Supporting Information

Sulfonic-acid functionalized hypercrosslinked porous organic polymer as a highly efficient heterogeneous catalyst for synthesis of 2*H*-chromene derivatives

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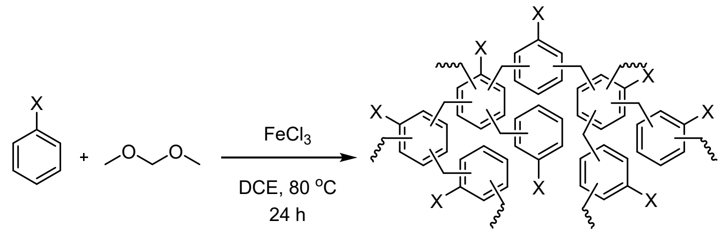
1. General information

All reactions were performed under an ambient atmosphere in oven-dried glassware with magnetic stirrer. Reactions conducted above an ambient temperature were heated by an anodized aluminium block. Starting materials, reagents, and organic solvents were purchased from commercial sources (Sigma Aldrich, TCI, Merck, and Alfa Aesar) and were used without further purification unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on alumina sheets pre-coated with a Merck silica gel 60 F254 plate and compounds were visualized under UV light. Purification of reaction products was carried out by column chromatography, in which a Merck silica gel 60 (0.063–0.200 mm) was used as a stationary phase. Proton nuclear magnetic resonance (^{1}H NMR) and proton-decoupled carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance 400 MHz and JEOL 400 MHz NMR spectrometer in deuterated chloroform ($CDCl_3$) and deuterated acetone ($(CD_3)_2CO$). The chemical shifts were recorded in part per million (ppm) relative to the resonance of the residual protonated solvent (^{1}H: $CDCl_3$, δ = 7.24 ppm; acetone-d_6, δ = 2.05 ppm and ^{13}C: $CDCl_3$, δ = 77.23 ppm; acetone-d_6, δ = 29.84 ppm). Data are reported as following: (brs = broad, s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, td = triplet of doublet; coupling constants, *J*, in Hz, integration). Melting points were determined in open glass capillaries using a Buchi melting point M-565 apparatus. FTIR spectra were recorded on a Perkin Elmer Frontier FTIR spectrometer. The catalytic surface areas and nitrogen adsorption-desorption isotherms (77 K) were obtained using micromeritics 3Flex surface area analyser. TGA was performed under a flow of nitrogen by heating from room temperature to 900 °C/min on TA Instruments SDT 2960. SEM and EDX data were obtained from Field Emission Scanning Electron Microscopes (FE-SEM) (HITACHI SU-8010. Mass spectrometric data were obtained with high resolution mass spectra (HRMS) on a Bruker micrOTOF spectrometer in the ESI mode.

2. Synthesis of HCP-H and HCP-SO_3H

2.1 Typical procedure for a synthesis of HCP-H

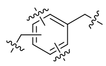


To a solution of benzene (4.68 g, 60 mmol, 1.0 equiv.) and dimethoxymethane (9.13 g, 120 mmol, 2.0 equiv.) in dichloroethane (120 mL) was added $FeCl_3$ (19.5 g, 120 mmol, 2.0 equiv.). The reaction was stirred under reflux for 24 hours. The reaction was filtered. The brown solid was washed with methanol by a Soxhlet extractor until the yellow liquid became colourless. The brown solid was dried in the oven for 24 hours. The reaction gave the brown solid product (6.30 g, quantitative yield).

The yield of HCP was calculated form the stoichiometry of the expected structure, based on the Equation 1.

$$Yield(\%) = \frac{m_{actual}}{n \times MW_{expected}} \times 100 \qquad (Eq. 1)$$

where m_{actual} is the actual mass of the resulting HCP, n is number of monomer mole, and $MW_{expected}$ is the molecular weight of the expected HCP structure.

For example, the expected structure of HCP-H **1a** is  (a benzene with 2 methylene carbon and 4 linkages to other repeating units), whose molecular weight is 102.13 g/mol. The yield of HCP-H is 103%.[1]

2.2 Optimization of the synthesis of sulfonic-acid functionalized HCP-H (HCP-H-SO_3H)

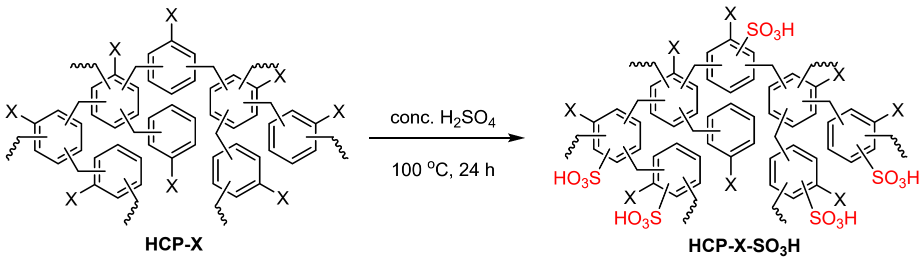
Different conditions including the concentration of H_2SO_4, the reaction temperature, the ratio of HCP-H to H_2SO_4, and time were investigated to optimize the sulfonation reactions of the HCP. Yields and acid contents were used to evaluate the optimal conditions. The acid concentrations of HCPs were evaluated by a back titration using NaOH and HCl solutions.

The results of the synthesis of HCP-H-SO_3H using different conditions were shown in Table S2.1. Increasing the concentration of H_2SO_4 led to higher acid contents of the materials without significantly affecting the yields. The acid content significantly increased from 0.26 mmol g^{-1} when H_2SO_4 (3 M) was used to 3.28 mmol g^{-1} when the conc. H_2SO_4

(18 M) was used. Therefore, conc. H_2SO_4 was further used to investigate the effect of the reaction temperature. The acid contents decreased when the reaction temperature was lowered. The temperature of 100 °C was then selected for further optimization. The ratio of HCP and H_2SO_4 were varied to optimize the amount of H_2SO_4 needed for the reaction. The 1:50 ratio of HCP:H_2SO_4 gave the highest acid content of 4.16 mmol g^{-1}. Further increasing the amount of H_2SO_4 did not increase the acid content. Finally, the reaction time was studied. Lowering the reaction time did not led to lower yields and acid contents in the materials. Thus, the sulfonation reaction using 50 equivalents of the conc. H_2SO_4 at 100 °C and 24 h was selected as optimal conditions for further sulfonation reactions.

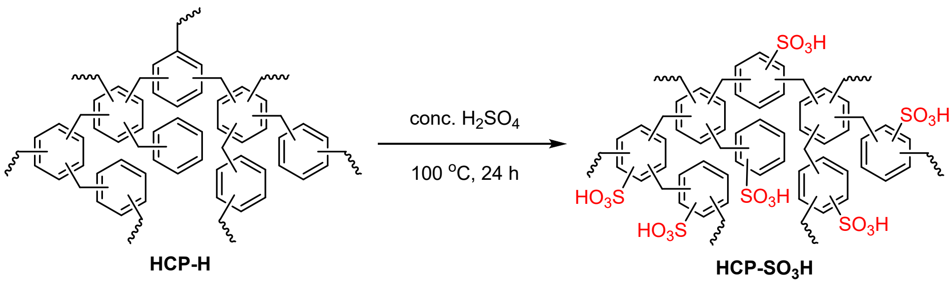
After sulfonation reaction with H_2SO_4, HCP-H-SO_3H was obtained as dark brown solid. The product has similar morphology to the HCP-H but darker in color. Dispersion in water was also improved after sulfonation. The sulfonation reaction was confirmed by IR spectroscopy.

Table S2.1 Optimization of the synthetic conditions for sulfonation



Entry	[H_2SO_4] (M)	Temperature (°C)	HCP-H:H_2SO_4	Time (h)	Yield (%)	Acid concentration (mmol/g)
1	3	100	1:20	24	48	0.26
2	4.5	100	1:20	24	49	0.31
3	6	100	1:20	24	48	1.14
4	9	100	1:20	24	49	1.22
5	18	100	1:20	24	66	3.28
6	18	80	1:20	24	62	2.84
7	18	60	1:20	24	59	2.11
8	18	100	1:10	24	69	2.72
9	**18**	**100**	**1:50**	**24**	**78**	**4.16**
10	18	100	1:100	24	66	3.23
11	18	100	1:50	1	58	2.75
12	18	100	1:50	3	63	3.00
13	18	100	1:50	6	62	3.03
14	18	100	1:50	12	68	3.37

2.1 Typical procedure for a synthesis of HCP-H-SO_3H



The reaction of HCP-H (2.01 g, 20 mmol, 1 equiv.) in conc. H_2SO_4 (56 mL, 50 equiv.) was stirred at 100 °C for 24 hours. The resulting black solid was filtered and washed with water until the pH is 7. The solid was dried in an oven for 24 hours. The reaction gave the black solid product (2.80 g, 78% yield).

The acid concentration was calculated by a back-titration method. HCP-H-SO_3H (20 mg, 0.2 mmol, 1 equiv.) was stirred with 0.0250 M NaOH (10 mL) for 1 hour. The reaction was filtered and washed with water until the pH is 7. The volume of the filtrate was adjusted to 100 mL by addition of water. This solution (10.0 mL) was pipetted into a flask containing 0.0250 M HCl solution (10 mL). The solution was titrated with 0.0125M NaOH. The acid concentration of HCP-SO_3H is determined to be 4.16 mmol/gram of HCP-H-SO_3H.

The acid content of HCP-X-SO_3H was calculated form back titration, following;

1) To determine amount of NaOH in excess from the titration result from Equation 2

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

$$mol_{excess\ NaOH} = C_{HCl}V_{HCl} - C_{NaOH}V_{NaOH} \qquad (Eq. 2)$$

Where $mol_{excess\ NaOH}$ is amount of excess NaOH, C_{HCl} is concentration of HCl solution (0.0250 M) in the flask, V_{HCl} is volumn of HCl solution in the flask, C_{NaOH} is concentration of titrant NaOH solution (0.0125 M) in the burette, and V_{NaOH} is volumn of used NaOH solution in the burette until the end point.

2) To determine amount of acid in HCP-X-SO_3H from Equation 3

$$HCP\text{-}X\text{-}SO_3H(s) + NaOH(aq) \rightarrow HCP\text{-}X\text{-}SO_3Na(s) + H_2O(l)$$

$$mol_{HCP\text{-}X\text{-}SO_3H} = mol_{reacted\ NaOH} = C_{NaOH}V_{NaOH} - mol_{excess\ NaOH} \qquad (Eq. 3)$$

Where $mol_{HCP\text{-}X\text{-}SO_3H}$ is amount of excess acid that contained in the HCP after sulfonation, C_{NaOH} is concentration of NaOH solution (0.0250 M) that was added to reacted with HCP-X-SO_3H, V_{NaOH} is volumn of NaH solution that was added, $mol_{excess\ NaOH}$ is amount of excess NaOH.

3. FTIR spectra

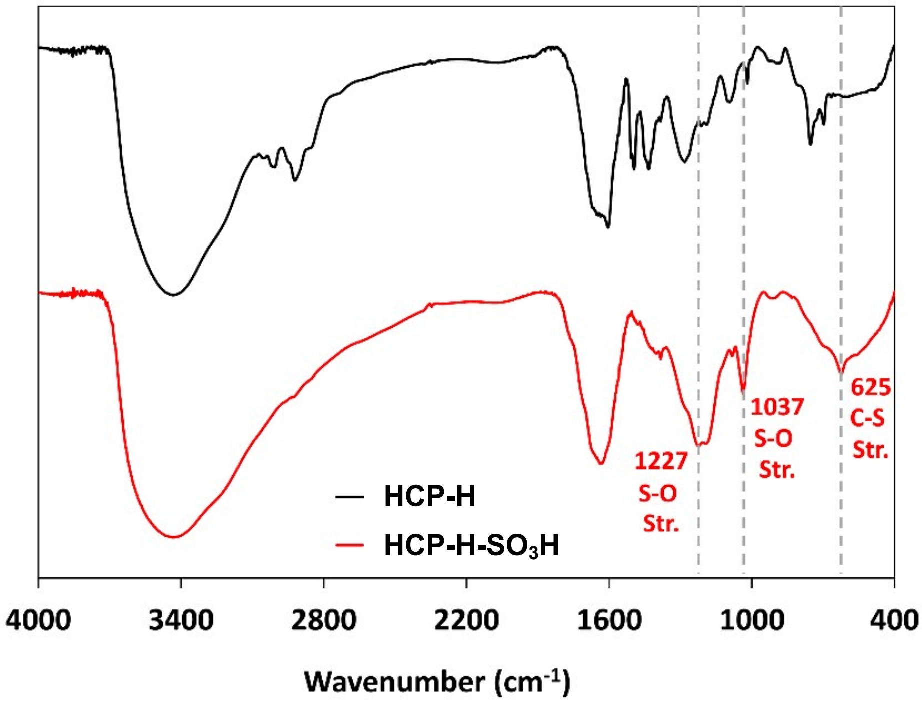


Fig. S3.1 IR spectra of HCP-H and HCP-H-SO_3H

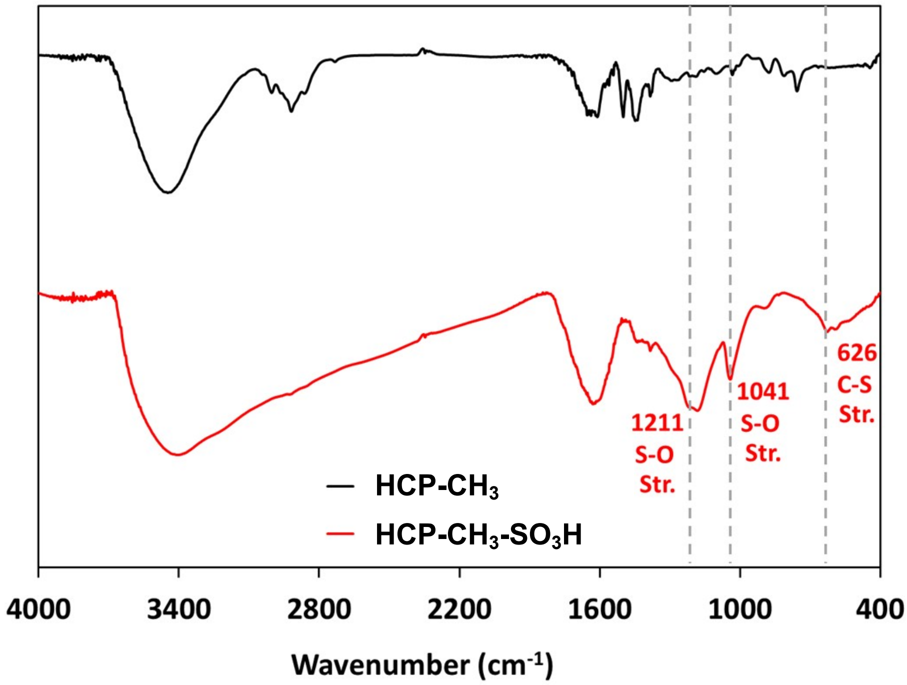


Fig. S3.2 IR spectra of $HCP-CH_3$ and $HCP-CH_3-SO_3H$

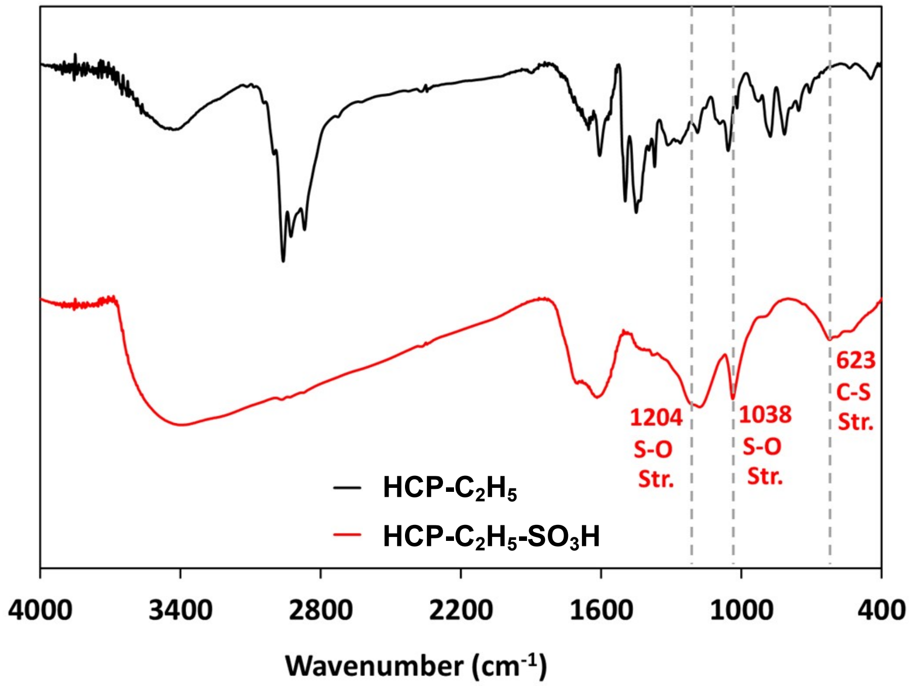


Fig. S3.3 IR spectra of $HCP-C_2H_5$ and $HCP-C_2H_5-SO_3H$

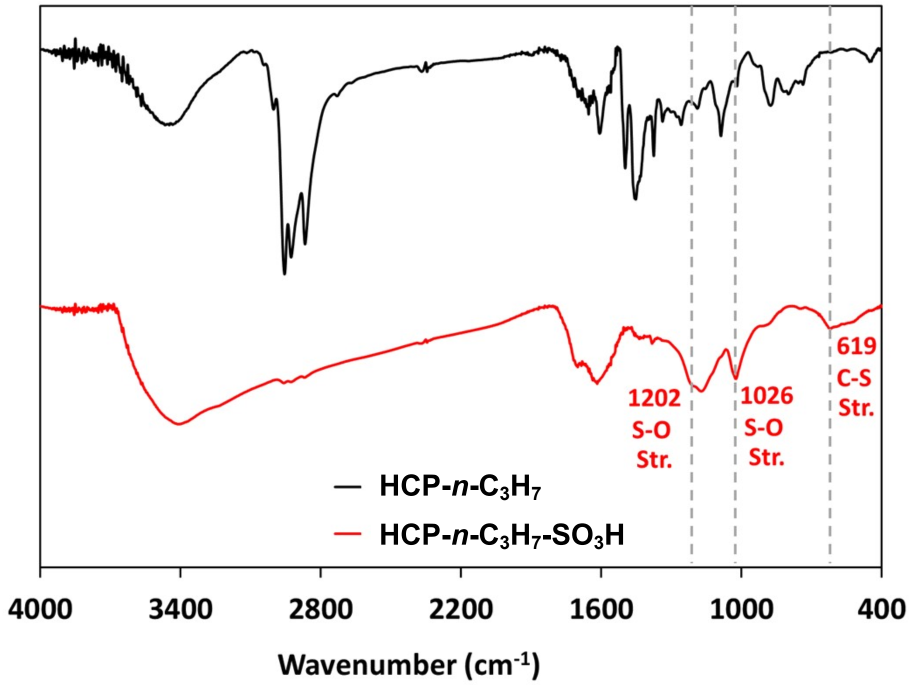


Fig. S3.4 IR spectra of HCP-*n*-C_3H_7 and HCP-*n*-C_3H_7-SO_3H

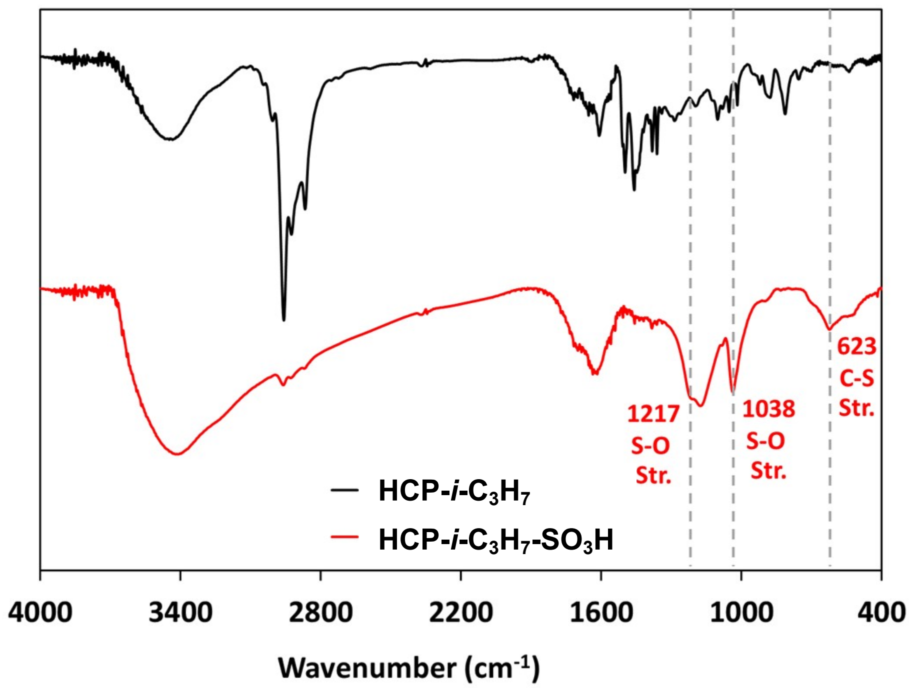


Fig. S3.5 IR spectra of HCP-*i*-C_3H_7 and HCP-*i*-C_3H_7-SO_3H

4. FE-SEM image and SEM-EDX elemental mappings

4.1 FE-SEM image and SEM-EDX elemental mappings of HCP-H

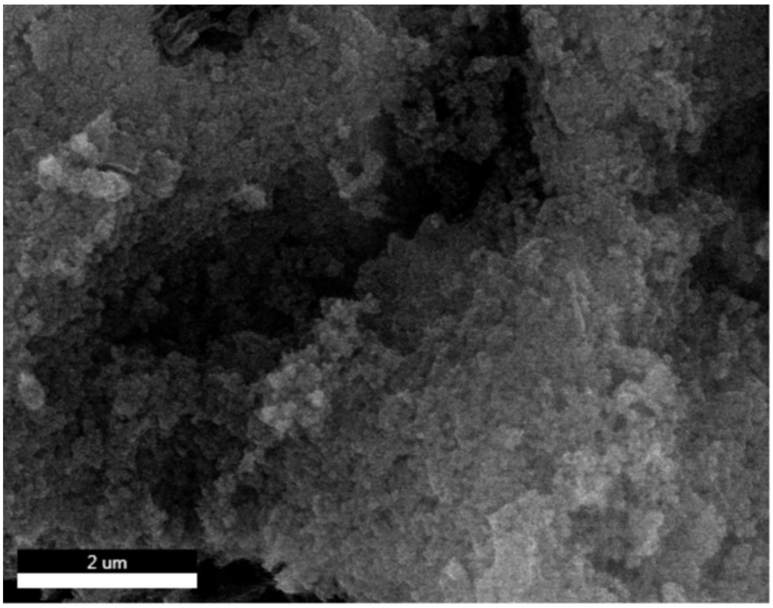


Fig. S4.1 FE-SEM image of HCP-H

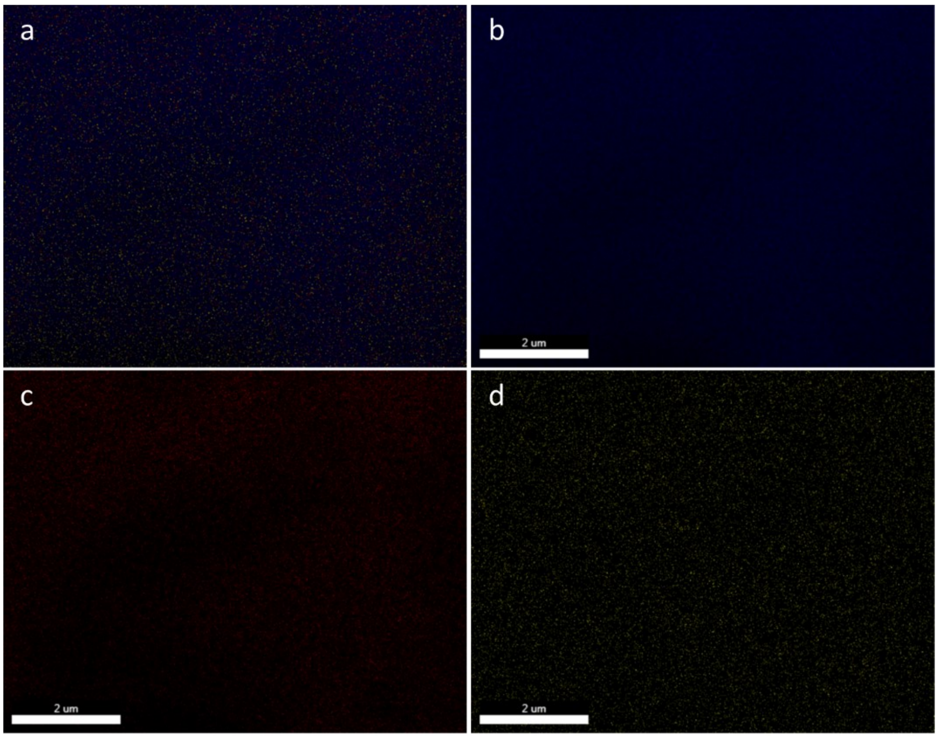


Fig. S4.2 SEM-EDX elemental mappings of HCP-H (a) carbon, oxygen, and sulfur, (b) carbon, (c) oxygen, and (d) sulfur

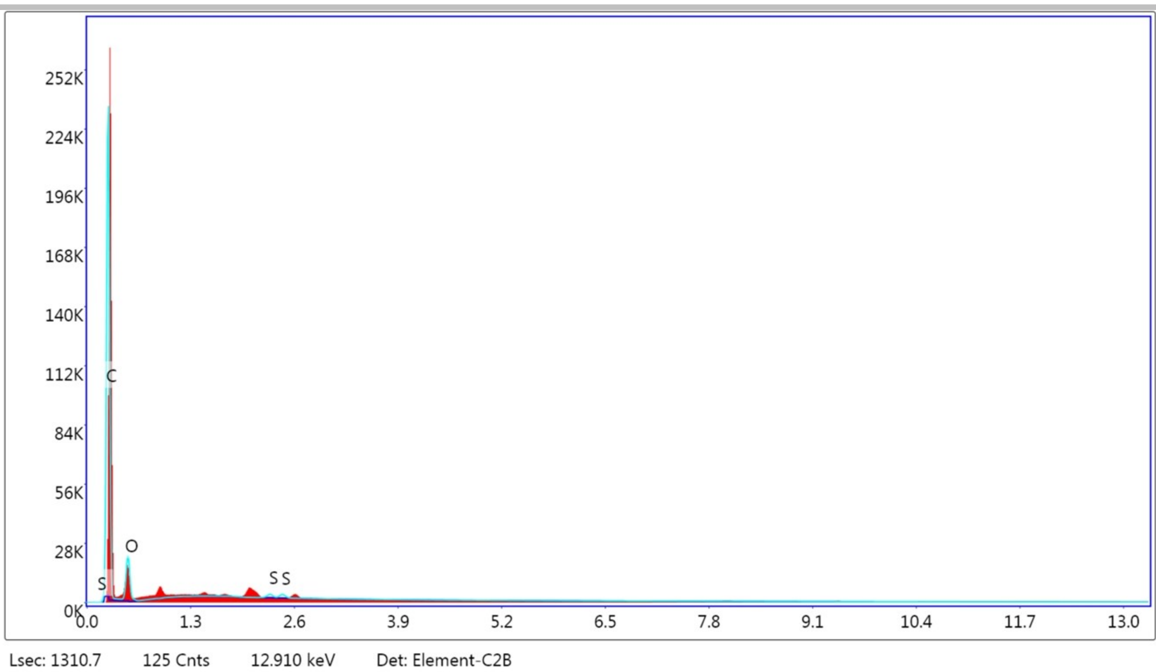


Figure 3.3 SEM-EDX elemental analysis HCP-H

Table S4.1 SEM-EDX elemental analysis HCP-H

Element	Weight %	Atomic %	Net	Error %	K_{ratio}	Z	A	F
C	75.80	80.79	818.45	3.86	0.5479385	1.0109	0.7152	1.0000
O	23.83	19.07	84.50	10.76	0.0290061	0.9655	0.1261	1.0000
S	0.37	0.15	10.06	3.01	0.0031772	0.8563	0.9957	1.0137

4.2 FE-SEM image and SEM-EDX elemental mappings of HCP-H-SO_3H

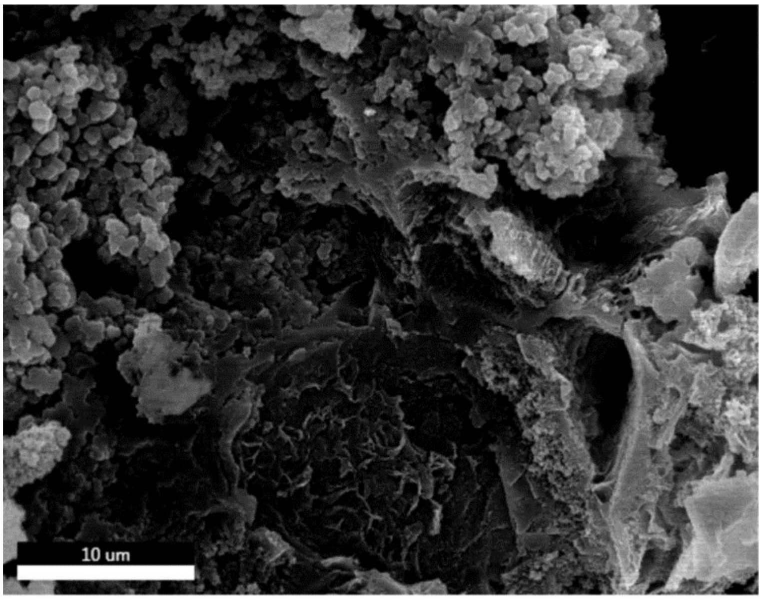


Fig. S4.4 FE-SEM image of HCP-H-SO_3H

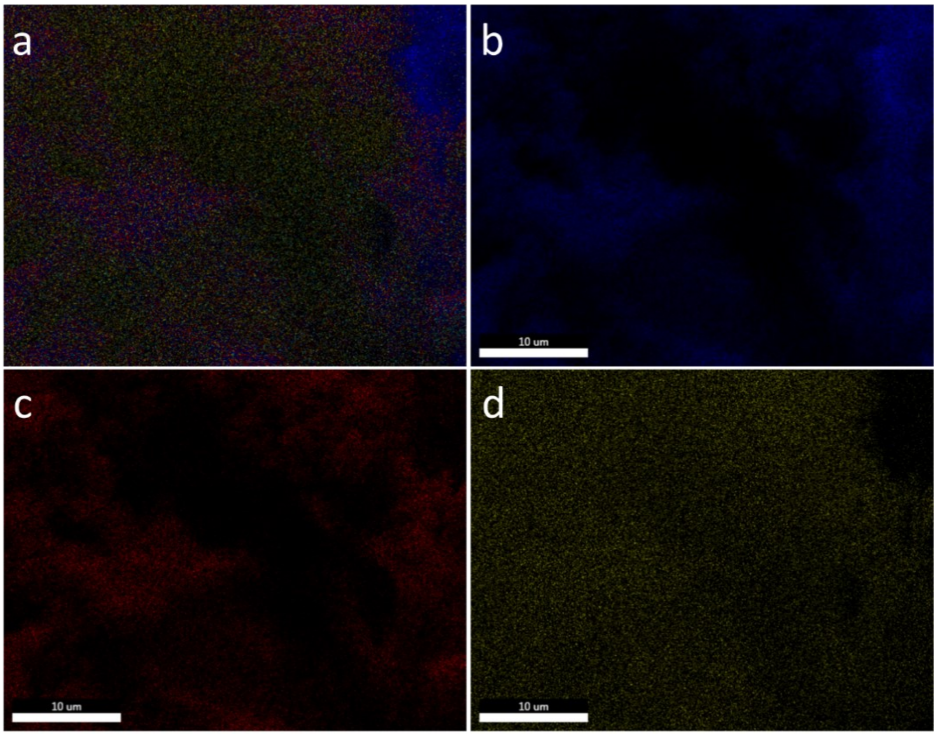


Fig. S4.5 SEM-EDX elemental mappings of HCP-H-SO_3H (a) carbon, oxygen, and sulfur, (b) carbon, (c) oxygen, and (d) sulfur

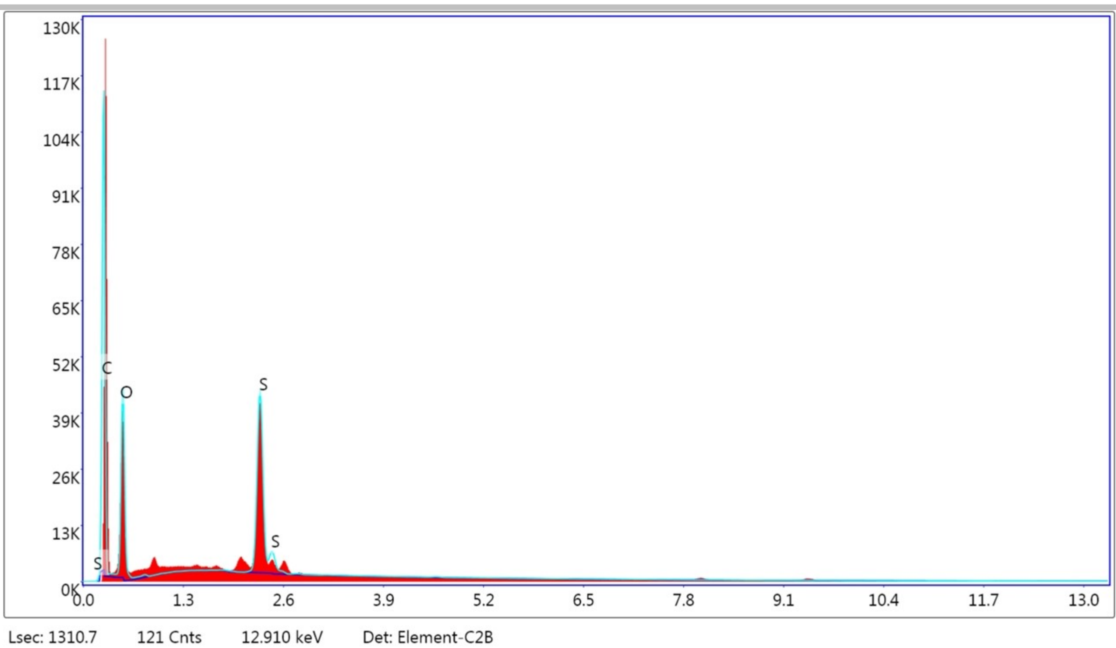


Fig. S4.6 SEM-EDX elemental analysis of HCP-H-SO_3H

Table S4.2 SEM-EDX elemental analysis of HCP-H-SO_3H

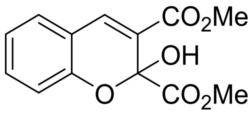
Element	Weight %	Atomic %	Net Int.	Error %	K_{ratio}	Z	A	F
C	59.22	68.24	399.20	7.87	0.194470	1.0254	0.3203	1.0000
O	32.65	28.25	185.59	9.95	0.046358	0.9800	0.1449	1.0000
S	8.13	3.51	303.00	1.48	0.069653	0.8703	0.9789	1.0061

5. Synthesis of 2*H*-chromene derivatives

5.1 Typical procedure for synthesis of 2*H*-chromenes (3)

To a suspension of salicylaldehydes (**1a–j**, 1.0 mmol, 1.0 equiv.) and HCP-H-SO_3H (0.10 mmol, 10 mol%) in ethanol (2.0 mL) was added dialkyl acetylenedicarboxylate (**2a–b**, 1.5 mmol, 1.5 equiv.) and pyrrolidine (24.6 µL, 0.30 mmol, 30 mol%). The reaction mixture was filtered through a PTFE syringe filter, and the filter was thoroughly washed successively with water, methanol, and acetone. The filtrate was stirred at 75 °C for 16 hours. The reaction mixture was extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed *in vacuo*, and the crude product was purified by flash column chromatography (silica gel: EtOAc/Hexane, 1/2, v/v) to give the pure product **3**.

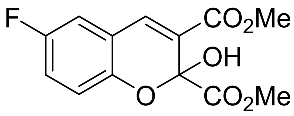
2-Hydroxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (3aa).



A white solid (208.3 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.80 (s, 1H, C*H*), 7.34 (td, *J* = 7.8 and 1.5 Hz, 1H, CH_{Ar}), 7.30 (dd, *J* = 7.6 and 1.2 Hz, 1H, CH_{Ar}), 7.03 (t, *J* = 7.5 Hz, 1H, CH_{Ar}), 6.97 (d, *J* = 8.2 Hz, 1H, CH_{Ar}), 5.10 (brs, 1H, O*H*), 3.88 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.9, 164.7, 151.5, 135.6, 133.0, 129.4, 122.8, 121.3, 118.2, 117.1, 93.2, 54.3, 52.4; IR (KBr) $ν_{max}$ 3459, 3042, 3019, 1962, 2924, 2856, 1737, 1704, 1637, 1608, 1572, 1458, 1444, 1325, 1259, 1282, 1217, 1141, 1117, 1047, 1000, 757 cm^{-1}; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{12}O_6Na$: 287.0526; found 287.0536.

Analytical data of the compound is consistent with the reported literature values.[2]

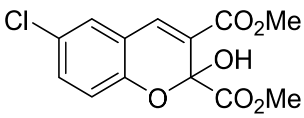
6-Fluoro-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (3ba).



A white solid (224.9 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.71 (s, 1H, C*H*), 7.08–6.99 (m, 2H, 2 × CH_{Ar}), 6.95–6.91 (m, 1H, CH_{Ar}), 5.11 (brs, 1H, O*H*), 3.88 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.7, 164.3, 159.2, 156.8, 147.4, 134.5, 122.7, 119.7, 119.4, 119.0, 118.9, 118.3, 118.3, 114.9, 114.6, 93.3, 54.3, 52.5; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{11}FO_6Na$: 305.0432; found 305.0439.

Analytical data of the compound is consistent with the reported literature values.[2]

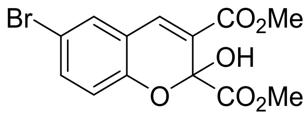
6-Chloro-2-hydroxy-2H-chromene-2,3-dicarboxylic acid dimethyl ester (3ca).



A white solid (255.4 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.69 (s, 1H, C*H*), 7.29–7.27 (m, 2H, 2 × CH_{Ar}), 6.90 (d, *J* = 8.7 Hz, 1H, CH_{Ar}), 5.18 (brs, 1H, O*H*), 3.87 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.5, 164.3, 149.9, 134.2, 132.5, 128.5, 127.6, 122.5, 119.4, 118.5, 93.3, 54.3, 52.5; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{11}ClO_6Na$: 321.0136; found 321.0145.

Analytical data of the compound is consistent with the reported literature values.[2]

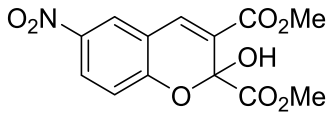
6-Bromo-2-hydroxy-2H-chromene-2,3-dicarboxylic acid dimethyl ester (3da).



A white solid (294.4 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.68 (s, 1H, C*H*), 7.41–7.39 (m, 2H, 2 × CH_{Ar}), 6.85–6.83 (m, 1H, CH_{Ar}), 5.22 (brs, 1H, O*H*), 3.86 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.4, 164.2, 150.4, 135.3, 134.1, 131.4, 122.5, 119.9, 118.8, 114.7, 93.2, 54.3, 52.5; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{11}BrO_6Na$: 364.9631; found 364.9638.

Analytical data of the compound is consistent with the reported literature values.[2]

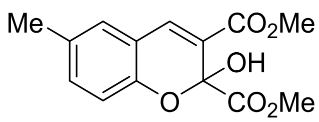
2-Hydroxy-6-nitro-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (3ea).



A white solid (303.3 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 8.25–8.22 (m, 2H, 2 × CH_{Ar}), 7.81 (s, 1H, C*H*), 7.08 (d, *J* = 8.5 Hz, 1H, CH_{Ar}), 5.29 (brs, 1H, O*H*), 3.90 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 168.9, 163.8, 156.1, 143.0, 133.6, 127.8, 124.9, 123.6, 118.3, 117.9, 93.9, 54.6, 52.8; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{11}NO_8Na$: 332.0377; found 332.0386.

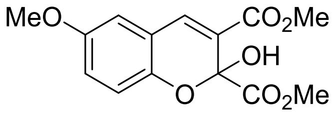
Analytical data of the compound is consistent with the reported literature values.[2]

2-Hydroxy-6-methyl-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (3fa).



A white solid (175.3 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (s, 1H, C*H*), 7.14 (dd, *J* = 8.3 and 1.7 Hz, 1H, CH_{Ar}), 7.08 (s, 1H, CH_{Ar}), 6.86 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 4.99 (brs, 1H, O*H*), 3.86 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.0, 164.7, 149.3, 135.7, 133.7, 132.1, 129.4, 121.2, 117.9, 116.7, 93.2, 54.2, 52.3, 20.6; IR (KBr) ν_{max} IR (KBr): 3434, 3022, 2964, 2926, 2860, 1751, 1716, 1643, 1579, 1488, 1439, 1300, 1269, 1251, 1217, 1141, 1091, 1036, 1004, 822 cm^{-1}; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{14}H_{14}O_6Na$: 301.0683; found 301.0680.

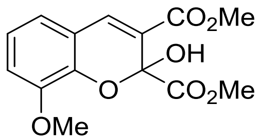
2-Hydroxy-6-methyoxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (3ga).



A yellow solid (227.0 mg, 77% yield). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.73 (s, 1H, C*H*), 6.93–6.87 (m, 2H, 2 × CH_{Ar}), 6.79 (d, *J* = 2.2 Hz, 1H, CH_{Ar}), 5.09 (brs, 1H, O*H*), 3.86 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.9, 164.6, 154.9, 145.5, 135.5, 121.9, 119.5, 118.5, 117.8, 112.7, 93.2, 56.0, 54.1, 52.3; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{14}O_7Na$: 317.0632; found 317.0635.

Analytical data of the compound is consistent with the reported literature values.[2]

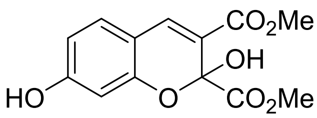
2-Hydroxy-8-methyoxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (3ha).



A yellow solid (246.1 mg, 84% yield). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.78 (s, 1H, C*H*), 7.00–6.91 (m, 3H, 3 × CH_{Ar}), 5.16 (brs, 1H, O*H*), 3.88 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.7, 164.6, 148.4, 140.9, 135.6, 122.5, 121.5, 121.2, 119.0, 115.6, 93.2, 56.5, 54.3, 52.4; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{14}O_7Na$: 317.0632; found 317.0635.

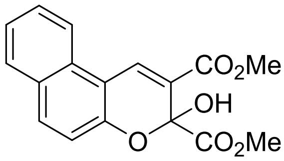
Analytical data of the compound is consistent with the reported literature values.[2]

2,7-Dihydroxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (3ia).



A white solid (141.2 mg, 50% yield). ^1H NMR (400 MHz, $(CD_3)_2CO$), δ (ppm) 7.76 (s, 1H, C*H*), 7.34 (d, *J* = 8.4 Hz, 1H, CH_{Ar}), 6.60 (dd, *J* = 8.4 and 2.0 Hz, 1H, CH_{Ar}), 6.45 (d, *J* = 2.0 Hz, 1H, CH_{Ar}), 3.78 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $(CD_3)_2CO$), δ (ppm) 169.9, 165.3, 162.7, 154.1, 135.3, 131.5, 119.8, 111.7, 111.2, 103.9, 94.9, 53.5, 52.0; IR (KBr) ν_{max} 3394, 2948, 2848, 1761, 1689, 1621, 1575, 1444, 1318, 1286, 1225, 1160, 1152, 1221 cm^{-1}; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{12}O_7Na$: 303.0475; found 303.0477.

3-Hydroxy-3*H*-benzo[*f*]chromene-2,3-dicarboxylic acid dimethyl ester (3ja).

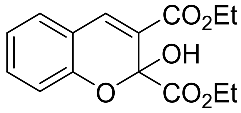


A yellow solid (200.4 mg, 64% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H, C*H*), 8.13 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 7.84 (d, *J* = 8.9 Hz, 1H, CH_{Ar}), 7.78 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 7.57 (td, *J* = 7.6 and 1.1 Hz, 1H, CH_{Ar}), 7.41 (td, *J* = 7.6 and 0.7 Hz, 1H, CH_{Ar}), 7.17 (d, *J* = 8.9, 1H, CH_{Ar}), 5.18 (brs, 1H, O*H*), 3.91 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3); ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 170.0, 164.9, 150.7, 133.7, 131.2, 130.5, 129.8, 129.0, 128.1, 125.0, 121.3, 119.4, 117.8, 111.2, 93.3, 54.4, 52.4, 29.9; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{17}H_{14}O_6Na$: 337.0683; found 337.0685.

Analytical data of the compound is consistent with the reported literature values.[3]

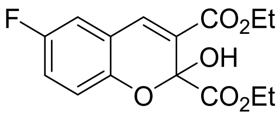
2-Hydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (3ab).



A white solid (271.4 mg, 93% yield). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.78 (s, 1H, C*H*), 7.34–7.28 (m, 2H, 2 × CH_{Ar}), 7.00 (td, *J* = 7.5 and 0.8 Hz, 1H, CH_{Ar}), 6.96 (d, *J* = 8.1 Hz, 1H, CH_{Ar}), 5.19 (brs, 1H, O*H*), 4.40 – 4.20 (m, 4H, 2 × OCH_2), 1.31–1.25 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.3, 164.1, 151.5, 135.2, 132.7, 129.2, 122.5, 121.7, 118.3, 117.0, 93.2, 63.5, 61.3, 14.3, 14.0; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{15}H_{16}O_6Na$: 315.0839; found 315.0844.

Analytical data of the compound is consistent with the reported literature values.[2]

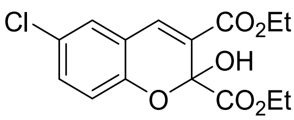
6-Fluoro-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (3bb).



A white solid (301.1 mg, 97% yield). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.69 (s, 1H, C*H*), 7.04–6.97 (m, 2H, 2 × CH_{Ar}), 6.93–6.88 (m, 1H, CH_{Ar}), 5.21 (brs, 1H, O*H*), 4.37–4.20 (m, 4H, 2 × OCH_2), 1.30–1.24 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.1, 163.8, 159.0, 156.6, 147.4, 134.2, 123.1, 119.4, 119.1, 119.1, 119.0, 118.2, 118.1, 114.7, 114.5, 93.3, 63.6, 61.4, 14.2, 13.9; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{15}H_{15}FO_6Na$: 333.0745; found 333.0752.

Analytical data of the compound is consistent with the reported literature values.[2]

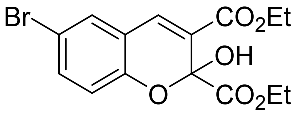
6-Chloro-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (3cb).



A white solid (316.9 mg, 98% yield). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.74 (s, 1H, C*H*), 7.32–7.29 (m, 2H, 2 × CH_{Ar}), 6.94 (d, *J* = 9.2 Hz, 1H, CH_{Ar}), 5.29 (brs, 1H, O*H*), 4.43–4.26 (m, 4H, 2 × OCH_2), 1.36–1.30 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.0, 163.7, 149.9, 133.9, 132.2, 128.3, 127.4, 122.9, 119.5, 118.4, 93.3, 63.7, 61.5, 14.2, 14.0; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{15}H_{15}ClO_6Na$: 349.0449; found 349.0452.

Analytical data of the compound is consistent with the reported literature values.[2]

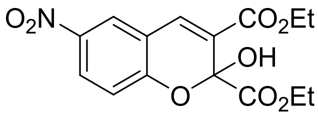
6-Bromo-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (3db).



A white solid (367.7 mg, 99% yield). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.68 (s, 1H, C*H*), 7.40–7.38 (m, 2H, 2 × CH_{Ar}), 6.84 (d, *J* = 8.4 Hz, 1H, C*H*), 5.22 (brs, 1H, O*H*), 4.37–4.20 (m, 4H, 2 × OCH_2), 1.30–1.25 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm) 169.0, 163.7, 150.5, 135.1, 133.8, 131.3, 122.9, 120.1, 118.8, 114.5, 93.3, 63.7, 61.5, 14.2, 14.0; LC-HRMS (ESI+): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{15}BrO_6Na$: 392.9944; found 392.9953.

Analytical data of the compound is consistent with the reported literature values.[2]

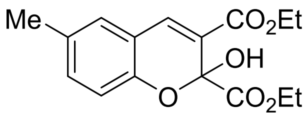
2-Hydroxy-6-nitro-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (3eb).



A white solid (335.4 mg, 99% yield). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm) 8.22 (d, *J* = 2.6 Hz, 1H, CH_{Ar}), 8.18 (dd, *J* = 9.0 and 2.6 Hz, 1H, CH_{Ar}), 7.79 (s, 1H, C*H*), 7.04 (d, *J* = 9.0 Hz, 1H, CH_{Ar}), 5.48 (brs, 1H, O*H*), 4.38–4.22 (m, 4H, 2 × OCH_2), 1.30–1.24 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm) 168.3, 163.3, 156.1, 142.8, 133.2, 127.5, 124.8, 123.9, 118.3, 117.7, 93.9, 64.0, 61.8, 14.2, 13.9; LC-HRMS (ESI+): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{15}NO_8Na$: 360.0690; found 360.0697.

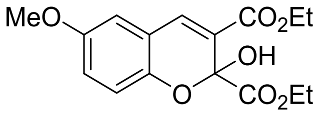
Analytical data of the compound is consistent with the reported literature values.[2]

2-Hydroxy-6-methyl-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (3fb).



A white solid (235.3 mg, 77% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.74 (s, 1H, C*H*), 7.13 (dd, *J* = 8.3 and 1.6 Hz, 1H, CH_{Ar}), 7.08 (s, 1H, CH_{Ar}), 6.86 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 4.95 (brs, 1H, O*H*), 4.38–4.21 (m, 4H 2 × OCH_2), 2.27 (s, 3H, CH_3), 1.31–1.25 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 169.5, 164.2, 149.4, 135.4, 133.5, 131.9, 129.3, 121.6, 118.0, 116.7, 93.2, 63.5, 61.3, 20.6, 14.3, 14.0; IR (KBr) ν_{max} 3448, 2989, 1748, 1708, 1640, 1579, 1384, 1298, 1265, 1244, 1220, 1147, 1132, 1093, 1041, 1021 cm^{-1}; LC-HRMS (ESI+): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{18}O_6Na$: 329.0996; found 329.0993.

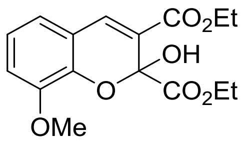
2-Hydroxy-6-methyoxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (3gb).



A yellow solid (311.1 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.73 (s, 1H, C*H*), 6.93–6.87 (m, 2H, 2 × CH_{Ar}), 6.80 (d, *J* = 1.8 Hz, 1H, CH_{Ar}), 5.10 (brs, 1H, O*H*), 4.39–4.21 (m, 4H, 2 × OCH_2), 3.75 (s, 3H, OCH_3), 1.31–1.25 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.5, 164.1, 155.0, 145.6, 135.3, 122.3, 119.3, 118.6, 117.8, 112.7, 93.3, 63.6, 61.3, 56.0, 14.3, 14.0; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{16}H_{18}O_7Na$: 345.0945; found 345.0953.

Analytical data of the compound is consistent with the reported literature values.[2]

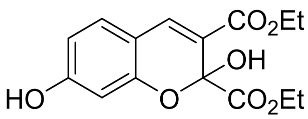
2-Hydroxy-8-methyoxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (3hb).



A yellow solid (318.5 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.75 (s, 1H, C*H*), 6.96–6.88 (m, 3H, 3 × CH_{Ar}), 5.25 (brs, 1H, O*H*), 4.40–4.19 (m, 4H, 2 × OCH_2), 3.81 (s, 3H, OCH_3), 1.29–1.23 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.1, 164.0, 148.3, 140.9, 135.2, 122.2, 121.8, 121.0, 119.0, 115.4, 93.2, 63.5, 61.2, 56.4, 14.2, 13.9; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{16}H_{18}O_7Na$: 345.0948; found 345.0953.

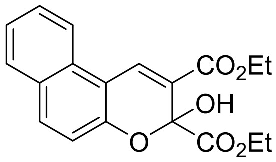
Analytical data of the compound is consistent with the reported literature values.[2]

2,7-Dihydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (3ib).



A white solid (229.8 mg, 75% yield). ^{1}H NMR (400 MHz, $(CD_3)_2CO$), δ (ppm) 7.74 (s, 1H, C*H*), 7.32 (d, *J* = 8.4 Hz, 1H, CH_{Ar}), 6.58 (dd, *J* = 8.4 and 2.1 Hz, 1H, CH_{Ar}), 6.44 (d, *J* = 2.1 Hz, 1H, CH_{Ar}), 4.31–4.16 (m, 4H, 2 × OCH_2), 1.26 (t, *J* = 7.1 Hz, 3H, CH_3), 1.23 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $(CD_3)_2CO$), δ (ppm) 169.4, 164.8, 162.8, 154.1, 135.1, 131.4, 120.1, 111.7, 111.1, 104.0, 94.9, 63.0, 61.1, 14.5, 14.2; IR (KBr) ν_{max} 3454, 3405, 2986, 2916, 1741, 1680, 1618, 1573, 1313, 1282, 1224, 1149, 1123 cm^{-1}; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{15}H_{16}O_7Na$: 331.0788; found 331.0789.

3-Hydroxy-3*H*-benzo[*f*]chromene-2,3-dicarboxylic acid diethyl ester (3jb).



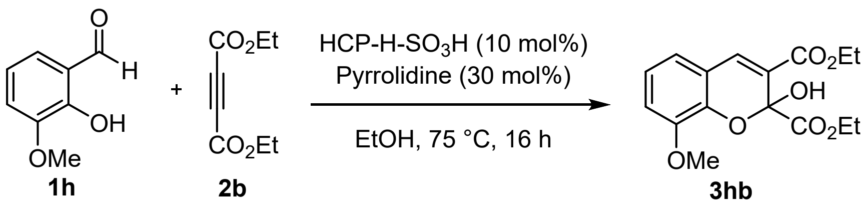
A yellow solid (284.9 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.56 (s, 1H, C*H*), 8.12 (d, *J* = 8.2 Hz, 1H, CH_{Ar}), 7.81 (d, *J* = 8.9 Hz, 1H, CH_{Ar}), 7.76 (d, *J* = 8.2 Hz, 1H, CH_{Ar}), 7.56 (td, *J* = 7.6 and 1.2 Hz, 1H, CH_{Ar}), 7.40 (td, *J* = 7.6 and 0.7 Hz, 1H, CH_{Ar}), 7.16 (d, *J* = 8.9 Hz, 1H, CH_{Ar}), 5.31 (brs, 1H, O*H*), 4.44–4.28 (m, 4H, 2 × OCH_2), 1.37–1.29 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.5, 164.4, 150.7, 133.5, 130.9, 130.4, 129.7, 128.9, 127.9, 124.8, 121.2, 119.8, 117.8, 111.2, 93.4, 63.7, 61.3, 14.4, 14.0; LC-HRMS (ESI+): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{18}O_6Na$: 365.0996; found 365.0995.

Analytical data of the compound is consistent with the reported literature values.[3]

5.2 Recycling of the HCP-H-SO_3H catalyst

To a suspension of 2-hydroxy-3-methoxybenzaldehyde **1h** (1.0 mmol, 1.0 equiv.) and HCP-H-SO_3H (0.10 mmol, 10 mol%) in ethanol (2.0 mL) was added diethyl acetylenedicarboxylate **2b** (1.5 mmol, 1.5 equiv.) and pyrrolidine (24.6 µL, 0.30 mmol, 30 mol%). The reaction was stirred at 75 °C for 16 hours. The reaction mixture was filtered through a PTFE syringe filter, and the filter was thoroughly washed successively with water, methanol, and acetone. The filtrate was extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed in vacuo, and the crude product was purified by flash column chromatography (silica gel: EtOAc/Hexane) to give the pure product **3hb**.

To recycle the HCP-H-SO_3H catalyst, the catalyst was removed from the syringe filter and dried overnight in an oven at 120 °C. The recovered HCP-H-SO_3H catalyst was subsequently reused in the next cycle.



Run	Yield of 3hb (%)[a]	Recovery of HCP-H-SO_3H (%)[b]
1	99	>99
2	99	>99
3	99	>99
4	98	>99

5	96	>99

[a] Reaction conditions: **1h** (1.0 mmol, 1.0 equiv.) and **2b** (1.5 mmol, 1.5 equiv,), HCP-H-SO_3H (10 mol%), and pyrrolidine (30 mol%) in EtOH (2.0 mL) at 75 °C for 16 h. The recovery of HCP-H-SO_3H was determined by weighing the catalyst after recovery.

5.3 Calculation of E-factor value for synthesis of 2H-chromene 3aa

1a 122.1 mg; **2a** 213.2 mg; 21.3 mg; 1.578 g (2 mL); **3aa** 208.3 mg

$$E - factor = \frac{Total\ mass\ of\ waste}{Total\ mass\ of\ product}$$

Total amount of reactants: 122.1 mg + 213.2 mg + 21.3 mg + 1578.0 mg = 1934.6 mg

Amount of final product: 208.3 mg

Amount of waste: 1934.6 mg – 208.3 mg = 1726.3 mg

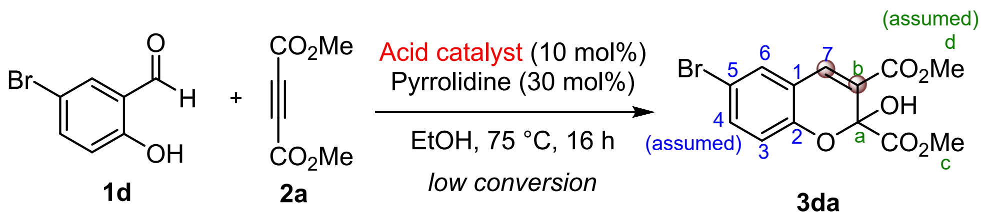
$$E - factor = \frac{1726.3\ mg}{208.3\ mg} = 8.29$$

6. ^{13}C Kinetic isotopic effect at natural abundance

The reaction between 5-bromosalicylaldehyde (**1d**) and dimethyl acethylenedicarboxylate (**2a**) were chosen to determine the ^{13}C kinetic isotope effects (KIEs) at natural abundance (Scheme 5.1). The cyclization reaction catalyzed by PTSA·H_2O was repeated three times, giving the following yields: 58.0 mg (17%), 56.1 mg (16%), and 49.9 mg (15%). The cyclization reaction catalyzed by HCP-SO_3H was repeated three times, giving the following yields: 20.0 mg (6%), 35.5 mg (10%), and 28.1 mg (8%). The percent yield of the product was assumed as the percent conversion. Two reference starting materials (**1d** and **2a**) were used. The NMR samples were prepared in deuterated chloroform ($CDCl_3$). The quantitative ^{13}C NMR spectra were taken at 100 MHz on a Bruker Avance 400 MHz NMR spectrometer with inverse-gated ^{1}H decoupling which used 30° pulses (zgig30 pulse program). Acquisition parameters were as follows: acquisition time 5.2 s; spectral width 240 ppm, size of fid 250k; recovery delays 75 s; size of real spectrum 64k points; transmitter frequency offset 110 ppm; number of dummy scans 8; pre-scan delay 50 µsec; number of scans 512 according to sample concentration. ^{13}C NMR measurements were carried out for the KIE values of 6-bromo-hydroxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3da**). ^{13}C NMR data were processed using 1 Hz exponential multiplication. For the KIE determination, the integration of C4 was set to 100 when **1d** was used as a reference, and the integration of the methyl group was set to 100 when **2a** as a reference. The average integration values for the other carbons were used to calculate the KIE values following Equation 5.[4]

$$KIE_{calc} = \frac{ln(1-F)}{ln[1-\left(F\frac{R_P}{R_0}\right)]} \qquad (Eq. 5)$$

Scheme S6.1 The model reaction of **1d** and **2a** for the determination of ^{13}C KIEs at natural abundance



6.1 ^{13}C KIEs at natural abundance of product 3da from the synthesis of 2*H*-chromenes catalyzed by PTSA·H_2O

Table S6.1 ^{13}C Integrations of the initial 5-bromosalicylaldehyde (**1d**)

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**121.8**	99.62	99.22	99.18	98.59	99.24	99.17	0.369594
2	**160.6**	103.79	103.26	102.59	103.27	103.46	103.274	0.43844
3	**119.9**	99.28	99.31	99.86	97.27	99.74	99.092	1.050271
4	**139.8**	100.00	100.00	100.00	100.00	100.00	100.00	0
5	**111.5**	100.20	99.36	98.30	99.14	99.86	99.372	0.729191
6	**135.7**	100.89	100.31	98.46	99.25	99.22	99.626	0.965831
7	**195.5**	101.15	100.79	100.06	100.50	101.08	100.716	0.448141

Table S6.2 ^{13}C Integrations of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 17% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	97.27	98.48	100.02	100.57	97.05	98.678	1.585298
2	**150.4**	99.58	104.22	103.68	104.32	104.01	103.162	2.017329918
4	**135.3**	100.00	100.00	100.00	100.00	100.00	100.00	0
5	**114.7**	98.21	98.31	100.19	99.92	98.57	99.04	0.940691
6	**131.4**	99.19	99.72	100.04	99.71	98.26	99.384	0.698305
7	**134.1**	94.73	96.68	98.59	98.87	97.08	97.19	1.666298

Table S6.3 Calculated ^{13}C KIEs of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 17% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	1.02147	1.007702	0.990658	0.984697	1.02401	1.005708	0.017715
2	**150.4**	1.040772	0.990022	0.995695	0.988978	0.992221	1.001538	0.022082998
4	**135.3**	1	1	1	1	1	1	0
5	**114.7**	1.013005	1.011874	0.991025	0.993971	1.008943	1.003764	0.010442
6	**131.4**	1.004832	0.998964	0.995451	0.999074	1.015281	1.00272	0.007786
7	**134.1**	1.069448	1.045883	1.023702	1.020523	1.041166	1.040144	0.019672

Table S6.4 ^{13}C Integrations of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 16% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	98.45	99.22	99.66	99.81	98.26	99.08	0.699678
2	**150.4**	102.17	103.72	103.75	103.71	103.08	103.286	0.683981
4	**135.3**	100.00	100.00	100.00	100.00	100.00	100.00	0
5	**114.7**	99.54	99.30	99.36	98.23	99.72	99.23	0.582666
6	**131.4**	99.52	99.77	99.95	99.93	98.55	99.544	0.581704
7	**134.1**	97.24	97.21	97.96	97.34	97.41	97.432	0.305729

Table S6.5 Calculated ^{13}C KIEs of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 16% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	1.008039	0.999446	0.994595	0.992951	1.01018	1.001042	0.007779
2	**150.4**	1.011877	0.995273	0.994957	0.995379	1.002069	0.999911	0.007322
4	**135.3**	1	1	1	1	1	1	0
5	**114.7**	0.998145	1.000797	1.000133	1.012779	0.996164	1.001603	0.006505
6	**131.4**	1.001171	0.998413	0.996437	0.996656	1.012001	1.000936	0.00647
7	**134.1**	1.039289	1.039641	1.030923	1.03812	1.037303	1.037055	0.003552

Table S6.6 ^{13}C Integrations of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 15% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	99.51	99.88	99.68	99.28	99.41	99.552	0.234457
2	**150.4**	103.09	103.5	102.77	104.79	103.26	103.482	0.777991
4	**135.3**	100.00	100.00	100.00	100.00	100.00	100.00	0
5	**114.7**	99.60	97.62	98.88	98.95	100.28	99.066	0.987158
6	**131.4**	99.85	99.04	100.18	98.07	98.8	99.188	0.843309
7	**134.1**	96.22	97.65	97.95	97.66	96.74	97.244	0.731252

Table S6.7 Calculated ^{13}C KIEs of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 15% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	0.996244	0.992186	0.994376	0.998782	0.997346	0.995787	0.002577
2	**150.4**	1.001962	0.9976	1.005391	0.984097	1.000149	0.99784	0.00819
4	**135.3**	1	1	1	1	1	1	0
5	**114.7**	0.997484	1.019727	1.005469	1.004688	0.990047	1.003483	0.01102
6	**131.4**	0.997534	1.006504	0.993921	1.01744	1.00919	1.004918	0.009394
7	**134.1**	1.051356	1.03451	1.031038	1.034394	1.045173	1.039294	0.008589

Table S6.8 ^{13}C Integrations of initial dimethyl acetylenedicarboxylate (**2a**)

C	ppm	n1	n2	n3	n4	n5	Average	SD
a&b	**74.6**	103.01	103.19	101.23	102.77	103.22	102.684	0.832334
C=O	**152.2**	101.31	100.62	100.22	101.07	101.50	100.944	0.521565
c&d	**53.5**	100.00	100.00	100.00	100.00	100.00	100.00	0

Table S6.9 ^{13}C Integrations of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 17% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	103.43	102.33	102.4	103.76	103.5	103.084	0.668229
b	**122.5**	100.90	100.8	100.97	99.88	101.19	100.748	0.505935
c	**54.3**	98.29	98.35	100.32	101.39	99.42	99.554	1.32504
d	**52.5**	100.00	100.00	100.00	100.00	100.00	100.00	0

Table S6.10 Calculated ^{13}C KIEs of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 17% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	0.992071	1.003803	1.003049	0.9886	0.991333	0.995771	0.007111
b	**122.5**	1.019434	1.020544	1.018659	1.030857	1.016229	1.021145	0.005656
c	**54.3**	1.019123	1.018441	0.996494	0.984929	1.006413	1.00508	0.014639
d	**52.5**	1	1	1	1	1	1	0

Table S6.11 ^{13}C Integrations of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 16% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	101.69	103.57	103.09	102.27	102.96	102.716	0.738295
b	**122.5**	101.30	100.20	100.72	100.25	101.44	100.782	0.575951
c	**54.3**	100.12	100.15	100.47	100.23	100.02	100.198	0.169617
d	**52.5**	100.00	100.00	100.00	100.00	100.00	100.00	0

Table S6.12 Calculated ^{13}C KIEs of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 16% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	1.010744	0.990596	0.995671	1.00445	0.997053	0.999703	0.007916
b	**122.5**	1.015017	1.027248	1.021433	1.026687	1.01348	1.020773	0.006396
c	**54.3**	0.998682	0.998354	0.994858	0.997478	0.99978	0.99783	0.001855
d	**52.5**	1	1	1	1	1	1	0

Table S6.13 ^{13}C Integrations of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 15% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	102.05	102.8	103.78	103.48	102.66	102.954	0.686717
b	**122.5**	101.86	100.16	100.30	100.67	99.81	100.56	0.789335
c	**54.3**	99.33	99.16	100.71	98.87	101.58	99.93	1.162691
d	**52.5**	100.00	100.00	100.00	100.00	100.00	100.00	0

Table S6.14 Calculated ^{13}C KIEs of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 15% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	1.006829	0.99876	0.988391	0.991544	1.000257	0.997156	0.007316
b	**122.5**	1.008892	1.027698	1.026125	1.02199	1.031649	1.023271	0.008751
c	**54.3**	1.007414	1.009312	0.99225	1.012563	0.982901	1.000888	0.012728
d	**52.5**	1	1	1	1	1	1	0

Table S6.15 Average calculated KIE values of the synthesis of **3da** in the presence of PTSA•H_2O as a catalyst

C	ppm	KIE #1	KIE #2	KIE #3	Average	SD
1	**119.9**	1.005708	1.001042	0.995787	1.000846	0.004963
2	**150.4**	1.001538	0.999911	0.99784	0.999763	0.001854
4	**135.3**	1	1	1	1	0
5	**114.7**	1.003764	1.001603	1.003483	1.00295	0.001175
6	**131.4**	1.00272	1.000936	1.004918	1.002858	0.001995
7	**134.1**	1.040144	1.037055	1.039294	1.038831	0.001596
a	**93.2**	0.995771	0.999703	0.997156	0.997543	0.001994
b	**122.5**	1.021145	1.020773	1.023271	1.02173	0.001348
c	**54.3**	1.00508	0.99783	1.000888	1.001266	0.00364
d	**52.5**	1	1	1	1	0

6.2 ^{13}C KIEs at natural abundance of product 3da from synthesis of 2*H*-chromenes catalyzed by HCP-SO_3H

Table S6.16 ^{13}C Integrations of initial 5-bromosalicylaldehyde (**1a**)

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**121.8**	102.5444	100.2894	99.0478	97.7741	99.9095	99.91304	1.75993
2	**160.6**	103.9992	104.9984	102.8561	102.5136	101.5147	103.1764	1.35091
4	**139.8**	100.00	100.00	100.00	100.00	100.00	100.00	0
5	**111.5**	100.9913	99.8836	97.655	99.1149	100.4213	99.61322	1.295005
6	**135.7**	101.3004	100.487	97.0879	99.2239	98.0413	99.2281	1.722514
7	**195.5**	104.7261	103.5833	103.8457	100.7828	100.5464	102.6969	1.9047

Table S6.17 ^{13}C Integrations of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 6% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	99.96	99.94	99.38	100.54	100.33	100.03	0.44317
2	**150.4**	103.19	103.59	103.15	103.33	101.99	103.05	0.61709
4	**135.3**	100.00	100.00	100.00	100.00	100.00	100.00	0
5	**114.7**	99.99	99.82	99.86	99.31	99.97	99.79	0.277759
6	**131.4**	98.55	99.45	99.48	98.03	99.50	99.002	0.6757
7	**134.1**	97.50	98.06	98.98	99.57	100.82	98.986	1.300992

Table S6.18 Calculated ^{13}C KIEs of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 6% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	0.999484	0.999703	1.005896	0.993145	0.995432	0.998732	0.004872
2	**150.4**	0.999855	0.995611	1.000281	0.998366	1.012786	1.00138	0.006633
4	**135.3**	1	1	1	1	1	1	0
5	**114.7**	0.995858	0.997723	0.997283	1.003356	0.996077	0.998059	0.003064
6	**131.4**	1.007563	0.997547	0.997217	1.013434	0.996996	1.002551	0.007548
7	**134.1**	1.058581	1.051971	1.041273	1.034517	1.020462	1.041361	0.014939

Table S6.19 ^{13}C Integrations of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 10% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	99.75	99.88	99.39	99.98	100.06	99.812	0.262812
2	**150.4**	103.16	103.48	103.04	102.88	103.76	103.264	0.353949
4	**135.3**	100.00	100.00	100.00	100.00	100.00	100.00	0
5	**114.7**	100.05	99.74	100.05	98.98	99.70	99.704	0.437299
6	**131.4**	99.42	98.38	98.83	99.93	98.34	98.98	0.687059
7	**134.1**	99.63	97.72	99.43	101.11	96.02	98.782	1.956724

Table S6.20 Calculated ^{13}C KIEs of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 10% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	1.001797	1.000364	1.005785	0.999264	0.998386	1.001119	0.002903
2	**150.4**	1.000175	0.996775	1.001455	1.003167	0.993817	0.999078	0.00376
4	**135.3**	1	1	1	1	1	1	0
5	**114.7**	0.995201	0.998603	0.995201	1.007032	0.999043	0.999016	0.004836
6	**131.4**	0.997878	1.009476	1.004428	0.992279	1.009927	1.002798	0.007631
7	**134.1**	1.033834	1.055975	1.036113	1.017251	1.076421	1.043919	0.022779

Table S6.21 ^{13}C Integrations of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 8% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	99.54	99.79	100.17	99.65	99.77	99.784	0.238076
2	**150.4**	103.19	103.93	102.77	102.80	102.87	103.112	0.486847
4	**135.3**	100.00	100.00	100.00	100.00	100.00	100.00	0
5	**114.7**	99.87	98.73	100.7	99.01	99.76	99.614	0.776614
6	**131.4**	98.37	99.20	98.98	99.21	99.35	99.022	0.387776
7	**134.1**	95.84	98.80	100.71	98.13	100.55	98.806	1.995051

Table S6.22 Calculated ^{13}C KIEs of **3da** (carbon atoms from 5-bromosalicylaldehyde) from the reaction with 8% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
1	**119.9**	1.004119	1.001355	0.99718	1.002902	1.001576	1.001427	0.002621
2	**150.4**	0.999855	0.992029	1.004347	1.004025	1.003274	1.000706	0.005169
4	**135.3**	1	1	1	1	1	1	0
5	**114.7**	0.997174	1.009833	0.988136	1.006697	0.998383	1.000045	0.008557
6	**131.4**	1.009589	1.000311	1.002755	1.000201	0.998651	1.002301	0.00433

7	**134.1**	1.078628	1.043351	1.021685	1.05115	1.023468	1.043656	0.023289

Table S6.23 ^{13}C Integrations of initial dimethyl acetylenedicarboxylate (**2a**)

C	ppm	n1	n2	n3	n4	n5	Average	SD
a&b	**74.6**	103.1087	103.2563	99.6901	102.4178	99.9672	101.688	1.729402
C=O	**152.2**	100.1908	98.4536	97.3499	99.9135	98.9211	98.96578	1.148286
c&d	**53.5**	100.00	100.00	100.00	100.00	100.00	100.00	0

Table S6.24 ^{13}C Integrations of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 6% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	102.24	100.98	101.76	101.03	101.84	101.57	0.547174
b	**122.5**	99.65	99.19	99.45	100.46	99.64	99.678	0.475363
c	**54.3**	99.56	100.31	99.97	100.37	99.8	100.002	0.341862
d	**52.5**	100.00	100.00	100.00	100.00	100.00	100.00	0

Table S6.25 Calculated ^{13}C KIEs of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 6% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	0.994065	1.007707	0.999222	1.007159	0.99836	1.001303	0.005931
b	**122.5**	1.02248	1.027681	1.024735	1.013436	1.022592	1.022185	0.005327
c	**54.3**	1.004858	0.996603	1.00033	0.995948	1.002203	0.999988	0.003759
d	**52.5**	1	1	1	1	1	1	0

Table S6.26 ^{13}C Integrations of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 10% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	100.55	102.59	101.54	101	102.99	101.734	1.035437
b	**122.5**	99.38	100.18	99.74	99.24	99.24	99.556	0.404327
c	**54.3**	101.66	98.76	100.41	99.97	99.30	100.02	1.112452
d	**52.5**	100.00	100.00	100.00	100.00	100.00	100.00	0

Table S6.27 Calculated ^{13}C KIEs of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 10% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	1.012441	0.990335	1.001602	1.007488	0.986103	0.999594	0.01117
b	**122.5**	1.025527	1.016546	1.021468	1.027113	1.027113	1.023554	0.004547

c	**54.3**	0.98205	1.013801	0.995511	1.00033	1.007749	0.999888	0.012175
d	**52.5**	1	1	1	1	1	1	0

Table S6.28 ^{13}C Integrations of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 8% conversion

C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	101.98	101.49	101.31	101.95	102.02	101.75	0.326726
b	**122.5**	99.33	99.48	99.46	99.84	99.83	99.588	0.232744
c	**54.3**	100.75	99.22	99.92	100.12	100.02	100.006	0.545875
d	**52.5**	100.00	100.00	100.00	100.00	100.00	100.00	0

Table S6.29 Calculated ^{13}C KIEs of **3da** (carbon atoms from dimethyl acetylenedicarboxylate) from the reaction with 8% conversion

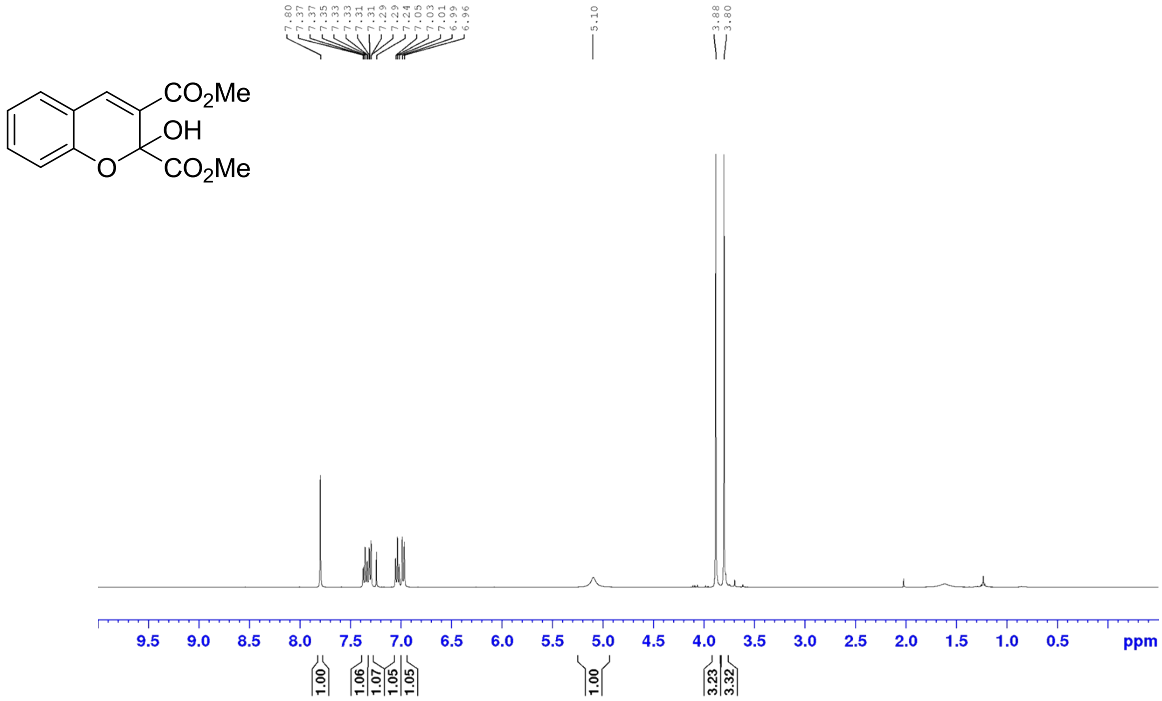
C	ppm	n1	n2	n3	n4	n5	Average	SD
a	**93.2**	0.996853	1.002145	1.004102	0.997175	0.996423	0.999339	0.003533
b	**122.5**	1.026093	1.024396	1.024622	1.020345	1.020458	8%	0.002622
c	**54.3**	0.991817	1.008641	1.00088	0.998682	0.99978	0.99996	0.006004
d	**52.5**	1	1	1	1	1	1	0

Table S6.30 Average calculated KIE values of the synthesis of **3da** in the presence of HCP-SO_3H as a catalyst

C	ppm	KIE #1	KIE #2	KIE #3	Average	SD
1	**119.9**	0.998732	1.001119	1.001427	1.000426	0.001475
2	**150.4**	1.00138	0.999078	1.000706	1.000388	0.001184
4	**135.3**	1	1	1	1	0
5	**114.7**	0.998059	0.999016	1.000045	0.99904	0.000993
6	**131.4**	1.002551	1.002798	1.002301	1.00255	0.000248
7	**134.1**	1.041361	1.043919	1.043656	1.042979	0.001407
a	**93.2**	1.001303	0.999594	0.999339	1.000079	0.001068
b	**122.5**	1.022185	1.023554	1.023183	1.022974	0.000708
c	**54.3**	0.999988	0.999888	0.99996	0.999946	5.16E-05
d	**52.5**	1	1	1	1	0

7. NMR Spectra

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

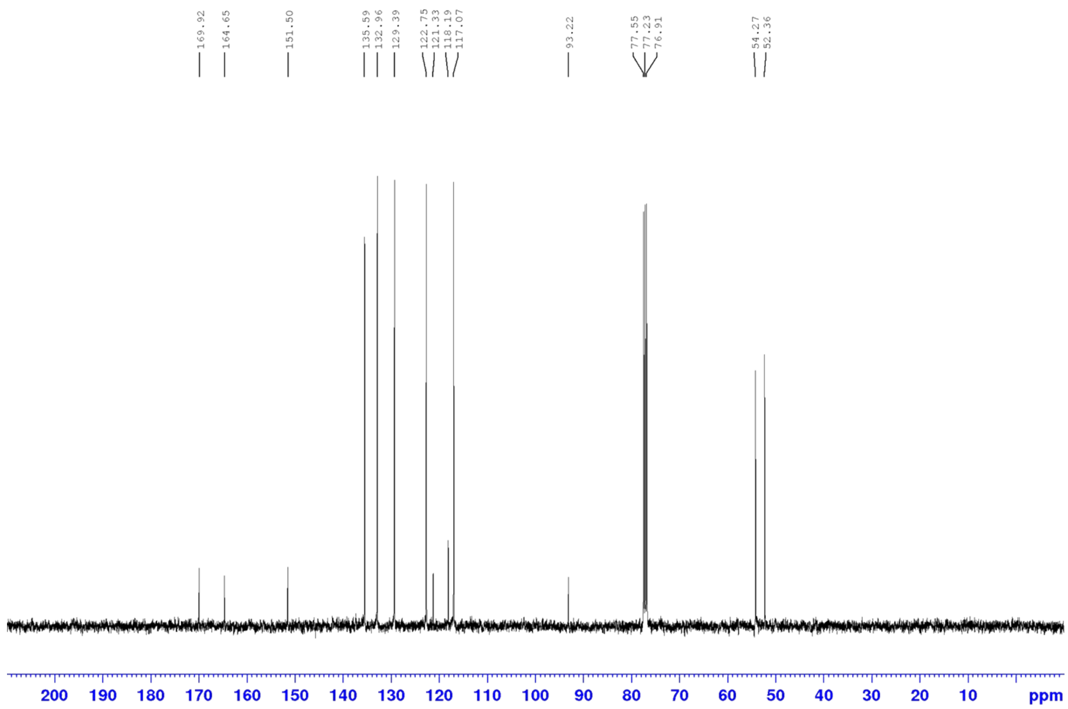
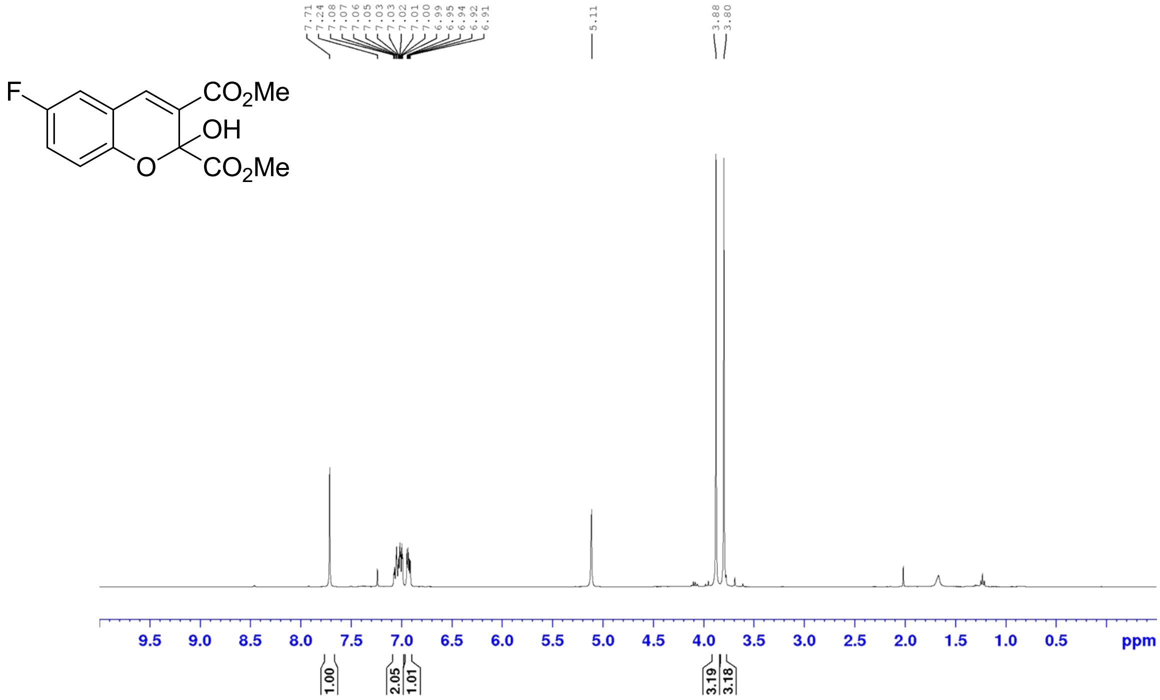


Fig. S7.1 NMR spectra of 2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3aa**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

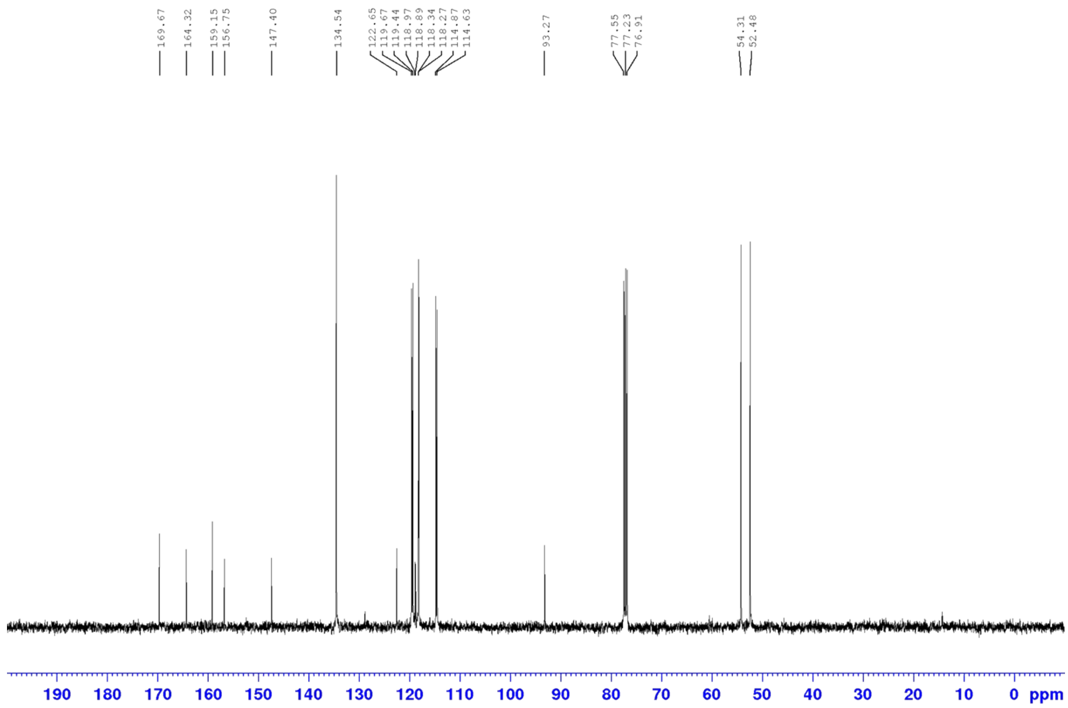
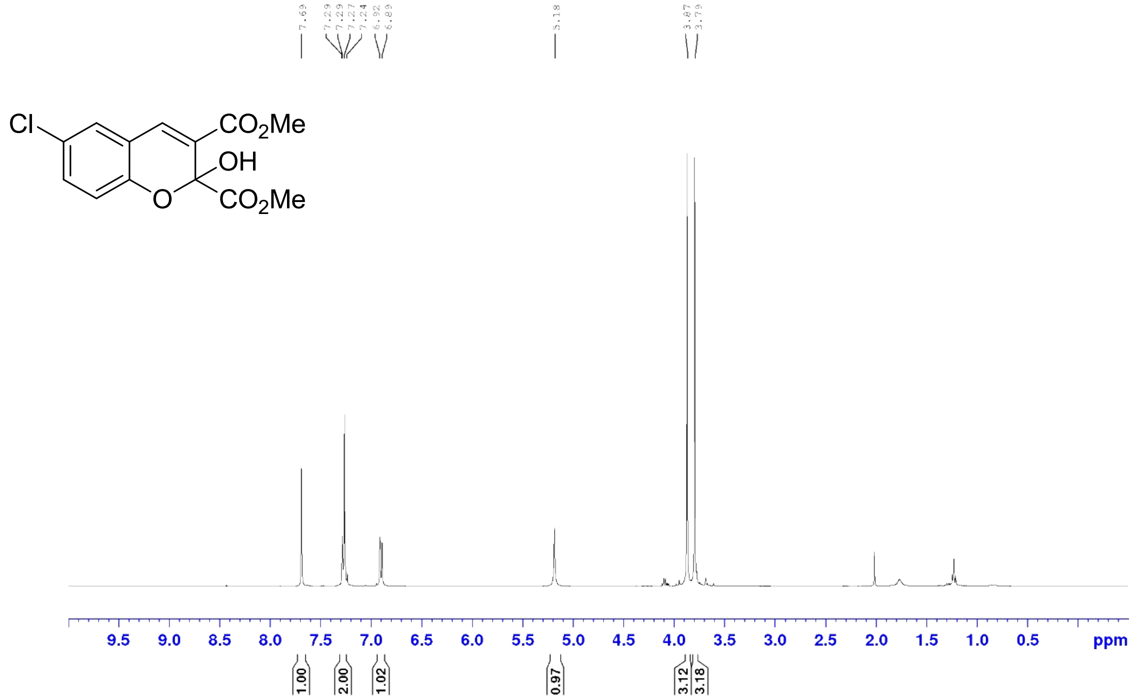


Fig. S7.2 NMR spectra of 6-fluoro-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3ba**)

^1H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

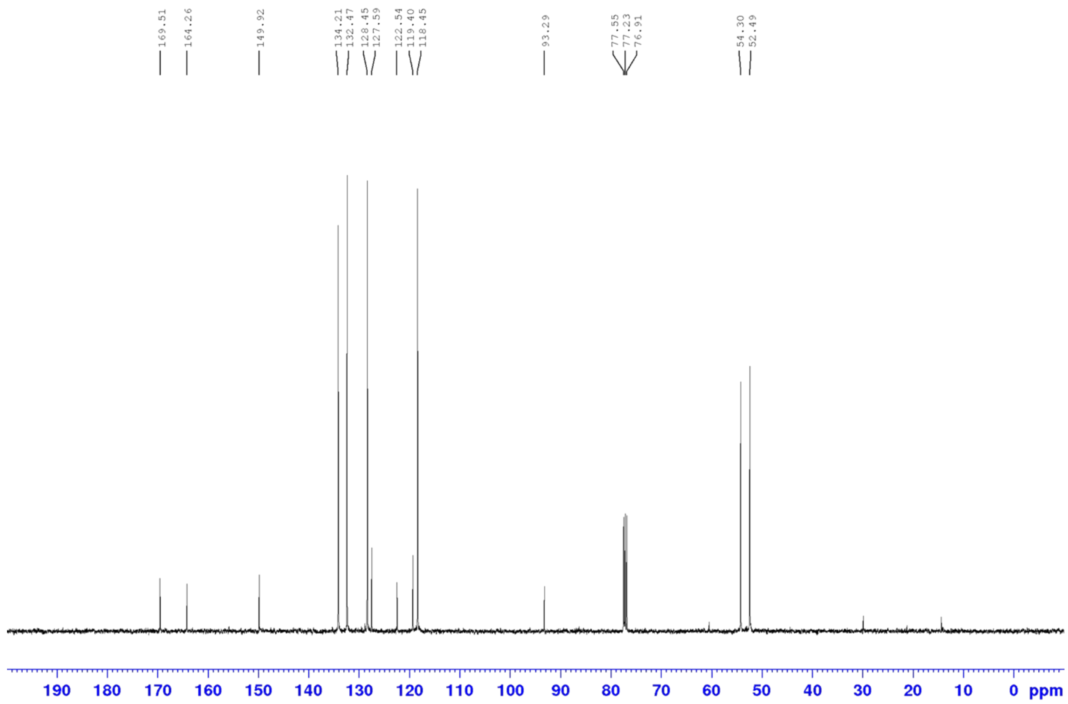
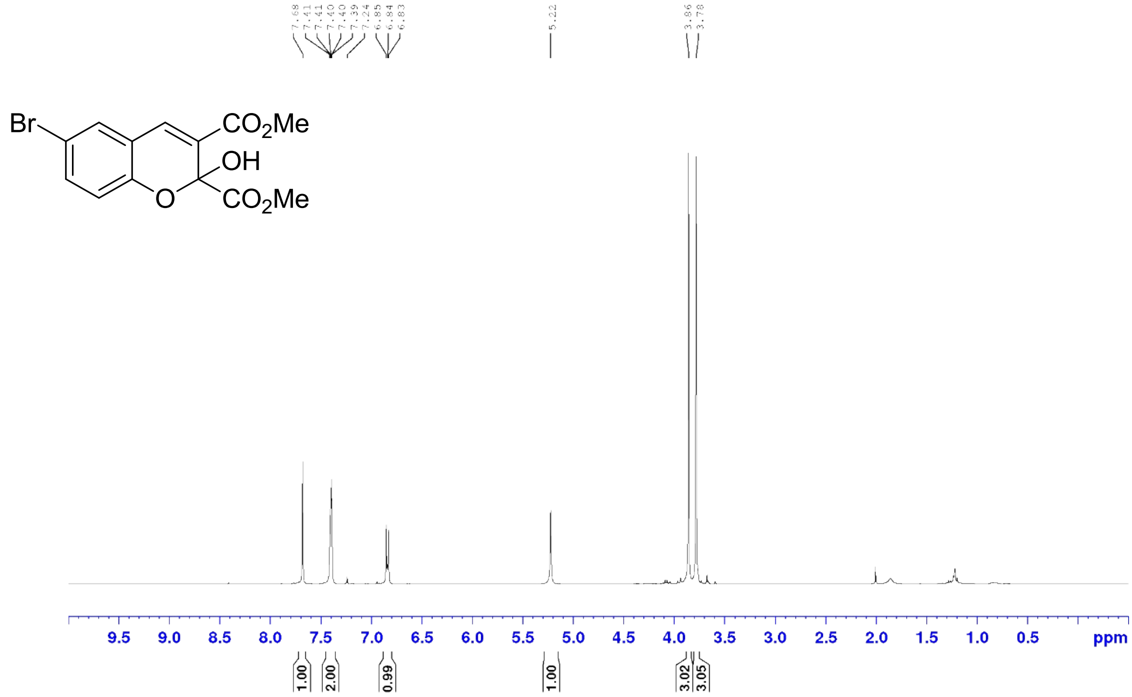


Fig. S7.3 NMR spectra of 6-chloro-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3ca**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

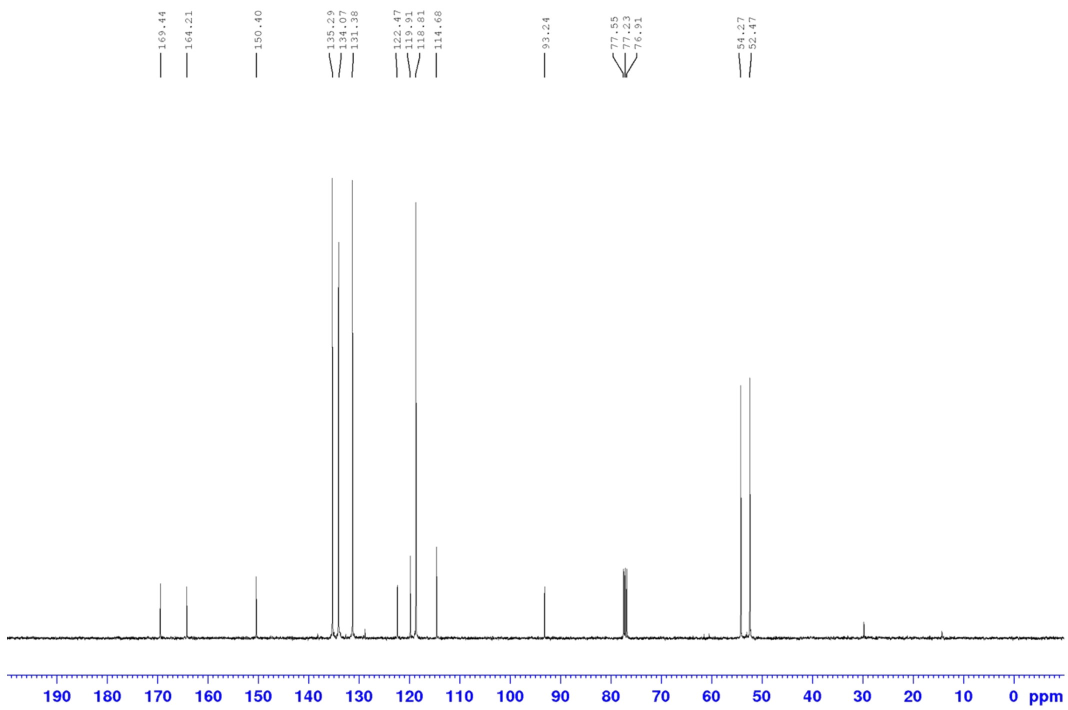
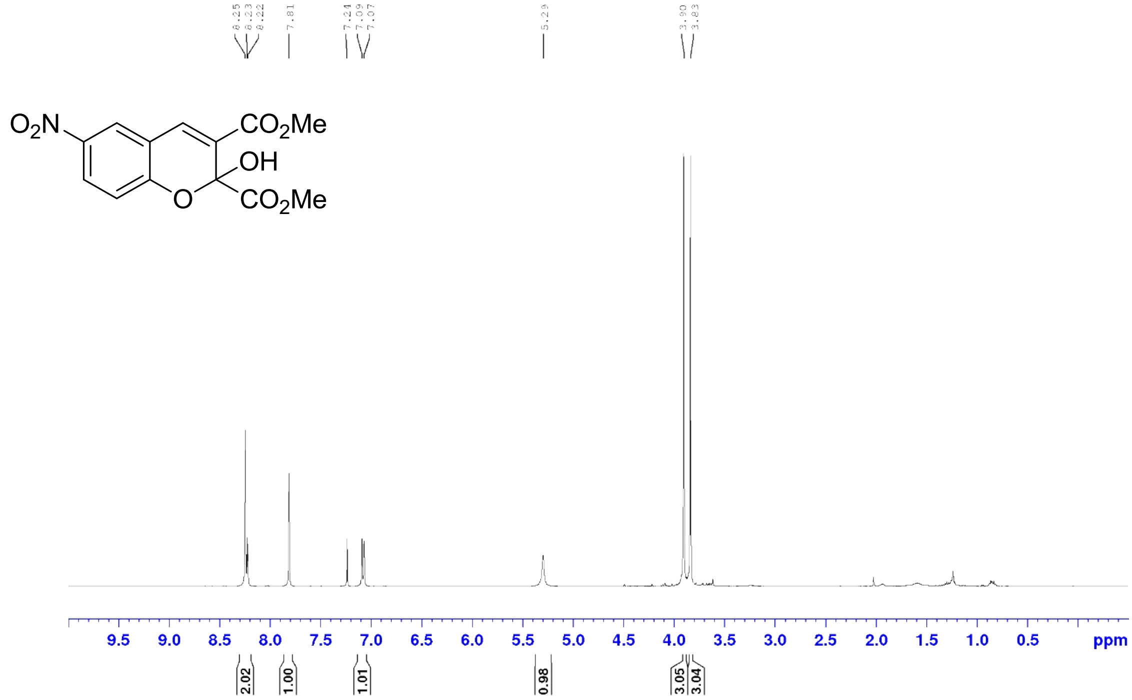


Fig. S7.4 NMR spectra of 6-bromo-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3da**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

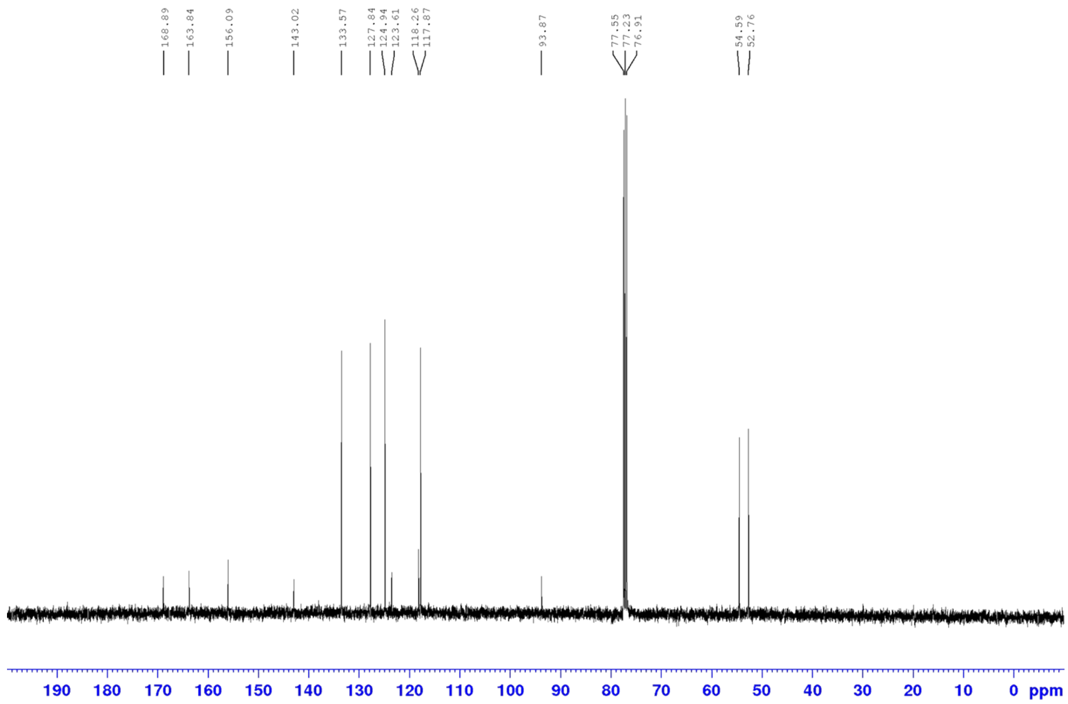
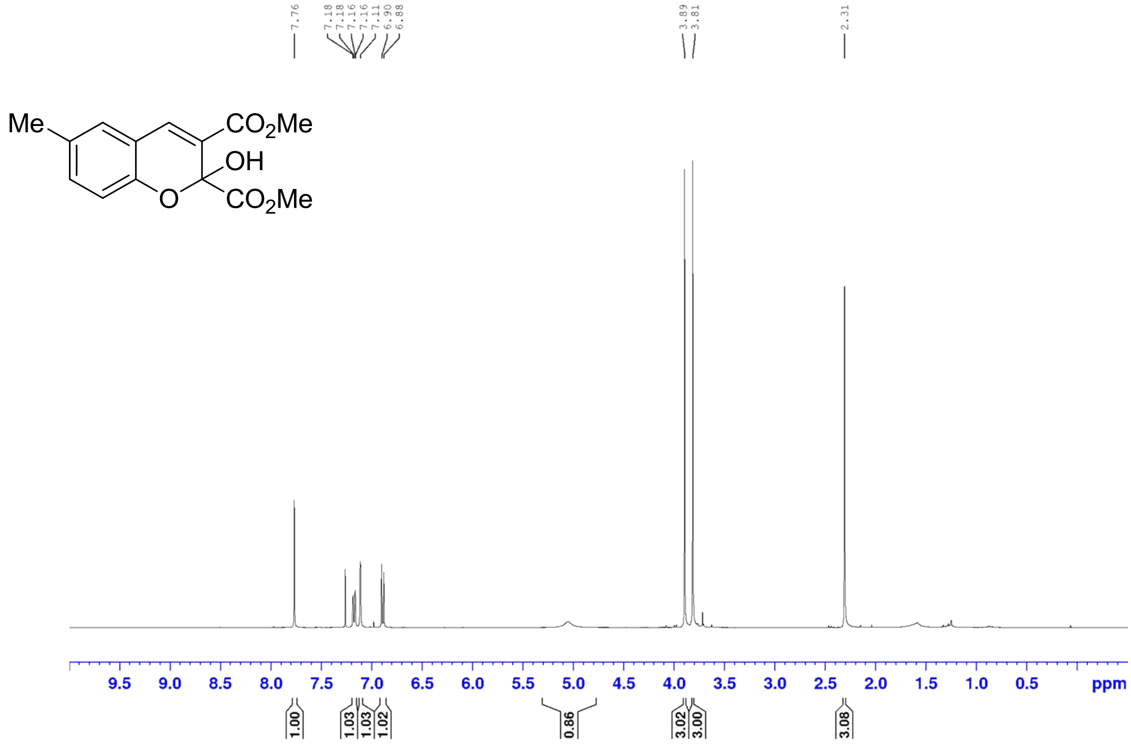


Fig. S7.5 NMR spectra of 2-hydroxy-6-nitro-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3ea**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

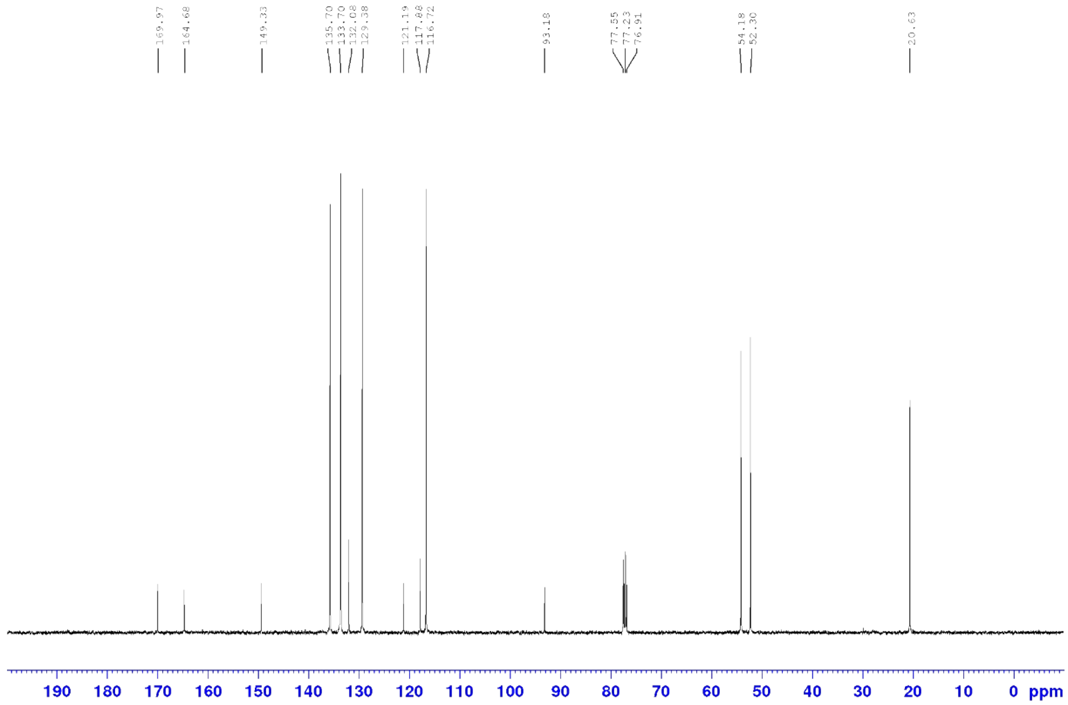
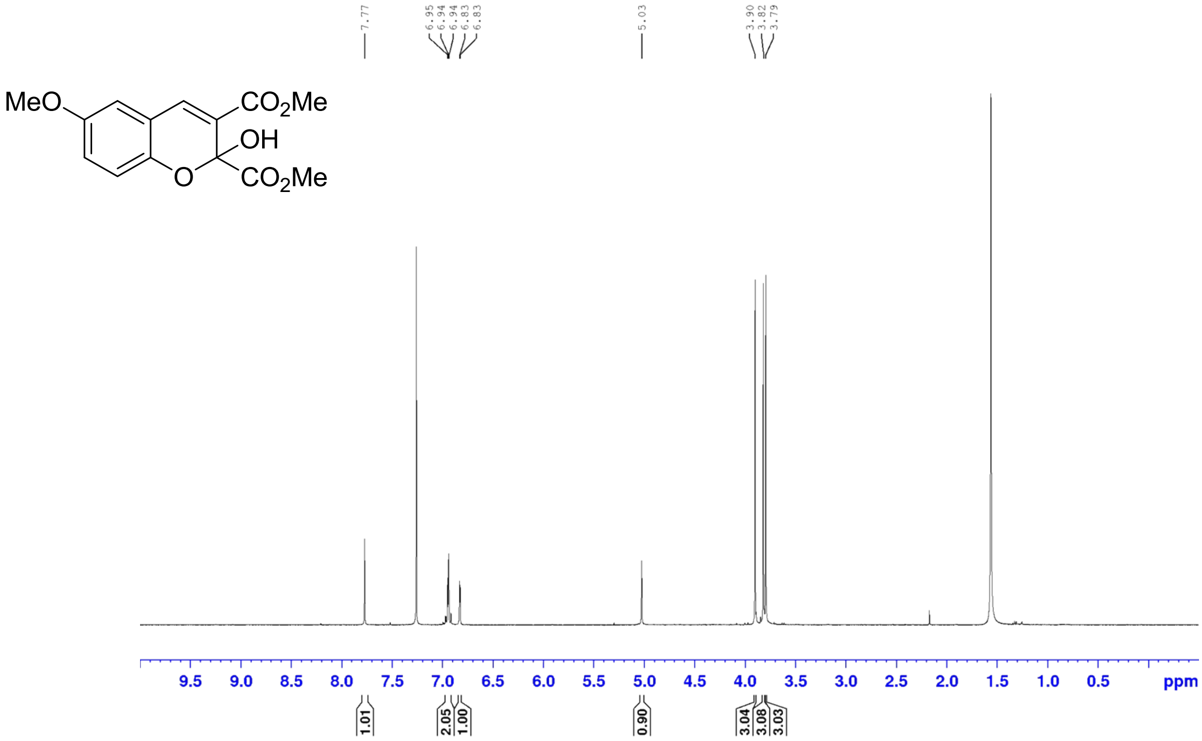


Fig. S7.6 NMR spectra of 2-hydroxy-6-methyl-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3fa**)

^1H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

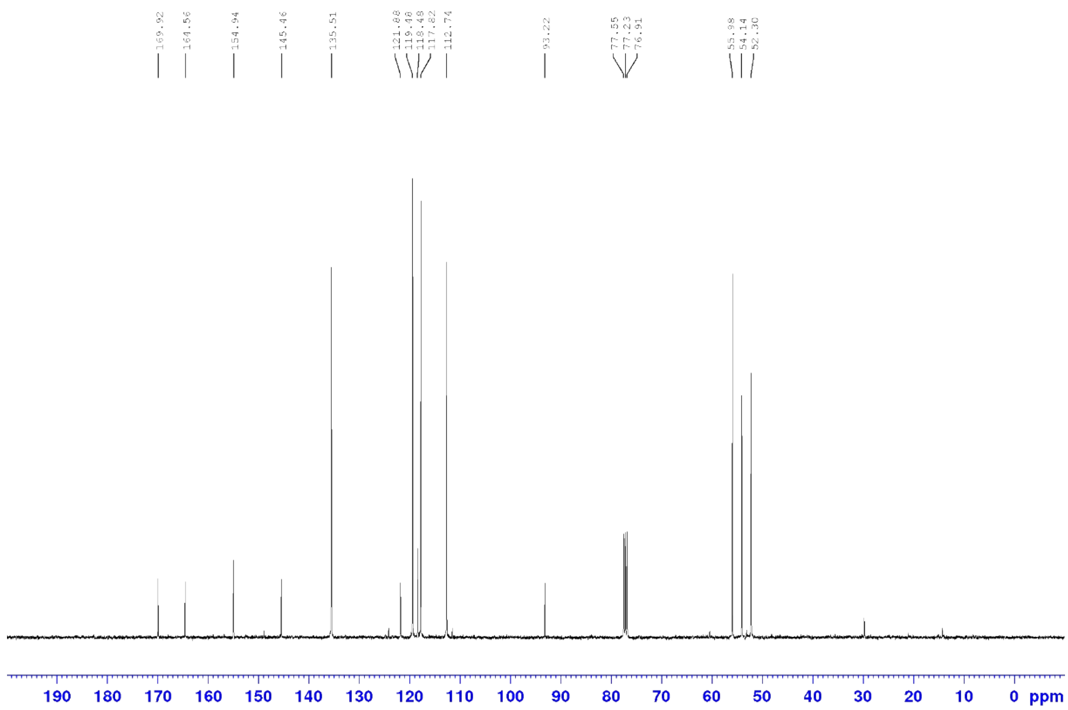
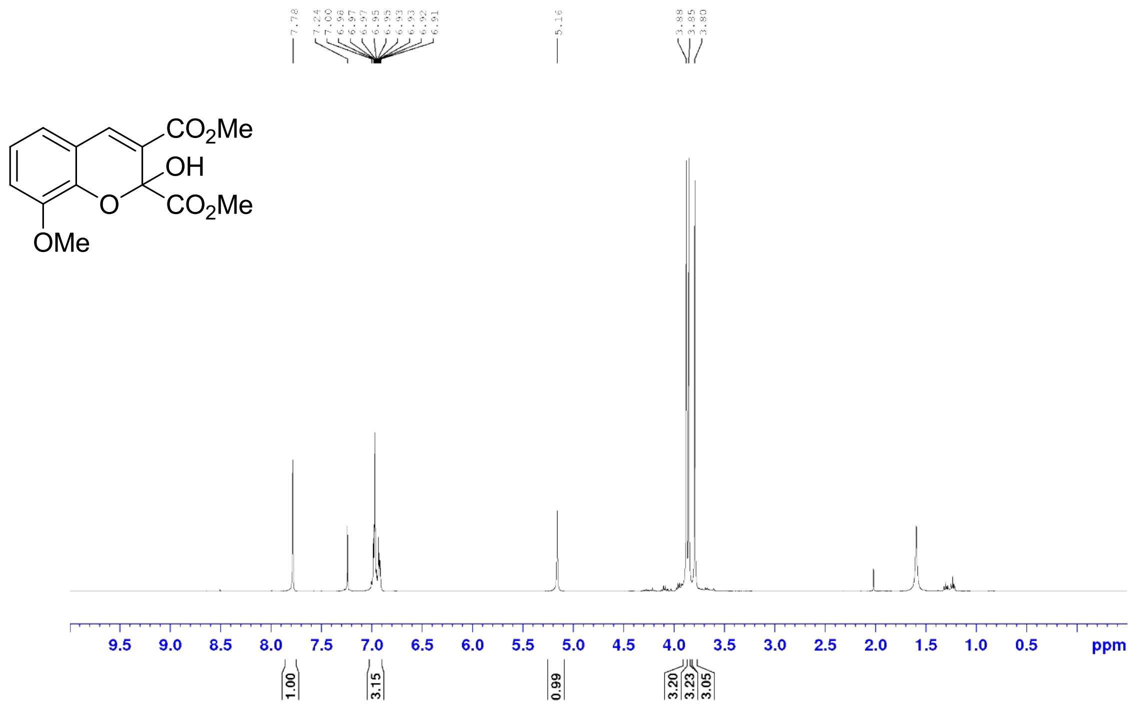


Fig. S7.7 NMR spectra of 2-hydroxy-6-methyoxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3ga**)

[1]H NMR with $CDCl_3$, 400 MHz



[13]C NMR with $CDCl_3$, 100 MHz

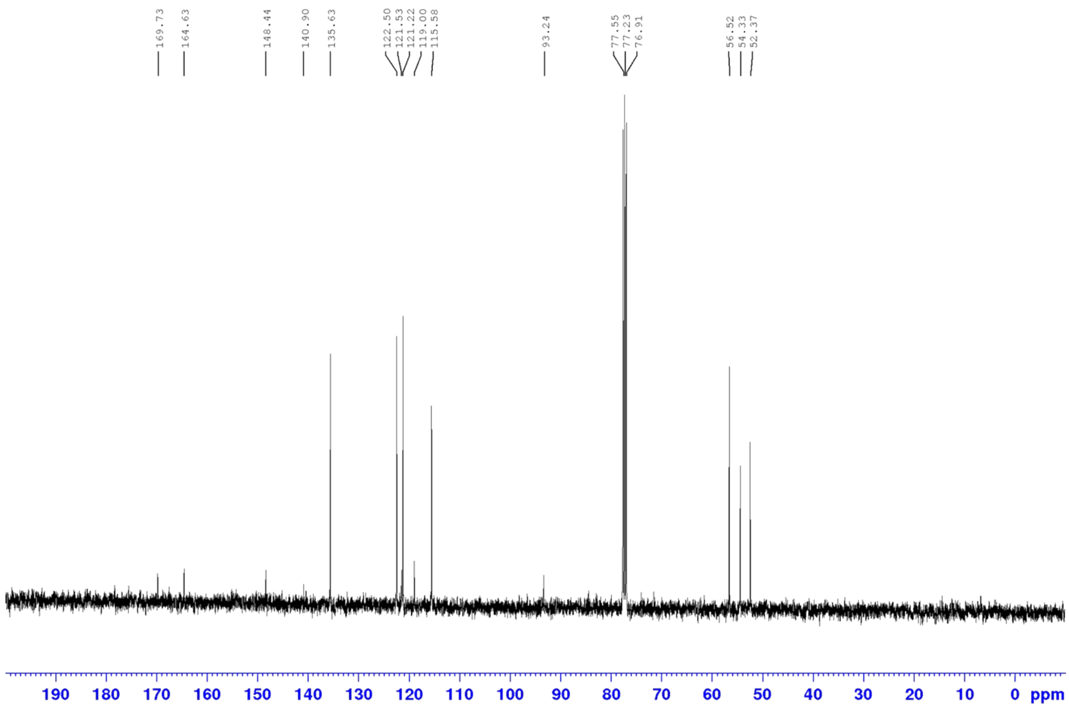
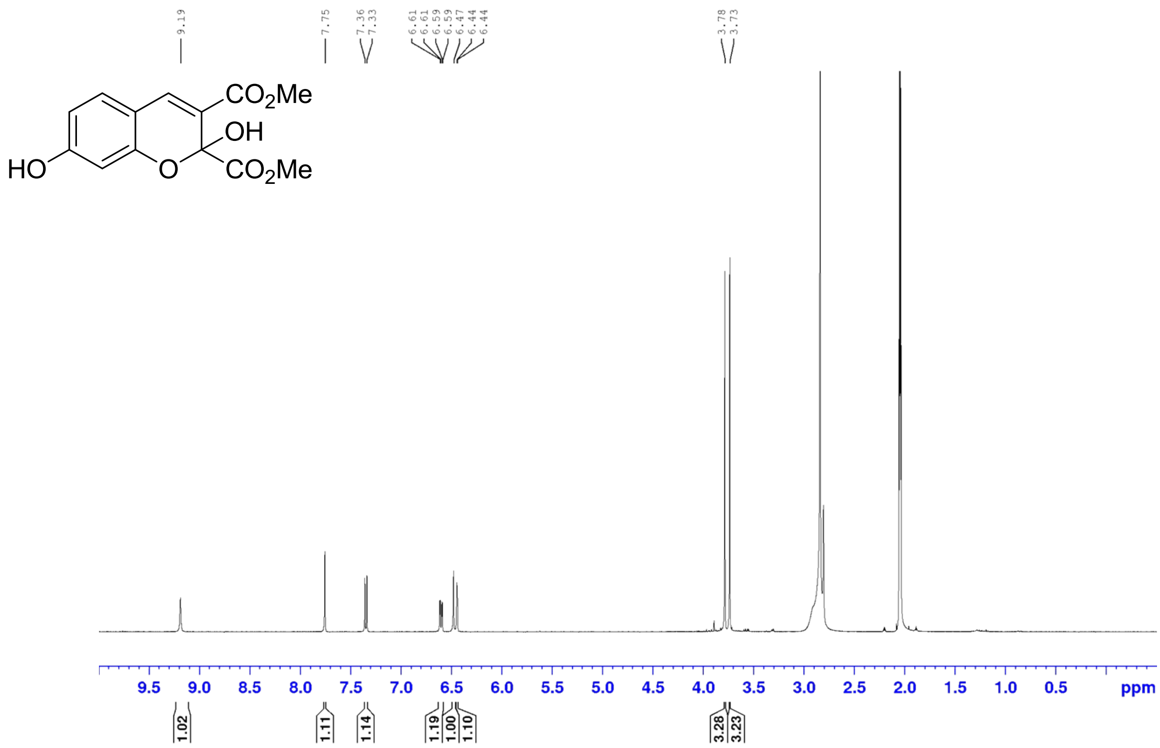


Fig. S7.8 NMR spectra of 2-hydroxy-8-methyoxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3ha**)

^{1}H NMR with acetone-d_6, 400 MHz



^{13}C NMR with acetone-d_6, 100 MHz

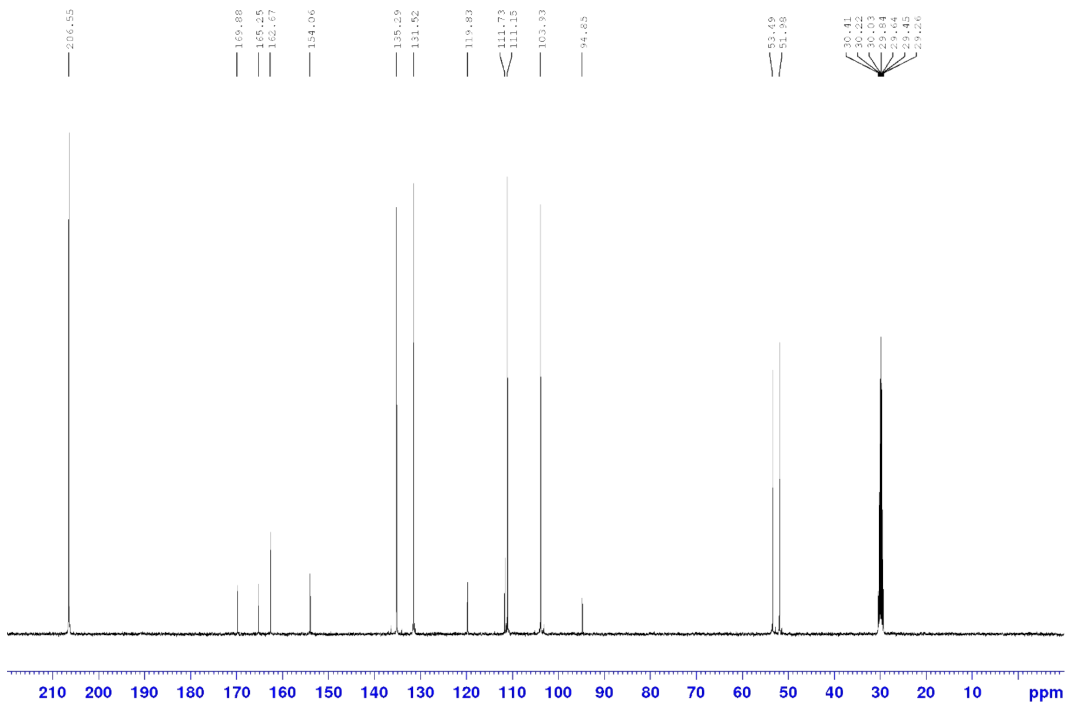
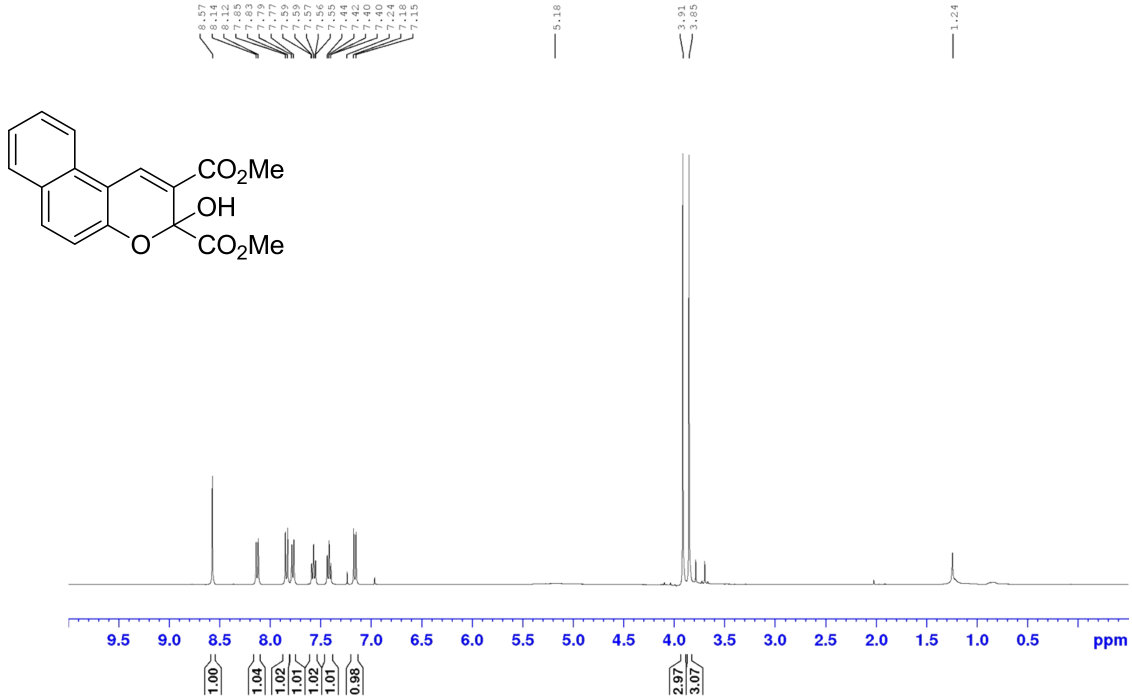


Fig. S7.9 NMR spectra of 2,7-dihydroxy-2*H*-chromene-2,3-dicarboxylic acid dimethyl ester (**3ia**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

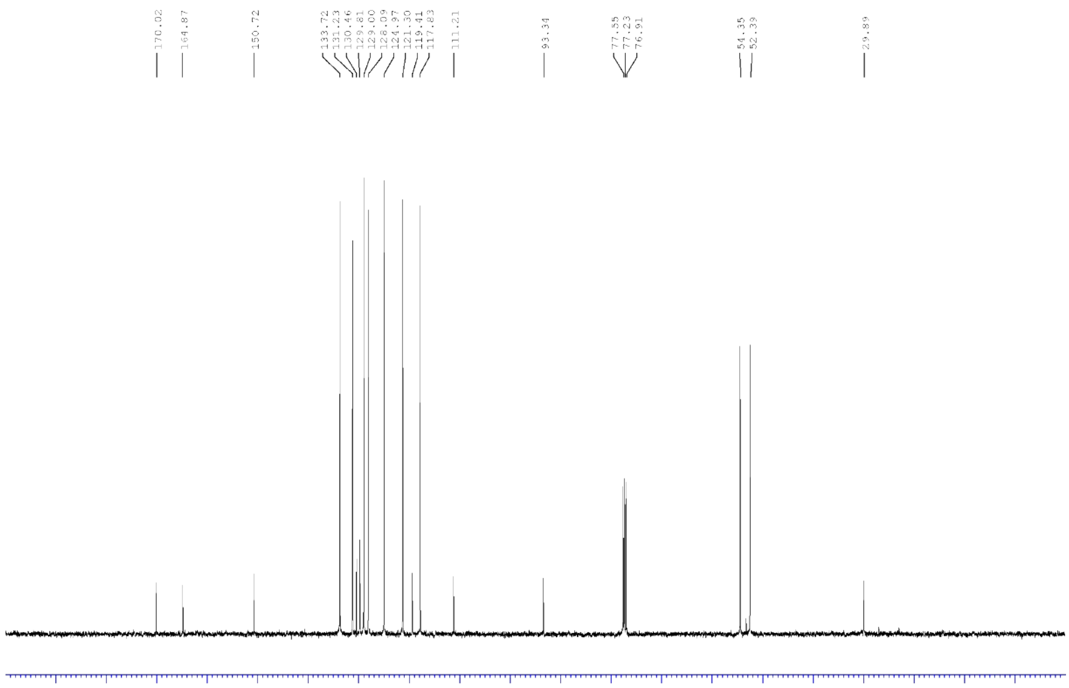
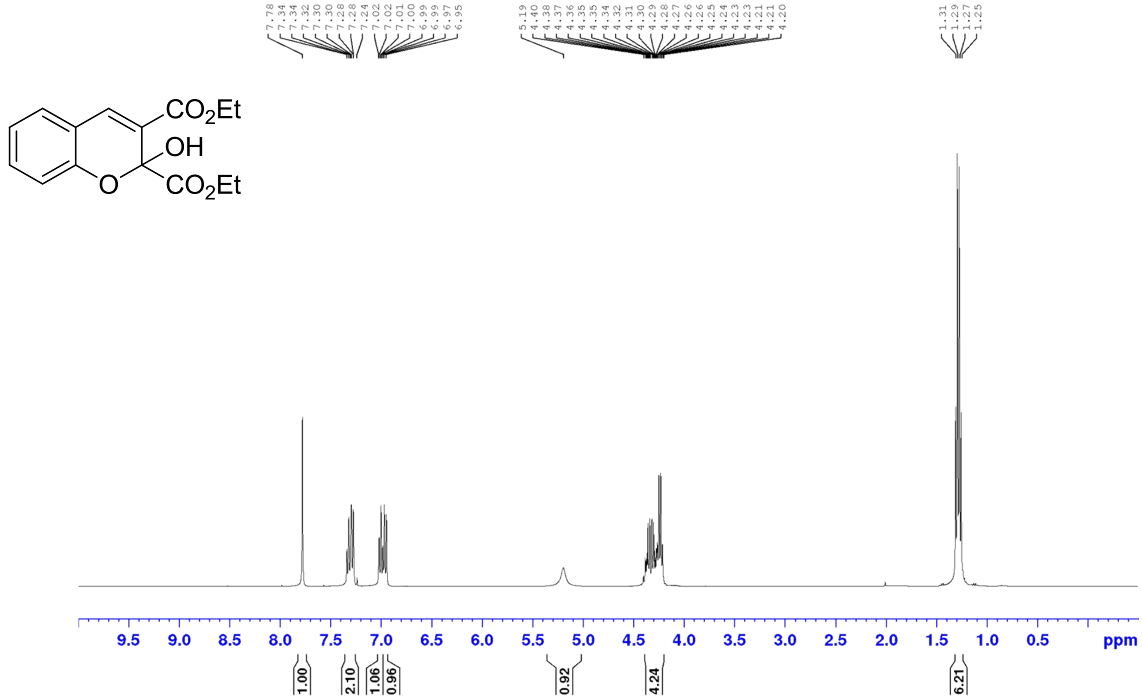


Fig. S7.10 NMR spectra of 3-hydroxy-3*H*-benzo[*f*]chromene-2,3-dicarboxylic acid dimethyl ester (**3ja**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

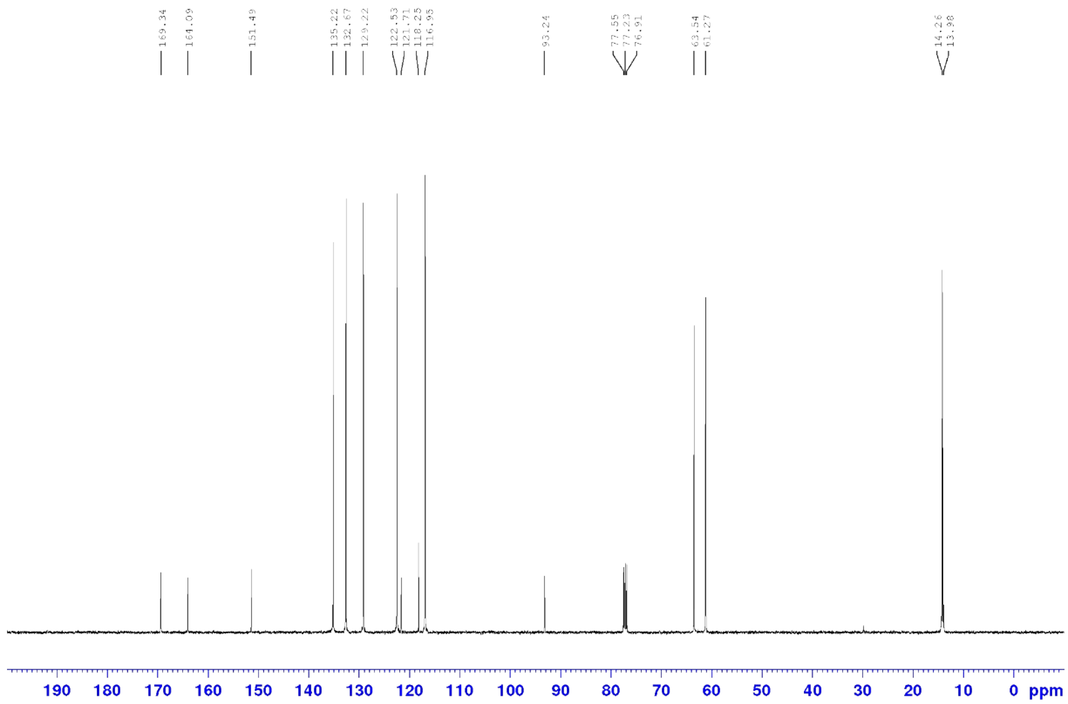
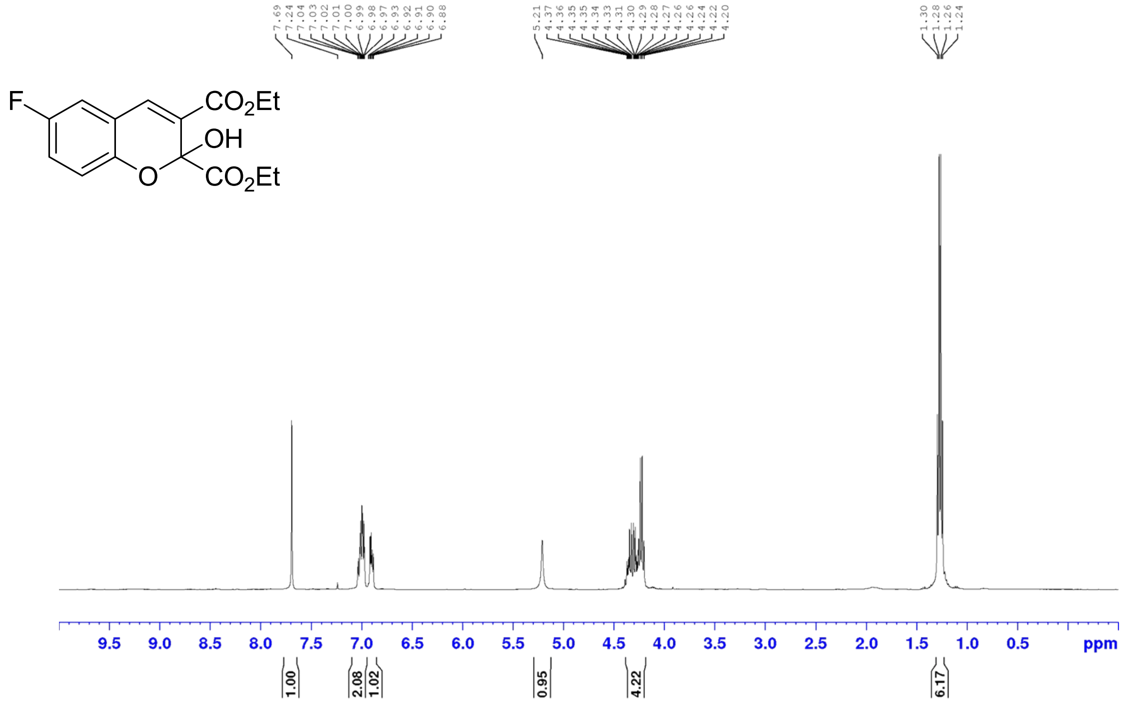


Fig. S7.11 NMR spectra of 2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (**3ab**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

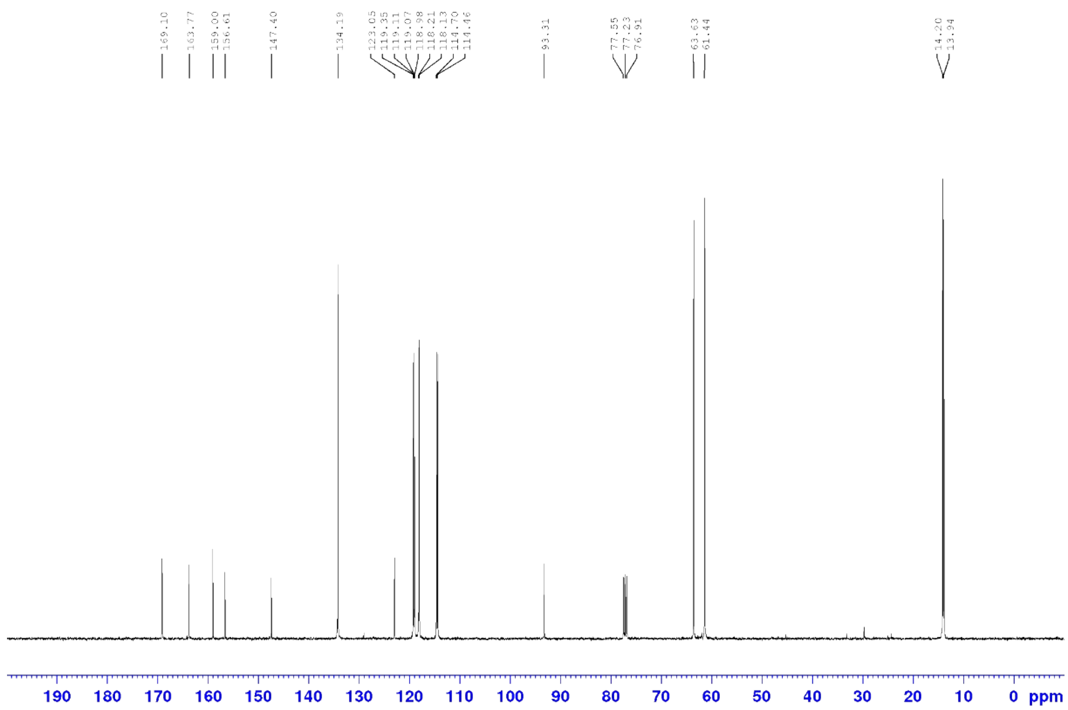
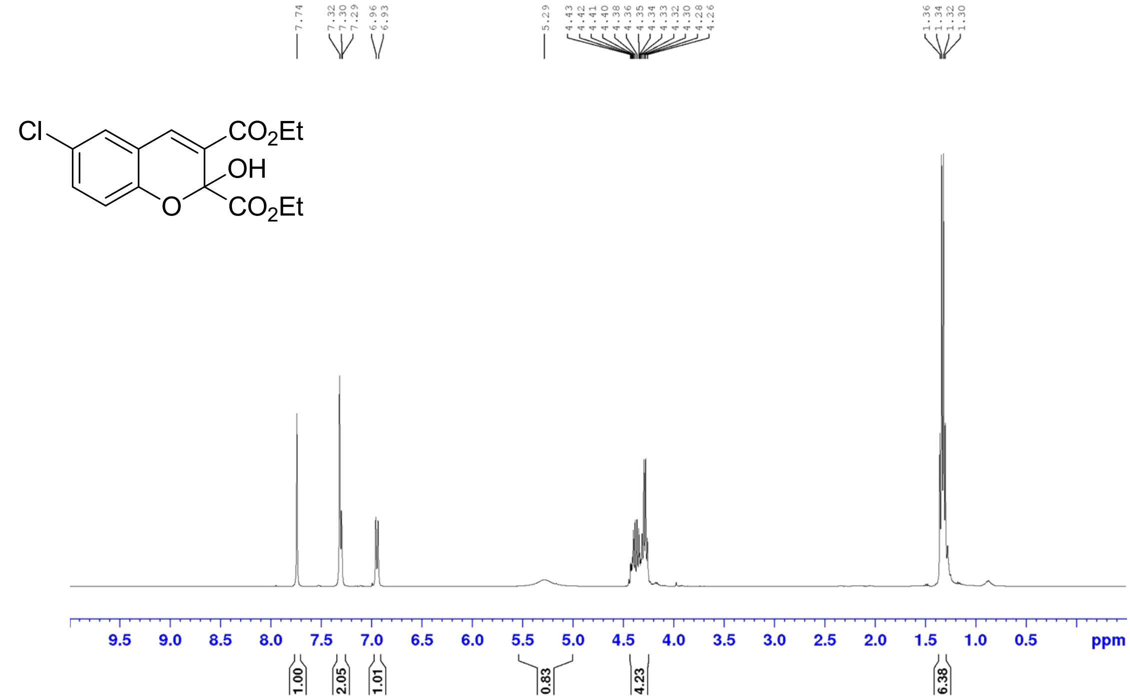


Fig. S7.12 NMR spectra of 6-fluoro-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (**3bb**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

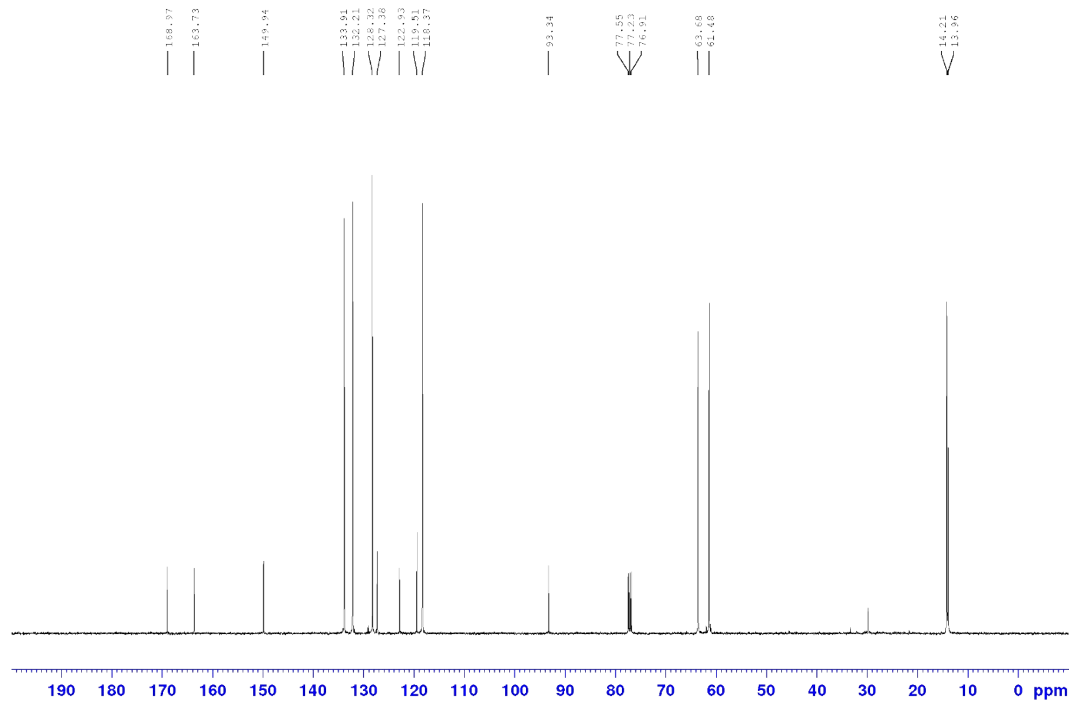
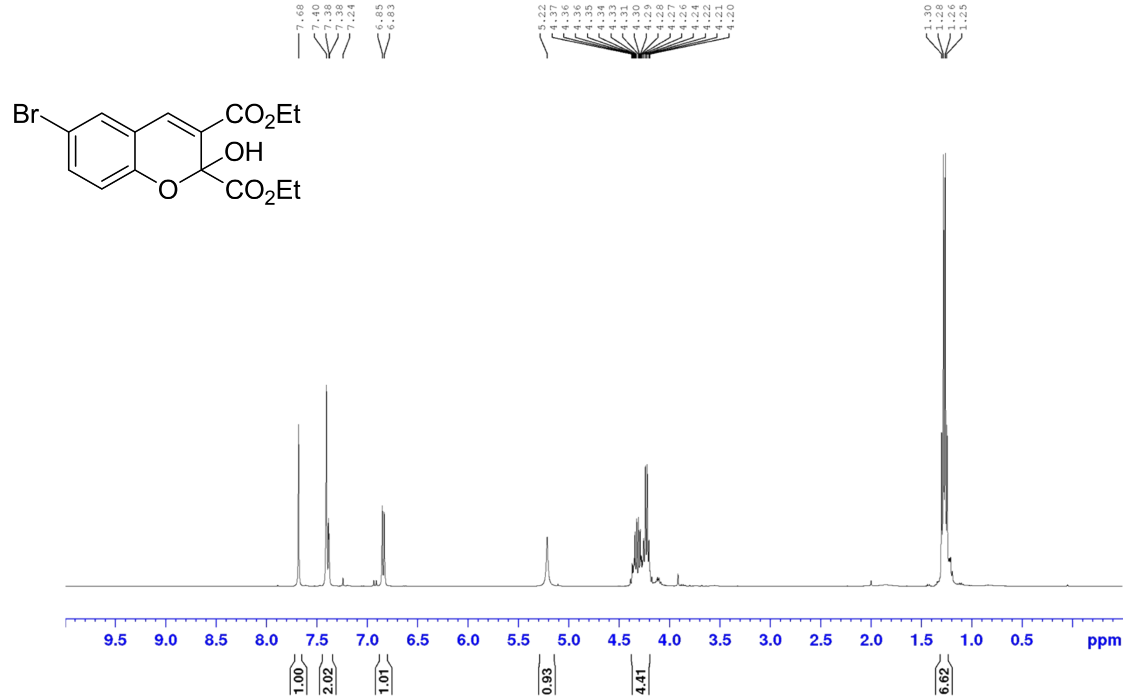


Fig. S7.13 NMR spectra of 6-chloro-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (**3cb**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

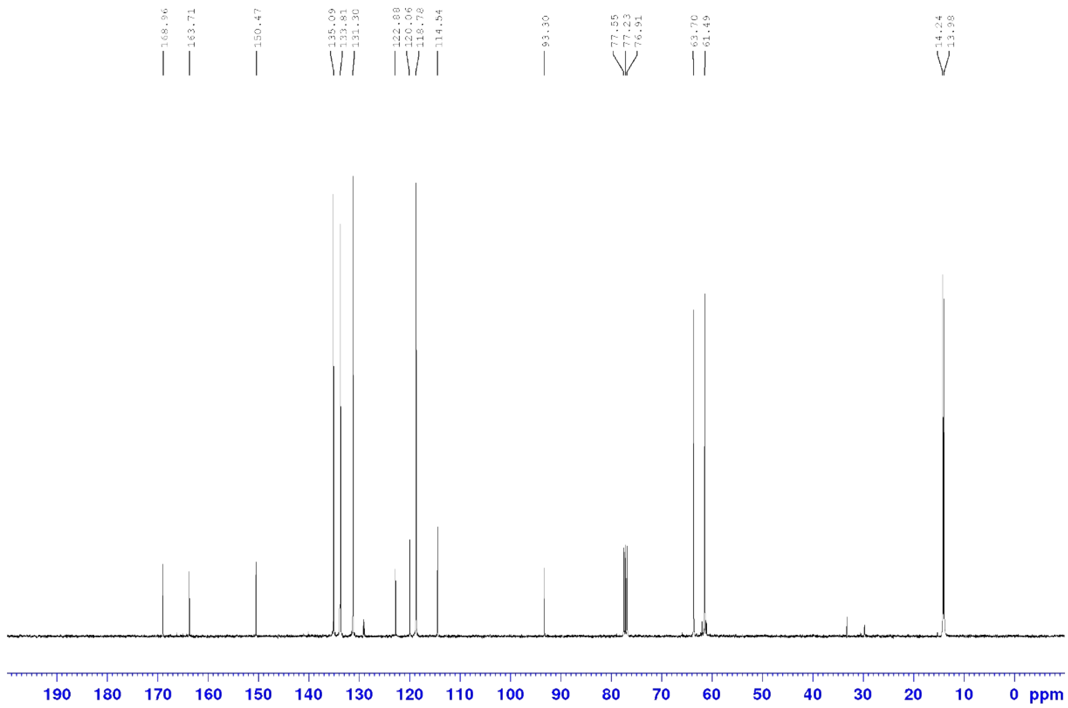
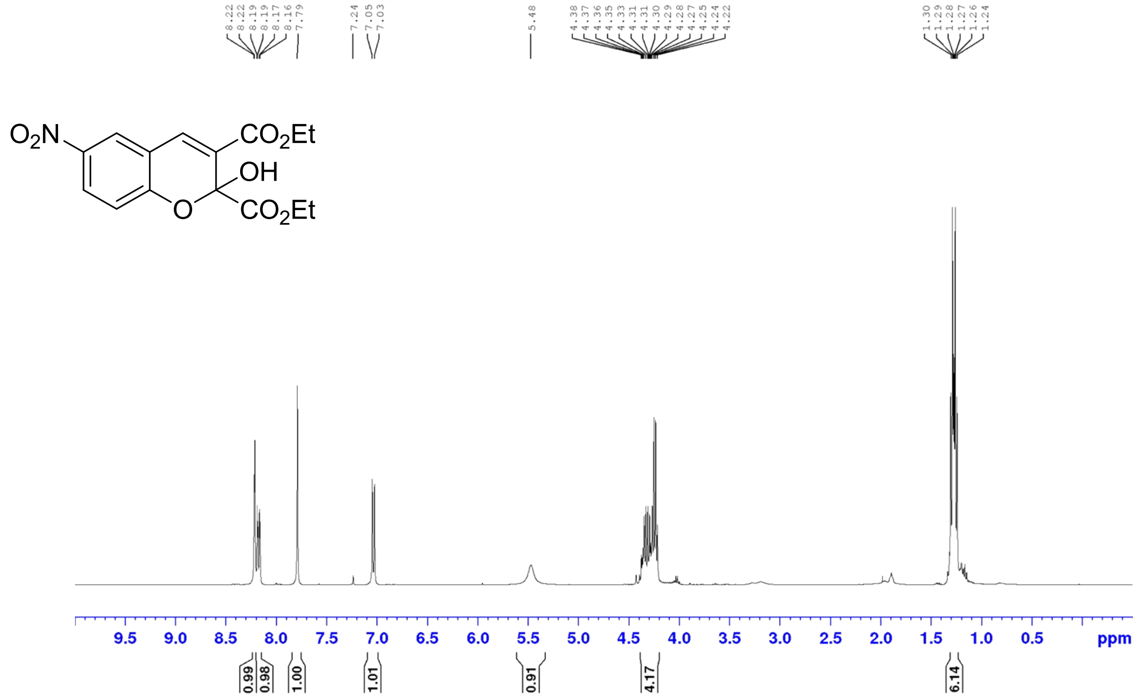


Fig. S7.14 NMR spectra of 6-bromo-2-hydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (**3db**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

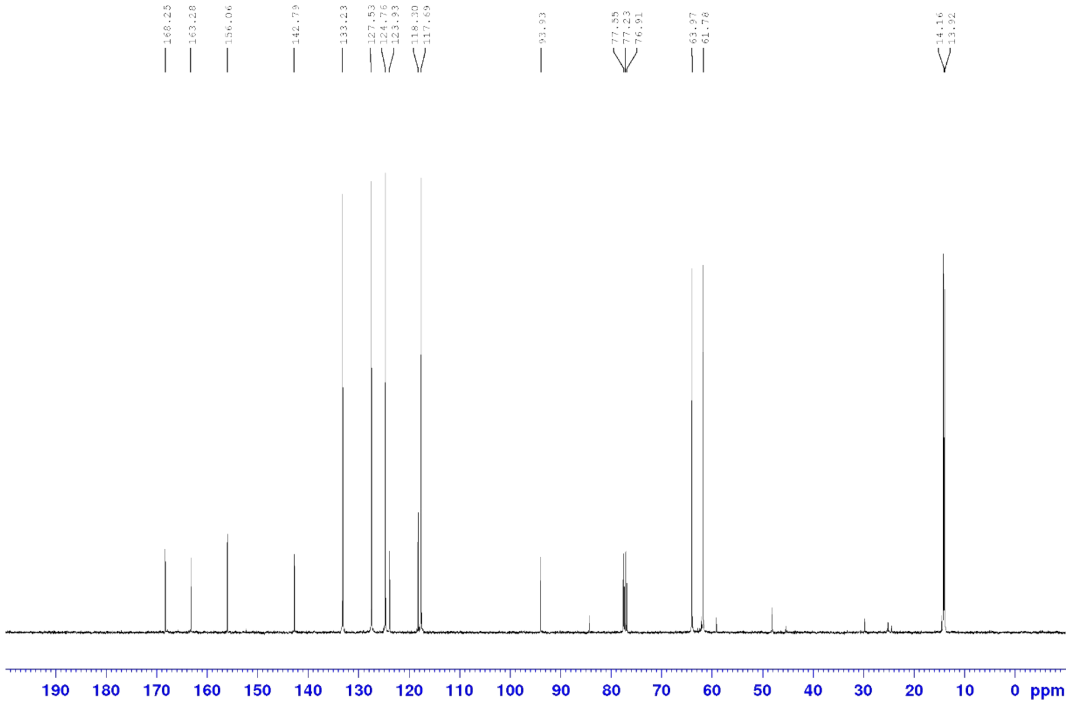
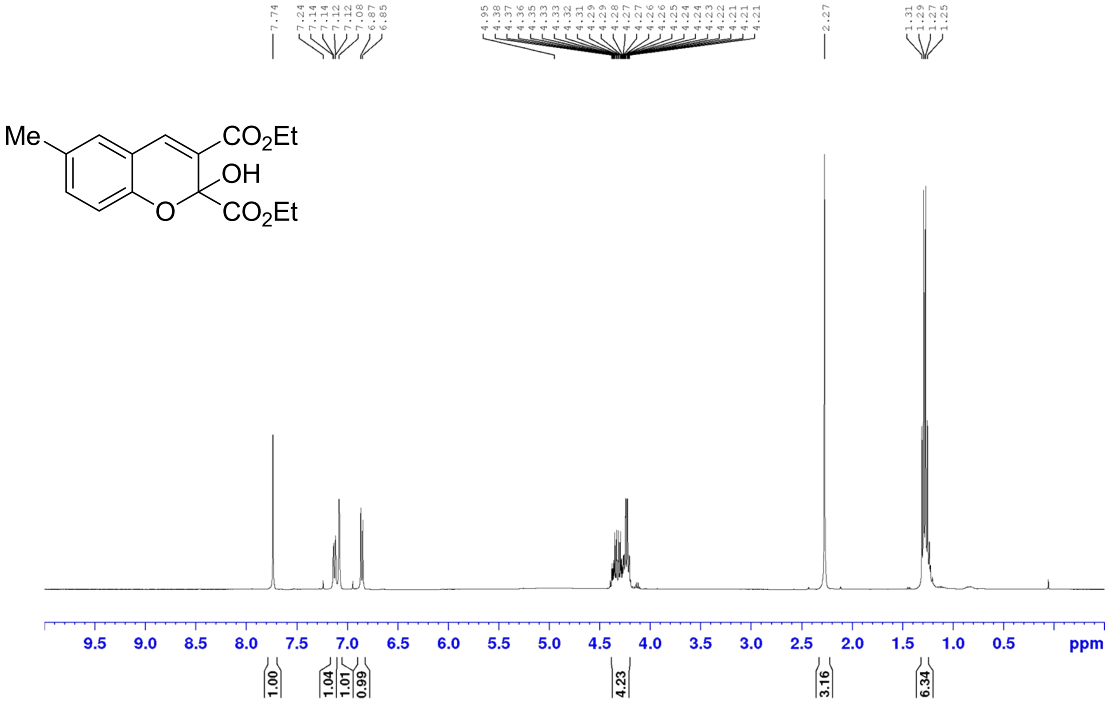


Fig. S7.15 NMR spectra of 2-hydroxy-6-nitro-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (**3eb**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

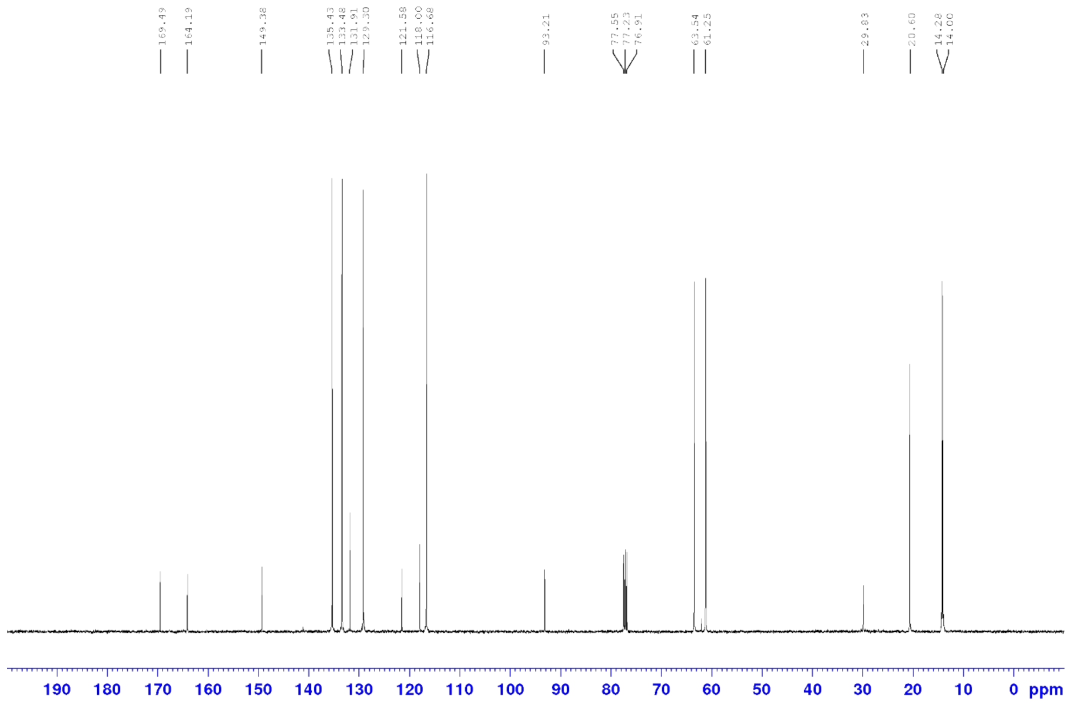
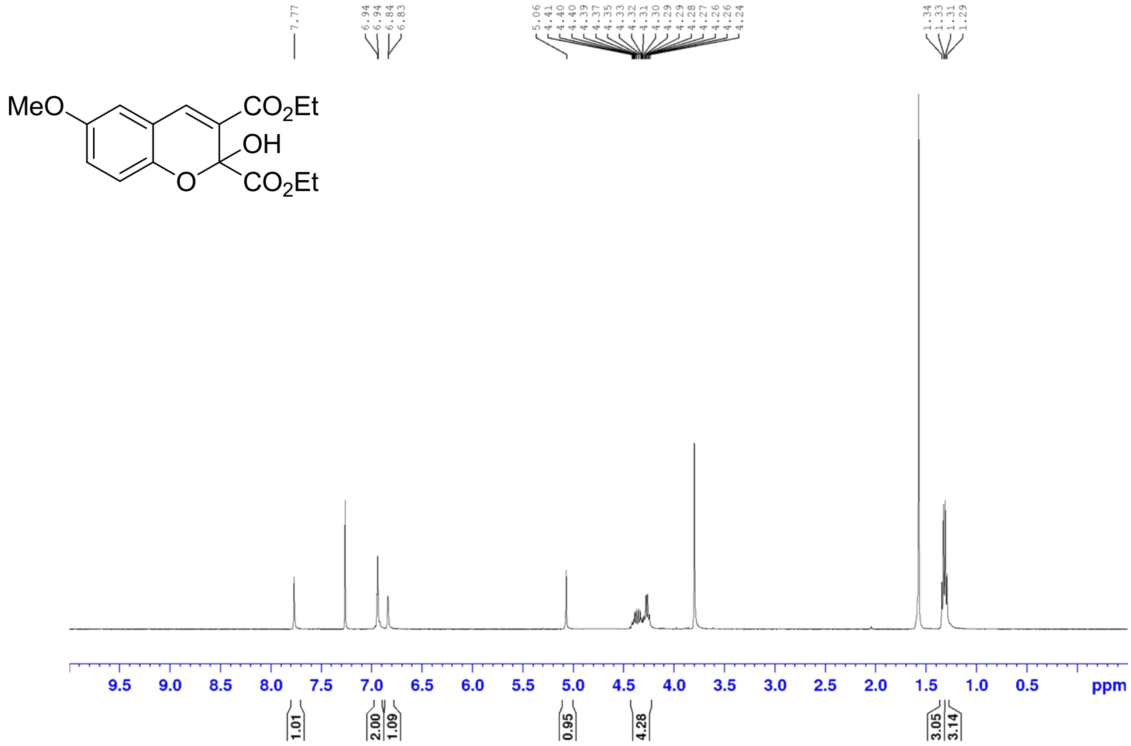


Fig. S7.16 NMR spectra of 2-hydroxy-6-methyl-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (**3fb**)

[1]H NMR with $CDCl_3$, 400 MHz



[13]C NMR with $CDCl_3$, 100 MHz

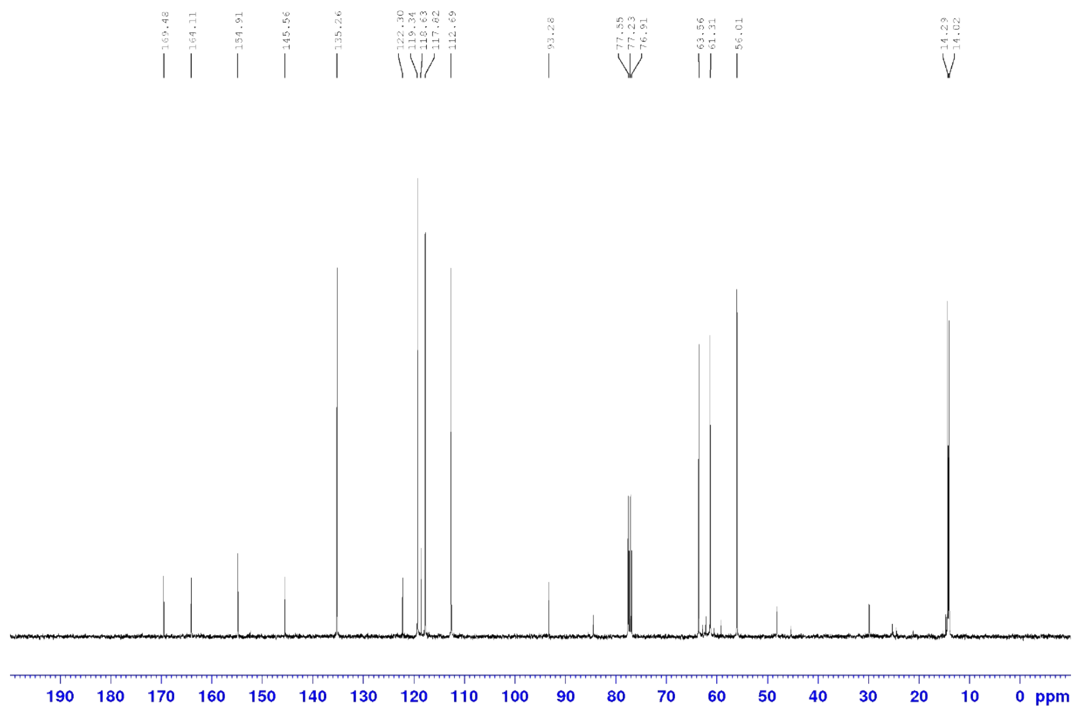
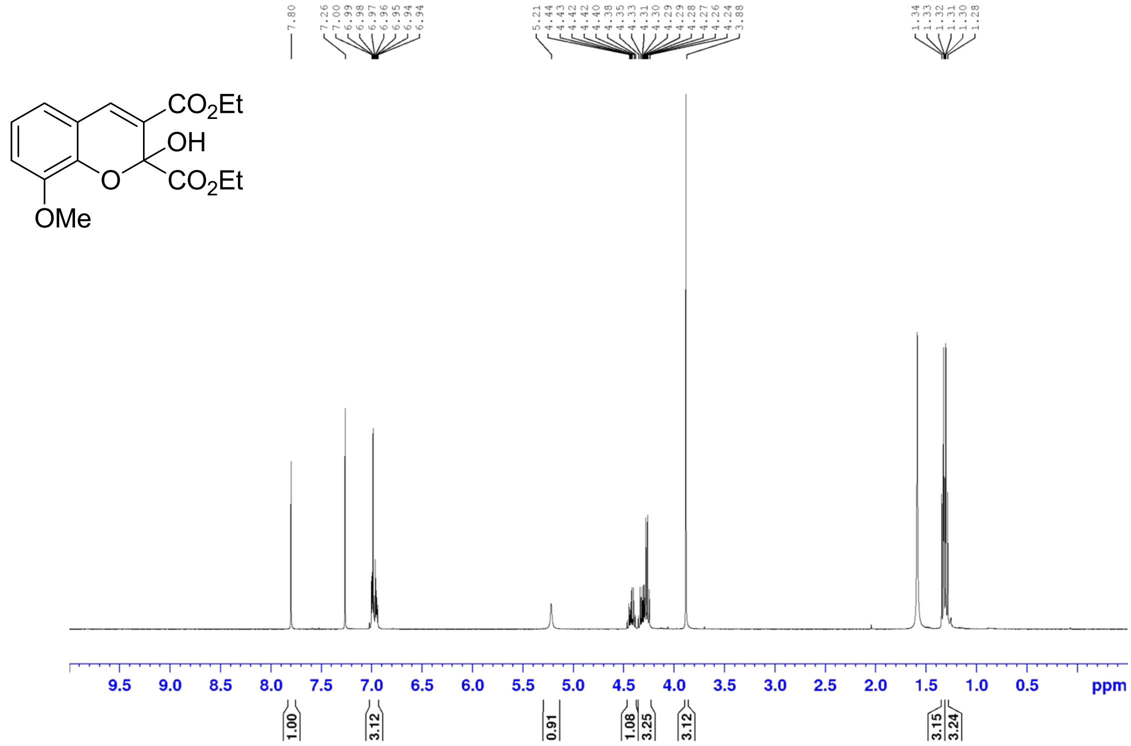


Fig. S7.17 NMR spectra of 2-hydroxy-6-methyoxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (**3gb**)

^1H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

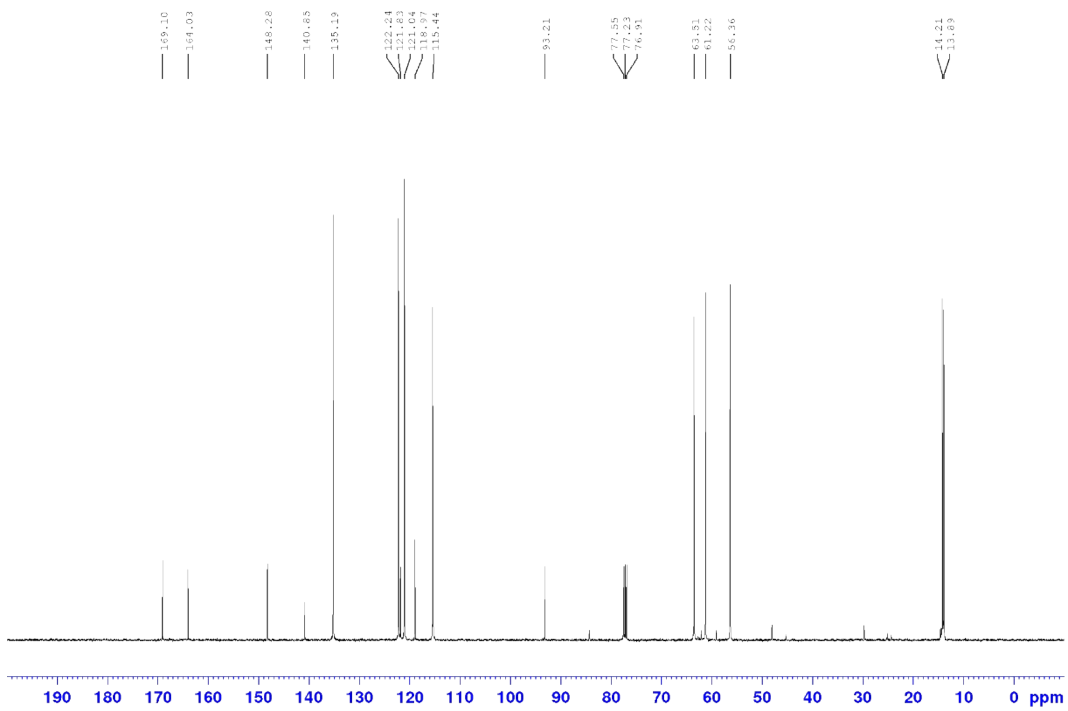
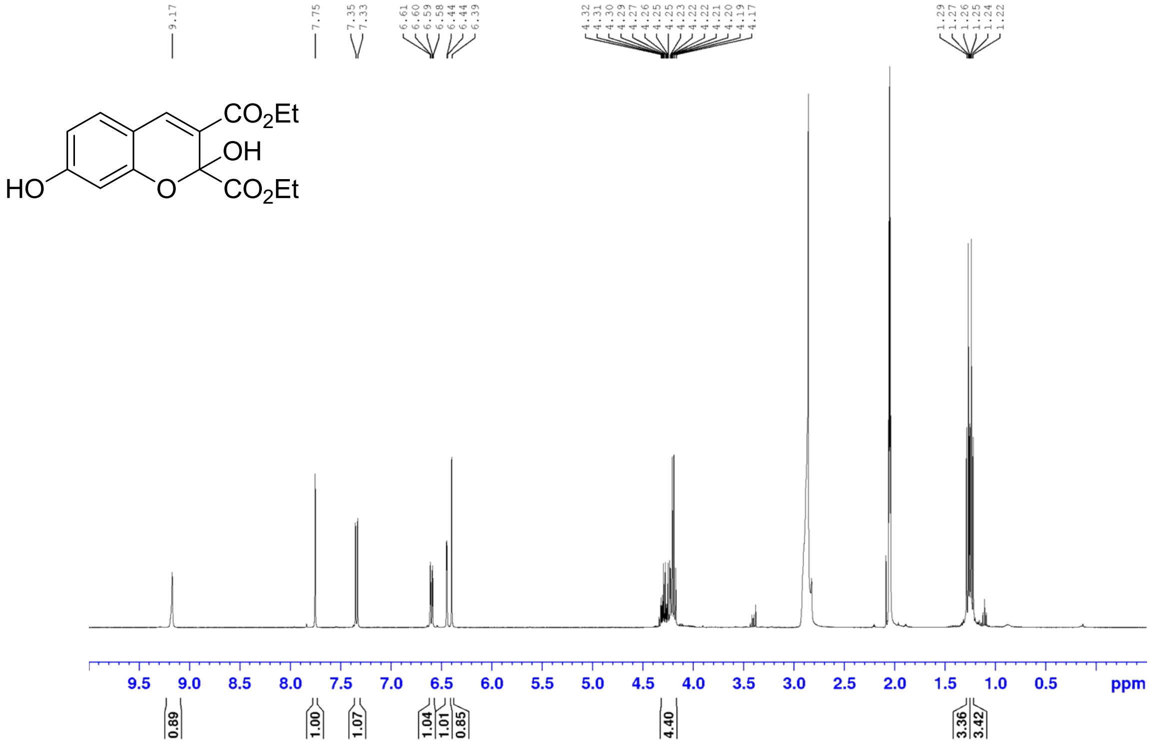


Fig. S7.18 NMR spectra of 2-hydroxy-8-methyoxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (**3hb**)

^{1}H NMR with acetone-d_6, 400 MHz



^{13}C NMR with acetone-d_6, 100 MHz

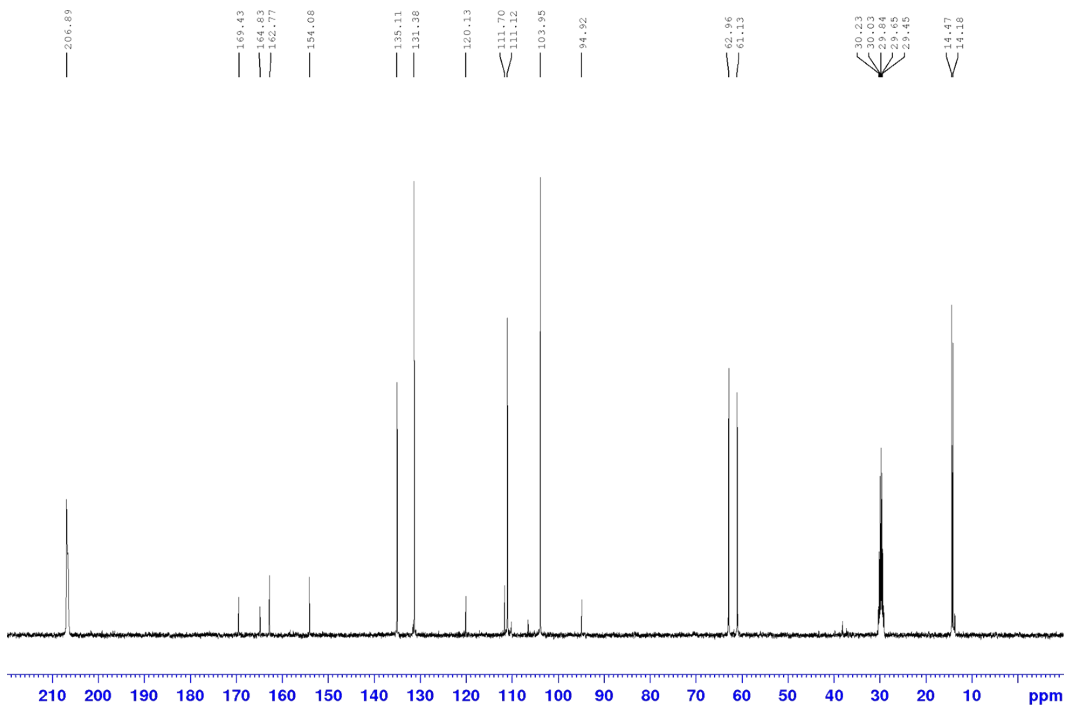
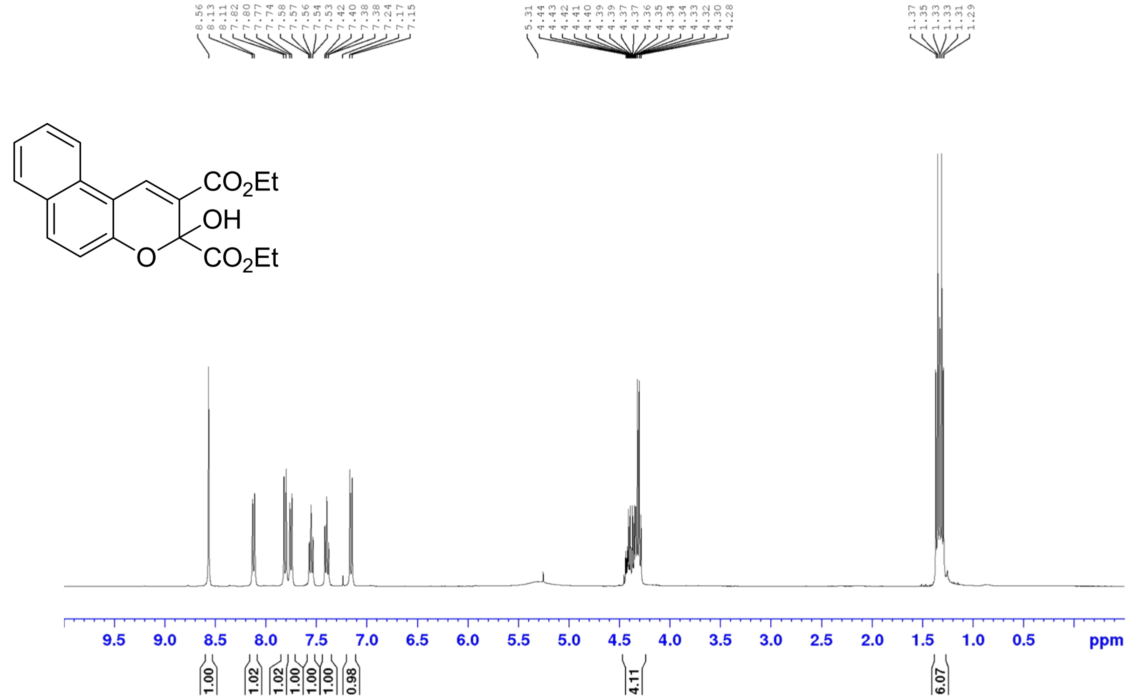


Fig. S7.19 NMR spectra of 2,7-dihydroxy-2*H*-chromene-2,3-dicarboxylic acid diethyl ester (**3ib**)

^{1}H NMR with $CDCl_3$, 400 MHz



^{13}C NMR with $CDCl_3$, 100 MHz

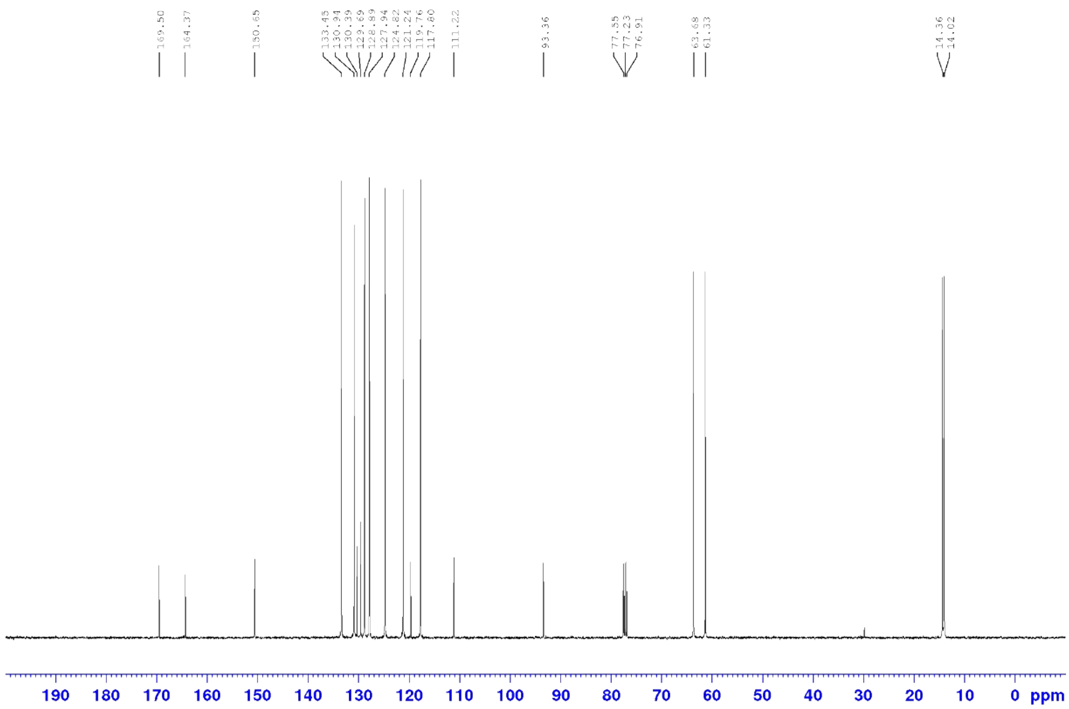


Fig. S7.20 NMR spectra of 3-hydroxy-3*H*-benzo[*f*]chromene-2,3-dicarboxylic acid diethyl ester (**3jb**)

References

[1] (a) R. Dawson, L. A. Stevens, T. C. Drage, C. E. Snape, M. W. Smith, D. J. Adams and A. I. Cooper, Impact of Water Coadsorption for Carbon Dioxide Capture in Microporous Polymer Sorbents, Journal of the American Chemical Society, 2012, 134, 10741-10744; (b) C. Wilson, M. J. Main, N. J. Cooper, M. E. Briggs, A. I. Cooper and D. J. Adams, Swellable functional hypercrosslinked polymer networks for the uptake of chemical warfare agents, Polymer Chemistry, 2017, 8, 1914–1922.

[2] S. Somprasong, W. Prasitwatcharakorn, T. Luanphaisarnnont, *Tetrahedron Lett.* **2020**, 61, 152402.

[3] N. Noshiranzadeh, A. Ramazani, *Synth. Commun.* **2007**, 37, 3181–3189.

[4] a) D. A. Singleton, A. A. Thomas, *J. Am. Chem. Soc.* **1995**, 117, 9357–9758; b) D. E. Frantz, D. A. Singleton, J. P. Snyder, *J. Am. Chem. Soc.* **1997**, 119, 3383–3384; c) M. J. Vetticatt, D. A. Singleton, *Org. Lett.* **2012**, 14, 9, 2370–2373; d) S. Xiang, M. P. A. Mayer, *J. Am. Chem. Soc.* **2014**, 136, 16, 5832–5835; e) D. E. Frantz, D. A. Singleton, *J. Am. Chem. Soc.* **2000**, 122, 3288–3295.