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Synthesis of 7-Hydroxydibenzopyran-6-ones via Benzannulation of Coumarins

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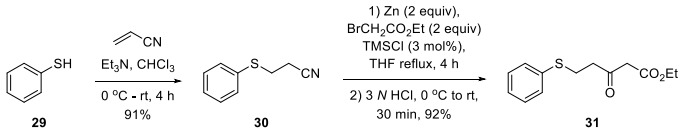
Experimental section

The solvents were dried according to standard procedures.[1] All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Column chromatography was carried on silica gel (100-200 mesh, AVRA Synthesis Private Limited) using increasing percentage of ethyl acetate in hexanes. The melting points were determined on a BUCHI M-560 equipment using open-ended capillary tubes. IR spectra were recorded as KBr pellets on a Nicolet-6700 spectrometer. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and DEPT-135 spectra were recorded for ($CDCl_3$ or 1:1 mixture of $CDCl_3$ and CCl_4, or DMSO- d_6) solutions on Bruker – Avance 400 MHz spectrometer with tetramethylsilane (TMS) as the internal standard; *J*-values are in Hz. ^{1}H NMR are reported as follows: chemical shift (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet and br s = broad singlet), coupling constant (*J*) and integrations). The ^{13}C NMR spectra were recorded with broad-band ^{1}H decoupling. The DEPT-135 NMR spectra were recorded for each sample to support assigned structure. ^{19}F NMR spectra were recorded on Bruker-400 (376 MHz) spectrometer with $CFCl_3$ as the external standard. High-resolution mass spectra were recorded on a Water Q-TOF micro mass spectrometer and Agilent 6350 B Q-TOF mass spectrometer using electro spray ionization mode. The microwave (MW) promoted reactions were carried out using Anton-Paar monomode microwave reactor. Salicylaldehydes were purchased from Sigma Aldrich Chemicals Private Limited, except 2,4-dihydroxybenzaldehyde was synthesised by published procedure.[2] Boronic acids were purchased from AVRA Synthesis Private Limited. DDQ, triflic anhydride and Pd catalysts were purchased from AVRA Synthesis Private Limited. The β-keto esters **31** were prepared by following our published procedure.[3]

Blaise reaction: Synthesis of Ethyl 3-oxo-5-(phenylthio)pentanoate **31**

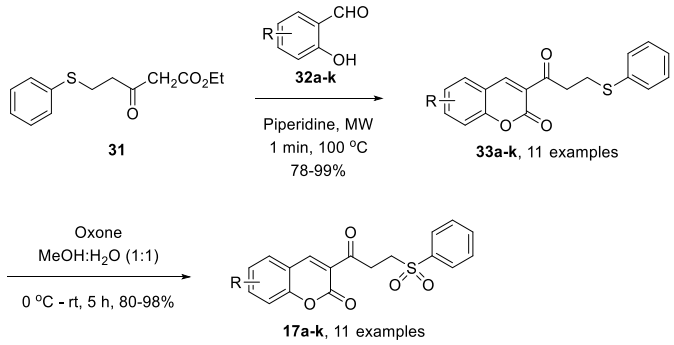


Scheme 1. Synthesis of β-keto ester **31**.

Zn (678 mg, 6.13 mmol, 2 equiv) and 3 mL of THF was placed in a three necked round bottomed flask. To this suspension, trimethylsilyl chloride (24 mg, 3 mol%) was added and refluxed for 25 minutes. To this activated Zn, THF solutions of 3-(phenylthio)propanenitrile **30** (502 mg, 6.13 mmol, 2 equiv) in 3mL THF and ethyl bromoacetate (1.25 g, 6.13 mmol, 2 equiv) in 3 mL of THF were added simultaneously to above activated Zn by using with two syringes about 25 minutes. The reaction was monitored by thin layer chromatography (TLC)

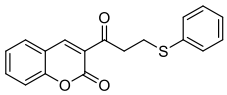
by using silica gel and hexanes/ethyl (9:1) acetate as eluent. After 4 h reflux, both the starting materials were completely absent and the reaction mixture was cooled to room temperature and under centrifuged to separate the Zn. THF solution was cooled to 0 ^{o}C and acidified with 3 *N* HCl and pH was adjusted to and stirred for 30 minutes at room temperature and extracted with 2 X 20 mL of DCM and organic layer was washed with 2 X 10 mL of water, 20 mL of brine and dried over anhydrous Na_2SO_4. DCM was removed by using a rotary evaporator to get the crude product and which was subjected to column chromatography by using hexanes/ethyl acetate (9:1) to provide **31** yellow colour liquid. Rf = 0.5 (hexanes/ EtOAc 9:1); IR (KBr) Data (ν): 3459, 3332, 2981, 2933, 1741, 1716, 1562, 1481, 1164, 1025, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$+CCl_4) 7.34 - 7.13 (m, 5H), 4.15 (q, *J* = 6.9 Hz, 2H), 3.35 (s, 2H), 3.1 (t, *J* = 6.9Hz, 2H), 2.83 (t, *J* = 6.9 Hz, 2H), 1.25 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+CCl_4) 200.1, 166.5, 129.5, 128.9, 126.2, 96.1, 61.1, 49.1, 42.4, 27.1, 14.1 ppm.

Synthesis of 3-acylcoumarins



Scheme 2. Synthesis of 3-acylcoumarins from β-keto ester and 2-hydroxy benzaldehydes

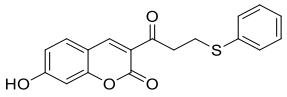
Representative procedure for synthesis of chromen-2-ones: **3-(3-(Phenylthio)propanoyl)-2*H*-chromen-2-one 33a**.



To ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol) taken in a conical flask, 2-hydroxybenzaldehyde **32a** (242 mg, 1.98 mmol, 1.0 equiv) and a catalytic amount of piperidine (33 mg, 20 mol%) were added. Resulting viscous liquid was exposed to MW at 100 ^{o}C for 2 min by which time the condensation was complete (TLC). The crude reaction mixture was dissolved in 10 mL of dichloromethane (DCM) and the resulting solution was washed with 10 mL of water, 10 mL of brine. The organic solution was dried over anhydrous Na_2SO_4 and then the solvent was removed under reduced pressure by using a rotary evaporator to get the crude product as a brown solid. The crude solid was recrystallized by using a mixture of methanol and DCM (9:1) to get crystalline colourless product **33a** in 92% yield (572 mg). Rf = 0.5

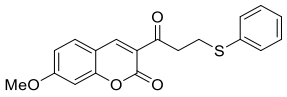
(hexanes: EtOAc 9:1); Mp: 133 - 134 ºC; IR (KBr) (ν): 3072, 2985, 1610, 1512, 1438, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.65-7.58 (m, 2H), 7.36-7.28 (m, 4H), 7.26-7.21 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 3.44 (t, *J* = 7.0 Hz, 2H), 3.24 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 159.0, 155.5, 147.7, 136.0, 134.5, 130.4, 129.9, 129.1, 126.4, 125.0, 124.4, 118.5, 116.8, 42.5, 28.2. HRMS (ESI): m/z calcd for $C_{18}H_{14}O_3SNa$ [M+Na] 333.0561 found, 333.0562

7-Hydroxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 33b.



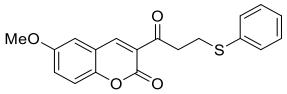
Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 2,4-dihydroxybenzaldehyde **32b** (273 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 7-hydroxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33b** as a yellow coloured solid in 85% yield (550 mg). Rf = 0.4 (hexanes: EtOAc 1:1); Mp: 218 - 219 ºC; IR (KBr) (ν): 3346, 3047, 1697, 1614, 1545, 1443, 1297, 1165 cm^{-1}; ^1H NMR (400 MHz, DMSO- d_6) δ 8.53 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.75 (t, *J* = 8.4 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 2H), 6.84 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.74 (d, *J* = 1.7 Hz, 1H), 3.60 (t, *J* = 7.0 Hz, 2H), 3.37 (t, *J* = 7.1 Hz, 2H).; ^{13}C NMR (100 MHz, DMSO- d_6) δ 192.7, 164.4, 159.0, 157.2, 148.47, 138.6, 133.9, 132.8, 129.4, 127.6, 117.9, 114.3, 110.7, 101.7, 49.8, 34.8. HRMS (ESI): m/z calcd for $C_{18}H_{14}O_4SNa$ [M+Na] 349.0510, found 349.0509.

7-Methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 33c.



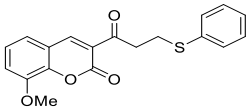
Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 2-hydroxy-4-methoxybenzaldehyde **32c** (300 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 7-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33c** as a light yellow solid in 98% yield (663 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 139 - 142 ºC; IR (KBr) (ν): 3052, 1735, 1683, 1548, 1350, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.27 (m, 2H), 7.17 (dt, *J* = 9.2, 4.3 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 3.91 (s, 3H), 3.48 (t, *J* = 7.1 Hz, 2H), 3.28 (t, *J* = 7.0 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 165.4, 159.5, 157.7, 148.2, 136.1, 131.5, 129.4, 128.9, 126.1, 120.0, 113.9, 112.0, 100.2, 56.0, 42.3, 27.9. HRMS (ESI): m/z calcd for $C_{19}H_{16}O_4SNa$ [M+Na] 363.0667, found, 363.0665.

6-Methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 33d.



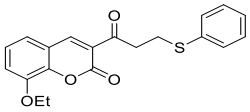
Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 2-hydroxy-5-methoxybenzaldehyde **32d** (301 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 6-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33d** as a yellow solid in 96% yield (650 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 143 - 145 ºC; IR (KBr) (ν): 2936, 1715, 1675, 1567, 737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.35 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.27 (dd, *J* = 12.2, 4.8 Hz, 3H), 7.22 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.19-7.13 (m, 1H), 7.02 (d, *J* = 2.8 Hz, 1H), 3.85 (s, 3H), 3.48 (t, *J* = 7.0 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 159.2, 156.4, 149.9, 147.7, 136.0, 129.6, 129.0, 126.3, 124.2, 123.1, 118.5, 117.8, 111.2, 56.0, 42.5, 28.0. HRMS (ESI): m/z calcd for $C_{19}H_{16}O_4S$ [M+H] 341.0769, found, 341.0813.

8-Methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 33e.



Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 2-hydroxy-3-methoxybenzaldehyde **32e** (301 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 8-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33e** as a yellow solid in 96% yield (650 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 143 - 145 ºC; IR (KBr) (ν): 2936, 1715, 1675, 1567, 1490, 737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.35 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.27 (dd, *J* = 12.2, 4.8 Hz, 3H), 7.22 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.19-7.13 (m, 1H), 7.02 (d, *J* = 2.8 Hz, 1H), 3.85 (s, 3H), 3.48 (t, *J* = 7.0 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 158.5, 148.1, 147.0, 144.9, 135.9, 129.5, 128.9, 126.2, 124.9, 124.1, 121.3, 118.8, 116.0, 56.3, 42.4, 27.9. HRMS (ESI): m/z calcd for $C_{19}H_{16}O_4S$ [M+H] 341.0769, found, 341.1002.

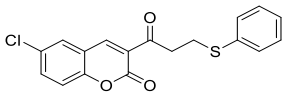
8-Ethoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 33f.



Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 3-ethoxy-2-hydroxybenzaldehyde **32f** (330 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 8-ethoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33f** as a yellow coloured solid in 99% yield (697 mg). Rf = 0.48 (hexanes: EtOAc 9:1); Mp: 173 - 174 ºC; IR (KBr) (ν): 2978, 1732, 1470, 1282, 1111, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.36 (dd,

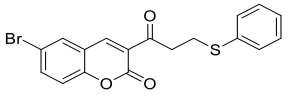
J = 8.2, 1.0 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.13 (m, 3H), 4.19 (q, *J* = 7.0 Hz, 2H), 3.49 (t, *J* = 6.9 Hz, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 1.51 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 158.7, 148.1, 146.4, 145.1, 136.0, 129.6, 129.0, 126.3, 124.9, 124.1, 121.3, 118.9, 117.3, 65.1, 42.4, 28.0, 14.7. HRMS (ESI): m/z calcd for $C_{20}H_{18}O_4SNa$ [M+Na] 377.0823, found, 377.0821.

6-Chloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 33g.



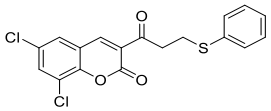
Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 2-hydroxy-5-chlorobenzaldehyde **32g** (317 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 6-chloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33g** as a yellow coloured solid in 97% yield (670 mg). Rf = 0.53 (hexanes: EtOAc 9:1); Mp: 143 - 144 ºC; IR (KBr) (ν): 3051, 1736, 1686, 1512, 1180, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.77 (d, *J* = 2.3 Hz, 1H), 7.72 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.36 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.28 (dd, *J* = 5.8, 4.4 Hz, 2H), 7.25 (d, *J* = 6.1 Hz, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 3.48 (t, *J* = 6.9 Hz, 2H), 3.28 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 158.3, 153.8, 146.4, 135.8, 134.3, 130.3, 129.6, 129.1, 128.9, 126.3, 125.0, 119.1, 42.4, 27.9. HRMS (ESI): m/z calcd for $C_{18}H_{13}ClO_3SNa$ [M+Na] 367.0172, found, 367.0172.

6-Bromo-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 33h.



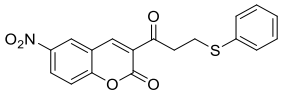
Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 2-hydroxy-5-bromobenzaldehyde **32h** (396 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 6-bromo-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33h** as a colourless solid in 98% yield (760 mg). Rf = 0.52 (hexanes: EtOAc 9:1); Mp: 153 - 155 ºC; IR (KBr) (ν): 3052, 1735, 1683, 1548, 1474, 1350, 1181, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.77 (d, *J* = 2.3 Hz, 1H), 7.72 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.36 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.20 – 7.15 (m, 1H), 3.48 (t, *J* = 6.9 Hz, 2H), 3.28 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 158.3, 153.8, 146.4, 135.8, 134.3, 130.3, 129.6, 129.1, 128.9, 126.3, 125.0, 119.1, 42.4, 27.9. HRMS (ESI): m/z calcd for $C_{18}H_{13}BrO_3SNa$ [M+Na] 410.9666, found, 410.9665.

6,8-Dichloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 33i.



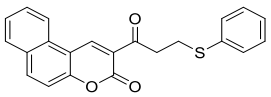
Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 2-hydroxy-3,5-dichlorobenzaldehyde **32i** (378 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 6,8-dichloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33i** as a yellow solid in 78% yield (590 mg). Rf = 0.6 (hexanes: EtOAc 9:1); Mp: 152 - 154 ºC; IR (KBr) (ν): 3064, 2918, 1754, 1677, 1604, 1553, 736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.46 (d, *J* = 2.4 Hz, 1H), 7.29-7.25 (m, 2H), 7.21-7.17 (m, 2H), 7.12-7.07 (m, 1H), 3.40 (t, *J* = 6.9 Hz, 2H), 3.19 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 157.4, 149.5, 146.2, 135.7, 134.2, 130.2, 129.8, 129.1, 127.8, 126.5, 125.6, 122.8, 120.0, 42.5, 27.9 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{12}Cl_2O_3S$ [M+H] 378.9884, found, 378.9901.

6-Nitro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one 33j.



Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 2-hydroxy-5-nitrobenzaldehyde **32j** (330 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 6-nitro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33j** as a light yellow solid in 88% yield (620 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 160 - 163 ºC; IR (KBr) (ν): 3059, 2919, 1751, 1688, 1616, 1351, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.5 Hz, 1H), 8.54 (s, 1H), 8.49 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.51 (d, *J* = 9.1 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 3.48 (t, *J* = 6.8 Hz, 2H), 3.29 (t, *J* = 6.8 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 158.3, 157.5, 146.4, 144.4, 135.7, 129.7, 129.1, 128.8, 126.5, 126.0, 125.9, 118.2, 118.0, 42.5, 27.9. HRMS (ESI): m/z calcd for $C_{18}H_{13}NO_5S$ [M+H] 356.0514, found, 356.05247.

2-(3-(Phenylthio)propanoyl)-3*H*-benzo[*f*]chromen-3-one 33k.

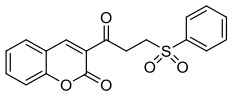


Reaction of ethyl 3-oxo-5-(phenylthio)pentanoate **31** (500 mg, 1.98 mmol), 2-hydroxy-1-naphthaldehyde **32k** (340 mg, 1.98 mmol, 1.0 equiv) and piperidine (33 mg, 20 mol%) afforded 2-(3-(phenylthio)propanoyl)-3*H*-benzo[*f*]chromen-3-one **33k** as a yellow solid in 92% yield (655 mg). Rf = 0.6 (hexanes: EtOAc 9:1); Mp: 158 - 159 ºC; IR (KBr) (ν): 2911, 1726, 1678, 1551, 737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.28 (d, *J* = 6.3 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.38

(d, *J* = 7.9 Hz, 3H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 3.54 (t, *J* = 6.8 Hz, 2H), 3.32 (t, *J* = 6.8 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 159.2, 156.1, 143.6, 136.5, 136.1, 130.2, 129.8, 129.6, 129.4, 129.3, 129.0, 126.7, 126.3, 121.9, 121.7, 116.5, 112.8, 42.5, 28.0. HRMS (ESI): m/z calcd for $C_{22}H_{16}O_3S$ [M+H] 361.0820, found, 361.0824.

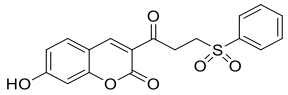
Representative procedure for oxidation of sulphide into sulfone:

3-(3-(Phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17a.



To the cooled (0 ^{o}C) and stirred solution of the coumarin **33a** (200 mg, 0.64 mmol, 1 equiv, turbid solution) in 1:1 mixture of MeOH and water (10 mL), oxone® (1.18 g, 1.93 mmol, 3 equiv) was added in four portions during 15 min. Resulting turbid reaction mixture was stirred for 1 h at 0 ^{o}C. Then the stirring was continued 3 h at rt by which time the oxidation was complete (TLC). Methanol was then removed under reduced pressure. Resulting crude reaction mixture was diluted with 10 mL DCM and 10 mL water. The aqueous layer was extracted with 3 x 20 mL of DCM. Organic layer was washed with 10 mL of water, 10 mL of brine and dried over anhydrous Na_2SO_4. DCM was removed under reduced pressure to afford the crude product. This crude product was recrystallized from methanol/DCM (9:1) to get the sulfone **17a** as white solid in 95% yield (209 mg). Rf = 0.5 (hexanes: EtOAc 3:1); Mp: 146 ^{o}C; IR (KBr) (ν): 3069, 1747, 1607, 1382, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.01-7.92 (m, 2H), 7.72-7.54 (m, 5H), 7.40-7.32 (m, 2H), 3.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 158.9, 155.3, 148.5, 138.8, 134.9, 133.9, 130.4, 129.4, 128.2, 125.2, 123.2, 118.0, 116.7, 50.8, 35.9. HRMS (ESI): m/z calcd for $C_{18}H_{14}O_5SNa$ [M+Na] 365.0460, found, 365.0460.

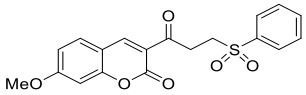
7-Hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17b.



Reaction of 7-hydroxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33b** (202 mg, 0.62 mmol), oxone® (1.13 g, 1.86 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 7-hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17b** as a yellow solid in 89% yield (194 mg). Rf = 0.4 (MeOH: DCM 9.5:0.5); Mp: 210 ^{o}C; IR (KBr) (ν): 3415, 2928, 1719, 1700, 1676, 1618, 739 cm^{-1}; ^{1}H NMR (400 MHz, DMSO- d_6) δ 11.16 (s, 1H) 8.48 (s, 1H), 7.88 (d, *J* = 7.0 Hz, 2H), 7.72-7.60 (m, 4H), 6.79 (dd, *J* = 7.0, 2.0 Hz, 1H), 6.67 (s, 1H), 3.52-3.33 (m, 4H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 192.5, 164.8, 158.9, 157.4, 148.7, 138.9, 133.7,

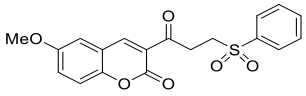
132.7, 132.6, 129.3, 127.7, 117.7, 114.4, 110.6, 101.8, 50.2, 35.0. HRMS (ESI): m/z calcd for $C_{18}H_{14}O_6SNa$ [M+Na] 381.0409 found, 381.0409.

7-Methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17c.



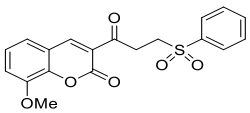
Reaction of 7-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33c** (202 mg, 0.58 mmol), oxone® (1.08 g, 1.74 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 7-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17c** as a yellow solid in 98% yield (213 mg). Rf = 0.6 (hexanes: EtOAc 3:1); Mp: 127-128 ºC; IR (KBr) (ν): 2928, 1719, 1700, 1676, 1618, 1149, 739 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.77-7.61 (m, 1H), 7.05-6.85 (m, 2H), 3.90 (s, 3H), 3.56 (t, *J* = 7.0 Hz, 2H), 3.38 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.5, 165.0, 158.6, 157.2, 148.3, 138.7, 133.6, 132.1, 129.2, 127.6, 118.9, 113.5, 111.6, 100.0, 56.1, 50.0, 34.9. HRMS (ESI): m/z calcd for $C_{19}H_{16}O_6SNa$ [M+Na] 395.0565, found, 395.0565.

6-Methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17d.



Reaction of 6-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33d** (202 mg, 0.58 mmol), oxone® (1.08 g, 1.74 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 6-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **17d** as a light yellow solid in 96% yield (210 mg). Rf = 0.5 (hexanes: EtOAc 8:2); Mp: 153 - 154 ºC; IR (KBr) (ν): 2935, 1724, 1683, 1560, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.00 – 7.94 (m, 2H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.04 (d, *J* = 2.8 Hz, 1H), 3.87 (s, 3H), 3.58 (t, *J* = 3.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 159.1, 156.4, 149.9, 148.3, 138.8, 133.9, 129.4, 128.2, 123.5, 123.3, 118.3, 117.8, 111.1, 55.9, 50.9, 36.0 ppm. HRMS (ESI): m/z calcd for $C_{19}H_{16}O_3S$ [M+H] 373.0668, found, 373.0659.

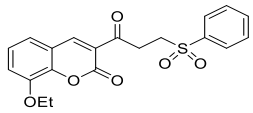
8-Methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17e.



Reaction of 8-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33e** (202 mg, 0.58 mmol), oxone® (1.08 g, 1.74 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 8-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **17e** as a yellow solid in 96% yield (210 mg). Rf = 0.45 (hexanes: EtOAc 8:2); Mp: 158 - 160 ºC; IR (KBr) (ν): 2935, 1724, 1683,

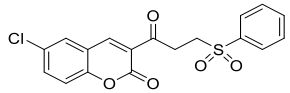
1560, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.98 – 7.94 (m, 2H), 7.67 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 1.2 Hz, 1H), 7.22 (s, 2H), 3.98 (s, 3H), 3.59 (dd, *J* = 4.4, 3.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 158.4, 148.7, 147.0, 144.9, 138.8, 133.9, 129.4, 129.3, 128.2, 125.0, 124.1, 123.3, 121.4, 118.6, 116.3, 56.3, 50.8, 35.9. HRMS (ESI): m/z calcd for $C_{19}H_{16}O_3S$ [M+H] 373.0668, found, 373.0660.

8-Ethoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17f.



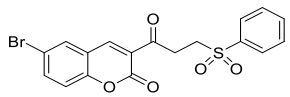
Reaction of 8-ethoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33f** (204 mg, 0.57 mmol), oxone® (1.04 g, 1.71 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 8-ethoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17f** as a yellow coloured solid in 99% yield (217 mg). Rf = 0.5 (hexanes: EtOAc 3:1); Mp: 219 ºC; IR (KBr) (ν): 2928, 1719, 1700, 1676, 1618, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.95 (t, *J* = 11.8 Hz, 2H), 7.68 – 7.52 (m, 3H), 7.26 – 7.14 (m, 3H), 4.18 (dd, *J* = 15.2, 8.6 Hz, 2H), 3.56 (d, *J* = 23.4 Hz, 4H), 1.55 – 1.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 158.7, 148.1, 146.4, 145.1, 136.0, 129.6, 129.0, 126.3, 124.9, 124.1, 121.3, 118.9, 117.3, 65.1, 42.4, 28.0, 14.7. HRMS (ESI): m/z calcd for $C_{20}H_{18}O_6S$ [M+H] 387.0824, found, 387.08752.

6-Chloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17g.



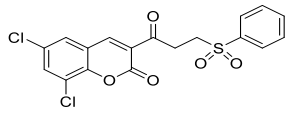
Reaction of 6-chloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33g** (202 mg,0.58 mmol), Oxone® (1.07 g, 1.74 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 6-chloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17g** as a colourless solid in 99% yield (215 mg). Rf = 0.55 (hexanes: EtOAc 3:1); Mp: 210 ºC; IR (KBr) (ν): 3053, 1735, 1685, 1556, 739 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.48 (s, 1H), 7.96-7.86 (m, 2H), 7.65 (dt, *J* = 14.0, 7.3 Hz, 4H), 6.78 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.67 (d, *J* = 1.4 Hz, 1H), 3.51 (t, J = 7.2 Hz, 2H), 3.37-3.33 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.5, 164.8, 158.9, 157.4, 148.7, 138.9, 133.7, 132.6, 129.3, 127.7, 117.7, 114.4, 110.6, 101.8, 50.2, 35.0. HRMS (ESI): m/z calcd for $C_{18}H_{13}ClO_5SNa$ [M+Na] 399.0070, found, 399.0071.

6-Bromo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17h.



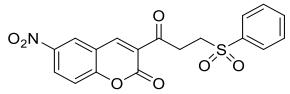
Reaction of 6-bromo-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33h** (201 mg, 0.51 mmol), oxone® (947 mg, 1.53 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 6-bromo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17h** as a colourless solid in 99% yield (214 mg). Rf = 0.55 (hexanes: EtOAc 3:1); Mp: 165 ºC; IR (KBr) (ν): 2928, 1719, 1700, 1676, 1618, 739 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (s, 1H), 8.16 (d, *J* = 1.6 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.83 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 1H), 3.57 (t, *J* = 7.1 Hz, 2H), 3.41 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.7, 157.6, 153.5, 146.4, 138.7, 136.7, 133.6, 132.6, 129.2, 127.6, 124.1, 119.7, 118.2, 116.4, 49.8, 34.9. HRMS (ESI): m/z calcd for $C_{18}H_{13}BrO_5SNa$ [M+Na] 442.9565, found, 442.9562.

6,8-Dichloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17i.



Reaction of 6,8-dichloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33i** (200 mg, 0.53 mmol), oxone® (0.97 g, 1.58 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 6,8-dichloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17i** as a light yellow solid in 92% yield (200 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 126 ºC; IR (KBr) (ν): 2976, 1751, 1688, 1607, 737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 5.6 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.69 – 7.65 (m, 1H), 7.64 – 7.49 (m, 4H), 3.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 157.4, 149.5, 146.2, 135.7, 134.2, 130.2, 129.8, 129.1, 127.8, 126.5, 125.6, 122.8, 120.0, 42.5, 27.9 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{12}O_5S$ [M+H] 410.9782, found, 410.9865.

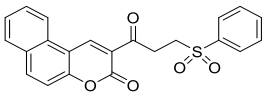
6-Nitro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17j.



Reaction of 6-nitro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33j** (201 mg, 0.56 mmol), oxone® (1.03 g, 1.69 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 6-nitro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17j** as a light yellow solid in 92% yield (200 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 171 - 173 ºC; IR (KBr) (ν): 2942, 1742, 1683, 1615, 1534, 1348, 788 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.5 Hz, 1H), 8.57 (s, 1H), 8.53 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 9.1 Hz, 1H), 3.59 (dt, *J* = 10.5, 5.2 Hz, 4H);^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 158.3, 157.4, 146.9, 144.4, 138.7, 134.0, 129.4, 129.0, 128.1, 126.0, 125.1,

118.1, 118.0, 50.7, 35.7 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{13}NO_7S$ [M+H] 388.0413, found, 388.0435.

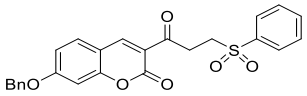
2-(3-(Phenylsulfonyl)propanoyl)-3*H*-benzo[*f*]chromen-3-one 17k.



Reaction of 2-(3-(phenylthio)propanoyl)-3*H*-benzo[*f*]chromen-3-one **33k** (200 mg, 0.55 mmol), oxone® (1.02 g, 1.66 mmol, 3 equiv), methanol (5 mL) and water (5 mL) afforded 2-(3-(phenylsulfonyl)propanoyl)-3*H*-benzo[*f*]chromen-3-one **17k** as a yellow solid in 96% yield (207 mg). Rf = 0.45 (hexanes: EtOAc 8:2); Mp: 199 - 201 ºC; IR (KBr) (ν): 3067, 2917, 1727, 1680, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 9.1 Hz, 1H), 8.00 – 7.91 (m, 3H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.62 (dt, *J* = 20.7, 7.3 Hz, 4H), 7.47 (d, *J* = 9.0 Hz, 1H), 3.63 (dd, *J* = 7.2, 4.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 159.2, 156.5, 144.3, 139.0, 137.1, 134.0, 130.4, 129.9, 129.6, 129.5, 129.4, 128.4, 126.9, 121.8, 121.3, 116.6, 112.9, 51.1, 36.2. HRMS (ESI): m/z calcd for $C_{22}H_{16}O_5S$ [M+H] 393.0718, found, 393.0785.

Conversion of the phenolic hydroxyl to benzyl ether

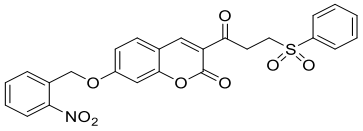
7-(Benzyloxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17l.



To the mixture of 7-hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17b** (200 mg, 0.55 mmol), benzyl bromide (114 mg, 0.67 mmol, 1.2 equiv), K_3PO_4 (178 mg, 0.83 mmol, 1.5 equiv) and TBAB (90 mg, 0.27 mmol, 0.5 equiv) taken in a 25 mL rb flask, 5 mL of water was added. Resulting reaction mixture was stirred at open atm for 30 minutes by which time benzyl ether formation was complete (TLC). The reaction mixture was diluted with 20 mL of DCM. The DCM solution washed with water (10 mL) followed by brine (10 mL) and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure to afford the crude product. Trituration with hexane to afforded 7-(benzyloxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17l** as a white solid in 96% yield (237 mg) Rf = 0.5 (hexanes: EtOAc 7:3); Mp: 168 - 170 ºC; IR (KBr) (ν): 2923, 1726, 1677, 1616, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.95 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.68 – 7.63 (m, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.42 (s, 2H), 7.41 (d, *J* = 2.9 Hz, 2H), 6.97 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.88 (d, *J* = 2.2 Hz, 1H), 5.16 (s, 2H), 3.56 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 164.8, 159.5, 157.8, 148.7, 138.9, 135.2, 133.9, 131.9, 129.4, 128.9, 128.7, 128.3, 127.6, 119.4,

114.8, 112.1, 101.4, 71.0, 51.0, 36.0. HRMS (ESI): m/z calcd for $C_{25}H_{20}O_6S$ [M+H] 449.0981, found, 449.0813.

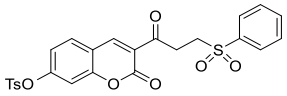
7-((2-Nitrobenzyl)oxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one 17m.



By following the general procedure described above, the reaction of 7-hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17b** (200 mg, 0.55 mmol) with 2-nitrobenzylbromide (144 mg, 0.67 mmol, 1.2 equiv) in the presence of K_3PO_4 (178 mg, 0.83 mmol, 1.5 equiv) and TBAB (90 mg, 0.27 mmol, 0.5 equiv) afforded 7-((2-nitrobenzyl)oxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17m** as a light yellow solid in 90% yield (245 mg) Rf = 0.5 (hexanes: EtOAc 7:3); Mp: 188 ºC; IR (KBr) (ν): 2923, 1731, 1683, 1626, 1550, 1336, 1305, 1148, 1026, 761 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 8.61 (s, 1H), 8.16 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.92 (dd, *J* = 5.6, 2.9 Hz, 3H), 7.81 – 7.73 (m, 3H), 7.67 (t, *J* = 7.5 Hz, 3H), 7.19 (d, *J* = 2.2 Hz, 1H), 7.11 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.63 (s, 2H), 3.63 (t, *J* = 7.3 Hz, 2H), 3.39 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.9, 163.4, 158.7, 156.9, 148.1, 147.5, 138.7, 134.1, 133.9, 132.5, 131.3, 129.5, 129.3, 127.7, 125.0, 119.7, 113.9, 112.3, 101.2, 67.3, 49.8, 34.9 ppm. HRMS (ESI): m/z calcd for $C_{25}H_{19}NO_8S$ [M+H] 494.0831, found, 494.0913.

Tosylation of the the phenolic hydroxyl group:

2-Oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl 4-methylbenzenesulfonate 17n.

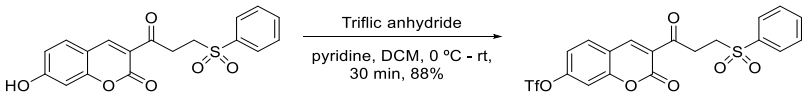


To the solution of 7-hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17b** (200 mg, 0.55 mmol) and NEt_3 (53 mg, 0.55 mmol, 1.0 equiv) in dry DCM (5 mL), *p*-tosylchloride (100 mg, 0.61 mmol, 1.2 equiv) in dry DCM (5 mL) was added at rt. Resulting solution was heated to reflux in an oil bath (bath tempt = 45 ºC) for 4 h by which time the tosylation was complete (TLC). The cooled reaction mixture was diluted with 10 mL of DCM and the solution was washed water (10 mL) followed by brine (10 mL). Then the solvent was evaporated under reduced pressure to obtain the crude solid. The solid was triturated with hexane to get pure product **17n** as a white solid in 94% yield (265 mg) Rf = 0.6 (hexanes: EtOAc 7:3); Mp: 166 ºC; IR (KBr) (ν): 3063, 2946, 1736, 1690, 1612, 1560, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.96 – 7.91 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.55 (m, 3H), 7.35 (dd, *J* = 8.6, 0.6 Hz, 2H), 7.09 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.96 (d, *J* = 2.3 Hz,

1H), 3.55 (s, 4H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 158.4, 155.9, 154.0, 147.6, 146.5, 138.9, 134.0, 131.8, 131.7, 130.3, 129.5, 128.5, 128.3, 123.2, 120.0, 116.9, 110.8, 50.9, 35.9, 21.9. HRMS (ESI): m/z calcd for $C_{25}H_{20}O_8S_2$ [M+H] 513.0600, found, 513.0668.

Trifluromethylsulfonylation of the phenolic hydroxyl group:

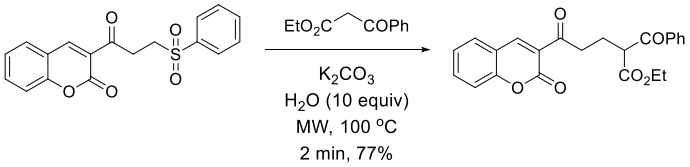
2-Oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl trifluoromethanesulfonate 17o.[4]



The cooled (0 ºC) solution of 7-hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17b** (200 mg, 0.55 mmol), dry pyridine (88 mg, 1.11 mmol, 2.0 equiv) in dry DCM (5 mL), triflic anhydride (190 mg, 0.67 mmol, 1.2 equiv) in 3 mL DCM was added drop-wise during 10 min. The reaction mixture was warmed to rt (35 ºC) during 30 min by which time conversion was complete (TLC). The reaction mixture was then diluted with 10 mL of DCM. To the cooled solution Na_2CO_3 (10 mg) was added to quench excess triflic acid. The DCM solution was then washed with water (10 mL) followed by brine (10 mL). Solvent was removed under reduced pressure after drying over anhydrous Na_2SO_4 to get the crude solid, which was triturated with hexanes (2 x 10 mL) to afford 2-oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl trifluoromethanesulfonate **17o** as a white solid in 88% yield (238 mg) Rf = 0.5 (Hexanes: EtOAc 7:3); Mp: 156 ºC; IR (KBr) (ν): 2985, 1743, 1694, 1611, 1425, 1234, 891 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.95 – 7.92 (m, 2H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 6.7 Hz, 2H), 7.32 (d, *J* = 2.2 Hz, 1H), 7.28 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.56 (d, *J* = 7.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 157.9, 155.8, 5152.8, 147.1, 138.8, 134.1, 132.3, 129.6, 128.2, 124.1, 120.3, 118.7 (q, *J* = 321 Hz), 118.0, 117.1, 114.9, 111.7, 110.5, 50.8, 35.9. HRMS (ESI): m/z calcd for $C_{19}H_{13}F_3O_8S_2$ [M+H] 491.0004, found, 491.0042.

Reaction of sulfone coumarin-sulfone and active methylene compunds

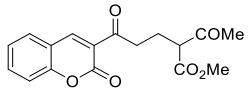
Ethyl-2-benzoyl-5-oxo-5-(2-oxo-2*H*-chromen-3-yl)pentanoate 22a.



In a conical flask 3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17a** (200 mg, 0.58 mmol, 1 equiv) was taken and added ethyl benzoylacetate **21a** (224 mg, 1.16 mmol, 1 equiv), K_2CO_3 (161 mg, 1.16 mmol, 2 equiv) and water (0.2 mL, 10 equiv). The reaction mixture was

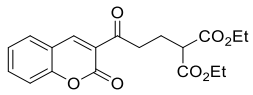
irradiated with microwaves at 100 ºC for 2 minutes. After absence sulfone coumarin, reaction mixture was dissolved in 10 mL of water and extracted with 2 x 10 mL of DCM. Organic layer was washed with 10 mL of brine and dried over anhydrous Na_2SO_4 to get crude product, which was subjected to column chromatography to purify by using silica gel (100 – 200 mesh) and hexane, ethyl acetate as eluent to furnish the pure product of ethyl-2-benzoyl-5-oxo-5-(2-oxo-2*H*-chromen-3-yl)pentanoate **22a** as a white solid in 77% yield (175 mg). Mp: 137 - 139 ºC, IR (KBr) Data (ν): 3059, 2981, 1732, 1728, 1685, 1610, 1560, 1448, 1179, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$+CCl_4) δ 8.48 (s, 1H), 8.05-8.00 (m, 2H), 7.66-7.61 (m, 2H), 7.57-7.52 (m, 1H), 7.50-7.44 (m, 2H), 7.33 (ddd, *J* = 8.5, 7.6, 3.8 Hz, 2H), 4.45 (dd, *J* = 7.9, 6.5 Hz, 1H), 4.14 (qd, *J* = 7.1, 3.7 Hz, 2H), 3.26 (td, *J* = 6.9, 1.9 Hz, 2H), 2.35 (ddd, *J* = 10.3, 6.9, 2.9 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$+CCl_4) δ 195.3, 194.4, 169.4, 158.5, 155.2, 147.2, 136.0, 134.1, 133.2, 130.0, 128.6, 128.5, 124.7, 124.2, 118.1, 116.5, 61.1, 52.8, 39.8, 22.8, 13.9. HRMS (ESI): m/z calcd for $C_{23}H_{20}O_6Na$ [M+Na] 415.1158, found, 415.1158

Methyl-2-acetyl-5-oxo-5-(2-oxo-2*H*-chromen-3-yl)pentanoate 22b.



Reaction of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17a** (202 mg, 0.58 mmol), methyl acetoactate **21b** (135 mg, 1.16 mmol, 1 equiv), K_2CO_3 (161 mg, 1.16, 1.equiv) and water (0.2 mL, 10 equiv) afforded methyl-2-acetyl-5-oxo-5-(2-oxo-2*H*-chromen-3-l)pentanoate **22b** as a white solid in 55% yield (101 mg). Mp. 123 - 124 ºC, IR (KBr) Data (ν): 2954, 1742, 1712, 1680, 1611, 1242, 1175, 763cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$+CCl_4) δ 8.48-8.44 (m, 1H), 7.63 (dd, *J* = 12.2, 4.6 Hz, 2H), 7.36-7.30 (m, 2H), 3.74 (s, 3H), 3.57-3.53 (m, 1H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$+CCl_4) δ 197.7, 179.1, 160.9, 153.1, 137.4, 131.7, 131.4, 128.3, 124.6, 118.7, 116.4, 105.3, 41.8, 32.3, 24.8, 21.0. HRMS (ESI): m/z calcd for $C_{17}H_{16}O_6Na$ [M+Na] 339.0845, found, 339.0844.

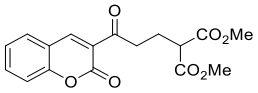
Diethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate 22c.



Reaction of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17a** (201mg, 0.58 mmol, 1 equiv) diethyl malanoate **21c** (187 mg, 1.16 mmol, 1 equiv), K_2CO_3 (161 mg, 1.16 mmol, 2 equiv) and water (0.2 mL, 10 equiv) afforded diethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate **22c** as a white solid in 49% yield (102 mg). Mp: 137 - 139 ºC, IR (KBr) Data (ν): 3059, 2981, 2246, 1732, 1728, 1685, 1610, 1560, 1448, 1179, 758 cm^{-1}; ^{1}H NMR

(400 MHz, $CDCl_3$+CCl_4) δ 8.48 (s, 1H), 8.05-8.00 (m, 2H), 7.66-7.61 (m, 2H), 7.57-7.52 (m, 1H), 7.50-7.44 (m, 2H), 7.33 (ddd, *J* = 8.5, 7.6, 3.8 Hz, 2H), 4.17 (m, 4H), 3.41 (q, *J* = 7.1, 1H), 3.26 (td, *J* = 6.9, 1.9 Hz, 2H), 2.27 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$+CCl_4) δ 195.6, 168.7, 158.5, 155.5, 147.5, 134.1, 130.0, 124.7, 124.1, 118.2, 116.5, 61.1, 50.6, 39.6, 22.6, 14.0. HRMS (ESI): m/z calcd for $C_{19}H_{20}O_7Na$ [M+Na] 383.1009, found, 383.1012.

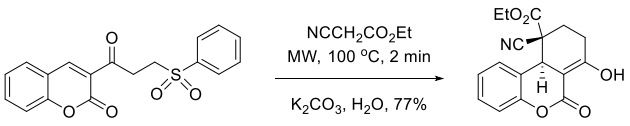
Dimethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate 22d.



Reaction of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17a** (201mg, 0.58 mmol), dimethyl malonate **21d** (154 mg, 1.16 mmol, 1.0 equiv), K_2CO_3 (161 mg, 1.16 mmol, 1.0 equiv) and water (0.2 mL, 10 equiv) afforded dimethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate **22d** as a white solid in 52% yield (101 mg). Rf = 0.5 (hexanes: EtOAc 8:2) Mp: 134 - 135 ºC, IR (KBr) Data (ν): 2921, 2848, 1702, 1638, 1344, 1225, 1113, 963, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 7.7, 6.9 Hz, 2H), 3.71 (s, 6H), 3.49 (t, *J* = 7.5 Hz, 1H), 3.19 (dd, *J* = 8.0, 6.2 Hz, 2H), 2.31 – 2.23 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 169.5, 159.0, 155.2, 147.7, 134.5, 130.2, 125.0, 124.0, 118.2, 116.6, 52.5, 50.4, 39.7, 22.8. HRMS (ESI): m/z calcd for $C_{17}H_{16}O_7$ [M+H] 333.0896, found, 333.0893.

Representative procedure for Michael addition-cyclization cascade

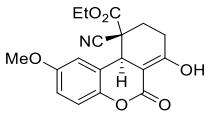
Ethyl 10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19a.



A 10 mL conical flask charged with an intimate mixture of the sulfone **17a** (200 mg, 0.5 mmol, 1 equiv), K_2CO_3 (162 mg, 1.16 mmol, 2 equiv), ethyl cyanoacetate (132 mg, 1.1 mmol, 2 equiv) and water (0.2 mL, 10 equiv) was placed in a MW oven and irradiated with microwaves at 100 ºC for 2 minutes by which time TLC indicated that the sulfone was consumed. The crude reaction mixture was diluted with 10 mL of DCM. The DCM layer was washed with 10 mL of water, 10 mL brine, and dried over anhydrous Na_2SO_4. The organic solvent was removed under reduced pressure to get the crude product. A column chromatographic purification using silica gel (100-200 mesh) and eluting with increasing amount of ethyl acetate in Hexanes (5 to 25%) furnished analytically pure product **19a** as a white solid in 77% yield (142 mg). Rf = 0.4

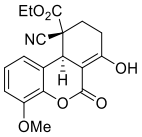
(hexanes: EtOAc 8:2); Mp: 126-128 ºC; IR (KBr) (ν): 3450, 2982, 2247, 1737, 1680, 1607, 1229, 855, 754 cm $^{-1;}$ ^{1}H NMR (400 MHz, CDCl3) δ 12.86 (s, 1H), 7.36 – 7.30 (m, 1H), 7.17 (td, *J* = 7.7, 1.1 Hz, 1H), 7.12 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 4.63 (s, 1H), 4.46 (m, 2H), 2.95 (m, 1H), 2.70 – 2.61 (m, 1H), 2.52 – 2.45 (m, 1H), 2.38 (m, 1H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 168.7, 168.5, 150.6, 129.5, 125.3, 125.2, 120.1, 117.9, 116.1, 91.2, 64.1, 46.9, 38.7, 30.8, 26.2, 14.0. HRMS (ESI): m/z calcd for $C_{17}H_{15}NO_5Na$ [M+H] 314.0150, found, 314.1025.

Ethyl 10-cyano-7-hydroxy-2-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19d.



Reaction of 6-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17d** (201 mg, 0.53 mmol), ethyl cyanoacetate (121 mg, 1.07 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (148 mg, 1.07 mmol, 2 equiv) afforded ethyl 10-cyano-7-hydroxy-2-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19d** as a yellow solid in 72% yield (133 mg). Rf = 0.5 (hexanes: EtOAc 8:2); Mp: 156-158 ºC; IR (KBr) (ν): 3438, 3074, 2971, 2249, 1728, 1690, 1603, 1503, 1259, 1200, 850 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.92 (s, 1H), 7.03 (d, *J* = 8.88 Hz, 1H), 6.83 (m, 1H), 6.55 (m, 1H), 4.58 (d, *J* = 1.4 Hz, 1H), 4.46 (m, 2H), 3.75 (s, 3H), 2.92 (d, *J* = 2.76 Hz, 1H), 2.65 (m, 1H), 2.44 (m, 1H), 2.40 (m, 1H), 1.44 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 168.8, 156.7, 144.4, 120.9, 118.5, 116.0, 113.9, 111.5, 91.1, 64.1, 55.7, 47.0, 39.0, 30.9, 26.2, 14.0. HRMS (ESI): m/z calcd for $C_{18}H_{17}NO_6$ [M+H] 344.1108, found, 344.1151.

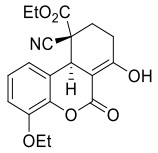
Ethyl 10-cyano-7-hydroxy-4-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19e.



Reaction of 8-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17e** (200 mg, 0.58 mmol), ethyl cyanoacetate (121 mg, 1.07 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (148 mg, 1.07 mmol, 2 equiv) afforded ethyl 10-cyano-7-hydroxy-4-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19e** as a light yellow solid in 75% yield (138 mg). Rf = 0.5 (hexanes: EtOAc 8:2); Mp: 152 ºC; IR (KBr) (ν): 3441, 2978, 2942, 2250, 1734, 1685, 1605, 1177, 833 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 12.83 (s, 1H), 7.12 (t, *J* = 8.16 Hz,

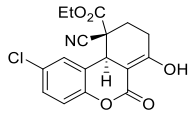
1H), 6.93 (d, *J* = 8.28 Hz, 1H), 6.60 (m, 1H), 4.62 (d, *J* = 1.64, 1H), 4.46 (m, 2H), 3.88 (s, 3H), 2.94 (d, *J* = 2.76, 1H), 2.66 (m, 1H), 2.45 (m, 1H), 2.40 (m, 1H), 1.43 (t, *J* = 7.12 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 168.7, 168.2, 148.3, 140.0, 125.1, 121.1, 116.4, 116.2, 112.1, 91.1, 64.0, 56.2, 47.0, 38.8, 30.9, 26.2, 14.0 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{17}NO_6$ [M+H] 344.1056, found, 344.1140.

Ethyl 10-cyano-4-ethoxy-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19f.



Reaction of 8-ethoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17f** (201 mg, 0.51 mmol), ethyl cyanoacetate (117 mg, 1.03 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (143 mg, 1.03 mmol, 2 equiv) afforded ethyl 10-cyano-4-ethoxy-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19f** as a light yellow solid in 74% yield (136 mg). Rf = 0.6 (hexanes: EtOAc 8:2); Mp: 162 ºC; IR (KBr) (ν): 3433, 2986, 2939, 2249, 1731, 1687, 1605, 1469, 1187, 1073, 854 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.86 (s, 1H), 7.12 (t, *J* = 8.12 Hz, 1H), 6.91 (d, *J* = 8.28 Hz, 1H), 6.58 (m, 1H), 4.60 (d, *J* = 1.36, 1H), 4.45 (m, 2H), 4.11 (m, 2H), 2.93 (d, *J* = 2.76, 1H), 2.65 (m, 1H), 2.44 (m, 1H), 2.39 (m, 1H), 1.46 (t, *J* = 7.00 Hz, 3H), 1.42 (t, *J* = 7.20 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 168.7, 168.3, 147.6, 140.3, 125.0, 121.2, 116.3, 116.1, 113.4, 91.2, 64.9, 64.0, 47.0, 38.9, 30.9, 26.2, 14.8, 14.0. HRMS (ESI): m/z calcd for $C_{19}H_{19}NO_6$ [M+H] 358.1212, found, 358.1297.

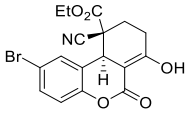
Ethyl 2-chloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19g.



Reaction of 6-chloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17g** (200 mg, 0.53 mmol), ethyl cyanoacetate (120 mg, 1.06 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (146 mg, 1.06 mmol, 2 equiv) afforded ethyl 2-chloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19g** as a light yellow solid in 74% yield (137 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 170 ºC; IR (KBr) (ν): 3445, 2980, 2870, 2248, 1729, 1695, 1601, 1480, 830 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.82 (s, 1H), 7.29 (m, 1H), 7.06 (d, *J* = 8.68 Hz, 1H), 6.99 (m, 1H), 4.58 (m, 2H), 4.44 (m, 1H), 2.93 (m, 1H), 2.68 (m, 1H), 2.46 (m, 1H), 2.40 (m, 1H), 1.48 (t, *J* = 7.16 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7,

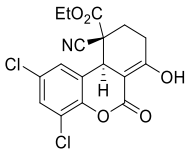
168.4, 167.9, 149.2, 130.4, 129.6, 125.6, 121.6, 119.2, 115.8, 90.5, 64.4, 46.8, 39.0, 30.8, 26.2, 14.0 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{14}ClNO_5$ [M+H] 348.0561, found, 348.0636.

Ethyl 2-bromo-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19h.



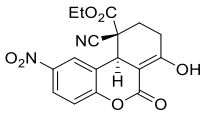
Reaction of 6-bromo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17h** (201 mg, 0.58 mmol), ethyl cyanoacetate (108 mg, 0.95 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (131 mg, 0.95 mmol, 2 equiv) afforded ethyl 2-bromo-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19h** as a light yellow solid in 72% yield (135 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 174-176 ºC; IR (KBr) (ν): 3448, 2978, 2878, 2247, 1735, 1696, 1602, 1484, 1409, 1068, 832 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.82 (s, 1H), 7.44 (m, 1H), 7.13 (q, *J* = 2.08 Hz, 1H), 7.00 (d, *J* = 8.64 Hz, 1H), 4.58 (m, 2H), 4.43 (m, 1H), 2.93 (m, 1H), 2.68 (m, 1H), 2.46 (d, *J* = 1.88 Hz, 1H), 2.40 (m, 1H), 1.50 (t, *J* = 7.16 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 168.4, 167.8, 149.7, 132.5, 128.5, 122.1, 119.7, 117.9, 115.8, 90.6, 64.4, 46.9, 39.0, 30.8, 26.3, 14.1. HRMS (ESI): m/z calcd for $C_{17}H_{14}BrNO_5$ [M +H] 392.0055, found, 392.0131.

Ethyl 2,4-dichloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19i.



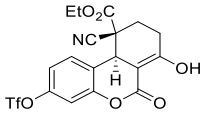
Reaction of 6,8-dichloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17i** (200 mg, 0.48 mmol), ethyl cyanoacetate (110 mg, 0.97 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (135 mg, 0.97 mmol, 2 equiv) afforded ethyl 2,4-dichloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19i** as a light yellow solid in 70% yield (128 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 166-168 ºC; IR (KBr) (ν): 3421, 2984, 2249, 1738, 1694, 1601, 1458, 1260, 1174, 815 cm^{-1}; ^1H-NMR (400 MHz, $CDCl_3$): δ 12.69 (s, 1H), 7.42 (m, 1H), 6.91 (m, 1H), 4.60 (m, 1H), 4.55 (m, 1H), 4.44 (m, 1H), 2.96 (d, *J* = 2.68 Hz, 1H) 2.70 (m, 1H), 2.48 (m, 1H), 2.41 (m, 1H), 1.48 (t, *J* = 7.12 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 168.3, 167.0, 145.5, 130.3, 130.1, 124.2, 124.0, 123.1, 115.6, 90.2, 64.5, 46.7, 39.3, 30.8, 26.3, 14.1. HRMS (ESI): m/z calcd for $C_{17}H_{13}Cl_2NO_5$ [M+H] 382.0210, found, 382.0225.

Ethyl 10-cyano-7-hydroxy-2-nitro-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19j.



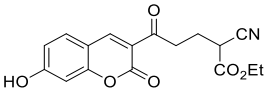
Reaction of 6-nitro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17j** (201 mg, 0.51 mmol), ethyl cyanoacetate (117 mg, 1.03 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (143 mg, 1.03 mmol, 2 equiv) afforded ethyl 10-cyano-7-hydroxy-2-nitro-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19j** as a light yellow coloured solid in 72% yield (133 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 155 ºC; IR (KBr) (ν): 3462, 3083, 2986, 2247, 1742, 1701, 1599, 1539. 1345, 1230, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.69 (s, 1H), 8.23 (ddd, *J* = 8.9, 2.5, 0.8 Hz, 1H), 8.02 (dd, *J* = 2.5, 1.3 Hz, 1H), 7.27 – 7.24 (d, *J* = 9.2 Hz, 1H), 4.67 (d, *J* = 1.3 Hz, 1H), 4.61 (s, 1H), 4.48 (m, 1H), 2.95 (m, 1H), 2.76 – 2.66 (m, 1H), 2.51 (m, 1H), 2.47 – 2.38 (m, 1H), 1.53 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 168.3, 166.8, 155.0, 144.6, 125.4, 121.8, 121.4, 119.0, 115.6, 89.7, 65.0, 46.7, 39.2, 30.6, 26.3, 14.0. HRMS (ESI): m/z calcd for $C_{17}H_{14}N_2O_7$ [M+H] 359.0801, found, 359.0863.

Ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19o.



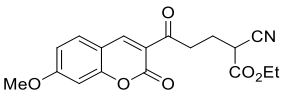
The reaction of 2-oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl trifluoromethanesulfonate **17o** (201 mg, 0.40 mmol, 2 equiv), ethyl cyanoacetate (92 mg, 0.81 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (112 mg, 0.81 mmol) afforded ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19o** as a white solid in 75% yield (141 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 142 ºC; IR (KBr) (ν): 3462, 3083, 2986, 2247, 1742, 1701, 1599, 1539. 1345, 1230, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.69 (s, 1H), 7.12 (m, 2H), 7.09 (m, 1H), 4.62 (d, 1H, *J* = 2.48 Hz), 4.48 (dd, 2H, *J* = 2.4 Hz), 2.96 (d, 1H, *J* = 2.72 Hz), 2.70 (m, 1H), 2.50 (m, 1H), 2.42 (m, 1H), 1.4 53 (t, 3H, *J* = 7.12 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 168.3, 167.4, 151.5, 149.2, 126.9, 120.9, 120.3, 118.7 (q, *J* = 320 Hz), 117.1, 115.7, 111.6, 90.3, 64.4, 46.7, 38.6, 30.7, 26.3, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -72.65 (s, 3F). HRMS (ESI): m/z calcd for $C_{18}H_{14}F_3NO_8S$ [M+H] 462.0392, found, 462.0480.

Ethyl 2-cyano-5-(7-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-oxopentanoate 22f.



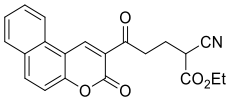
Reaction of 7-hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17b** (201 mg, 0.60 mmol), ethyl cyanoacetate (137 mg, 1.2 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (168 mg, 1.2 mmol, 2 equiv) afforded ethyl 2-cyano-5-(7-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-oxopentanoate **22f** as a yellow solid in 83% yield (165 mg). Rf = 0.4 (hexanes: EtOAc 6:4); Mp: 170-174 ºC; IR (KBr) (ν): 3340, 2985, 2250, 1743, 1694, 1611, 1425, 891 cm^{-1}. ^1H NMR (400 MHz, DMSO- d_6) δ 11.18 (s, 1H), 8.62 (s, 1H), 7.80 (d, J = 8.6 Hz, 1H), 6.85 (dd, J = 8.6, 2.1 Hz, 1H), 6.75 (d, J = 1.9 Hz, 1H), 4.28 – 4.23 (m, 1H), 4.23 – 4.16 (m, 2H), 3.19 (t, J = 7.4 Hz, 2H), 2.29 – 2.08 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 195.1, 166.2, 164.3, 159.0, 157.2, 148.2, 132.8, 118.5, 117.3, 114.3, 110.8, 101.7, 62.2, 36.1, 23.5, 13.8. HRMS (ESI): m/z calcd for $C_{17}H_{15}NO_5$ [M+H] 330.0899, found, 330.0981.

Ethyl 2-cyano-5-(7-methoxy-2-oxo-2*H*-chromen-3-yl)-5-oxopentanoate 22g.



Reaction of 7-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17c** (201 mg, 0.53 mmol), ethyl cyanoacetate (121 mg, 1.07 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (148 mg, 1.07 mmol, 2 equiv) afforded ethyl 2-cyano-5-(7-methoxy-2-oxo-2*H*-chromen-3-yl)-5-oxopentanoate **22g** as a yellow solid in 78% yield (144 mg). Rf = 0.5 (hexanes: EtOAc 8:2); Mp: 143-145 ºC; IR (KBr) (ν): 3055, 2946, 2254, 1741, 1713, 1672, 1624, 1445, 1228, 857 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.82 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.75 (m, 1H), 3.36 (m, 2H), 2.44 – 2.25 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 166.0, 165.6, 159.6, 157.9, 148.5, 131.7, 119.7, 116.4, 114.2, 112.0, 100.3, 63.0, 56.2, 39.0, 36.5, 24.1, 14.1 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{17}NO_6$ [M+H] 345.1056, found, 345.0848

Ethyl 2-cyano-5-oxo-5-(3-oxo-3*H*-benzo[*f*]chromen-2-yl)pentanoate 22o.



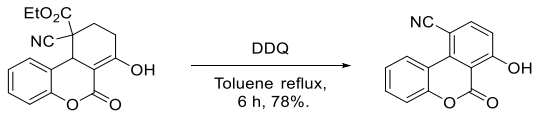
Reaction of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-benzo[*f*]chromen-2-one **17k** (201 mg, 0.51 mmol), ethyl cyanoacetate (115 mg, 1.02 mmol, 2 equiv), water (0.2 mL) and K_2CO_3 (140 mg, 1.02 mmol, 2 equiv) afforded ethyl 2-cyano-5-oxo-5-(2-oxo-2*H*-benzo[*f*]chromen-3-yl)pentanoate **22o** as a yellow solid in 82% yield (152 mg). Rf = 0.5 (hexanes: EtOAc 8:2);

Mp: 163-165 ^{o}C; IR (KBr) (ν): 2986, 2916, 2249, 1736, 1683, 1559, 1263, 1196, 1027, 821 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 9.04 Hz, 1H), 7.78 (d, *J* = 8.04 Hz, 1H), 7.76 (m, 1H), 7.63 (t, *J* = 7.92 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 4.32 (t, *J* = 14.28 Hz, 2H), 3.80 (d, J = 1.8 Hz, 1H), 3.45 (m, 2H), 2.45 (m, 2H), 1.36 (t, *J* = 7.12 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 166.0, 159.2, 156.3, 143.9, 136.8, 130.3, 129.8, 129.5, 129.4, 126.8, 121.7, 121.6, 116.5, 116.4, 112.8, 63.0, 39.2, 36.6, 24.2, 14.1. HRMS (ESI): m/z calcd for $C_{21}H_{17}NO_5$ [M+H] 364.1107, found, 364.1084.

Method A

Synthesis of dibenzopyrans: Oxidation with DDQ for the formation of dibenzopyran-6-ones

7-Hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20a.

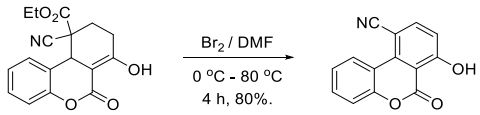


To the solution of tetrahydro-6*H*-benzo[*c*]chromene **19a** (200 mg, 0.61 mmol, 1 equiv) in toluene (10 mL) DDQ (277 mg, 1.22 mmol, 2 equiv) was added. The reaction mixture was heated to reflux for 6 h by which time aromatization was complete (TLC). Then the reaction mixture was cooled to room temperature and filtered it using celite. The filtrate was evaporated by using rotary evaporator to get the crude product. Purification by column chromatography using silica gel (100-200 mesh) and 10% ethyl acetate in hexanes as eluent furnished dibenzopyran-6-one in 78% yield.

Method B

Oxidation with bromine for the formation of dibenzopyran-6-ones:

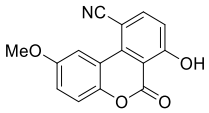
7-Hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20a.



To cooled (0 ^{o}C) and stirred solution of ethyl 10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19a** (200 mg, 0.61 mmol) in 5 mL of dimethylformamide (DMF) a solution of bromine (1.27 mmol, 2 equiv) in 5 mL of dimethylformamide was added drop-wise. The reaction mixture was allowed to warm to rt and then heated to 80 °C during 30 min. Then kept at this temperature for 3.5 h by which time the oxidation (TLC) was complete. The DMF was removed under reduced pressure and the residue was diluted with 10 mL DCM and 10 mL water. Separated aqueous layer was extracted with DCM (2 x 25 mL). Combined organic solutions were washed with 10% aqueous sodium

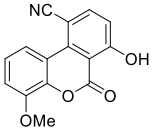
bisulfide (2 x 10 mL), 10% aqueous acetic acid (2 x 25 mL), and with water (10 mL). The DCM solution was dried (Na_2SO_4) before removing the solvent under reduced pressure. The crude product was purified by column chromatography using silica gel (100-200 mesh) and 10% ethyl acetate in hexanes as eluent to afford 7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20a** as a white solid in 80% yield (122 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 197-199 °C. IR (KBr) (ν): 3463, 2943, 2219, 1693, 1452, 1355, 763 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 12.39 (s, 1H), 9.16 (d, *J* = 7.48 Hz, 1H), 8.00 (d, *J* = 8.76 Hz, 1H), 7.65 (t, *J* = 7.24 Hz, 1H), 7.47 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 164.6, 150.5, 143.8, 137.7, 132.8, 125.9, 125.4, 119.4, 118.1, 117.6, 116.5, 107.0, 96.9. HRMS (ESI): m/z calcd for $C_{14}H_7NO_3$ [M+H] 238.0426, found, 238.0500.

7-Hydroxy-2-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20b



Oxidation of ethyl 10-cyano-7-hydroxy-2-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19d** (200 mg, 0.58 mmol) with bromine (186 mg, 1.16 mmol, 2 equiv) in DMF (10 mL) afforded 7-hydroxy-2-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20b** as white solid in 78% yield (121 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 227-228 °C. IR (KBr) (ν): 3440, 2928, 2219, 1688, 1438, 1212, 823 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 12.53 (s, 1H), 8.72 (d, *J* = 2.4 Hz, 1H,), 8.01 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 9.08 Hz, 1H), 7.20 (m, 1H), 7.17 (m, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.3, 148.2, 144.0, 140.6, 138.0, 125.5, 119.5, 117.6, 117.3, 116.4, 114.5, 107.1, 97.3, 56.5. HRMS (ESI): m/z calcd for $C_{15}H_9NO_4$ [M+H] 268.0532, found, 268.1067.

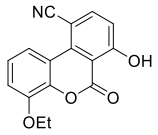
7-Hydroxy-4-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20c



Oxidation of ethyl 10-cyano-7-hydroxy-4-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19e** (201 mg, 0.58 mmol) with bromine (186 mg, 1.16 mmol, 2 equiv) in DMF (10 mL) afforded 7-hydroxy-4-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20c** as white solid in 74% yield (126 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 234 °C. IR (KBr) (ν): 3439, 2923, 2220, 1689, 1446, 1206, 822 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 12.43 (s, 1H), 8.77 (d, *J* = 8.36 Hz, 1H), 8.01 (d, *J* = 8.76 Hz, 1H), 7.40 (t, *J* = 8.08 Hz, 1H), 7.20 (m, 2H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.3,

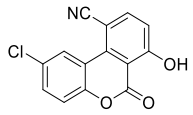
148.2, 143.9, 140.6, 138.0, 125.5, 119.5, 117.6, 117.3, 116.4, 114.4, 107.1, 97.3, 56.5. HRMS (ESI): m/z calcd for $C_{15}H_9NO_4$ [M+Na] 268.0532, found, 268.0609.

4-Ethoxy-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20d



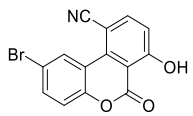
Oxidation of ethyl 10-cyano-4-ethoxy-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19f** (201 mg, 0.56 mmol) with bromine (179 mg, 1.12 mmol, 2 equiv) in DMF (10 mL) afforded 4-ethoxy-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20d** as white solid in 80% yield (127 mg). Rf = 0.56 (hexanes: EtOAc 9:1); Mp: 164 -166 ºC. IR (KBr) (ν): 3458, 2924,2218, 1697, 1457, 1210, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.47 (s, 1H), 8.75 (d, *J* = 1.2 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.38 (t, *J* = 8.28 Hz, 1H), 7.19 (m, 1H), 7.16 (m, 1H), 4.24 (q, *J* = 13.96 Hz, 2H), 1.55 (t, *J* = 7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.5, 147.5, 143.9, 140.7, 138.1, 125.5, 119.5, 117.5, 117.4, 116.3, 115.6, 107.1, 97.2, 65.2, 14.8. HRMS (ESI): m/z calcd for $C_{16}H_{11}NO_4$ [M+H] 282.0688, found, 282.0769.

2-Chloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20e



Oxidation of ethyl 2-chloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19g** (201 mg, 0.57 mmol) with bromine (184 mg, 1.15 mmol, 2 equiv) in DMF (10 mL) afforded 2-chloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20e** as white solid in 76% yield (120 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 184 ºC. IR (KBr) (ν): 3360, 3084, 2923, 2220, 1699, 1570, 1459, 1210, 803 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 12.32 (s, 1H), 9.20 (d, *J* = 2.28 Hz, 1H), 8.03 (d, *J* = 8.84 Hz, 1H), 7.60 (d, *J* = 2.28 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.3, 149.0, 143.8, 136.4, 132.9, 131.6, 125.0, 119.5, 118.9, 118.4, 117.7, 107.0, 97.3 ppm. HRMS (ESI): m/z calcd for $C_{14}H_6ClNO_3$ [M+H] 272.0036, found, 272.0114.

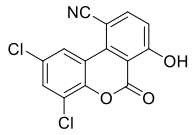
2-Bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20f



Oxidation of ethyl 2-bromo-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19h** (200 mg, 0.51 mmol) with bromine (163 mg, 1.02

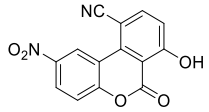
mmol, 2 equiv) in DMF (10 mL) afforded 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f** as a white solid in 78% yield (154 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 192-195 °C. IR (KBr) (ν): 3443, 2923, 2220, 1699, 1580, 1448, 778 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.31 (s, 1H), 9.36 (d, *J* = 2.16 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 2.16 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.2, 149.5, 143.8, 136.2, 135.8, 128.0, 119.8, 119.0, 118.9, 118.4, 118.2, 107.0, 97.3. HRMS (ESI): m/z calcd for $C_{14}H_6BrNO_3$ [M+H] 315.9531, found, 315.9609.

2,4-Dichloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20g



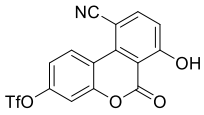
Oxidation of ethyl 2,4-dichloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19i** (201 mg, 0.52 mmol) with bromine (168 mg, 1.05 mmol, 2 equiv) in DMF (10 mL) afforded 2,4-dichloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20g** as white solid in 73% yield (119 mg). Rf = 0.55 (hexanes: EtOAc 9:1); Mp: 182 °C. IR (KBr) (ν): 3453, 2928, 2221, 1695, 1580, 1448, 803 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.20 (s, 1H), 9.17 (d, *J* = 2.2 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 163.3, 145.2, 144.1, 135.9, 133.0, 131.3, 124.3, 123.6, 119.0, 118.9, 118.7, 107.0, 97.8. HRMS (ESI): m/z calcd for $C_{14}H_5Cl_2NO_3$ [M+H] 305.9646, found, 305.9254.

7-Hydroxy-2-nitro-6-oxo-6*H*-benzo[*c*]chromene-10-carbon 20h



Oxidation of ethyl 10-cyano-7-hydroxy-2-nitro-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19j** (201 mg, 0.55 mmol) with bromine (178 mg, 1.11 mmol, 2 equiv) in DMF (10 mL) afforded 7-hydroxy-2-nitro-6-oxo-6*H*-benzo[*c*]chromene-10-carbon **20h** as white solid in 72% yield (115 mg). Rf = 0.48 (hexanes: EtOAc 9:1); Mp: 192 °C. IR (KBr) (ν): 3442, 3086, 2220, 1700, 1613, 1525, 1455, 1346, 1177, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.08 (s, 1H), 10.25 (d, *J* = 2.48 Hz, 1H), 8.52 (dd, *J* = 9.2, 2.44 Hz, 1H), 8.11 (d, *J* = 8.84 Hz, 1H), 7.62 (d, *J* = 8.82 Hz, 1H), 7.30 (d, *J* = 8.84 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 163.5, 154.0, 145.1, 144.0, 135.8, 127.4, 121.8, 119.4, 119.2, 118.4, 117.2, 106.9, 97.9. ppm. HRMS (ESI): m/z calcd for $C_{14}H_6N_2O_5Na$ [M+Na] 305.0177, found, 305.0160.

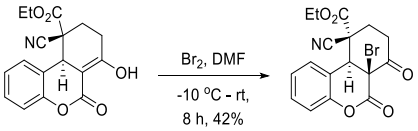
10-Cyano-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromen-3-yl trifluoromethanesulfonate 20i



Oxidation of ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19o** (200 mg, 0.43 mmol) with bromine (139 mg, 0.86 mmol, 2 equiv) in DMF (10 mL) afforded 10-cyano-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromen-3-yl trifluoromethanesulfonate **20i** as white solid in 70% yield (117 mg). Rf = 0.54 (hexanes: EtOAc 9:1); Mp: 173 ^{o}C. IR (KBr) (ν): 3371, 3060, 2924, 2218, 1690, 1593, 1466, 1434, 1211, 1130, 847 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.18 (s, 1H), 9.35 (d, *J* = 9.7 Hz, 1H), 8.05 (d, *J* = 8.9 Hz, 1H), 7.41 (dd, *J* = 4.8, 2.5 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 163.8, 151.3, 151.0, 144.0, 136.3, 127.6, 120.3, 119.0, 118.9, 118.8 (q, *J* = 321 Hz), 117.1, 116.8, 111.6, 106.8, 97.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -72.46 (s, 3F). HRMS (ESI): m/z calcd for $C_{15}H_6F_3NO_6S$ [M+H] 385.9868, found, 385.9953

Bromine mediated reaction at lower temperature

Ethyl 6a-bromo-10-cyano-6,7-dioxo-6a,7,8,9,10,10a-hexahydro-6*H*-benzo[*c*]chromene-10-carboxylate 24

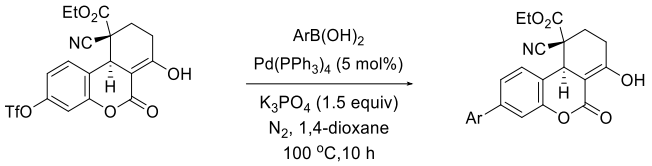


To the cooled (-10 ^{o}C) and stirred solution of ethyl 10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19a** (50 mg, 0.15 mmol) in 5 mL of dimethylformamide (DMF) a solution of bromine (0.32 mmol, 2 equiv) in 5 mL of dimethylformamide was added drop-wise. The reaction mixture was allowed to warm to rt. for 8 h. After the reaction, DMF was removed under reduced pressure and the residue was diluted with 10 mL DCM and 10 mL water. Separated aqueous layer was extracted with DCM (2 x 10 mL). Combined organic solutions were washed with 10% aqueous sodium bisulfide (2 x5 mL), 10% aqueous acetic acid (2 x 10 mL), and with water (10 mL). Then dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using silica gel (100-200 mesh) and 20% ethyl acetate in hexanes as eluent to afford ethyl 6a-bromo-10-cyano-6,7-dioxo-6a,7,8,9,10,10a-hexahydro-6*H*-benzo[*c*]chromene-10-carboxylate **24** as a white solid in 42% yield (24 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 182-185 ^{o}C. IR (KBr) (ν): 3463, 2943, 2218, 1705, 1692, 1455, 1355, 763

cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.13 (dd, *J* = 7.7, 1.4 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.20 (s, 1H), 3.35 – 3.22 (m, 1H), 2.96 (d, *J* = 15.2 Hz, 1H), 2.59 (ddd, *J* = 14.0, 5.3, 2.9 Hz, 1H), 2.50 – 2.39 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 166.2, 161.1, 151.1, 131.5, 128.3, 125.7, 118.2, 118.1, 114.7, 64.5, 61.6, 53.3, 51.6, 35.4, 33.6, 14.0. HRMS (ESI): m/z calcd for $C_{17}H_{14}BrNO_5$ [M+H] 392.0055, found, 392.0199.

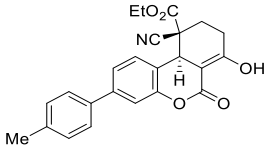
a) Representative procedure for Suzuki coupling involving aryl triflates

Ethyl 10-cyano-7-hydroxy-6-oxo-3-phenyl-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19p.



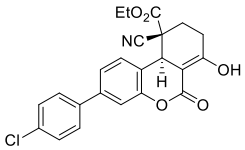
The mixture of the triflate **19o** (100 mg, 0.21 mmol), phenylboronic acid (34 mg, 0.28 mmol, 1.3 equiv), K_3PO_4 (69 mg, 0.32 mmol, 1.5 equiv), and $Pd(PPh_3)_4$ (4 mg, 5 mol%) in degassed 1,4-dioxane was stirred at 100 °C overnight, under N_2 atm. After completion of the coupling reaction (TLC), the reaction mixture was cooled to rt, diluted with DCM (10 mL) and decanted. The residue was extracted with DCM (10 mL) two more times. The solvent was removed from the combined DCM layers and the residue was subjected to column chromatography by using silica gel (100 – 200 mesh), hexane and EtOAc (5% to 15%) as eluent to afforded ethyl 10-cyano-7-hydroxy-6-oxo-3-phenyl-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19p** as light yellow solid in 90% yield (84 mg). Rf = 0.4 (hexanes: EtOAc 7:3); Mp: 155-158 °C. IR (KBr) (ν): 3367, 2982, 2247, 1744, 1684, 1615, 1408, 1232, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 12.88 (s, 1H), 7.56 (m, 2H), 7.46 (m, 2H), 7.41 (m, 2H), 7.35 (m, 1H), 7.09 (d, 1H, *J* = 8.08 Hz), 4.65 (s, 1H), 4.49 (m, 2H), 2.96 (d, 1H, *J* = 2.6 Hz), 2.69 (m, 1H), 2.49 (m, 1H), 2.43 (m, 1H), 1.46 (t, *J* = 7.12 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 168.7, 168.5, 151.0, 142.8, 139.1, 129.0, 128.2, 127.0, 123.8, 118.8, 116.3, 116.1, 91.2, 64.1, 47.0, 38.7, 30.8, 26.3, 14.0. HRMS (ESI): m/z calcd for $C_{23}H_{19}NO_5$ [M+H] 390.1263, found, 390.1334.

Ethyl 10-cyano-7-hydroxy-6-oxo-3-(p-tolyl)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19q.



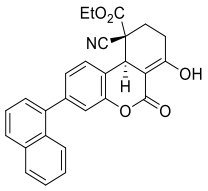
The coupling reaction of ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19o** (100 mg, 0.21 mmol), *p*-tolylboronic acid (38 mg, 0.28 mmol, 1.3 equiv), K_3PO_4 (69 mg, 0.32 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (4 mg, 5 mol%) afforded ethyl 10-cyano-7-hydroxy-6-oxo-3-(p-tolyl)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19q** as light yellow solid in 82% yield (79 mg). Rf = 0.5 (hexanes: EtOAc 7:3); Mp: 181-183 ºC. IR (KBr) (ν): 3468, 2991, 2920, 2248, 1745, 1680, 1613, 1404, 1233, 799 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 12.81 (s, 1H), 7.39 (d, 2H, *J* = 7.88 Hz), 7.32 (d, 1H, *J* = 7.92 Hz), 7.26 (s, 1H), 7.19 (d, 2H, *J* = 7.52 Hz), 7.00 (d, 1H, *J* = 8.04 Hz), 4.57 (s, 1H), 4.42 (t, 2H, *J* = 5.76 Hz), 2.88 (s, 1H), 2.60 (m, 1H), 2.32 (m, 5H), 1.39 (t, 3H, *J* = 7.08 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 168.7, 168.6, 151.0, 142.8, 138.1, 136.2, 129.8, 126.8, 125.6, 123.6, 118.4, 116.2, 116.1, 91.3, 64.1, 47.1, 38.7, 30.9, 26.3, 21.2, 14.1. HRMS (ESI): m/z calcd for $C_{24}H_{21}NO_5$ [M+H] 404.4340, found, 404.1490.

Ethyl 3-(4-chlorophenyl)-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19r.



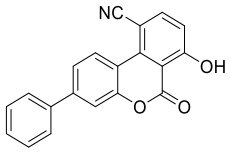
The reaction of ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19o** (100 mg, 0.21 mmol), 4-chlorophenylboronic acid (43 mg, 0.28 mmol, 1.3 equiv), K_3PO_4 (69 mg, 0.32 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (4 mg, 5 mol%) afforded **e**thyl 3-(4-chlorophenyl)-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19r** as light yellow solid in 78% yield (79 mg). Rf = 0.4 (hexanes: EtOAc 7:3); Mp: 157-158 ºC. IR (KBr) (ν): 3467, 3070, 2919, 2220, 1759, 1693, 1616, 1416, 1229, 800 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 12.85 (s, 1H), 7.48 (m, 2H), 7.42 (m, 2H), 7.36 (dd, *J* = 8.2, 1.6 Hz, 1H,), 7.29 (d, 1H, *J* = 1.76 Hz), 7.08 (d, 1H, *J* = 8 Hz), 4.64 (s, 1H), 4.49 (q, 2H), 2.96 (d, 1H, *J* = 2.64 Hz), 2.69 (m, 1H), 2.52 (m, 1H), 2.43 (m, 1H), 1.46 (t, 3H, *J* = 7.12 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 168.7, 168.4, 151.1, 141.5, 137.6, 134.4, 129.2, 128.3, 125.8, 123.6, 119.2, 116.2, 116.1, 91.1, 64.2, 47.0, 38.7, 30.8, 26.3, 14.1. HRMS (ESI): m/z calcd for $C_{23}H_{18}ClNO_5$ [M+H] 424.0874, found, 424.0938

Ethyl 10-cyano-7-hydroxy-3-(naphthalen-1-yl)-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate 19s.



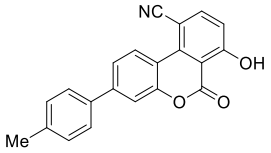
The reaction of ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19o** (100 mg, 0.21 mmol), 1-naphthylboronic acid (48 mg, 0.28 mmol, 1.3 equiv), K_3PO_4 (69 mg, 0.32 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (4 mg, 5 mol%) afforded ethyl 10-cyano-7-hydroxy-3-(naphthalen-1-yl)-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19s** as light yellow colour solid in 86% yield (90 mg). Rf = 0.5 (hexanes: EtOAc 7:3); Mp: 217-218 ºC. IR (KBr) (ν): 3473, 3055, 2985, 2245, 1747, 1675, 1407, 1221, 776 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 12.91 (s, 1H), 7.92 (m, 3H), 7.54 (m, 3H), 7.40 (m, 1H), 7.33 (m, 1H), 7.29 (m, 1H), 7.15 (m, 1H), 4.73 (t, 1H, *J* = 1.2 Hz), 4.51 (m, 2H), 3.00 (m, 1H), 2.72 (m, 1H), 2.52 (m, 1H), 2.43 (m, 1H), 1.47 (t, 3H, *J* = 7.12 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 168.7, 168.6, 150.5, 142.4, 138.1, 133.8, 131.2, 128.5, 128.4, 127.0, 126.9, 126.5, 126.1, 125.6, 125.4, 125.1, 119.4, 118.9, 116.2, 91.3, 64.2, 47.0, 38.8, 30.9, 26.3 14.1. HRMS (ESI): m/z calcd for $C_{27}H_{21}NO_5$ [M+H] 440.4670, found, 440.1485.

7-Hydroxy-6-oxo-3-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile 20j.



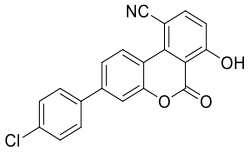
The reaction of ethyl 10-cyano-7-hydroxy-6-oxo-3-phenyl-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19p** (100 mg, 0.25 mmol) in toluene (10 mL) DDQ (116 mg, 0.51 mmol, 2 equiv) afforded 7-hydroxy-6-oxo-3-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile **20j** as white solid in 75% yield (60 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 218-220 ºC. IR (KBr) (ν): 3364, 3076, 2922, 2217, 1679, 1601, 1458, 1184, 784 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 12.39 (s, 1H), 9.25 (d, 1H, *J* = 8.8 Hz), 8.01 (d, 1H, *J* = 8.8 Hz), 7.71 (m, 2H), 7.66 (m, 2H), 7.53 (m, 2H), 7.46 (m, 1H), 7.15 (d, 1H, *J* = 8.76 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.8, 151.1, 145.8, 143.8, 138.3, 137.7, 129.3, 129.1, 127.2, 125.9, 124.4, 119.5, 117.4, 115.9, 115.3, 106.8, 96.8. HRMS (ESI): m/z calcd for $C_{20}H_{11}NO_3$ [M+H] 314.0739, found, 314.0805.

7-Hydroxy-6-oxo-3-(p-tolyl)-6*H*-benzo[*c*]chromene-10-carbonitrile 20k.



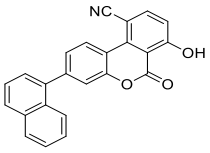
The reaction of ethyl 10-cyano-7-hydroxy-6-oxo-3-(p-tolyl)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19q** (100 mg, 0.24 mmol) in toluene (10 mL) DDQ (112 mg, 0.49 mmol, 2 equiv) afforded 7-hydroxy-6-oxo-3-(p-tolyl)-6*H*-benzo[*c*]chromene-10-carbonitrile **20k** as white solid in 78% yield (63 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 215 ^{o}C. IR (KBr) (ν): 3387, 3076, 2917, 2218, 1675, 1615, 1461, 1191, 804 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.40 (s, 1H), 9.23 (d, 1H, *J* = 8.6 Hz), 8.00 (d, 1H, *J* = 8.76 Hz), 7.69 (m, 1H,), 7.61 (d, 1H,), 7.57 (d, 2H, *J* = 8.04), 7.32 (m, 2H), 7.14 (d, 1H, *J* = 8.8 Hz), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.9, 151.1, 145.7, 143.8, 139.3, 137.8, 135.3, 130.0, 127.0, 125.8, 124.2, 119.5, 117.3, 115.5, 115.0, 106.8, 96.7, 21.3. HRMS (ESI): m/z calcd for $C_{21}H_{13}NO_3$ [M+H] 328.0895, found, 328.0957.

3-(4-Chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20l.



The reaction of ethyl 10-cyano-7-hydroxy-2-nitro-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19r** (101 mg, 0.23 mmol) in toluene (10 mL) DDQ (107 mg, 0.47 mmol, 2 equiv) afforded 3-(4-chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20l** as white solid in 68% yield (55 mg). Rf = 0.5 (hexanes: EtOAc 9:1); Mp: 211 ^{o}C. IR (KBr) (ν): 3328, 3076, 2919, 2220, 1693, 1616, 1593, 1417, 1220, 800 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.37 (s, 1H), 9.27 (d, 1H, *J* = 8.44 Hz), 8.02 (d, 1 H, *J* = 8.2 Hz), 7.67 (d, 1H, *J* = 8.36 Hz), 7.61 (m, 3H), 7.49 (d, 2H. *J* = 7.44 Hz), 7.17 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 164.8, 151.1, 144.5, 143.9, 137.6, 136.7, 135.4, 129.6, 128.5, 126.1, 125.6, 124.2, 119.5, 117.6, 115.8, 106.9, 96.9. HRMS (ESI): m/z calcd for $C_{20}H_{10}ClNO_3$ [M+H] 348.0349, found, 348.0185.

7-Hydroxy-3-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 20m.

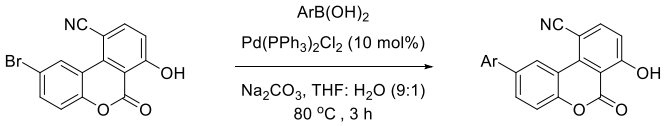


The reaction of ethyl 10-cyano-7-hydroxy-3-(naphthalen-1-yl)-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19s** (100 mg, 0.22 mmol) in toluene (10 mL) DDQ (103

mg, 0.45 mmol, 2 equiv) afforded 7-hydroxy-3-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20m** as white solid in 80% yield (64 mg). Rf = 0.6 (hexanes: EtOAc 9:1); Mp: 217-219 ^{o}C. IR (KBr) (ν): 3320, 2922, 2220, 1697, 1615, 1465, 1119, 791 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.42 (s, 1H), 9.33 (d, *J* = 8.44 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.95 (m, 3H), 7.65 (m, 1H), 7.60 (m, 5H), 7.19 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.8, 150.6, 145.9, 143.9, 137.8, 137.4, 133.9, 130.9, 129.1, 128.7, 127.8, 127.3, 126.9, 126.3, 125.5, 125.3, 125.2, 119.5, 119.2, 117.6, 115.5, 107.0, 96.9. HRMS (ESI): m/z calcd for $C_{24}H_{13}NO_3$ [M+H] 364.0895, found, 364.0960.

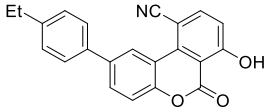
b) Representative procedure for Suzuki Coupling reaction

7-Hydroxy-6-oxo-2-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile 28a



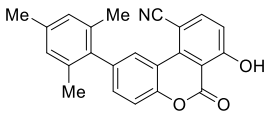
To the solution of 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f** (50 mg, 0.15 mmol) in 2.0 mL of THF, phenylboronic acid (38 mg, 0.31 mmol, 2 equiv), Na_2CO_3 (50 mg, 0.47 mmol, 3 equiv), $PdCl_2(PPh_3)_2$ (11 mg, 10 mol%), 2.0 mL H_2O were sequentially added. Resulting mixture was heated in a pre-heated oil-bath (80 ^{o}C) for 3 h by which time the coupling was complete (TLC). After cooling to rt, the resulting reaction mixture was diluted with DCM (20 mL). The organic solution was washed with water (2 x 10 mL), brine (10 mL), and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure resulted in the crude product, which was purified by column chromatography using silica gel (100 – 200 mesh) eluting with a mixture of hexane and ethyl acetate (5% to 15%) to afford 7-hydroxy-6-oxo-2-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile **28a** as a white solid in 76% yield (38 mg). Rf = 0.5 (hexanes: EtOAc 8:2); Mp: 180-182 ^{o}C; IR (KBr) (ν): 3361, 3088, 2985, 1743, 1694, 1611, 1425, 1284, 891 cm $^{-1}$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.41 (s, 1H), 9.48 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.89 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.72 (d, *J* = 1.4 Hz, 1H), 7.70 – 7.69 (m, 1H), 7.51 (dt, *J* = 7.8, 3.3 Hz, 3H), 7.44 – 7.39 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.7, 149.9, 143.8, 139.1, 139.0, 137.9, 131.4, 129.4, 128.3, 127.2, 123.6, 118.5, 117.7, 116.8, 112.8, 107.2, 97.1. HRMS (ESI): m/z calcd for $C_{20}H_{11}NO_3$ [M+H] 314.0739, found, 314.0813.

2-(4-Ethylphenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 28b.



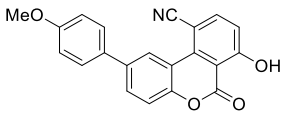
Following the general procedure, the Suzuki coupling reaction of 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f** (50 mg, 0.15 mmol) and 4-ethylphenylboronic acid (48 mg, 0.31 mmol, 2 equiv) in the presence of Na_2CO_3 (50 mg, 0.47 mmol, 3 equiv), $PdCl_2(PPh_3)_2$ (11 mg, 0.10 equiv) afforded 2-(4-ethylphenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28b** as a white solid in 77% yield (42 mg). Rf = 0.5 (hexanes: EtOAc 8:2); Mp: 175-177 ºC; IR (KBr) (ν): 3364, 2905, 2219, 1685, 1586, 1457, 1220, 813 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 12.39 (s, 1H), 9.41 (d, *J* = 2.1 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.84 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.7, 149.7, 144.5, 143.7, 138.9, 137.9, 136.2, 131.1, 128.9, 127.0, 123.6, 119.5, 118.4, 117.6, 116.7, 107.1, 97.1, 28.6, 15.6. HRMS (ESI): m/z calcd for $C_{22}H_{15}NO_3$ [M+H] 342.1052, found, 342.1123.

7-Hydroxy-2-mesityl-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 28c



The Suzuki coupling reaction of 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f** (50 mg, 0.15 mmol) and 2,4,6-trimethylphenylboronic acid (52 mg, 0.31 mmol, 2 equiv) in the presence of Na_2CO_3 (50 mg, 0.47 mmol, 3 equiv), $PdCl_2(PPh_3)_2$ (11 mg, 0.10 equiv) afforded 7-hydroxy-2-mesityl-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28c** as a white solid in 80% yield (45 mg). Rf = 0.6 (hexanes: EtOAc 8:2); Mp: 221-223 ºC; IR (KBr) (ν): 3381, 2918, 2217, 1707, 1567, 1451, 1168, 780 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 12.44 (s, 1H), 8.98 (d, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 6.96 (s, 2H), 2.34 (s, 3H), 2.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 164.9, 149.4, 143.8, 139.0, 138.0, 137.4, 136.7, 135.9, 134.4, 128.6, 126.1, 119.2, 118.1, 117.6, 116.5, 107.1, 97.1, 21.1, 21.0. HRMS (ESI): m/z calcd for $C_{23}H_{17}NO_3$ [M+H] 356.1208, found, 356.1274.

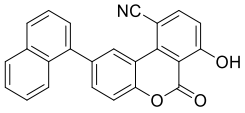
7-Hydroxy-2-(4-methoxyphenyl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 28d



The Suzuki coupling reaction of 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f** (50 mg, 0.15 mmol) and 4-methoxyphenylboronic acid (48 mg, 0.31 mmol, 2 equiv) in the presence of Na_2CO_3 (50 mg, 0.47 mmol, 3 equiv), $PdCl_2(PPh_3)_2$ (11 mg, 0.10 equiv) afforded 7-hydroxy-2-(4-methoxyphenyl)-6-oxo-6*H*-benzo[*c*]chromene-10-

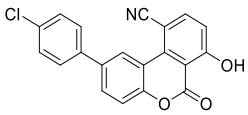
carbonitrile **28d** as a white solid in 75% yield (41 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 232 ºC; IR (KBr) (ν): 3440, 2924, 2850, 2214, 1685, 1589, 1457, 1218, 813 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.42 (s, 1H), 9.38 (d, *J* = 2.4 Hz, 1H), 8.09 – 7.95 (m, 1H), 7.83 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 164.6, 159.7, 149.3, 143.6, 138.4, 137.8, 131.1, 130.6, 128.0, 122.7, 119.5, 118.3, 117.5, 116.5, 114.6, 107.0, 96.8, 55.3. HRMS (ESI): m/z calcd for $C_{21}H_{13}NO_4$ [M+H] 344.0845, found, 344.0923.

7-Hydroxy-2-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 28e



The Suzuki coupling reaction of 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f** (50 mg, 0.15 mmol) and 1-naphthylboronic acid (55 mg, 0.31 mmol, 2 equiv) in the presence of Na_2CO_3 (50 mg, 0.47 mmol, 3 equiv), $PdCl_2(PPh_3)_2$ (11 mg, 0.10 equiv) afforded 7-hydroxy-2-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28e** as a white solid in 76% yield (44 mg). Rf = 0.53 (hexanes: EtOAc 8:2); Mp: 252-254 ºC; IR (KBr) (ν): 3375, 2925, 2859, 2221, 1687, 1590, 1459, 1220, 807 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.43 (s, 1H), 9.35 (d, *J* = 1.9 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.91 (m, 3H), 7.79 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.59 – 7.46 (m, 5H), 7.17 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.8, 149.9, 143.9, 138.8, 138.0, 137.8, 134.7, 134.0, 131.3, 128.7, 128.6, 127.6, 126.7, 126.5, 126.2, 125.6, 125.3, 119.2, 117.9, 117.7, 116.7, 107.2, 97.2. HRMS (ESI): m/z calcd for $C_{24}H_{13}NO_3$ [M+H] 364.0895, found, 364.0960.

2-(4-Chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile 28f

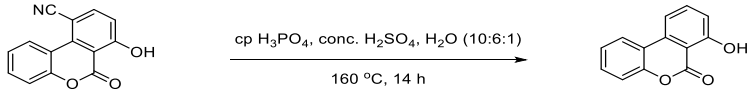


The Suzuki coupling reaction of 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f** (50 mg, 0.15 mmol) and 4-chlorophenylboronic acid (50 mg, 0.31 mmol, 2 equiv) in the presence of Na_2CO_3 (50 mg, 0.47 mmol, 3 equiv), $PdCl_2(PPh_3)_2$ (11 mg, 0.10 equiv) afforded 2-(4-chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28f** as a white solid in 72% yield (40 mg). Rf = 0.4 (hexanes: EtOAc 8:2); Mp: 224-225 ºC; IR (KBr) (ν): 3443, 2917, 2852, 2214, 1694, 1586, 1455, 1224, 808 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.38 (s, 1H), 9.45 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.84 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 164.7, 150.1, 143.8, 137.8, 137.5,

134.5, 131.1, 129.6, 128.4, 123.6, 119.6, 118.7, 117.9, 116.9, 107.2, 97.1. HRMS (ESI): m/z calcd for $C_{20}H_{10}ClNO_3$ [M+H] 348.0349, found, 348.0420.

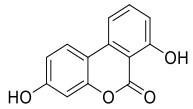
c) Representative procedure for the reductive decyanation

7-Hydroxy-6*H*-benzo[*c*]chromen-6-one 2b



A 25 ml rb flask was charged sequentially with 7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20a** (105 mg, 0.42mmol), H_3PO_4 (5 mL), water (0.5 mL) and conc.H_2SO_4 (3 mL). The rb was placed in a pre-heated (160 °C) oil-bath for 13 h. by which time the reductive decynanation was complete. The cooled (5 ºC, ice-water) reaction mixture was diluted with ice-cold water (10 mL) and EtOAc (10 mL) carefully. The aqueous layer was extracted with EtOAc (3 x 10 mL). Combined EtOAc solutions was washed with dilute and cold sodium bicarbonate solution (0.1 M, 10 mL x 2), brine (10 mL). Resulting EtOAc solution was dried over anhydrous Na_2SO_4. Removal of solvent followed by column chromatography by using silica gel (100 – 200 mesh) hexane and EtOAc (5% to 15%) as eluent afforded 7-hydroxy-6*H*-benzo[*c*]chromen-6-one **2b** as white solid in 70% yield (63 mg). Rf = 0.6 (hexanes: EtOAc 8:2); Mp: 165 °C. IR (KBr) (ν): 3229, 2925, 1695, 1617, 1288, 1216, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.93 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.65 (t, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.30 (m, 2H), 7.01 (dd, *J* = 8.3, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 162.4, 150.5, 137.3, 135.2, 130.6, 125.2, 123.4, 118.2, 117.7, 116.5, 112.2, 106.1. HRMS (ESI): m/z calcd for $C_{13}H_8O_3$ [M+H] 213.0473, found, 213.0550.

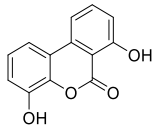
3,7-Dihydroxy-6*H*-benzo[*c*]chromen-6-one 2c



Reaction of 3,7-dihydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20i** (100 mg, 0.39 mmol), H_3PO_4 (5 mL), H_2SO_4 (3 mL) and 0.5 mL of water afforded 3,7-dihydroxy-6*H*-benzo[*c*]chromen-6-one **2c** as white solid in 65% yield (55 mg). Rf = 0.6 (hexanes: EtOAc 8:2); Mp: 215-217 °C. IR (KBr) (ν): 3319, 3202, 1674, 1616, 1466, 1244, 797 cm^{-1}; ^1H-NMR (400 MHz, DMSO-d_6) δ 11.04 (s, 1H), 10.59 (s, 1H), 7.86 (d, *J* = 8.72 Hz, 1H), 7.61 (t, *J* = 8.00 Hz, 1H), 7.43 (d, *J* = 8.04 Hz, 1H), 6.82 (d, *J* = 8.24 Hz, 1H), 6.76 (dd, *J* = 8.8, 2.32 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.1, 161.5, 160.2, 151.6,

137.9, 135.9, 125.4, 114.6, 114.1, 112.1, 109.7, 104.6, 103.1 ppm. HRMS (ESI): m/z calcd for $C_{13}H_8O_4$ [M+H] 229.0423, found, 229.0508.

4,7-Dihydroxy-6*H*-benzo[*c*]chromen-6-one 2d



Reaction of 7-hydroxy-4-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20c** (100 mg, 0.37 mmol), H_3PO_4 (5 mL), H_2SO_4 (3 mL) and 0.5 mL of water afforded 4,7-dihydroxy-6*H*-benzo[*c*]chromen-6-one **2d** as white solid in 60% yield (50 mg). Rf = 0.6 (hexanes: EtOAc 8:2); Mp: 180-184 °C. IR (KBr) (ν): 3389, 3078, 1716, 1618, 1571, 1460, 1195, 771 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 10.18 (s, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.55 (m, 2H), 7.15 (t, *J* = 7.9 Hz 1H), 7.07 (d, *J* = 2.24 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.9, 160.1, 145.5, 140.1, 137.2, 132.7, 124.5, 118.7, 118.0, 117.1, 113.3, 112.2, 107.6. HRMS (ESI): m/z calcd for $C_{13}H_8O_4$ [M+H] 229.0423, found, 229.0498.

X-ray crystallography data

The X-ray diffraction measurements were carried out at 293 K on Oxford CrysAlis CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å).

X-ray crystallography of 20i

Single crystals of $C_{15}H_6NO_6F_3S$ **20i**, the crystal was kept at 293(2) K during data collection. Using Olex2,[5] the structure was solved with the ShelXS[6] structure solution program using direct methods and refined with the ShelXL[7] refinement package using Least Squares minimisation. Anisotropic displacement parameters were included for all non-hydrogen atoms.

Table 1. **Crystal data of 2oi**

Identification code	HSPR-MP-II-114-AS
Empirical formula	$C_{15}H_6NO_6F_3S$
Formula weight	385.27
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.6654(4)

b/Å	9.6240(5)
c/Å	12.5534(7)
α/°	102.129(4)
β/°	104.972(5)
γ/°	94.329(5)
Volume/Å^3	753.35(7)
Z	2
ρ_{calc}mg/mm^3	1.698
μ/mm^{-1}	0.286
F(000)	388.0
Crystal size/mm^3	0.62 x 0.38 x 0.08
2Θ range for data collection	6.36 to 58.7°
Index ranges	$-8 \leq h \leq 8$, $-12 \leq k \leq 13$, $-16 \leq l \leq 17$
Reflections collected	16636
Independent reflections	3703[R(int) = 0.0352]
Data/restraints/parameters	3703/0/236
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0487, wR_2 = 0.1273
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.1408
Largest diff. peak/hole / e Å^{-3}	0.39/-0.44
CCDC No	2174559

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 20i. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	550.6(9)	709.7(5)	8564.7(4)	44.19(18)
O1	3280(2)	-1667.2(15)	4493.3(12)	42.5(3)
C2	35(3)	-2862.9(18)	4627.8(15)	31.6(4)
O3	371(3)	687.1(15)	7289.0(12)	49.6(4)
O4	4681(2)	-2437.3(17)	3131.3(14)	54.0(4)
C5	-75(3)	-3961.4(18)	3597.5(15)	30.9(4)
C6	1503(3)	-3791.3(19)	3050.7(16)	34.9(4)
C7	1707(3)	-1745.6(19)	5016.1(15)	34.2(4)

O8	2925(3)	-4612.6(19)	1480.2(15)	61.4(5)
C9	1897(3)	-604(2)	5936.5(16)	39.7(4)
C10	3234(3)	-2628(2)	3530.5(17)	38.7(4)
C11	-3307(3)	-5546(2)	3551.3(18)	42.1(5)
C12	-1449(3)	-2798(2)	5242.5(16)	38.7(4)
C13	-1326(3)	-1672(2)	6149.2(17)	42.6(5)
C14	1462(3)	-4746(2)	2019.7(18)	43.9(5)
C15	-1660(3)	-5143.8(19)	3086.2(16)	36.2(4)
C16	339(4)	-593(2)	6463.8(16)	39.6(4)
N17	-4648(3)	-5986(2)	3849.0(19)	60.3(6)
C18	-1656(4)	-6070(2)	2063.8(19)	48.5(5)
O19	-747(3)	1690(2)	8909.0(16)	74.9(6)
O20	484(4)	-669.5(18)	8752.5(15)	84.6(7)
C21	3191(5)	1640(5)	9208(3)	85.6(10)
F22	3614(4)	1770(3)	10317.2(17)	139.1(11)
C23	-157(4)	-5881(2)	1530(2)	54.6(6)
F24	3352(4)	2898(3)	8978(2)	132(1)
F25	4494(4)	885(4)	8807(3)	158.3(13)

Table 3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 20i. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	59.6(4)	39.4(3)	31.4(3)	1.81(19)	16.6(2)	-1.2(2)
O1	38.9(7)	41.2(7)	40.9(8)	-2.2(6)	14.1(6)	-11.3(6)
C2	33.1(9)	29.7(8)	29.0(9)	5.3(7)	6.1(7)	-0.4(7)
O3	81.6(11)	33.2(7)	32.0(7)	1.3(5)	19.2(7)	3.6(7)
O4	45.3(9)	60(1)	54.4(10)	1.7(7)	25.0(7)	-11.1(7)
C5	31.4(9)	27.8(8)	30.5(9)	4.6(7)	6.2(7)	1.0(7)
C6	35.6(10)	31.7(9)	35.1(10)	3.6(7)	10.5(8)	1.3(7)
C7	34.8(9)	34.0(9)	30.9(9)	5.0(7)	8.6(7)	-3.1(7)
O8	68.5(11)	58.3(10)	58.3(10)	-5.6(8)	38.7(9)	-3.9(8)
C9	45.9(11)	33.2(9)	33.5(10)	2.3(7)	7.7(8)	-7.3(8)
C10	37.2(10)	38.5(10)	39(1)	6.0(8)	12.7(8)	-0.9(8)
C11	40.4(11)	32.4(9)	46.2(11)	1.4(8)	9.0(9)	-5.8(8)
C12	39.2(10)	37.2(10)	37.3(10)	3.8(8)	12.9(8)	-3.5(8)
C13	47.5(11)	43.6(11)	36.6(10)	5.0(8)	17.1(9)	0.7(9)
C14	49.5(12)	39.8(10)	42.5(11)	1.8(8)	20.5(9)	3.3(9)
C15	35.3(10)	30.6(9)	37.8(10)	3.3(7)	7.2(8)	-1.8(7)
C16	56.3(12)	32.7(9)	26.4(9)	1.9(7)	10.8(8)	2.6(8)
N17	54.4(12)	51.1(11)	71.3(14)	4.8(10)	24.8(11)	-15.3(9)
C18	50.5(13)	35.9(10)	48.3(12)	-6.7(9)	12.4(10)	-7.5(9)
O19	81.7(14)	91.4(14)	56.5(11)	4.4(10)	33.7(10)	29.1(11)
O20	166(2)	44.5(10)	44.9(10)	10.6(7)	37.4(12)	-2.2(11)

C21	63.0(19)	128(3)	54.7(17)	15.6(18)	7.9(14)	-6.5(19)
F22	104.0(17)	224(3)	50.8(11)	19.6(14)	-17.4(11)	-40.9(17)
C23	65.8(15)	43.9(12)	44.9(12)	-11.2(9)	20.7(11)	-5.2(10)
F24	143(2)	117.6(18)	108.5(18)	11.4(14)	27.1(15)	-75.8(16)
F25	64.8(14)	294(4)	137(2)	76(2)	36.8(15)	54(2)

Table 4. Bond Lengths for 20i

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O3	1.5701(15)	C6	C14	1.414(3)
S1	O19	1.404(2)	C7	C9	1.388(3)
S1	O20	1.3955(18)	O8	C14	1.336(3)
S1	C21	1.810(3)	C9	C16	1.368(3)
O1	C7	1.378(2)	C11	C15	1.434(3)
O1	C10	1.351(2)	C11	N17	1.140(3)
C2	C5	1.470(2)	C12	C13	1.377(3)
C2	C7	1.398(2)	C13	C16	1.376(3)
C2	C12	1.401(3)	C14	C23	1.390(3)
O3	C16	1.428(2)	C15	C18	1.401(3)
O4	C10	1.215(2)	C18	C23	1.360(3)
C5	C6	1.413(3)	C21	F22	1.324(4)
C5	C15	1.409(2)	C21	F24	1.305(4)
C6	C10	1.453(3)	C21	F25	1.305(4)

Table 5. Bond Angles for 20i.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	S1	C21	99.19(13)	O4	C10	O1	116.06(17)
O19	S1	O3	106.53(11)	O4	C10	C6	125.03(18)
O19	S1	C21	104.88(17)	N17	C11	C15	173.6(2)
O20	S1	O3	111.76(9)	C13	C12	C2	122.23(18)
O20	S1	O19	122.92(14)	C16	C13	C12	118.22(19)
O20	S1	C21	108.81(18)	O8	C14	C6	122.88(18)
C10	O1	C7	121.73(14)	O8	C14	C23	117.51(19)
C7	C2	C5	118.24(16)	C23	C14	C6	119.61(19)
C7	C2	C12	116.13(16)	C5	C15	C11	125.21(17)
C12	C2	C5	125.57(16)	C18	C15	C5	120.04(18)
C16	O3	S1	122.87(12)	C18	C15	C11	114.70(16)
C6	C5	C2	117.30(15)	C9	C16	O3	116.58(17)
C15	C5	C2	125.52(17)	C9	C16	C13	123.14(18)
C15	C5	C6	117.13(16)	C13	C16	O3	119.90(19)

C5	C6	C10	121.14(16)	C23	C18	C15	122.44(18)
C5	C6	C14	121.42(16)	F22	C21	S1	107.5(2)
C14	C6	C10	117.44(17)	F24	C21	S1	110.6(3)
O1	C7	C2	122.50(16)	F24	C21	F22	110.7(3)
O1	C7	C9	114.31(15)	F24	C21	F25	108.9(3)
C9	C7	C2	123.16(17)	F25	C21	S1	109.1(3)
C16	C9	C7	117.04(17)	F25	C21	F22	110.0(3)
O1	C10	C6	118.91(17)	C18	C23	C14	119.33(19)

Table 6. Torsion Angles for 20i .

A	B	C	D	Angle/˚
S1	O3	C16	C9	-120.51(18)
S1	O3	C16	C13	66.4(3)
O1	C7	C9	C16	177.56(17)
C2	C5	C6	C10	3.9(3)
C2	C5	C6	C14	-176.31(18)
C2	C5	C15	C11	-6.6(3)
C2	C5	C15	C18	176.10(19)
C2	C7	C9	C16	-0.7(3)
C2	C12	C13	C16	-1.1(3)
O3	S1	C21	F22	179.4(3)
O3	S1	C21	F24	58.5(3)
O3	S1	C21	F25	-61.3(3)
C5	C2	C7	O1	-2.3(3)
C5	C2	C7	C9	175.84(18)
C5	C2	C12	C13	-174.73(19)
C5	C6	C10	O1	-2.5(3)
C5	C6	C10	O4	177.6(2)
C5	C6	C14	O8	179.8(2)
C5	C6	C14	C23	-0.2(3)
C5	C15	C18	C23	0.2(4)
C6	C5	C15	C11	175.71(18)
C6	C5	C15	C18	-1.6(3)
C6	C14	C23	C18	-1.2(4)
C7	O1	C10	O4	178.53(18)
C7	O1	C10	C6	-1.4(3)
C7	C2	C5	C6	-1.5(3)
C7	C2	C5	C15	-179.20(18)
C7	C2	C12	C13	2.6(3)
C7	C9	C16	O3	-170.46(17)
C7	C9	C16	C13	2.4(3)
O8	C14	C23	C18	178.8(2)

C10	O1	C7	C2	3.9(3)
C10	O1	C7	C9	-174.43(18)
C10	C6	C14	O8	-0.4(3)
C10	C6	C14	C23	179.6(2)
C11	C15	C18	C23	-177.3(2)
C12	C2	C5	C6	175.74(18)
C12	C2	C5	C15	-1.9(3)
C12	C2	C7	O1	-179.82(17)
C12	C2	C7	C9	-1.7(3)
C12	C13	C16	O3	171.08(18)
C12	C13	C16	C9	-1.6(3)
C14	C6	C10	O1	177.66(18)
C14	C6	C10	O4	-2.3(3)
C15	C5	C6	C10	-178.25(17)
C15	C5	C6	C14	1.6(3)
C15	C18	C23	C14	1.2(4)
N17	C11	C15	C5	-165(2)
N17	C11	C15	C18	12(2)
O19	S1	O3	C16	-142.07(18)
O19	S1	C21	F22	69.5(3)
O19	S1	C21	F24	-51.5(3)
O19	S1	C21	F25	-171.3(2)
O20	S1	O3	C16	-5.3(2)
O20	S1	C21	F22	-63.7(3)
O20	S1	C21	F24	175.3(2)
O20	S1	C21	F25	55.5(3)
C21	S1	O3	C16	109.3(2)

Table 7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 20i.

Atom	***x***	***y***	***z***	**U(eq)**
H8	3763	-3889	1821	92
H9	3034	121	6183	48
H12	-2556	-3541	5031	46
H13	-2340	-1642	6539	51
H18	-2719	-6843	1738	58
H23	-213	-6505	845	66

X-ray crystallography of 19p

Single crystals of $C_{24}H_{19}NO_5$ **19p**, the crystal was kept at 293(2) K during data collection.

Using Olex2, the structure was solved with the olex2.solve structure solution program using

Charge Flipping and refined with the ShelXL, refinement package using Least Squares minimisation.

Table 8. Crystal data of 19p

Identification code	HSPR-MP-85-AS
Empirical formula	$C_{24}H_{19}NO_5$
Formula weight	389.39
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.7089(8)
b/Å	14.3510(12)
c/Å	14.2749(15)
α/°	90.00
β/°	106.946(10)
γ/°	90.00
Volume/Å^3	1902.6(3)
Z	3
ρ_{calc}mg/mm^3	1.149
m/mm^{-1}	0.181
F(000)	687.0
Crystal size/mm^3	0.75 ×0.44 × 0.42
2Θ range for data collection	5.98 to 58.34°
Index ranges	$-13 \leq h \leq 13$, $-18 \leq k \leq 17$, $-18 \leq l \leq 18$
Reflections collected	10689
Independent reflections	4413[R(int) = 0.0264]
Data/restraints/parameters	4413/0/264
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.1027
Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1179
Largest diff. peak/hole / e Å^{-3}	0.19/-0.18
CCDC No	2153368

Table 9. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 19p. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
O1	5386(1)	3325.9(7)	9206.1(7)	40.9(3)
O2	6302.4(11)	2253.7(8)	8483.5(8)	51.0(3)
O3	2772.0(12)	5693.8(8)	6178.5(10)	59.2(4)
O4	5081.2(13)	1830.4(8)	6683.2(9)	58.6(3)
C5	4437.4(14)	3162.2(10)	7449.5(10)	34.6(3)
C6	5419.4(15)	2880.2(10)	8373.5(11)	37.3(3)
C7	4041.1(15)	4041.4(10)	10117.7(11)	36.5(3)
O8	500.9(12)	5327.5(10)	6077.9(9)	65.0(4)
C9	4203.0(14)	3879.5(10)	9205.6(10)	33.5(3)
C10	3642.9(14)	4078.3(10)	7395.5(10)	33.3(3)
C11	3291.3(14)	4244.2(10)	8348.1(10)	34.4(3)
C12	1958.3(17)	4937.1(12)	9364.4(11)	44.1(4)
C13	2148.7(16)	4772.7(11)	8456.8(11)	44.3(4)
C14	2732.1(15)	4791.0(11)	11198.4(11)	38.1(3)
N15	340.2(17)	2983.7(12)	6616.7(12)	66.3(5)
C16	2912.8(15)	4585.2(10)	10220.1(11)	36.5(3)
C17	2039.4(18)	5591.8(12)	11355.6(13)	50.8(4)
C18	2336.3(14)	4130.6(11)	6452.3(10)	37.8(4)
C19	1182.2(16)	3505.7(12)	6549.2(12)	45.1(4)
C20	2831.2(17)	3809.1(12)	5565.7(11)	44.6(4)
C21	3274.2(17)	4198.4(12)	11992.2(12)	46.5(4)
C22	4340.3(15)	2611.1(11)	6661.7(11)	40.9(4)
C23	1732.3(17)	5116.9(12)	6224.0(11)	43.8(4)
C24	3338.7(16)	2809.3(12)	5675.0(11)	46.8(4)
C25	2423(2)	5206.6(15)	13036.8(14)	62.9(5)
C26	3117.0(19)	4412.3(14)	12901.7(13)	57.8(5)
C27	1886(2)	5803.3(14)	12264.2(14)	63.0(5)
C28	2376(2)	6661.3(13)	5927.7(18)	71.6(6)
C29	3563(3)	7104.3(17)	5663(2)	108.9(10)

Table 10. Anisotropic Displacement Parameters ($Å^2×10^3$) for 19p. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

O1	35.9(5)	50.0(6)	31.8(6)	-2.7(5)	1.9(4)	9.2(5)
O2	50.3(6)	50.9(7)	44.9(7)	-1.8(5)	2.8(5)	18.3(5)
O3	51.8(7)	43.2(7)	79.6(10)	13.8(6)	14.4(6)	12.1(6)
O4	59.9(7)	53.4(7)	52.0(8)	-15.8(6)	-0.2(6)	18.0(6)
C5	32.2(7)	35.0(8)	33.3(8)	-1.8(6)	4.2(6)	0.2(6)
C6	33.7(7)	37.1(8)	38.0(9)	-3.5(7)	5.7(6)	0.3(6)
C7	37.6(7)	35.1(8)	32.0(8)	0.7(6)	2.9(6)	-2.4(6)
O8	47.7(7)	79.3(9)	65.9(9)	16.1(7)	13.1(6)	24.6(7)
C9	30.5(7)	32.0(7)	34.7(8)	-2.7(6)	4.1(6)	-1.6(6)
C10	31.2(7)	34.9(8)	30.0(8)	-1.6(6)	2.9(6)	-1.3(6)
C11	36.0(7)	31.9(8)	31.5(8)	-2.7(6)	3.9(6)	-1.9(6)
C12	43.8(8)	47.7(9)	38.7(9)	-4.2(7)	8.8(7)	10.2(7)
C13	45.2(8)	47.7(9)	34.2(9)	-0.9(7)	2.3(6)	11.3(7)
C14	36.1(7)	40.9(9)	37.7(9)	-3.4(7)	11.4(6)	-8.8(6)
N15	56.0(9)	74.1(11)	71.3(12)	-21.4(9)	22.5(8)	-19.5(8)
C16	37.7(7)	35.9(8)	34.1(8)	-3.2(6)	7.7(6)	-5.9(6)
C17	55.4(10)	52.6(11)	48.2(11)	0.0(8)	21.4(8)	2.9(8)
C18	34.2(7)	45.2(9)	30.6(8)	-1.1(7)	4.0(6)	2.4(6)
C19	37.8(8)	55(1)	38.9(9)	-10.6(8)	5.4(6)	-1.4(8)
C20	43.0(8)	56.6(10)	31.1(8)	-2.0(7)	6.2(6)	5.9(7)
C21	48.0(9)	49.6(10)	42.5(10)	2.3(8)	14.5(7)	-3.3(7)
C22	37.3(7)	42.1(9)	39.9(9)	-5.3(7)	6.1(6)	2.7(7)
C23	43.3(8)	53.8(10)	30.5(9)	3.5(7)	5.0(6)	10.0(8)
C24	43.6(8)	56.6(11)	35.8(9)	-11.0(7)	4.9(7)	3.7(7)
C25	67.9(12)	82.9(15)	46.2(11)	-8.1(10)	29.9(9)	-7.7(11)
C26	58.7(10)	74.7(13)	42.3(11)	8.3(9)	18.3(8)	-6.3(10)
C27	70.4(12)	68.3(13)	60.3(13)	-8(1)	34.6(10)	6.4(10)
C28	74.7(13)	47.2(11)	93.6(17)	19.5(10)	25.7(11)	22.6(10)
C29	99.2(19)	57.9(14)	183(3)	40.6(17)	62.0(19)	20.3(13)

Table 11. Bond Lengths for 19p.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C6	1.3583(17)	C12	C13	1.381(2)
O1	C9	1.3964(16)	C12	C16	1.395(2)
O2	C6	1.2204(17)	C14	C16	1.487(2)
O3	C23	1.322(2)	C14	C17	1.382(2)
O3	C28	1.457(2)	C14	C21	1.392(2)
O4	C22	1.3270(18)	N15	C19	1.133(2)
C5	C6	1.442(2)	C17	C27	1.382(2)
C5	C10	1.5149(19)	C18	C19	1.473(2)
C5	C22	1.355(2)	C18	C20	1.549(2)
C7	C9	1.376(2)	C18	C23	1.530(2)
C7	C16	1.387(2)	C20	C24	1.510(2)
O8	C23	1.1911(17)	C21	C26	1.385(2)
C9	C11	1.3872(19)	C22	C24	1.487(2)

C10	C11	1.514(2)	C25	C26	1.366(3)
C10	C18	1.5595(18)	C25	C27	1.373(3)
C11	C13	1.389(2)	C28	C29	1.459(3)

Table 12. Bond Angles for 19p.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	O1	C9	119.80(11)	C7	C16	C14	121.58(13)
C23	O3	C28	117.29(14)	C12	C16	C14	121.36(14)
C6	C5	C10	118.76(12)	C27	C17	C14	121.70(17)
C22	C5	C6	117.56(13)	C19	C18	C10	109.84(12)
C22	C5	C10	123.57(13)	C19	C18	C20	108.73(12)
O1	C6	C5	119.35(13)	C19	C18	C23	109.17(12)
O2	C6	O1	115.42(13)	C20	C18	C10	108.85(11)
O2	C6	C5	125.23(14)	C23	C18	C10	113.15(12)
C9	C7	C16	120.42(13)	C23	C18	C20	106.99(12)
C7	C9	O1	114.61(12)	N15	C19	C18	176.13(17)
C7	C9	C11	123.49(13)	C24	C20	C18	111.60(13)
C11	C9	O1	121.89(13)	C26	C21	C14	120.59(16)
C5	C10	C18	111.07(11)	O4	C22	C5	124.56(14)
C11	C10	C5	109.60(12)	O4	C22	C24	112.57(13)
C11	C10	C18	115.35(11)	C5	C22	C24	122.84(14)
C9	C11	C10	118.70(13)	O3	C23	C18	109.82(12)
C9	C11	C13	115.62(14)	O8	C23	O3	125.05(16)
C13	C11	C10	125.62(13)	O8	C23	C18	125.08(16)
C13	C12	C16	121.54(15)	C22	C24	C20	112.53(13)
C12	C13	C11	121.84(14)	C26	C25	C27	119.63(17)
C17	C14	C16	120.91(14)	C25	C26	C21	120.72(17)
C17	C14	C21	117.54(15)	C25	C27	C17	119.82(18)
C21	C14	C16	121.54(14)	O3	C28	C29	107.89(17)

Table 13. Torsion Angles for 19p.

A	B	C	D	Angle/°
O1	C9	C11	C10	-3.4(2)
O1	C9	C11	C13	179.24(13)
O4	C22	C24	C20	-163.03(14)
C5	C10	C11	C9	29.67(17)
C5	C10	C11	C13	-153.28(14)
C5	C10	C18	C19	72.41(15)
C5	C10	C18	C20	-46.52(16)
C5	C10	C18	C23	-165.32(12)
C5	C22	C24	C20	18.8(2)
C6	O1	C9	C7	159.49(13)
C6	O1	C9	C11	-21.59(19)
C6	C5	C10	C11	-34.97(17)

C6	C5	C10	C18	-163.61(13)
C6	C5	C22	O4	0.2(2)
C6	C5	C22	C24	178.19(14)
C7	C9	C11	C10	175.40(13)
C7	C9	C11	C13	-1.9(2)
C9	O1	C6	O2	-163.82(13)
C9	O1	C6	C5	15.74(19)
C9	C7	C16	C12	1.1(2)
C9	C7	C16	C14	-178.47(13)
C9	C11	C13	C12	1.3(2)
C10	C5	C6	O1	13.9(2)
C10	C5	C6	O2	-166.57(14)
C10	C5	C22	O4	176.45(14)
C10	C5	C22	C24	-5.6(2)
C10	C11	C13	C12	-175.82(15)
C10	C18	C19	N15	-73(3)
C10	C18	C20	C24	62.04(16)
C10	C18	C23	O3	54.57(17)
C10	C18	C23	O8	-127.66(16)
C11	C10	C18	C19	-53.07(16)
C11	C10	C18	C20	-172.00(12)
C11	C10	C18	C23	69.20(17)
C13	C12	C16	C7	-1.7(2)
C13	C12	C16	C14	177.86(14)
C14	C17	C27	C25	-0.4(3)
C14	C21	C26	C25	0.2(3)
C16	C7	C9	O1	179.66(12)
C16	C7	C9	C11	0.8(2)
C16	C12	C13	C11	0.5(2)
C16	C14	C17	C27	-178.72(15)
C16	C14	C21	C26	178.80(14)
C17	C14	C16	C7	153.19(14)
C17	C14	C16	C12	-26.4(2)
C17	C14	C21	C26	0.0(2)
C18	C10	C11	C9	155.91(13)
C18	C10	C11	C13	-27.0(2)
C18	C20	C24	C22	-47.08(18)
C19	C18	C20	C24	-57.58(16)
C19	C18	C23	O3	177.20(13)
C19	C18	C23	O8	-5.0(2)
C20	C18	C19	N15	46(3)
C20	C18	C23	O3	-65.30(15)
C20	C18	C23	O8	112.47(17)
C21	C14	C16	C7	-25.6(2)
C21	C14	C16	C12	154.90(15)

C21	C14	C17	C27	0.1(2)
C22	C5	C6	O1	-169.69(13)
C22	C5	C6	O2	9.8(2)
C22	C5	C10	C11	148.87(14)
C22	C5	C10	C18	20.2(2)
C23	O3	C28	C29	-165.02(19)
C23	C18	C19	N15	162(3)
C23	C18	C20	C24	-175.37(12)
C26	C25	C27	C17	0.6(3)
C27	C25	C26	C21	-0.5(3)
C28	O3	C23	O8	-0.2(2)
C28	O3	C23	C18	177.61(15)

Table 14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 19p.

Atom	*x*	*y*	*z*	U(eq)
H4	5640	1757	7233	88
H7	4692	3785	10669	44
H10	4315	4570	7340	40
H12	1175	5291	9406	53
H13	1494	5023	7903	53
H17	1667	5999	10836	61
H20A	2037	3872	4971	54
H20B	3608	4208	5506	54
H21	3746	3654	11911	56
H24A	2510	2401	5559	56
H24B	3820	2674	5183	56
H25	2315	5343	13648	75
H26	3488	4011	13426	69
H27	1421	6348	12352	76
H28A	2203	6980	6482	86
H28B	1504	6690	5382	86
H29A	3712	6793	5105	163
H29B	4424	7064	6204	163
H29C	3335	7747	5506	163

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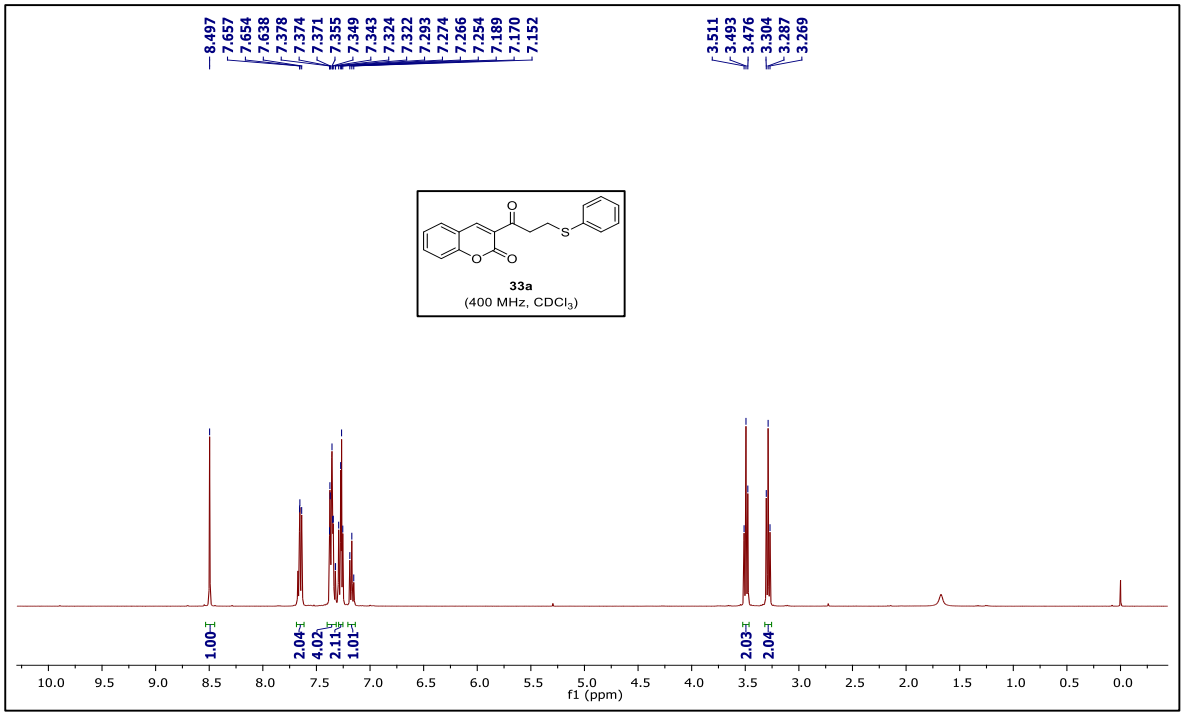
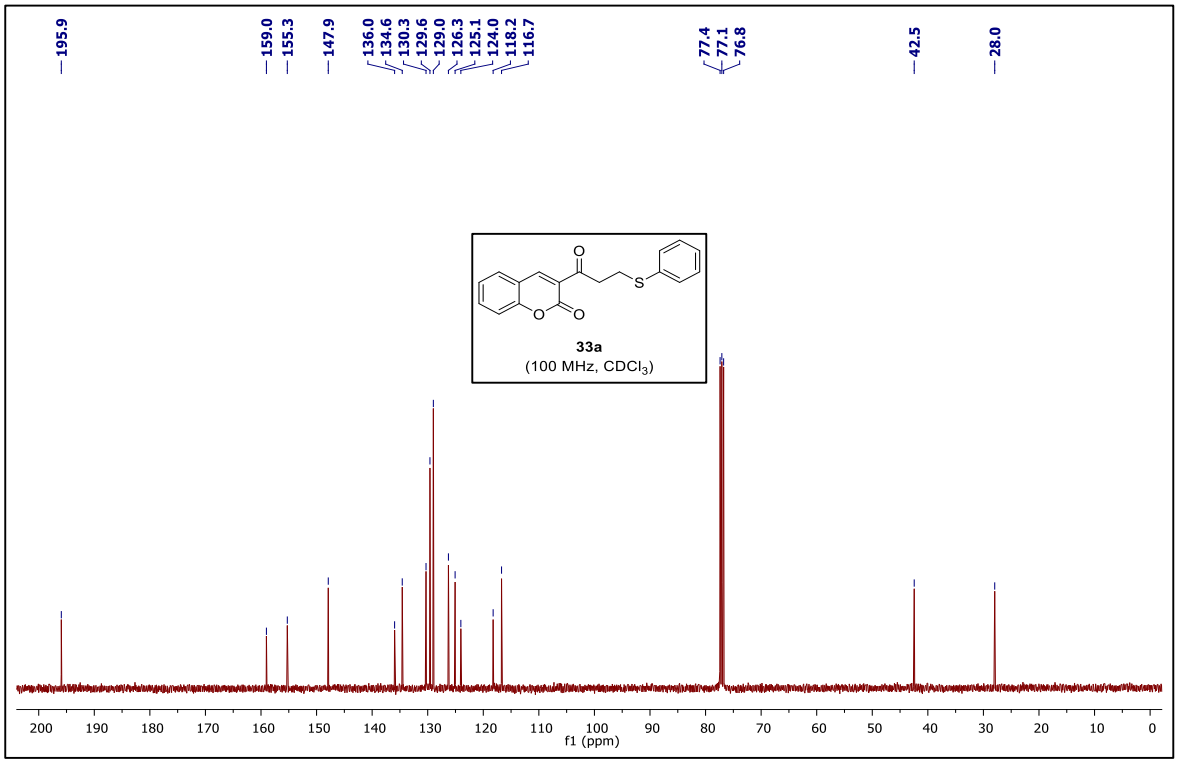
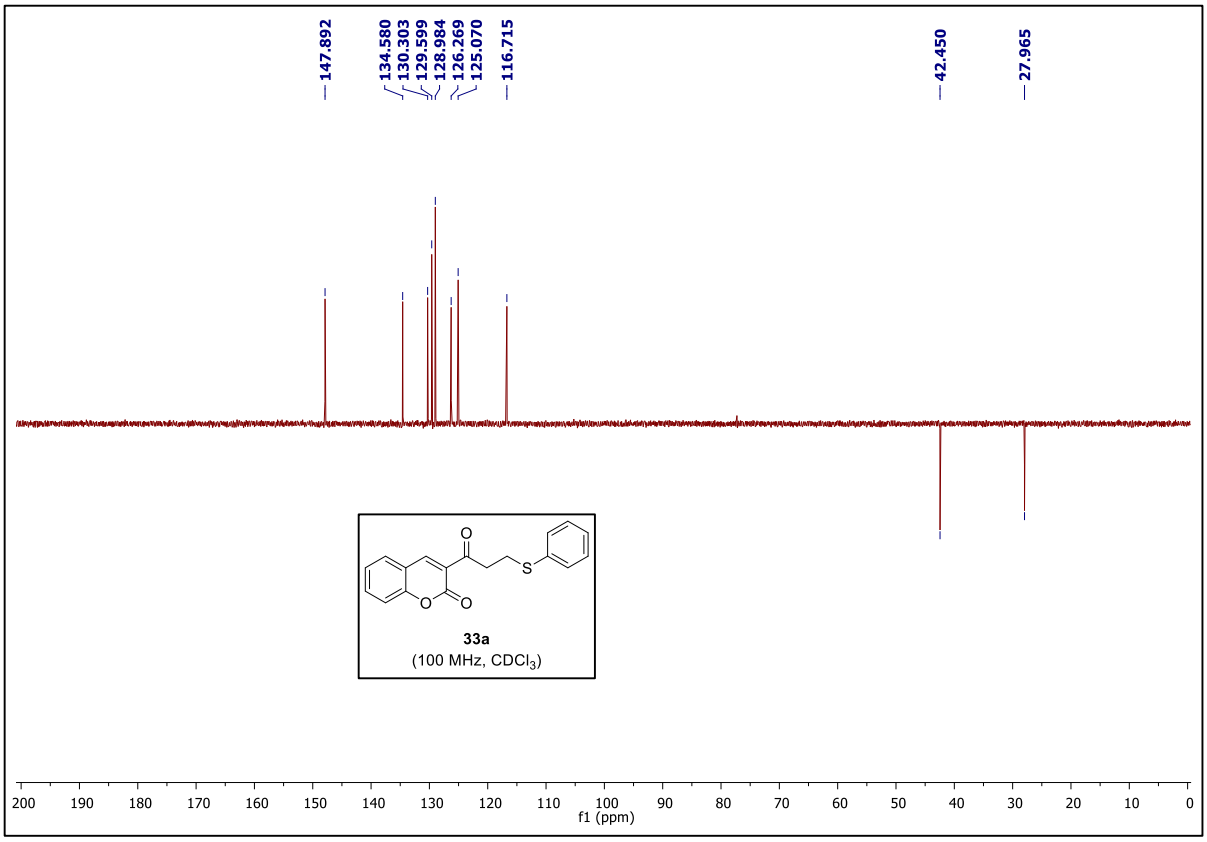


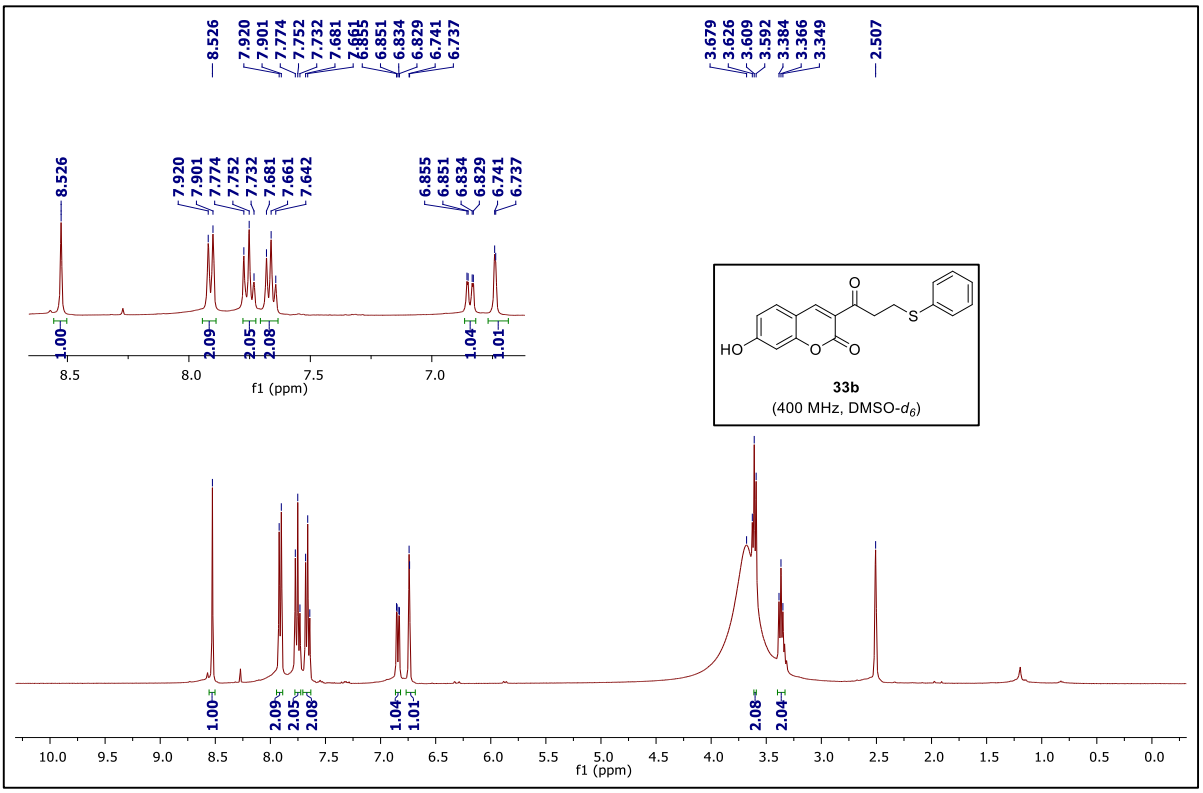
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33a**.



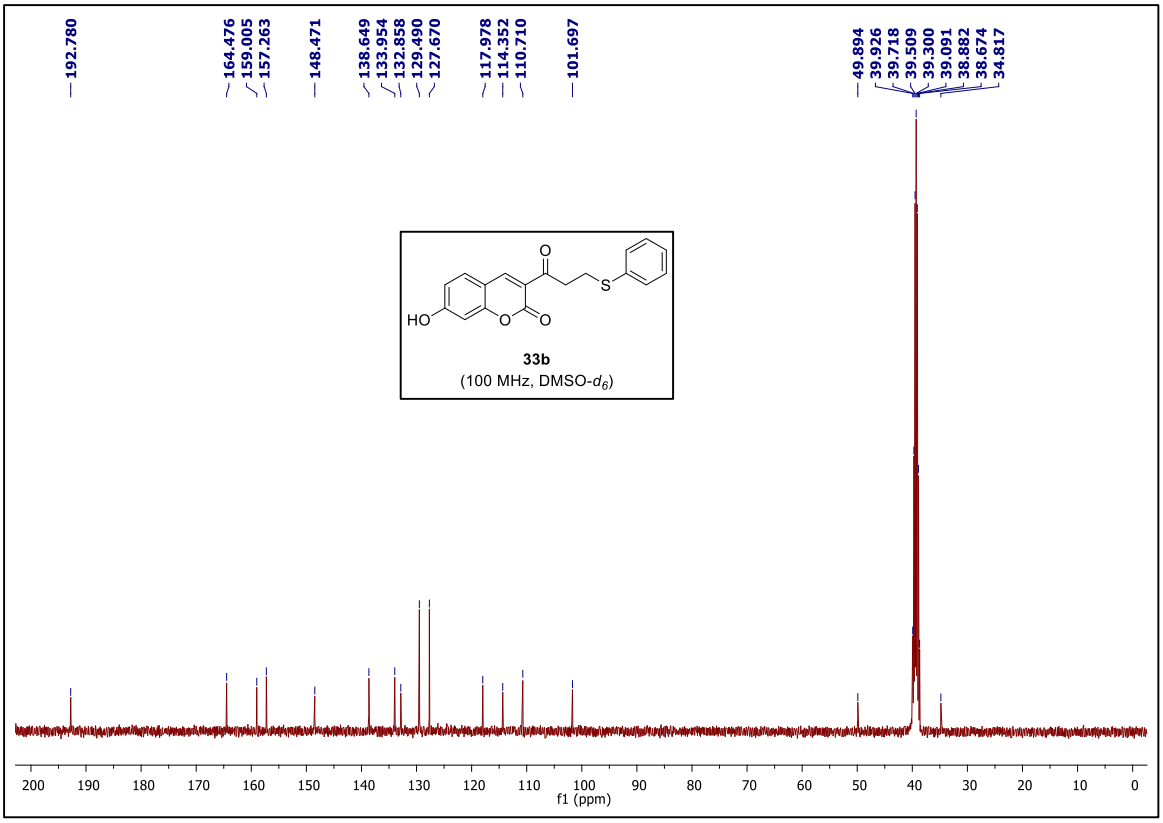
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(3-(phenylthio)propanoyl)-2*H*- chromen-2-one **33a**.



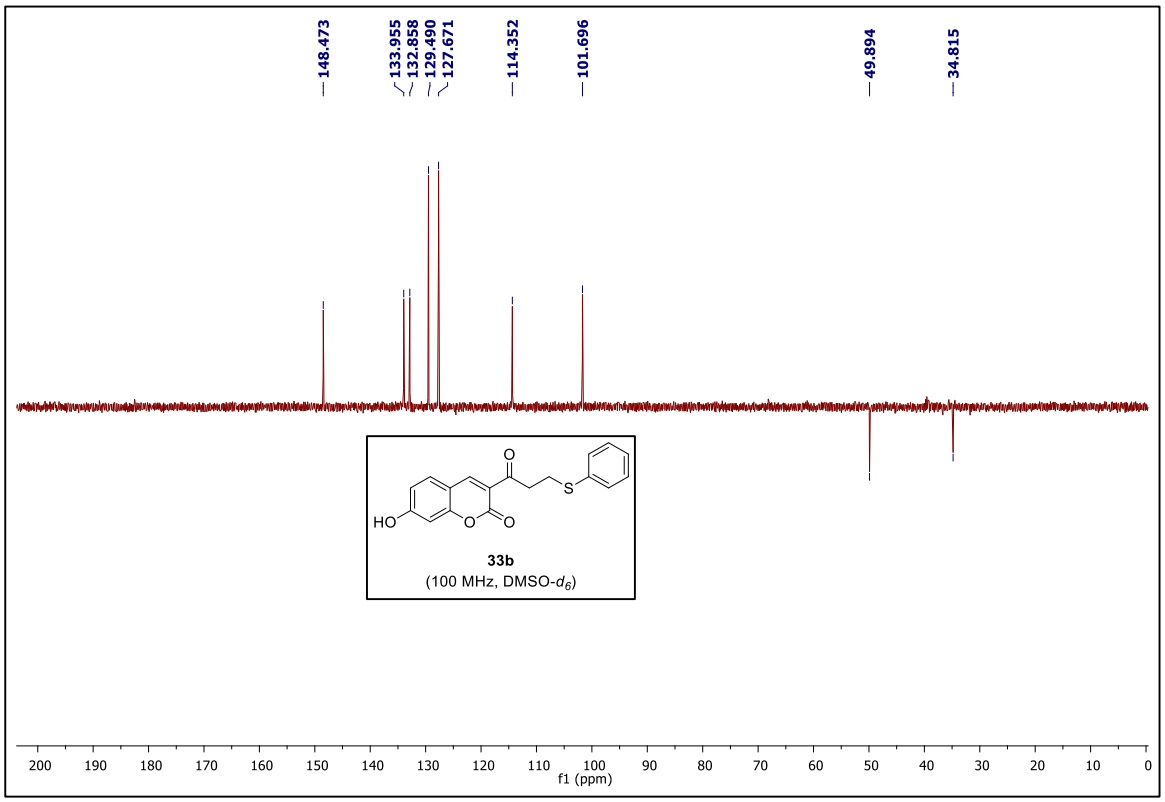
DEPT-135 NMR spectrum of 3-(3-(phenylthio)propanoyl)-2*H*-benzo[h]chromen-2-one **33a**.



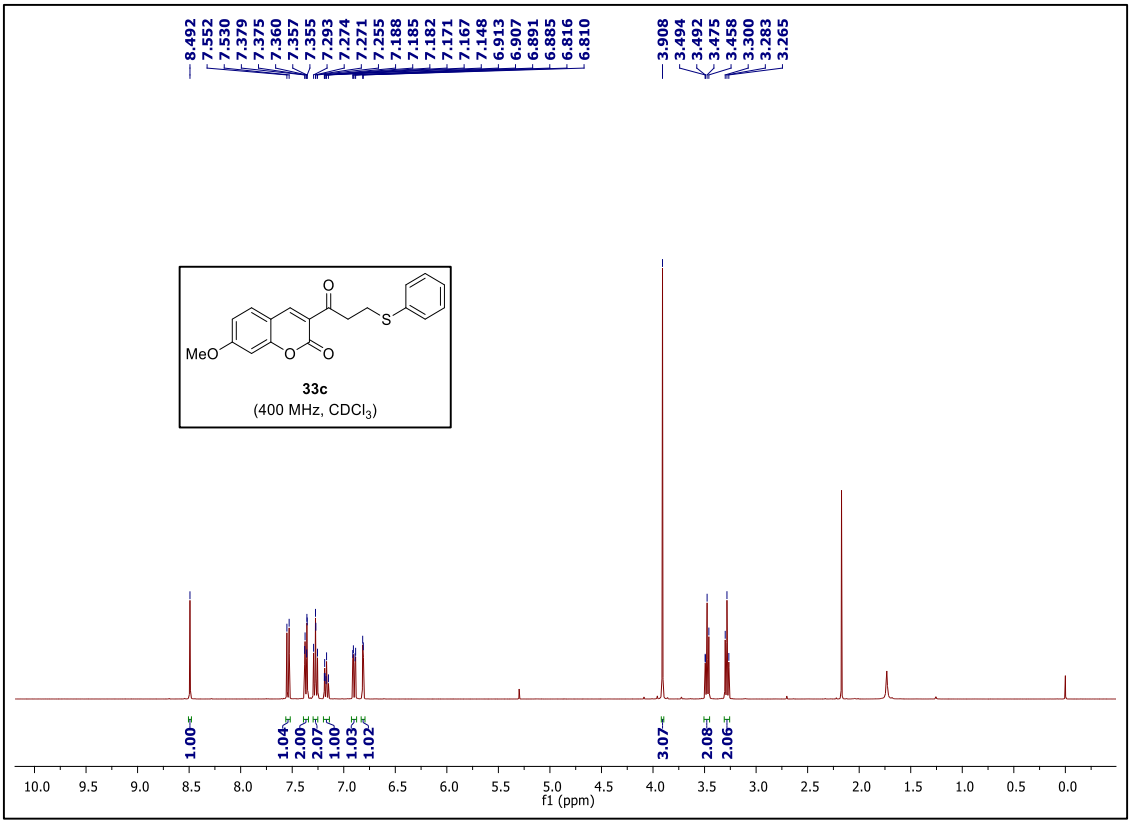
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 7-hydroxy-3-(3- phenylthio)propanoyl)-2*H*-chromen-2-one **33b**.



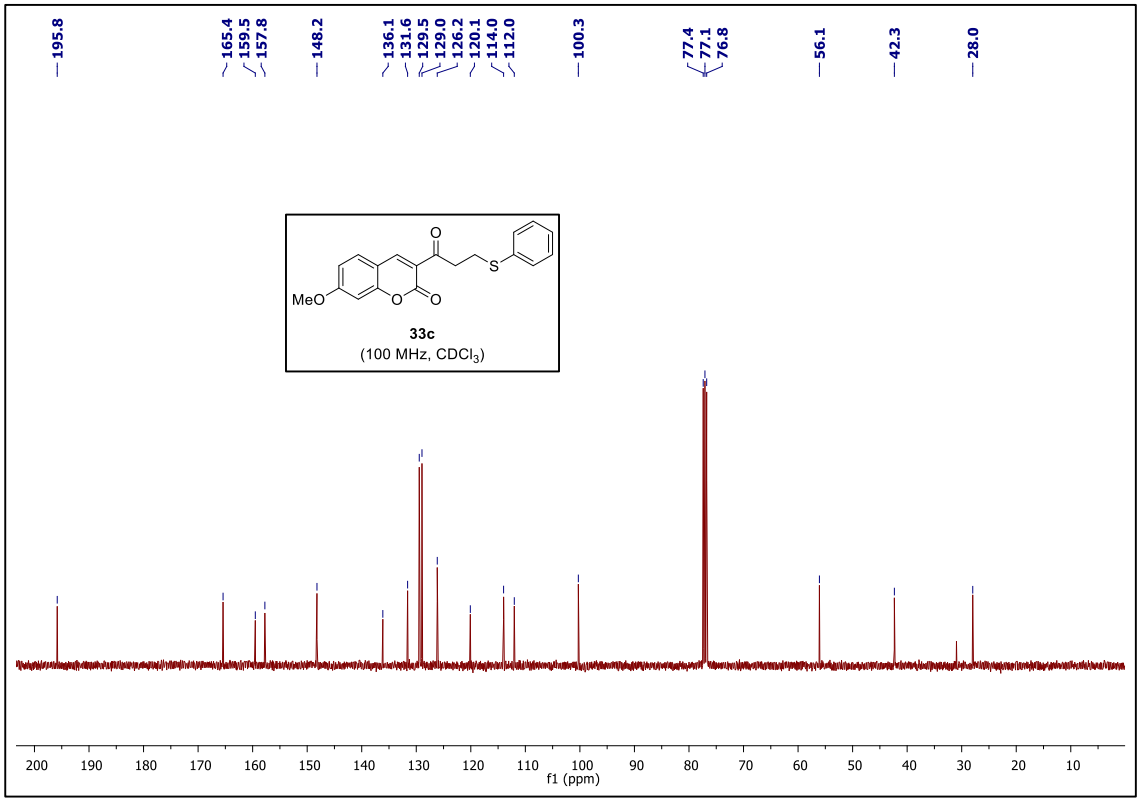
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 7-hydroxy-3-(3- phenylthio)propanoyl)-2*H*-chromen-2-one **33b**.



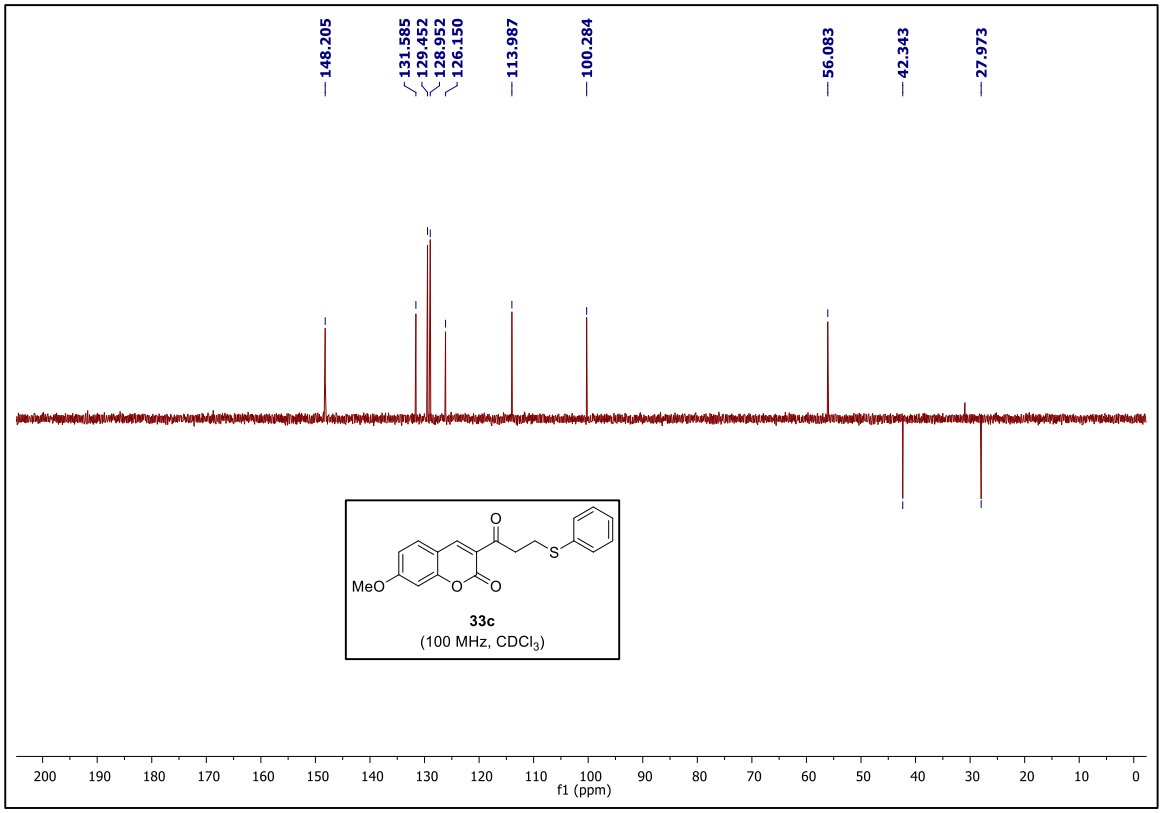
DEPT-135 NMR spectrum of 7-hydroxy-3-(3- phenylthio)propanoyl)-2*H*-chromen-2-one **33b**.



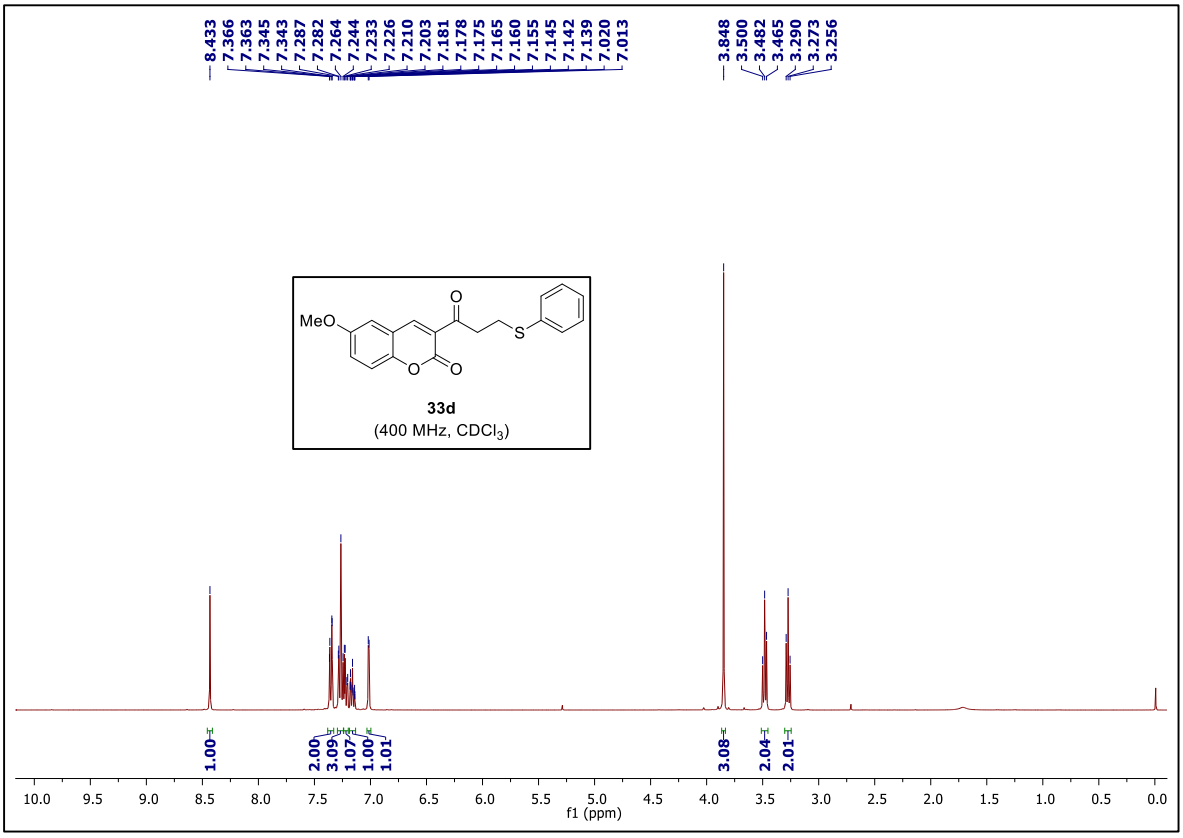
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33c**.



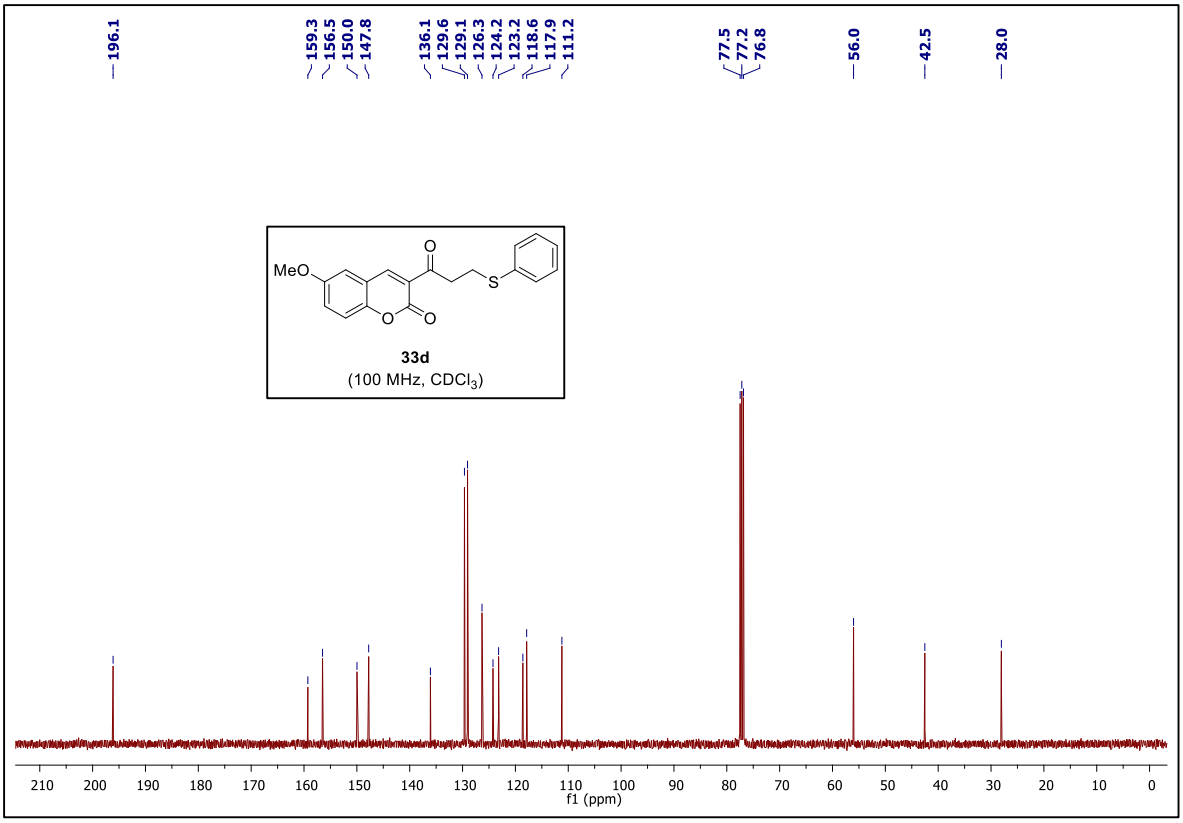
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33c**.



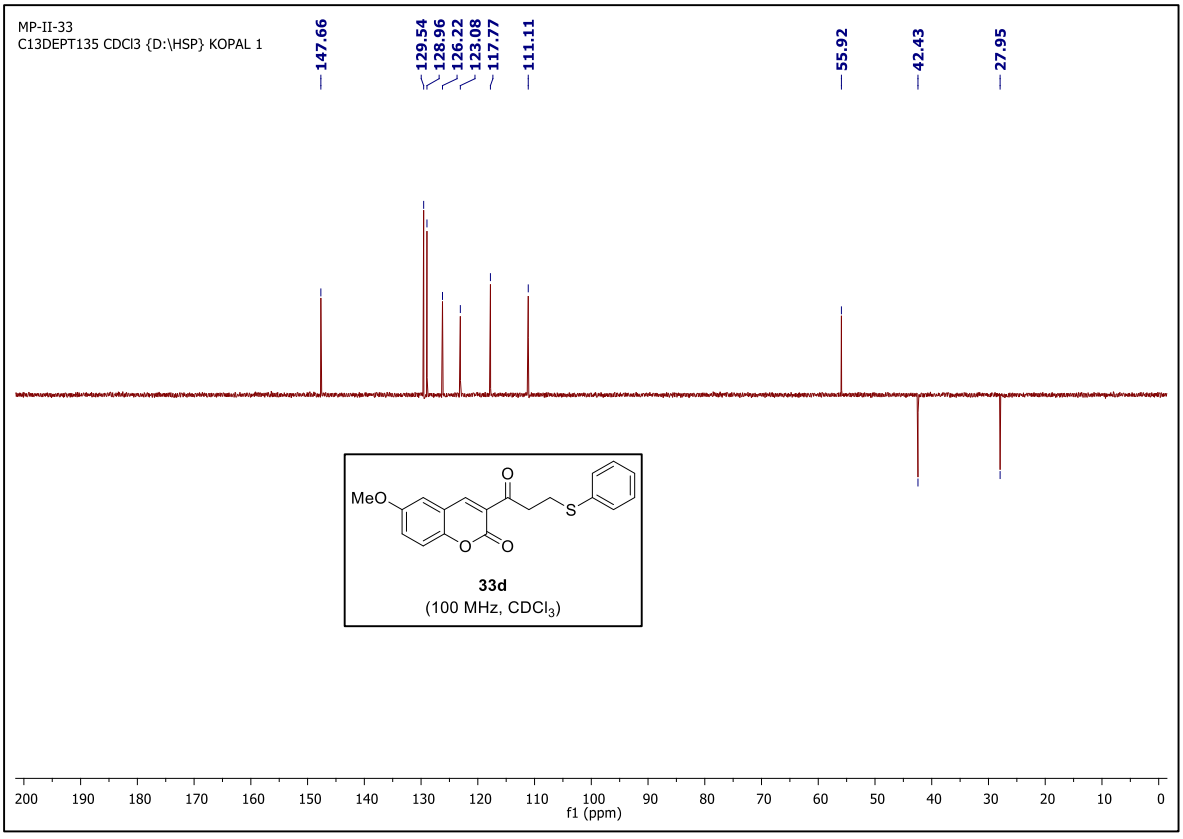
DEPT-135 NMR spectrum of 7-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33c**.



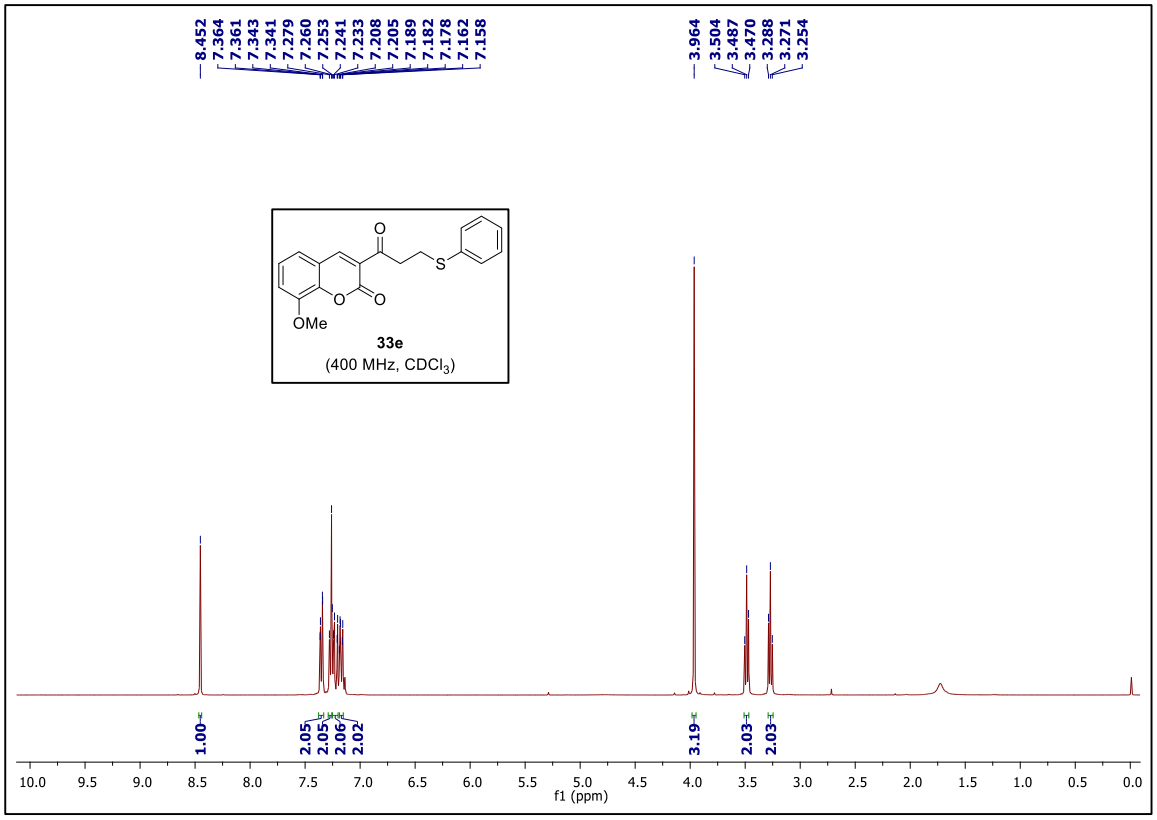
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-methoxy-3-(3-(phenylthio)propanoyl)-2$_H$-chromen-2-one **33d**.



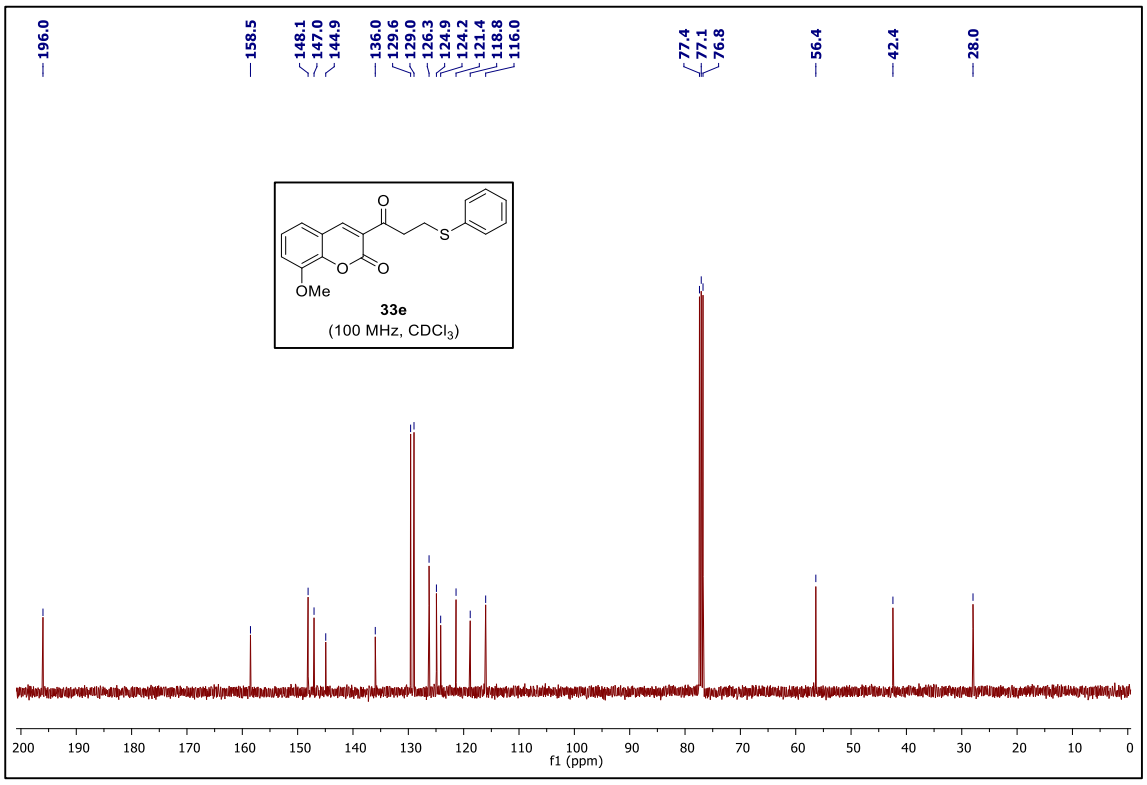
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33d**.



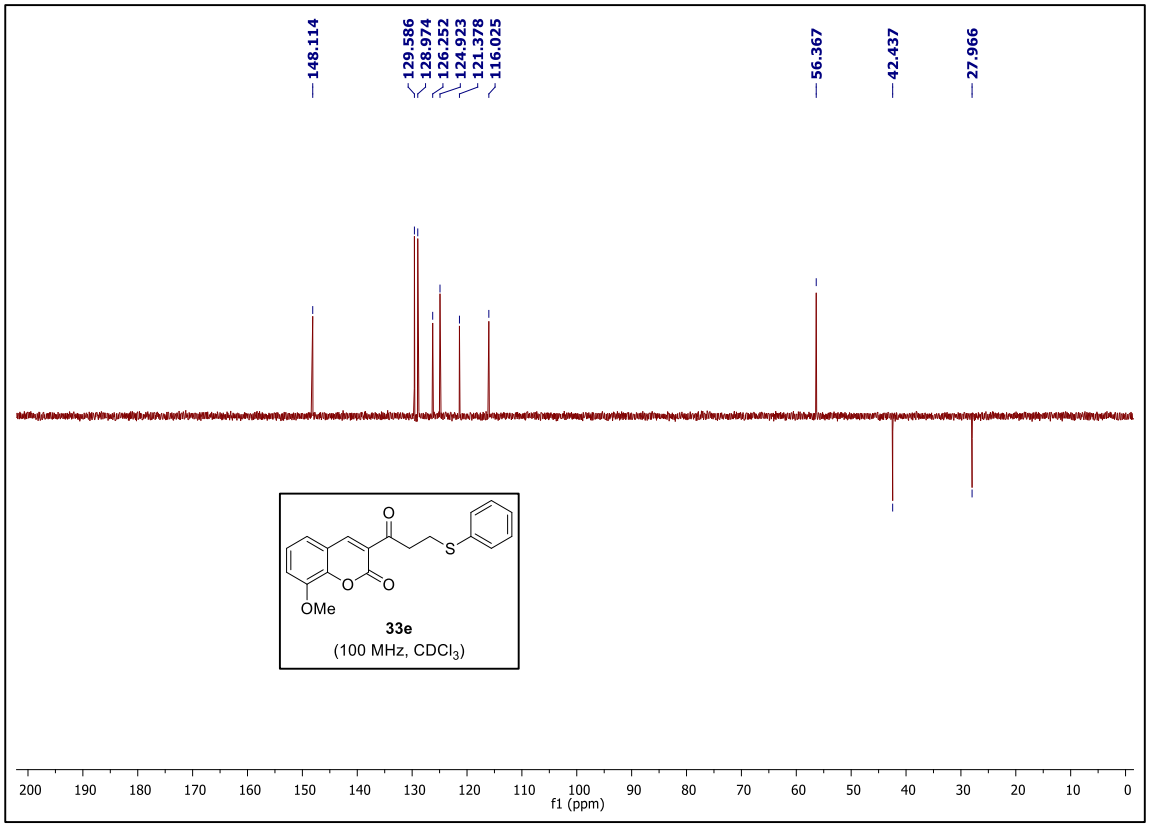
DEPT-135 NMR spectrum of 6-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33d**.



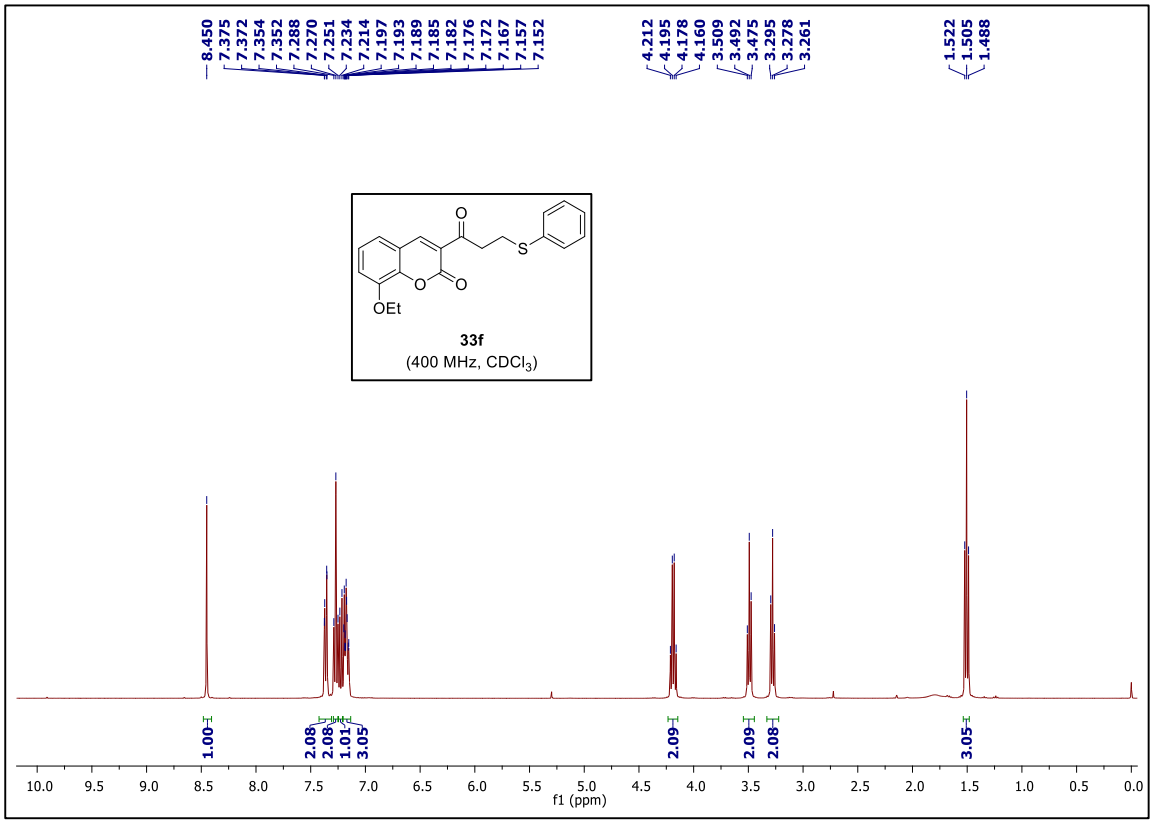
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33e**.



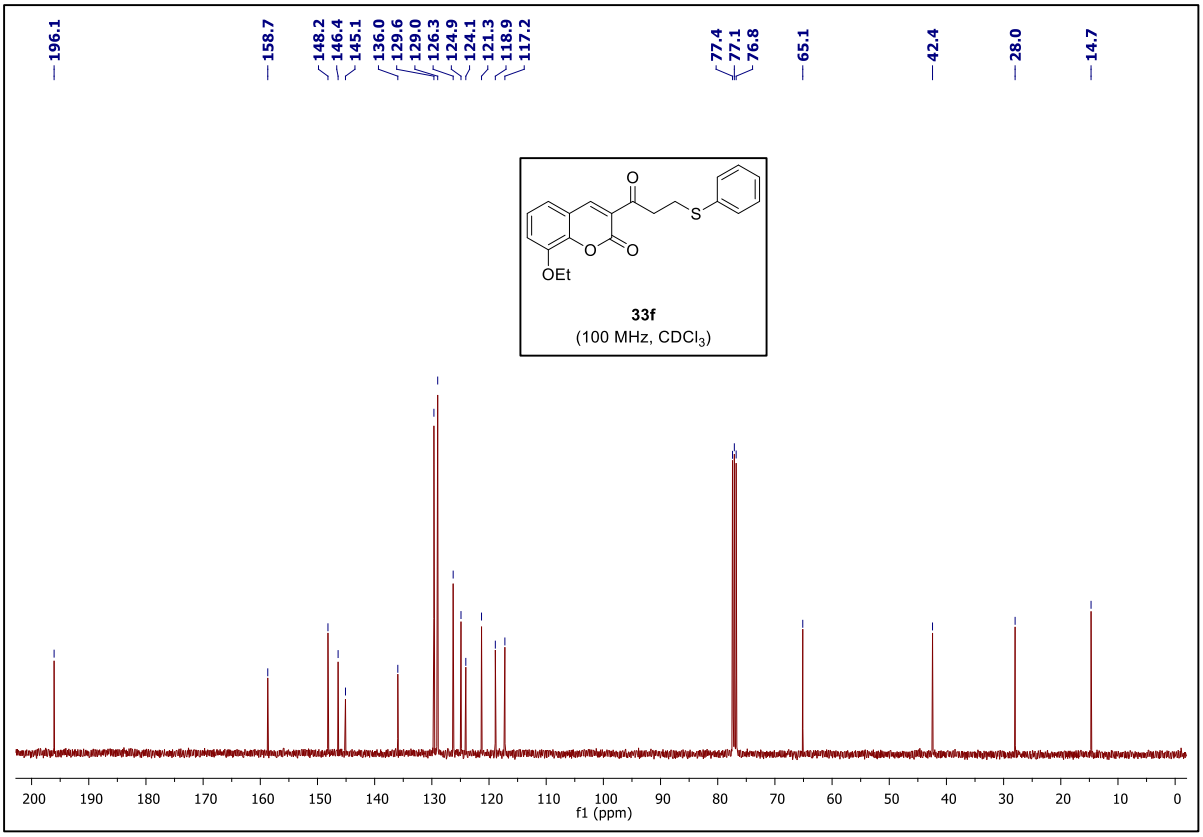
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33e**.



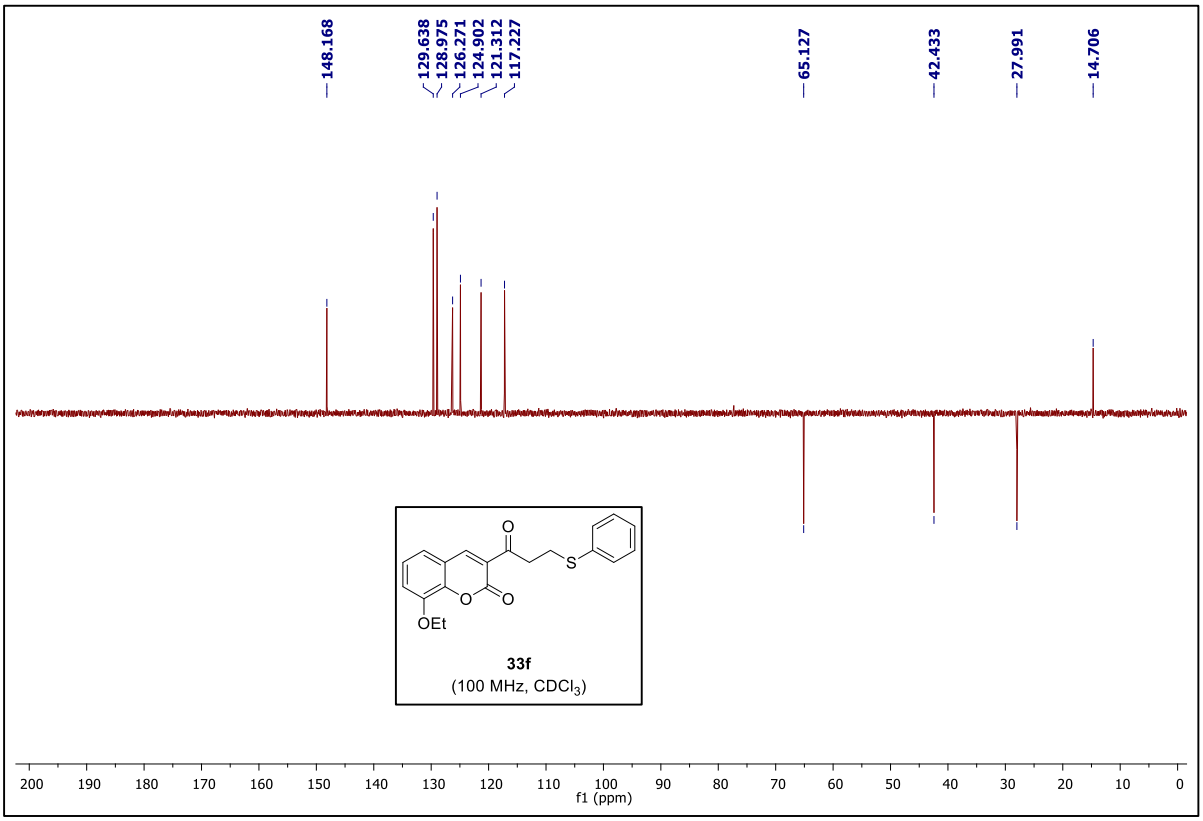
DEPT-135 NMR spectrum of 8-methoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33e**.



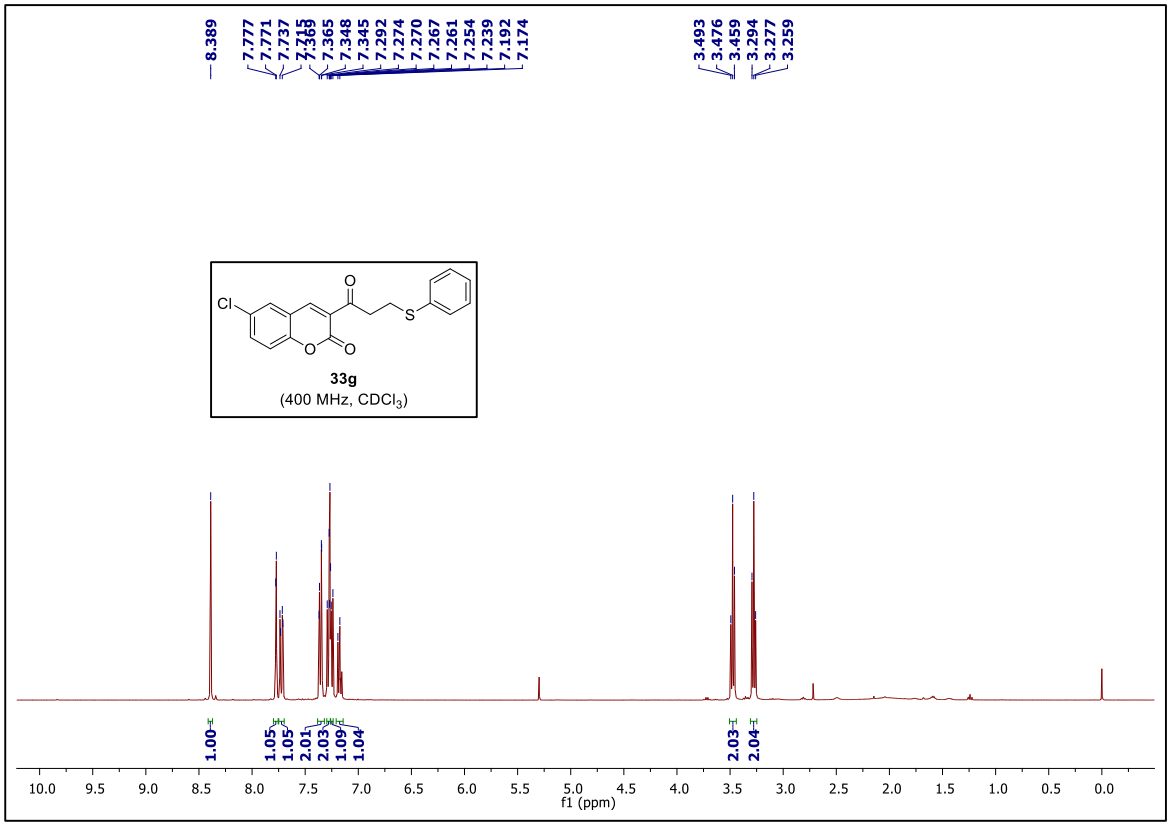
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8-ethoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33f**.



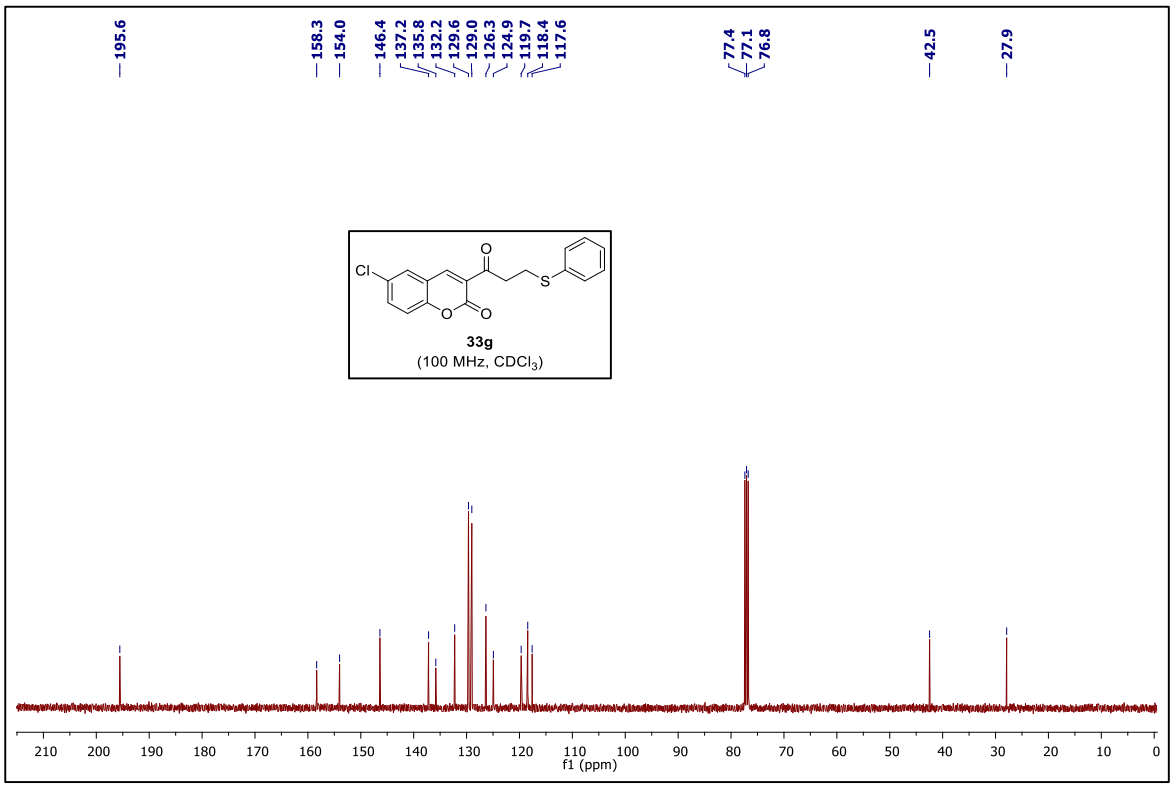
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8-ethoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33f**.



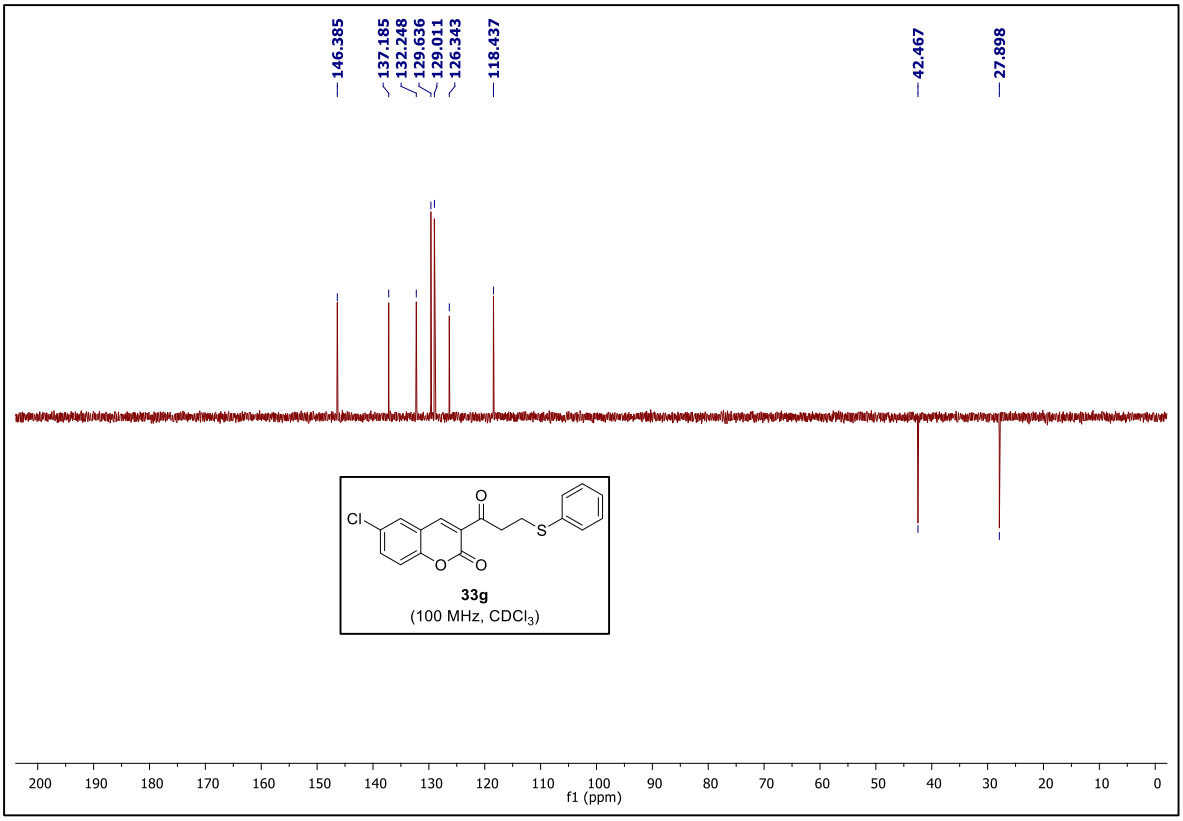
DEPT-135 NMR spectrum of 8-ethoxy-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33f**.



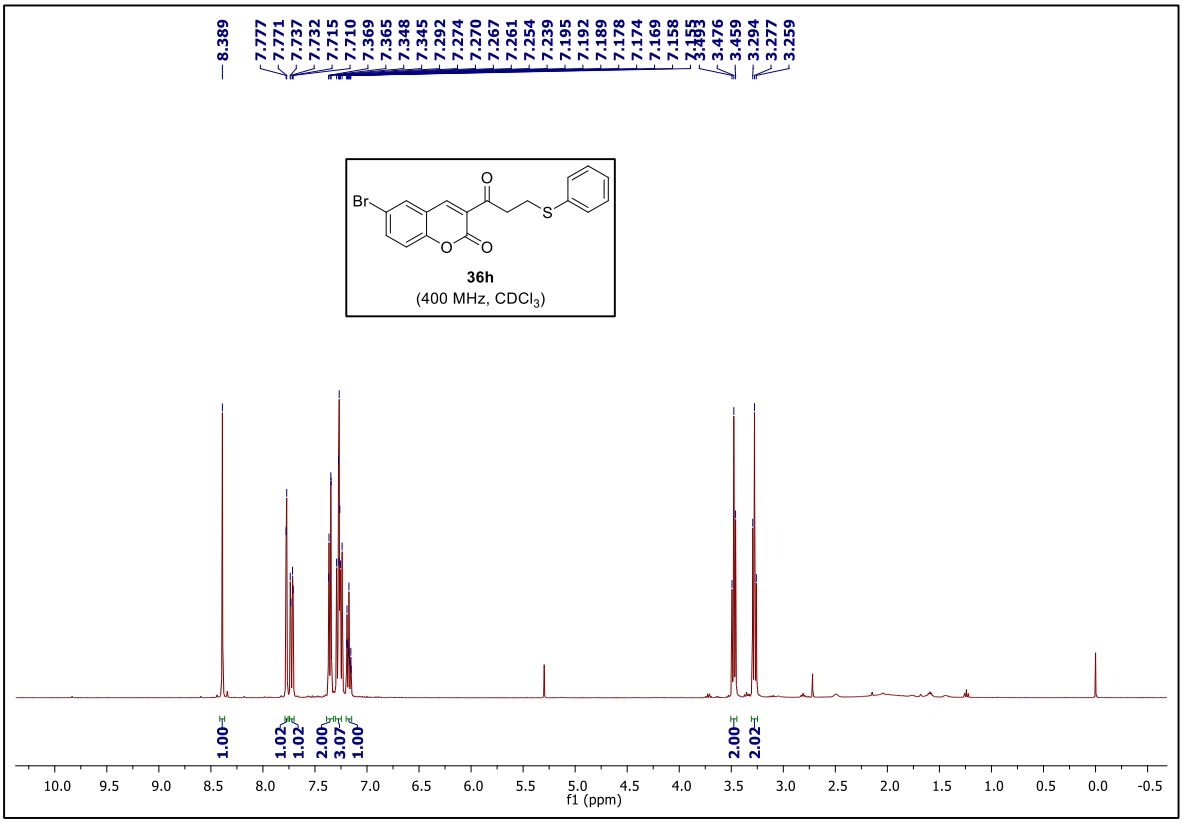
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-chloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33g**.



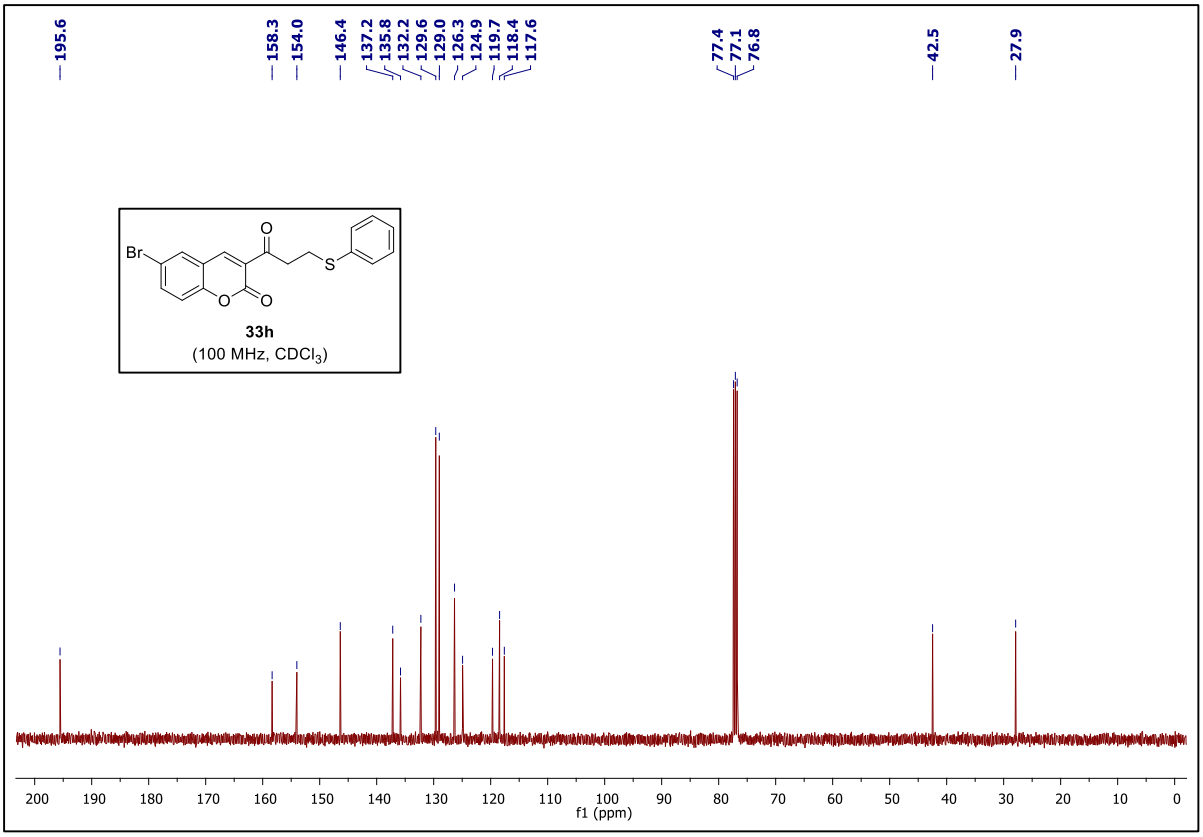
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6-chloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33g**.



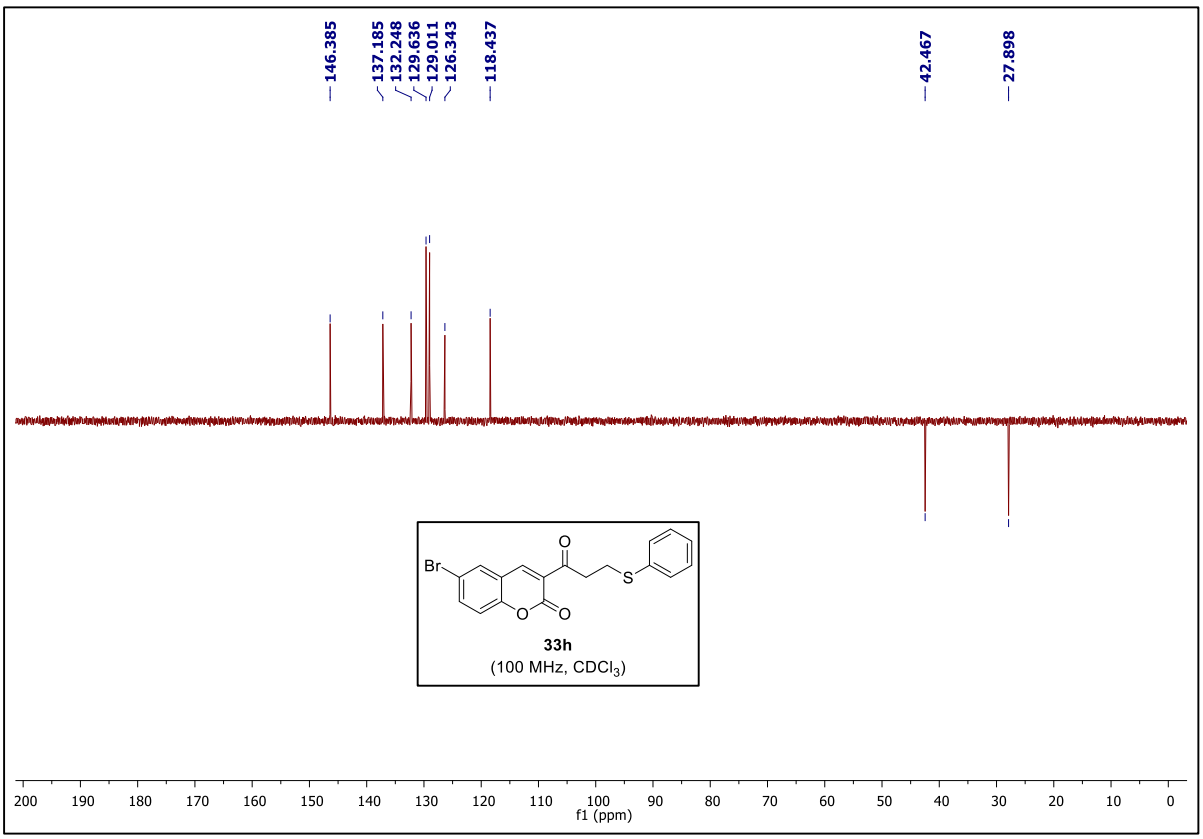
DEPT-135 NMR spectrum of 6-chloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33g**.



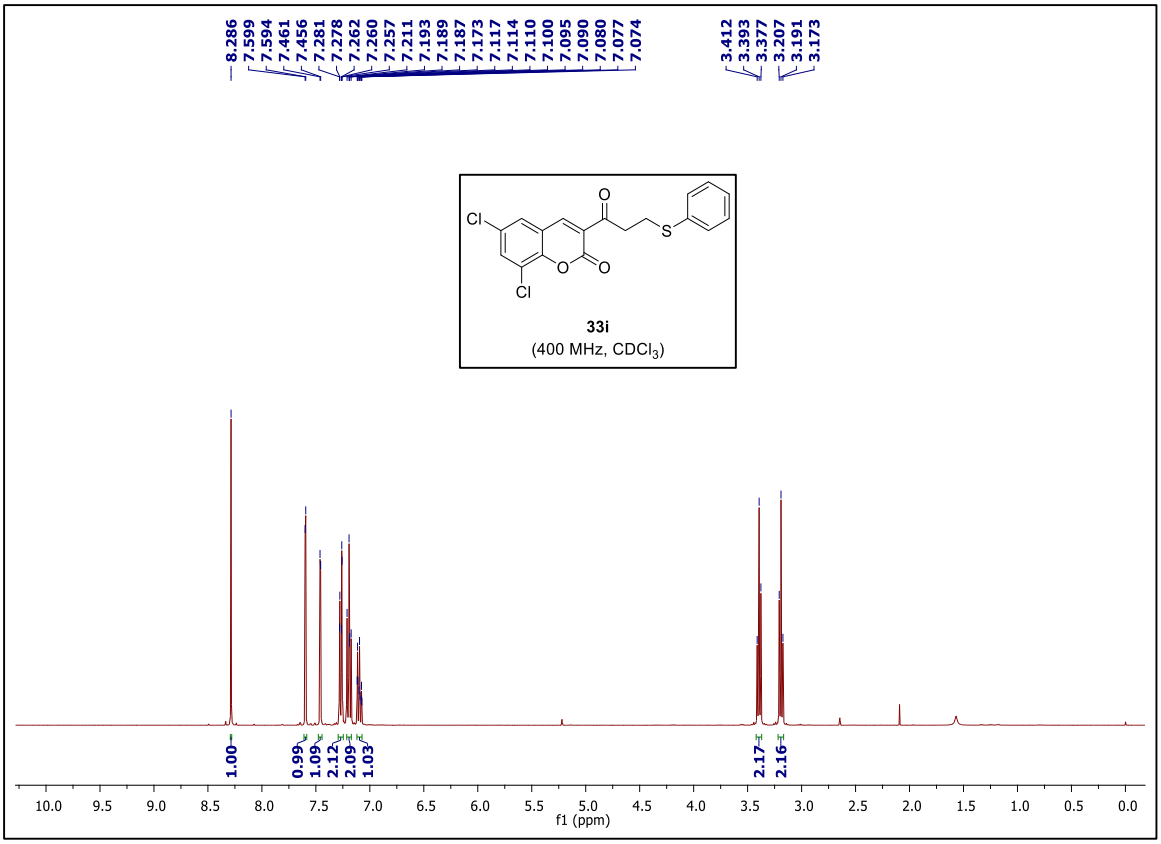
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-bromo-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33h**.



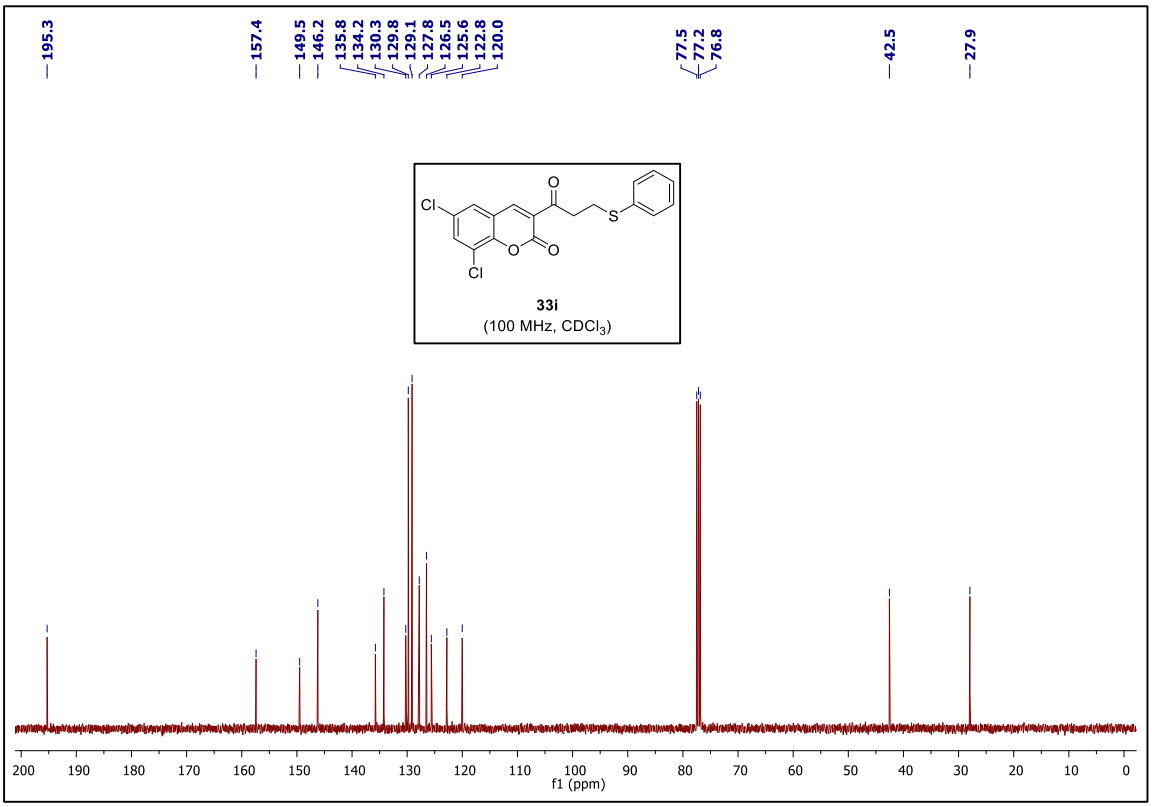
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6-bromo-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33h**.



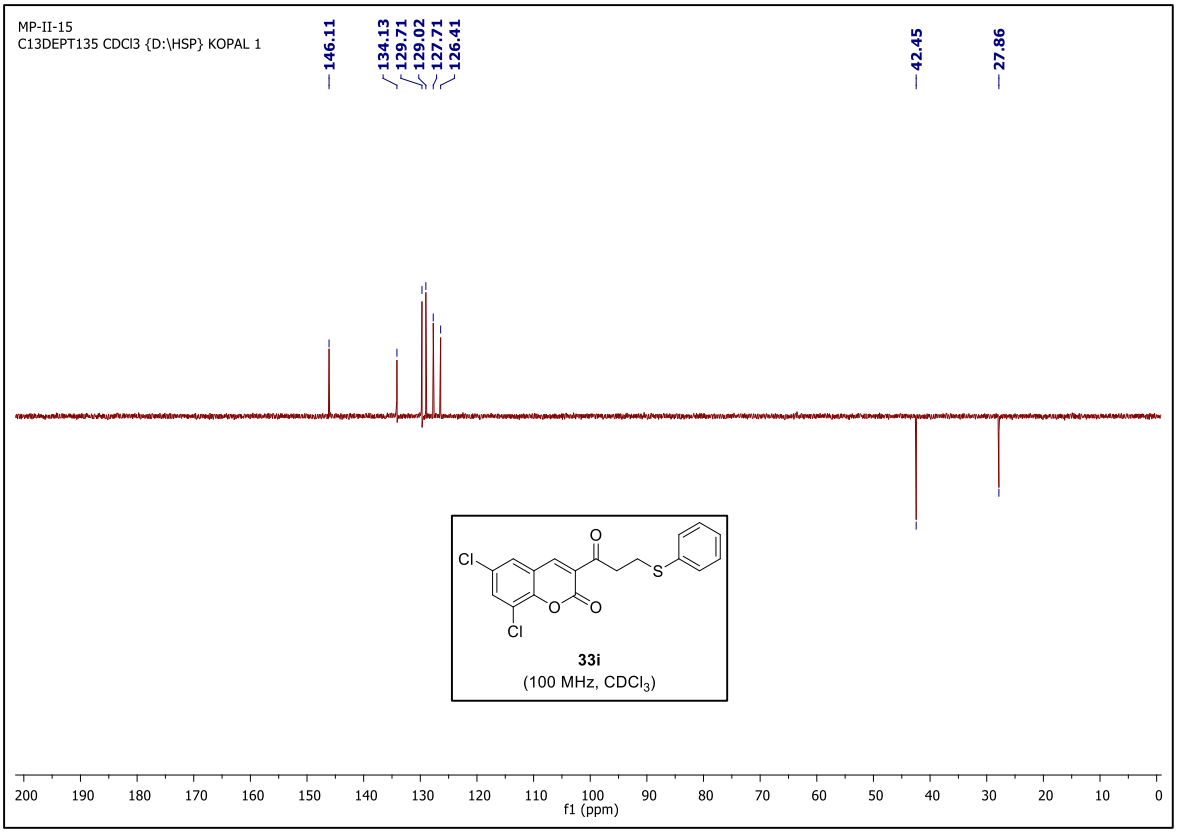
DEPT-135 NMR spectrum of 6-bromo-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33h**.



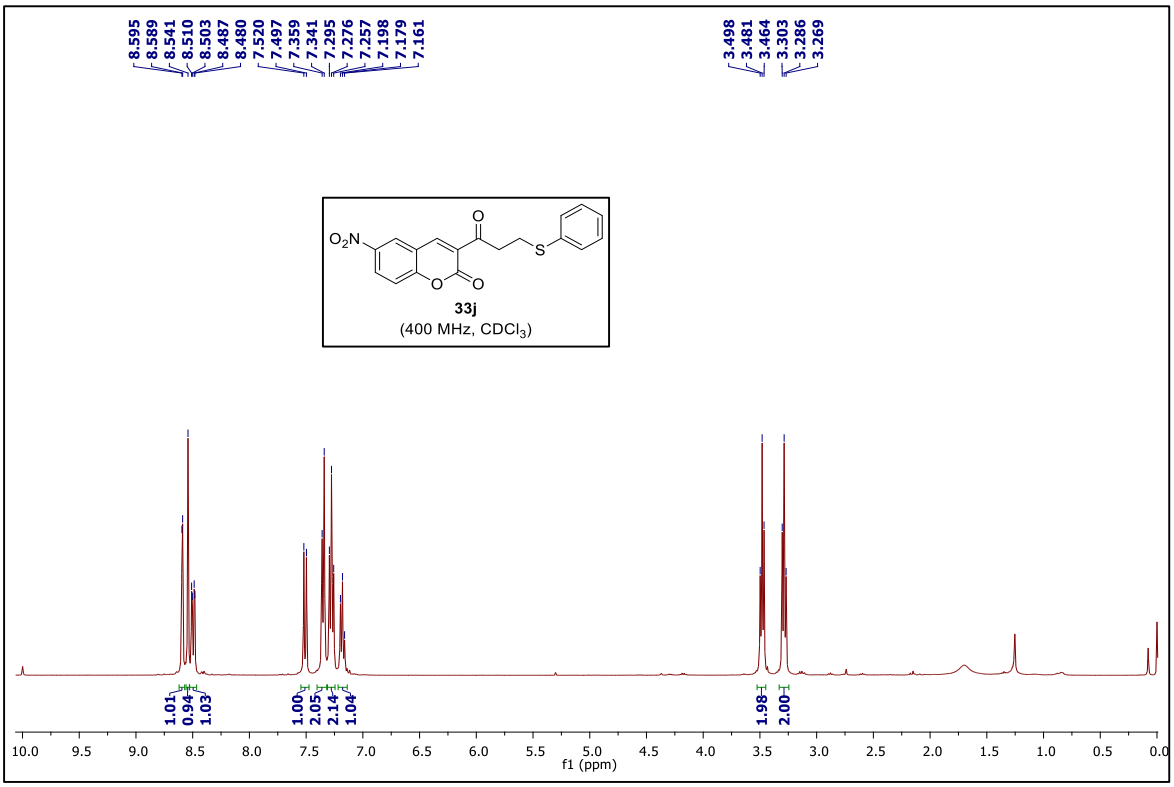
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6,8-dichloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33i**.



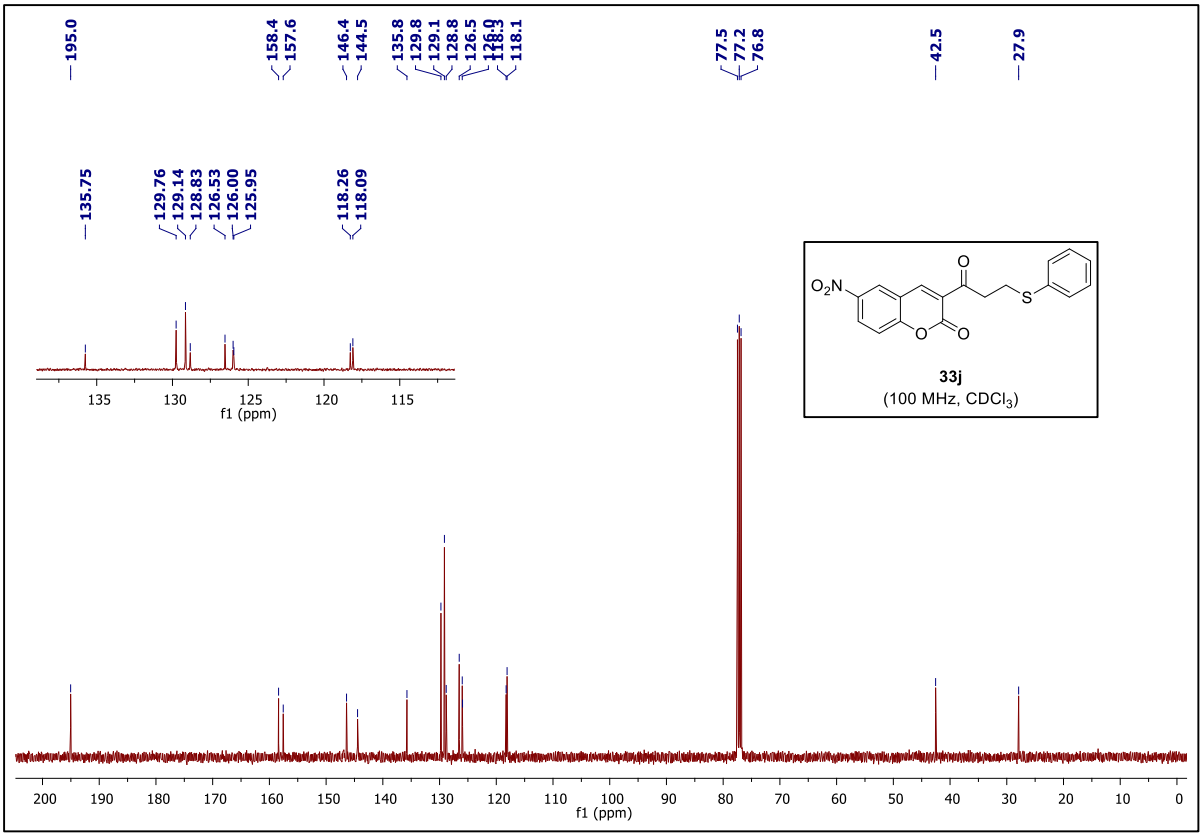
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6,8-dichloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33i**.



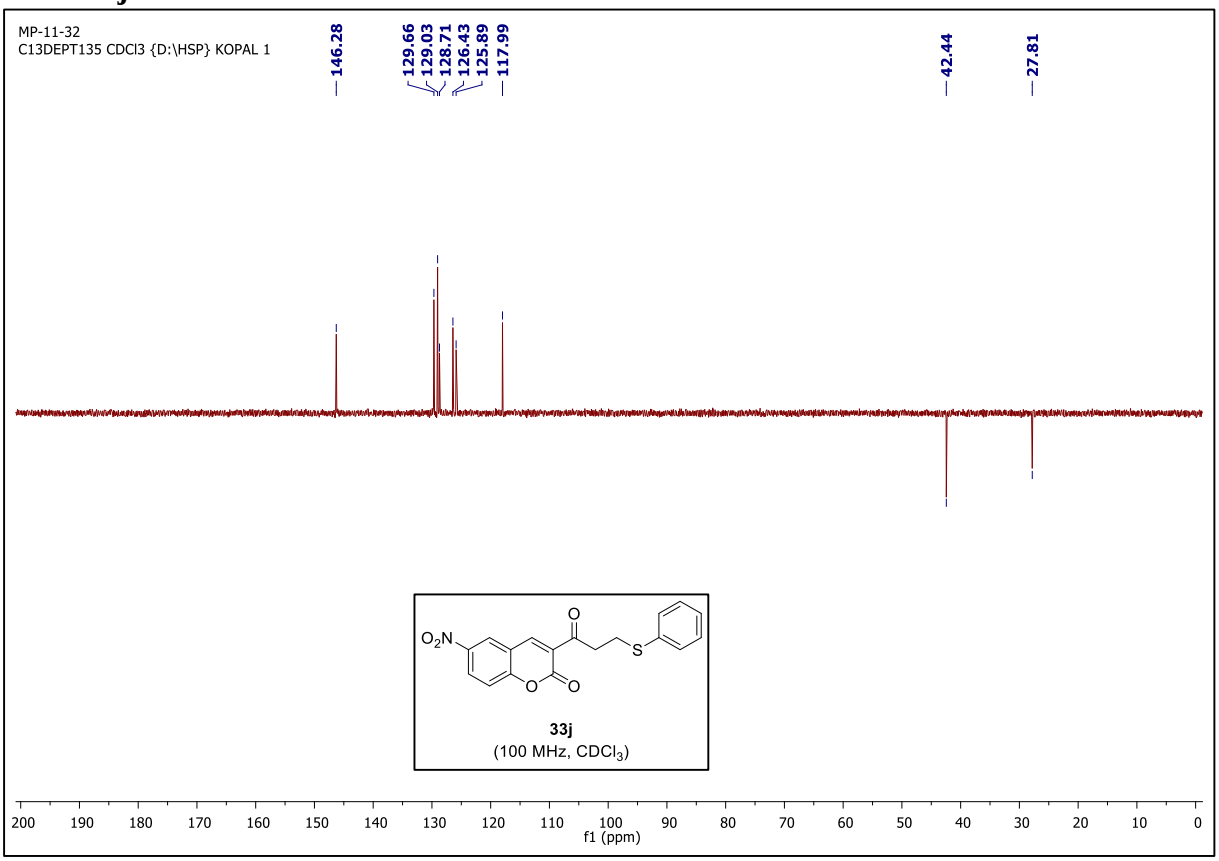
DEPT-135 NMR spectrum of 6,8-dichloro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33i**.



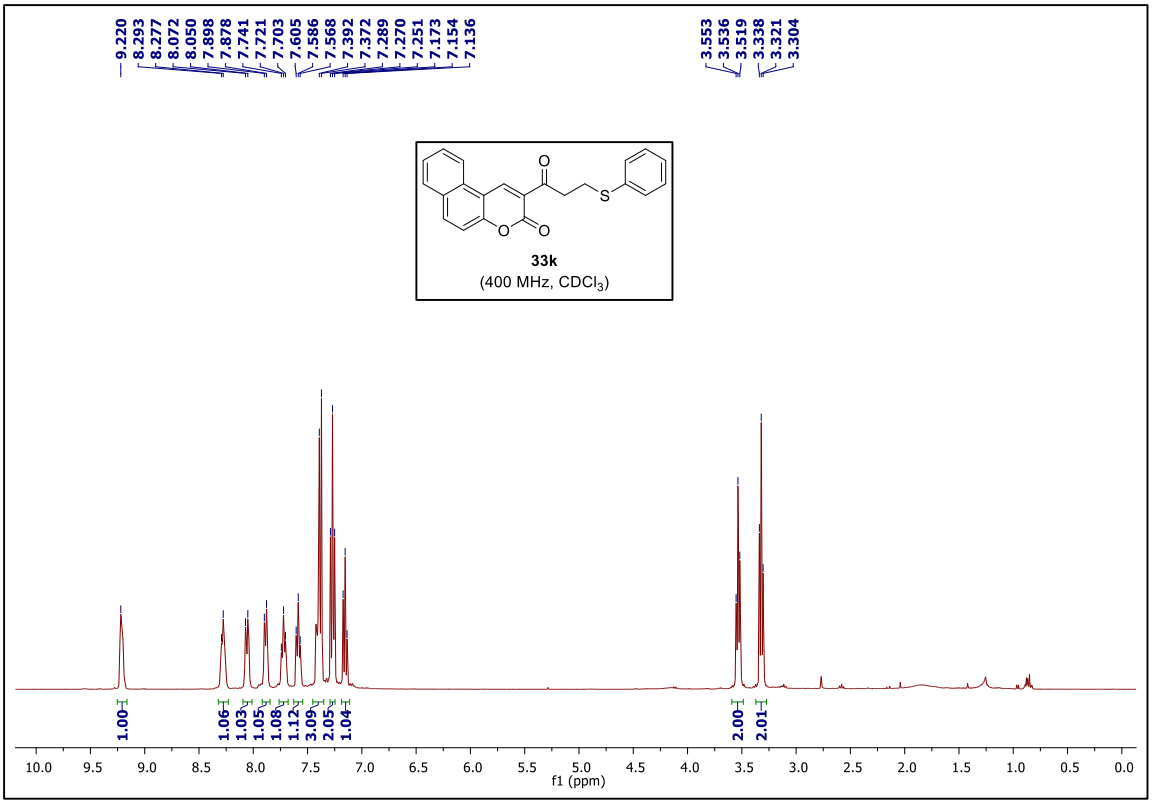
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-nitro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33j**.



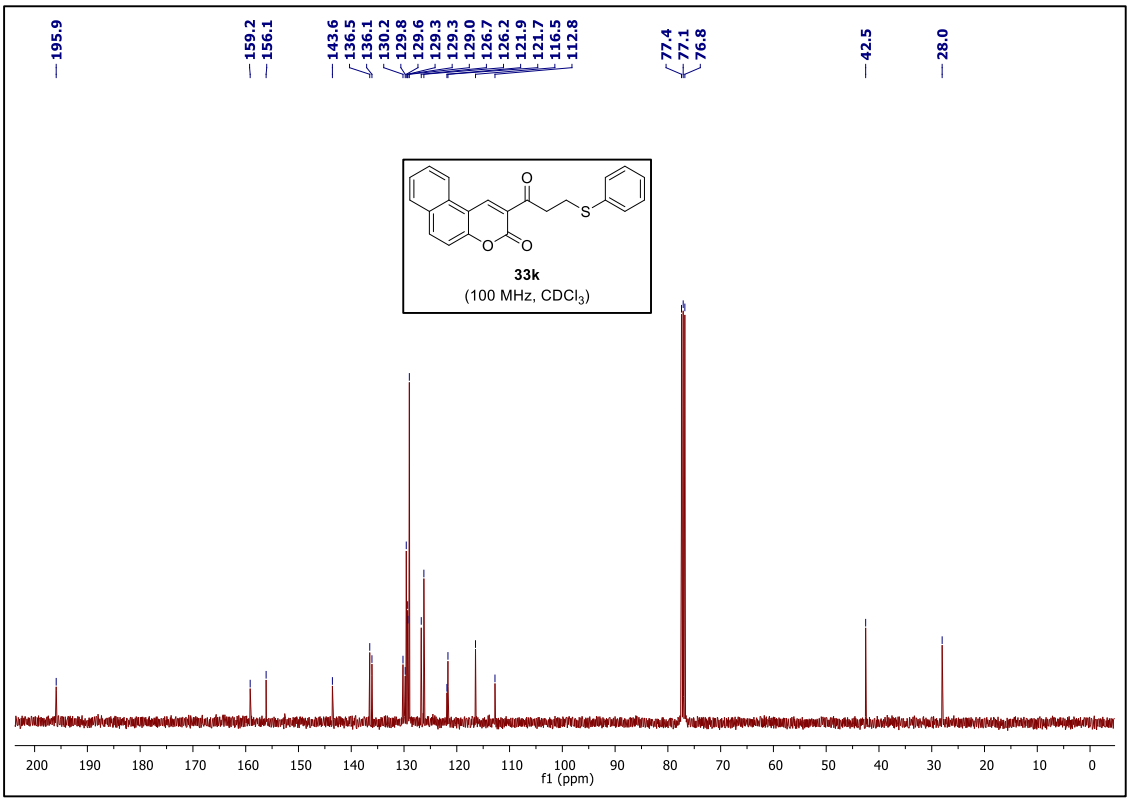
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6-nitro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33j**.



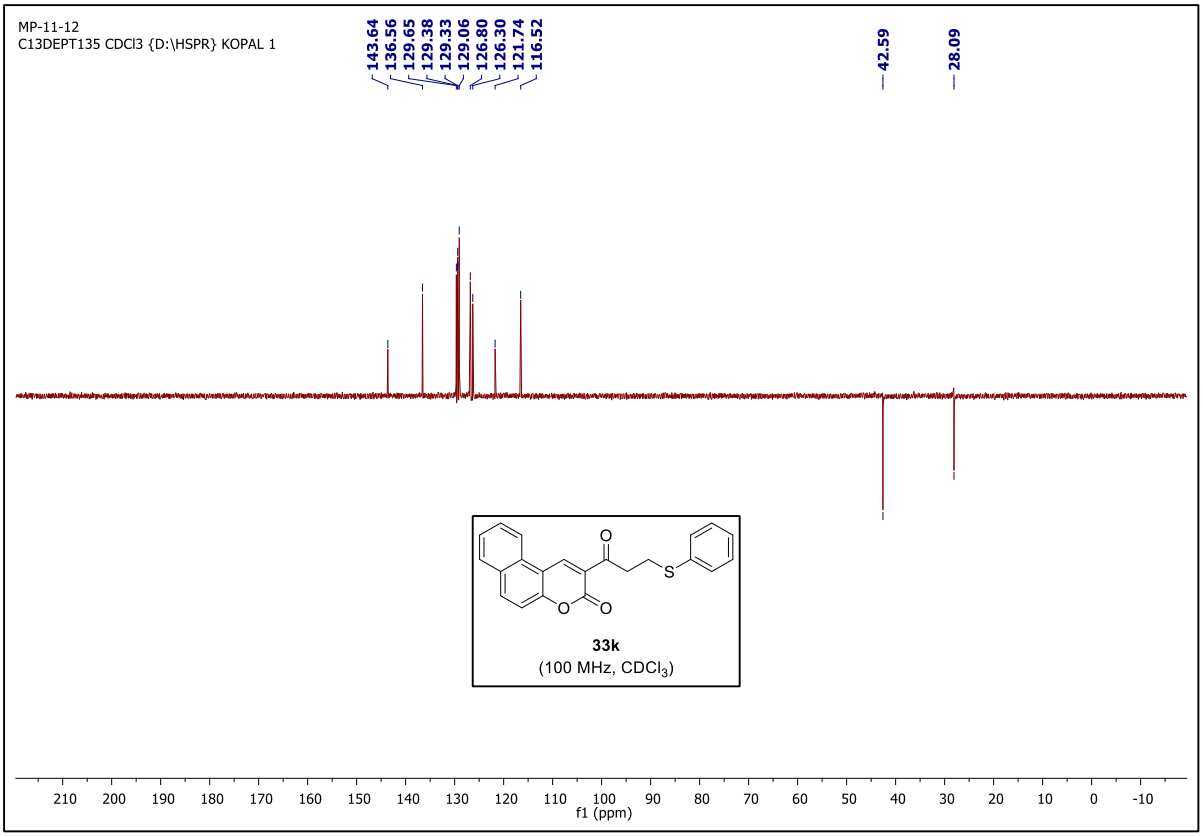
DEPT-135 NMR spectrum of 6-nitro-3-(3-(phenylthio)propanoyl)-2*H*-chromen-2-one **33j**.



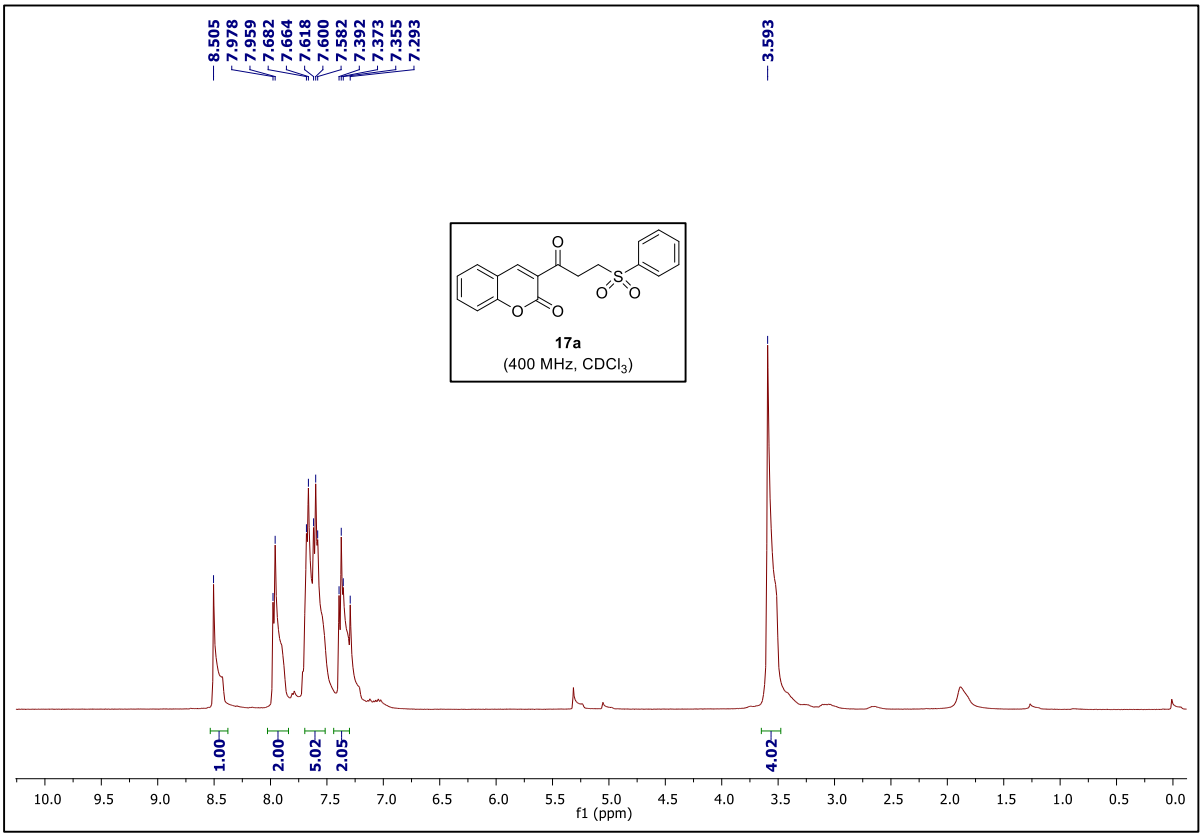
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(3-(phenylthio)propanoyl)-3*H*-benzo[*f*]chromen-3-one **33k**.



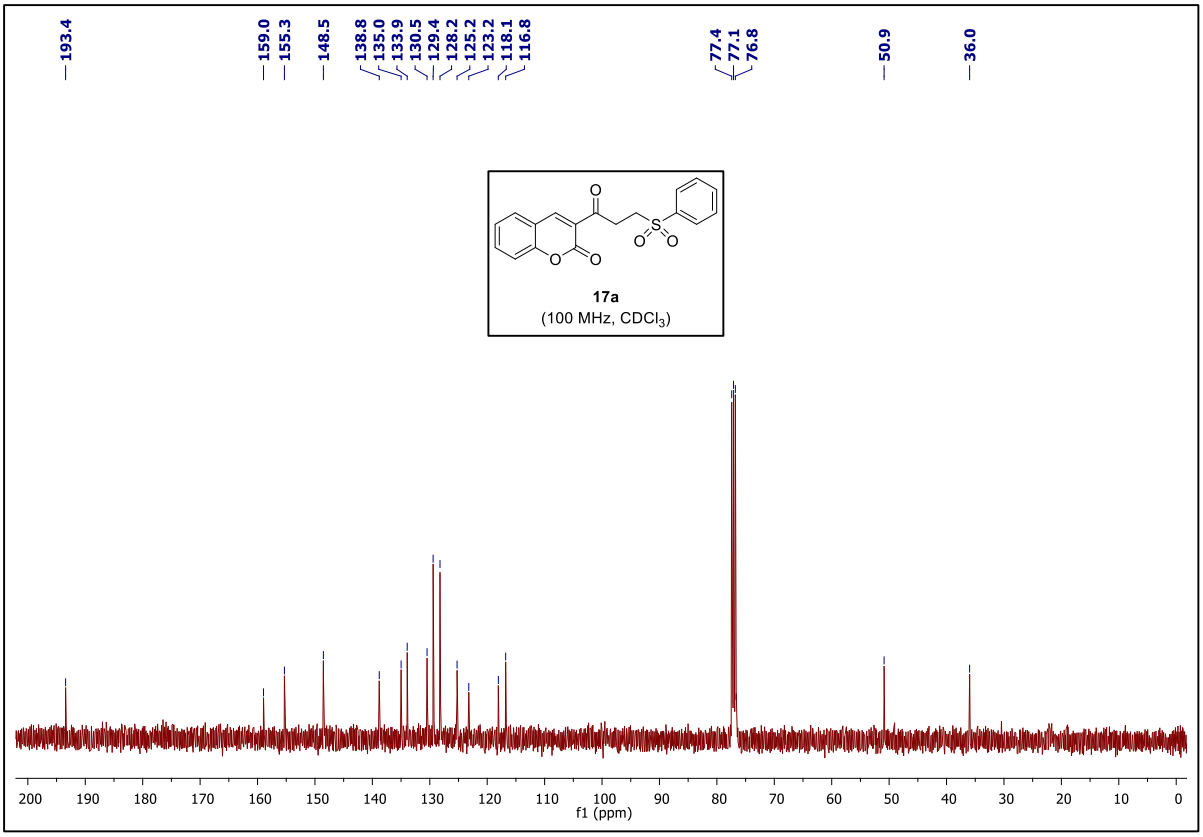
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(3-(phenylthio)propanoyl)-3*H*-benzo[*f*]chromen-3-one **33k**.



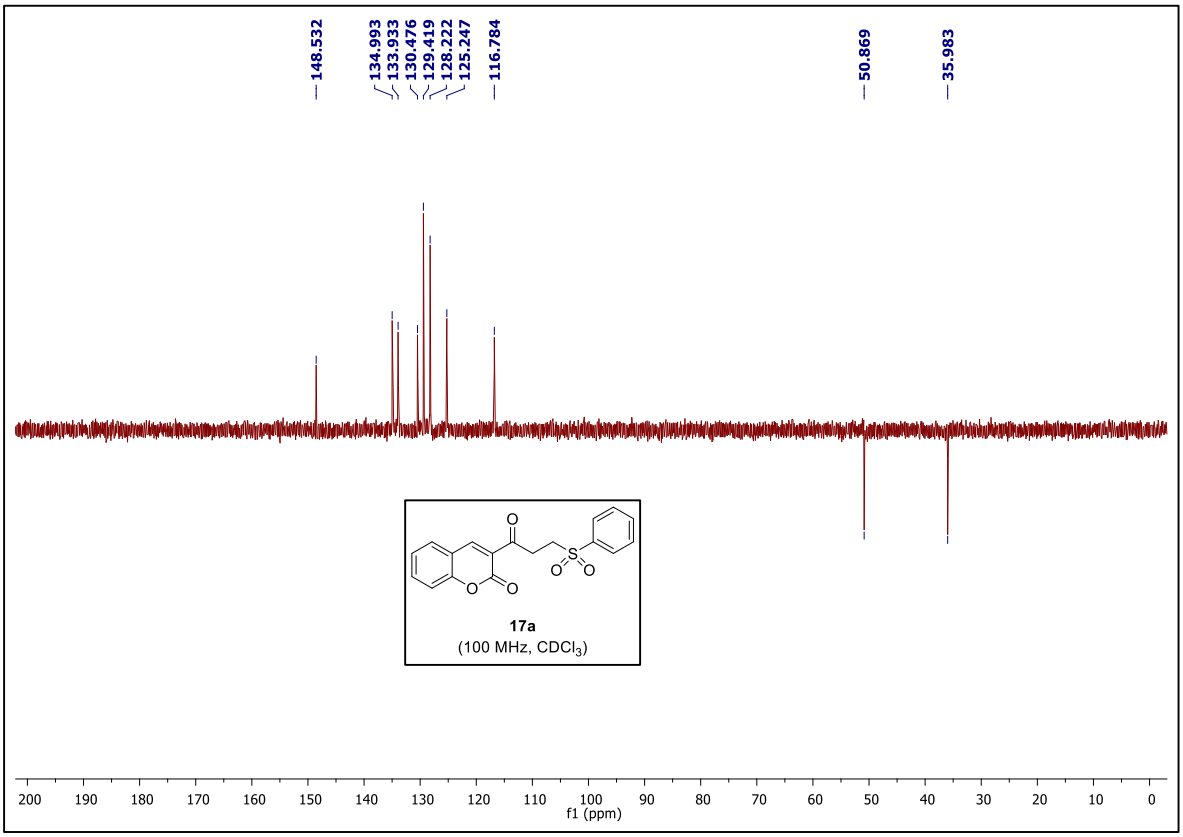
DEPT-135 NMR spectrum of 2-(3-(phenylthio)propanoyl)-3*H*-benzo[*f*]chromen-3-one **33k**.



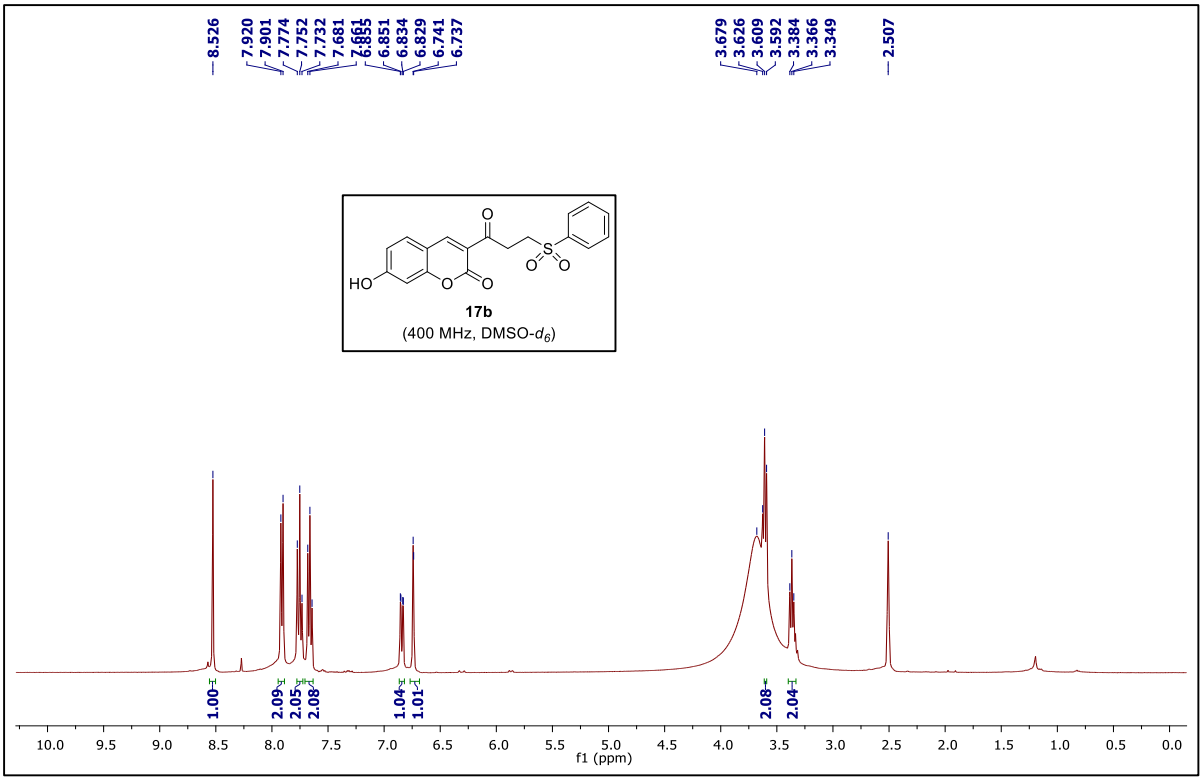
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17a**.



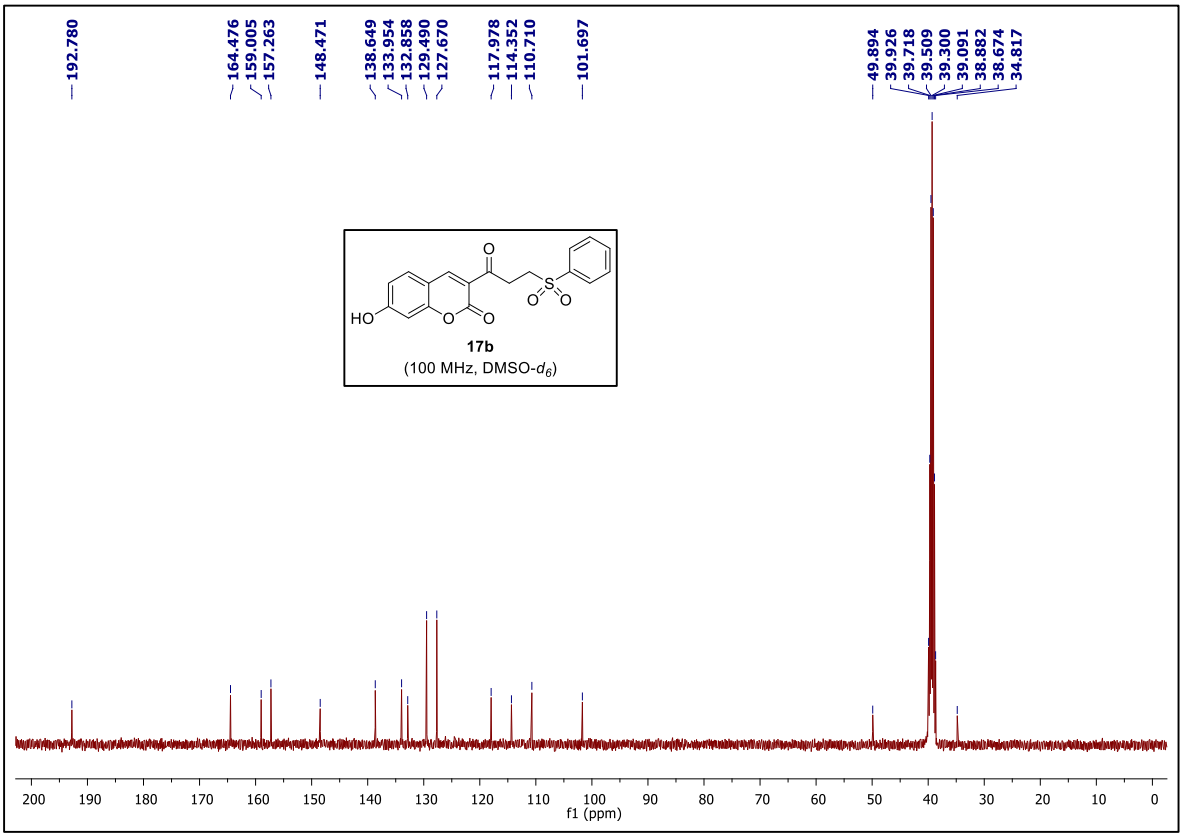
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17a**.



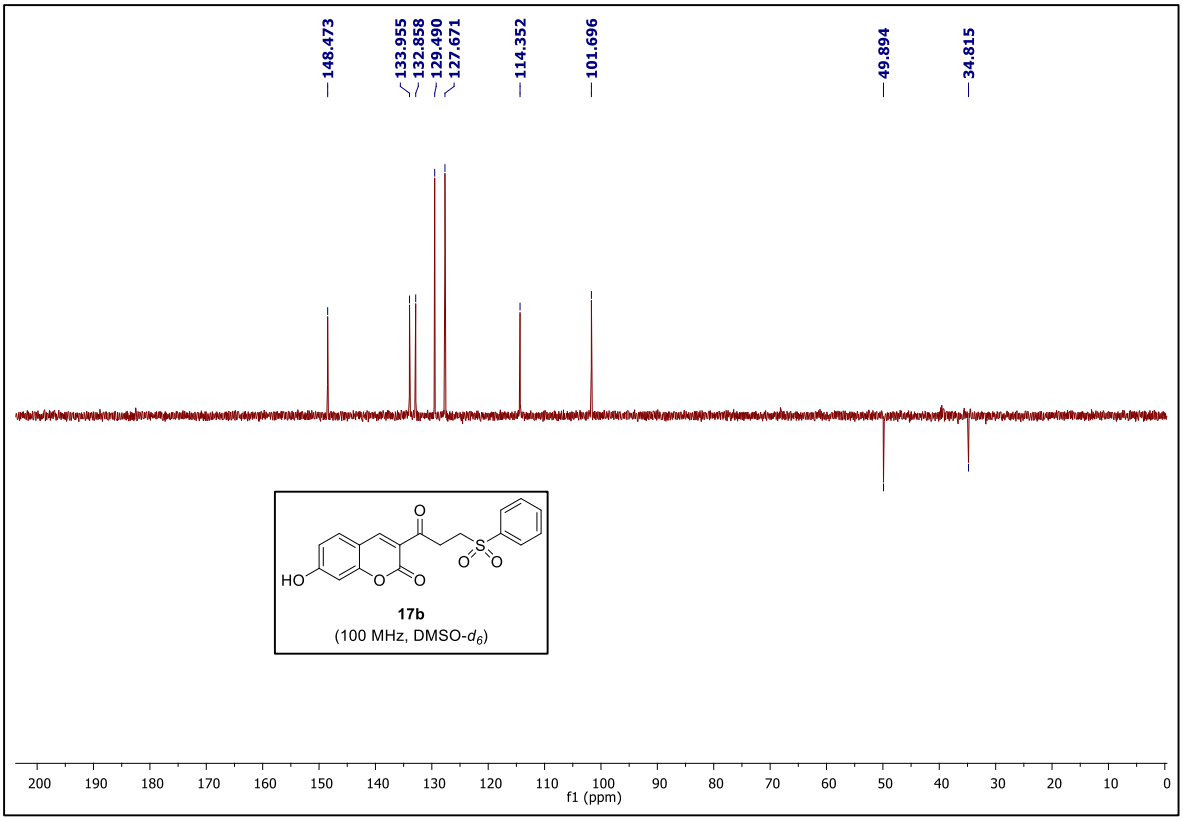
DEPT-135 NMR spectrum of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17a**.



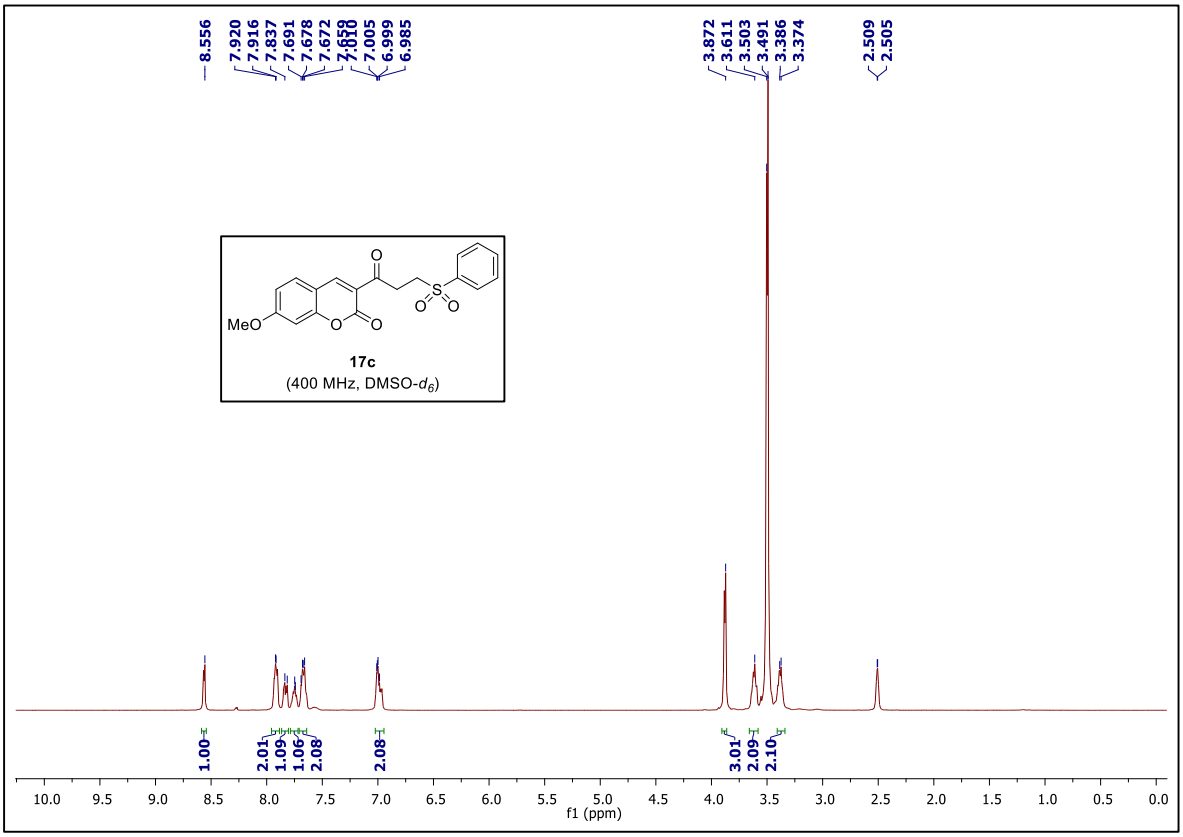
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 7-hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17b**.



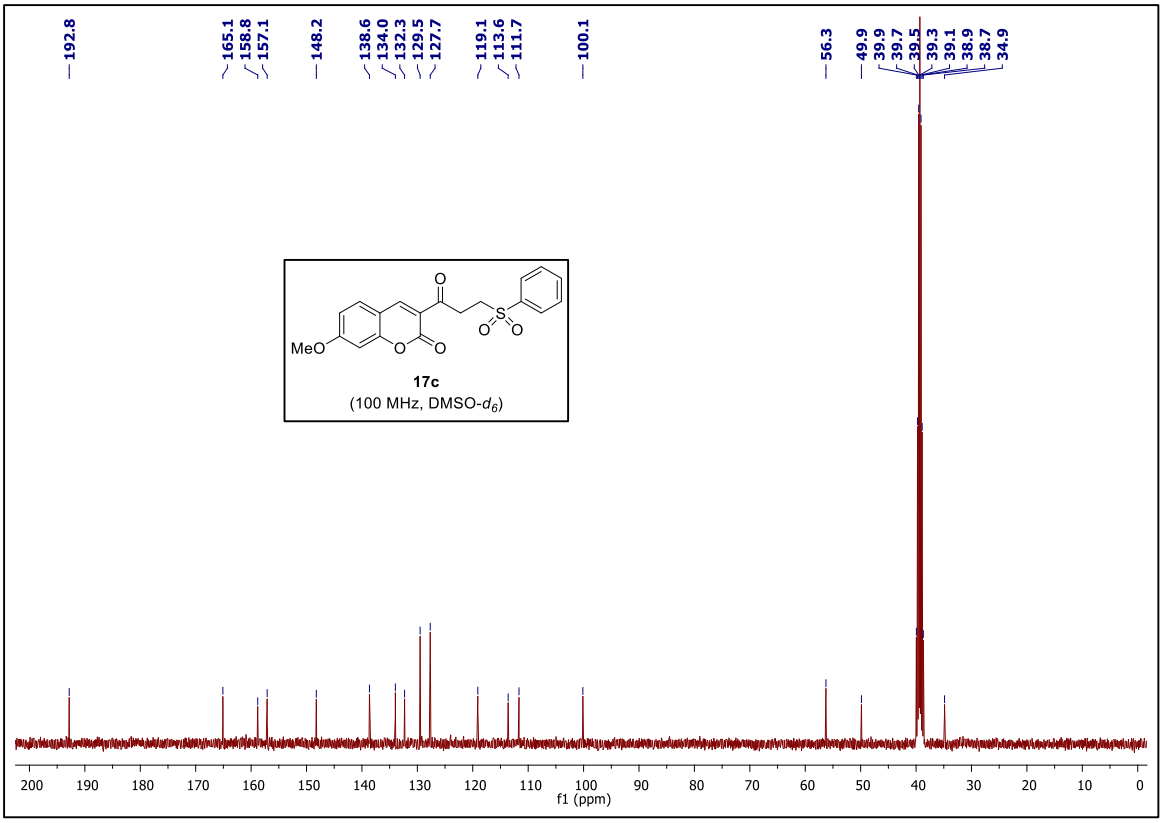
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 7-hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17b**.



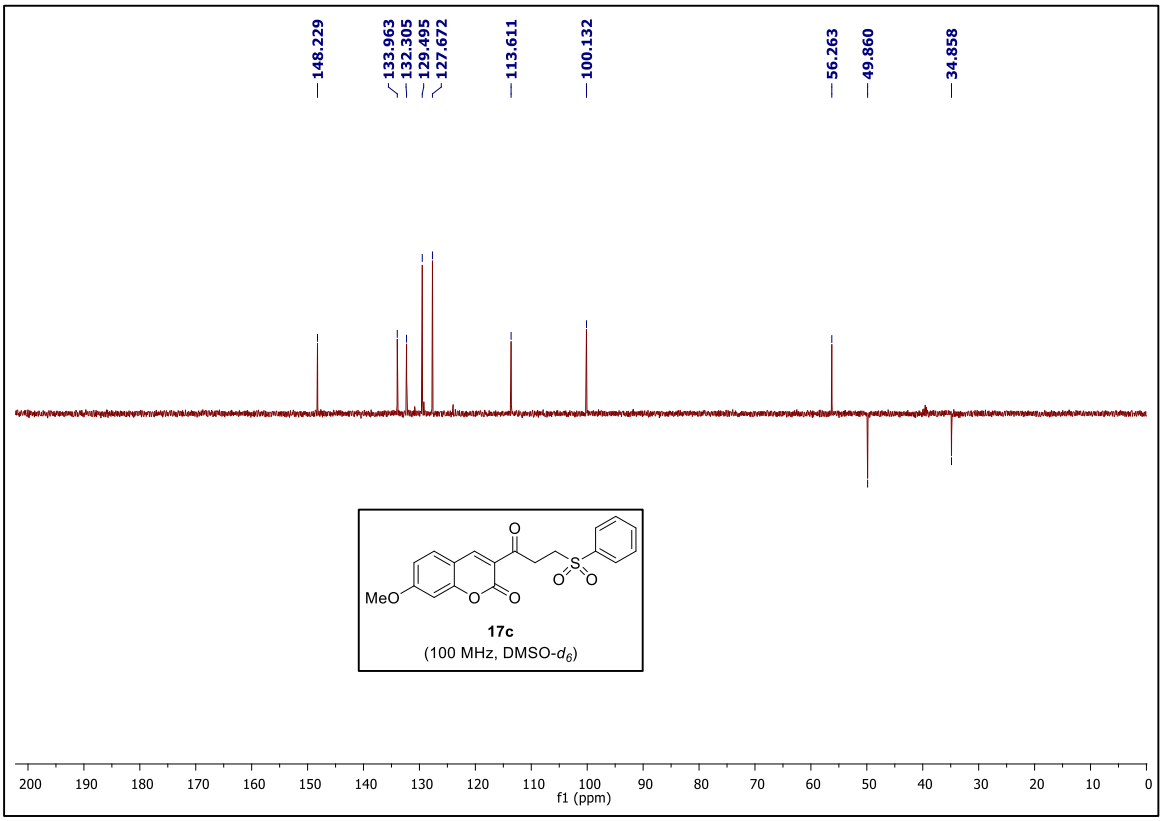
DEPT-135 NMR spectrum of 7-hydroxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17b**.



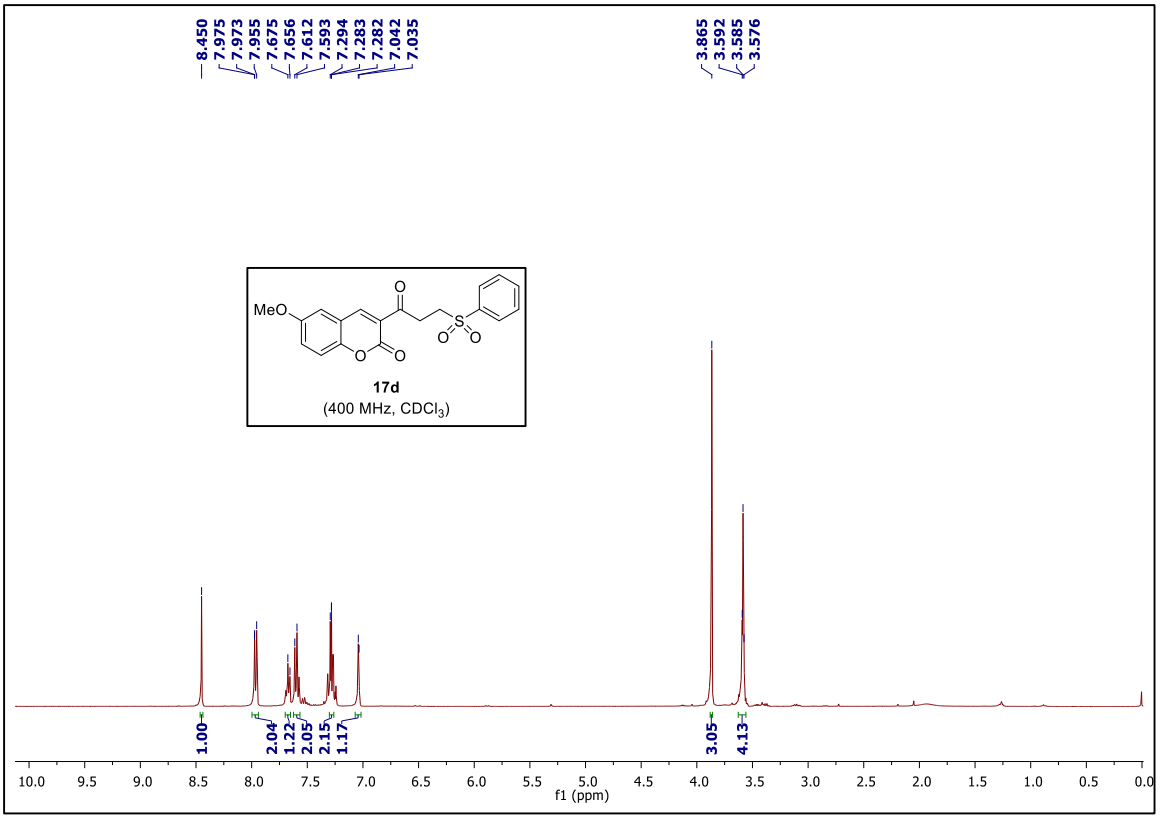
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 7-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17c**.



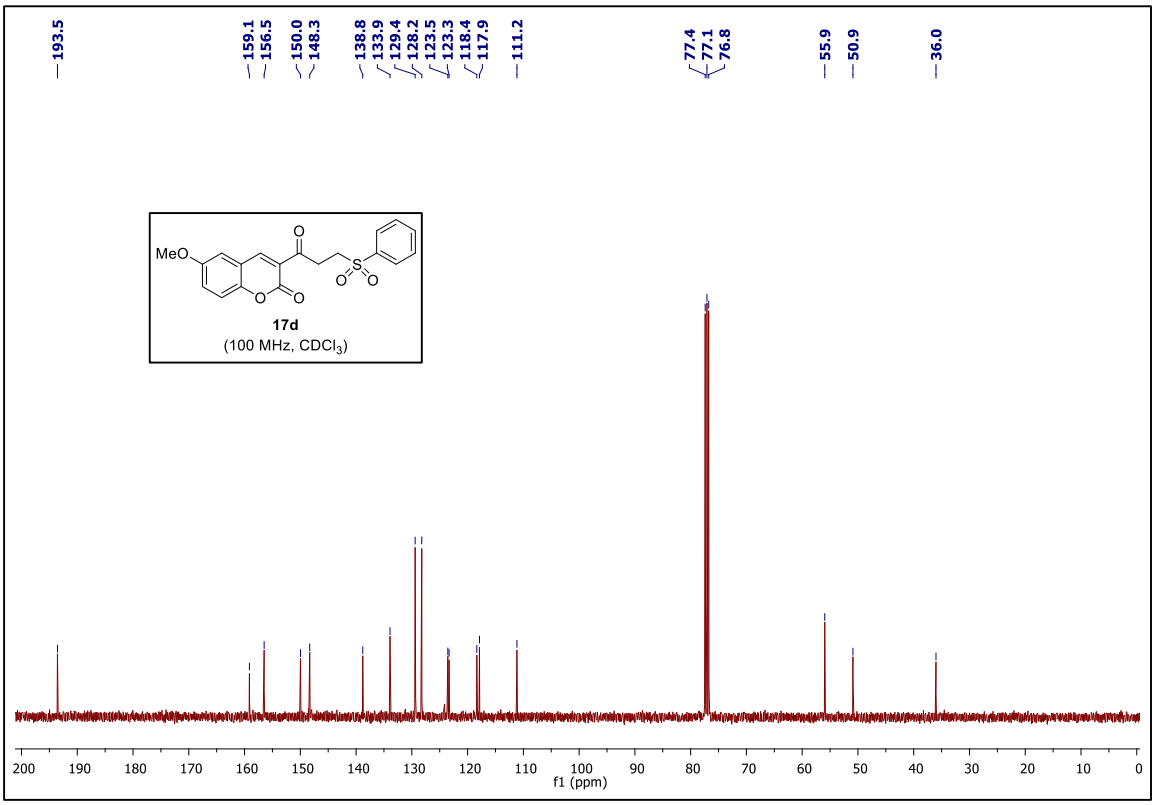
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 7-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17c**.



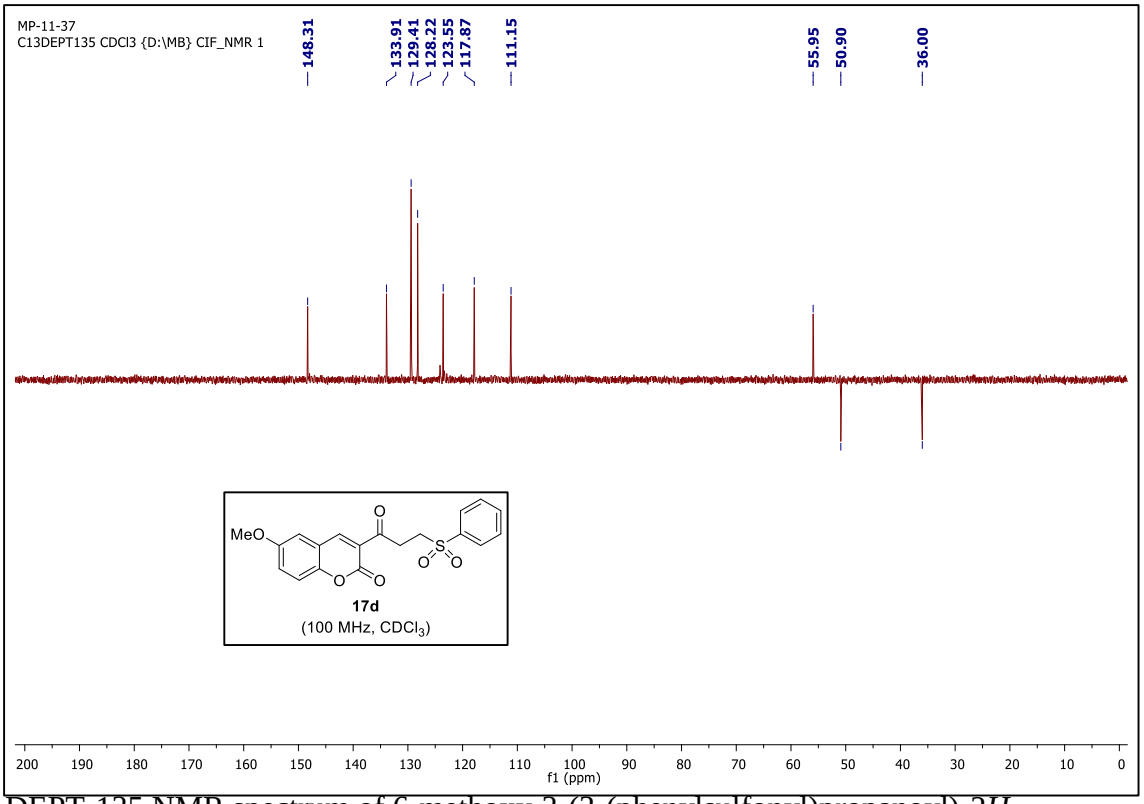
DEPT-135 NMR spectrum of 7-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17c**.



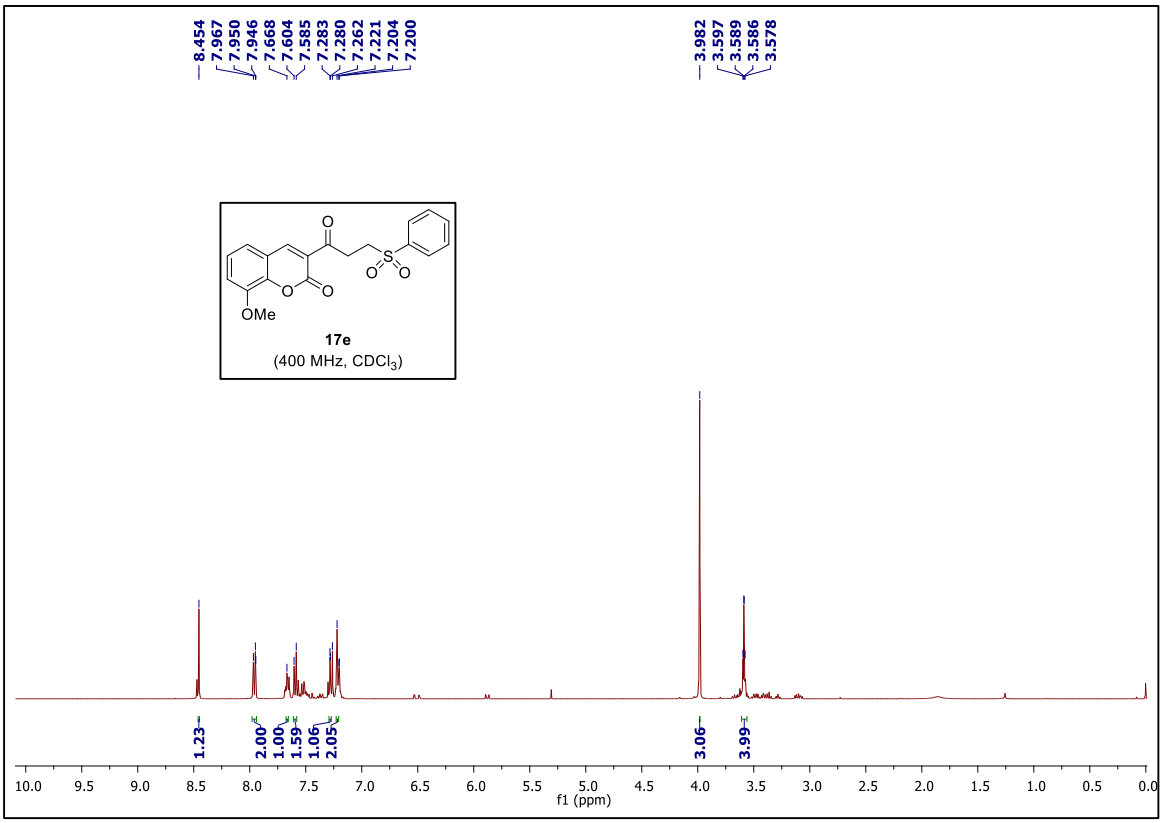
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17d**.



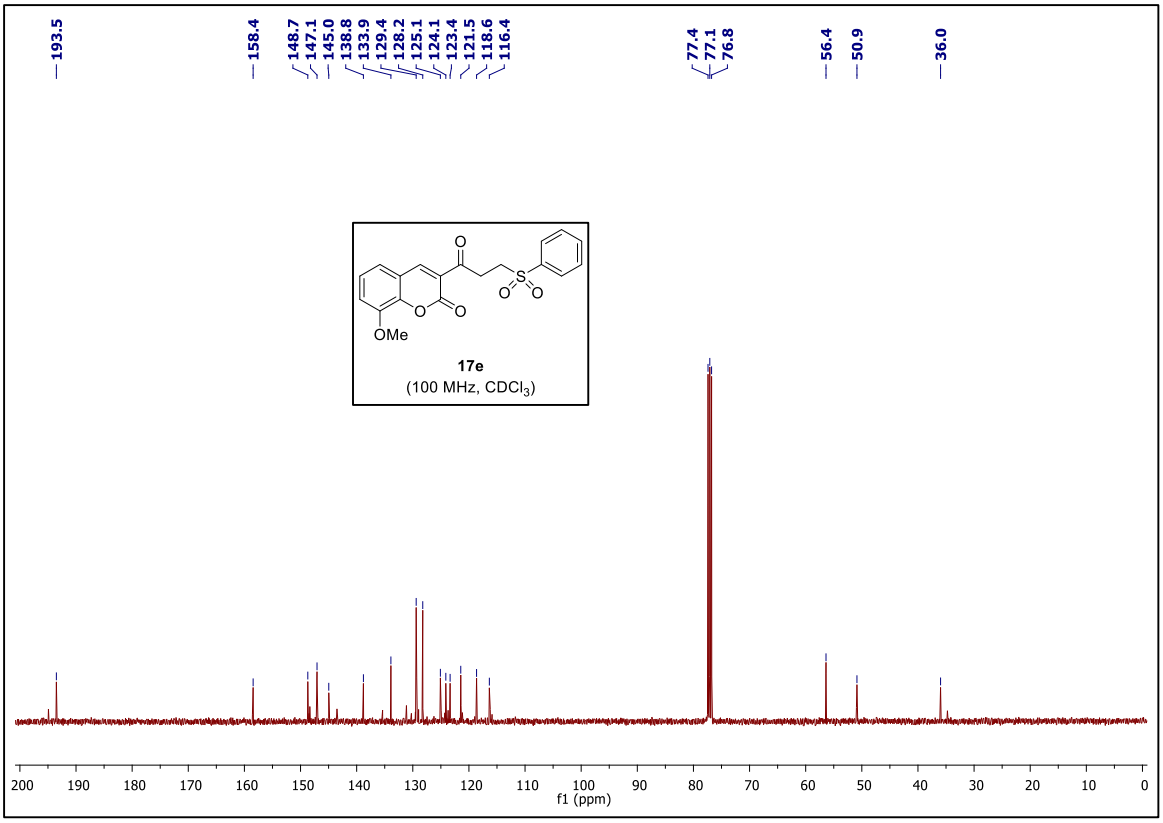
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17d**.



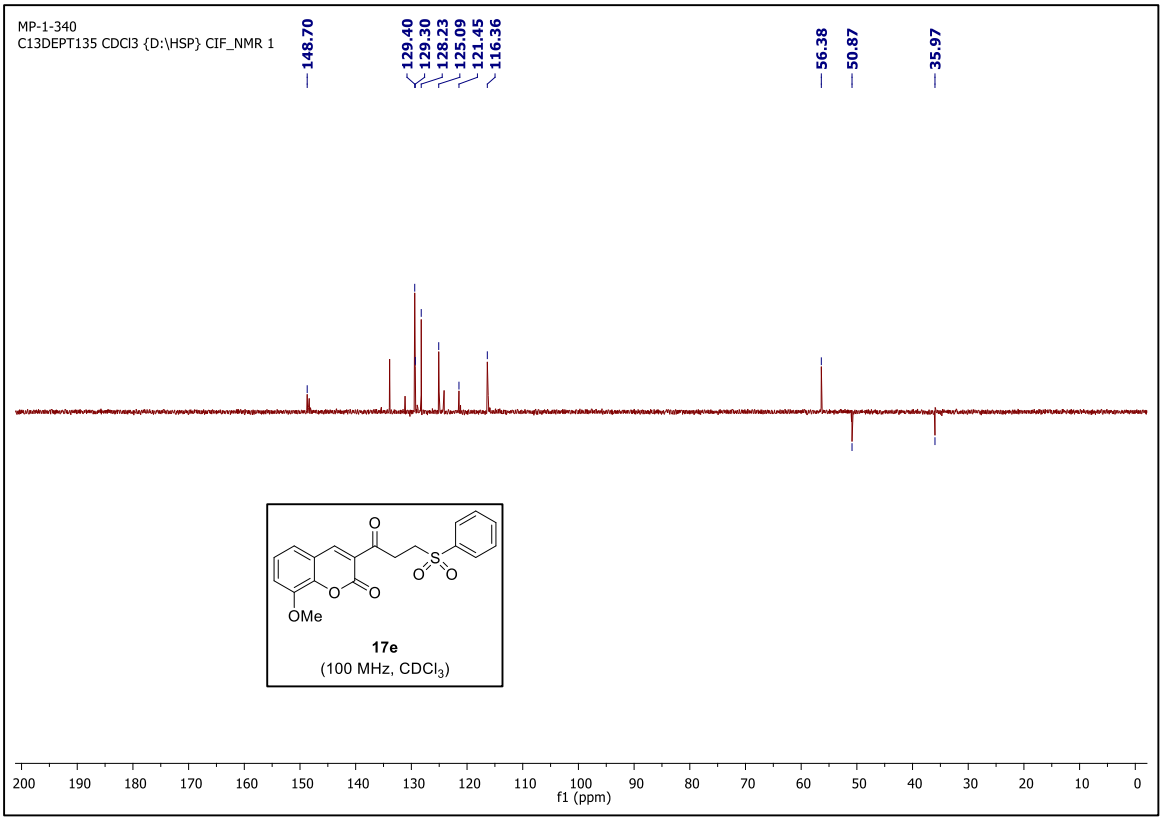
DEPT-135 NMR spectrum of 6-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17d**.



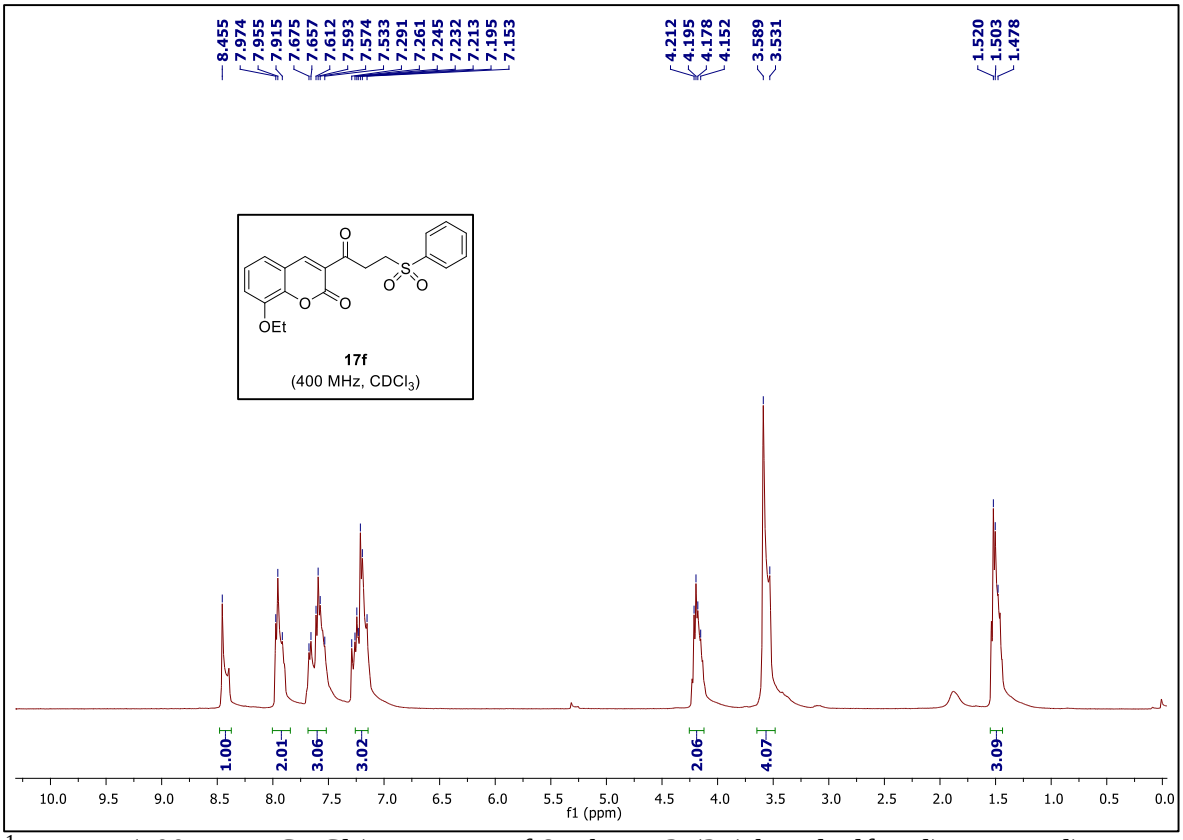
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17e**.



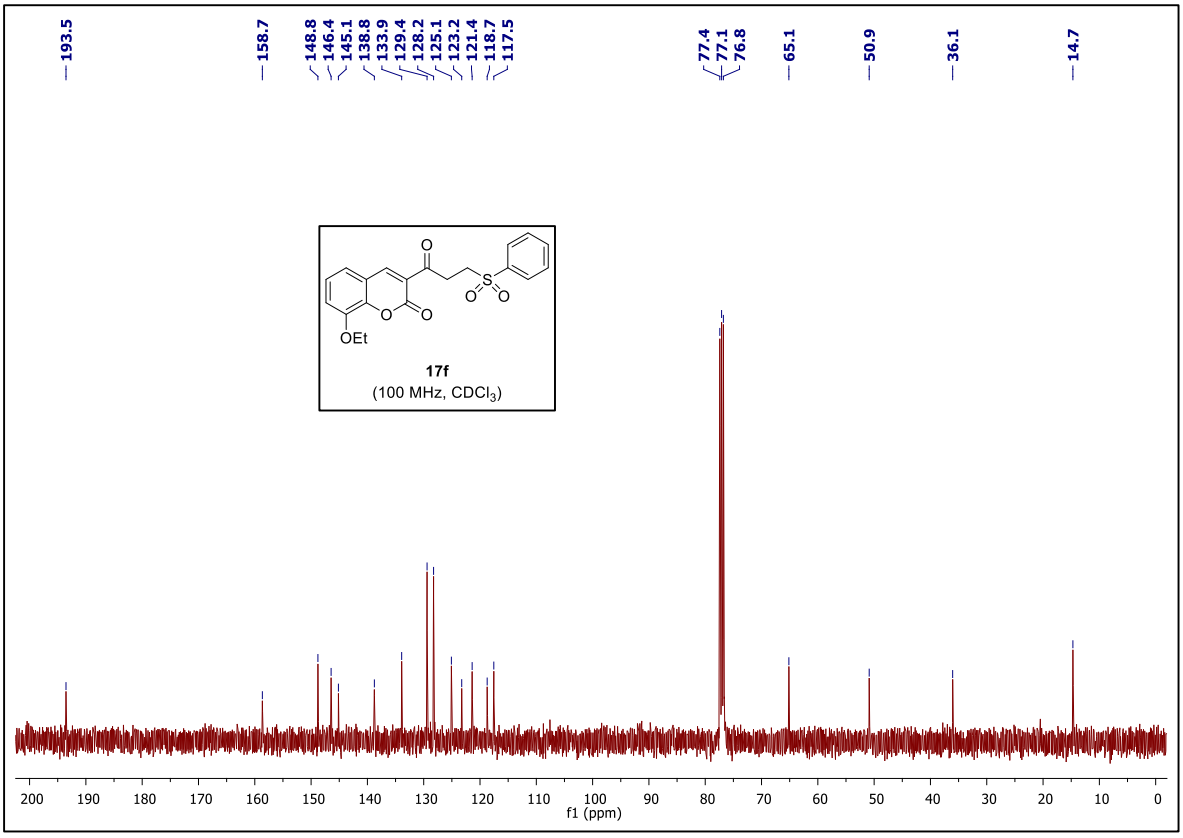
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17e**.



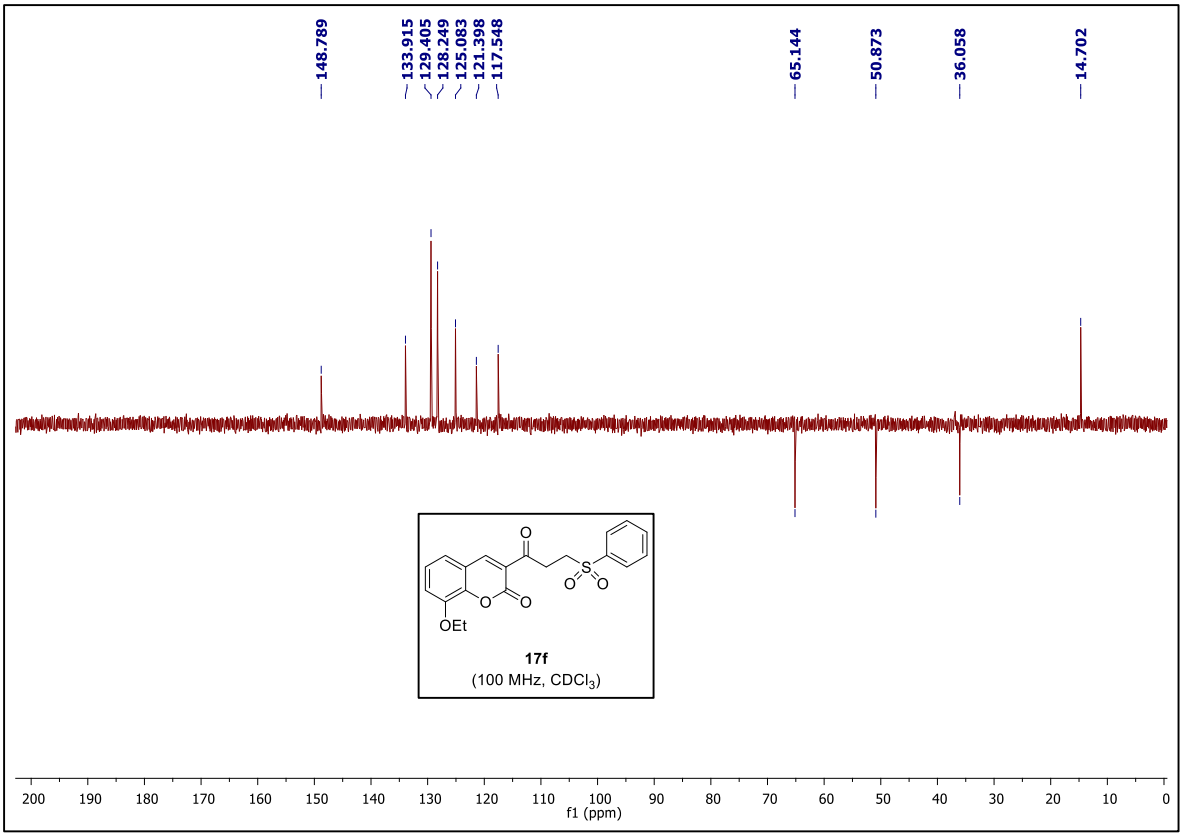
DEPT-135 NMR spectrum of 8-methoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17e**.



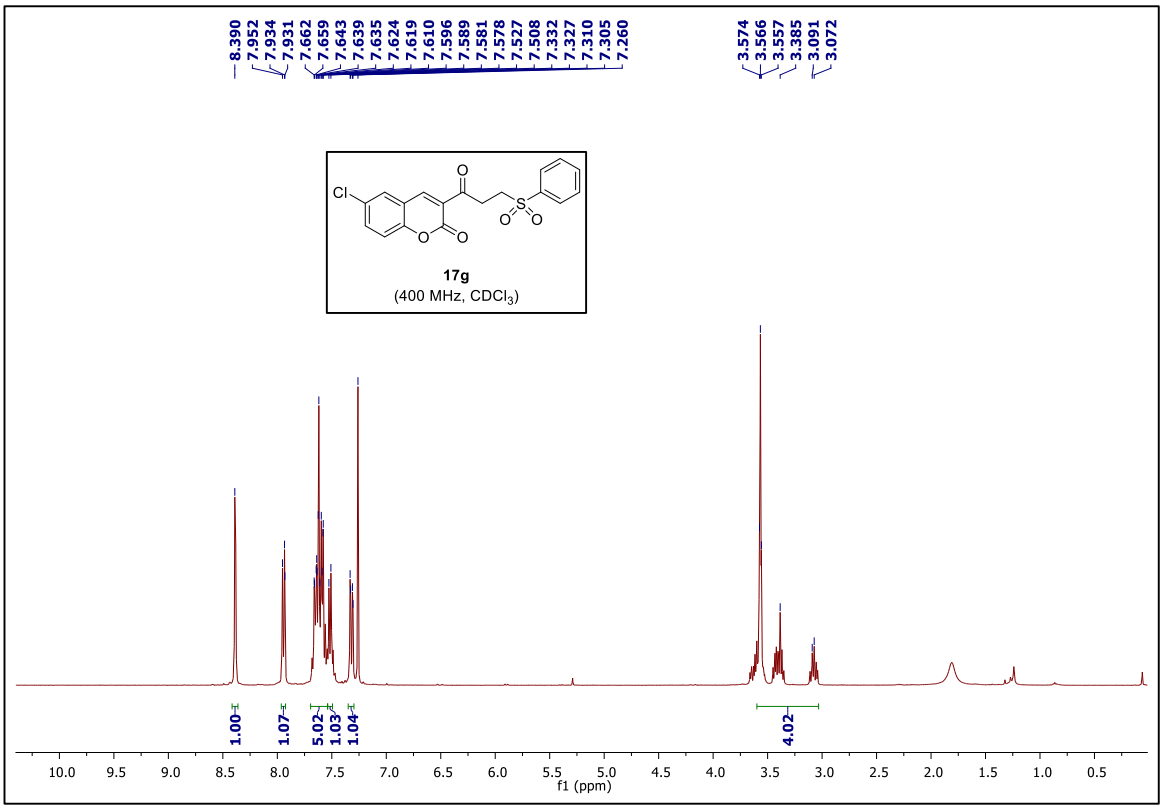
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8-ethoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17f**.



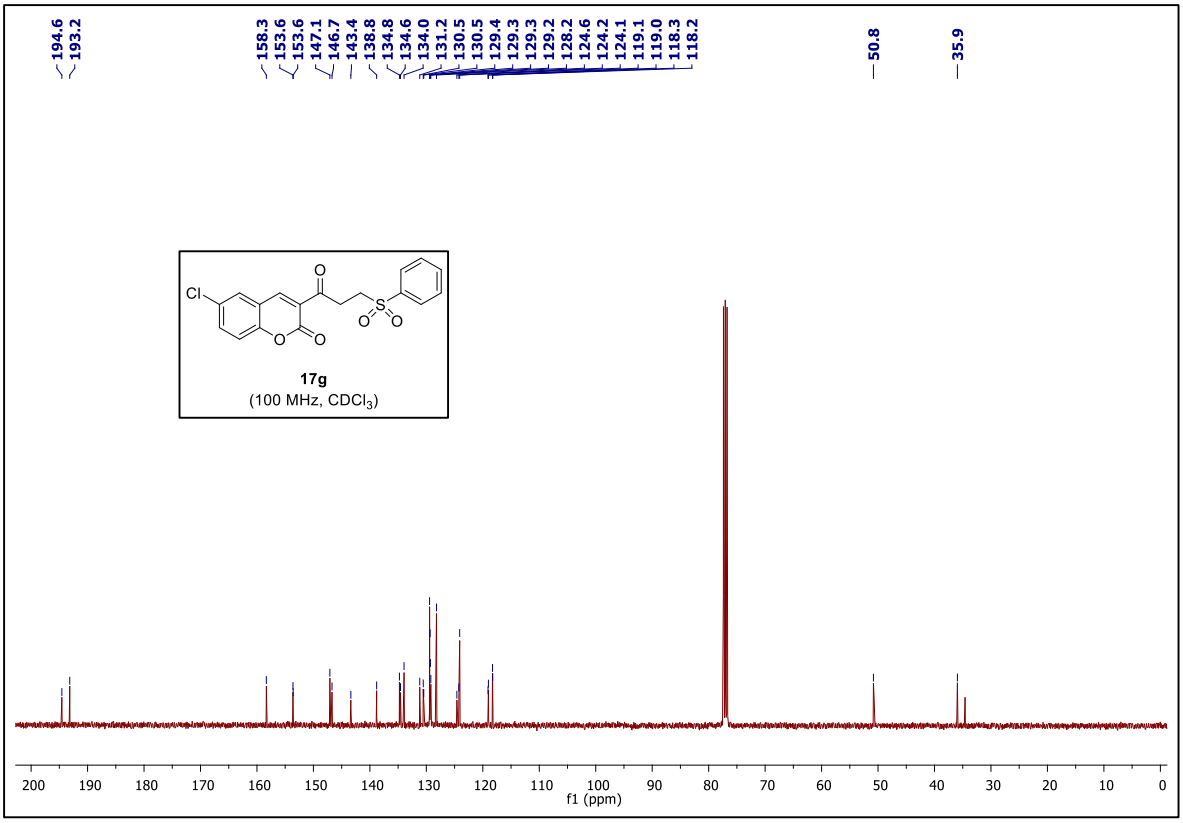
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8-ethoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17f.**



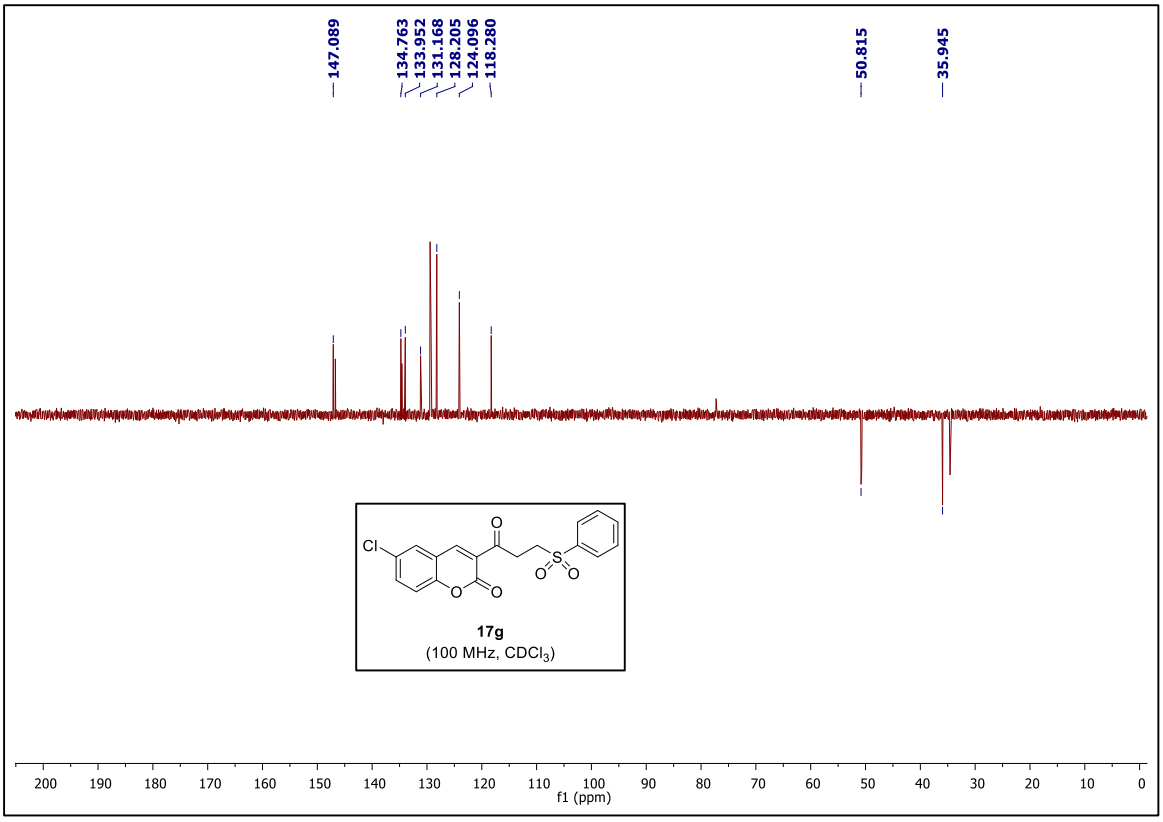
DEPT-135 NMR spectrum of 8-ethoxy-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17f**.



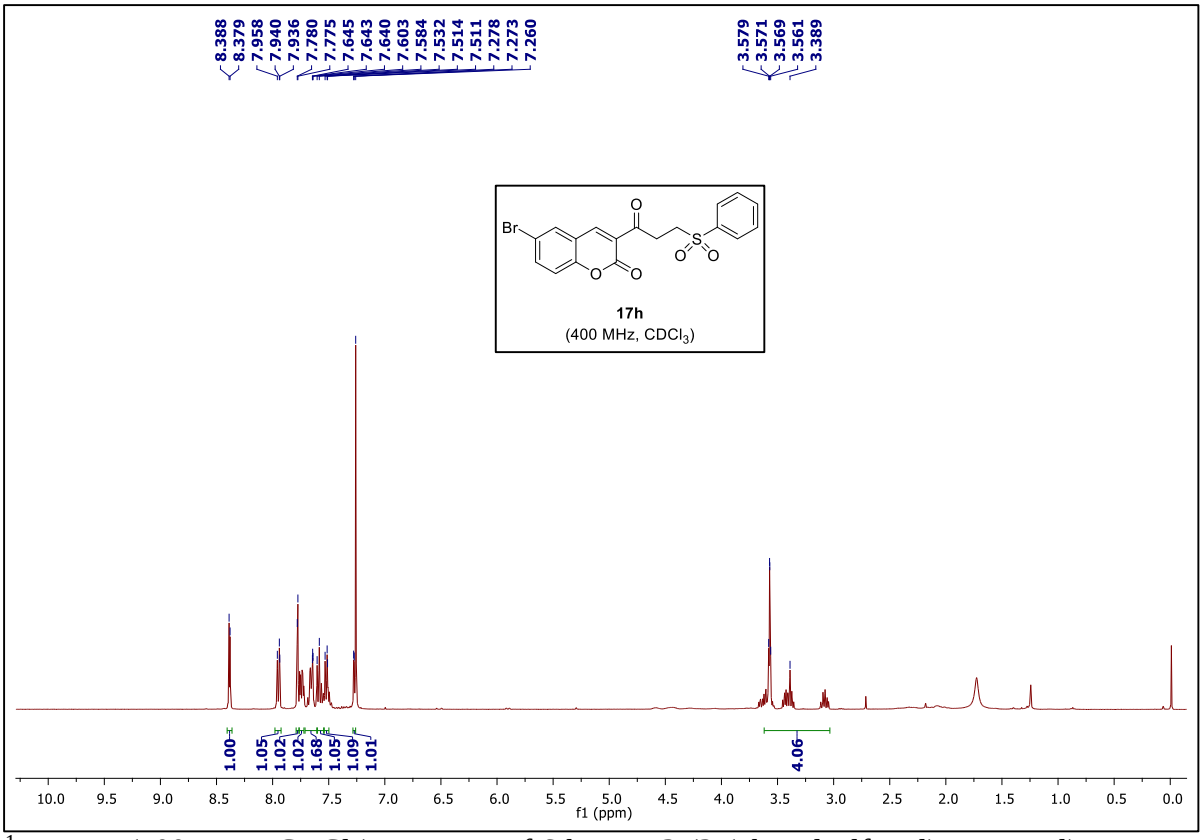
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-chloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17g**.



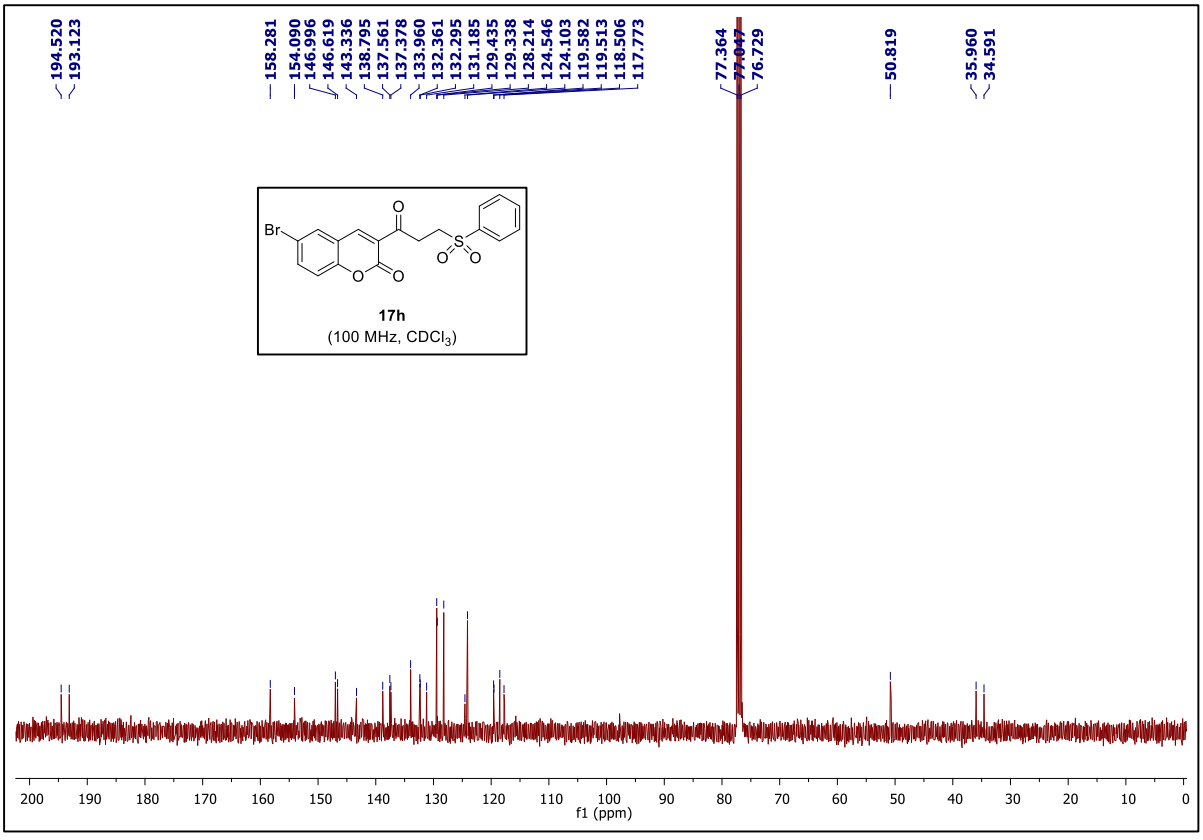
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6-chloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17g**.



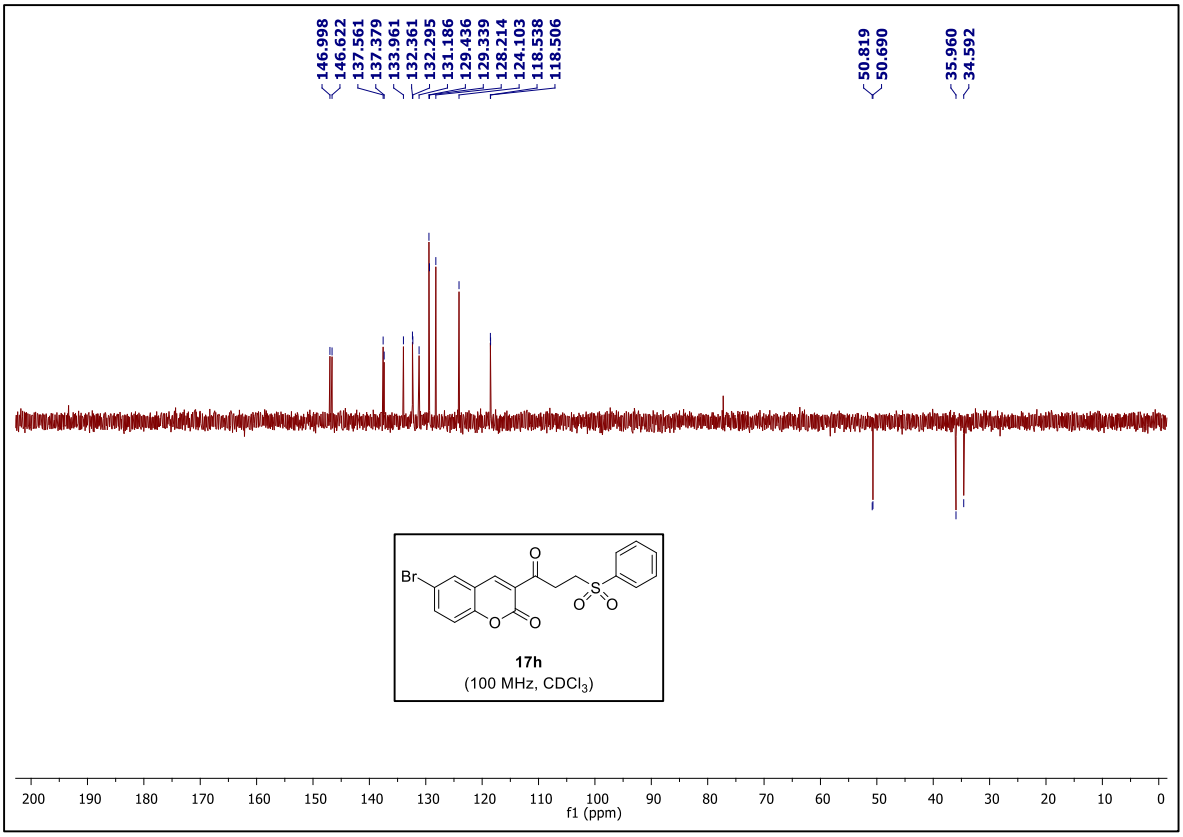
DEPT-135 NMR spectrum of 6-chloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17g**.



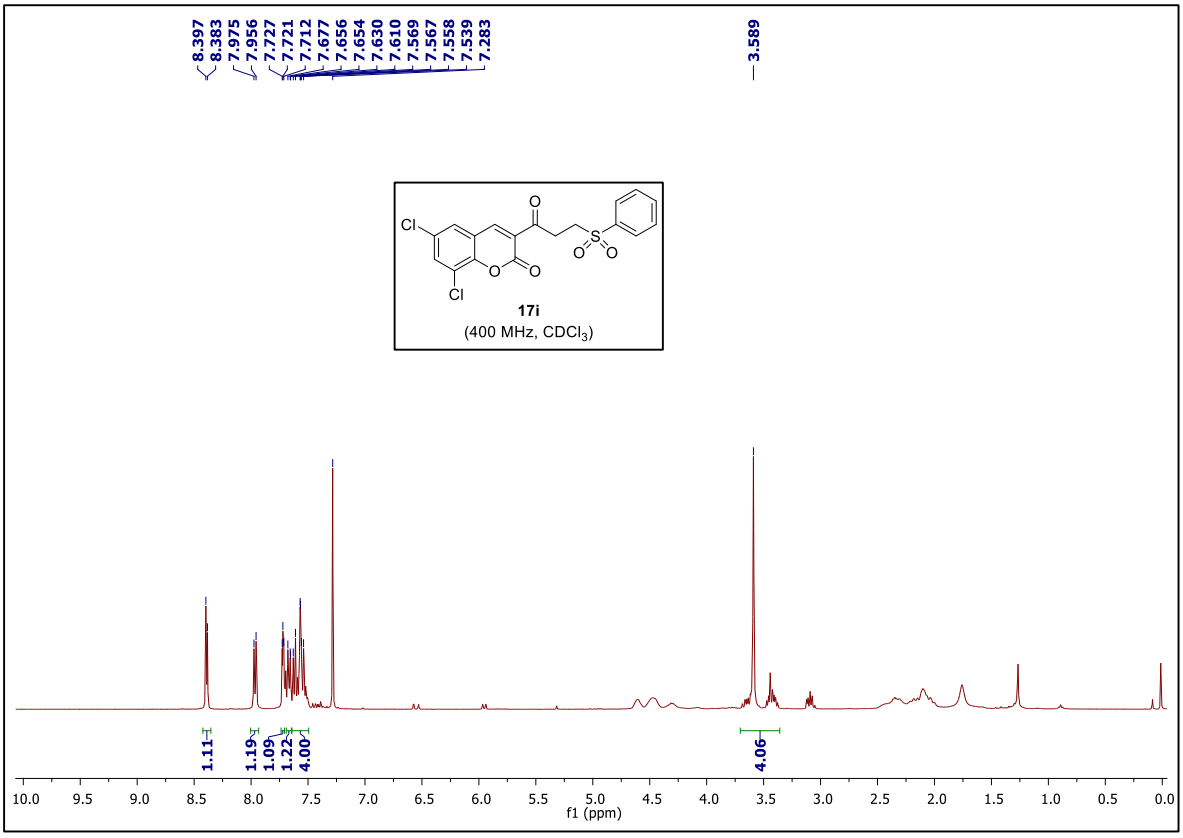
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-bromo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17h**.



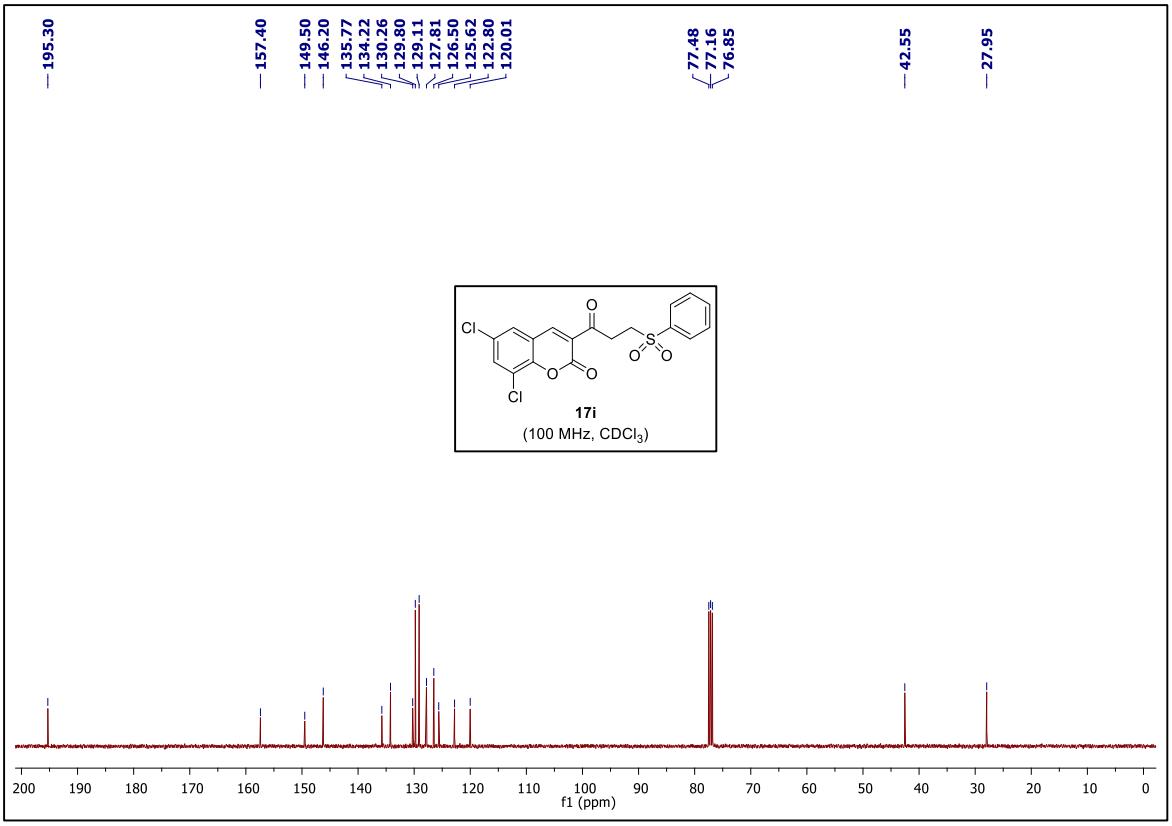
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6-bromo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17h**.



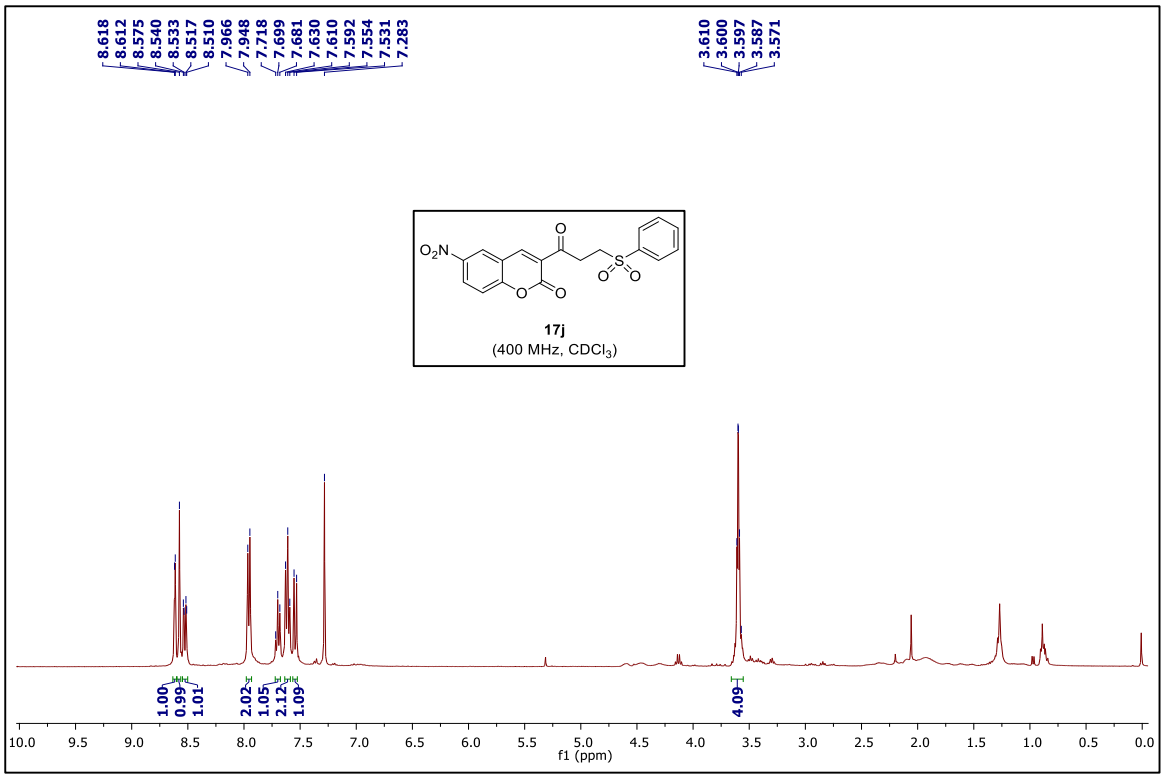
DEPT-135 NMR spectrum of 6-bromo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17h**.



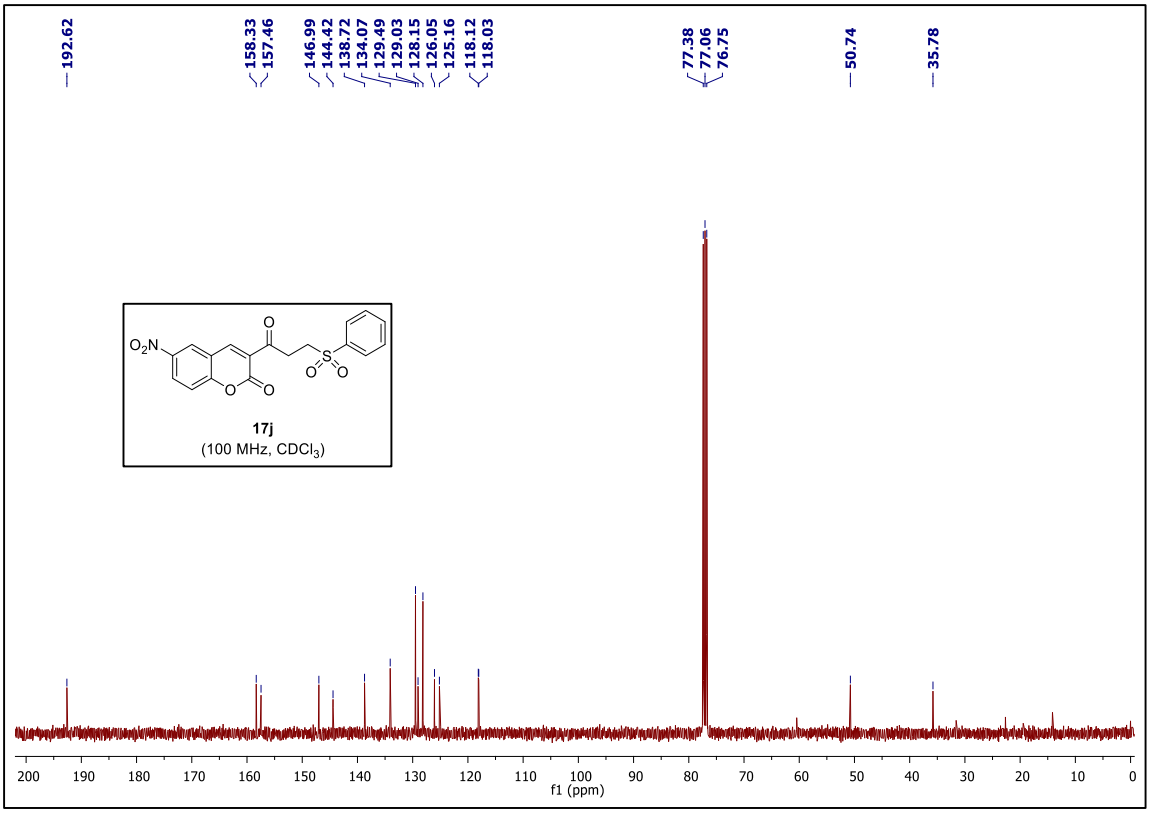
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6,8-dichloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17i.**



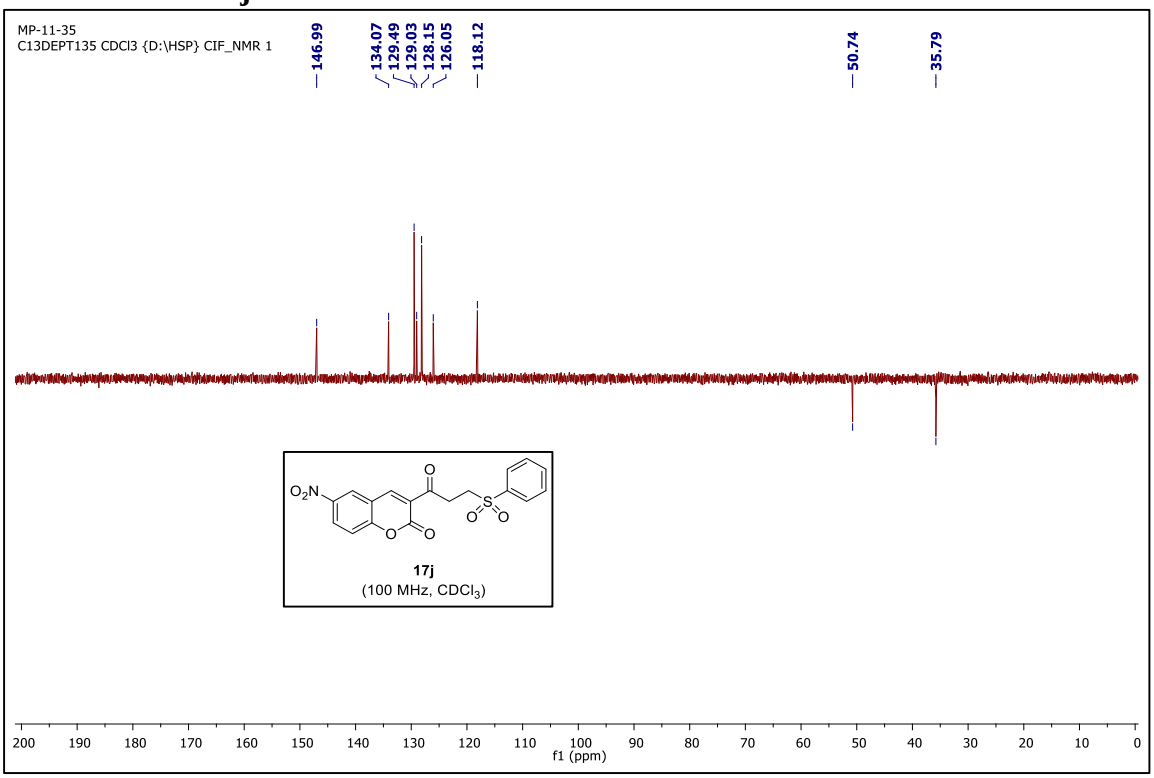
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6,8-dichloro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17i**.



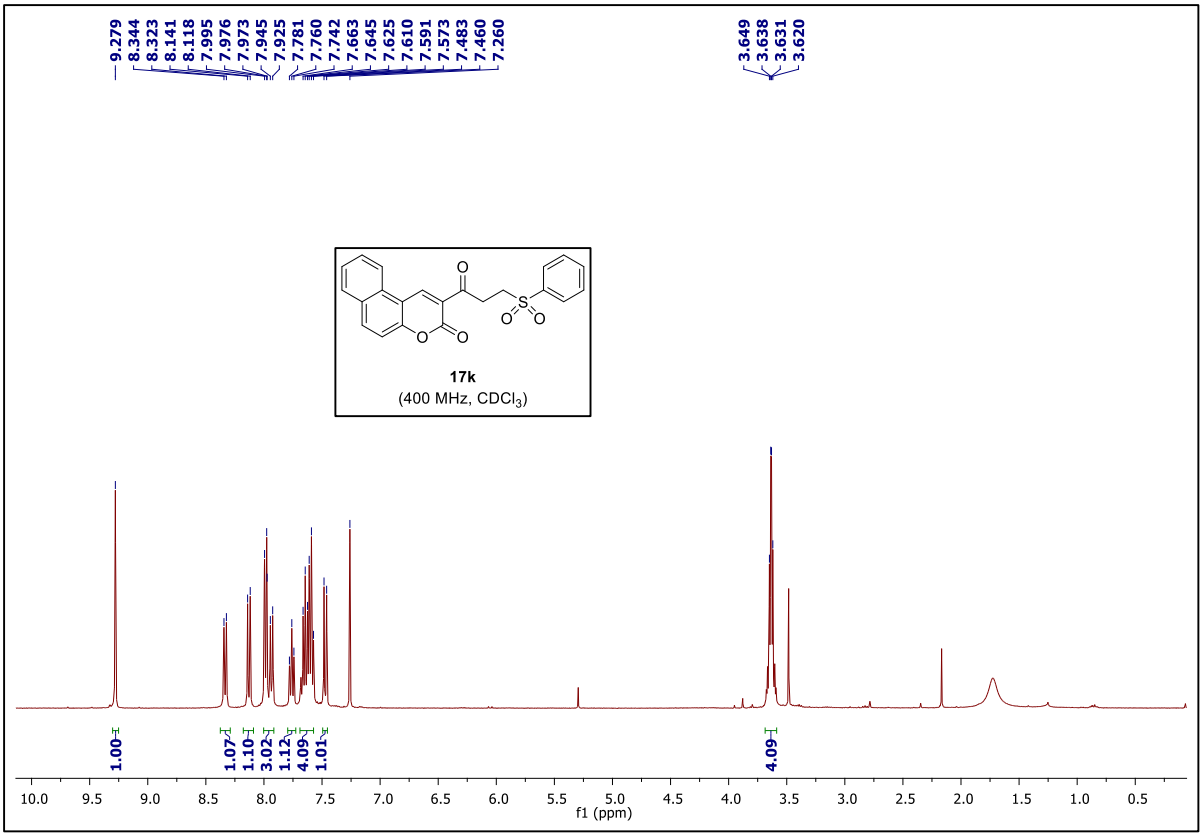
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-nitro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17j**.



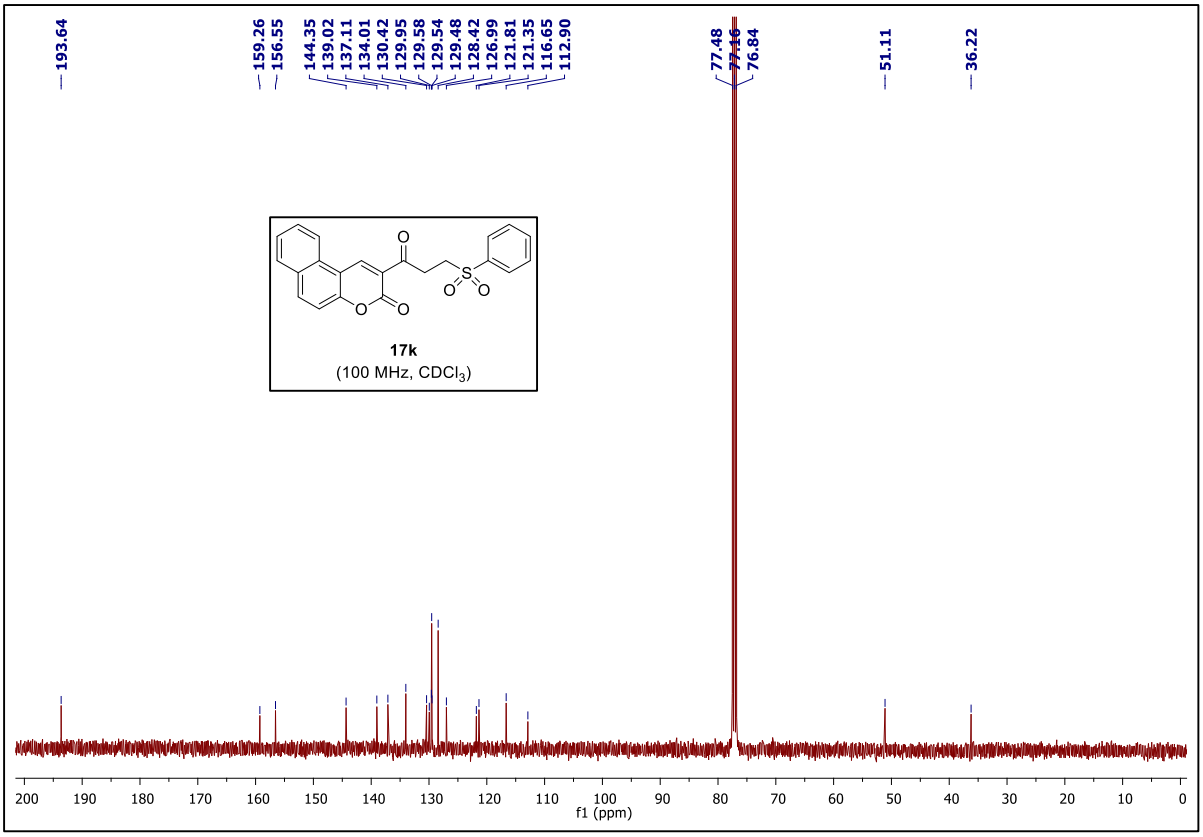
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6-nitro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17j**.



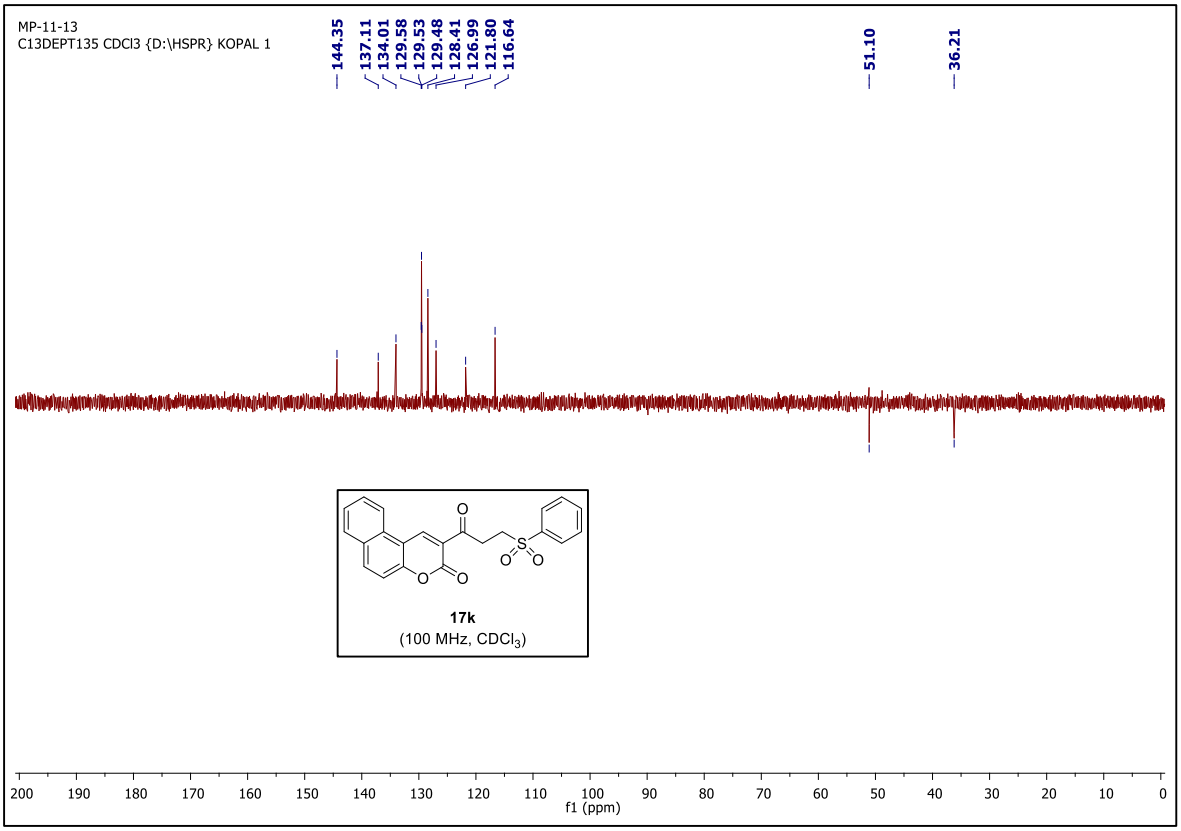
DEPT-135 NMR spectrum of 6-nitro-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17j**.



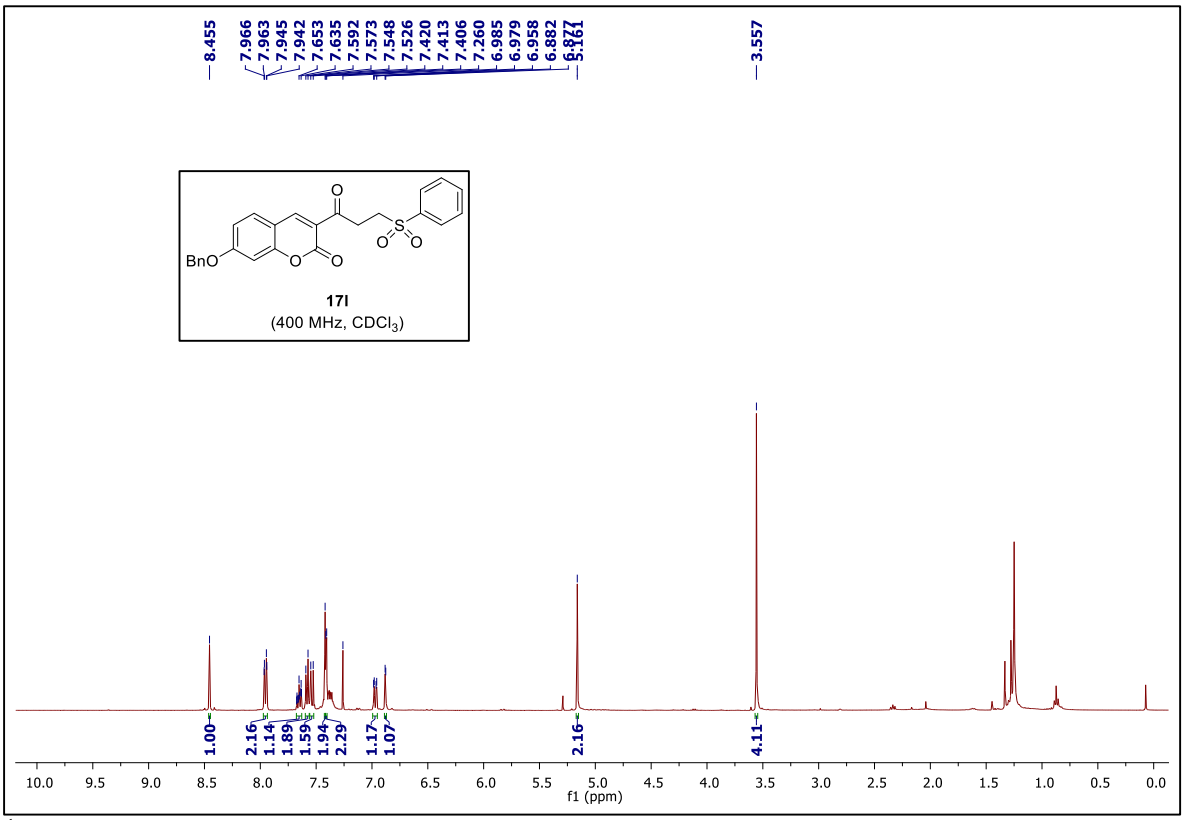
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-benzo[*f*]chromen-2-one **17k**.



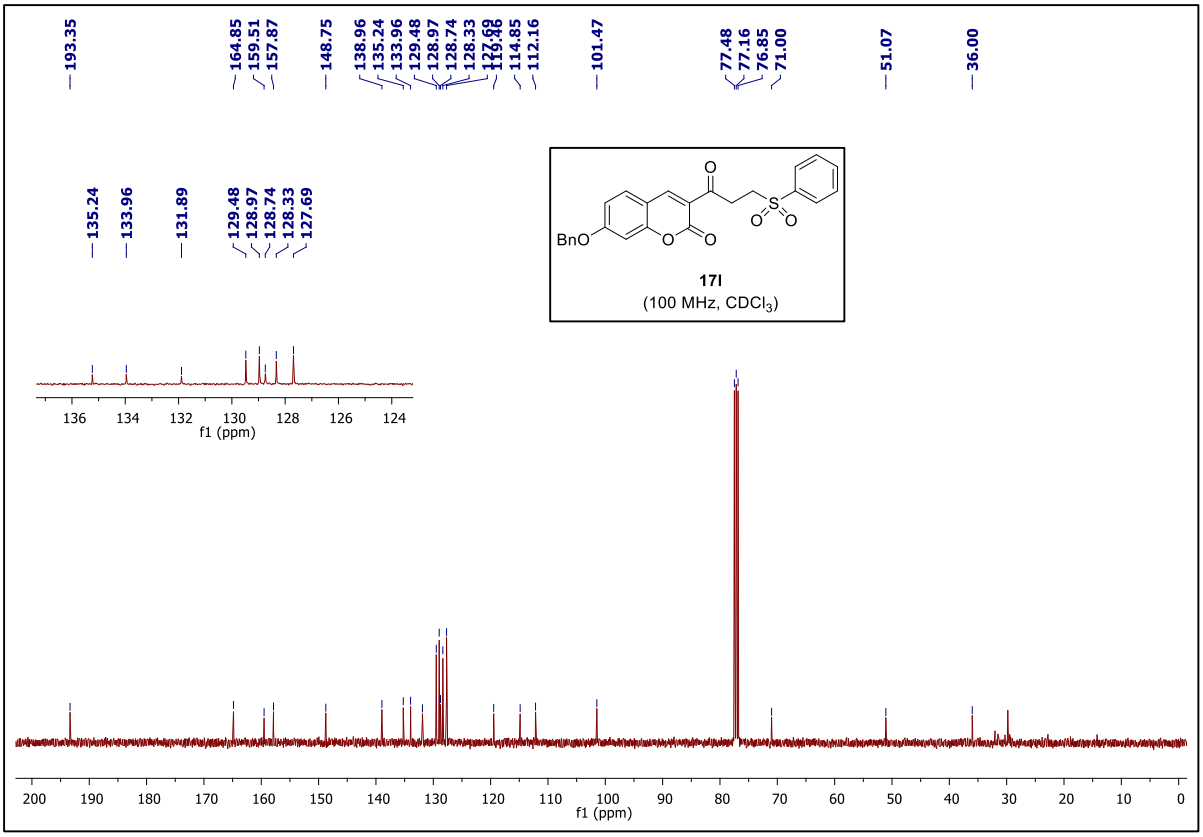
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-benzo[*f*]chromen-2-one **17k**.



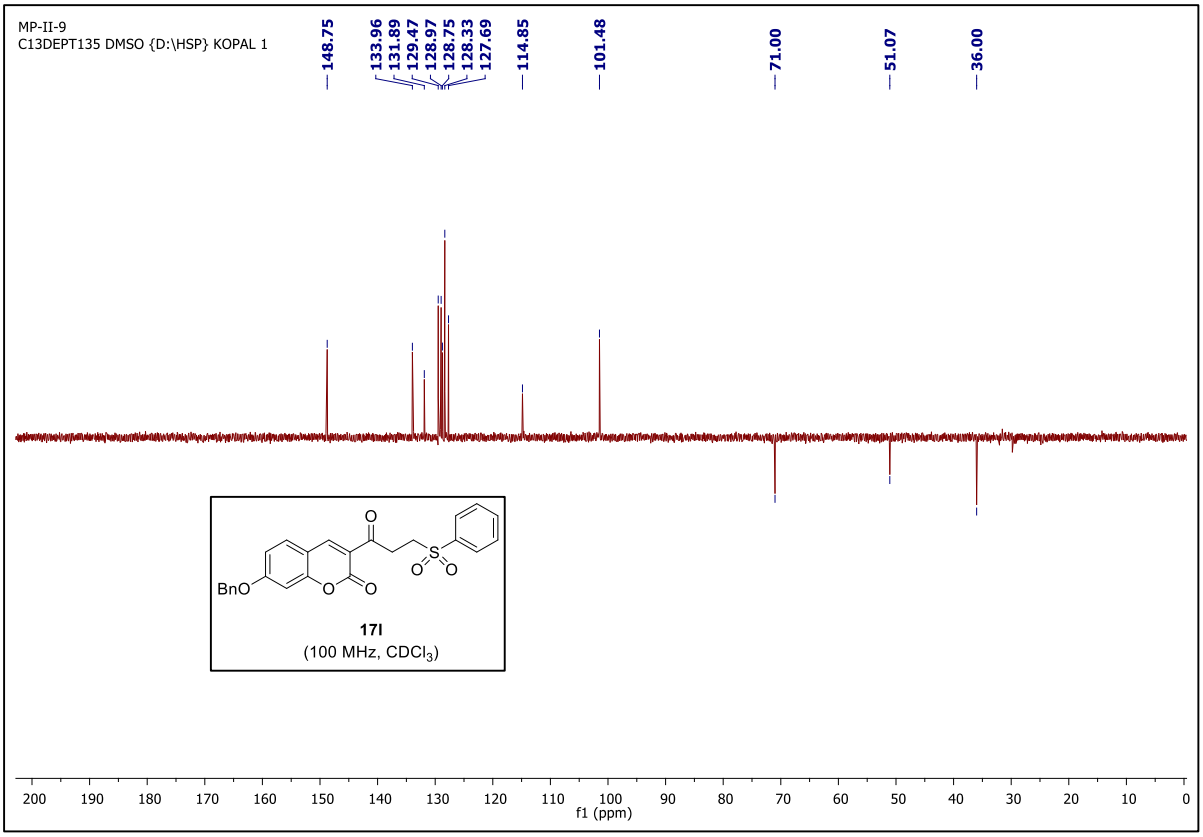
DEPT-135 NMR spectrum of 3-(3-(phenylsulfonyl)propanoyl)-2*H*-benzo[f]chromen-2-one **17k**.



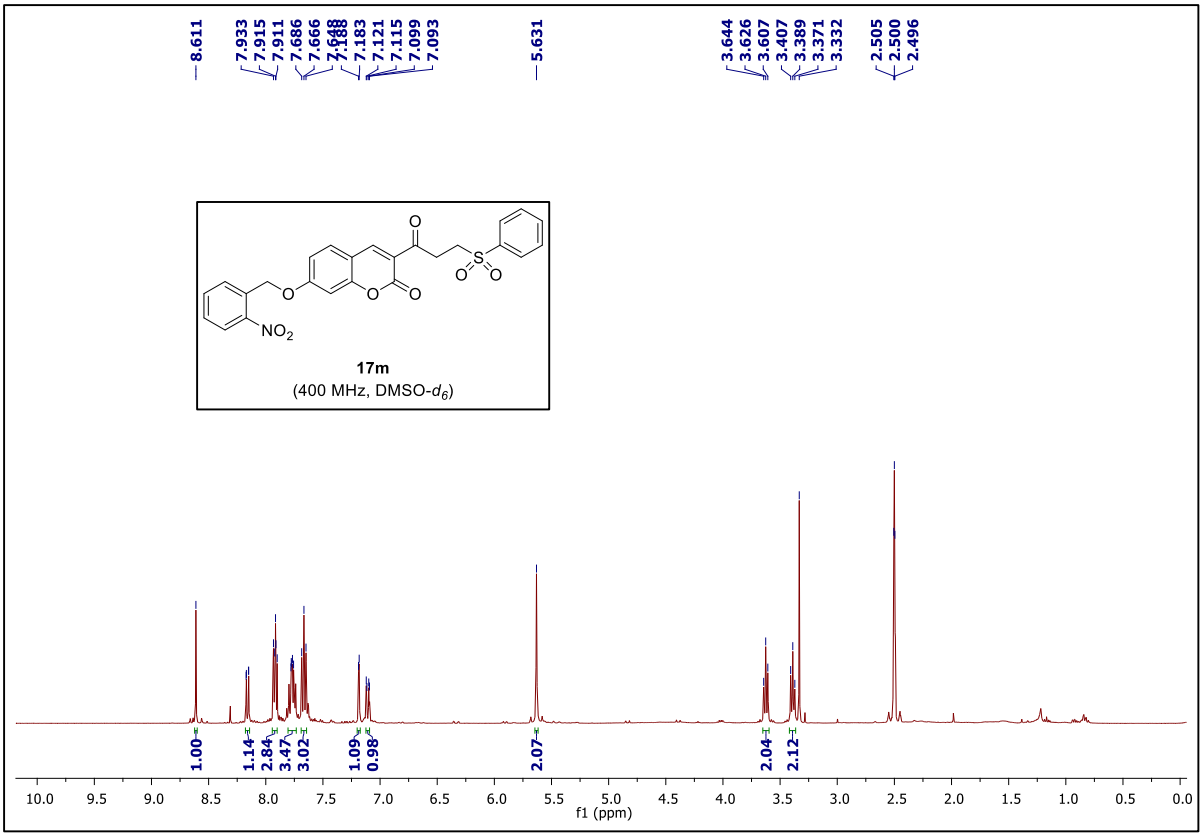
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-(benzyloxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17l**.



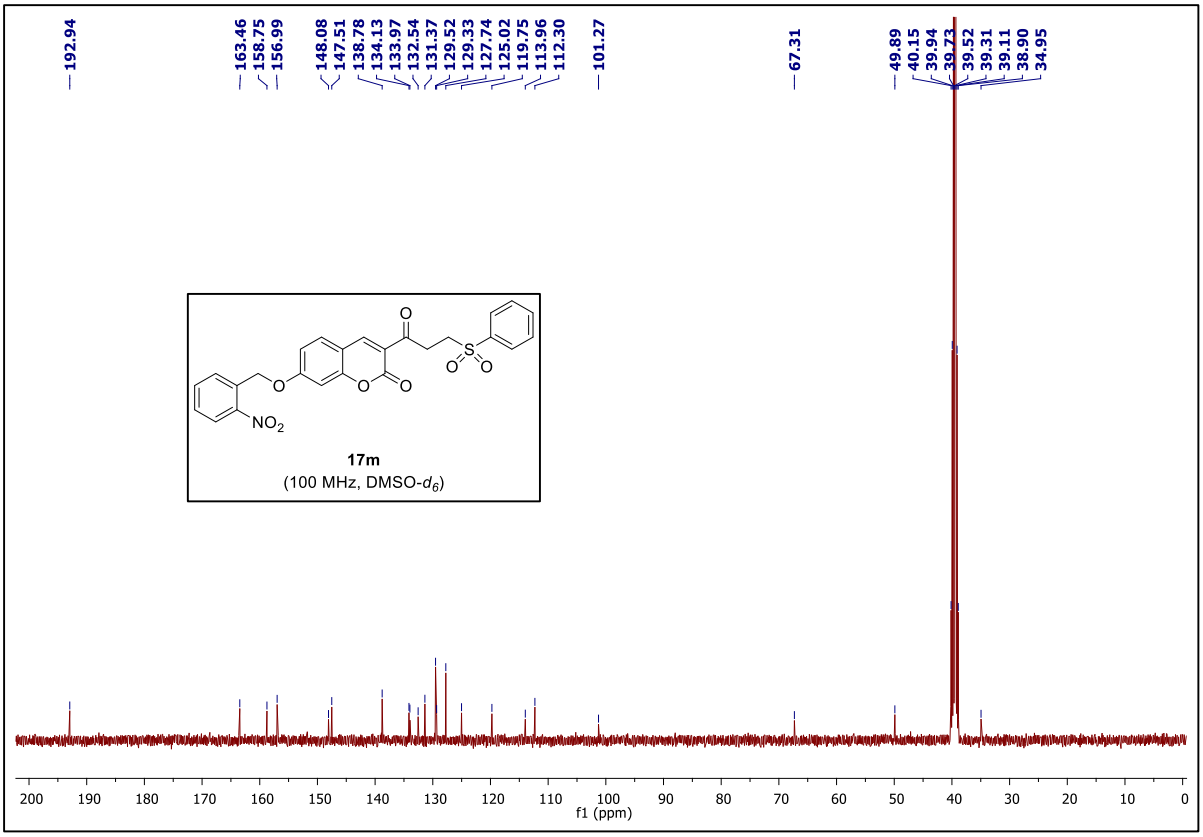
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-(benzyloxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17l**.



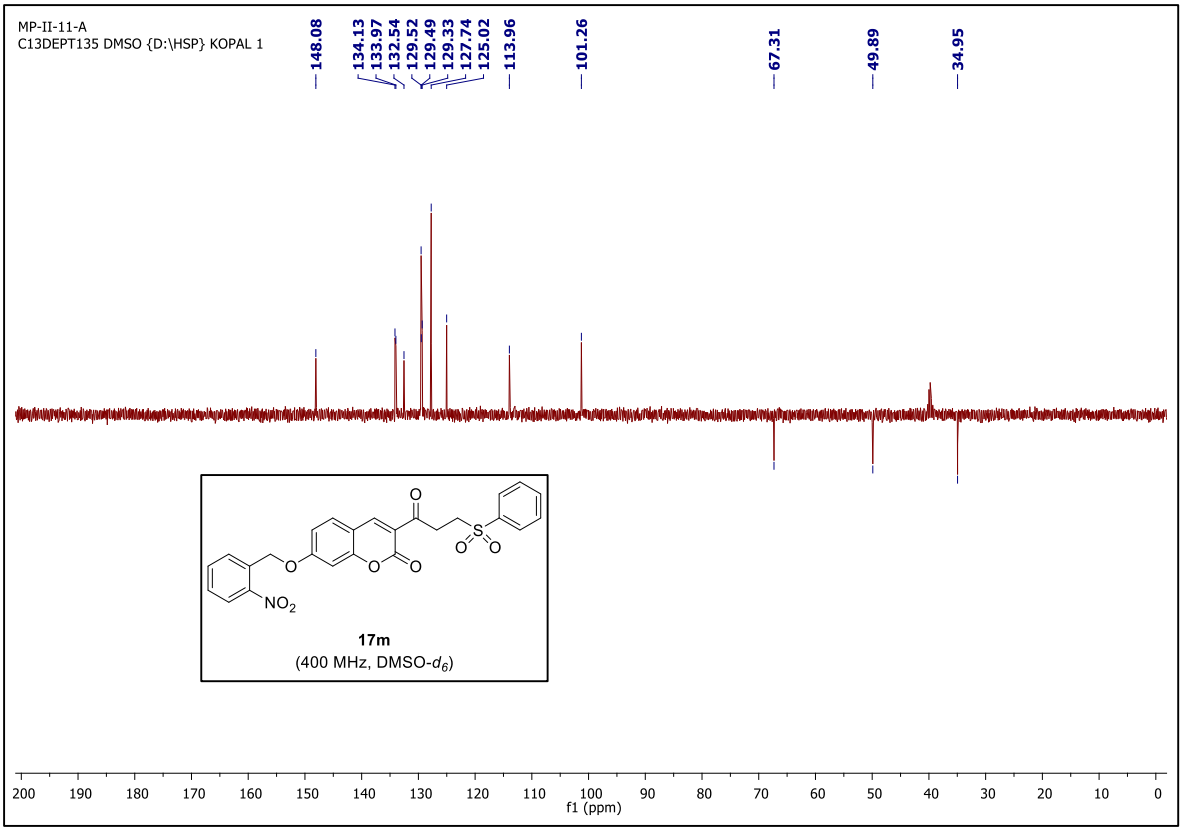
DEPT-135 NMR spectrum of 7-(benzyloxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17l**.



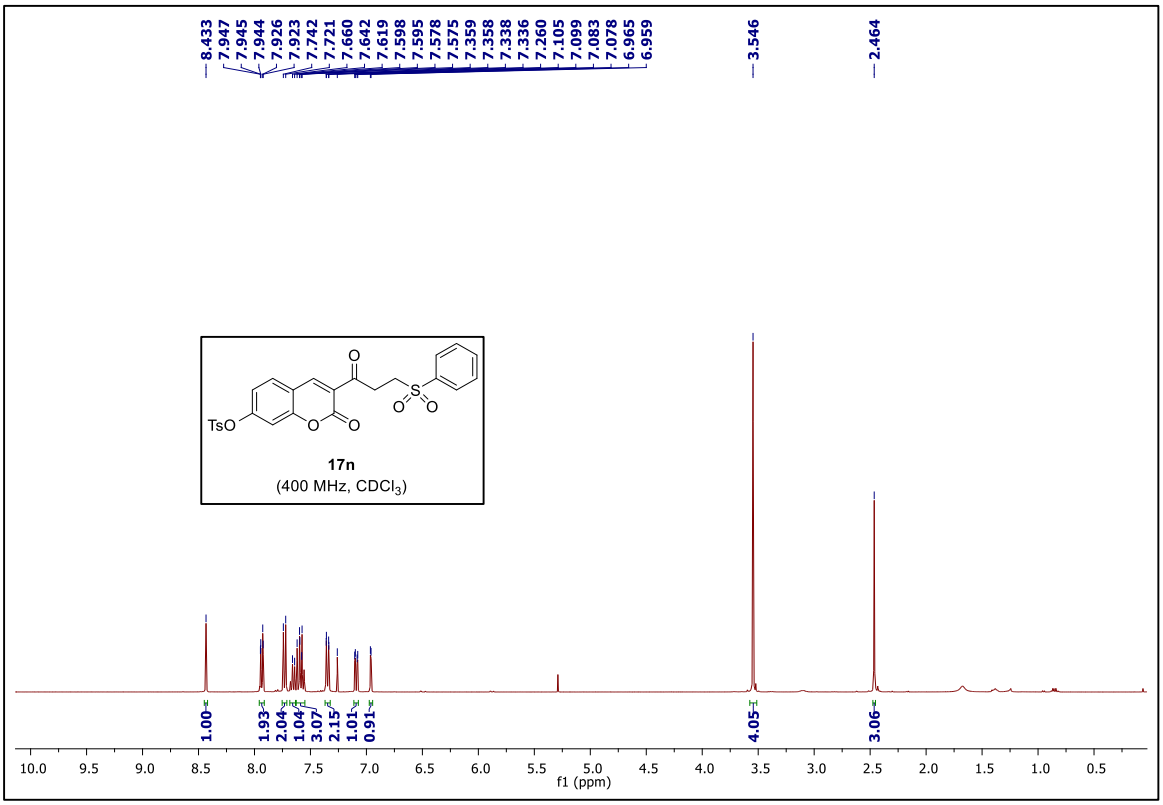
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 7-((2-nitrobenzyl)oxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17m**.



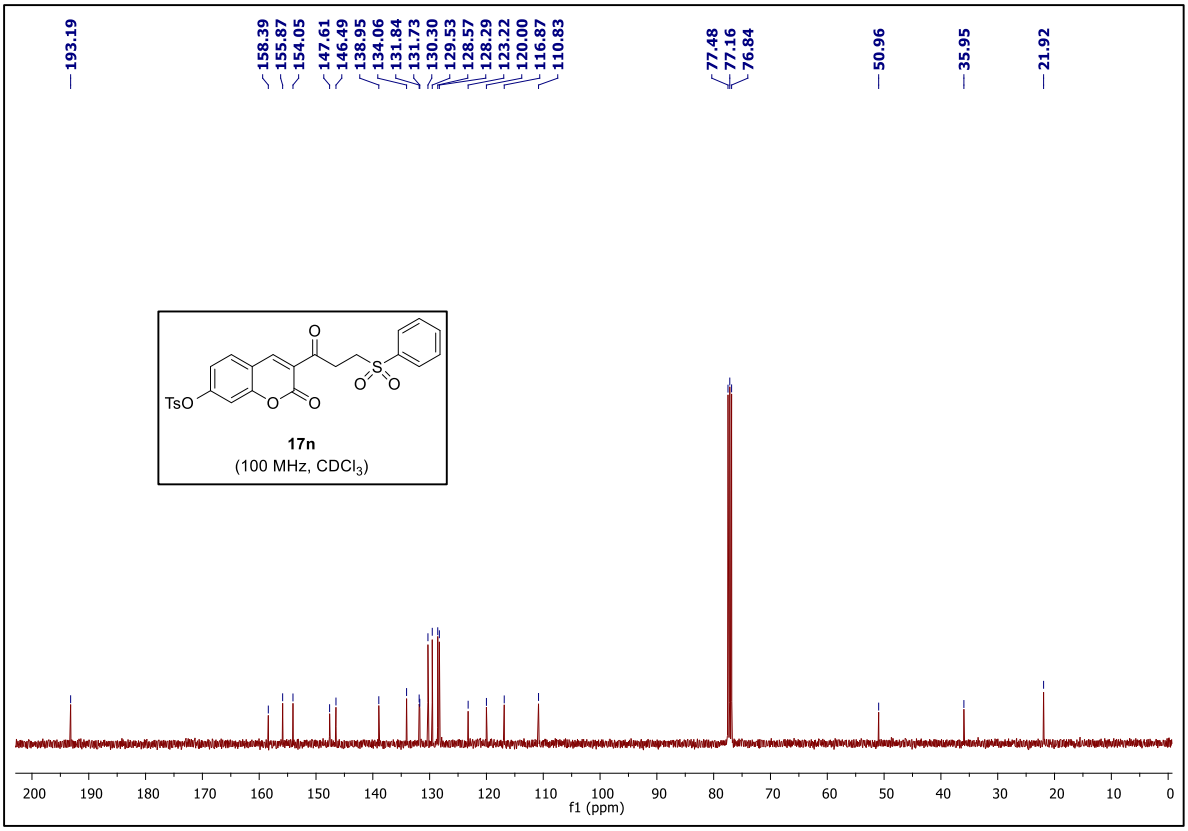
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 7-((2-nitrobenzyl)oxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17m**.



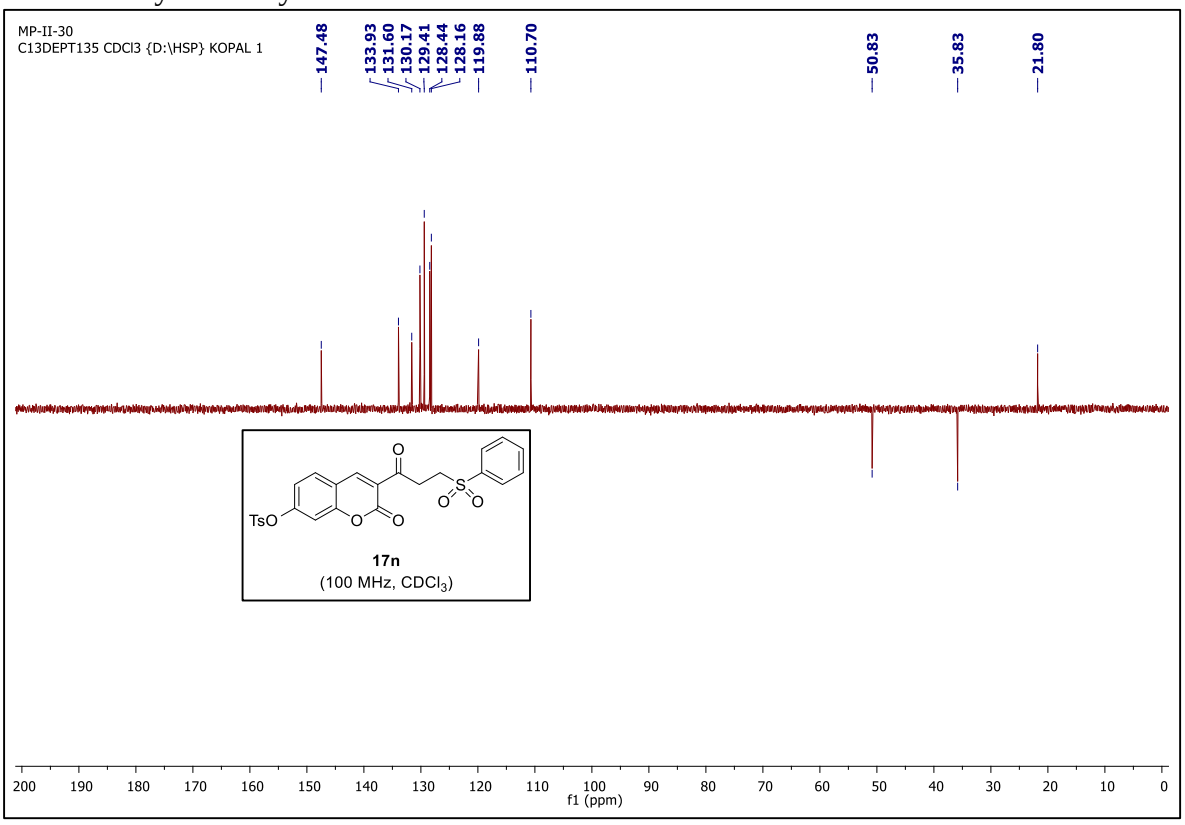
DEPT-135 NMR spectrum of 7-((2-nitrobenzyl)oxy)-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-2-one **17m**.



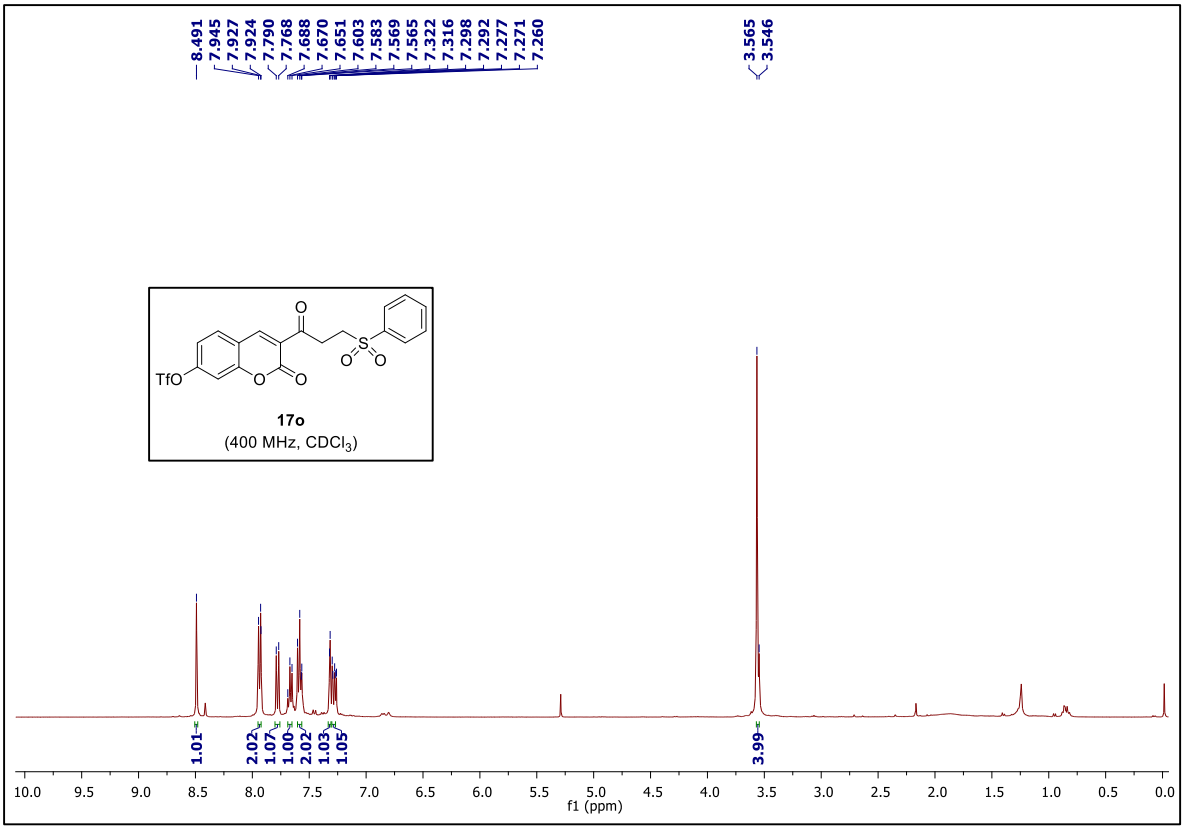
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl 4-methylbenzenesulfonate **17n**.



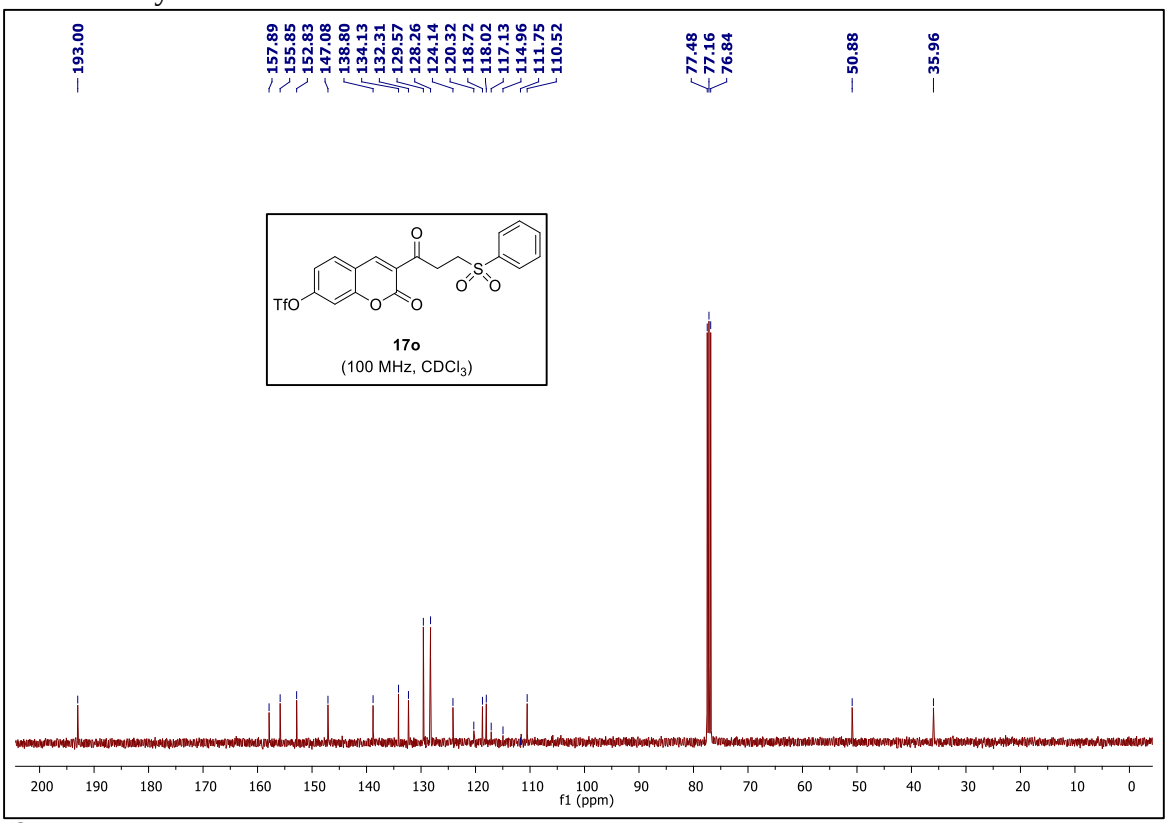
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl 4-methylbenzenesulfonate **17n**.



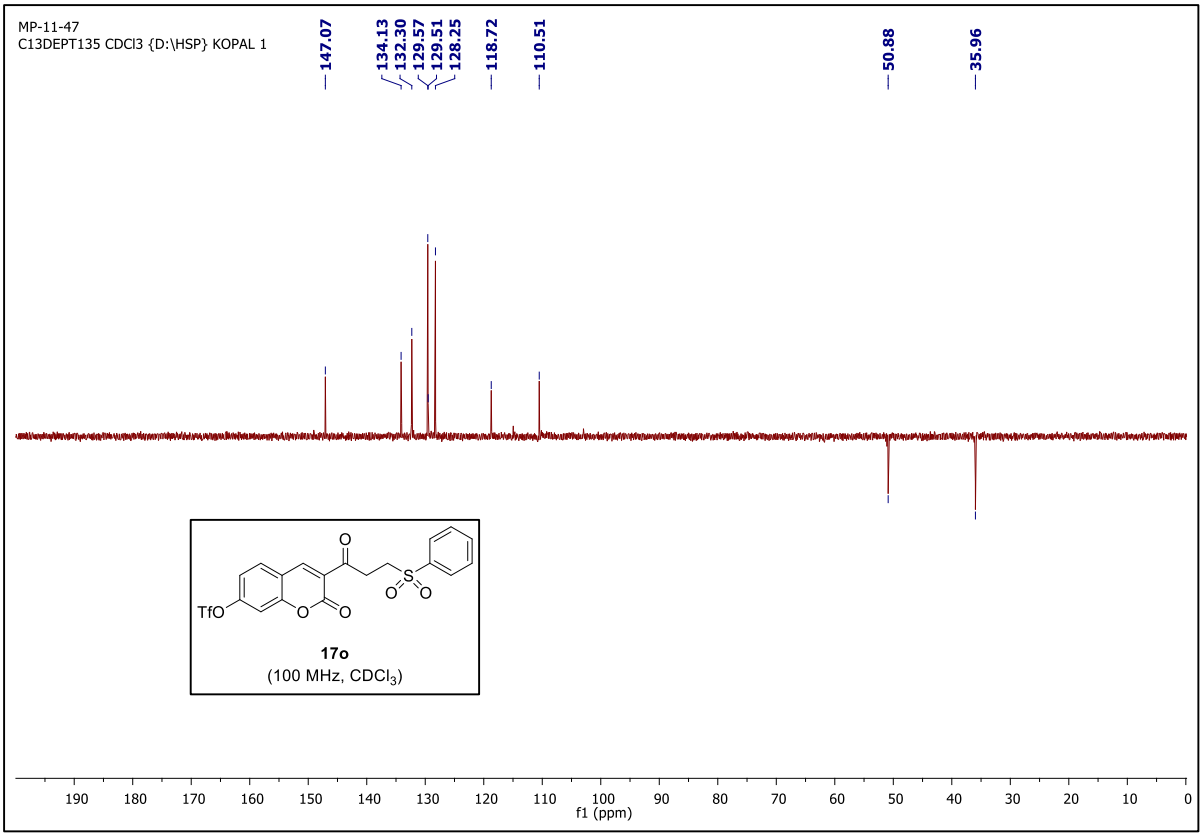
DEPT-135 NMR spectrum of 2-oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl 4-methylbenzenesulfonate **17n**.



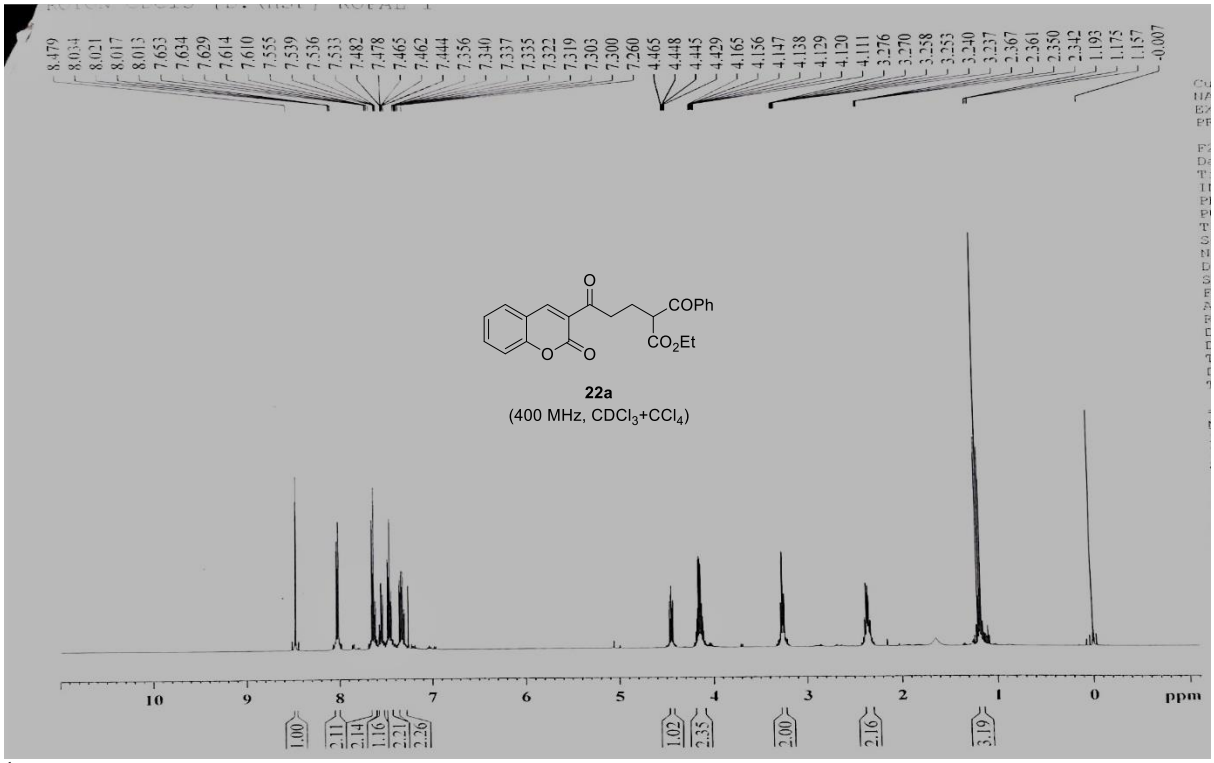
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl trifluoromethanesulfonate **17o**



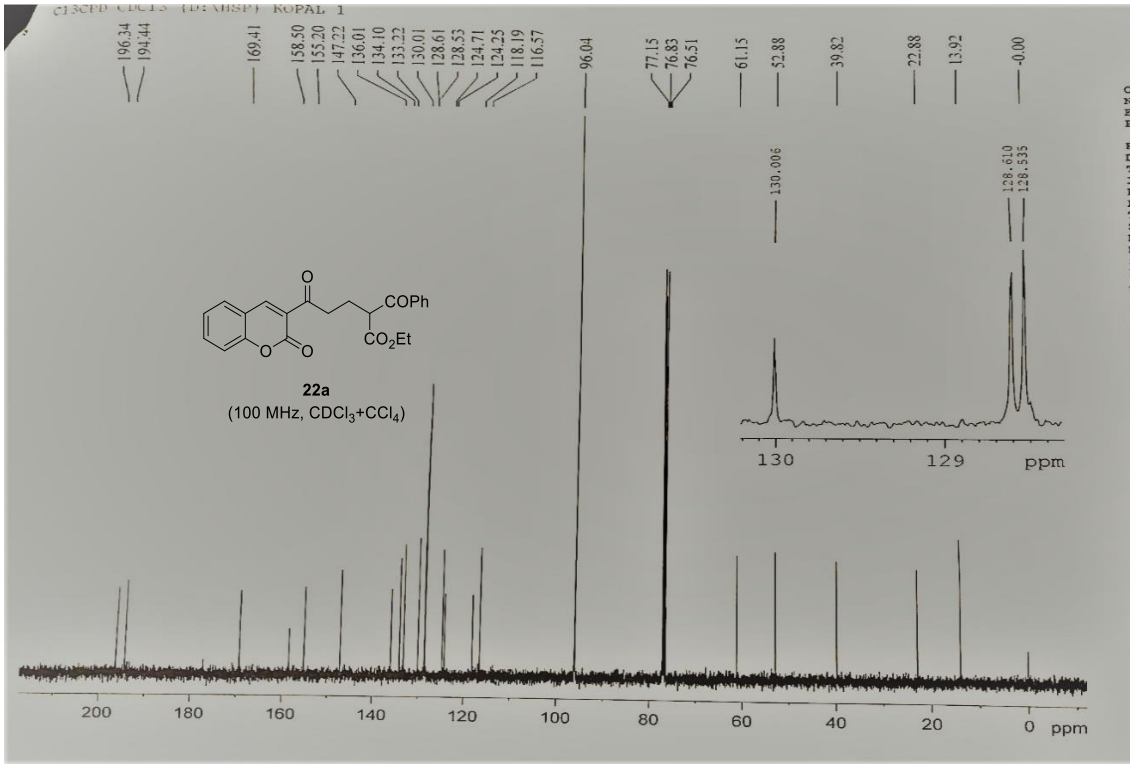
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl trifluoromethanesulfonate **17o**.



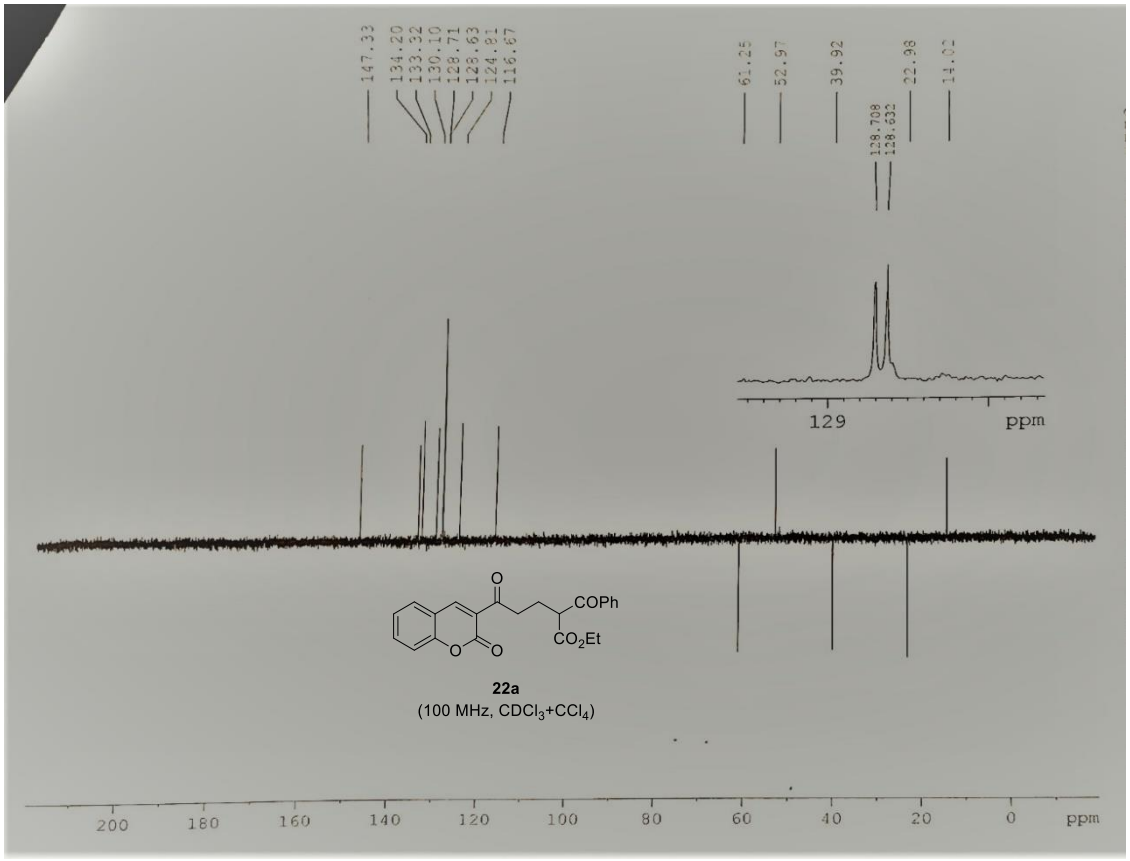
DEPT-135 NMR spectrum of 2-oxo-3-(3-(phenylsulfonyl)propanoyl)-2*H*-chromen-7-yl trifluoromethanesulfonate **17o**.



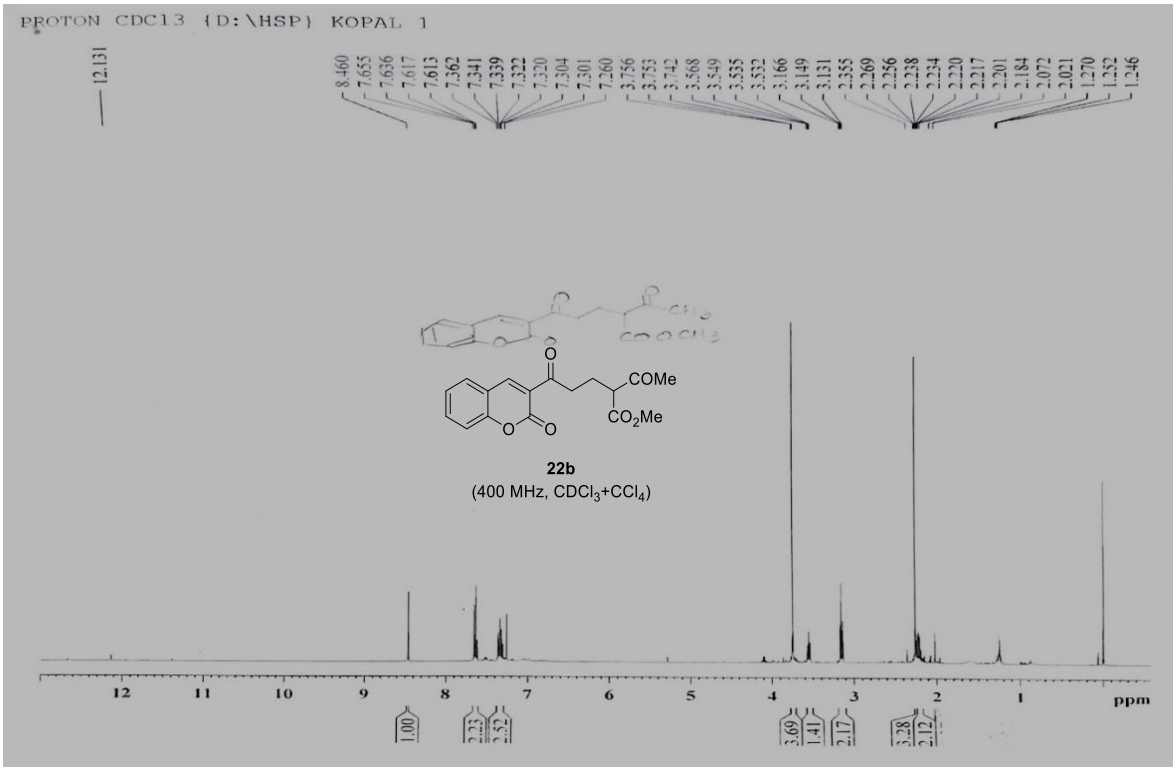
^{1}H NMR (400 MHz, $CDCl_3$+CCl_4) spectrum of ethyl-2-benzoyl-5-oxo-5-(2-oxo-2*H*-chromen-3-yl)pentanoate **22a.**



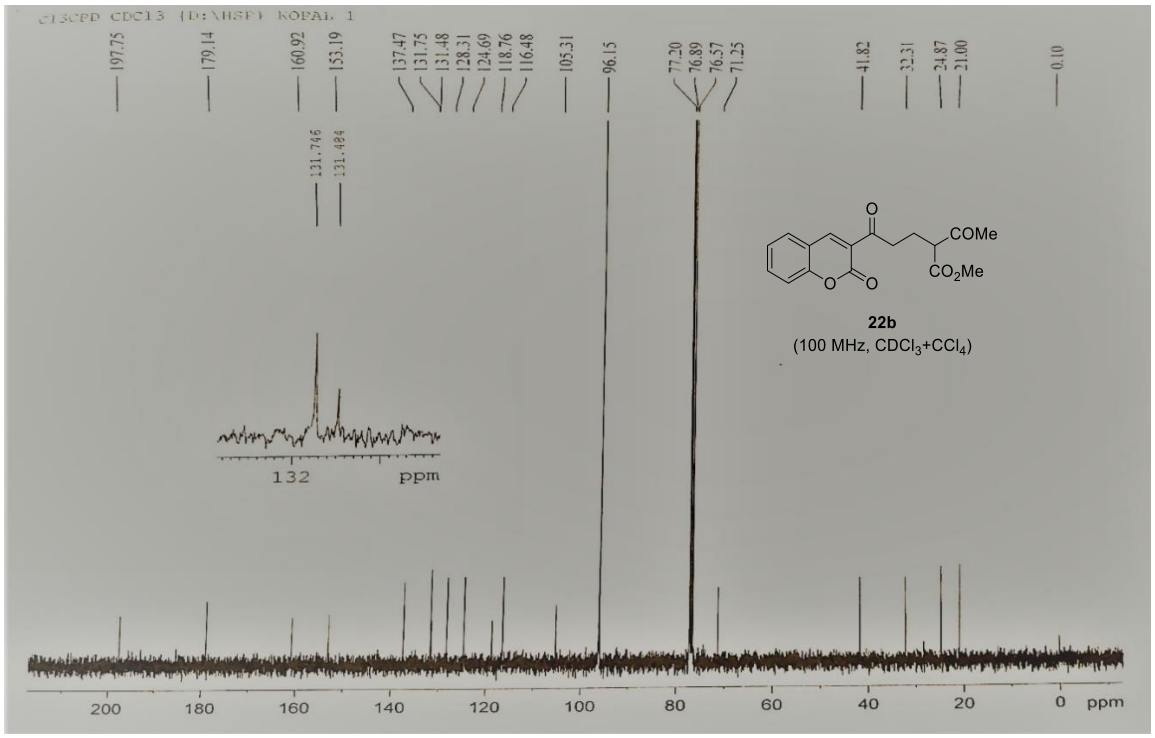
^{13}C NMR (100 MHz, $CDCl_3$+CCl_4) spectrum of ethyl-2-benzoyl-5-oxo-5-(2-oxo-2*H*-chromen-3-yl)pentanoate **22a**.



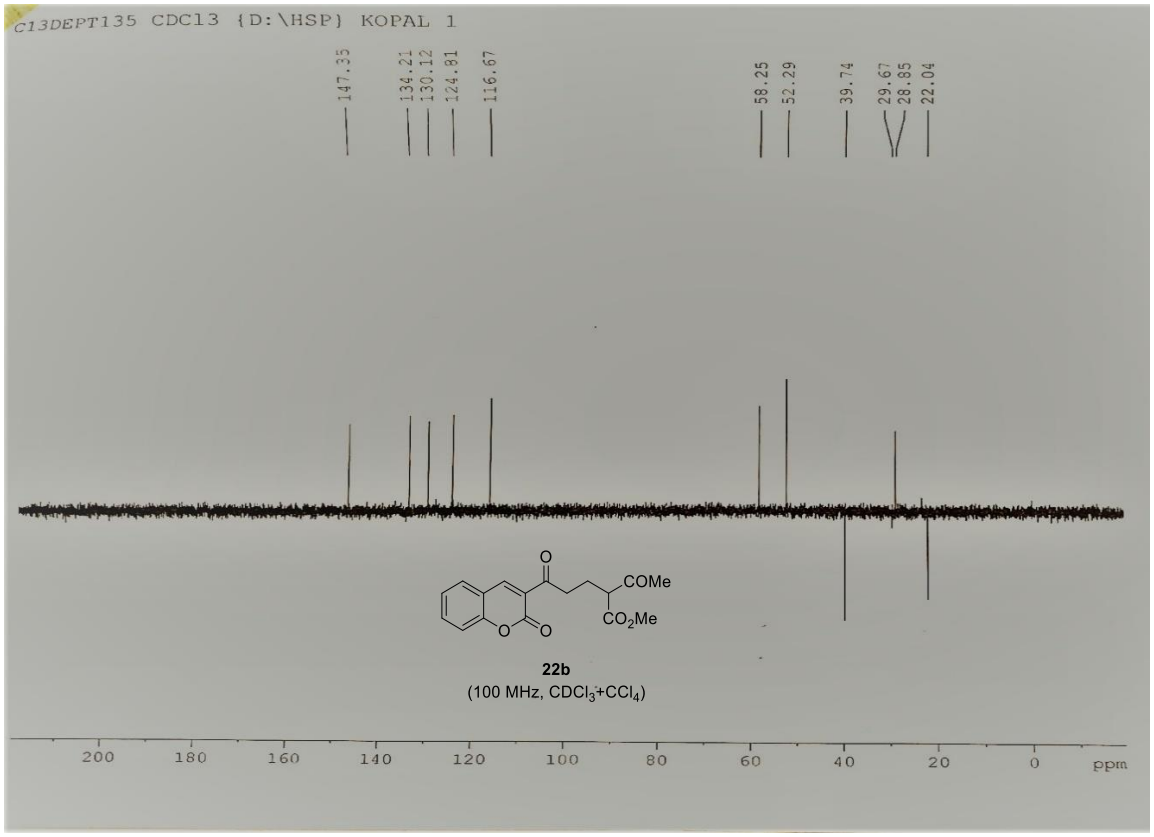
DEPT-135 NMR spectrum of ethyl-2-benzoyl-5-oxo-5-(2-oxo-2*H*-chromen-3-yl)pentanoate **22a**.



^{1}H NMR (400 MHz, $CDCl_3$+CCl_4) spectrum of methyl-2-acetyl-5-oxo-5-(2-oxo-2*H*-chromen-3-l)pentanoate **22b**.

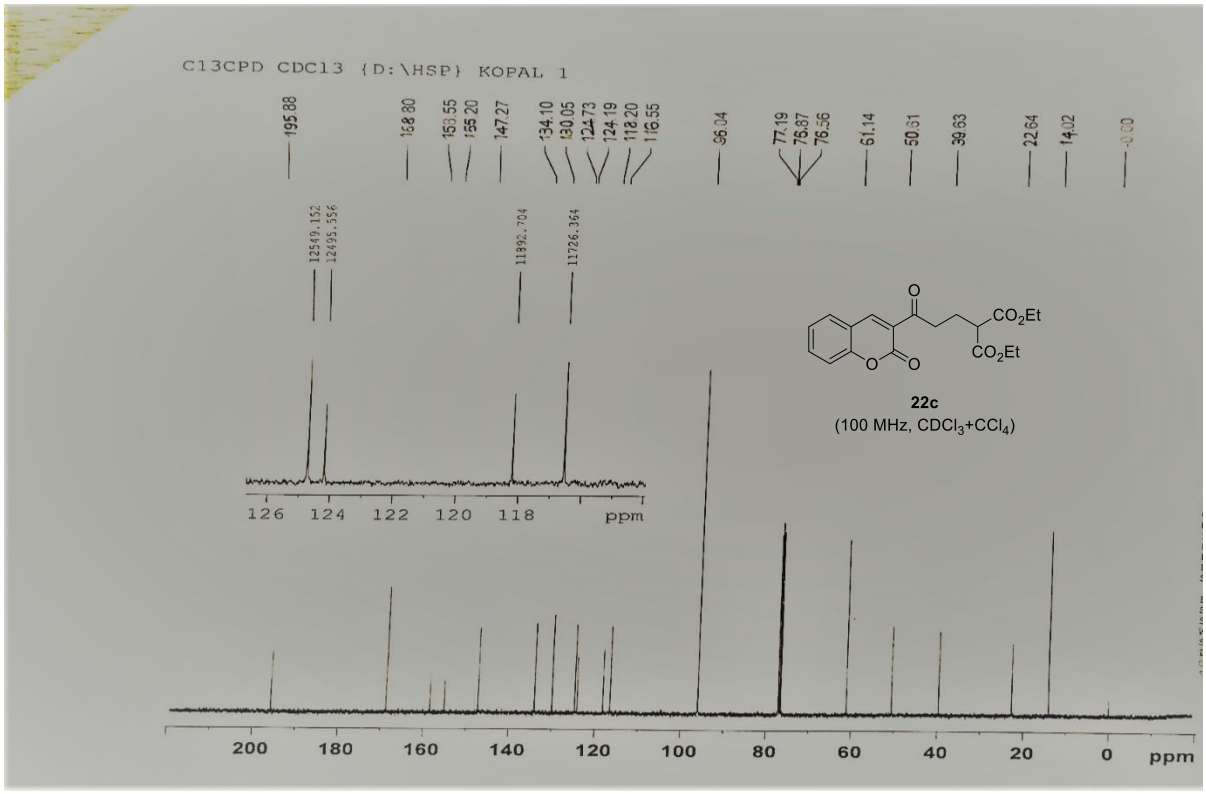


^{13}C NMR (100 MHz, $CDCl_3$+CCl_4) spectrum of methyl-2-acetyl-5-oxo-5-(2-oxo-2*H*-chromen-3-l)pentanoate **22b**.

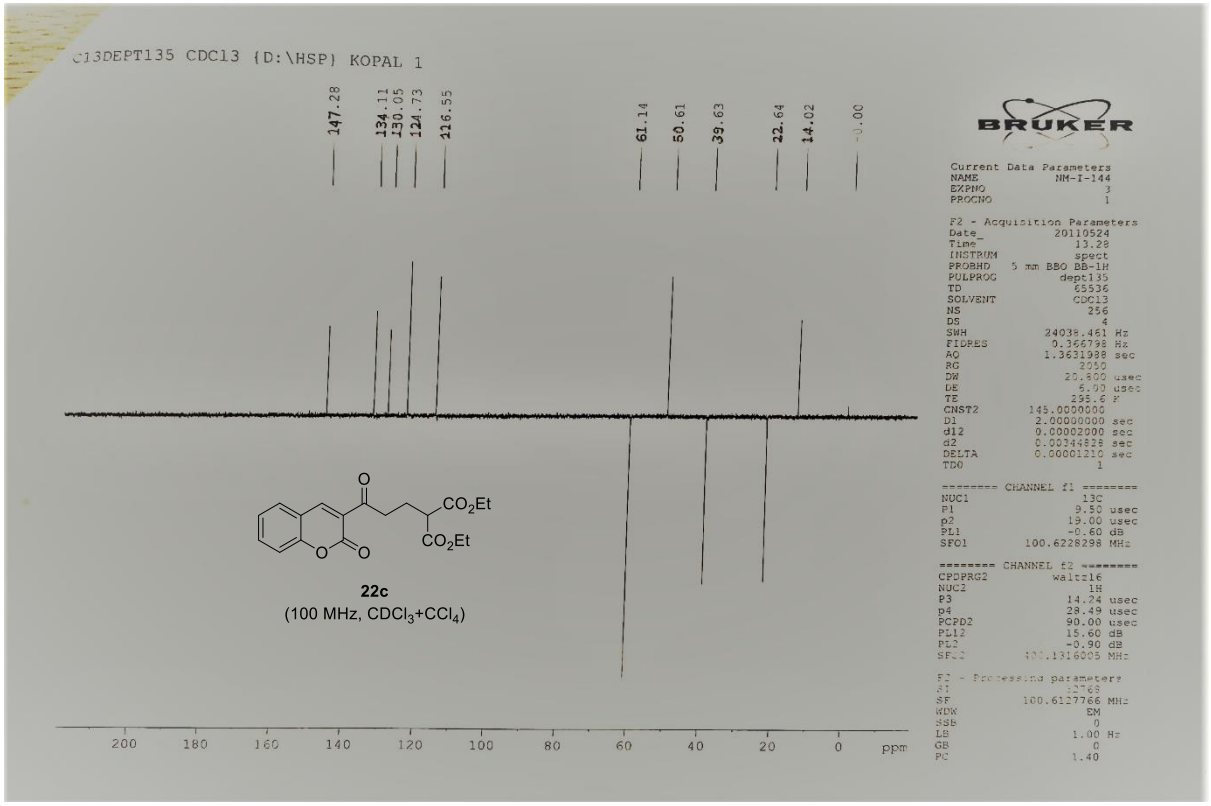


DEPT-135 NMR spectrum of methyl-2-acetyl-5-oxo-5-(2-oxo-2*H*-chromen-3-l)pentanoate **22b**.

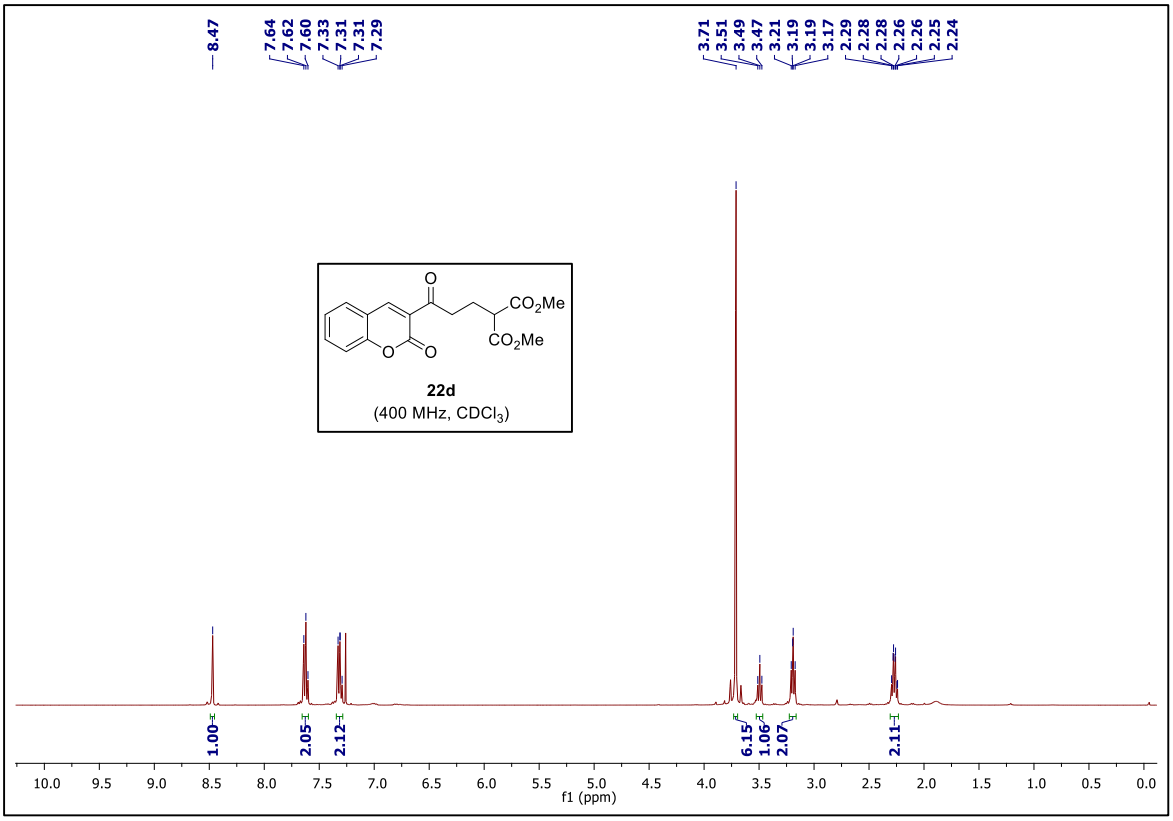
^{1}H NMR (400 MHz, $CDCl_3$+CCl_4) spectrum of diethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate **22c**.



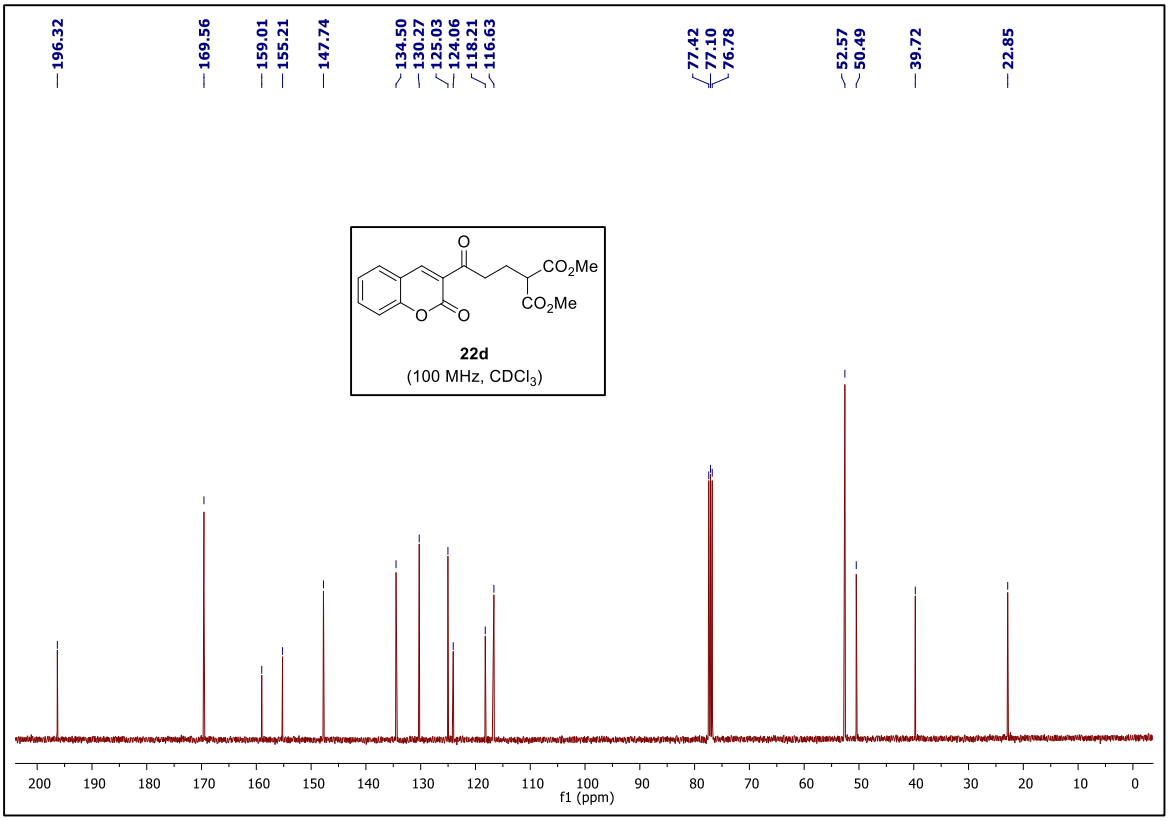
^{13}C NMR (100 MHz, $CDCl_3$+CCl_4) spectrum of diethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate **22c**.



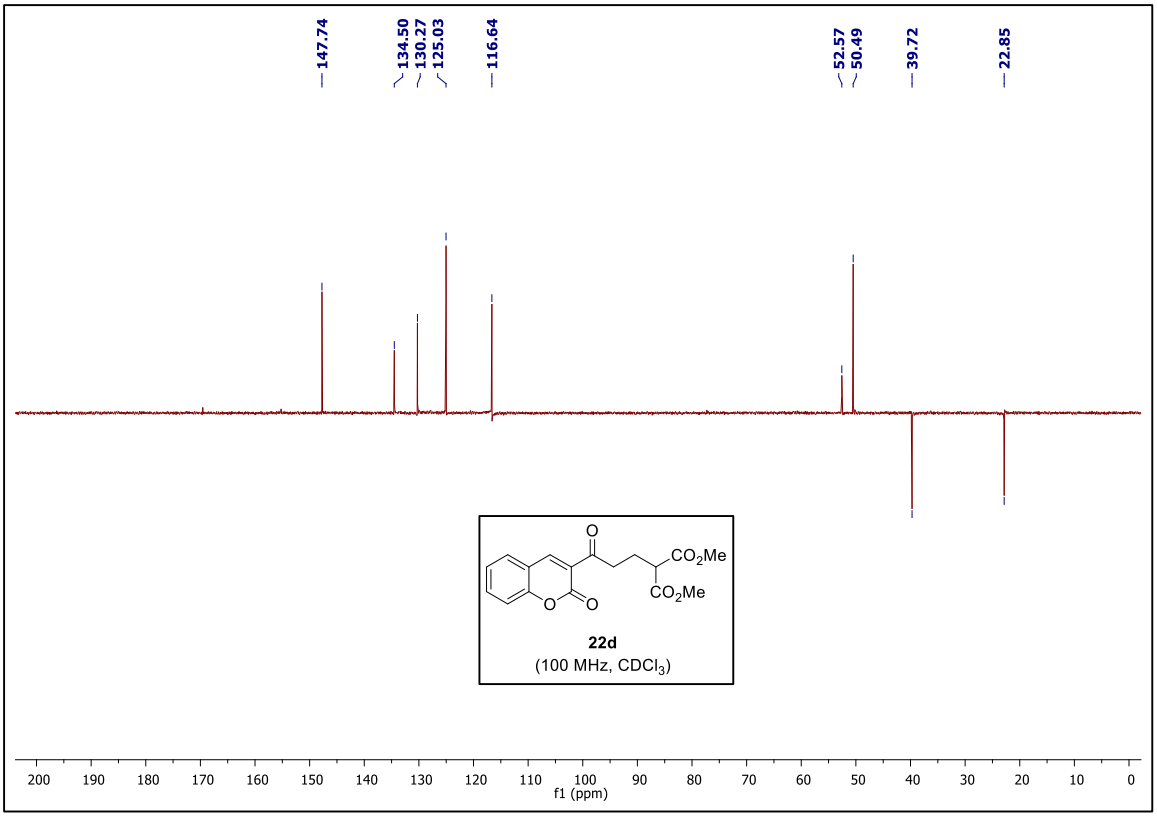
DEPT-135 NMR spectrum of diethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate **22c**.



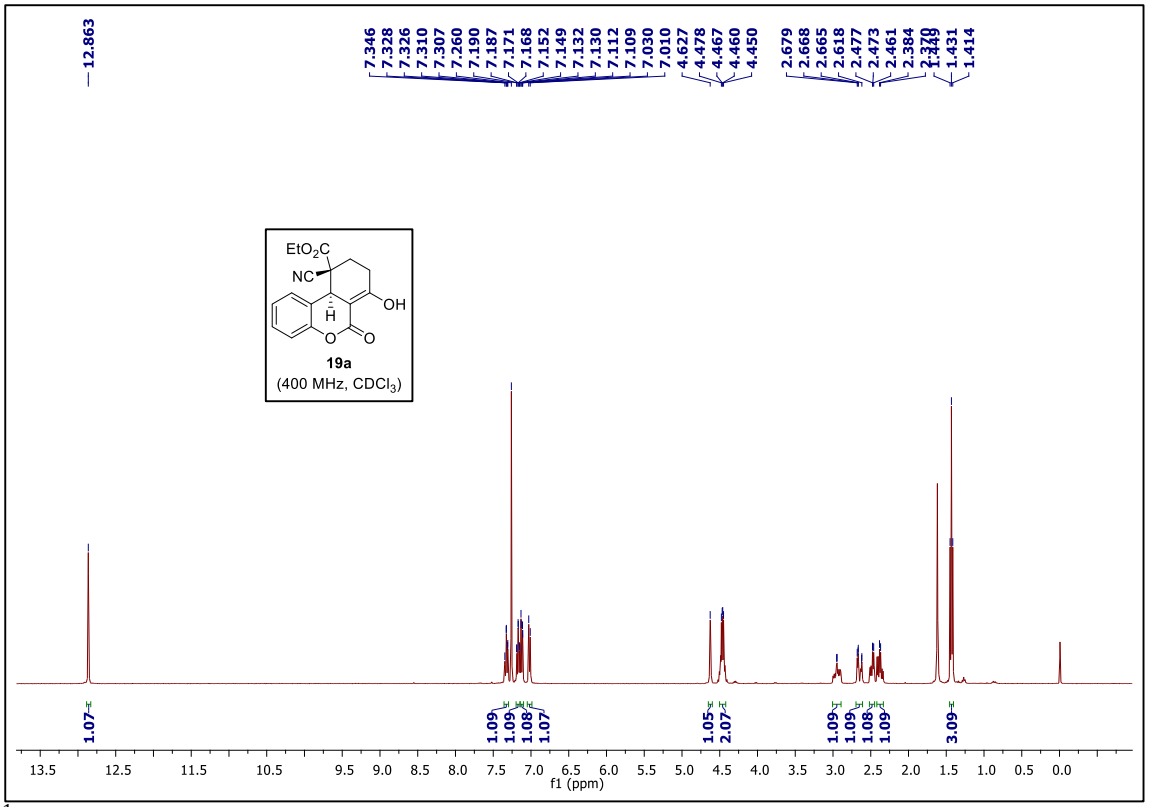
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of dimethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate **22d**.



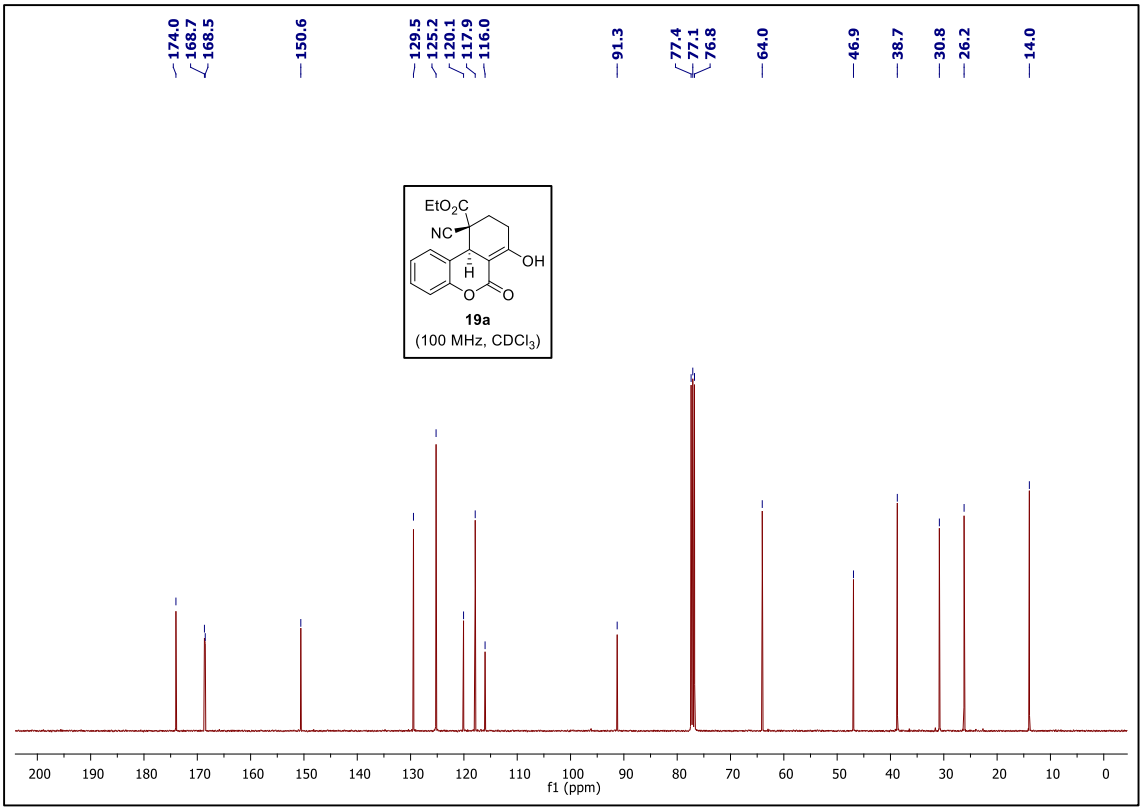
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of dimethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate **22d**.



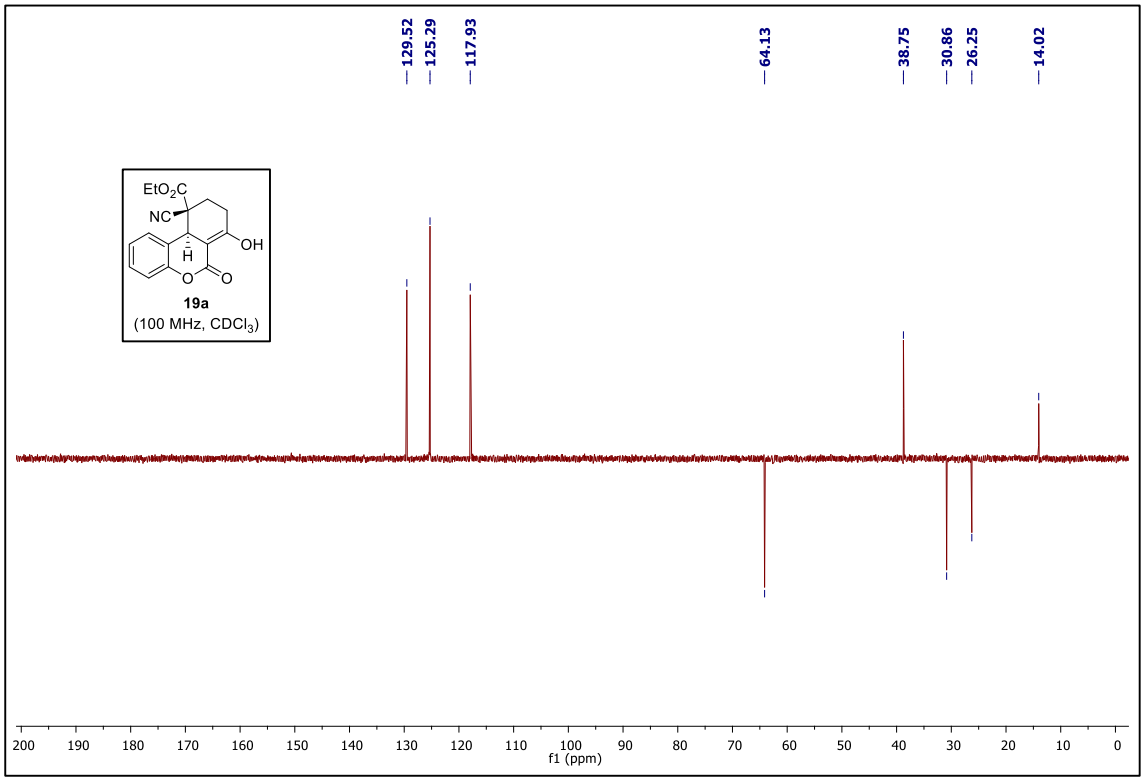
DEPT-135 NMR OF spectrum of dimethyl 2-(3-oxo-3-(2-oxo-2*H*-chromen-3-yl)propyl)malonate **22d**.



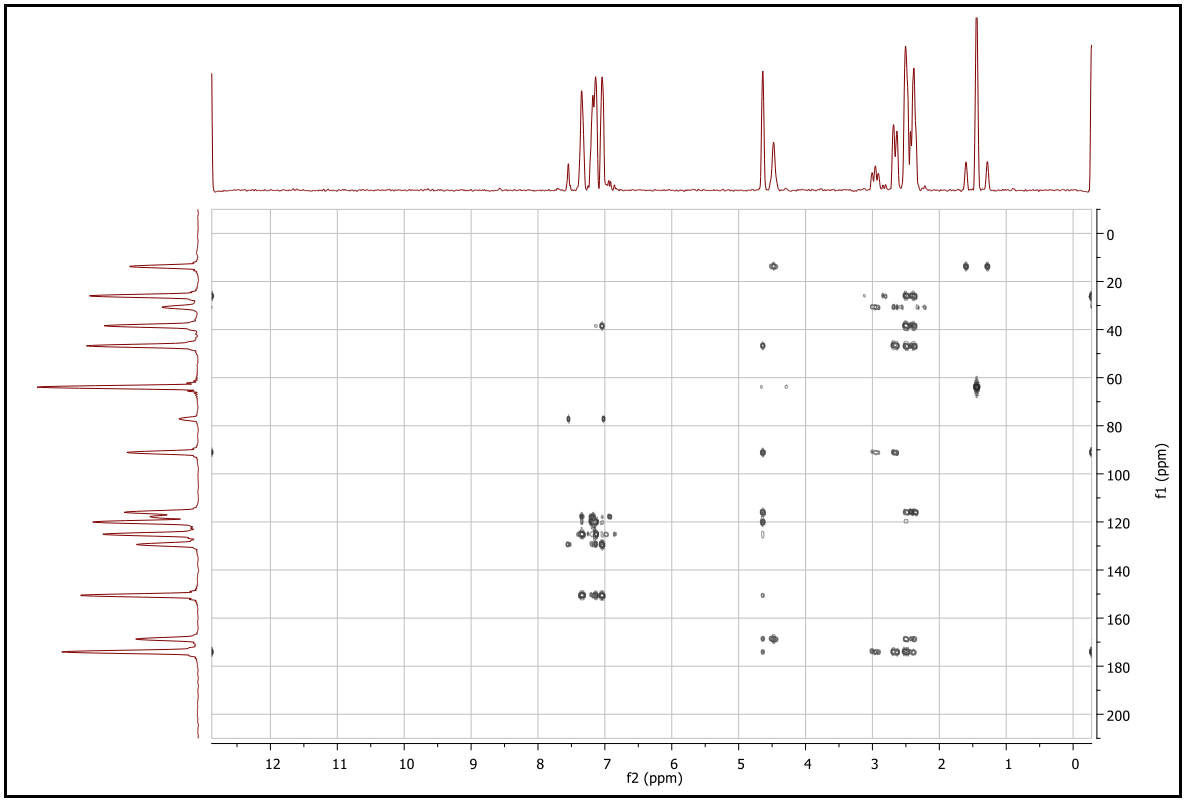
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19a**.



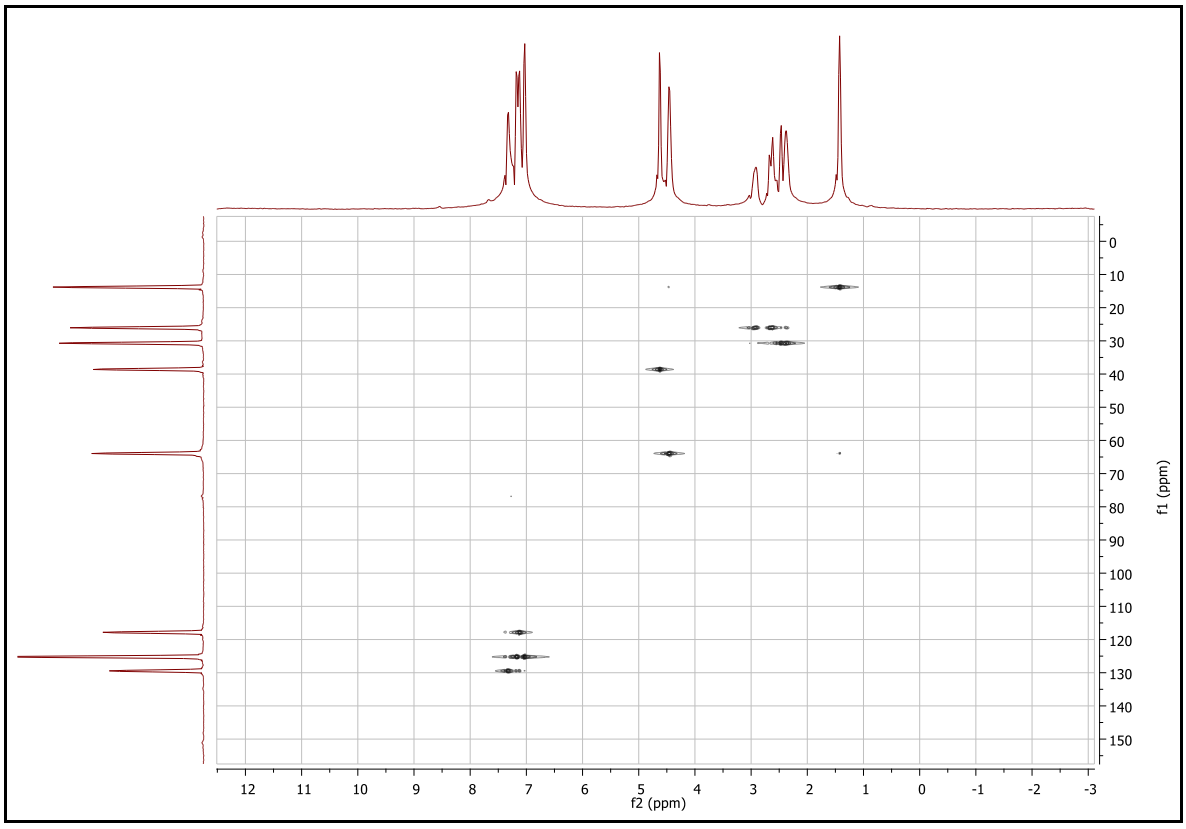
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19a**.



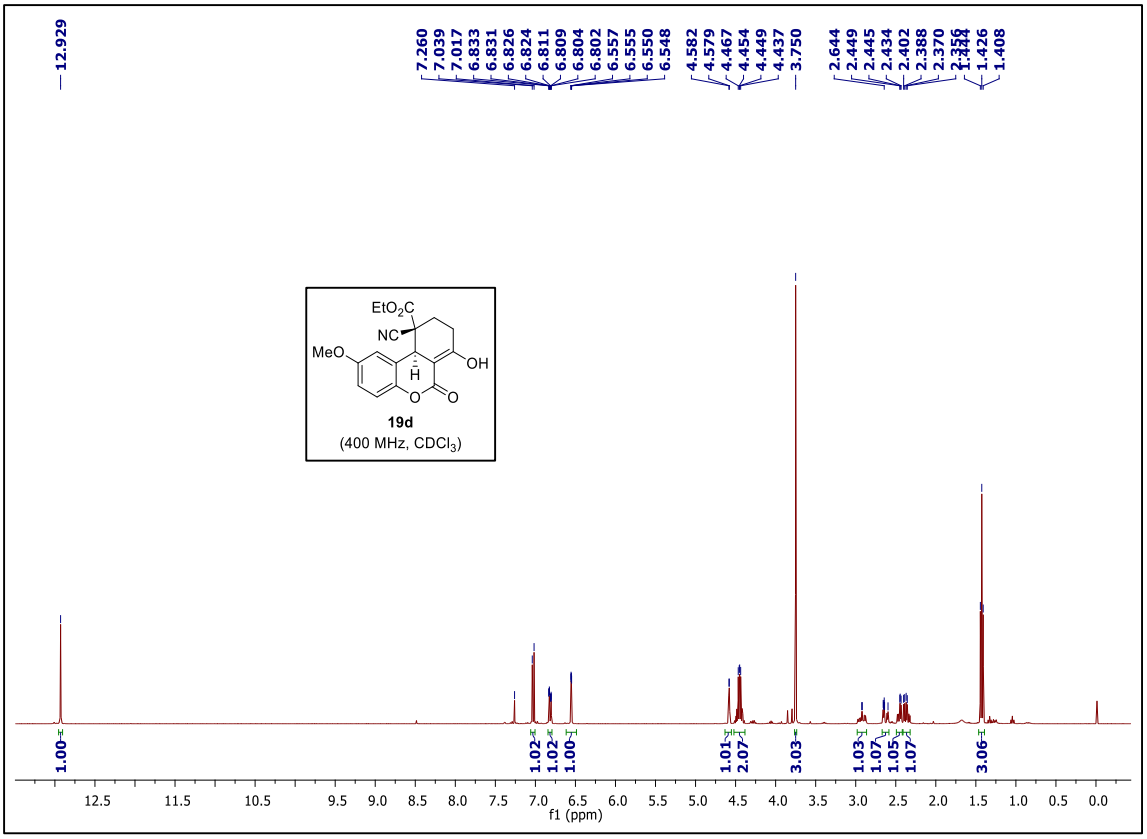
DEPT-135 NMR spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19a**.



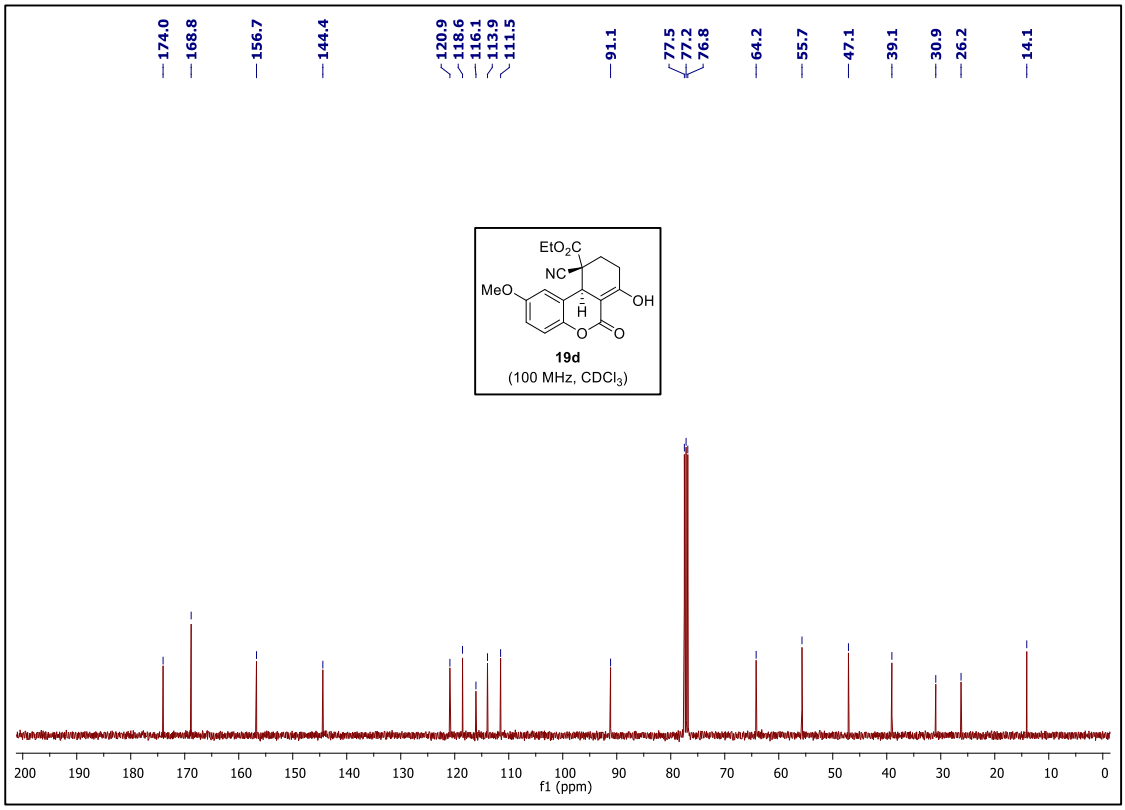
HMBC spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19**.



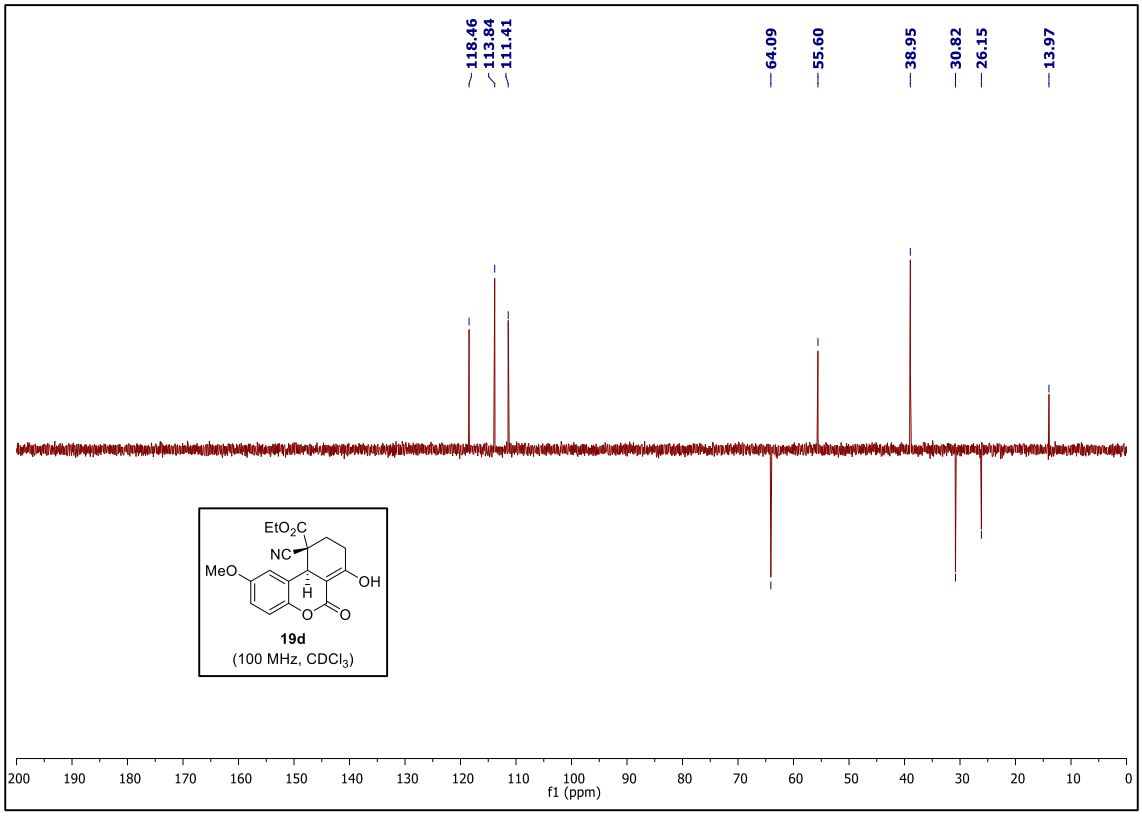
HSQC spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19a**



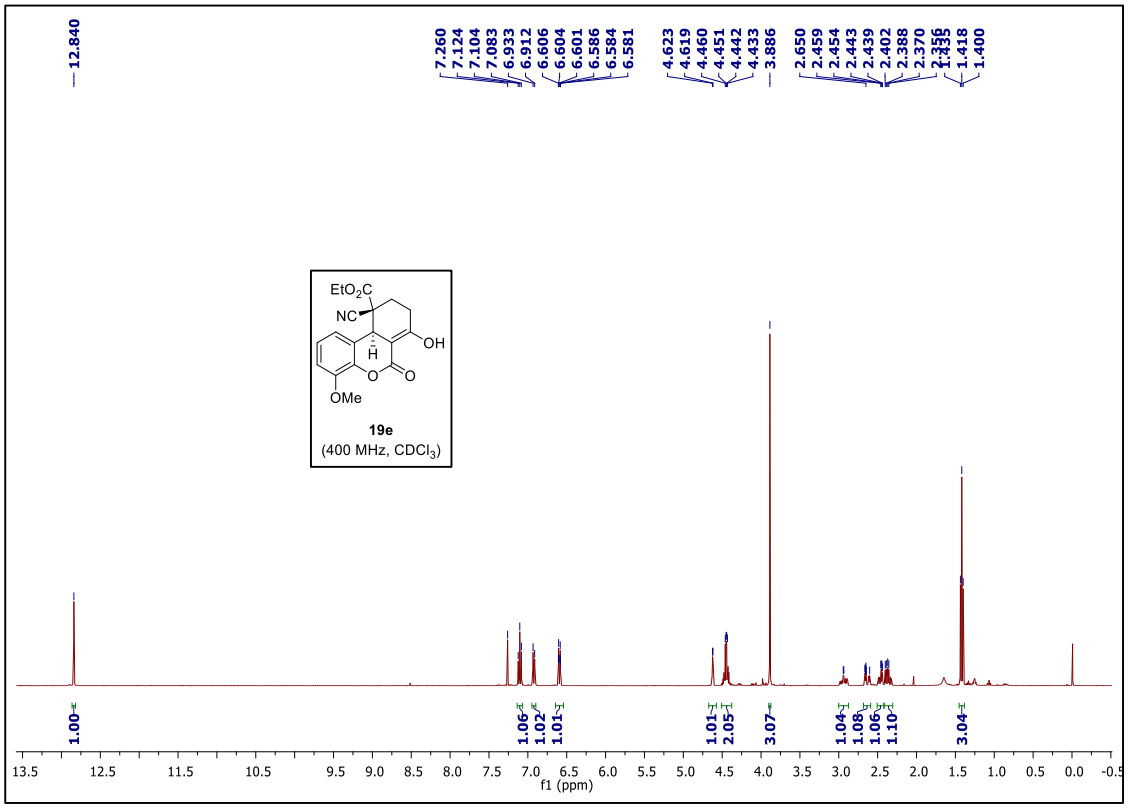
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-2-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19d**.



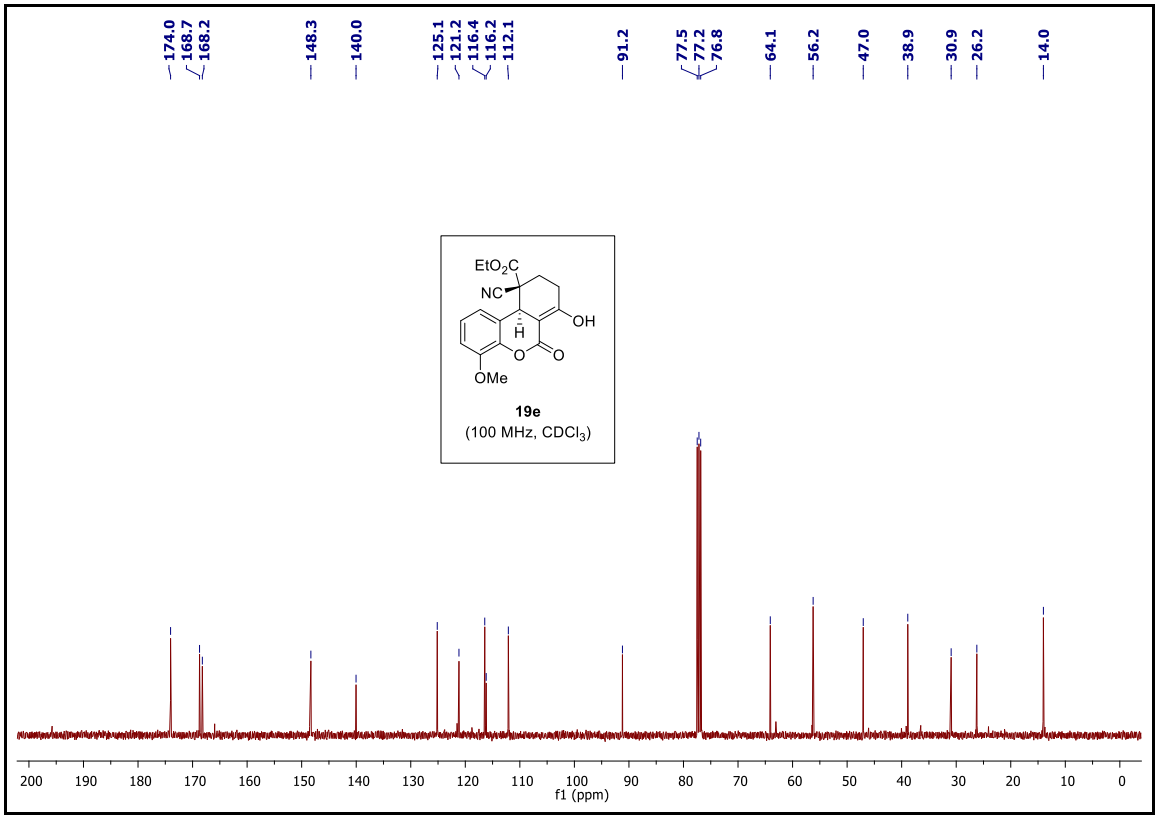
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-2-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19d**.



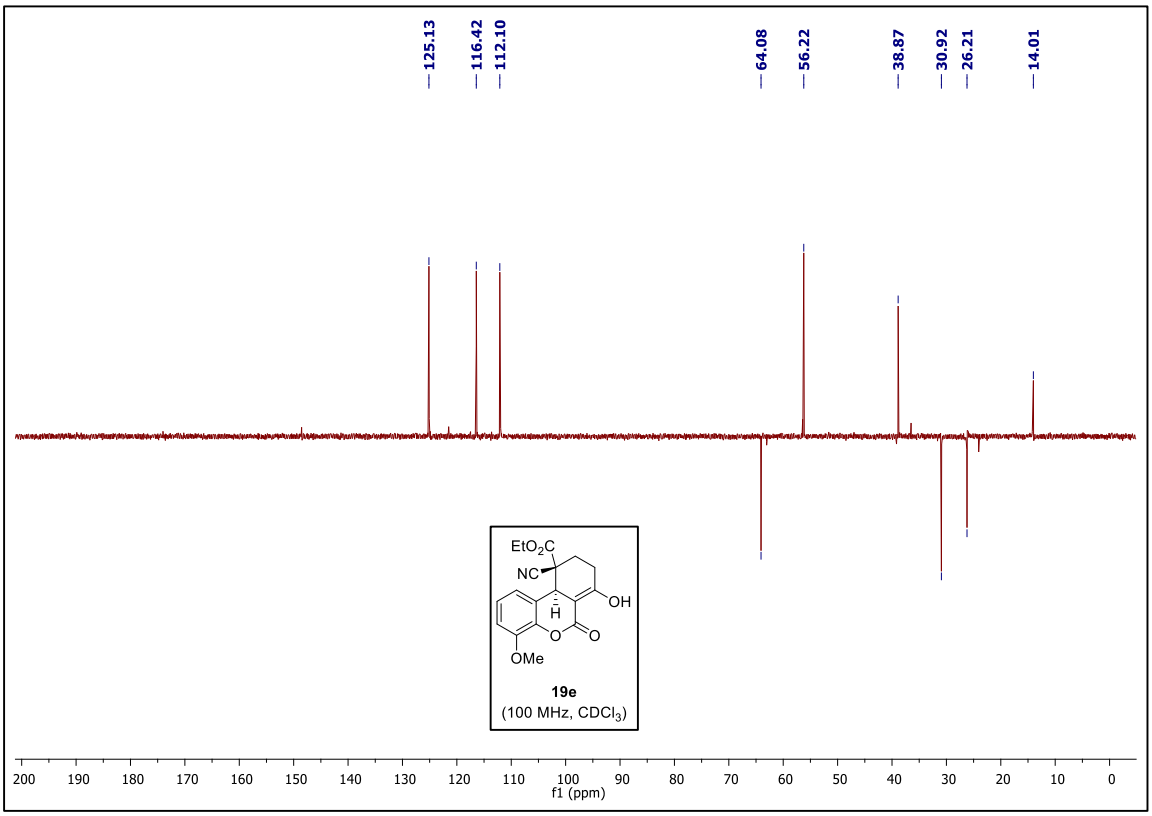
DEPT-135 NMR spectrum of ethyl 10-cyano-7-hydroxy-2-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19d**.



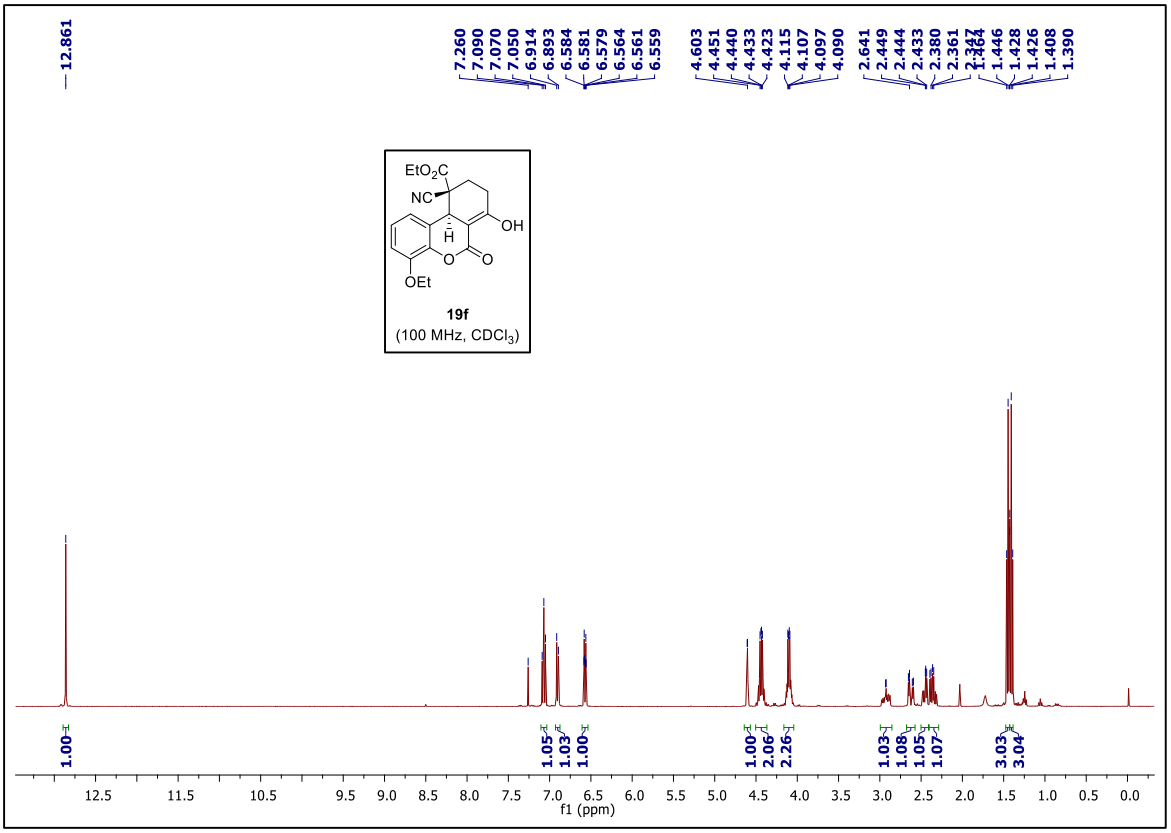
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-4-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19e**.



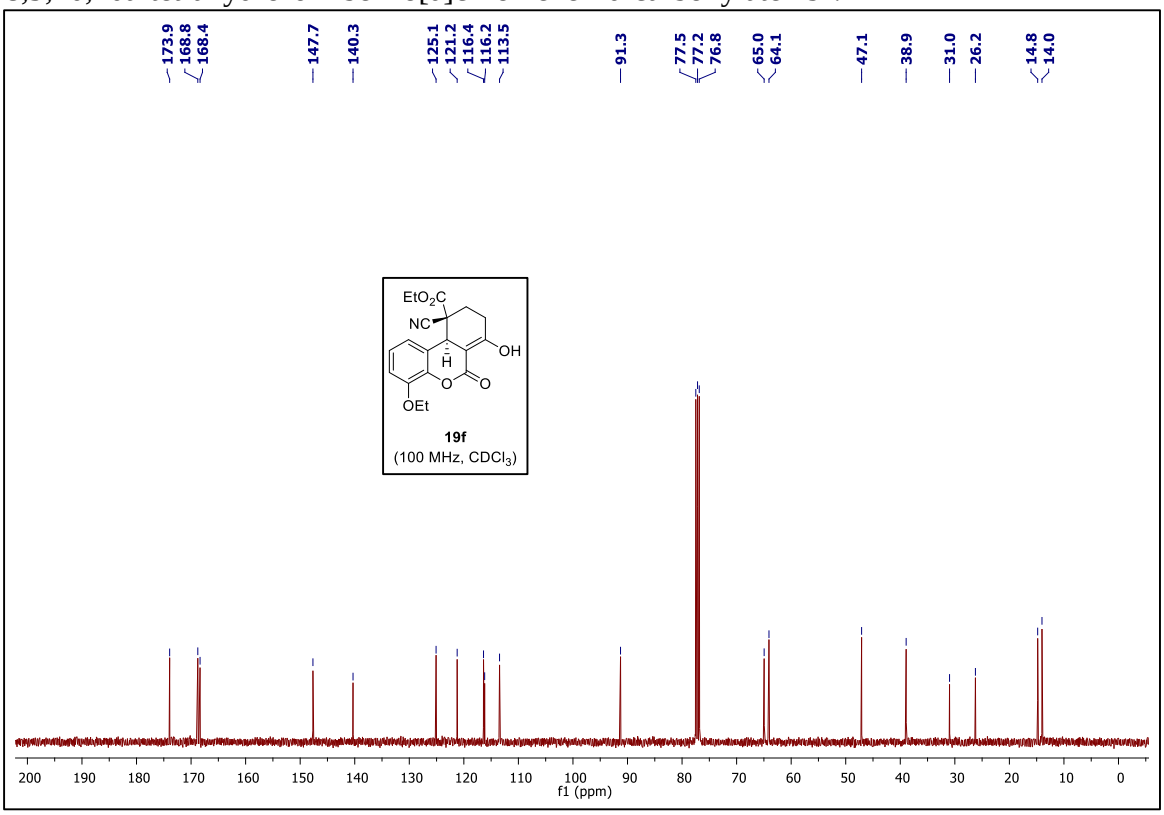
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-4-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19e**



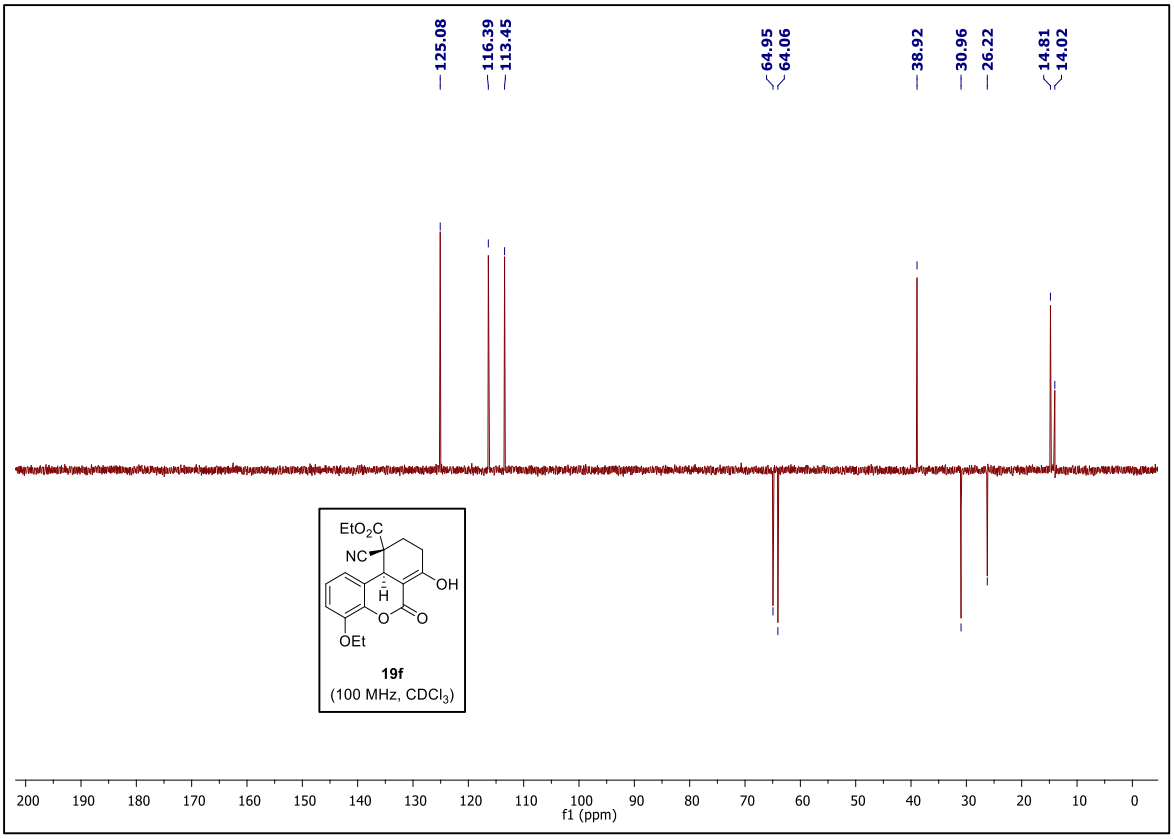
DEPT-135 NMR spectrum of ethyl 10-cyano-7-hydroxy-4-methoxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19e**



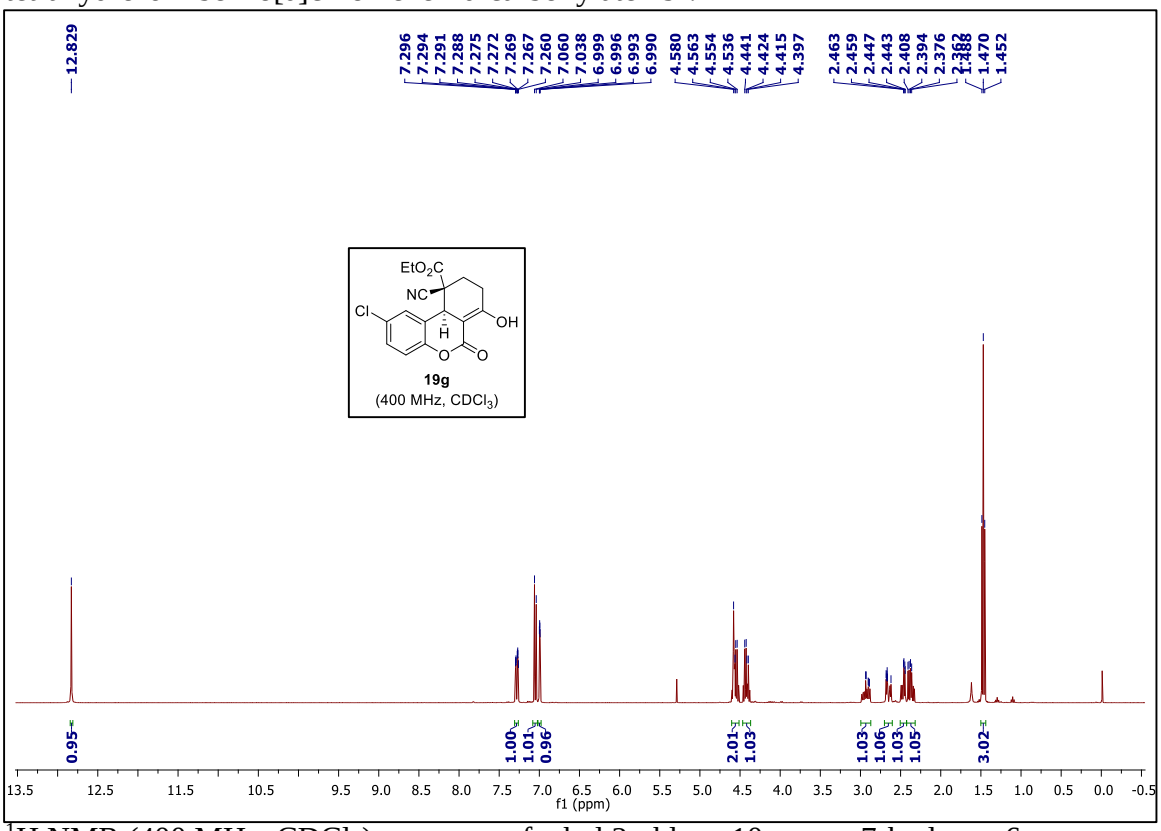
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-4-ethoxy-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19f**.



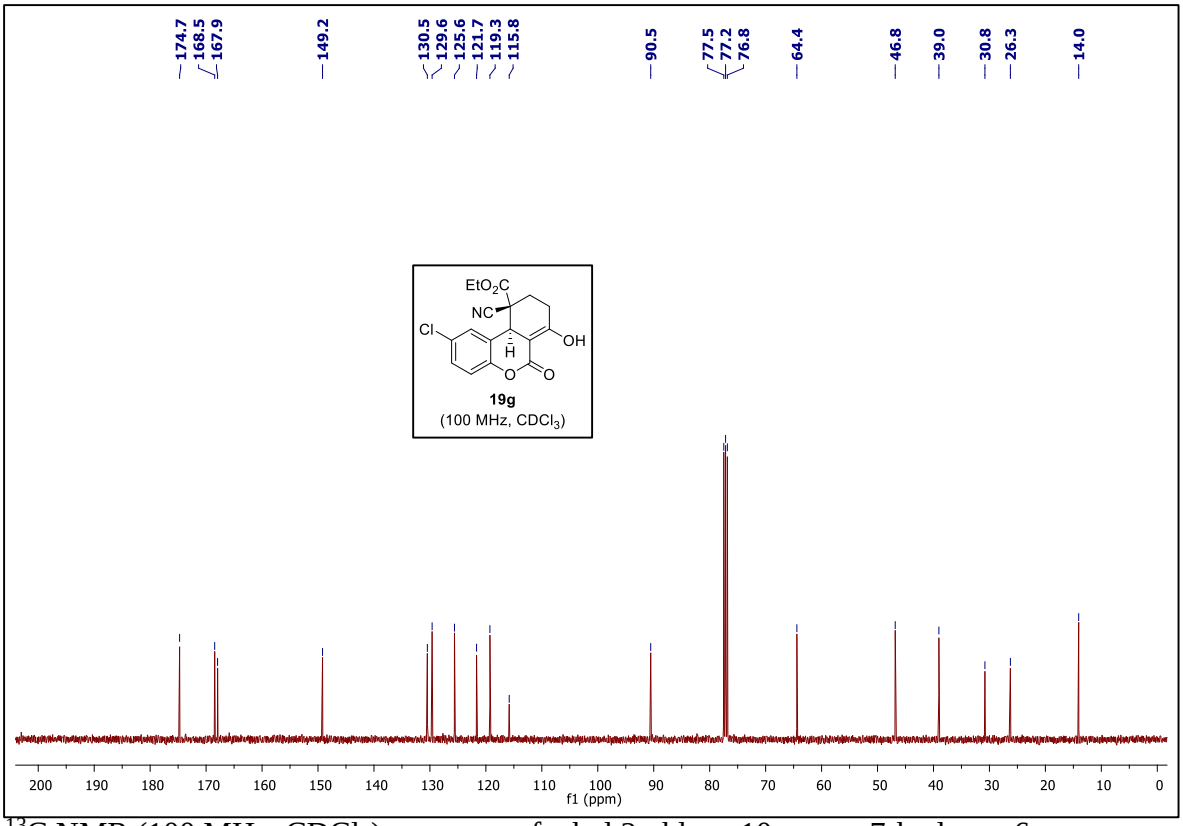
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-4-ethoxy-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **No**



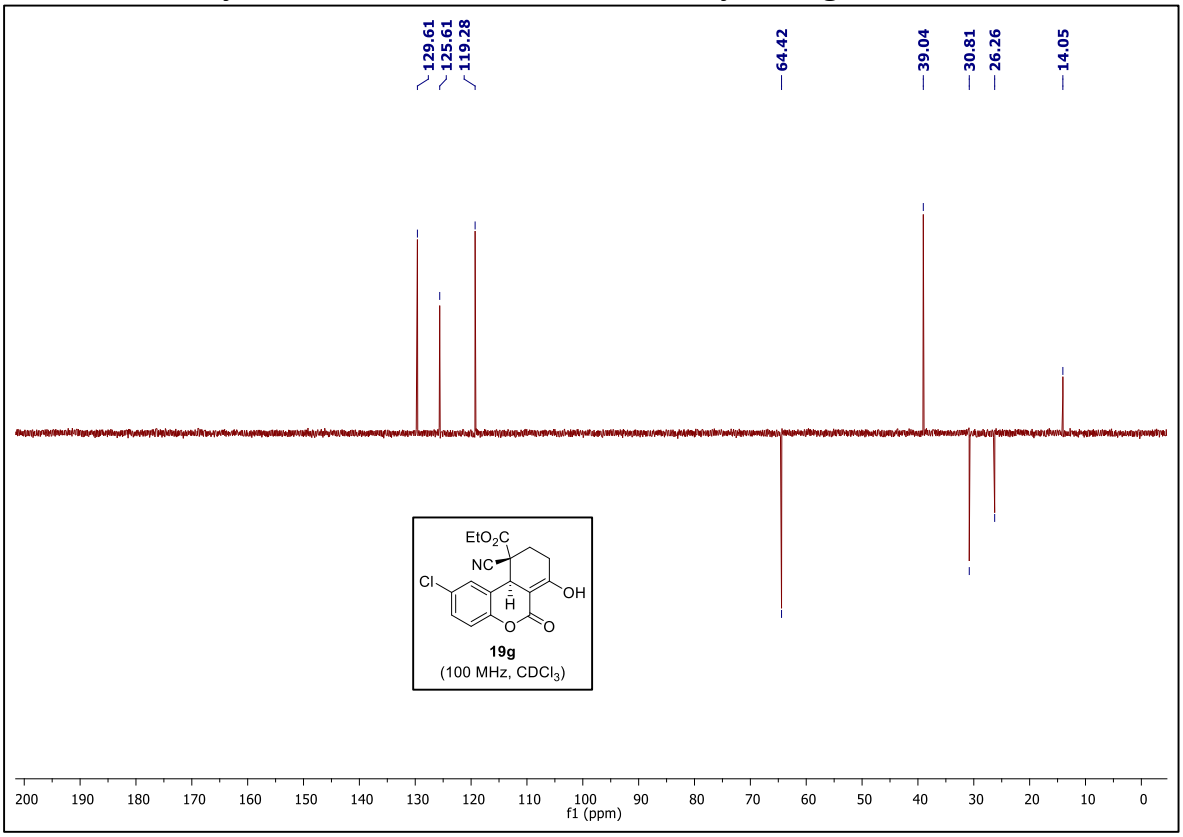
DEPT-135 NMR spectrum of ethyl 10-cyano-4-ethoxy-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19f**.



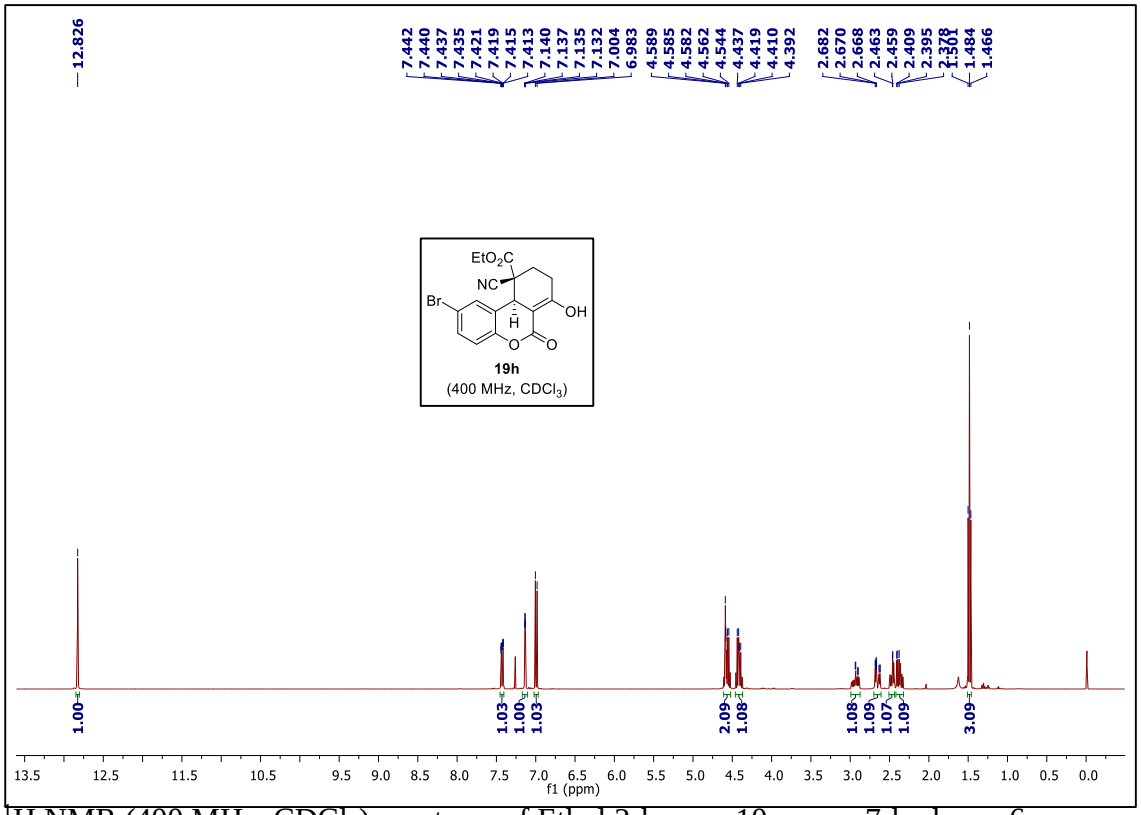
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 2-chloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19g**



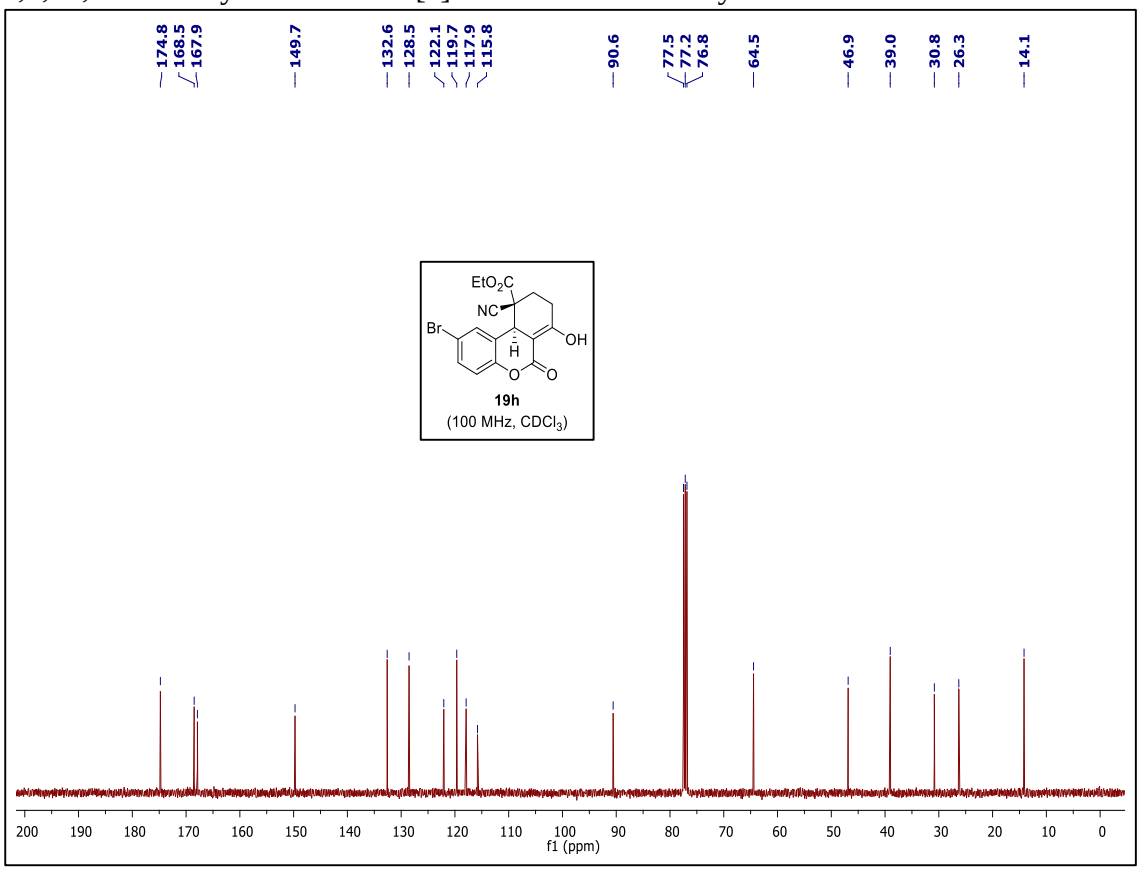
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 2-chloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19g**.



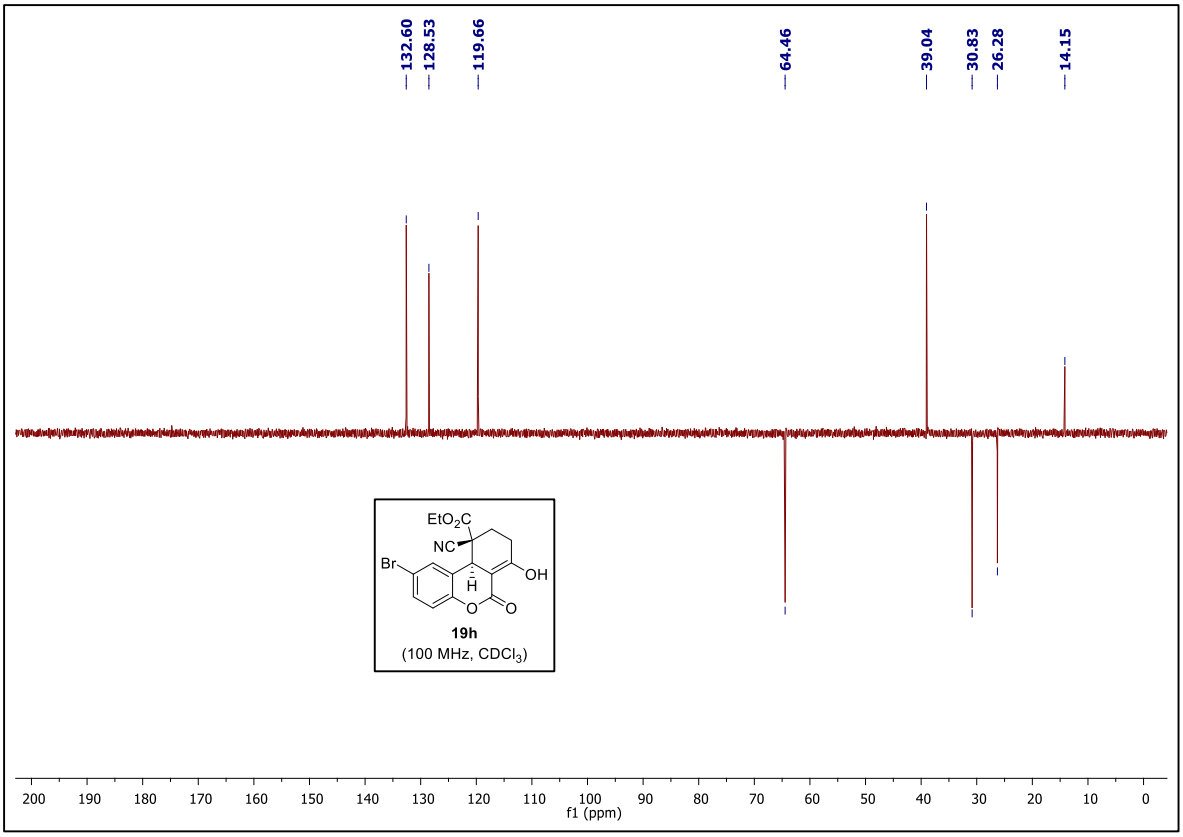
DEPT-135 NMR spectrum of ethyl 2-chloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19g**



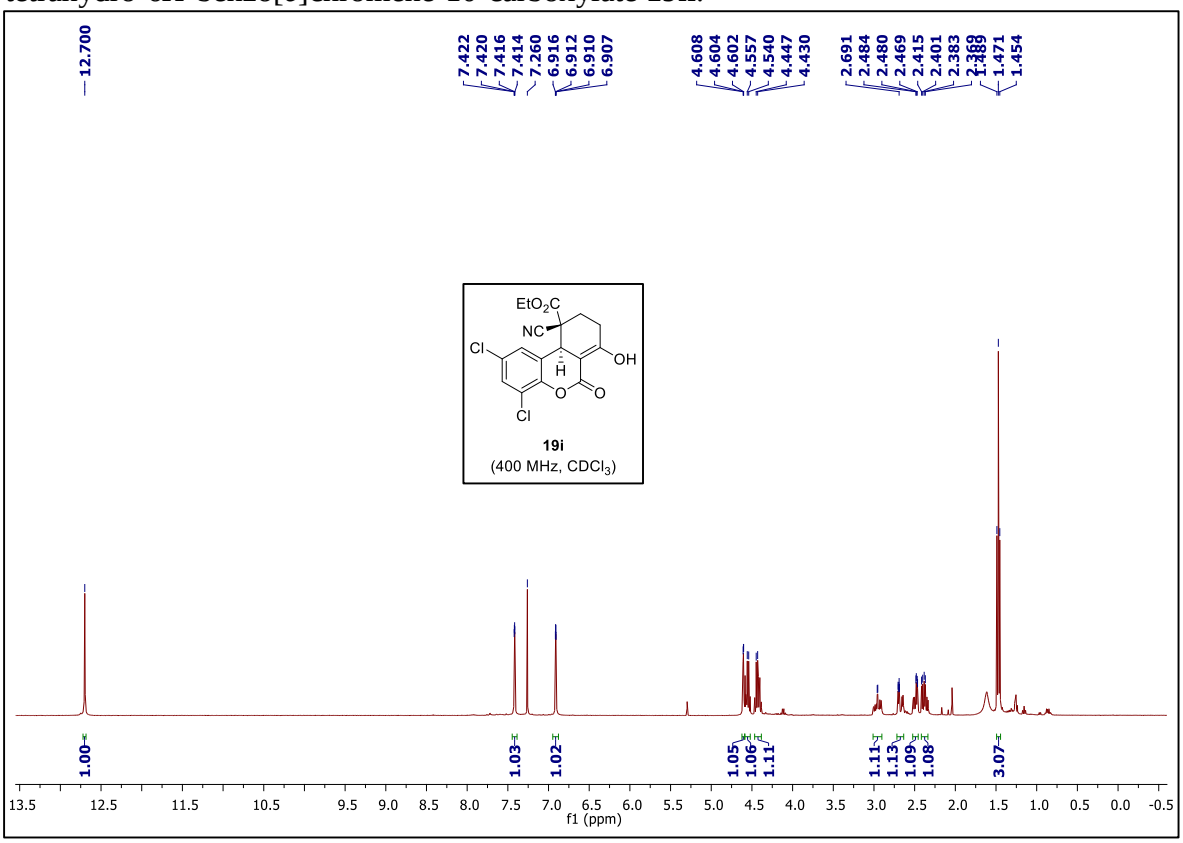
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Ethyl 2-bromo-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19h**



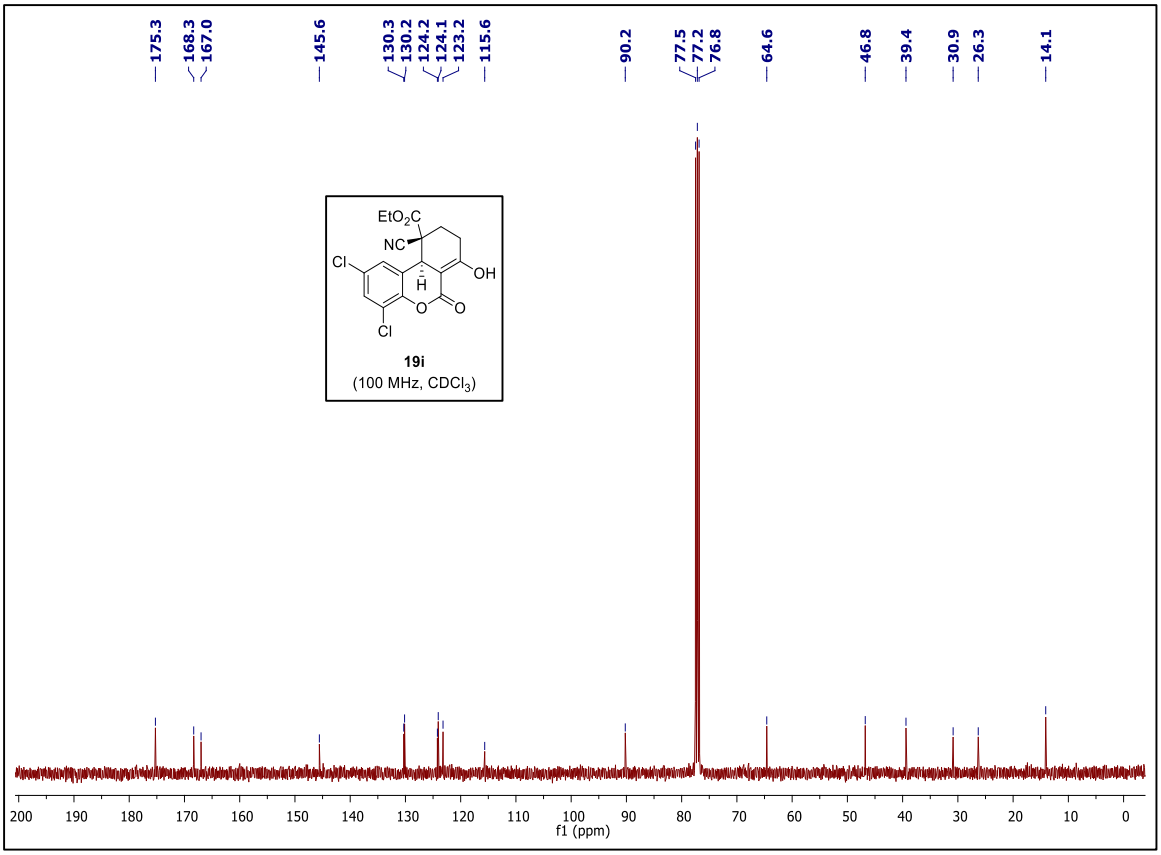
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Ethyl 2-bromo-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19h**.



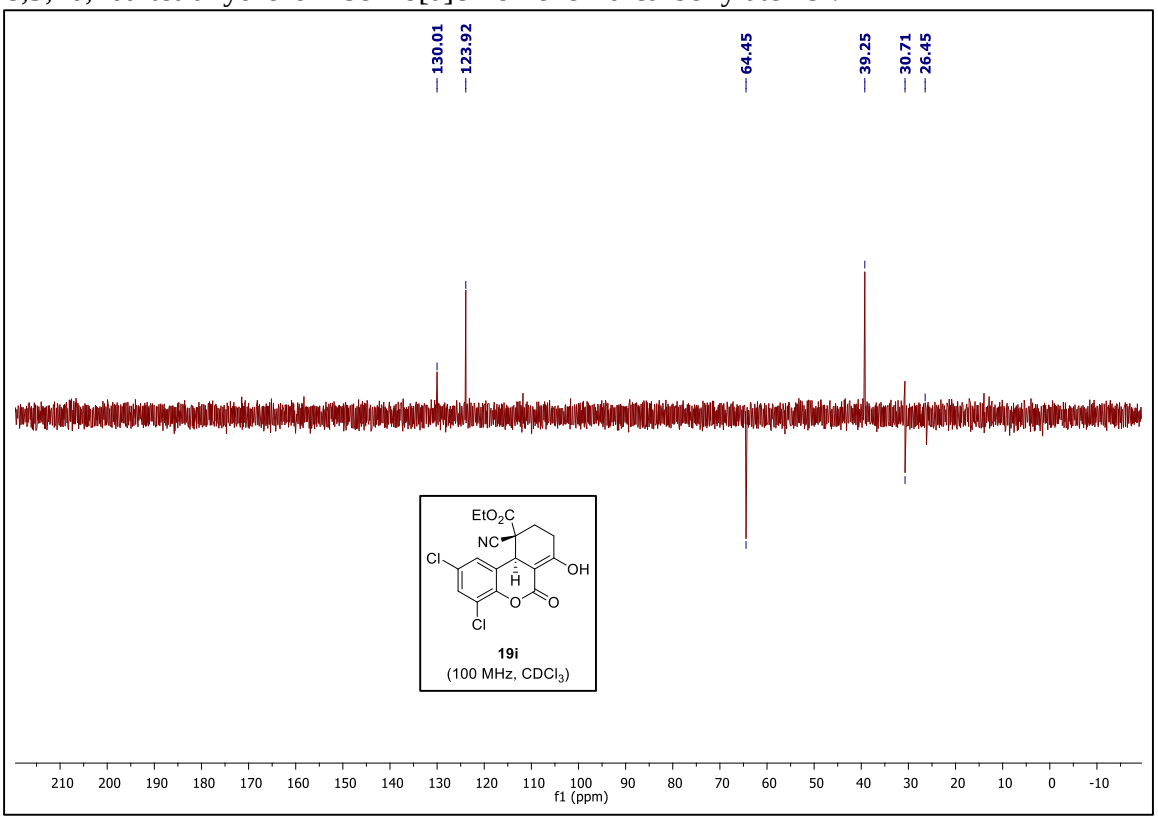
DEPT-135 NMR spectrum of ethyl 2-bromo-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19h**.



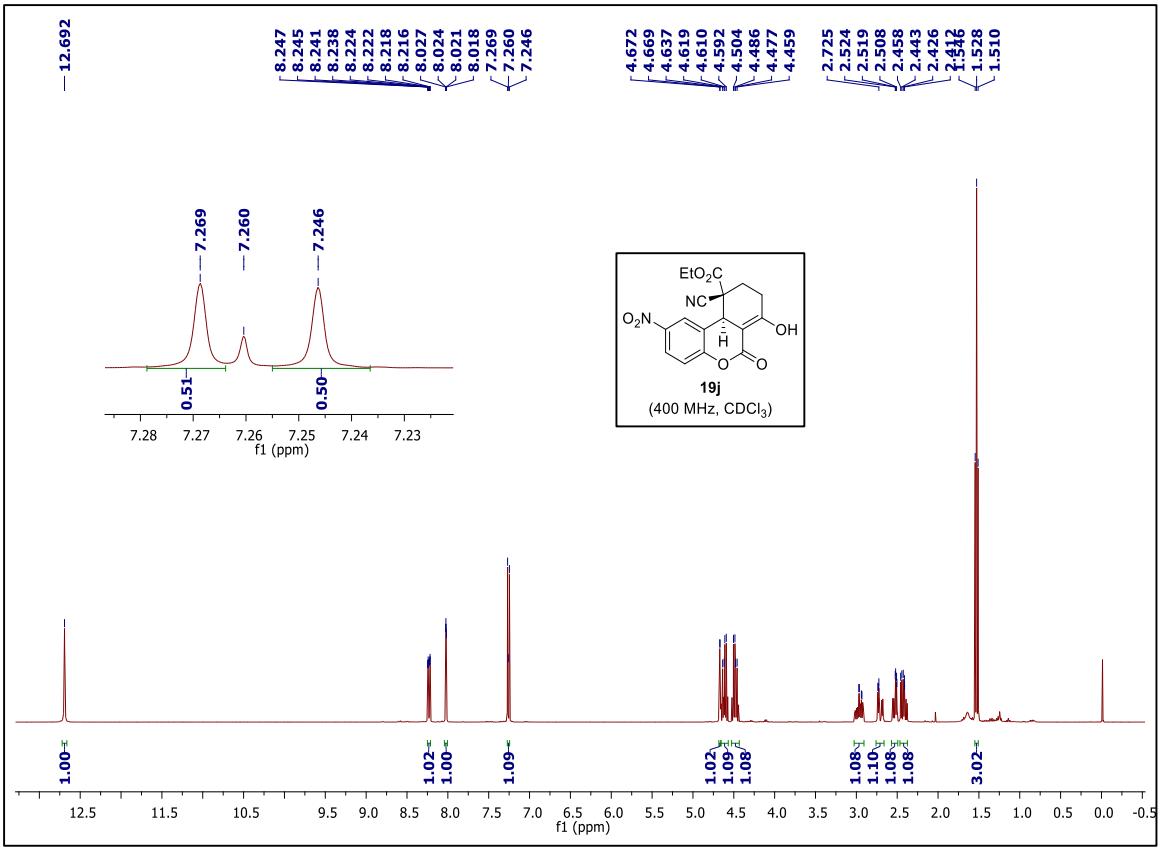
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 2,4-dichloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19i**



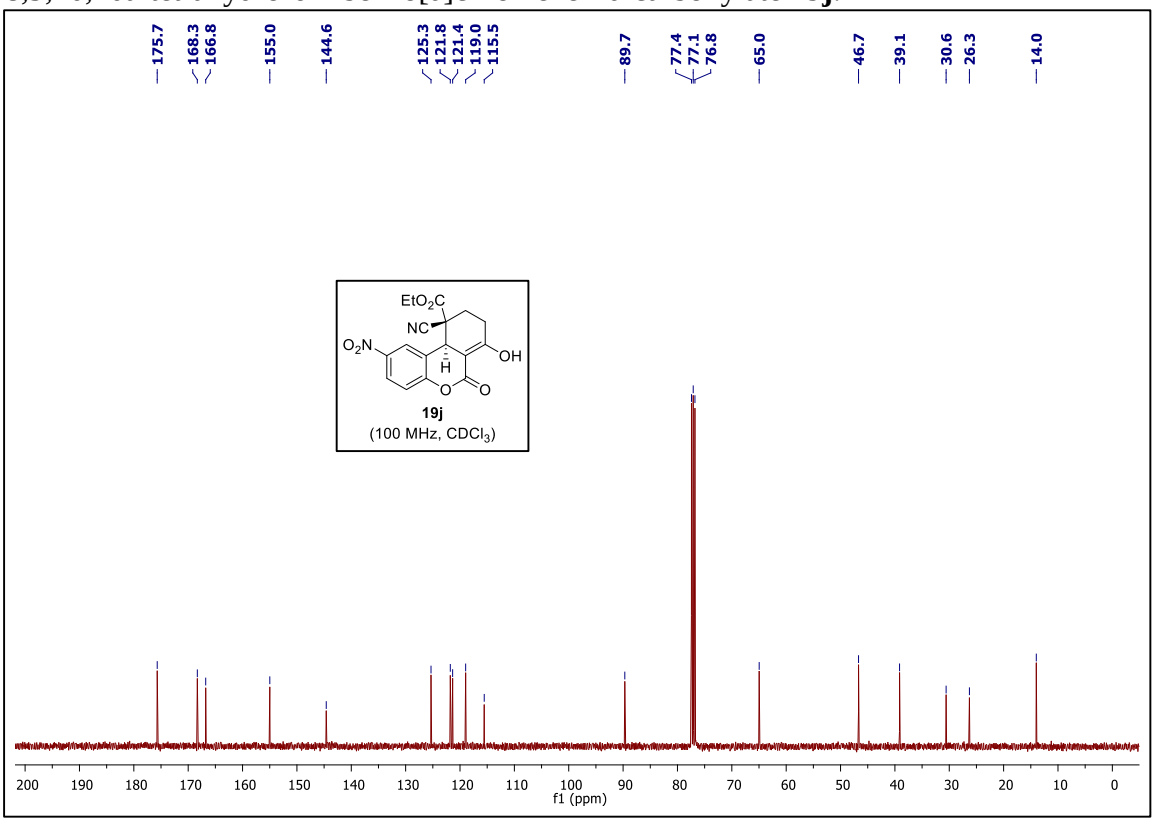
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 2,4-dichloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19i**.



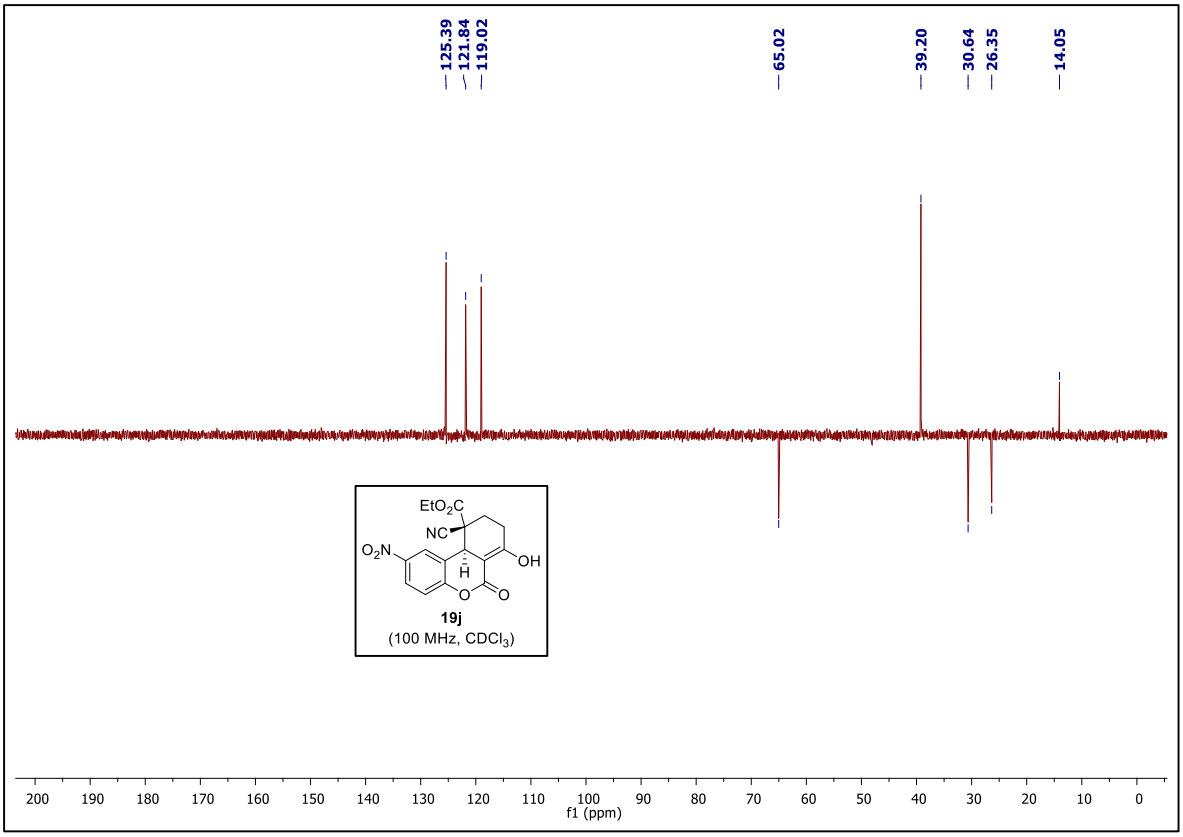
DEPT-135 NMR spectrum of ethyl 2,4-dichloro-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19i**.



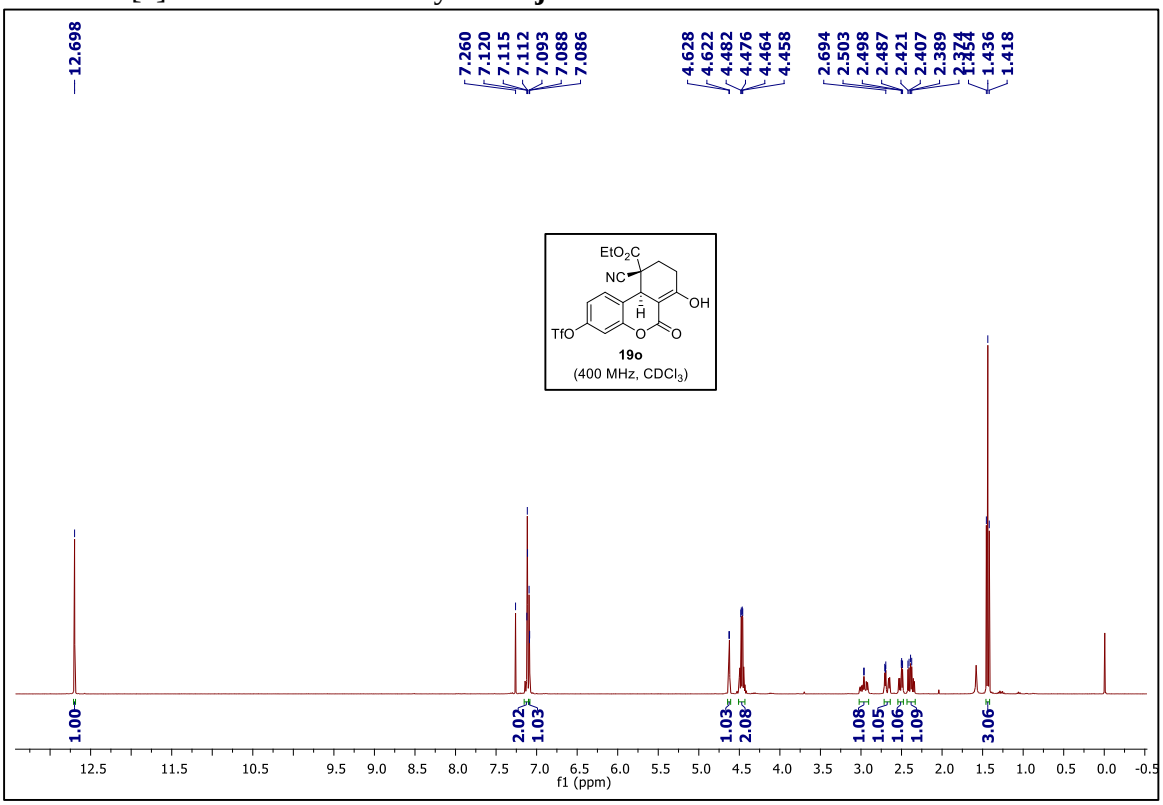
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-2-nitro-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19j**.



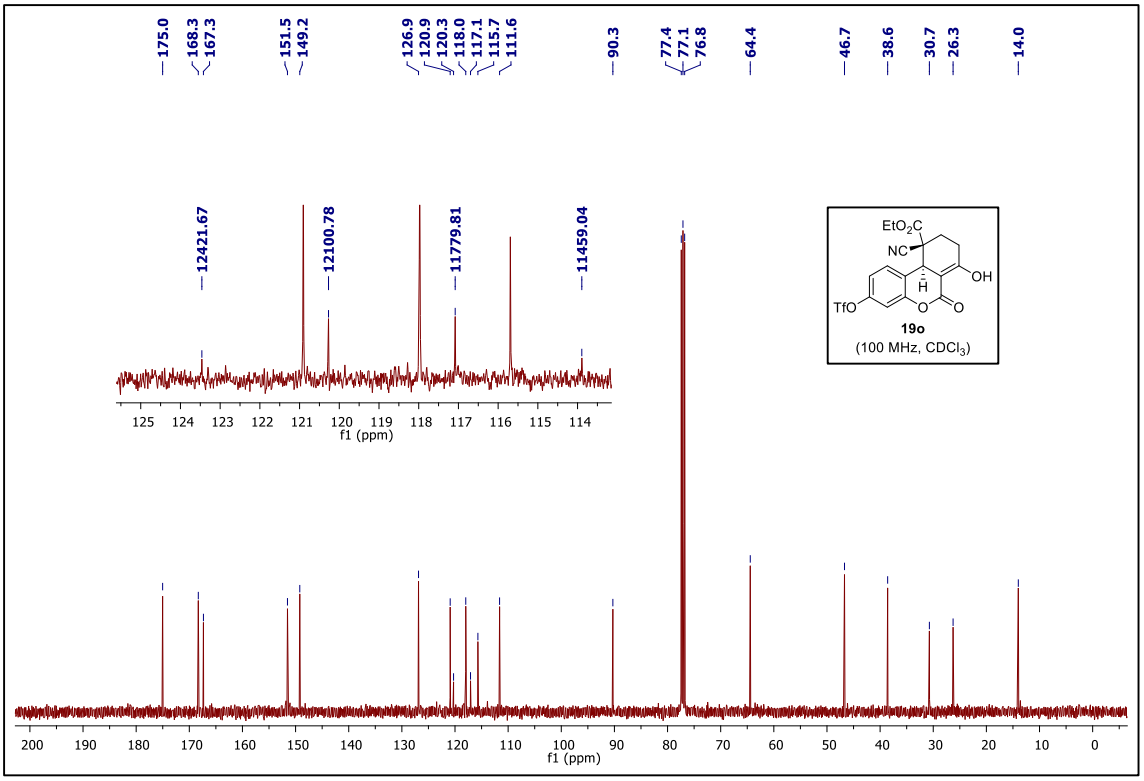
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-2-nitro-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19j**



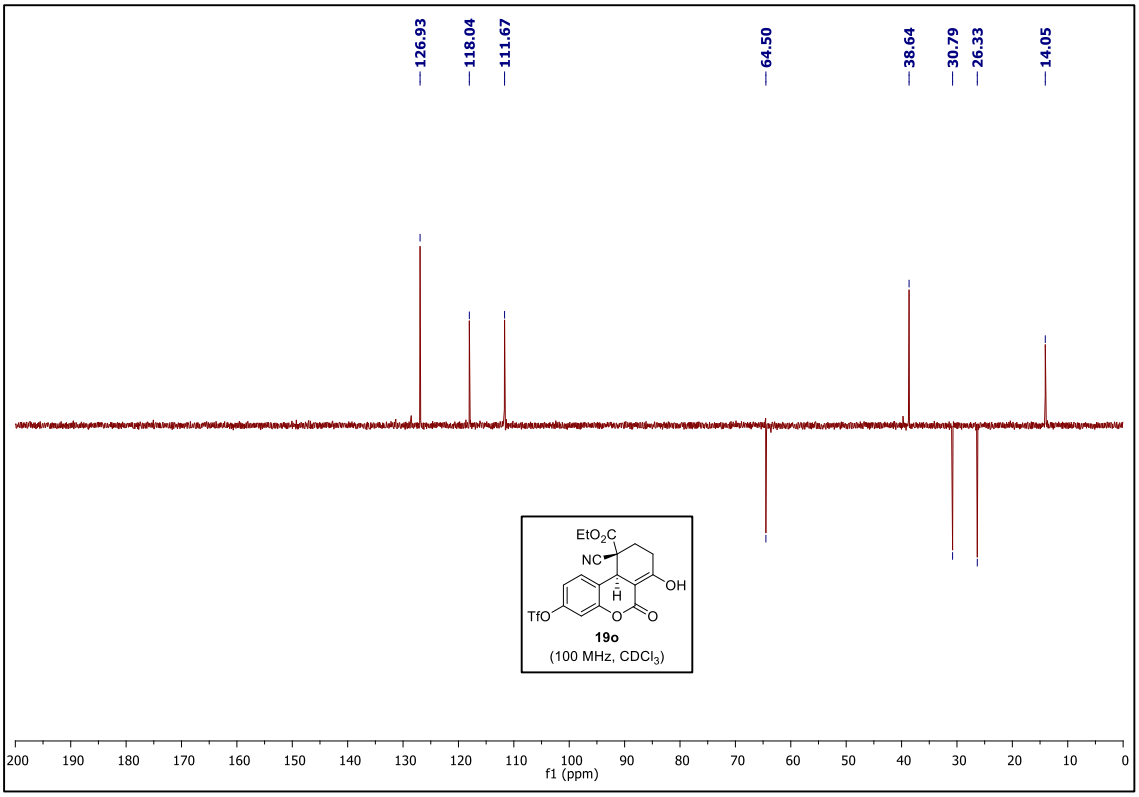
DEPT-135 NMR spectrum of ethyl 10-cyano-7-hydroxy-2-nitro-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19j**.



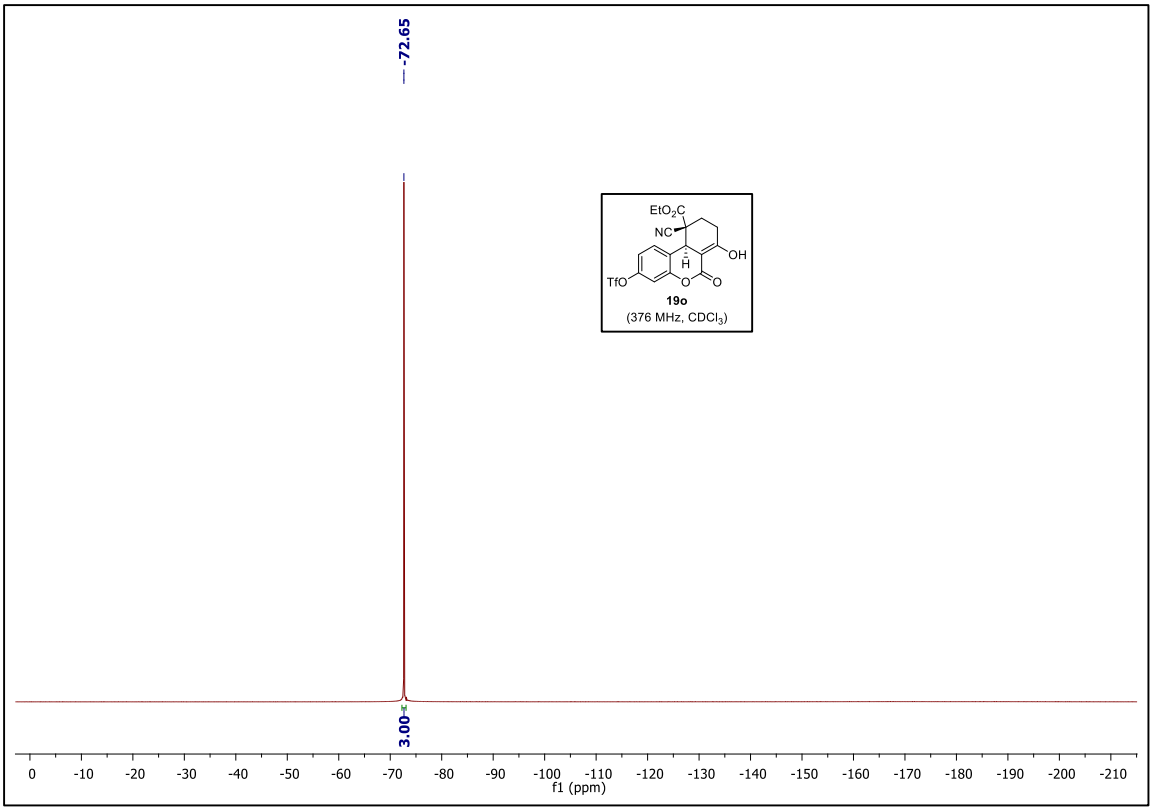
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19o**.



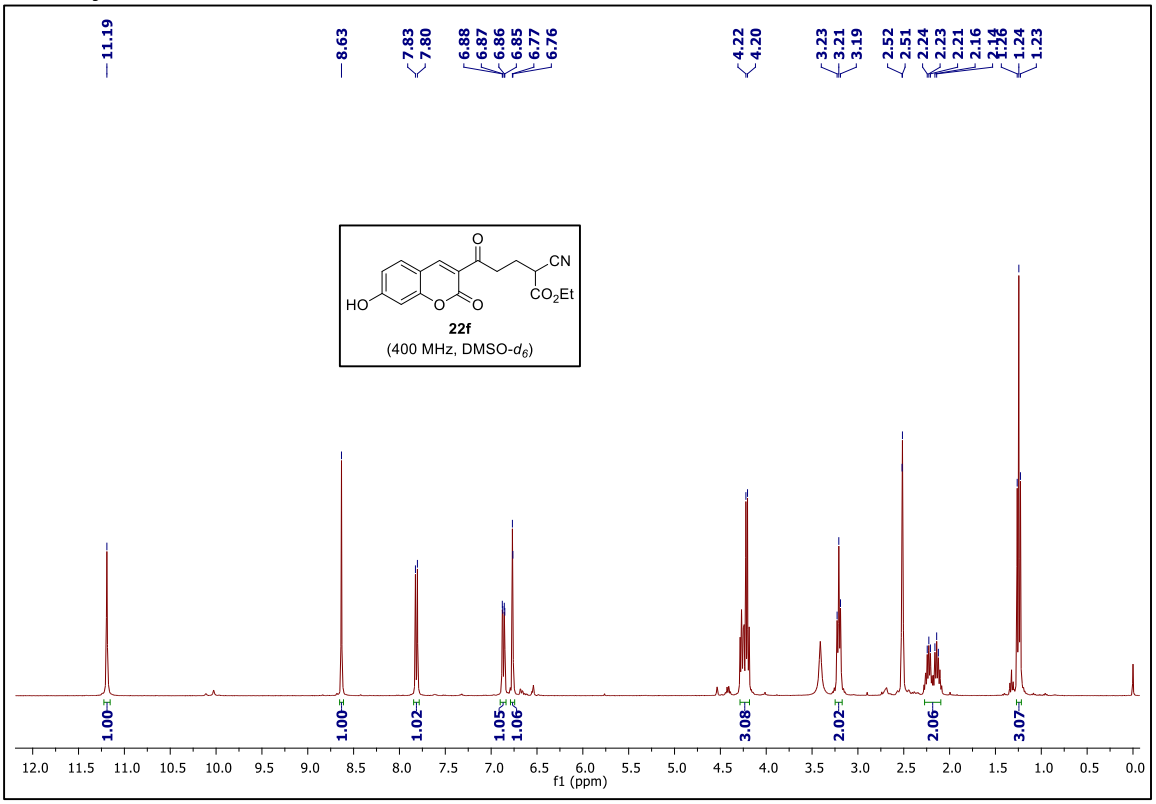
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19o**.



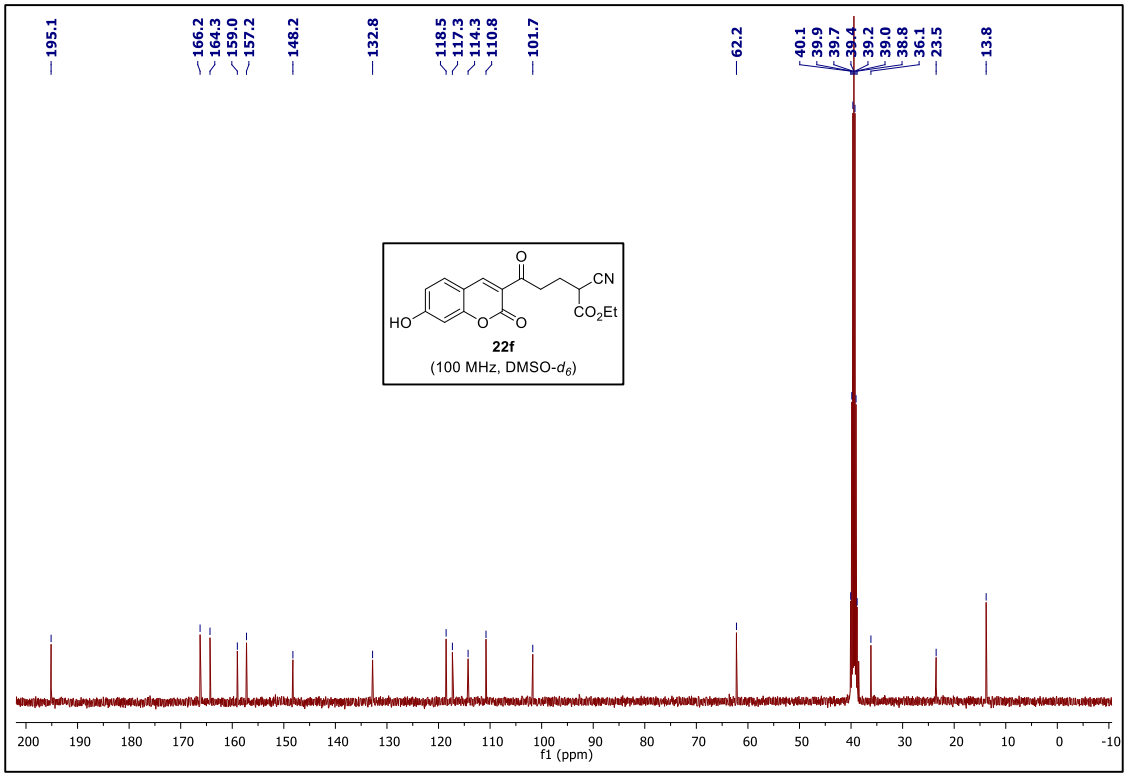
DEPT-135 NMR spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19o**.



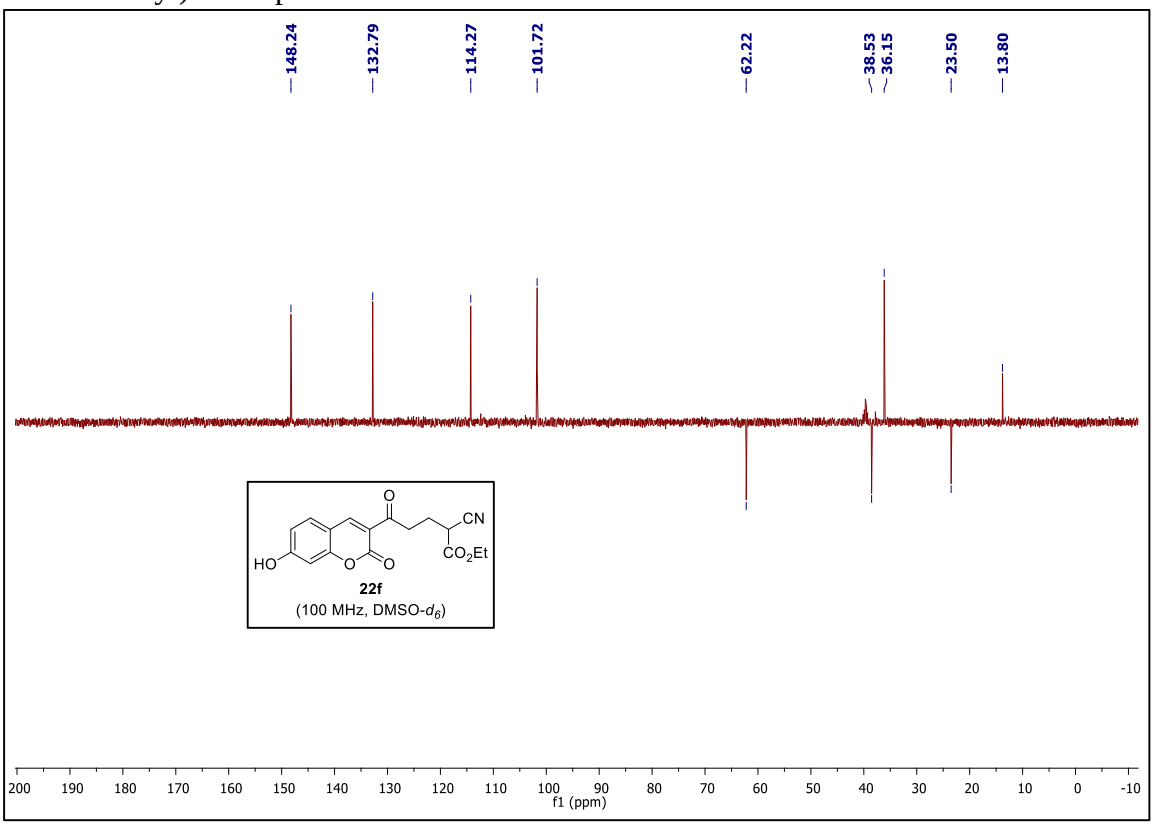
^{19}F NMR (376 MHz, $CDCl_3$, Reference = $CFCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-(((trifluoromethyl)sulfonyl)oxy)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19o**.



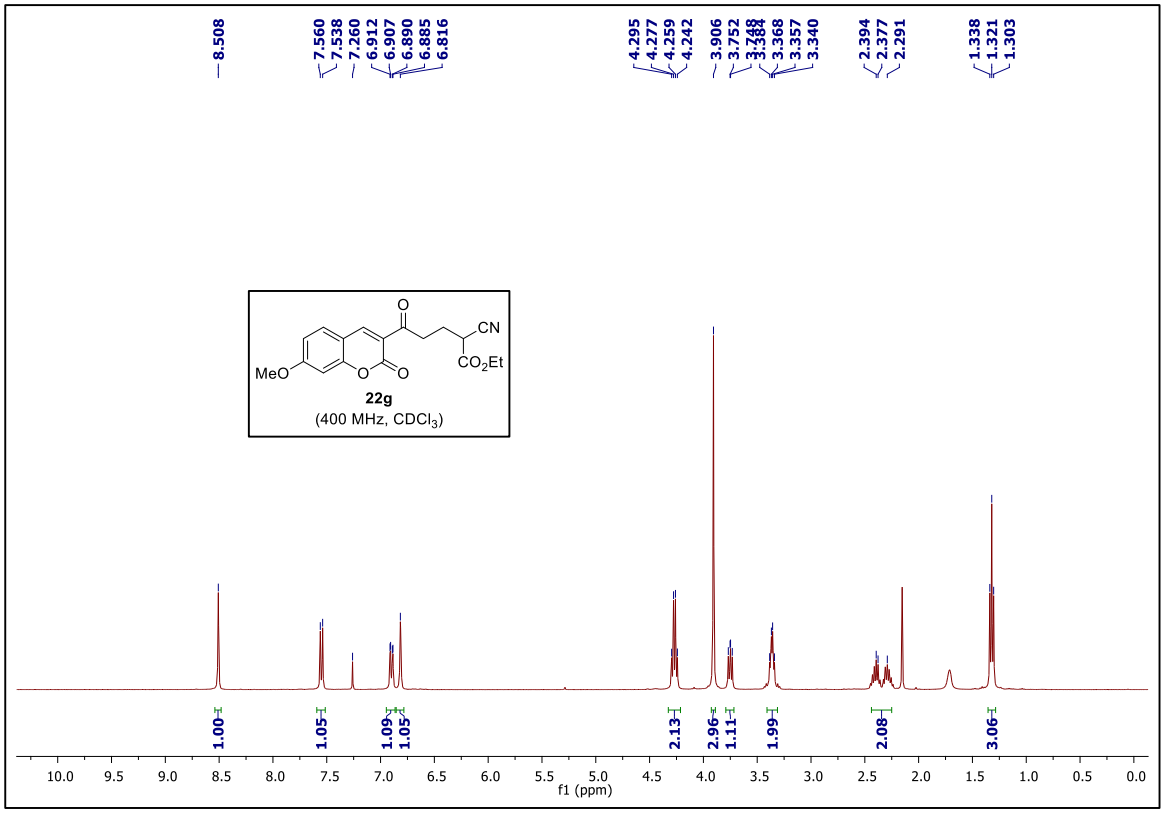
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of ethyl 2-cyano-5-(7-hydroxy-2-oxo-*2H*-chromen-3-yl)-5-oxopentanoate **22f**.



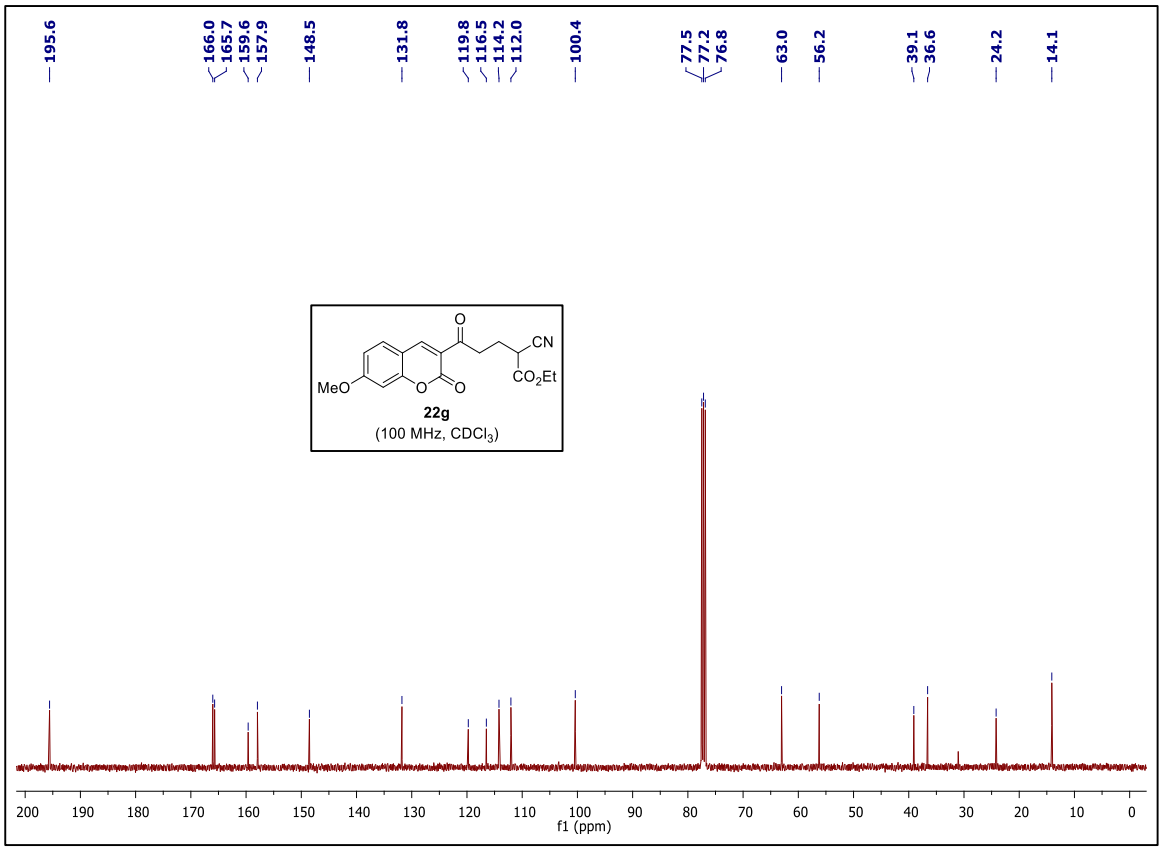
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of ethyl 2-cyano-5-(7-hydroxy-2-oxo-*2H*-chromen-3-yl)-5-oxopentanoate **22f.**



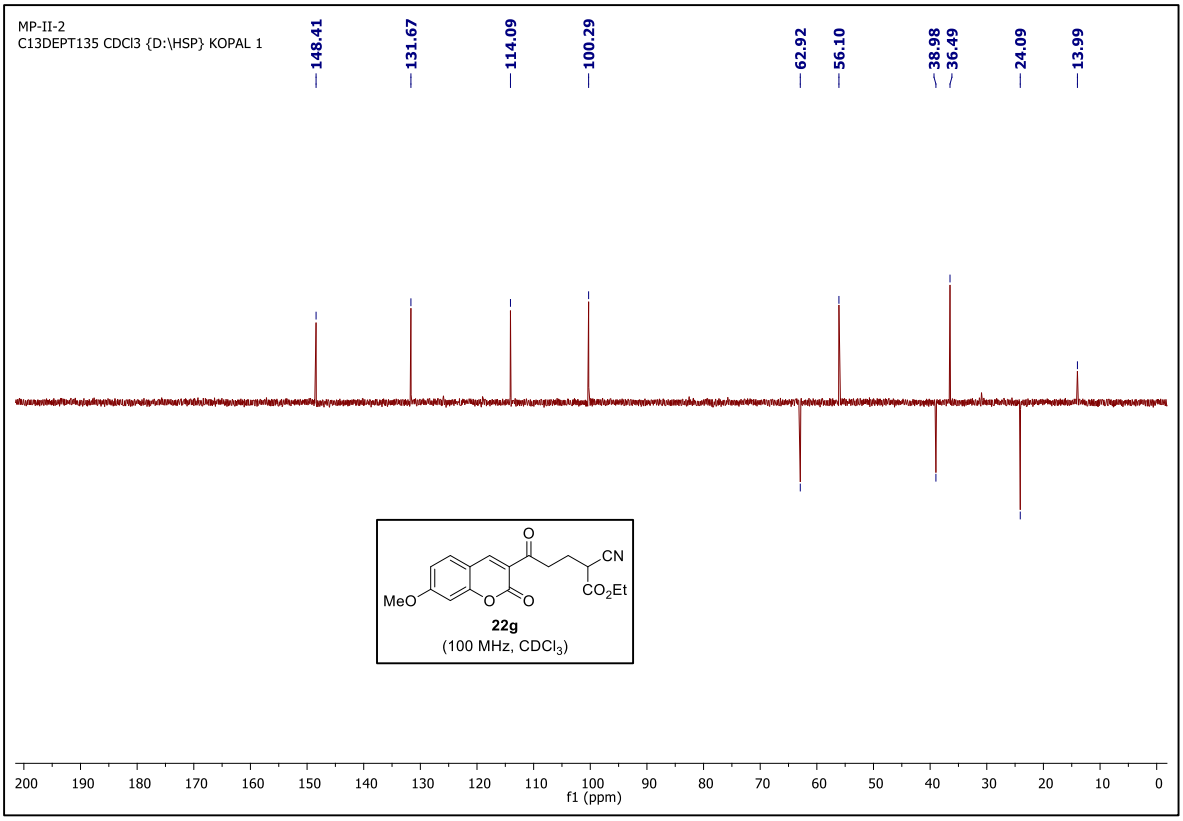
DEPT-135 NMR spectrum of ethyl 2-cyano-5-(7-hydroxy-2-oxo-*2H*-chromen-3-yl)-5-oxopentanoate **22f**.



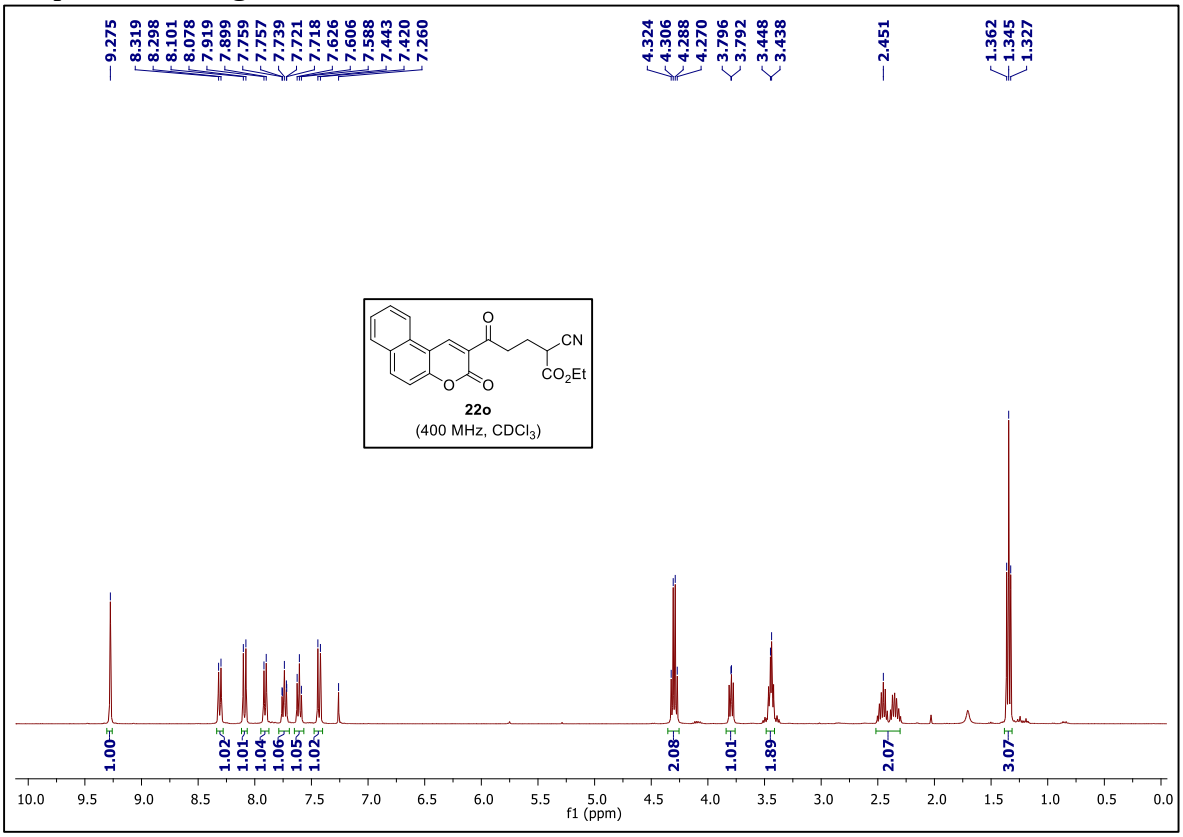
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 2-cyano-5-(7-methoxy-2-oxo-2*H*-chromen-3-yl)-5-oxopentanoate **22g**.



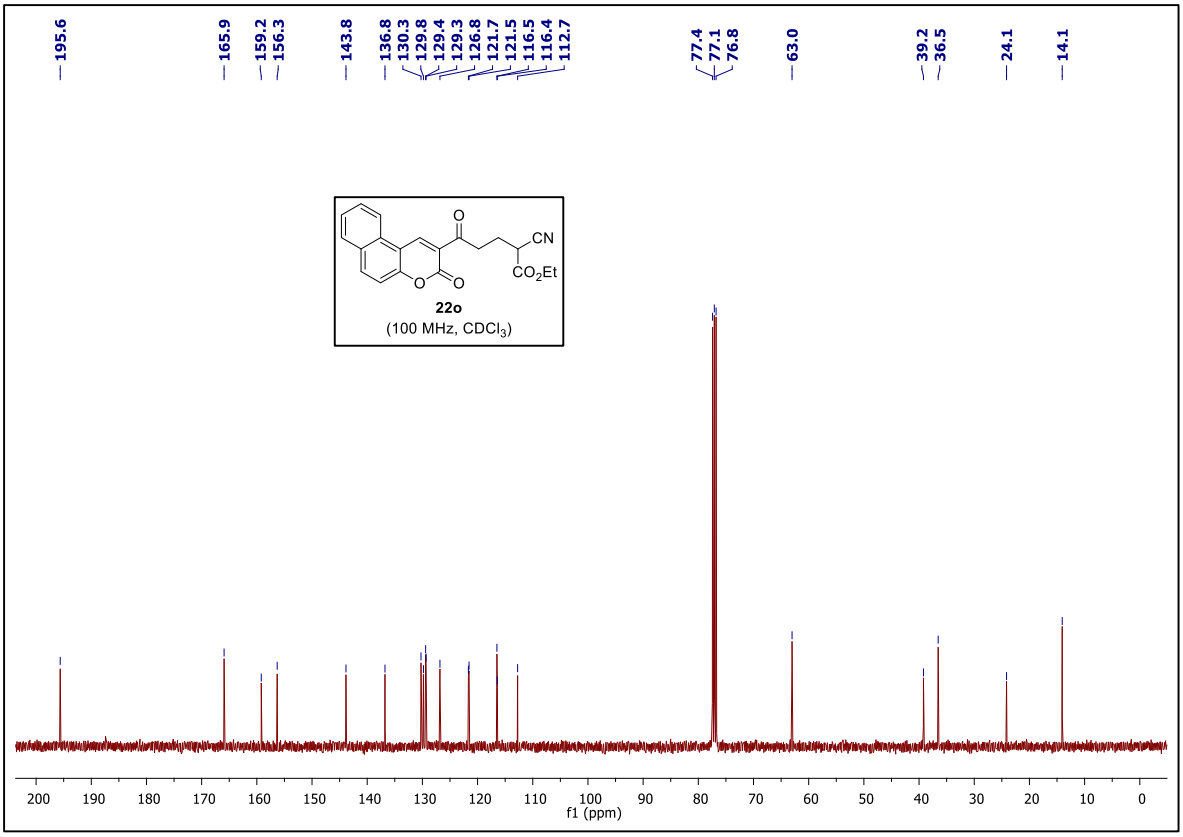
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 2-cyano-5-(7-methoxy-2-oxo-2*H*-chromen-3-yl)-5-oxopentanoate **22g**



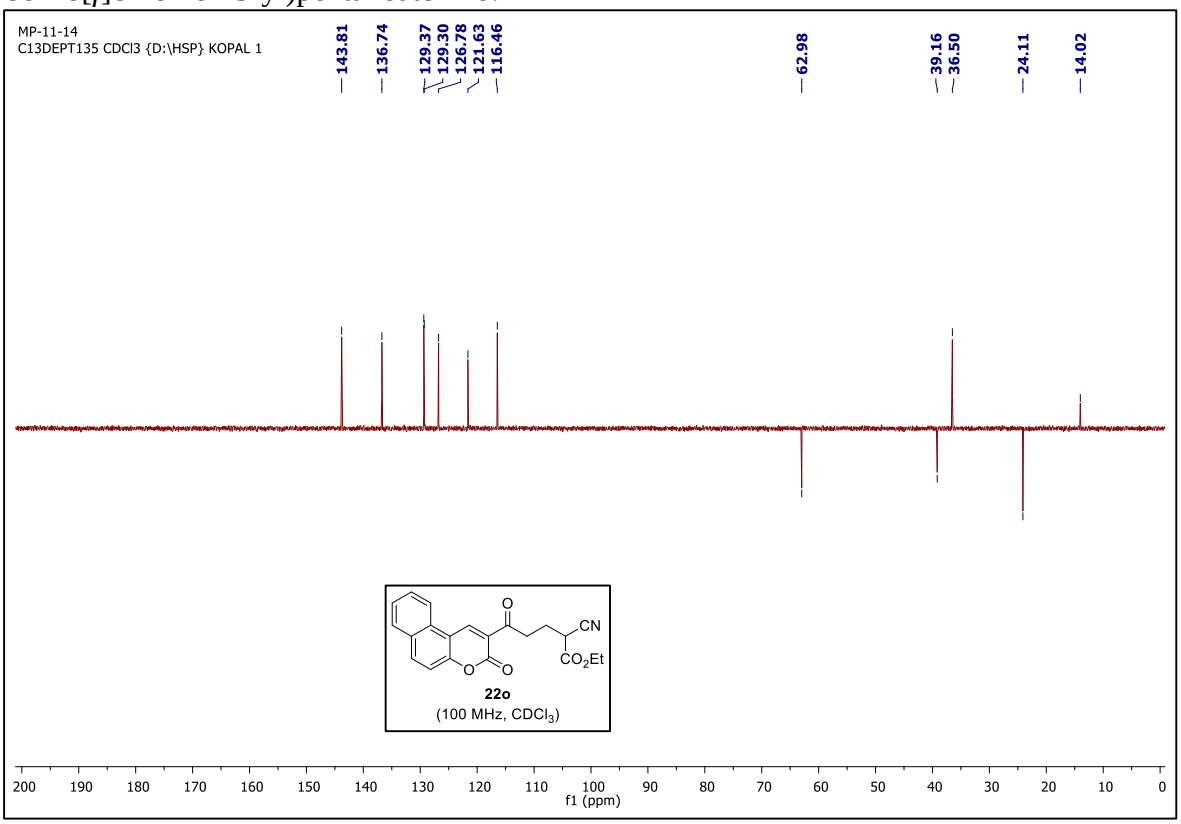
DEPT-135 NMR spectrum of ethyl 2-cyano-5-(7-methoxy-2-oxo-2*H*-chromen-3-yl)-5-oxopentanoate **22g**.



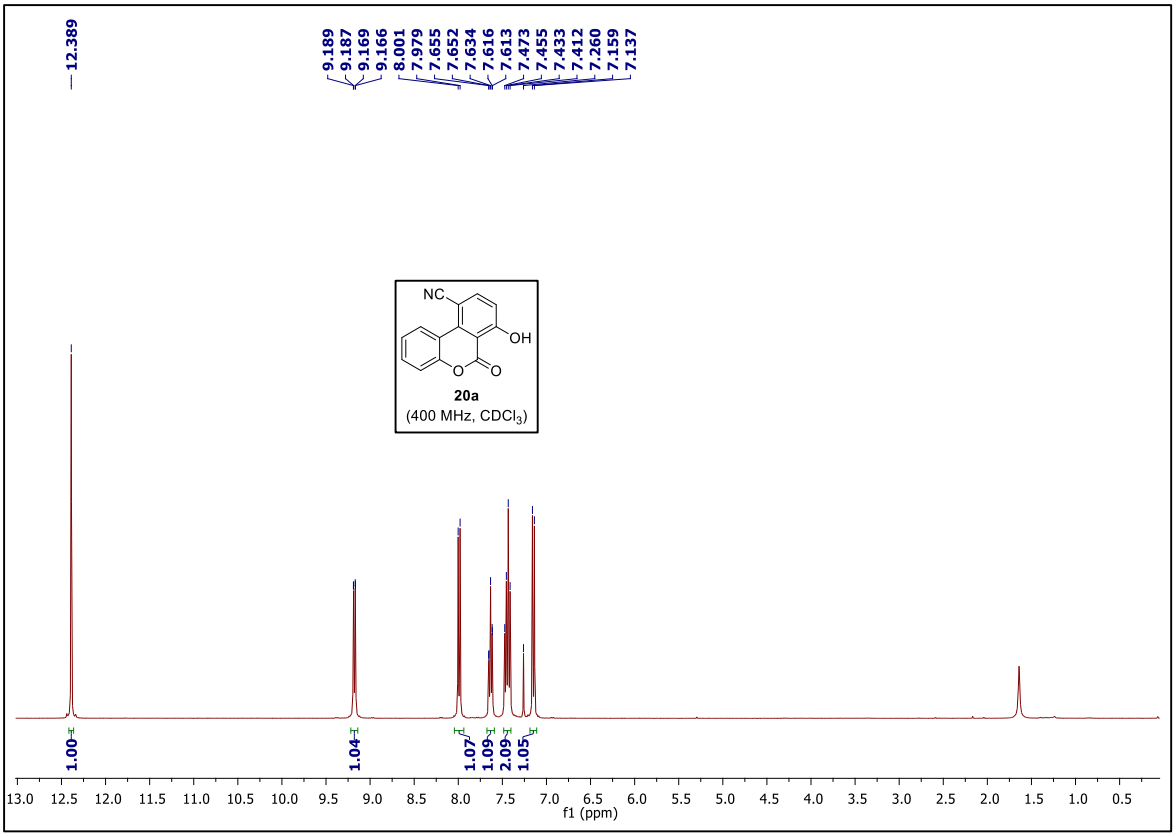
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 2-cyano-5-oxo-5-(2-oxo-2*H*-benzo[*f*]chromen-3-yl)pentanoate **22o**



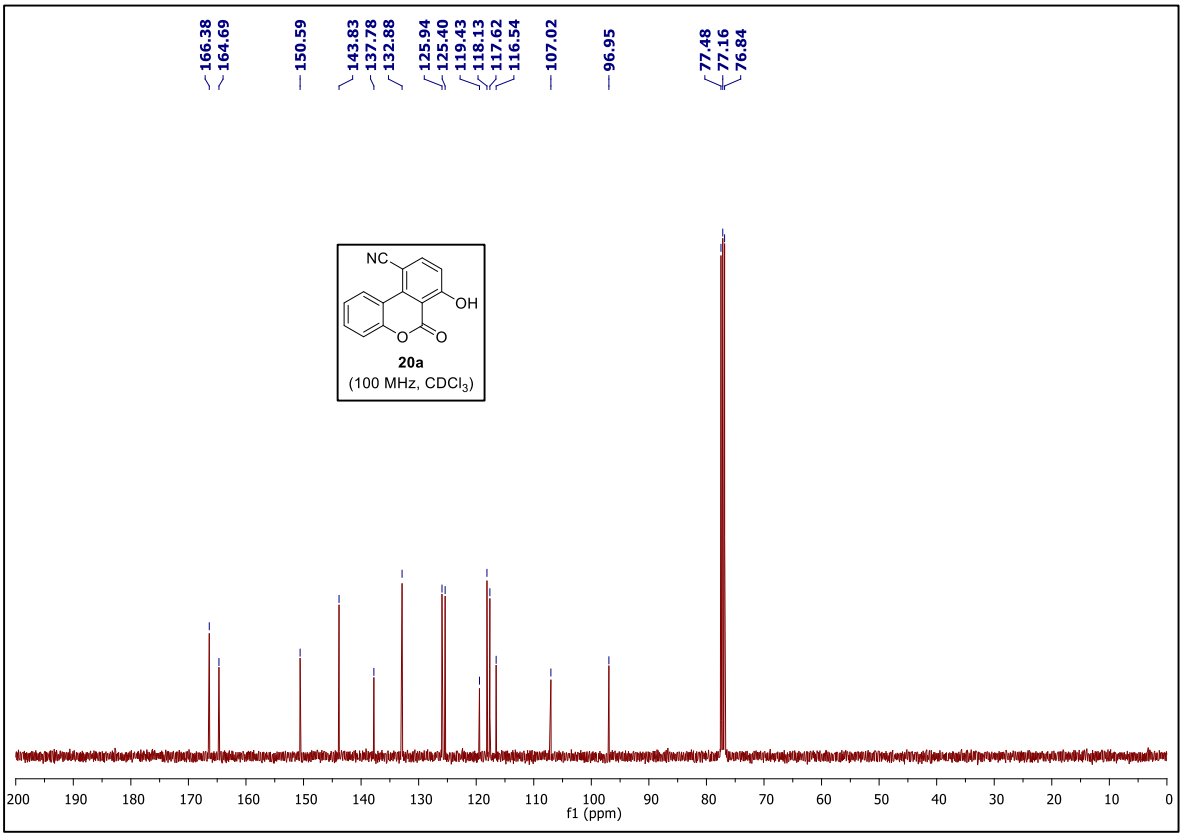
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 2-cyano-5-oxo-5-(2-oxo-2*H*-benzo[*f*]chromen-3-yl)pentanoate **22o**.



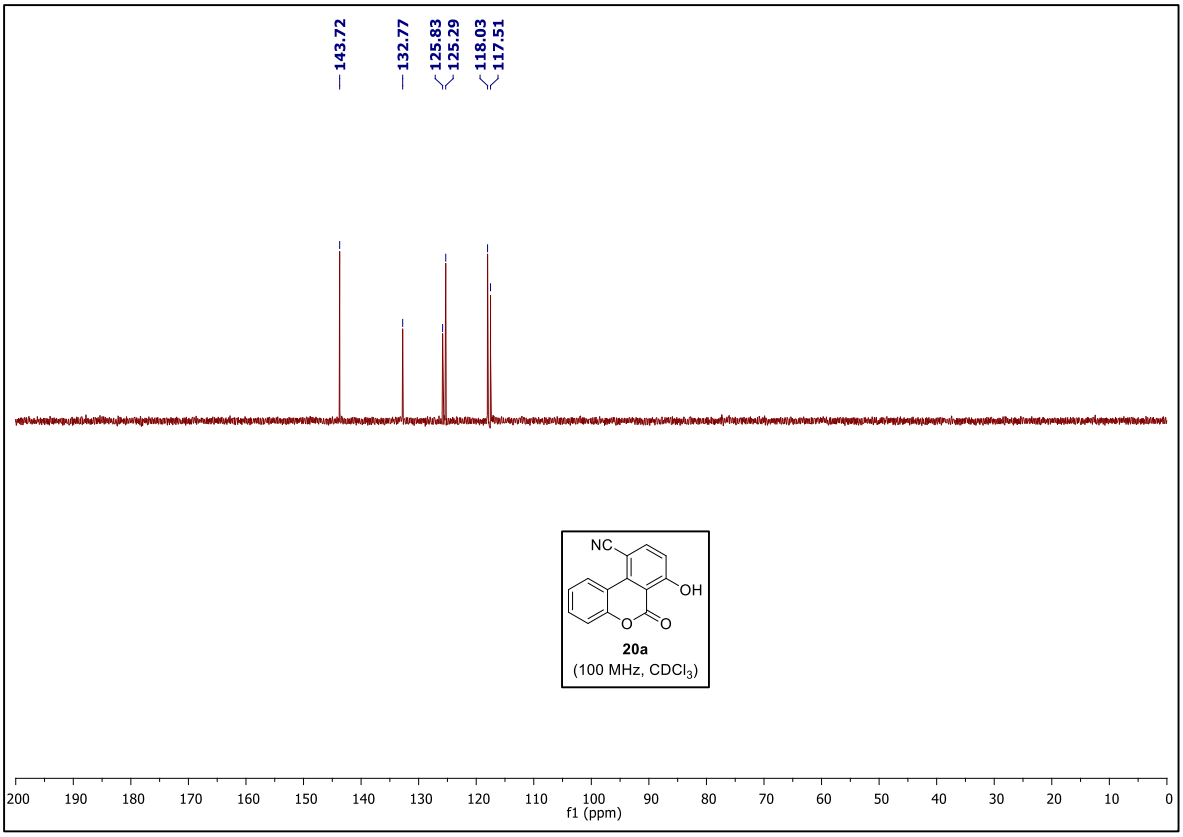
DEPT-135 NMR spectrum of ethyl 2-cyano-5-oxo-5-(2-oxo-2*H*-benzo[*f*]chromen-3-yl)pentanoate **22o**



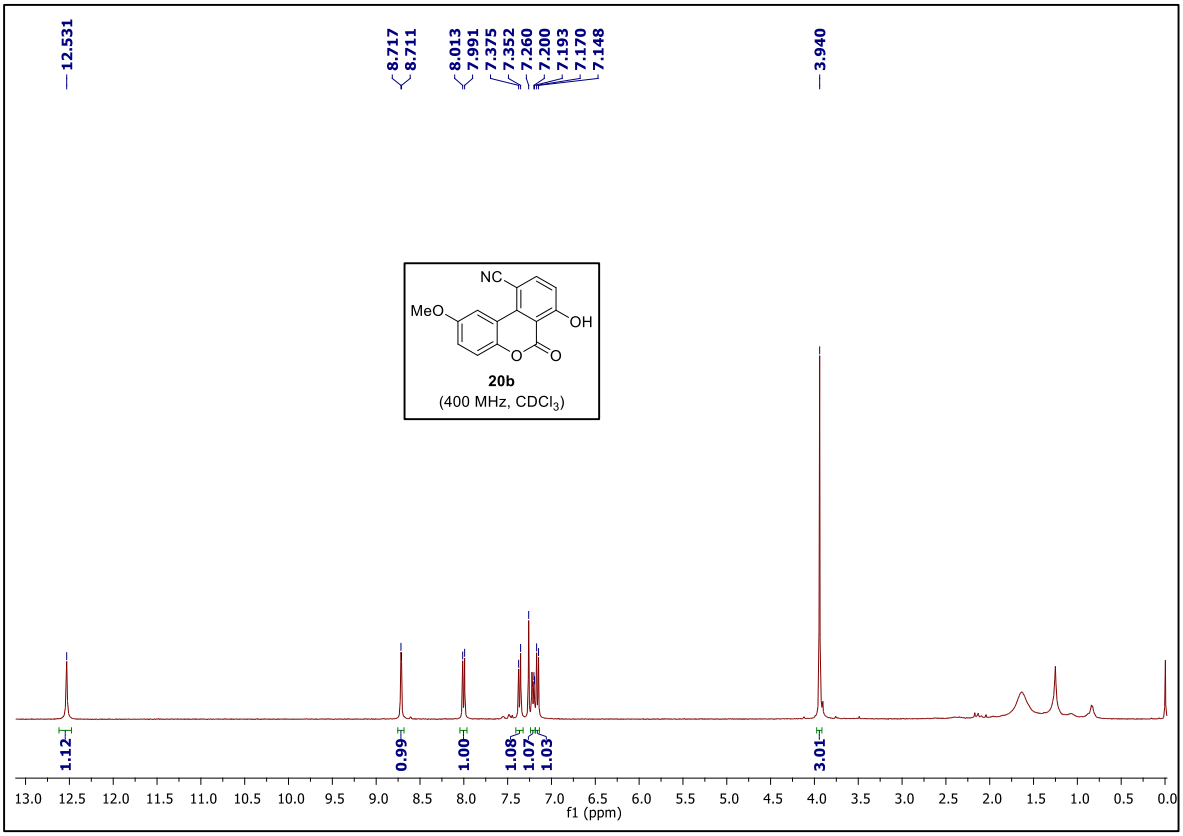
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20a**.



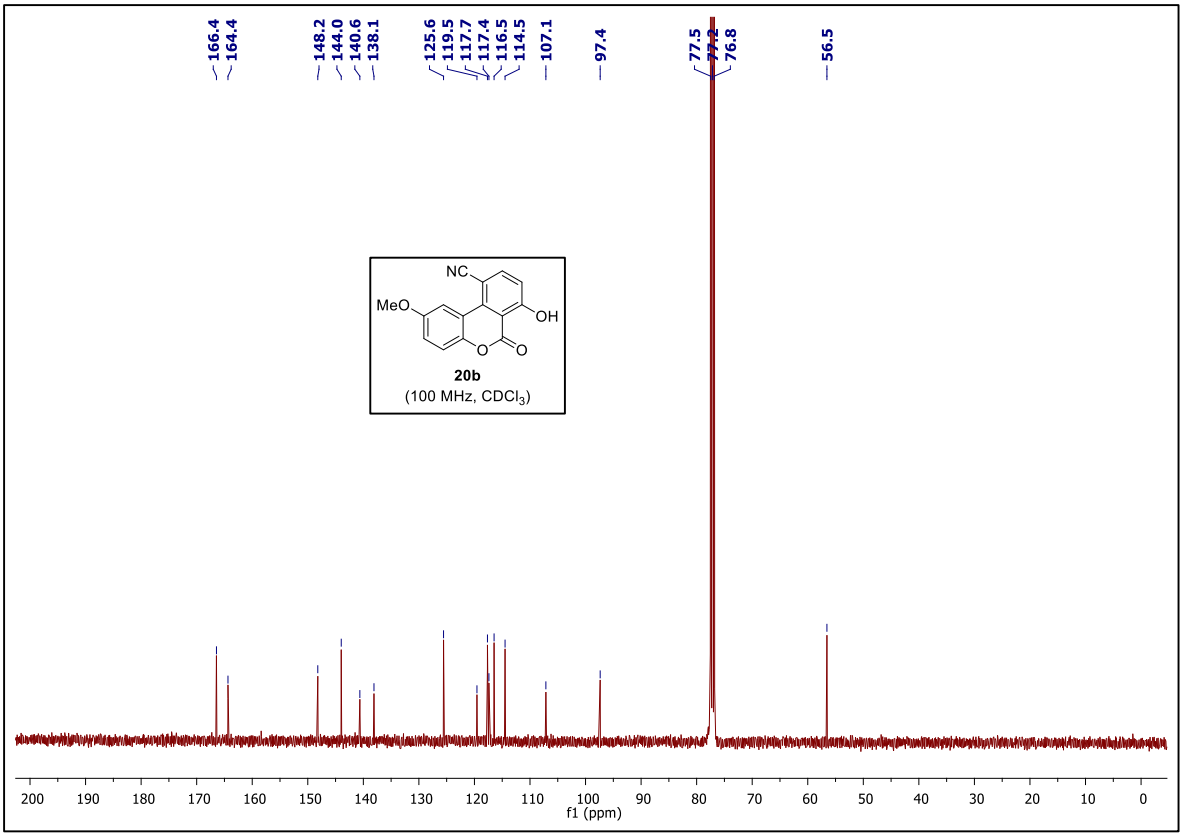
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20a**.



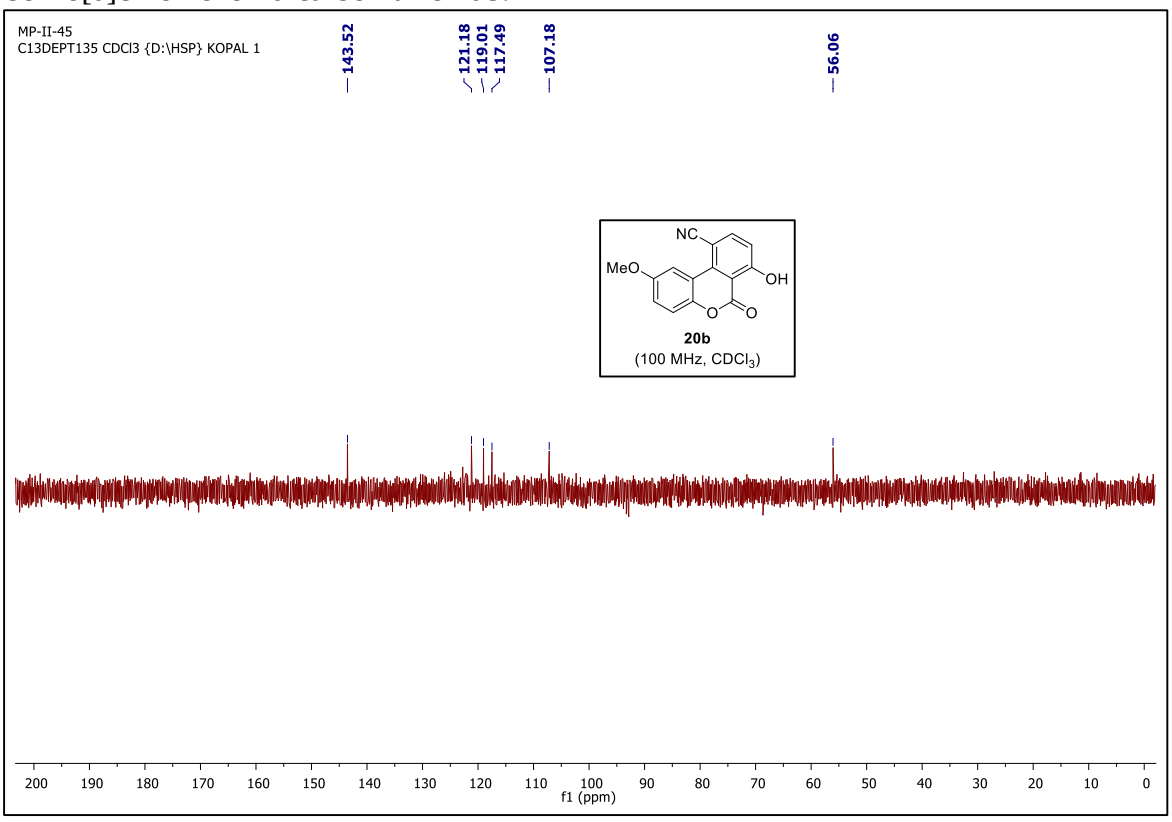
DEPT-135 NMR spectrum of 7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20a**.



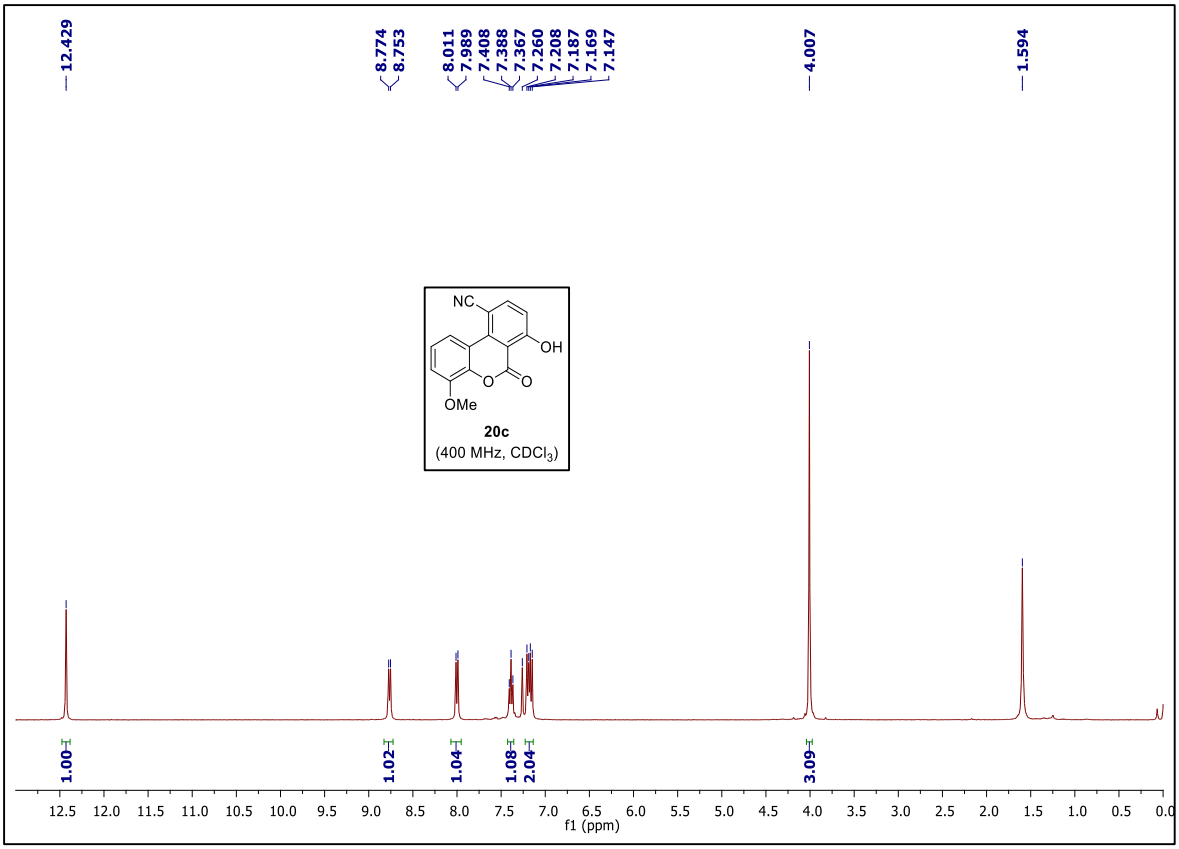
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20b**



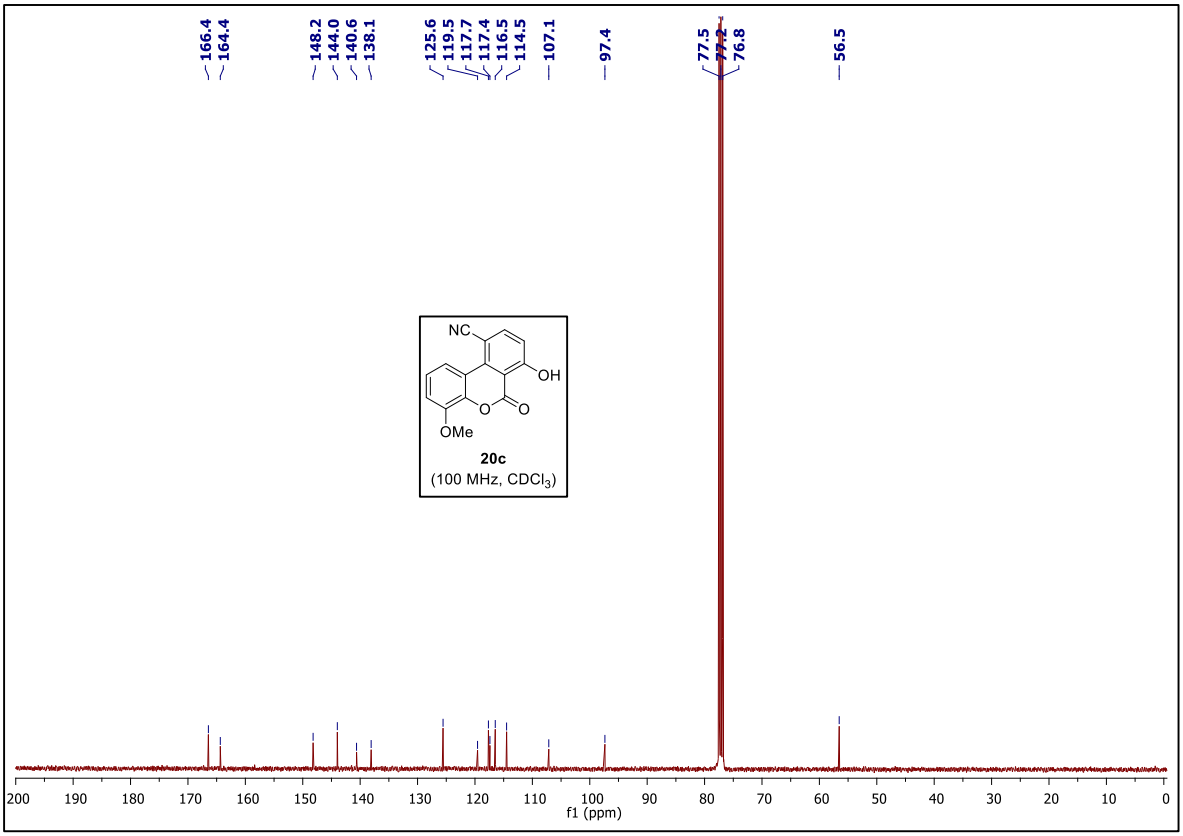
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20b**.



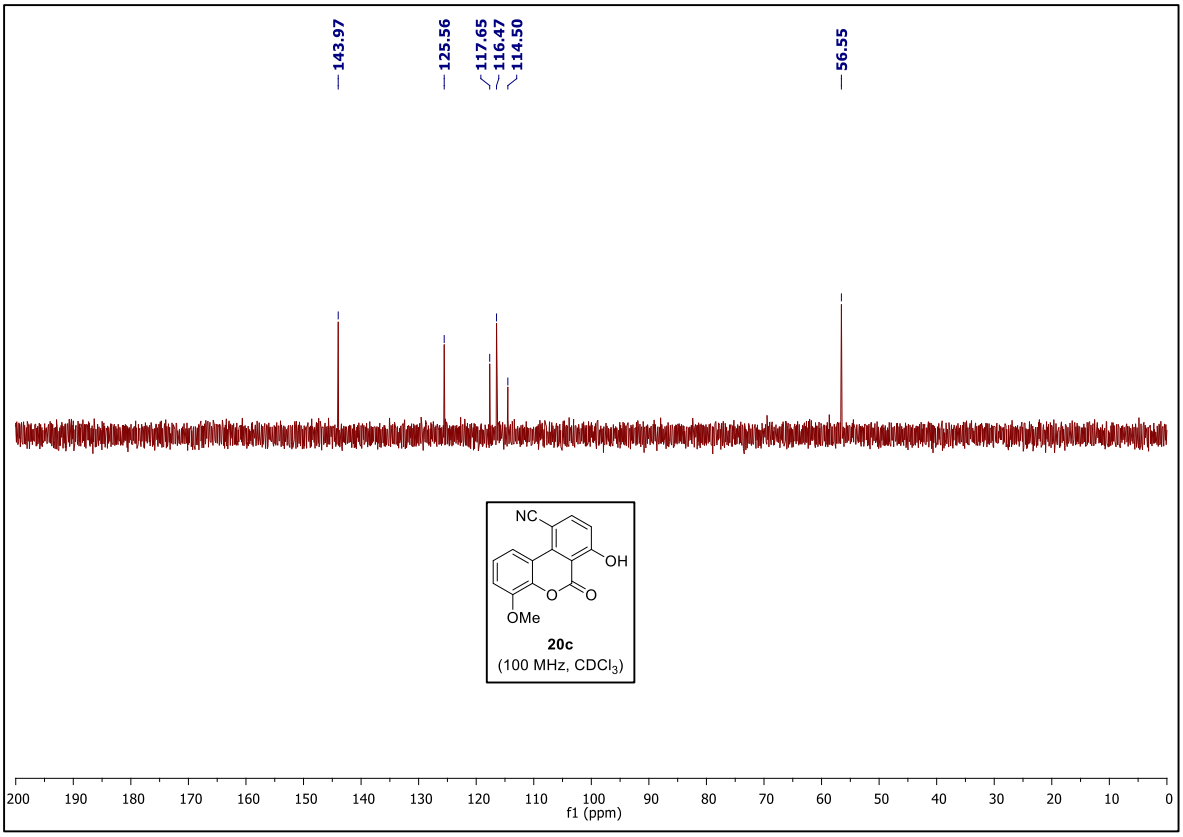
DEPT-135 NMR spectrum of 7-hydroxy-2-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20b**.



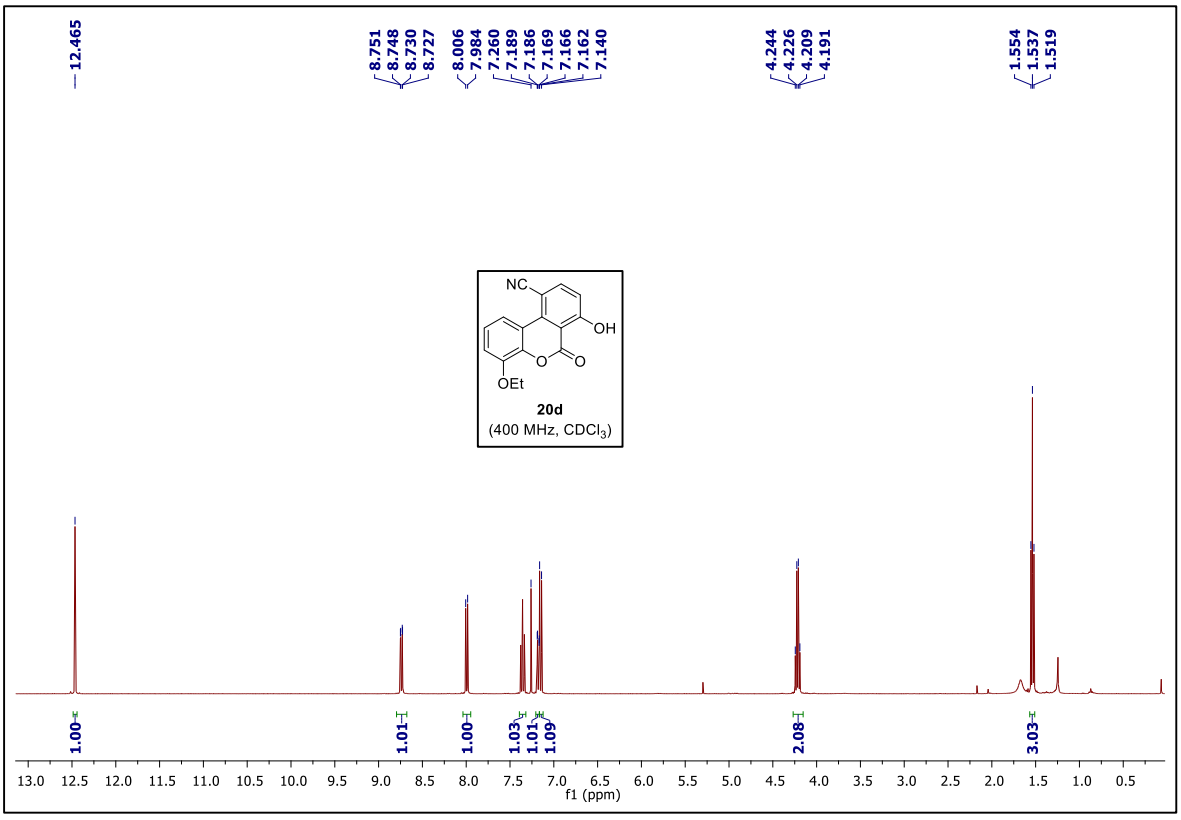
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-4-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20c**.



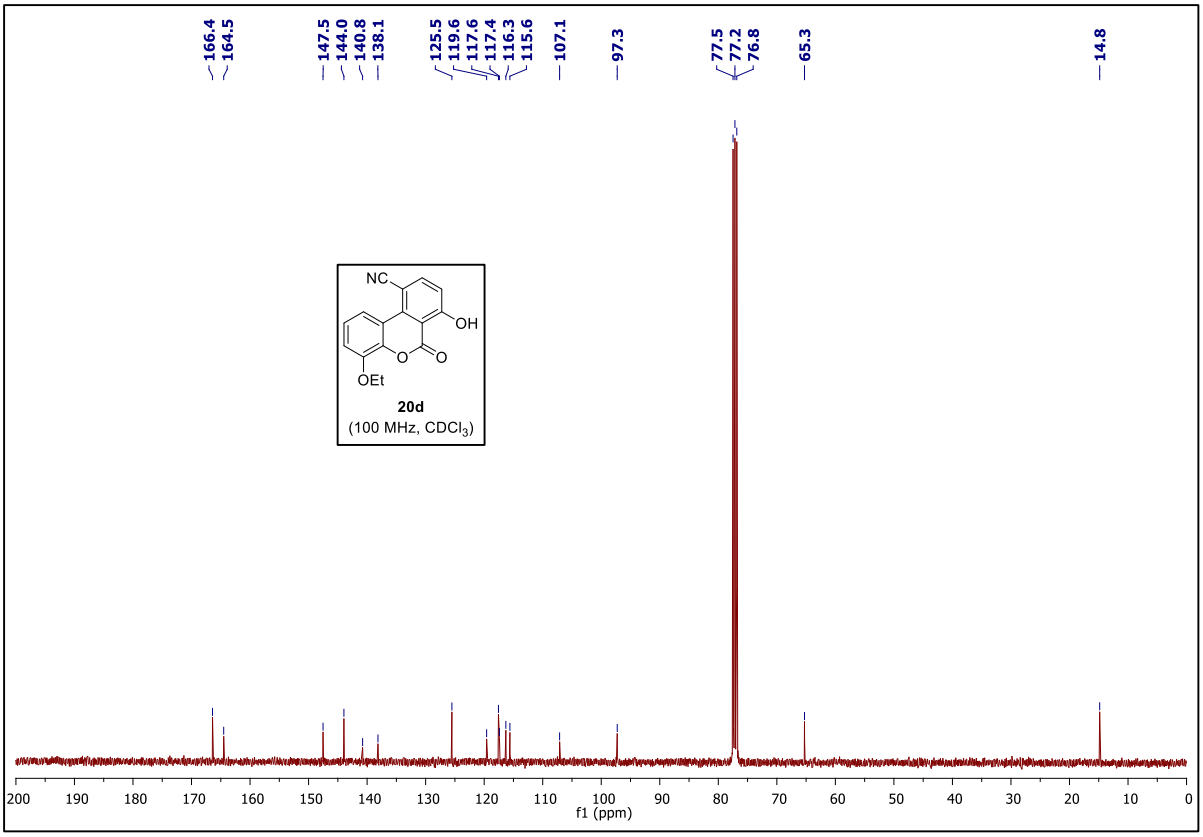
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-4-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20c**.



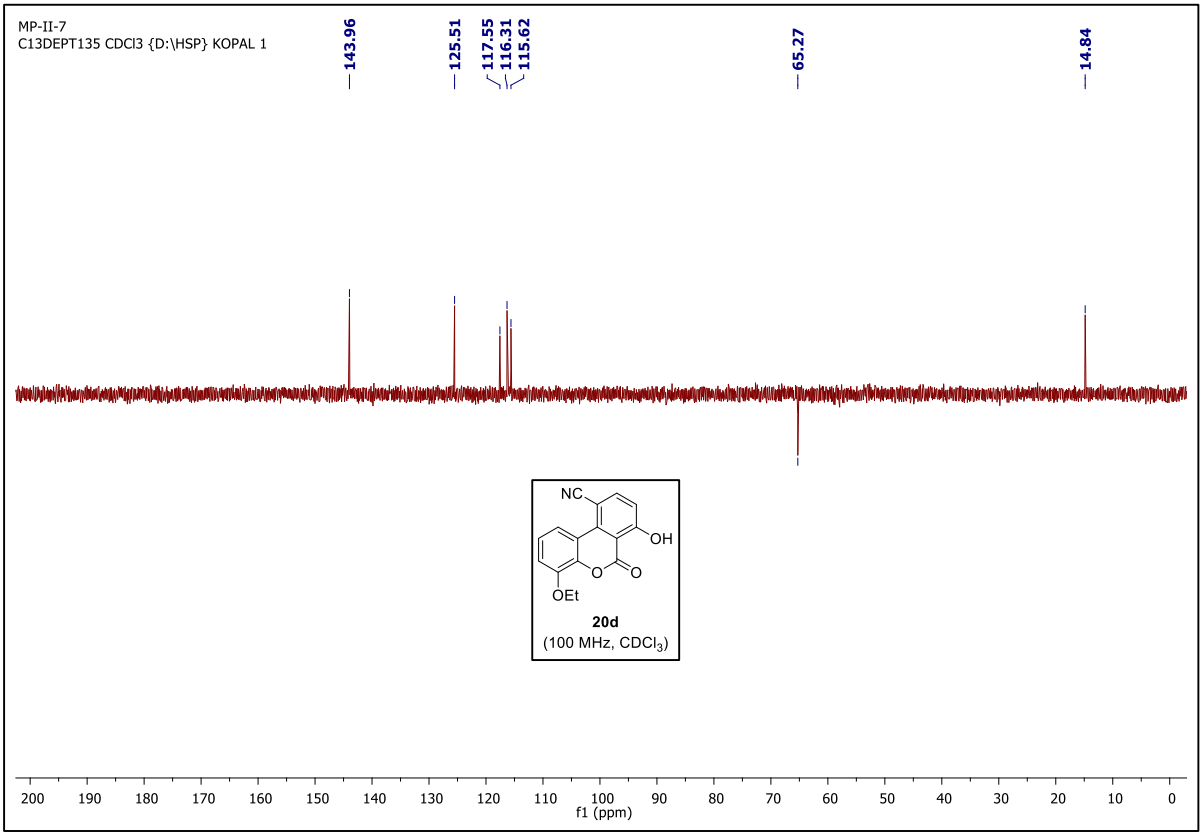
DEPT-135 NMR spectrum of 7-hydroxy-4-methoxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20c**.



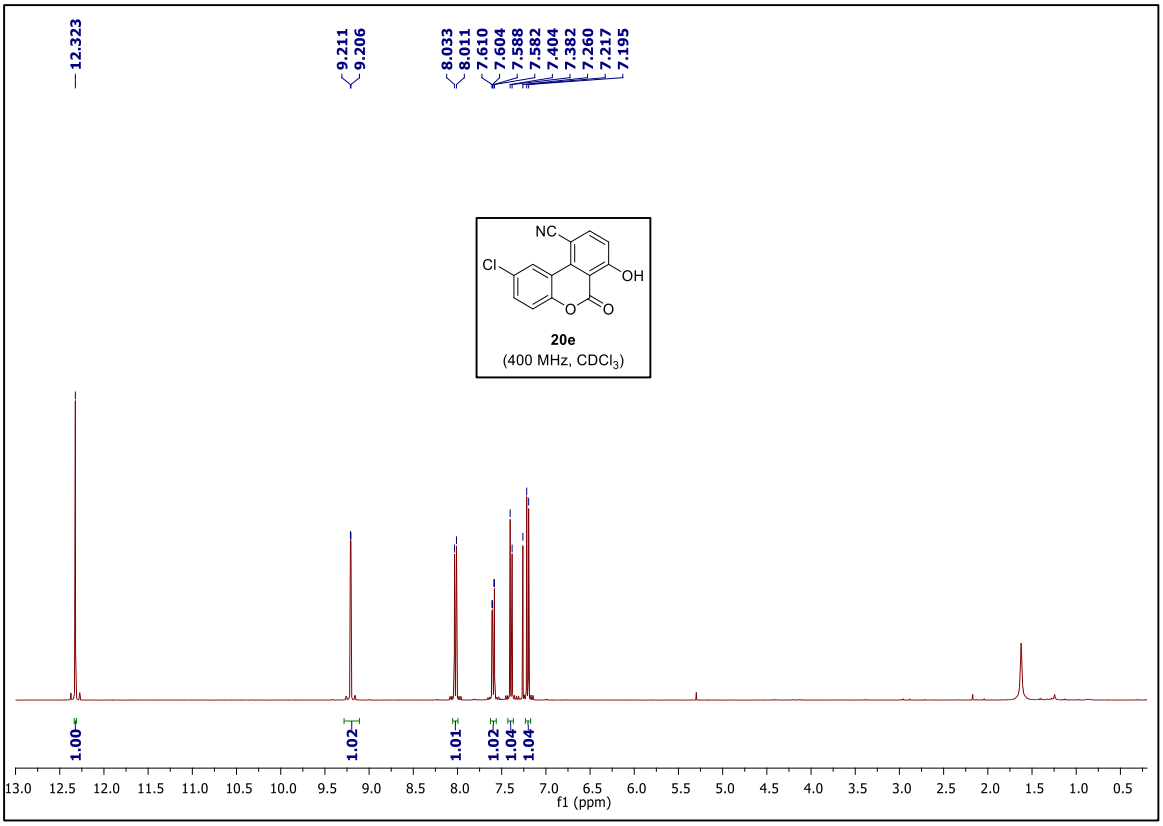
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-ethoxy-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20d**



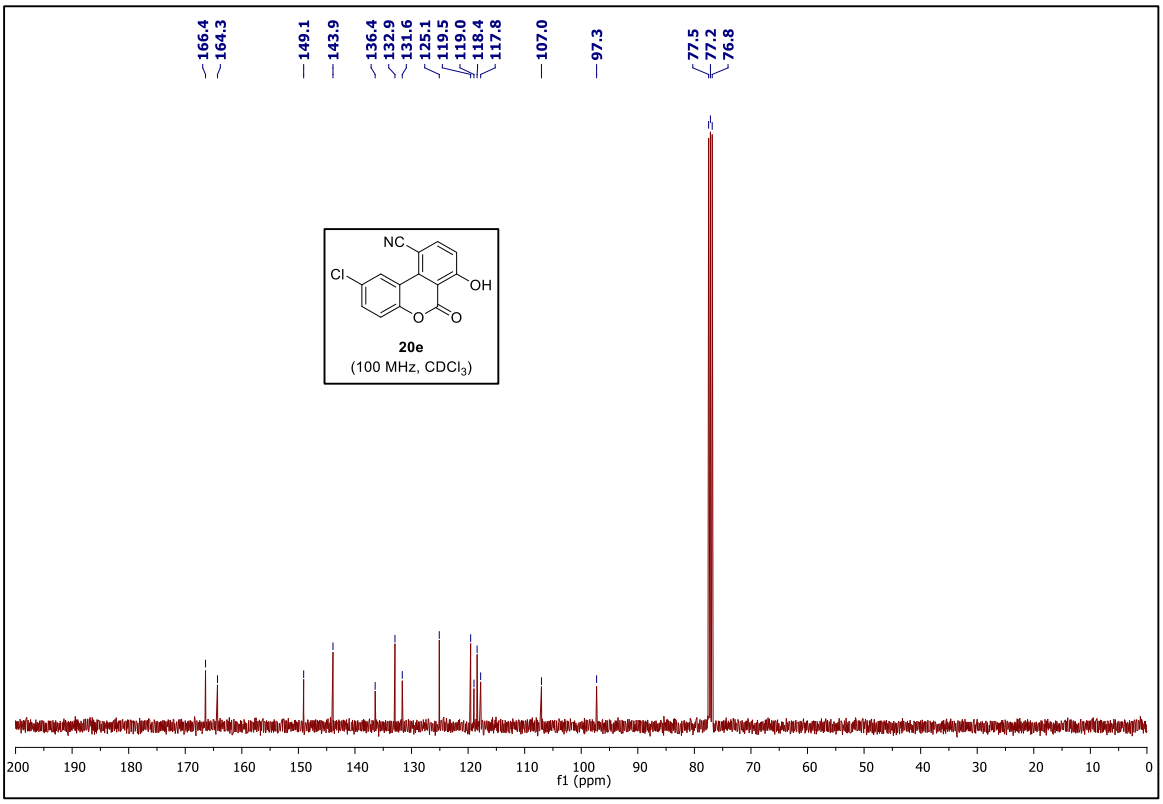
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4-ethoxy-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20d**.



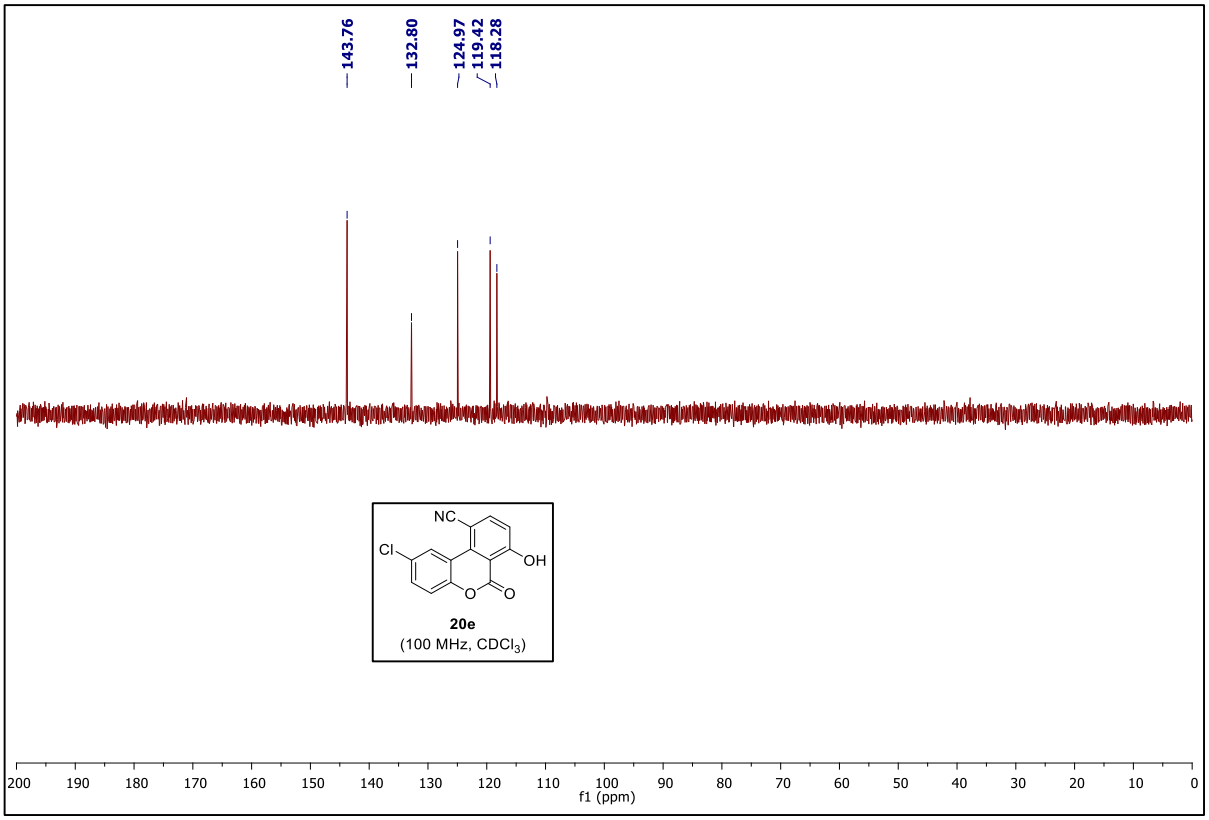
DEPT-135 NMR spectrum of 4-ethoxy-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20d**.



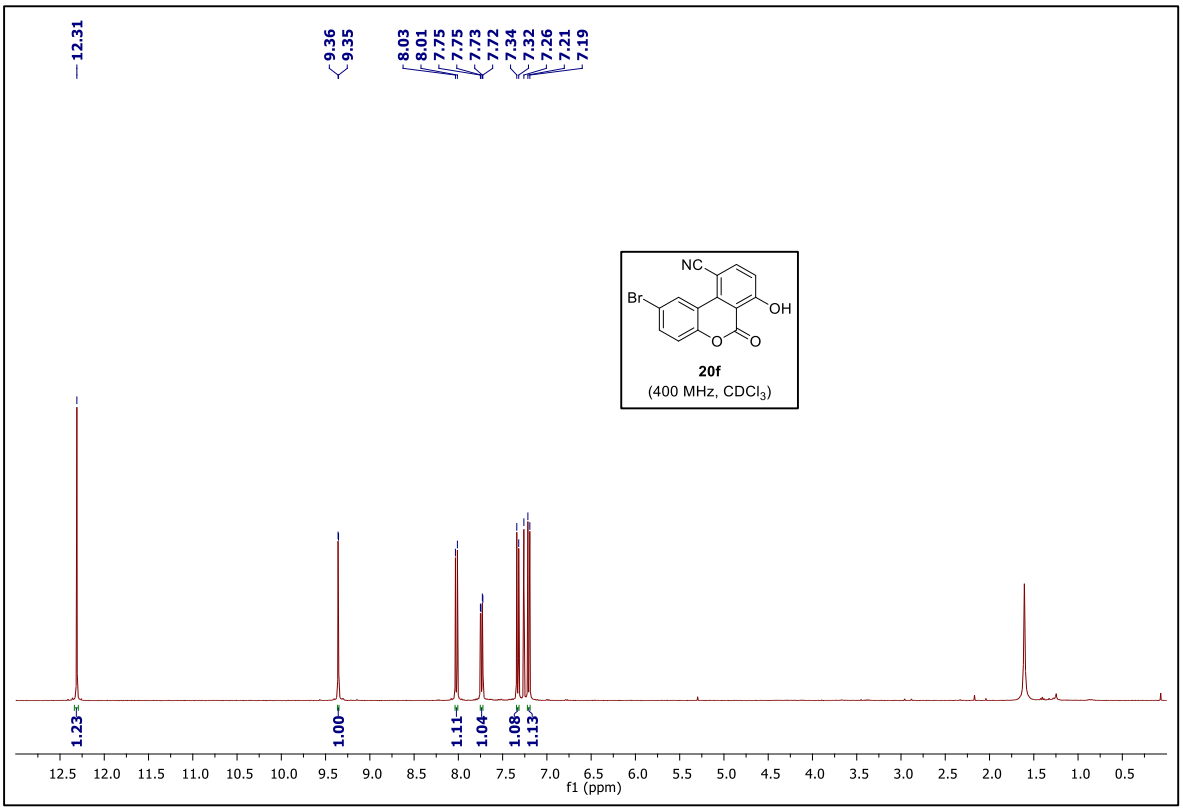
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-chloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20e**.



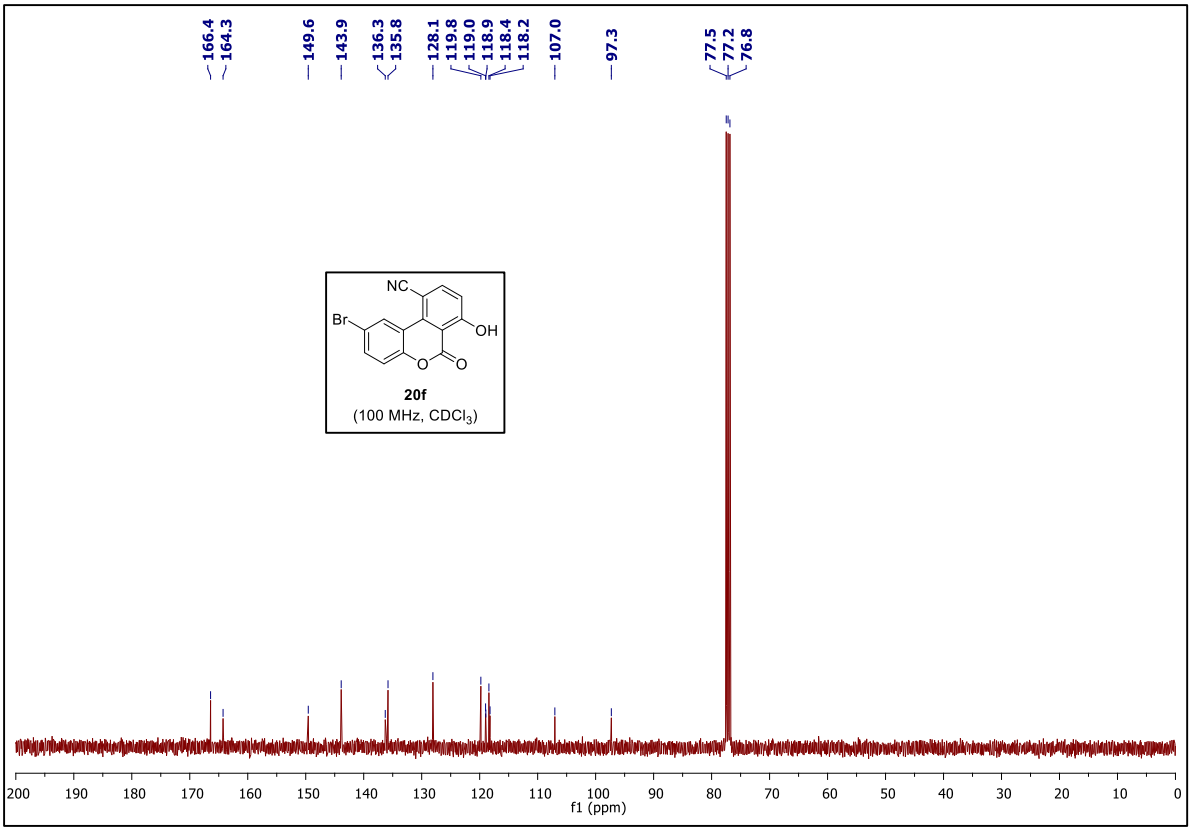
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-chloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20e**.



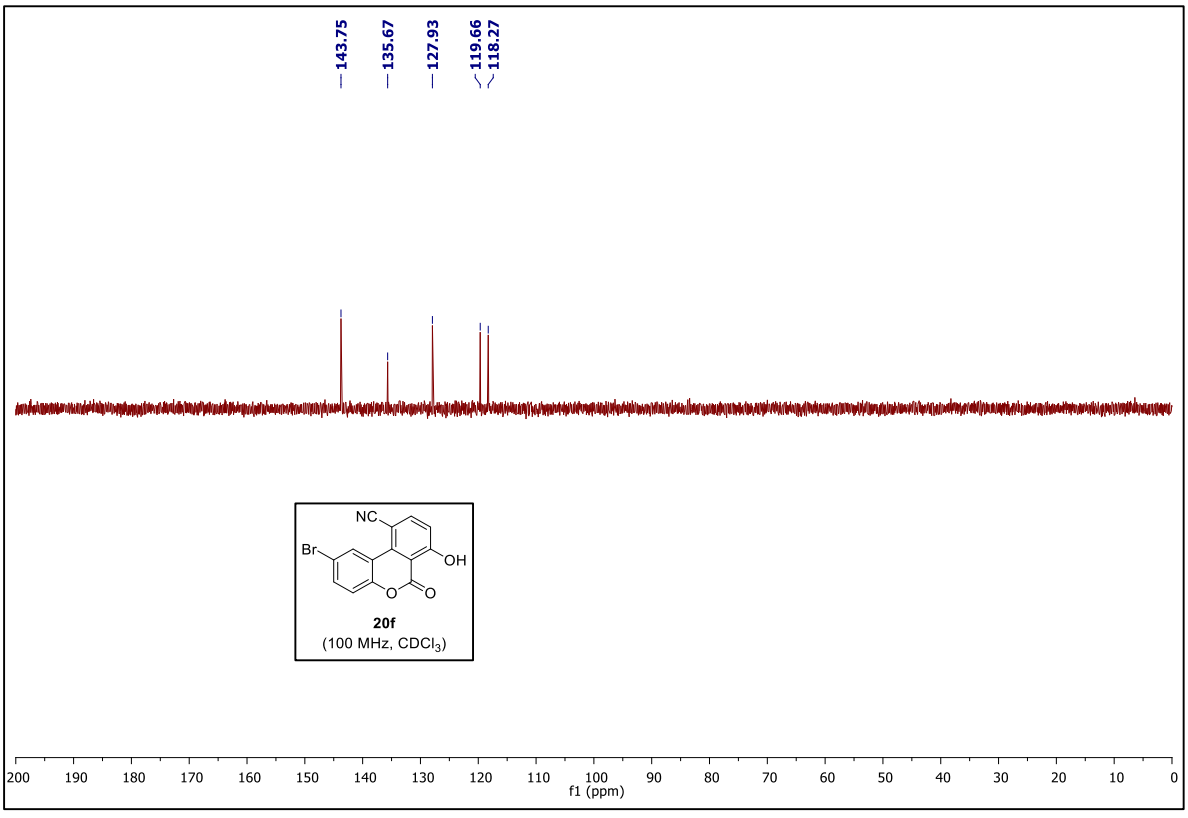
DEPT-135 NMR spectrum of 2-chloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20e**.



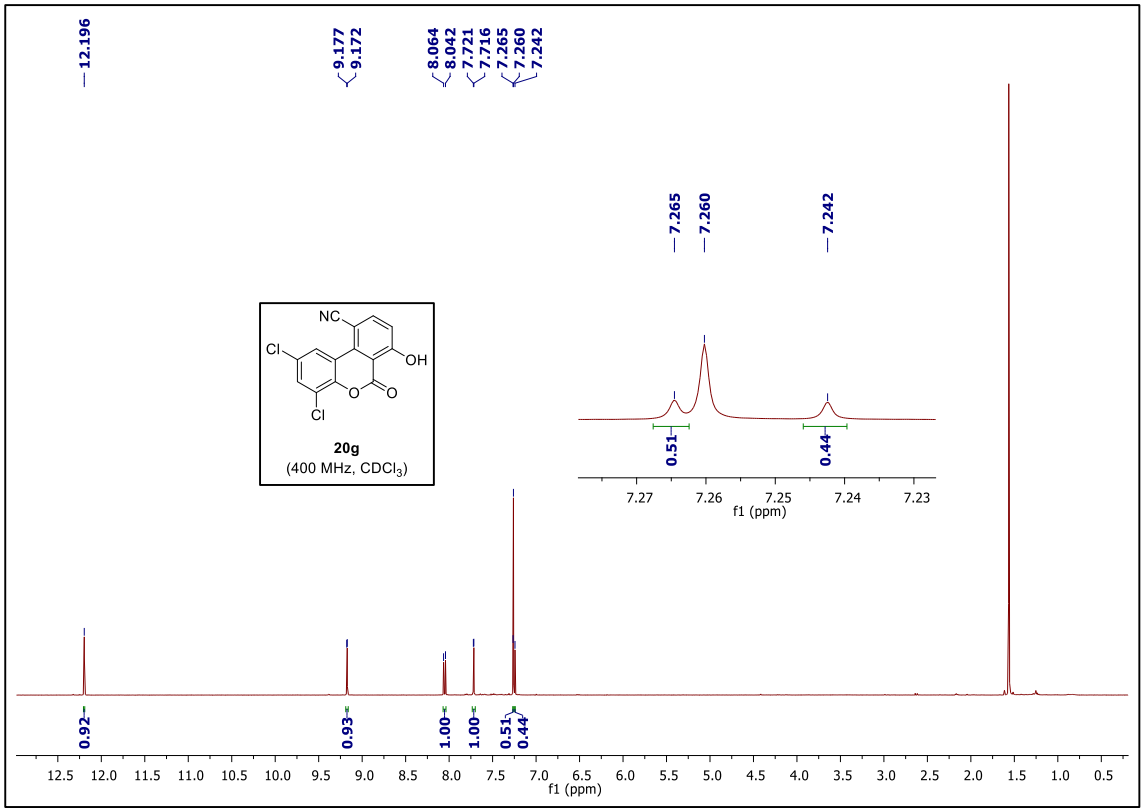
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f**



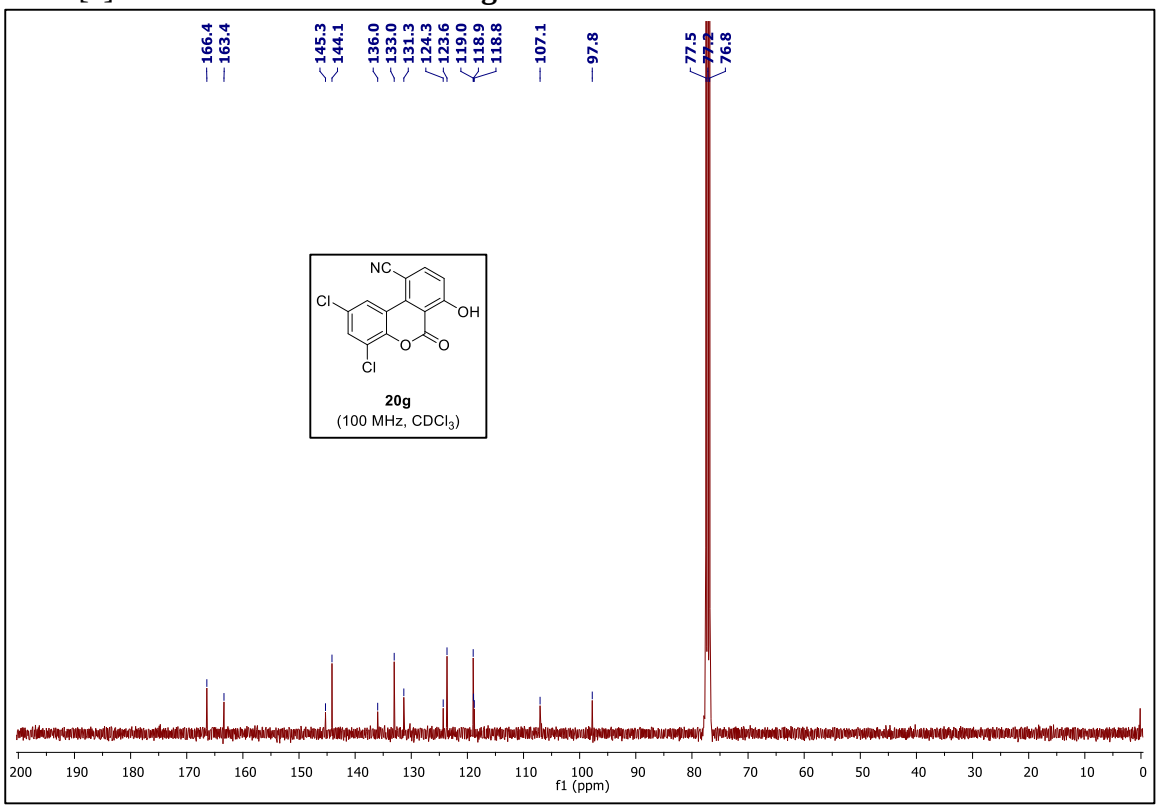
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f**.



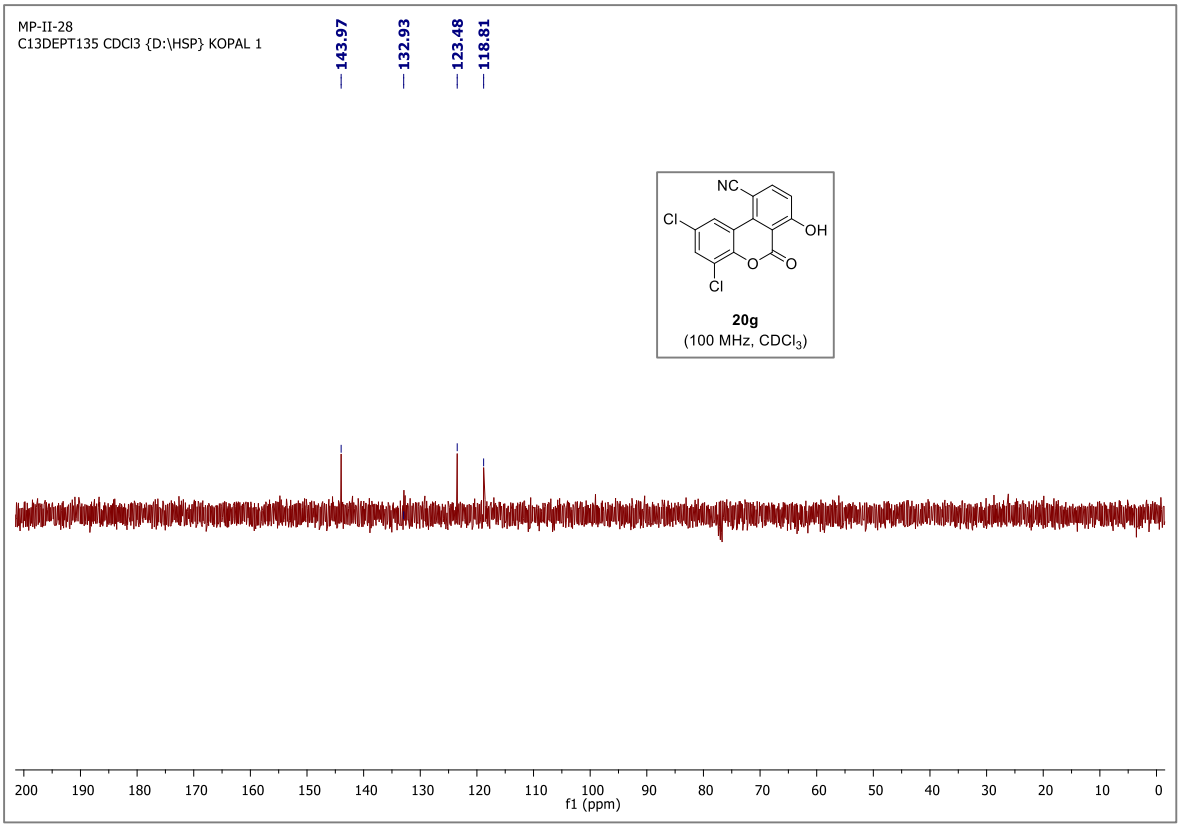
DEPT-135 NMR spectrum of 2-bromo-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20f**.



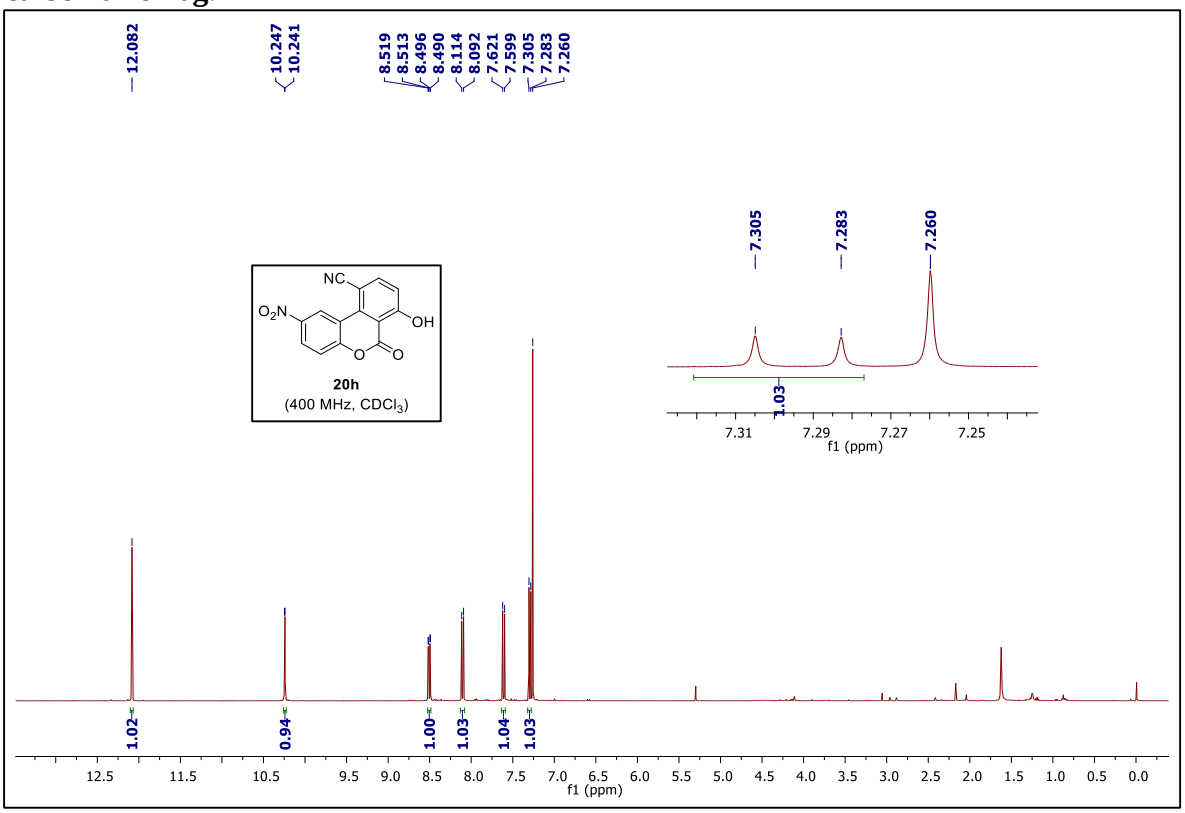
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2,4-dichloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20g**.



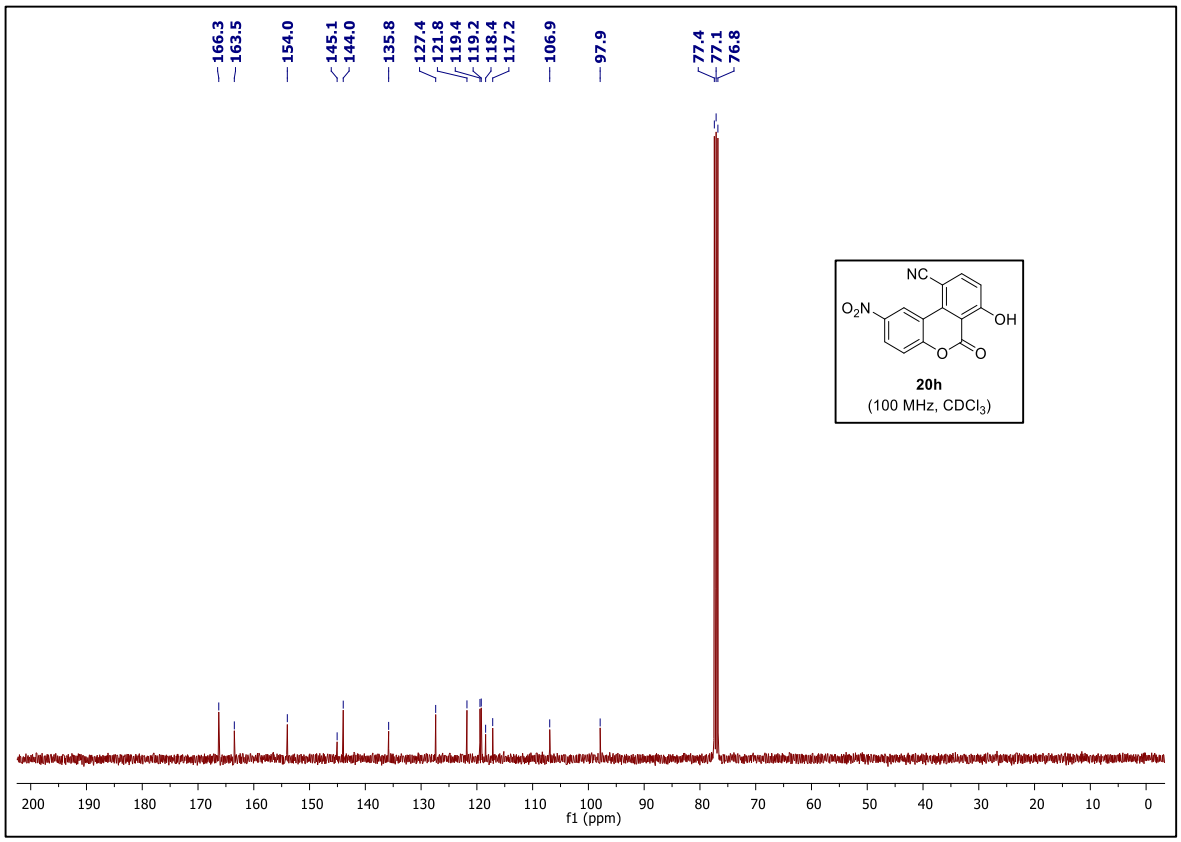
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2,4-dichloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20g**.



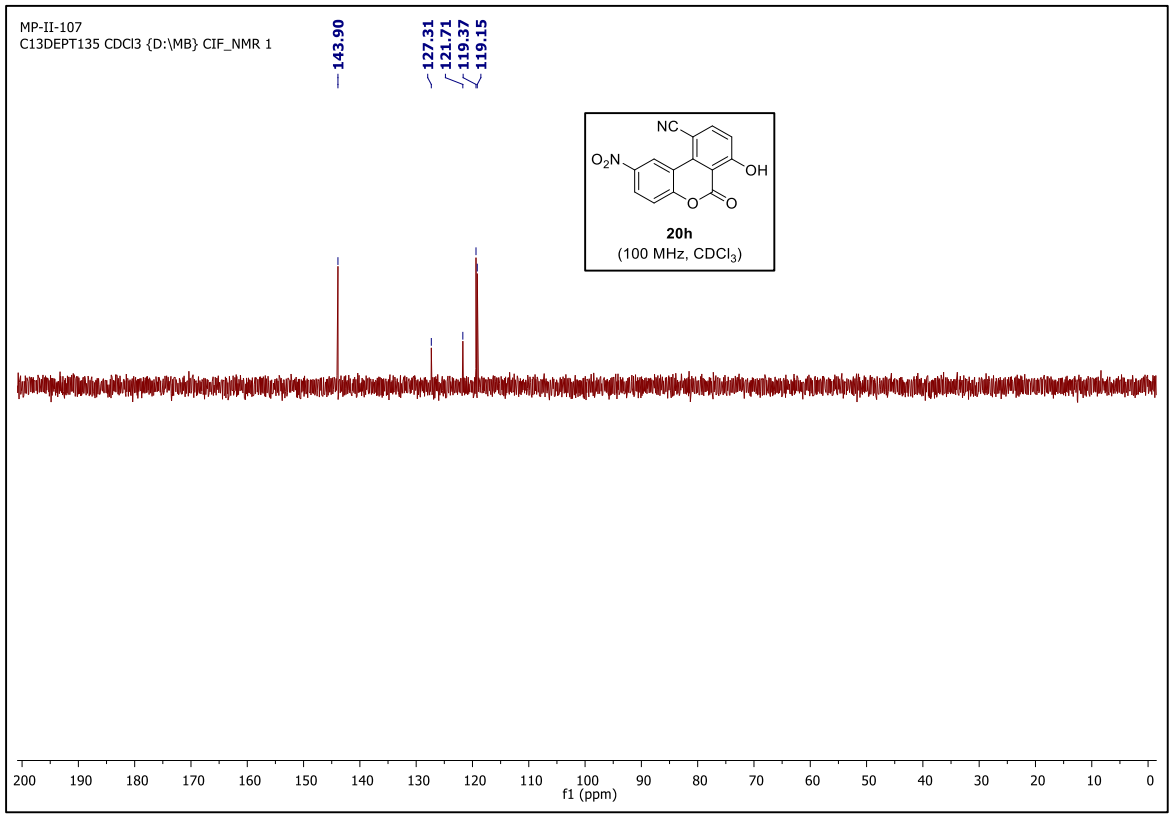
DEPT-135 NMR spectrum of 2,4-dichloro-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20g**.



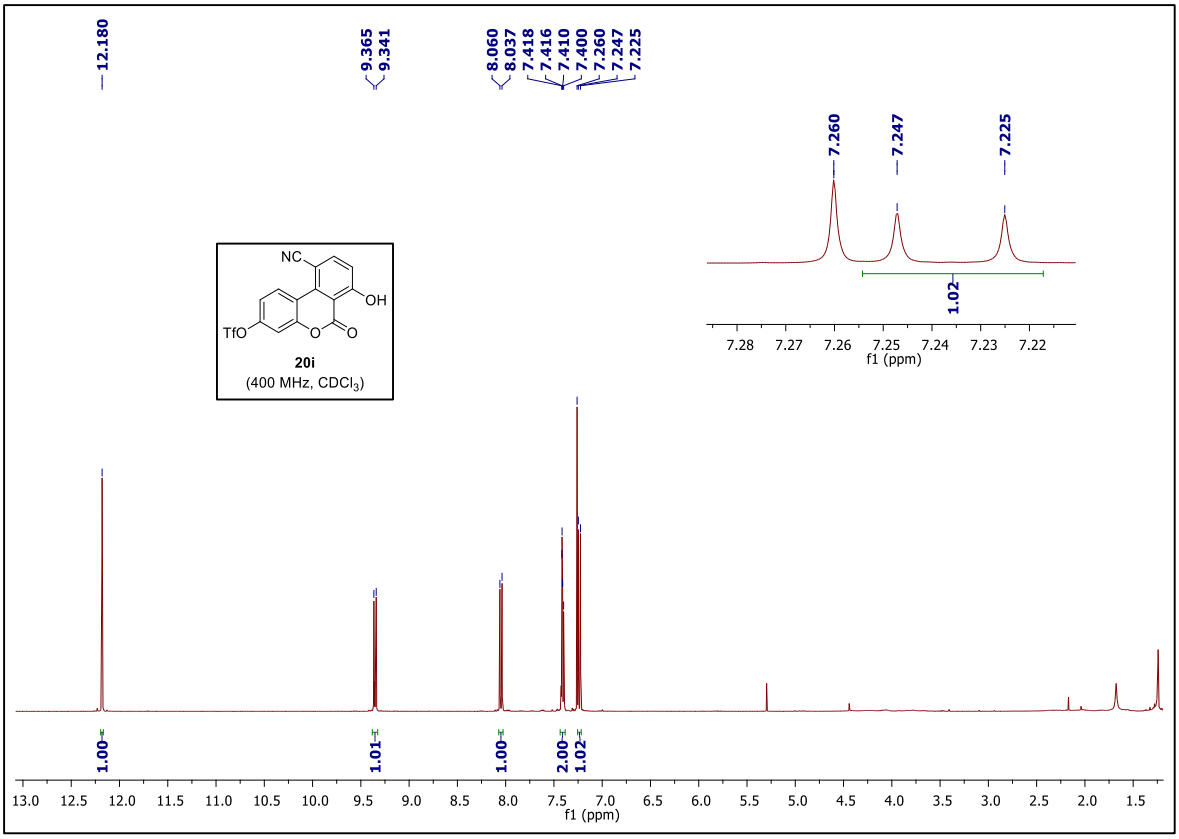
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-nitro-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20h**.



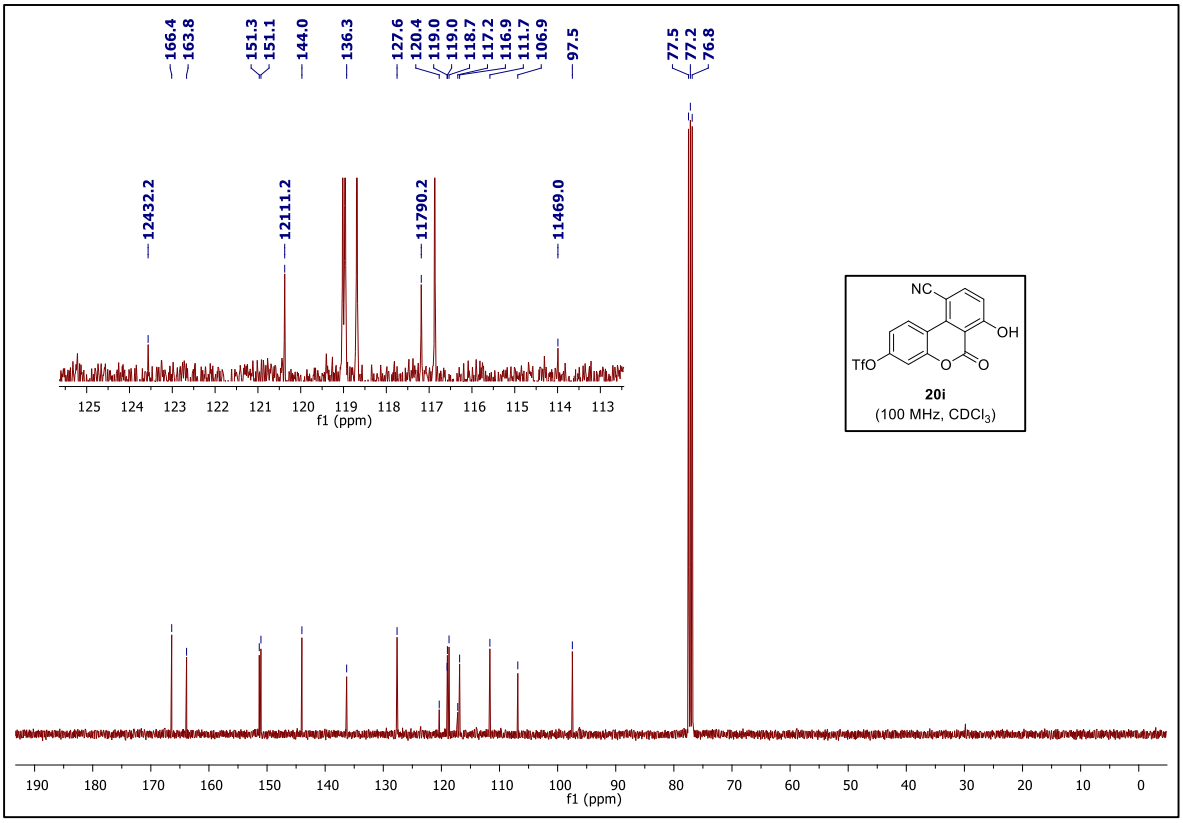
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-nitro-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20h**.



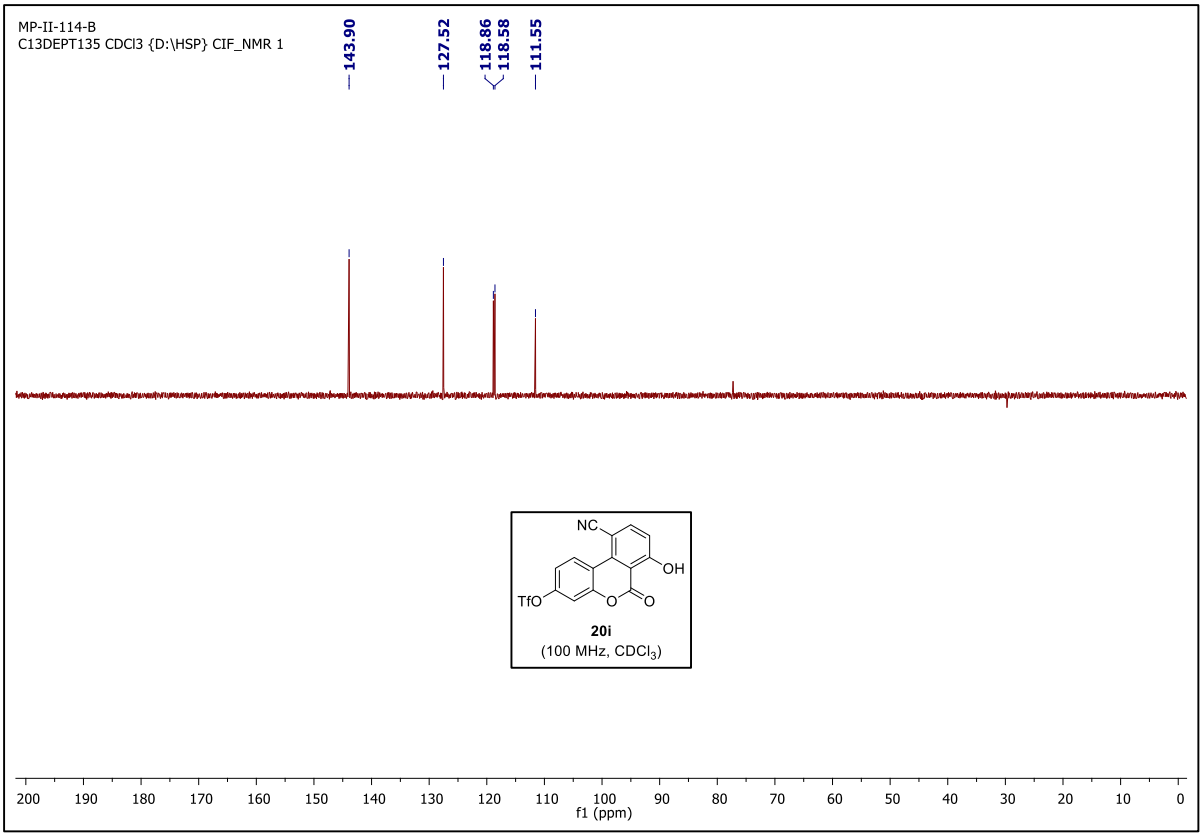
DEPT-135 NMR spectrum of 7-hydroxy-2-nitro-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20h**.



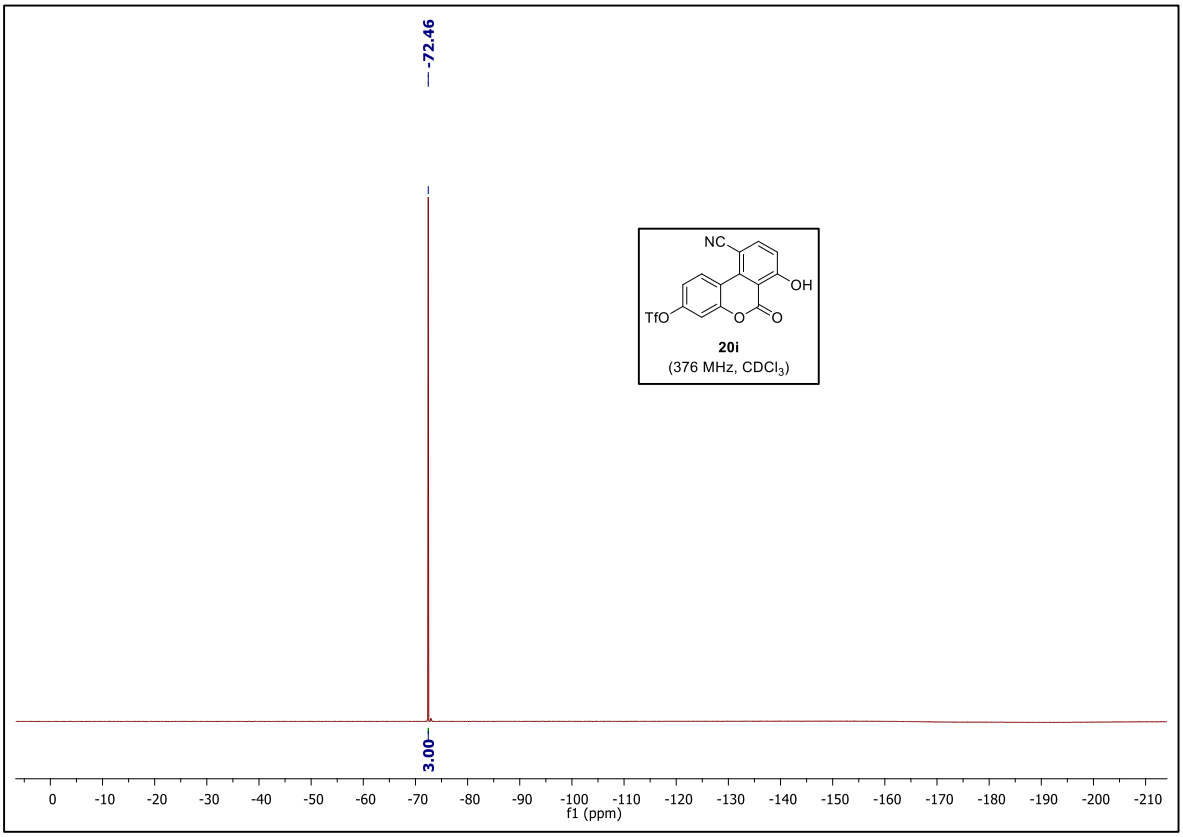
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 10-cyano-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromen-3-yl trifluoromethanesulfonate **20i**.



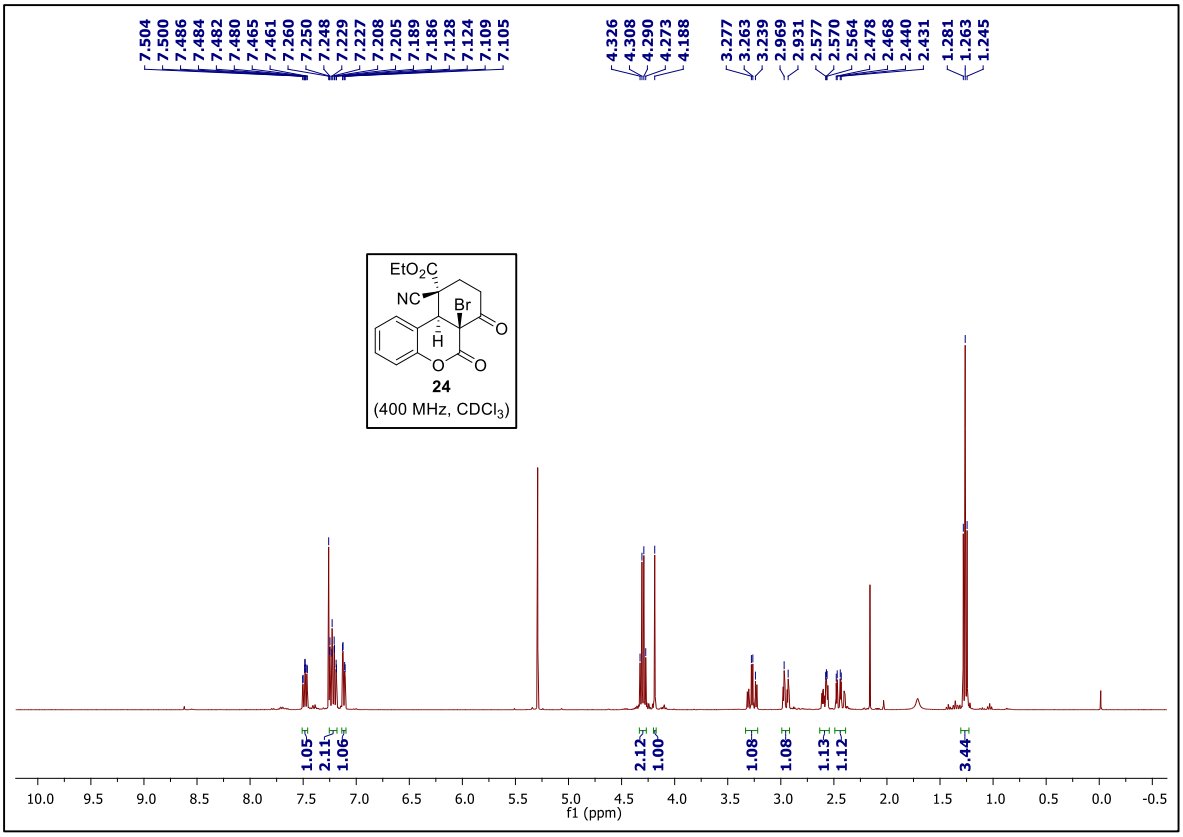
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 10-cyano-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromen-3-yl trifluoromethanesulfonate **20i**



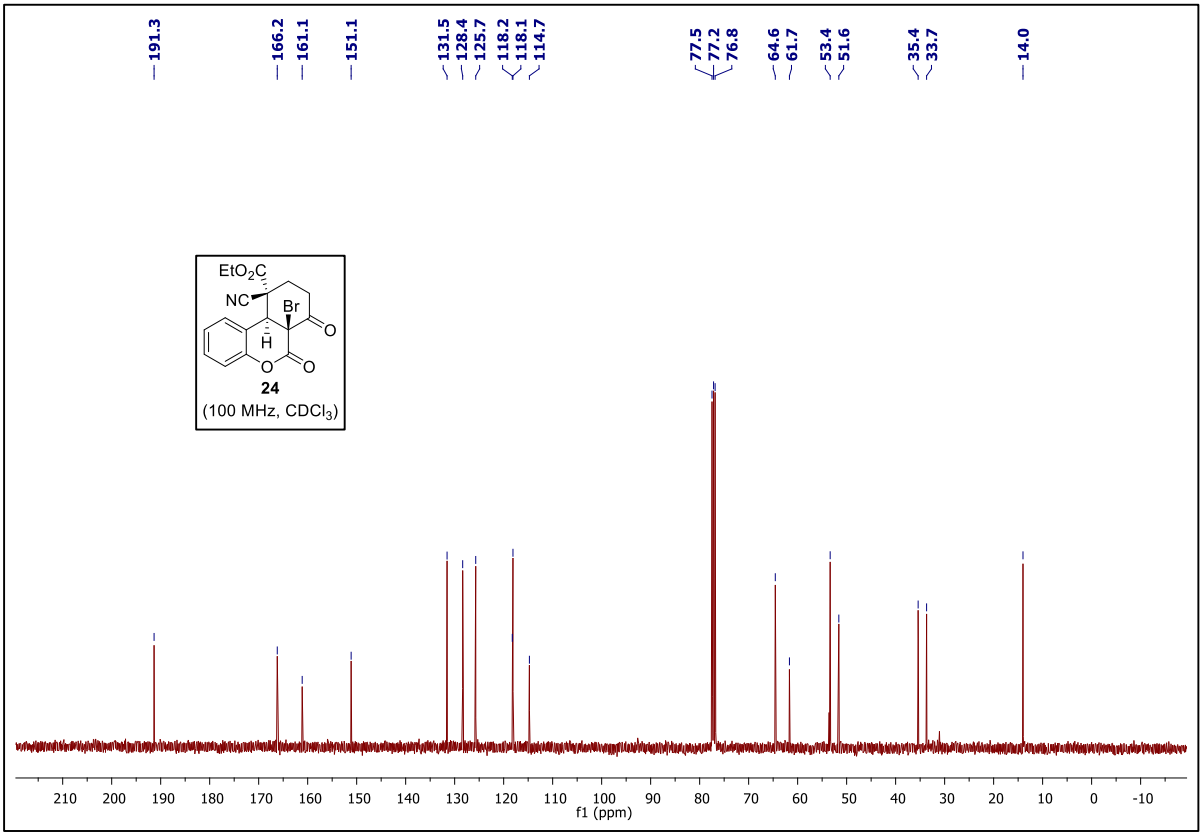
DEPT-135 NMR spectrum of 10-cyano-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromen-3-yl trifluoromethanesulfonate **20i**.



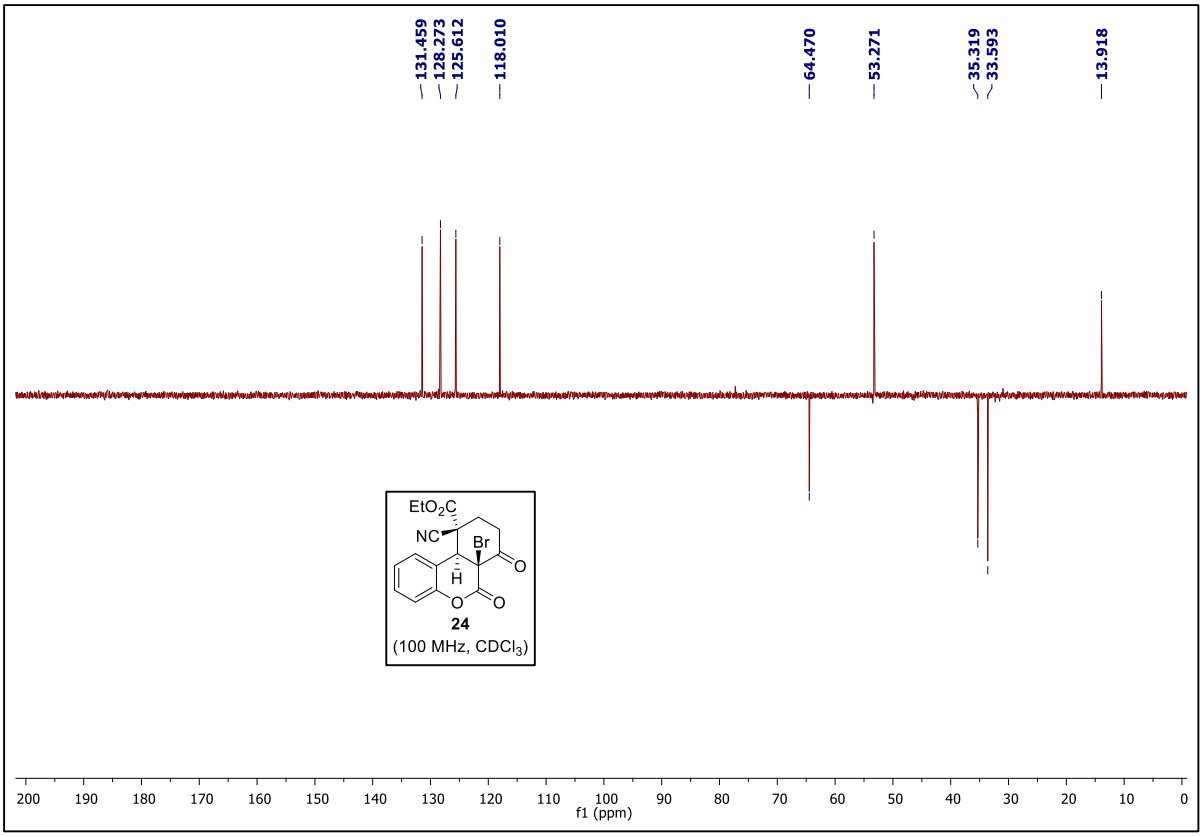
^{19}F NMR (376 MHz, $CDCl_3$; Reference = $CFCl_3$) spectrum of 10-cyano-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromen-3-yl trifluoromethanesulfonate **20i**.



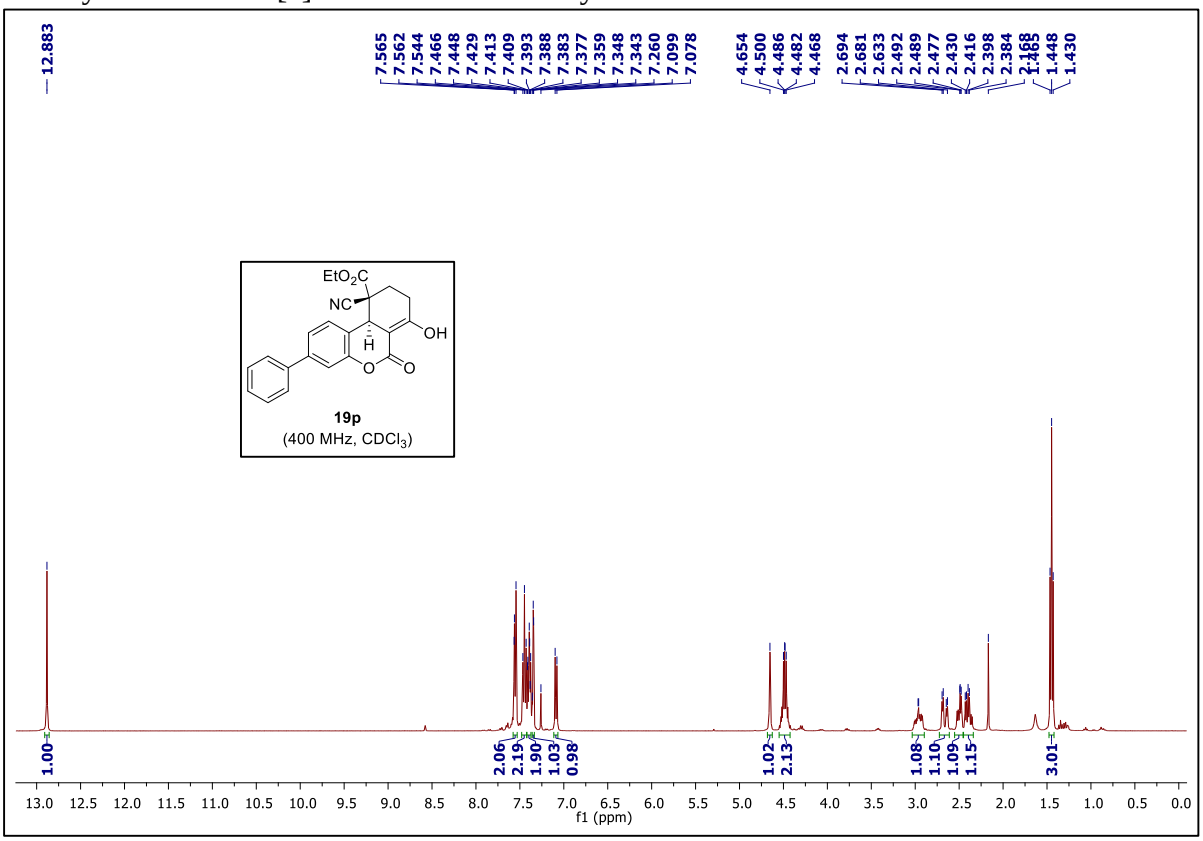
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 6a-bromo-10-cyano-6,7-dioxo-6a,7,8,9,10,10a-hexahydro-6*H*-benzo[*c*]chromene-10-carboxylate **24**.



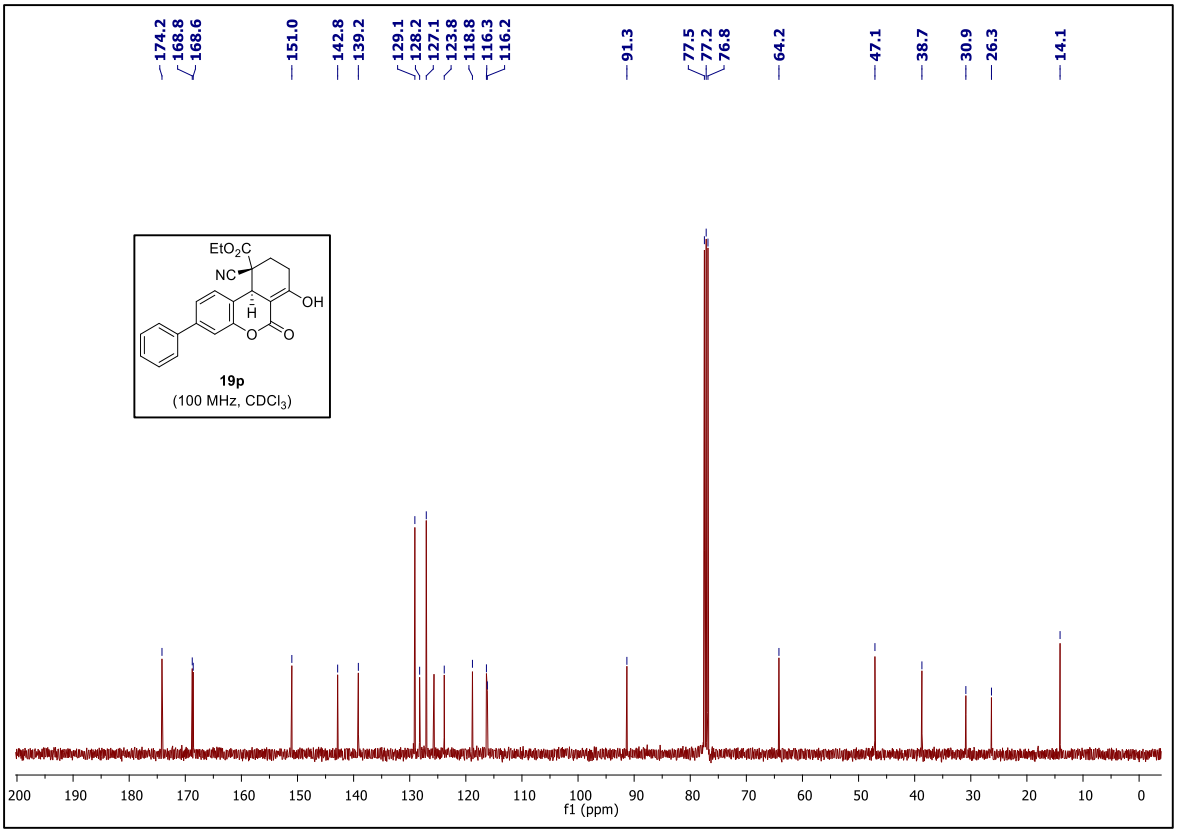
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 6a-bromo-10-cyano-6,7-dioxo-6a,7,8,9,10,10a-hexahydro-6*H*-benzo[*c*]chromene-10-carboxylate **24**.



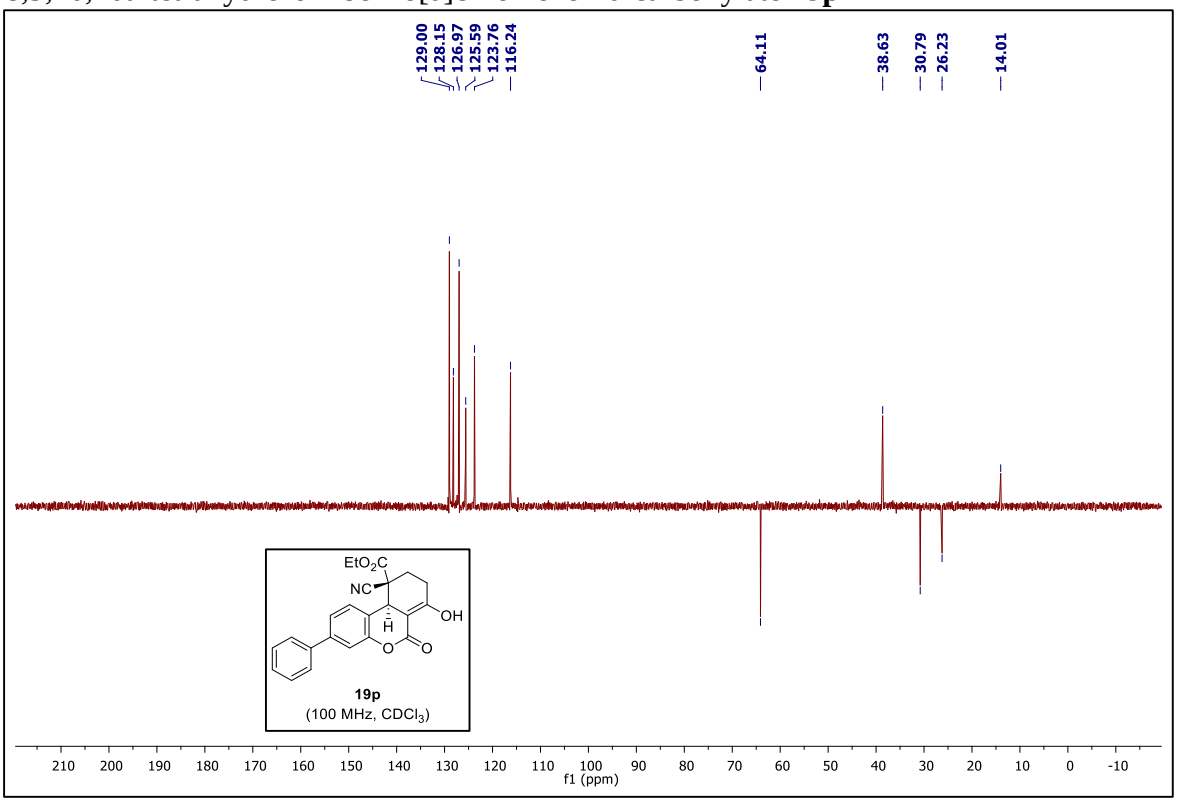
DEPT-135 NMR spectrum of ethyl 6a-bromo-10-cyano-6,7-dioxo-6a,7,8,9,10,10a-hexahydro-6*H*-benzo[*c*]chromene-10-carboxylate **24**.



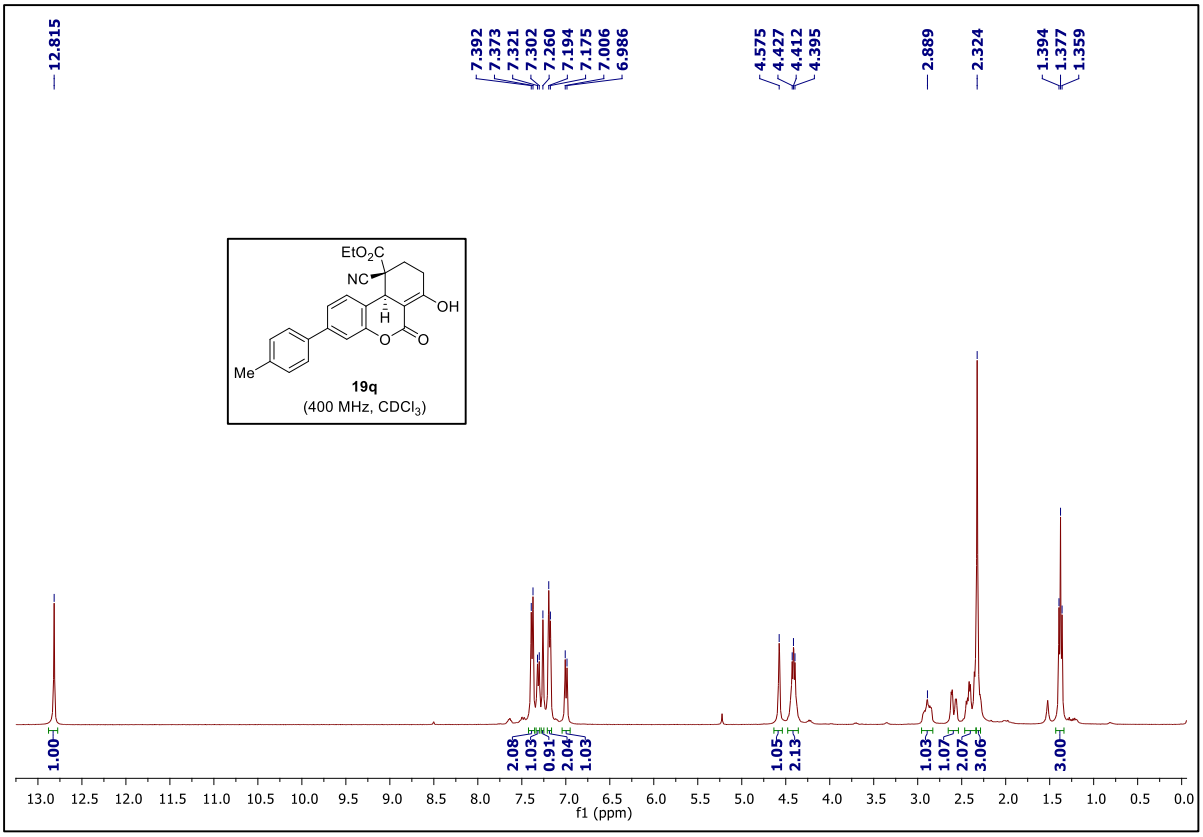
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-phenyl-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19p**.



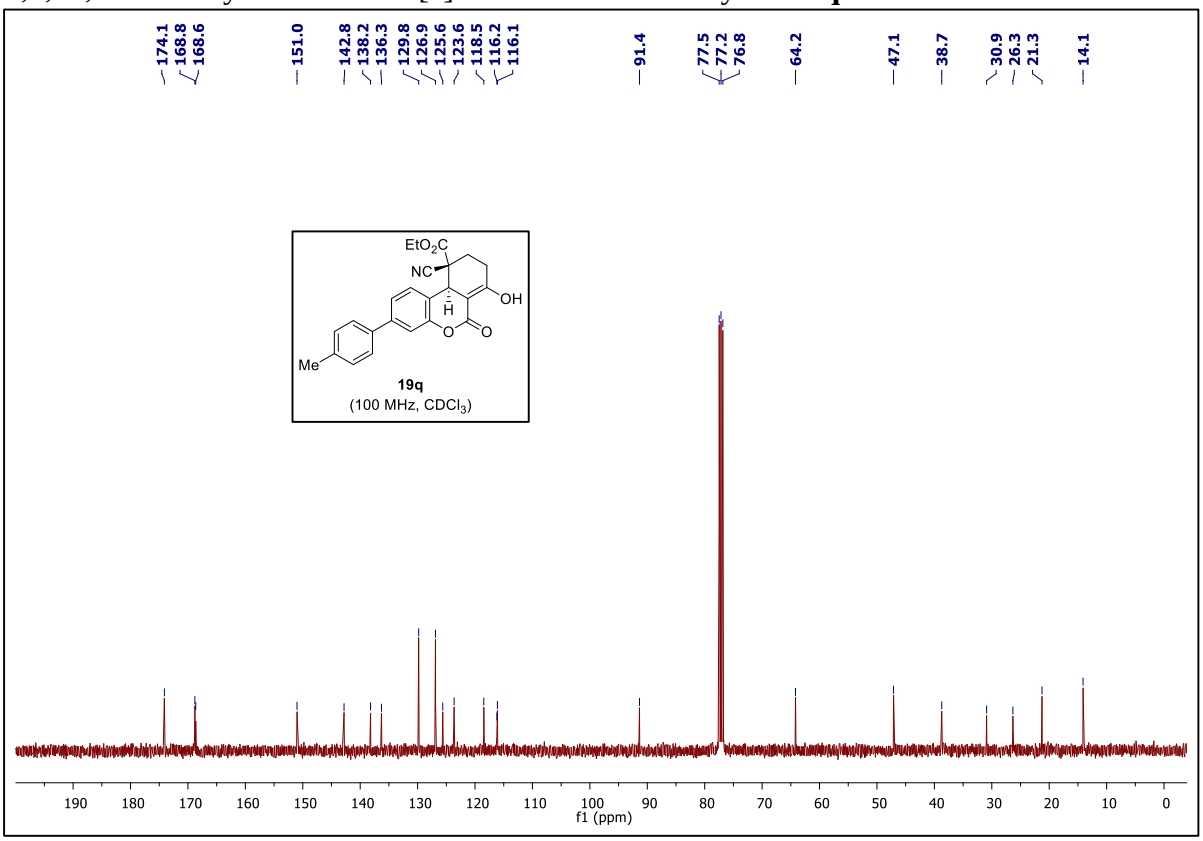
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-phenyl-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19p**



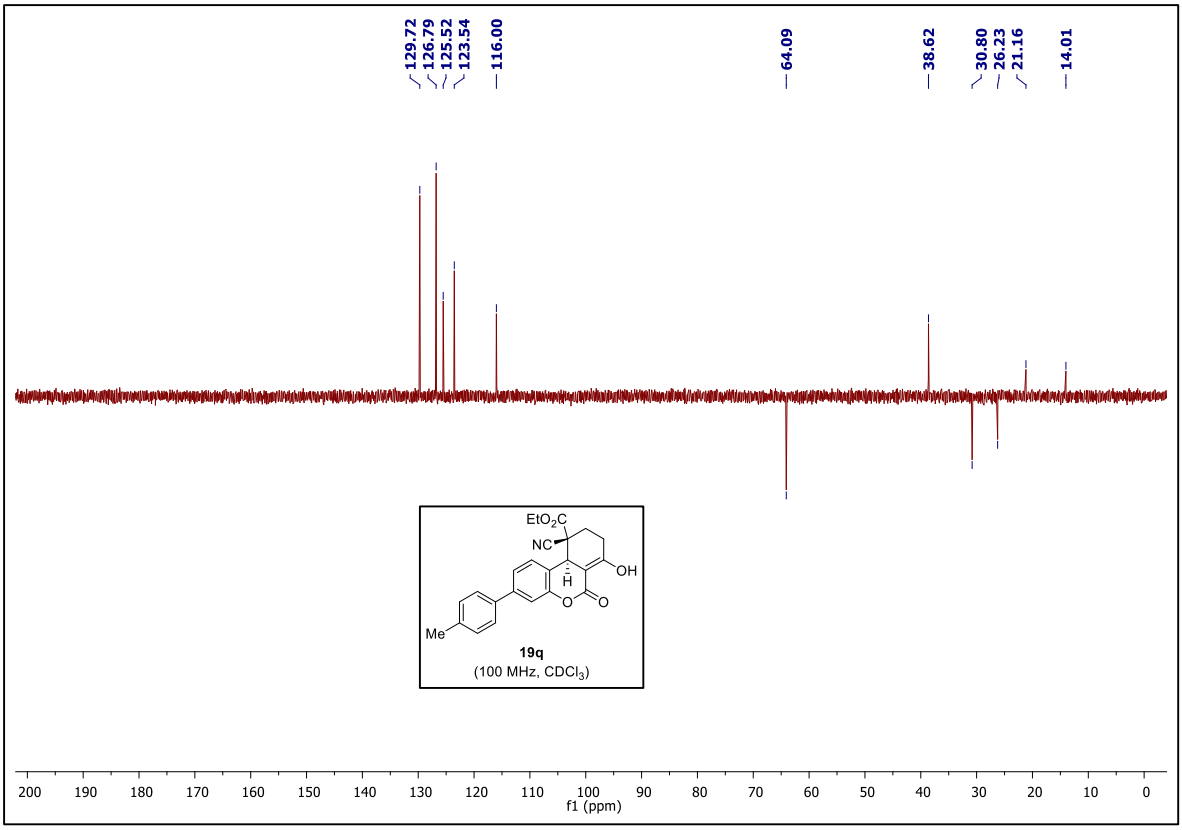
DEPT-135 NMR spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-phenyl-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19p**



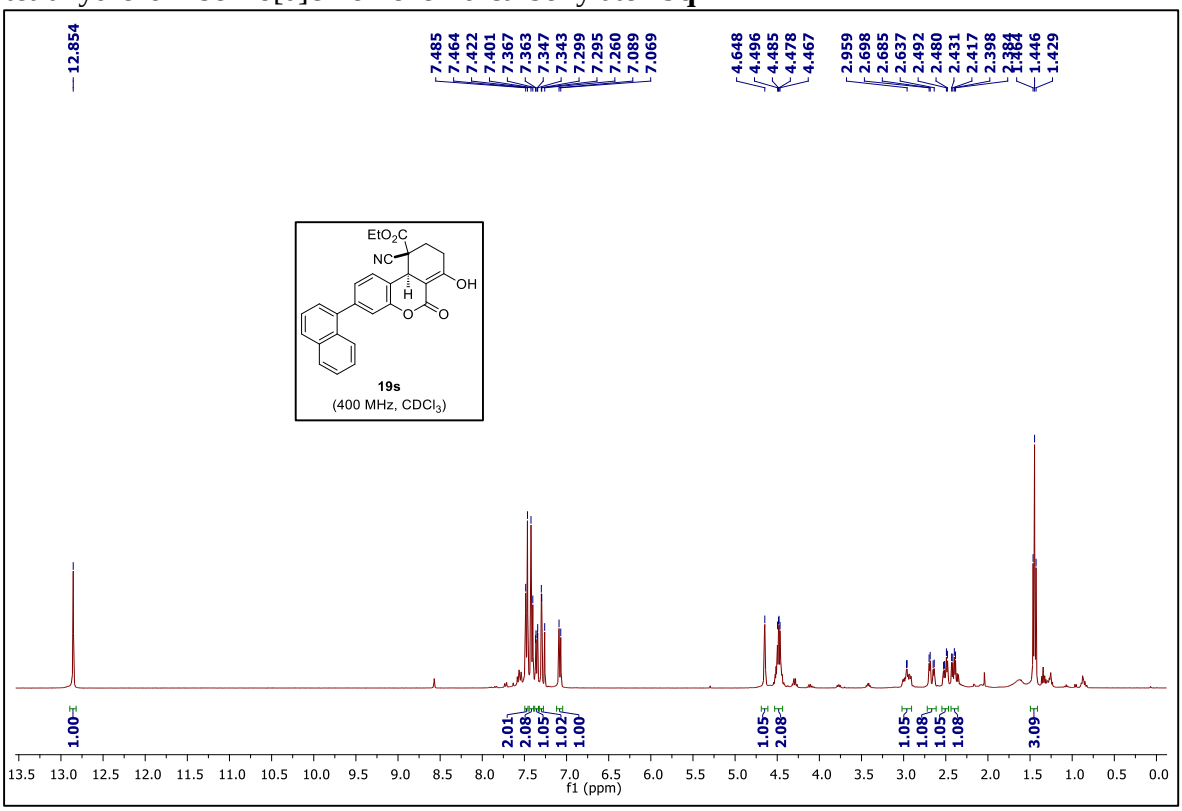
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-(p-tolyl)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19q**.



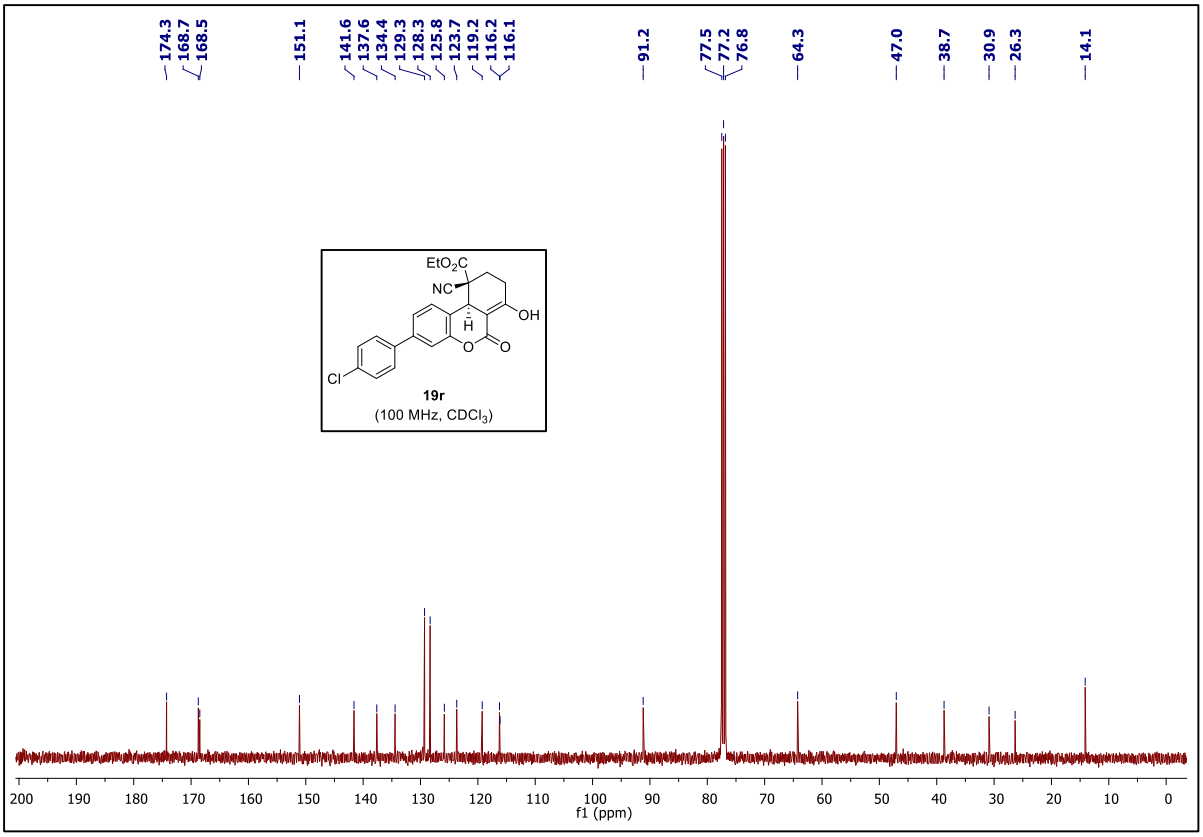
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-(p-tolyl)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19q**



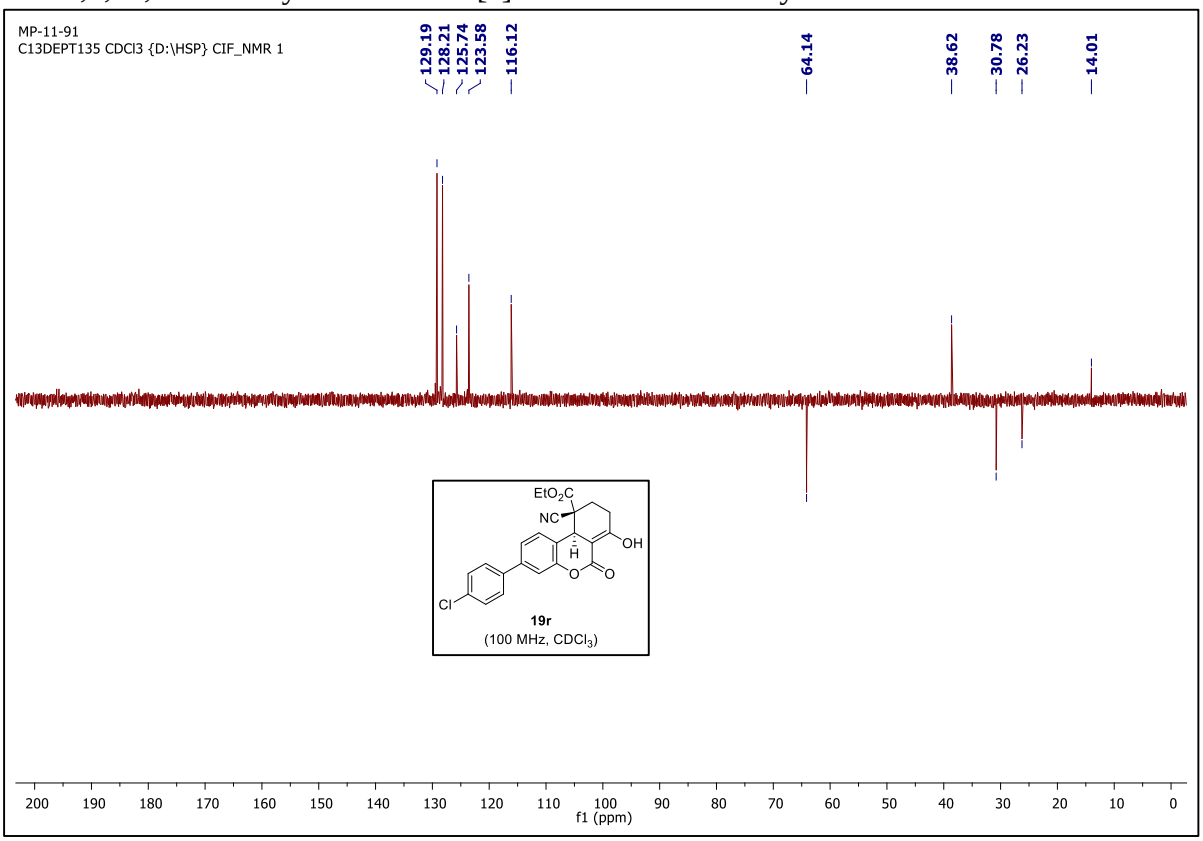
DEPT-135 NMR spectrum of ethyl 10-cyano-7-hydroxy-6-oxo-3-(p-tolyl)-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19q**



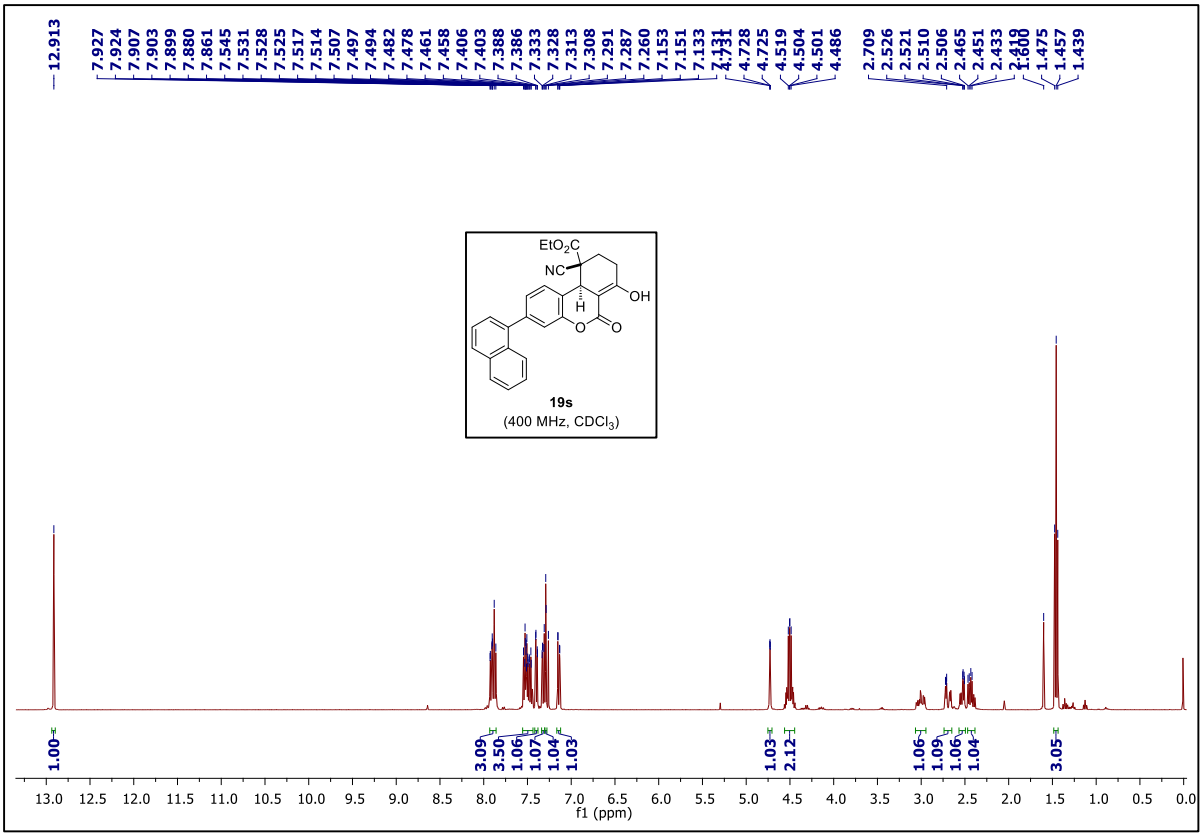
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 3-(4-chlorophenyl)-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19r**



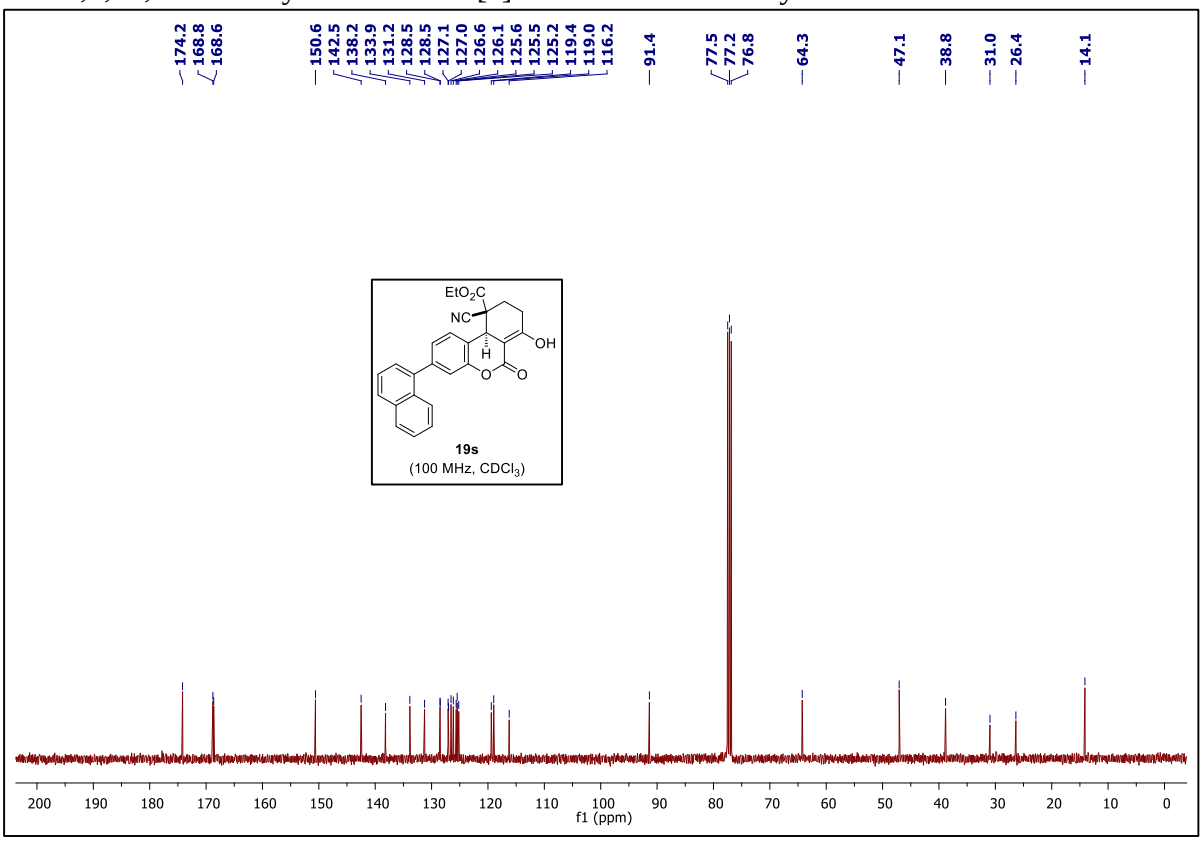
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 3-(4-chlorophenyl)-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19r**



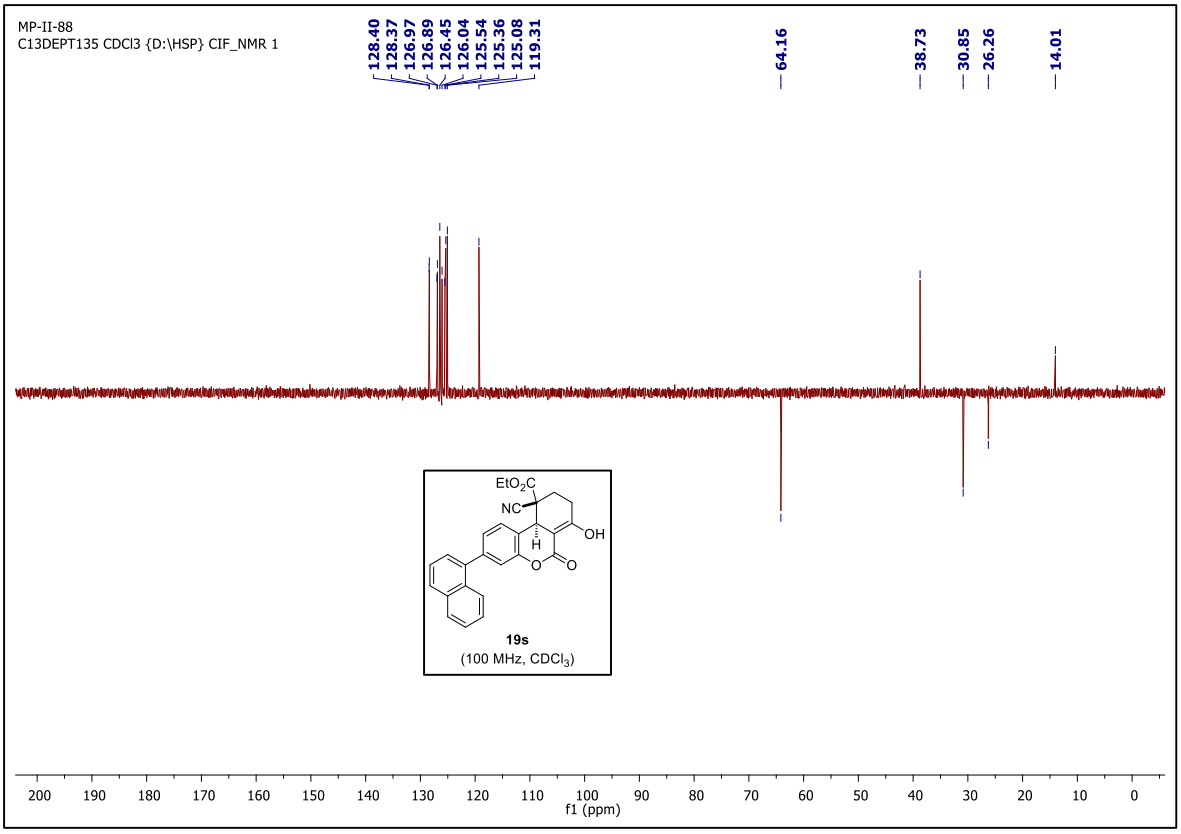
DEPT-135 NMR spectrum of ethyl 3-(4-chlorophenyl)-10-cyano-7-hydroxy-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19r**.



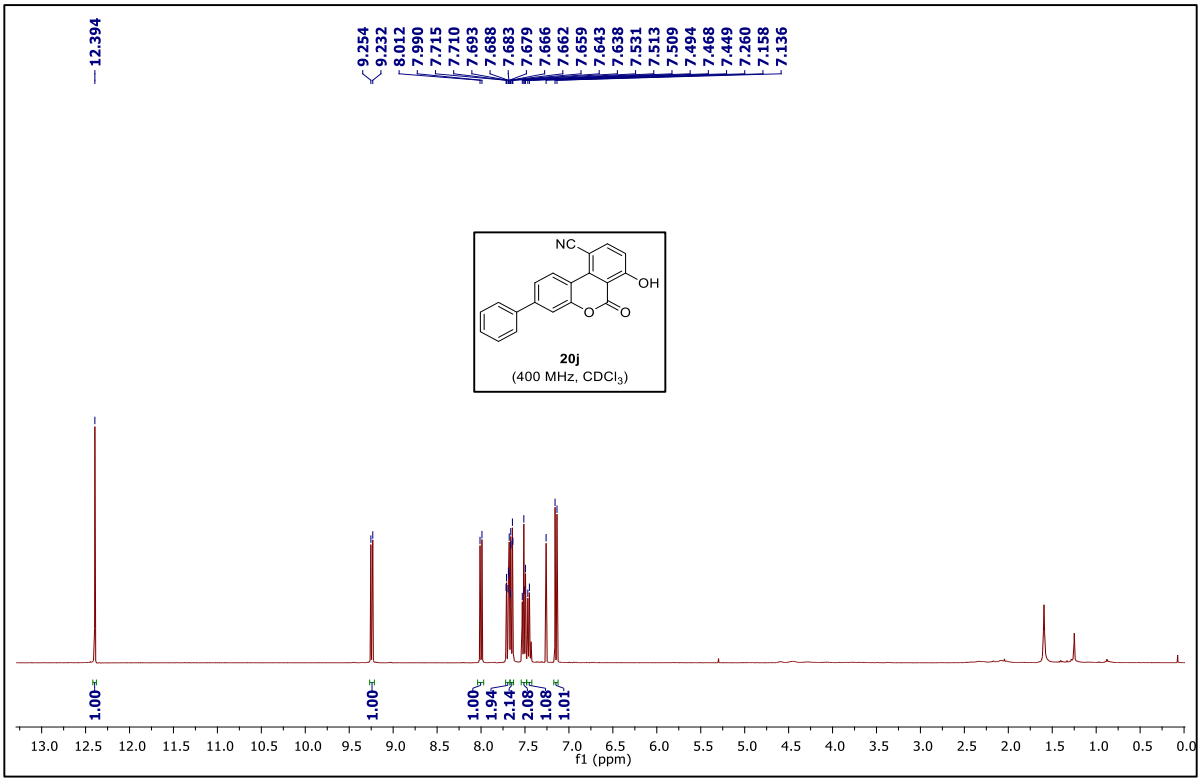
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-3-(naphthalen-1-yl)-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19s**.



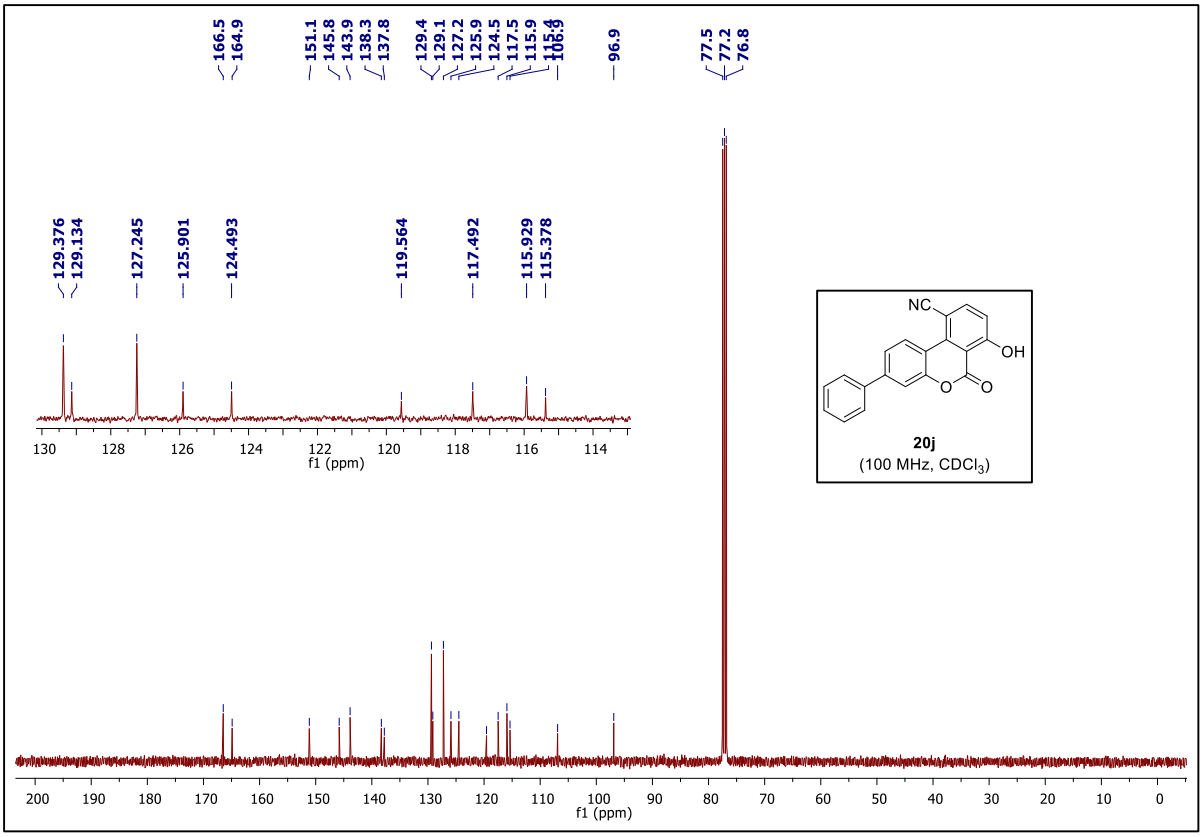
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ethyl 10-cyano-7-hydroxy-3-(naphthalen-1-yl)-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19s**



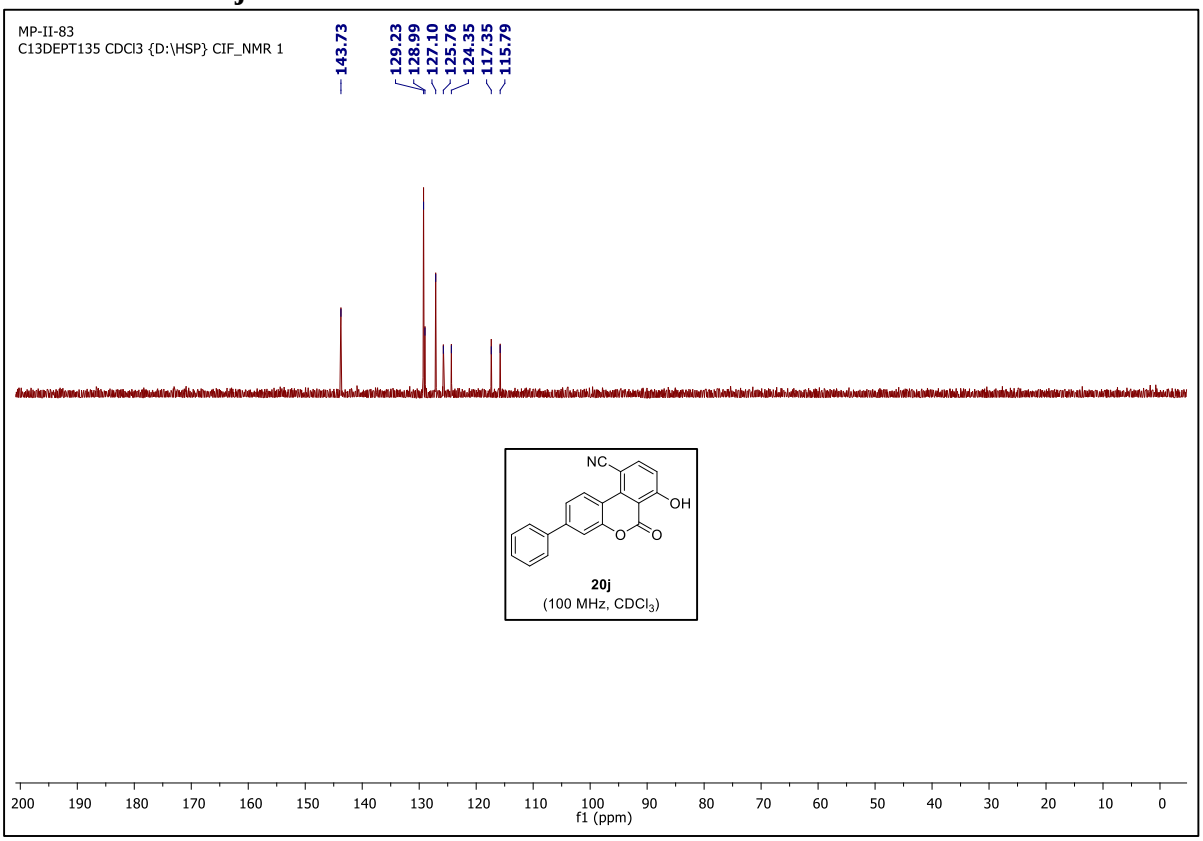
DEPT-135 NMR spectrum of ethyl 10-cyano-7-hydroxy-3-(naphthalen-1-yl)-6-oxo-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene-10-carboxylate **19s**.



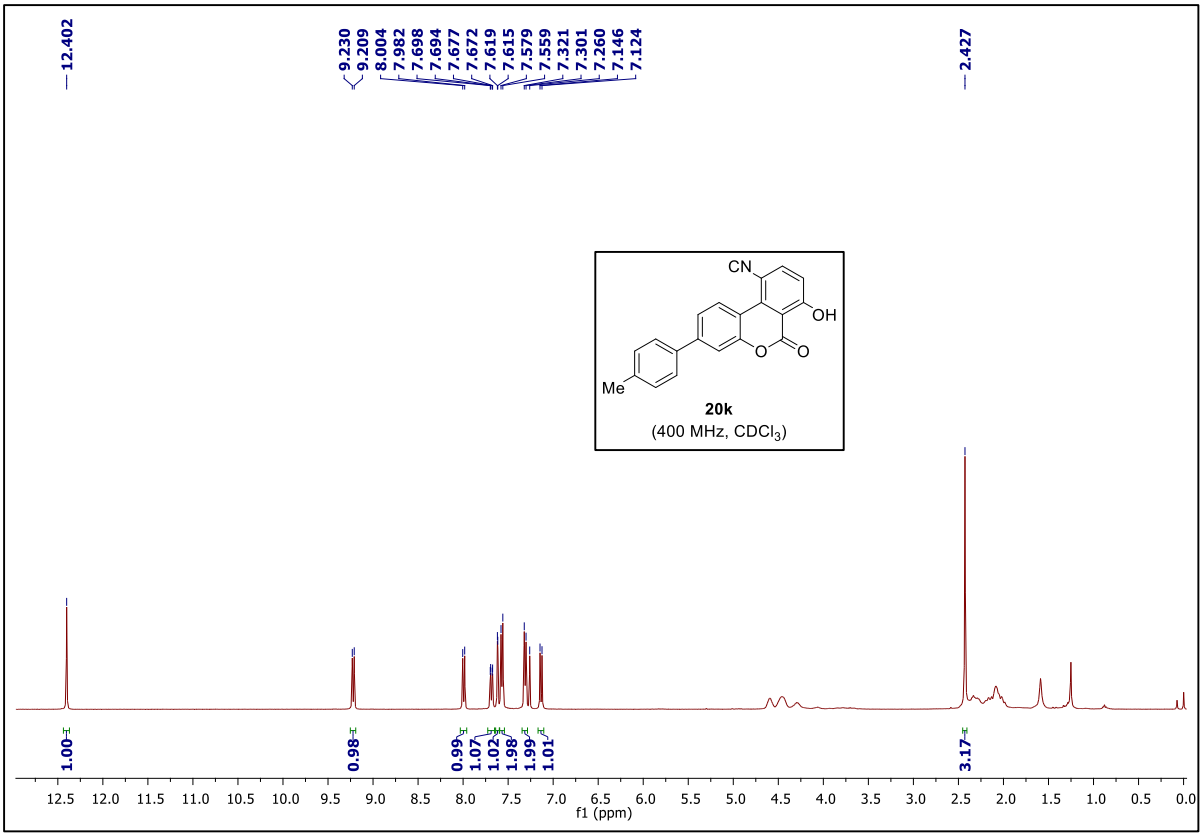
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-6-oxo-3-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile **20j**



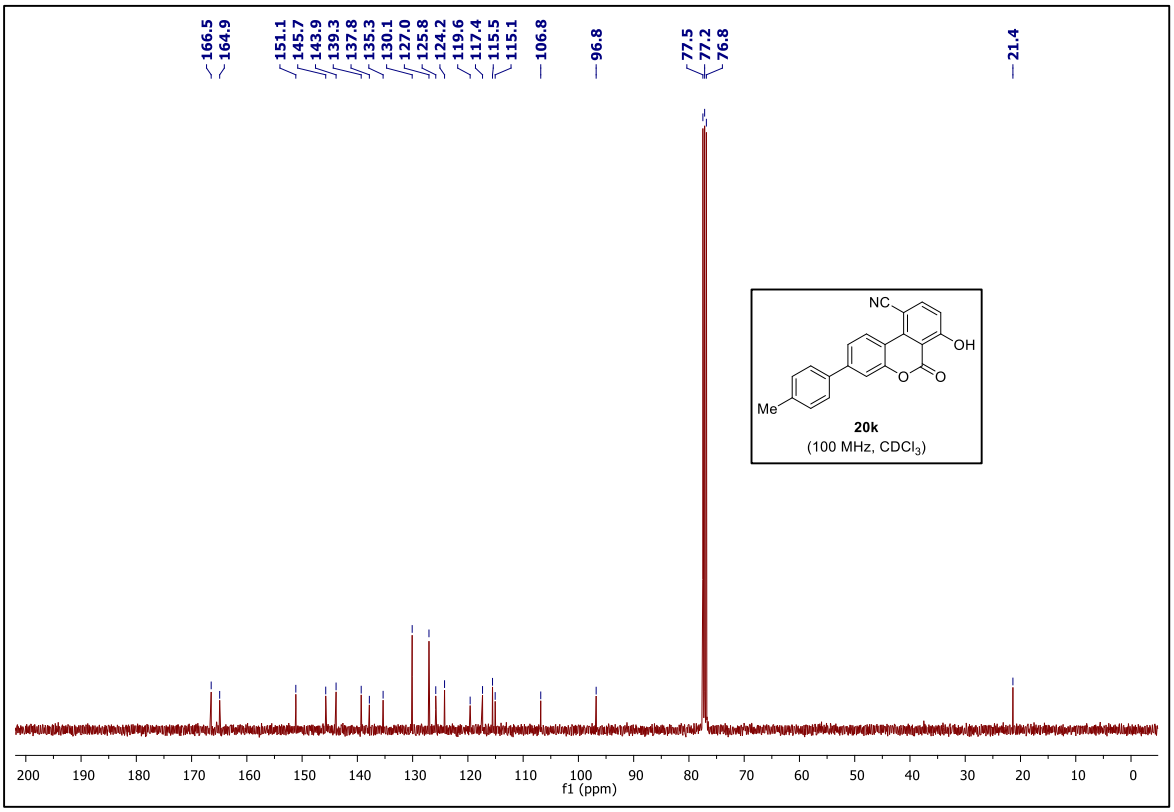
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-6-oxo-3-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile **20j**.



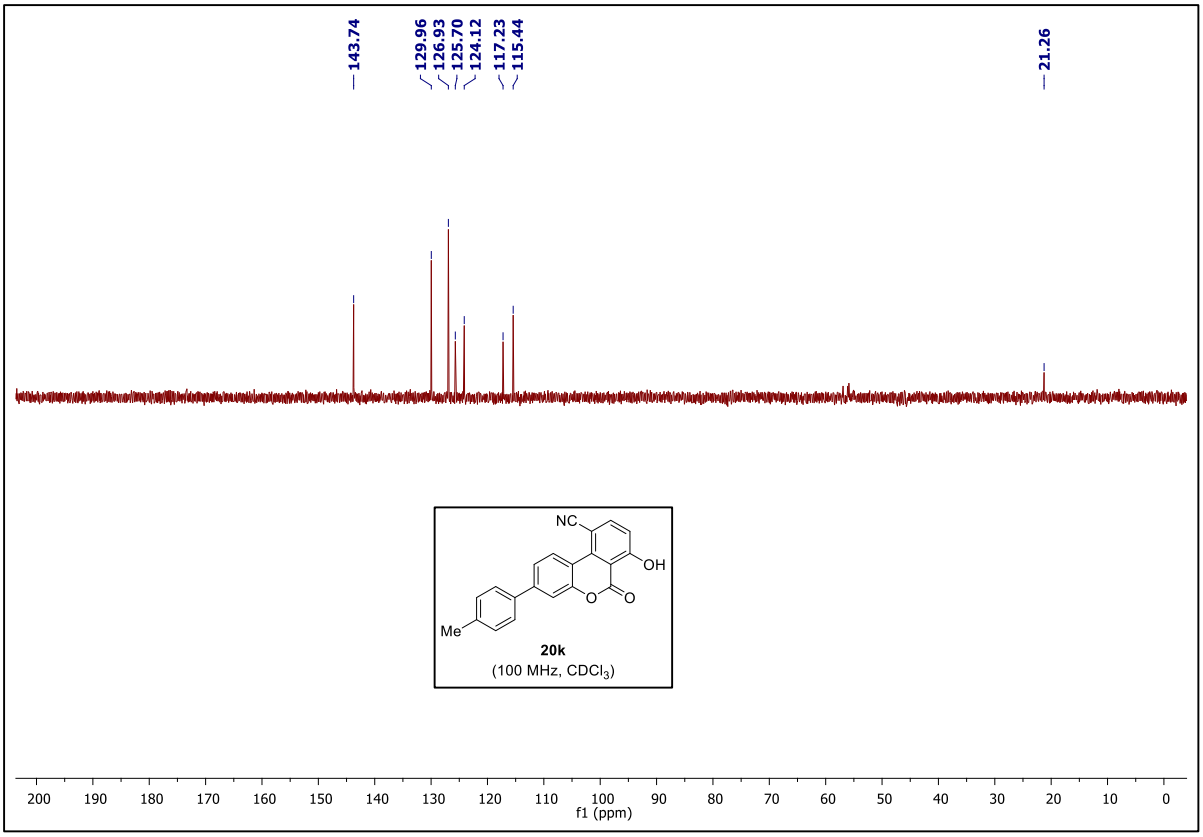
DEPT-135 NMR spectrum of 7-hydroxy-6-oxo-3-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile **20j**.



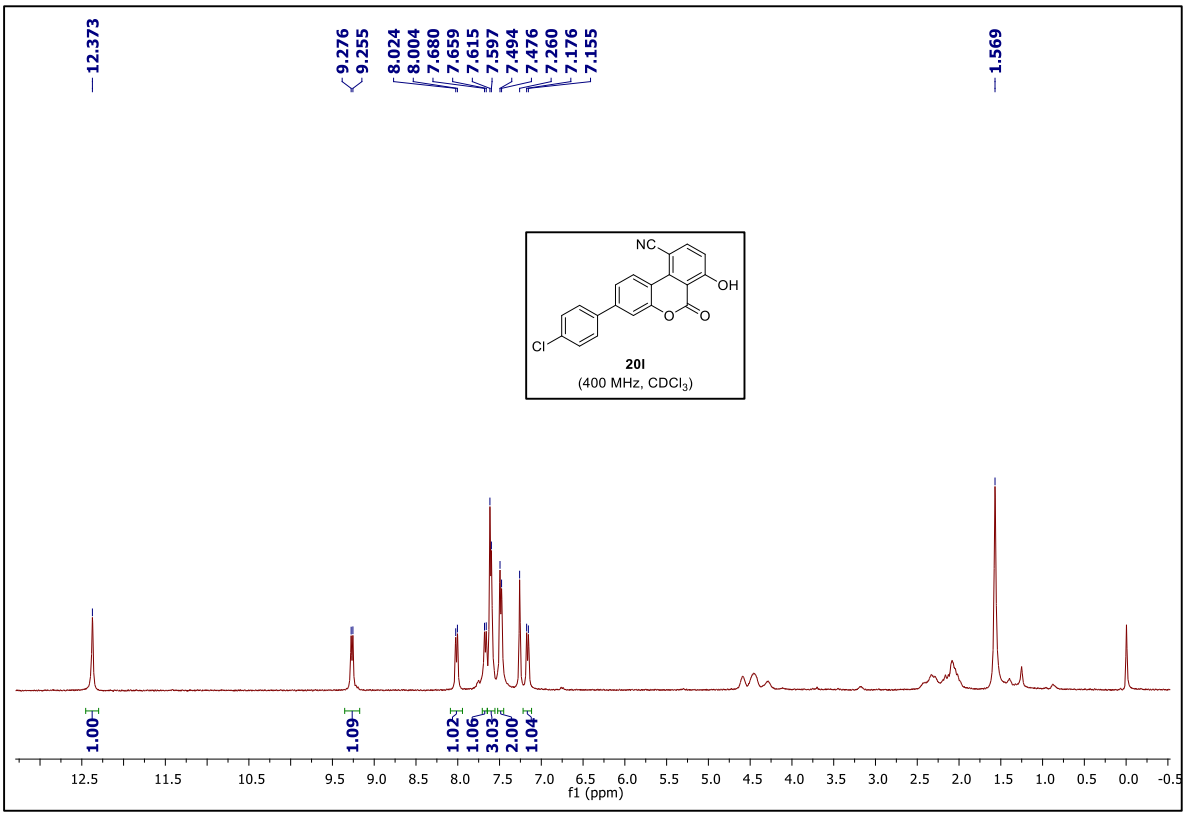
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-6-oxo-3-(p-tolyl)-6*H*-benzo[*c*]chromene-10-carbonitrile **20k**.



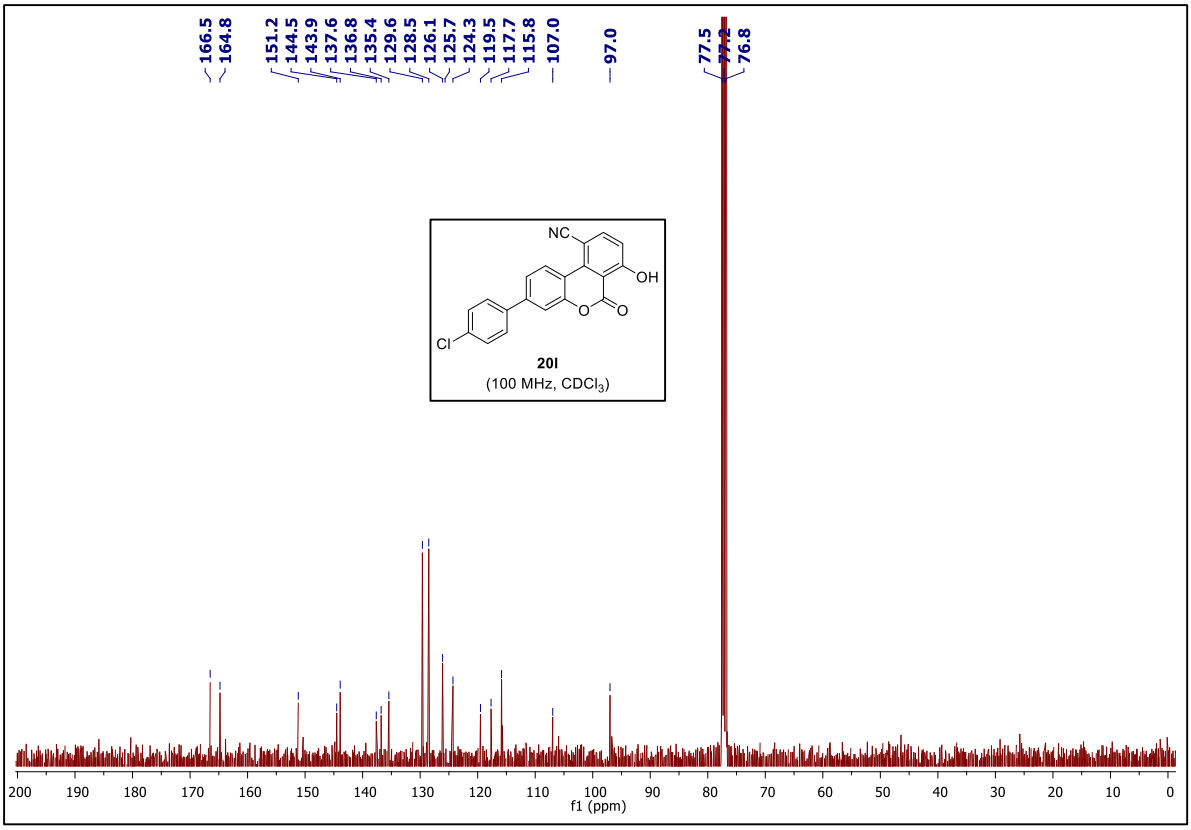
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-6-oxo-3-(p-tolyl)-6*H*-benzo[*c*]chromene-10-carbonitrile **20k**.



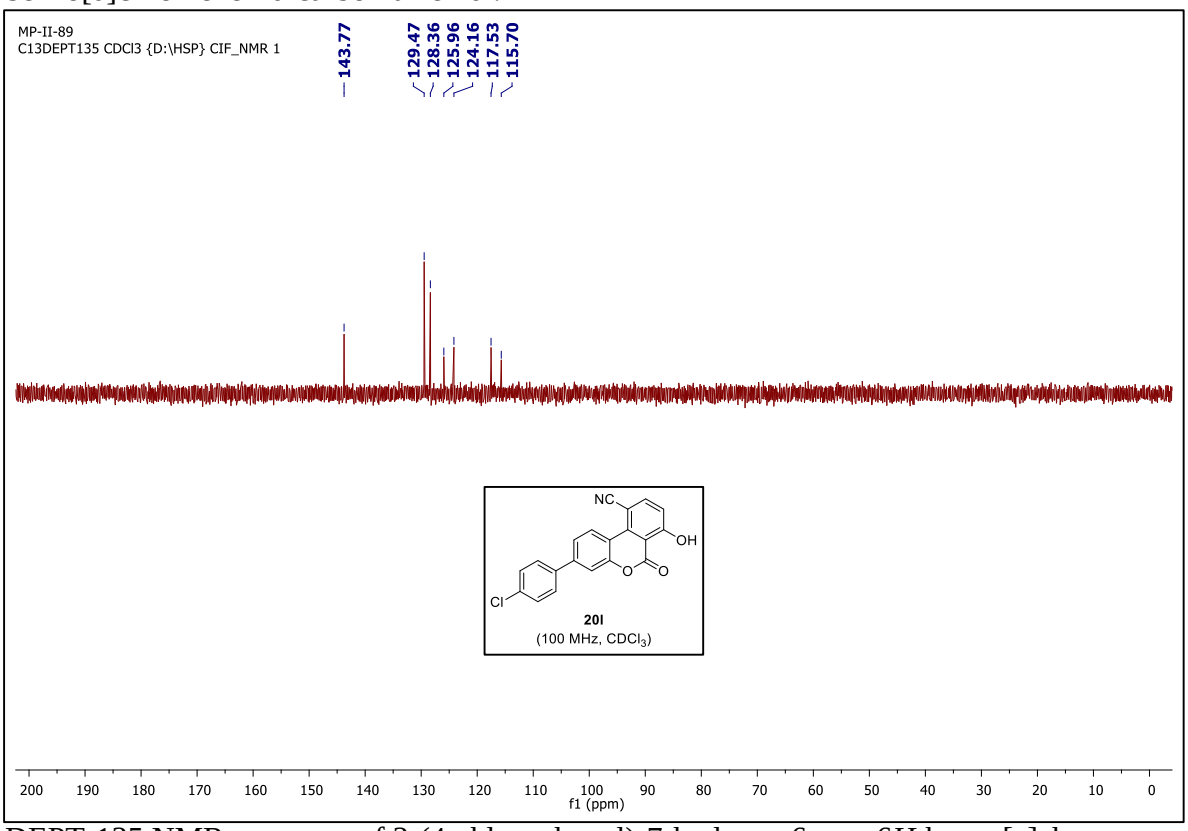
DEPT-135 NMR spectrum of 7-hydroxy-6-oxo-3-(p-tolyl)-6*H*-benzo[*c*]chromene-10-carbonitrile **20k**.



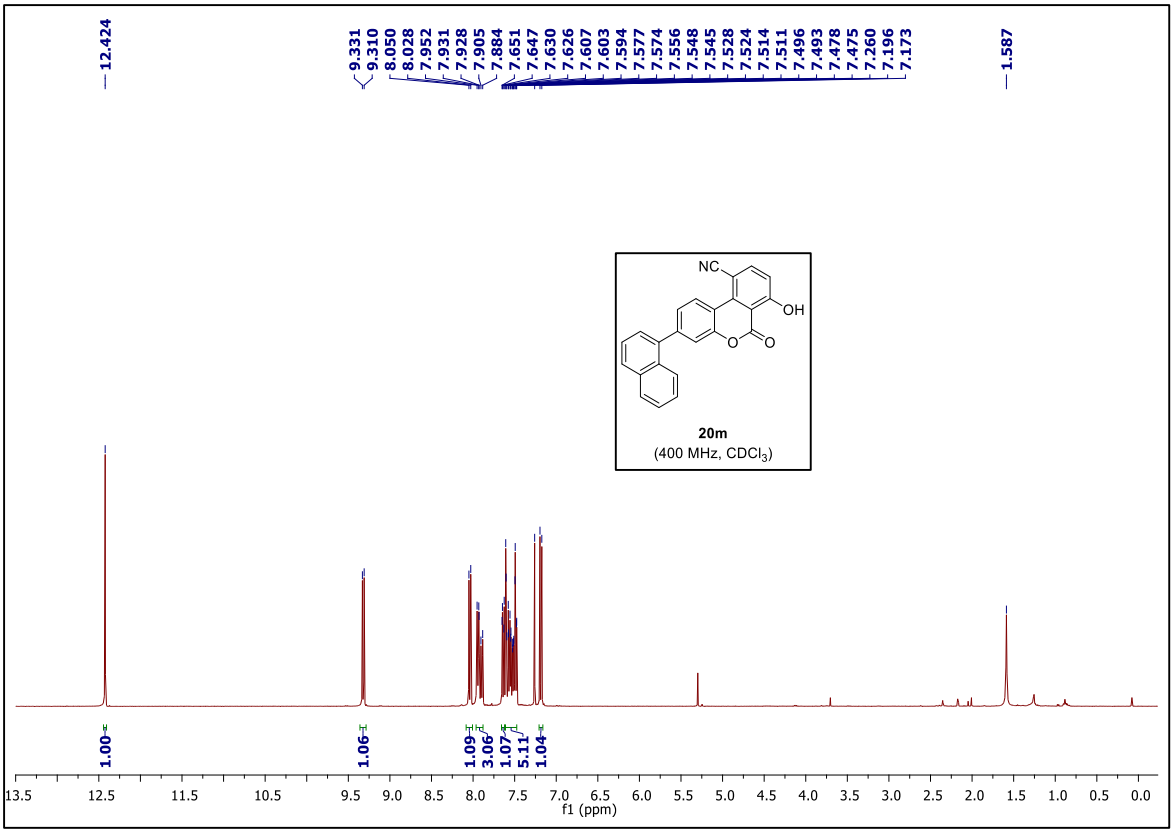
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(4-chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20l**.



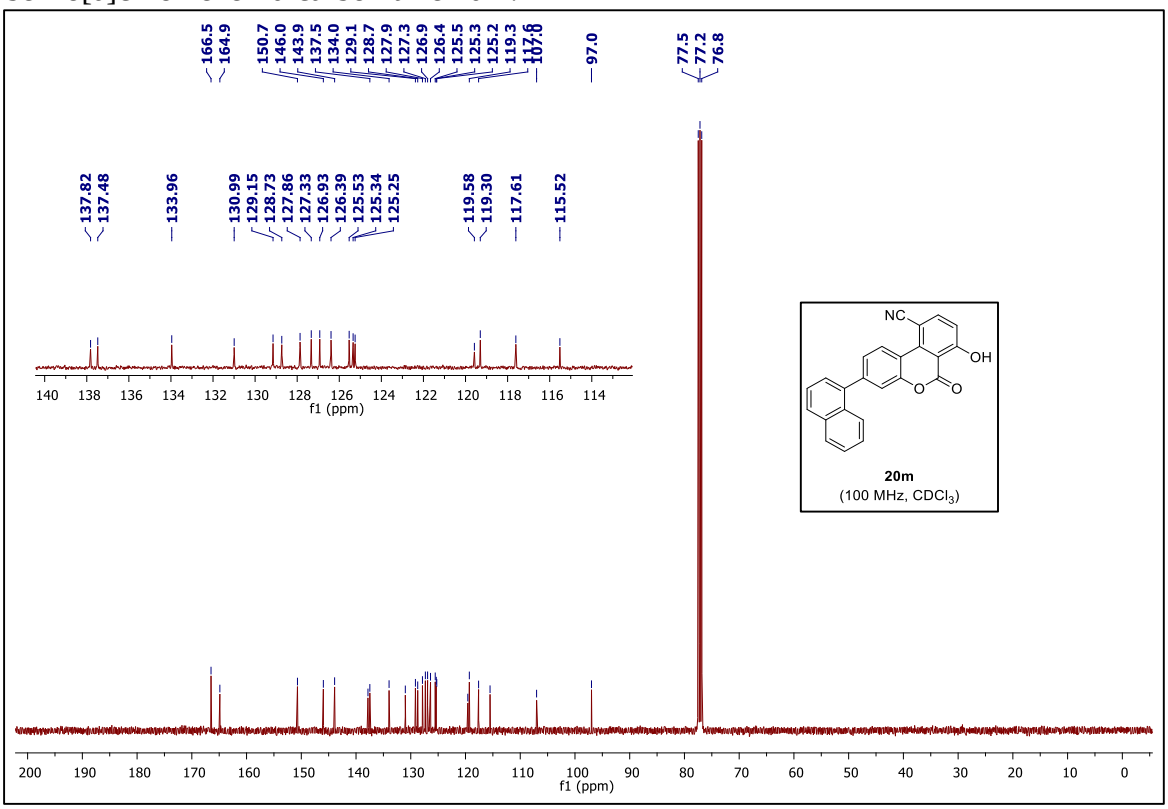
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(4-chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20l**.



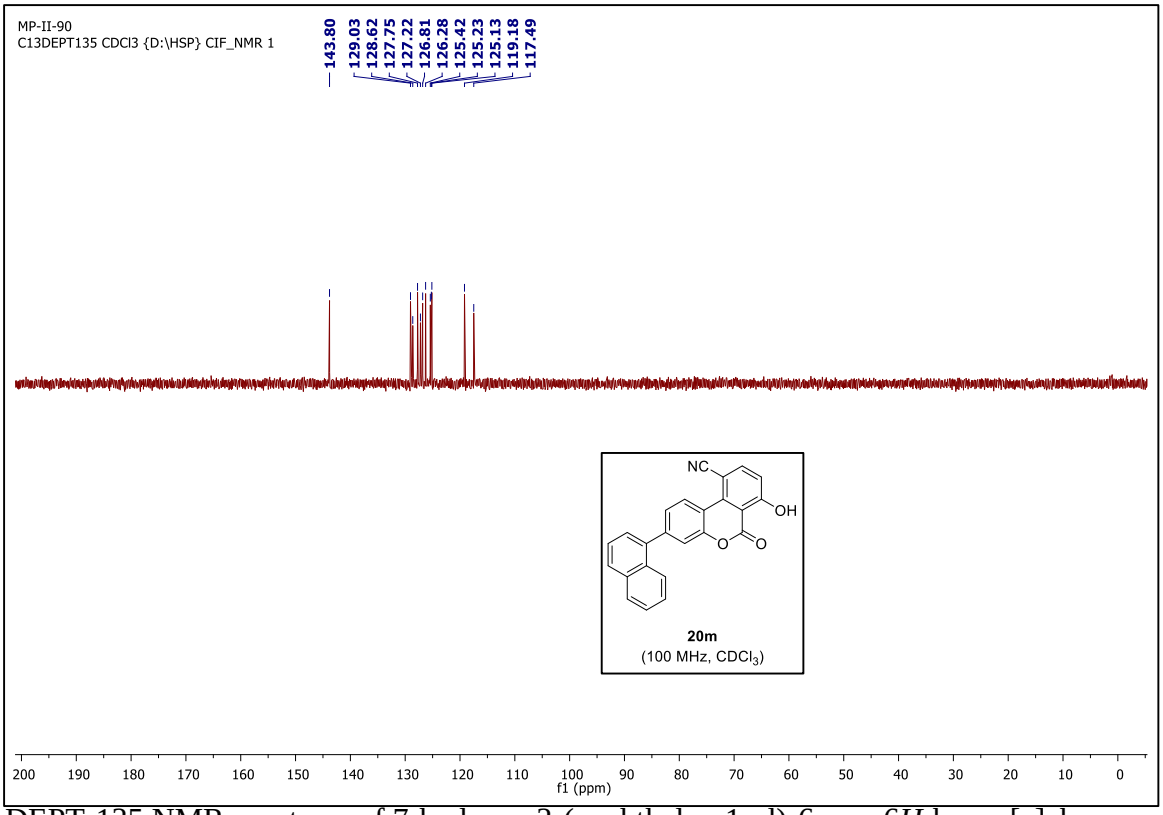
DEPT-135 NMR spectrum of 3-(4-chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20l**.



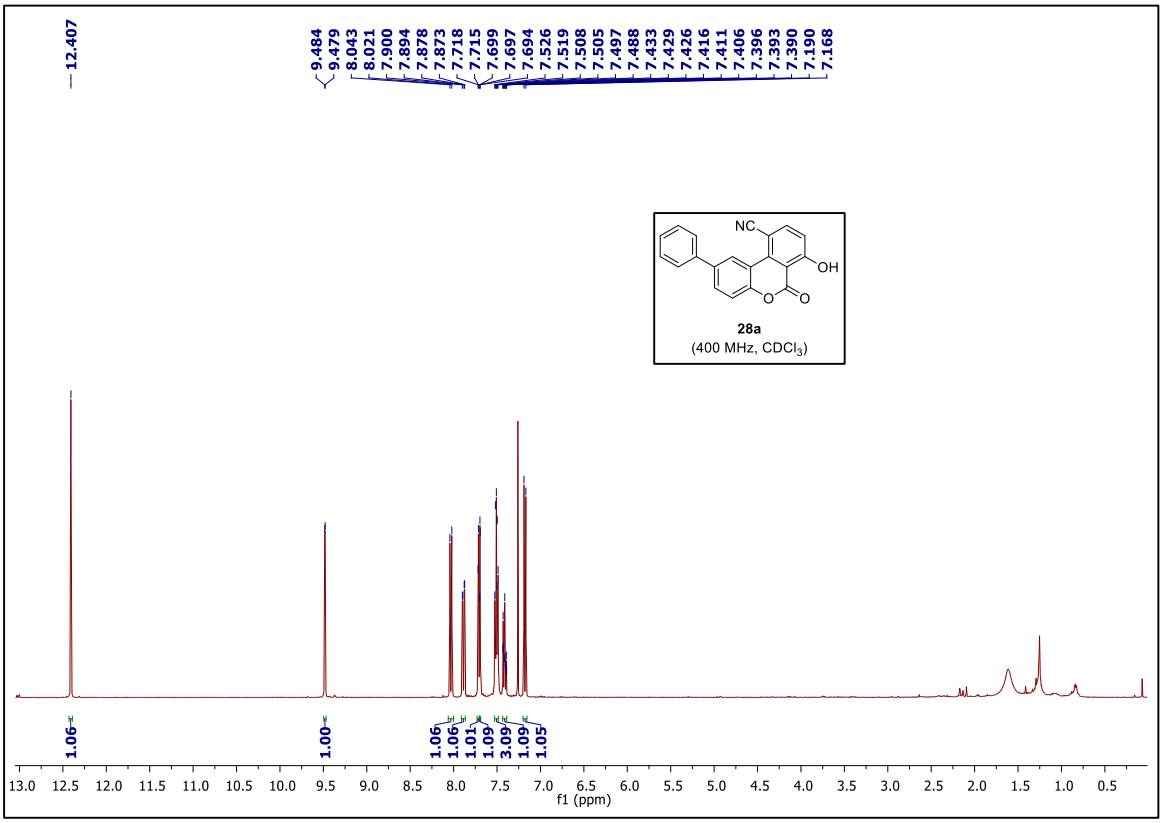
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-3-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20m**.



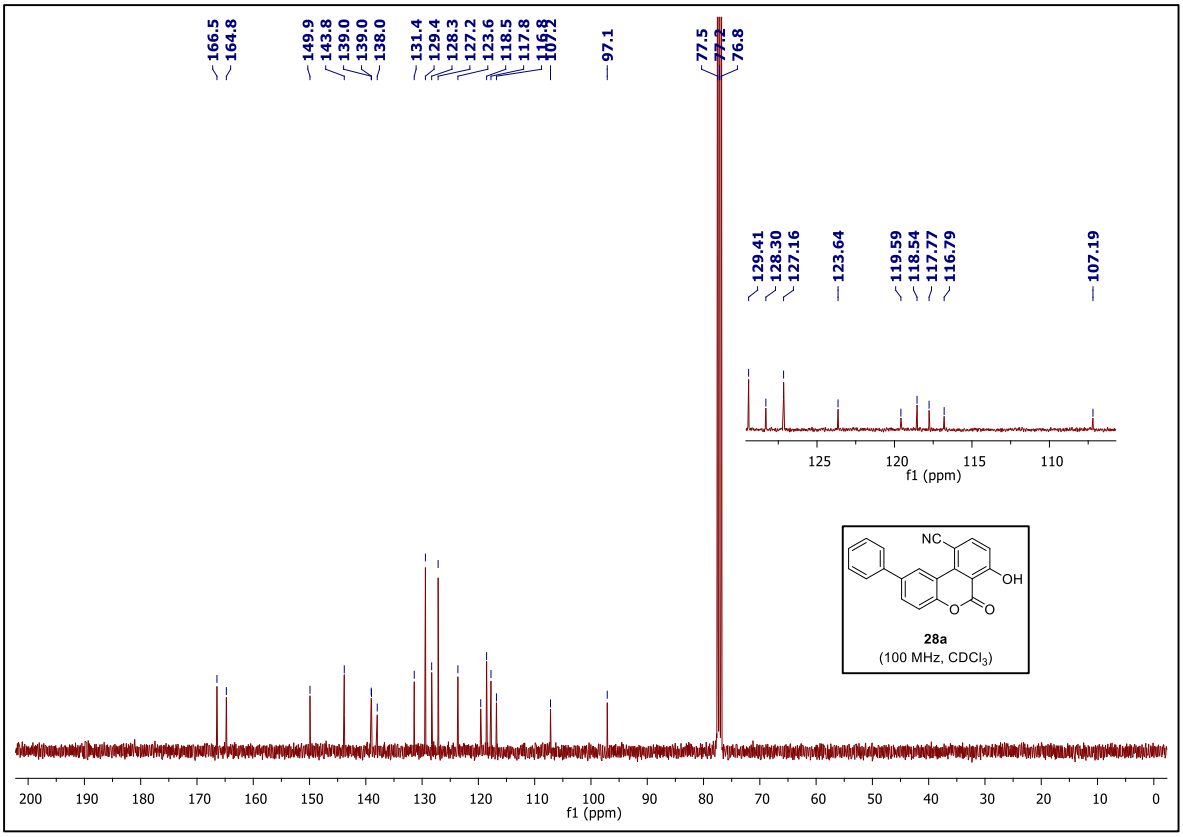
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-3-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20m**



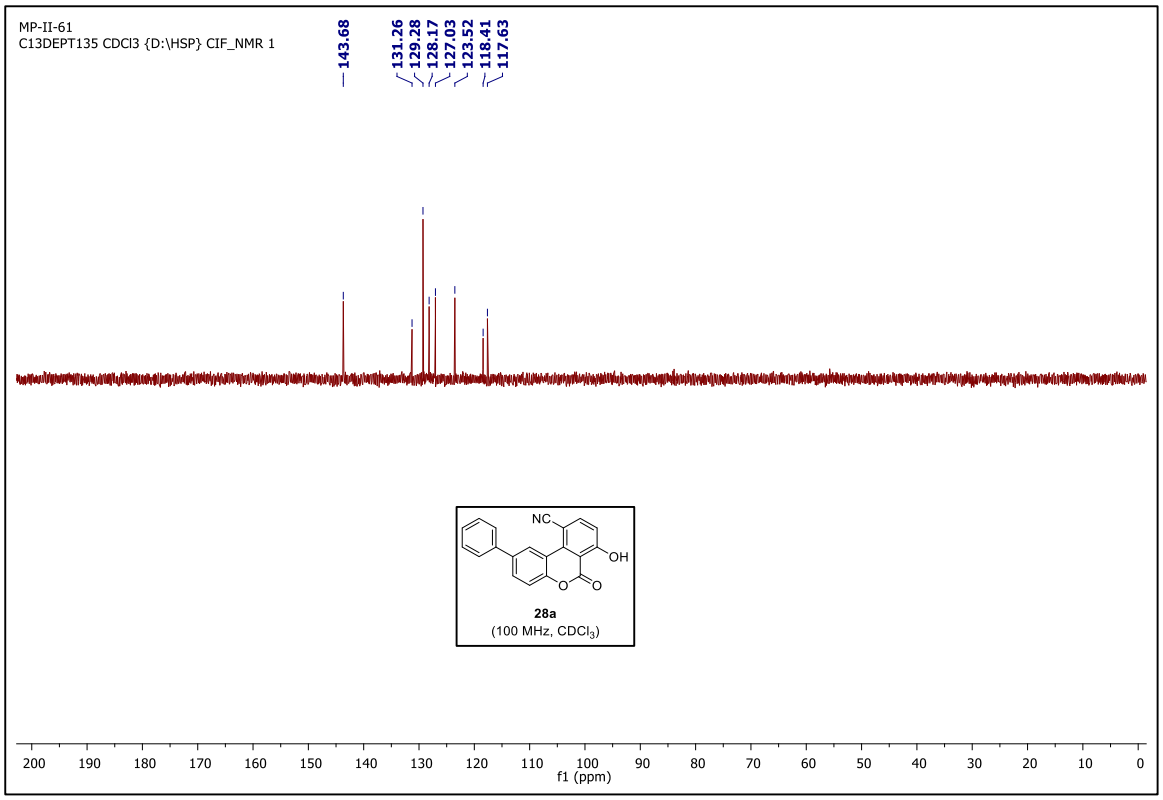
DEPT-135 NMR spectrum of 7-hydroxy-3-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **20m**.



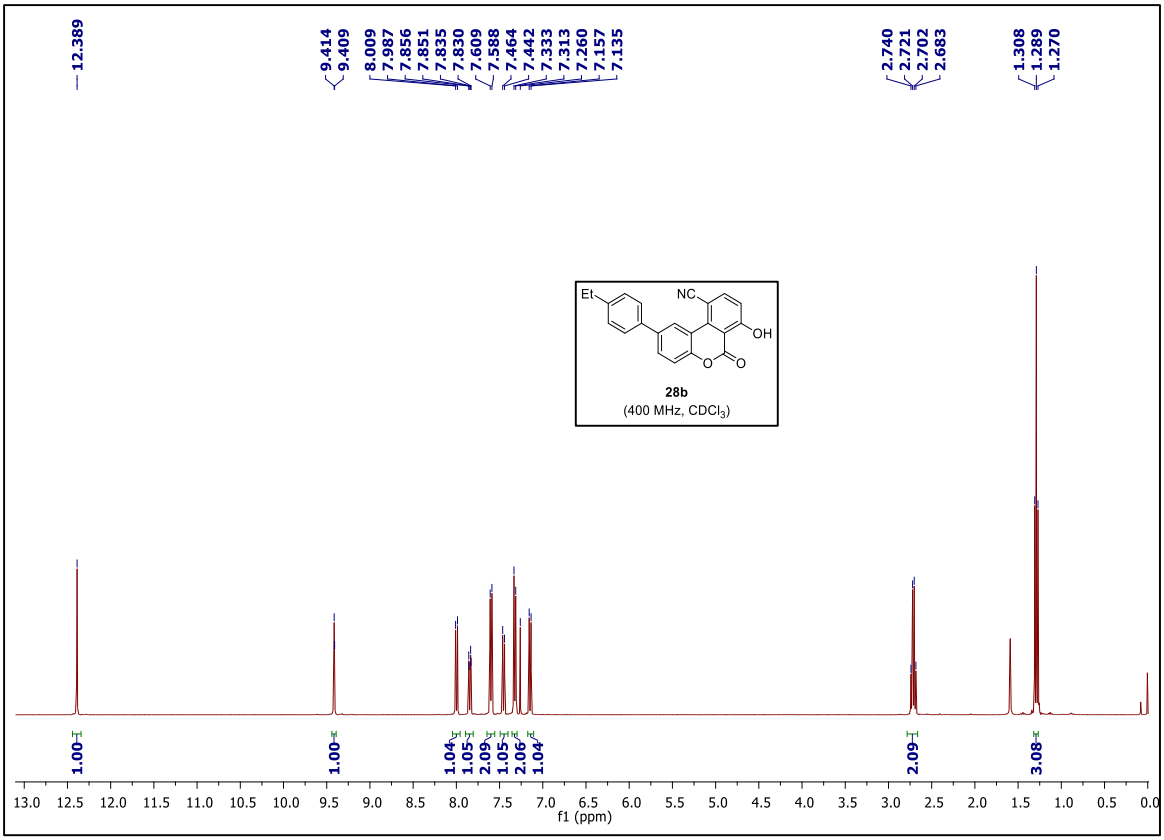
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-6-oxo-2-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile **28a**



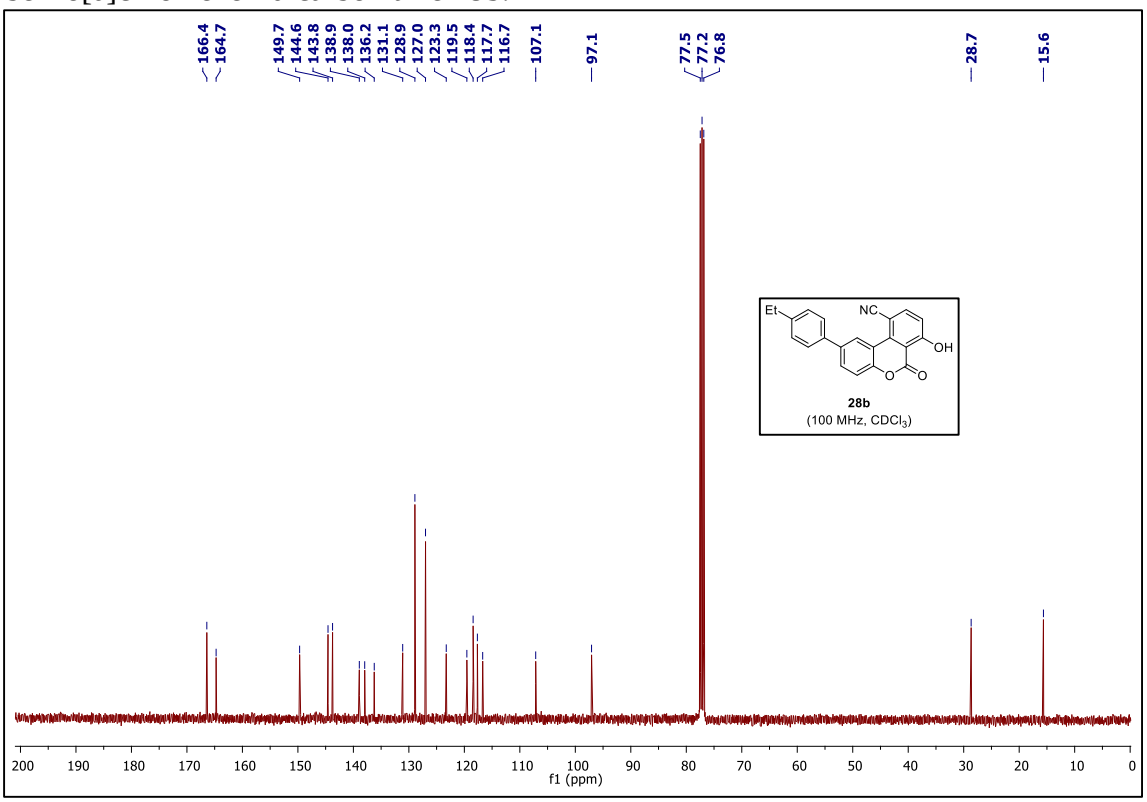
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-6-oxo-2-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile **28a**.



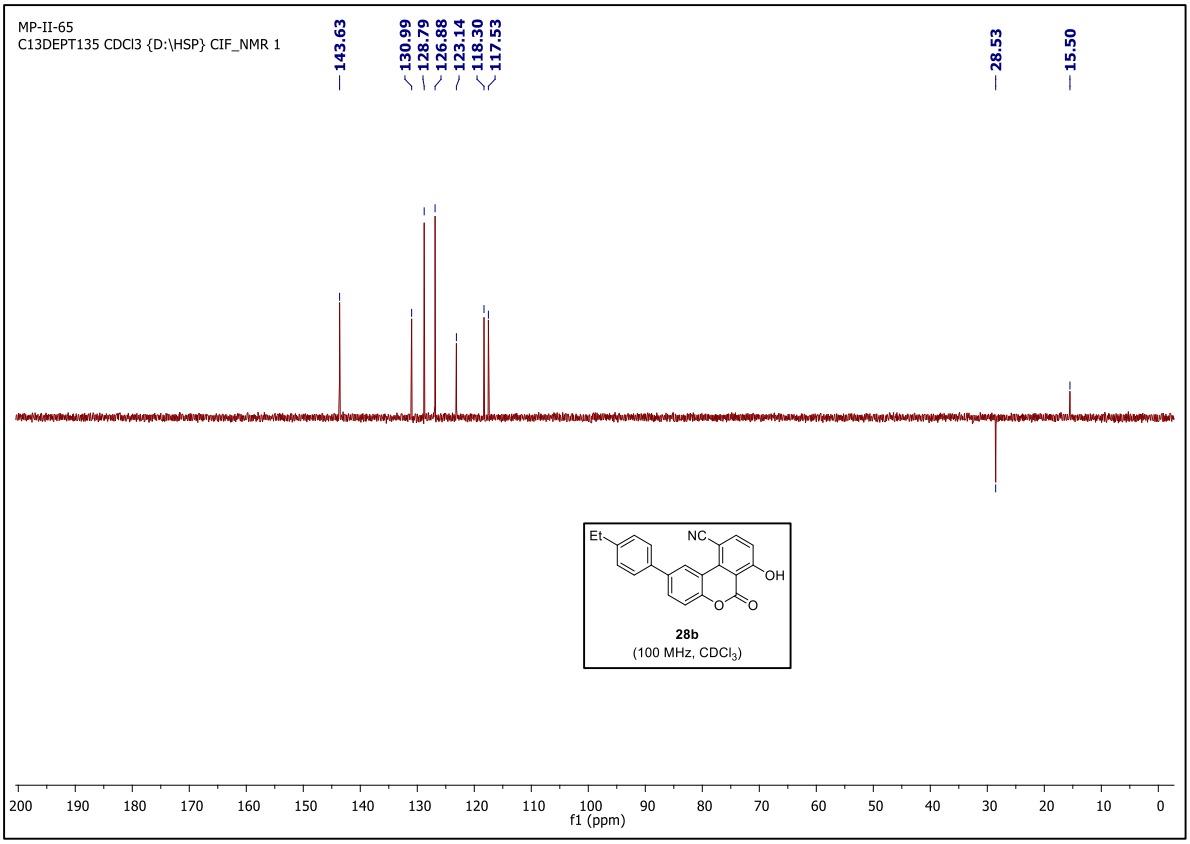
DEPT-135 NMR spectrum of 7-hydroxy-6-oxo-2-phenyl-6*H*-benzo[*c*]chromene-10-carbonitrile **28a**.



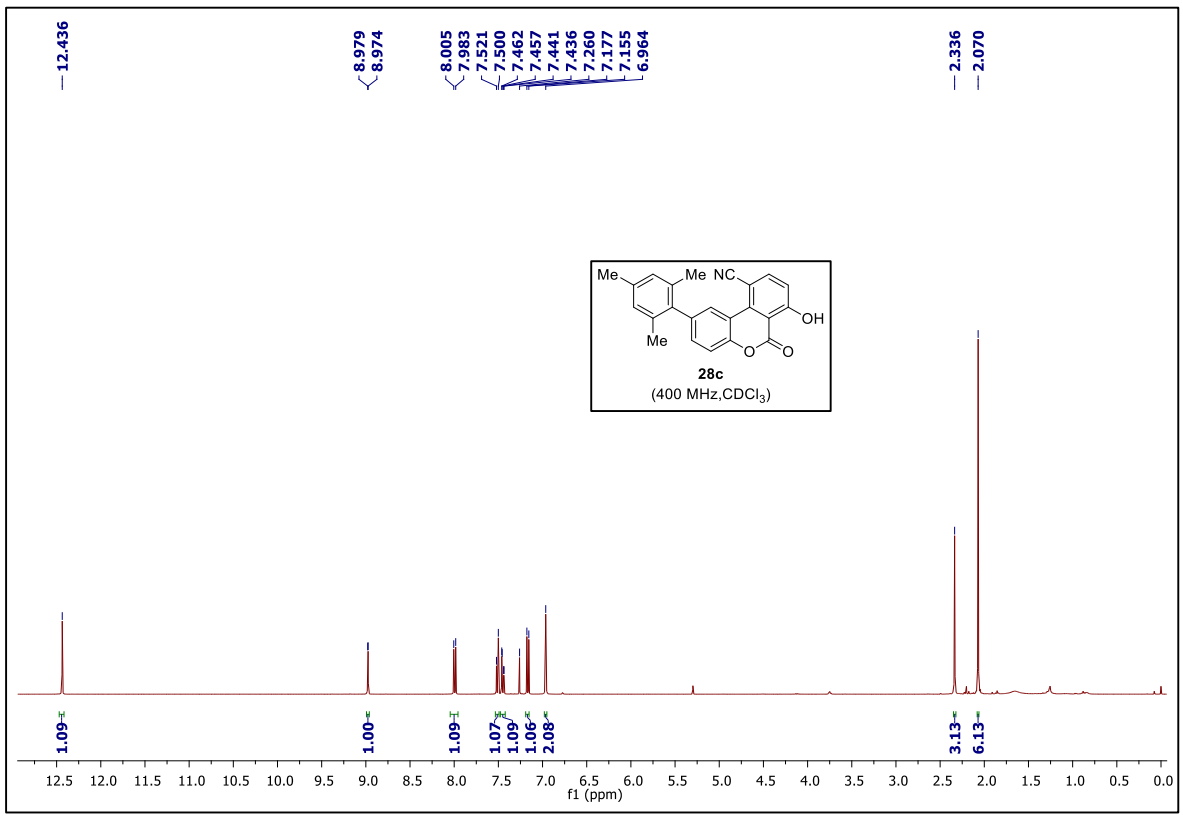
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-ethylphenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28b**.



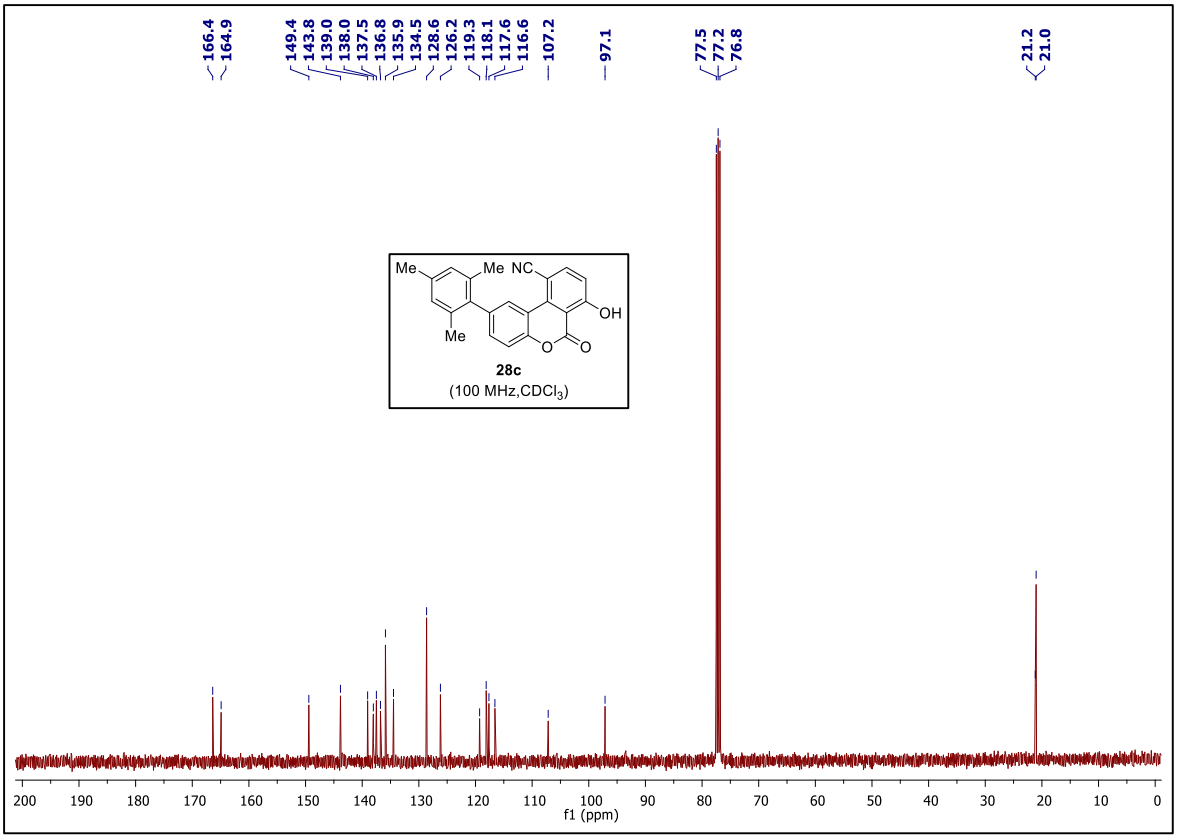
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-ethylphenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28b**.



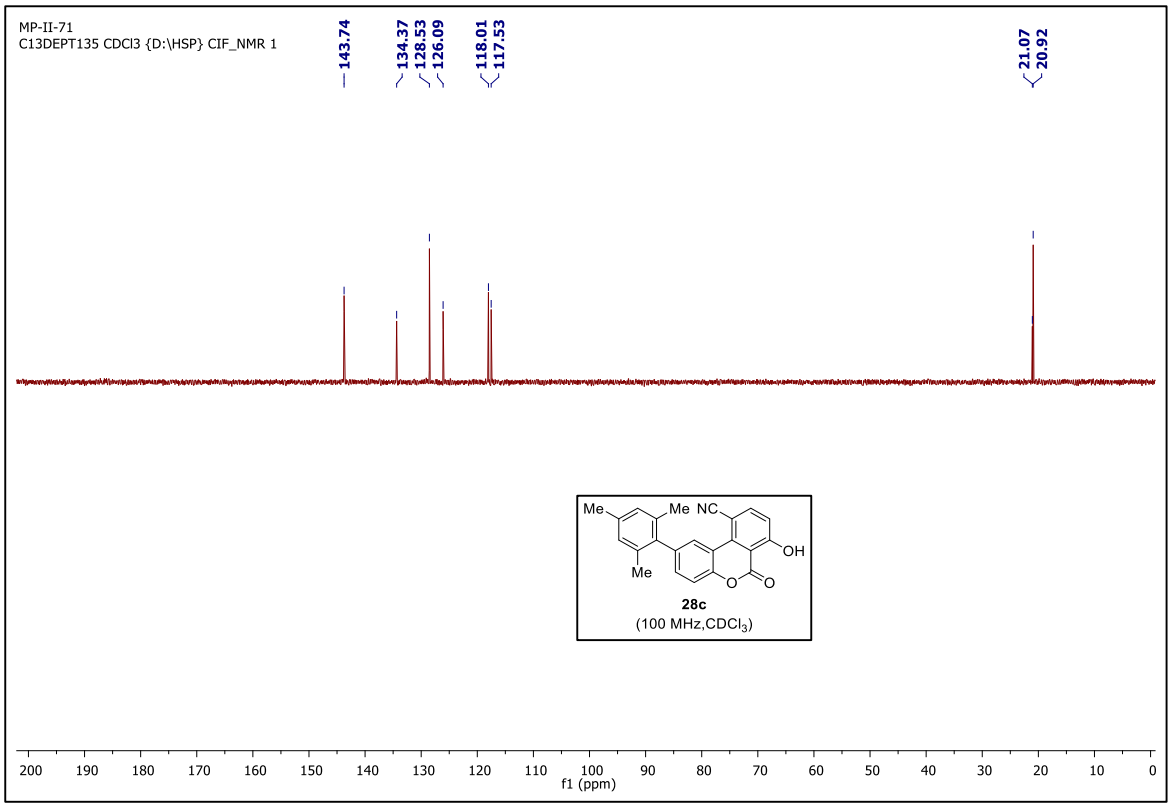
DEPT-135 NMR spectrum of 2-(4-ethylphenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28b**.



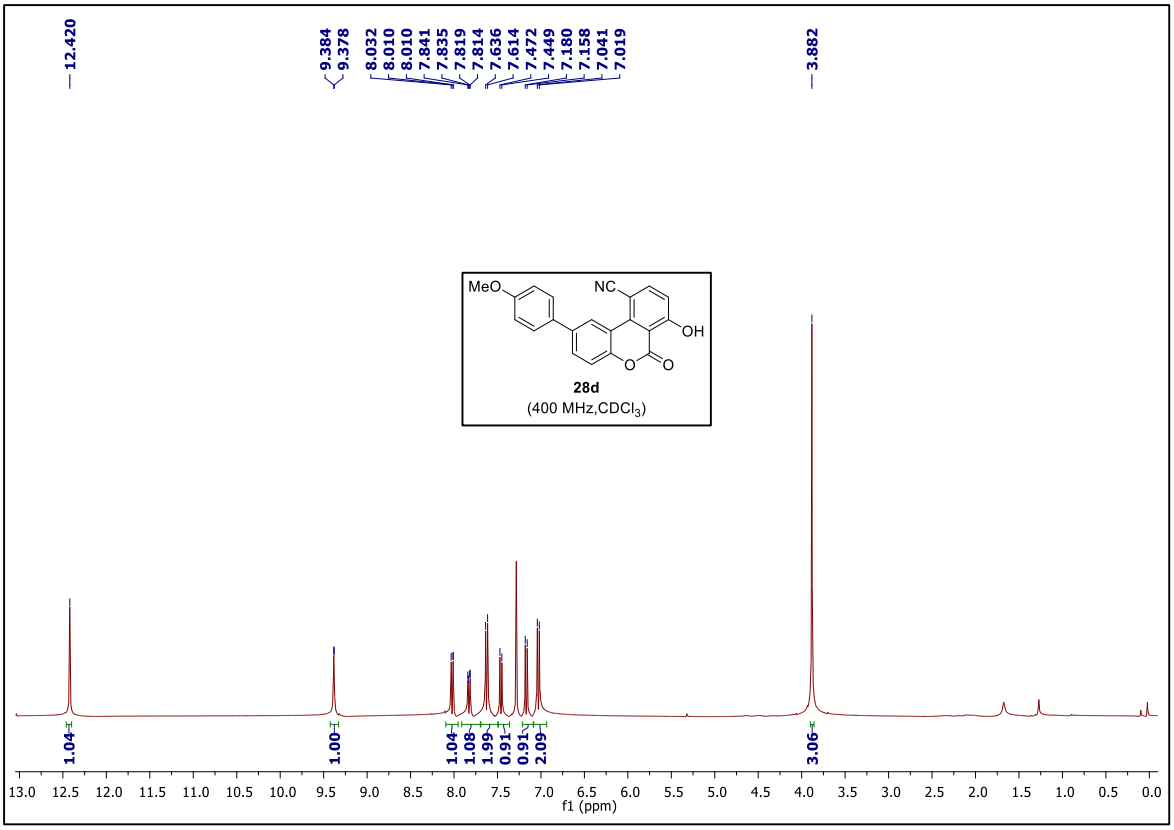
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-mesityl-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28c**.



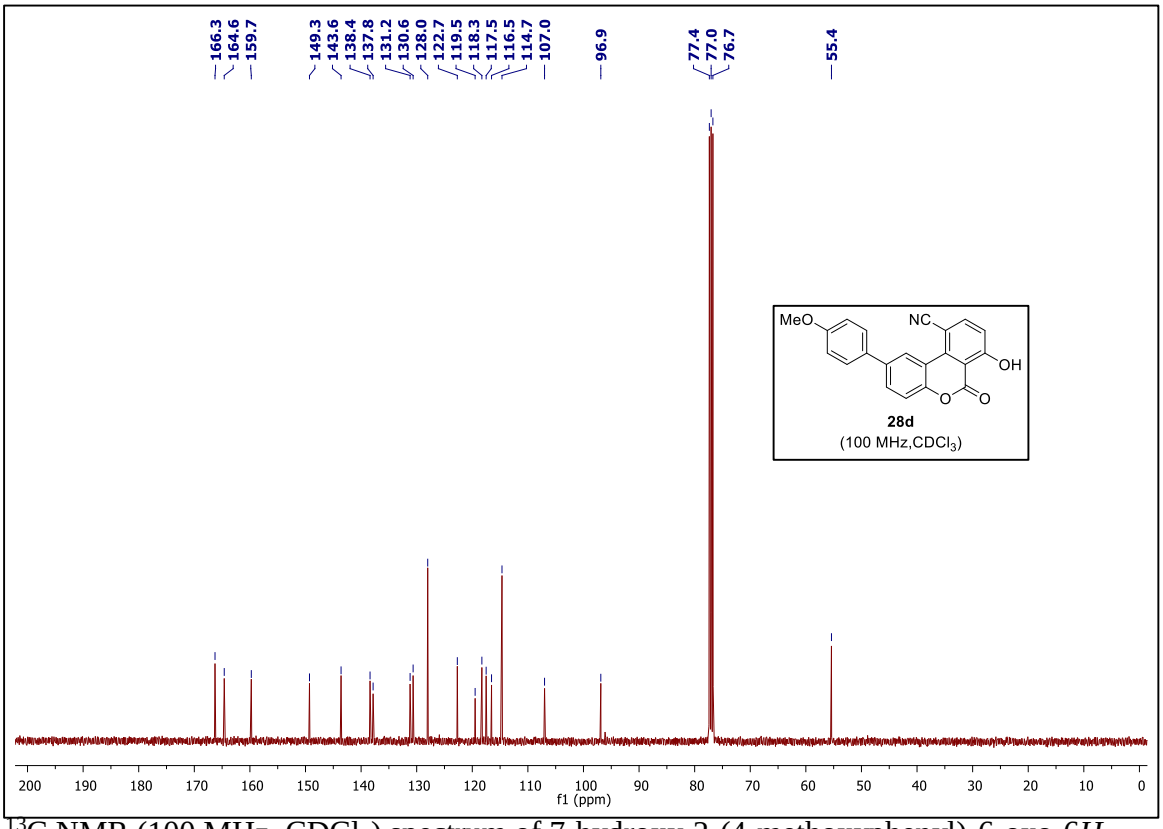
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-mesityl-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28c**.



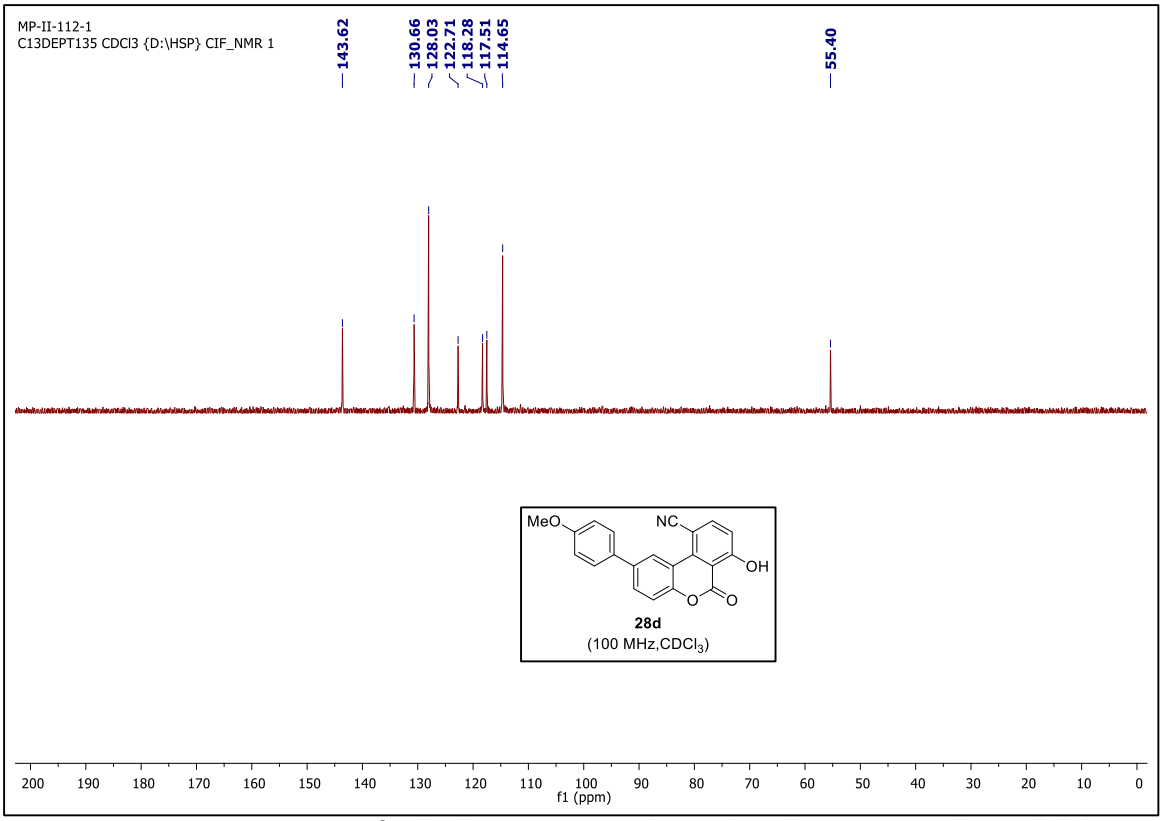
DEPT-135 NMR spectrum of 7-hydroxy-2-mesityl-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28c**.



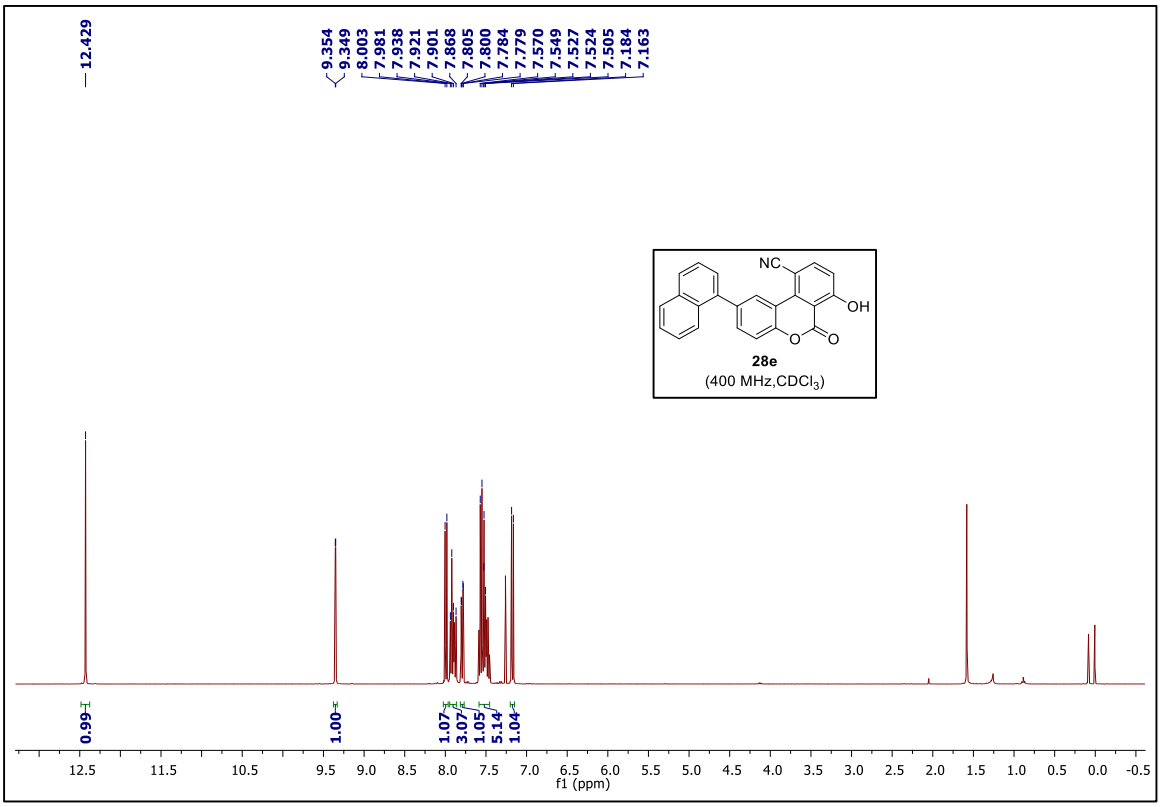
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-(4-methoxyphenyl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28d**.



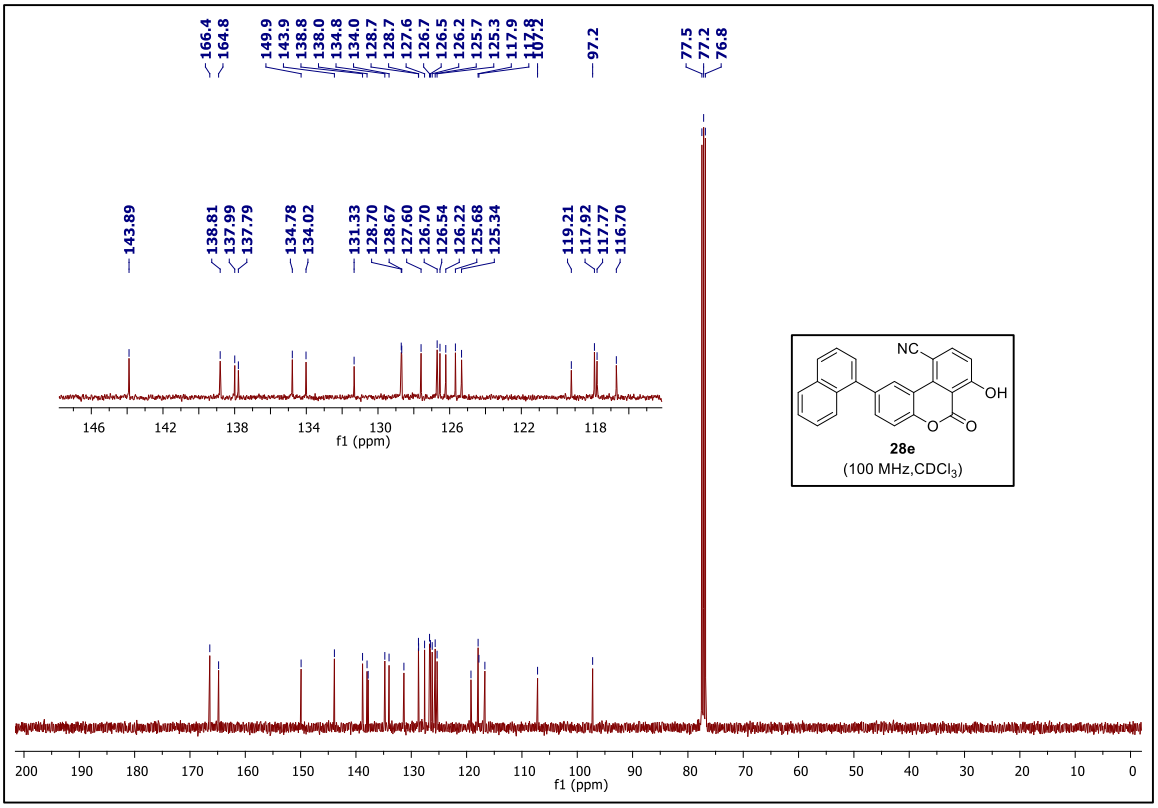
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-(4-methoxyphenyl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28d**.



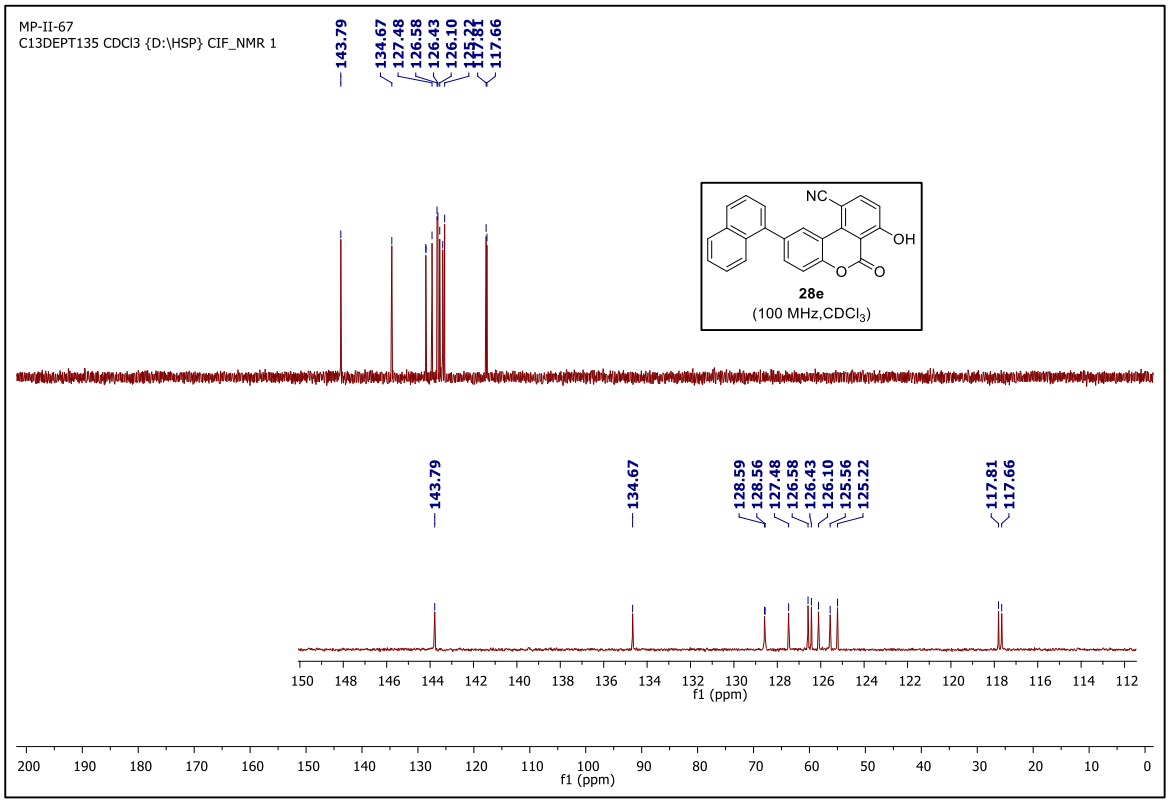
DEPT-135 NMR spectrum of 7-hydroxy-2-(4-methoxyphenyl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28d**.



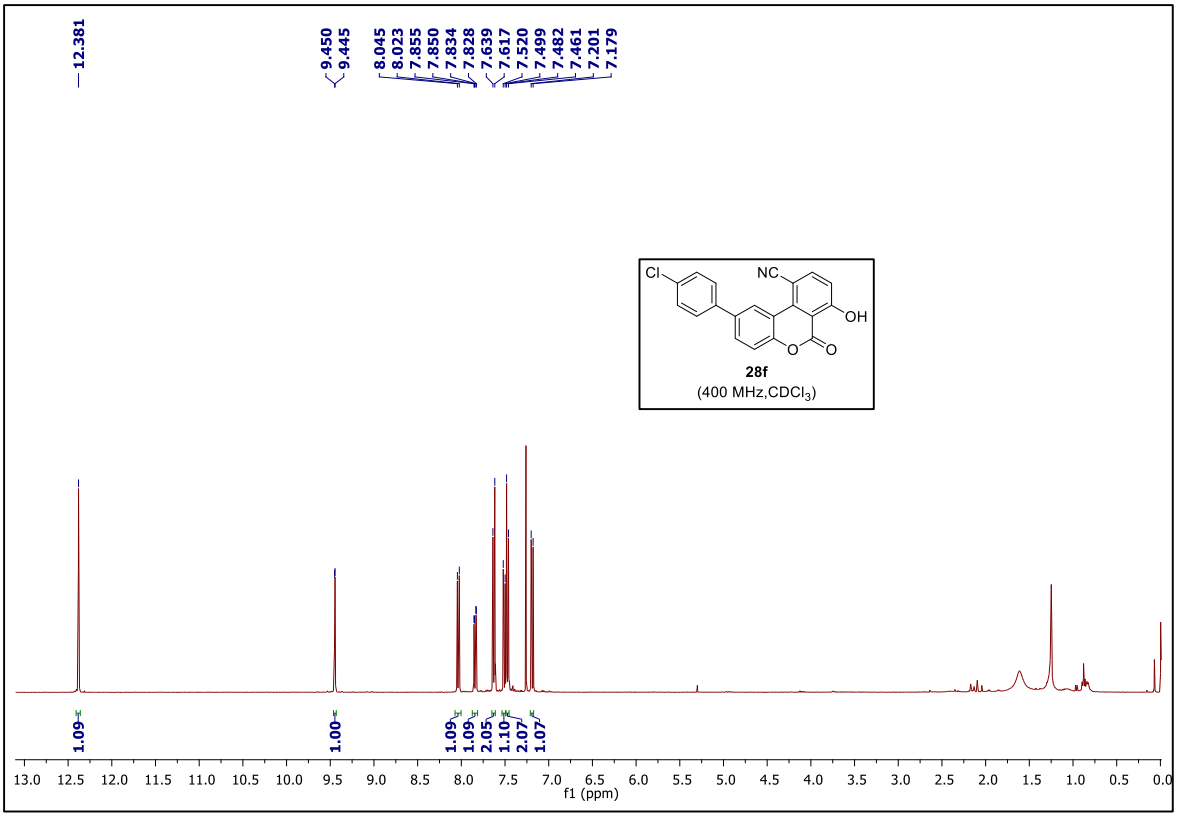
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28e**.



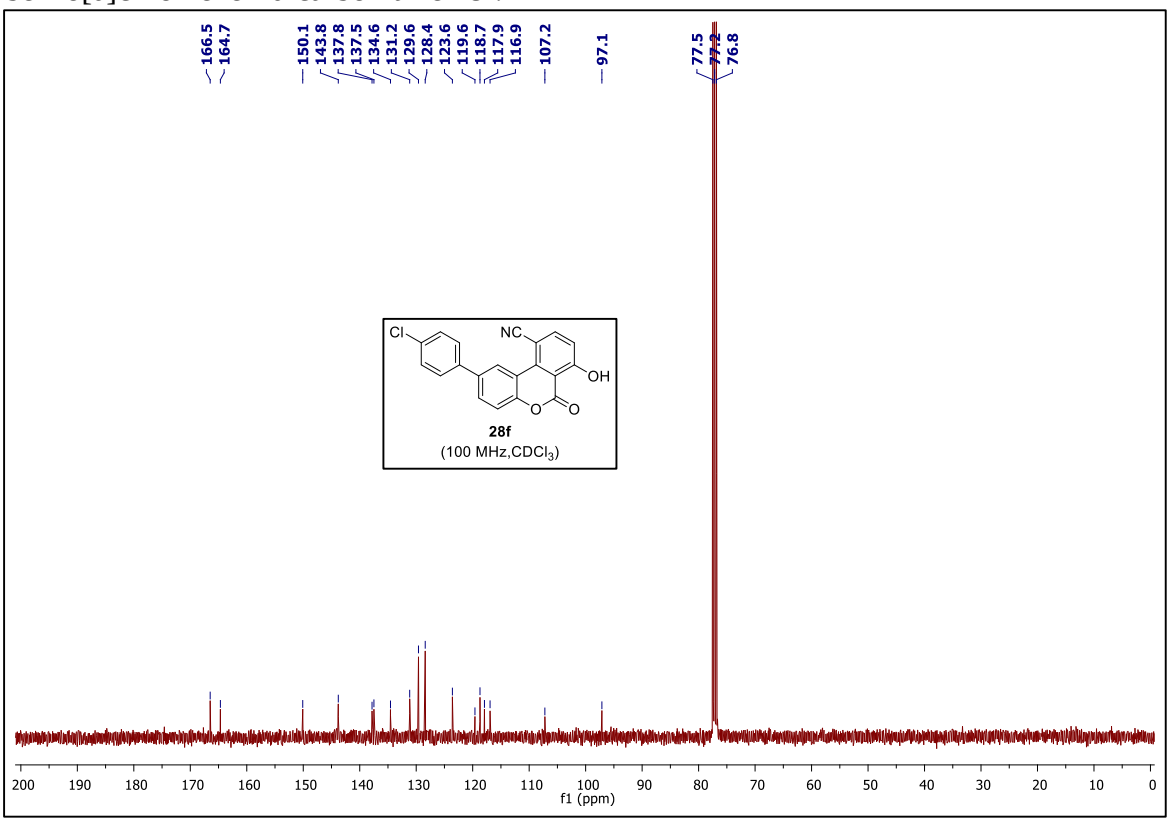
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-2-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28e**.



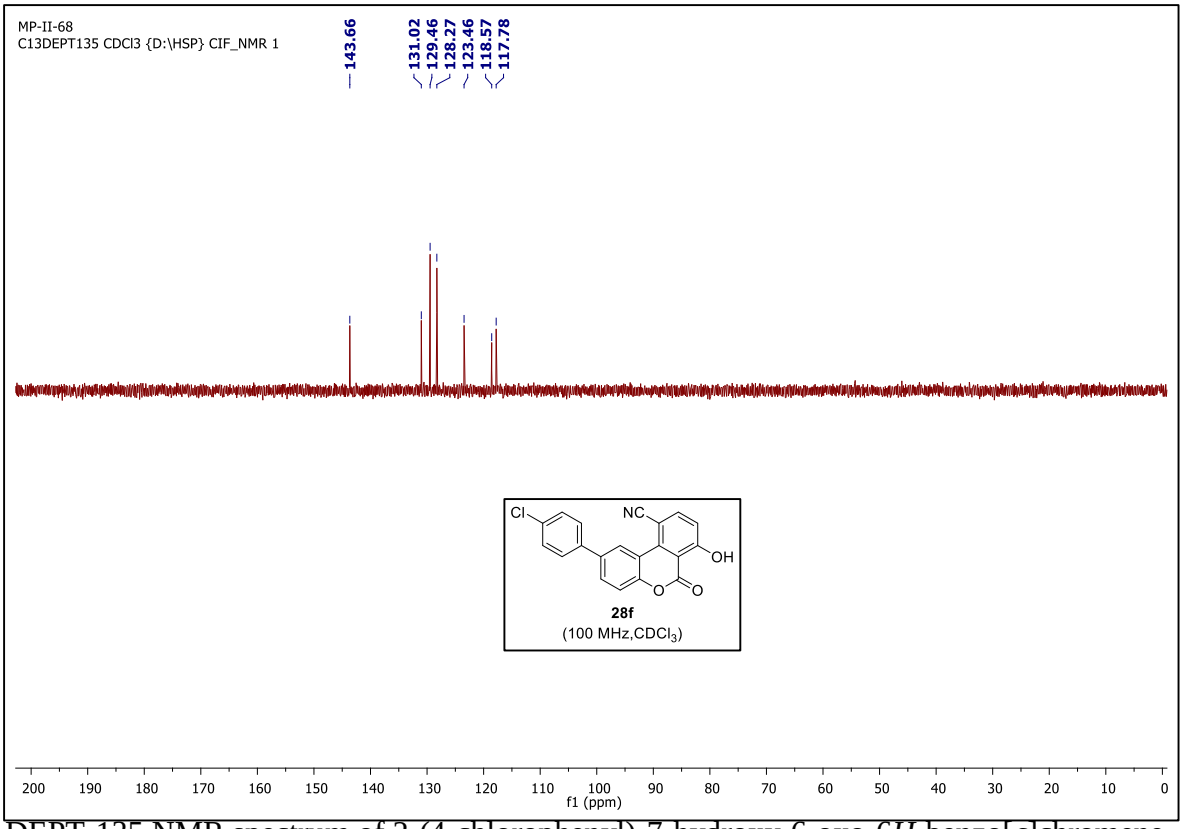
DEPT-135 NMR spectrum of 7-hydroxy-2-(naphthalen-1-yl)-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28e**



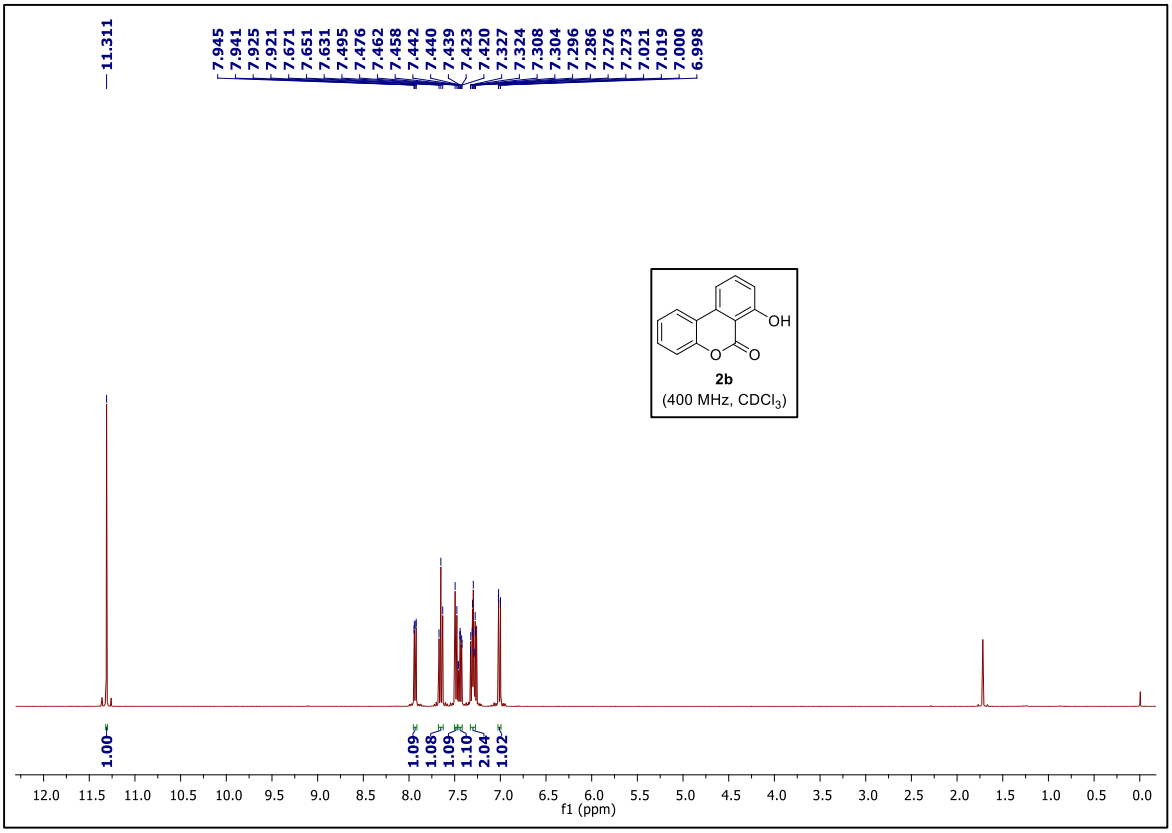
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28f**.



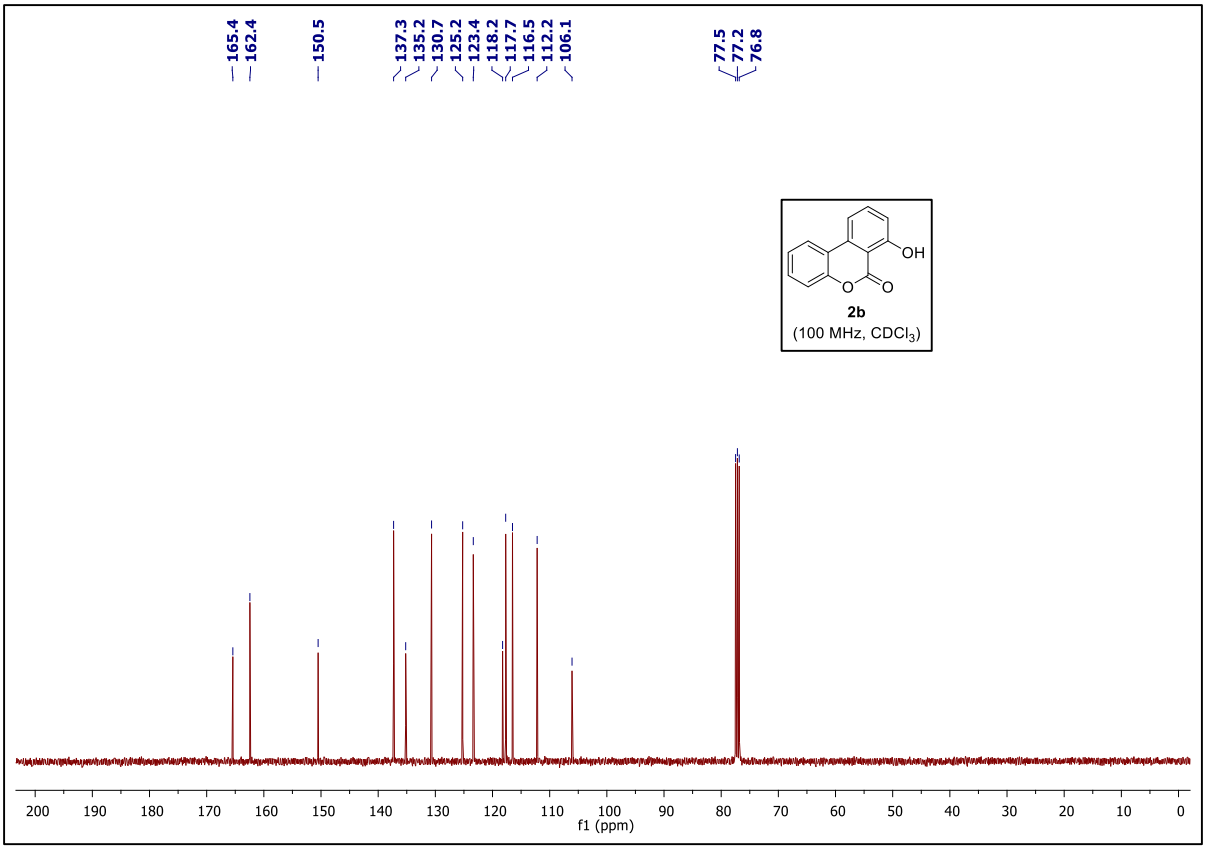
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28f**



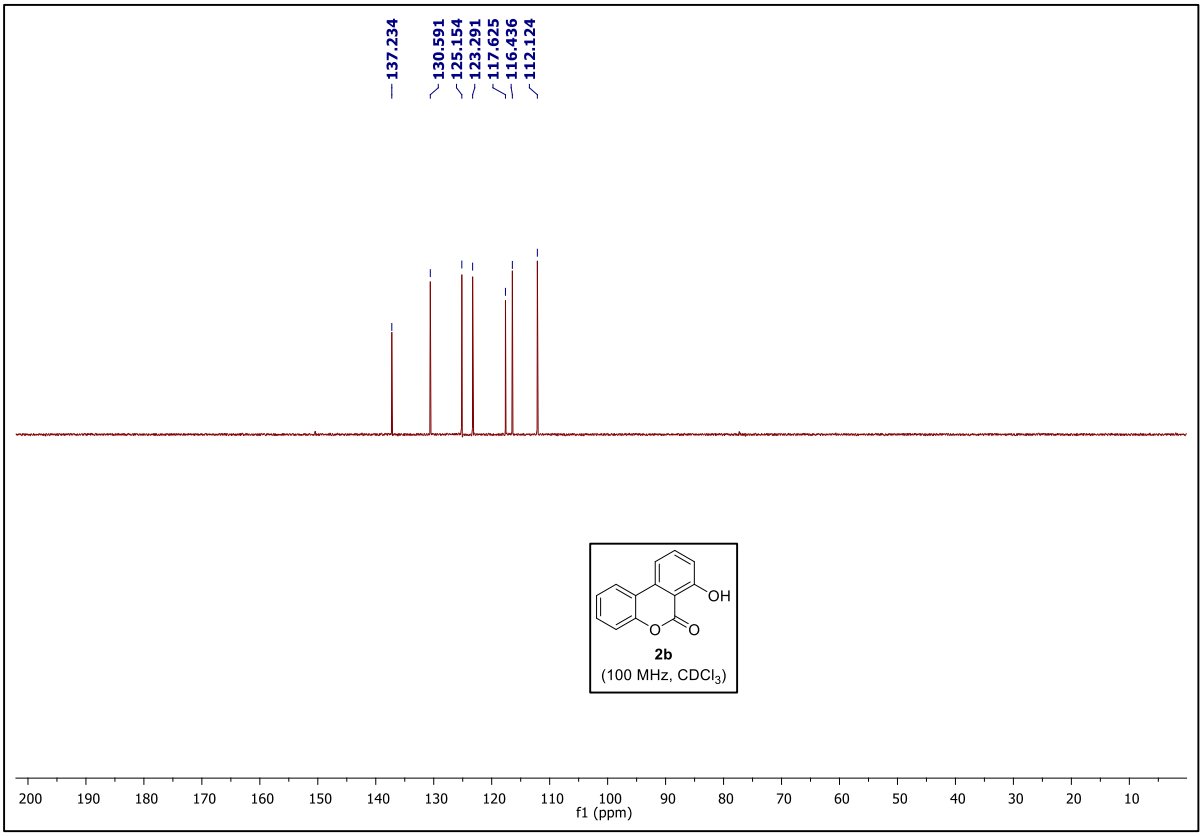
DEPT-135 NMR spectrum of 2-(4-chlorophenyl)-7-hydroxy-6-oxo-6*H*-benzo[*c*]chromene-10-carbonitrile **28f**.



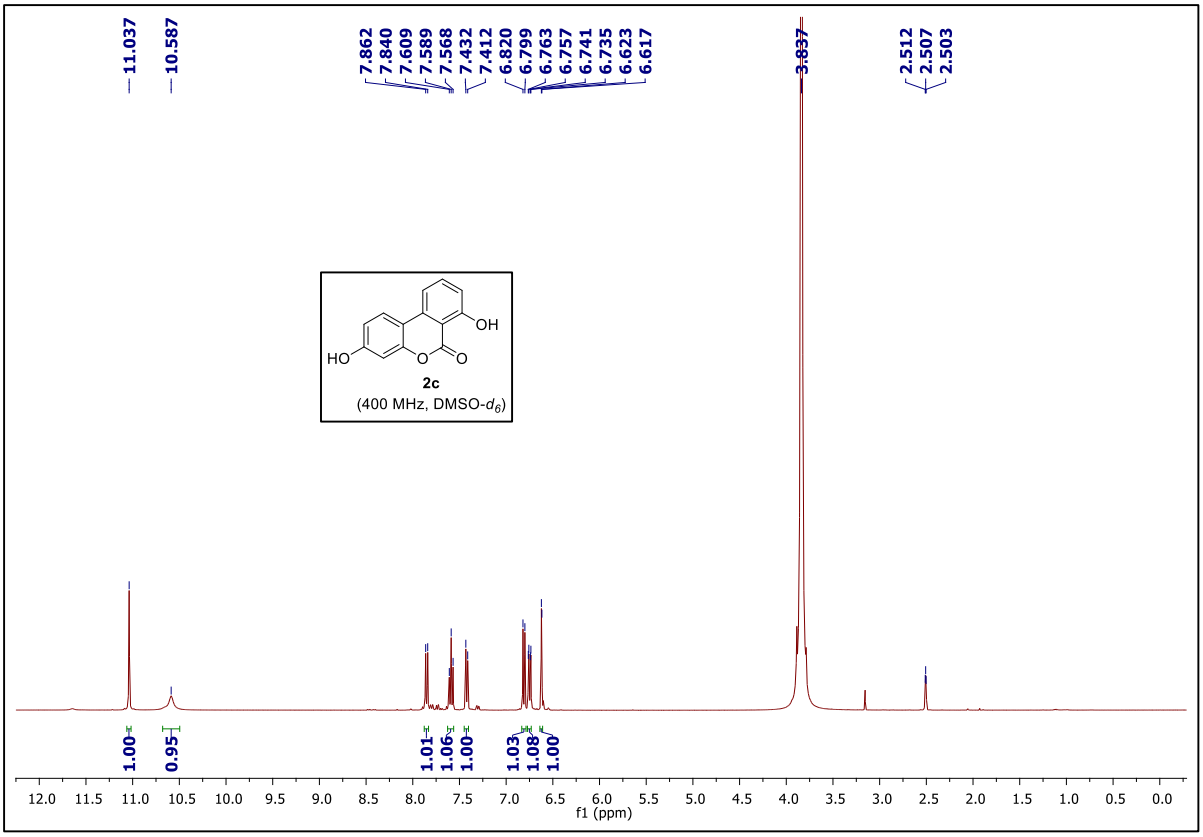
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7-hydroxy-6*H*-benzo[*c*]chromen-6-one **2b**.



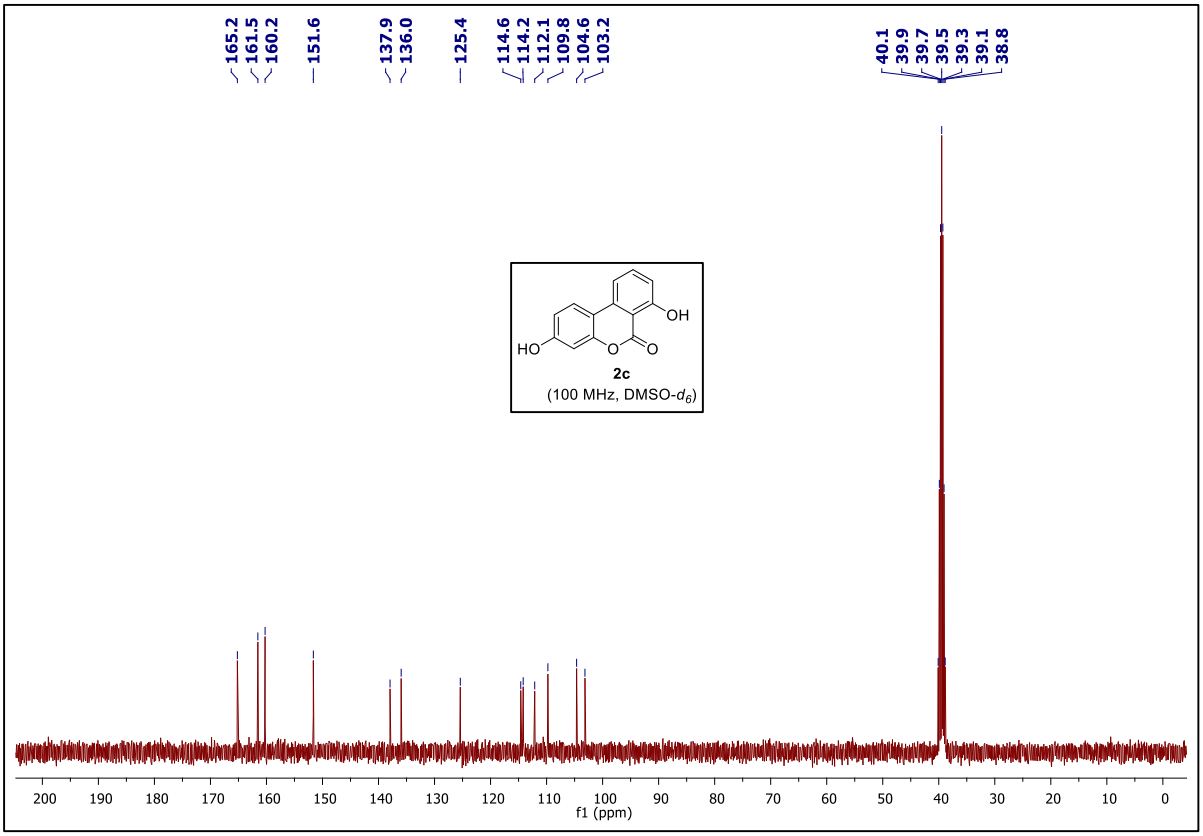
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7-hydroxy-6*H*-benzo[*c*]chromen-6-one **2b**.



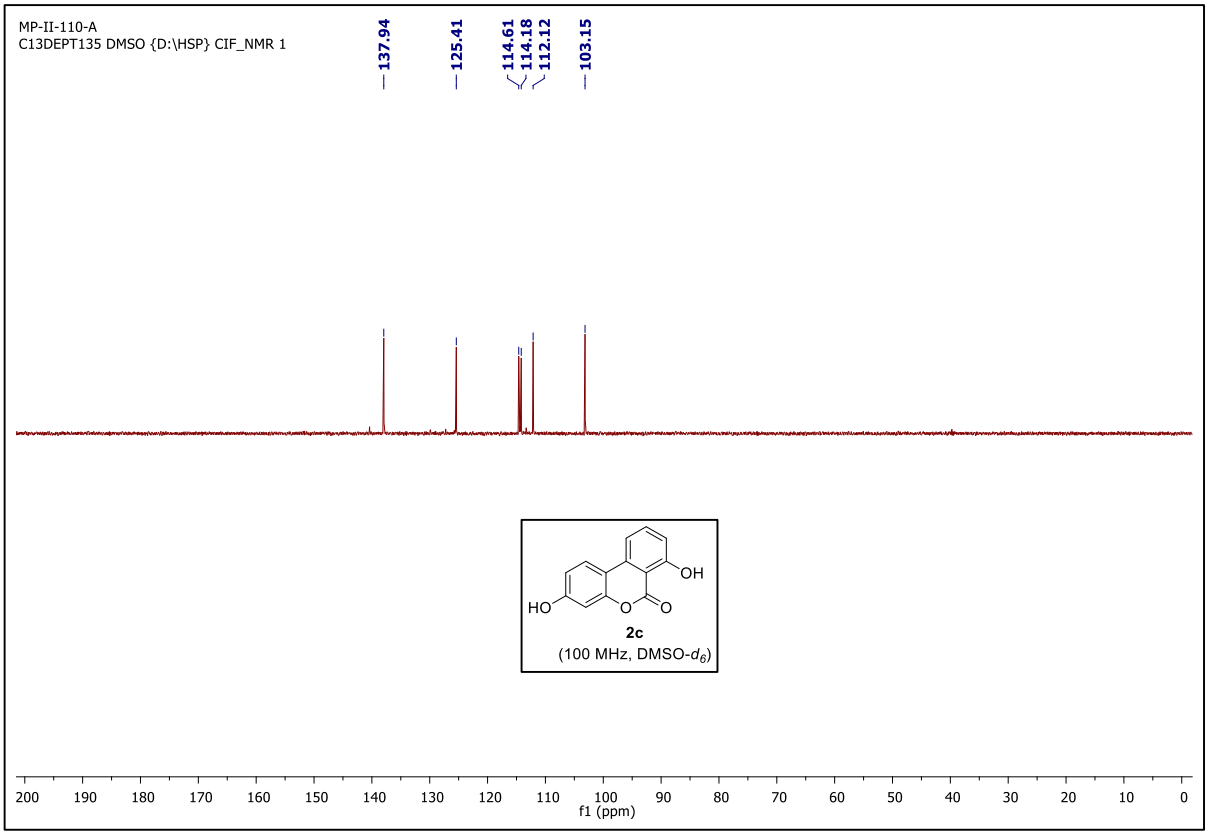
DEPT-135 NMR spectrum of 7-hydroxy-6*H*-benzo[*c*]chromen-6-one **2b**



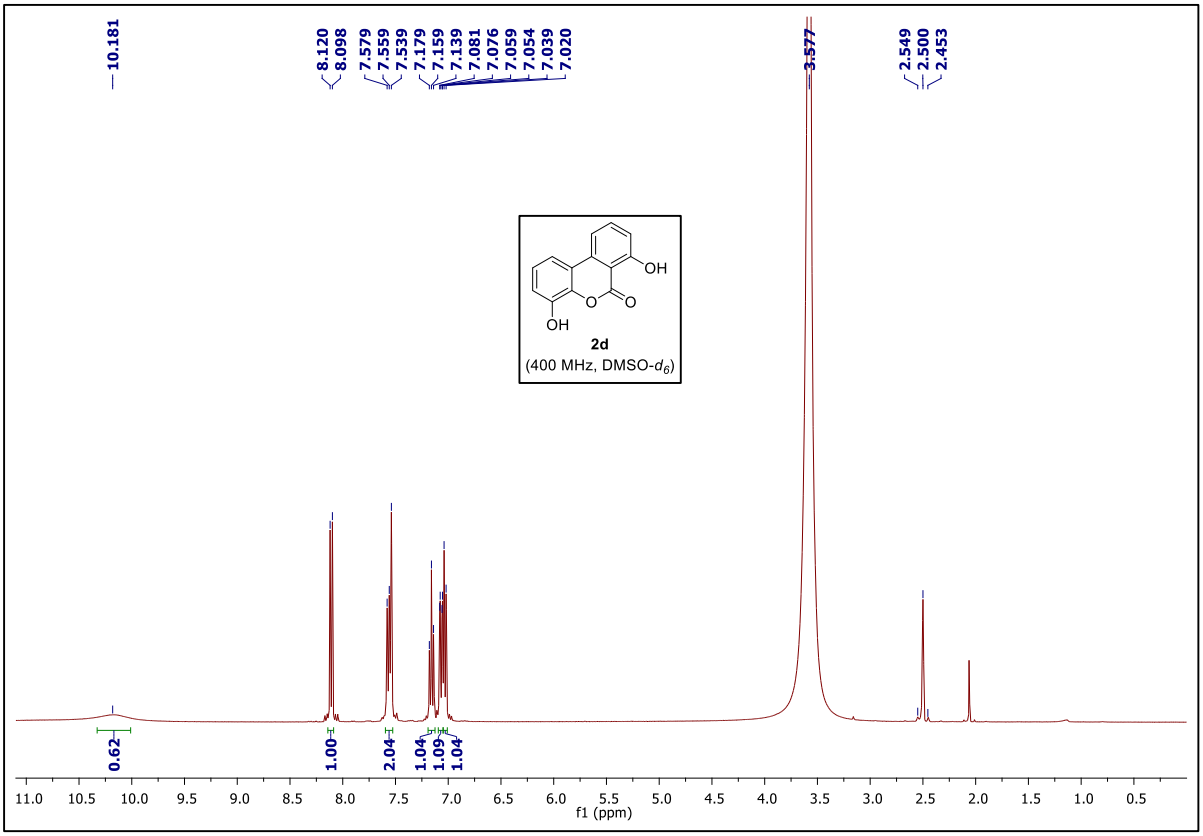
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3,7-dihydroxy-6*H*-benzo[*c*]chromen-6-one **2c**.



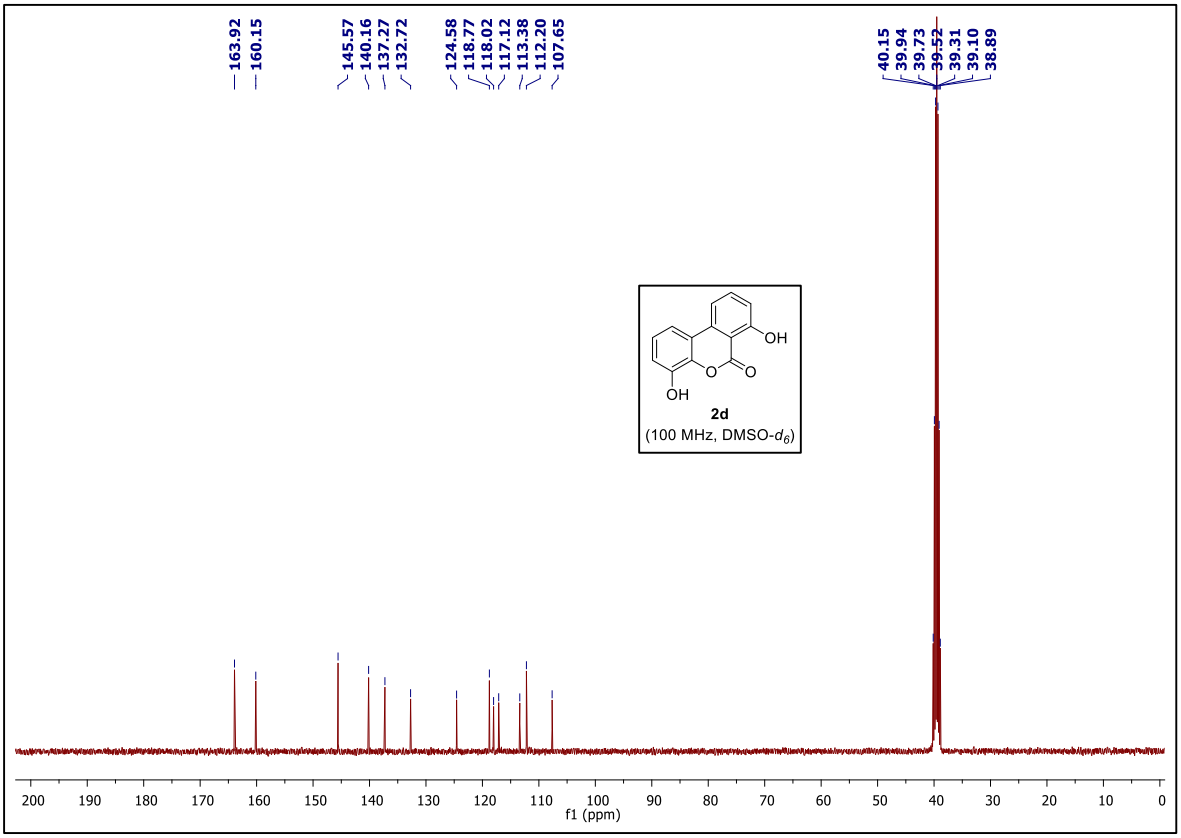
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 3,7-dihydroxy-6*H*-benzo[*c*]chromen-6-one **2c**.



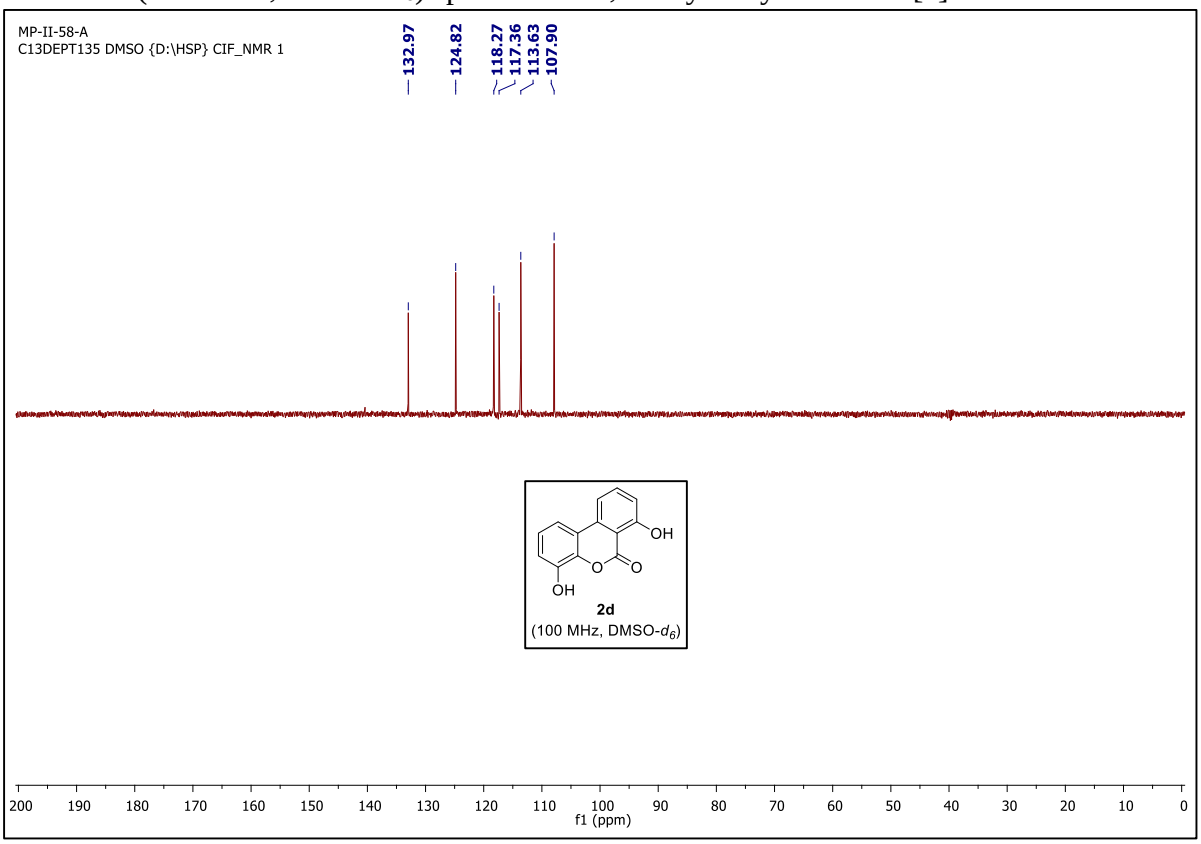
DEPT-135 NMR spectrum of 3,7-dihydroxy-6*H*-benzo[*c*]chromen-6-one **2c**.



^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 2,7-dihydroxy-6*H*-benzo[*c*]chromen-6-one **2d**



^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 2,7-dihydroxy-6*H*-benzo[*c*]chromen-6-one **2d**.



DEPT-135 NMR spectrum of 2,7-dihydroxy-6*H*-benzo[*c*]chromen-6-one **2d**.