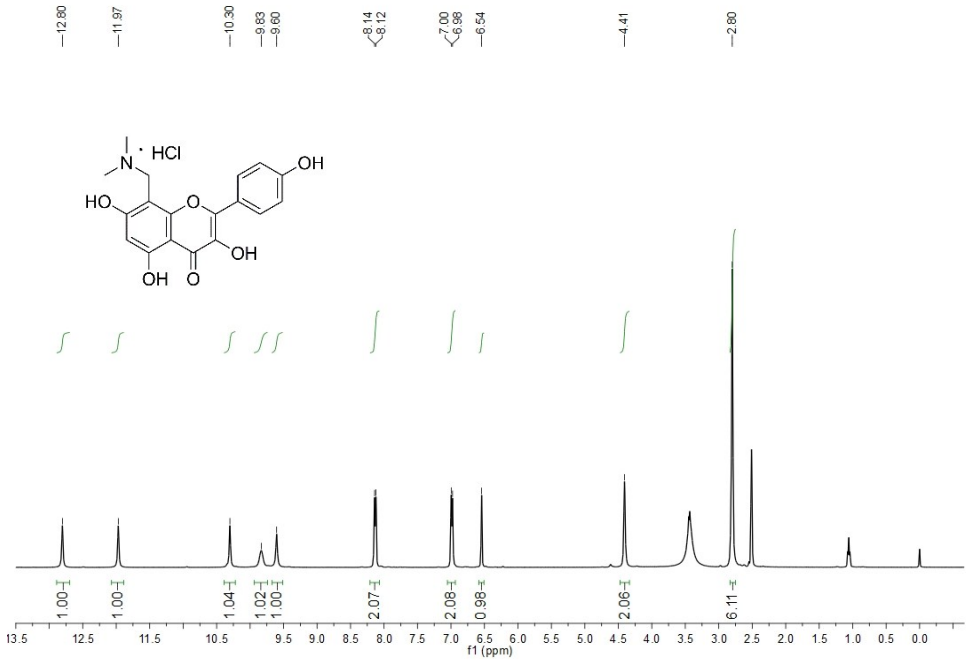
IR of 5f



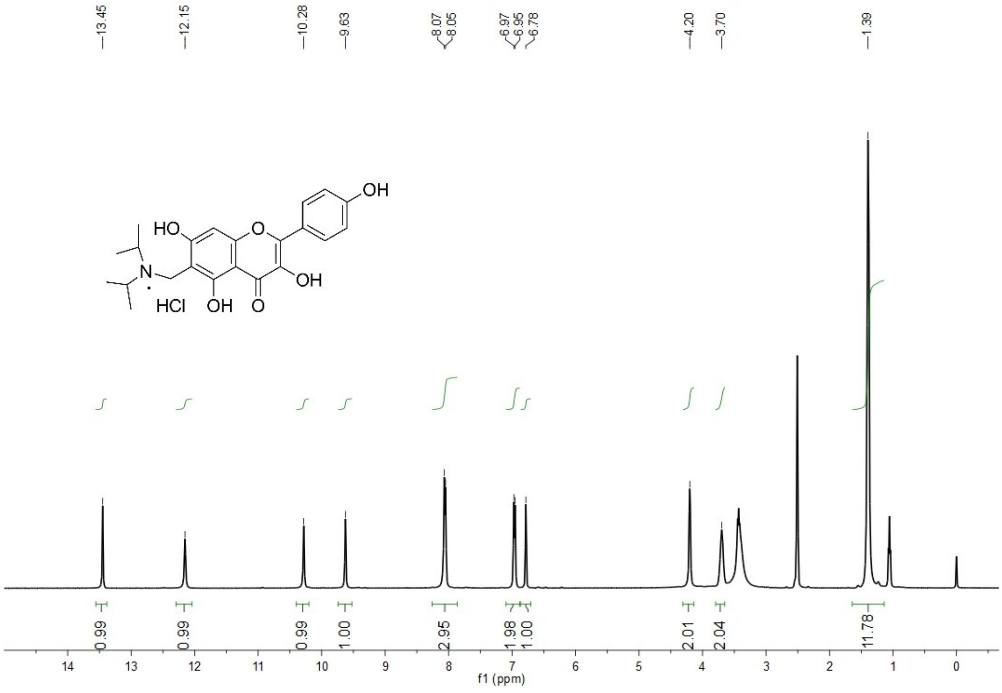
IR of 5h



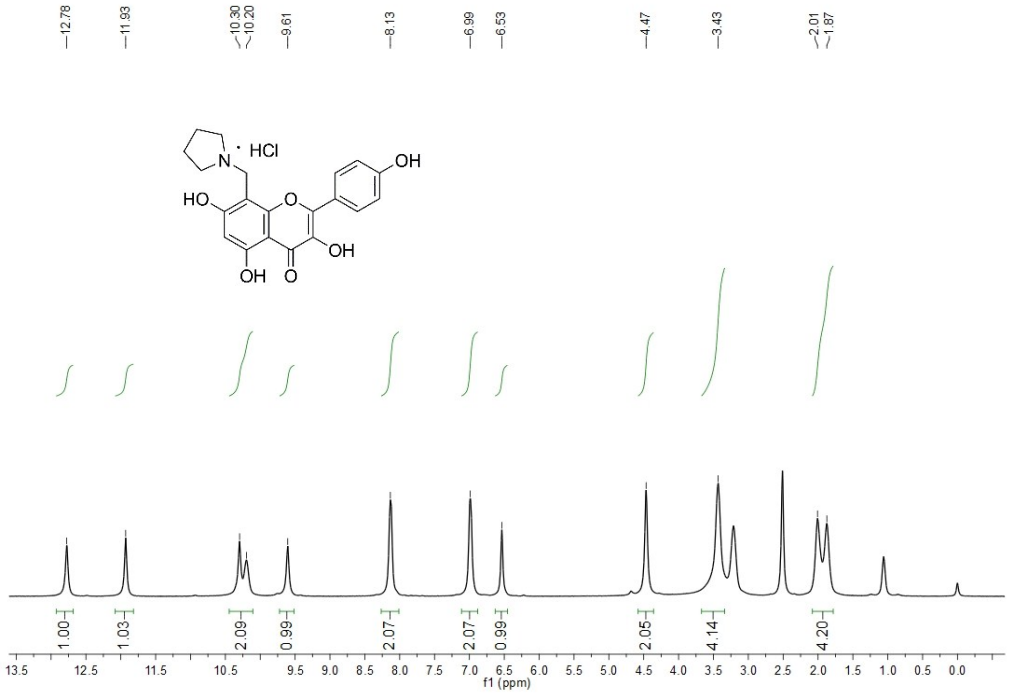
H NMR of 4a



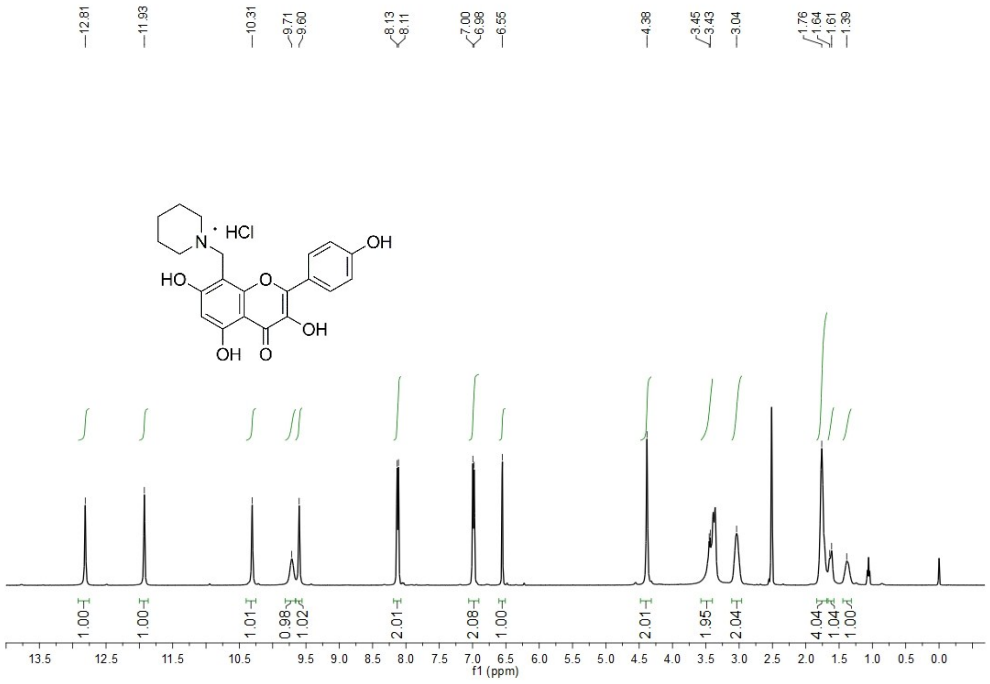
H NMR of 4b



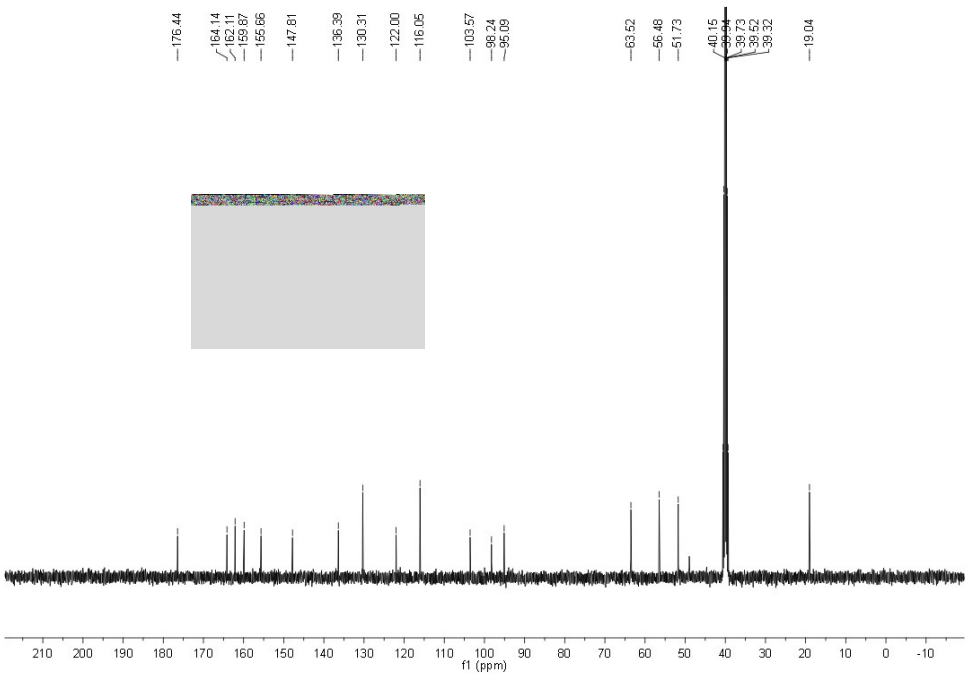
H NMR of 4c



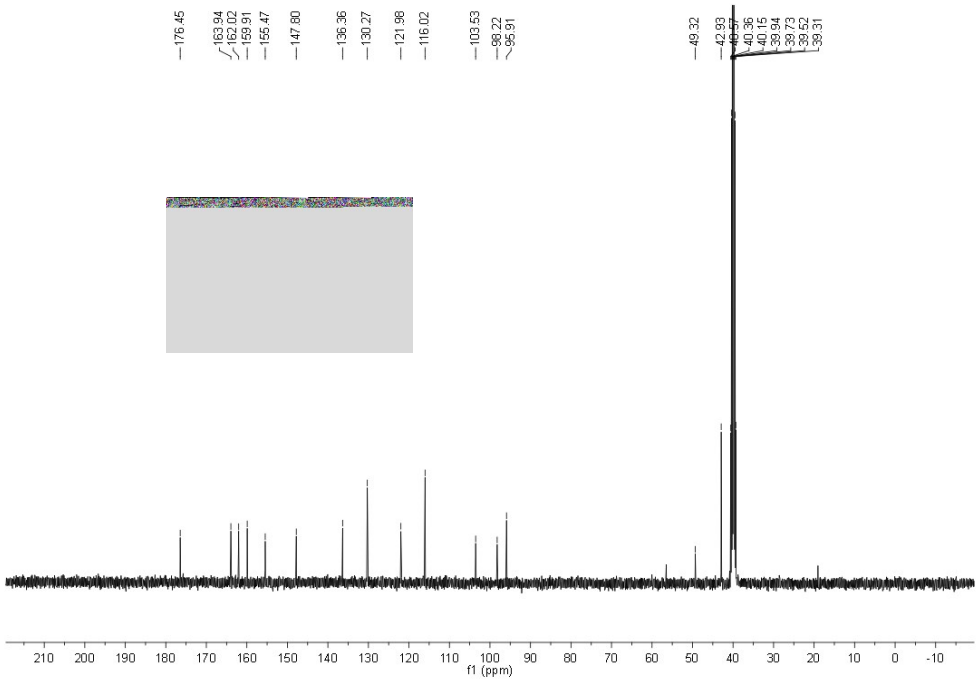
H NMR of 4d



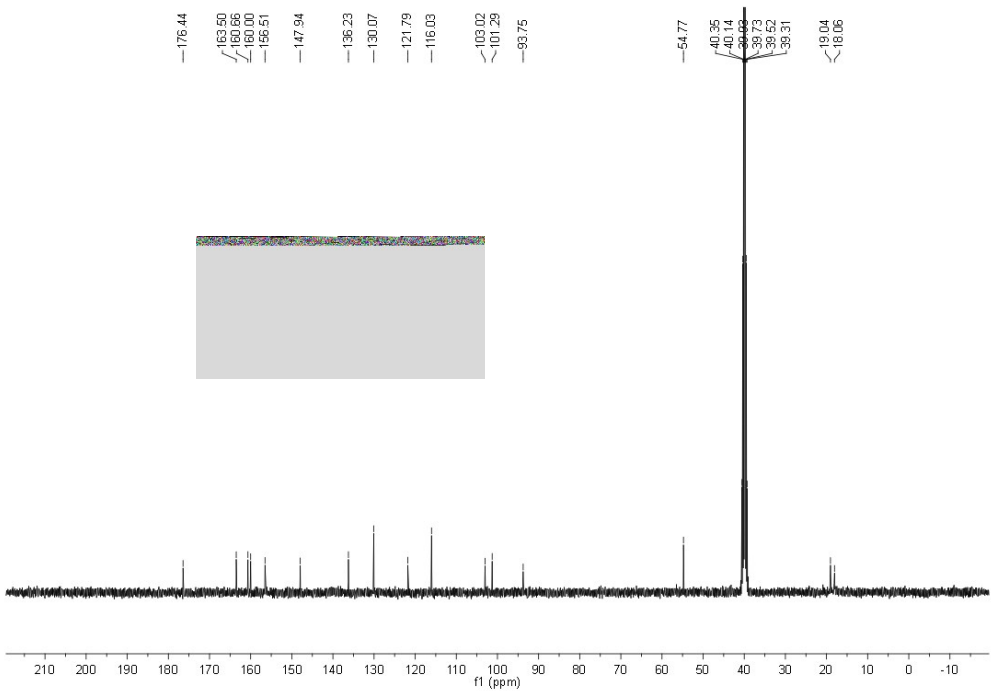
H NMR of 4e



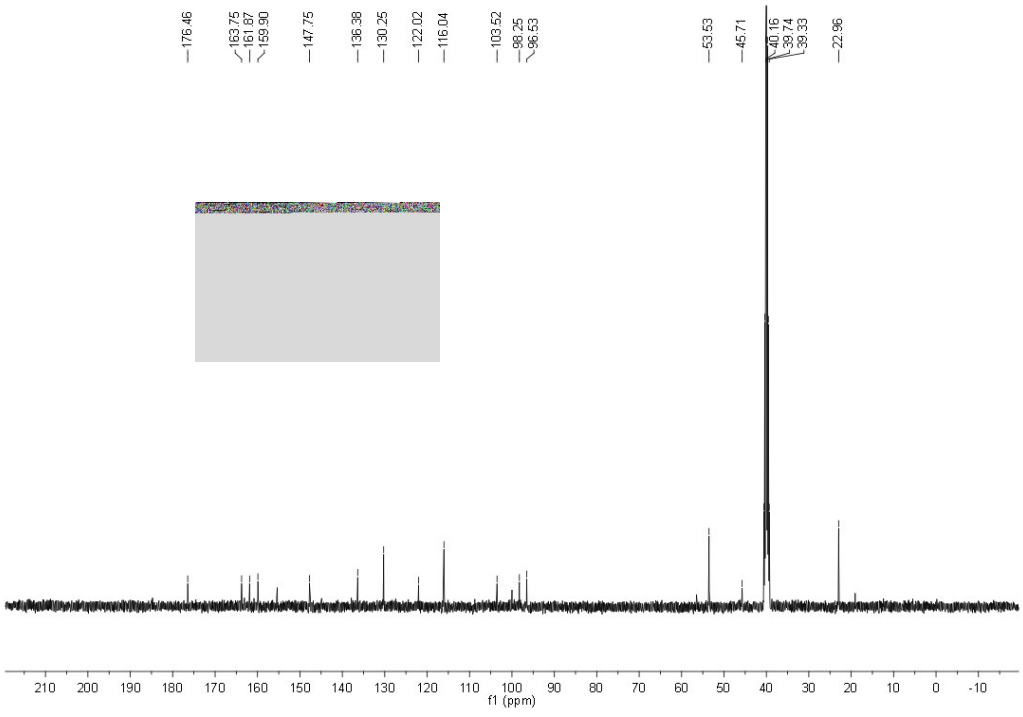
C NMR of 4a



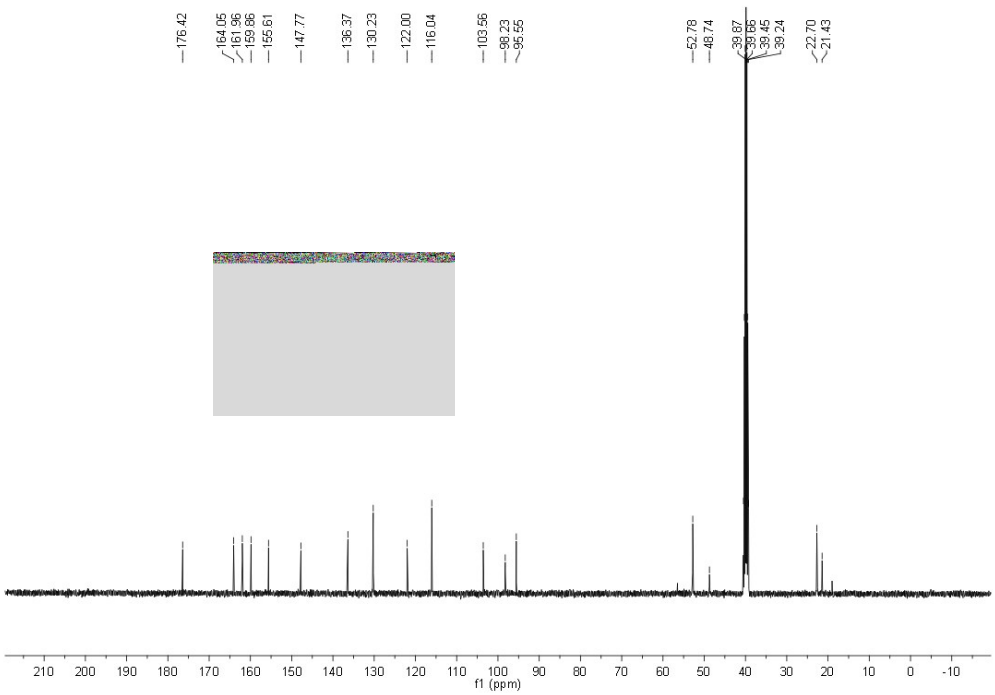
C NMR of 4b



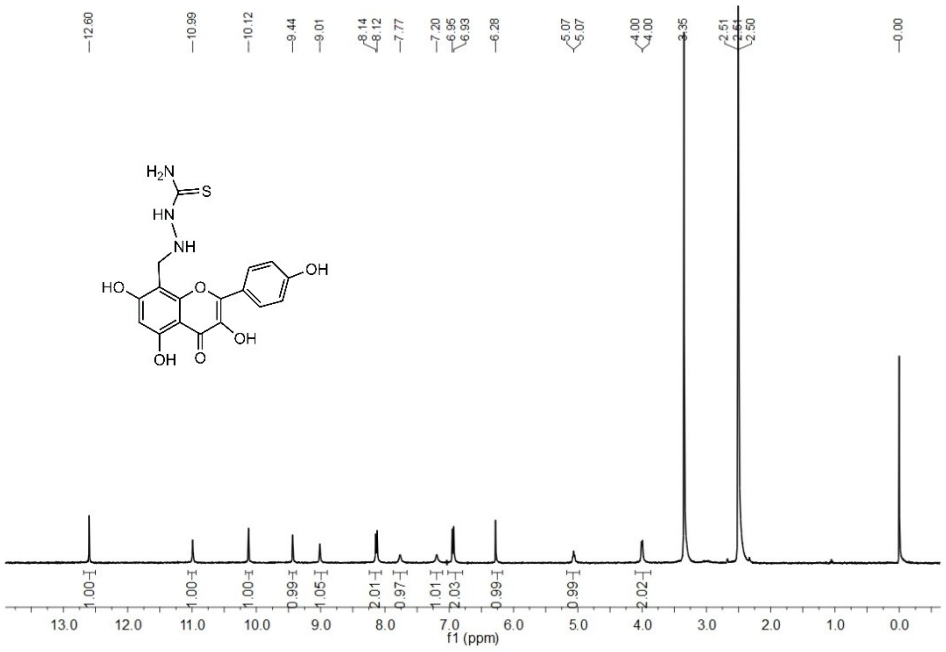
C NMR of 4c



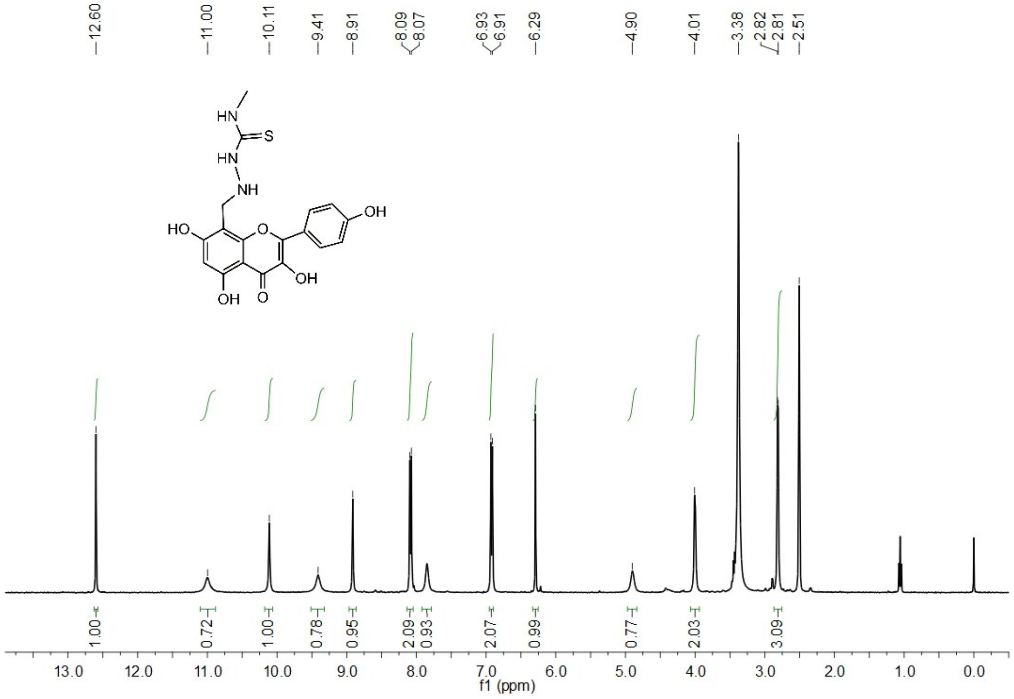
C NMR of 4d



C NMR of 4e



^{1}H NMR of 5a



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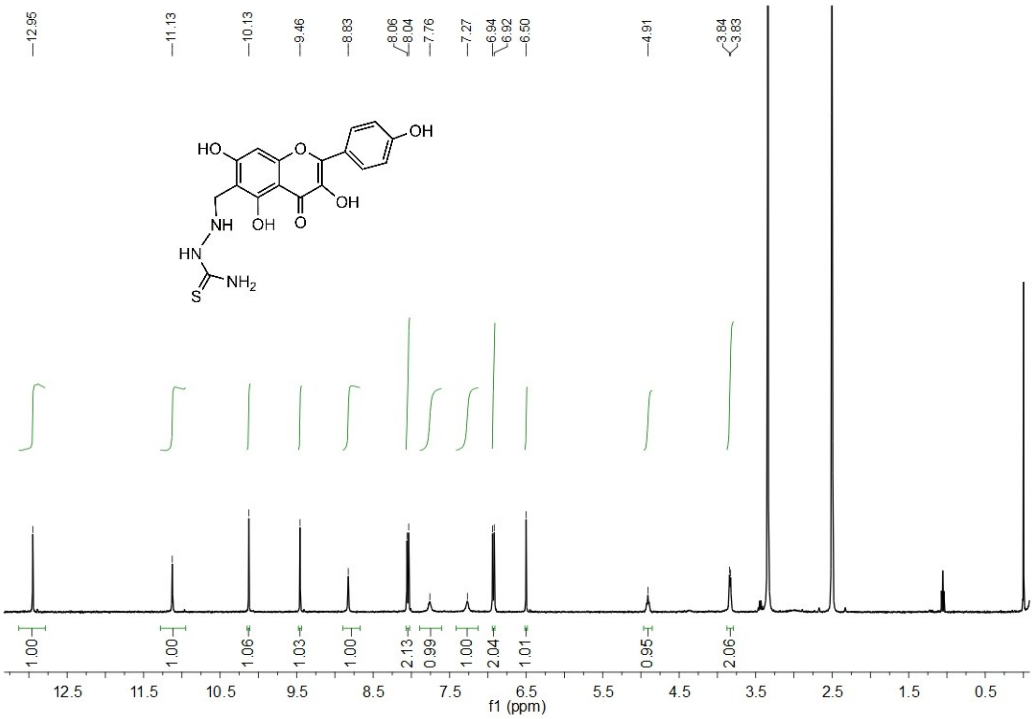

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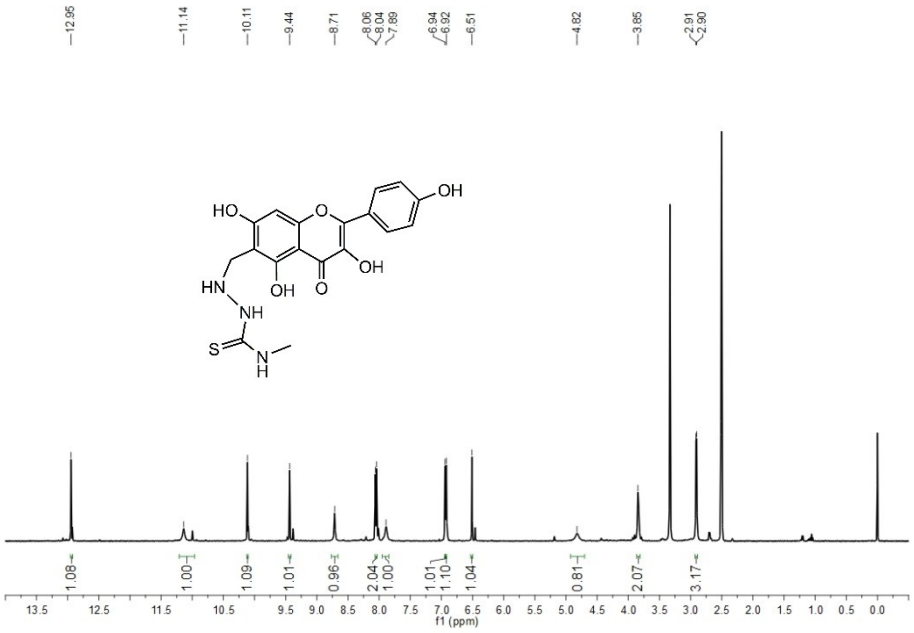
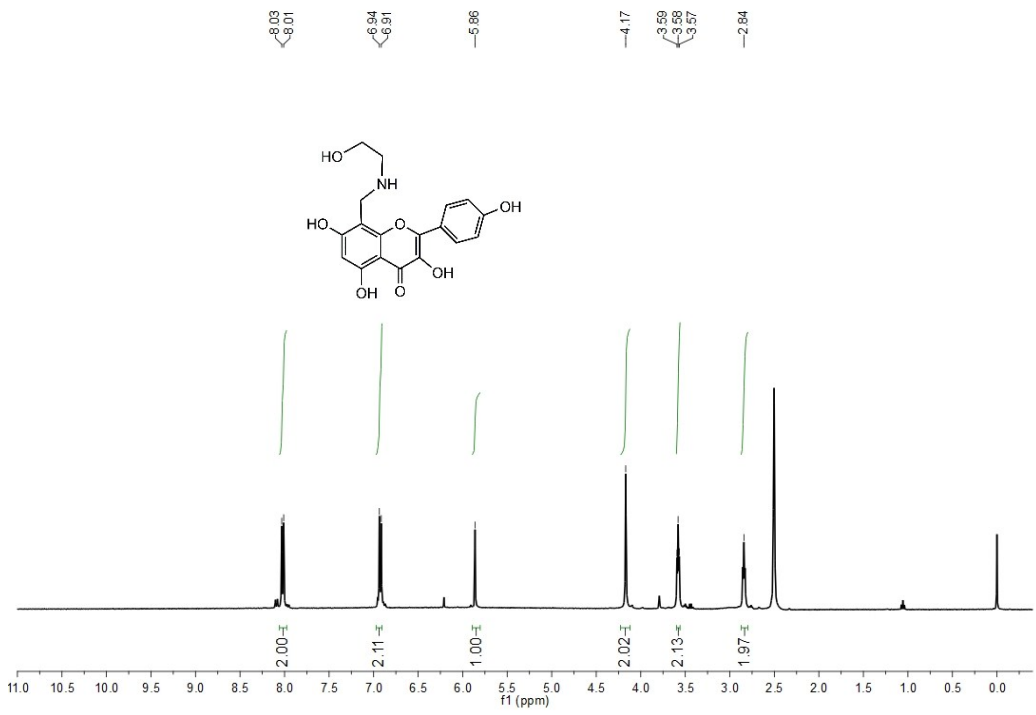
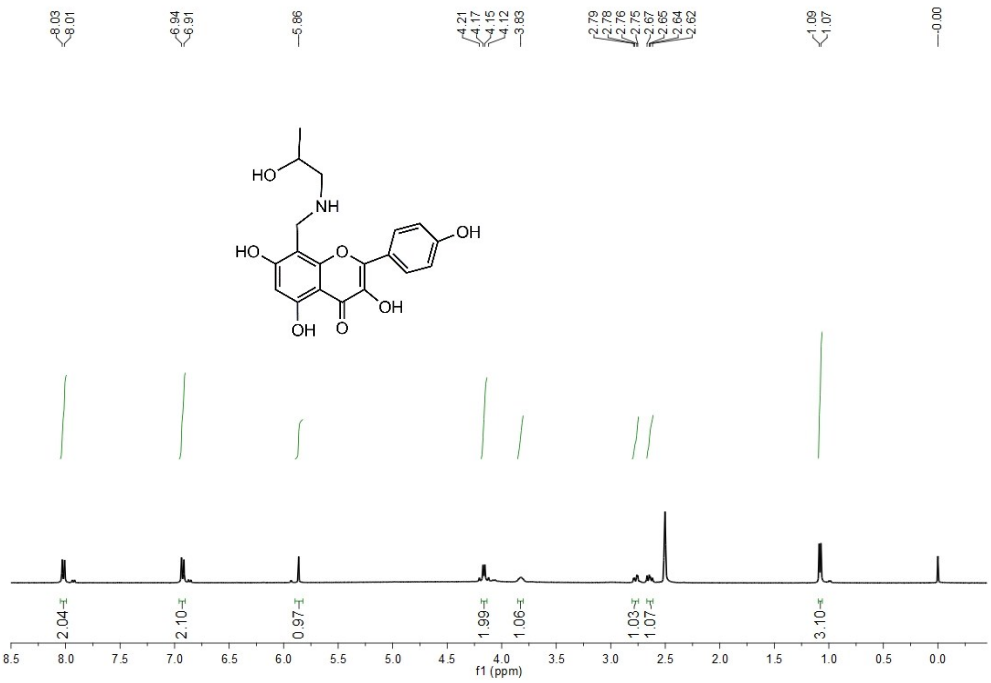


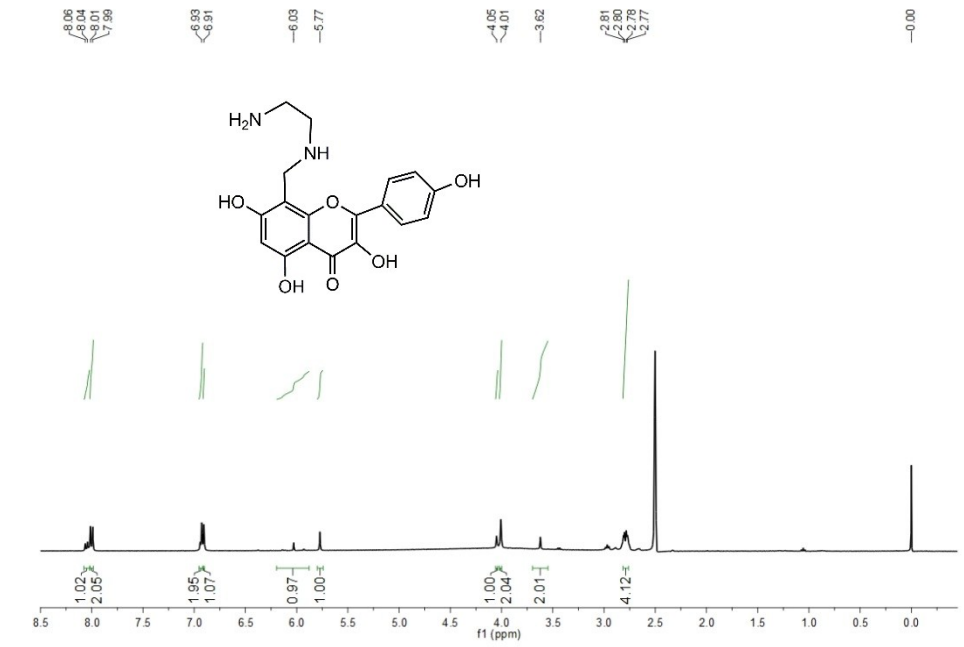
^{1}H NMR of 5d



^{1}H NMR of 5e



^{1}H NMR of 5f



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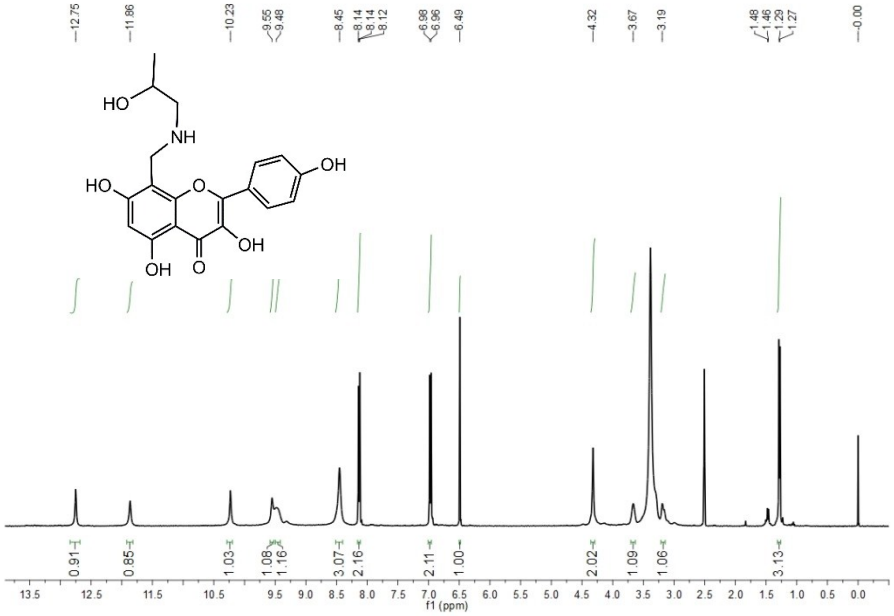

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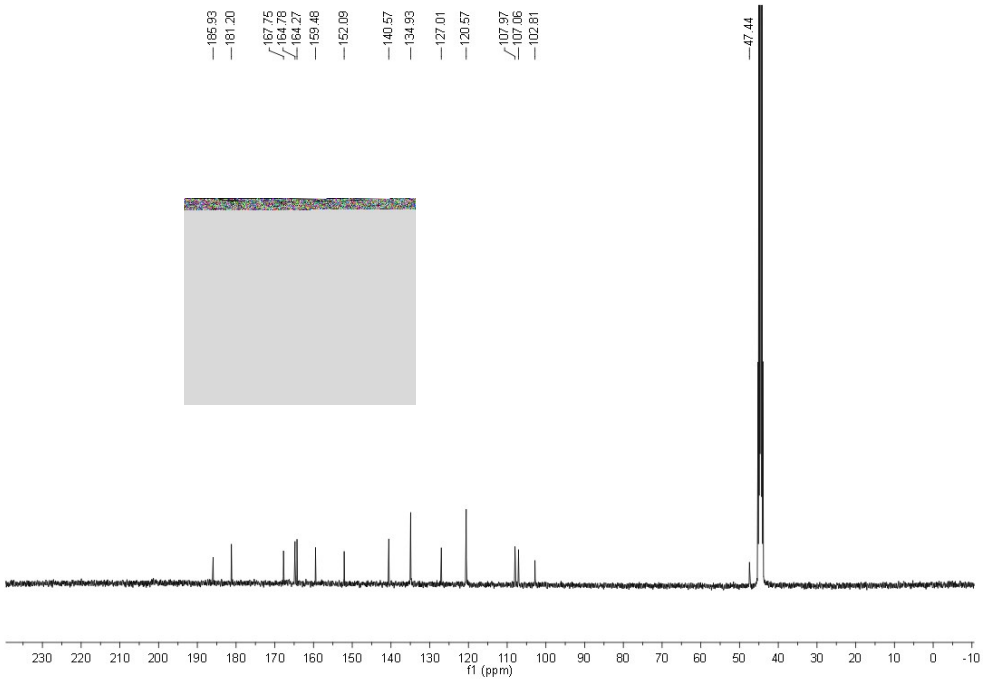

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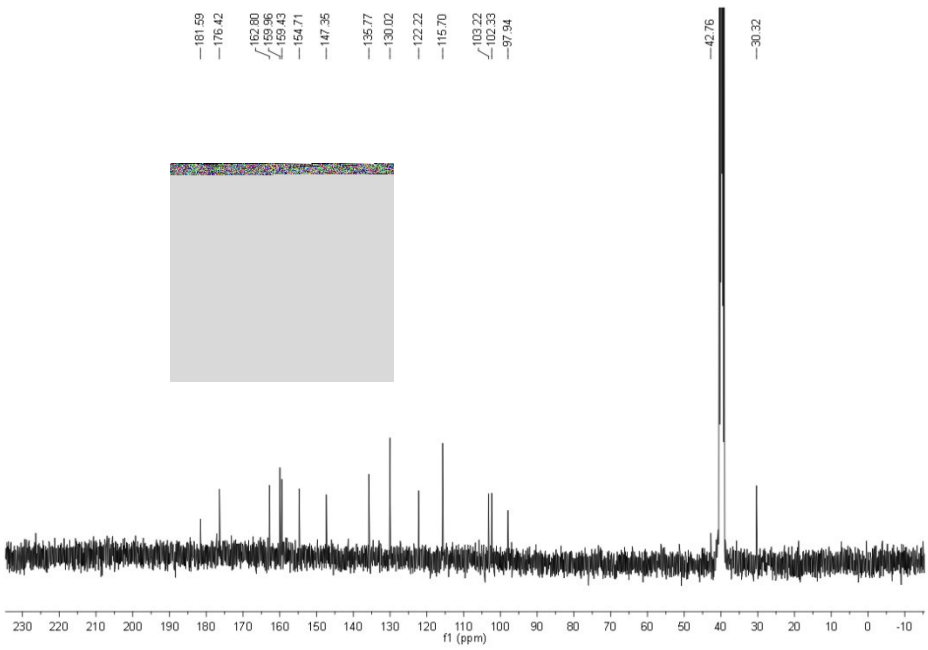

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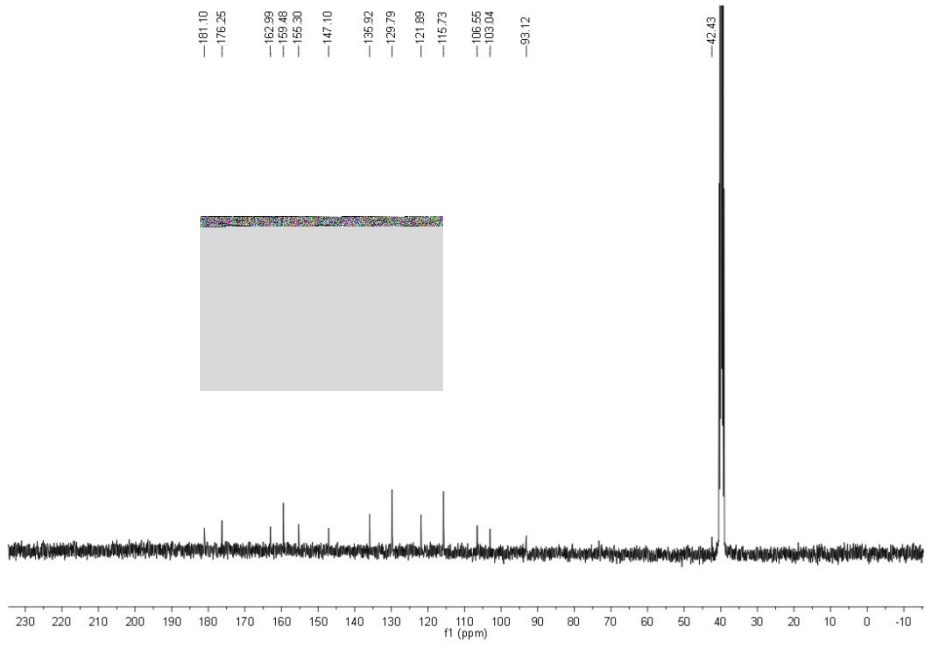

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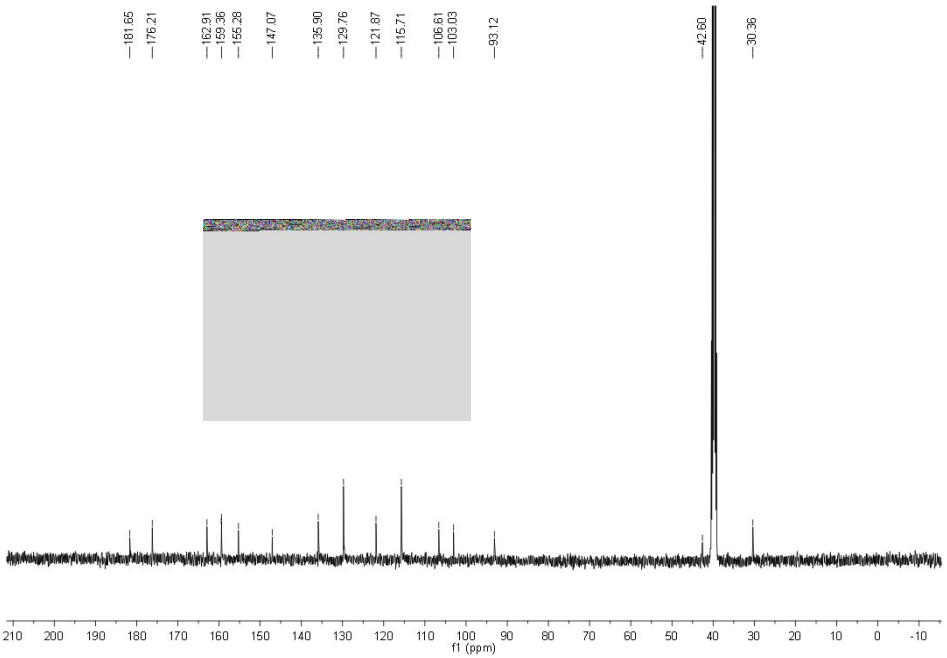
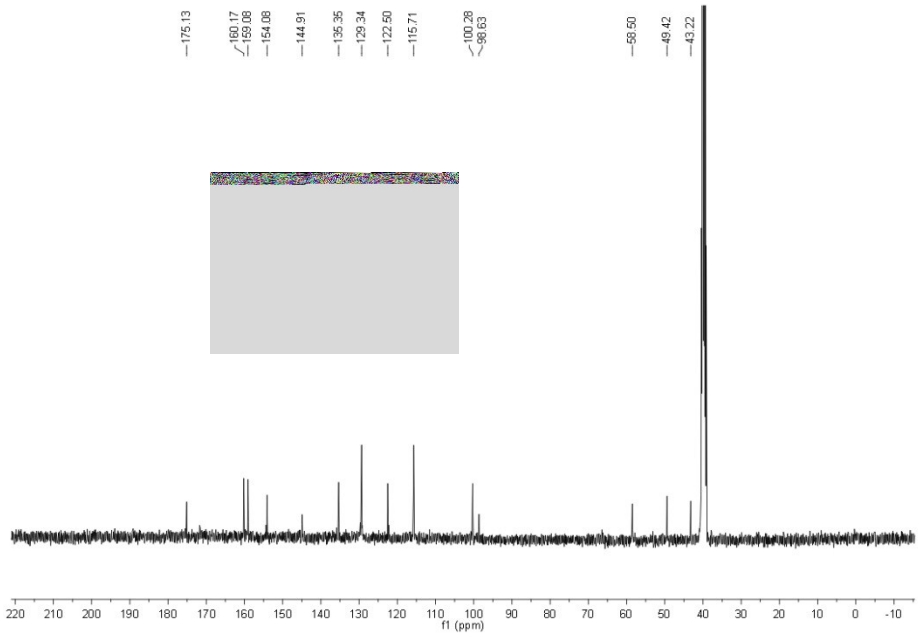


^{13}C NMR of 5d



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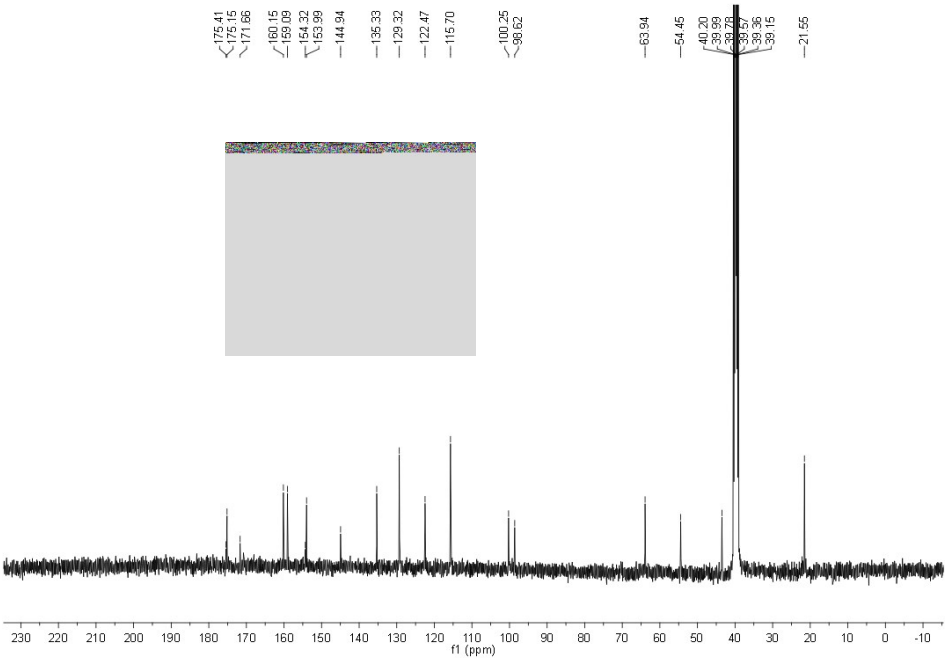
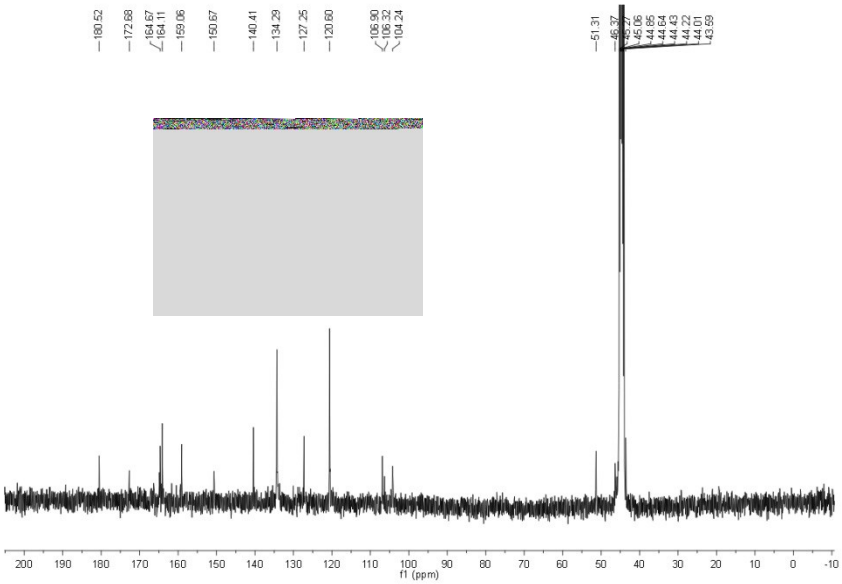
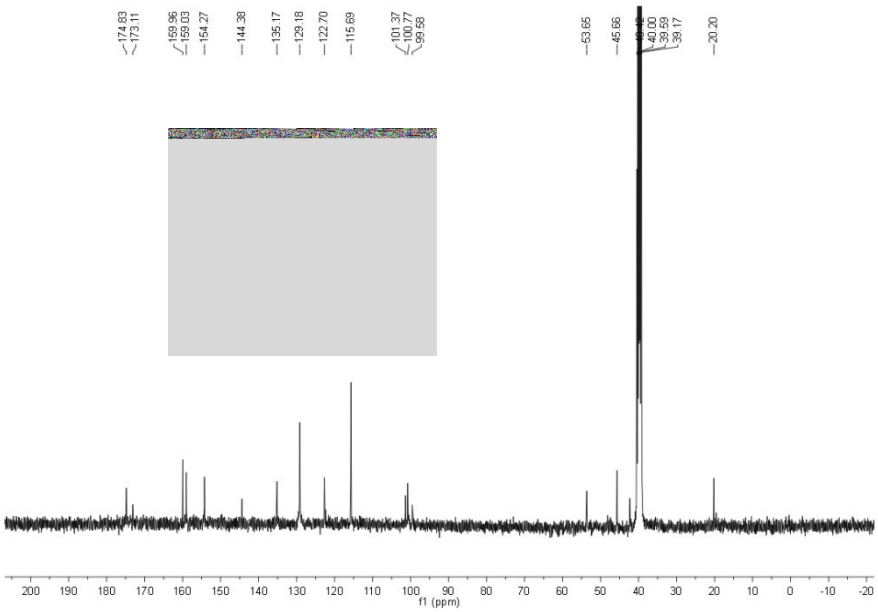


^{13}C NMR of 5f



^{13}C NMR of 5g



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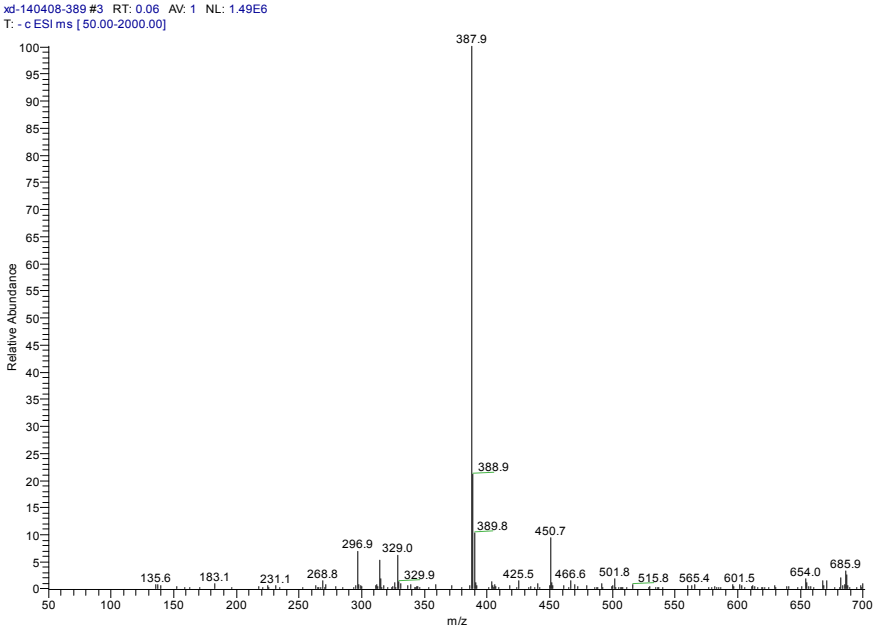
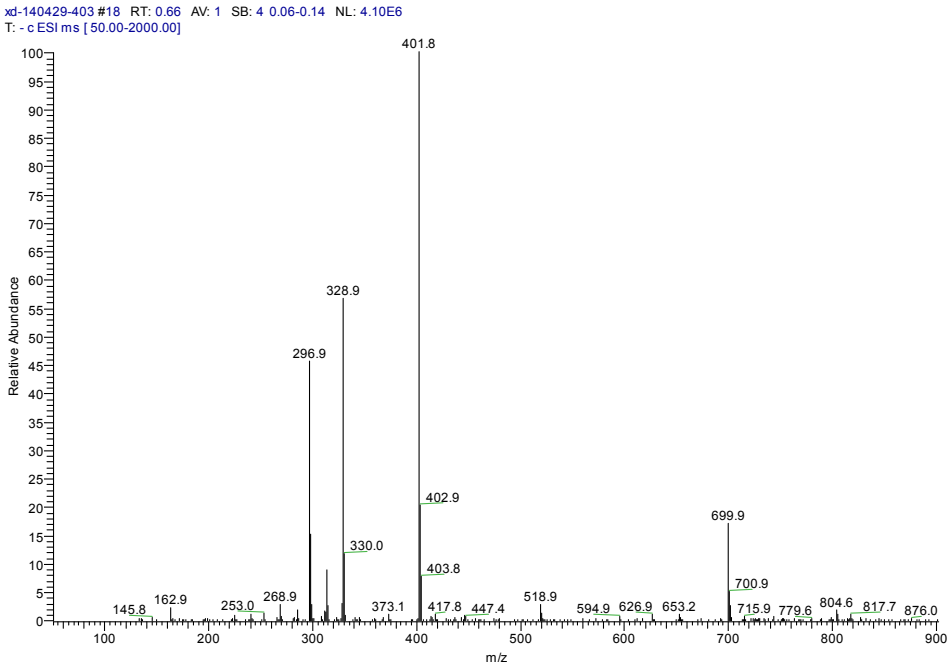
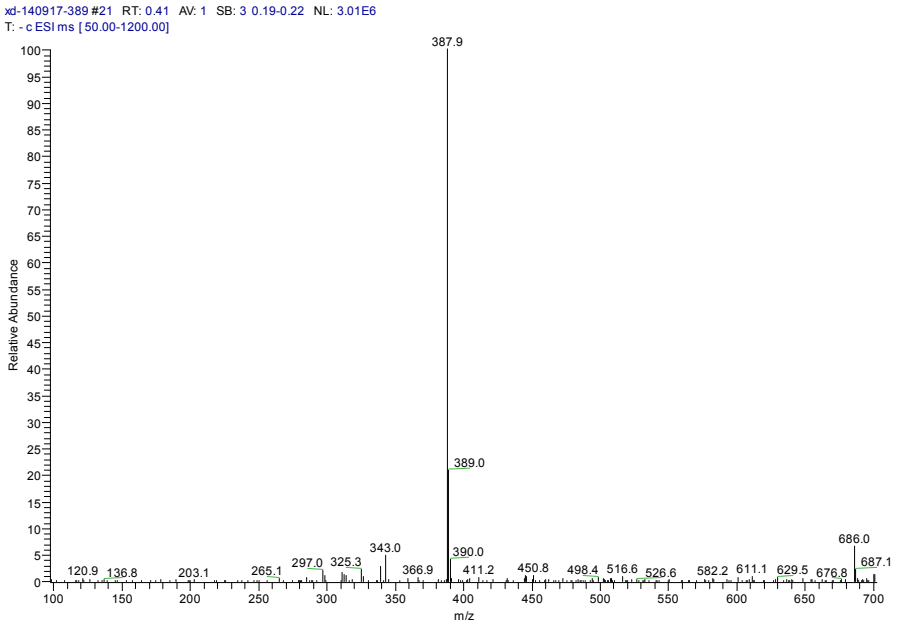


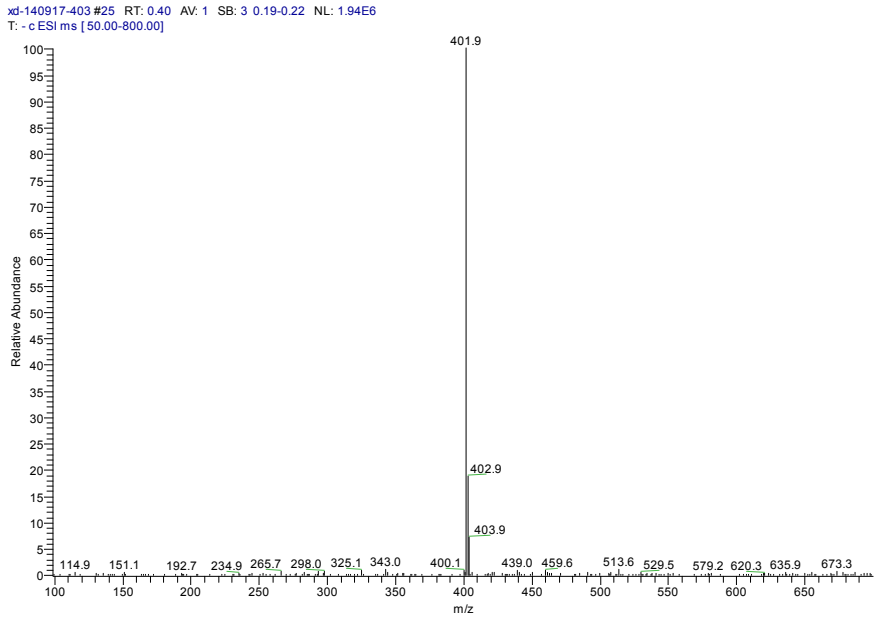
MS of 5a



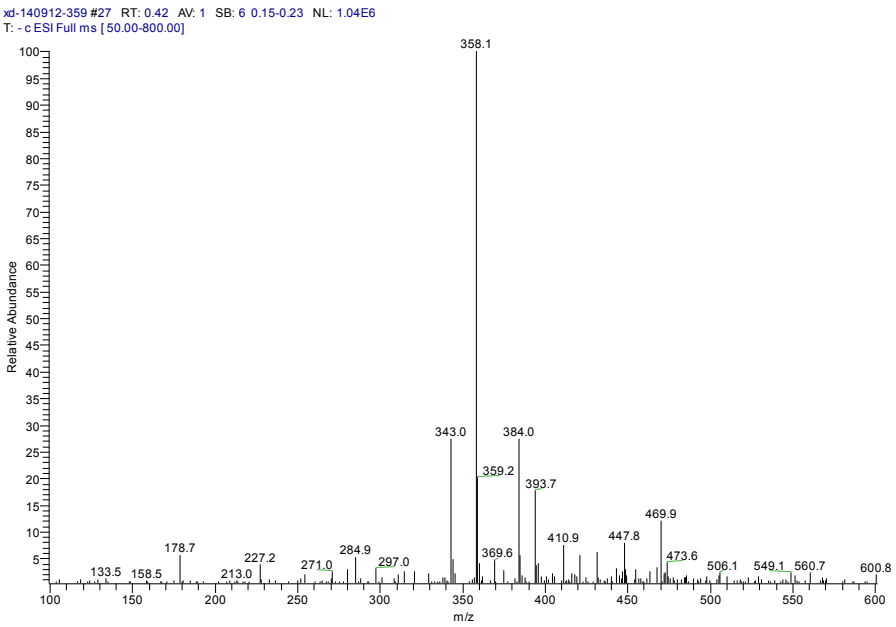
MS of 5b



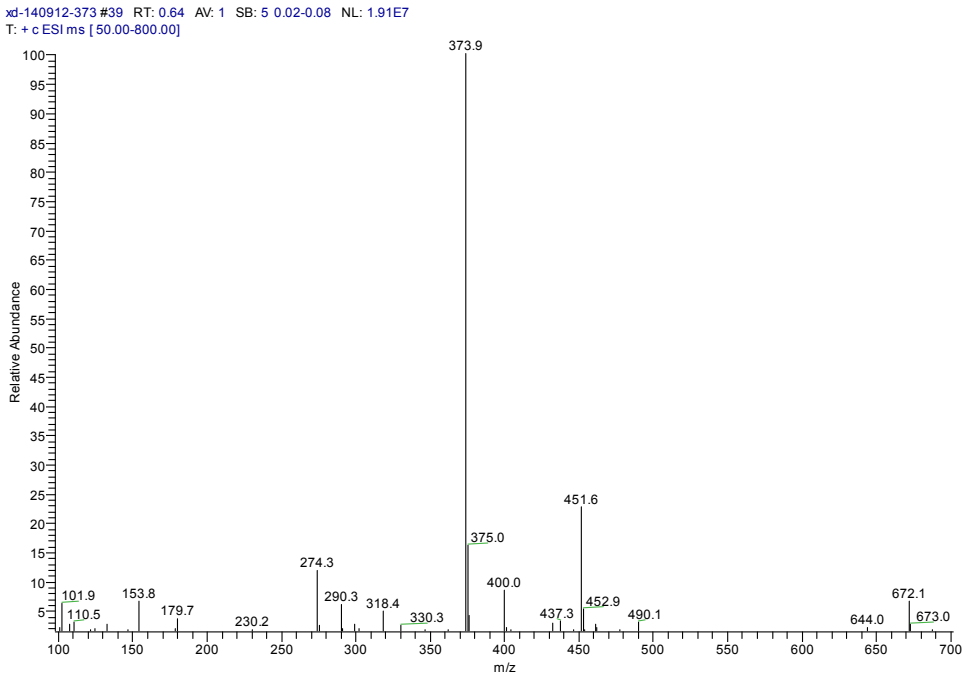
MS of 5c



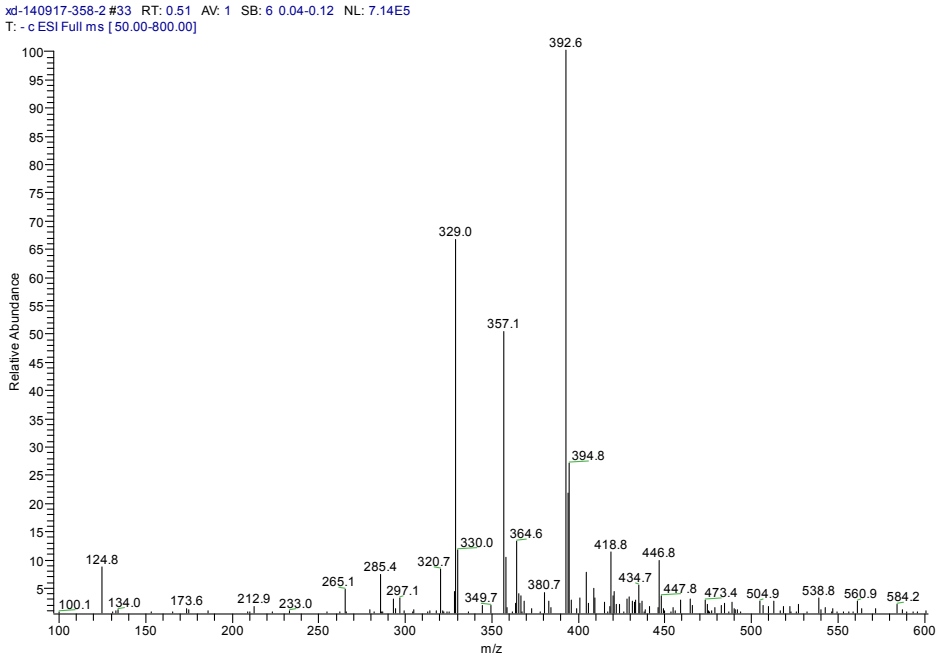
MS of 5d



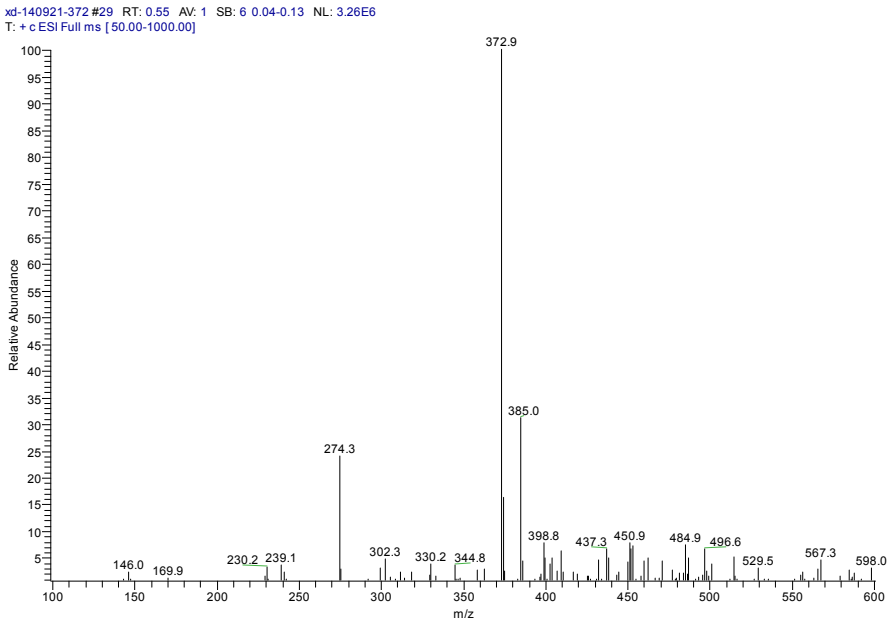
MS of 5e



MS of 5f



MS of 5g


xd-140921-372 #29 RT: 0.55 AV: 1 SB: 6 0.04-0.13 NL: 3.26E6
T: + c ESI Full ms [50.00-1000.00]
Relative Abundance
m/z
372.9
385.0
274.3
398.8
437.3
450.9
484.9
496.6
529.5
567.3
598.0
146.0
169.9
230.2
239.1
302.3
330.2
344.8

MS of 5h

Table S1-S6

Table S1. Standard Orientation of the Transition State [morpholine···kaempferol···ethylenediamine]

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	2.3622670	1.8147910	0.3456670
2	C	2.1747580	3.0781380	-0.2172810
3	C	0.9100970	3.4931570	-0.6342980
4	C	-0.2388140	2.6459830	-0.4940000
5	C	-0.0315410	1.3797030	0.0508840
6	C	1.2635670	0.8976420	0.4524930
7	C	-1.5987080	3.0281700	-0.8780480
8	C	-2.6350360	2.0175060	-0.6375730
9	C	-2.3608780	0.7902340	-0.1046350
10	O	-1.0389690	0.5091920	0.2256260
11	C	-3.2620940	-0.3228260	0.1836520
12	C	-2.7525010	-1.5914110	0.5399540
13	C	-3.5937010	-2.6583700	0.8205460
14	C	-4.9836780	-2.4869680	0.7552790
15	C	-5.5106870	-1.2388230	0.4012600
16	C	-4.6636910	-0.1721120	0.1188410
17	O	3.5910230	1.5207470	0.7617810
18	O	0.7106960	4.7008720	-1.1648410
19	O	-3.8745440	2.4007820	-1.0012060
20	O	-1.9485980	4.1029640	-1.3807350
21	O	-5.7552660	-3.5678610	1.0428120
22	C	1.4408450	-0.4171890	0.8974860
23	H	3.0299440	3.7418360	-0.2956180
24	H	-1.6813560	-1.7485520	0.5845630
25	H	-3.1971610	-3.6325680	1.0863090
26	H	-6.5870640	-1.0964550	0.3468260
27	H	-5.0929790	0.7823050	-0.1533790
28	H	3.7032200	0.7197320	1.3644310
29	H	1.5405880	5.1989460	-1.2191120
30	H	-3.7592170	3.3089970	-1.3606060
31	H	-6.6950060	-3.3526460	0.9644050
32	H	0.6134900	-1.1072930	0.8920740
33	H	2.4248400	-0.8459000	0.9835170
34	N	1.7341700	-1.7987180	-1.4433190
35	C	2.0535270	-3.2270800	-1.2564950
36	C	2.7421170	-1.1311070	-2.2902380
37	C	3.0236360	-1.9060320	-3.5805450
38	C	2.3628110	-3.9354150	-2.5801330
39	O	3.3907400	-3.2505920	-3.2865030

40	H	0.8203870	-1.7174440	-1.8892230
41	H	1.2172230	-3.7178260	-0.7455340
42	H	2.9346730	-3.2937190	-0.6049660
43	H	3.6711680	-1.0528950	-1.7120330
44	H	2.4006110	-0.1151150	-2.5162430
45	H	3.8615560	-1.4674340	-4.1292180
46	H	2.1350620	-1.8955510	-4.2345150
47	H	2.7260060	-4.9523800	-2.4079080
48	H	1.4529910	-3.9910680	-3.2019920
49	N	1.3712030	-0.3526350	3.1355180
50	H	0.4404980	-0.7118430	3.3403270
51	H	1.3650540	0.6378770	3.3764310
52	C	2.3967490	-1.0886850	3.9046900
53	H	2.0912020	-1.2052170	4.9527580
54	H	2.4720170	-2.0984770	3.4822010
55	N	4.3810570	-0.3603070	2.5466890
56	H	5.2924070	0.0933020	2.6168920
57	H	4.5796470	-1.3078030	2.2250190
58	C	3.7626160	-0.4056100	3.8931130
59	H	4.4011950	-0.9294510	4.6157580
60	H	3.6633680	0.6272410	4.2474050

SCF Done: E(RB3LYP) = -1545.86238760 A.U.

Zero-point correction= 0.493105 (Hartree/Particle)

Thermal correction to Energy= 0.523919

Thermal correction to Enthalpy= 0.524863

Thermal correction to Gibbs Free Energy= 0.425856

Sum of electronic and zero-point Energies= -1545.369283

Sum of electronic and thermal Energies= -1545.338468

Sum of electronic and thermal Enthalpies= -1545.337524

Sum of electronic and thermal Free Energies= -1545.436531

Low frequencies --- -149.3169 -6.7486 -4.5433 -0.0058 -0.0053 -0.0041

Low frequencies --- 4.9744 8.8495 11.3835

****** 1 imaginary frequencies (negative Signs) ******

Table S2. Standard Orientation of the Transition State [morpholine···kaempferol···1,2-diaminopropane]

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-2.2236780	1.7285780	-0.0851180
2	C	-2.0212620	2.9908520	0.4774710
3	C	-0.7383790	3.4346540	0.7957260
4	C	0.4171080	2.6198190	0.5520660
5	C	0.1989450	1.3549130	0.0087340
6	C	-1.1120110	0.8438290	-0.2948530

7	C	1.7926680	3.0319990	0.8348030
8	C	2.8311910	2.0490080	0.5058630
9	C	2.5465210	0.8201930	-0.0182720
10	O	1.2106630	0.5118380	-0.2540280
11	C	3.4489980	-0.2697800	-0.3814850
12	C	2.9417890	-1.5391490	-0.7386770
13	C	3.7838260	-2.5854470	-1.0864710
14	C	5.1724400	-2.3924950	-1.0888680
15	C	5.6973410	-1.1430880	-0.7363470
16	C	4.8496190	-0.0968290	-0.3874390
17	O	-3.4723170	1.4072430	-0.4021740
18	O	-0.5270940	4.6411550	1.3248610
19	O	4.0849930	2.4590590	0.7805610
20	O	2.1547300	4.1107720	1.3203960
21	O	5.9449740	-3.4542430	-1.4387530
22	C	-1.2904630	-0.4676280	-0.7449000
23	H	-2.8838080	3.6307000	0.6343120
24	H	1.8723960	-1.7129430	-0.7336220
25	H	3.3890990	-3.5599440	-1.3538670
26	H	6.7726920	-0.9836000	-0.7346520
27	H	5.2777200	0.8588040	-0.1179700
28	H	-3.6327270	0.6093510	-1.0167420
29	H	-1.3623790	5.1159570	1.4536470
30	H	3.9750930	3.3614730	1.1561380
31	H	6.8839750	-3.2247190	-1.4045990
32	H	-0.4472670	-1.1328100	-0.8310750
33	H	-2.2654830	-0.9244430	-0.7502100
34	N	-1.3242620	-1.8895280	1.5952800
35	C	-1.8104210	-3.2737610	1.4422280
36	C	-2.1232450	-1.1491310	2.5909370
37	C	-2.2880510	-1.9263750	3.9002280
38	C	-1.9871220	-3.9837710	2.7890450
39	O	-2.8252990	-3.2219660	3.6504490
40	H	-0.3510840	-1.9105650	1.9000850
41	H	-1.1145670	-3.8301180	0.8038310
42	H	-2.7821580	-3.2359270	0.9326230
43	H	-3.1140170	-0.9630680	2.1583040
44	H	-1.6506450	-0.1784850	2.7763560
45	H	-2.9889360	-1.4233150	4.5719800
46	H	-1.3165530	-2.0175910	4.4151270
47	H	-2.4708610	-4.9562720	2.6622990
48	H	-1.0045880	-4.1428460	3.2653920
49	N	-1.4409660	-0.3569800	-2.9837880
50	H	-0.5368450	-0.7098500	-3.2924920

51	H	-1.4572400	0.6398350	-3.1964080
52	C	-2.5405480	-1.0715450	-3.6658550
53	H	-2.3470330	-1.1478050	-4.7438580
54	H	-2.5663940	-2.0971240	-3.2768600
55	N	-4.4095710	-0.4298090	-2.1003170
56	H	-4.4254190	-1.4008340	-1.7875990
57	C	-3.9010590	-0.4009770	-3.4876130
58	H	-4.6076210	-0.8942640	-4.1716900
59	H	-3.8458000	0.6493690	-3.8014170
60	C	-5.7955420	0.0899310	-2.0139100
61	H	-6.4810180	-0.4414120	-2.6865290
62	H	-6.1540750	-0.0080300	-0.9871690
63	H	-5.7980410	1.1510350	-2.2758050

SCF Done: E(RB3LYP) = -1585.17154050 A.U.

Zero-point correction= 0.520591 (Hartree/Particle) 0.02748485

Thermal correction to Energy= 0.552883

Thermal correction to Enthalpy= 0.553827

Thermal correction to Gibbs Free Energy= 0.451491

Sum of electronic and zero-point Energies= -1584.650950

Sum of electronic and thermal Energies= -1584.618658

Sum of electronic and thermal Enthalpies= -1584.617714

Sum of electronic and thermal Free Energies= -1584.720050

Low frequencies --- -147.5241 -6.9518 -7.3167 -0.0097 -0.0101 -1.7354

Low frequencies --- 0.0026 10.7349 14.6511

****** 1 imaginary frequencies (negative Signs) ******

Table S3. Standard Orientation of the Transition State [morpholine···kaempferol···isopropanolamine]

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-2.0873890	1.9829920	-0.3073500
2	C	-1.7506060	3.3072630	-0.0320140
3	C	-0.4174460	3.6787280	0.1465640
4	C	0.6420060	2.7198230	0.0442320
5	C	0.2821380	1.3977450	-0.2204370
6	C	-1.0808610	0.9683040	-0.3693160
7	C	2.0621290	3.0401250	0.1986310
8	C	2.9889480	1.9124400	0.0512970
9	C	2.5683390	0.6385790	-0.2056590
10	O	1.1999690	0.4230880	-0.3352500
11	C	3.3490390	-0.5852580	-0.3704490
12	C	2.7102580	-1.8407470	-0.4803430
13	C	3.4353040	-3.0127670	-0.6395610
14	C	4.8353700	-2.9653470	-0.6947960

15	C	5.4898280	-1.7321990	-0.5863540
16	C	4.7591730	-0.5593800	-0.4262050
17	O	-3.3854900	1.7303890	-0.5117930
18	O	-0.0724610	4.9420720	0.4042070
19	O	4.2866490	2.2426590	0.2026600
20	O	2.5441110	4.1532150	0.4418430
21	O	5.4894720	-4.1459570	-0.8516930
22	C	-1.4007170	-0.3910780	-0.5372620
23	H	-2.5442650	4.0461170	0.0141370
24	H	1.6296900	-1.9015300	-0.4321280
25	H	2.9393770	-3.9744360	-0.7181920
26	H	6.5751220	-1.6847570	-0.6274770
27	H	5.2866850	0.3808010	-0.3436970
28	H	-3.5915130	0.8354970	-0.8694470
29	H	-0.8539360	5.5133360	0.4542120
30	H	4.2778980	3.2086760	0.3873970
31	H	6.4471040	-4.0110810	-0.8704580
32	H	-0.6162110	-1.1293810	-0.5179610
33	H	-2.4054790	-0.7578140	-0.4065530
34	N	-1.4151850	-1.2525590	2.0043780
35	C	-2.0526710	-2.5772780	2.1316750
36	C	-2.0787100	-0.2557120	2.8665720
37	C	-2.2451310	-0.7534670	4.3056200
38	C	-2.2226210	-3.0016610	3.5945160
39	O	-2.9250540	-2.0047260	4.3278640
40	H	-0.4346050	-1.3265070	2.2760110
41	H	-1.4556450	-3.3165520	1.5853890
42	H	-3.0412160	-2.5224590	1.6584080
43	H	-3.0689760	-0.0490100	2.4427450
44	H	-1.5017290	0.6751890	2.8447860
45	H	-2.8505920	-0.0597290	4.8952380
46	H	-1.2592300	-0.8544470	4.7906100
47	H	-2.8114370	-3.9197380	3.6728970
48	H	-1.2356430	-3.1802300	4.0543150
49	N	-1.6662640	-0.7032810	-2.7082030
50	H	-0.7669540	-1.0910900	-2.9875970
51	H	-1.7334380	0.2202460	-3.1356580
52	C	-4.1432290	-0.9267840	-3.0076960
53	H	-4.1494720	0.0124340	-3.5813720
54	C	-2.7721490	-1.5858330	-3.1385270
55	H	-2.6432820	-1.8898120	-4.1853540
56	H	-2.7425050	-2.4907720	-2.5220460
57	O	-4.3438610	-0.5951600	-1.6076810
58	H	-5.2937590	-0.5253360	-1.4335680

59	C	-5.2556340	-1.8390530	-3.5128830
60	H	-6.2321850	-1.3551190	-3.4038280
61	H	-5.1223230	-2.0587280	-4.5762370
62	H	-5.2702390	-2.7841460	-2.9605820

SCF Done: E(RB3LYP) = -1605.04606746 A.U.

Zero-point correction= 0.507945 (Hartree/Particle)

Thermal correction to Energy= 0.540232

Thermal correction to Enthalpy= 0.541177

Thermal correction to Gibbs Free Energy= 0.439321

Sum of electronic and zero-point Energies= -1604.538123

Sum of electronic and thermal Energies= -1604.505835

Sum of electronic and thermal Enthalpies= -1604.504891

Sum of electronic and thermal Free Energies= -1604.606747

Low frequencies --- -172.3236 -5.8643 -4.8261 -3.0118 -0.0039 -0.0028

Low frequencies --- -0.0010 11.1408 15.7411

****** 1 imaginary frequencies (negative Signs) ******

Table S4. Standard Orientation of the Transition State [morpholine···kaempferol···ethanolamine]

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	2.3205050	1.8471700	0.4562250
2	C	2.1227700	3.1312300	-0.0481810
3	C	0.8570480	3.5425840	-0.4684260
4	C	-0.2747930	2.6683850	-0.3853410
5	C	-0.0516180	1.3823810	0.1080840
6	C	1.2436660	0.9066890	0.5096870
7	C	-1.6357830	3.0412820	-0.7761400
8	C	-2.6570500	2.0039500	-0.5935920
9	C	-2.3687630	0.7610870	-0.1065570
10	O	-1.0465820	0.4878710	0.2301570
11	C	-3.2552360	-0.3765180	0.1256790
12	C	-2.7296900	-1.6532670	0.4249980
13	C	-3.5573620	-2.7428850	0.6541920
14	C	-4.9493680	-2.5867460	0.5929400
15	C	-5.4920290	-1.3308150	0.2942820
16	C	-4.6585300	-0.2414180	0.0631870
17	O	3.5574460	1.5606000	0.8800990
18	O	0.6447110	4.7696110	-0.9478840
19	O	-3.8980860	2.3799280	-0.9600430
20	O	-1.9965550	4.1295160	-1.2403840
21	O	-5.7072310	-3.6894760	0.8288460
22	C	1.4343880	-0.4289080	0.9079050
23	H	2.9676610	3.8116330	-0.0822710

24	H	-1.6566000	-1.7986750	0.4639140
25	H	-3.1485910	-3.7231520	0.8753380
26	H	-6.5700670	-1.2002750	0.2430450
27	H	-5.0997590	0.7187050	-0.1667330
28	H	3.6466070	0.7196450	1.3834730
29	H	1.4659710	5.2842790	-0.9651460
30	H	-3.7944820	3.3035760	-1.2813770
31	H	-6.6495630	-3.4837700	0.7557820
32	H	0.6136060	-1.1242250	0.8456240
33	H	2.4187230	-0.8609200	0.9863710
34	N	1.8034460	-1.6628450	-1.4701050
35	C	2.1618650	-3.0864570	-1.3192720
36	C	2.8211140	-0.9363470	-2.2540740
37	C	3.1685230	-1.6549170	-3.5611650
38	C	2.5359050	-3.7377620	-2.6554380
39	O	3.5646410	-2.9984240	-3.3035680
40	H	0.9044930	-1.5933380	-1.9472390
41	H	1.3244310	-3.6199000	-0.8549770
42	H	3.0214570	-3.1473070	-0.6396870
43	H	3.7267010	-0.8570780	-1.6400620
44	H	2.4597170	0.0780980	-2.4549560
45	H	4.0112160	-1.1730850	-4.0644450
46	H	2.3021990	-1.6443260	-4.2444110
47	H	2.9248960	-4.7486860	-2.5057330
48	H	1.6489910	-3.7989690	-3.3091110
49	N	1.3089470	-0.4581960	3.1019640
50	H	0.3610690	-0.7914130	3.2691220
51	H	1.3397210	0.5127610	3.4127220
52	C	3.6903230	-0.6945070	3.8113830
53	H	4.3469960	-1.3386780	4.4043760
54	H	3.6904500	0.3062790	4.2648700
55	C	2.2937970	-1.2946550	3.8209870
56	H	2.0001860	-1.4370170	4.8698060
57	H	2.3120440	-2.2798580	3.3439980
58	O	4.1792110	-0.6118100	2.4559960
59	H	5.1466340	-0.6068830	2.4607680

SCF Done: E(RB3LYP) = -1565.72239921 A.U.

Zero-point correction= 0.480450 (Hartree/Particle)

Thermal correction to Energy= 0.511256

Thermal correction to Enthalpy= 0.512200

Thermal correction to Gibbs Free Energy= 0.413683

Sum of electronic and zero-point Energies= -1565.241949

Sum of electronic and thermal Energies= -1565.211143

Sum of electronic and thermal Enthalpies= -1565.210199

Sum of electronic and thermal Free Energies= -1565.308716

Low frequencies --- -174.0901 -5.5002 -2.9480 -0.0002 0.0004 0.0011

Low frequencies --- 4.5184 9.6168 12.6566

****** 1 imaginary frequencies (negative Signs) ******

Table S5. Standard Orientation of the Transition State [morpholine···kaempferol···thiosemicarbazide]

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-1.8559970	2.2351520	-0.2144850
2	C	-1.4372060	3.5237610	0.1034590
3	C	-0.0845170	3.8011760	0.3152710
4	C	0.9116440	2.7780710	0.1990560
5	C	0.4692230	1.4894810	-0.0995860
6	C	-0.9178130	1.1539640	-0.2731050
7	C	2.3494070	3.0035090	0.3666320
8	C	3.2022070	1.8224910	0.1901980
9	C	2.7007430	0.5857370	-0.0979370
10	O	1.3216400	0.4599680	-0.2384890
11	C	3.4036930	-0.6807040	-0.2874120
12	C	2.6984910	-1.9045590	-0.2890780
13	C	3.3500720	-3.1158840	-0.4716400
14	C	4.7391770	-3.1394280	-0.6619210
15	C	5.4584000	-1.9377920	-0.6596980
16	C	4.8014190	-0.7257530	-0.4742780
17	O	-3.1720020	2.0645780	-0.4077280
18	O	0.3377550	5.0304640	0.6109350
19	O	4.5180920	2.0594620	0.3534900
20	O	2.8988170	4.0755180	0.6447400
21	O	5.3188700	-4.3555490	-0.8372080
22	C	-1.3240050	-0.1858440	-0.4095800
23	H	-2.1808380	4.3126130	0.1543520
24	H	1.6272070	-1.9084880	-0.1245720
25	H	2.8070990	-4.0550640	-0.4591860
26	H	6.5357660	-1.9460450	-0.8043130
27	H	5.3767070	0.1901540	-0.4741860
28	H	-3.3977240	1.3159230	-1.0019320
29	H	-0.4039580	5.6528050	0.6613330
30	H	4.5763680	3.0167080	0.5701390
31	H	6.2765340	-4.2709100	-0.9439980
32	H	-0.6117400	-0.9772680	-0.2388730
33	H	-2.3650730	-0.4575050	-0.3131900
34	N	-1.7719520	-0.9407660	2.2473540
35	C	-1.4286640	-2.3360450	2.5842900

36	C	-3.1738540	-0.6377090	2.6008260
37	C	-3.5245370	-1.0668650	4.0281220
38	C	-1.8359310	-2.7120870	4.0124000
39	O	-3.2170020	-2.4430770	4.2291760
40	H	-1.1561350	-0.3127490	2.7635910
41	H	-0.3517540	-2.4835580	2.4435590
42	H	-1.9568580	-2.9920190	1.8799510
43	H	-3.8226270	-1.1785360	1.8996330
44	H	-3.3528610	0.4345030	2.4659220
45	H	-4.5947890	-0.9554720	4.2222890
46	H	-2.9720080	-0.4503590	4.7576870
47	H	-1.6938990	-3.7807720	4.1955150
48	H	-1.2260820	-2.1499310	4.7401700
49	N	-1.4059040	-0.6263970	-2.4929380
50	N	-2.2788400	-1.6616760	-2.8986350
51	C	-3.6237150	-1.3825040	-2.9945620
52	S	-4.2273450	0.1889780	-2.8970470
53	H	-0.4910300	-0.7854370	-2.9199020
54	H	-1.8100390	0.2380060	-2.8768900
55	H	-1.9916440	-2.5773560	-2.5702500
56	N	-4.4099560	-2.4572980	-3.2060530
57	H	-4.0392910	-3.3483140	-3.5112180
58	H	-5.3960340	-2.2915270	-3.3521110

SCF Done: E(RB3LYP) = -1958.85975720 A.U.

Zero-point correction= 0.458858 (Hartree/Particle)

Thermal correction to Energy= 0.490866

Thermal correction to Enthalpy= 0.491810

Thermal correction to Gibbs Free Energy= 0.390545

Sum of electronic and zero-point Energies= -1958.400899

Sum of electronic and thermal Energies= -1958.368891

Sum of electronic and thermal Enthalpies= -1958.367947

Sum of electronic and thermal Free Energies= -1958.469212

Low frequencies --- -195.0181 -3.7581 -0.0001 0.0012 0.0016 1.8145

Low frequencies --- 5.0212 14.0442 17.3504

****** 1 imaginary frequencies (negative Signs) ******

Table S6. Standard Orientation of the Transition State [morpholine···kaempferol···4-methylthiosemicarbazide]

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-1.3980290	2.4846140	-0.5095000
2	C	-0.8069490	3.7437800	-0.4618050
3	C	0.5786220	3.8767290	-0.3435060
4	C	1.4344620	2.7288780	-0.2824630

5	C	0.8224350	1.4761500	-0.3090510
6	C	-0.6035890	1.2980460	-0.3730900
7	C	2.8957910	2.7929440	-0.2038280
8	C	3.5871260	1.4990680	-0.1771260
9	C	2.9232480	0.3065100	-0.2058510
10	O	1.5334270	0.3372090	-0.2687420
11	C	3.4560980	-1.0534450	-0.1800610
12	C	2.6126960	-2.1541270	0.0879180
13	C	3.1008460	-3.4528980	0.1055240
14	C	4.4588940	-3.6915290	-0.1492530
15	C	5.3136960	-2.6138880	-0.4121910
16	C	4.8206610	-1.3131590	-0.4261090
17	O	-2.7312100	2.4514890	-0.6321310
18	O	1.1640410	5.0735700	-0.3073740
19	O	4.9293790	1.5884350	-0.1073090
20	O	3.5864040	3.8172450	-0.1541200
21	O	4.8756020	-4.9845680	-0.1213550
22	C	-1.1799430	0.0280510	-0.2177410
23	H	-1.4434390	4.6183650	-0.5503960
24	H	1.5639530	-1.9874430	0.3049330
25	H	2.4531230	-4.2951420	0.3248980
26	H	6.3684310	-2.7889300	-0.6086740
27	H	5.4985320	-0.4953000	-0.6300150
28	H	-3.0771230	1.6521910	-1.0933540
29	H	0.5082640	5.7856210	-0.3620730
30	H	5.1160270	2.5533440	-0.0799490
31	H	5.8256290	-5.0461180	-0.2926060
32	H	-0.5656340	-0.8039880	0.0875220
33	H	-2.2415830	-0.0753580	-0.0489590
34	N	-1.6572810	-0.1296810	2.5534720
35	C	-1.5234340	-1.4721930	3.1501830
36	C	-2.9974750	0.4360490	2.8072260
37	C	-3.4102080	0.3329950	4.2778690
38	C	-1.9851320	-1.5152340	4.6105650
39	O	-3.3119080	-1.0133680	4.7332980
40	H	-0.9530370	0.4871060	2.9577400
41	H	-0.4798460	-1.7971020	3.0693310
42	H	-2.1412300	-2.1645950	2.5630200
43	H	-3.7200750	-0.1232430	2.1985110
44	H	-3.0142680	1.4790910	2.4734030
45	H	-4.4520660	0.6338030	4.4181930
46	H	-2.7727170	0.9847490	4.8994610
47	H	-2.0032590	-2.5407510	4.9899100
48	H	-1.3008120	-0.9226370	5.2414300

49	N	-1.4428740	-0.8349840	-2.1799680
50	N	-2.4992860	-1.7618460	-2.3311110
51	C	-3.7802850	-1.2752620	-2.4581080
52	S	-4.0861770	0.3728870	-2.7217250
53	H	-0.5976380	-1.2352890	-2.5917320
54	H	-1.7271200	-0.0103390	-2.7261940
55	H	-2.3441970	-2.6328060	-1.8365970
56	N	-4.7598210	-2.1933500	-2.4196500
57	H	-5.6909180	-1.8184360	-2.5428250
58	C	-4.5862540	-3.6420180	-2.3492290
59	H	-4.1798260	-3.9547590	-1.3790450
60	H	-5.5643780	-4.1085520	-2.4629610
61	H	-3.9366600	-4.0011190	-3.1549600

SCF Done: E(RB3LYP) = -1998.17295221 A.U.

Zero-point correction= 0.486345 (Hartree/Particle)

Thermal correction to Energy= 0.519834

Thermal correction to Enthalpy= 0.520779

Thermal correction to Gibbs Free Energy= 0.416175

Sum of electronic and zero-point Energies= -1997.686607

Sum of electronic and thermal Energies= -1997.653118

Sum of electronic and thermal Enthalpies= -1997.652173

Sum of electronic and thermal Free Energies= -1997.756777

Low frequencies --- -192.1683 -4.5317 -1.0679 0.0103 0.0085 2.0644

Low frequencies --- 0.0138 15.7122 18.0526

****** 1 imaginary frequencies (negative Signs) ******

Determination of stoichiometry of complex and the stability constant of complex

According to the Beer-Lambert law, the stoichiometry of complex is measured by Job's method for concentration continuous variation[1]. Equimolar solutions of metal ion and ligand (50 μmol·L^{-1} for each) are prepared. For example, 10.00, 9.00, 8.00, 7.00, 6.00, 5.00, 4.00, 3.00, 2.00, 1.00 and 0.00 mL ligand solutions (50 um/L in EtOH) were placed in 11 small beakers, respectively. Then, 0.00, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, 9.00 and 10.00 mL solutions of metal ion (50 um/L in EtOH) were added in turn. The plot of absorbance (with λ_{max}) versus mole fraction (x_L) of ligand (L/(M+L)) indicates that the stoichiometry of complex is 1:1 (metal:ligand).

Then, the stability constant (k) can be calculated by the following equation:

$k = (1-\alpha)/c\alpha^2$

Where, c is the initial concentration (here, $c = 2.5 \times 10^{-5}$ mol/L) and α is the dissociation degree of the complex.

α can be calculated by the following equation:

$\alpha = (A_0-A)/A_0$

Where, A is the absorbance value of maximum absorbance found from the abovementioned A-x_L graph, A_0 is the absorbance at the stoichiometric molar- ratio of the ligand and the metal in complex. For example, values of α for some ligands with Lu are 0.1698(5a), 0.1463(5b), 0.1389(5c), 0.1026(5d), and 0.1667(5g). Thus, the corresponding stability constant values are 1.15×10^6, 1.59×10^6, 1.78×10^6, 3.41×10^6 and 1.12×10^6.

Notes and references

1 U. B. Barache, A. B. Shaikh, T. N. Lokhande, G. S. Kamble, M. A. Anuse, S. H. Gaikwad, *Spectrochim. Acta A*, 2018, **189**, 443–453.