

# Supporting Information

## Enantioselective synthesis of spiro[indoline-3,4'-pyrano[2,3-c]pyrazole] derivatives via organocatalytic asymmetric Michael/cyclization cascade reaction

Jin Xie,<sup>a</sup> Xiao-Yu Xing,<sup>a</sup> Feng Sha,<sup>\*,a</sup> Zhi-Yan Wu<sup>b</sup>, Xin-Yan Wu<sup>\*, a</sup>

<sup>a</sup> *Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China*

<sup>b</sup> *Quanzhou High School, Guilin, Guangxi 541500*

E-mail: [xinyanwu@ecust.edu.cn](mailto:xinyanwu@ecust.edu.cn)

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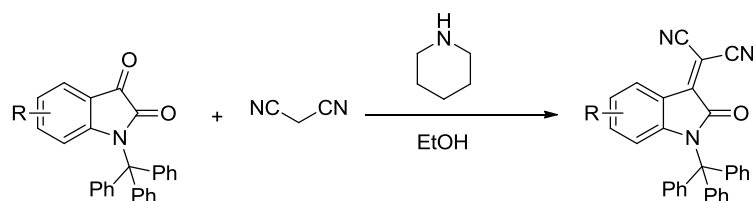
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## 1. General Information

Melting points were taken without correction.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 300 spectrometer or Bruker 400 spectrometer.  $^1\text{H}$  NMR spectra were referenced to tetramethylsilane ( $\delta$  0.00 ppm) using  $\text{CDCl}_3$  as solvent or referenced to solvent protons ( $\delta$  2.50 ppm) using  $\text{DMSO-}d_6$  as solvent.  $^{13}\text{C}$  NMR spectra were referenced to solvent carbons ( $\delta$  77.0 ppm for  $\text{CDCl}_3$  or  $\delta$  39.52 ppm for  $\text{DMSO-}d_6$ ). IR spectra were recorded on Nicolet Magna-I 550 spectrometer. High resolution mass spectra (HRMS) were performed on an electron spray ionization time-of-flight (ESI-TOF) mass spectrometer. Thin-layer chromatography (TLC) was performed on 10-40  $\mu\text{m}$  silica gel plates. Column chromatography was performed, using silica gel (300-400 mesh) eluted with ethyl acetate and  $\text{CH}_2\text{Cl}_2$ .

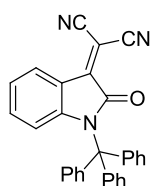
Pyrazolones **1a-1e**<sup>1</sup> and isatyliidene malononitriles **2a-2d**, **2q-2s**<sup>2</sup> were prepared according to literature procedures.

## 2. Synthesis of Isatyliidene Malononitriles 2e-2p



To a solution of the *N*-substituted isatins (5.0 mmol) in anhydrous ethanol (10 mL) malonodinitrile was added, as well as one drop piperidine as catalyst. The resulting mixture was stirred until the reaction completed (monitored by TLC). The solvent was removed under reduced pressure and the residue was purified by column chromatography ( $\text{CH}_2\text{Cl}_2$ ) to give the desired product **2**.

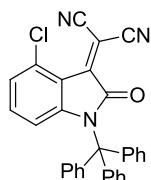
### 2-(2-oxo-1-tritylindolin-3-ylidene)malononitrile (2e)



Red solid, mp: 236.2-239.1  $^{\circ}\text{C}$ ,  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz):  $\delta$  7.98 (d,  $J = 7.6$  Hz, 1H), 7.48 (d,  $J = 7.6$  Hz, 6H), 7.31 (t,  $J = 7.6$  Hz, 7H), 7.28-7.19 (m, 3H), 7.13 (t,  $J = 7.6$  Hz, 1H), 6.29 (d,  $J = 8.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100 MHz):  $\delta$  163.4, 149.9, 146.4, 141.1, 135.9, 128.8, 127.9, 127.1, 125.2,

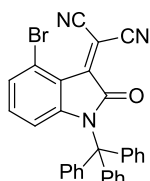
123.3, 119.3, 116.5, 113.1, 111.9, 80.6, 74.4; IR (KBr, cm<sup>-1</sup>):  $\nu$  3421, 3036, 2225, 1719, 1593, 1579, 1490, 1461, 1448, 1340, 1311, 1279, 1209, 1188, 1210, 1186, 1111, 1033, 1002, 794, 773, 764, 744, 722, 706, 697, 644; HRMS (ESI) calcd for C<sub>30</sub>H<sub>19</sub>KN<sub>3</sub>O ([M+K]<sup>+</sup>): 476.1165, found: 476.1163.

### 2-(4-chloro-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2f)



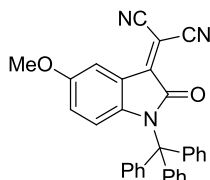
Red solid, mp: 219.2-223.1 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.41 (d,  $J$  = 6.6 Hz, 6H), 7.31-7.23 (m, 9H), 7.09 (t,  $J$  = 8.4 Hz, 1H), 6.97 (d,  $J$  = 8.1 Hz, 1H), 6.32 (d,  $J$  = 8.1 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  164.4, 148.2, 147.8, 140.5, 135.8, 134.2, 128.9, 128.1, 127.5, 125.3, 117.7, 115.0, 113.2, 112.2, 85.7, 75.7; IR (KBr, cm<sup>-1</sup>):  $\nu$  3420, 2959, 2927, 2852, 1733, 1584, 1455, 1428, 1332, 1279, 1256, 1226, 1184, 1146, 1084, 1023, 760, 749, 704; HRMS (ESI) calcd for C<sub>30</sub>H<sub>18</sub>ClNaN<sub>3</sub>O ([M+Na]<sup>+</sup>): 494.1036, found: 494.1034.

### 2-(4-bromo-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2g)



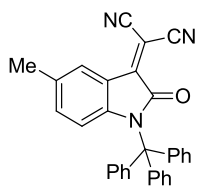
Red solid, mp: 217.4-220.3 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.42 (d,  $J$  = 7.5 Hz, 6H), 7.31-7.16 (m, 10H), 6.99 (t,  $J$  = 8.4 Hz, 1H), 6.37 (d,  $J$  = 8.4 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  164.7, 149.3, 148.5, 140.5, 135.7, 128.8, 128.1, 127.5, 122.2, 119.8, 115.4, 113.1, 111.9, 85.2, 75.7; IR (KBr, cm<sup>-1</sup>):  $\nu$  3421, 2957, 2923, 2849, 2314, 1730, 1635, 1583, 1454, 1428, 1329, 1273, 1263, 1220, 1177, 1138, 1088, 766, 750, 704; HRMS (ESI) calcd for C<sub>30</sub>H<sub>18</sub>BrNaN<sub>3</sub>O ([M+Na]<sup>+</sup>): 538.0531, found: 538.0539.

### 2-(5-methoxy-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2h)



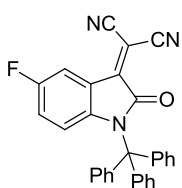
Red solid, mp: 196.9-199.1 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.63 (d,  $J$  = 2.7 Hz, 1H), 7.41 (d,  $J$  = 6.9 Hz, 6H), 7.30-7.17 (m, 9H), 6.74 (dd,  $J_1$  = 9.0 Hz,  $J_2$  = 2.7 Hz, 1H), 6.23 (d,  $J$  = 9.3 Hz, 1H), 3.74 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  163.4, 155.5, 150.0, 141.4, 140.8, 129.0, 128.0, 127.3, 123.4, 119.6, 117.9, 112.7, 111.1, 109.3, 81.3, 75.3, 55.6; IR (KBr, cm<sup>-1</sup>):  $\nu$  3434, 2957, 2927, 2850, 2228, 1727, 1581, 1484, 1449, 1308, 1274, 1265, 1230, 1193, 1164, 1121, 1089, 1035, 902, 873, 851, 821, 800, 764, 748, 727, 704; HRMS (ESI) calcd for C<sub>31</sub>H<sub>21</sub>NaN<sub>3</sub>O<sub>2</sub> ([M+Na]<sup>+</sup>): 490.1531, found: 490.1531.

### 2-(5-methyl-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2i)



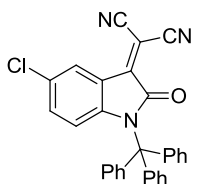
Red solid, mp: 226.7-228.4 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.90 (s, 1H), 7.41 (d,  $J = 7.8$  Hz, 6H), 7.28-7.23 (m, 9H), 6.97 (d,  $J = 8.4$  Hz, 1H), 6.21 (d,  $J = 8.4$  Hz, 1H), 3.24 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  163.4, 149.8, 145.1, 140.8, 137.1, 133.2, 128.9, 127.9, 127.3, 126.0, 119.0, 116.7, 112.7, 111.2, 80.8, 75.2, 20.6; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3422, 2958, 2924, 2227, 1725, 1616, 1579, 1482, 1451, 1314, 1270, 1242, 1196, 1160, 1129, 1087, 1036, 1003, 903, 822, 795, 726, 704; HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{21}\text{NaN}_3\text{O}$  ( $[\text{M}+\text{Na}]^+$ ): 474.1582, found: 474.1578.

### 2-(5-fluoro-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2j)



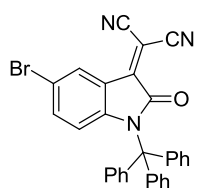
Red solid, mp: 224.2-228.2 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.83 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 2.4$  Hz, 1H), 7.41-7.38 (m, 6H), 7.31-7.21 (m, 9H), 6.89 (dt,  $J_1 = 8.8$  Hz,  $J_2 = 2.8$  Hz, 1H), 6.30 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 4.0$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  163.0, 159.9, 156.6, 149.1, 143.5, 140.5, 128.9, 128.1, 127.5, 123.0 (d,  $J_{\text{C-F}} = 23.3$  Hz), 119.6 (d,  $J_{\text{C-F}} = 8.6$  Hz), 118.1 (d,  $J_{\text{C-F}} = 7.4$  Hz), 112.5 (d,  $J_{\text{C-F}} = 25.1$  Hz), 111.4 (d,  $J_{\text{C-F}} = 107.8$  Hz), 82.9, 75.6; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3447, 2227, 1729, 1587, 1480, 1451, 1316, 1301, 1268, 1223, 1185, 1167, 1155, 1114, 1084, 1036, 1006, 980, 903, 872, 823, 810, 743, 726, 704; HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{18}\text{FNaN}_3\text{O}$  ( $[\text{M}+\text{Na}]^+$ ): 478.1332, found: 478.1332.

### 2-(5-chloro-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2k)



Red solid, mp: 210.3-212.6 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.07 (s, 1H), 7.39 (d,  $J = 7.2$  Hz, 6H), 7.27 (d,  $J = 7.5$  Hz, 9H), 7.13 (d,  $J = 8.7$  Hz, 1H), 6.29 (d,  $J = 9.3$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  162.8, 148.5, 145.6, 140.4, 135.7, 128.9, 128.1, 127.5, 125.3, 120.0, 118.0, 112.1, 110.6, 82.9, 75.6; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3427, 2957, 2928, 2853, 2320, 1726, 1598, 1457, 1304, 1267, 1182, 1125, 1088, 1052, 957, 903, 878, 821, 766, 745, 726, 704; HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{18}\text{ClNaN}_3\text{O}$  ( $[\text{M}+\text{Na}]^+$ ): 494.1036, found: 494.1033.

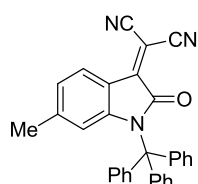
### 2-(5-bromo-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2l)



Red solid, mp: 225.4-227.8 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.21 (s, 1H), 7.39 (d,  $J = 6.9$  Hz, 6H), 7.31-7.24 (m, 10H), 6.23 (d,  $J = 9.0$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  162.7, 148.3, 146.1, 140.4, 138.5, 128.9, 128.2, 128.1, 127.6, 120.4, 118.3, 116.4, 112.1, 110.6, 82.9, 75.6; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3423, 2958, 2926, 2850, 2222, 1723, 1592, 1463, 1302, 1267, 1186, 1127, 1080, 1033,

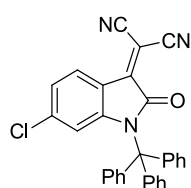
951, 902, 881, 819, 766, 747, 724, 701; HRMS (ESI) calcd for  $C_{30}H_{18}BrNaN_3O$  ( $[M+Na]^+$ ): 538.0531, found: 538.0529.

### 2-(6-methyl-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2m)



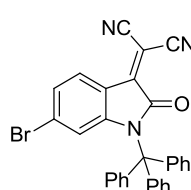
Red solid, mp: 239.5-242.1 °C,  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  7.99 (d,  $J = 8.1$  Hz, 1H), 7.41 (d,  $J = 7.2$  Hz, 6H), 7.31-7.23 (m, 9H), 6.82 (d,  $J = 7.8$  Hz, 1H), 6.03 (s, 1H), 2.11 (s, 3H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  163.7, 149.3, 148.6, 147.6, 140.9, 129.0, 127.9, 127.3, 125.9, 124.3, 117.6, 116.8, 112.9, 111.3, 79.6, 75.3, 23.2; IR (KBr,  $cm^{-1}$ ):  $\nu$  3421, 2954, 2925, 2848, 2320, 1725, 1613, 1589, 1448, 1346, 1273, 1260, 1192, 1124, 1090, 900, 817, 764, 749, 723, 701; HRMS (ESI) calcd for  $C_{31}H_{21}NaN_3O$  ( $[M+Na]^+$ ): 474.1582, found: 474.1581.

### 2-(6-chloro-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2n)



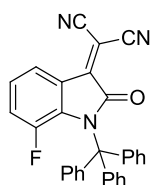
Red solid, mp: 258.1-258.5 °C,  $^1H$  NMR ( $DMSO-d_6$ , 400 MHz):  $\delta$  7.97 (d,  $J = 8.4$  Hz, 1H), 7.46 (d,  $J = 8.0$  Hz, 6H), 7.35 (t,  $J = 7.6$  Hz, 6H), 7.30-7.26 (m, 4H), 6.08 (d,  $J = 1.6$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  163.2, 148.2, 148.1, 142.6, 140.4, 128.9, 128.2, 127.6, 127.2, 126.6, 123.7, 117.5, 117.3, 112.5, 110.9, 107.6, 75.8; IR (KBr,  $cm^{-1}$ ):  $\nu$  3431, 2956, 2921, 2849, 2223, 1726, 1641, 1631, 1591, 1421, 1344, 1270, 1244, 1190, 1119, 1082, 1051, 980, 956, 936, 906, 819, 794, 768, 747, 726, 698; HRMS (ESI) calcd for  $C_{30}H_{18}ClNaN_3O$  ( $[M+Na]^+$ ): 494.1036, found: 494.1030.

### 2-(6-bromo-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2o)



Red solid, mp: 238.4-242.6 °C,  $^1H$  NMR ( $DMSO-d_6$ , 400 MHz):  $\delta$  7.88 (d,  $J = 8.4$  Hz, 1H), 7.45 (d,  $J = 8.0$  Hz, 6H), 7.42-7.39 (m, 1H), 7.35 (t,  $J = 7.6$  Hz, 6H), 7.29 (d,  $J = 7.2$  Hz, 3H), 6.23 (s, 1H);  $^{13}C$  NMR ( $DMSO-d_6$ , 100 MHz):  $\delta$  163.2, 148.8, 147.1, 140.7, 128.8, 128.0, 127.4, 126.4, 126.2, 119.0, 118.6, 113.1, 111.8, 81.2, 74.8; IR (KBr,  $cm^{-1}$ ):  $\nu$  3428, 2960, 2930, 2312, 1726, 1640, 1633, 1590, 1411, 1334, 1270, 1242, 1188, 1160, 1120, 1072, 1012, 922, 902, 864, 819, 797, 725, 698; HRMS (ESI) calcd for  $C_{30}H_{18}BrNaN_3O$  ( $[M+Na]^+$ ): 538.0531, found: 538.0526.

### 2-(7-fluoro-2-oxo-1-tritylindolin-3-ylidene)malononitrile (2p)



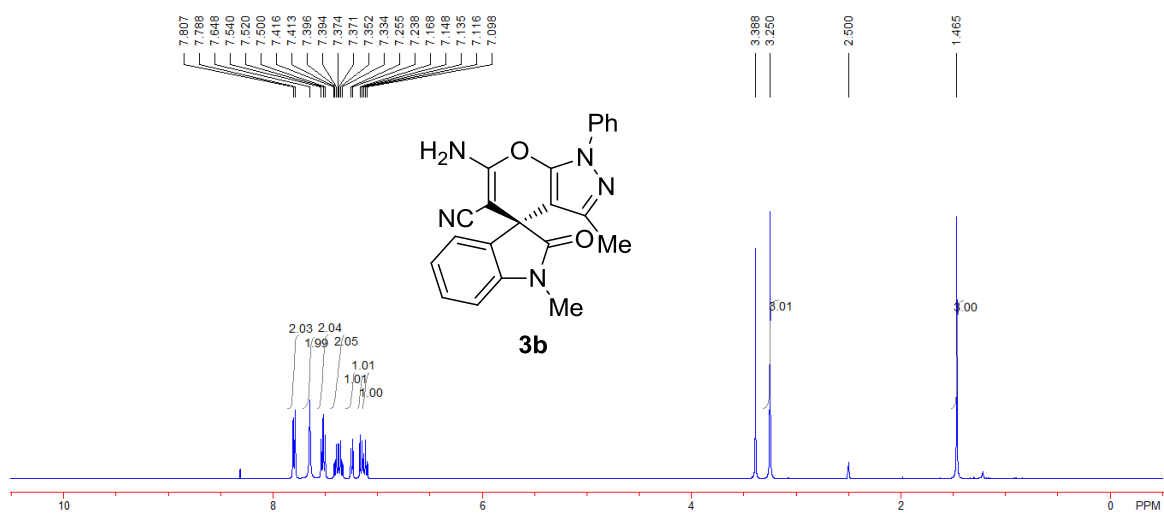
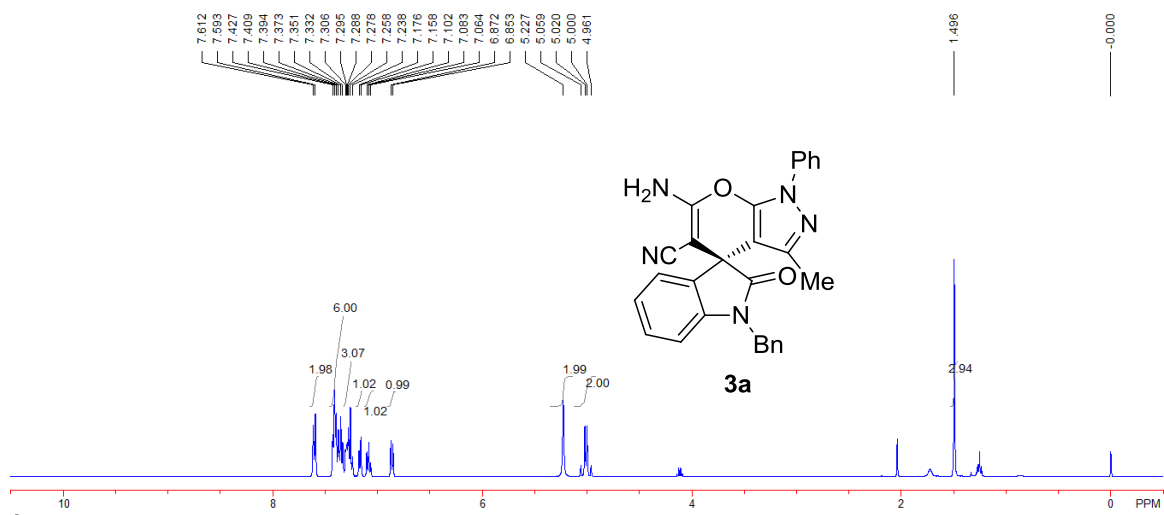
Red solid, mp: 228.9-229.9 °C,  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  8.08 (d,  $J$

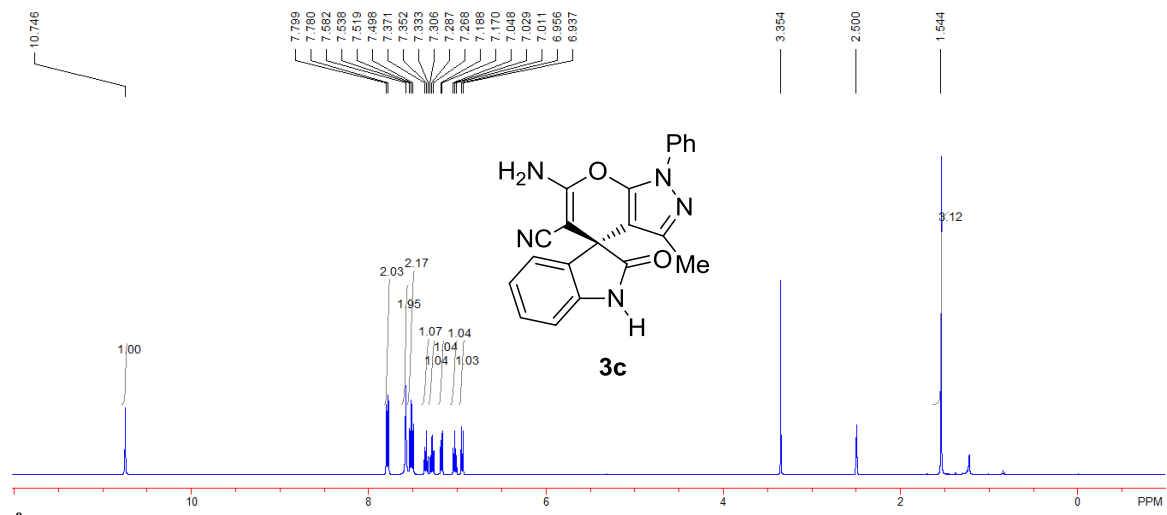
= 7.8 Hz, 1H), 7.39-7.36 (m, 6H), 7.28-7.23 (m, 9H), 7.07-6.93 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  162.6, 148.9, 148.2, 144.9, 142.1, 133.5 (d,  $J_{\text{C-F}} = 9.2$  Hz), 128.5, 127.7, 127.1, 126.5 (d,  $J_{\text{C-F}} = 23.3$  Hz), 125.2 (d,  $J_{\text{C-F}} = 7.4$  Hz), 122.5, 121.2, 111.6 (d,  $J_{\text{C-F}} = 123.2$  Hz), 83.0, 76.0; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3408, 2955, 2927, 2849, 1729, 1643, 1594, 1492, 1450, 1301, 1266, 1250, 1207, 1190, 1157, 1088, 923, 902, 862, 838, 801, 763, 745, 725, 702; HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{18}\text{FNaN}_3\text{O}$  ( $[\text{M}+\text{Na}]^+$ ): 478.1332, found: 478.1330.

### 3. References

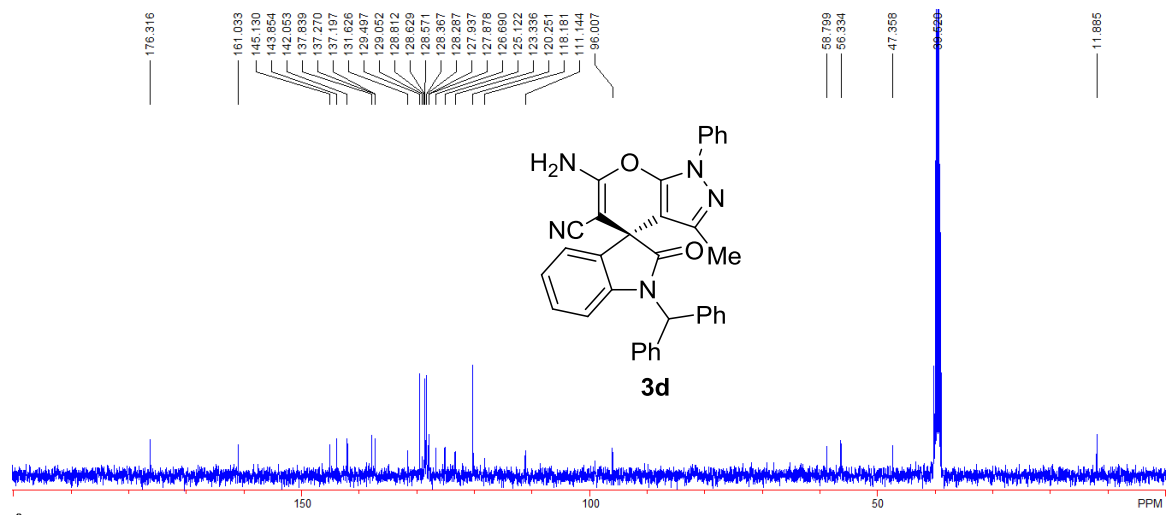
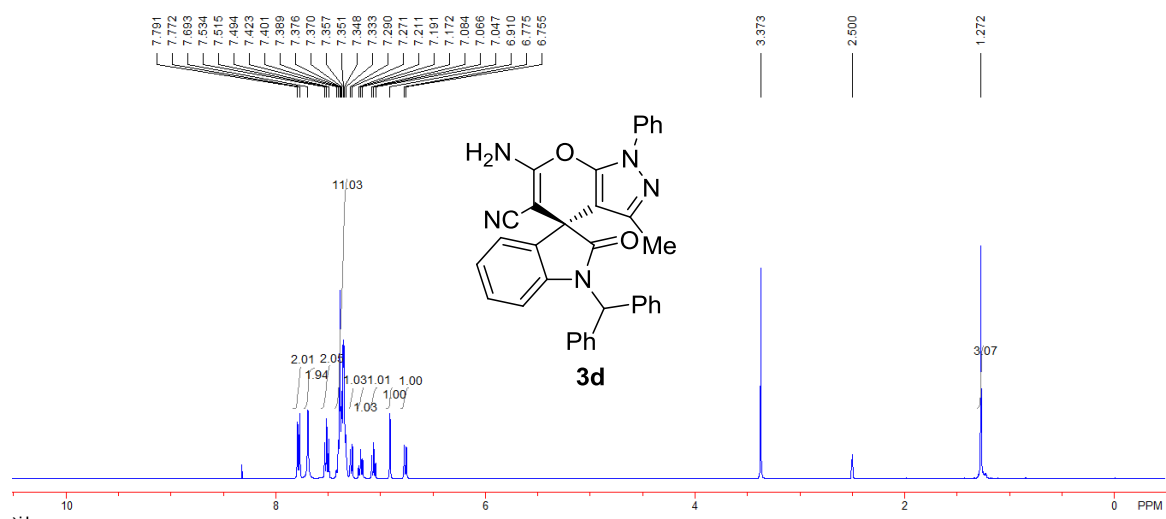
- [1] (a) G. Rassu, V. Zambrano, L. Pinna, C. Curti, L. Battistini, A. Sartori, G. Pelosi, G. Casiraghi and F. Zanardi, *Adv. Synth. Catal.*, 2014, **356**, 2330-2336; (b) X. Tang, J. Chang, C. Liu and B. Zhang, *Tetrahedron Lett.*, 2014, **55**, 6534-6537; (c) C. Xie, Z. Lu, W. Zhou, J. Han and Y. Pan, *Tetrahedron Lett.*, 2012, **53**, 6650-6653.
- [2] (a) W.-B. Chen, Z.-J. Wu, Q.-L. Pei, L.-F. Cun, X.-M. Zhang and W.-C. Yuan, *Org. Lett.*, 2010, **12**, 3132-3135; (b) F.-F. Pan, W. Yu, Z.-H. Qi, C. Qiao and X.-W. Wang, *Synthesis*, 2014, **46**, 1143-1156; (c) T. Z. Li, J. Xie, Y. Jiang, F. Sha and X. Y. Wu, *Adv. Synth. Catal.*, 2015, **357**, 3507-3511.

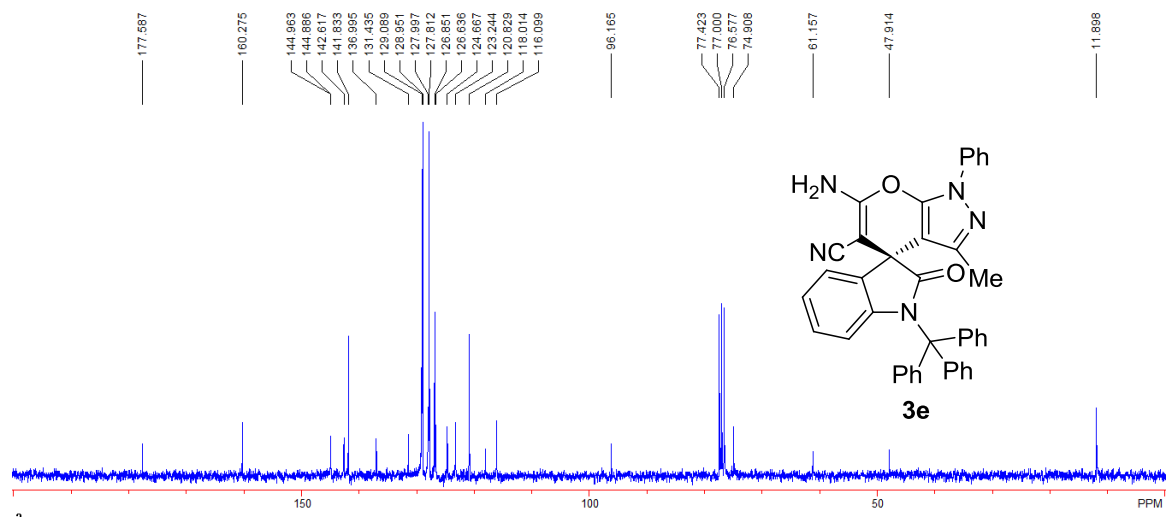
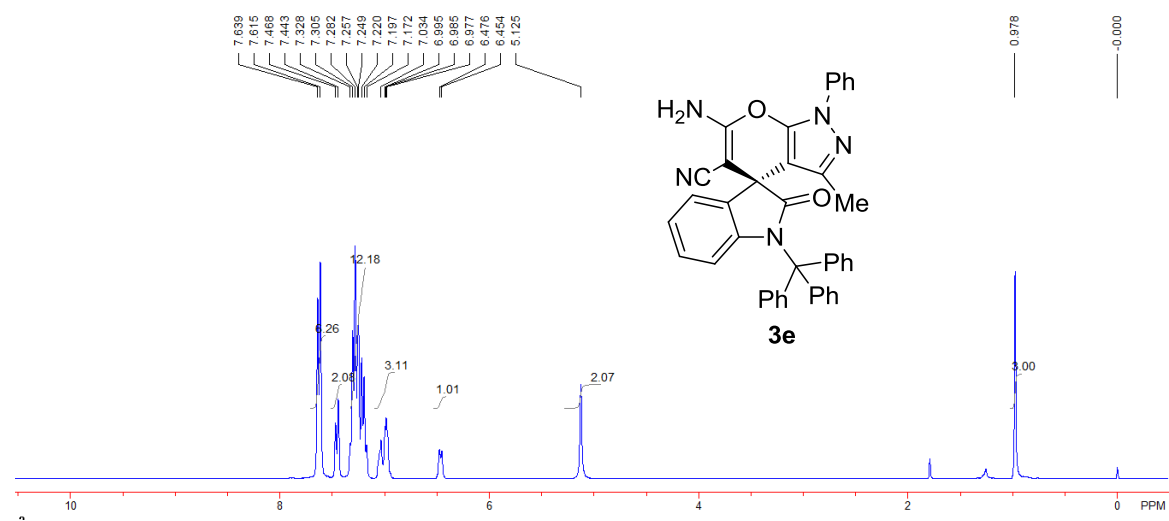
## 4. Copies of NMR Spectra of the Products 3

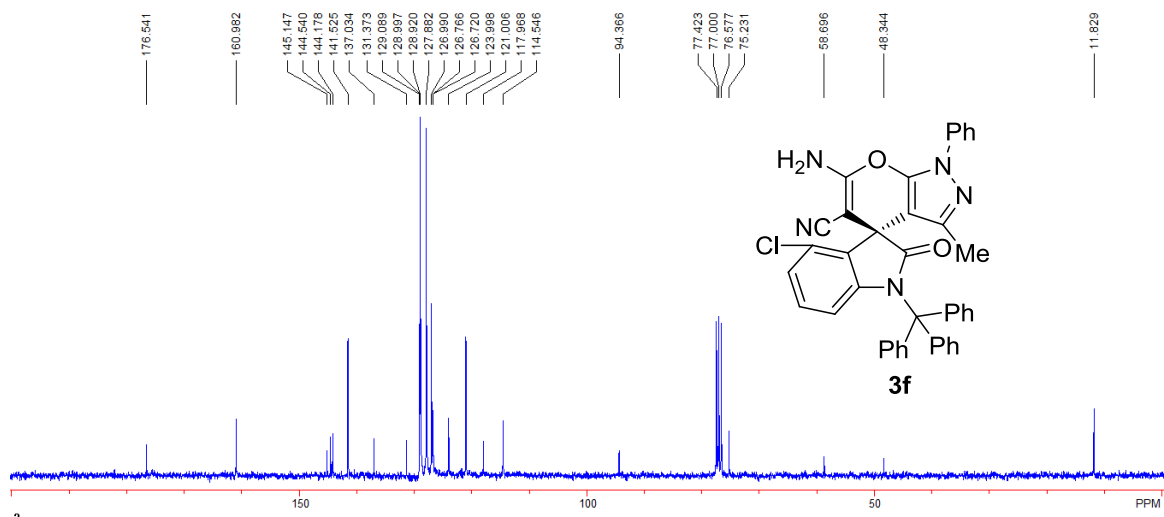
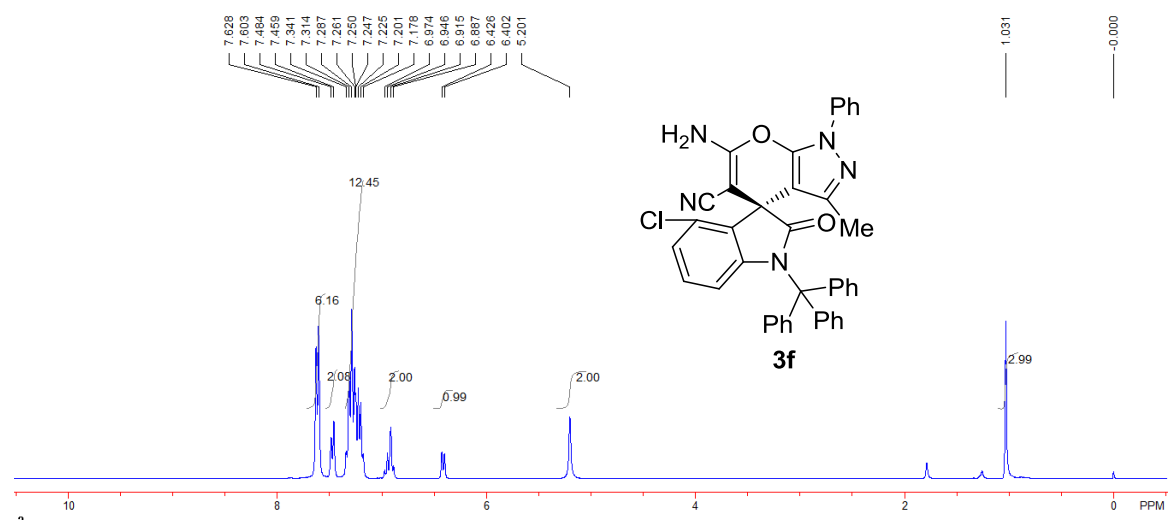


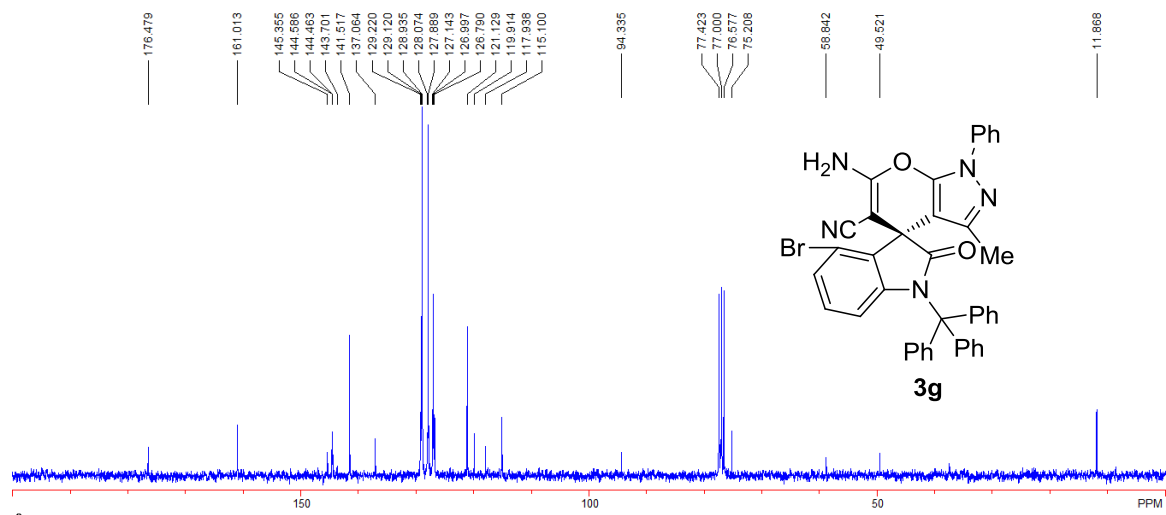
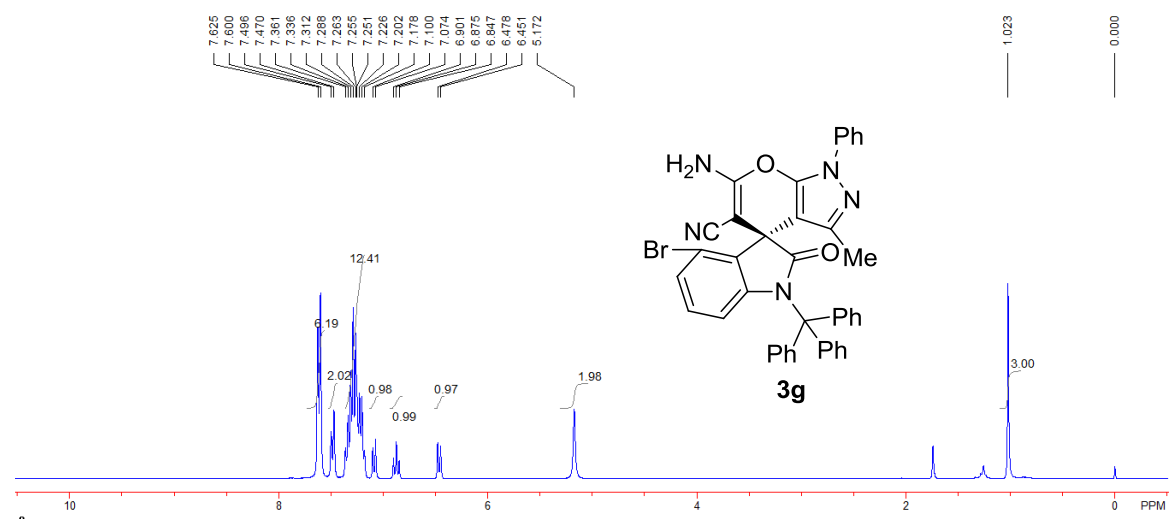


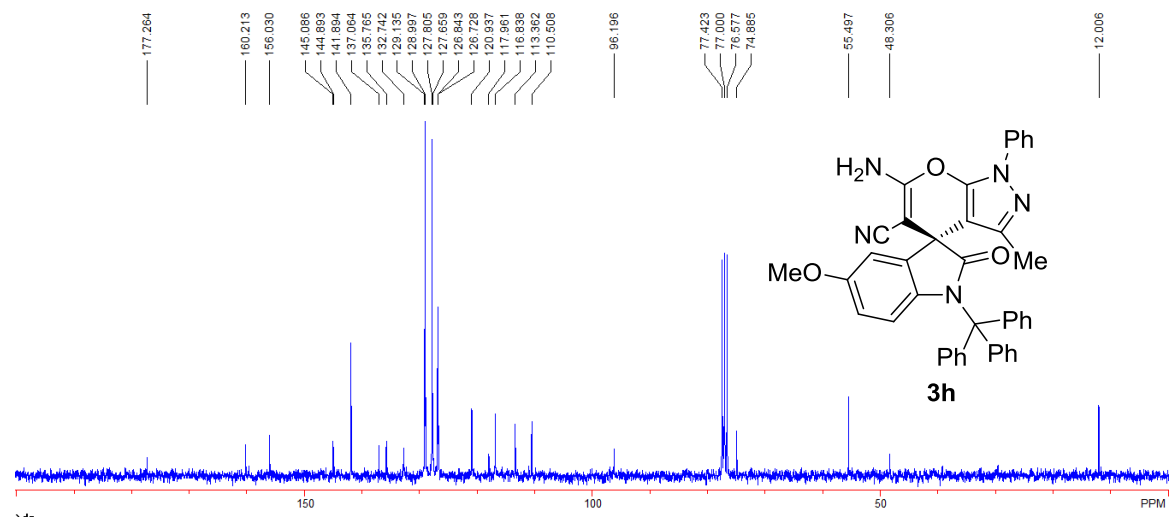
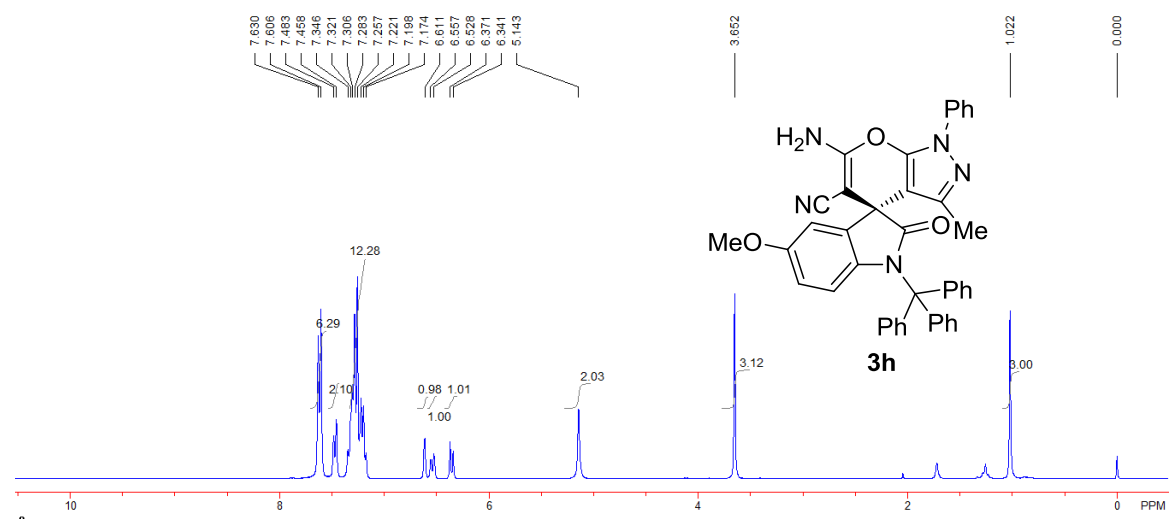


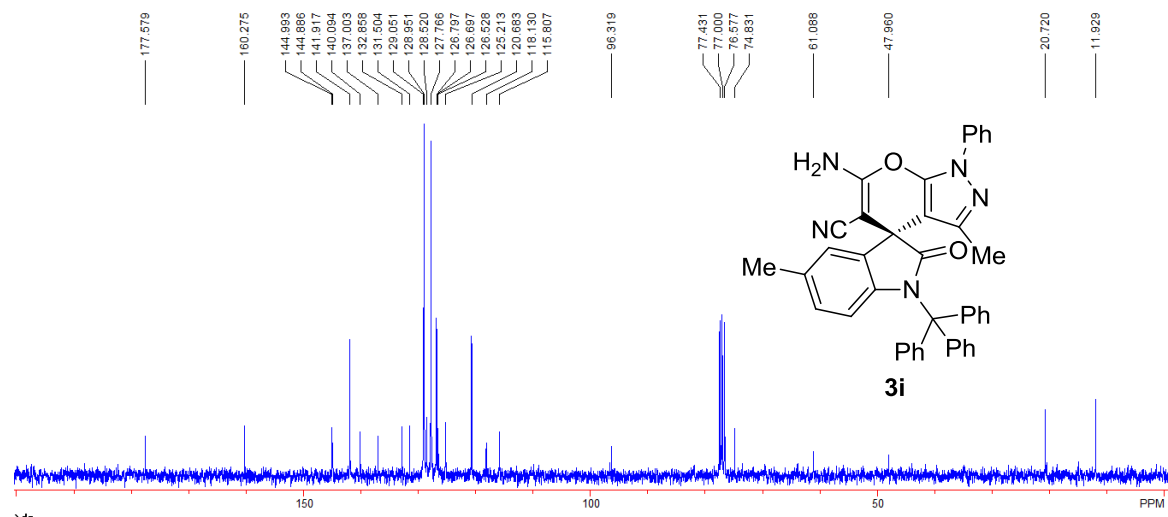
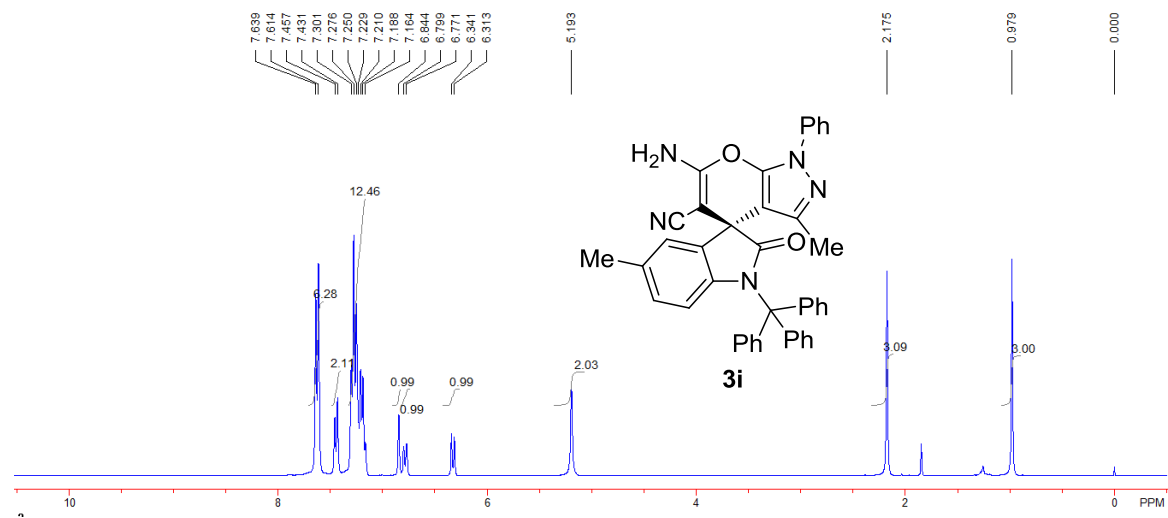


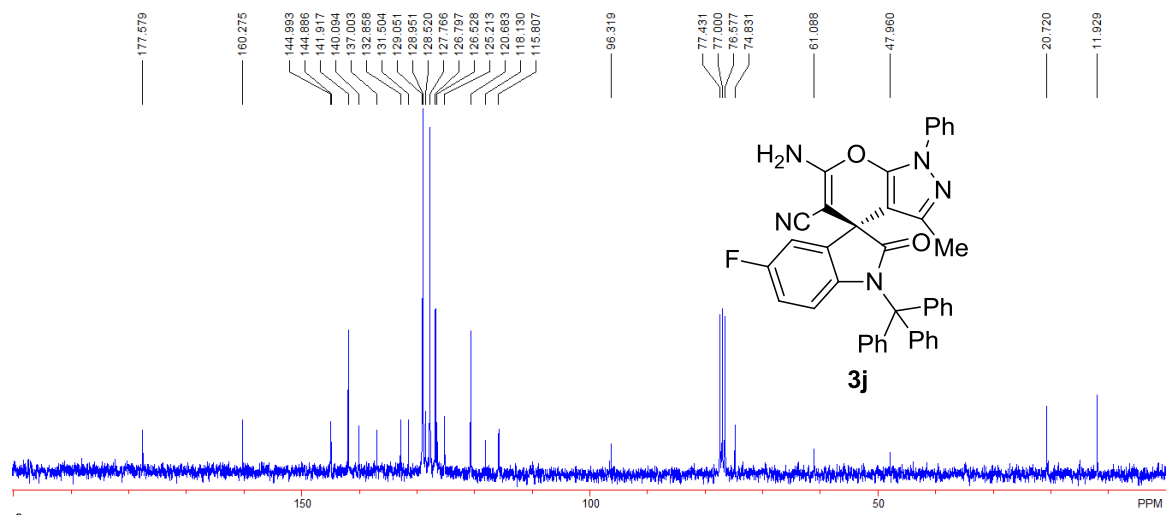
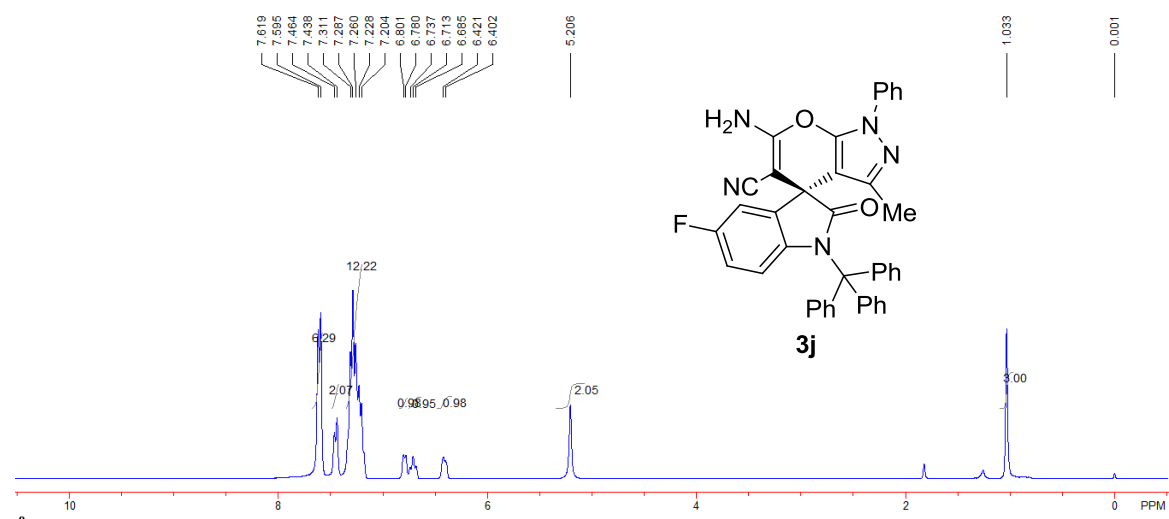


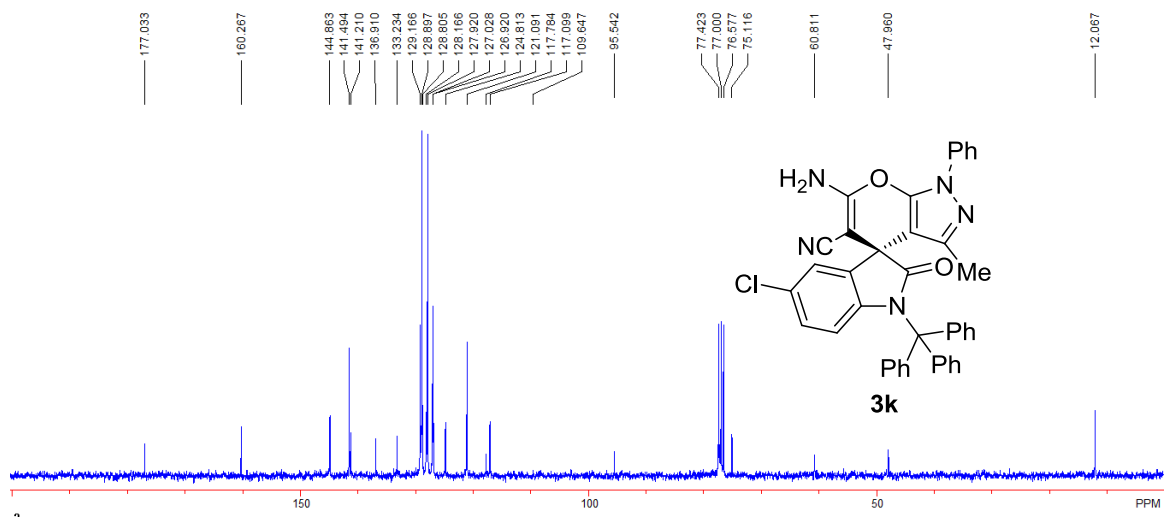
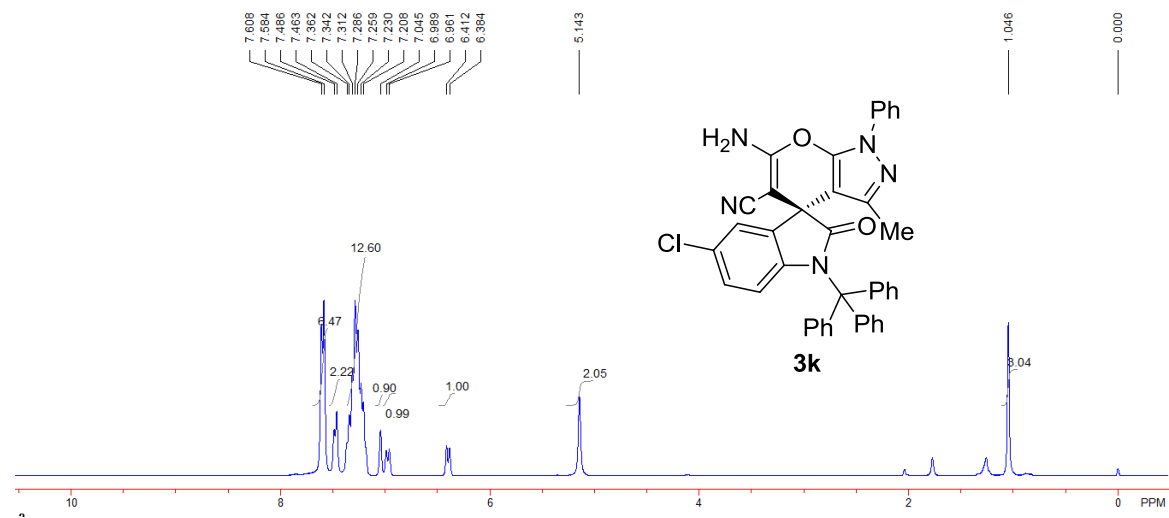




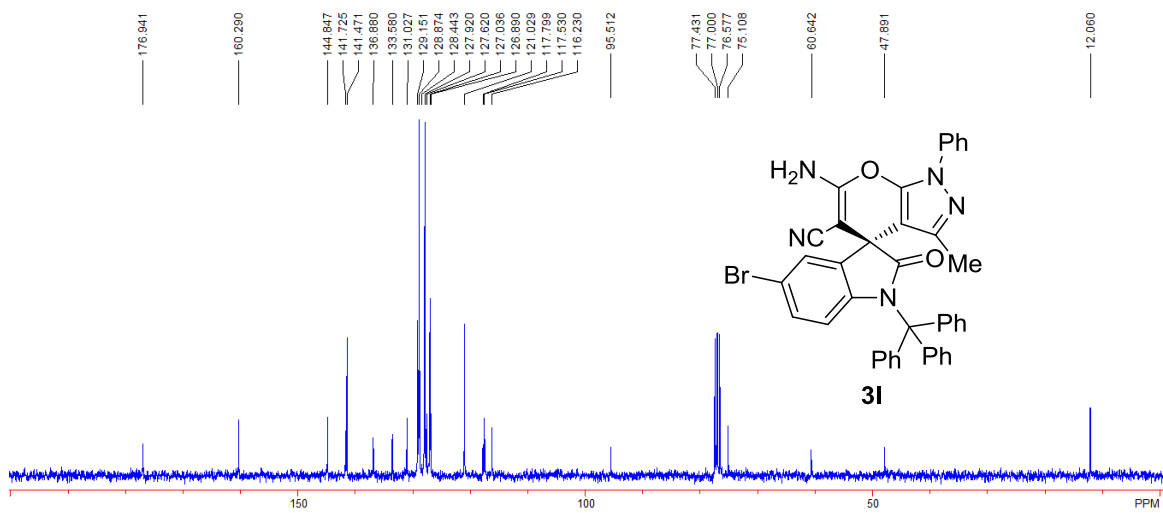
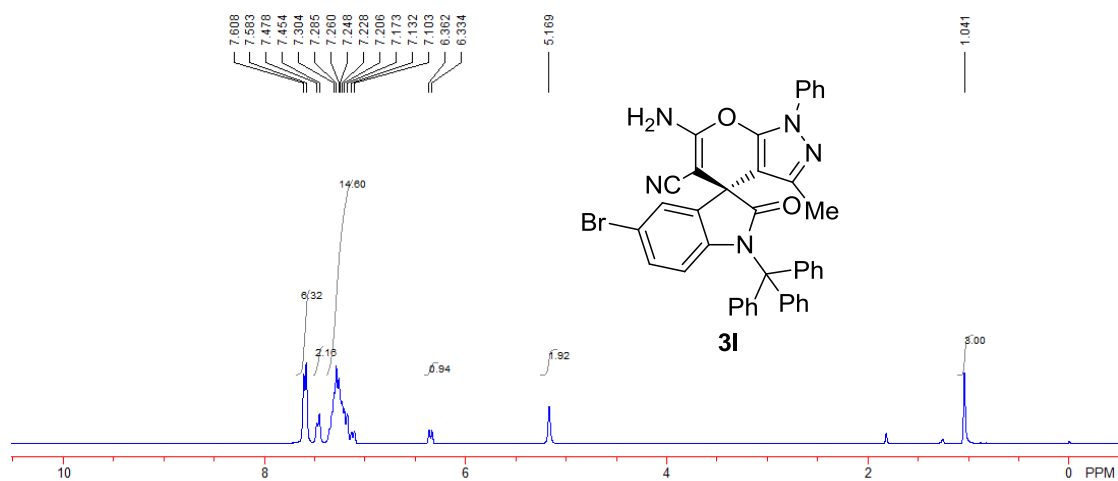


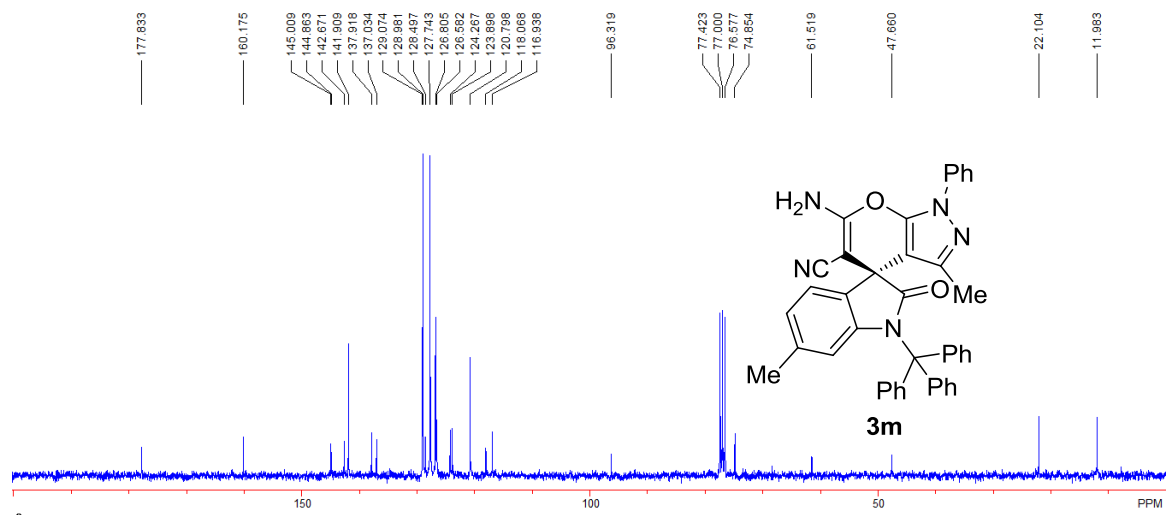
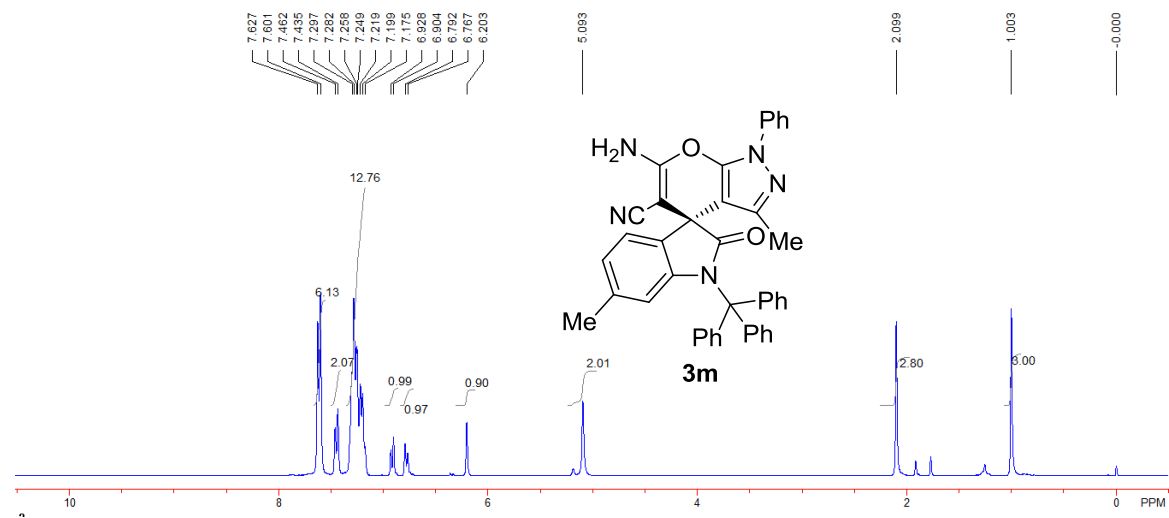


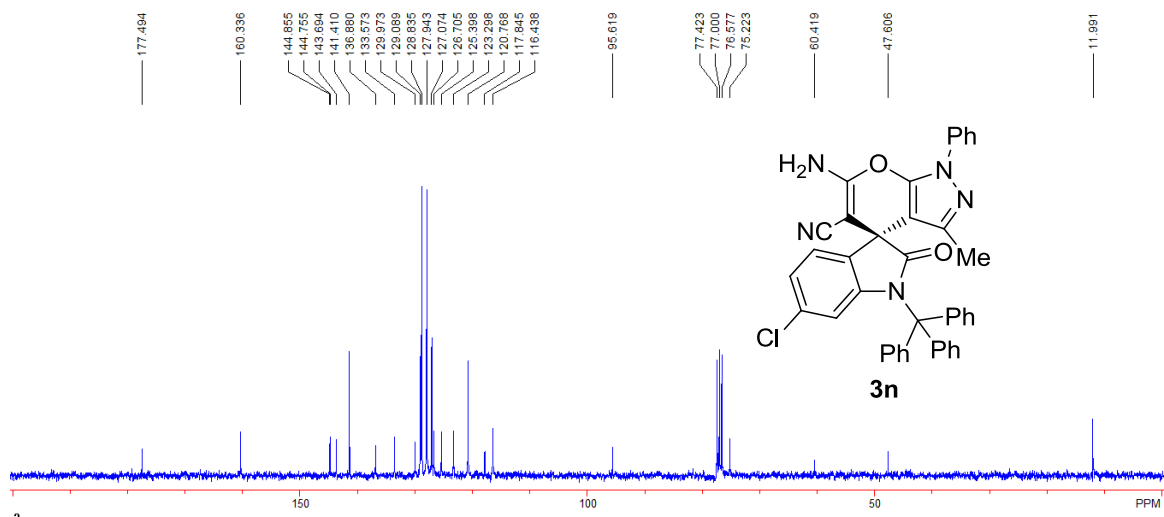
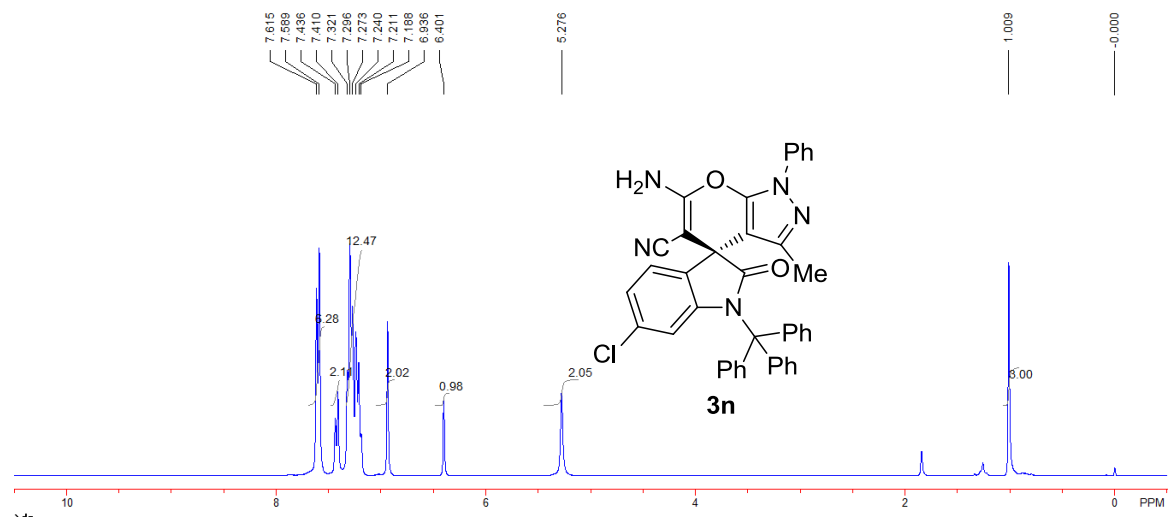


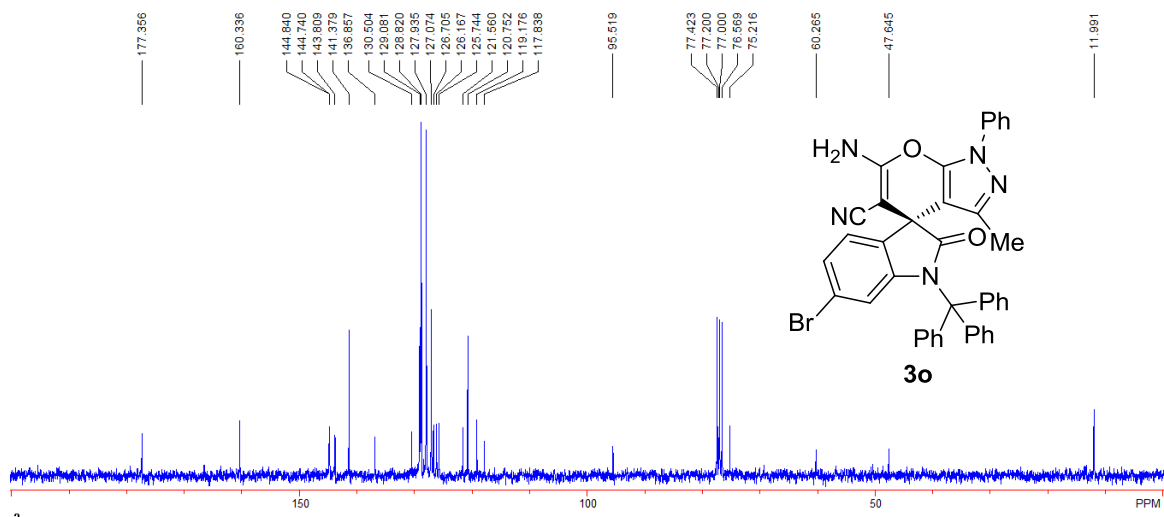
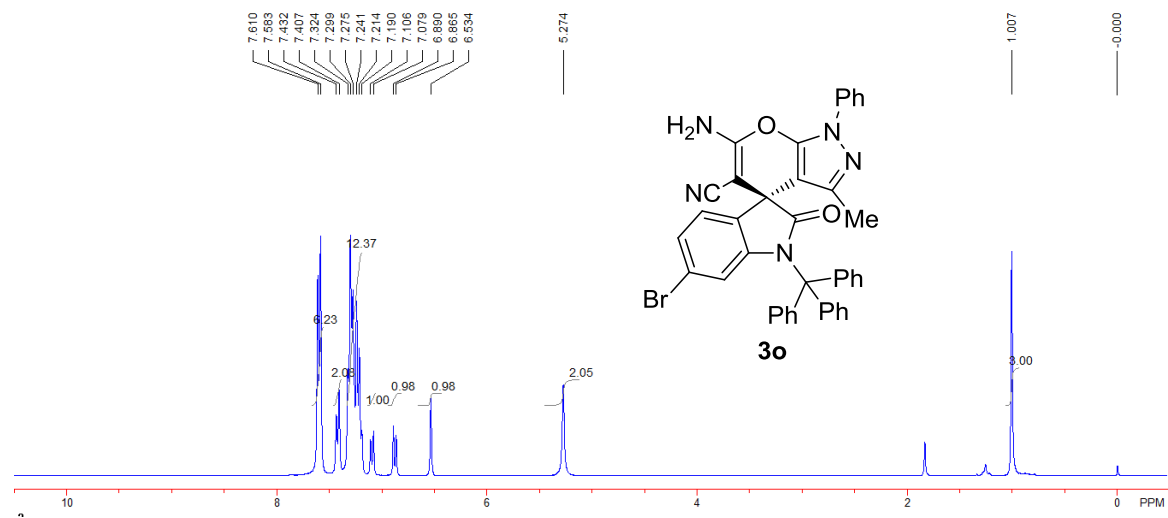


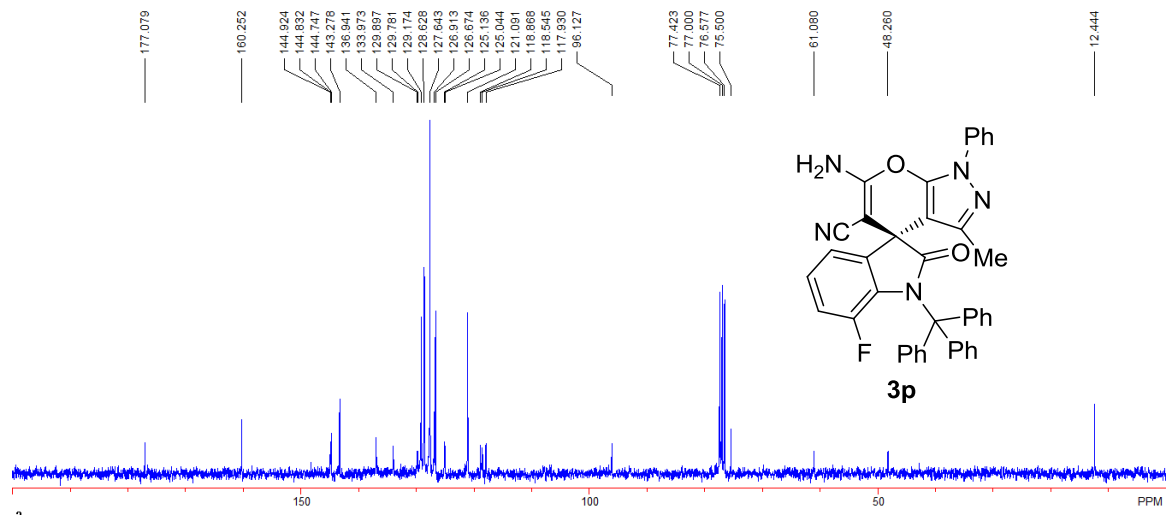
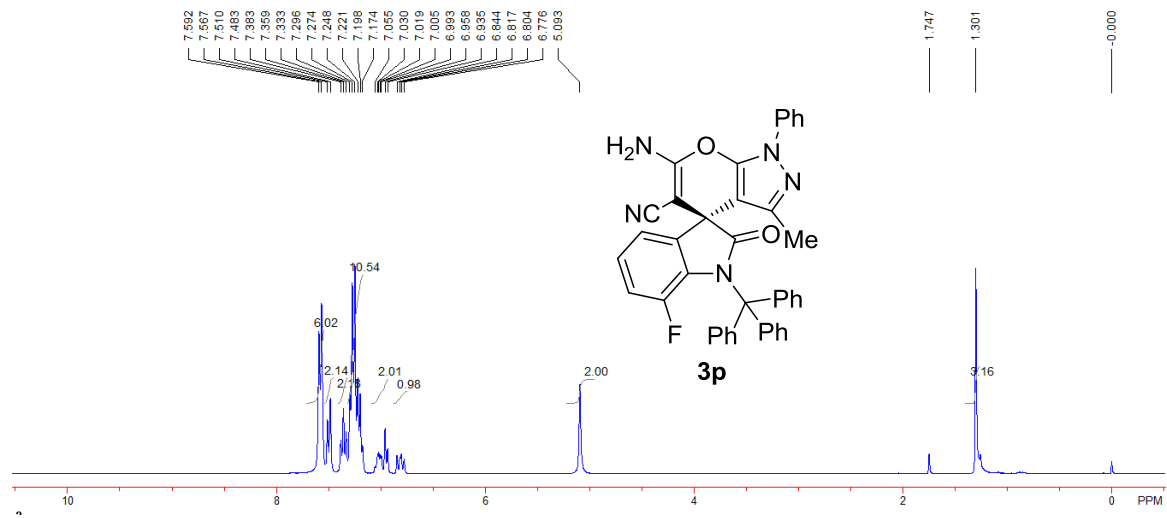


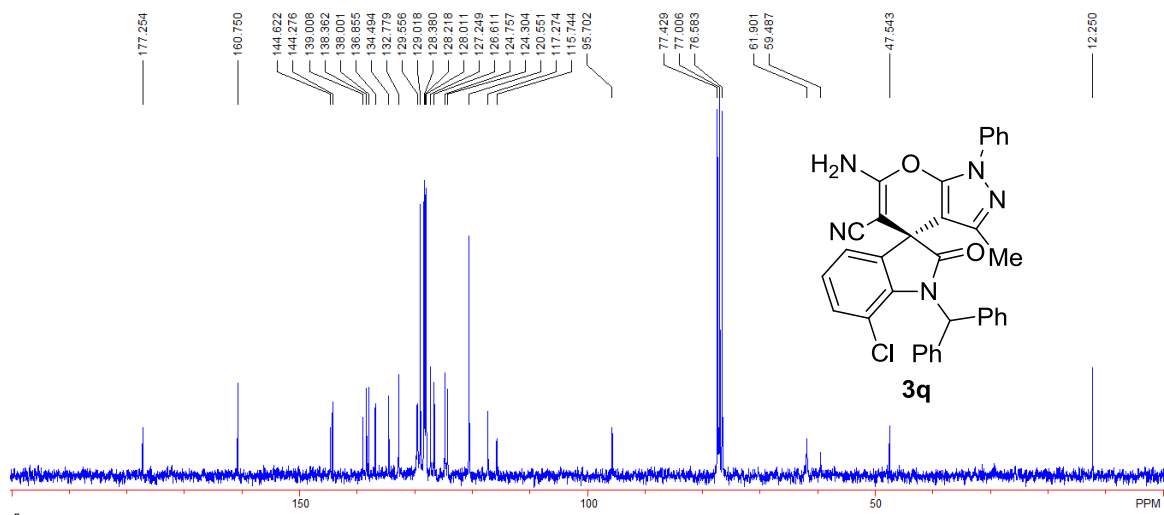
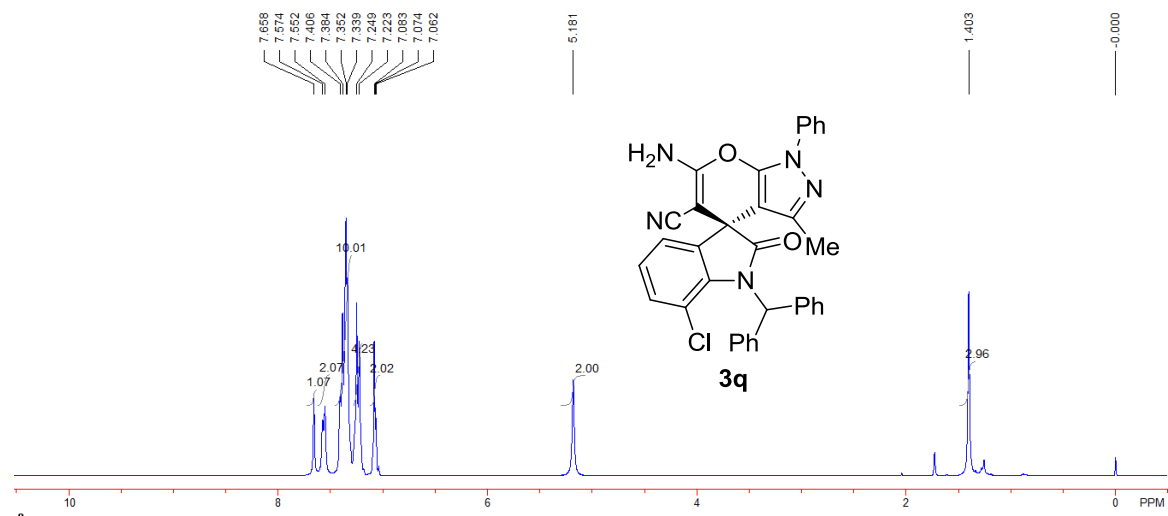


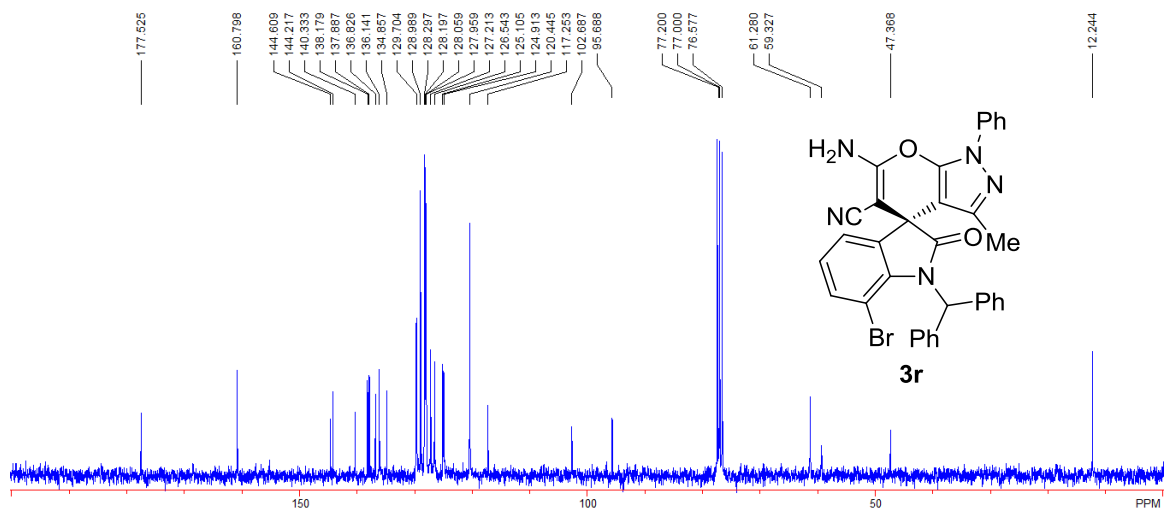
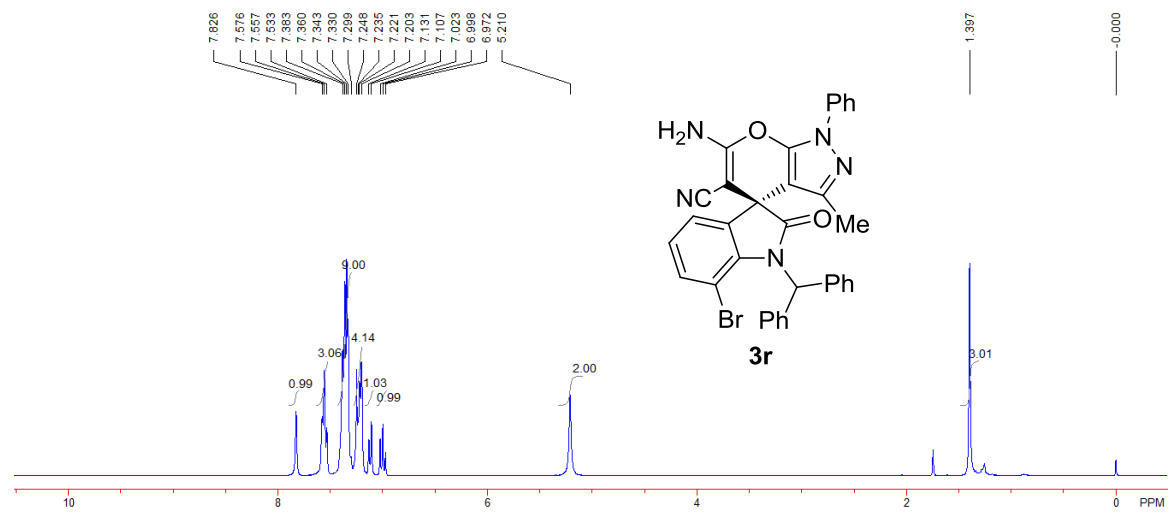


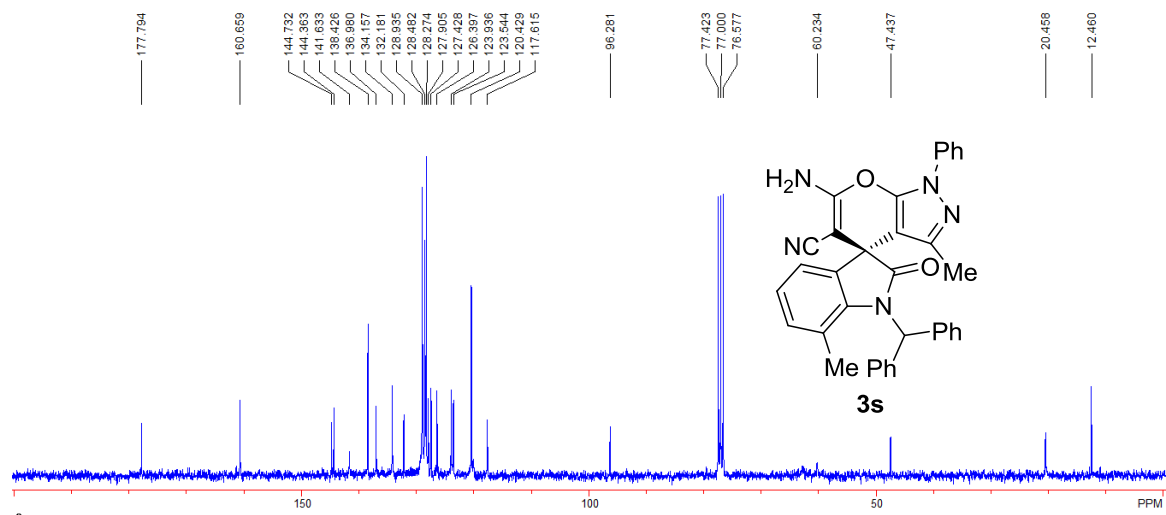
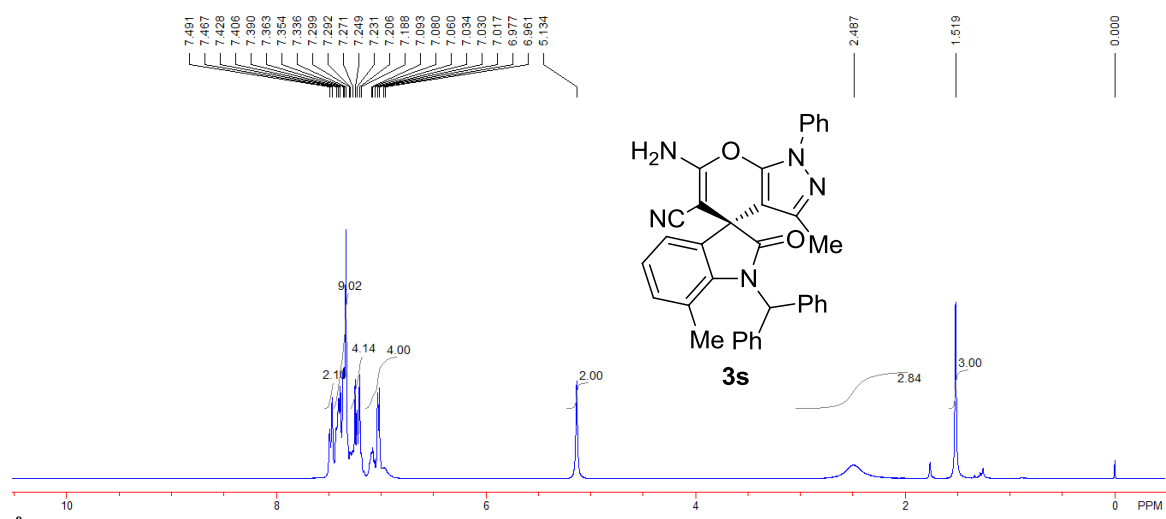




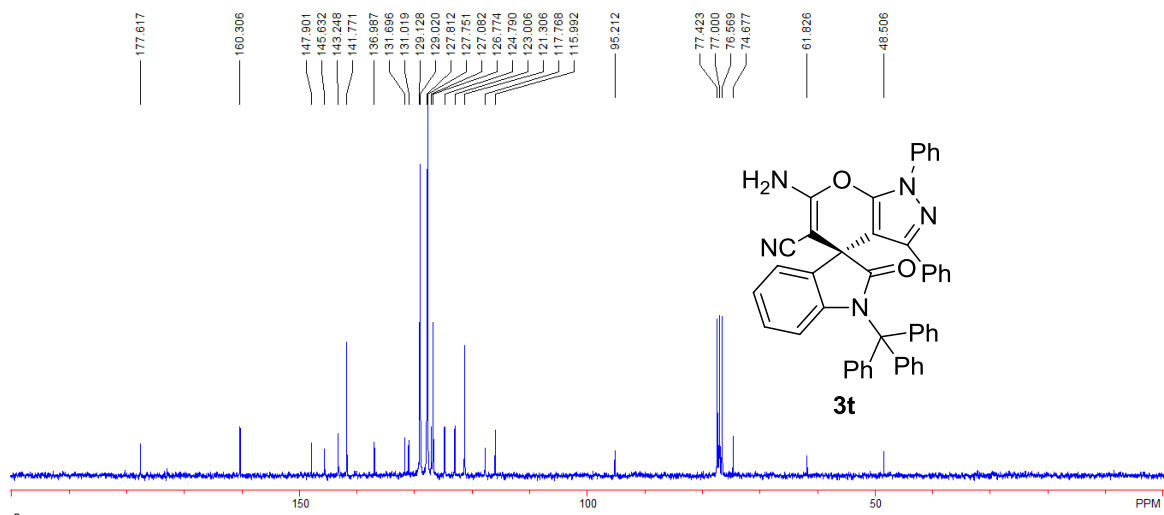
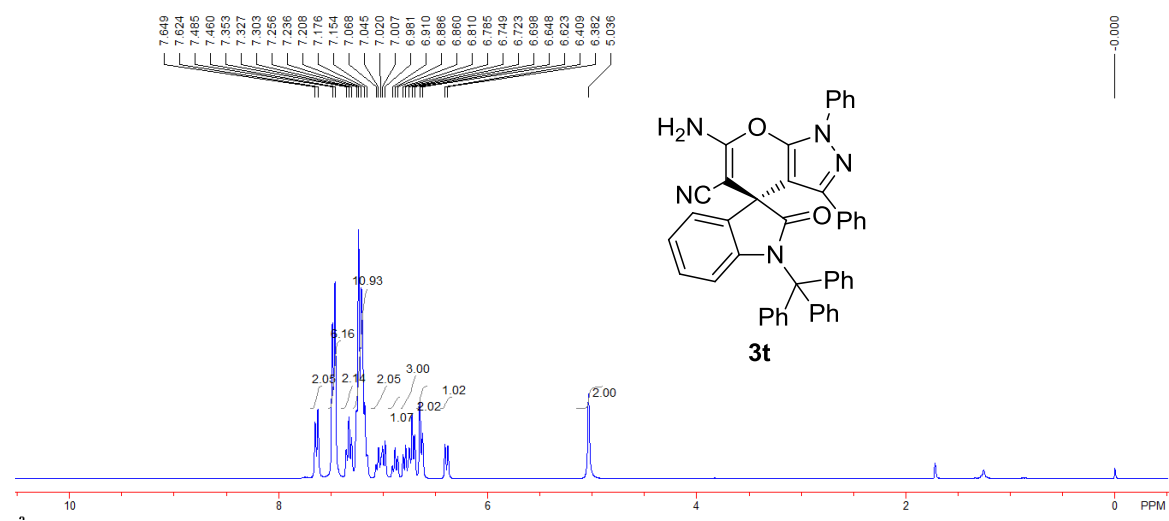


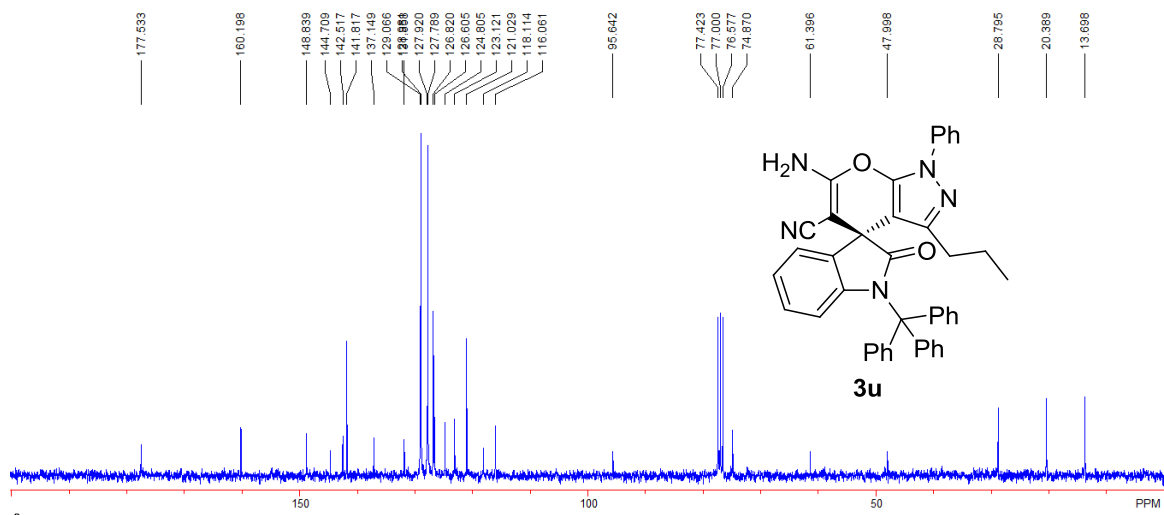
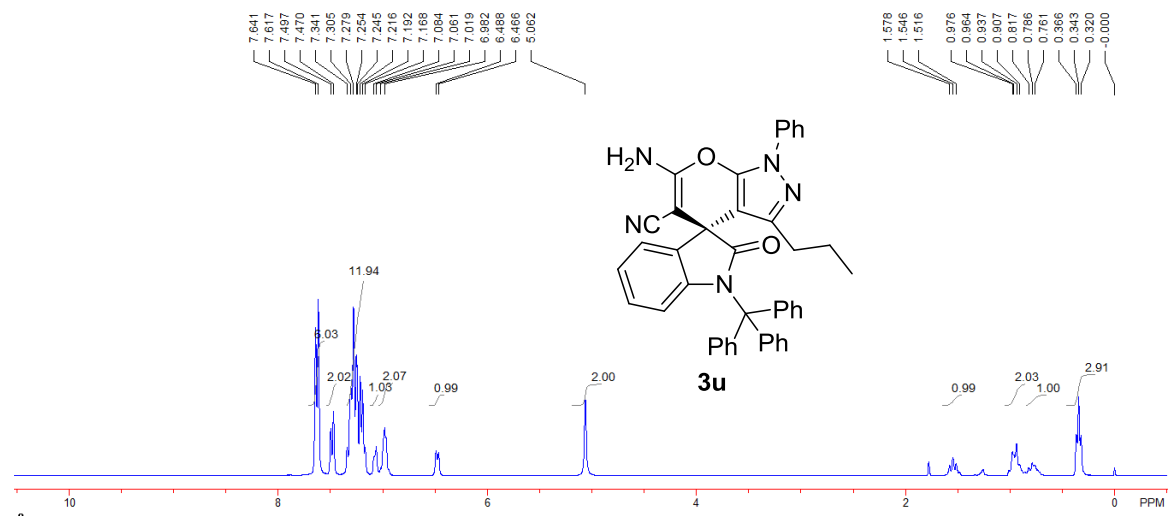


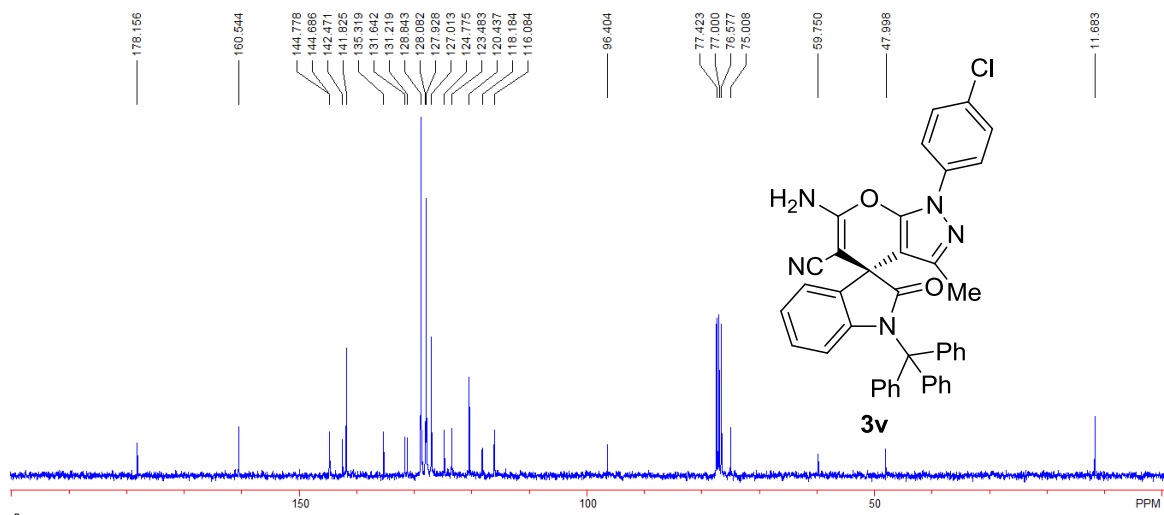
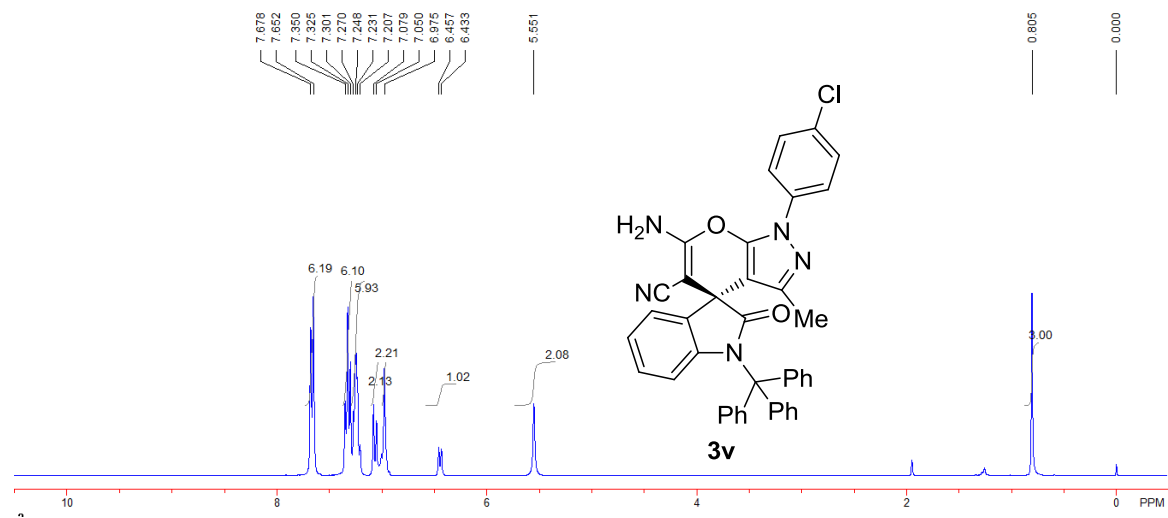


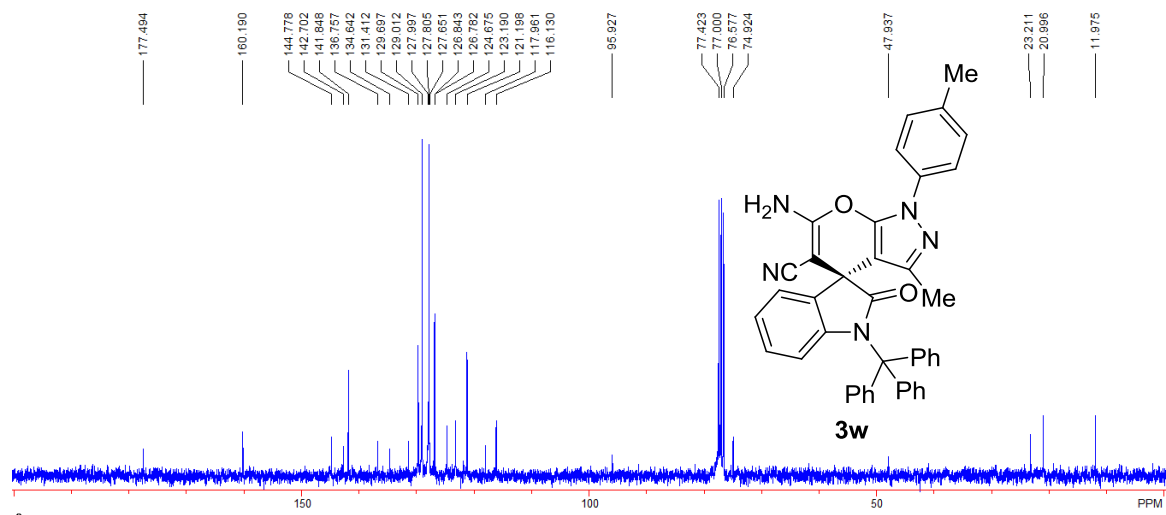
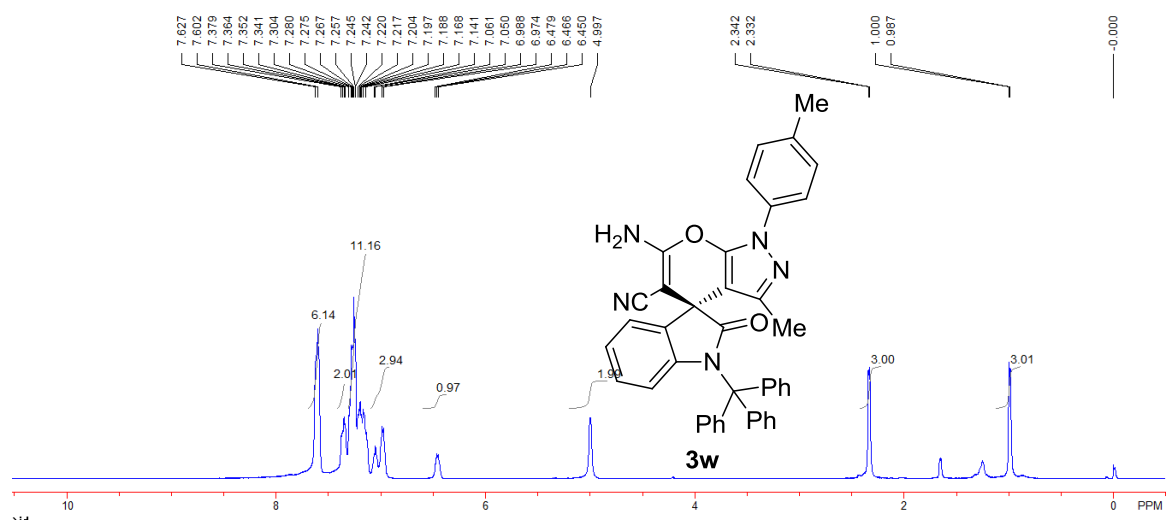




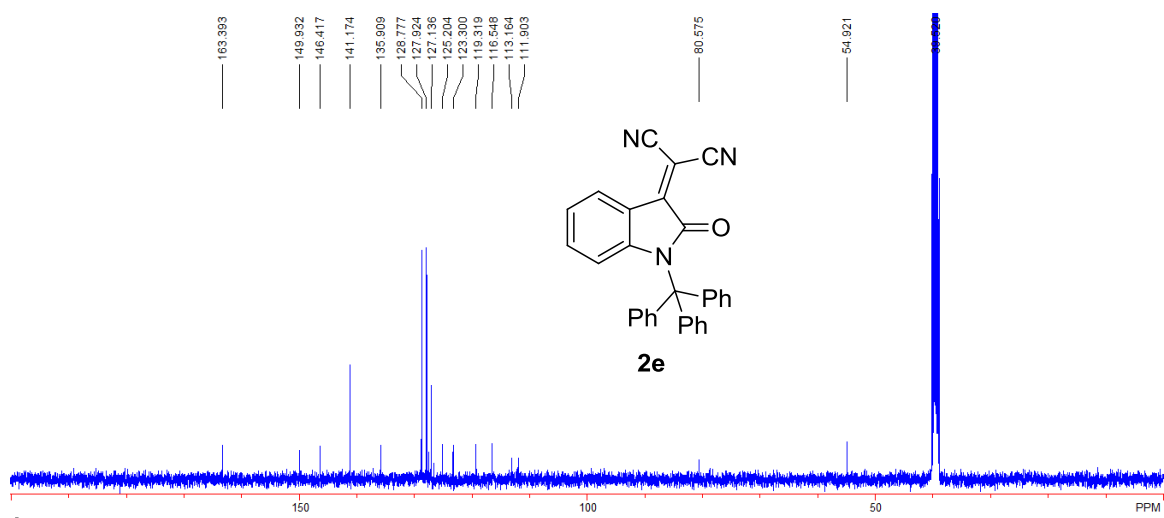
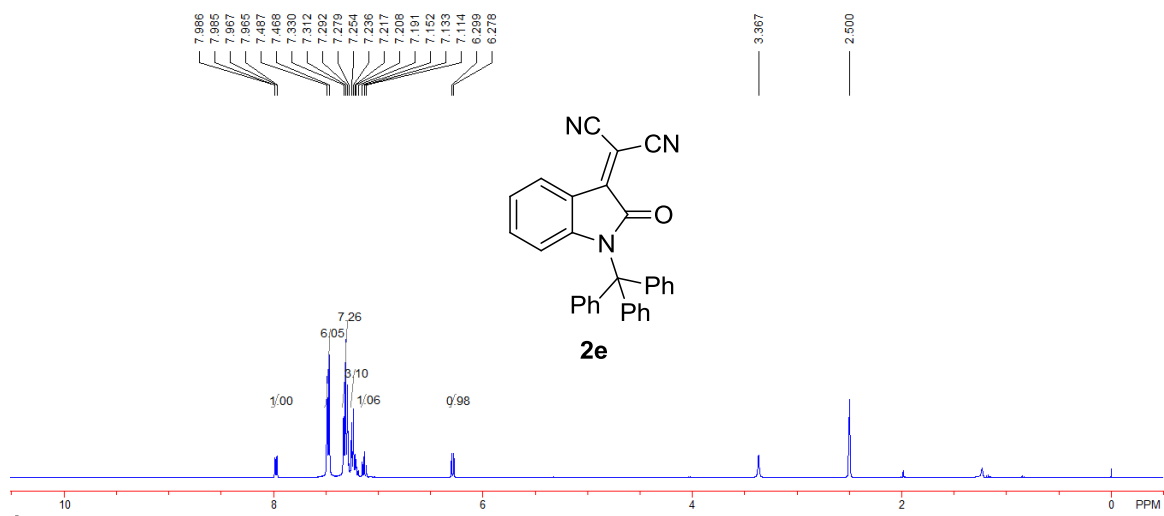


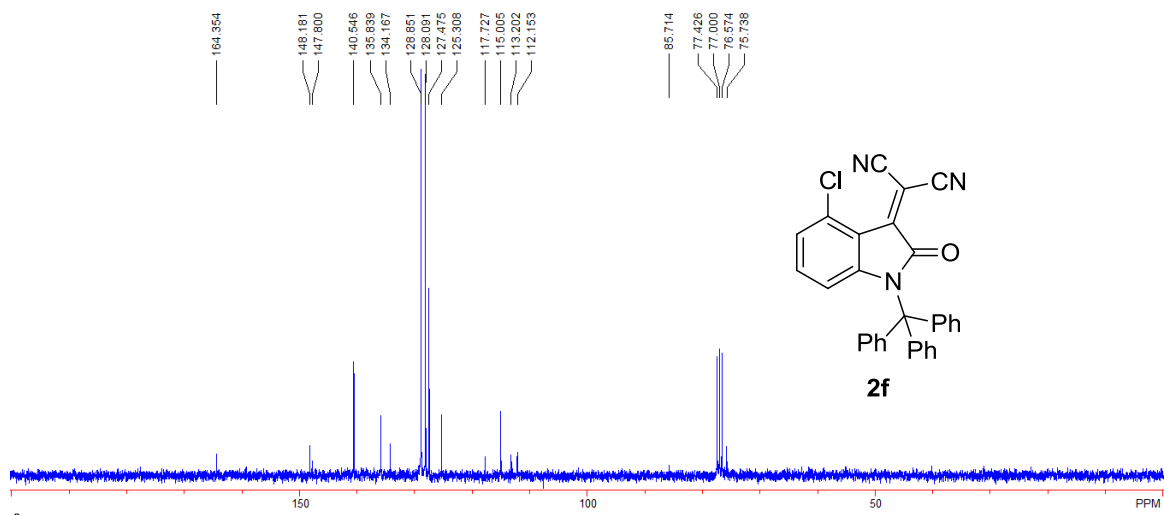
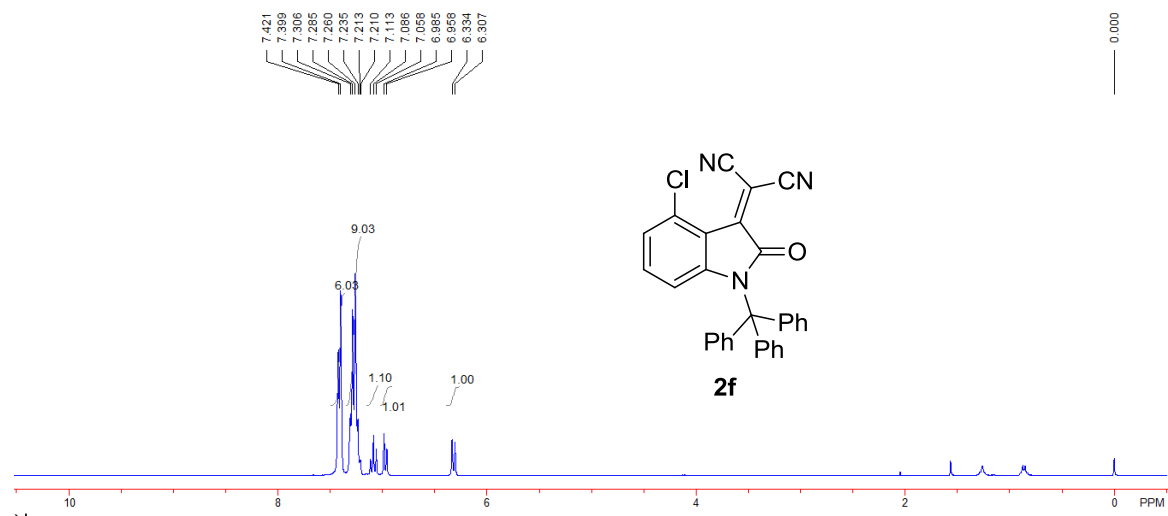


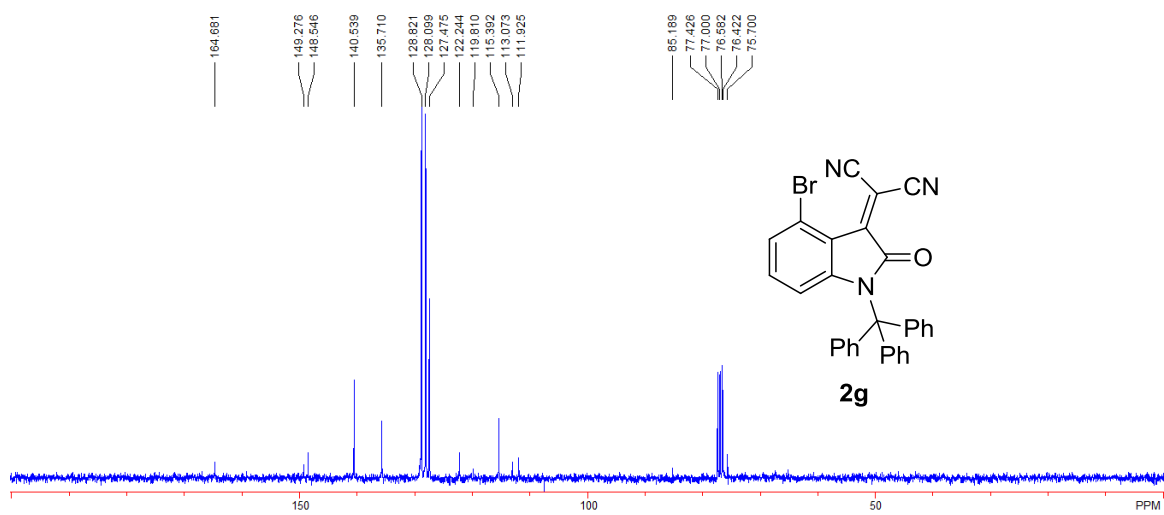
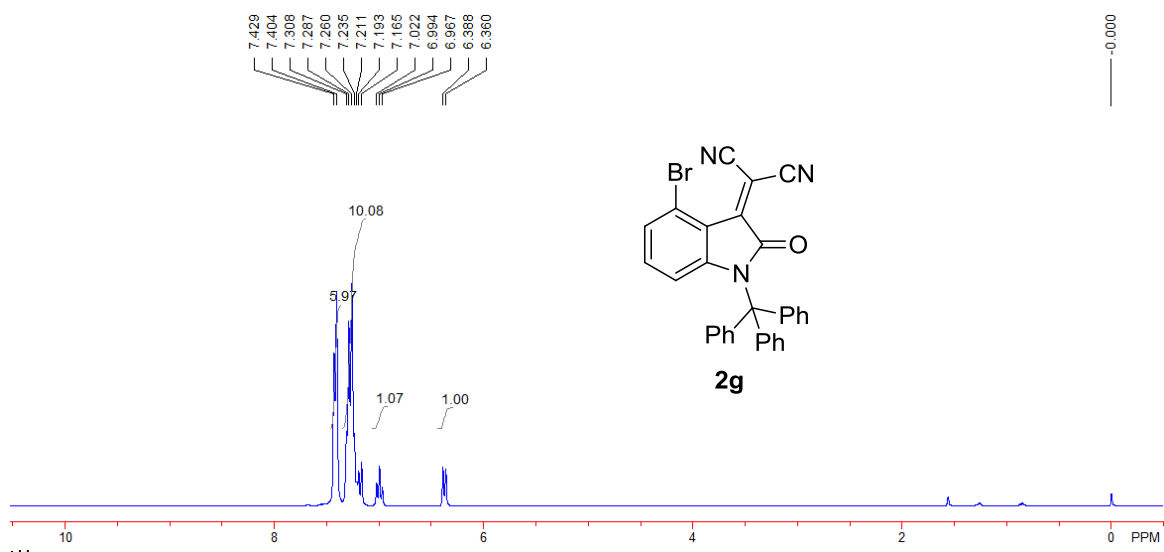


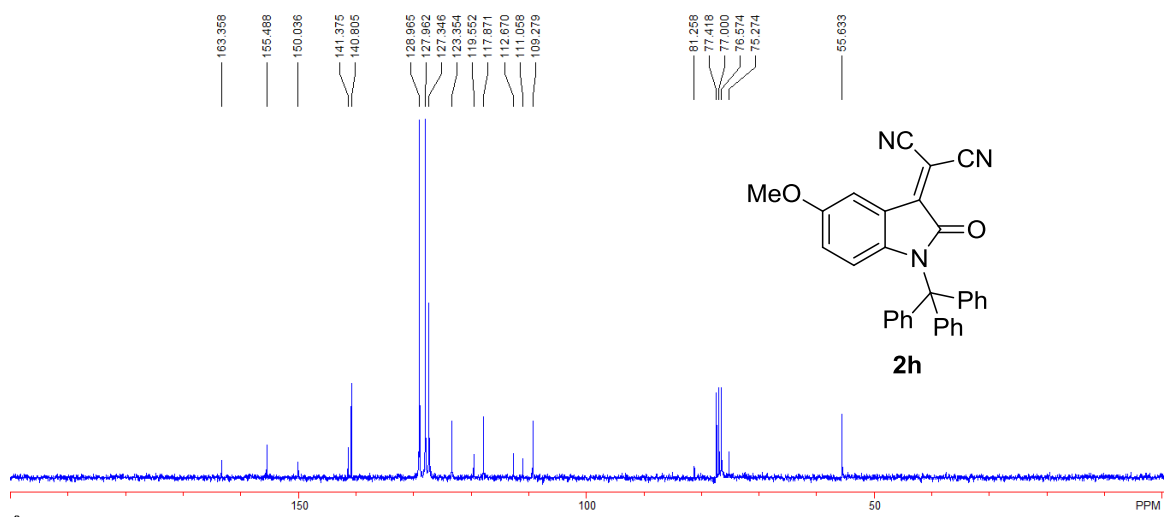
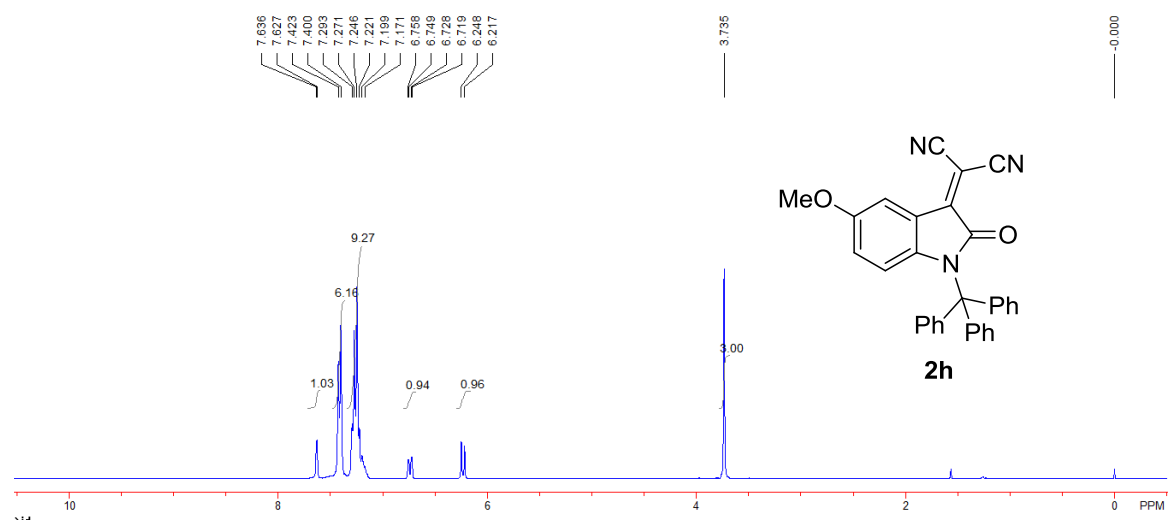


## 5. Copies of NMR Spectra of Substrates 2e-2p

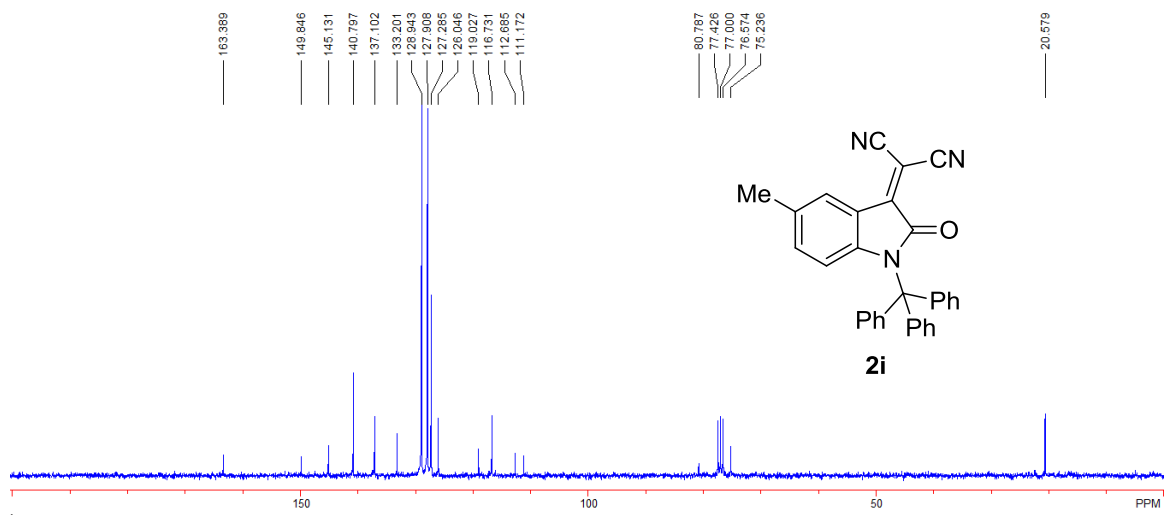
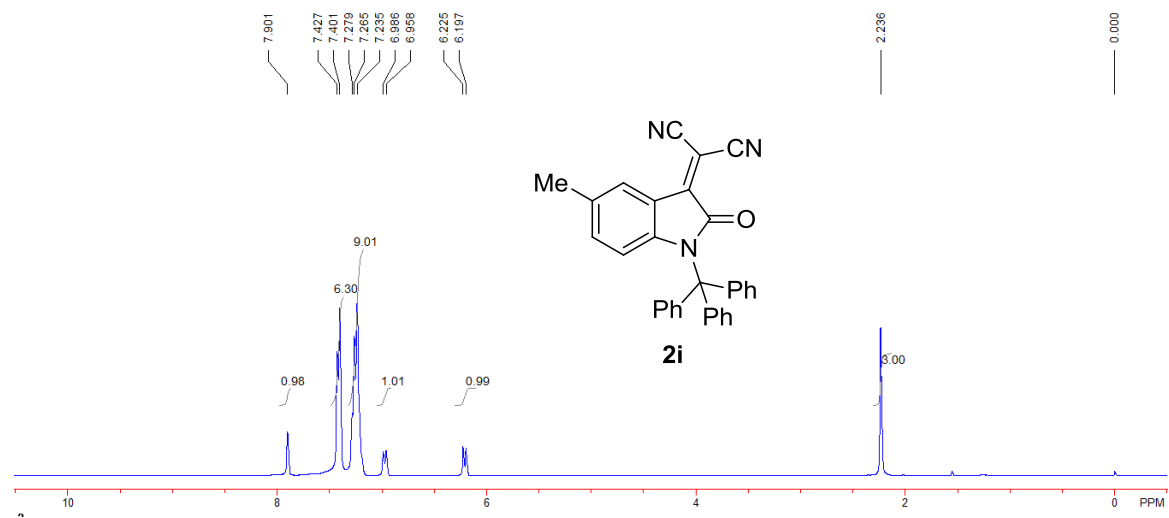


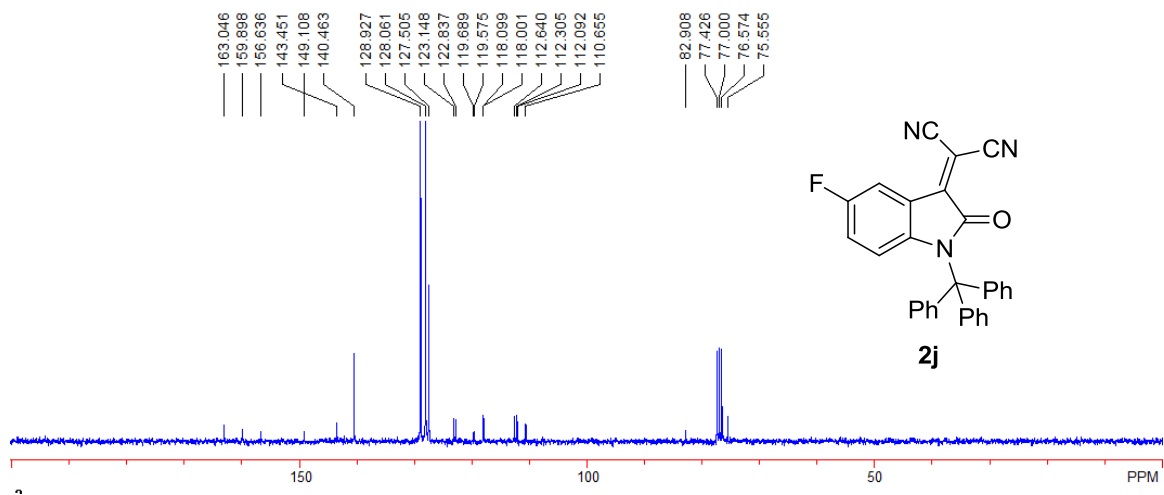
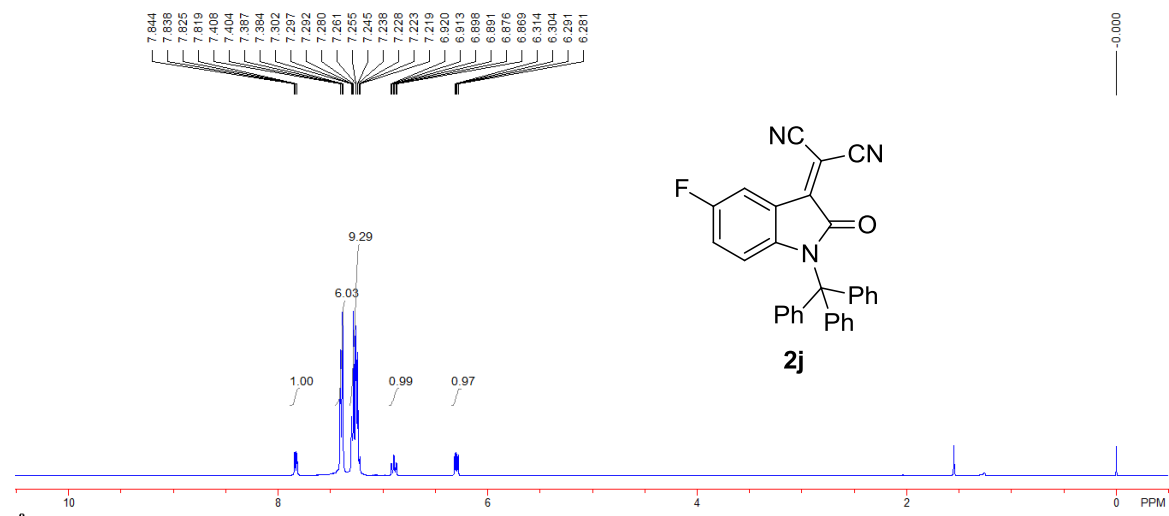


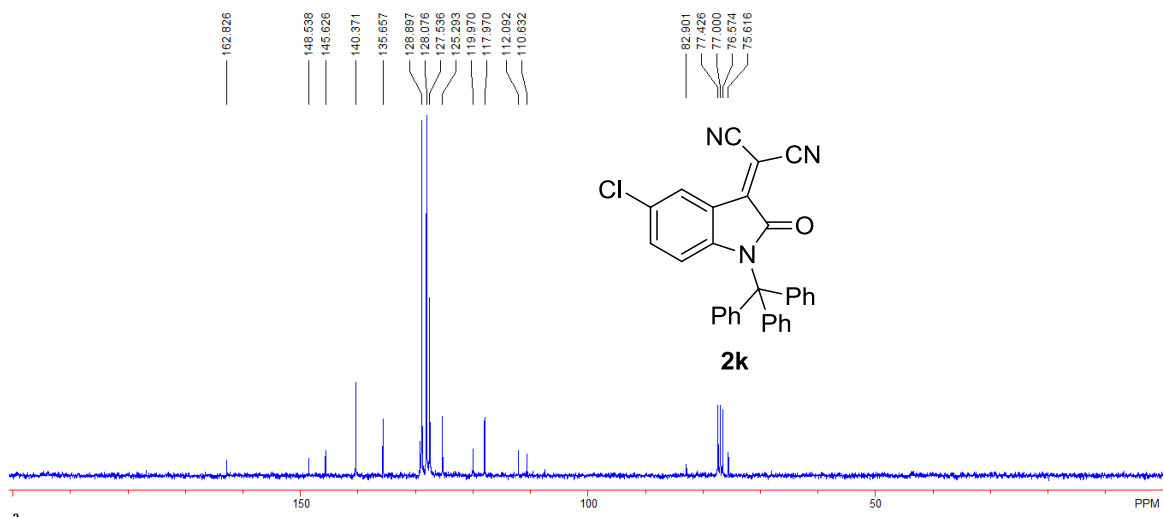
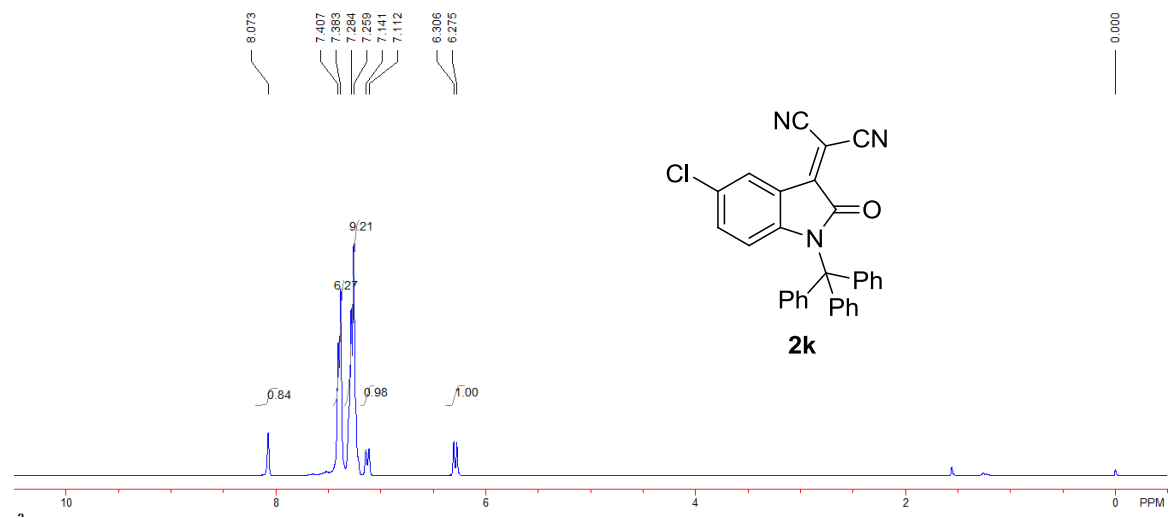


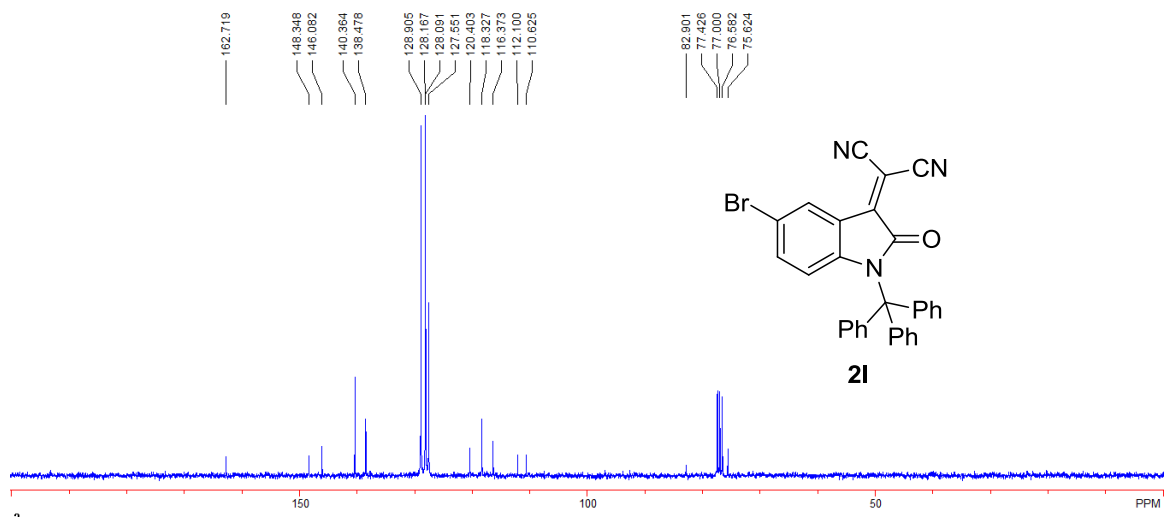
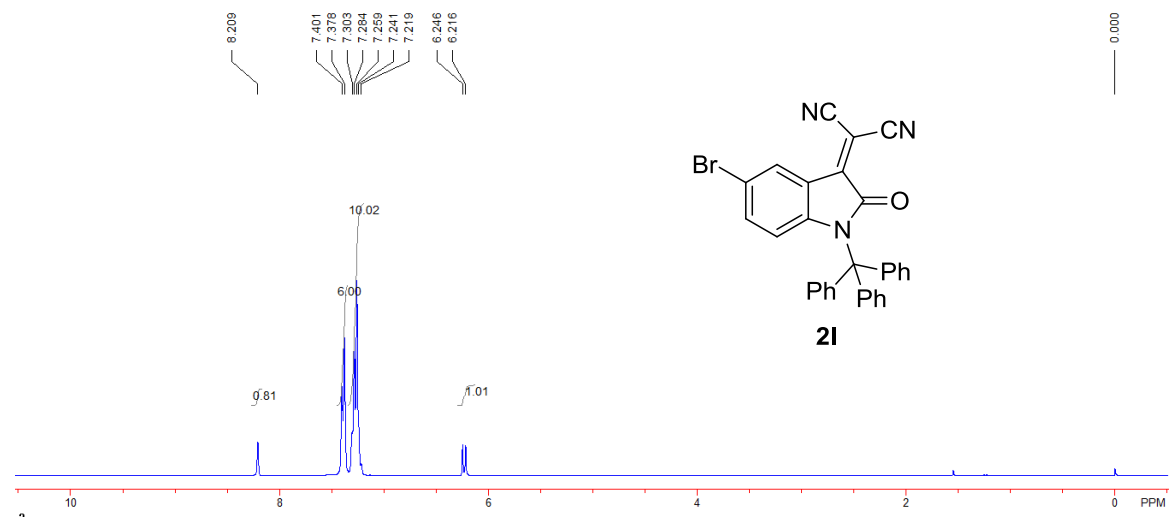


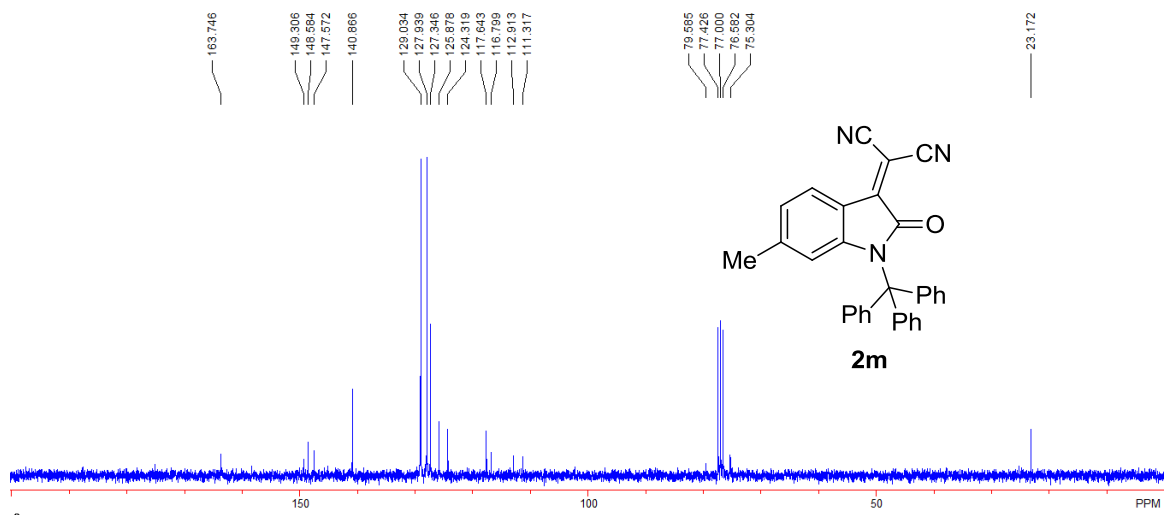
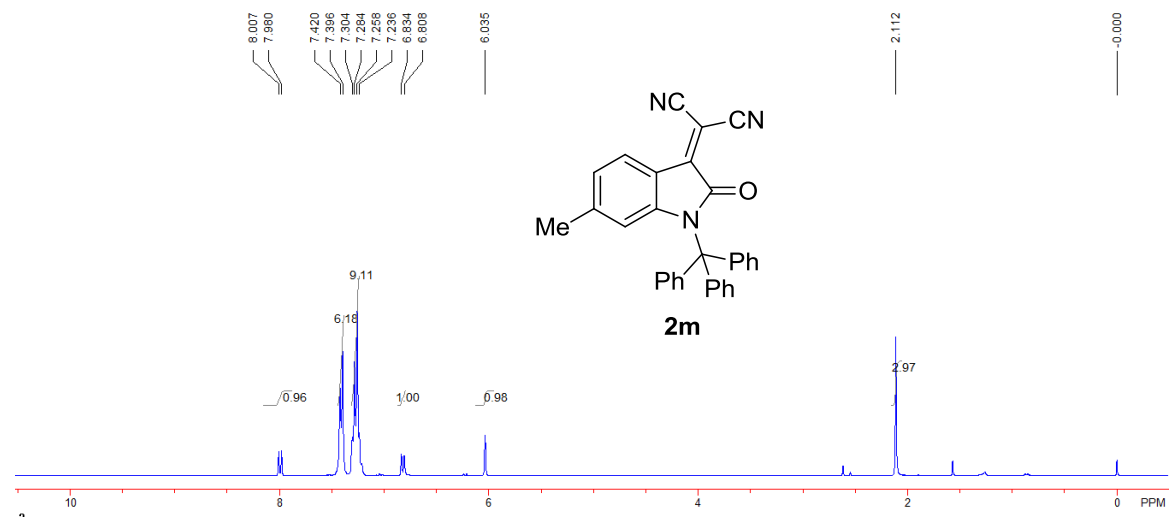


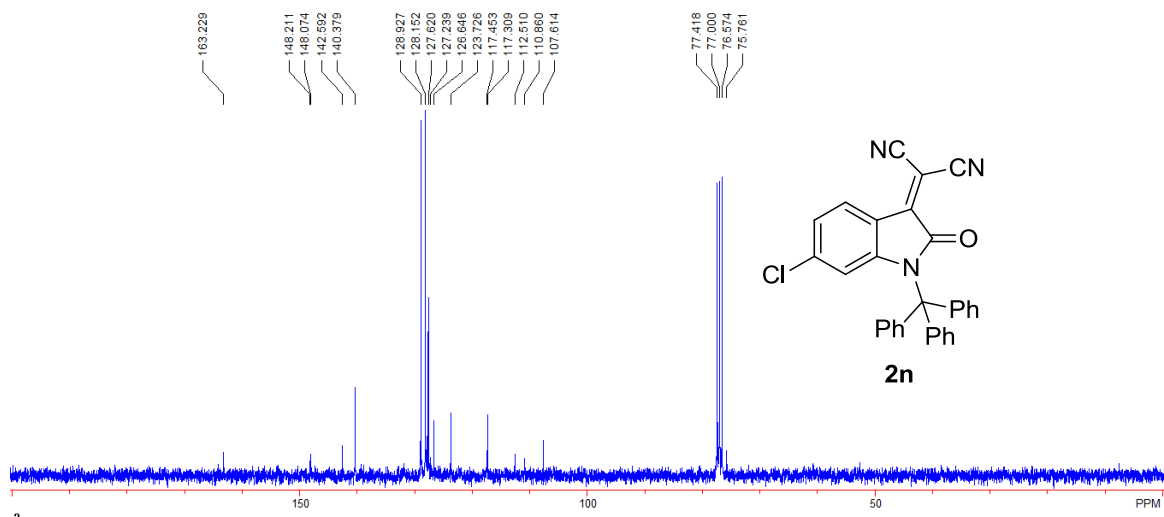
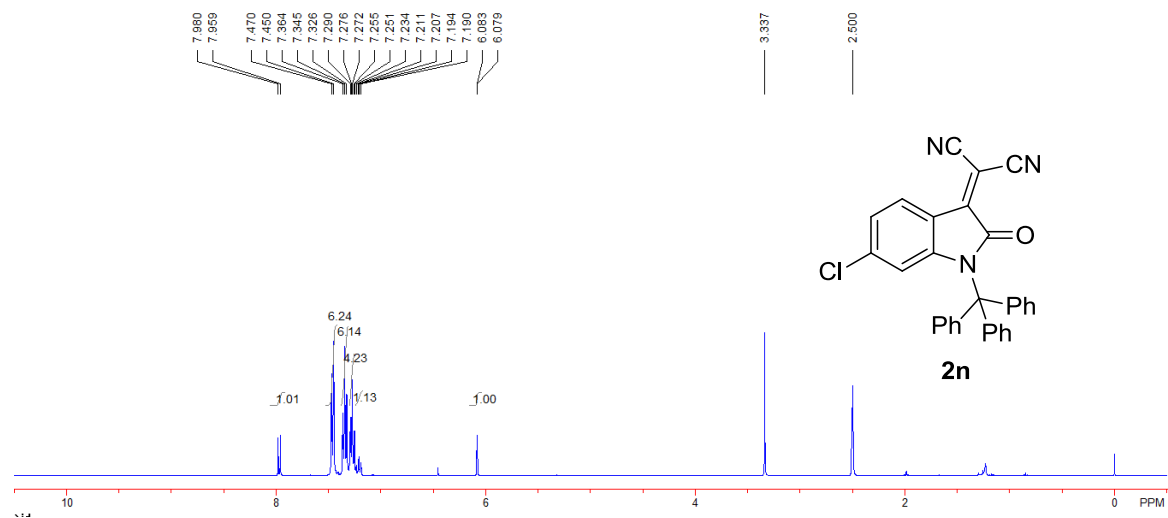


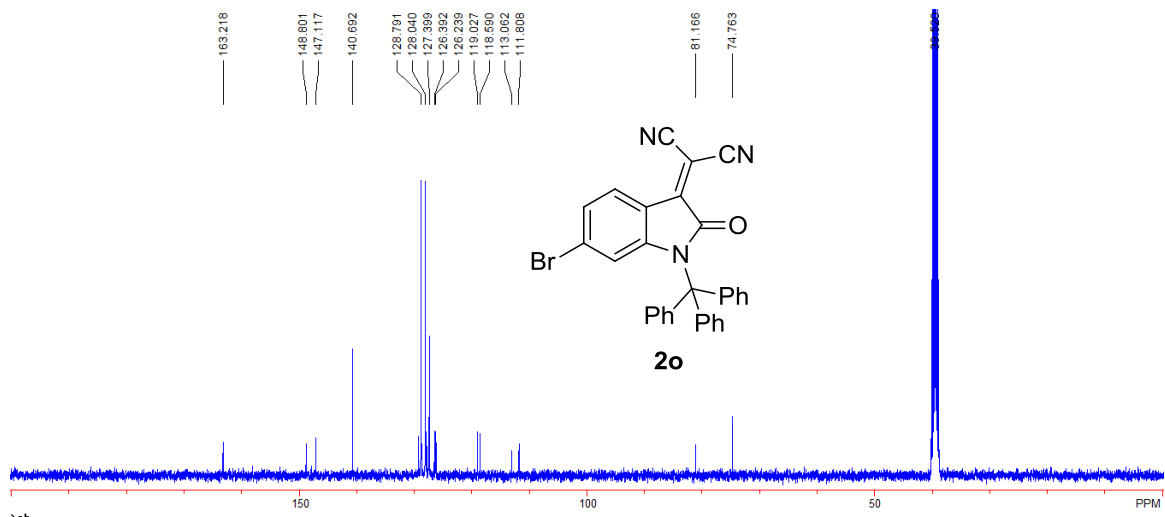
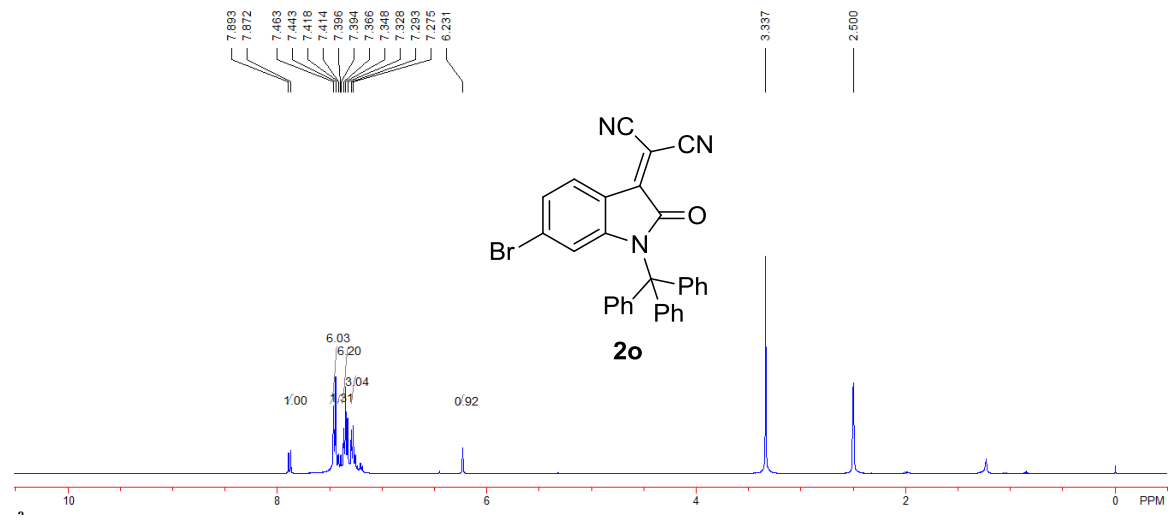


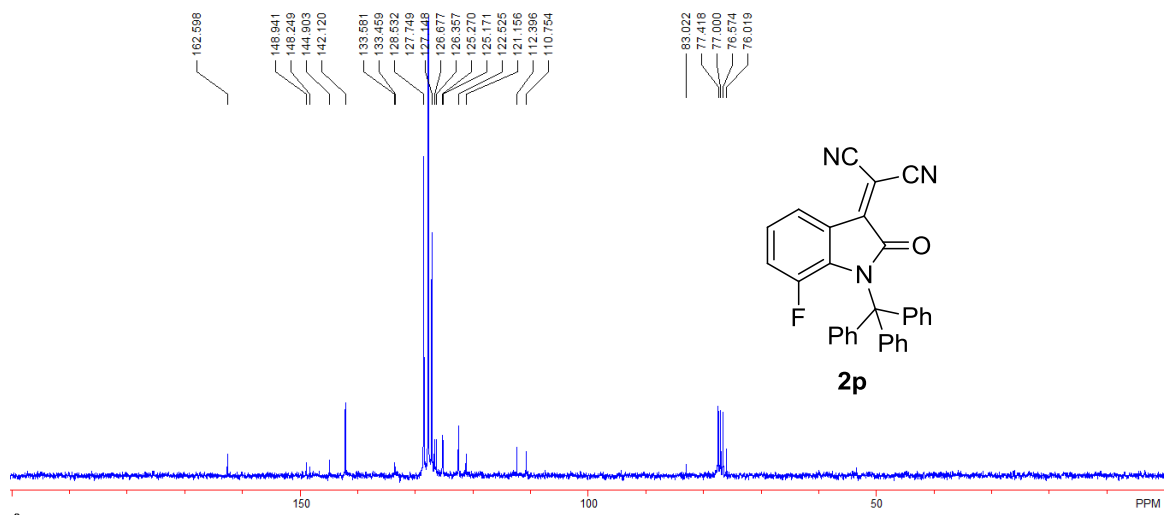
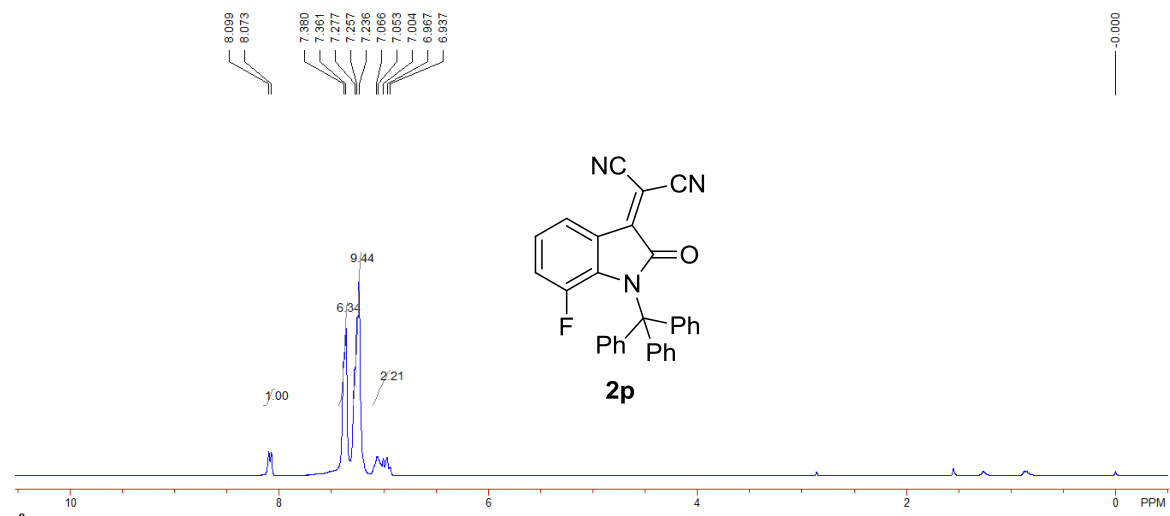






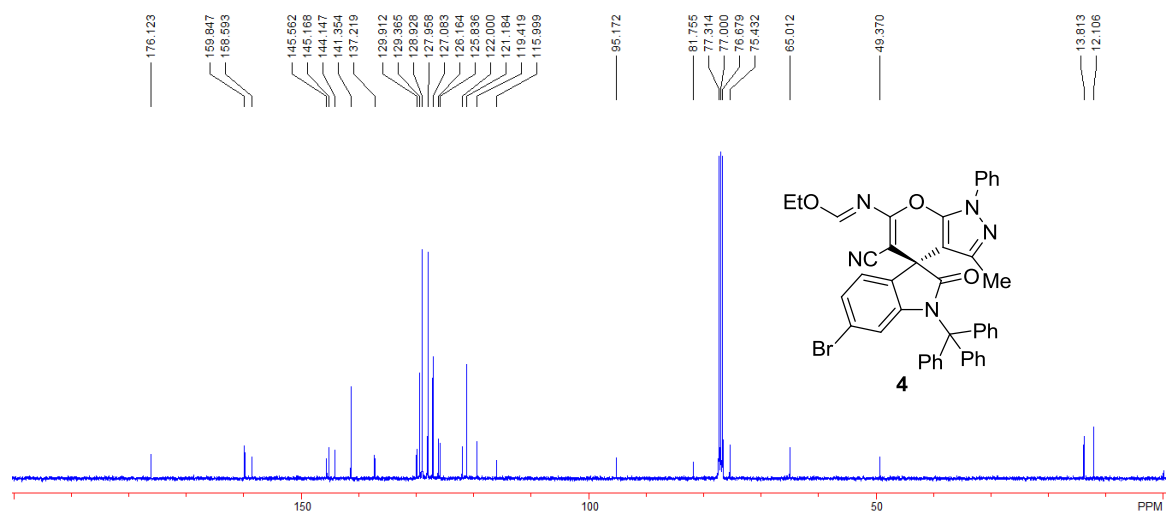
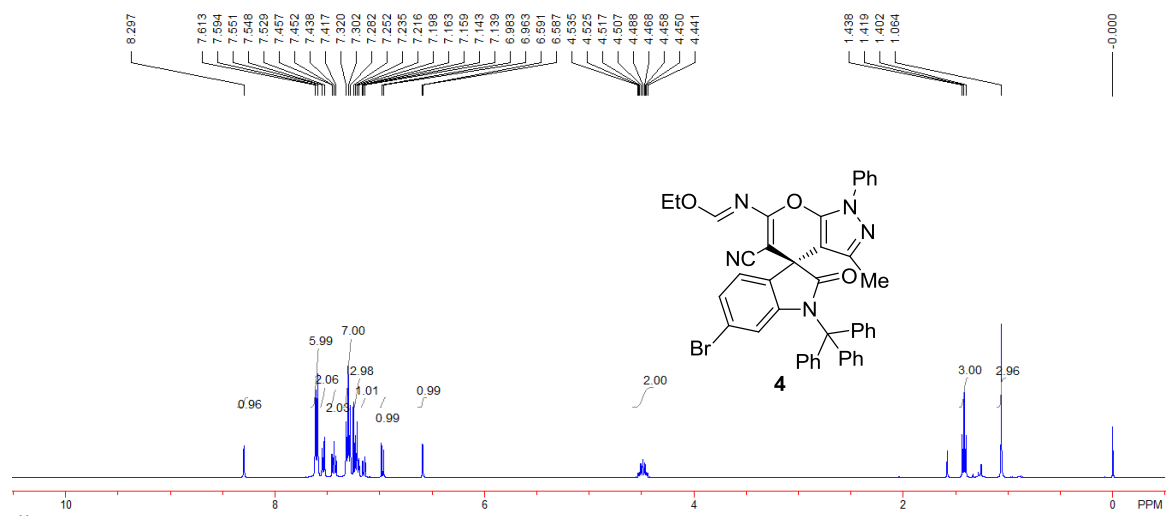


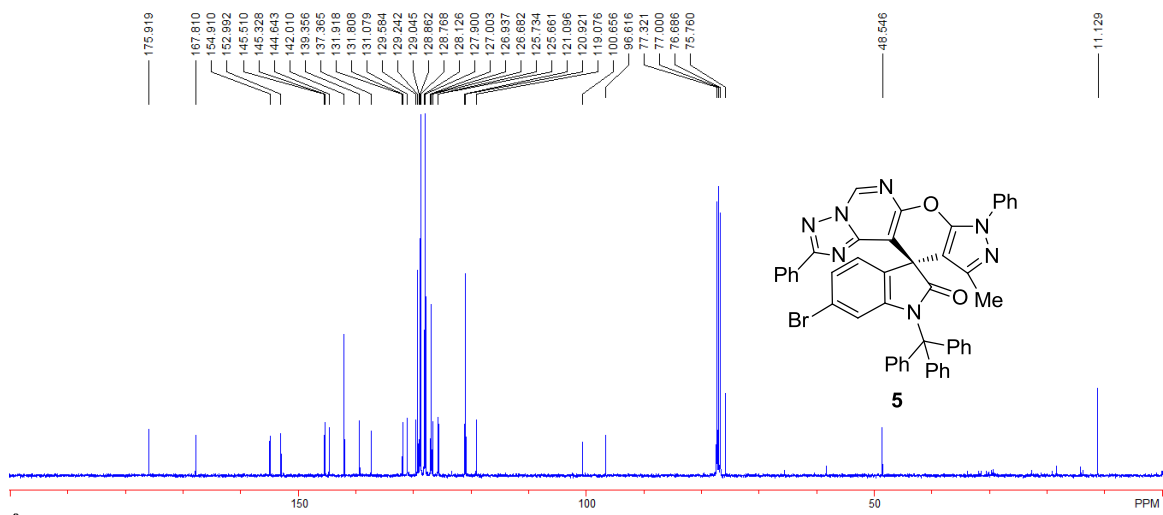
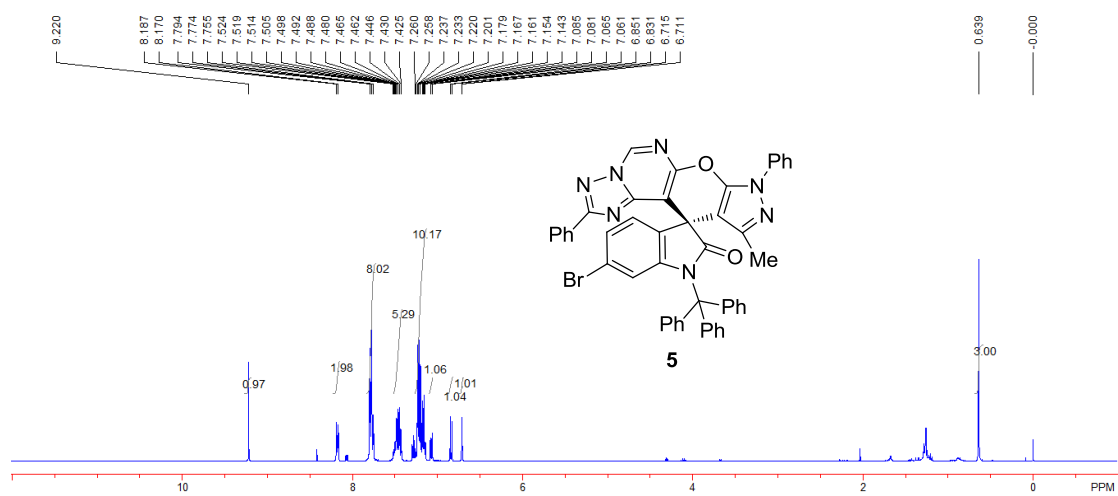


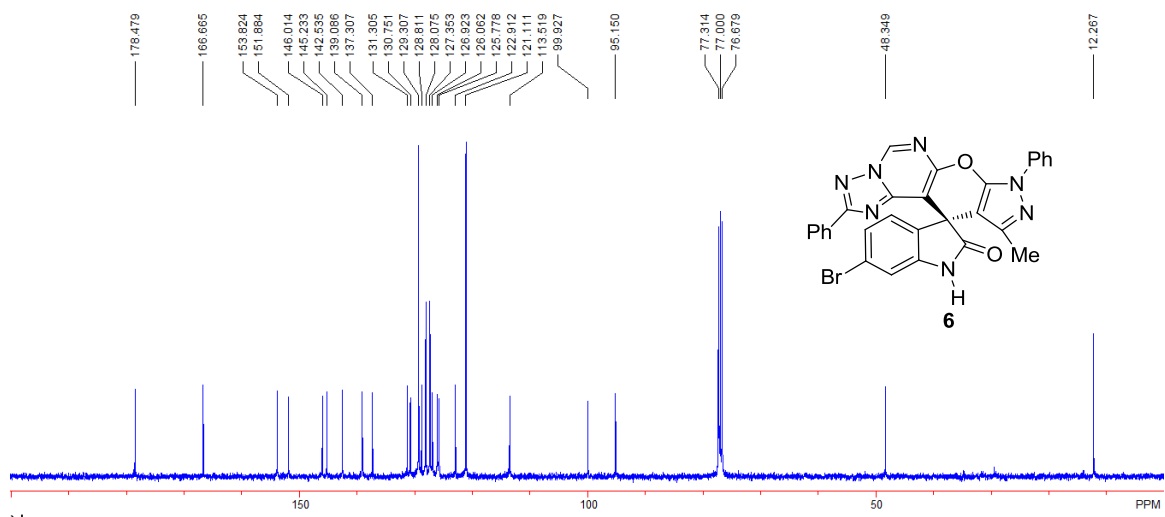
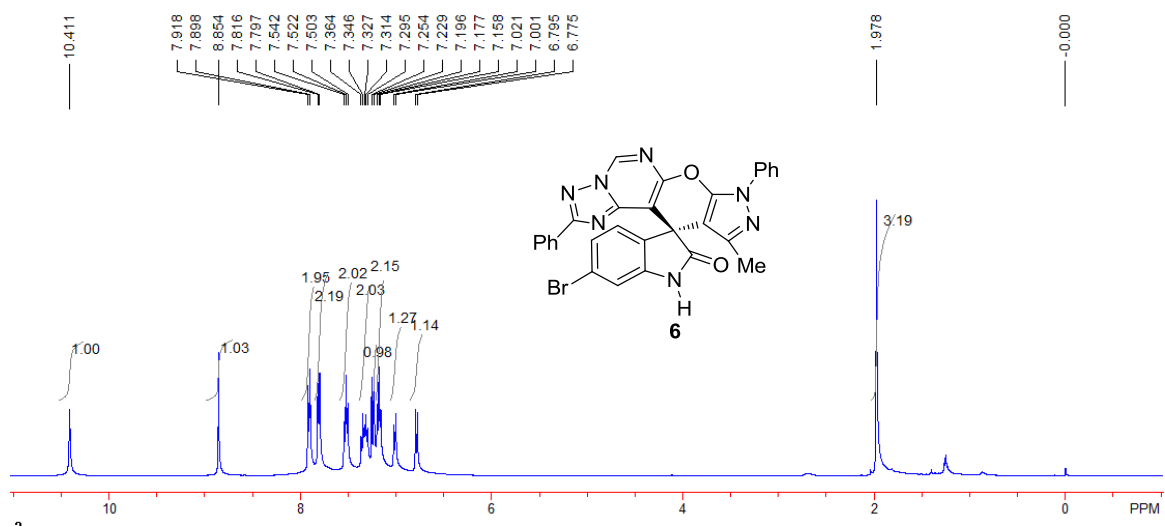




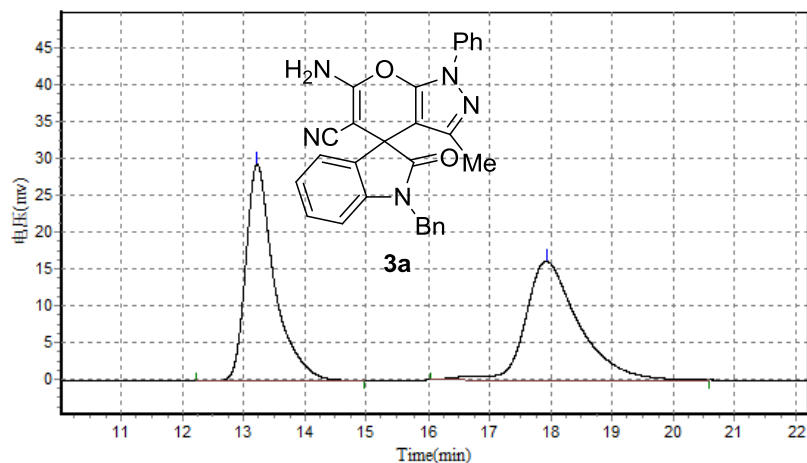
## 6. Copies of NMR Spectra of Compounds 4-6





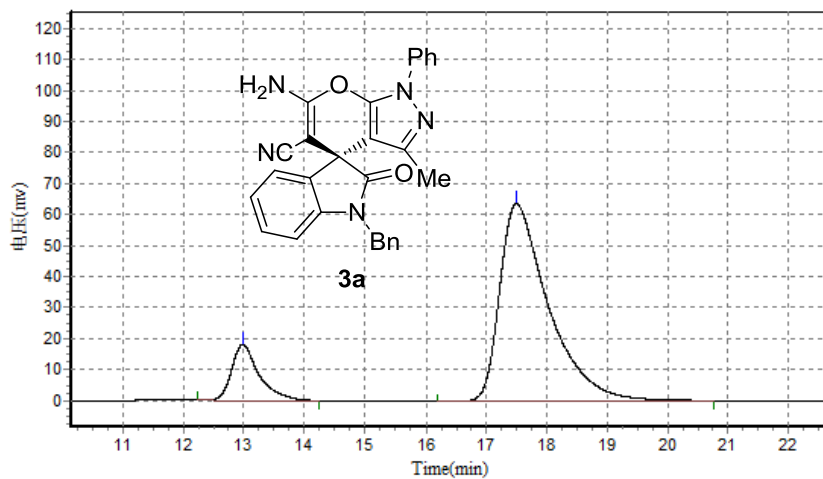


## 7. Copies of HPLC Spectra of the Products 3-6



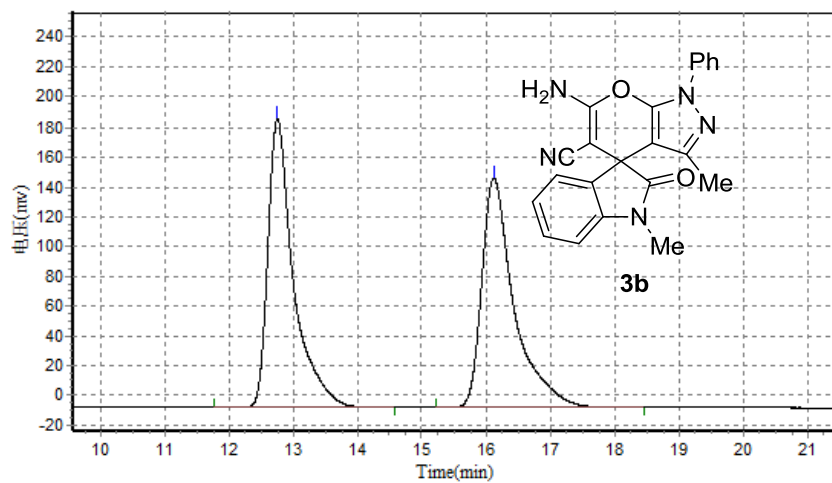
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.215	29398.352	948061.438	49.5254
2		17.920	16141.455	966233.313	50.4746
<b>Total</b>			45539.807	1914294.750	100.0000



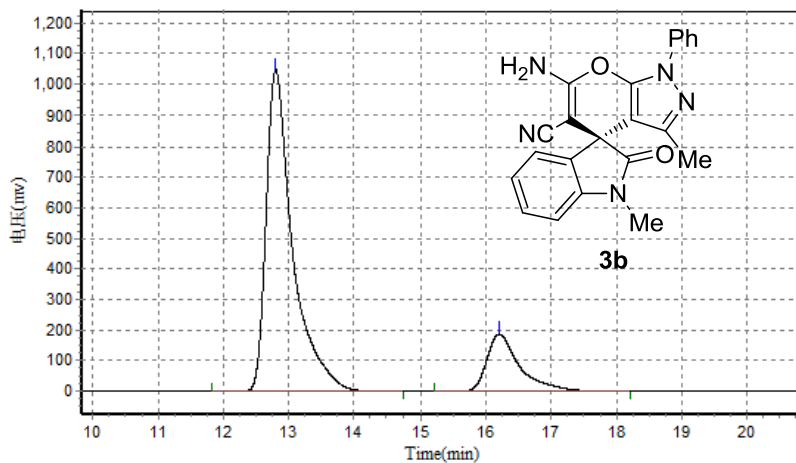
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.982	17866.266	559602.313	13.6290
2		17.493	63418.699	3546360.750	86.3710
<b>Total</b>			81284.965	4105963.063	100.0000



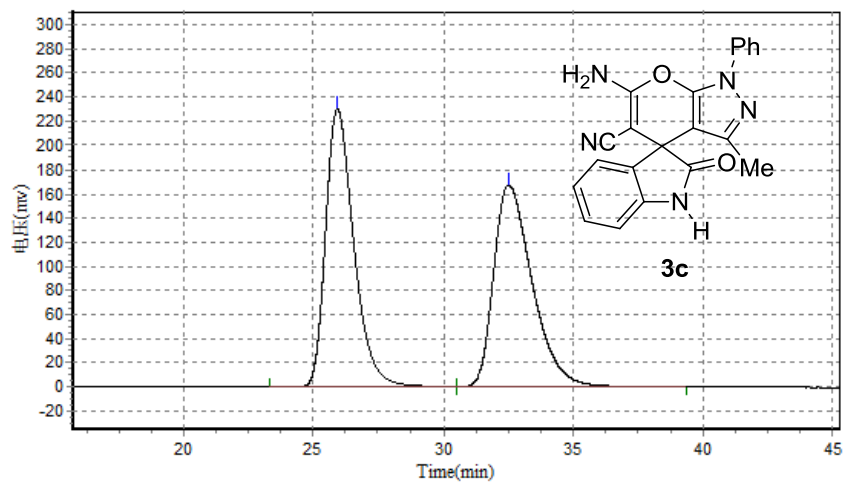
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.752	193474.156	5336085.000	49.7665
2		16.107	154043.156	5386163.500	50.2335
<b>Total</b>			347517.313	10722248.500	100.0000



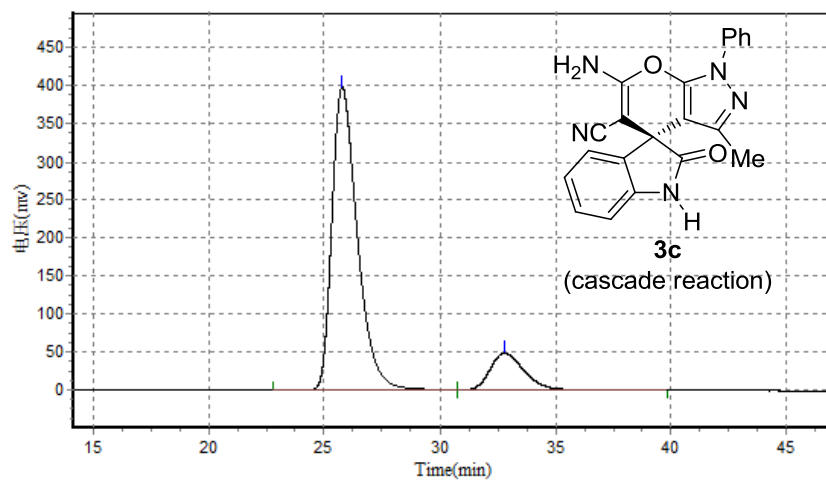
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.802	1048450.250	29540124.000	81.7248
2		16.203	187999.594	6605741.000	18.2752
<b>Total</b>			1236449.844	36145865.000	100.0000



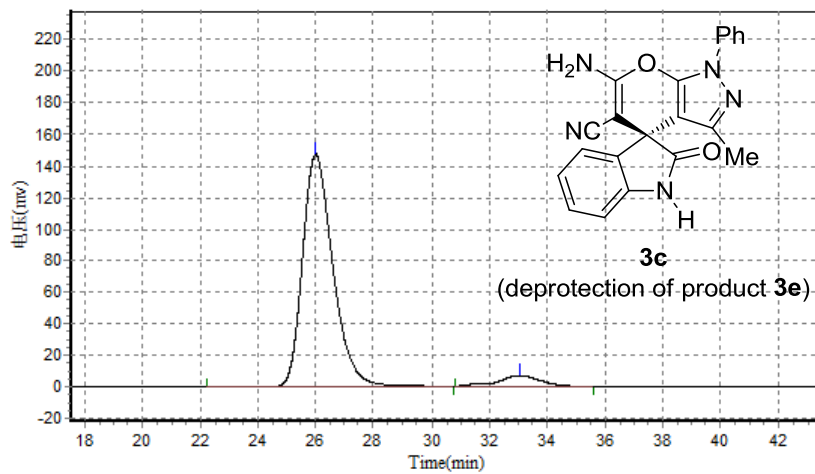
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.928	230979.734	17436902.000	50.0493
2		32.493	168336.797	17402566.000	49.9507
<b>Total</b>			399316.531	34839468.000	100.0000



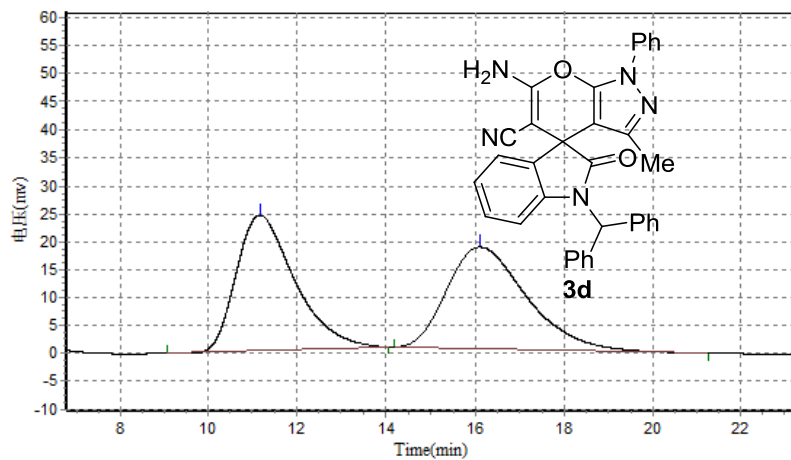
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.788	397743.531	30526372.000	85.1202
2		32.782	49210.301	5336307.000	14.8798
<b>Total</b>			446953.832	35862679.000	100.0000



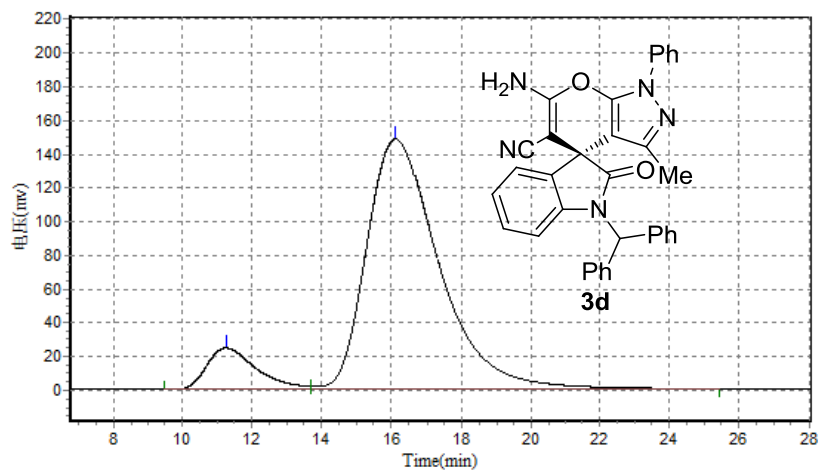
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.998	147409.844	10851318.000	93.6468
2		33.022	6925.049	736175.375	6.3532
<b>Total</b>			154334.893	11587493.375	100.0000



### Results

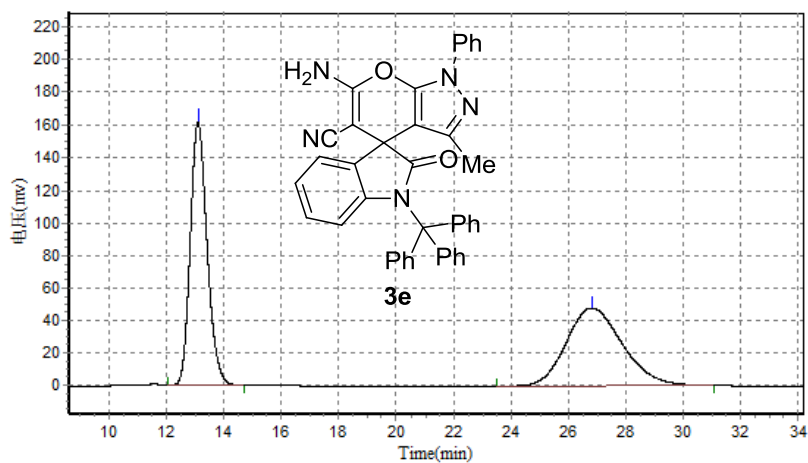
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.153	24229.164	2229062.500	49.4497
2		16.103	18234.375	2278673.000	50.5503
<b>Total</b>			42463.539	4507735.500	100.0000



### Results

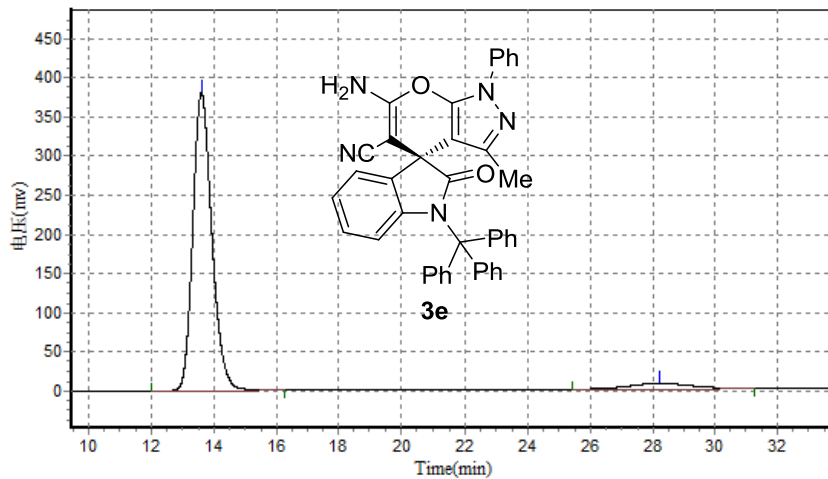
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.255	24556.166	2432425.250	10.2320
2		16.135	148199.188	21340214.000	89.7680
<b>Total</b>			172755.354	23772639.250	100.0000





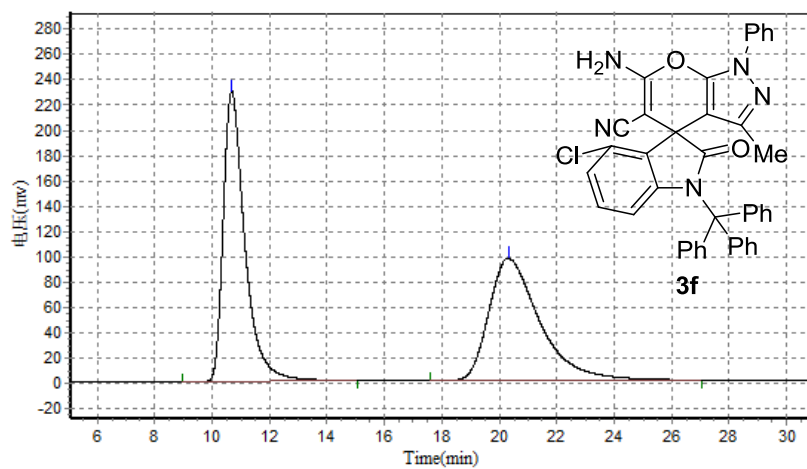
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.117	161876.297	6598503.500	50.3424
2		26.817	47898.715	6508754.500	49.6576
<b>Total</b>			209775.012	13107258.000	100.0000



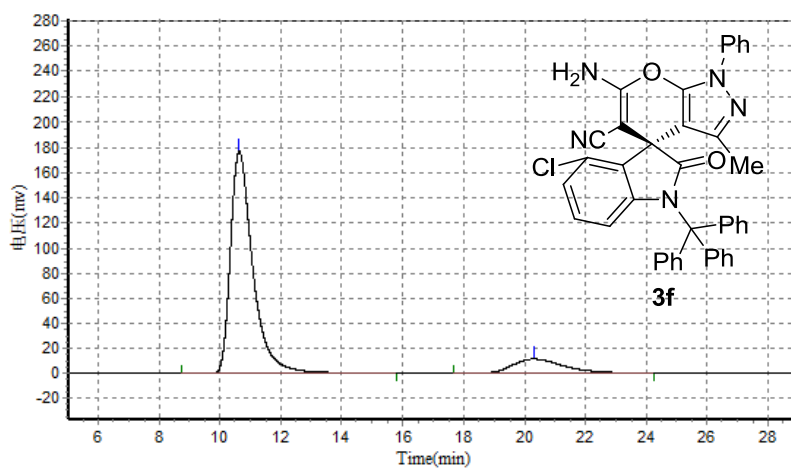
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.607	380218.781	16011022.000	94.3866
2		28.217	6963.194	952217.125	5.6134
<b>Total</b>			387181.976	16963239.125	100.0000



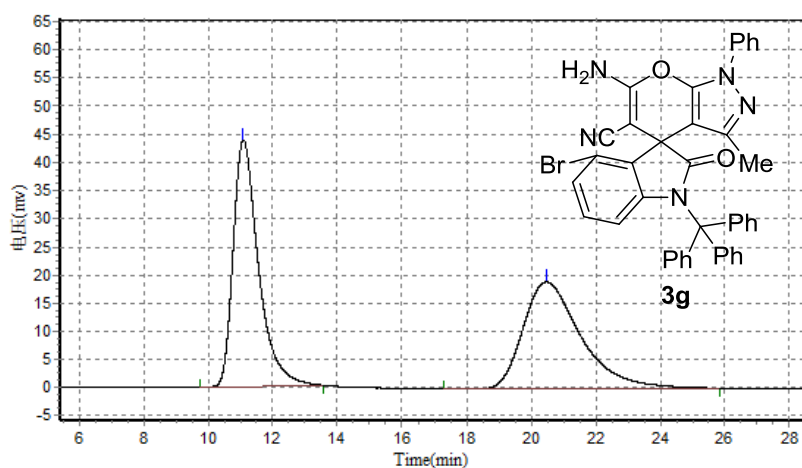
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.687	228566.203	11998230.000	50.2430
2		20.313	96267.781	11882179.000	49.7570
<b>Total</b>			324833.984	23880409.000	100.0000



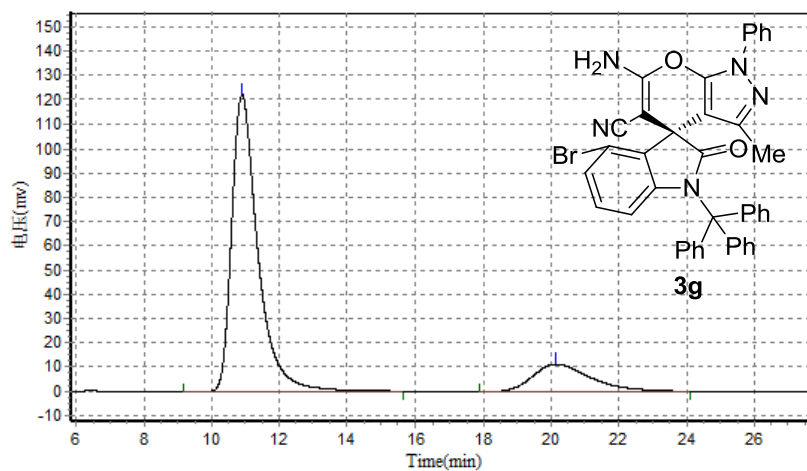
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.638	177125.063	9102100.000	86.9193
2		20.308	11473.305	1369799.375	13.0807
<b>Total</b>			188598.367	10471899.375	100.0000



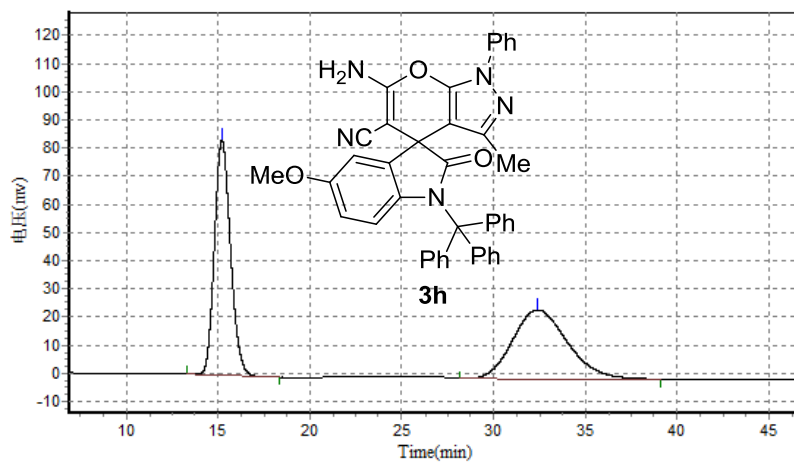
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.090	43940.750	2395284.750	50.2664
2		20.460	19044.061	2369893.000	49.7336
<b>Total</b>			62984.811	4765177.750	100.0000



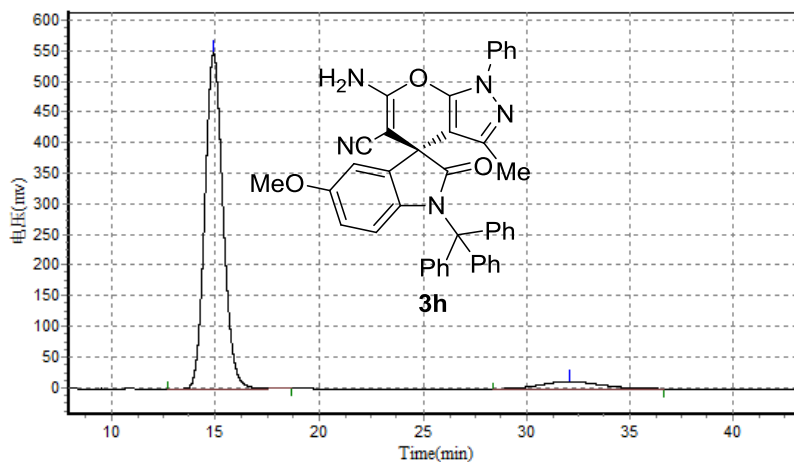
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.893	121963.195	6552413.500	83.0525
2		20.143	11268.212	1337066.625	16.9475
<b>Total</b>			133231.407	7889480.125	100.0000



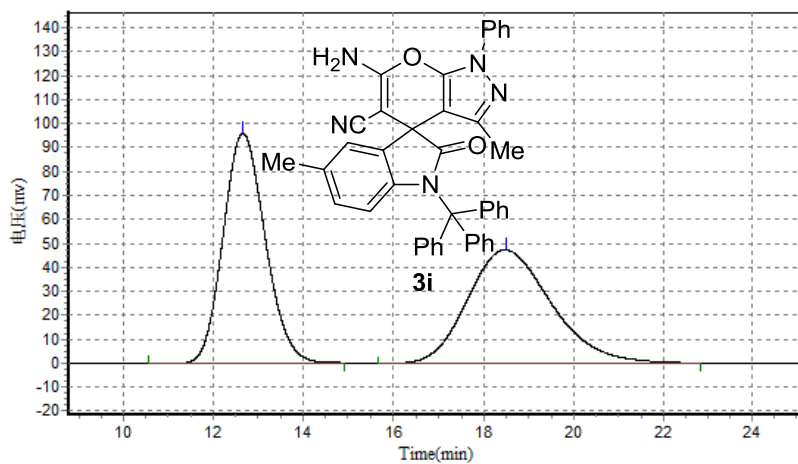
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.220	83493.469	5080126.000	50.3593
2		32.365	24360.365	5007645.000	49.6407
<b>Total</b>			107853.834	10087771.000	100.0000



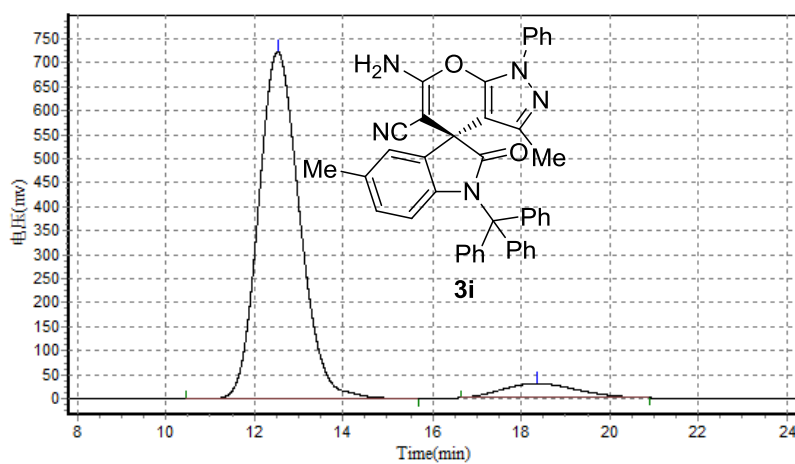
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.903	548680.188	33522758.000	93.4823
2		32.070	11669.442	2337250.500	6.5177
<b>Total</b>			560349.630	35860008.500	100.0000



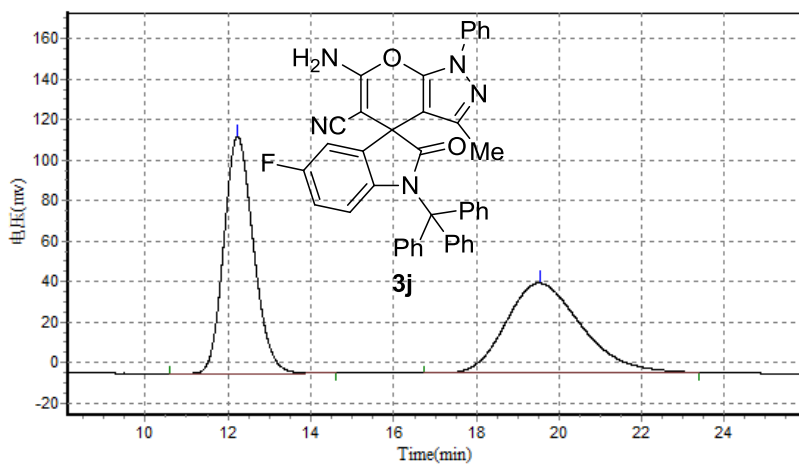
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.655	96079.391	6265504.000	50.4283
2		18.485	47381.934	6159073.000	49.5717
<b>Total</b>			143461.324	12424577.000	100.0000



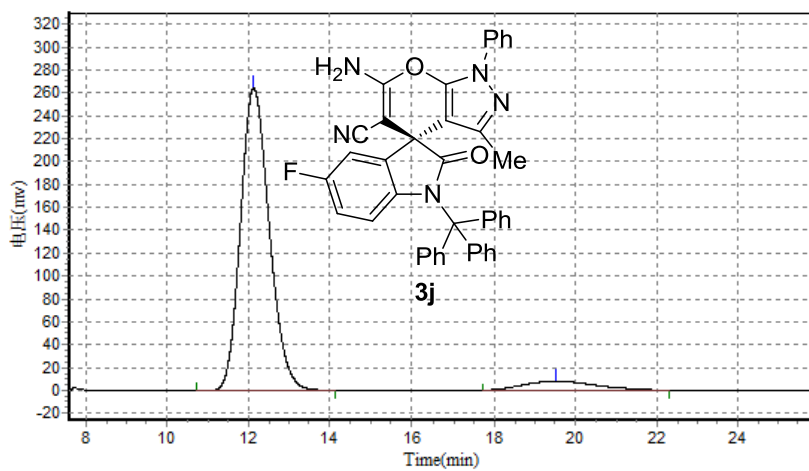
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.525	722871.875	46492300.000	93.0241
2		18.355	29609.029	3486480.000	6.9759
<b>Total</b>			752480.904	49978780.000	100.0000



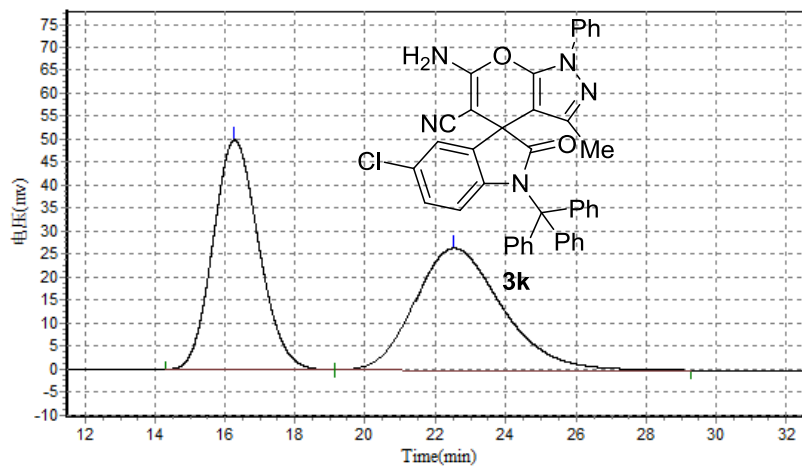
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.238	117178.258	5836971.000	50.9010
2		19.532	44374.809	5630325.000	49.0990
<b>Total</b>			161553.066	11467296.000	100.0000



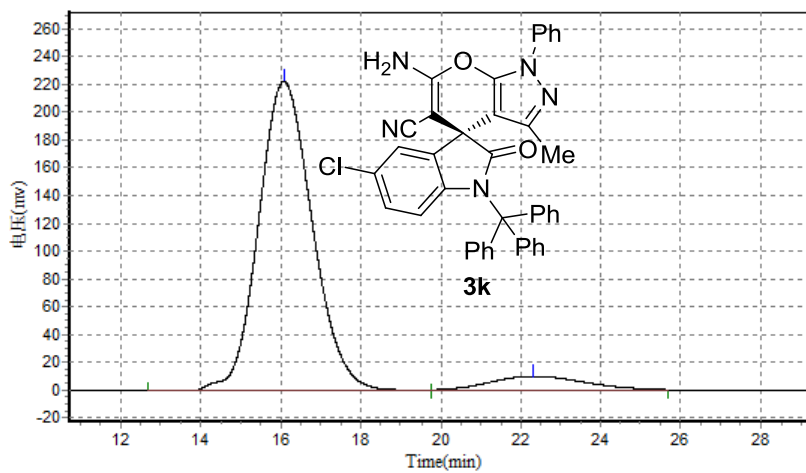
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.127	264565.031	12983120.000	92.9136
2		19.530	7912.599	990211.125	7.0864
<b>Total</b>			272477.630	13973331.125	100.0000



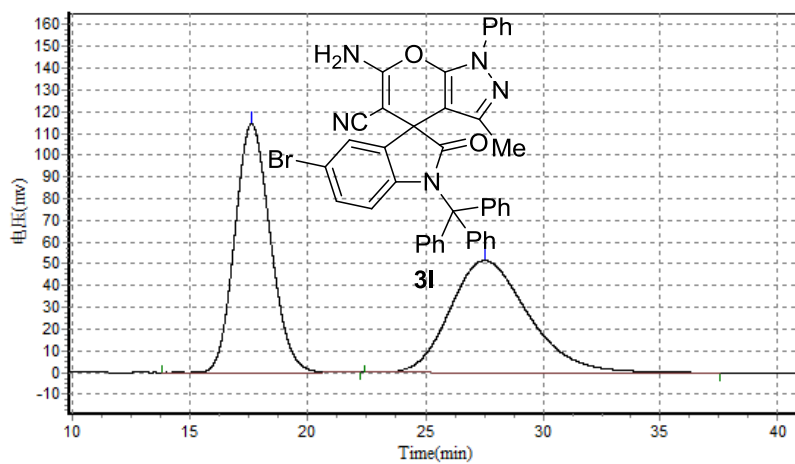
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.265	49854.809	4506595.000	49.8633
2		22.505	26408.949	4531296.000	50.1367
<b>Total</b>			76263.758	9037891.000	100.0000



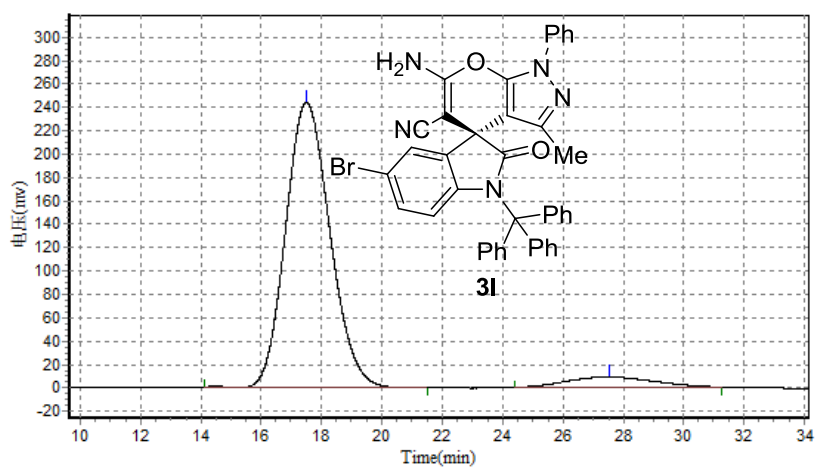
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.077	221857.469	20695688.000	92.8411
2		22.283	9855.474	1595829.875	7.1589
<b>Total</b>			231712.942	22291517.875	100.0000



### Results

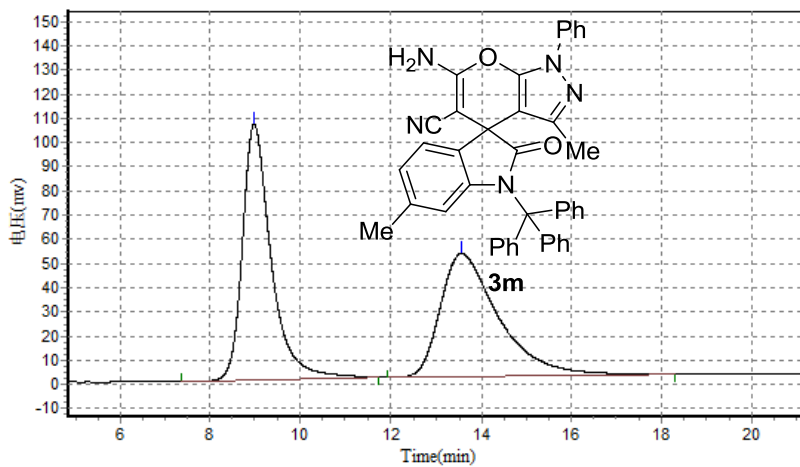
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.623	114371.641	12030132.000	50.1790
2		27.503	51531.730	11944315.000	49.8210
<b>Total</b>			165903.371	23974447.000	100.0000



### Results

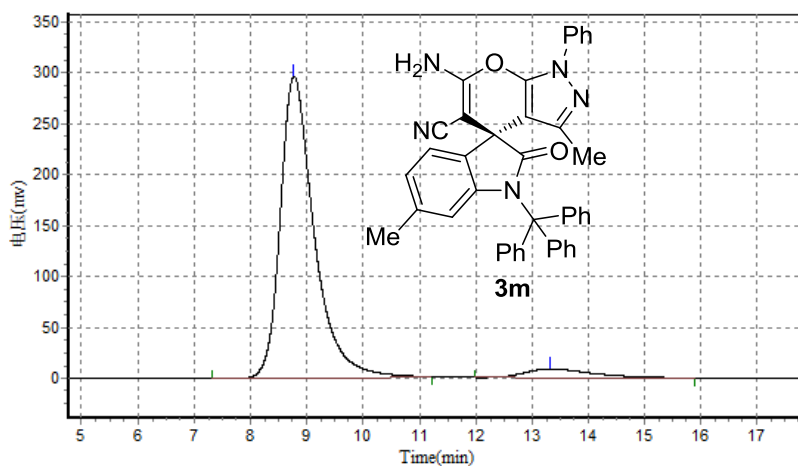
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.508	244467.438	25037932.000	93.3628
2		27.527	8779.376	1779949.000	6.6372
<b>Total</b>			253246.813	26817881.000	100.0000





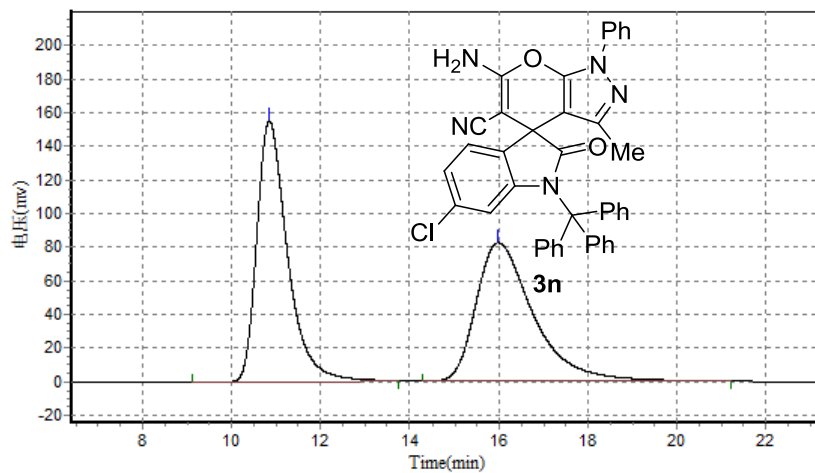
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.978	105580.281	4661290.500	50.6485
2		13.553	50718.289	4541934.000	49.3516
<b>Total</b>			156298.570	9203224.500	100.0000



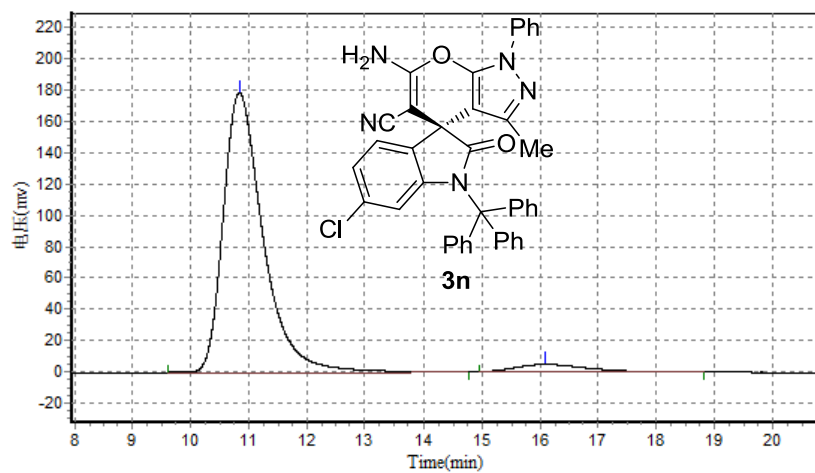
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.780	295990.125	12340196.000	94.5615
2		13.318	8598.358	709716.875	5.4385
<b>Total</b>			304588.483	13049912.875	100.0000



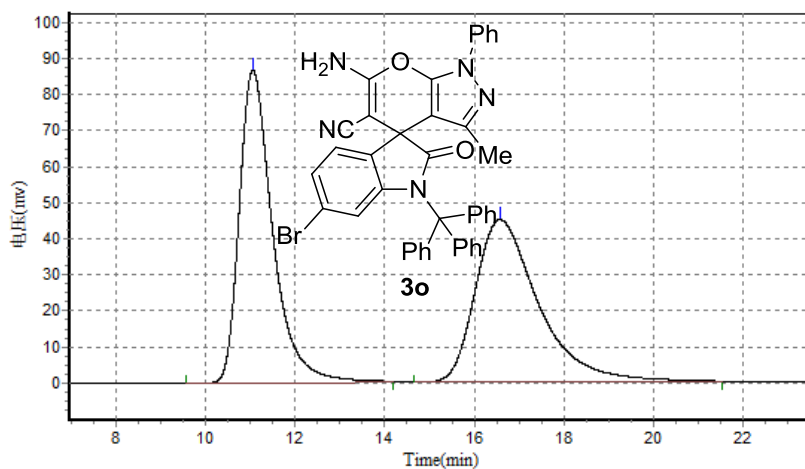
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.855	154879.750	7402522.000	50.1323
2		15.983	82273.047	7363449.000	49.8677
<b>Total</b>			237152.797	14765971.000	100.0000



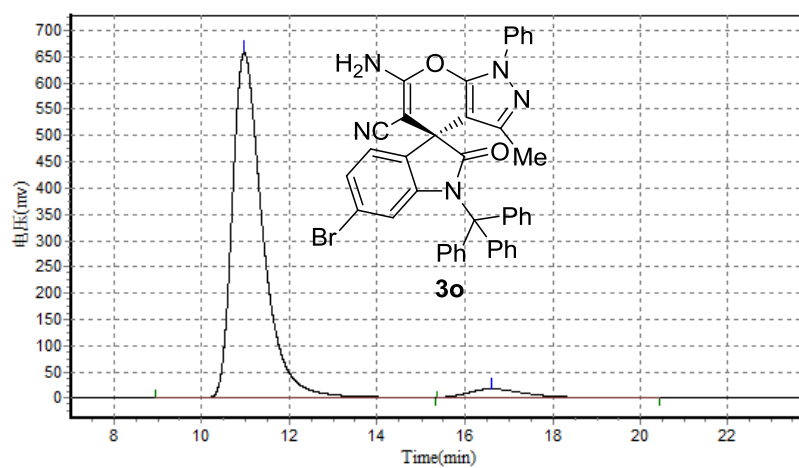
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.840	178048.031	8499101.000	95.4226
2		16.078	4767.599	407699.406	4.5774
<b>Total</b>			182815.630	8906800.406	100.0000



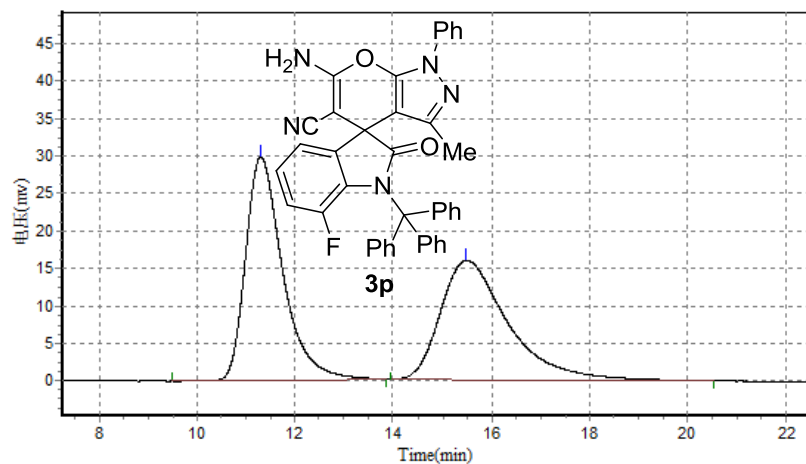
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.058	86584.563	4468051.000	50.4660
2		16.552	44847.074	4385529.000	49.5340
<b>Total</b>			131431.637	8853580.000	100.0000



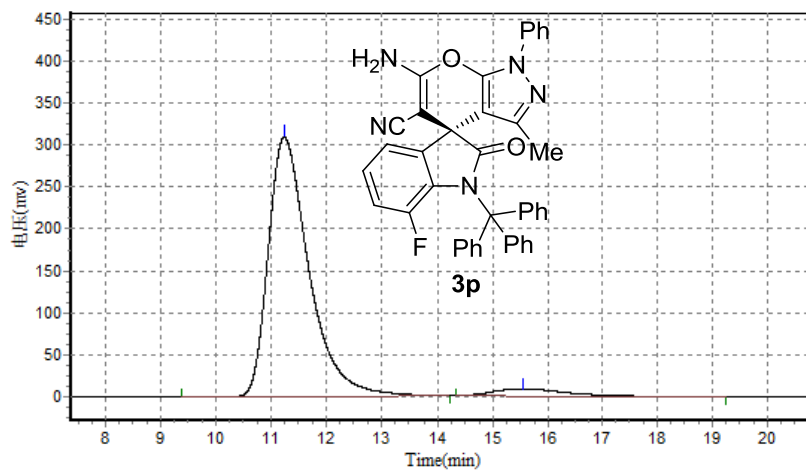
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.977	656811.250	31713452.000	95.4779
2		16.600	16548.471	1502030.875	4.5221
<b>Total</b>			673359.721	33215482.875	100.0000



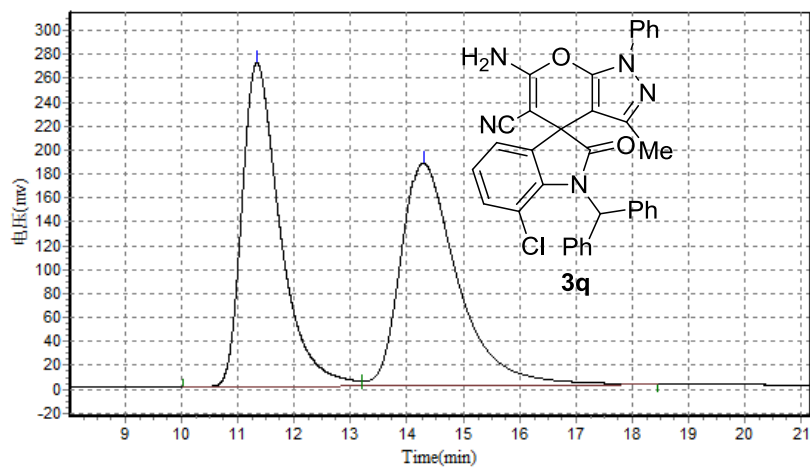
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.302	29807.932	1563996.125	50.6474
2		15.475	15909.587	1524011.250	49.3526
<b>Total</b>			45717.519	3088007.375	100.0000



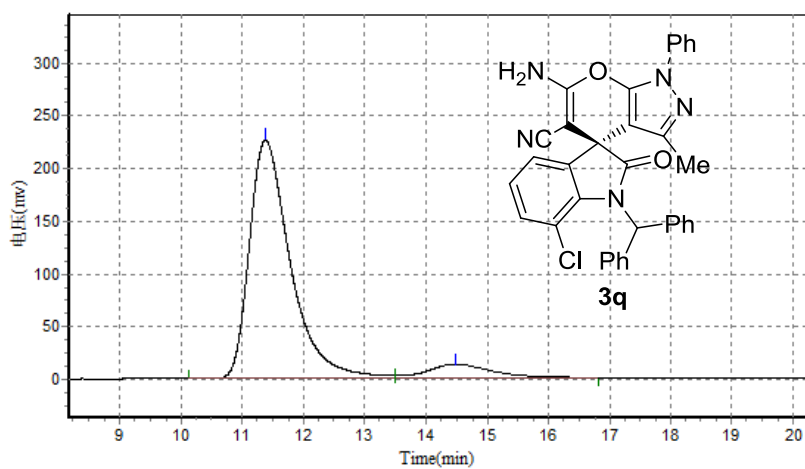
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.245	308388.906	15821498.000	95.4276
2		15.540	8534.312	758086.563	4.5724
<b>Total</b>			316923.218	16579584.563	100.0000



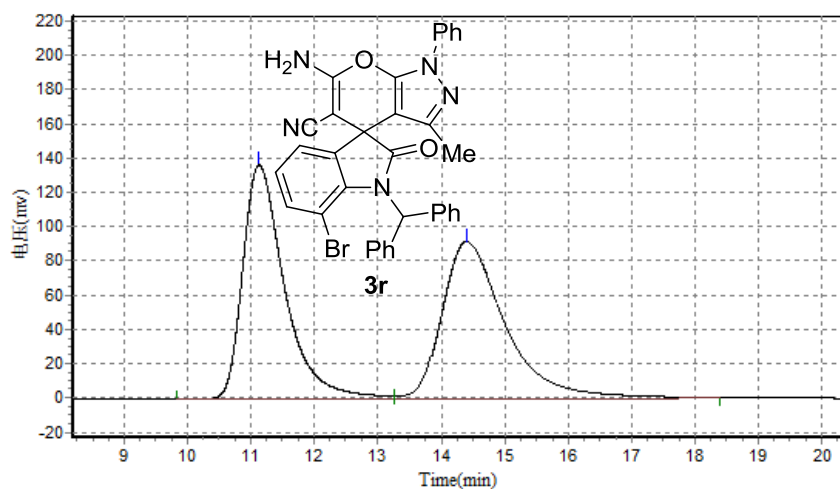
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.345	269823.719	12659516.000	49.6670
2		14.278	185822.766	12829261.000	50.3330
<b>Total</b>			455646.484	25488777.000	100.0000



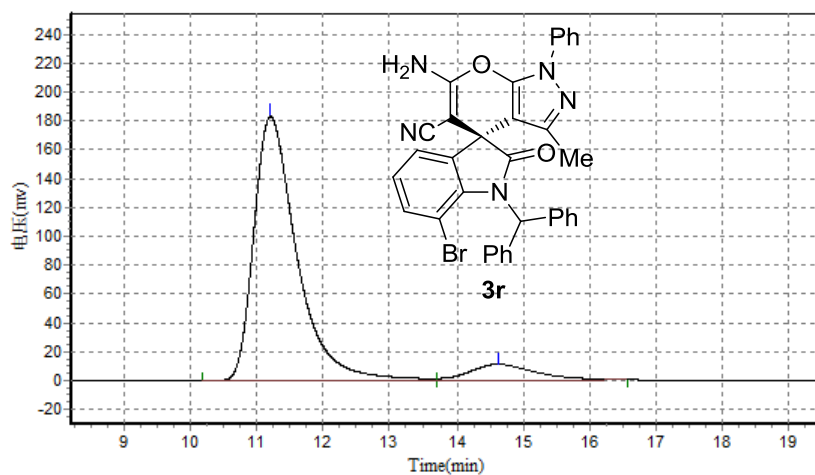
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.383	225990.063	10562122.000	91.6289
2		14.475	13123.521	964939.063	8.3711
<b>Total</b>			239113.583	11527061.063	100.0000



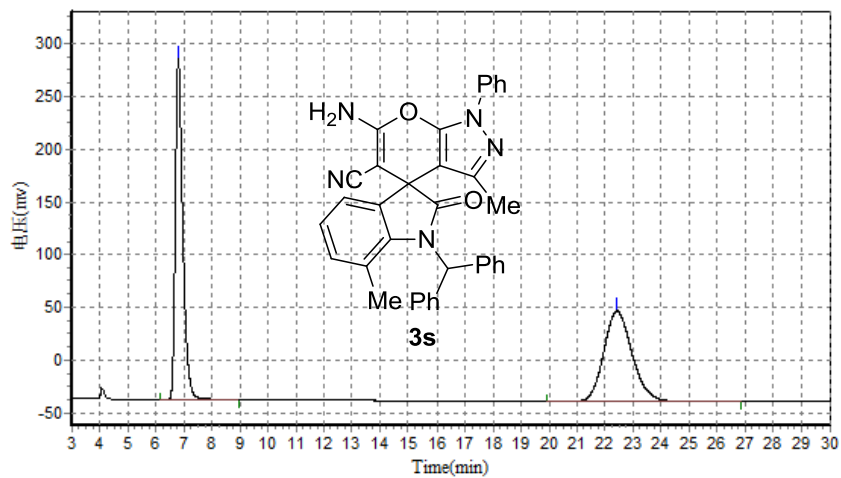
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.140	136503.734	6226538.000	49.8223
2		14.402	91559.969	6270948.500	50.1777
<b>Total</b>			228063.703	12497486.500	100.0000



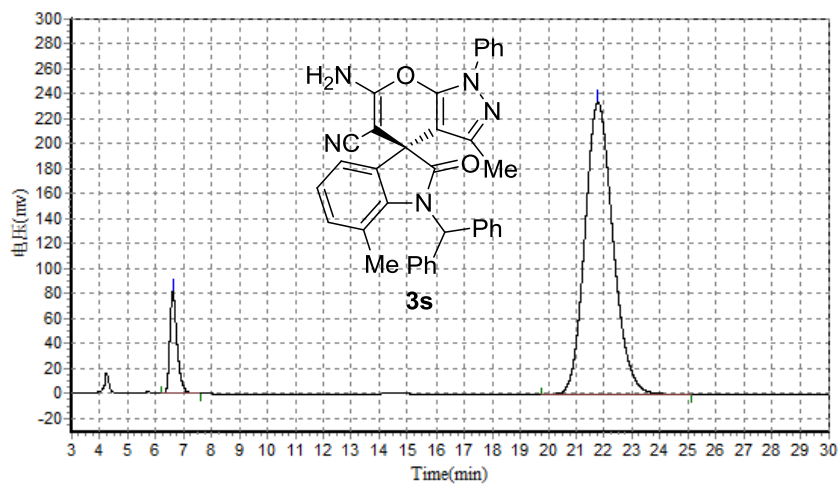
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.208	182974.656	8224511.500	91.6623
2		14.623	10868.662	748108.938	8.3377
<b>Total</b>			193843.318	8972620.438	100.0000



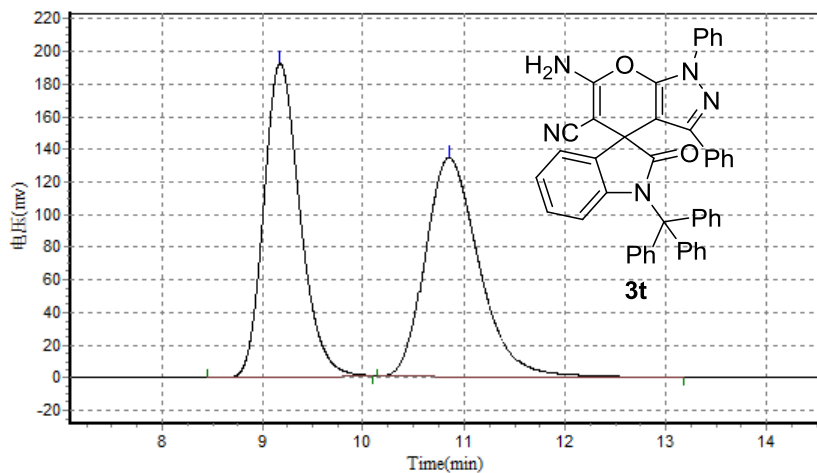
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.793	322834.906	5991547.500	50.1082
2		22.422	85467.125	5965668.500	49.8918
<b>Total</b>			408302.031	11957216.000	100.0000



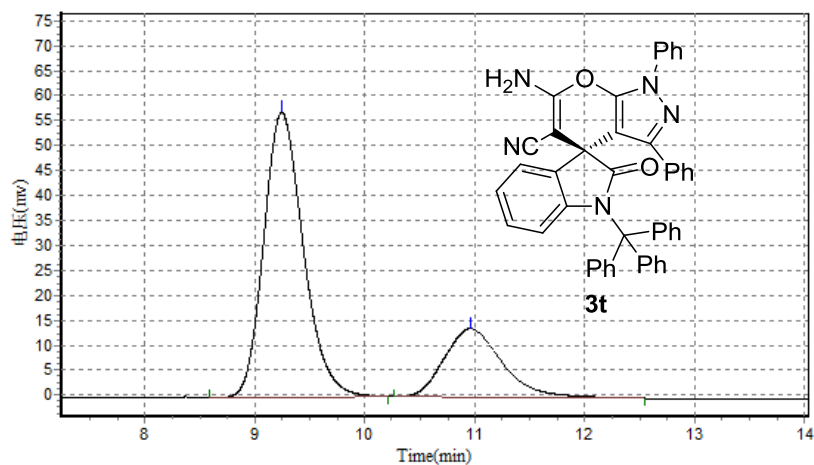
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.610	81637.617	1459728.750	8.2108
2		21.780	234204.188	16318475.000	91.7892
<b>Total</b>			315841.805	17778203.750	100.0000



### Results

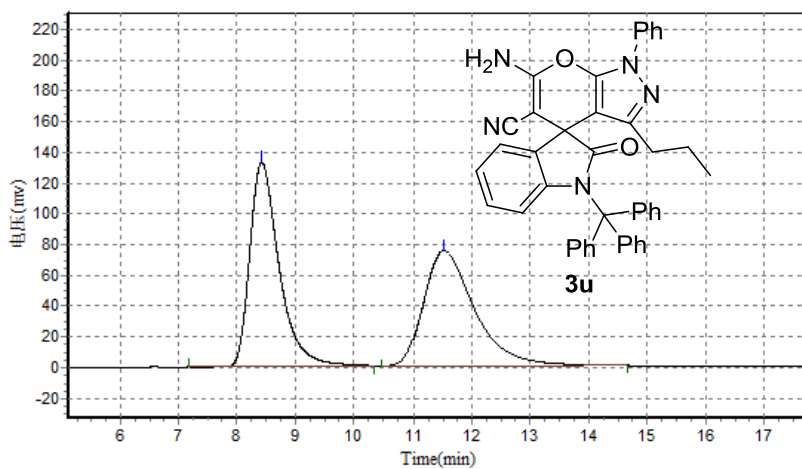
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.178	192081.984	4783971.500	49.4046
2		10.845	133789.375	4899280.000	50.5954
<b>Total</b>			325871.359	9683251.500	100.0000



### Results

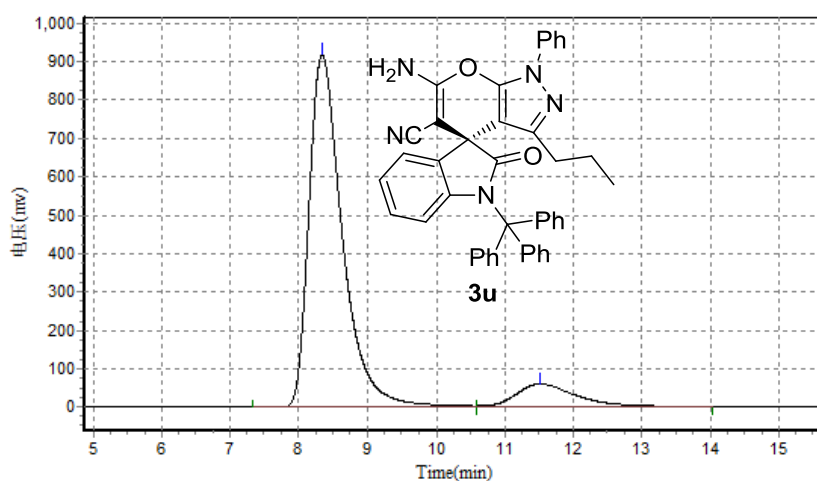
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.248	56979.449	1428357.750	73.6783
2		10.957	13742.665	510283.406	26.3217
<b>Total</b>			70722.114	1938641.156	100.0000





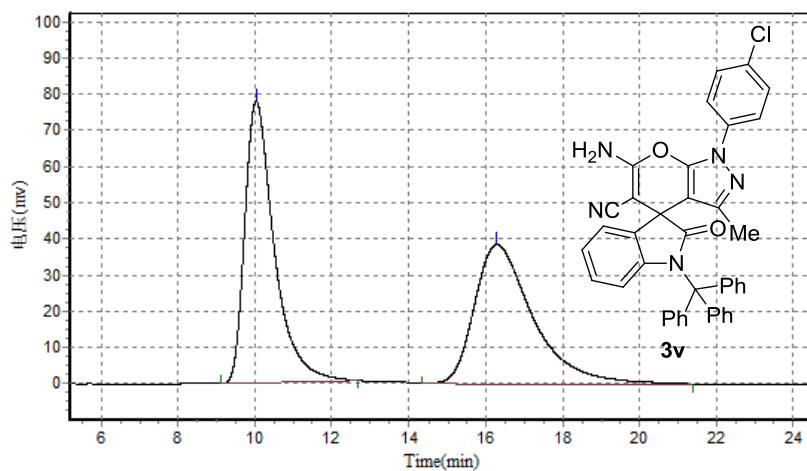
**Results**

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.425	132598.563	4613695.500	50.4017
2		11.527	75094.297	4540144.000	49.5982
<b>Total</b>			207692.859	9153839.500	100.0000



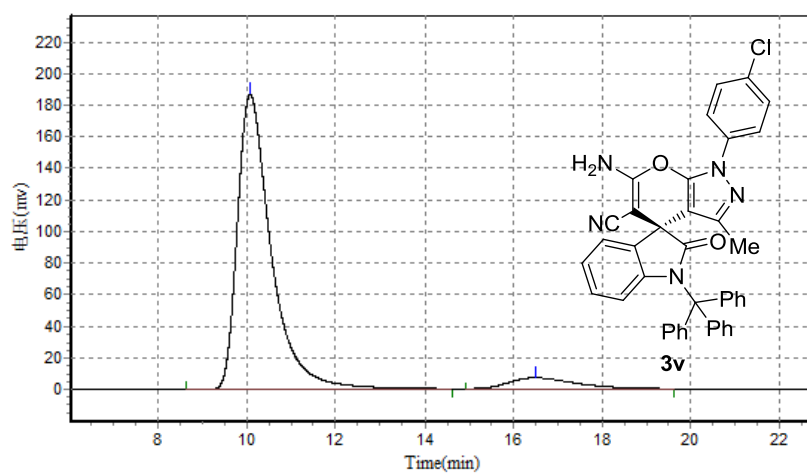
**Results**

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.343	916348.188	31153746.000	89.5444
2		11.520	59677.898	3637629.750	10.4556
<b>Total</b>			976026.086	34791375.750	100.0000



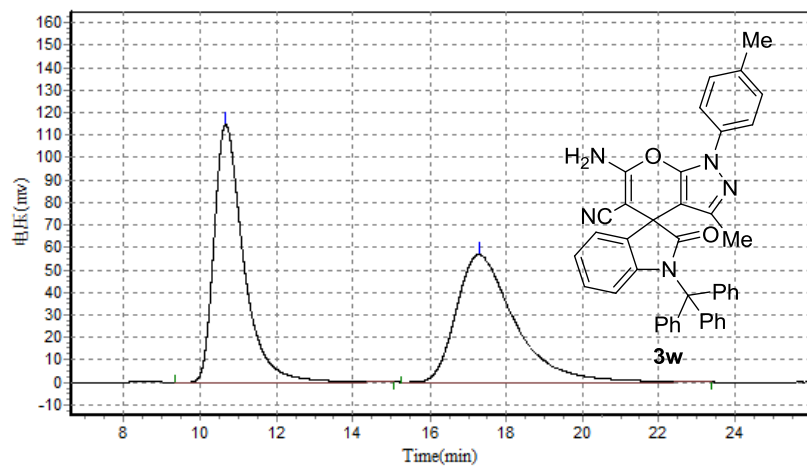
**Results**

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.042	77886.844	4141922.750	50.7817
2		16.277	38284.449	4014401.750	49.2183
<b>Total</b>			116171.293	8156324.500	100.0000



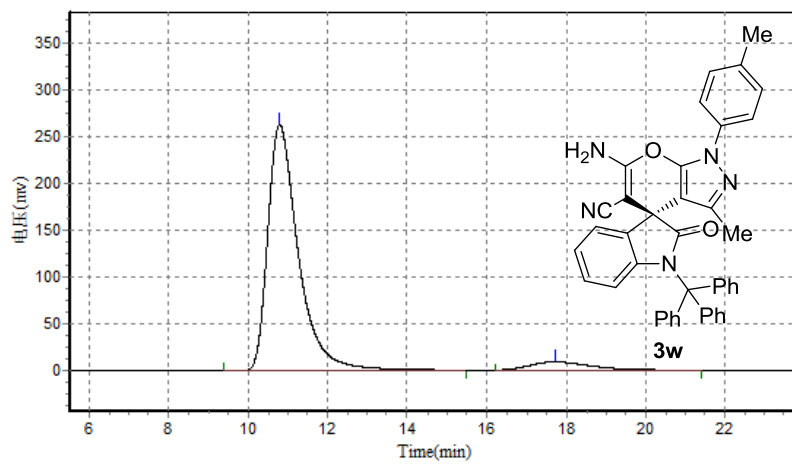
**Results**

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.083	186771.609	9887684.000	93.1662
2		16.512	6950.479	725269.125	6.8338
<b>Total</b>			193722.089	10612953.125	100.0000



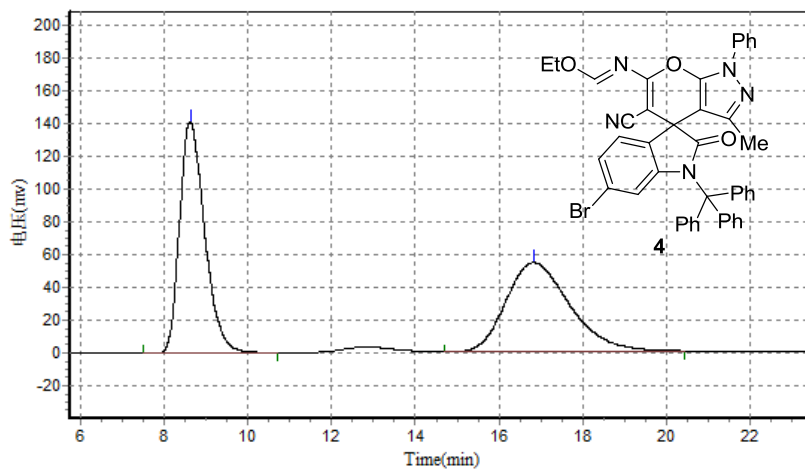
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.673	114884.930	6166986.000	50.4627
2		17.280	56677.547	6053885.000	49.5373
<b>Total</b>			171562.477	12220871.000	100.0000



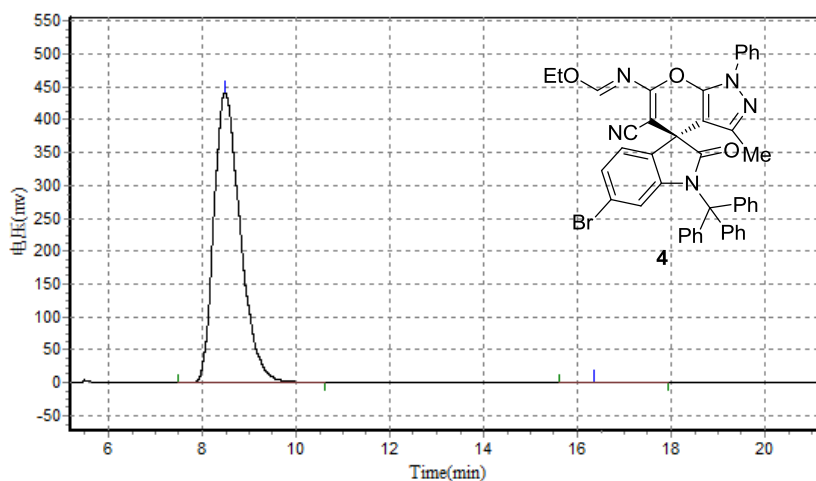
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.802	262995.219	14043461.000	93.8016
2		17.703	8730.875	927987.375	6.1984
<b>Total</b>			271726.094	14971448.375	100.0000



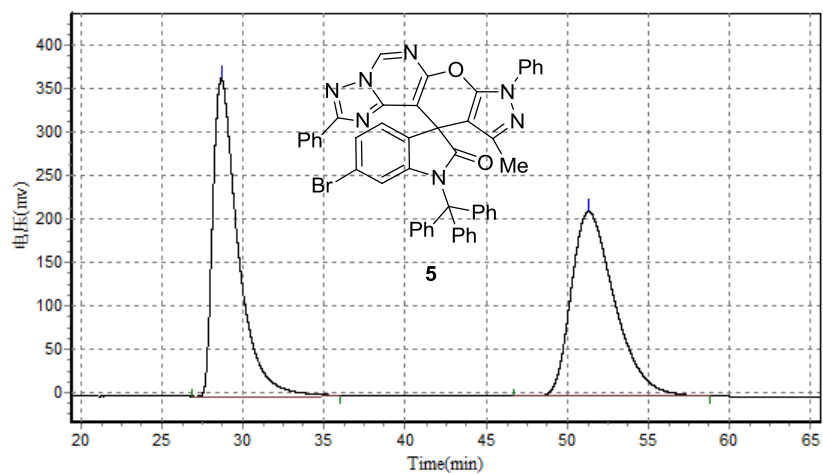
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.625	141019.484	5889653.000	50.6711
2		16.817	54140.922	5733649.000	49.3289
<b>Total</b>			195160.406	11623302.000	100.0000



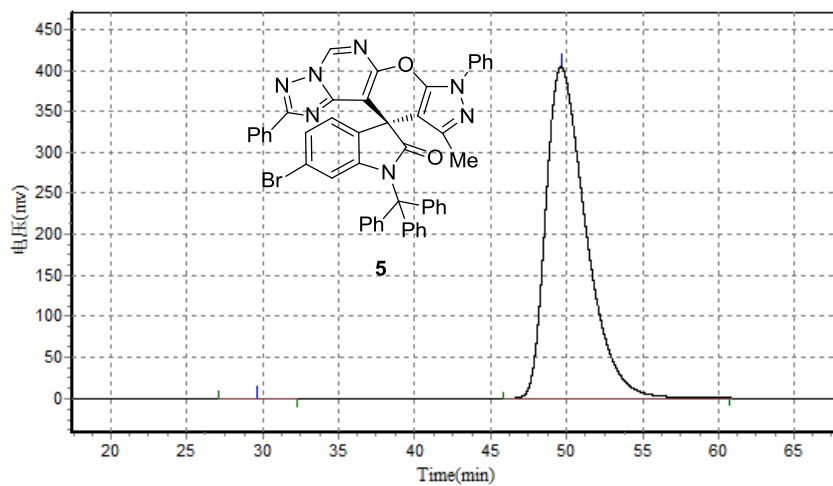
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.487	440001.500	17245668.000	99.9478
2		16.360	131.000	8999.499	0.0522
<b>Total</b>			440132.500	17254667.499	100.0000



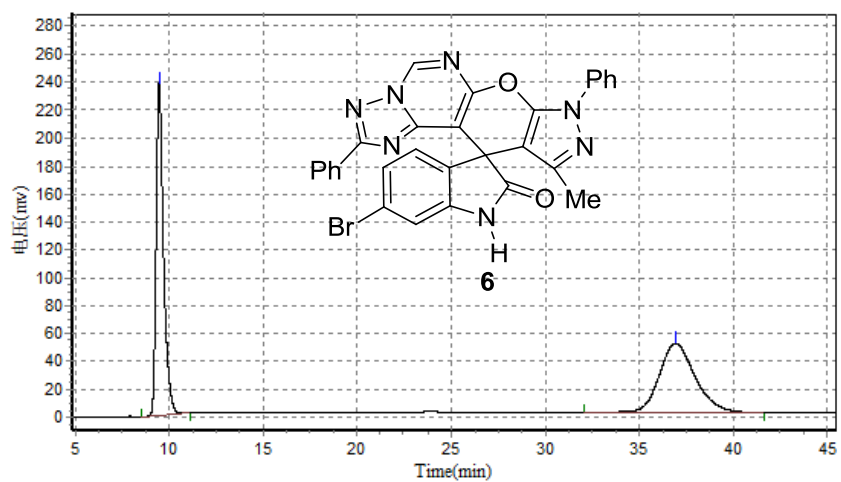
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.662	365716.125	39499360.000	49.9359
2		51.330	212505.734	39600808.000	50.0641
<b>Total</b>			578221.859	79100168.000	100.0000



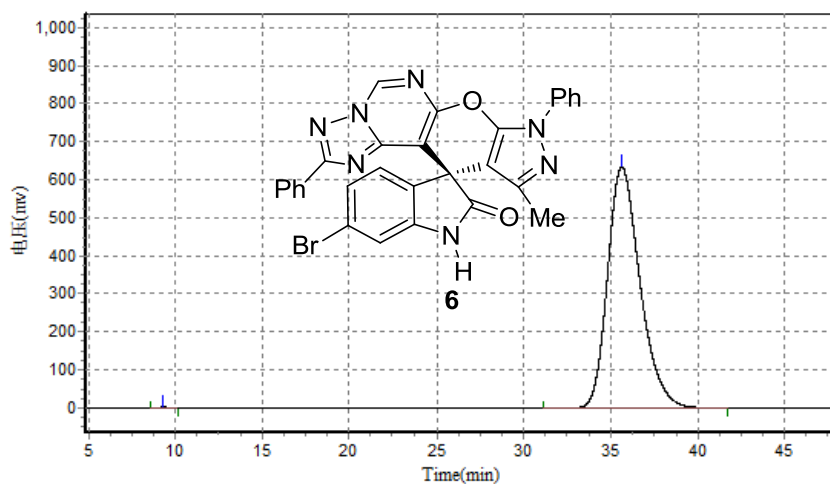
### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		29.613	495.914	55803.703	0.0751
2		49.615	403985.375	74213592.000	99.9249
<b>Total</b>			404481.289	74269395.703	100.0000



### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.453	237734.250	6489347.500	49.6040
2		36.952	49661.109	6592947.500	50.3960
<b>Total</b>			287395.359	13082295.000	100.0000



### Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.310	2273.719	55934.598	0.0680
2		35.627	634383.875	82229544.000	99.9320
<b>Total</b>			636657.594	82285478.598	100.0000

## 8. X-ray Structure and Crystal Data for Compound 4

The crystal data of **4** have been deposited in CCDC with number 1468155.

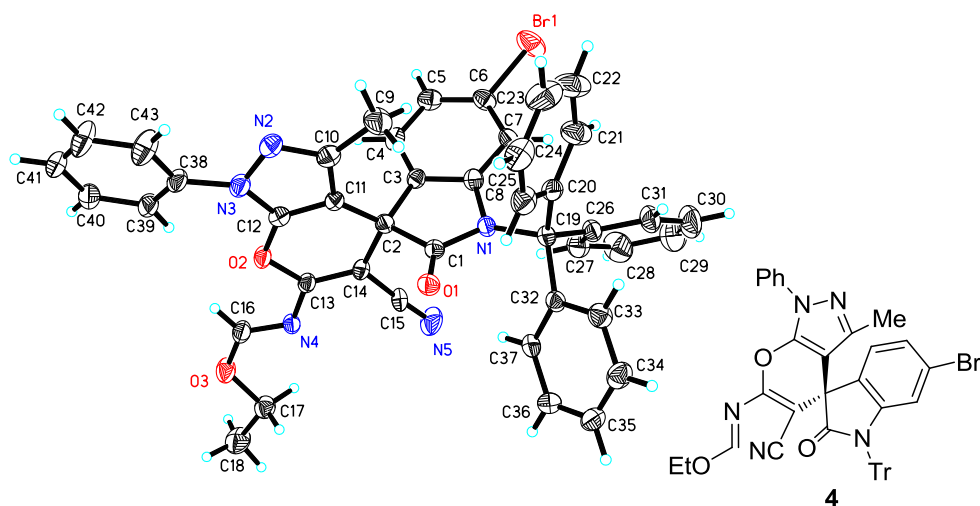


Table 1. Crystal data and structure refinement for **4**.

Identification code	<b>4</b>
Empirical formula	$C_{43}H_{32}BrN_5O_3$
Formula weight	746.64
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	$a = 13.218(2)$ Å = 90 ° $b = 16.657(3)$ Å = 92.527(3) ° $c = 16.344(3)$ Å = 90 °
Volume	$3595.2(10)$ Å <sup>3</sup>
Z	4
Density (calculated)	1.379 Mg/m <sup>3</sup>
Absorption coefficient	1.192 mm <sup>-1</sup>
F(000)	1536
Crystal size	0.15 x 0.12 x 0.08 mm <sup>3</sup>
Theta range for data collection	1.542 to 27.705 °

Index ranges	-17<=h<=17, -21<=k<=18, -20<=l<=21
Reflections collected	29858
Independent reflections	15941 [R(int) = 0.0554]
Completeness to theta = 26.000 °	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6136
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	15941 / 1 / 941
Goodness-of-fit on F <sup>2</sup>	0.866
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.0811
R indices (all data)	R1 = 0.1338, wR2 = 0.1057
Absolute structure parameter	-0.003(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.287 and -0.263 e.Å <sup>-3</sup>