Supplementary Material

Theoretical and experimental investigation of NMR, IR and UV-Visible spectra of hydroxyl-substituted 4-chloromethylcoumarin derivatives

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Table S1 The calculated geometrical parameters for bond-length distances

Bond lengths (Å)	Calculated values				
	Compound				
	A	B	C	D	E
C2 – O1	1.37	1.37	1.37	1.37	1.37
C2 – $O_{carbonyl}$	1.20	1.19	1.20	1.19	1.19
C2 – C3	1.46	1.46	1.46	1.46	1.45
C3 – C4	1.34	1.34	1.34	1.34	1.34
C4 – C11	1.50	1.50	1.50	1.50	1.50
C4 – C10	1.45	1.44	1.45	1.45	1.45
C10 – C9	1.39	1.40	1.39	1.40	1.40
C9 – O1	1.36	1.36	1.36	1.35	1.35
C10 – C5	1.40	1.40	1.40	1.40	1.41
C5 – C6	1.38	1.38	1.37	1.38	1.38
C6 – C7	1.40	1.40	1.41	1.39	1.39
C7 – C8	1.38	1.38	1.38	1.39	1.38
C8 – C9	1.39	1.38	1.39	1.39	1.39
C5 – $O_{5\text{-hydroxyl}}$					1.35
C6 – $O_{6\text{-hydroxyl}}$	1.36		1.37		
C7 – $O_{7\text{-hydroxyl}}$		1.35	1.35	1.36	1.35
C8 – $O_{8\text{-hydroxyl}}$				1.35	
C3 – H8					
C3 – H7	1.08	1.08	1.08	1.08	1.08
C11 – H5	1.09	1.09	1.09	1.09	1.08
C11 – H6	1.08	1.08	1.08	1.08	1.08
C11 – H7					
C11 – Cl	1.80	1.79	1.80	1.80	1.79
C5 – H4	1.08	1.08	1.08	1.08	
C6 – H3		1.08		1.08	1.08
C7 – H2	1.08				
$O_{5\text{-hydroxyl}}$ – H4					0.96
$O_{6\text{-hydroxyl}}$ – H3	0.96		0.96		
$O_{7\text{-hydroxyl}}$ – H2		0.96	0.96	0.96	0.96
$O_{8\text{-hydroxyl}}$ – H1				0.96	
C8 – H1	1.08	1.08	1.08		1.08

*Compound A = 4-chloromethyl-6-hydroxyl-coumarin, Compound B = 4-chloromethyl-7-hydroxyl-coumarin, Compound C = 4-chloromethyl-6,7-dihydroxyl-coumarin, Compound D = 4-chloromethyl-7,8-dihydroxyl-coumarin, Compound E = 4-chloromethyl-5,7-dihydroxyl-coumarin.

Table S2 Z-matrix

Compound **A** (4-chloromethyl-6-hydroxyl-coumarin)

X	Y	Z
-5.090062	-1.79114	0.001559
-3.749655	-1.8249	-0.03021
-3.006521	-0.57633	-0.04437
-3.741649	0.605325	-0.01255
-5.843369	-0.53777	0.020143
-1.017387	-1.40471	-0.12166
-5.692403	-2.68802	0.01563
-1.608543	-0.4987	-0.0736
-3.108031	1.841618	-0.00347
-1.732366	1.90317	-0.0313
-0.977989	0.728545	-0.06756
-3.71304	2.736572	0.024834
0.374014	0.866925	-0.09749
0.796575	0.006804	-0.15303
-5.103054	0.610226	0.016305
-7.036291	-0.45706	0.04225
-3.030545	-3.13653	-0.01839
-2.236775	-3.14949	0.724461
-3.718006	-3.95312	0.172983
-2.258683	-3.46975	-1.60492
-1.215364	2.852297	-0.02888

Energy: -1071.12791061 a.u.

-672143.4752 Kcal/mol

M06-2X/6-311+G(2df,2p)

Compound **B** (4-chloromethyl-7-hydroxyl-coumarin)

X	Y	Z
-8.195663	-1.98677	0.104389
-6.853875	-2.03293	0.112333
-6.096357	-0.79837	0.118596
-6.815432	0.401546	0.116297
-8.930237	-0.72557	0.098887
-4.113441	-1.62703	0.119246
-8.807888	-2.87659	0.100616
-4.700511	-0.71892	0.134262
-6.18709	1.634339	0.131096
-4.804036	1.678083	0.148195
-4.055244	0.497642	0.151287
-2.973707	0.544258	0.160821
-8.171117	0.418854	0.102551
10.120123	-0.61841	0.093451
-4.223551	2.899396	0.160426
-3.267185	2.814377	0.167454
-6.150503	-3.3537	0.137983
-5.384008	-3.38547	0.908342
-6.855045	-4.1632	0.296302
-5.329683	-3.67976	-1.42415
-6.770117	2.543302	0.127249

Energy: -1071.13099889 a.u.

-672145.4131 Kcal/mol

M06-2X/6-311+G(2df,2p)

Compound **C** (4-chloromethyl-6,7-dihydroxyl-coumarin)

X	Y	Z
-5.097571	-1.79854	-0.02928
-3.754404	-1.82123	-0.03798
-3.019353	-0.57508	-0.00664
-3.757499	0.606058	0.035461
-5.854816	-0.55162	0.009186
-1.013511	-1.37727	-0.05767
-5.692598	-2.69987	-0.05066
-1.618587	-0.48074	-0.00542
-3.145049	1.850889	0.080921
-1.769186	1.922626	0.081031
-1.004156	0.743775	0.037493
-3.74099	2.750999	0.113708
-1.159444	3.121836	0.120416
-0.204939	2.988864	0.108135
0.348657	0.941097	0.039679
0.816096	0.107968	-0.0508
-5.115745	0.602223	0.039647
-7.047532	-0.46779	0.018246
-3.029699	-3.1304	-0.05011
-2.261584	-3.17005	0.718523
-3.719273	-3.95611	0.087314
-2.202506	-3.40483	-1.6203

Energy: -1146.35984472 a.u.

-719352.2662 Kcal/mol

M06-2X/6-311+G(2df,2p)

Compound **D** (4-chloromethyl-7,8-dihydroxyl-coumarin)

X	Y	Z
-8.193707	-1.96931	0.102064
-6.852817	-2.01972	0.109249
-6.087786	-0.78674	0.110525
-6.816607	0.405984	0.109663
-8.928797	-0.70702	0.089926
-4.110808	-1.63417	0.10148
-8.807007	-2.85874	0.104591
-4.69259	-0.72432	0.125332
-6.17901	1.641802	0.12913
-4.790103	1.669131	0.147701
-4.047377	0.494839	0.145287
-2.966097	0.545633	0.152438
-8.170107	0.434906	0.096033
-10.118851	-0.60373	0.078205
-6.911915	2.772881	0.132433
-6.313577	3.527558	0.148399
-4.243105	2.916889	0.166673
-3.284839	2.867957	0.185114
-6.154909	-3.34287	0.145889
-5.377946	-3.36498	0.905707
-6.860634	-4.14604	0.327165
-5.355096	-3.70075	-1.42117

Energy: -1146.3550447 a.u.

-719349.2541 Kcal/mol

M06-2X/6-311+G(2df,2p)

Compound **E** (4-chloromethyl-5,7-dihydroxyl-coumarin)

X	Y	Z
-7.286182	-0.12584	-0.19075
-5.906834	-0.16329	-0.17114
-5.136947	1.016153	-0.08597
-5.853217	2.220876	-0.07005
-7.237577	2.281714	-0.09204
-7.948466	1.097189	-0.14321
-7.86582	-1.03691	-0.25599
-3.689014	1.103546	-0.01003
-7.722622	3.247531	-0.06871
-3.860272	3.555905	-0.02315
-3.104377	2.315298	0.0096
-2.032749	2.431014	0.074618
-5.228348	3.420197	-0.03123
-3.402018	4.659438	-0.02816
-2.798965	-0.10125	0.089145
-3.063182	-0.87953	-0.61503
-1.763805	0.19367	-0.04483
-2.915221	-0.82122	1.727659
-5.252728	-1.34471	-0.25612
-5.878878	-2.07177	-0.21396
-9.298726	1.059054	-0.16343
-9.65674	1.949675	-0.12927

Energy: -1146.35851953 a.u.

-719351.4346 Kcal/mol

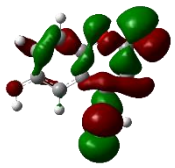
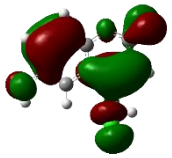
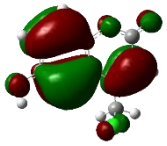
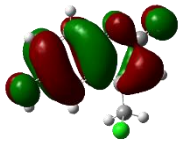
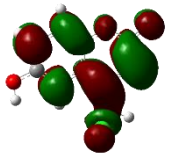
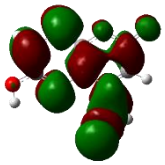
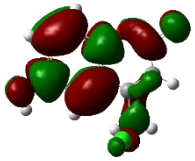
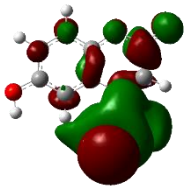
M06-2X/6-311+G(2df,2p)

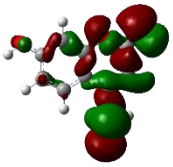
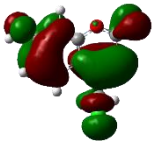
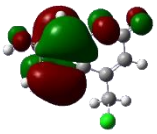
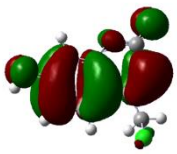
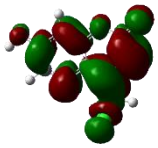
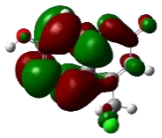
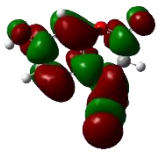
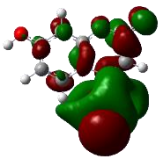
Table S3 Calculated charge of coumarin derivatives

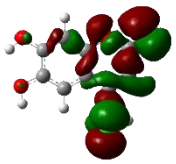
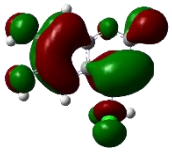
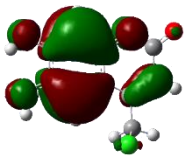
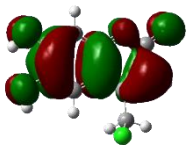
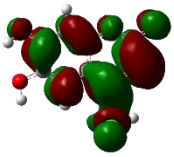
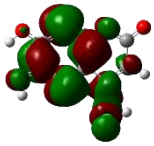
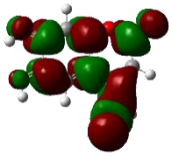
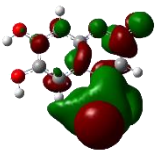
Atom	Compound				
	A	B	C	D	E
H1	0.17	0.18	0.18	0.28	0.15
H2	0.17	0.25	0.29	0.26	0.26
H3	0.26	0.14	0.27	0.14	0.15
H4	0.16	0.18	0.17	0.18	0.27
H5	0.17	0.18	0.18	0.18	0.18
H6	0.17	0.17	0.17	0.16	0.16
H7	0.18	0.18	0.18	0.18	0.18
H8					
C2	0.41	0.42	0.40	0.41	0.42
C3	-0.16	-0.21	-0.29	-0.39	-0.27
C4	0.85	0.61	0.78	0.87	0.88
C5	-0.37	-0.43	-0.55	-0.42	-0.72
C6	-0.52	-0.14	-0.04	-0.18	-0.03
C7	0.35	-0.24	-0.00	-0.06	-0.34
C8	-0.35	-0.21	-0.20	-0.04	-0.56
C9	-0.46	-0.18	-0.26	-0.10	-0.10
C10	0.35	0.45	0.60	0.36	1.02
C11	-0.12	-0.12	-0.15	-0.13	-0.08
Cl	-0.26	-0.26	-0.25	-0.25	-0.28
O1	-0.27	-0.27	-0.27	-0.29	-0.27
O $_{(Carbonyl)}$	-0.41	-0.40	-0.41	-0.40	-0.41
O $_{(5\text{-}Hydroxyl)}$	-	-	-	-	-0.32
O $_{(6\text{-}Hydroxyl)}$	-0.33	-	-0.42	-	-
O $_{(7\text{-}Hydroxyl)}$	-	-0.31	-0.35	-0.38	-0.31
O $_{(8\text{-}Hydroxyl)}$	-	-	-	-0.39	-

*Compound A = 4-chloromethyl-6-hydroxyl-coumarin, Compound B = 4-chloromethyl-7-hydroxyl-coumarin, Compound C = 4-chloromethyl-6,7-dihydroxyl-coumarin, Compound D = 4-chloromethyl-7,8-dihydroxyl-coumarin, Compound E = 4-chloromethyl-5,7-dihydroxyl-coumarin.

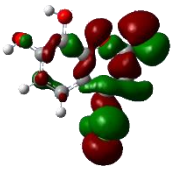
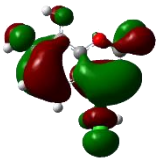
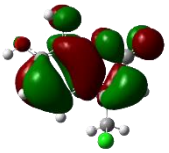
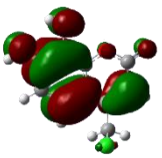
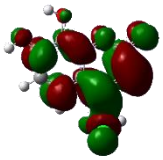
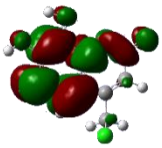
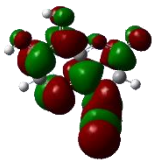
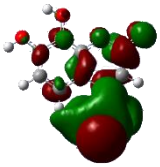
Table S4 Calculated energy levels of HOMO, LUMO and energy gap (eV)

Compound A		
H - 3	-0.45eV	
H - 2	-0.43 eV	
H -1	-0.36 eV	
H	-0.32 eV	
L	0.05 eV	
L + 1	0.13 eV	
L + 2	0.14 eV	
L + 3	0.20 eV	
Gap	**-0.37 eV**	

Compound B		
H - 3	-0.44 eV	
H - 2	-0.42 eV	
H -1	-0.36 eV	
H	-0.32 eV	
L	0.06 eV	
L + 1	0.12 eV	
L + 2	0.14 eV	
L + 3	0.20 eV	
Gap	**-0.38 eV**	

Compound C		
H - 3	-0.44 eV	
H - 2	-0.42 eV	
H -1	-0.36 eV	
H	-0.31 eV	
L	0.05 eV	
L + 1	0.13 eV	
L + 2	0.14 eV	
L + 3	0.20 eV	
Gap	**-0.36 eV**	

Compound D

H - 3	-0.44 eV	
H - 2	-0.42 eV	
H -1	-0.33 eV	
H	-0.32 eV	
L	0.06 eV	
L + 1	0.13 eV	
L + 2	0.15 eV	
L + 3	0.21 eV	
Gap	**-0.38 eV**	

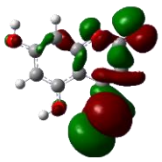
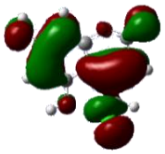
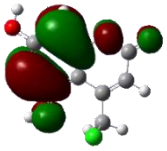
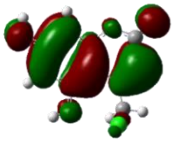
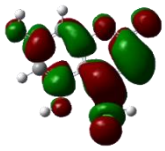
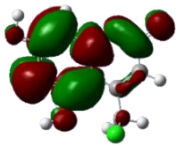
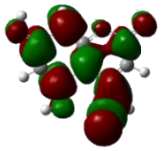
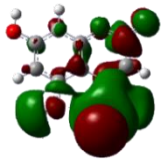
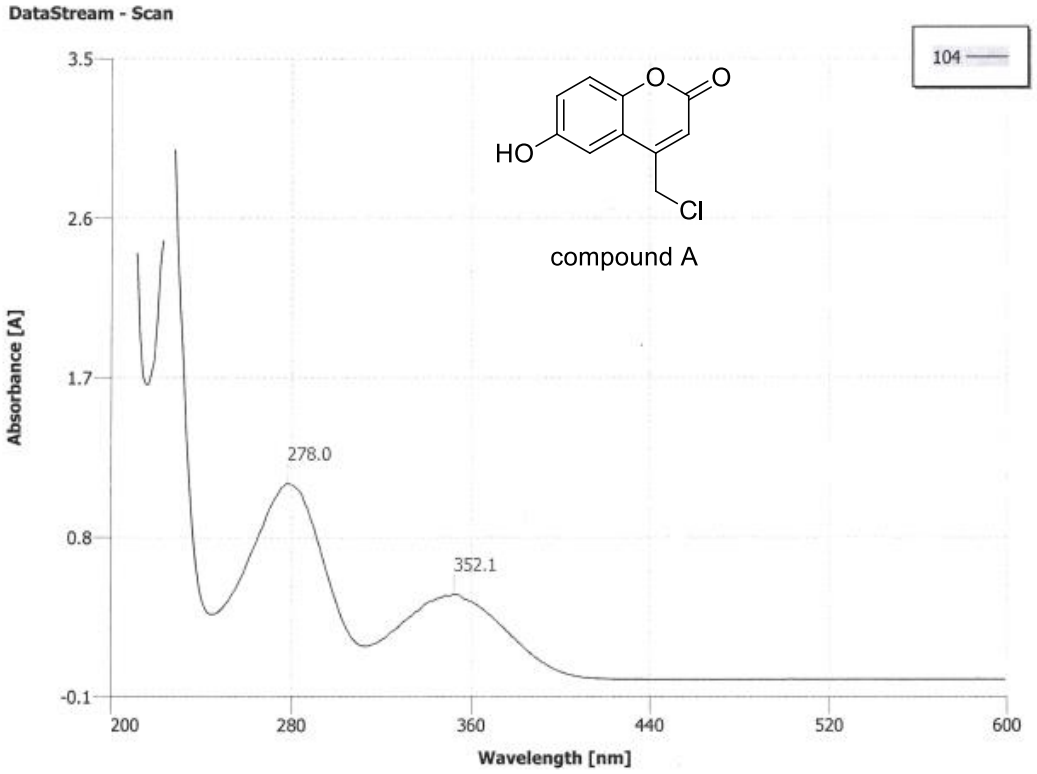
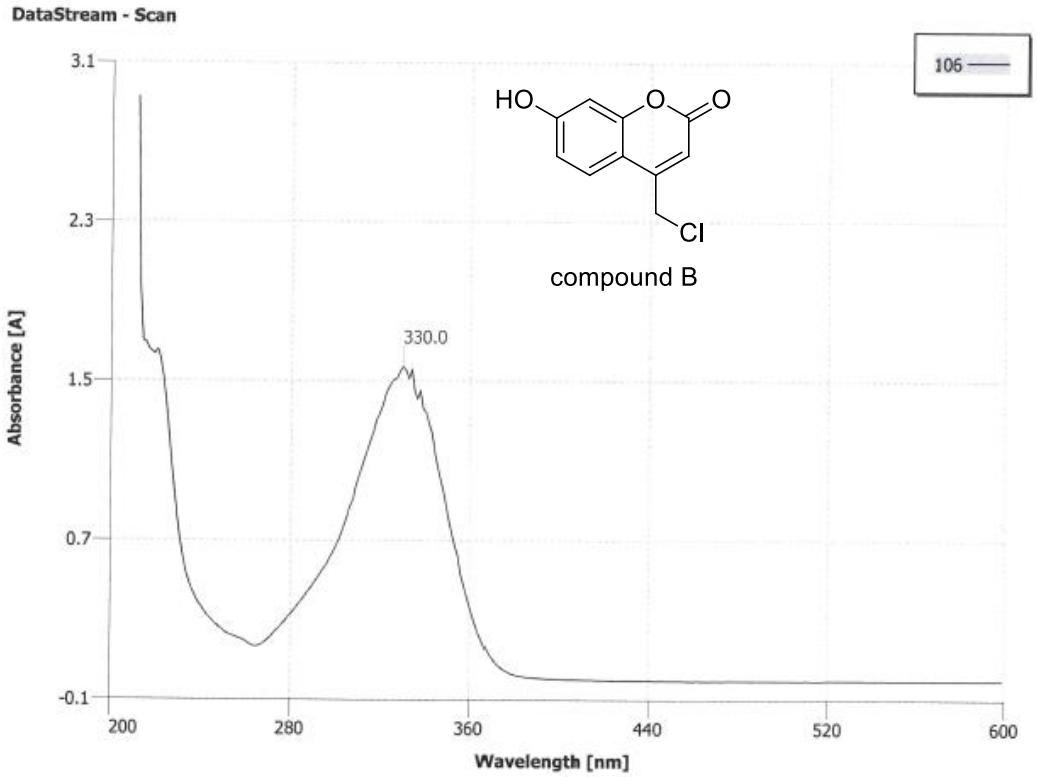
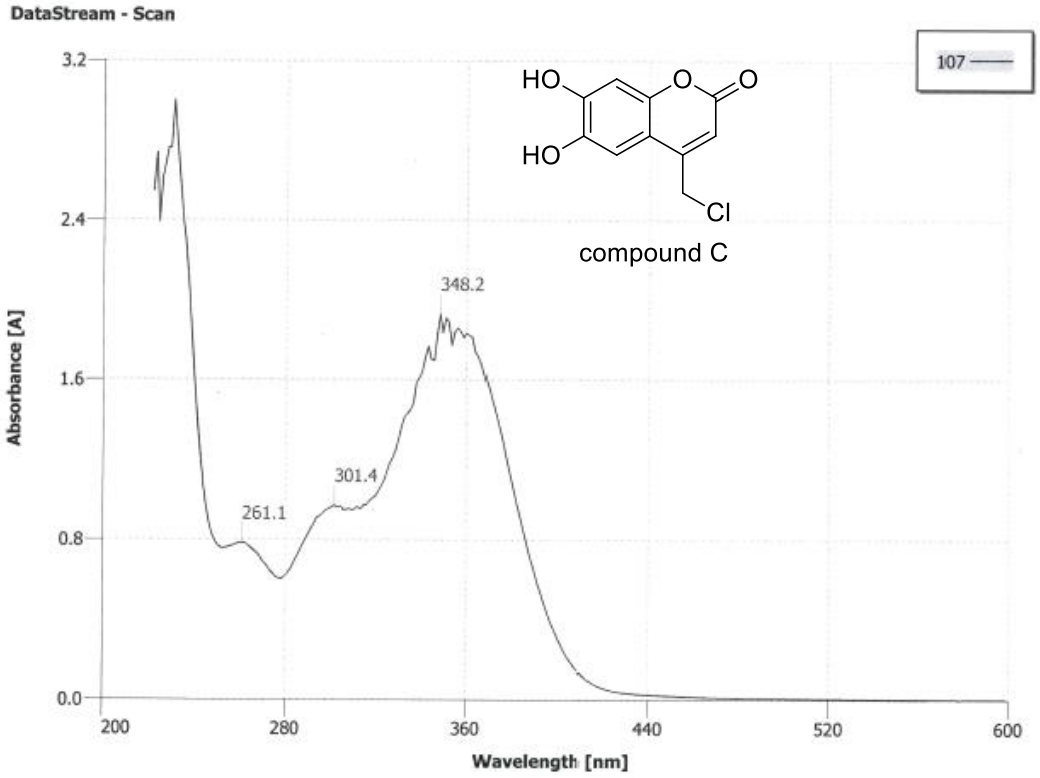
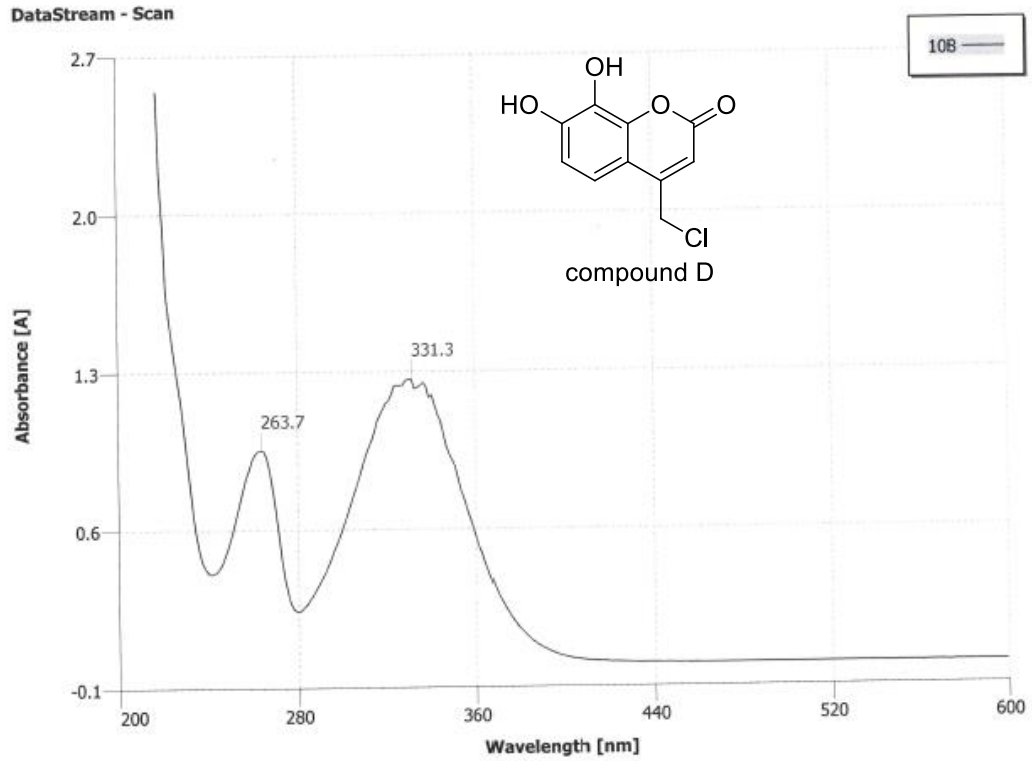
Compound E		
H - 3	-0.44 eV	
H - 2	-0.42 eV	
H -1	-0.35 eV	
H	-0.32 eV	
L	0.06 eV	
L + 1	0.13 eV	
L + 2	0.15 eV	
L + 3	0.22 eV	
Gap	**-0.38 eV**	

Figure S1 UV-Visible spectra of coumarin compounds **A**, **B**, **C**, **D** and **E**









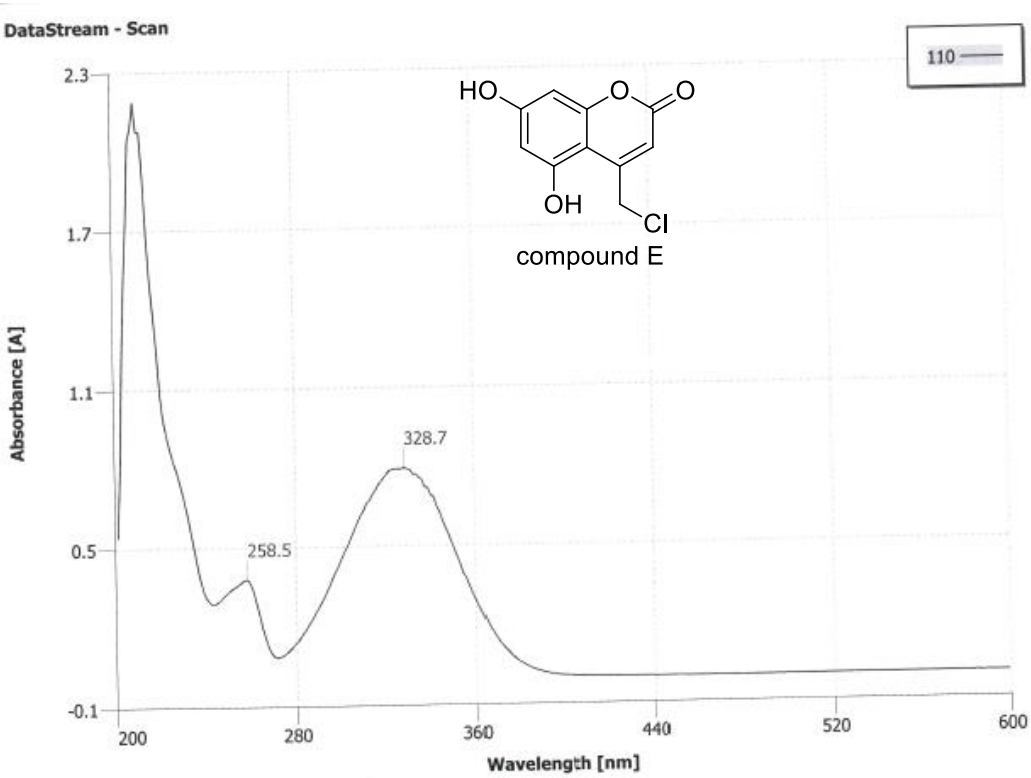
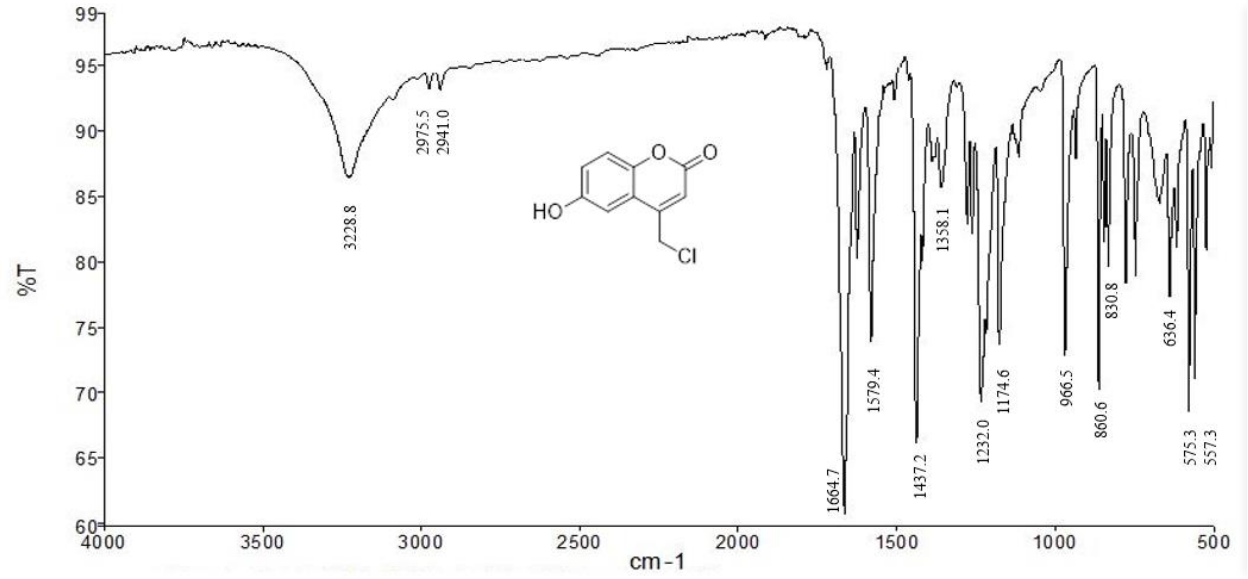
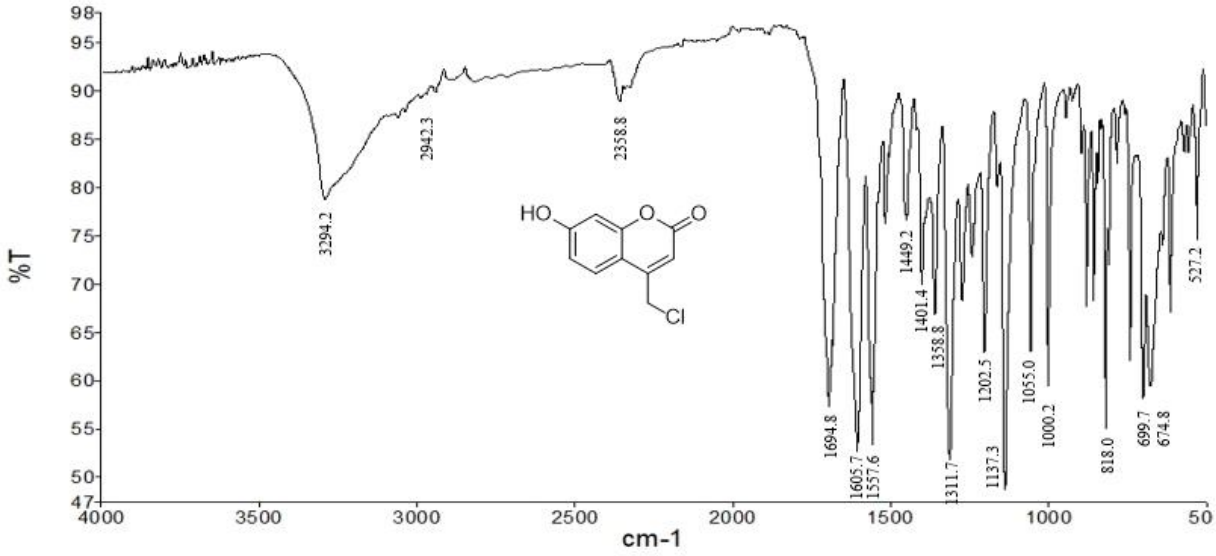


Figure S2 IR spectrum of coumarin compounds **A**, **B**, **C**, **D** and **E**

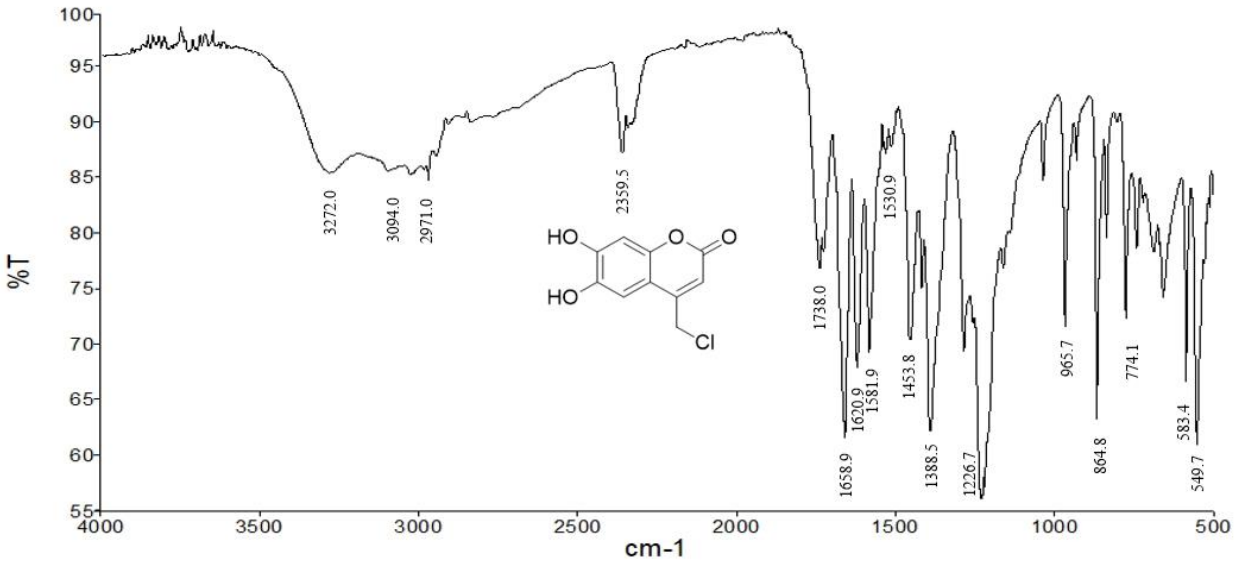
Compound A



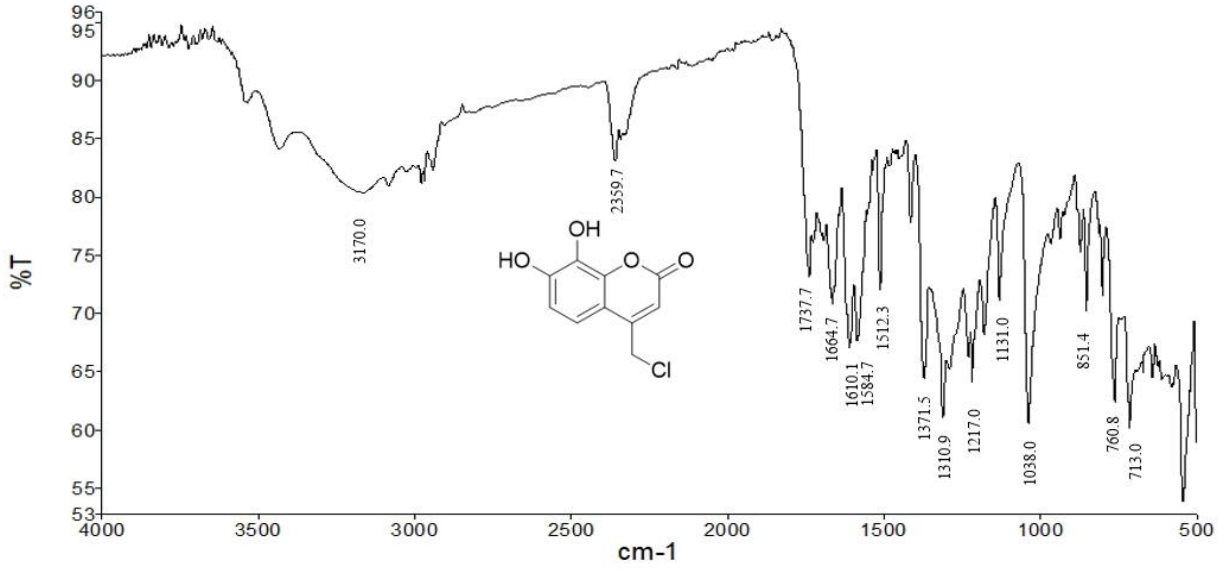
Compound B



Compound C



Compound D



Compound E

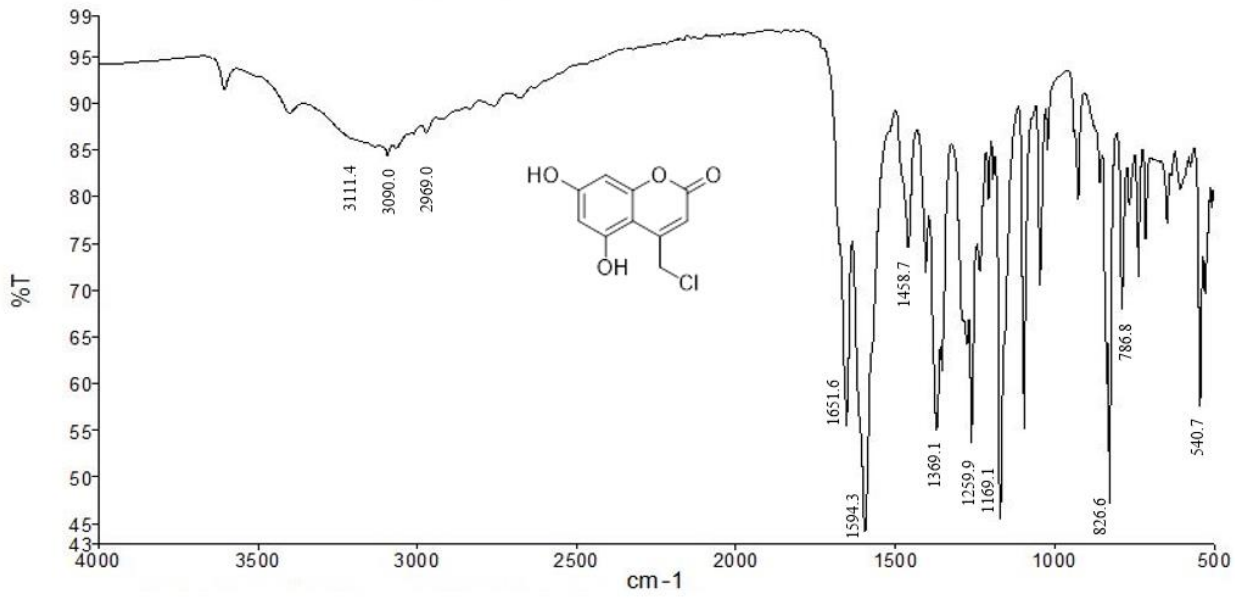
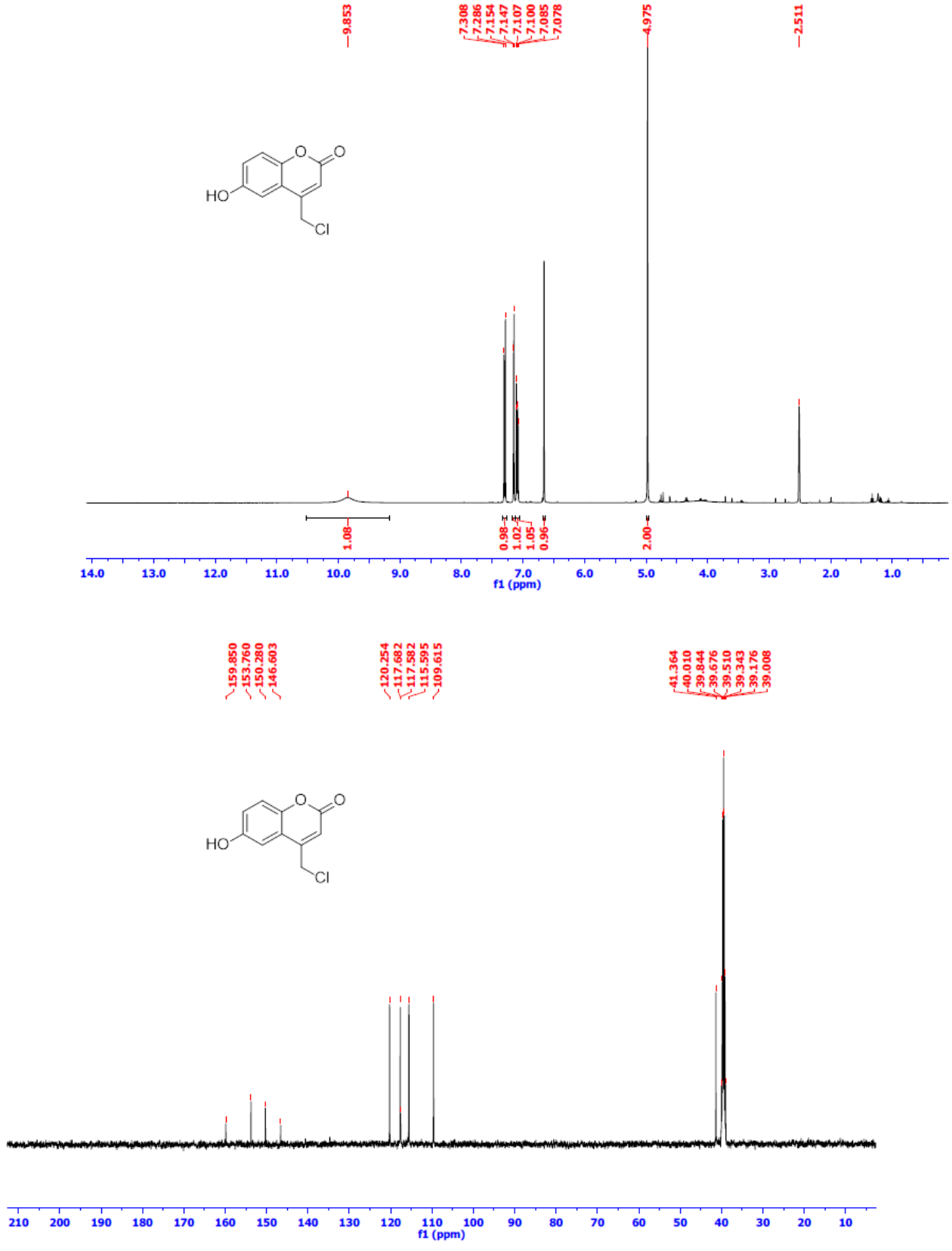
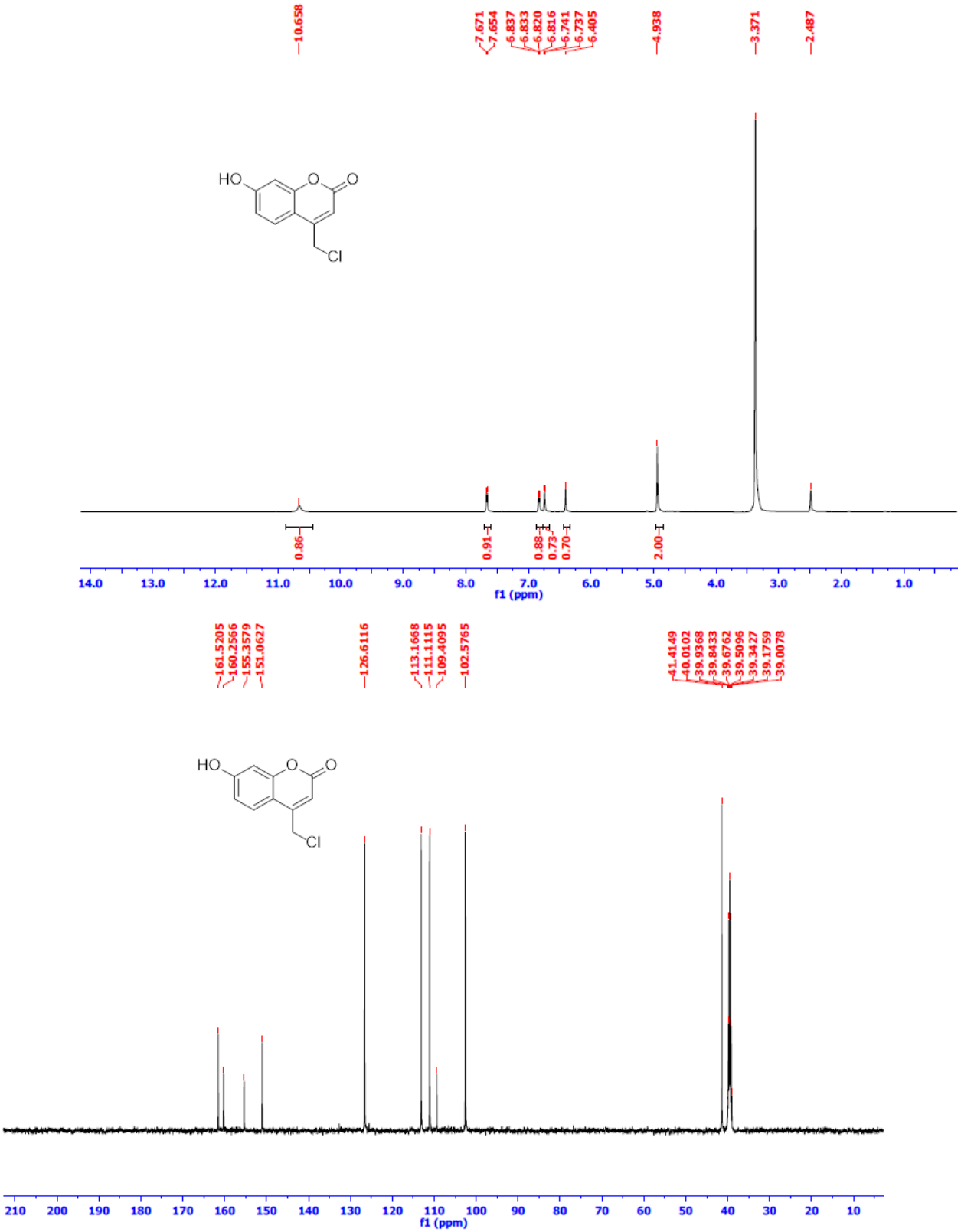


Figure S3 ^{1}H-NMR and ^{13}C-NMR spectra of coumarin compounds **A**, **B**, **C**, **D** and **E**

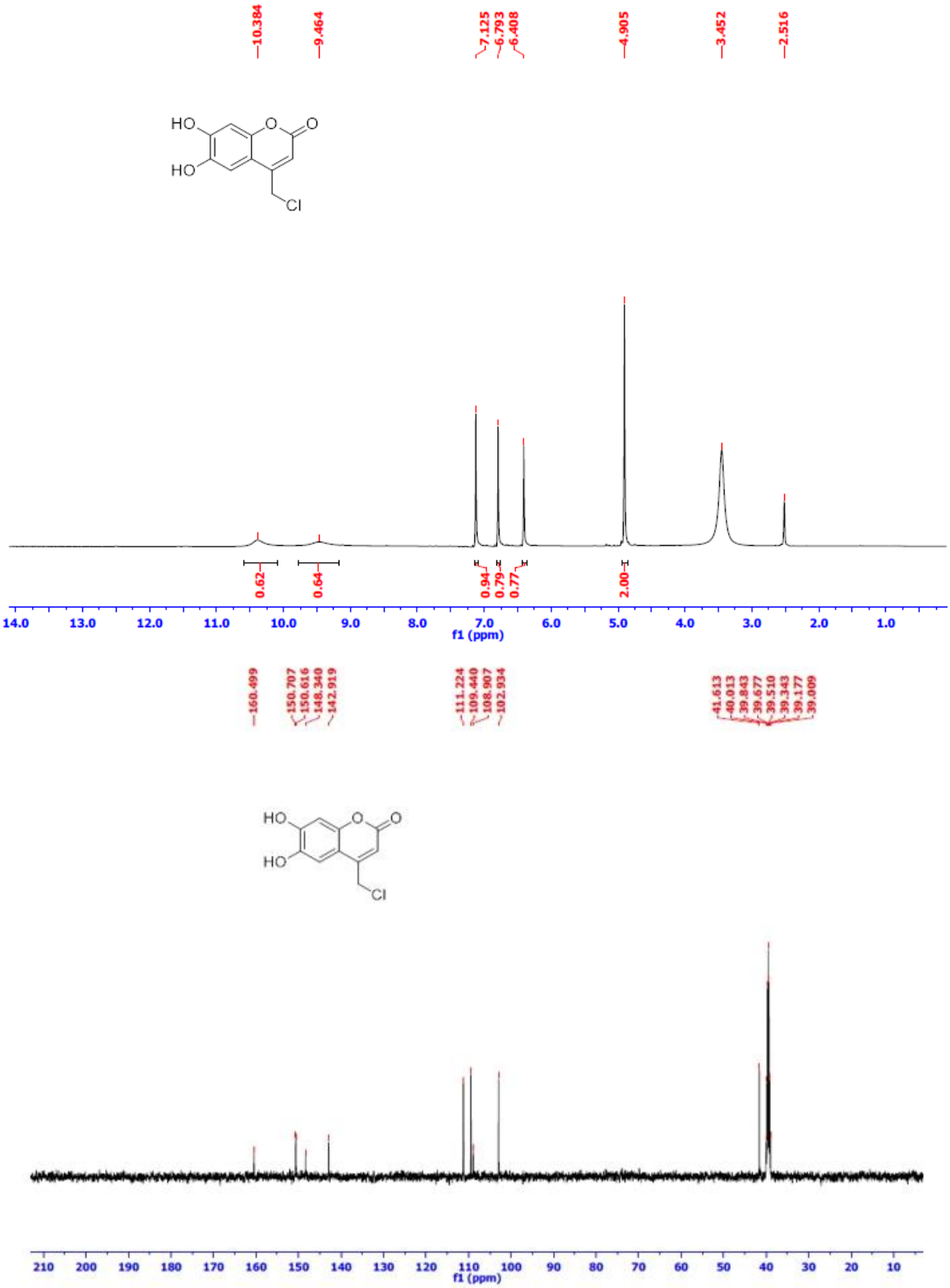
^{1}H-NMR and ^{13}C-NMR spectra of 4-chloromethyl-6-hydroxyl-coumarin (compound **A**)



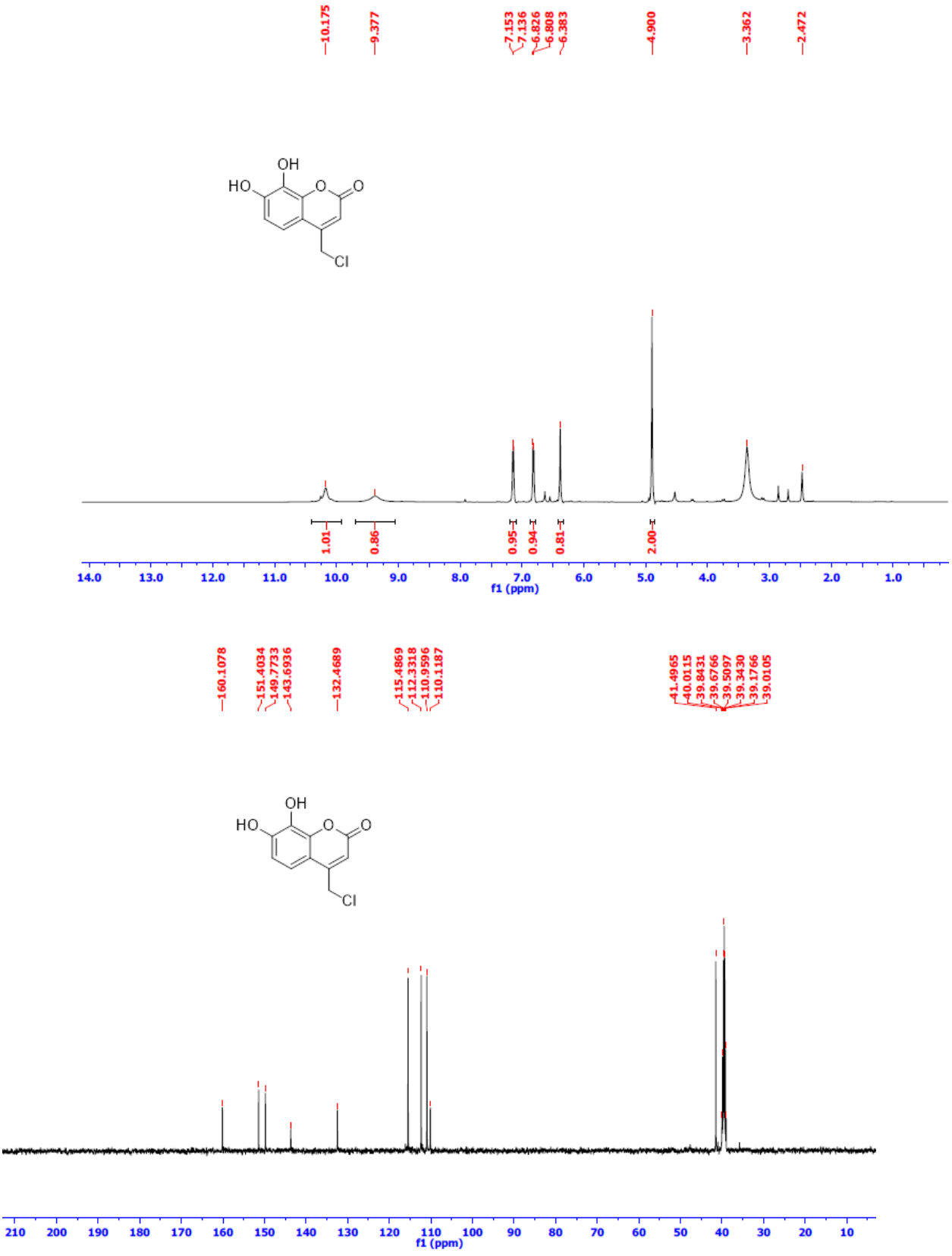
^{1}H-NMR and ^{13}C-NMR spectra of 4-chloromethyl-7-hydroxyl-coumarin (compound **B**)



^{1}H-NMR and ^{13}C-NMR spectra of 4-chloromethyl-6,7-dihydroxylcoumarin (compound **C**)



^{1}H-NMR and ^{13}C-NMR spectra of 4-chloromethyl-7,8-dihydroxyl-coumarin (compound **D**)



^{1}H-NMR and ^{13}C-NMR spectra of 4-chloromethyl-5,7-dihydroxyl-coumarin (compound **E**)

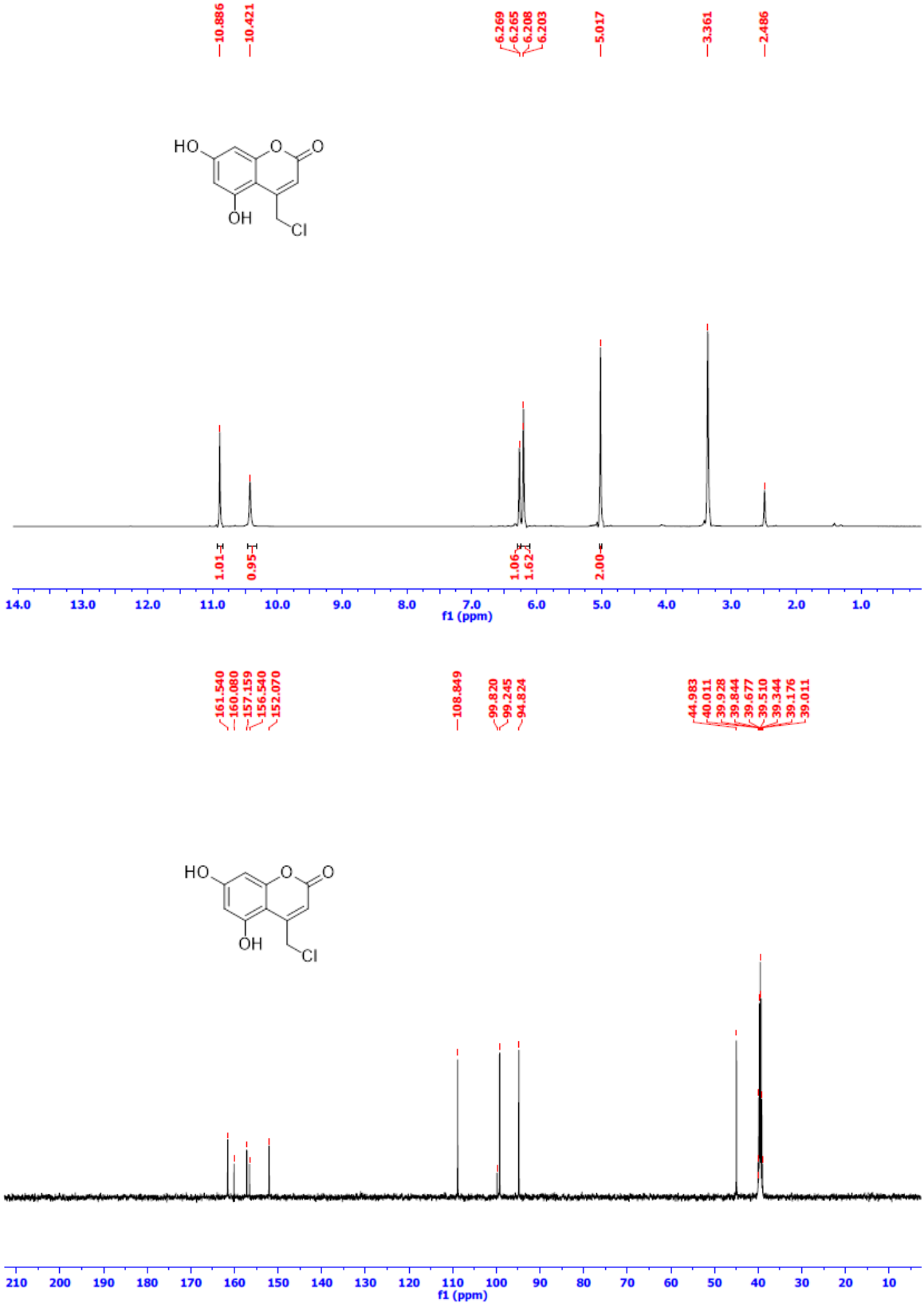
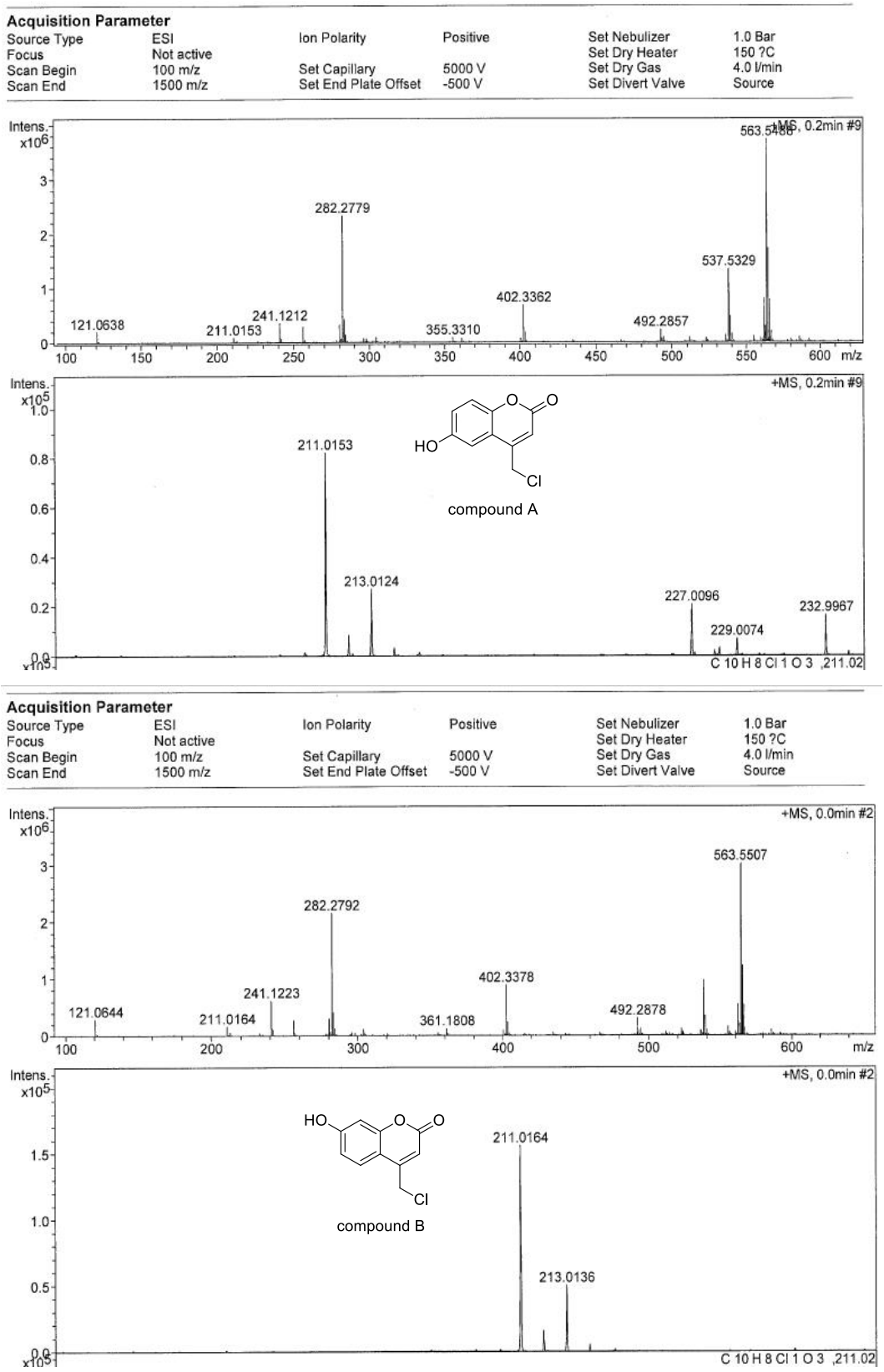
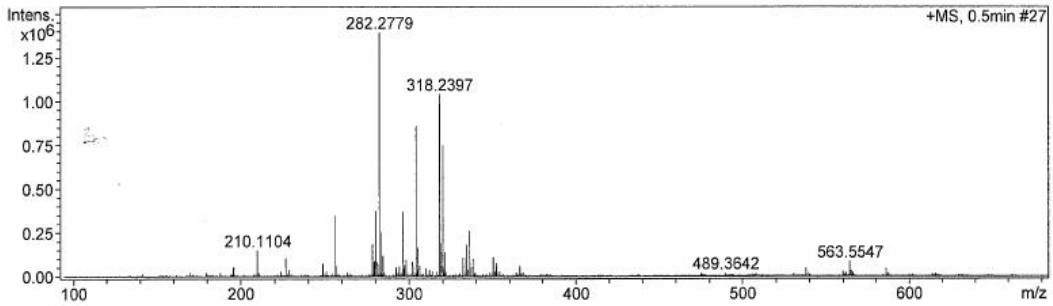


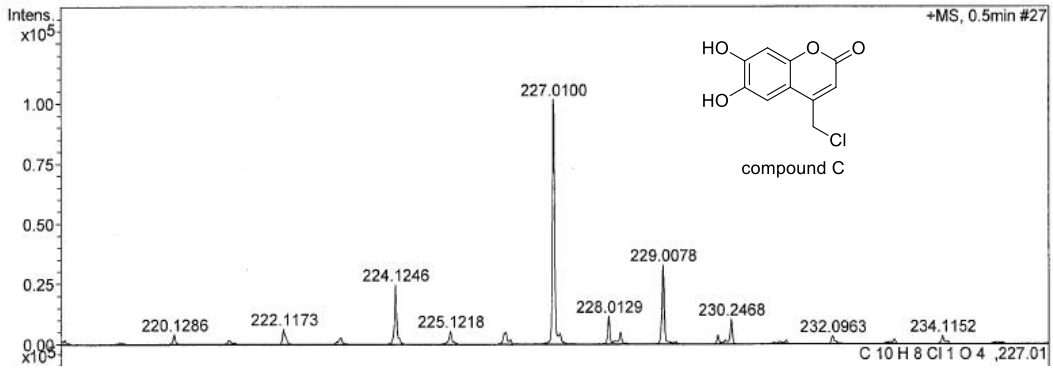
Figure S4 High resolution mass spectrometry of coumarin compounds **A**, **B**, **C, D** and **E**



Acquisition Parameter

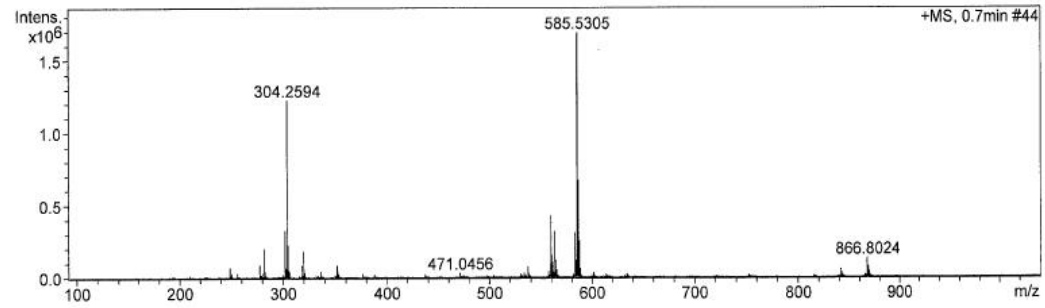
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	150 ?C
Scan Begin	100 m/z	Set Capillary	5000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

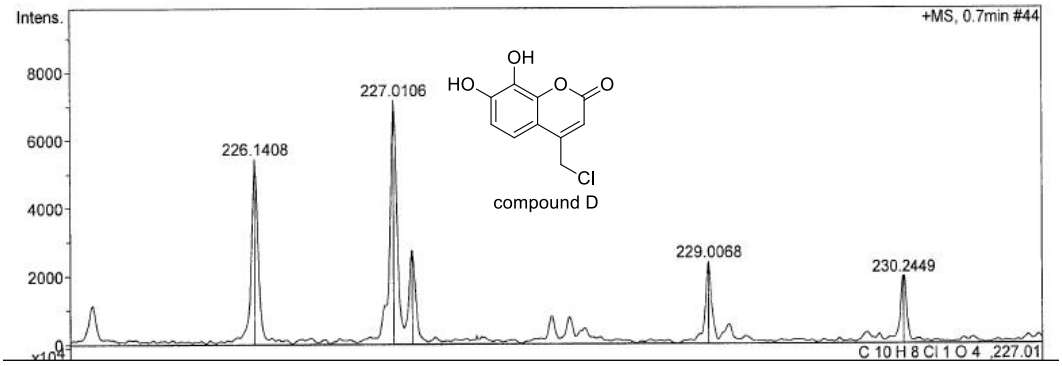




Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	150 ?C
Scan Begin	100 m/z	Set Capillary	5000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source





Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	150 ?C
Scan Begin	100 m/z	Set Capillary	5000 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source