Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Pd/Cu-Catalyzed Dual C-H Bond Carbonylation towards the Synthesis of Fluorazones

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1. General

All reactions were carried out in oven-dried Schlenk tube under a mixed oxygen and carbon monoxide atmosphere with a balloon. Toluene and DMSO were dried by activated molecular sieve. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. GC yields were recorded with a SHIMADZU GC-2014 gas chromatograph instrument with a FID detector and biphenyl was added as an internal standard. ^{1}H and ^{13}C NMR data were recorded with Bruker Advanced II (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform; 39.6 ppm, DMSO-d_6), respectively. High resolution massspectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion ($[M]^+$) or $[M+H]^+$.

2. Preparation of *N*-aryl Pyrroles

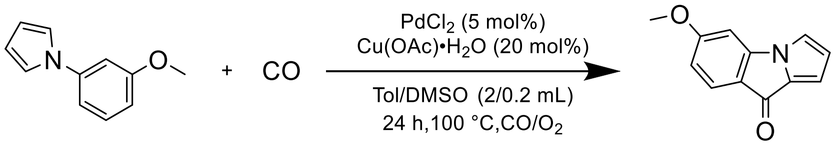
General procedure to synthesize *N*-substituted pyrrole was employed from Jean-Paul Lellouche and Subrata Ghosh[1]. Sodium acetate (20 mmol) was dissolved, under stirring, in water (40 mL) at room temperature. To this solution, required amine (20.6 mmol) was added followed by glacial acetic acid (10ml). The reaction mixture was heated at 75 ^{o}C for about 10 minutes followed by addition of 2, 5-dimethoxytetrahydrofuran (DMT) (20.6 mmol) in a drop wise manner into the vigorously stirred reaction mixture. Further, the reaction mixture was allowed to stir at this temperature (70 ^{o}C) for 2.5h. After cooling to room temperature, reaction mixture was extracted with ethyl acetate (50ml), washed with brine, dried over anhydrous sodium sulphate and evaporated under reduced pressure. The crude compound was purified on silica gel using ethyl acetate and petroleum ether as eluent.

3. Pd/Cu-Catalyzed Dual C-H Bond Carbonylation to Fluorazones

General Procedure: In an oven-dried Schlenk tube equipped with a stir-bar, $PdCl_2$ (1.8 mg, 5 mol%), $Cu(OAc)_2 \cdot H_2O$ (8.0 mg, 20 mol%) were combined. A balloon filled with CO and air (the ratio is 7:1) was connected to the Schlenk tube via the side tube and purged for 3 times. Then DMSO (0.3mL) and toluene (3.0mL) were added to the tube via a syringe. At last, *N*-aryl pyrrole was added to the tube. The Schlenk tube was heated at 100 ^{o}C for 24 hours and then cooled to room temperature. After the balloon gas was released carefully, the reaction was quenched by water and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with hexane and ethyl acetate.

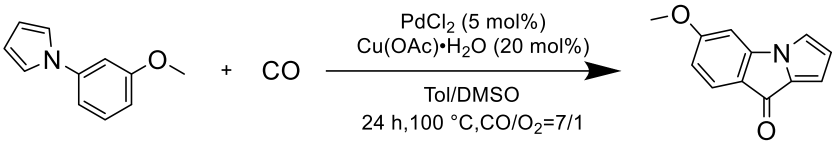
4. Optimization of Pd-Catalyzed Dual C-H Bond Carbonylation of 1a

Optimization of CO/O_2 ratio:



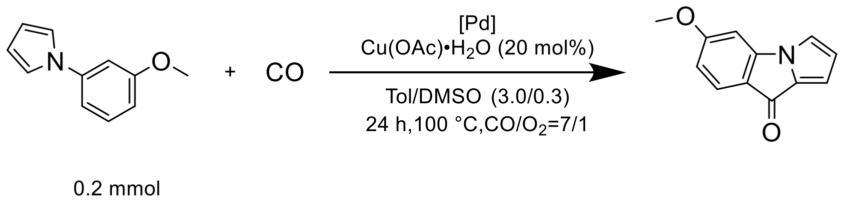
entry	CO/O_2	Yield%
1	3/1	51
2	1/3	45
3	7/1	72
4	1/7	45
5	1/1	54

Optimization of solvent:



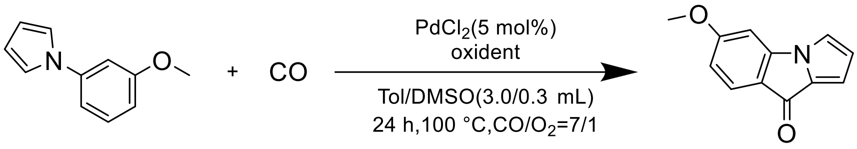
entry	solvent	Yield%
1	3.0/0.3 ml	73
2	3.0/0.4 ml	51
3	3.0/0.1 ml	57
4	3.0/0.2 ml	73
5	2.0/0.2 ml	52
6	1.0/0.1 ml	46
7	DMSO(3ml)	7
8	Toluene(3ml)	none

Optimization of Palladium catalyst precursor:



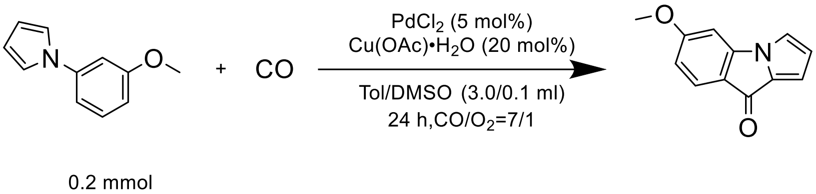
Entry	[Pd]	Yield%
1	$PdCl_2$ (5 mol%)	76
2	$Pd(CF_3COO)_2$ (5 mol%)	19
3	$PdCl_2(PPh_3)_2$ (5 mol%)	11
4	$Pd(OAc)_2$ (5 mol%)	53

Optimization of oxidant:



entry	oxident	Yield%
1	$Cu(OAc)_2$•H_2O(20 mol%)	74
2	$Cu(OAc)_2$•H_2O(20 mol%), $AgCO_3$(2 eq.)	none
3	$AgCO_3$(2 eq.)	none
4	MnO_2(2 eq.)	none
5	BQ(2 eq.)	none
6	$Cu(OPiv)_2$ (20 mol%)	61

Optimization of temperature:



entry	Tem.	Yield%
1	100 °C	70
2	105 °C	62
3	90 °C	33
4	95 °C	47

5. Preparation of *d*$_5$-*N*-phenyl Pyrrole

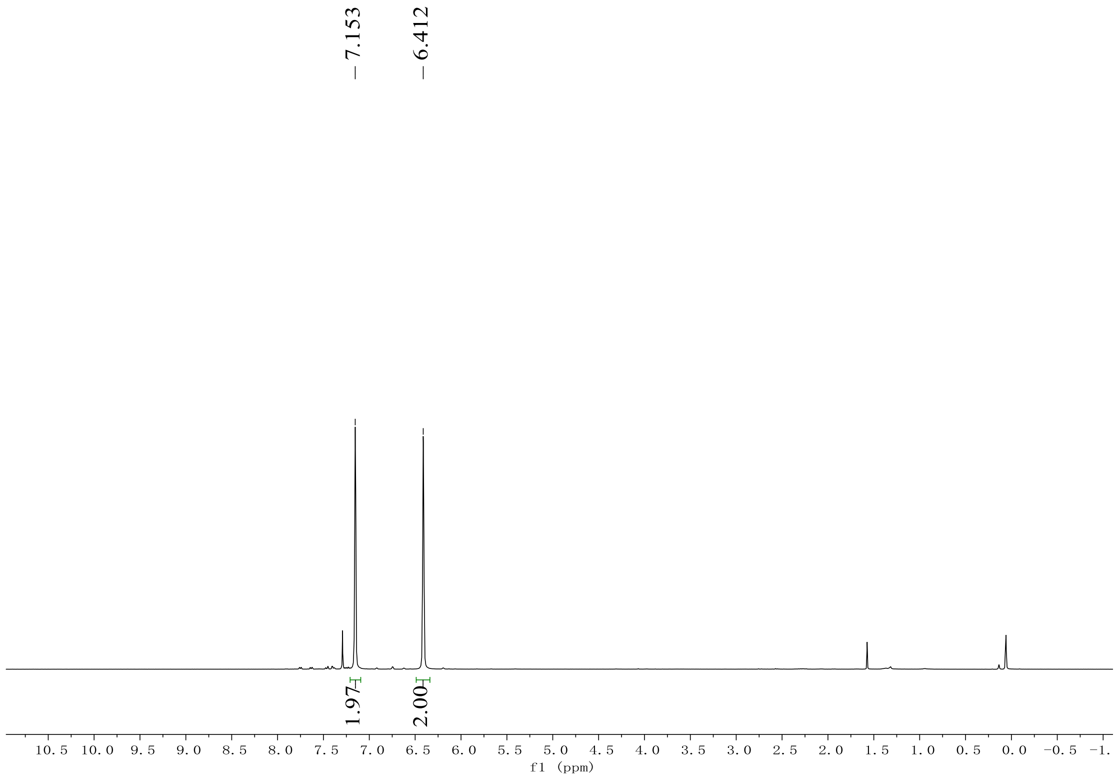
General procedure[2]: Concentrated nitric acid (1.0 mL) and concentrated sulfuric acid (1.0 mL) were mixed together in a round-bottom flask held in an ice-water bath. Then, *d*^{6}-benzene (1.3 g) was added drop-wise at room temperature into the mixture of acids and the reaction mixture was allowed to stir at 60 ^{o}C for 1 hour. The reaction mixture was poured into ice-water and extracted with ethyl acetate. The organic layer was washed with water, $NaHCO_3$ solution, brine and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography using EtOAc: petroleum ether (1:19) as the eluant to obtain *d*^{5}-nitrobenzene.

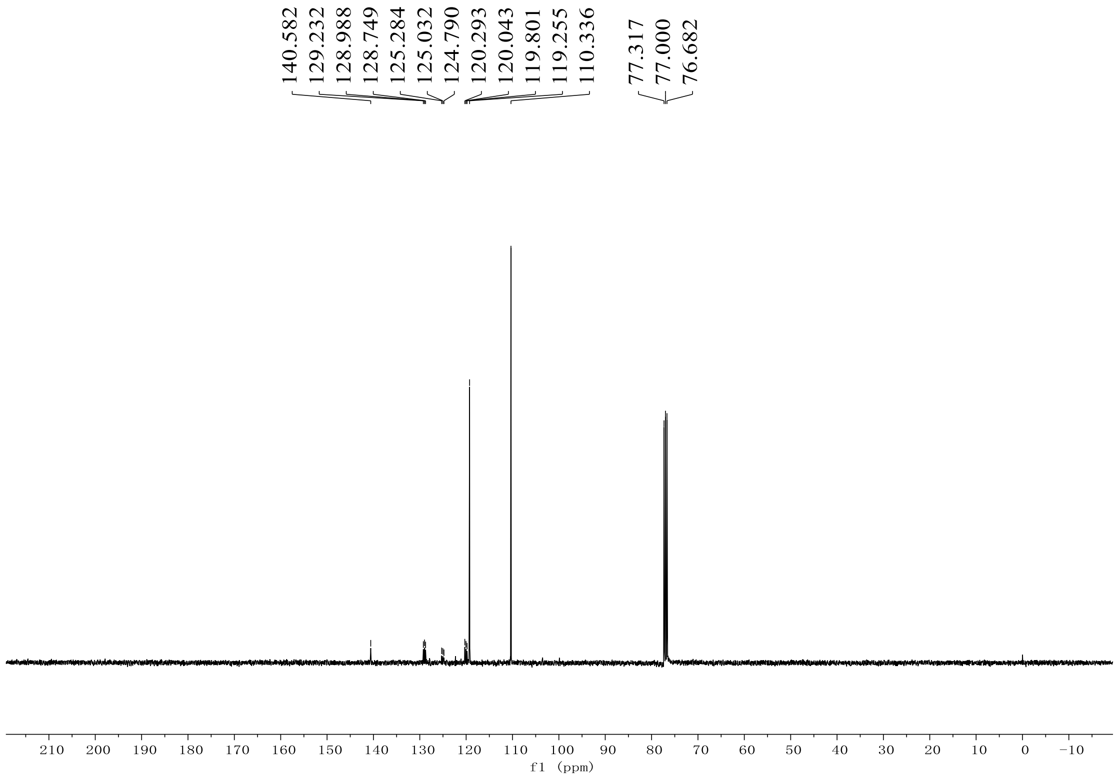
To a mixture of the above *d*^{5}-nitrobenzene (7 mmol) and concentrated aq HCl (11 M, 7.0 mL) in EtOH (15 mL), Sn powder (3.5 g, 29 mmol) was added in several portions, and the resulting mixture was stirred at room temperature under air. After 6 h, volatile materials were evaporated in vacuo, and residue was dissolved in water and diethyl ether. The mixture was neutralized with saturated aq K_2CO_3 and then filtered through a pad of Celite. The filtrate was extracted with ethyl acetate, concentrated under reduced pressure, and purified by column chromatography on silica gel with petroleum ether and ethyl acetate (3/1, v) to afford aniline-*d*$_5$.

According to the preparation of *N*-aryl pyrroles, *d*^{5}-*N*-phenyl pyrrole could be obtained utilizing *d*^{5}-aniline and 2, 5-dimethoxytetrahydrofuran as the reactant, sodium acetate as the base, AcOH/water as the solvent.

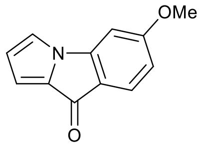
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (s, 2 H), 6.41 (s, 2 H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.58, 128.99 (t, *J* = 24.4 Hz), 125.03 (t, *J* = 24.7 Hz), 120.04 (t, *J* = 24.7 Hz), 119.26, 110.34.


7.153
6.412
1.97
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)


140.582
129.232
128.988
128.749
125.284
125.032
124.790
120.293
120.043
119.801
119.255
110.336
77.317
77.000
76.682
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

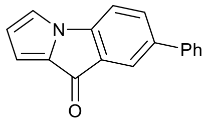
6. Analytical Data of Products



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J*=8.4 Hz, 1H), 7.03 (dd, *J* = 2.4, 0.8 Hz, 1H), 6.72 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.64 (d, *J* = 2.0 Hz, 1H), 6.57 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.28 (dd, *J* = 3.8, 2.6 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.15, 165.15, 145.79, 132.87, 126.02, 122.97, 118.80, 115.60, 113.07, 108.89, 98.11, 55.90.

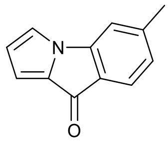
HRMS (ESI) calcd for $C_{12}H_9NO_2$ $[M+H]^+$: 200.0706; found: 200.0702.



^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.85 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.73 (d, *J* = 1.6 Hz, 1H), 7.70-7.67 (m, 2H), 7.67-7.66 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.48-7.42 (m, 2H), 7.37 (tt, *J* = 7.2, 1.6 Hz, 1H), 6.86 (dd, *J* = 4.0, 0.8 Hz, 1H), 6.39 (dd, *J* = 3.6, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 178.53, 142.65, 138.88, 137.86, 133.09, 131.32, 130.30, 129.09, 127.82, 126.57, 122.17, 121.96, 116.28, 114.43, 112.11.

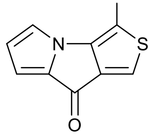
HRMS (ESI) calcd for $C_{17}H_{11}NO$ $[M+H]^+$: 246.0913; found: 246.0905.



^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.61 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.01-6.98 (m, 1H), 6.79 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.35 (dd, *J* = 3.6, 2.4 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 178.72, 145.99, 143.86, 131.31, 127.06, 126.10, 123.92, 121.61, 115.94, 113.84, 112.35, 21.87.

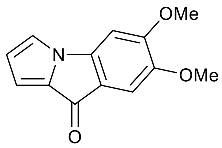
HRMS (ESI) calcd for $C_{12}H_9NO$ $[M+H]^+$: 184.0757; found: 184.0749



^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.30 (s, 1H), 7.75 (dd, *J* = 2.6, 1.0 Hz, 1H), 6.92 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.44 (dd, *J* = 3.6, 2.8 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 172.06, 160.67, 144.20, 138.65, 138.02, 132.10, 124.40, 116.44, 114.75, 109.49, 52.91.

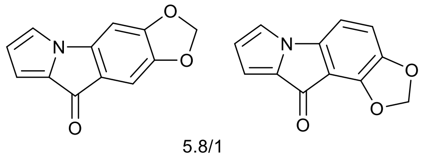
HRMS (ESI) calcd for $C_{11}H_7NO_3S$ $[M+H]^+$: 234.0219; found: 234.0214



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.36 (s, 1H), 7.05 (s, 1H), 6.70 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.25 (dd, *J* = 3.6, 2.4 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 178.77, 154.57, 146.54, 139.57, 131.48, 121.40, 120.32, 114.92, 113.54, 107.18, 97.22, 56.44, 56.11,

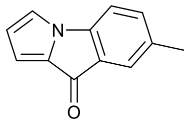
HRMS (ESI) calcd for $C_{13}H_{11}NO_3$ [M+H]$^+$: 230.0812; found: 230.0805



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 (dd, *J* = 2.6, 1.0 Hz, 0.16H), 7.48 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.27 (s, 1H), 7.00 (s, 1H), 6.94 (q, *J* = 8.0 Hz, 0.34H), 6.74 (dd, *J* = 4.0, 0.8 Hz, 0.17H), 6.71 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.32 (dd, *J* = 3.6, 2.4 Hz, 0.17H), 6.25 (dd, *J* = 3.6, 2.8 Hz, 1H), 6.16 (s, 0.32H), 6.11 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 178.11, 175.78, 152.81, 147.22, 145.18, 144.29, 140.94, 136.66, 131.50, 131.11, 122.22, 121.66, 121.56, 115.73, 115.02, 113.89, 112.99, 111.54, 111.14, 104.15, 103.42, 103.36, 102.71, 95.03.

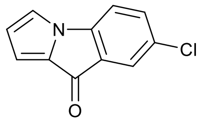
HRMS (ESI) calcd for $C_{12}H_7NO_3$ [M+H]$^+$: 214.0499; found:214.0493



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 (dd, *J* = 2.8, 1.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.37-7.32 (m, 1H), 7.34-7.31 (m , 1H), 6.80 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.34 (dd, *J* = 3.8, 2.6 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 178.96, 141.40, 135.32, 134.97, 131.08, 129.62, 124.47, 121.87, 115.82, 113.98, 111.38, 20.60.

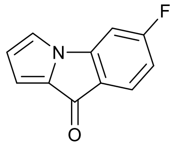
HRMS (ESI) calcd for $C_{12}H_9NO$ [M+H]$^+$: 184.0757; found:184.0749



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.63 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.56 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.51 (dd, *J* = 2.2, 0.6 Hz, 1H), 6.88 (dd, *J* = 4.0, 0.8 Hz, 1H), 6.39 (dd, *J* = 3.8, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 177.21, 142.04, 134.24, 131.24, 131.12, 130.01, 123.89, 122.72, 116.61, 115.11, 113.32,

HRMS (ESI) calcd for $C_{11}H_6ClNO$ [M+H]$^+$: 204.0211; found:204.0201

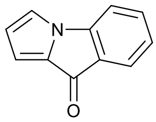


^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.58-7.53 (m, 2H), 7.00 (ddd, *J* = 9.6, 8.4, 3.6 Hz, 1H), 6.86 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.40 (dd, *J* = 3.6, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 177.54, 166.40 (d, *J* = 252.1 Hz), 145.49 (d, *J* = 13.6 Hz), 131.65, 126.19 (d, *J* = 11.3 Hz), 125.91 (d, *J* = 2.5 Hz), 122.24, 116.53, 114.53, 112.06 (d, *J* = 23.4 Hz), 100.92 (d, *J* = 29.0 Hz).

^{19}F NMR (377 MHz, DMSO) δ -102.88.

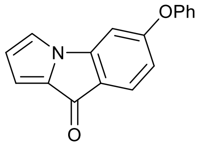
HRMS (ESI) calcd for $C_{11}H_6FNO$ $[M+H]^+$: 188.0506; found:188.0498



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.57 (dt, *J* = 7.4, 1.2 Hz, 1 H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.20 (td, *J* = 7.2, 1.6 Hz, 1H), 6.84 (dd, *J* = 4.0, 0.8 Hz, 1H), 6.37 (dd, *J* = 3.8, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 178.81, 143.50, 135.00, 130.96, 129.48, 125.81, 124.05, 122.06, 116.18, 114.28, 111.69.

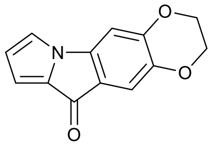
HRMS (ESI) calcd for $C_{11}H_7NO$ $[M+H]^+$: 170.0600; found:170.0591



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.52-7.44 (m, 3H), 7.30-7.23 (m, 2H), 7.20-7.15 (m, 2H), 6.80 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.64 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.34 (dd, *J* = 3.8, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 177.90, 163.04, 155.05, 145.61, 131.78, 130.49, 125.90, 125.00, 124.15, 122.01, 120.00, 116.04, 113.83, 113.63, 102.26.

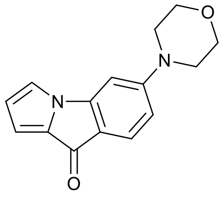
HRMS (ESI) calcd for $C_{17}H_{11}NO_2$ $[M+H]^+$: 262.0863; found:262.0853



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.15 (s, 1H), 6.98 (s, 1H), 6.72 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.28 (dd, *J* = 3.8, 2.6 Hz, 1H), 4.36-4.23 (m, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 178.11, 148.65, 140.96, 138.40, 131.61, 122.34, 121.50, 115.35, 113.42, 113.19, 101.72, 64.94, 63.82.

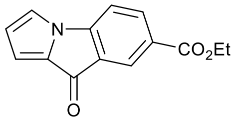
HRMS (ESI) calcd for $C_{13}H_9NO_3$ $[M+H]^+$: 228.0655; found:228.0647



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 (d, *J* = 2.8 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 6.65 (d, *J* = 3.6 Hz, 1H), 6.58 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.30 (dd, *J* = 3.6, 2.4 Hz, 1H), 3.74 (t, *J* = 4.8 Hz, 4H),3.35 (t, J = 4.8Hz, 4H).

^{13}C NMR (101 MHz, DMSO-*d_6*) δ 178.19, 155.98, 145.99, 132.39, 125.43, 120.36, 118.57, 115.21, 112.02, 108.78, 97.23, 65.83, 47.06.

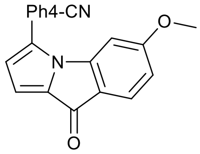
HRMS (ESI) calcd for $C_{15}H_{14}N_2O_2$ $[M+H]^+$: 255.1128; found:255.1118



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 1.6 Hz, 1H), 8.19 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 2.4, 0.8 Hz, 1H), 6.84 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.38 (dd, *J* = 3.8, 2.6 Hz, 1H), 4.38 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.46, 165.19, 146.53, 136.35, 132.53, 130.22, 127.90, 125.74, 119.89, 116.94, 114.88, 110.03, 61.33, 14.25.

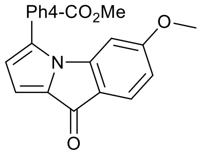
HRMS (ESI) calcd for $C_{14}H_{11}NO_3$ $[M+H]^+$: 242.0812; found: 242.0802



^{1}H NMR (400 MHz, DMSO-*d_6*) δ 8.02 (d, *J*= 8.4 Hz, 2H), 7.87 (dt, *J*=8.4, 1.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.54 (d, *J* = 3.6 Hz, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 3.74 (s, 3H).

^{1}H NMR (400 MHz, DMSO-*d_6*) δ 8.03, 8.01, 7.89, 7.88, 7.88, 7.87, 7.86, 7.86, 7.52, 7.50, 6.91, 6.90, 6.74, 6.73, 6.72, 6.71, 6.55, 6.54, 6.46, 6.45, 3.74.

HRMS (ESI) calcd for $C_{19}H_{13}N_2O_2$ $[M+H]^+$: 301.0972; found: 301.0980.

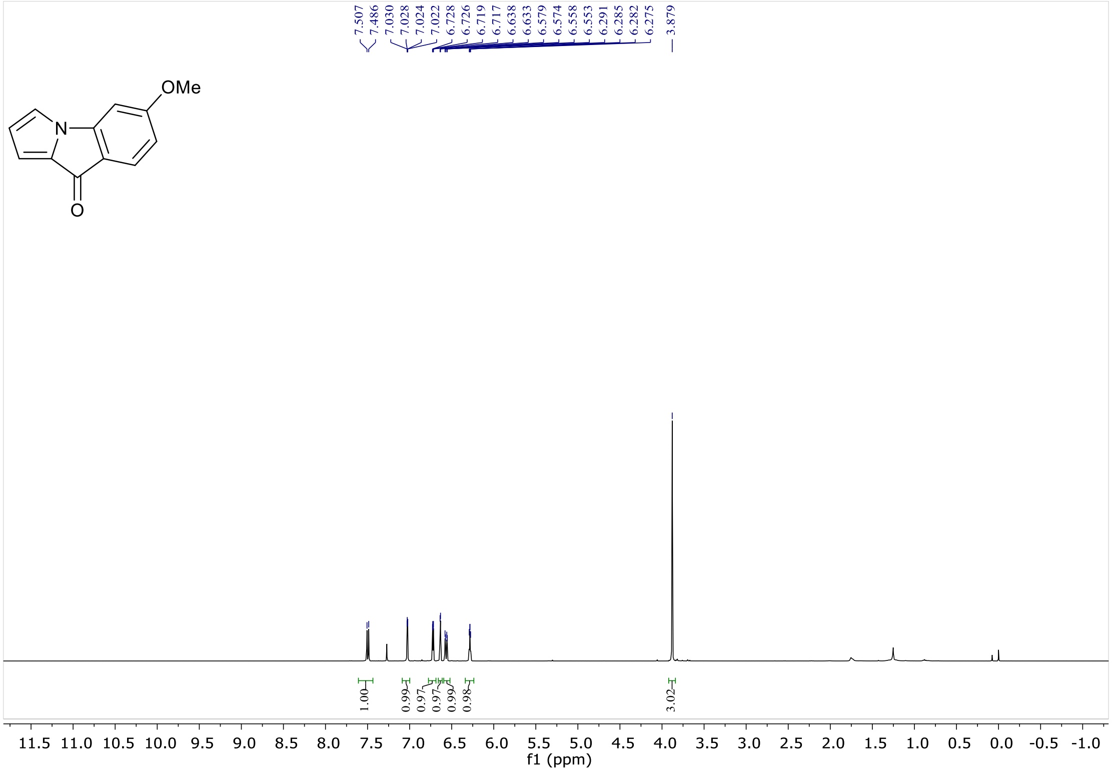


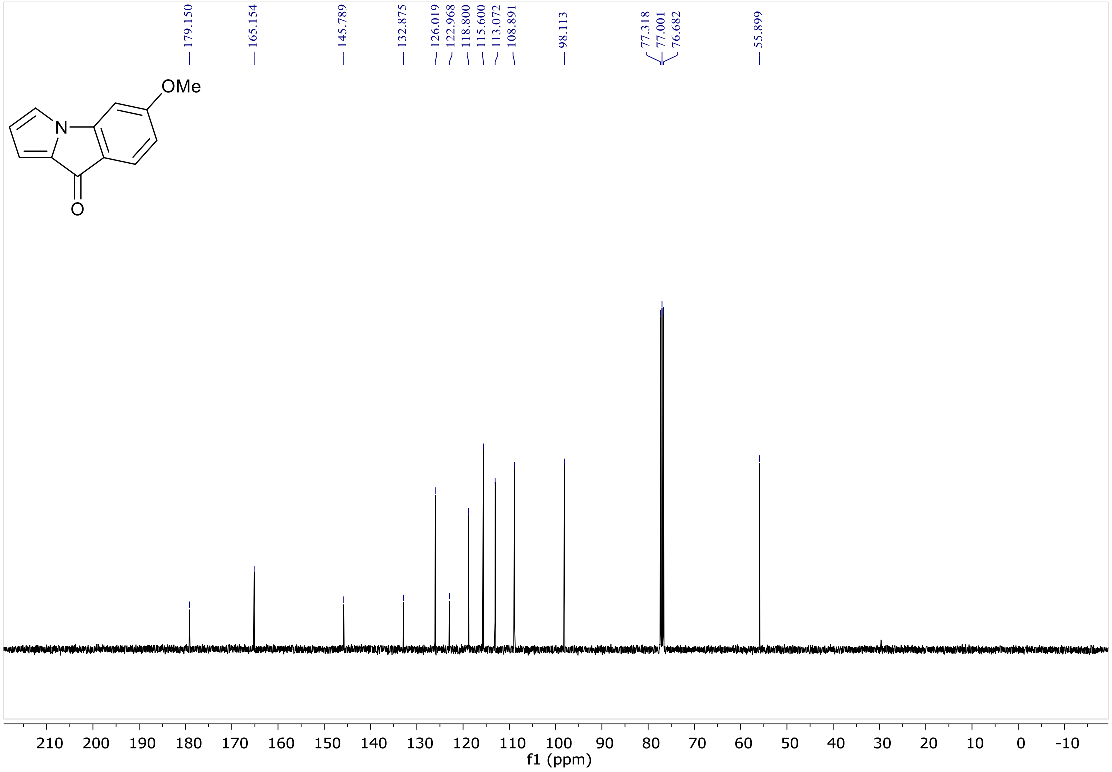
^{1}H NMR (400 MHz, DMSO-*d_6*) δ 8.10-8.06 (m, 2H), 7.80-7.76 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 3.6 Hz, 1H), 6.70 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.50 (d, *J* = 3.6 Hz, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H), 3.71 (s, 3H).

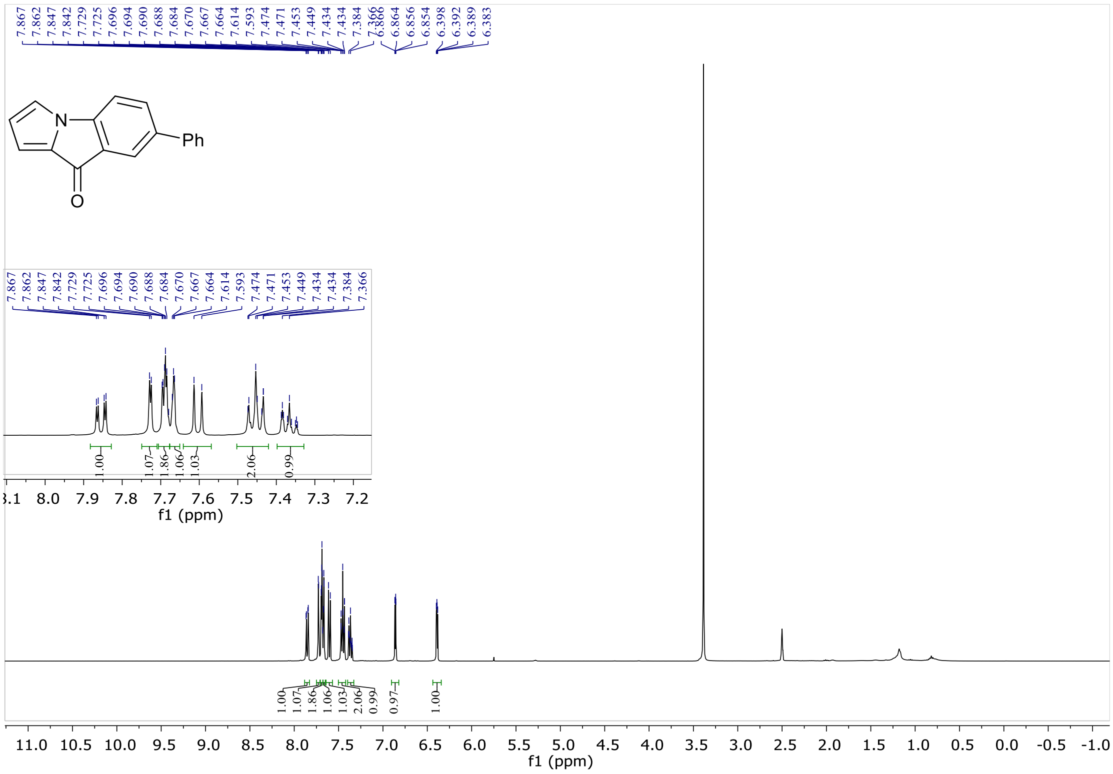
^{13}C NMR (101 MHz, DMSO-*d_6*) δ 177.67, 165.86, 164.82, 145.55, 135.86, 134.73, 134.26, 130.07, 129.72, 129.15, 126.05, 122.60, 117.63, 113.64, 109.37, 100.04, 56.01, 52.51.

HRMS (ESI) calcd for $C_{20}H_{16}NO_4$ $[M+H]^+$: 334.1074; found: 334.1084.

7.NMR Spectra of Products



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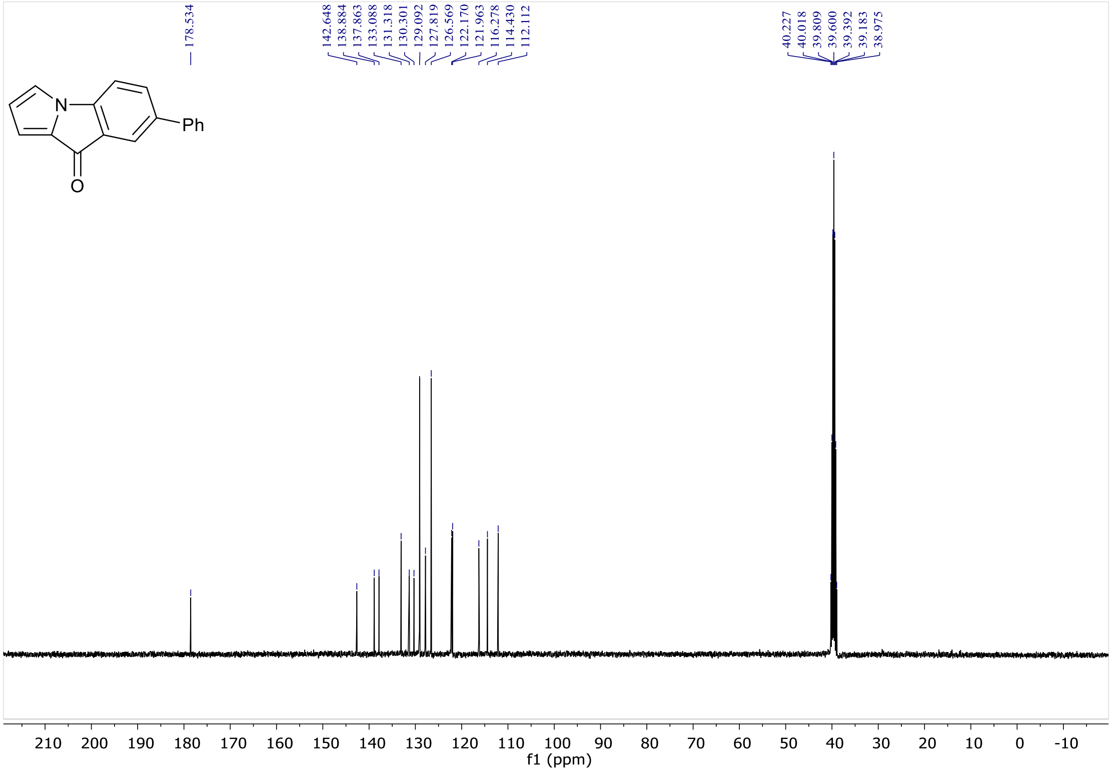
7.862
7.847
7.842
7.729
7.725
7.696
7.694
7.690
7.688
7.684
7.670
7.667
7.664
7.614
7.593
7.474
7.471
7.453
7.449
7.434
7.434
7.384
7.366
6.866
6.864
6.856
6.854
6.398
6.392
6.389
6.383
N
Ph
O
1.00
1.07
1.86
1.06
1.03
2.06
0.99
0.97
1.00
f1 (ppm)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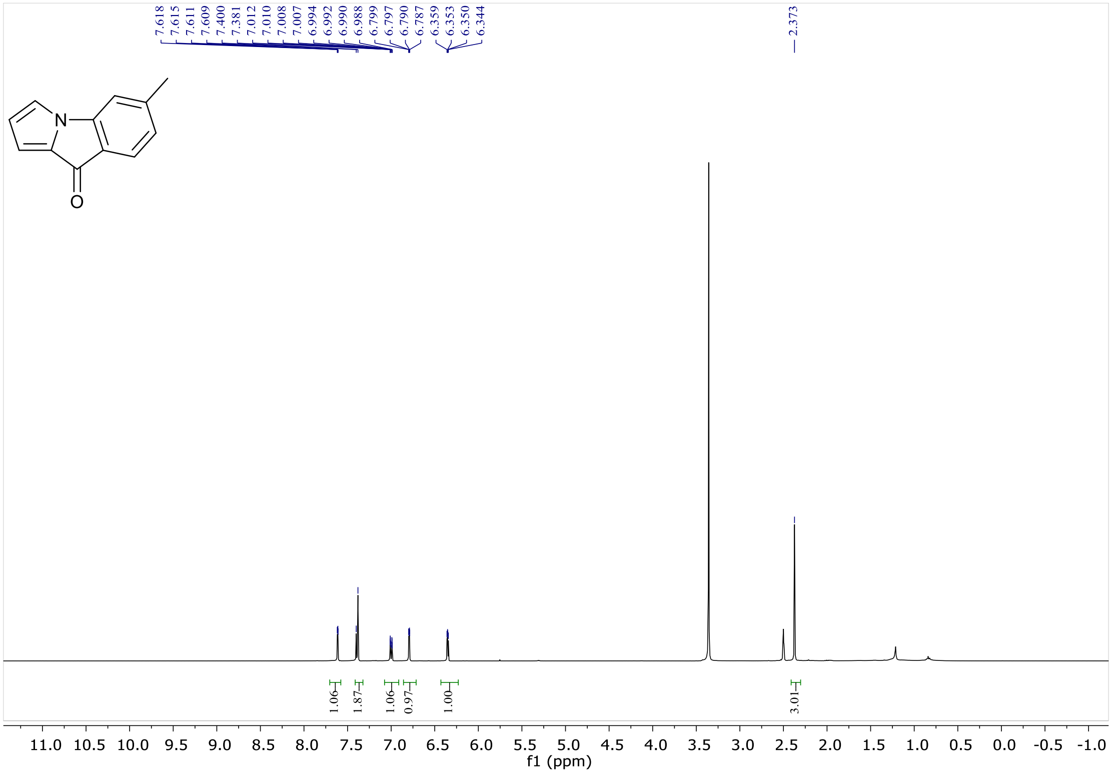
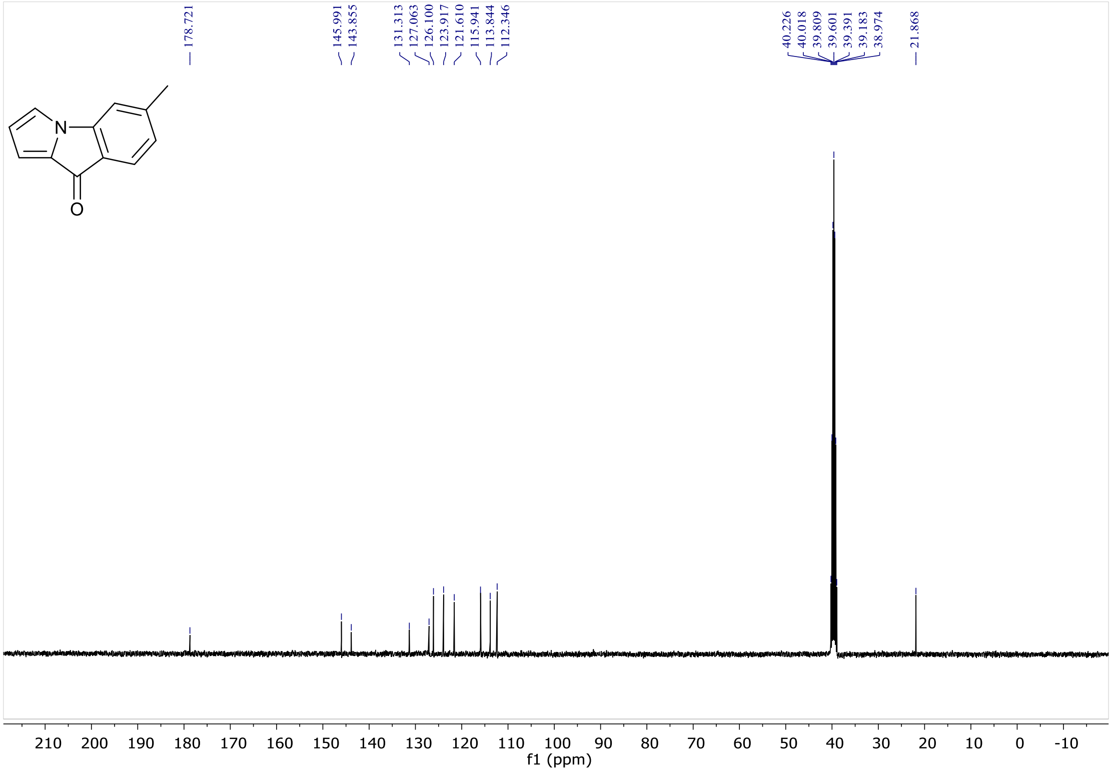
142.648
138.884
137.863
133.088
131.318
130.301
129.092
127.819
126.569
122.170
121.963
116.278
114.430
112.112
40.227
40.018
39.809
39.600
39.392
39.183
38.975
N
Ph
O
f1 (ppm)


7.618
7.615
7.611
7.609
7.400
7.381
7.012
7.010
7.008
7.007
6.994
6.992
6.990
6.988
6.799
6.797
6.790
6.787
6.359
6.353
6.350
6.344
2.373
N
O
1.06
1.87
1.06
0.97
1.00
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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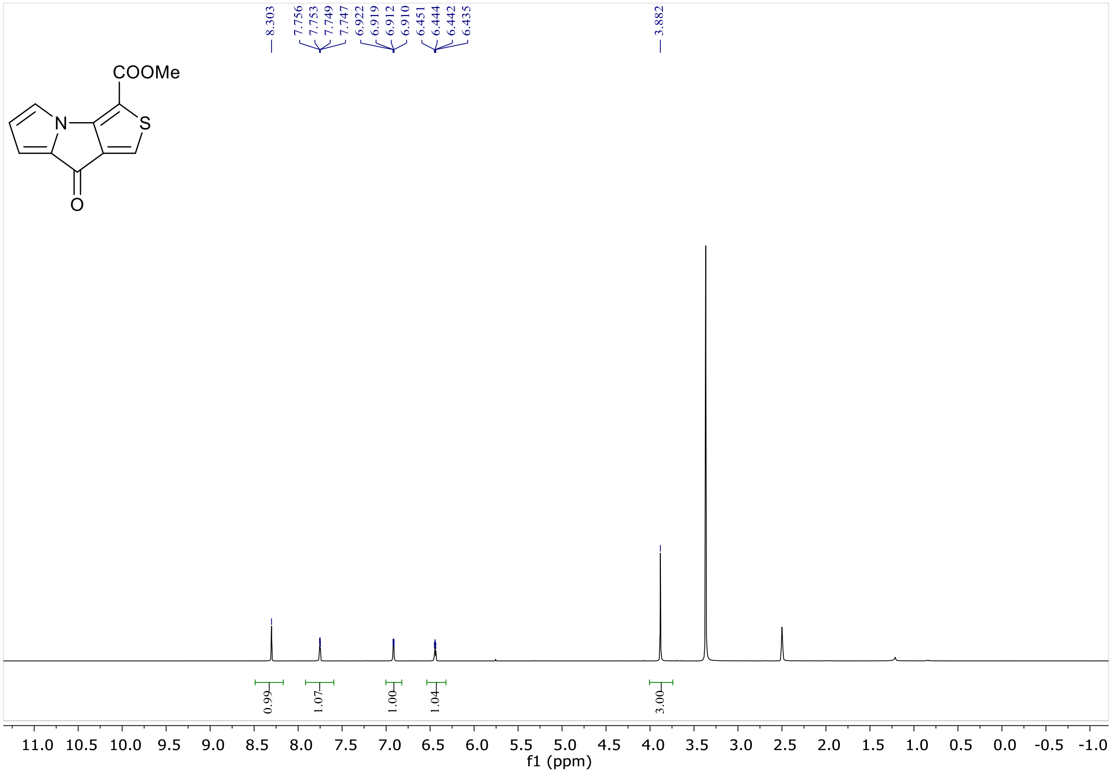
145.991
143.855
131.313
127.063
126.100
123.917
121.610
115.941
113.844
112.346
40.226
40.018
39.809
39.601
39.391
39.183
38.974
21.868
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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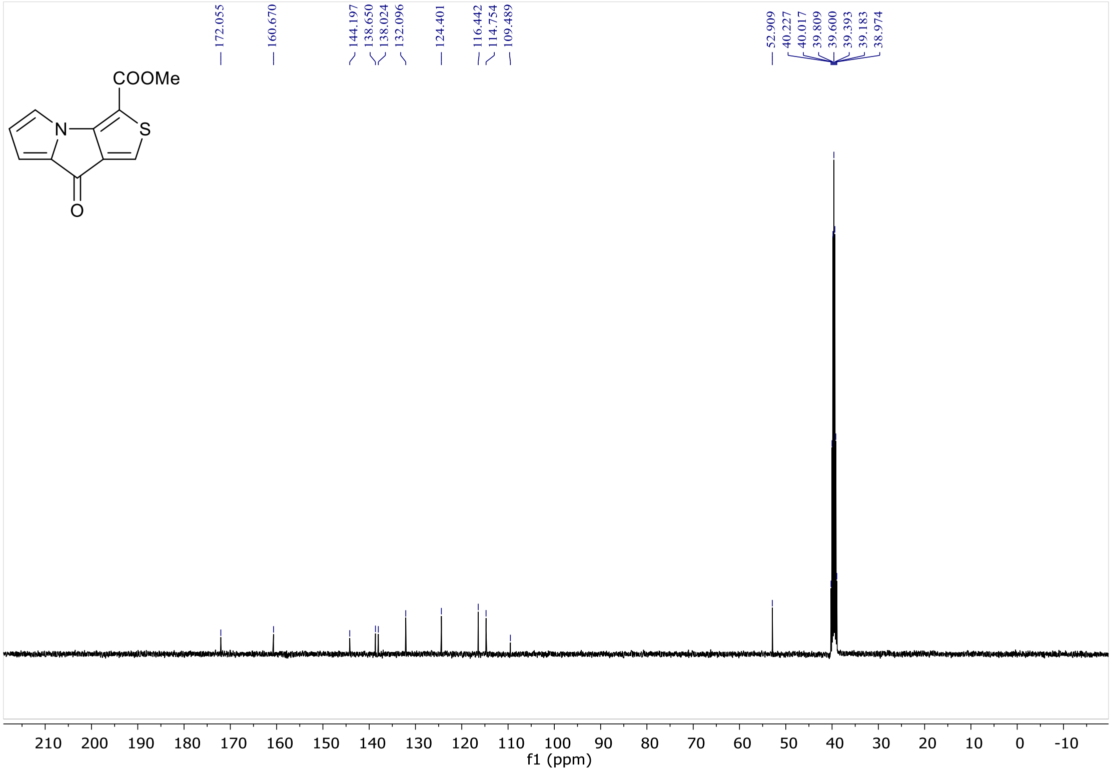
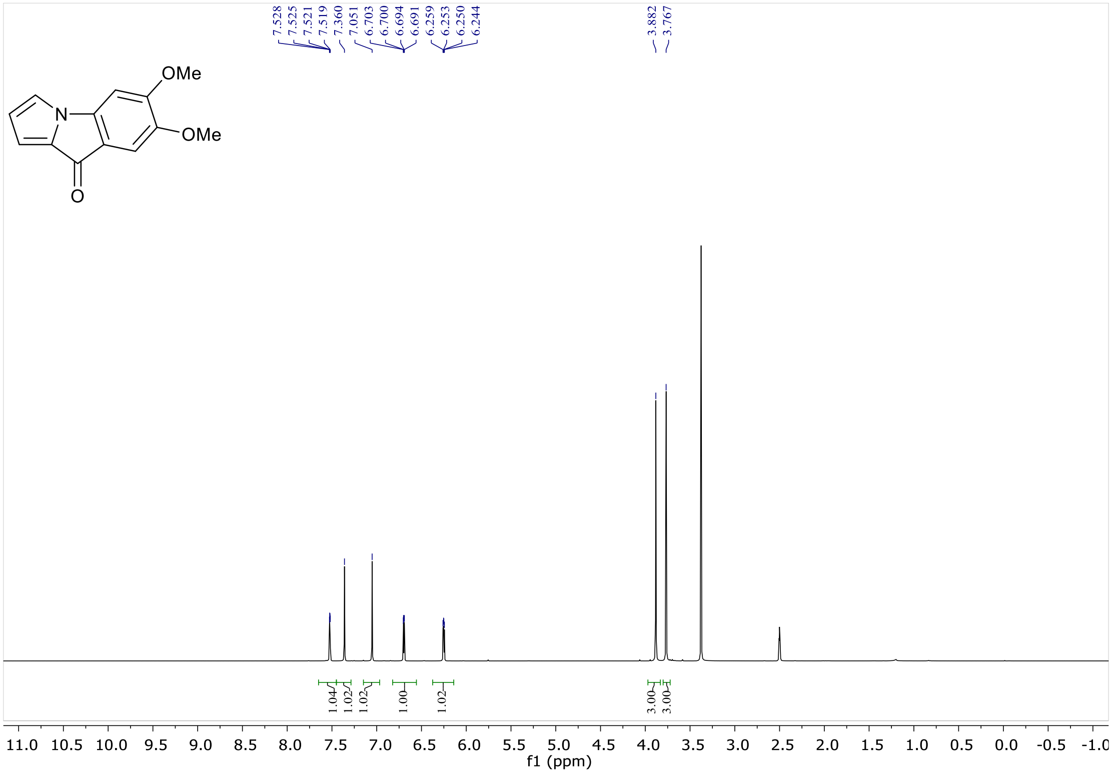
7.756
7.753
7.749
7.747
6.922
6.919
6.912
6.910
6.451
6.444
6.442
6.435
3.882
COOMe
N
S
O
0.99
1.07
1.00
1.04
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


172.055
160.670
144.197
138.650
138.024
132.096
124.401
116.442
114.754
109.489
52.909
40.227
40.017
39.809
39.600
39.393
39.183
38.974
COOMe
N
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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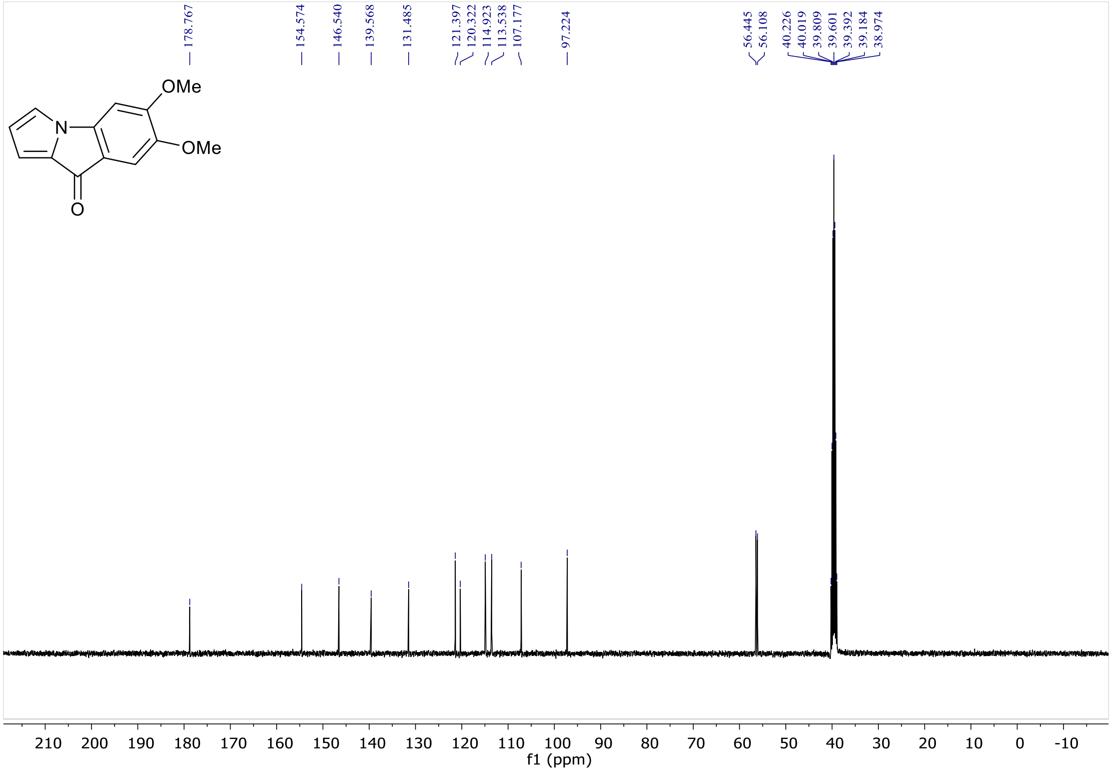
7.525
7.521
7.519
7.360
7.051
6.703
6.700
6.694
6.691
6.259
6.253
6.250
6.244
3.882
3.767
OMe
OMe
N
O
1.04
1.02
1.02
1.00
1.02
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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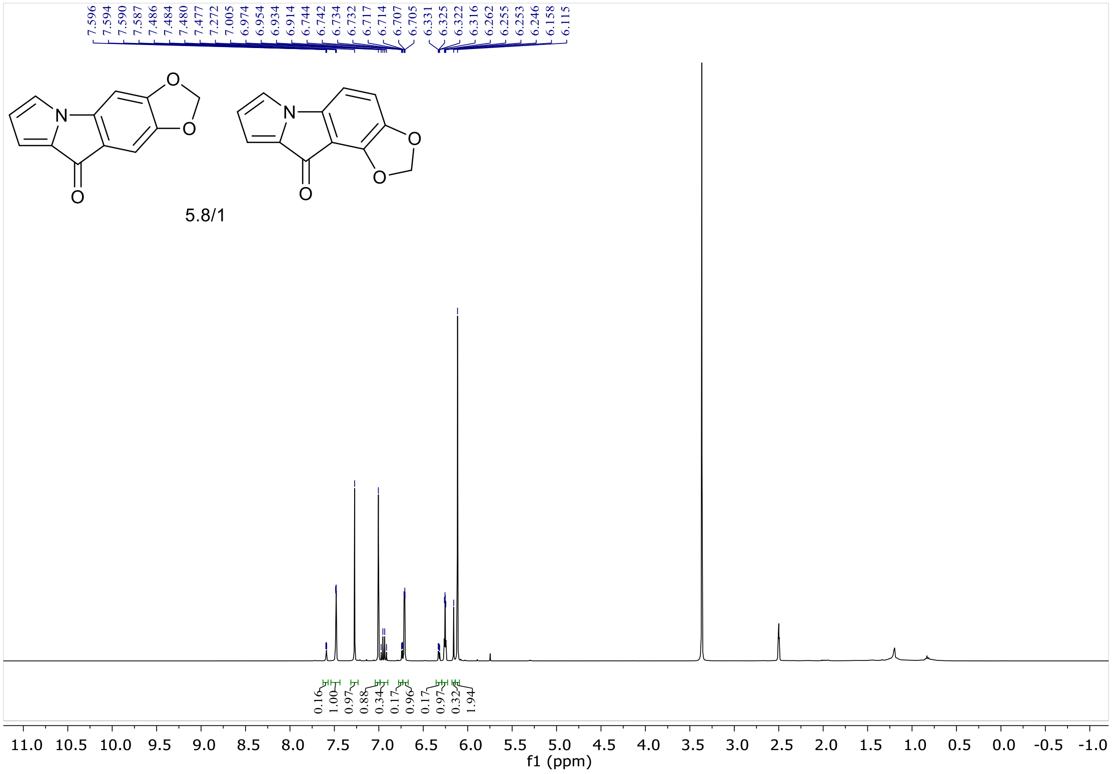
146.540
139.568
131.485
121.397
120.322
114.923
113.538
107.177
97.224
56.445
56.108
40.226
40.019
39.809
39.601
39.392
39.184
38.974
OMe
OMe
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.590
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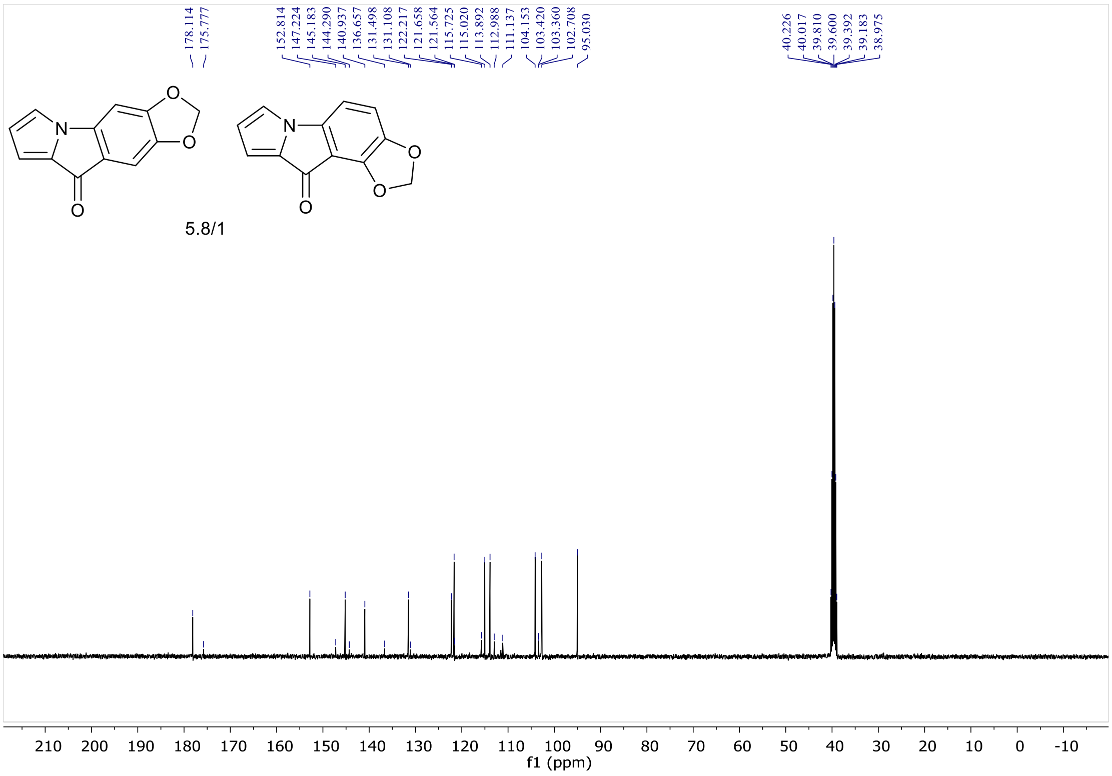
7.484
7.480
7.477
7.272
7.005
6.974
6.954
6.934
6.914
6.744
6.742
6.734
6.732
6.717
6.714
6.707
6.705
6.331
6.325
6.322
6.316
6.262
6.255
6.253
6.246
6.158
6.115
N
O
O
O
N
O
O
O
5.8/1
0.16
1.00
0.97
0.88
0.34
0.17
0.96
0.17
0.97
0.32
1.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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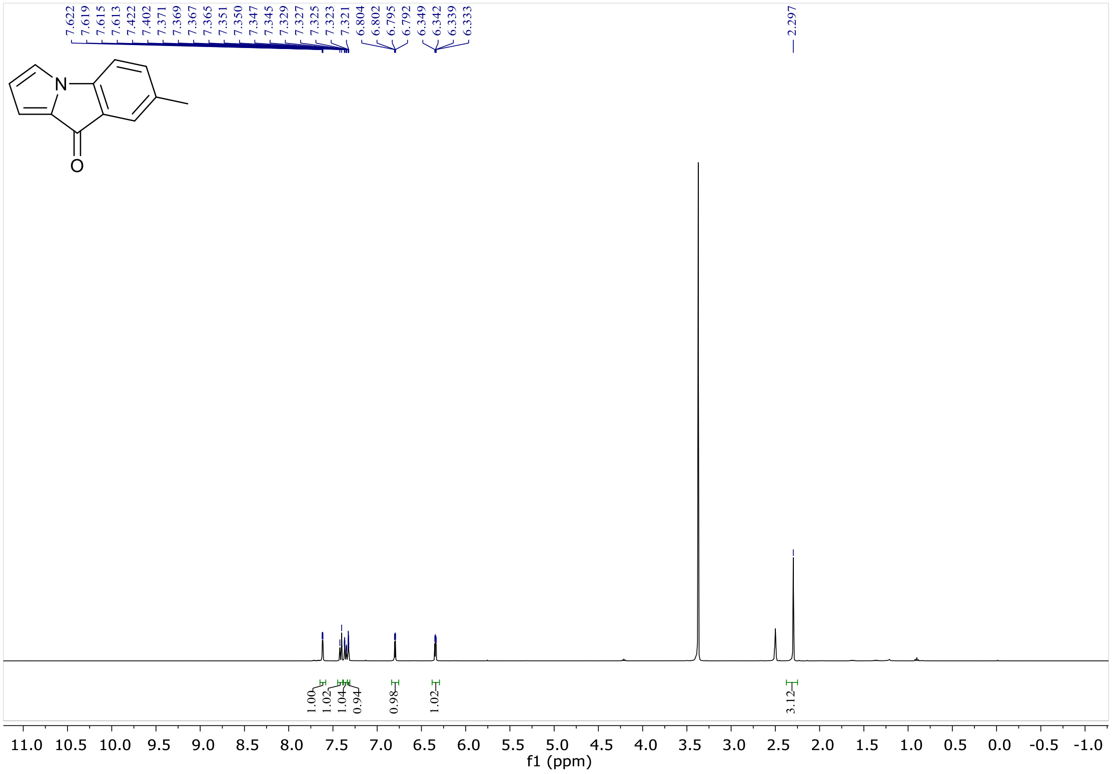
115.725
115.020
113.892
112.988
111.137
104.153
103.420
103.360
102.708
95.030
40.226
40.017
39.810
39.600
39.392
39.183
38.975
N
O
O
O
N
O
O
O
5.8/1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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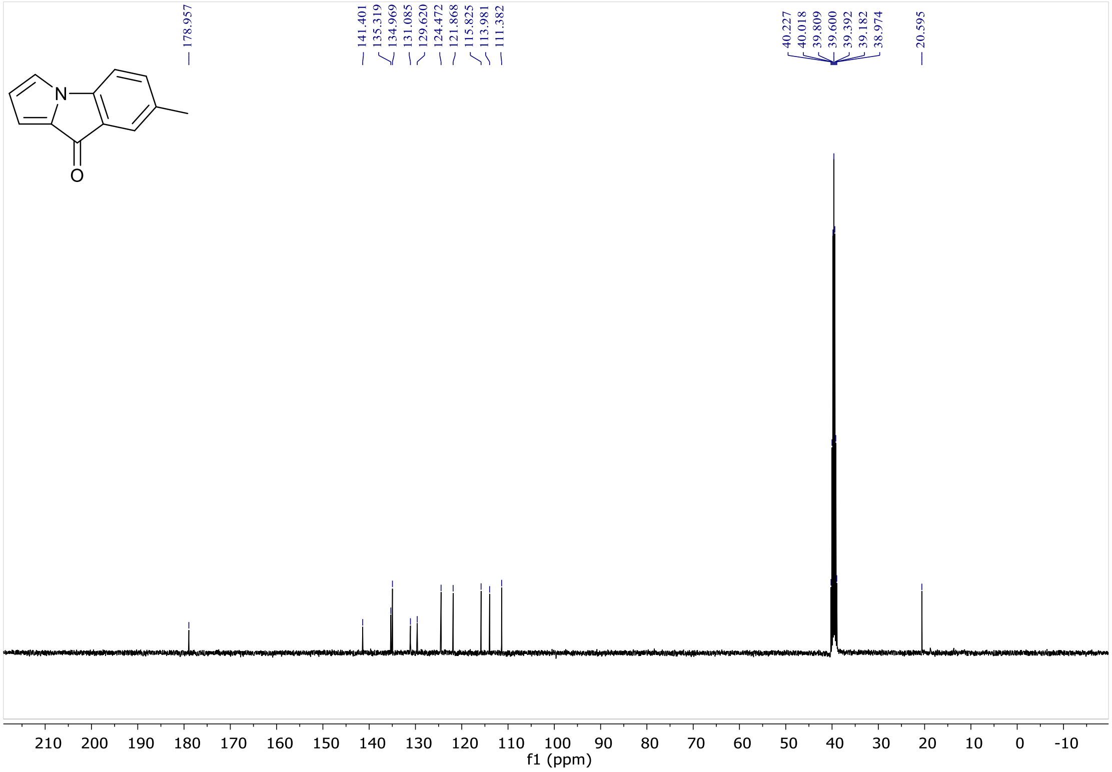
7.369
7.367
7.365
7.351
7.350
7.347
7.345
7.329
7.327
7.325
7.323
7.321
6.804
6.802
6.795
6.792
6.349
6.342
6.339
6.333
2.297
N
O
1.00
1.02
1.04
0.94
0.98
1.02
3.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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121.868
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113.981
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40.227
40.018
39.809
39.600
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20.595
N
O
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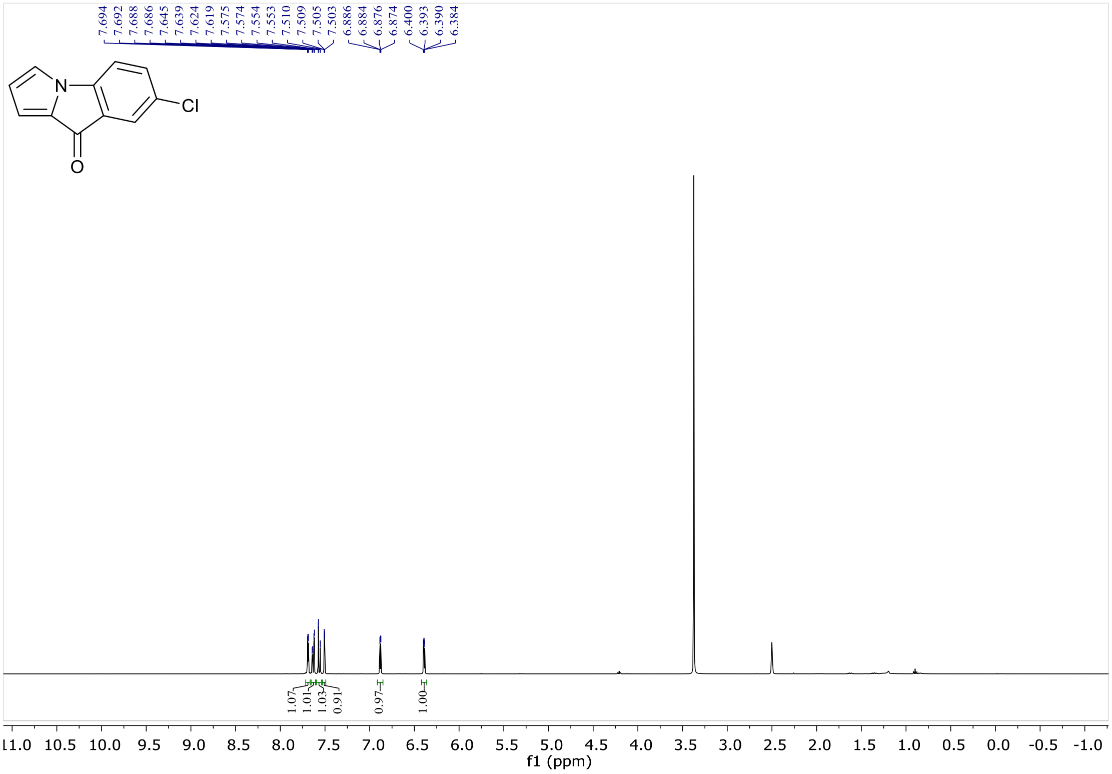
f1 (ppm)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7.639
7.624
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7.574
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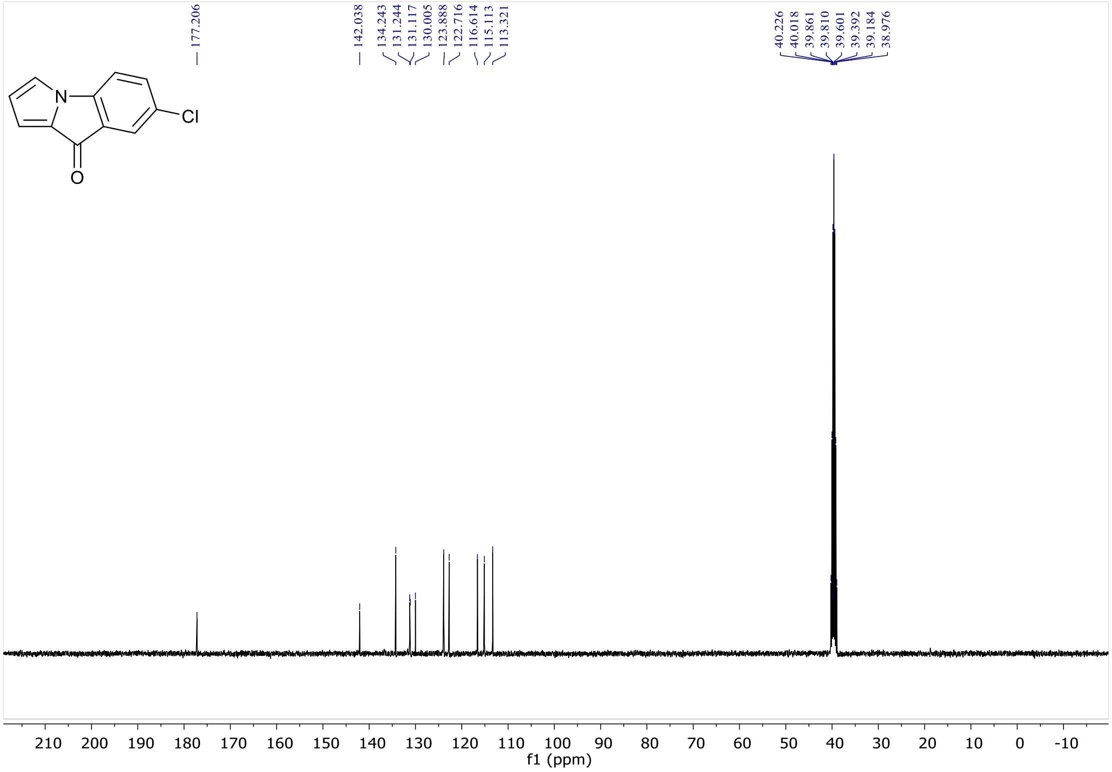
7.509
7.505
7.503
6.886
6.884
6.876
6.874
6.400
6.393
6.390
6.384
N
Cl
O
1.07
1.01
1.03
0.91
0.97
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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115.113
113.321
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40.018
39.861
39.810
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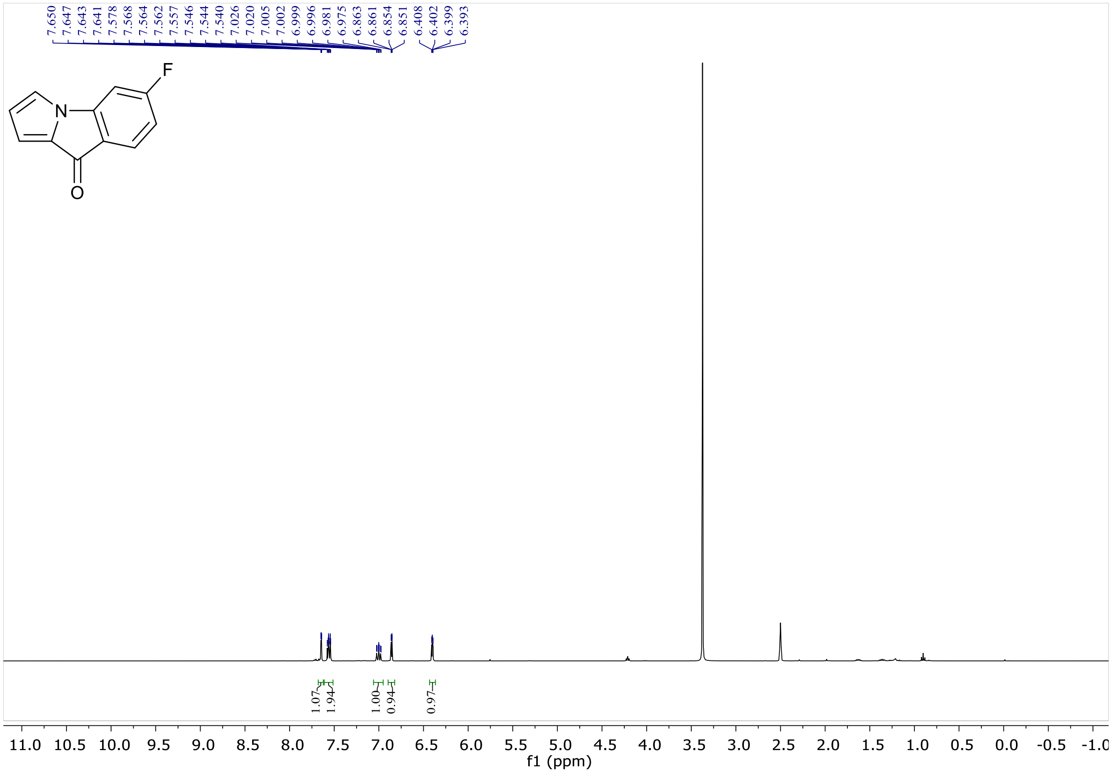
38.976
N
Cl
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.562
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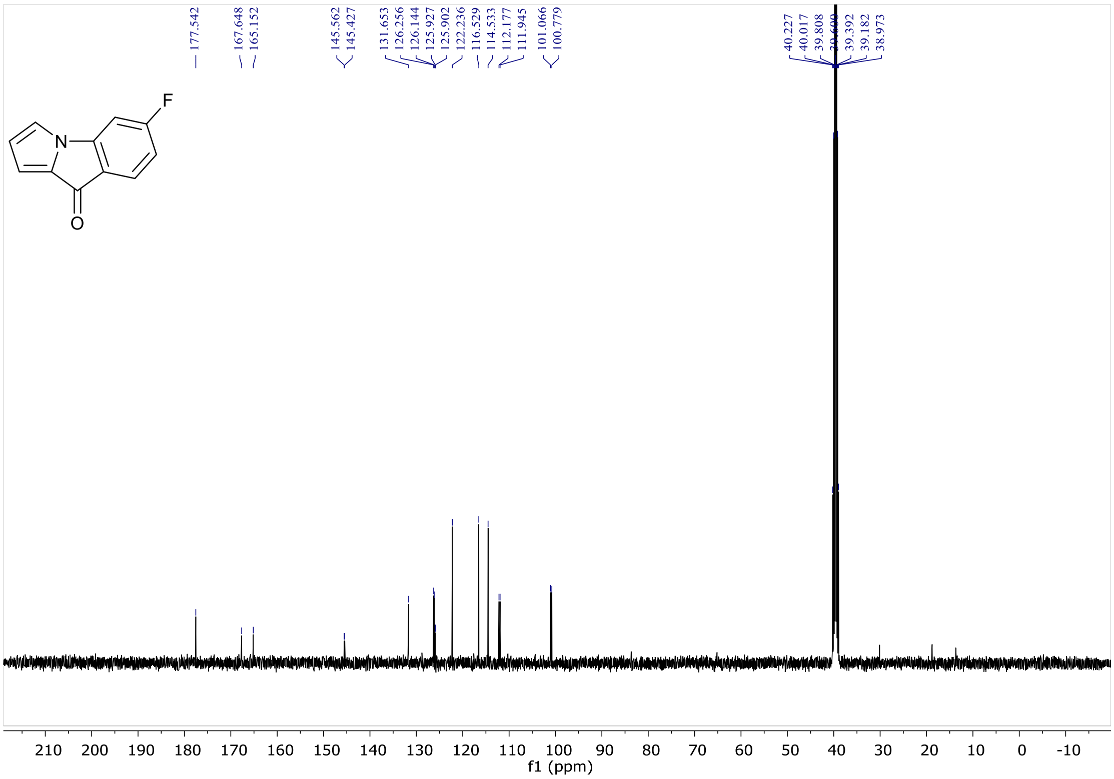
7.544
7.540
7.026
7.020
7.005
7.002
6.999
6.996
6.981
6.975
6.863
6.861
6.854
6.851
6.408
6.402
6.399
6.393
F
N
O
1.07
1.94
1.00
0.94
0.97
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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114.533
112.177
111.945
101.066
100.779
40.227
40.017
39.808
39.600
39.392
39.182
38.973
F
N
O
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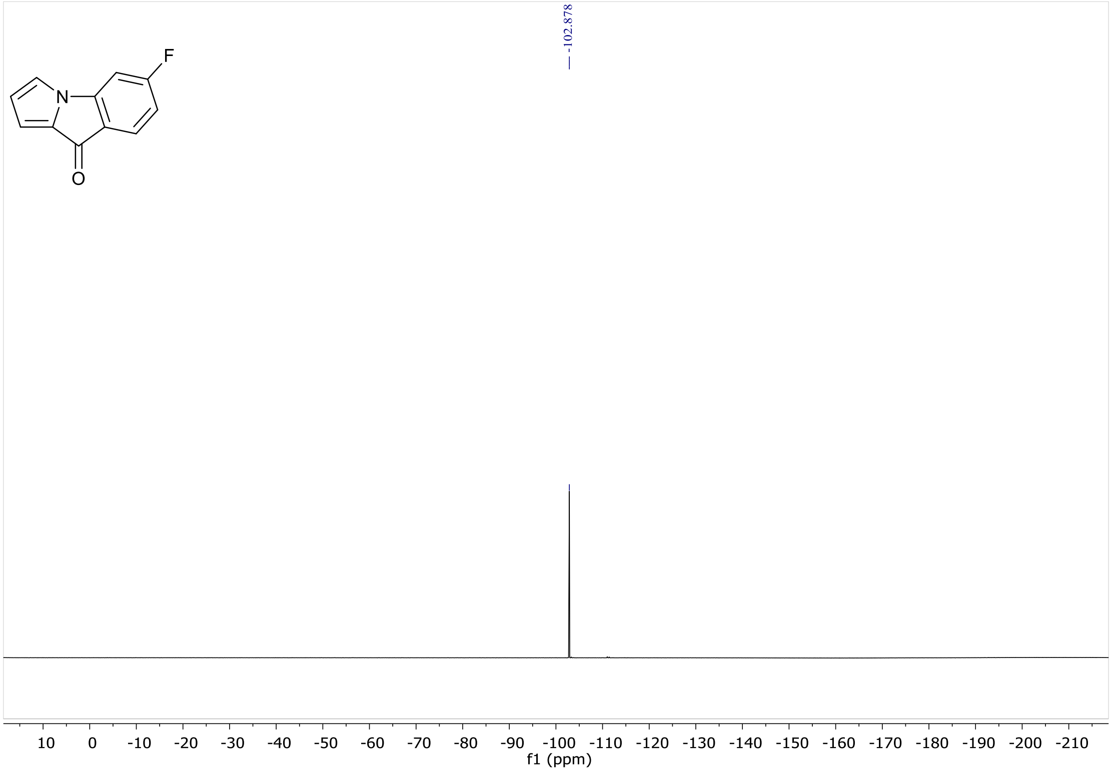
f1 (ppm)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-180
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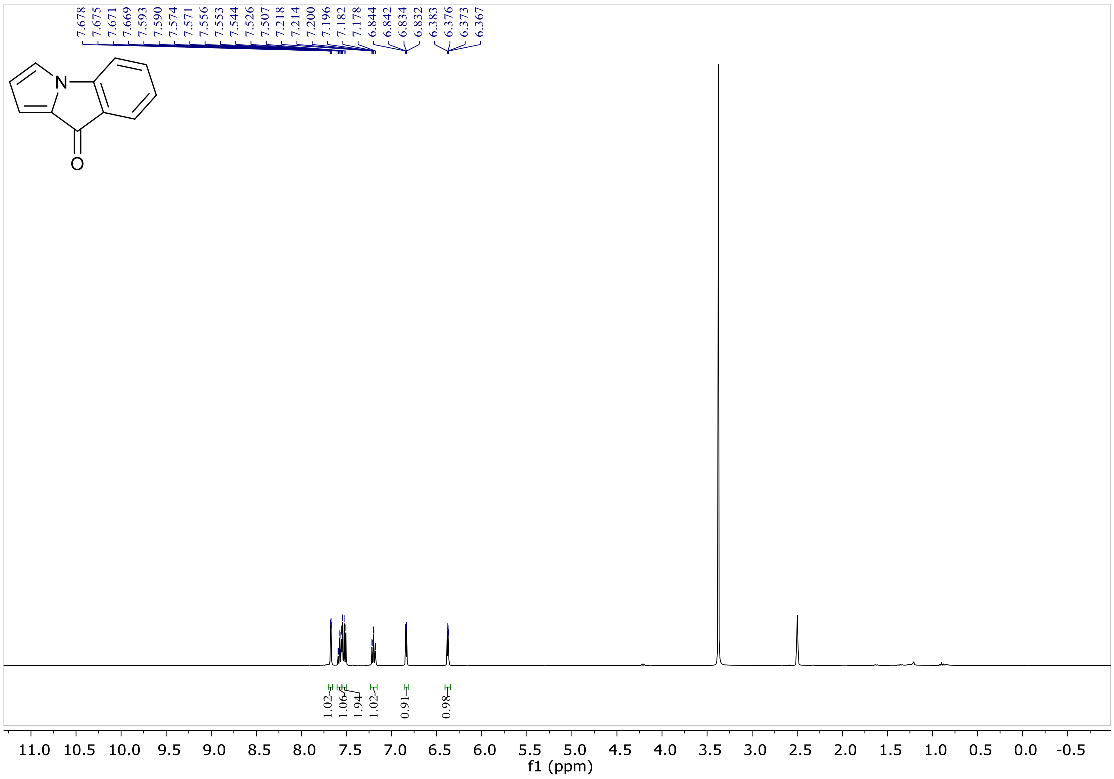
f1 (ppm)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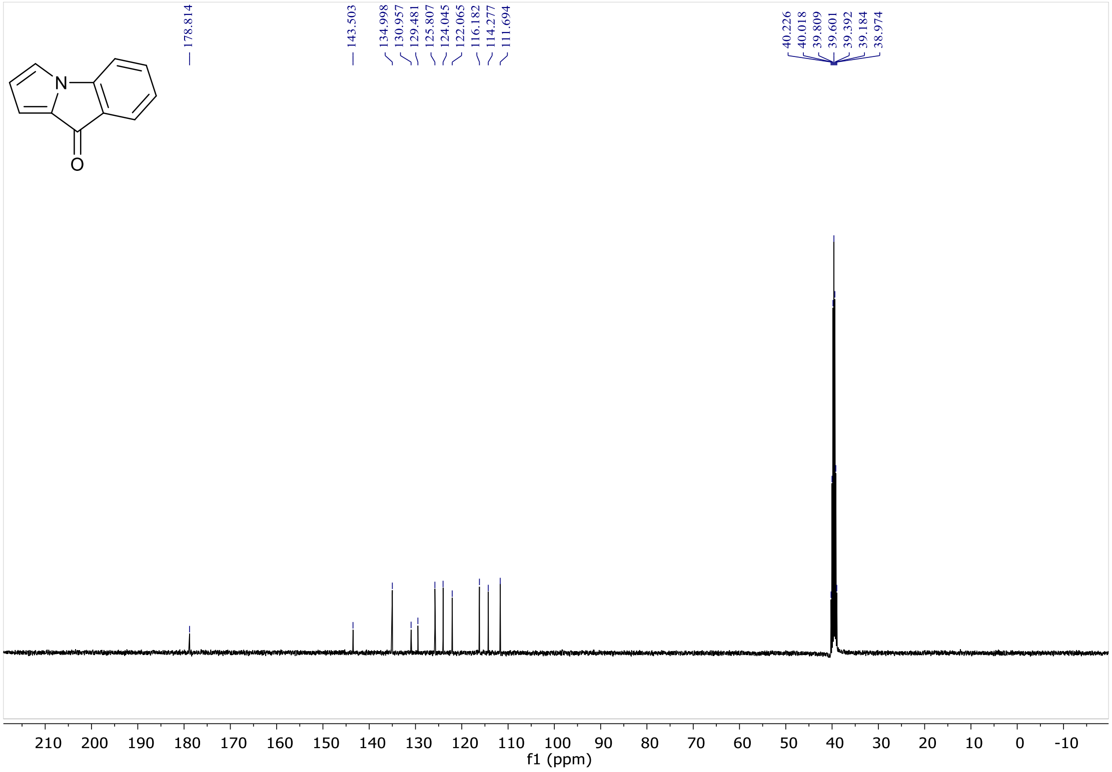
7.507
7.218
7.214
7.200
7.196
7.182
7.178
6.844
6.842
6.834
6.832
6.383
6.376
6.373
6.367
N
O
1.02
1.06
1.94
1.02
0.91
0.98
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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134.998
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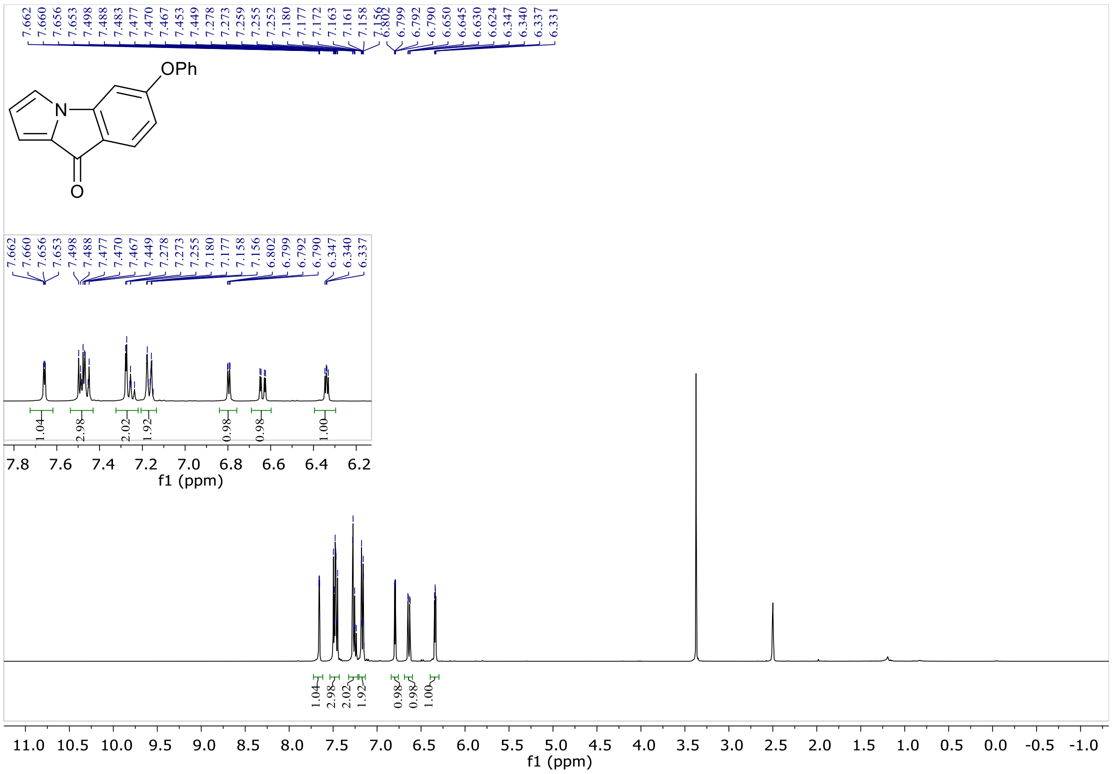
125.807
124.045
122.065
116.182
114.277
111.694
40.226
40.018
39.809
39.601
39.392
39.184
38.974
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.488
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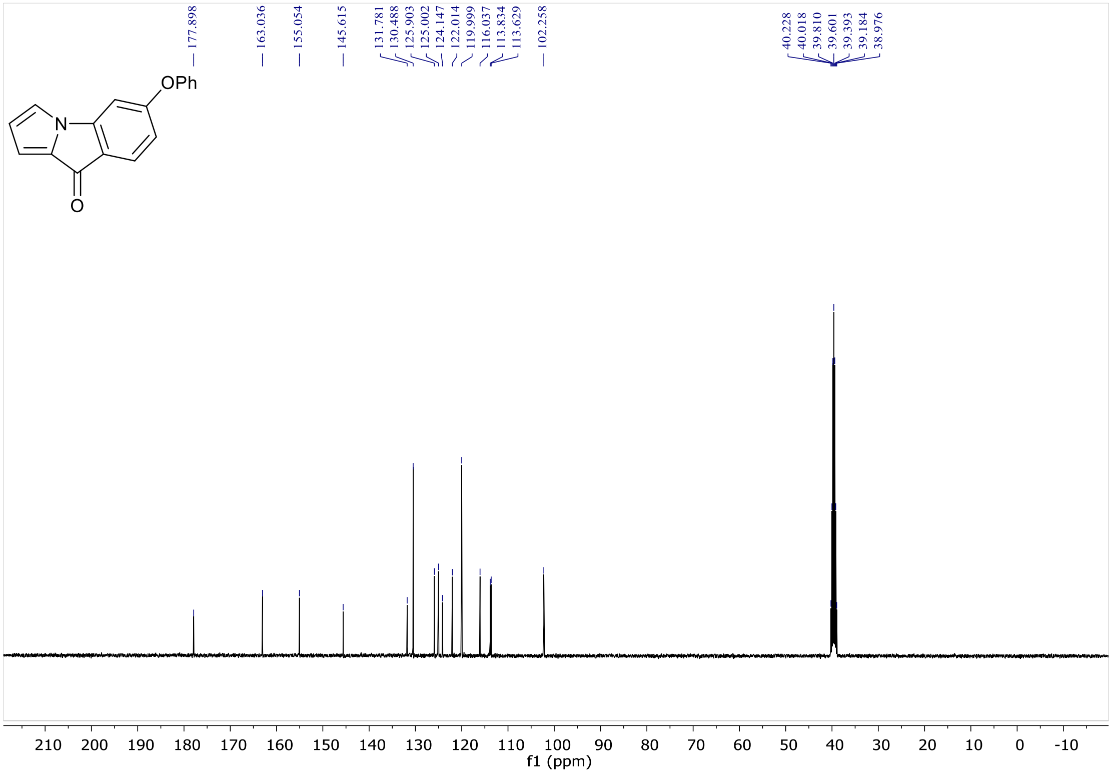
7.453
7.449
7.278
7.273
7.259
7.255
7.252
7.180
7.177
7.172
7.163
7.161
7.158
7.156
6.802
6.799
6.792
6.790
6.650
6.645
6.630
6.624
6.347
6.340
6.337
6.331
OPh
N
O
1.04
2.98
2.02
1.92
0.98
0.98
1.00
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2
f1 (ppm)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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125.002
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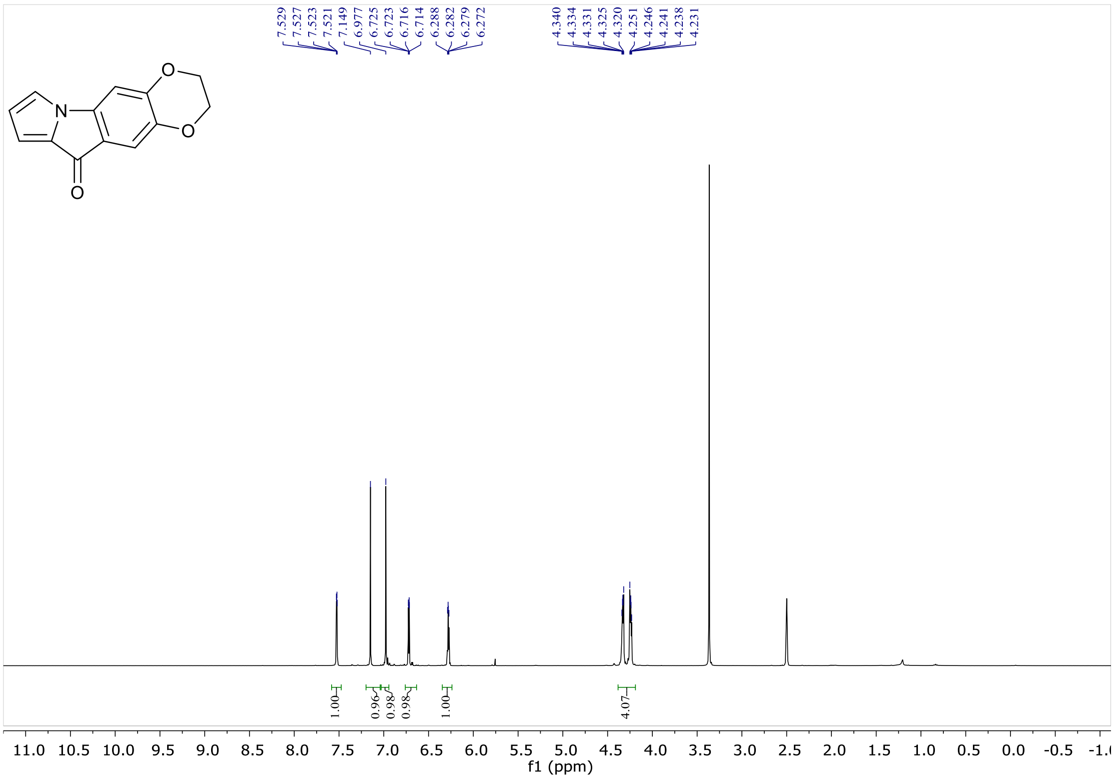
122.014
119.999
116.037
113.834
113.629
102.258
40.228
40.018
39.810
39.601
39.393
39.184
38.976
OPh
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.149
6.977
6.725
6.723
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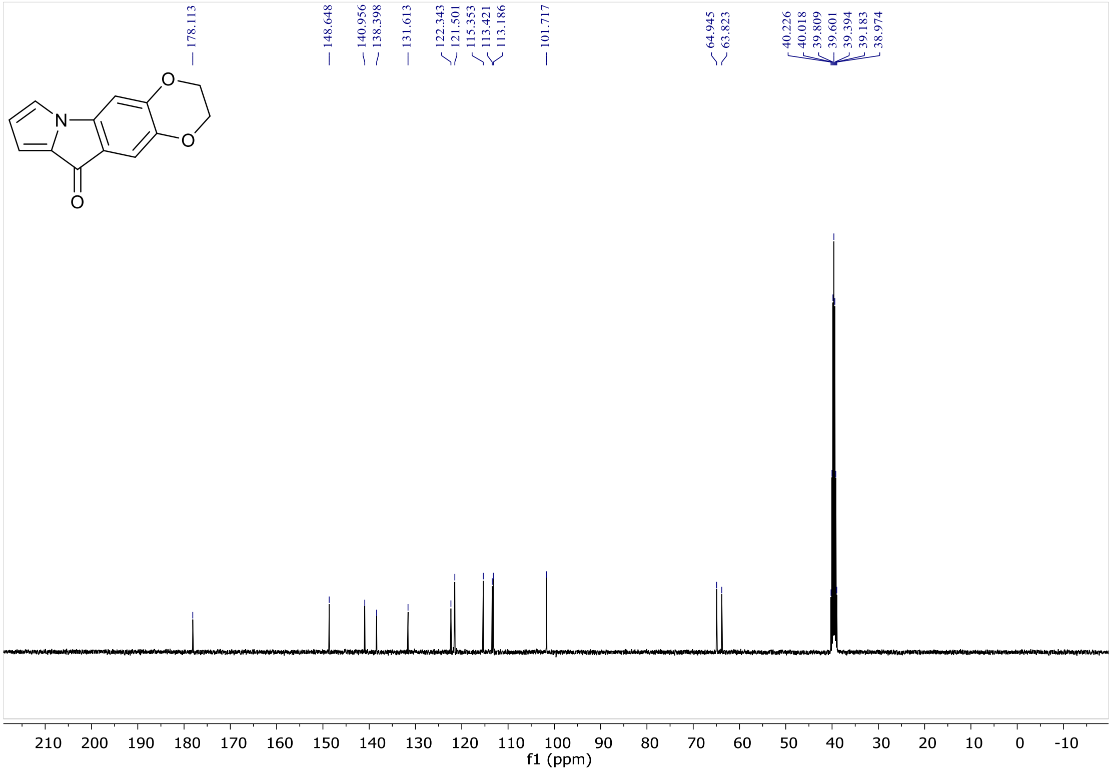
6.714
6.288
6.282
6.279
6.272
4.340
4.334
4.331
4.325
4.320
4.251
4.246
4.241
4.238
4.231
N
O
O
O
1.00
0.96
0.98
0.98
1.00
4.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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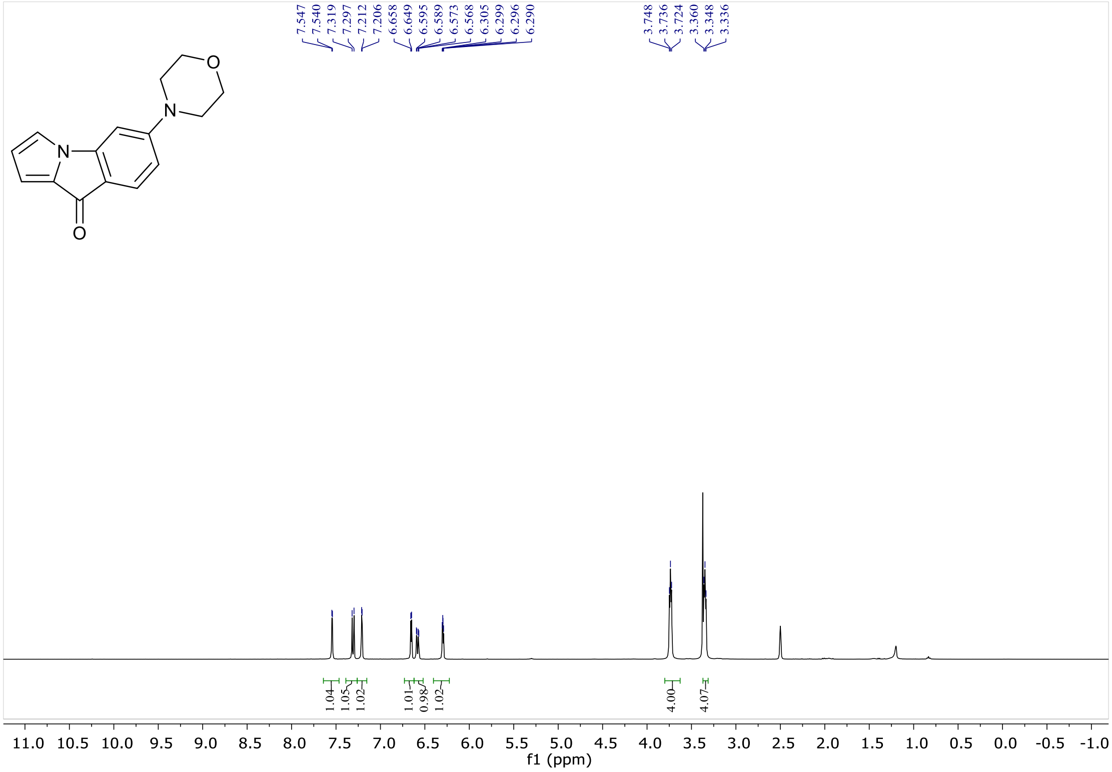
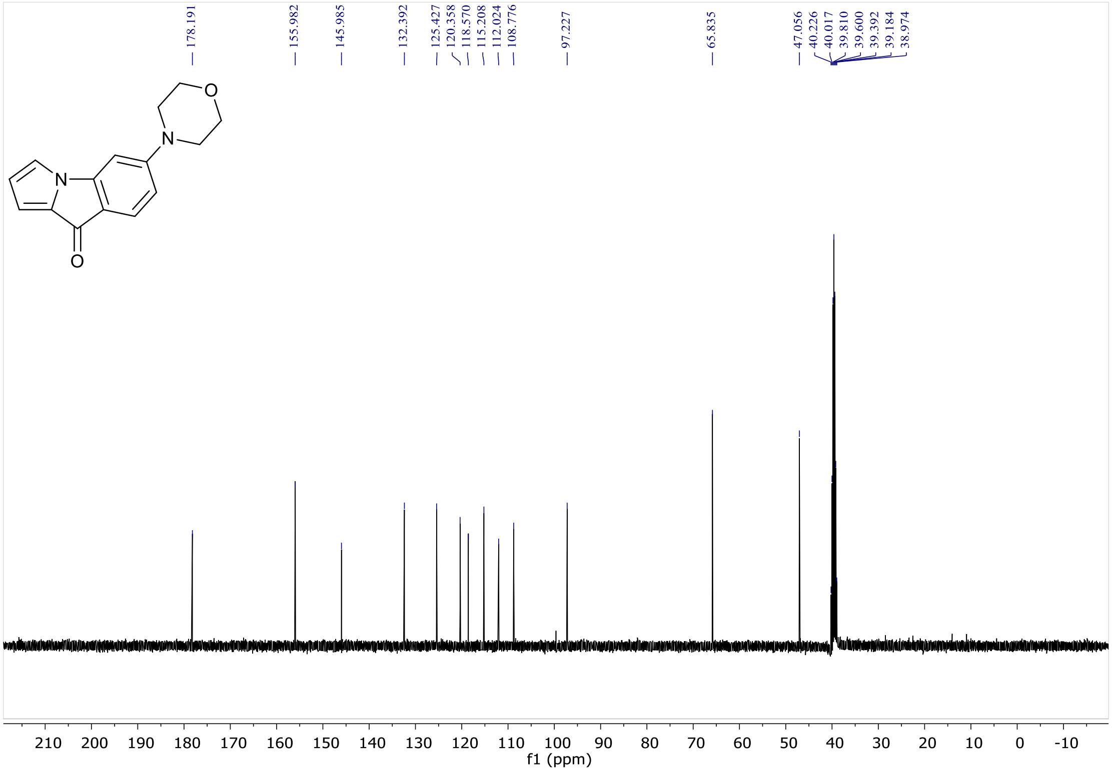
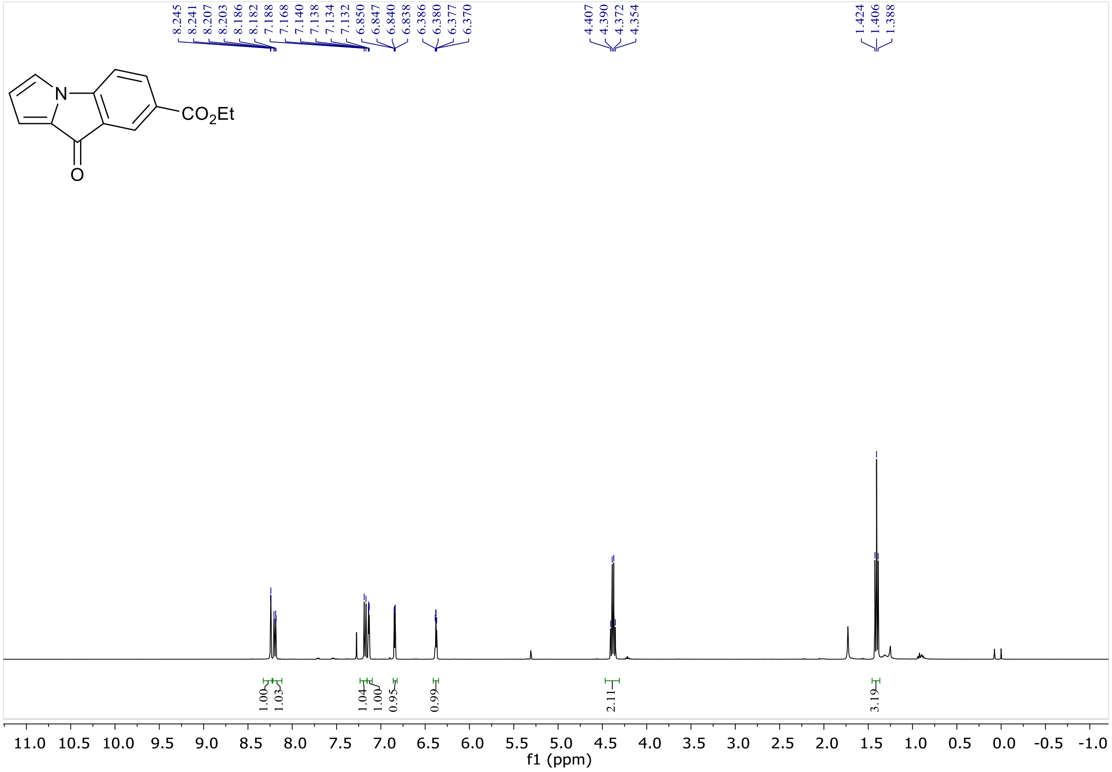
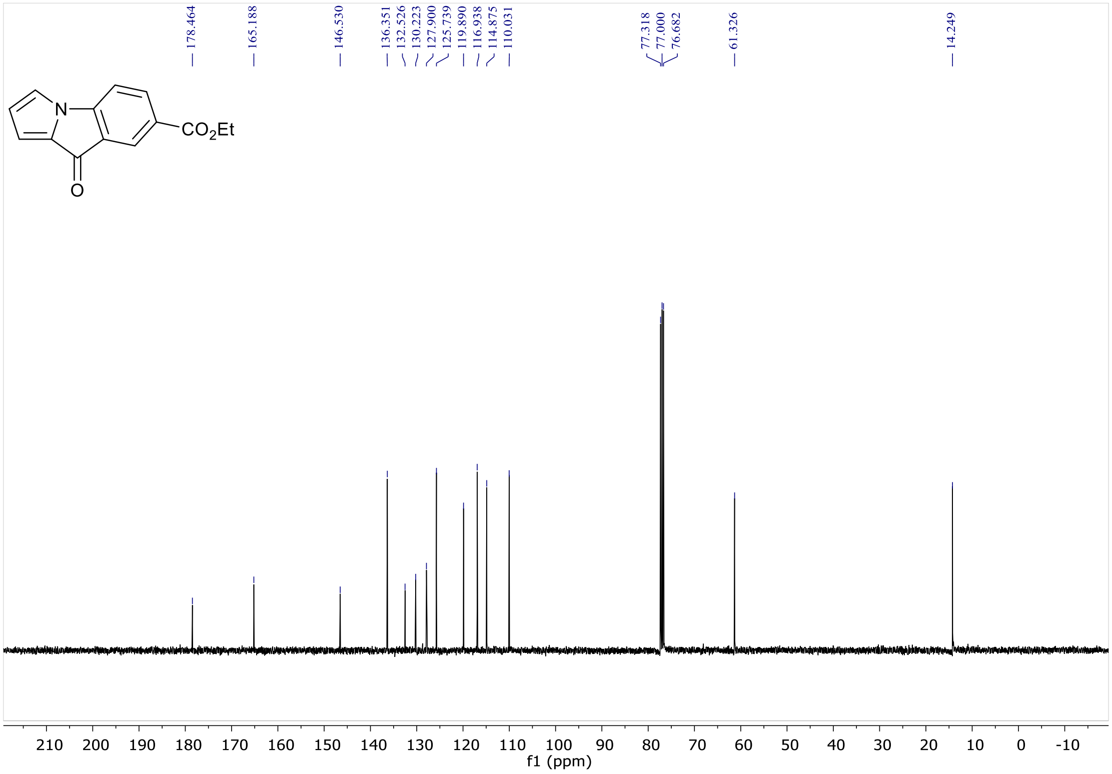
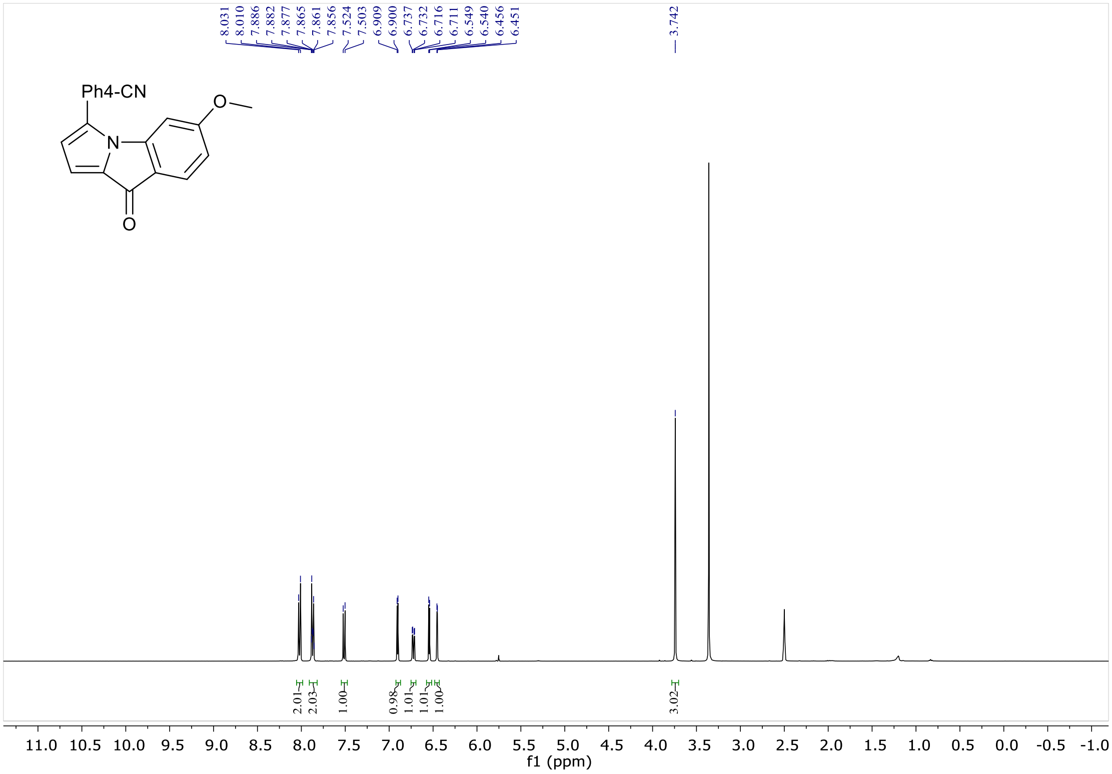
101.717
64.945
63.823
40.226
40.018
39.809
39.601
39.394
39.183
38.974
O
O
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

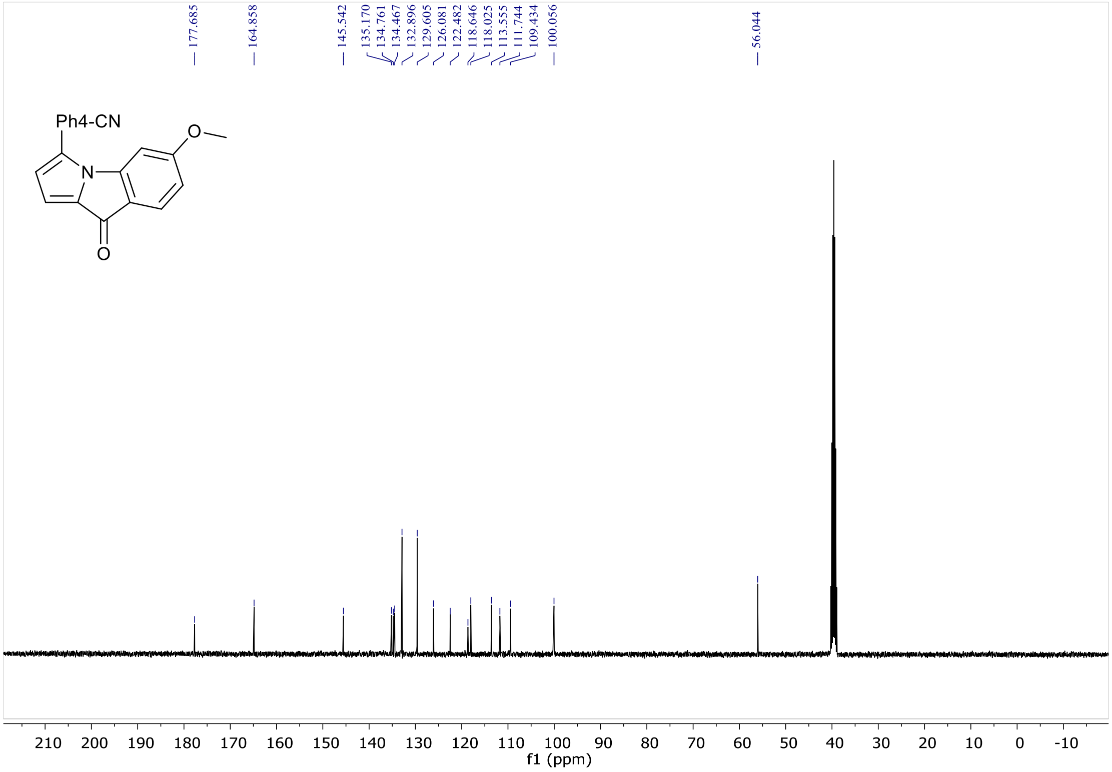

7.547
7.540
7.319
7.297
7.212
7.206
6.658
6.649
6.595
6.589
6.573
6.568
6.305
6.299
6.296
6.290
3.748
3.736
3.724
3.360
3.348
3.336
O
N
N
O
1.04
1.05
1.02
1.01
0.98
1.02
4.00
4.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

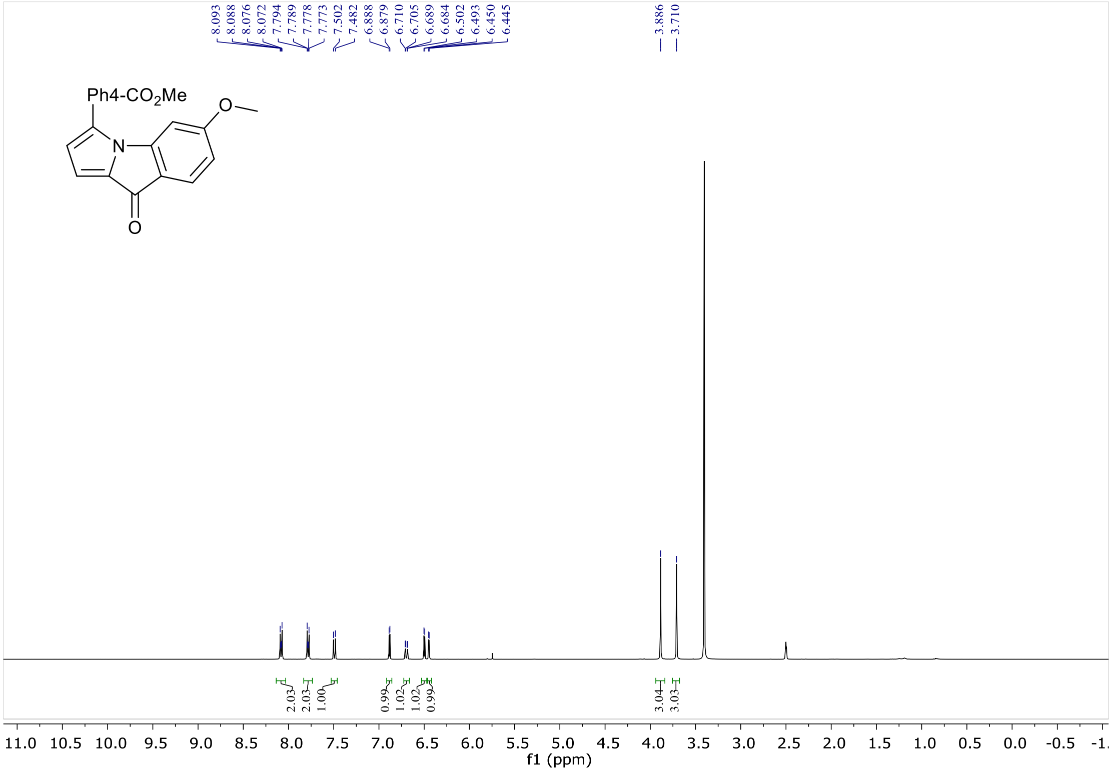

178.191
155.982
145.985
132.392
125.427
120.358
118.570
115.208
112.024
108.776
97.227
65.835
47.056
40.226
40.017
39.810
39.600
39.392
39.184
38.974
O
N
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

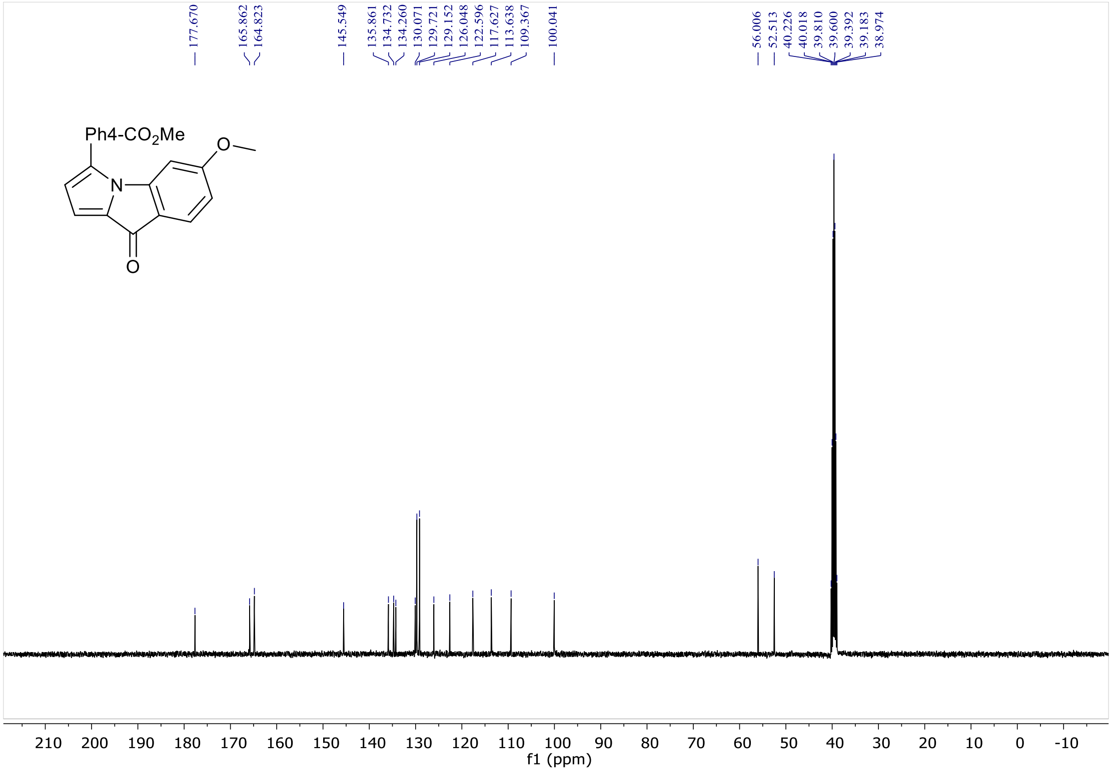

8.245
8.241
8.207
8.203
8.186
8.182
7.188
7.168
7.140
7.138
7.134
7.132
6.850
6.847
6.840
6.838
6.386
6.380
6.377
6.370
4.407
4.390
4.372
4.354
1.424
1.406
1.388
N
CO_2Et
O
1.00
1.03
1.04
1.00
0.95
0.99
2.11
3.19
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


178.464
165.188
146.530
136.351
132.526
130.223
127.900
125.739
119.890
116.938
114.875
110.031
77.318
77.000
76.682
61.326
14.249
N
CO_2Et
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.031
8.010
7.886
7.882
7.877
7.865
7.861
7.856
7.524
7.503
6.909
6.900
6.737
6.732
6.716
6.711
6.549
6.540
6.456
6.451
3.742
Ph4-CN
N
O
O
2.01
2.03
1.00
0.98
1.01
1.01
1.00
3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


177.685
164.858
145.542
135.170
134.761
134.467
132.896
129.605
126.081
122.482
118.646
118.025
113.555
111.744
109.434
100.056
56.044
Ph4-CN
N
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.093
8.088
8.076
8.072
7.794
7.789
7.778
7.773
7.502
7.482
6.888
6.879
6.710
6.705
6.689
6.684
6.502
6.493
6.450
6.445
3.886
3.710
Ph4-CO2Me
N
O
O
2.03
2.03
1.00
0.99
1.02
1.02
0.99
3.04
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)



8.Reference

[1] Sunil Kumar, Sada Krishnakanth, Jomon Mathew, Zvika Pomerantz, Jean-Paul Lellouche, and Subrata Ghosh, *J. Phys. Chem. C*, **2014**, *118*, 2570-2579.

[2] Riko Odani, Koji Hirano, Tetsuya Satoh, and Masahiro Miura, *J. Org. Chem.* **2013**, *78*, 11045-11052