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SUPPORTING INFORMATION

Iodine-mediated formal [3+2] annulation for synthesis of Furocoumarin from oxime esters

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Section S1. *Catalysis: Materials and Instrumentation*

Chemical used in this work. All chemicals were purchased from Sigma – Aldrich, Acros Organics, and Fisher and used without further purification unless otherwise noted.

Analytical techniques.

Single crystals suitable for X-ray analysis were obtained by re-crystallization from methanol. The single crystal data for a colorless plate-shaped crystal (0.25 × 0.25 × 0.012 mm^3) was collected on a Bruker D8 QUEST diffractometer at 100 K with Mo Kα radiation (λ = 0.71076 Å) using a TRIUMP monochromator, operated at 50 kV and 30.0 mA. The raw data was processed with the Bruker APEX3 software package[1] and then integrated with the Bruker SAINT package[2] using a narrow-frame algorithm – corrected for absorption using the SADABS procedure.[3] The structures were solved by intrinsic phasing methods. The refinement was performed by full-matrix least squares on F^2 (SHELXL-2014)[4] using the Olex2 software package.[5]

The products were indicated by GC-MS, analysis data were recorded on a Shimadzu GCMS-QP2010 Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, film thickness = 0.25 μm). The temperature program for GC-MS analysis heated samples at 50 °C for 2 min, from 50 °C to 280 °C at rate of 10 °C/min, then held at 280 °C for 5 min. MS spectra were compared with the spectra gathered in the NIST library.

Gas chromatography (GC) analysis were performed using a Shimadzu GC 2010-Plus equipped with a FID detector and a SPB-5 column (length = 30 m, inner diameter = 0.25 mm, film thickness = 0.25 μm). The temperature program for GC analysis heated sample at 100 °C for 1 minute, from 100 °C to 120 °C at rate of 20 °C/minute, held at 120 °C for 2 minutes. And then from 120 °C to 280 °C at rate of 40 °C/minute, held 280 °C for 1 minute. 1,2-dichlorobenzene was used as internal standard.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 500 MHz spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C, respectively, using tetramethylsilane as standard. The chemical shifts (δ) are expressed as values in parts per million (ppm) and the coupling constant (*J*) is given in hertz (Hz). Spin multiplicities are described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), and *m* (multiplet).

Section S2. *Synthesis of starting materials*

Synthesis of ketoximes

In a typical procedure, the mixture of ketone derivatives (22 mmol), hydroxylamine hydrochloride $NH_2OH.HCl$ (33 mmol) was stirred in 10 mL EtOH at 60 ^oC for 1h. During the reaction, K_2CO_3 (22 mmol) was added dropwise into this mixture. When the reaction was completed (TLC), the mixture was cooled to room temperature, and the desired product was extracted with EtOAc (20 mL), then washed the mixture with deionized water (3 x 10 mL) and dried the organic phase over anhydrous Na_2SO_4 before removed under reduced pressure to give corresponding ketoxime derivatives.

Synthesis of ketoxime carboxylates

In a typical procedure, the mixture of ketoxime (22 mmol), acetic anhydride (44.4 mmol, 2.0 eq.) was stirred in 10 mL EtOAc at room temperature for 1h. During the reaction, K_2CO_3 (22 mmol) was added dropwise into this mixture. When the reaction was completed (TLC), the mixture was cooled to room temperature, diluted with EtOAc (25 mL) and washed with H_2O (20 mL) and brine (10 mL). The organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the ketoxime acetates with hexane/ethyl acetate as the eluent.

Section S3. *GC yield measurement*

After the transformations were completed, samples were withdrawn from reactors, quenched with water and then eluted with ethyl acetate. Subsequently, the organic layer was carefully shaken with anhydrous Na_2SO_4 before being analyzed by GC system. GC yields of the desired products was determined as following

$$\text{GC yield (\%)} = \frac{n_{Pr} \times 100\%}{n_{Pr}'} = \left(\frac{S_{Pr}}{S_{IS}} \times 0{,}823 + 0.0127\right) \times n_{IS} \times \frac{100\%}{n_{Pr}'}$$

In which:

n_{Pr} (mg): Mole of 3-Phenyl-4H-furo[3,2-c]chromen-4-one product obtained

$n_{Pr'}$ (mg): Calculated mole of 3-Phenyl-4H-furo[3,2-c]chromen-4-one when yield = 100%

n_{IS} (mg): Mole of n-hexadecane in sample

S_{Pr}: Peak area of 2-(3-oxo-3-phenylpropyl) isoindoline-1,3-dione in sample

S_{IS}: Peak area of n-hexadecane in sample

This formula was determined, relied on the calibration curve achieved by the following process: diphenylether (42,3 mg) and 3-Phenyl-4H-furo[3,2-c]chromen-4-one (19,6 mg) were added to two distinct 8 mL volumetric flasks. After that, to dissolve these substances, the flasks were supplemented by dichlobenzene until the solvent masses reach 6494,8 mg and 1995,4 mg, respectively.

	Product	**Internal standard**
Mass (mg)	19,6	42,3
Dichlobenzene (mg)	1995,4	6494,8
C% (w/w)	**0,9727**	**0.6471**

*Table **Error! No text of specified style in document.**-1:Calibration curve preparation for 3-Phenyl-4H-furo[3,2-c]chromen-4-one*

Different fractions of the two solutions were then withdrawn and attributed to six 1,5 mL GC vials which were analyzed by GC method later. The areal ratio of 3-Phenyl-4H-furo[3,2-c]chromen-4-one to diphenylether were obtained via GC data. As a result, the calibration curve was illustrated in Figure 3-1.

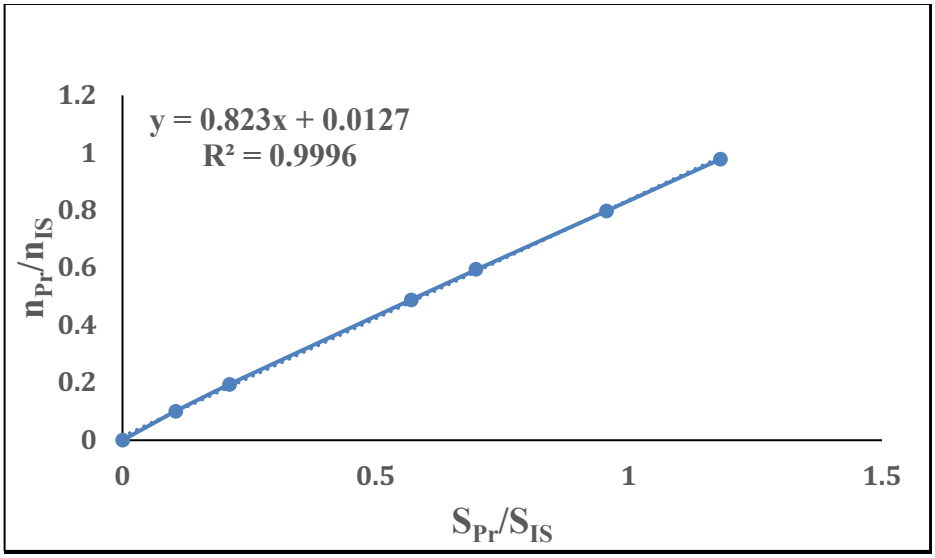


Figure **Error! No text of specified style in document.**-1 Calibration curve of 3-Phenyl-4H-furo[3,2-c]chromen-4-one

Section S4. *Crystal data*

CIF deposit number: 2026801

Crystal data and structure refinement for 3a

Identification code	3a
Empirical formula	$C_{17}H_{10}O_3$
Formula weight	262.25
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbca
a/Å	13.2356(8)
b/Å	7.1744(4)
c/Å	25.3234(16)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2404.6(2)
Z	8
ρ_{calc}g/cm^3	1.449
μ/mm^{-1}	0.100
F(000)	1088.0
Crystal size/mm^3	0.25 × 0.25 × 0.012
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.156 to 52.772
Index ranges	$-16 \le h \le 16$, $-8 \le k \le 8$, $-31 \le l \le 31$
Reflections collected	25205
Independent reflections	2450 [R_{int} = 0.1303, R_{sigma} = 0.0499]
Data/restraints/parameters	2450/0/181
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0518, wR_2 = 0.1000
Final R indexes [all data]	R_1 = 0.0962, wR_2 = 0.1151
Largest diff. peak/hole / e Å^{-3}	0.23/-0.21

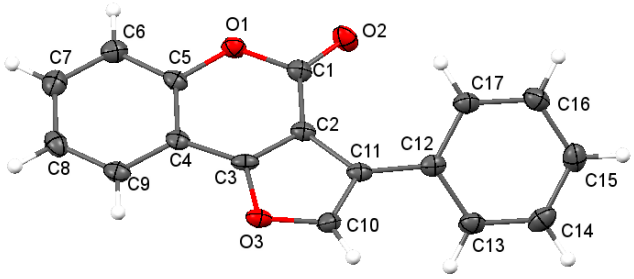
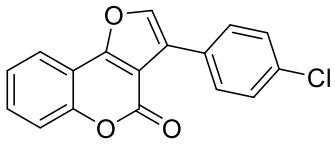


Figure S1. ORTEP representation of the asymmetric unit of compound 3a displayed with 50% probability. Atom colors: O, red; C, grey; H, white.

Section S5 *NMR of products*

Spectroscopic data for 3-(4-chlorophenyl)-4*H*-furo[3,2-*c*]coumarin (HP1)



^{1}H NMR (500 MHz, DMSO-d_6): δ 8.54 (d, J = 1.0 Hz, 1H), 7.99 (dt, J = 7.8, 1.5 Hz, 1H), 7.86 (dd, J = 8.4, 2 Hz, 2H), 7.67 (ddd, J = 8.5, 7.3, 1.3 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.49 – 7.45 (t, J = 7.5 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 158.22, 157.10, 152.00, 143.49, 132.87, 131.47, 130.24, 128.41, 127.99, 124.95, 124.20, 120.98, 116.82, 112.07, 107.74.

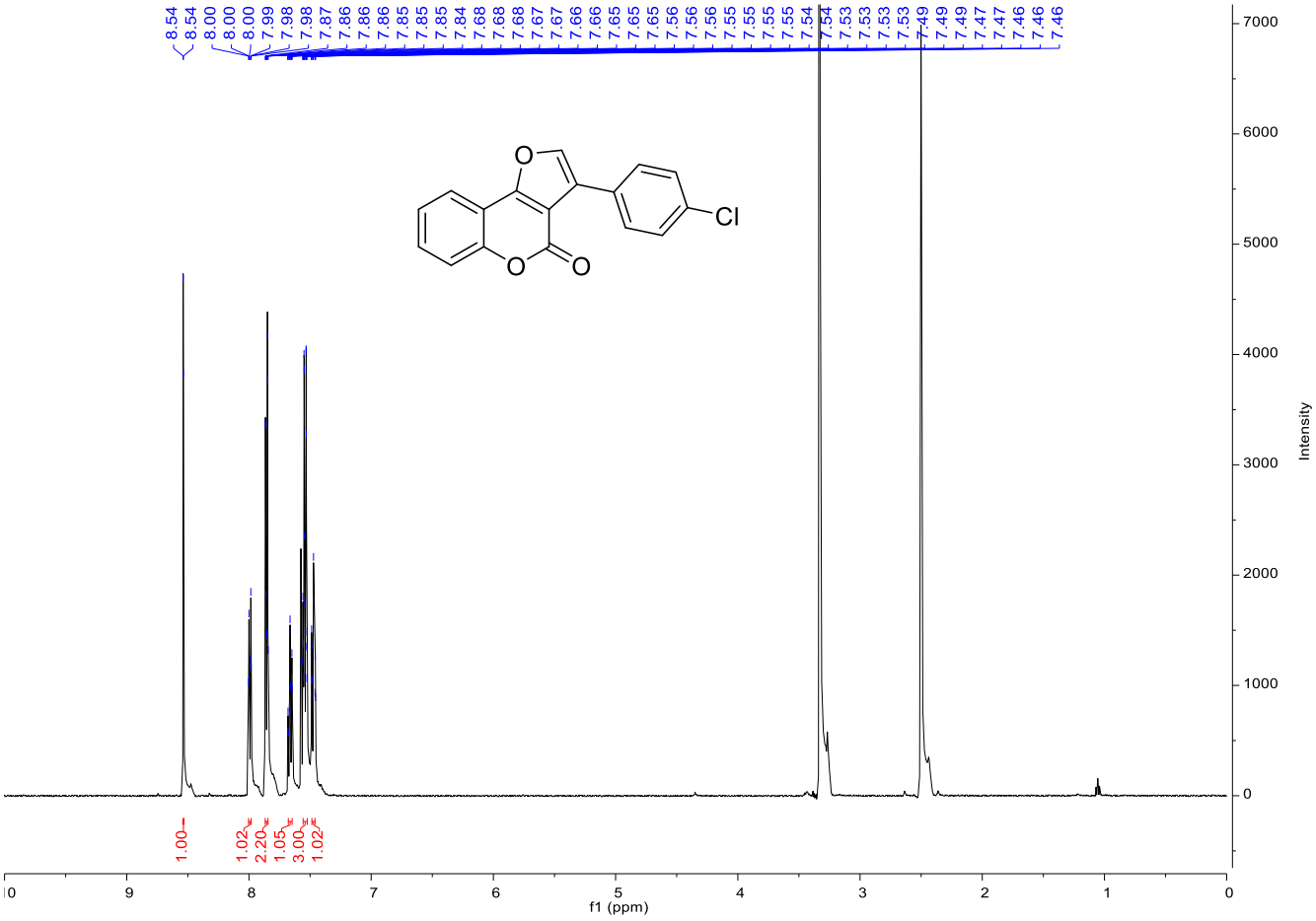


Fig. Sx. ^{1}H-NMR spectra of 3-(4-chlorophenyl)-4*H*-furo[3,2-*c*]coumarin.

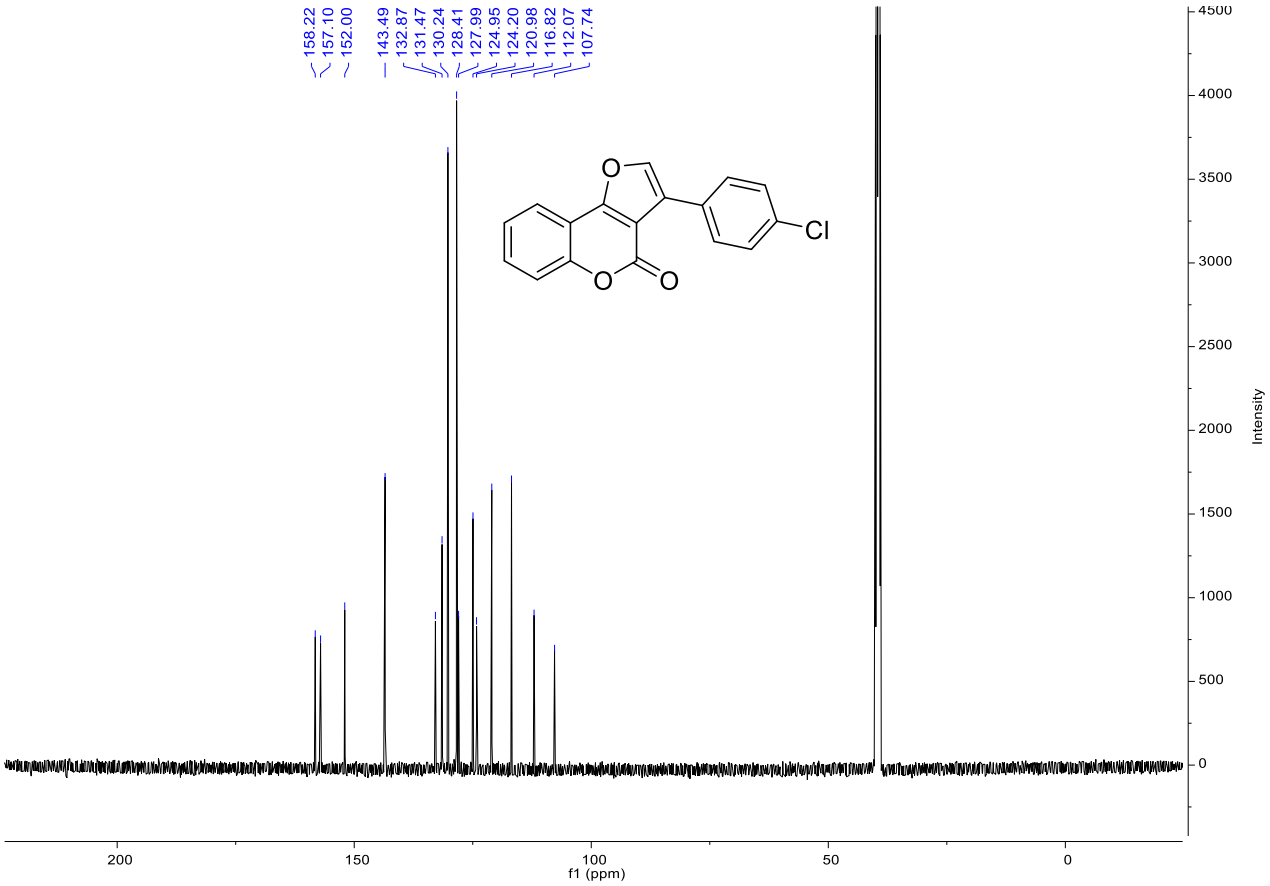
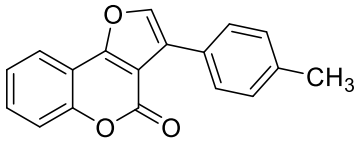


Fig. Sx. ^{13}C-NMR spectra of 3-(4-chlorophenyl)-4*H*-furo[3,2-*c*]coumarin.

Spectroscopic data for 3-(4-methylphenyl)-4*H*-furo[3,2-*c*]coumarin (HP2)



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.39 (d, J = 1.4 Hz, 1H), 7.93 (dt, J = 7.8, 1.8 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.62 (ddd, J = 8.7, 7.3, 1.5 Hz, 1H), 7.51 (dd, J = 8.5, 1.1 Hz, 1H), 7.43 (td, J = 7.5, 1.1 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, DMSO) δ 158.01, 157.02, 151.92, 142.75, 137.46, 131.26, 128.89, 128.36, 126.08, 125.29, 124.82, 120.87, 116.73, 112.11, 107.81, 20.80.

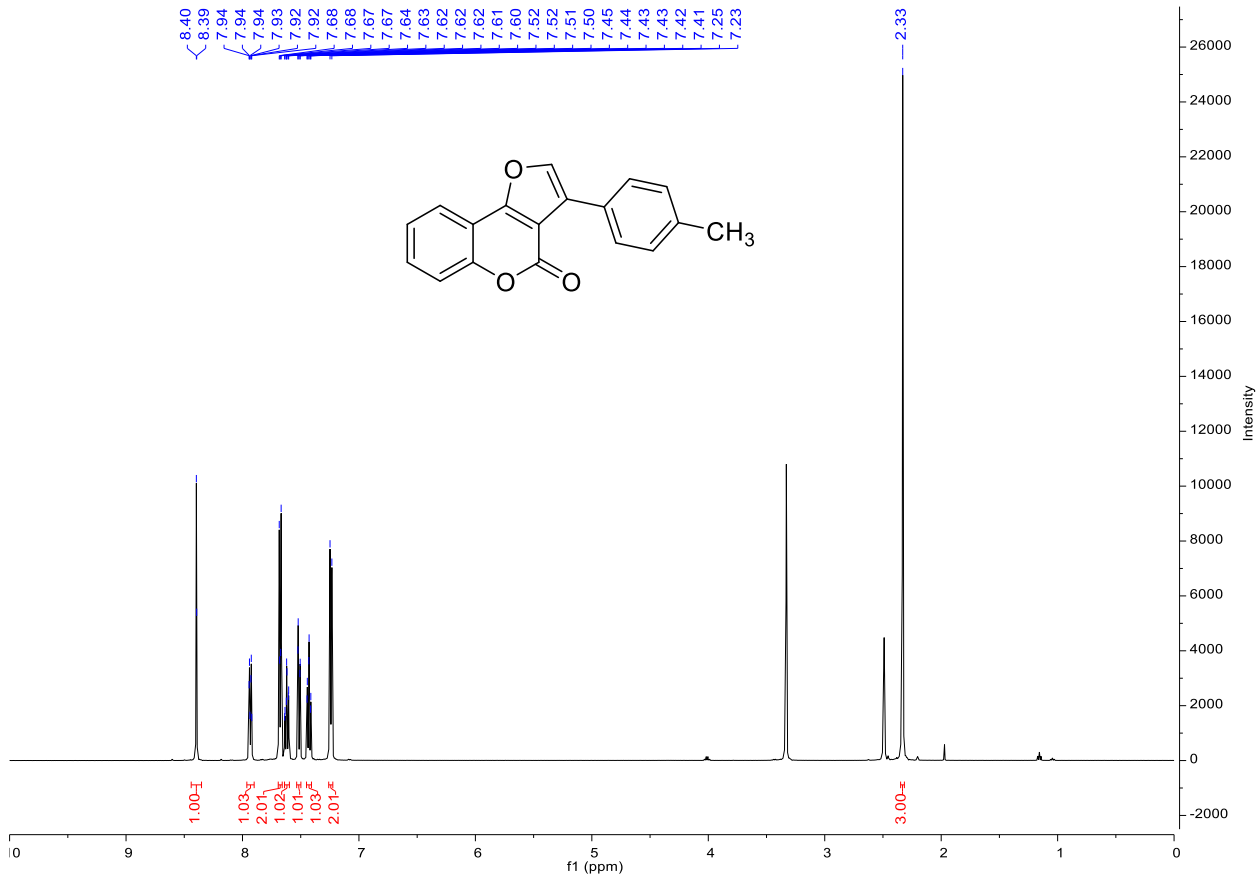


Fig. Sx. ^{1}H-NMR spectra of 3-(4-methylphenyl)-4*H*-furo[3,2-*c*]coumarin.

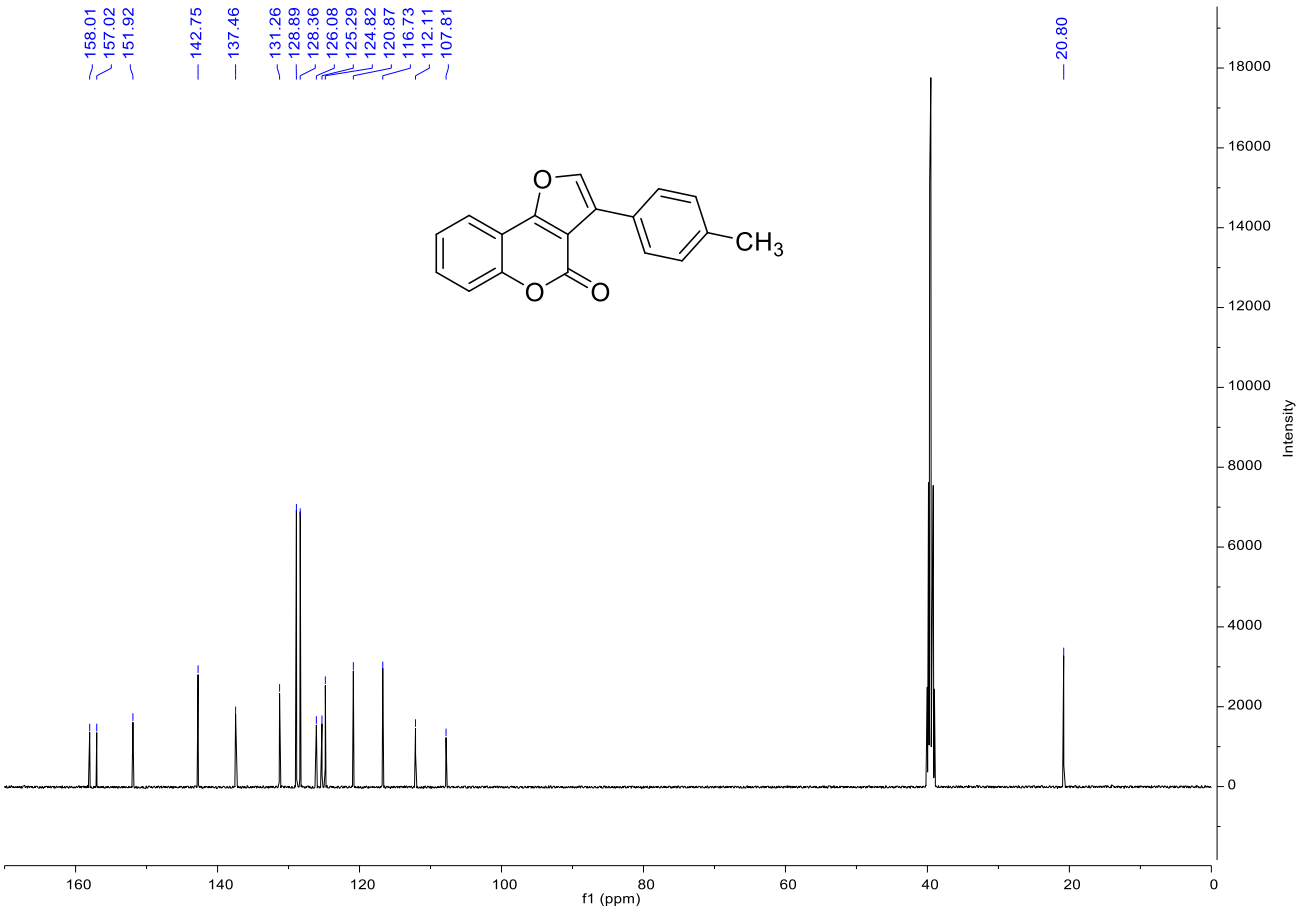
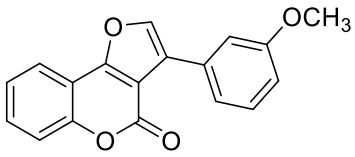


Fig. Sx. ^{13}C-NMR spectra of 3-(4-methylphenyl)-4*H*-furo[3,2-*c*]coumarin.

Spectroscopic data for 3-(4-methoxyphenyl)-4*H*-furo[3,2-*c*]coumarin (HP3)



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 (s, 1H), 8.00 (dd, J = 7.8, 1.6 Hz, 1H), 7.66 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 7.56 (dd, J = 8.4, 1.0 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.39 – 7.35 (m, 2H), 6.97 (dt, J = 7.4, 2.2 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (126 MHz, DMSO) δ 159.17, 158.18, 157.06, 151.98, 143.38, 131.41, 130.27, 129.44, 125.25, 124.91, 120.98, 120.67, 116.79, 114.29, 113.61, 112.12, 107.83, 55.12.

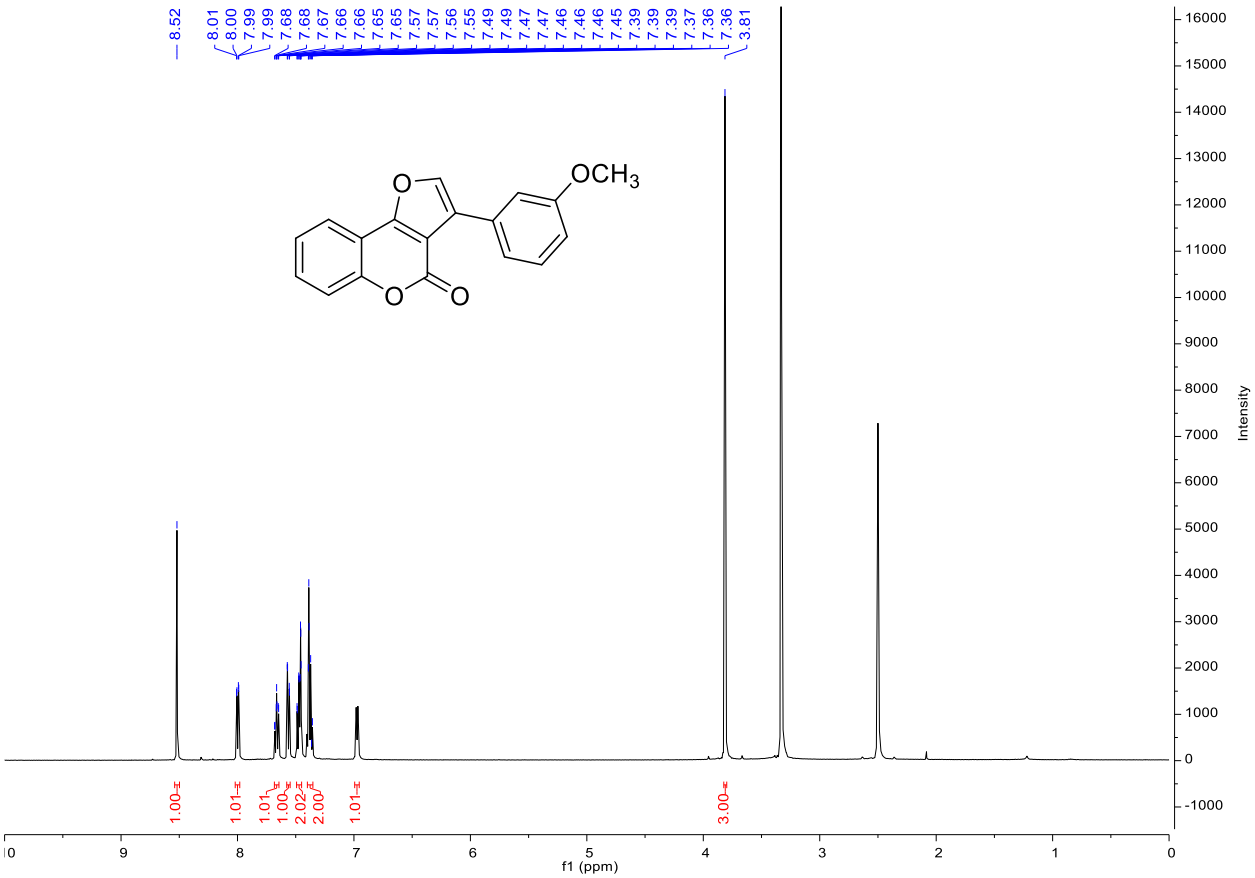


Fig. Sx. ^{1}H-NMR spectra of 3-(4-methoxyphenyl)-4*H*-furo[3,2-*c*]coumarin.

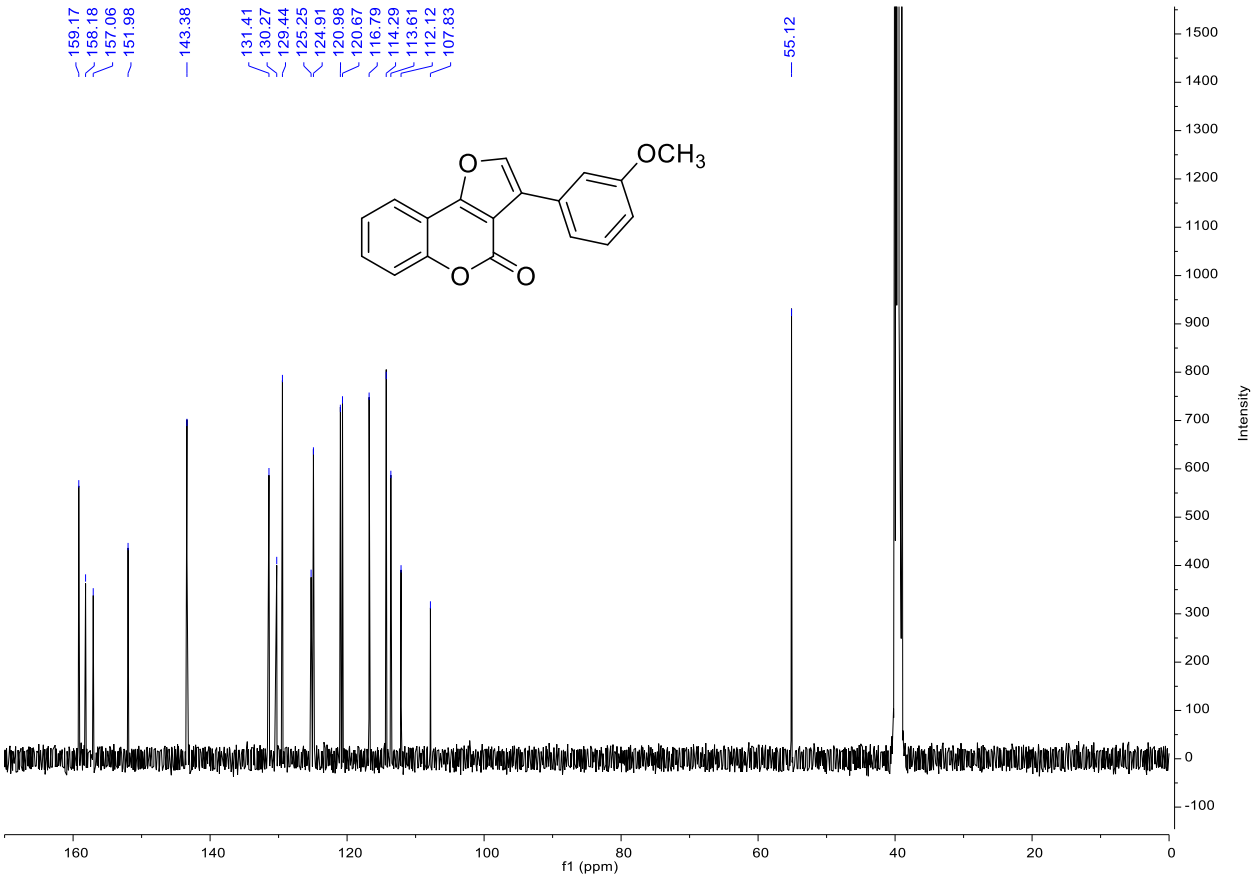
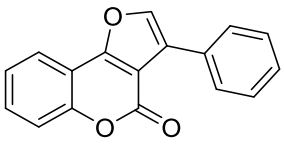


Fig. Sx. ^{13}C-NMR spectra of 3-(4-methoxyphenyl)-4*H*-furo[3,2-*c*]coumarin.

Spectroscopic data for 3-phenyl-4*H*-furo[3,2-*c*]coumarin (HP4)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.80 – 7.75 (m, 3H), 7.54 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.48 – 7.44 (m, 3H), 7.38 (dt, *J* = 14.8, 7.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.96, 152.81, 141.38, 131.08, 129.24, 128.83, 128.71, 128.52, 126.94, 124.62, 121.13, 117.30, 112.97, 108.68.

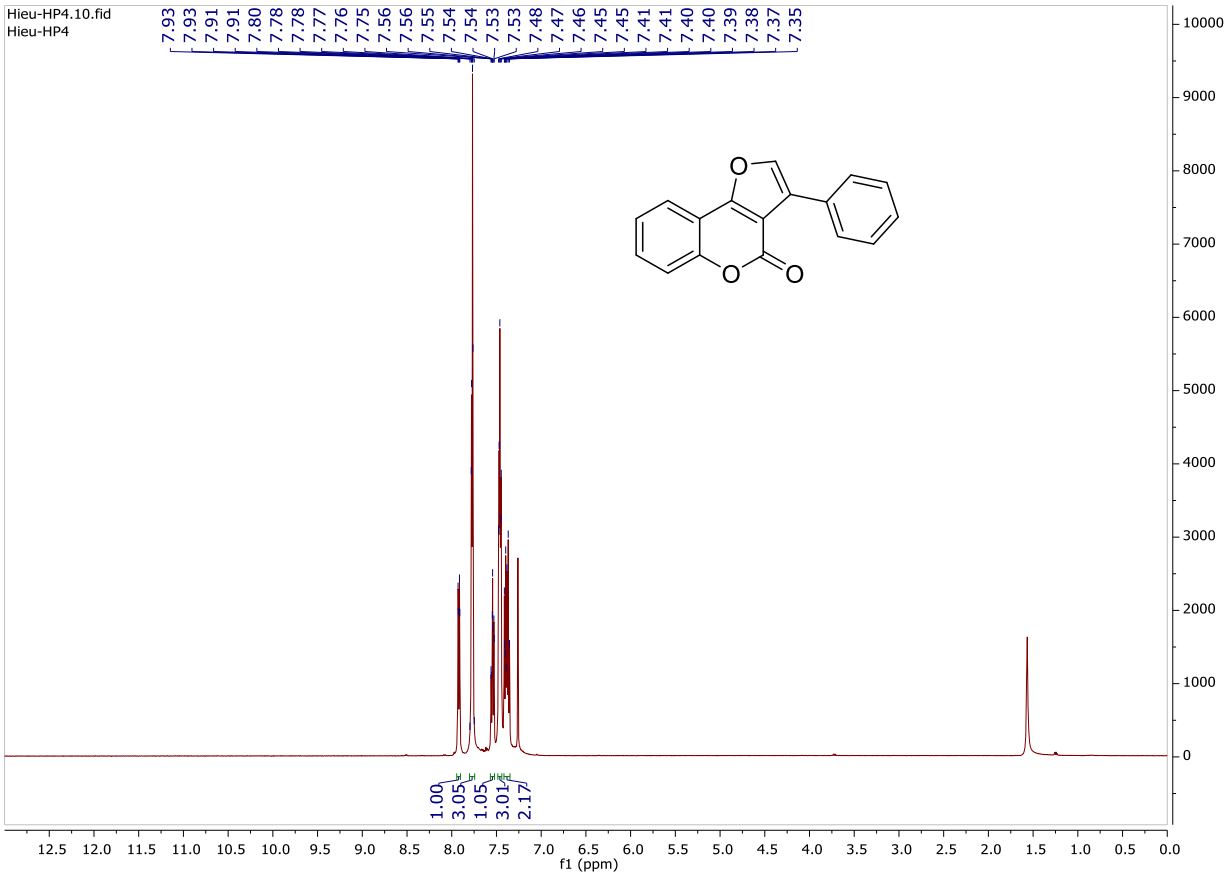


Fig. Sx. ^{1}H-NMR spectra of 3-phenyl-4*H*-furo[3,2-*c*]coumarin.

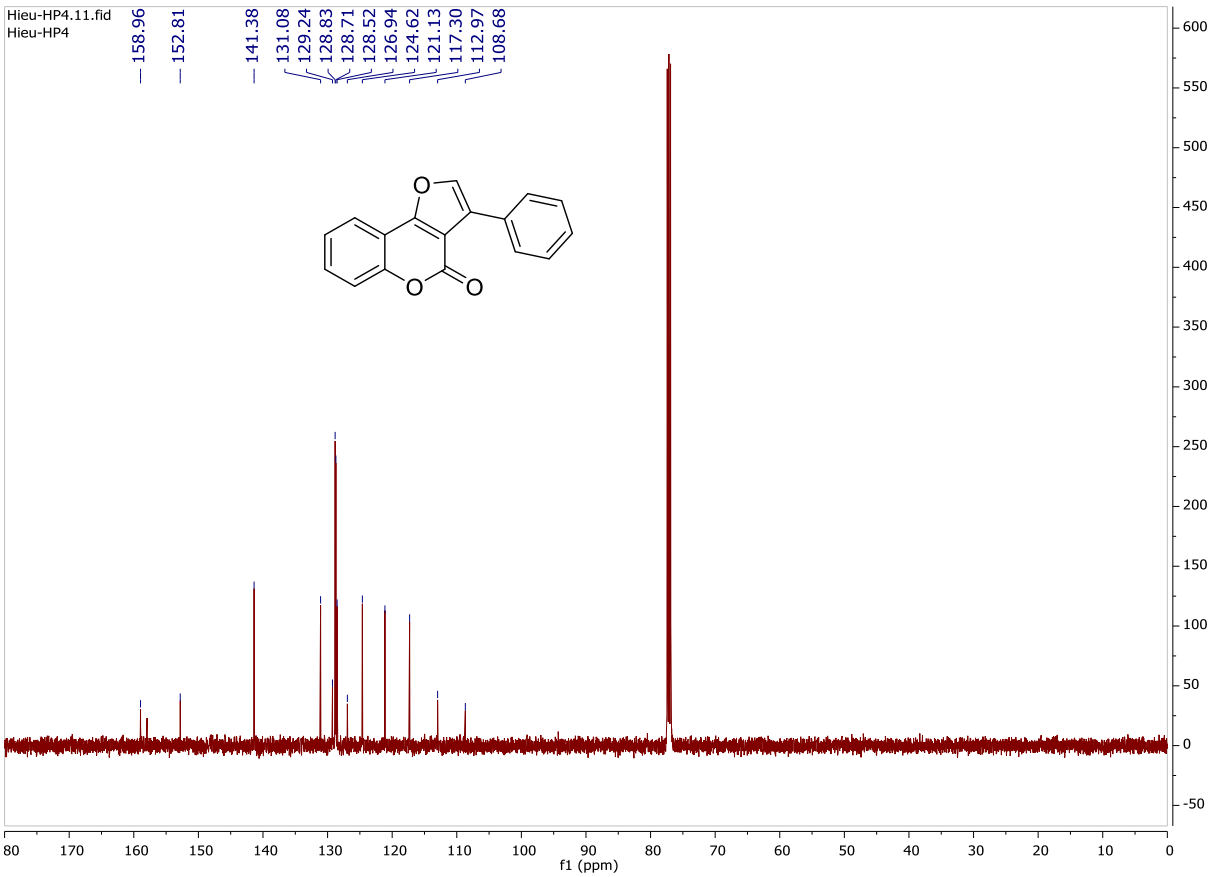
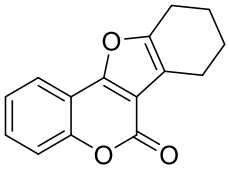
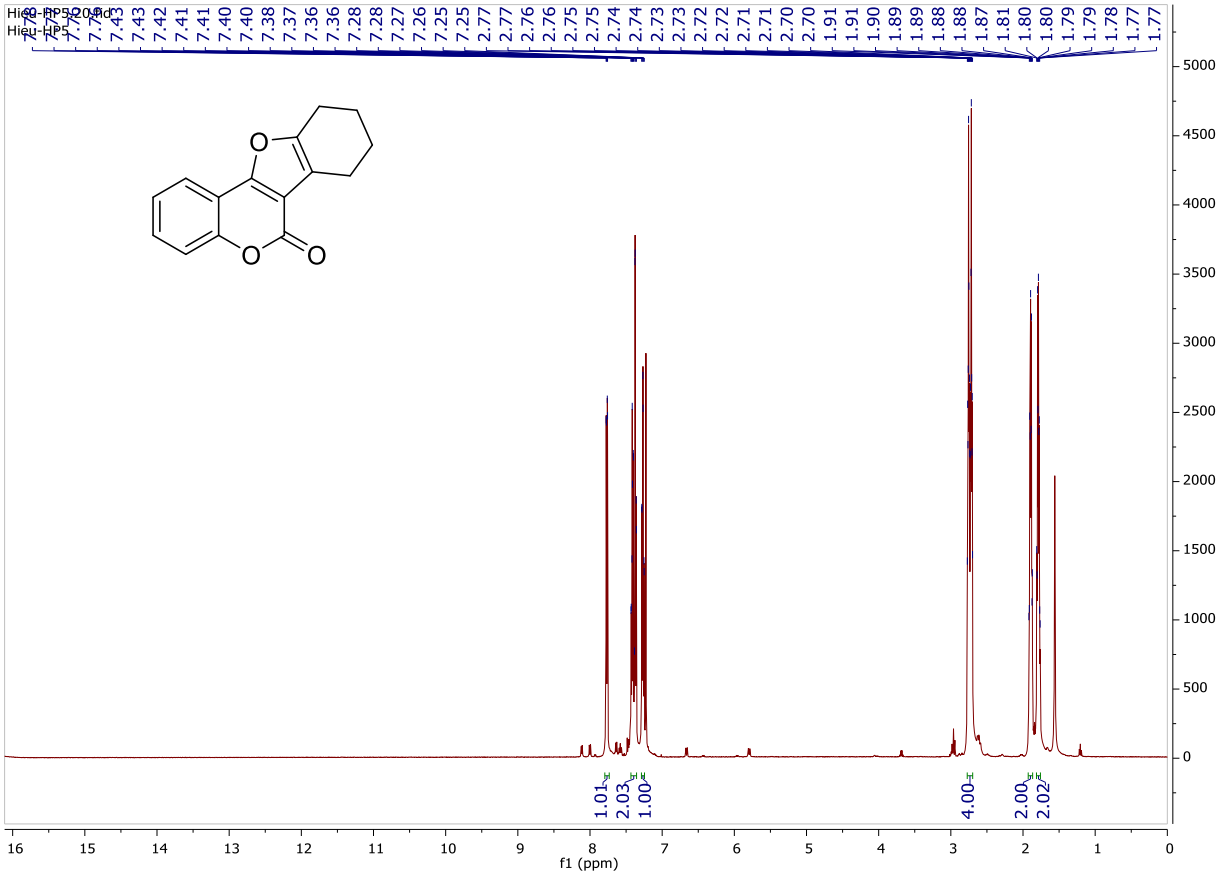


Fig. Sx. ^{13}C-NMR spectra of 3-phenyl-4*H*-furo[3,2-*c*]coumarin.

Spectroscopic data for 7,8,9,10-tetrahydro-6*H*-benzofuro[3,2-*c*]coumarin (HP5)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.27 (td, *J* = 7.6, 1.3 Hz, 1H), 2.77 – 2.70 (m, 4H), 1.93 – 1.87 (m, 2H), 1.81 – 1.76 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.91, 156.14, 154.44, 152.39, 129.90, 124.42, 120.58, 117.32, 116.93, 113.46, 110.58, 23.33, 22.61, 22.46, 21.12.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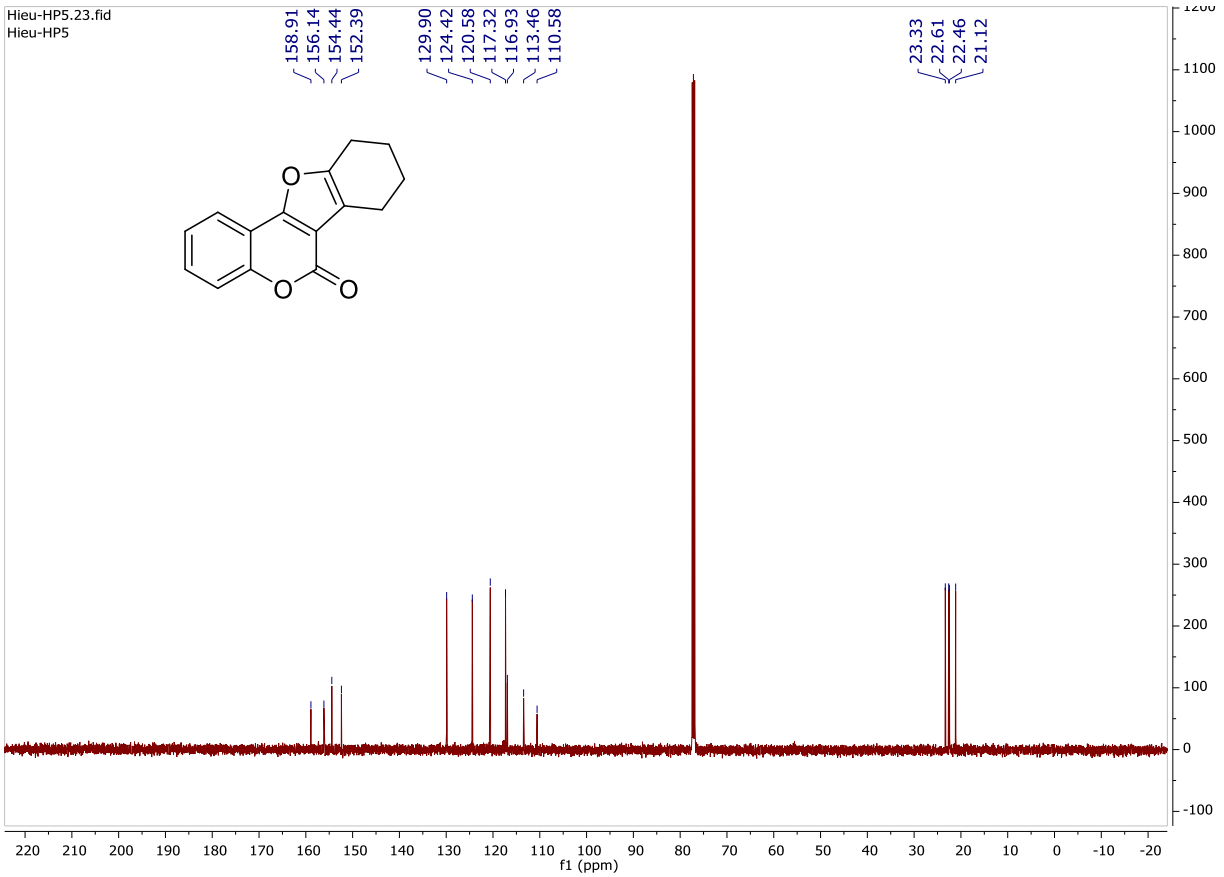
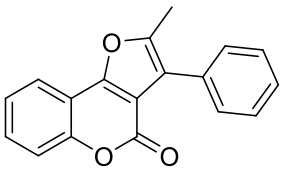
Hieu-HPS
7.77 7.77 7.76 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.38 7.37 7.36 7.36 7.28 7.28 7.27 7.26 7.25 7.25 2.77 2.77 2.76 2.76 2.75 2.75 2.74 2.74 2.73 2.73 2.72 2.72 2.71 2.71 2.70 2.70 1.91 1.91 1.90 1.89 1.89 1.88 1.88 1.87 1.81 1.80 1.80 1.79 1.79 1.78 1.77 1.77
O
O
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.01
2.03
1.00
4.00
2.00
2.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

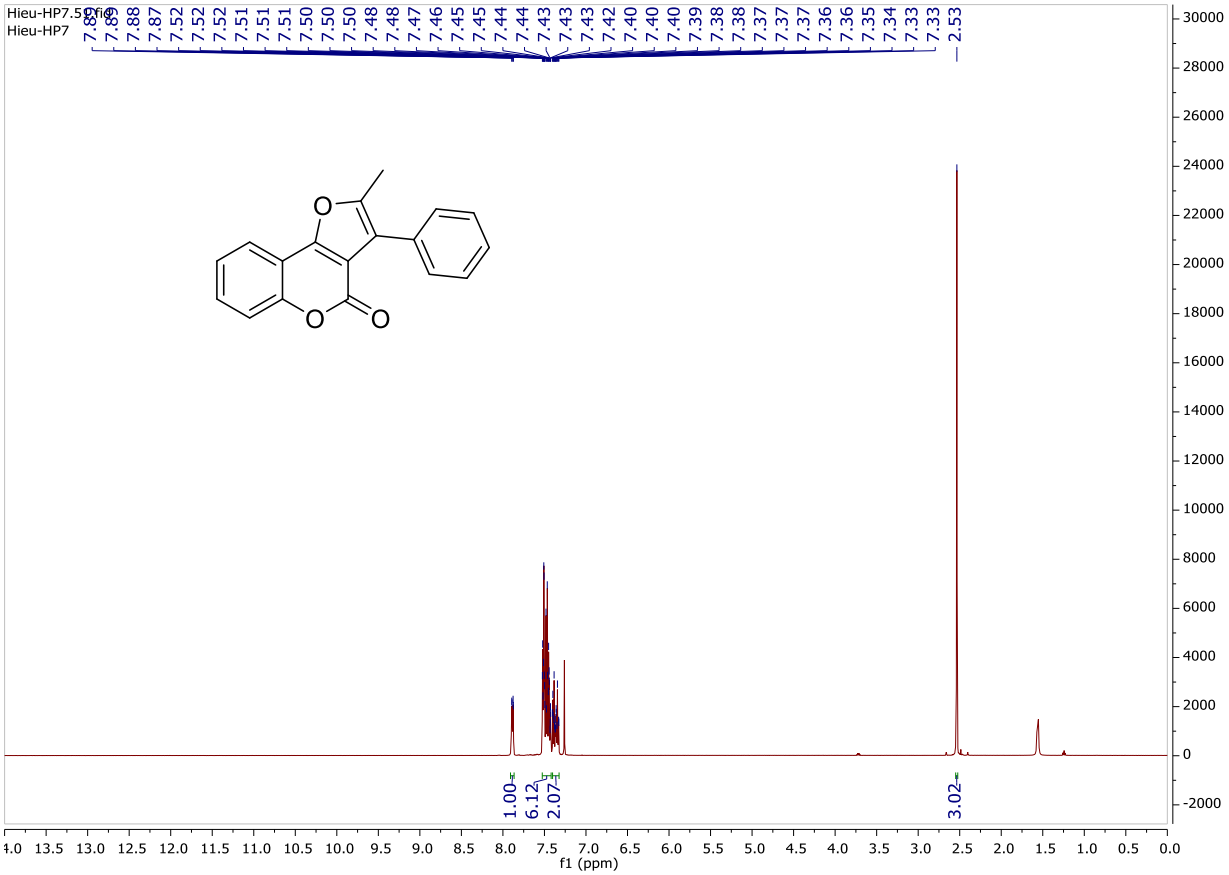


Spectroscopic data for2-methyl-3-phenyl-4H-furo[3,2-c]coumarin (HP7)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (ddd, *J* = 7.8, 1.6 Hz, 0.5 Hz, 1H), 7.53 – 7.33 (m, 8H), 2.53 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.84, 156.43, 152.50, 151.81, 130.39, 130.14, 130.02, 128.34, 127.90, 124.41, 120.72, 120.64, 117.23, 112.96, 109.81, 12.73.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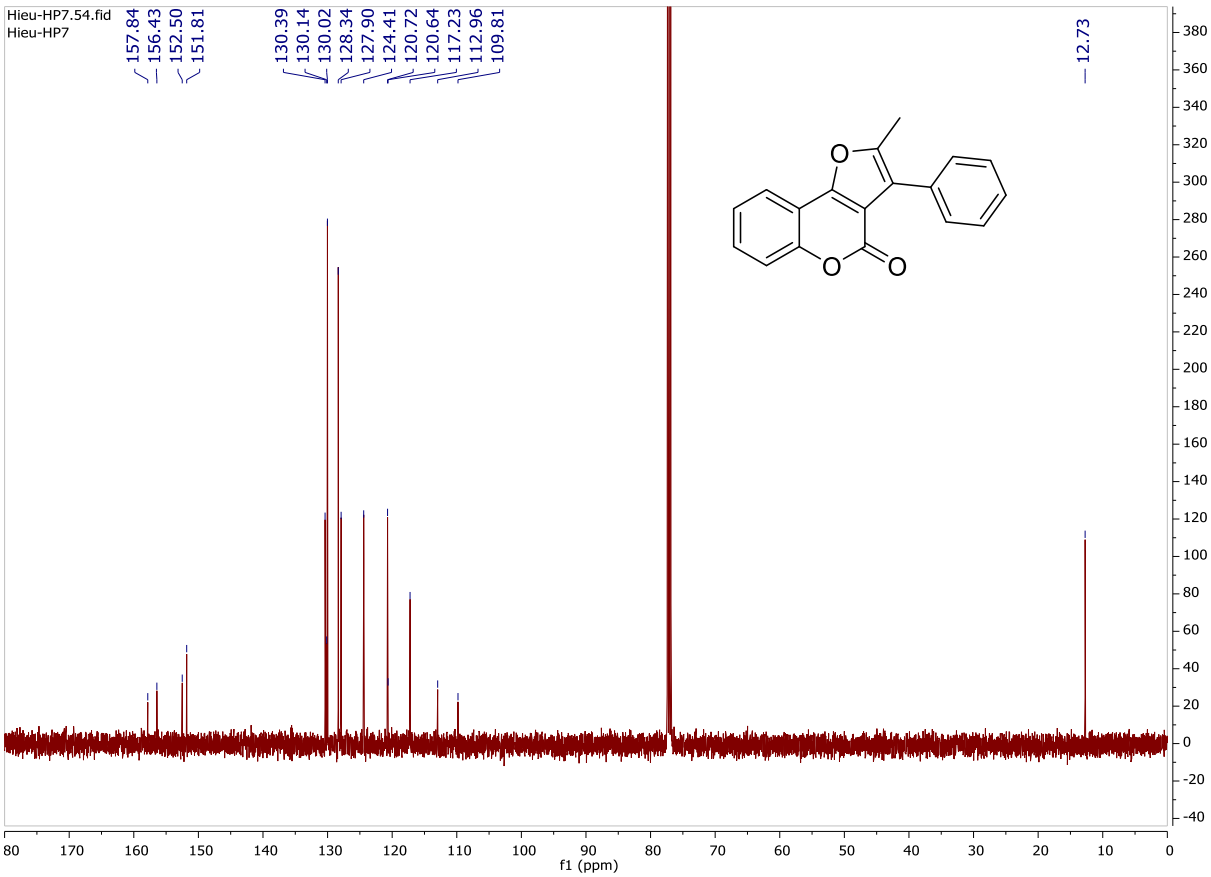
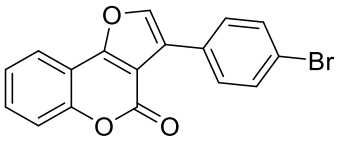
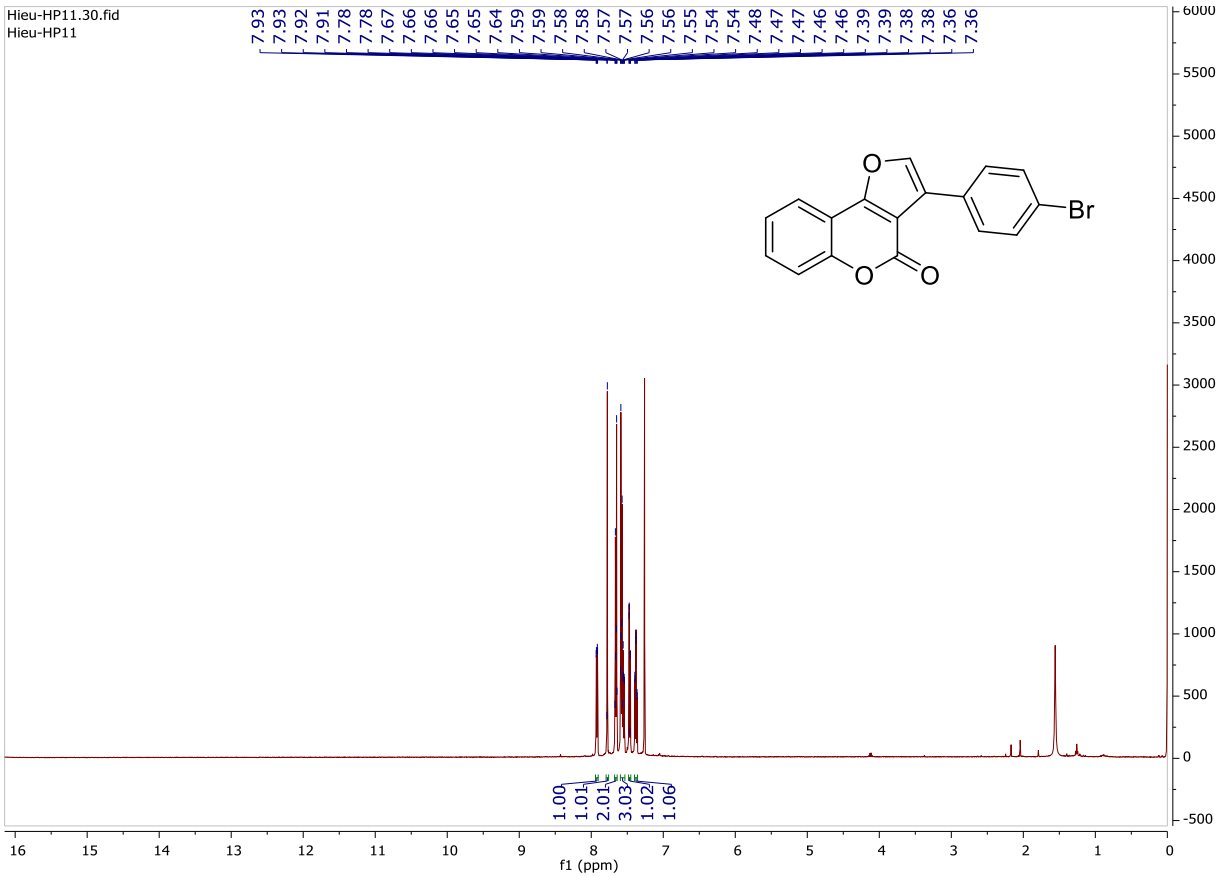
6.12
2.07
3.02
f1 (ppm)



Spectroscopic data for 3-(4-bromophenyl)-4H-furo[3,2-c]coumarin (HP11)



^{1}H NMR (500 MHz $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.78 (s, 1H), 7.67 –7.53 (m, 5H), 7.47 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.38 (td, *J* = 7.5, 1.1 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.16, 157.96, 152.83, 141.39, 141.34, 131.91, 131.30, 130.40, 128.19, 125.96, 124.74, 122.80, 121.19, 117.36, 112.83, 108.46.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Hieu-HP11
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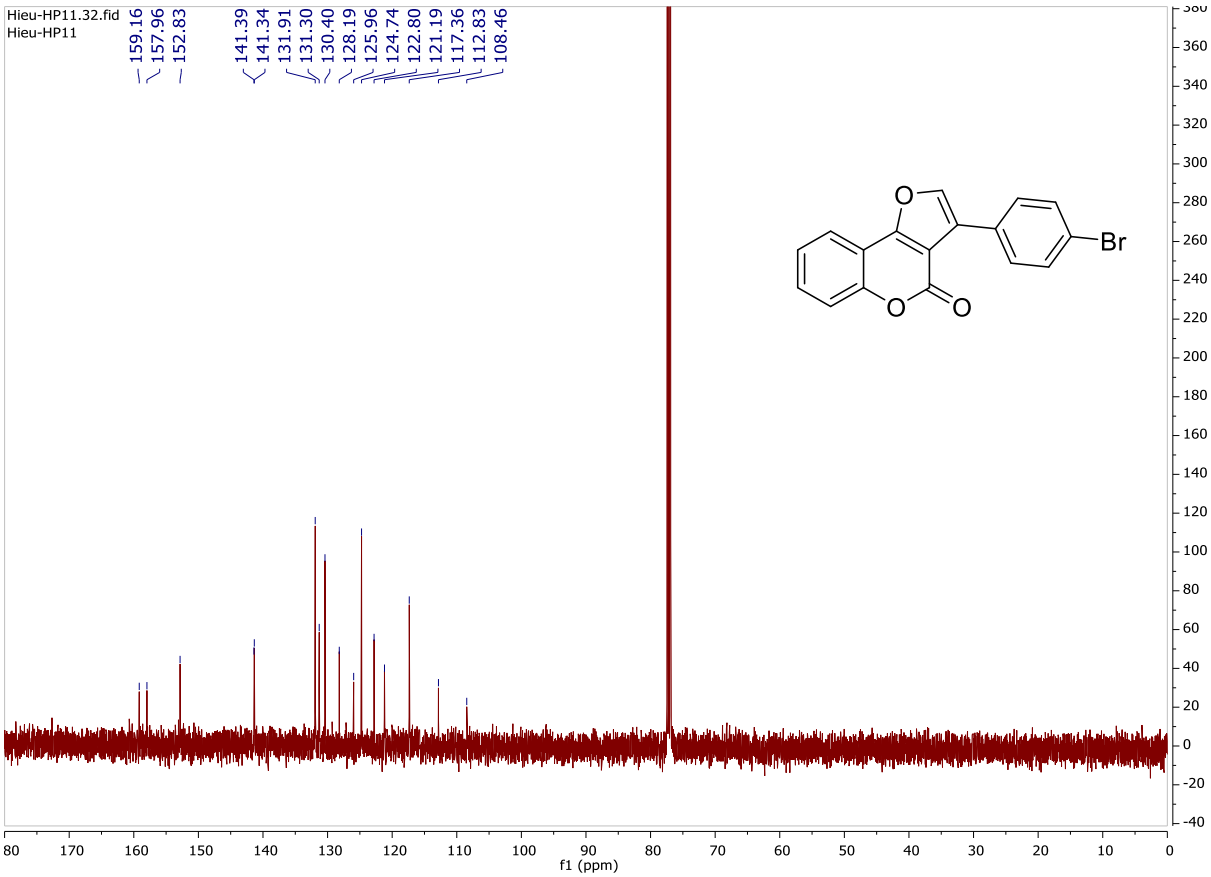
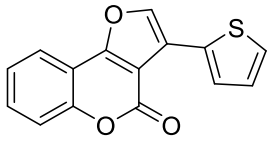
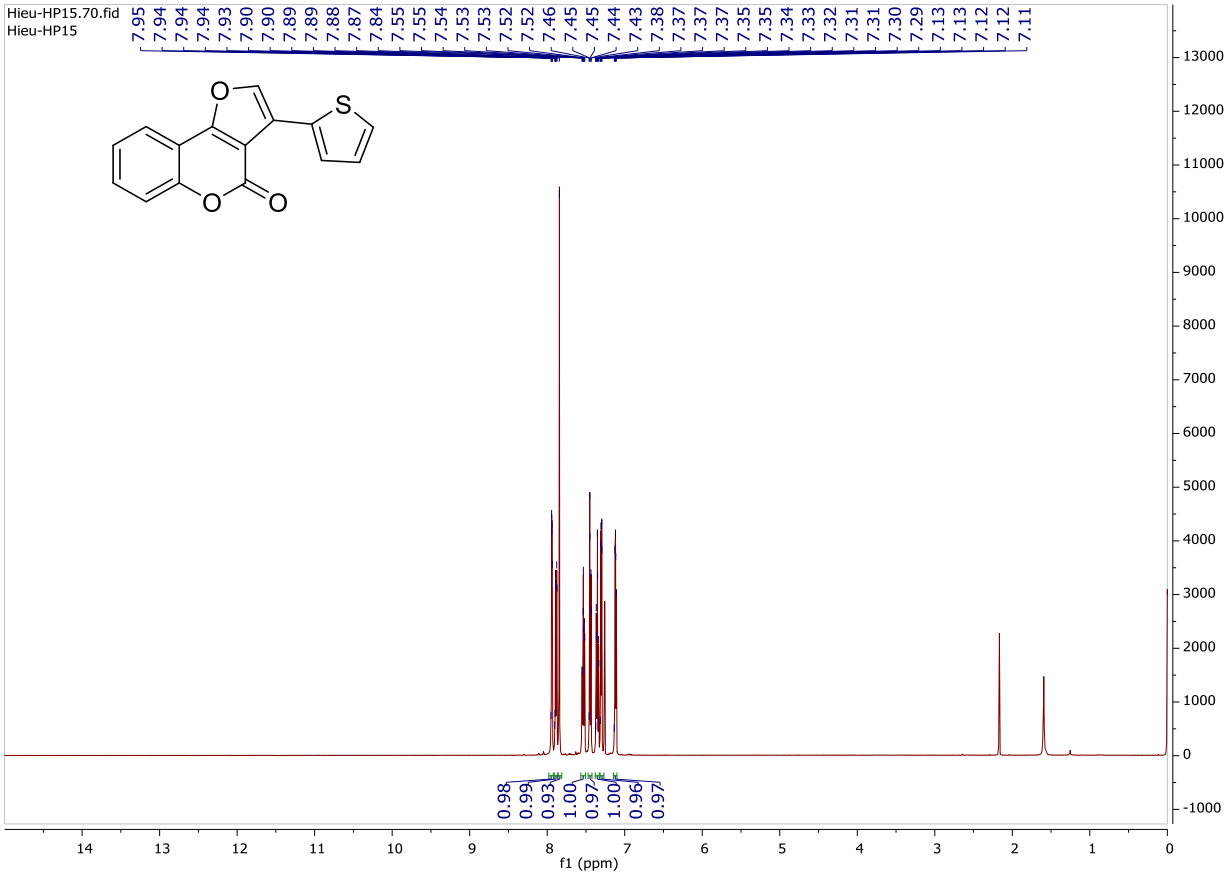
Br
1.00 1.01 2.01 3.03 1.02 1.06
f1 (ppm)

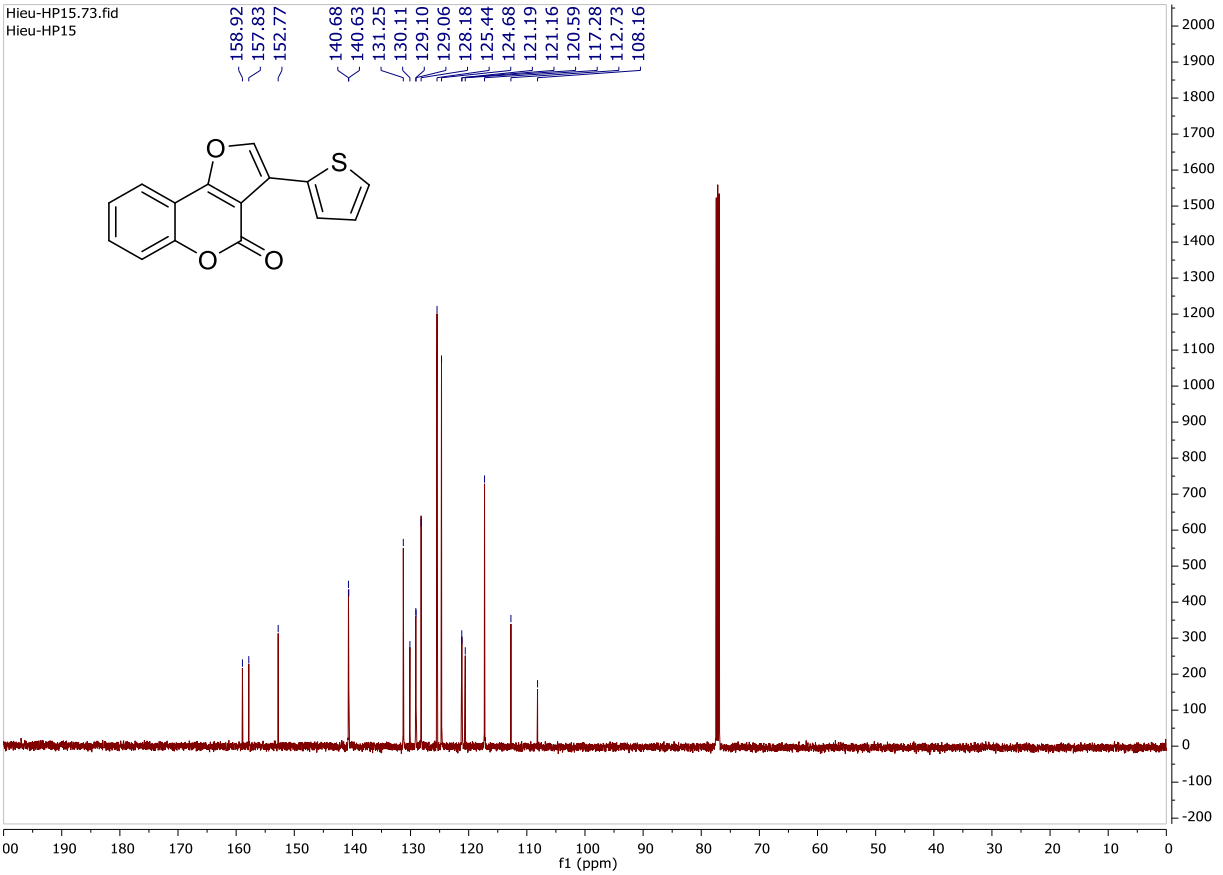


Spectroscopic data for 3-(thiophen-2-yl)-4H-furo[3,2-c]coumarin (HP15)

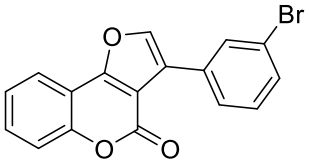


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.84 (s, 1H), 7.53 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.44 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.35 (td, *J* = 7.5, 1.1 Hz, 1H), 7.30 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.92, 157.83, 152.77, 140.68, 140.63, 131.25, 130.11, 129.10, 129.06, 128.18, 125.44, 124.68, 121.19, 121.16, 120.59, 117.28, 112.73, 108.16.


Hieu-HP15.70.fid
Hieu-HP15
7.95 7.94 7.94 7.94 7.93 7.90 7.90 7.89 7.89 7.88 7.87 7.84 7.55 7.55 7.54 7.53 7.53 7.52 7.52 7.46 7.45 7.45 7.44 7.43 7.38 7.37 7.37 7.37 7.35 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.13 7.13 7.12 7.12 7.11
O
S
O
O
0.98 0.99 0.93 1.00 0.97 1.00 0.96 0.97
13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

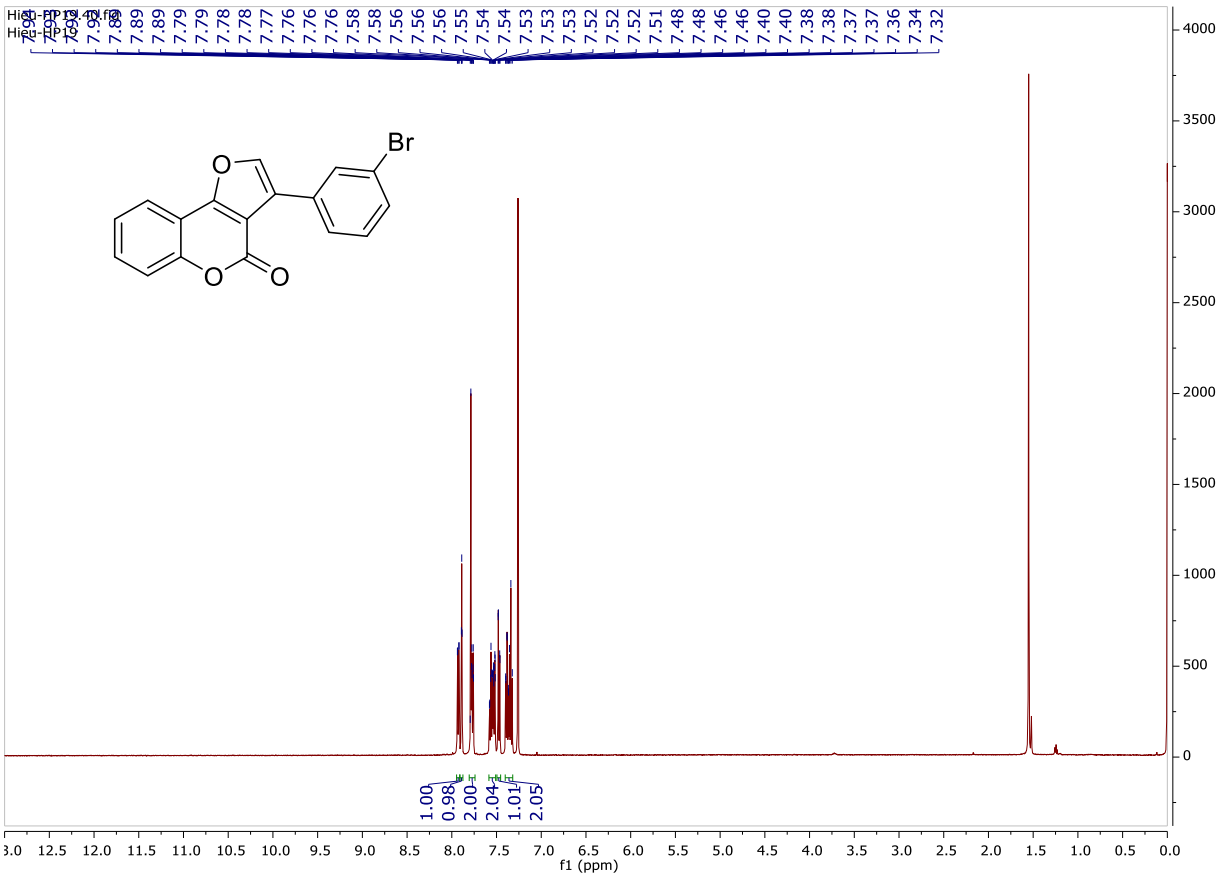


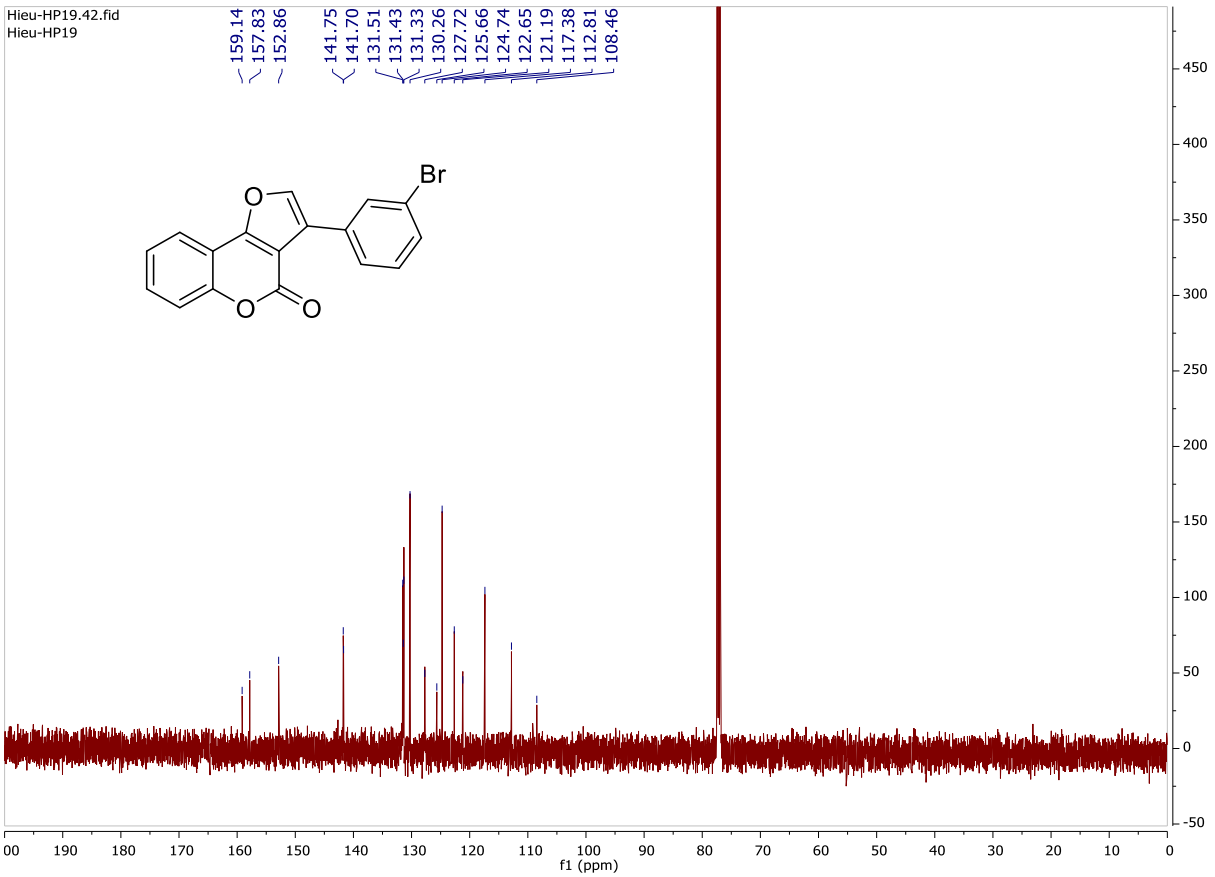
Spectroscopic data for 3-(3-bromophenyl)-4H-furo[3,2-c]coumarin (HP19)



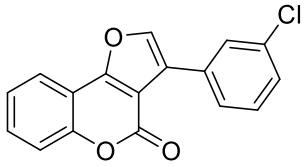
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.89 (t, *J* = 1.8 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.58 – 7.51 (m, 2H), 7.47 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.40 – 7.32 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.14, 157.83, 152.86, 141.75, 141.70, 131.51, 131.43, 131.33, 130.26, 127.72, 125.66, 124.74, 122.65, 121.19, 117.38, 112.81, 108.46.


Hieu-hp19.4.fid
Hieu-hp19
Br
O
O
O
1.00
0.98
2.00
2.04
1.01
2.05
f1 (ppm)

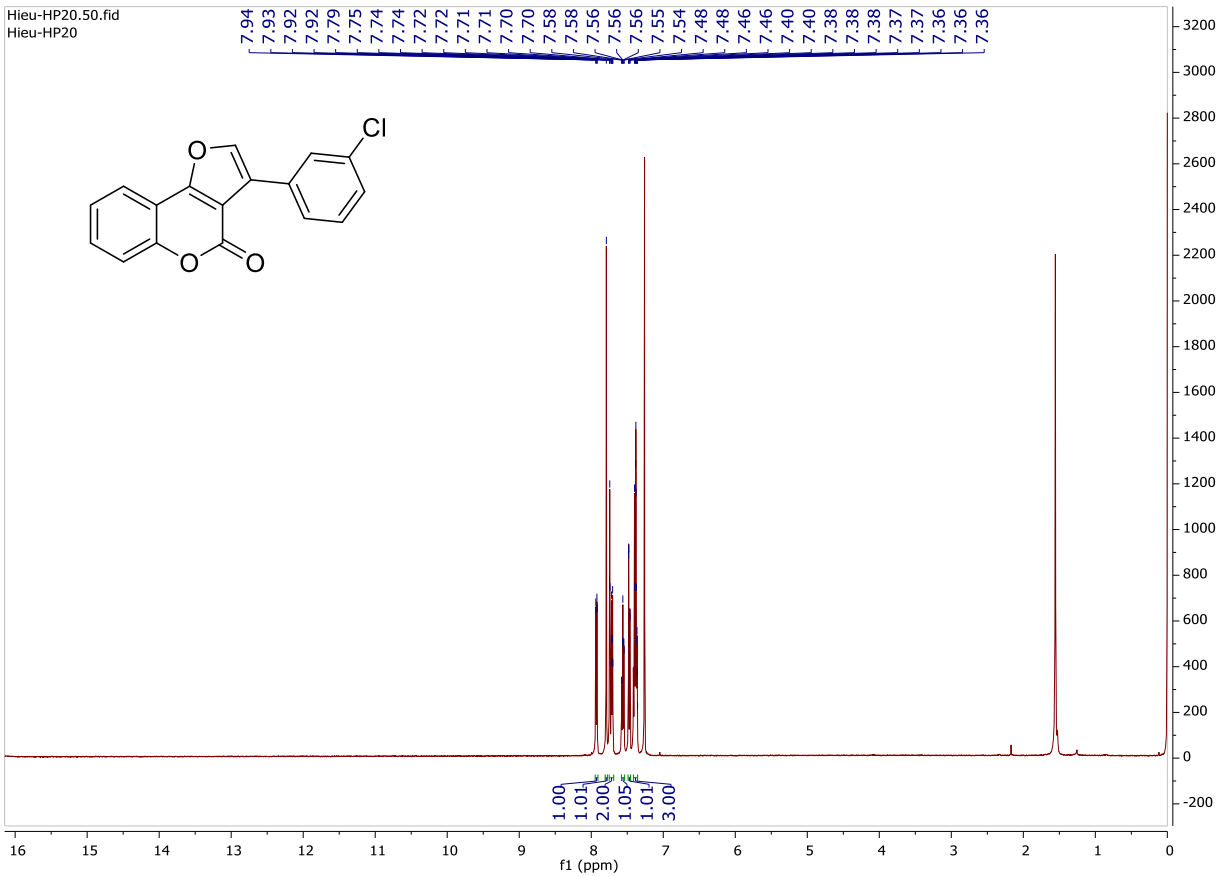


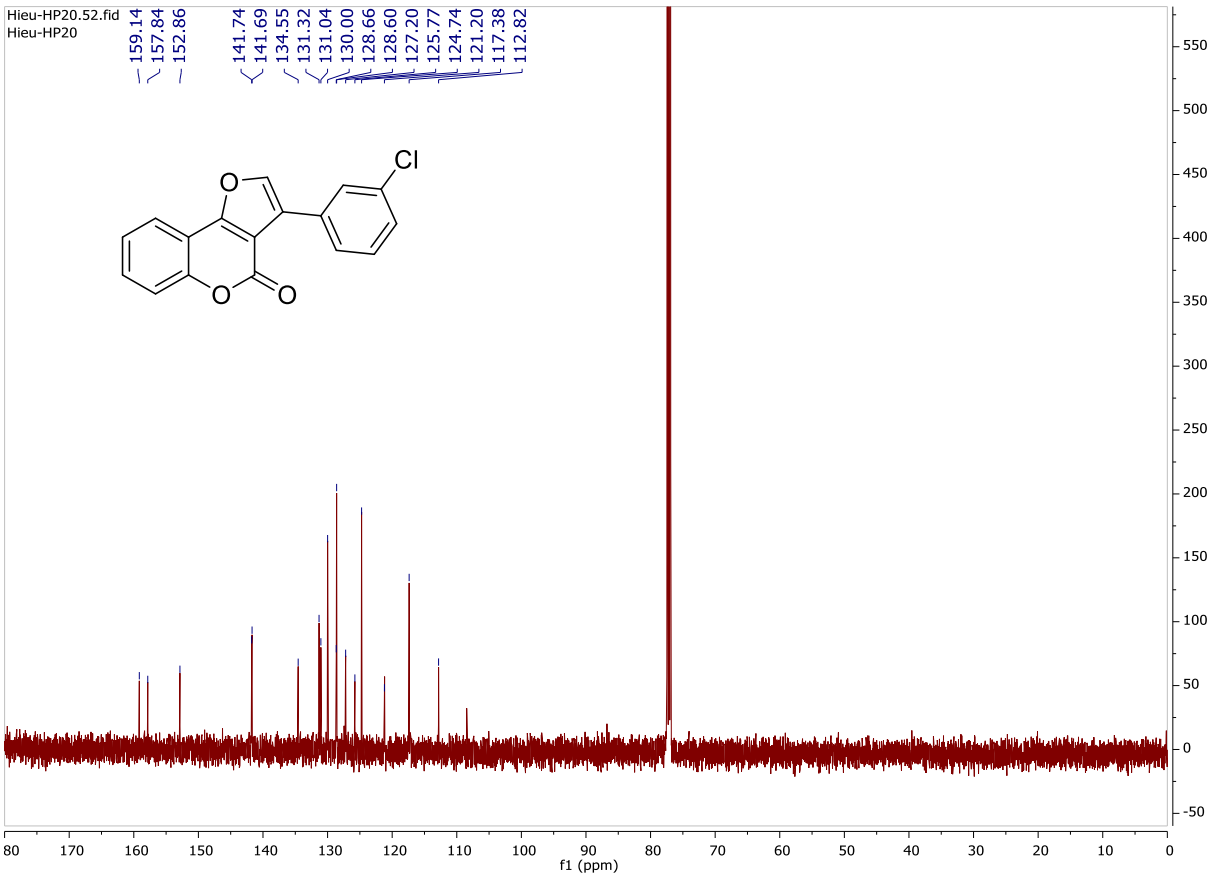
Spectroscopic data for 3-(3-chlorophenyl)-4H-furo[3,2-c]coumarin (HP20)



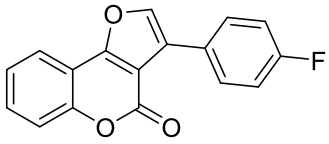
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.79 (s, 1H), 7.75 – 7.69 (m, 2H), 7.56 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.47 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.41 – 7.36 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.14, 157.84, 152.86, 141.74, 141.69, 134.55, 131.32, 131.04, 130.00, 128.66, 128.60, 127.20, 125.77, 124.74, 121.20, 117.38, 112.82.


Hieu-HP20.50.fid
Hieu-HP20
7.94 7.93 7.92 7.92 7.79 7.75 7.74 7.74 7.72 7.72 7.71 7.71 7.70 7.70 7.58 7.56 7.56 7.56 7.55 7.54 7.48 7.48 7.46 7.46 7.40 7.40 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.36
Cl
O
O
O
1.00 1.01 2.00 1.05 1.01 3.00
f1 (ppm)

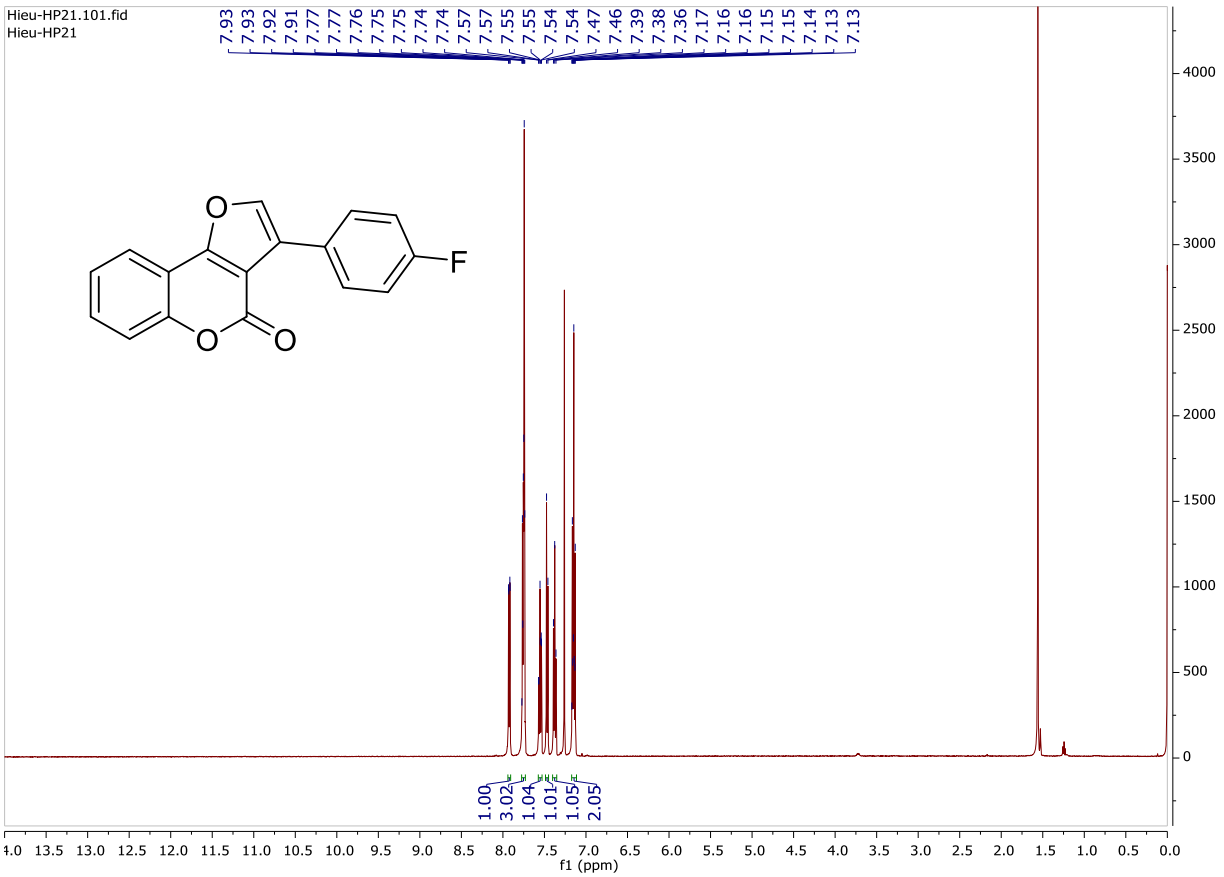


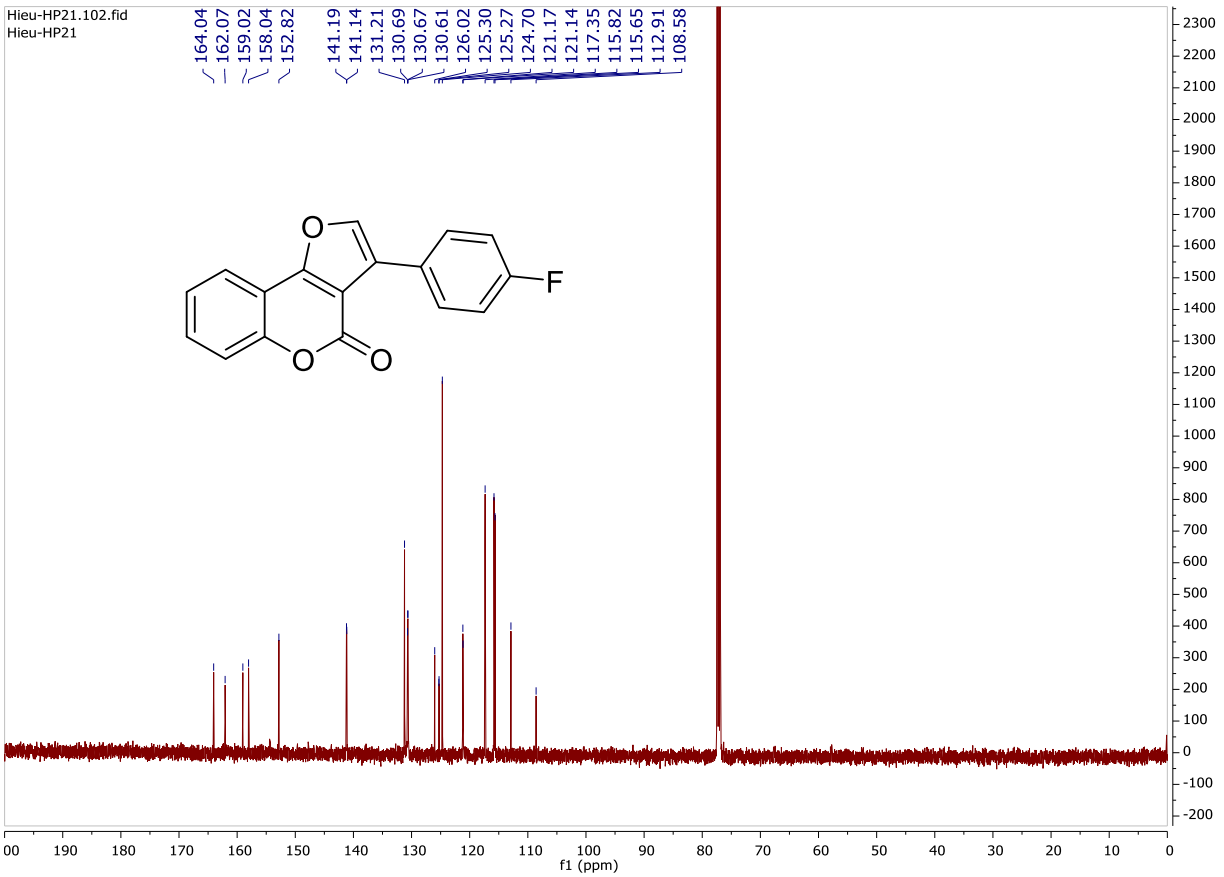
Spectroscopic data for 3-(3-fluorophenyl)-4H-furo[3,2-c]coumarin (HP21)



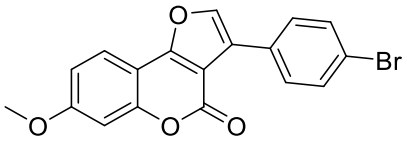
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.78 – 7.73 (m, 3H), 7.55 (td, *J* = 7.8, 7.1, 1.6 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.12 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.04, 162.07, 159.02, 158.04, 152.82, 141.19, 141.14, 131.21, 130.69, 130.67, 130.61, 126.02, 125.30, 125.27, 124.70, 121.17, 121.14, 117.35, 115.82, 115.65, 112.91, 108.58.


Hieu-HP21.101.fid
Hieu-HP21
7.93 7.93 7.92 7.91 7.77 7.77 7.76 7.75 7.75 7.74 7.74 7.57 7.57 7.55 7.55 7.54 7.54 7.47 7.46 7.39 7.38 7.36 7.17 7.16 7.16 7.15 7.15 7.14 7.13 7.13
O
F
O
O
1.00 3.02 1.04 1.01 1.05 2.05
4000
3500
3000
2500
2000
1500
1000
500
0
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

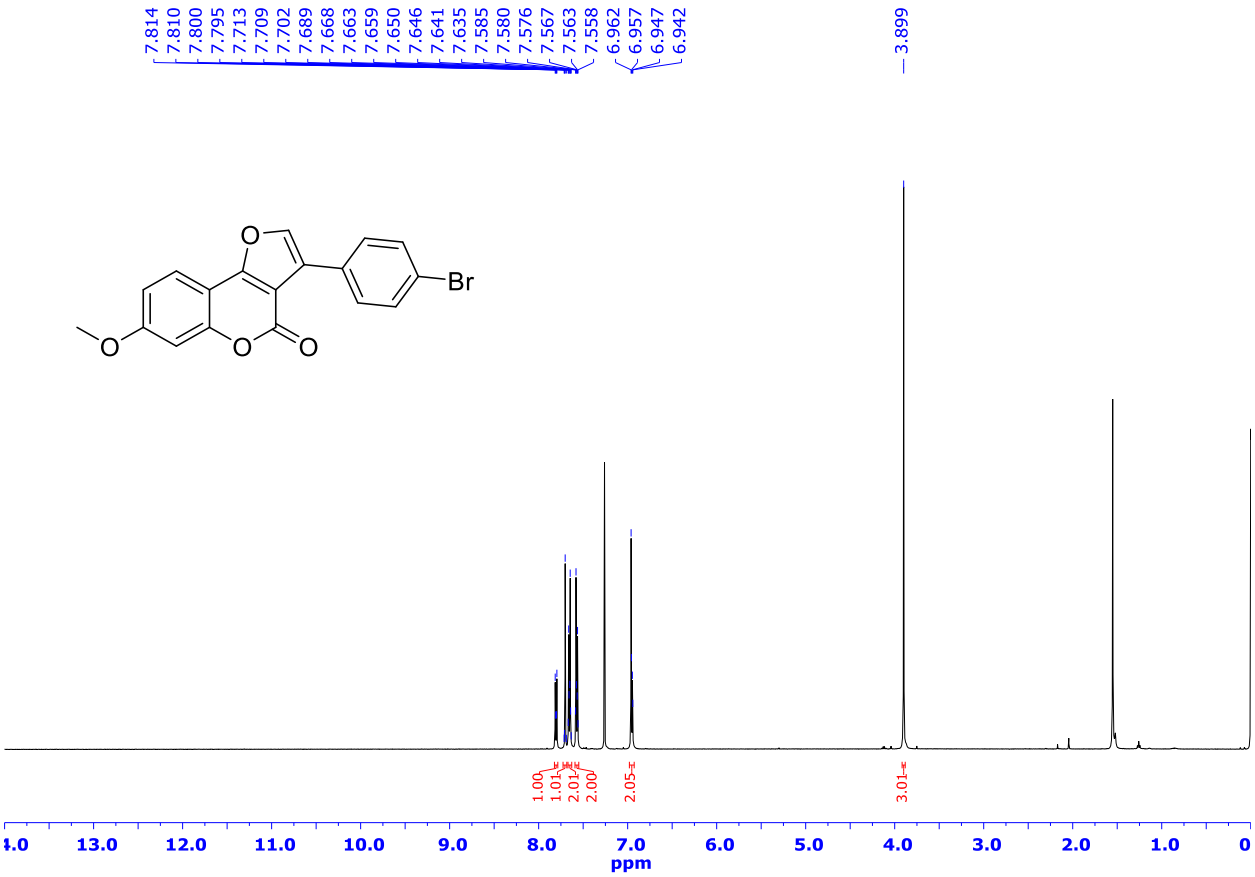


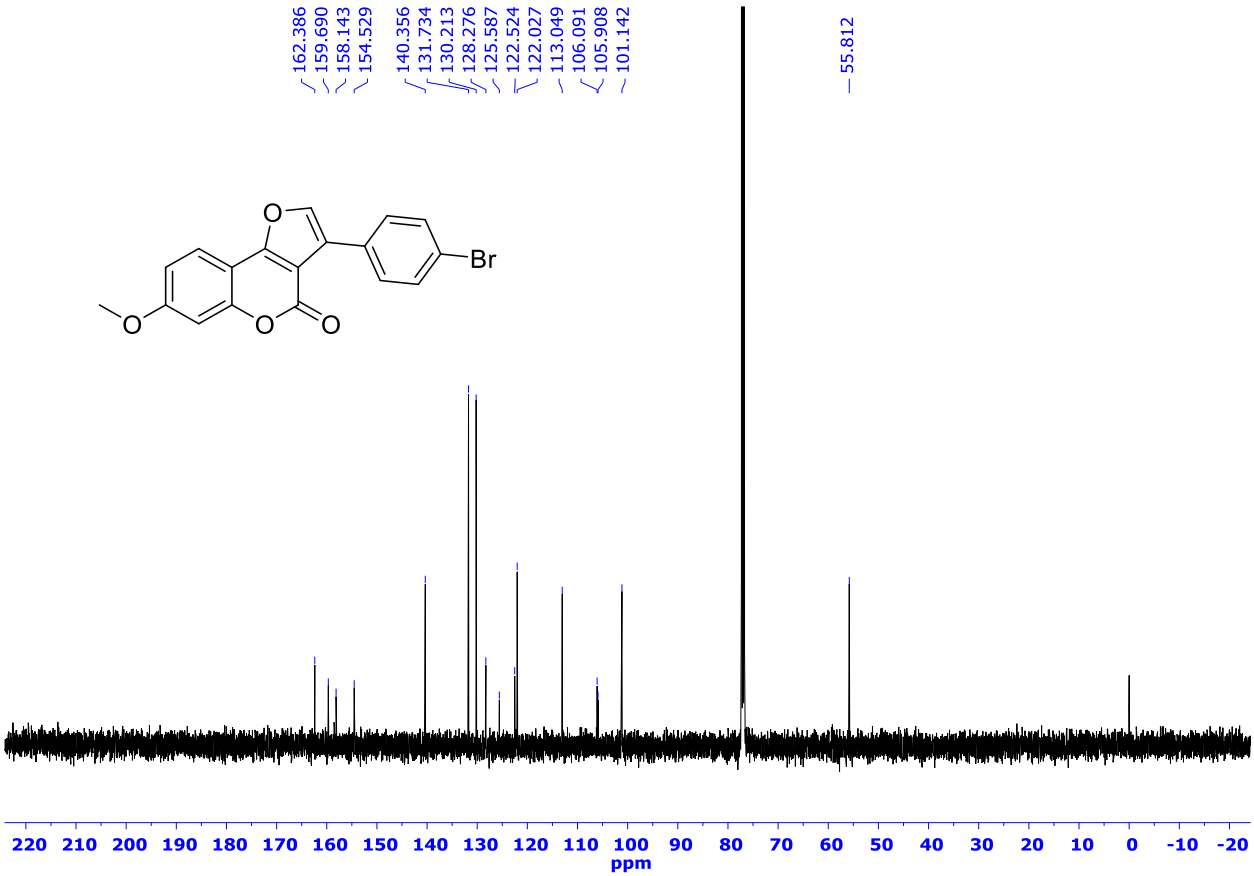
Spectroscopic data for 3-(4-bromophenyl)-7-methoxy-4H-furo[3,2-c]coumarin (HP24)



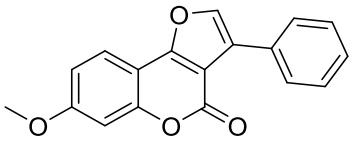
^{1}H NMR (500 MHz, CDCl3) δ 7.82 – 7.78 (m, 1H), 7.70 (s, 1H), 7.67 – 7.63 (m, 2H), 7.59 – 7.55 (m, 2H), 6.98 – 6.93 (m, 2H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.39, 159.69, 158.14, 154.53, 140.36, 131.73, 130.21, 128.28, 125.59, 122.52, 122.03, 113.05, 106.09, 105.91, 101.14, 55.81.


7.814
7.810
7.800
7.795
7.713
7.709
7.702
7.689
7.668
7.663
7.659
7.650
7.646
7.641
7.635
7.585
7.580
7.576
7.567
7.563
7.558
6.962
6.957
6.947
6.942
3.899
O
Br
O
O
O
1.00
1.01
2.01
2.00
2.05
3.01
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm

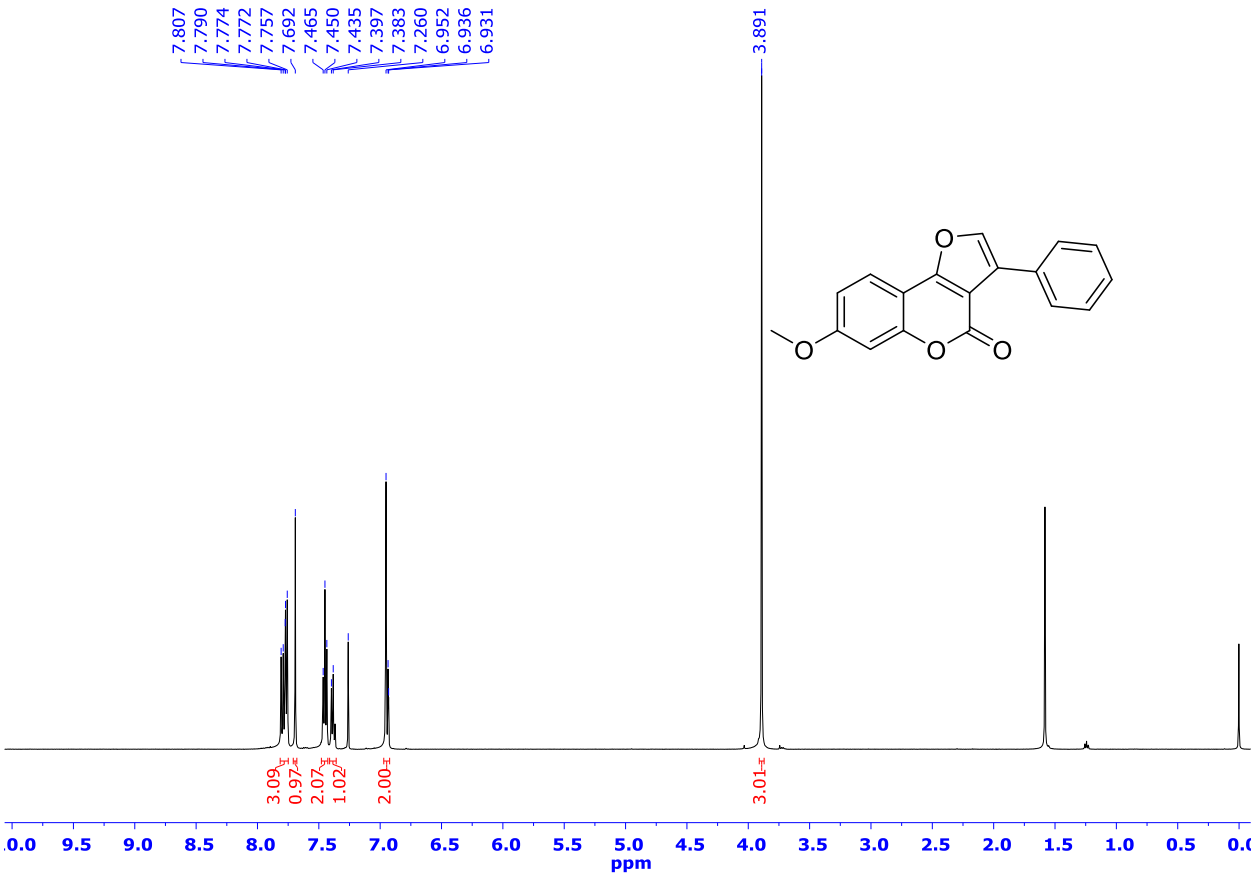


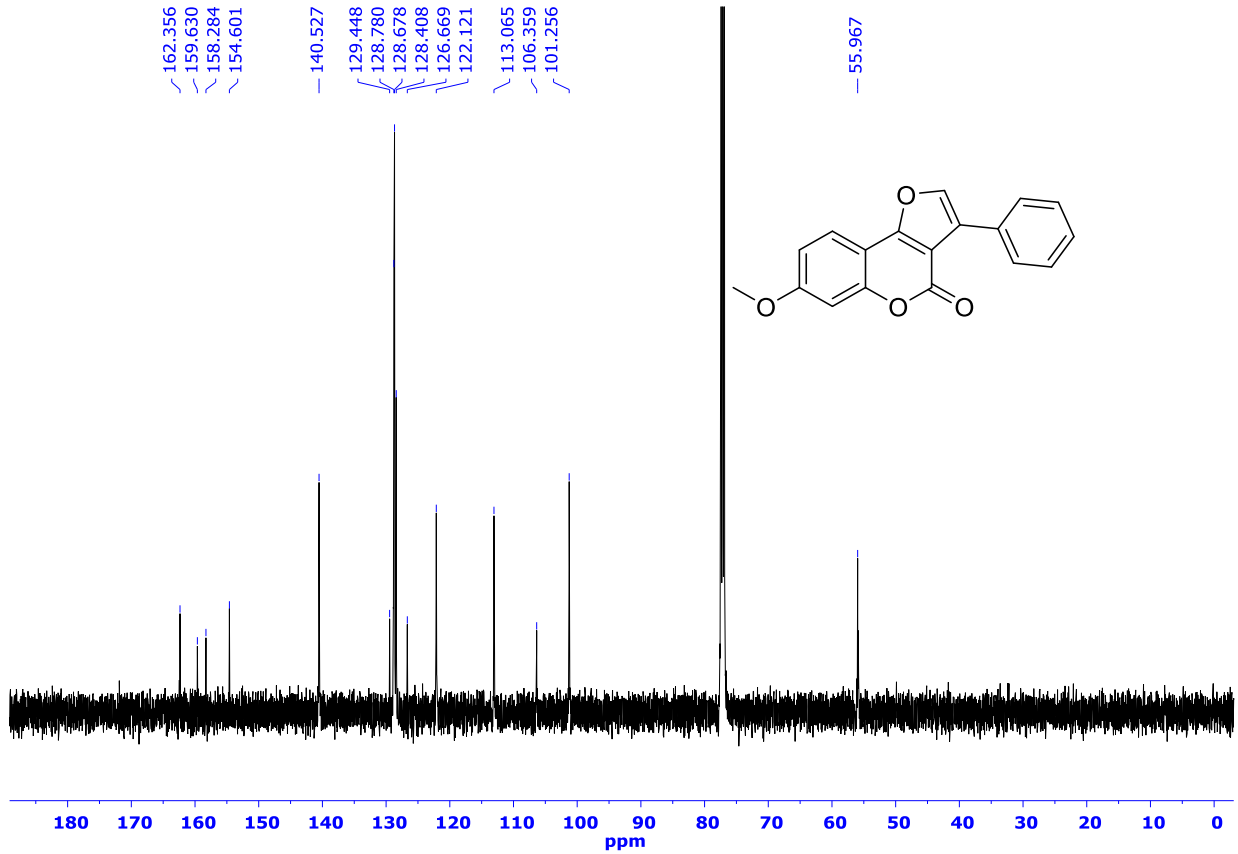
Spectroscopic data for 3-phenyl-7-methoxy-4H-furo[3,2-c]coumarin (HP25)



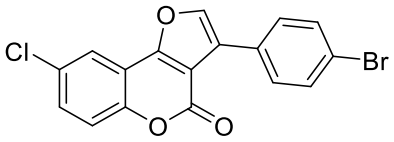
^{1}H NMR (500 MHz, CDCl3) δ 7.81 – 7.75 (m, 3H), 7.69 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 1H), 6.97 – 6.92 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.36, 159.63, 158.28, 154.60, 140.53, 129.45, 128.78, 128.68, 128.41, 126.67, 122.12, 113.07, 106.36, 101.26, 55.97.

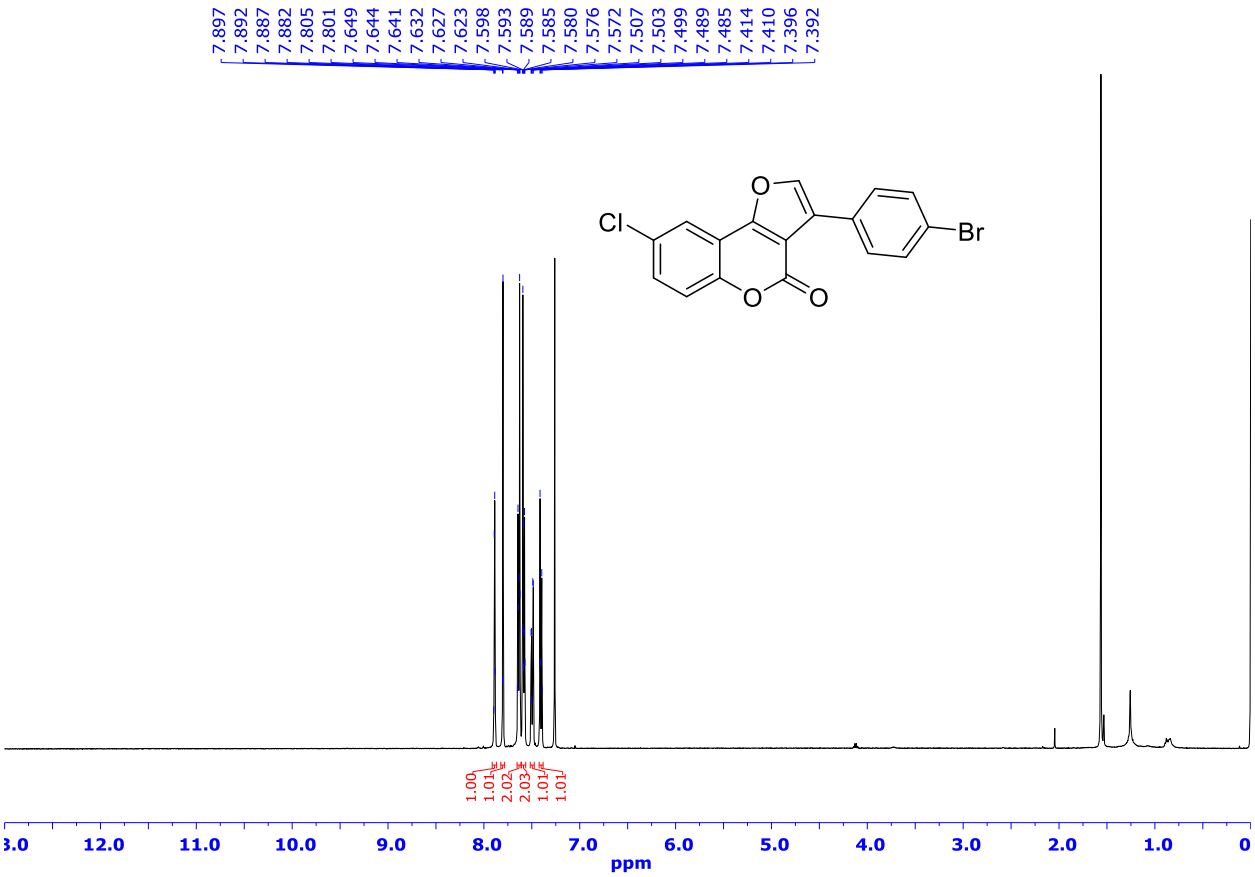

7.807
7.790
7.774
7.772
7.757
7.692
7.465
7.450
7.435
7.397
7.383
7.260
6.952
6.936
6.931
3.891
O
O
O
O
3.09
0.97
2.07
1.02
2.00
3.01
ppm

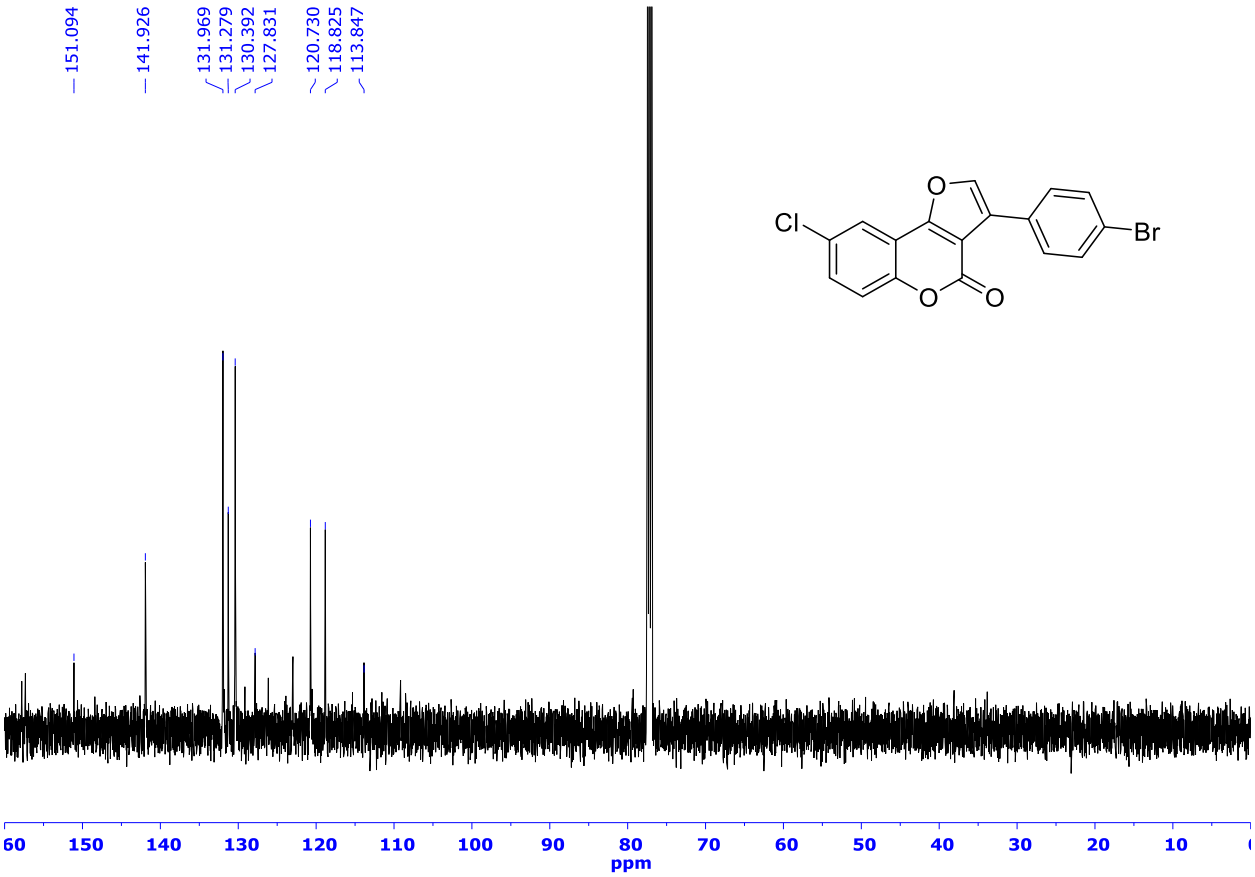


Spectroscopic data for 3-(4-bromophenyl)-8-chloro-4H-furo[3,2-c]coumarin (HP26)

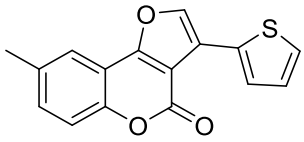


^{1}H NMR (500 MHz, CDCl3) δ 7.89 (t, *J* = 2.5 Hz, 1H), 7.80 (s, 1H), 7.66 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 7.50 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.09, 141.93, 131.97, 131.28, 130.39, 127.83, 120.73, 118.82, 113.85.


7.897
7.892
7.887
7.882
7.805
7.801
7.649
7.644
7.641
7.632
7.627
7.623
7.598
7.593
7.589
7.585
7.580
7.576
7.572
7.507
7.503
7.499
7.489
7.485
7.414
7.410
7.396
7.392
Cl
O
Br
O
O
1.00
1.01
2.02
2.03
1.01
1.01
3.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm

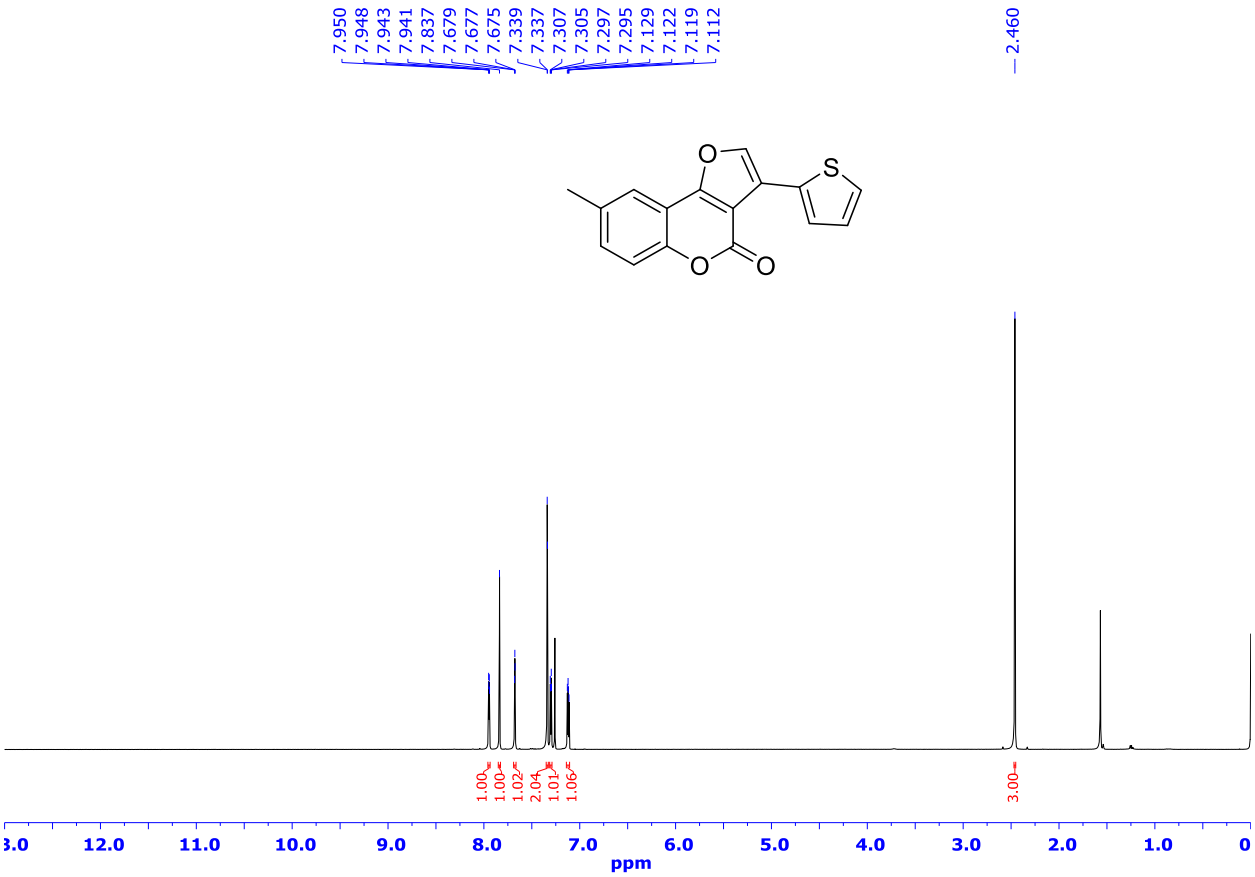


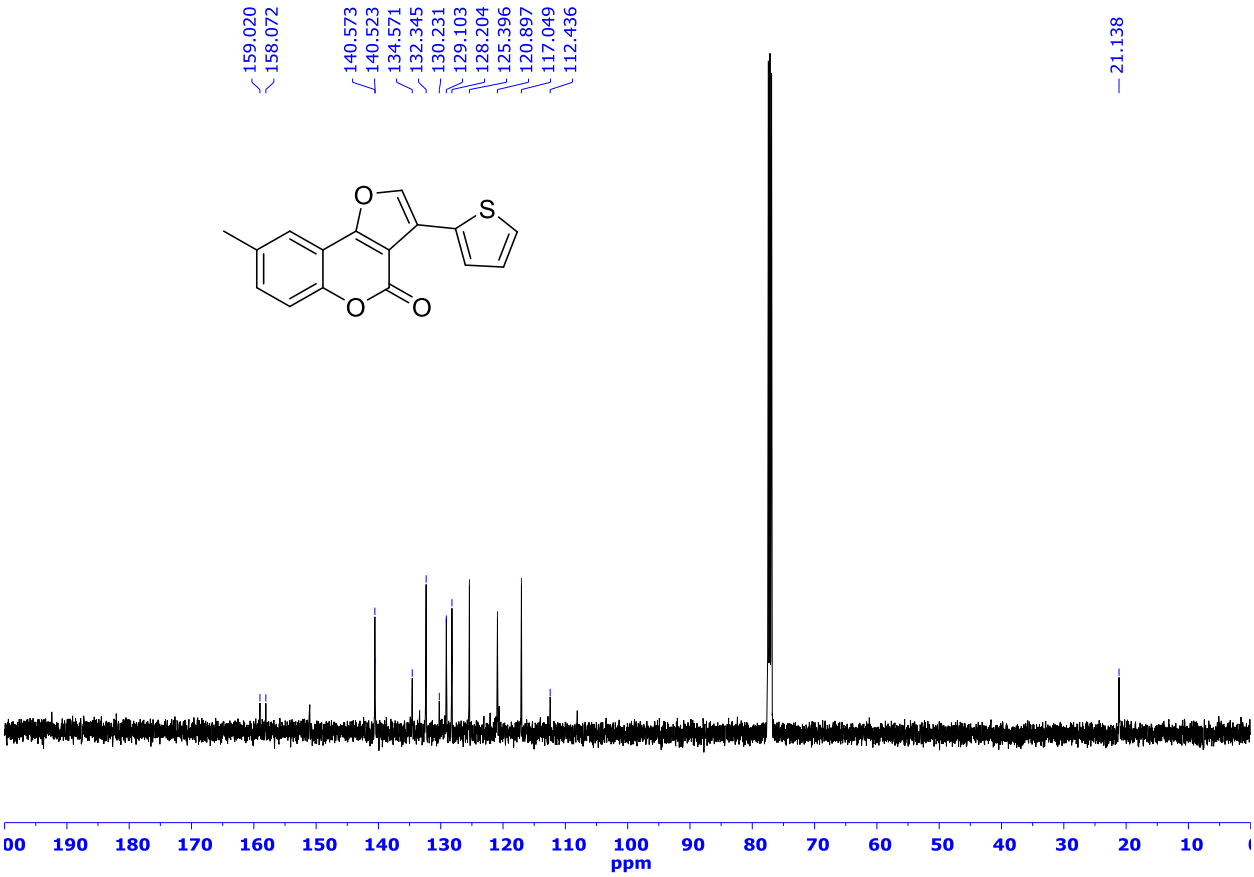
Spectroscopic data for 8-methyl-(3-thiophen-2-yl)-4H-furo[3,2-c]coumarin (HP27)



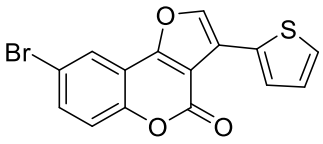
^{1}H NMR (500 MHz, CDCl3) δ 7.95 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.84 (s, 1H), 7.69 – 7.67 (m, 1H), 7.34 (d, *J* = 1.2 Hz, 2H), 7.30 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.02, 158.07, 140.57, 140.52, 134.57, 132.35, 130.23, 129.10, 128.20, 125.40, 120.90, 117.05, 112.44, 21.14.


7.950
7.948
7.943
7.941
7.837
7.679
7.677
7.675
7.339
7.337
7.307
7.305
7.297
7.295
7.129
7.122
7.119
7.112
2.460
O
S
O
O
1.00
1.00
1.02
2.04
1.01
1.06
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm

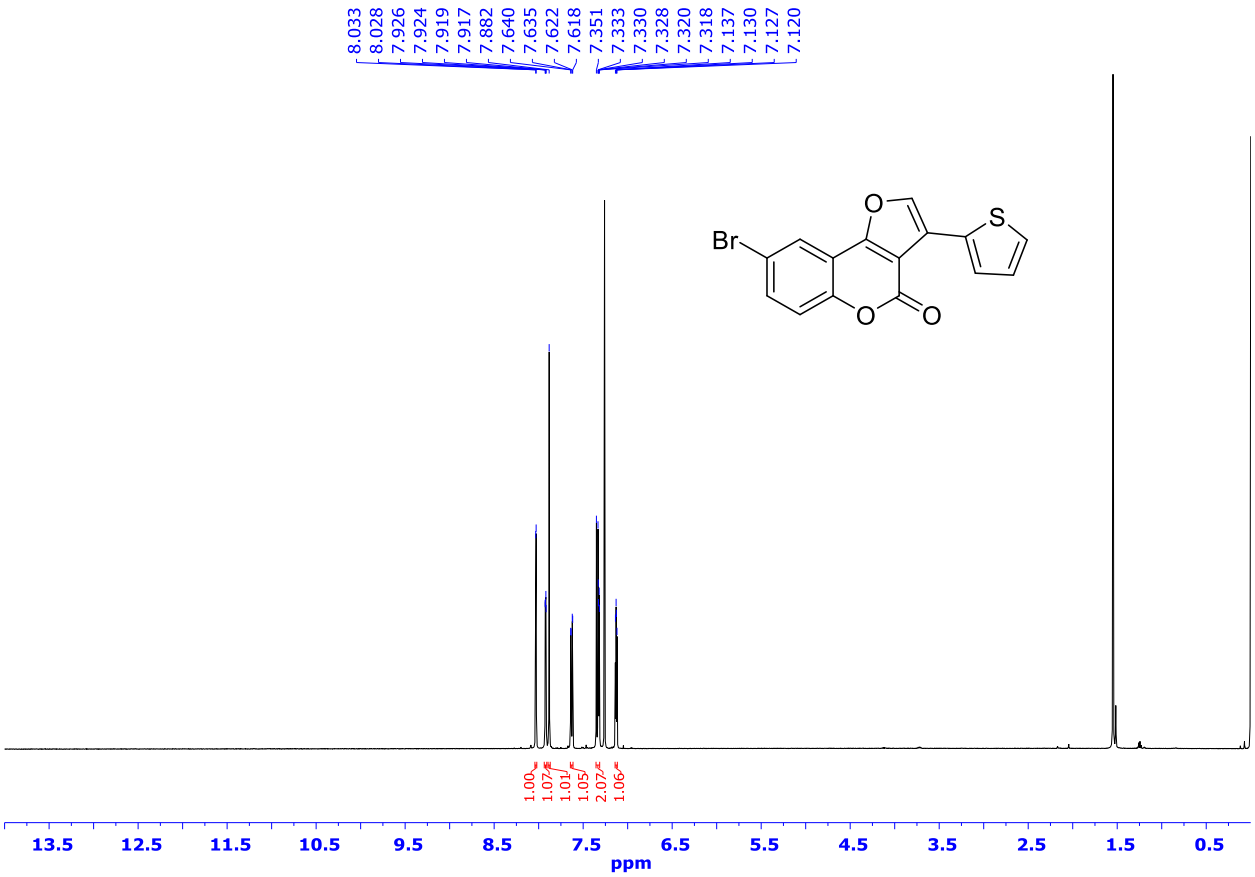


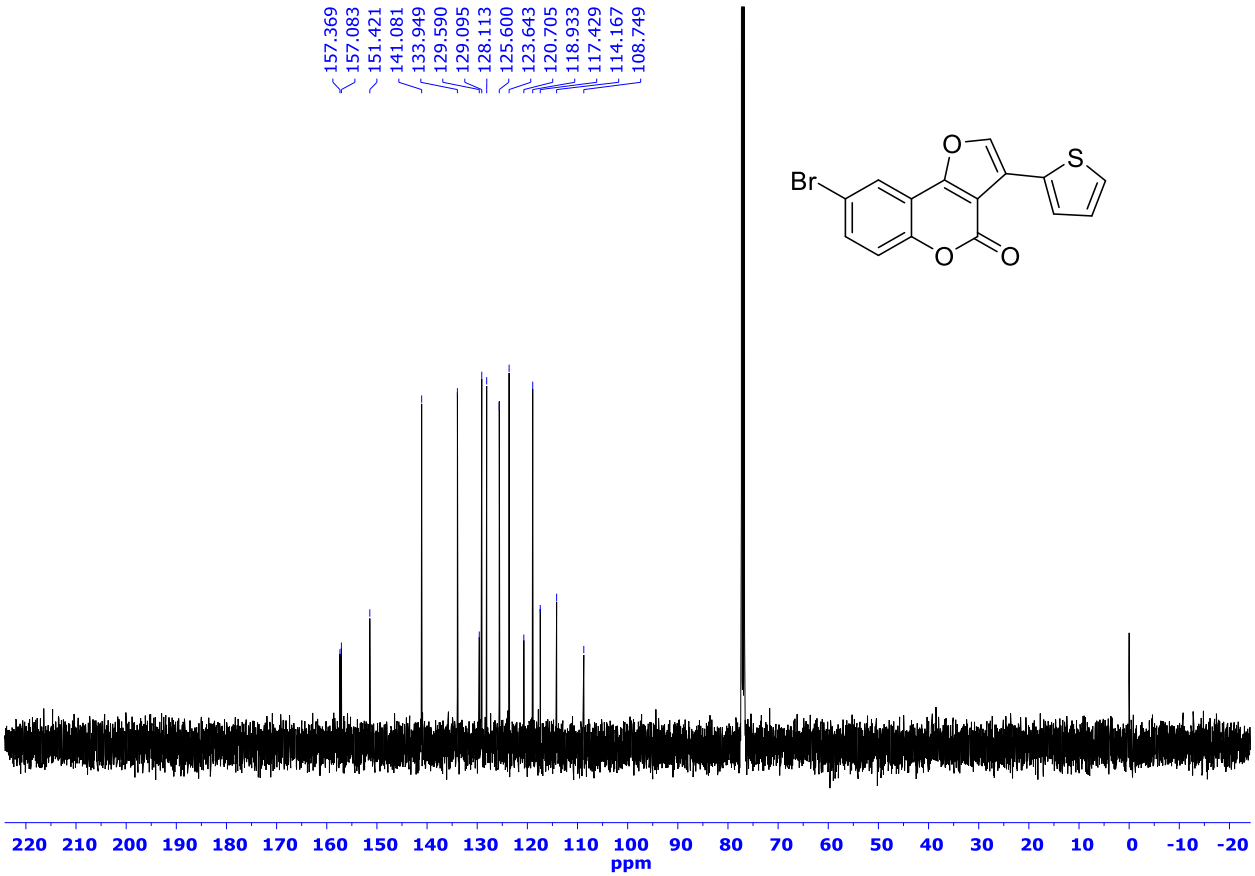
Spectroscopic data for 8-bromo-(3-thiophen-2-yl)-4H-furo[3,2-c]coumarin (HP28)



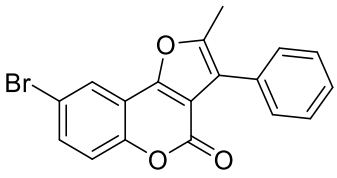
^{1}H NMR (500 MHz, CDCl3) δ 8.03 (d, *J* = 2.3 Hz, 1H), 7.92 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.88 (s, 1H), 7.63 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.13 (dd, *J* = 5.1, 3.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.37, 157.08, 151.42, 141.08, 133.95, 129.59, 129.10, 128.11, 125.60, 123.64, 120.70, 118.93, 117.43, 114.17, 108.75.

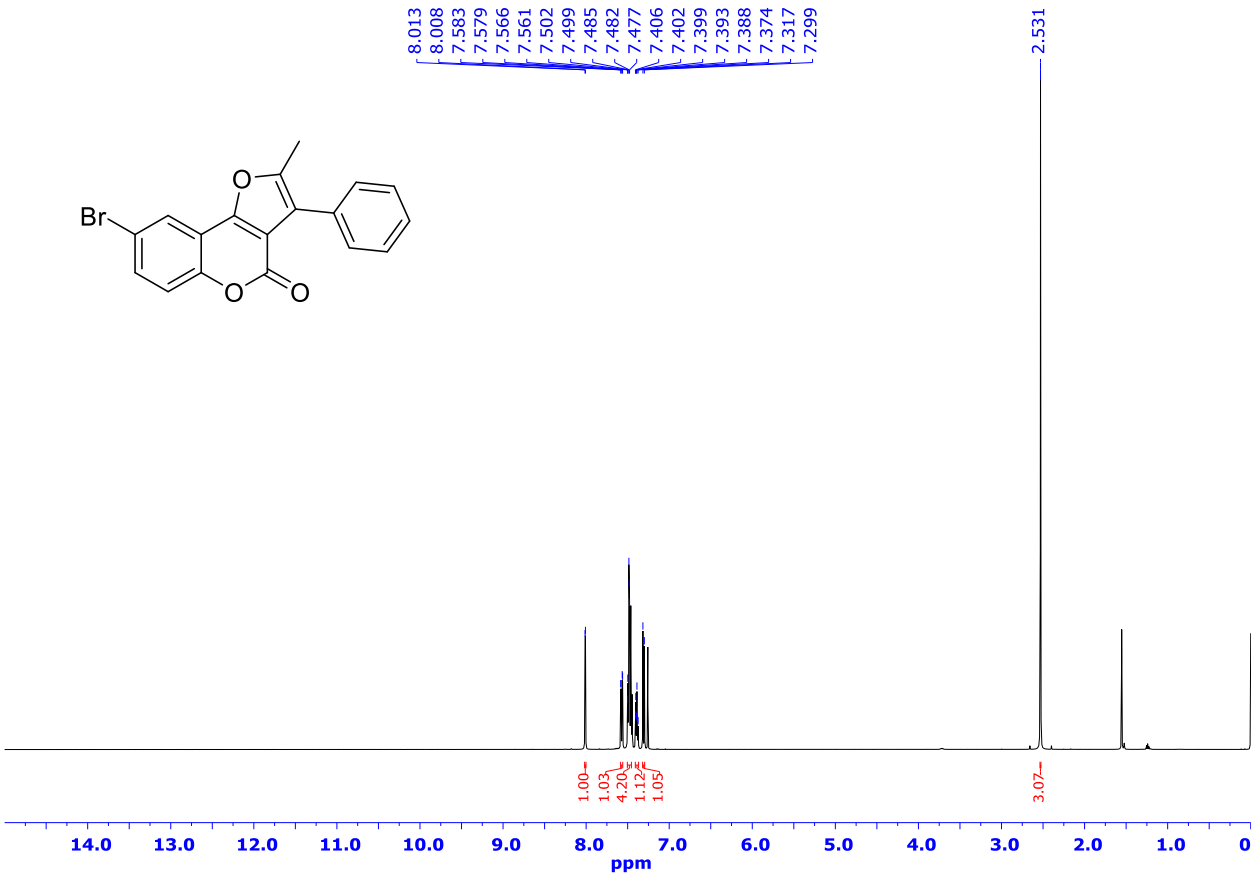

8.033
8.028
7.926
7.924
7.919
7.917
7.882
7.640
7.635
7.622
7.618
7.351
7.333
7.330
7.328
7.320
7.318
7.137
7.130
7.127
7.120
Br
O
S
O
O
1.00
1.07
1.01
1.05
2.07
1.06
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm

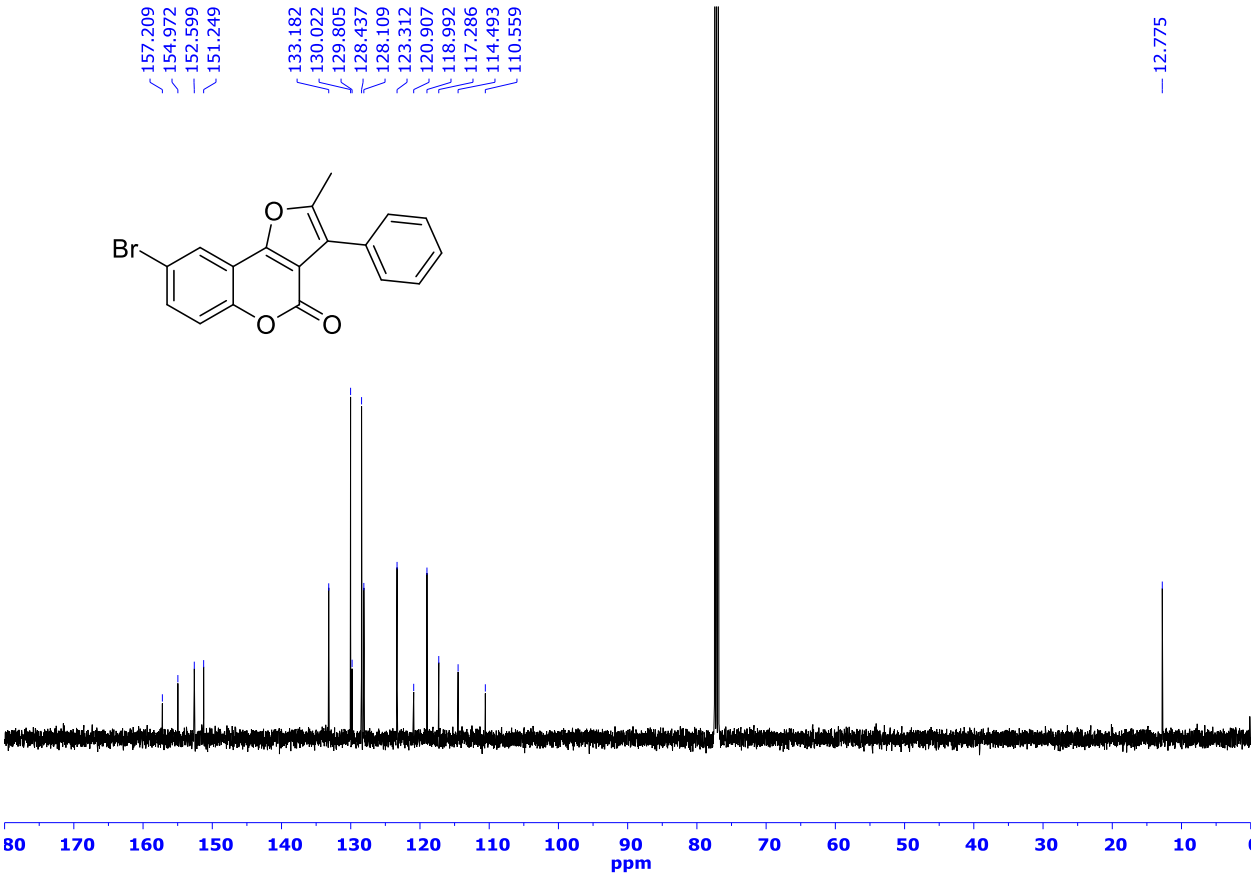


Spectroscopic data for 8-bromo-2-methyl-3-phenyl-4H-furo[3,2-c]coumarin (HP29)

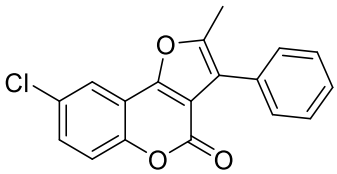


^{1}H NMR (500 MHz, CDCl3) δ 8.01 (d, *J* = 2.4 Hz, 1H), 7.57 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.51 – 7.44 (m, 4H), 7.42 – 7.36 (m, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 2.53 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.21, 154.97, 152.60, 151.25, 133.18, 130.02, 129.81, 128.44, 128.11, 123.31, 120.91, 118.99, 117.29, 114.49, 110.56, 12.77.


8.013
8.008
7.583
7.579
7.566
7.561
7.502
7.499
7.485
7.482
7.477
7.406
7.402
7.399
7.393
7.388
7.374
7.317
7.299
2.531
Br
O
O
O
1.00
1.03
4.20
1.12
1.05
3.07
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm

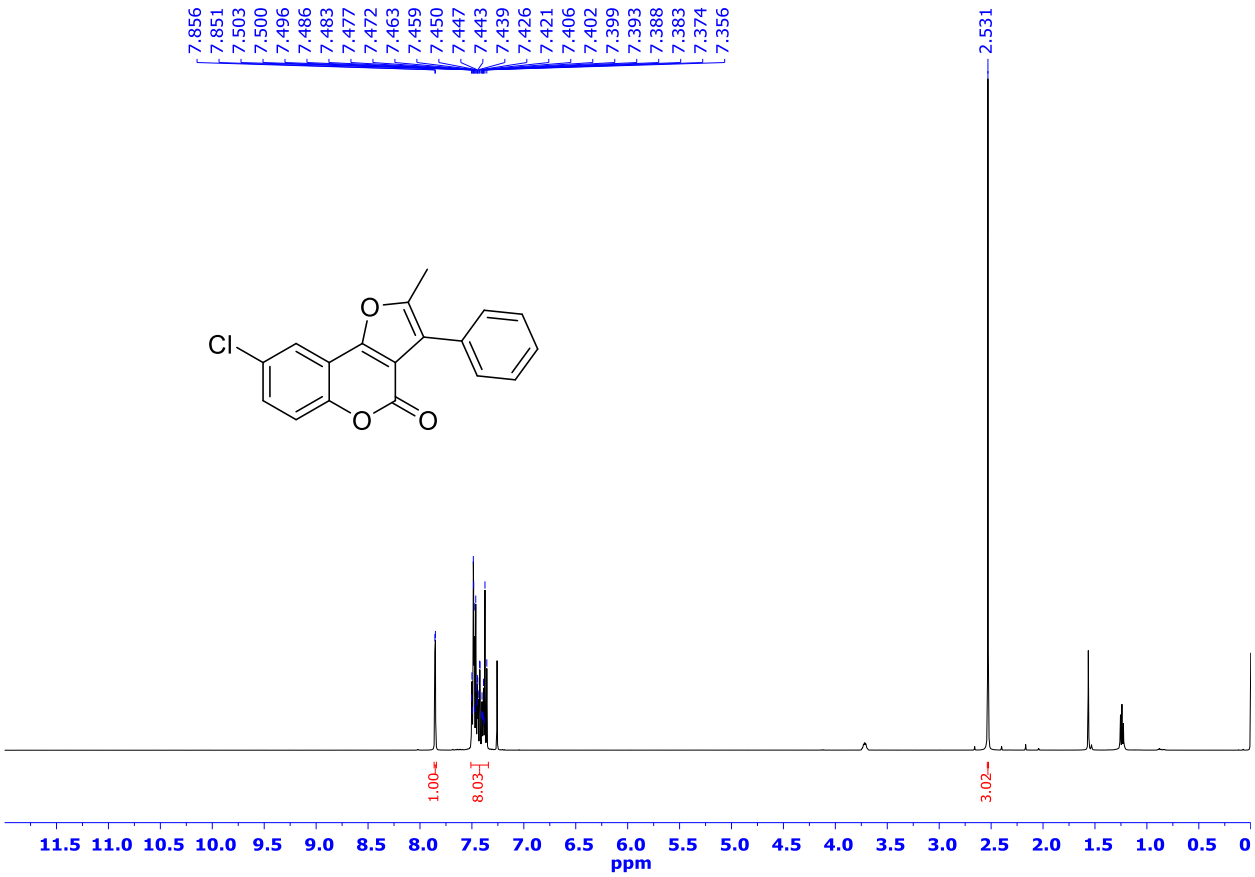


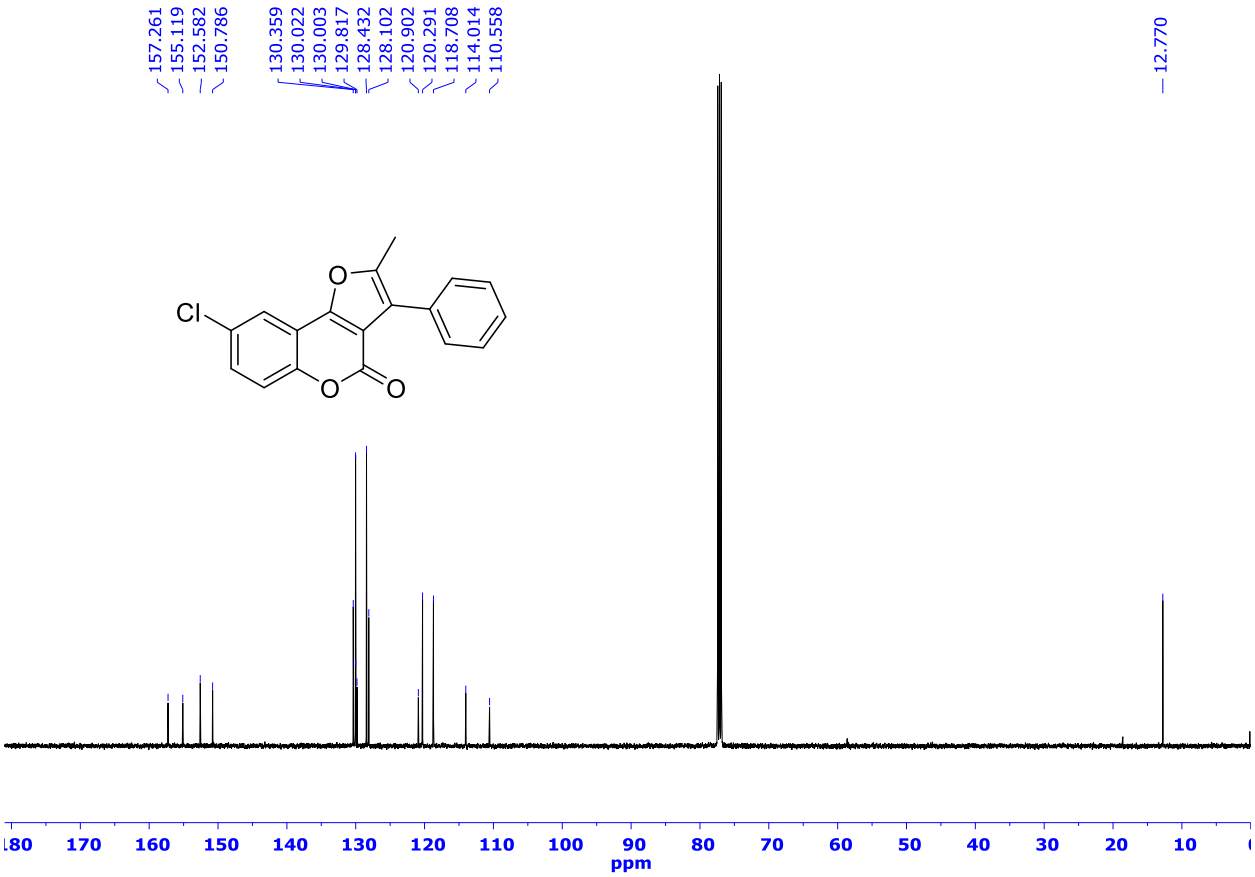
Spectroscopic data for 8-chloro-2-methyl-3-phenyl-4H-furo[3,2-c]coumarin (HP30)



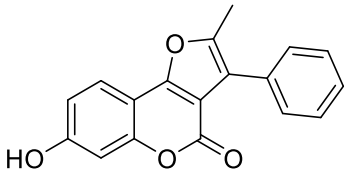
^{1}H NMR (500 MHz, CDCl3) δ 7.85 (d, *J* = 2.4 Hz, 1H), 7.52 – 7.34 (m, 8H), 2.53 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.26, 155.12, 152.58, 150.79, 130.36, 130.02, 130.00, 129.82, 128.43, 128.10, 120.90, 120.29, 118.71, 114.01, 110.56, 12.77.

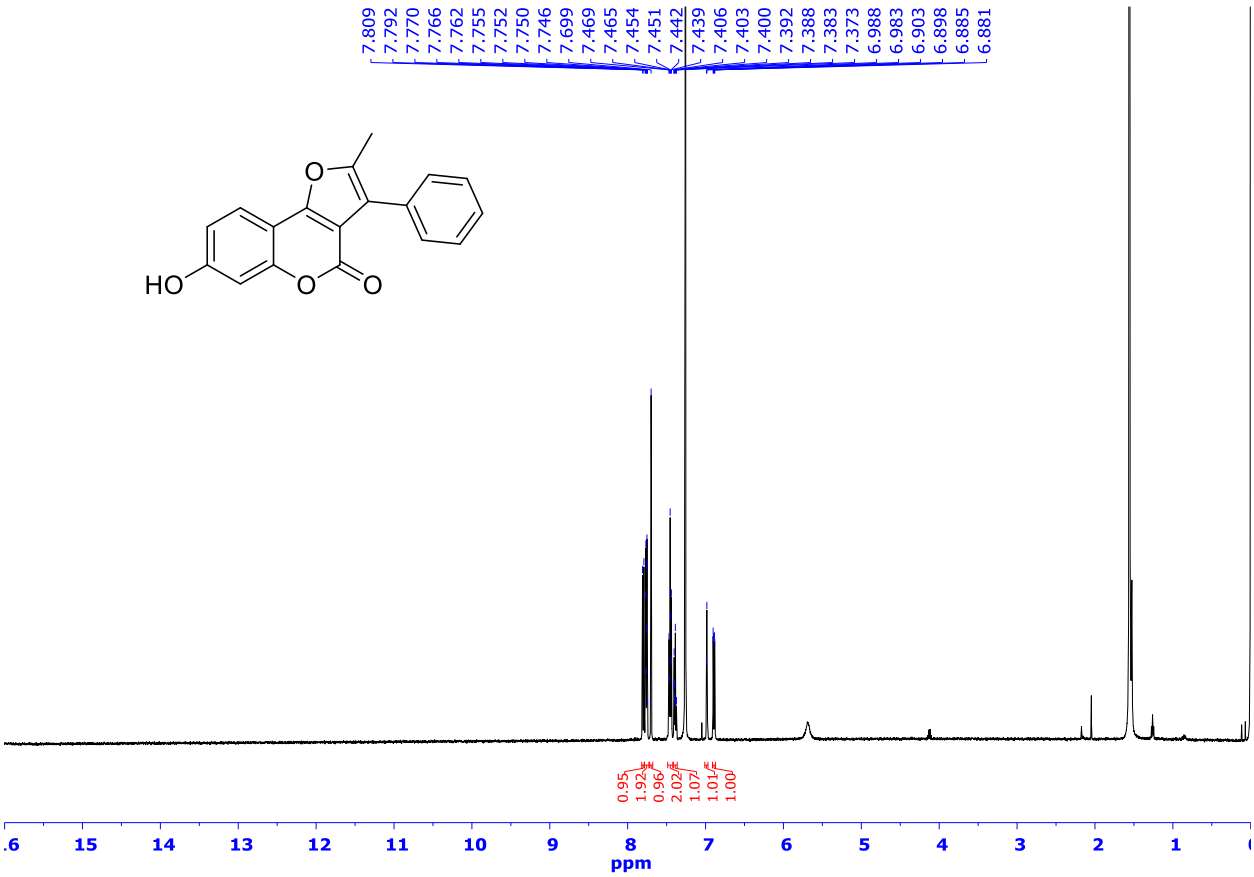

7.856
7.851
7.503
7.500
7.496
7.486
7.483
7.477
7.472
7.463
7.459
7.450
7.447
7.443
7.439
7.426
7.421
7.406
7.402
7.399
7.393
7.388
7.383
7.374
7.356
2.531
Cl
O
O
O
1.00
8.03
3.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
ppm

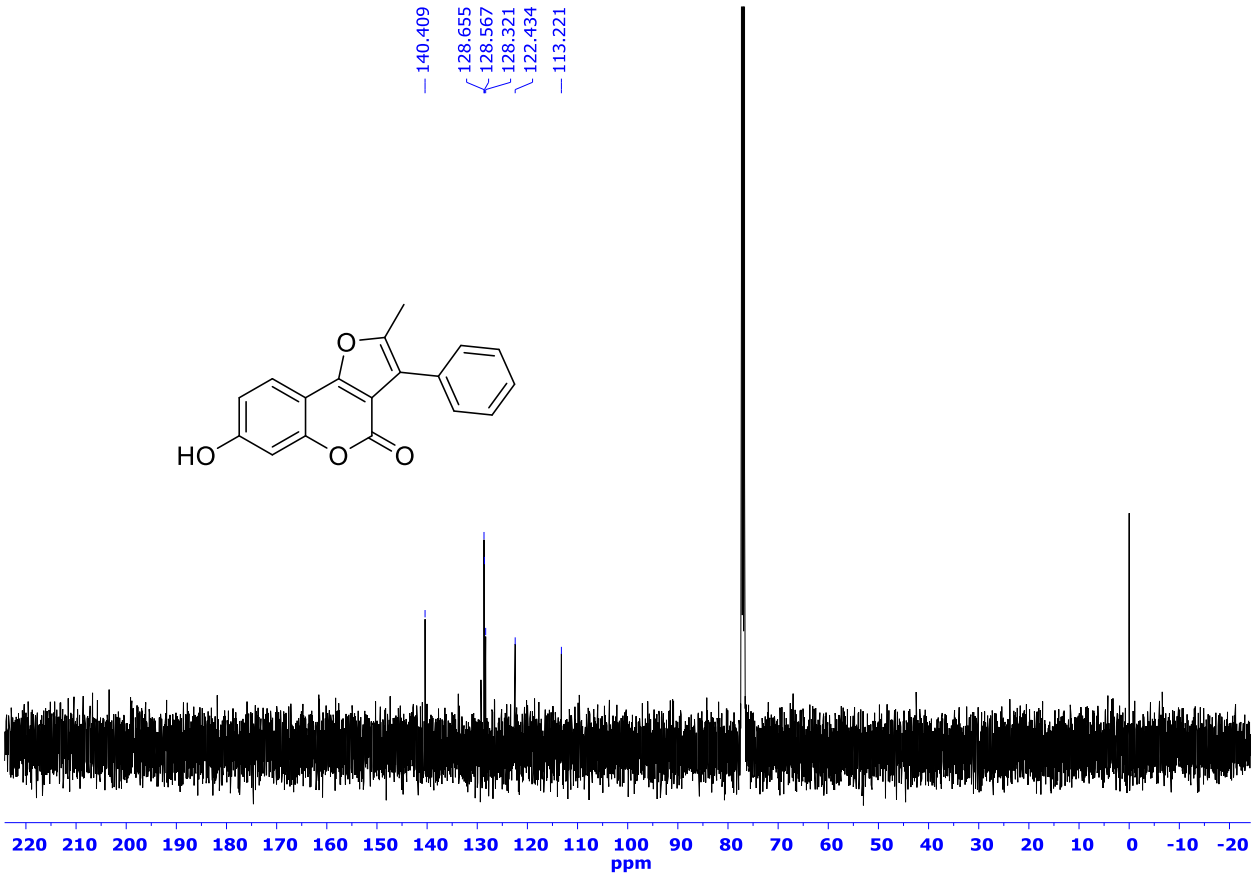


Spectroscopic data for 7-hydroxy-2-methyl-3-phenyl-4H-furo[3,2-c]coumarin (HP31)

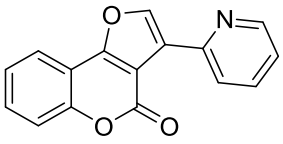


^{1}H NMR (500 MHz, CDCl3) δ 7.80 (d, *J* = 8.6 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.70 (s, 1H), 7.45 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.41 – 7.37 (m, 1H), 6.99 (d, *J* = 2.6 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.41, 128.65, 128.57, 128.32, 122.43, 113.22.

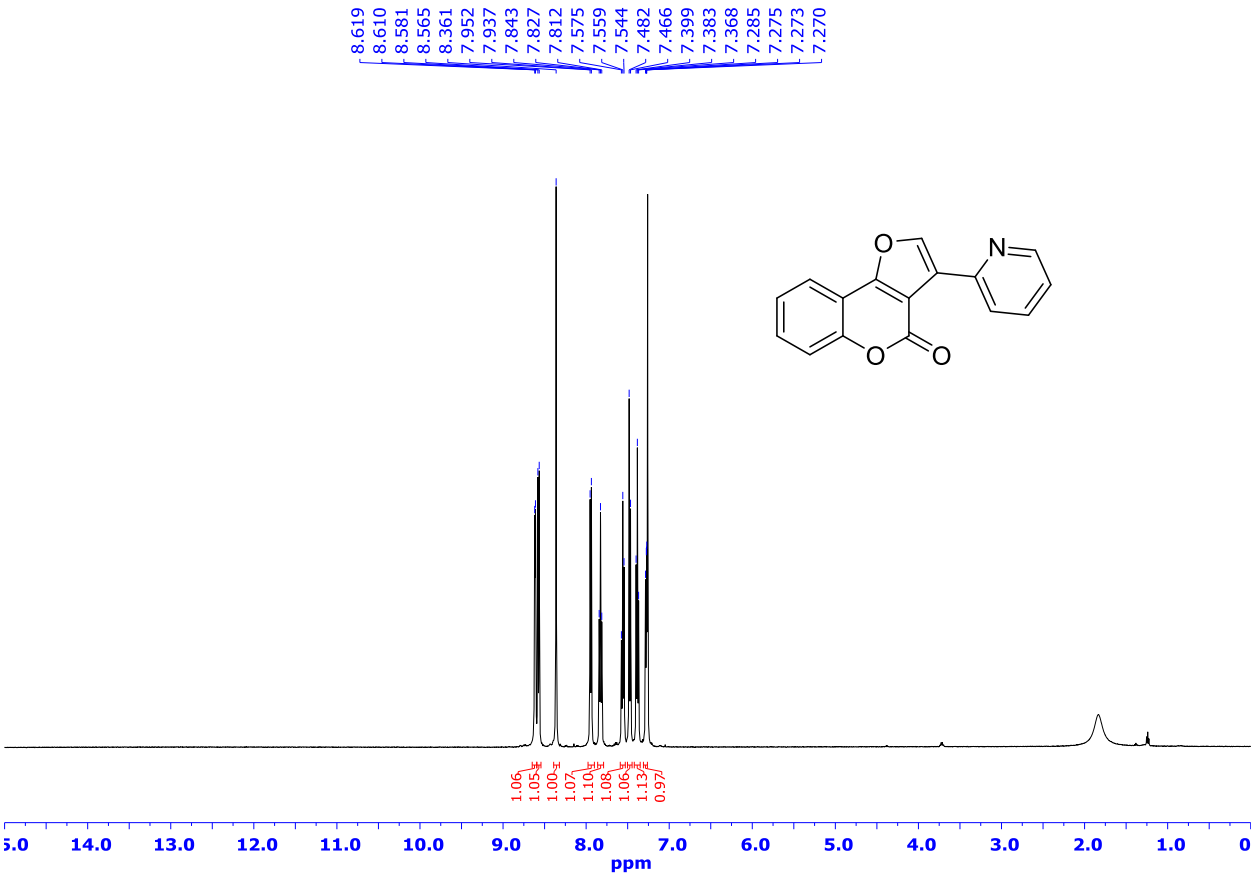

7.809
7.792
7.770
7.766
7.762
7.755
7.752
7.750
7.746
7.699
7.469
7.465
7.454
7.451
7.442
7.439
7.406
7.403
7.400
7.392
7.388
7.383
7.373
6.988
6.983
6.903
6.898
6.885
6.881
HO
O
O
O
0.95
1.92
0.96
2.02
1.07
1.01
1.00
.6
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

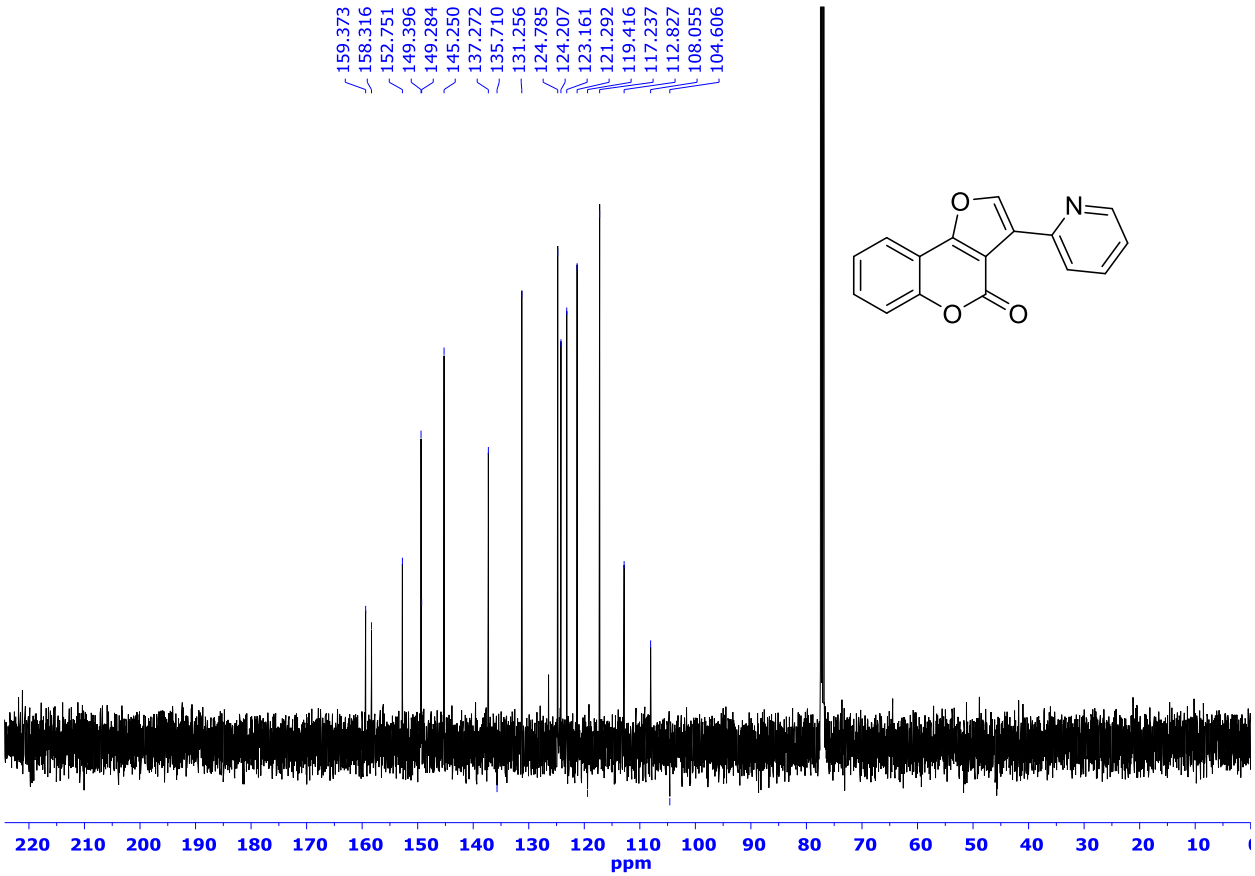


Spectroscopic data for 3-(pyridin-2-yl)-4H-furo[3,2-c]coumarin (HP8)

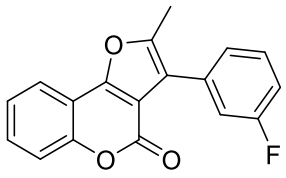


^{1}H NMR (500 MHz, CDCl3) δ 8.61 (d, *J* = 4.6 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.36 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.28 (dd, *J* = 4.1, 3.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.37, 158.32, 152.75, 149.40, 149.28, 145.25, 137.27, 135.71, 131.26, 124.78, 124.21, 123.16, 121.29, 119.42, 117.24, 112.83, 108.06, 104.61.

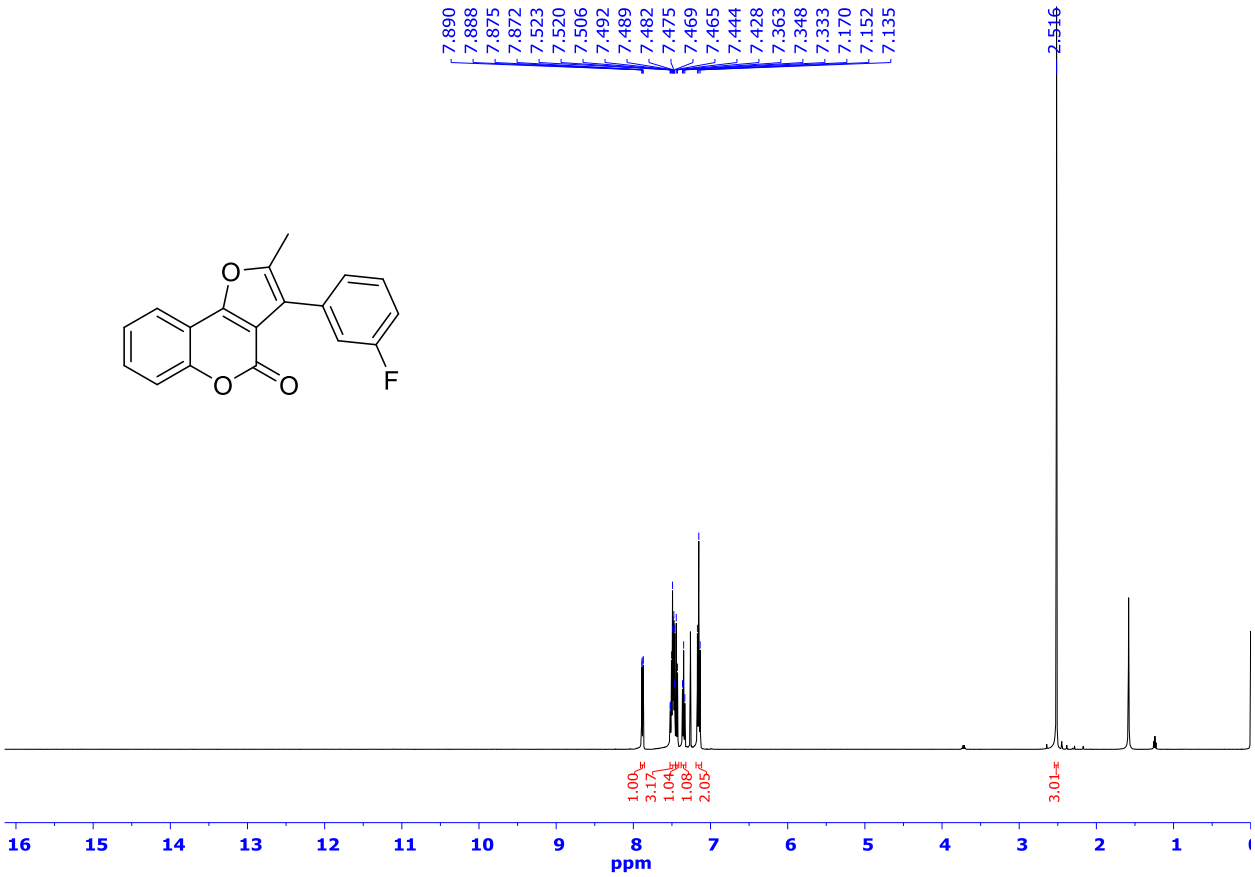

8.619
8.610
8.581
8.565
8.361
7.952
7.937
7.843
7.827
7.812
7.575
7.559
7.544
7.482
7.466
7.399
7.383
7.368
7.285
7.275
7.273
7.270
O
N
O
O
1.06
1.05
1.00
1.07
1.10
1.08
1.06
1.13
0.97
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm

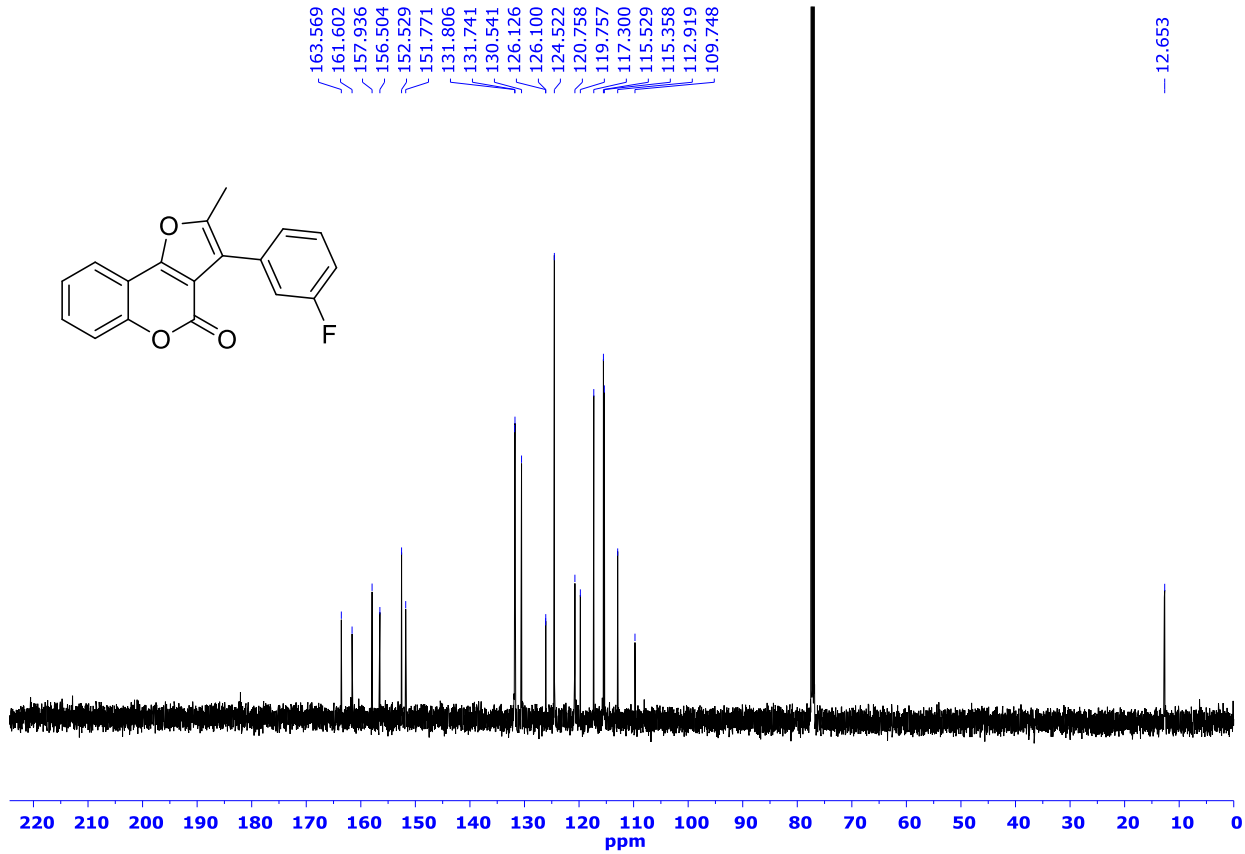


Spectroscopic data for 3-(3-fluorophenyl)-2-methyl-4H-furo[3,2-c]coumarin (HP8)

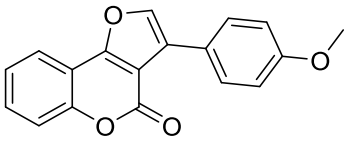


^{1}H NMR (500 MHz, CDCl3) δ 7.88 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 8.7 Hz, 2H), 2.52 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.57, 161.60, 157.94, 156.50, 152.53, 151.77, 131.81, 131.74, 130.54, 126.13, 126.10, 124.52, 120.76, 119.76, 117.30, 115.53, 115.36, 112.92, 109.75, 12.65.


7.890
7.888
7.875
7.872
7.523
7.520
7.506
7.492
7.489
7.482
7.475
7.469
7.465
7.444
7.428
7.363
7.348
7.333
7.170
7.152
7.135
2.516
O
O
O
F
1.00
3.17
1.04
1.08
2.05
3.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

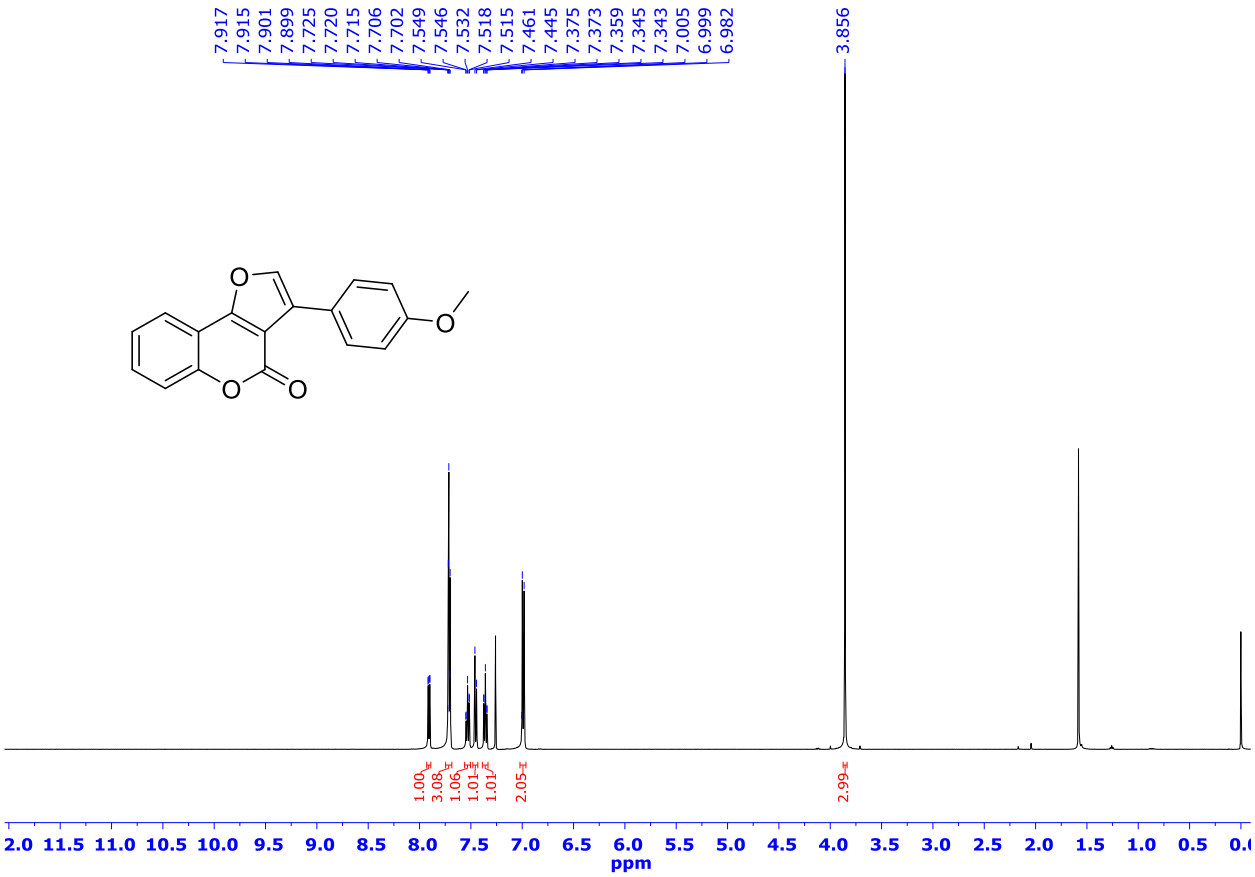


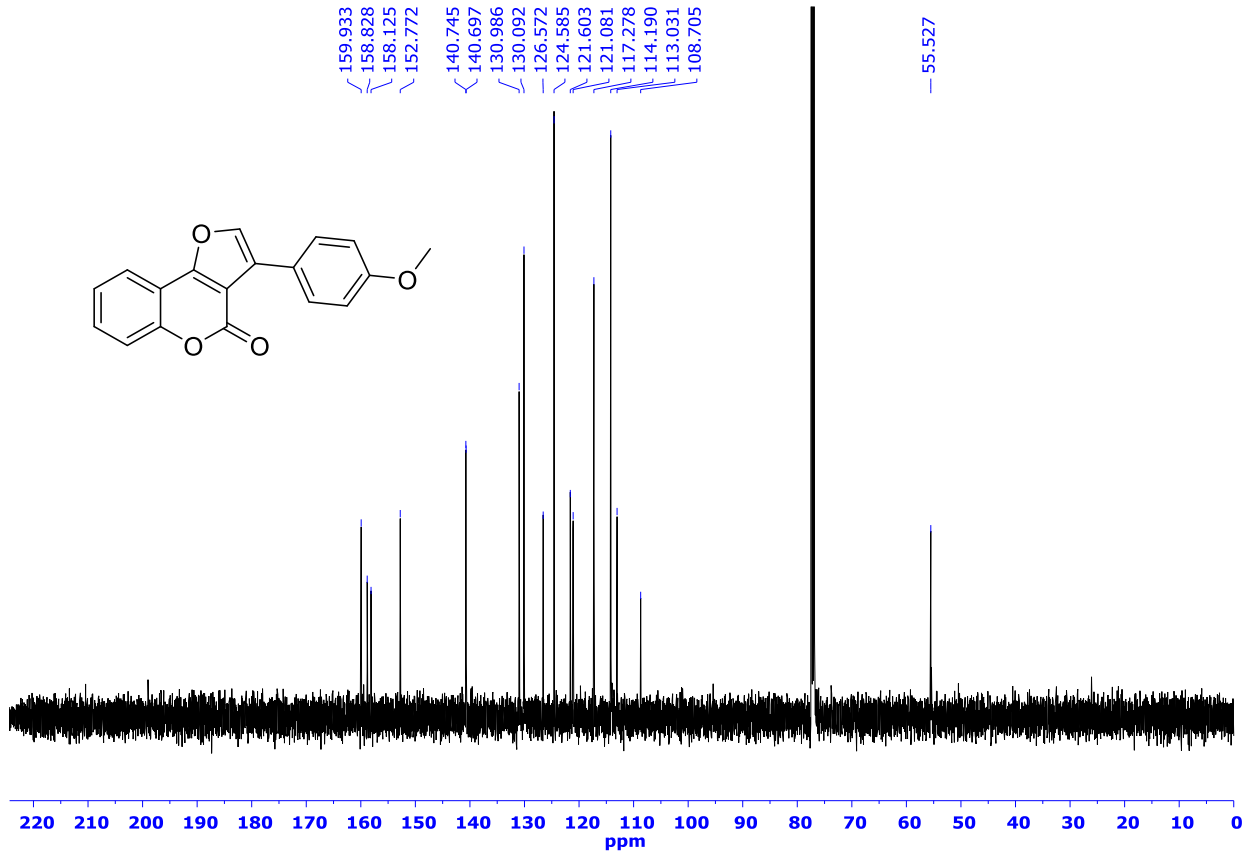
Spectroscopic data for 3-(4-methoxyphenyl)-4H-furo[3,2-c]coumarin (HP8)



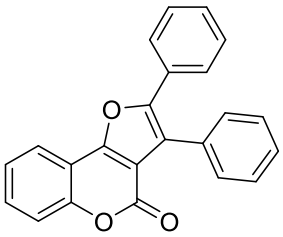
^{1}H NMR (500 MHz, CDCl3) δ 7.91 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.56 – 7.50 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.00 (t, *J* = 5.8 Hz, 2H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.93, 158.83, 158.13, 152.77, 140.74, 140.70, 130.99, 130.09, 126.57, 124.59, 121.60, 121.08, 117.28, 114.19, 113.03, 108.70, 55.53.


7.917
7.915
7.901
7.899
7.725
7.720
7.715
7.706
7.702
7.549
7.546
7.532
7.518
7.515
7.461
7.445
7.375
7.373
7.359
7.345
7.343
7.005
6.999
6.982
3.856
O
O
O
O
1.00
3.08
1.06
1.01
1.01
2.05
2.99
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

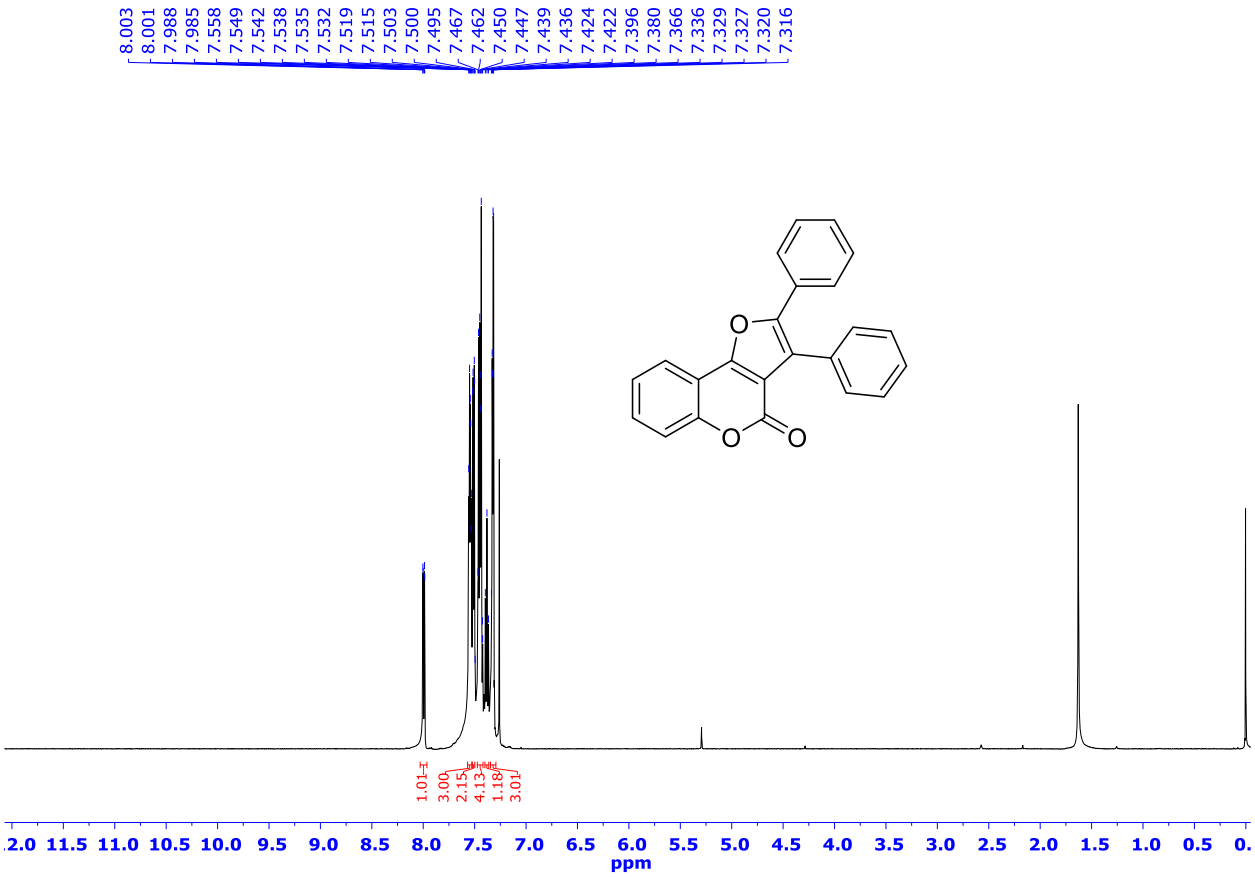


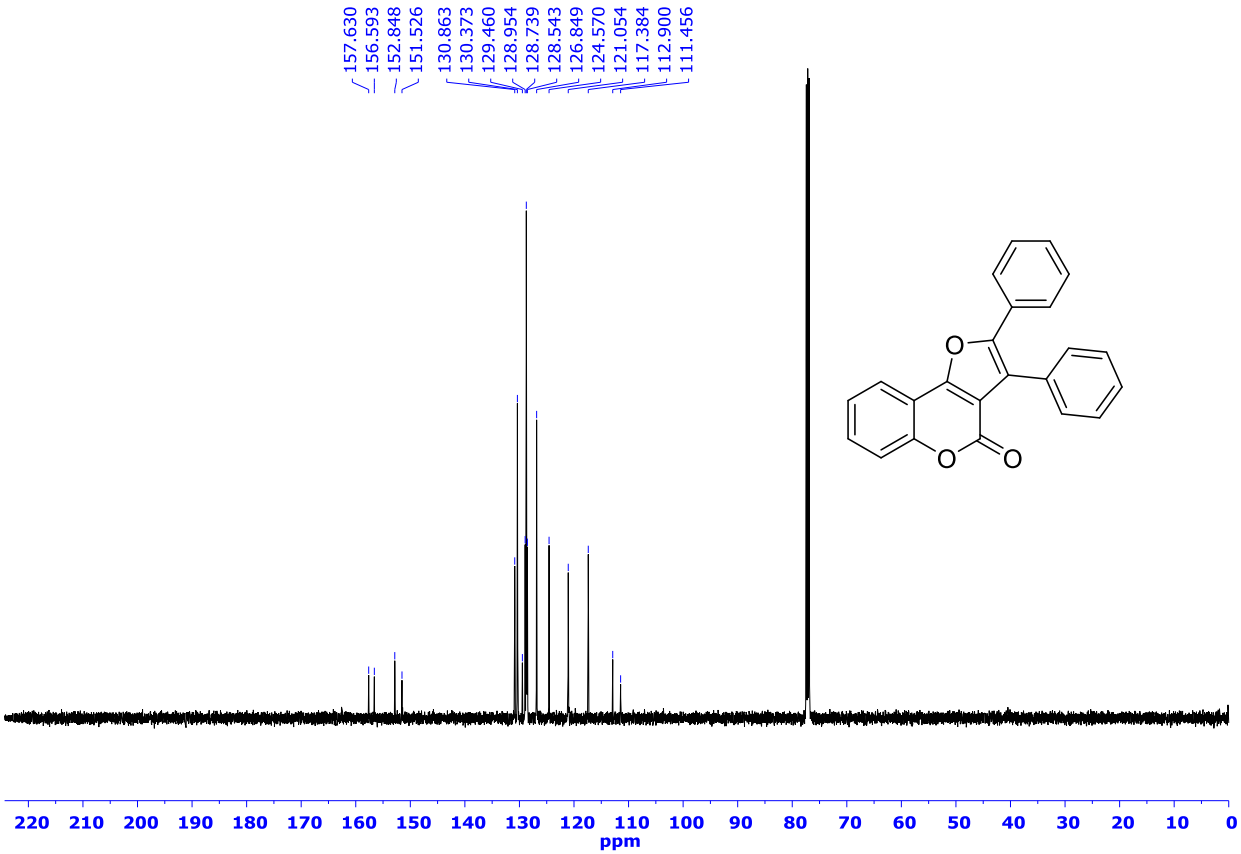
Spectroscopic data for 2,3-diphenyl-4H-furo[3,2-c]coumarin (HP8)



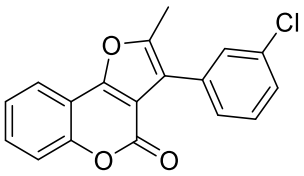
^{1}H NMR (500 MHz, CDCl3) δ 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.57 – 7.53 (m, 3H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.47 – 7.42 (m, 4H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.29 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.63, 156.59, 152.85, 151.53, 130.86, 130.37, 129.46, 128.95, 128.74, 128.54, 126.85, 124.57, 121.05, 117.38, 112.90, 111.46

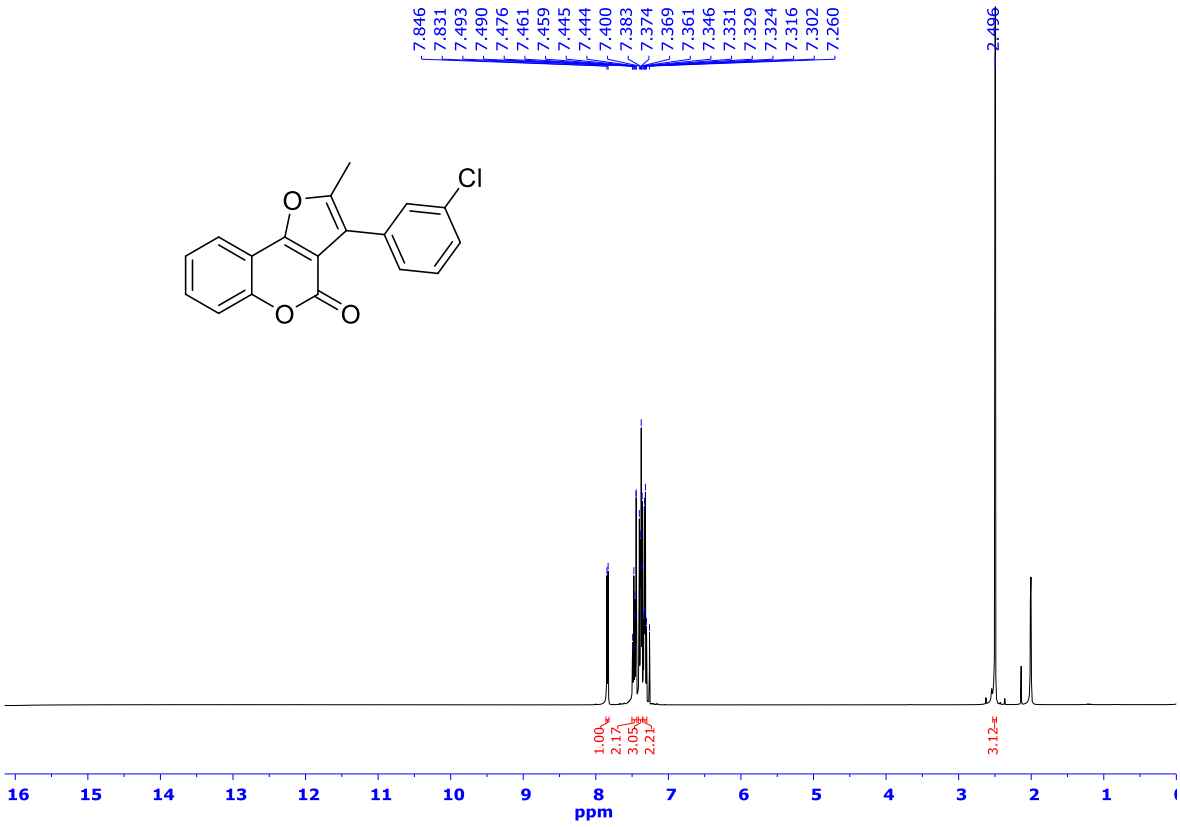

8.003
8.001
7.988
7.985
7.558
7.549
7.542
7.538
7.535
7.532
7.519
7.515
7.503
7.500
7.495
7.467
7.462
7.450
7.447
7.439
7.436
7.424
7.422
7.396
7.380
7.366
7.336
7.329
7.327
7.320
7.316
O
O
O
1.01
3.00
2.15
4.13
1.18
3.01
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
ppm

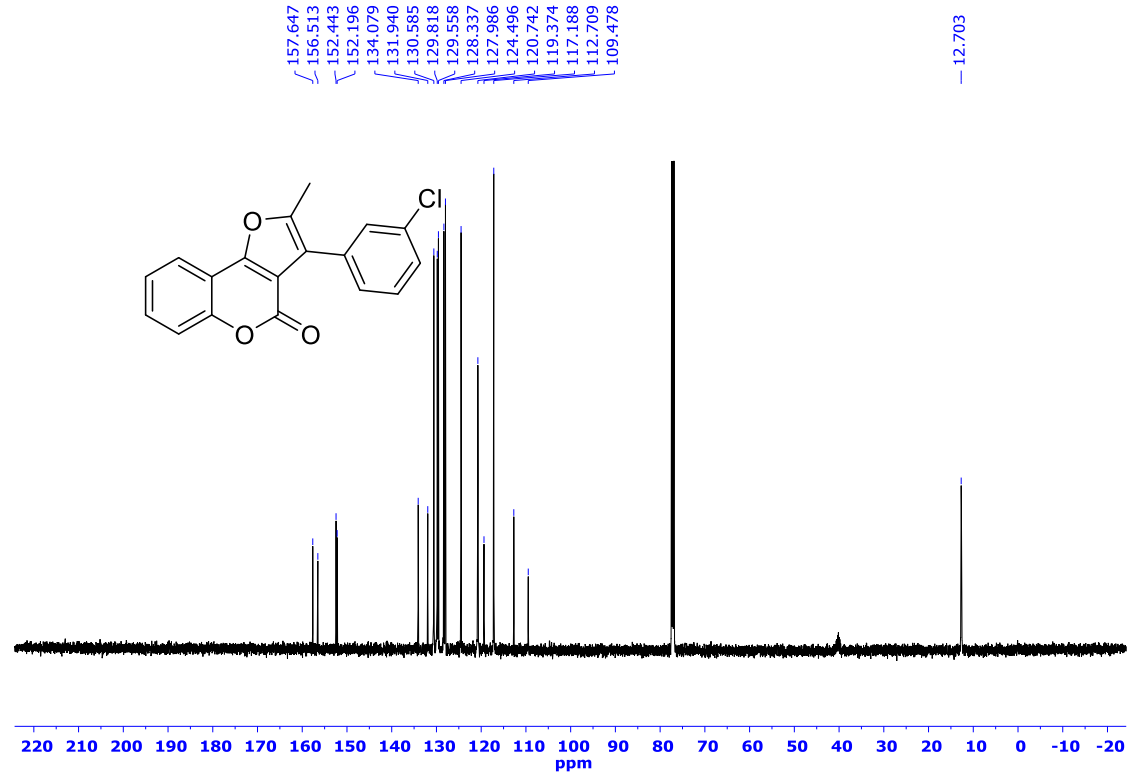


Spectroscopic data for 3-(3-chlorophenyl)-2-methyl-4H-furo[3,2-c]coumarin (HP17)



^{1}H NMR (500 MHz, CDCl3) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.41 – 7.35 (m, 3H), 7.32 (dt, *J* = 11.1, 7.4 Hz, 2H), 2.50 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.65, 156.51, 152.44, 152.20, 134.08, 131.94, 130.58, 129.82, 129.56, 128.34, 127.99, 124.50, 120.74, 119.37, 117.19, 112.71, 109.48, 12.70.


7.846
7.831
7.493
7.490
7.476
7.461
7.459
7.445
7.444
7.400
7.383
7.374
7.369
7.361
7.346
7.331
7.329
7.324
7.316
7.302
7.260
2.496
Cl
O
O
O
1.00
2.17
3.05
2.21
3.12
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm


157.647
156.513
152.443
152.196
134.079
131.940
130.585
129.818
129.558
128.337
127.986
124.496
120.742
119.374
117.188
112.709
109.478
12.703
Cl
O
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
ppm

Section S7. *Reference*

(1) Bruker. *APEX3* v2015.5-2. (Bruker AXS Inc., Madison, Wisconsin, U.S.A. 2015).

(2) Bruker. *SAINT* v8.37A. (Bruker AXS Inc., Madison, Wisconsin, U.S.A. 2015).

(3) Bruker. *SADABS* -2016/2. (Bruker AXS Inc., Madison, Wisconsin, U.S.A. 2016).

(4) Sheldrick, G. A Short History of Shelx. *Acta Cryst.* **2008**, *A64*, 112-122.

(5) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. Olex2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339-341.