Electronic Supplementary Material (ESI) for ChemComm.

Visible-light-enabled cascade cross-dehydrogenative-coupling/ cyclization to construct *α*-chromone substituted *α*-amino acid derivatives

Zhi-Qiang Zhu,* Jia-Yu Hu, Zong-Bo Xie, Zhang-Gao Le*

Jiangxi Province Key Laboratory of Synthetic Chemistry, School of Chemistry and Materials Science, East China University of Technology, Nanchang, 330013, China

Supporting Information

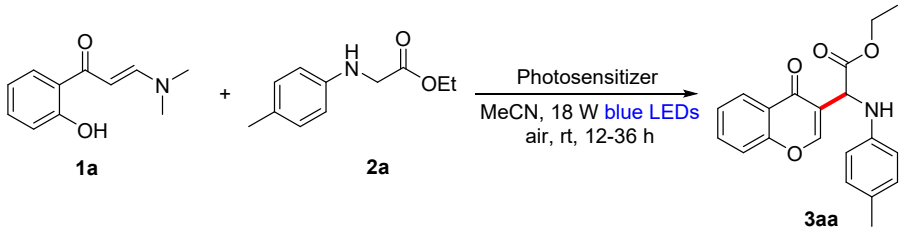
Contents

1. General Information

Unless otherwise indicated, all reagents were purchased from commercial distributors and used without further purification. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded at 400 MHz, 100 MHz and 471 MHz, using tetramethylsilane as an internal reference. High-resolution mass spectra (HRMS) were measured on a quadrupole time-of-flight (Q-TOF) mass spectrometer instrument with an electrospray ionization (ESI) source. Melting points were uncorrected. Blue Led light were purchased from Ouying Lighting Co., Ltd. (18 W/5313 A/455 nm), The distance between the light source and the irradiation instrument is 8 cm. Flash column chromatography was performed over silica gel 200-300 mesh. Thin-layer chromatography (TLC) was carried out with silica gel GF254 plates. *o*-Hydroxyaryl enaminones **1** and *N*-arylglycine esters **2** were prepared according to the previous reported protocols.[1-2]

2. Optimization of the Reaction Conditions

Table S1. Screening of photosensitizers[a]

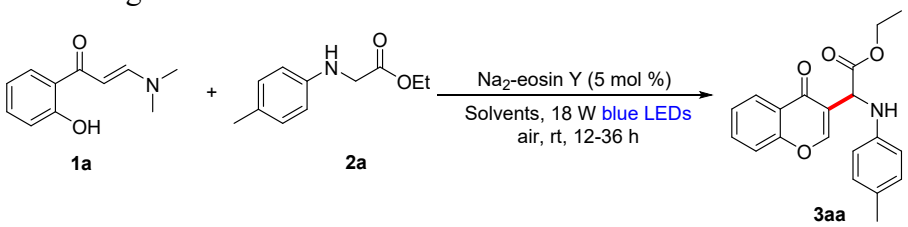


Entry	Photosensitizer (5 mol %)	Yield(%) [b]
1	$Ru(bpy)Cl\cdot 6H_2O$	26
2	$Ir(bpy)_3$	19
3	4CzPIN	9
4	**Na_2-eosin Y**	**35**
5	Acr^{+}-Mes-ClO_4^{-}	trace
6	Rose bengal	21
7	Methylene Blue hydrate	trace
8	Eosin B	27
9	Rhodamine B	8

(a) Reaction condition: **1a** (0.2 mmol), **2a** (0.4 mmol), Photosensitizer (5 mol%), MeCN (2 mL) under

irradiation of 18 W blue LEDs for 12-36 h; (b) Isolated yields based on **1a**.

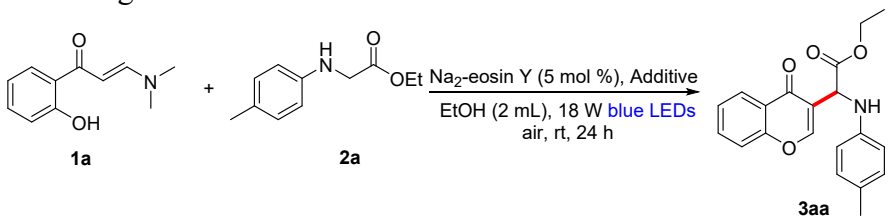
Table S2. Screening of solvents[a]



Entry	Solvent (2 mL)	Yield (%)[b]
1	Acetone	23
2	Toluene	trace
3	THF	31
4	**EtOH**	**49**
5	DMSO	24
6	DCE	<10
7	1,4-Dioxane	trace

(a) Reaction condition: **1a** (0.2 mmol), **2a** (0.4 mmol), Na_2-eosin Y (5 mol %), Solvent (2 mL) under irradiation of 18 W blue LEDs for 12-36 h; (b) Isolated yields based on **1a**.

Table S3. Screening of additives[a]



Entry	Additive (2.0 equiv)	Yield (%)[b]
1	KF	<10
2	Cs_2CO_3	N.R.
3	Na_2HPO_4	20%
4	*t*-BuOK	N.R.
5	DBU	N.R.
6	Citric Acid	66
7	**Citric Acid·H_2O**	**68 (46)[c]**
8	Boric Acid	N.R.
9	Acetic Acid	57

(a) Reaction condition: **1a** (0.2 mmol), **2a** (0.4 mmol), Na_2-eosin Y (5 mol %), EtOH (2 mL), Additives (2.0 equiv), under irradiation of 18 W blue LEDs for 24 h; (b) Isolated yields based on **1a**.; (c) 1 equiv. Citric Acid.H_2O was used.

3. General Procedure for Synthesis of Products

Synthesis of 3-aminoalkylation chromones 3. To a 10 mL overdried reaction tube were added *o*-hydroxyarylenaminones **1** (0.2 mmol, 1.0 equiv), *α*-amino acid derivatives **2** (0.4 mmol, 2.0 equiv), Na_2-eosin Y (5 mol%), Citric Acid·H_2O (2.0 equiv), and EtOH (2 mL, 0.1 M). The reaction mixture was performed under irradiation of 18 W blue LED lights at room temperature (25 ± 2 ℃) for 24 h. After the reaction was completed, the resulting mixture was concentrated under a vacuum, and the residue was subjected to column chromatography (silica gel, PE to PE/EA = 10:1 as an eluent) to afford the target corresponding products **3**.

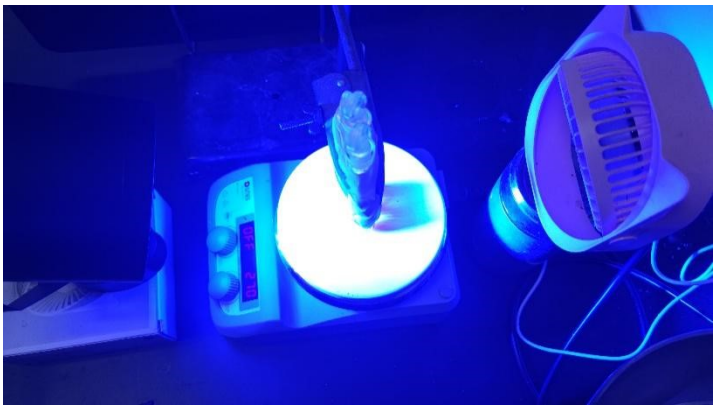
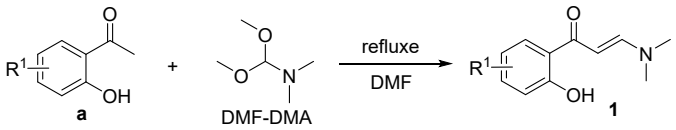


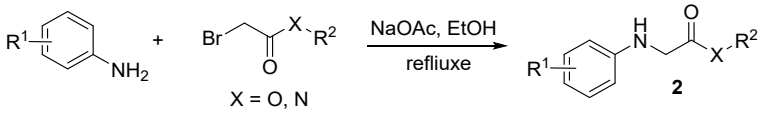
Figure S1. The reaction and cooling setup of the reactor

Synthesis of *o*-hydroxyarylenaminones 1. The corresponding 2-hydroxyacetophenones **a** (50 mmol) and DMF-DMA (23.8 g, 200 mmol) were refluxed in DMF (100 mL) and stirred at 80 ℃ for 1 h. All reactions were monitored by TLC until the disappearance of corresponding **a**, which was indicative of the reaction being completed. The reaction mixture was poured into brine (250 mL), an orange precipitate appeared, which was filtered and dried, and the corresponding *o*-hydroxyarylenaminones **1** were obtained.



Scheme S1. Synthesis of *o*-hydroxyphenyl enaminones 1

Synthesis of *N*-arylglycine esters 2. In a 50 mL oven dried round bottom flask equipped with a magnetic stirring bar, *p*-methoxyanilines (20 mmol, 1 eq.), bromoacetates (22 mmol, 1.1 eq.) and anhydrous sodium acetate (22 mmol, 1.1 eq.) were taken and then 20 mL ethanol was added. The reaction mixture was stirred in oil bath (90 ºC) for 24 h under N_2 atmosphere. After cooling, the solvent was evaporated and residue was subjected to column chromatography (230-400 mesh silica gel). The resulting product was crystalized then gave the product **2** as off-white solid. Following the general procedure, other glycine derivatives also were prepared.



Scheme S2. Synthesis of *N*-arylglycine esters 2

4. Radical Trapping Experiments

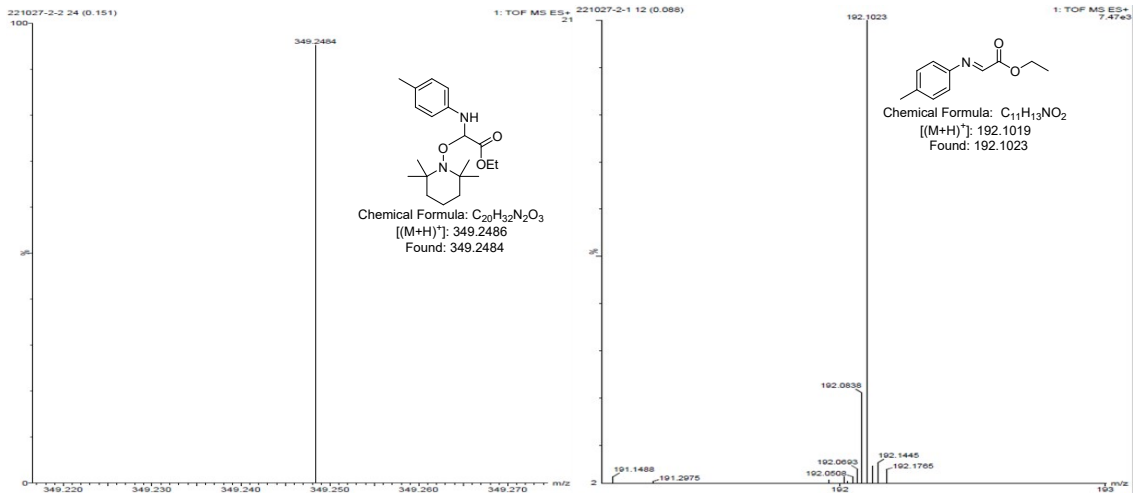


Figure S2. HR-MS Spectra of TEMPO-adduct and imine intermediate.

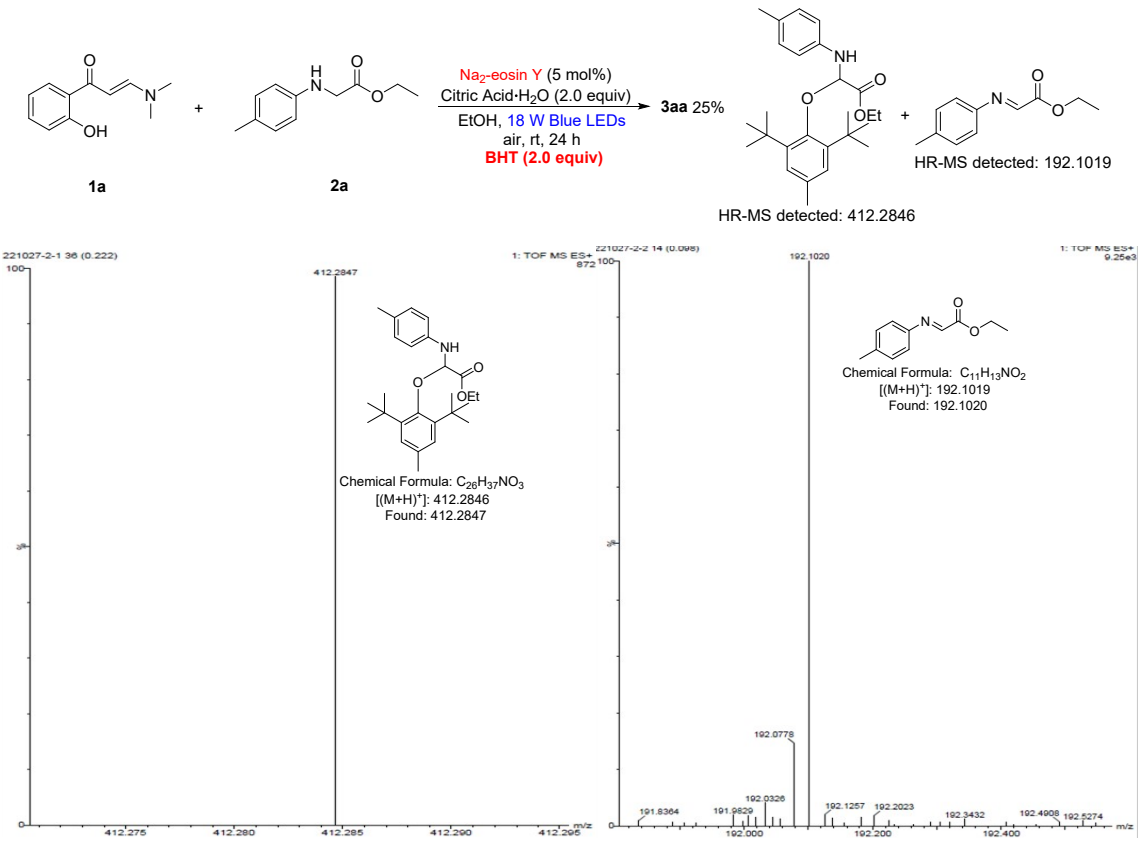


Figure S3. HR-MS Spectra of BHT-adduct and intermediate.

5. Cyclic Voltammetry (CV)

Cyclic voltammograms were recorded with a CHI604E electrochemical analyzer/workstation (Shanghai Chen Hua Instrument Co., Ltd). Cyclic voltammograms of **1a** (0.01 M) and **2a** (0.01 M) were performed in a three-electrode cell connected to an electrochemical cell at room temperature. The working electrode was a steady glassy carbon disk electrode while the counter electrode was a platinum wire. The glassy carbon disk electrode is a cylindrical working electrode with a base area of 0.07 cm^2 and the polishing procedure is: take a small amount of micron Al_2O_3 on the grinding disc, then drop a small amount of deionized water, so that the electrode keeps the path of a circular movement at a uniform speed, and finally clean the surface of the electrode with deionized water and dry it. A saturated calomel electrode (SCE) was used as the reference electrode. A 0.1 M solution of $^nBu_4NBF_4$ in EtOH purged with nitrogen was added into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 0.10 V/s, ranging from -2.5.0 V to 2.5 V.

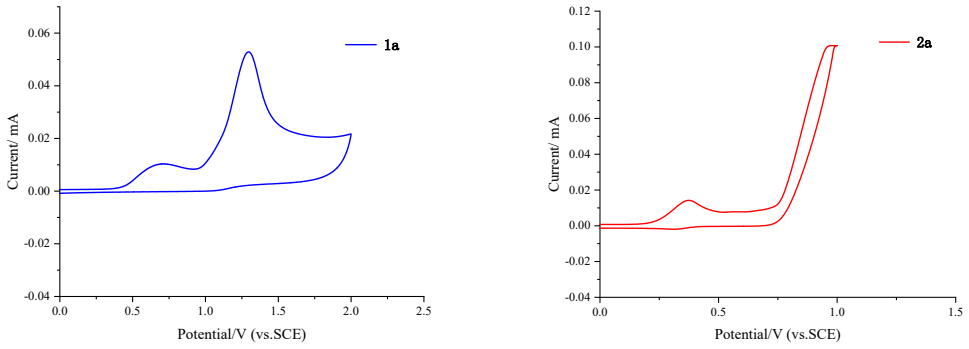


Figure S4. Cyclic voltammograms of reaction substrates

6. Fluorescence Quenching Experiments

The fluorescence quenching experiment was taken using a Perkin Elmer LS55 fluorescence spectrophotometer (USA). The experiments were carried out in 0.0005 mmol/L of Na_2-eosin Y/EtOH at 32 °C. The concentrations of quenchers (*o*-hydroxyarylenaminone **1a** and *N*-(4-methylphenyl)glycine ethyl ester **2a**) in EtOH were 0 mmol/L, 0.5 mmol/L, 1.0 mmol/L, 1.5 mmol/L, 2.0 mmol/L, 2.5 mmol/L, 3.0 mmol/L.

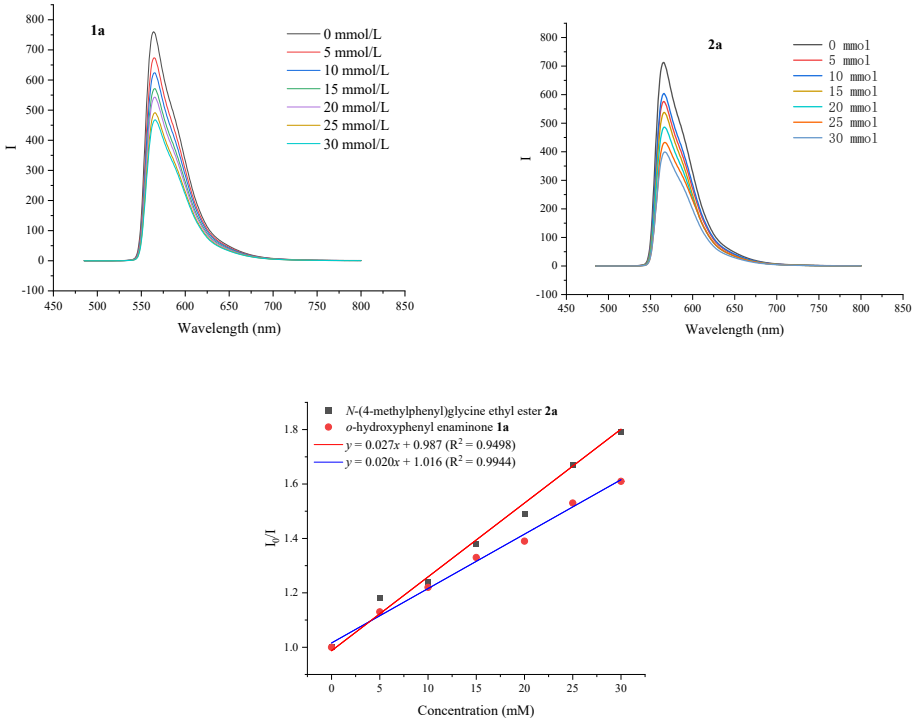


Figure S5. Fluorescence Quenching of Na_2-eosin Y by Reaction Substrates

To probe the interaction of Eosin Y with substrates, fluorescence quenching experiments of Na_2-eosin Y with *o*-hydroxyarylenaminone **1a** and *N*-(4-methylaryl)glycine ethyl ester **2a** were investigated, respectively (Figure S5). The results showed that *N*-(4-methylaryl)glycine ethyl ester **2a** more significantly bursted the fluorescence emission of Na_2-eosin Y in the excited state compared to *o*-hydroxyarylenaminone **1a**, and this tendency was also visible in the corresponding Stern-Volmer plots. Therefore, the substrate **2a** was preferentially oxidized by Na_2-eosin Y in the excited state.

7. UV-Visible Spectroscopy

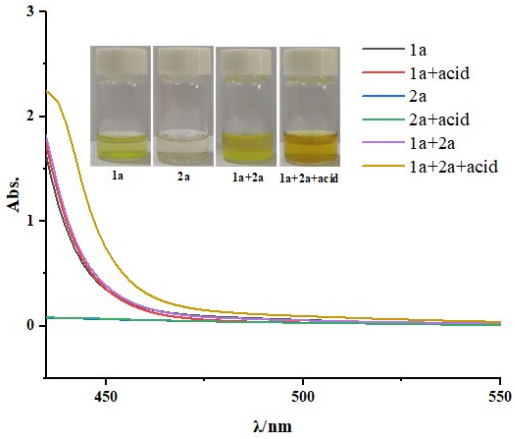


Figure S6. UV-Visible absorption spectra (c = 6e^{-4} M)

8. X-ray Crystallography Date of 3aa

3.1 The crystal of **3aa** was grown in the air by slow evaporation of the solvents (a mixture of *n*-hexane / dichloromethane) at room temperature.

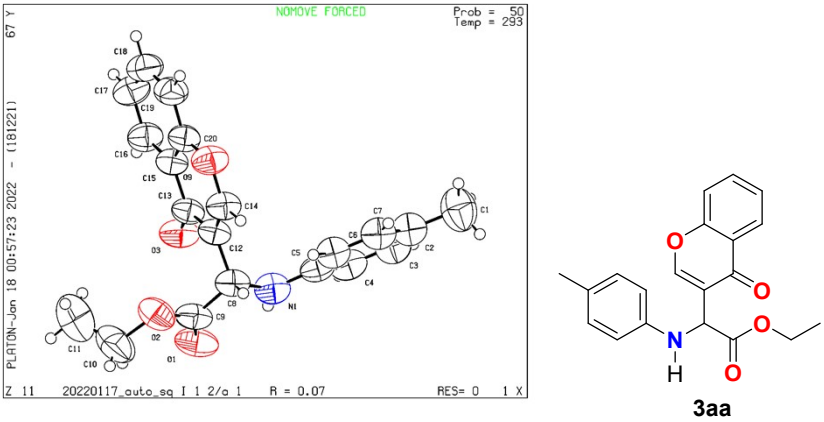


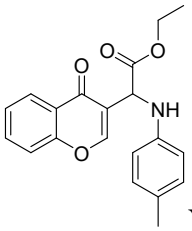
Figure S7. The thermal ellipsoid plot of **3aa**.

Table S4. Crystal data and structure refinement for **3aa.**

Identification code	2237743
Empirical formula	$C_{20}H_{19}NO_4$
Formula weight	337.36
Temperature/K	293
Wavelength/Å	1.54184
Crystal system	Monoclinic
Space group	I2/a
a (Å)	11.6169(4)
b (Å)	15.6243(6)
c (Å)	23.3222(12)
α (º)	90
β (º)	94.169(4)
γ (º)	90
Volume/ Å^3	4221.9(3)
Z	8
Calculated density (mg/m^3)	1.061
Absorption coefficient (mm^{-1})	0.606
F (000)	1424.0
Crystal size/mm	0.1 x 0.08 x 0.02
Theta range for data collection / º	6.816 to 137.446
Limiting indices	$-13\leq h\leq 11$, $-18\leq k\leq 17$, $-25\leq l\leq 27$
Reflections collected / unique	2755 / 3840 [R (int) = 0.0670]
Completeness to theta	98.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F_2
Data / restraints / parameters	3844 / 0 / 228
Goodness-of-fit on F_2	1.119
Final R indices [I>2 sigma (I)]	$R_1 = 0.0670$, $wR_2 = 0.2122$
R indices (all data)	$R_1 = 0.0779$, $wR_2 = 0.2255$
Largest diff. peak / hole / (e.A^{-3})	0.32/-0.34

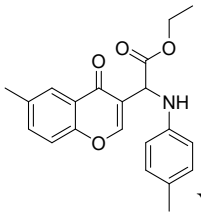
9. Characterization Data

Ethyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3aa)



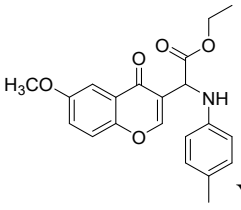
Yield 65% (34 mg); yellow solid; mp 130.9-131.2 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.25 (dd, *J*=8.0, 1.7 Hz, 1H), 8.06 (s, 1H), 7.66 (ddt, *J*=8.4, 7.0, 1.4 Hz, 1H), 7.45–7.39 (m, 2H), 6.96 (d, *J*=8.1 Hz, 2H), 6.60–6.55 (m, 2H), 5.28 (s, 1H), 4.30–4.16 (m, 2H), 2.20 (s, 3H), 1.23 (t, *J*=7.1 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 176.63, 171.46, 156.40, 154.38, 143.40, 134.01, 129.92, 127.97, 126.05, 125.48, 123.96, 121.86, 118.29, 114.00, 62.19, 53.29, 20.49, 14.18; HRMS (ESI) calcd for $C_{20}H_{19}NO_4$ $(M+H)^+$ 338.1387, found 338.1396.

Ethyl-2-(6-methyl-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ab)



Yield 65% (34 mg); yellow solid; mp 124.3-125.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.02 (m, 2H), 7.47 (dd, *J*=8.6, 2.3 Hz, 1H), 7.32 (d, *J*=8.6 Hz, 1H), 6.95 (d, *J*=8.2 Hz, 2H), 6.57 (d, *J*=8.4 Hz, 2H), 5.27 (s, 1H), 4.22 (q, *J*=14.9, 7.3 Hz, 1H), 2.45 (s, 3H), 2.20 (s, 3H), 1.23 (t, *J*=7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.7, 171.6, 154.8, 154.3, 143.6, 135.5, 135.2, 130.0, 128.0, 125.4, 123.8, 121.8, 118.1, 114.2, 62.1, 53.5, 21.1, 20.5, 14.2; HRMS (ESI) calcd for $C_{21}H_{21}NO_4$ $(M+H)^+$ 352.1543, found 352.1546.

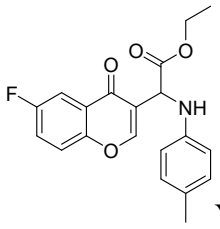
Ethyl-2-(6-methoxy-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ac)



Yield 65% (34 mg); yellow solid; mp 121.2-123.4 °C; ^{1}H NMR (400

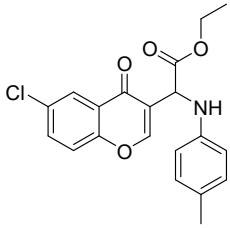
MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.60 (d, *J*=3.0 Hz, 1H), 7.36 (d, *J*=9.2 Hz, 1H), 7.26 (d, *J*=2.8 Hz, 1H), 6.95 (d, *J*=8.0 Hz, 2H), 6.56 (d, *J*=8.0 Hz, 2H), 5.29 (s, 1H), 4.22 (q, *J*=18.8, 7.2 Hz, 1H), 3.89 (s, 4H), 2.20 (s, 3H), 1.23 (t, *J*=7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.5, 171.5, 157.2, 154.2, 151.3, 143.5, 129.9, 128.0, 124.6, 124.2, 121.1, 119.7, 114.0, 105.0, 62.2, 56.0, 53.4, 20.5, 14.2; HRMS (ESI) calcd for $C_{21}H_{21}NO_5$ $(M+H)^+$ 368.1492, found 368.1495.

Ethyl-2-(6-fluoro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ad)



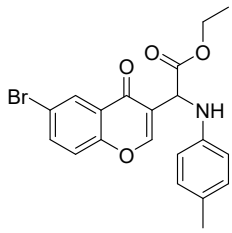
Yield 65% (34 mg); yellow solid; mp 113.6-114.9 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 8.53 (s, 1H), 7.77-7.73 (m, 2H), 6.89 (d, *J*=8.1 Hz, 2H), 6.62 (d, *J*=8.4 Hz, 2H), 5.84 (d, *J*=9.1 Hz, 1H), 5.25 (d, *J*=9.1 Hz, 1H), 4.12 (qd, *J*=7.1, 2.7 Hz, 2H), 2.12 (s, 3H), 1.13 (t, *J*=7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.8, 171.2, 159.6 (d, $J_{C\text{-}F}$=248.36 Hz), 154.5, 152.6, 143.3, 129.8, 128.0, 125.1 (d, $J_{C\text{-}F}$= 7.47 Hz), 125.1 (d, $J_{C\text{-}F}$= 25.65 Hz), 121.3, 125.1 (d, $J_{C\text{-}F}$= 8.08 Hz), 114.0, 125.1 (d, $J_{C\text{-}F}$=23.84 Hz), 62.1, 53.3, 20.3, 14.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.54. HRMS (ESI) calcd for $C_{20}H_{18}FNO_4$ $(M+H)^+$ 356.1293, found 356.1299.

Ethyl-2-(6-chloro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ae)



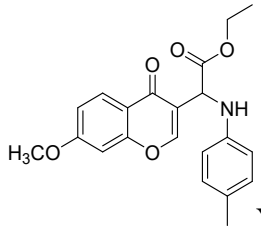
Yield 65% (34 mg); yellow solid; mp 131.7-132.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J*=2.6 Hz, 1H), 8.05 (s, 1H), 7.60 (dd, *J*=8.9, 2.6 Hz, 1H), 7.39 (d, *J*=9.0 Hz, 1H), 6.96 (d, *J*=8.3 Hz, 2H), 6.55 (d, *J*=8.4 Hz, 2H), 5.27 (s, 1H), 4.23 (q, *J*=16.9, 7.2 Hz, 1H), 2.20 (s, 3H), 1.23 (t, *J*=7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.5, 171.2, 154.7, 154.5, 143.3, 134.2, 131.5, 130.0, 128.1, 125.5, 124.9, 122.0, 120.0, 114.0, 62.3, 53.2, 20.5, 14.2; HRMS (ESI) calcd for $C_{20}H_{18}ClNO_4$ $(M+H)^+$ 372.0997, found 372.1002.

Ethyl-2-(6-bromo-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3af)



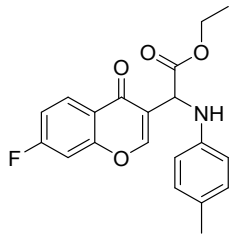
Yield 65% (34 mg); yellow solid; mp 126.7-128.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J*=2.5 Hz, 1H), 8.05 (s, 1H), 7.72 (dd, *J*=8.9, 2.5 Hz, 1H), 7.31 (d, *J*=8.9 Hz, 1H), 6.95 (d, *J*=8.2 Hz, 2H), 6.55 (d, *J*=8.4 Hz, 2H), 5.27 (s, 1H), 4.23 (q, *J*=14.3, 7.1 Hz, 1H), 2.20 (s, 4H), 1.23 (t, *J*=7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.3, 171.2, 155.2, 154.5, 143.3, 136.9, 129.9, 128.6, 128.1, 125.2, 122.2, 120.2, 118.9, 114.0, 62.2, 53.3, 20.4, 14.1; HRMS (ESI) calcd for $C_{20}H_{18}BrNO_4$ $(M+H)^+$ 416.0492, found 416.0498.

Ethyl-2-(7-methoxy-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ag)



Yield 65% (34 mg); yellow solid; mp 130.4-131.7 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.41 (s, 1H), 7.96 (dd, *J*=8.9, 1.7 Hz, 1H), 7.13 (t, *J*=2.3 Hz, 1H), 7.07 (dd, *J*=8.9, 2.3 Hz, 1H), 6.89 (d, *J*=7.9 Hz, 2H), 6.61 (d, *J*=8.3 Hz, 2H), 5.78 (d, *J*=9.2 Hz, 1H), 5.21 (d, *J*=9.2 Hz, 1H), 4.11 (q, 2H), 3.87 (d, *J*=2.1 Hz, 3H), 2.12 (d, *J*=1.9 Hz, 3H), 1.12 (t, *J*=7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.6, 171.5, 156.5, 154.4, 143.5, 134.0, 130.0, 128.0, 126.1, 125.5, 124.1, 122.0, 118.3, 114.1, 62.2, 53.4, 20.5, 14.2; HRMS (ESI) calcd for $C_{21}H_{21}NO_5$ $(M+H)^+$ 368.1492, found 368.1501.

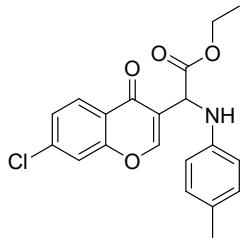
Ethyl-2-(7-fluoro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ah)



Yield 65% (34 mg); yellow solid; mp 121.6-123.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J*=8.9, 6.2 Hz, 1H), 8.03 (s, 1H), 7.19-7.08 (m, 2H), 6.96 (d, *J*=8.0 Hz, 2H), 6.56 (d, 2H), 5.26 (s, 1H), 4.23 (q, 1H), 2.20 (s, 3H), 1.23 (t, *J*=7.1 Hz, 3H);

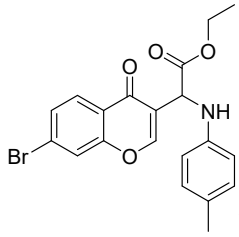
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.6, 171.2, 165.8 (d, J_{C-F}=256.44 Hz), 154.4, 143.3, 129.9, 128.6 (d, J_{C-F}=10.61 Hz), 128.1, 122.1, 120.8 (d, J_{C-F}=2.63 Hz), 119.8, 114.3 (d, J_{C-F}=23.13 Hz), 114.0, 104.8 (d, J_{C-F}=25.35 Hz), 62.1, 53.3, 20.3, 14.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -102.18. HRMS (ESI) calcd for $C_{20}H_{18}FNO_4$ $(M+H)^+$ 356.1293, found 356.1293.

Ethyl-2-(7-chloro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ai)



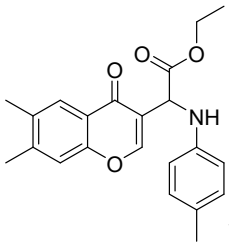
Yield 65% (34 mg); yellow solid; mp 121.7-123.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J*=8.6 Hz, 1H), 8.02 (s, 1H), 7.44 (d, *J*=1.9 Hz, 1H), 7.38 (dd, *J*=8.6, 2.0 Hz, 1H), 6.96 (d, *J*=8.3 Hz, 2H), 6.55 (d, 2H), 5.26 (s, 1H), 4.23 (q, *J*=15.1, 7.3 Hz, 1H), 2.20 (s, 3H), 1.23 (t, *J*=7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.8, 171.2, 156.5, 154.4, 143.3, 140.1, 129.9, 128.1, 127.4, 126.4, 122.5, 122.3, 118.3, 114.0, 62.2, 53.3, 20.5, 14.2; HRMS (ESI) calcd for $C_{20}H_{18}ClNO_4$ $(M+H)^+$ 372.0997, found 372.1000.

Ethyl-2-(7-bromo-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3aj)



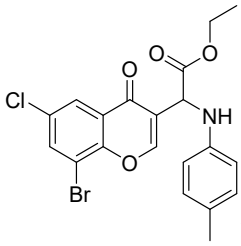
Yield 65% (34 mg); yellow solid; mp 118.2-119.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J*=8.5 Hz, 1H), 8.01 (s, 1H), 7.62 (s, 1H), 7.53 (d, *J*=8.7, 1.7 Hz, 1H), 6.96 (d, *J*=7.9 Hz, 2H), 6.55 (d, *J*=7.9 Hz, 2H), 5.25 (s, 1H), 4.23 (q, *J*=14.6, 7.4 Hz, 1H), 2.20 (s, 4H), 1.23 (t, *J*=7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.9, 171.2, 156.4, 154.3, 143.3, 130.0, 129.2, 128.3, 128.2, 127.5, 122.8, 122.3, 121.4, 114.0, 62.3, 53.3, 20.5, 14.2; HRMS (ESI) calcd for $C_{20}H_{18}BrNO_4$ $(M+H)^+$ 416.0492, found 416.0510.

Ethyl-2-(6,7-dimethyl-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ak)



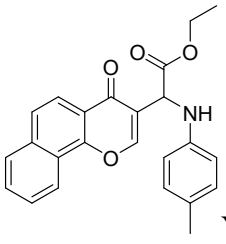
Yield 65% (34 mg); yellow solid; mp 127.4-128.6 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.41 (s, 1H), 7.79 (s, 1H), 7.41 (s, 1H), 6.89 (d, *J*=8.1 Hz, 2H), 6.61 (d, *J*=8.5 Hz, 2H), 5.80 (d, *J*=9.2 Hz, 1H), 5.23 (d, *J*=9.1 Hz, 1H), 4.11 (q, *J*=7.0 Hz, 2H), 2.33 (s, 3H), 2.30 (s, 3H), 2.12 (s, 3H), 1.12 (t, *J*=7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.5, 171.6, 155.0, 154.0, 144.5, 143.6, 134.8, 129.9, 127.9, 125.6, 121.9, 121.6, 118.3, 114.1, 62.0, 53.5, 20.4, 19.4, 14.1; HRMS (ESI) calcd for $C_{22}H_{23}NO_4$ $(M+H)^+$ 366.1700, found 366.1707.

Ethyl-2-(8-bromo-6-chloro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3al)



Yield 65% (34 mg); yellow solid; mp 128.7-129.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J*=2.5 Hz, 1H), 8.13 (s, 1H), 7.88 (d, *J*=2.6 Hz, 1H), 6.96 (d, *J*=8.0 Hz, 2H), 6.54 (d, *J*=8.3 Hz, 2H), 5.27 (s, 1H), 4.23 (q, *J*=18.4, 7.1 Hz, 1H), 2.20 (s, 3H), 1.24 (t, *J*=7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.0, 170.9, 154.7, 151.7, 142.9, 137.2, 131.7, 130.0, 128.5, 125.6, 125.0, 122.2, 114.1, 62.5, 53.2, 20.5, 14.20; HRMS (ESI) calcd for $C_{20}H_{17}BrClNO_4$ $(M+H)^+$ 450.0102, found 450.0109.

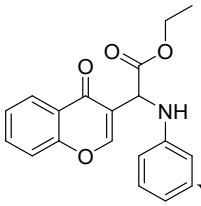
Ethyl-2-(4-oxo-4*H*-benzo[h]chromen-3-yl)-2-(*p*-tolylamino)acetate (3am)



Yield 65% (34 mg); yellow solid; mp 134.7-135.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J*=8.7 Hz, 1H), 8.25 (s, 1H), 8.17 (d, *J*=8.8 Hz, 1H), 7.91 (d, 1H), 7.76 (d, *J*=8.8 Hz, 1H), 7.72-7.61 (m, 1H), 6.97 (d, *J*=8.0 Hz, 2H), 6.61 (d, *J*=8.4 Hz, 2H), 5.37 (s, 1H), 4.26 (q, 1H), 2.20 (s, 3H), 1.24 (t, *J*=7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.4, 171.4, 154.0, 153.5, 143.4, 135.9, 129.9, 129.6, 128.2, 128.0, 127.4, 125.7,

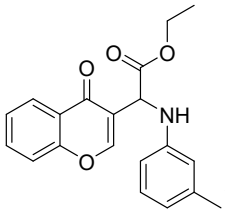
124.0, 123.3, 122.3, 120.8, 120.3, 114.1, 62.2, 53.4, 20.5, 14.2; HRMS (ESI) calcd for $C_{24}H_{21}NO_4$ $(M+H)^+$ 388.1543, found 388.1551.

Ethyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3ba)



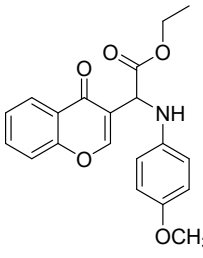
Yield 65% (34 mg); yellow solid; mp 132.4-134.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J*=7.9, 1.7 Hz, 1H), 8.06 (s, 1H), 7.67 (ddd, *J*=8.6, 7.1, 1.7 Hz, 1H), 7.43 (td, *J*=8.0, 7.5, 1.4 Hz, 2H), 7.15 (dd, *J*=8.5, 7.3 Hz, 2H), 6.73 (td, *J*=7.3, 1.1 Hz, 1H), 6.67-6.63 (m, 2H), 5.31 (s, 1H), 4.23 (q, 1H), 1.23 (t, *J*=7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.6, 171.4, 156.5, 154.4, 145.8, 134.1, 129.5, 126.2, 125.6, 124.1, 121.9, 118.8, 118.3, 113.9, 62.3, 53.1, 14.2; HRMS (ESI) calcd for $C_{19}H_{17}NO_4$ $(M+H)^+$ 324.1230, found 324.1239.

Ethyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(*m*-tolylamino)acetate (3ca)



Yield 65% (34 mg); yellow solid; mp 131.6-132.8 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.51 (s, 1H), 8.08 (dd, *J*=8.0, 1.7 Hz, 1H), 7.82 (ddd, *J*=8.7, 7.1, 1.7 Hz, 1H), 7.66 (d, 1H), 7.51 (t, 1H), 6.97 (t, *J*=7.7 Hz, 1H), 6.56-6.49 (m, 2H), 6.42 (d, *J*=7.4 Hz, 1H), 5.94 (d, *J*=9.0 Hz, 1H), 5.26 (d, *J*=9.0 Hz, 1H), 4.12 (q, *J*=6.9, 3.8 Hz, 2H), 2.17 (s, 3H), 1.13 (t, *J*=7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.6, 171.4, 156.4, 154.3, 145.8, 139.2, 134.0, 129.3, 126.0, 125.5, 124.0, 121.9, 119.6, 118.3, 114.8, 110.7, 62.2, 53.0, 21.6, 14.2; HRMS (ESI) calcd for $C_{20}H_{19}NO_5$ $(M+H)^+$ 338.1387, found 338.1397.

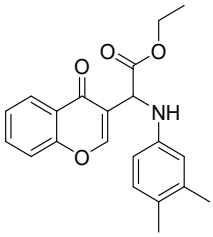
Ethyl-2-((4-methoxyphenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3da)



Yield 65% (34 mg); yellow solid; mp 134.1-135.7 °C; ^{1}H NMR (500

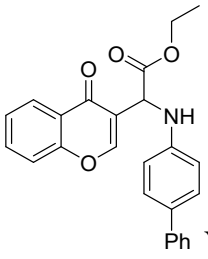
MHz, DMSO-d_6) δ 8.49 (s, 1H), 8.07 (dd, *J*=8.0, 1.7 Hz, 1H), 7.81 (ddd, *J*=8.6, 7.0, 1.7 Hz, 1H), 7.64 (d, *J*=8.4 Hz, 1H), 7.55-7.47 (m, 1H), 6.73-6.66 (m, 3H), 5.66 (d, *J*=9.4 Hz, 1H), 5.21 (d, *J*=9.3 Hz, 1H), 4.11 (q, *J*=7.1, 2.7 Hz, 2H), 3.62 (s, 3H), 1.12 (t, *J*=7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.6, 171.5, 156.5, 154.4, 153.1, 140.0, 134.0, 126.1, 125.5, 124.0, 122.0, 118.3, 115.6, 115.0, 62.1, 55.8, 54.3, 14.2; HRMS (ESI) calcd for $C_{18}H_{17}NO_2$ $(M+H)^+$ 354.1336, found 354.1344.

Ethyl-2-((3,4-dimethylphenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ea)



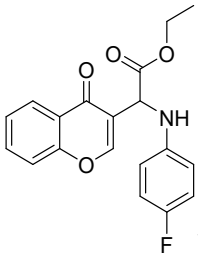
Yield 65% (34 mg); yellow solid; mp 132.7-134.2 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.25 (d, *J*=7.9 Hz, 1H), 8.06 (s, 1H), 7.67 (ddd, *J*=8.6, 7.1, 1.5 Hz, 2H), 7.42 (t, 3H), 6.91 (d, *J*=8.1 Hz, 1H), 6.51 (s, 1H), 6.41 (dd, *J*=8.4, 2.5 Hz, 1H), 5.27 (s, 1H), 4.23 (q, *J*=22.6, 7.1, 1.3 Hz, 2H), 2.13 (d, *J*=19.7 Hz, 8H), 1.23 (td, *J*=7.1, 1.2 Hz, 4H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.6, 171.5, 156.4, 154.3, 143.8, 137.6, 134.0, 130.4, 126.8, 126.1, 125.5, 124.0, 121.9, 118.3, 115.9, 111.1, 62.2, 53.4, 20.1, 18.8, 14.2; HRMS (ESI) calcd for $C_{21}H_{21}NO_4$ $(M+H)^+$ 352.1543, found 352.1546.

Ethyl-2-([1,1'-biphenyl]-4-ylamino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3fa)



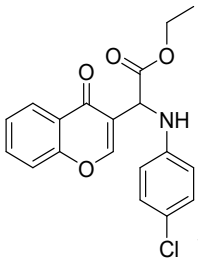
Yield 65% (34 mg); yellow solid; mp 141.7-143.3 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 8.56 (s, 1H), 8.09 (dd, *J*=8.0, 1.7 Hz, 1H), 7.82 (ddd, *J*=8.7, 7.0, 1.8 Hz, 1H), 7.66 (d, *J*=8.4 Hz, 1H), 7.53 (ddd, *J*=7.0, 4.3, 1.4 Hz, 3H), 7.43 (d, 2H), 7.36 (t, *J*=7.7 Hz, 2H), 7.22 (t, *J*=7.2, 1.3 Hz, 1H), 6.82 (d, 2H), 6.26 (d, *J*=8.9 Hz, 1H), 5.35 (d, *J*=8.8 Hz, 1H), 4.15 (q, *J*=7.0 Hz, 2H), 1.14 (t, *J*=7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.5, 171.3, 156.4, 154.4, 145.2, 141.1, 134.0, 131.6, 128.7, 128.1, 126.4, 126.3, 126.1, 125.5, 124.0, 121.8, 118.3, 114.1, 62.2, 53.1, 14.2; HRMS (ESI) calcd for $C_{25}H_{21}NO_4$ $(M+H)^+$ 400.1543, found 400.1550.

Ethyl-2-((4-fluorophenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ga)



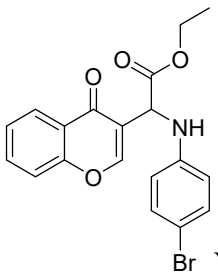
Yield 65% (34 mg); yellow solid; mp 135.4-136.8 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.25 (dd, *J*=8.0, 1.7 Hz, 1H), 8.05 (s, 1H), 7.69 (ddd, *J*=8.7, 6.9, 1.7 Hz, 1H), 7.47–7.41 (m, 2H), 6.86 (t, *J*=8.7 Hz, 2H), 6.58 (dd, *J*=8.9, 4.3 Hz, 2H), 5.23 (s, 1H), 4.30–4.15 (m, 2H), 1.22 (t, *J*=7.1 Hz, 3H).; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.4, 171.2, 157.7, 156.6, 155.3, 154.3, 142.2, 134.0, 125.7 (d, $J_{C\text{-}F}$=53.13 Hz), 123.9, 121.7, 118.2, 115.8 (d, $J_{C\text{-}F}$=22.62 Hz), 114.9 (d, $J_{C\text{-}F}$=7.58 Hz), 62.1, 53.8, 14.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -126.34. HRMS (ESI) calcd for $C_{19}H_{16}FNO_4$ $(M+Na)^+$ 364.0956, found 364.0959.

Ethyl-2-((4-chlorophenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ha)



Yield 65% (34 mg); yellow solid; mp 131.9-133.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$)δ 8.25 (dd, *J*=7.9, 1.7 Hz, 1H), 8.05 (s, 1H), 7.69 (td, *J*=7.8, 7.0, 1.7 Hz, 1H), 7.50-7.40 (m, 2H), 7.09 (dd, *J*=8.7, 1.7 Hz, 2H), 6.57 (d, *J*=8.3 Hz, 2H), 5.25 (s, 1H), 4.34-4.15 (m, 2H), 1.23 (td, *J*=7.1, 1.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 176.5, 171.1, 156.3, 154.3, 144.3, 134.1, 129.2, 126.0, 125.6, 123.8, 123.3, 121.4, 118.3, 114.9, 62.3, 52.9, 14.1; HRMS (ESI) calcd for $C_{19}H_{16}ClNO_4$ $(M+Na)^+$ 380.0660, found 380.0668.

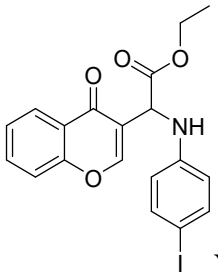
Ethyl-2-((4-bromophenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ia)



Yield 65% (34 mg); yellow solid; mp 127.1-129.6 °C; ^{1}H NMR (500

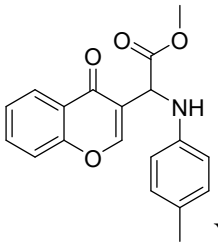
MHz, Chloroform-*d*) δ 8.24 (dd, *J*=8.1, 1.7 Hz, 1H), 8.04 (s, 1H), 7.69 (ddd, *J*=8.7, 7.1, 1.7 Hz, 1H), 7.48-7.42 (m, 2H), 7.22 (d, 2H), 6.52 (d, *J*=8.8 Hz, 2H), 5.24 (s, 1H), 4.23 (q, *J*=25.1, 7.1 Hz, 1H), 1.23 (t, *J*=7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 176.6, 171.1, 156.4, 154.4, 144.8, 134.2, 132.2, 126.1, 125.7, 123.9, 121.5, 118.4, 115.5, 110.5, 62.4, 52.9, 14.2; HRMS (ESI) calcd for $C_{19}H_{16}BrNO_4$ $(M+Na)^+$ 424.0155, found 424.0171.

Ethyl-2-((4-bromophenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ja)



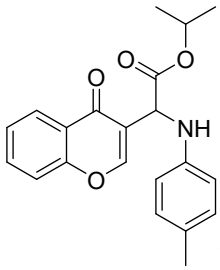
Yield 65% (34 mg); yellow solid; mp 132.2-134.1 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.25 (dd, *J*=8.1, 1.7 Hz, 1H), 8.05 (s, 1H), 7.68 (ddt, *J*=8.5, 7.1, 1.4 Hz, 1H), 7.47–7.41 (m, 2H), 6.85 (t, *J*=8.7 Hz, 2H), 6.58 (dd, *J*=8.9, 4.3 Hz, 2H), 5.22 (s, 1H), 4.29–4.15 (m, 2H), 1.22 (t, *J*=7.1 Hz, 3H).; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 176.5, 171.3, 156.4, 154.4, 134.1, 126.1, 125.6, 124.0, 118.3, 116.0, 115.8, 115.1, 115.0, 62.2, 53.9, 27.0, 14.1; HRMS (ESI) calcd for $C_{19}H_{16}INO_4$ $(M+H)^+$ 450.0197, found 450.0202.

Methyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3ka)



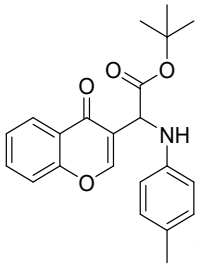
Yield 65% (34 mg); yellow solid; mp 126.5-127.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, 1H), 8.06 (s, 1H), 7.66 (td, *J*=7.6, 7.1, 1.7 Hz, 1H), 7.42 (t, *J*=7.4 Hz, 2H), 6.96 (d, *J*=8.1 Hz, 2H), 6.57 (d, *J*=8.4 Hz, 2H), 5.31 (s, 1H), 3.76 (s, 3H), 2.20 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 176.7, 172.0, 156.5, 154.4, 143.5, 134.0, 130.0, 128.1, 126.1, 125.5, 124.0, 121.9, 118.3, 114.1, 53.3, 53.0, 20.5; HRMS (ESI) calcd for $C_{19}H_{17}NO_4$ $(M+Na)^+$ 346.1050, found 346.1054.

Isopropyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3la)



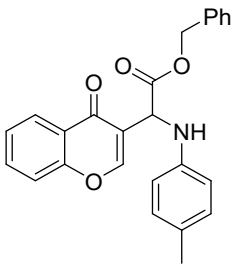
Yield 65% (34 mg); yellow solid; mp 145.5-147.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J*=8.0, 1.7 Hz, 1H), 8.04 (s, 1H), 7.66 (ddd, *J*=8.6, 7.1, 1.7 Hz, 1H), 7.44-7.39 (m, 2H), 6.96 (d, *J*=8.2 Hz, 2H), 6.58 (d, *J*=8.4 Hz, 2H), 5.23 (s, 1H), 5.08 (p, *J*=6.2 Hz, 1H), 2.20 (s, 3H), 1.26 (d, *J*=6.3 Hz, 3H), 1.16 (d, *J*=6.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.5, 171.0, 156.5, 154.3, 143.7, 133.9, 129.9, 128.0, 126.1, 125.5, 124.1, 122.1, 118.3, 114.2, 69.9, 53.7, 21.8, 21.6, 20.5; HRMS (ESI) calcd for $C_{21}H_{21}NO_4$ $(M+H)^+$ 352.1543, found 352.1552.

***Tert*-butyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3ma)**



Yield 65% (34 mg); yellow solid; mp 142.8-145.2 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.26 (dt, *J*=8.1, 2.0 Hz, 1H), 8.04 (d, *J*=2.1 Hz, 1H), 7.69-7.64 (m, 1H), 7.45-7.40 (m, 2H), 6.96 (dd, *J*=8.5, 2.2 Hz, 2H), 6.57 (dd, *J*=8.6, 2.3 Hz, 2H), 5.20 (d, *J*=2.1 Hz, 1H), 2.20 (s, 3H), 1.43 (d, *J*=2.1 Hz, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.5, 170.5, 156.5, 154.1, 143.7, 133.9, 129.9, 127.8, 126.1, 125.4, 124.1, 122.5, 118.3, 114.0, 82.7, 53.9, 28.0, 20.5; HRMS (ESI) calcd for $C_{22}H_{23}NO_4$ $(M+H)^+$ 366.1700, found 366.1718.

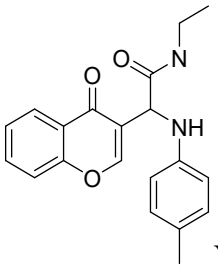
Benzyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3na)



Yield 65% (34 mg); yellow solid; mp 137.4-138.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J*=8.2, 1.7 Hz, 1H), 7.94 (s, 1H), 7.59 (ddd, *J*=8.7, 7.2, 1.7 Hz,

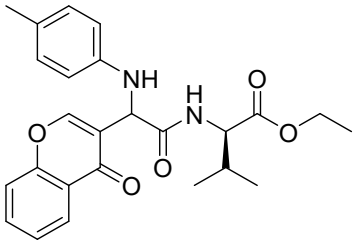
1H), 7.38-7.32 (m, 2H), 7.19 (d, *J*=1.8 Hz, 6H), 6.89 (d, *J*=8.1 Hz, 2H), 6.54-6.49 (m, 2H), 5.27 (s, 1H), 5.13 (q, 2H), 2.14 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 176.6, 171.3, 156.4, 154.4, 143.5, 135.5, 134.0, 129.9, 128.5, 128.3, 128.1, 128.0, 126.1, 125.5, 124.0, 121.7, 118.3, 114.2, 67.6, 53.7, 20.5; HRMS (ESI) calcd for $C_{25}H_{21}NO_4$ $(M+H)^+$ 422.1363, found 422.1367.

3-(2-(Ethyl-l2-azanyl)-2-oxo-1-(*p*-tolylamino)ethyl)-4*H*-chromen-4-one (3oa)



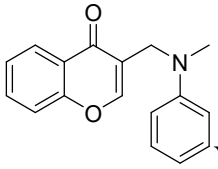
Yield 65% (34 mg); yellow solid; mp 127.6-128.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J*=8.5, 1.7 Hz, 1H), 8.12 (s, 1H), 7.71 (td, *J*=7.6, 7.1, 1.7 Hz, 1H), 7.50-7.45 (m, 2H), 6.94 (d, *J*=8.1 Hz, 2H), 6.47 (d, *J*=8.3 Hz, 2H), 5.13 (s, 1H), 3.38-3.31 (m, 1H), 3.26-3.20 (m, 1H), 2.20 (s, 3H), 1.12 (t, *J*=7.3 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 179.0, 169.8, 156.7, 155.4, 143.4, 134.3, 130.0, 127.5, 125.8, 125.7, 123.7, 121.6, 118.5, 113.7, 53.7, 34.8, 20.4, 14.8; HRMS (ESI) calcd for $C_{20}H_{19}N_2O_3$ $(M+H)^+$ 359.1361, found 359.1384.

Ethyl-(2-(4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetyl)-D-valinate (3pa)



Yield 65% (34 mg); yellow solid; mp 131.5-132.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dt, *J*=8.2, 2.3 Hz, 1H), 8.13 (d, *J*=14.1 Hz, 1H), 7.97 (dd, *J*=30.2, 8.6 Hz, 1H), 7.70 (tdd, *J*=7.1, 3.5, 1.7 Hz, 1H), 7.50-7.43 (m, 2H), 6.94 (dd, *J*=8.5, 2.5 Hz, 2H), 6.52-6.46 (m, 2H), 5.27 (d, *J*=12.4 Hz, 2H), 4.45 (ddd, *J*=8.6, 4.8, 1.6 Hz, 1H), 4.26-4.19 (m, 1H), 4.03-3.95 (m, 1H), 2.20 (s, 3H), 1.29 (s, 1H), 1.07-0.96 (m, 6H), 0.79 (dd, *J*=18.3, 6.9 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 179.0, 171.1, 170.2, 156.6, 155.4, 143.3, 134.2, 129.9, 127.7, 125.9, 125.6, 123.7, 121.2, 118.4, 113.8, 61.0, 58.1, 53.7, 30.9, 20.4, 19.2, 17.7, 14.0; HRMS (ESI) calcd for $C_{25}H_{28}N_2O_5$ $(M+H)^+$ 437.2071, found 437.2079.

3-((Methyl(phenyl)amino)methyl)-4*H*-chromen-4-one (3qa)



Yield 65% (34 mg); yellow solid; mp 119.3-121.4 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.09 (d, *J*=2.7 Hz, 2H), 7.79 (ddd, *J*=8.7, 7.0, 1.7 Hz, 1H), 7.61 (d, *J*=8.4 Hz, 1H), 7.49 (t, *J*=7.5 Hz, 1H), 7.15 (dd, *J*=8.7, 7.1 Hz, 2H), 6.76 (d, *J*=8.2 Hz, 2H), 6.63 (t, *J*=7.2 Hz, 1H), 4.34 (s, 2H), 3.00 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.1, 156.7, 152.9, 149.1, 133.7, 129.4, 125.7, 125.2, 123.8, 120.3, 118.3, 117.1, 112.4, 49.3, 39.0; HRMS (ESI) calcd for $C_{17}H_{15}NO_2$ $(M+H)^+$ 266.1176, found 266.1185.

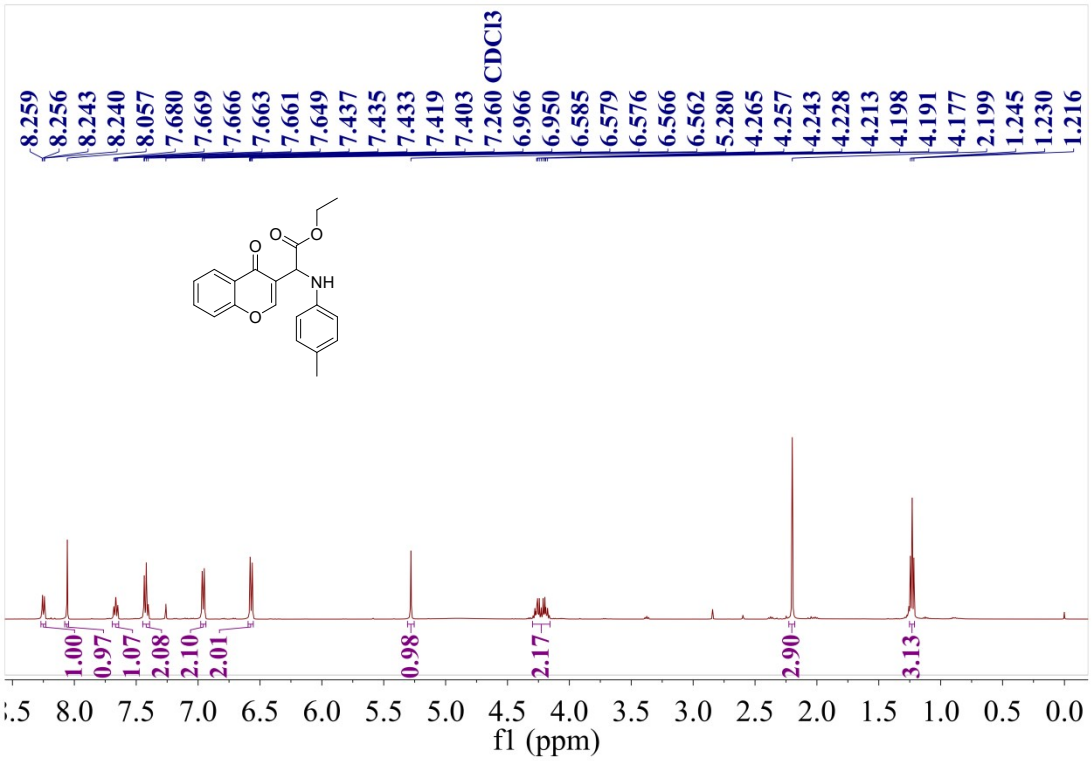
10. References

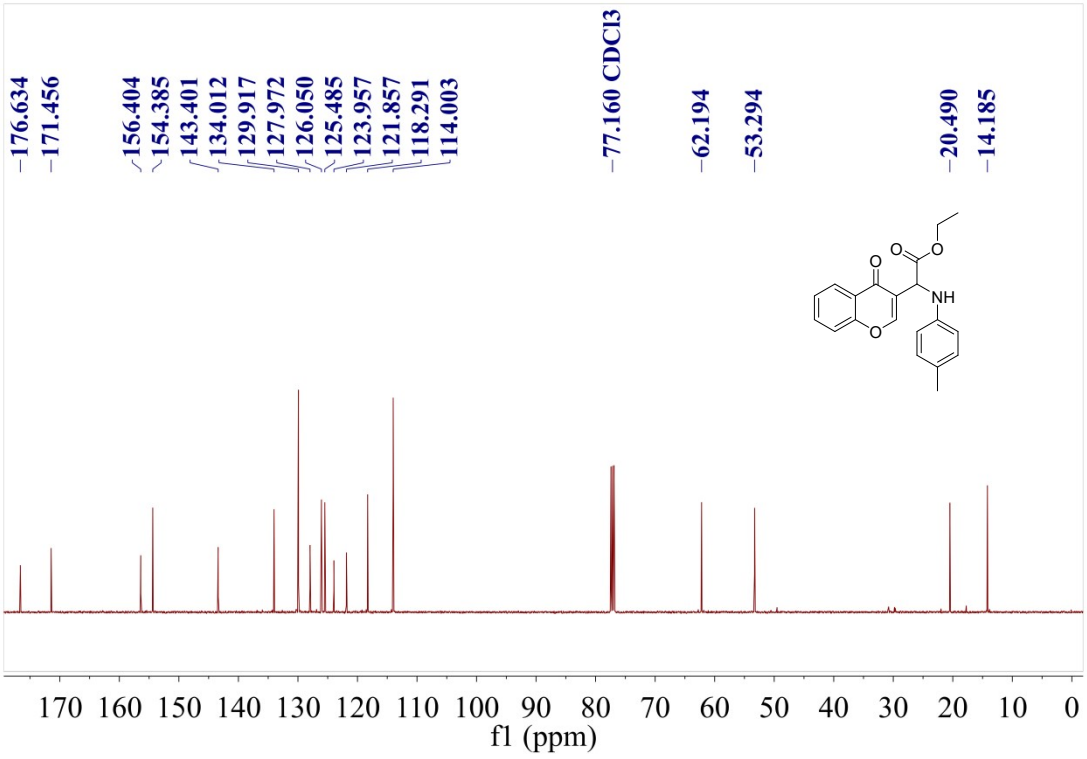
[1] D. A. Vasselin, A. D. Westwell, C. S. Matthews, T. D. Bradshaw and M. F. G. Stevens, *Journal of Medicinal Chemistry* **2006**, *49*, 3973-3981.

[2] R. Rohlmann, T. Stopka, H. Richter and O. G. Mancheño, *J. Org. Chem*. **2013**, *78*, 6050-6064.

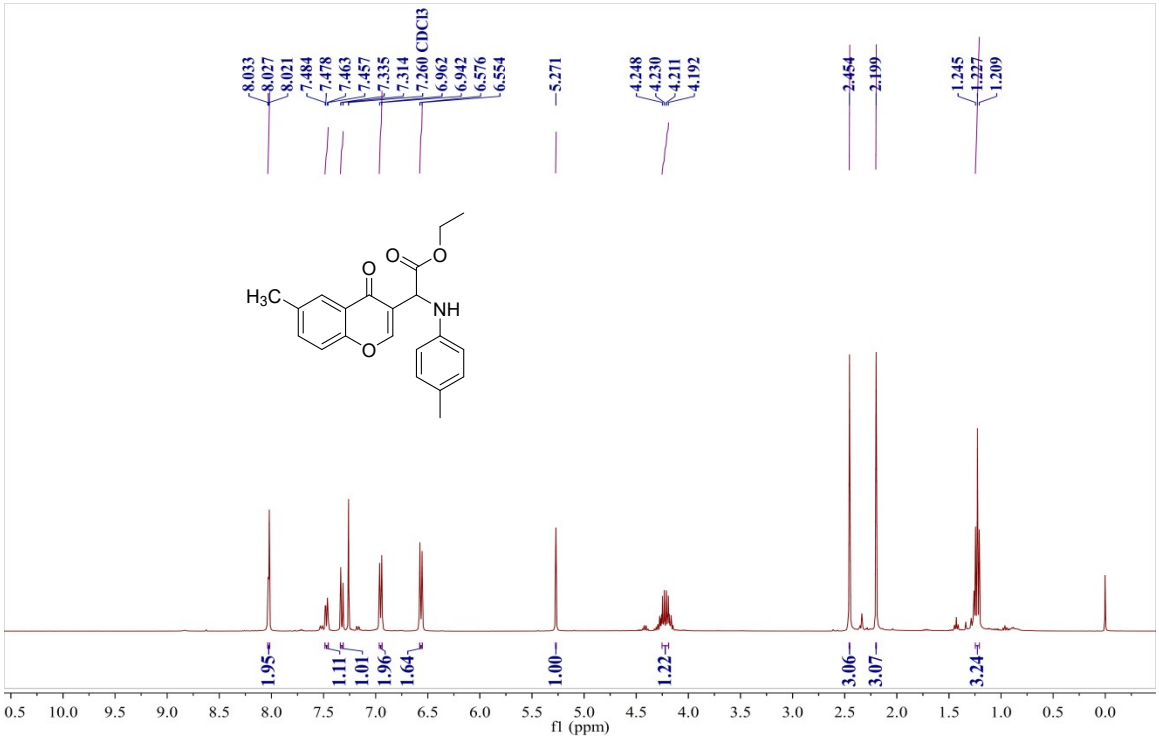
11. NMR Spectra of Products

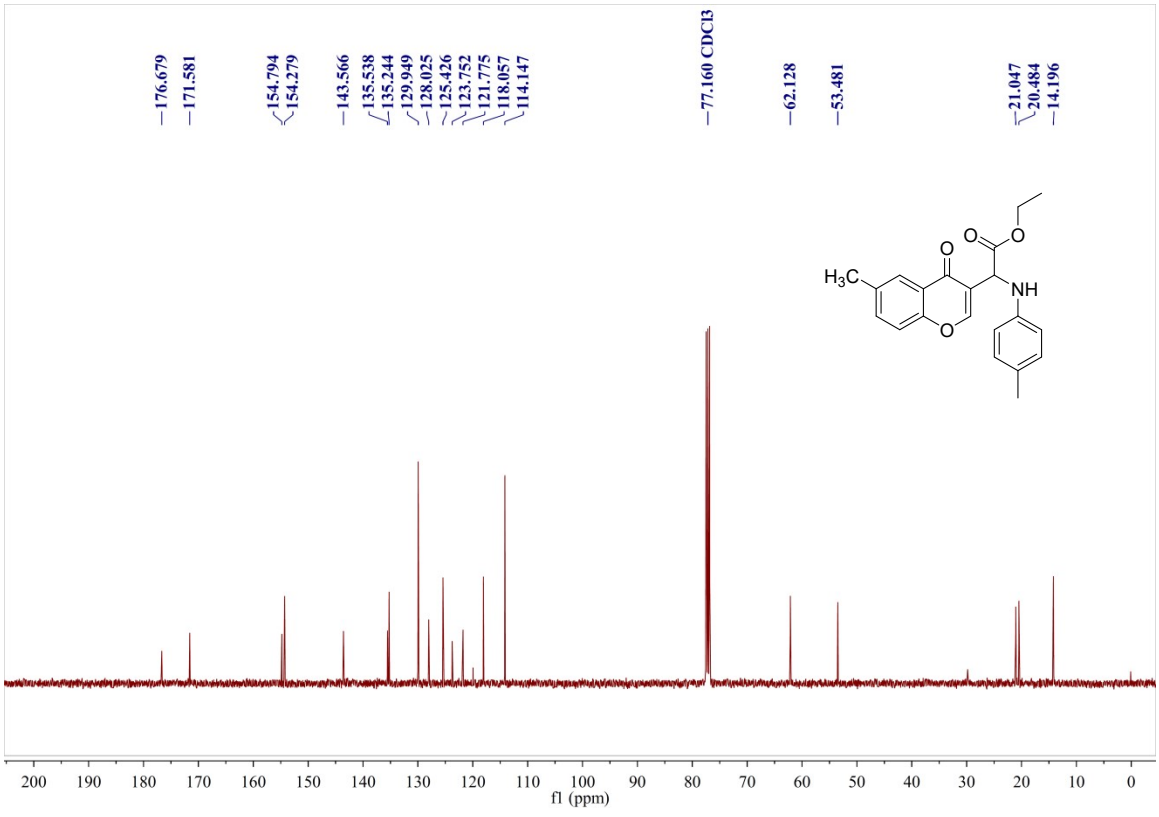
Ethyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3aa)



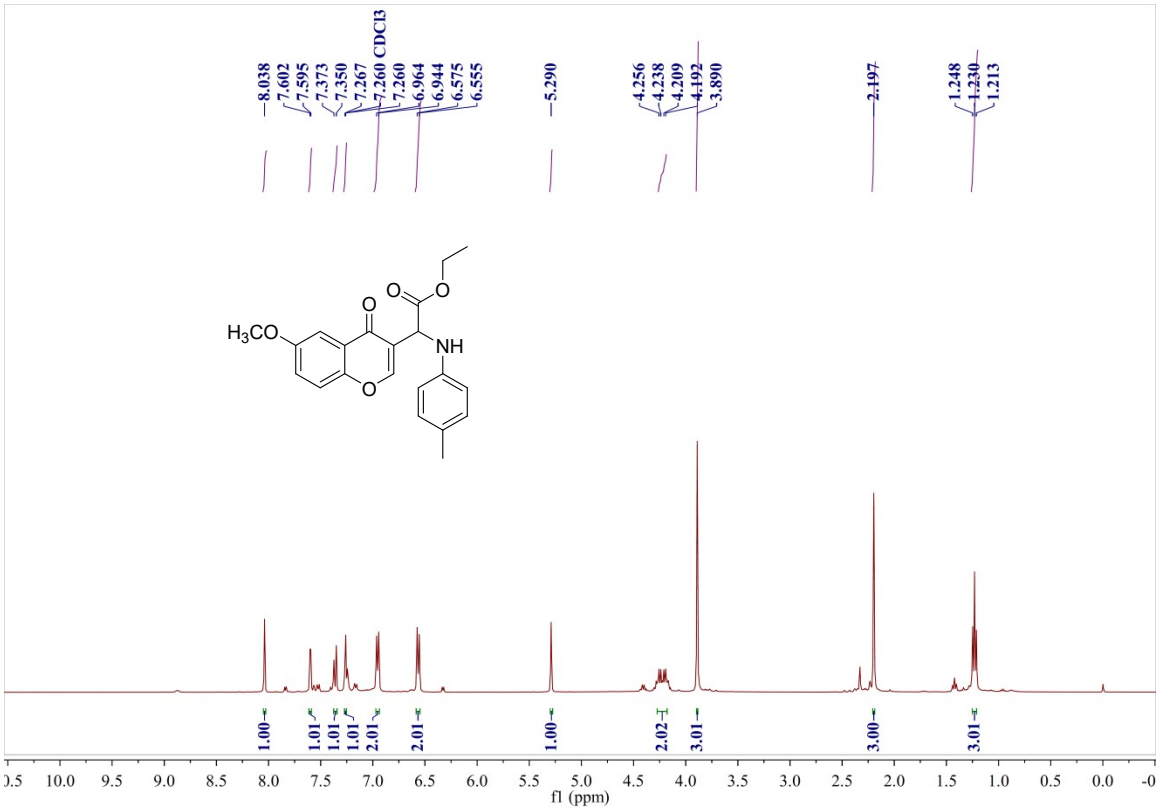


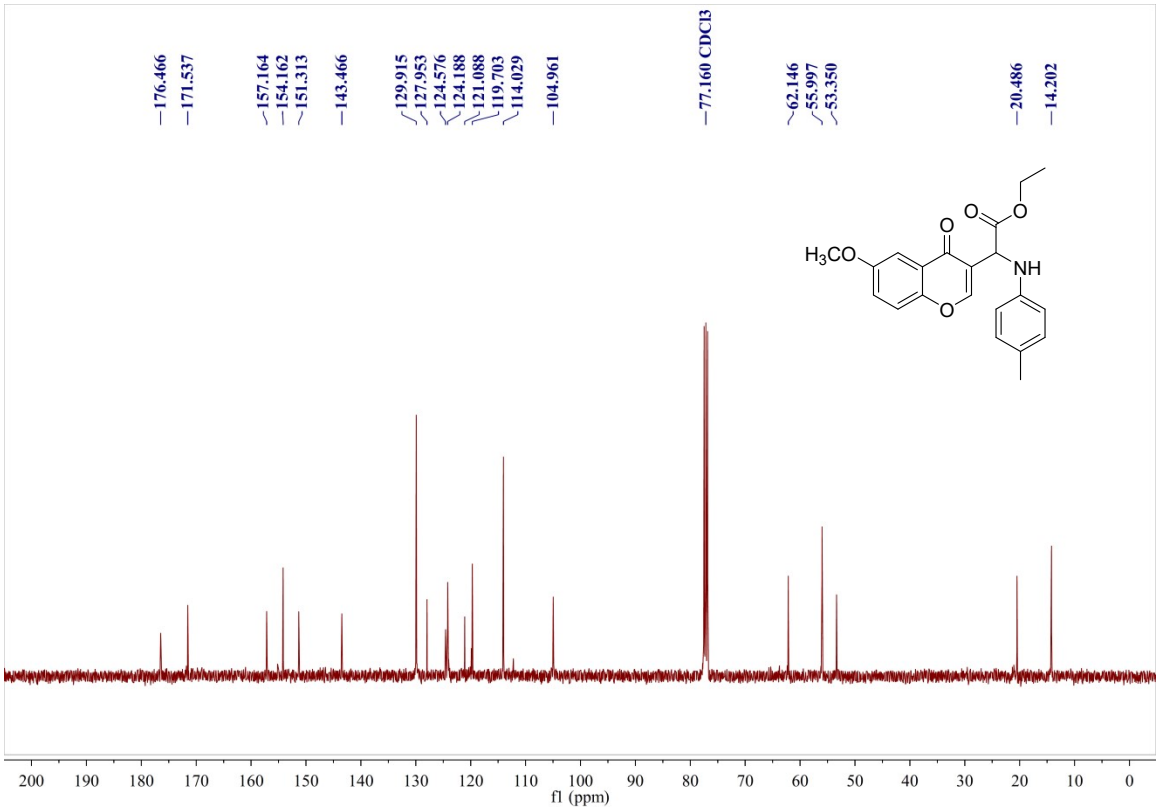
Ethyl-2-(6-methyl-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ab)



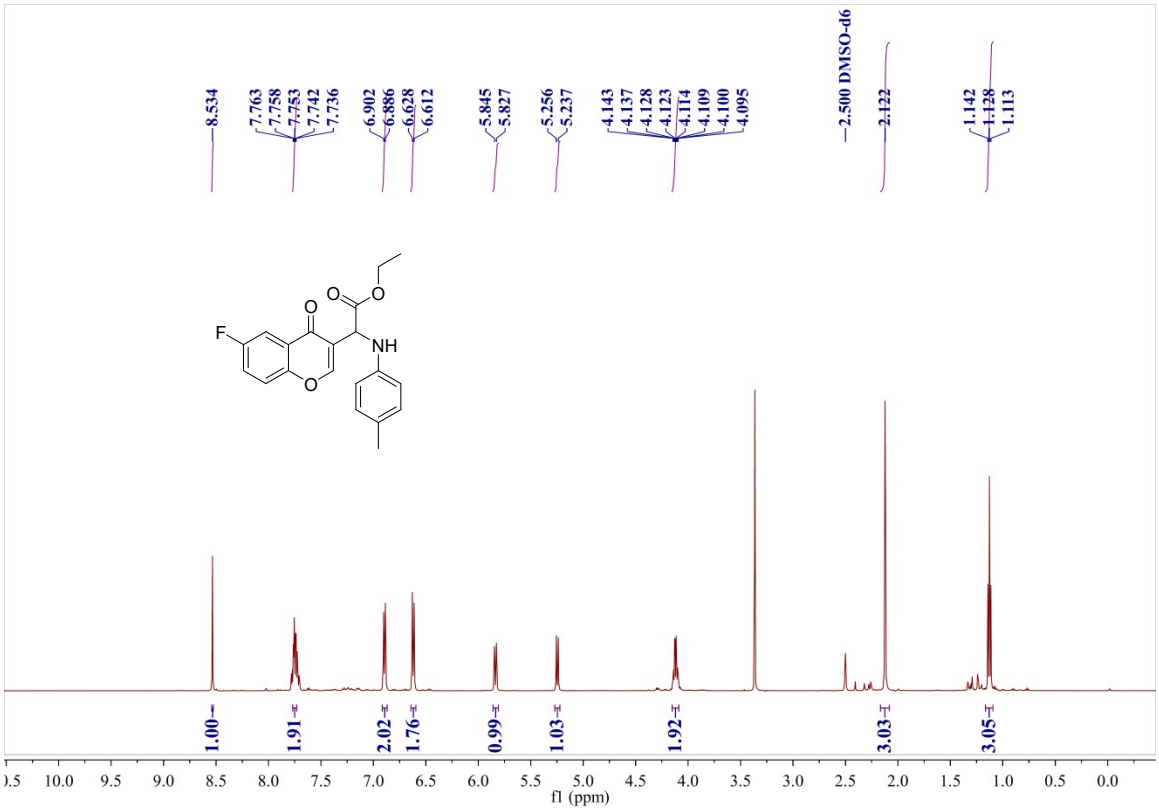


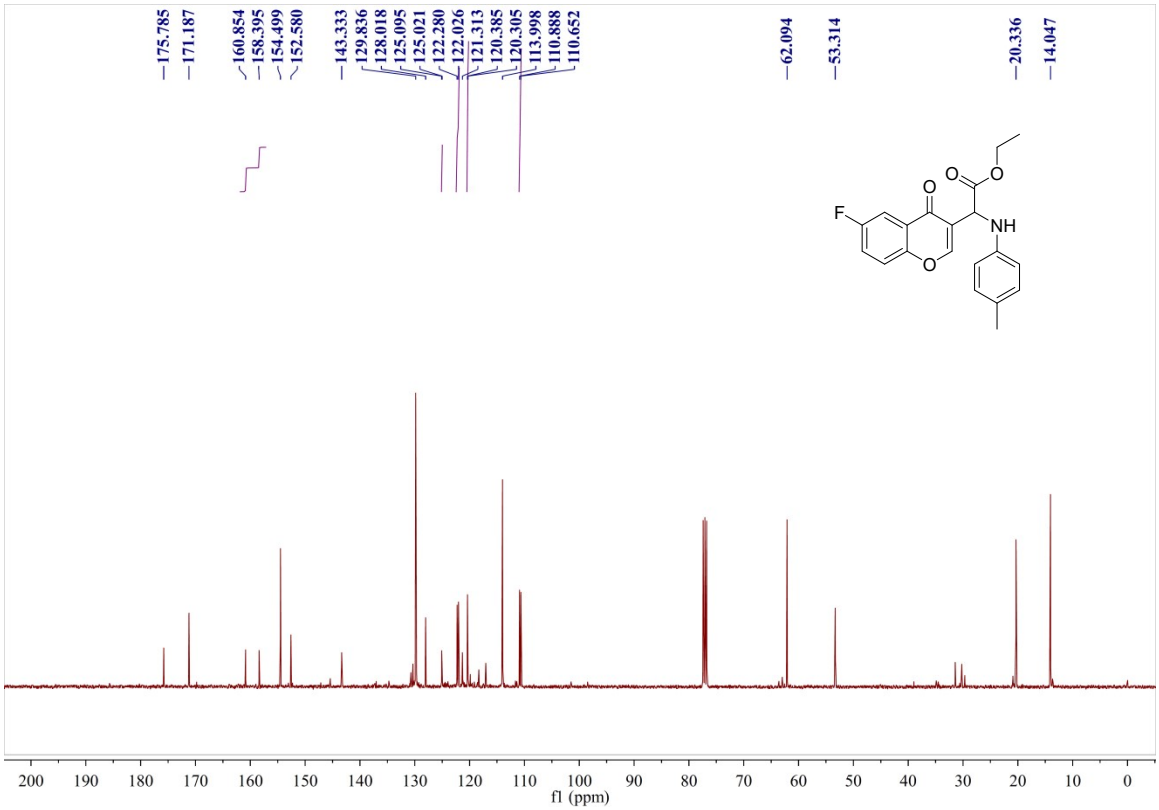
Ethyl-2-(6-methoxy-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ac)

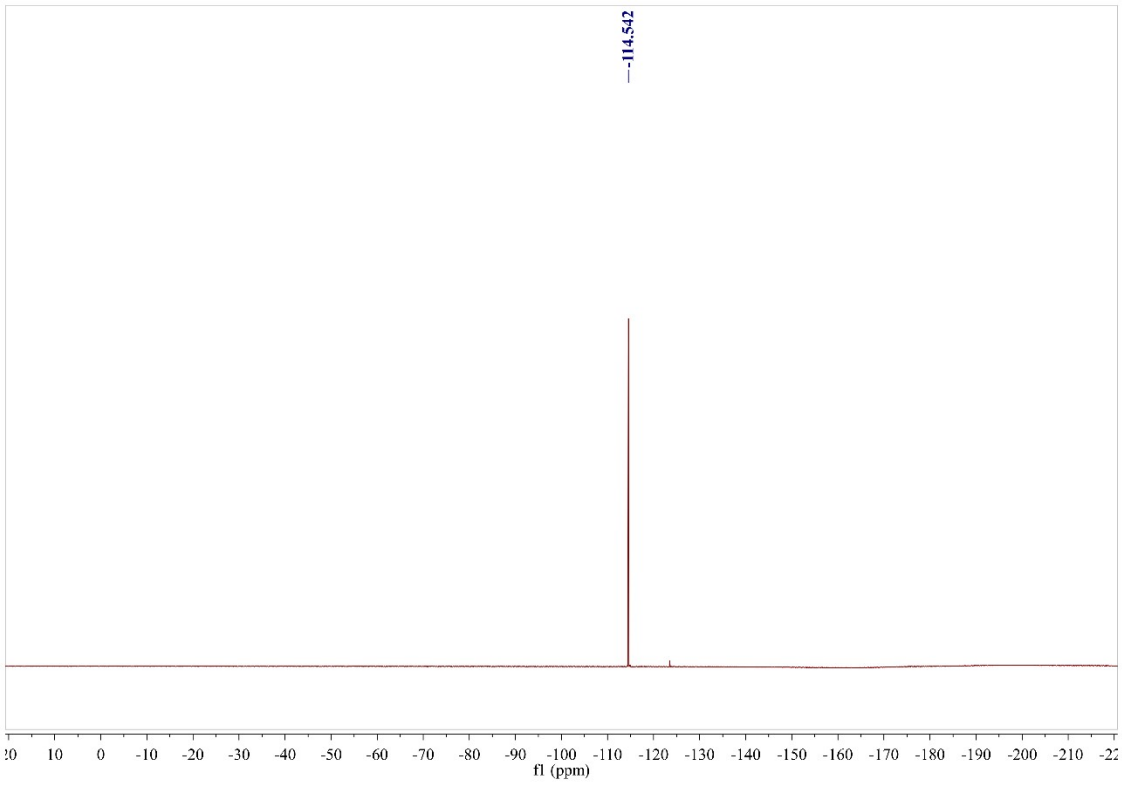




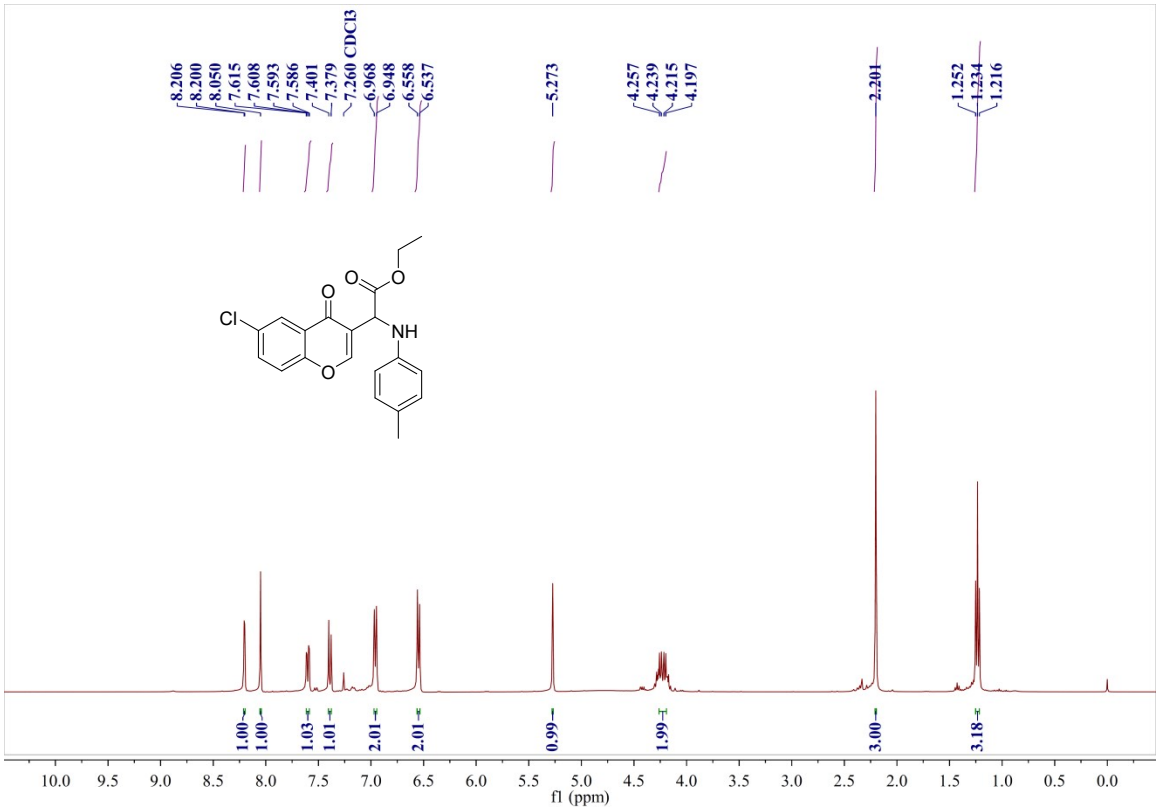
Ethyl-2-(6-fluoro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ad)

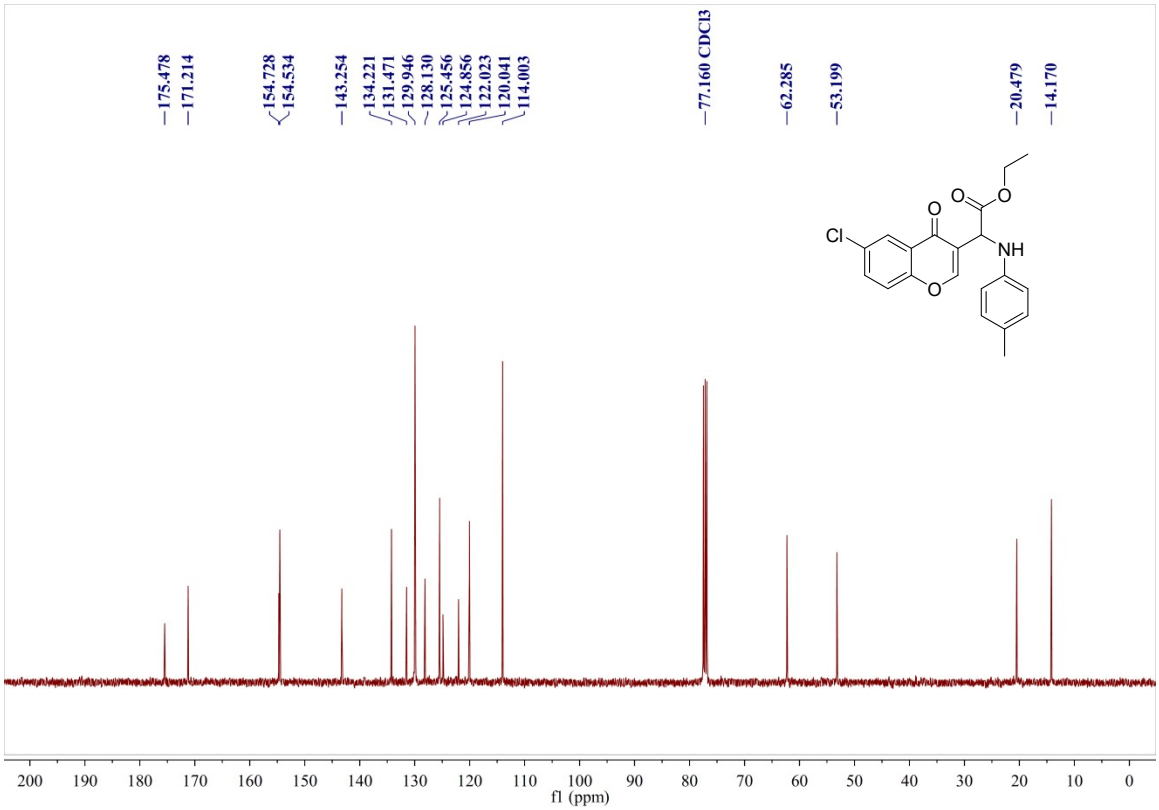




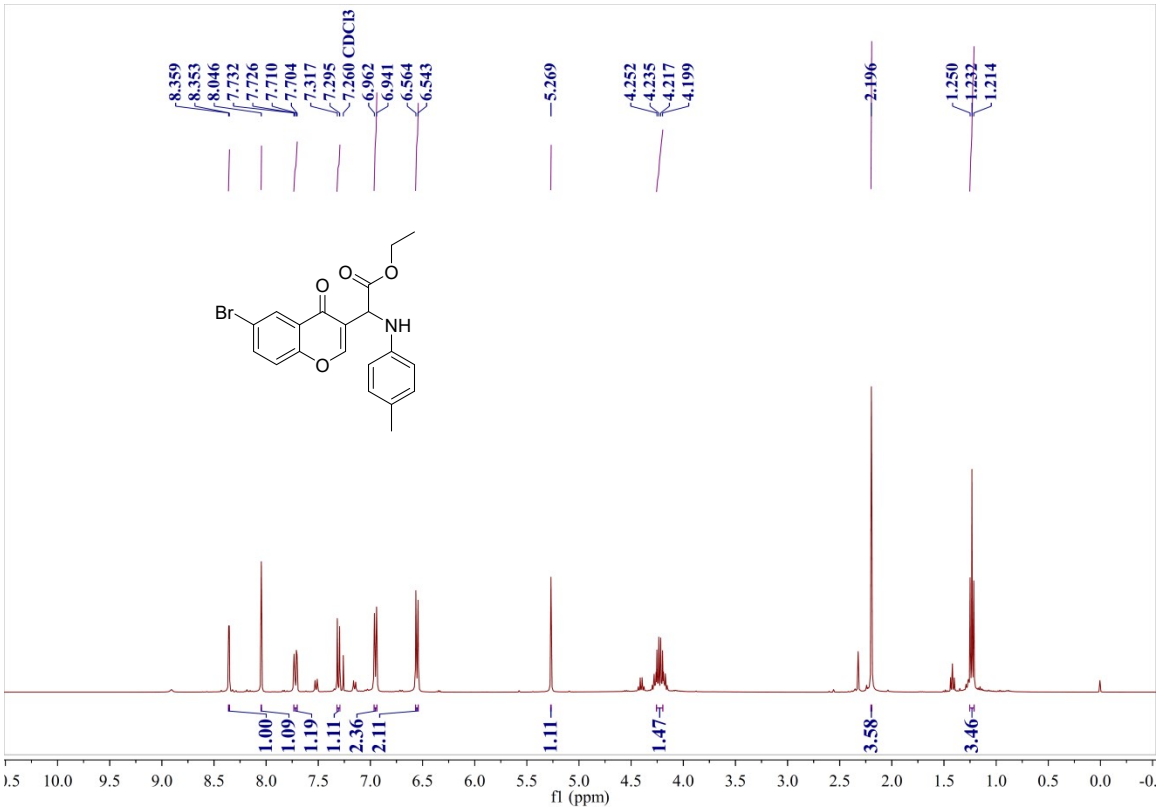

-114.542
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

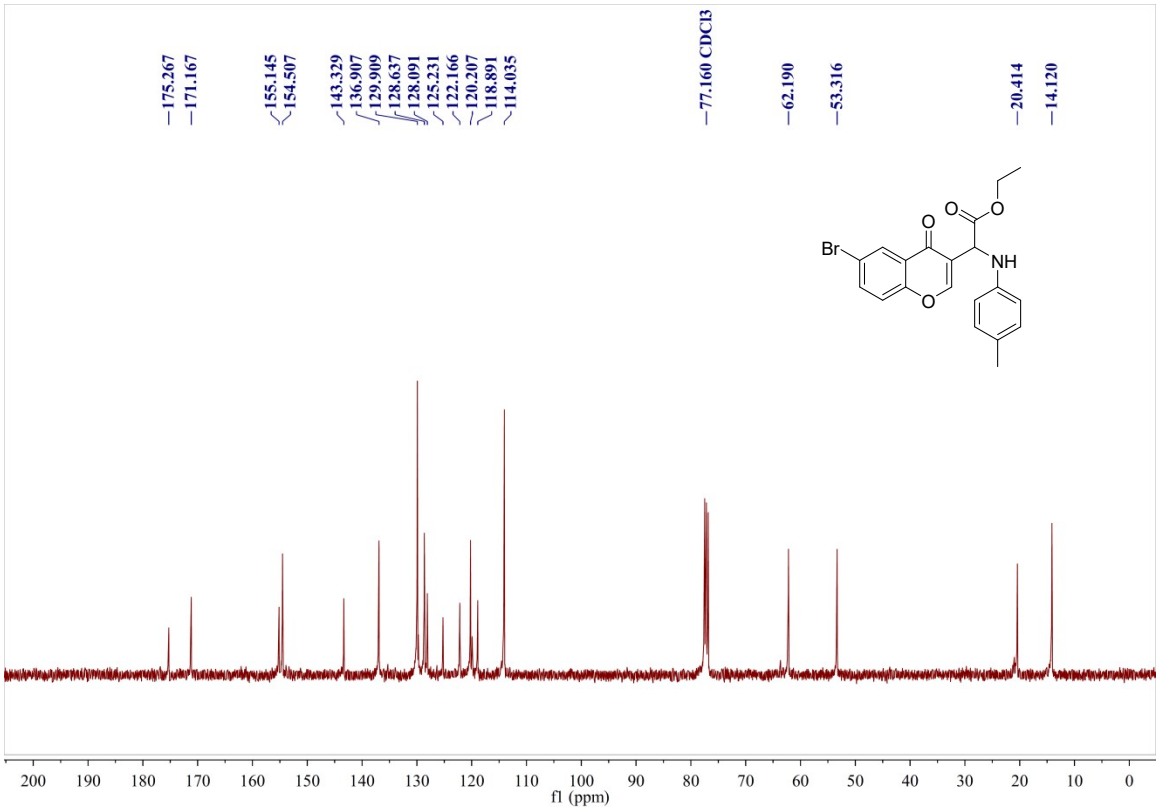
Ethyl-2-(6-chloro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ae)



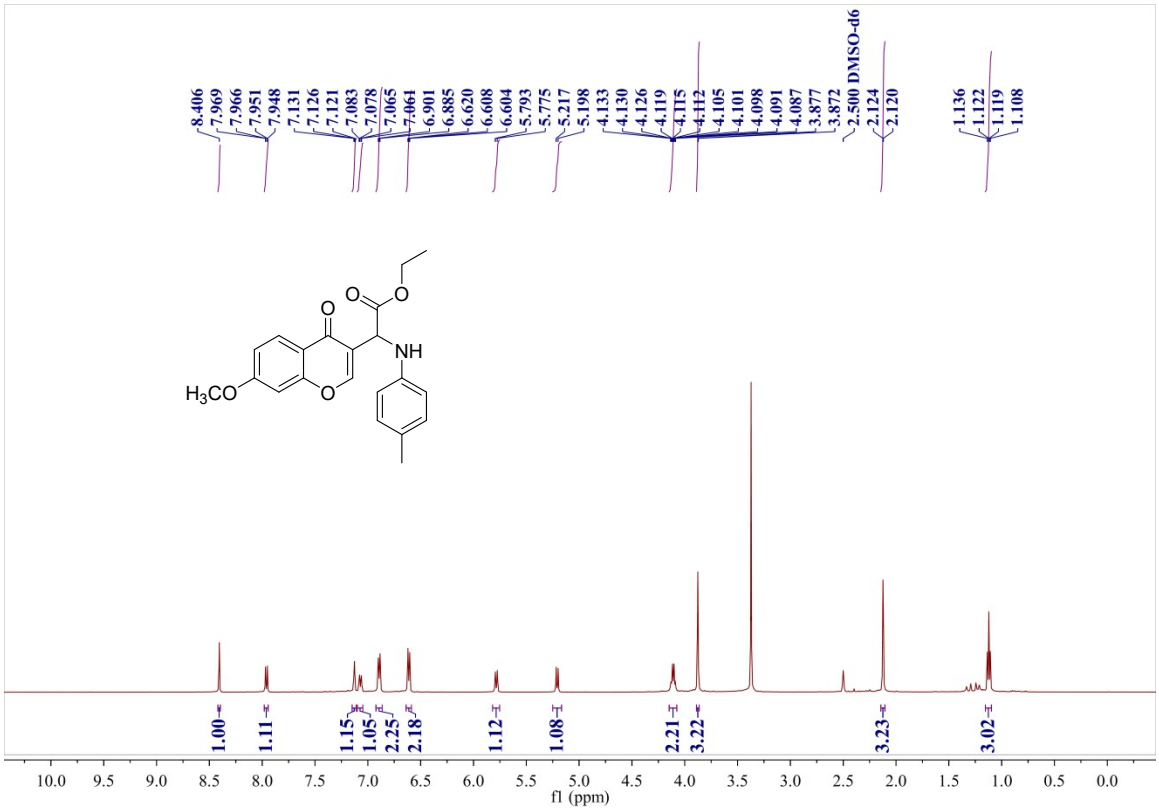


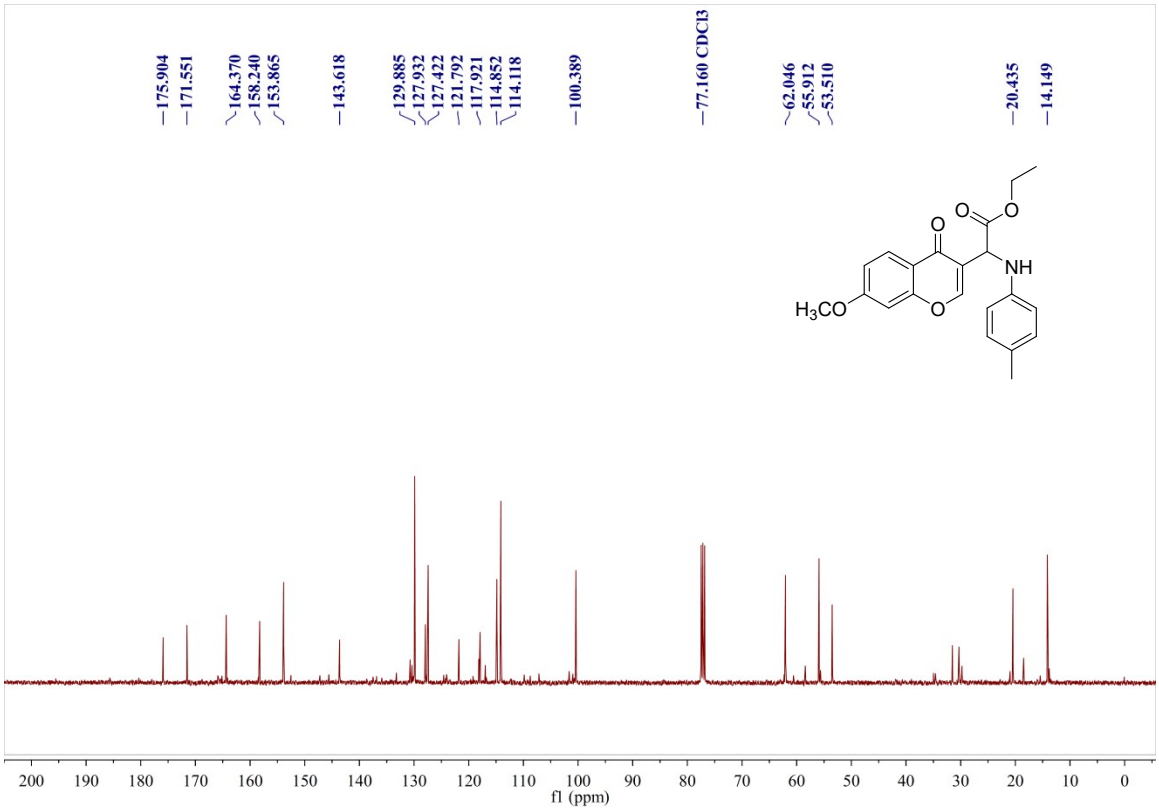
Ethyl-2-(6-bromo-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3af)



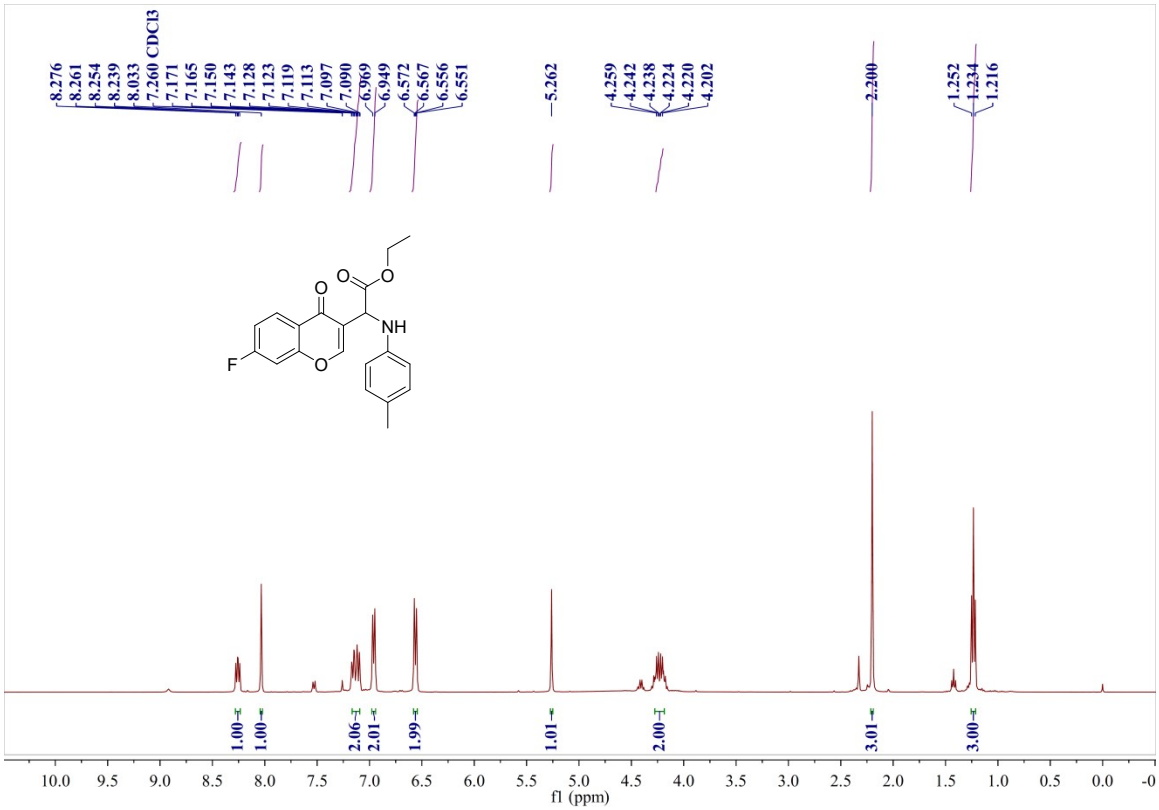


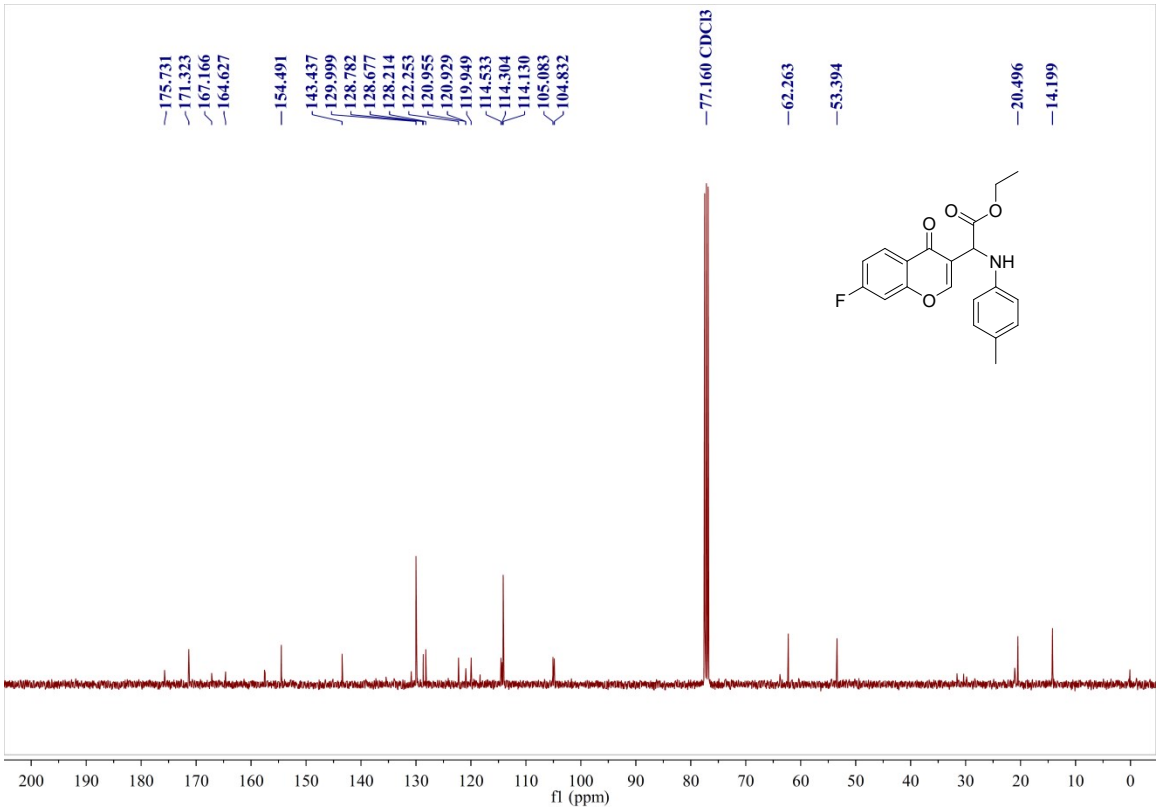
Ethyl-2-(7-methoxy-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ag)

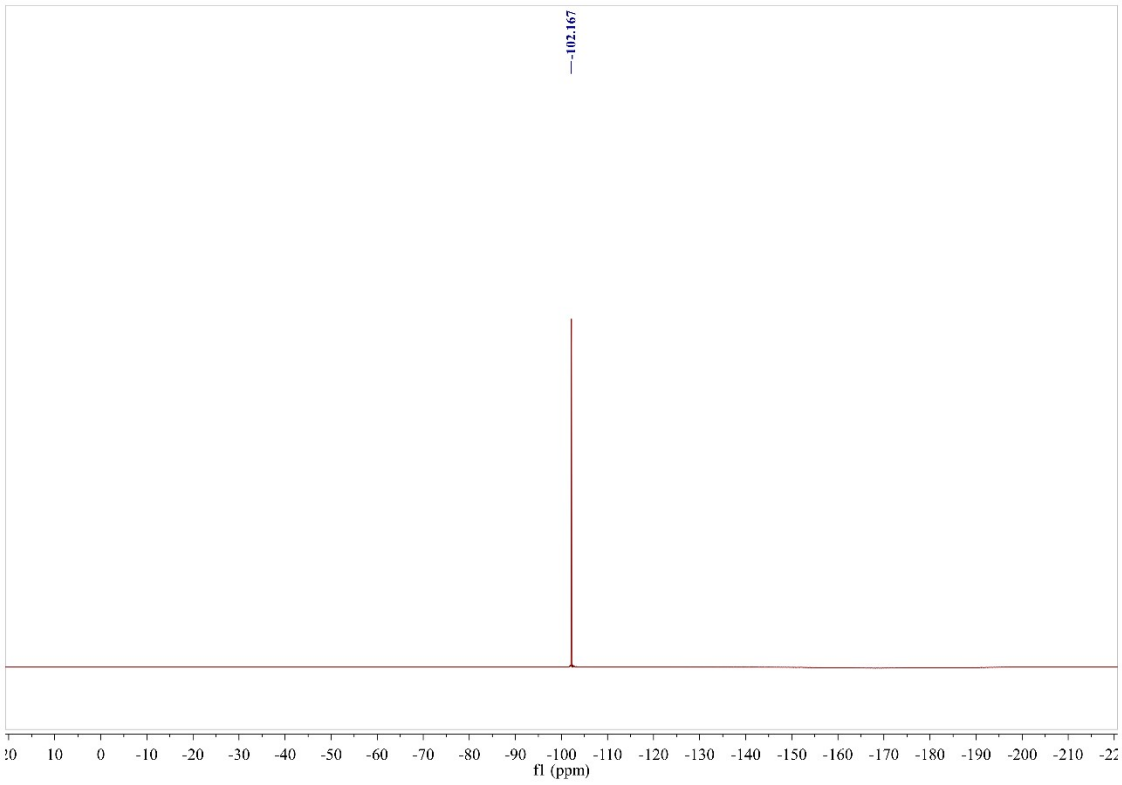




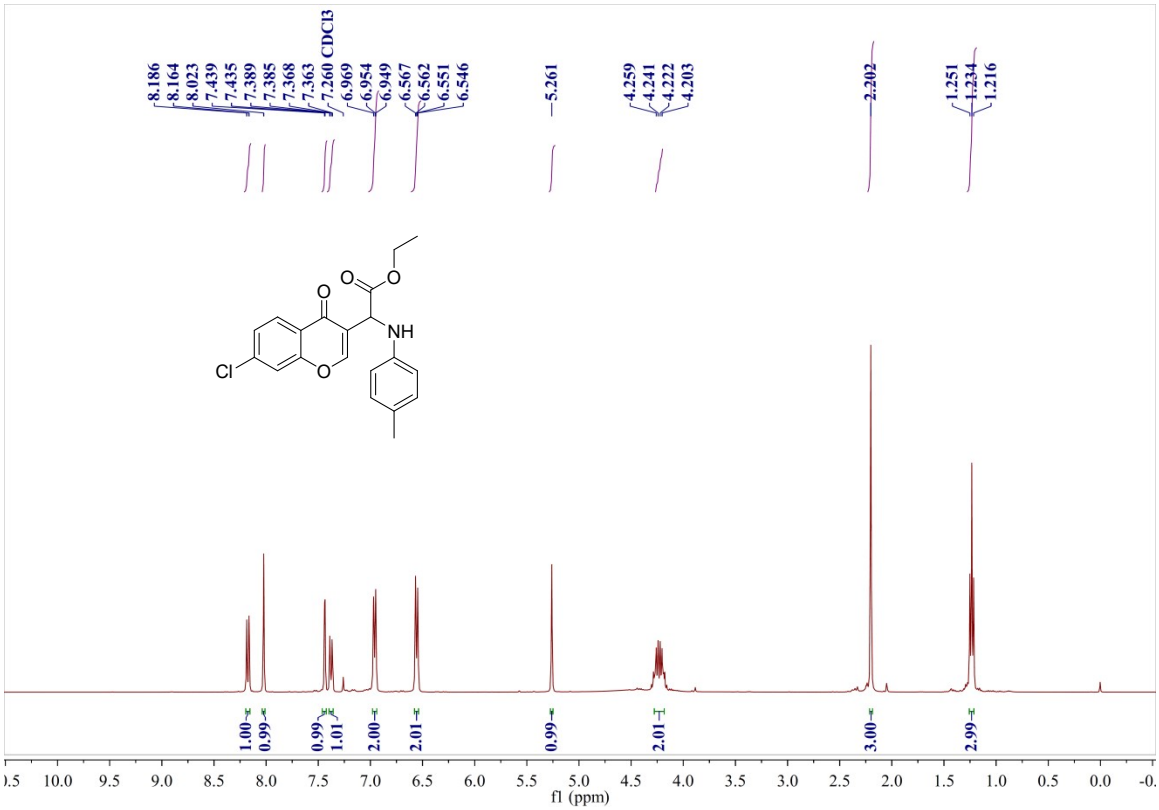
Ethyl-2-(7-fluoro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ah)

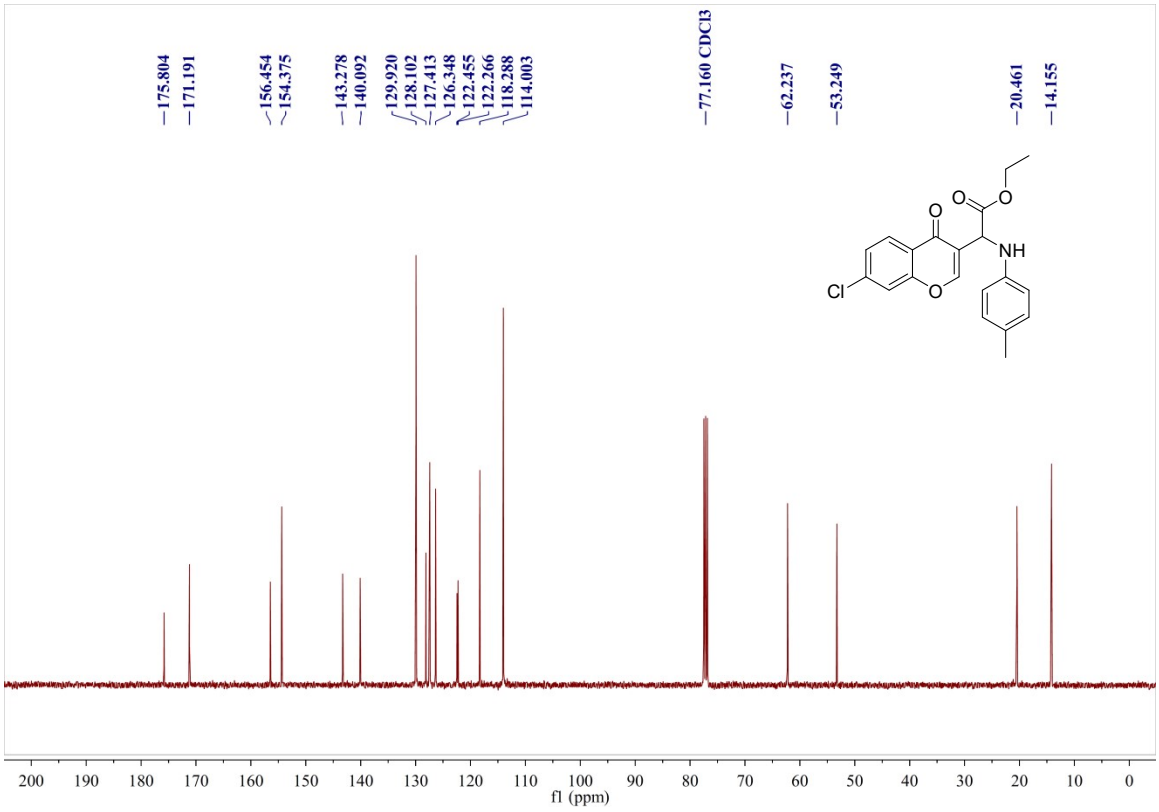




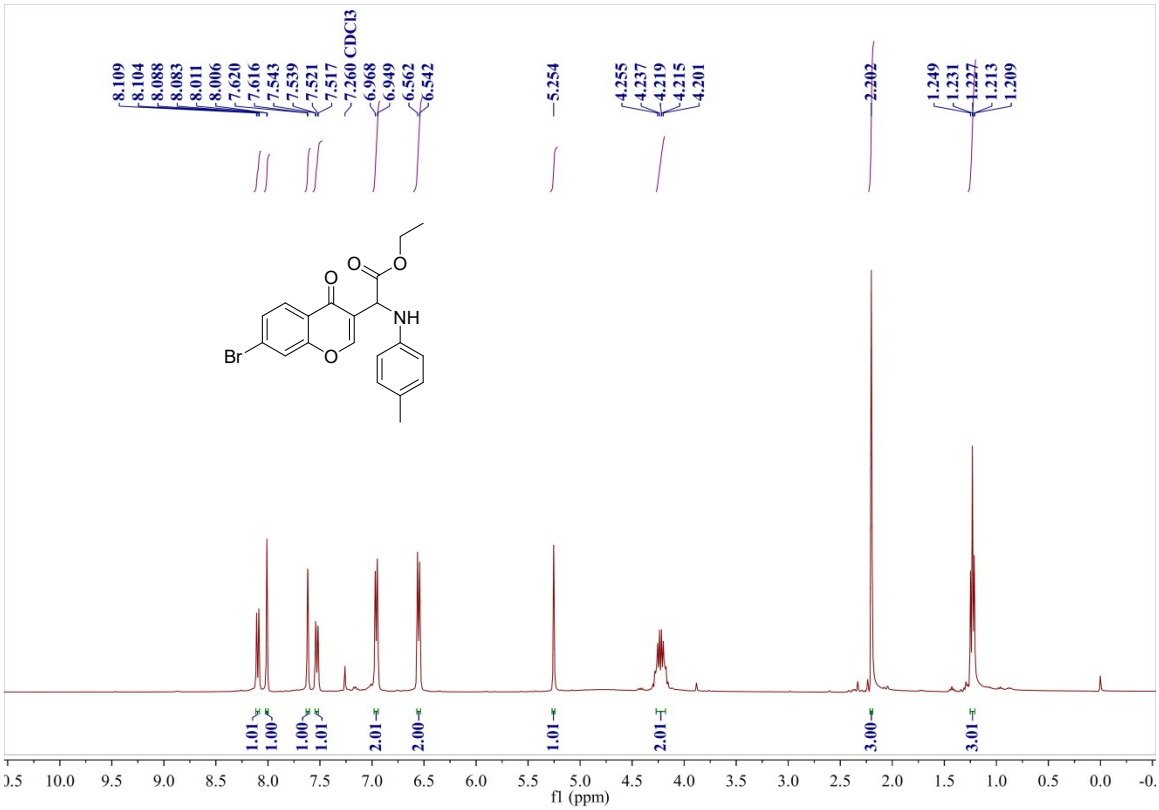

-102.167
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

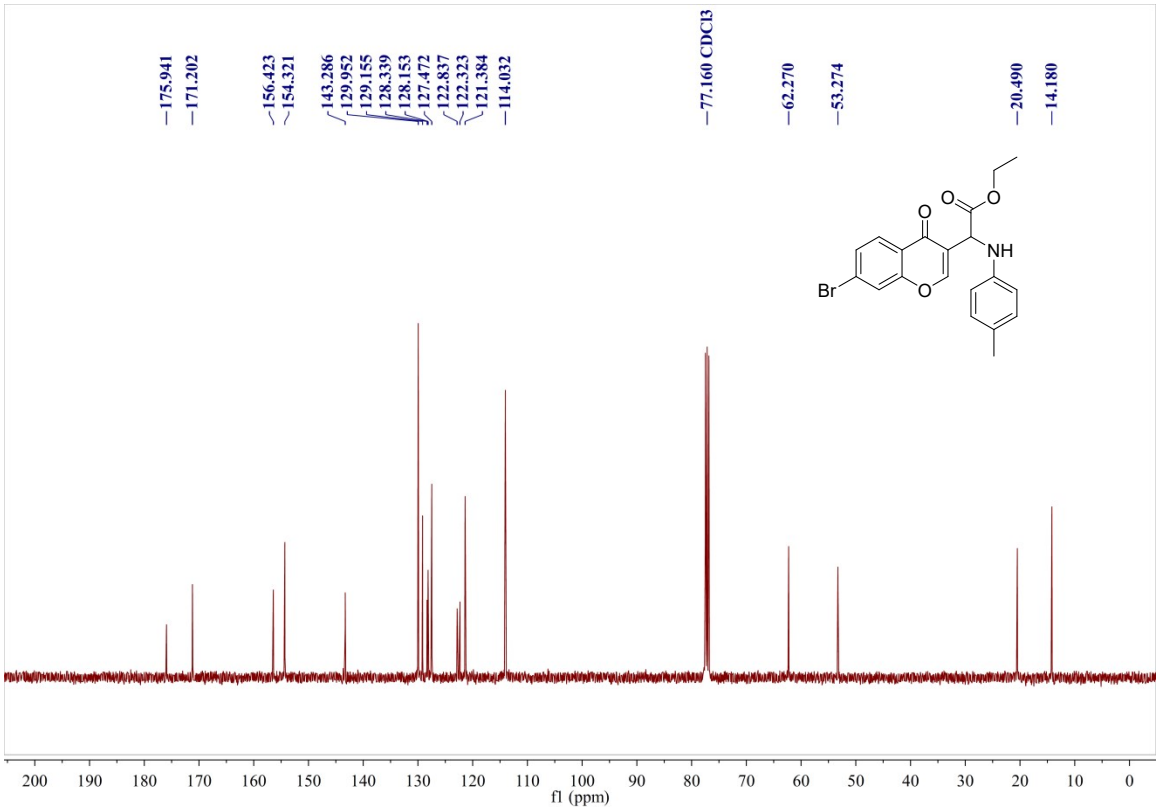
Ethyl-2-(7-chloro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ai)



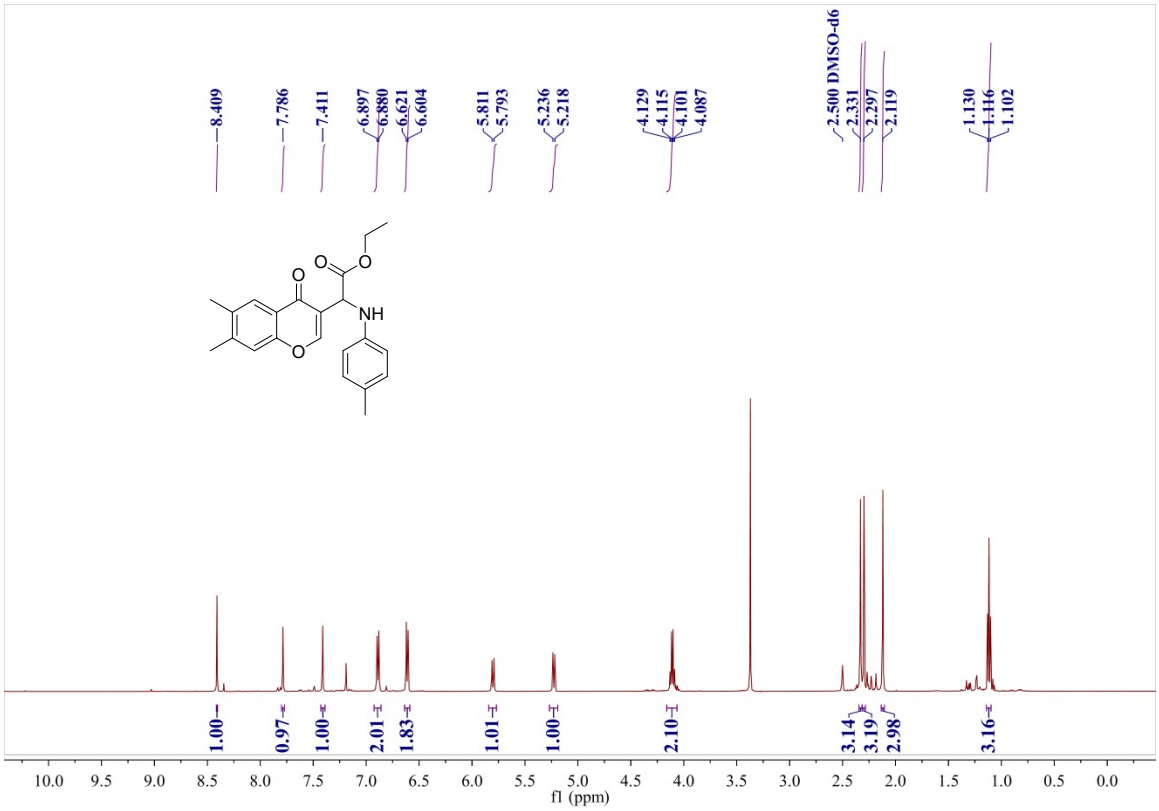


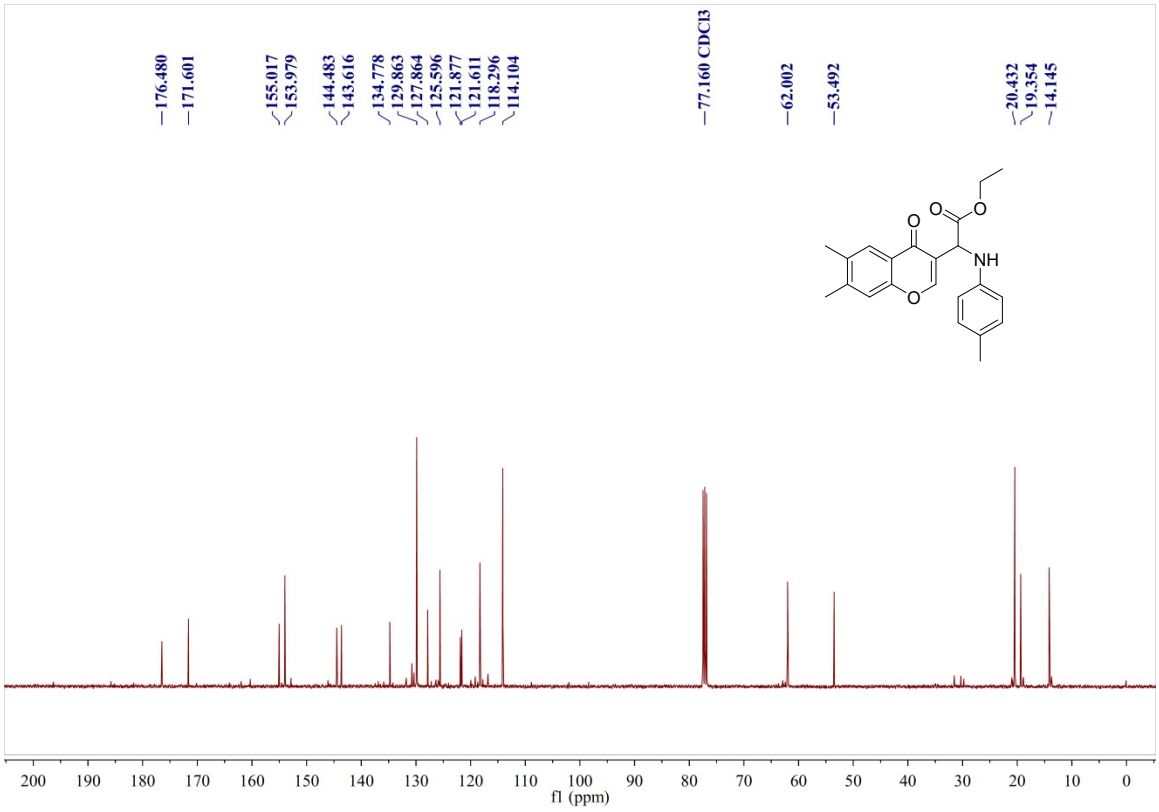
Ethyl-2-(7-bromo-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3aj)



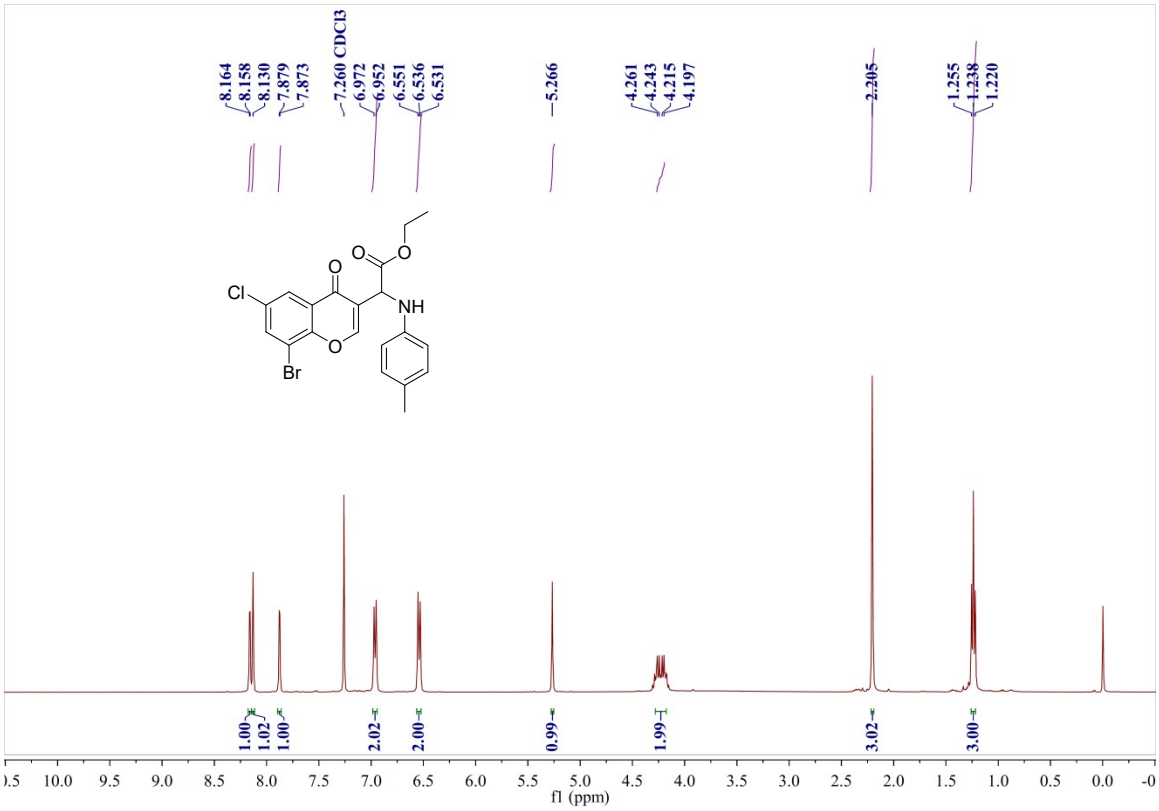


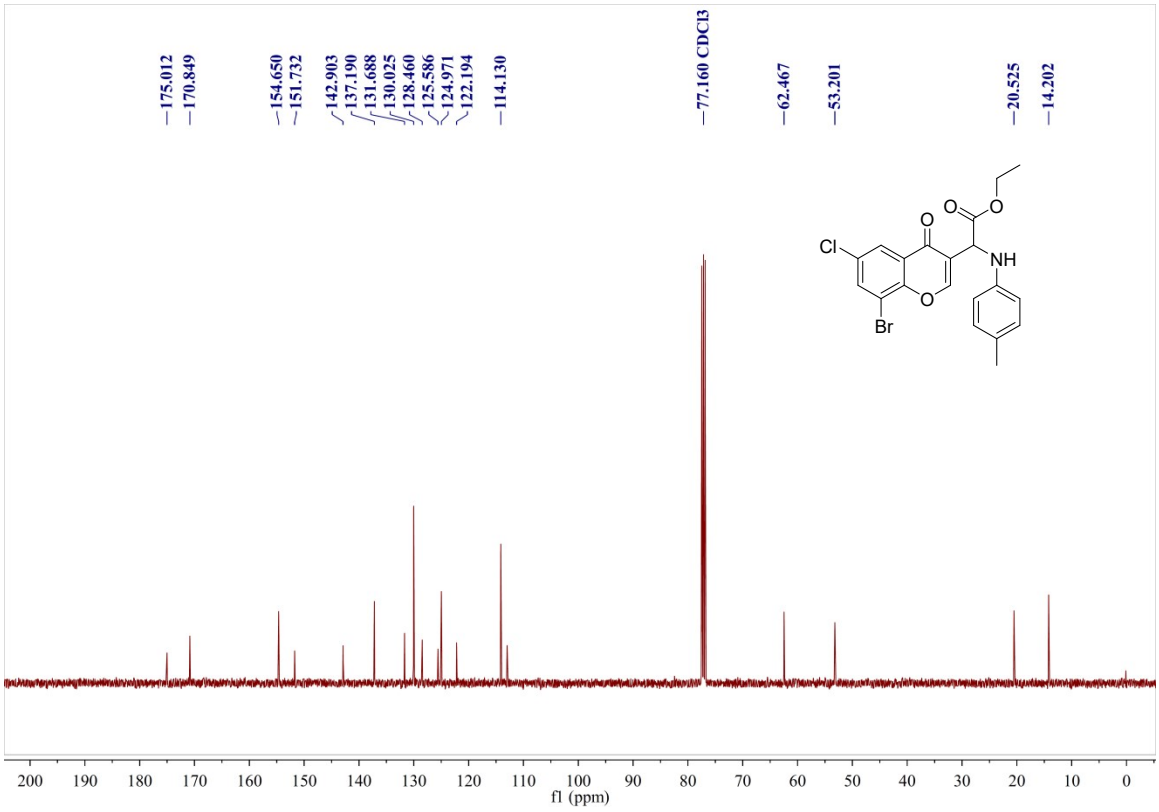
Ethyl-2-(6,7-dimethyl-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3ak)



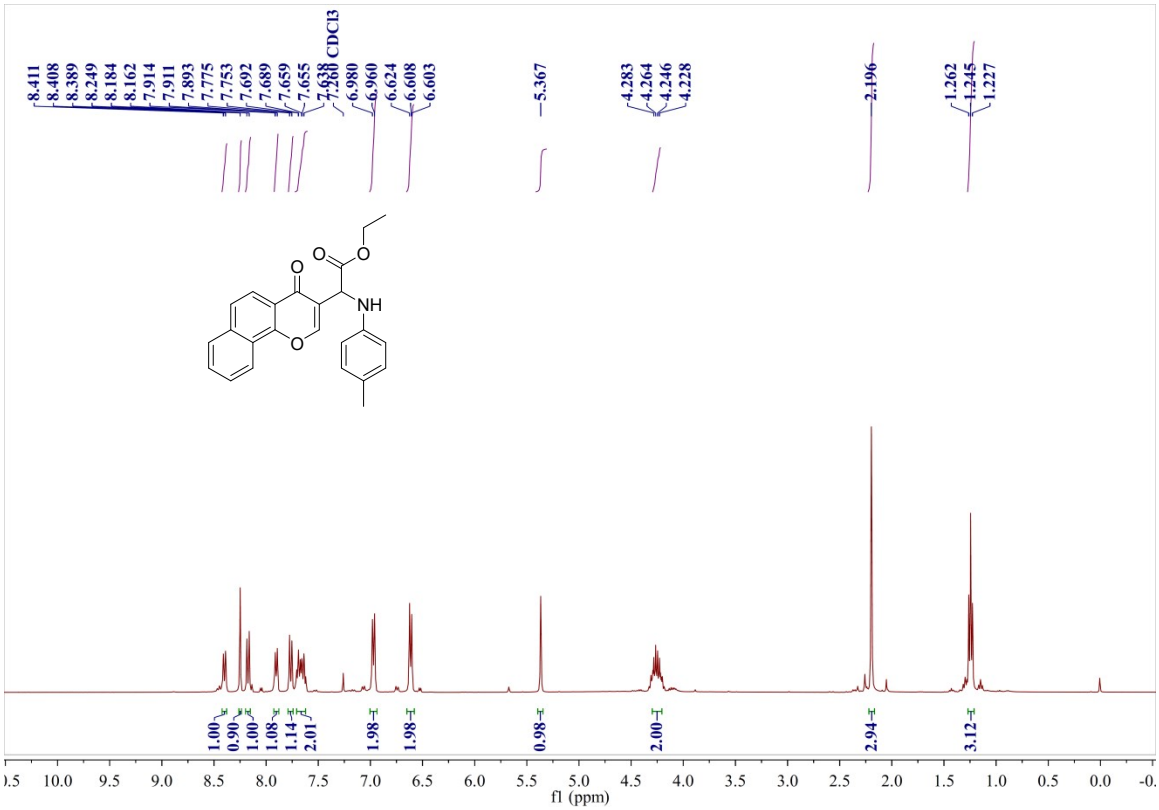


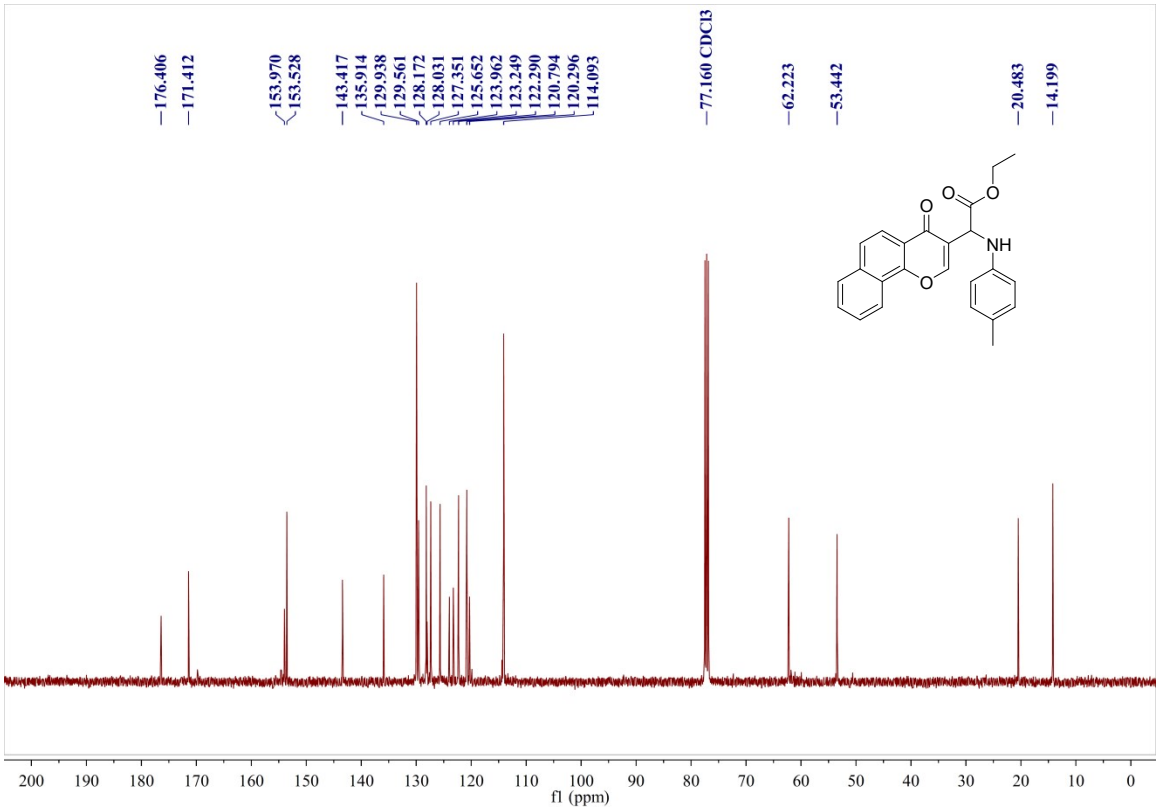
Ethyl-2-(8-bromo-6-chloro-4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetate (3al)



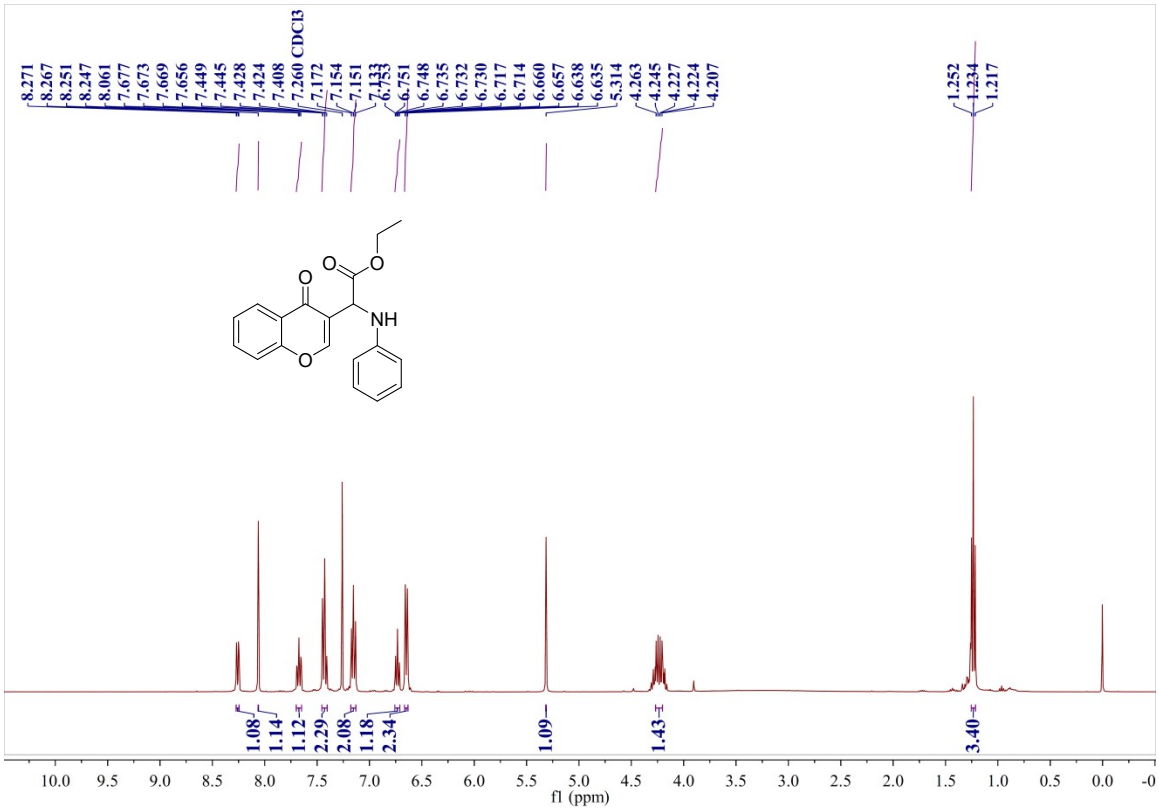


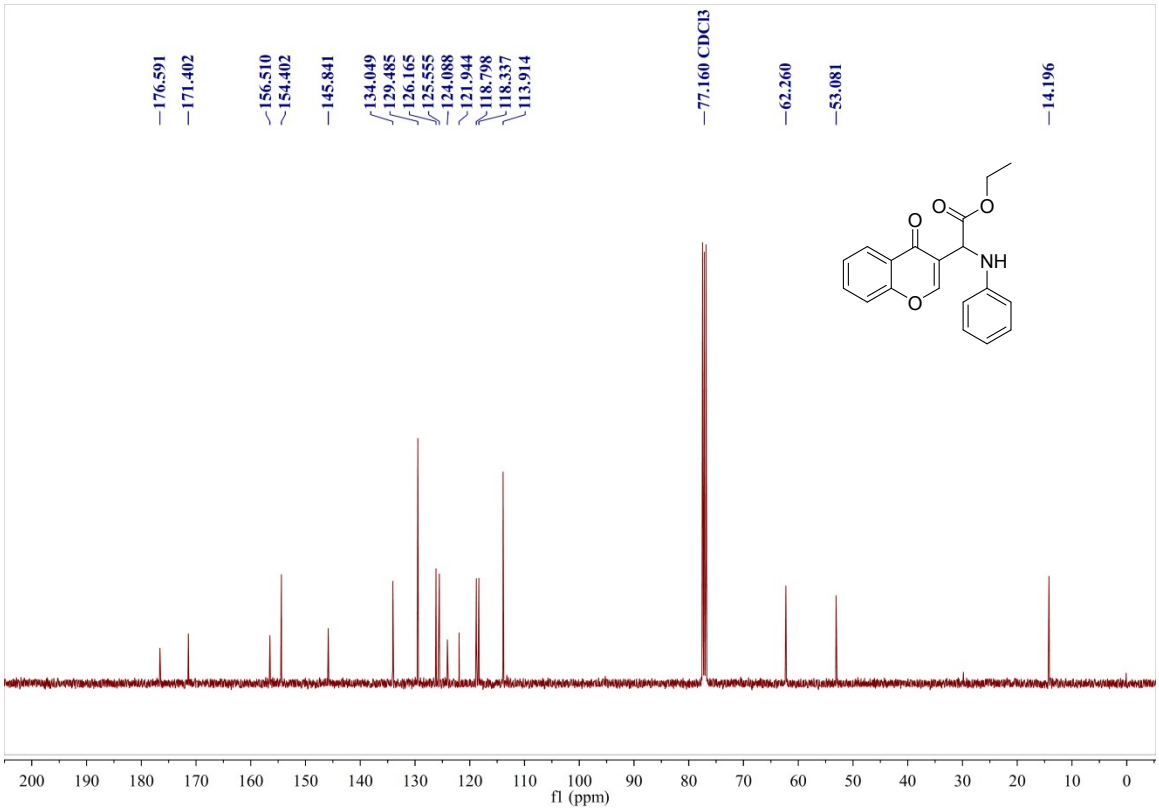
Ethyl-2-(4-oxo-4*H*-benzo[h]chromen-3-yl)-2-(*p*-tolylamino)acetate (3am)



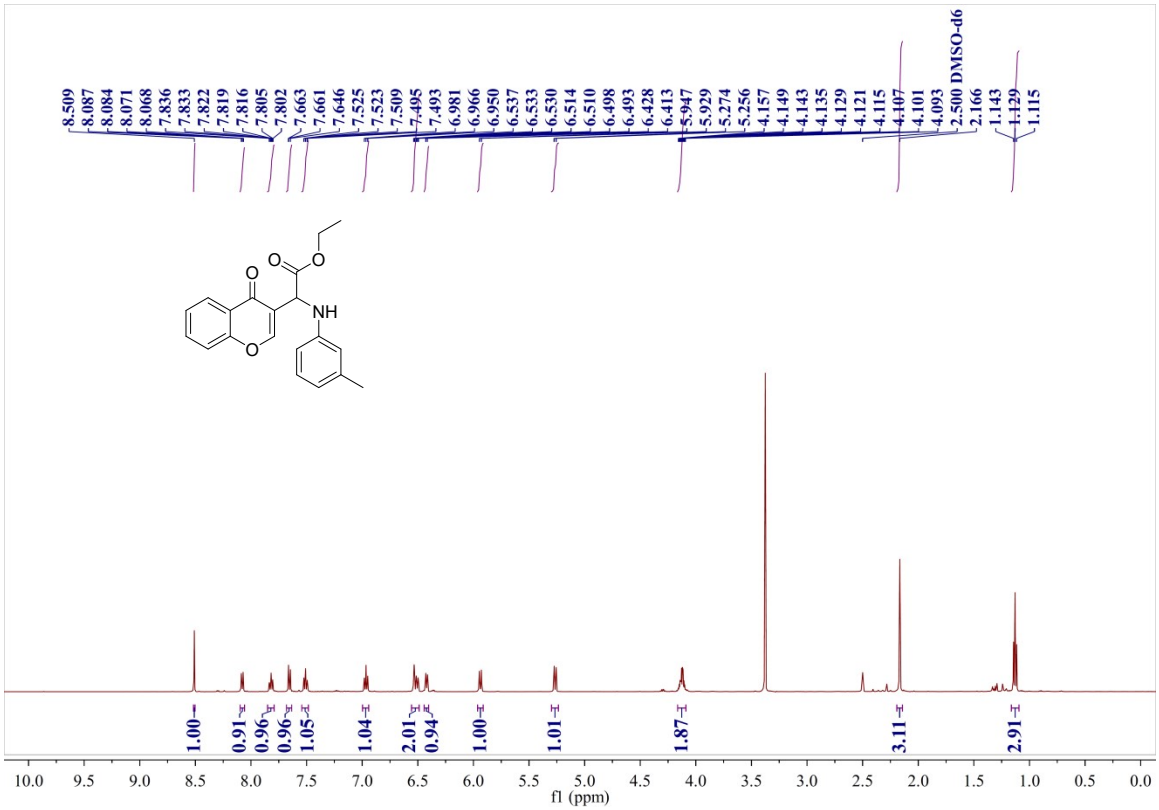


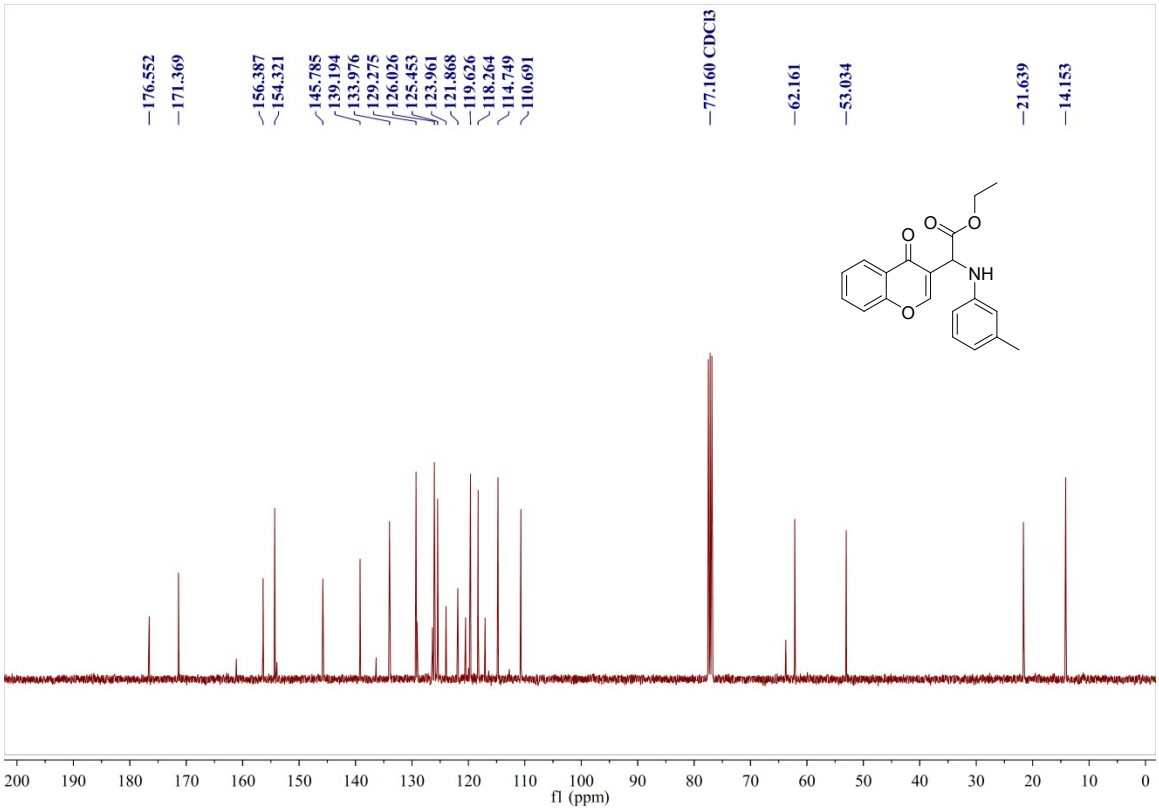
Ethyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3ba)



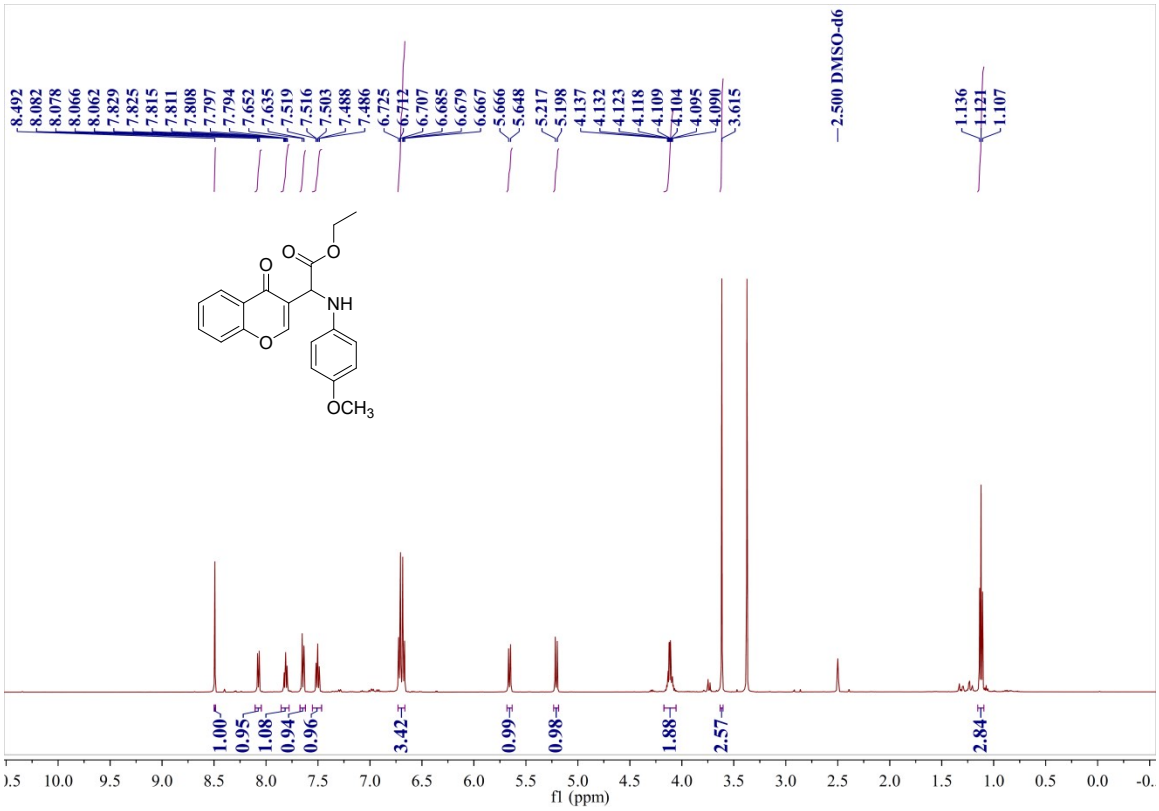


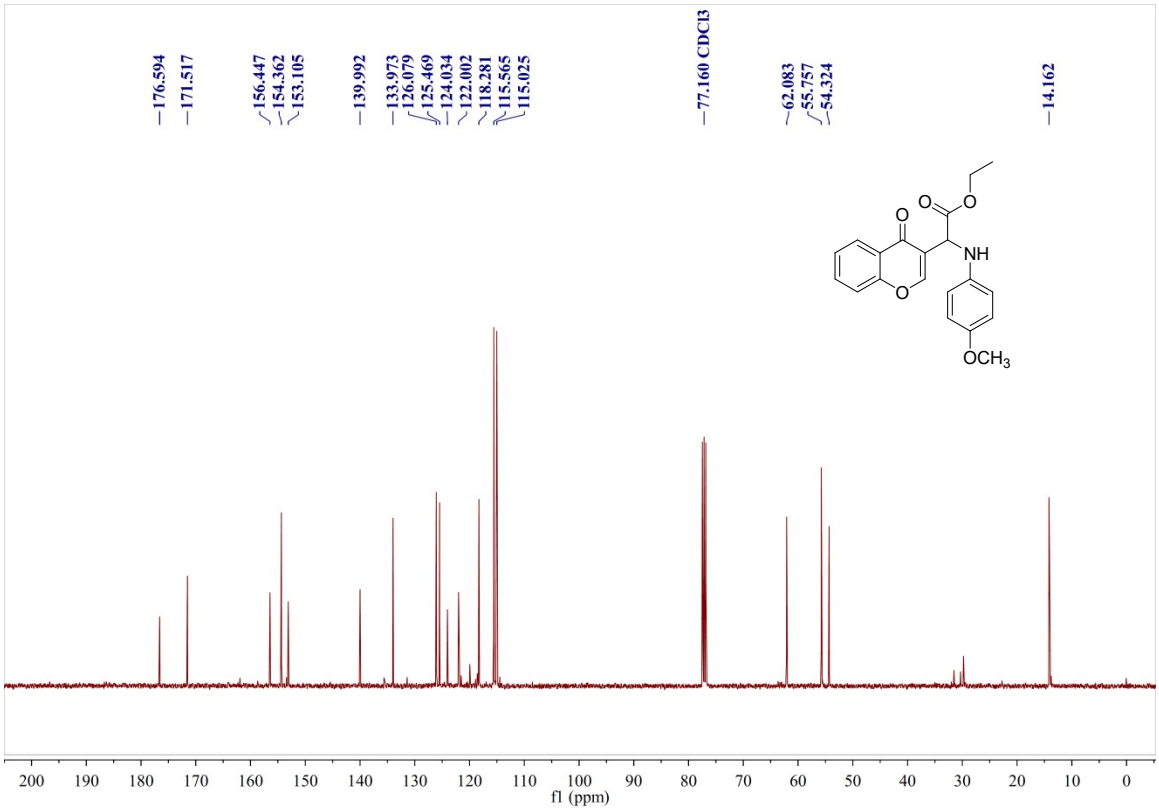
Ethyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(*m*-tolylamino)acetate (3ca)



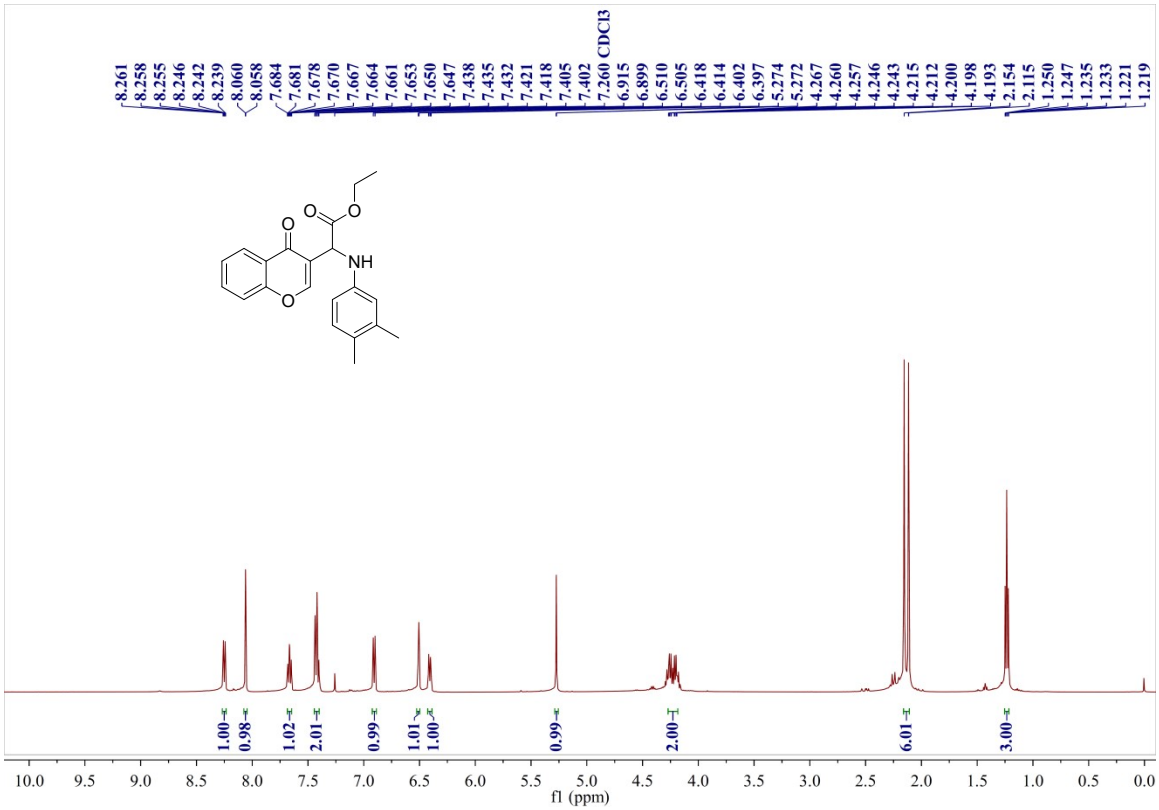


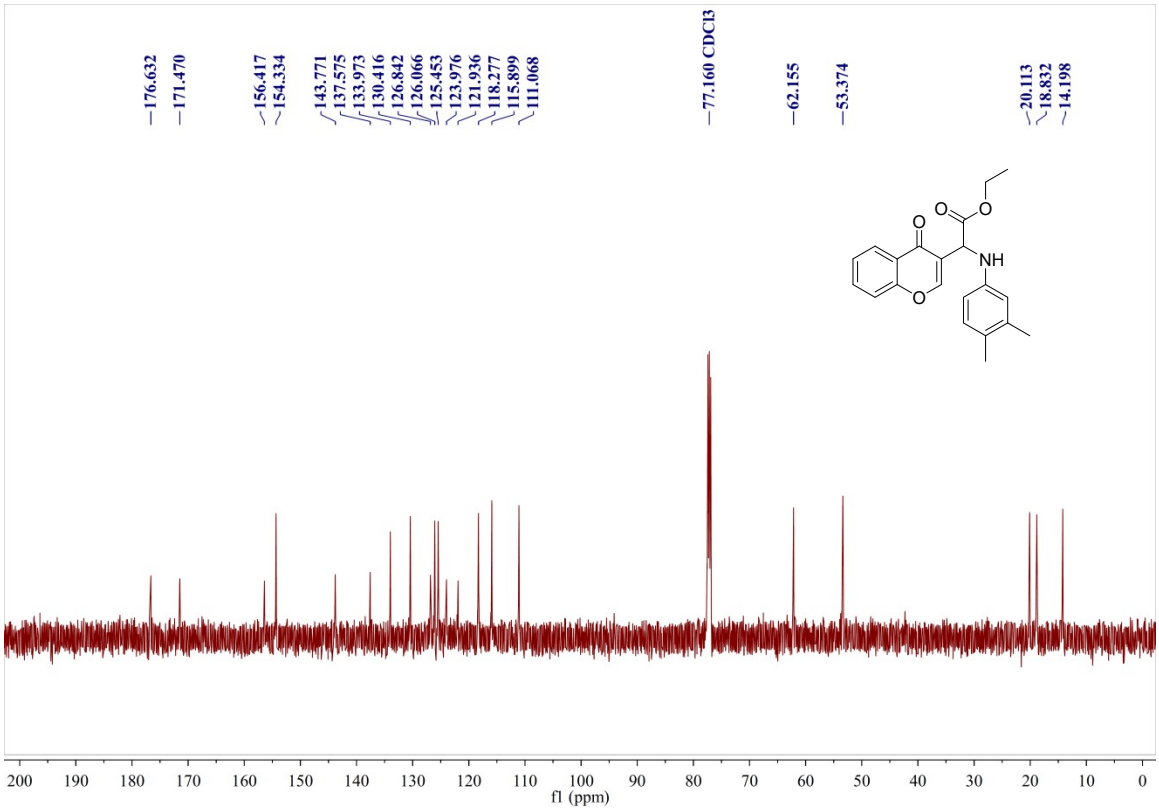
Ethyl-2-((4-methoxyphenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3da)



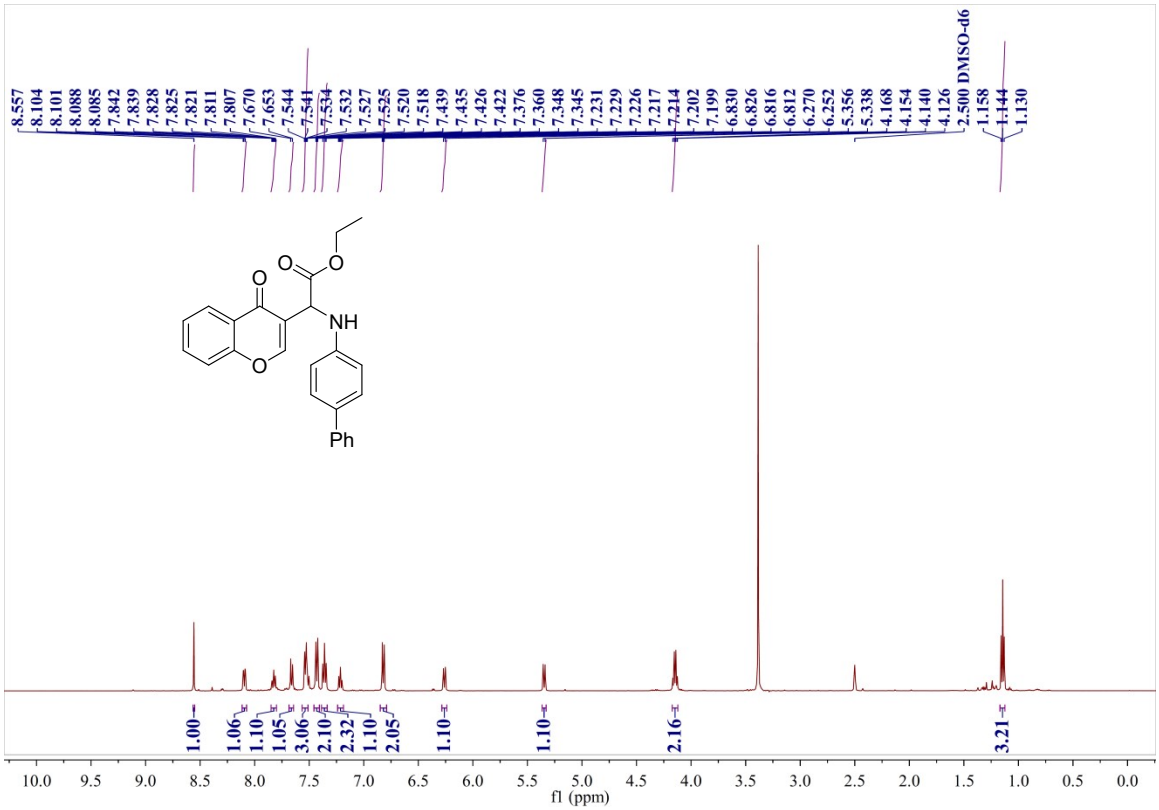


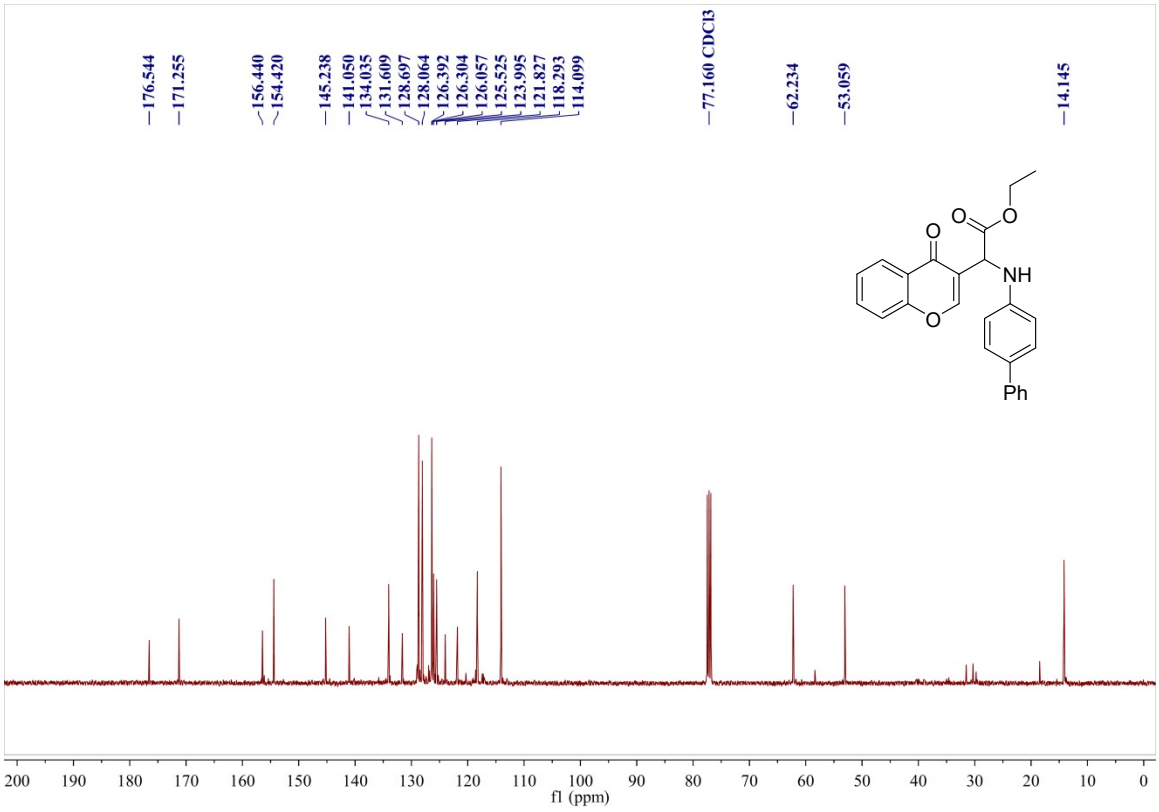
Ethyl-2-((3,4-dimethylphenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ea)



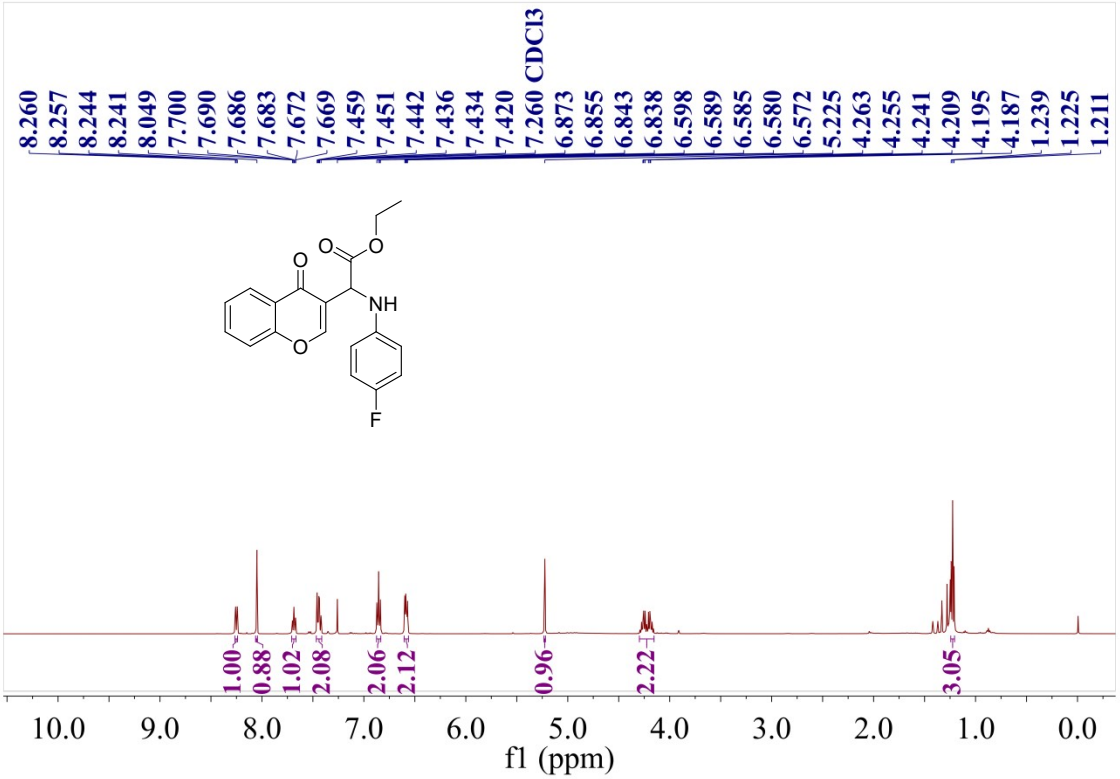


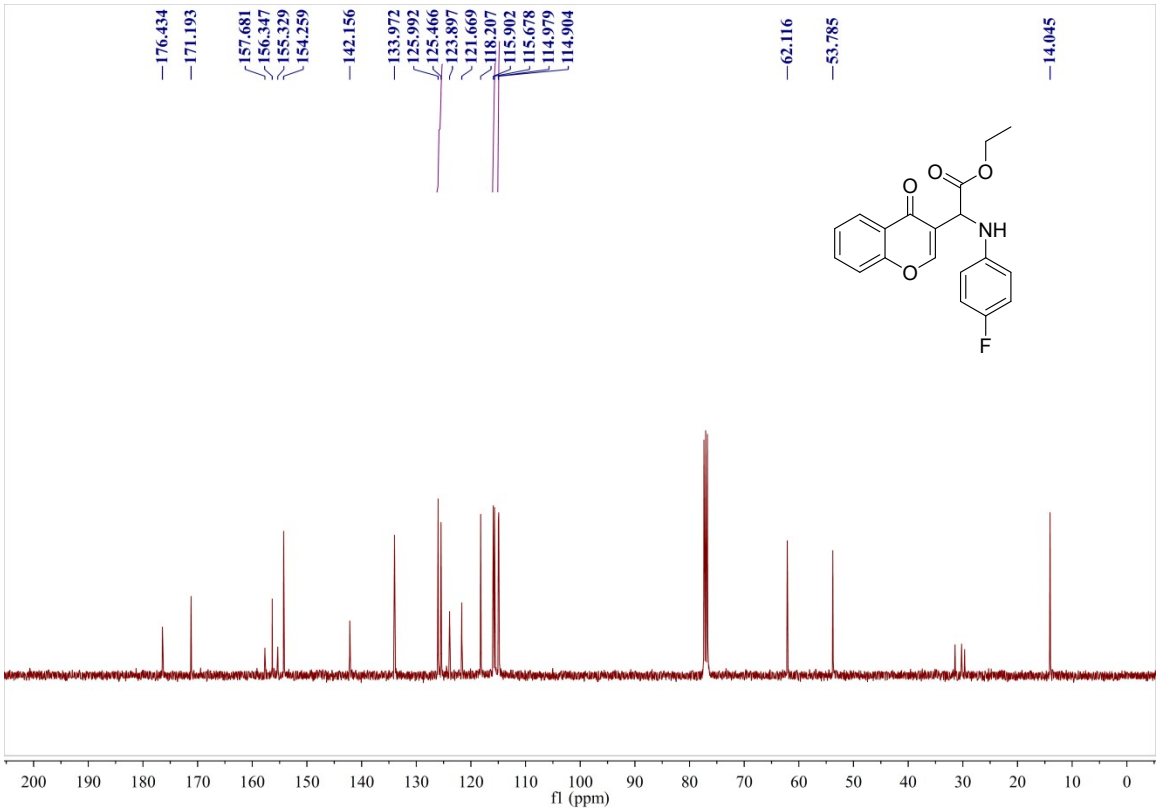
Ethyl-2-([1,1'-biphenyl]-4-ylamino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3fa)

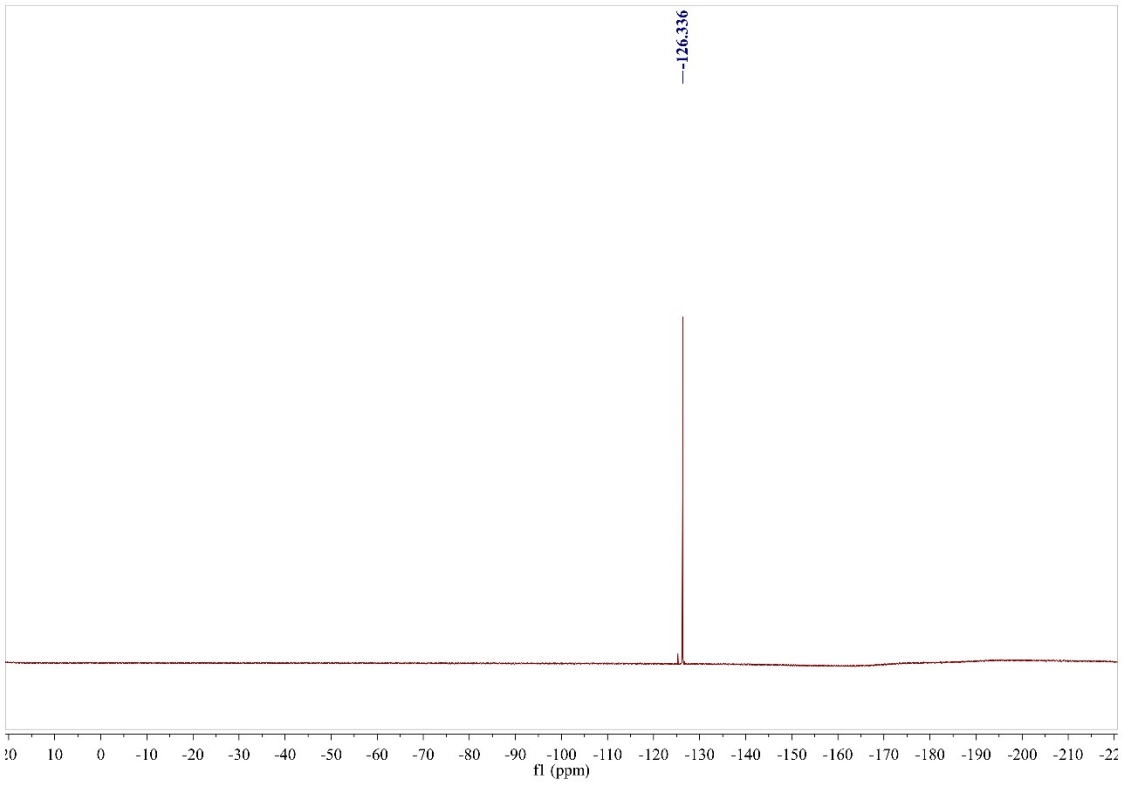




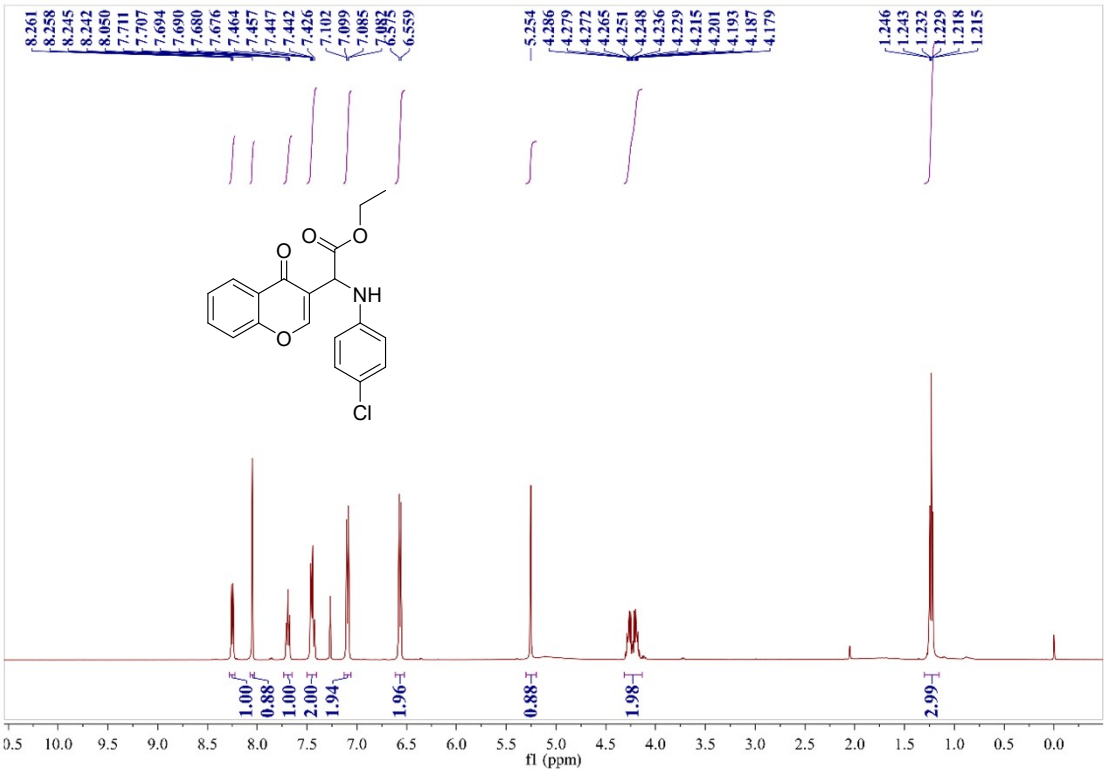
Ethyl-2-((4-fluorophenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ga)

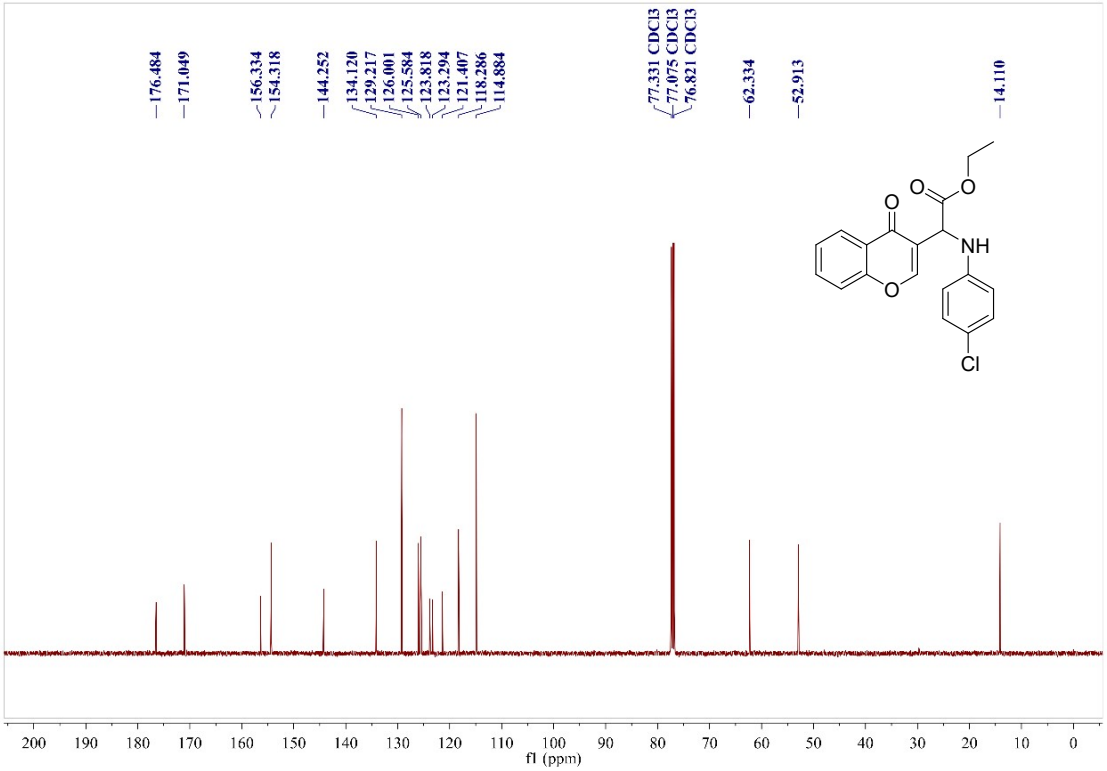




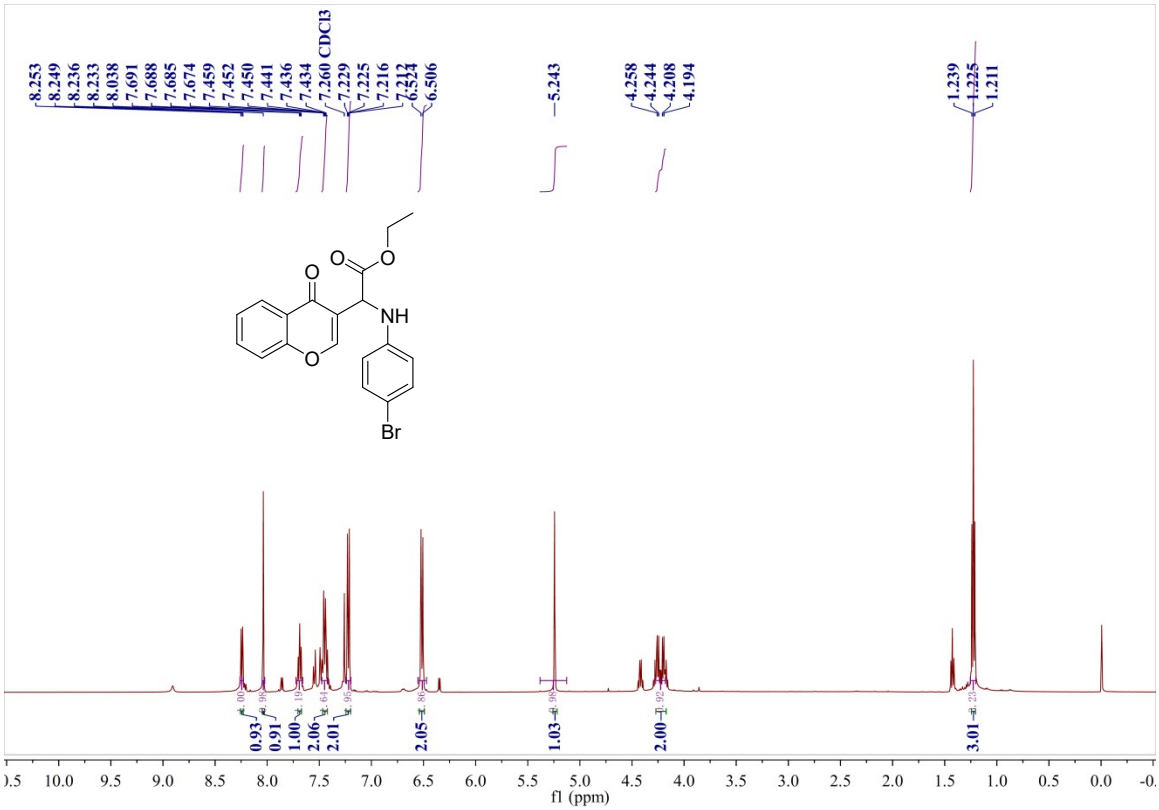

-126.336
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

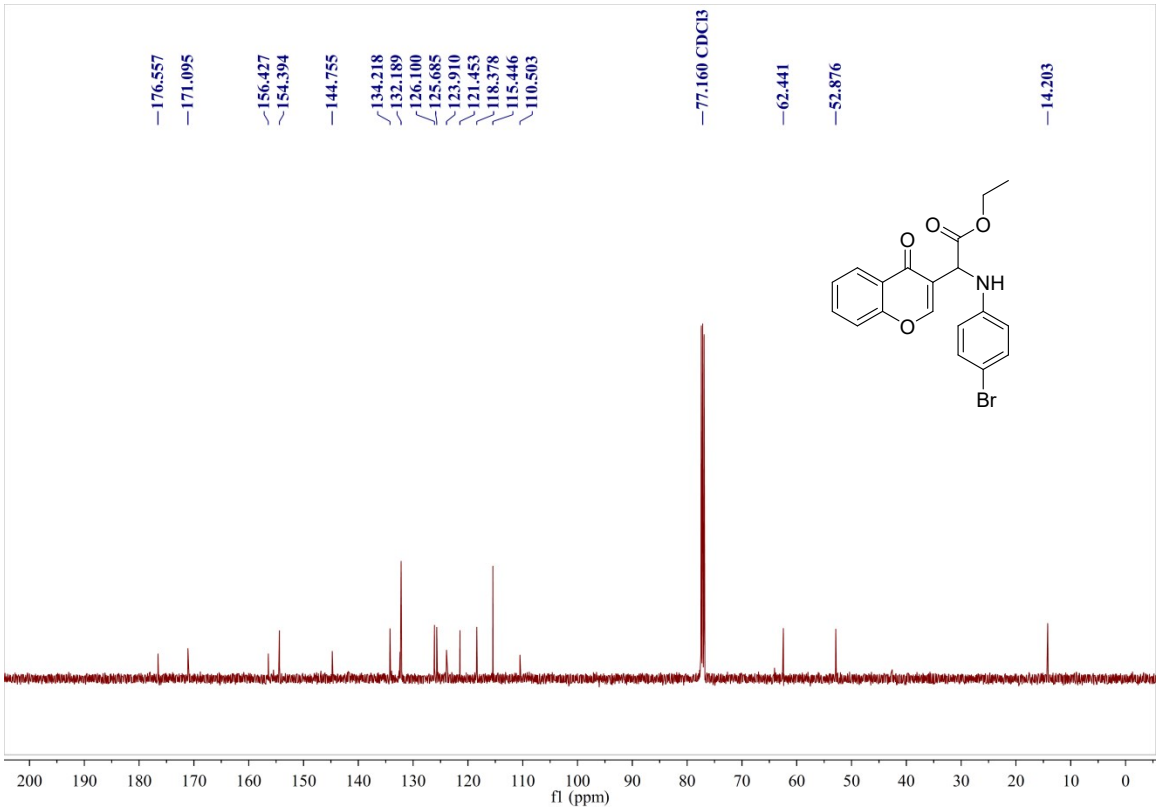
Ethyl-2-((4-chlorophenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ha)



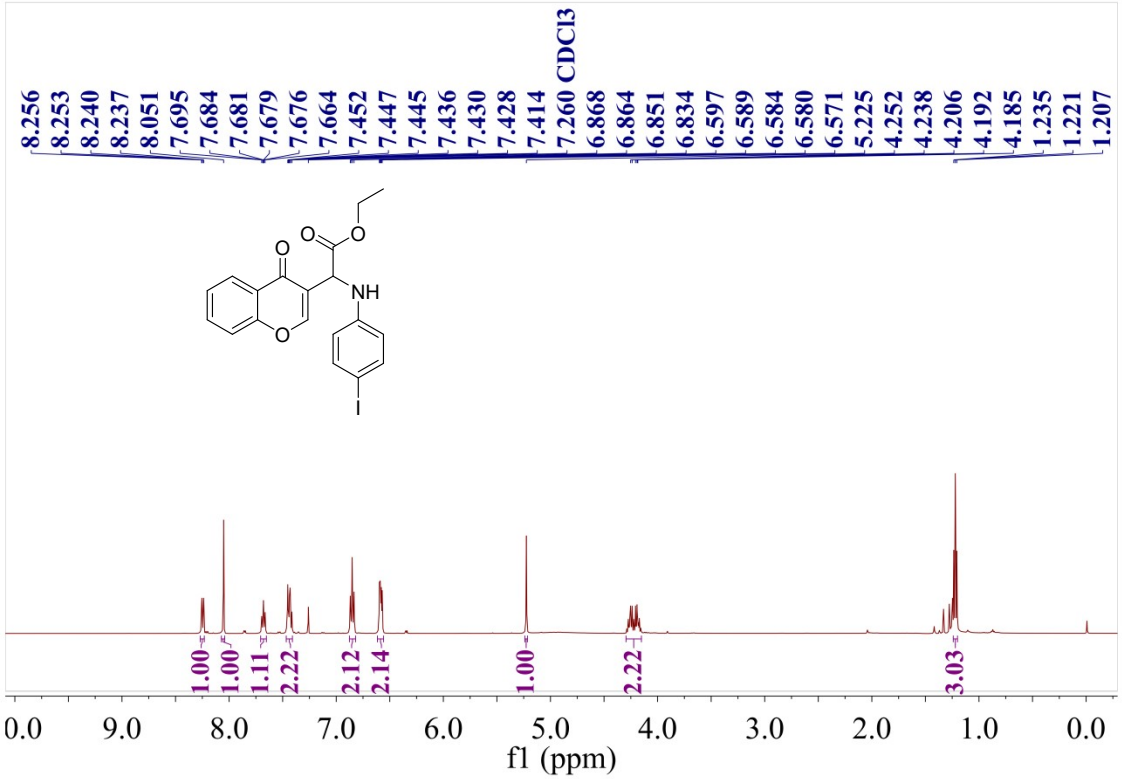


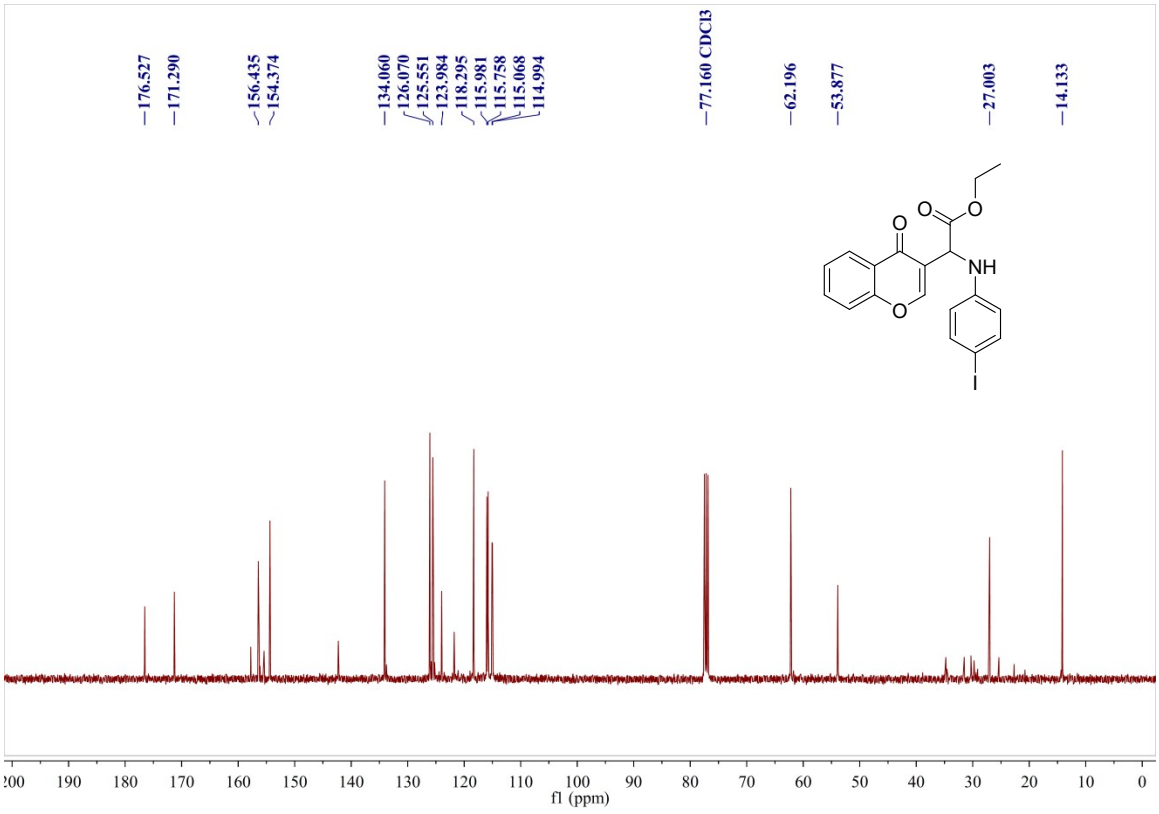
Ethyl-2-((4-bromophenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ia)



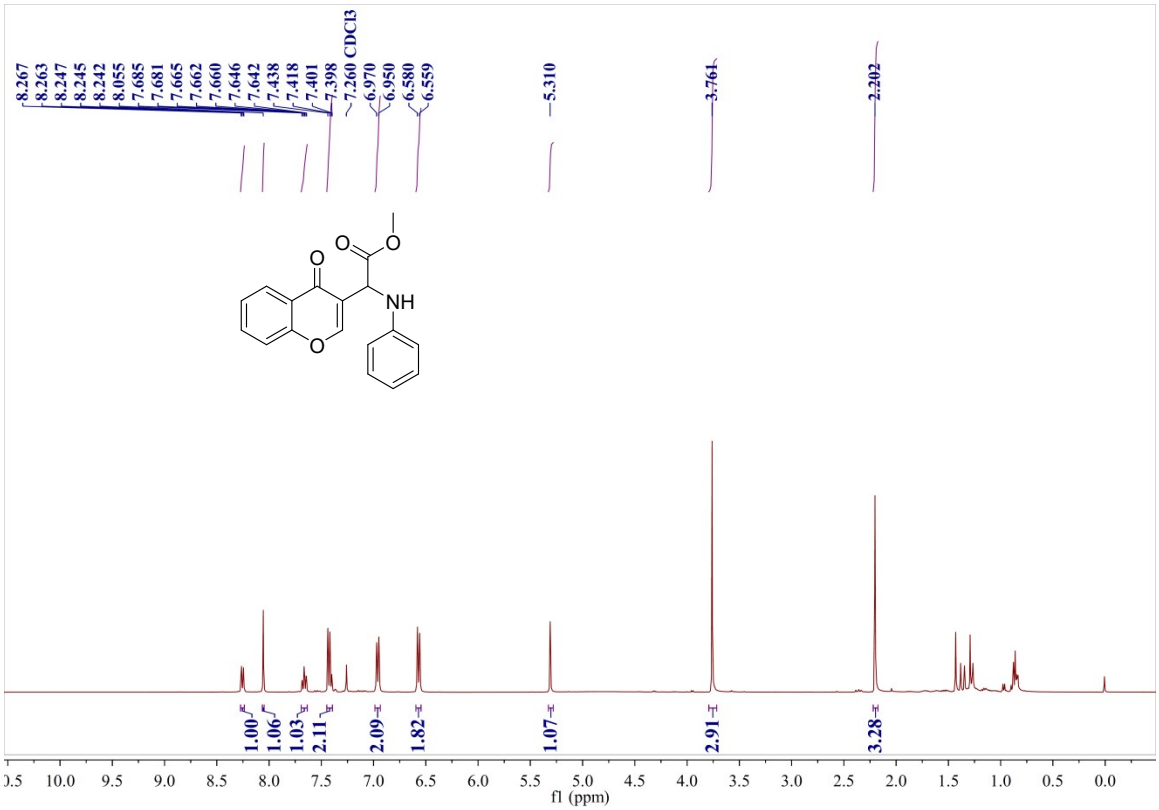


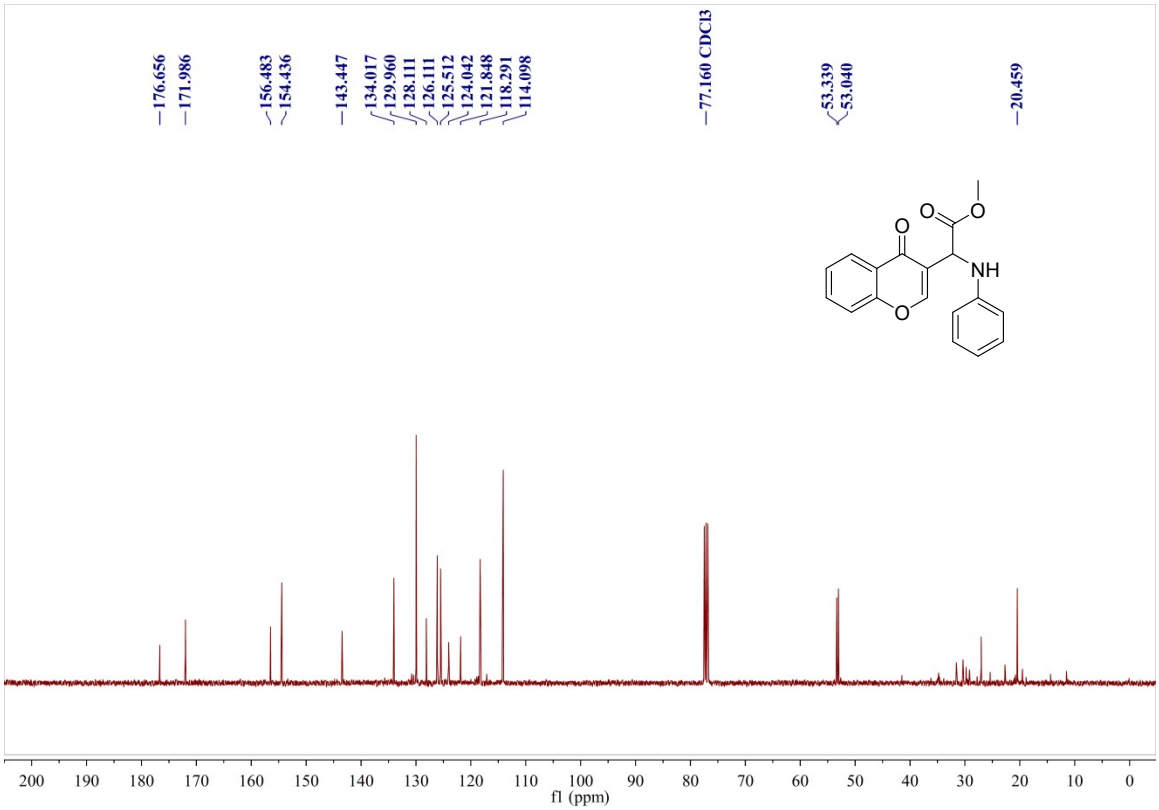
Ethyl-2-((4-bromophenyl)amino)-2-(4-oxo-4*H*-chromen-3-yl)acetate (3ja)



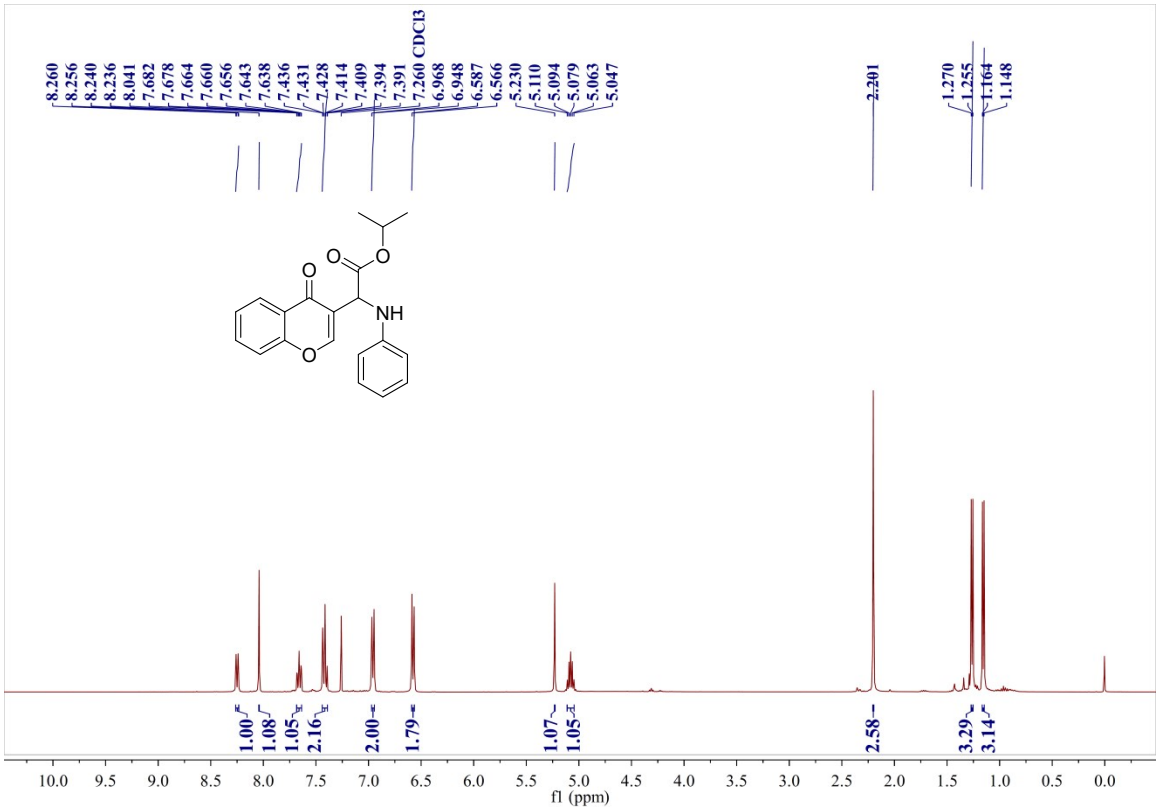


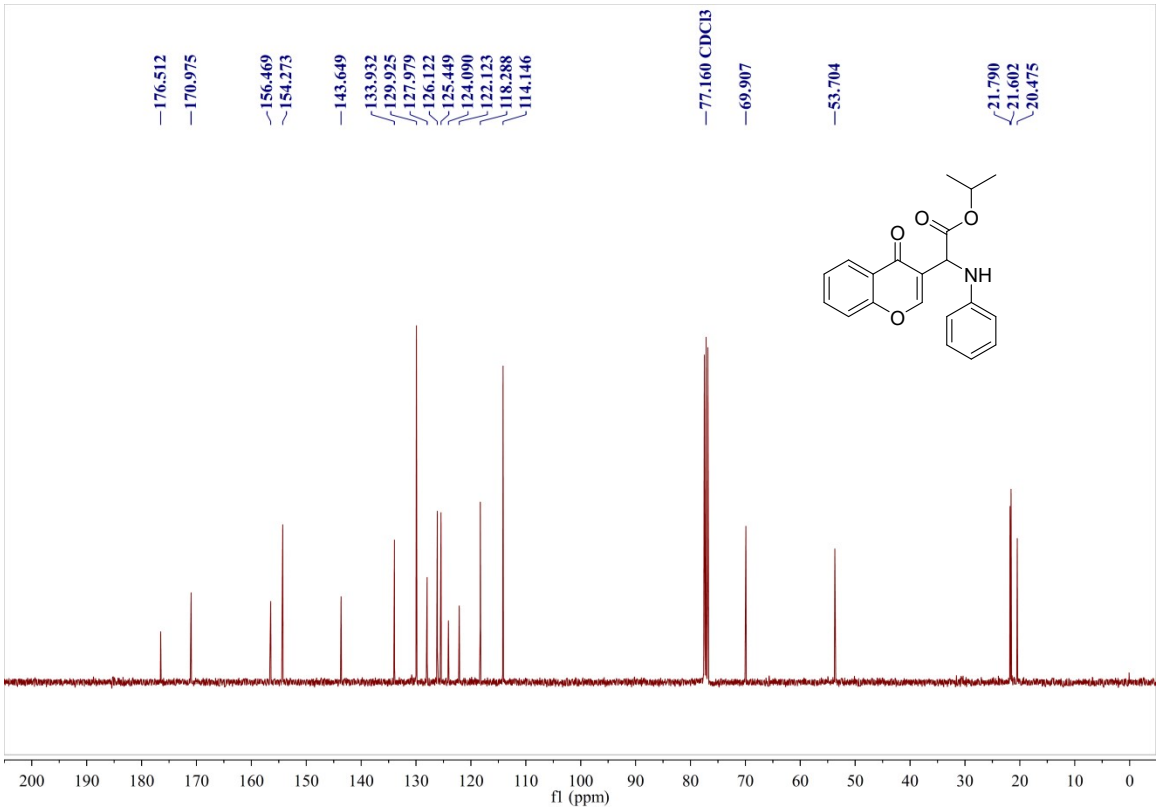
Methyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3ka)



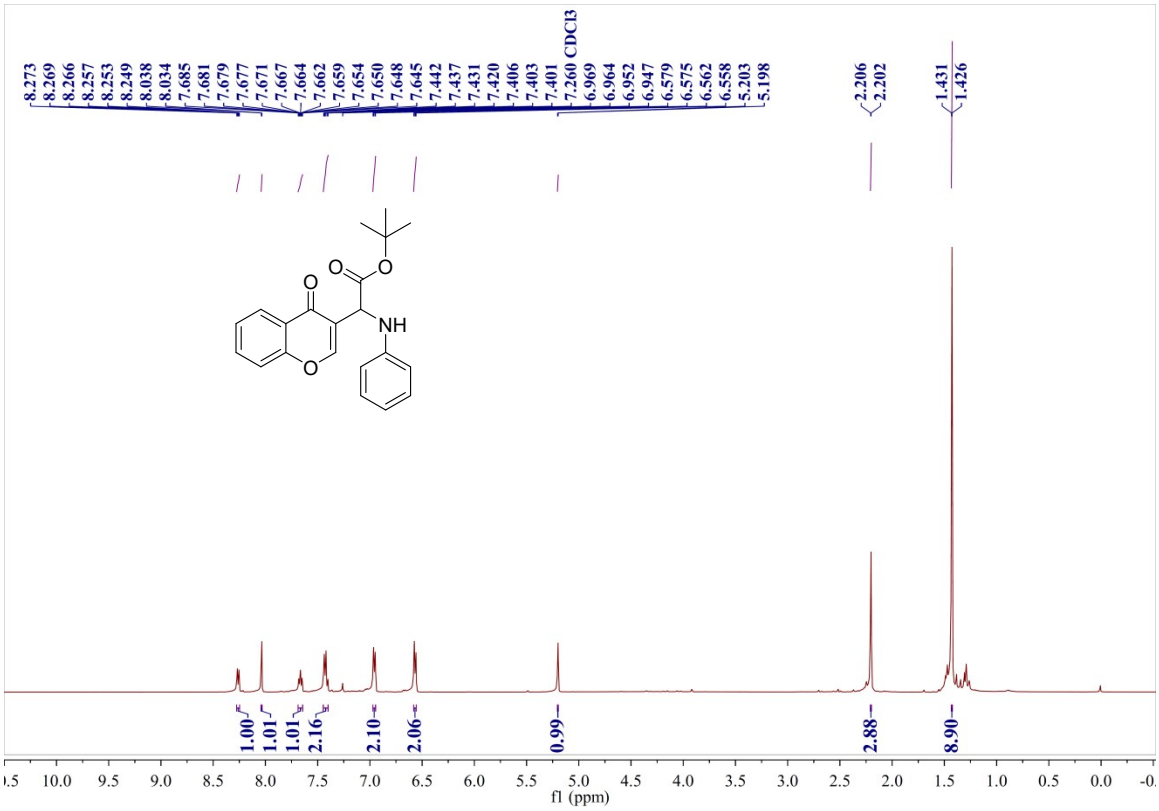


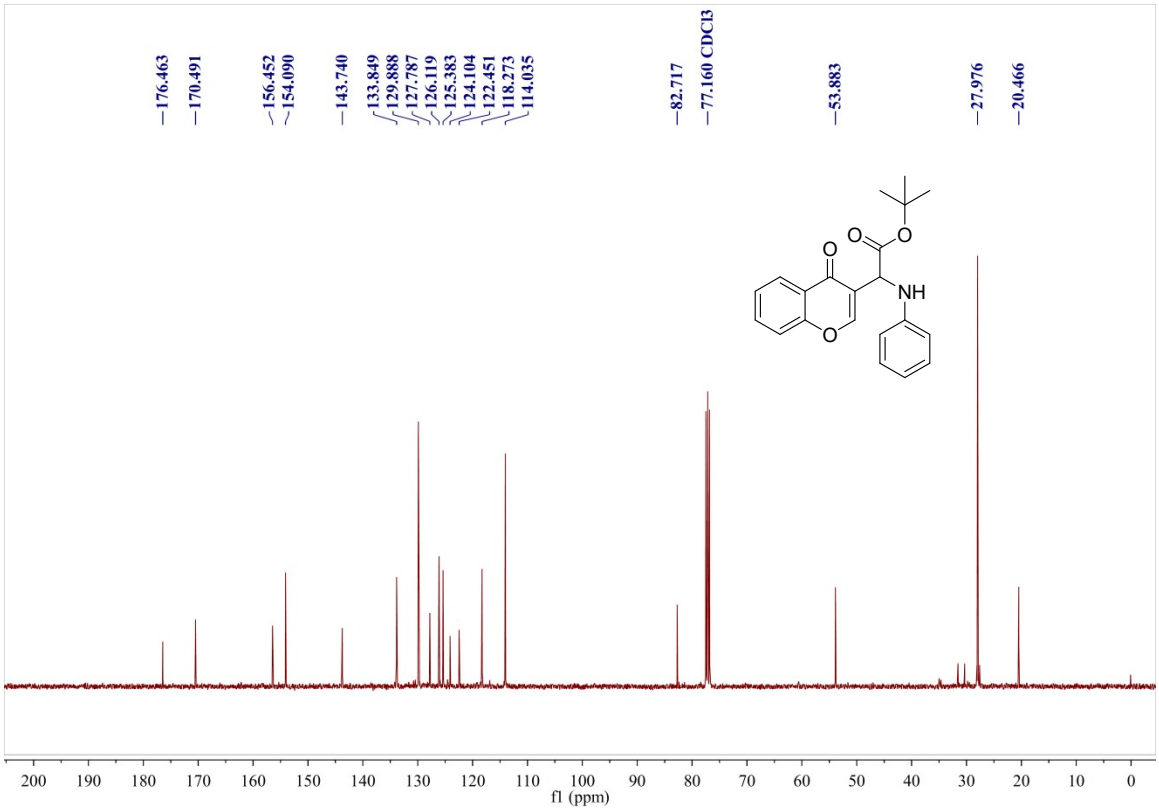
Isopropyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3la)



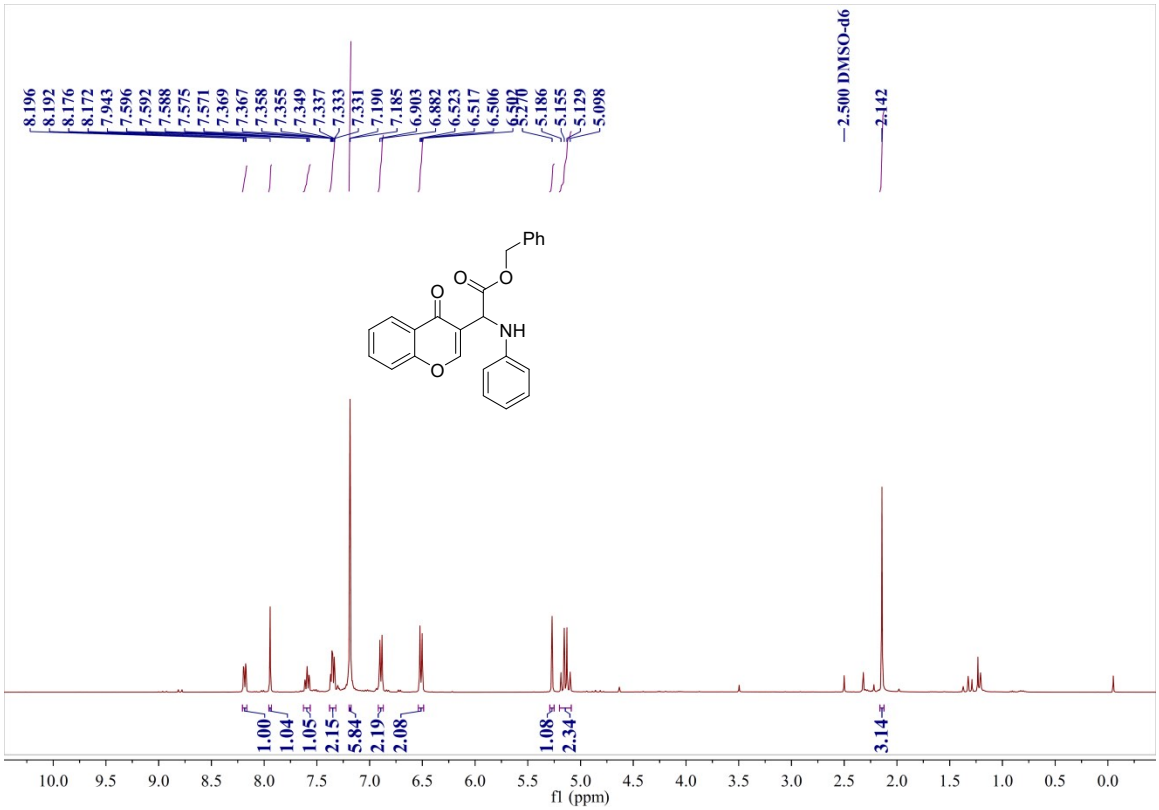


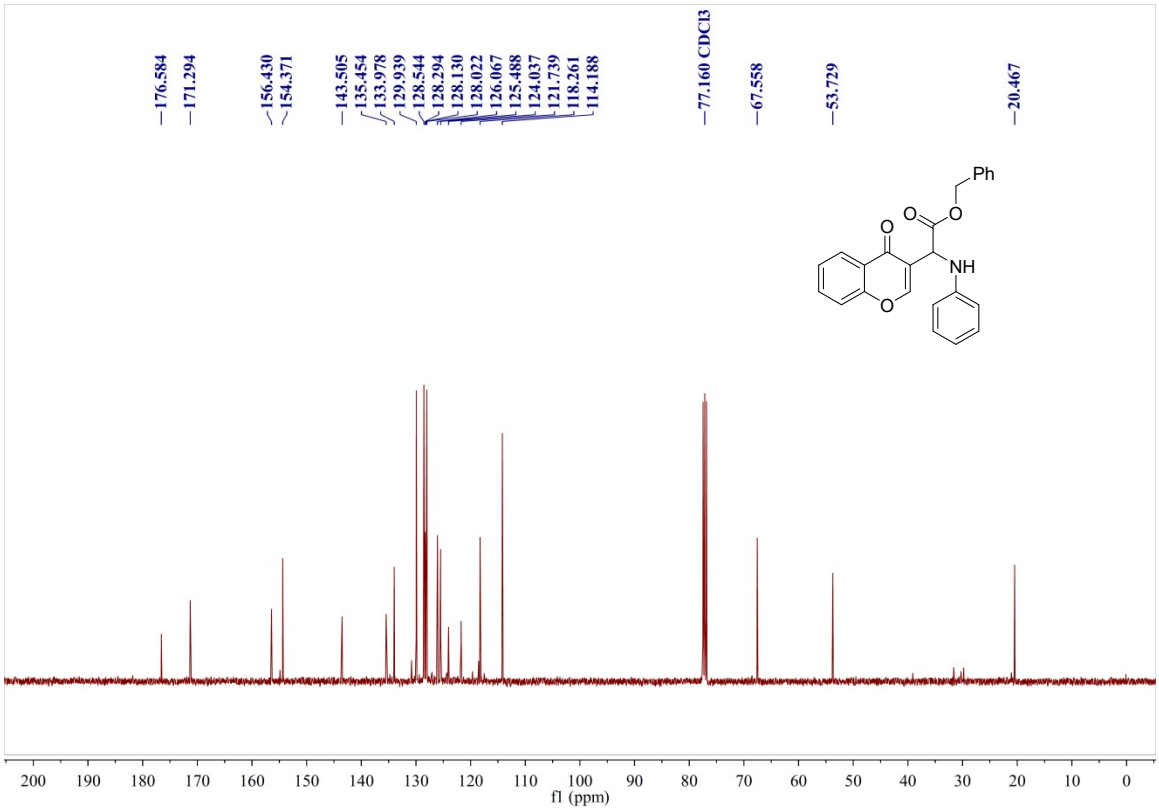
Tert-butyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3ma)



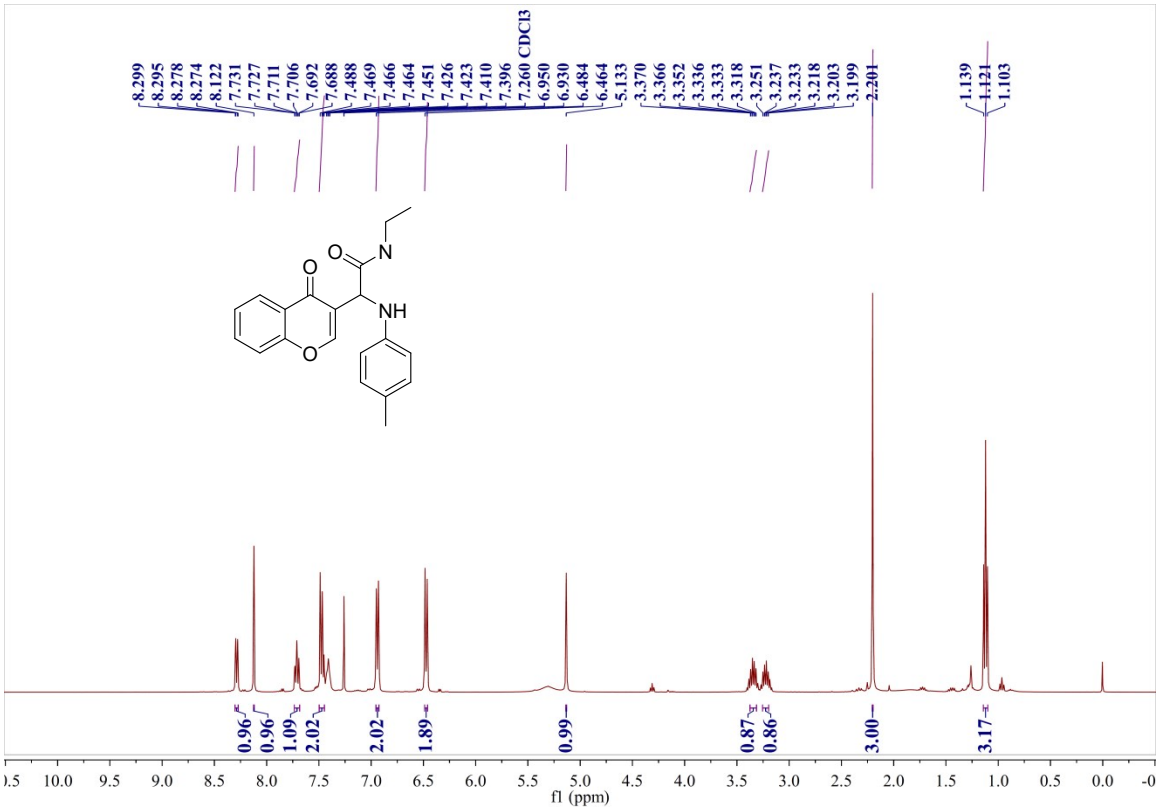


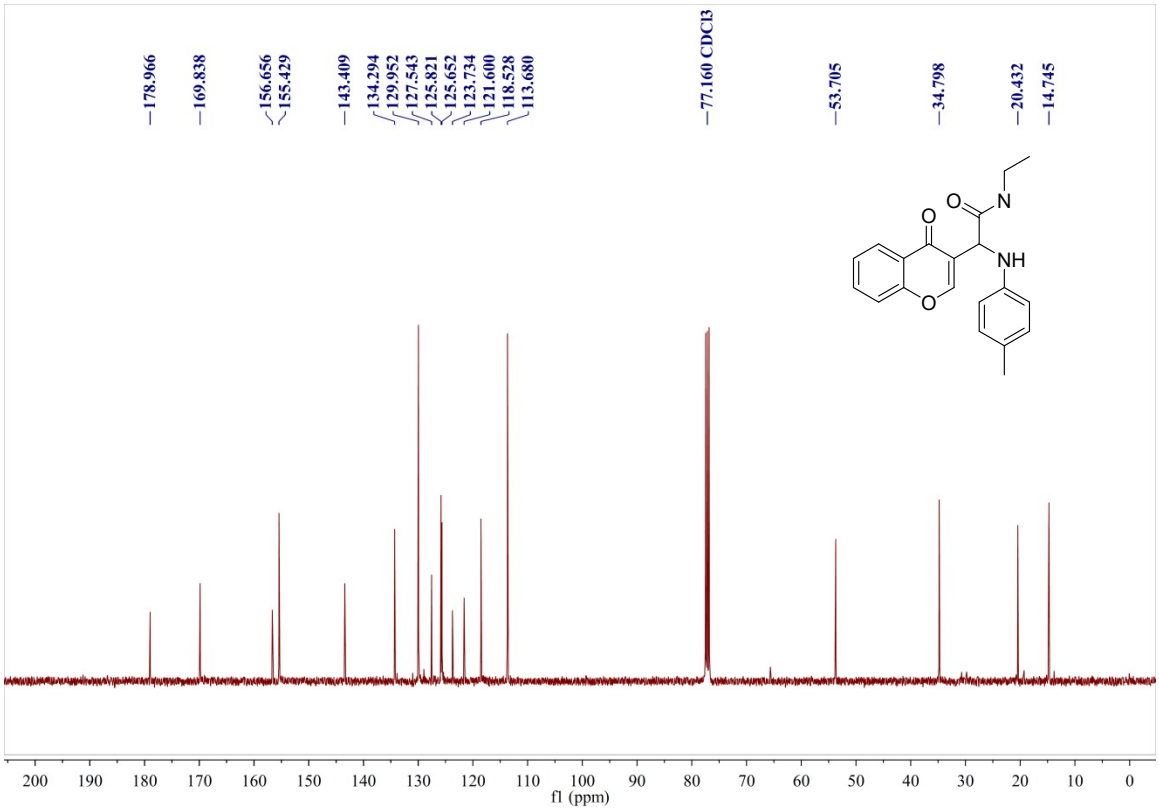
Benzyl-2-(4-oxo-4*H*-chromen-3-yl)-2-(phenylamino)acetate (3na)



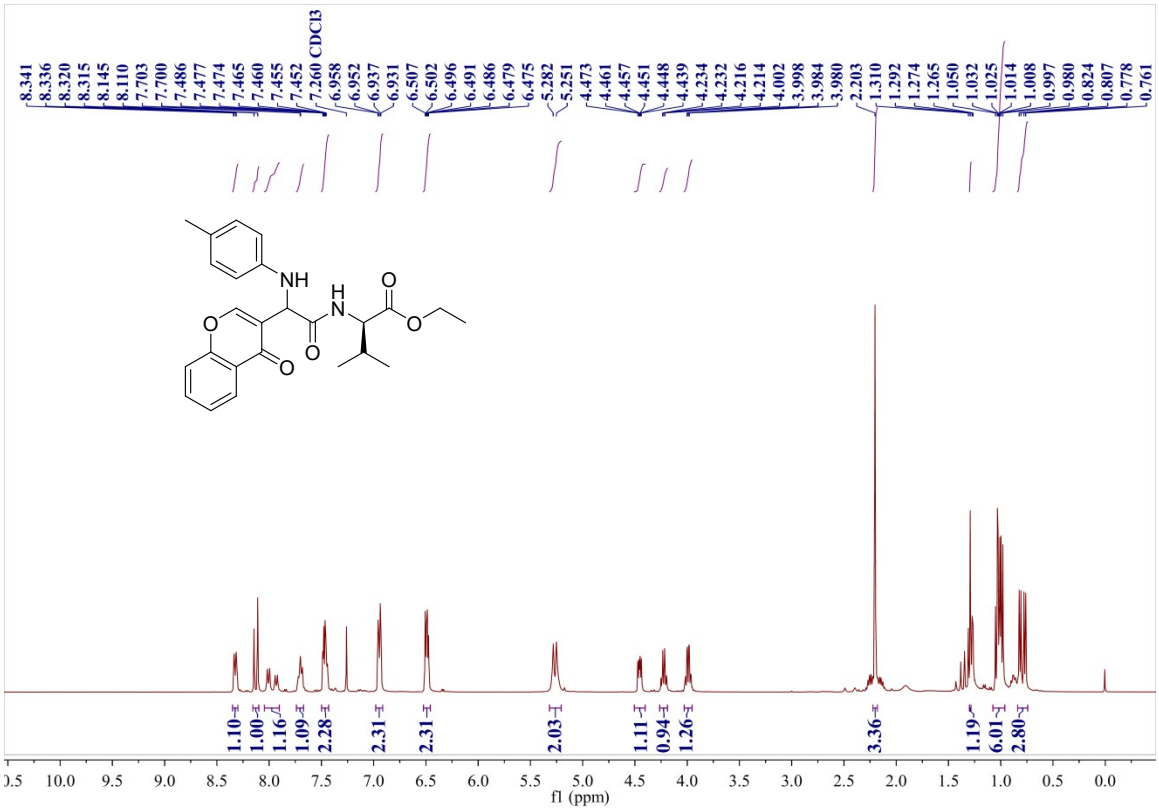


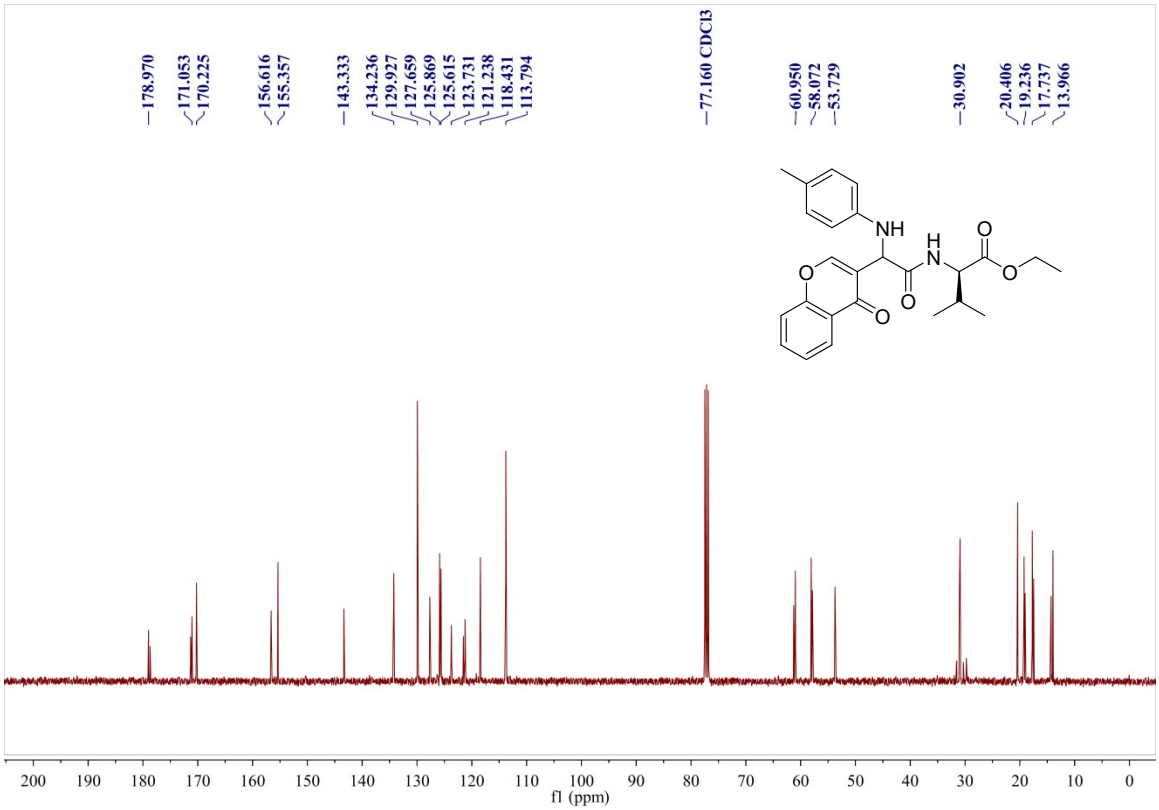
3-(2-(Ethyl-l2-azanyl)-2-oxo-1-(*p*-tolylamino)ethyl)-4*H*-chromen-4-one (3oa)





Ethyl-(2-(4-oxo-4*H*-chromen-3-yl)-2-(*p*-tolylamino)acetyl)-D-valinate (3pa)





3-((Methyl(phenyl)amino)methyl)-4*H*-chromen-4-one (3qa)