Supporting Information

Development of hydrogelator based Gel Entrapped Base Catalysts (GEBC) as heterogeneous basic catalysts for the synthesis of 3-acetylcoumarins

Nilesh N. Korgavkar and Shriniwas D. Samant*

Department of Chemistry, Institute of Chemical Technology, N.M. Parekh Road, Matunga, Mumbai 400 019, India

Tel No.- *022-33612606*

e-mail- **samantsd.ict@gmail.com**

Table S1
Gelation study with divalent cations

Sr. No.	Salt of divalent cation	M. W.	Solution prepared (0.5 M)	Conc (%)	Remarks
1	$MgCl_2.6H_2O$	203.30	2.0 g in 20 mL	10	Do not formed gel
2	$CaCl_2$	111.00	1.1 g in 20 mL	5.5	Formed gel beads
3	$SrCl_2.6H_2O$	266.62	2.6 g in 20 mL	13	Formed gel beads
4	$BaCl_2.2H_2O$	244.28	2.4 g in 20 mL	12	Formed gel beads
5	$Mg(NO_3)_2.6H_2O$	256.41	2.5 g in 20 mL	12.5	Do not formed gel
6	$Ba(NO_3)_2.6H_2O$	261.32	2.6 g in 20 mL	13	Formed gel beads
7	$Ba(OH)_2$	315.48	3.1 g in 20 mL (do not dissolved completely)	15.5	Formed gel beads

Homogeneous colloidal solution of Na-Alg-Water-base was added dropwise in an aqueous solution of divalent cations.

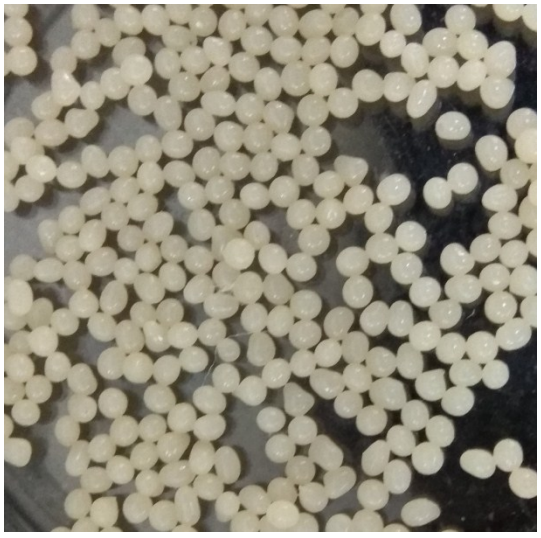


Figure S1. Gel entrapped base catalyst, Ca Alg-Base

Table S2.
Effect of divalent cations on base entrapment efficiency of alginate beads GEBCs

Entry	GEBC System	Cation (Concentration)	EE (%)
1	Ca5 Alg6-Mor13	Ca^{2+} (5%, 0.5 M)	20 (± 2)
2	Ca10 Alg6-Mor13	Ca^{2+} (10%, 1.0 M)	25 (± 1)
3	Ca15 Alg6-Mor13	Ca^{2+} (15%, 1.5 M)	18 (± 1)
4	Ca20 Alg6-Mor13	Ca^{2+} (20%, 2.0 M)	15 (± 1)
5	Ba12 Alg6-Mor13	Ba^{2+} (12%, 0.5 M)	19 (± 1)
6	Ba24 Alg6-Mor13	Ba^{2+} (24%, 1.0 M)	25 (± 1)
7	Sr13 Alg6-Mor13	Sr^{2+} (13%, 0.5 M)	19 (± 1)
8	Sr26 Alg6-Mor13	Sr^{2+} (26%, 1.0 M)	23 (± 1)
9	Ca10 Alg6-Pip9	Ca^{2+} (10%, 1.0 M)	27 (± 1)
10	Ba24 Alg6-Pip9	Ba^{2+} (24%, 1.0 M)	26 (± 1)
11	Sr26 Alg6-Pip9	Sr^{2+} (26%, 1.0 M)	26 (± 1)

In (Ca5 Alg6-Mor13) Ca5 the integer 5 showing w/w% concentration of $CaCl_2$ solution and Alg6-Mor13 corresponds to Na Alg 6% + Morpholine 13% + Water 81%

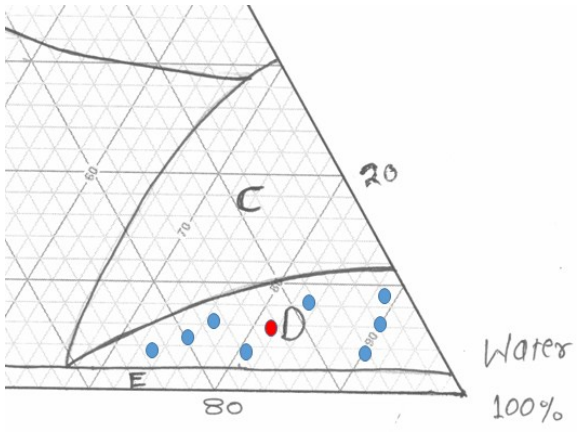


Figure S2: Part of ternary phase diagram for (Na Alg-Water-Morpholine) system showing the points selected to study the entrapment efficiency (EE)

Table S3

Entrapment efficiency for different combinations of phase D

Sr. No.	GEBC System	Composition of system	EE (%)
1	Ca10 Alg4-Mor06	Na Alg 4% + Morpholine 6% + Water 90%	10 (± 2)
2	Ca10 Alg6-Mor04	Na Alg 6% + Morpholine 4% + Water 90%	10 (± 2)
3	Ca10 Alg4-Mor14	Na Alg 4% + Morpholine 14% + Water 82%	14 (± 1)
4	Ca10 Alg6-Mor13	Na Alg 6% + Morpholine 13% + Water 81%	25 (± 1)
5	Ca10 Alg8-Mor08	Na Alg 8% + Morpholine 8% + Water 84%	20 (± 1)
6	Ca10 Alg4-Mor23	Na Alg 4% + Morpholine 23% + Water 73%	10 (± 2)
7	Ca10 Alg5-Mor20	Na Alg 5% + Morpholine 20% + Water 75%	10 (± 2)
8	Ca10 Alg8-Mor15	Na Alg 8% + Morpholine 15% + Water 77%	22 (± 1)
9	Ca10 Alg4-Pip06	Na Alg 4% + Piperidine 6% + Water 92%	26 (± 1)
10	Ca10 Alg6-Pip04	Na Alg 4% + Piperidine 6% + Water 92%	25 (± 1)
11	Ca10 Alg4-Pip11	Na Alg 4% + Piperidine 6% + Water 92%	22 (± 1)
12	Ca10 Alg6-Pip09	Na Alg 4% + Piperidine 6% + Water 92%	28 (± 1)
13	Ca10 Alg4-Pip13	Na Alg 4% + Piperidine 6% + Water 92%	16 (± 2)
14	Ca10 Alg6-Pip13	Na Alg 4% + Piperidine 6% + Water 92%	18 (± 1)
15	Ca10 Alg4-Pip18	Na Alg 4% + Piperidine 6% + Water 92%	10(± 2)

In (Ca10 Alg6-Mor13) Ca10 the integer 10 showing w/w% concentration of $CaCl_2$ solution and Alg6-Mor13 corresponds to Na Alg 6% + Morpholine 13% + Water 81%

Figure S3. Set-up used to perform the reaction in continuous flow

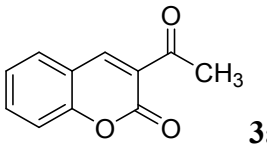
Table S4.
Reaction of salicylaldehyde and methyl/ethyl acetoacetate

Entry	2a/b Me/Et acetoacetate	Solvent	Base	Yield (%)	Remark
1	2a	Methanol	Morpholine	78	Good yield
2	2a	Methanol	Piperidine	82	Good yield
3	2a	Methanol	TEA	26	Poor yield
4	2b	Ethanol	Morpholine	80	Good yield
5	2b	Ethanol	Piperidine	82	Good yield
6	2b	Ethanol	TEA	30	Poor yield

Reaction conditions: Salicylaldehyde (4.0 mmol), methyl/ethyl acetoacetate (4.0 mmol), base (25 mol%), methanol/ethanol 20 mL, rt (27-30 °C), 1h

Structures and characterization

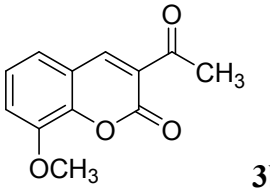
1] 3-acetyl-2*H*-chromen-2-one ($C_{11}H_8O_3$)



3a

Pale yellow solid, mp- 117-118°C, IR (KBr, cm^{-1}) 2979(C^{sp2}-H str.), 2924 (C^{sp3}-H str.), 1720(C=O str.), 1705(C=O str.), 1686, 1650(C=C str. olefinic), 1600 & 1486 (C=C str. aromatic), 1449 & 1353 (CH_3 bending), 1224, 1200, 1162, 1104 (C-O str.), 968, 932, 776, 761 (out of plane bending vibration of C-H for substituted phenyl); ^{1}H-NMR δ_H (400 MHz, $CDCl_3$) 2.75 (3H, s), 8.53 (1H, s), 7.67 (1H, dd, *J* = 4.1, 1.6 Hz), 7.39 – 7.34 (1H, m), 7.72 – 7.68 (1H, m), 7.44 – 7.39 (1H, m)

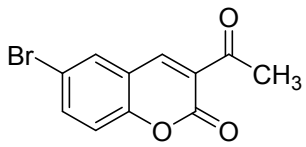
2] 3-acetyl-8-methoxy-2*H*-chromen-2-one ($C_{12}H_{10}O_4$)



3b

Pale yellow solid, mp- 165-166°C, IR (KBr, cm^{-1}), 2979(C^{sp2}-H str.), 2921 (C^{sp3}-H str.), 1722(C=O str.), 1705(C=O str.), 1688, 1649(C=C str. olefinic), 1600 & 1497 (C=C str. aromatic), 1471 & 1367 (CH_3 bending), 1277, 1230, 1205, 1194, 1025, (C-O str.), 953, 932, 890, 798, 763 (out-of-plane bending vibration of C-H for substituted phenyl); ^{1}H-NMR δ H (400 MHz, $CDCl_3$) 2.75 (3H, s), 8.49 (1H, s), 7.23 (1H, dd, *J*= 7.9, 1.7 Hz), 7.28 (1H, t, J = 7.8 Hz), 7.20 (1 H, dd, *J* =7.8, 1.7 Hz), 4.00 (3H, s)

3] 3-acetyl-6-bromo-2*H*-chromen-2-one ($C_{11}H_7BrO_3$)

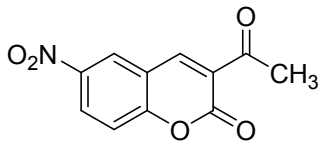


3c

White solid, mp- 217-218°C, IR (KBr, cm^{-1}), 3042, 2976(C^{sp2}-H str.), 2921 (C^{sp3}-H str.), 1722(C=O str.), 1705(C=O str.), 1689, 1649(C=C str. olefinic), 1604 & 1496 (C=C str. aromatic), 1449 & 1363 (CH_3 bending), 1225, 1203, 1068, 1027 (C-O str.), 968, 932, 833,

776, 761 (out-of-plane bending vibration of C-H for substituted phenyl), 556; ^{1}H-NMR δ_H (400 MHz, $CDCl_3$) 2.74 (3H, s), 8.42 (1H, s), 7.80 (1H, d, *J* = 2.3 Hz), 7.75 (1H, dd, *J* = 8.8, 2.3 Hz), 7.29 (1H, d, *J* = 4.4 Hz)

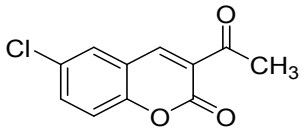
4] 3-acetyl-6-nitro-2*H*-chromen-2-one ($C_{11}H_7NO_5$)



3d

Pale yellow solid, mp-195-196°C, IR (KBr, cm^{-1}), 3101(C^{sp2}-H str.), 2927 (C^{sp3}-H str.), 1751(C=O str.), 1721(C=O str.), 1679, 1648(C=C str. olefinic), 1605 & 1496 (C=C str. aromatic), 1474 & 1357 (CH_3 bending), 1535 & 1345 (-NO2 symmetric and asymmetric str.), 1238, 1212, 1200, 1129, 1112 (C-O str.), 958, 932, 820, 766, 748 (out-of-plane bending vibration of C-H for substituted phenyl); ^{1}H-NMR δ_H (400 MHz, $CDCl_3$) 2.77 (3H, s), 8.57 (1H, s), 8.62 (1H, d, *J* = 2.4 Hz), 8.53 (1H, dd, *J* = 9.1, 2.6 Hz), 7.55 (1H, d, *J* = 9.1 Hz)

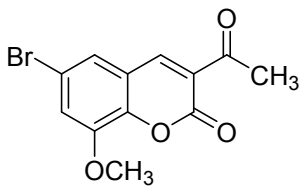
5] 3-acetyl-6-chloro-2*H*-chromen-2-one ($C_{11}H_7ClO_3$)



3e

White solid, mp- 221-222°C, IR (KBr, cm^{-1})3043, 2979(C^{sp2}-H str.), 2924 (C^{sp3}-H str.), 1722(C=O str.), 1705(C=O str.), 1689, 1649(C=C str. olefinic), 1607 & 1497 (C=C str. aromatic), 1450 & 1354 (CH_3 bending), 1227, 1203, 1080, 1027 (C-O str.), 981, 932, 835, 768, 762 (out-of-plane bending vibration of C-H for substituted phenyl), 563; ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 2.74 (3H, s), 8.43 (1H, s), 7.65 (1H, d, *J* = 2.4 Hz), 7.61 (1H, dd, *J* = 8.8, 2.4 Hz), 7.35 (1H, d, *J* = 8.8 Hz)

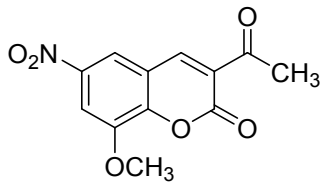
6] 3-acetyl-6-bromo-8-methoxy-2*H*-chromen-2-one ($C_{12}H_9BrO_4$)



3f

White solid, mp- 204-205°C, IR (KBr, cm^{-1}), 3049, 2976(C^{sp2}-H str.), 2936 (C^{sp3}-H str.), 1721(C=O str.), 1705(C=O str.), 1675, 1649(C=C str. olefinic), 1603 & 1500 (C=C str. aromatic), 1459 & 1355 (CH_3 bending), 1237, 1203, 1185, 1142, 1037 (C-O str.), 993, 933, 841, 835, 768, 730 (out-of-plane bending vibration of C-H for substituted phenyl), 554 (C-Br str.); ^{1}H-NMR δ_H (400 MHz, $CDCl_3$) 2.74 (3H, s), 8.38 (1H, s), 7.37 (1 H, d, J = 2.0 Hz), 7.27 (1H, d, J = 2.0 Hz), 4.00 (3H, s)

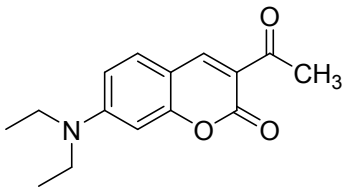
7] 3-acetyl-6-bromo-8-methoxy-2*H*-chromen-2-one ($C_{12}H_9NO_6$)



3g

white solid, mp- 215-216°C, IR (KBr, cm^{-1}), 2976(C^{sp2}-H str.), 2924 (C^{sp3}-H str.), 1751, 1720(C=O str.), 1705(C=O str.), 1663, 1649(C=C str. olefinic), 1605 & 1467 (C=C str. aromatic), 1449 & 1322 (CH_3 bending), 1567, 1335 (-NO_2 symmetric and asymmetric str.), 1235, 1212, 1100, 1078 (C-O str.), 833, 768, 748, 692 (out-of-plane bending vibration of C-H for substituted phenyl); ^{1}H-NMR, δ_H (400 MHz, $CDCl_3$) 2.76 (3H, s), 8.53 (1H, s), 8.20 (1H, d, J = 2.4 Hz), 8.02 (1H, d, J = 2.4 Hz), 4.12 (3H, s)

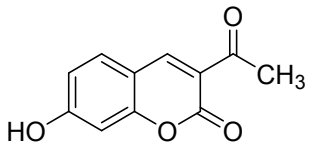
9] 3-acetyl-7-(N,N-diethylamino)-2*H*-chromen-2-one ($C_{15}H_{17}NO_3$)



3h

Yellow solid, mp- 148-149°C, IR (KBr, cm^{-1}), 3119, 2965(C^{sp2}-H str.), 2930 (C^{sp3}-H str.), 1722(C=O str.), 1714(C=O str.), 1661(C=C str. olefinic), 1612 & 1505 (C=C str. aromatic), 1476 & 1360 (CH_3 bending), 1214, 1187, 1135, 1094, 1075, 966, 950 (C-O str.), 816, 803, 758, 702 (out-of-plane bending vibration for substituted phenyl); ^{1}H-NMR δ_H (400 MHz, $CDCl_3$) 2.70 (3 H, s), 8.45 (1H, s), 7.42 (1H, d, J = 9.0 Hz), 6.62 (1H, dd, J = 2.5 Hz), 6.48 (1H, d), 3.48 (4H, q, J = 7.1 Hz), 1.26 (6H, t, J = 7.1 Hz).

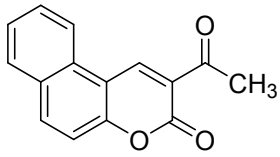
9] 3-acetyl-7-hydroxy-2*H*-chromen-2-one ($C_{11}H_8O_4$)



3i

Buff coloured solid- mp- 240-241°C, IR (KBr, cm^{-1}), 3214 (-OH str), 3067, 3046(C^{sp2}-H str), 2921 (C^{sp3}-H str.), 1723(C=O str.), 1705(C=O str.), 1680, 1648 (C=C str. olefinic), 1606 & 1505 (C=C str. aromatic), 1451 & 1357 (CH_3 bending), 1215, 1165, 1135, 979, 932, 848 (C-O str.), 824, 768, 733, 692, 613 (out-of-plane bending vibration of C-H for substituted phenyl); ^{1}H-NMR δ_H (400 MHz, DMSO) 2.55 (3H, s), 8.60 (1H, s), 7.79 (1H, d, *J* = 8.6 Hz), 6.86 (1H, dd, *J* = 8.6, 2.2 Hz), 6.76 (1H, d, *J* = 2.2 Hz)

10]2-acetyl-3H-benzo[f]chromen-3-one ($C_{15}H_{10}O_3$)

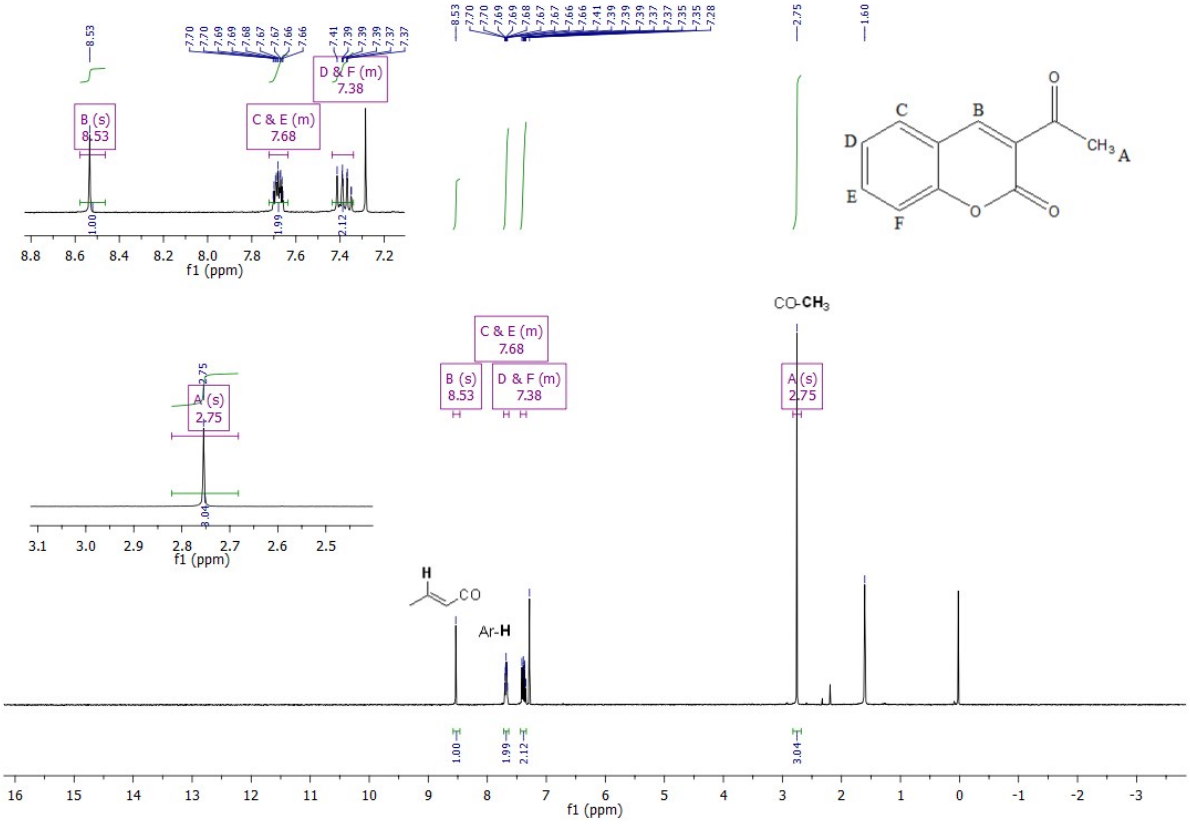


3j

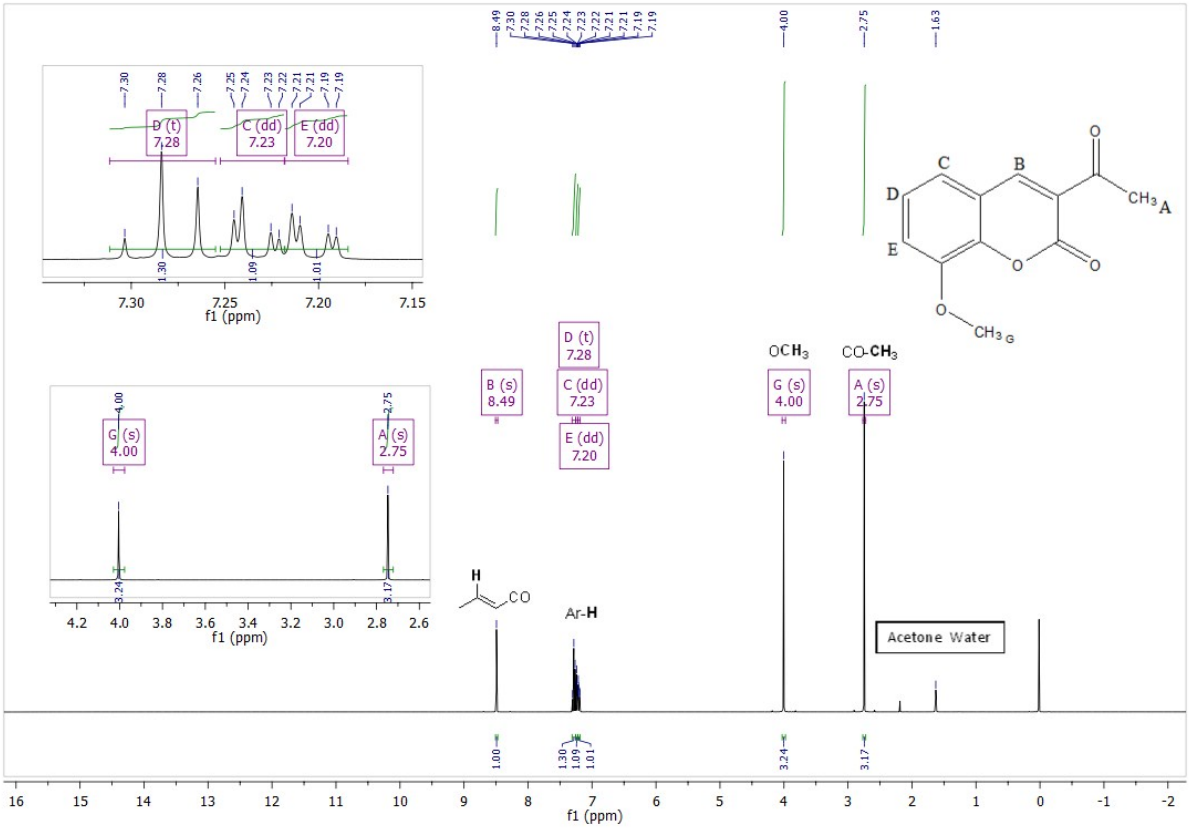
Yellow solid, mp- 181-182°C , IR (KBr, cm^{-1}) , 3066, 2976(C^{sp2}-H str.), 2930 (C^{sp3}-H str.), 1723(C=O str.), 1705(C=O str.), 1674, 1650 (C=C str. olefinic), 1596 & 1500 (C=C str. aromatic), 1476 & 1360 (CH_3 bending), 1214, 1187, 1135, 1094, 1075, 966, 950 (C-O str.), 816, 803, 758, 702 (out-of-plane bending vibration of C-H for substituted phenyl); ^{1}H-NMR δ_H (400 MHz, $CDCl_3$) 2.82 (3H, s), 9.37 (1H, s), 7.52 (1H, d, *J* = 9.0 Hz), 7.96 (1H, d, *J* = 8.1 Hz), 8.14 (1H, d, *J* = 9.0 Hz), 7.79 (1H, ddd, *J* = 8.4, 7.0, 1.3 Hz), 7.65 (1H, ddd, *J* = 8.1, 7.0, 1.1 Hz), 8.42 (1H, d, *J* = 8.3 Hz)

^{1}H NMR Spectra-

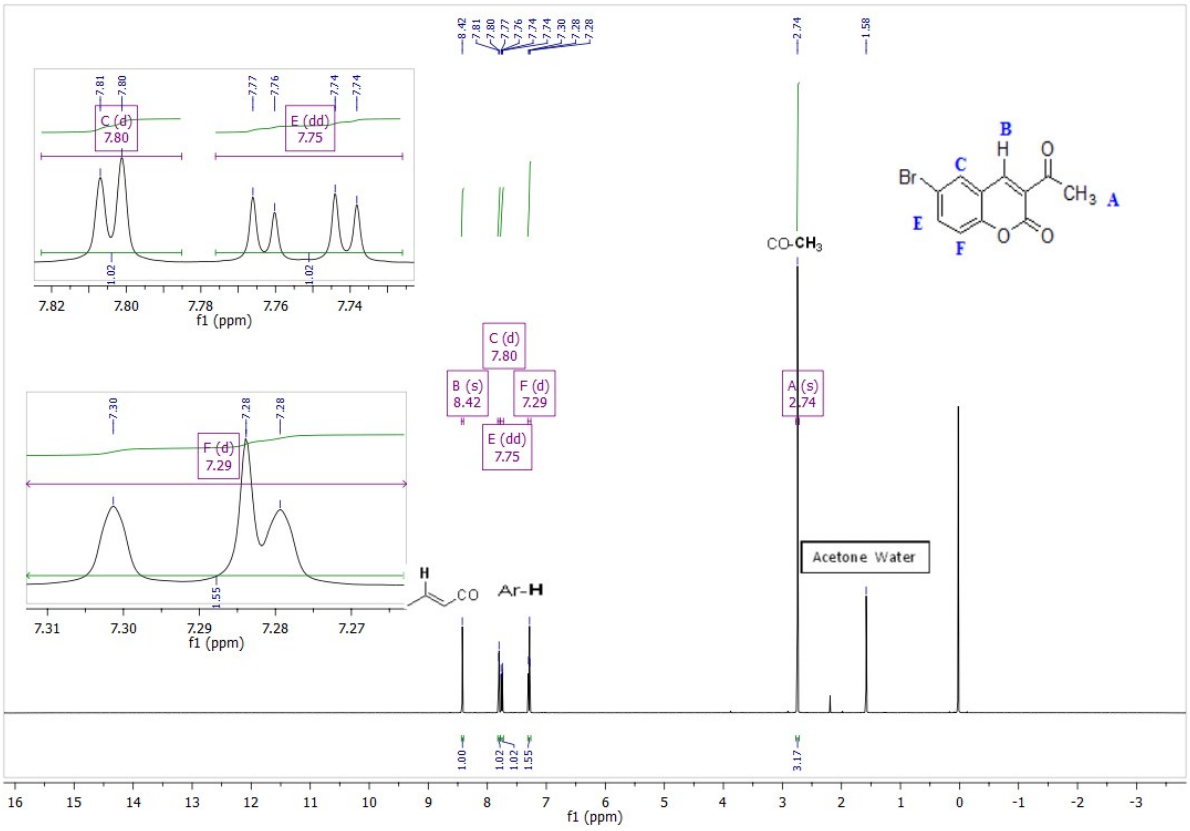
1] 3-acetyl-2*H*-chromen-2-one ($C_{11}H_8O_3$) – $CDCl_3$, 400 MHz



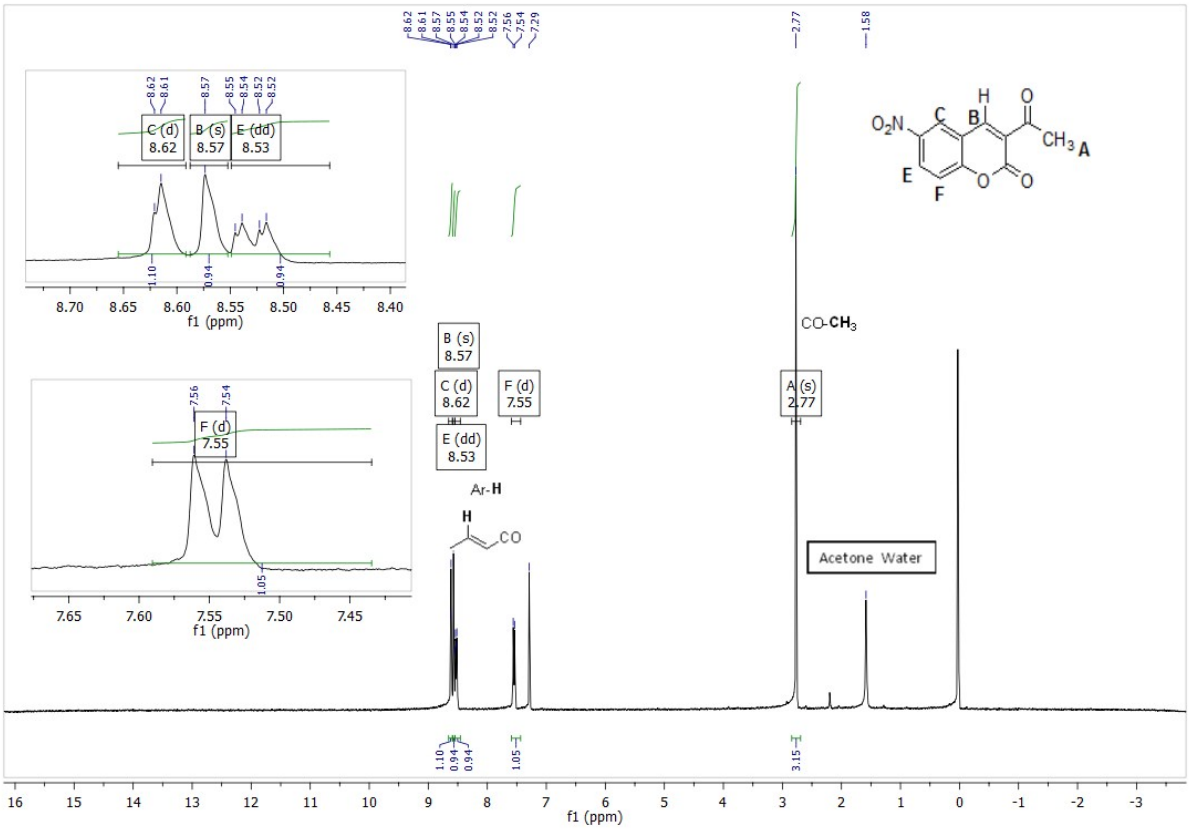
2] 3-acetyl-8methoxy-2*H*-chromen-2-one ($C_{12}H_{10}O_4$)- $CDCl_3$, 400 MHz



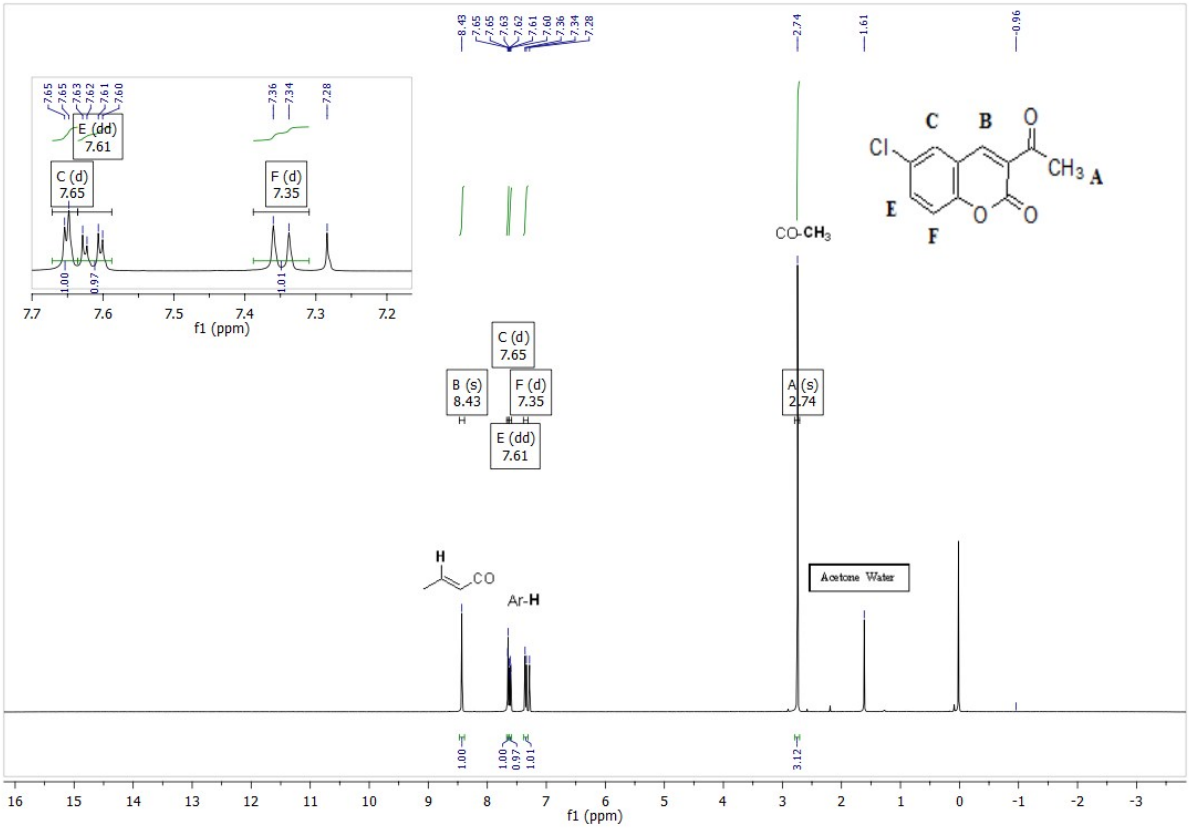
3] 3-acetyl-6-bromo-2*H*-chromen-2-one ($C_{11}H_7BrO_3$)- $CDCl_3$, 400 MHz



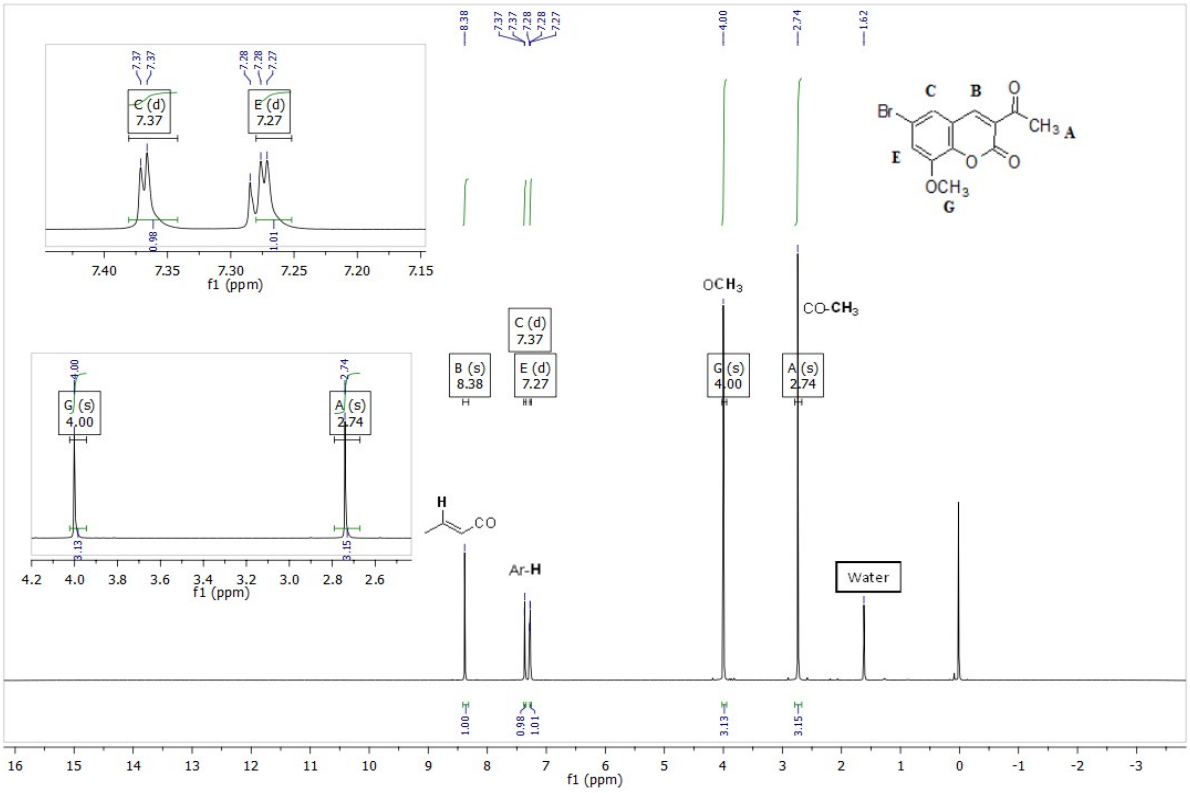
4] 3-acetyl-6-nitro-2*H*-chromen-2-one ($C_{11}H_7NO_5$)- $CDCl_3$, 400 MHz



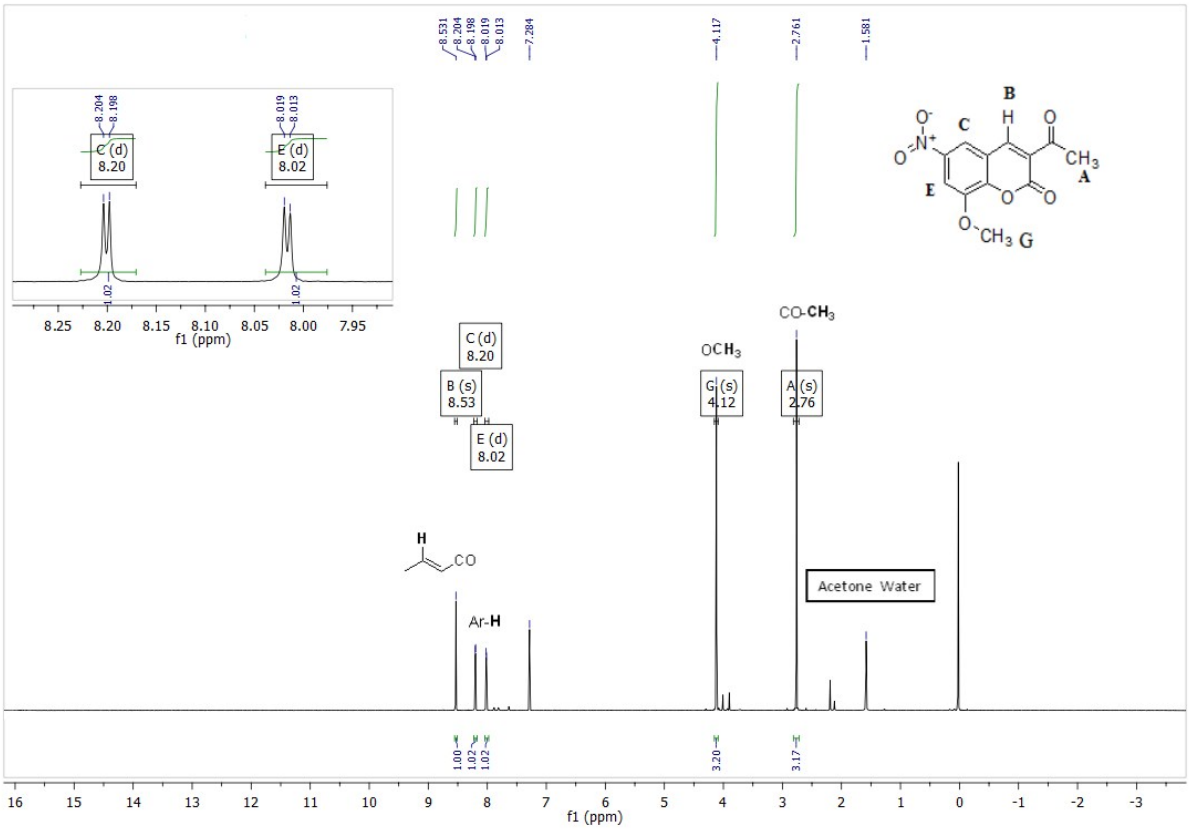
5] 3-acetyl-6-chloro-2*H*-chromen-2-one ($C_{11}H_7ClO_3$)- $CDCl_3$, 400 MHz



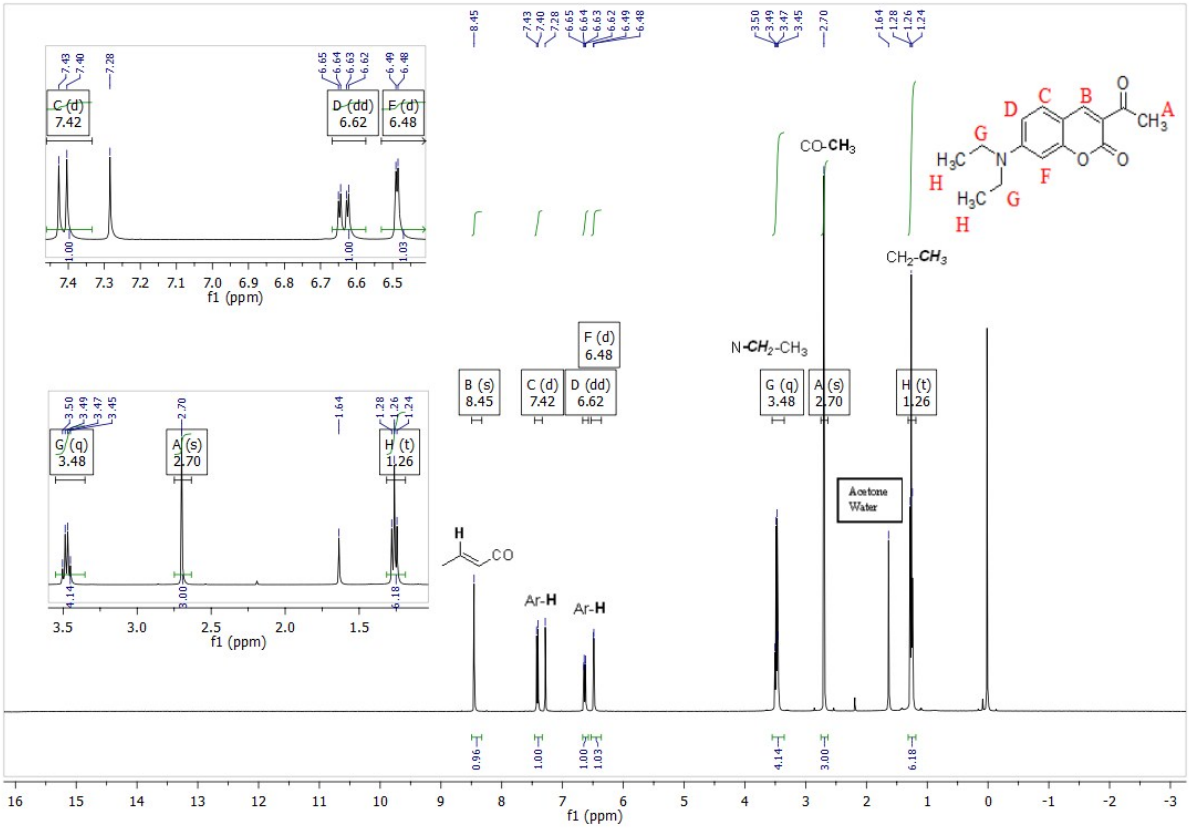
6] 3-acetyl-6-bromo-8-methoxy-2*H*-chromen-2-one ($C_{12}H_9BrO_4$)- $CDCl_3$, 400 MHz



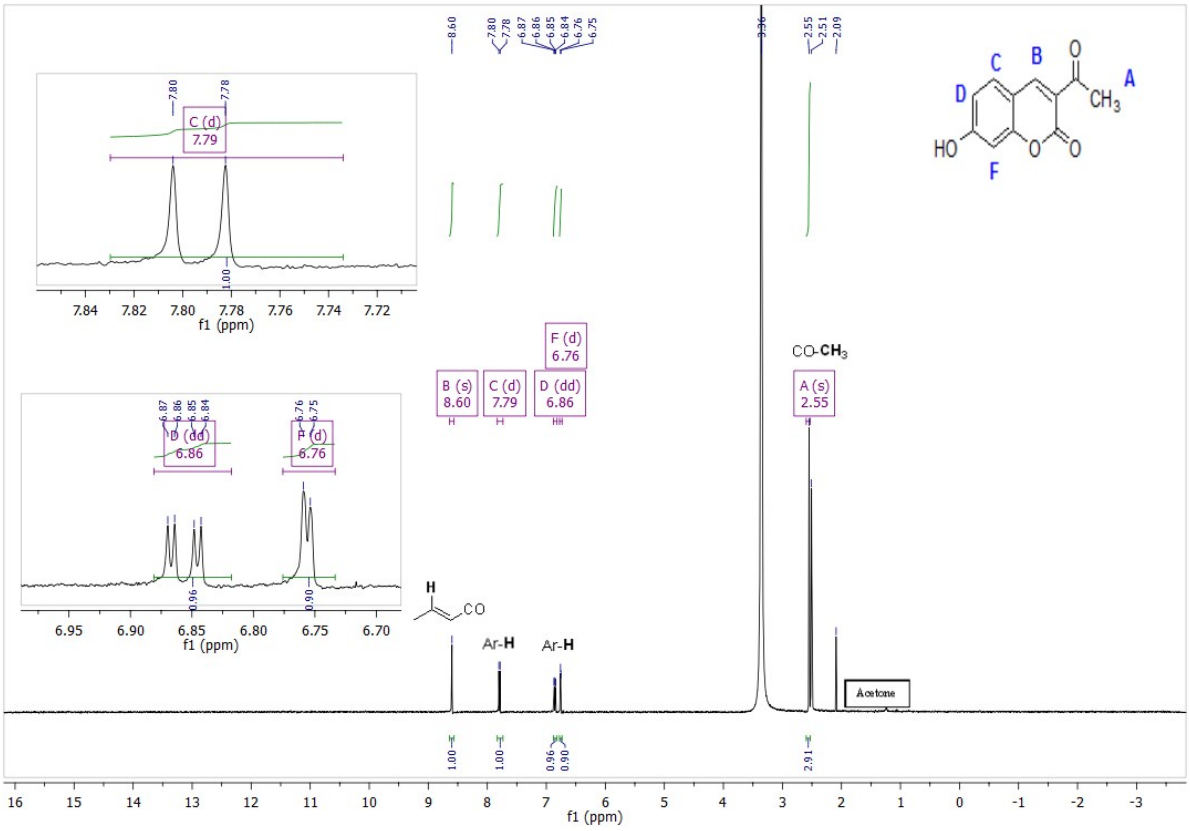
7] 3-acetyl-6-nitro-8-methoxy-2*H*-chromen-2-one ($C_{12}H_9NO_6$)- $CDCl_3$, 400 MHz



8] 3-acetyl-7-(N,N-diethylamino)-2*H*-chromen-2-one ($C_{15}H_{17}NO_3$)- $CDCl_3$, 400 MHz



9] 3-acetyl-7-hydroxy-2*H*-chromen-2-one ($C_{11}H_8O_4$) – DMSO-d6, 400 MHz



10] 2-acetyl-3H-benzo[f]chromen-3-one ($C_{15}H_{10}O_3$)- $CDCl_3$, 400 MHz