# Structural characterization of mono and dihydroxylated umbelliferone derivatives

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## 1. Materials

Deuterated chloroform ($CDCl_3$), deuterated dimethylsulfoxide (DMSO-$d^6$), resorcinol ($C_6H_6O_2$), ethyl acetoacetate ($C_6H_{10}O_3$, EtOAc), 2-bromoethanol ($C_2H_5BrO$), anhydrous pyridine ($C_5H_5N$), 4-dimethylaminopyridine (DMAP) and Dowex® H+ resin were supplied by Sigma–Aldrich, and used as received. Dichloromethane ($CH_2Cl_2$), 1,4-dioxane ($C_4H_8O_2$), concentrated sulphuric acid ($H_2SO_4$), ethyl acetate ($C_4H_8O_2$, EtOAc), ethanol ($C_2H_5OH$, EtOH), N,N-dimethylformamide ($C_3H_7NO$, DMF), potassium carbonate ($K_2CO_3$), sodium bisulphite ($NaHSO_3$), sodium carbonate ($Na_2CO_3$), brine solution, anhydrous magnesium sulphate ($MgSO_4$), toluene ($C_7H_8$), diethyl ether ($(C_2H_5)_2O$) and methanol ($CH_3OH$, MeOH) were supplied by Scharlau, and used as received.

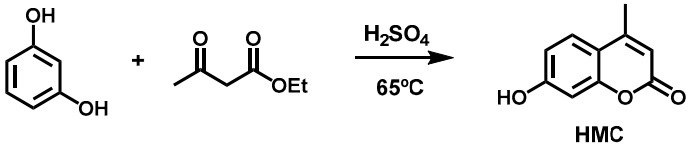
## 2. Synthesis of coumarin derivatives

### *2.1 Synthesis of 7-hydroxy-4-methylcoumarin (HMC)*

HMC was synthesized according to previous literature [1,2]. Resorcinol (11.0 g, 0.1 mol) and ethyl acetoacetate (13.0 g, 0.1 mol) were completely dissolved in 40 mL 1,4-dioxane. Then, concentrated sulphuric acid (3 mL) was dropwise added to the system, which was subsequently warmed up to 65ºC for 3 h as can be seen in Scheme S1. Afterwards, the suspension was cooled down to room temperature and poured into 300 mL ice water to obtain a yellowish precipitate. The crude product was dried in a vacuum oven and recrystallized twice in ethyl acetate to obtain white crystals of HMC with a yield of 70%, which was kept away from light. Colourless crystals suitable for single-crystal X ray diffraction analysis were obtained from ethyl acetate/ethanol (3:1) mixture. The 1H and 13C-NMR spectra are collected in Figure S1 and ATR-FTIR and its MS spectra are collected in Figure S2.

$^1$H NMR (300 MHz, DMSO-$d^6$, δ): 10.49 (s, 1H, –OH), 7.57 (d, J= 8.7 Hz, 1H, Ar–H), 6.78 (dd, J= 8.7 Hz J=2.3, 1H, Ar–H), 6.68 (d, J=2.3 Hz, 1H, Ar–H), 6.11 (s, 1H, C–H), 2.36 (s, 3H, –$CH_3$).

$^{13}$C NMR (101 MHz, DMSO-$d^6$, δ): 161.24, 160.44, 154.91, 153.56, 126.58, 112.94, 112.09, 110.34, 102.27, 39.52, 18.19.




**Scheme S1**:Synthetic route for the preparation of HMC.

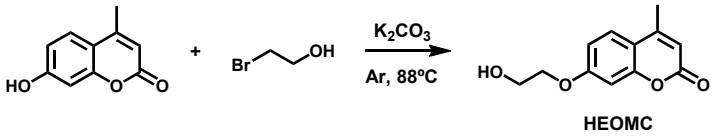
### *2.2 Synthesis of 7-(2-hydroxyethoxy)-4-methylcoumarin (HEOMC)*

The synthetic procedure for HEOMC is described as follows (Scheme S2), according to previous literature [3]. In a 150 mL two-neck round-bottom flask, (4 g, $2.3 \times 10^{-2}$ mol) of previously synthesized HMC was dissolved in 20 mL N,N-dimethylformamide. Then, a solution of (4.3 g, $3.4 \times 10^{-2}$ mol) of 2-bromoethanol in 10 mL DMF was dropwise added to the reaction and (6.3 g, $45.6 \times 10^{-2}$mol) potassium carbonate was added one-off under stirring. The reaction mixture was stirred for 18 h at 88ºC under an argon atmosphere. The reaction was monitored by

TLC. When the reaction was completed, the mixture was cooled down to room temperature, poured into 70 mL ice water and filtrated to get the crude product. The solid was then recrystallized twice in ethyl acetate to obtain colourless crystals of HEOMC suitable for single crystal X-ray diffraction analysis with a yield of 86%. The 1H and 13C-NMR spectra are collected in Figure S3 and ATR-FTIR and its MS spectra are collected in Figure S4.

$^{1}$H NMR (400MHz, DMSO-d6, δ): 7.49 (d, 1H; J=8.8 Hz, Ar-H), 6.86 (dd, 1H; $J_1$=8.8 Hz, $J_2$=2.4 Hz, Ar-H), 6.81 (d, 1H, J=2.4 Hz, Ar-H), 6.13 (s, 1H, -CH), 4.53 (t, 2H, J=4.8 Hz, Ar-O-$CH_2$-), 4.25 (t, 2H, J=4.8 Hz, -$CH_2$-OCO-), 4.19 (d, 2H, J=11.2 Hz, -$CH_2$-OH), 3.64 (d, 2H, J=11.2 Hz, -$CH_2$-OH), 2.39 (s, 3H, -$CH_3$), 1.08 (s, 3H, -$CH_3$).

$^{13}$C NMR (101 MHz, DMSO-d6, δ): 161.79, 160.17, 154.69, 153.36, 126.34, 113.00, 112.39, 111.06, 101.12, 70.29, 59.39, 39.50, 18.12.

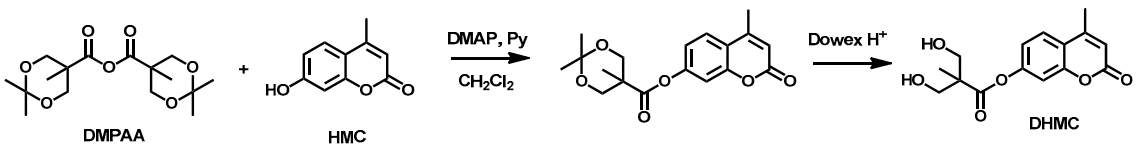



**Scheme S2:** Synthetic route for the preparation of HEOMC

The synthesis of both DHMC and DHEOMC require the synthesis of the same intermediate compound, isopropylidene-2.2-bis-(methoxy)propionic anhydride (DMPAA), which was synthesized according to literature [4,5].

*2.3 Synthesis of 4-methylcoumarin-7-yl-3-hydroxy-2-(hidroxymethyl)-2-methylpropanoate DHMC*

Then, DMPAA and HMC were reacted to produce an ester. The synthesis of the coumarin diol derivative was carried out following the route presented in Scheme S3. 7-hydroxy-4-methylcoumarin (HMC) (15.4 g, $8.6 \times 10^{-2}$mol) were added together with 4-dimethylaminopyridine (DMAP) (2.1 g, $1.7 \times 10^{-2}$ mol) and dissolved in 238 mL of anhydrous pyridine and diluted with 537 mL of dichloromethane. The anhydride (DMPAA) (43.4 g, $13.1 \times 10^{-2}$ mol) were added and reacted under stirring for 9 hours at room temperature. The excess of the anhydride was decomposed by stirring the reaction overnight (18 h) with 85 mL of a pyridine: water solution in a 1: 1 ratio. Subsequently, the following washes of the organic phase were carried out: 1M sodium bisulphite, sodium carbonate 10 % (w/t) and brine solution. The organic phase was dried over anhydrous magnesium sulphate and the solvent was removed at low pressure. 25.4 g (0.076 mol) of isopropyl-[2,2-bis-(methoxy)]-propanoate of 4-methylcoumarin were obtained, with a yield of 68%.




**Scheme S3:** Synthetic route for the preparation of DHMC.

Finally, the protecting group was easily removed yielding the HMC ester diol. The compound synthesized in the previous step (HMC-ester) was weighted, (25.4 g, $7.6 \times 10^{-2}$mol), and dissolved in 500 mL of methanol. Six teaspoon of the Dowex $H^+$ resin was added, and the mixture was stirred at room temperature for 3 hours. The resin was filtered and washed with 50 mL of methanol. The organic solvent was evaporated on a rotary evaporator and a white solid was obtained. The product was purified twice by recrystallization in ethyl acetate, obtaining a final yield of 30%. Then, the solid was recrystallized twice in ethyl acetate to obtain colourless crystals suitable for single crystal X-ray diffraction analysis. The 1H and 13C-NMR spectra are collected in Figure S5 and ATR-FTIR and its MS spectra are collected in Figure S6.

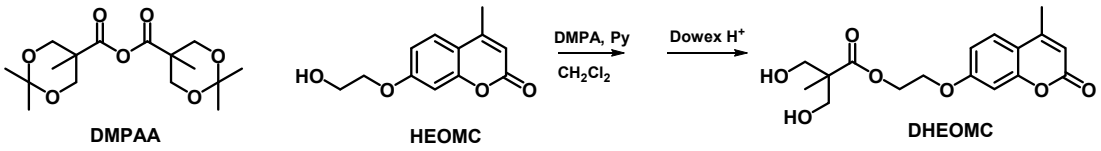
$^1$H NMR (400MHz, DMSO-d6, δ): 7.82 (d, J= 2.2Hz, 1H, Ar-H), 7.11 (m, 2H, Ar-H), 6.38 (s, 1H, -CH), 3.65 (m, 2H, OH), 3.51 (m, 4H, -$CH_2$-O), 2.44 (s, 3H, -$CH_3$), 1.17 (s, 3H, -$CH_3$).

$^{13}$C NMR (101 MHz, DMSO-d6, δ): 173.33, 159.60, 153.50, 153.35, 152.96, 126.33, 118.50, 117.37, 113.67, 110.00, 63.99, 51.23, 39.50, 18.18, 16.80.

*2.4 Synthesis of 2-((4-methylcoumarin-7-yl)oxy)ethyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate DHEOMC*

The synthesis of the DHEOMC followed the same procedure than the synthesis of the DHMC and it is shown in Scheme S4.

7-hydroxyethoxy-4-methylcoumarin (HMC) (15.1, 0.07 mol) were dissolved together with 4.16 g (0.03 mol) of 4-dimethylamino pyridine (DMAP) with a mixture of 138 mL of anhydrous pyridine and 554 mL of dichloromethane. 34 g (0.1 mol) of anhydride (DMPAA) were slowly added and left to react for 9 hours at room temperature. The excess of the anhydride was destroyed by stirring the reaction overnight with 66 mL of a pyridine:water solution in a 1:1 ratio. Subsequently, the organic phase was extracted consecutively with 1 M sodium bisulphite, 10%, sodium carbonate and brine solution. Finally, the organic phase was dried over anhydrous magnesium sulphate, which was then removed by filtration and the resulting solution was evaporated on a rotary evaporator, leaving a viscous orange solid. The yield was 73%.




**Scheme S4:** Synthetic route for the preparation of DHEOMC.

For the deprotection step, 20.9 g (6.021 mmol) of the 4-methylcoumarin-7-ethoxyl ester of 2,2,5-trimethyl-[1,3] dioxan-5-(yl)acetic acid in 200 mL of methanol (MeOH) were dissolved and they added approximately 10 g of Dowex $H^+$ resin. The reaction was allowed to react at room temperature with stirring for 3 hours, the resin was filtered and washed with methanol. The methanol was evaporated on a rotary evaporator to give the desired compound (white crystals). The product obtained was purified by recrystallization from toluene. Colourless crystals suitable for single-crystal X ray diffraction analysis were obtained from ethyl acetate/diethyl ether (1:1) mixture. The 1H and 13C-NMR spectra are collected in Figure S7 and ATR-FTIR and its MS spectra are collected in Figure S8.

$^{1}$H RMN (400MHz, DMSO-d$^{6}$, δ): 7.51 (d, 1H; J=8.8 Hz, Ar-H), 6.87 (dd, 1H; J1=8.8 Hz, J2=2.4 Hz, Ar-H), 6.83 (d, 1H, J=2.4 Hz, Ar-H), 6.15 (s, 1H, CH), 4.56 (t, 2H, J=4.8 Hz, OCO-$CH_2$), 4.27 (t, 2H, J=4.8 Hz, $CH_2$-O-Ar), 3.92 (d, 2H, J=11.2 Hz, -$CH_2$OH), 3.74 (d, 2H, J=11.2 Hz, -$CH_2$OH), 2.40 (s, 3H, -CH3), 1.08 (s, 3H, -CH3).

$^{13}$C NMR (101 MHz, DMSO-d$^{6}$, δ): 174.70, 161.36, 160.13, 154.67, 153.35, 126.48, 113.31, 112.48, 111.29, 101.40, 66.64, 63.81, 62.04, 50.33, 39.50, 18.14, 16.84.

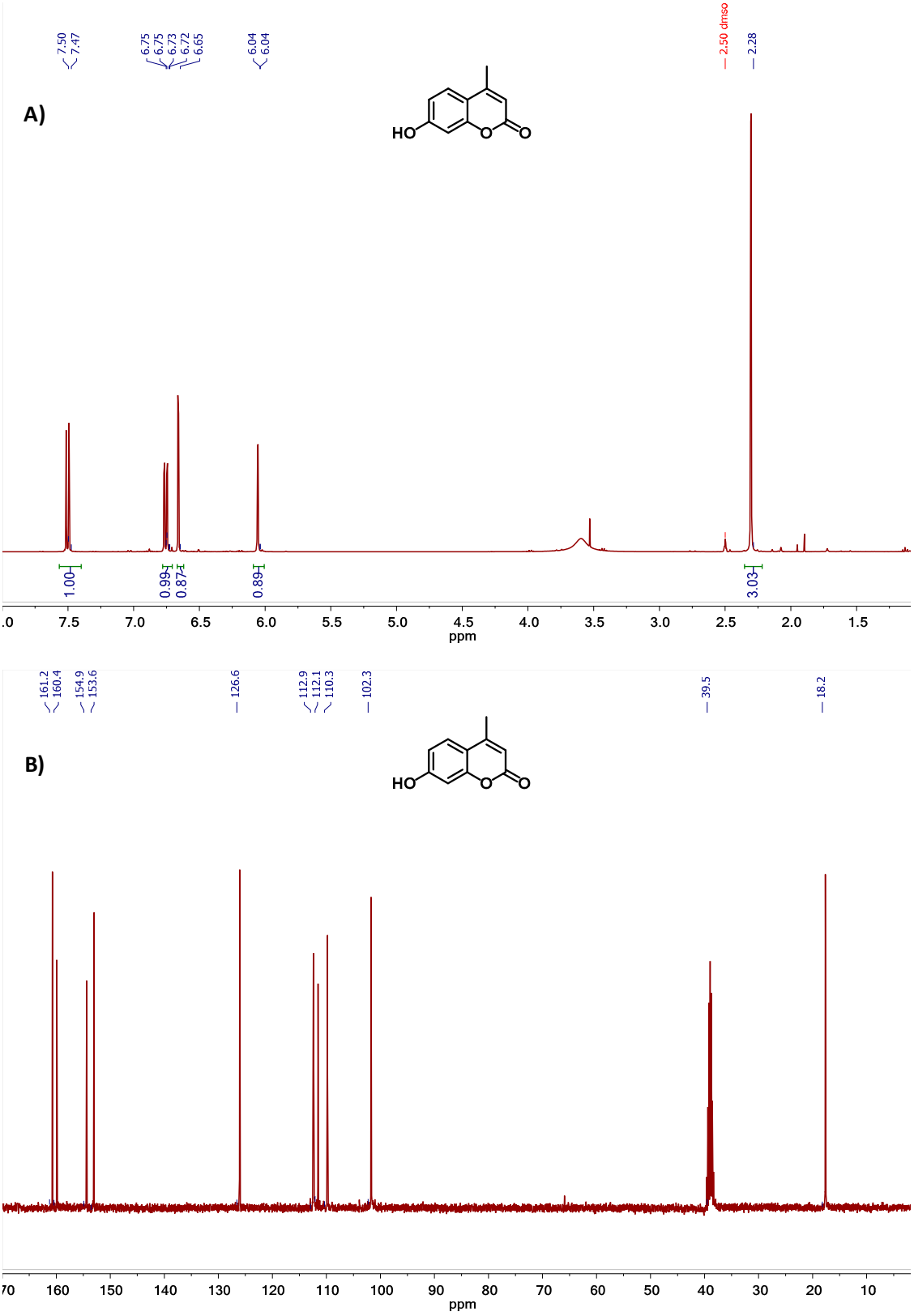
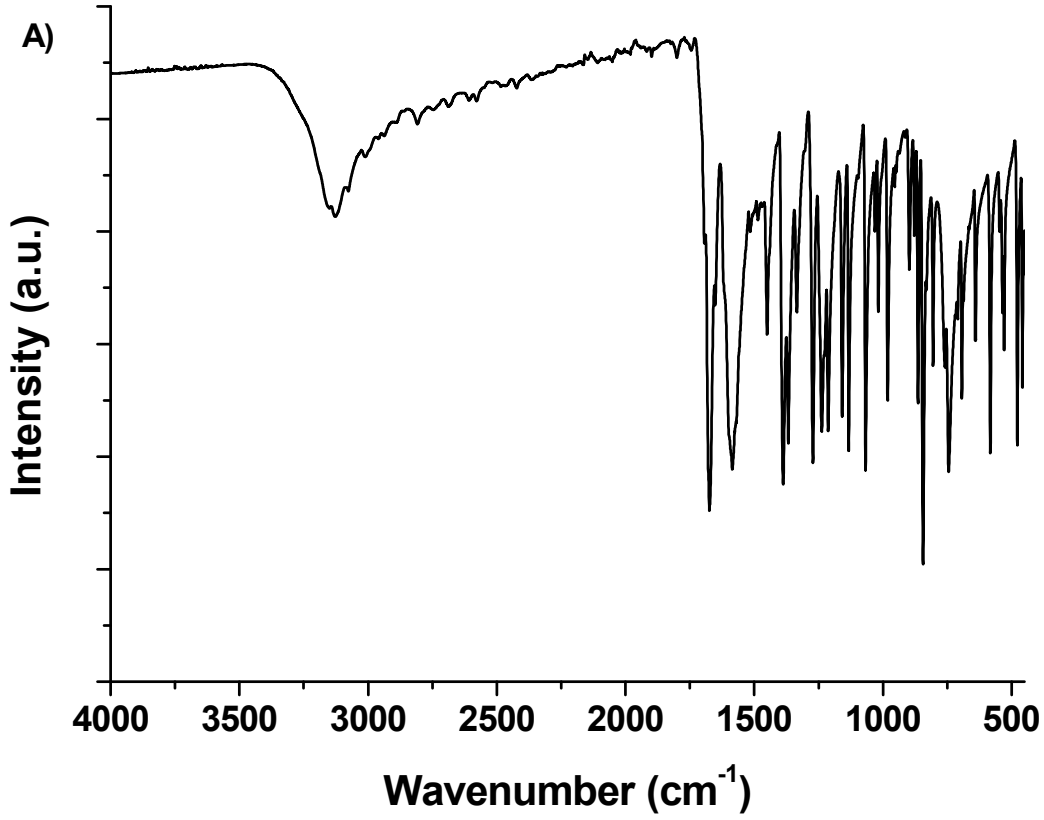



**Figure S1**: A) 1H-NMR and B) 13C-NMR spectra of HMC.

A)



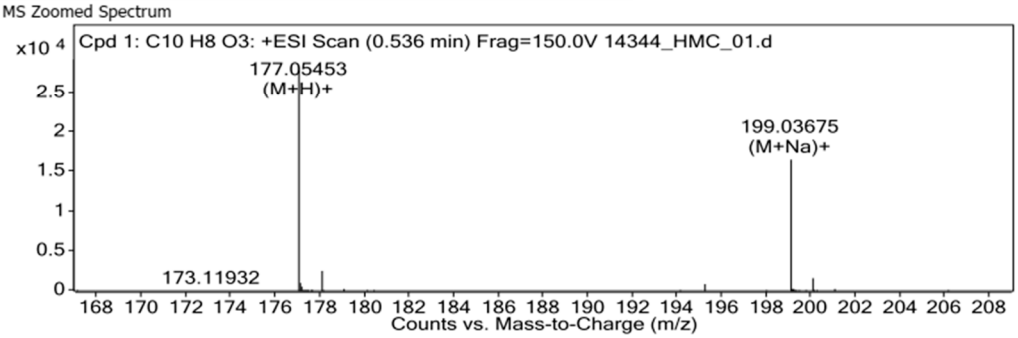

B)

**Compound Table**

| Compound Label | RT | Mass | Abund | Formula | Tgt Mass | Diff (ppm) |
|---|---|---|---|---|---|---|
| Cpd 1: C10 H8 O3 | 0.536 | 176.0473 | 27792 | C10 H8 O3 | 176.04734 | -0.26 |

| Compound Label | RT | Algorithm | Mass |
|---|---|---|---|
| Cpd 1: C10 H8 O3 | 0.536 | Find By Formula | 176.0473 |

MS Zoomed Spectrum




**MS Spectrum Peak List**

| m/z | Calc m/z | Diff(ppm) | z | Abund | Formula | Ion |
|---|---|---|---|---|---|---|
| 177.05453 | 177.05462 | -0.53 | | 27792 | C10 H9 O3 | (M+H)+ |
| 177.09319 | | | | 1028 | | |
| 177.14197 | | | | 354 | | |
| 177.17808 | | | | 620 | | |
| 177.27521 | | | | 171 | | |
| 178.05903 | 178.05801 | 5.72 | | 2590 | C10 H9 O3 | (M+H)+ |
| 179.05683 | 179.06007 | -18.09 | | 299 | C10 H9 O3 | (M+H)+ |
| 199.03675 | 199.03657 | 0.94 | 1 | 16542 | C10 H8 Na O3 | (M+Na)+ |
| 200.03935 | 200.03995 | -3.02 | 1 | 1724 | C10 H8 Na O3 | (M+Na)+ |
| 201.04329 | 201.04201 | 6.38 | 1 | 230 | C10 H8 Na O3 | (M+Na)+ |

**Figure S2:** A) ATR-FTIR and B) Mass spectra of HMC

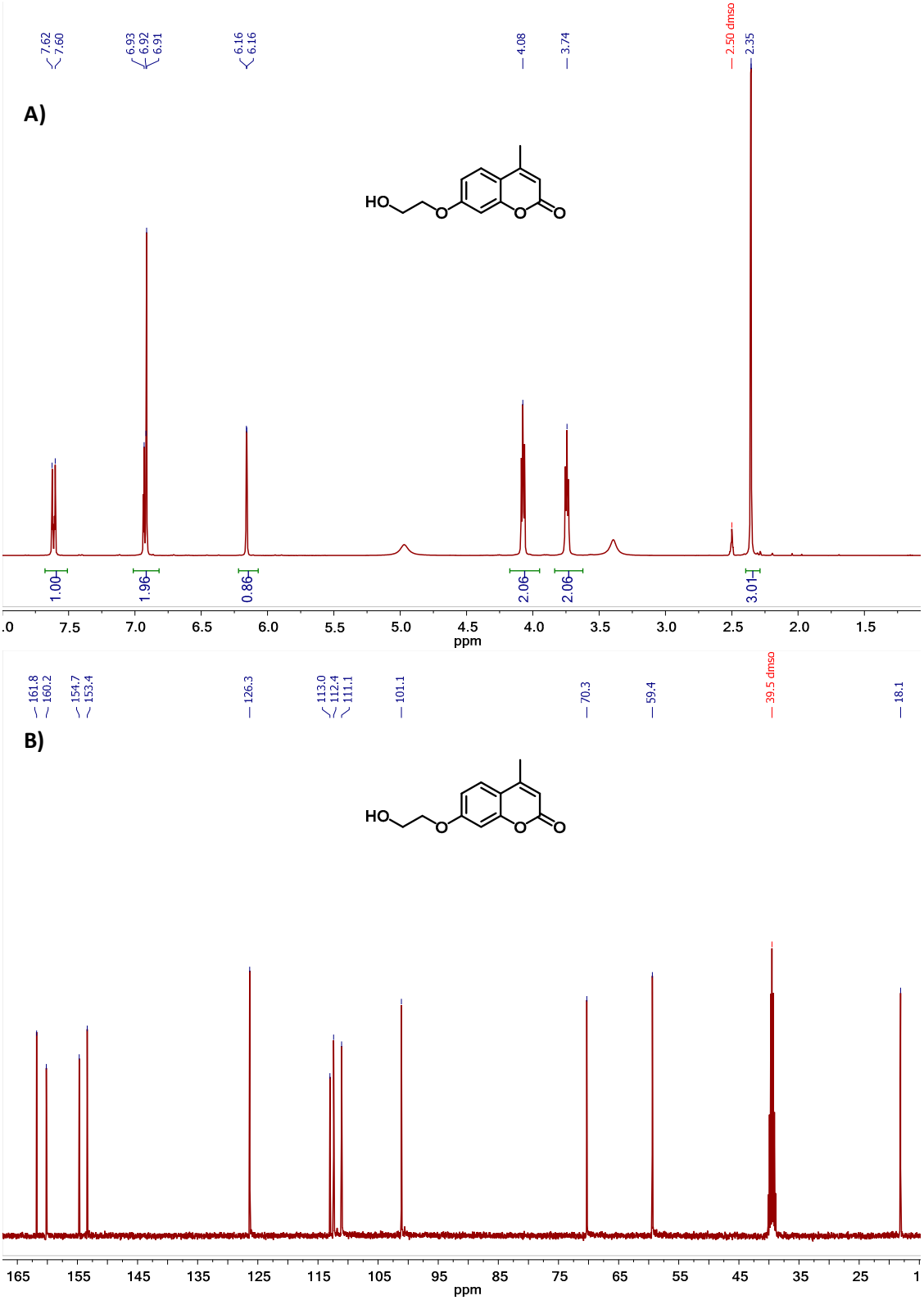
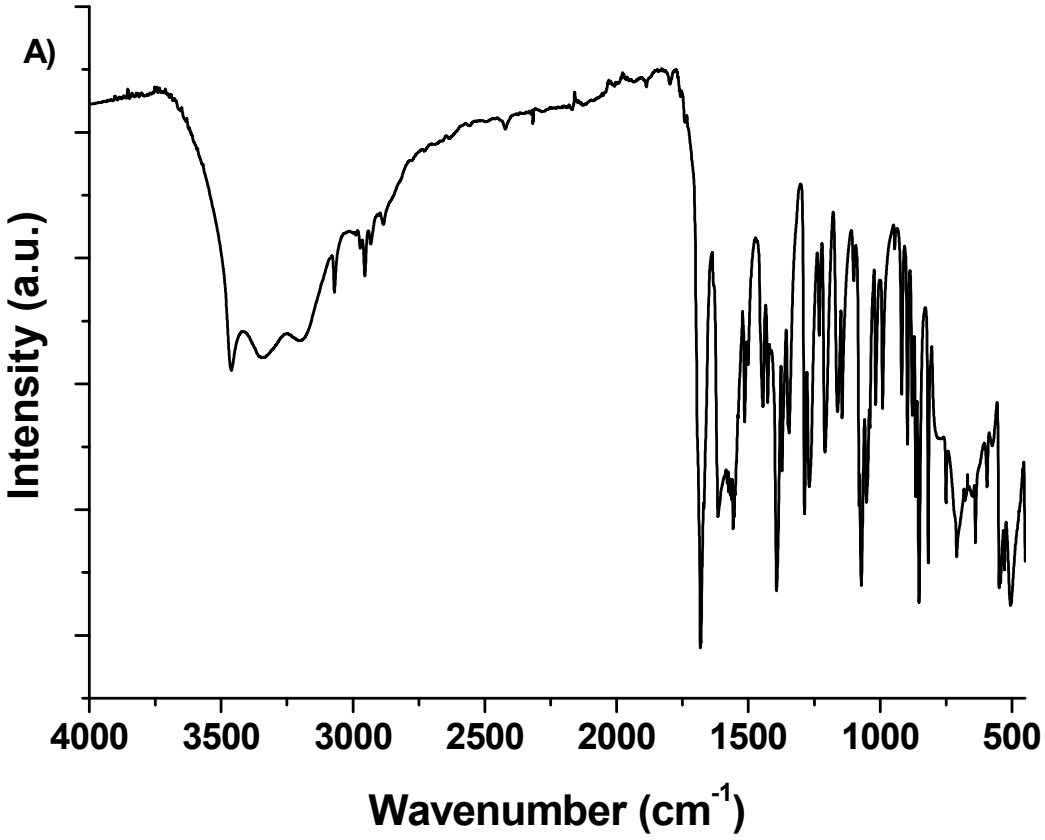



**Figure S3:** A) 1H-NMR and B) 13C-NMR spectra of HEOMC



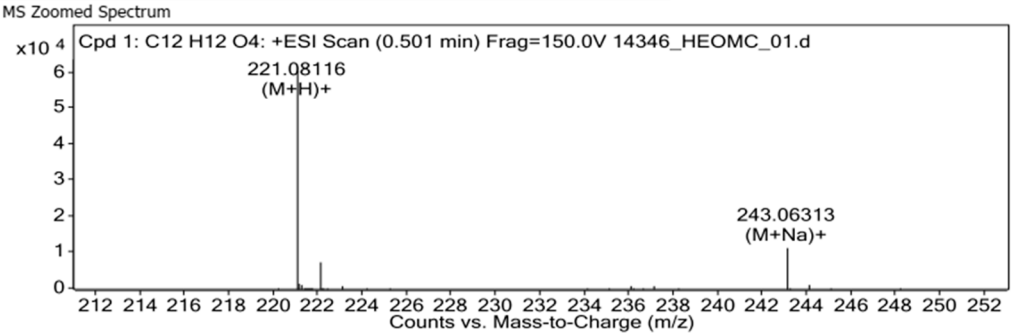

B)

**Compound Table**

| Compound Label | RT | Mass | Abund | Formula | Tgt Mass | Diff (ppm) |
|---|---|---|---|---|---|---|
| Cpd 1: C12 H12 O4 | 0.501 | 220.07388 | 60537 | C12 H12 O4 | 220.07356 | 1.47 |

| Compound Label | RT | Algorithm | Mass |
|---|---|---|---|
| Cpd 1: C12 H12 O4 | 0.501 | Find By Formula | 220.07388 |

MS Zoomed Spectrum




**MS Spectrum Peak List**

| *m/z* | *Calc m/z* | Diff(ppm) | z | Abund | Formula | Ion |
|---|---|---|---|---|---|---|
| 221.08116 | 221.08084 | 1.46 | | 60537 | C12 H13 O4 | (M+H)+ |
| 221.13282 | | | | 1786 | | |
| 221.21828 | | | | 1464 | | |
| 221.26871 | | | | 466 | | |
| 222.08424 | 222.08423 | 0.05 | | 7636 | C12 H13 O4 | (M+H)+ |
| 222.13774 | | | | 379 | | |
| 223.08575 | 223.08635 | -2.68 | | 899 | C12 H13 O4 | (M+H)+ |
| 225.19838 | | | | 448 | | |
| 243.06313 | 243.06278 | 1.42 | 1 | 11524 | C12 H12 Na O4 | (M+Na)+ |
| 244.06534 | 244.06618 | -3.42 | 1 | 1412 | C12 H12 Na O4 | (M+Na)+ |

**Figure S4:** A) ATR-FTIR and B) Mass spectra of HEOMC

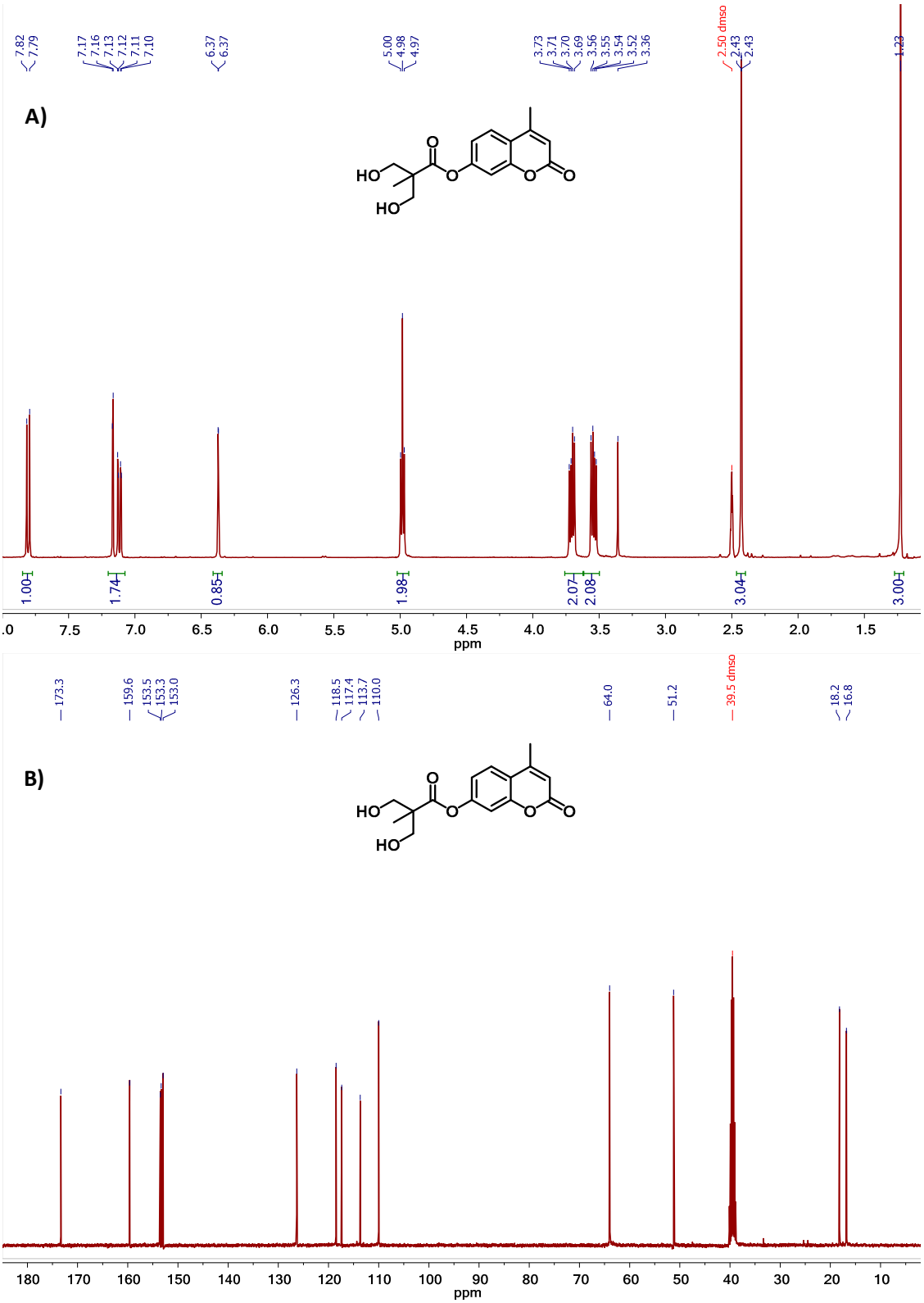
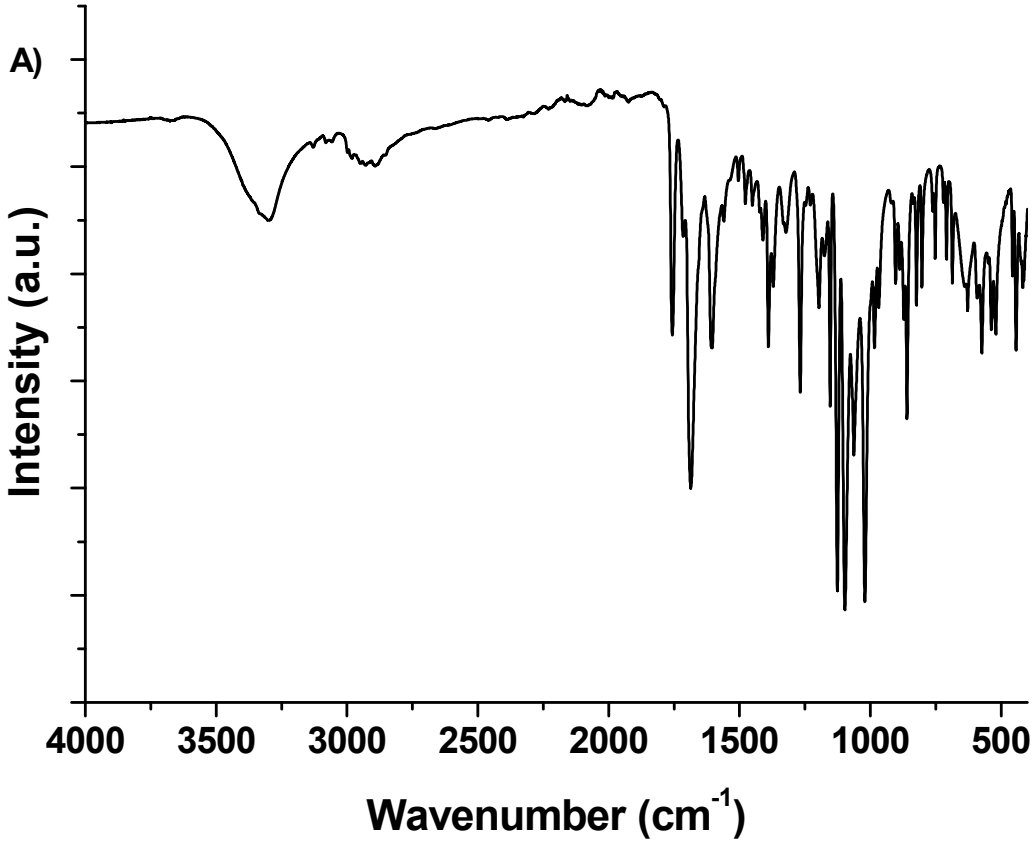



**Figure S5:** A) 1H-NMR and B) 13C-NMR spectra of DHMC



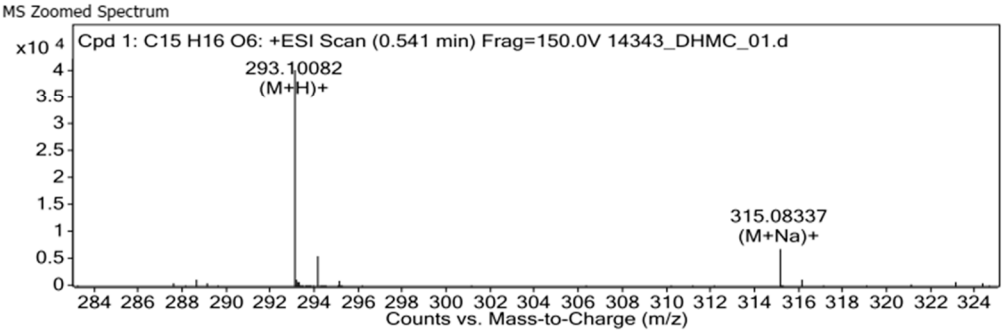

B)

**Compound Table**

| Compound Label | RT | Mass | Abund | Formula | Tgt Mass | Diff (ppm) |
|---|---|---|---|---|---|---|
| Cpd 1: C15 H16 O6 | 0.541 | 292.09355 | 40162 | C15 H16 O6 | 292.09469 | -3.9 |

| Compound Label | RT | Algorithm | Mass |
|---|---|---|---|
| Cpd 1: C15 H16 O6 | 0.541 | Find By Formula | 292.09355 |

MS Zoomed Spectrum




**MS Spectrum Peak List**

| m/z | Calc m/z | Diff(ppm) | z | Abund | Formula | Ion |
|---|---|---|---|---|---|---|
| 225.19548 | | | | 74597 | | |
| 225.24799 | | | | 2017 | | |
| 225.33407 | | | | 1974 | | |
| 226.19834 | | | | 9363 | | |
| 227.20273 | | | | 962 | | |
| 293.10082 | 293.10196 | -3.9 | 1 | 40162 | C15 H17 O6 | (M+H)+ |
| 294.10405 | 294.10537 | -4.46 | 1 | 5692 | C15 H17 O6 | (M+H)+ |
| 295.10475 | 295.10752 | -9.4 | 1 | 1024 | C15 H17 O6 | (M+H)+ |
| 315.08337 | 315.08391 | -1.71 | 1 | 6867 | C15 H16 Na O6 | (M+Na)+ |
| 316.08596 | 316.08731 | -4.26 | 1 | 1284 | C15 H16 Na O6 | (M+Na)+ |

**Figure S6:** A) ATR-FTIR and B) Mass spectra of DHMC

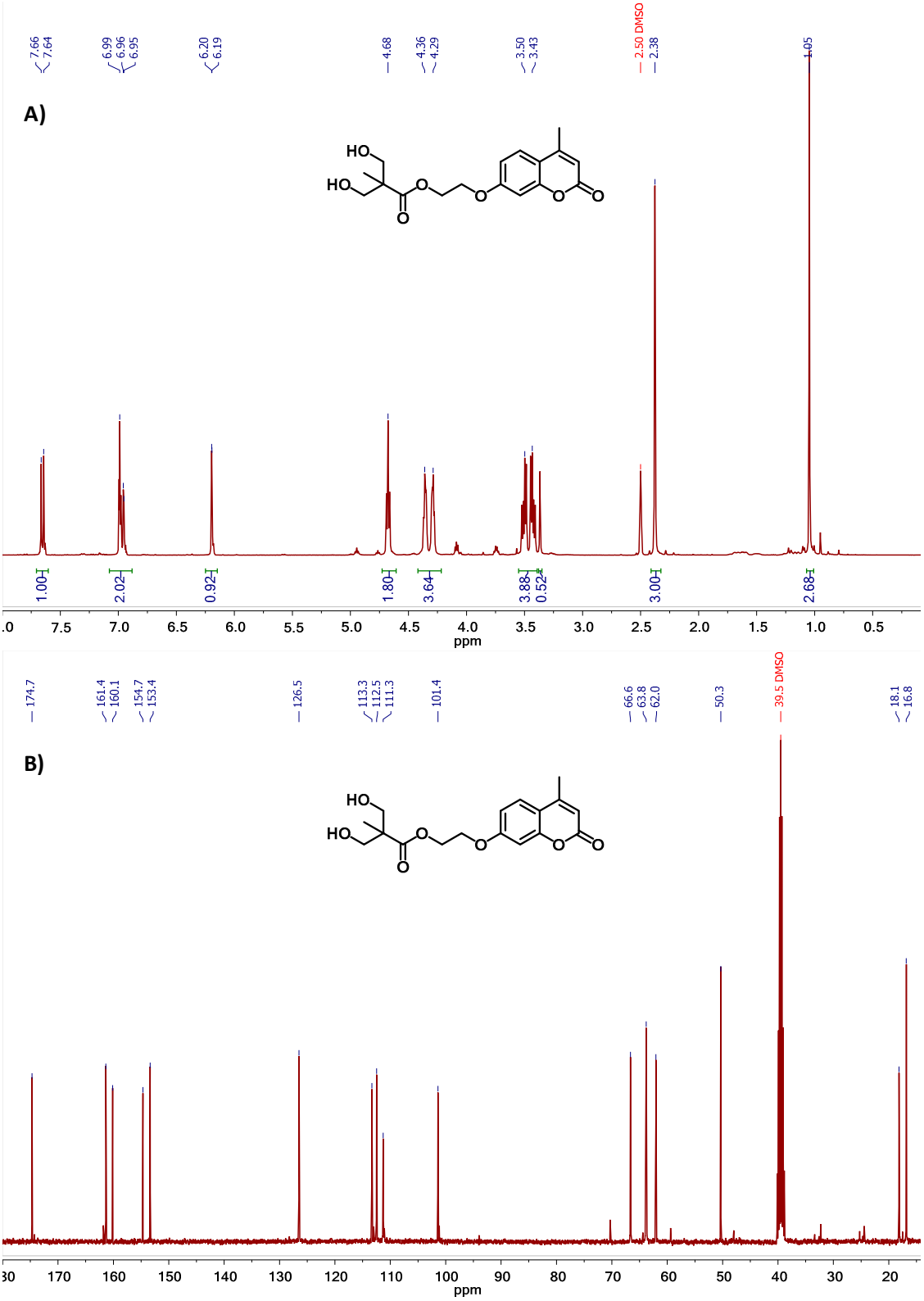
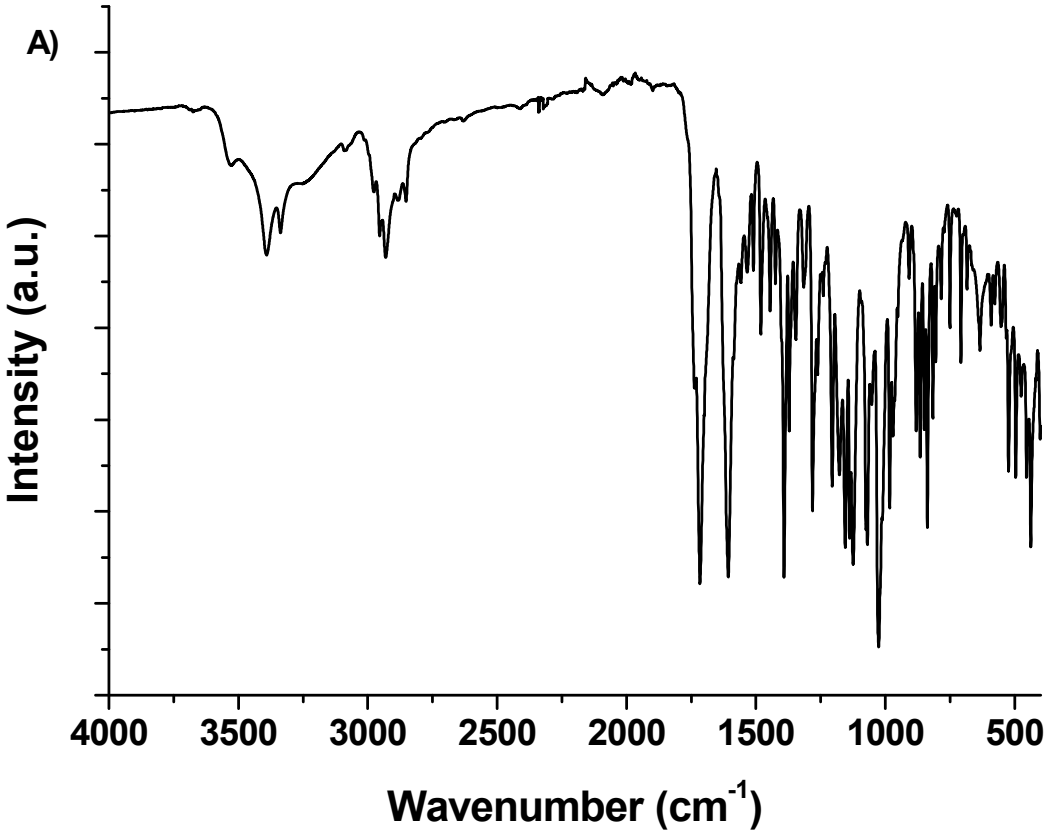



**Figure S7:** A) 1H-NMR and B) 13C-NMR spectra of DHEOMC

A)



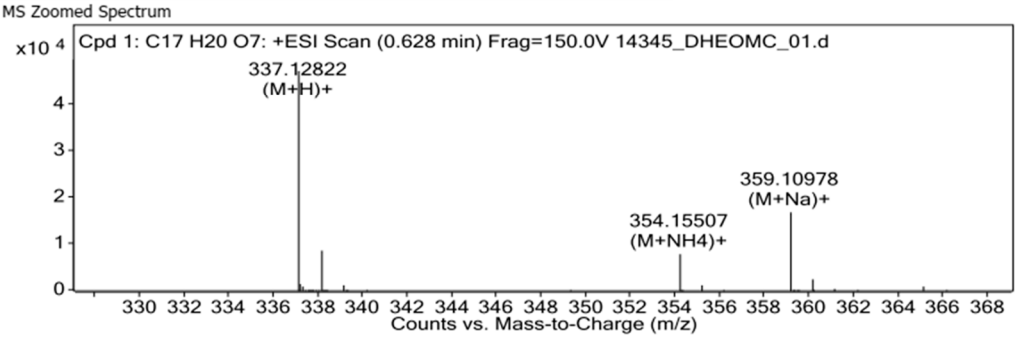

B)

**Compound Table**

| Compound Label | RT | Mass | Abund | Formula | Tgt Mass | Diff (ppm) |
|---|---|---|---|---|---|---|
| Cpd 1: C17 H20 O7 | 0.628 | 336.12093 | 47454 | C17 H20 O7 | 336.1209 | 0.08 |

| Compound Label | RT | Algorithm | Mass |
|---|---|---|---|
| Cpd 1: C17 H20 O7 | 0.628 | Find By Formula | 336.12093 |

MS Zoomed Spectrum




**MS Spectrum Peak List**

| m/z | Calc m/z | Diff(ppm) | z | Abund | Formula | Ion |
|---|---|---|---|---|---|---|
| 337.12822 | 337.12818 | 0.13 | | 47454 | C17 H21 O7 | (M+H)+ |
| 337.18691 | | | | 1584 | | |
| 337.29695 | | | | 1080 | | |
| 338.13154 | 338.13158 | -0.13 | | 8643 | C17 H21 O7 | (M+H)+ |
| 339.13109 | 339.13381 | -8.03 | | 1391 | C17 H21 O7 | (M+H)+ |
| 354.15507 | 354.15473 | 0.96 | 1 | 8063 | C17 H24 N O7 | (M+NH4)+ |
| 355.15692 | 355.15802 | -3.09 | 1 | 1265 | C17 H24 N O7 | (M+NH4)+ |
| 359.10978 | 359.11012 | -0.95 | 1 | 17027 | C17 H20 Na O7 | (M+Na)+ |
| 360.11358 | 360.11353 | 0.16 | 1 | 2648 | C17 H20 Na O7 | (M+Na)+ |
| 361.11537 | 361.11575 | -1.05 | 1 | 603 | C17 H20 Na O7 | (M+Na)+ |

**Figure S8:** A) ATR-FTIR and B) Mass spectra of DHEOMC

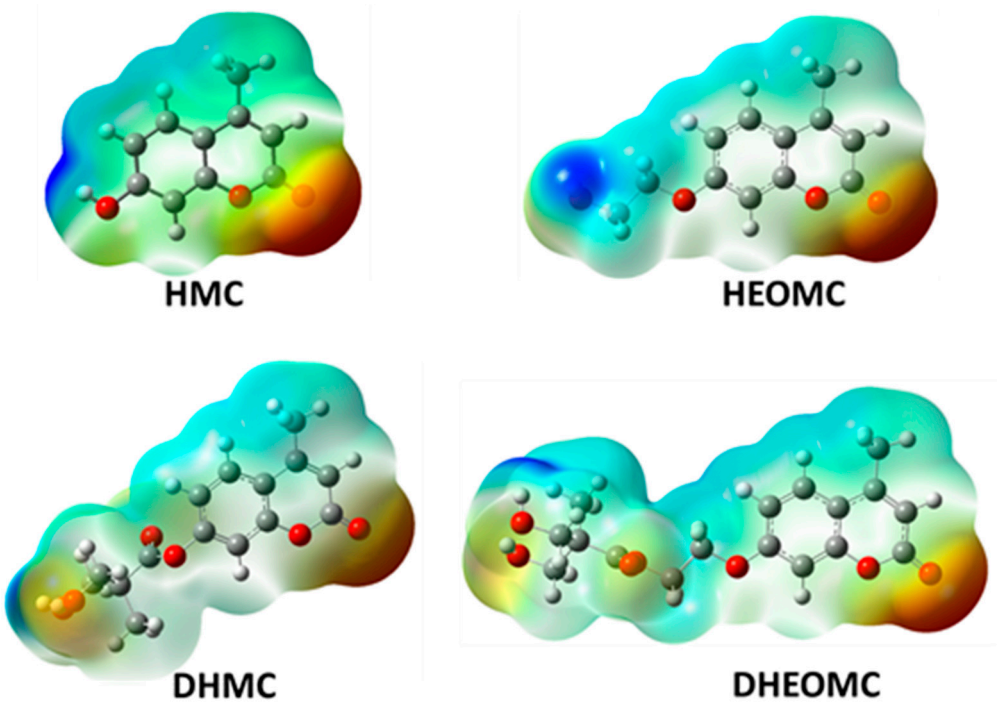



**Figure S9:** Electrostatic potential surfaces for the coumarins studied. Contour values range from -0.080 to 0.080 Hartree/e.

**Table S1*:*** Experimental and theoretical vertical excitation energies and oscillator strength for the first two excited states. The labels 1, 2, 1′ and 2′ correspond to HOMO, LUMO, HOMO-1 and LUMO+1, respectively.

| Coumarin | Transition (weight) | Theoretical Excitation (nm) | Oscillator Strength | Experimental Absorption (nm) |
|---|---|---|---|---|
| HMC | S1: 1-> 1′ (0.95) | 306 | 0.3980 | 317 |
| | S2: 2-> 1′ (0.84) | 278 | 0.0063 | |
| | 1 -> 2′ (0.14) | | | |
| HEOMC | S1: 1-> 1′ (0.96) | 310 | 0.4660 | 319 |
| | S2: 2-> 1′ (0.87) | 282 | 0.0034 | |
| | 1 -> 2′ (0.11) | | | |
| DHMC | S1: 1-> 1′ (0.88) | 295 | 0.3136 | 313 |
| | 2->1′ (0.07) | | | |
| | 2->2′ (0.02) | | | |
| | S2: 2-> 1′ (0.81) | 272 | 0.1408 | |
| | 1->1′ (0.07) | | | |
| | 1->2′ (0.09) | | | |
| DHEOMC | S1: 1-> 1′ (0.96) | 309 | 0.4934 | 318 |
| | S2: 2-> 1′ (0.86) | 281 | 0.0037 | |
| | 1 -> 2′ (0.11) | | | |

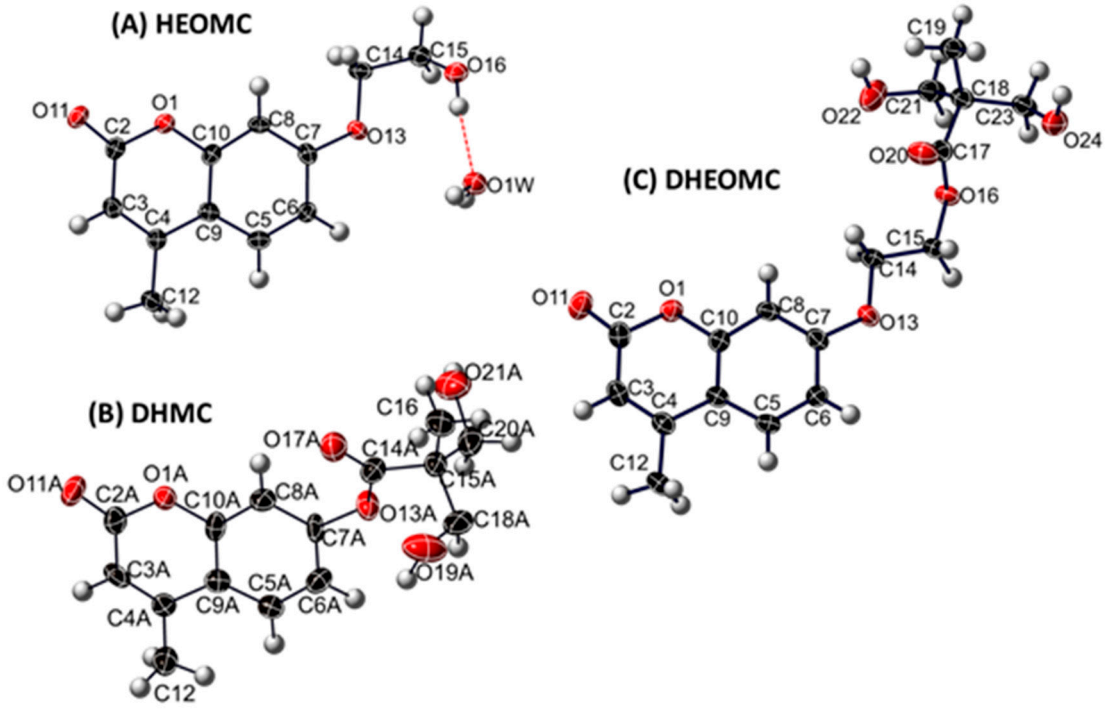



**Figure S10:** ORTEP view of the asymmetric units in (A) HEOMC, (B) DHMC and (C) DHEOMC depicted at the 50% probability level, together with atom labelling. Colour code: C, black, O, red, H, white.

**Table S2:** Geometrical parameters (Å, °) of intermolecular π-π interactions in HEOMC, DHMC and DHEOMC.

| Centroids (Cg) | Cg···Cg | ANG | Cg···plane | | Slippage |
|---|---|---|---|---|---|
| **HEOMC** | | | | | |
| **Cg1-Cg2**$^{i}$ | 3.574(2) | 2.27(13) | 3.441(2) | 3.459(2) | 0.900 |
| **Cg2-Cg1**$^{i}$ | 3.574(2) | 2.27(13) | 3.459(2) | 3.441(2) | 0.966 |
| **DHMC** | | | | | |
| **Cg1-Cg4**$^{ii}$ | 3.603(5) | 3.9(4) | 3.311(4) | 3.349(4) | 1.331 |
| **Cg1-Cg4**$^{iii}$ | 3.571(5) | 3.9(4) | 3.525(4) | 3.478(4) | 0.806 |
| **Cg2-Cg3**$^{ii}$ | 3.547(5) | 3.7(4) | 3.456(4) | 3.496(4) | 0.599 |
| **Cg2-Cg3**$^{iii}$ | 3.602(5) | 3.7(4) | 3.385(4) | 3.331(4) | 1.371 |
| **DHEOMC** | | | | | |
| **Cg1-Cg1**$^{iv}$ | 3.342(2) | 0.03(10) | 3.279(8) | 3.279(8) | 0.645 |

Cg = Centroid of the interacting ring. Cg1: O1, C2, C3, C4, C9, C10; Cg2: C5, C6, C7, C8, C10, C9.

Cg···Cg: distance between centroids; ANG: dihedral angle between planes containing both rings; Cg···plane: distance from one centroid to the plane containing the other ring. Slippage: distance between one centroid and its perpendicular projection to the plane containing the second ring. Symmetry codes: (i) -x, 1-y, 2-z; (ii) x, y, z; (iii) x, 1+y, z; (iv) 1-x, 1-y, 1-z.

**Table S3:** Geometrical parameters for O-H··O hydrogen bonds and C-H··O-type contacts in HEOMC, DHMC and DHEOMC.

| D–H···A | D···A (Å) | Angle (°) |
|---|---|---|
| | **HEOMC** | |
| $O_{1W}$–$H_{1WA}$···$O_{11}^{i}$ | 2.874(3) | 175 |
| $O_{1W}$–$H_{1WB}$···$O_{16}^{ii}$ | 2.712(3) | 175 |
| $O_{16}$–$H_{16}$···$O_{1W}^{iii}$ | 2.716(3) | 171 |
| $C_{12}$–$H_{12C}$···$O_{11}^{iv}$ | 3.468(3) | 167 |
| $C_{8}$–$H_{8}$···$O_{11}^{v}$ | 3.573(4) | 166 |
| | **DHMC** | |
| $O_{19A}$–$H_{19A}$···$O_{41A}^{vi}$ | 2.673(14) | 163 |
| $O_{21A}$–$H_{21A}$···$O_{19A}^{vii}$ | 2.690(12) | 158 |
| $O_{49A}$–$H_{49A}$···$O_{51A}^{vii}$ | 2.694(12) | 158 |
| $C_{3A}$–$H_{3A}$···$O_{49A}^{viii}$ | 3.336(15) | 152 |
| $C_{5A}$–$H_{5A}$···$O_{17A}^{ix}$ | 3.446(15) | 172 |
| $C_{12}$–$H_{12}$···$O_{17A}^{ix}$ | 3.301(13) | 158 |
| $C_{20A}$–$H_{20B}$···$O_{11A}^{iv}$ | 3.397(14) | 155 |
| $C_{33A}$–$H_{33A}$···$O_{21A}^{viii}$ | 3.313(13) | 150 |
| $C_{35A}$–$H_{35A}$···$O_{47A}^{viii}$ | 3.470(16) | 175 |
| $C_{50A}$–$H_{50A}$···$O_{41A}^{x}$ | 3.387(15) | 163 |
| | **DHEOMC** | |
| $O_{22}$–$H_{22}$···$O_{20}^{xi}$ | 2.904(2) | 137 |
| $O_{24}$–$H_{24}$···$O_{22}^{iv}$ | 2.746(2) | 163 |
| $C_{3}$–$H_{3}$···$O_{11}^{xii}$ | 3.578(2) | 171 |
| $C_{21}$–$H_{21A}$···$O_{11}^{xiii}$ | 3.403(3) | 132 |
| $C_{19}$–$H_{19A}$···$O_{11}^{xiii}$ | 3.458(4) | 137 |

D = donor; A = acceptor. Symmetry codes: (i) 1/2-x, -1/2+y, 3/2-z; (ii) x, y, -1+z; (iii) -1/2+x, 1/2-y, 1/2+z; (iv) -1+x, y, z; (v) 1-x, 1-y, 2-z; (vi) x, 1+y, z; (vi) x, -1+y, z; (viii) x, 1-y, -1/2+z; (ix) x, 2-y, -1/2+z; (x) 1+x, 1-y, ½+z; (xi) -1-x, -y, -z; (xii) 2-x, 1-y, 1-z; (xiii) –x, -y, -z.

**Table S4:** DSC results.

| COUMARIN | DSC Heating | | | | DSC Cooling | | | |
|---|---|---|---|---|---|---|---|---|
| | **Tm-onset (ºC)** | **Tm-peak (ºC)** | **Tm-endset (ºC)** | **ΔHm (J/g)** | **Tc-onset (ºC)** | **Tc-peak (ºC)** | **Tc-endset (ºC)** | **ΔHc (J/g)** |
| HMC | 185.2 | 187.9 | 189.4 | 127.7 | 153.6 | 151.5 | 149.9 | -93.2 |
| DHMC | 119.3 | 120.9 | 122.6 | 93.9 | -- | -- | -- | -- |
| HEOMC | 148.9 | 149.3 | 150.9 | 130.4 | 77.0 | 73.9 | 71.6 | -71.3 |
| DHEOMC | 120.3 | 122.7 | 124.2 | 122.9 | -- | -- | -- | -- |

Tm-onset: onset melting temperature

Tm-peak: peak melting temperature

Tm-endset: endset melting temperature

ΔHm: melting enthalpy

Tc-onset: onset crystallization temperature

Tc-peak: peak crystallization temperature

Tc-endset: endset crystallization temperature

ΔHc: crystallization enthalpy

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