Base-Promoted Synthesis of Coumarins from Salicylaldehydes and Aryl-Substituted 1, 1-Dibromo-1-alkenes under Transition-Metal-Free Conditions

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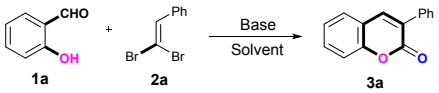
1. General information

All the chemicals and solvents were used as received without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. NMR spectra of the products were recorded using a Bruker Avance TM spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics microTOF-Q_spectrometer.

2. Experimental procedure for the base-promoted tandem reaction

2.1 Optimization of reaction conditions

Table 1. Optimization of reaction conditions[a]



Entry	Base	Additive	Solvent	Yield[b] (%)
1	Na_2CO_3	--	DMF	Trace
2	**Na_2CO_3**	**Et_2NH**	**DMF**	**85**
3	--	Et_2NH	DMF	n. d.[c]
4	Cs_2CO_3	Et_2NH	DMF	77
5	K_2CO_3	Et_2NH	DMF	68
6	K_3PO_4	Et_2NH	DMF	46
7	NaOAc	Et_2NH	DMF	50
8	*t*-BuOK	Et_2NH	DMF	53
9	Na_2CO_3	Et_2NH	DMAc	30
10	Na_2CO_3	Et_2NH	Toluene	n. d.[c]
11	Na_2CO_3	Et_2NH	1,4-dioxane	Trace
12	Na_2CO_3	Et_2NH	NMP	84
13[d]	Na_2CO_3	Et_2NH	DMF	61
14[e]	Na_2CO_3	Et_2NH	DMF	59

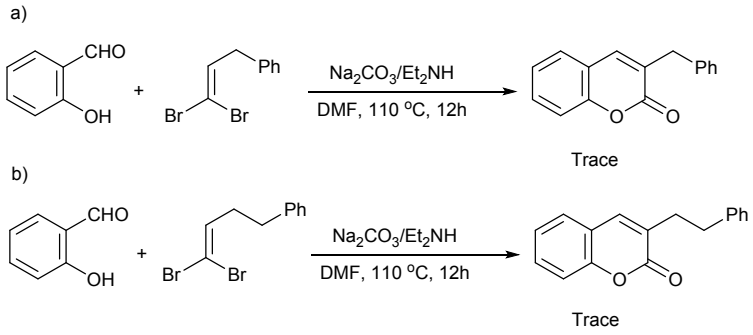
[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.5 mmol), base (2.0 mmol), Et_2NH (0.50 mL) and in solvent (5.0 mL) at 110 ºC for 12 h in air. [b] Isolated yields. [c] n.d.= no desired product. [d]120 ºC. [e]100 ºC

2.2 Experimental procedure for the base-promoted tandem reaction of the aryl-substituted 1, 1-dibromoalkenes with salicylaldehydes

A mixture of salicylaldehydes (1.0 mmol), aryl-substituted 1, 1-dibromoalkenes (1.5 mmol), Et_2NH (0.50 mL), sodium carbonate (2.0 mmol) and DMF (5.0 mL) was stirred at 110 ºC in air for 12 h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the corresponding product.

2.3 Experimental procedure for the base-promoted tandem reaction of the alkyl-substituted 1, 1-dibromoalkenes with salicylaldehydes

A mixture of salicylaldehydes (1.0 mmol), alkyl-substituted 1, 1-dibromoalkenes (1.5 mmol), Et2NH (0.50 mL), sodium carbonate (2.0 mmol) and DMF (5.0 mL) was stirred at 110 oC in air for 12 h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na2SO4, and concentrated in vacuum. The residue was determined by GC-MS, only a trace of desired product was obtained (Scheme 1).

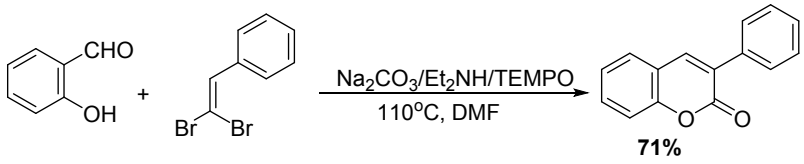


Scheme 1

3. Experiments on investigation of mechanism

3.1 Base-promoted tandem reaction of salicylaldehydes, (2, 2-dibromovinyl)benzene and TMPO

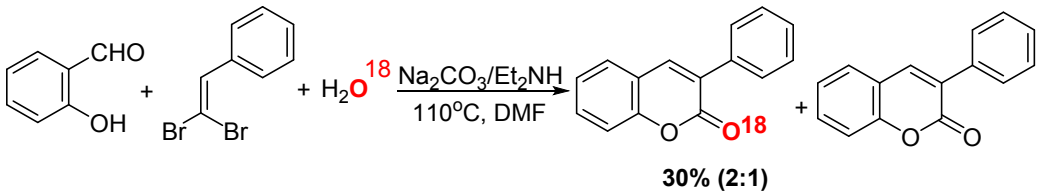
A mixture of salicylaldehydes (1.0 mmol), 1, 1-dibromoalkenes (1.5 mmol), 2, 2, 6, 6-tetramethylpiperidine-N-oxyl (2.0 mmol), Et_2NH (0.50 mL), sodium carbonate (2.0 mmol) and DMF (5.0 mL) was stirred at 110 ºC in air for 12 h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na_2SO_4, and concentrated in *vacuum*. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the corresponding product in 71% yield (Scheme 2).



Scheme 2

3.2 Base-promoted tandem reaction of salicylaldehydes and (2, 2-dibromovinyl)benzene in H_2O^{18}

A mixture of salicylaldehydes (1.0 mmol), 1, 1-dibromoalkenes (1.5 mmol), Et_2NH (0.50 mL), sodium carbonate (2.0 mmol), H_2O^{18} (20 mmol) and DMF (5.0 mL) was stirred at 110 ºC in air atmosphere for 12 h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the corresponding product in 30% yield (Scheme 3). The product was determined by GC-MS (**Figure 1**).



Scheme 3

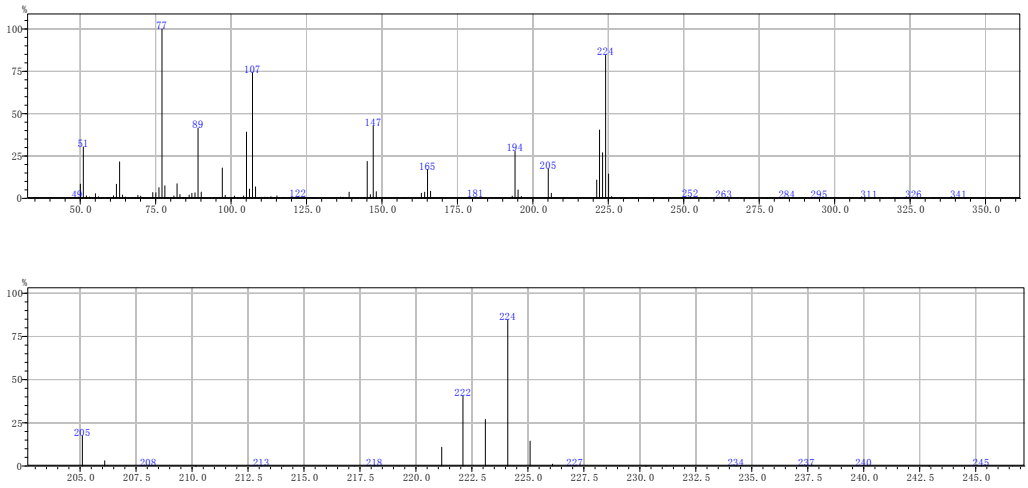
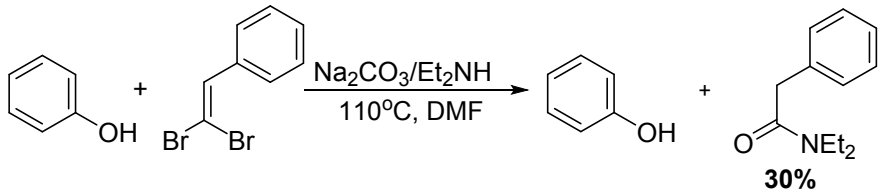


Figure 1. The GC-MS specturm of coumarin

3.3 Base-promoted tandem reaction of phenol and (2, 2-dibromovinyl)benzene.

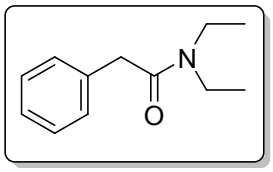
A mixture of phenol (1.0 mmol), (2, 2-dibromovinyl)benzene (1.5 mmol), Et_2NH (0.50 mL), sodium carbonate (2.0 mmol) and DMF (5.0 mL) was stirred at 110 ºC in air for 12 h. After

cooling to room temperature, the resultant reaction mixture was determined by TLC and GC-MS. The *N*, *N*-diethyl-2-phenylacetamide was obtained in 30% yield (Scheme 4).

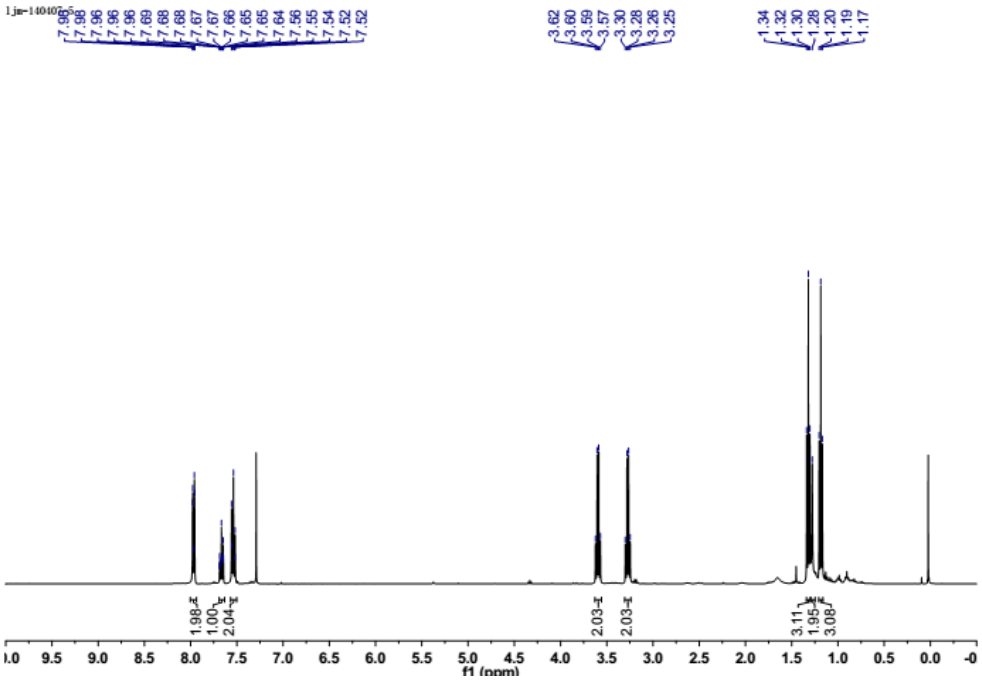


Scheme 4

***N*, *N*-diethyl-2-phenylacetamide**

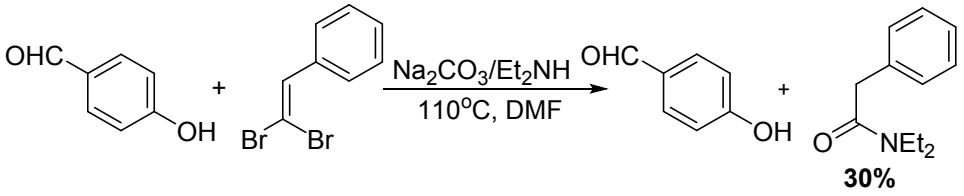


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 2H), 7.69-7.64 (m, 1H), 7.56-7.52 (m, 2H), 3.60 (q, *J* = 8.0 Hz, 2H), 3.27 (q, *J* = 8.0 Hz, 2H), 1.32 (t, *J* = 8.0 Hz , 3H), 1.28 (s, 2H), 1.19 (t, *J* = 8.0 Hz, 3H). ESI-MS: *m/z* = 191 [M^+].



3.4 Base-promoted tandem reaction of *p*-hydroxybenzaldehyde and (bromoethynyl)benzene.

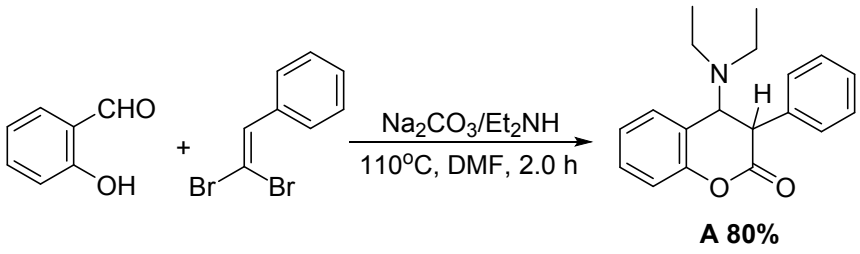
A mixture of *p*-hydroxybenzaldehyde (1.0 mmol), (2, 2-dibromovinyl)benzene (1.5 mmol), Et_2NH (0.50 mL), sodium carbonate (2.0 mmol) and DMF (5.0 mL) was stirred at 110 ºC in air for 12 h. After cooling to room temperature, the resultant reaction mixture was determined by TLC and GC-MS. The *N*, *N*-diethyl-2-phenylacetamide was obtained in 30% yield (Scheme 5).



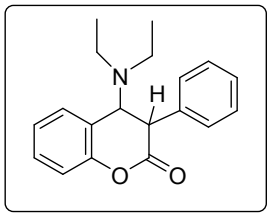
Scheme 5

3.5 Detection and isolation of intermediate A

A mixture of salicylaldehydes (1.0 mmol), 1, 1-dibromoalkenes (1.5 mmol), Et_2NH (0.50 mL), sodium carbonate (2.0 mmol) and DMF (5.0 mL) was stirred at 110 ºC in air atmosphere for 2.0 h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the corresponding product **A** in 25% yield (Scheme 6).

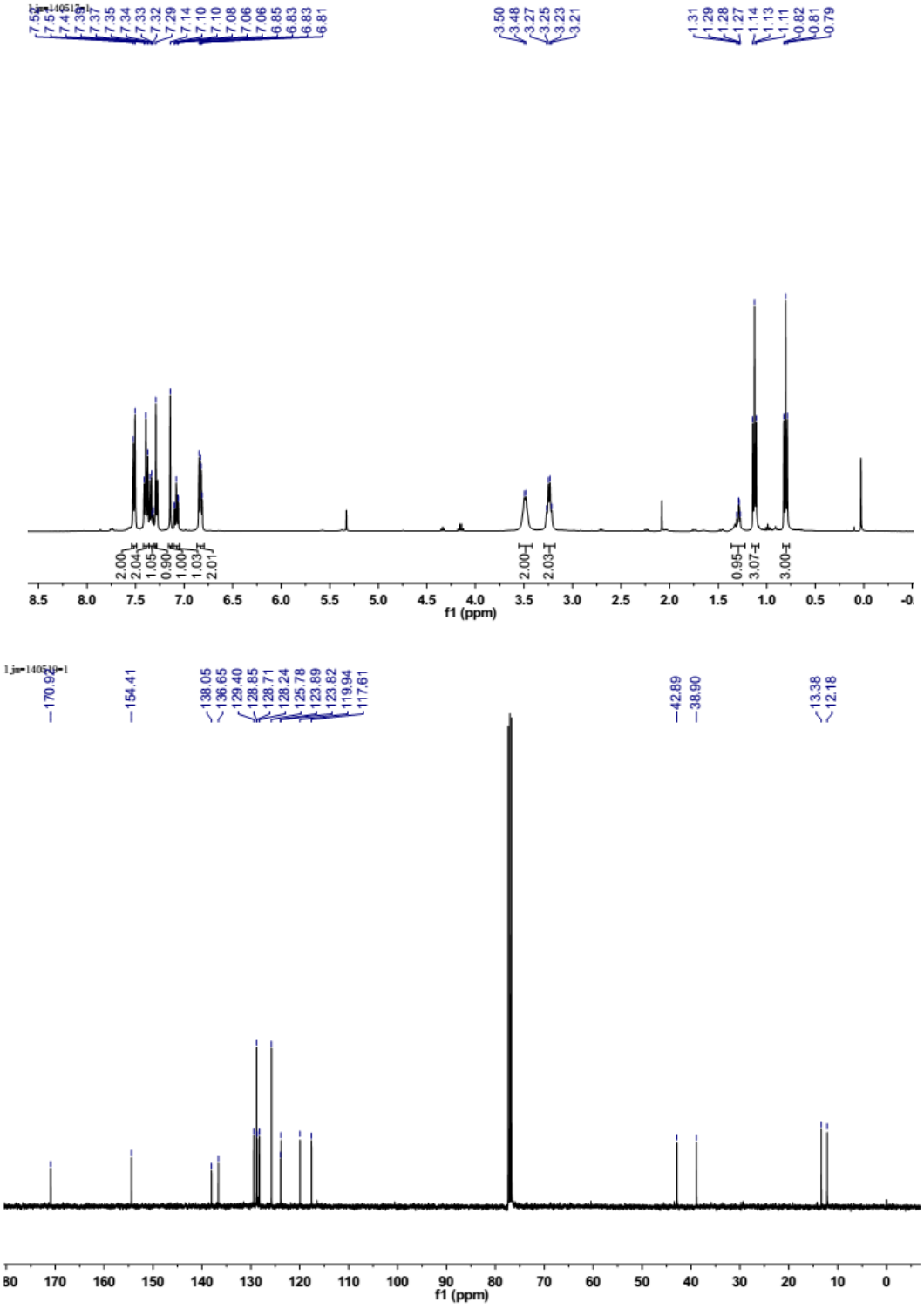


Scheme 6



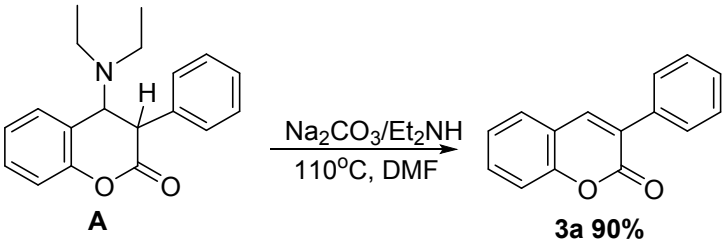
^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 4.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.35-7.32 (m, 1H), 7.29 (s, 1H), 7.14 (s, 1H), 7.10-7.08 (s, 1H), 6.85-6.81(m, 2H), 3.49 (d, *J* = 8.0 Hz, 2H), 3.25

(dd, J = 8.0 Hz, 2H), 1.31-1.27 (m, 1H), 1.13 (t, J = 6.0 Hz, 3H), 0.81 (t, J = 6.0 Hz, 3H),^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 154.4, 138.1, 136.7, 129.4, 128.9, 128.7, 128.2, 125.8, 123.9, 123.8, 120.0, 117.6, 42.9, 38.9, 13.4, 12.2. LC-MS: m/z = 296 (M+H).



3.6 Reaction of intermediate A

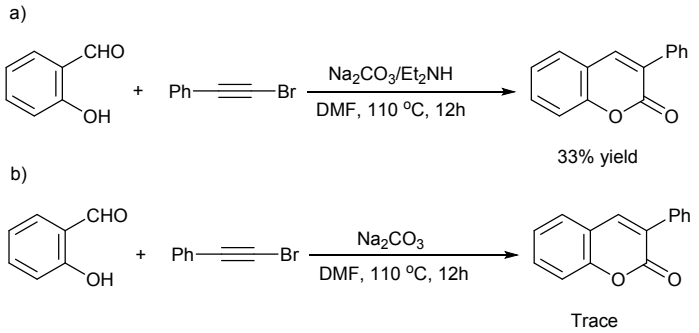
A mixture of intermediate **A** (0.50 mmol), Et_2NH (0.25 mL), sodium carbonate (1.0 mmol) and DMF (2.5 mL) was stirred at 110 ºC in air atmosphere for 12 h. After cooling to room temperature, water (20 mL) was added and the aqueous phase was extracted by EtOAc (5×20 mL). The combined organic phases were dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the corresponding product in 90% yield (Scheme 7).



Scheme 7

3.7 Base-promoted tandem reaction of salicylaldehydes and alkynyl bromide

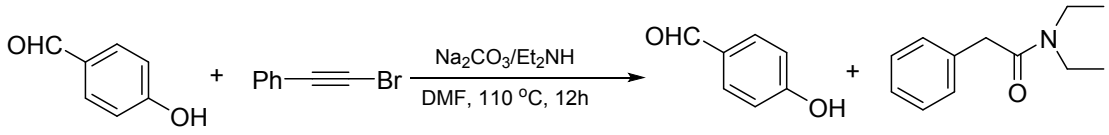
A mixture of salicylaldehydes (1.0 mmol), (bromoethynyl)benzene (1.5 mmol), Et_2NH (0.50 mL), sodium carbonate (2.0 mmol) and DMF (5.0 mL) was stirred at 110 ºC in air atmosphere for 12 h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the corresponding product **3a** in 33% yield (Scheme 8).



Scheme 8

3.4 Base-promoted tandem reaction of *p*-hydroxybenzaldehyde and (bromoethynyl)benzene.

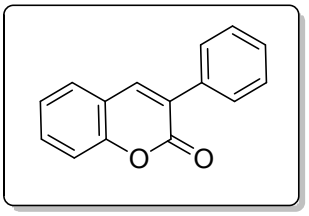
A mixture of *p*-hydroxybenzaldehyde (1.0 mmol), (bromoethynyl)benzene (1.5 mmol), Et_2NH (0.50 mL), sodium carbonate (2.0 mmol) and DMF (5.0 mL) was stirred at 110 ºC in air for 12 h. After cooling to room temperature, the resultant reaction mixture was determined by TLC and GC-MS. The *N*, *N*-diethyl-2-phenylacetamide was obtained in 22% yield (Scheme 9).



Scheme 9

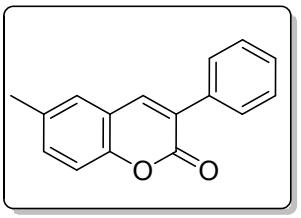
4. Characterization data for products

3-phenyl-2H-chromen-2-one 3a[1]



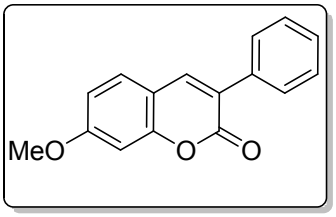
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.69 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.59-7.49 (m, 2H), 7.49 -7.33 (m, 4H), 7.30 (t, *J* = 7.6, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 153.5, 139.9, 134.7, 131.4, 128. 9, 128.5, 127.9, 124.5, 119.7, 116.5. ESI-MS: *m/z* = 222 [M^+].

7-methyl-2-phenyl-4H-chromen-4-one 3b



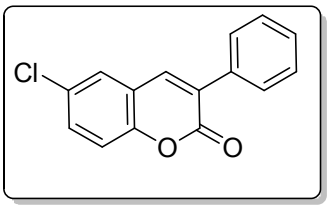
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.72-7.67 (m, 2H), 7.48-7.38 (m, 3H), 7.36-7.31 (m, 2H), 7.25 (t, J =2.4 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ160.8, 151.7, 139.9, 134.9, 134.2, 132.5, 128.8, 128.6, 128.5, 128.3, 127.7, 119.4, 116.2, 20.8. HRMS, calculated for $C_{16}H_{12}NaO_2$ [M+Na^+]: 259.0726, found: 259.0730.

6-methoxy-3-phenyl-2H-chromen-2-one 3c



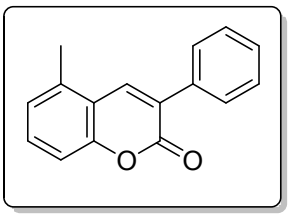
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.73 -7.68 (m, 2H), 7.49 -7.37 (m, 3H), 7.32-7.24 (m, 1H), 7.11 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.97 (d, *J* = 2.9 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 156.2, 148.0, 139.7, 134.8, 128.9, 128.7, 128.6, 128.5, 120.0, 119.2, 117.5, 109.9, 55.9. HRMS, calculated for $C_{16}H_{12}NaO_3$ [M+Na^+]: 275.0680, found: 275.0679.

6-chloro-3-phenyl-2H-chromen-2-one 3d



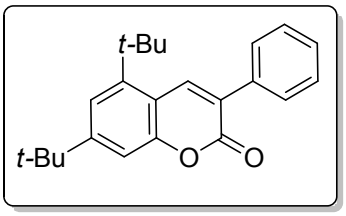
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.69 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.53 (d, *J* = 2.3 Hz, 1H), 7.50-7.40 (m, 4H), 7.31 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 151.9, 138.4, 134.3, 131.3, 129.7, 129.6, 129.2, 128.6, 128.6, 127.1, 120.7, 117.9. HRMS, calculated for $C_{15}H_9ClNaO_2$ [M+Na^+]: 279.0183, found: 279.0179.

5-methyl-3-phenyl-2H-chromen-2-one 3e



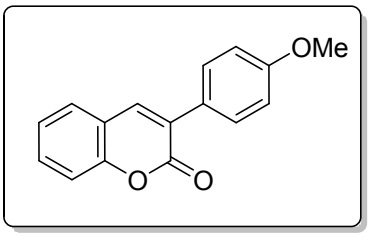
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.72 (d, *J* = 7.2, 2H), 7.49-7.39 (m, 5H), 7.19 (t, *J* = 3.6, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 151.9, 140.3, 134.8, 132.7, 128.8, 128.5, 128.5, 127.9, 125.9, 125.6, 124.1, 119.4, 15.5. HRMS, calculated for $C_{16}H_{13}O_2$ [M+H^+]: 237.0903, found: 237.0906.

5, 7-di-*tert*-butyl-3-phenyl-2H-chromen-2-one 3f



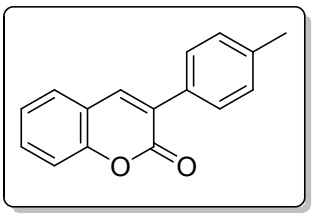
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.74 (m, 2H), 7.43 (t, *J* = 7.2, 1H), 7.41-7.36 (m, 4H), 1.55 (s, 9H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 150.3, 146.7, 141.3, 137.0, 135.0, 128.6, 128.5, 128.4, 127.1, 126.7, 122. 6, 119.6, 35.1, 34.7, 31.1, 30.0. HRMS, calculated for $C_{23}H_{27}O_2$ [M+H$^+$]: 335.1999, found: 335.2006.

3-(4-methoxyphenyl)-2H-chromen-2-one 3g[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.72 (dt, *J* = 9.6, 2.8 Hz, 2H), 7.43 (t, *J* = 1.6 Hz, 2H), 7.28-7.19 (m, 2H), 6.92 (d, *J* =9.6, 2.8 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 153.3, 138.5, 131.0, 129.9, 127.9, 127.7, 127.1, 124.5, 119.9, 116.4, 113.9, 55.4. ESI-MS: *m/z* = 252 [M$^+$].

3-(p-tolyl)-2H-chromen-2-one 3h[2]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.46-7.42 (m, 2H), 7.29 (s, 1H), 7.23-7.17 (m, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 153.44, 139.2, 139.0, 131.8, 131.2, 129.2, 128.4, 127.8, 124.5, 119.8, 116.4, 21.3. HRMS, calculated for $C_{16}H_{13}O_2$ (M+H$^+$): 237.0903, found: 237.0907 (M+H$^+$).

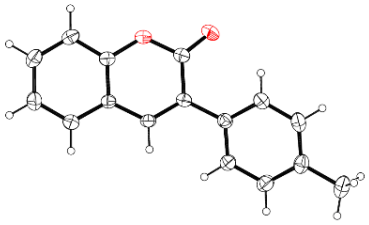
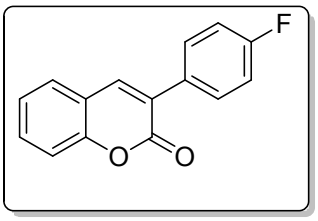


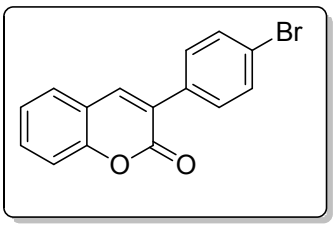
Figure 3. Single crystal structure of coumarin **3h**

3-(4-fluorophenyl)-2H-chromen-2-one 3i



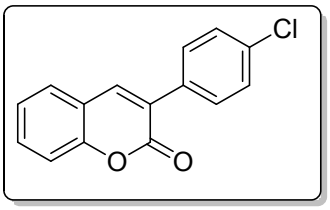
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.73-7.68 (m, 2H), 7.56-7.52 (m, 2H), 7.39 (d, *J*= 8.4 Hz, 1H), 7.33-7.29 (m, 1H), 7.17-7.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 161.9, 160.6, 153.5, 139.7, 131.5, 130.7, 130.7, 130.5, 130.4, 127.9, 127.4, 124.6, 119.6, 116.5, 115.6, 115.4. HRMS, calculated for $C_{15}H_9FNaO_2$ [M+Na^+]: 263.0479, found: 263.0482.

3-(4-bromocyclohexa-2,4-dien-1-yl)-2H-chromen-2-one 3j



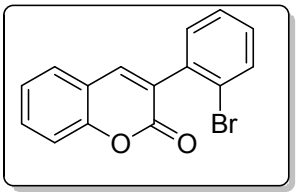
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.9 Hz, 1H), 7.57 (ddt, *J* = 12.5, 9.2, 5.2 Hz, 6H), 7.42 -7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 160.3, 153.5, 140.0, 133.5, 131.7, 131.6, 130.1, 128.0, 127.1, 124.7, 123.2, 119.5, 116.5. HRMS, calculated for $C_{15}H_9BrNaO_2$ [M+Na^+]: 322.9678, found: 322.9673.

3-(4-chlorophenyl)-2H-chromen-2-one 3k



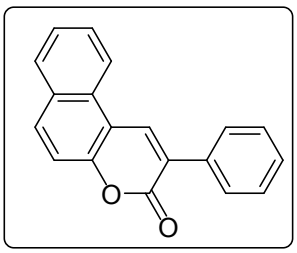
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.69 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.53 (d, *J* = 2.3 Hz, 1H), 7.50-7.40 (m, 4H), 7.31 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 151.9, 138.4, 134.3, 133.3, 129.7, 129.6, 129.2, 128.6, 129.6, 127.1, 117.9. HRMS, calculated for $C_{15}H_9ClNaO_2$ [M+Na^+]: 279.0183, found: 279.0181.

3-(2-bromocyclohexa-2,4-dien-1-yl)-2H-chromen-2-one 3l



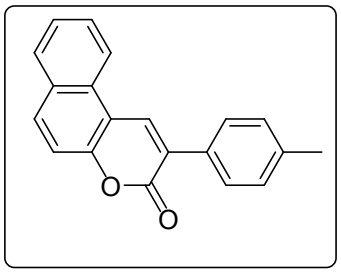
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.61-7.52 (m, 2H), 7.40 (d, *J* = 4.6 Hz, 3H), 7.36-7.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 153.9, 142.6, 135.8, 133.1, 131.9, 131.4, 130.3, 128.8, 128.2, 127.5, 124.7, 123.6. HRMS, calculated for $C_{15}H_9BrNaO_2$ [M+Na^+]: 322.9678, found: 322.9675.

2-phenyl-3H-benzo[f]chromen-3-one 3m



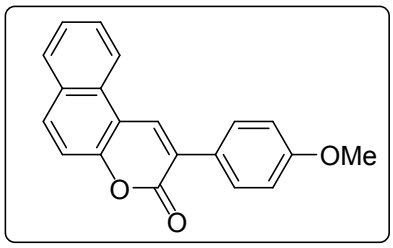
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.90 (t, *J* = 6.9 Hz, 1H), 7.83-7.76 (m, 2H), 7.73-7.64 (m, 1H), 7.56 (td, *J* = 7.7, 3.7 Hz, 1H), 7.53-7.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 153.2, 135.7, 135.1, 132.7, 130.4, 129.1, 129.1, 128.9, 128.6, 128.6, 128.2, 127.3, 126.0, 121.4, 116.7, 113.7. HRMS, calculated for $C_{19}H_{12}NaO_2$ [M+Na^+]: 295.0730, found: 295.0730.

2-(p-tolyl)-3H-benzo[f]chromen-3-one 3n



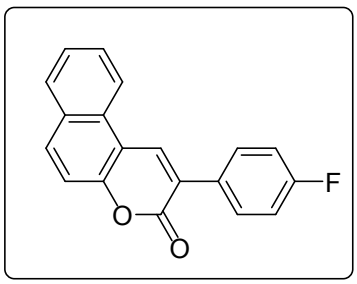
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.93 (dd, *J* = 18.4, 8.5 Hz, 2H), 7.74-7.64 (m, 3H), 7.57 (dd, *J* = 11.1, 3.9 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.28 (t, *J* = 8.8 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 153.0, 139.0, 135.0, 132.5, 132.2, 130.4, 129.3, 129.1, 129.4, 128.5, 128.1, 127.3, 126.0, 121.5, 116.7, 113.8, 21.3. HRMS, calculated for $C_{20}H_{14}NaO_2$ [M+Na$^+$]: 309.0873, found: 309.0876.

2-(4-methoxyphenyl)-3H-benzo[f]chromen-3-one 3o



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.95 (dd, *J* = 15.1, 8.6 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.73-7.68 (m, 1H), 7.61-7.56 (m, 1H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 160.2, 152.8, 134.3, 132.3, 130.4, 129.9, 129.1, 128.1, 127.5, 126.8, 126.0, 121.5, 116.7, 114.0, 113.9, 55.4. HRMS, calculated for $C_{20}H_{14}NaO_3$ [M+Na$^+$]: 325.0835, found: 325.0838.

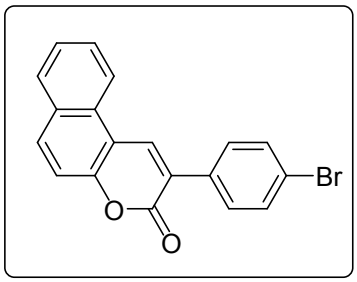
2-(4-fluorophenyl)-3H-benzo[f]chromen-3-one 3p



^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (s, 1H), 8.76 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.01-7.90 (m, 2H), 7.81-7.72 (m, 1H), 7.69-7.60 (m, 2H), 7.42-7.29 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.5, 161.0, 159.8, 152.6, 136.6, 133.0, 131.2, 131.2,

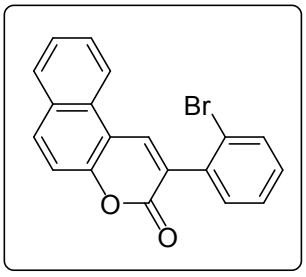
131.1, 131.0, 130.0, 128.9, 128.8, 128.2, 126.1, 125.1, 116.4, 115.1, 114.9, 113.6. HRMS, calculated for $C_{19}H_{11}FNaO_2$ [M+Na$^+$]: 313.0642, found: 313.0635.

2-(4-bromophenyl)-3H-benzo[f]chromen-3-one 3q



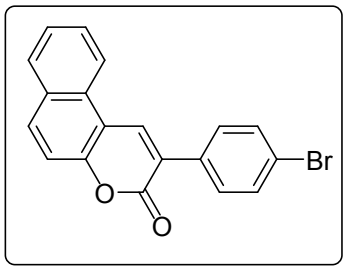
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.75 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 9.1 Hz, 1H), 8.09-8.05 (m, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.77-7.68 (m, 3H), 7.66-7.6**0** (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.1, 153.4, 135.9, 134.2, 133.0, 131.6, 130.4, 130.3, 129.1, 129.1, 128.3, 126.1, 125.9, 122.9, 121.5, 116.6, 113.6. HRMS, calculated for $C_{19}H_{11}BrNaO_2$ [M+Na$^+$]: 372.9835, found: 372.9838.

2-(2-bromophenyl)-3H-benzo[f]chromen-3-one 3r



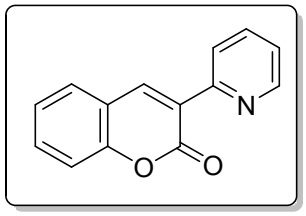
^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.77-7.64 (m, 2H), 7.64-7.40 (m, 4H), 7.32 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 153.8, 138.6, 136.1, 133.2, 131.5, 130.4, 130.2, 129.2, 129.1, 128.4, 127.6, 127.6, 126.1, 123.7, 121.5, 116.9, 113.2. HRMS, calculated for $C_{19}H_{12}BrO_2$ [M+H$^+$]: 351.0015, found: 351.0020.

2-(4-bromophenyl)-3H-benzo[f]chromen-3-one 3s



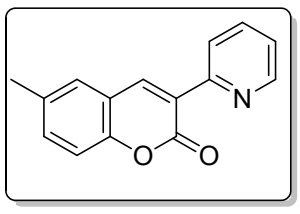
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 1H), 8.76 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.96-7.89 (m, 2H), 7.75 (dd, *J* = 11.3, 4.1 Hz, 1H), 7.61 (ddd, *J* = 19.3, 9.4, 7.0 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.6, 152.7, 136.9, 133.6, 133.3, 133.2, 130.6, 130.0, 130.0, 128.8, 128.2, 128.2, 126.1, 124.8, 122.8, 116.4, 113.6. HRMS, calculated for $C_{19}H_{11}ClNaO_2$ [M+Na$^+$]: 329.0333, found: 329.0337.

3-(pyridin-2-yl)naphthalen-2(1H)-one 4a



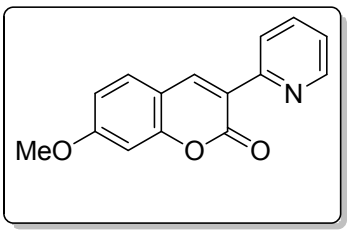
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82-8.73 (m, 1H), 8.69 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.42 (d, *J* = 8.1 Hz, 1H), 7.79 (tt, *J* = 5.6, 2.8 Hz, 1H), 7.65 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.60-7.53 (m, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.35-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 153.9, 151.3, 149.3, 142.5, 136.8, 132.2, 128.9, 125.3, 124.6, 124.1, 123.5, 119.5, 116.4. HRMS, calculated for $C_{14}H_9NNaO_2$ [M+Na$^+$]: 246.0527, found: 246.0525.

6-methyl-3-(pyridin-2-yl)-2H-chromen-2-one 4b



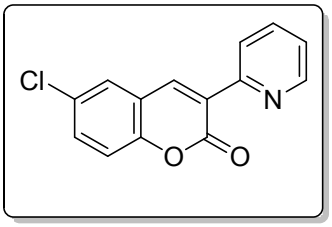
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75-8.65 (m, 2H), 8.41 (t, *J* = 7.1 Hz, 1H), 7.79 (td, *J* = 7.8, 1.7 Hz, 1H), 7.42 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.33-7.25 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 152.1, 151.4, 149.3, 142.6, 136.7, 134.3, 133.1, 128.6, 125.2, 124.1, 123.4, 119.3, 116.1, 20.8. HRMS, calculated for $C_{15}H_{12}NO_2$ [M+H$^+$]: 238.0861, found: 238.0863.

6-methoxy-3-(pyridin-2-yl)-2H-chromen-2-one 4c



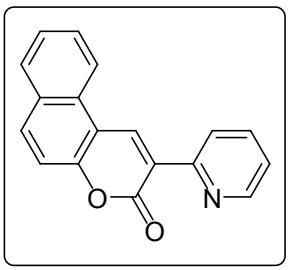
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.69 (d, *J* = 4.1 Hz, 1H), 8.44 (d, *J* = 8.1 Hz, 1H), 7.80 (td, *J* = 7.9, 1.7 Hz, 1H), 7.31 (t, *J* = 6.5 Hz, 2H), 7.15 (dd, *J* = 9.0, 2.9 Hz, 1H), 7.07 (d, *J* = 2.8 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 156.1, 151.3, 149.4, 148.4, 142.3, 136.77, 125.6, 124.1, 123.5, 120.2, 119.8, 117.4, 110.3, 107.0, 55.8. HRMS, calculated for $C_{15}H_{12}NO_3$ [M+H$^+$]: 254.0807, found: 254.0812.

6-chloro-3-(pyridin-2-yl)-2H-chromen-2-one 4d



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76-8.66 (m, 2H), 8.42 (d, *J* = 8.1 Hz, 1H), 7.87-7.78 (m, 1H), 7.62 (t, *J* = 5.6 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.34 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 152.3, 150.7, 149.3, 141.3, 137.1, 132.1, 129.9, 127.9, 124.3, 123.9, 120.5, 117.8. HRMS, calculated for $C_{14}H_8ClNNaO_2$ [M+Na$^+$]: 258.0312, found: 258.0316.

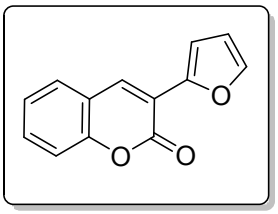
2-(pyridin-2-yl)-3H-benzo[f]chromen-3-one 4e



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.74 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.90 (t, *J* = 5.7 Hz, 1H), 7.81 (td, *J* = 7.8, 1.9 Hz, 1H), 7.73-7.67 (m, 1H), 7.57 (ddd, *J* = 8.0, 5.2, 1.0 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H),

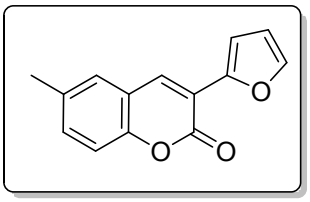
7.36-7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 153.8, 151.4, 149.4, 138.3, 136.8, 133.7, 130.3, 129.6, 129.0, 128.4, 126.2, 124.0, 123.8, 123.4, 122.2, 116.5, 113.6. HRMS, calculated for $C_{18}H_{12}NO_2$ [M+H$^+$]: 274.0857, found: 274.0856.

3-(furan-2-yl)-2H-chromen-2-one 5a



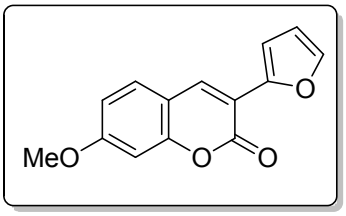
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.57 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54-7.47 (m, 2H), 7.40-7.33 (m, 2H), 7.33-7.27 (m, 1H), 6.55 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 152.7, 147.6, 143.2, 133.9, 131.1, 127.9, 124.7, 119.4, 118.1, 116.5, 112.9, 112.4. HRMS, calculated for $C_{13}H_8NaO_3$ [M+Na$^+$]: 235.0362, found: 235.0366.

3-(furan-2-yl)-6-methyl-2H-chromen-2-one 5b



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.52 (d, *J* = 1.3 Hz, 1H), 7.40-7.13 (m, 4H), 6.54 (dd, *J* = 3.4, 1.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 150.8, 147.8, 143.1, 134.3, 133.9, 132.2, 127.7, 119.1, 118.0, 116.2, 112.7, 112.4, 20.8. HRMS, calculated for $C_{14}H_{10}NaO_3$ [M+Na$^+$]: 249.0515, found: 249.0522.

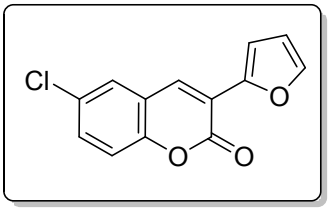
3-(furan-2-yl)-7-methoxy-2H-chromen-2-one 5c



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.50-7.43 (m, 2H), 7.27 (d, *J* = 3.9 Hz, 1H), 6.89-6.82 (m, 2H), 6.53 (dd, *J* = 3.4, 1.8 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.4,

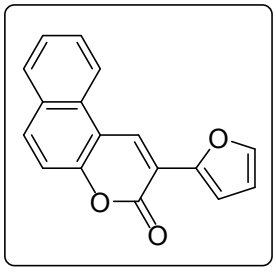
154.4, 147.9, 142.7, 134.3, 128.9, 115.0, 113.0, 113.0, 112.3, 111.6, 100.5, 55.8. HRMS, calculated for $C_{14}H_{11}O_4$ [M+H$^+$]): 243.0652, found: 243.0659.

6-chloro-3-(furan-2-yl)-2H-chromen-2-one 5d



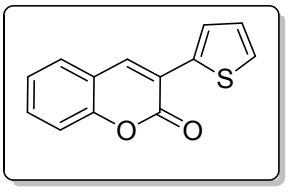
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.46 (d, *J* = 2.2 Hz, 2H), 7.36 (dt, *J* = 9.8, 4.9 Hz, 1H), 7.31 (d, *J* = 3.4 Hz, 1H), 7.25-7.17 (m, 1H), 6.48 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 149.9, 146.2, 142.7, 131.2, 129.8, 128.9, 126.0, 119.4, 118.0, 116.8, 112.7, 111.6. HRMS, calculated for $C_{13}H_7ClNaO_3$ [M+Na$^+$]: 268.9970, found: 268.9976.

2-(furan-2-yl)-3H-benzo[f]chromen-3-one 5e



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.93 (dd, *J* = 16.1, 8.5 Hz, 2H), 7.71 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.62-7.53 (m, 2H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.42 (d, *J* = 3.4 Hz, 1H), 6.59 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 152.2, 148.0, 143.3, 132.4, 130.5, 129.6, 129.1, 129.0, 128.2, 126.1, 121.8, 117.1, 116.7, 113.7, 112.9, 112.6. HRMS, calculated for $C_{17}H_{10}NaO_3$ [M+Na$^+$]: 285.0513, found: 285.0518.

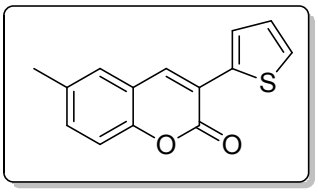
3-(thiophen-2-yl)-2H-chromen-2-one 5f



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.85-7.75 (m, 1H), 7.58-7.47 (m, 2H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.38-7.26 (m, 2H), 7.13 (t, *J* = 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 152.6,

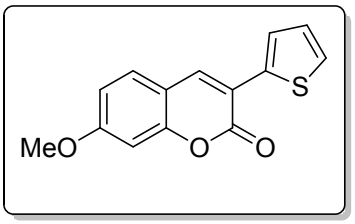
135.9, 135.5, 131.2, 127.8, 127.6, 127.1, 124.7, 121.7, 119.4, 116.4. HRMS, calculated for $C_{13}H_9O_2S$ [M+H$^+$]: 229.0318, found: 229.0313.

6-methyl-3-(thiophen-2-yl)-2H-chromen-2-one 5g



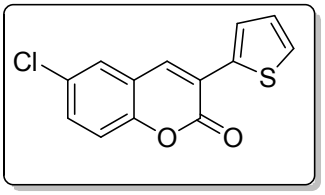
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.82-7.77 (m, 1H), 7.43 (dt, *J*= 5.2, 1.1 Hz, 1H), 7.32 (d, *J*= 9.2 Hz, 2H), 7.28-7.24 (m, 1H), 7.13 (ddd, *J*= 5.0, 3.8, 1.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6) δ 159.6, 150.8, 136.6, 135.8, 134.6, 132.9, 129.2, 128.5, 127.8, 127.0, 120.9, 119.5, 116.2, 20.8. HRMS, calculated for $C_{14}H_{10}NaO_2S$ [M+Na$^+$]: 265.0294, found: 265.0294.

7-methoxy-3-(thiophen-2-yl)-2H-chromen-2-one 5h



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.75 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.42-7.37 (m, 1H), 7.13 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.92-6.86 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 159.8, 154.6, 136.4, 136.0, 128.7, 127.5, 126.9, 126.3, 118.6, 113.1, 100.4, 55.8. HRMS, calculated for $C_{14}H_{10}NaO_3S$ [M+Na$^+$]: 281.0243, found: 281.0241.

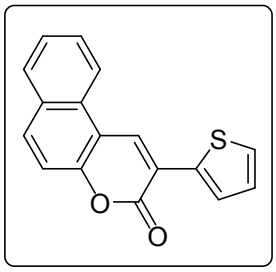
6-chloro-3-(thiophen-2-yl)-2H-chromen-2-one 5i



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.82 (dt, *J* = 3.7, 1.0 Hz, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.50-7.40 (m, 2H), 7.37-7.21 (m, 2H), 7.15 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.0,

151.2, 135.5, 135.2, 131.4, 129.8, 129.0, 128.0, 127.7, 127.6, 122.1, 121.2, 118.4. HRMS, calculated for $C_{13}H_8ClO_2S$ [M+H$^+$]: 262.9930, found: 262.9935.

2-(thiophen-2-yl)-3H-benzo[f]chromen-3-one 5j



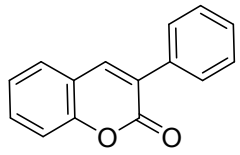
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 3.4 Hz, 1H), 8.33 (dd, *J* = 8.9, 3.2 Hz, 1H), 8.02- 7.86 (m, 3H), 7.77-7.68 (m, 1H), 7.59 (dd, *J* = 9.2, 5.7 Hz, 1H), 7.48 (td, *J* = 8.4, 7.4, 3.5 Hz, 2H), 7.32-7.10 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.6, 152.1, 135.8, 133.2, 132.4, 130.6, 129.7, 129.3, 128.6, 127.7, 127.5, 126.7, 123.4, 120.5, 116.9, 114.1. HRMS, calculated for $C_{17}H_{10}NaO_2S$ [M+Na$^+$]: 301.0294, found: 301.0300.

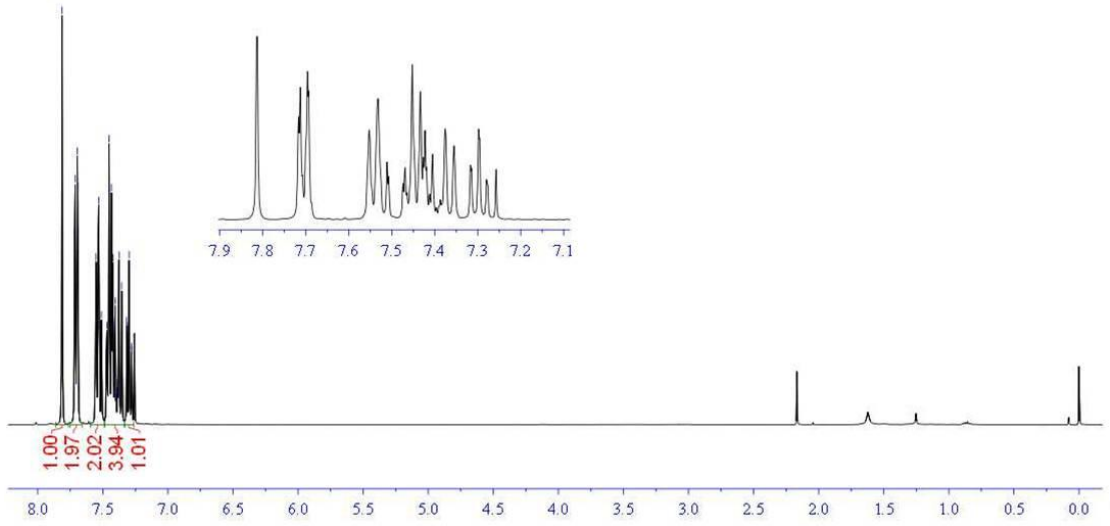
References

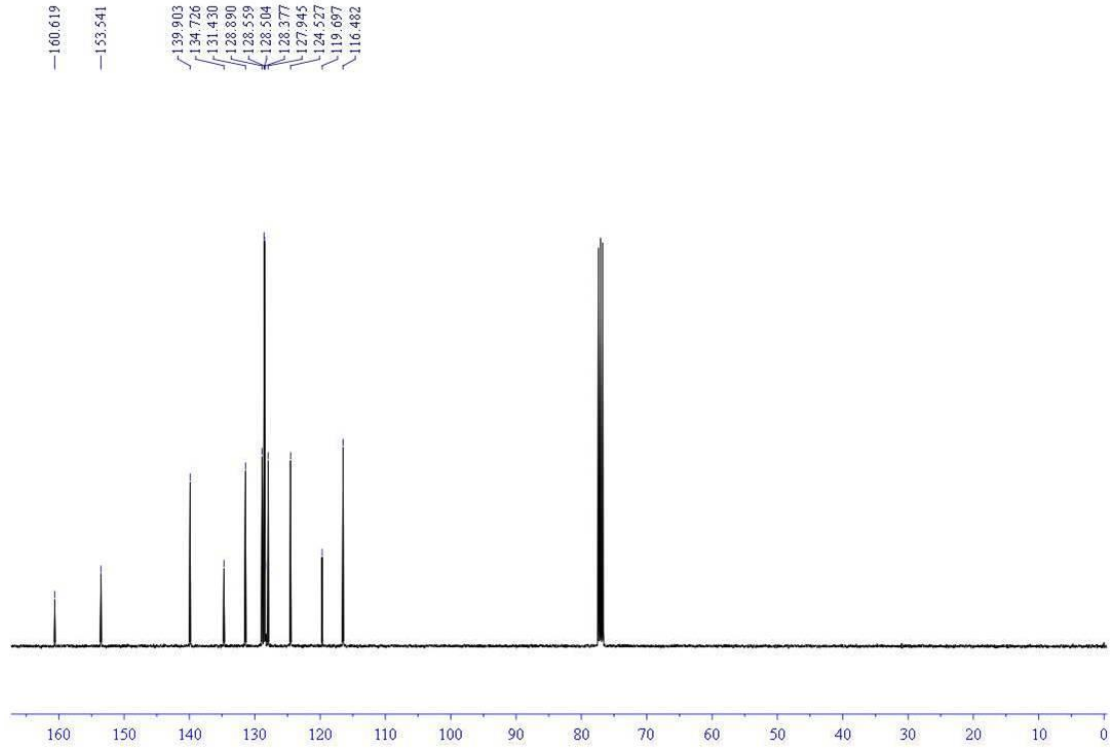
1. Matos, M. J.; Vazquez-Rodriguez, S.; Borges, F.; Santana, L. ; Uriarte, E. *Tetrahedron Lett.* **2011**, *52*, 1225.
2. CCDC 947235 (**3h**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

5. ^{1}H NMR and ^{13}C NMR copies of products

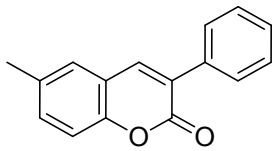
3-phenyl-2H-chromen-2-one 3a

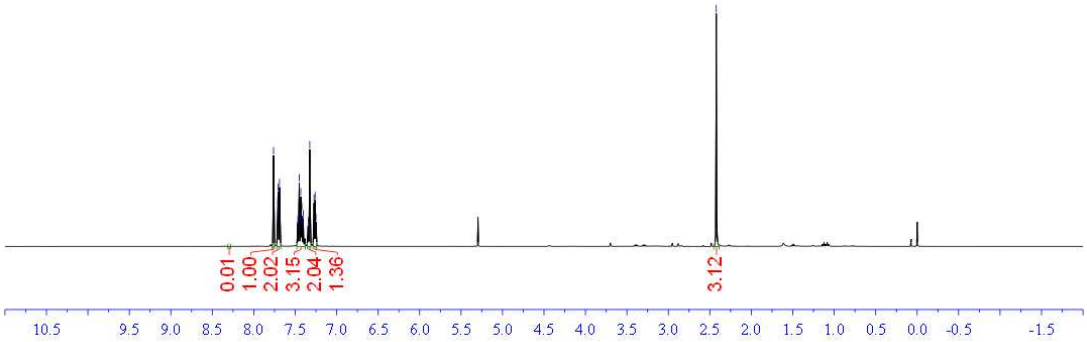


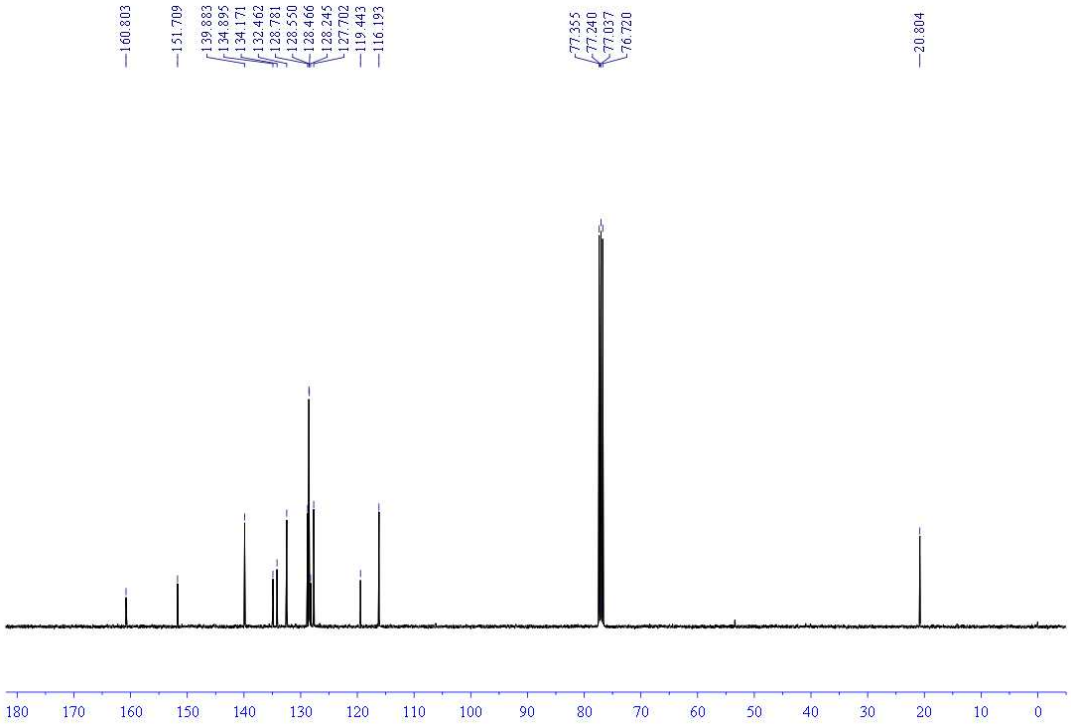




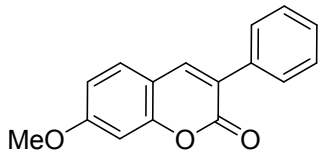
7-methyl-2-phenyl-4H-chromen-4-one 3b

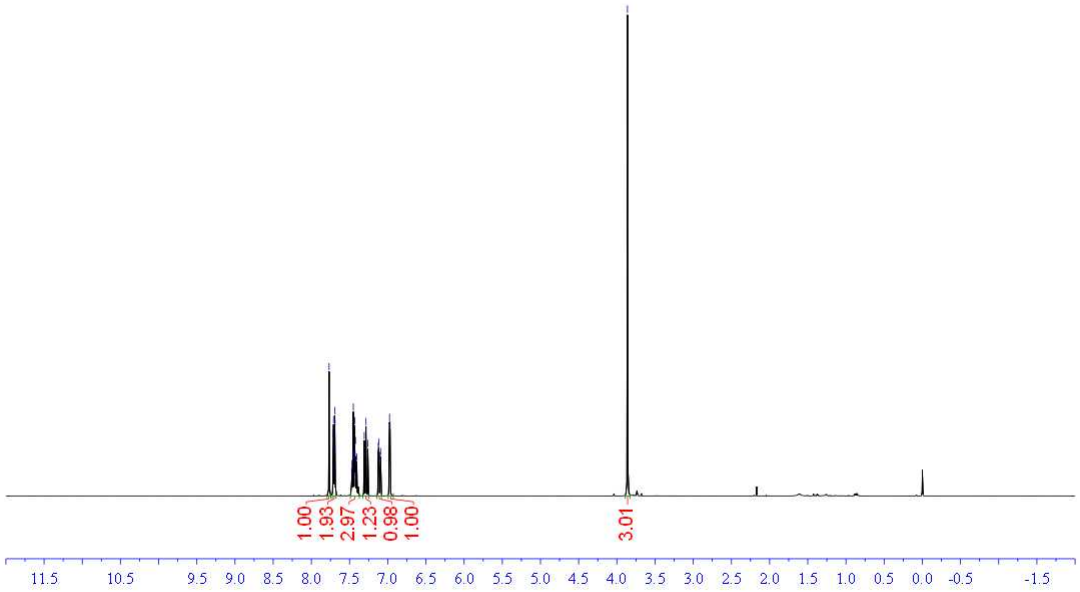


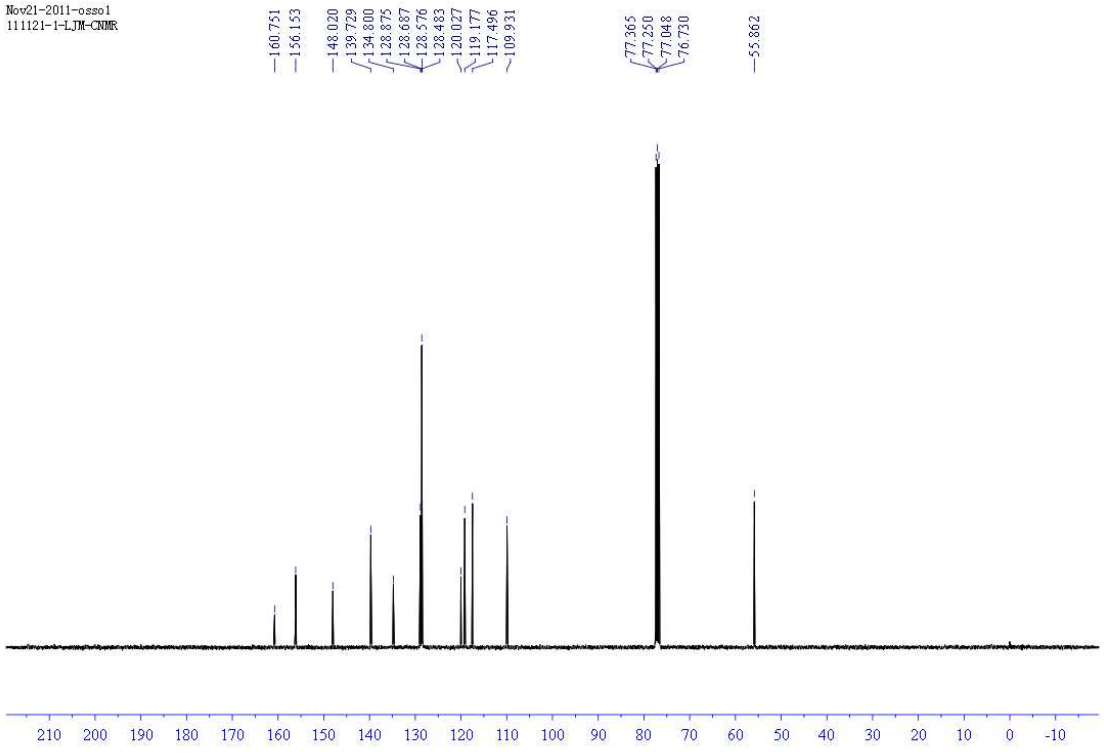




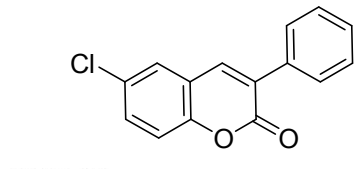
6-methoxy-3-phenyl-2H-chromen-2-one 3c

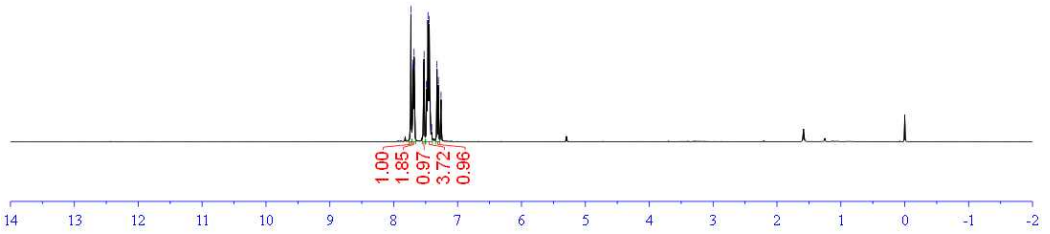


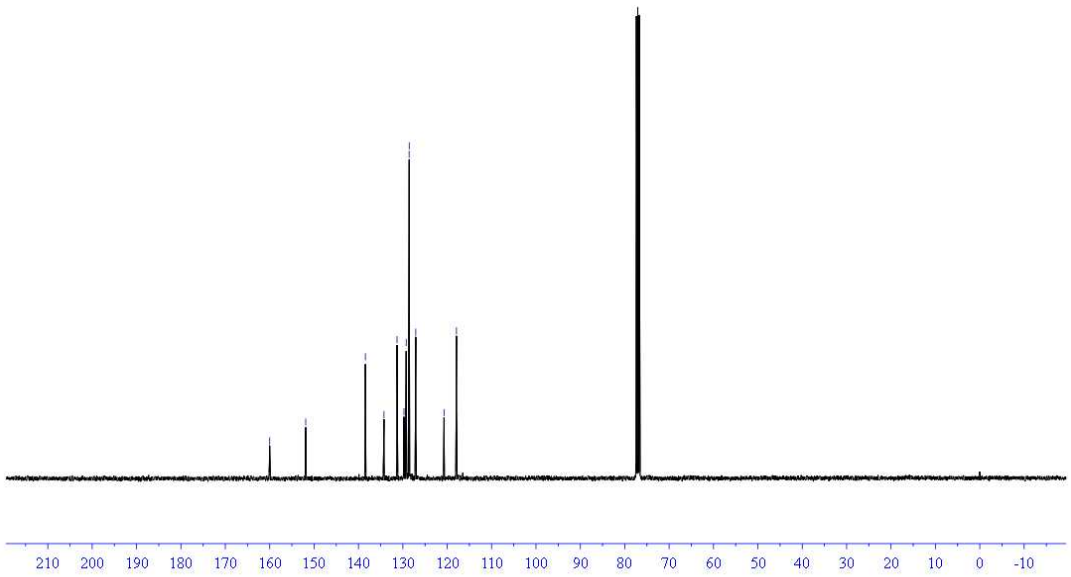




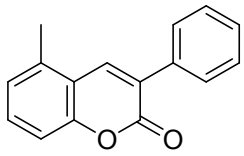
6-chloro-3-phenyl-2H-chromen-2-one 3d

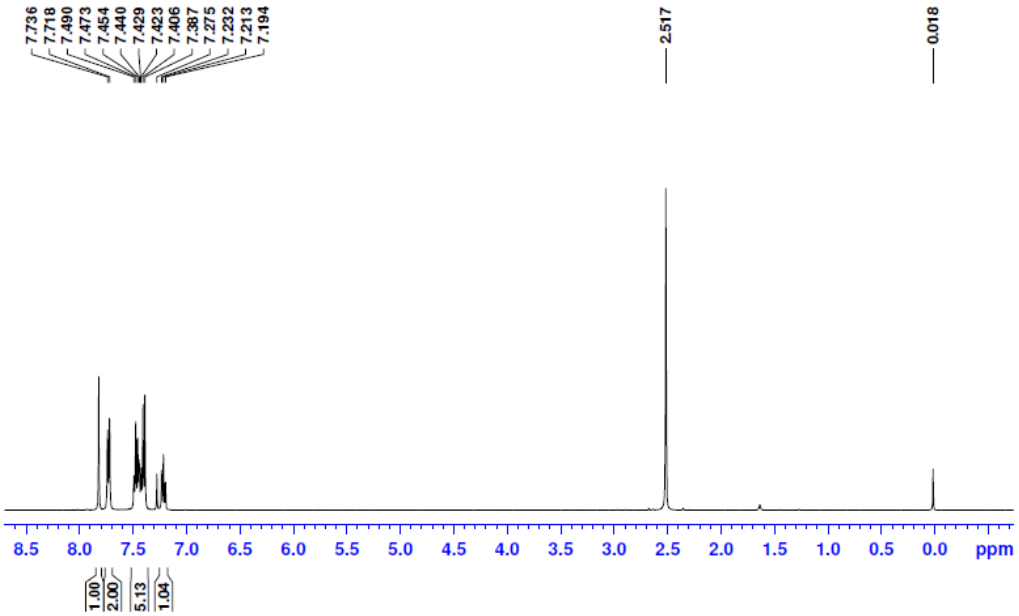


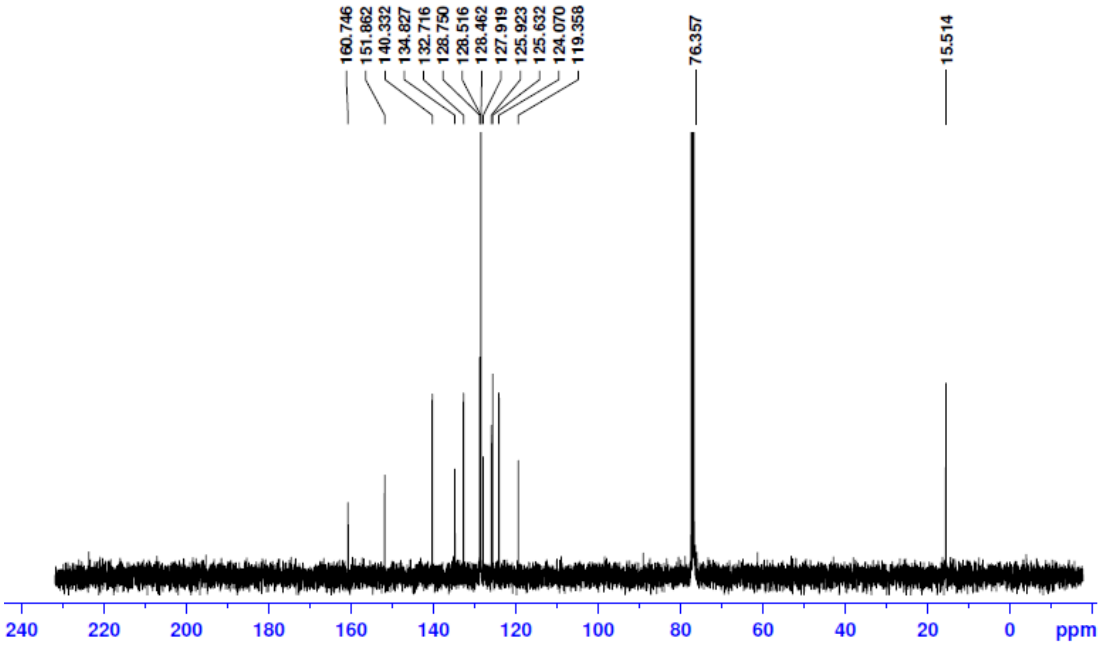




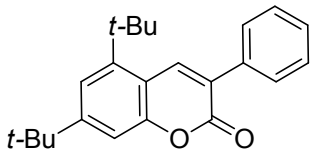
5-methyl-3-phenyl-2H-chromen-2-one 3e

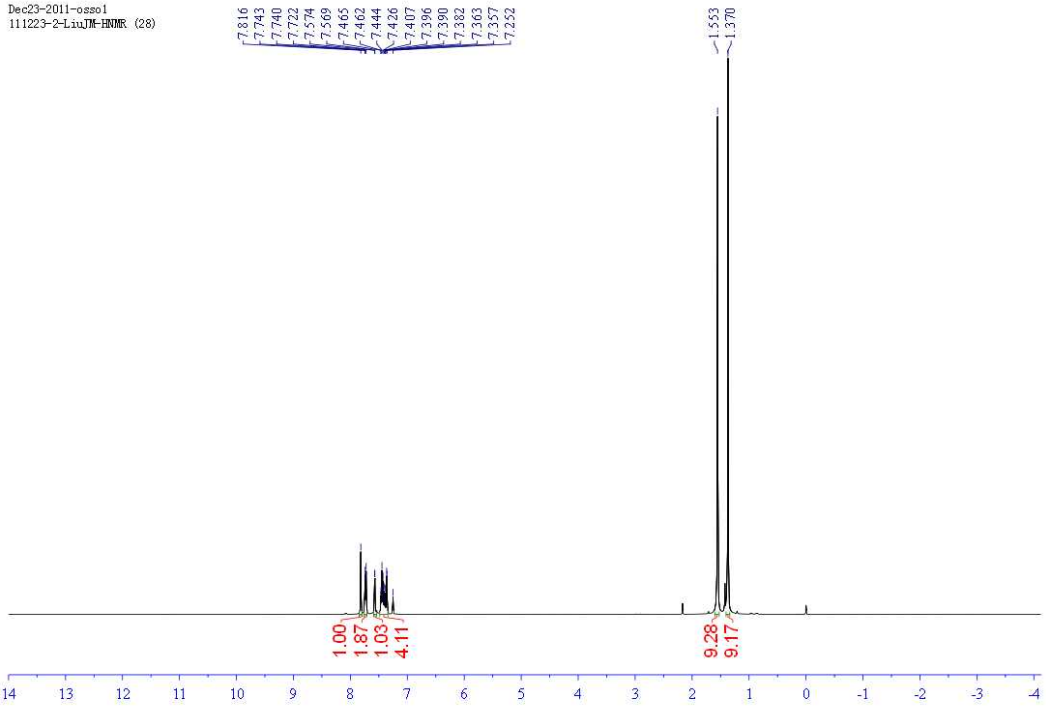


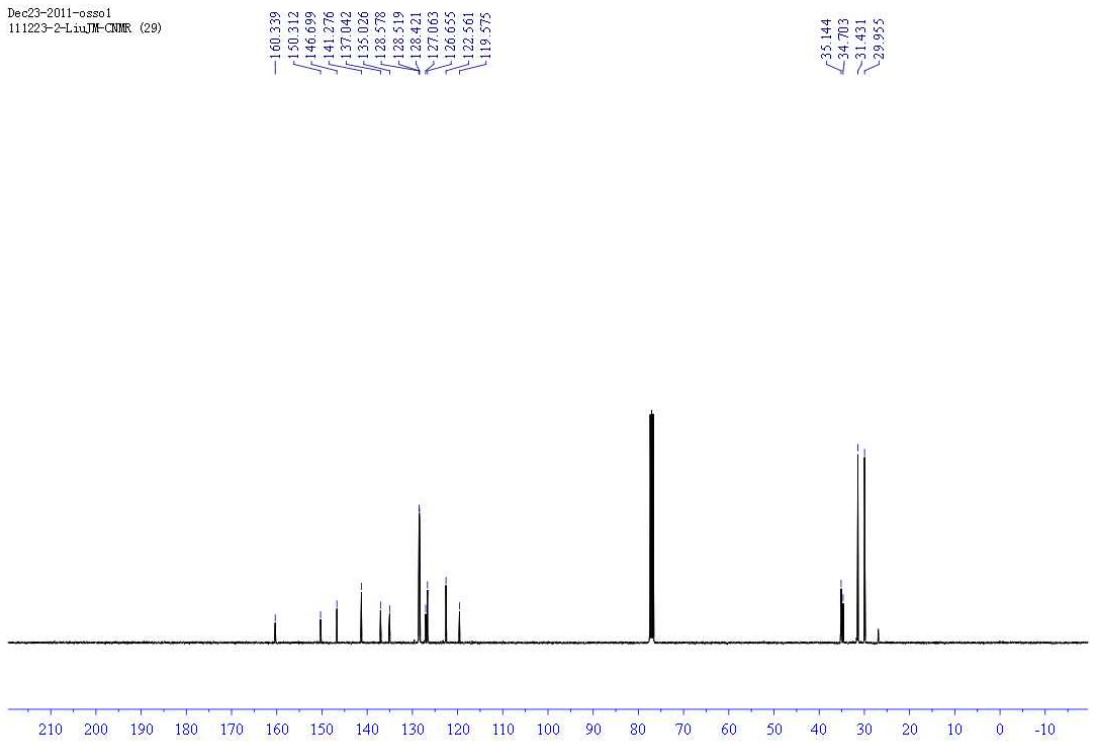




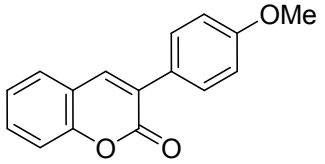
5, 7-di-*tert*-butyl-3-phenyl-2H-chromen-2-one 3f

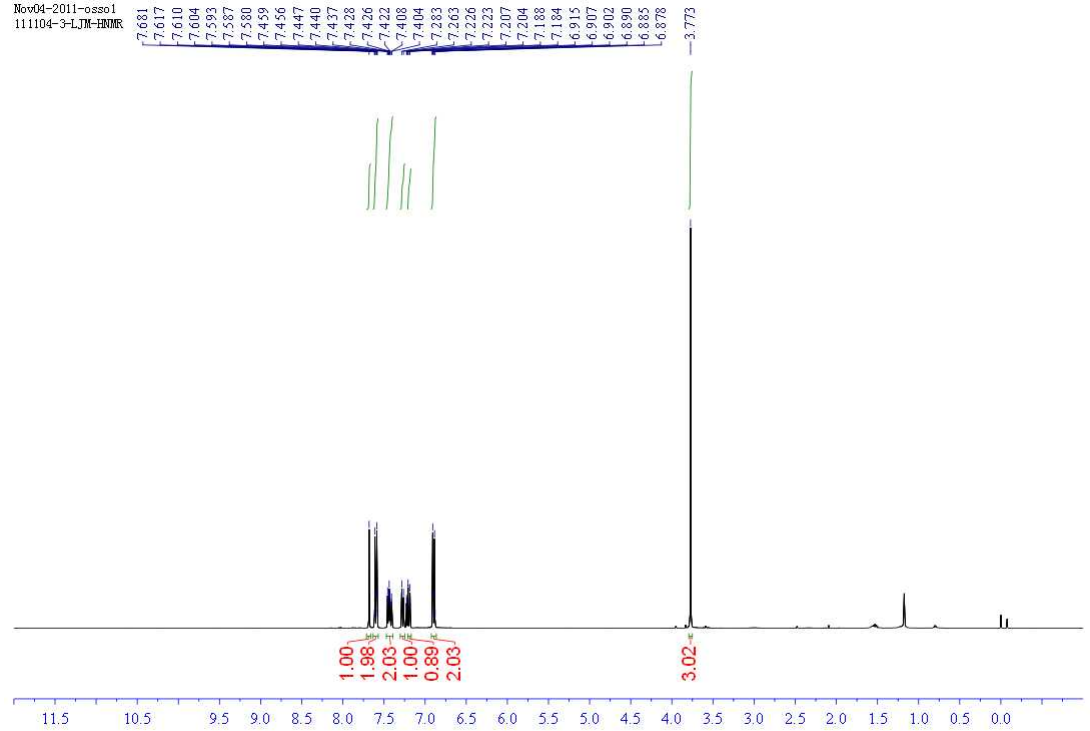


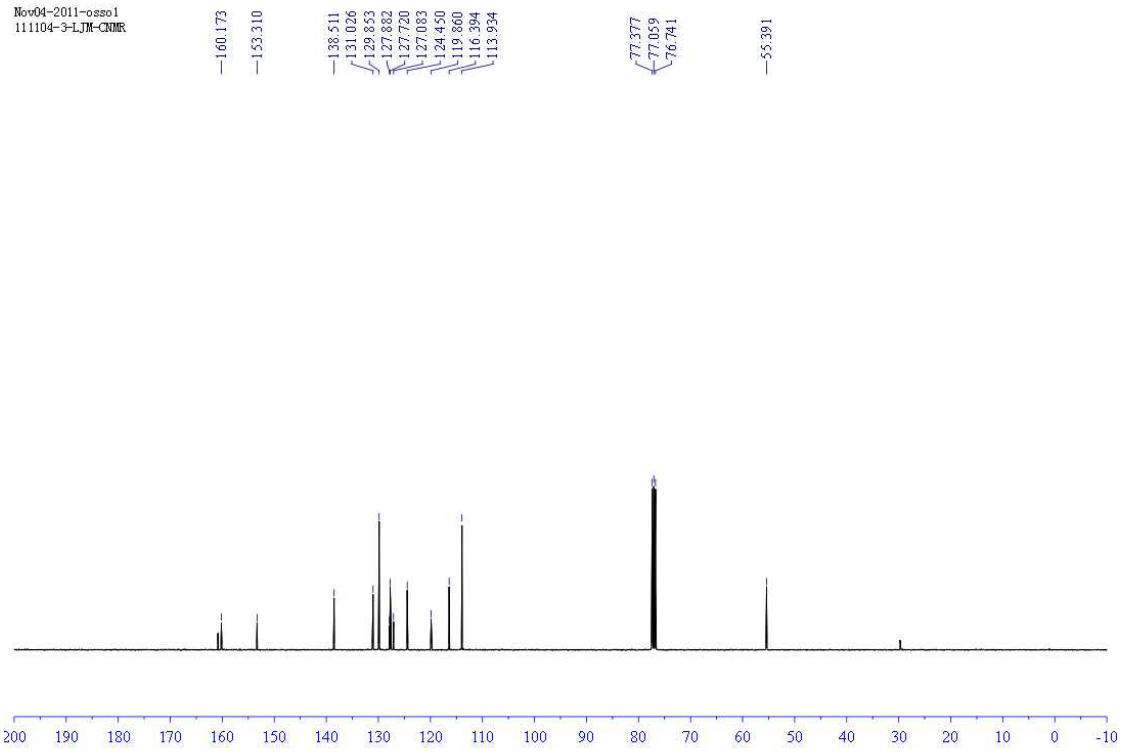




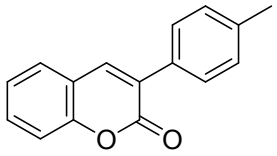
3-(4-methoxyphenyl)-2H-chromen-2-one 3g

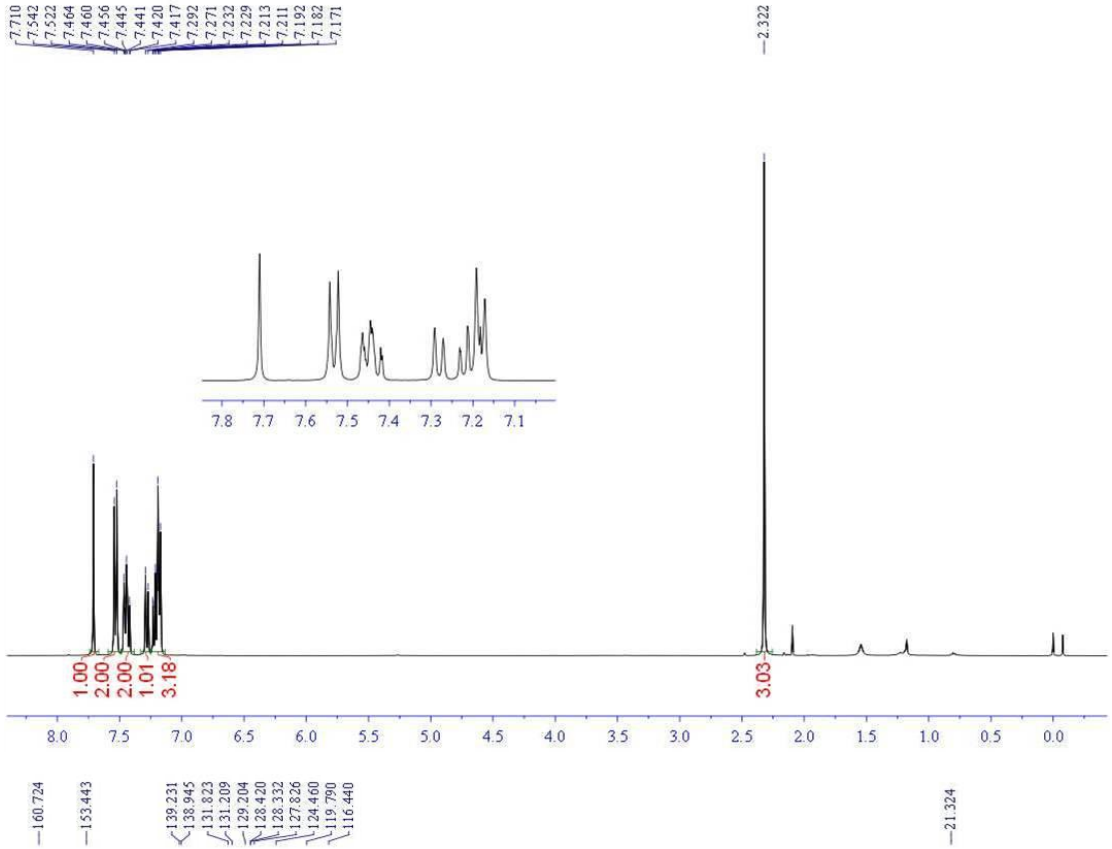


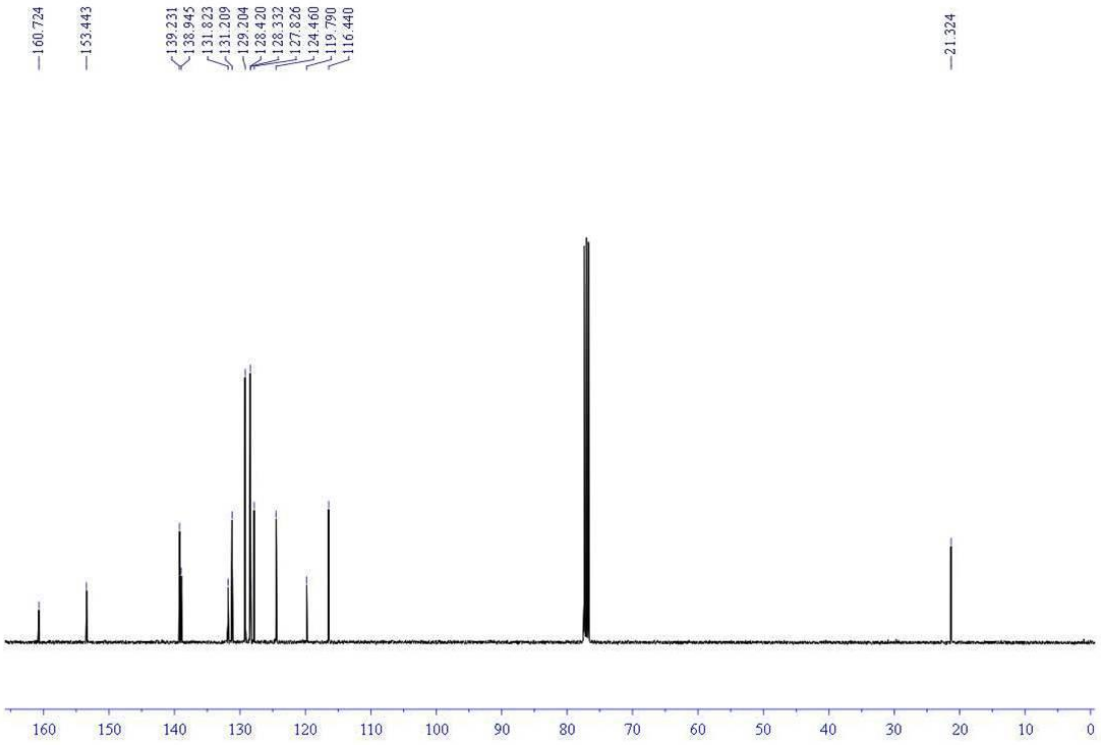




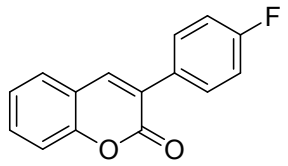
3-(p-tolyl)-2H-chromen-2-one 3h

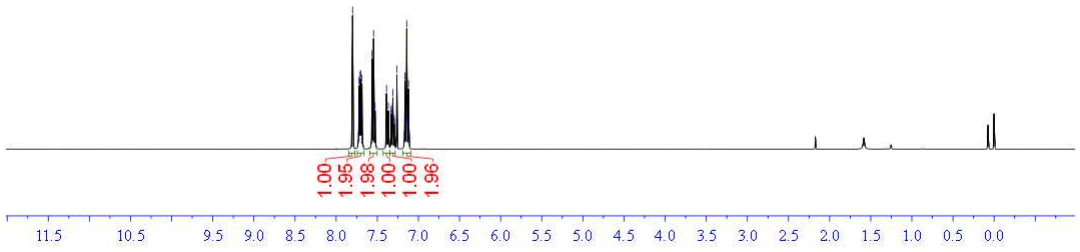


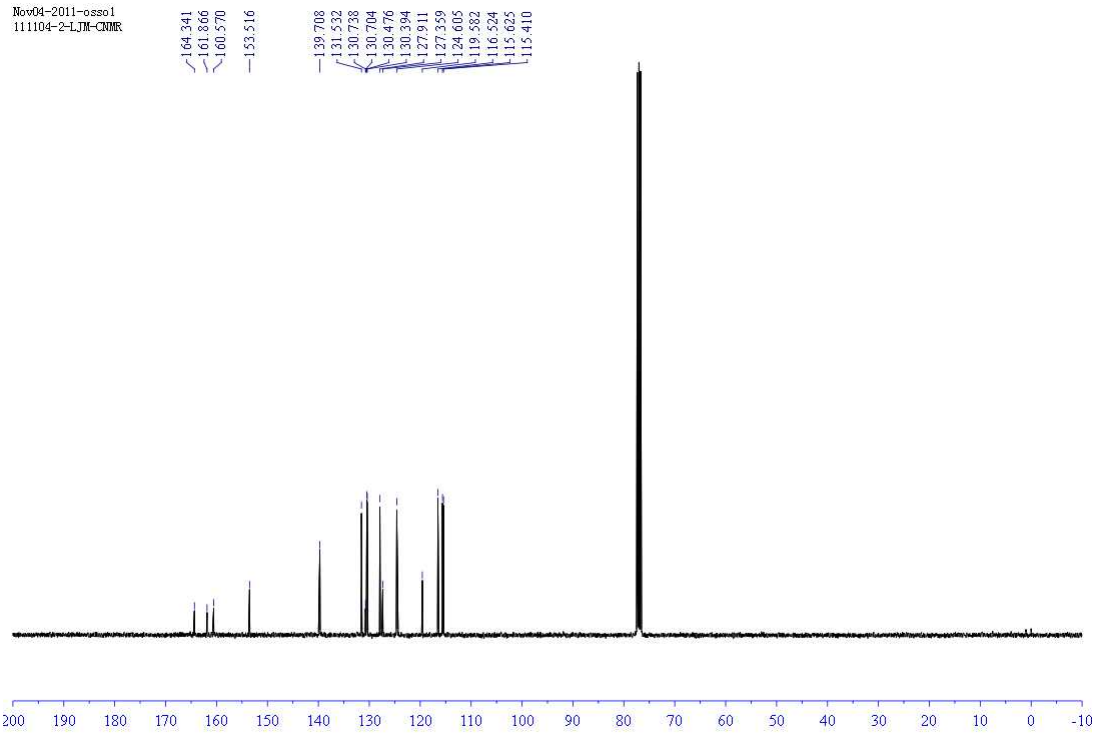




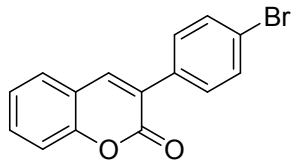
3-(4-fluorophenyl)-2H-chromen-2-one 3i

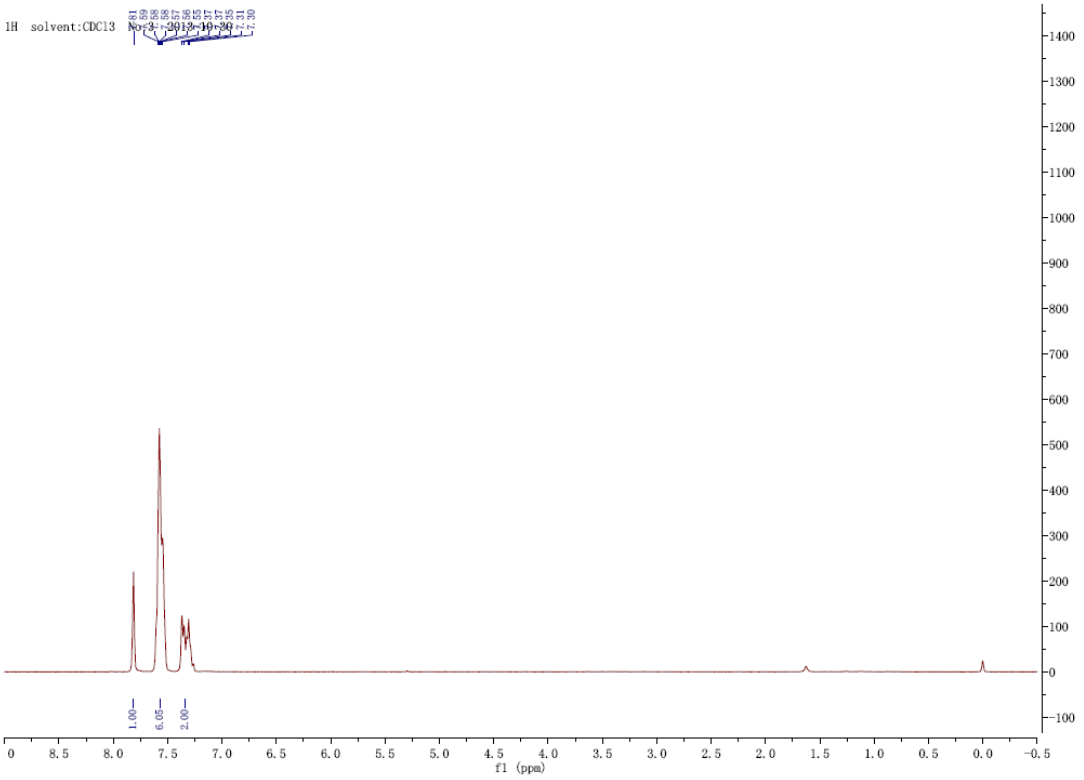


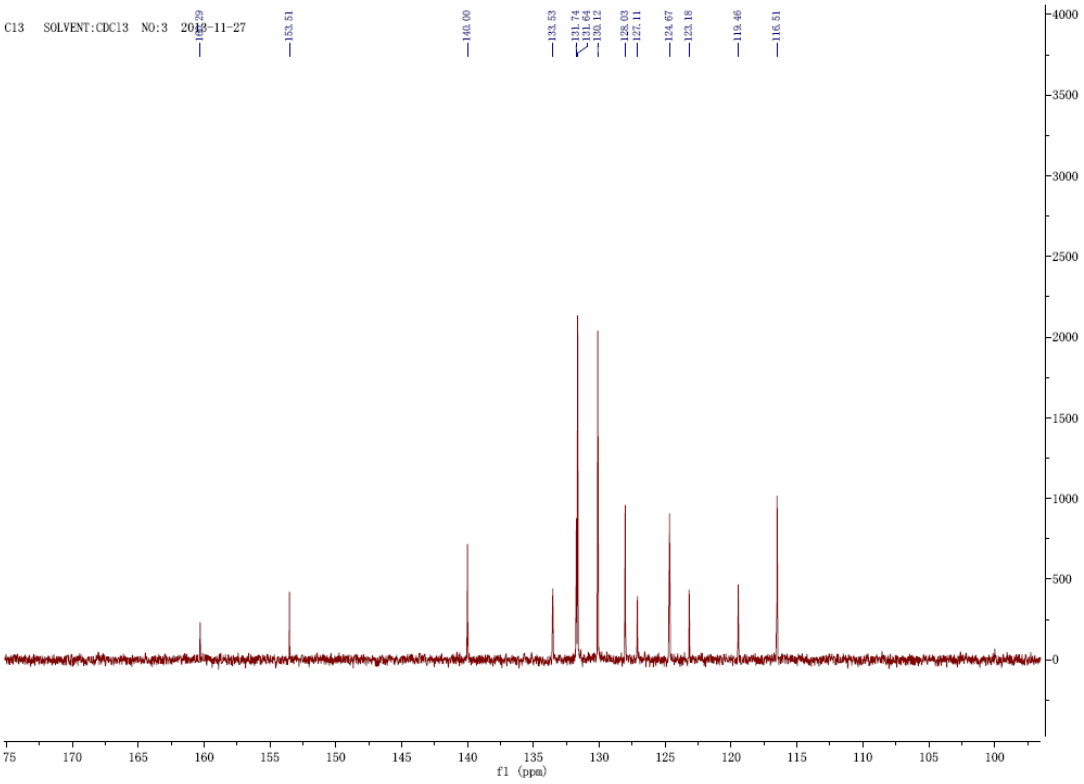




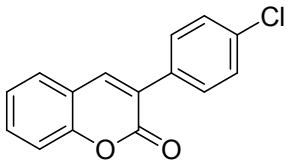
3-(4-bromocyclohexa-2,4-dien-1-yl)-2H-chromen-2-one 3j

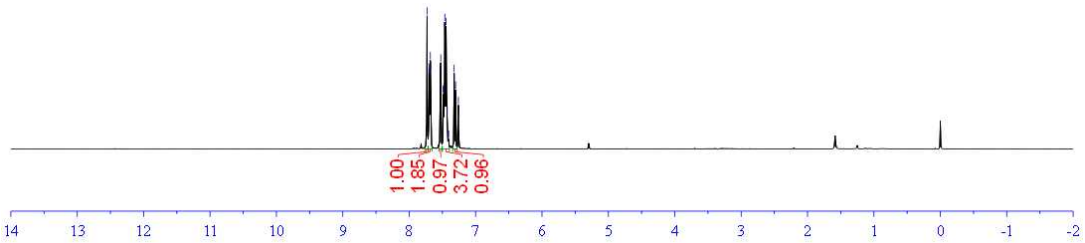


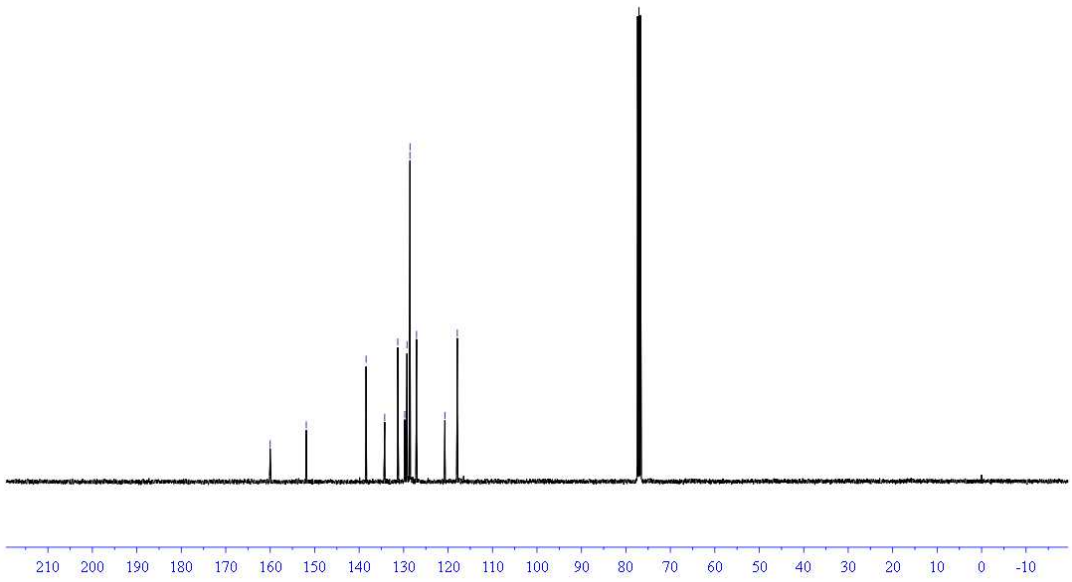




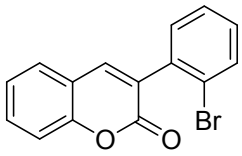
3-(4-chlorophenyl)-2H-chromen-2-one 3k

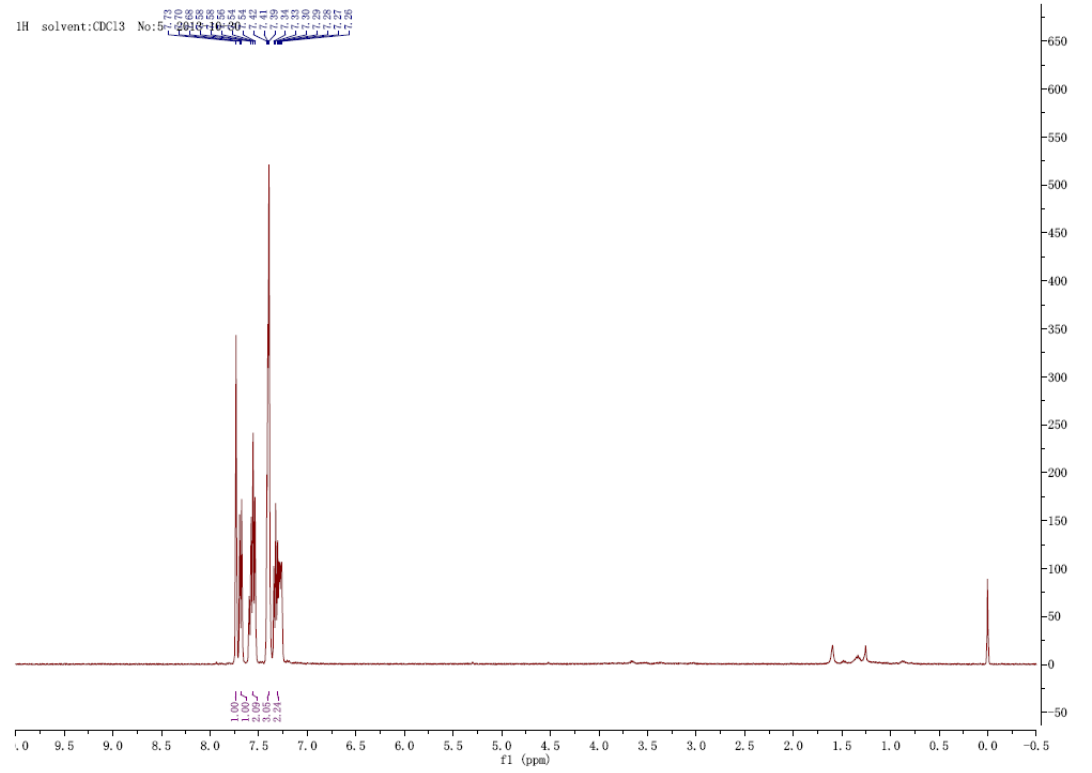


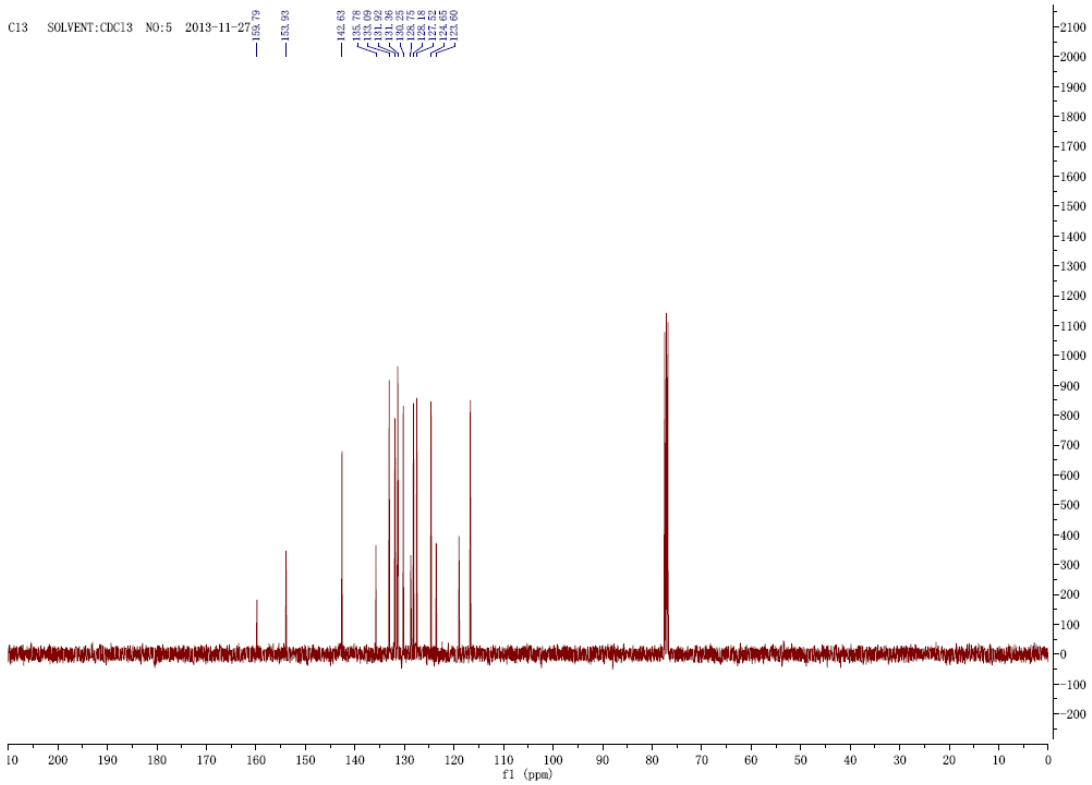




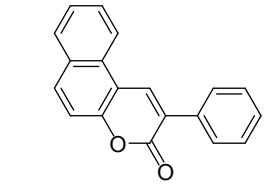
3-(2-bromocyclohexa-2,4-dien-1-yl)-2H-chromen-2-one 3l

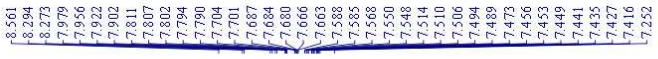


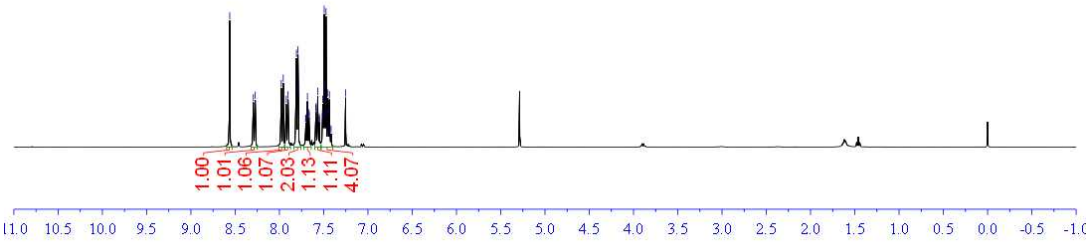


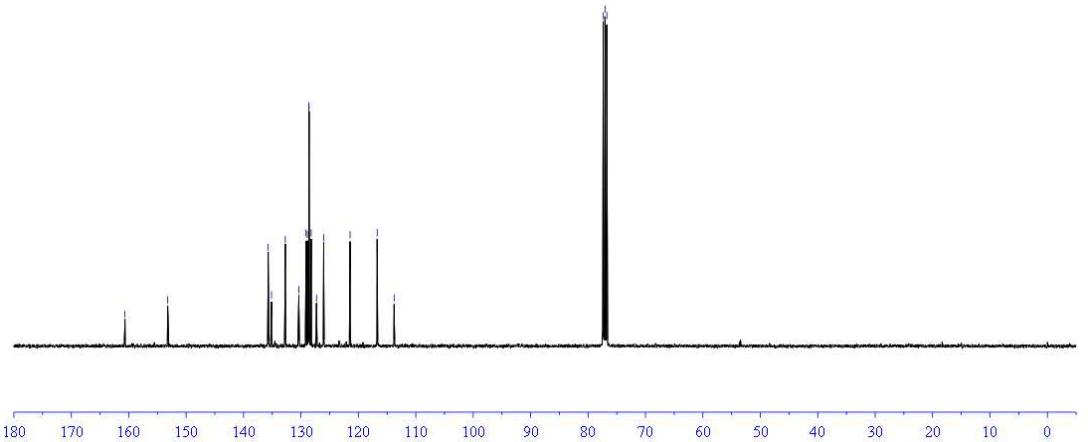


2-phenyl-3H-benzo[f]chromen-3-one 3m

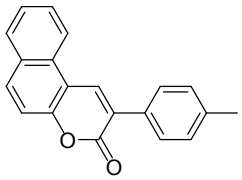


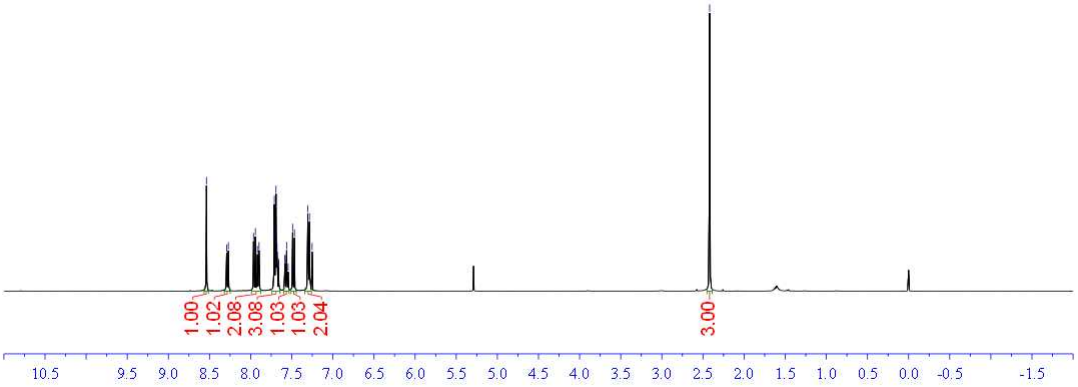


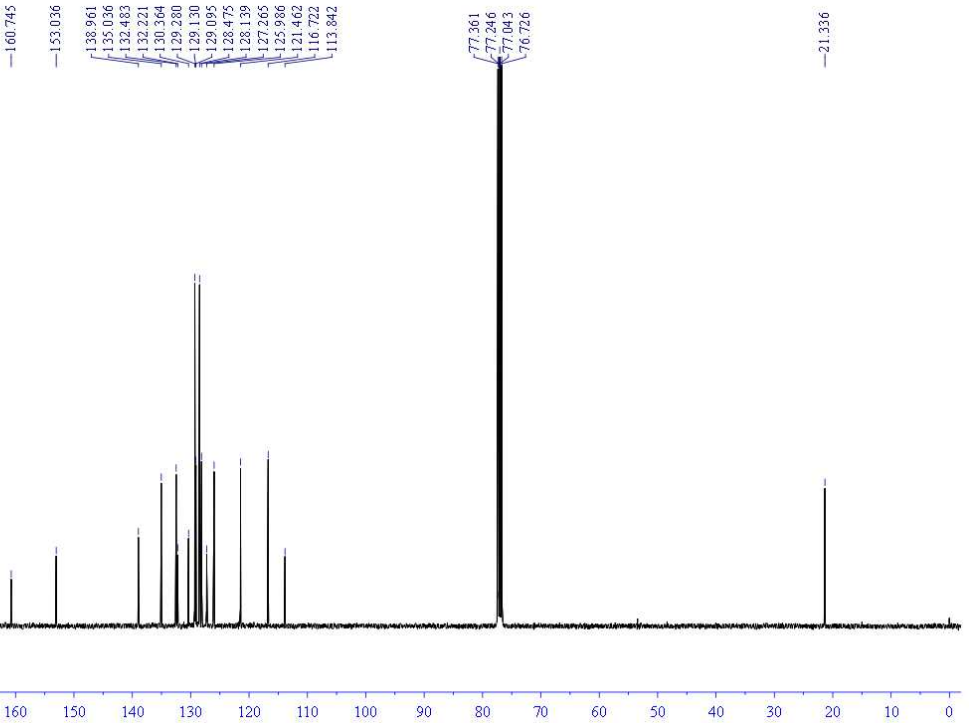




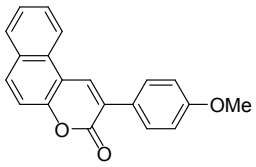
2-(p-tolyl)-3H-benzo[f]chromen-3-one 3n

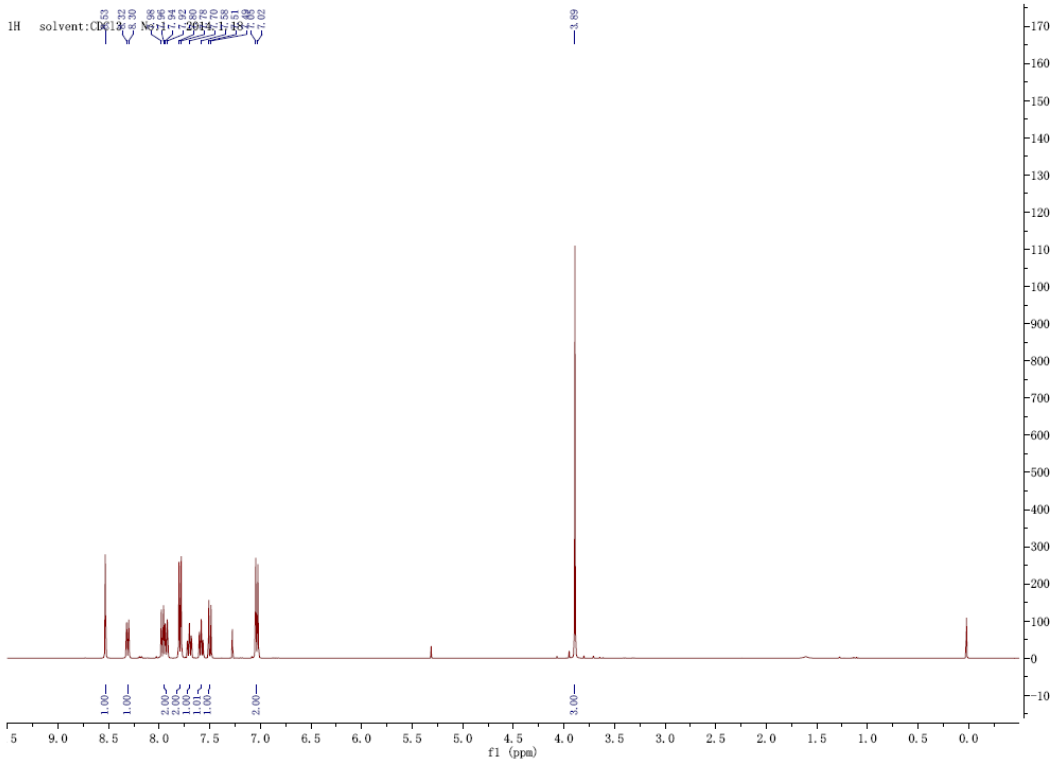


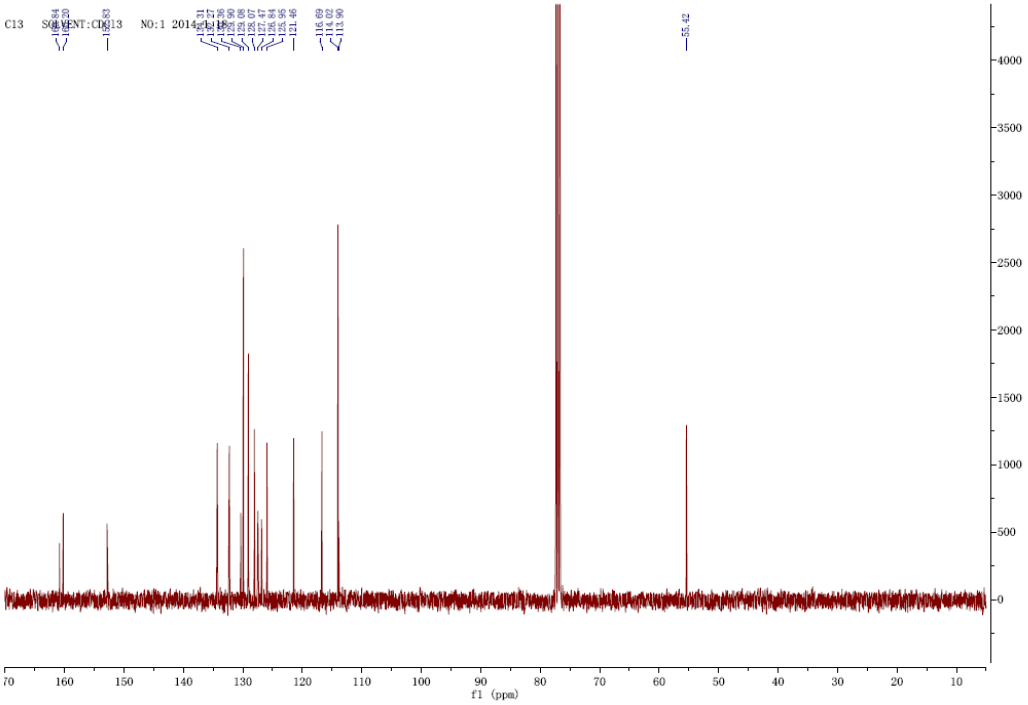




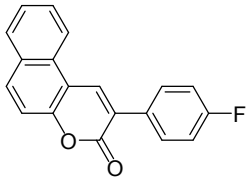
2-(4-methoxyphenyl)-3H-benzo[f]chromen-3-one 3o

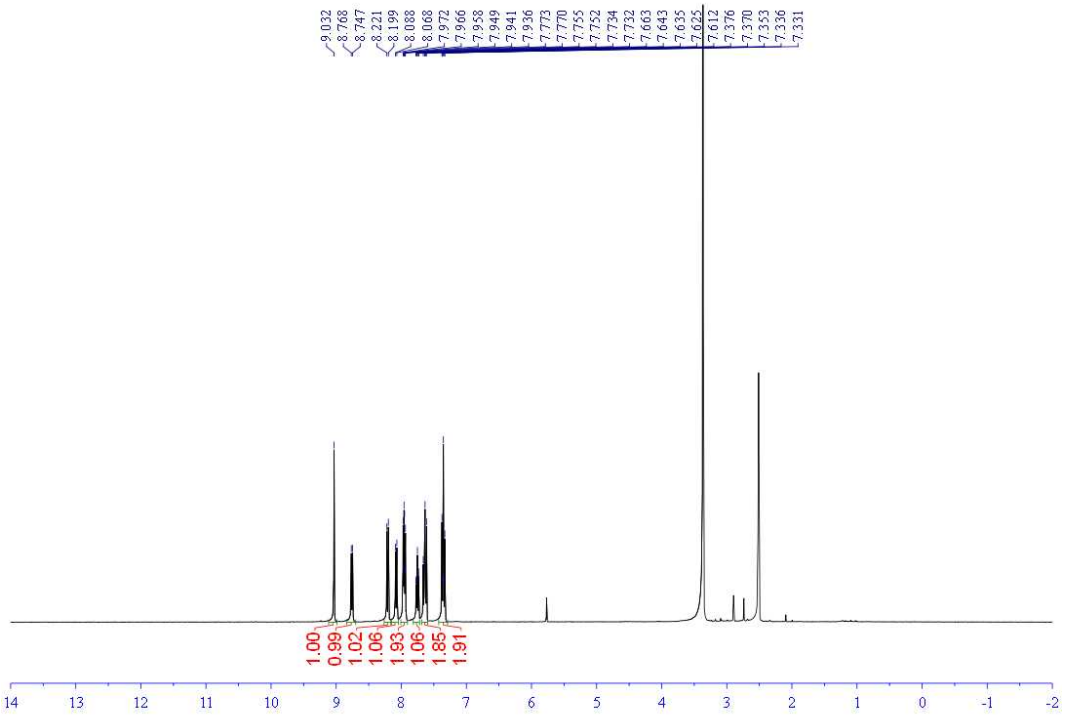


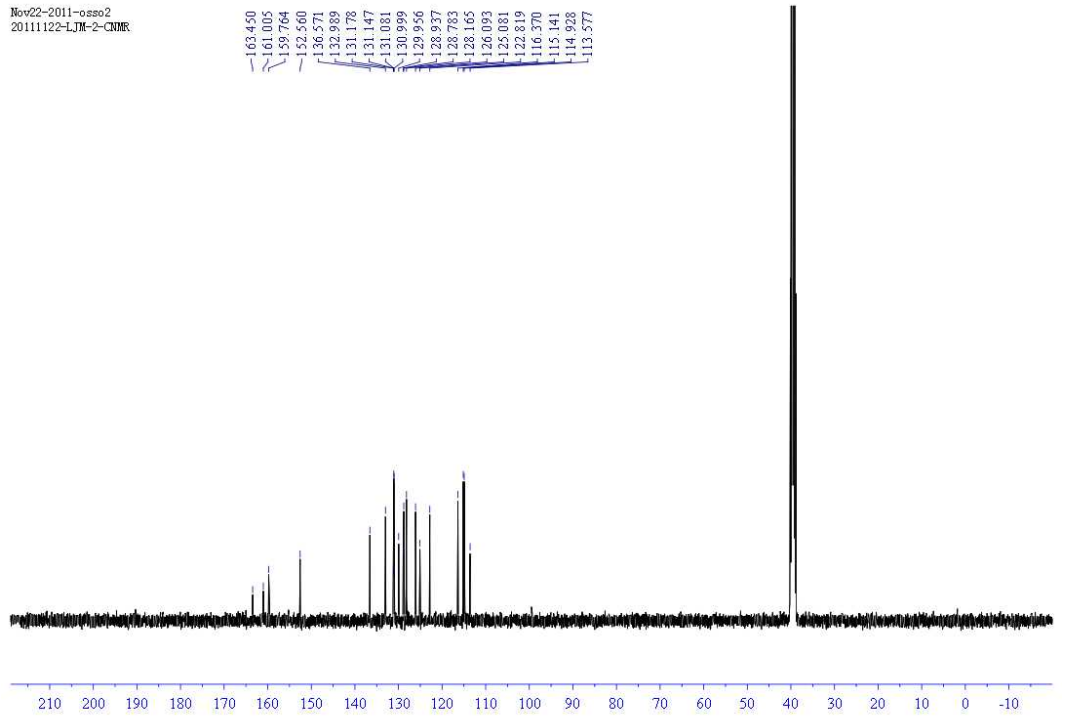




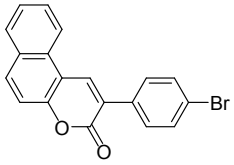
2-(4-fluorophenyl)-3H-benzo[f]chromen-3-one 3p

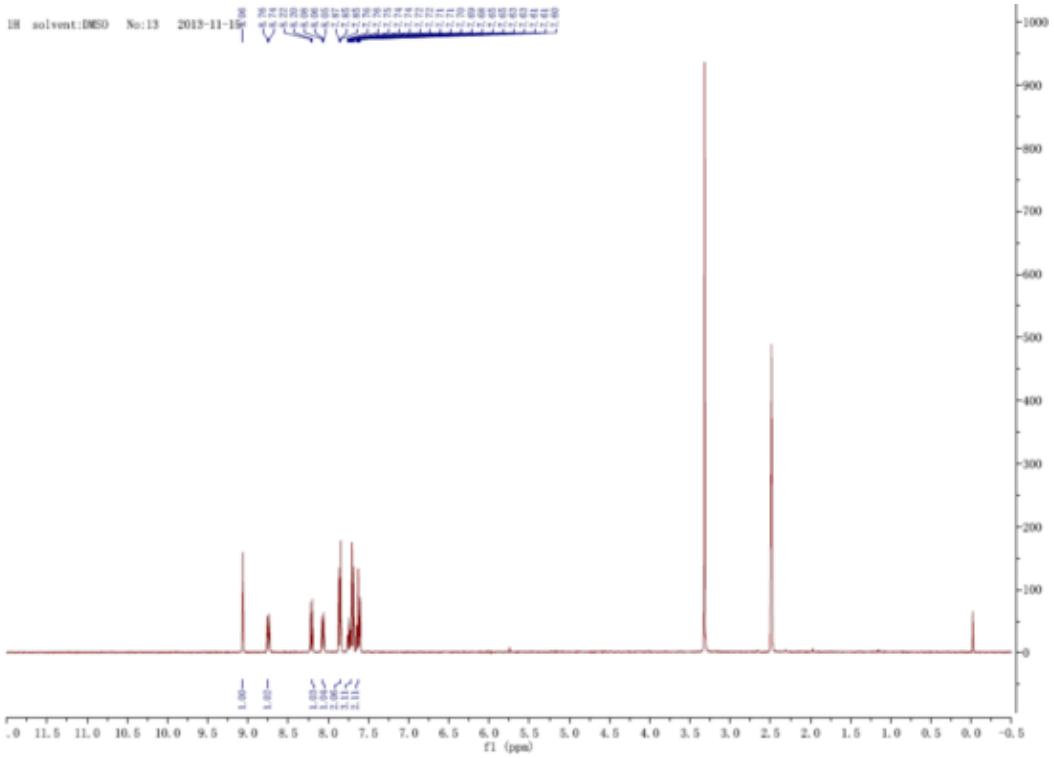


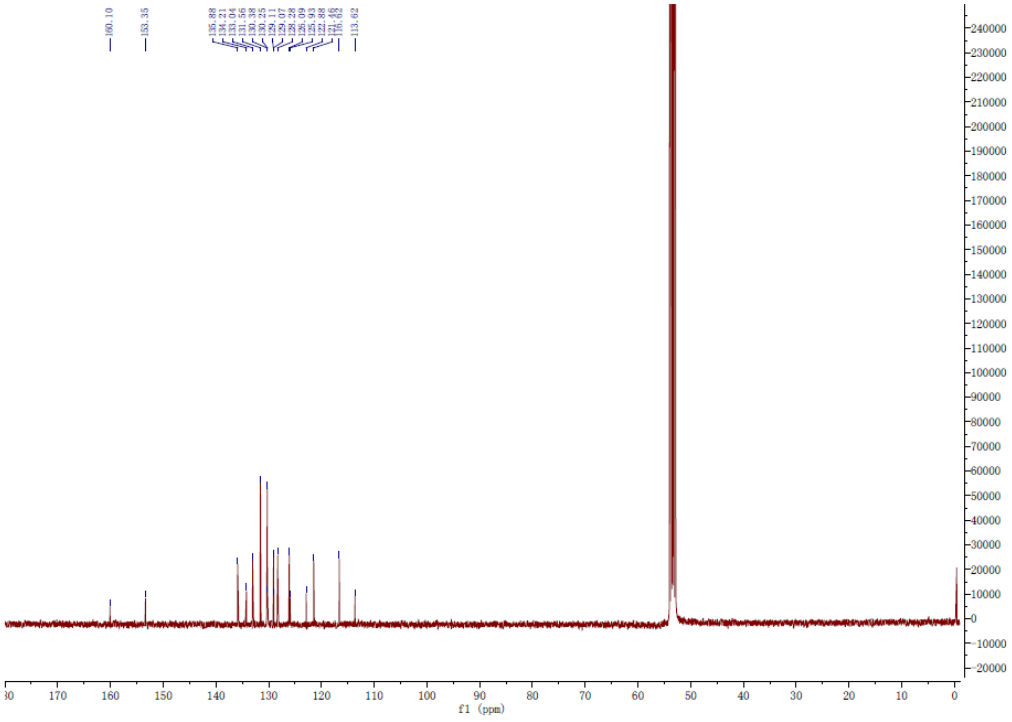




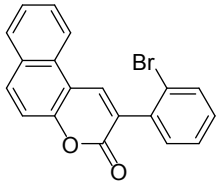
2-(4-bromophenyl)-3H-benzo[f]chromen-3-onee 3q

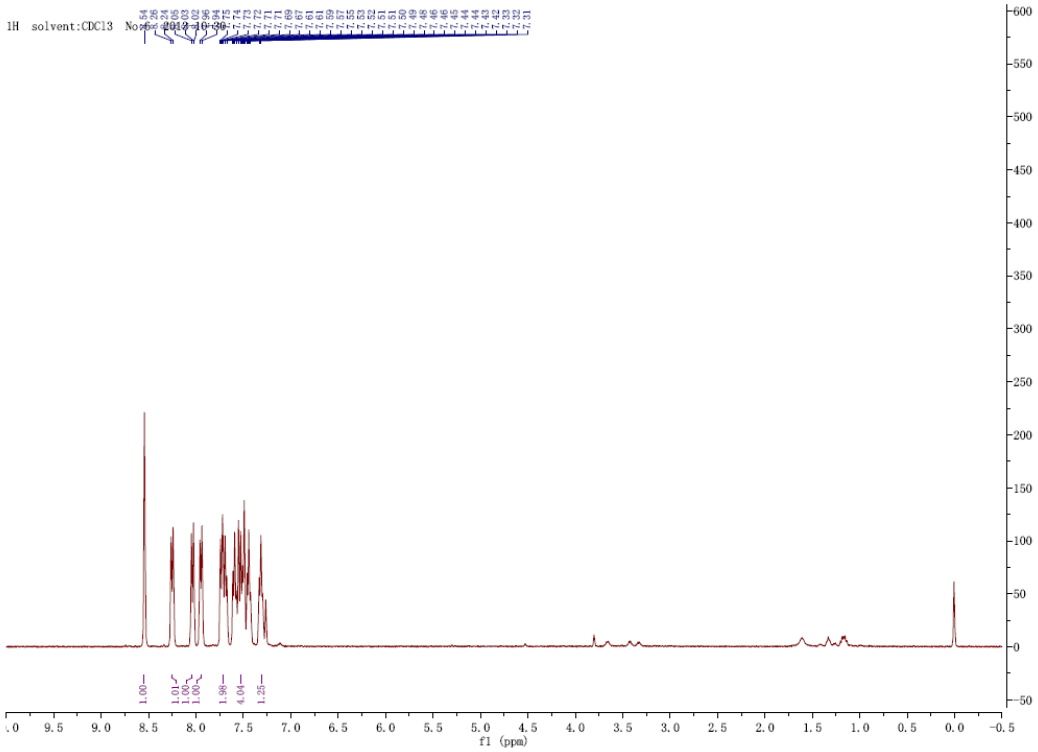


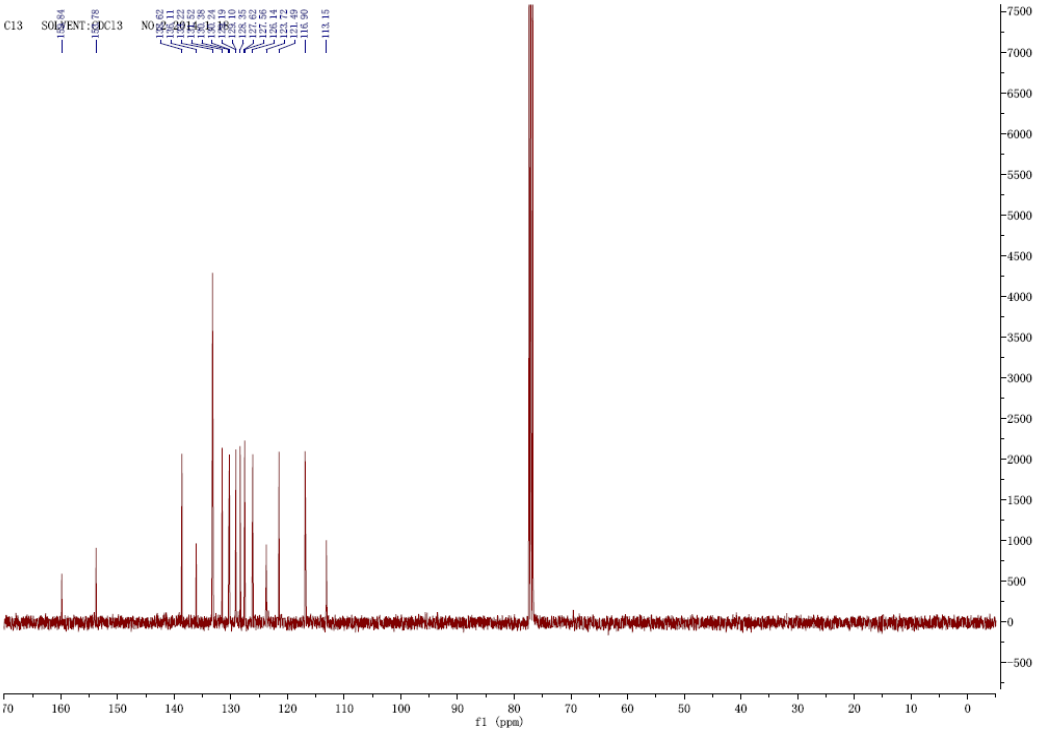




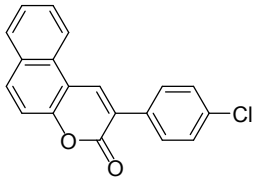
2-(2-bromophenyl)-3H-benzo[f]chromen-3-one 3r

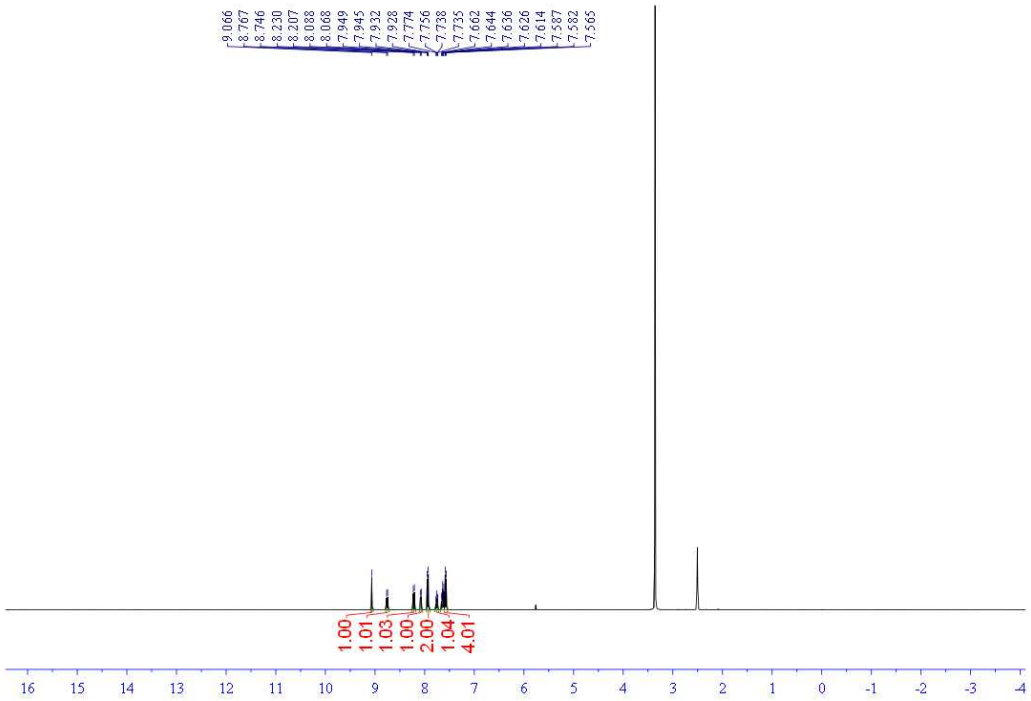


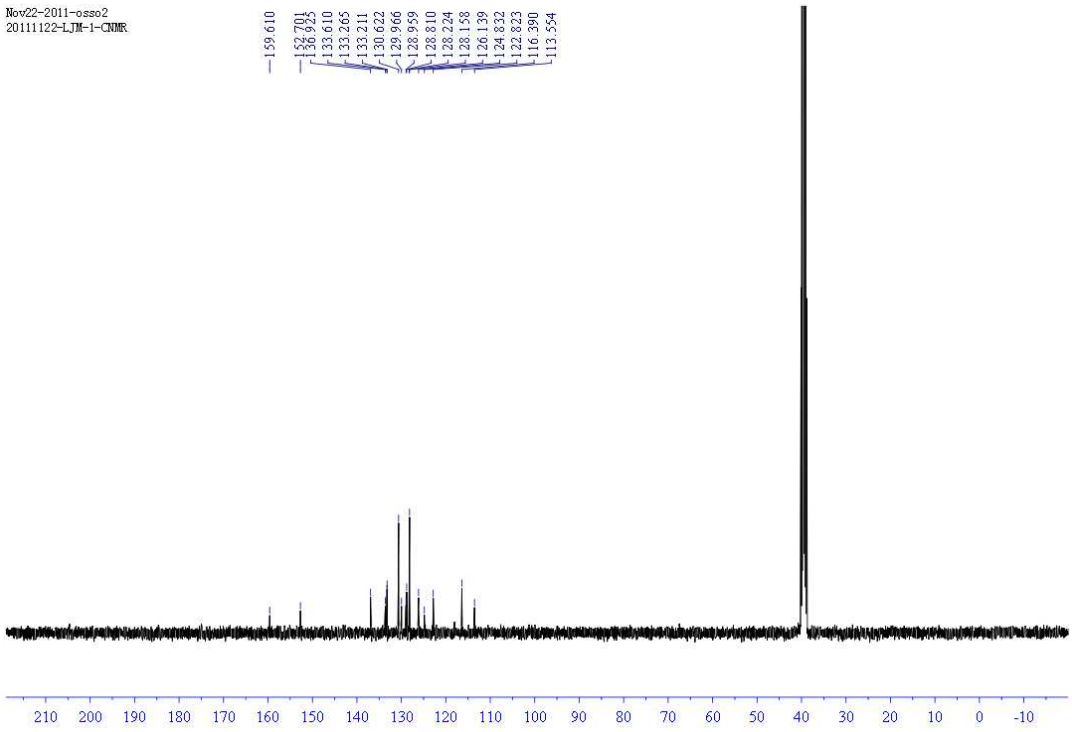




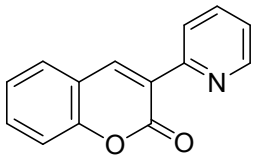
2-(4-chlorophenyl)-3H-benzo[f]chromen-3-one 3s

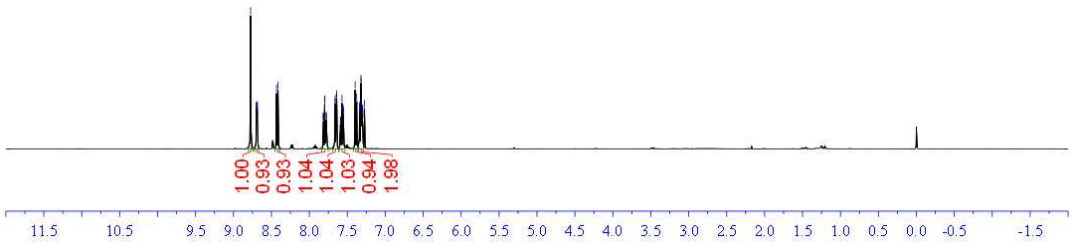


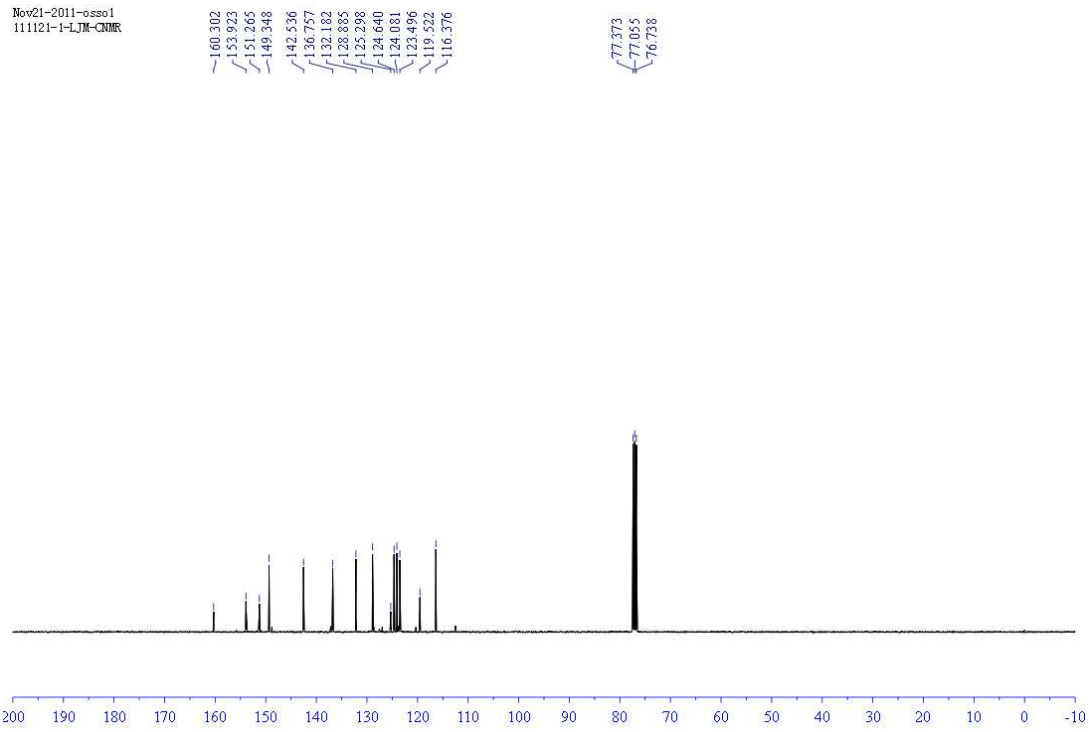




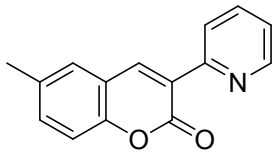
3-(pyridin-2-yl)naphthalen-2(1H)-one 4a

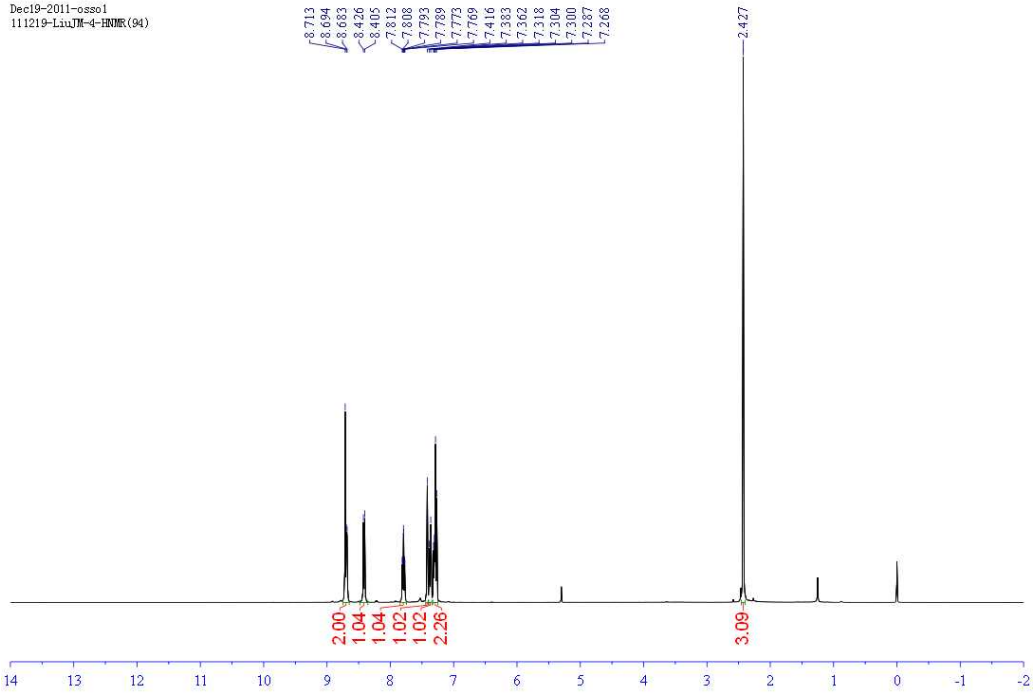


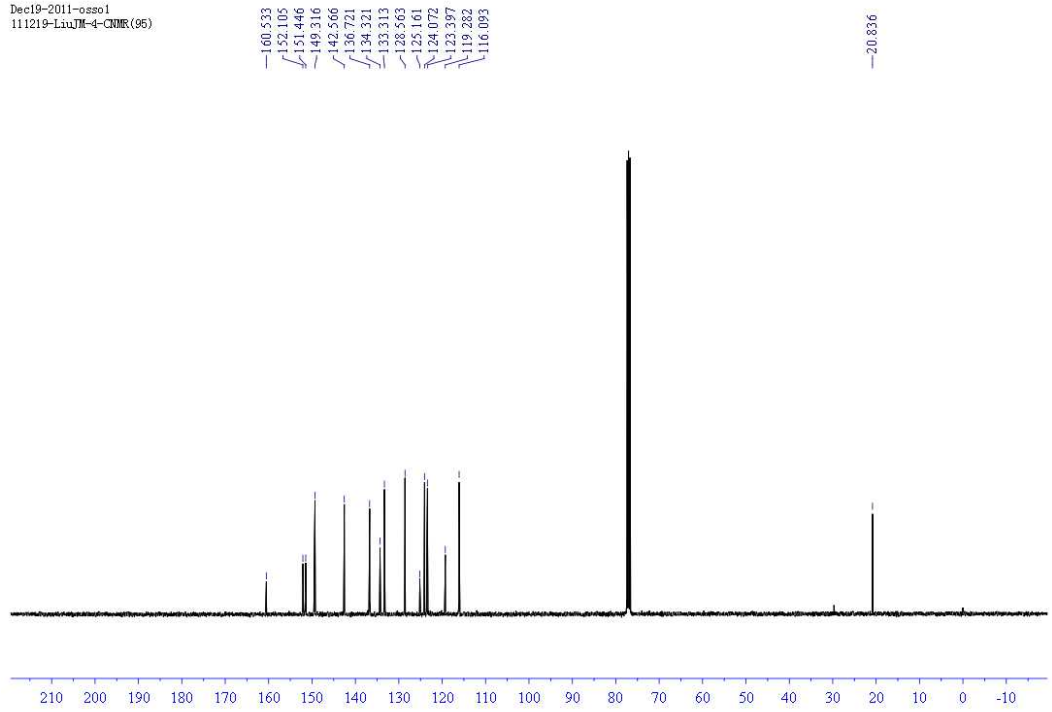




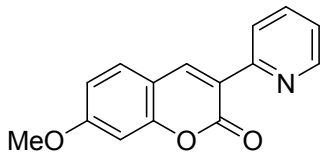
6-methyl-3-(pyridin-2-yl)-2H-chromen-2-one 4b

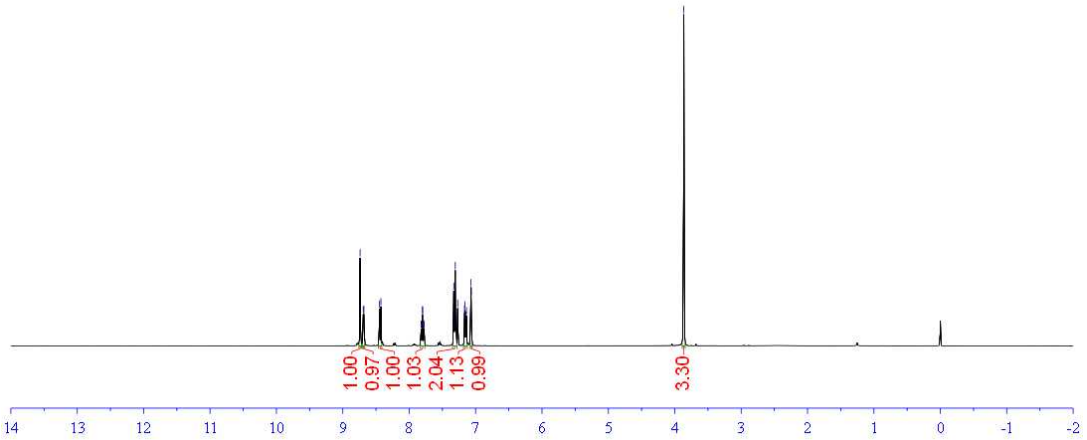


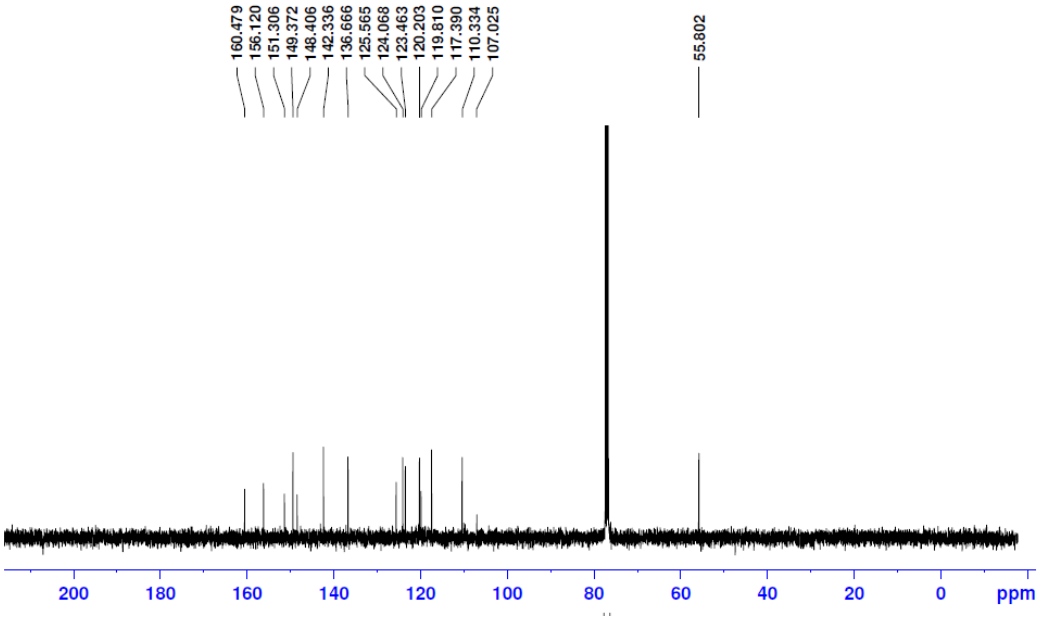




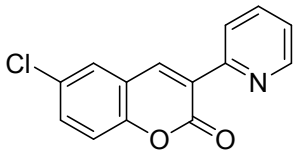
6-methoxy-3-(pyridin-2-yl)-2H-chromen-2-one 4c

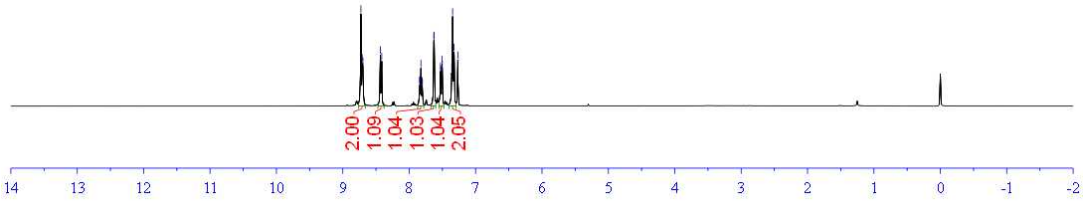


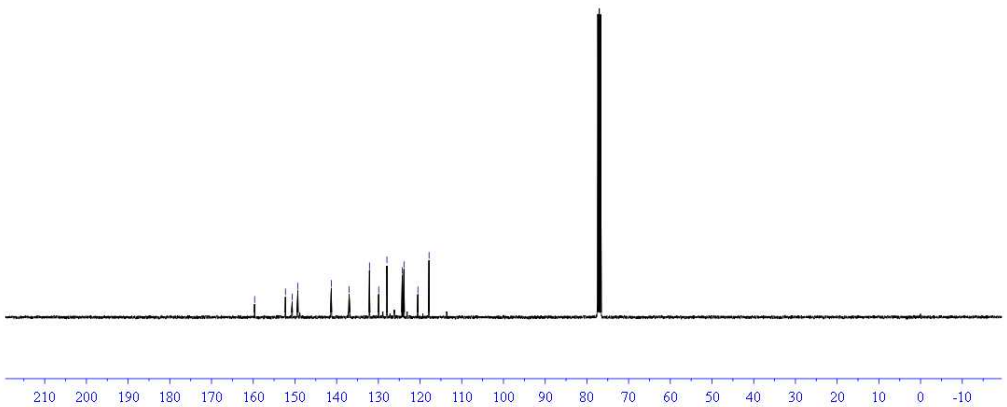




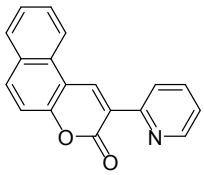
6-chloro-3-(pyridin-2-yl)-2H-chromen-2-one 4d

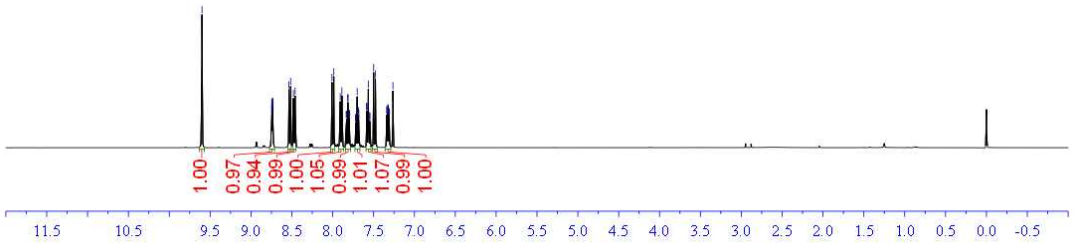


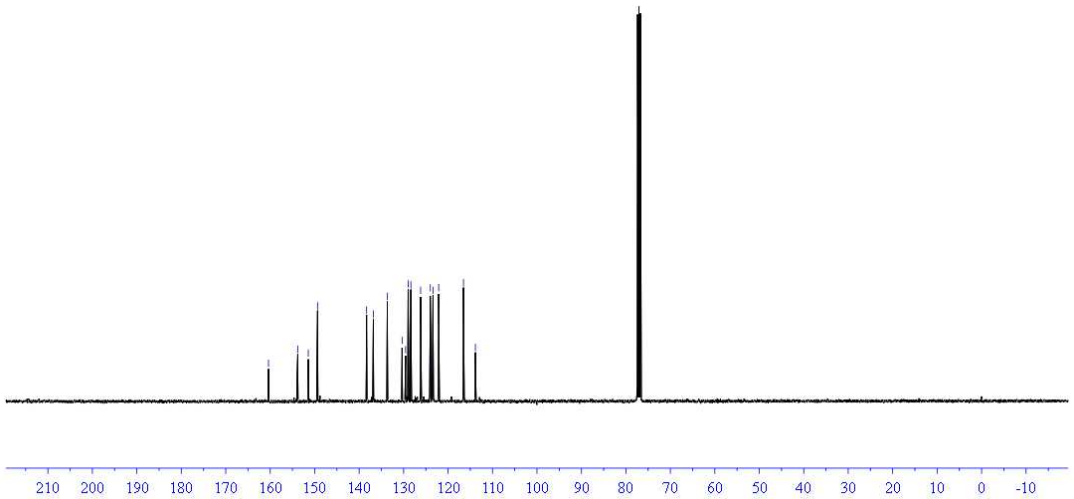




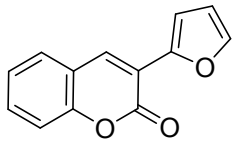
2-(pyridin-2-yl)-3H-benzo[f]chromen-3-one 4e

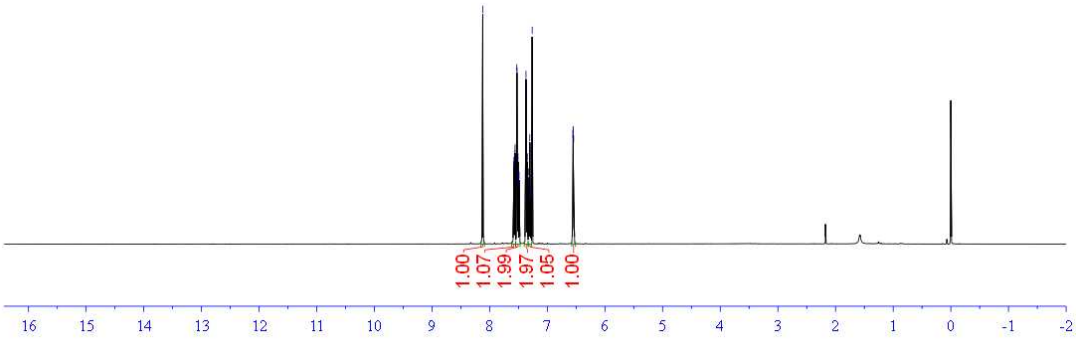


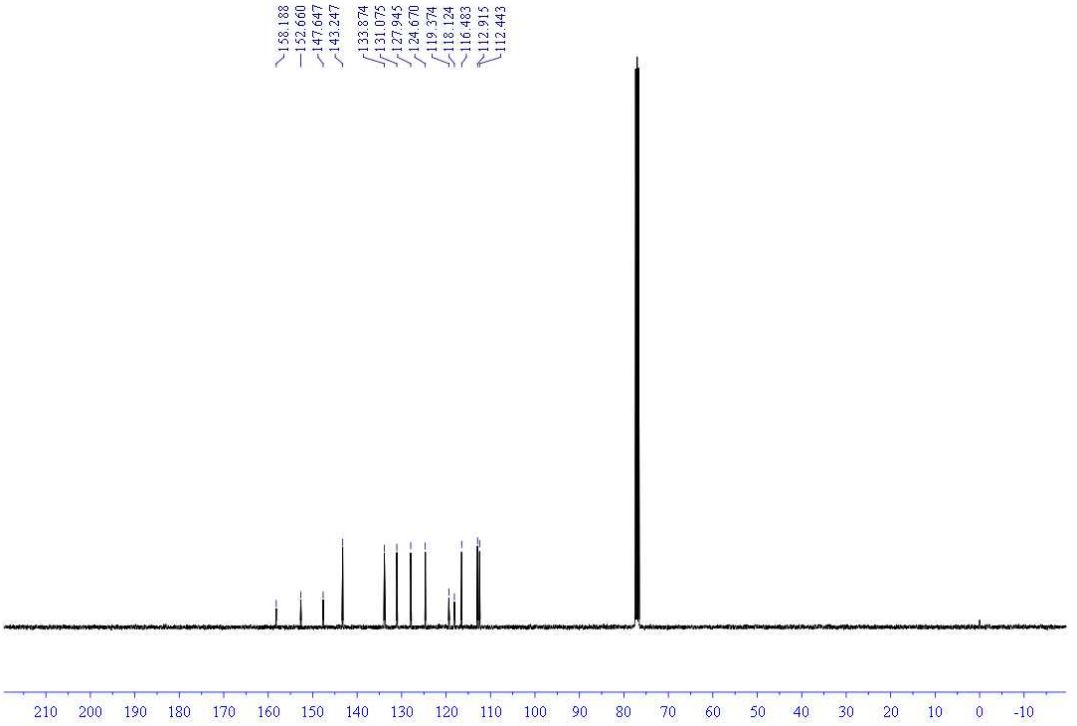




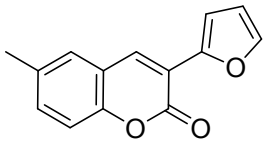
3-(furan-2-yl)-2H-chromen-2-one 5a

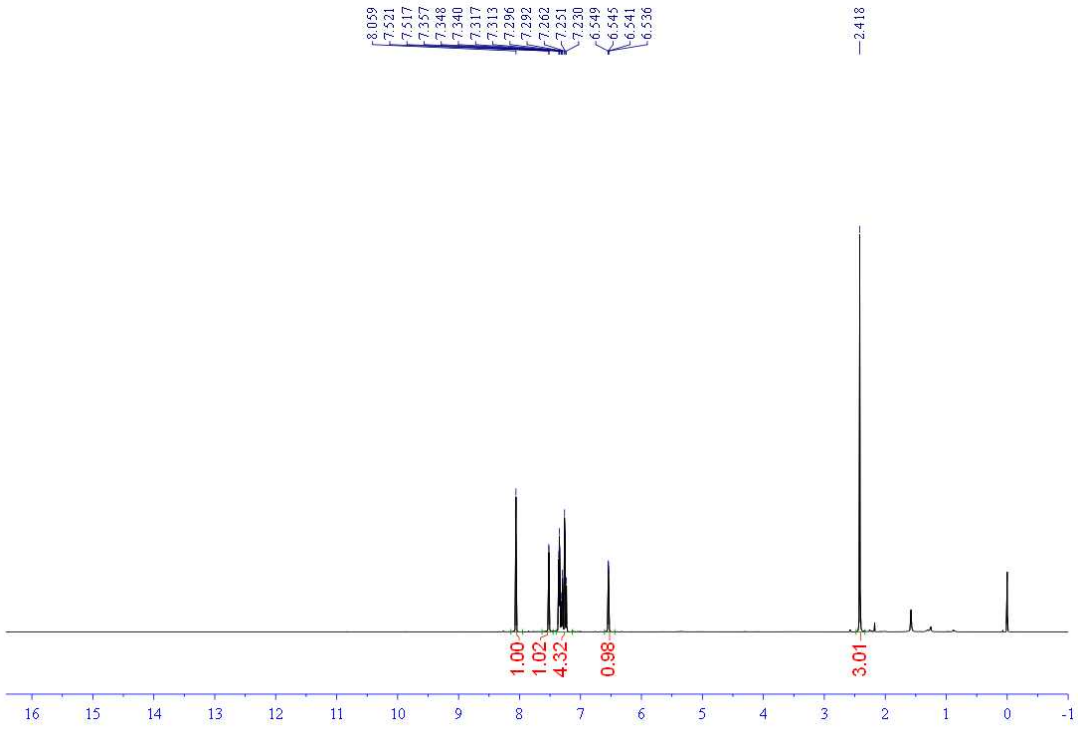


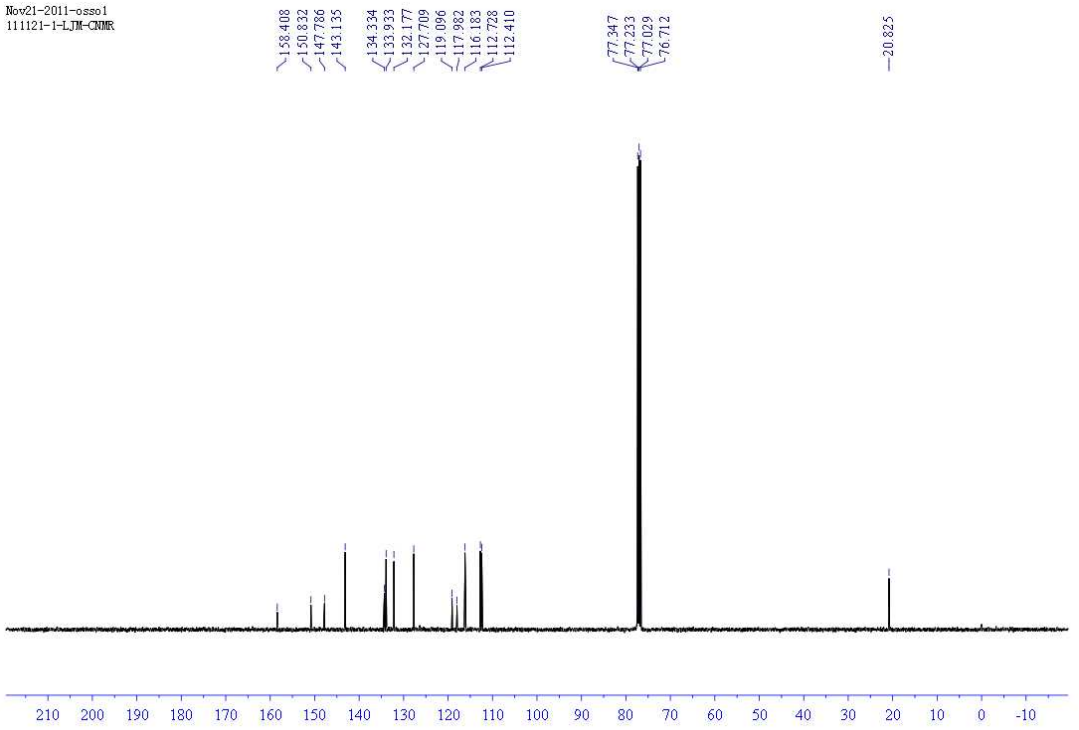




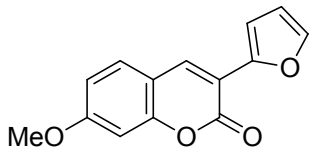
3-(furan-2-yl)-6-methyl-2H-chromen-2-one 5b

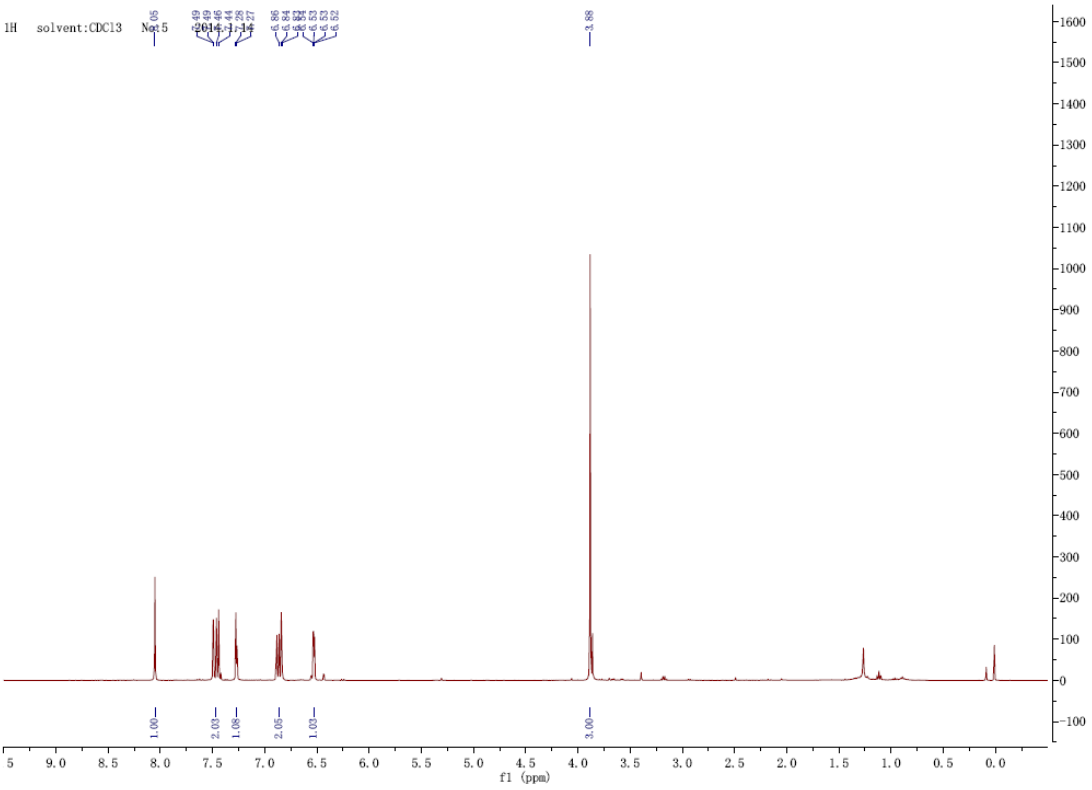


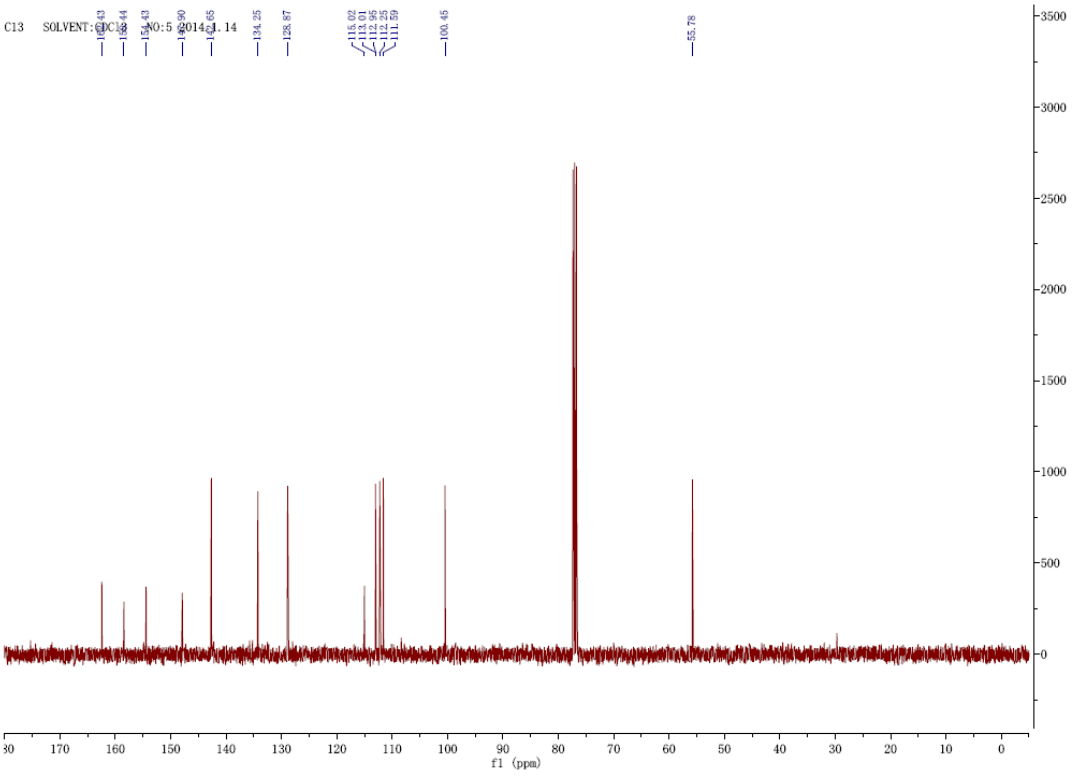




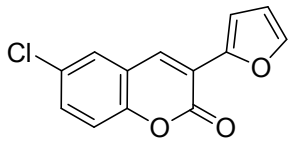
3-(furan-2-yl)-7-methoxy-2H-chromen-2-one 5c

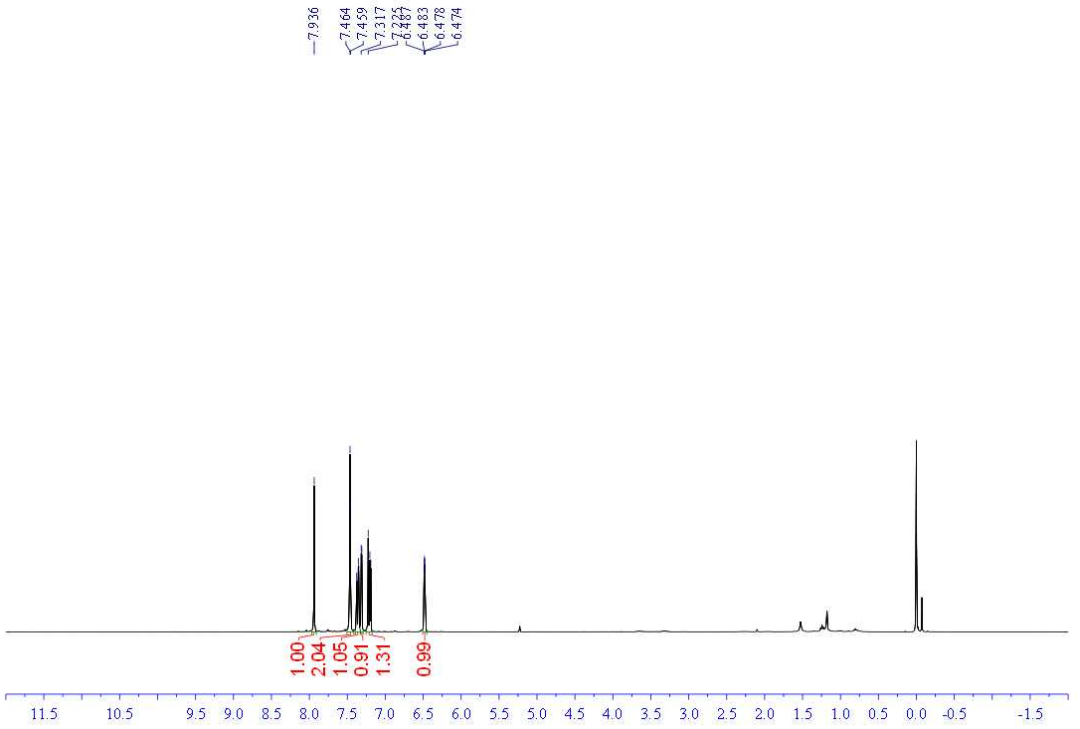


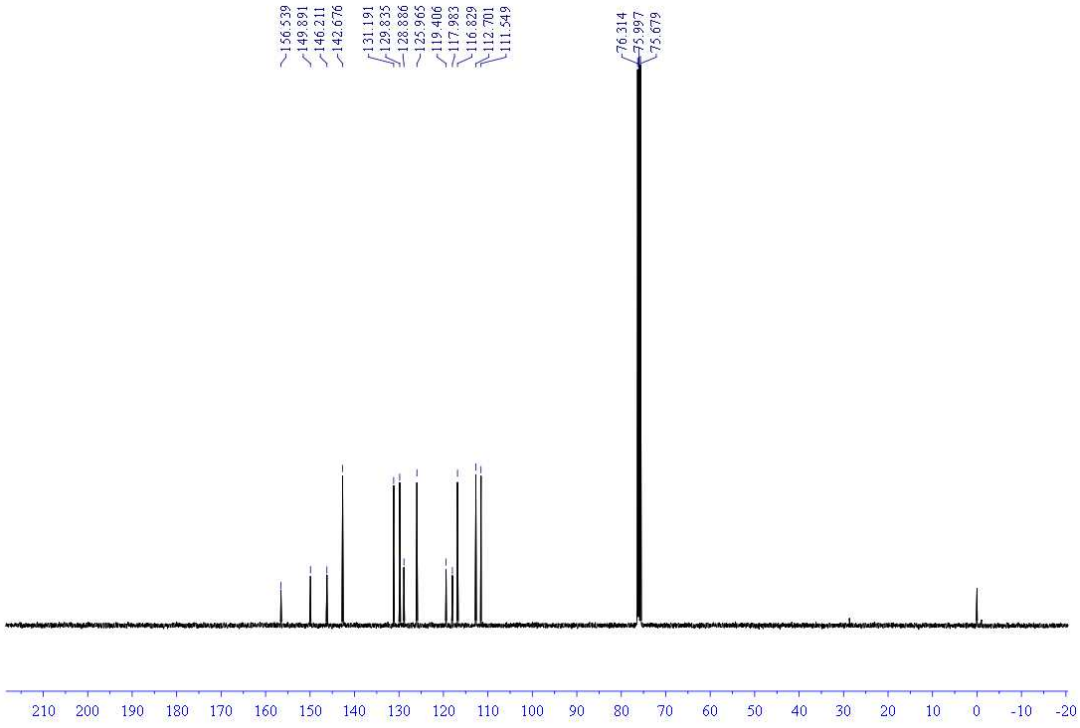




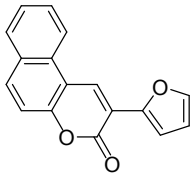
6-chloro-3-(furan-2-yl)-2H-chromen-2-one 5d

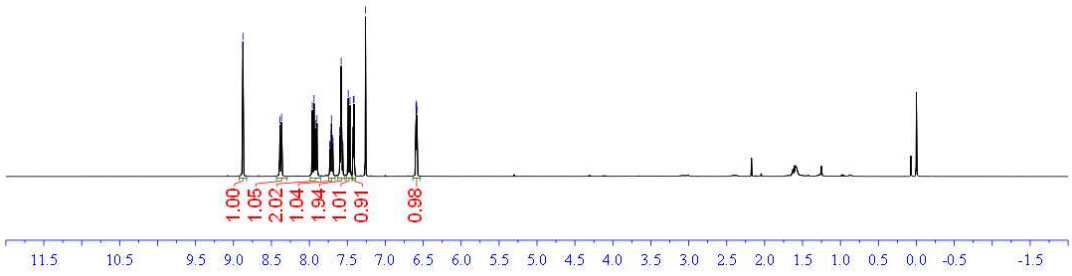


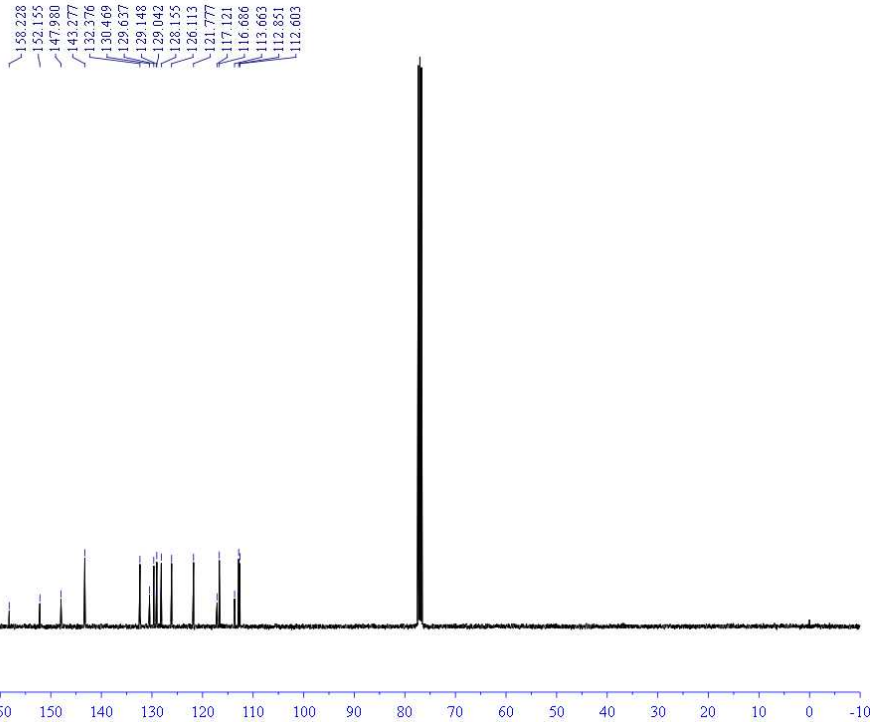




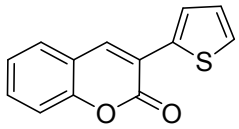
2-(furan-2-yl)-3H-benzo[f]chromen-3-one 5e

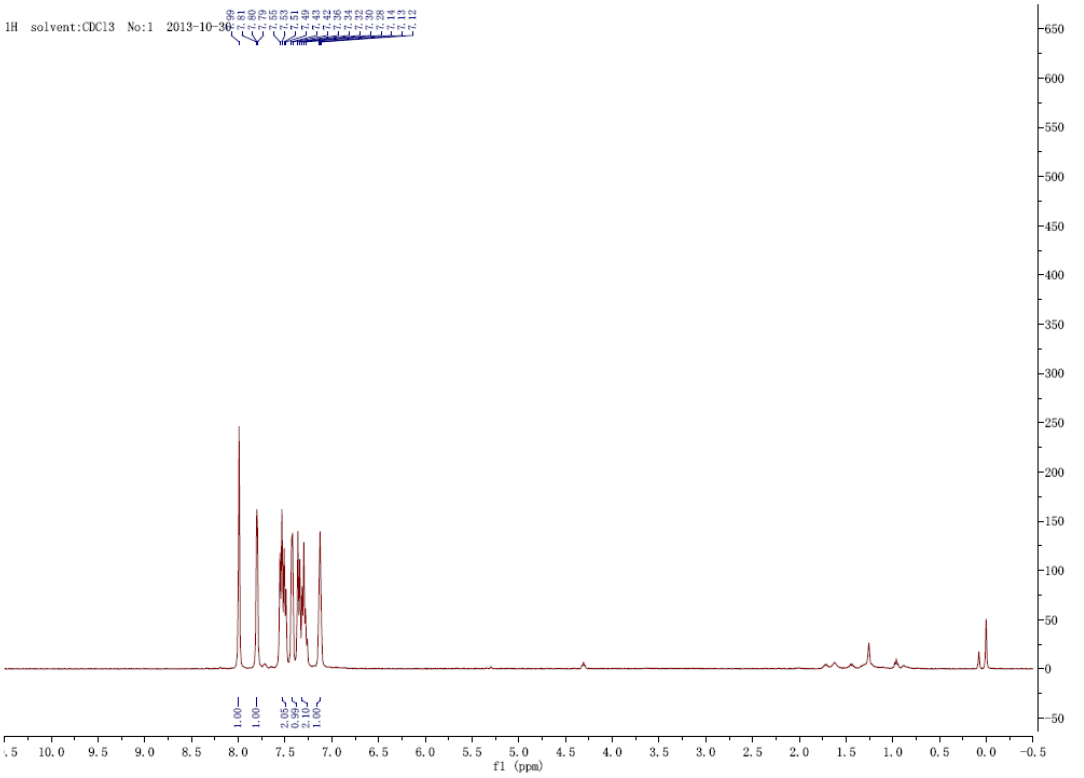


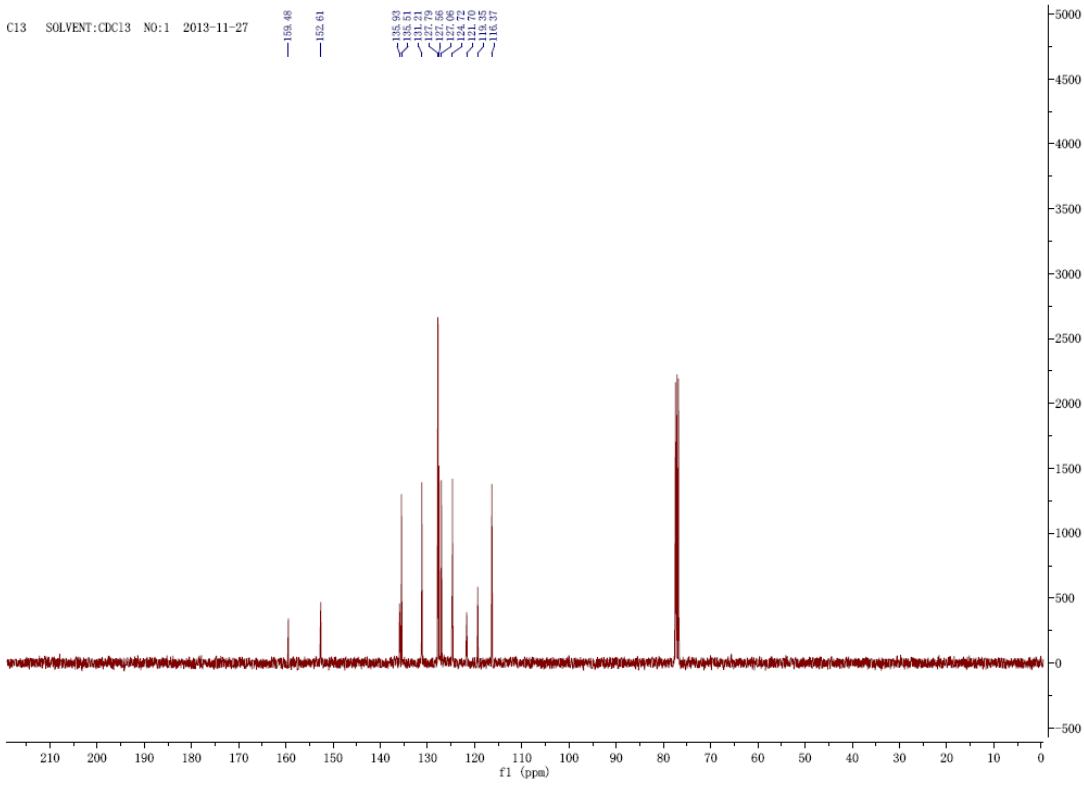




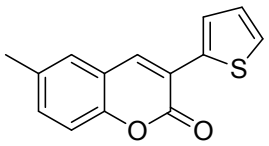
3-(thiophen-2-yl)-2H-chromen-2-one 5f

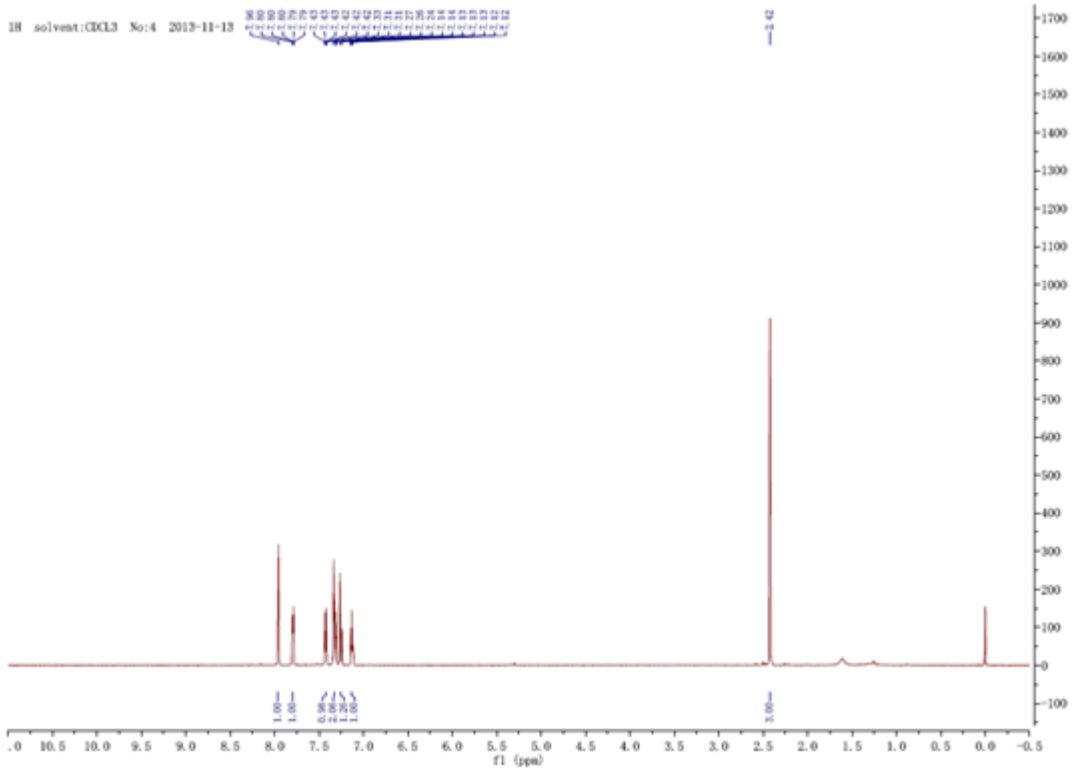


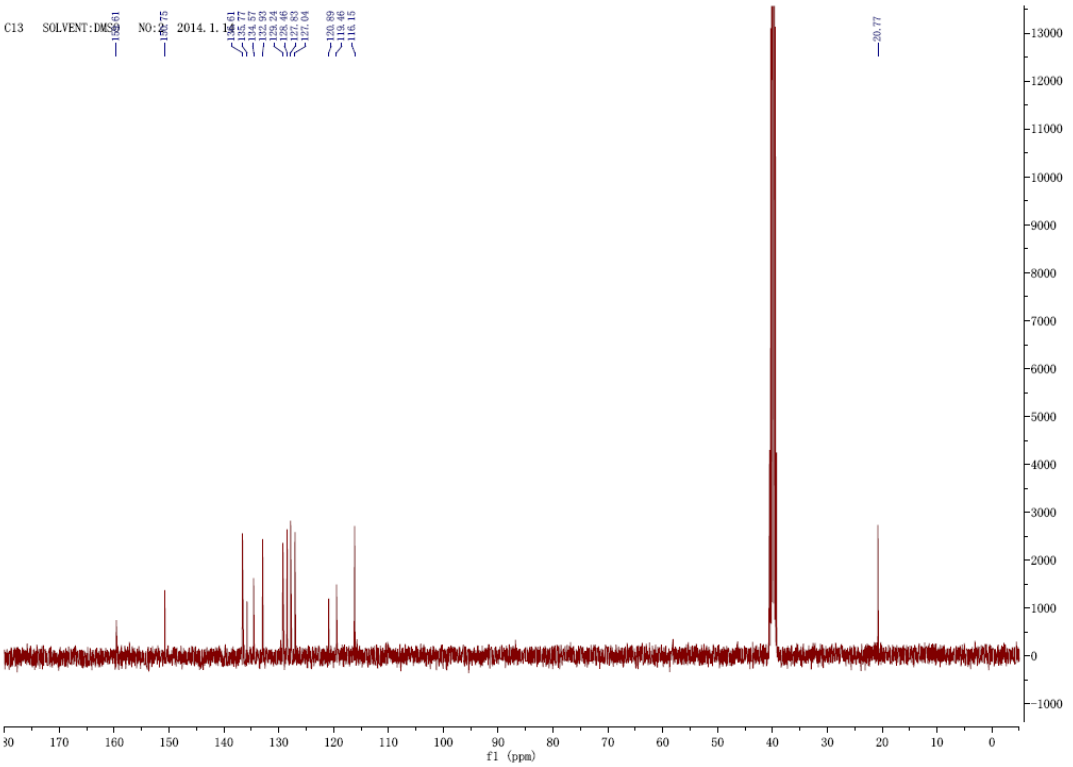




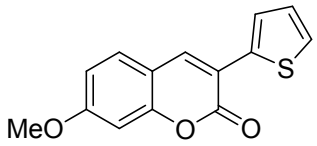
6-methyl-3-(thiophen-2-yl)-2H-chromen-2-one 5g

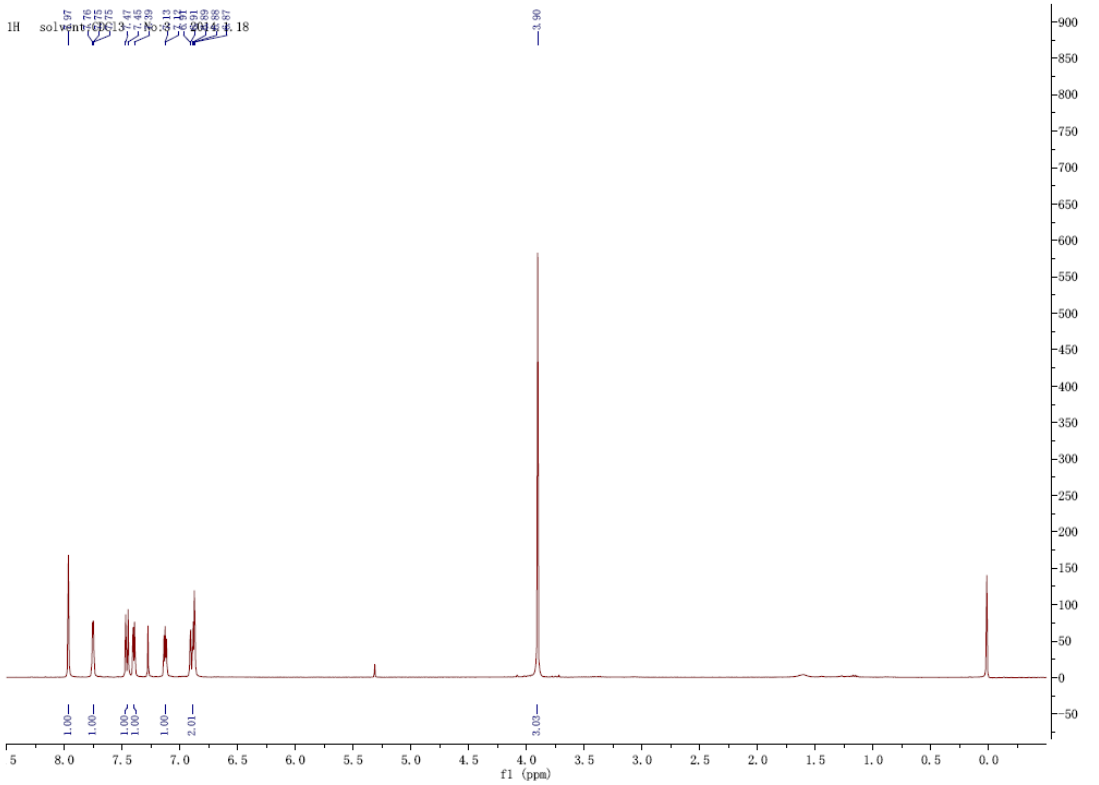


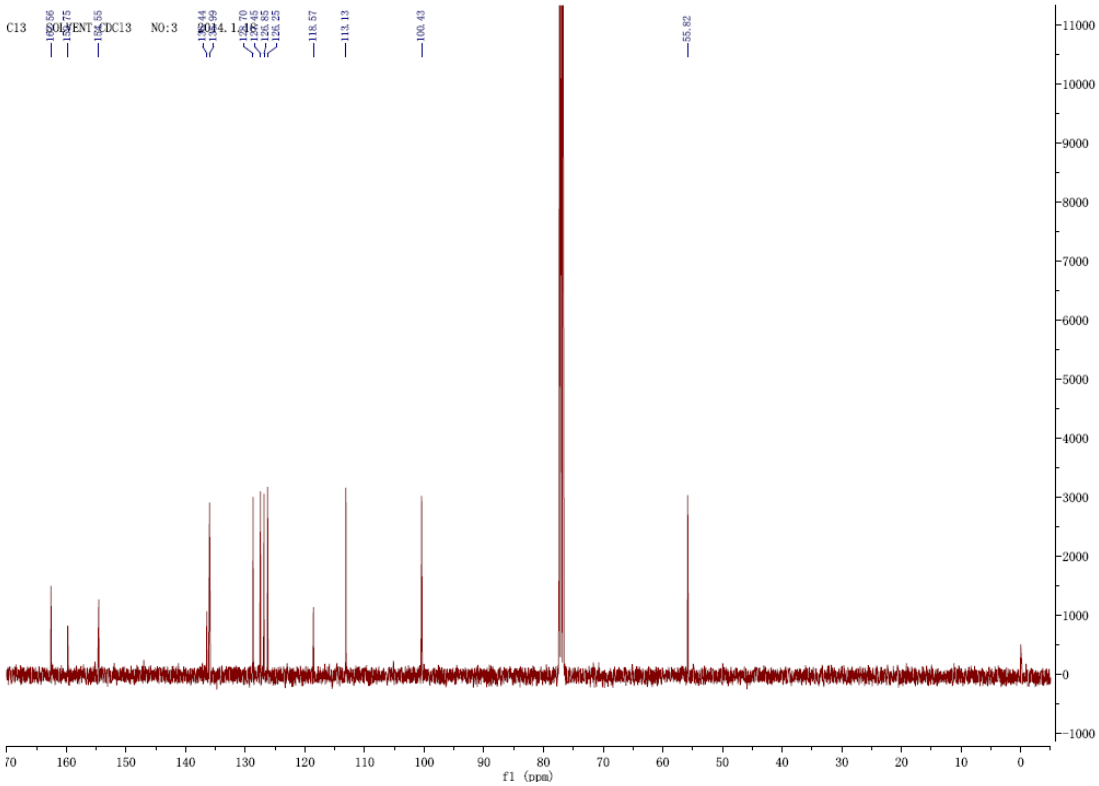




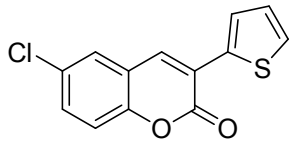
7-methoxy-3-(thiophen-2-yl)-2H-chromen-2-one 5h

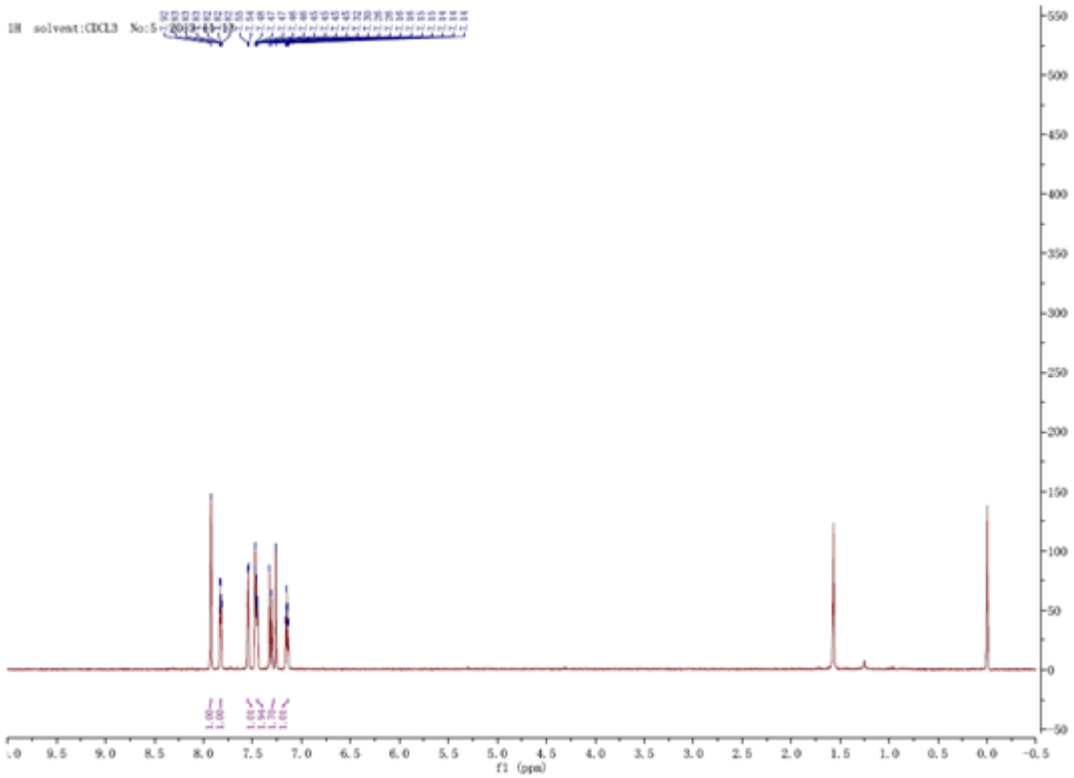


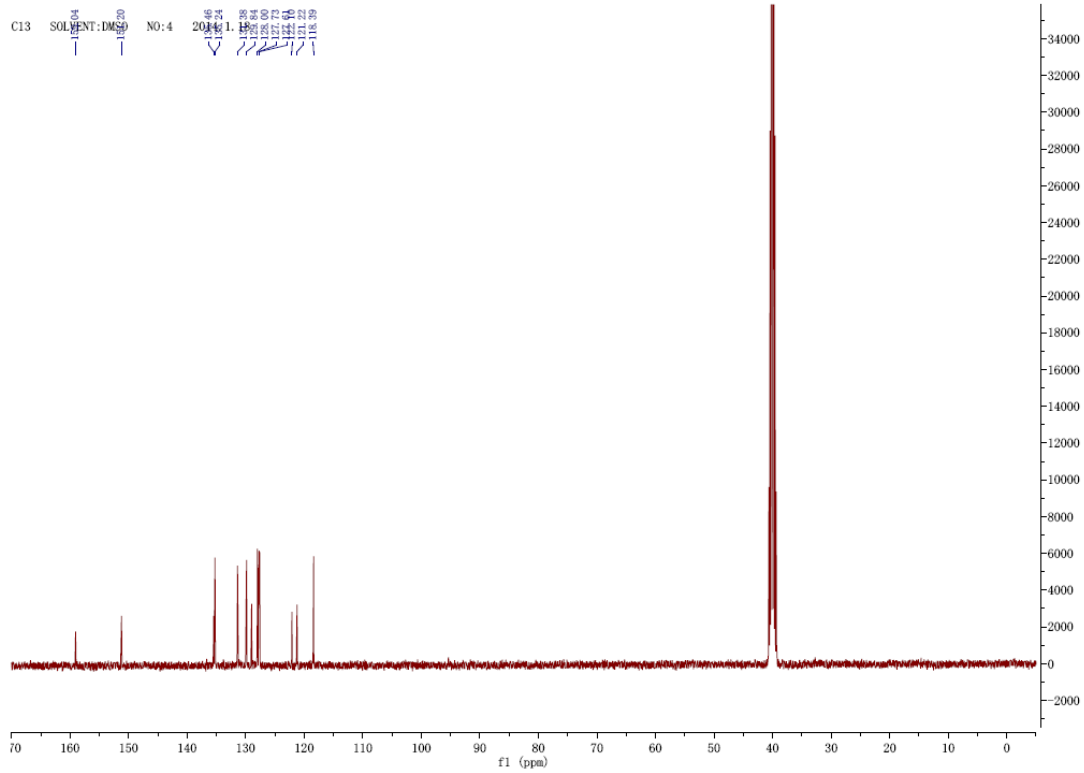




6-chloro-3-(thiophen-2-yl)-2H-chromen-2-one 5i







2-(thiophen-2-yl)-3H-benzo[f]chromen-3-one 5j