Supplementary Information (SI) for Materials Advances.

Enhanced anticorrosion performance of Antipyrine Derivatives on Mild Steel in an Acidic Environment: An Experimental and Theoretical Analysis

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Supporting Information

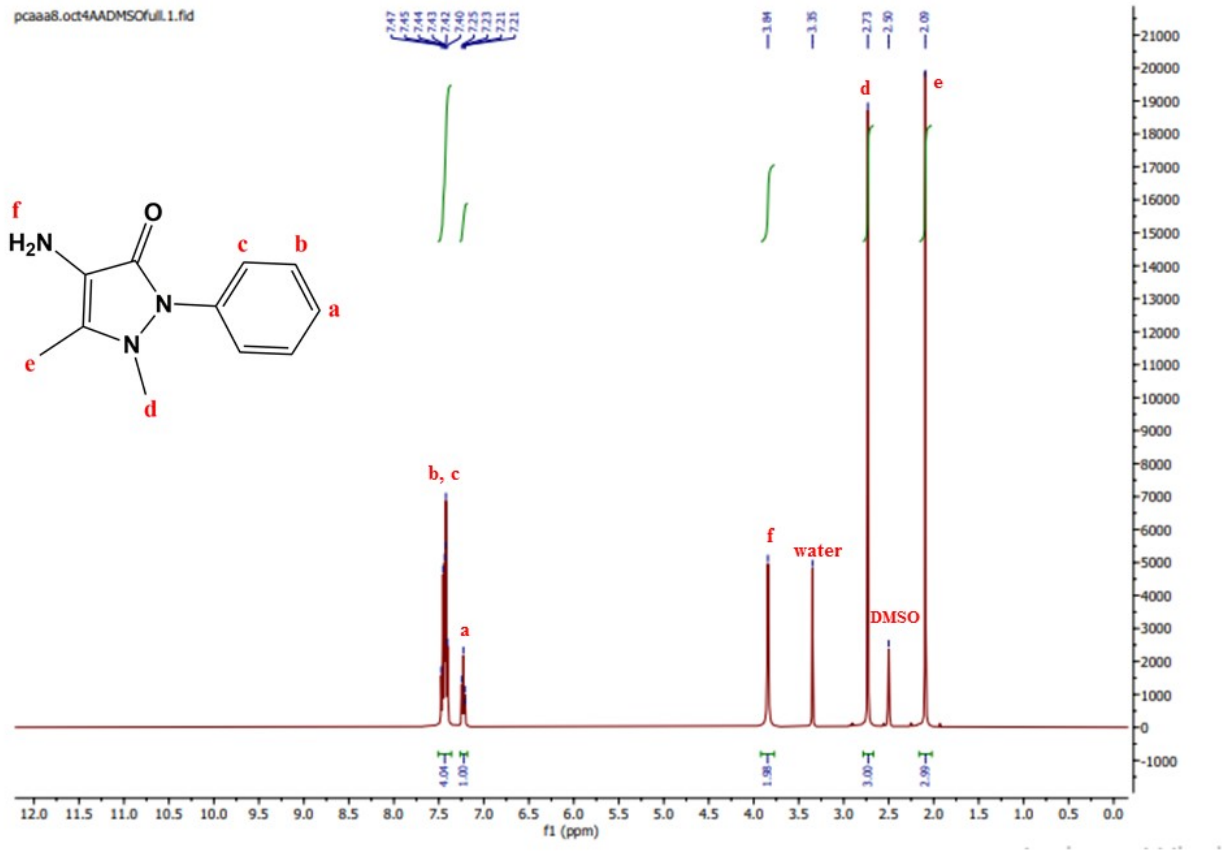


Figure S1: ^{1}H-NMR spectrum of 2.

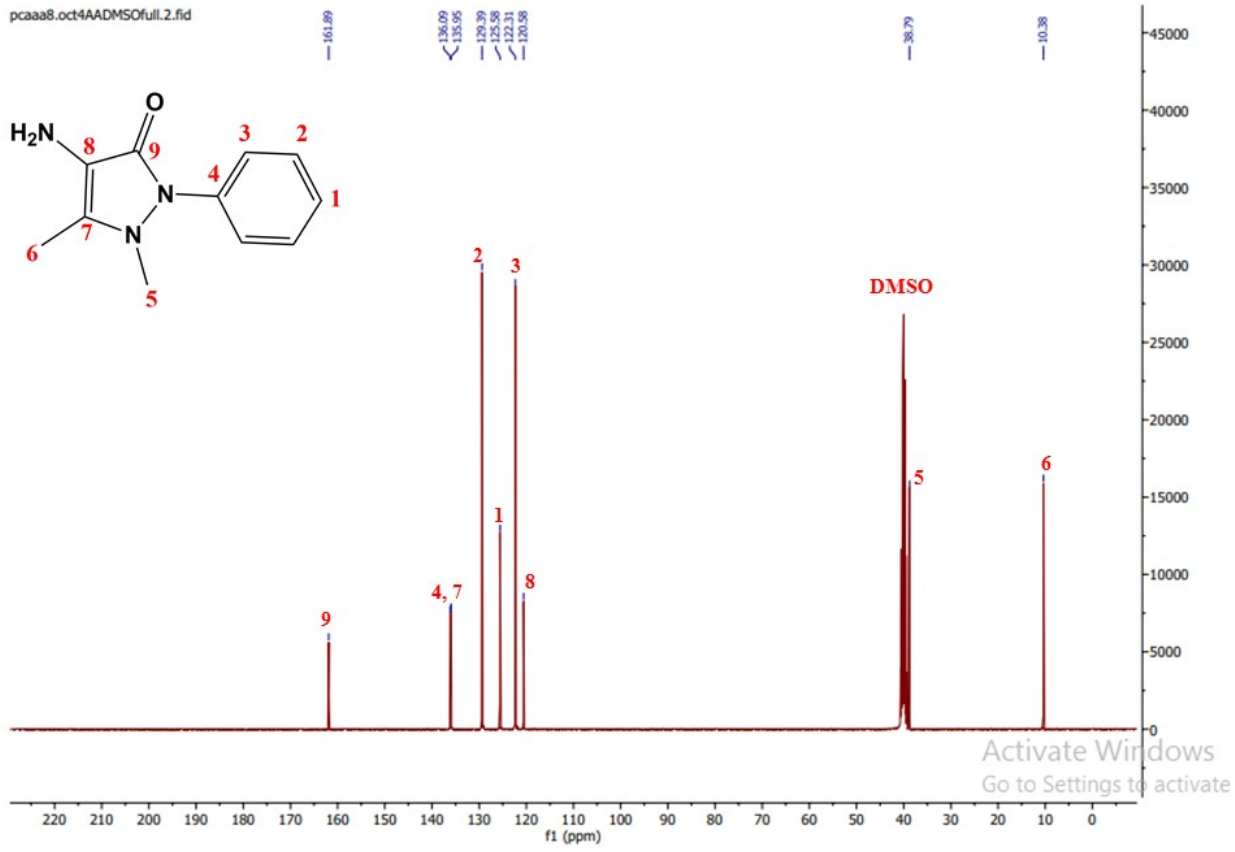


Figure S2: ^{13}C-NMR spectrum of 2.

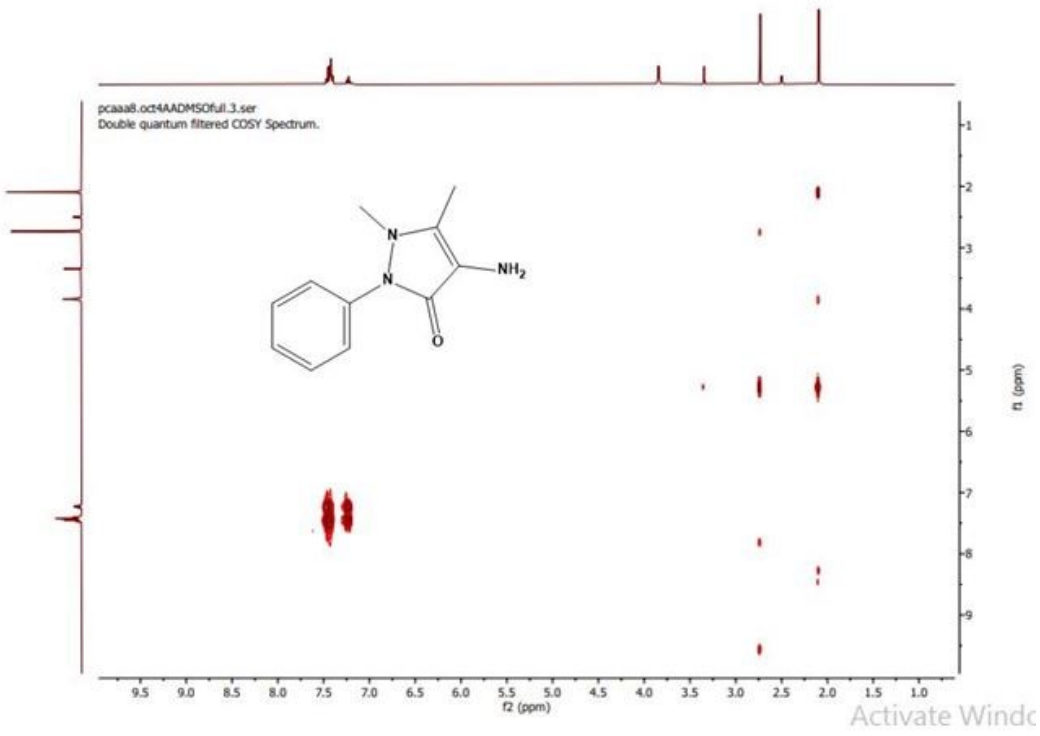


Figure S3: COSY spectrum of 2.

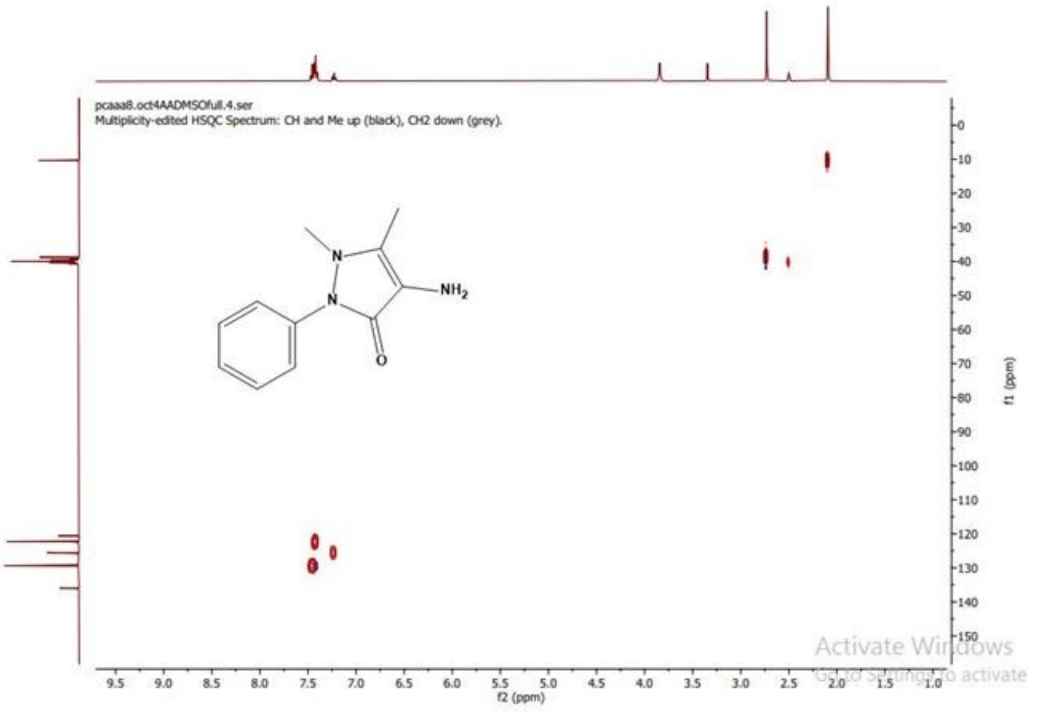
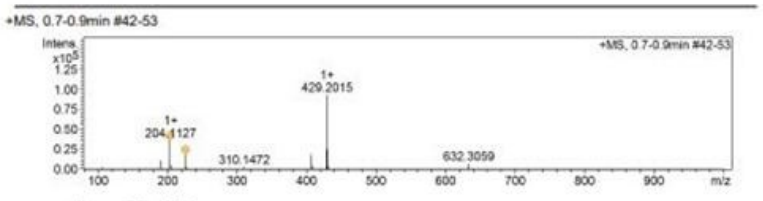
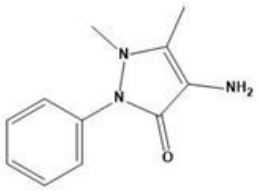


Figure S4: HSQC spectrum of 2.



#	m/z	I %
1	107.0379	2.3
2	175.0272	1.1
3	185.1144	1.4
4	191.0911	12.0
5	193.0880	1.1
6	204.1127	38.8
7	205.1159	5.3
8	226.0952	20.5
9	227.0980	2.7
10	263.1872	1.2
11	310.1472	3.1
12	407.2198	19.8
13	408.2228	5.0
14	429.2015	100.0
15	430.2043	27.2
16	431.2063	3.9
17	497.1901	1.1
18	591.2820	1.0
19	632.3059	7.7
20	633.3083	3.0



Generate Molecular Formula Parameters

Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C11 H13 N3 O1 **Adduct(s):** H, Na, NH4, C3H5N2, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	204.1127	204.1131	2.00	0.0027	C11H14N3O	M+H	1.0078
1	226.0952	226.0951	0.50	0.0004	C11H13N3NaO	M+Na	22.9898

Note: Sigma fits < 0.05 indicates high probability of correct MF

Figure S5: HRMS spectrum of 2.

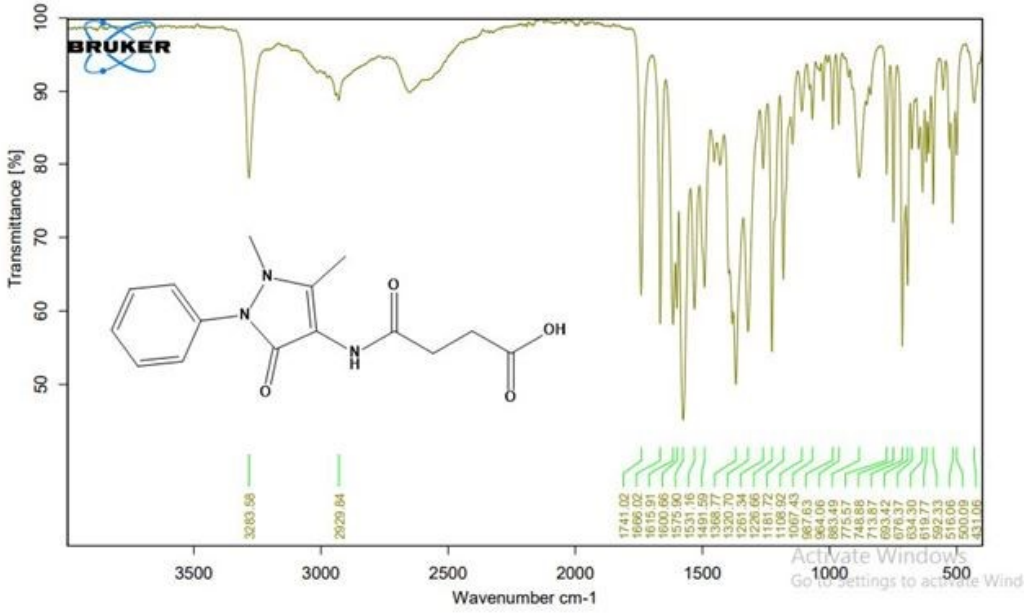


Figure S6: IR spectrum of 4.

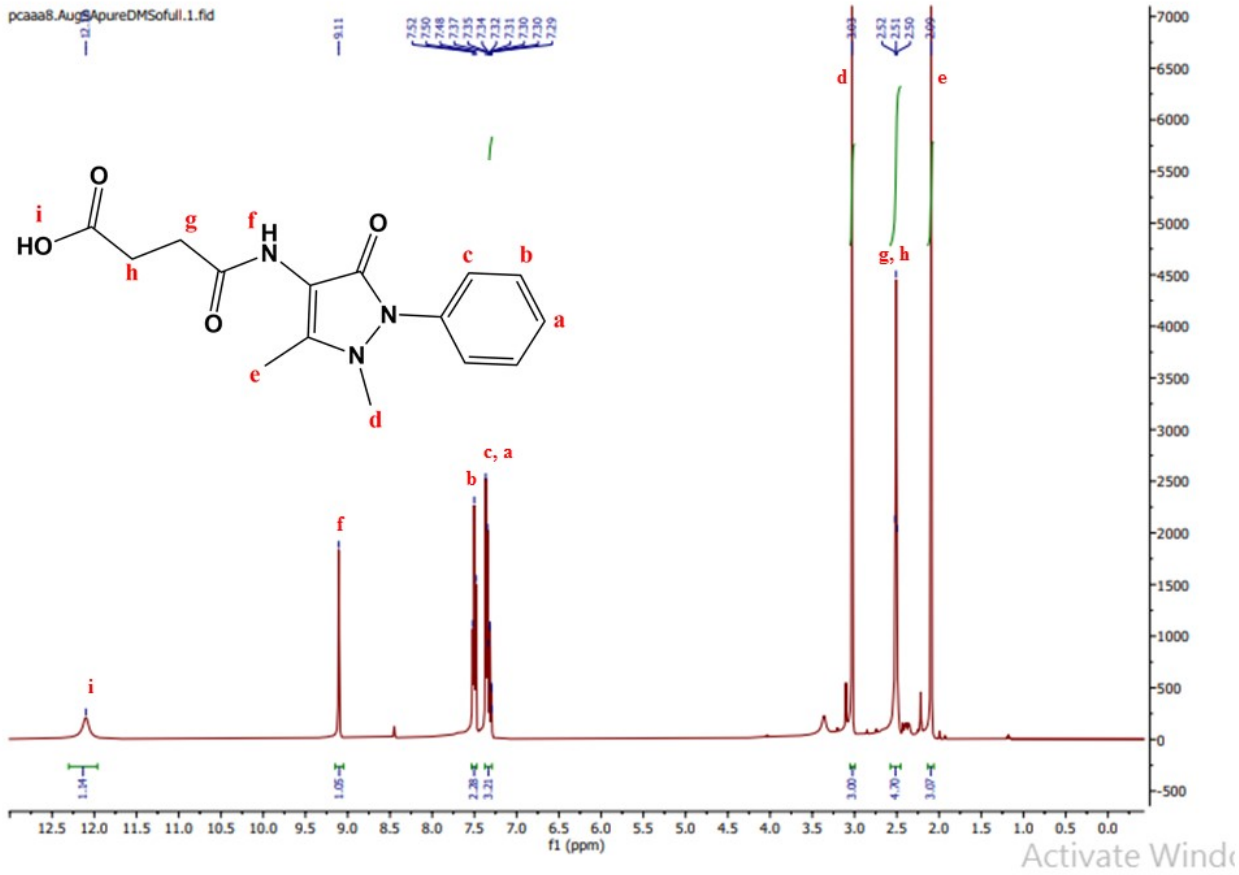


Figure S7: ^{1}H-NMR spectrum of 4.

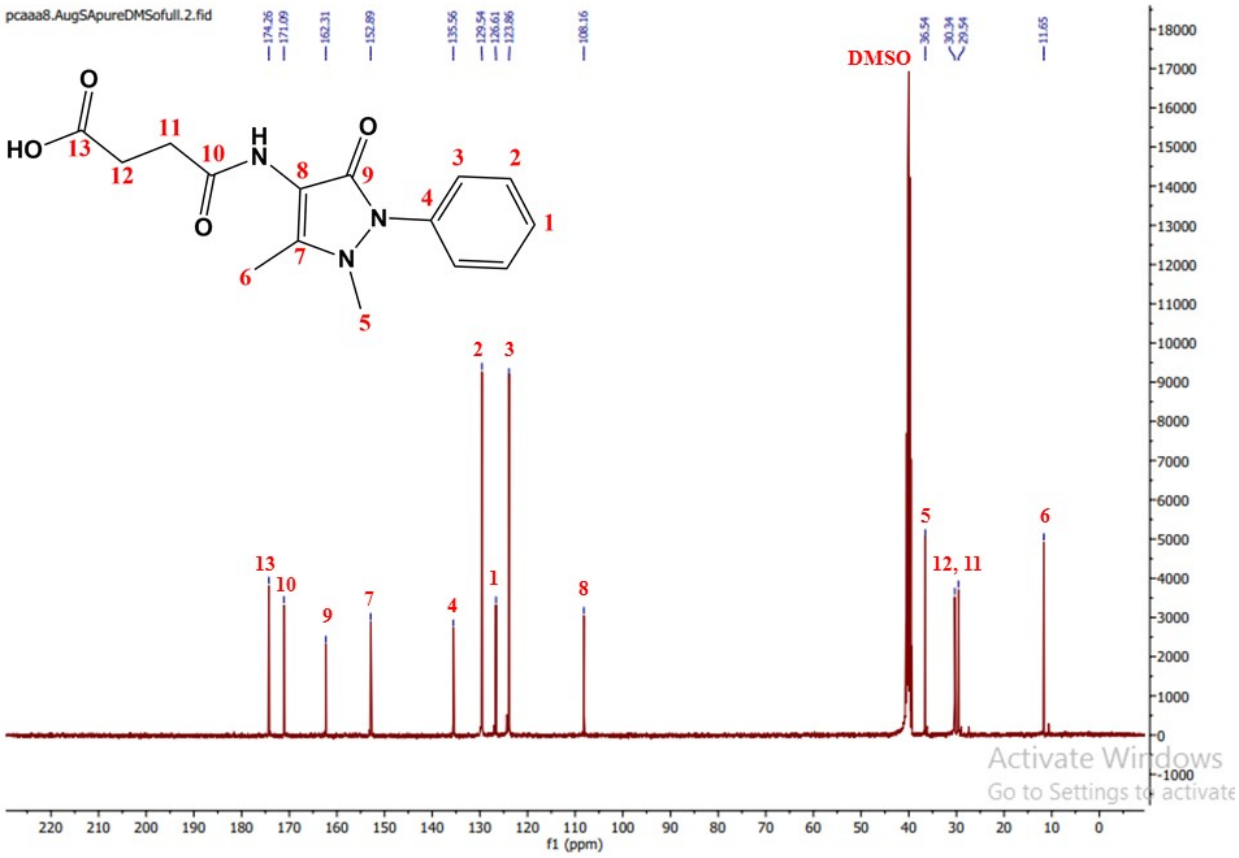


Figure S8: ^{13}C-NMR spectrum of 4.

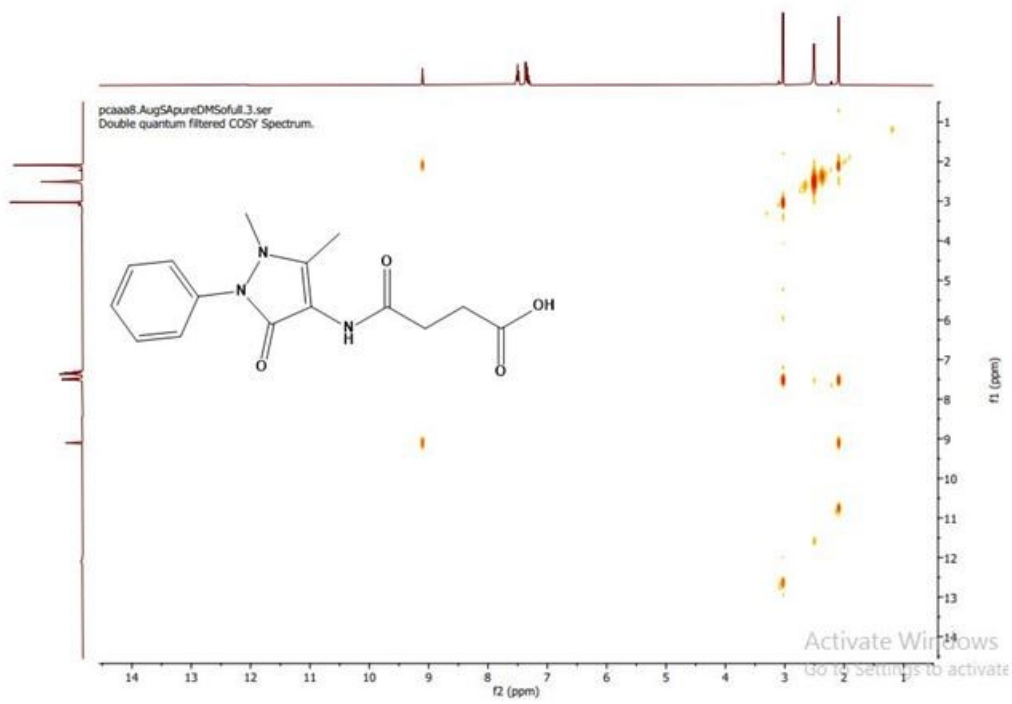


Figure S9: COSY spectrum of 4.

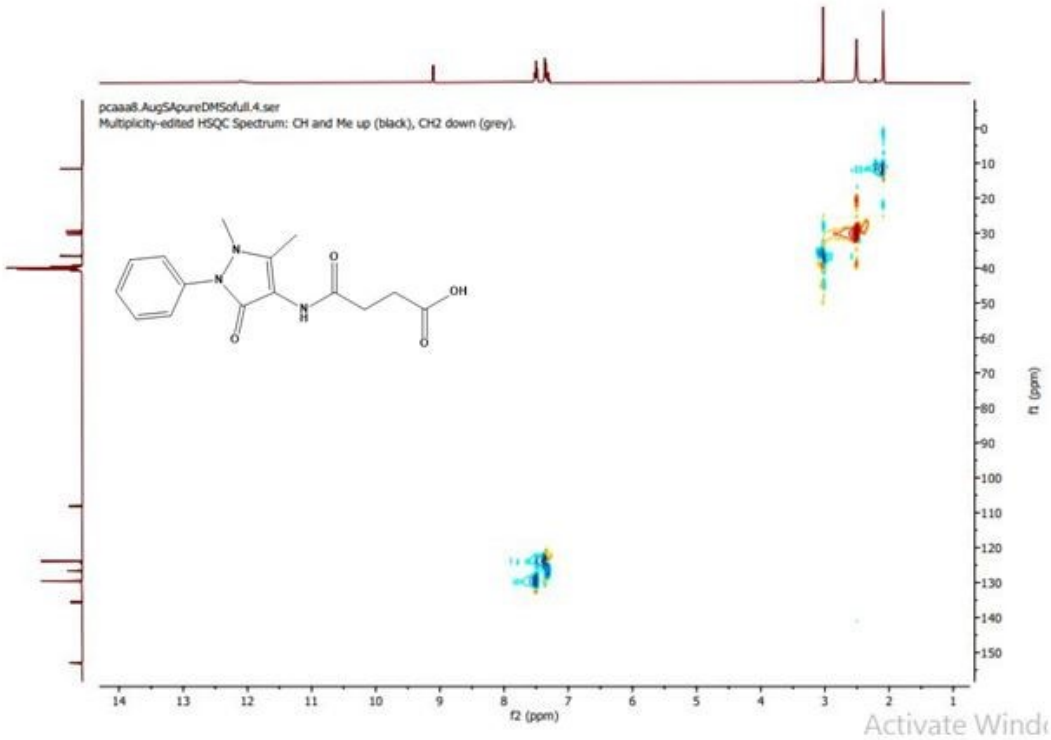
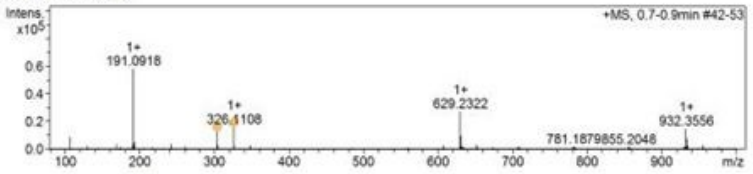
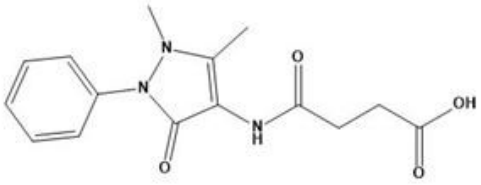


Figure S10: HSQC spectrum of 4.

+MS, 0.7-0.9min #42-53



#	m/z	I %
1	107.0370	15.6
2	130.1567	3.9
3	169.1092	6.1
4	191.0918	100.0
5	192.0936	6.2
6	193.0881	9.3
7	242.2839	7.3
8	304.1290	22.2
9	305.1431	5.1
10	326.1108	27.5
11	327.1131	4.9
12	348.0932	4.8
13	607.2500	4.5
14	629.2322	47.1
15	630.2352	17.3
16	651.2135	5.6
17	932.3556	25.5
18	933.3578	13.6
19	934.3612	4.1
20	954.3372	5.0



Generate Molecular Formula Parameters

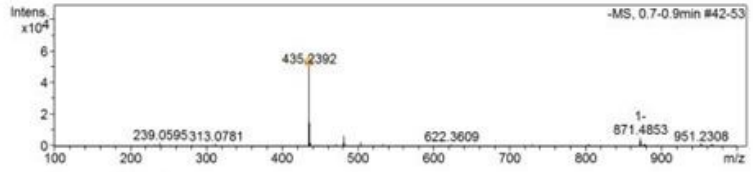
Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C15 H17 N3 O4 **Adduct(s):** H, Na, NH4, C3H5N2, radical

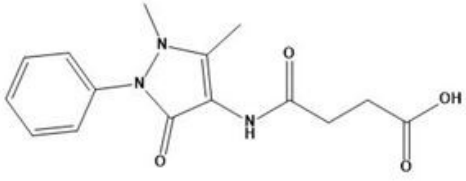
#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	326.1108	326.1111	0.90	0.0015	C15H17N3NaO4	M+Na	22.9898

Figure S11: HRMS Positive spectrum of 4.

-MS, 0.7-0.9min #42-53



#	m/z	I %
1	239.0595	3.9
2	313.0781	2.4
3	435.2392	100.0
4	436.2427	29.8
5	437.2461	4.3
6	471.2172	2.1
7	481.2452	13.4
8	482.2478	4.2
9	503.2266	4.7
10	533.2183	1.8
11	622.3609	2.0
12	803.1909	2.1
13	871.4853	10.8
14	872.4882	6.0
15	877.2041	1.9
16	878.2080	1.8
17	951.2308	2.5
18	952.2245	2.1
19	953.2269	1.7
20	965.2038	2.0



Generate Molecular Formula Parameters

Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
-1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C25 H32 N4 O3 **Adduct(s):** H, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	435.2392	435.2402	2.20	0.0050	C25H31N4O3	M- H	1.0078

Note: Sigma fits < 0.05 indicates high probability of correct MF

Figure S12: HRMS Negative spectrum of 4.

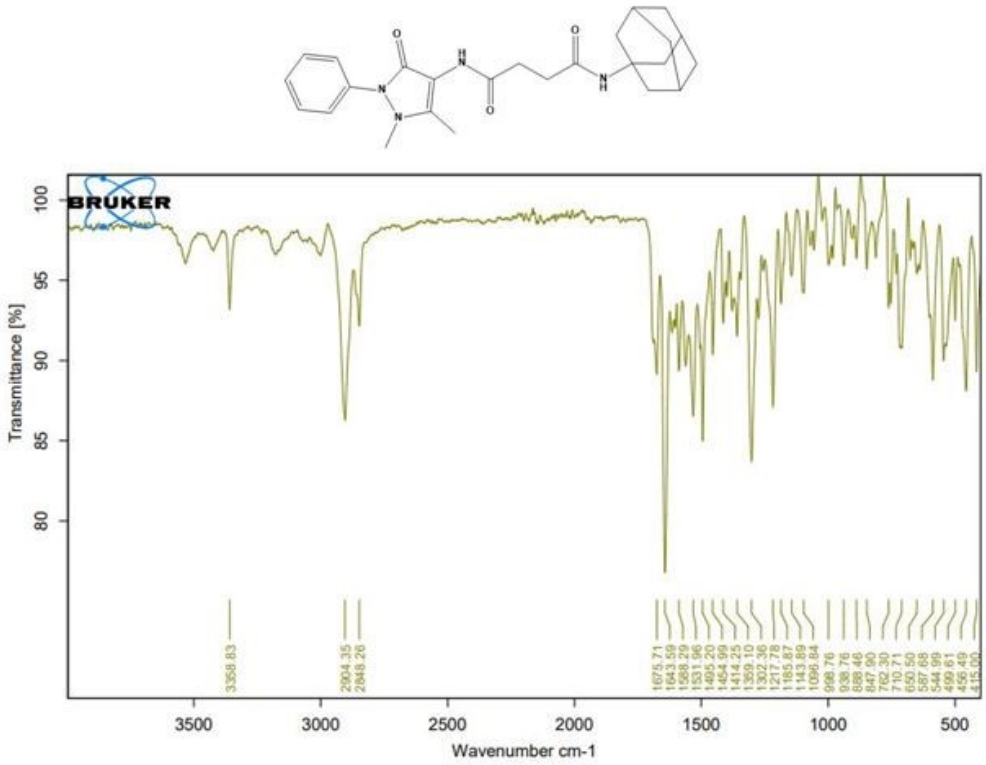


Figure S13: IR spectrum of M1.

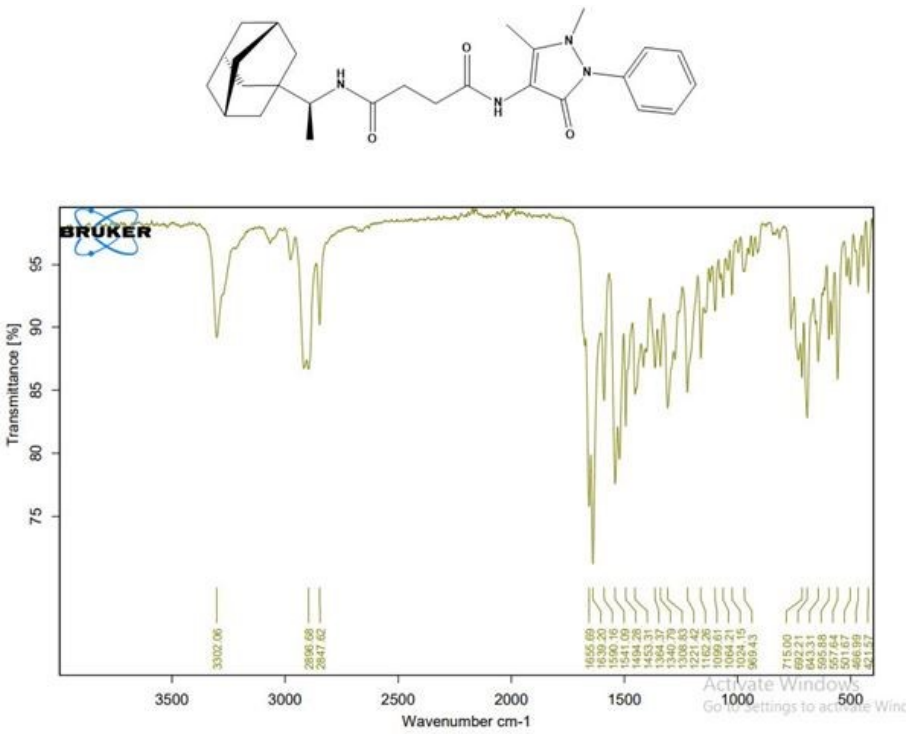


Figure S14: IR spectrum of M2.

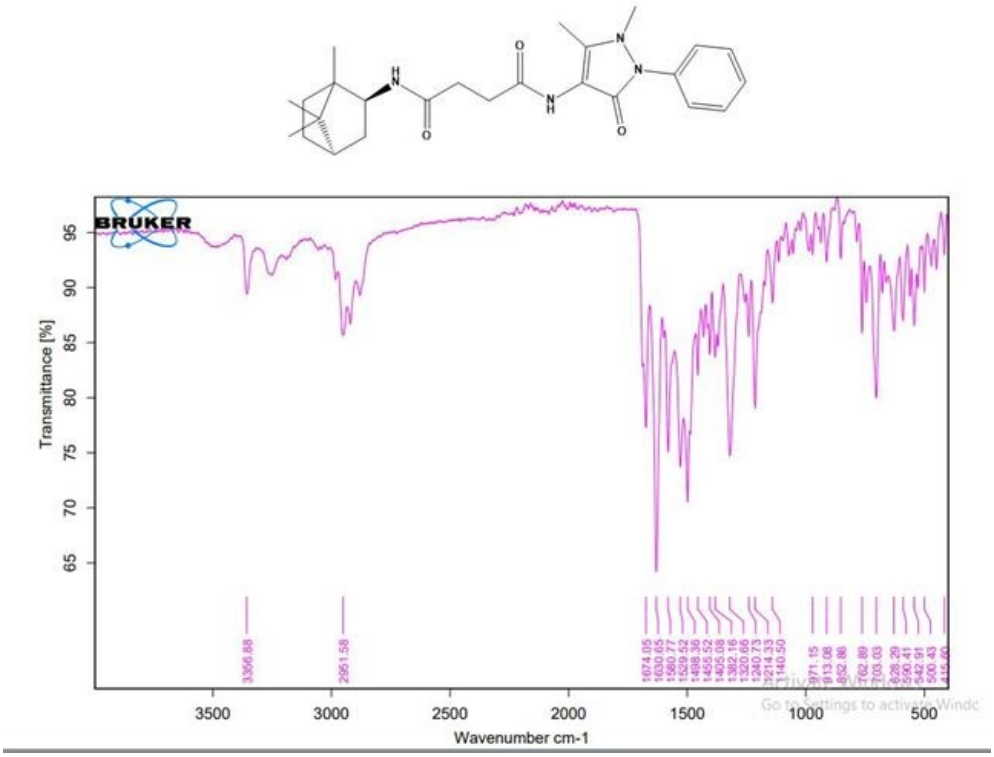


Figure S15: IR spectrum of M3.

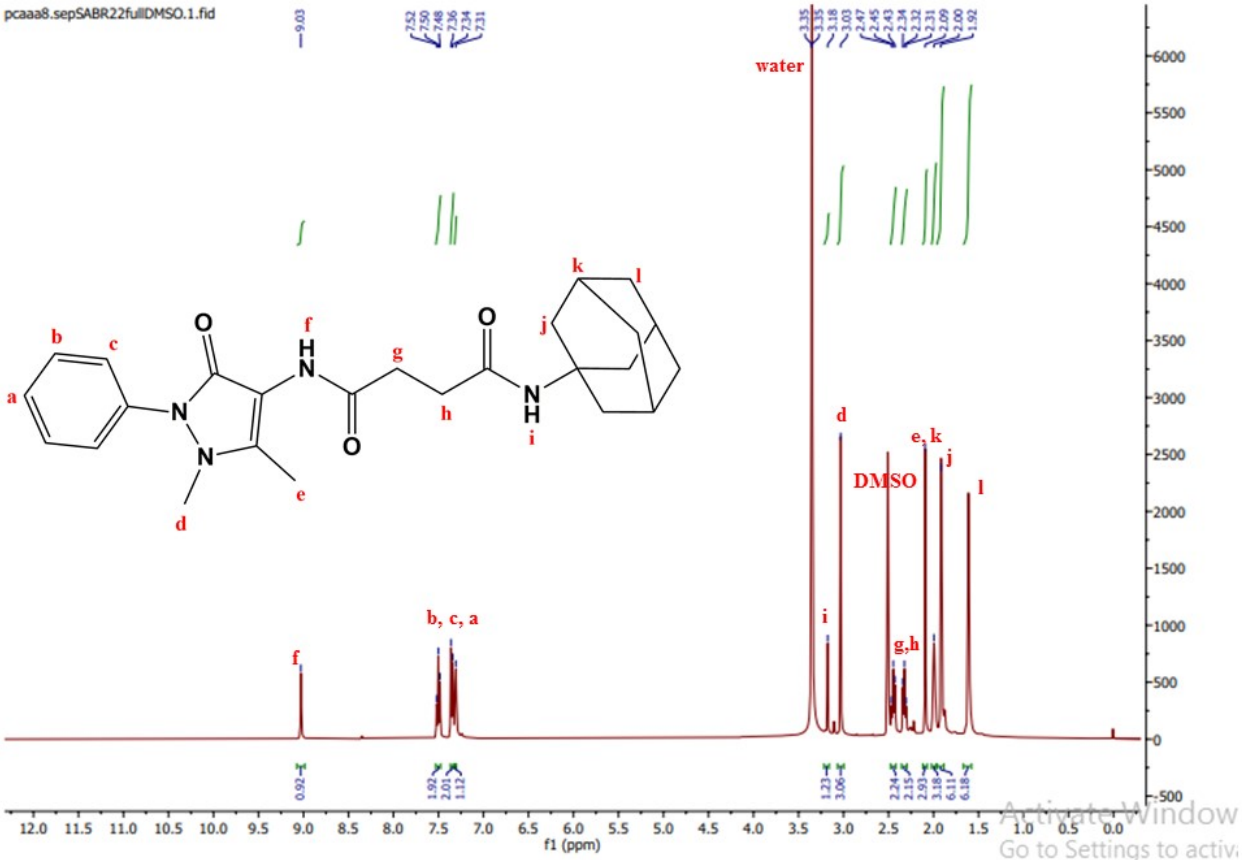


Figure S16: ^{1}H-NMR spectrum of M1.

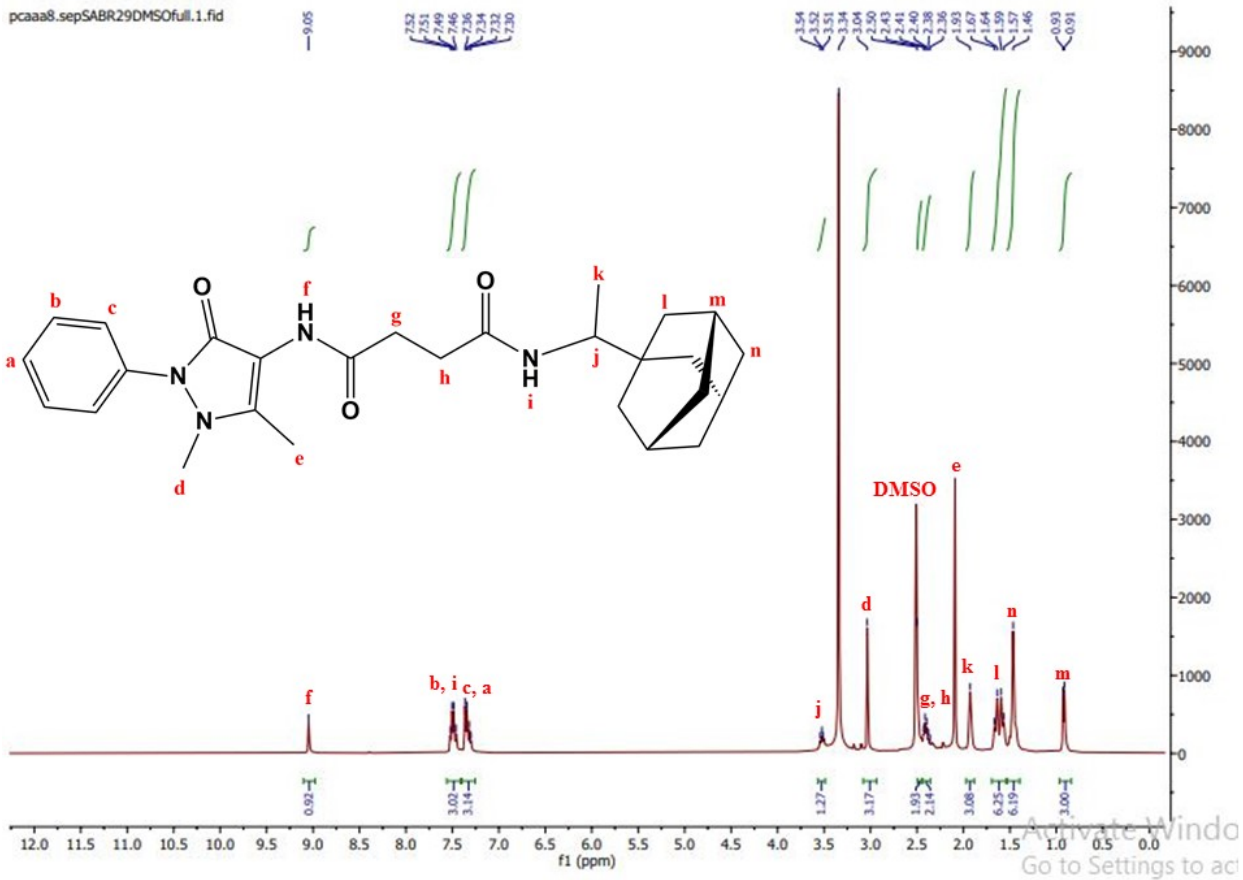


Figure S17: ^{1}H-NMR spectrum of M2.

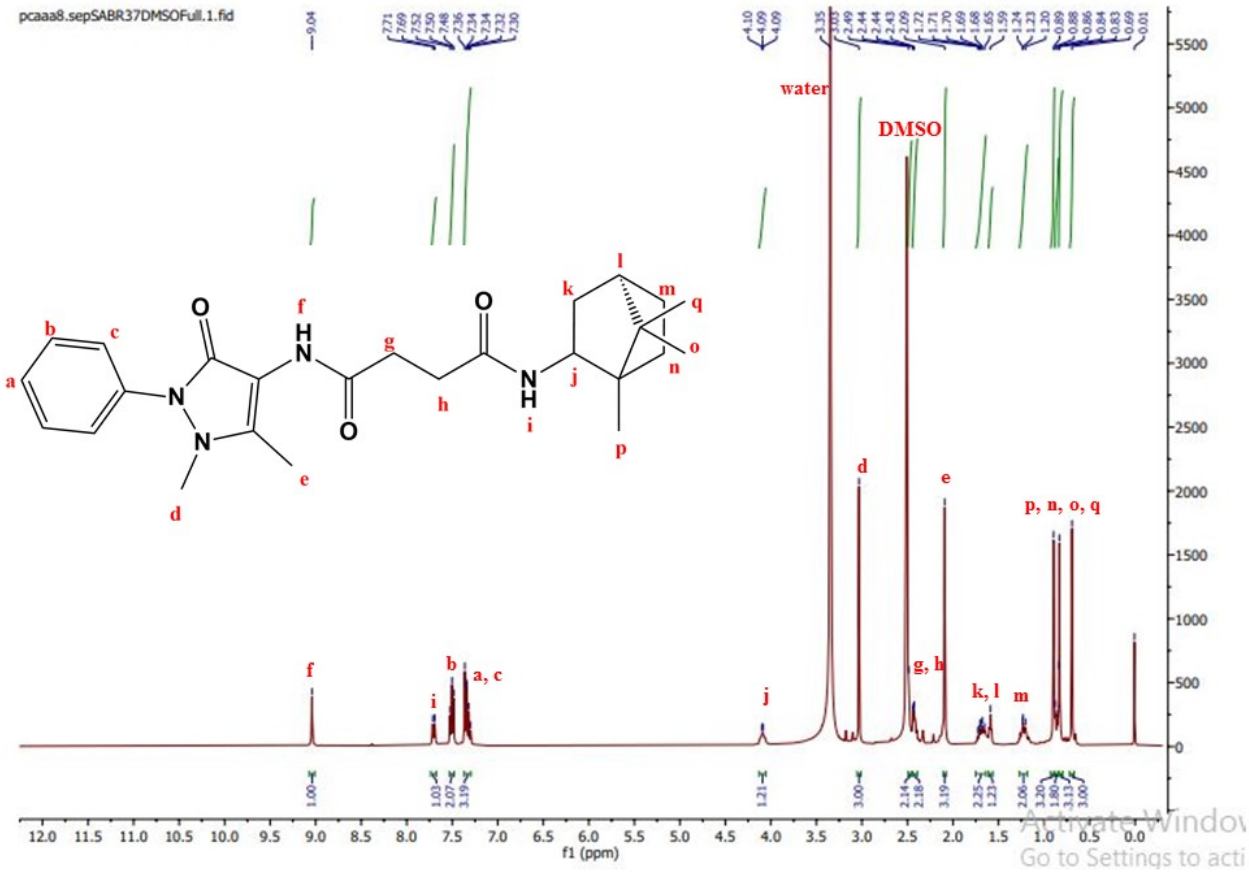


Figure S18: ^{1}H-NMR spectrum of M3.

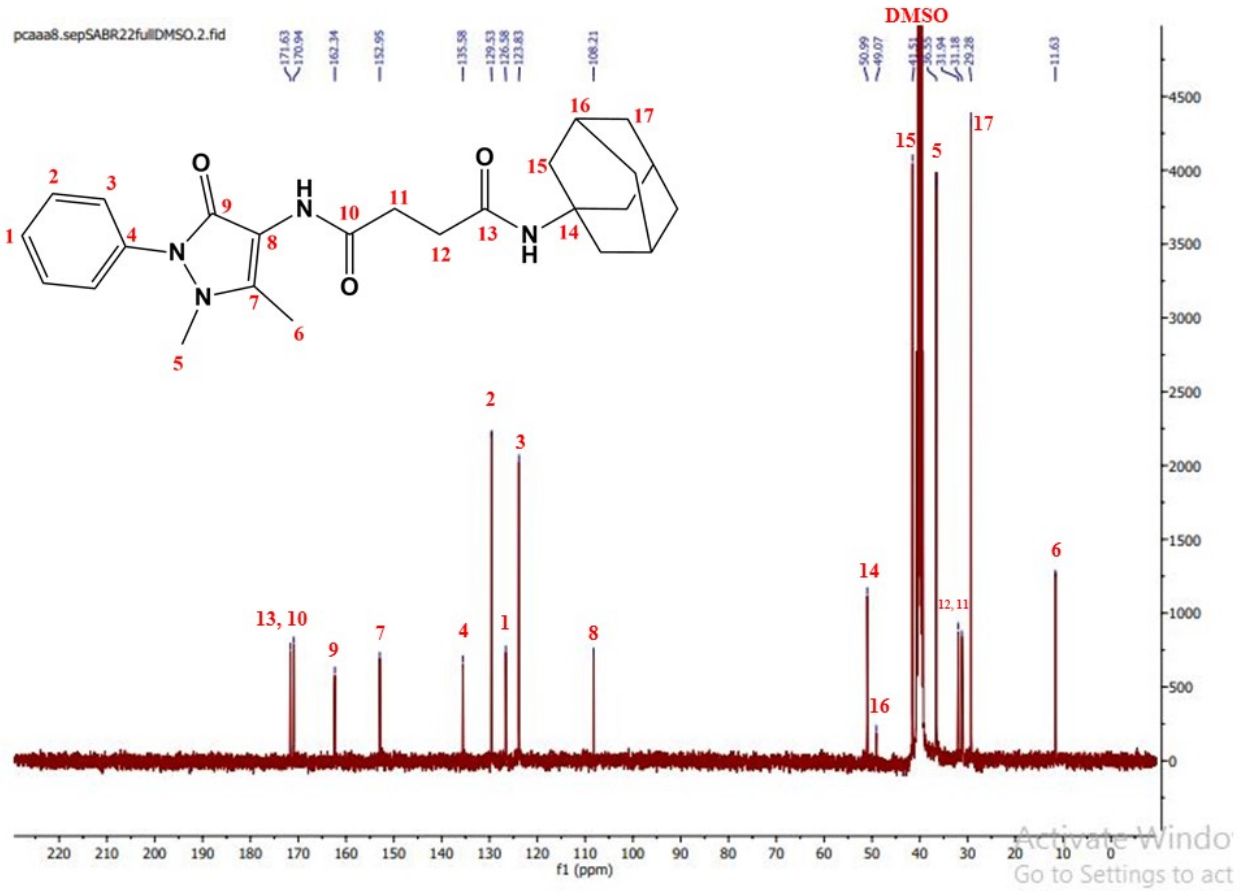


Figure S19: ^{13}C-NMR spectrum of M1.

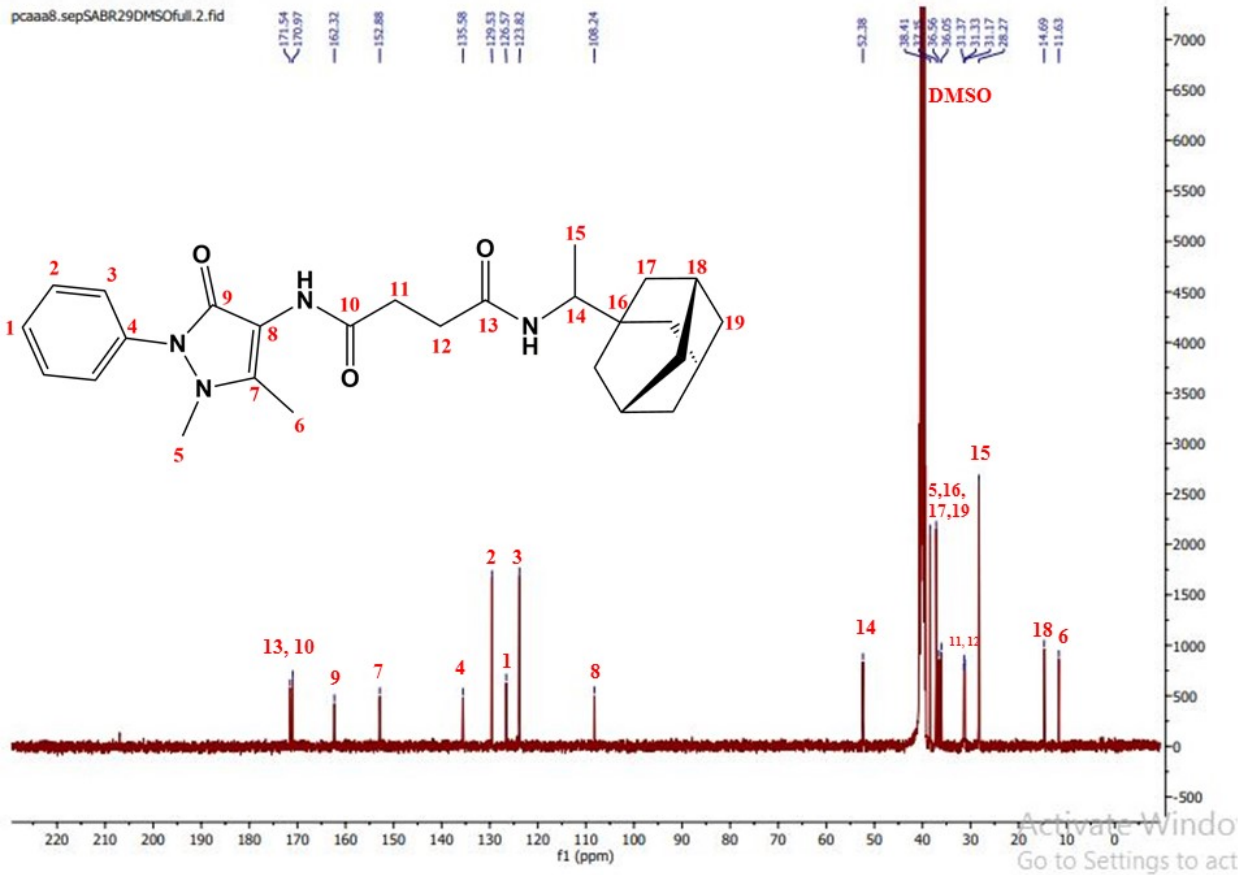


Figure S20: ^{13}C-NMR spectrum of M2.

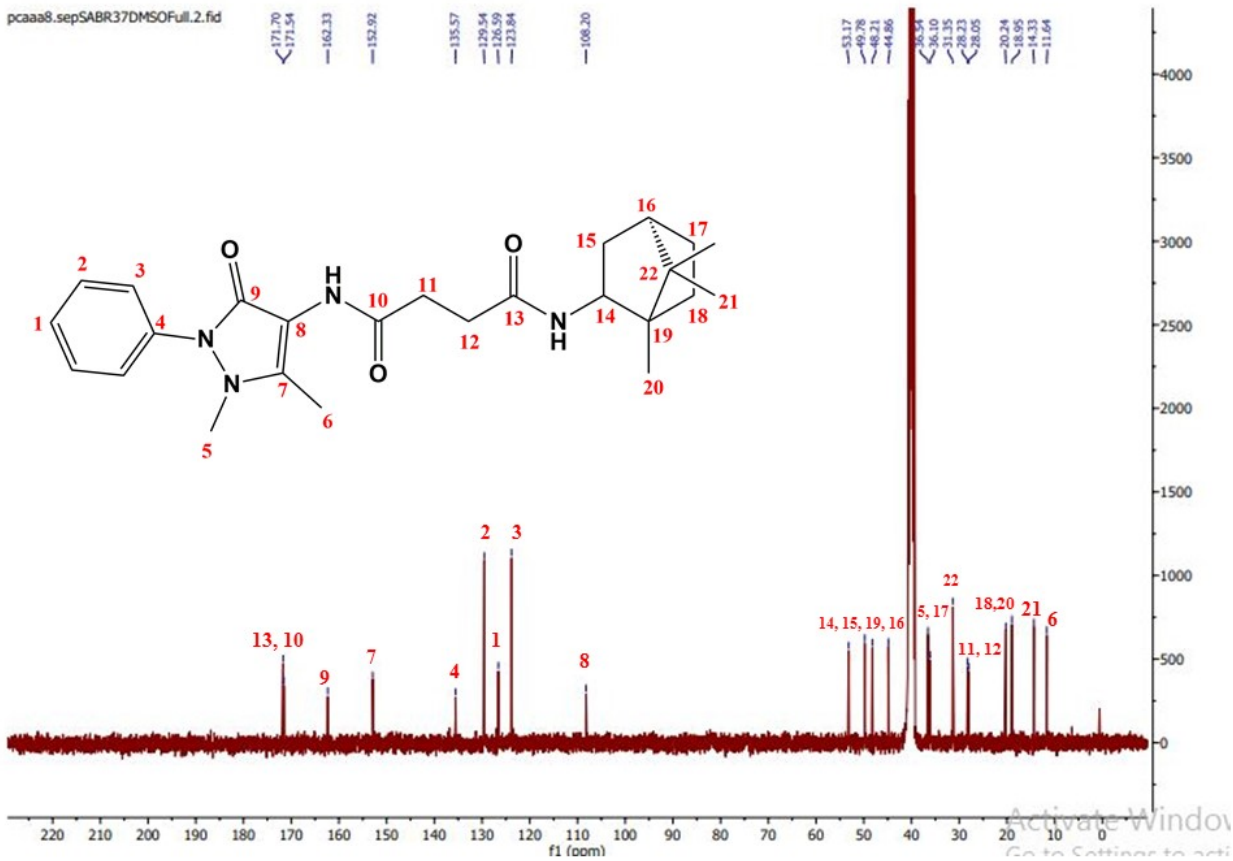


Figure S21: ^{13}C-NMR spectrum of M3.

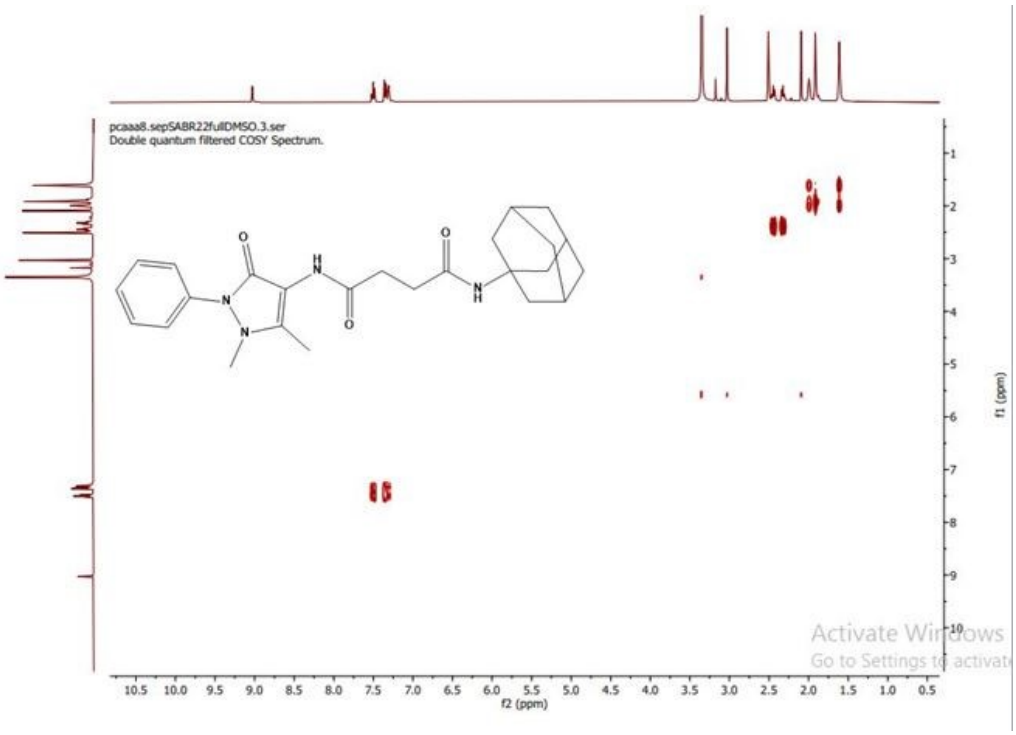


Figure S22: COSY spectrum of M1.

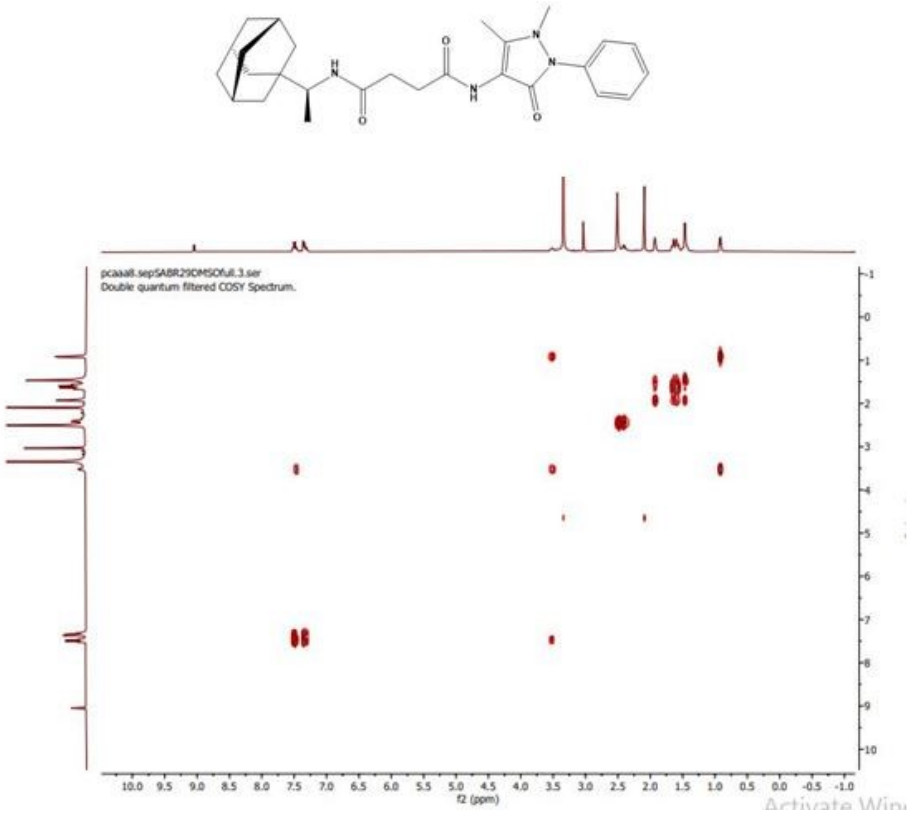


Figure S23: COSY spectrum of M2.

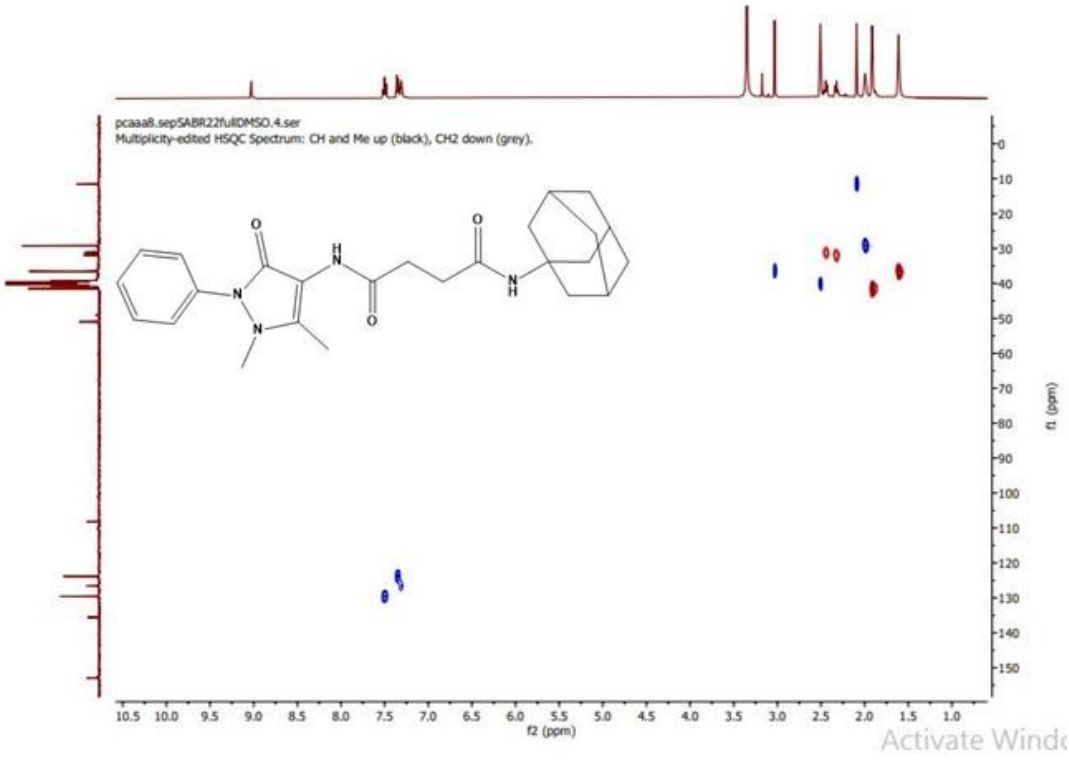


Figure S24: HSQC spectrum of M1.

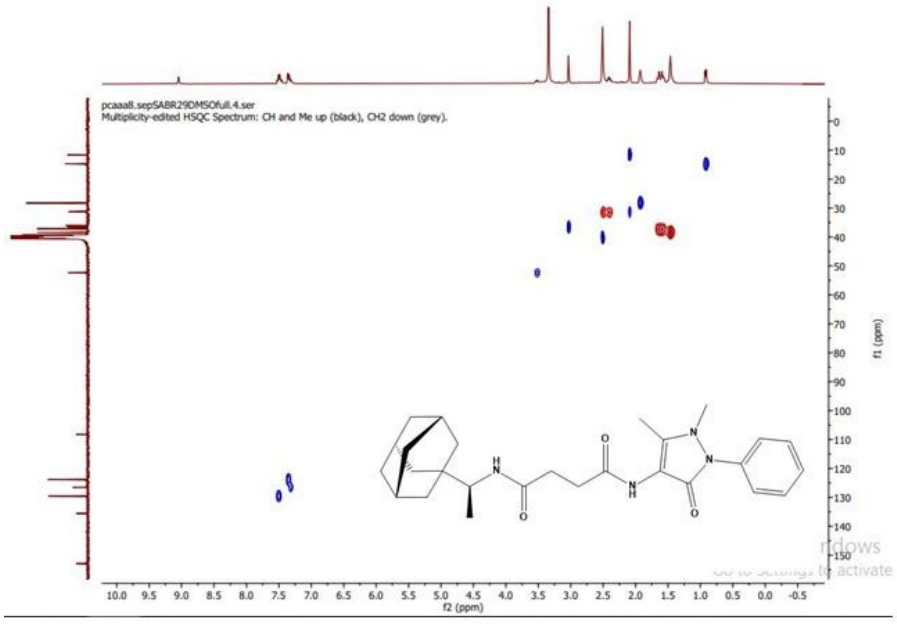


Figure S25: HSQC spectrum of M2.

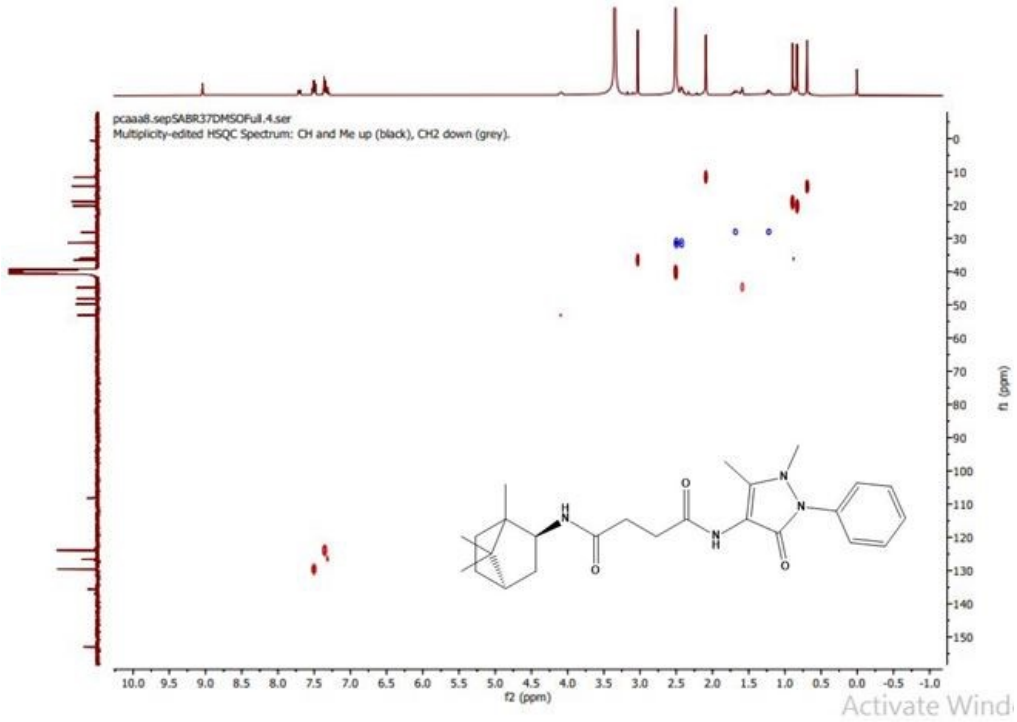
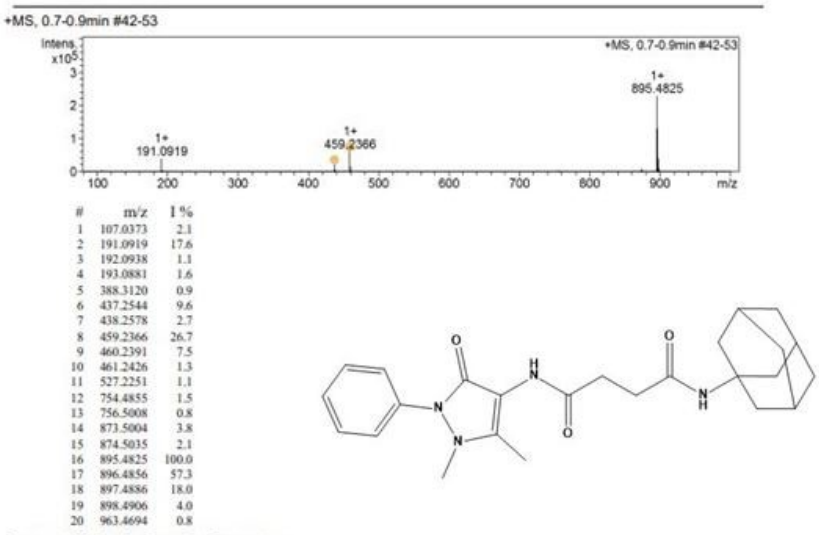


Figure S26: HSQC spectrum of M3.



#	m/z	I %
1	107.0373	2.1
2	191.0919	17.6
3	192.0938	1.1
4	193.0881	1.6
5	388.3120	0.9
6	437.2544	9.6
7	438.2578	2.7
8	459.2366	26.7
9	460.2391	7.5
10	461.2426	1.3
11	527.2251	1.1
12	754.4855	1.5
13	756.5008	0.8
14	873.5004	3.8
15	874.5035	2.1
16	895.4825	100.0
17	896.4856	57.3
18	897.4886	18.0
19	898.4906	4.0
20	963.4694	0.8

Generate Molecular Formula Parameters

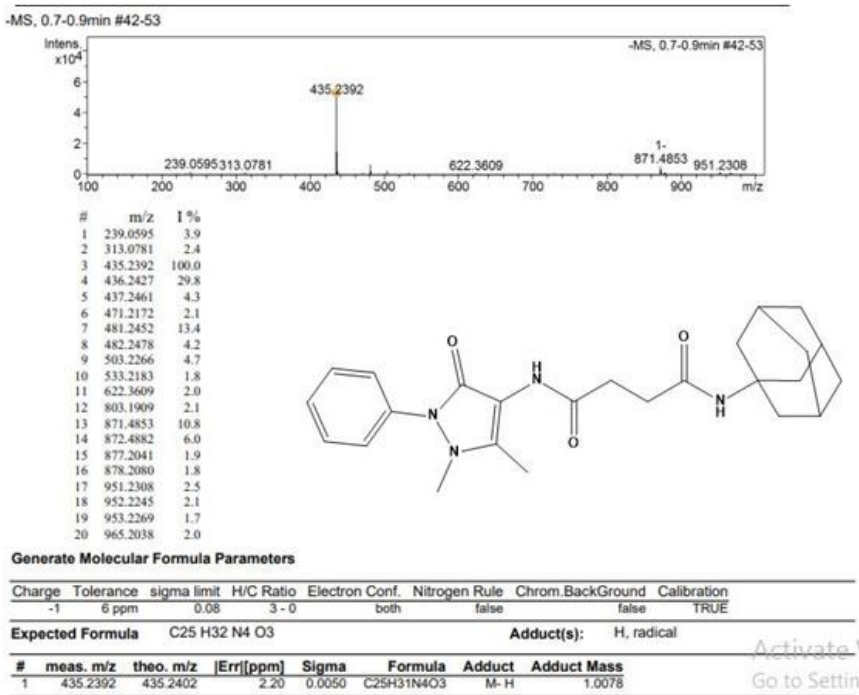
Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C25 H32 N4 O3 **Adduct(s):** H, Na, NH4, C3H5N2, radical

#	meas. m/z	theo. m/z	[Err[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	437.2544	437.2547	0.80	0.0077	C25H33N4O3	M+H	1.0078
1	459.2366	459.2367	0.00	0.0058	C25H32N4NaO3	M+Na	22.9898

Note: Sigma fits < 0.05 indicates high probability of correct MF

Figure S27: HRMS positive spectrum of M1.



#	m/z	I %
1	239.0595	3.9
2	313.0781	2.4
3	435.2392	100.0
4	436.2427	29.8
5	437.2461	4.3
6	471.2172	2.1
7	481.2452	13.4
8	482.2478	4.2
9	503.2266	4.7
10	533.2183	1.8
11	622.3609	2.0
12	803.1909	2.1
13	871.4853	10.8
14	872.4882	6.0
15	877.2041	1.9
16	878.2080	1.8
17	951.2308	2.5
18	952.2245	2.1
19	953.2269	1.7
20	965.2038	2.0

Generate Molecular Formula Parameters

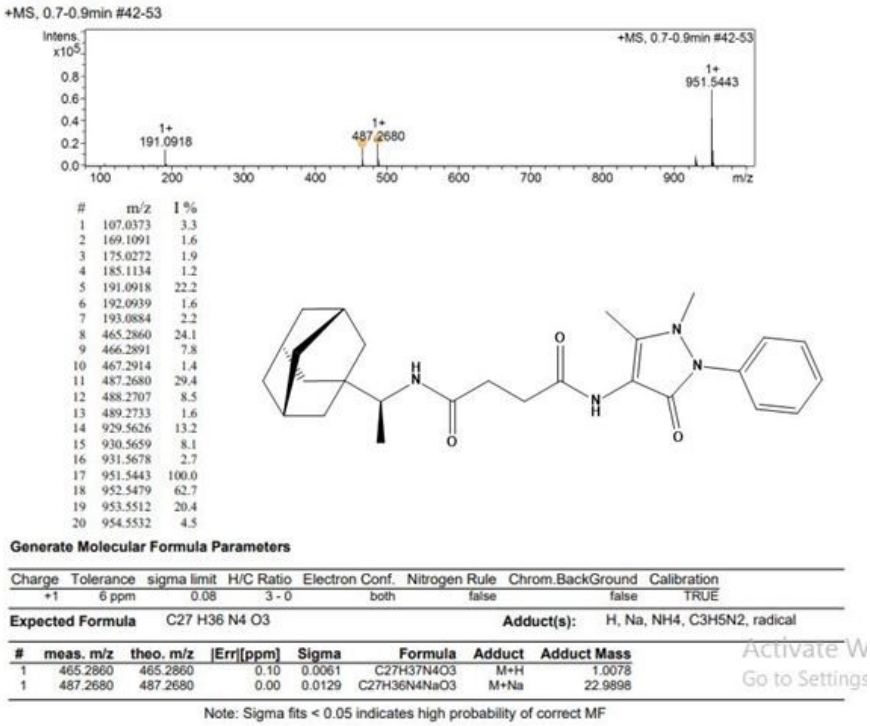
Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
-1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C25 H32 N4 O3 **Adduct(s):** H, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	435.2392	435.2402	2.20	0.0050	C25H31N4O3	M- H	1.0078

Note: Sigma fits < 0.05 indicates high probability of correct MF

Figure S28: HRMS negative spectrum of M1.



#	m/z	I %
1	107.0373	3.3
2	169.1091	1.6
3	175.0272	1.9
4	185.1134	1.2
5	191.0918	22.2
6	192.0939	1.6
7	193.0884	2.2
8	465.2860	24.1
9	466.2891	7.8
10	467.2914	1.4
11	487.2680	29.4
12	488.2707	8.5
13	489.2733	1.6
14	929.5626	13.2
15	930.5659	8.1
16	931.5678	2.7
17	951.5443	100.0
18	952.5479	62.7
19	953.5512	20.4
20	954.5532	4.5

Generate Molecular Formula Parameters

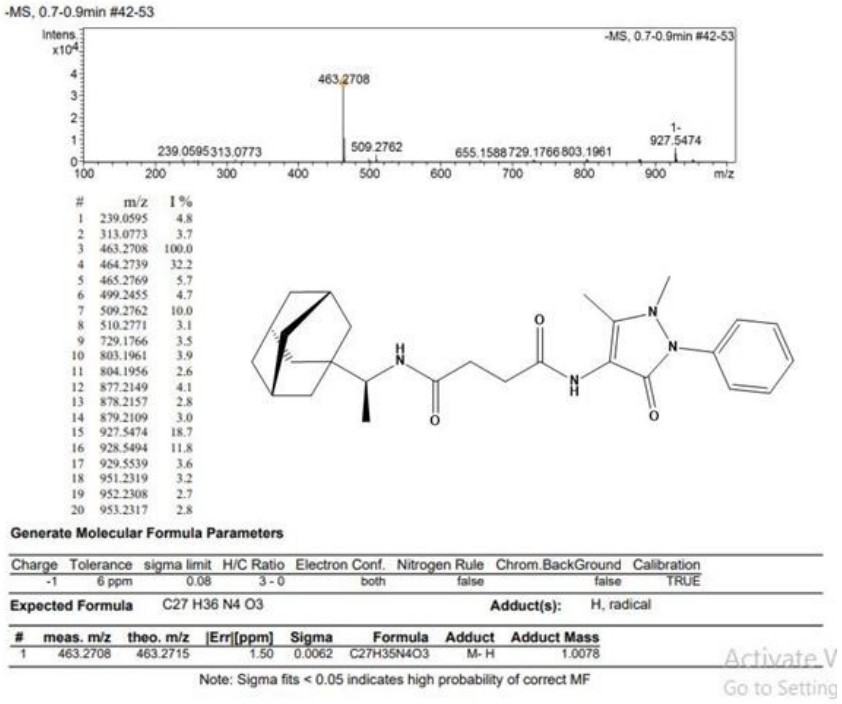
Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C27 H36 N4 O3 **Adduct(s):** H, Na, NH4, C3H5N2, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	465.2860	465.2860	0.10	0.0061	C27H37N4O3	M+H	1.0078
1	487.2680	487.2680	0.00	0.0129	C27H36N4NaO3	M+Na	22.9898

Note: Sigma fits < 0.05 indicates high probability of correct MF

Figure S29: HRMS positive spectrum of M2.



#	m/z	I %
1	239.0595	4.8
2	313.0773	3.7
3	463.2708	100.0
4	464.2739	32.2
5	465.2769	5.7
6	499.2455	4.7
7	509.2762	10.0
8	510.2771	3.1
9	729.1766	3.5
10	803.1961	3.9
11	804.1956	2.6
12	877.2149	4.1
13	878.2157	2.8
14	879.2109	3.0
15	927.5474	18.7
16	928.5494	11.8
17	929.5539	3.6
18	951.2319	3.2
19	952.2308	2.7
20	953.2317	2.8

Generate Molecular Formula Parameters

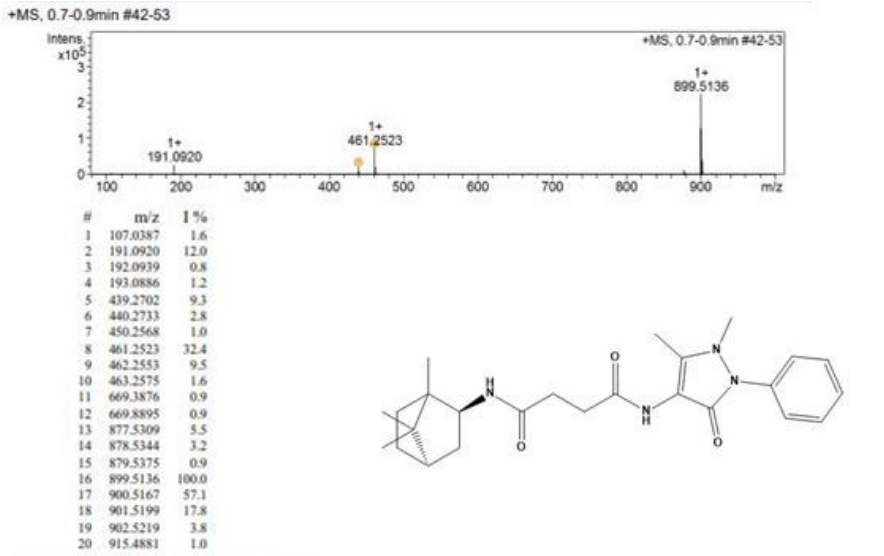
Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
-1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C27 H36 N4 O3 **Adduct(s):** H, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	463.2708	463.2715	1.50	0.0062	C27H35N4O3	M- H	1.0078

Note: Sigma fits < 0.05 indicates high probability of correct MF

Figure S30: HRMS negative spectrum of M2.



#	m/z	I %
1	107.0387	1.6
2	191.0920	12.0
3	192.0939	0.8
4	193.0886	1.2
5	439.2702	9.3
6	440.2733	2.8
7	450.2568	1.0
8	461.2523	32.4
9	462.2553	9.5
10	463.2575	1.6
11	669.3876	0.9
12	669.8895	0.9
13	877.5309	5.5
14	878.5344	3.2
15	879.5375	0.9
16	899.5136	100.0
17	900.5167	57.1
18	901.5199	17.8
19	902.5219	3.8
20	915.4881	1.0

Generate Molecular Formula Parameters

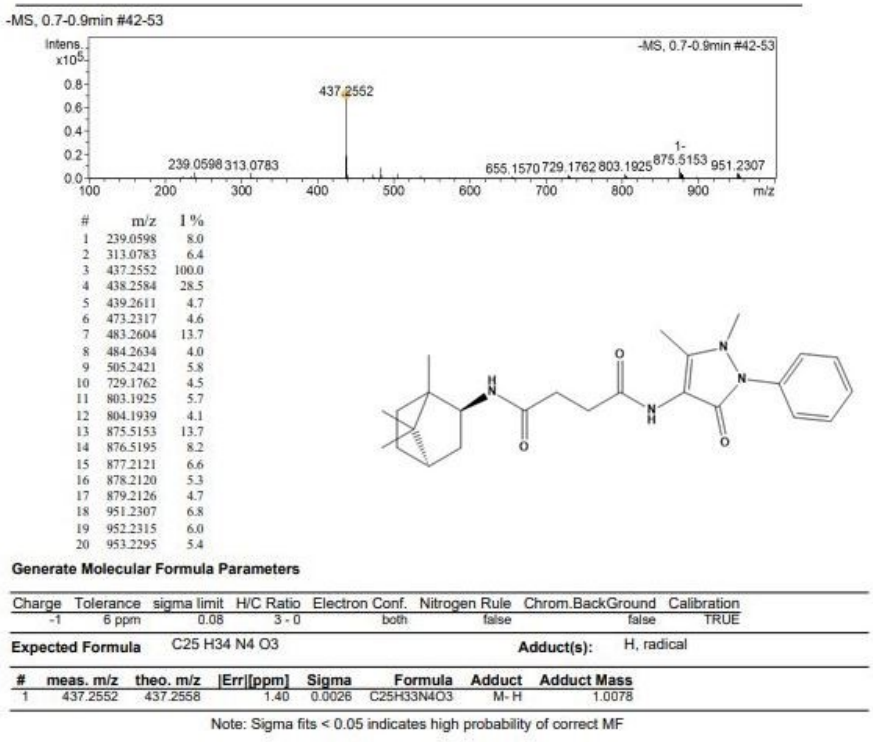
Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C25 H34 N4 O3 **Adduct(s):** H, Na, NH4, C3H5N2, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	439.2702	439.2704	0.50	0.0065	C25H35N4O3	M+H	1.0078
1	461.2523	461.2523	0.10	0.0028	C25H34N4NaO3	M+Na	22.9898

Note: Sigma fits < 0.05 indicates high probability of correct MF

Figure S31: HRMS positive spectrum of M3.



#	m/z	I %
1	239.0598	8.0
2	313.0783	6.4
3	437.2552	100.0
4	438.2584	28.5
5	439.2611	4.7
6	473.2317	4.6
7	483.2604	13.7
8	484.2634	4.0
9	505.2421	5.8
10	729.1762	4.5
11	803.1925	5.7
12	804.1939	4.1
13	875.5153	13.7
14	876.5195	8.2
15	877.2121	6.6
16	878.2120	5.3
17	879.2126	4.7
18	951.2307	6.8
19	952.2315	6.0
20	953.2295	5.4

Generate Molecular Formula Parameters

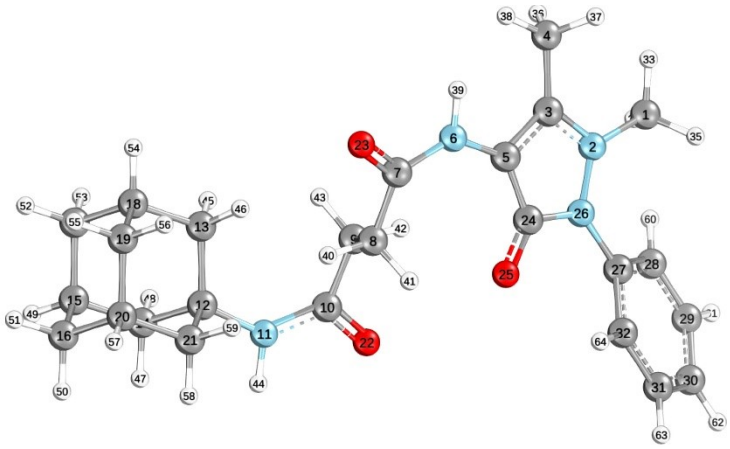
Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
-1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C25 H34 N4 O3 **Adduct(s):** H, radical

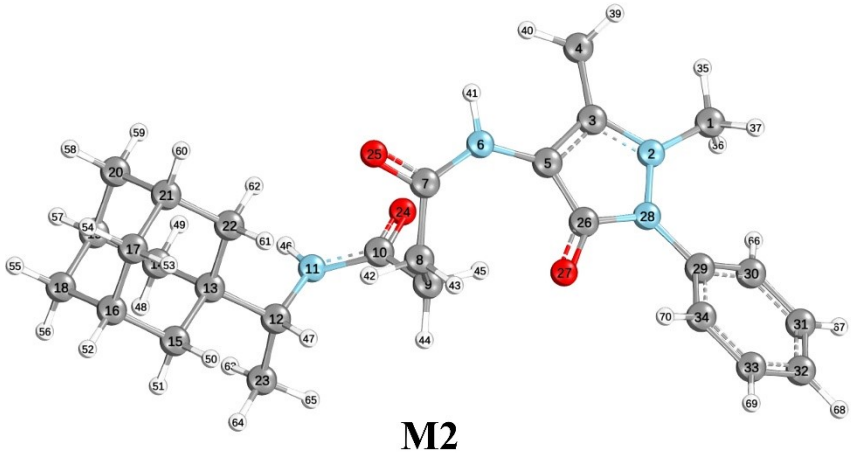
#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	437.2552	437.2558	1.40	0.0026	C25H33N4O3	M- H	1.0078

Note: Sigma fits < 0.05 indicates high probability of correct MF

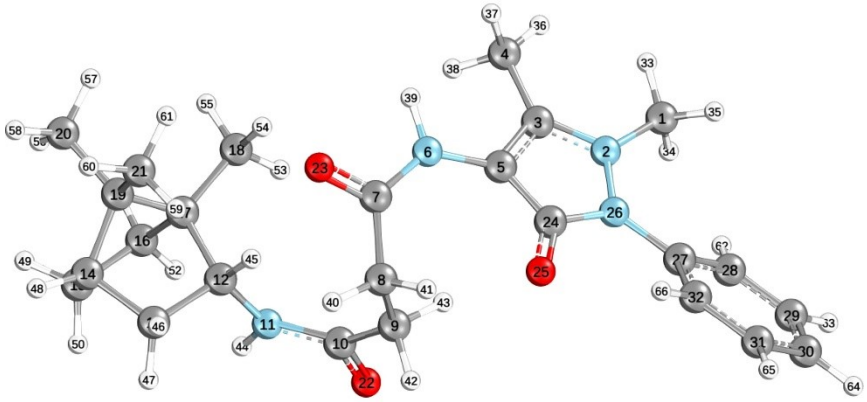
Figure S32: HRMS positive spectrum of M3.



M1



M2



M3

Figure S33: 3D optimized structures of molecules M1, M2 and M3 with atoms numbers.

3.2.1.4. Adsorption isotherms

Temkin isotherm:

$$\theta = -\frac{-1}{2a}\ln\left(K_{ads}\right) + \frac{-1}{2a}ln(C_{inh}) \quad (1)$$

Freundlich isotherm:

$$ln\theta = \ln\left(K_{ads}\right) + aln(C_{inh}) \quad (2)$$

Flory-Huggins isotherm:

$$log(\frac{\theta}{1-\theta}) = \log\left(K_{ads}\right) + ylog(C_{inh}) \quad (3)$$

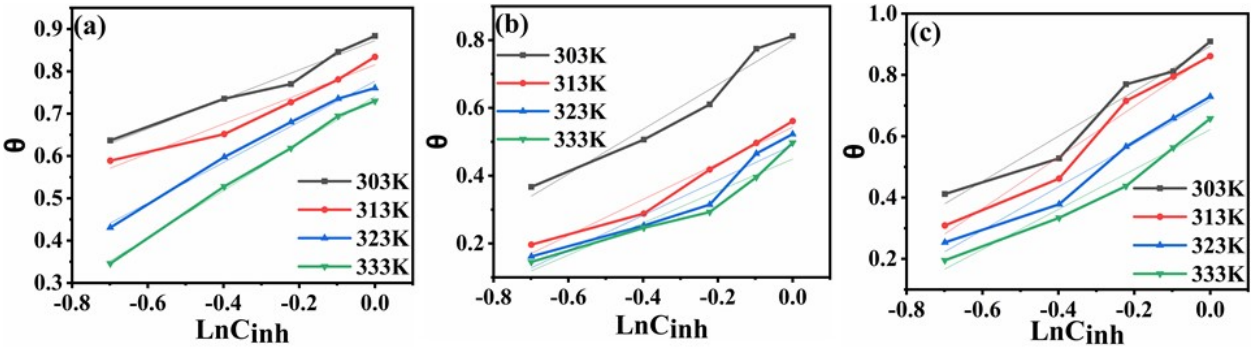


Figure S34. Temkin isotherm of M1 (a), M2 (b) and M3 (c)

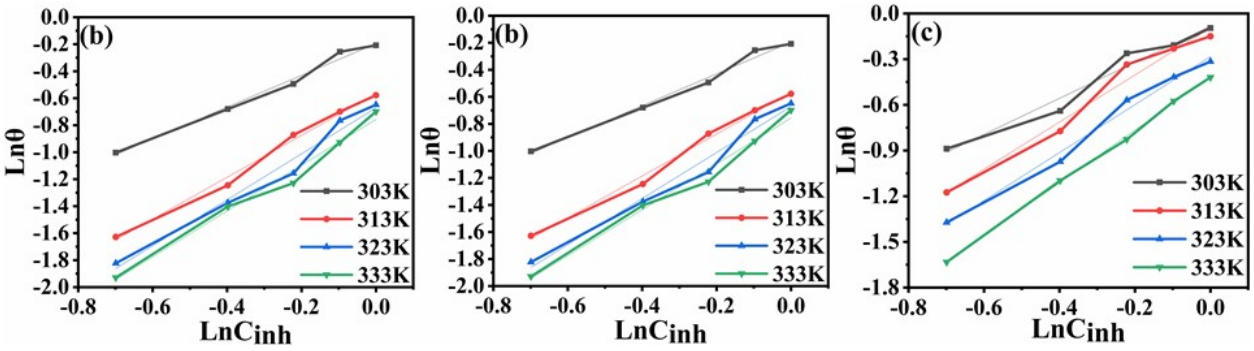


Figure S35. Freundlich isotherm of M1 (a), M2 (b) and M3 (c)

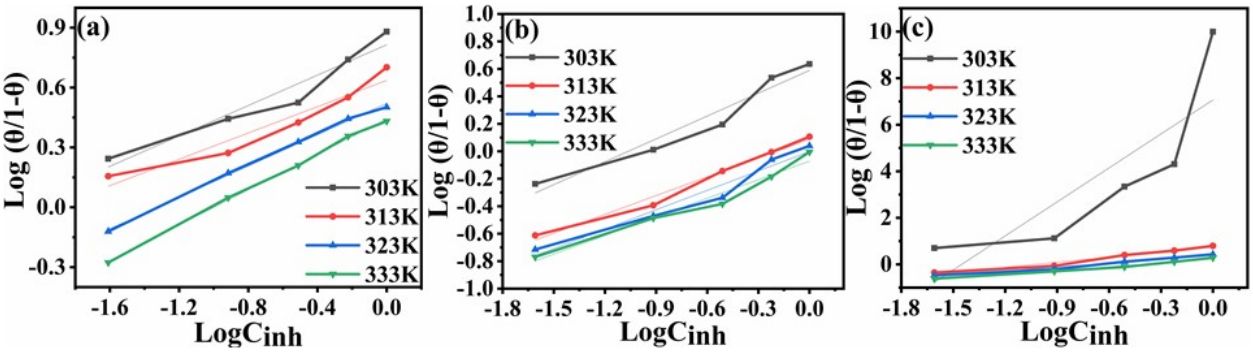


Figure S36. Flory-Huggins isotherm of M1 (a), M2 (b) and M3 (c)

Table S11. Comparison of R^2 values of Temkin, Freundlich, Flory–Huggins and Langmuir isotherms

Temperature (K)	Temkin Isotherm (R^2)	Freundlich Isotherm (R^2)	Flory–Huggins Isotherm (R^2)	Langmuir isotherms (R^2) (Best fitted)
M1				
303	0.99	0.97	0.99	0.99
313	0.98	0.96	0.99	0.99
323	0.95	0.97	0.91	0.99
333	0.96	0.98	0.91	0.99
M2				
303	0.89	0.97	0.95	0.96
313	0.88	0.97	0.94	0.98
323	0.95	0.98	0.97	0.93
333	0.94	0.98	0.92	0.96
M3				
303	0.95	0.99	0.97	0.99
313	0.96	0.98	0.96	0.99
323	0.95	0.96	0.95	0.99
333	0.93	0.95	0.58	0.97