Supplementary Information

Applications of oxidative and reductive methodologies on coumarinyl ketones

Ranjit Kumar Shit*[a] & Nitai Chand Sinha[b]

[a] Department of Chemistry, Vidyasagar College, Kolkata 700 006, West Bengal, India

[b] Department of Chemistry, Jadavpur University, Kolkata 700 032, West Bengal, India

E-mail: rshit123@gmail.com, sinha.nitai1234@gmail.com

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Table S2

^{1}H NMR

1a : 2.41 (3H, s, 4-CH_3), 3.89 (3H, s, 7-OCH_3), 6.16 (1H, s, 3-H), 6.93 (1H, d, J = 8.7, 6-H),

7.63 (1H, d, J = 8.7, 5-H), 9.49 (8-O-COCHO)

1c : 1.68 (3H,d, J= 6.6Hz, 8-CH(OH)CH_2) , 2.43 (3H , broad s , 4-CH_3), 3.97 (3H, s, J=8.8Hz ,3-H), 6.80 (1H, s , CH_2OH)
6.85 (1H, d, J=9Hz, 3-H) , 7.35 (1H, s , J =9Hz , 5-H) , 7.63 (1H, d, J=8.8Hz ,4-H)

1e : 1.68 (3H , d , J=7.0Hz , 8-CH(OCOCH_3)CH_3 , 2.03(3H , s , 8-CH(OCOCH_3)CH_3) ,

2.39(3H , d , J=0.9Hz , 4-CH_3) , 3.97(3H , s , 7-OCH_3) , 6.15(1H , broad s , 3-H), 6.49(1H, q,

J=7.0 Hz , 8-CH(OCOCH_3)CH_3) , 6.86 (1H , d , J=9.0Hz , 6-H), 7.52(1H, d , J=9.0Hz,5-H)

2a : 1.62 (2H,s, COCH_2) , 3.87 (3H , s- , OCH_3)

6.24 (1H, d, J=8.8Hz ,3-H), 6.80 (1H, s- , CH_2OH)
6.85 (1H, d, J=9Hz, 3-H) , 7.35 (1H, s , J =9Hz , 5-H) , 7.63 (1H, d, J=8.8Hz ,4-H)
2c : 1.67 (3H , d , J=6.6Hz , 8-CH(OH)CH_3) , 3.94 (3H , s , 7-OCH_3) , 5.94(1H, dq, J=6.6 & 15Hz, 8-CH(OH)CH_3) , 6.16 (1H , d , J=9.4Hz , 3-H), 6.9091H , d , J=9.2 Hz, 6-H) , 7.45 (1H , d , J=9.2Hz, 5-H), 7.57(1H , d , J=9.4Hz , 4-H) , 9.69(1H , broad d , J=15Hz , 8-CH(OH)CH_3)
2e : 2.02 (3H ,s-, OCOCH_3), 3.08 (2H , s, CH_2 of epoxide) , 3.85 (3H, s-, OCH_3) , 6.27 (1H , d , J=8.8Hz , 3-H) , 6.83 (1H , d , J=9 Hz , 6-H) , 7.33 (1H , d , J=9Hz , 5-H) , 7.68 (1H , d , J=8.8 Hz , 4-H)
3a : 2.40 (3H, sharp s, 4-CH3), 2.55 (3H, sharp s, 8-COCOCH3), 3.90 (3H, sharp s, 7-O-CH3), 6.15 (1H, s, 3-H), 6.90 (1H, d, J = 9.0, 6-H), 7.67 (1H, d, J = 9.0, 5-H)
3c : 1.12 (3H, t , J=7.2Hz, 8- CH(OH)CH_2CH_3) , 1.81 (2H , dq , J=7.4 Hz & 7.2Hz , 8-CH(OH)CH_2CH_3) , 2.42(3H , s , 4-CH_3) , 3.91 (3H , s , 7-OCH_3) , 3.95 (1H, broad s, 8-CH(OH)CH_2CH_3), 4.89 (1H , broad t , J=7.0 Hz, 8- CH(OH)CH_2CH_3) , 6.15(1H , broad s , 3-H), 6.86 (1H , d , J=8.8 Hz,6-H), 7.38(1H , d , J=8.7Hz , 5-H)
4a : 2.57 (3H, sharp s, 8-COCOCH_3), 3.91 (3H, sharp s, 7-OCH_3), 6.15 (1H, d, J = 9.0, 3-H), 6.92 (1H, d, J = 9.2, 6-H), 7.67 (1H, d, J = 9.2, 5-H), 7.72 (1H, d, J = 9.0, 4-H)
4b : 1.62(2H, s, COCH2), 3.85(3H, s, OCH3), 6.26(1H, s, CH2OH), 6.28(1H, d, J=8Hz, 3-H), 6.85(1H, d, J=9Hz, 6-H), 7.36(1H, d, J=-9Hz, 5-H), 7.62(1H, d, J=8Hz, 4-H)

4d : 1.11 (3H ,t , J=7.8 Hz ,8-$COCH_2CH_3$), 2.86 (2H , q , J=7.8 Hz , 8- CO_2CH_2Me), 3.89 (3H, s- , OCH_3) , 7.39 and 6.12 (each 1H, d , J=13.8 Hz , 3'H , 2' –H) , 7.57 and 6.88 (each 1H ,d, J=8Hz , 5-H , 6-H) , 13.68 (1H , s, Phenolic OH)
4e : 1.98 (3H, s- , $OCOCH_3$), 1.282(2H , s , 2' – CH_2), 6.82 (1H, d, J=9Hz , 3-H) , 6.86 (1H, d , J=9Hz, 6-H), 7.33 (1H, d , J=9Hz, 5-H) , 7.56 (1H , d , J=9Hz , 4-H)
5a : 1.20 (3H, t, J = 7.2, 8-$COCOCH_2CH_3$), 2.98 (2H, q, J = 7.2, 8-$COCOCH_2CH_3$), 3.90 (1H, sharp s, 7-OCH_3), 6.15 (1H, d, J = 8.8, 3-H), 6.94 (1H, d, J = 9.2, 6-H), 7.67 (1H, d, J = 9.0, 5-H), 7.72 (1H, d, J = 8.8, 4-H)
5b : 1.22 (3H, t, J = 7.2, 8-$COCOCH_2CH_3$), 3.90 (3H, sharp s, 7-OCH_3), 6.22 (1H, s, 3-H), 6.90 (1H, d, J = 9.0, 6-H), 7.68 (1H, d, J = 9.0, 5-H), 8.80 (1H, s, 4-CHO)
5c: 0.99 (3H , t , J=7.2Hz , 8- $CH(OH)CH_2CH_2CH_3$) , 1.77 (2H , sextet, J=7.2Hz, 8- $CH(OH)CH_2CH_2CH_3$), 1.81 (2H ,q , J=7.2Hz , 8- $CH(OH)CH_2CH_2CH_3$)
6a : 1.20 (3H, t, J = 7.2, 8-$COCOCH_2CH_3$), 2.98 (2H, q, J = 7.2, 8-$COCOCH_2CH_3$), 3.90 (1H, sharp s, 7-OCH_3), 6.15 (1H, d, J = 8.8, 3-H), 6.94 (1H, d, J = 9.2, 6-H), 7.67 (1H, d, J = 9.0, 5-H), 7.72 (1H, d, J = 8.8, 4-H)
6d : 1.05 (3H, t , J=8Hz, 8- $COCH_2CH_2CH_3$) , 1.76 (2H , sextet , J=7.2 Hz , 8- $COCH_2CH_2CH_3$) , 3.31(1H , t , J=8Hz, 8- $COCH_2CH_2CH_3$) , 3.90 (3H , s- , OCH_3) , 7.83 and 6.80 (each 1H, d , J=13.8 Hz 3'-H , 2'-H) , 7.98 and 6.80 (each 1H , J=8Hz ,5-H ,6-H)
7d: 6.40 & 7.94 (each 1H , d , J=13.8HZ , 3'-H , 2'-H) , 6.94 &7.54 (each 1H, d, J=8HZ, 5-H, 6-H) , 7.44(2H , t, J=7Hz, m-H) , 7.54 (1H , J=8Hz , p-H) , 7.58(1H , d , J=8Hz , o-H) , 3.88(3H , s- , OCH_3)
7a : 3.86 (3H, sharp s, 7-OCH_3), 6.12 (1H, broad s, 3-H), 7.03 (1H, d, J = 9.0, 6-H), 7.46 (2H, t, J = 7.2, *m*-H), 7.60 (1H, t, J = 7.2, *p*-H), 7.84 (2H, broad d, J = 7.2, *O*-H), 8.70 (1H, d, J = 9.0, 5-H), 10.07 (1H, s, 4-CHO)
7c : 3.46(1H, br.d, J=2.8Hz, 8-CHOHPh), 3.85(3H, s, OCH_3), 6.37(1H, s, alcoholic OH), 6.67(1H, d, J=9.2Hz, 3-H), 6.86(1H, d, J=8Hz, 6-H), 7.28(1H, d, J=8Hz, 5-H), 7.32-7.36(5H, complex, C_6H_5), 7.57(1H, d, J=9.2Hz, 5-H)
7e : 2.16 (3H, s, 8-CH($OCOCH_3$)C_6H_5), 2.38 (3H, d, J = 1.0 HZ, 4-CH_3), 3.94 (3H, s, 7-OCH_3), 6.10 (1H, broad s, 3-H), 6.86 (1H, d, J = 9.0 HZ, 6-H), 7.25 (1H, d, J = 9.0 HZ, 5-H), 7.51 (1H, s, 8-CH($OCOCH_3$) C_6H_5), 7.56 (5H, complex, C_6H_5)
9c : 1.61 (3H, d, J = 6.6 Hz, 8-$CH(OH)CH_3$), 2.37 (3H, broad s, 4-CH_3), 5.91 (1H, q, J = 6.6 Hz, 8-$CH(OH)CH_3$), 6.05 (1H, broad s, 3-H), 6.84 (1H, d, J = 8.7 Hz, 6-H), 7.39 (1H, d, J = 8.7 Hz, 5-H), 10.03 (1H, broad s, 7-OH)
9e : 1.67 (3H, d, J = 6.9 Hz, 8-$CH(OCOCH_3)CH_3$), 1.99 (3H, s, 8-$CH(OCOCH_3)CH_3$), 2.40 (3H, broad s, 4-CH_3), 2.42 (3H, s, 7-$OCOCH_3$), 6.29 (1H, broad s, 3-H), 6.46 (1H, q, J = 6.9 Hz, 8-$CH(OCOCH_3)CH_3$), 7.0 (1H, d, J = 9.0 Hz, 6-H), 7.56 (1H, d, J = 9.0 Hz, 5-H)
11c : 1.01 (3H, t, J = 7.4 Hz, 8-$CH(OH)CH_2CH_3$),1.92 (2H, dq, J = 7.4 & 7.2 Hz, 8-$CH(OH)CH_2CH_3$), 2.36 (3H, d, J = 0.94 Hz, 4-CH_3), 4.48 (1H, d, J = 3.8 Hz, 8-$CH(OH)CH_3$), 5.69 (1H, dt, J = 7.2 & 3.8 Hz, 8-$CH(OH)CH_2CH_3$), 6.03 (1H, broad q, J = 0.9 Hz, 3-H), 6.83 (1H, d, J = 8.8 HZ, 6-H), 7.38 (1H, d, J = 8.8 Hz, 5-H), 9.80 (1H, s, 7-OH)
11e : 0.93 (3H, t, J = 7.4 Hz, 8-$CH(OCOCH_3)CH_AH_BCH_3$), 2.02 (1H, quintet, J = 7.4 Hz, H_A of 8-$CH(OCOCH_3)CH_AH_BCH_3$), 2.10 (1H, quintet, J = 7.4 Hz, H_B of 8-$CH(OCOCH_3)CH_AH_BCH_3$), 2.15 (3H, broad s, 8-$CH(OCOCH_3)CH_AH_BCH_3$), 2.31 (3H, s, 7-$OCOCH_3$), 2.42 (3H, d, J = 1.1 Hz, 4-CH_3), 6.24 (1H, t, J = 1.1 & 15 Hz, 8-

C*H*($OCOCH_3$)$CH_AH_BCH_3$), 6.27 (1H, broad s, 3-H), 7.01 (1H, d, J = 8.7 Hz, 6-H), 7.58 (1H, d, J = 8.7 Hz, 5-H)
13c : 2.40 (3H, broad s, 4-C*H*$_3$), 3.83 (1H, d, J = 2.7 Hz, 8-C*H*(OH)C_6H_5), 6.16 (1H, broad s, 3-H), 6.72 (1H, d, J = 2.8 Hz, 8-CH(O*H*)C_6H_5), 6.86 (1H, d, J = 8.7 Hz, 6-H), 7.32 (5H, complex, C_6*H*$_5$), 7.57 (1H, d, J = 8.7 Hz, 5-H), 9.67 (1H, sharp s, 7-OH)

Table S3 : ^{13}C NMR

1c: 160.79 (4^o, C-2), 159.82 (4^o, C-7), 152.54 (4^o, C-8a), 144.60 (4^o, C-4), 127.2 (3^o, C-5), 120.24 (4^o, C-8), 114.2 (4^o, C-4a), 112.12 (3^o, C-3), 107.90 (3^o, C-6), 69.29 (3^o, 8-*C*H(OH)CH_3), 56.24 (1^o, 7-O*C*H$_3$), 23.2 (1^o, 8-CH(OH)*C*H$_3$), 18.72 (1^o, 4-*C*H$_3$).
2a : 197.8 (8-CO*C*H$_2$), 64.6(C-2) , 161.8 (C-7), 155.8 (C-8a), 143.1(C-4), 129.5(C-5), 112.9(C-4a), 112.3(C-3), 100.2(C-6), 56.7(-O*C*H$_3$), 13.7(2'-C)
2c: 160.24 (4^o, C-2), 159.01(4^o, C-7), 152.23 (4^o, C-8a), 146.2 (3^o, C-4), 127.2 (3^o, C-5), 120.12 (4^o, C-8), 114.2 (4^o, C-4a), 112.8 (3^o, C-3), 108.23 (3^o, C-6), 69.2 (3^o, 8-*C*H(OH)CH_3), 56.44 (1^o, 7-O*C*H$_3$), 23.8 (1^o, 8-CH(OH)*C*H$_3$).
3a : 197.27 (4^o, 8-CO*C*OCH$_3$), 191.16 (4^o, 8-*C*OCOCH$_3$), 159.98 (4^o, C-2), 158.04 (4^o, C-7), 152.8 (4^o, C-8a), 151.8 (4^o, C-4), 127.35 (3^o, C-5), 115.2 (4^o, C-8), 114.2 (4^o, C-4a), 112.86 (3^o, C-3), 108.1 (3^o, C-6), 56.28 (1^o, 7-O*C*H$_3$), 18.72 (1^o, 4-*C*H$_3$), 7.53 (1^o, 8-COCO*C*H$_3$)
3c: 161.29 (4^o, C-2), 159.50 (4^o, C-7), 154.46 (4^o, C-8a), 152.82 (4^o, C-4a), 129.82 (3^o, C-5), 122.53 (4^o, C-8), 113.15 (3^o, C-6), 112.15 (4^o, C-4), 99.02 (3^o, C-3), 70.92 (3^o, 8-*C*H(OH)CH_2CH_3), 55.91 (1^o, 7-O*C*H$_3$), 30.42 (1^o, 8-CH(OH)*C*H$_2$CH$_3$), 18.17 (1^o, 4-*C*H$_3$), 10.25 (1^o, 8-CH(OH)CH$_2$*C*H$_3$).
4a : 197.27 (4^o, 8-CO*C*OCH$_3$), 190.16 (4^o, 8-*C*OCOCH$_3$), 160.86 (4^o, C-2), 159.23 (4^o, C-7), 152.99 (4^o, C-8a), 151.81 (3^o, C-4), 128.69 (3^o, C-5), 115.07 (4^o, C-8), 114.12 (4^o, C-4a), 112.86 (3^o, C-3), 107.43 (3^o, C-6), 56.28 (1^o, 7-O*C*H$_3$), 7.52 (1^o, 8-COCO*C*H$_3$)
4b : 192.88 & 184.6 (8-COCO), 162.8 (C-2), 156.8 (C-4), 152.0 (C-8a), 143.5 (C-4), 129.0 (C-5), 112.8 (C-4a), 112.8 (C-8), 109.6 (C-6), 100.8 (C-3), 55.4 (C-7), 29.6 (COCOCH)
5a : 200.30 (4^o, 8-*C*OCOCH$_2$CH$_3$), 197.24 (4^o, 8-CO*C*OCH$_2$CH$_3$), 160.86 (4^o, C-2), 159.23 (4^o, C-7), 152.93 (4^o, C-8a), 151.89 (4^o, C-4), 128.77 (3^o, C-5), 115.08 (4^o, C-8), 144.3 (4^o, C-4a), 112.76 (3^o, C-3), 107.62 (3^o, C-6), 56.55 (1^o, 7-O*C*H$_3$), 29.75 (2^o, 8-COCO*C*H$_2$CH$_3$), 18.63 (1^o, 4-*C*H$_3$), 8.10 (1^o, 8-COCOCH$_2$*C*H$_3$)
5c: 160.41 (4^o, C-2), 159.83 (4^o, C-7), 152.57 (4^o, C-8a), 151.84 (4^o, C-4a), 124.28 (3^o, C-5), 122.4 (4^o, C-8), 114.25 (4^o, C-4), 112.29 (3^o, C-6), 107.49 (3^o, C-3), 69.26 (3^o, 8-*C*H(OH)$CH_2CH_2CH_3$), 56.13 (1^o, 7-O*C*H$_3$), 39.79 (2^o, 8-CH(OH)*C*H$_2$CH$_2$CH$_3$), 19.37 (2^o, 8-CH(OH)CH$_2$*C*H$_2$CH$_3$),18.82 (1^o, 4-*C*H$_3$), 13.95 (1^o, 8-CH(OH)CH$_2$CH$_2$*C*H$_3$).
6a : 201.2 (4^o, 8-*C*OCOCH$_2$CH$_3$), 198.03 (4^o, 8-CO*C*OCH$_2$CH$_3$), 161.01 (4^o, C-2), 159.1 (4^o, C-7), 153.01 (4^o, C-8a), 152.1 (3^o, C-4), 128.72 (3^o, C-5), 115.02 (4^o, C-8), 114.3 (4^o, C-4a), 112.80 (3^o, C-3), 107.62 (3^o, C-6), 57.01 (1^o, 7-O*C*H$_3$), 30.02 (2^o, 8-COCO*C*H$_2$CH$_3$), 11.2 (1^o, 8-COCOCH$_2$*C*H$_3$)
7a : 191.60 (4^o, 8-*C*OC_6H_5), 160.03 (3^o, 4-*C*HO), 159,35 (4^o, C-2), 152.40 (4^o, C-7), 143.30 (4^o, Ph-C), 136.74 (4^o, C-8a), 134.03 (4^o, C-4), 129.78 (3^o, *m*-C) 128.92 (3^o, *o*-C), 126.23 (3^o, *p*-C), 123.27 (3^o, C-5), 117.35 (4^o, C-8), 114.2 (4^o, C-4a), 108.67 (3^o, C-6), 107.94 (3^o, C-3), 56.44 (1^o, 7-O*C*H$_3$)

7c : 161.24 (4°, C-2), 160.46 (4°, C-7), 152.23 (4°, C-8a), 144.2 (4°, C-4), 143.2 (4°, Ph-C), 129.69 (3°, *m*-C), 128.91 (3°, *o*-C), 126.24 (3°, *p*-C), 116.4 (3°, C-5), 114.2 (4°, C-8), 113.42 (4°, C-4a), 112.02 (3°, C-6), 108.1 (3°, C-3), 70.2 (3°, 8-*C*H(OH)Ph), 56.29 (1°, 7-O*C*H$_3$), 18.24 (1°, 4-*C*H$_3$).
8c: 160.78 (4°, C-2), 159.83 (4°, C-7), 152.4 (4°, C-8a), 144.06 (3°, C-4), 143.2 (4°, Ph-C), 129.2 (3°, *m*-C), 128.92 (3°, *o*-C), 126.53 (3°, *p*-C), 115.08 (3°, C-5), 114.12 (4°, C-8), 112.8 (4°, C-4a), 112.06 (3°, C-6), 108.9 (3°, C-3), 70.46 (3°, 8-*C*H(OH)Ph), 56.24(1°, 7-O*C*H$_3$).
9c: 160.12 (4°, C-2), 153.91 (4°, C-7), 152.04 (4°, C-8a), 150.60 (4°, C-4), 126.18 (3°, C-5), 119.37 (4°, C-8), 114.01 (4°, C-4a), 112.64 (3°, C-3), 107.43 (3°, C-6), 69.29 (3°, 8-*C*HOHCH$_3$), 23.2 (1°, 8-CH(OH)*C*H$_3$), 18.72 (1°, 4-*C*H$_3$).
9e : 160.51 (4°, 8-CH(O*C*OCH$_3$) CH$_3$), 159.68 (4°, 7- O*C*OCH$_3$), 152.70 (4°, C-2), 151.31 (4°, C-7), 124.32 (4°, C-8a), 120.39 (4°, C-4), 116.1 (4°, C-4a), 114.23 (3°, C-5), 112.21 (4°, C-8), 107.56 (3°, C-6), 106.8 (3°, C-3), 64.89 (3°, 8-*C*H(OCOCH$_3$)CH$_3$), 23.35 (1°, 8-CH(OCOCH$_3$)*C*H$_3$), 19.04 (1°, 7-OCO*C*H$_3$), 18.72 (1°, 4-*C*H$_3$), 10.30 (1°, 8-CH(OCO*C*H$_3$)CH$_3$).
11c: 161.81 (4°, C-2), 160.58(4°, C-7), 153.97 (4°, C-4), 150.83 (4°, C-8a), 124.50 (3°, C-5), 114.73 (4°, C-8), 114.56 (3°, C-6), 112.56 (4°, C-4a), 110.70 (3°, C-3), 70.88 (3°, 8-*C*H(OH)CH$_2$CH$_3$), 29.85 (2°, 8-CH(OH) *C*H$_2$CH$_3$), 18.72 (1°, 4-*C*H$_3$), 9.48 (1°, 8-CH(OH) CH$_2$*C*H$_3$) .
11e : 170.15 (4°, 7- O*C*OCH$_3$), 169.10 (4°, 8-CH(O*C*OCH$_3$)CH$_2$CH$_3$), 159.79 (4°, C-2), 152.26 (4°, C-7), 151.95 (4°, C-8a), 151.32 (4°, C-4), 124.54 (3°, C-5), 120.99 (4°, C-4a), 119.71(3°, C-6), 118.08 (4°, C-8), 114.68 (3°, C-3), 69.46 (3°, 8-*C*H(OCOCH$_3$)CH$_2$CH$_3$), 26.24 (2°, 8-CH(OCOCH$_3$)*C*H$_2$CH$_3$), 21.0 (1°, 7-OCO*C*H$_3$), 18.92 (1°, 4-*C*H$_3$) 10.29 (1°, 8-CH(OCO*C*H$_3$)CH$_2$CH$_3$), 8.69 (1o, 8-CH(OCOCH$_3$)CH$_2$*C*H$_3$).
13c: 161.23 (4°, C-2), 160.58 (4°, C-7), 152.23 (4°, C-8a), 144.6 (4°, C-4), 141.89 (4°, Ph-C), 129.78 (3°, *m*-C), 128.92 (3°, *o*-C), 126.23 (3°, *p*-C), 116.1 (3°, C-5), 114.2 (4°, C-8), 113.28 (4°, C-4a), 112.01 (3°, C-6), 107.8 (3°, C-3), 69.2 (3°, 8-*C*H(OH)Ph), 18.17 (1°, 4-*C*H$_3$).

Table S4 : Cross peaks [δ(^{1}H) vs δ(^{1}H)] observed in COSY

Compound number	Serial number	Protons attached / bound / on: chemical shift (δ) relevant protons are italicized or numbered	Protons attached / bound / on: chemical shift (δ) relevant protons are italicized or numbered
3c	1	6-CH(OH)CH$_2$C*H*$_3$ (0.98)	6-CH(OH)C*H*$_2$CH$_3$ (1.80)
	2	6-CH(OH)C*H*$_2$CH$_3$ (1.80)	6-CH(OH)CH$_2$C*H*$_3$ (1.80) and 6-C*H*(OH)CH$_2$CH$_3$ (4.90)

	3	4-C*H*$_3$ (2.42)	3-H (6.15)
	4	6-C*H*(OH)CH$_2$CH$_3$ (4.90)	6-CH(OH)CH$_2$CH$_3$ (1.80)
5c	1	8-CH(OH) CH$_2$CH$_2$C*H*$_3$ (0.99)	8-CH(OH)CH$_2$C*H*$_2$CH$_3$ (1.77)
	2	8-CH(OH)CH$_2$C*H*$_2$CH$_3$ (1.77)	8-CH(OH)CH$_2$CH$_2$C*H*$_3$ (0.99) and 8-CH(OH) C*H*$_2$CH$_2$CH$_3$ (1.81)
	3	4-C*H*$_3$ (2.40)	3-H (6.15)
	4	8-C*H*(OH)CH$_2$CH$_2$CH$_3$ (5.37)	8-CH(OH)C*H*$_2$CH$_2$CH$_3$ (1.81)
	5	6-H (6.88)	5-H (7.49)
11e	1	8-CH(OCOCH$_3$)CH$_A$H$_B$C*H*$_3$ (0.93)	8-CH(OCOCH$_3$)C*H*$_A$H$_B$CH$_3$ (2.02) and 8-CH(OCOCH$_3$)CH$_A$*H*$_B$CH$_3$ (2.10)
	2	8-CH(OCOCH$_3$)C*H*$_A$H$_B$CH$_3$ (2.02)	8-CH(OCOCH$_3$)CH$_A$H$_B$C*H*$_3$ (0.93) and 8-CH(OCOCH$_3$)CH$_A$*H*$_B$CH$_3$ (2.10) and 8-C*H*(OCOCH$_3$)CH$_A$H$_B$CH$_3$ (6.27)
	3	8-CH(OCOCH$_3$)CH$_A$*H*$_B$CH$_3$ (2.10)	8-CH(OCOCH$_3$)CH$_A$H$_B$C*H*$_3$ (0.93) and 8-CH(OCOCH$_3$)C*H*$_A$H$_B$CH$_3$ (2.02) and 8-C*H*(OCOCH$_3$)CH$_A$H$_B$CH$_3$ (6.27)
	4	4-CH$_3$ (2.42)	3-H (6.24)
	5	8-C*H*(OCOCH$_3$)CH$_A$H$_B$CH$_3$ (6.24)	8-CH(OCOCH$_3$)C*H*$_A$H$_B$CH$_3$ (2.02) and 8-C*H*(OCOCH$_3$)CH$_A$*H*$_B$CH$_3$ (2.10)
	6	6-H (7.01)	5-H (7.58)

Table S5 : Cross peaks [δ ^{1}H and ^{13}C] observed in HMQC

Compound No.	Entry no.	Protons attached/ bound on; chemical shift (δ) (relevant protons are italicized/numbered)	Carbons attached/ bound on; chemical shift (δ) relevant carbons are italicized/numbered)
4	1	8-COCH$_2$CH$_3$ (1.19)	8-COCH$_2$CH$_3$ (7.52)

	2	4-CH_3 (2.39)	4-CH_3 (18.73)
	3	8-$COCH_2CH_3$ (2.86)	8-$COCH_2CH_3$ (38.17)
	4	7-OCH_3 (3.89)	7-OCH_3 (56.29)
	5	3-H (6.12)	3-C (110)
	6	6-H (6.89)	6-C (107.43)
	7	5-H (7.57)	5-C (126.81)
4b	1	3-H (6.21)	112.8
	2	6-H (6.85)	110.8 , 29.5
	3	5-H (7.39)	128.7
	4	4-H (7.53)	142.8
4d	1	8-$COCH_2C\mathit{H}_3$ (1.11)	8-$COCH_2CH_3$ (7.32)
	2	3-H (2.39)	3-C (142.2)
	3	8-$COC\mathit{H}_2CH_3$ (2.86)	8-$COCH_2CH_3$ (38.17)
	4	7-$OC\mathit{H}_3$ (3.89)	7-OCH_3 (56.29)
	5	2-H(6.12)	2-C(112.76)
	6	6-*H* (6.89)	6-*C* (100.3)
	7	5-*H* (7.57)	5-*C* (126.8)
11e	1	8-$CH(OCOCH_3)CH_AH_BC\mathit{H}_3$ (0.93)	8-$CH(OCOCH_3)CH_AH_BCH_3$ (8.69)
	2	8-$CH(OCOCH_3)C\mathit{H}_AH_BCH_3$ (2.02)	8-$CH(OCOCH_3)CH_AH_BCH_3$ (26.24)
	3	8-$CH(OCOCH_3)CH_A\mathit{H}_BCH_3$ (2.10)	8-$CH(OCOCH_3)CH_AH_BCH_3$ (26.24)
	4	8-$CH(OCOC\mathit{H}_3)CH_AH_BCH_3$ (2.10)	8-$CH(OCOCH_3)CH_AH_BCH_3$ (20.77)
	5	7- $OCOC\mathit{H}_3$ (2.31)	7- $OCOCH_3$ (21.0)

	6	4-C*H*$_3$ (2.42)	4-*C*H$_3$ (18.92)
	7	8-C*H*(OCOCH$_3$)CH$_A$H$_B$CH$_3$ (6.24)	8-*C*H(OCOCH$_3$)CH$_A$H$_B$CH$_3$ (69.46)
	8	3-H (6.27)	C- 3 (114.68)
	9	6-H (7.01)	C- 6 (119.7)
	10	5-H (7.58)	C- 5 (124.54)

Table S6 : HMSC of compound 2a

Compound No.	Entry no.	Protons attached/ bound on; chemical shift (δ) (relevant protons are italicized/numbered)	Carbons attached/ bound on; chemical shift (δ) relevant carbons are italicized/numbered)
2a	1	3-H(6.34)	C-3(113.2)
	2	6-H(6.85)	C-6(112.3)
	3	5-H(7.55)	C-5(128.7)
	4	4-H(7.85)	C-4(162.7)
	5	2′-H(1.62)	C-2′(25.1)

Table S7 : HMBC spectral studies Cross peaks [δ(^{1}H) vs δ(^{13}C)] observed in HMBC spectral studies

Compound number	Entry number	Protons attached / bound / on: chemical shift (δ) relevant protons are italicized or numbered	Chemical shift (δ) of Carbons attached / bound / having relationship as: relevant carbons are italicized or numbered		
			2-bond	3-bond	4-bond
4a	1	H-3(6.34)	C-4(142.8) C-2(164.1)	C-4a(112.8)	
	2	H-6(6.90)	C-5(128.9) C-7(15.99) C-8(125)	C-4a(112.8)	
	3	H-5(7.35)	C-6(113.2) C-7(162.1)	C-4a(112.8)	

	4	H-4(7.68)	C-3(113.2) C-4a(112.8)	C-2(164.1) C-5(128.9)	
	5	H-3′(1.62)	C-2′(184.2)	C-1′(192.6)	
11c	1	8-$CH(OH)CH_2C\mathit{H}_3$ (1.01)	8-$CH(OH)\mathit{C}H_2CH_3$ (29.85)	8-$\mathit{C}H(OH)CH_2CH_3$ (70.88)	
	2	8-$CH(OH)C\mathit{H}_2CH_3$ (1.92)	8-$CH(OH)CH_2\mathit{C}H_3$ (9.48) and 8-$\mathit{C}H(OH)CH_2CH_3$ (70.88) and C-8 (114.73)		
	3	4-$C\mathit{H}_3$ (2.36)	C-4 (153.94)	C-3 (110.70)	
	4	8-$C\mathit{H}(OH)CH_2CH_3$ (5.69)	8-$CH(OH)CH_2CH_3$ (29.85) and C-8 (114.73)	8-$CH(OH)CH_2\mathit{C}H_3$ (9.48)	
	5	3-H (6.03)	C-2 (161.81)	4-$\mathit{C}H_3$ (18.87) and C-4a (112.56)	
	6	6-H (6.83)	C-5 (124.50) and C-7 (160.58)	C-8 (114.73)	C-8a (150.83)
	7	5-H (7.38)	C-6 (114.56) and C-4a (112.56)	C-7 (160.58) and C-8a (150.83)	

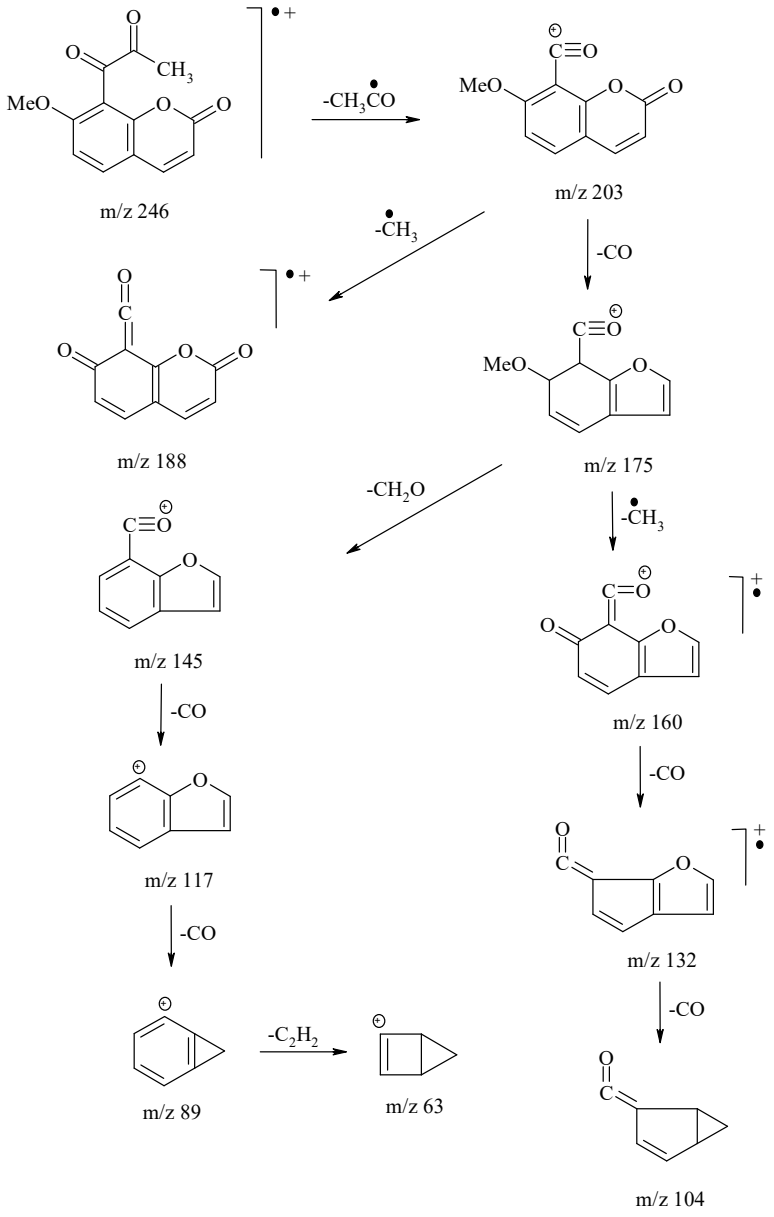
	8	7-OH (9.80)	C-6 (114.56) and C-7 (161.81)		C-4a (112.56) and C-5 (124.50)

Table S8. Significant ion peaks of 7-methoxy-8-coumarinyl ketones and its selenium dioxide oxidation products

Compound No.	m/z of the ion peaks for the fragments recorded (relative intensity in percent and probable rationalization if any)
3a	260 (1.0, $M^{\bullet+}$), 217 (100, $M^{\bullet+}$-$COCH_3$), 202 (6.2, $M^{\bullet+}$-$COCH_3$-CH_3), 189 (9.0, $M^{\bullet+}$-$COCH_3$-CO), 174 (20.2, $M^{\bullet+}$-$COCH_3$-CO-CH_3), 159 (2.62, M $M^{\bullet+}$-$COCH_3$-CO-CH_2O), 146 (10.2, $M^{\bullet+}$-$COCH_3$-CO-CH_3-CO), 131 (4.85, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-CO), 118 (4.77, $M^{\bullet+}$-$COCH_3$-CO-CH_3-2CO), 103 (12.2, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-2CO), 77 (8.01, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-2CO-C_2H_2), 43 (87, CH_3-C≡O^+)
4a	246 (1.0, $M^{+\bullet}$), 203 (100, $M^{\bullet+}$-$COCH_3$), 188 (5.10, $M^{\bullet+}$-$COCH_3$-CH_3), 175 (8.50, $M^{\bullet+}$-$COCH_3$-CO), 160 (22.41, $M^{\bullet+}$-$COCH_3$-CO-CH_3), 145 (2.68, $M^{\bullet+}$-$COCH_3$-CO-CH_2O), 132 (8.13, $M^{\bullet+}$-$COCH_3$-CO-CH_3-CO), 117 (4.81, $M^{\bullet+}$-$COCH_3$-CO=CH_2O-CO), 104 (4.77, $M^{\bullet+}$-$COCH_3$-CO-CH_3-2CO), 89 (11.21, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-2CO), 63 (7.96, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-2CO-C_2H_2), 43 (83.5, CH_3-C≡O^+)
4b	262 (10, $M^{\bullet+}$), 232 (21, $M^{\bullet+}$-30), 231 (36, $M^{\bullet+}$-31), 203 (100, $M^{\bullet+}$-59), 175 (25, $M^{\bullet+}$-87), 160 (31, $M^{\bullet+}$-102), 145 (48, $M^{\bullet+}$-117), 104 (67, $M^{\bullet+}$-158), 89 (71, $M^{\bullet+}$-173)
5a	274 (63.2, $M^{\bullet+}$), 245 (5.2, $M^{\bullet+}$-29), 217 (100, $M^{\bullet+}$-C_2H_5CO), 202 (28.2, $M^{\bullet+}$-C_2H_5CO-CH_3), 189 (19.1, $M^{\bullet+}$-C_2H_5CO-CO), 161 ($M^{\bullet+}$-C_2H_2CO-2CO), 175 ($M^{\bullet+}$-C_2H_5CO-CO-CH_3+H^+)

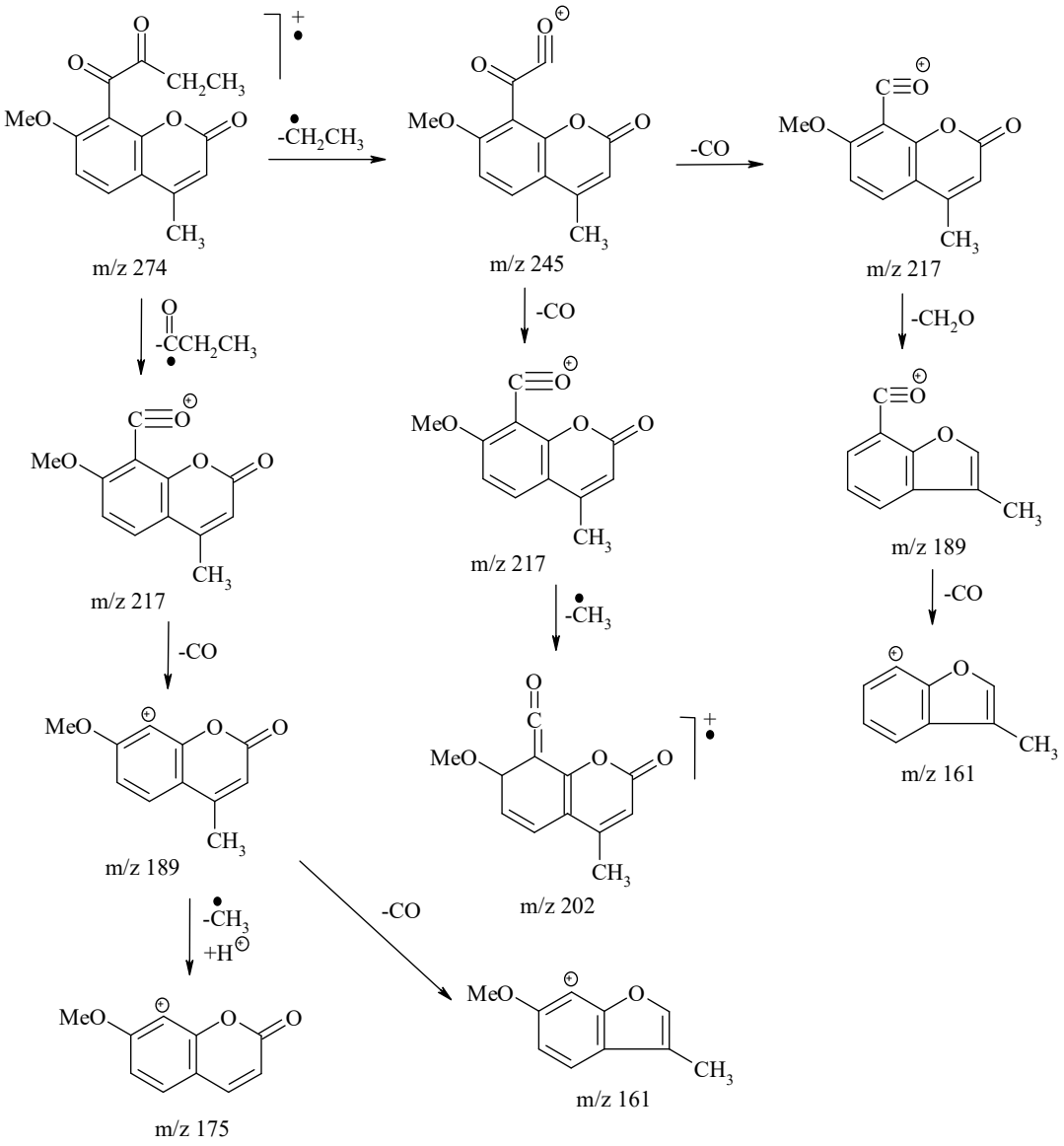
Mass spectral analysis of typical members **4a** and **5a** among the representative oxidized products are being logically delineated in Scheme **1** and **2**.

Mass spectral fragmentation of the compound 4a



Scheme S1

Mass spectral fragmentation of 5a



Scheme S2

Table S9

Electron spray ionization of 7-methoxy-8-coumarinyl ketones and its selenium dioxide oxidation products

Compound No.	m/z of ion peaks recorded	
4	$[M-H]^+$ at m/z 247.90	$[M+Na]^+$ at 269.09
4a	$[M-H]^+$ at m/z	$[M+Na]^+$ at 246.1
3a	$[M-H]^+$ at m/z 261.1	$[M+Na]^+$ at 283.1
6a	$[M-H]^+$ at m/z 261.1	$[M+Na]^+$ at 283.1
7a	$[M-H]^+$ at m/z 309.1	$[M+Na]^+$ at 331.1
11c	$[M+H]^+$ at 235.10	$[M+Na]^+$ at 257.10
3c	$[M+H]^+$ at 263.3	$[M+Na]^+$ at 285.3
8c	$[M+H]^+$ at 283.3	$[M+Na]^+$ at 295.3
11e	$[M+H]^+$ at 319.2	$[M+Na]^+$ at 341.12
1e	$[M+H]^+$ at 277.13	$[M+Na]^+$ at 299.13