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A Facile, Choline Chloride/Urea Catalyzed Solid Phase Synthesis of Coumarins via Knoevenagel Condensation

Hosanagara N. Harishkumar[1], Kittappa M. Mahadevan[1*], Hittalumane C. Kiran Kumar[1], and Nayak D. Satyanarayan[2]

[1,] Department of Post Graduate Studies and Research in Chemistry, School of Chemical Sciences Kuvempu University, Shankaraghatta, Karnataka 577 451, India.

[2] Department of Pharmaceutical Chemistry, Kuvempu University, Post Graduate Center, Kadur-577548, Karnataka, India.

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1: General Information

All the melting points were recorded in open capillaries. The purity of the compounds was monitored by TLC on silica gel and was purified by recrystallization with ethonal. ^{1}H NMR spectra were recorded on a Bruker-400MHz spectrometer using TMS as an internal standard. IR spectra were obtained using a FTS-135 spectrometer instrument. Mass spectra was recorded on a JEOL SX 102/DA-6000 (10 kV) FAB mass spectrometer.

2: Optimization Table

Table1. Reaction yield and melting points of newly synthesized compounds 3a-k.

Entry	R^1	R^2	R^3	R^4	Yield (%)	Mp(obs)/(litr) ^oC
3a	H	H	H	H	98	191-192/193-194[22]
3b	Cl	H	H	H	97	118-120/120-121[22]
3c	Br	H	H	H	93	195-198/195-196[22]
3d	H	Et_2N	H	H	96	243-248/222-224[22]
3e	H	OH	H	H	97	259-262/261-263[22]
3f	H	Morpholine	H	H	96	243-244
3g	H	$CH(CH_3)_2$	H	H	95	106-109
3h	H	H	H	OCH_3	97	215-216/218[7]
3i	CH_3	H	H	H	95	163-164/166[7]
3j	H	OCH_3	H	H	96	190-195/192-194[22]
3k	H	F	H	H	98	200-203

Table 2. Reaction yield and melting points of newly synthesized compounds 5a-j.

Entry	R^1	R^2	R^4	R^3	Yield (%)	Mp(obs)/(litr) ^oC
5a	H	H	Et	COOMe	96	121-122/124[23]
5b	H	H	Et	COOEt	95	92-93/93-94[23]
5c	H	H	Et	CN	98	180-182/184-185[23]
5d	H	Et_2N	Et	COOMe	94	149-152/151-153[23]
5e	H	Et_2N	Et	COOEt	98	80-82/77-78[23]
5f	H	Et_2N	Et	CN	98	225-226/229[23]
5g	H	$CH(CH_3)_2$	Et	CN	92	125-127
5h	H	Morpholine	Et	CN	96	262-264
5i	H	OMe	Et	CN	95	221-223/224-226[23]
5j	H	Cl	Et	CN	98	189-192

3: Spectral data of reported compounds

2-oxo-2H-chromene-3-carboxylic acid (3a)

White crystalline solid: IR (KBr): ν = 1716 (C=O)cm^{-1}, 1676 (C=O)cm^{-1}: ^{1}H NMR (400 MHz, DMSO-d_6), (δ/ppm): 13.24 (s, 1H), 8.74 (s, 1H), 7.88-7.91 (d, 1H, J=4.0 Hz.), 7.74-7.70 (t, 1H, J= 8.0 Hz), 7.44-7.37 (dd, 2H, J= 12.0 Hz). ^{13}C NMR (100 MHz,DMSO-d_6) (δ/ppm): 163.9, 156.6, 154.4, 148.3, 134.2, 130.1, 124.8, 118.3, 117.9, 116.1. MS.m/z = 189 (M-1). Anal. Calcd for $C_{10}H_6O_4$: C,63.16 %; H, 3.18 %. Found: C, 63.12 %; H, 3.13 %.

6-chloro-2-oxo-2H-chromene-3-carboxylic acid (3b)

White crystalline solid: IR(KBr): ν = 1716 (C=O)cm^{-1}, 1676 (C=O)cm^{-1}, ^{1}H NMR (400 MHz,DMSO-d_6): (δ/ppm): 13.4 (s, 1H), 8.69 (s, 1H), 8.03 (d, 1H, J =2.56Hz), 7.73-7.76 (dd, 1H, J = 4.0 & 8.0 Hz), 7.48 (d, 1H, J = 9.72 Hz). ^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm): 164.2, 156.5, 153.5, 147.5, 134.0, 129.4, 128.8, 119., 119.8, 118.6. MS.m/z = 227 (M+3), Anal. Calcd for $C_{10}H_5ClO_4$: C,:53.48; %; H, 2.24 %. Found: C,53.41 %, H, 2.21%.

7-(diethyl amino)-2-oxo-2H-chromene-3-corboxylic acid (3d)

Yellow crystalline solid: IR (KBr): ν = 1709 (C=O)cm^{-1}, 1672 (C=O)cm^{-1}. ^{1}H NMR(400 MHz,$CDCl_3$-d_6): (δ/ppm): 12.33 (s, 1H), 8.62 (s, 1H), 7.43 (d, ,1H, J = 9.2 Hz), 6.69 (dd, ,1H, J = 2.4 Hz, 9.0 Hz), 6.51 (s, 1H), 3.45-3.51 (m, 4H), 1.50 (t, 6H, J = 7.2 Hz). ^{13}C NMR (100 MHz,$CDCl_3$-d_6): (δ/ppm): 165.5, 164.4, 158.0, 153.7, 150.2, 131.9, 110.9, 108.5, 105.5, 96.8, 45.3, 12.3: MS. m/z = 261.7 (M+1). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36 %; H, 5.79 %, N, 5.36 %. Found: C, 64.27 % H, 5.685; N,5.25 %.

7-(morpholin-4-yl)-2-oxo-2H-chromene-3-carboxylic acid (3f).

Orange crystalline solid: IR (KBr): ν = 1716 (C=O)cm^{-1}, 1676 (C=O)cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): (δ/ppm): 12.41 (br, 1H), 8.58 (s, 1H), 7.68 (d, , 1H, *J* = 9.0 Hz), 7.03 (dd, 1H, *J* = 2.2, 8.9 Hz), 6.85 (d, 1H, *J* = 2.2 Hz), 3.72-3.75 (m, 4H), 3.42-3.44 (m, 4H). ^{13}C NMR(100 MHz, DMSO-d_6): (δ/ppm): 164.8, 159.0, 157.8, 155.7, 149.6, 131.8, 111.7, 110.5, 109.4, 98.9, 66.1, 47.03. MS.m/z = 276 (M+1),277(M+2). Anal.Calcd for $C_{14}H_{13}NO_5$: C, 61.09 %; H, 4.76 %; N, 5.09 %. Found:C, 60.96 %; H, 5.04 %, N, 4.85 %.

2-oxo-7-(propan-2-yl)-2H-chromene-3-carboxylic acid (3g).

White crystalline solid: IR (KBr): ν = 1740 (C=O)cm^{-1}, 1680 (C=O)cm^{-1}: ^{1}H NMR(400 MHz,DMSO-d_6): (δ/ppm): 13.12 (br,s,1H), 8.71 (s,1H), 7.82(d, ,1H, *J* = 8.41 Hz), 7.3-7.33(m, 2H), 3.01-3.04(m,1H), 1.24 (d, 6H, *J* = 7.0 Hz). ^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm): 164.5, 157.4, 156.6, 155.2, 148.8, 130.5, 123.9, 117.6, 116.4, 114.1, 34.2, 23.7. MS.m/z = 233 (M+1). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23 %, H, 5.21 %. Found: C, 67.29%; H, 5.31%.

8-Methoxy-2-oxo-2H-chromene-3-carboxylic acid (3h)

White crystalline solid: IR (KBr): ν = 1685(C=O)cm^{-1}, 1676 (C=O)cm^{-1}: ^{1}H NMR(400 MHz, DMSO-d_6 **)**: (δ/ppm): 13.29 (br, s, 1H), 8.71 (s, 1H), 7.41-7.44 (m, 2H), 7.30-7.34 (t, 1H, J = 8.0 Hz) , 3.90 (s, 3H,-OCH_3). ^{13}C NMR(100MHz,DMSO-d_6): (δ/ppm): 164.0, 156.4, 148.6, 146.2, 143.8, 124.7, 121.1, 118.5, 116.2, 56.6, Ms.m/z = 221 (M+1). Anal.Calcd for $C_{11}H_8O_5$: C, 60.01 %; H,3.66%. Found: C, 60.03 %, H, 3.62 %.

6-Methyl-2-oxo-2H-chromene-3-carboxylic acid (3i)

White crystalline solid: IR (KBr): ν = 1736 (C=O)cm^{-1}, 1679 (C=O)cm^{-1}: ^{1}H NMR(400 MHz, DMSO-d_6): (δ/ppm): 13.23 (br, s, 1H), 8.65 (s, 1H), 7.68 (s, 1H), 7.54 (d, 1H, *J* = 8.4 Hz), 7.33 (d, ,1H, *J* = 8.48 Hz).2.36(s,3H). ^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm)164.9, 157.6, 154.4, 148.3, 135.2, 130.1, 124.8, 118.3, 117.9, 116.1. MS.m/z = 205 (M+1). Anal.Calcd for: $C_{11}H_8O_4$: C, 64.71 %; H, 3.95 %. Found: C, 64.70 %; H, 3.93 %.

7-Methoxy-2-oxo-2H-chromene-3-carboxylic acid (3j)

White crystalline solid: IR (KBr): ν = 1745 (C=O)cm^{-1}, 1675 (C=O)cm^{-1}: ^{1}H NMR(400 MHz, DMSO-d_6): (δ/ppm):12.98(s,1H), 8.73(s, 1H), 7.83 (d, 1H, *J* = 8.6 Hz), 7.03 (m, ,2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm): 165.12, 164.62, 157.67, 157.36, 149.54, 132.03, 114.31, 113.77, 112.08, 100.75, 56.71. MS.m\z = 221 (m+1). Anal.Calcd for: $C_{11}H_8O_5$: C, 60.01 %; H, 3.66 %. Found: C, 59.98 %; H, 3.63 %.

7-Fluoro-2-oxo-2H-chromene-3-carboxylic acid(3k)

White crystalline solid: IR (KBr): ν = 1735 (C=O)cm^{-1}, 1693 (C=O)cm^{-1} ^{1}H NMR (400 MHz, DMSO-d_6): (δ/ppm):13.39 (s,1H), 8.7 (s, 1H), 7.79 (dd, 1H, *J* = 2.9, 8.3 Hz), 7.58-7.68 (m,

1H),7.48-7.52 (m,1H).^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm): 163.7, 159.1, 156.7, 156.3, 150.9, 147.2, 121.6, 121.3, 119.4, 118.9, 118.8, 118.2, 118.1, 115.1, 114.9. MS,m/z = 206 (M-2). Anal.Calcd for: $C_{10}H_5FO_4$,C, 57.71 %; H, 2.42 %. Found: C, 57.69 %; H, 2.40 %.

Ethyl-2-oxo-2H-chromene-3-carboxylate (5b)

White crystalline solid: IR (KBr): ν = 1706 (C=O)cm^{-1}, 1676 (C=O)cm^{-1}.^{1}H NMR(400 MHz,DMSO-d_6) (δ/ppm): 8.76 (s, 1H), 7.93 (d, 1H, J = 6.52 Hz), 7.76-7.75 (m, 1H), 7.46-7.46 (m, 2H) 4.32 (q, ,2H, J = 7.08 Hz), 1.32 (t, 3H, J = 7.08Hz).^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm):165, 163, 153, 151.3, 128.7, 128.3, 127.2, 126.1,123.2, 121.4, 60.4, 14.1. MS.m/z = 219 (M+1). Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.06 %; H, 4.62 %. Found: C, 65.98 %;H, 4.59 %.

Ethyl-7-(diethyl amino)-2-oxo-2H-chromene-3-carboxylate (5e)

Yellow crystalline solid: IR (KBr): ν = 1716 (C=O)cm^{-1}, 1676 (C=O)cm^{-1}. ^{1}H NMR (400 MHz,DMSO-d_6): (δ/ppm): 8.54 (s, 1H), 7.61-7.64 (d, 1H. J = 12 Hz), 6.75-6.78 (d, 1H, J = 12.0 Hz), 6.53 (s, 1H), 4.20-4.25(q, 2H, J=8 Hz), 3.4-3.5(q, 4H, J=8.0 Hz), 1.26-1.30(t, 3H, J=8.0 Hz), 1.12-1.16(t, 6H, J=8.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): (δ/ppm): 165.2, 163.7, 152.5, 151, 144.2, 128.1, 123.6, 117.8, 110.1, 106.5, 60.05, 49.1, 33.84, 14.04, MS.m/z = 290.2 (M+1). Anal.Calcd for $C_{16}H_{19}NO_4$: C, 66.42 %; H, 6.62 %;N, 4.84 %;. Found: C, 66.39 %; H, 6.61 %; N, 4.81 %.

7-(diethylamino)-2-oxo-2H-chromene-3carbonitrile (5f)

Yellow crystalline solid: IR (KBr): ν = 1716 (C=O)cm^{-1},2230(C≡N) ^{1}H NMR(300 MHz,DMSO-d_6): (δ/ppm): 8.30 (s, 1H), 8.91 (s, 1H), 7.71-7.74 (d, 1H, J = 9.0 Hz,), 7.02-7.05 (d, 1H J=9.0 Hz), 4.20-4.13 (m, 4H), 1.12 (t, 6H, J = 9.4 Hz). ^{13}C NMR(100 MHz,DMSO-d_6): (δ/ppm): 163.6, 160.1, 152.3, 145, 128.1, 118, 110.1, 106.3, 100.3, 59.8, 49.1,15.2 MS.m/z = 242(M+). Anal.Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41 %; H, 5.82 % ; N, 11.56 %. Found: C, 69.31 %, H, 5.80 %; N, 11.47 %.

2-oxo-7-(propan-2-yl)-2H-chromene-3-carbonitrile (5g)

White crystalline solid: IR (KBr): ν = 1722 (C=O)cm^{-1}, 2232(C≡N), ^{1}H NMR(300 MHz,DMSO-d_6): (δ/ppm,): 8.91 (s, 1H), 7.73 (d, 1H, *J* = 7.9 Hz), 7.40 (t, 2H *J* = 8.8 Hz), 3.02-3.09 (m, 1H),

1.25 (d, 6H, *J* = 6.86 Hz). ^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm): 158.0, 157.6, 154.8, 153.7, 130.3, 124.5, 116.0, 115.2, 114.8, 101.3, 34.3, 23.6. MS.m/z = 214 (M+1). Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.23 %; H, 5.20 %; N, 6.57 %. Found: C, 73.22 %; H, 5.35 %; N, 5.61 %.

7-(morpholin-4-yl)-2-oxo-2H-chromene-3-carbonitrile (5h)

White crystalline solid: IR (KBr): ν = 1731 (C=O)cm^{-1},2203(C≡N), ^{1}H NMR(400 MHz, DMSO-d_6): (δ/ppm): 8.64 (s, 1H), 7.57 (d, 1H, *J* = 9.0 Hz), 7.04-7.09 (m, 2H),6.9(d,1H, *J* =2.2) 3.73(q.4H, *J* = 5.0Hz,14.0Hz),3.47(t,4H, *J* = 4.6Hz) ^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm): 165.8, 157.8, 157.0, 153.6, 131.7, 115.4, 114.3, 111.7, 101.4, 97.9, 57.17, 23.5, 19.6, 13.9.MS.m/z = 257 (M+1). Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62 %; H, 4.72 %; N, 10.93 %. Found: C, 65.51 %; H, 4.69 %; N, 10.89 %;

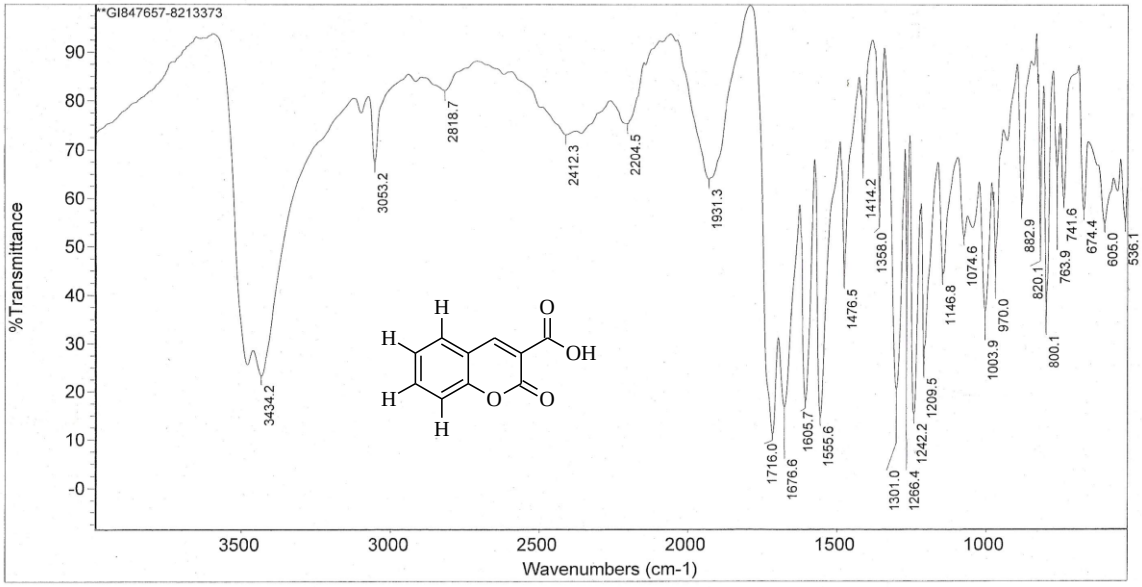
7-methoxy-2-oxo-2H-chromene-3-carbonitrile (5i)

White crystalline solid: IR (KBr): ν = 1707 (C=O)cm^{-1}, 2229 (C≡N)cm^{-1}. ^{1}H NMR(400 MHz,DMSO-d_6): (δ/ppm): 8.84 (s, 1H), 7.73 (d, ,1H, J = 8.7 Hz), 7.05-7.12 (m, 2H), 3.91(s, 3H). ^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm): 165.8, 157.8, 157.0, 153.6, 131.7, 115.5, 114.3, 111.7, 101.4, 97.9, 56.9. MS.m/z = 202 (M+1),202(M+2), Anal.Calcd for $C_{10}H_5NO_3$: C, 64.18 %; H, 2.69 %; N, 7.48 %.Found: C, 64.11 %; H, 2.71 %; N, 7.43 %.

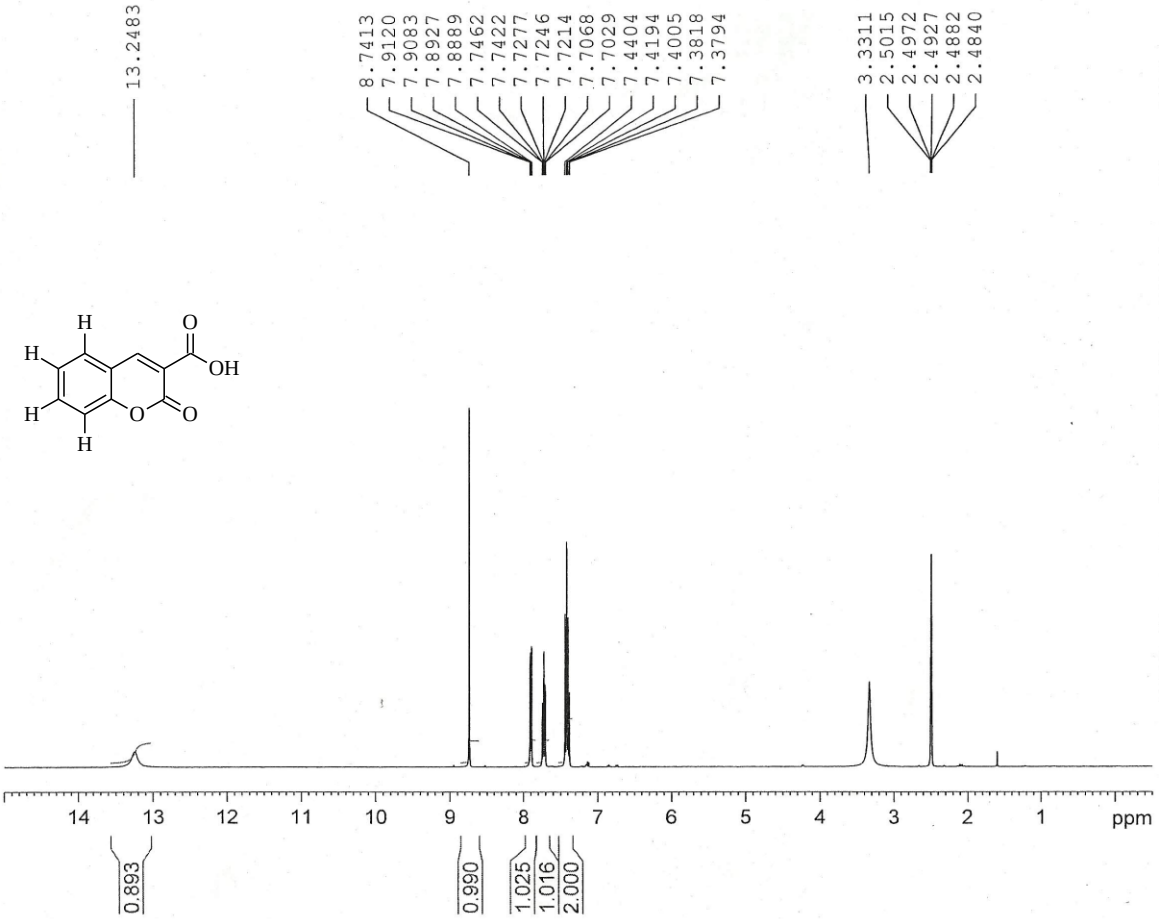
7-chloro-2-oxo-2H-chromene-3-carbonitrile (5j)

White crystalline solid: IR (KBr): ν = 1716 (C=O)cm^{-1}, 1676 (C=O)cm^{-1} ^{1}H NMR(400 MHz,DMSO-d_6): (δ/ppm): 7.55-7.57 (m, 1H), 8.95 (s, 1H), 7.77-7.85 (m, 2H), ^{13}C NMR (100 MHz,DMSO-d_6): (δ/ppm),: 165.7, 157.6, 154.9, 153.0, 131.69, 126.30, 117.50, 111.65, 101.38, 97.83. MS.m/z = 208 (M+3). Anal.Calcd for $C_{10}H_4NO_2$: C, 58.42 %; H, 1.96%; N, 6.81%. Found: C, 58.49 %; H, 1.92 %; N, 6.80 %.

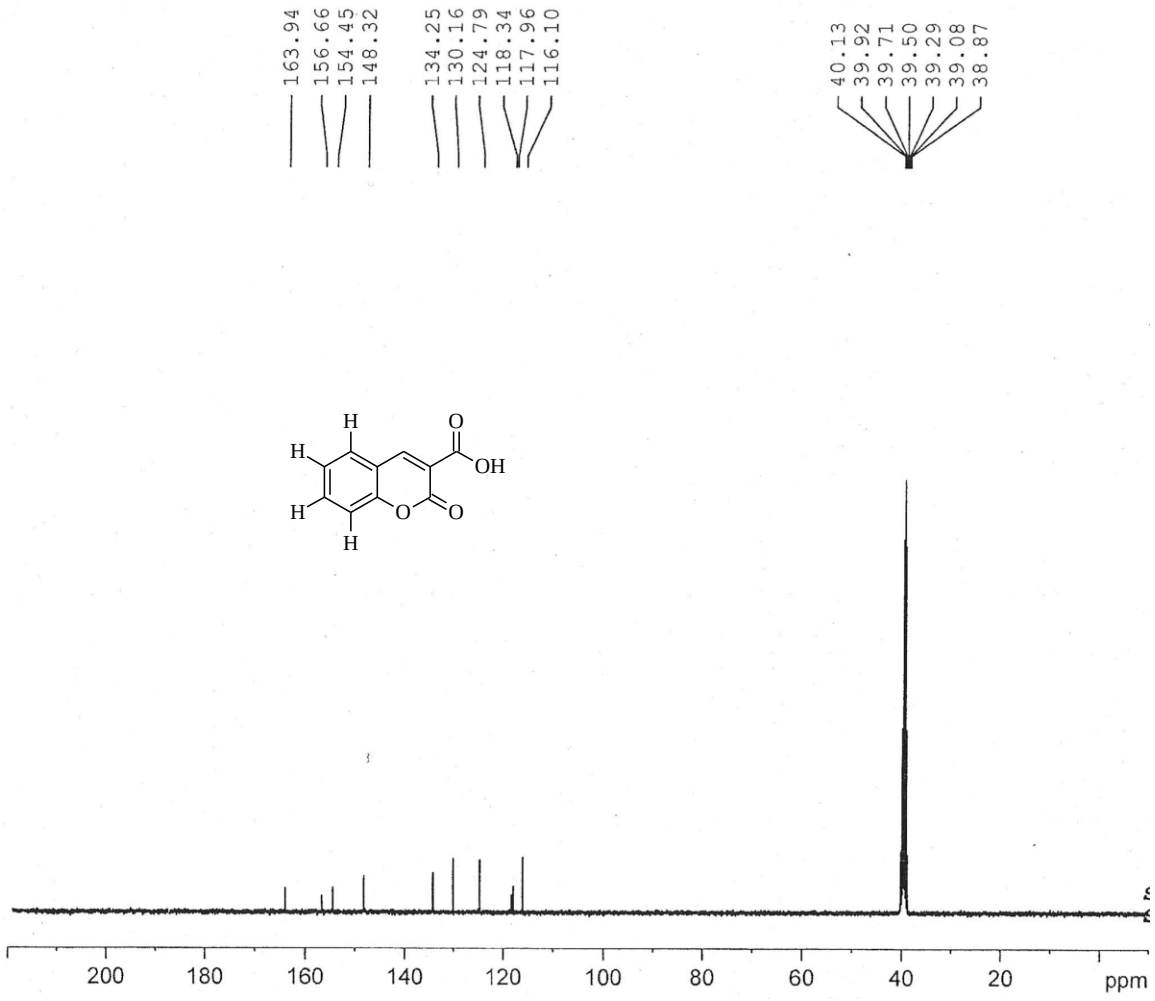
4: Spectra of reported compounds



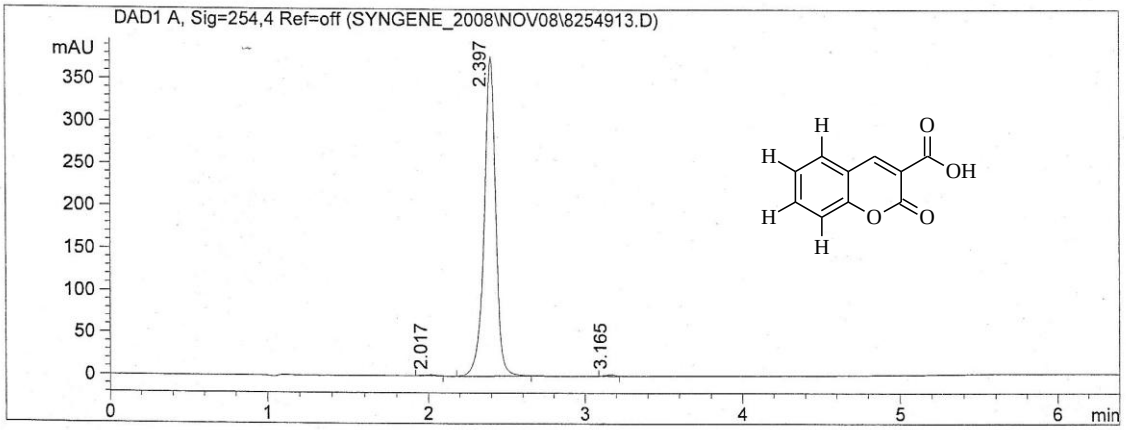
1. IR Spectrum of 2-oxo-2*H*-chromene-3-carboxylic acid (3a)



2. ^{1}H-NMR Spectrum of 2-oxo-2*H*-chromene-3-carboxylic acid (3a)



3. ^{13}C Spectrum of 2-oxo-2*H*-chromene-3-carboxylic acid (3a)



Peak No	RT min	Area	Area %
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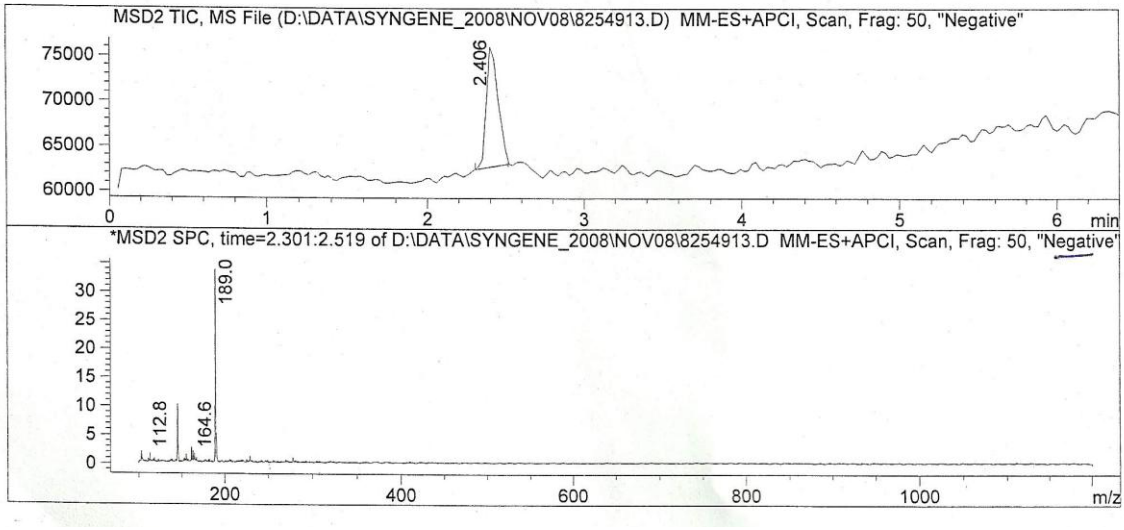
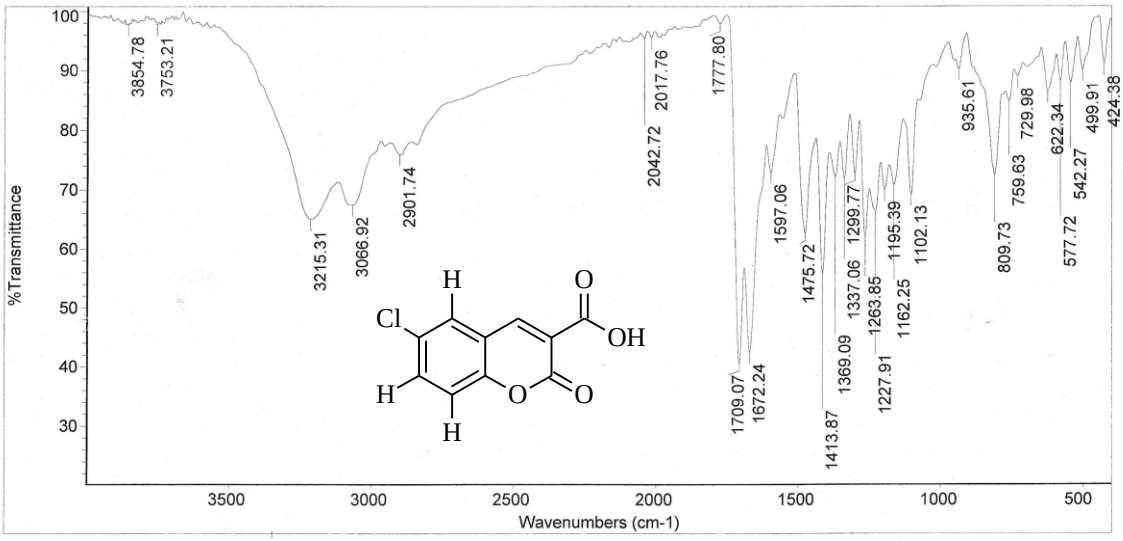
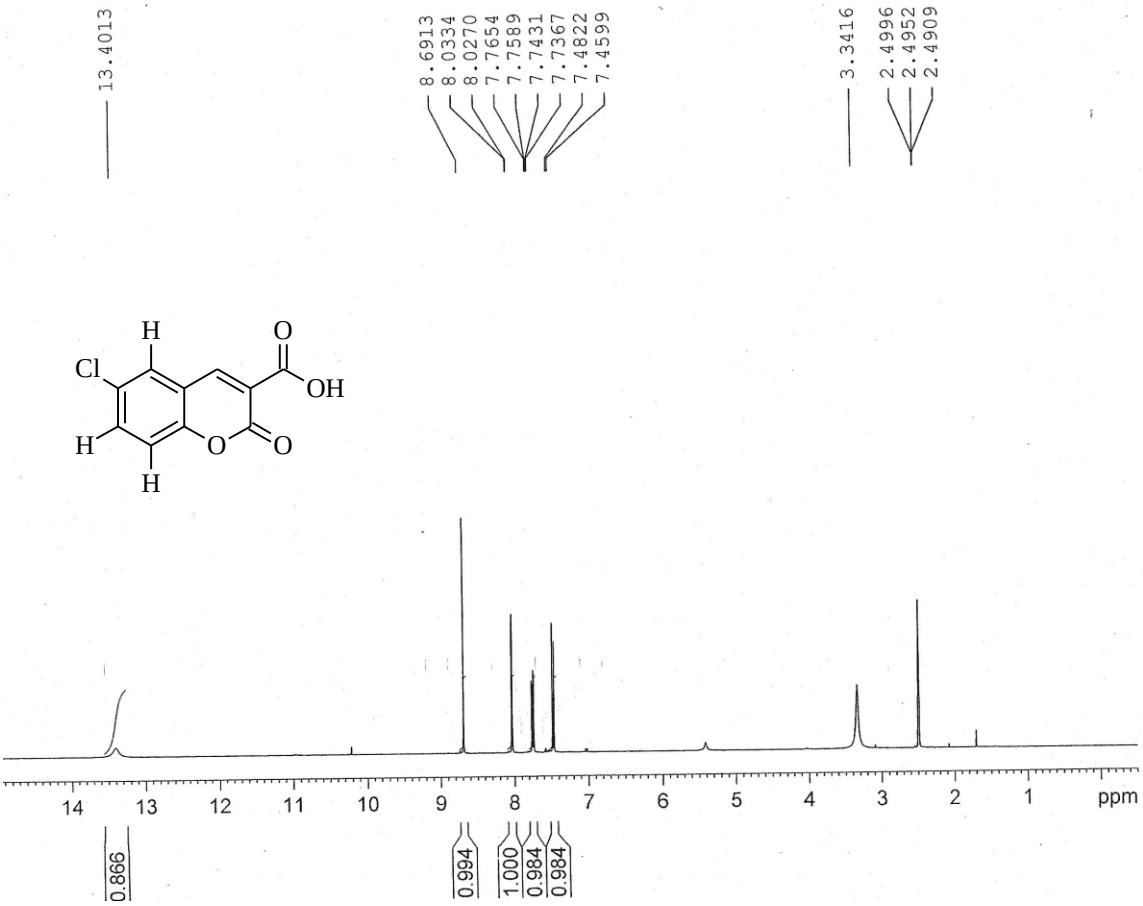
2	2.397	1.907e+003	99.154
3	3.165	8.444e+000	0.439



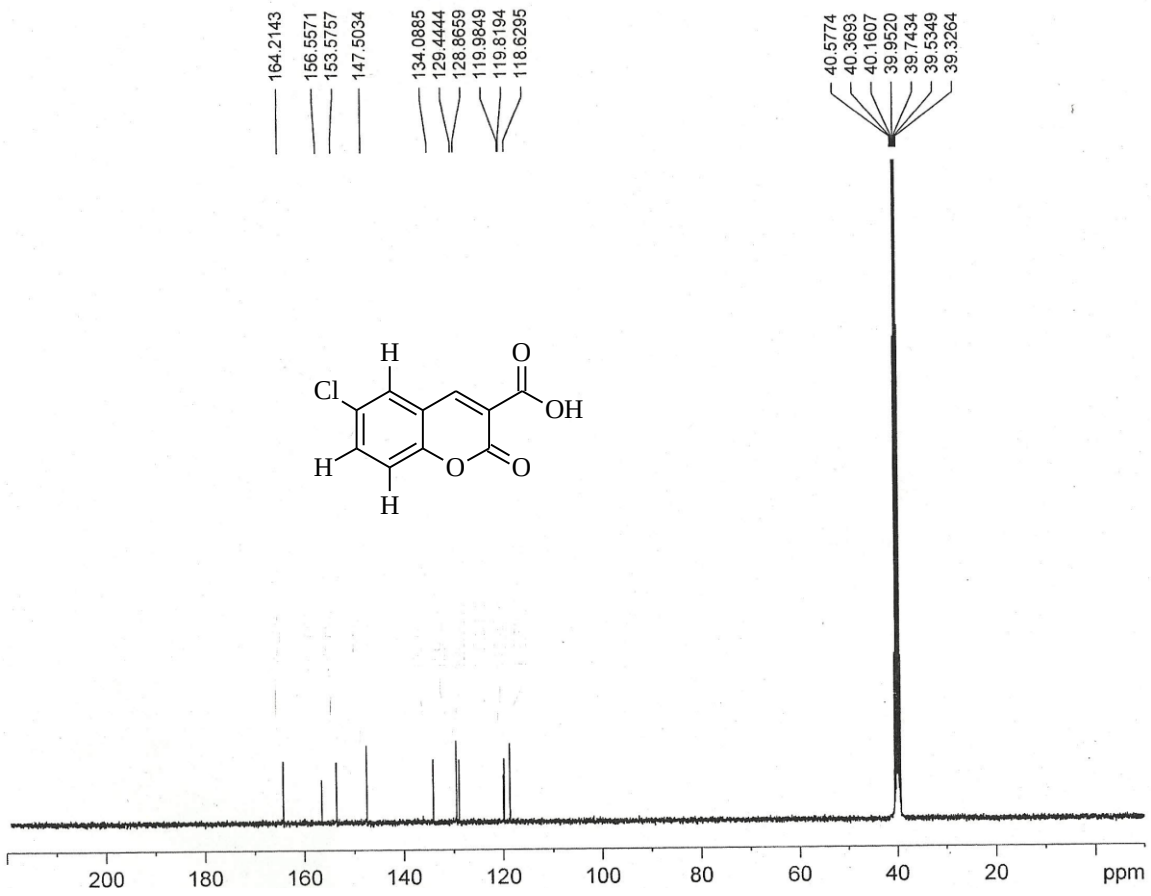
4. Mass Spectrum of 2-oxo-2*H*-chromene-3-carboxylic acid (3a)



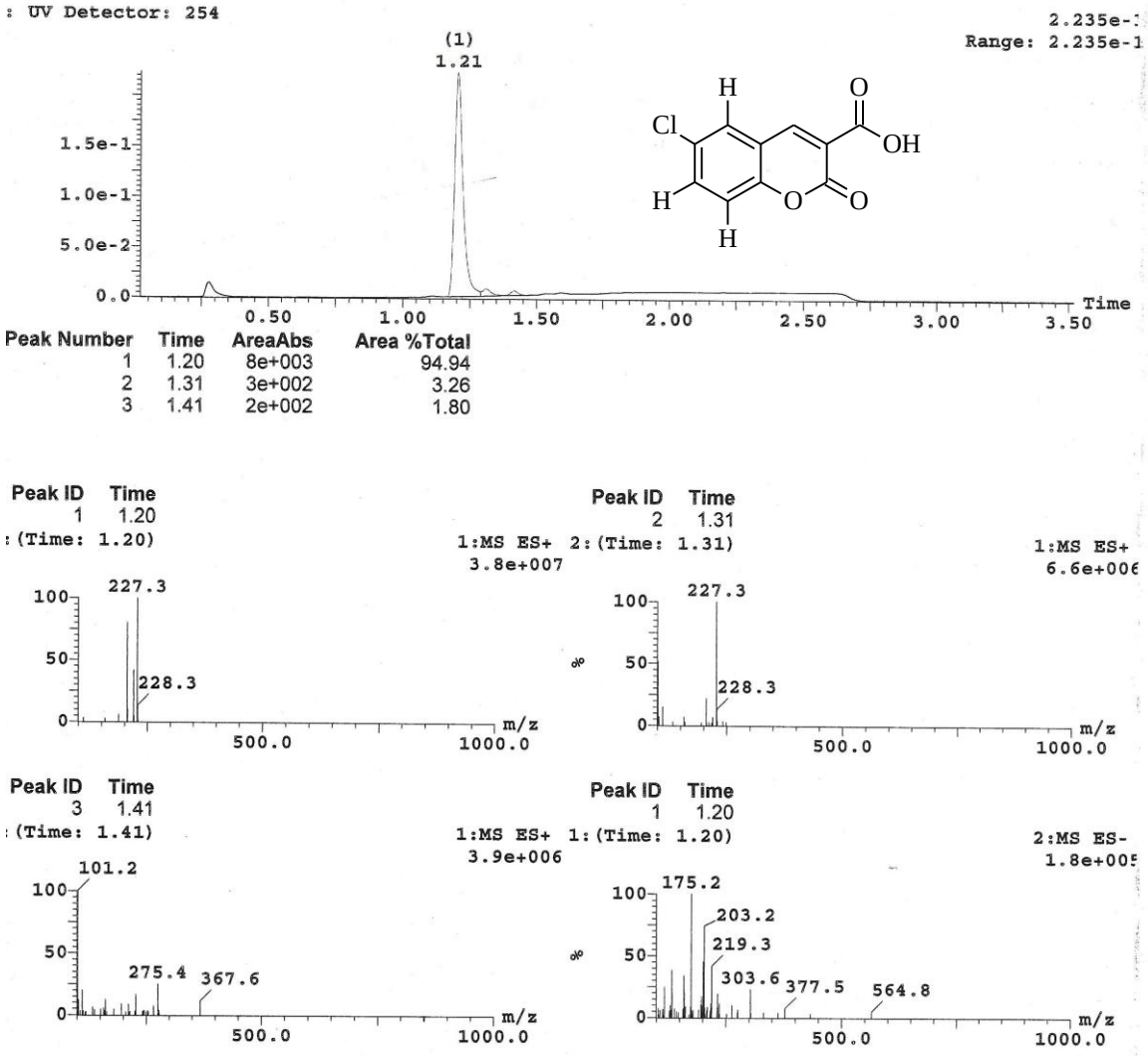
5. IR Spectrum of 6-chloro-2-oxo-2*H*-chromene-3-carboxylic acid (3b)



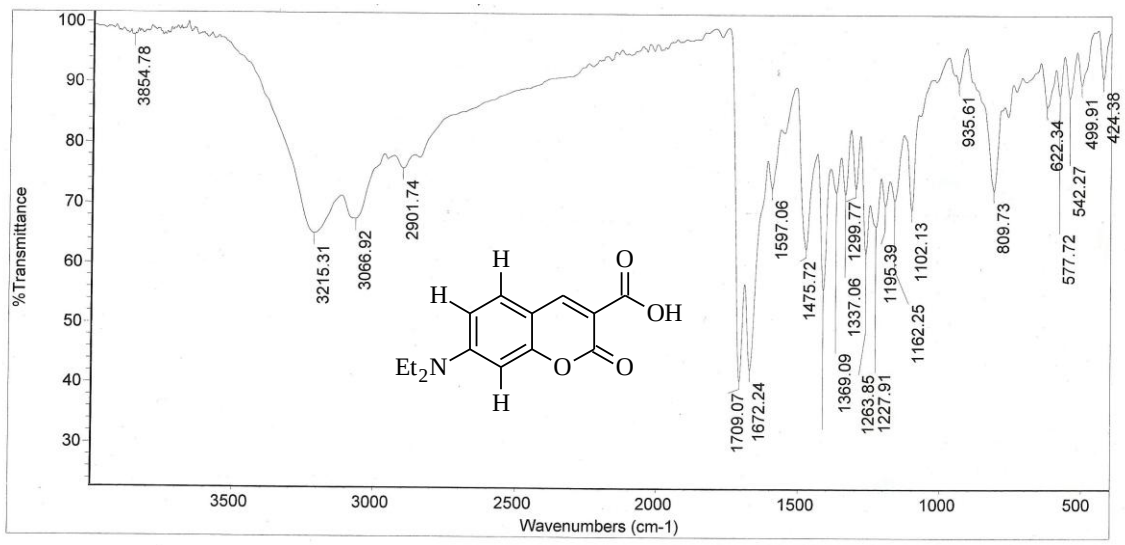
6. ^{1}H-NMR Spectrum of 6-chloro-2-oxo-2*H*-chromene-3-carboxylic acid (3b)



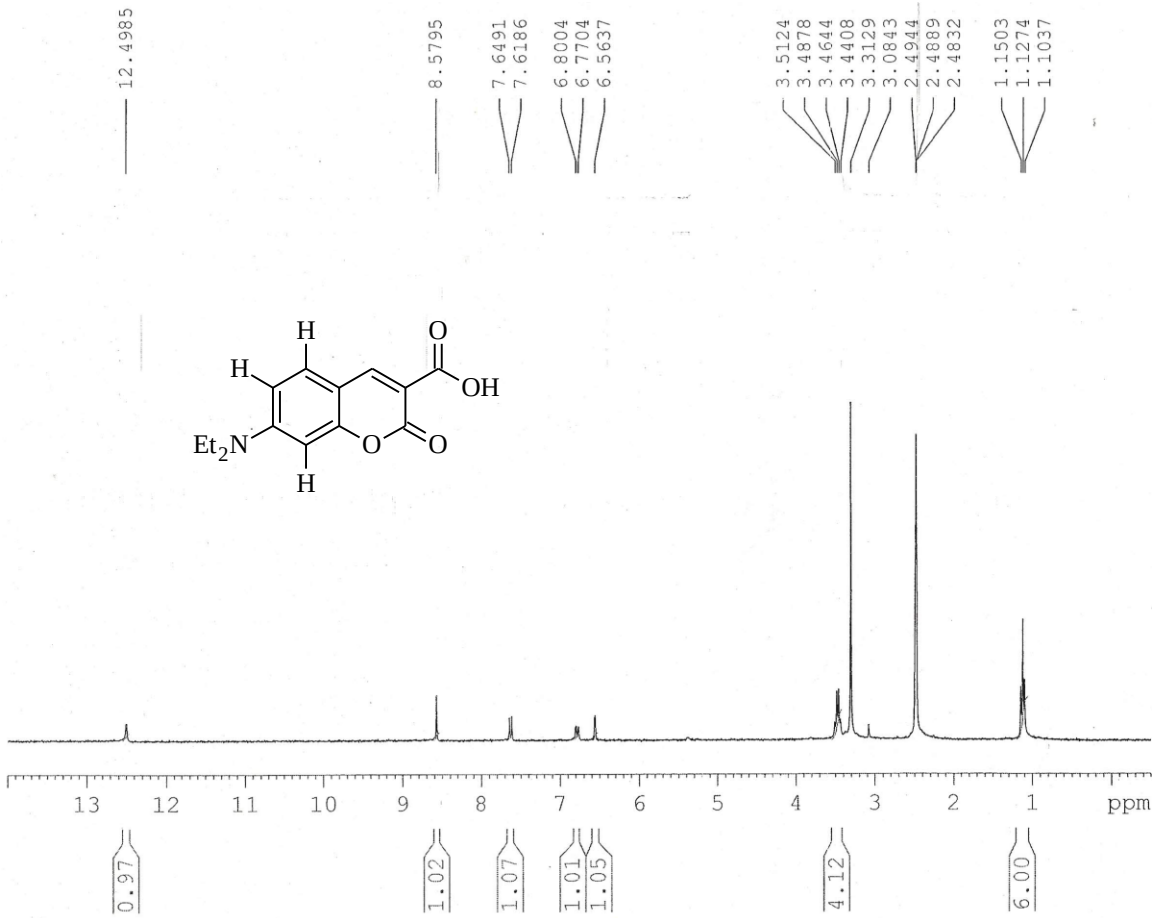
7. ^{13}C Spectrum of 6-chloro-2-oxo-2*H*-chromene-3-carboxylic acid (3b)



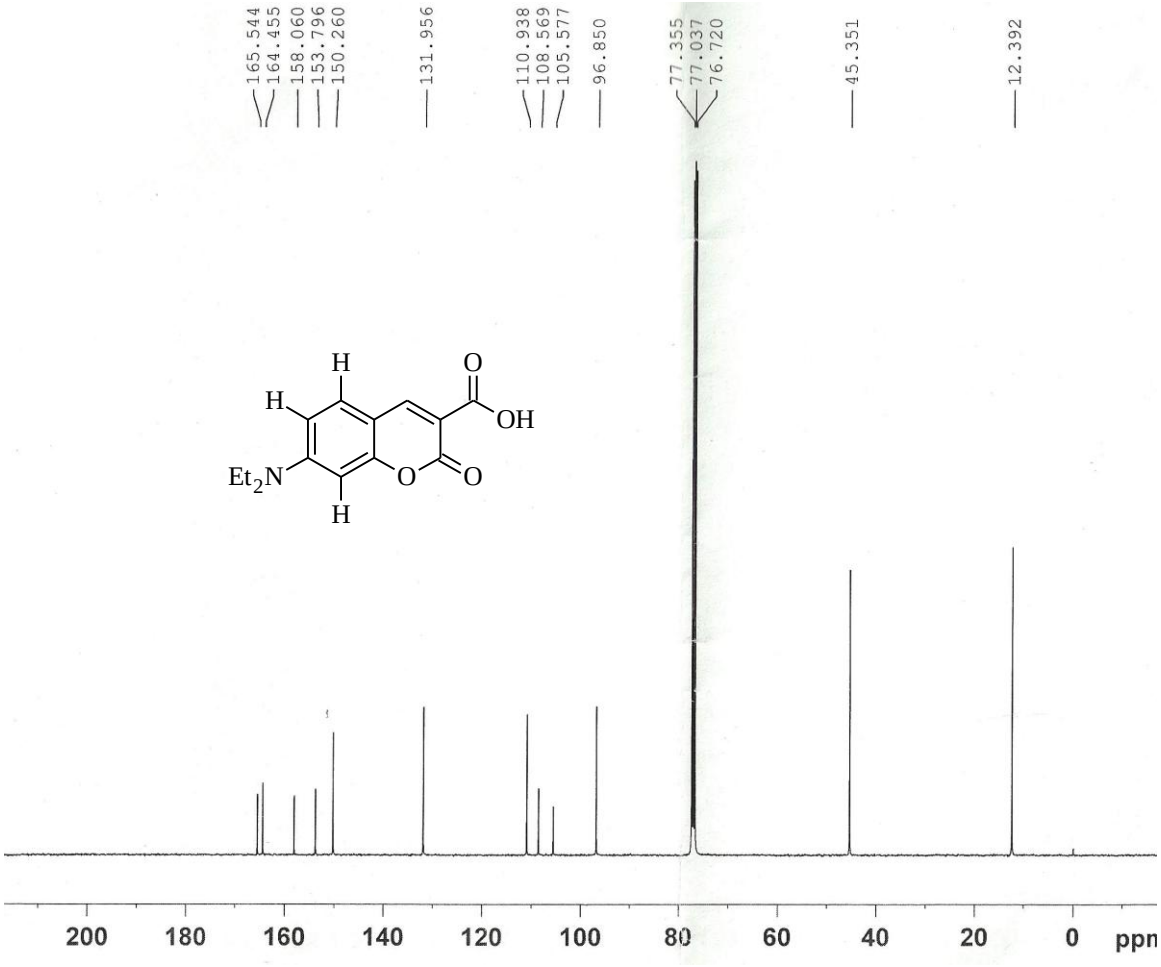
8. Mass Spectrum of 6-chloro-2-oxo-2*H*-chromene-3-carboxylic acid (3b)



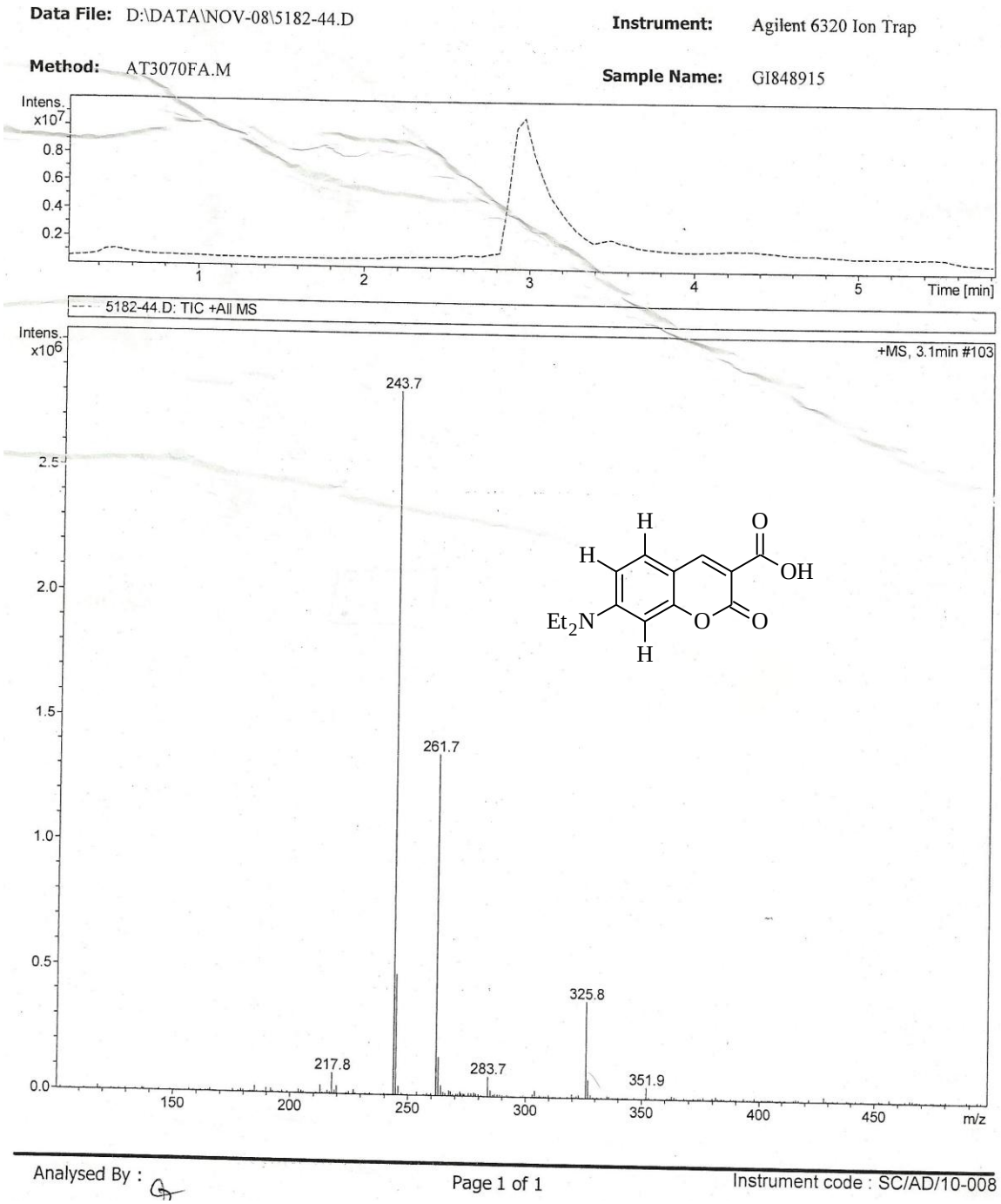
9. IR Spectrum of 7-(diethyl amino)-2-oxo-2*H*-chromene-3-corboxylic acid (3d)



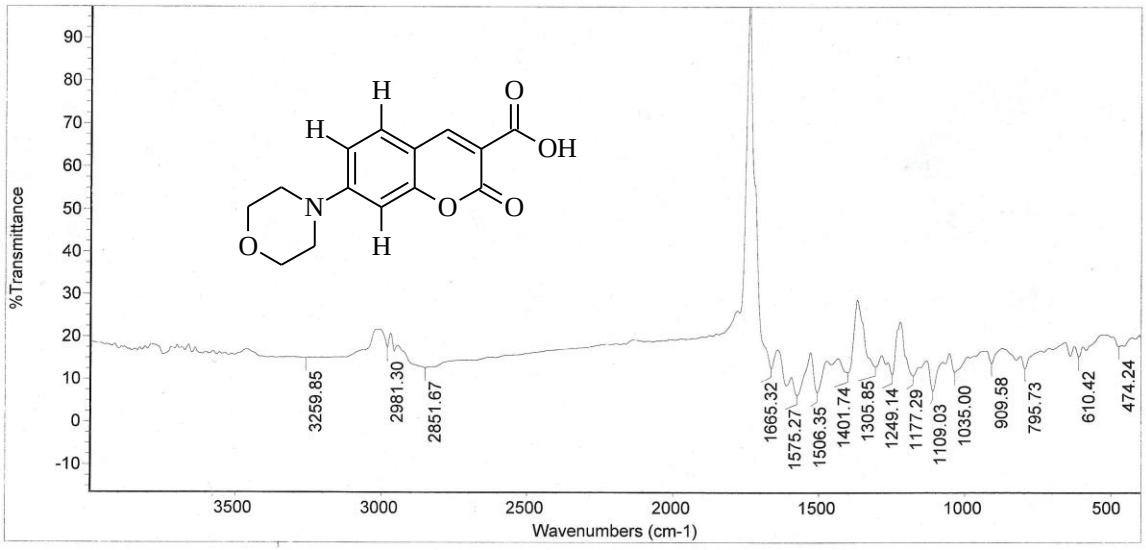
10. ^{1}H-NMR Spectrum of 7-(diethyl amino)-2-oxo-2*H*-chromene-3-corboxylic acid (3d)



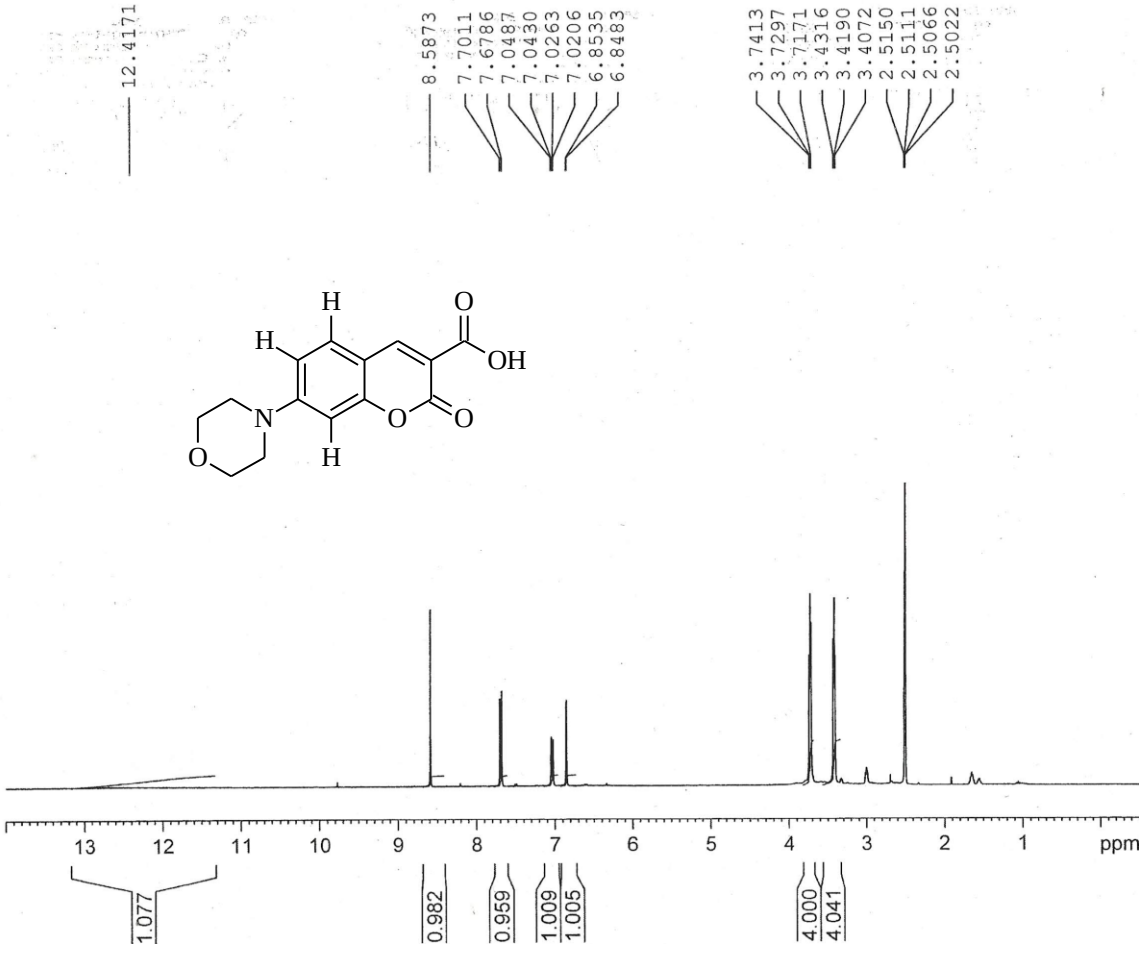
11. ^{13}C Spectrum of 7-(diethyl amino)-2-oxo-2*H*-chromene-3-corboxylic acid (3d)



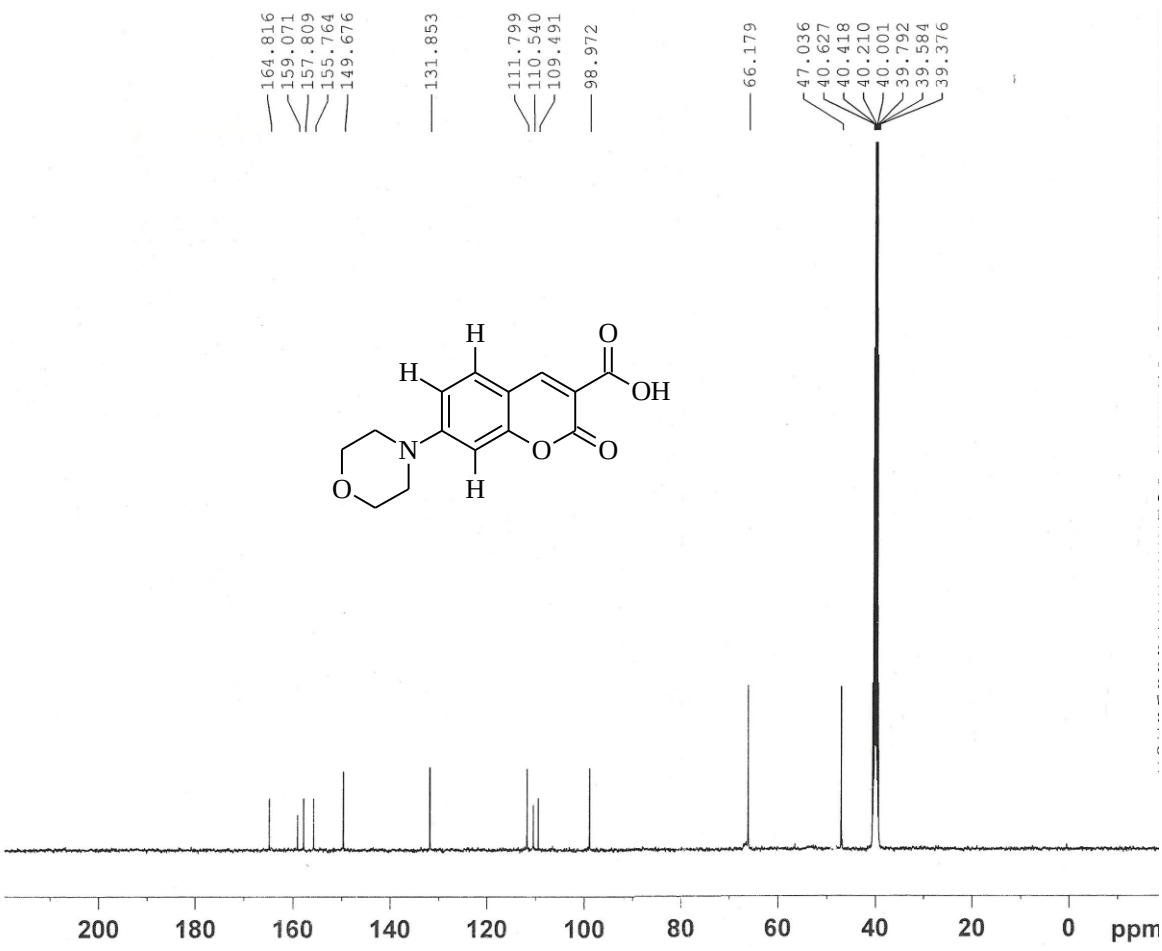
12. Mass Spectrum of 7-(diethyl amino)-2-oxo-2*H*-chromene-3-corboxylic acid (3d)



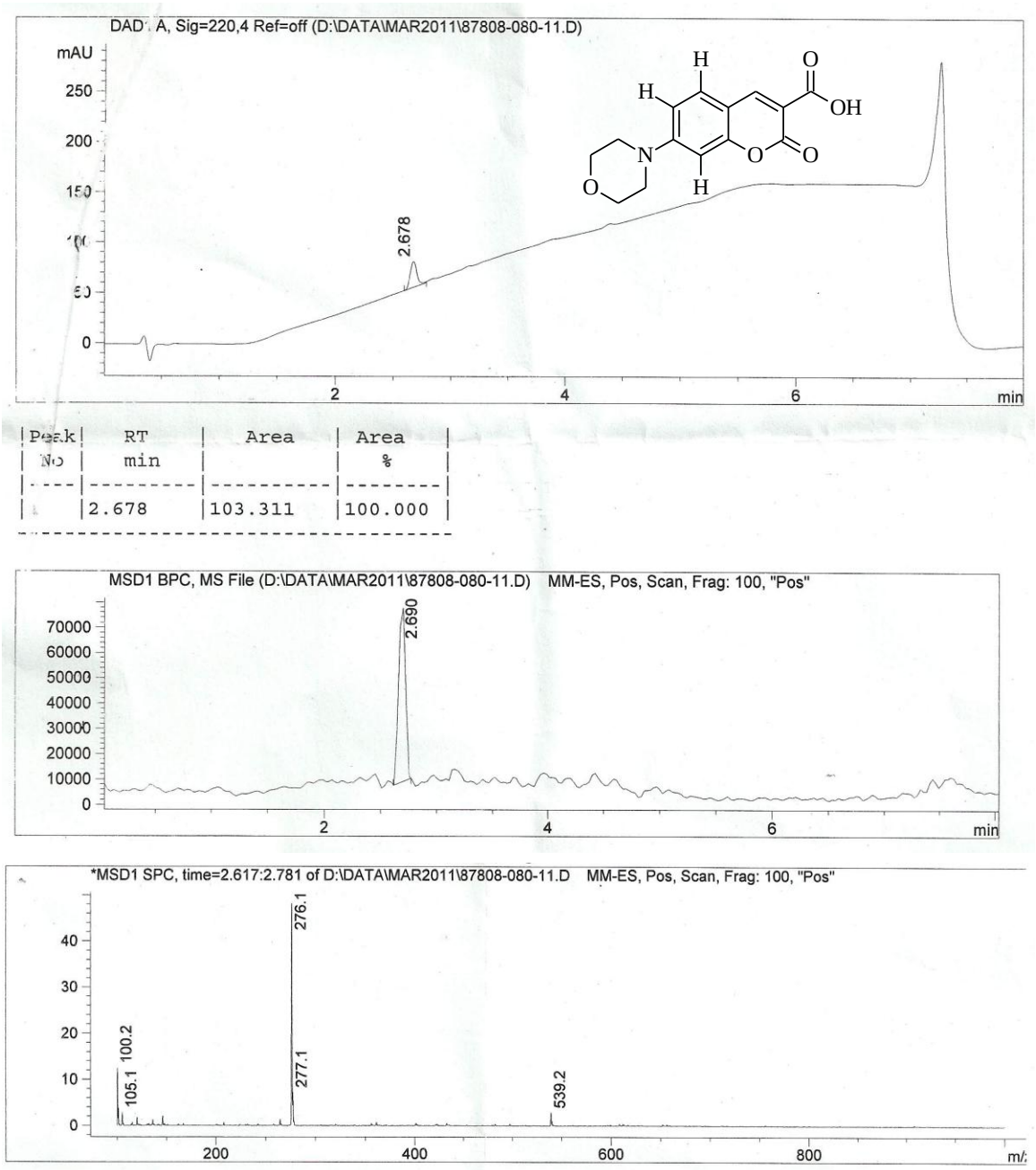
13. IR Spectrum of 7-(morpholin-4-yl)-2-oxo-2*H*-chromene-3-carboxylic acid (3f)



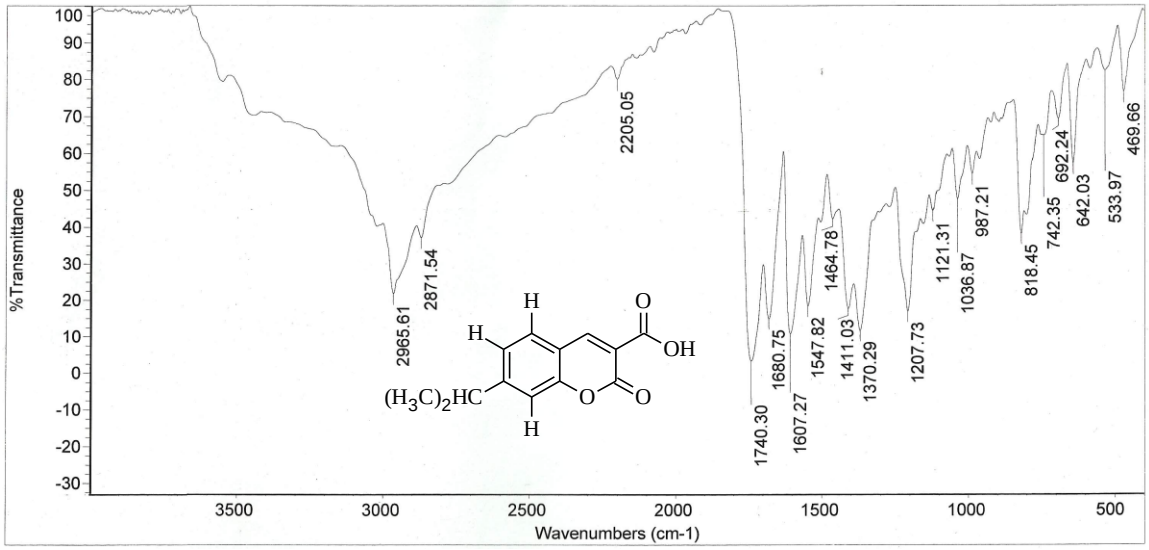
14. ^{1}H-NMR Spectrum of 7-(morpholin-4-yl)-2-oxo-2*H*-chromene-3-carboxylic acid (3f)



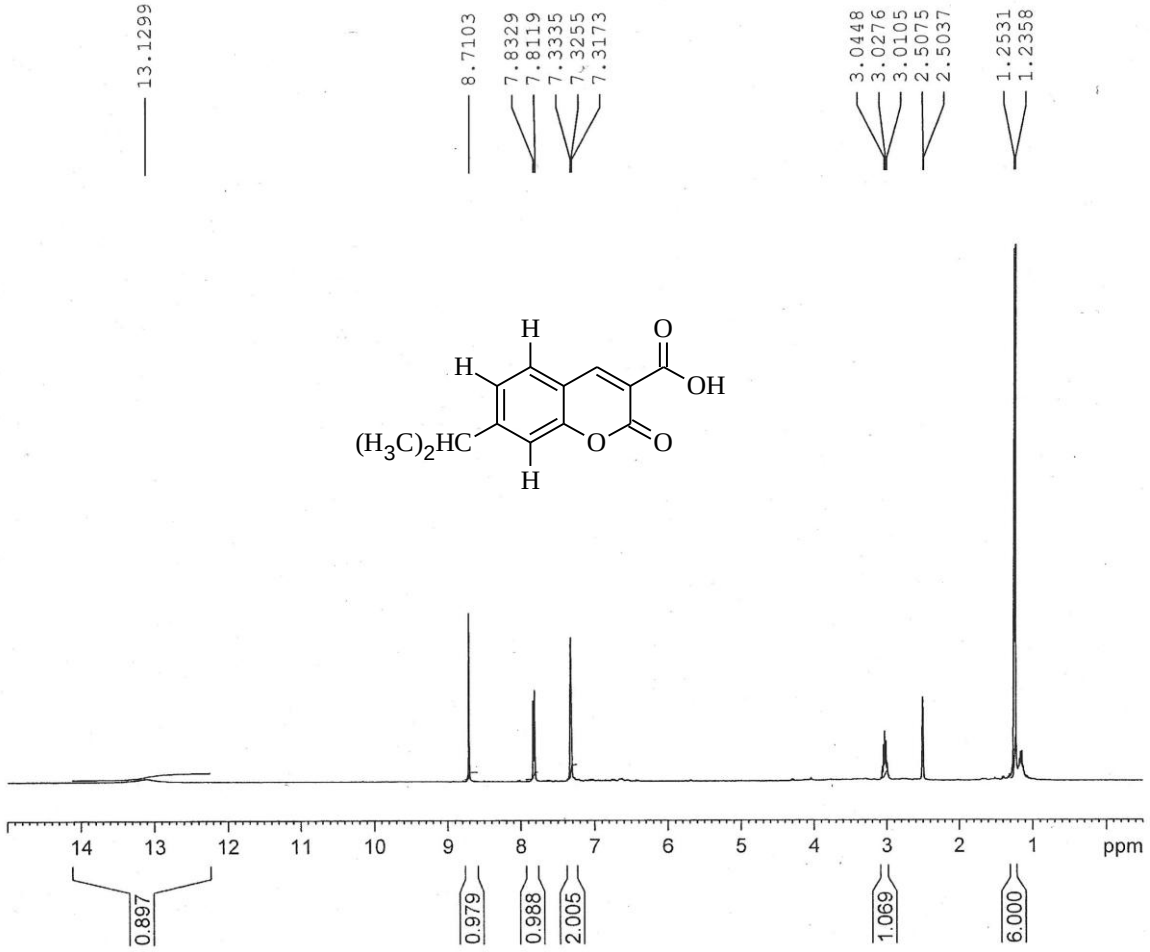
15. ^{13}C Spectrum of 7-(morpholin-4-yl)-2-oxo-2*H*-chromene-3-carboxylic acid (3f)



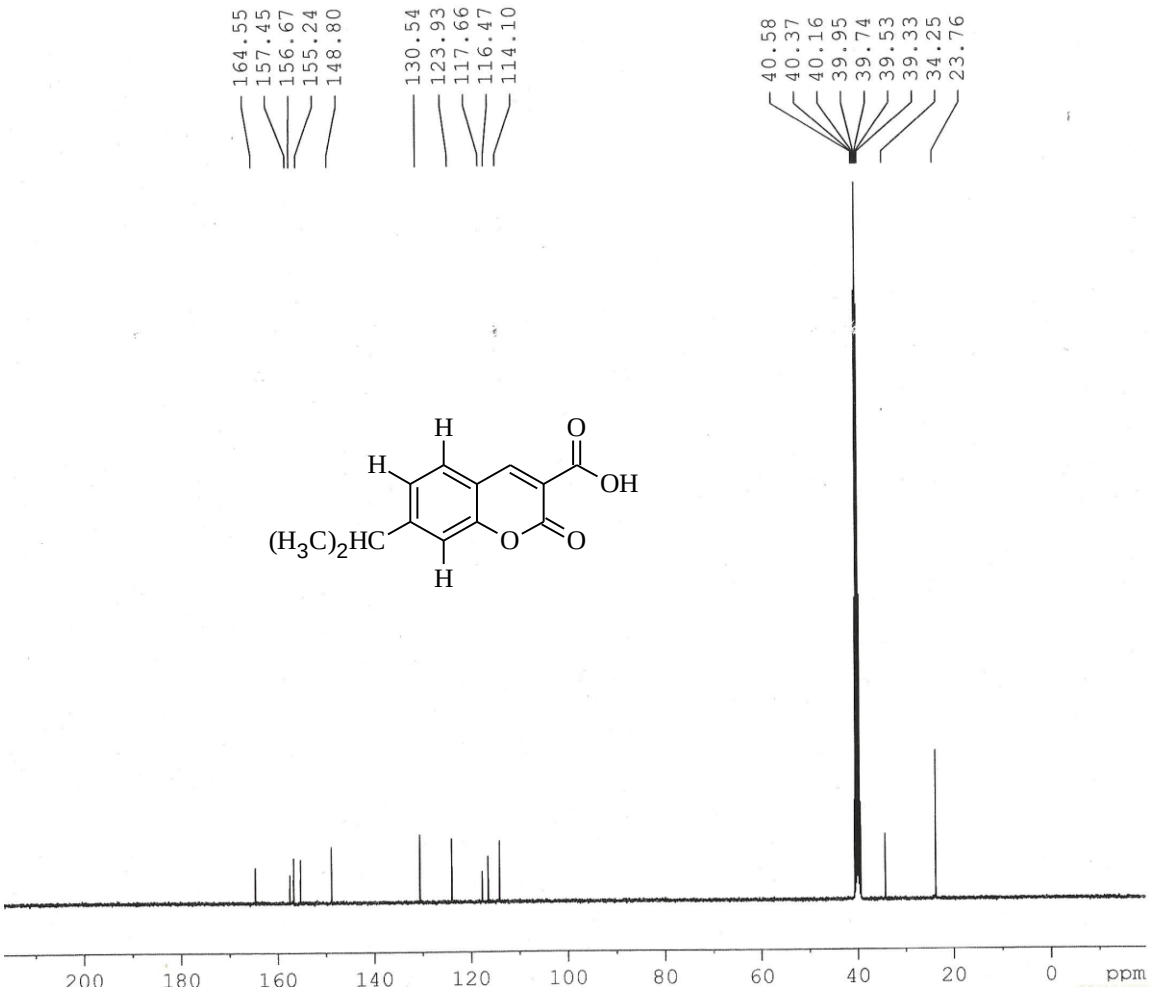
16. Mass Spectrum of 7-(morpholin-4-yl)-2-oxo-2*H*-chromene-3-carboxylic acid (3f)



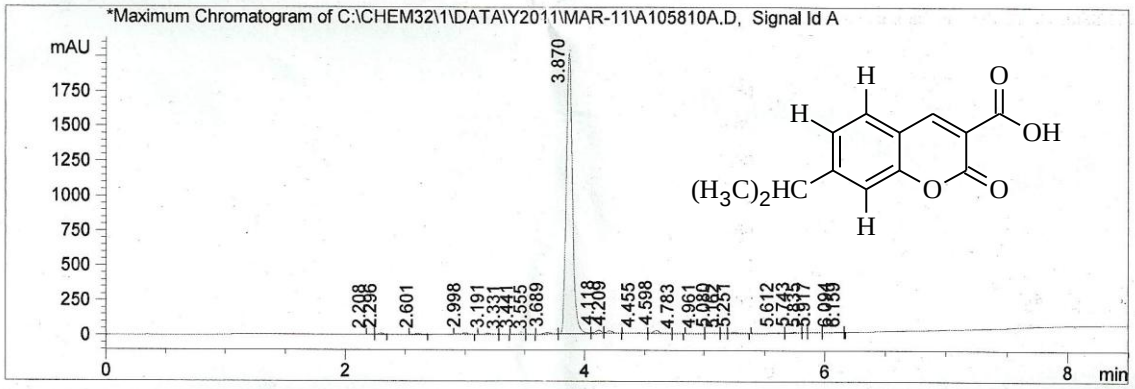
17. IR Spectrum of 2-oxo-7-(propan-2-yl)-2*H*-chromene-3-carboxylic acid (3g)



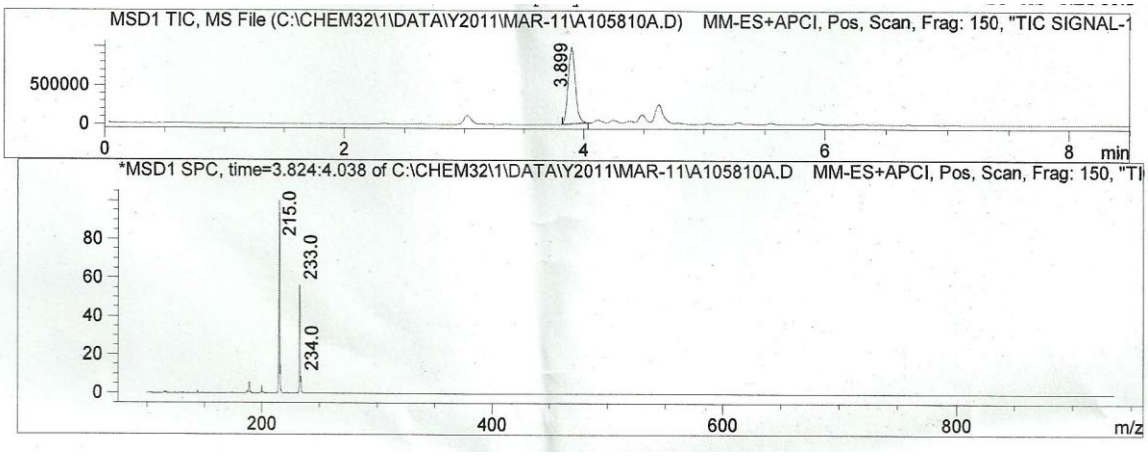
18. ^{1}H-NMR Spectrum of 2-oxo-7-(propan-2-yl)-2*H*-chromene-3-carboxylic acid (3g)



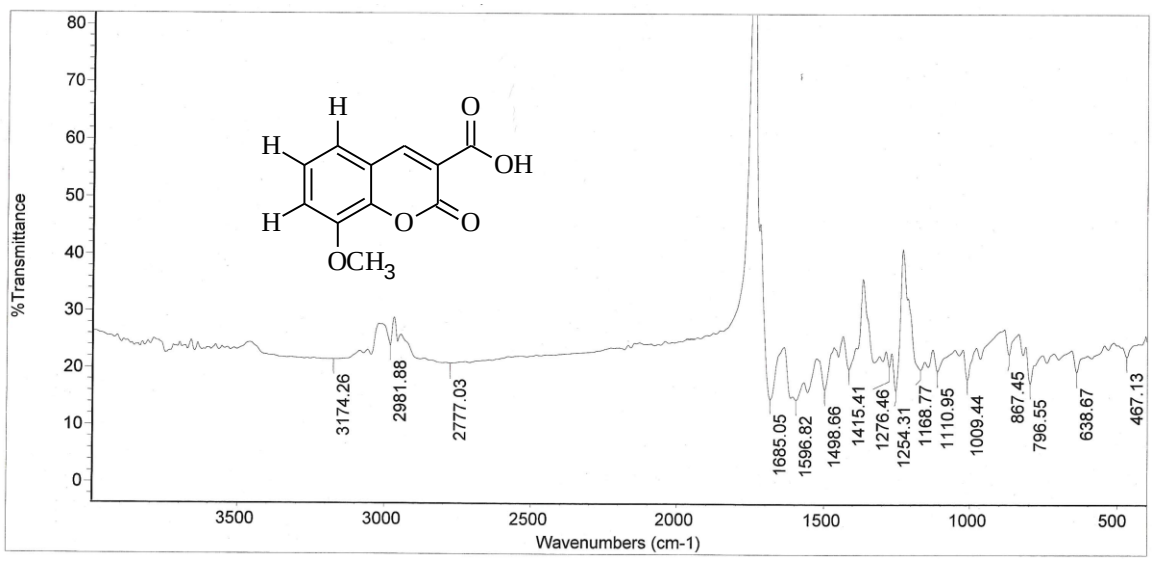
19. ^{13}C Spectrum of 2-oxo-7-(propan-2-yl)-2*H*-chromene-3-carboxylic acid (3g)



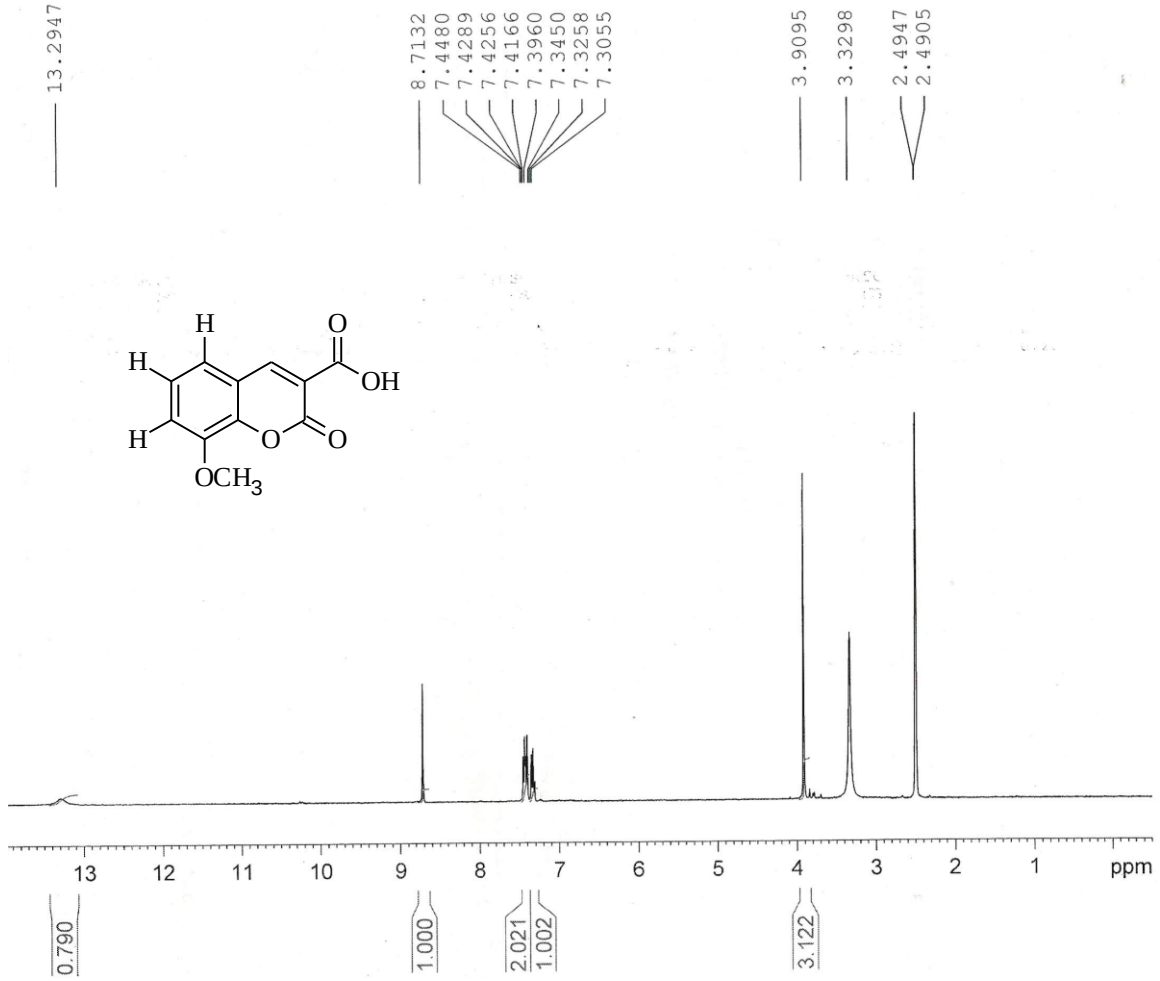
Peak No	RT min	Area	Area %
1	2.208	5.059e+000	0.063
2	2.296	2.450e+001	0.307
3	2.601	2.020e+001	0.253
4	2.998	4.080e+001	0.511
5	3.191	3.349e+001	0.420
6	3.331	1.087e+000	0.014
7	3.441	7.431e+000	0.093
8	3.555	2.233e+000	0.028
9	3.689	6.130e+001	0.768
10	3.870	7.296e+003	91.420
11	4.118	1.090e+002	1.366
12	4.209	8.621e+001	1.080
13	4.455	4.438e+001	0.556
14	4.598	8.921e+001	1.118
15	4.783	4.141e+000	0.052
16	4.961	1.007e+001	0.126
17	5.080	2.181e+001	0.273
18	5.162	7.337e+000	0.092
19	5.251	3.733e+001	0.468
20	5.612	2.677e+001	0.336
21	5.743	2.471e+001	0.310
22	5.835	1.275e+000	0.016
23	5.917	1.043e+001	0.131
24	6.094	1.515e+001	0.190
25	6.159	8.235e-001	0.010



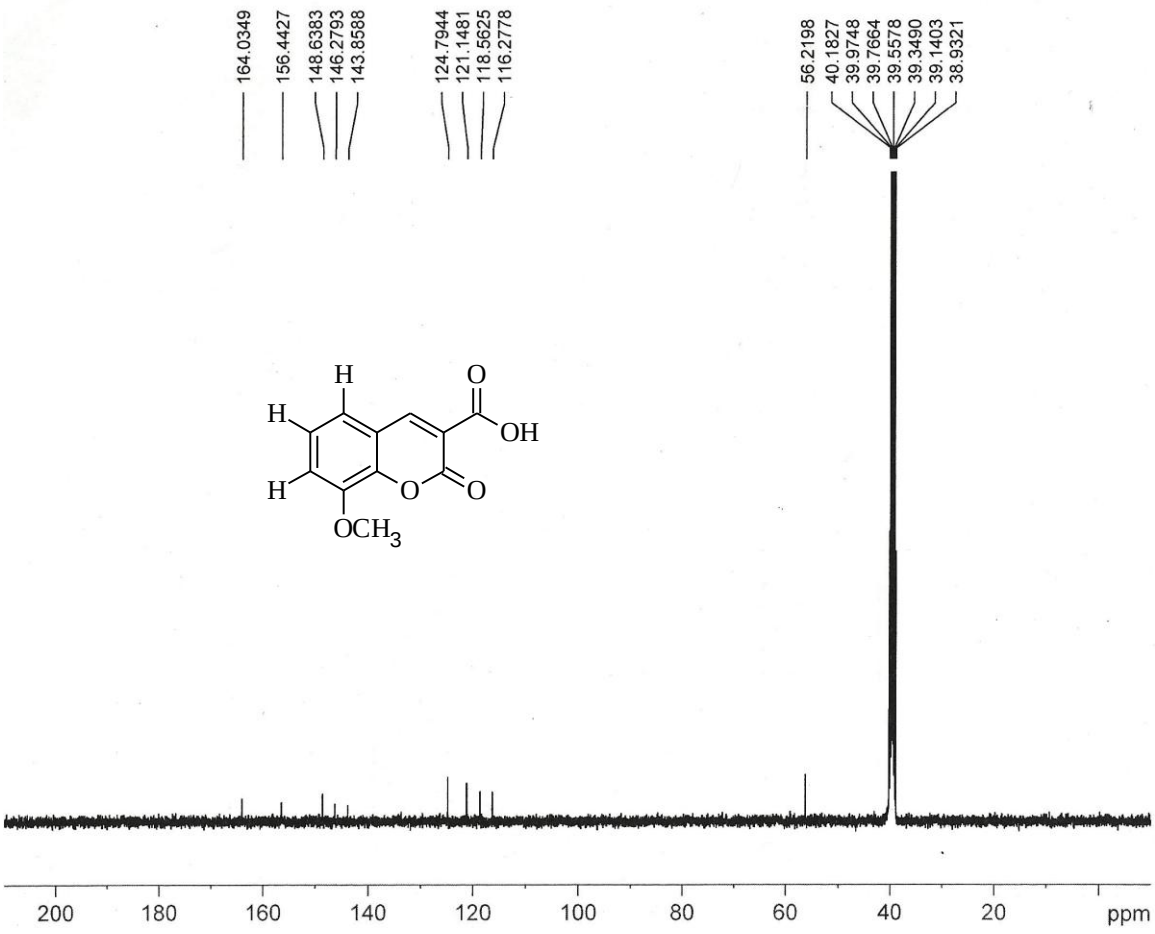
20. Mass Spectrum of 2-oxo-7-(propan-2-yl)-2*H*-chromene-3-carboxylic acid (3g)



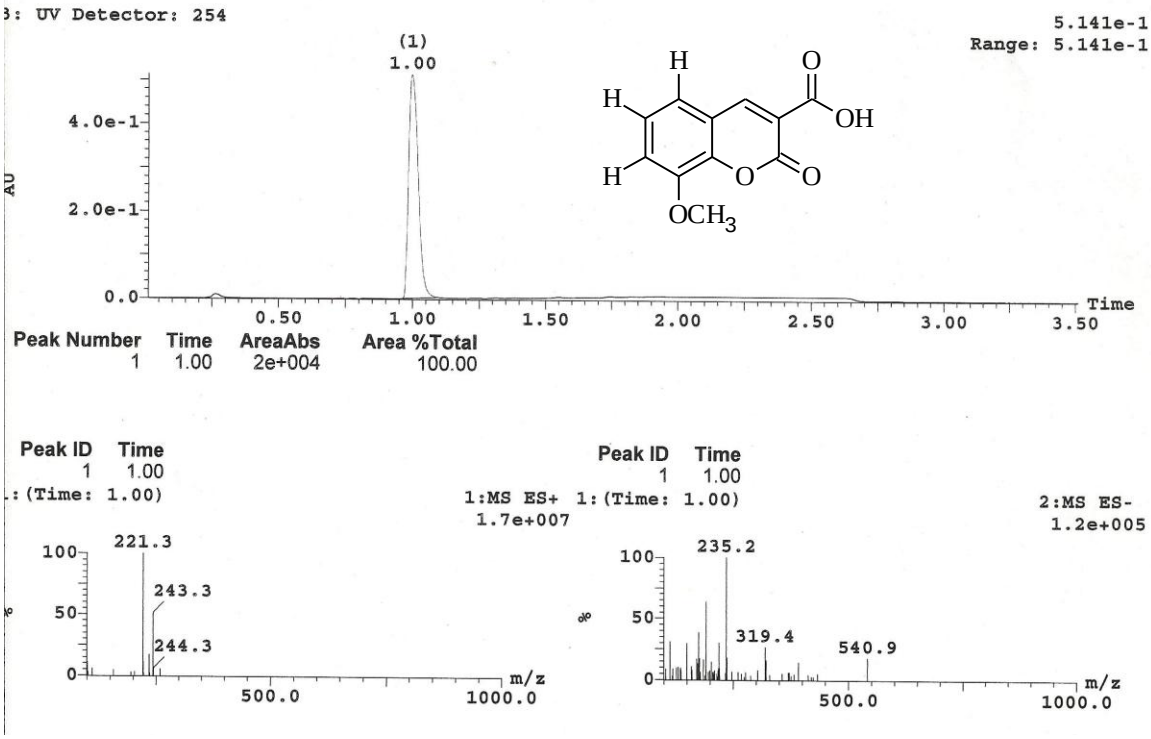
21. IR Spectrum of 8-Methoxy-2-oxo-2*H*-chromene-3-carboxylic acid (3h)



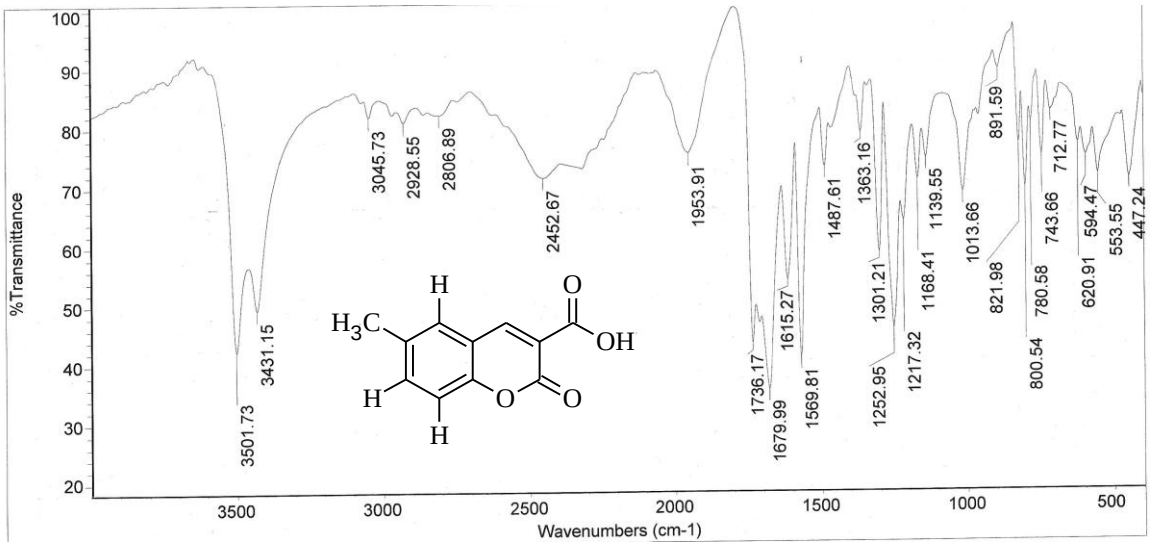
22. ^{1}H-NMR Spectrum of 8-Methoxy-2-oxo-2*H*-chromene-3-carboxylic acid (3h)



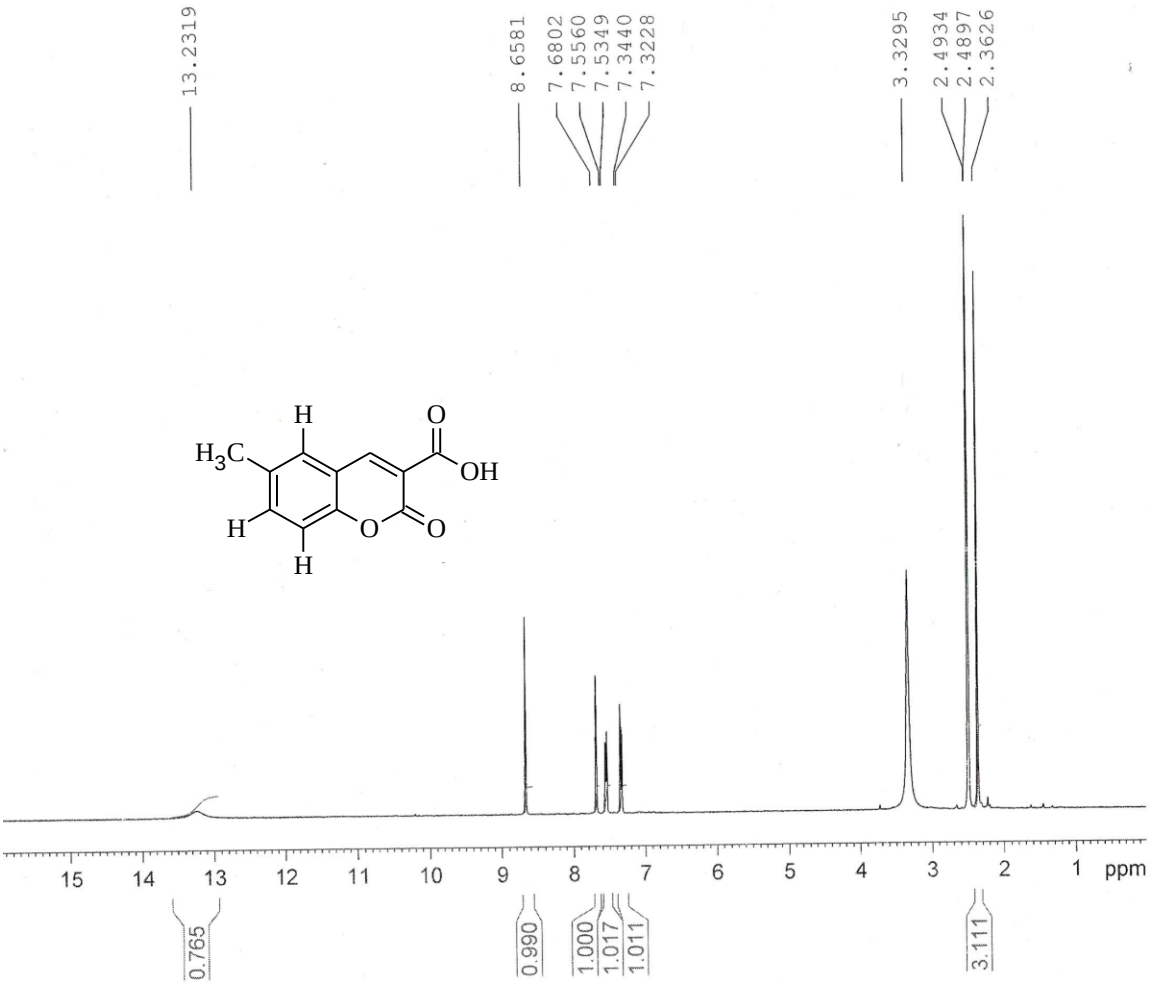
23. ^{13}C Spectrum of 8-Methoxy-2-oxo-2*H*-chromene-3-carboxylic acid (3h)



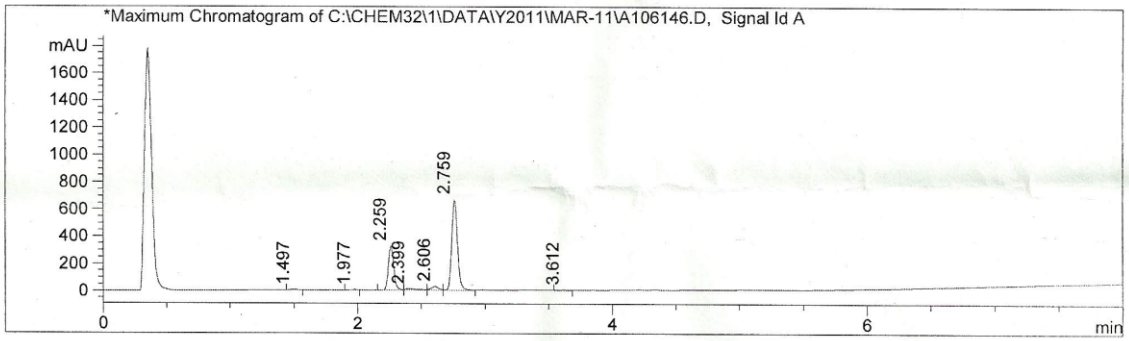
24. Mass Spectrum of 8-Methoxy-2-oxo-2*H*-chromene-3-carboxylic acid (3h)



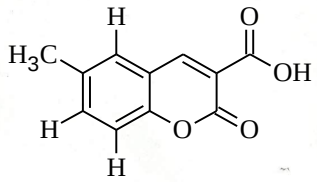
25. IR Spectrum of 6-Methyl-2-oxo-2*H*-chromene-3-carboxylic acid (3i)

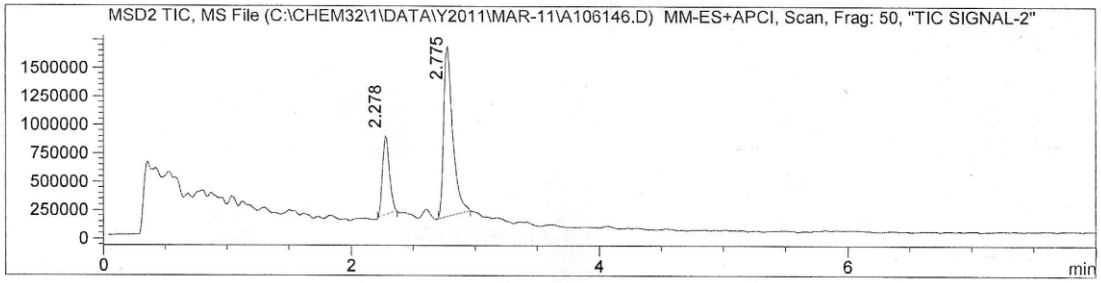


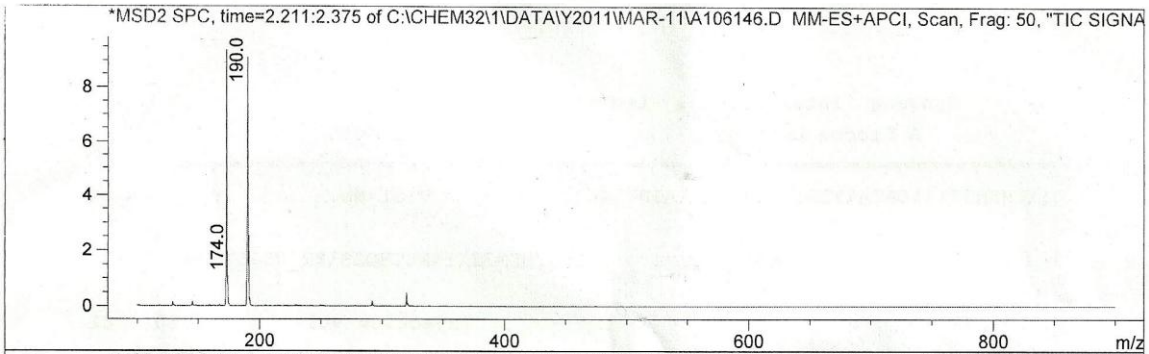
26. ^{1}H-NMR Spectrum of 6-Methyl-2-oxo-2*H*-chromene-3-carboxylic acid (3i)

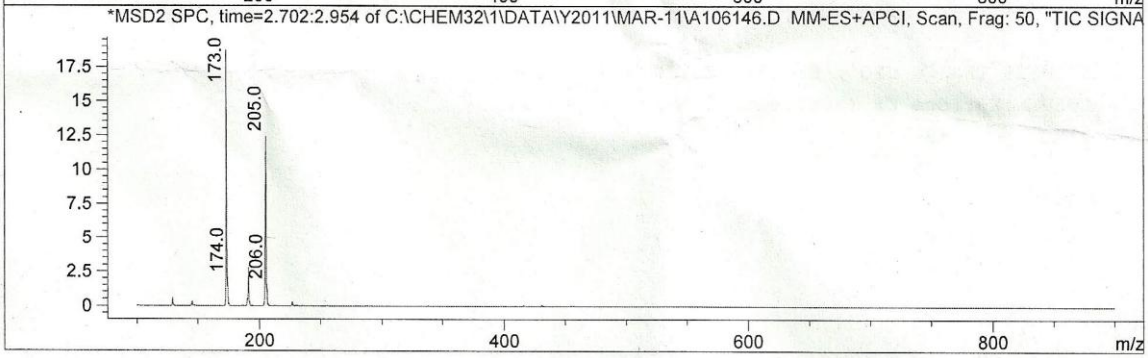


Peak No	RT min	Area	Area %
1	1.497	2.752e+001	0.835
2	1.977	1.498e+001	0.455
3	2.259	9.533e+002	28.936
4	2.399	8.687e+001	2.637
5	2.606	1.211e+002	3.675
6	2.759	2.061e+003	62.557
7	3.612	2.983e+001	0.905

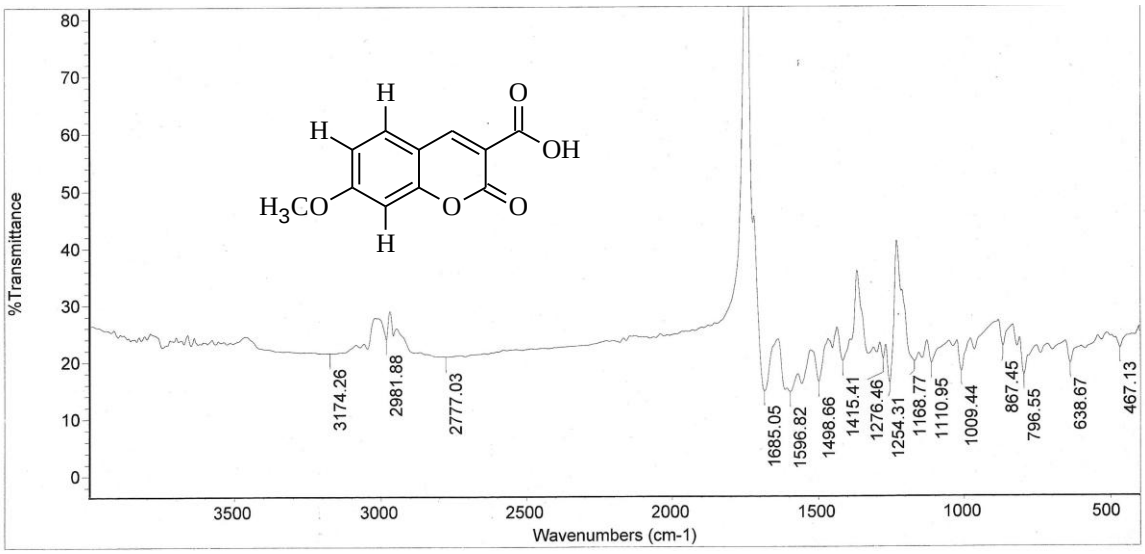




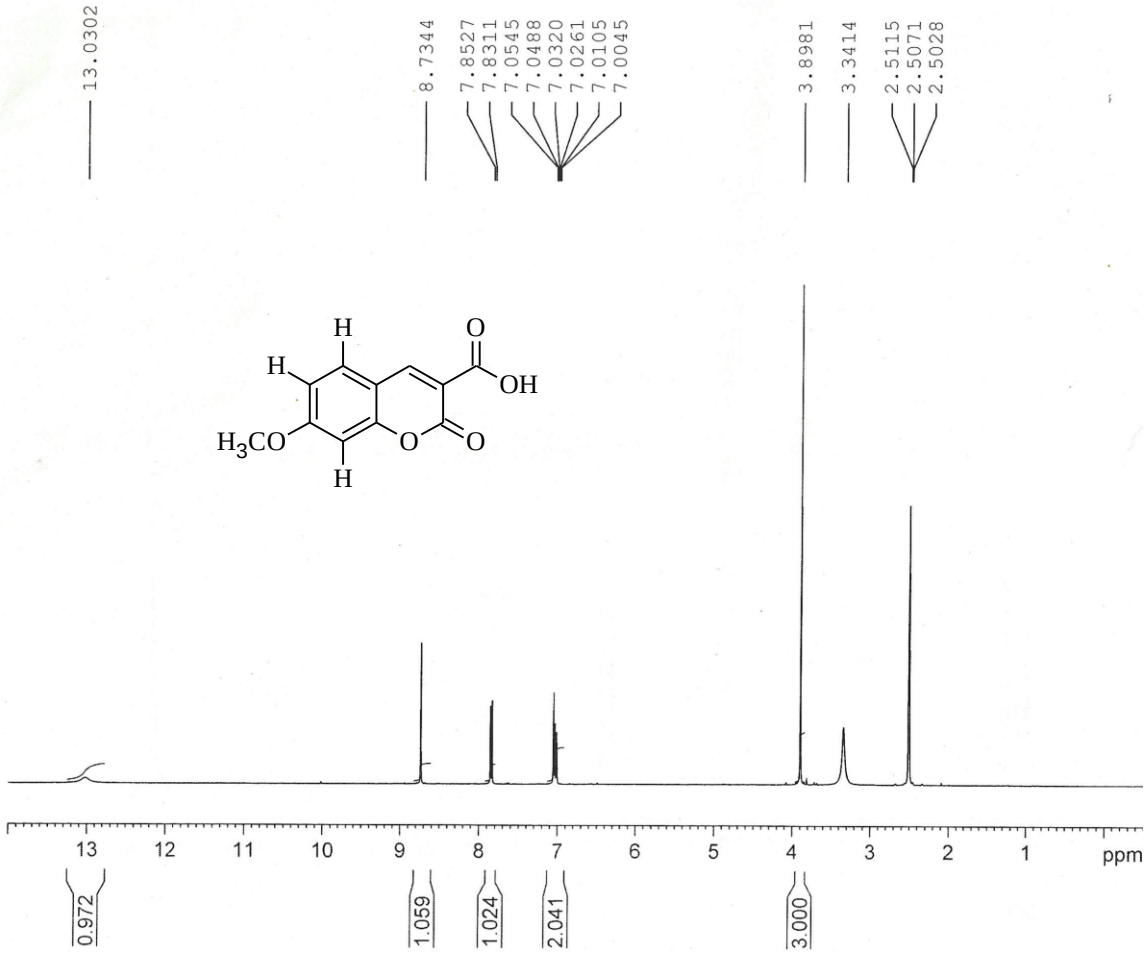




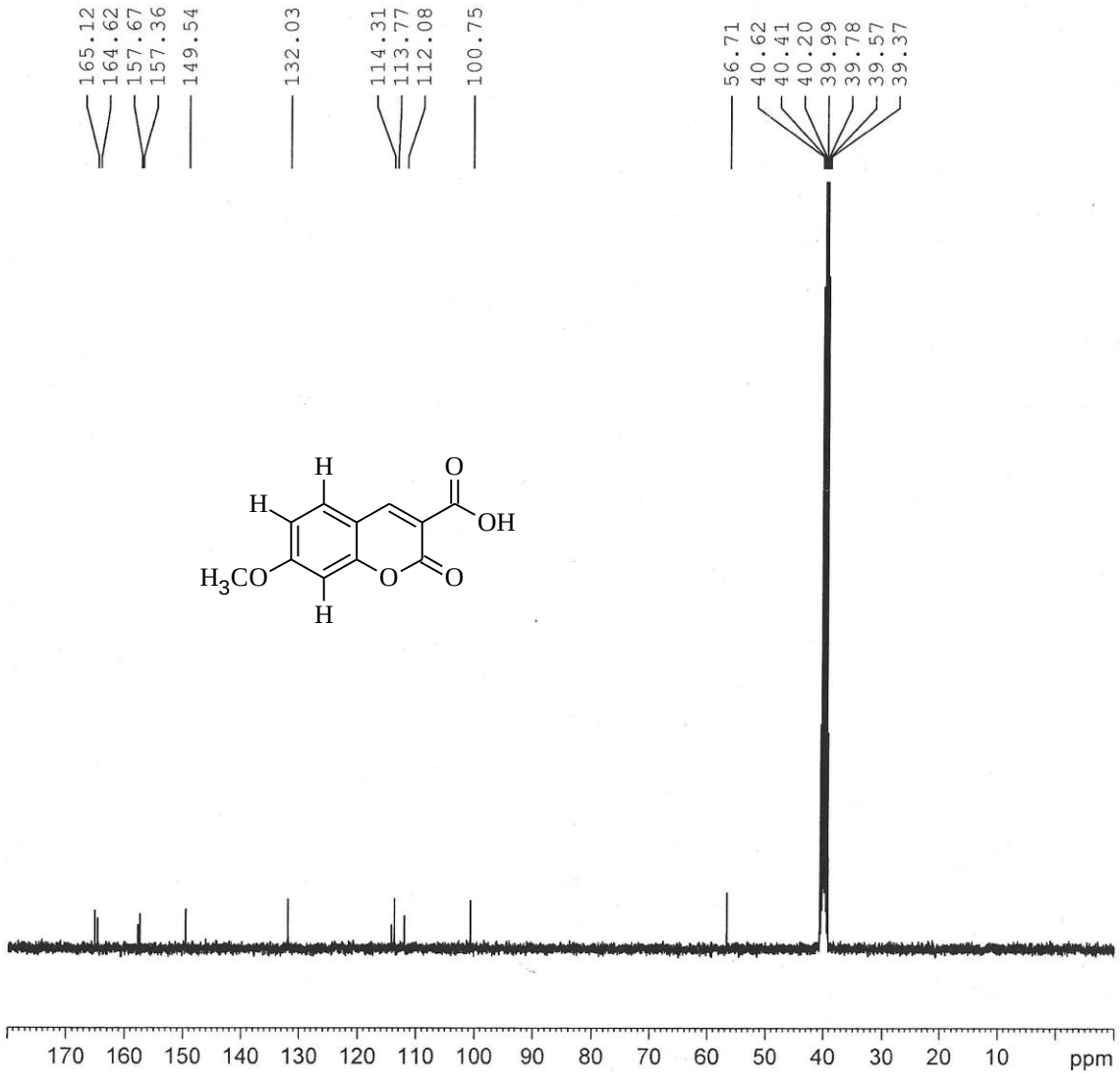
27. Mass Spectrum of 6-Methyl-2-oxo-2*H*-chromene-3-carboxylic acid (3i)



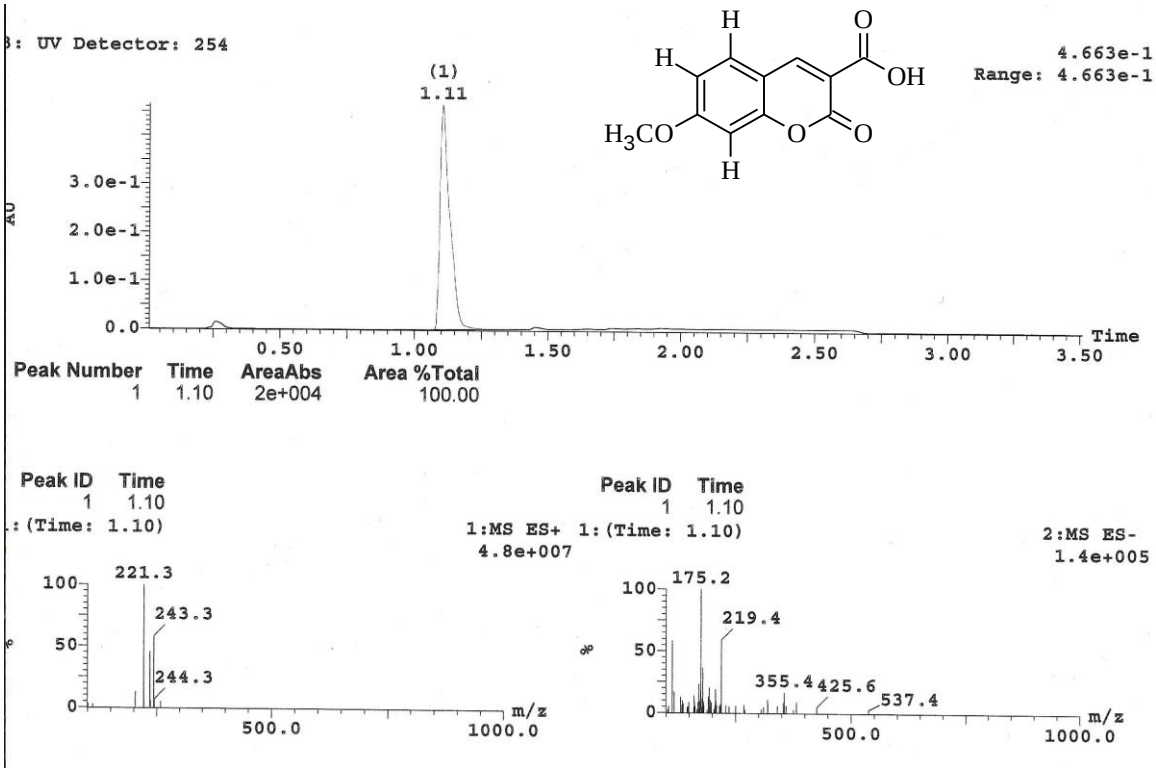
28. IR Spectrum of 7-Methoxy-2-oxo-2*H*-chromene-3-carboxylic acid (3j)



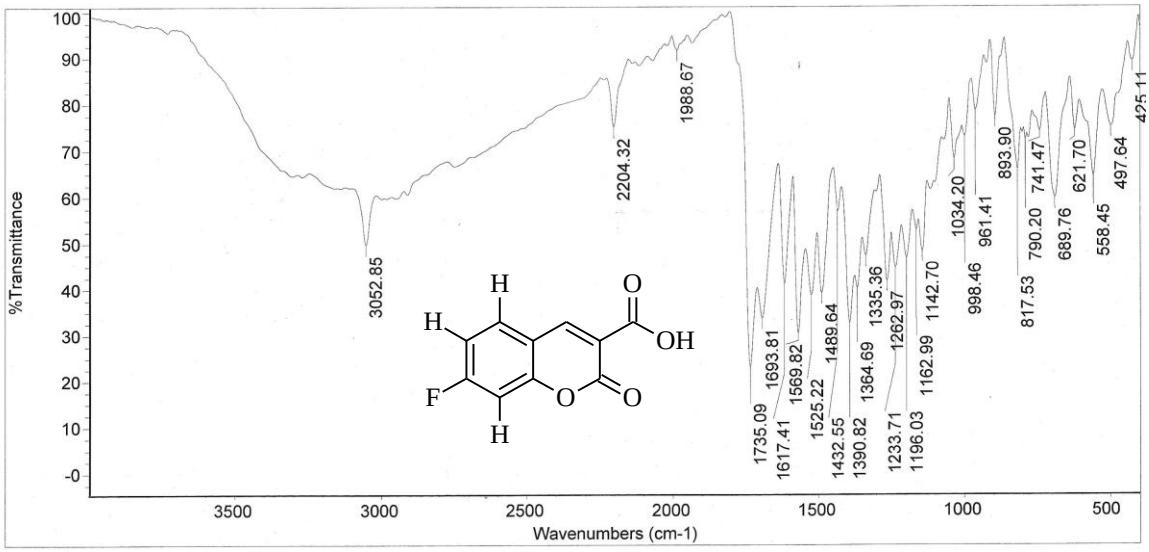
29. ^{1}H-NMR Spectrum of 7-Methoxy-2-oxo-2*H*-chromene-3-carboxylic acid (3j)



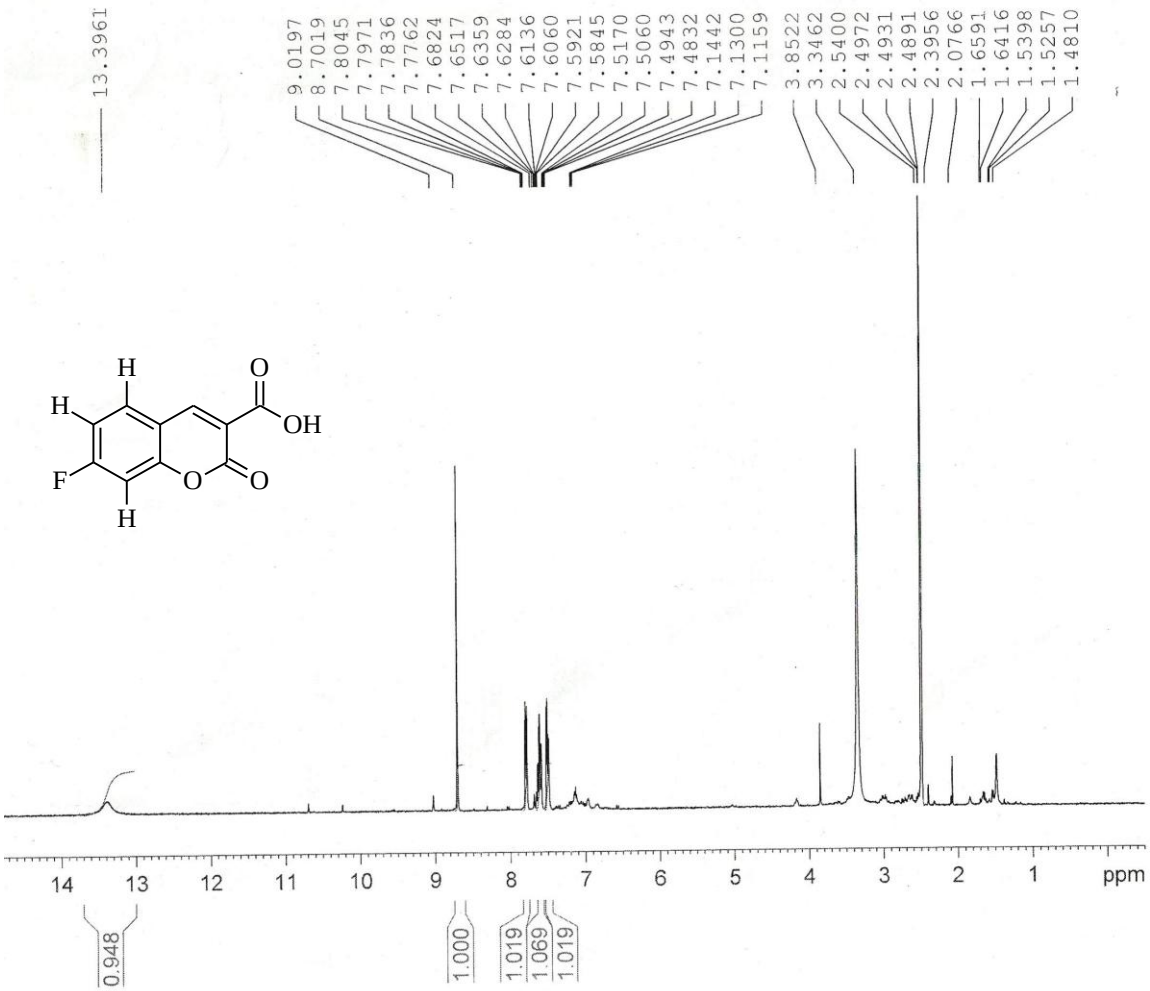
30. ^{13}C Spectrum of 7-Methoxy-2-oxo-2*H*-chromene-3-carboxylic acid (3j)



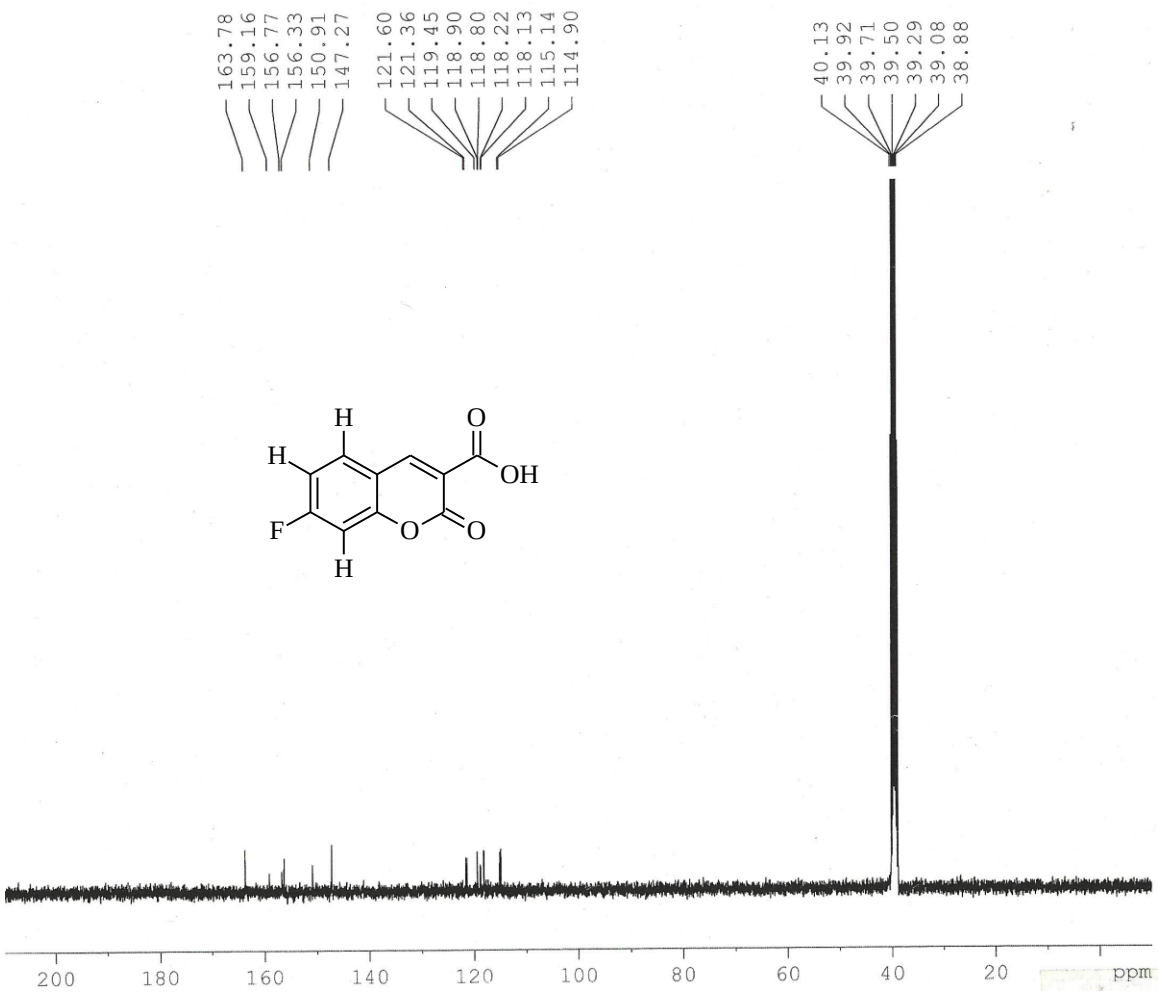
31. Mass Spectrum of 7-Methoxy-2-oxo-2*H*-chromene-3-carboxylic acid (3j)



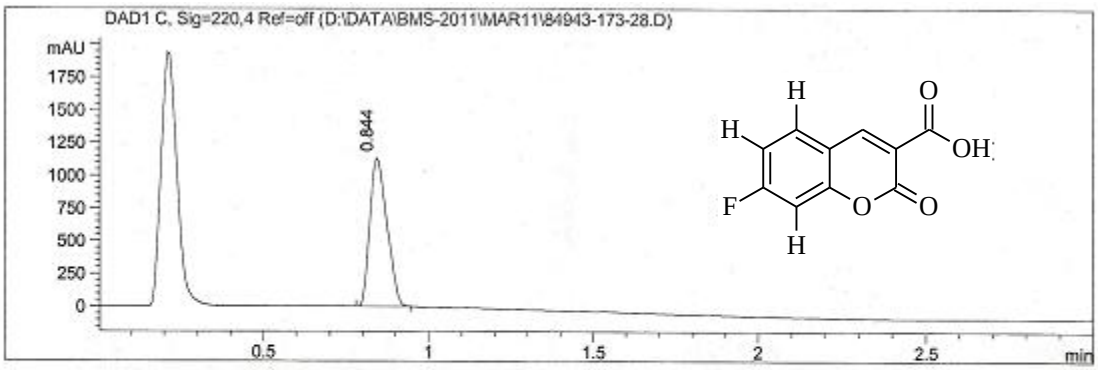
32. IR Spectrum of 7-Fluoro-2-oxo-2*H*-chromene-3-carboxylic acid (3k)



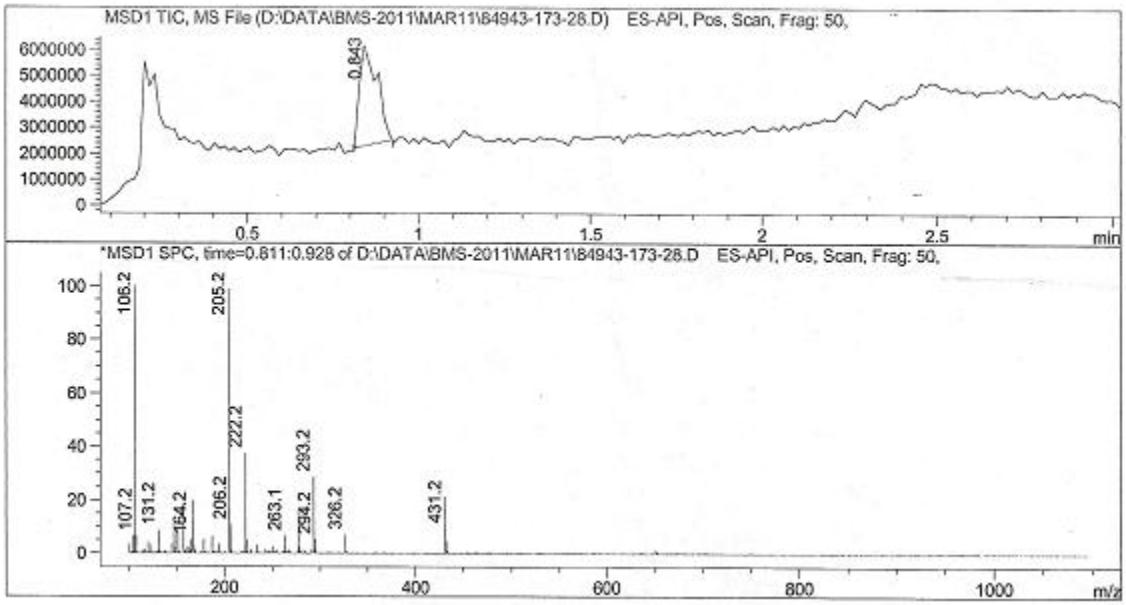
33. ^{1}H-NMR Spectrum of 7-Fluoro-2-oxo-2*H*-chromene-3-carboxylic acid (3k)



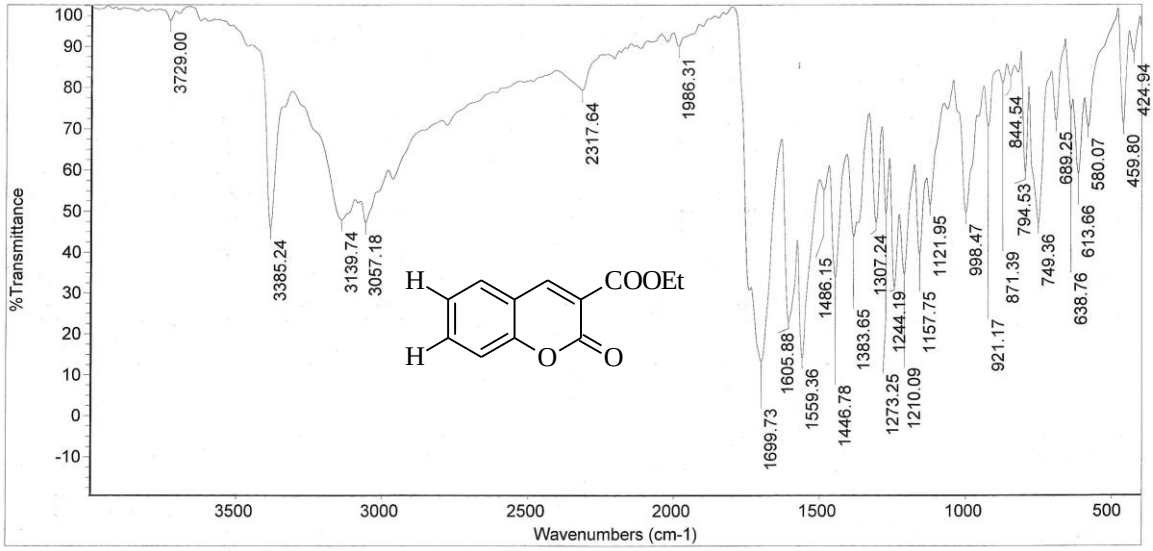
34. ^{13}C Spectrum of 7-Fluoro-2-oxo-2*H*-chromene-3-carboxylic acid (3k)



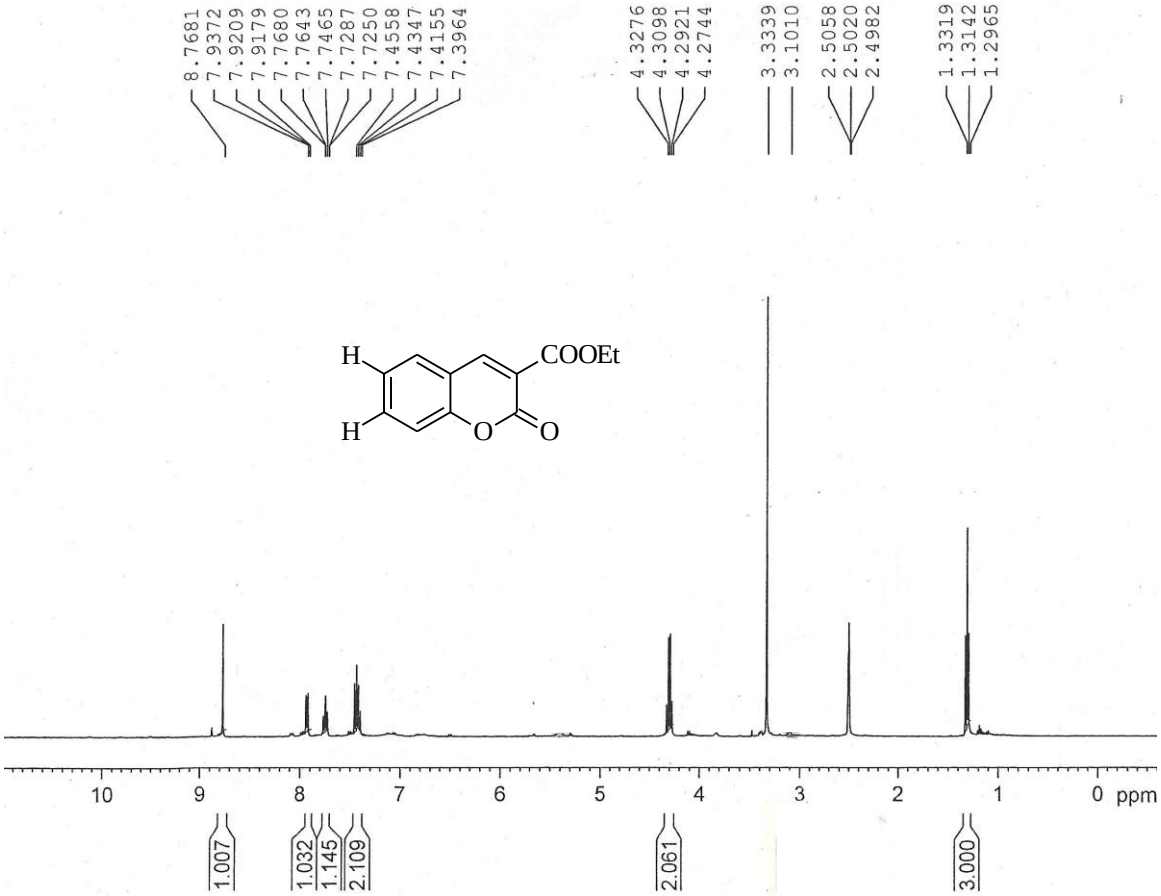
Peak No	RT min	Area	Area %
1	0.844	4.116e+003	100.000



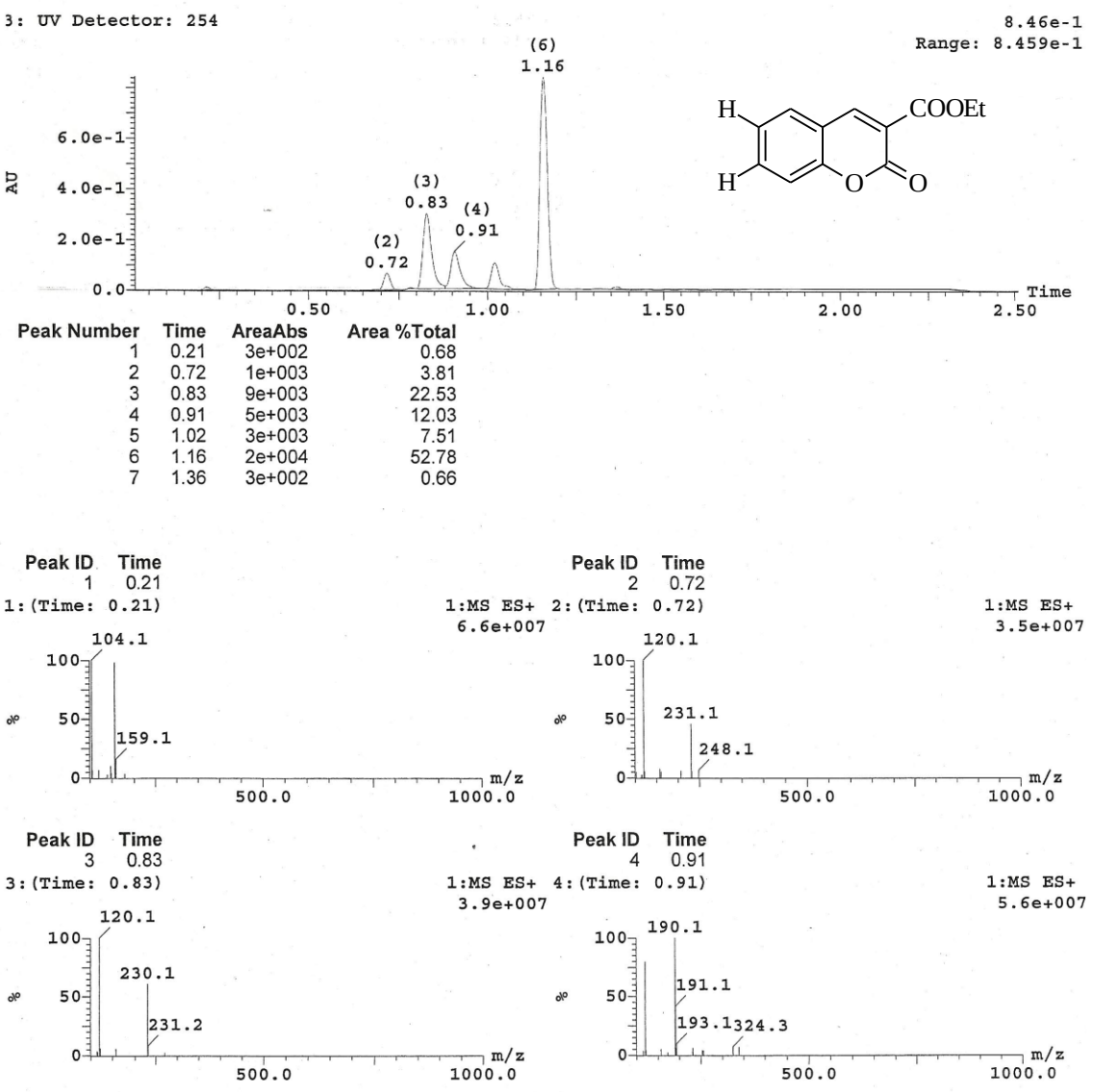
35. Mass Spectrum of 7-Fluoro-2-oxo-2*H*-chromene-3-carboxylic acid (3k)



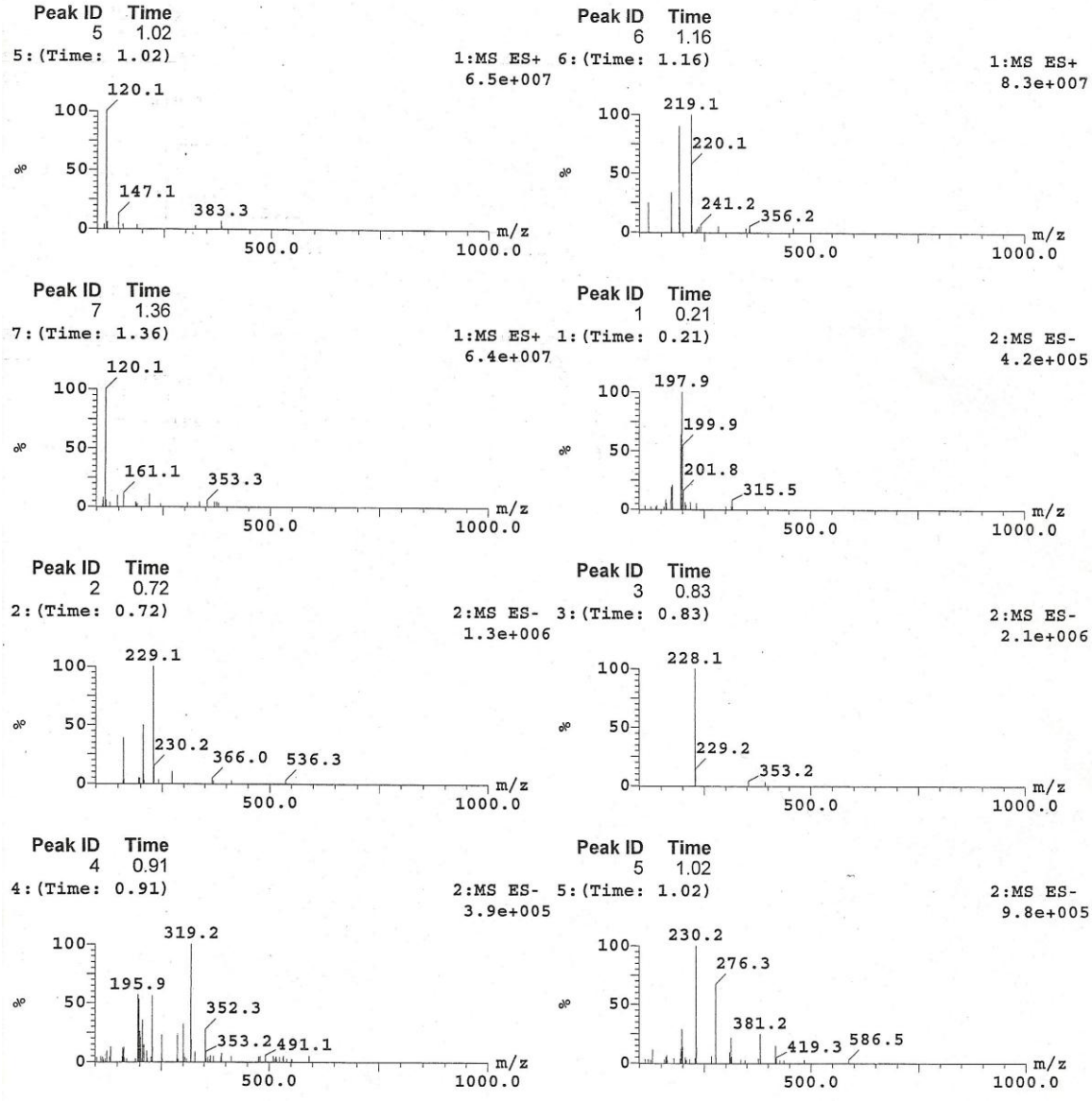
36. IR Spectrum of Ethyl-2-oxo-2*H*-chromene-3-carboxylate (5b)



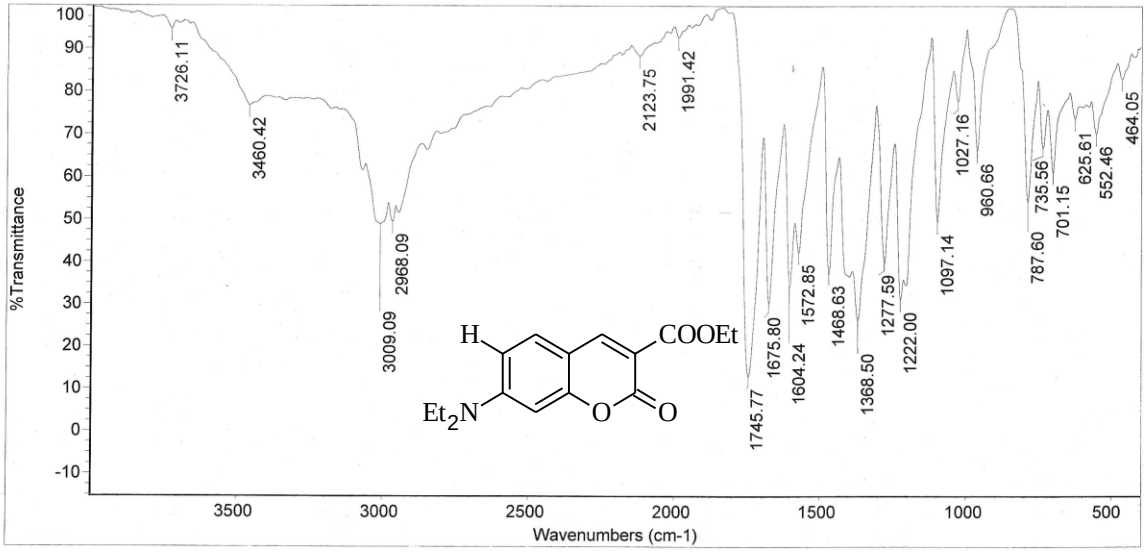
37. ^{1}H-NMR Spectrum of Ethyl-2-oxo-2*H*-chromene-3-carboxylate (5b)



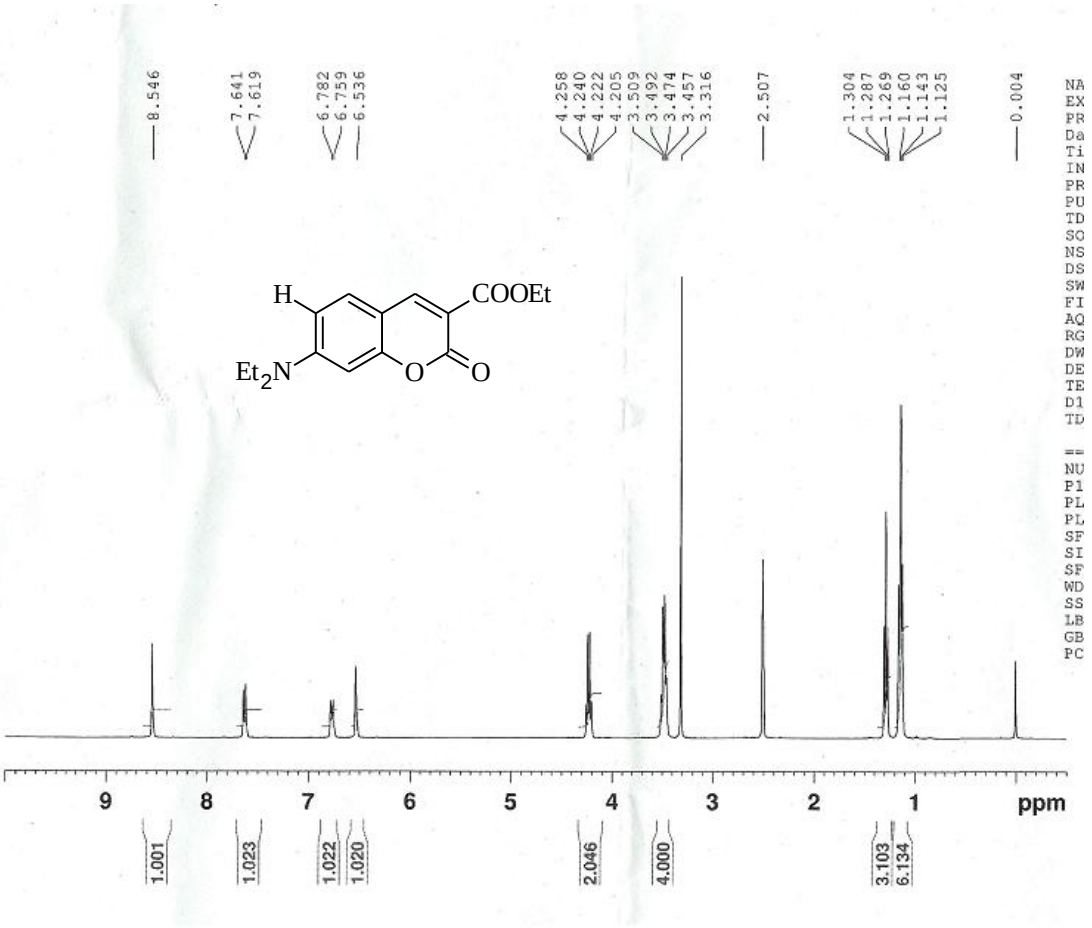
38. Mass Spectrum of Ethyl-2-oxo-2*H*-chromene-3-carboxylate (5b) (Continued)



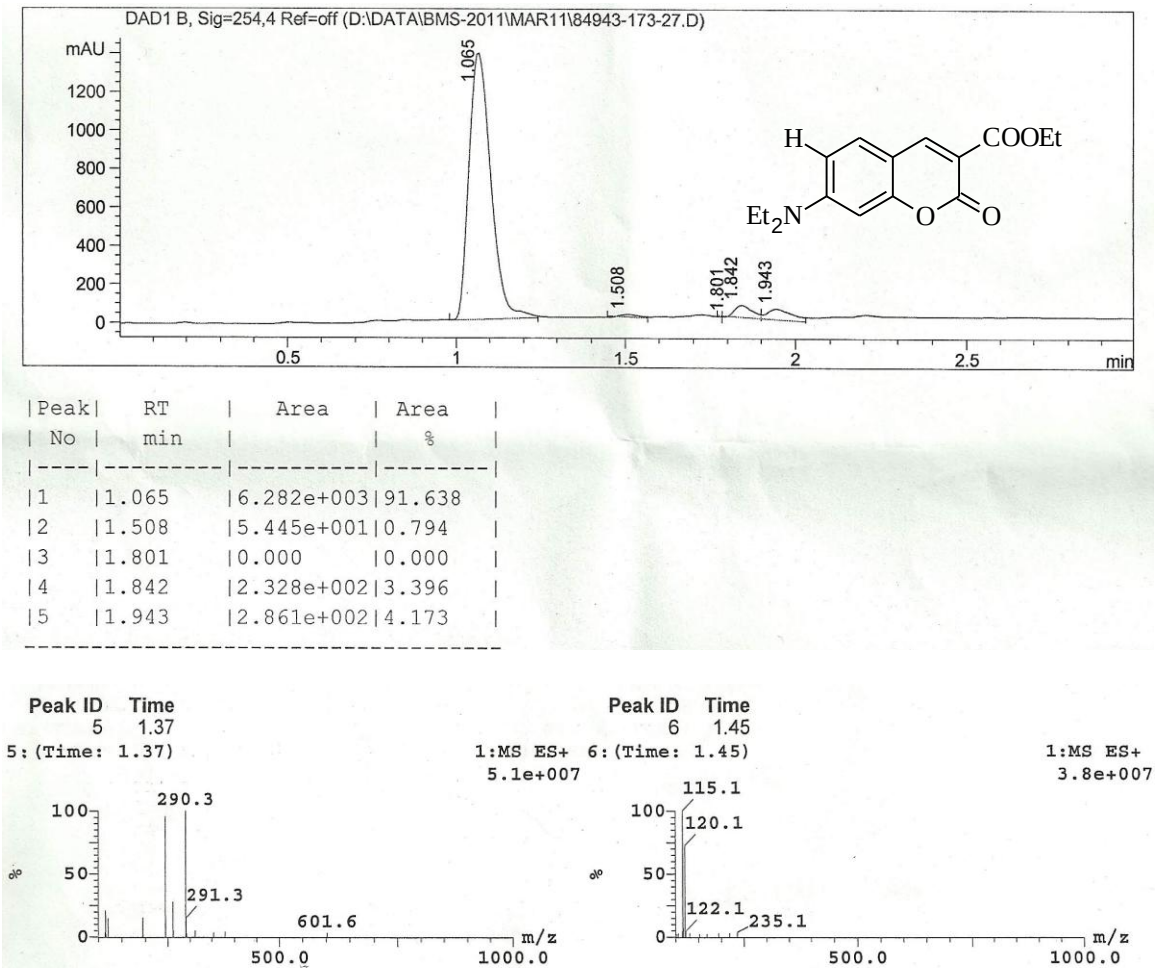
38. Mass Spectrum of Ethyl-2-oxo-2*H*-chromene-3-carboxylate (5b)



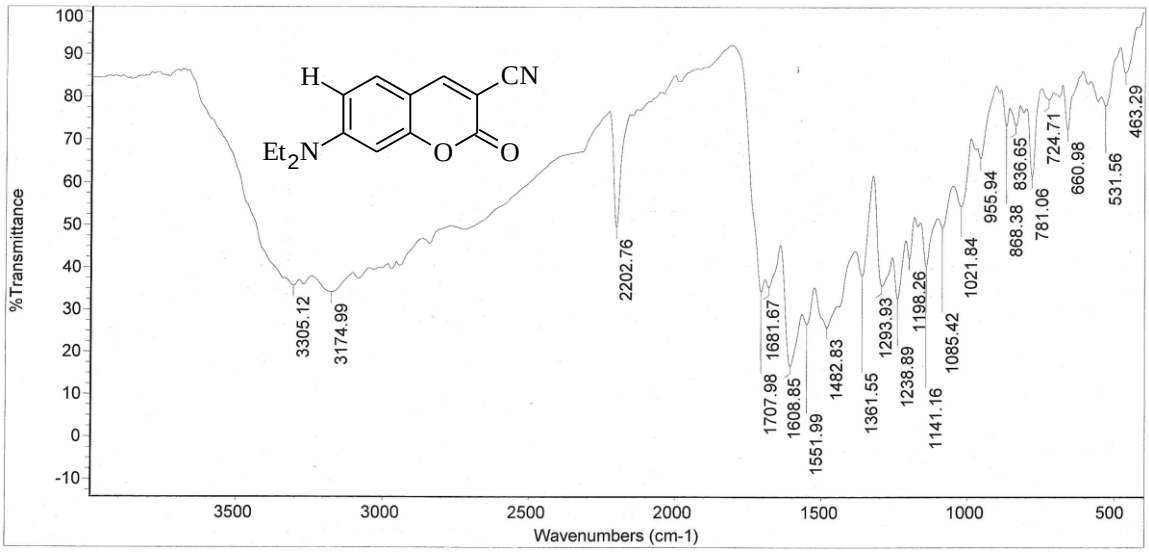
39. IR Spectrum of Ethyl-7-(diethyl amino)-2-oxo-2*H*-chromene-3-carboxylate (5e)



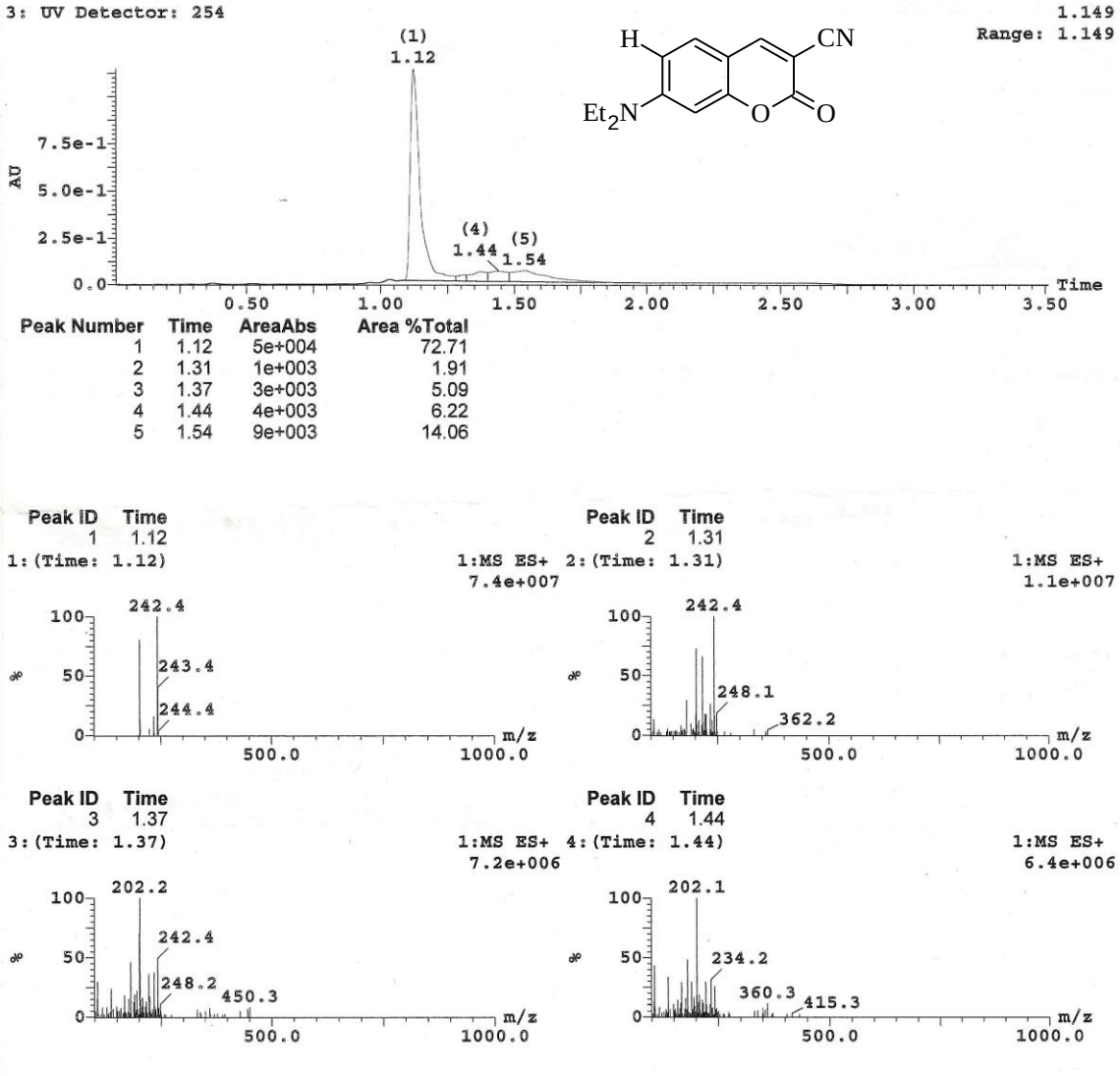
40. ^{1}H NMR Spectrum of Ethyl-7-(diethyl amino)-2-oxo-2*H*-chromene-3-carboxylate (5e)



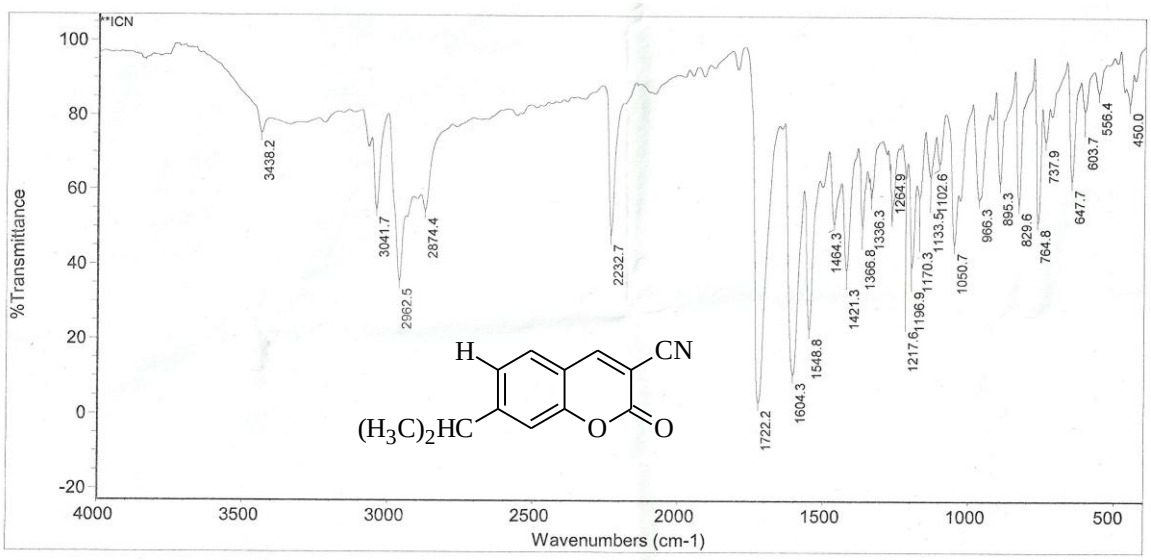
41. Mass Spectrum of Ethyl-7-(diethyl amino)-2-oxo-2*H*-chromene-3-carboxylate (5e)



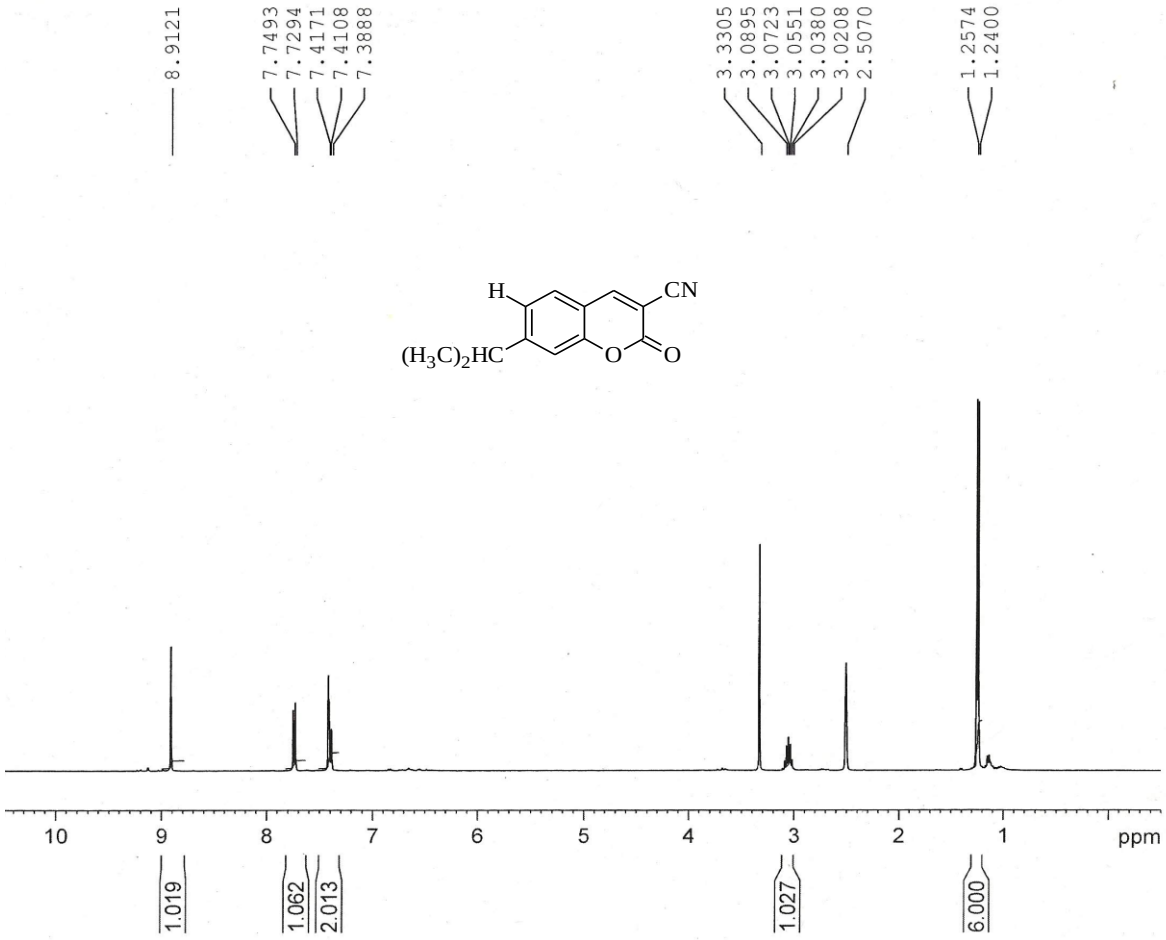
42. IR Spectrum of 7-(diethylamino)-2-oxo-2*H*-chromene-3-carbonitrile (5f)



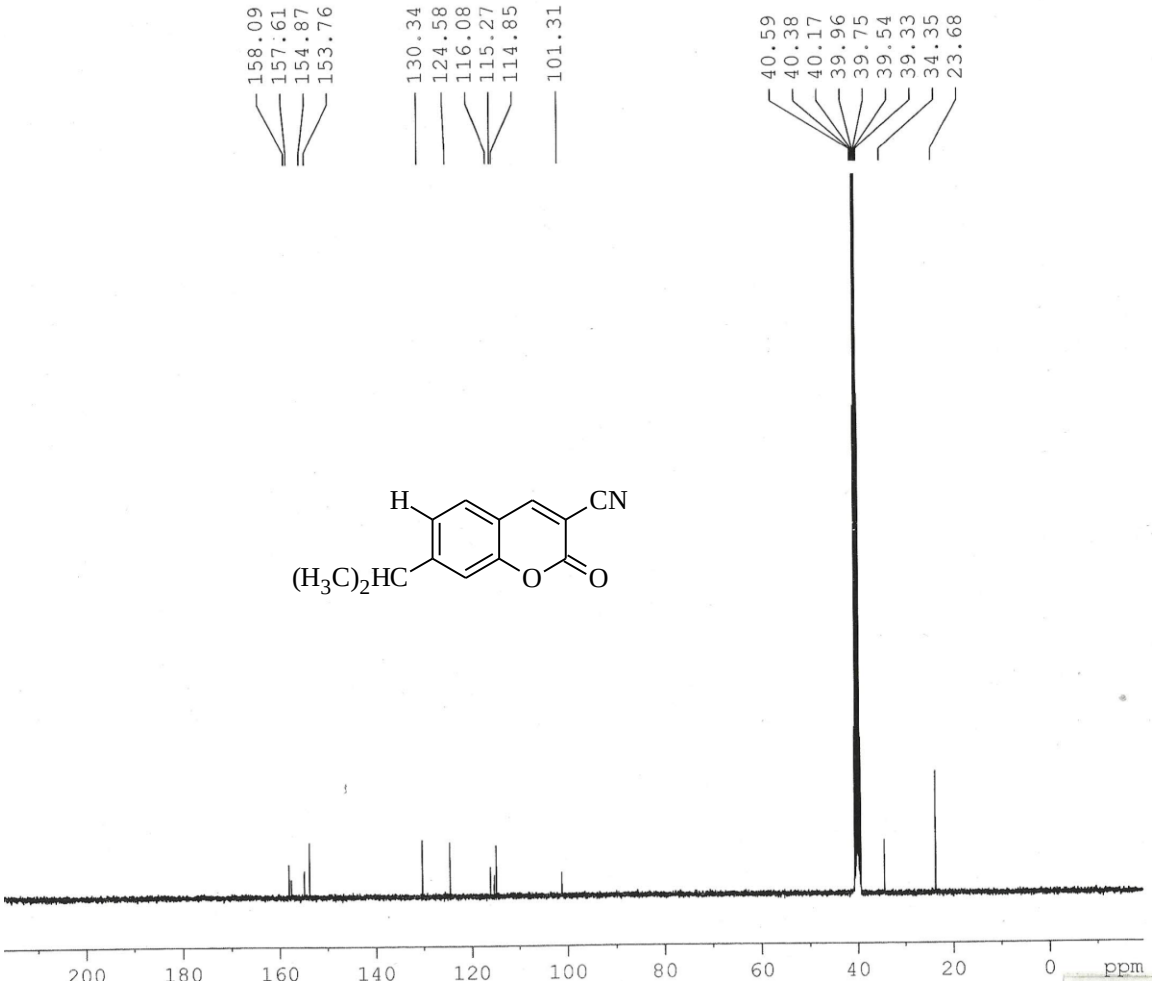
43. Mass Spectrum of 7-(diethylamino)-2-oxo-2*H*-chromene-3carbonitrile (5f)



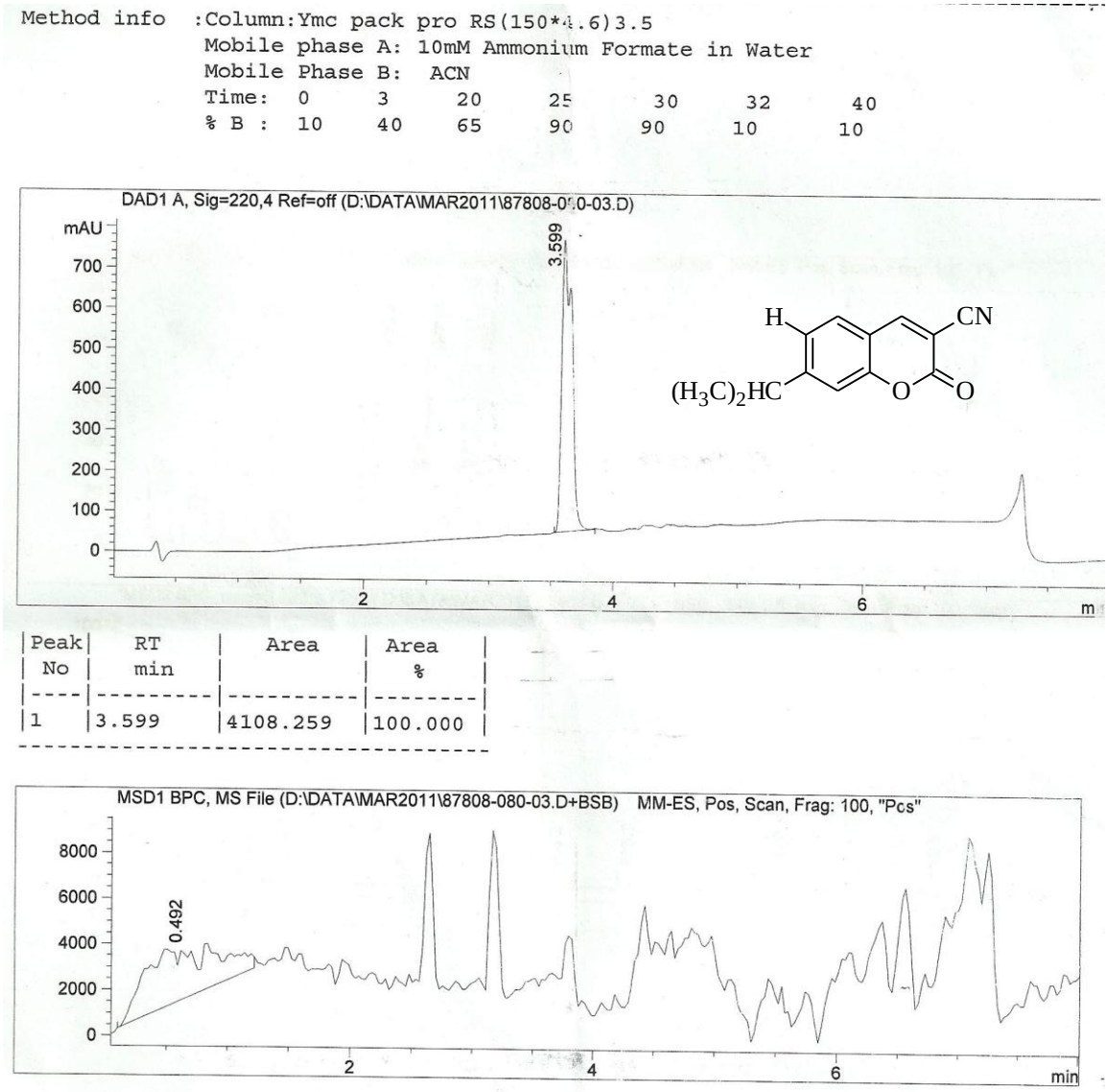
44. IR Spectrum of 2-oxo-7-(propan-2-yl)-2*H*-chromene-3-carbonitrile (5g)



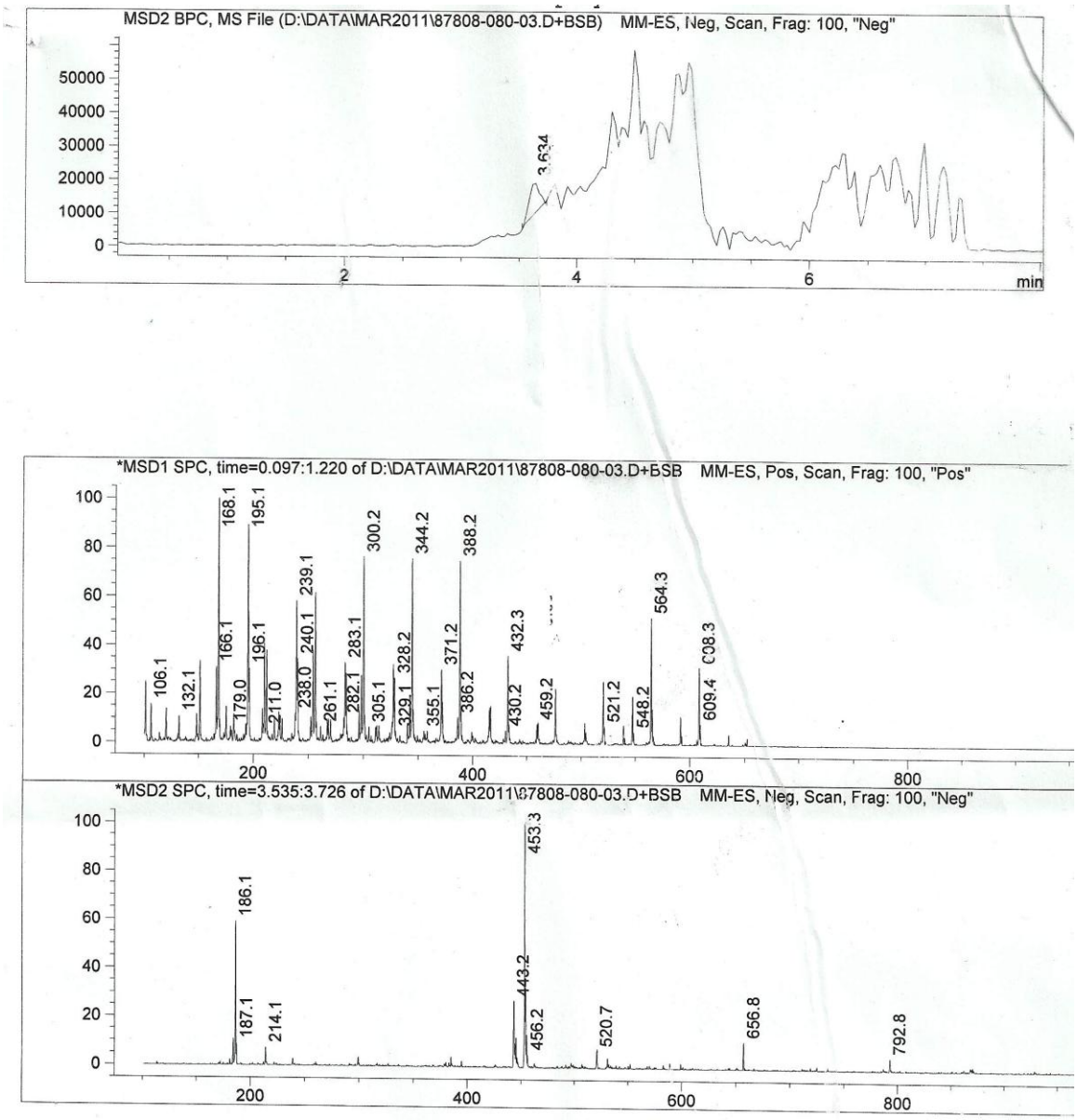
45. ^{1}H-NMR Spectrum of 2-oxo-7-(propan-2-yl)-2*H*-chromene-3-carbonitrile (5g)



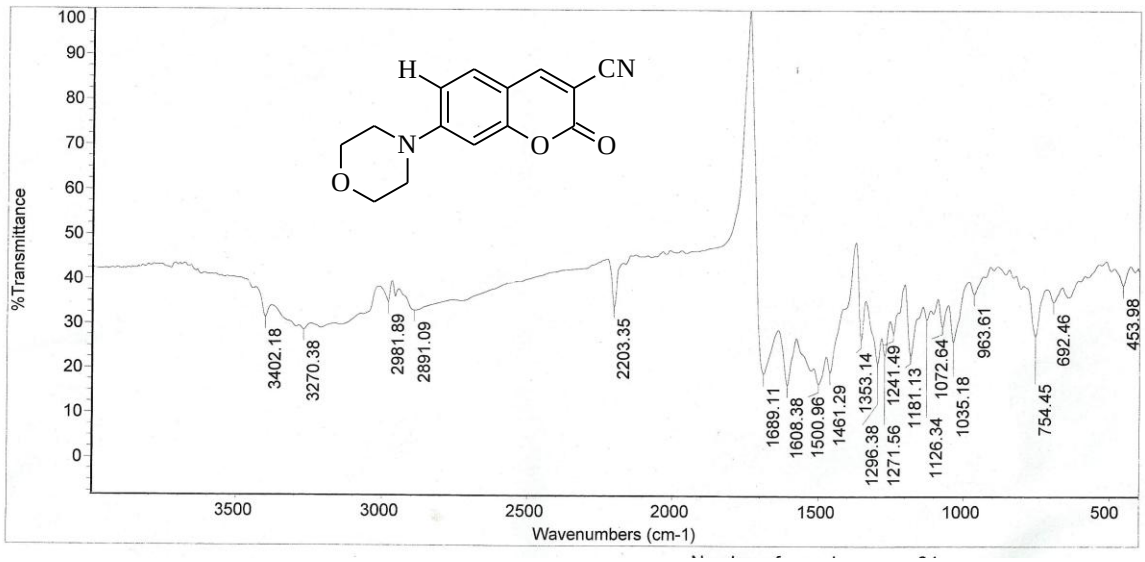
46. ^{13}C Spectrum of 2-oxo-7-(propan-2-yl)-2*H*-chromene-3-carbonitrile (5g)



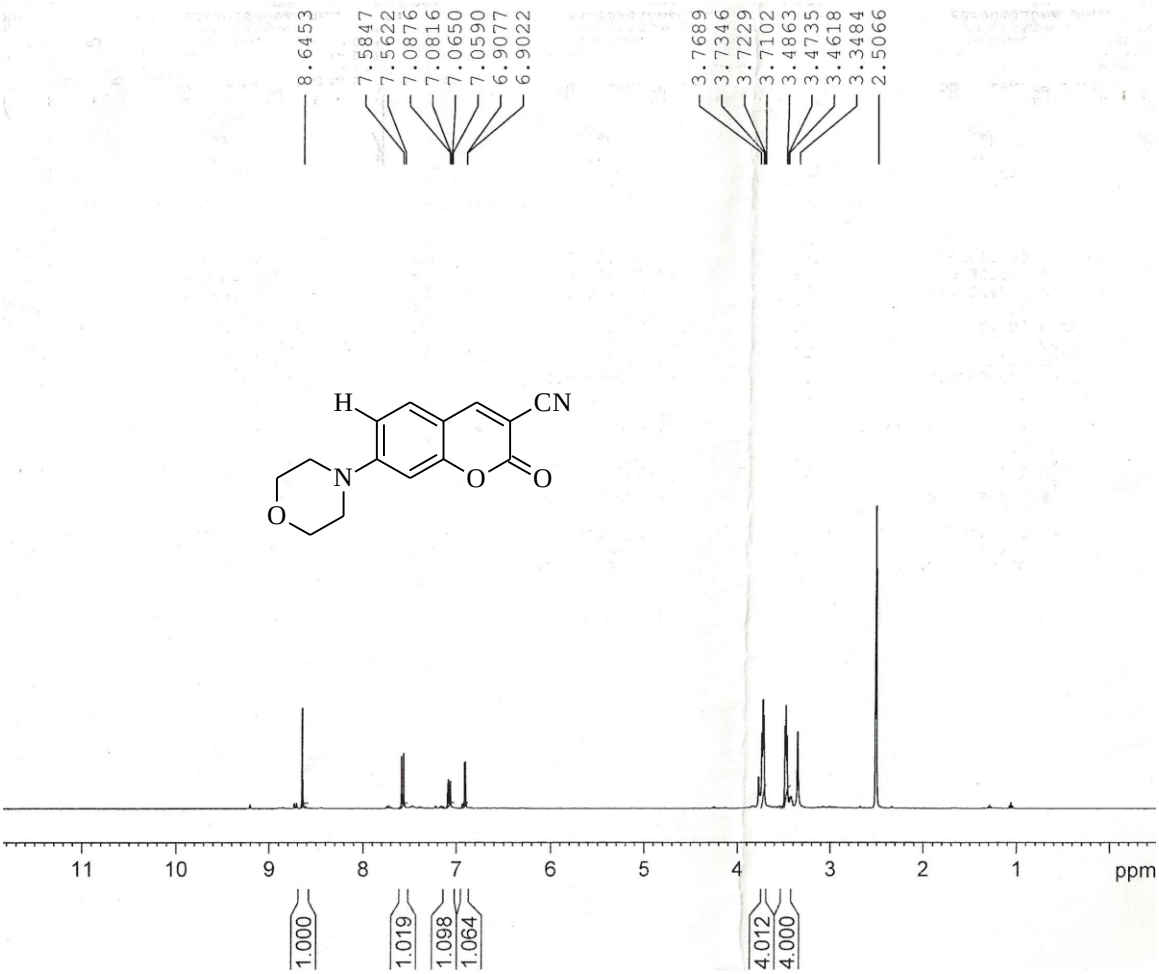
47. Mass Spectrum of 2-oxo-7-(propan-2-yl)-2*H*-chromene-3-carbonitrile (5g) (Continued)



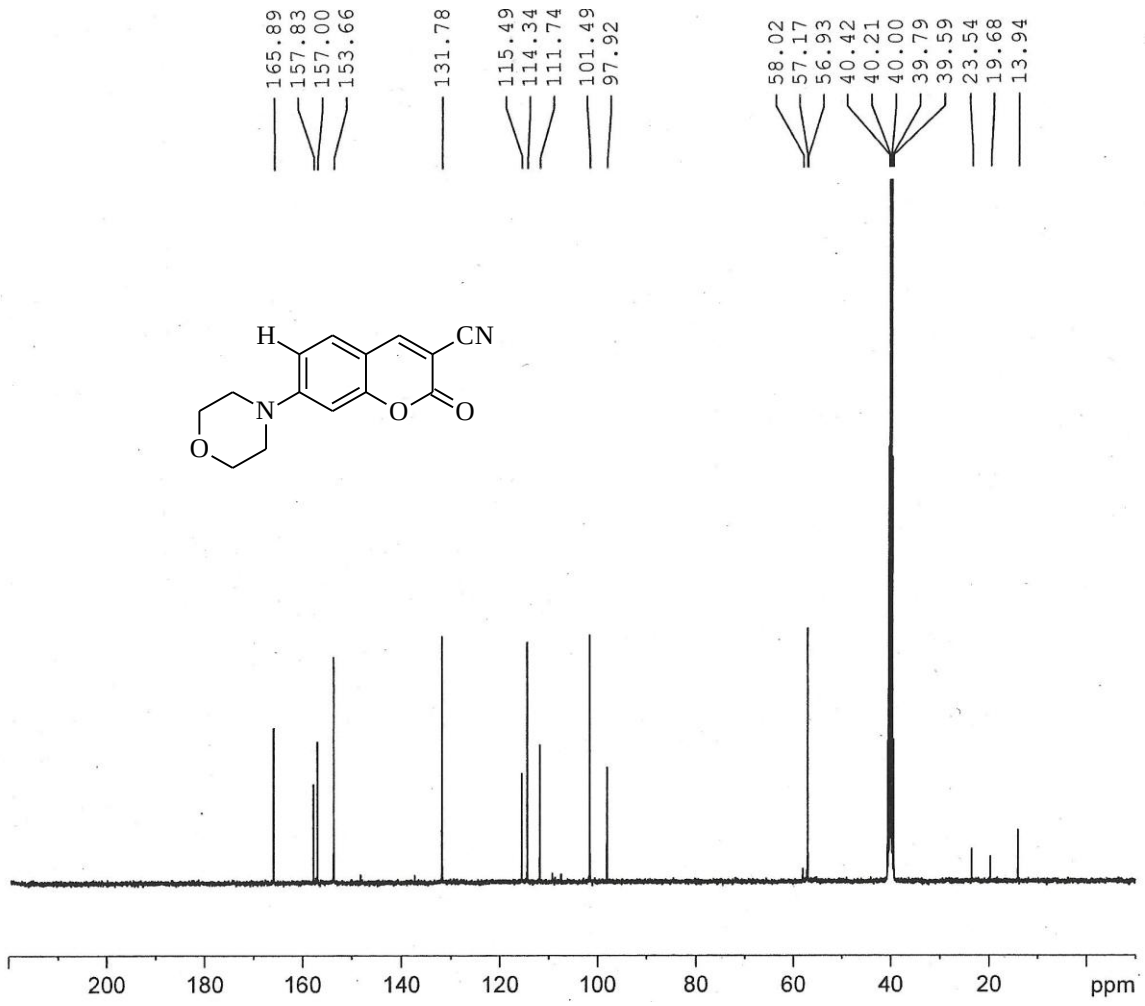
47. Mass Spectrum of 2-oxo-7-(propan-2-yl)-2*H*-chromene-3-carbonitrile (5g)



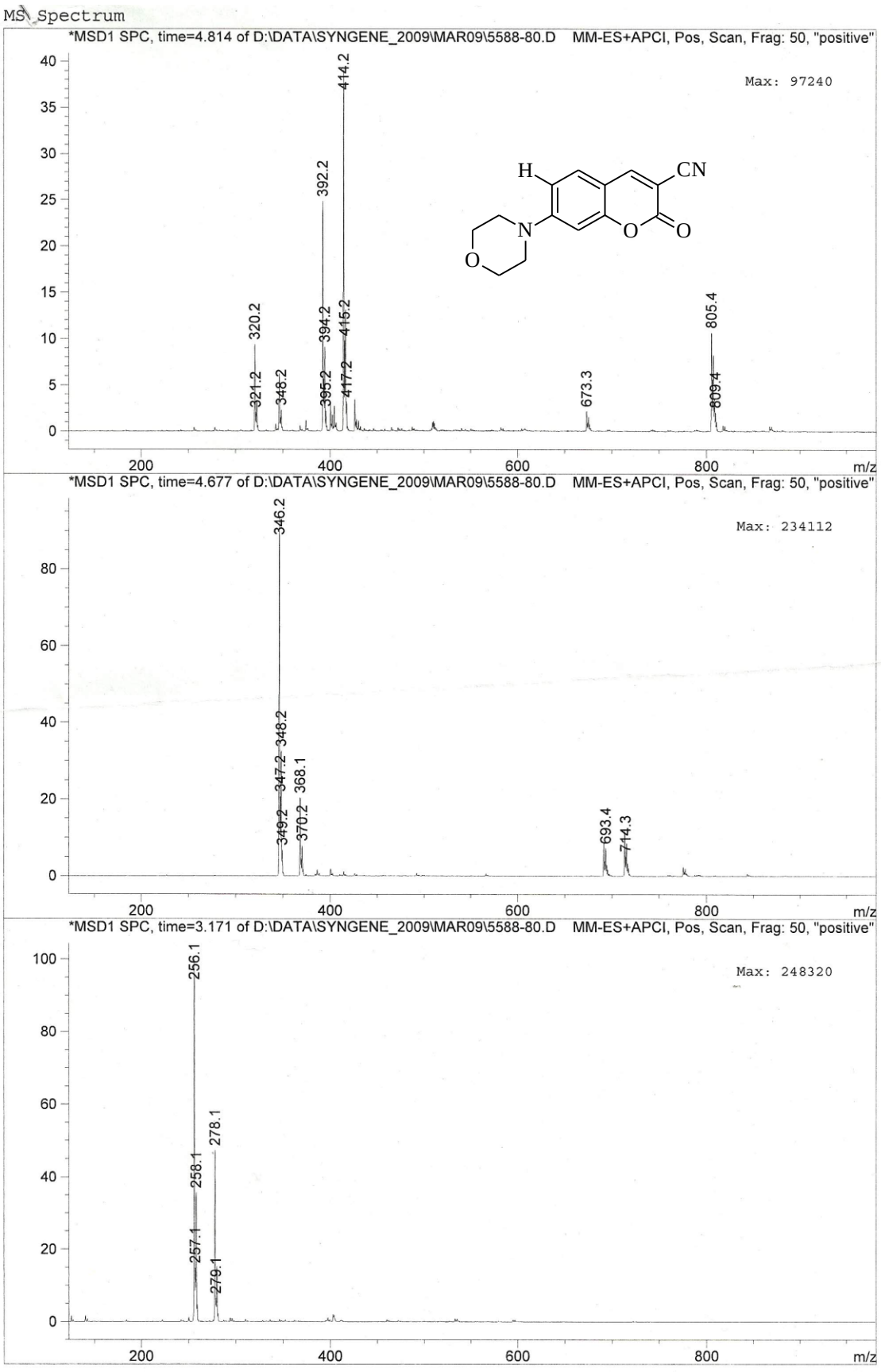
48. IR Spectrum of 7-(morpholin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (5h)



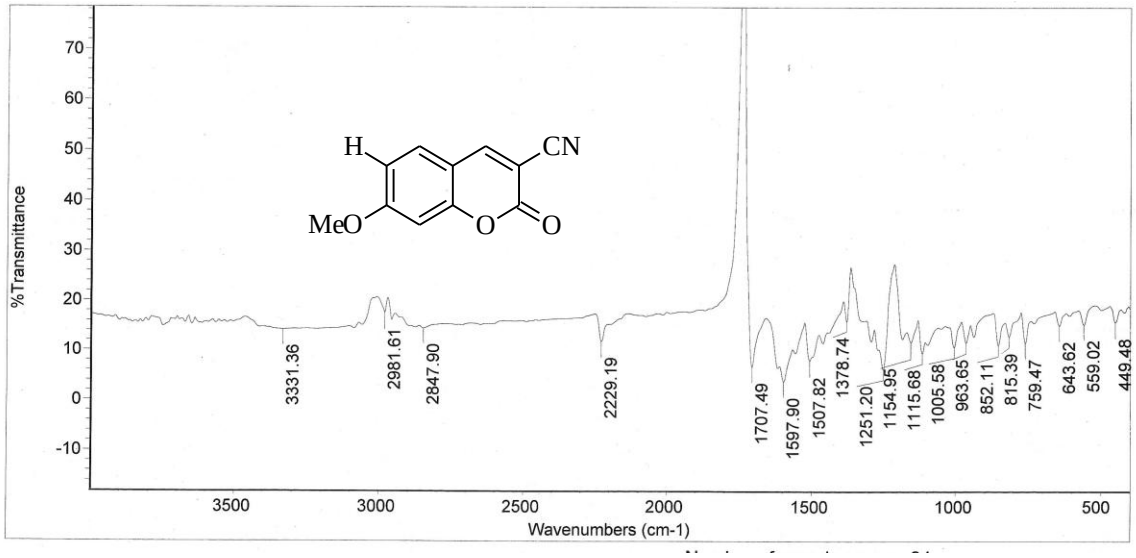
49. ^{1}H-NMR Spectrum of 7-(morpholin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (5h)



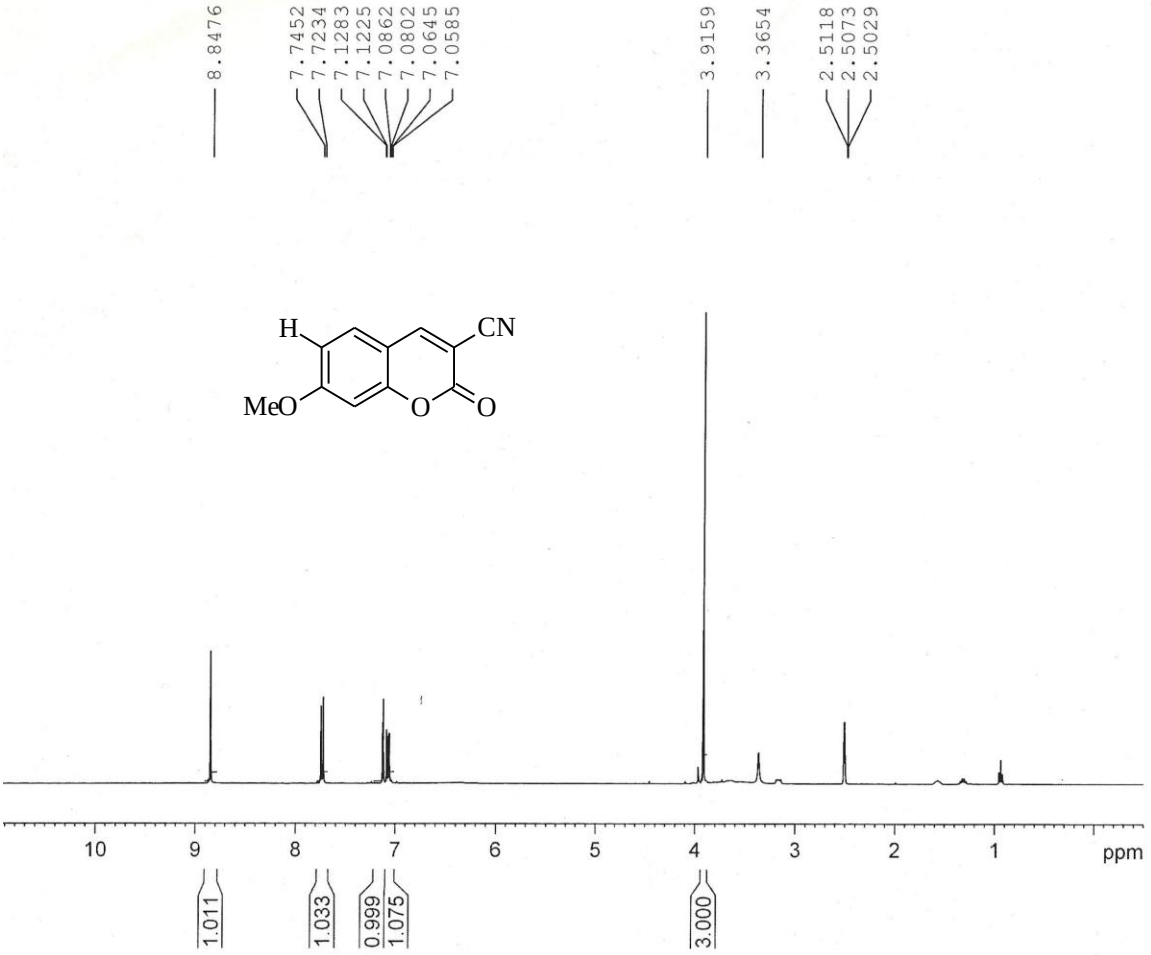
50. ^{13}C Spectrum of 7-(morpholin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (5h)



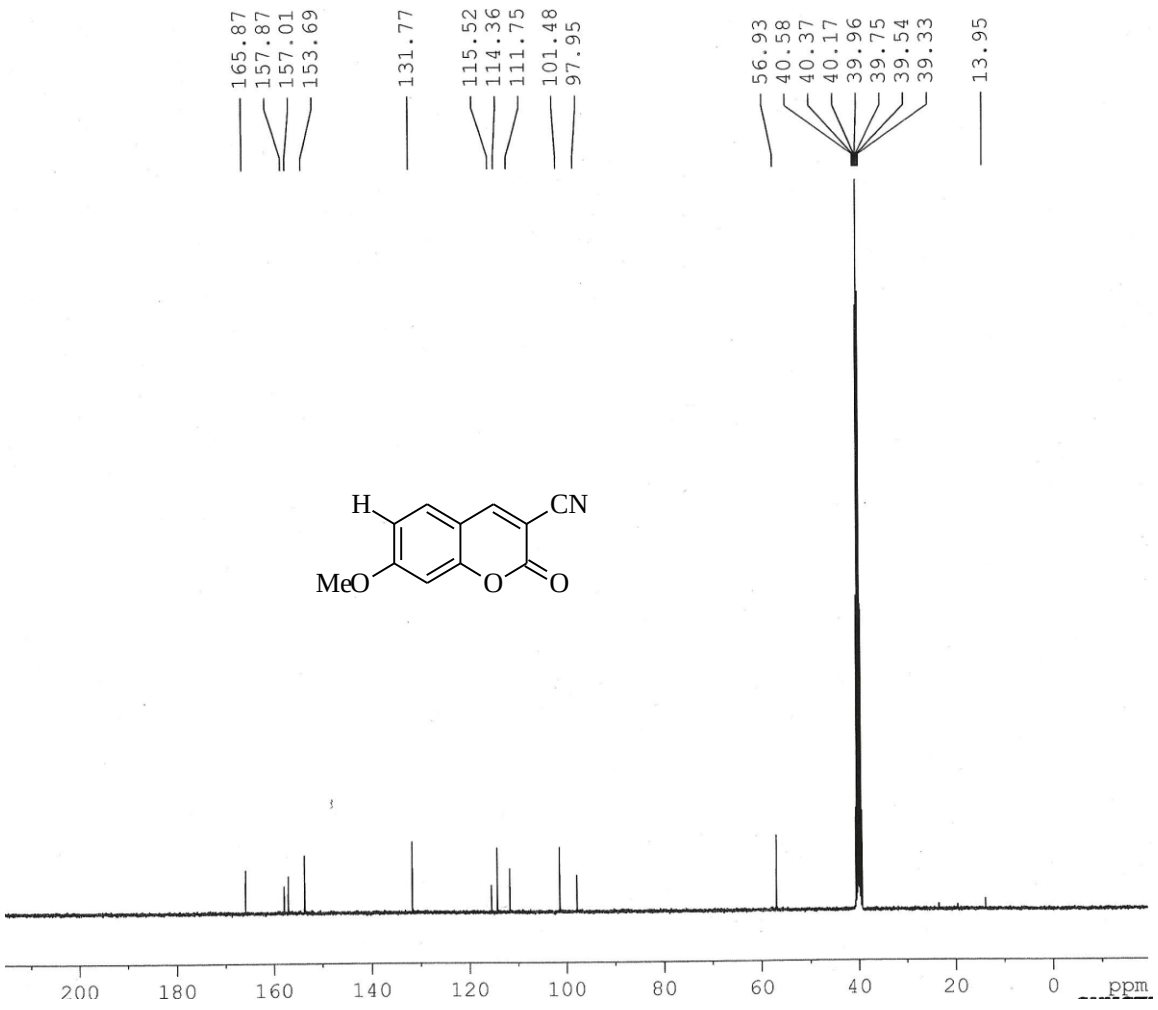
51. Mass Spectrum of 7-(morpholin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (5h)



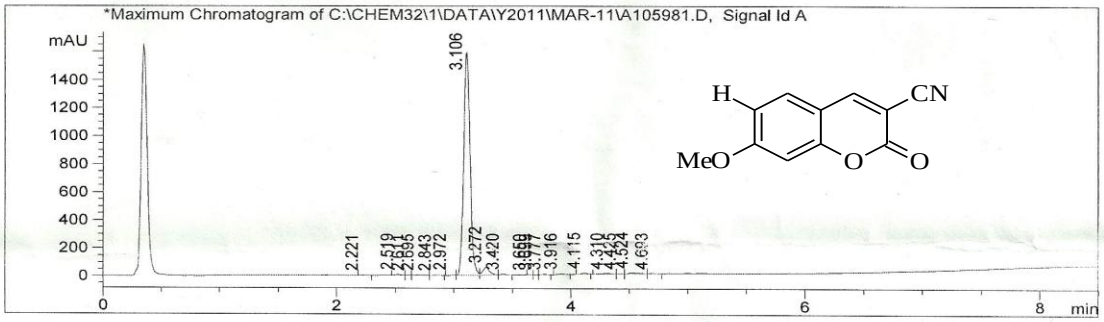
52. IR Spectrum of 7-methoxy-2-oxo-2H-chromene-3-carbonitrile (5i)



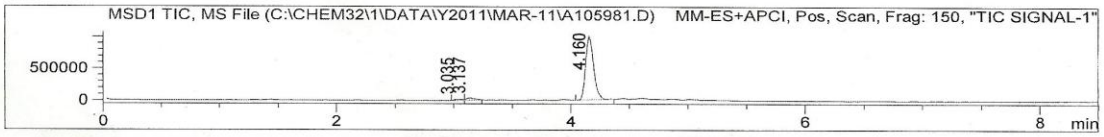
53. ^{1}H-NMR Spectrum of 7-methoxy-2-oxo-2*H*-chromene-3-carbonitrile (5i)

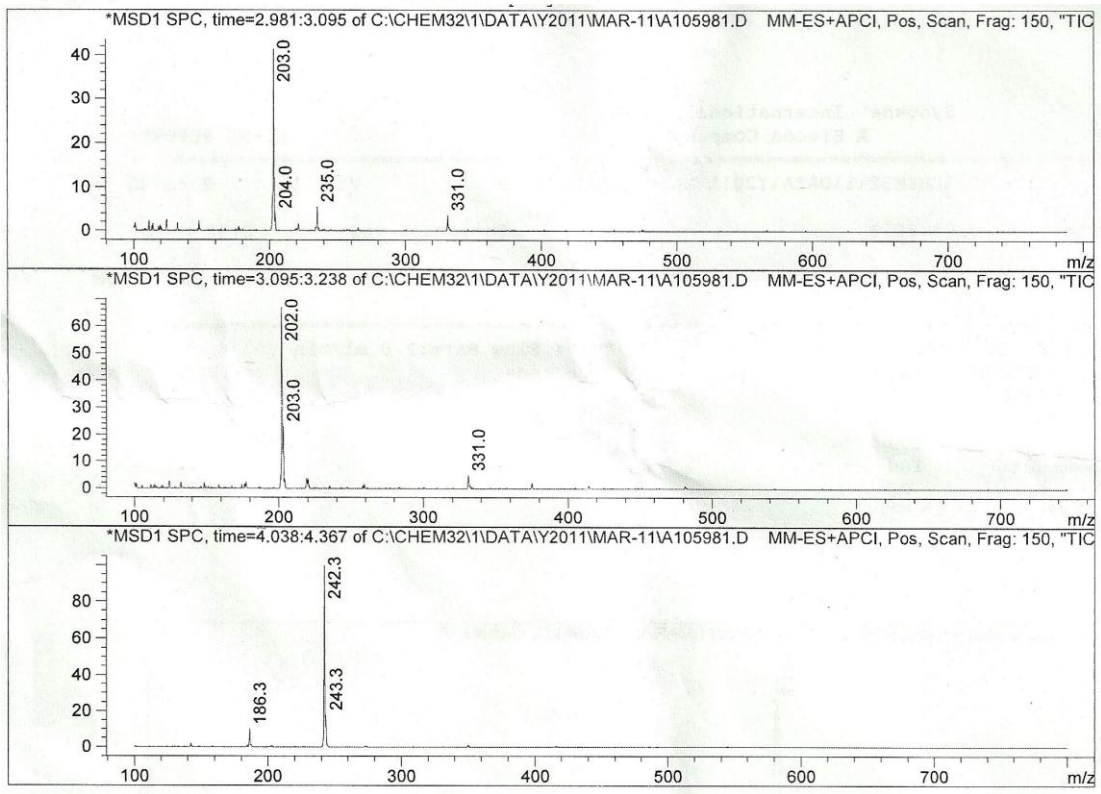


54. ^{13}C Spectrum of 7-methoxy-2-oxo-2*H*-chromene-3-carbonitrile (5i)

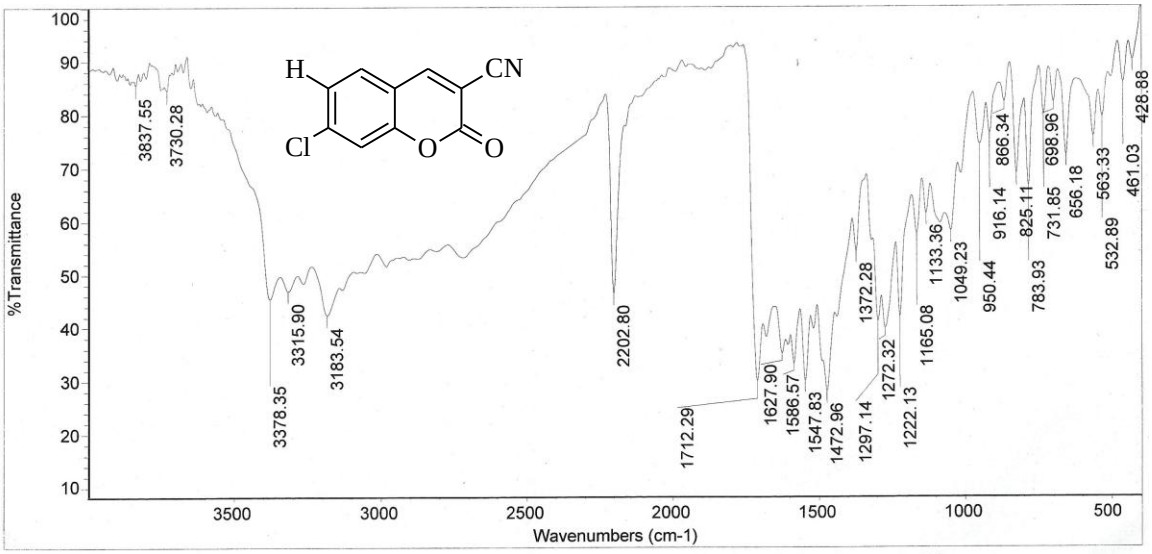


Peak No	RT min	Area	Area %
1	2.221	1.354e+001	0.208
2	2.519	3.494e+001	0.537
3	2.611	8.656e+000	0.133
4	2.695	2.291e+001	0.352
5	2.843	1.431e+001	0.220
6	2.972	8.959e+000	0.138
7	3.106	5.989e+003	91.972
8	3.272	2.229e+002	3.423
9	3.420	2.737e+001	0.420
10	3.650	5.458e+000	0.084
11	3.699	3.612e+000	0.055
12	3.777	1.306e+001	0.201
13	3.916	1.943e+001	0.298
14	4.115	2.595e+001	0.399
15	4.310	3.834e+001	0.589
16	4.425	9.446e+000	0.145
17	4.524	4.582e+001	0.704
18	4.693	8.062e+000	0.124

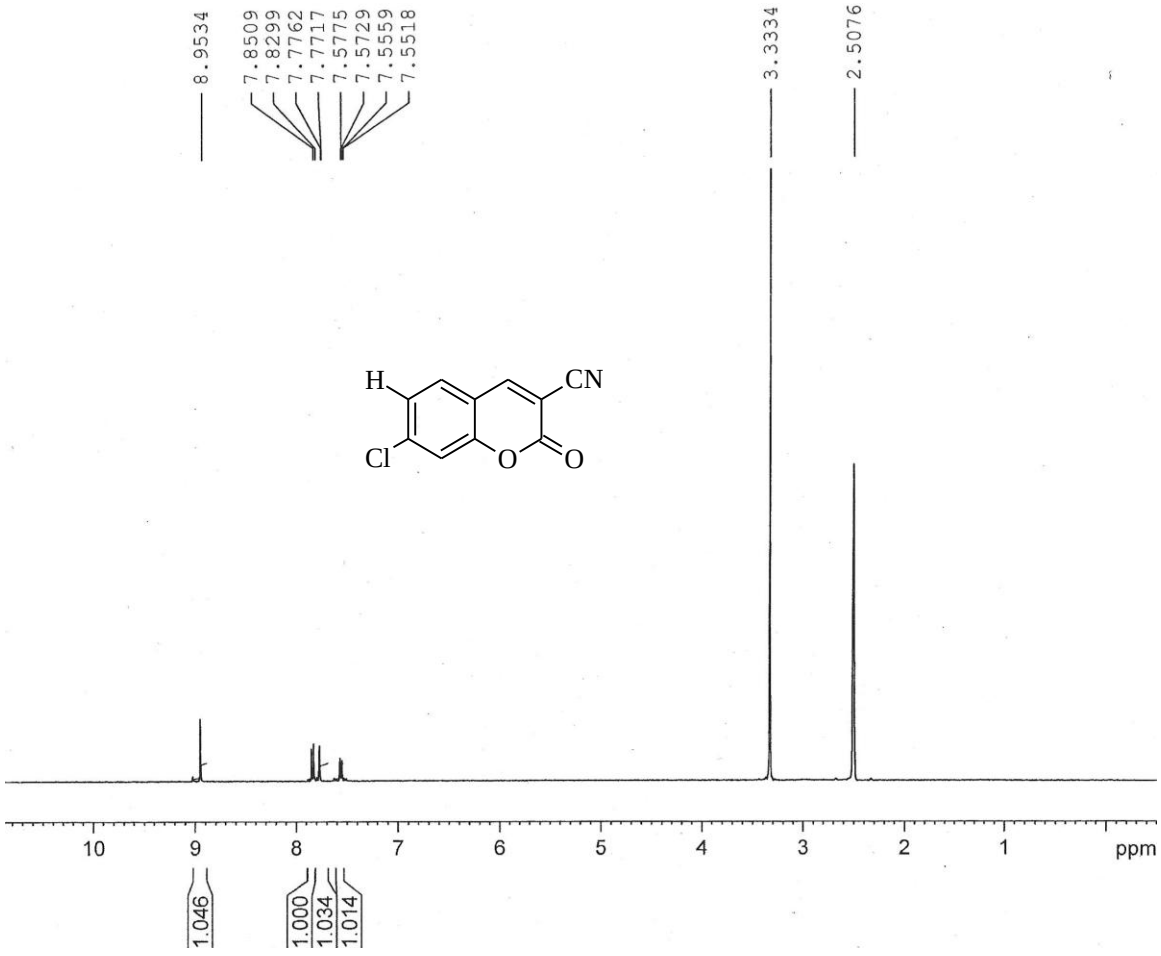




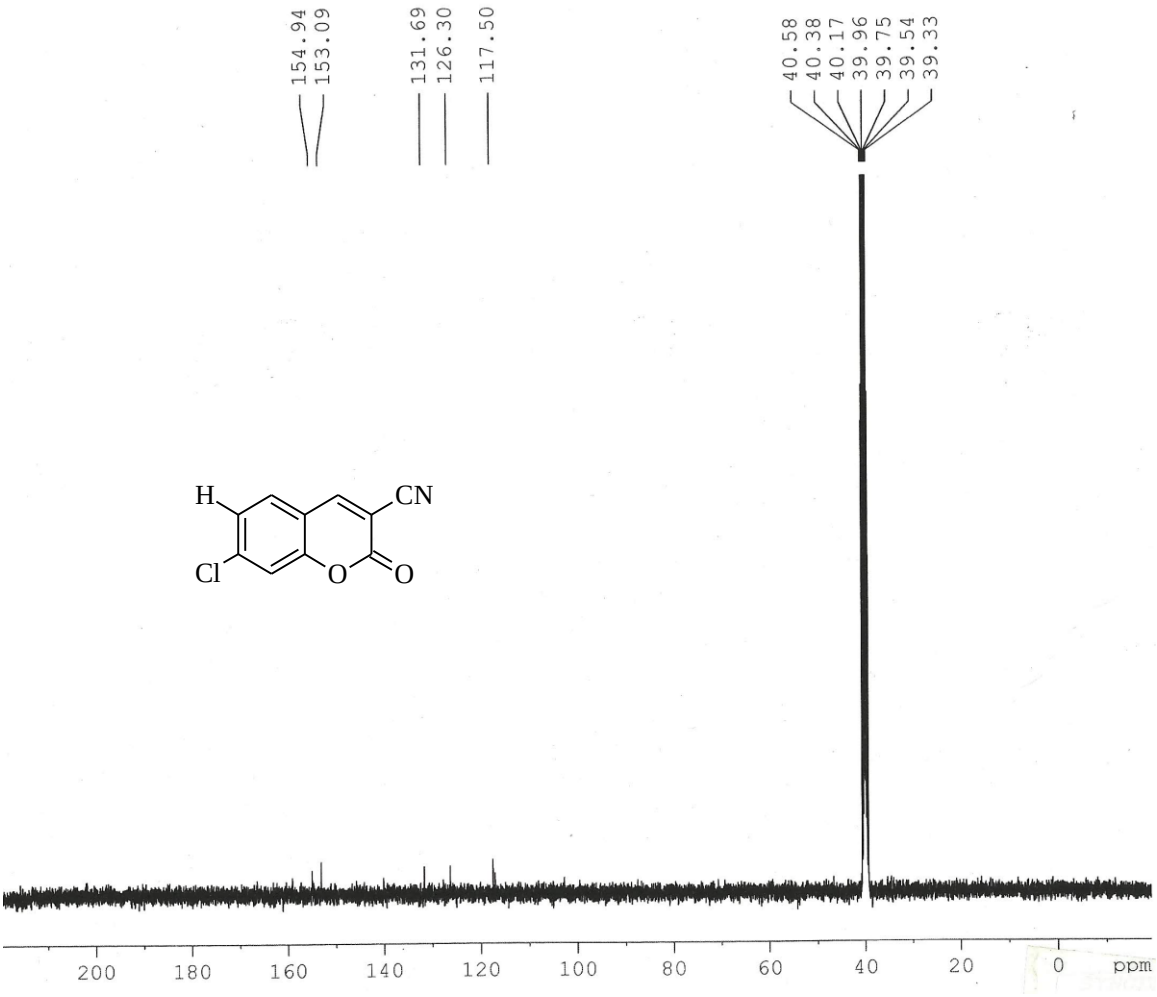
55. Mass Spectrum of 7-methoxy-2-oxo-2*H*-chromene-3-carbonitrile (5i)



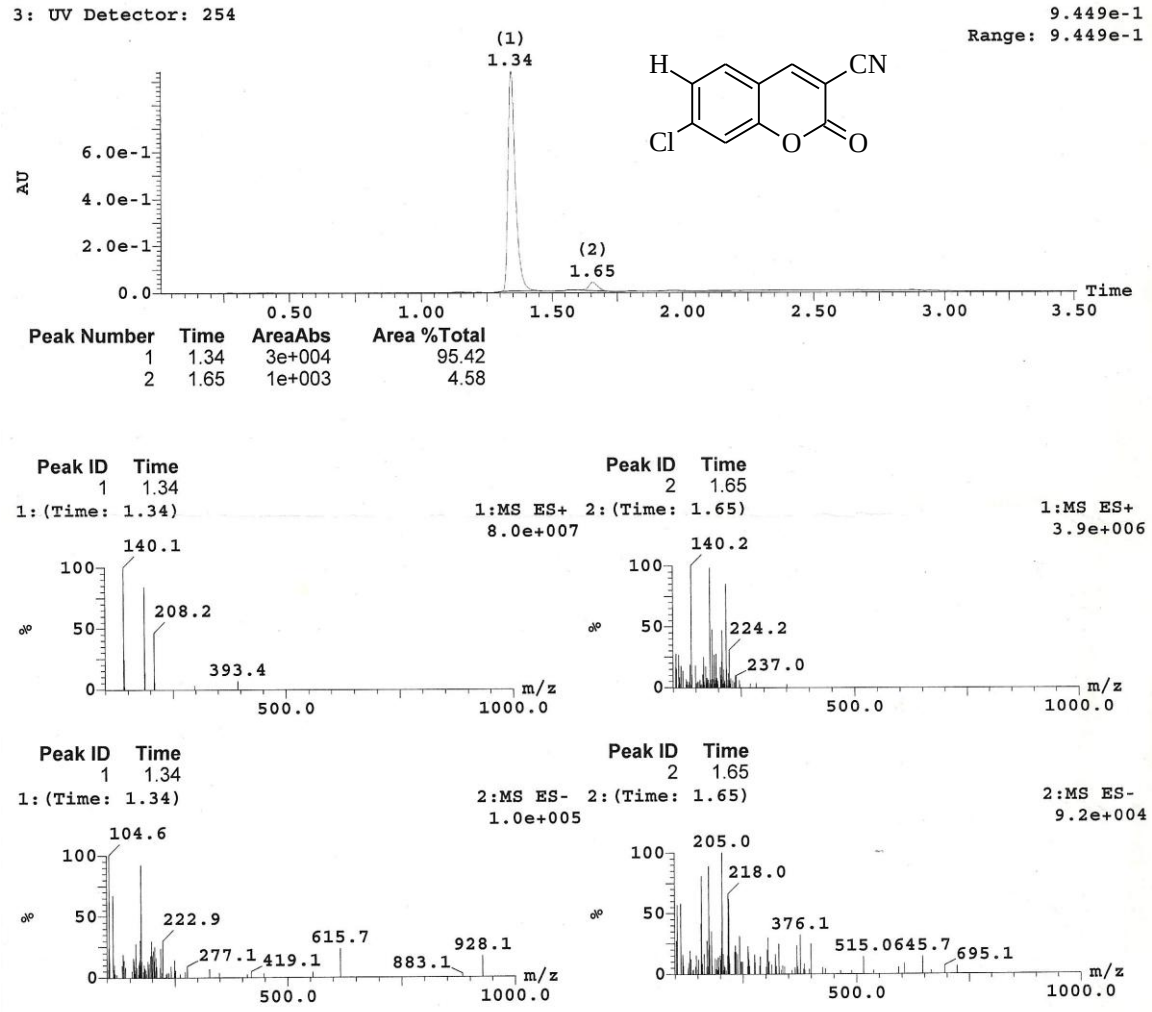
56. IR Spectrum of 7-chloro-2-oxo-2*H*-chromene-3-carbonitrile (5j)



57. ^{1}H-NMR Spectrum of 7-chloro-2-oxo-2*H*-chromene-3-carbonitrile (5j)



58. ^{13}C Spectrum of 7-chloro-2-oxo-2*H*-chromene-3-carbonitrile (5j)



59. Mass Spectrum of 7-chloro-2-oxo-2*H*-chromene-3-carbonitrile (5j)