Supporting Information

Synthesis of 10*H*-Indolo[1,2-a]indol-10-ones via Palladium-Catalyzed C-H Bond Activation and Difluorocarbene Transfer

Chengxian Hu‡, Dan Mou‡, Xi Zhang, Ying Fu*, Congde Huo*, Zhengyin Du*

* Email: clinton_du@126.com; fu_yingmail@126.com; huocongde1978@hotmail.com

‡ These authors contributed equally.

Key Laboratory of Eco-functional Polymer Materials of the Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, P. R. China.

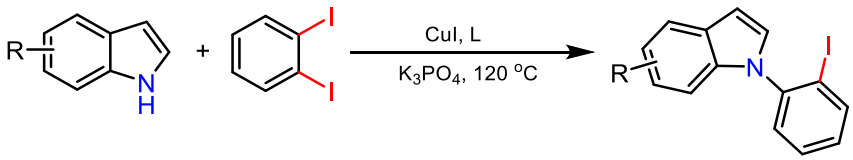
Contents

1. General Information

All chemicals were purchased from Energy Chemical Reagent, Ltd, Zane Chemical Technology company, Aladdin Ltd, Crystal pure bio-tech company and so forth. Unless otherwise stated, all experiments were conducted in a seal tube under argon atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on Nuclear Magnetic Resonance spectrometer (400 MHz for ^{1}H or 600 MHz for ^{1}H, 151 MHz for ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR， δ = 77.00 for ^{13}C-NMR) as an internal reference. High resolution mass spectra were recorded using ZAB-HS Bifocal high resolution mass spectrometer. Coupling constants (*J*) were reported in Hertz (Hz).

2. Synthetic Methods of Starting Materials[1]



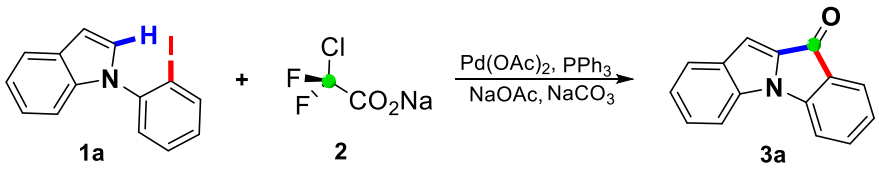
The appropriate quantity of CuI and ligand benzotriazole were added to a 5 mL of round bottom flask containing aryl halide (0.5 mmol), nitrogen heterocycles (0.55 mmol, 1.1 equiv), and KO-*t*-Bu or K_3PO_4 (1.0 mmol, 2.0 equiv) in 2.0 mL of DMSO. The flask was sealed with a cap containing a PTFE septum. The mixture was then heated at 120 ^{o}C until the aryl halides were consumed, as determined by TLC. The reaction mixture was washed with ethyl acetate and water. The organic layer was then washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo and the crude residue was purified by column chromatography on silica gel using hexanes or a mixture of hexane and ethylacetate as eluents. These compounds were characterized by ^{1}H NMR and ^{13}C NMR and they keep consistent with previous literature.

3. Catalyst-Loading Effects

At the initial stage of the exploration of this reaction, the loads of palladium catalyst and phosphorous ligand are examined in the presence of sodium acetate and sodium

carbonate. The results are listed in Table S1. It is found that the optimal loads for the generation of **3a** were finalized with $Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%), NaOAc (1.0 equiv), Na_2CO_3 (2.0 equiv.), sodium chlorodi-flfluoroacetate **2** (2.0 equiv) in DMSO (3 mL) at 90 °C for about 10 hours in the argon atmosphere.

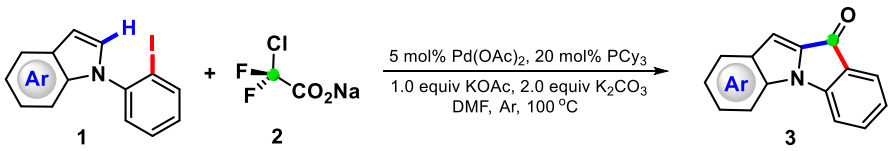
Table S1 Catalyst-loading effects.



Entry[a]	$Pd(OAc)_2$ (mol%)	PPh_3 (mol%)	NaOAc (mol%)	Na_2CO_3 (mol%)	Yield[b] (%)
1	5	10	50	100	30
2	10	10	50	100	24
3	20	10	50	100	19
4	5	0	50	100	n.r.
5	5	5	50	100	trace
6	5	15	50	100	33
7	5	20	50	100	35
8	5	30	50	100	22
9	5	20	0	100	27
10	5	20	100	100	38
11	5	20	150	100	34
12	5	20	100	0	n.r.
13	5	20	100	200	43
14	5	20	100	300	40
15 [c]	5	20	100	200	25
16 [d]	5	20	100	200	39

[a]Reaction conditions: 1-(2-iodophenyl)-1H-indole **1a** (0.2 mmol), sodium chlorodiflfluoroacetate **2** (0.4 mmol, 2.0 equiv), solvent (3 mL), 90 °C, and argon, for about 10 hours until **1a** is completely reaction in a sealed Schlenk tube. [b]Isolated yield. [c]sodium chlorodiflfluoroacetate **2** (0.2 mmol, 1.0 equiv), [d]sodium chlorodiflfluoroacetate **2** (0.6 mmol, 3.0 equiv).

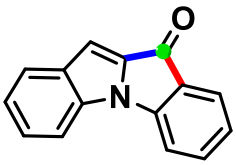
4. General Procedure for the Synthesis of Product 3



A dry sealed tube equipped with a magnetic stir bar was charged with 1-(2-iodophenyl)-1*H*-indoles **1** (0.2 mmol), Sodium chlorodifluoroacetate **2** (0.4 mmol, 2 equiv), $Pd(OAc)_2$ (2.2 mg, 5 mol%), PCy_3 (11.2 mg, 20 mol%), KOAc (0.2 mmol, 1.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv) and DMF (3 mL) under argon atmosphere. The mixture was heated in an oil bath at 100 ^{o} C overnight. Upon completion of the reaction, ethyl acetate was added to the mixture, and then washed with saturated brine. The combined water layers were extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether/Ethyl acetate = 20:1) to give the desired product **3**.

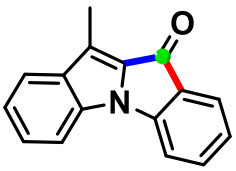
5. Characterization Data of Product 3

10*H*-indolo[1,2-a]indol-10-one (3a):



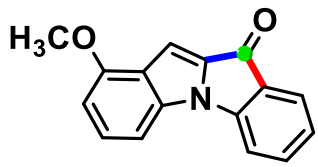
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3a** (36.8 mg, 84% yield). Yellow solid. M.p. 164-166 ^{o}C. (161.4-162.2 ^{o}C.)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.50 - 7.44 (m, 2H), 7.40 - 7.36 (m, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.13 - 7.07 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.5, 145.5, 135.7, 135.4, 134.2, 132.6, 129.4, 128.1, 125.1, 125.0, 123.8, 122.0, 111.3, 111.3, 107.9.

11-Methyl-10*H*-indolo[1,2-a]indol-10-one (3b):



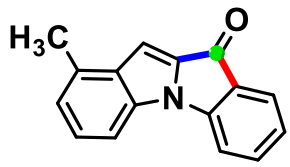
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3b** (40.1 mg, 86% yield). Yellow solid. M.p. 134-136 °C. (121-123 °C.)[3]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.42 - 7.36 (m, 2H), 7.27 (d, *J* = 5.9 Hz, 1H), 7.12 - 7.07 (m, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.9, 145.0, 135.0, 134.1, 133.5, 132.8, 129.8, 128.2, 124.8, 123.1, 122.8, 122.3, 121.3, 111.17, 111.0, 9.3.

1-Methoxy-10*H*-indolo[1,2-a]indol-10-one (3c):



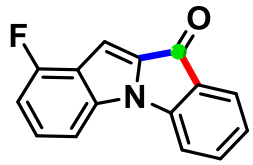
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3c** (44.4 mg, 89% yield). Orange solid. M.p. 169-171 °C. (164.3-165.6 °C.)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.31 - 7.27 (m, 2H), 7.22 (s, 1H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.48 (d, *J* = 7.9 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.2, 156.0, 145.4, 135.4, 135.2, 134.5, 129.6, 129.5, 125.03, 123.9, 123.5, 111.3, 105.9, 104.2, 101.7, 55.4.

1-Methyl-10*H*-indolo[1,2-a]indol-10-one (3d):



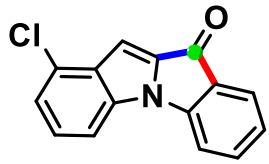
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3d** (39.6 mg, 85% yield). Orange solid. M.p. 172-174 °C. (163.4-164.8 °C.)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.48 (td, *J* = 7.7, 1.3 Hz, 1H), 7.31 - 7.28 (m, 3H), 7.13 (s, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.91 - 6.88 (m, 1H), 2.50 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.5, 145.5, 135.3, 135.2, 134.8, 134.2, 132.6, 129.5, 128.2, 125.0, 123.8, 122.2, 111.3, 108.8, 106.5, 19.3.

1-Fluoro-10*H*-indolo[1,2-*a*]indol-10-one (3e):



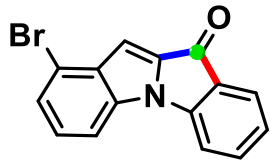
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3e** (29.9 mg, 63% yield). Yellow solid. M.p. 203-205 °C. (197.4-198.9 °C.)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.33 - 7.29 (m, 1H), 7.26 - 7.18 (m, 2H), 7.10 (d, *J* = 6.0 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.75 (t, *J* = 8.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.0, 158.1 (d, J_{C-F} = 253.72 Hz), 145.1, 135.6 (d, J_{C-F} = 253.72 Hz), 135.5, 135.4, 129.2, 128.9 (d, J_{C-F} = 8.05 Hz), 125.2, 124.30, 121.8 (d, J_{C-F} = 22.00 Hz), 111.4, 107.3 (d, J_{C-F} = 4.07 Hz), 106.9 (d, J_{C-F} = 19.00 Hz), 103.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.7.

1-Chloro-10*H*-indolo[1,2-a]indol-10-one (3f):



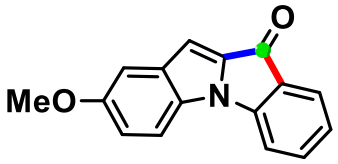
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3f** (27.8 mg, 55% yield). Yellow solid. M.p. 239-241 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.55 (td, *J* = 7.7, 1.3 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.24 (s, 1H), 7.13 (dt, *J* = 7.5, 3.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.2, 145.2, 135.7, 135.6, 134.6, 131.4, 120.0, 129.2, 128.5, 125.4, 124.4, 121.7, 111.5, 109.8, 106.0. HRMS (ESI) m/z calcd for $C_{15}H_8ClNO^+$, $(M+K)^+$ 291.9926, found 291.9924.

1-Bromo-10*H*-indolo[1,2-a]indol-10-one (3g):



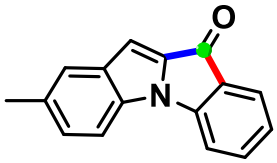
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3g** (29.8 mg, 50% yield). Yellow solid. M.p. 221-223 °C. (215.6-216.8 °C.)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 6.8 Hz, 2H), 7.20 (s, 1H), 7.14 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.2, 145.3, 135.6, 134.3, 133.3, 129.2, 128.7, 125.4, 124.9, 124.5, 118.6, 114.4, 111.5, 110.3, 107.7.

2-Methoxy-10*H*-indolo[1,2-a]indol-10-one (3h):



The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3h** (45.9 mg, 92% yield). Orange solid. M.p. 151-152 °C. (137.7-138.4 °C.)[3]. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 1H), 7.47 (td, *J* = 7.7, 1.3 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.27 - 7.24 (m, 2H), 7.06 - 7.04 (m, 1H), 7.04 (d, *J* = 2.9 Hz, 1H), 7.02 (d, *J* = 7.1 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.7, 145.6, 135.9, 135.4, 132.9, 132.8, 131.5, 129.9, 129.4, 125.1, 124.5, 123.6, 111.14, 110.9, 107.6, 21.3.

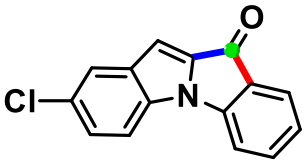
2-Methyl-10*H*-indolo[1,2-a]indol-10-one (3i):



The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3i** (40.6 mg, 87% yield). Orange solid. M.p. 142-143 °C. (129.0-129.8 °C.)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 1H), 7.49 (td, *J* = 7.7, 1.3 Hz, 1H), 7.42 - 7.37 (m, 2H), 7.30 (s, 1H), 7.23 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.08 - 7.03 (m, 2H), 2.41 (s, 3H). ^{13}C

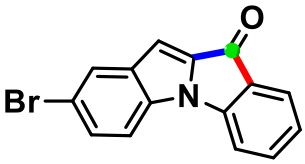
NMR (151 MHz, $CDCl_3$) δ 181.6, 145.6, 135.9, 135.4, 132.9, 131.5, 129.8, 129.4, 125.0, 124.5, 123.6, 111.1, 110.9, 107.6, 21.3.

2-Chloro-10*H*-indolo[1,2-a]indol-10-one (3j):



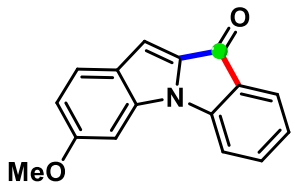
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3j** (33.4 mg, 66% yield). Yellow solid. M.p. 209-211 °C. (199.3-200.4 °C.)[2]. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.3, 145.2, 136.7, 135.7, 133.5, 132.4, 129.2, 128.3, 127.5, 125.3, 124.3, 124.2, 112.2, 111.3, 106.8.

2-Bromo-10*H*-indolo[1,2-a]indol-10-one (3k):



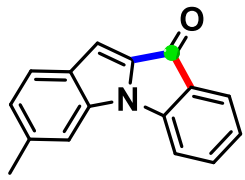
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3k** (36.4 mg, 61% yield). Orange solid. M.p. 218-220 °C. (214.3-215.2 °C.)[2]. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.53 (td, *J* = 7.7, 1.3 Hz, 1H), 7.50 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.3, 145.2, 136.5, 135.7, 134.1, 132.7, 130.9, 129.2, 127.4, 125.4, 124.3, 114.9, 112.5, 111.4, 106.7.

3-Methoxy-10*H*-indolo[1,2-a]indol-10-one (3l):



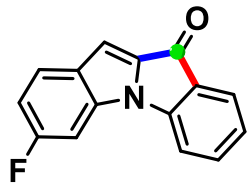
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3l** (43.4 mg, 87% yield). Yellow solid. M.p. 167-169 °C. (160.1-161.2 °C.)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.0 Hz, 1H), 7.43 - 7.38 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.75 (s, 1H), 6.68 (dd, *J* = 8.8, 2.2 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.7, 160.9, 144.9, 135.5, 135.2, 134.9, 129.7, 126.7, 125.6, 124.9, 123.7, 112.1, 111.0, 108.6, 94.4, 55.6.

3-Methyl-10*H*-indolo[1,2-a]indol-10-one (3m):



The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3m** (38.2 mg, 82% yield). Yellow solid. M.p. 178-179 °C. (174.0-174.3 °C.)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.2 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 13.3 Hz, 1H), 7.11 - 7.04 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.4, 145.4, 138.8, 135.4, 135.2, 134.8, 130.5, 129.6, 125.0, 124.5, 123.9, 123.7, 111.3, 111.3, 108.1, 22.3.

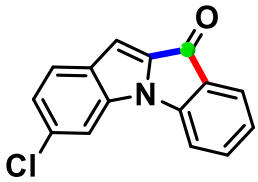
3-Fluoro-10*H*-indolo[1,2-*a*]indol-10-one (3n):



The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3n** (28.0 mg, 59% yield). Yellow solid. M.p. 218-220 °C. (203.9-204.9 °C.)[2]. ^{1}H NMR (400

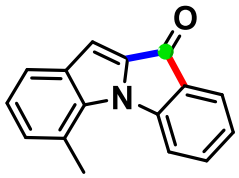
MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.60 (dd, *J* = 8.8, 5.4 Hz, 1H), 7.54 (td, *J* = 7.7, 1.3 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.20 (dd, *J* = 9.2, 2.2 Hz, 1H), 7.15 - 7.10 (m, 2H), 6.91 (td, *J* = 9.1, 2.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.0, 163.3 (d, J_{C-F} = 247.38 Hz), 145.0, 136.6 (d, J_{C-F} = 3.71 Hz), 135.5, 134.4 (d, J_{C-F} = 12.55 Hz), 129.4, 129.1, 126.2 (d, J_{C-F} = 10.54 Hz), 125.3, 124.3, 111.3, 111.1 (d, J_{C-F} = 24.99 Hz), 108.0, 98.1 (d, J_{C-F} = 27.33 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.3.

3-Chloro-10*H*-indolo[1,2-a]indol-10-one (3o):



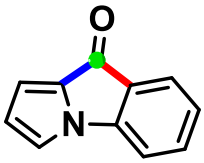
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3o** (25.3 mg, 50% yield). Yellow solid. M.p. 227-229 °C. (216.8-217.1 °C.)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.2 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.44 (s, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.09 - 7.05 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.1, 144.9, 136.2, 135.56, 134.2, 134.1, 131.0, 129.2, 125.7, 125.3, 124.3, 122.8, 111.4, 111.3, 107.6.

4-Methyl-10*H*-indolo[1,2-a]indol-10-one (3p):[4]



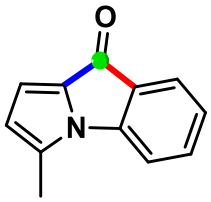
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3p** (33.1 mg, 71% yield). Orange solid. M.p. 196-198 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.46 - 7.43 (m, 2H), 7.17 - 7.13 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 2.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.6, 146.7, 137.5, 135.8, 135.5, 133.7, 131.1, 129.7, 125.1, 123.8, 123.0, 122.5, 121.1, 113.4, 108.9.

9*H*-pyrrolo[1,2-a]indol-9-one (3q):[5]



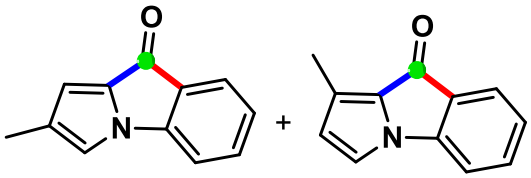
The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3q** (21.6mg, 64% yield). Yellow solid. M.p. 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.11 - 7.05 (m, 2H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.74 (d, *J* = 3.8 Hz, 1H), 6.29 - 6.24 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.6, 143.7, 134.1, 131.9, 130.2, 125.4, 124.4, 119.5, 115.9, 113.9, 110.3.

3-Methyl-9*H*-pyrrolo[1,2-a]indol-9-one (3r):[5]



The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3r** (27.8 mg, 76% yield). Yellow solid. M.p. 138-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.71 - 6.68 (m, 1H), 5.97 (d, *J* = 3.6 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 143.9, 133.9, 133.8, 131.0, 125.0, 124.6, 115.4, 114.4, 111.1, 13.4.

1-Methyl-9H-pyrrolo[1,2-a]indol-9-one and 2-Methyl-9*H*-pyrrolo[1,2-a]indol-9-one (3s):[5]



The reaction was performed following the general procedure. Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3s** (25.0 mg, 68% yield). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 1H),

7.51 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.06 - 7.02 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.93 (s, 1H), 6.82 (s, 1H), 6.56 (s, 1H), 6.07 (s, 1H), 2.31 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.8, 179.7, 144.0, 143.3, 133.9, 133.7, 131.7, 130.7, 129.9, 129.4, 129.0, 127.0, 124.9, 124.8, 124.3, 124.2, 119.2, 118.0, 117.3, 114.8, 109.9, 109.8, 12.1, 11.7. HRMS (ESI) m/z calcd for $C12H9NO^+$, $(M+Na)^+$ 206.0576, found 206.0576.

6. References

(1) A. K. Verma, J. Singh and R. C. Larock, Tetrahedron 2009, 65, 8434-8439.

(2) X. Wang, Z. Li, S. Cao and H. Rao, Adv. Syn. Catal. 2016, 358, 13, 2059-2065.

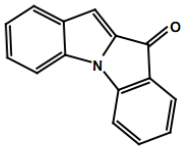
(3) S. Zou, Y. Liu and C. Xi. ACS. Omega, 2019, 4, 20, 18734-18740.

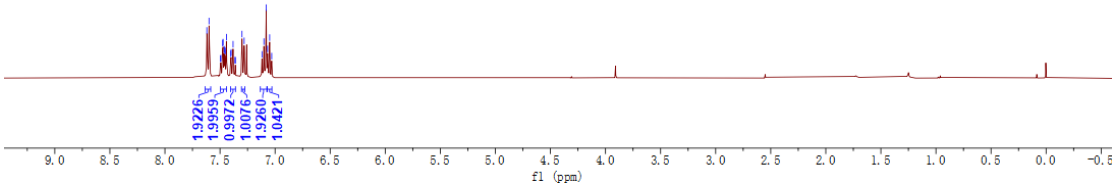
(4) M. Liu, Y. W. Liu, H. Xu and H. X. Dai, Tetrahedron Lett. 2019, 60, 151061.

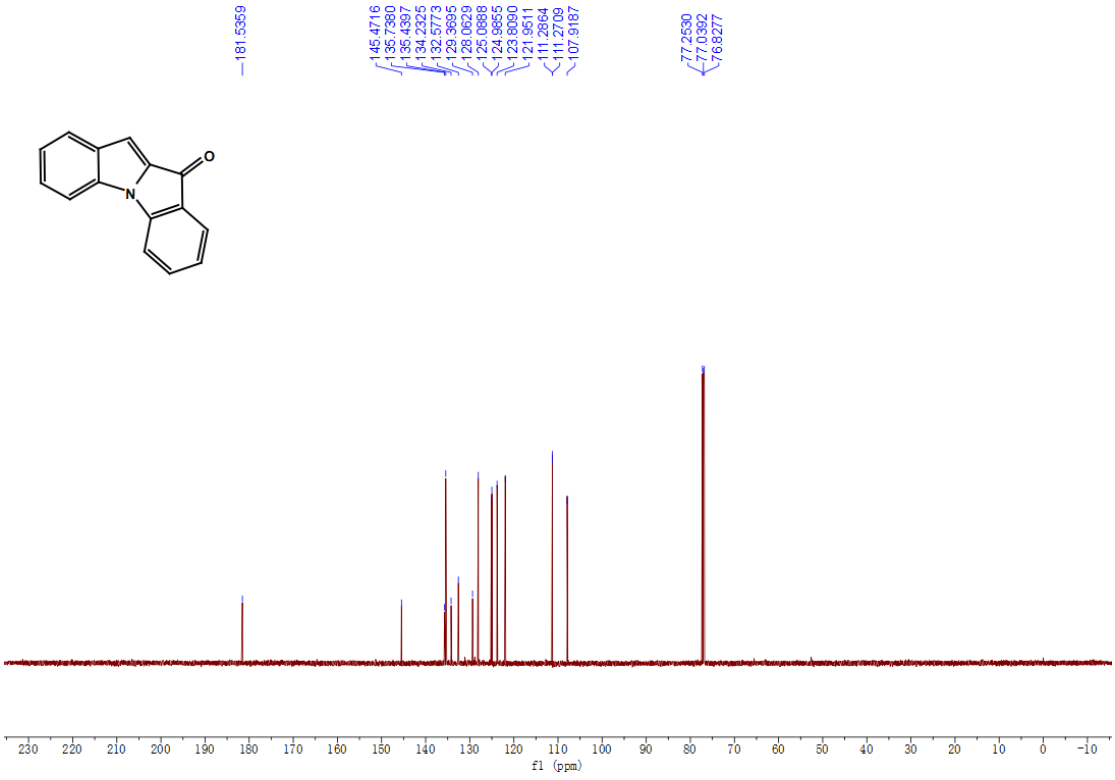
(5) Y. Ramtohul and R. Giacometti, Synlett .2009, 12, 2010-2016.

7. NMR Spectra Copies of Product 3

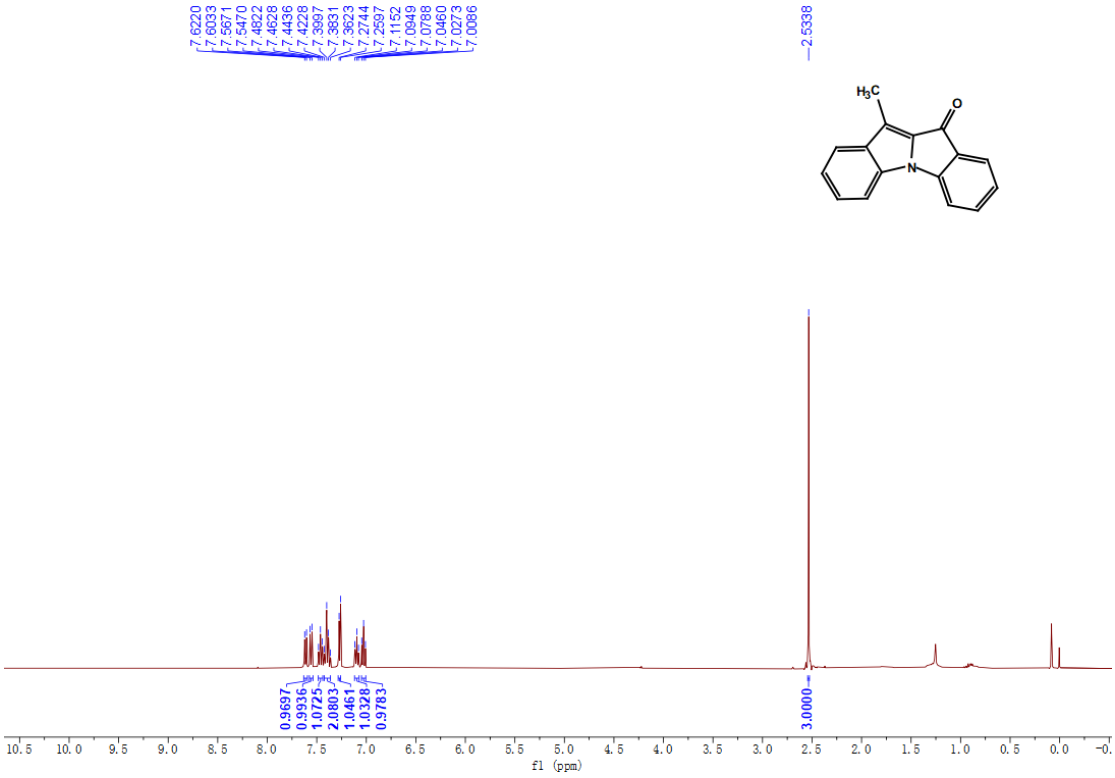
10*H*-indolo[1,2-a]indol-10-one (3a)

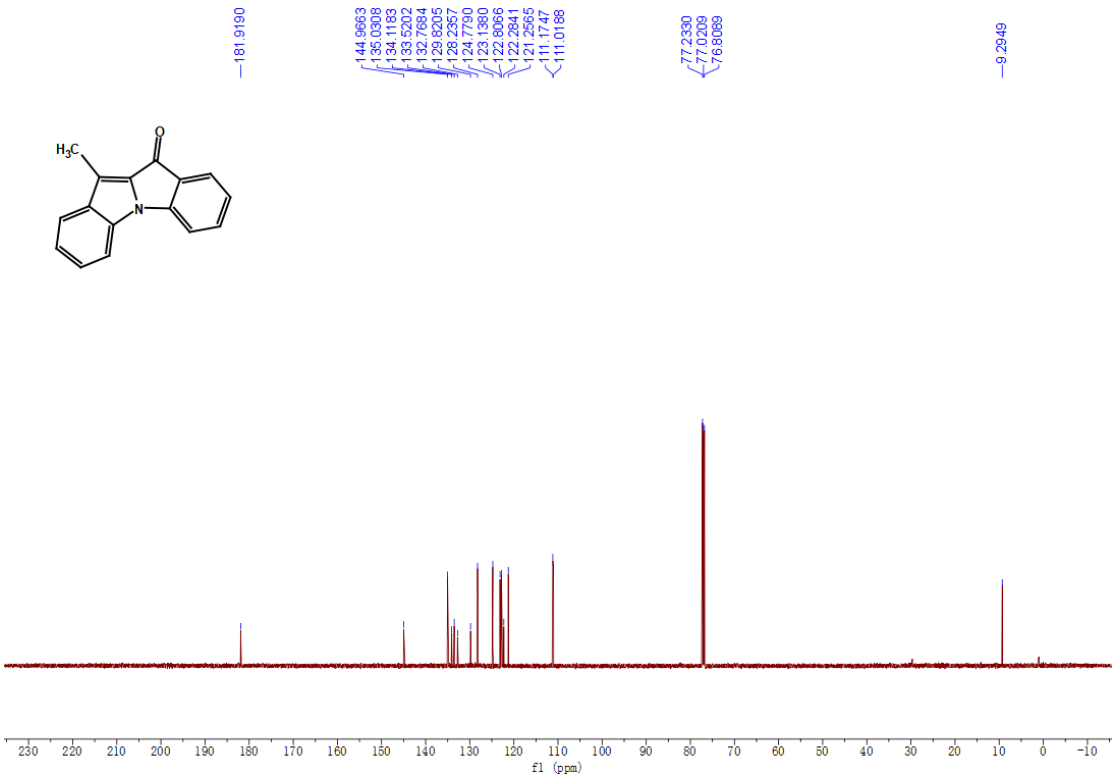




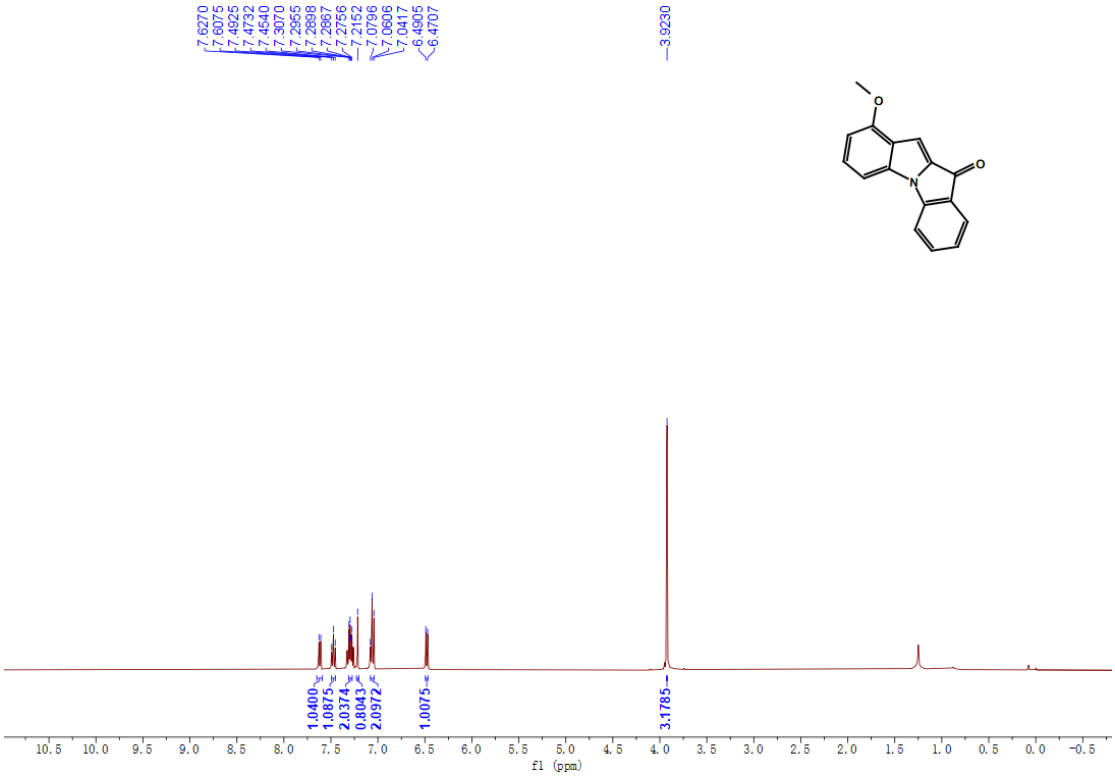


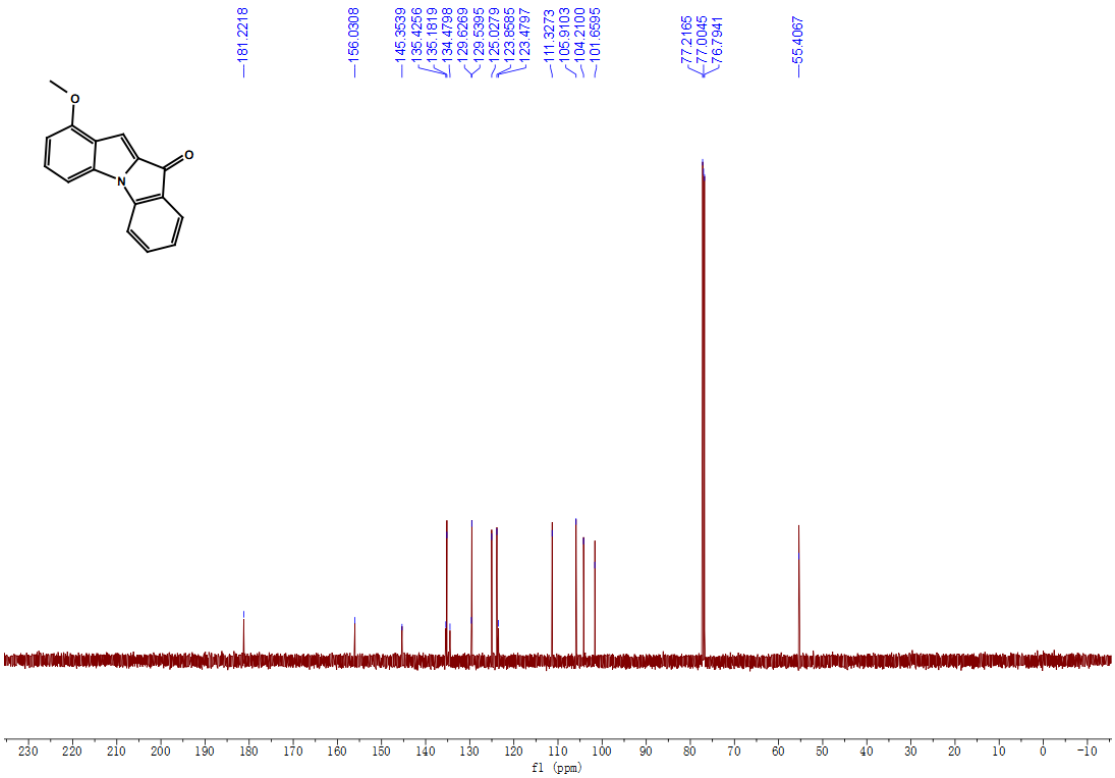
11-Methyl-10*H*-indolo[1,2-a]indol-10-one (3b)



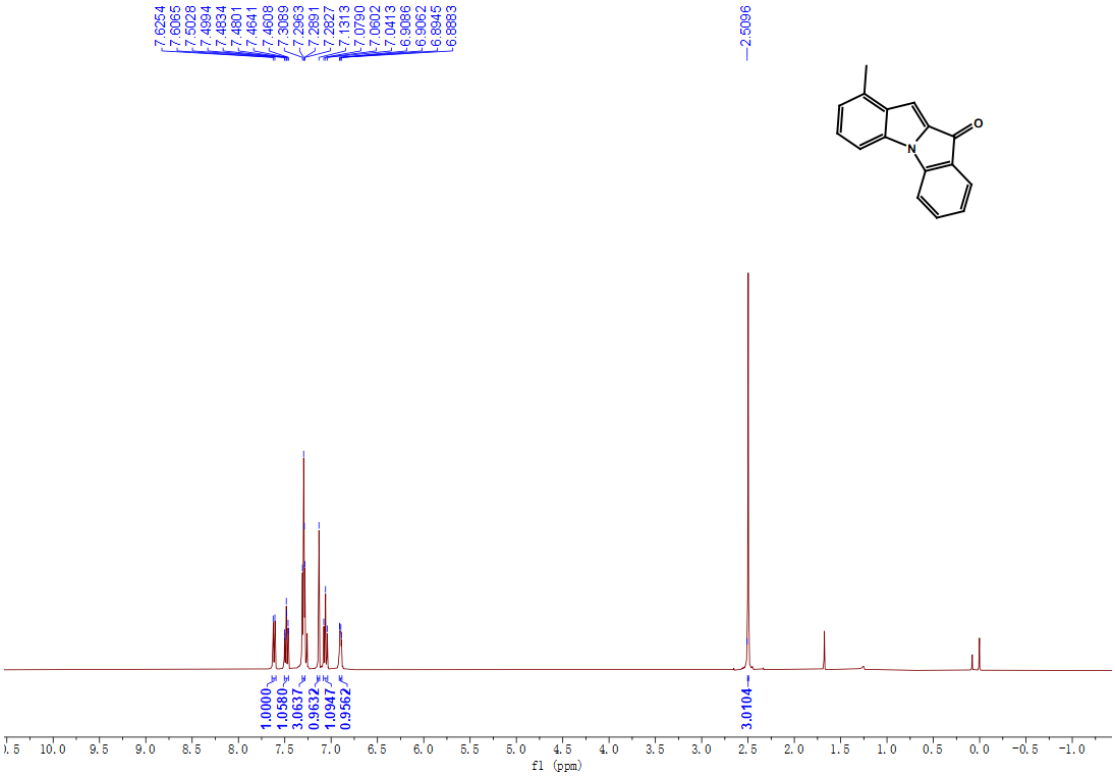


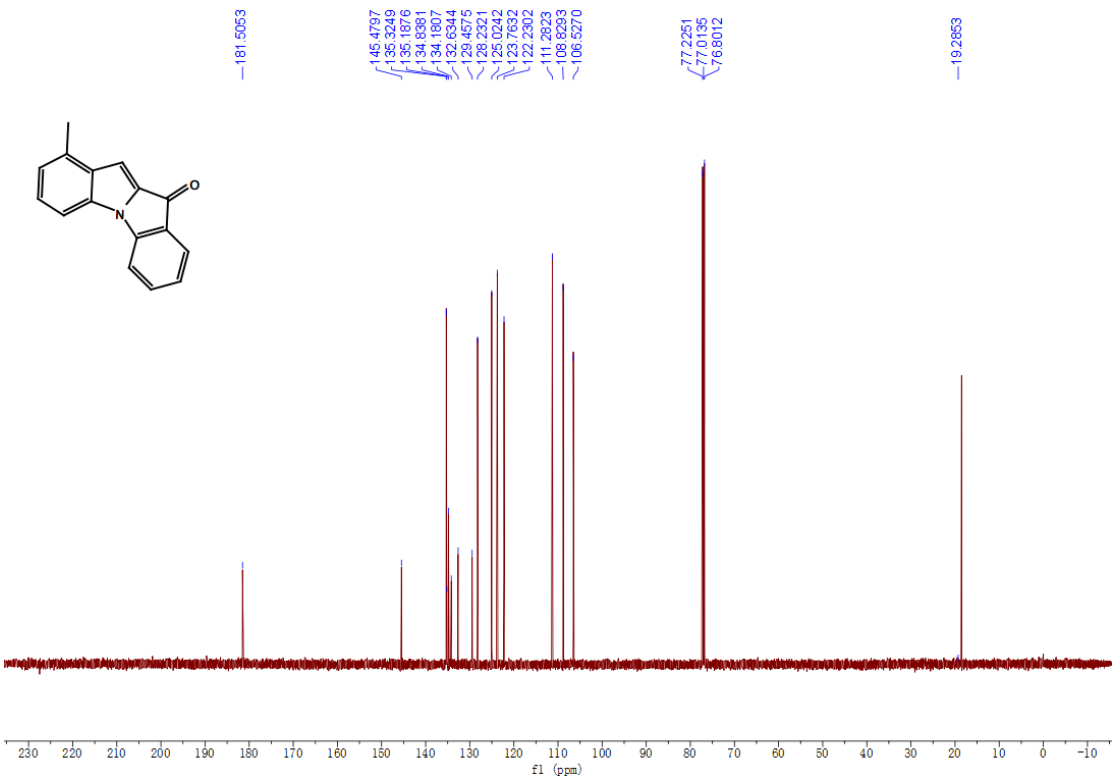
1-Methoxy-10*H*-indolo[1,2-a]indol-10-one (3c)



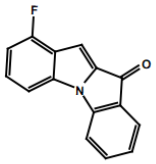


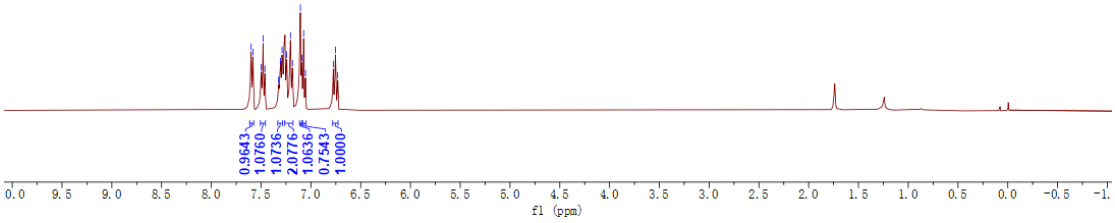
1-Methyl-10*H*-indolo[1,2-a]indol-10-one (3d)

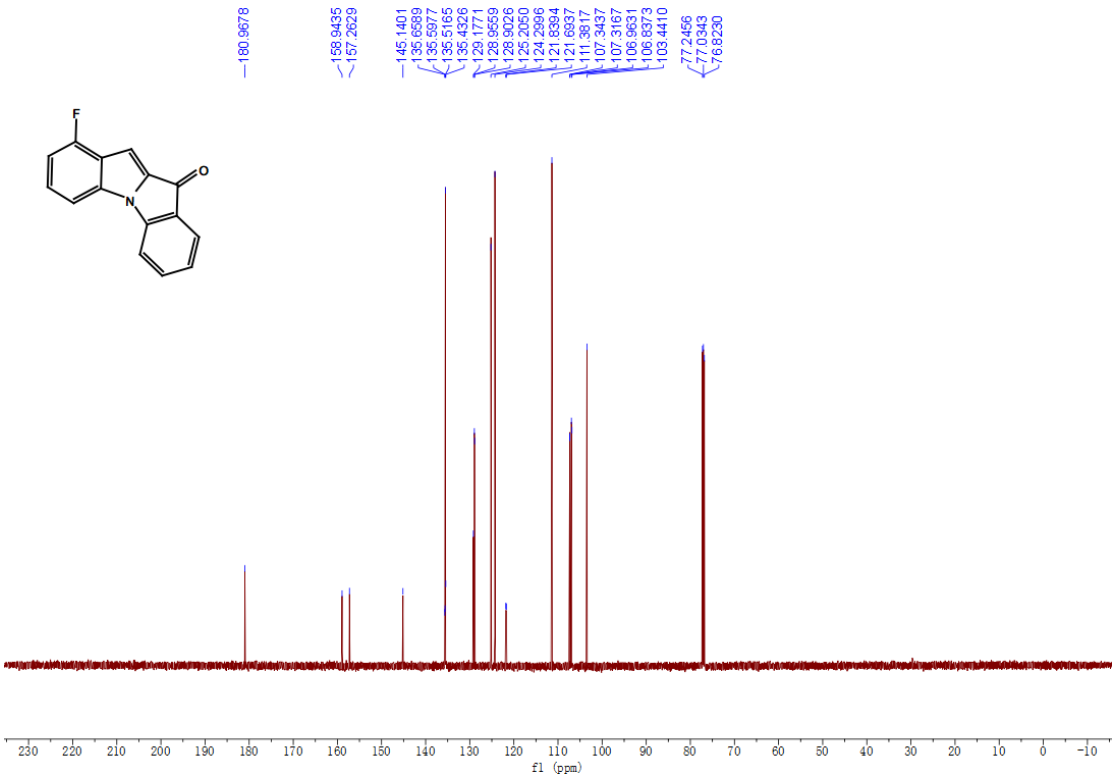


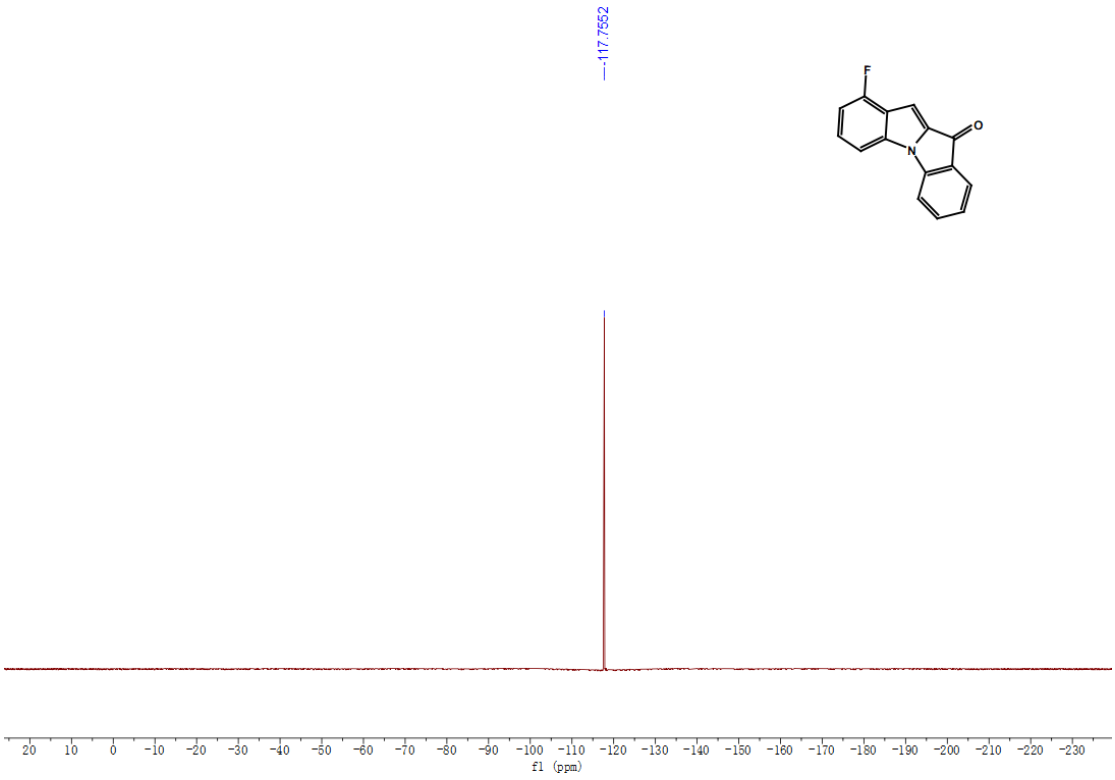


1-Fluoro-10*H*-indolo[1,2-*a*]indol-10-one (3e)

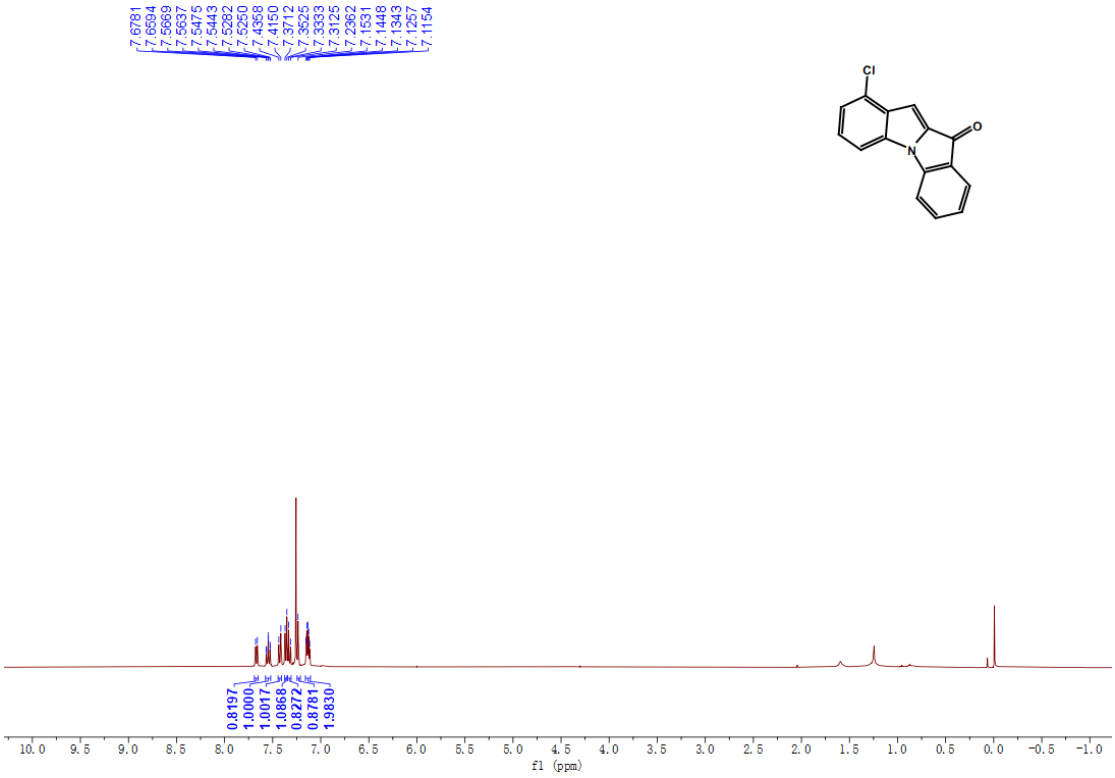


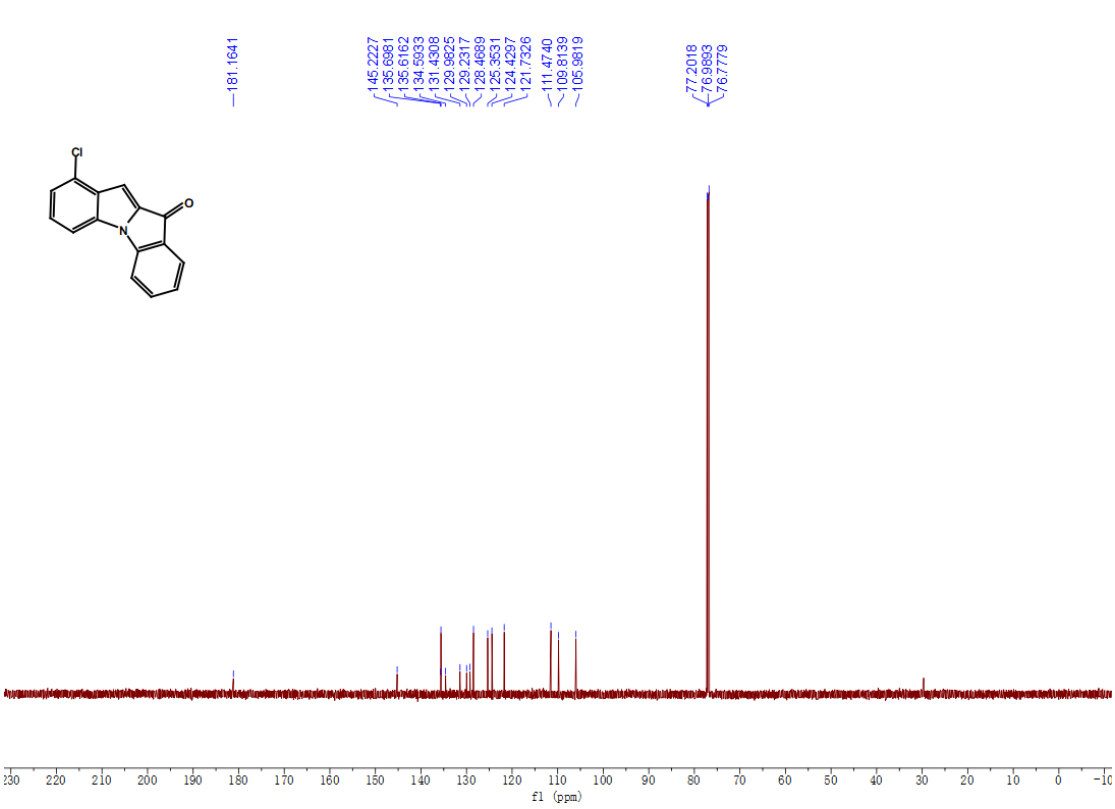




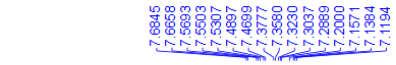

-117.7552
F
O
N
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

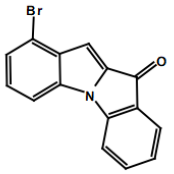
1-Chloro-10*H*-indolo[1,2-a]indol-10-one (3f)

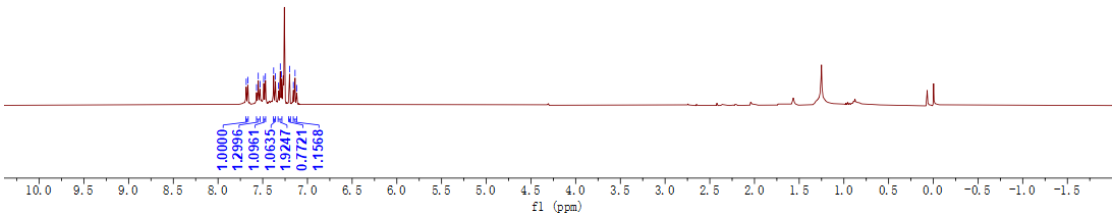


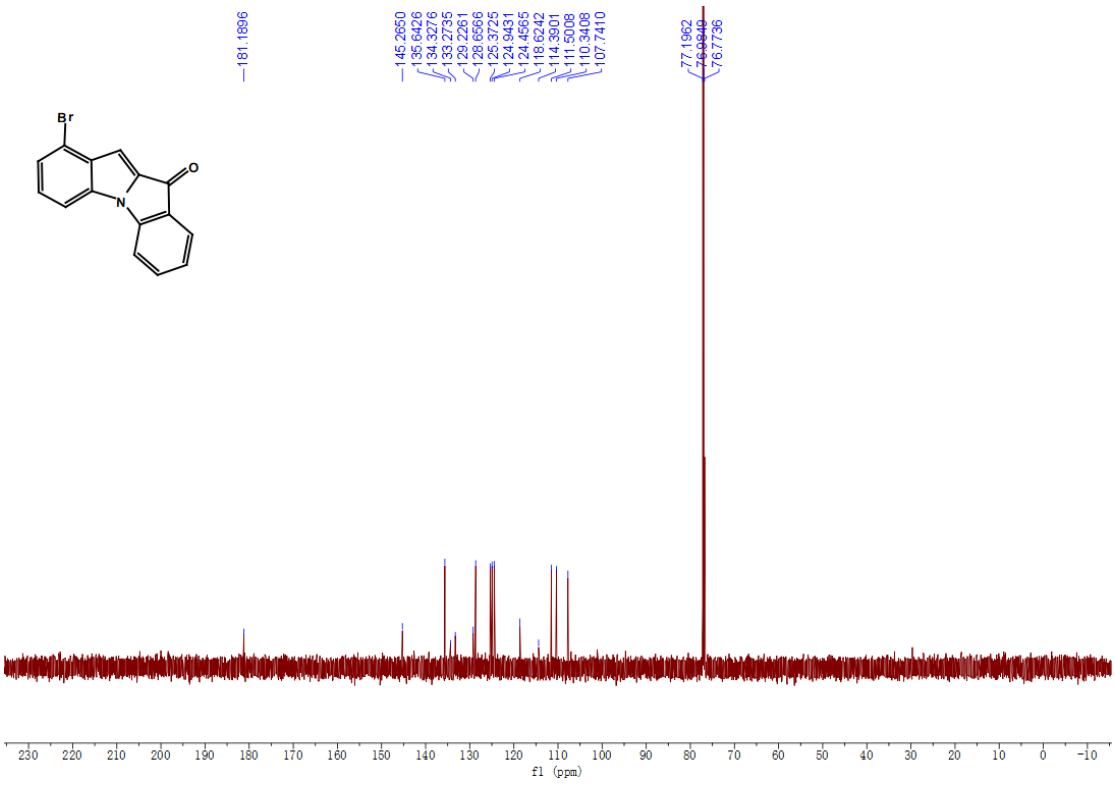


1-Bromo-10*H*-indolo[1,2-a]indol-10-one (3g)

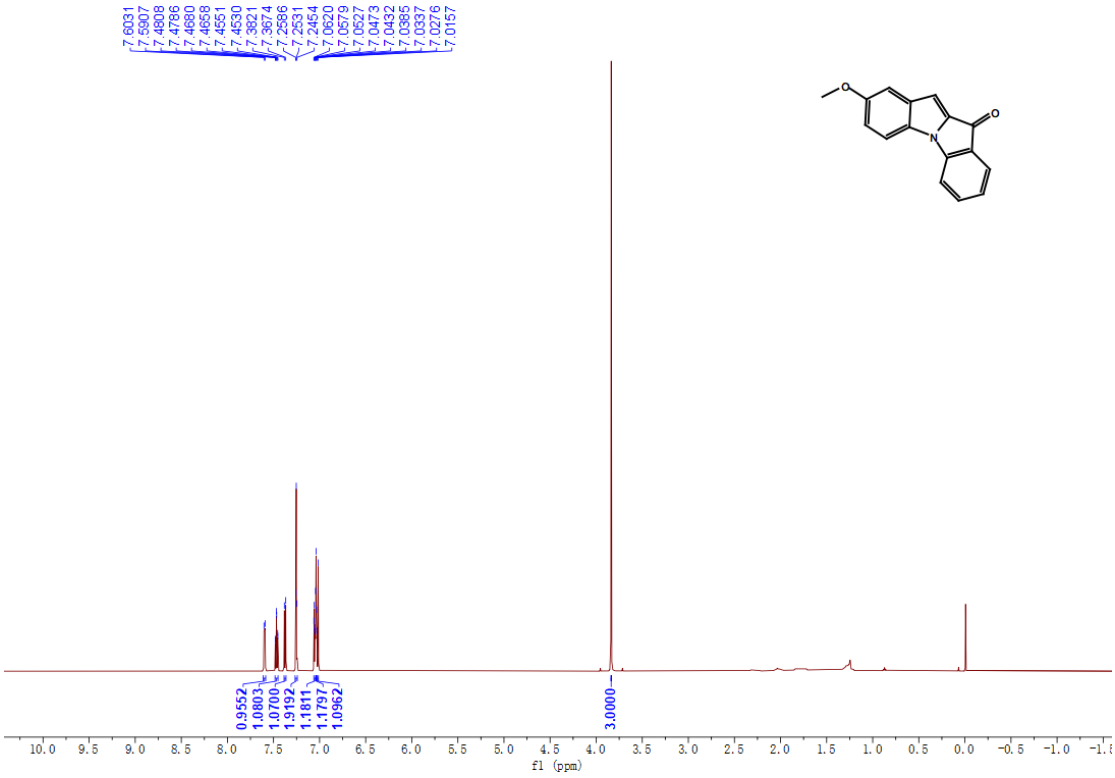


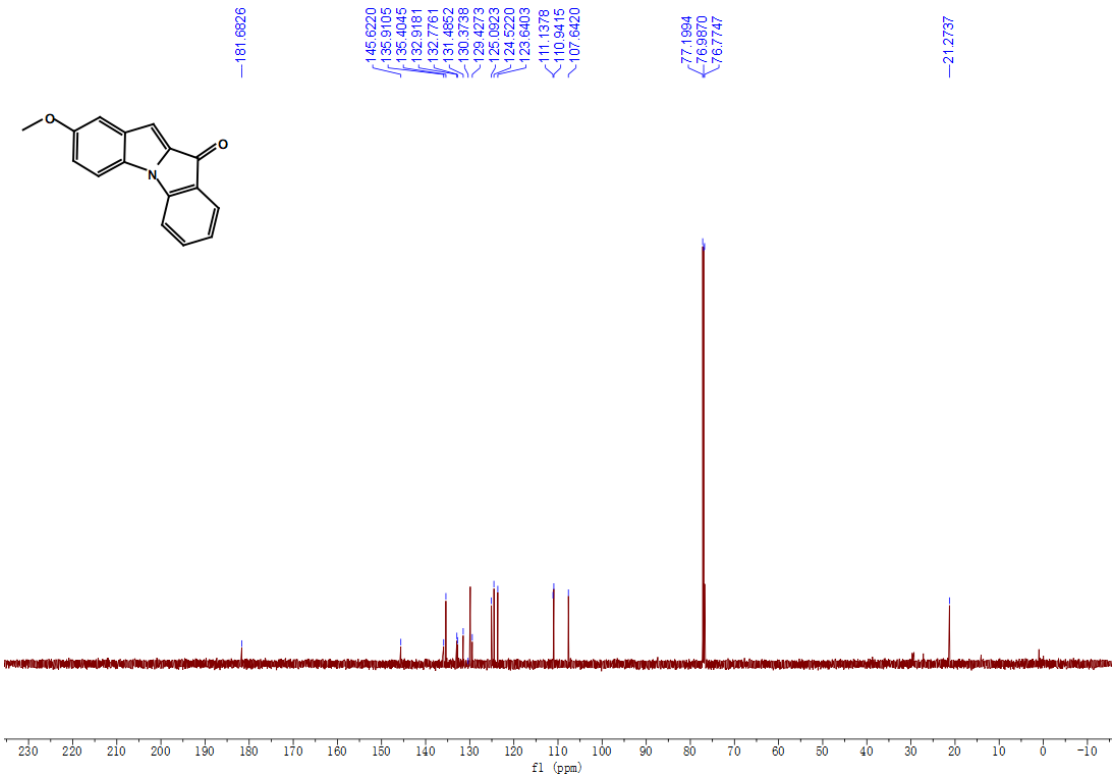




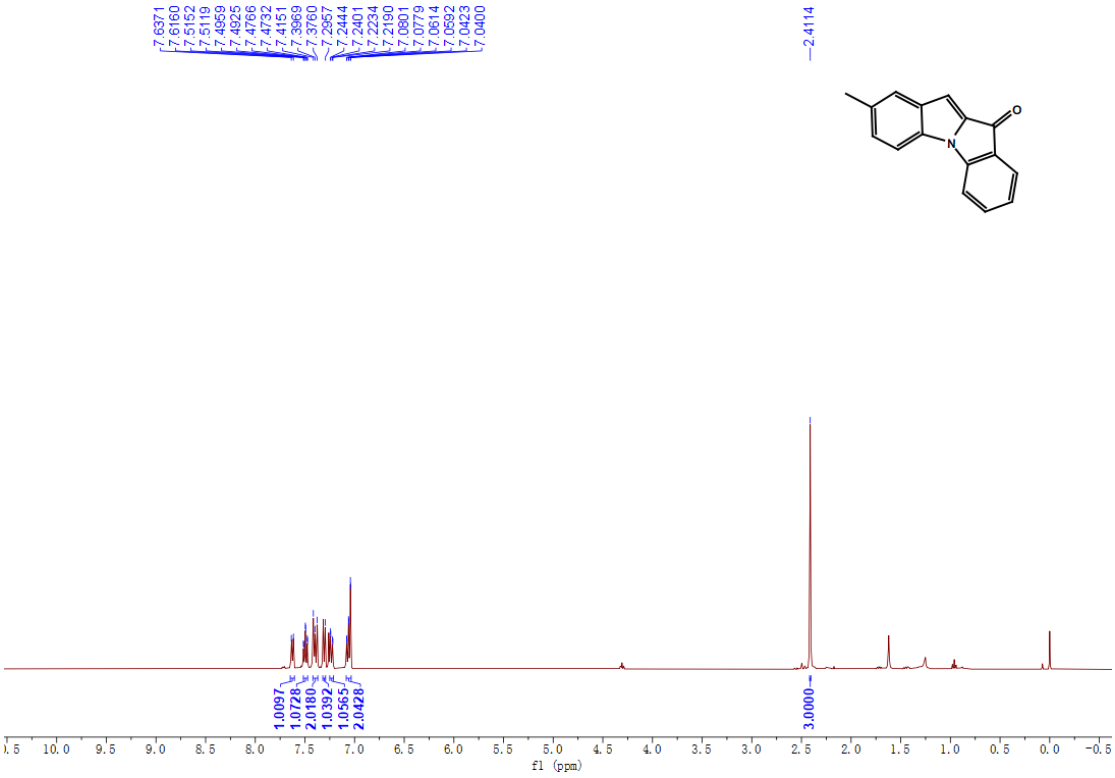


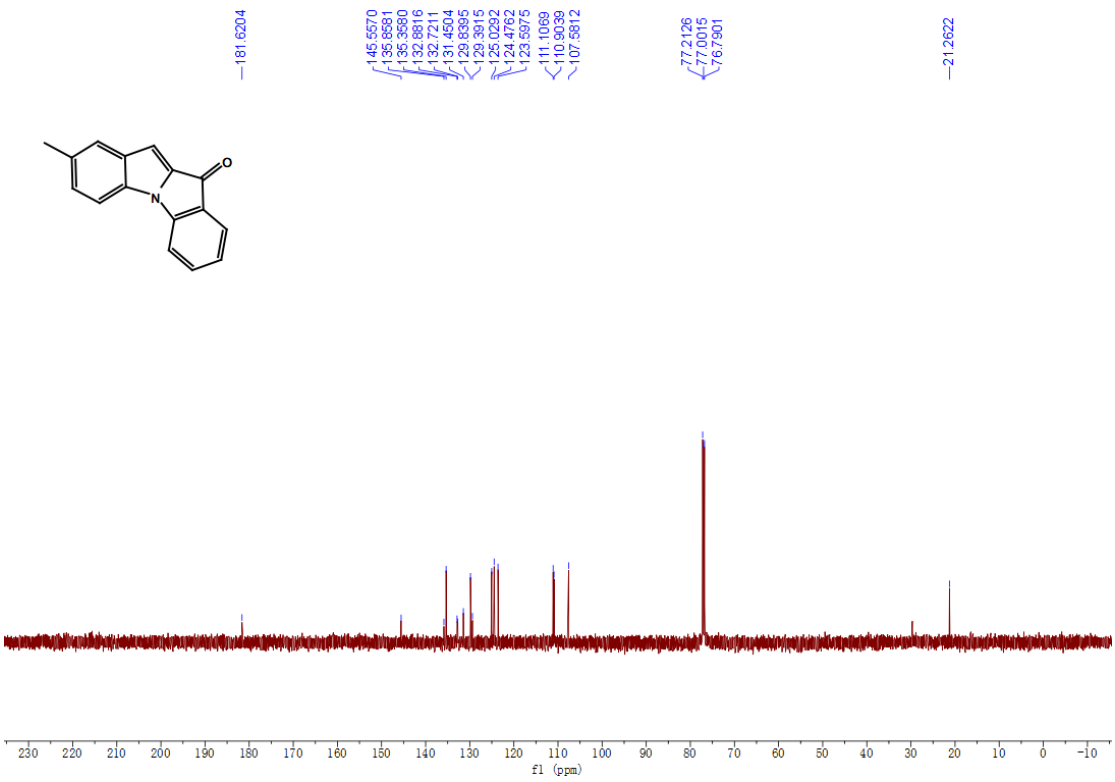
2-Methoxy-10*H*-indolo[1,2-a]indol-10-one (3h)



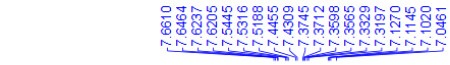


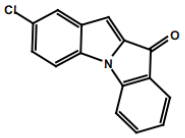
2-Methyl-10*H*-indolo[1,2-a]indol-10-one (3i)

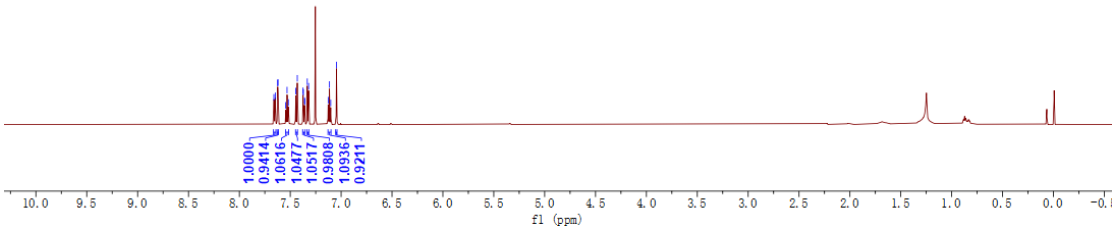


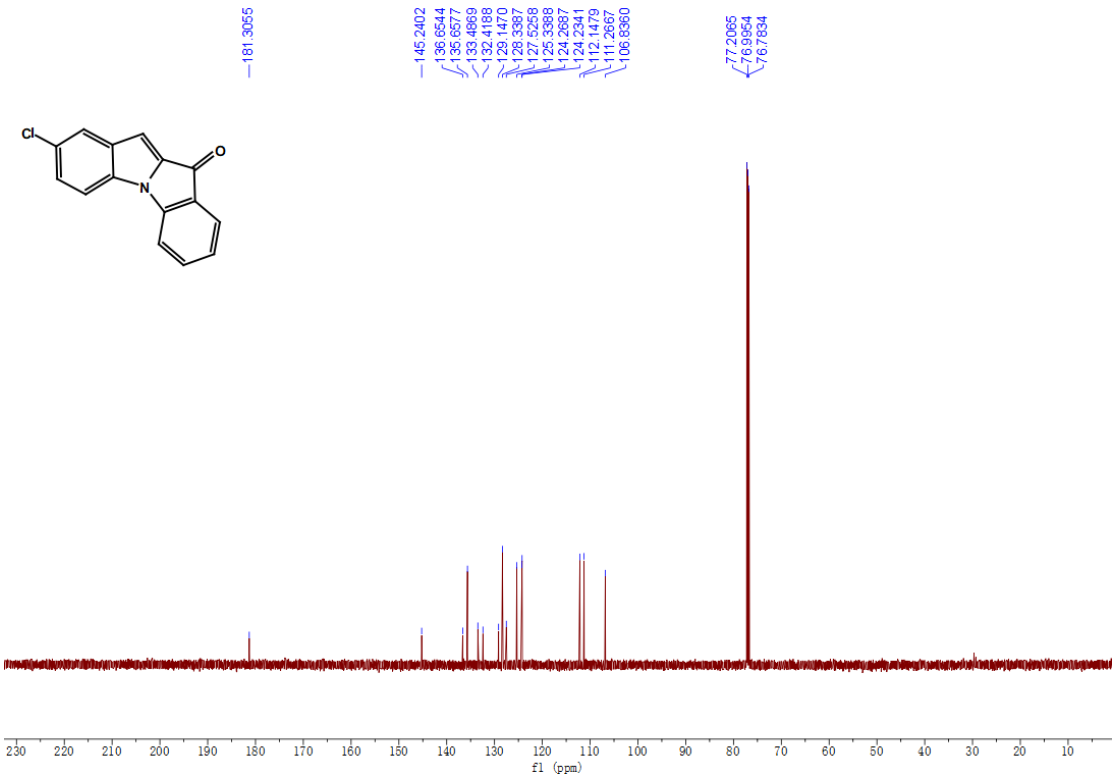


2-Chloro-10*H*-indolo[1,2-a]indol-10-one (3j)

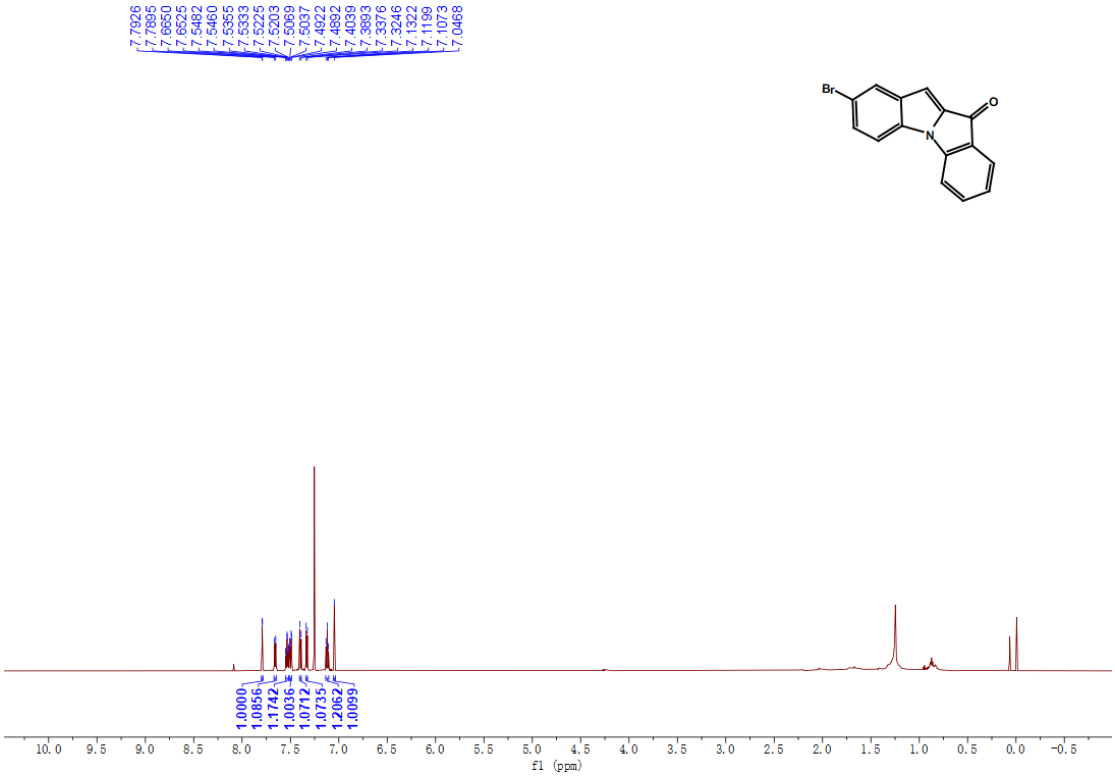


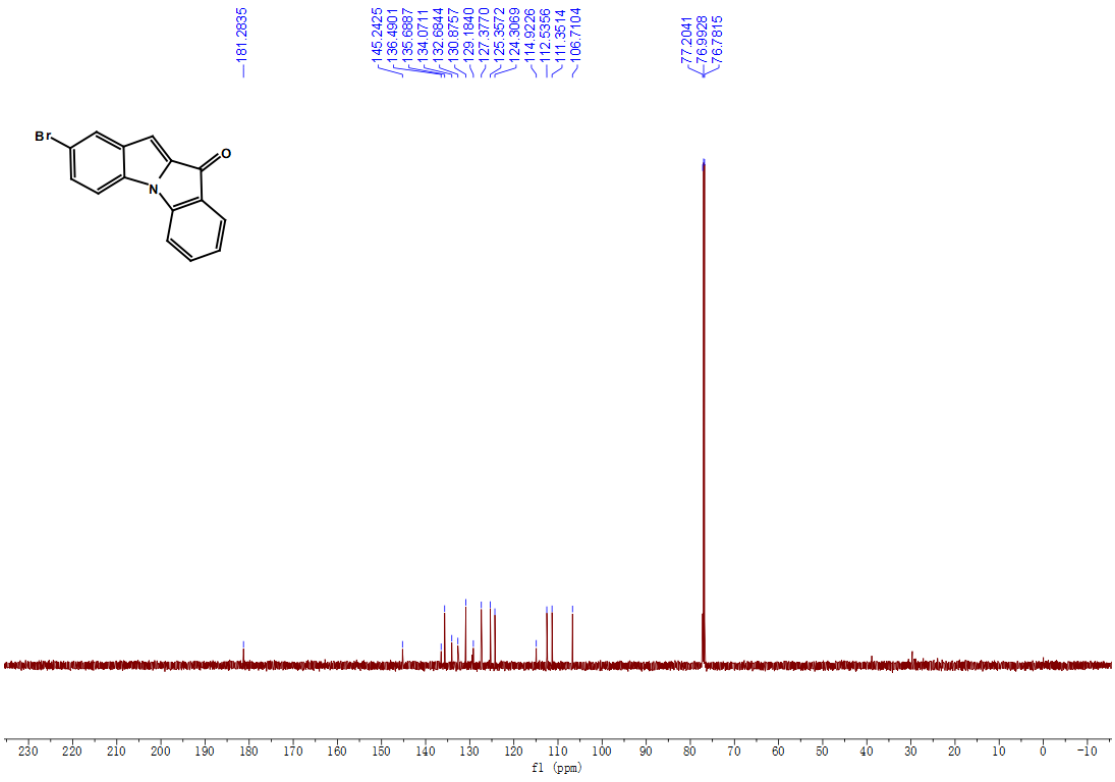




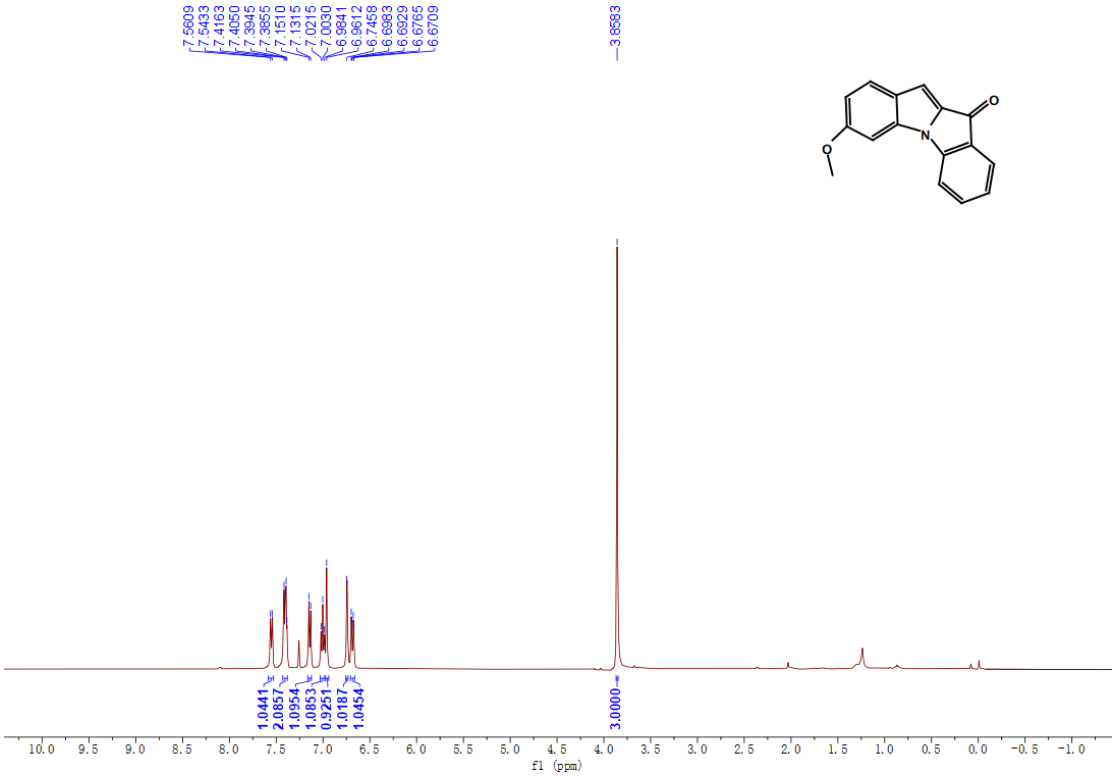


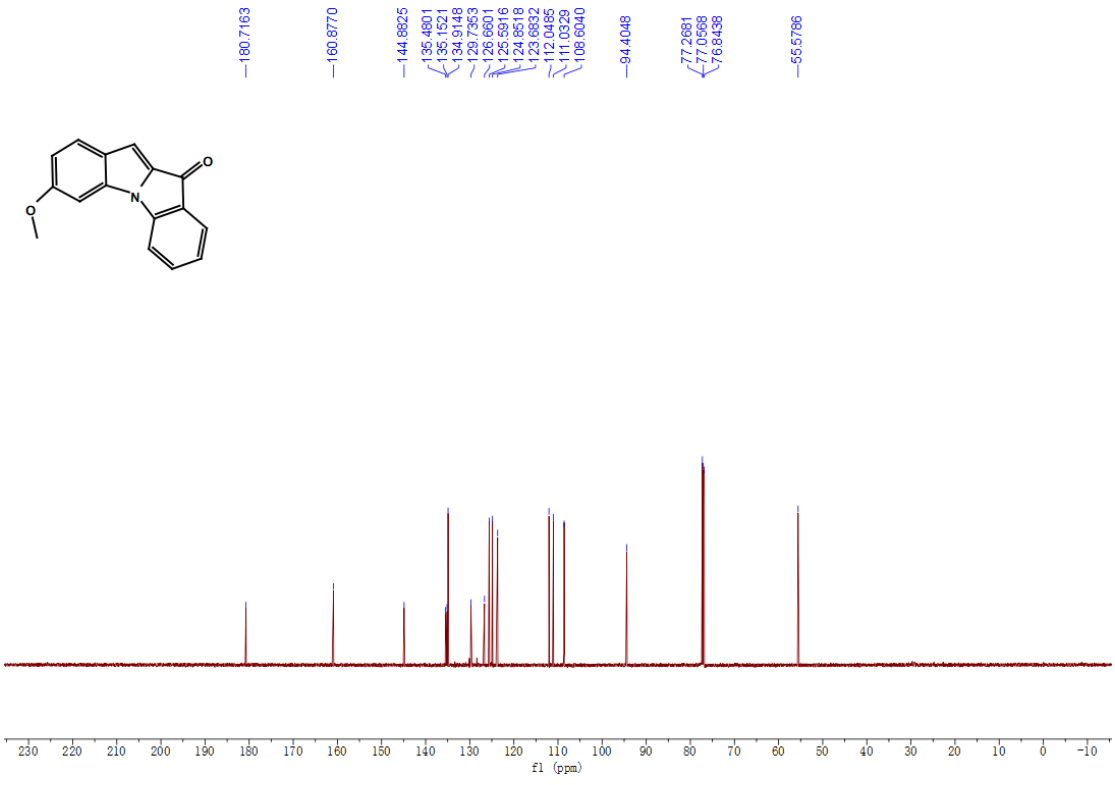
2-Bromo-10*H*-indolo[1,2-a]indol-10-one (3k)



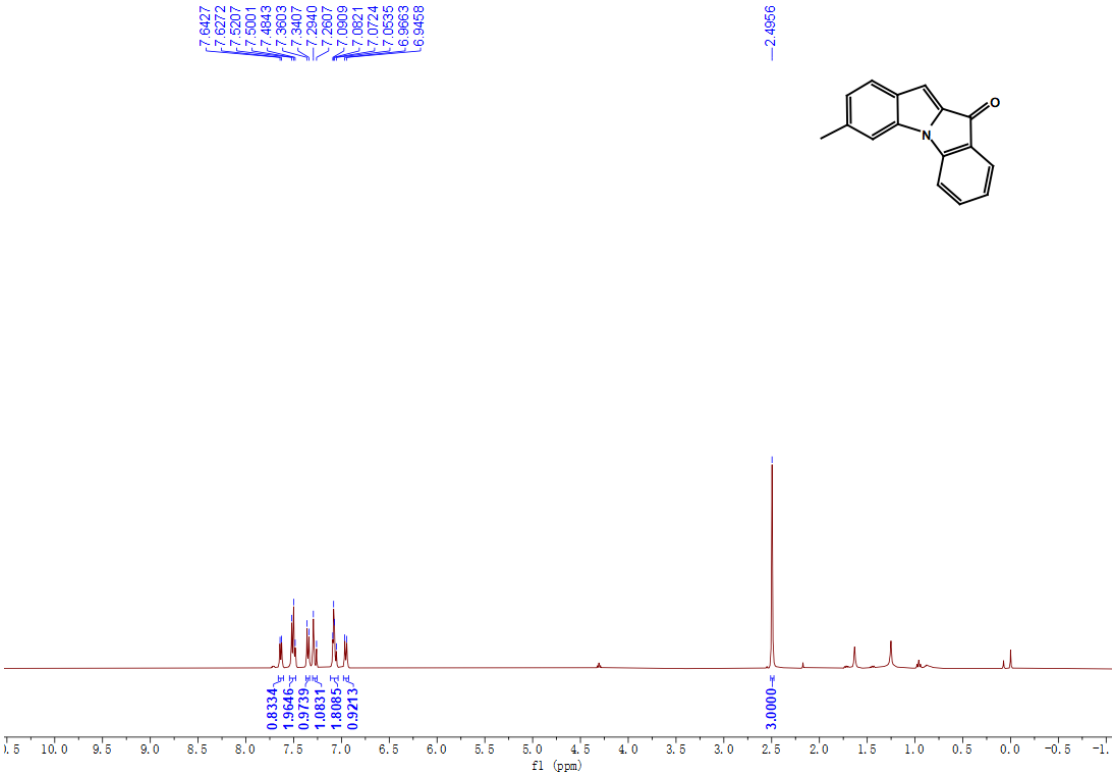


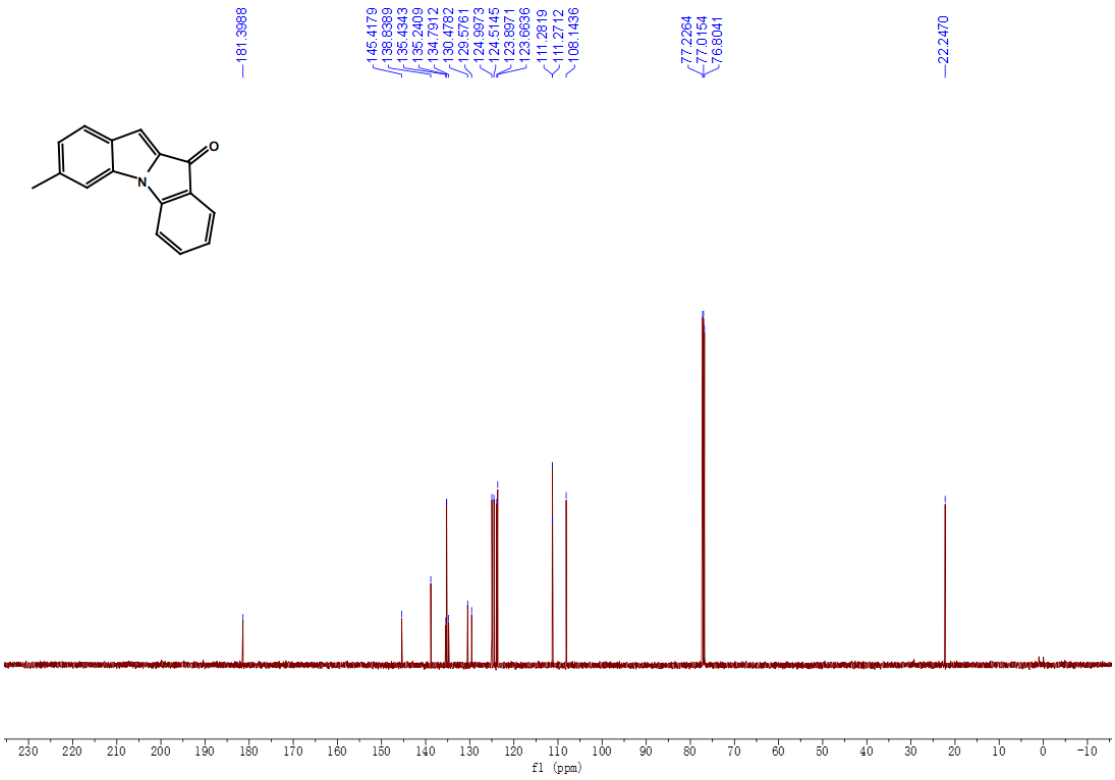
3-Methoxy-10*H*-indolo[1,2-a]indol-10-one (3l)



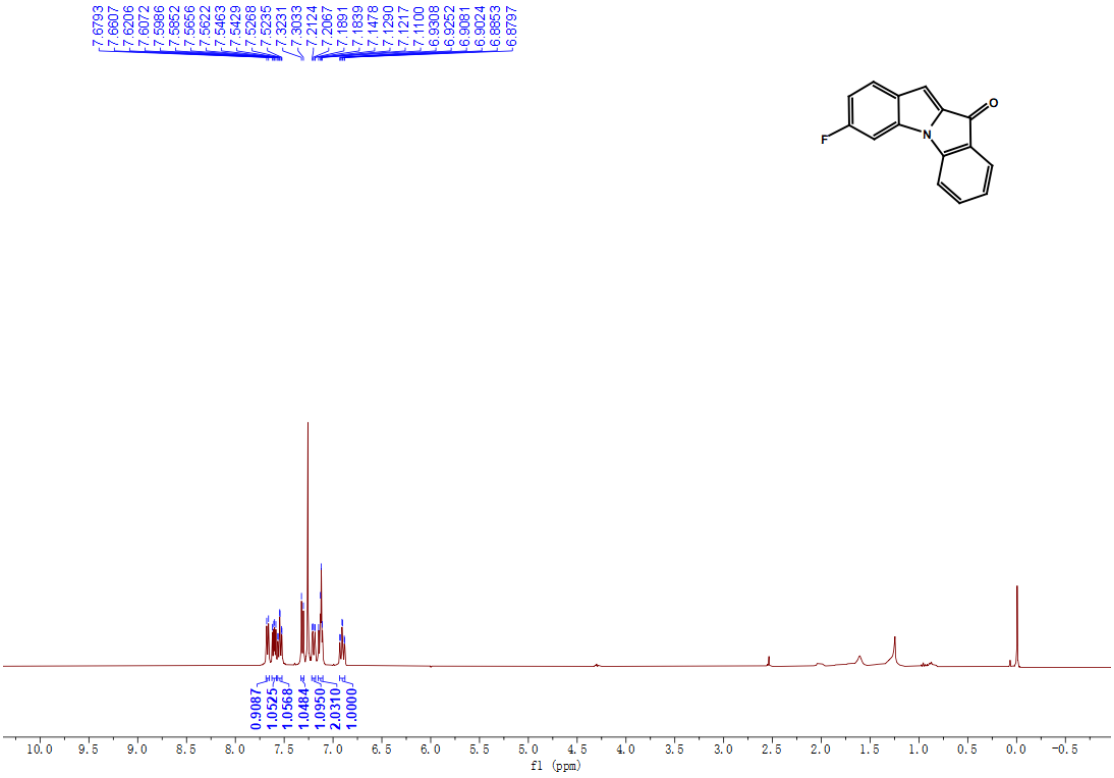


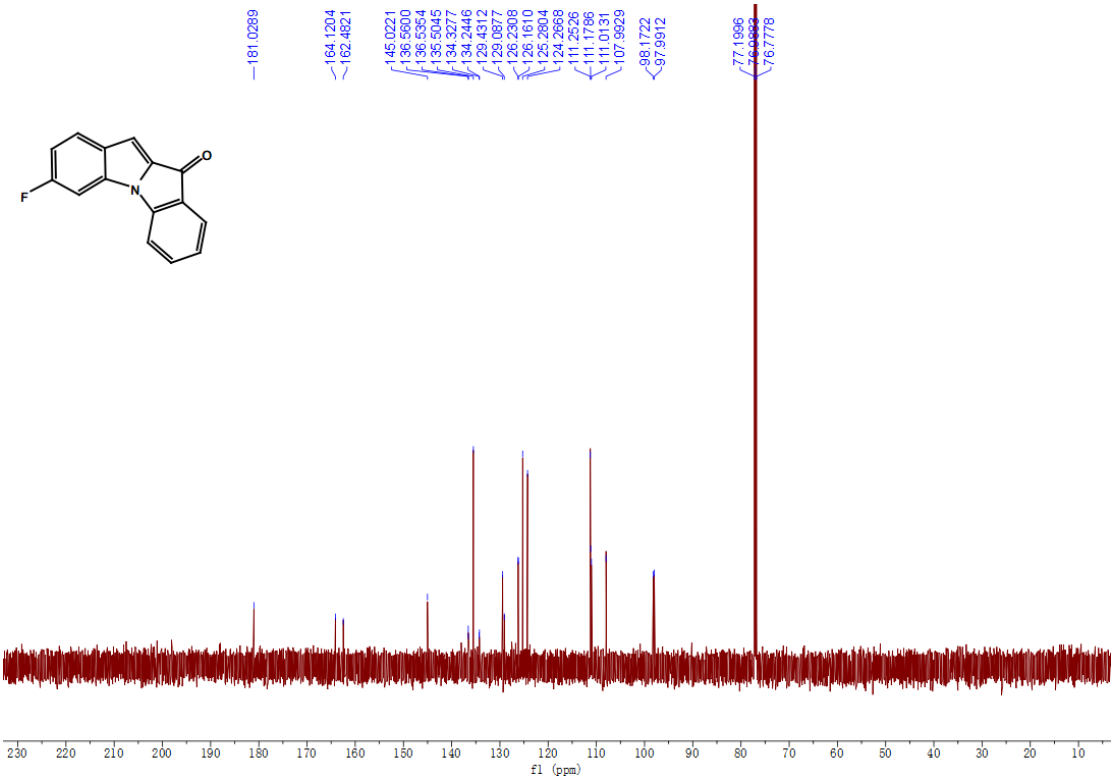
3-Methyl-10*H*-indolo[1,2-a]indol-10-one (3m)

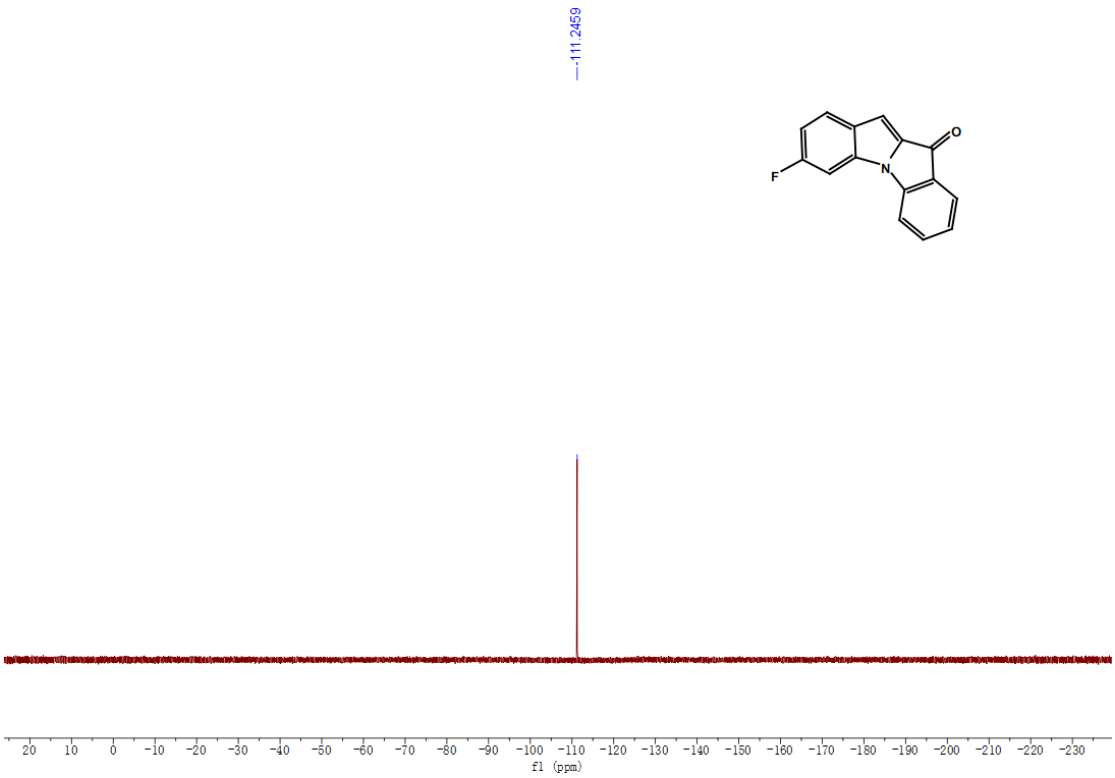




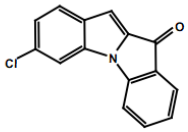
3-Fluoro-10*H*-indolo[1,2-*a*]indol-10-one (3n)

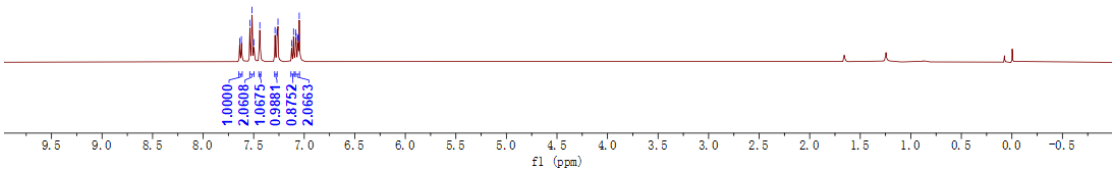


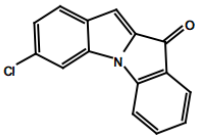


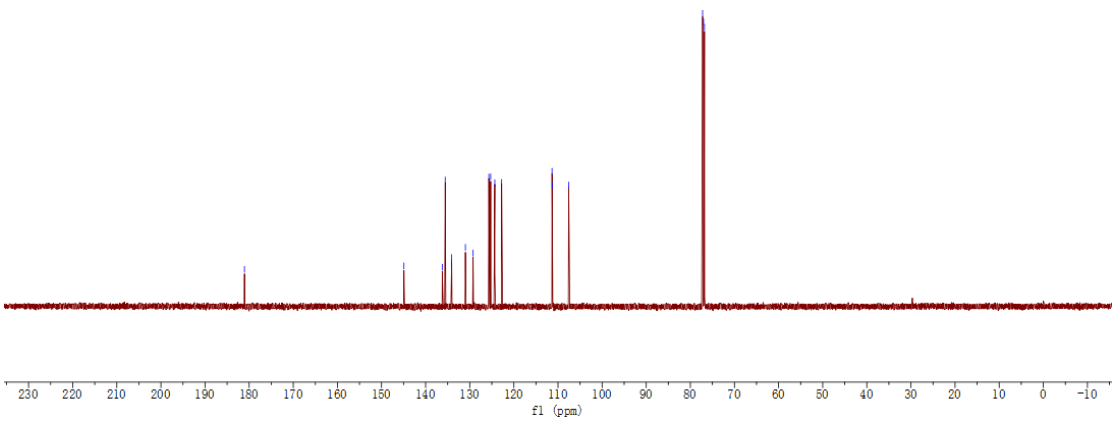

-111.2459
F
N
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

3-Chloro-10*H*-indolo[1,2-a]indol-10-one (3o)

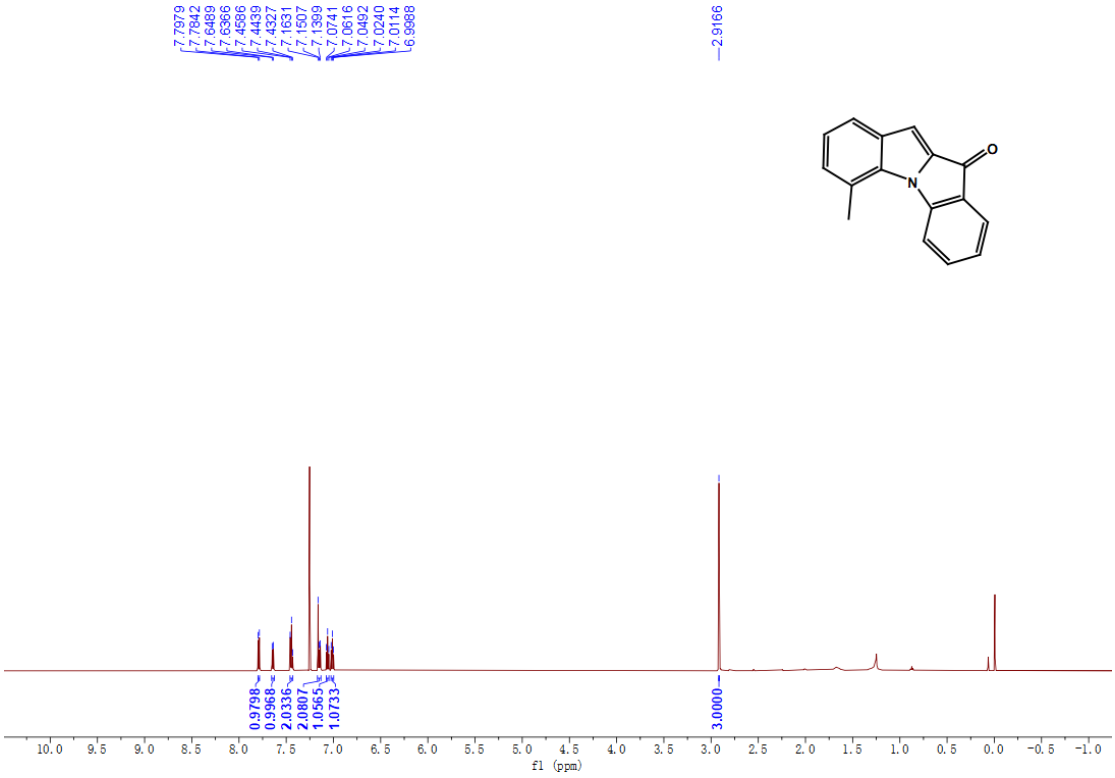


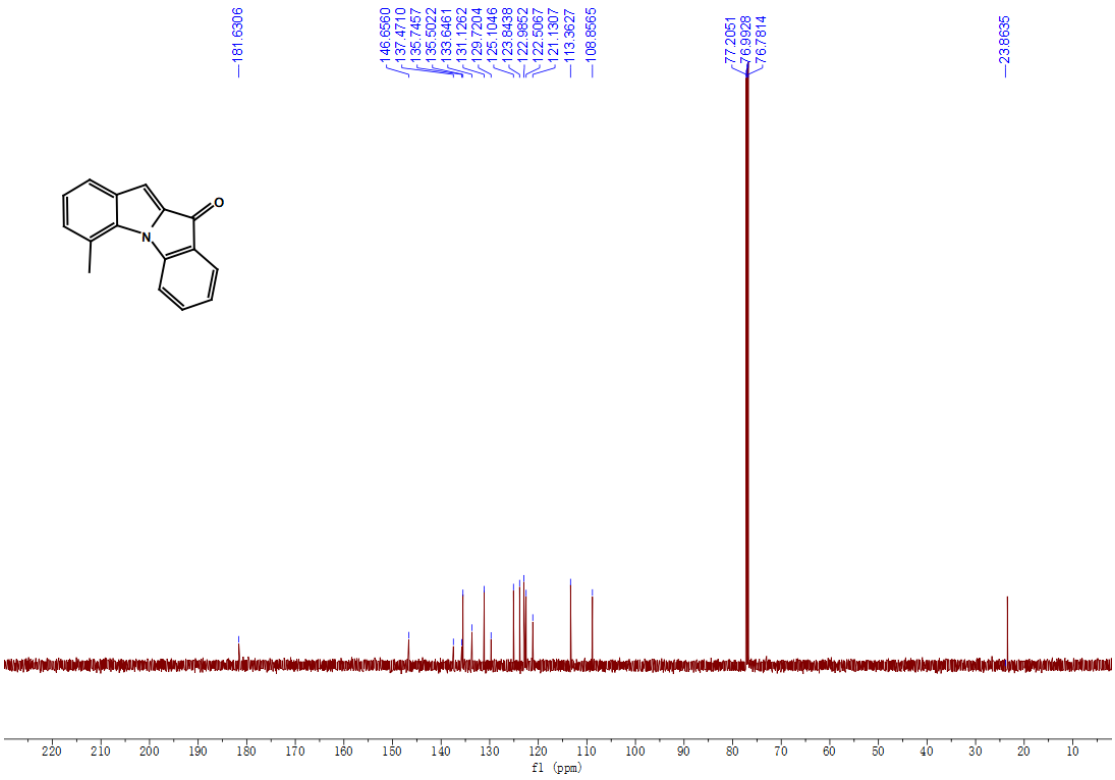




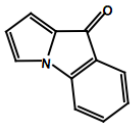


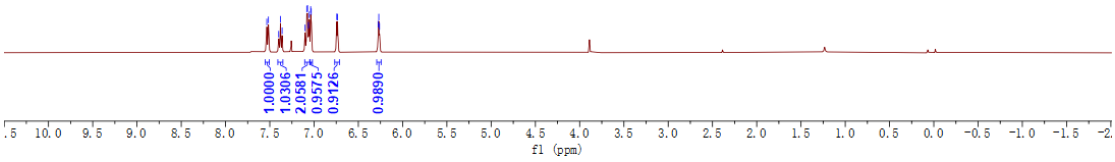
4-Methyl-10*H*-indolo[1,2-a]indol-10-one (3p)

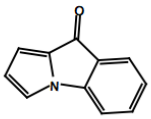


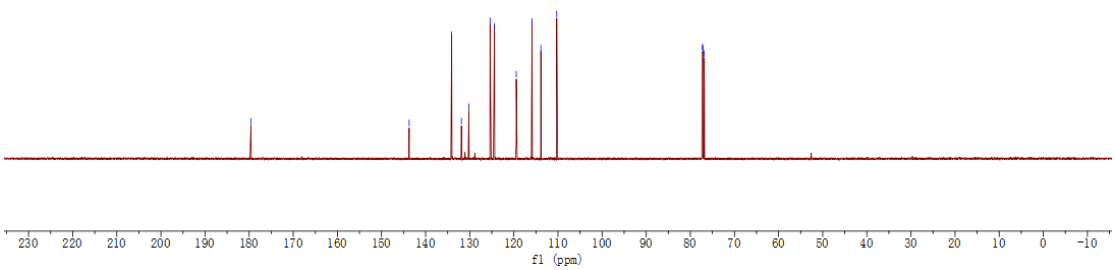


9*H*-pyrrolo[1,2-a]indol-9-one (3q)

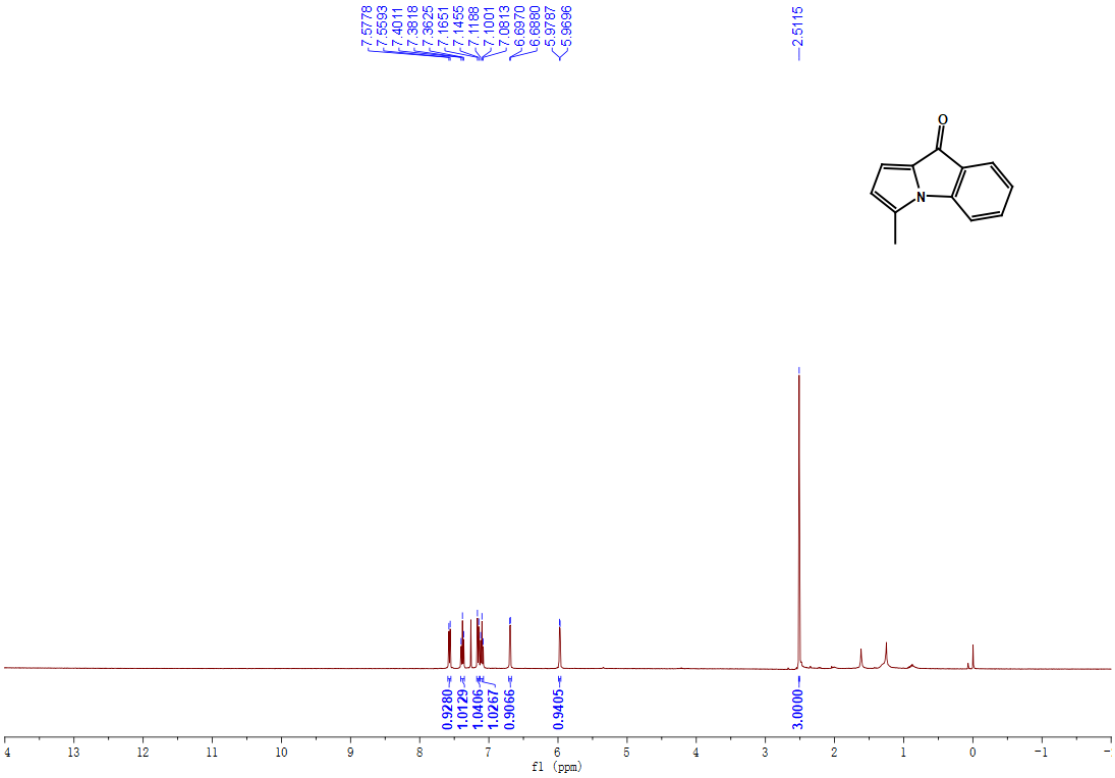


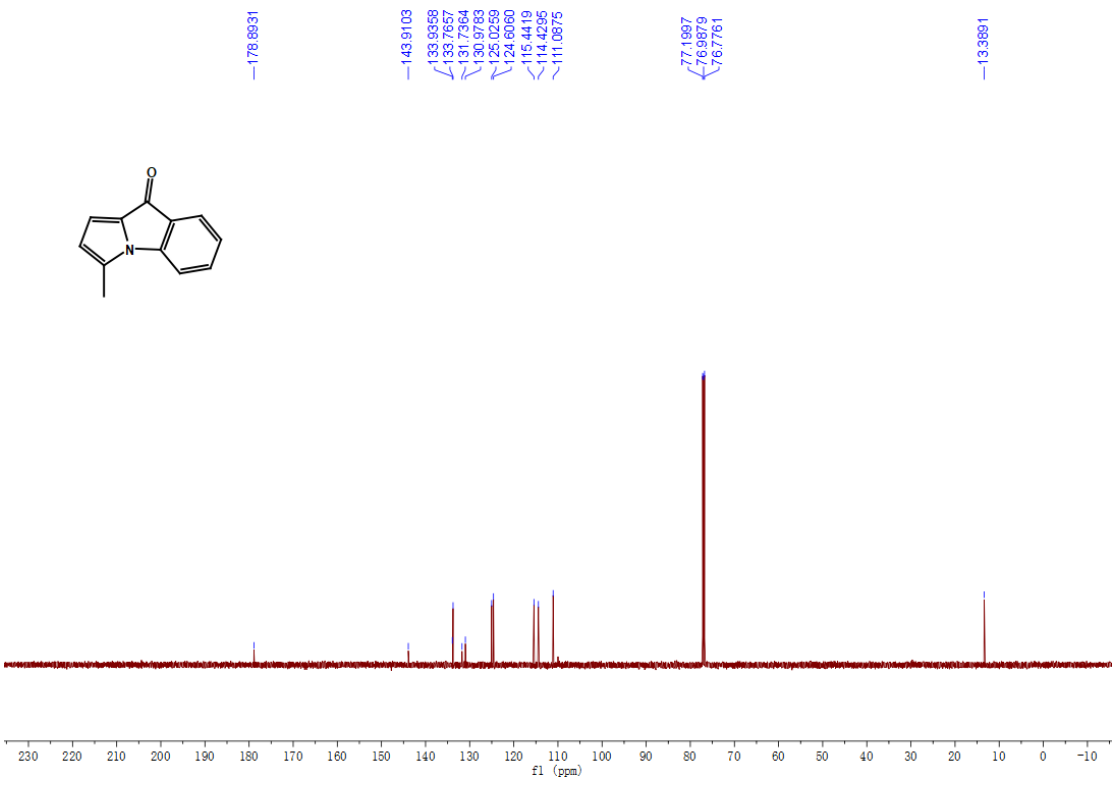




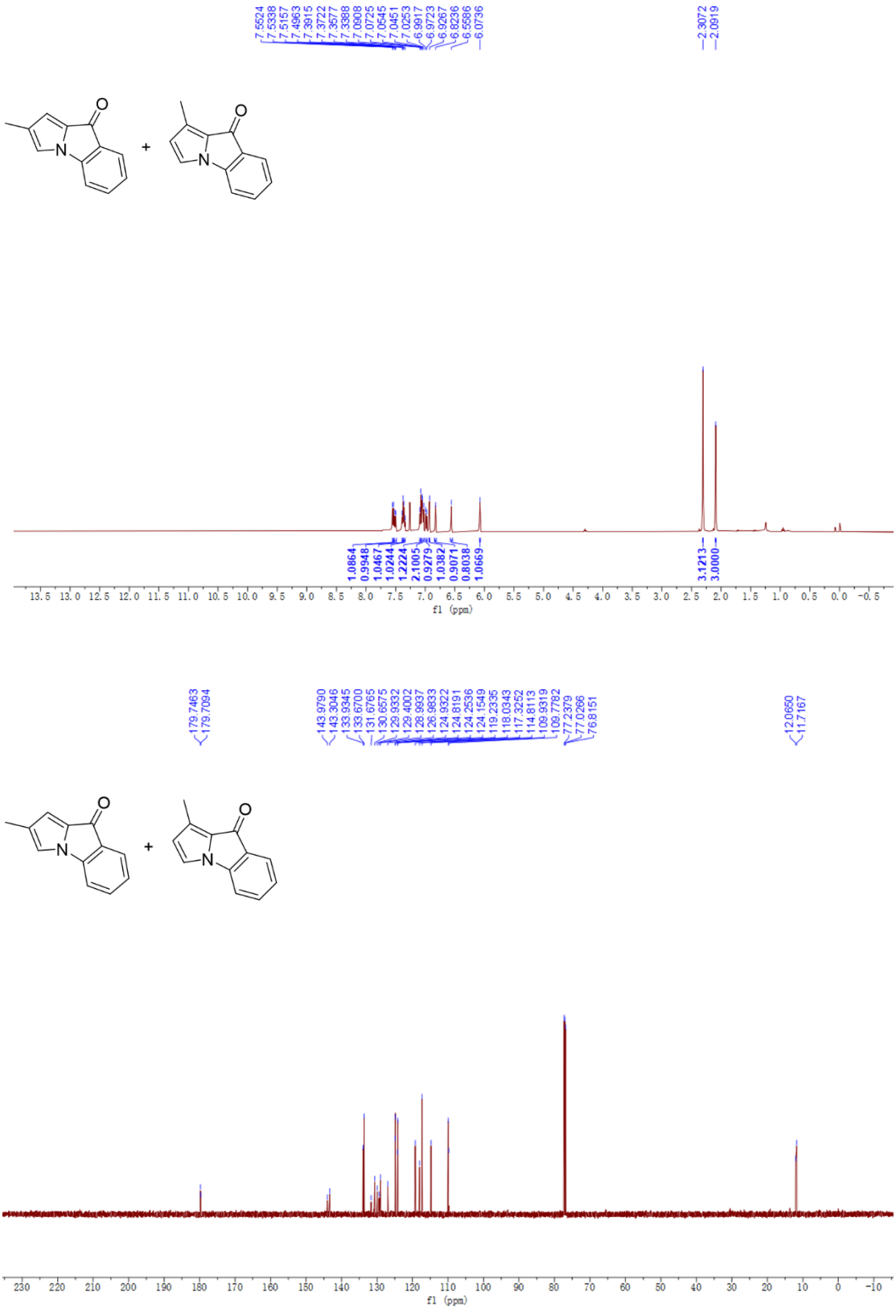


3-Methyl-9*H*-pyrrolo[1,2-a]indol-9-one (3r)





1-Methyl-9*H*-pyrrolo[1,2-a]indol-9-one and 2-Methyl-9*H*-pyrrolo[1,2-a]indol-9-one (3s)

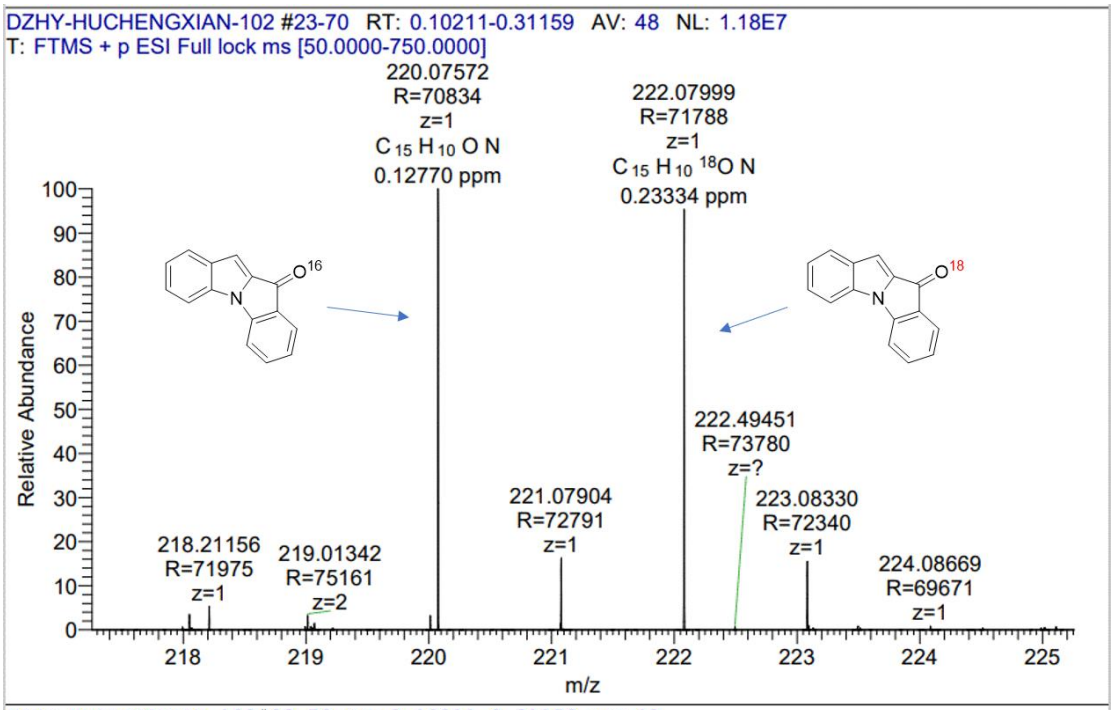


8. HRMS Spectra Copies of Some Product

Product 3a and O^{18}

HRMS (ESI) m/z calcd for $C_{15}H_8ClN^{16}O^+$, $(M+H)^+$ 220.0757, found 220.0757.

HRMS (ESI) m/z calcd for $C_{15}H_8ClN^{18}O^+$, $(M+H)^+$ 222.0799, found 222.0799.

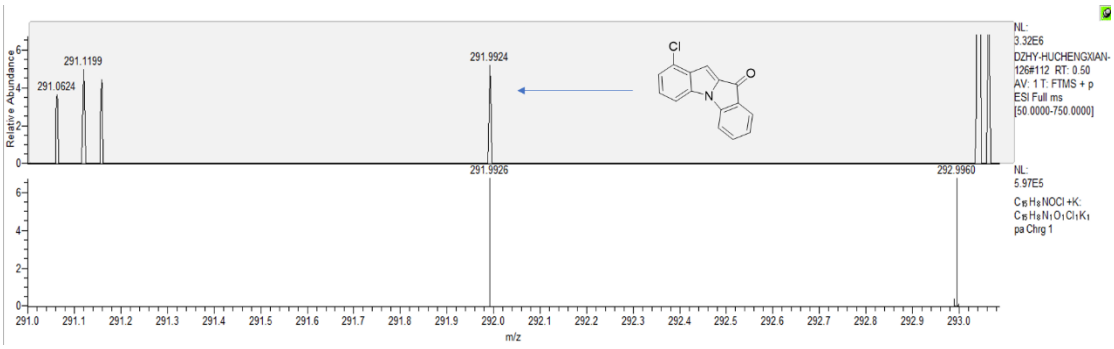


DZHY-HUCHENGXIAN-102#23-70 RT: 0.10211-0.31159 AV: 48
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 217.25628-225.25608

m/z	Intensity	Relative	Resolution	Charge	Delta (ppm)	Composition
218.21156	629212.4	5.27	71975.31	1.00		
220.07572	11948536.0	100.00	70833.92	1.00	0.13	$C_{15}H_{10}ON$
221.07904	1916985.6	16.04	72791.03	1.00		
222.07999	11294737.0	94.53	71788.45	1.00	0.23	$C_{15}H_{10}{}^{18}ON$
223.08330	1829972.3	15.32	72339.55	1.00		

Product 3f

HRMS (ESI) m/z calcd for $C_{15}H_8ClNO^+$, $(M+K)^+$ 291.9926, found 291.9924.



Product 3s

HRMS (ESI) m/z calcd for $C_{12}H_9NO^+$, $(M+Na)^+$ 206.0576, found 206.0576.