Supporting Information

Meglumine sulfate catalyzed solvent free one-pot synthesis of coumarins under microwave and thermal conditions

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General procedure for the synthesis of coumarines

Phenol derivative (2.5 mmol), β -diketne (2.5 mmol) and catalytic amount of meglumine sulfate (0.04 g) were mixed and heated at 100°C in thermal conditions. In microwave conditions, the reaction mixture subjected to microwave irradiation at power of 600W and 60-70°C for 6 minutes. The progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was cooled to room temperature and 10 ml of EtOH was added. Then, obtained mixture poured into crushed ice and stirred for 10 min. The crude product was collected by filtration, washed with ice cold distilled water and recrystallized from hot ethanol to afford pure corresponding pure product.

The characterization data for synthesized coumarons are given below:

7-hydroxy-4-methyl-chromen-2-one (3a). Yellow powder: m.p 185-186°C; IR (KBr) $\nu_{\max}$: 3498, 3113, 1605, 1669, 1450, 1390, 1213 cm^{-1} ; ^1H NMR (Acetone- d_6 , 400 MHz): δ 9.62 (s, 1H, OH), 7.52 (d, J = 8.4 Hz, 1H, H-5), 6.83 (d, J = 8.4 Hz, 1H, H-6), 6.38 (s, 1H, H-8), 6.25 (s, 1H, H-3), 2.56 (s, 3H, CH_3 -C-4) ppm; ^{13}C NMR (100 MHz, Acetone- d_6): δ 161.18 (C-2), 160.39 (C-7), 155.39 (C-4), 153.15 (C-9), 126.36 (C-5), 112.70 (C-10), 112.61 (C-6), 110.75 (C-3), 102.39

(C-8), 17.67 (CH₃) ppm; Anal. Found: C, 67.97; H, 4.49; O, 27.25%. Calcd for C₁₀H₈O₃: C, 68.18; H, 4.55; O, 27.27%.

7,8-Dihydroxy-4-methyl-chromen-2-one (3b). Orange powder: m.p 243-245°C; IR (KBr) $\nu_{\max}$: 3413, 3233, 1690, 1584, 1485, 11371, 1057 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 9.96 (s, 1H, OH), 9.10 (s, 1H, OH), 7.06 (d, J=8.4 Hz, 1H, H-5), 6.79 (d, J=8.4 Hz, 1H, H-6), 6.12 (s, 1H, H-3), 3.11 (s, 3H, CH₃-C-4) ppm; Anal. Found: C, 62.41; H, 4.15; O, 33.31%. Calcd for C₁₀H₈O₄: C, 62.46; H, 4.16; O, 33.33%.

4-methyl-benzo[h]chromen-2-one (3c). Yellow powder: m.p 153-155°C; IR (KBr) $\nu_{\max}$: 3057, 2917, 1910, 1714, 1373, 1471, 1080 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 7.59-8.57 (m, 6H, ArH), 6.38 (s, 1H, H-3), 2.53 (s, 3H, CH₃-C-4) ppm; Anal. Found: C, 79.92; H, 4.75; O, 15.21%. Calcd for C₁₄H₁₀O₂: C, 80.00; H, 4.76; O, 15.23%.

5,7-Dihydroxy-4-methyl-chromen-2-one (3d). Orange powder: m.p 282-285°C; IR (KBr) $\nu_{\max}$: 3435, 3137, 2687, 1668, 1551, 1471, 1390, 1299, 1158 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 10.53 (s, 1H, OH), 10.31 (s, 1H, OH), 6.23 (s, 1H, H-3), 6.14 (s, 1H, H-8), 5.83 (s, 1H, H-6), 3.29 (s, 3H, CH₃-C-4) ppm; Anal. Found: C, 62.43; H, 4.13; O, 33.32%. Calcd for C₁₀H₈O₄: C, 62.5; H, 4.16; O, 33.33%.

5-hydroxy-4,7-dimethyl-chromen-2-one (3e). Yellow powder: m.p 250-253°C; IR (KBr) $\nu_{\max}$: 3272, 2979, 2922, 1822, 1681, 1603, 1385, 1281, 1093 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 10.51 (s, 1H, OH), 6.58 (s, 1H, H-8), 6.53 (s, 1H, H-6), 6.01 (s, 1H, H-3), 2.49 (s, 3H, CH₃), 2.23

(s, 3H) ppm; Anal. Found: C, 64.46; H, 5.24; O, 25.25%. Calcd for $C_{11}H_{10}O_3$: C, 64.47; H, 5.26; O, 25.26%.

7-hydroxy-4-phenyl-chromen-2-one (3f): Bright pink powder: m.p 257-259°C; IR (KBr) $\nu_{\max}$: 3104, 2802, 2599, 1696, 1610, 1444, 1375, 1238 cm^{-1} ; ^1H NMR (DMSO- d_6 , 400 MHz): δ 10.42 (s, 1H, OH), 7.46-7.49 (m, 5H, Ph), 7.19 (d, J = 8.4 Hz, 1H, H-5), 6.76 (s, 2H, H-6, H-8), 6.09 (s, 1H, H-3) ppm; Anal. Found: C, 70.85; H, 3.92; O, 25.18%. Calcd for $C_{15}H_{10}O_4$: C, 70.87; H, 3.94; O, 25.19%.

7,8-Dihydroxy-4-phenyl-chromen-2-one (3g). Bright yellow powder: m.p 194-197°C; IR (KBr) $\nu_{\max}$: 3402, 1890, 1696, 1606, 1450, 1356, 1210, 1071 cm^{-1} ; ^1H NMR (DMSO- d_6 , 400 MHz): δ 10.24 (s, 1H, OH), 9.48 (s, 1H, OH), 7.5 (m, 5H, ArH), 6.7 (d, J =2.8 Hz, H-5, H-6), 6.12 (s, 1H, ArH) ppm; ^{13}C NMR (DMSO- d_6 , 100 MHz): δ 160.57 (C=O), 156.42 (C-4), 150.09 (C-9), 144.35 (C-7), 135.91 (C-8), 133.09-128.88 (6C of ph), 117.77 (C-10), 112.79 (C-6), 111.96 (C-5) ppm; Anal. Found: C, 70.85; H, 3.93; O, 25.17%. Calcd for $C_{15}H_{10}O_4$: C, 70.87; H, 3.94; O, 25.19%.

5,7-Dihydroxy-4-phenyl-chromen-2-one (3h). Bright orange powder: m.p 245-247°C; IR (KBr) $\nu_{\max}$: 3217, 1665, 1609, 1460, 1371, 1295, 1146, 1073; ^1H NMR (DMSO- d_6 , 400 MHz): δ 10.42 (s, 1H, OH), 10.13 (s, 1H, OH), 7.33 (s, 5H, ArH), 6.24 (s, 1H, H-3), 6.13 (s, 1H, H-8), 5.7 (s, 1H, H-6) ppm; ^{13}C NMR (DMSO- d_6 , 100 MHz): δ 162.18 (C=O), 160.40 (C-7), 157.57 (C-4), 157.21 (C-5), 156.3 (C-4), 140.02-127.73 (6C of ph), 110.62 (C-10), 101.03 (C-3), 99.58 (C-8),

95.10 (C-6) ppm; Anal. Found: C, 70.86; H, 3.92; O, 25.20%. Calcd for C₁₅H₁₀O₄: C, 70.87; H, 3.94; O, 25.19%.

7-amino-4-methyl-chromen-2-one (3i). Bright yellow powder: m.p 222-223 °C; IR (KBr) $\nu_{\max}$: 3356, 2989, 1696, 1651, 1486, 1213, 1092 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 7.34 (d, J=8.7 Hz, 1H, H-5), 6.74 (d, J=8.7 Hz, 1H, H-6), 6.39 (s, 1H, H-8), 5.84 (s, 1H, H-3), 3.92 (s, 2H, NH₂), 2.32 (s, 3H, CH₃-C-4) ppm; Anal. Found: C, 68.55; H, 5.13; O, 18.30%. Calcd for C₁₀H₉O₂: C, 68.57; H, 5.14; O, 18.29%.

7-methoxy-4-methyl-chromen-2-one (3j). White powder m.p 160-161 °C; IR (KBr) $\nu_{\max}$: 3355, 2983, 1698, 1649, 1482, 1207, 1113 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 7.52 (d, J=8.1, 1H, H-5), 6.86 (d, J=8.1, 1H, H-6), 6.38 (s, 1H, H-8), 6.25 (s, 1H, H-3), 3.68 (s, 3H, OCH₃), 2.56 (s, 3H, CH₃-C-4) ppm; Anal. Found: C, 69.47; H, 5.24; O, 25.25%. Calcd for C₁₁H₁₀O₃: C, 69.47; H, 5.26; O, 25.26%.

4-methyl-chromen-2-one (3l). Bright pink powder :m.p 77-79 °C; IR (KBr) $\nu_{\max}$: 3342, 2983, 1690, 1490, 1210, 1027 cm⁻¹; ¹H NMR (CDCl₃, 400MHz): δ 7.63 (d, J=6.0 Hz, 1H, H-5), 7.18-7.48 (m, 3H, H-6, H-8), 6.36 (s, 1H, H-3), 2.38 (s, 3H, CH₃-C-4) ppm; Anal. Found: C, 74.95; H, 5.01; O, 20.05%. Calcd for C₁₀H₈O₂: C, 75.00; H, 5.00; O, 20.00%.

6-hydroxy-4-methyl-chromen-2-one (3m): Yellow powder m.p 180-182 °C; IR (KBr) $\nu_{\max}$: 3377, 2981, 1682, 1617, 1493, 1201, 1099 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 8.92 (s, 1H, OH), 7.25 (s, 1H, H-5), 6.86 (d, J = 8.4 Hz, 1H, H-8), 6.58 (d, J = 8.4 Hz, 1H, H-7), 6.32 (s, 1H,

H-3), 2.38 (s, 3H, CH₃-C-4) ppm; Anal. Found: C, 68.21; H, 4.58; O, 27.26%. Calcd for C₁₀H₈O₃: C, 68.18; H, 4.55; O, 27.27%.

¹H NMR of 3a

^{13}C NMR of 3a

¹H NMR of 3b

¹H NMR of 3C

^1H NMR of 3d

¹H NMR of 3e

¹H NMR of 3f

¹H NMR of 3g

^{13}C NMR of 3g

Expand ^{13}C NMR of 3g

¹H NMR of 3h

¹³CNMR of 3h

^1H NMR of 3i

¹H NMR of 3j

^1H NMR of 31

^1H NMR of 3m