Supporting Information for

A sustainable innovation for the tandem synthesis of sugar-containing coumarin Derivatives Catalyzed by Lipase TL IM from *Thermomyces lanuginosus* under Continuous-flow Microreactors

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Materials

Unless otherwise stated, all chemicals were obtained from commercial sources and used without further purification. Lipozyme TL IM from *Thermomyces lanuginosus* was purchased from Novo Nordisk. Salicylaldehyde, 3-Methoxysalicylaldehyde and Diethyl malonate were purchased from Aldrich, 5-Chlorosalicylaldehyde, Dimethyl malonate and Di-tert-Butyl malonate were purchased from Energy Chemical. 2,4-Dihydroxybenzaldehyde and 5-Methylsalicyladehyde were purchased from Macklin. D-glucose, D-mannose, Sucrose, Maltose were purchased from China pharmaceutical group chemical reagents Co., Ltd. Harvard Apparatus PHD 2000 syringe pumps were purchased from Harvard.

Purification of the Products

When the conversion of salicylaldehyde to coumarin derivatives reached the maximum value (determined by TLC), 20 ml of water was then added to the resulting mixture, and the resulting mixture was extracted three times with 20mL of EA. The combined extracts were dried over anhydrous Na_2SO_4 and the solvents were then removed under reduced pressure. The crude products were purified by column chromatography with petroleum ether/ethyl acetate (3:1, by vol) as eluent. The purification was monitored by TLC. The fractions containing the main products were pooled, the solvent evaporated, and the residue analyzed by ^{1}H NMR, ^{13}C NMR, ESI-MS.

When the conversion of coumarin to sugar-containing coumarin derivatives reached the maximum value (determined by TLC), the reaction was terminated by filtering the enzyme, and the tert-amyl alcohol solvent was evaporated under reduced pressure. The products (**5a, 5b, 5e, 5f, 5i, 5j, 5m, 5n, 5q, 5r**) were eluted by

dichloromethane: methanol (10:1.5, by vol), The products (**5c, 5d, 5g, 5h, 5k, 5l, 5o, 5p, 5s, 5t**) were eluted by dichloromethane: methanol (10:2, by vol). The purification was monitored by TLC. The fractions containing the main products were pooled, the solvent evaporated, and the residue analyzed by ^{1}H NMR, ^{13}C NMR, ESI-MS.

Thin-Layer Chromatography

Analytical TLC was performed on silica gel 60 plates (Merck) using ethyl acetate: methanol: water (1.7:0.2:0.1, by vol) as developing solvent. Spots were detected by ultraviolet irradiation at 254 nm.

Experiment

General Procedure for Sugar-containing Coumarin Derivatives Synthesis in Continuous Flow Microreactors

Method A: 20 mmol salicylaldehyde derivative (salicylaldehyde, 5-chlorosalicylaldehyde, 5-methylsalicyladehyde, 2,4-dihydroxybenzaldehyde or 3-methoxysalicylaldehyde) was dissolved in 2.5 mL DMSO solution (feed **1**). 40 mmol diester malonate derivative (dimethyl malonate, diethyl malonate or di-tert-butyl malonate) was dissolved in 2.5 mL DMSO solution (feed **2**). Two solutions were put into 10 mL injector respectively. The mixture of 870 mg catalyst (104.4 mg K_2CO_3 and 765.6 mg lipozyme TL IM) was filled in PFA tubing (inner diameter ID=2.0 mm, length=100 cm). Feed **1** and **2** were mixed together at 31.2 μL min^{-1} flow rate in a Y-mixer at 40 °C and the resulting stream (62.4μL min^{-1}) was connected to a sample vial which was used to collect the final mixture. The reaction temperature was controlled by a water bath thermostat. Then 9.48 mL tert-amyl alcohol was slowly dripped with 0.52 mL reaction solution (feed **3**). 0.5 mmol sugar compounds (D-glucose, D-mannose, sucrose or maltose) were dissolved in 0.52 mL DMSO, and 9.48 mL *tert*-amyl alcohol was slowly dripped (feed **4**). 870 mg lipozyme TL IM was filled in PFA tubing (inner diameter ID=2.0 mm, length=100 cm). Feed **3** and **4** were mixed together at 7.8 μL min^{-1}flow rate in a Y-mixer at 35 °C and the resulting stream (15.6 μL min^{-1}) was connected to a sample vial which was used to collect the final mixture. The final mixture was then evaporated, and the oily residue was submitted to column chromatography on silica gel (200–300 mesh). The fractions containing the main products were pooled, the solvent evaporated, and the residue analyzed by ^{1}H NMR, ^{13}C NMR, ESI-MS.

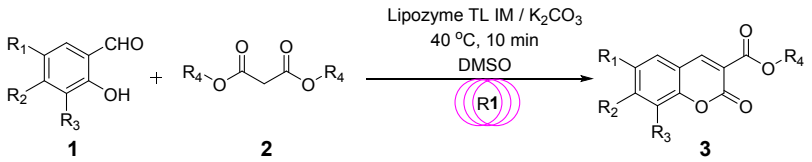
General Procedure for Sugar-containing Coumarin Derivatives Synthesis in shaker reactor.

Method B: 0.25 mmol salicylaldehyde derivative (salicylaldehyde, 5-chlorosalicylaldehyde, 5-methylsalicyladehyde, 2,4-dihydroxybenzaldehyde or 3-methoxysalicylaldehyde) was added in to 5 mL DMSO and 0.5 mmol diester malonate derivative (dimethyl malonate, diethyl malonate or di-tert-butyl malonate) was added. The 145 mg catalyst (25 mg K_2CO_3 and 120 mg lipozyme TL IM) was then added and the suspension maintained at

55 °C for 16 h under shaker reactors. Aliquots were withdrawn at different times, analyzed by TLC. When the conversion of salicylaldehyde derivative to intermidiates reached the maximum value (determined by TLC), the mixture was cooled and filtered. The reaction liquid was extracted by ice water and ethyl acetate, and the residue was submitted to column chromatography on silica gel (200–300 mesh). The intermediates were eluted by ethyl acetate: petroleum ether (1:3, by vol). The purification was monitored by TLC. The fractions containing the main products were pooled, the solvent evaporated. 0.5 mmol intermediates (**3b, 3e, 3h, 3k, 3n**) were added in to 0.26 mL DMSO and 0.125 mmol of sugar compounds (D-glucose, D-mannose, sucrose or maltose), slowly dripping 4.74 mL tert-amyl alcohol after full dissolution. The biocatalyst (40 mg/mL, 200 mg) was then added and the suspension maintained at 45 °C for 24 h under shaker reactors. Aliquots were withdrawn at different times, analyzed by TLC. When the conversion of sugar-containing coumarin derivatives to target products reached the maximum value (determined by TLC). The tert-amyl alcohol was evaporated under reduced pressure, and the oily residue was submitted to column chromatography on silica gel (200–300 mesh). The purification was monitored by TLC. The fractions containing the main products were pooled, the solvent evaporated, and the residue analyzed by ^{1}H NMR, ^{13}C NMR, ESI-MS.

Exploration of Reaction

Table S1 Continuous flow for the synthesis of coumarin derivatives[a]

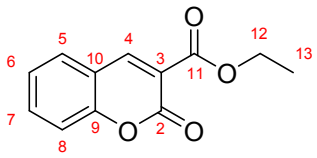


Entry	R_1	R_2	R_3	R_4	Product	Yield[b] (%)
1	H	H	H	CH_2CH_3	**3a**	92
2	H	H	H	CH_3	**3b**	94
3	H	H	H	$C(CH_3)_3$	**3c**	66
4	Cl	H	H	CH_2CH_3	**3d**	91
5	Cl	H	H	CH_3	**3e**	94
6	Cl	H	H	$C(CH_3)_3$	**3f**	64
7	CH_3	H	H	CH_2CH_3	**3g**	94
8	CH_3	H	H	CH_3	**3h**	95
9	CH_3	H	H	$C(CH_3)_3$	**3i**	68
10	H	H	OCH_3	CH_2CH_3	**3j**	87
11	H	H	OCH_3	CH_3	**3k**	89
12	H	H	OCH_3	$C(CH_3)_3$	**3l**	58

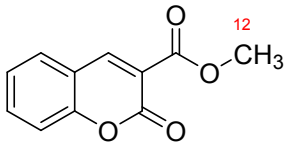
13	H	OH	H	CH_2CH_3	**3m**	78
14	H	OH	H	CH_3	**3n**	84
15	H	OH	H	$C(CH_3)_3$	**3o**	55

[a] Reaction conditions: feed **1**, salicylaldehyde derivative (2 mmol) was dissolved in 10 mL DMSO; feed **2**, diester malonate derivative (1 mmol) was dissolved in 10 mL DMSO, reacted in continuous flow microreactors catalyzed by mixed catalyst K_2CO_3/lipozyme TL IM (104.4 mg K_2CO_3 and 765.6 mg lipozyme TL IM) at 40 °C for 10 min. [b] Isolated yields.

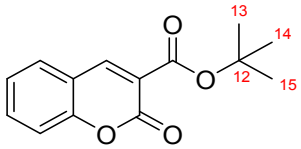
Experimental data of products



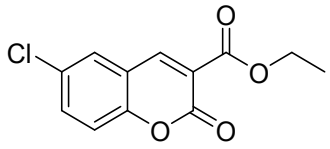
Ethyl coumarin-3-carboxylate (3a)[S1]**:** white solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.54 (s, 1H, H-4), 7.68 – 7.61 (m, 2H, H-5, H-7), 7.39 – 7.33 (m, 2H, H-6, H-8), 4.43 (q, *J* = 7.1 Hz, 2H, H-12), 1.42 (t, *J* = 7.1 Hz, 3H, H-13). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.06 (C-11), 156.71 (C-2), 155.16 (C-9), 148.59 (C-4), 134.32 (C-7), 129.48 (C-5), 124.83 (C-6), 118.34 (C-10), 117.88 (C-3), 116.80 (C-8), 62.00 (C-12), 14.24 (C-13).



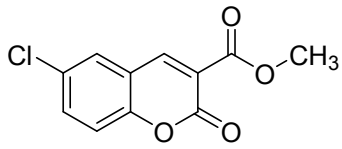
Methyl coumarin-3-carboxylate (3b)[S1]: white solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.58 (s, 1H, H-4), 7.69 – 7.61 (m, 2H, H-5, H-7), 7.39 – 7.33 (m, 2H, H-6, H-8), 3.96 (s, 3H, H-12). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.71 (C-11), 156.70 (C-2), 155.22 (C-9), 149.17 (C-4), 134.49 (C-7), 129.57 (C-5), 124.90 (C-6), 117.93 (C-10), 117.85 (C-8), 116.81 (C-3), 52.94 (C-12).



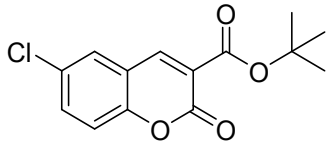
Tert-butyl coumarin-3-carboxylate (3c)[S2]: white solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.40 (s, 1H, H-4), 7.65 – 7.58 (m, 2H, H-5, H-7), 7.36 – 7.31 (m, 2H, H-6, H-8), 1.61 (s, 9H, H-13, H-14, H-15). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.93 (C-11), 156.83 (C-2), 155.02 (C-9), 147.43 (C-4), 133.92 (C-7), 129.30 (C-5), 124.67 (C-6), 119.69 (C-10), 117.96 (C-8), 116.70 (C-3), 82.83 (C-12), 28.11 (3C, C-13, C-14, C-15).



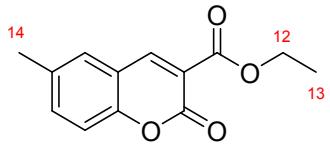
Ethyl 6-chlorocoumarin-3-carboxylate (3d)[S1]: white solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.45 (s, 1H, H-4), 7.62 – 7.58 (m, 2H, H-5, H-7), 7.35 – 7.31 (m, 1H, H-8), 4.44 (q, *J* = 7.1 Hz, 2H, H-12), 1.43 (t, *J* = 7.1 Hz, 3H, H-13). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.70 (C-11), 156.06 (C-2), 153.50 (C-9), 147.14 (C-4), 134.17 (C-7), 130.17 (C-5), 128.45 (C-6), 119.56 (C-10), 118.84 (C-3), 118.30 (C-8), 62.25 (C-12), 14.22 (C-13).



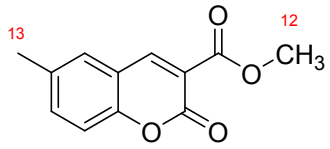
Methyl 6-chlorocoumarin-3-carboxylate (3e) [S1]: white solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (s, 1H, H-4), 8.07 (d, *J* = 2.6 Hz, 1H, H-5), 7.79 (dd, *J* = 8.9, 2.6 Hz, 1H, H-7), 7.50 (d, *J* = 8.9 Hz, 1H, H-8), 3.85 (s, 3H, H-12). ^{13}C NMR (126 MHz, DMSO) δ 162.83 (C-11), 155.48 (C-2), 153.17 (C-9), 147.66 (C-4), 133.89 (C-7), 129.08 (C-5), 128.45 (C-6), 119.14 (C-10), 118.51 (C-8), 118.18 (C-3), 52.52 (C-12).



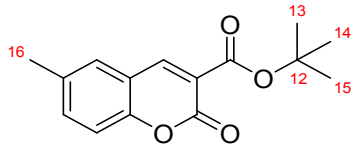
Tert-butyl 6-chlorocoumarin-3-carboxylate (3f): white solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.38 (s, 1H, H-4), 7.60 – 7.56 (m, 2H, H-5, H-7), 7.33 – 7.30 (m, 1H, H-8), 1.60 (s, 9H, H-13, H-14, H-15). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.65 (C-11), 156.26 (C-2), 153.51 (C-9), 147.02 (C-4), 134.25 (C-7), 130.30 (C-5), 128.44 (C-6), 119.68 (C-10), 118.97 (C-8), 118.43 (C-3), 82.90 (C-12), 28.12 (3C, C-13, C-14, C-15).



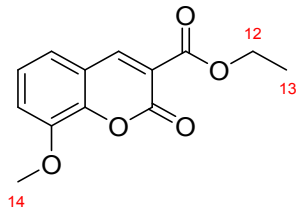
Ethyl 6-methylcoumarin-3-carboxylate (3g) [S1]: white solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.59 (s, 1H, H-4), 7.48 (dd, *J* = 8.6, 2.0 Hz, 1H, H-7), 7.41 (d, *J* = 2.0 Hz, 1H, H-5), 7.26 (d, *J* = 8.6 Hz, 1H, H-8), 4.39 (q, *J* = 7.1 Hz, H-12), 2.43 (s, 3H, H-14), 1.40 (t, *J* = 7.1 Hz, 3H, H-13). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.12 (C-11), 157.43 (C-2), 153.08 (C-9), 148.71 (C-4), 135.30 (C-6), 135.04 (C-7), 129.31 (C-5), 117.76 (C-3), 117.53 (C-)10, 115.79 (C-8), 61.49 (C-12), 19.21 (C-14), 13.51 (C-13).



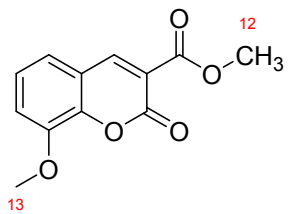
Methyl 6-methylcoumarin-3-carboxylate (3h) [S1]: white solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.51 (s, 1H, H-4), 7.46 (dd, *J* = 8.6, 2.1 Hz, 1H, H-7), 7.39 (d, *J* = 2.1 Hz, 1H, H-5), 7.25 (d, *J* = 8.6 Hz, 1H, H-8), 3.95 (s, 3H, H-12), 2.43 (s, 3H, H-13). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.84 (C-11), 156.94 (C-2), 153.39 (C-9), 149.15 (C-4), 135.63 (C-6), 134.73 (C-7), 129.15 (C-5), 117.73 (C-10), 117.60 (C-8), 116.49 (C-3), 52.86 (C-12), 20.68 (C-13).



Tert-butyl 6-methylcoumarin-3-carboxylate (3i) [S2]: white solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50 (s, 1H, H-4), 7.45 (dd, *J* = 8.5, 2.0 Hz, 1H, H-7), 7.41 (d, *J* = 2.0 Hz, 1H, H-5), 7.24(d, *J* = 8.5 Hz, 1H, H-8), 2.43 (s, 3H, H-16), 1.60 (s, 9H, H-13, H-14, H-15). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.99 (C-11), 157.43 (C-2), 153.10 (C-9), 148.65 (C-4), 135.21 (C-6), 135.11 (C-7), 129,44 (C-5), 117.82 (C-10), 117.46 (C-8), 115.68 (C-3), 82.70 (C-12), 28.01 (3C, C-13, C-14, C-15), 19.20 (C-16).

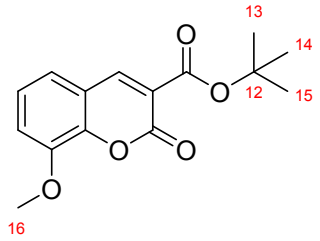


Ethyl 8-methoxycoumarin-3-carboxylate (3j) [S3]: light yellow solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50 (s, 1H, H-4), 7.30 – 7.23 (m, 1H, H-5), 7.19-7.17 (m, 2H, H-6, H-7), 4.42 (q, *J* = 7.1 Hz, 2H, H-12), 3.98 (s, 3H, H-14), 1.41 (t, *J* = 7.1 Hz, 3H, H-13). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.09 (C-11), 156.11 (C-2), 148.77 (C-8), 147.06 (C-9), 144.87 (C-4), 124.66 (C-6), 120.57 (C-5), 118.53 (C-3), 118.45 (C-7), 115.78 (C-10), 61.96 (C-12), 56.31 (C-14), 14.22 (C-13).

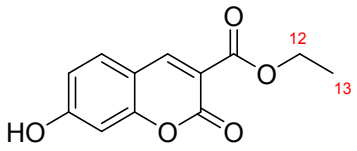


Methyl 8-methoxycoumarin-3-carboxylate (3k) [S4]: light yellow solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.56 (s, 1H, H-4), 7.29-7.28 (m, 1H, H-5), 7.20-7.18 (m, 2H, H-6, H-7) , 3.98 (s, 3H, H-13), 3.96 (s, 3H, H-12). ^{13}C NMR

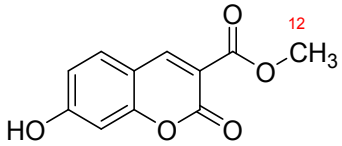
(126 MHz, $CDCl_3$) δ 163.83 (C-11), 156.14 (C-2), 149.41 (C-8), 147.10 (C-9), 144.96 (C-4), 124.74 (C-6), 120.65 (C-5), 118.45 (C-3), 118.17 (C-7), 115.90 (C-10), 56.33 (C-13), 52.94 (C-12).



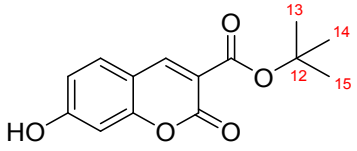
Tert-butyl 8-methoxycoumarin-3-carboxylate (3l): light yellow solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.53 (s, 1H, H-4), 7.29-7.25 (m, 1H, H-5), 7.20-7.17 (m, 2H, H-6, H-7), 3.97 (s, 3H, H-16), 1.61 (s, 9H, H-13, H-14, H-15). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.98 (C-11), 156.07 (C-2), 148.92 (C-8), 147.00 (C-9), 144.78 (C-4), 124.53 (C-6), 120.51 (C-5), 118.59 (C-3), 118.40 (C-7), 115.67 (C-10), 82.81 (C-12), 56.32 (C-16), 28.02 (3C, C-13, C-14, C-15).



Ethyl 7-hydroxycoumarin-3-carboxylate (3m) [S3]: light yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.71 (s, 1H, H-4), 7.75 (d, J = 8.6 Hz, 1H, H-5), 6.85 (dd, J = 8.6, 2.3 Hz, 1H, H-6), 6.74 (d, J = 2.3 Hz, 1H, H-8), 4.38 (q, J = 7.1 Hz, 2H, H-12), 1.41 (t, J = 7.1 Hz, 3H, H-13). ^{13}C NMR (126 MHz, DMSO) δ 164.52 (C-11), 163.61 (C-7), 158.40 (C-2), 157.74 (C-9), 149.88 (C-4), 131.39 (C-5), 114.64 (C-10), 112.20 (C-3), 110.78 (C-6), 102.36 (C-8), 61.53 (C-12), 13,94 (C-13).

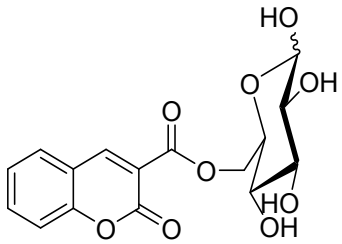


Methyl 7-hydroxycoumarin-3-carboxylate (3n) [S5]: light yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.70 (s, 1H, H-4), 7.76 (d, J = 8.6 Hz, 1H, H-5), 6.85 (dd, J = 8.6, 2.3 Hz, 1H, H-6), 6.73 (dd, J = 2.2, 0.6 Hz, 1H, H-8), 3.80 (s, 3H, H-12). ^{13}C NMR (126 MHz, DMSO) δ 164.19 (C-11), 163.51 (C-7), 157.17 (C-2), 156.39 (C-9), 149.76 (C-4), 132.18 (C-5), 114.06 (C-10), 111.76 (C-3), 110.44 (C-6), 101.80 (C-8), 52.13 (C-12).

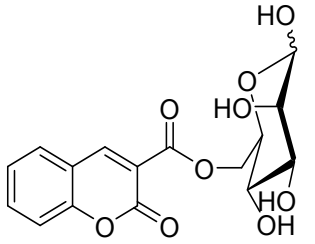


Tert-butyl 7-hydroxycoumarin-3-carboxylate (3o): light yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.67 (s, 1H, H-4), 7.76 (d, J = 8.5 Hz, 1H, H-5), 6.88 (dd, J = 8.5, 2.2 Hz, 1H, H-6), 6.73 (d, J = 2.2, Hz, 1H, H-8), 1.60 (s,

9H, H-13, H-14, H-15). ^{13}C NMR (126 MHz, DMSO) δ 164.55 (C-11), 163.62 (C-7), 158.50 (C-2), 157.89 (C-9), 149.92 (C-4), 131.23 (C-5), 114.64 (C-10), 112.21 (C-3), 110.78 (C-6), 102.18 (C-8), 82.84 (C-12), 28.09 (3C, C-13, C-14, C-15).

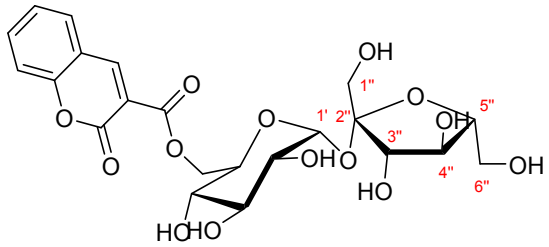


6'-O-D-glucosyl coumarin-3-carboxylate (5a) : white solid, mp 200-203 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.71 (s, 0.28H, H-4 of β-D-glucose), 8.69 (s, 0.72H, H-4 of α-D-glucose), 7.94-7.89 (m, 1H, H-5), 7.78-7.72 (m, 1H, H-7), 7.45-7.40 (m, 2H, H-8, H-6), 6.71 (d, *J* = 6.7 Hz, 0.28H, C1'-OH of β-D-glucose), 6.38 (d, *J* = 3.7 Hz, 0.72H, C1'-OH of α-D-glucose), δ 5.20 (d, *J* = 4.9 Hz, 0.28H, C1'-H of β-D-glucose), 5.14 (d, *J* = 5.6 Hz, 0.72H, C1'-H of α-D-glucose), 5.00 (d, *J* = 3.9 Hz, 0.28H, C4'-OH of β-D-glucose), 4.96-4.93 (m, 1H, C2'-OH of β-D-glucose, C4'-OH of α-D-glucose), 4.80 (d, *J* = 4.7 Hz, 0.72H, C2'-OH of β-D-glucose), 4.57 (d, *J* = 6.6 Hz, 0.72H, C3'-OH of α-D-glucose), 4.54 (dd, *J* = 11.8, 1.9 Hz, 0.28H, C6'-Ha of β-D-glucose), 4.49 (dd, *J* = 11.7, 2.1 Hz, 0.72H, C6'-Ha of α-D-glucose), 4.36 (dd, *J* = 7.7, 6.5 Hz, 0.28H, C3'-OH of β-D-glucose), 4.34-4.27 (m, 1H, C6'-Hb of D-glucose), 3.93 (ddd, *J* = 10.1, 6.0, 2.1 Hz, 0.72H, C5'-H of α-D-glucose), 3.53-3.47 (m, 1H, C3'-H of α-D-glucose, C5'-H of β-D-glucose), 3.25 – 3.17 (m, 2H, C2'-H, C4'-H of α-D-glucose, C2'-H, C3'-H of -D-glucose), 2.97 (td, *J* = 8.0, 4.2 Hz, 0.28H, C4'-H of β-D-glucose). ^{13}C NMR (126 MHz, DMSO) δ 162.53, 162.49 (C-11), 155.93 (C-2), 154.55, 154.53 (C-9), 148.65, 148.54 (C-4), 134.58, 134.56 (C-7), 130.27 (C-5), 124.88 (C-6), 117.72 (C-10), 117.69, 117.61 (C-8), 116.20 (C-3), 97.00 (C-1' of β-D-glucose), 92.38 (C-1' of α-D-glucose), 76.46 (C-3' of β-D-glucose), 74.71 (C-2' of β-D-glucose), 73.49 (C-5' of β-D-glucose), 72.91 (C-3' of α-D-glucose), 72.16 (C-2' of α-D-glucose), 70.57 (C-4' of α-D-glucose), 70.17 (C-4' of β-D-glucose), 69.20 (C-5' of α-D-glucose), 65.22 (C-6' of D-glucose). HRMS: $C_{16}H_{16}O_9Na$ for $[M+Na]^+$, calculated 375.0692, found 375.0693.

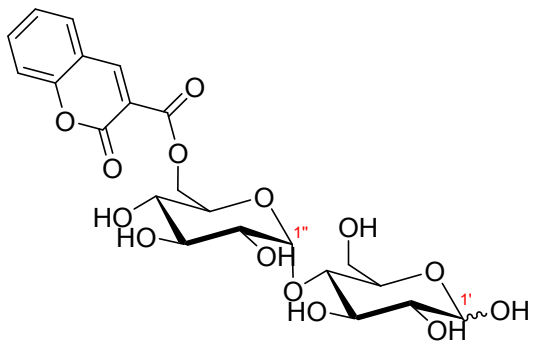


6'-O-D-mannosyl coumarin-3-carboxylate (5b) : white solid, mp 171-172 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.74 (s, 1H, H-4), 7.89 (dd, *J* = 7.8, 1.6 Hz, 1H, H-5), 7.76 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H, H-7), 7.49 – 7.40 (m, 2H,

H-8, H-6), 6.41 (d, *J* = 4.4 Hz, 1H, C1'-OH of D-mannose), 5.01 (d, *J* = 5.6 Hz, 1H, C1'-H of D-mannose), 4.90 (d, *J* = 4.4 Hz, 1H, C4'-OH of D-mannose), 4.72 (d, *J* = 4.1 Hz, 1H, C3'-OH of D-mannose), 4.64 (d, *J* = 5.5 Hz, 1H, C2'-OH of D-mannose), 4.55 (dd, *J* = 11.6, 2.2 Hz, 1H, C6'-Ha of D-mannose), 4.30 (dd, *J* = 11.6, 6.2 Hz, 1H, C6'-Hb of D-mannose), 3.84 (ddd, *J* = 8.7, 6.2, 2.1 Hz, 1H, C5'-H of D-mannose), 3.63 – 3.56 (m, 2H, C2'-H, C3'-H of D-mannose), 3.55 (dd, *J* = 9.4, 5.5 Hz, 1H, C4'-H of D-mannose). ^{13}C NMR (126 MHz, DMSO) δ 162.43 (C-11), 156.06 (C-2), 154.52 (C-9), 148.53 (C-4), 134.59 (C-7), 130.23 (C-5), 124.96 (C-6), 117.88 (C-10), 117.77 (C-8), 116.28 (C-3), 94.16 (C-1'), 71.36 (C-2'), 70.53 (C-3'), 70.34 (C-5'), 67.13 (C-4'), 65.16 (C-6'). HRMS: $C_{16}H_{16}O_9Na$ for $[M+Na]^+$, calculated 375.0692, found 375.0693.

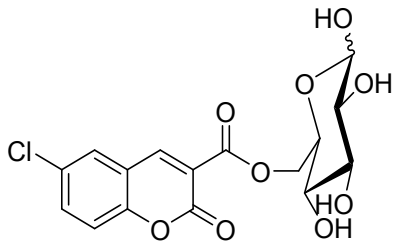


6'-O-D-sucrosyl coumarin-3-carboxylate (5c): syrup liquid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.74 (s, 1H, H-4), 7.94 (dd, *J* = 7.8, 1.6 Hz, 1H, H-1), 7.75 (ddd, *J* = 8.4, 7.3, 1.6 Hz, 1H, H-7), 7.46-7.39 (m, 2H, H-8, H-6), 5.23 (d, *J* = 3.7 Hz, 1H, C1'-H), 5.16 (d, *J* = 5.9 Hz, 1H, C4'-OH), 5.12 (dd, *J* = 9.3, 6.0 Hz, 2H, C3'-OH, C2'-OH), 4.93 (d, *J* = 4.8 Hz, 1H, C3"-OH), 4.83 (t, *J* = 6.3 Hz, 1H, C1"-OH), 4.66 (d, *J* = 7.9 Hz, 1H, C4"-OH), 4.49 (dd, *J* = 11.8, 1.9 Hz, 1H, C6'-Ha), 4.41 (dd, *J* = 6.0, 4.9 Hz, 1H, C6"-OH), 4.27 (dd, *J* = 11.8, 6.0 Hz, 1H, C6'-Hb), 4.11-4.06 (m, 1H, C5'-H), 3.91 (t, *J* = 8.1 Hz, 1H, C3"-H), 3.79 (td, *J* = 8.0, 5.9 Hz, 1H, C5"-H), 3.56 (tdd, *J* = 11.8, 9.2, 5.9 Hz, 3H, C4"-H, C6"-Ha, C6"-Hb), 3.50-3.46 (m, 1H, C3'-H), 3.42 (d, *J* = 6.3 Hz, 2H, C1"-Ha, C1"-Hb), 3.30-3.20 (m, 2H, C2'-H, C4'-H). ^{13}C NMR (126 MHz, DMSO) δ 162.25 (C-11), 155.95 (C-2), 154.54 (C-9), 148.80 (C-4), 134.52 (C-7), 130.45 (C-5), 124.80 (C-6), 117.78 (C-10), 117.27 (C-8), 116.13 (C-3), 103.99 (C-2"), 91.63 (C-1'), 82.50 (C-5"), 76.89 (C-3"), 74.44 (C-4"), 72.68 (C-3'), 71.50 (C-2'), 70.17 (C-5'), 70.08 (C-4'), 65.03 (C-6'), 62.50 (C-1"), 62.16 (C-6"). HRMS: $C_{22}H_{26}O_{14}Na$ for $[M+Na]^+$, calculated 537.1220, found 537.1218.



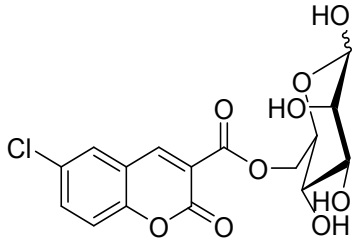
6''-O-D-maltosyl coumarin-3-carboxylate (5d) : syrup liquid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.77 (s, 0.5H,

H-4 of β-D-maltose), 8.75 (s, 0.5H, H-4 of α-D-maltose), 7.94 (td, *J* = 8.2, 1.6 Hz, 1H, H-5), 7.75 (ddd, *J* = 8.4, 7.3, 1.6 Hz, 1H, H-7), 7.47-7.37 (m, 2H, H-8, H-6), 6.69 (d, *J* = 6.4 Hz, 0.5H, C1'-OH of β-D-maltose), 6.36 (d, *J* = 3.9 Hz, 0.5H, C1'-OH of α-D-maltose), 5.56 (t, *J* = 6.2 Hz, 1H, C2"-OH of D-maltose), 5.51 (d, *J* = 3.0 Hz, 0.5H, C3'-OH of β-D-maltose), 5.35 (d, *J* = 3.1 Hz, 0.5H, C3'-OH of α-D-maltose), 5.28 (t, *J* = 5.8 Hz, 1H, C4"-OH of D-maltose), 5.07 (d, *J* = 4.0 Hz, 1.5H, C3"-OH of D-maltose), 5.04 (d, *J* = 3.7 Hz, 0.5H, C1"-H of D-maltose), 4.98 (d, *J* = 4.9 Hz, 0.5H, C1'-H of α-D-maltose), 4.92 (t, *J* = 4.1 Hz, 0.5H, C2'-OH of β-D-maltose), 4.63 (d, *J* = 6.8 Hz, 0.5H, C2'-OH of α-D-maltose), 4.57-4.52 (m, 1H, C6'-OH of D-maltose), 4.51 (t, *J* = 2.2 Hz, 0.5H, C6"-Ha of α-D-maltose), 4.45 (t, *J* = 6.0 Hz, 0.5H, C6"-Hb of β-D-maltose), 4.33 (dd, *J* = 7.7, 6.4 Hz, 0.5H, C1'-H of β-D-maltose), 4.25 (ddd, *J* = 11.7, 6.9, 2.6 Hz, 1H, C6"-Hb of D-maltose), 3.88 (dtd, *J* = 8.7, 6.7, 1.9 Hz, 1H, C6'-Ha of D-maltose), 3.72-3.65 (m, 1.5H, C5'-H, C6'-Hb of α-D-maltose, C6'-Hb of β-D-maltose), 3.61 (dd, *J* = 6.3, 3.5 Hz, 1H, C5"-H of D-maltose), 3.59-3.52 (m, 0.5H, C5'-H of β-D-maltose), 3.49-3.42 (m, 1.5H, C3'-H, C3"-H of α-D-maltose, C3"-H of β-D-maltose), 3.36-3.28 (m, 2H, C2"-H, C4'-H of α-D-maltose, C3'-H, C4'-H of β-D-maltose), 3.26-3.22 (m, 0.5H, C2'-H of α-D-maltose), 3.22-3.15 (m, 1.5H, C4"-H of α-D-maltose, C2"-H, C4"-H of β-D-maltose), 2.99-2.93 (m, 0.5H, C2'-H of β-D-maltose). ^{13}C NMR (126 MHz, DMSO) δ 162.14 (C-11), 155.91, 155.90 (C-2), 154.59 (C-9), 148.83, 148.80 (C-4), 134.62 (C-7), 130.48, 130.42 (C-5), 124.88 (C-6), 117.80 (C-10), 117.16 (C-8), 116.17, 116.15 (C-3), 101.00 (C-1" of β-D-maltose), 100.91 (C-1" of α-D-maltose), 96.81 (C-1' of β-D-maltose), 92.13 (C-1' of α-D-maltose), 80.68 (C-4' of α-D-maltose), 80.18 (C-4' of β-D-maltose), 76.56 (C-3' of β-D-maltose), 75.12 (C-5' of β-D-maltose), 74.31 (C-2' of β-D-maltose), 73.12 (C-3' of α-D-maltose), 73.09 (C-3" of α-D-maltose), 72.98 (C-3" of β-D-maltose), 72.47 (C-2" of β-D-maltose), 72.34 (C-2" of α-D-maltose), 71.86 (C-5" of α-D-maltose), 70.62 (C-5" of β-D-maltose), 70.59 (C-2' of α-D-maltose), 70.35 (C-5' of α-D-maltose), 70.22 (C-4" of α-D-maltose), 70.17 (C-4" of β-D-maltose), 65.24 (C-6" of D-maltose), 60.73 (C-6' of β-D-maltose), 60.61 (C-6' of α-D-maltose). HRMS: $C_{22}H_{26}O_{14}Na$ for $[M+Na]^+$, calculated 537.1220, found 537.1221.

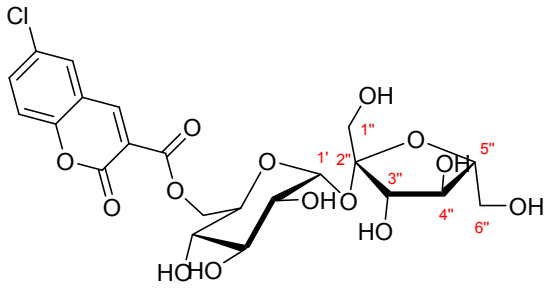


6'-O-D-glucosyl 6-chlorocoumarin-3-carboxylate (5e) : white solid, mp 208-209 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.68 (s, 0.23H, H-4 of β-D-glucose), 8.66 (s, 0.77H, H-4 of α-D-glucose), 8.06 (d, *J* = 2.6 Hz, 1H, H-5), 7.77 (dd, *J* = 8.9, 2.6 Hz, 1H, H-7), 7.49 (d, *J* = 8.8 Hz, 1H, H-8), 6.71 (d, *J* = 6.6 Hz, 0.23H, C1'-OH of β-D-glucose), 6.38 (d, *J* = 3.9 Hz, 0.77H, C1'-OH of α-D-glucose), 5.19 (d, *J* = 5.0 Hz, 0.23H, C1'-H of β-D-glucose), 5.13 (d, *J* =

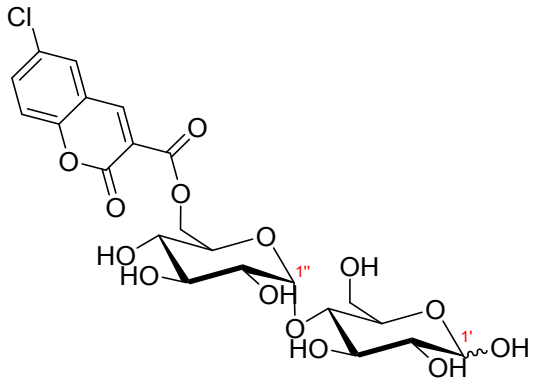
5.7 Hz, 0.77H, C1'-H of α-D-glucose), 5.00 (d, *J* = 4.3 Hz, 0.23H, C4'-OH of β-D-glucose), 4.94 (dd, *J* = 9.6, 4.6 Hz, 1H, C4'-OH of α-D-glucose, C2'-OH of β-D-glucose), 4.81 (d, *J* = 4.7 Hz, 0.77H, C2'-OH of α-D-glucose), 4.58 (d, *J* = 6.7 Hz, 0.77H, C3'-OH of α-D-glucose), 4.53 (dd, *J* = 11.8, 1.9 Hz, 0.23H, , C6'-Ha of β-D-glucose), 4.49 (dd, *J* = 11.7, 2.1 Hz, 0.77H, C6'-Ha of α-D-glucose), 4.39 – 4.27 (m, 1.23H, C3'-OH of β-D-glucose, C6'-Hb of D-glucose), 3.91 (ddd, *J* = 10.0, 5.8, 2.0 Hz, 0.77H, C5'-H of α-D-glucose), 3.49 (td, *J* = 9.1, 4.6 Hz, 1H, C5'-H of β-D-glucose, C3'-H of α-D-glucose), 3.21 (ddt, *J* = 12.2, 9.2, 4.6 Hz, 2H, , C4'-H of α-D-glucose, C3'-H of β-D-glucose, C2'-H of D-glucose), 2.96 (td, *J* = 8.2, 4.7 Hz, 0.23H, C4'-H of β-D-glucose). ^{13}C NMR (126 MHz, DMSO) δ 162.32, 162.28 (C-11), 155.53 (C-2), 153.18 (C-9), 147.43, 147.32 (C-4), 133.94, 133.91 (C-7), 129.12 (C-5), 128.52 (C-6), 119.12 (C-10), 118.81, 118.74 (C-8), 118.25 (C-3), 97.01 (C1' of β-D-glucose), 92.39 (C1' of α-D-glucose), 76.45 (C3' of β-D-glucose), 74.68 (C2' of β-D-glucose), 73.48 (C5' of β-D-glucose), 72.90 (C3' of α-D-glucose), 72.14 (C2' of α-D-glucose), 70.50 (C4' of α-D-glucose), 70.10 (C4' of β-D-glucose), 69.18 (C5' of α-D-glucose), 65.36 (C6' of β-D-glucose), 65.32 (C6' of α-D-glucose). HRMS: $C_{16}H_{15}ClO_9Na$ for $[M+Na]^+$, calculated 409.0297, found 409.0302.



6'-O-D-mannosyl 6-chlorocoumarin-3-carboxylate (5f) : white solid, mp 188-190 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.69 (s, 1H, H-4), 8.01 (d, *J* = 2.6 Hz, 1H, H-5), 7.77 (dd, *J* = 8.9, 2.6 Hz, 1H, H-7), 7.49 (d, *J* = 8.8 Hz, 1H, H-8), 6.40 (d, *J* = 4.4 Hz, 1H, C1'-OH of D-mannose), 4.99 (d, *J* = 5.6 Hz, 1H, C4'-OH of D-mannose), 4.90 (dd, *J* = 4.4, 1.4 Hz, 1H, C1'-H of D-mannose), 4.73 (d, *J* = 4.0 Hz, 1H, C3'-OH of D-mannose), 4.65 (d, *J* = 5.3 Hz, 1H, C2'-OH of D-mannose), 4.58 (dd, *J* = 11.5, 2.1 Hz, 1H, C6'-Ha of D-mannose), 4.31 (dd, *J* = 11.6, 6.0 Hz, 1H, C6'-Hb of D-mannose), 3.85 (ddd, *J* = 8.4, 6.1, 2.1 Hz, 1H, C5'-H of D-mannose), 3.63-3.58 (m, 2H, C2'-H, C3'-H of D-mannose), 3.58-3.53 (m, 1H, C4'-H of D-mannose). ^{13}C NMR (126 MHz, DMSO) δ 162.19 (C-11), 155.59 (C-2), 153.12 (C-9), 147.20 (C-4), 133.89 (C-7), 128.97 (C-5), 128.57 (C-6), 119.11 (C-10), 119.04 (C-8), 118.29 (C-3), 94.13 (C-1'), 71.34 (C-2'), 70.52 (C-3'), 70.30 (C-5'), 67.07 (C-4'), 65.19 (C-6'). HRMS: $C_{16}H_{15}ClO_9Na$ for $[M+Na]^+$, calculated 409.0302, found 409.0303.

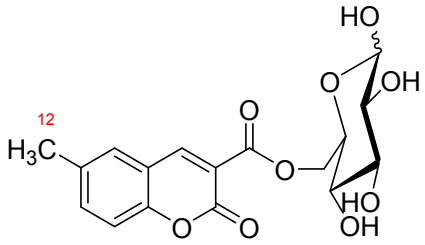


6'-O-D-sucrosyl 6-chlorocoumarin-3-carboxylate (5g) : syrup liquid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.70 (s, 1H, H-4), 8.07 (d, J = 2.6 Hz, 1H, H-5), 7.77 (dd, J = 8.9, 2.6 Hz, 1H, H-7), 7.48 (d, J = 8.8 Hz, 1H, H-8), 5.21 (d, J = 3.7 Hz, 1H, C1'-OH), 5.16 (d, J = 5.9 Hz, 1H, C4'-OH), 5.12 (d, J = 5.6 Hz, 1H, C3'-OH), 5.09 (d, J = 6.3 Hz, 1H, C2'-OH), 4.93 (d, J = 4.8 Hz, 1H, C3"-OH), 4.83 (t, J = 6.3 Hz, 1H, C1"-OH), 4.68 (d, J = 7.8 Hz, 1H, C4"-OH), 4.47 (dd, J = 11.8, 1.8 Hz, 1H, C6'-Ha), 4.41 (dd, J = 6.0, 4.9 Hz, 1H, C6"-OH), 4.27 (dd, J = 11.8, 6.1 Hz, 1H, C6"-Hb), 4.07 (ddd, J = 10.1, 6.0, 1.9 Hz, 1H, C5'-H), 3.90 (t, J = 8.1 Hz, 1H, C3"-H), 3.78 (td, J = 8.0, 5.9 Hz, 1H, C5"-H), 3.59 – 3.50 (m, 3H, C4"-H, C6"-Ha, C6"-Hb), 3.48 – 3.44 (m, 1H, C3'-H), 3.40 (d, J = 6.3 Hz, 2H, C1"-Ha, C1"-Hb), 3.29 – 3.18 (m, 2H, C2"-H, C4'-H). ^{13}C NMR (126 MHz, DMSO) δ 161.98 (C-11), 155.53 (C-2), 153.17 (C-9), 147.56 (C-4), 133.87 (C-7), 129.29 (C-5), 128.45 (C-6), 119.16 (C-10), 118.37 (C-8), 118.16 (C-3), 103.95 (C-2"), 91.53 (C-1'), 82.45 (C-5"), 76.78 (C-3"), 74.38 (C-4"), 72.69 (C-3'), 71.48 (C-2'), 70.13 (C-5'), 70.02 (C-4'), 65.16 (C-6'), 62.47 (C-1"), 62.17 (C-6"). HRMS: $C_{22}H_{25}ClO_{14}Na$ for $[M+Na]^+$, calculated 571.0831, found 571.0830.



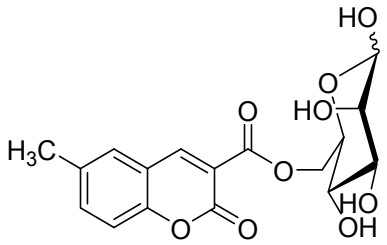
6''-O-D-maltosyl 6-chlorocoumarin-3-carboxylate (5h) : syrup liquid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (s, 0.5H, H-4 β-D-maltose), 8.71 (s, 0.5H, H-4 of α-D-maltose), 8.05 (dd, J = 4.1, 2.6 Hz, 1H, H-5), 7.81-7.74 (m, 1H, H-7), 7.49 (d, J = 8.9 Hz, 1H, H-8), 6.68 (d, J = 6.2 Hz, 0.5H, C1'-OH of β-D-maltose), 6.36 (d, J = 4.4 Hz, 0.5H, C1'-OH of α-D-maltose), 5.58 (d, J = 5.1 Hz, 0.5H, C2"-OH of β-D-maltose), 5.51 (dd, J = 9.3, 4.0 Hz, 1H, C2"-OH of α-D-maltose, C3"-OH of β-D-maltose), 5.32 (d, J = 3.1 Hz, 0.5H, C3'-OH of α-D-maltose), 5.27 (t, J = 5.9 Hz, 1H, C4'-OH of D-maltose), 5.05 (m, 2H, C3"-OH of D-maltose, C1"-H of D-maltose), 4.96 (d, J = 4.4 Hz, 0.5H, C1'-H of α-D-maltose), 4.92 (t, J = 4.0 Hz, 0.5H, C2'-OH of β-D-maltose), 4.62 (d, J = 6.6 Hz, 0.5H, C2'-OH of α-

D-maltose), 4.57 (d, *J* = 6.1 Hz, 0.5H, C6'-OH of β-D-maltose), 4.54-4.46 (m, 1.5H, C6''-Ha of D-maltose, , C6'-OH of α-D-maltose), 4.33 (dd, *J* = 7.6, 6.2 Hz, 0.5H, C1'-H of β-D-maltose), 4.27 (ddd, *J* = 11.5, 7.0, 4.2 Hz, 1H, C6''-Hb of D-maltose), 3.87 (tdd, *J* = 9.0, 6.8, 2.0 Hz, 1H, C6'-H of D-maltose), 3.72-3.65 (m, 1.5H, , C6'-Hb of D-maltose, , C5'-H of α-D-maltose), 3.60 (dddd, *J* = 19.0, 13.6, 8.6, 5.0 Hz, 1H,, C5''-H of D-maltose), 3.52 (td, *J* = 12.0, 11.4, 5.3 Hz, 0.5H, C5'-H of β-D-maltose), 3.48-3.39 (m, 1.5H, C3''-H of D-maltose, , C3'-H of α-D-maltose), 3.34-3.29 (m, 2H, , C4'-H of D-maltose, C2''-H of α-D-maltose, C3'-H of β-D-maltose), 3.26-3.14 (m, 2H, C4''-H of D-maltose, C2'-H of α-D-maltose, C2''-H of β-D-maltose), 2.96 (ddd, *J* = 9.2, 7.7, 4.8 Hz, 0.5H, C2'-H of β-D-maltose). ^{13}C NMR (126 MHz, DMSO) δ 161.92, 161.89 (C-11), 155.47 (C-2), 153.20 (C-9), 147.55, 147.43 (C-4), 133.95 (C-7), 129.15 (C-5), 128.53 (C-6), 119.16 (C-10), 118.33, 118.30 (C-8), 118.20 (C-3), 101.01 (C-1'' of β-D-maltose), 100.85 (C-1'' of α-D-maltose), 96.79 (C-1' of β-D-maltose), 92.10 (C-1' of α-D-maltose), 80.44 (C-4' of D-maltose), 76.54 (C-3' of β-D-maltose), 75.10 (C-5' of β-D-maltose), 74.25 (C-2' of β-D-maltose), 73.07 (C-3' of α-D-maltose), 73.02 (C-3'' of α-D-maltose), 72.40 (C-3'' of β-D-maltose), 72.30 (C-2'' of D-maltose), 71.86 (C-5'' of α-D-maltose), 70.57 (C-5'' of β-D-maltose), 70.51 (C-2' of α-D-maltose), 70.29 (C-5' of α-D-maltose), 70.16 (C-4'' of α-D-maltose), 70.07 (C-4'' of β-D-maltose), 65.31 (C-6'' of D-maltose), 60.73 (C-6' of β-D-maltose), 60.58 (C-6' of α-D-maltose). HRMS: $C_{22}H_{25}ClO_{14}Na$ for $[M+Na]^+$, calculated 571.0831, found 571.0833

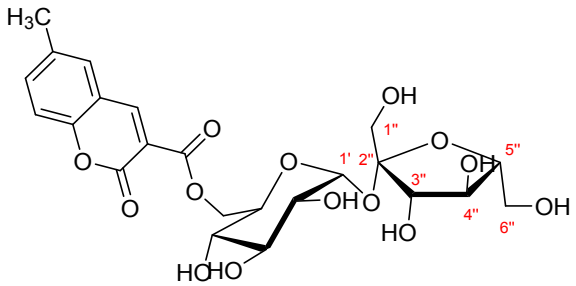


6'-O-D-glucosyl 6-methylcoumarin-3-carboxylate (5i) : white solid, mp 195-196 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.60 (s, 0.75H, H-4 of β-D-glucose), 8.58 (s, 0.25H, , H-4 of α-D-glucose), 7.66 (d, *J* = 2.2 Hz, 1H, H-5), 7.55 (dd, *J* = 8.5, 2.1 Hz, 1H, H-7), 7.32 (d, *J* = 8.5 Hz, 1H, H-8), 6.74 (s, 0.75H, C1'-OH of β-D-glucose), 6.40 (s, 0.25H, C1'-OH of α-D-glucose), 5.40-4.85 (m, 3H, C1'-H, C2'-OH, C3'-OH of D-glucose), 4.68 (d, *J* = 6.7 Hz, 0.25H, C3'-OH of α-D-glucose), 4.52 (dd, *J* = 11.7, 1.9 Hz, 0.75H, C6'-Ha of β-D-glucose), 4.48 (dd, *J* = 11.7, 2.1 Hz, 0.25H, C6'-Ha of α-D-glucose), 4.36 (d, *J* = 7.7 Hz, 0.75H, C3'-OH of β-D-glucose), 4.29 (td, *J* = 12.2, 6.1 Hz, 1H, C6'-Hb of D-glucose), 3.92 (ddd, *J* = 10.1, 5.8, 2.1 Hz, 0.25H, C5'-H of α-D-glucose), 3.48 (ddd, *J* = 9.5, 6.1, 1.7 Hz, 1H, C3'-H of α-D-glucose, C5'-H of β-D-glucose), 3.22 (m, 2H, C2'-H of D-glucose, C4'-H of α-D-glucose, C3'-H of β-D-glucose), 3.01 – 2.95 (m, 0.75H, C4'-H of β-D-glucose), 2.36 (s, 3H, H-12). ^{13}C NMR (126 MHz, DMSO) δ 162.61, 162.57 (C-11), 156.12 (C-2), 152.74, 152.72 (C-9), 148.59, 148.48 (C-4), 135.57, 135.55 (C-6), 134.29 (C-7), 129.72 (C-5), 117.56 (C-10), 117.49, 117.45 (C-8), 116.02 (C-3), 97.06 (C1' of β-D-glucose), 92.44 (C1' of

α-D-glucose), 76.49 (C3' of β-D-glucose), 74.75 (C2' of β-D-glucose), 73.51 (C5' of β-D-glucose), 72.95 (C3' of α-D-glucose), 72.21 (C2' of α-D-glucose), 70.58 (C4' of α-D-glucose), 70.18 (C4' of β-D-glucose), 69.22 (C5' of α-D-glucose), 65.19 (C6'), 20.22 (C-12). HRMS: $C_{17}H_{18}O_9Na$ for $[M+Na]^+$, calculated 389.0843, found 389.0851.

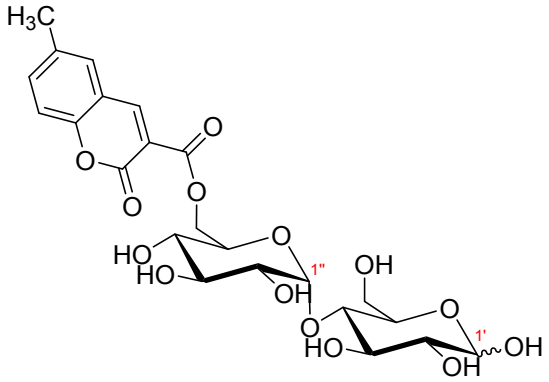


6'-O-D-mannosyl 6-methylcoumarin-3-carboxylate (5j) : white solid, mp 178-179 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.64 (s, 1H, H-4), 7.64 (d, J = 2.1 Hz, 1H, H-5), 7.55 (dd, J = 8.5, 2.1 Hz, 1H, H-7), 7.32 (d, J = 8.4 Hz, 1H, H-8), 6.43 (s, 1H, C1'-OH), 5.19-4.96 (m, 1H, C4'-OH), 4.91 (s, 1H, C1'-H), 4.77 (s, 1H, C3'-OH), 4.57 (dd, J = 11.5, 2.1 Hz, 1H, C6'-Ha), 4.30 (dd, J = 11.6, 5.9 Hz, 1H, C6'-Hb), 3.85 (ddd, J = 8.4, 5.9, 2.1 Hz, 1H, C5'-H), 3.65-3.54 (m, 3H, C2'-H, C2'-OH, C3'-H), 3.54-3.46 (m, 1H, C4'-H), 2.37 (s, 3H, H-12). ^{13}C NMR (126 MHz, DMSO) δ 162.49 (C-11), 156.20 (C-2), 152.66 (C-9), 148.44 (C-4), 135.51 (C-6), 134.31 (C-7), 129.65 (C-5), 117.74 (C-10), 117.47 (C-8), 116.04 (C-3), 94.20 (C-1'), 71.39 (C-2'), 70.57 (C-3'), 70.37 (C-5'), 67.11 (C-4'), 65.00 (C-6'), 20.19 (C-12). HRMS: $C_{17}H_{18}O_9Na$ for $[M+Na]^+$, calculated 389.0843, found 389.0847.



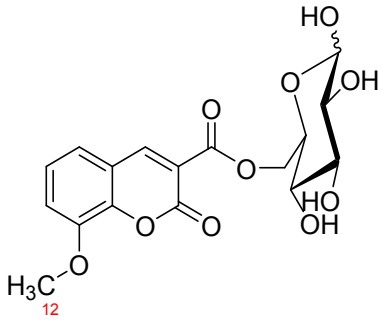
6'-O-D-sucrosyl 6-methylcoumarin-3-carboxylate (5k) : syrup liquid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.66 (s, 1H, H-4), 7.72 (d, J = 2.1 Hz, 1H, H-5), 7.56 (dd, J = 8.5, 2.1 Hz, 1H, H-7), 7.34 (d, J = 8.4 Hz, 1H, H-8), 5.23 (d, J = 3.7 Hz, 1H, C1'-H), 5.19 (d, J = 6.0 Hz, 1H, C4'-OH), 5.14 (dd, J = 10.0, 6.0 Hz, 2H, C2'-OH, C3'-OH), 4.96 (d, J = 4.8 Hz, 1H, C3"-OH), 4.86 (t, J = 6.3 Hz, 1H, C1"-OH), 4.69 (d, J = 7.9 Hz, 1H, C4"-OH), 4.49-4.44 (m, 1H, C6'-Ha), 4.42 (t, J = 5.5 Hz, 1H, C6"-OH), 4.27 (dd, J = 11.8, 5.9 Hz, 1H, C6'-Hb), 4.07 (ddd, J = 10.1, 5.8, 1.8 Hz, 1H, C5'-H), 3.91 (t, J = 8.1 Hz, 1H, C3"-H), 3.79 (td, J = 7.9, 5.8 Hz, 1H, C5"-H), 3.62-3.51 (m, 3H, C4"-H, C6"-Ha, C6"-Hb), 3.49-3.45 (m, 1H, C3'-H), 3.45-3.42 (m, 2H, C1"-Ha, C1"-Hb), 3.31 – 3.21 (m, 2H, C2'-H, C4'-H), 2.37 (s, 3H, H-12). ^{13}C NMR (126 MHz, DMSO) δ 162.35 (C-11), 156.17 (C-2), 152.76 (C-9), 148.77 (C-4), 135.52 (C-6), 134.19 (C-7), 129.97 (C-5), 117.53 (C-10), 117.19 (C-8), 115.95 (C-3), 104.04 (C-2"), 91.67 (C-1'), 82.55 (C-5"), 76.90 (C-3"), 74.44 (C-4"), 72.71 (C3'), 71.54 (C-2'), 70.17 (C-5'), 70.08 (C-4'), 65.00 (C-6'), 62.51, (C-1")

62.18 (C-6"), 20.23 (C-12). HRMS: $C_{23}H_{28}O_{14}Na$ for $[M+Na]^+$, calculated 551.1377, found 551.1377.

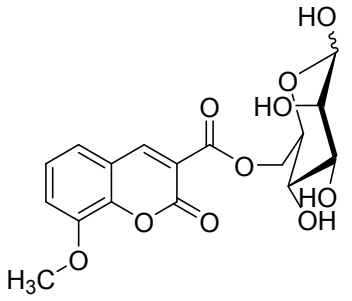


6''-O-D-maltosyl 6-methylcoumarin-3-carboxylate (5l) : syrup liquid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.69 (s, 0.5H, H-4 of β-D-maltose), 8.68 (s, 0.5H, H-4 of α-D-maltose), 7.71 (dd, *J* = 6.8, 2.0 Hz, 1H, H-5), 7.56 (dd, *J* = 8.5, 2.1 Hz, 1H, H-7), 7.33 (d, *J* = 8.5 Hz, 1H, H-8), 6.72 (d, *J* = 6.4 Hz, 0.5H, C1'-OH of β-D-maltose), 6.38 (d, *J* = 4.6 Hz, 0.5H, C1'-OH of α-D-maltose), 5.57 (dd, *J* = 6.2, 3.1 Hz, 1H, C2"-OH of D-maltose), 5.52 (d, *J* = 3.0 Hz, 0.5H, C3'-OH of β-D-maltose), 5.36 (d, *J* = 3.1 Hz, 0.5H, C3'-OH of α-D-maltose), 5.29 (t, *J* = 5.6 Hz, 1H, C4"-OH of D-maltose), 5.08 (t, *J* = 4.0 Hz, 1.5H, C3"-OH of D-maltose, C1"-H of β-D-maltose), 5.05 (d, *J* = 3.7 Hz, 0.5H, C1"-H of α-D-maltose), 5.00 (d, *J* = 4.9 Hz, 0.5H, C1'-H of α-D-maltose), 4.92 (t, *J* = 4.1 Hz, 0.5H, C2'-OH of β-D-maltose), 4.66 (d, *J* = 6.9 Hz, 0.5H, C2'-OH of α-D-maltose), 4.61 (t, *J* = 6.0 Hz, 0.5H, C6'-OH of β-D-maltose), 4.54-4.47 (m, 1.5H, C6"-Ha of D-maltose, C6'-OH of α-D-maltose), 4.34 (dd, *J* = 7.7, 6.4 Hz, 0.5H, C1'-H of β-D-maltose), 4.24 (ddd, *J* = 11.8, 7.0, 2.3 Hz, 1H, C6"-Hb of D-maltose), 3.87 (dtd, *J* = 9.1, 7.1, 1.9 Hz, 1H, C6'-Ha of D-maltose), 3.73-3.65 (m, 1.5H, C6'-Hb of D-maltose, C5'-H of α-D-maltose), 3.62 (d, *J* = 5.6 Hz, 1H, C5"-H of D-maltose), 3.55 (dt, *J* = 11.8, 6.0 Hz, 0.5H, C5'-H of β-D-maltose), 3.50-3.43 (m, 1.5H, C3"-H of D-maltose, C3'-H of α-D-maltose), 3.37-3.29 (m, 2H, C4'-H of D-maltose, C2"-H of α-D-maltose, C3'-H of β-D-maltose), 3.25-3.15 (m, 2H, C4"-H of D-maltose, C2'-H of α-D-maltose, C2"-H of β-D-maltose), 2.96 (ddd, *J* = 9.0, 7.7, 4.7 Hz, 0.5H, C2'-H of β-D-maltose), 2.38 (s, 3H, H-12). ^{13}C NMR (126 MHz, DMSO) δ 162.21 (C-11), 156.09, 156.07 (C-2), 152.76 (C-9), 148.73, 148.68 (C-4), 135.58 (C-6), 134.30, 134.26 (C-7), 129.88, 129.84 (C-5), 117.54 (C-10), 117.06 (C-8), 115.95 (C-3), 100.98 (C-1" of β-D-maltose), 100.87 (C-1" of α-D-maltose), 96.83 (C-1' of β-D-maltose), 92.16 (C-1' of α-D-maltose), 80.60 (C-4' of α-D-maltose), 80.07 (C-4' of β-D-maltose), 76.61 (C-3' of β-D-maltose), 75.16 (C-5' of β-D-maltose), 74.32 (C-2' of β-D-maltose), 73.11 (C-3' of α-D-maltose), 73.09 (C-3" of α-D-maltose), 73.02 (C-3" of β-D-maltose), 72.47 (C-2" of β-D-maltose), 72.35 (C-2" of α-D-maltose), 71.88 (C-5" of α-D-maltose), 70.60 (C-5" of β-D-maltose), 70.57 (C-2' of α-D-maltose), 70.38 (C-5' of α-D-maltose), 70.24 (C-4" of α-D-maltose), 70.18 (C-4" of β-D-maltose), 65.24 (C-6" of β-D-maltose), 65.20 (C-6" of α-D-maltose), 60.73 (C-6' of

β-D-maltose), 60.61 (C-6' of α-D-maltose), 20.22 (H-12). HRMS: $C_{23}H_{28}O_{14}Na$ for $[M+Na]^+$, calculated 551.1377, found 551.1379.

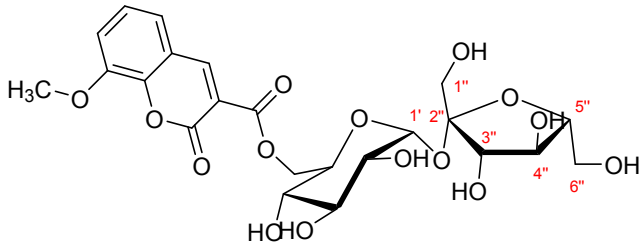


6'-O-D-glucosyl 8-methoxycoumarin-3-carboxylate (5m) : light yellow solid, mp 151-153 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.67 (s, 0.5H, H-4 of β-D-glucose), 8.65 (s, 0.5H, H-4 of α-D-glucose), 7.45-7.39 (m, 2H, H-5, H-7), 7.33 (t, J = 7.9 Hz, 1H, H-6), 6.72 (s, 0.5H, C1'-OH of β-D-glucose) , 6.39 (s, 0.5H, C1'-OH of α-D-glucose) 5.35-4.78 (m, 3H, C1'-H of D-glucose, C4'-OH of D-glucose, C2'-OH of β-D-glucose), 4.70-4.47 (m, 1.5H, C3'-OH of α-D-glucose, C6'-Ha of D-glucose), 4.36 (d, J = 7.7 Hz, 0.5H, C3'-OH of β-D-glucose), 4.30 (td, J = 12.1, 6.2 Hz, 1H, C6'-Hb of D-glucose), 3.92 (s, 3H, H-12), 3.91 (s, 0.5H, C5'-H of α-D-glucose), 3.51-3.47 (m, 1H, C5'-H of β-D-glucose, C3'-H of α-D-glucose), 3.24-3.18 (m, 2H, C2'-H of D-glucose, C3'-H of β-D-glucose, C4'-H of α-D-glucose), 2.97 (t, J = 8.2 Hz, 0.5H, C4'-H of β-D-glucose). ^{13}C NMR (126 MHz, DMSO) δ 162.53, 162.49 (C-11), 155.67 (C-2), 148.93, 148.81 (C-8), 146.26 (C-9), 143.92 (C-4), 124.84 (C-6), 121.16 (C-5), 118.23 (C-3), 117.79, 117.72 (C-7), 116.51 (C-10), 97.02 (C1' of β-D-glucose), 92.41 (C1' of α-D-glucose), 76.46 (C3' of β-D-glucose), 74.72 (C2' of β-D-glucose), 73.50 (C5' of β-D-glucose), 72.91 (C3' of α-D-glucose), 72.18 (C2' of α-D-glucose), 70.59 (C4' of α-D-glucose), 70.19 (C4' of β-D-glucose), 69.21 (C5' of α-D-glucose), 65.26 (C6' of D-glucose), 56.21, 56.17 (C-12). HRMS: $C_{17}H_{18}O_{10}Na$ for $[M+Na]^+$, calculated 405.0798, found 405.0799.

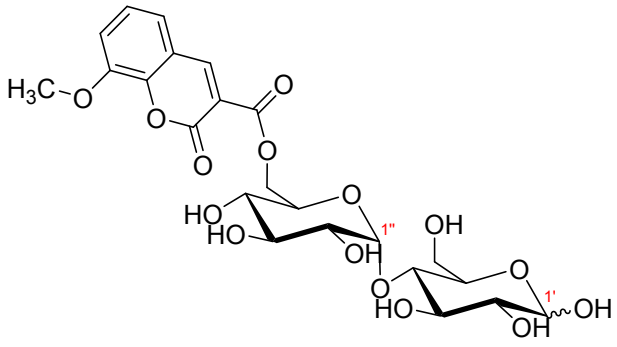


6'-O-D-mannosyl 8-methoxycoumarin-3-carboxylate (5n) : light yellow solid, mp 147-148 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.68 (s, 1H, H-4), 7.41 (ddd, J = 8.2, 4.1, 1.5 Hz, 2H, H-5, H-7), 7.34 (t, J = 7.9 Hz, 1H, H-6), 6.41 (s, 1H, C1'-OH), 5.17-4.94 (m, 1H, C4'-OH), 4.91 (m, 1H, C1'-H), 4.71 (s, 1H, C3'-OH), 4.56 (dd, J = 11.6, 2.1 Hz, 1H, C6'-Ha), 4.31 (dd, J = 11.6, 6.2 Hz, 1H, C6'-Hb), 3.92 (s, 3H, H-12), 3.86 (ddd, J = 9.5, 6.1, 2.1 Hz, 1H,

C5'-H), 3.61 (d, *J* = 7.4 Hz, 2H, C2'-OH, C3'-H), 3.56 (t, *J* = 9.3 Hz, 1H, C2'-H), 3.48-3.39 (m, 1H, C4'-H). ^{13}C NMR (126 MHz, DMSO) δ 162.36 (C-11), 155.71 (C-2), 148.69 (C-8), 146.27 (C-9), 143.84 (C-4), 124.83 (C-6), 121.07 (C-5), 118.22 (C-3), 117.94 (C-7), 116.47 (C-10), 94.16 (C-1'), 71.35 (C-2'), 70.52 (C-3'), 70.34 (C-5'), 67.14 (C-4'), 65.15 (C-6'), 56.19 (C-12). HRMS: $C_{17}H_{18}O_{10}Na$ for $[M+Na]^+$, calculated 405.0798, found 405.0800.

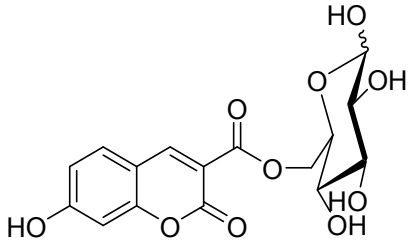


6'-O-D-sucrosyl 8-methoxycoumarin-3-carboxylate (5o) : syrup liquid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.71 (s, 1H, H-4), 7.51-7.41 (m, 2H,H-5, H-7), 7.38-7.30 (m, 1H, H-6), 5.23 (d, *J* = 3.7 Hz, 1H, C1'-H), 5.14 (dt, *J* = 8.8, 6.1 Hz, 3H, C2'-OH,C3'-OH, C4'-OH), 4.94 (d, *J* = 4.6 Hz, 1H, C3"-OH), 4.83 (t, *J* = 6.4 Hz, 1H, C1"-OH), 4.66 (d, *J* = 7.9 Hz, 1H, C4"-OH), 4.48 (dd, *J* = 11.9, 2.0 Hz, 1H, C6'-Ha), 4.40 (t, *J* = 4.9 Hz, 1H, C6"-OH), 4.27 (dd, *J* = 11.8, 6.0 Hz, 1H, C6'-Hb), 4.07 (ddd, *J* = 10.0, 6.0, 1.9 Hz, 1H, C5'-H), 3.93 (s, 3H, H-12), 3.90 (t, *J* = 8.1 Hz, 1H, C3"-H), 3.78 (td, *J* = 7.9, 5.6 Hz, 1H, C5"-H), 3.61-3.50 (m, 3H, C4"-H, C6"-Ha, C6"-Hb), 3.50-3.45 (m, 1H, C3'-H), 3.42 (d, *J* = 6.1 Hz, 2H, C1"-Ha, C1"-Hb), 3.30-3.20 (m, 2H, C2'-H, C4'-H). ^{13}C NMR (126 MHz, DMSO) δ 162.26 (C-11), 155.69 (C-2), 149.05 (C-8), 146.22 (C-9), 143.93 (C-4), 124.73 (C-6), 121.37 (C-5), 118.31 (C-3), 117.42 (C-7), 116.49 (C-10), 103.99 (C-2"), 91.63 (C1'), 82.50 (C-5"), 76.86 (C-3"), 74.41 (C-4"), 72.66 (C-3'), 71.50 (C-2'), 70.17 (C-5'), 70.06 (C-4'), 65.05 (C-6'), 62.51 (C-1"), 62.14 (C-6"), 56.21 (C-12). HRMS: $C_{23}H_{28}O_{15}Na$ for $[M+Na]^+$, calculated 567.1326, found 567.1327.



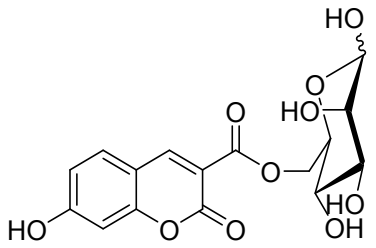
6''-O-D-maltosyl 8-methoxycoumarin-3-carboxylate (5p) : syrup liquid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.73 (s, 0.5H, H-4 of β-D-maltose), 8.72 (s, 0.5H, H-4 of α-D-maltose), 7.53-7.37 (m, 2H, H-5, H-7), 7.37-7.29 (m, 1H, H-6), 6.69 (d, *J* = 5.4 Hz, 0.5H, C1'-OH of β-D-maltose), 6.36 (d, *J* = 4.4 Hz, 0.5H, C1'-OH of α-D-maltose), 5.56 (d, *J* = 7.1 Hz, 1H, C2"-OH of D-maltose), 5.52 (d, *J* = 3.0 Hz, 0.5H, C3'-OH of β-D-maltose), 5.36 (d, *J* = 3.0 Hz, 0.5H, C3'-OH of α-D-maltose), 5.29 (s, 1H, C4"-OH of D-maltose), 5.09-5.05 (m, 1.5H, C3"-OH of D-maltose, C1"-

H of β-D-maltose), 5.04 (d, *J* = 3.7 Hz, 0.5H, C1"-H of α-D-maltose), 4.99 (s, 0.5H, C1'-H of α-D-maltose), 4.91 (t, *J* = 4.0 Hz, 0.5H, C2'-OH of β-D-maltose), 4.64 (d, *J* = 6.7 Hz, 0.5H, C2'-OH of α-D-maltose), 4.55-4.52 (m, 1H, C6"-Ha of D-maltose), 4.51 (t, *J* = 2.1 Hz, 0.5H, C6'-OH of β-D-maltose), 4.44 (d, *J* = 6.9 Hz, 0.5H, C6'-OH of α-D-maltose), 4.35-4.30 (m, 0.5H, C1'-H of β-D-maltose), 4.25 (ddd, *J* = 11.8, 7.0, 2.7 Hz, 1H, C6"-Hb of D-maltose), 3.92 (s, 3H, H-12), 3.91-3.84 (m, 1H, C6'-Ha of D-maltose), 3.73-3.64 (m, 1.5H, C6'-Hb of D-maltose, C5'-H of α-D-maltose), 3.60 (dd, *J* = 6.0, 3.4 Hz, 1H, C5"-H of D-maltose), 3.55 (dt, *J* = 11.6, 5.8 Hz, 0.5H, C5'-H of D-maltose), 3.49-3.43 (m, 1.5H, C3"-H of D-maltose, C3'-H of α-D-maltose), 3.36-3.28 (m, 2H, C4'-H of D-maltose, C2"-H of α-D-maltose, C3'-H of β-D-maltose), 3.27-3.13 (m, 2H, C4"-H of D-maltose, C2'-H of α-D-maltose, C2"-H of β-D-maltose), 2.99-2.93 (m, 0.5H, C2'-H of β-D-maltose). ^{13}C NMR (126 MHz, DMSO) δ 162.16 (C-11), 155.64 (C-2), 149.09, 149.05 (C-8), 146.25 (C-9), 143.96 (C-4), 124.82 (C-6), 121.37, 121.32 (C-5), 118.32 (C-3), 117.30 (C-7), 116.57 (C-10), 101.01 (C-1" of β-D-maltose), 100.94 (C-1" of α-D-maltose), 96.82 (C-1' of β-D-maltose), 92.15 (C-1' of α-D-maltose), 80.67 (C-4' of α-D-maltose), 80.21 (C-4' of β-D-maltose), 76.57 (C-3' of β-D-maltose), 75.13 (C-5' of β-D-maltose), 74.30 (C-2' of β-D-maltose), 73.13 (C-3' of α-D-maltose), 73.10 (C-3" of α-D-maltose), 72.99 (C-3" of β-D-maltose), 72.48 (C-2" of β-D-maltose), 72.36 (C-2" of α-D-maltose), 71.87 (C-5" of α-D-maltose), 70.63 (C-5" of β-D-maltose), 70.60 (C-2' of α-D-maltose), 70.36 (C-5' of α-D-maltose), 70.22 (C-4" of α-D-maltose), 70.17 (C-4" of β-D-maltose), 65.27 (C-6" of D-maltose), 60.72 (C-6' of β-D-maltose), 60.59 (C-6' of α-D-maltose), 56.24 (C-12). HRMS: $C_{23}H_{28}O_{15}Na$ for $[M+Na]^+$, calculated 567.1320, found 567.1318.



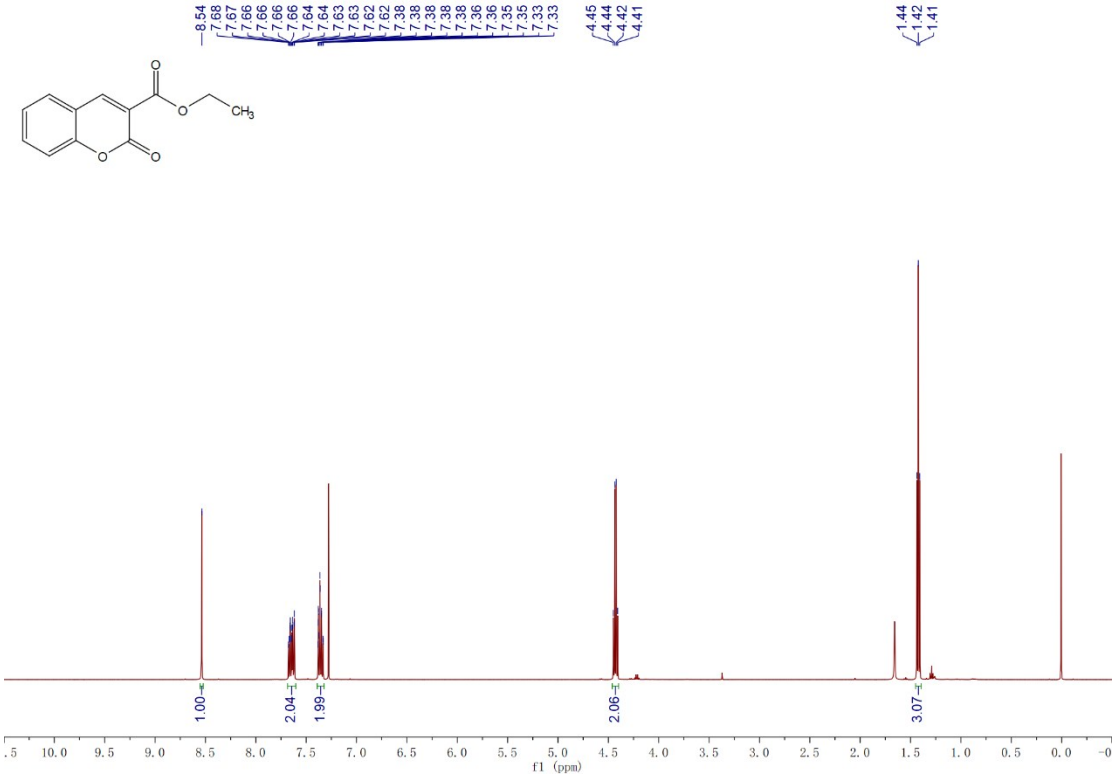
6'-O-D-glucosyl 7-hydroxycoumarin-3-carboxylate (5q) : light yellow solid, mp 201-203 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.64 (s, 0.5H, H-4 of β-D-glucose), 8.62 (s, H-4 of α-D-glucose), 7.76 (d, *J* = 8.6 Hz, 1H, H-5), 6.85 (dd, *J* = 8.6, 2.3 Hz, 1H, H-6), 6.74 (d, *J* = 2.2 Hz, 1H, H-8), 6.69 (s, 0.5H, C1'-OH of β-D-glucose), 6.36 (s, 0.5H, C1'-OH of α-D-glucose), 5.16 (s, 0.5H, C1'-H of β-D-glucose), 5.11 (s, 0.5H, C1'-H of α-D-glucose), 4.98 (s, 0.5H, C4'-OH of β-D-glucose), 4.93 (d, *J* = 3.6 Hz, 1H, C2'-OH of β-D-glucose, C4'-OH of α-D-glucose), 4.79 (s, 0.5H, C2'-OH of α-D-glucose), 4.56 (s, 0.5H, C3'-OH of α-D-glucose), 4.51-4.42 (m, 1H, C6'-Ha of D-glucose), 4.34 (d, *J* = 7.8 Hz, 1H, C3'-OH of β-D-glucose), 4.26 (ddd, *J* = 13.6, 11.7, 6.2 Hz, 1H, C6'-Hb of D-glucose), 3.89 (ddd, *J* = 10.1, 6.0, 2.1 Hz, 0.5H, C5'-H of α-D-glucose), 3.48-3.45 (m, 1H, C5'-H of β-D-glucose, C3'-H of α-D-glucose), 3.21-3.16 (m, 2H, C2'-H of D-glucose, C3'-H of β-D-glucose, C4'-H of α-D-glucose), 2.95 (t, *J* = 8.1 Hz, 0.5H,

C4'-H of β-D-glucose). ^{13}C NMR (126 MHz, DMSO) δ 164.31, 164.28 (C-11), 162.88, 162.83 (C-7), 157.18, 157.15 (C-2), 156.39 (C-9), 149.40, 149.29 (C-4), 132.11 (C-5), 114.14, 114.12 (C-10), 111.99, 111.91 (C-3), 110.30 (C-6), 101.88 (C-8), 96.98 (C1' of β-D-glucose), 92.36 (C1' of α-D-glucose), 76.47 (C3' of β-D-glucose), 74.71 (C2' of β-D-glucose), 73.55 (C5' of β-D-glucose), 72.91 (C3' of α-D-glucose), 72.17 (C2' of α-D-glucose), 70.61 (C4' of α-D-glucose), 70.22 (C4' of β-D-glucose), 69.24 (C5' of α-D-glucose), 64.82 (C-6'). HRMS: $C_{16}H_{16}O_{10}Na$ for $[M+Na]^+$, calculated 391.066, found 391.0652.



6'-O-D-mannosyl 7-hydroxycoumarin-3-carboxylate (5r) : light yellow solid, mp 175-176 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.65 (s, 1H, H-4), 7.72 (d, J = 8.5 Hz, 1H, H-5), 6.86 (dd, J = 8.6, 2.2 Hz, 1H, H-6), 6.75 (d, J = 2.2 Hz, 1H, H-8), 6.38 (s, 1H, C1'-OH), 5.05-4.92 (m, 1H, C4'-OH), 4.89 (s, 1H, C1'-H), 4.70-4.60 (m, 1H, C3'-OH), 4.51 (dd, J = 11.6, 2.2 Hz, 1H, C6'-Ha), 4.27 (dd, J = 11.4, 6.3 Hz, 1H, C6'-Hb), 3.83 (ddd, J = 8.8, 6.3, 2.1 Hz, 1H, C5'-H), 3.62-3.56 (m, 2H, C2'-OH, C3'-H), 3.53 (t, J = 9.6 Hz, 2H, C2'-H, C4'-H). ^{13}C NMR (126 MHz, DMSO) δ 164.20 (C-11), 162.71 (C-7), 157.08 (C-2), 156.44 (C-9), 149.24 (C-4), 132.01 (C-5), 114.11 (C-10), 112.17 (C-3), 110.29 (C-6), 101.90 (C-8), 94.11 (C-1'), 71.34 (C-2'), 70.54 (C-3'), 70.35 (C-5'), 67.19 (C-4'), 64.81 (C-6'). HRMS: $C_{16}H_{16}O_{10}Na$ for $[M+Na]^+$, calculated 391.066, found 391.0653.

3a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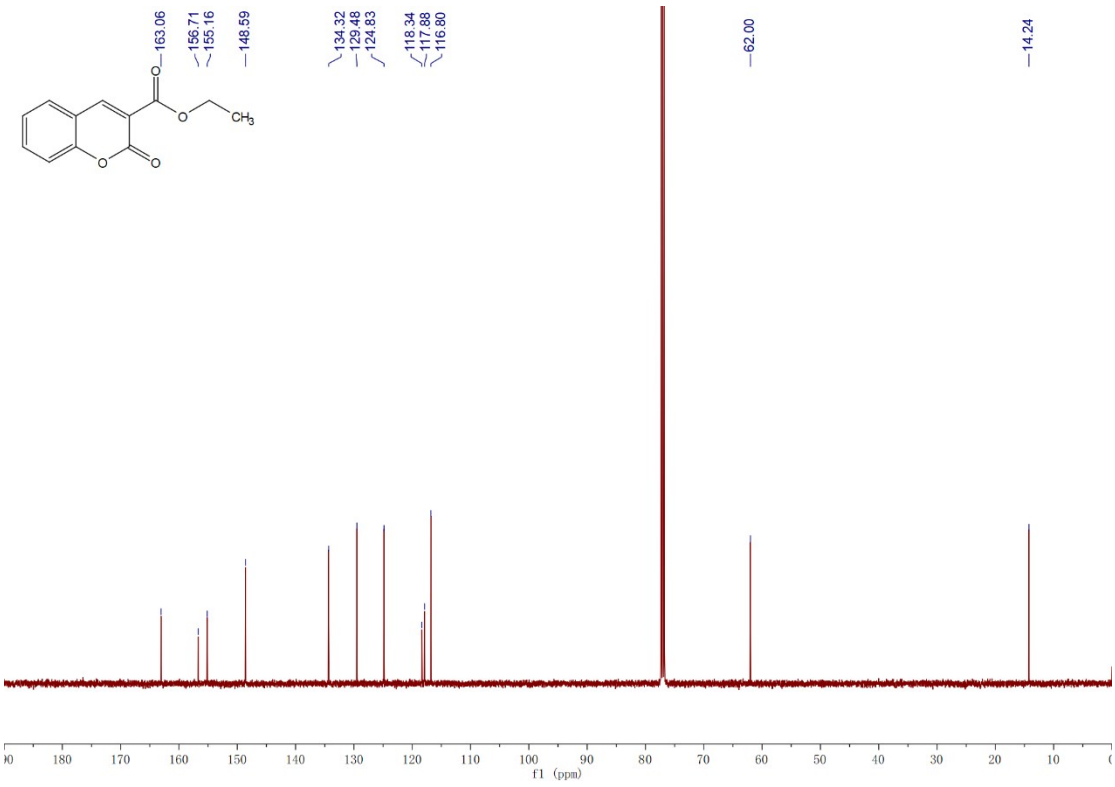
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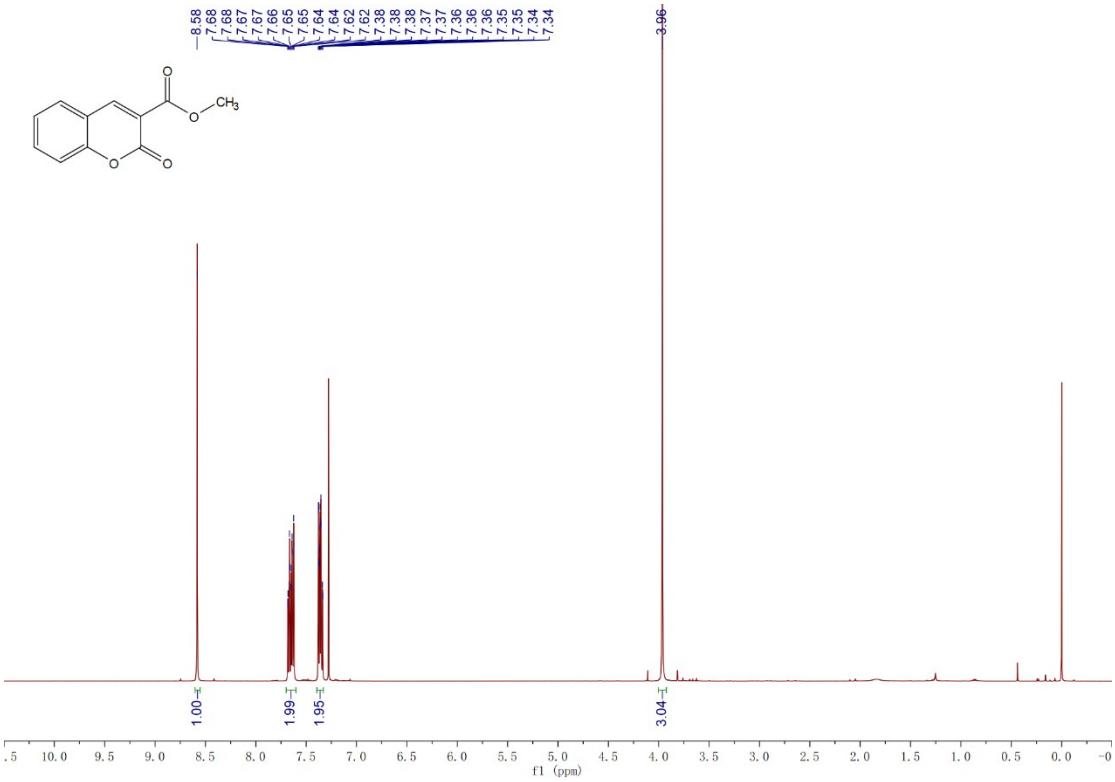
3b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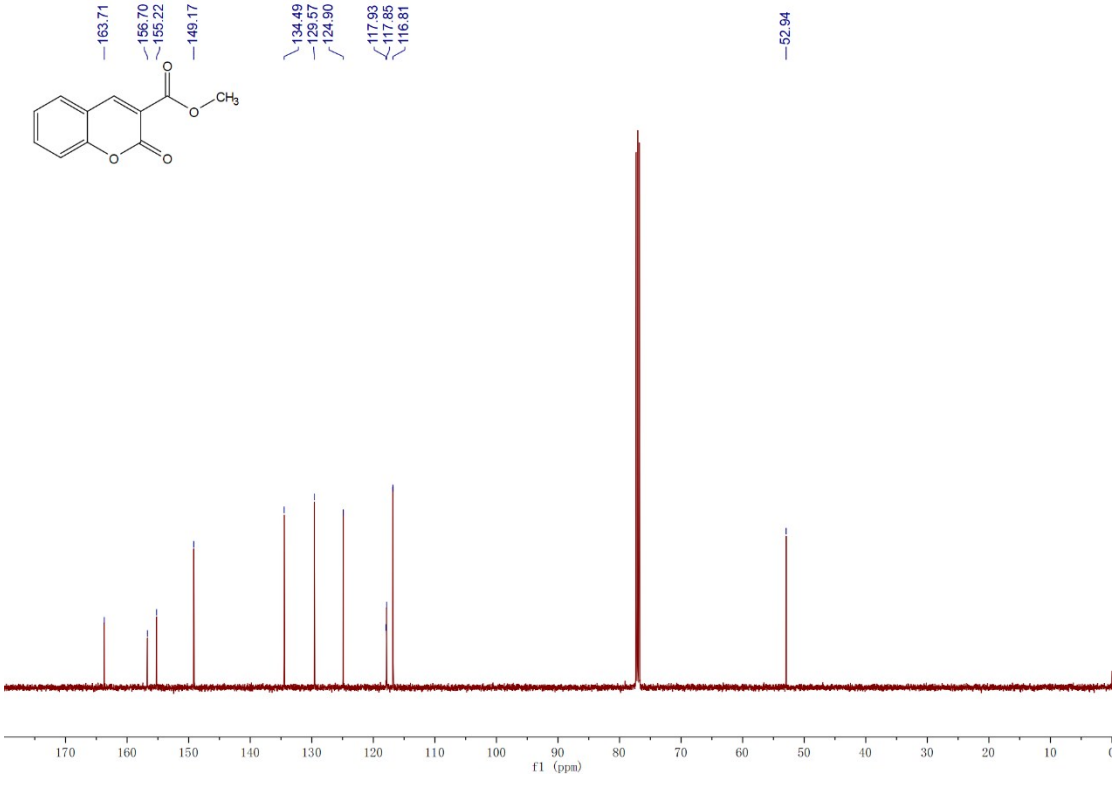
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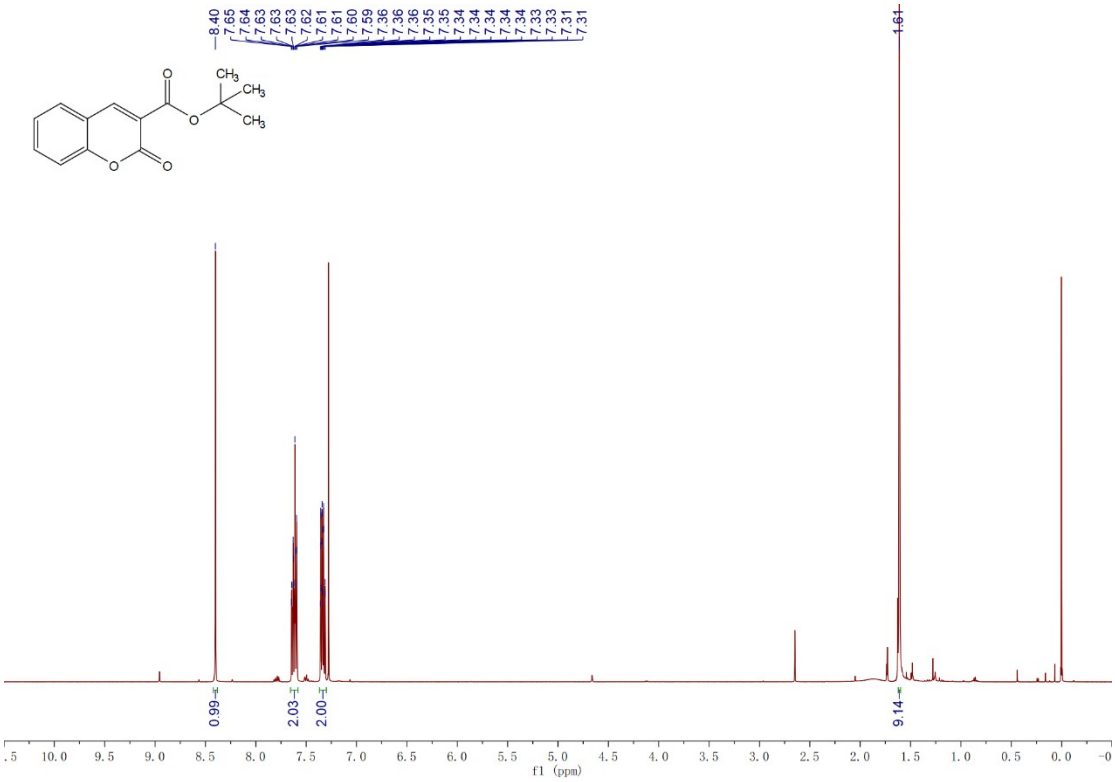
3c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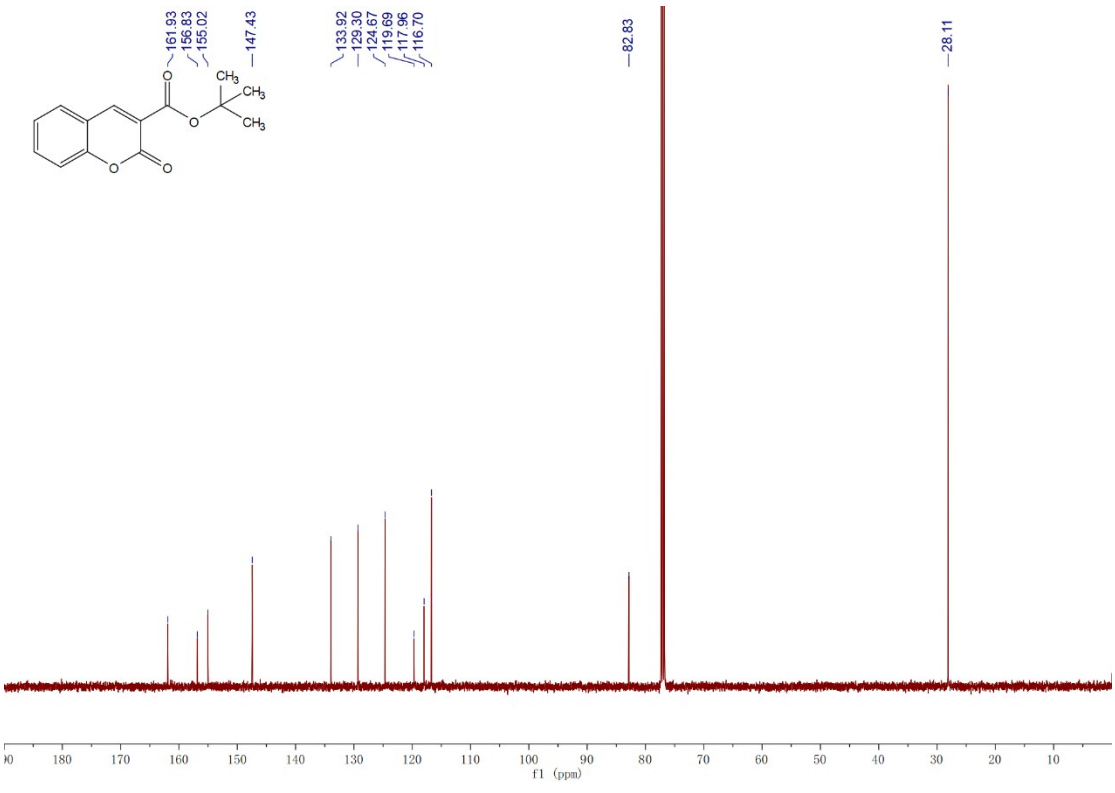
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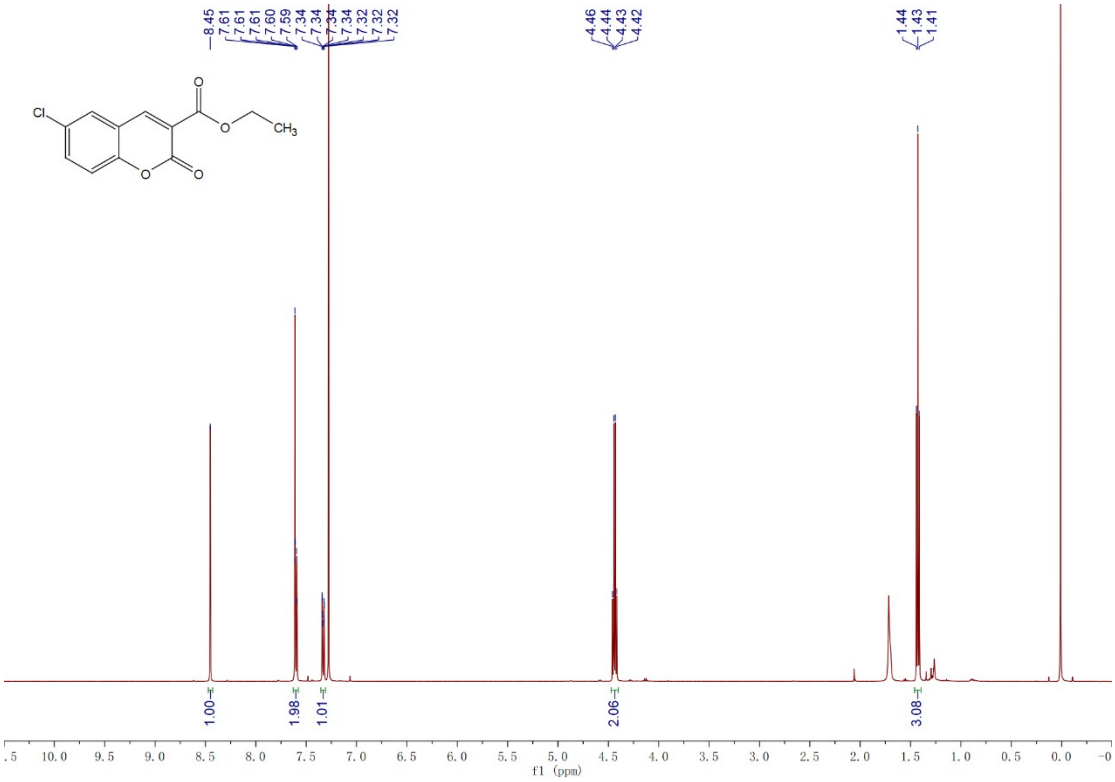
3d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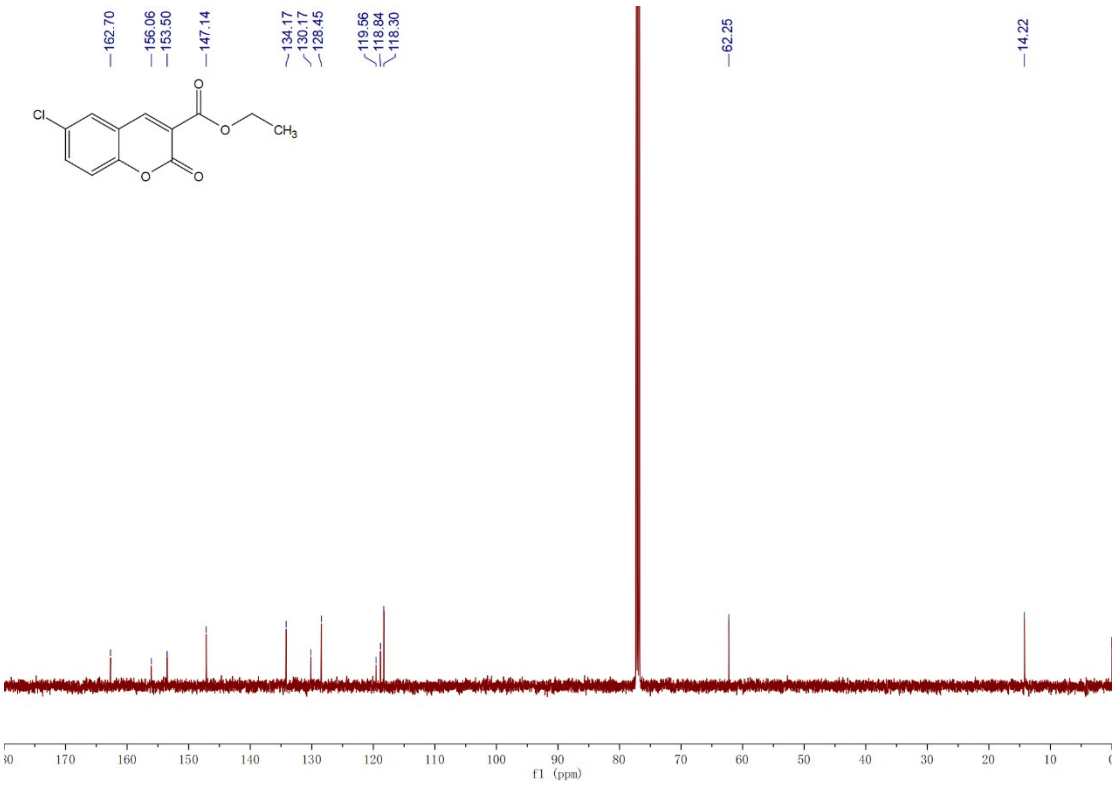
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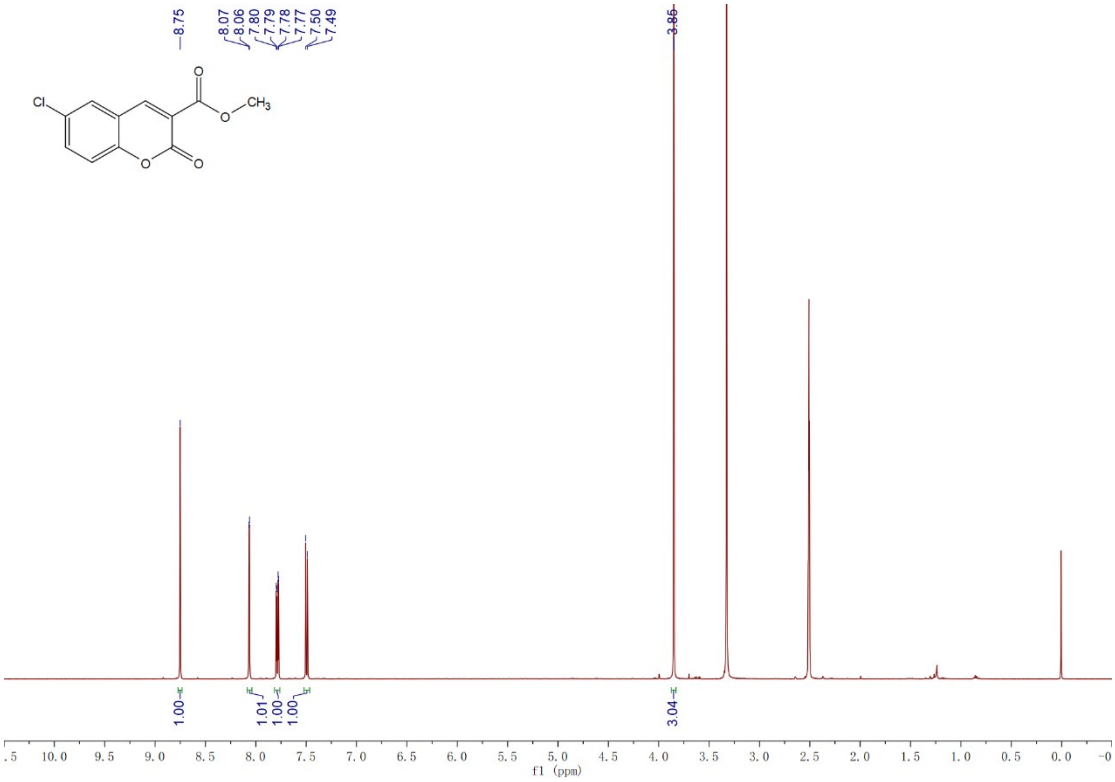
3e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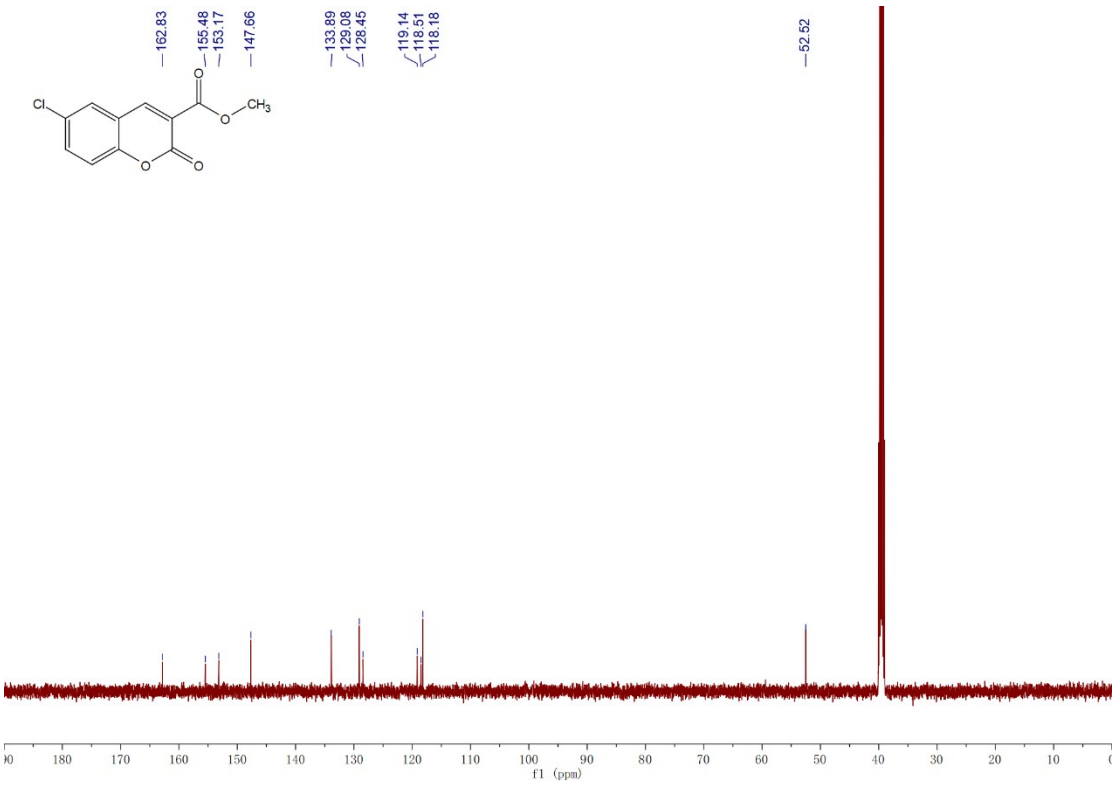
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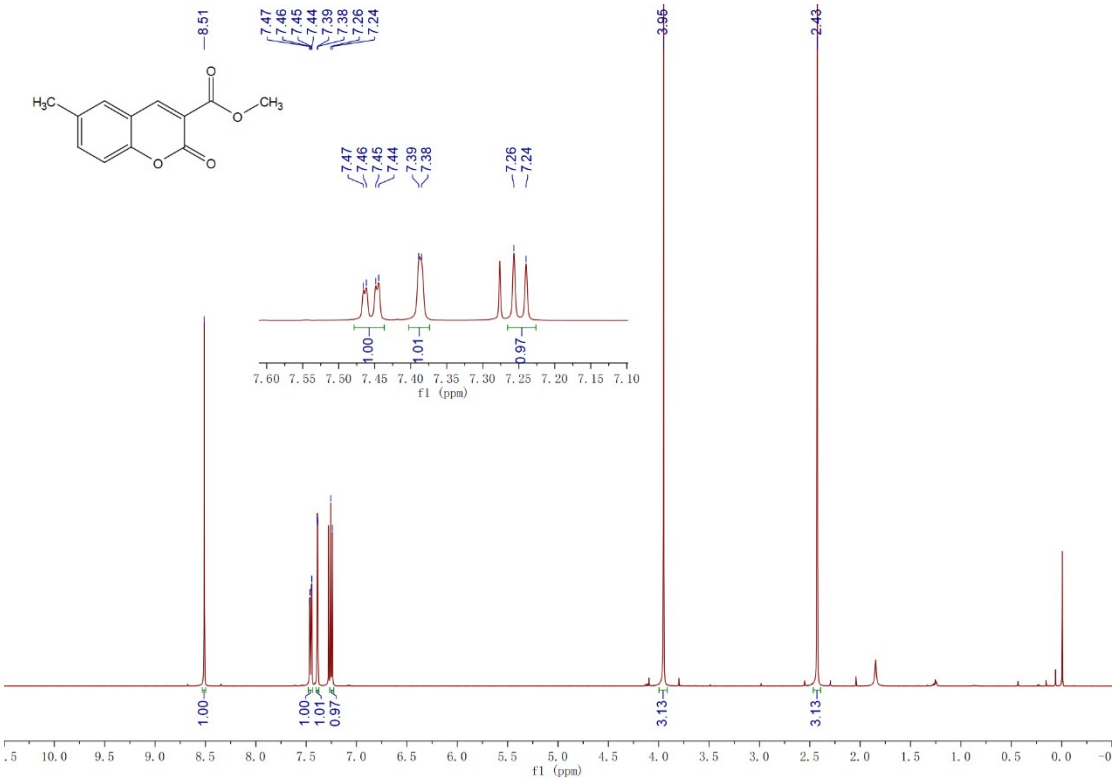
3h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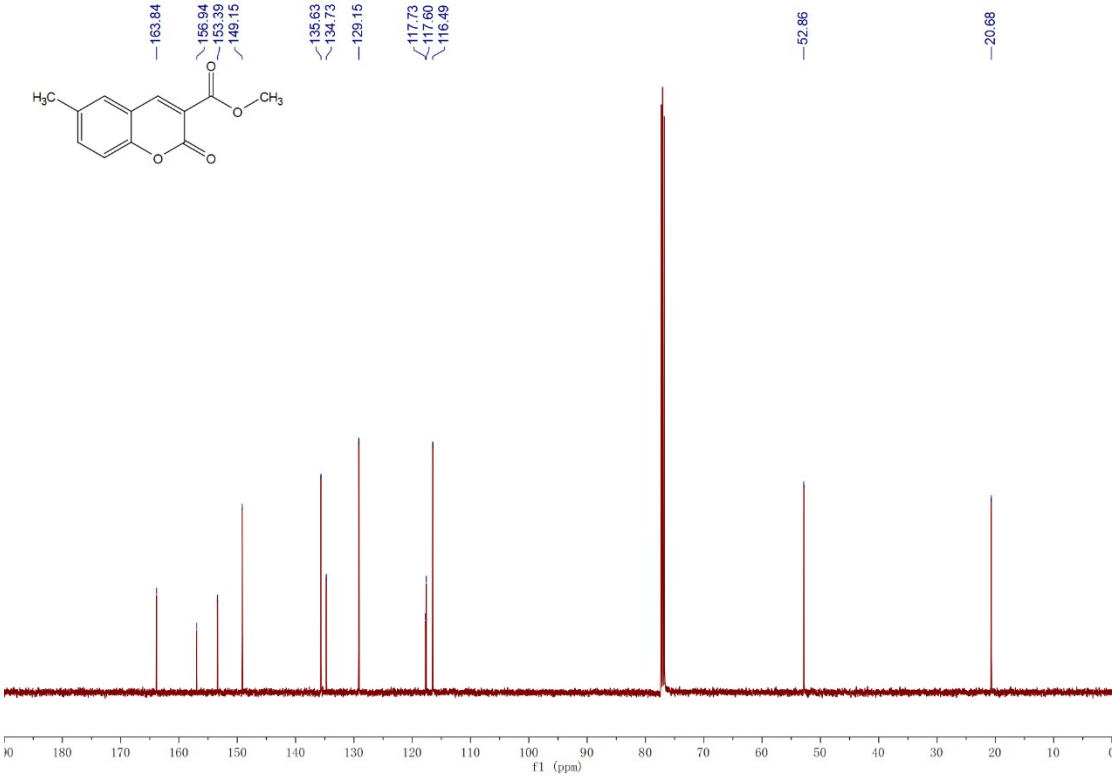
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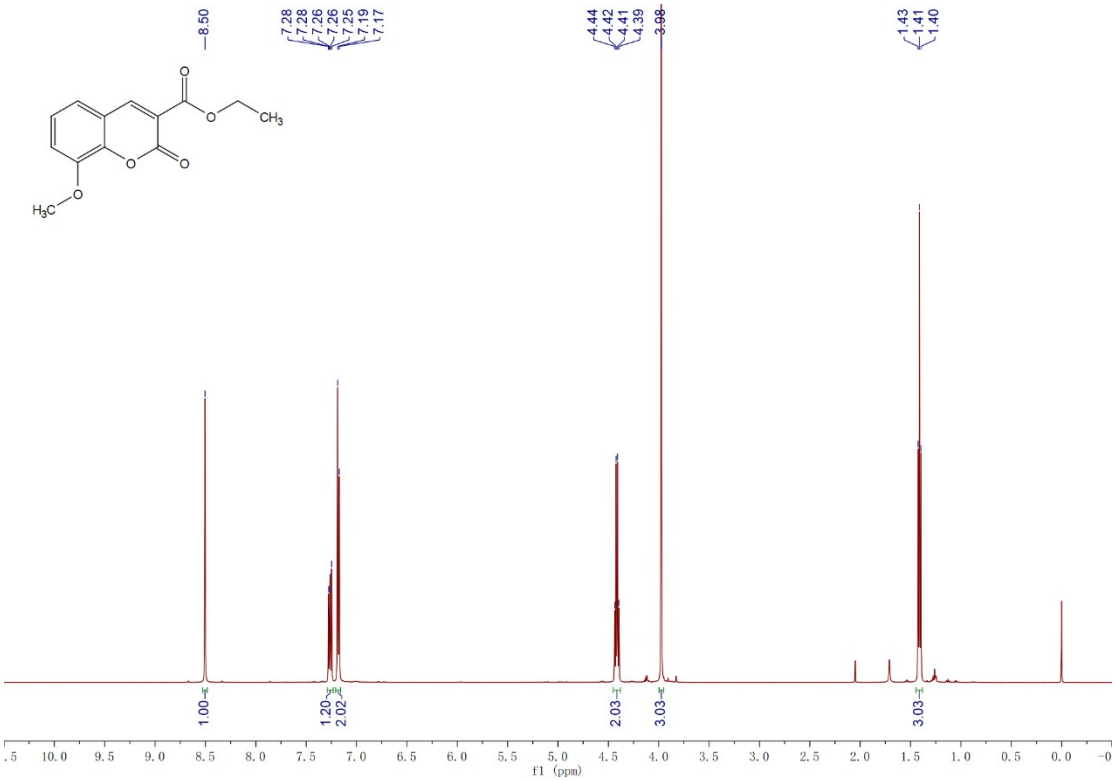
3j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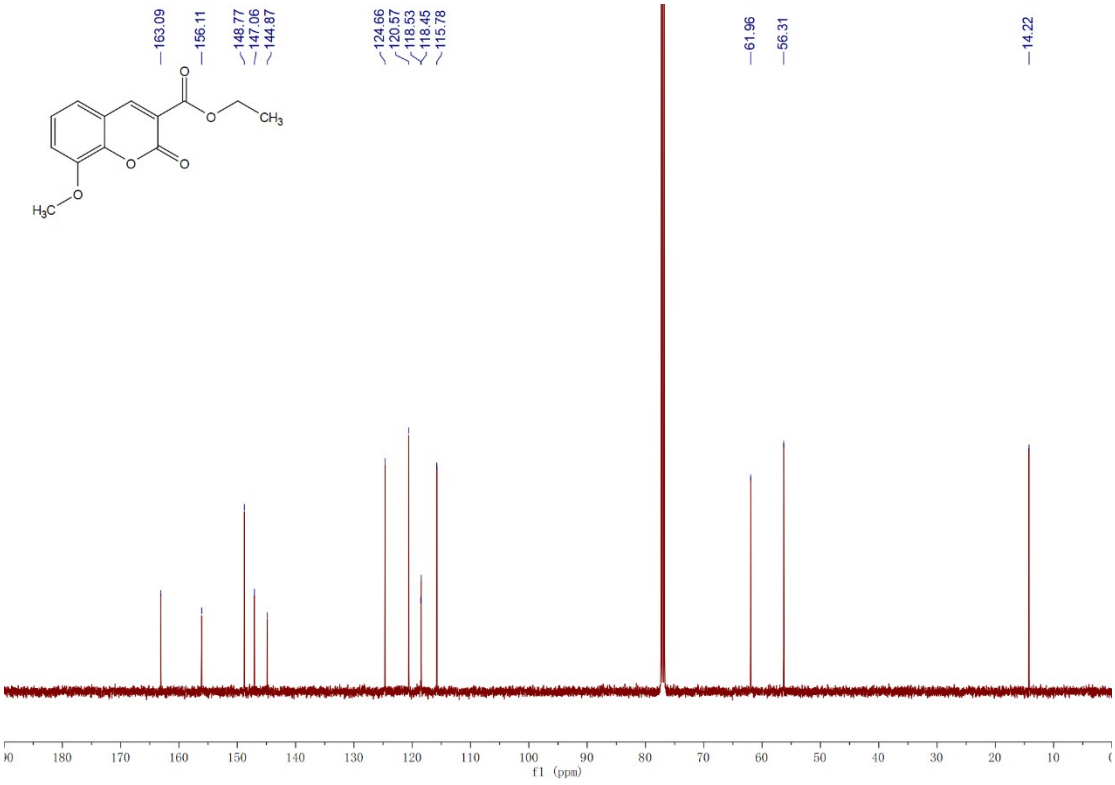
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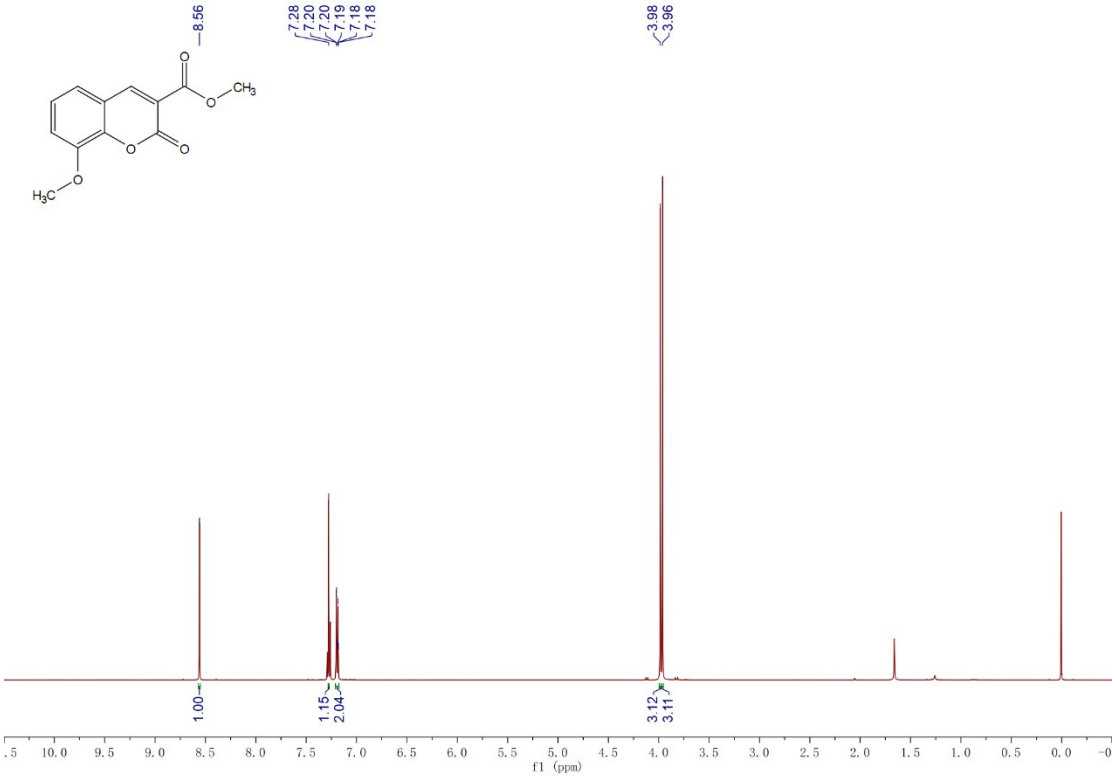
3k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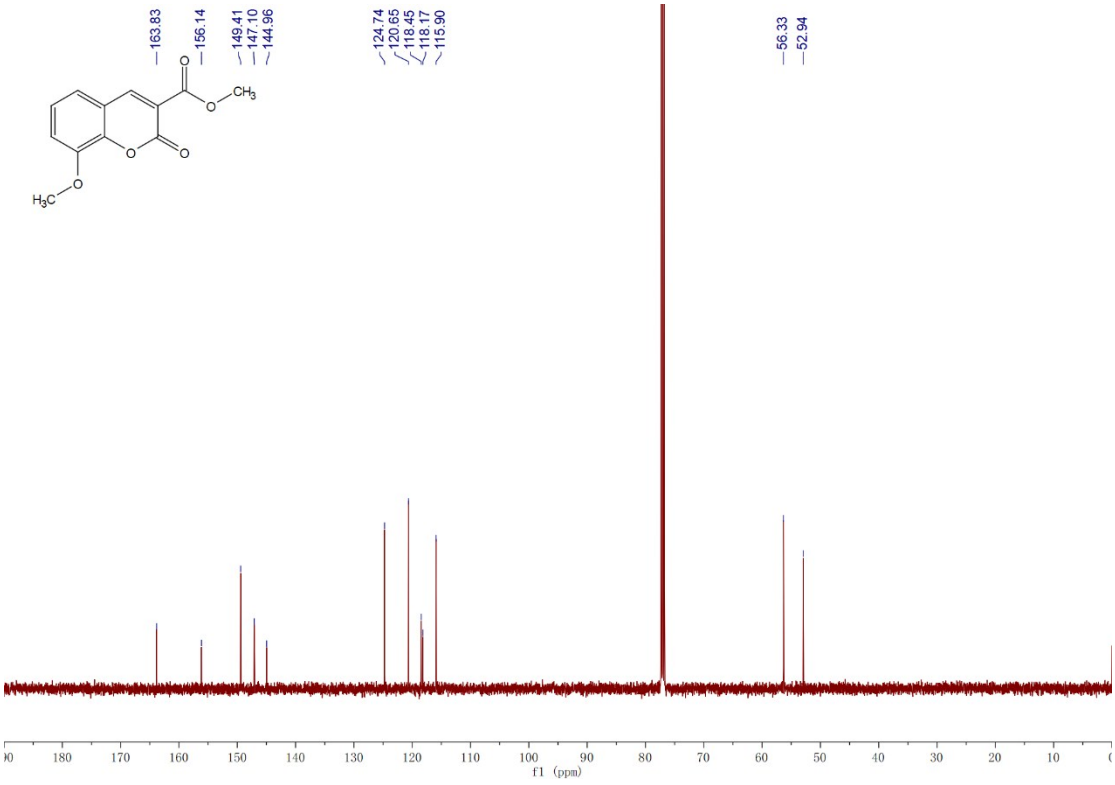
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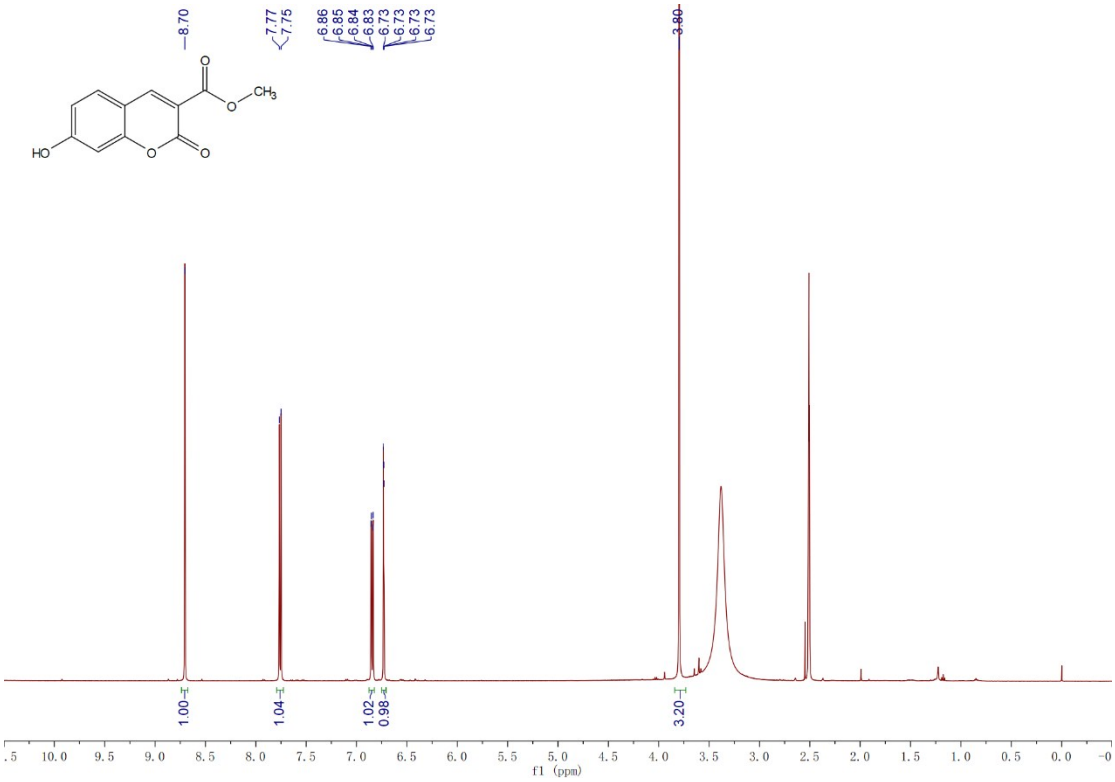
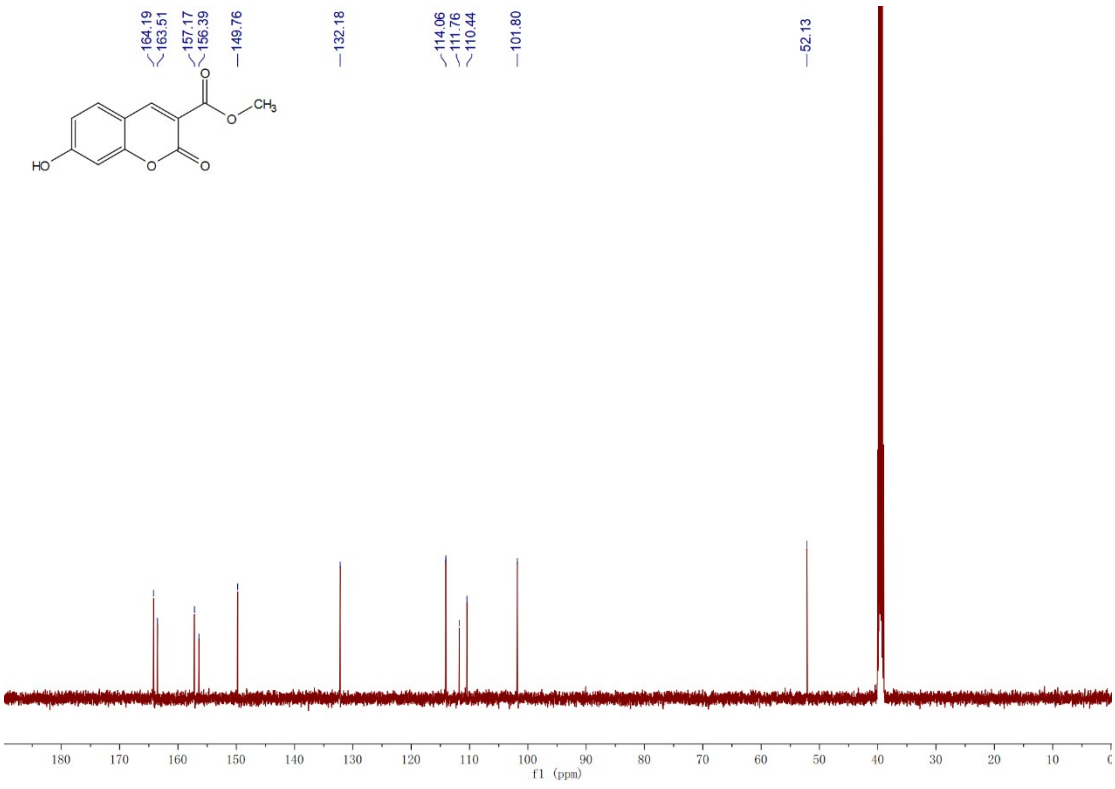
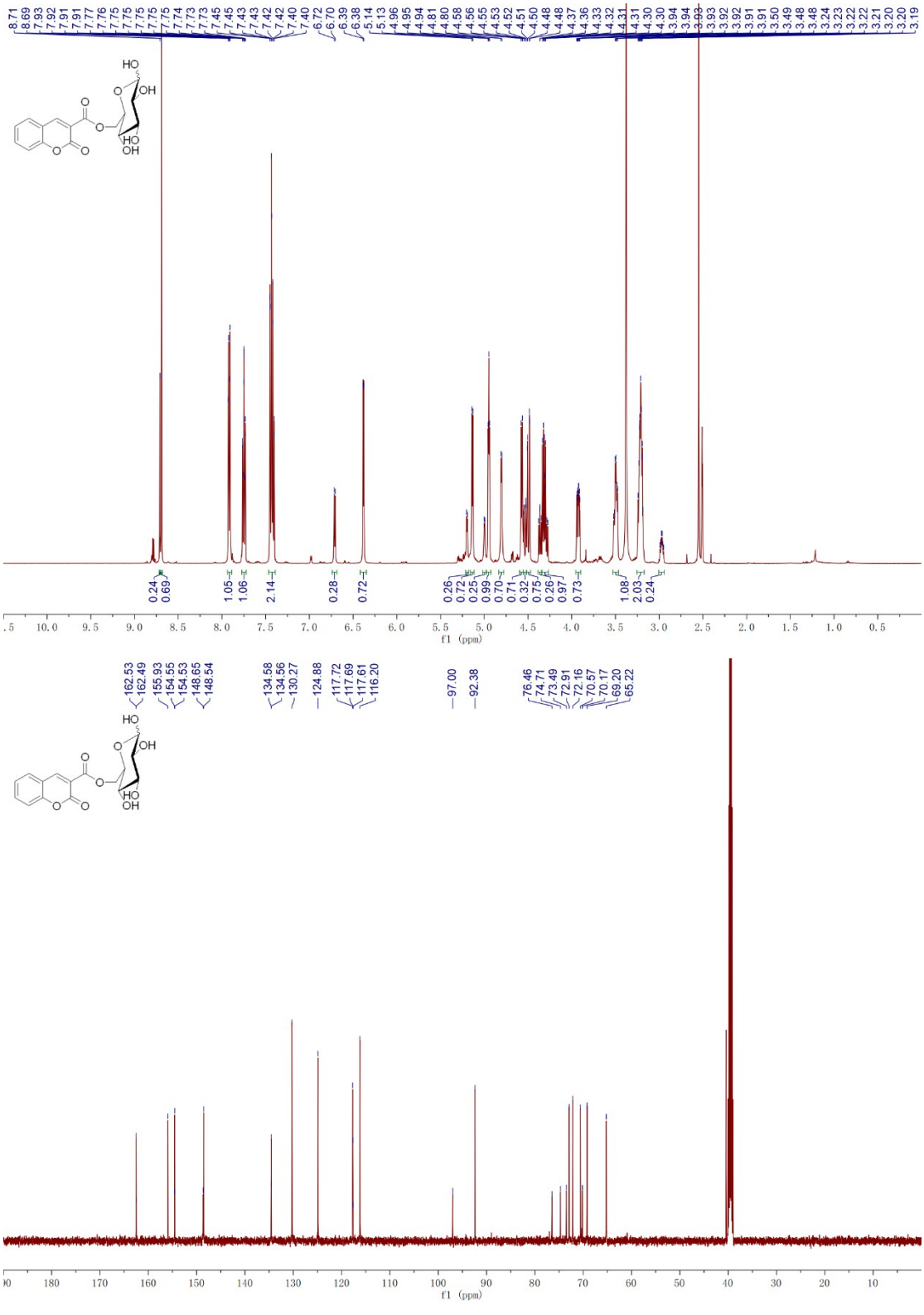
f1 (ppm)

3n

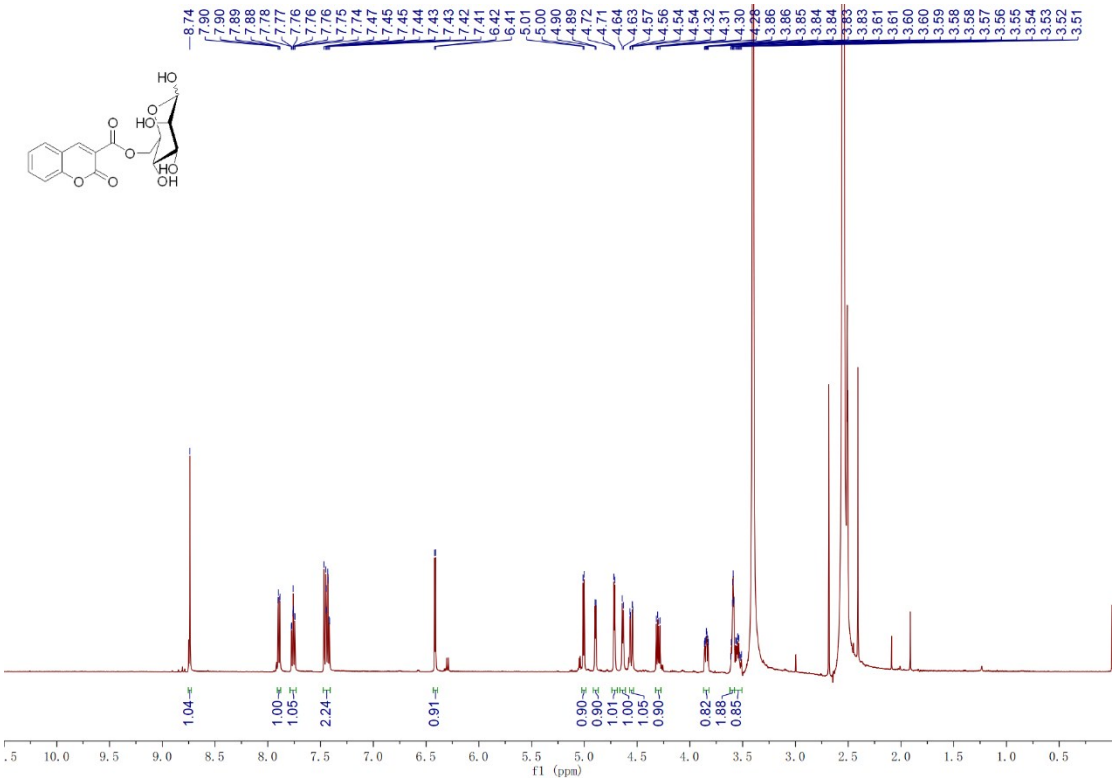

8.70
7.77
7.75
6.86
6.85
6.84
6.83
6.73
6.73
6.73
6.73
3.80
HO
O
O
O
O
CH3
1.00
1.04
1.02
0.98
3.20
f1 (ppm)

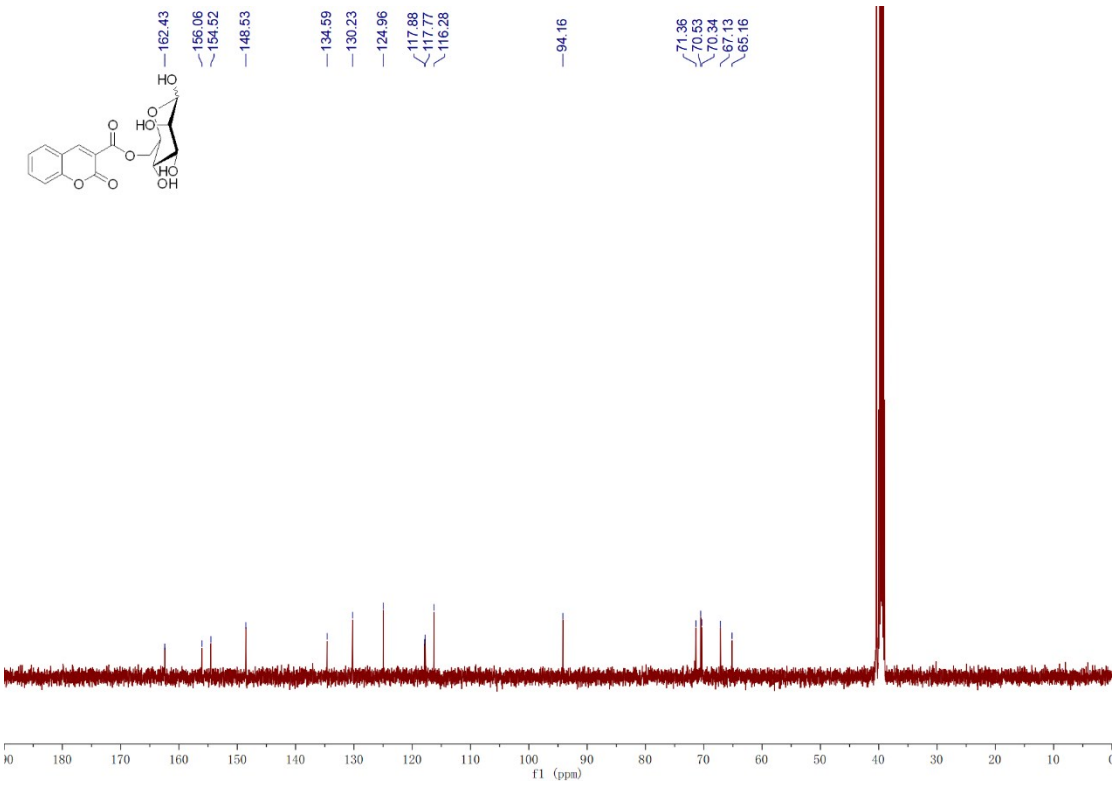

164.19
163.51
157.17
156.39
149.76
132.18
114.06
111.76
110.44
101.80
52.13
HO
O
O
O
O
CH3
f1 (ppm)

5a

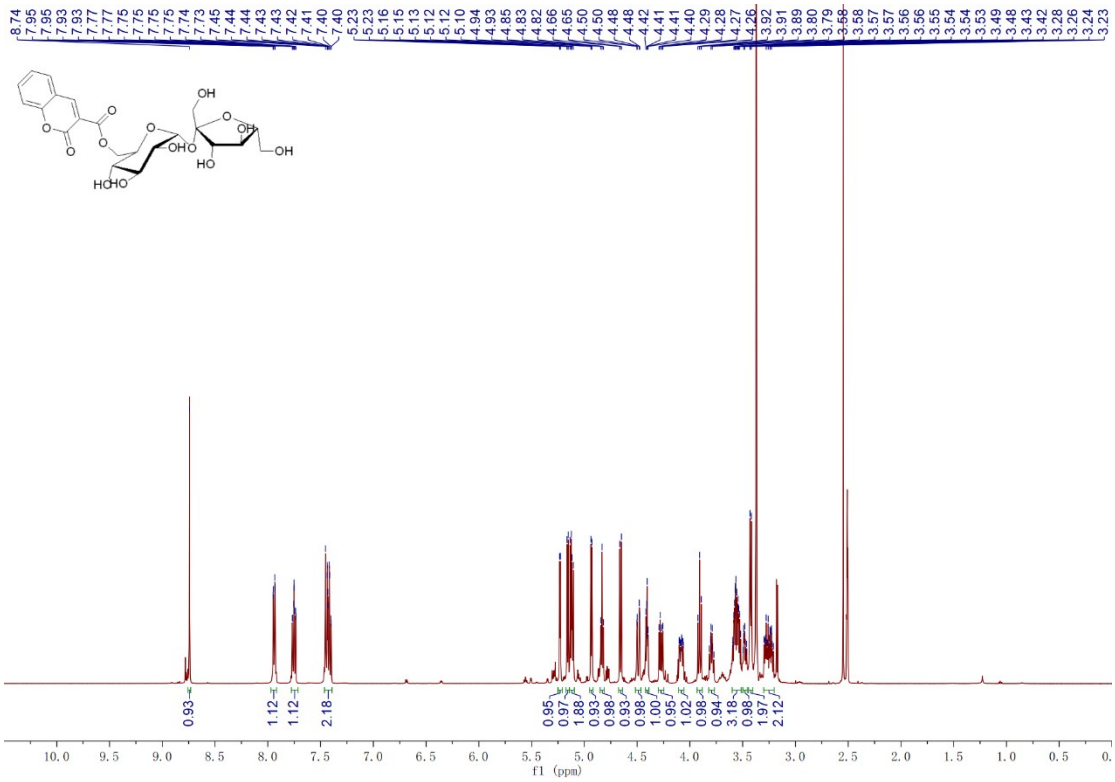

8.71
8.69
7.93
7.92
7.91
7.91
7.77
7.76
7.75
7.75
7.75
7.75
7.74
7.73
7.73
7.45
7.45
7.43
7.43
7.42
7.42
7.40
7.40
6.72
6.70
6.39
6.38
5.14
5.13
4.96
4.95
4.94
4.81
4.80
4.58
4.56
4.55
4.53
4.52
4.51
4.50
4.48
4.48
4.37
4.36
4.33
4.32
4.31
4.31
4.30
4.30
3.94
3.94
3.93
3.92
3.91
3.91
3.50
3.49
3.48
3.48
3.24
3.23
3.22
3.22
3.21
3.20
3.20
3.19
HO
O
OH
HO
OH
O
O
O
O
0.24
0.69
1.05
1.06
2.14
0.28
0.72
0.26
0.72
0.25
0.99
0.70
0.71
0.32
0.75
0.26
0.97
0.73
1.08
2.03
0.24
f1 (ppm)
162.53
162.49
155.93
154.55
154.53
148.65
148.54
134.58
134.56
130.27
124.88
117.72
117.69
117.61
116.20
97.00
92.38
76.46
74.71
73.49
72.91
72.16
70.57
70.17
69.20
65.22
f1 (ppm)

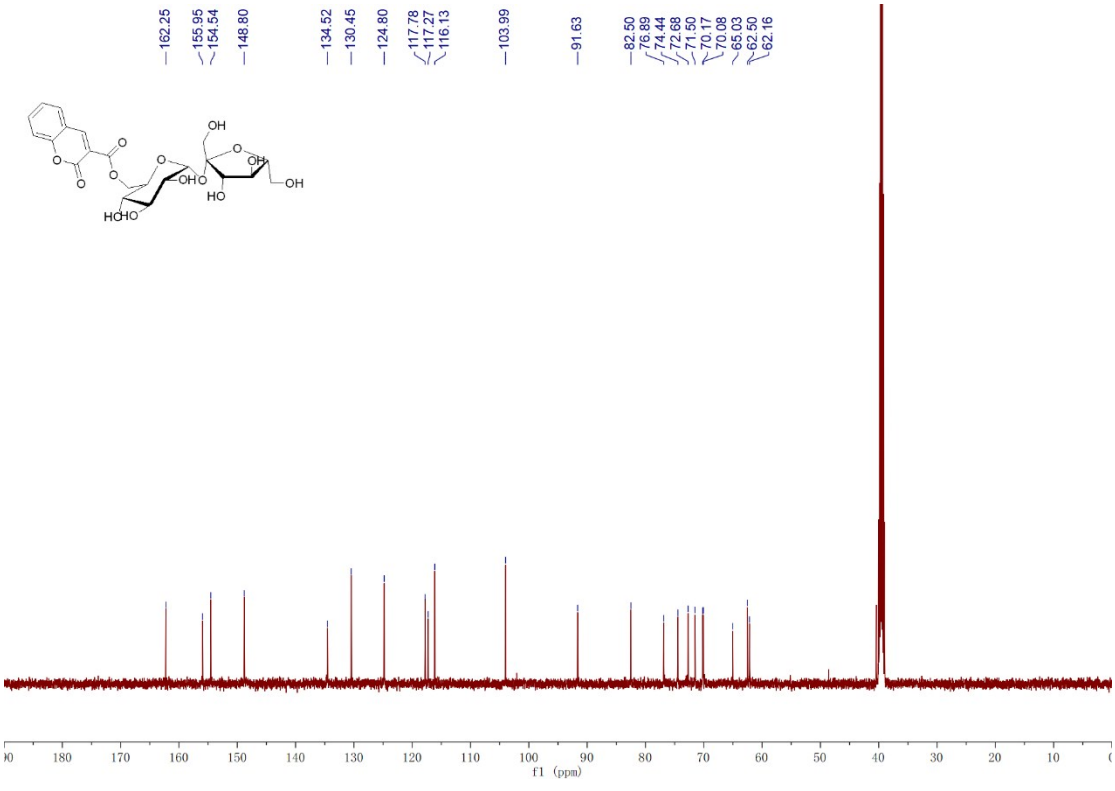
5b


8.74
7.90
7.90
7.89
7.88
7.78
7.77
7.76
7.76
7.76
7.75
7.74
7.47
7.45
7.45
7.44
7.43
7.43
7.42
7.41
6.42
6.41
5.01
5.00
4.90
4.89
4.72
4.71
4.64
4.63
4.57
4.56
4.54
4.54
4.32
4.31
4.30
4.28
3.86
3.86
3.85
3.84
3.84
3.83
3.83
3.61
3.61
3.60
3.60
3.59
3.58
3.58
3.57
3.56
3.55
3.54
3.53
3.52
3.51
HO
O
HO
O
O
HO
OH
O
O
1.04
1.00
1.05
2.24
0.91
0.90
0.90
1.01
1.00
1.05
0.90
0.82
1.88
0.85
f1 (ppm)

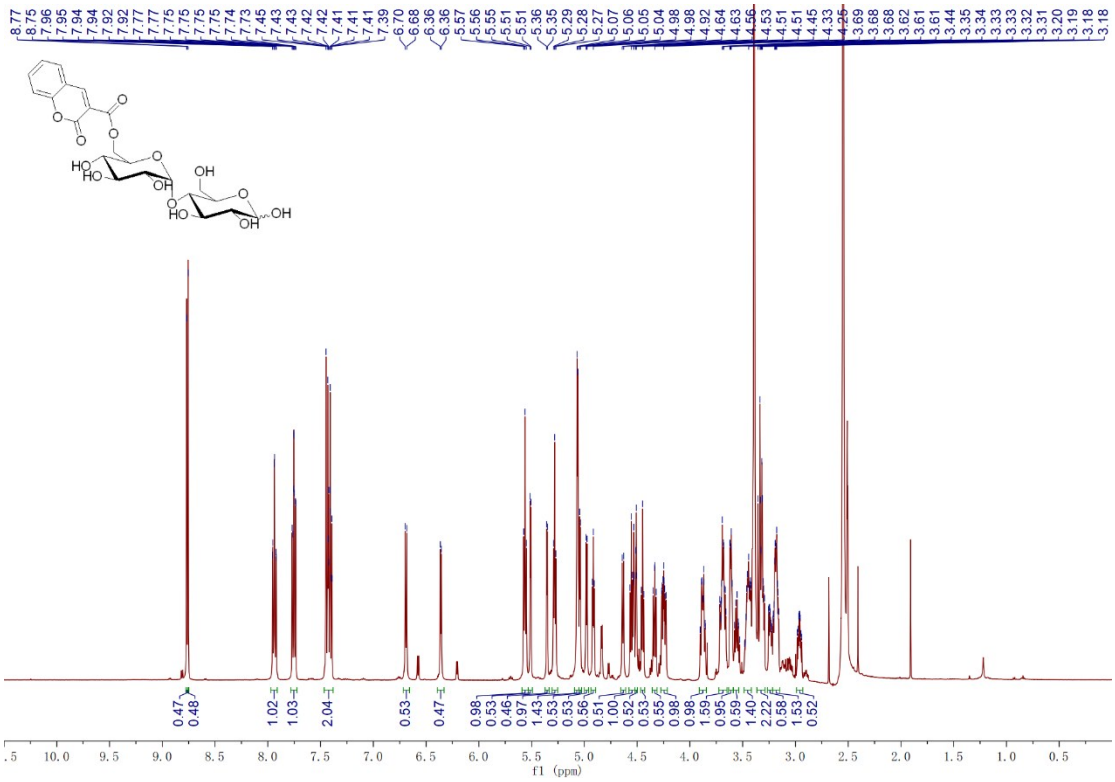

162.43
156.06
154.52
148.53
134.59
130.23
124.96
117.88
117.77
116.28
94.16
71.36
70.53
70.34
67.13
65.16
HO
O
HO
O
O
HO
OH
O
O
f1 (ppm)

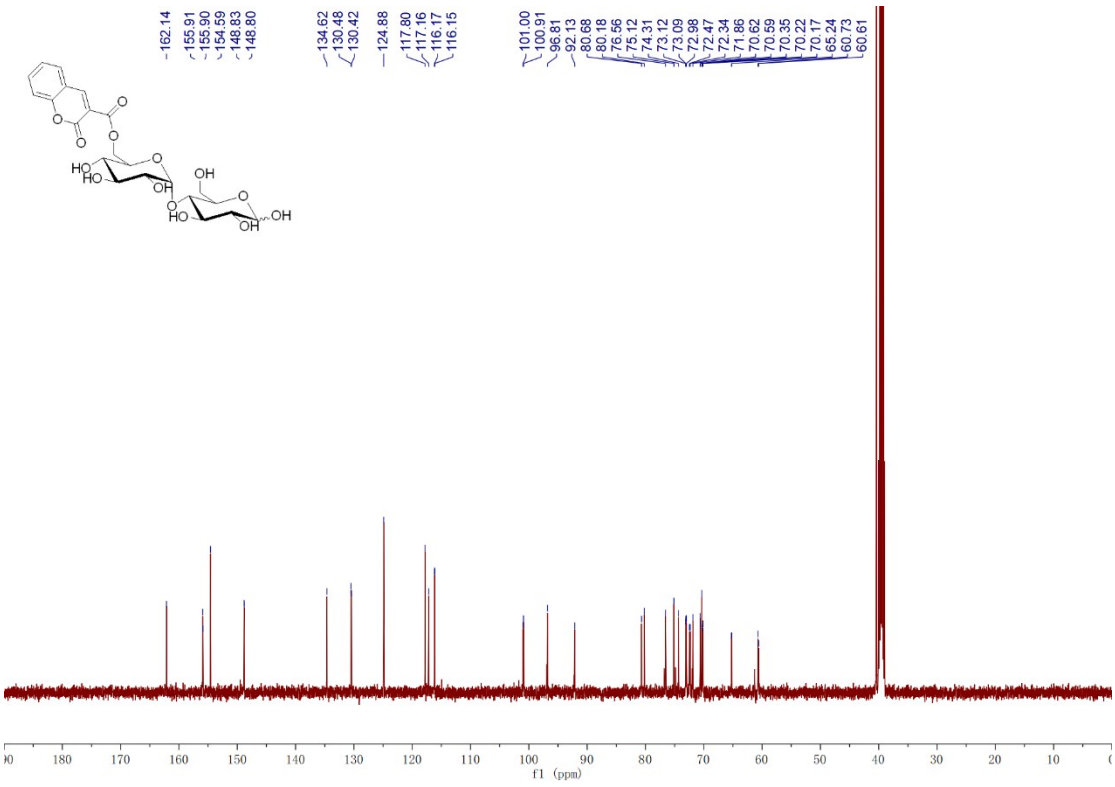
5c


8.74 7.95 7.95 7.93 7.93 7.77 7.77 7.75 7.75 7.75 7.75 7.74 7.73 7.45 7.44 7.44 7.43 7.43 7.42 7.41 7.40 7.40 5.23 5.23 5.16 5.15 5.13 5.12 5.10 4.94 4.93 4.85 4.83 4.82 4.66 4.65 4.50 4.50 4.48 4.48 4.42 4.41 4.41 4.40 4.29 4.28 4.27 4.26 3.92 3.91 3.89 3.80 3.79 3.58 3.57 3.57 3.56 3.56 3.55 3.54 3.54 3.53 3.49 3.48 3.43 3.42 3.28 3.26 3.24 3.23
OH
O
O
O
O
O
OH
OH
HO
HO
HO
0.93
1.12
1.12
2.18
0.95
0.97
1.88
0.93
0.98
0.93
0.98
1.00
0.95
1.02
0.98
0.94
3.18
0.98
1.97
2.12
f1 (ppm)

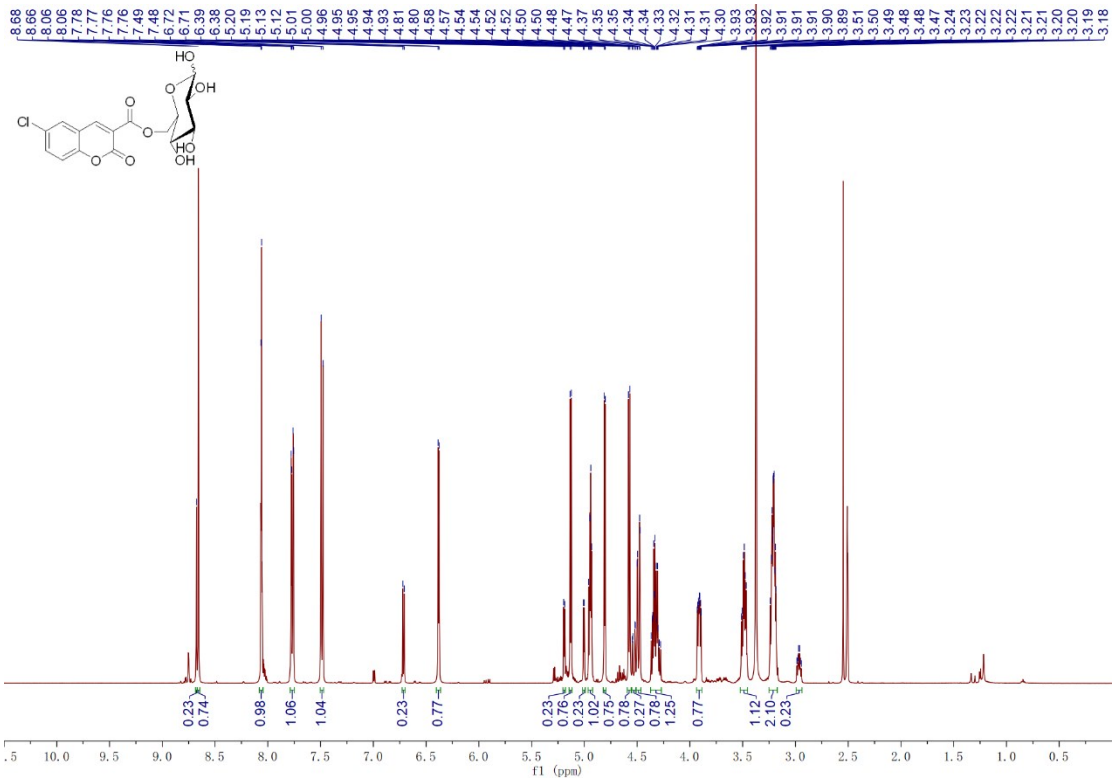

162.25
155.95
154.54
148.80
134.52
130.45
124.80
117.78
117.27
116.13
103.99
91.63
82.50
76.89
74.44
72.88
71.50
70.17
70.08
65.03
62.50
62.16
OH
O
O
O
O
O
OH
OH
HO
HO
HO
f1 (ppm)

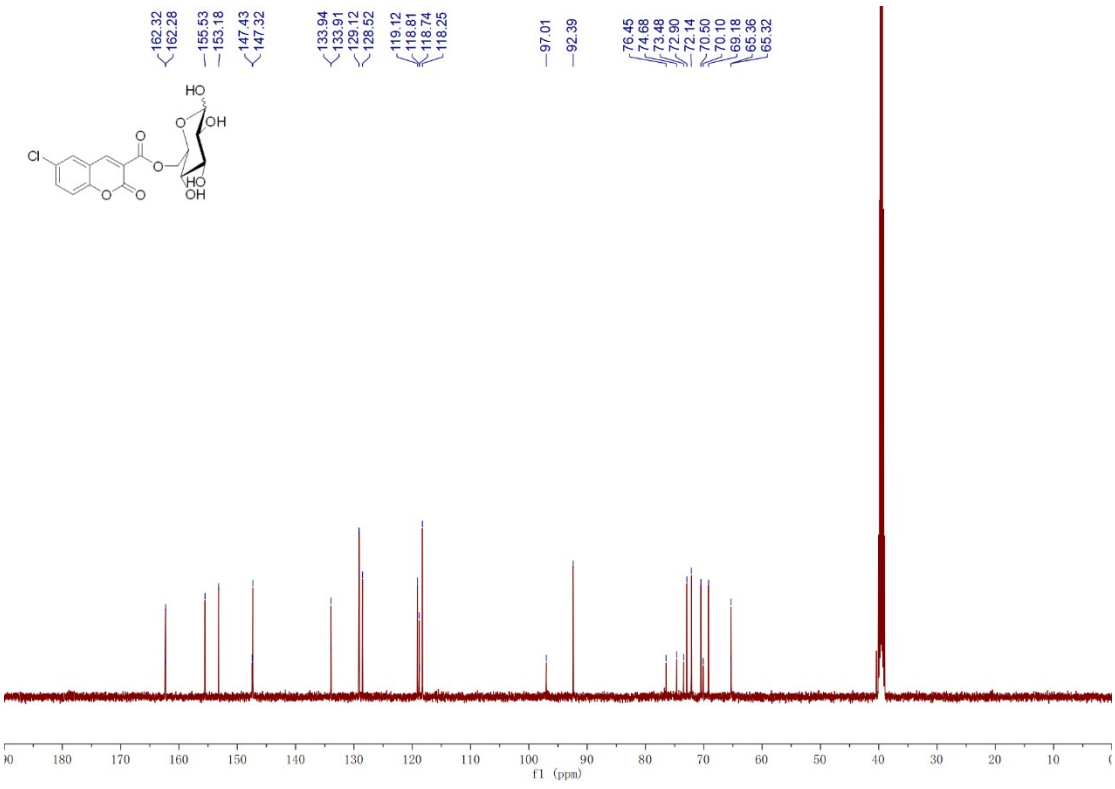
5d


8.77 8.75 7.96 7.95 7.94 7.94 7.92 7.92 7.77 7.77 7.75 7.75 7.75 7.75 7.74 7.73 7.45 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.39 6.70 6.68 6.36 6.36 5.57 5.56 5.55 5.55 5.51 5.51 5.36 5.35 5.29 5.28 5.27 5.07 5.06 5.05 5.04 4.98 4.98 4.92 4.64 4.63 4.56 4.53 4.51 4.51 4.45 4.33 4.26 3.69 3.68 3.68 3.62 3.61 3.61 3.44 3.35 3.34 3.33 3.33 3.32 3.31 3.20 3.19 3.18 3.18
0.47 0.48 1.02 1.03 2.04 0.53 0.47 0.98 0.53 0.46 0.97 1.43 0.53 0.53 0.56 0.51 1.00 0.52 0.53 0.55 0.98 0.98 1.59 0.95 0.59 1.40 2.22 0.58 1.53 0.52
f1 (ppm)

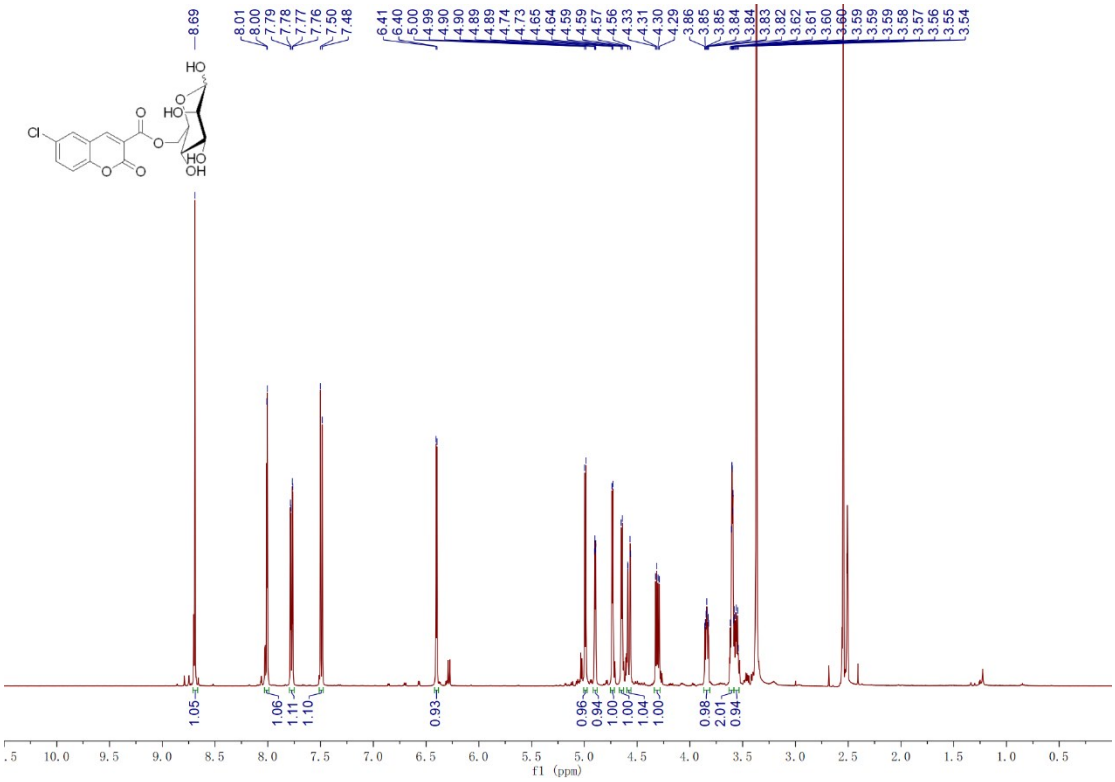

162.14 155.91 155.90 154.59 148.83 148.80 134.62 130.48 130.42 124.88 117.80 117.16 116.17 116.15 101.00 100.91 96.81 92.13 80.68 80.18 76.56 75.12 74.31 73.12 73.09 72.98 72.47 72.34 71.86 70.62 70.59 70.35 70.22 70.17 65.24 60.73 60.61
f1 (ppm)

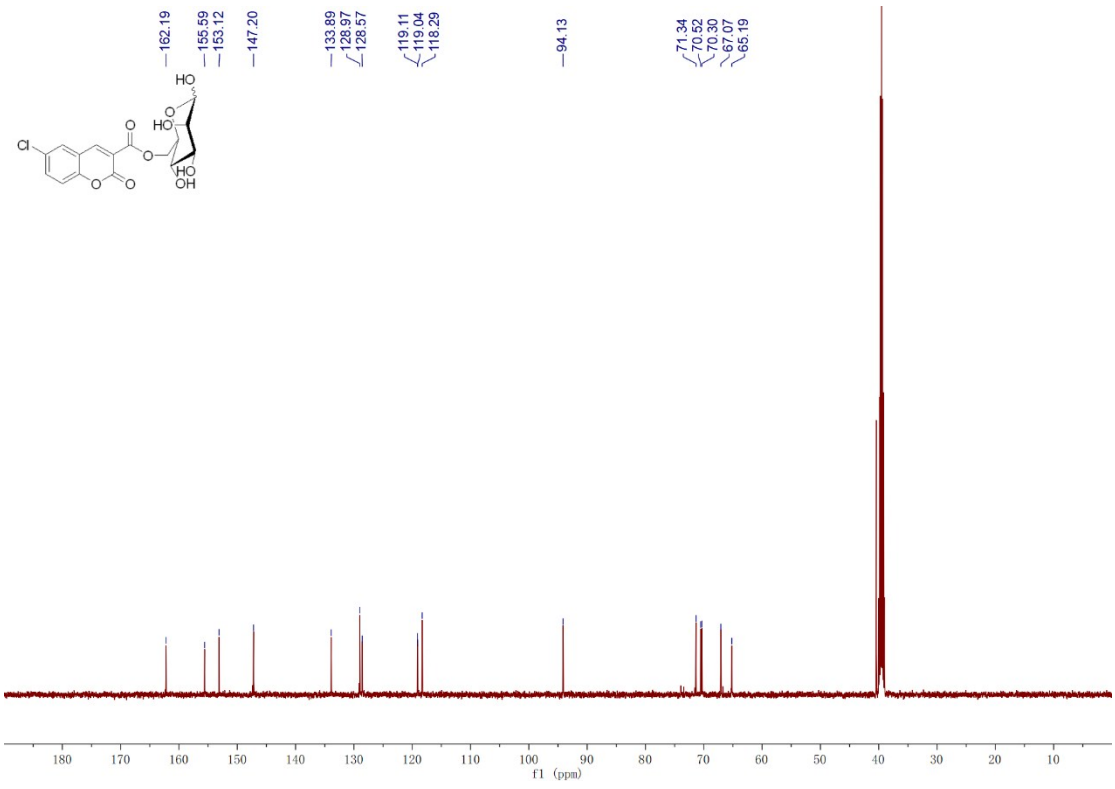
5e


8.68 8.66 8.06 8.06 7.78 7.77 7.76 7.76 7.49 7.48 6.72 6.71 6.39 6.38 5.20 5.19 5.13 5.12 5.01 5.00 4.96 4.95 4.95 4.94 4.93 4.81 4.80 4.58 4.57 4.54 4.54 4.52 4.52 4.50 4.50 4.48 4.47 4.37 4.35 4.35 4.34 4.34 4.33 4.32 4.31 4.31 4.30 3.93 3.93 3.92 3.91 3.91 3.90 3.89 3.51 3.50 3.49 3.48 3.48 3.47 3.24 3.23 3.22 3.22 3.22 3.21 3.21 3.20 3.20 3.19 3.18
HO
OH
O
Cl
O
O
HO
OH
0.23 0.74 0.98 1.06 1.04 0.23 0.77 0.23 0.76 0.23 1.02 0.75 0.78 0.27 0.78 1.25 0.77 1.12 2.10 0.23
f1 (ppm)

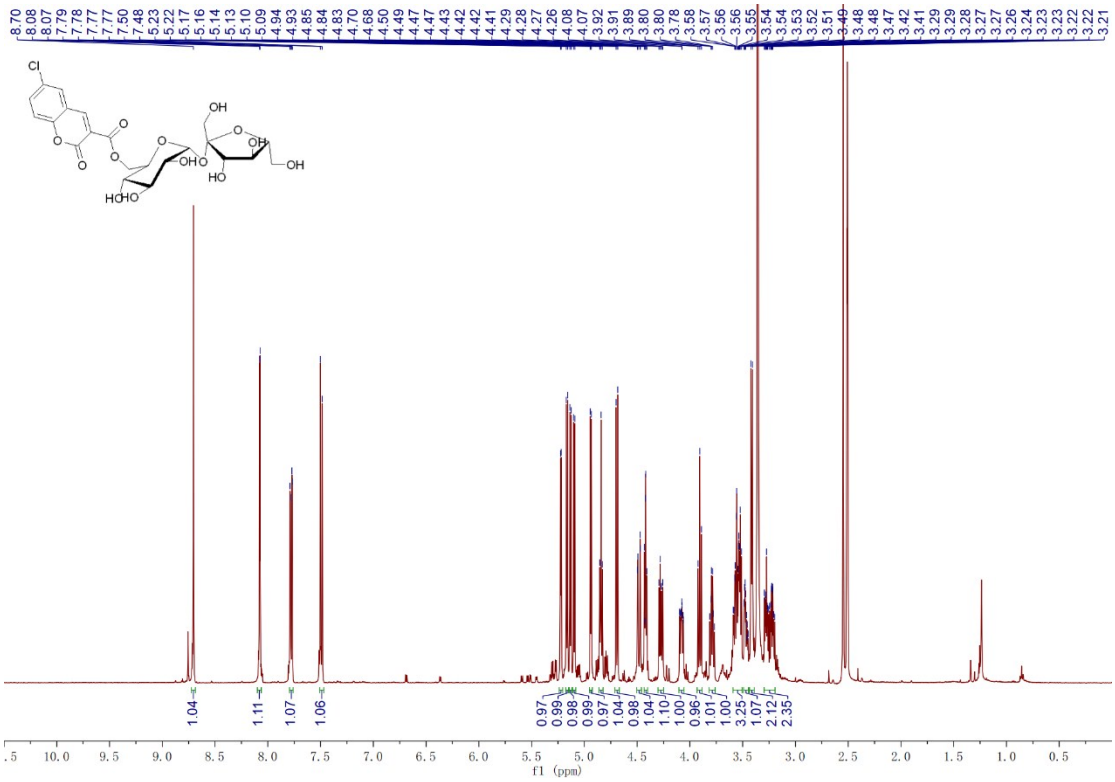

162.32 162.28 155.53 153.18 147.43 147.32 133.94 133.91 129.12 128.52 119.12 118.81 118.74 118.25 97.01 92.39 76.45 74.68 73.48 72.90 72.14 70.50 70.10 69.18 65.36 65.32
HO
OH
O
Cl
O
O
HO
OH
f1 (ppm)

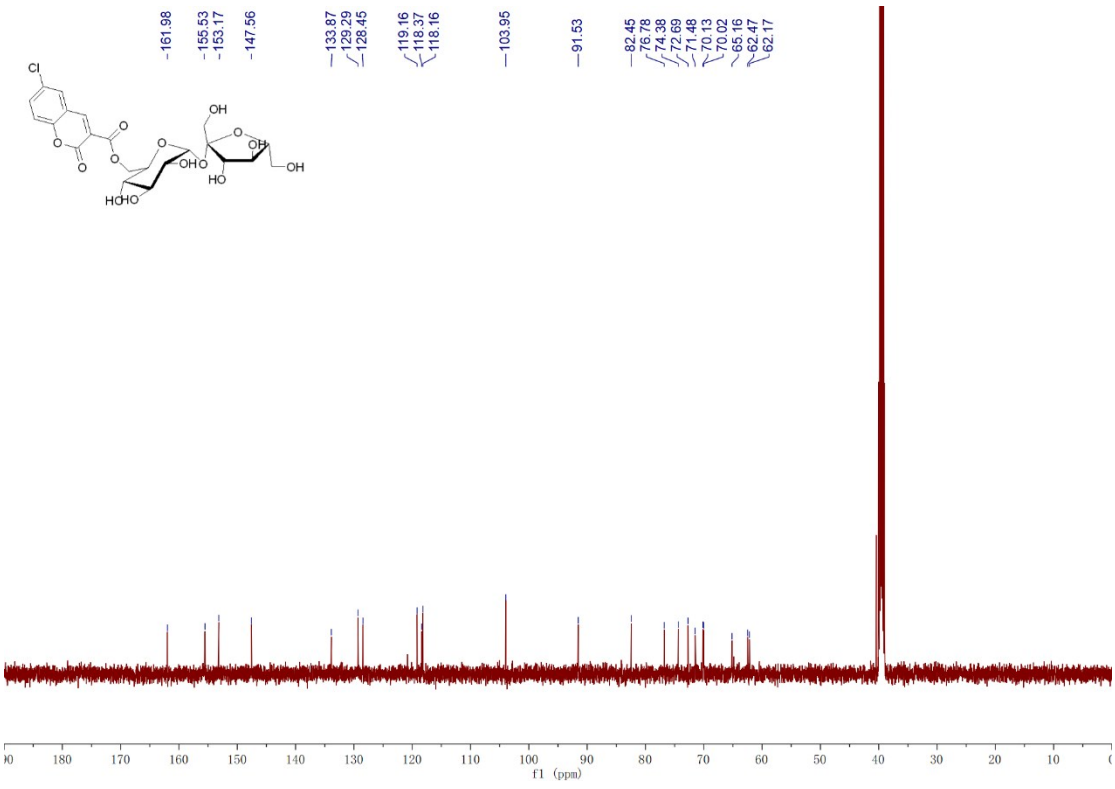
5f


8.69
8.01
8.00
7.79
7.78
7.77
7.76
7.50
7.48
6.41
6.40
5.00
4.99
4.90
4.90
4.89
4.89
4.74
4.73
4.65
4.64
4.59
4.59
4.57
4.56
4.33
4.31
4.30
4.29
3.86
3.85
3.85
3.84
3.84
3.83
3.82
3.62
3.61
3.60
3.60
3.59
3.59
3.59
3.58
3.57
3.56
3.55
3.54
HO
O
HO
Cl
O
O
HO
OH
1.05
1.06
1.11
1.10
0.93
0.96
0.94
1.00
1.00
1.04
1.00
0.98
2.01
0.94
f1 (ppm)

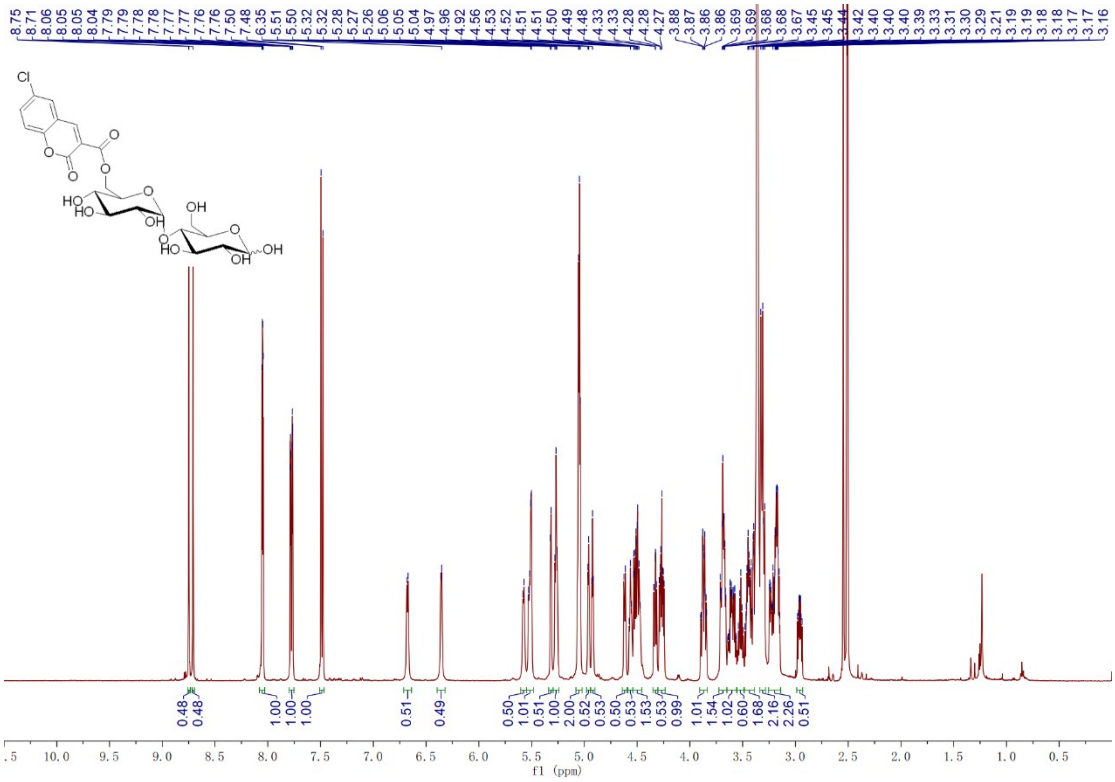

162.19
155.59
153.12
147.20
133.89
128.97
128.57
119.11
119.04
118.29
94.13
71.34
70.52
70.30
67.07
65.19
HO
O
HO
Cl
O
O
HO
OH
f1 (ppm)

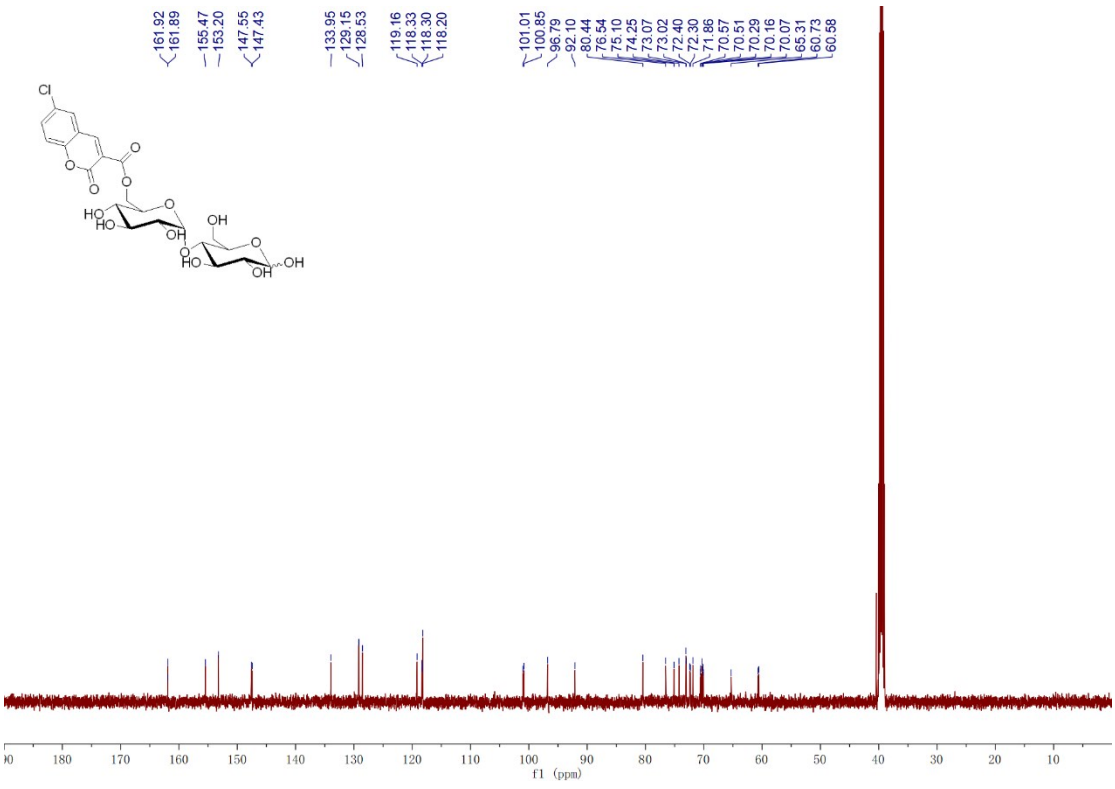
5g


8.70 8.08 8.07 7.79 7.78 7.77 7.77 7.50 7.48 5.23 5.22 5.17 5.16 5.14 5.13 5.10 5.09 4.94 4.93 4.85 4.84 4.83 4.70 4.68 4.50 4.49 4.47 4.47 4.43 4.42 4.42 4.41 4.29 4.28 4.27 4.26 4.08 4.07 3.92 3.91 3.89 3.80 3.80 3.78 3.58 3.57 3.56 3.56 3.55 3.54 3.54 3.53 3.52 3.51 3.49 3.48 3.48 3.47 3.42 3.41 3.29 3.29 3.28 3.27 3.27 3.26 3.24 3.23 3.23 3.22 3.22 3.21
Cl
O
O
O
O
O
OH
OH
OH
HO
HO
HO
1.04
1.11
1.07
1.06
0.97
0.99
0.98
0.99
0.97
1.04
0.98
1.04
1.10
1.00
0.96
1.01
1.00
3.25
1.07
2.12
2.35
f1 (ppm)

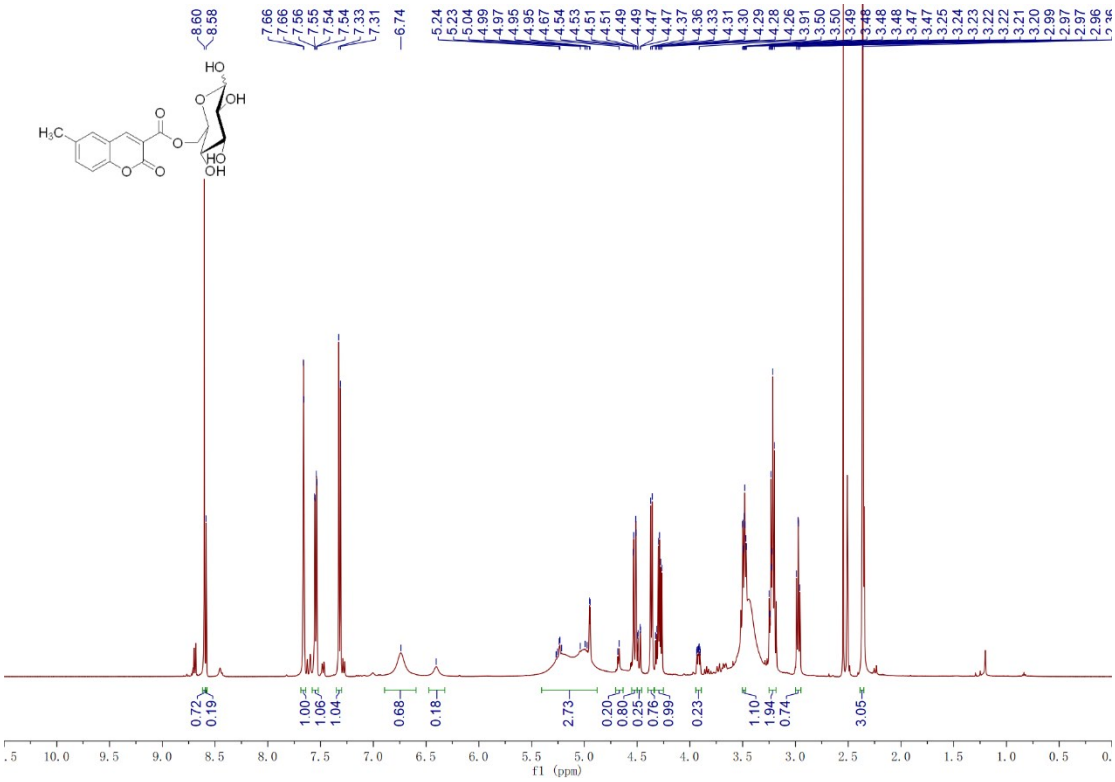

161.98
155.53
153.17
147.56
133.87
129.29
128.45
119.16
118.37
118.16
103.95
91.53
82.45
76.78
74.38
72.69
71.48
70.13
70.02
65.16
62.47
62.17
Cl
O
O
O
O
O
OH
OH
OH
HO
HO
HO
f1 (ppm)

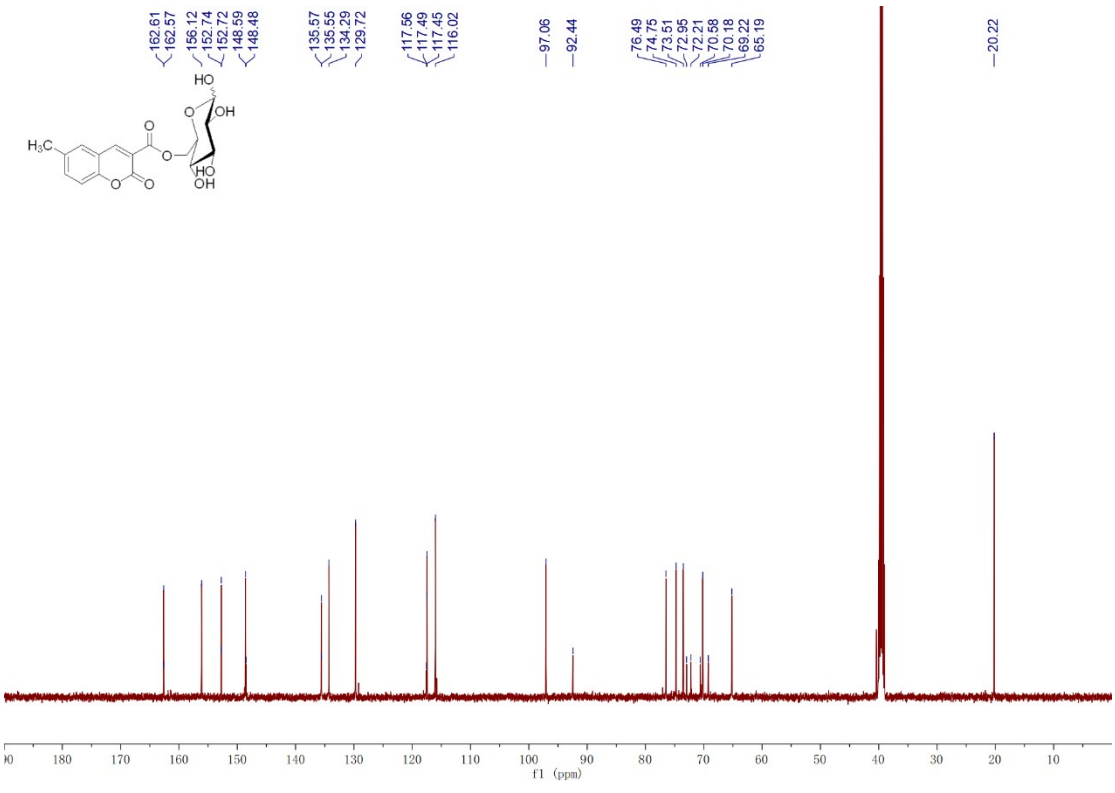
5h



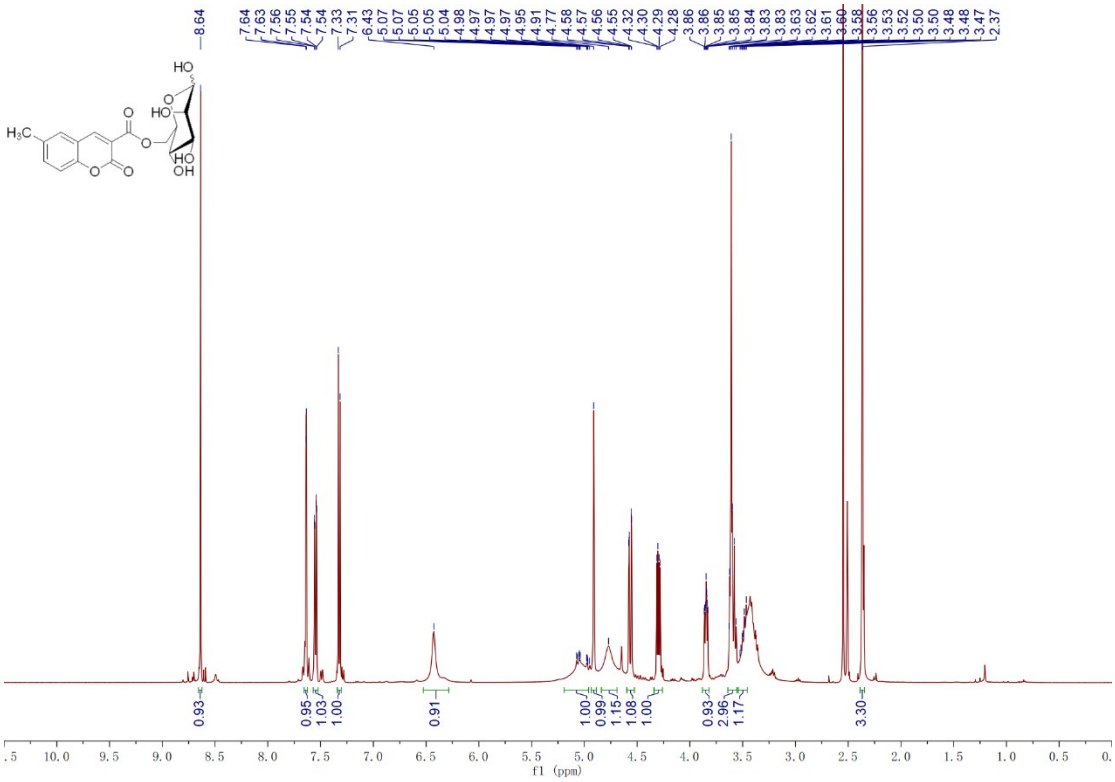


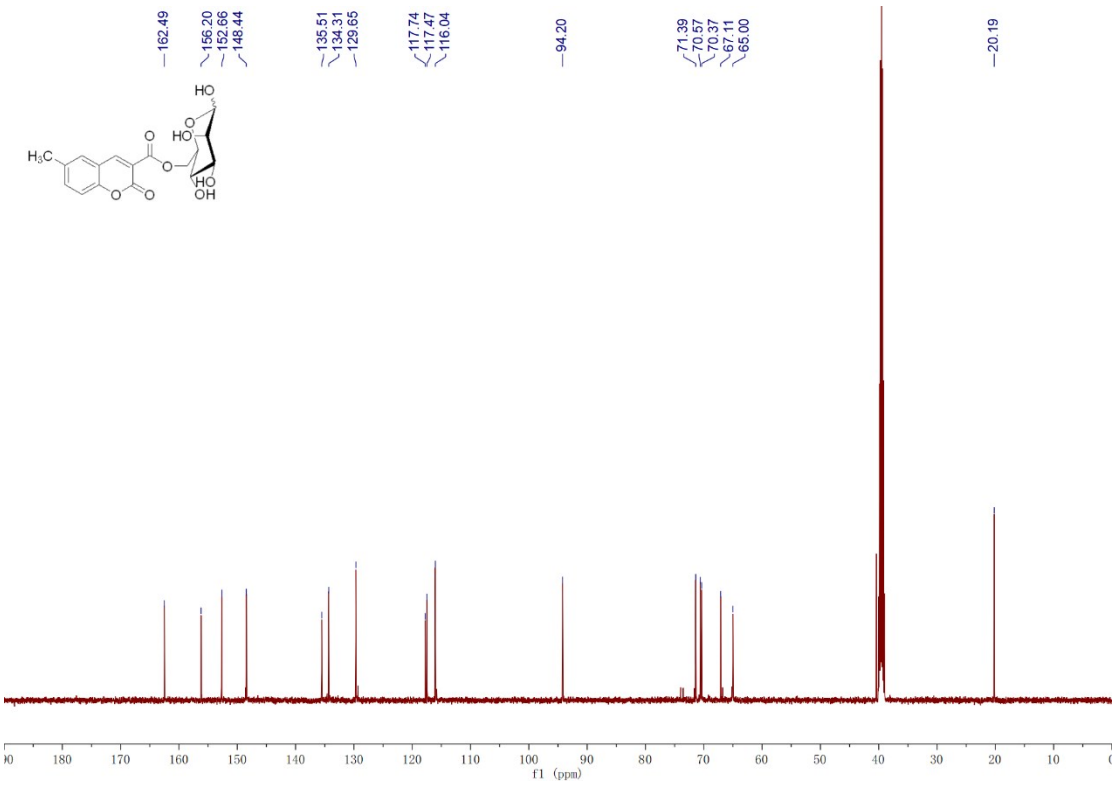
5i


8.60
8.58
7.66
7.66
7.56
7.55
7.54
7.54
7.33
7.31
6.74
5.24
5.23
5.04
4.99
4.97
4.95
4.95
4.67
4.54
4.53
4.51
4.51
4.49
4.49
4.47
4.47
4.37
4.36
4.33
4.31
4.30
4.29
4.28
4.26
3.91
3.50
3.50
3.49
3.48
3.48
3.48
3.47
3.47
3.25
3.24
3.23
3.22
3.22
3.21
3.20
2.99
2.97
2.96
HO
OH
O
O
HO
OH
H3C
O
O
0.72
0.19
1.00
1.06
1.04
0.68
0.18
2.73
0.20
0.80
0.25
0.76
0.99
0.23
1.10
1.94
0.74
3.05
f1 (ppm)

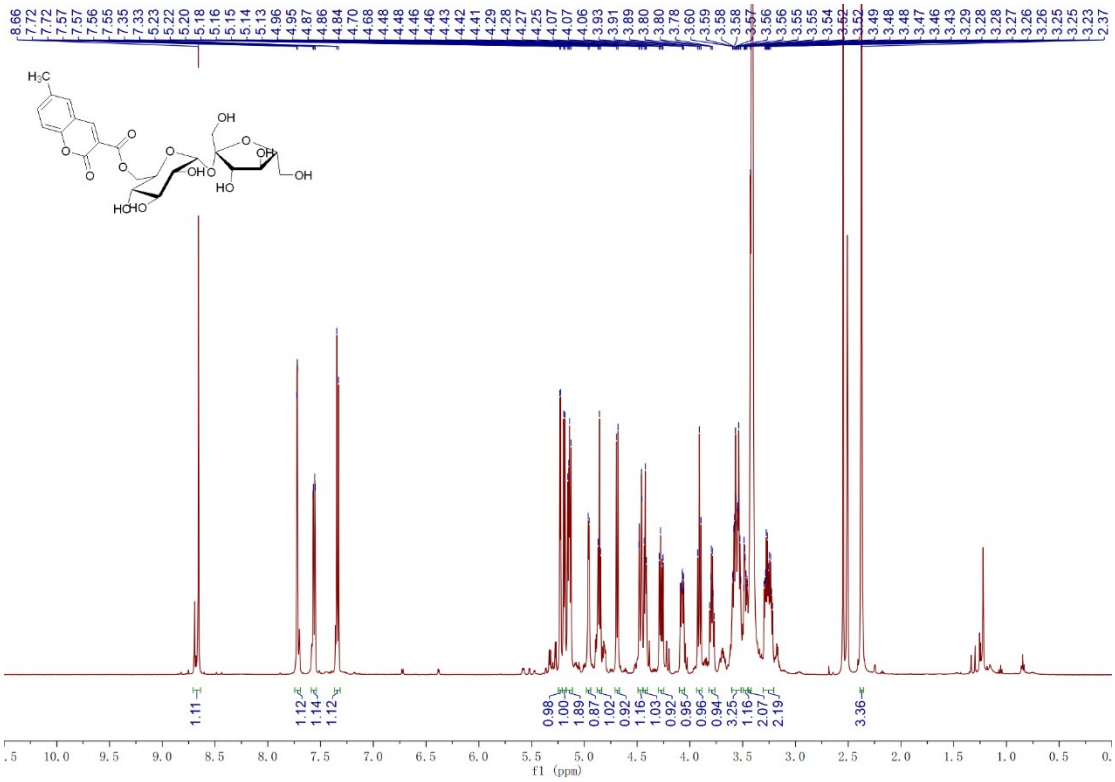

162.61
162.57
156.12
152.74
152.72
148.59
148.48
135.57
135.55
134.29
129.72
117.56
117.49
117.45
116.02
97.06
92.44
76.49
74.75
73.51
72.95
72.21
70.58
70.18
69.22
65.19
20.22
HO
OH
O
O
HO
OH
H3C
O
O
f1 (ppm)

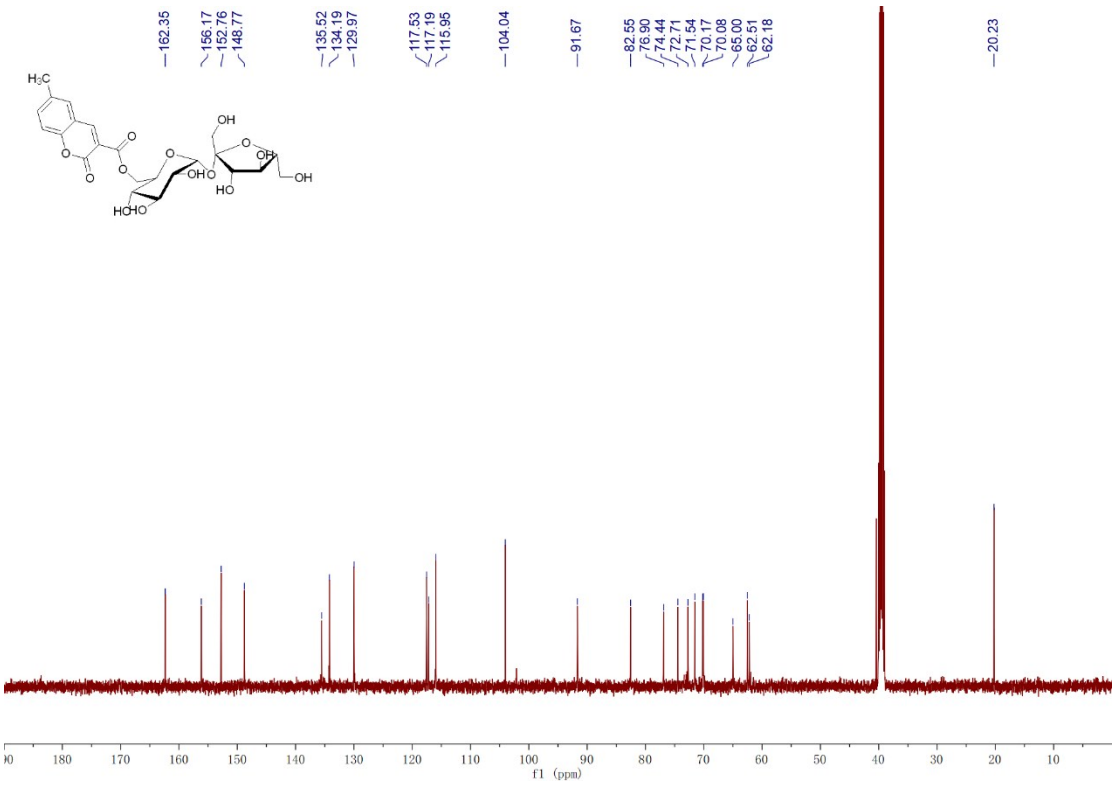
5j


8.64
7.64
7.63
7.56
7.55
7.54
7.54
7.33
7.31
6.43
5.07
5.07
5.05
5.05
5.04
4.98
4.97
4.97
4.97
4.95
4.91
4.77
4.58
4.57
4.56
4.55
4.32
4.30
4.29
4.28
3.86
3.86
3.85
3.85
3.84
3.83
3.83
3.63
3.62
3.61
3.60
3.58
3.56
3.53
3.52
3.50
3.50
3.48
3.48
3.47
2.37
0.93
0.95
1.03
1.00
0.91
1.00
0.99
1.15
1.08
1.00
0.93
2.96
1.17
3.30
f1 (ppm)

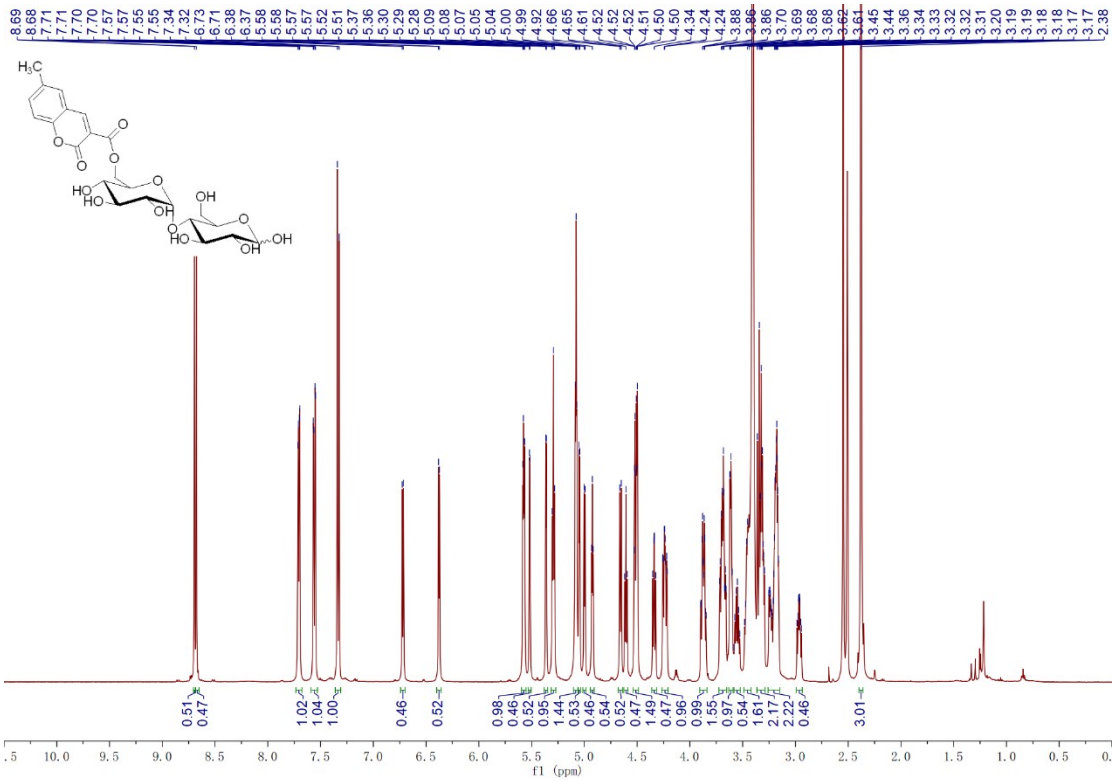

162.49
156.20
152.66
148.44
135.51
134.31
129.65
117.74
117.47
116.04
94.20
71.39
70.57
70.37
67.11
65.00
20.19
f1 (ppm)

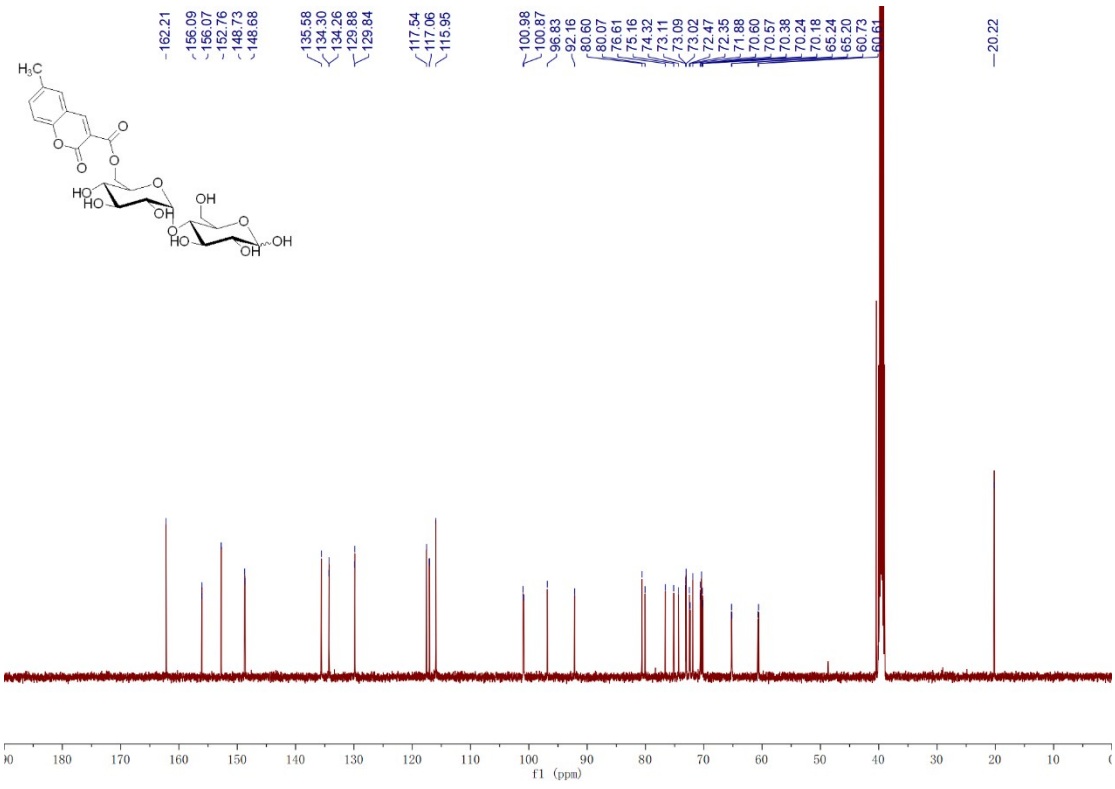
5k


8.66 7.72 7.72 7.57 7.57 7.56 7.55 7.35 7.33 5.23 5.22 5.20 5.18 5.16 5.15 5.14 5.13 4.96 4.95 4.87 4.86 4.84 4.70 4.68 4.48 4.48 4.46 4.46 4.43 4.42 4.41 4.29 4.28 4.27 4.25 4.07 4.07 4.06 3.93 3.91 3.89 3.80 3.80 3.78 3.60 3.59 3.58 3.58 3.57 3.56 3.56 3.55 3.55 3.54 3.52 3.49 3.48 3.48 3.47 3.46 3.43 3.29 3.28 3.28 3.27 3.26 3.26 3.25 3.25 3.23 2.37
1.11 1.12 1.14 1.12 0.98 1.00 1.89 0.87 1.02 0.92 1.16 1.03 0.92 0.95 0.96 0.94 3.25 1.16 2.07 2.19 3.36
f1 (ppm)

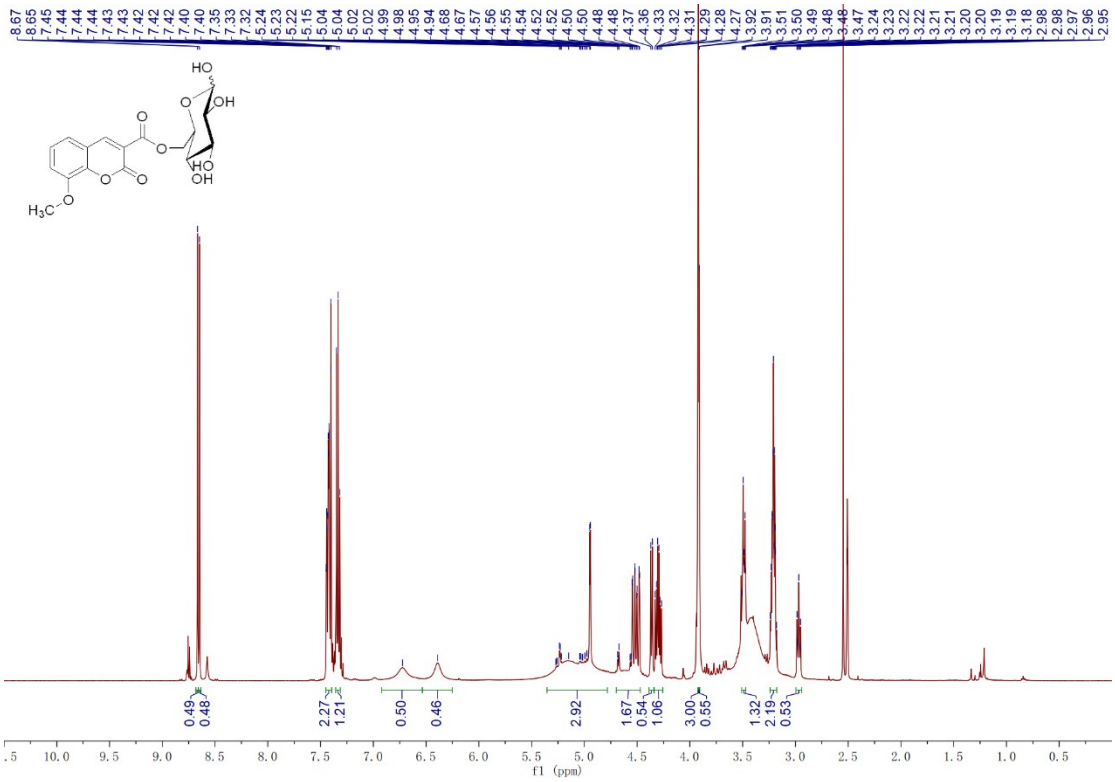

162.35 156.17 152.76 148.77 135.52 134.19 129.97 117.53 117.19 115.95 104.04 91.67 82.55 76.90 74.44 72.71 71.54 70.17 70.08 65.00 62.51 62.18 20.23
f1 (ppm)

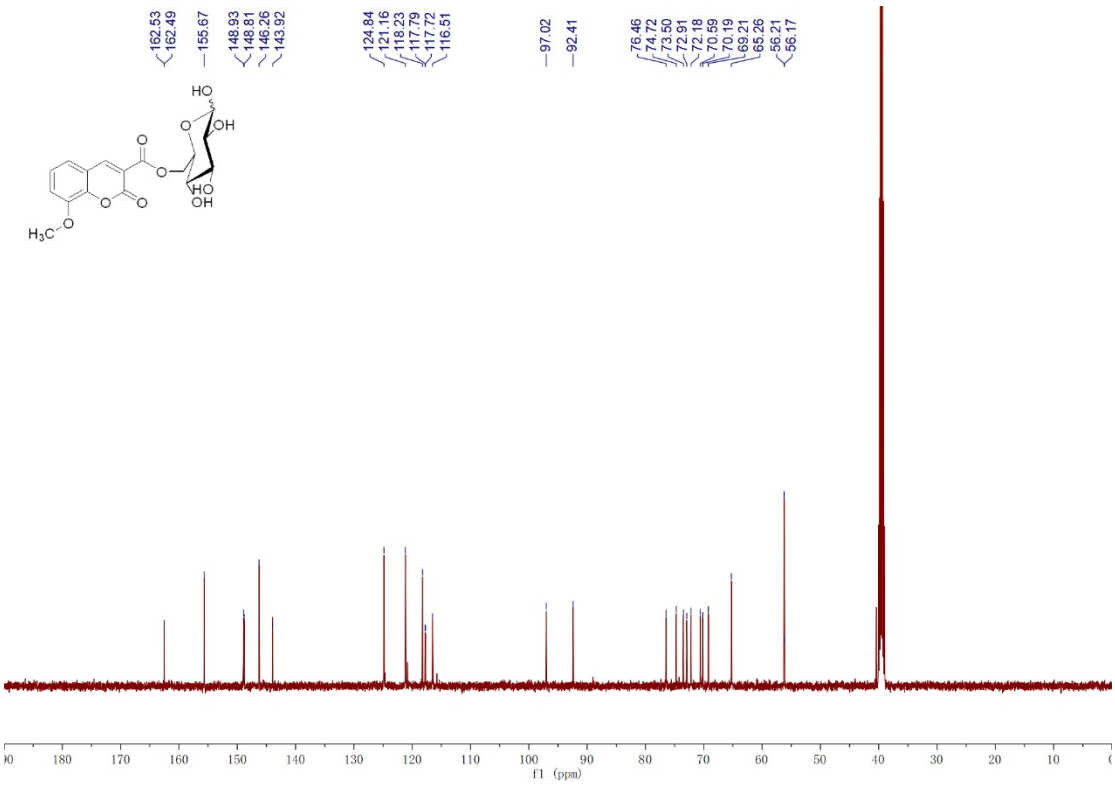
5l


8.69 8.68 7.71 7.71 7.70 7.70 7.57 7.57 7.55 7.55 7.34 7.32 6.73 6.71 6.38 6.37 5.58 5.58 5.57 5.57 5.52 5.51 5.37 5.36 5.30 5.29 5.28 5.09 5.08 5.07 5.05 5.04 5.00 4.99 4.92 4.66 4.65 4.61 4.52 4.52 4.52 4.51 4.50 4.50 4.34 4.24 4.24 3.88 3.86 3.86 3.70 3.69 3.68 3.68 3.62 3.61 3.45 3.44 3.36 3.34 3.33 3.32 3.32 3.31 3.20 3.19 3.19 3.18 3.17 3.17 2.38
0.51 0.47 1.02 1.04 1.00 0.46 0.52 0.98 0.46 0.52 0.95 1.44 0.53 0.46 0.54 0.52 0.47 1.49 0.47 0.96 0.99 1.55 0.97 0.54 1.61 2.17 2.22 0.46 3.01
f1 (ppm)

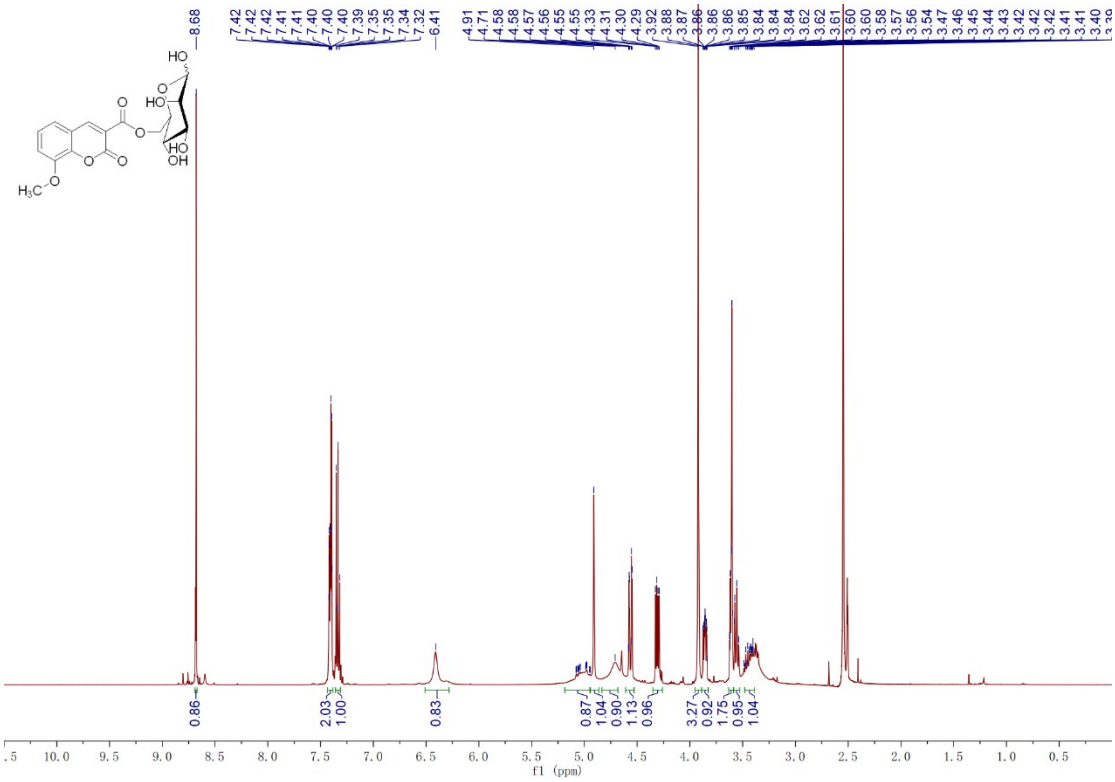

162.21 156.09 156.07 152.76 148.73 148.68 135.58 134.30 134.26 129.88 129.84 117.54 117.06 115.95 100.98 100.87 96.83 92.16 80.60 80.07 76.61 75.16 74.32 73.11 73.09 73.02 72.47 72.35 71.88 70.60 70.57 70.38 70.24 70.18 65.24 65.20 60.73 60.61 20.22
f1 (ppm)

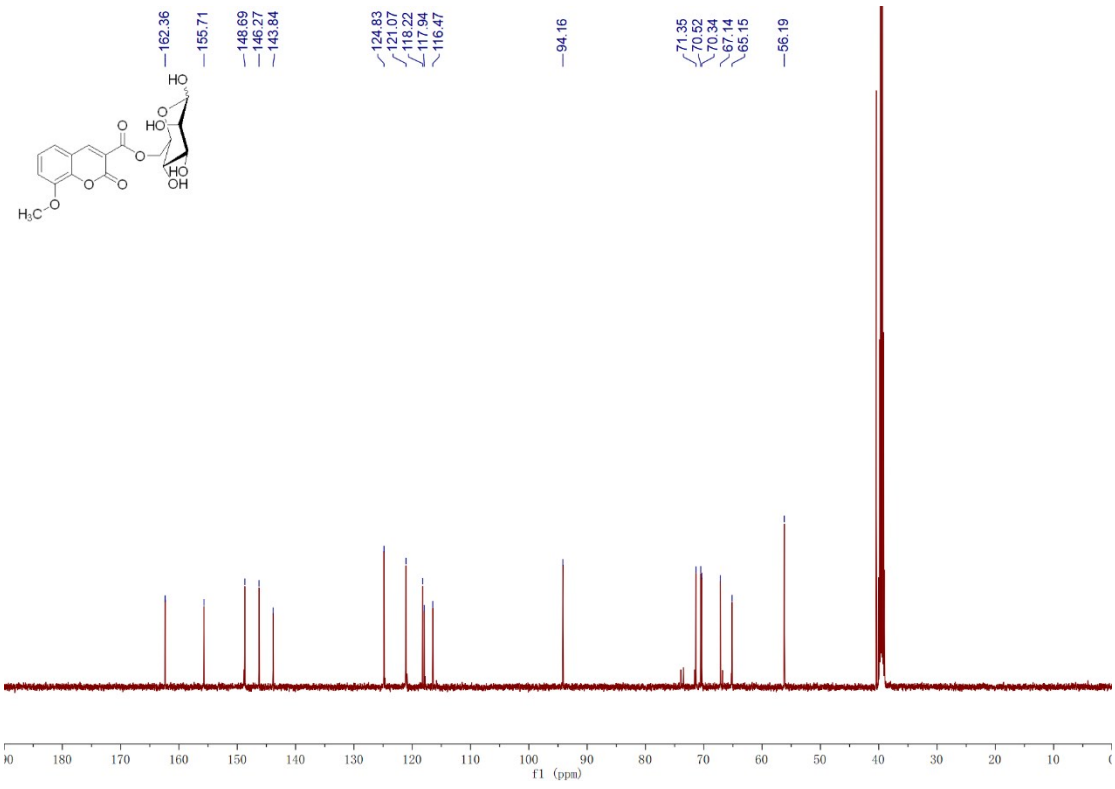
5m


8.67 8.65 7.45 7.44 7.44 7.44 7.43 7.42 7.42 7.42 7.40 7.40 7.35 7.33 7.32 5.24 5.23 5.22 5.15 5.04 5.04 5.02 5.02 4.99 4.98 4.95 4.94 4.68 4.67 4.57 4.56 4.55 4.54 4.52 4.52 4.50 4.50 4.48 4.48 4.37 4.36 4.33 4.32 4.31 4.29 4.28 4.27 3.92 3.91 3.51 3.50 3.49 3.48 3.48 3.47 3.24 3.23 3.22 3.22 3.21 3.21 3.20 3.19 3.19 3.18 2.98 2.98 2.97 2.96 2.95
HO
OH
HO
OH
O
O
O
O
O
H3C
0.49
0.48
2.27
1.21
0.50
0.46
2.92
1.67
0.54
1.06
3.00
0.55
1.32
2.19
0.53
f1 (ppm)

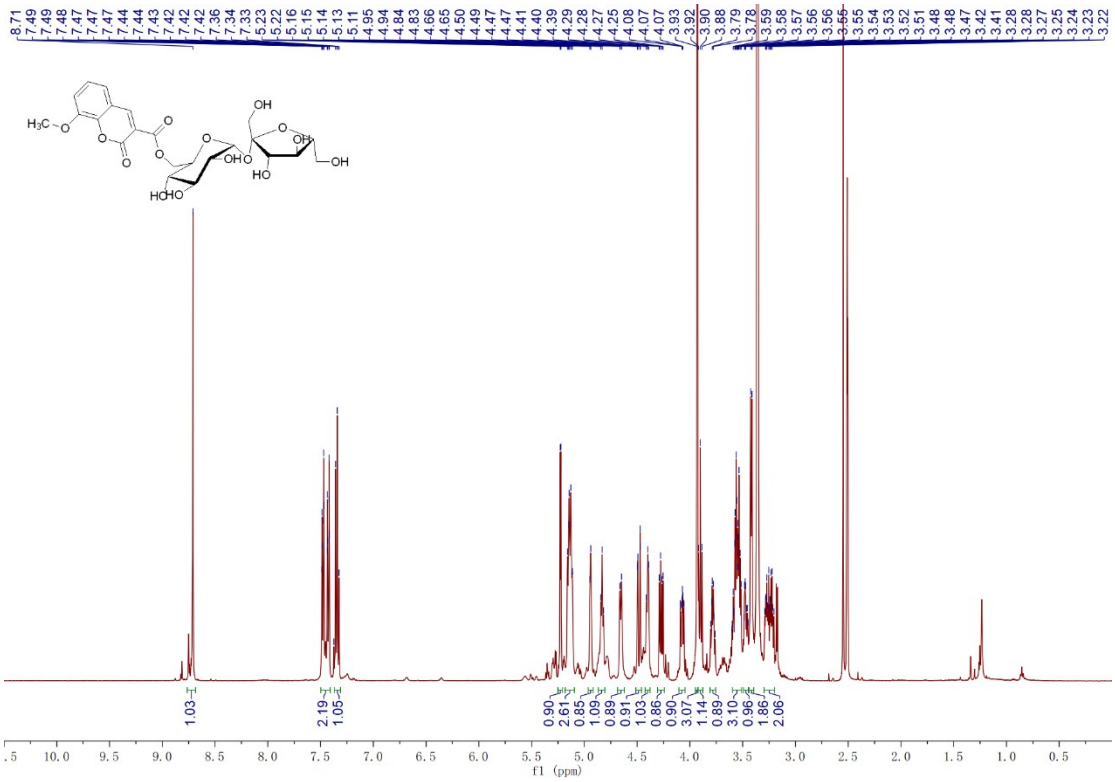

162.53
162.49
155.67
148.93
148.81
146.26
143.92
124.84
121.16
118.23
117.79
117.72
116.51
97.02
92.41
76.46
74.72
73.50
72.91
72.18
70.59
70.19
69.21
65.26
56.21
56.17
HO
OH
HO
OH
O
O
O
O
O
H3C
f1 (ppm)

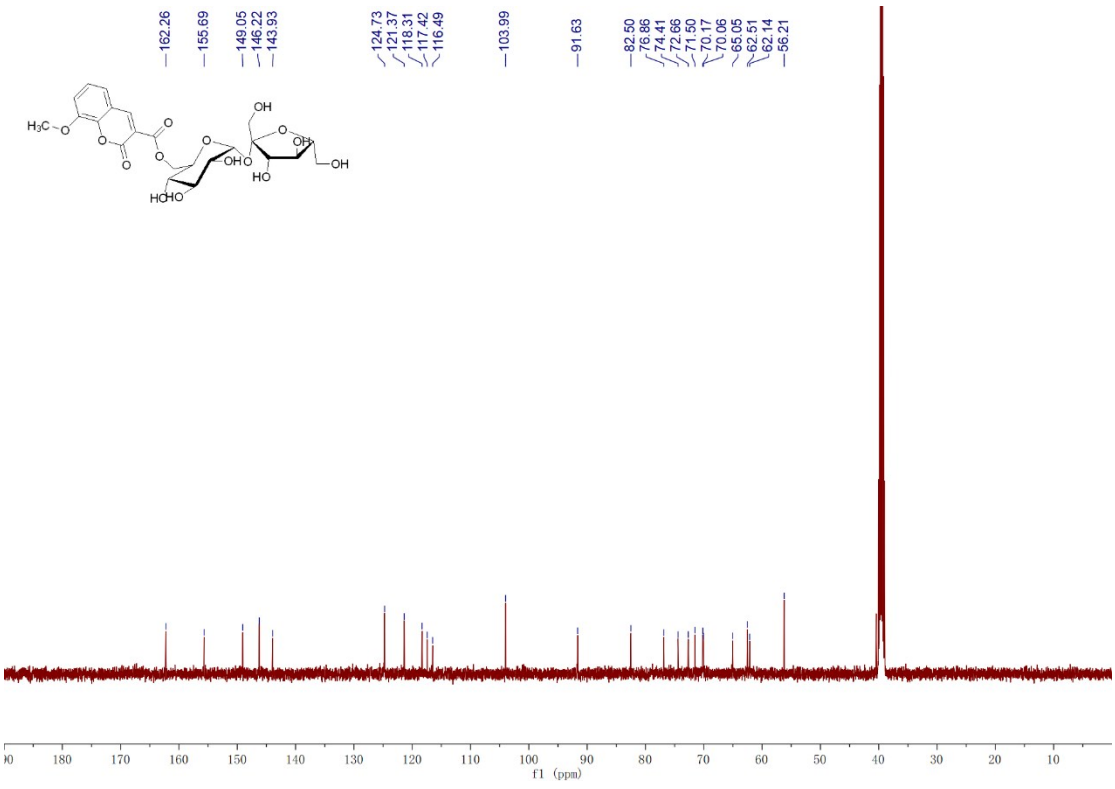
5n


8.68
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.35
7.35
7.34
7.32
6.41
4.91
4.71
4.58
4.58
4.57
4.56
4.55
4.55
4.33
4.31
4.30
4.29
3.92
3.88
3.87
3.86
3.86
3.86
3.85
3.84
3.84
3.84
3.62
3.62
3.61
3.60
3.60
3.58
3.57
3.56
3.54
3.47
3.46
3.45
3.44
3.43
3.42
3.42
3.42
3.41
3.41
3.40
0.86
2.03
1.00
0.83
0.87
1.04
0.90
1.13
0.96
3.27
0.92
1.75
0.95
1.04
f1 (ppm)

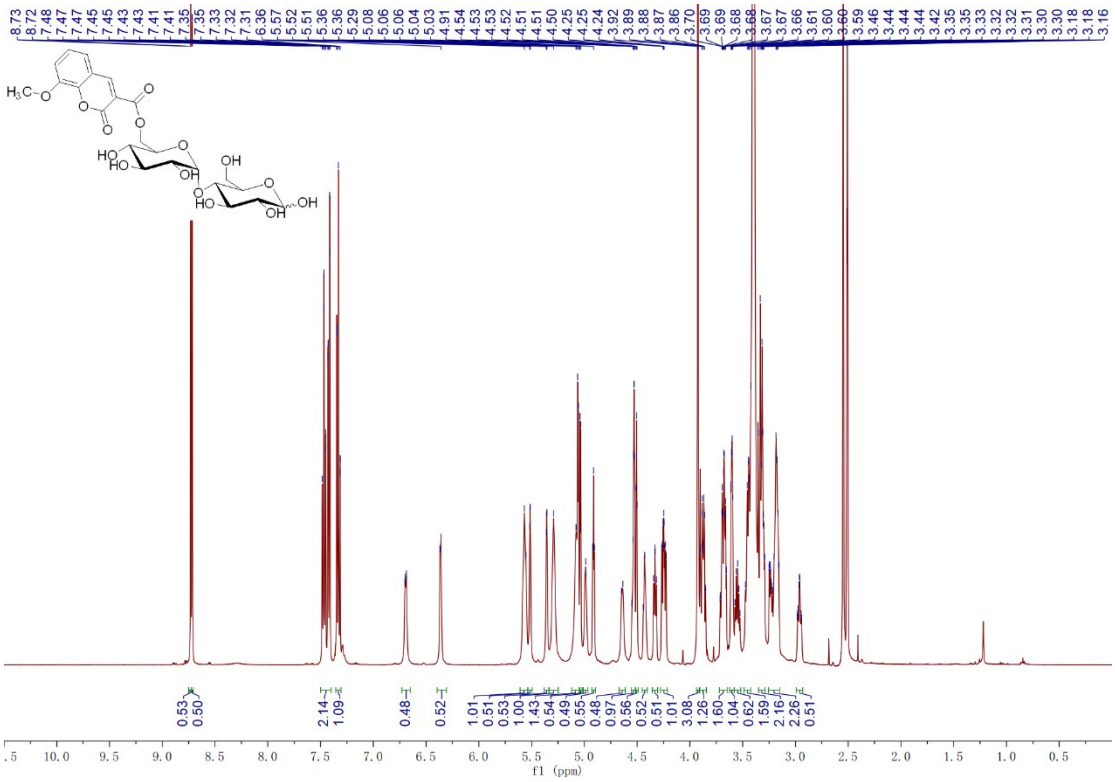

162.36
155.71
148.69
146.27
143.84
124.83
121.07
118.22
117.94
116.47
94.16
71.35
70.52
70.34
67.14
65.15
56.19
f1 (ppm)

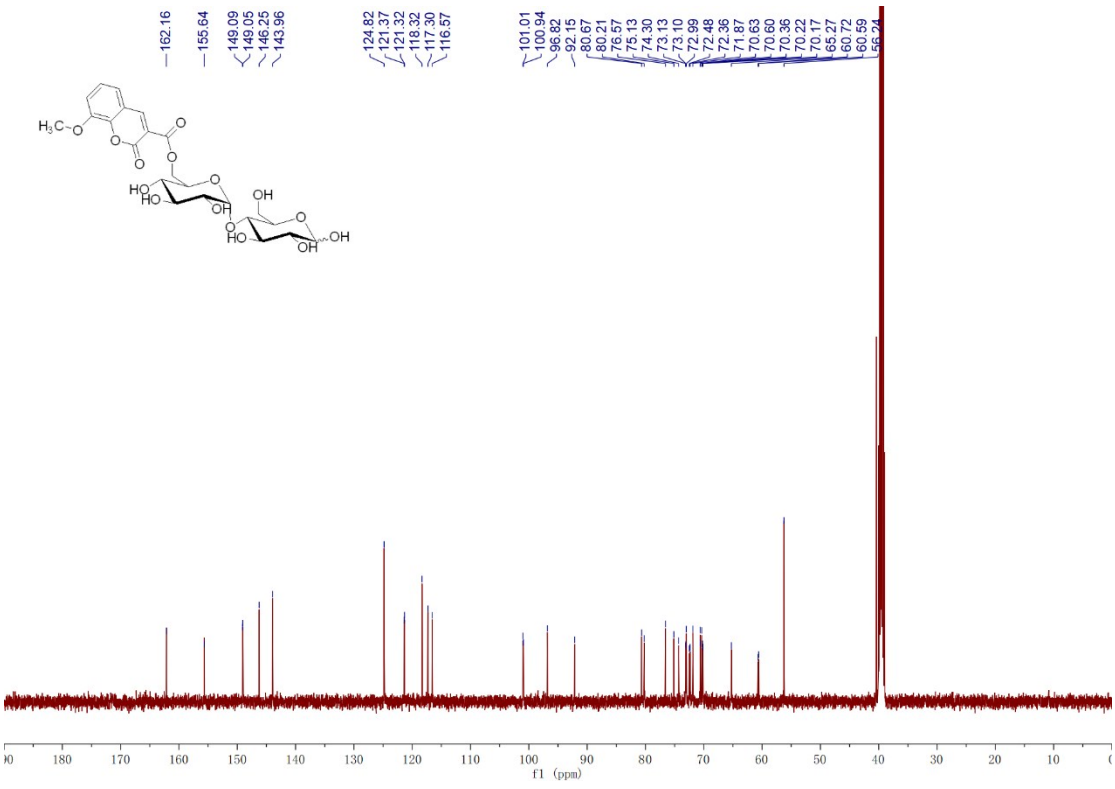
5o


8.71 7.49 7.49 7.48 7.47 7.47 7.47 7.44 7.44 7.43 7.42 7.42 7.42 7.36 7.34 7.33 5.23 5.22 5.16 5.15 5.14 5.13 5.11 4.95 4.94 4.84 4.83 4.66 4.65 4.50 4.49 4.47 4.47 4.41 4.40 4.39 4.29 4.28 4.27 4.25 4.08 4.07 4.07 4.01 3.93 3.92 3.90 3.88 3.79 3.78 3.59 3.58 3.57 3.56 3.56 3.55 3.54 3.53 3.52 3.51 3.48 3.48 3.47 3.42 3.41 3.28 3.28 3.27 3.25 3.24 3.23 3.22
1.03 2.19 1.05 0.90 2.61 0.85 1.09 0.89 0.91 1.03 0.86 0.90 3.07 1.14 0.89 3.10 0.96 1.86 2.06
f1 (ppm)

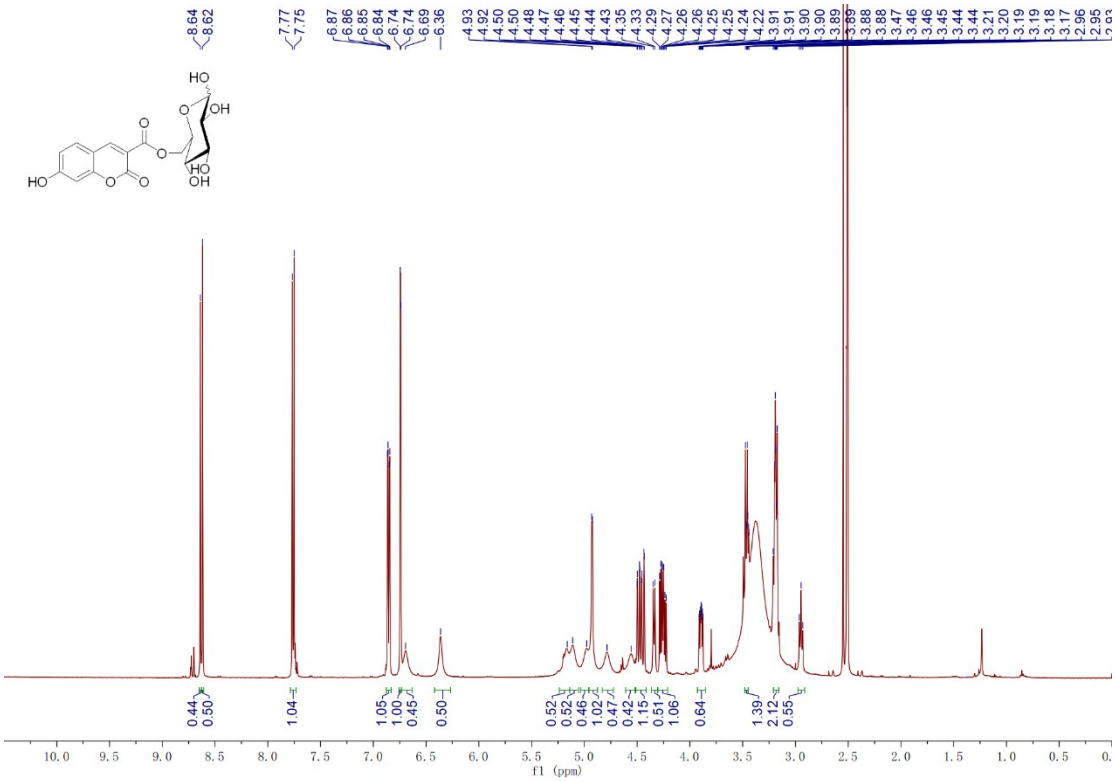

162.26 155.69 149.05 146.22 143.93 124.73 121.37 118.31 117.42 116.49 103.99 91.63 82.50 76.86 74.41 72.66 71.50 70.17 70.06 65.05 62.51 62.14 56.21
f1 (ppm)

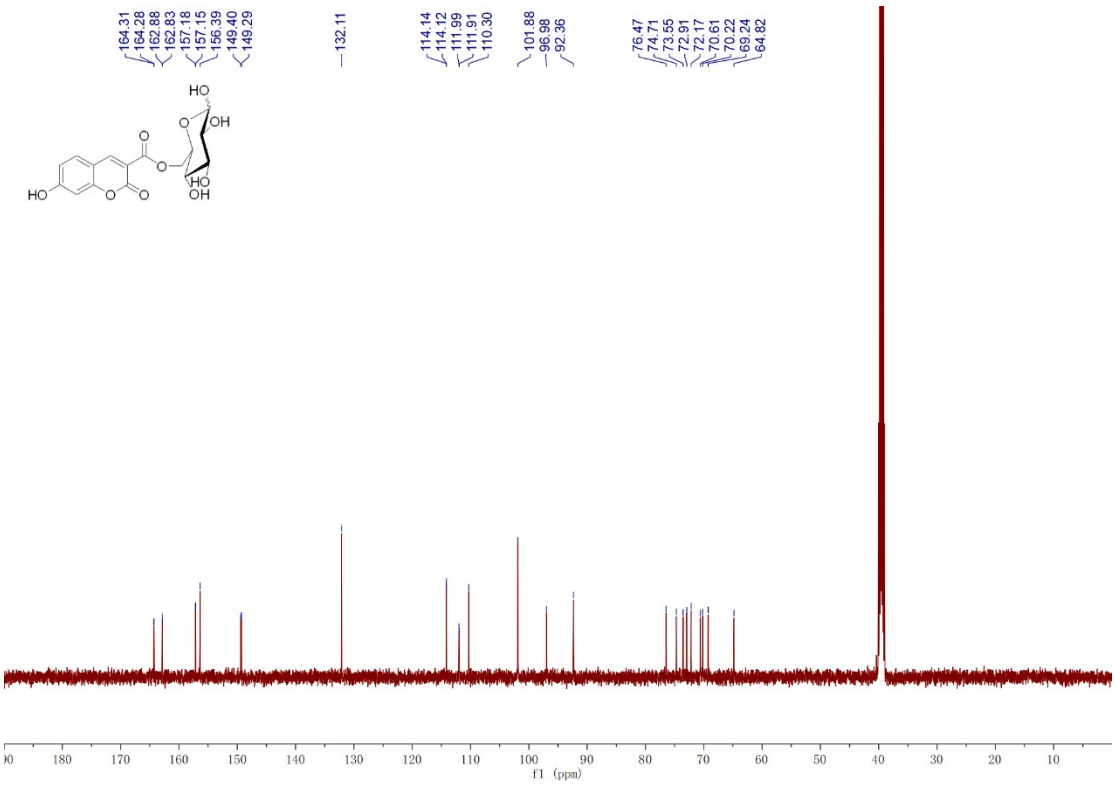
5p



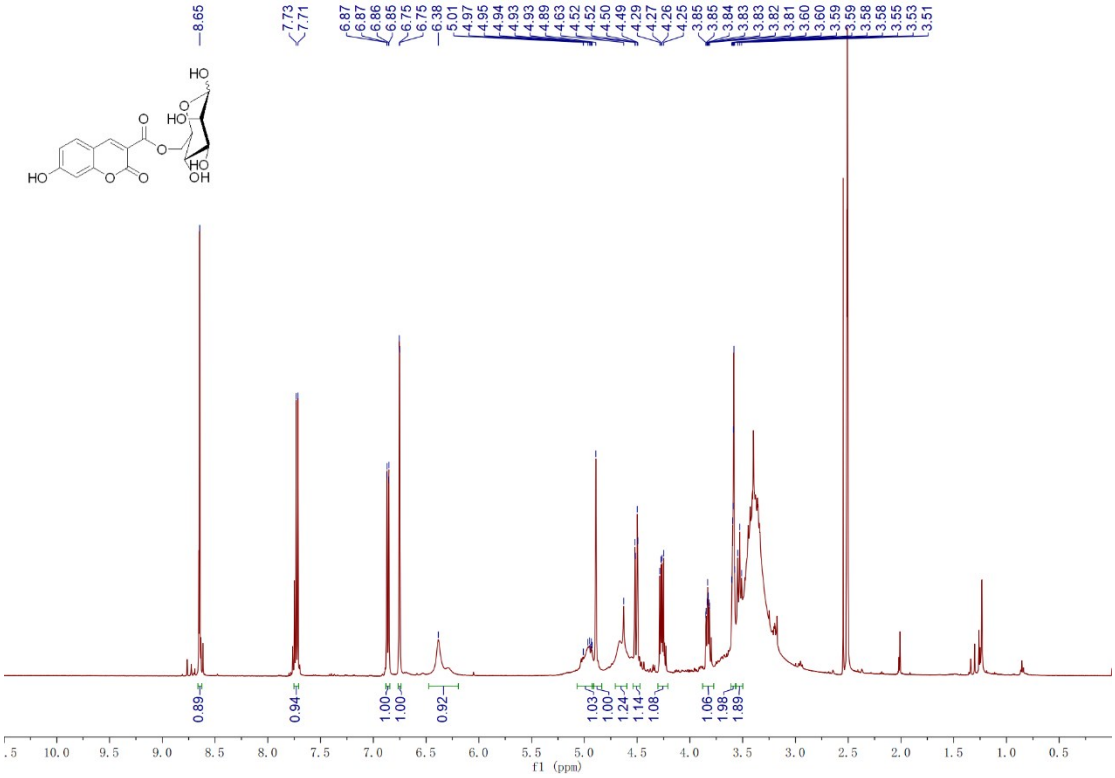


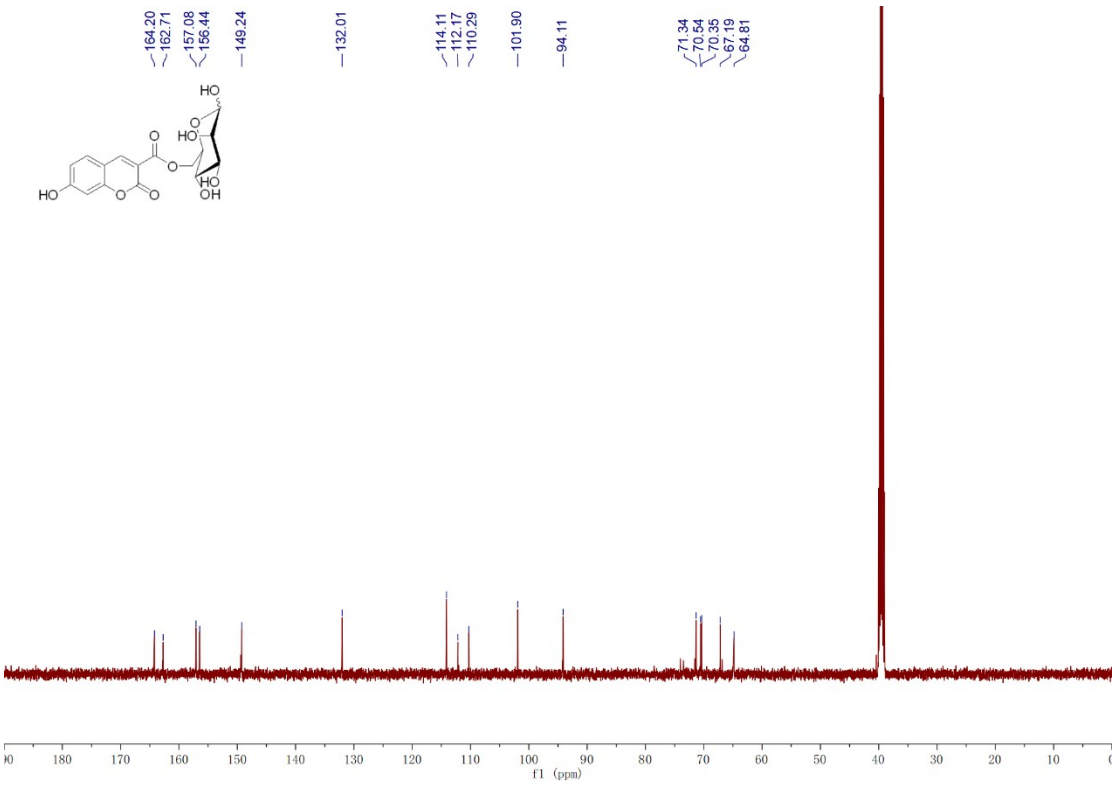
5q


8.64
8.62
7.77
7.75
6.87
6.86
6.85
6.84
6.74
6.74
6.69
6.36
4.93
4.92
4.50
4.50
4.48
4.47
4.46
4.45
4.44
4.43
4.35
4.33
4.29
4.27
4.26
4.26
4.25
4.25
4.24
4.22
3.91
3.91
3.90
3.90
3.89
3.89
3.88
3.88
3.47
3.46
3.46
3.45
3.44
3.44
3.21
3.20
3.19
3.19
3.18
3.17
2.96
2.95
HO
O
OH
HO
OH
O
O
HO
O
O
0.44
0.50
1.04
1.05
1.00
0.45
0.50
0.52
0.52
0.46
1.02
0.47
0.42
1.15
0.51
1.06
0.64
1.39
2.12
0.55
f1 (ppm)

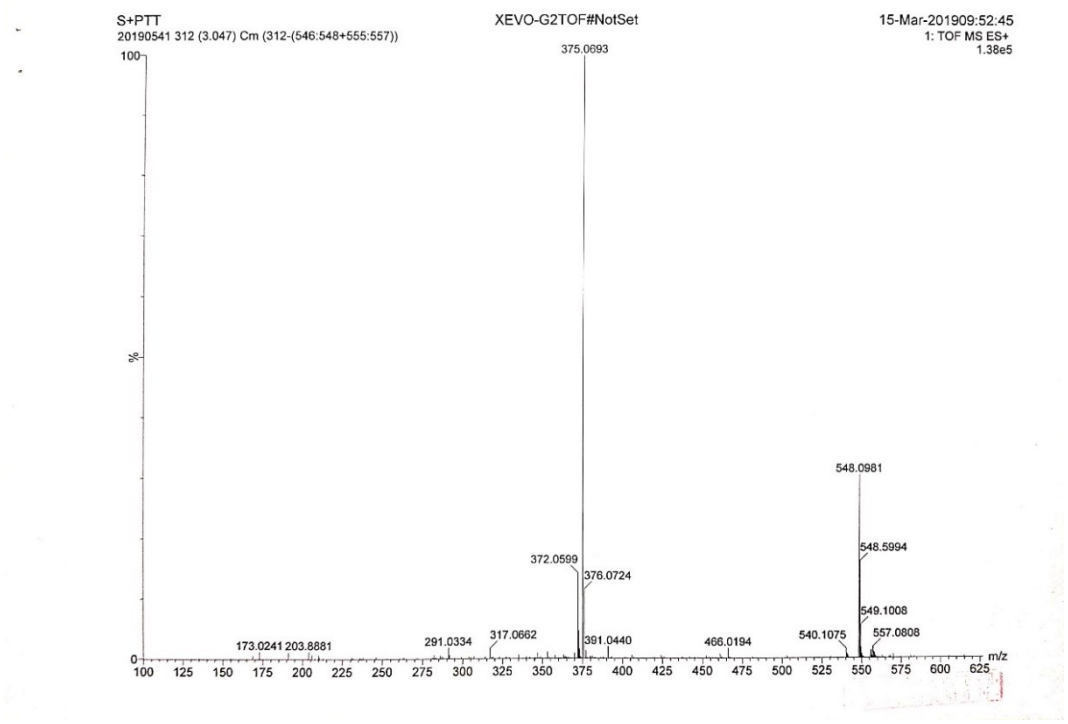

164.31
164.28
162.88
162.83
157.18
157.15
156.39
149.40
149.29
132.11
114.14
114.12
111.99
111.91
110.30
101.88
96.98
92.36
76.47
74.71
73.55
72.91
72.17
70.61
70.22
69.24
64.82
HO
O
OH
HO
OH
O
O
HO
O
O
f1 (ppm)

5r

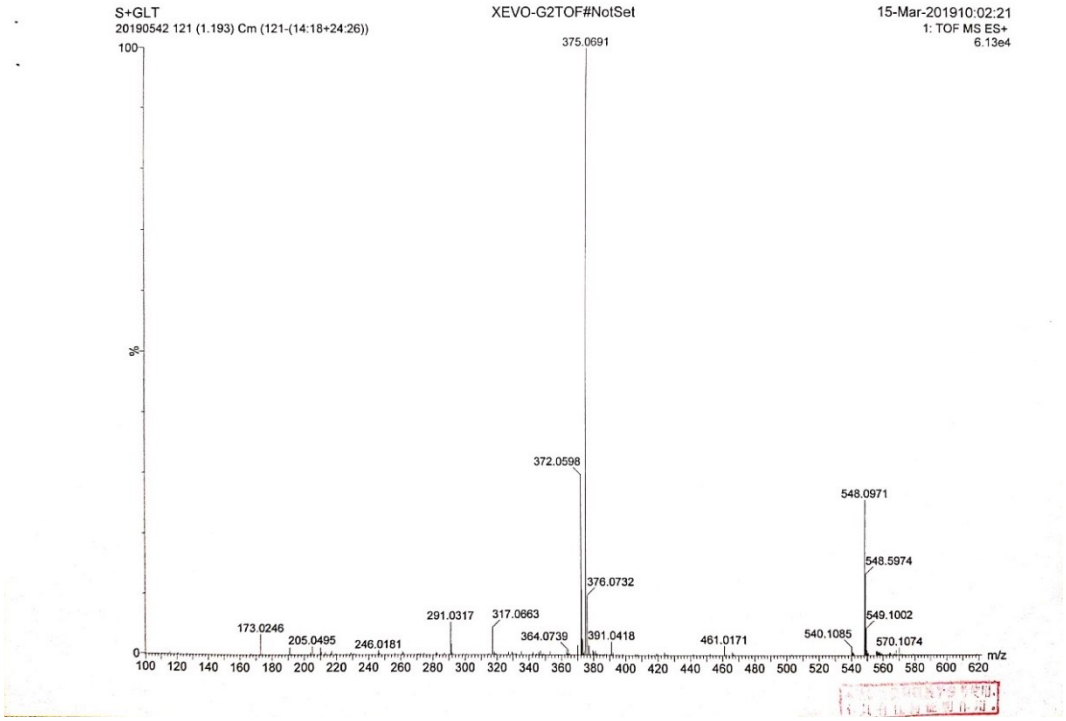

8.65
7.73
7.71
6.87
6.87
6.86
6.85
6.75
6.75
6.38
5.01
4.97
4.95
4.94
4.93
4.93
4.89
4.63
4.52
4.52
4.50
4.49
4.29
4.27
4.26
4.25
3.85
3.85
3.84
3.83
3.83
3.82
3.81
3.60
3.60
3.59
3.59
3.58
3.58
3.55
3.53
3.51
HO
HO
HO
HO
HO
OH
O
O
O
O
O
0.89
0.94
1.00
1.00
0.92
1.03
1.00
1.24
1.14
1.08
1.06
1.98
1.89
f1 (ppm)


164.20
162.71
157.08
156.44
149.24
132.01
114.11
112.17
110.29
101.90
94.11
71.34
70.54
70.35
67.19
64.81
HO
HO
HO
HO
HO
OH
O
O
O
O
O
f1 (ppm)

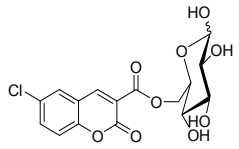
5a

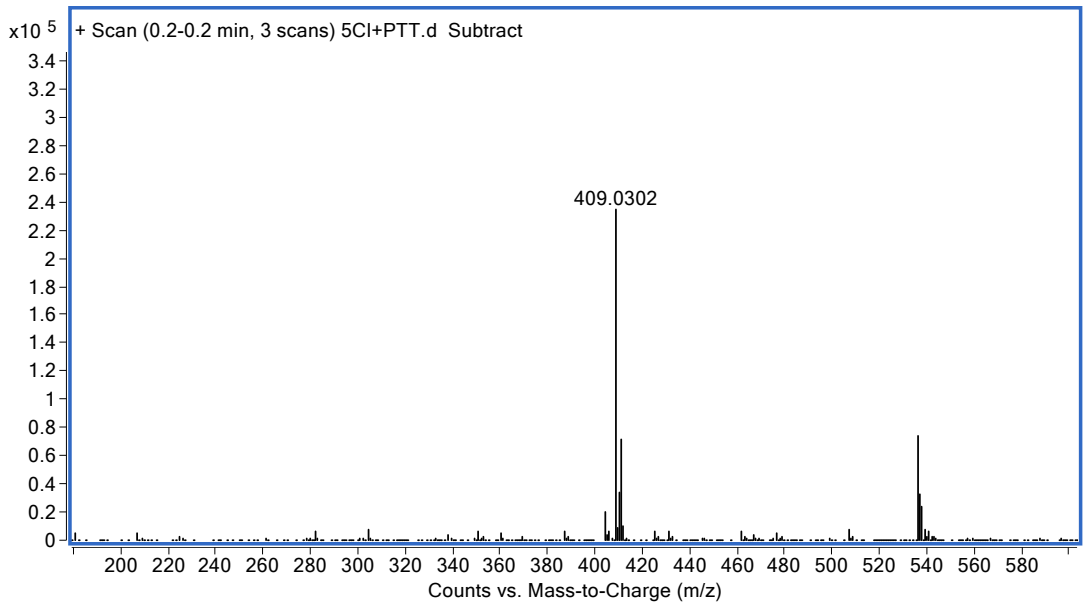

S+PTT
20190541 312 (3.047) Cm (312-(546:548+555:557))
XEVO-G2TOF#NotSet
15-Mar-201909:52:45
1: TOF MS ES+
1.38e5
100
%
0
375.0693
548.0981
548.5994
372.0599
376.0724
549.1008
557.0808
540.1075
173.0241
203.8881
291.0334
317.0662
391.0440
466.0194
m/z
100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625

5b


S+GLT
20190542 121 (1.193) Cm (121-(14:18+24:26))
XEVO-G2TOF#NotSet
15-Mar-201910:02:21
1: TOF MS ES+
6.13e4
100
%
0
375.0691
372.0598
548.0971
548.5974
376.0732
549.1002
291.0317
317.0663
173.0246
205.0495
246.0181
364.0739
391.0418
461.0171
540.1085
570.1074
m/z
100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620

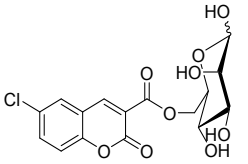
5e

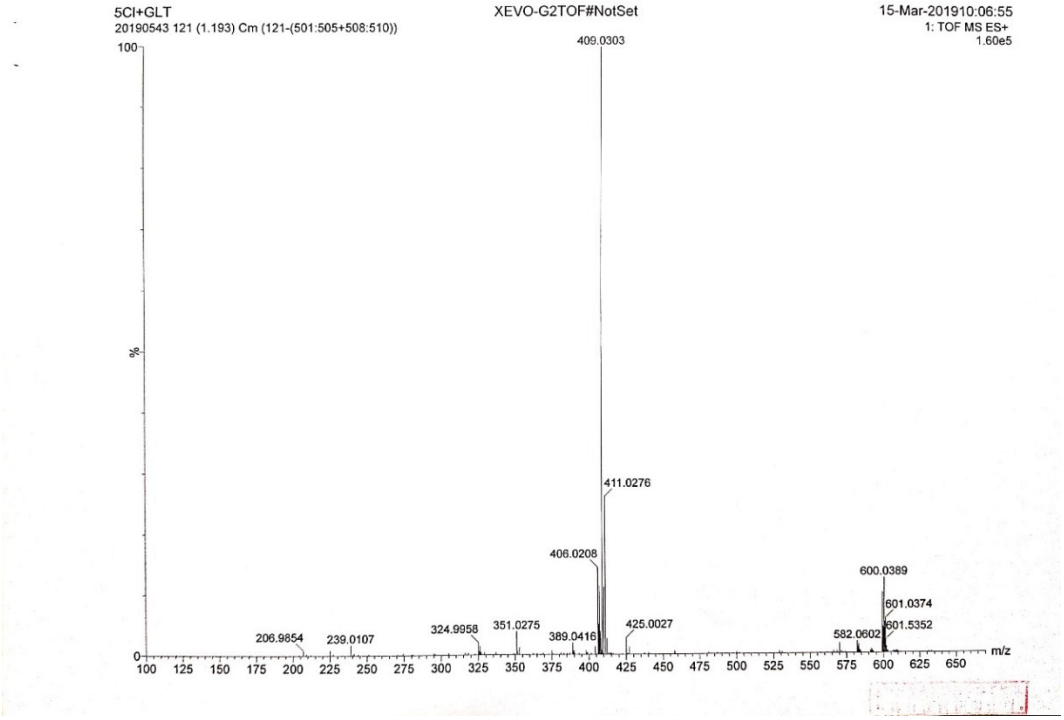

HO
O
OH
O
Cl
O
O
HO
OH
O


x10 5
+ Scan (0.2-0.2 min, 3 scans) 5Cl+PTT.d Subtract
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
409.0302
200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580
Counts vs. Mass-to-Charge (m/z)

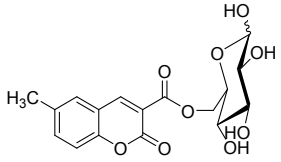
Formula (M)	Calc m/z	Diff (ppm)	Ion Formula	m/z
C16 H15 Cl O9	409.0297	-1.34	C16 H15 Cl Na O9	409.0302

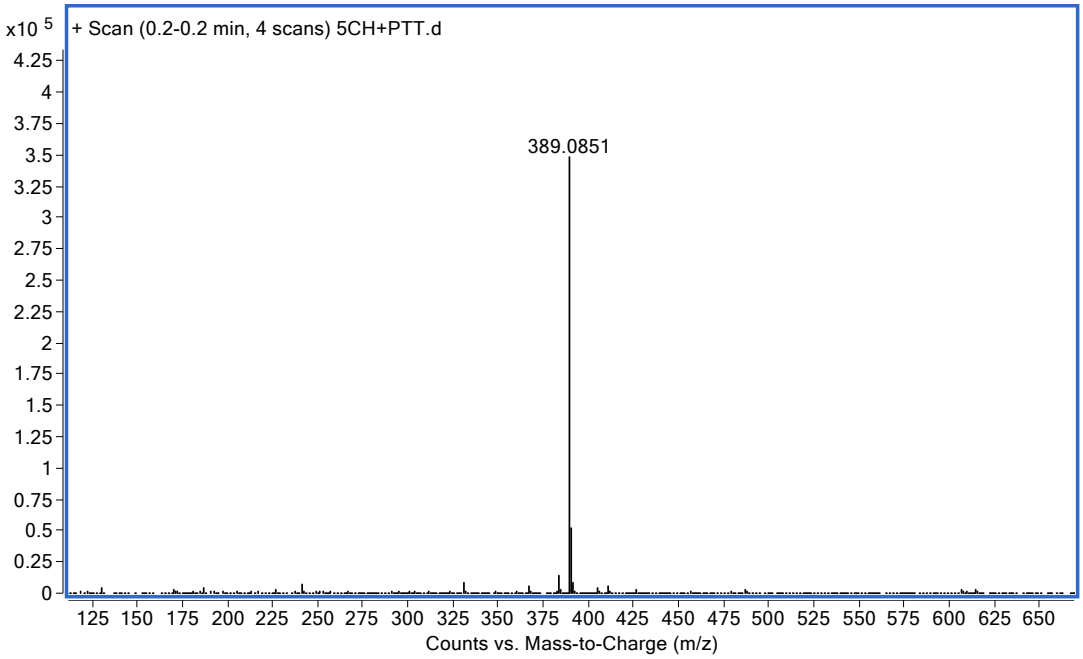
5f



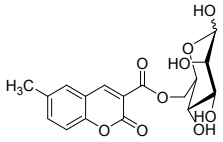


5i

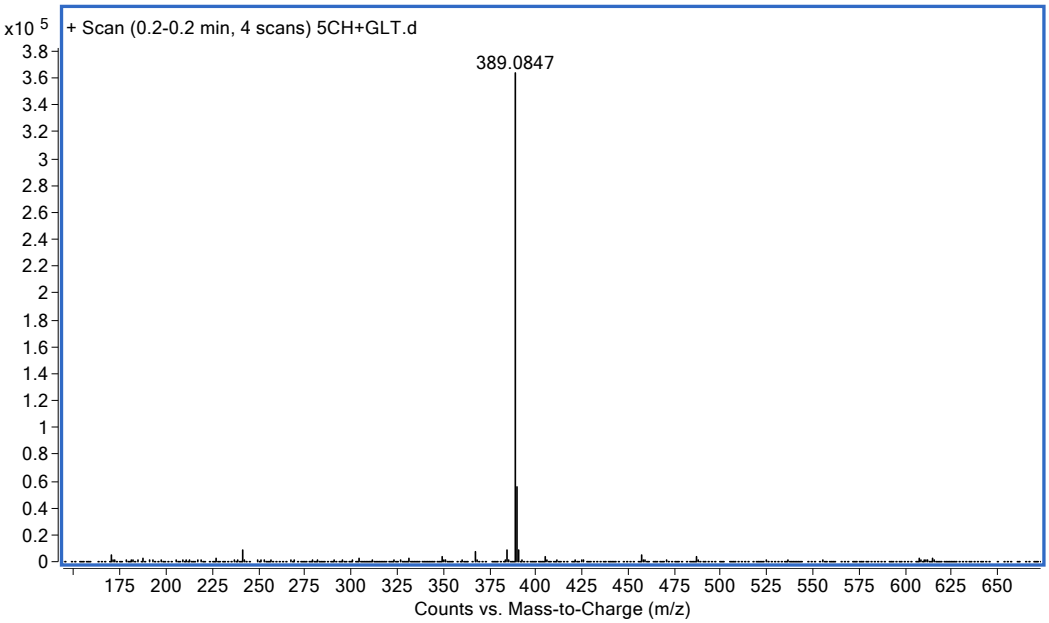




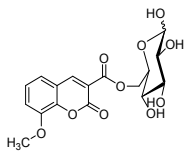
Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C17 H18 O9	C17 H18 Na O9	389.0851	389.0843	-2.18



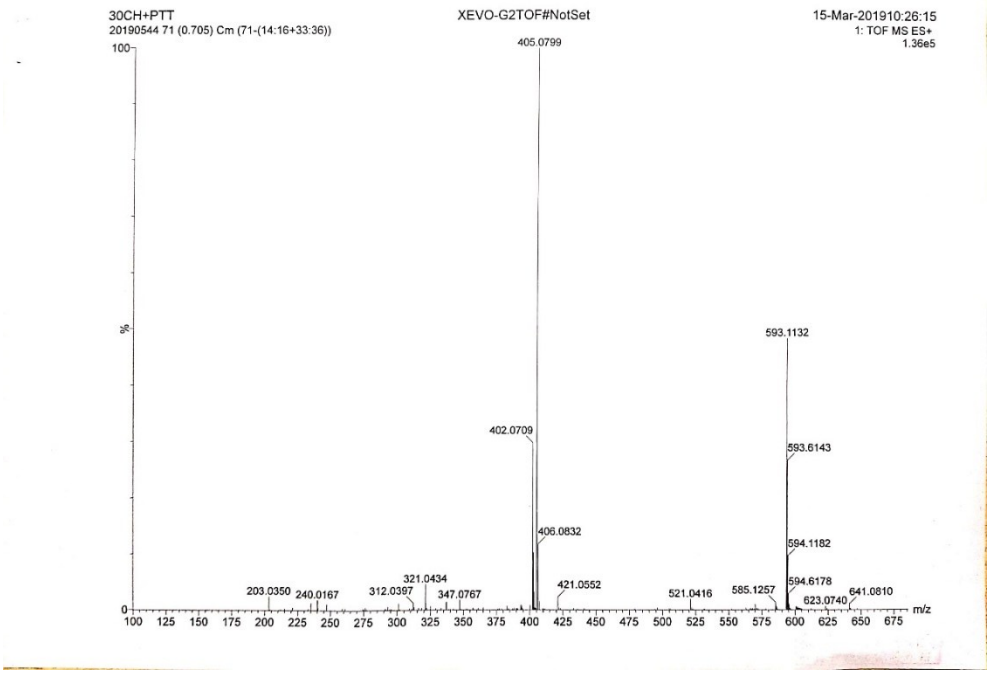
5j

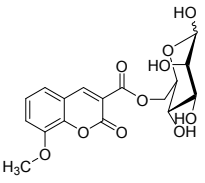


Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C17 H18 O9	C17 H18 Na O9	389.0847	389.0843	-1.08

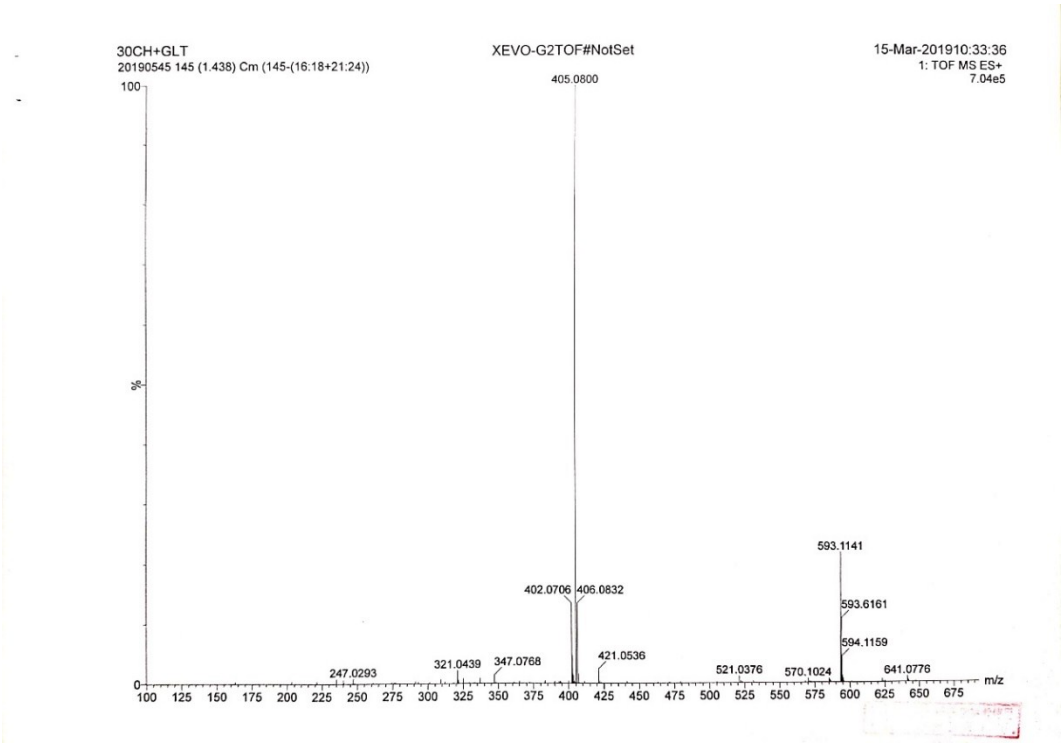


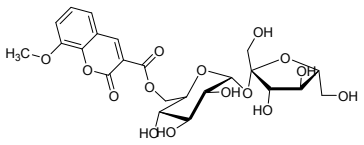
5m


30CH+PTT
20190544 71 (0.705) Cm (71-(14:16+33:36))
XEVO-G2TOF#NotSet
15-Mar-201910:26:15
1: TOF MS ES+
1.36e5
100
%
0
405.0799
593.1132
402.0709
593.6143
406.0832
594.1182
321.0434
203.0350
240.0167
312.0397
347.0767
421.0552
521.0416
585.1257
594.6178
623.0740
641.0810
m/z
100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650 675

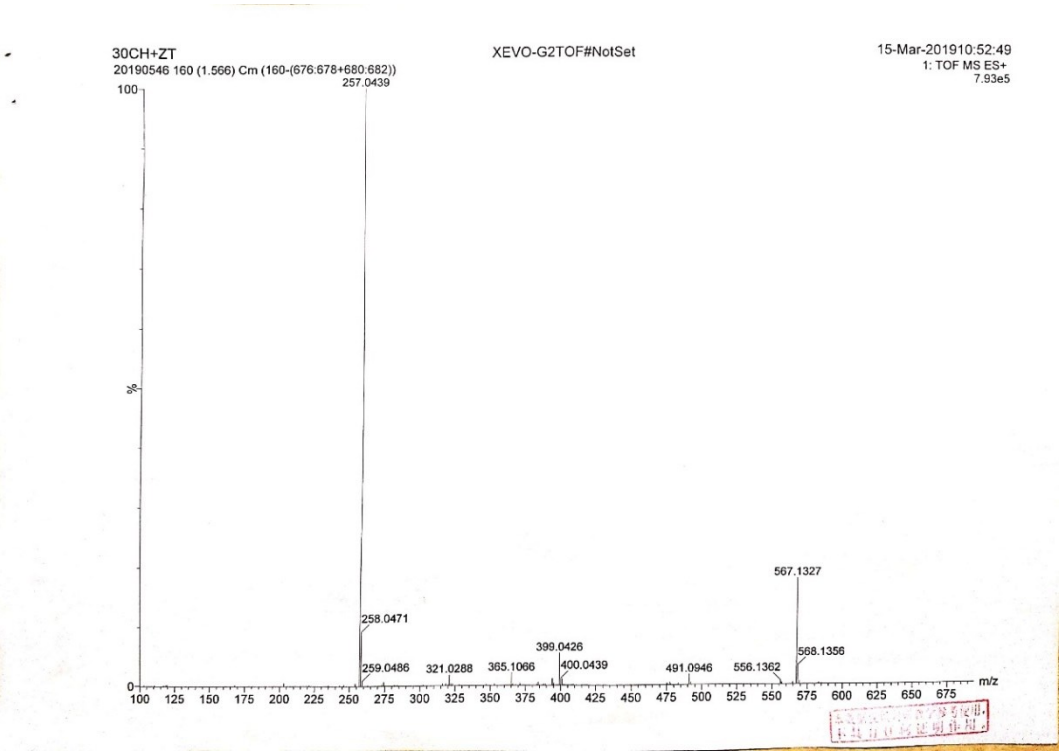

HO
O
HO
O
O
HO
OH
O
O
H3C
O

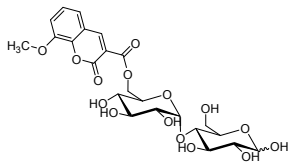
5n


30CH+GLT
20190545 145 (1.438) Cm (145-(16:18+21:24))
XEVO-G2TOF#NotSet
15-Mar-201910:33:36
1: TOF MS ES+
7.04e5
405.0800
593.1141
402.0706
406.0832
593.6161
594.1159
421.0536
321.0439
347.0768
247.0293
521.0376
570.1024
641.0776
%
m/z

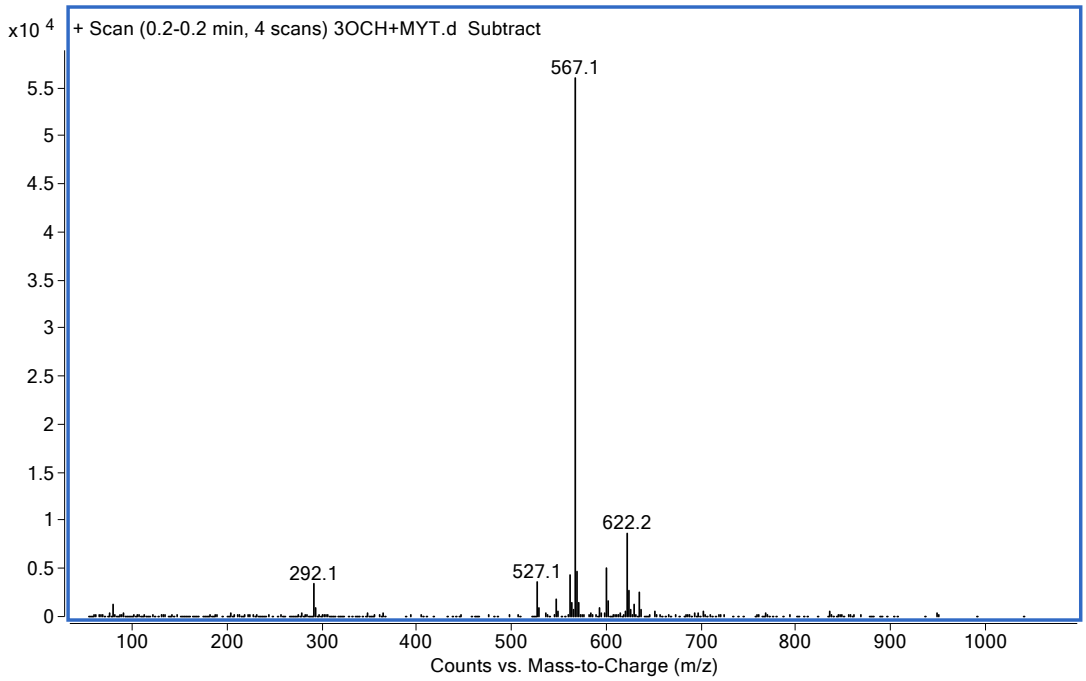

H3C
O
O
O
O
O
O
OH
HO
HO
OH
O
OH
HO
OH

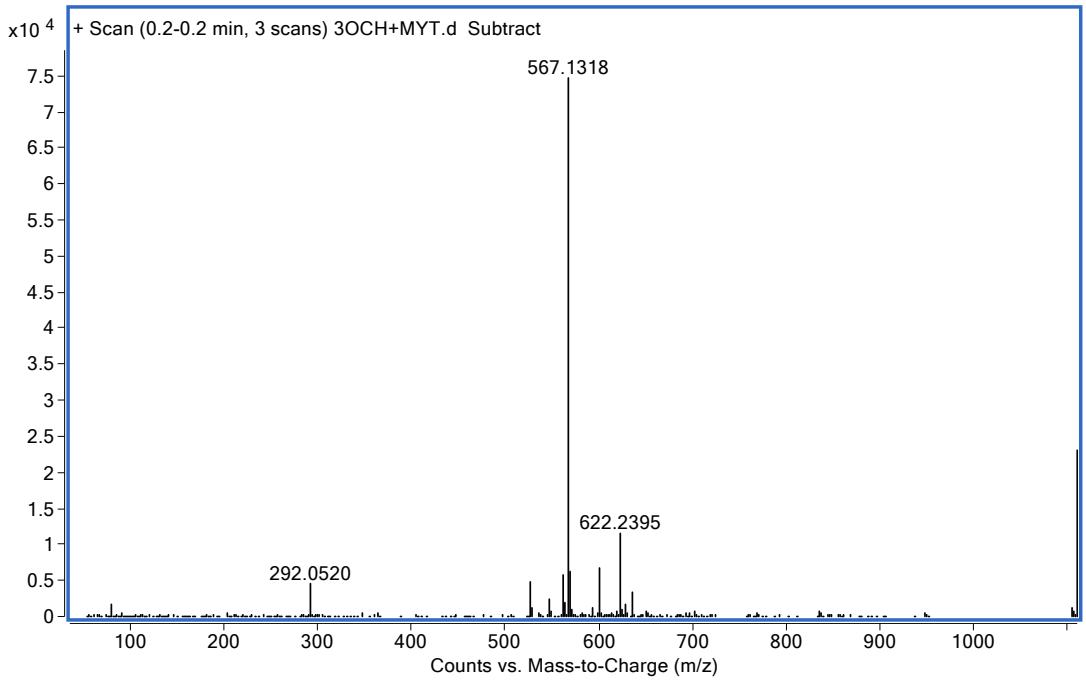
5o


30CH+ZT
20190546 160 (1.566) Cm (160-(676:678+680:682))
XEVO-G2TOF#NotSet
15-Mar-201910:52:49
1: TOF MS ES+
7.93e5
257.0439
258.0471
259.0486
321.0288
365.1066
399.0426
400.0439
491.0946
556.1362
567.1327
568.1356
m/z



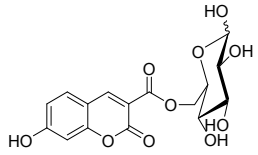
5p

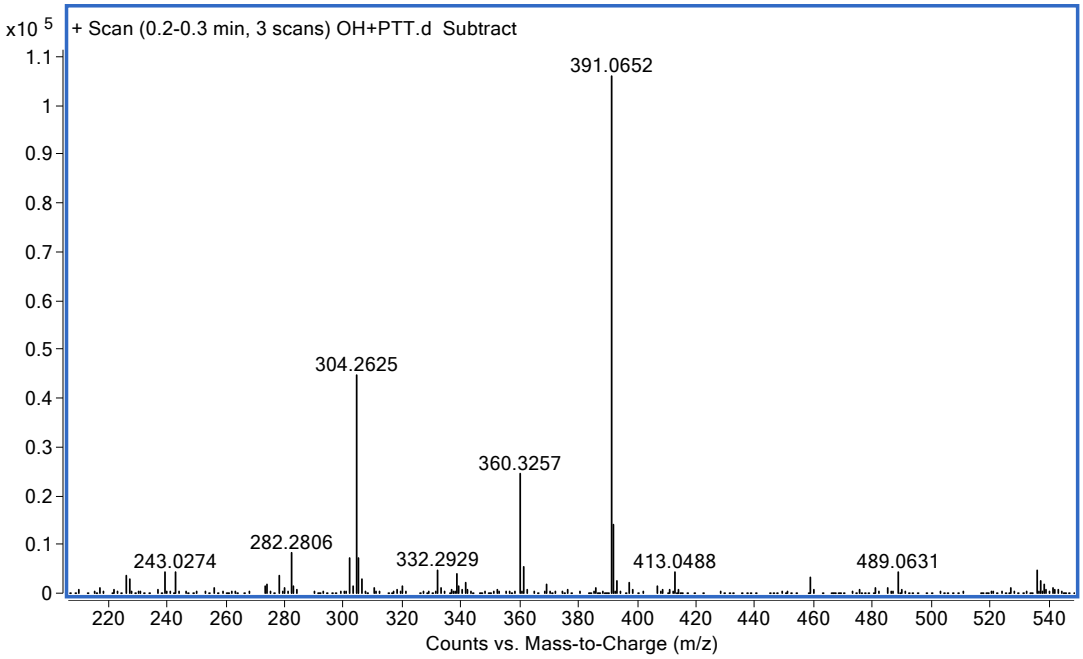




Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)	DBE
C23 H28 O15	C23 H28 Na O15	567.1318	567.132	0.44	10

5q





Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C16 H16 O10	C16 H16 Na O10	391.0652	391.066	1.98

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