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Supporting Information

for

Molecular diversity of the reactions of MBH carbonates of isatins and various nucleophiles

Zi-Ying Xiao, Jing Sun and Chao-Guo Yan

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Experimental procedures, ^{1}H, ^{13}C NMR, and HRMS spectra for all new compounds

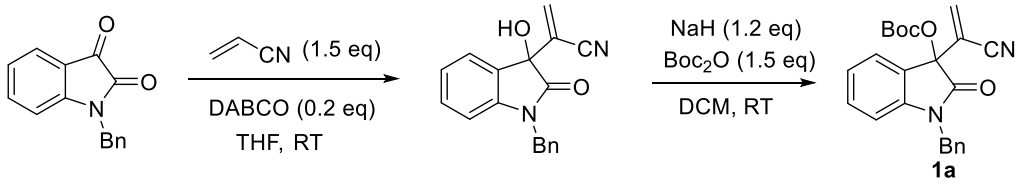
Table of contents

General information

The ^{1}H and $^{13}C\{1H\}$ spectra NMR spectra were recorded either with a Varian 400 (at 400 or 100 MHz) or a Bruker 600 (at 600 or 151 MHz) spectrometer. High-resolution mass spectra (HRMS) were recorded in ESI mode using a MicroTOF mass spectrometer. Single-crystal X-ray data were collected with a Bruker Smart APEX-2 CCD diffractometer. IR spectra were recorded using a Bruker Tensor 27 spectrometer (KBr disc). Melting points were determined with a micromelting point apparatus. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were monitored by observation under UV light (254 and 365 nm). Reagents and solvents were purchased as reagent grade and were used without further purification. All reactions were performed in standard glassware. Flash column chromatography was performed over silica gel (200–300 m) using a mixture of ethyl acetate (EtOAc) and petroleum ether (PE).

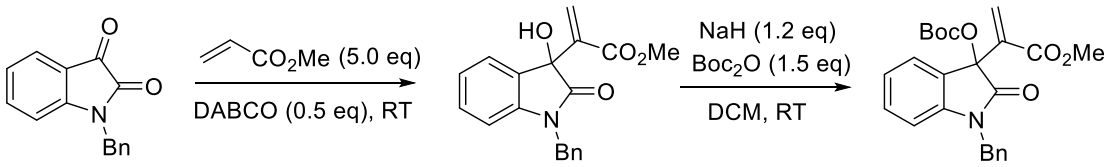
Preparation of the starting materials

1. General procedure for the synthesis of MBH nitriles of isatins 1a: In a flask, a mixture of vinyl cyanide (9 mmol), *N*-benzylisatin (6 mmol), and DABCO (1 mmol) in THF was stirred at room temperature. After the completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography over silica gel PE/EA 2:1 as the eluent to afford the *N*-benzylisatin-derived MBH adduct. The product was added slowly to a suspension of sodium hydride (1.2 equiv) in dry DCM at 0 °C under nitrogen, and the mixture was stirred for 20 min. Then the solution was added slowly to a solution of Boc_2O (1.5 equiv) in 4.0 mL dry DCM at room temperature and the mixture was stirred at room temperature overnight. The mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel using PE/EA 5:1 as the eluent to afford the desired products **1** as a yellow solid.



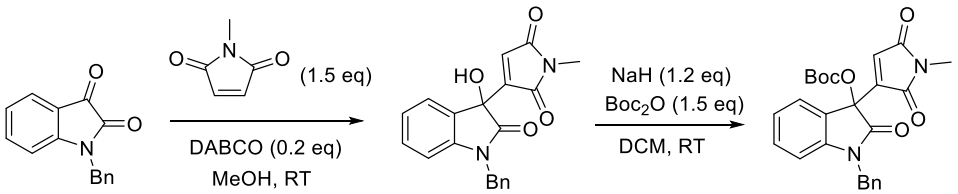
1a

2. General procedure for the synthesis of MBH acrylates of isatins 1b: Methyl acrylate (25 mmol), *N*-benzylisatin (5 mmol), and DABCO (2.5 mmol) were added to a flask, and the mixture was stirred at room temperature for 24 hours. After the completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography over silica gel PE/EA 2:1 as the eluent to afford the MBH acrylates of isatins. Then, the obtained product was added slowly to a suspension of sodium hydride (1.2 equiv) in dry DCM at 0 °C under nitrogen, and the mixture was stirred for 20 min. Then, the solution was added slowly to a solution of Boc_2O (1.5 equiv) in 4.0 mL dry DCM at room temperature and the mixture was stirred at room temperature overnight. The mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel using PE/EA 5:1 as the eluent to afford the desired products **1b** as a yellow solid.



1b

3. General procedure for the synthesis of MBH maleimides of isatins 4: In a flask, a mixture of *N*-methylmaleimide (9 mmol), *N*-benzylisatin (6 mmol), and DABCO (1 mmol) in MeOH was stirred at room temperature. After the completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by EtOH to afford the *N*-benzylisatin-derived MBH adduct. Then, the obtained product was added slowly to a suspension of sodium hydride (1.2 equiv) in dry DCM at 0 °C, and the mixture was stirred for 20 min. Then, the solution was added slowly to a solution of Boc_2O (1.5 equiv) in 4.0 mL dry DCM at room temperature and the mixture was stirred at room temperature overnight. The mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel using PE/EA 5:1 as the eluent to afford the desired products **4** as a yellow solid.



4

Preparation of compounds 3, 5, 6, 7 and 8

1. General procedure for the preparation of the compounds 3a–o

In a round flask, MBH carbonate of isatin **1** (0.1 mmol) and arylamine (0.1 mmol) were dissolved in toluene (5.0 mL). Then, DMAP (0.02 mmol) was added and the mixture was stirred at room temperature for about one hour. The solvent was removed by rotatory evaporation at reduced pressure. The residue was subjected to silica gel column chromatography with ethyl acetate and petroleum ether 1:8 (v/v) as eluent to give pure products **3a–o** for analysis.

2. General procedure for the preparation of the compounds 5a–n

In a round flask, MBH maleimide of isatin **4** (0.1 mmol) and arylamine (0.1 mmol) were dissolved in toluene (5.0 mL) and the mixture was stirred at 65 °C for about one hour. The solvent was removed by rotatory evaporation at reduced pressure. The residue was subjected to silica gel column chromatography with ethyl acetate, dichloromethane and petroleum ether 1:3:4 (v/v/v) as eluent to give pure products **5a–n** for analysis.

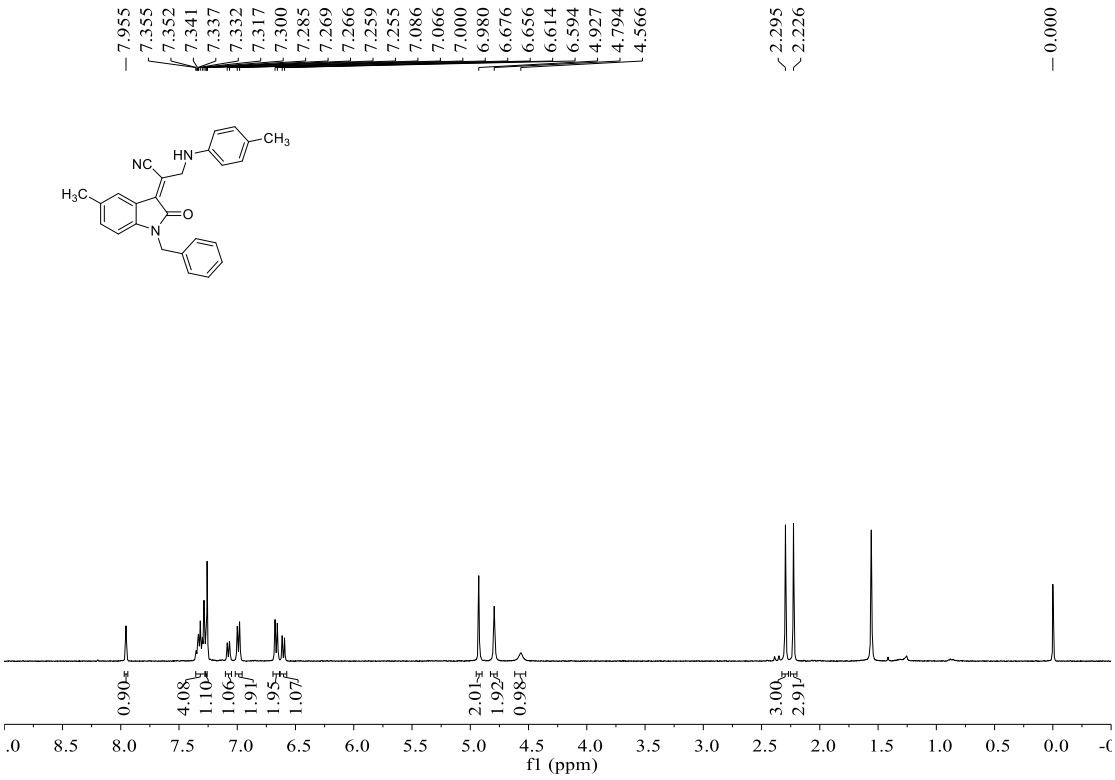
3. General procedure for the preparation of the compounds 6a–f

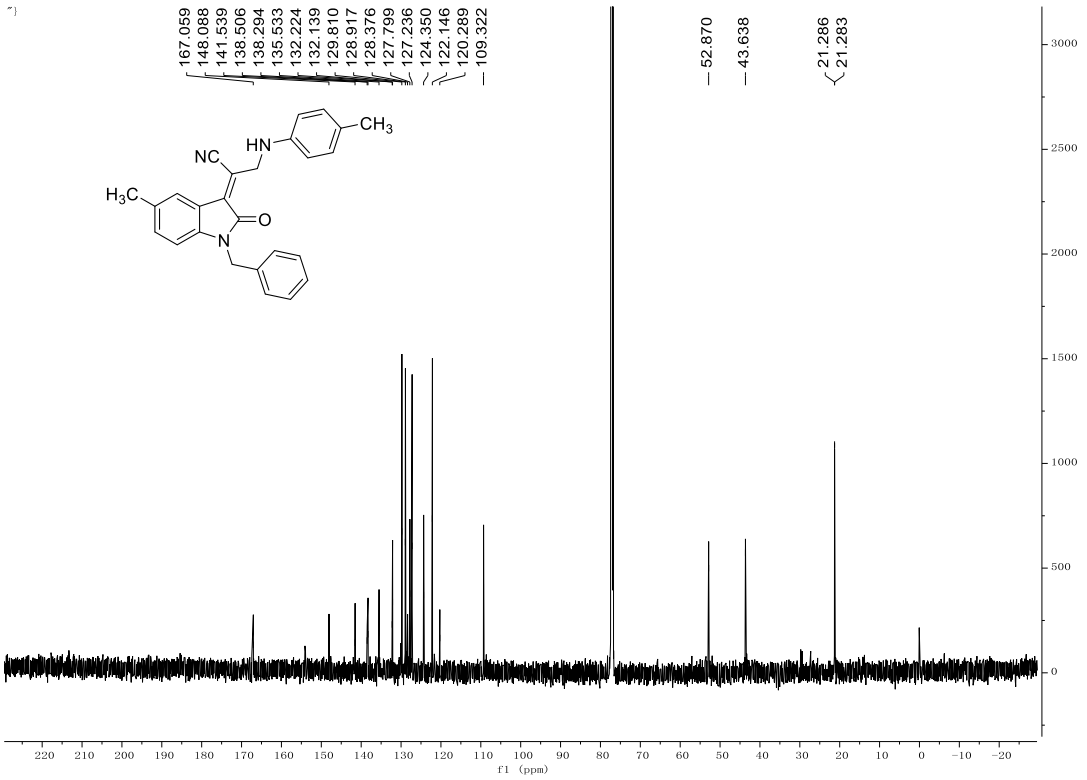
In a round flask, MBH carbonate of isatin **1** (0.1 mmol) and triphenylphosphine (0.1 mmol) were dissolved in acetonitrile (5.0 mL) and the mixture was stirred at room temperature for about two hours. The solvent was removed by rotatory evaporation at reduced pressure. The residue was subjected to silica gel column chromatography with ethyl acetate and petroleum ether 1:1 (v/v) as eluent to give pure products **6a–f** for analysis.

4. General procedure for the preparation of the compounds 7a–d and 8a–d

In a round flask, MBH carbonate of isatin (0.1 mmol), tri(*n*-butyl)phosphine (0.1 mmol) and DABCO (0.04 mmol) were dissolved in toluene (5.0 mL) and the mixture was stirred at 80 °C for about two hours. The solvent was removed by rotatory evaporation at reduced pressure. The residue was subjected to silica gel column chromatography with ethyl acetate, dichloromethane and petroleum ether 1:3:7 (v/v/v) as eluent to give pure product for analysis.

(*E*)-2-(1-Benzyl-5-methyl-2-oxoindolin-3-ylidene)-3-(*p*-tolylamino)propanenitrile (3a): red solid, 72%, 28 mg, m.p. 134-135 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H, ArH), 7.36-7.29 (m, 4H, ArH), 7.27-7.26 (m, 1H, ArH), 7.08 (d, *J* = 8.0 Hz, 1H, ArH), 6.99 (d, *J* = 8.0 Hz, 2H, ArH), 6.67 (d, *J* = 8.0 Hz, 2H, ArH), 6.60 (d, *J* = 8.0 Hz, 1H, ArH), 4.93 (s, 2H, CH), 4.79 (s, 2H, CH), 4.57 (s, 1H, CH), 2.30 (s, 3H, CH_3), 2.23 (s, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 167.1, 148.1, 141.5, 138.5, 138.3, 135.5, 132.2, 132.1, 129.8, 128.9, 128.4, 127.8, 127.2, 124.4, 122.2, 120.3, 109.3, 52.9, 43.6, 21.29, 21.28; IR (KBr) υ: 1699, 1607, 1521, 1489, 1455, 1439, 1375, 1318, 1302, 1248, 1191, 1129, 1082, 886, 809 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{24}N_3O$ ($[M+H]^+$): 394.1914, Found: 394.1905.

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124.350
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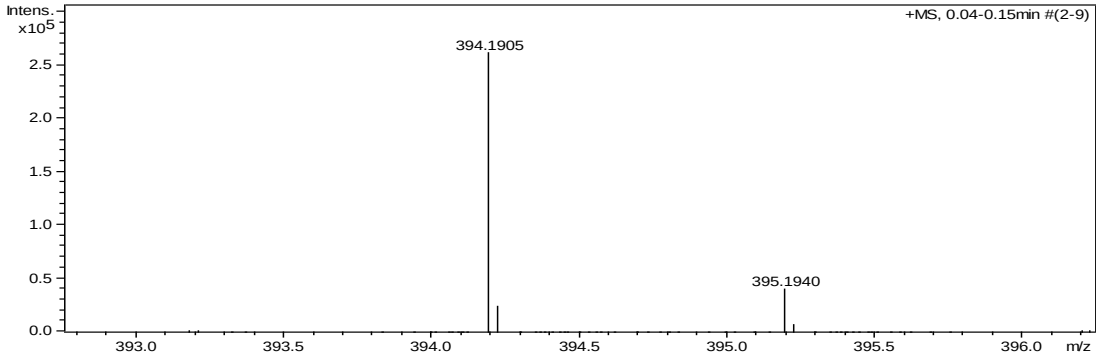
H3C
O
N
f1 (ppm)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x10^5
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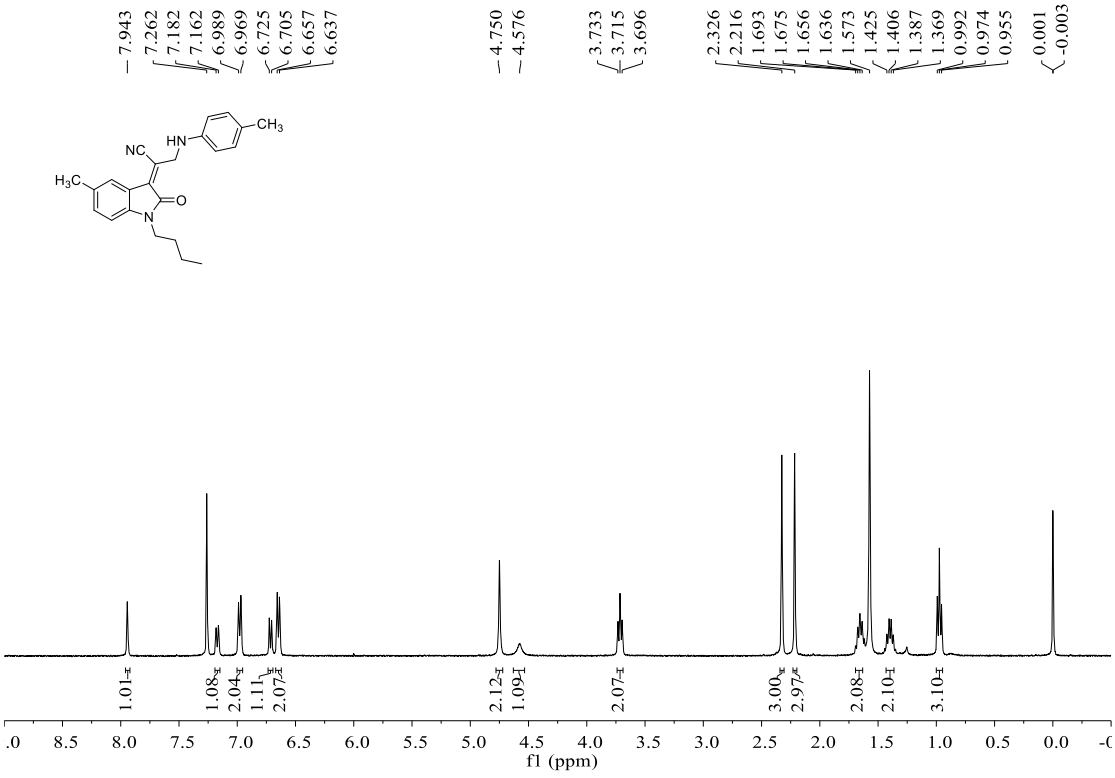
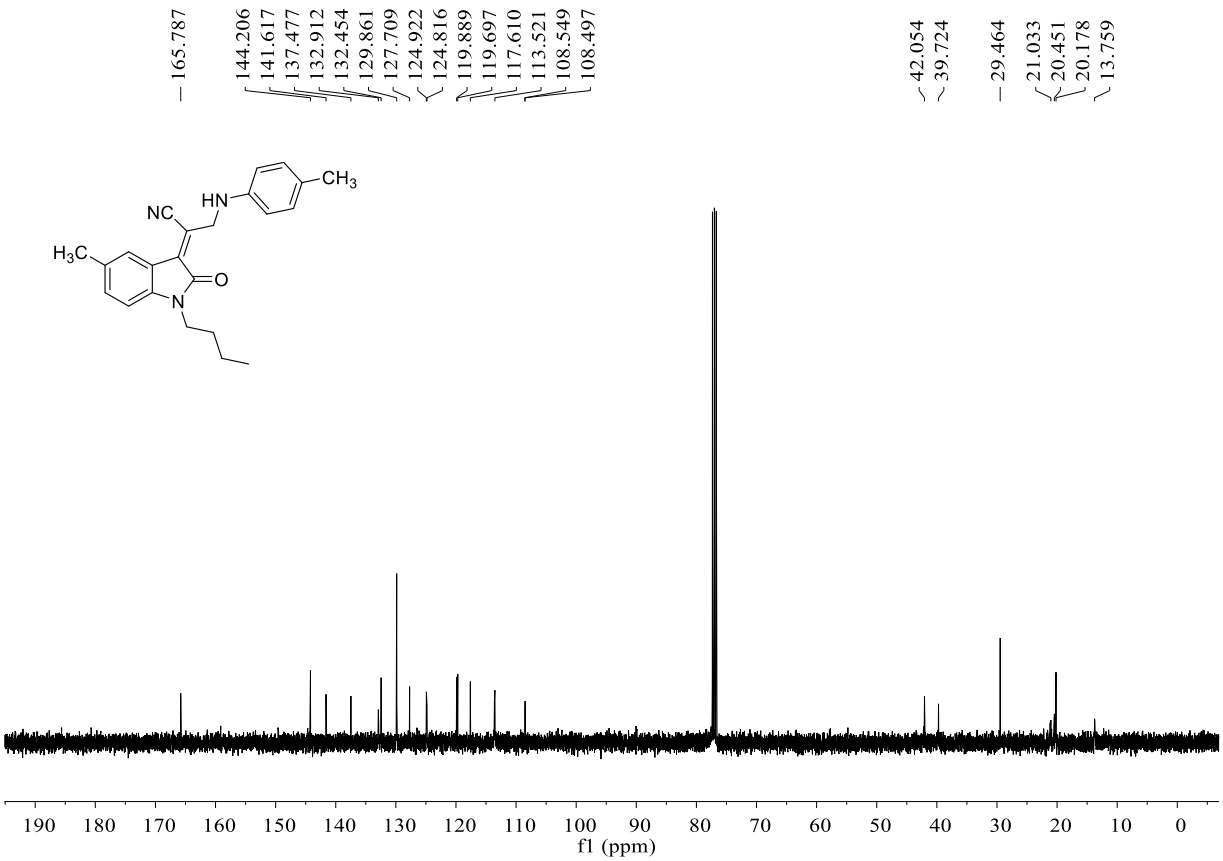
394.1905
395.1940
m/z

(*E*)-2-(1-Butyl-5-methyl-2-oxoindolin-3-ylidene)-3-(*p*-tolylamino)propanenitrile (3b): red solid, 68%, 24 mg, m.p. 136-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 1H, ArH), 7.17 (d, *J* = 8.0 Hz, 1H, ArH), 6.98 (d, *J* = 8.0 Hz, 2H, ArH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH), 6.65 (d, *J* = 8.0 Hz, 2H, ArH), 4.75 (s, 2H, CH), 4.58 (s, 1H, CH), 3.72 (t, *J* = 7.2 Hz, 2H, CH), 2.33 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.70-1.64 (m, 2H, CH), 1.43-1.37 (m, 2H, CH), 0.97 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.8, 144.2, 141.6, 137.5, 132.9, 132.5, 129.9, 127.7, 124.9, 124.8, 119.9, 119.7, 117.6, 113.5, 108.6, 108.5, 42.1, 39.7, 29.5, 21.0, 20.5, 20.2, 13.8; IR (KBr) υ: 1684, 1628, 1541, 1469, 1451, 1345, 1323, 1309, 1288, 1194, 1129, 1082, 886, 811 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{23}H_{26}N_3O$ ($[M+H]^+$): 360.2070, Found: 360.2063.

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113.521
108.549
108.497
42.054
39.724
29.464
21.033
20.451
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CH3
NC
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O
N
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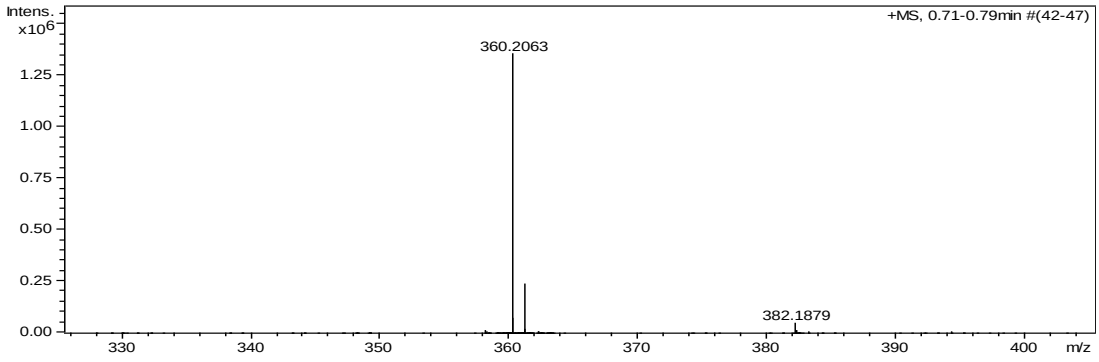
f1 (ppm)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x10^6
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1.00
0.75
0.50
0.25
0.00
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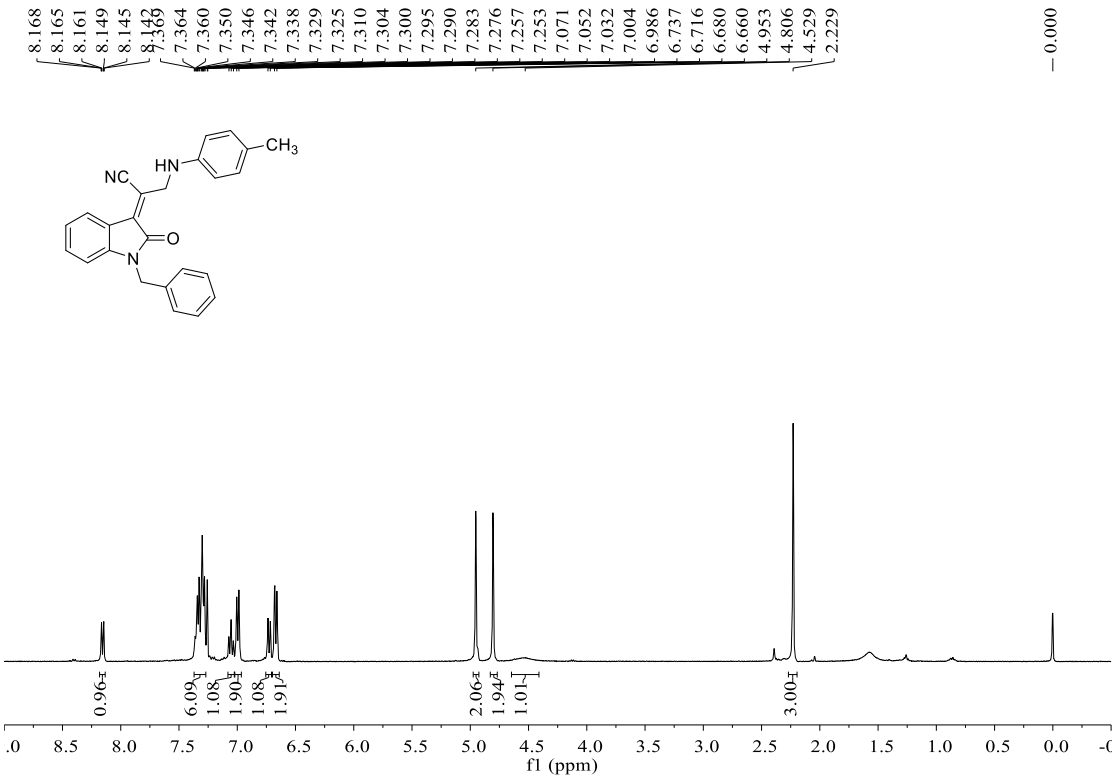
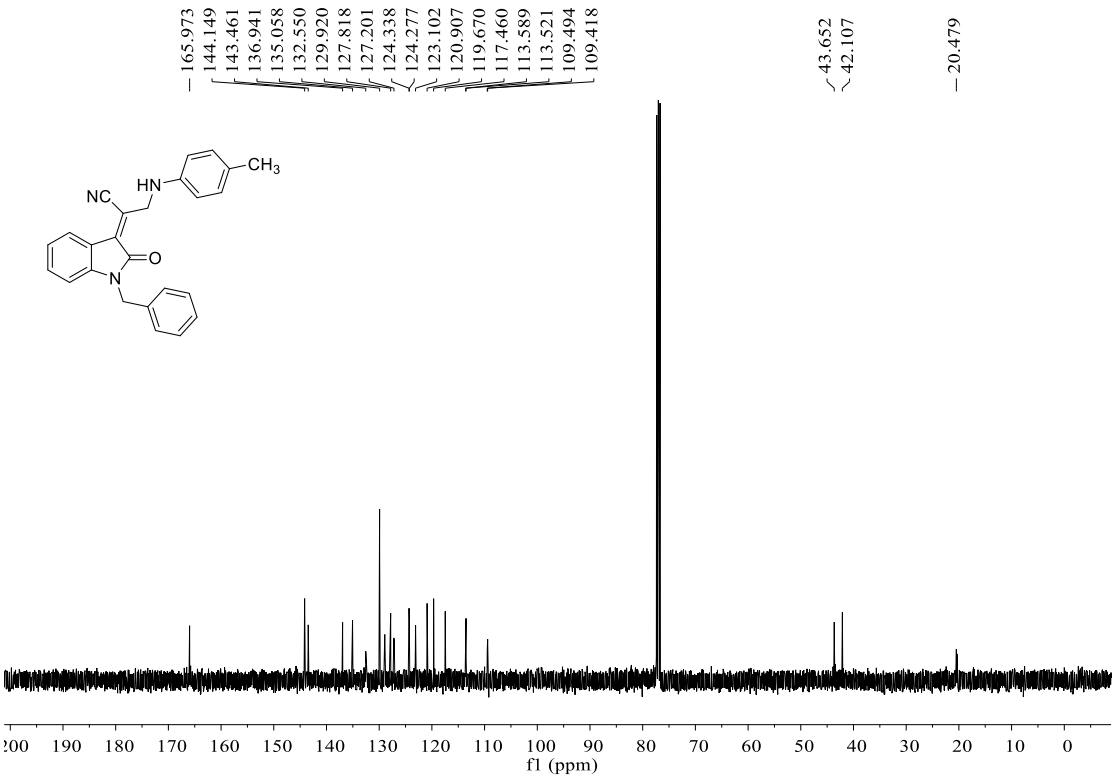
360.2063
382.1879
330 340 350 360 370 380 390 400 m/z

(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-3-(*p*-tolylamino)propanenitrile (3c): red solid, 65%, 24 mg, m.p. 136-137 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.0 Hz, 1H, ArH), 7.40-7.28 (m, 6H, ArH), 7.05 (t, *J* = 7.6 Hz, 1H, ArH), 7.0 (d, *J* = 7.2 Hz, 2H, ArH), 6.73 (d, *J* = 8.4 Hz, 1H, ArH), 6.67 (d, *J* = 8.0 Hz, 2H, ArH), 4.95 (s, 2H, CH), 4.81 (s, 2H, CH), 4.53 (s, 1H, CH), 2.23 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.0, 144.2, 143.5, 136.9, 135.1, 132.6, 129.9, 127.8, 127.2, 124.34, 124.28, 123.1, 120.9, 119.7, 117.5, 113.6, 113.5, 109.5, 109.4, 43.7, 42.1, 20.5; IR (KBr) υ: 1689, 1618, 1525, 1479, 1452, 1435, 1355, 1347, 1338, 1303, 1248, 1129, 886, 819, 789 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{22}N_3O$ ([M+H]$^+$): 380.1757, Found: 380.1753.

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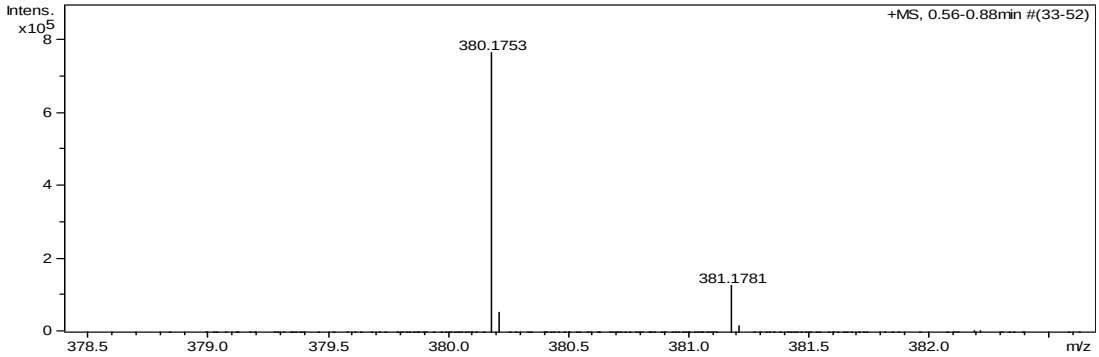
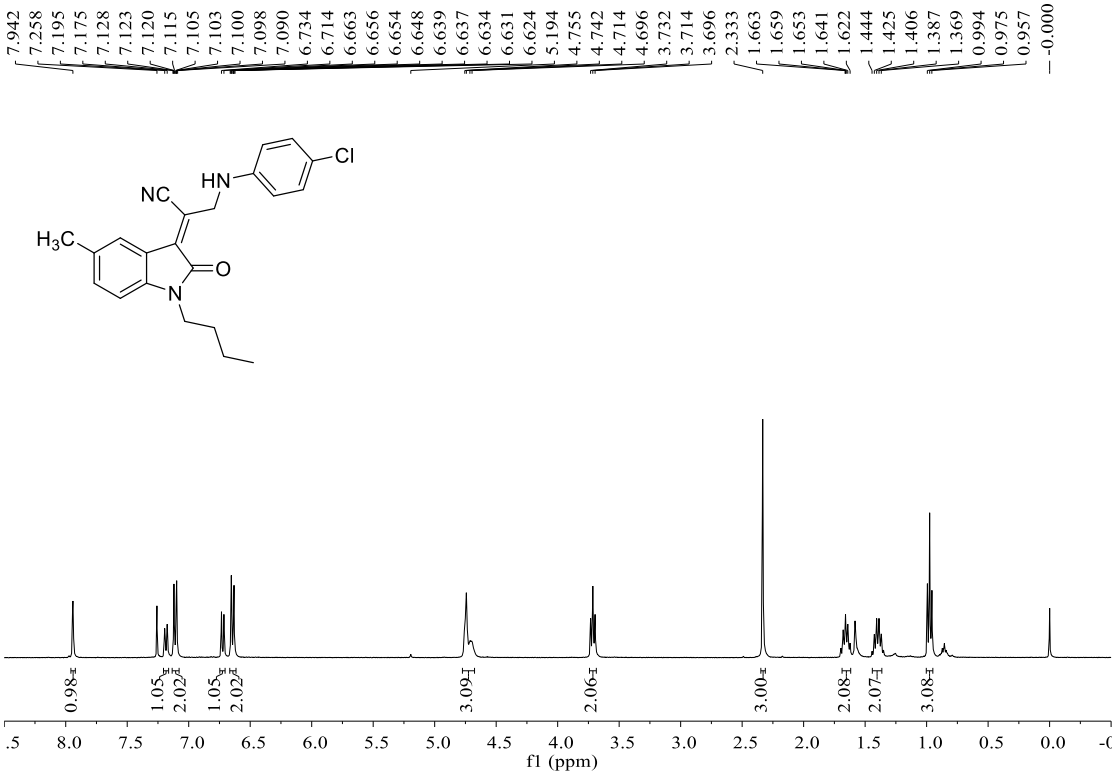
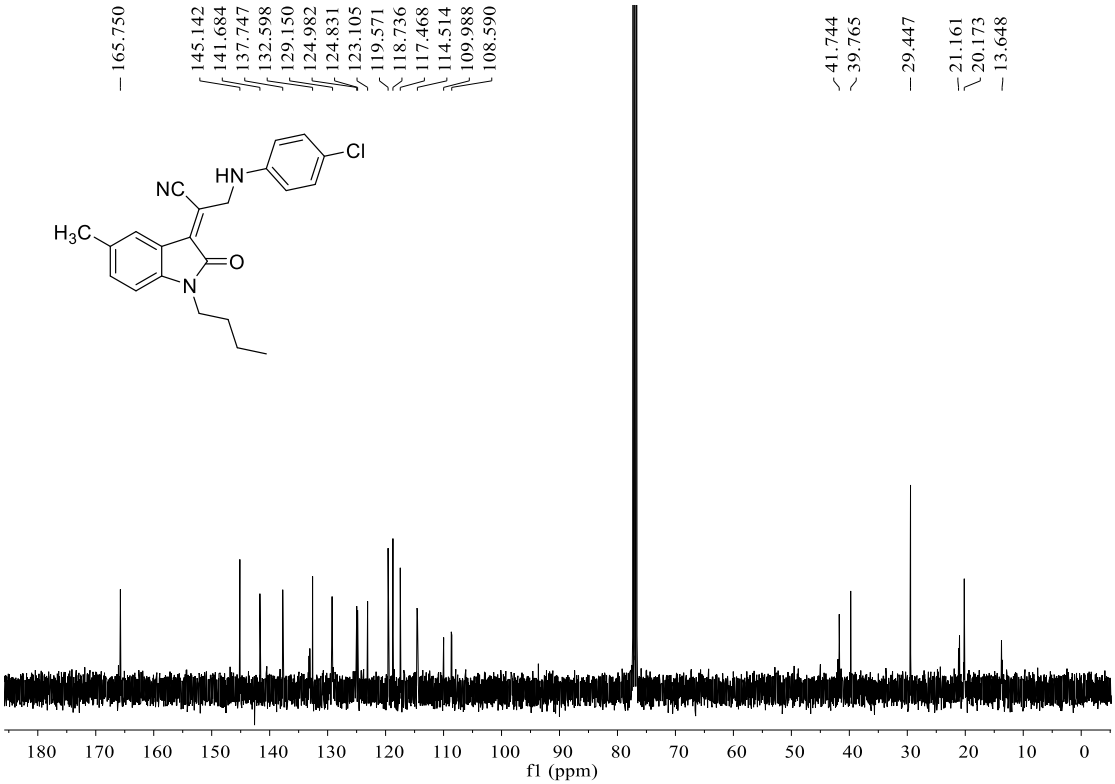
O
N
f1 (ppm)


Intens.
x10^5
+MS, 0.56-0.88min #(33-52)
380.1753
381.1781
m/z

(*E*)-2-(1-Butyl-5-methyl-2-oxoindolin-3-ylidene)-3-((4-chlorophenyl)amino)propanenitrile (3d): red solid, 58%, 22 mg, m.p. 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 1H, ArH), 7.19 (d, *J* = 8.0 Hz, 1H, ArH), 7.13-7.09 (m, 2H, ArH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH), 6.66-6.62 (m, 2H, ArH), 4.76-4.70 (m, 3H, CH), 3.71 (t, *J* = 7.2 Hz, 2H, CH), 2.33 (s, 3H, CH_3), 1.66-1.62 (m, 2H, CH), 1.44-1.37 (m, 2H, CH), 0.98 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.8, 145.1, 141.7, 137.8, 132.6, 129.2, 125.0, 124.8, 123.1, 119.6, 118.7, 117.5, 114.5, 111.0, 108.6, 41.7, 39.8, 29.5, 21.2, 20.2, 13.6; IR (KBr) υ: 1867, 1799, 1760, 1682, 1646, 1601, 1532, 1488, 1295, 1261, 1143, 1113, 1099, 979, 817 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{22}H_{23}ClN_3O$ ($[M+H]^+$): 380.1524, Found: 380.1527.

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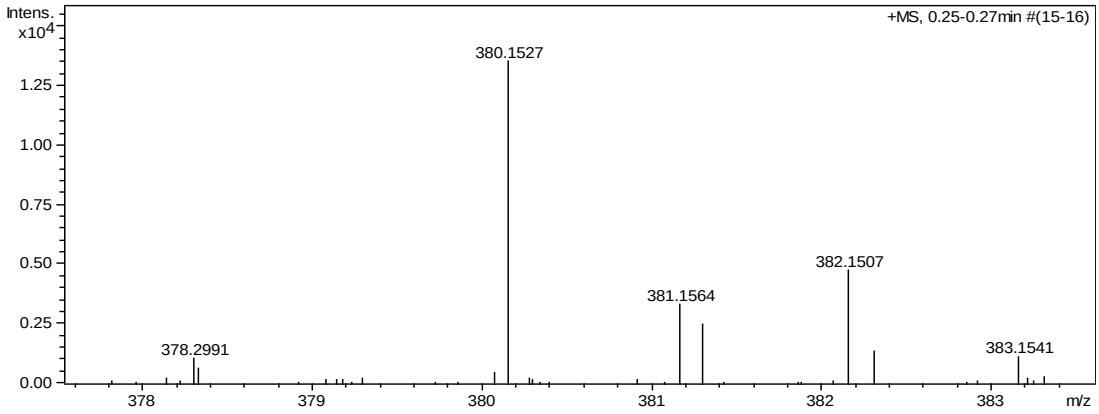
f1 (ppm)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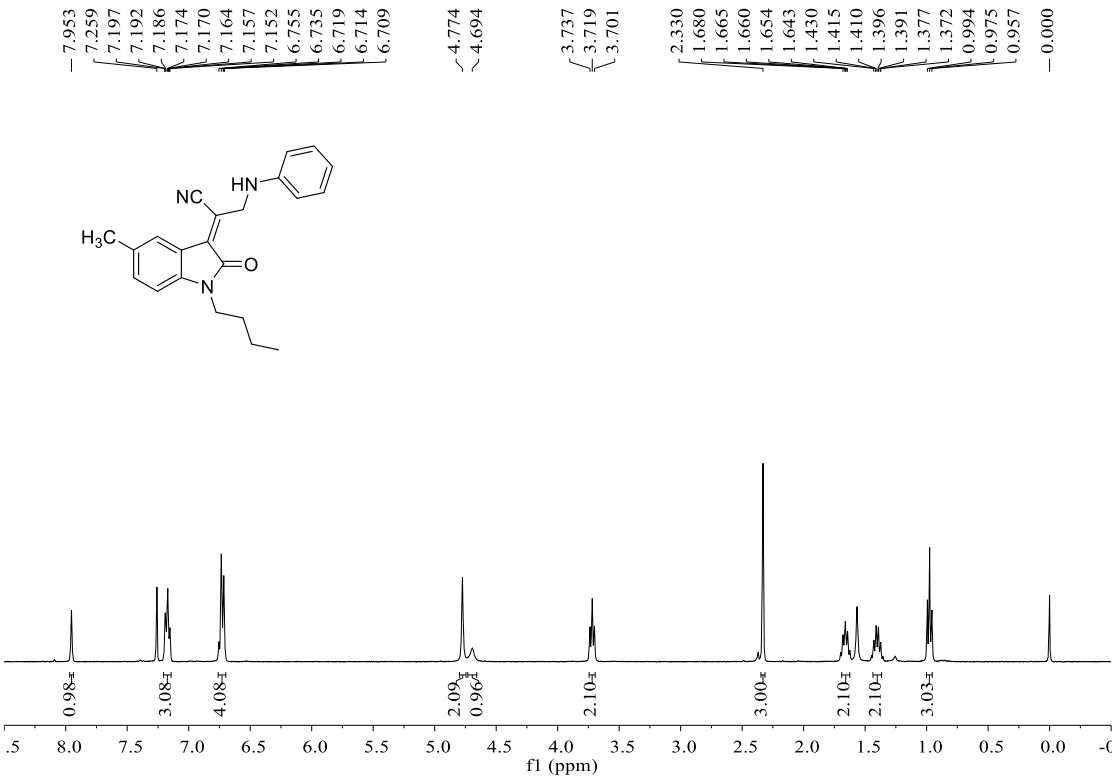
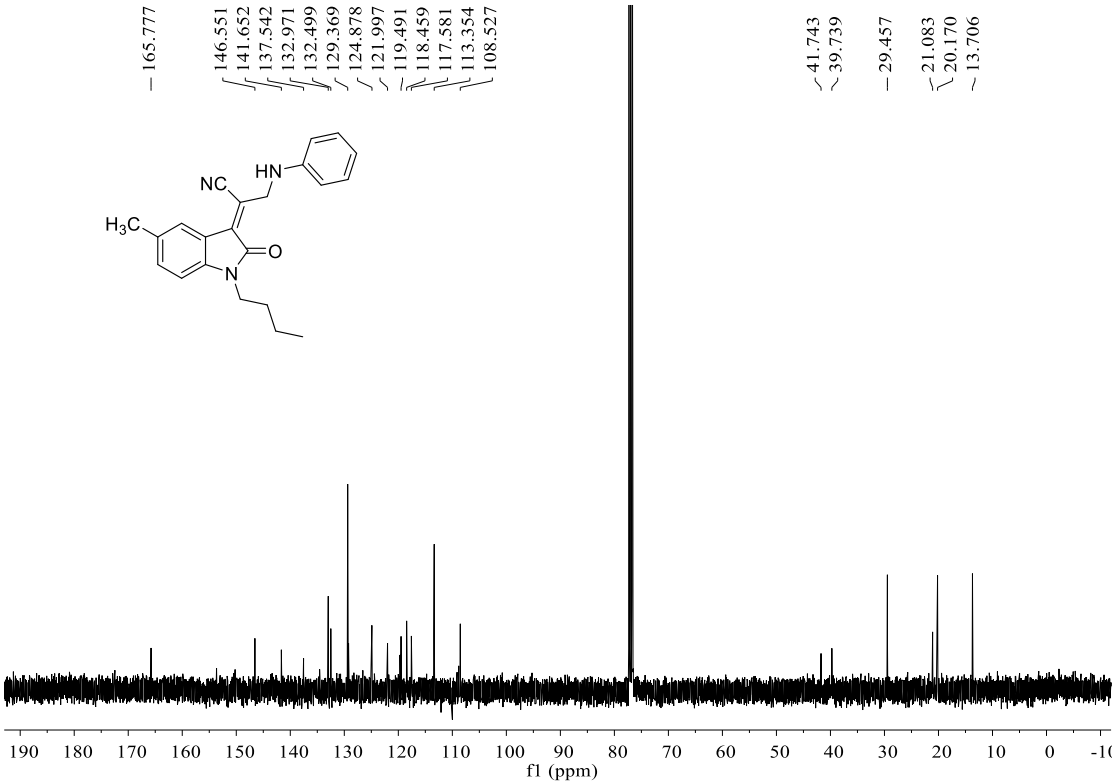
1.25
1.00
0.75
0.50
0.25
0.00
378
379
380
381
382
383
m/z

(*E*)-2-(1-Butyl-5-methyl-2-oxoindolin-3-ylidene)-3-(phenylamino)propanenitrile (3e): red solid, 72%, 25 mg, m.p. 132-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 1H, ArH), 7.20-7.15 (m, 3H, ArH), 6.76-6.71 (m, 4H, ArH), 4.77 (s, 2H, CH), 4.69 (s, 1H, CH), 3.72 (t, *J* = 7.2 Hz, 2H, CH), 2.33 (s, 3H, CH_3), 1.68-1.64 (m, 2H, CH), 1.43-1.37 (m, 2H, CH), 0.98 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.8, 146.6, 141.7, 137.5, 133.0, 132.5, 129.4, 124.9, 122.0, 119.5, 118.5, 117.6, 113.4, 108.5, 41.7, 39.7, 29.5, 21.1, 20.2, 13.7; IR (KBr) υ: 2962, 1684, 1603, 1532, 1488, 1358, 1264, 1203, 1119, 877, 809, 751 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{22}H_{24}N_3O$ ($[M+H]^+$): 346.1914, Found: 346.1918.

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108.527
41.743
39.739
29.457
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O
N
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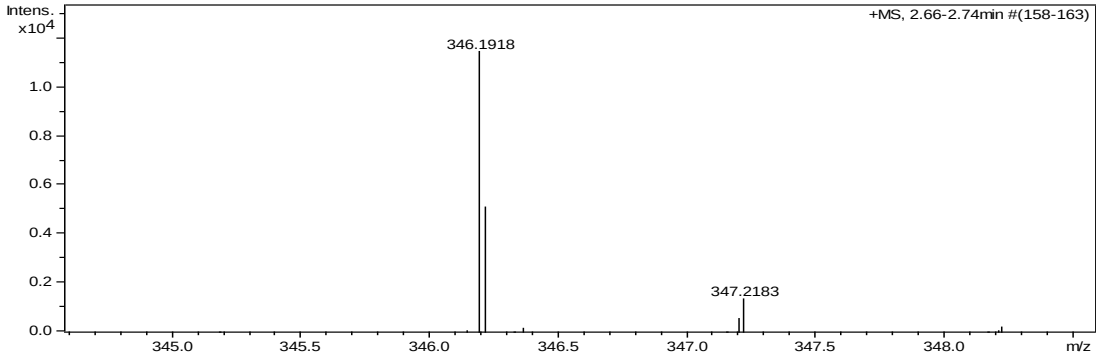
f1 (ppm)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+MS, 2.66-2.74min #(158-163)
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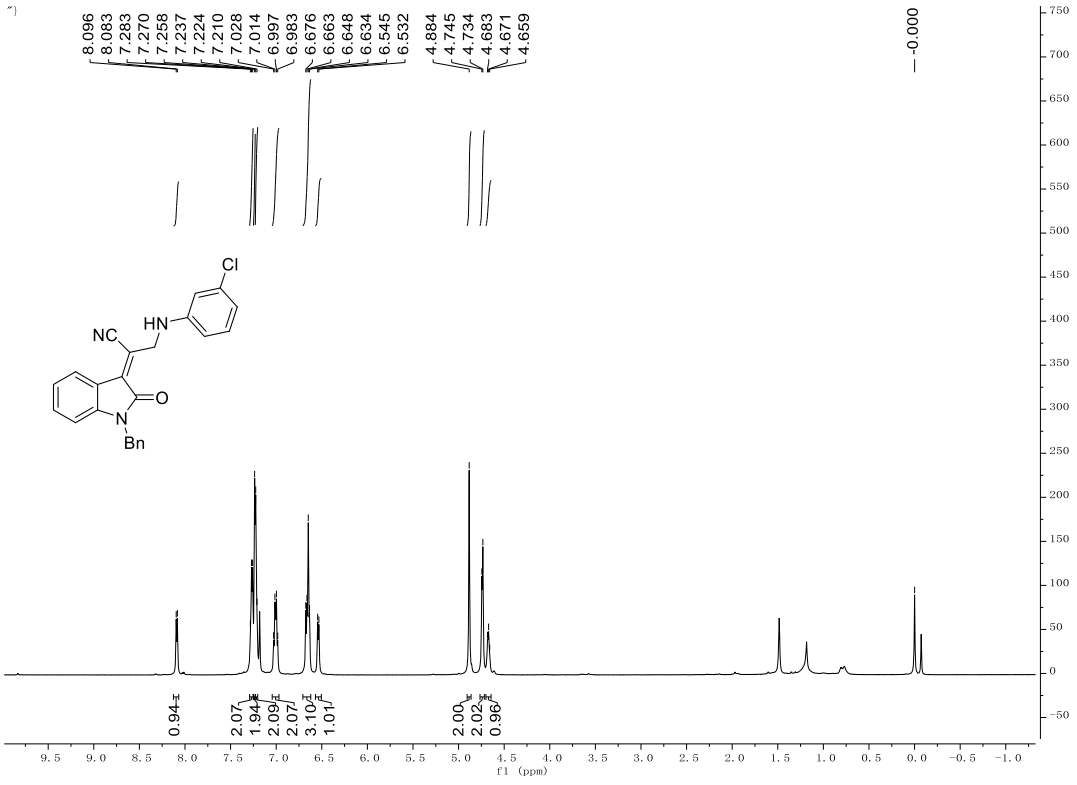
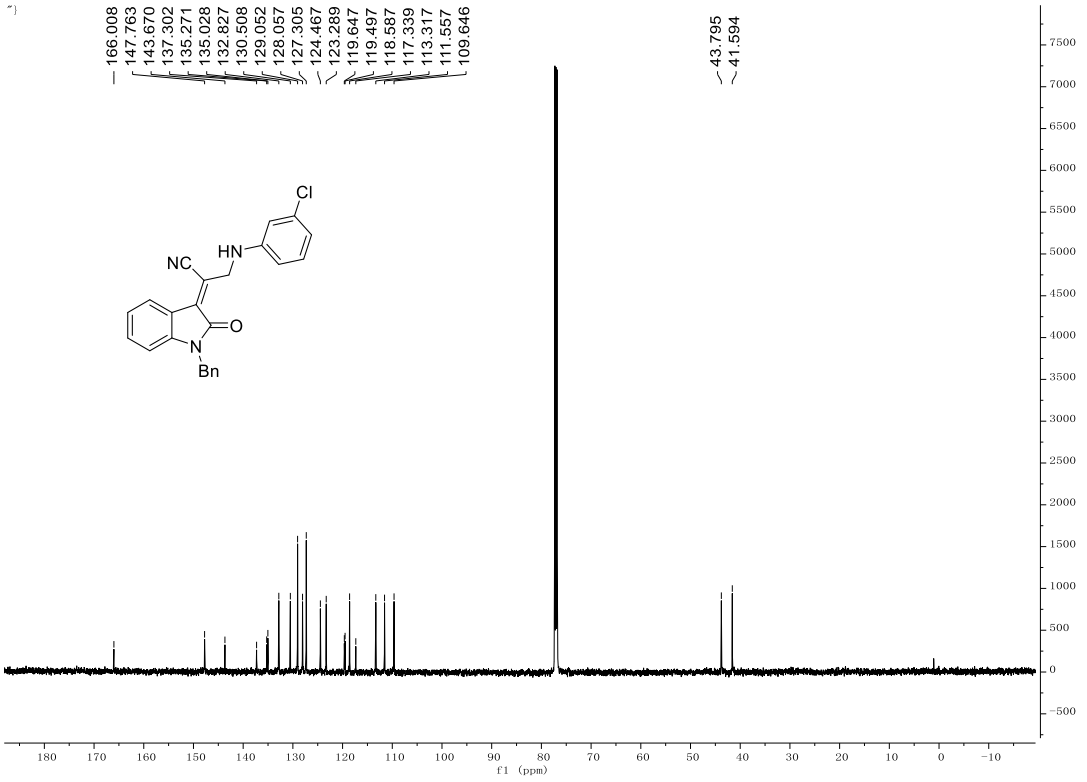
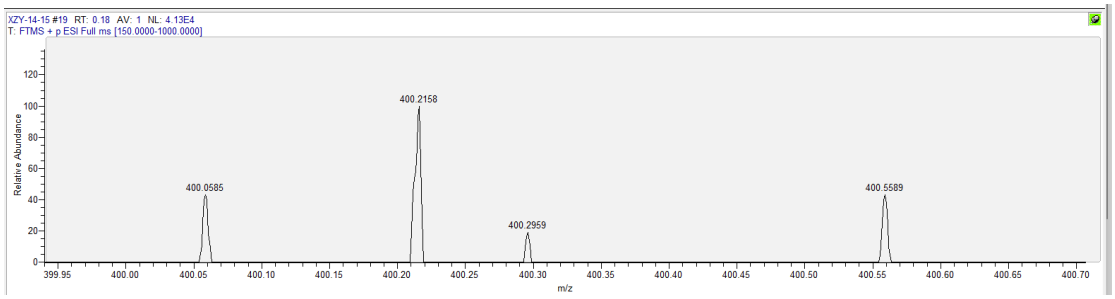
0.6
0.4
0.2
0.0
345.0
345.5
346.0
346.5
347.0
347.5
348.0
m/z

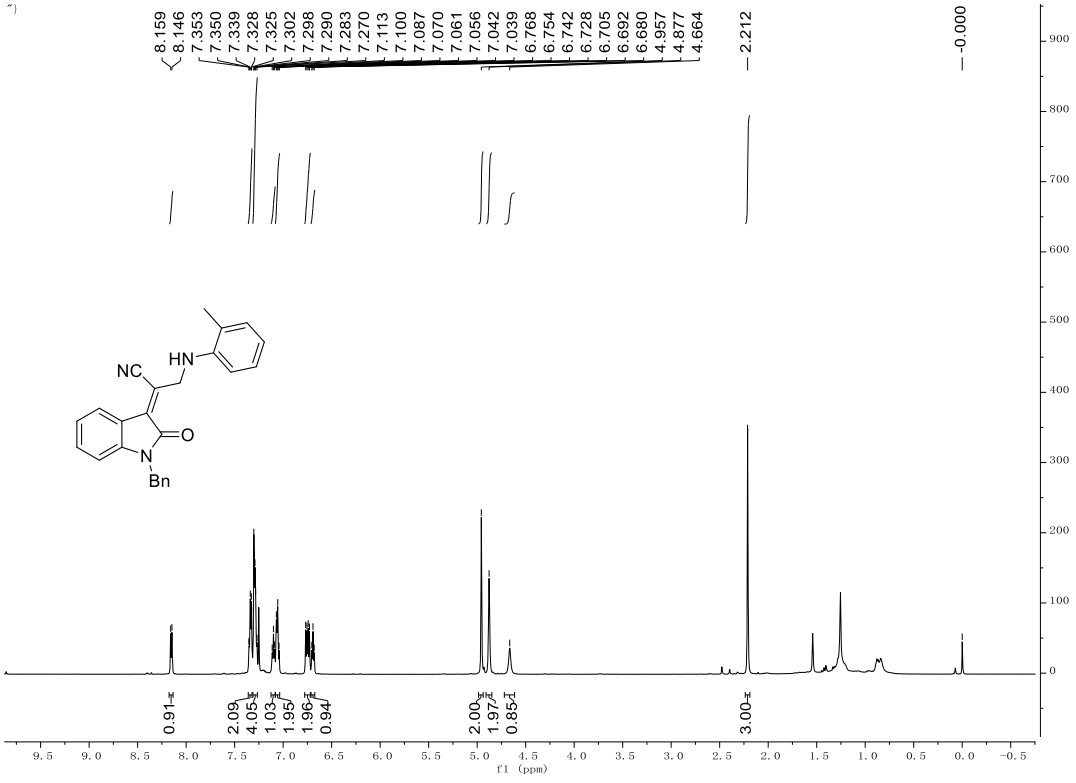
(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-3-((3-chlorophenyl)amino)propanenitrile (3f): yellow solid, 55%, 22 mg, m.p. 158-159 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 7.8 Hz, 1H, ArH), 7.27 (t, *J* = 7.5 Hz, 2H, ArH), 7.24 (s, 2H, ArH), 7.22 (d, *J* = 8.5 Hz, 2H, ArH), 7.01 (q, *J* = 8.3 Hz, 2H, ArH), 6.66 (q, *J* = 8.1 Hz, 3H, ArH), 6.54 (d, *J* = 8.2 Hz, 1H, ArH), 4.88 (s, 2H, CH), 4.74 (d, *J* = 6.9 Hz, 2H, CH), 4.67 (t, *J* = 7.2 Hz, 1H, NH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 166.0, 147.8, 143.7, 137.3, 135.3, 135.0, 132.8, 130.5, 129.1, 128.1, 127.3, 124.5, 123.3, 119.7, 119.5, 118.6, 117.3, 113.3, 111.6, 109.7, 43.8, 41.6; IR (KBr) υ: 1719, 1659, 1611, 1487, 1468, 1455, 1348, 1175, 1110, 1076, 754 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{19}ClN_3O$ ([M+H]$^{+}$): 400.2131, Found: 400.2158.

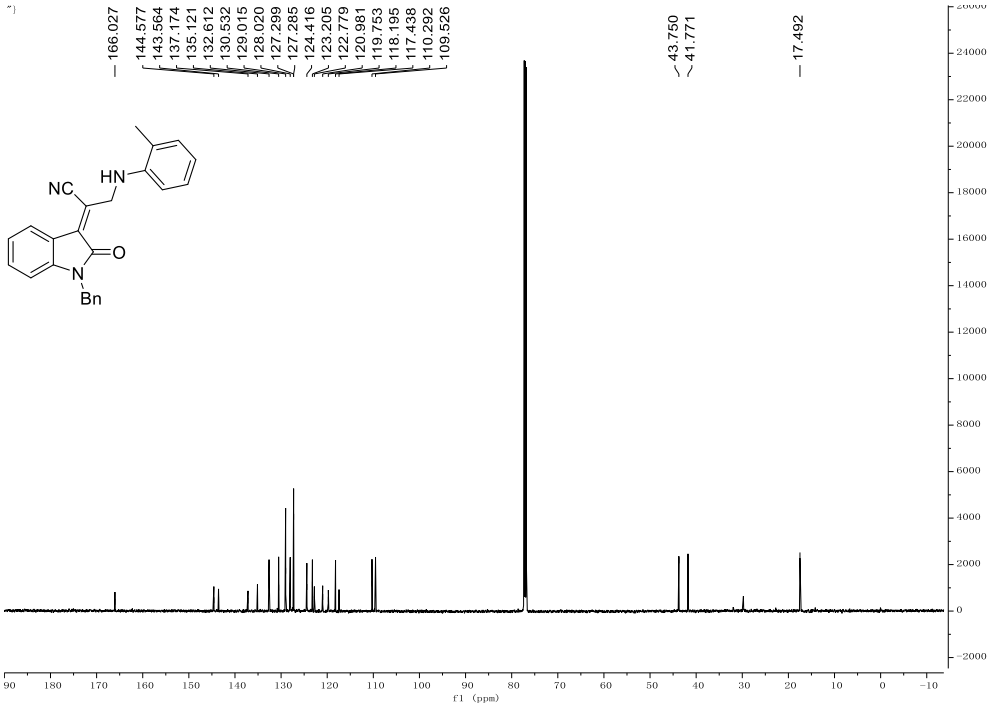


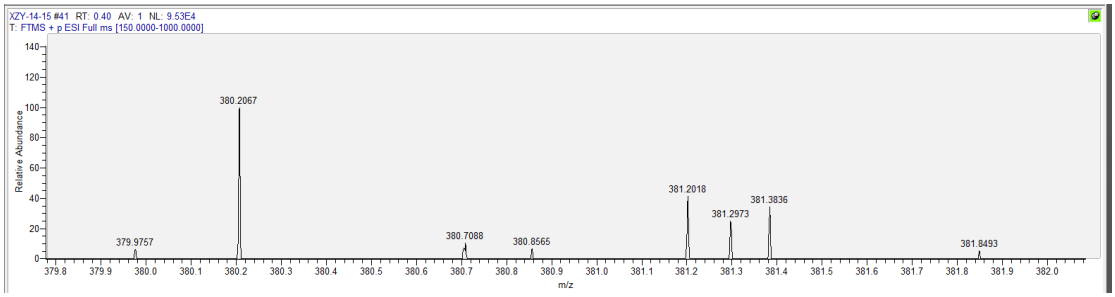

166.008
147.763
143.670
137.302
135.271
135.028
132.827
130.508
129.052
128.057
127.305
124.467
123.289
119.647
119.497
118.587
117.339
113.317
111.557
109.646
43.795
41.594
Cl
HN
NC
O
N
Bn
f1 (ppm)


XZY-14-15 #19 RT: 0.18 AV: 1 NL: 4.13E4
T: FTMS + p ESI Full ms [150.0000-1000.0000]
Relative Abundance
400.0585
400.2158
400.2959
400.5589
m/z

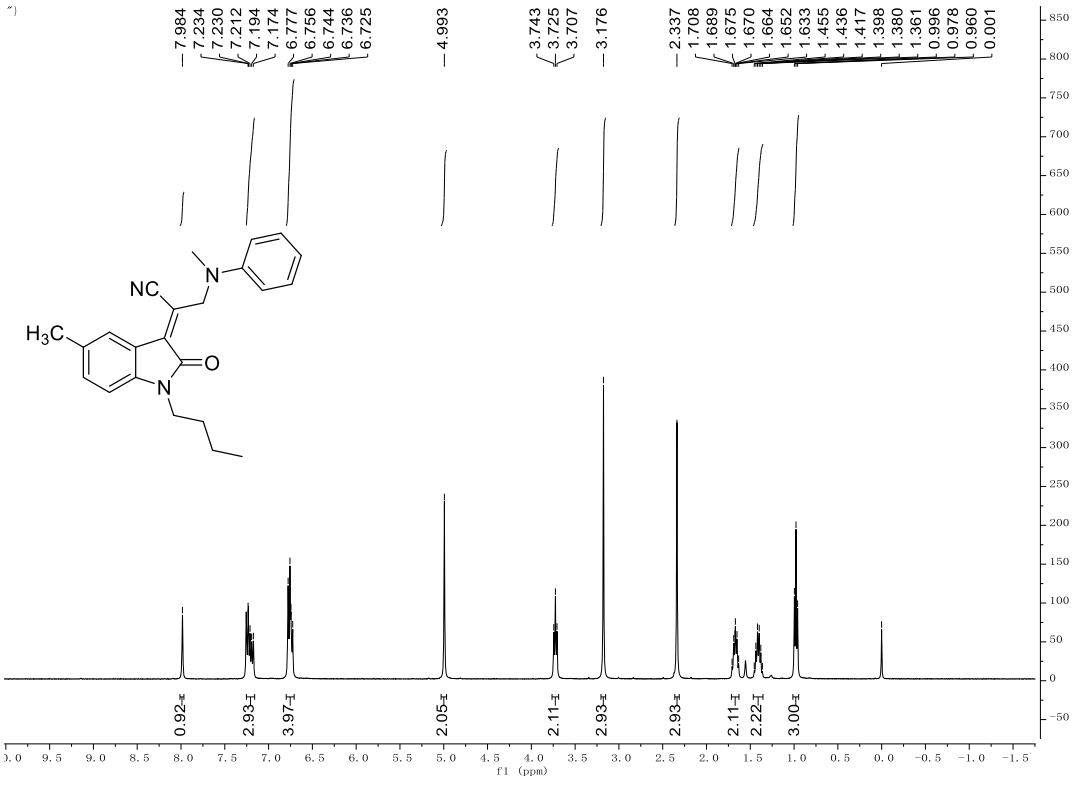
(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-3-(*o*-tolylamino)propanenitrile (3g): yellow solid, 58%, 22 mg, m.p. 159-160 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 7.8 Hz, 1H, ArH), 7.36-7.32 (m, 2H, ArH), 7.29 (dd, J_1 = 8.3 Hz, J_2=3.3 Hz, 4H, ArH), 7.10 (t, *J* = 7.7 Hz, 1H, ArH), 7.06 (dd, J_1 = 9.7 Hz, J_2 =6.6 Hz, 2H, ArH), 6.75 (dd, J_1 = 15.6 Hz, J_2 =8.0 Hz, 2H, ArH), 6.69 (t, *J* = 7.5 Hz, 1H, ArH), 4.96 (s, 2H, CH), 4.88 (s, 2H, CH), 4.66 (s, 1H, NH), 2.21 (s, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 166.0, 144.6, 143.6, 137.2, 135.1, 132.6, 130.5, 129.0, 128.0, 127.30, 127.29, 124.4, 123.2, 122.8, 121.0, 119.8, 118.2, 117.4, 110.3, 109.5, 43.8, 41.8, 17.5; IR (KBr) υ: 1720, 1610, 1487, 1468, 1455, 1438, 1361, 1299, 1177, 1107, 1081, 753 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{22}N_3O$ ([M+H]$^+$): 380.2057, Found: 380.2067.

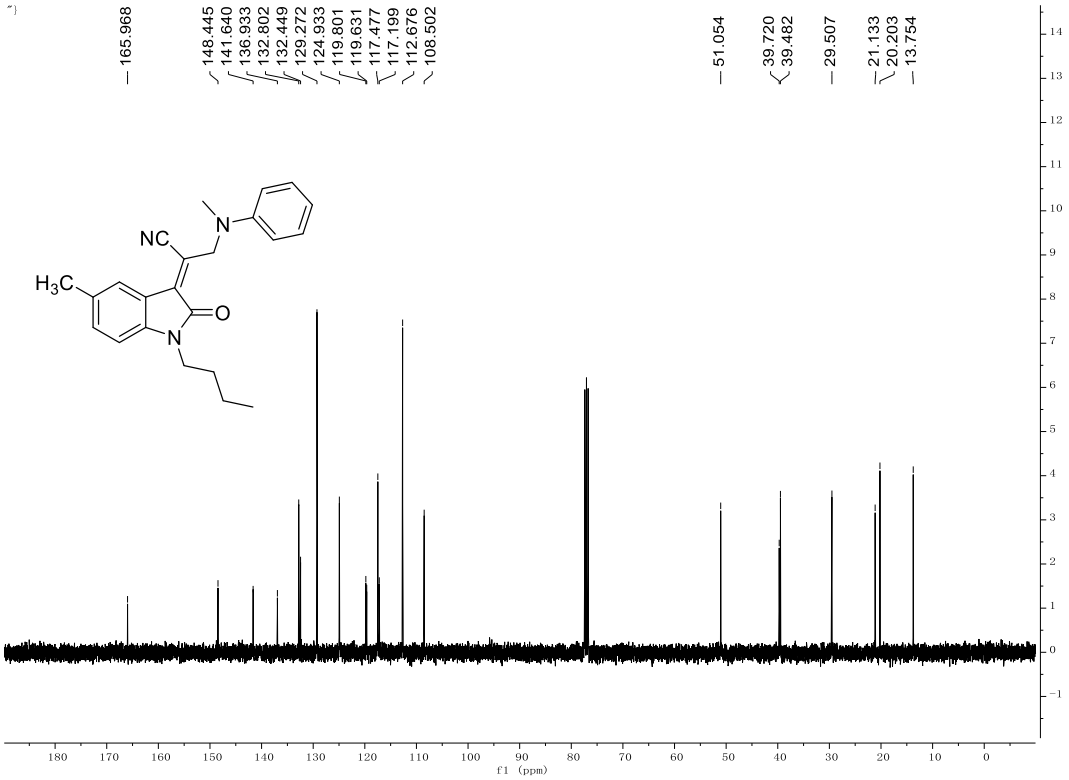


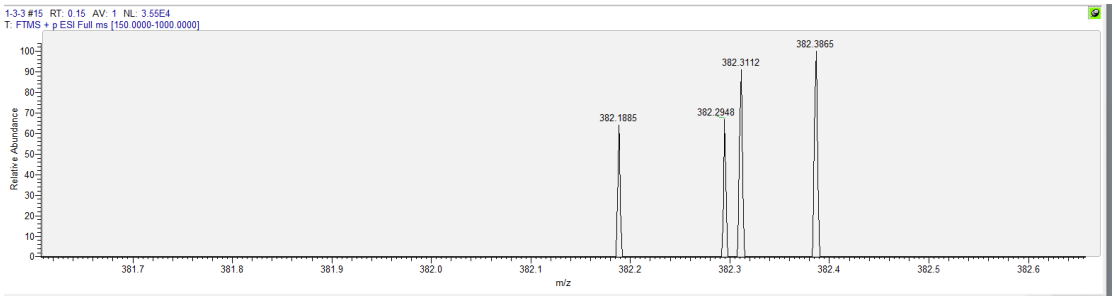

166.027
144.577
143.564
137.174
135.121
132.612
130.532
129.015
128.020
127.299
127.285
124.416
123.205
122.779
120.981
119.753
118.195
117.438
110.292
109.526
43.750
41.771
17.492
NC
HN
O
N
Bn
f1 (ppm)


XZY-14-15 #41 RT: 0.40 AV: 1 NL: 9.53E4
T: FTMS + p ESI Full ms [150.0000-1000.0000]
Relative Abundance
380.2067
381.2018
381.3836
381.2973
379.9757
380.7088
380.8565
381.8493
m/z

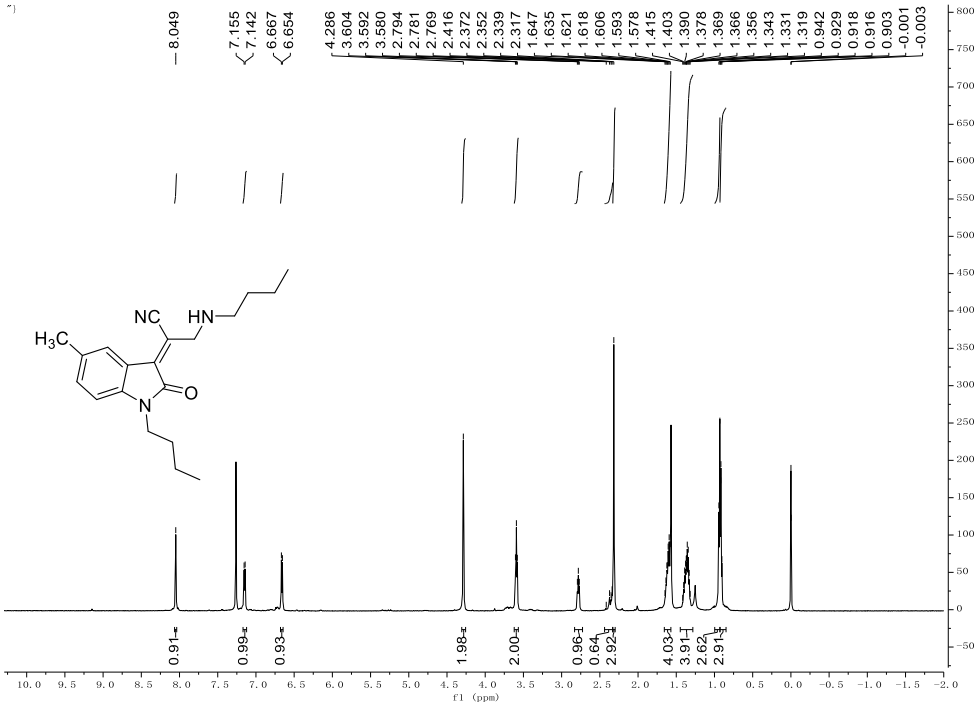
(*E*)-2-(1-Butyl-5-methyl-2-oxoindolin-3-ylidene)-3-(methyl(phenyl)amino)propanenitrile (3h): orange solid, 72%, 27 mg, m.p. 168-169 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (s, 1H, ArH), 7.25-7.16 (m, 3H, ArH), 6.75 (dd, J_1 = 12.8 Hz, J_1 = 8.1 Hz, 4H, ArH), 4.99 (s, 2H, CH), 3.73 (t, J = 7.2 Hz, 2H, CH), 3.18 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 1.72-1.63 (m, 2H, CH), 1.41 (h, J = 7.4 Hz, 2H, CH), 0.98 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0, 148.5, 141.6, 136.9, 132.8, 132.5, 129.3, 124.9, 119.8, 119.6, 117.5, 117.2, 112.7, 108.5, 51.1, 39.7, 39.5, 29.5, 21.1, 20.2, 13.8; IR (KBr) υ: 1722, 1489, 1468, 1405, 1388, 1361, 1265, 1137, 1102, 1081, 763 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{23}H_{25}N_3NaO$ ([M+Na]$^+$): 382.1890, Found: 382.1885.

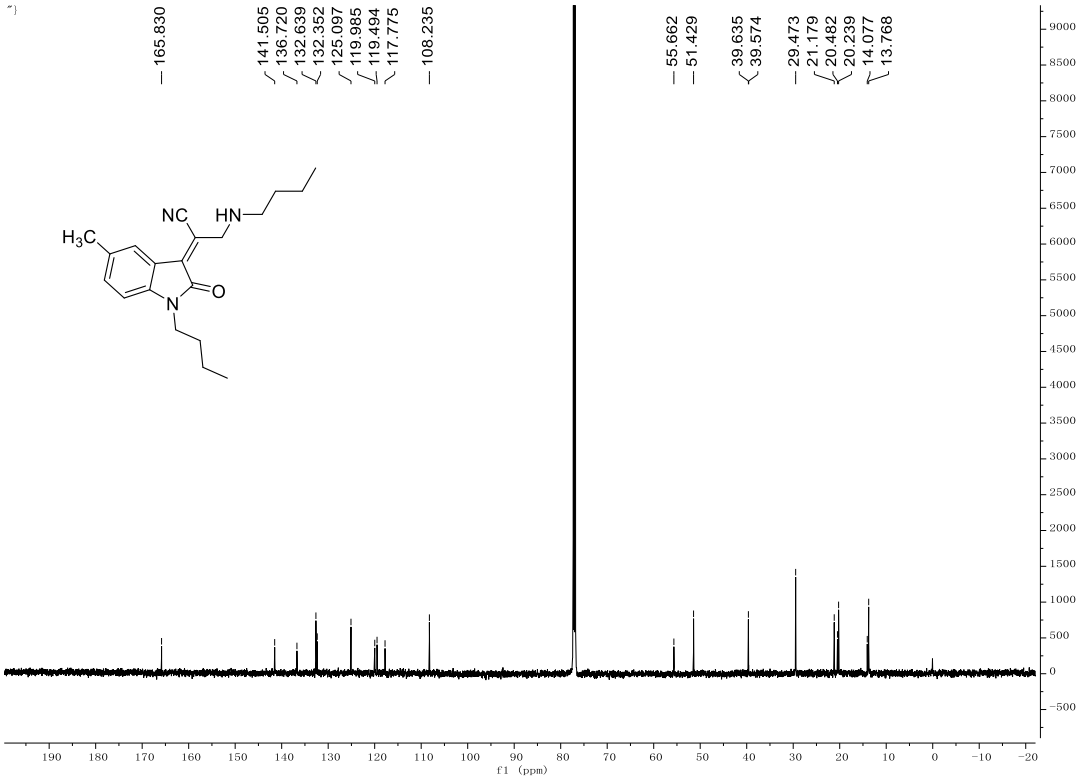


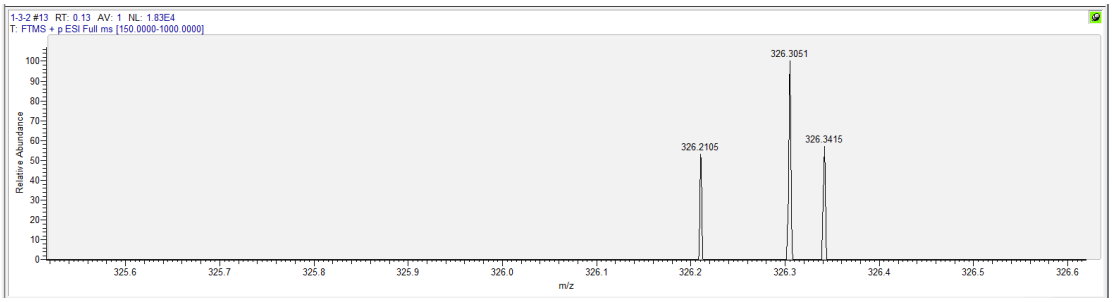

165.968
148.445
141.640
136.933
132.802
132.449
129.272
124.933
119.801
119.631
117.477
117.199
112.676
108.502
51.054
39.720
39.482
29.507
21.133
20.203
13.754
NC
N
H3C
O
N
f1 (ppm)


1-3-3 #15 RT: 0.15 AV: 1 NL: 3.55E4
T: FTMS + p ESI Full ms [150.0000-1000.0000]
382.3865
382.3112
382.2948
382.1885
Relative Abundance
m/z

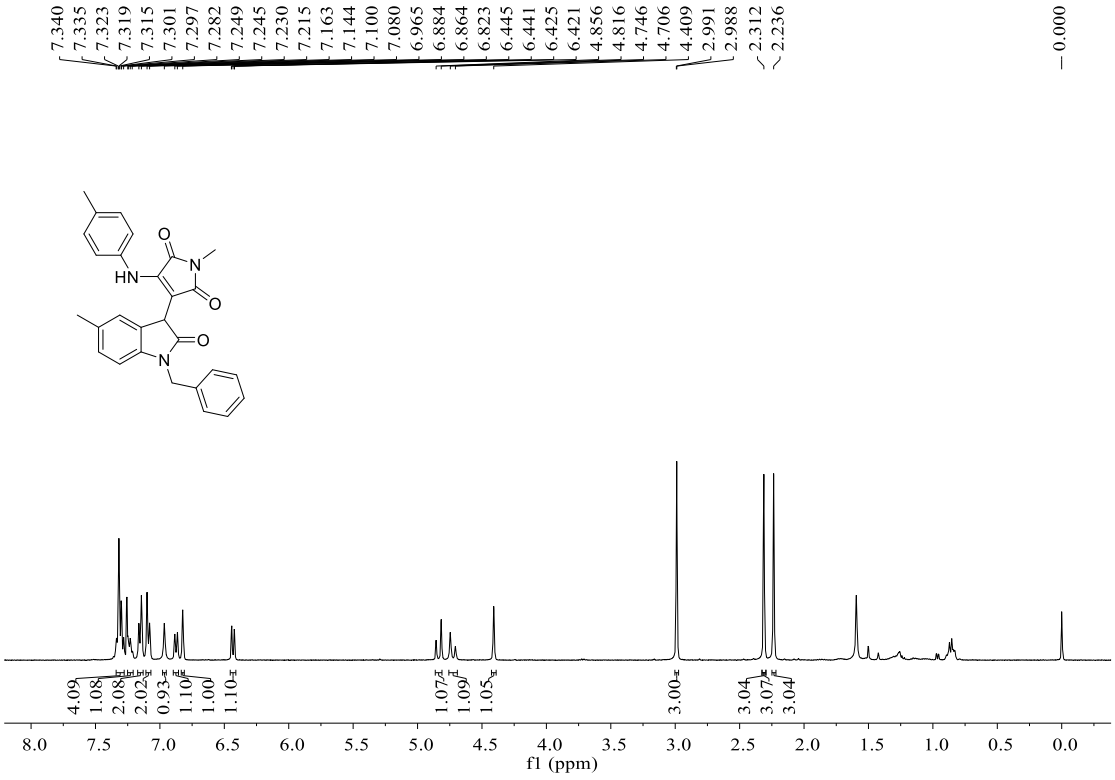
(*E*)-2-(1-Butyl-5-methyl-2-oxoindolin-3-ylidene)-3-(butylamino)propanenitrile (3i): red solid, 63%, 20 mg, m.p. 183-184 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.05 (s, 1H, ArH), 7.15 (d, *J* = 8.0 Hz, 1H, ArH), 6.66 (d, *J* = 7.9 Hz, 1H, ArH), 4.29 (s, 2H, CH), 3.59 (t, *J* = 7.3 Hz, 2H, CH), 2.78 (t, *J* = 7.5 Hz, 1H, CH), 2.42-2.34 (m, 1H, CH), 2.32 (s, 3H, CH_3), 1.67-1.57 (m, 4H, CH), 1.45-1.28 (m, 4H, CH), 0.94 (d, *J* = 7.7 Hz, 3H, CH_3), 0.93-0.85 (m, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 165.8, 141.5, 136.7, 132.6, 132.4, 125.1, 120.0, 119.5, 117.8, 108.2, 55.7, 51.4, 39.63, 39.57, 29.5, 21.2, 20.5, 20.2, 14.1, 13.8; IR (KBr) υ: 1732, 1642, 1464, 1427, 1398, 1371, 1316, 1254, 1197, 1168, 1061, 889, 767 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{20}H_{28}N_3O$ ($[M+H]^+$): 326.2127, Found: 326.2105.

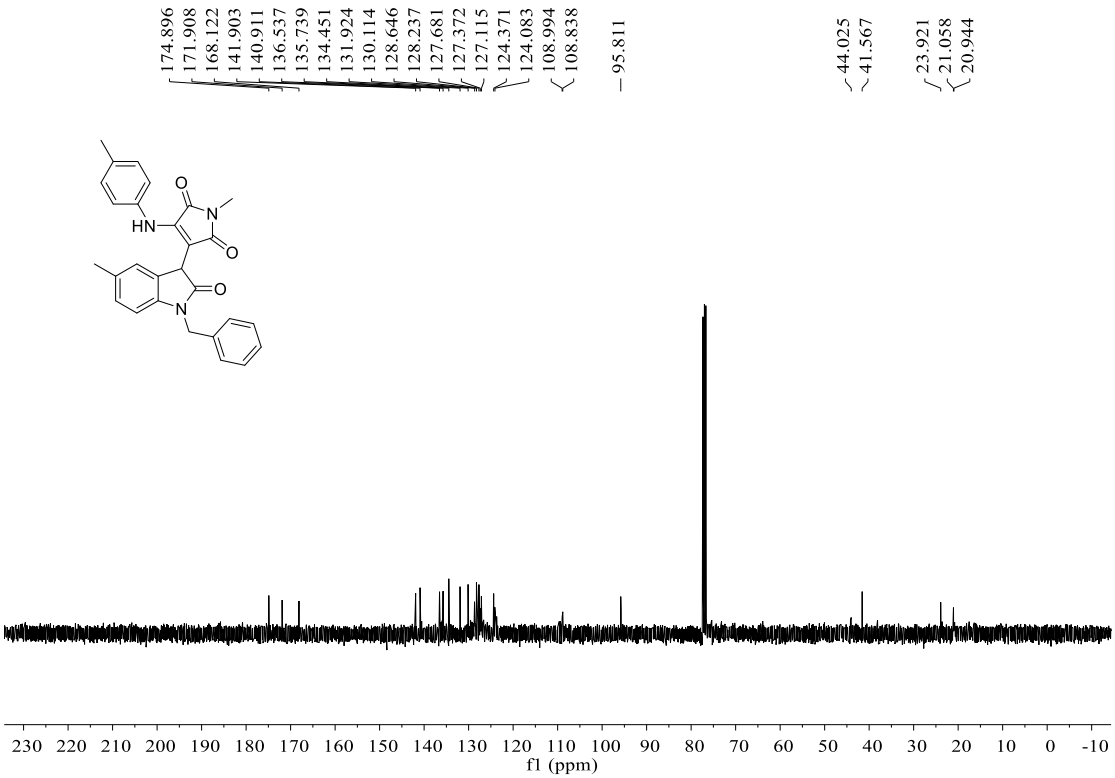


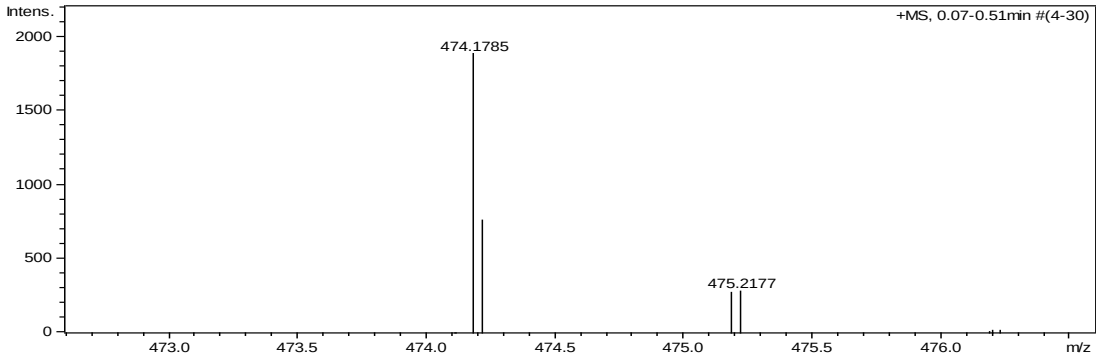

165.830
141.505
136.720
132.639
132.352
125.097
119.985
119.494
117.775
108.235
55.662
51.429
39.635
39.574
29.473
21.179
20.482
20.239
14.077
13.768
NC
HN
H3C
O
N
f1 (ppm)


1-3-2 #13 RT: 0.13 AV: 1 NL: 1.83E4
T: FTMS + p ESI Full ms [150.0000-1000.0000]
326.3051
326.2105
326.3415
Relative Abundance
m/z

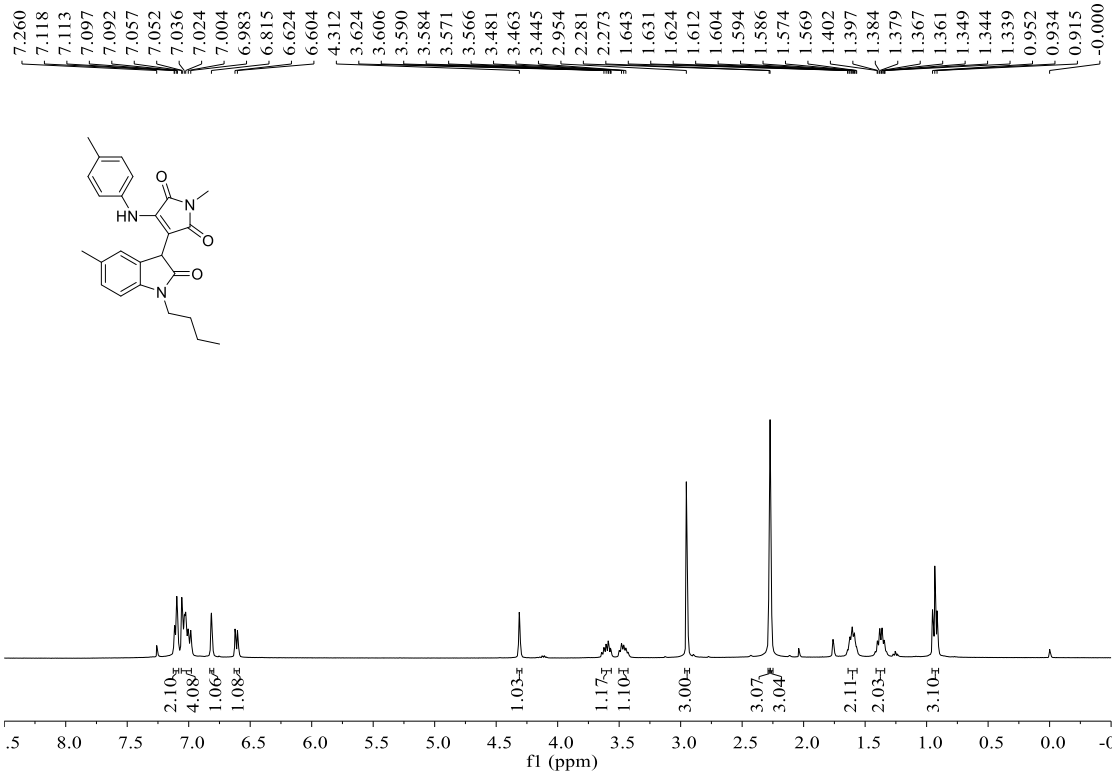
3-(1-Benzyl-5-methyl-2-oxoindolin-3-yl)-1-methyl-4-(*p*-tolylamino)-1*H*-pyrrole-2,5-dione (5a): yellow solid, 88%, 39 mg, m.p. 159-160 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.28 (m, 4H, ArH), 7.25-7.22 (m, 1H, ArH), 7.16-7.14 (d, *J* = 7.6 Hz, 2H, ArH), 7.10-7.08 (d, *J* = 8.0 Hz, 2H, ArH), 6.97 (s, 1H, ArH), 6.87 (d, *J* = 8.0 Hz, 1H, ArH), 6.82 (s, 1H, ArH), 6.43 (dd, *J* = 8.0 Hz, J_2 = 1.4 Hz, 1H, ArH), 4.84 (d, *J* = 16.0 Hz, 1H, CH), 4.73 (d, *J* = 16.0 Hz, 1H, CH), 4.41 (s, 1H, CH), 2.99 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.24 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.9, 171.9, 168.1, 141.9, 140.9, 136.5, 135.7, 134.5, 131.9, 130.1, 128.6, 128.2, 127.7, 127.4, 127.1, 124.4, 124.1, 123.7, 108.8, 95.8, 44.0, 41.6, 23.9, 21.1, 20.9; IR (KBr) υ: 1770, 1708, 1657, 1604, 1529, 1499, 1454, 1392, 1289, 1195, 1173, 999, 917, 823, 801, 765 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{28}H_{25}N_3NaO_3$ ([M+Na]$^{+}$): 474.1788, Found: 474.1785.

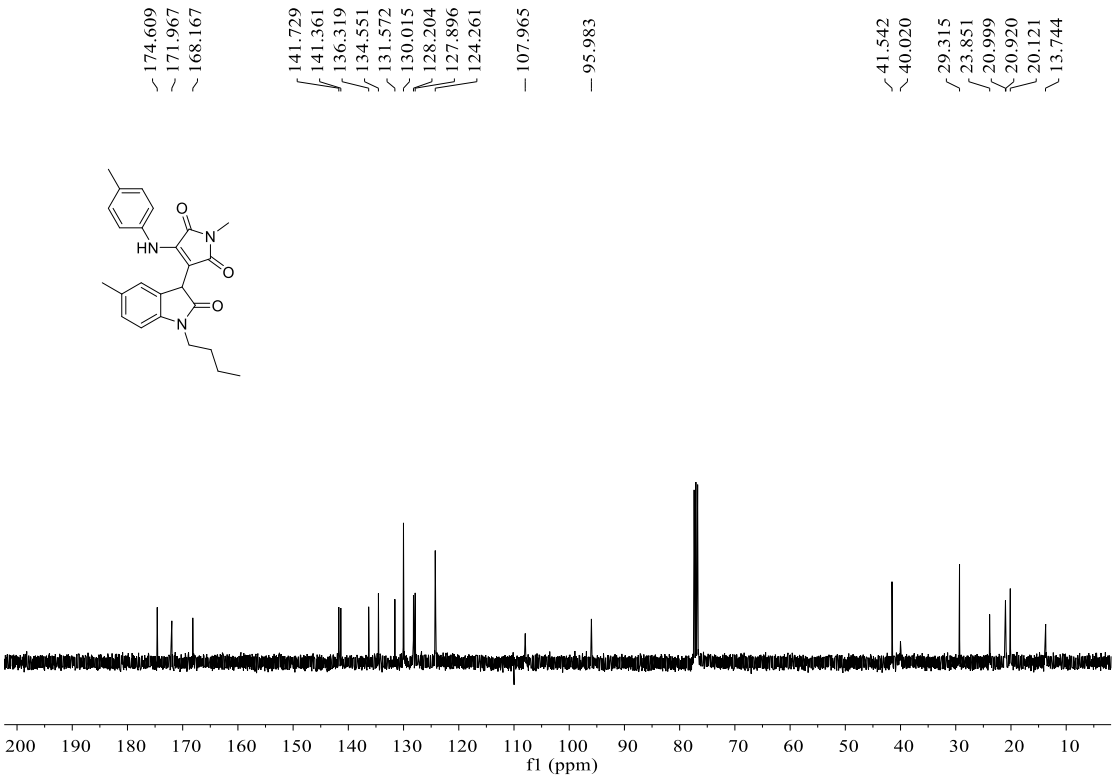


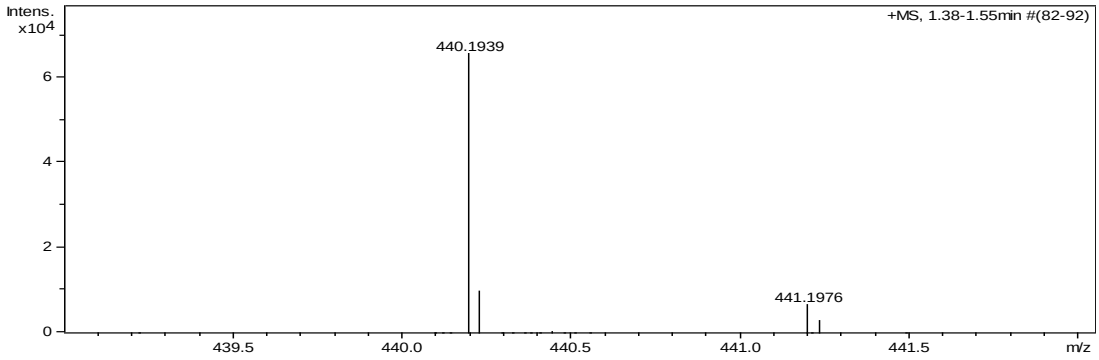

174.896
171.908
168.122
141.903
140.911
136.537
135.739
134.451
131.924
130.114
128.646
128.237
127.681
127.372
127.115
124.371
124.083
108.994
108.838
95.811
44.025
41.567
23.921
21.058
20.944
HN
O
N
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 0.07-0.51min #(4-30)
2000
1500
1000
500
0
474.1785
475.2177
473.0
473.5
474.0
474.5
475.0
475.5
476.0
m/z

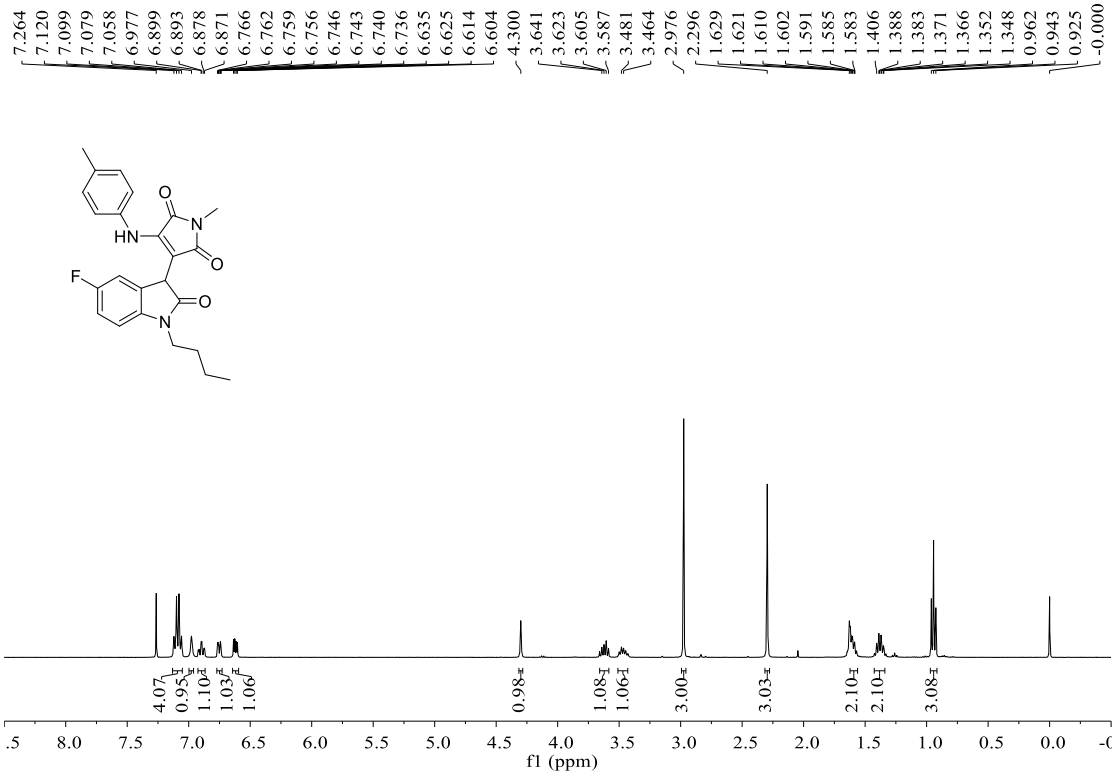
3-(1-Butyl-5-methyl-2-oxoindolin-3-yl)-1-methyl-4-(*p*-tolylamino)-1*H*-pyrrole-2,5-dione (5b): yellow solid, 85%, 35 mg, m.p. 165-167 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12-7.10 (m, 2H, ArH), 7.06-6.98 (m, 4H, ArH), 6.82 (s, 1H, ArH), 6.61 (d, *J* = 8.0 Hz, 1H, ArH), 4.31 (s, 1H, CH), 3.64-3.57 (m, 1H, CH), 3.50-3.43 (m, 1H, CH), 2.95 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 1.64-1.57 (m, 2H, CH), 1.40-1.34 (m, 2H, CH), 0.93 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 172.0, 168.2, 141.7, 141.4, 136.3, 134.6, 131.6, 130.0, 128.2, 127.9, 124.3, 108.0, 96.0, 41.5, 40.0, 29.3, 23.9, 21.0, 20.9, 20.1, 13.7; IR (KBr) υ: 1766, 1707, 1655, 1603, 1583, 1525, 1497, 1441, 1393, 1354, 1339, 1249, 1194, 1105, 1067, 1099, 990, 819 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{27}N_3NaO_3$ ([M+Na]$^+$): 440.1945, Found: 440.1939.

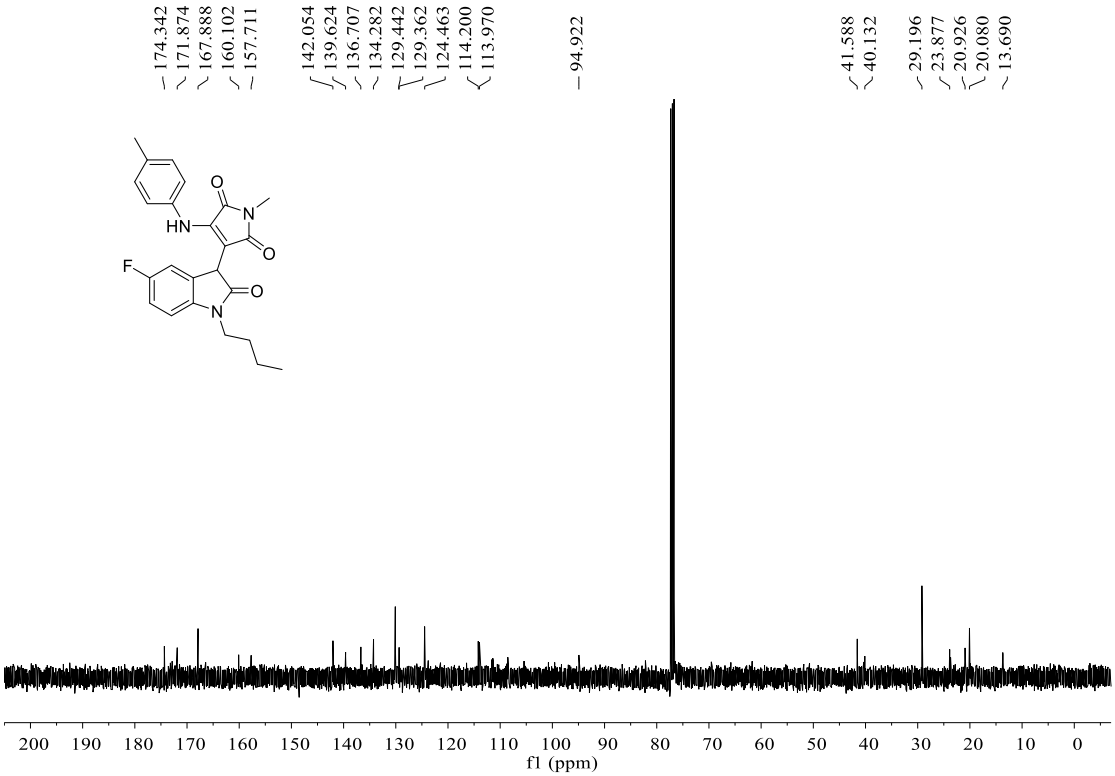


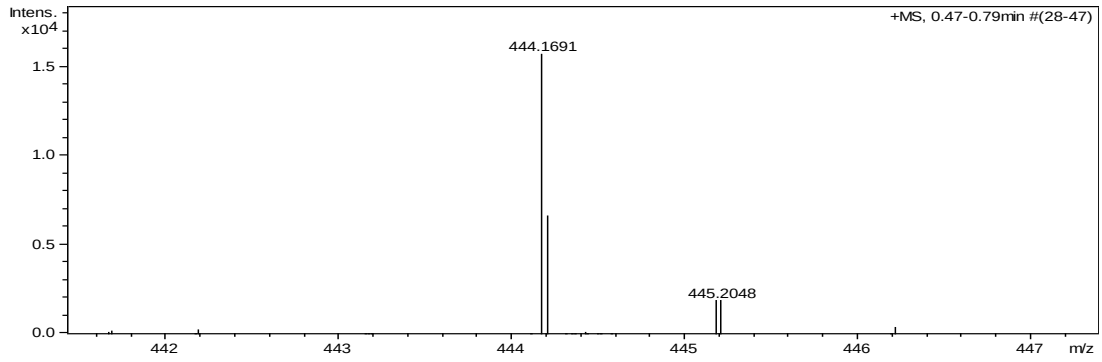

174.609
171.967
168.167
141.729
141.361
136.319
134.551
131.572
130.015
128.204
127.896
124.261
107.965
95.983
41.542
40.020
29.315
23.851
20.999
20.920
20.121
13.744
HN
O
N
O
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^4
+MS, 1.38-1.55min #(82-92)
440.1939
441.1976
6
4
2
0
439.5
440.0
440.5
441.0
441.5
m/z

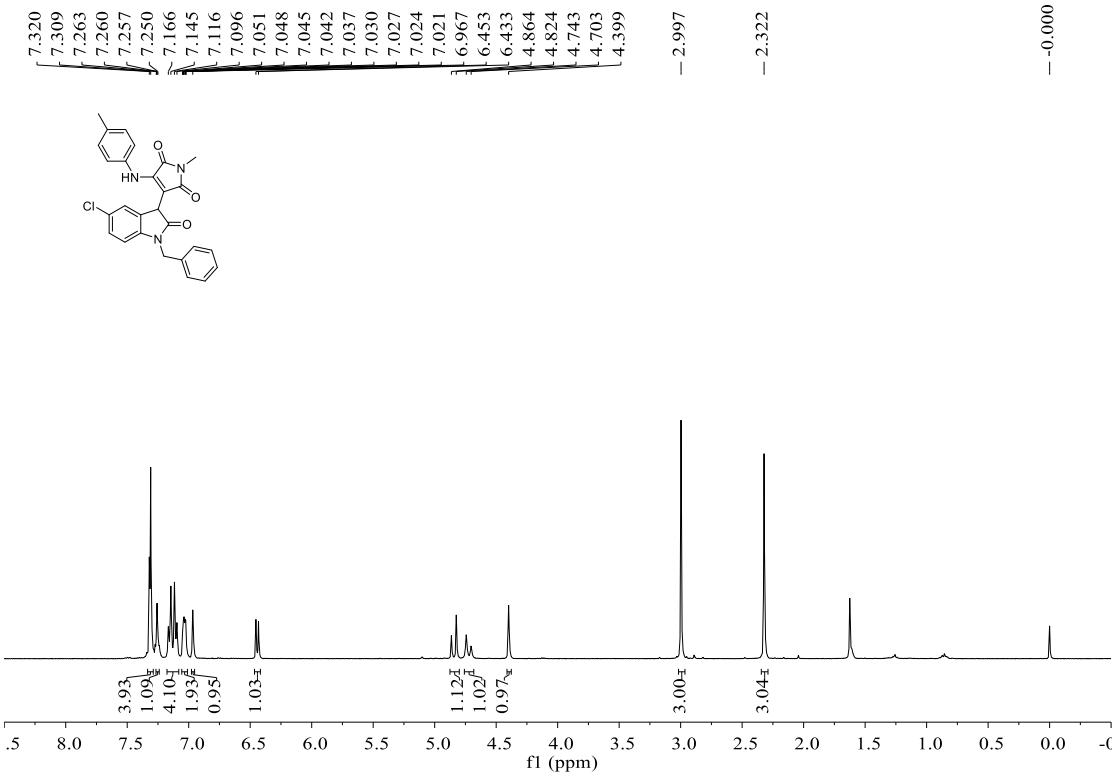
3-(1-Butyl-5-fluoro-2-oxoindolin-3-yl)-1-methyl-4-(*p*-tolylamino)-1*H*-pyrrole-2,5-dione (5c): yellow solid, 87%, 36 mg, m.p. 199-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (dd, J_1 = 16.4 Hz, J_2 = 8.4 Hz, 4H, ArH), 7.0 (s, 1H, ArH), 6.90 (td, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H, ArH), 6.77-6.74 (m, 1H, ArH), 6.62 (q, J = 4.0 Hz, 1H, ArH), 4.30 (s, 1H, CH), 3.66-3.59 (m, 1H, CH), 3.50-3.43 (m, 1H, CH), 2.98 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 1.61-1.57 (m, 2H, CH), 1.42-1.33 (m, 2H, CH), 0.94 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 171.9, 167.9, 160.1, 157.7, 142.1, 139.6, 136.7, 134.3, 129.44, 129.36, 124.5, 114.2, 114.0, 94.9, 41.6, 40.1, 29.2, 23.9, 20.9, 20.1, 13.7; IR (KBr) υ: 1771, 1704, 1660, 1491, 1455, 943, 858, 829, 815, 805, 793, 764 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{24}FN_3NaO_3$ ([M+Na]$^+$): 444.1694, Found: 444.1691.

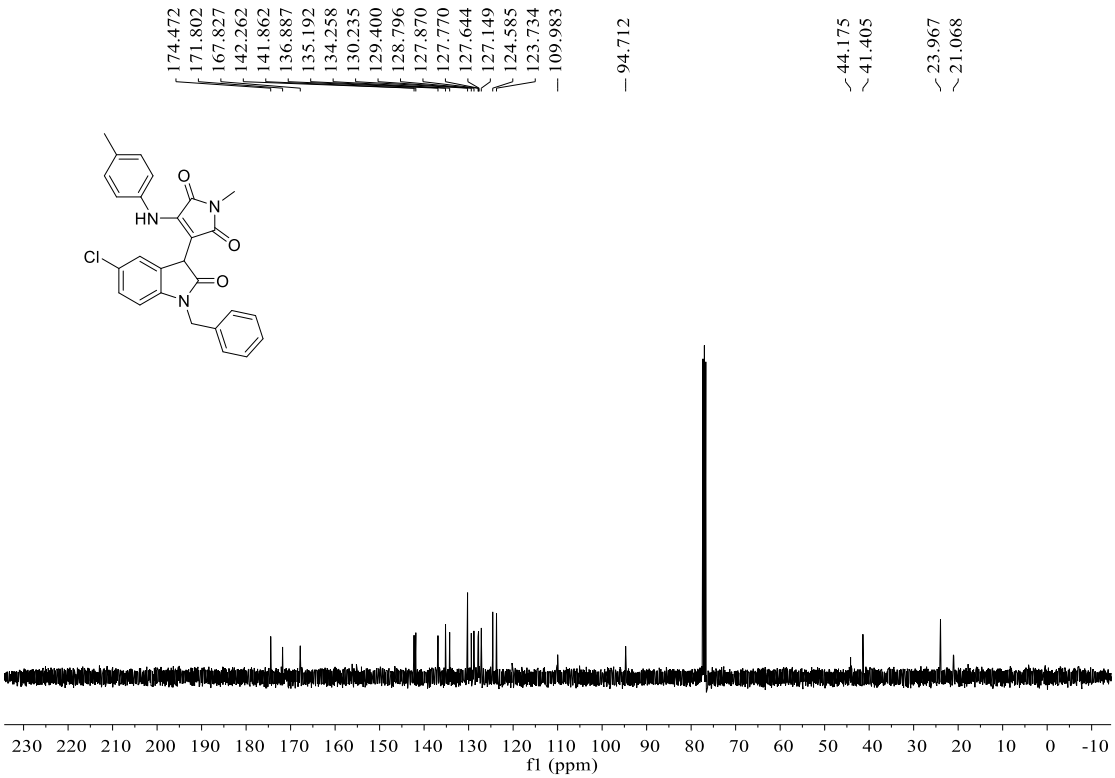


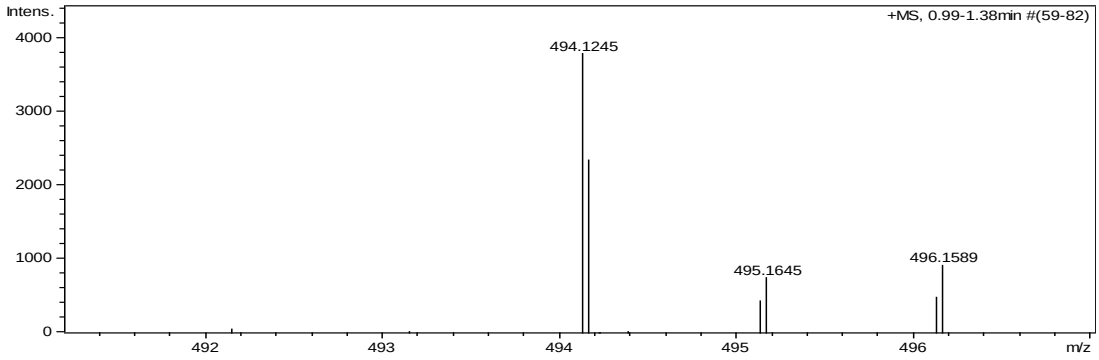

174.342
171.874
167.888
160.102
157.711
142.054
139.624
136.707
134.282
129.442
129.362
124.463
114.200
113.970
94.922
41.588
40.132
29.196
23.877
20.926
20.080
13.690
HN
O
N
O
F
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^4
+MS, 0.47-0.79min #(28-47)
444.1691
445.2048
1.5
1.0
0.5
0.0
442
443
444
445
446
447
m/z

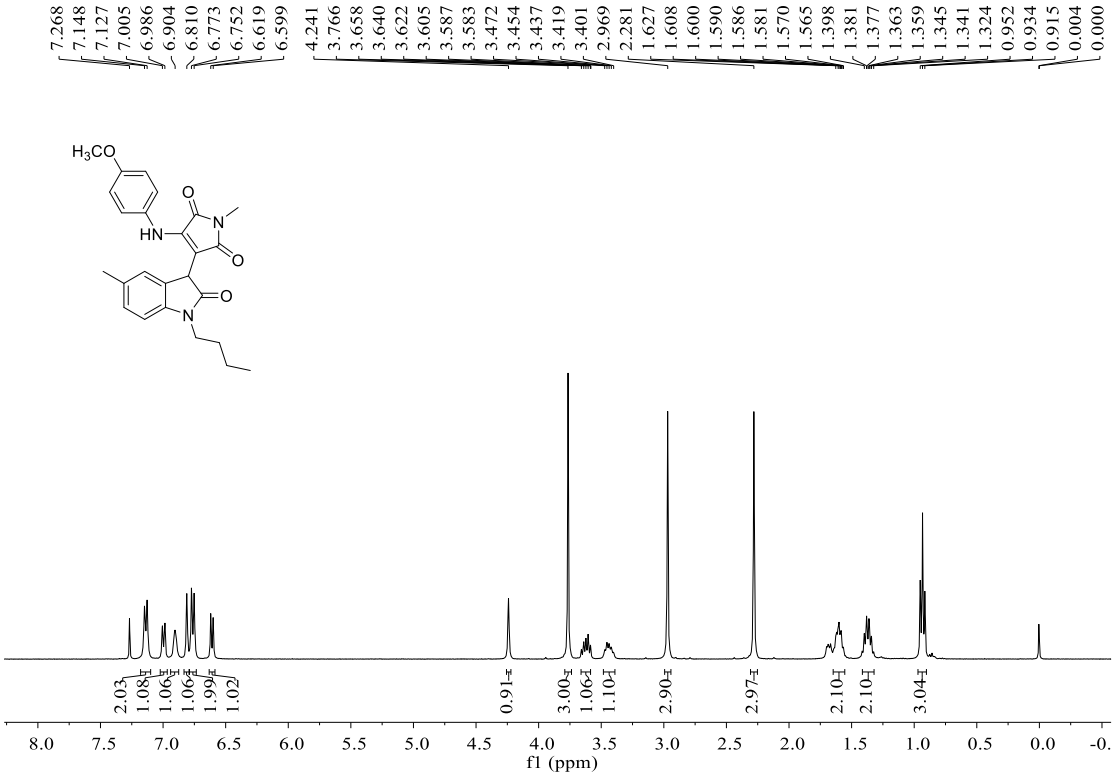
3-(1-Benzyl-5-chloro-2-oxoindolin-3-yl)-1-methyl-4-(*p*-tolylamino)-1*H*-pyrrole-2,5-dione (5d): yellow solid, 86%, 40 mg, m.p. 210-211 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.31 (m, 4H, ArH), 7.26-7.25 (m, 1H, ArH), 7.13 (dd, J_1 = 20.0 Hz, J_2 = 8.4 Hz, 4H, ArH), 7.05-7.02 (m, 2H, ArH), 6.97 (s, 1H, ArH), 6.44 (d, J = 8.0 Hz, 1H, ArH), 4.84 (d, J = 16.0 Hz, 1H, CH), 4.72 (d, J = 16.0 Hz, 1H, CH), 4.40 (s, 1H, CH), 3.0 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 171.8, 167.8, 142.3, 141.9, 136.9, 135.2, 134.3, 130.2, 129.4, 128.8, 127.9, 127.8, 127.6, 127.2, 124.6, 123.7, 110.0, 94.7, 44.2, 41.4, 24.0, 21.1; IR (KBr) υ: 1770, 1732, 1709, 1660, 1610, 1526, 1507, 1485, 1455, 1394, 1339, 1215, 1161, 1105, 1072, 999, 866, 813, 762 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{27}H_{22}ClN_3NaO_3$ ([M+Na]$^+$): 494.1242, Found: 494.1245.

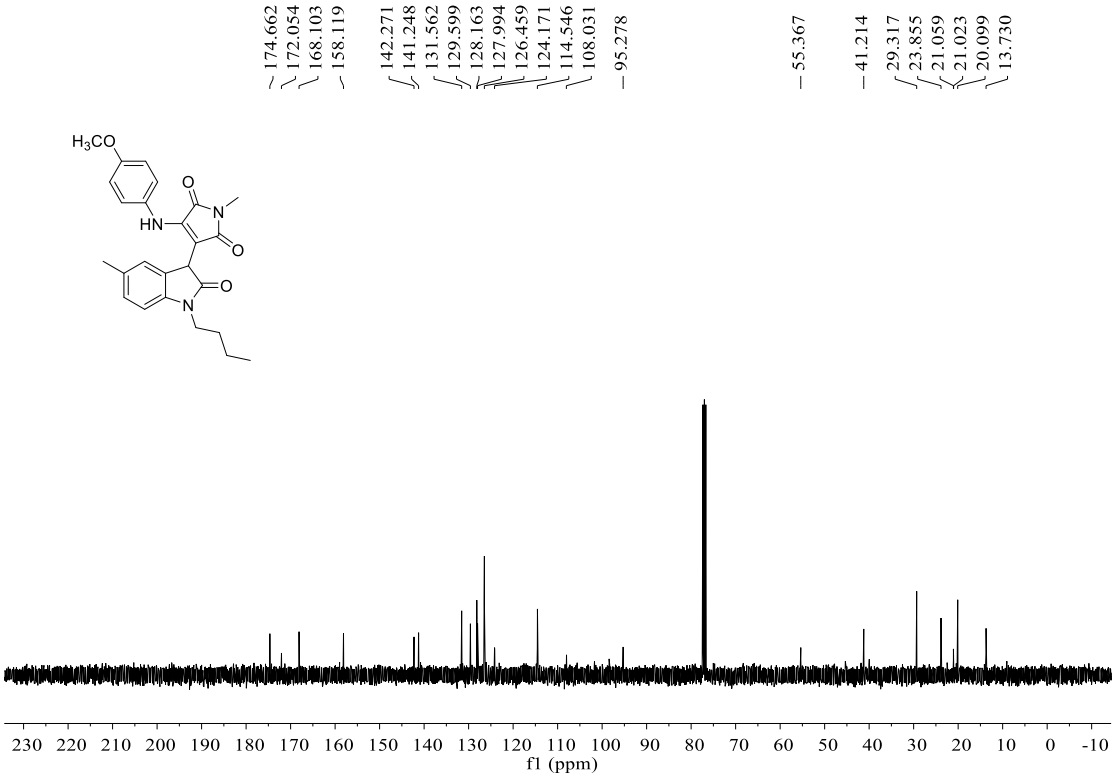


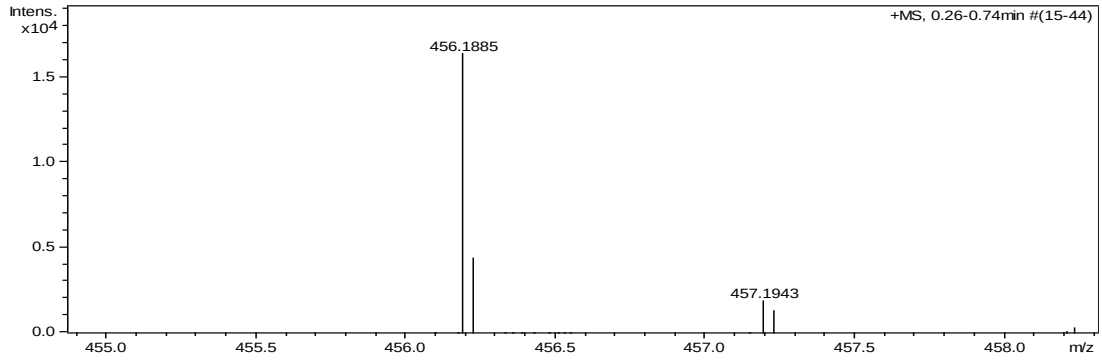

174.472
171.802
167.827
142.262
141.862
136.887
135.192
134.258
130.235
129.400
128.796
127.870
127.770
127.644
127.149
124.585
123.734
109.983
94.712
44.175
41.405
23.967
21.068
HN
O
N
O
Cl
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 0.99-1.38min #(59-82)
4000
3000
2000
1000
0
494.1245
495.1645
496.1589
492
493
494
495
496
m/z

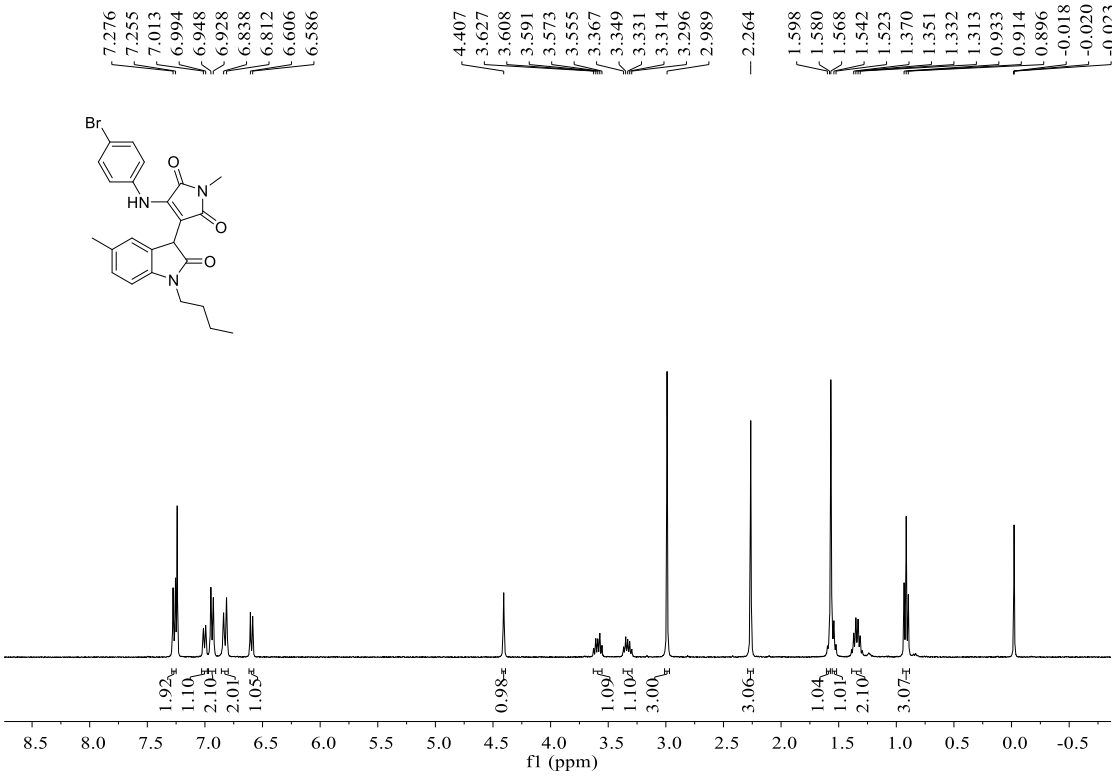
3-(1-Butyl-5-methyl-2-oxoindolin-3-yl)-4-((4-methoxyphenyl)amino)-1-methyl-1*H*-pyrrole-2,5-dione (5e): yellow solid, 88%, 38 mg, m.p. 163-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14 (d, *J* = 8.4 Hz, 2H, ArH), 7.0 (d, *J* = 7.6 Hz, 1H, ArH), 6.9 (s, 1H, ArH), 6.81 (s, 1H, ArH), 6.76 (d, *J* = 8.4 Hz, 2H, ArH), 6.61 (d, *J* = 7.6 Hz, 1H, ArH), 4.24 (s, 1H, CH), 3.77 (s, 3H, CH_3), 3.66-3.58 (m, 1H, CH), 3.47-3.40 (m, 1H, CH), 2.97 (s, 3H, CH_3), 2.28 (s, 3H, OCH_3), 1.63-1.56 (m, 2H, CH), 1.40-1.32 (m, 2H, CH), 0.93 (t, *J* = 7.2 Hz, 3H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.7, 172.1, 168.1, 158.1, 142.3, 141.3, 131.6, 129.6, 128.2, 128.0, 126.5, 124.2, 114.6, 108.0, 95.3, 55.4, 41.2, 29.3, 23.9, 21.1, 21.0, 20.1, 13.7; IR (KBr) υ: 1767, 1706, 1693, 1647, 1596, 1540, 1509, 1495, 1446, 1386, 1348, 1293, 1241, 1203, 1181, 1105, 1025, 996, 866, 832 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{27}N_3NaO_4$ ([M+Na]$^+$): 456.1894, Found: 456.1885.

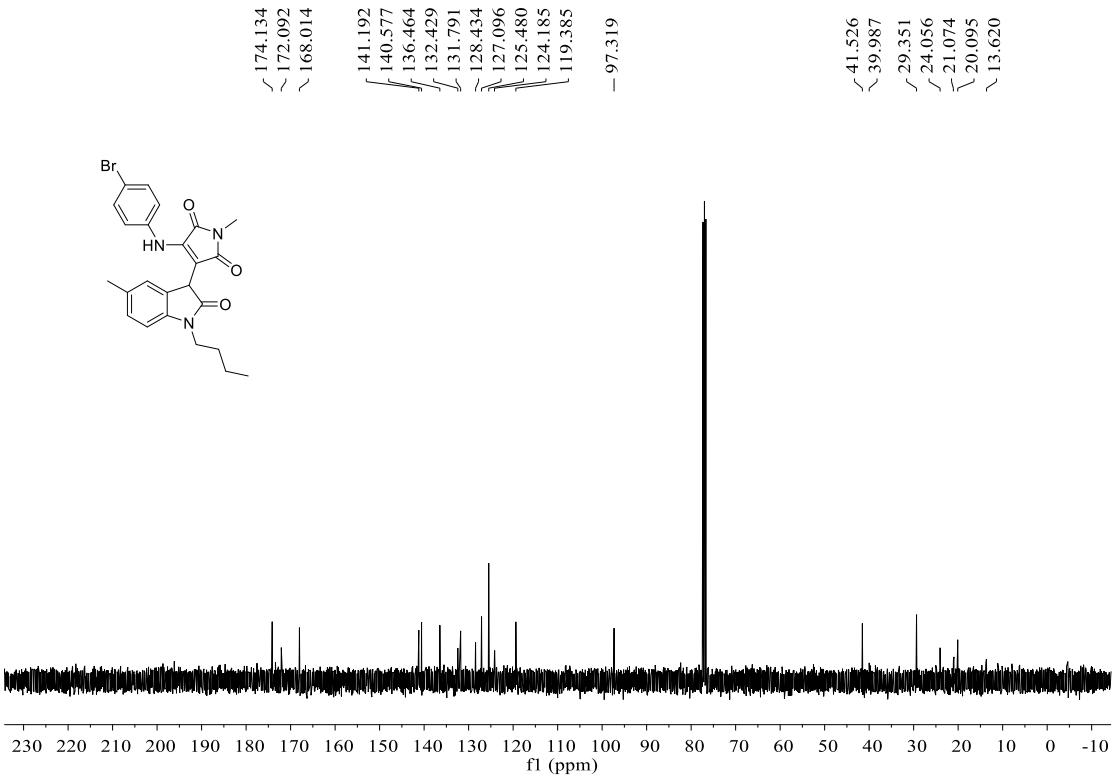


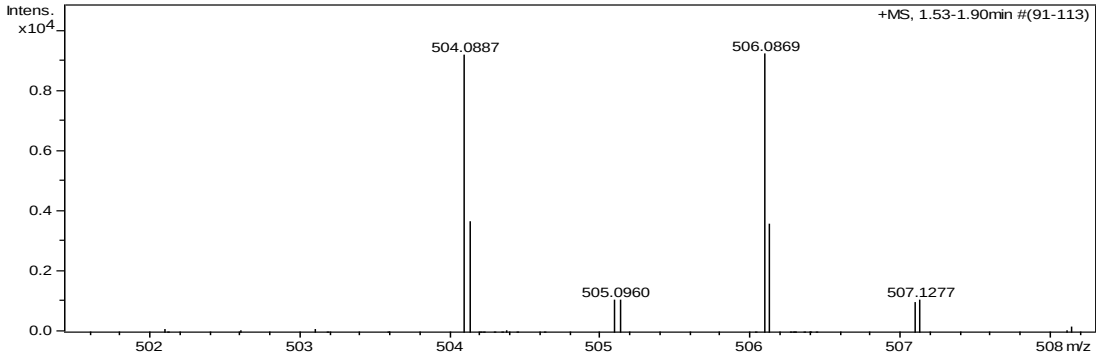

174.662
172.054
168.103
158.119
142.271
141.248
131.562
129.599
128.163
127.994
126.459
124.171
114.546
108.031
95.278
55.367
41.214
29.317
23.855
21.059
21.023
20.099
13.730
H3CO
HN
O
N
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 0.26-0.74min #(15-44)
456.1885
457.1943
1.5
1.0
0.5
0.0
455.0
455.5
456.0
456.5
457.0
457.5
458.0
m/z

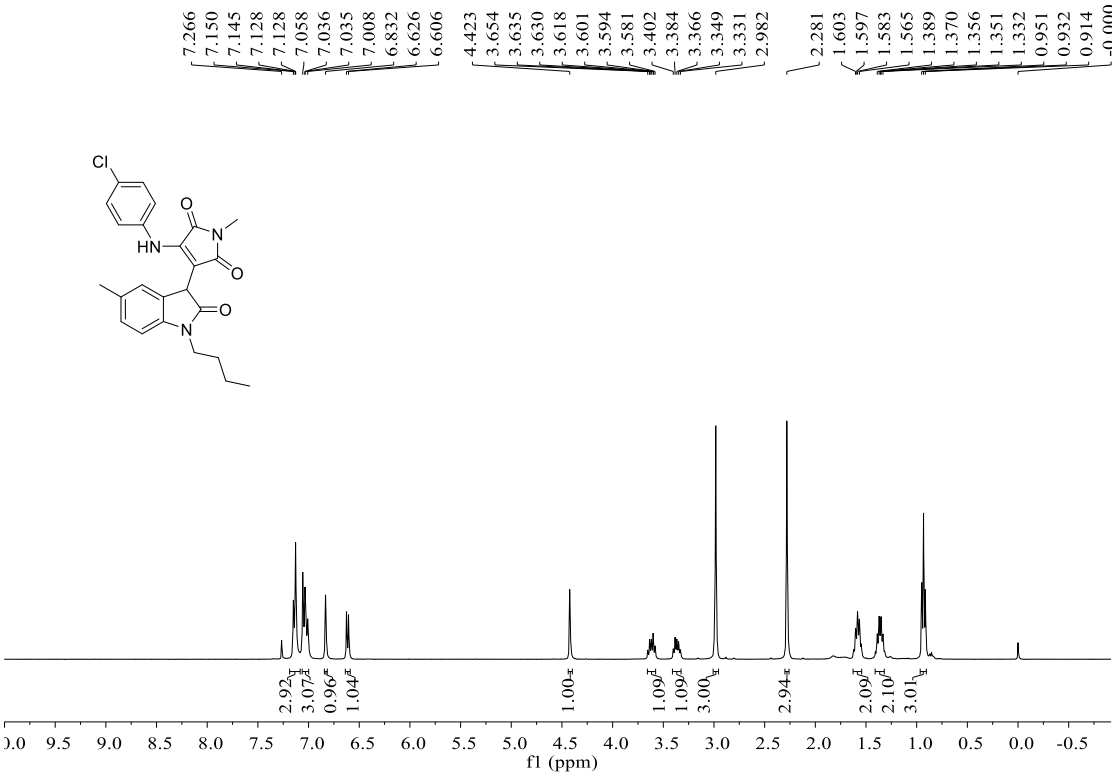
3-((4-Bromophenyl)amino)-4-(1-butyl-5-methyl-2-oxoindolin-3-yl)-1-methyl-1*H*-pyrrole-2,5-dione (5f): yellow solid, 72%, 34 mg, m.p. 178-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (s, 1H, ArH), 7.0 (d, *J* = 7.6 Hz, 2H, ArH), 6.94 (d, *J* = 8.0 Hz, 2H, ArH), 6.83 (d, *J* = 6.0 Hz, 2H, ArH), 6.60 (d, *J* = 8.0 Hz, 1H, ArH), 4.40 (s, 1H, CH), 3.63-3.56 (m, 1H, CH), 3.37-3.30 (m, 1H, CH), 2.99 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.60-1.58 (m, 1H, CH), 1.54-1.52 (m, 1H, CH), 1.39-1.31 (m, 2H, CH), 0.91 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 172.1, 168.0, 141.2, 140.6, 136.5, 132.4, 131.8, 128.4, 127.1, 125.5, 124.2, 119.4, 97.3, 41.5, 40.0, 29.4, 24.1, 21.1, 20.1, 13.6; IR (KBr) υ: 1705, 1663, 1624, 1602, 1583, 1527, 1497, 1456, 1404, 1388, 1342, 1243, 1200, 1175, 1148, 1074, 996, 863, 833, 762 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{24}BrN_3NaO_3$ ([M+Na]$^+$): 504.0893, Found: 504.0887.

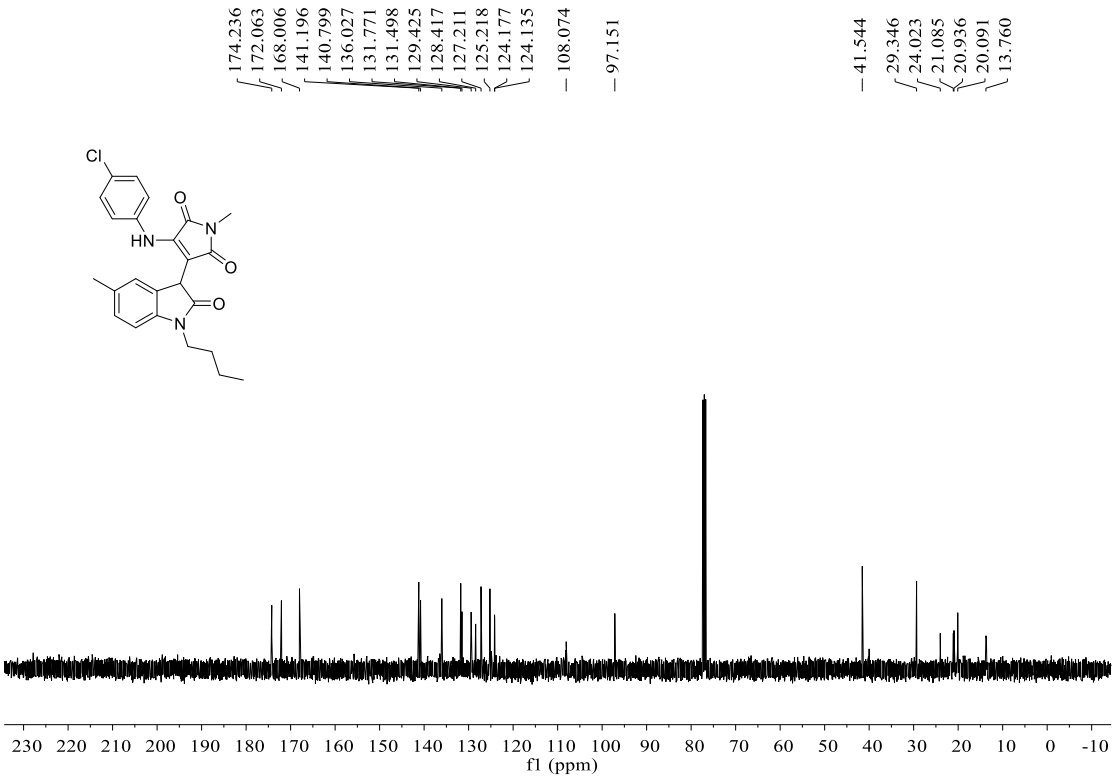


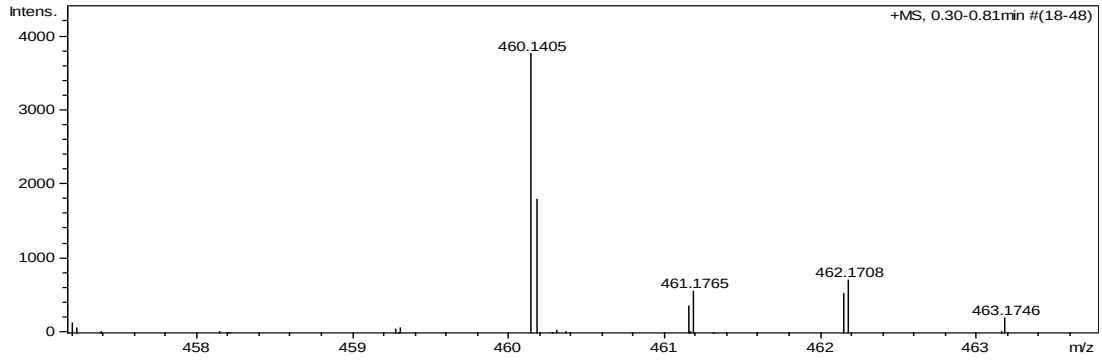

174.134
172.092
168.014
141.192
140.577
136.464
132.429
131.791
128.434
127.096
125.480
124.185
119.385
97.319
41.526
39.987
29.351
24.056
21.074
20.095
13.620
Br
HN
O
N
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 1.53-1.90min #(91-113)
504.0887
506.0869
505.0960
507.1277
0.0
0.2
0.4
0.6
0.8
502
503
504
505
506
507
508 m/z

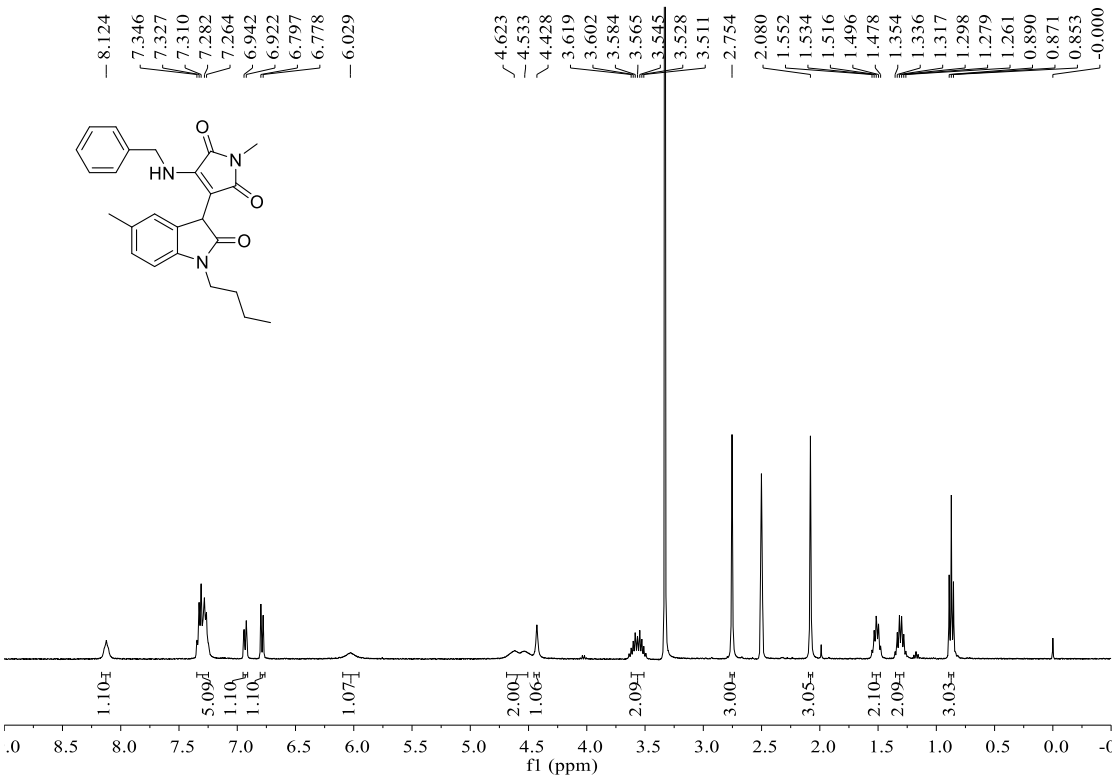
3-(1-Butyl-5-methyl-2-oxoindolin-3-yl)-4-((4-chlorophenyl)amino)-1-methyl-1*H*-pyrrole-2,5-dione (5g): yellow solid, 70%, 30 mg, m.p. 174-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15-7.13 (m, 3H, ArH), 7.06-7.01 (m, 3H, ArH), 6.83 (s, 1H, ArH), 6.62 (d, *J* = 8.0 Hz, 1H, ArH), 4.42 (s, 1H, CH), 3.65-3.58 (m, 1H, CH), 3.40-3.33 (m, 1H, CH), 2.98 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 1.62-1.55 (m, 2H, CH), 1.41-1.33 (m, 2H, CH), 0.93 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 172.1, 168.0, 141.2, 140.8, 136.0, 131.8, 131.5, 129.4, 128.4, 127.2, 125.2, 124.2, 124.1, 108.1, 97.2, 41.5, 29.4, 24.0, 21.1, 20.9, 20.1, 13.8; IR (KBr) υ: 1770, 1706, 1663, 1587, 1527, 1494, 1457, 1388, 1342, 1285, 1244, 1200, 1176, 1103, 996, 962, 936, 883, 836, 807 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{24}ClN_3NaO_3$ ([M+Na]$^+$): 460.1398, Found: 460.1405.

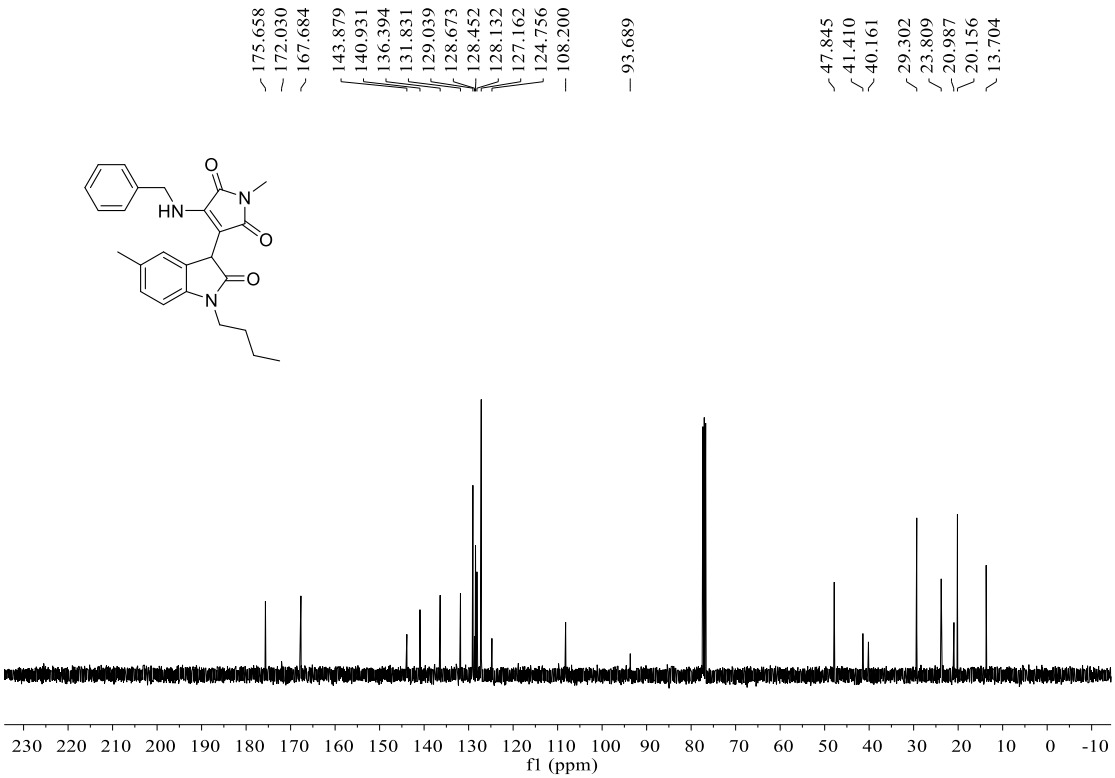


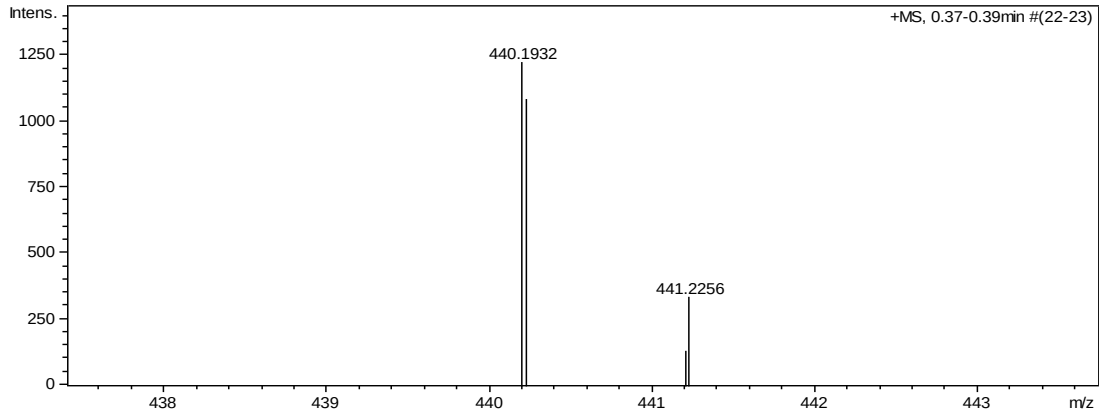

174.236
172.063
168.006
141.196
140.799
136.027
131.771
131.498
129.425
128.417
127.211
125.218
124.177
124.135
108.074
97.151
41.544
29.346
24.023
21.085
20.936
20.091
13.760
Cl
HN
O
N
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 0.30-0.81min #(18-48)
4000
3000
2000
1000
0
460.1405
461.1765
462.1708
463.1746
458
459
460
461
462
463
m/z

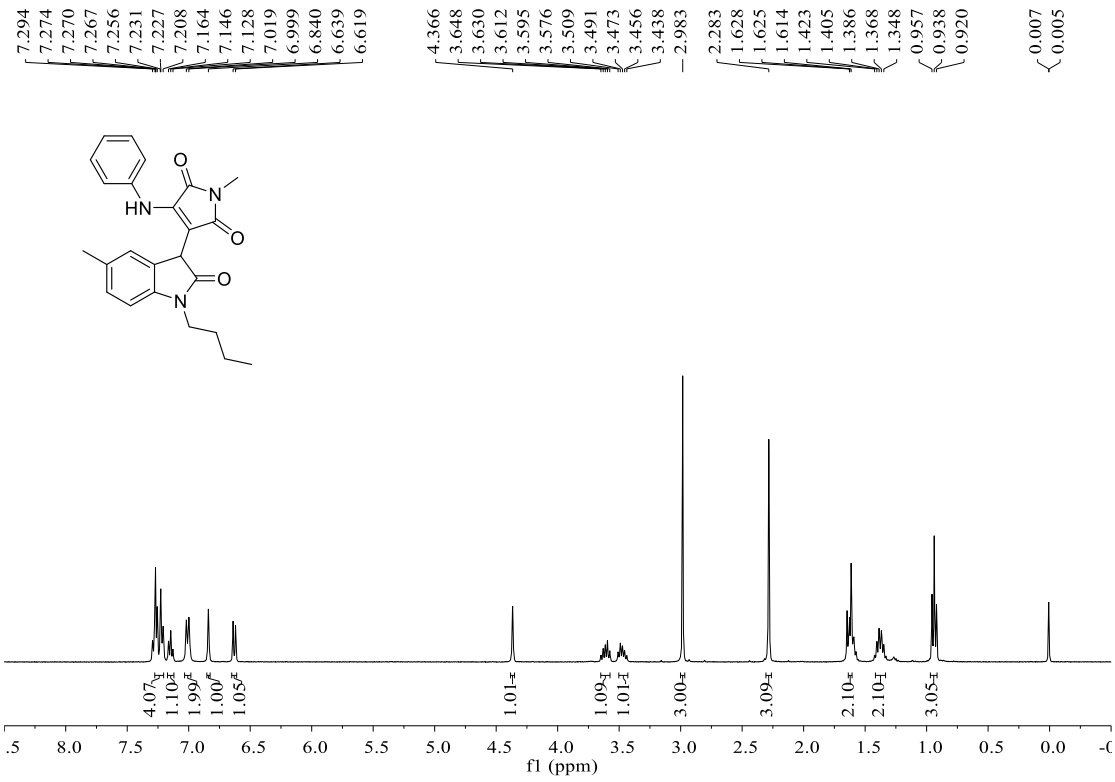
3-(Benzylamino)-4-(1-butyl-5-methyl-2-oxoindolin-3-yl)-1-methyl-1*H*-pyrrole-2,5-dione (5h): yellow solid, 84%, 35 mg, m.p. 172-173 °C; ^{1}H NMR (400 MHz, DMSO) δ: 8.12 (s, 1H, CH), 7.35-7.26 (m, 5H, ArH), 6.93 (d, *J* = 8.0 Hz, 1H, ArH), 6.79 (d, *J* = 7.6 Hz, 1H, ArH), 6.03 (s, 1H, ArH), 4.62-4.53 (m, 2H, CH), 4.43 (s, 1H, CH), 3.62-3.51 (m, 2H, CH), 2.75 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 1.55-1.48 (m, 2H, CH), 1.35-1.26 (m, 2H, CH), 0.87 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.7, 172.0, 167.7, 143.9, 140.9, 136.4, 131.8, 129.0, 128.7, 128.5, 128.1, 127.2, 124.8, 108.2, 93.7, 47.9, 41.4, 40.2, 29.3, 23.8, 21.0, 20.2, 13.7; IR (KBr) υ: 1717, 1687, 1661, 1603, 1534, 1496, 1455, 1387, 1343, 1203, 1105, 994, 963, 816, 775 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{27}N_3NaO_3$ ([M+Na]$^{+}$): 440.1945, Found: 440.1932.

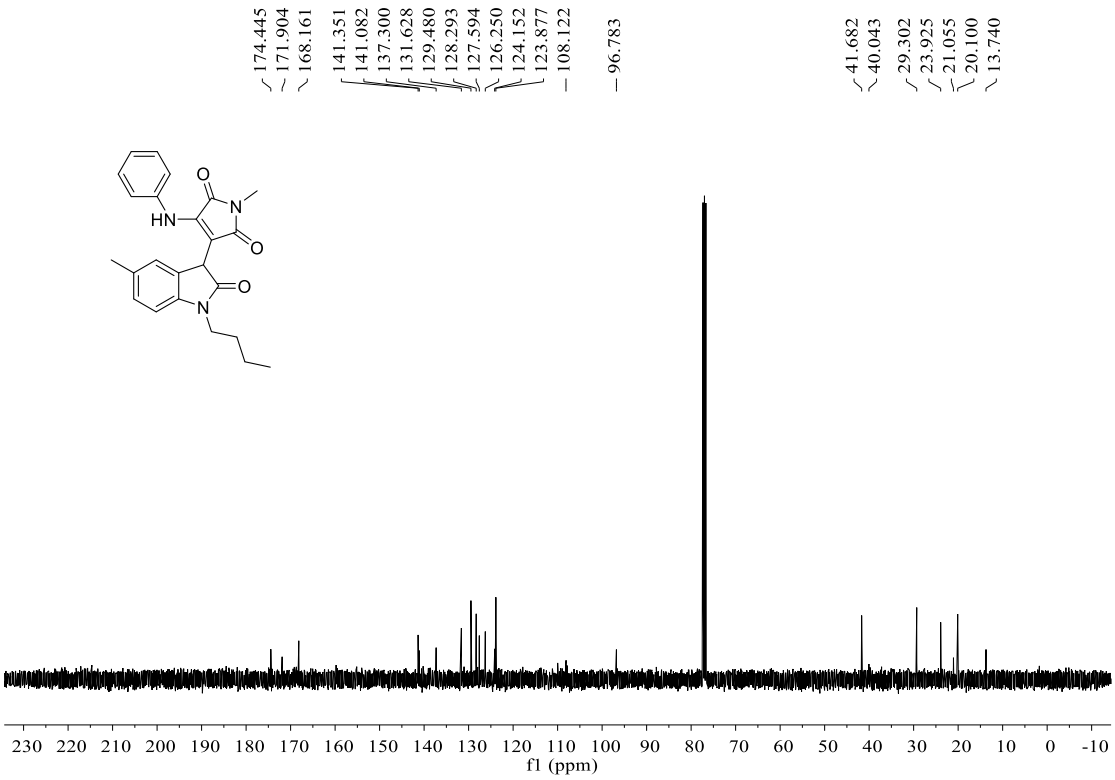


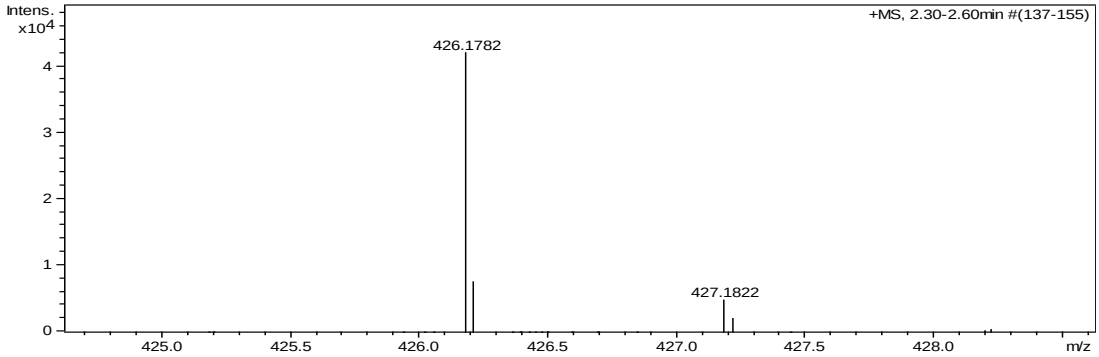

175.658
172.030
167.684
143.879
140.931
136.394
131.831
129.039
128.673
128.452
128.132
127.162
124.756
108.200
93.689
47.845
41.410
40.161
29.302
23.809
20.987
20.156
13.704
HN
O
N
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 0.37-0.39min #(22-23)
1250
1000
750
500
250
0
440.1932
441.2256
438
439
440
441
442
443
m/z

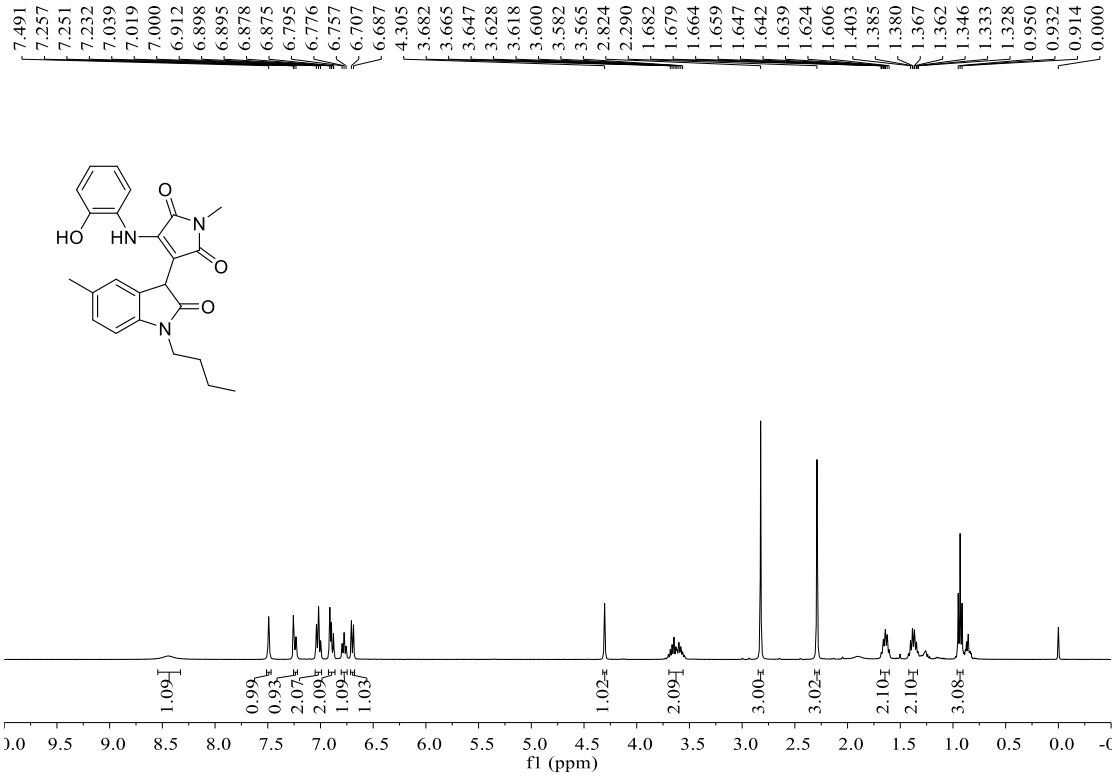
(*Z*)-3-(1-Butyl-5-methyl-2-oxoindolin-3-ylidene)-1-methyl-4-(phenylamino)pyrrolidine-2,5-dione (5i): yellow solid, 85%, 34 mg, m.p. 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27-7.21 (m, 4H, ArH), 7.15 (t, *J* = 7.2 Hz, 1H, ArH), 7.01 (d, *J* = 8.0 Hz, 2H, ArH), 6.84 (s, 1H, ArH), 6.63 (d, *J* = 8.0 Hz, 1H, ArH), 4.37 (s, 1H, CH), 3.65-3.58 (m, 1H, CH), 3.51-3.44 (m, 1H, CH), 2.98 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 1.63-1.61 (m, 2H, CH), 1.42-1.35 (m, 2H, CH), 0.94 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 171.9, 168.2, 141.4, 141.1, 137.3, 131.6, 129.5, 128.3, 127.6, 126.3, 124.2, 123.9, 108.1, 96.8, 41.7, 40.0, 29.3, 23.9, 21.1, 20.1, 13.7; IR (KBr) υ: 1717, 1685, 1623, 1548, 1489, 1458, 1378, 1343, 1218, 1201, 1199, 1145, 1104, 997, 967, 834, 776 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{25}N_3NaO_3$ ([M+Na]$^+$): 426.1788, Found: 426.1782.

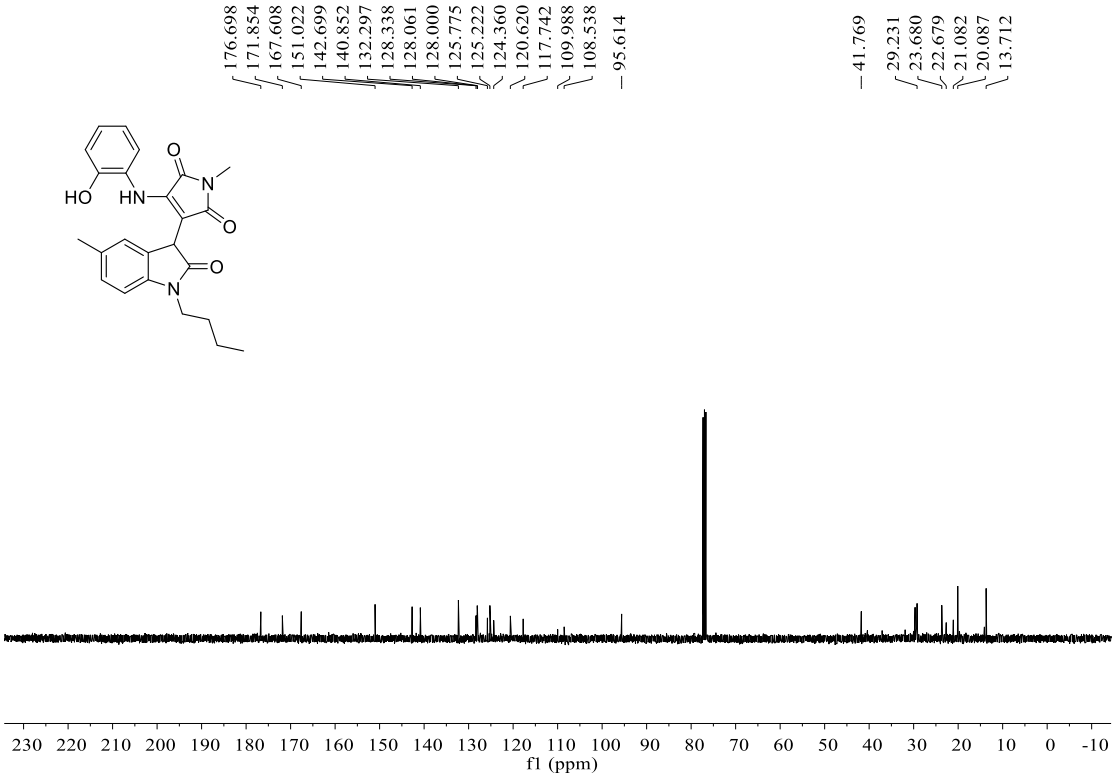


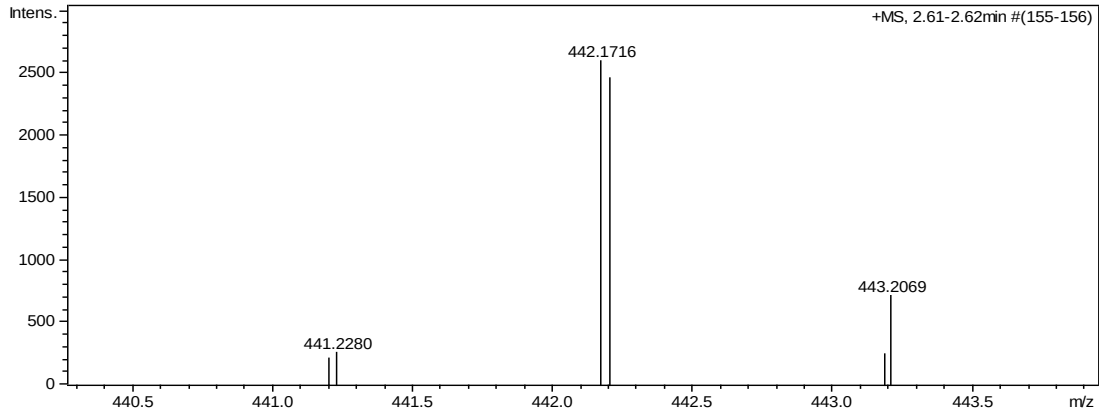

174.445
171.904
168.161
141.351
141.082
137.300
131.628
129.480
128.293
127.594
126.250
124.152
123.877
108.122
96.783
41.682
40.043
29.302
23.925
21.055
20.100
13.740
HN
O
N
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 2.30-2.60min #(137-155)
426.1782
427.1822
4
3
2
1
0
425.0
425.5
426.0
426.5
427.0
427.5
428.0
m/z

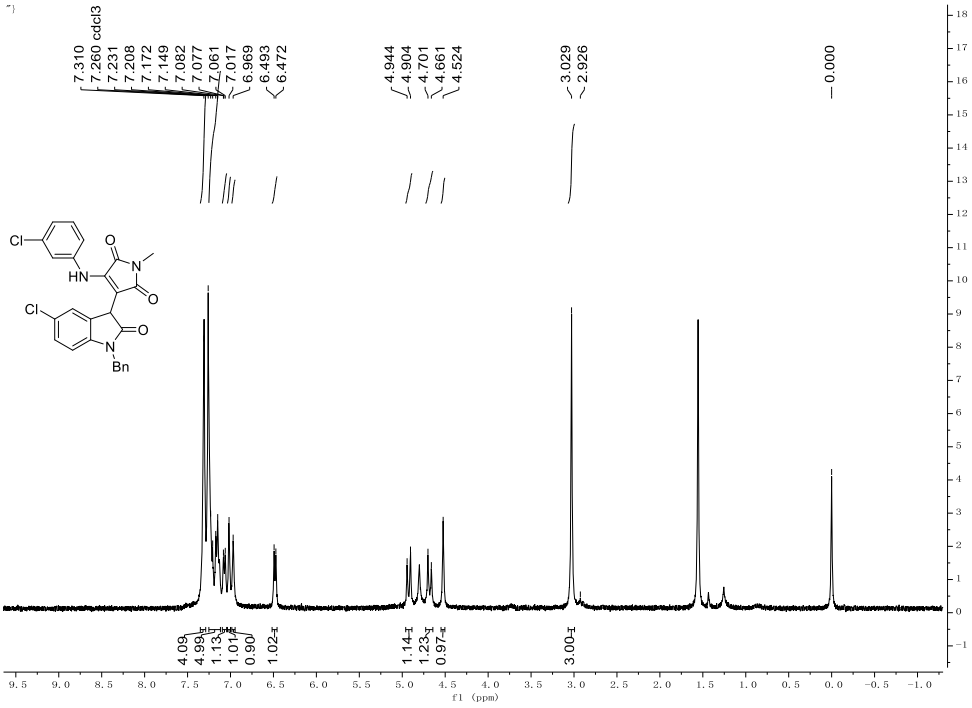
3-(1-Butyl-5-methyl-2-oxoindolin-3-yl)-4-((2-hydroxyphenyl)amino)-1-methyl-1*H*-pyrrole-2,5-dione (5j) yellow solid, 60%, 25 mg, m.p. 217-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (s, 1H, CH), 7.49 (s, 1H, ArH), 7.25-7.23 (m, 1H, ArH), 7.02 (t, *J* = 8.0 Hz, 2H, ArH), 6.91-6.88 (m, 2H, ArH), 6.78 (t, *J* = 7.6 Hz, 1H, ArH), 6.70 (d, *J* = 8.0 Hz,1H, ArH), 4.31 (s, 1H, CH), 3.70-3.55 (m, 2H, CH), 2.82 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 1.68-1.61 (m, 2H, CH), 1.42-1.31 (m, 2H, CH), 0.93 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 171.8, 167.6, 151.0, 142.7, 140.9, 132.3, 128.3, 128.1, 125.8, 124.4, 120.6, 117.7, 110.0, 108.5, 95.6, 41.8, 29.2, 23.7, 22.7, 21.1, 20.1, 13.7; IR (KBr) υ: 1704, 1659, 1596, 1528, 1494, 1456, 1387, 1228, 1106, 927, 877, 813, 771 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{25}N_3NaO_4$ ([M+Na]$^+$): 442.1737 , Found: 442.1716.

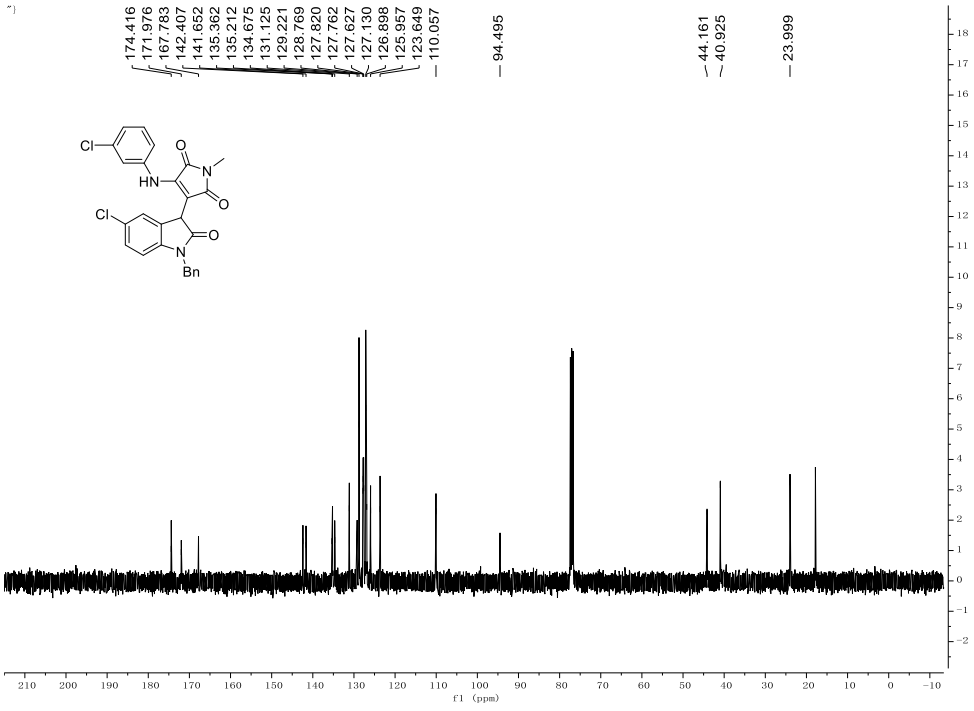


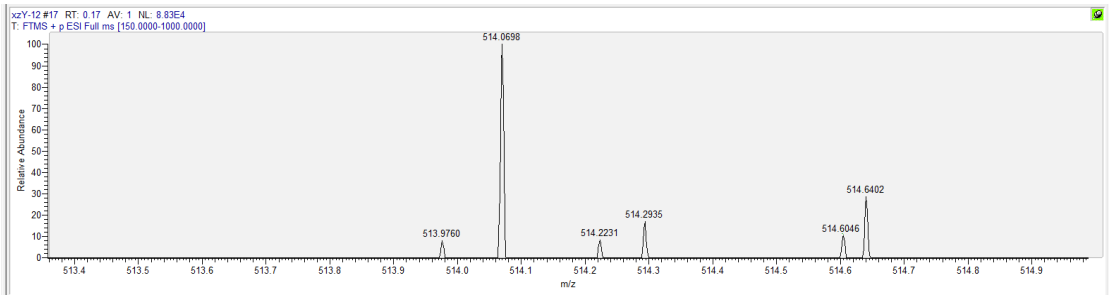

176.698
171.854
167.608
151.022
142.699
140.852
132.297
128.338
128.061
128.000
125.775
125.222
124.360
120.620
117.742
109.988
108.538
95.614
41.769
29.231
23.680
22.679
21.082
20.087
13.712
HO
HN
O
N
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 2.61-2.62min #(155-156)
442.1716
443.2069
441.2280
2500
2000
1500
1000
500
0
440.5
441.0
441.5
442.0
442.5
443.0
443.5
m/z

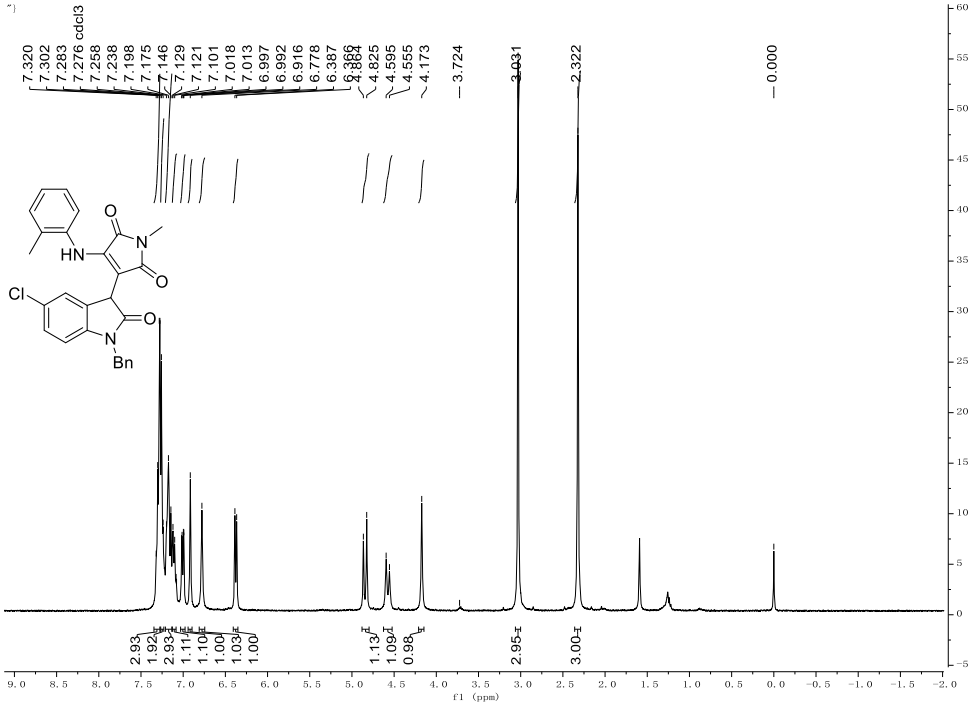
(*Z*)-3-(1-Benzyl-5-chloro-2-oxoindolin-3-ylidene)-4-((3-chlorophenyl)amino)-1-methylpyrrolidine-2,5-dione (5k): yellow solid, 49%, 24 mg, m.p. 182-183 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (s, 4H, ArH), 7.25-7.12 (m, 5H, ArH), 7.07 (d, *J* = 8.5 Hz, 1H, ArH), 7.02 (s, 1H, ArH), 6.97 (s, 1H, ArH), 6.48 (d, *J* = 8.3 Hz, 1H, ArH), 4.92 (d, *J* = 15.8 Hz, 1H, CH), 4.68 (d, *J* = 15.8 Hz, 1H, CH), 4.52 (s, 1H, CH), 3.03 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, CDCl3) δ: 174.4, 172.0, 167.8, 142.4, 141.7, 135.4, 135.2, 134.7, 131.1, 129.2, 128.8, 127.82, 127.76, 127.6, 127.1, 126.9, 126.0, 123.7, 110.1, 94.5, 44.2, 40.9, 24.0; IR (KBr) υ: 1772, 1707, 1667, 1610, 1593, 1531, 1484, 1456, 1392, 1340, 1260, 1173, 813, 760 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{19}Cl_2N_3NaO_3$ ([M+Na]$^{+}$): 514.0696, Found: 514.0698.

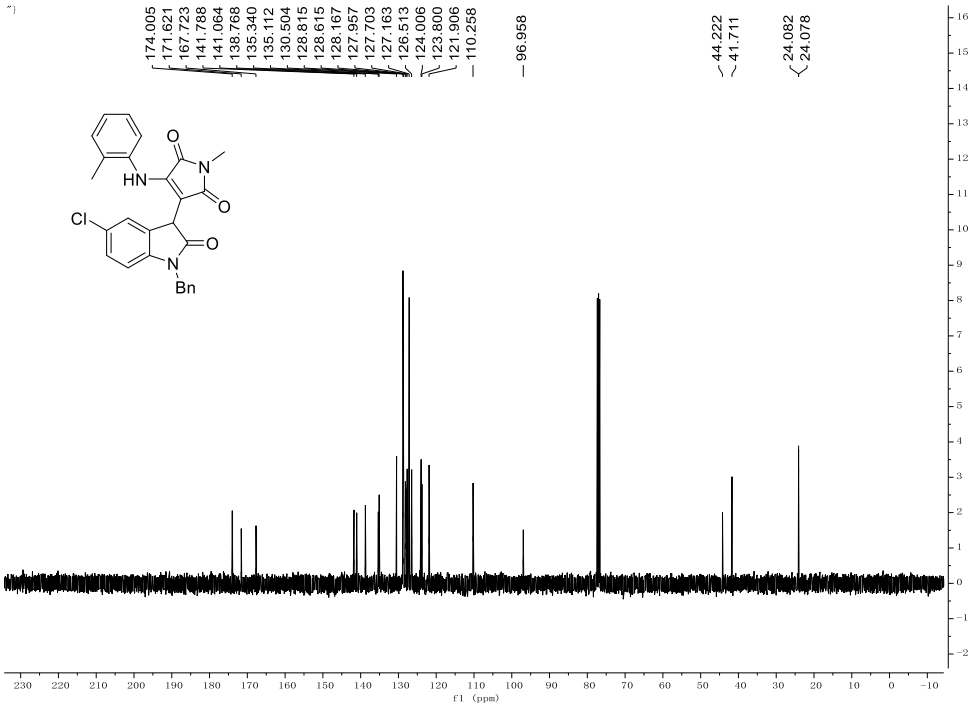


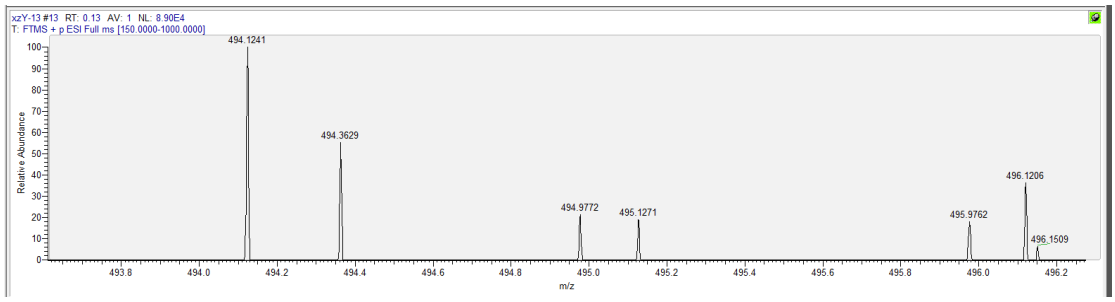

174.416
171.976
167.783
142.407
141.652
135.362
135.212
134.675
131.125
129.221
128.769
127.820
127.762
127.627
127.130
126.898
125.957
123.649
110.057
94.495
44.161
40.925
23.999
Cl
HN
O
N
O
Cl
O
N
Bn
f1 (ppm)


xzY-12 #17 RT: 0.17 AV: 1 NL: 8.83E4
T: FTMS + p ESI Full ms [150.0000-1000.0000]
514.0698
513.9760
514.2231
514.2935
514.6046
514.6402
Relative Abundance
m/z

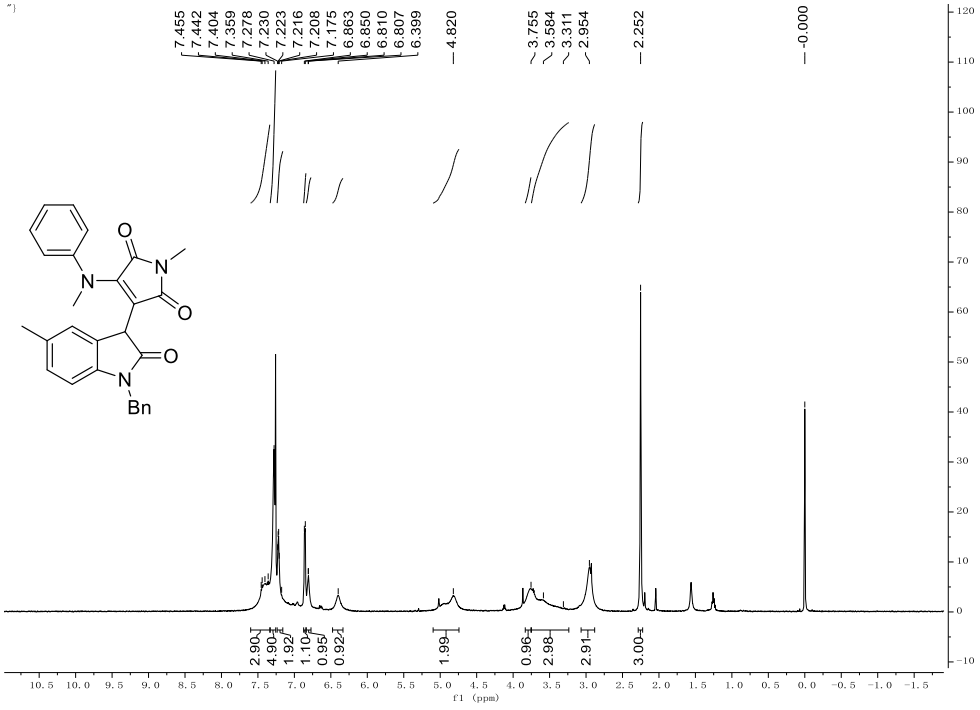
(*Z*)-3-(1-Benzyl-5-chloro-2-oxoindolin-3-ylidene)-1-methyl-4-(*o*-tolylamino)pyrrolidine-2,5-dione (5l): yellow solid, 55%, 26 mg, m.p. 184-185 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 7.4 Hz, 3H, ArH), 7.25 (d, *J* = 8.1 Hz, 2H, ArH), 7.16 (d, *J* = 11.5 Hz, 3H, ArH), 7.13-7.08 (m, 1H, ArH), 7.01 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1H, ArH), 6.92 (s, 1H, ArH), 6.78 (s, 1H, ArH), 6.38 (d, *J* = 8.3 Hz, 1H, ArH), 4.84 (d, *J* = 15.8 Hz, 1H, CH), 4.57 (d, *J* = 15.8 Hz, 1H, CH), 4.17 (s, 1H, CH), 3.03 (s, 3H, NCH_3), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl3) δ: 174.0, 171.6, 167.7, 141.8, 141.1, 138.8, 135.3, 135.1, 130.5, 128.8, 128.6, 128.2, 128.0, 127.7, 127.2, 126.5, 124.0, 123.8, 121.9, 110.3, 97.0, 44.2, 41.7, 24.082, 24.078; IR (KBr) υ: 1766, 1705, 1659, 1610, 1520, 1485, 1455, 1390, 1341, 1177, 1159, 1115, 810, 762 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{27}H_{22}ClN_3NaO_3$ ([M+Na]$^{+}$): 494.1242, Found: 494.1241.

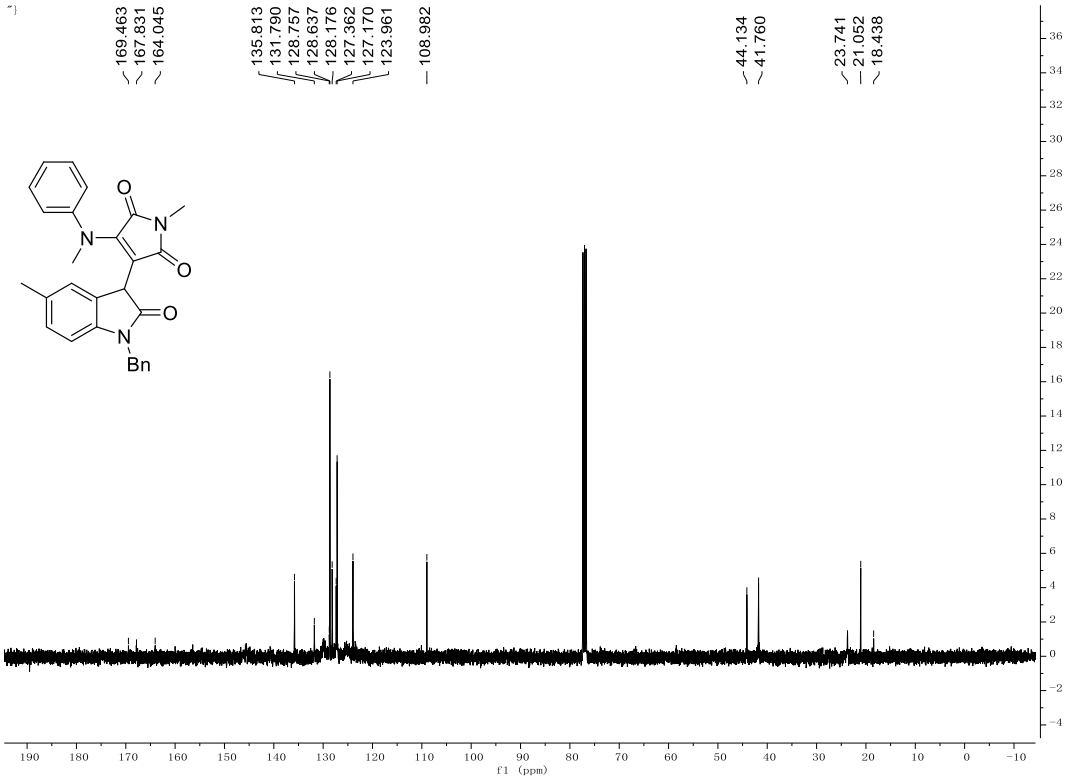


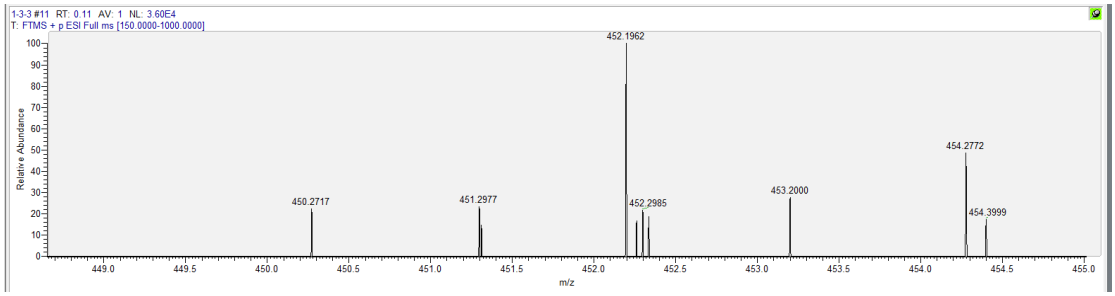

174.005
171.621
167.723
141.788
141.064
138.768
135.340
135.112
130.504
128.815
128.615
128.167
127.957
127.703
127.163
126.513
124.006
123.800
121.906
110.258
96.958
44.222
41.711
24.082
24.078
HN
O
N
O
Cl
O
N
Bn
f1 (ppm)


xzY-13 #13 RT: 0.13 AV: 1 NL: 8.90E4
T: FTMS + p ESI Full ms [150.0000-1000.0000]
494.1241
494.3629
494.9772
495.1271
495.9762
496.1206
496.1509
Relative Abundance
m/z

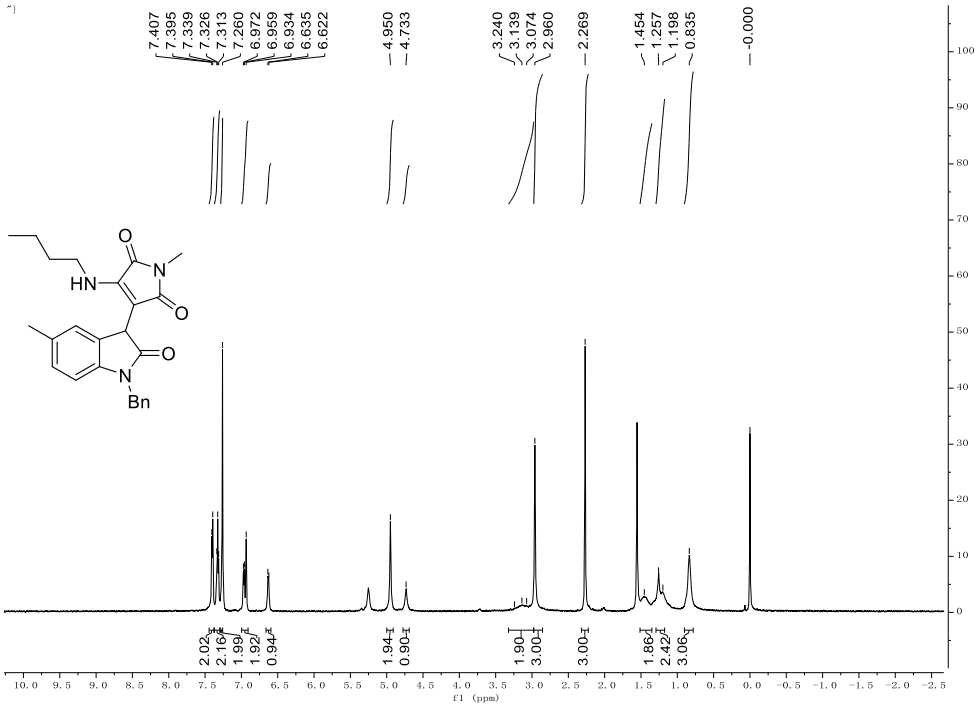
(*Z*)-3-(1-Benzyl-5-methyl-2-oxoindolin-3-ylidene)-1-methyl-4-(methyl(phenyl)amino)pyrrolidine-2,5-dione (5m): yellow solid, 75%, 34 mg, m.p. 194-195 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.48-7.35 (m, 3H, ArH), 7.28 (s, 5H, ArH), 7.22 (q, *J* = 4.7 Hz, 2H, ArH), 6.86 (d, *J* = 7.8 Hz, 1H, ArH), 6.84-6.77 (m, 1H, ArH), 6.40 (s, 1H, ArH), 4.82 (s, 2H, CH), 3.76 (s, 1H, CH), 3.58-3.11 (m, 3H, OCH_3), 2.95 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl3) δ: 169.5, 167.8, 164.1, 135.8, 131.8, 128.8, 128.6, 128.2, 127.4, 127.2, 124.0, 109.0, 44.1, 41.8, 23.7, 21.1, 18.4; IR (KBr) υ: 1756, 1747, 1653, 1611, 1523, 1435, 1392, 1351, 1175, 1169, 1113, 818, 763 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{28}H_{26}N_3O_3$ ($[M+H]^+$): 452.1969, Found: 452.1962.

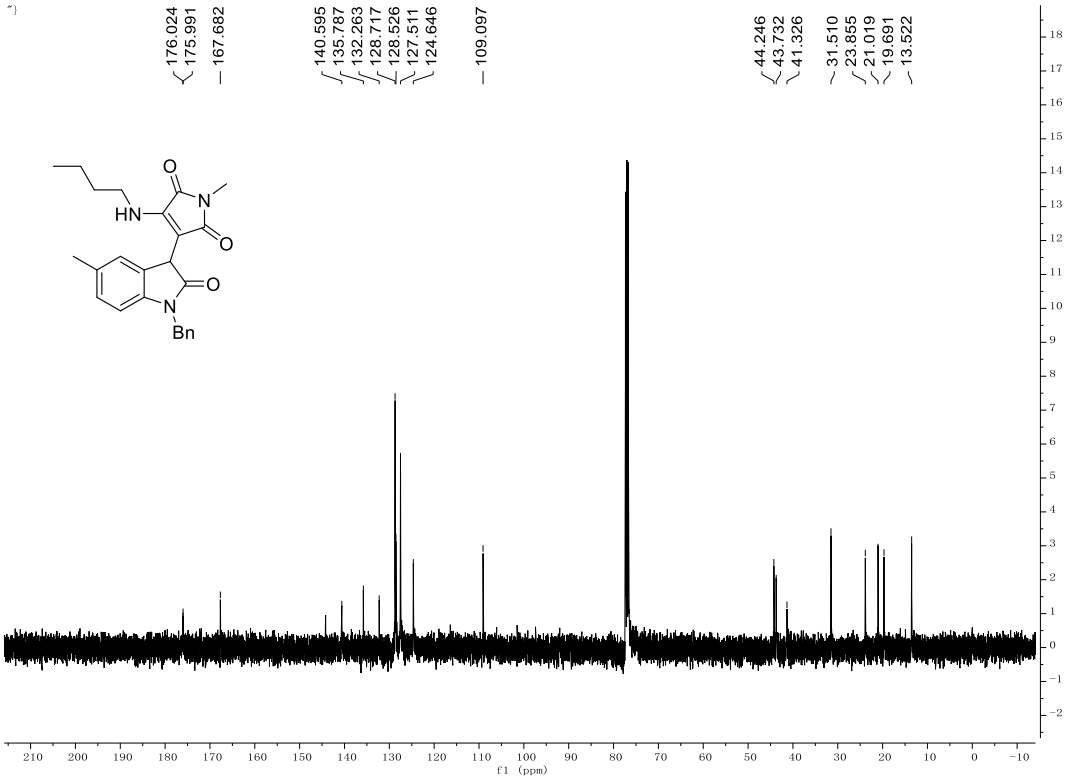


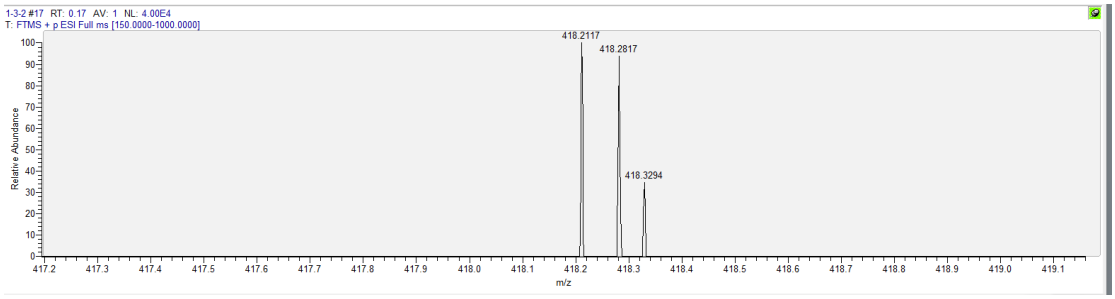

169.463
167.831
164.045
135.813
131.790
128.757
128.637
128.176
127.362
127.170
123.961
108.982
44.134
41.760
23.741
21.052
18.438
O
N
N
O
O
N
Bn
f1 (ppm)


1-3-3 #11 RT: 0.11 AV: 1 NL: 3.60E4
T: FTMS + p ESI Full ms [150.0000-1000.0000]
452.1962
454.2772
453.2000
450.2717
451.2977
452.2985
454.3999
Relative Abundance
m/z

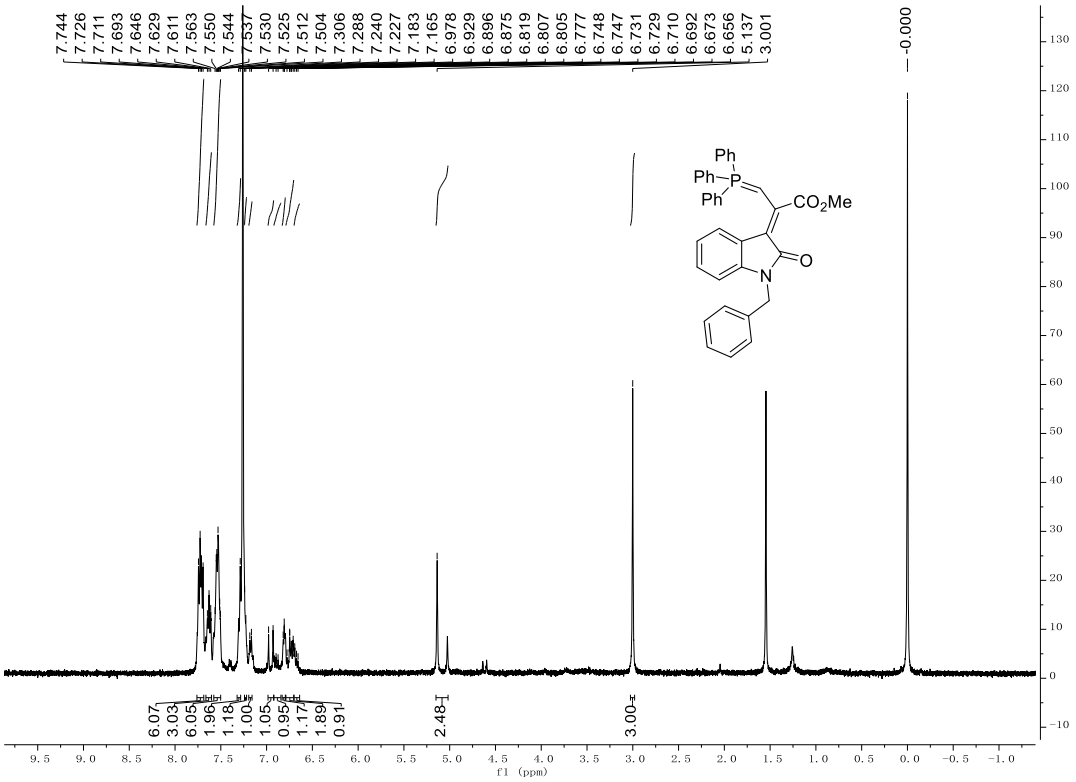
(*Z*)-3-(1-Benzyl-5-methyl-2-oxoindolin-3-ylidene)-4-(butylamino)-1-methylpyrrolidine-2,5-dione (5n): yellow solid, 55%, 23 mg, m.p. 184-185 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 7.5 Hz, 2H, ArH), 7.33 (t, *J* = 7.6 Hz, 2H, ArH), 7.26 (s, 2H, ArH), 7.00-6.91 (m, 2H, ArH), 6.63 (d, *J* = 8.0 Hz, 1H, ArH), 4.95 (s, 2H, CH), 4.73 (s, 1H, CH), 3.24-3.07 (m, 2H, CH), 2.96 (s, 3H, NCH_3), 2.27 (s, 3H, CH_3), 1.45 (s, 2H, CH), 1.46-1.20 (m, 2H, CH), 0.83 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl3) δ: 176.02, 175.99, 167.7, 140.6, 135.8, 132.3, 128.7, 128.5, 127.5, 124.7, 109.1, 44.3, 43.7, 41.3, 31.5, 23.9, 21.0, 19.7, 13.5; IR (KBr) υ: 1762, 1725, 1653, 1615, 1540, 1465, 1451, 1378, 1340, 1173, 1150, 1112, 814, 767 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{28}N_3O_3$ ($[M+H]^+$): 418.2125, Found: 418.2117.

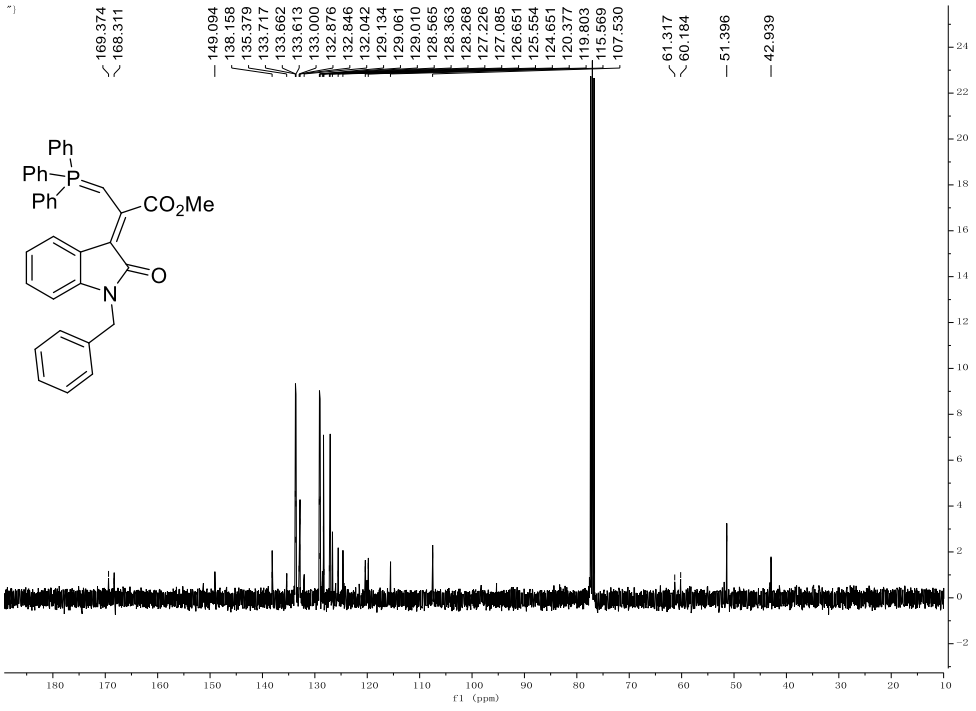


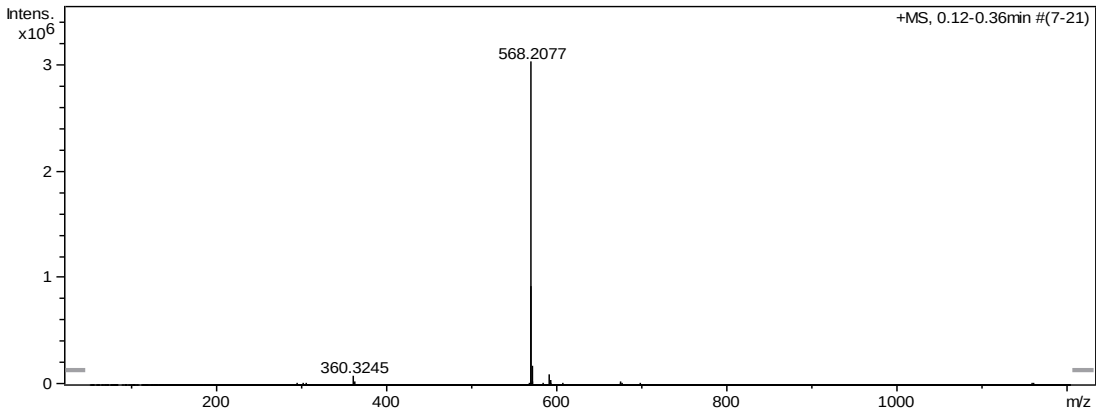

176.024
175.991
167.682
140.595
135.787
132.263
128.717
128.526
127.511
124.646
109.097
44.246
43.732
41.326
31.510
23.855
21.019
19.691
13.522
HN
O
N
O
O
N
Bn
f1 (ppm)


1-3-2 #17 RT: 0.17 AV: 1 NL: 4.00E4
T: FTMS + p ESI Full ms [150.0000-1000.0000]
418.2117
418.2817
418.3294
Relative Abundance
m/z

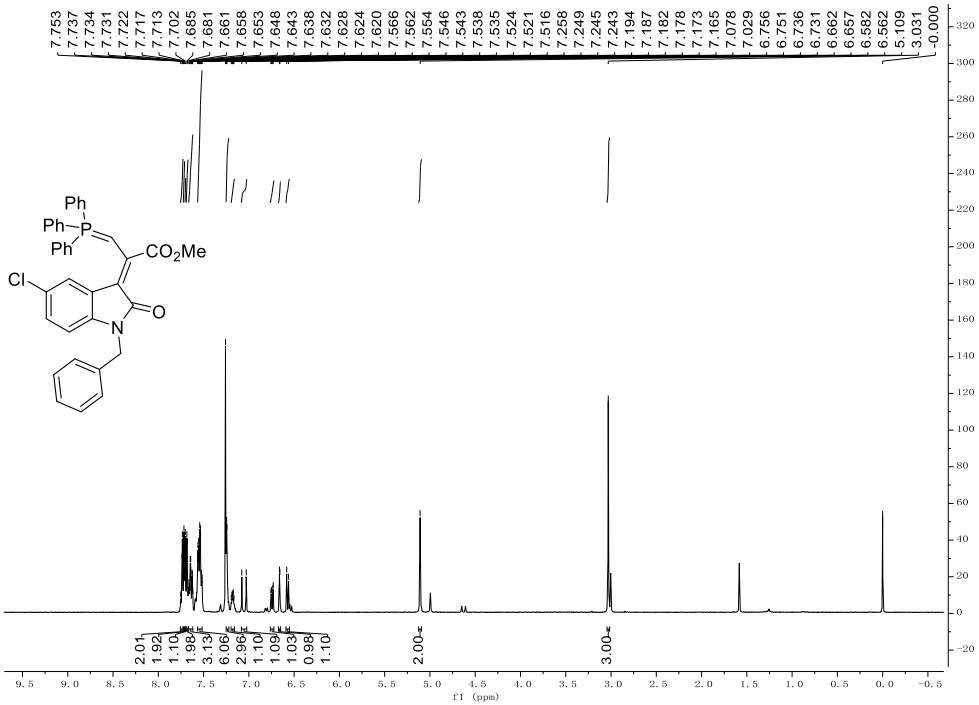
Methyl (*E*)-2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(triphenyl-λ^5-phosphaneylidene) propanoate (6a): orange solid, 90%, 49 mg, m.p. 214-215 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.74-7.69 (m, 6H, ArH), 7.66-7.60 (m, 3H, ArH), 7.58-7.50 (m, 6H, ArH), 7.30 (d, *J* = 7.4 Hz, 2H, ArH), 7.23 (d, *J* = 5.3 Hz, 1H, ArH), 7.17 (d, *J* = 7.2 Hz, 1H, ArH), 6.95 (d, *J* = 19.6 Hz, 1H, ArH), 6.89 (d, *J* = 8.7 Hz, 1H, ArH), 6.81 (d, *J* = 5.4 Hz, 1H, ArH), 6.79-6.70 (m, 2H, ArH), 6.70-6.64 (m, 1H, CH), 5.14 (s, 2H, CH), 3.00 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, CDCl3) δ: 169.4, 168.3, 149.1, 138.2, 135.4, 133.72, 133.66, 133.6, 133.0, 132.88, 132.85, 132.0, 129.13, 129.06, 129.0, 128.6, 128.4, 128.3, 127.2, 127.1, 126.7, 125.6, 124.7, 120.4, 119.8, 115.6, 107.5, 61.3, 60.2, 51.4, 42.9; IR (KBr) υ: 1722, 1634, 1489, 1472, 1436, 1410, 1344, 1299, 1209, 1172, 1101, 1044, 1015, 987, 917, 892, 849, 825, 780 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{31}NO_3P$ ($[M+H]^+$): 568.2036, Found: 568.2077.

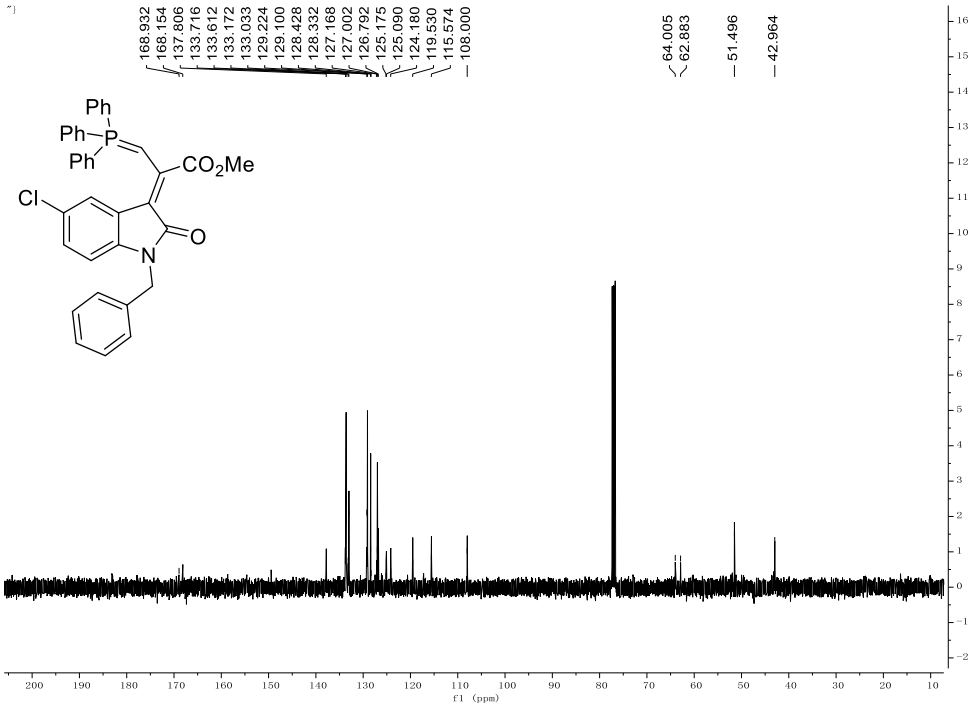


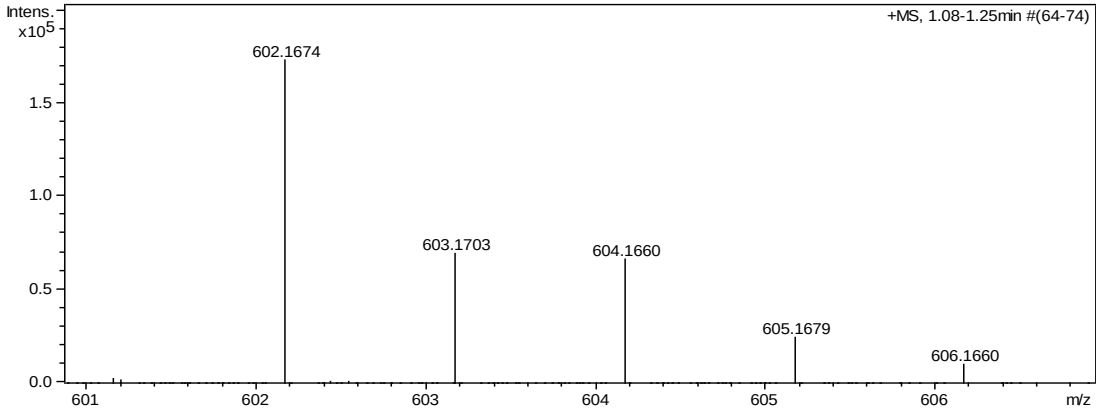

169.374
168.311
149.094
138.158
135.379
133.717
133.662
133.613
133.000
132.876
132.846
132.042
129.134
129.061
129.010
128.565
128.363
128.268
127.226
127.085
126.651
125.554
124.651
120.377
119.803
115.569
107.530
61.317
60.184
51.396
42.939
Ph
Ph
P
Ph
CO2Me
O
N
f1 (ppm)


Intens.
x10^6
+MS, 0.12-0.36min #(7-21)
568.2077
360.3245
m/z

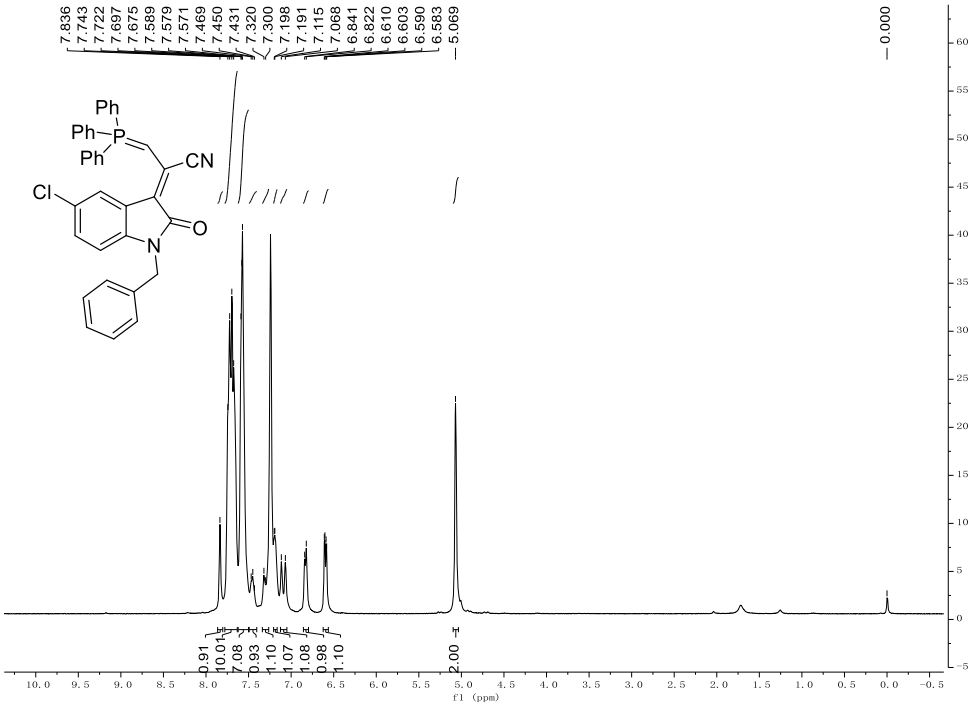
Methyl (*E*)-2-(1-benzyl-5-chloro-2-oxoindolin-3-ylidene)-3-(triphenyl-λ^5-phosphaneylidene) propanoate (6b): orange solid, 92%, 53 mg, m.p. 216-217 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75-7.73 (m, 2H, ArH), 7.72-7.71 (m, 2H, ArH), 7.70 (s, 1H, ArH), 7.68 (d, *J* = 1.6 Hz, 2H, ArH), 7.66-7.64 (m, 3H, ArH), 7.60-7.52 (m, 6H, ArH), 7.25-7.22 (m, 3H, ArH), 7.20-7.17 (m, 1H, ArH), 7.05 (d, *J* = 19.6 Hz, 1H, ArH), 6.74 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H, ArH), 6.66 (d, *J* = 2.0 Hz, 1H, ArH), 6.57 (d, *J* = 8.0 Hz, 1H, ArH), 5.11 (s, 2H, CH_2), 3.03 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, CDCl3) δ: 168.9, 168.2, 137.8, 133.7, 133.6, 133.2, 133.0, 129.2, 129.1, 128.4, 128.3, 127.2, 127.0, 126.8, 125.2, 125.1, 124.2, 119.5, 115.6, 108.0, 64.0, 62.9, 51.5, 43.0; IR (KBr) υ: 1720, 1624, 1484, 1435, 1412, 1336, 1299, 1282, 1160, 1098, 991, 856, 825, 812, 775 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{30}ClNO_3P$ ([M+H]$^+$): 602.1646, Found: 602.1674.

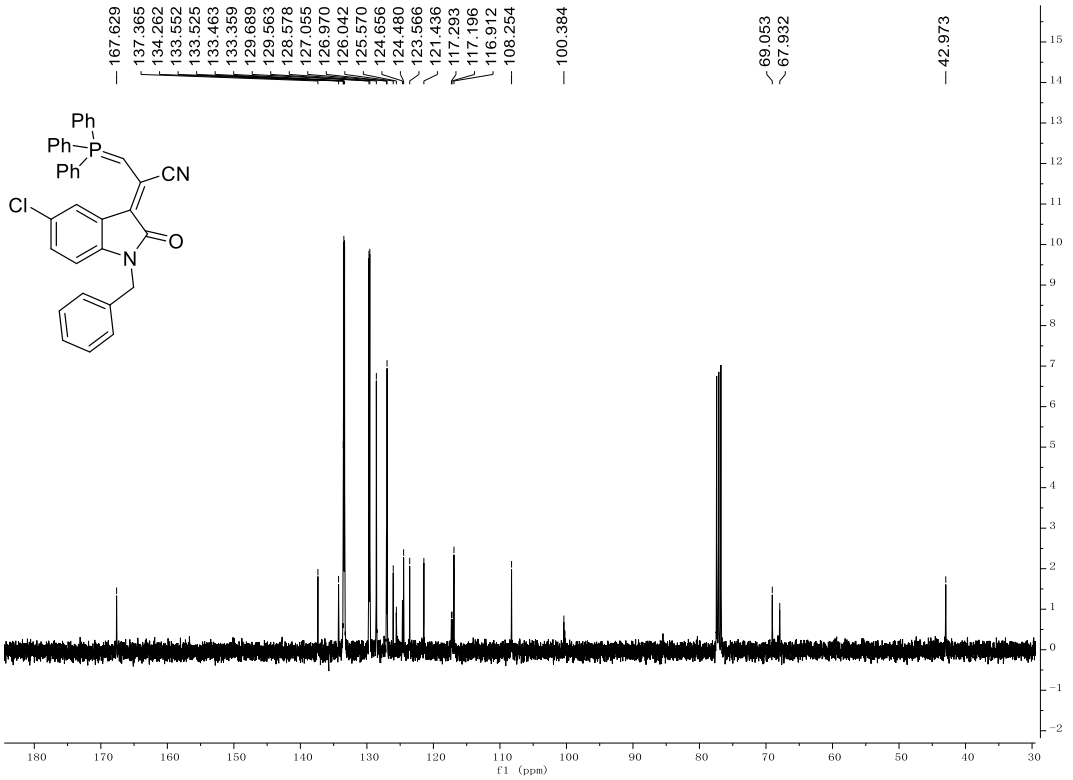


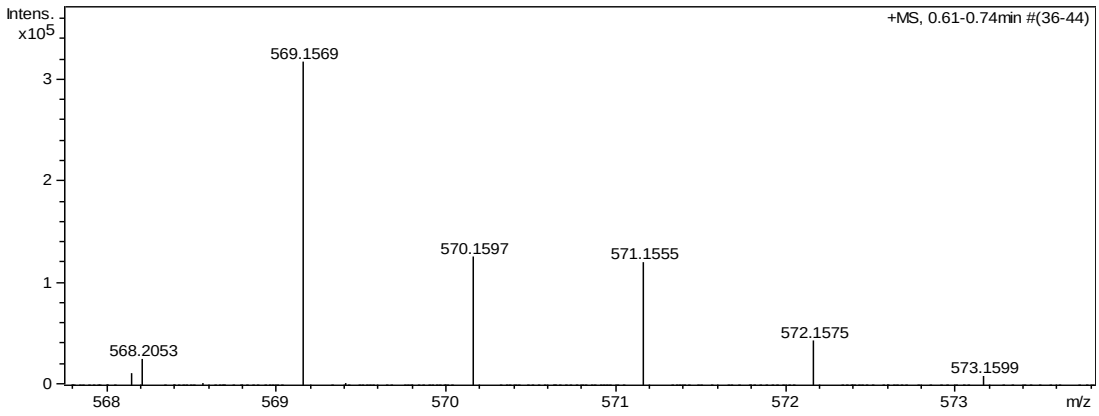

168.932
168.154
137.806
133.716
133.612
133.172
133.033
129.224
129.100
128.428
128.332
127.168
127.002
126.792
125.175
125.090
124.180
119.530
115.574
108.000
64.005
62.883
51.496
42.964
Ph
Ph
P
Ph
CO2Me
Cl
O
N
f1 (ppm)


Intens.
x10^5
+MS, 1.08-1.25min #(64-74)
602.1674
603.1703
604.1660
605.1679
606.1660
m/z

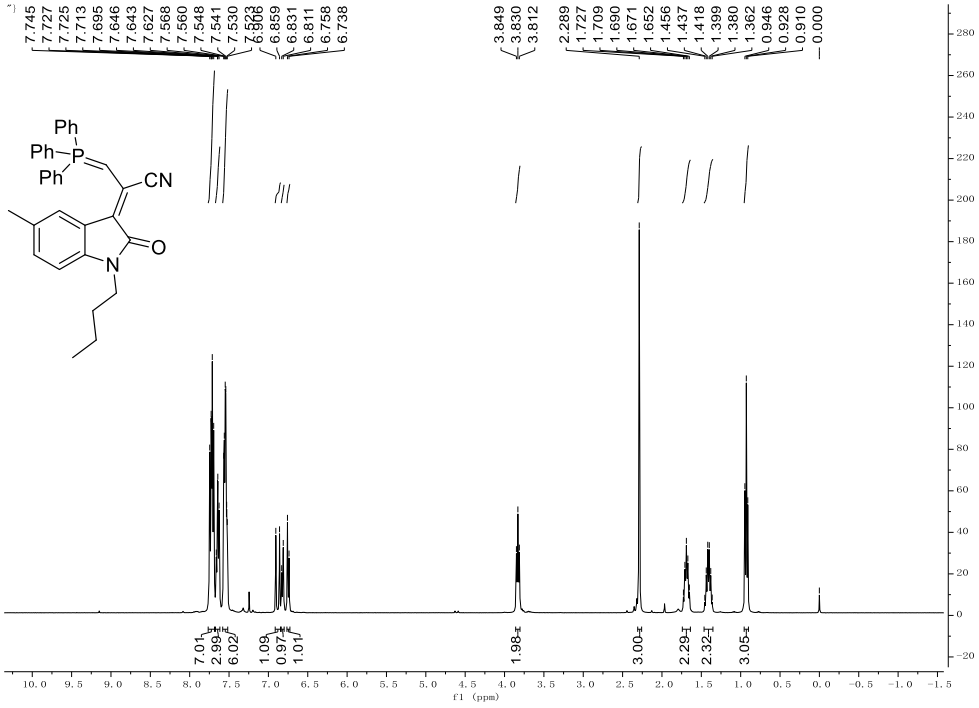
(*E*)-2-(1-Benzyl-5-chloro-2-oxoindolin-3-ylidene)-3-(triphenyl-λ^5-phosphaneylidene) propanenitrile (6c): orange solid, 84%, 45 mg, m.p. 210-211 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (s, 1H, ArH), 7.74-7.68 (m, 10H, ArH), 7.59-7.57 (m, 7H, ArH), 7.47-7.43 (m, 1H, ArH), 7.32-7.30 (m, 1H, ArH)7.20-7.19 (m, 1H, ArH), 7.09 (d, J = 18.8 Hz, 1H, ArH), 6.83 (d, J = 7.6 Hz, 1H, ArH), 6.60 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H, ArH), 5.07 (s, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl3) δ: 167.6, 137.4, 134.3, 133.55, 133.52, 133.46, 133.7, 129.7, 129.6, 128.6, 127.1, 127.0, 126.0, 125.6, 124.7, 124.5, 123.6, 121.4, 117.3, 117.2, 116.9, 108.3, 100.4, 69.1, 67.9, 43.0; IR (KBr) υ: 1630, 1484, 1435, 1407, 1336, 1182, 1166, 1103, 987, 859, 797 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{27}ClN_2OP$ ($[M+H]^+$): 569.1544, Found: 569.1569.

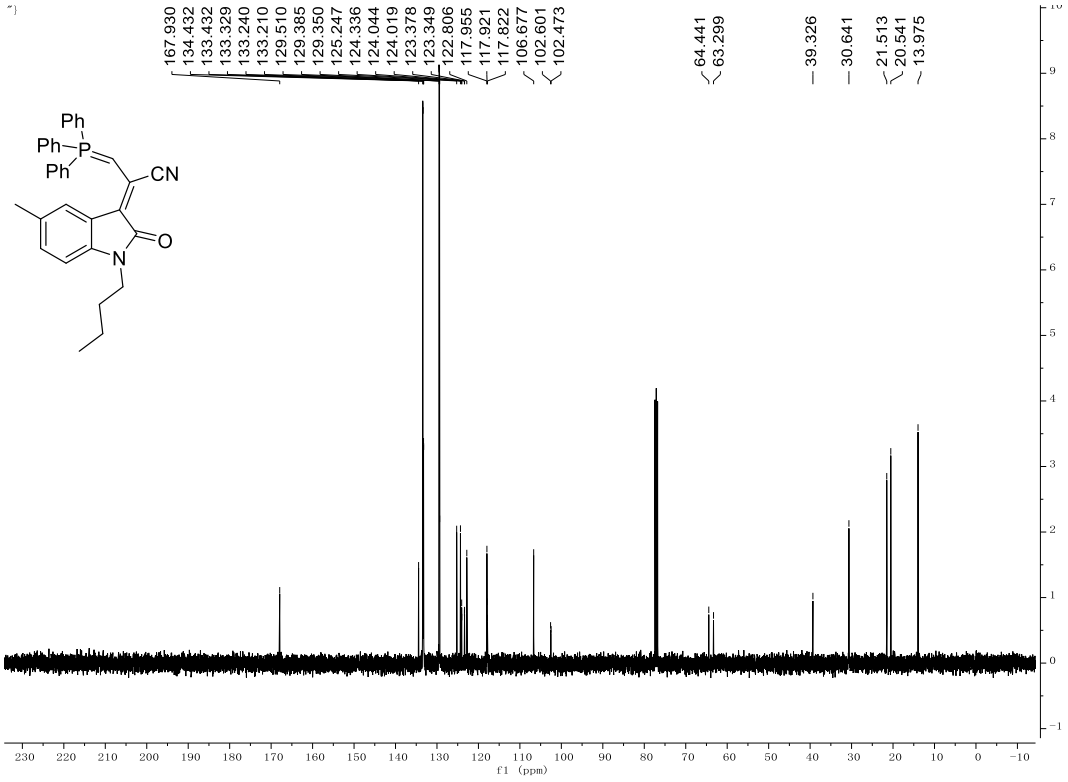


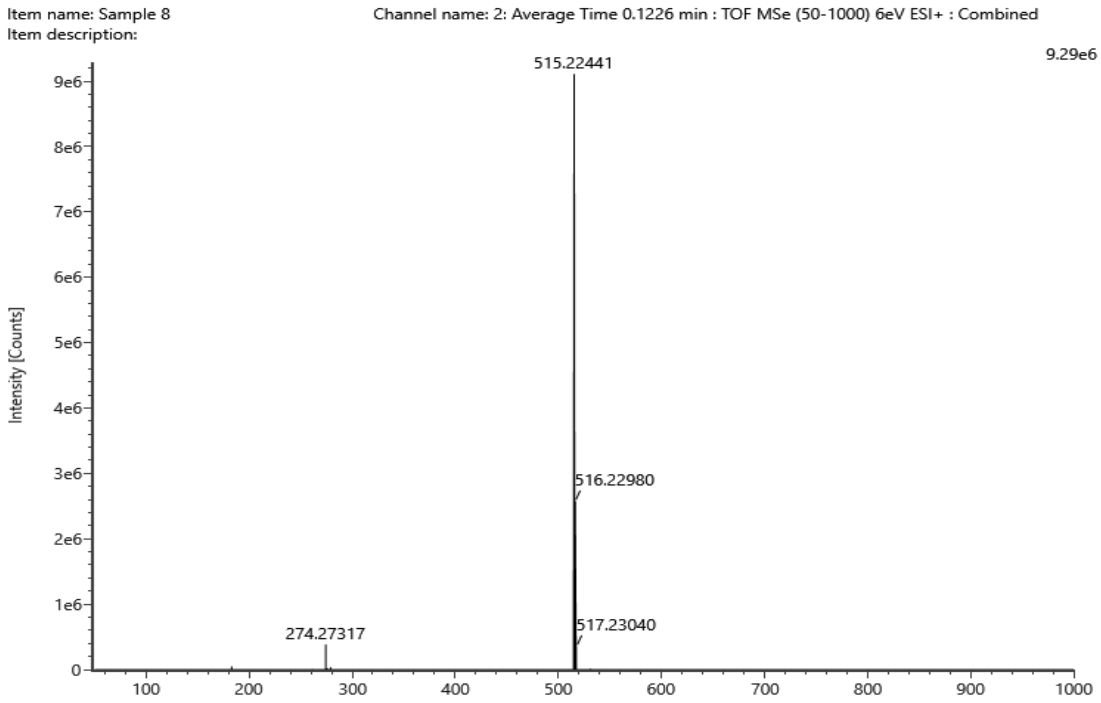

167.629
137.365
134.262
133.552
133.525
133.463
133.359
129.689
129.563
128.578
127.055
126.970
126.042
125.570
124.656
124.480
123.566
121.436
117.293
117.196
116.912
108.254
100.384
69.053
67.932
42.973
Ph
Ph
P
Ph
CN
Cl
O
N
f1 (ppm)


Intens.
x10^5
+MS, 0.61-0.74min #(36-44)
569.1569
570.1597
571.1555
572.1575
568.2053
573.1599
m/z

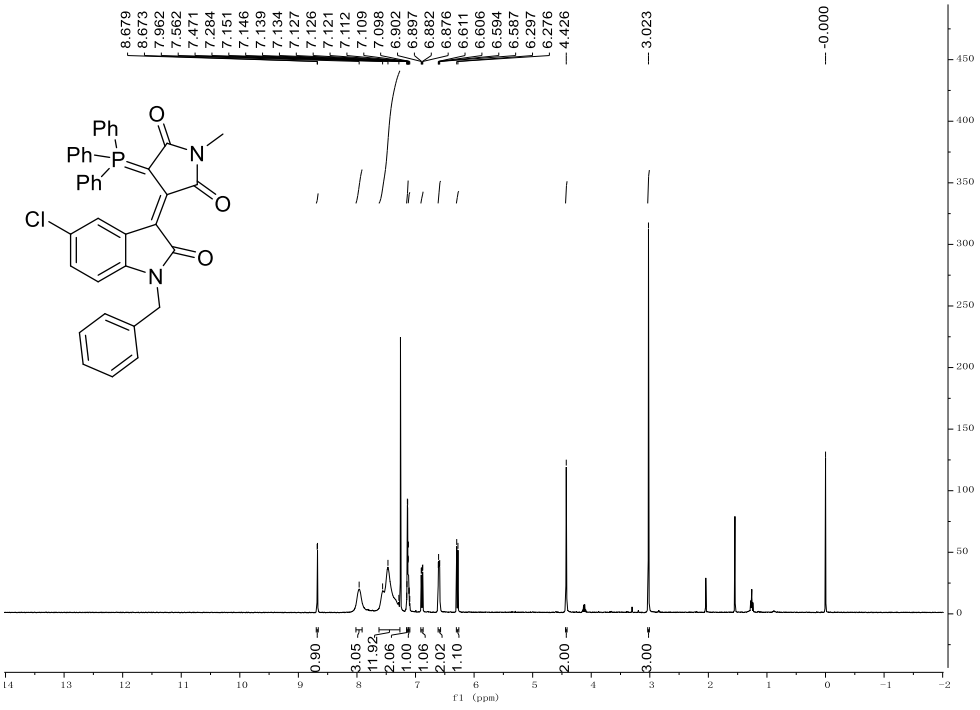
(*E*)-2-(1-Butyl-5-methyl-2-oxoindolin-3-ylidene)-3-(triphenyl-λ^5-phosphaneylidene) propanenitrile (6d): orange solid, 82%, 42 mg, m.p. 204-205 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.75-7.70 (m, 7H, ArH), 7.66-7.63 (m, 3H, ArH), 7.57-7.52 (m, 6H, ArH) , 6.88 (d, *J* = 18.8 Hz, 1H, ArH), 6.82 (d, *J* = 8.0 Hz, 1H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 3.83 (t, *J* = 7.6 Hz, 2H, CH), 2.29 (s, 3H, CH_3), 1.73-1.65 (m, 2H, CH), 1.46-1.36 (m, 2H, CH), 0.93 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl3) δ: 167.9, 134.4, 133.4, 133.3, 133.24, 133.21, 129.5, 129.39, 129.35, 125.3, 124.3, 124.0, 124.0, 123.38, 123.35, 122.8, 118.0, 117.9, 117.8, 106.7, 102.6, 102.5, 64.4, 63.3, 39.3, 30.6, 21.5, 20.5, 14.0; IR (KBr) υ: 1691, 1632, 1485, 1436, 1337, 1166, 1105, 859, 809 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{34}H_{32}N_2OP$ ($[M+H]^+$): 515.2247, Found: 515.2244.

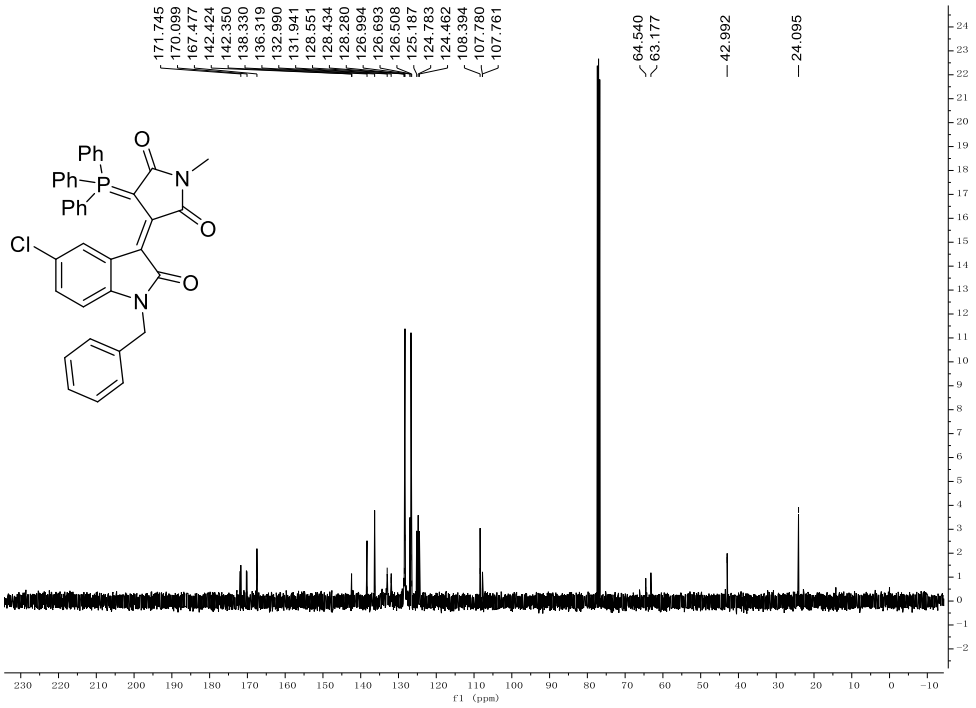


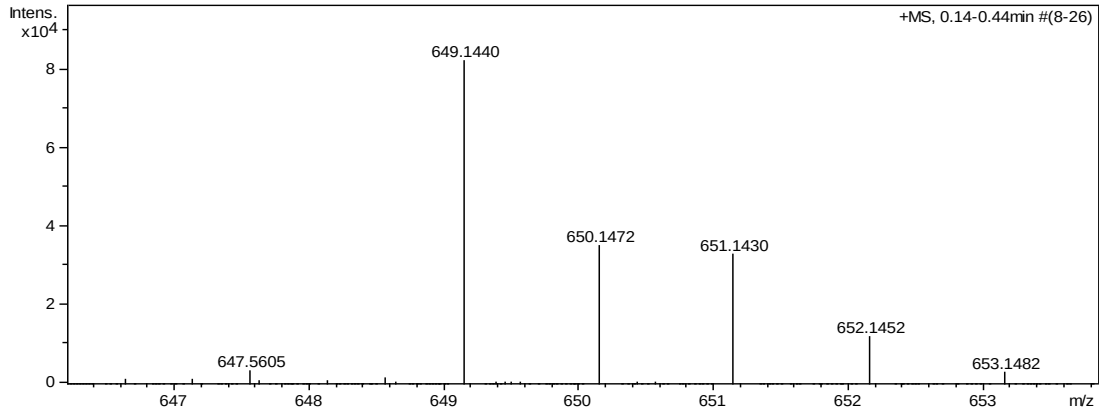

167.930
134.432
133.432
133.329
133.240
133.210
129.510
129.385
129.350
125.247
124.336
124.044
124.019
123.378
123.349
122.806
117.955
117.921
117.822
106.677
102.601
102.473
64.441
63.299
39.326
30.641
21.513
20.541
13.975
Ph
Ph
P
Ph
CN
O
N
f1 (ppm)


Item name: Sample 8
Item description:
Channel name: 2: Average Time 0.1226 min : TOF MSe (50-1000) 6eV ESI+ : Combined
9.29e6
515.22441
516.22980
517.23040
274.27317
Intensity [Counts]

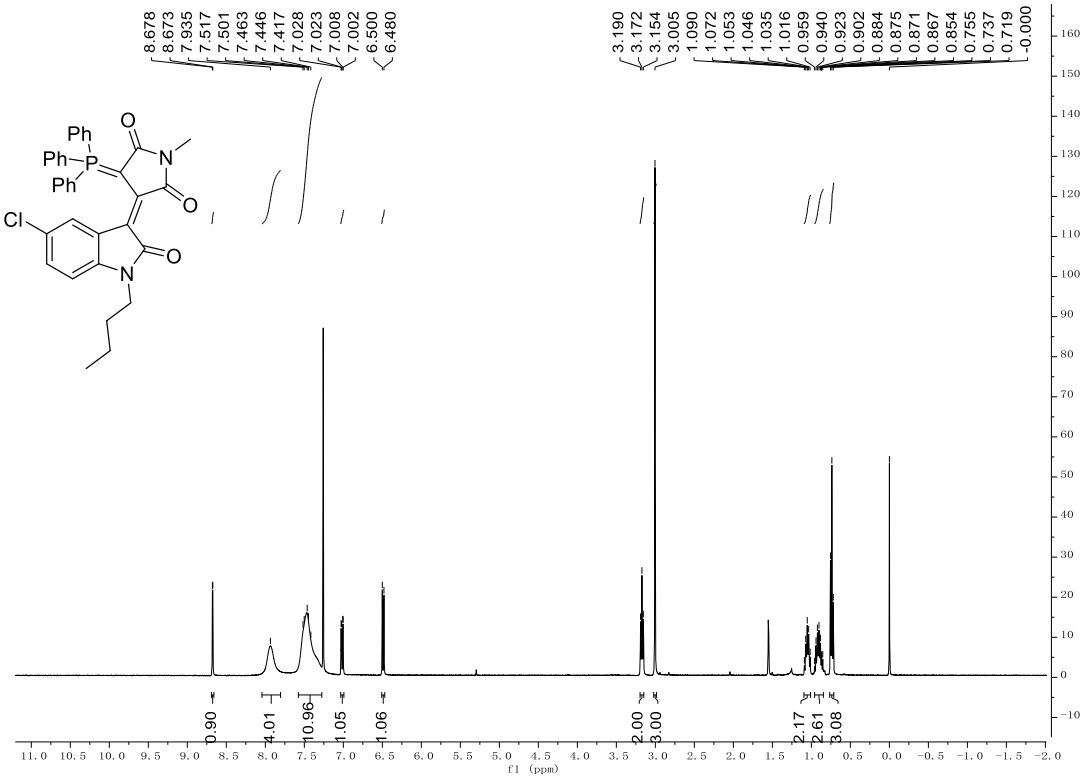
(*E*)-3-(1-Benzyl-5-chloro-2-oxoindolin-3-ylidene)-1-methyl-4-(triphenyl-λ^5-phosphaneylidene)pyrrolidine-2,5-dione (6e): purple solid, 92%, 57 mg, m.p. 203-204 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (d, *J* = 2.4 Hz, 1H, ArH), 7.96 (s, 3H, ArH), 7.56-7.47 (m, 12H, ArH), 7.15-7.13 (m, 2H, ArH), 7.12-7.10 (m, 1H, ArH), 6.89 (dd, J_1 = 2.0 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.61-6.59 (m, 2H, ArH), 6.29 (d, *J* = 7.6 Hz, 1H, ArH), 4.43 (s, 2H, CH), 3.02 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, CDCl3) δ: 171.7, 170.1, 167.5, 142.4, 142.4, 138.3, 136.3, 133.0, 131.9, 128.6, 128.4, 128.3, 127.0, 126.7, 126.5, 125.2, 124.8, 124.5, 108.4, 107.8, 107.8, 64.5, 63.2, 43.0, 24.1; IR (KBr) υ: 1665, 1538, 1435, 1380, 1321, 1159, 1094, 1030, 868, 796, 771 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{28}ClN_2NaO_3P$ ([M+Na]$^+$): 649.1418, Found: 649.1440.

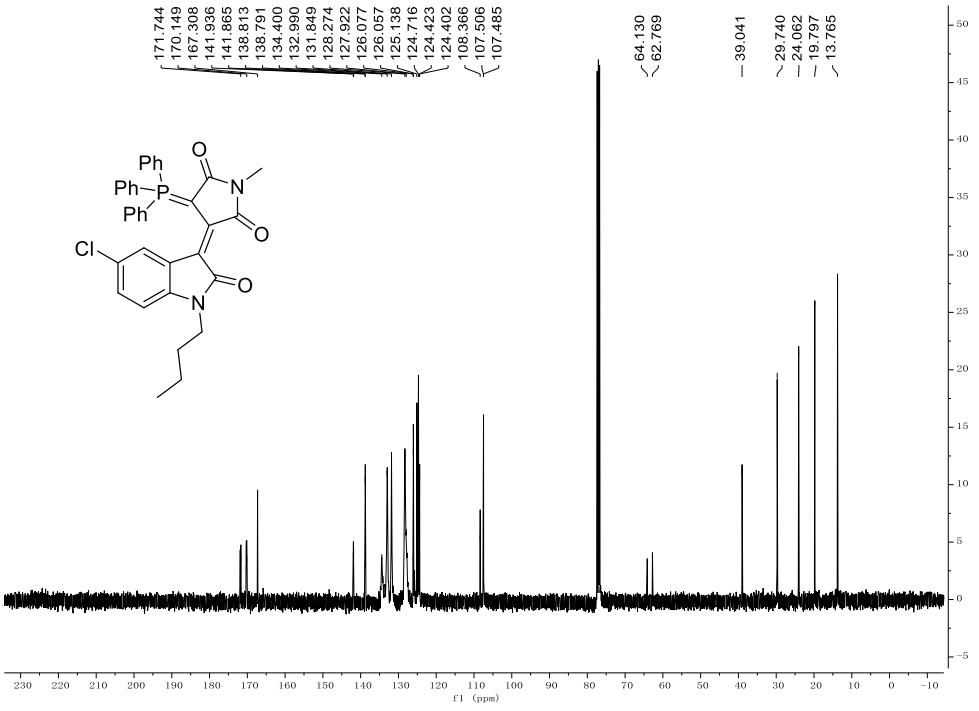


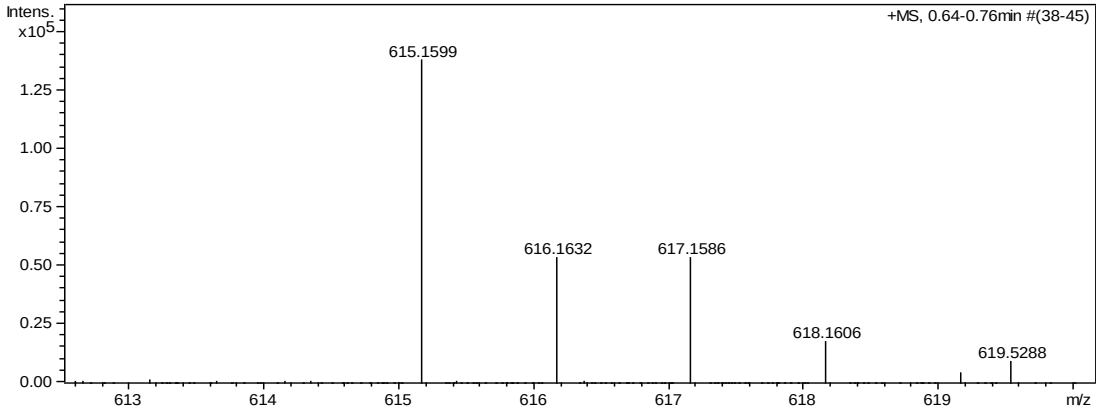

171.745
170.099
167.477
142.424
142.350
138.330
136.319
132.990
131.941
128.551
128.434
128.280
126.994
126.693
126.508
125.187
124.783
124.462
108.394
107.780
107.761
64.540
63.177
42.992
24.095
Ph
Ph
Ph
P
O
N
O
Cl
O
N
f1 (ppm)


Intens.
x10^4
+MS, 0.14-0.44min #(8-26)
649.1440
650.1472
651.1430
652.1452
647.5605
653.1482
m/z

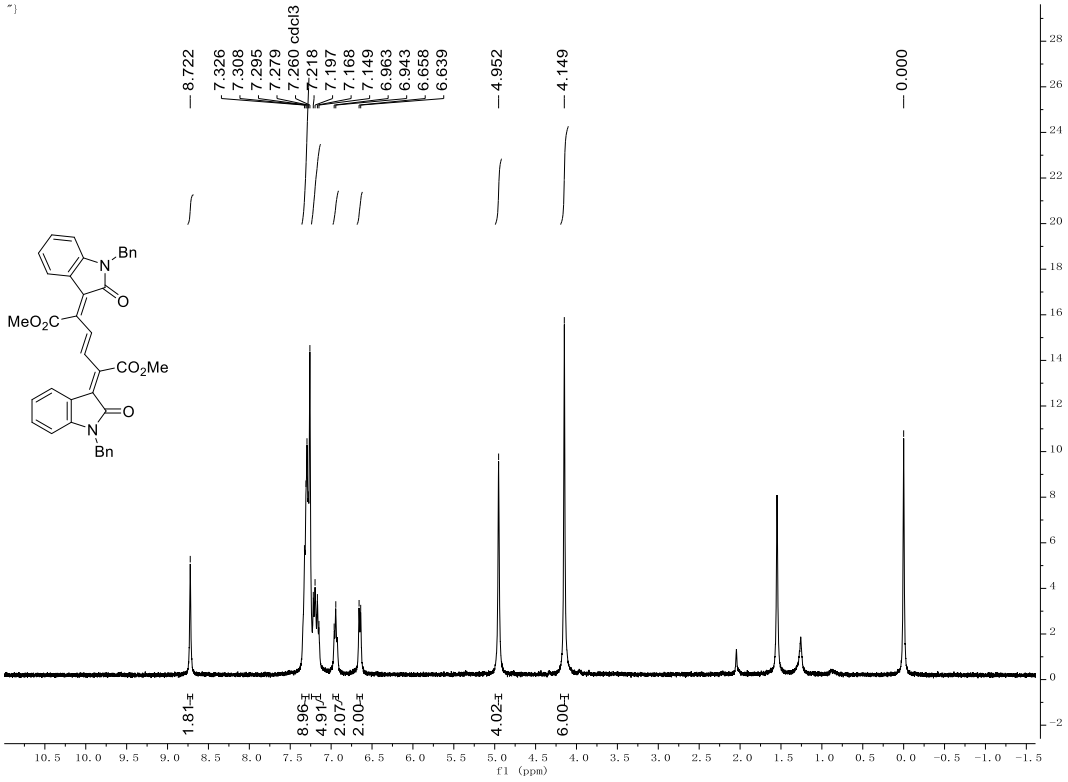
(*E*)-3-(1-Butyl-5-chloro-2-oxoindolin-3-ylidene)-1-methyl-4-(triphenyl-λ^5-phosphaneylidene) pyrrolidine-2,5-dione (6f): purple solid, 89%, 52 mg, m.p. 204-205 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.68 (d, *J* = 2.0 Hz, 1H, ArH), 7.94 (s, 4H, ArH), 7.52-7.42 (m, 11H, ArH), 7.16 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, ArH), 6.49 (d, *J* = 8.0 Hz, 1H, ArH), 3.17 (t, *J* = 7.2 Hz, 2H, CH), 3.01 (s, 3H, CH_3), 1.09-1.02 (m, 2H, CH), 0.96-0.85 (m, 2H, CH), 0.74 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.7, 170.2, 167.3, 141.94, 141.87, 138.81, 138.79, 134.4, 133.0, 131.9, 128.3, 127.9, 126.08, 126.06, 125.1, 124.7, 124.42, 124.40, 108.4, 107.51, 107.49, 64.1, 62.8, 39.0, 29.7, 24.1, 19.8, 13.8; IR (KBr) υ: 1718, 1664, 1605, 1574, 1540, 1467, 1435, 1380, 1316, 1278, 1176, 1109, 865, 794 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{30}ClN_2NaO_3P$ ($[M+Na]^+$): 615.1575, Found: 615.1599.

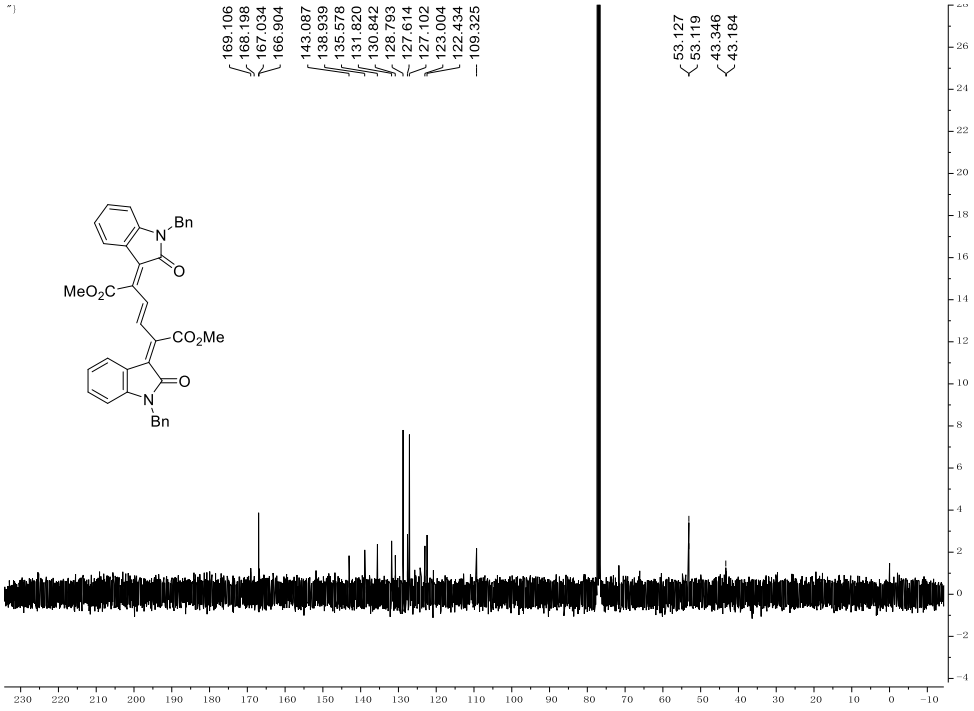


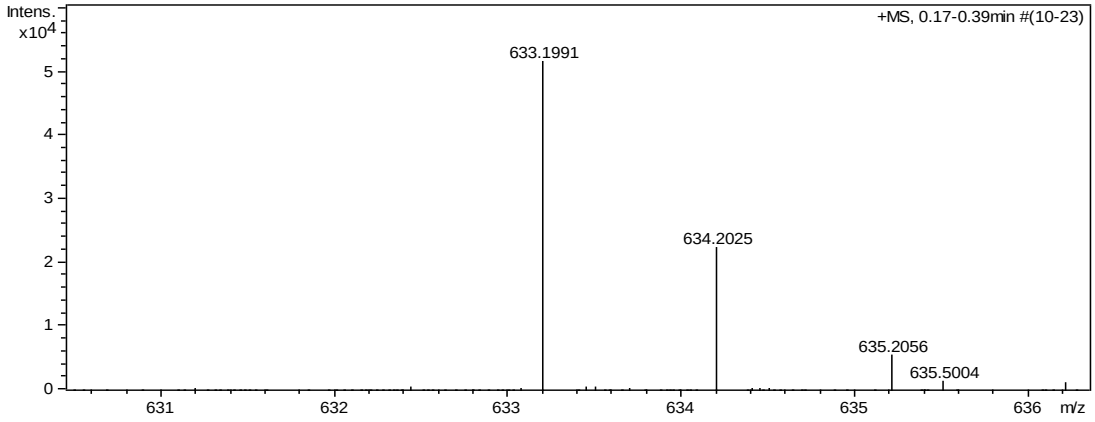

171.744
170.149
167.308
141.936
141.865
138.813
138.791
134.400
132.990
131.849
128.274
127.922
126.077
126.057
125.138
124.716
124.423
124.402
108.366
107.506
107.485
64.130
62.769
39.041
29.740
24.062
19.797
13.765
Ph
Ph
Ph
P
O
N
O
Cl
O
N
f1 (ppm)


Intens.
x10^5
+MS, 0.64-0.76min #(38-45)
615.1599
616.1632
617.1586
618.1606
619.5288
m/z

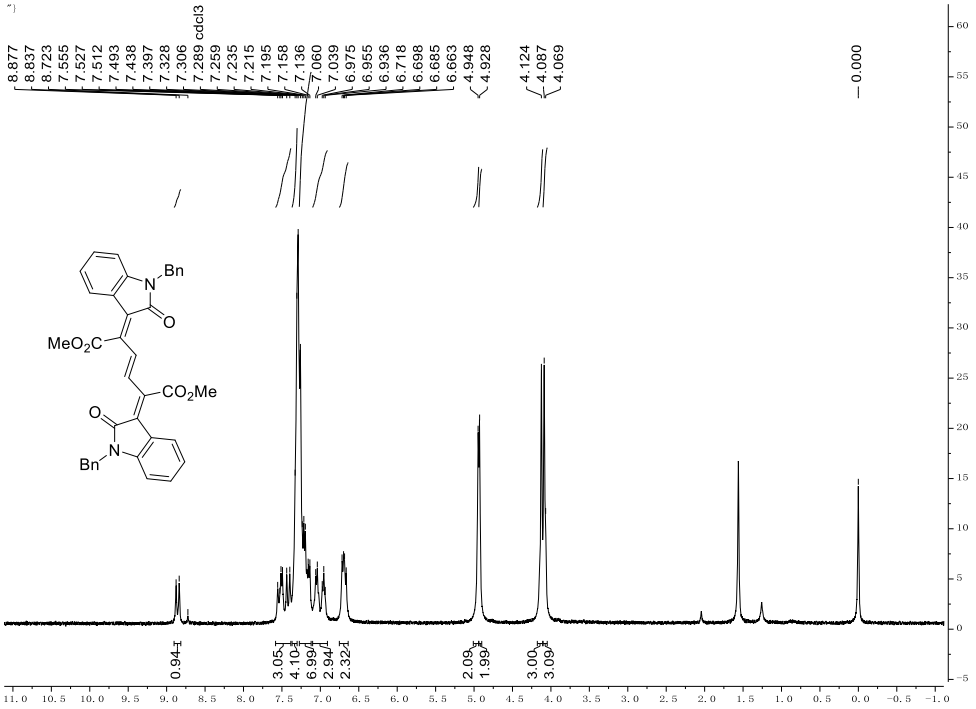
Dimethyl (*E*)-4-((*E*)-1-benzyl-2-oxoindolin-3-ylidene)-2-(((*Z*)-1-benzyl-2-oxoindolin-3-ylidene)methyl)pent-2-enedioate (7a): red solid, 63%, 38 mg, m.p. 230-231 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (s, 2H, ArH), 7.36-7.27 (m, 9H, ArH), 7.24-7.13 (m, 5H, ArH), 6.95 (d, *J* = 7.9 Hz, 2H, ArH), 6.65 (d, *J* = 7.9 Hz, 2H, ArH), 4.95 (s, 4H, CH), 4.15 (s, 6H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.1, 168.2, 167.0, 166.9, 143.1, 138.9, 135.6, 131.8, 130.8, 128.8, 127.6, 127.1, 123.0, 122.4, 109.3, 53.13, 53.12, 43.4, 43.2; IR (KBr) υ: 1736, 1692, 1611, 1497, 1482, 1470, 1434, 1379, 1359, 1298, 1180, 1158, 1108, 1080, 1059, 1044, 1017, 971cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{30}N_2NaO_6$ ([M+Na]$^{+}$): 633.1996, Found: 633.1991.

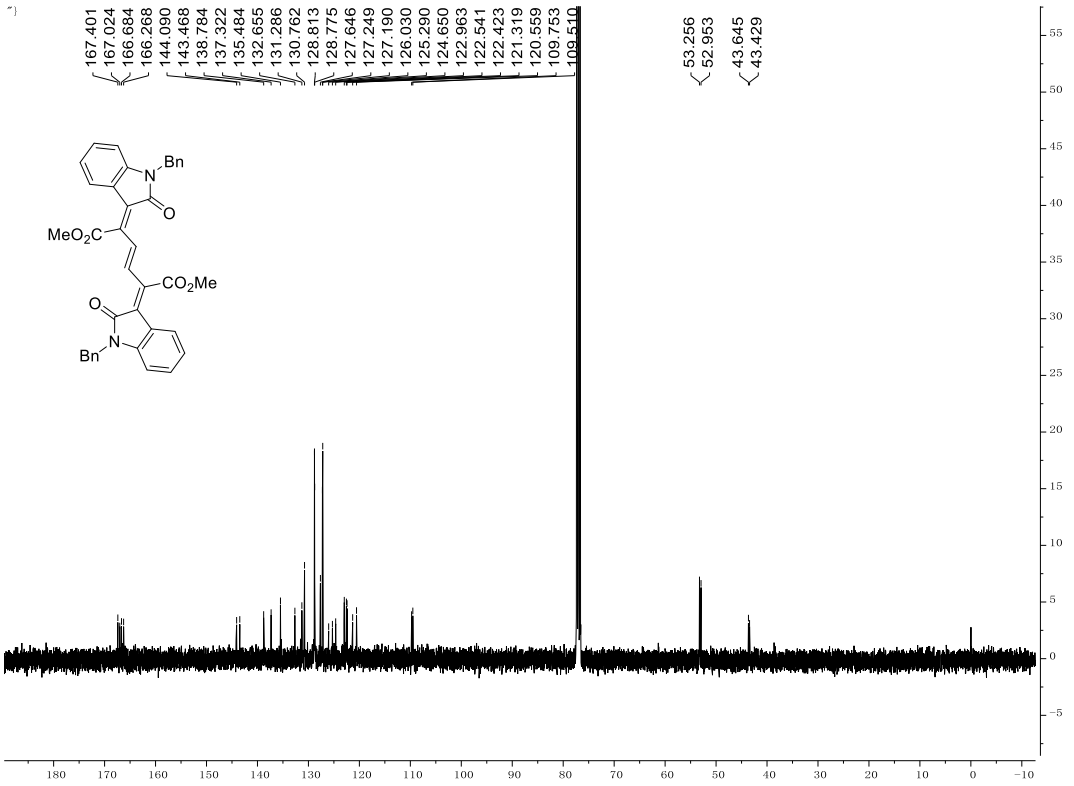


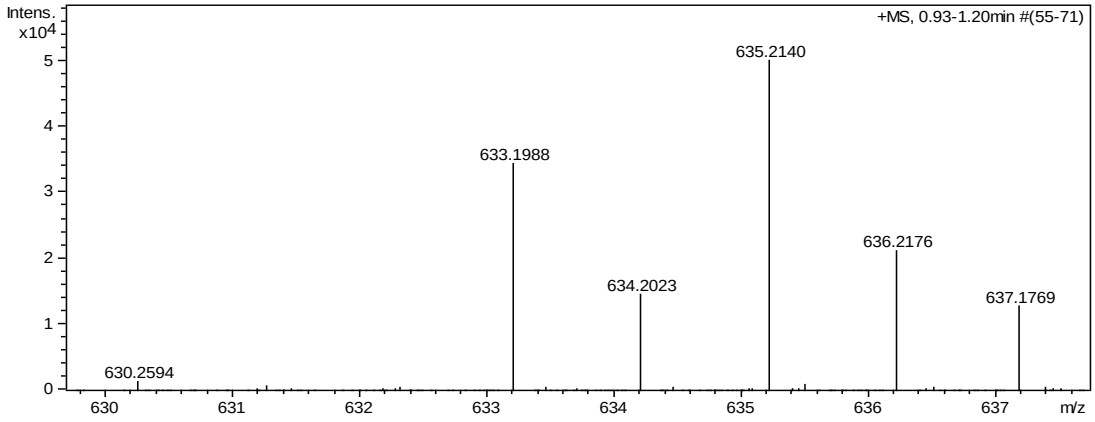

169.106
168.198
167.034
166.904
143.087
138.939
135.578
131.820
130.842
128.793
127.614
127.102
123.004
122.434
109.325
53.127
53.119
43.346
43.184
Bn
N
O
MeO2C
CO2Me
O
N
Bn


Intens.
x10^4
+MS, 0.17-0.39min #(10-23)
633.1991
634.2025
635.2056
635.5004
m/z

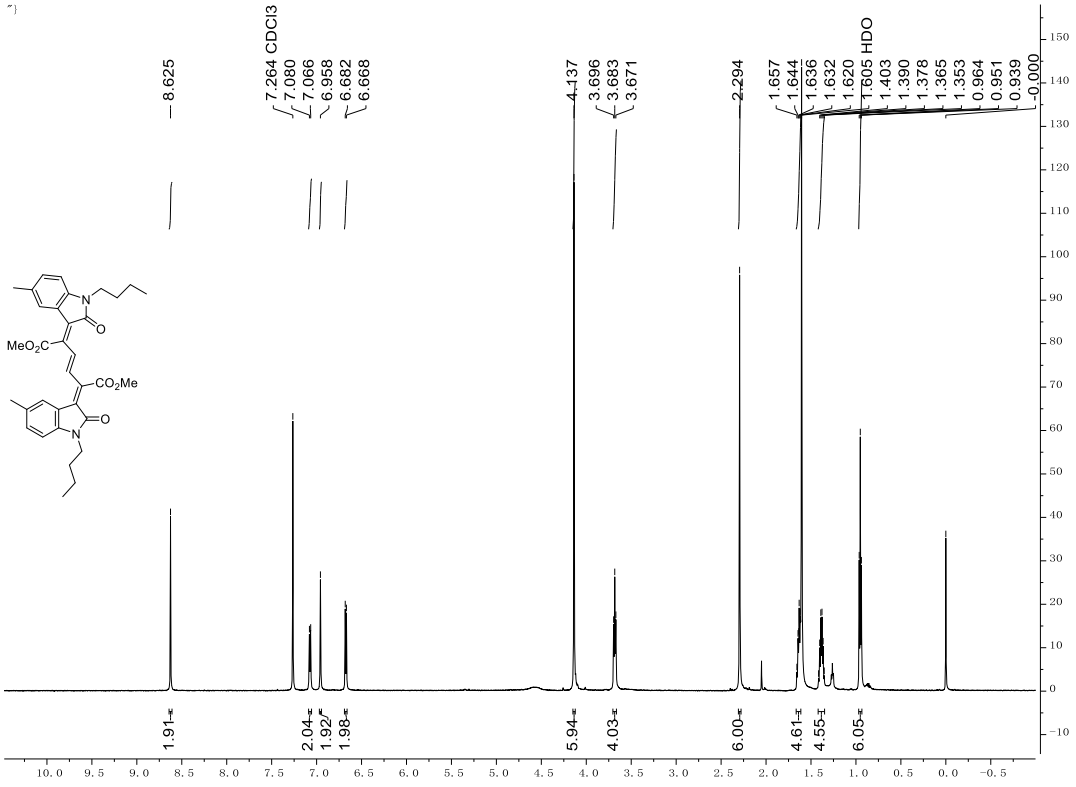
Dimethyl (*E*)-4-((*E*)-1-benzyl-2-oxoindolin-3-ylidene)-2-(((*E*)-1-benzyl-2-oxoindolin-3-ylidene)methyl)pent-2-enedioate (8a): red solid, 15%, 9 mg, m.p. 166-167 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (d, *J* = 16.1 Hz, 1H, CH), 7.58-7.38 (m, 3H, ArH), 7.32 (d, *J* = 8.9 Hz, 4H, ArH), 7.27-7.12 (m, 7H, ArH), 7.06-6.94 (m, 3H, ArH), 6.72-6.66 (m, 2H, ArH), 4.95 (s, 2H, CH), 4.93 (s, 2H, CH), 4.12 (s, 3H, OCH_3), 4.08 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.4, 167.0, 166.7, 166.3, 144.1, 143.5, 138.8, 137.3, 135.5, 132.7, 131.3, 130.8, 128.81, 128.78, 127.7, 127.3, 127.2, 126.0, 125.3, 124.7, 123.0, 122.5, 122.4, 121.3, 120.6, 109.8, 109.5, 53.3, 53.0, 43.6, 43.4; IR (KBr) υ: 1701, 1610, 1482, 1467, 1433, 1380, 1351, 1218, 1178, 1107, 973 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{30}N_2NaO_6$ ([M+Na]$^{+}$): 633.1996, Found: 699.1988.

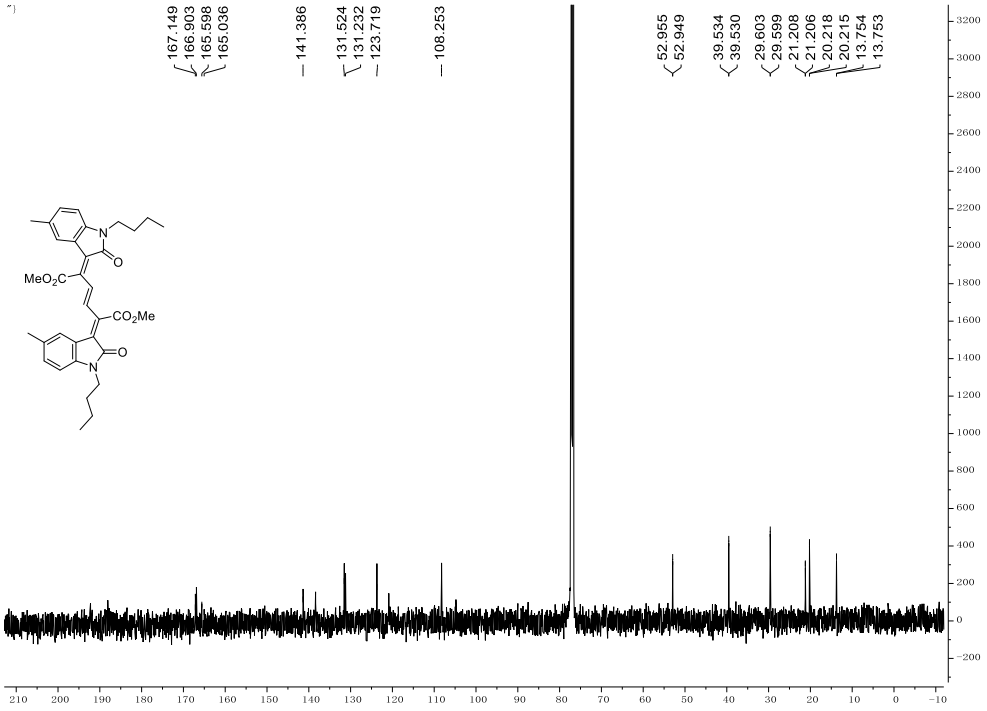


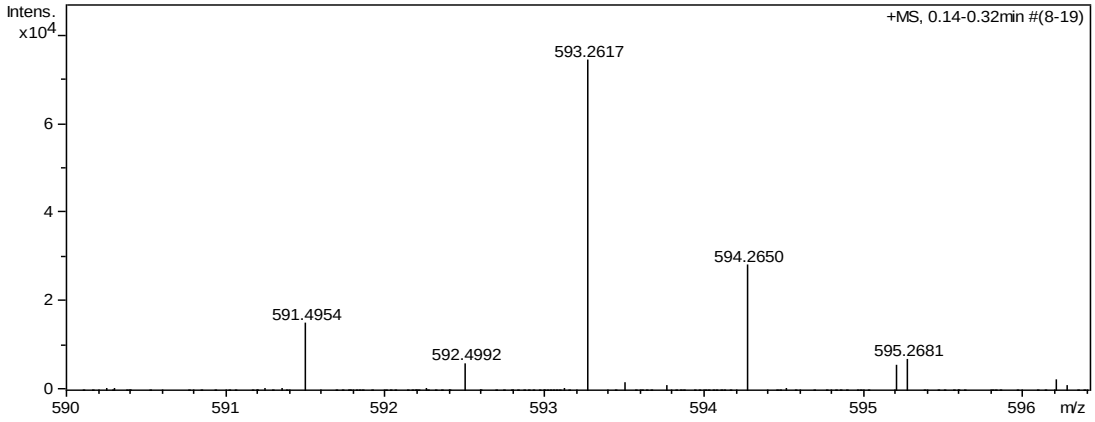

167.401
167.024
166.684
166.268
144.090
143.468
138.784
137.322
135.484
132.655
131.286
130.762
128.813
128.775
127.646
127.249
127.190
126.030
125.290
124.650
122.963
122.541
122.423
121.319
120.559
109.753
109.510
53.256
52.953
43.645
43.429
Bn
N
O
MeO2C
CO2Me
O
N
Bn


Intens.
x10^4
+MS, 0.93-1.20min #(55-71)
635.2140
633.1988
636.2176
634.2023
637.1769
630.2594
m/z

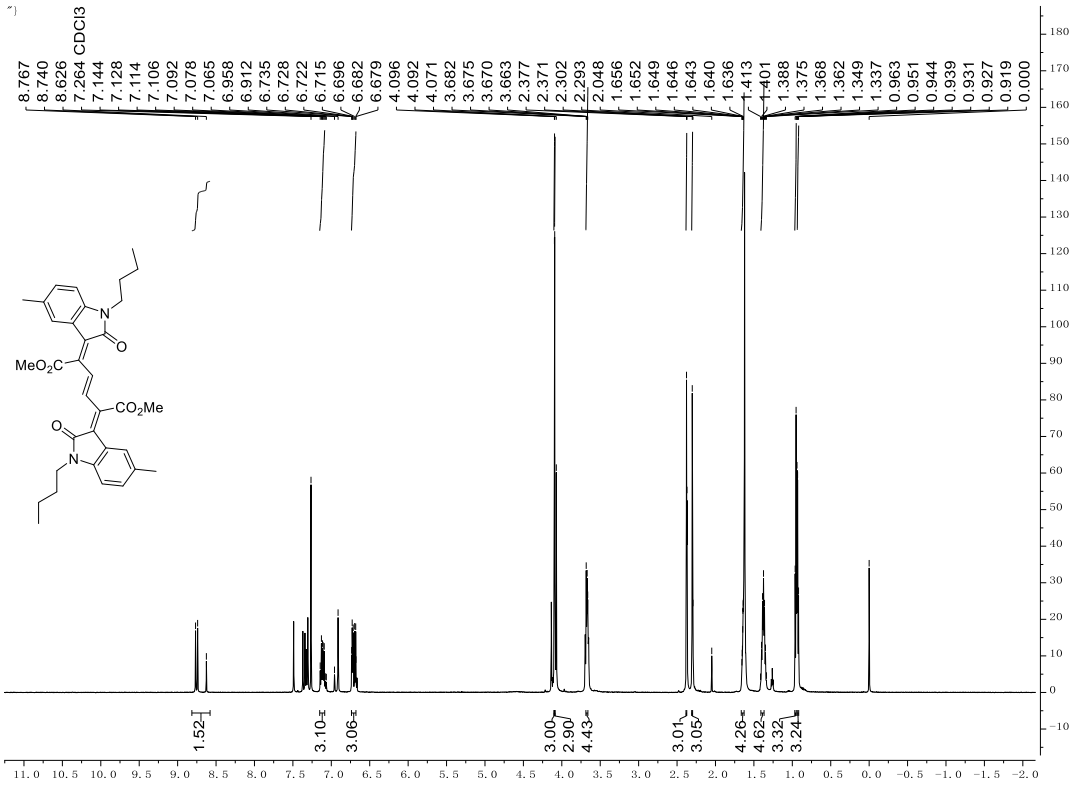
Dimethyl (*E*)-4-((*E*)-1-butyl-5-methyl-2-oxoindolin-3-ylidene)-2-(((*Z*)-1-butyl-5-methyl-2-oxoindolin-3-ylidene)methyl)pent-2-enedioate (7b): red solid, 62%, 35 mg, m.p. 233-234 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.63 (s, 2H, CH), 7.07 (d, *J* = 8.4 Hz, 2H, ArH), 6.96 (s, 2H, ArH), 6.67 (d, *J* = 8.0 Hz, 2H, ArH), 4.14 (s, 6H, OCH_3), 3.68 (t, *J* = 7.4 Hz, 4H, CH), 2.29 (s, 6H, CH_3), 1.66-1.61 (m, 4H,CH), 1.38 (h, *J* = 7.4 Hz, 4H, CH), 0.95 (t, *J* = 7.4 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.2, 166.9, 165.6, 165.0, 141.4, 131.5, 131.2, 123.7, 108.3, 52.96, 52.95, 39.534, 39.530, 29.603, 29.599, 21.208, 21.206, 20.218, 20.215, 13.754, 13,753; IR (KBr) υ: 1732, 1686, 1612, 1588, 1489, 1433, 1354, 1300, 1258, 1229, 1201, 1171, 1153, 1113, 1063, 988, 949, 911, 822cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{34}H_{38}N_2NaO_6$ ([M+Na]$^{+}$): 593.2622, Found: 593.2617.

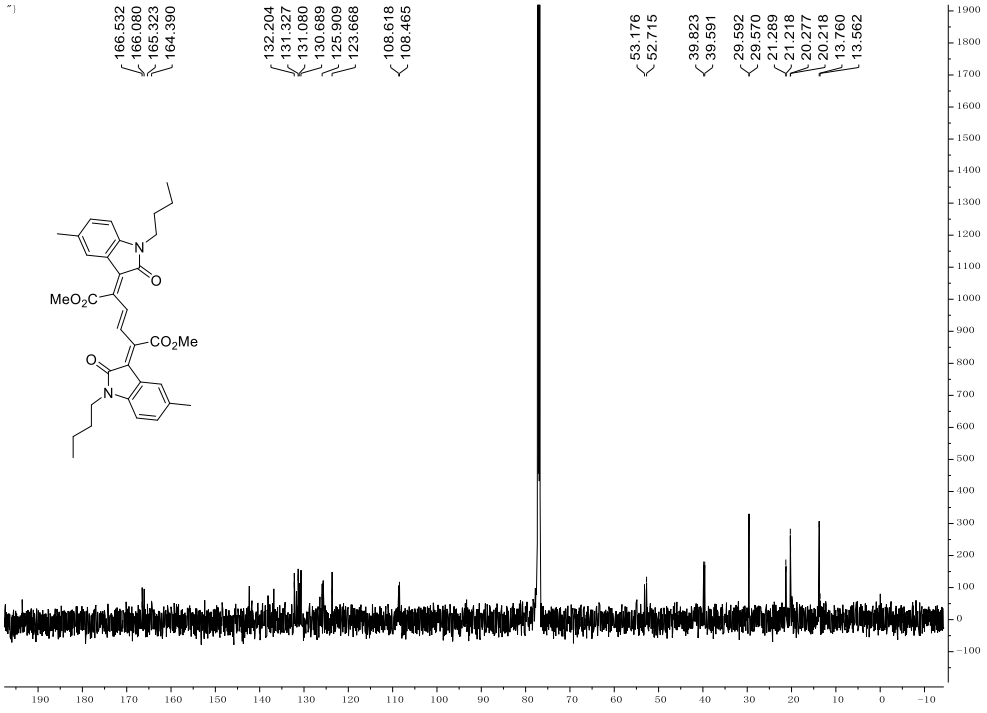


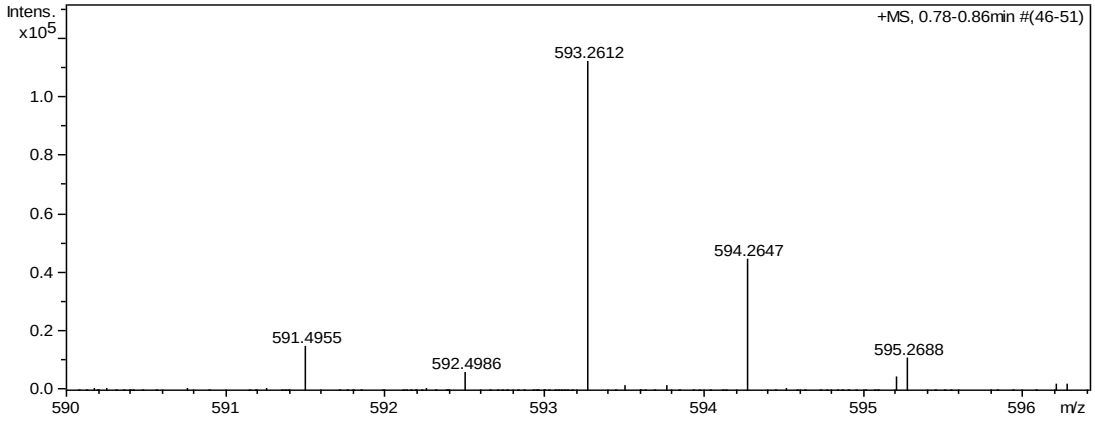

167.149
166.903
165.598
165.036
141.386
131.524
131.232
123.719
108.253
52.955
52.949
39.534
39.530
29.603
29.599
21.208
21.206
20.218
20.215
13.754
13.753
MeO2C
CO2Me
O
N


Intens.
x10^4
+MS, 0.14-0.32min #(8-19)
593.2617
594.2650
591.4954
592.4992
595.2681
m/z

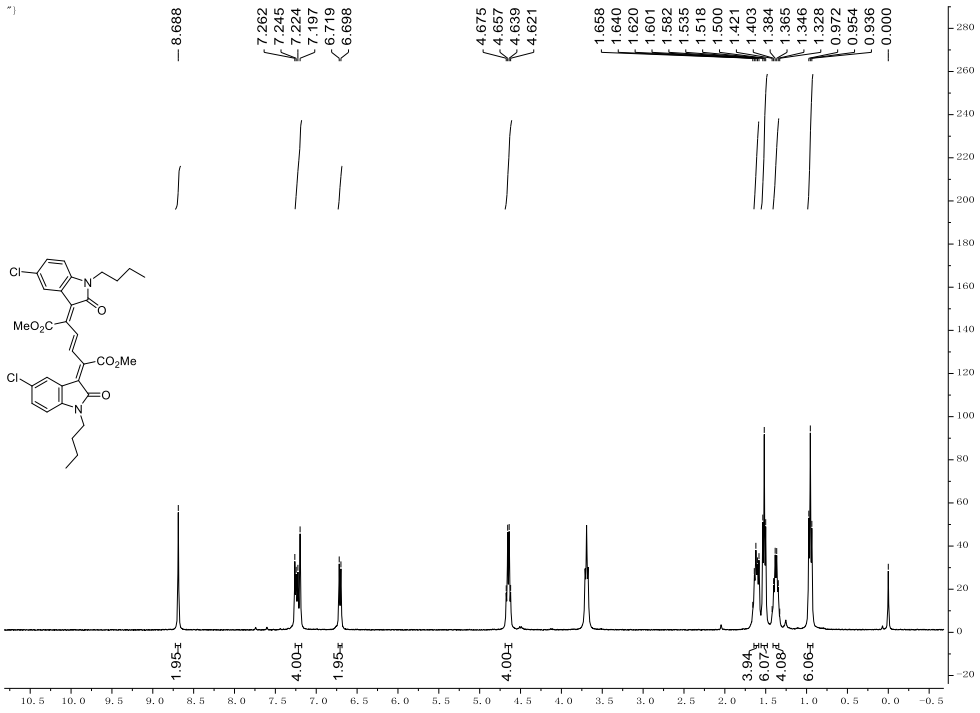
Dimethyl (*E*)-4-((*E*)-1-butyl-5-methyl-2-oxoindolin-3-ylidene)-2-(((*E*)-1-butyl-5-methyl-2-oxoindolin-3-ylidene)methyl)pent-2-enedioate (8b): red solid, 14%, 8 mg, m.p. 164-165 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.81-8.58 (m, 2H, CH), 7.15-7.09 (m, 3H, ArH), 6.74-6.68 (m, 3H, ArH), 4.10 (s, 3H, OCH_3), 4.09 (s, 3H, OCH_3), 3.69-3.66 (m, 4H, CH), 2.38 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 1.66-1.63 (m, 4H, CH), 1.38 (q, J_1 = 5.9 Hz, J_2 = 3.9 Hz, 4H, CH), 0.96 (d, J = 7.3 Hz, 3H, CH_3), 0.93 (d, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.5, 166.1, 165.3, 164.4, 132.2, 131.3, 131.1, 130.7, 125.9, 123.7, 108.6, 108.5, 53.2, 52.7, 39.8, 39.6, 29.59, 29.57, 21.3, 21.2, 20.3, 20.2, 13.8, 13.6; IR (KBr) υ: 1741, 1720, 1701, 1615, 1552, 1486, 1434, 1355, 1310, 1225, 1201, 1176, 1148, 1112, 1078, 987, 810 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{34}H_{38}N_2NaO_6$ ([M+Na]$^{+}$): 593.2622, Found: 593.2612.

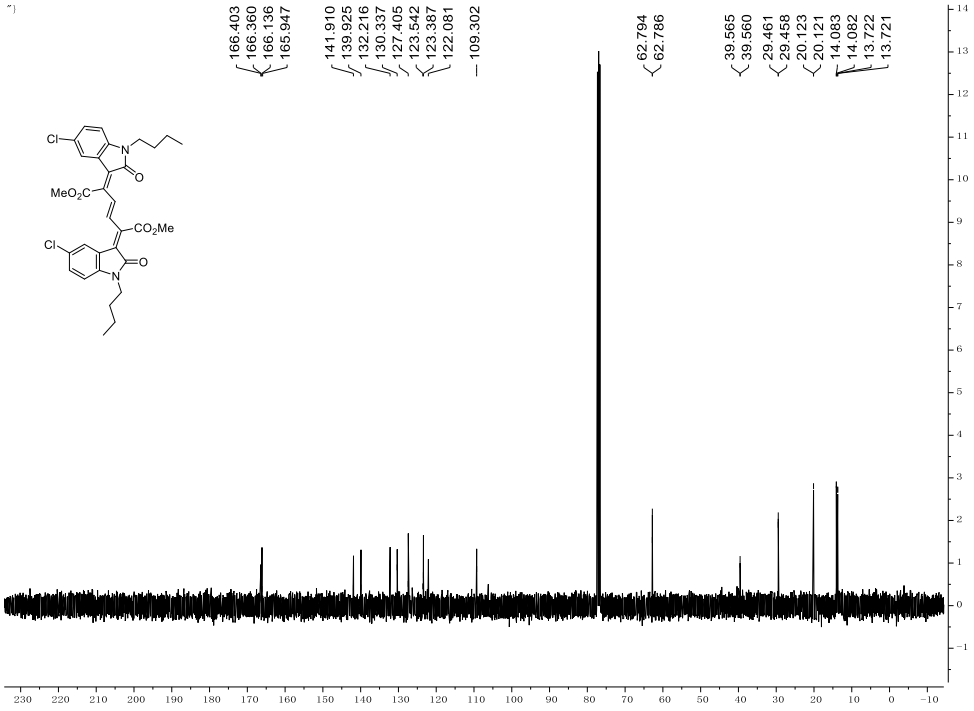


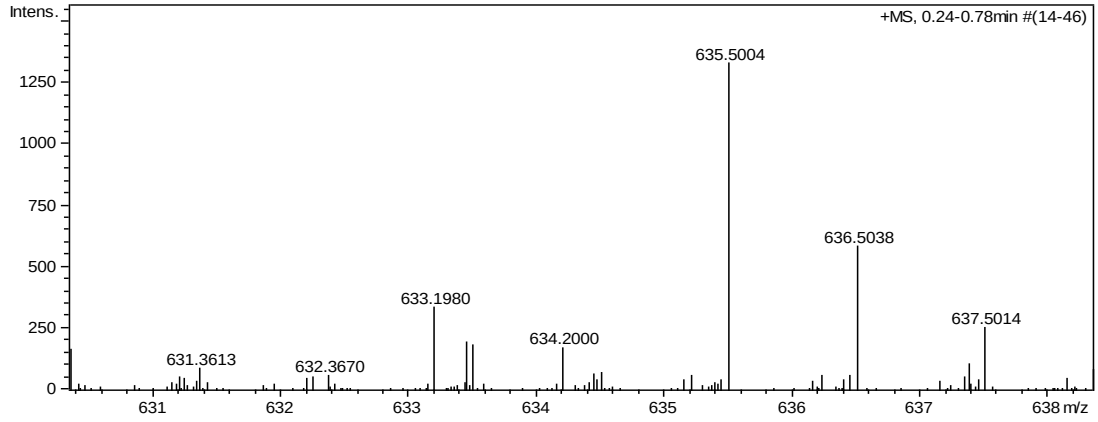

166.532
166.080
165.323
164.390
132.204
131.327
131.080
130.689
125.909
123.668
108.618
108.465
53.176
52.715
39.823
39.591
29.592
29.570
21.289
21.218
20.277
20.218
13.760
13.562
MeO2C
CO2Me
O
N


Intens.
x10^5
+MS, 0.78-0.86min #(46-51)
593.2612
594.2647
591.4955
592.4986
595.2688
m/z

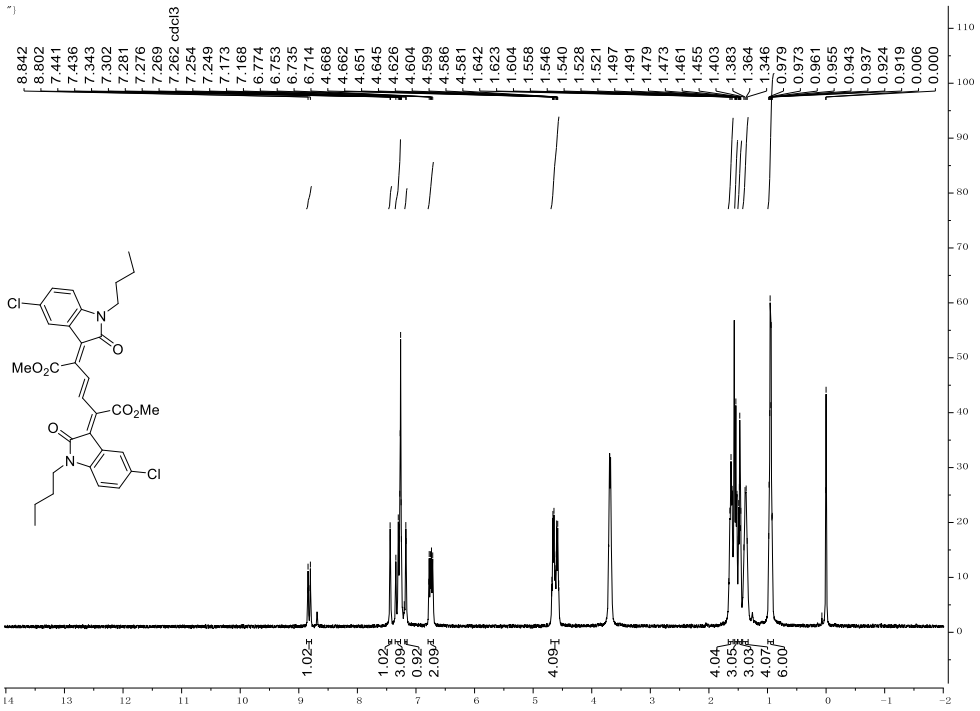
Dimethyl (*E*)-4-((*E*)-1-butyl-5-methyl-2-oxoindolin-3-ylidene)-2-(((*Z*)-1-butyl-5-methyl-2-oxoindolin-3-ylidene)methyl)pent-2-enedioate (7c): red solid, 66%, 40 mg, m.p. 237-238 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (s, 2H, CH), 7.26-7.18 (m, 4H, ArH), 6.71 (d, *J* = 8.4 Hz, 2H, ArH), 4.65 (q, *J* = 7.2 Hz, 4H, CH), 1.66-1.58 (m, 4H, CH), 1.52 (t, *J* = 7.2 Hz, 6H, OCH_3), 1.42-1.33 (m, 4H, CH), 0.95 (t, *J* = 7.3 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.40, 166.36, 166.1, 166.0, 141.9, 139.9, 132.2, 130.3, 127.4, 123.5, 123.4, 122.1, 109.3, 62.794, 62.786, 39.57, 39.56, 29.461, 29.458, 20.123, 20.121, 14.083, 14.082, 13.722, 13.721; IR (KBr) υ: 1728, 1691, 1608, 1477, 1435, 1349, 1272, 1210, 1188, 1176, 1109, 1014, 858, 808 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{32}H_{32}Cl_2N_2NaO_6$ ($[M+Na]^+$): 633.1950, Found: 633.1980.

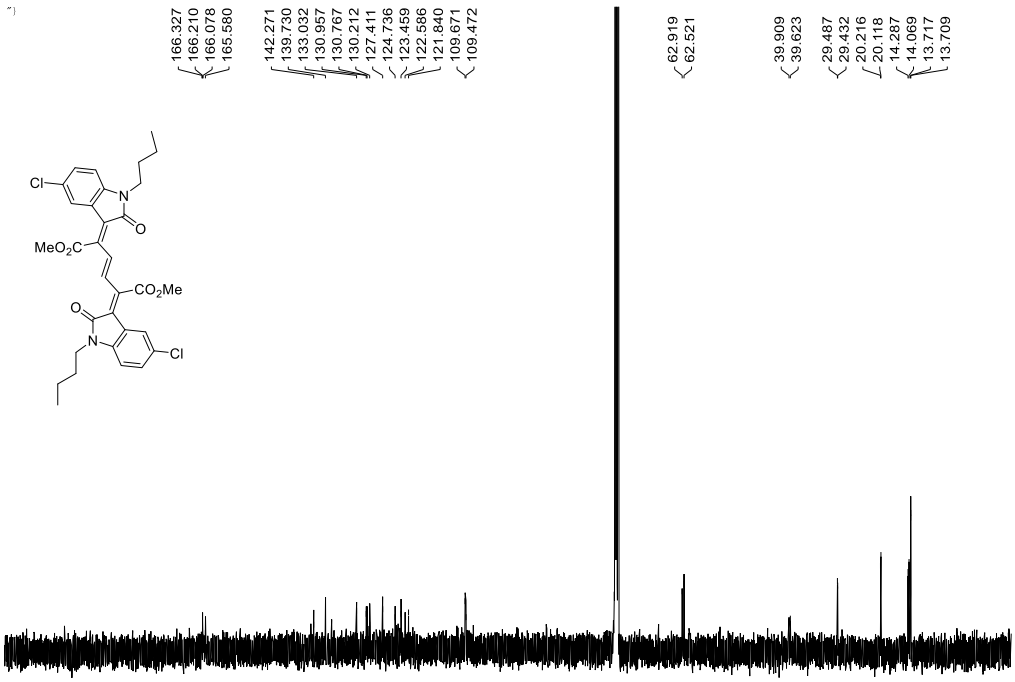


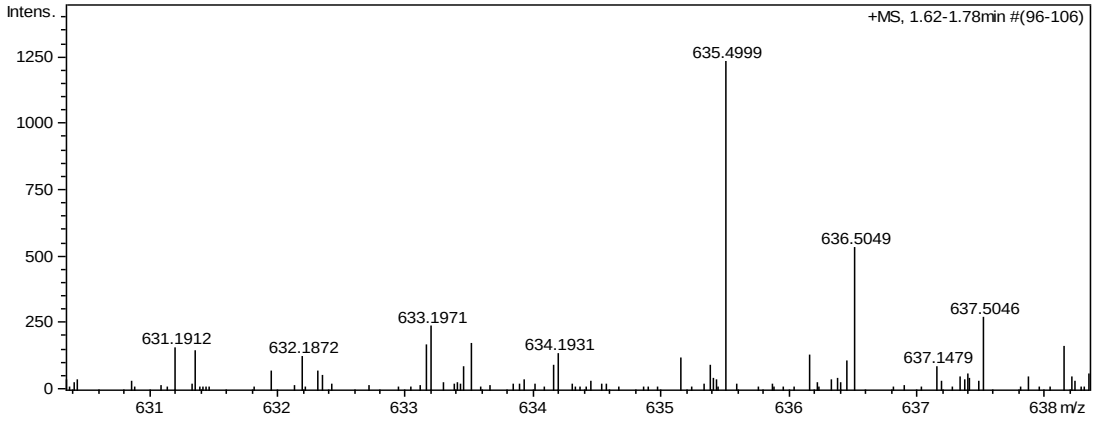

166.403
166.360
166.136
165.947
141.910
139.925
132.216
130.337
127.405
123.542
123.387
122.081
109.302
62.794
62.786
39.565
39.560
29.461
29.458
20.123
20.121
14.083
14.082
13.722
13.721
Cl
N
O
MeO2C
CO2Me
Cl
O
N


Intens.
+MS, 0.24-0.78min #(14-46)
635.5004
636.5038
633.1980
637.5014
634.2000
631.3613
632.3670
m/z

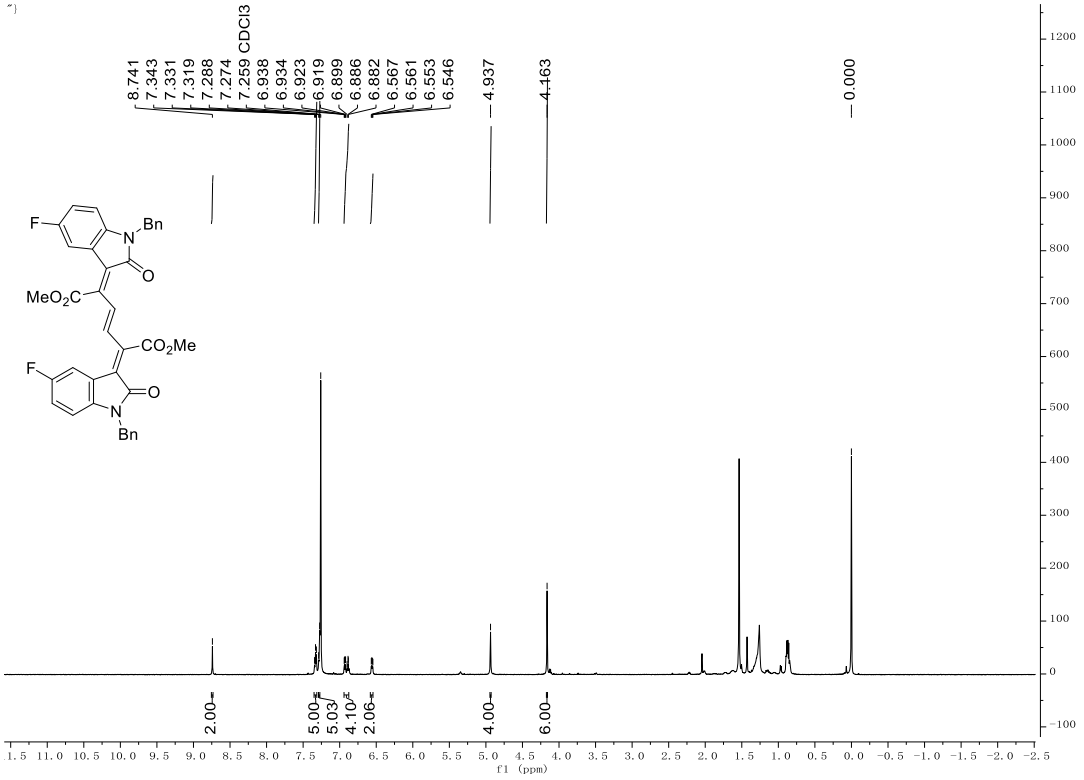
Dimethyl (*E*)-4-((*E*)-1-butyl-5-chloro-2-oxoindolin-3-ylidene)-2-(((*E*)-1-butyl-5-chloro-2-oxoindolin-3-ylidene)methyl)pent-2-enedioate (8c): red solid, 12%, 7 mg, m.p. 168-169 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.83 (dd, J_1 = 16.1 Hz, J_2 = 2.4 Hz, 1H, CH), 7.44 (d, J = 2.2 Hz, 1H, ArH), 7.36-7.28 (m, 3H, ArH), 7.17 (d, J = 2.1 Hz, 1H, ArH), 6.75 (dd, J_1 = 15.5 Hz, J_2 = 8.4 Hz, 2H, ArH), 4.62 (dd, J_1 = 24.9 Hz, J_2 =8.8 Hz, 4H, CH), 1.62 (t, J = 7.6 Hz, 4H, CH), 1.56-1.52(m, 3H, OCH_3), 1.43-1.33(m, 3H, OCH_3), 1.37 (q, J = 7.6 Hz, 4H, CH), 0.95 (q, J_1 = 7.2 Hz, J_2 =2.4 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 166.2, 166.1, 165.6, 142.3, 139.7, 133.0, 131.0, 130.8, 130.2, 127.4, 124.7, 123.5, 122.6, 121.8, 109.7, 109.5, 62.9, 62.5, 39.9, 39.6, 29.5, 29.4, 20.2, 20.1, 14.3, 14.1, 13.72, 13,71; IR (KBr) υ: 1729, 1709, 1608, 1474, 1438, 1348, 1192, 1110, 805 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{32}H_{32}Cl_2N_2NaO_6$ ([M+Na]$^{+}$): 633.1950, Found: 633.1971.

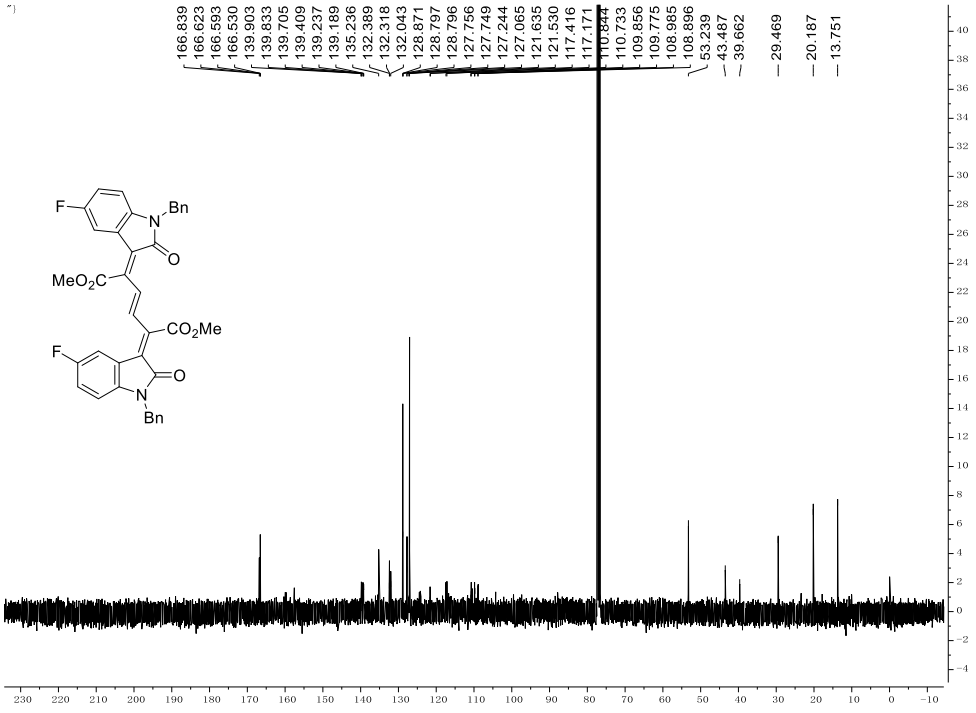



166.327
166.210
166.078
165.580
142.271
139.730
133.032
130.957
130.767
130.212
127.411
124.736
123.459
122.586
121.840
109.671
109.472
62.919
62.521
39.909
39.623
29.487
29.432
20.216
20.118
14.287
14.069
13.717
13.709
Cl
N
O
MeO2C
CO2Me
O
N
Cl


Intens.
+MS, 1.62-1.78min #(96-106)
1250
1000
750
500
250
0
635.4999
636.5049
637.5046
633.1971
631.1912
632.1872
634.1931
637.1479
631
632
633
634
635
636
637
638 m/z

Dimethyl (*E*)-4-((*E*)-1-benzyl-5-fluoro-2-oxoindolin-3-ylidene)-2-(((*Z*)-1-benzyl-5-fluoro-2-oxoindolin-3-ylidene)methyl)pent-2-enedioate (7d): red solid, 65%, 41 mg, m.p. 236-237 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.74 (s, 2H, CH), 7.33 (t, *J* = 7.4 Hz, 5H, ArH), 7.28 (d, *J* = 8.2 Hz, 5H, ArH), 6.94–6.88 (m, 4H, ArH), 6.56 (dd, *J* = 8.7, 4.1 Hz, 2H, ArH), 4.94 (s, 4H, CH), 4.16 (s, 6H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.8, 166.62, 166.59, 166.53, 139.9, 139.8, 139.7, 139.4, 139.2, 139.2, 135.2, 132.4, 132.3, 132.0, 128.9, 128.8, 127.8, 127.2, 127.1, 121.6, 121.5, 117.4, 117.2, 110.8, 110.7, 109.9, 109.8, 109.0, 108.9, 53.2, 43.5, 39.7, 29.5, 20.2, 13.8; IR (KBr) υ: 1737, 1691, 1618, 1483, 1456, 1336, 1280, 1226, 1167, 1107, 991, 855, 811 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{28}F_2N_2NaO_6$ ([M+Na]$^{+}$): 684.2027, Found: 684.2013.

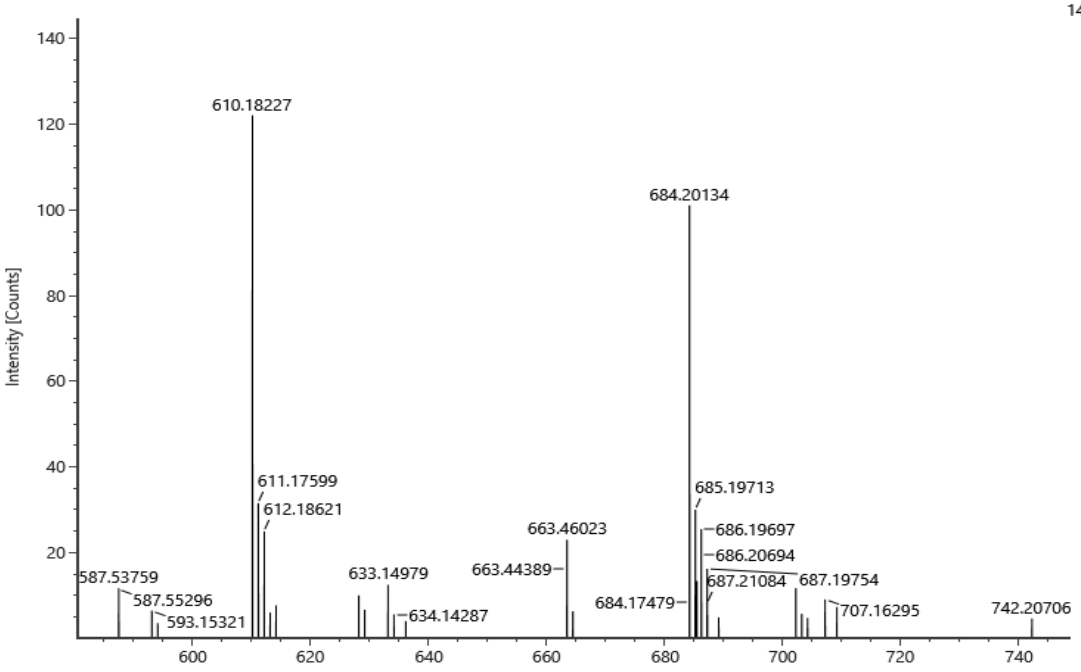




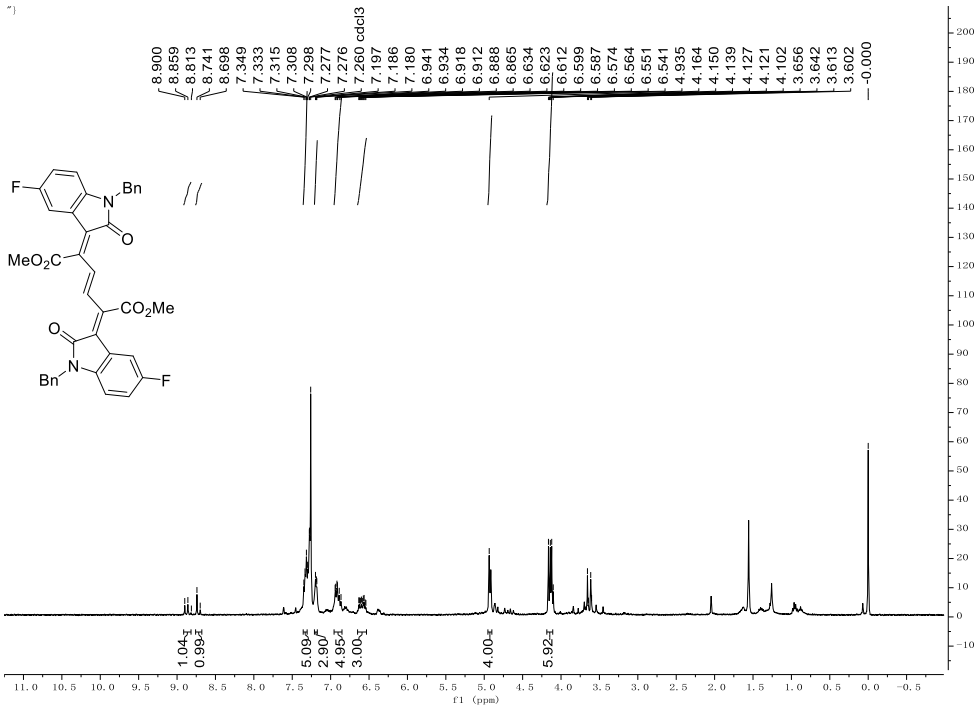
Item name: Sample 9
Item description:

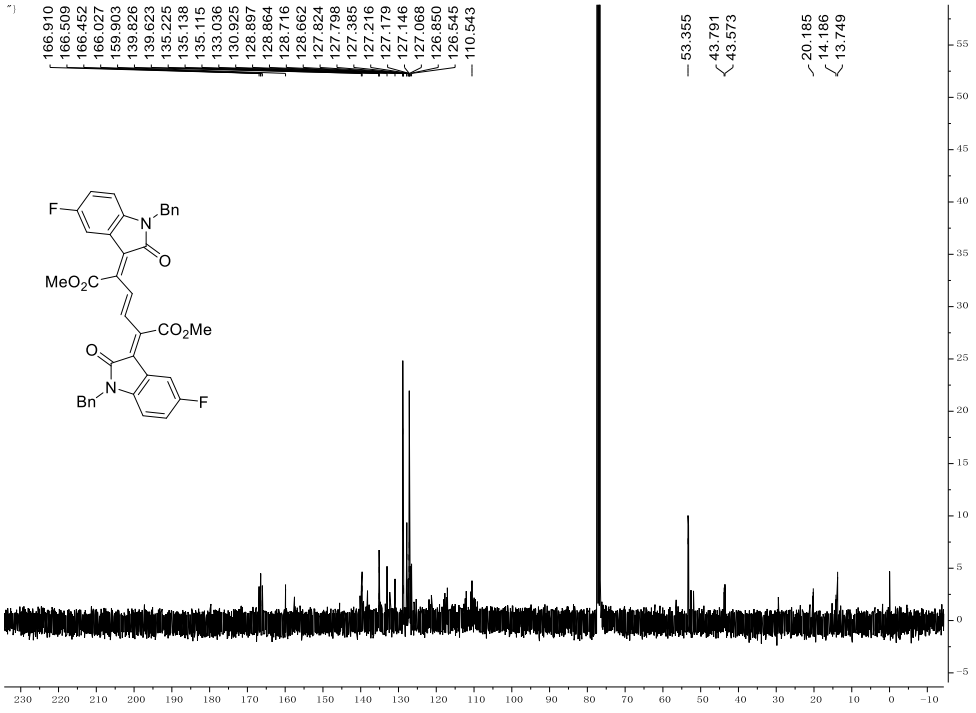
Channel name: 2: Average Time 0.1059 min : TOF MSe (50-1000) 6eV ESI+ : Combined

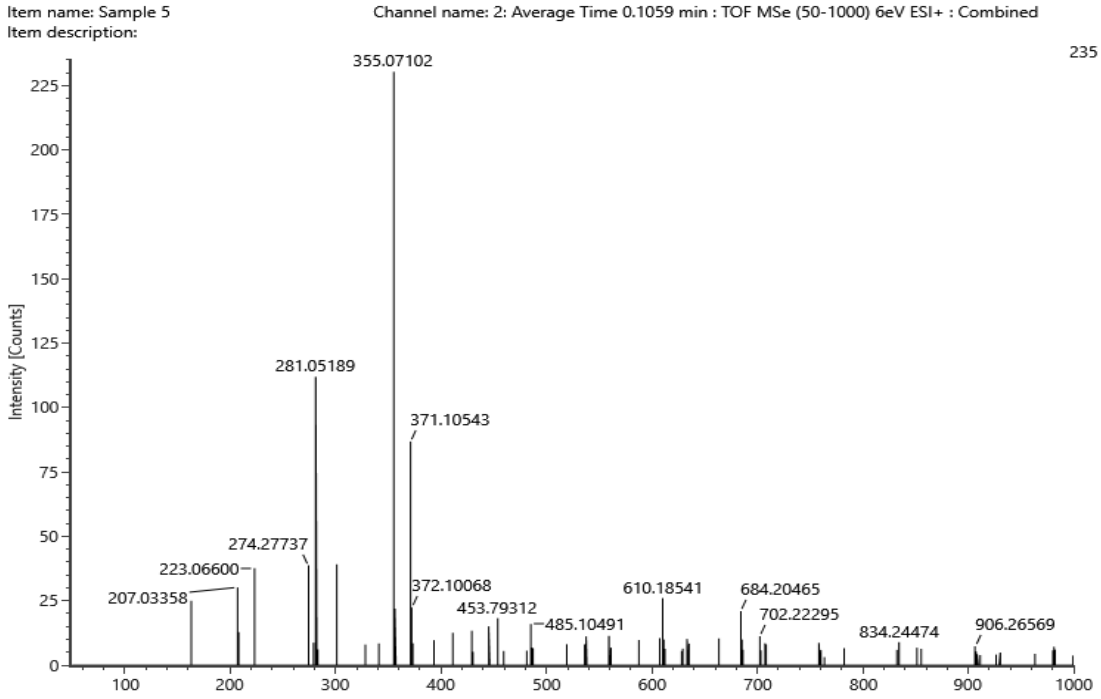
145



Dimethyl (*E*)-4-((*E*)-1-benzyl-5-fluoro-2-oxoindolin-3-ylidene)-2-(((*E*)-1-benzyl-5-fluoro-2-oxoindolin-3-ylidene)methyl)pent-2-enedioate (8d): red solid, 13%, 9 mg, m.p. 164-165 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.88 (d, *J* = 16.2 Hz, 1H, ArH), 8.72 (d, *J* = 17.0 Hz, 1H, ArH), 7.33 (q, J_1 = 4.6 Hz, J_2 = 3.1 Hz, 5H, ArH), 7.21-7.17 (m, 3H, ArH), 6.96-6.85 (m, 5H, ArH), 6.65-6.53 (m, 3H, ArH), 4.92 (d, *J* = 8.3 Hz, 4H, CH), 4.19-4.11 (m, 6H, OCH_3) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.9, 166.5, 139.8, 139.6, 135.2, 135.14, 135.12, 133.0, 130.9, 128.9, 128.7, 127.8, 127.4, 127.2, 127.1, 126.9, 126.5, 110.5, 53.4, 43.8, 43.6, 20.2, 14.2, 13.8; IR (KBr) υ: 1431, 1371, 1282, 1164, 1112, 1062, 993, 853, 810 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{29}F_2N_2O_6$ ([M+H]$^+$): 684.2027, Found: 684.2047.




166.910
166.509
166.452
166.027
159.903
139.826
139.623
135.225
135.138
135.115
133.036
130.925
128.897
128.864
128.716
128.662
127.824
127.798
127.385
127.216
127.179
127.146
127.068
126.850
126.545
110.543
53.355
43.791
43.573
20.185
14.186
13.749
F
N
Bn
O
MeO2C
CO2Me
O
N
Bn
F


Item name: Sample 5
Item description:
Channel name: 2: Average Time 0.1059 min : TOF MSe (50-1000) 6eV ESI+ : Combined
235
355.07102
281.05189
371.10543
274.27737
223.06600
207.03358
372.10068
453.79312
485.10491
610.18541
684.20465
702.22295
834.24474
906.26569
Intensity [Counts]