SUPPORTING INFORMATION

Copper(I)/Phosphine-Catalyzed Tandem Carboxylation/Annulation of Terminal Alkynes with Ambient Pressure of CO_2: One-Pot Access to 3a-Hydroxyisoxazolo[3,2-*a*]isoindol-8(3a*H*)-ones

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Contents Table

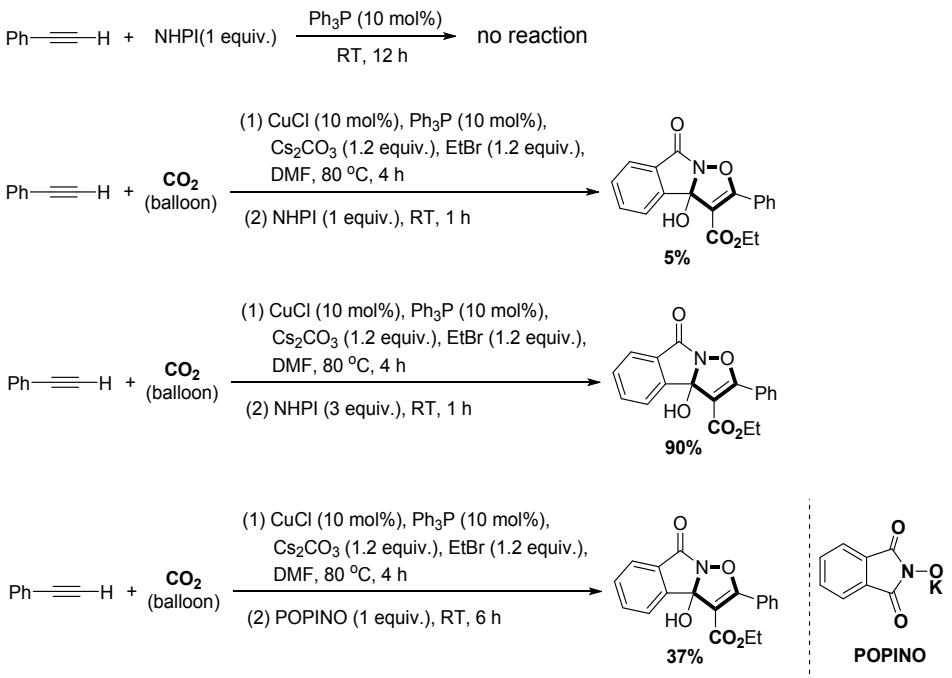
1. General Information

The starting materials were commercially available and all the reactions were carried out in dried glasswares with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 ^{o}C) and ethyl acetate. All products were characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy. NMR spectra were determined on Bruker 400. ^{1}H NMR chemical shifts were referenced to residual solvent as determined relative to DMSO-d_6 (2.50 ppm). The ^{13}C NMR chemical shifts were reported in ppm relative to the carbon resonance of DMSO-d_6 (central peak is 39.52 ppm). ^{1}H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, J, are reported in Hertz (Hz). High resolution mass spectrometry was conducted using a Varian 7.0 T FTICR-MS by ESI technique.

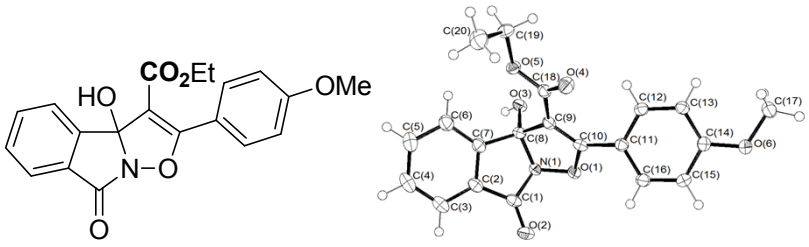
2. Preparation of potassium phthalimide-N-oxyl (POPINO)[32]

Into a 100 mL flask was added NHPI (1.63 g, 10 mmol) and KOH (0.056 g, 10 mmol). Then EtOH (50 ml) was added. After reflux conditions for 30 min, the obtained deep red solid was filtered, and washed with cold EtOH (50 mL).

3. Control experiments



4. Crystallography of compound 2b



Single-crystal structure of **2b**

Table S1. Crystal data and structure refinement.

Empirical formula	$C_{20}H_{17}NO_6$
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
space group	P2(1)/C
Unit cell dimensions	a = 7.8241(16) Å b = 24.301(5) Å c = 9.1574(18) Å alpha = 90 deg. beta = 93.76(3) deg. gamma = 90 deg.
Volume	1737.4(6) $Å^3$
Z	4
Calculated density	1.404 Mg/m^3
Absorption coefficient	0.105 mm^{-1}
F(000)	768
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	1.68 to 27.99 deg.
Reflections collected / unique	15793 / 4064 [R(int) = 0.0590]
Data / restraints / parameters	4064 / 0 / 248
Goodness-of-fit on F^2	0.979
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.1200
R indices (all data)	R1 = 0.0660, wR2 = 0.1305

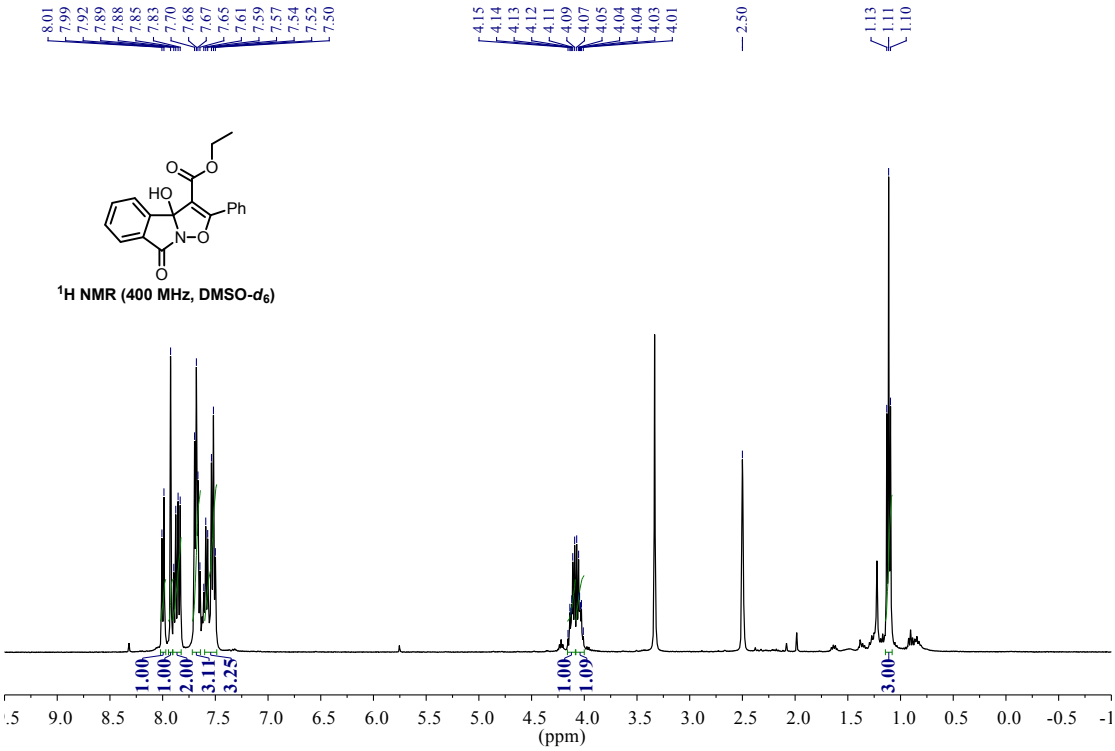
Table S2. Bond lengths [A] and angles [deg].

O(1)-C(10)	1.3835(17)
O(1)-N(1)	1.4338(16)
O(2)-C(1)	1.2178(19)
O(3)-C(8)	1.4046(17)
O(4)-C(18)	1.2147(18)
O(5)-C(18)	1.3399(18)

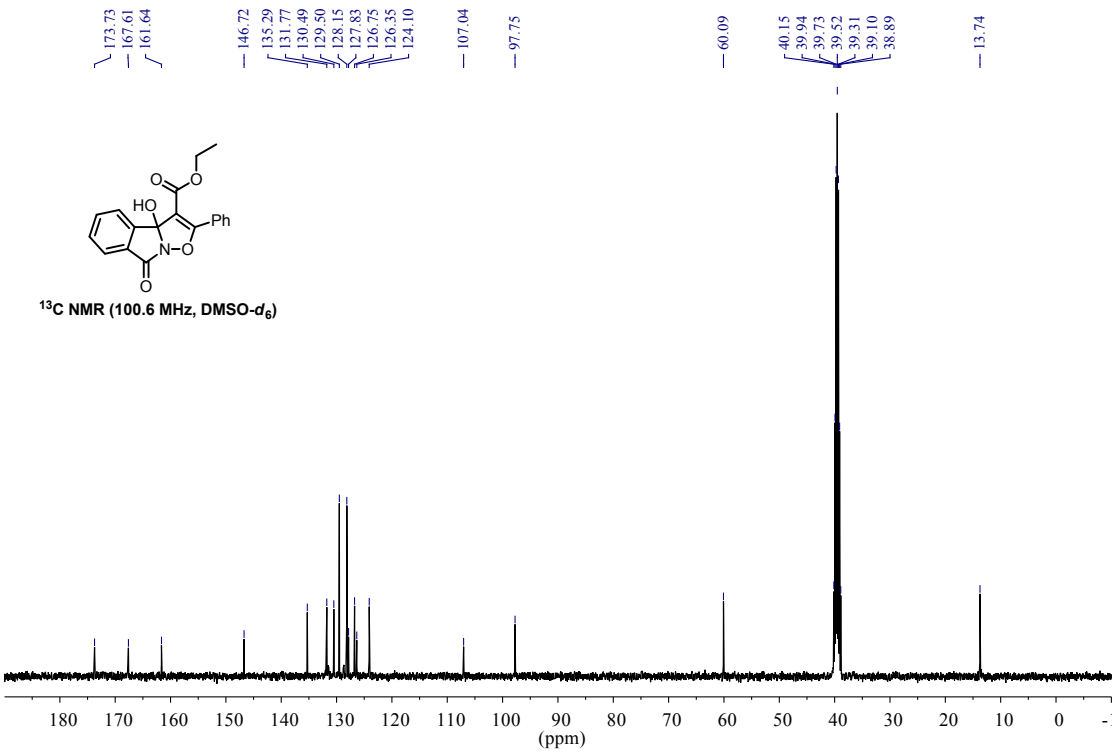
O(5)-C(19)	1.4610(17)
O(6)-C(14)	1.3597(19)
O(6)-C(17)	1.4328(19)
N(1)-C(1)	1.4114(18)
N(1)-C(8)	1.4921(19)
C(1)-C(2)	1.477(2)
C(2)-C(3)	1.385(2)
C(2)-C(7)	1.393(2)
C(3)-C(4)	1.386(3)
C(4)-C(5)	1.394(2)
C(5)-C(6)	1.396(2)
C(6)-C(7)	1.387(2)
C(7)-C(8)	1.521(2)
C(8)-C(9)	1.514(2)
C(9)-C(10)	1.342(2)
C(9)-C(18)	1.468(2)
C(10)-C(11)	1.468(2)
C(11)-C(12)	1.396(2)
C(11)-C(16)	1.396(2)
C(12)-C(13)	1.384(2)
C(13)-C(14)	1.388(2)
C(14)-C(15)	1.402(2)
C(15)-C(16)	1.384(2)
C(19)-C(20)	1.504(2)
C(10)-O(1)-N(1)	105.26(11)
C(18)-O(5)-C(19)	116.42(12)
C(14)-O(6)-C(17)	118.46(12)
C(1)-N(1)-O(1)	112.31(12)
C(1)-N(1)-C(8)	110.78(12)
O(1)-N(1)-C(8)	109.35(10)
O(2)-C(1)-N(1)	123.84(15)
O(2)-C(1)-C(2)	130.83(14)
N(1)-C(1)-C(2)	105.33(13)
C(3)-C(2)-C(7)	122.21(16)
C(3)-C(2)-C(1)	129.32(15)
C(7)-C(2)-C(1)	108.46(13)
C(2)-C(3)-C(4)	117.56(16)
C(3)-C(4)-C(5)	120.90(16)
C(4)-C(5)-C(6)	121.12(17)
C(7)-C(6)-C(5)	118.04(16)
C(6)-C(7)-C(2)	120.15(14)
C(6)-C(7)-C(8)	129.45(14)
C(2)-C(7)-C(8)	110.28(13)
O(3)-C(8)-N(1)	112.54(11)

O(3)-C(8)-C(9)	109.27(12)
N(1)-C(8)-C(9)	99.62(12)
O(3)-C(8)-C(7)	113.00(13)
N(1)-C(8)-C(7)	100.79(11)
C(9)-C(8)-C(7)	120.41(12)
C(10)-C(9)-C(18)	126.58(14)
C(10)-C(9)-C(8)	108.95(13)
C(18)-C(9)-C(8)	124.41(14)
C(9)-C(10)-O(1)	113.13(13)
C(9)-C(10)-C(11)	134.56(14)
O(1)-C(10)-C(11)	112.12(13)
C(12)-C(11)-C(16)	118.79(14)
C(12)-C(11)-C(10)	121.20(13)
C(16)-C(11)-C(10)	119.90(13)
C(13)-C(12)-C(11)	121.70(14)
C(12)-C(13)-C(14)	118.84(14)
O(6)-C(14)-C(13)	124.31(14)
O(6)-C(14)-C(15)	115.20(14)
C(13)-C(14)-C(15)	120.48(14)
C(16)-C(15)-C(14)	119.88(15)
C(15)-C(16)-C(11)	120.29(14)
O(4)-C(18)-O(5)	123.93(14)
O(4)-C(18)-C(9)	125.50(15)
O(5)-C(18)-C(9)	110.56(13)
O(5)-C(19)-C(20)	111.00(13)

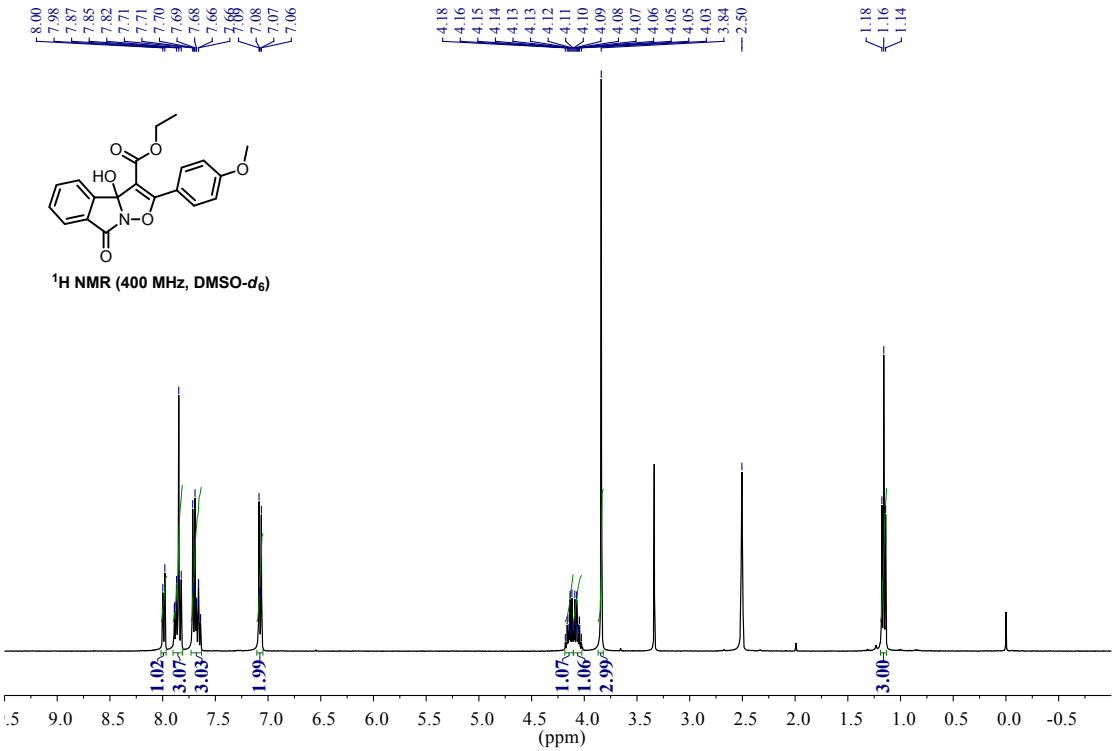
5. NMR Spectral Copies of the Products



^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100.6 MHz, DMSO-d_6)



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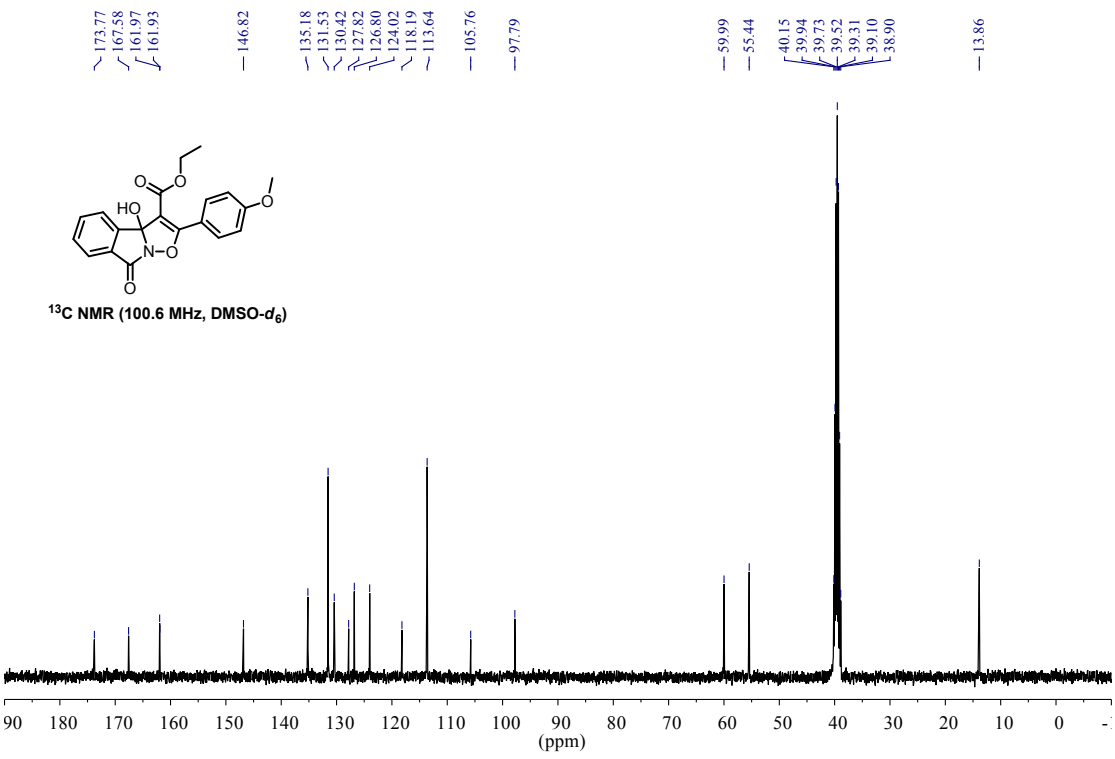
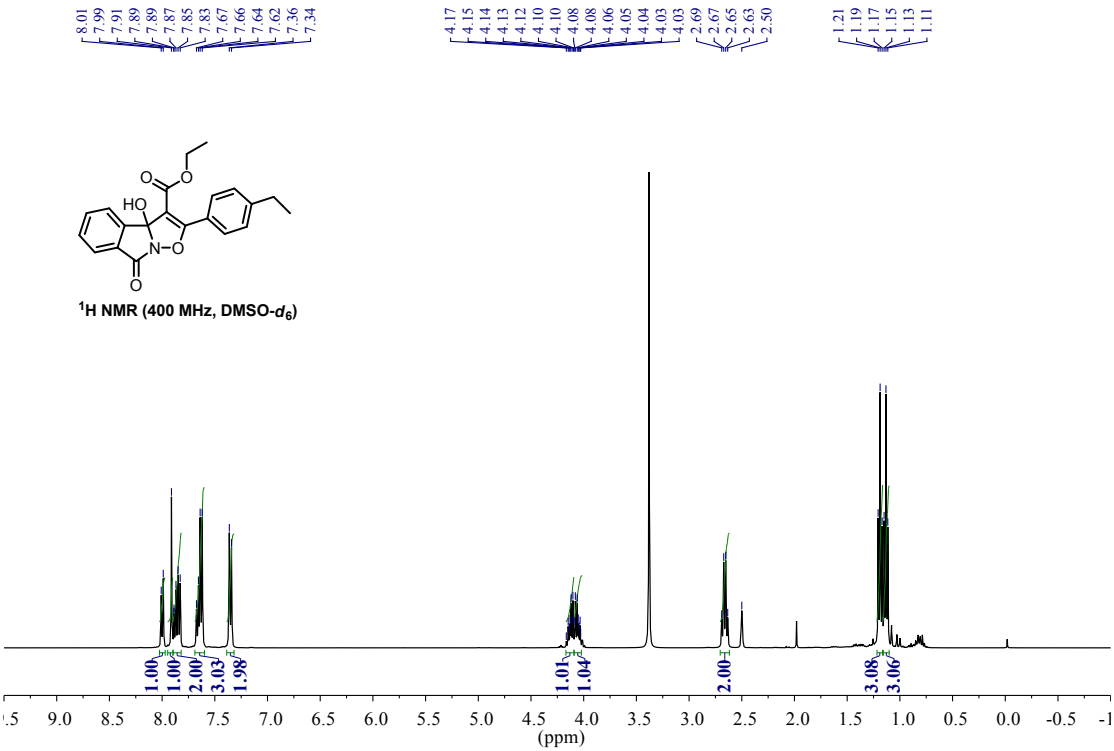
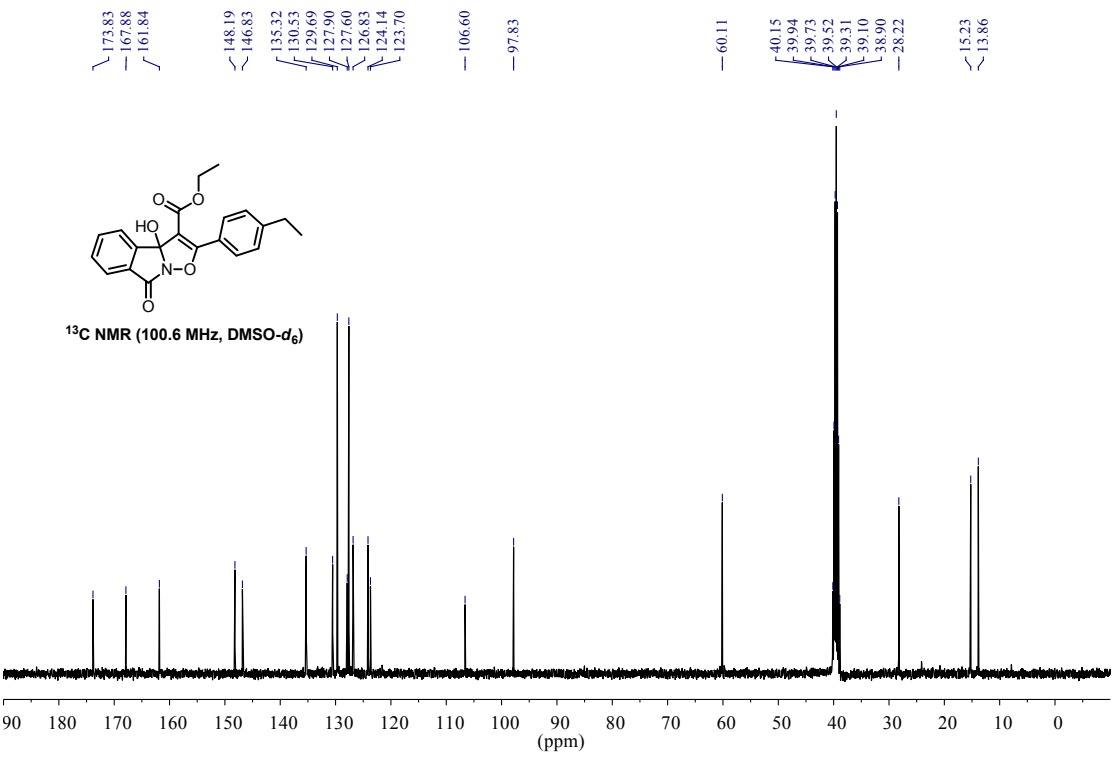


^{13}C NMR (100.6 MHz, DMSO-d_6)


8.01
7.99
7.91
7.89
7.89
7.87
7.85
7.83
7.67
7.66
7.64
7.62
7.36
7.34
4.17
4.15
4.14
4.13
4.12
4.10
4.10
4.08
4.08
4.06
4.05
4.04
4.03
4.03
2.69
2.67
2.65
2.63
2.50
1.21
1.19
1.17
1.15
1.13
1.11
HO
N–O
O
O
O
1H NMR (400 MHz, DMSO-d6)
1.00
1.00
2.00
3.03
1.98
1.01
1.04
2.00
3.08
3.06
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
(ppm)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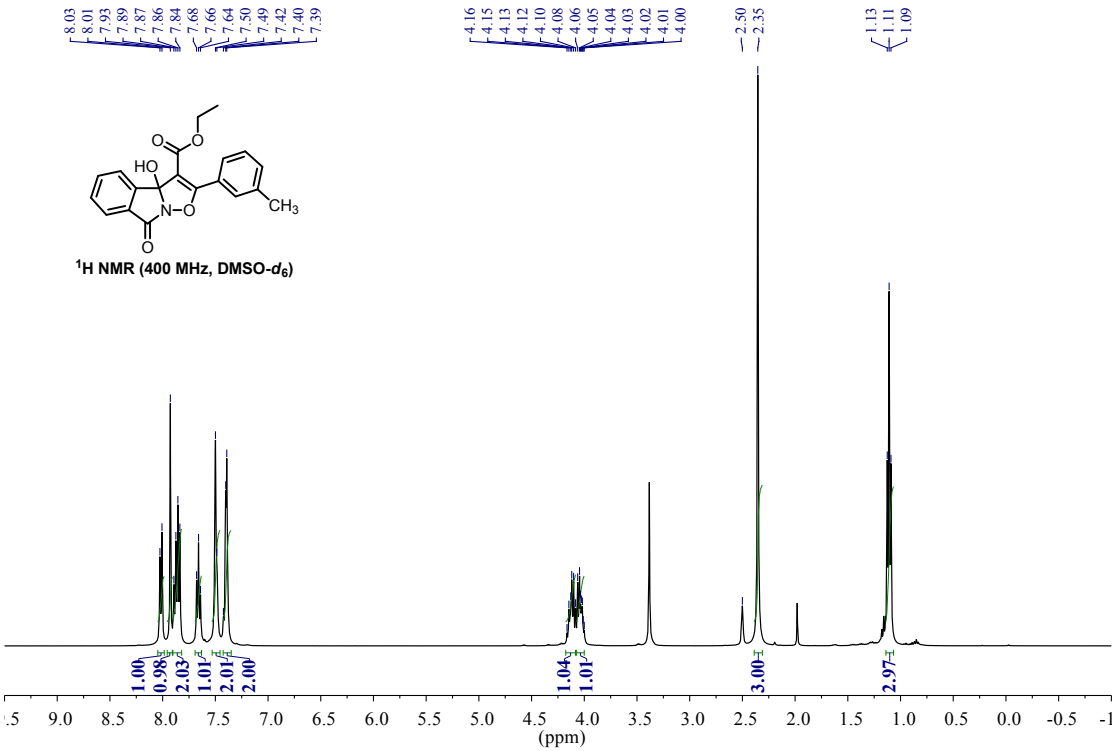
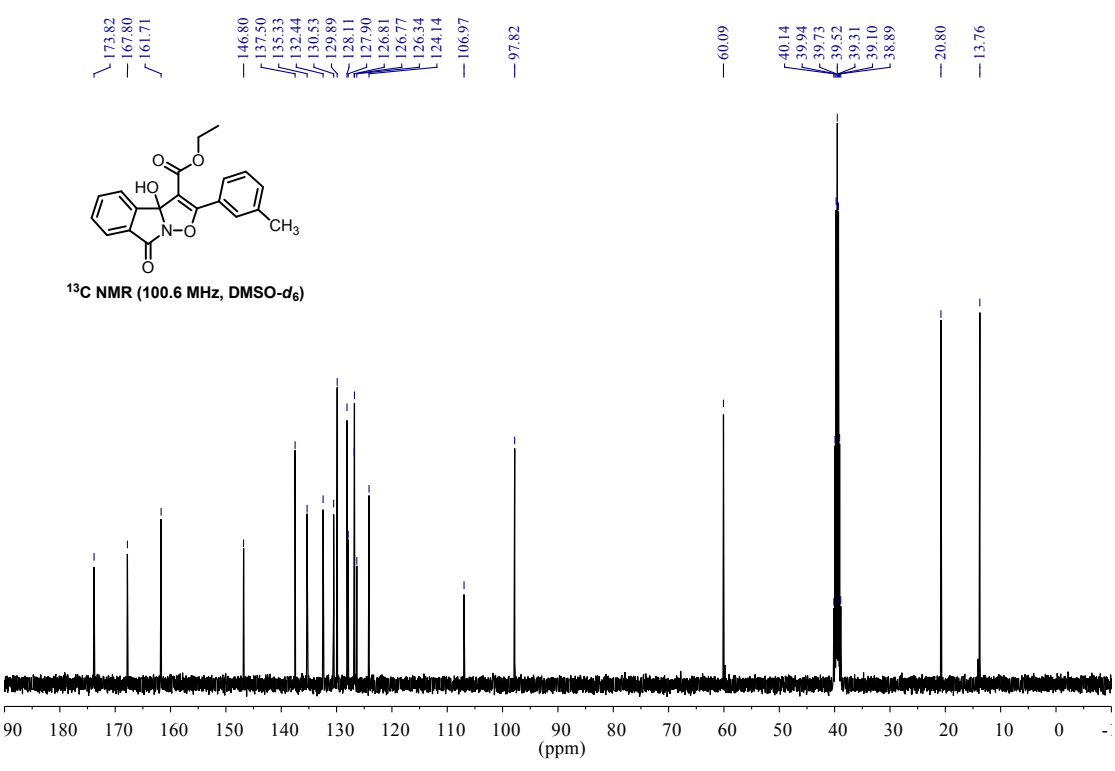
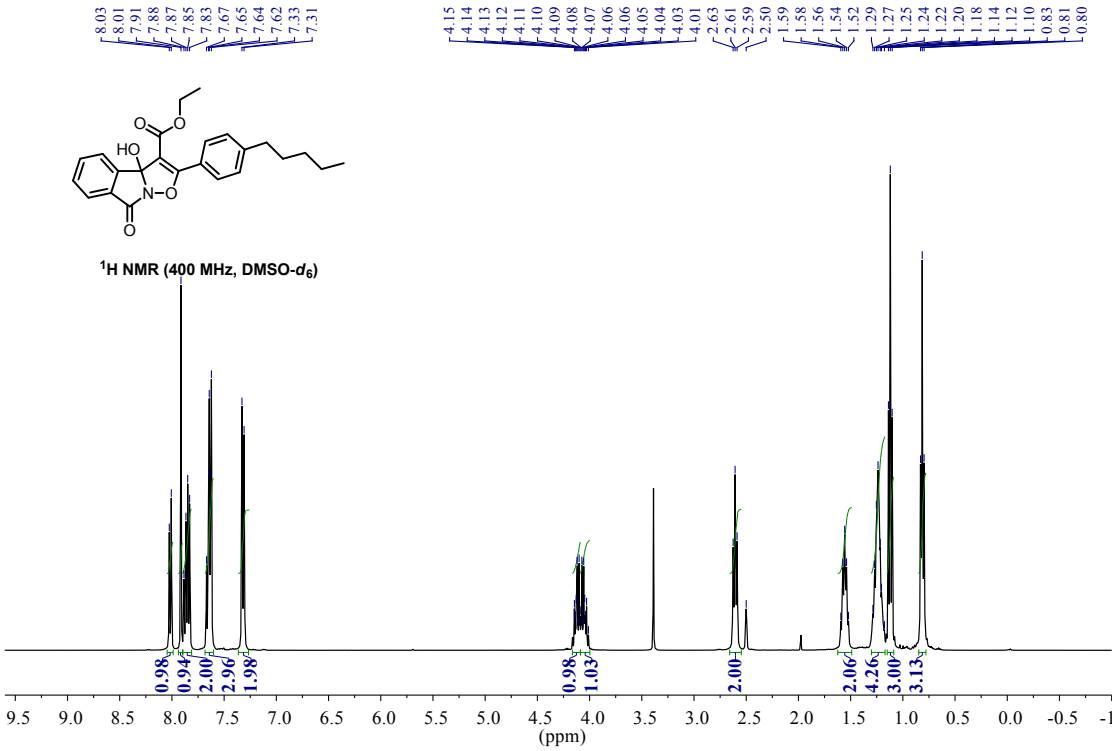
167.88
161.84
148.19
146.83
135.32
130.53
129.69
127.90
127.60
126.83
124.14
123.70
106.60
97.83
60.11
40.15
39.94
39.73
39.52
39.31
39.10
38.90
28.22
15.23
13.86
HO
N–O
O
O
O
13C NMR (100.6 MHz, DMSO-d6)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)



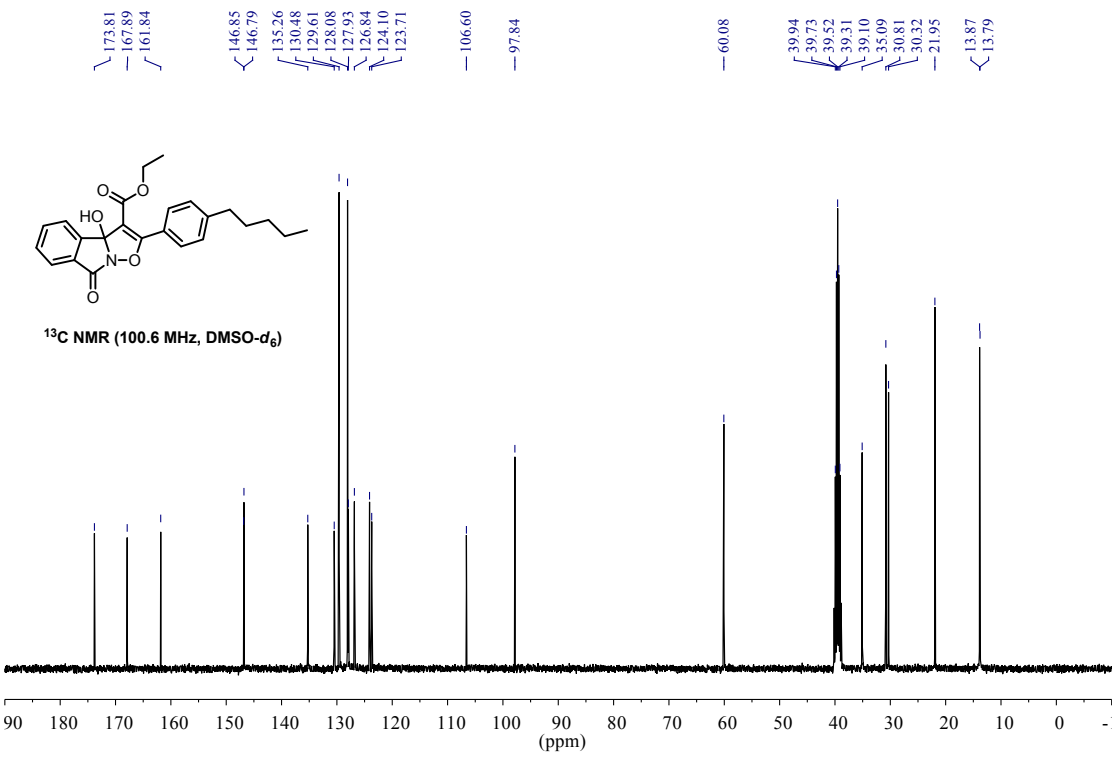
^{1}H NMR (400 MHz, DMSO-d_6)



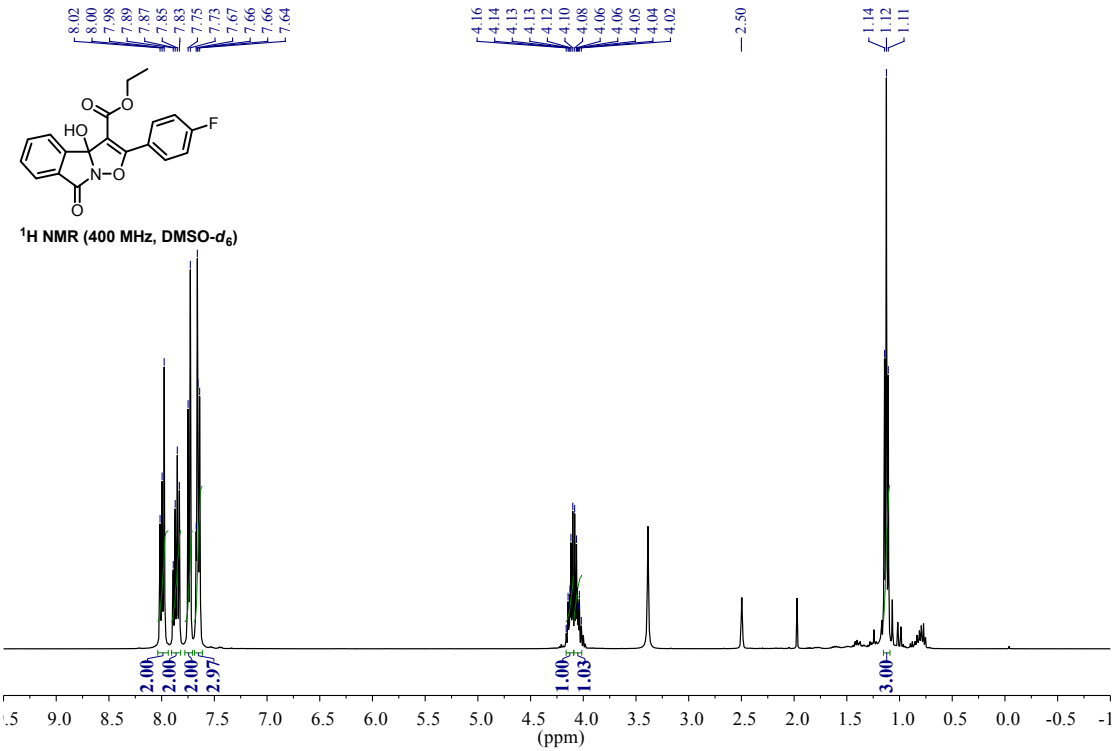
^{13}C NMR (100.6 MHz, DMSO-d_6)



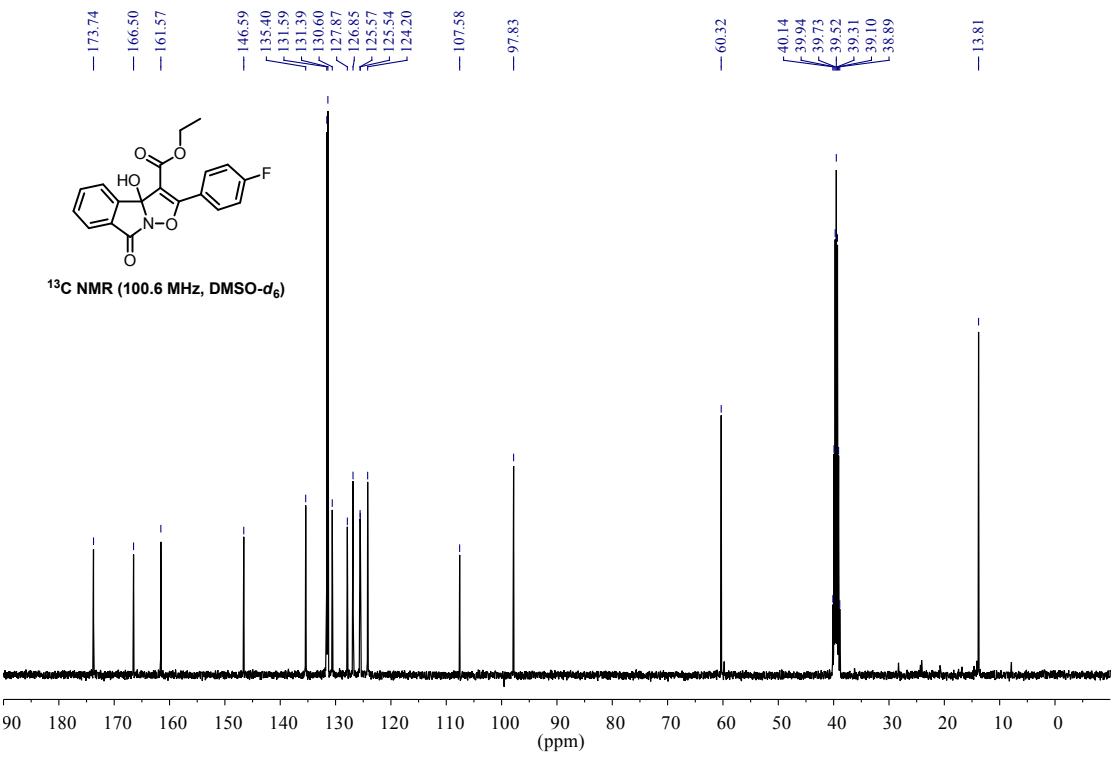
^{1}H NMR (400 MHz, DMSO-d_6)



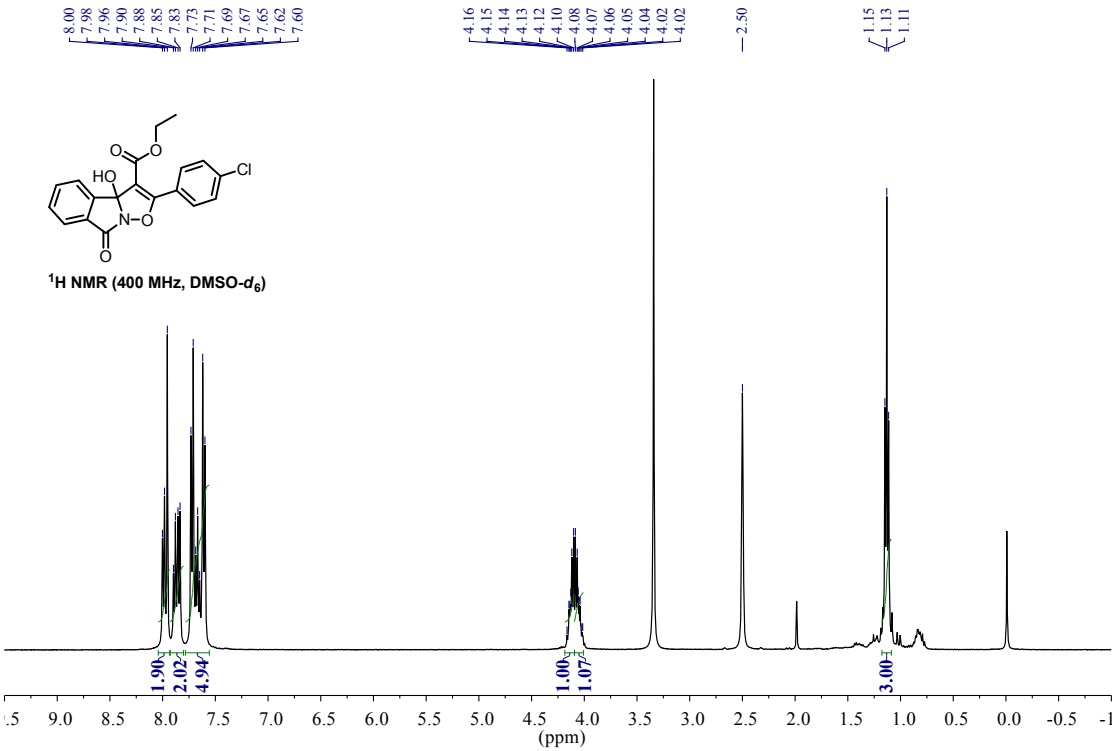
^{13}C NMR (100.6 MHz, DMSO-d_6)



^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100.6 MHz, DMSO-d_6)


8.00
7.98
7.96
7.90
7.88
7.85
7.83
7.73
7.71
7.69
7.67
7.65
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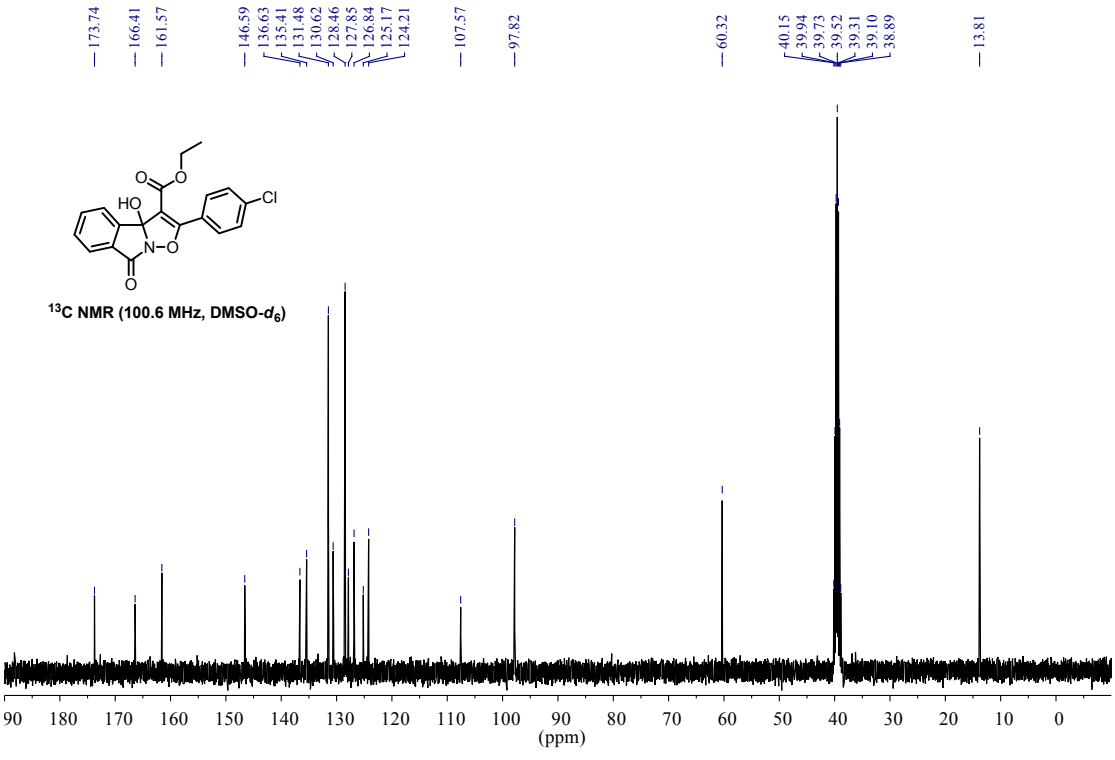
7.60
4.16
4.15
4.14
4.13
4.12
4.10
4.08
4.07
4.06
4.05
4.04
4.02
4.02
2.50
1.15
1.13
1.11
O
O
HO
N–O
O
Cl
1H NMR (400 MHz, DMSO-d6)
1.90
2.02
4.94
1.00
1.07
3.00
(ppm)


173.74
166.41
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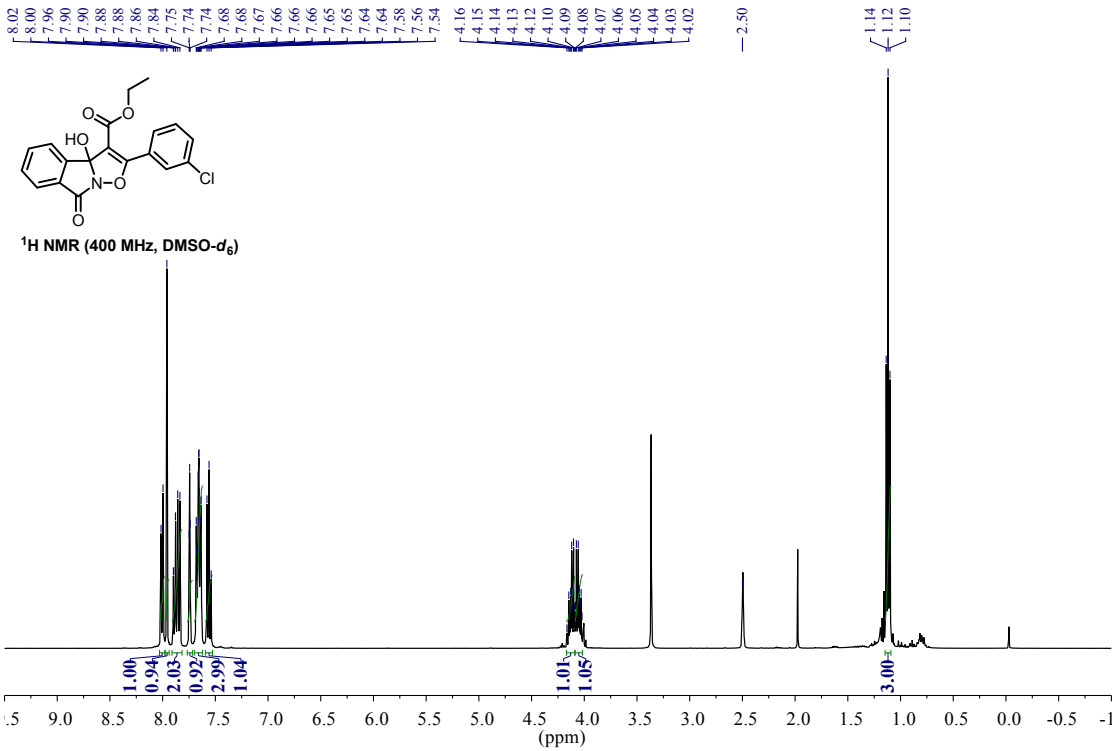
146.59
136.63
135.41
131.48
130.62
128.46
127.85
126.84
125.17
124.21
107.57
97.82
60.32
40.15
39.94
39.73
39.52
39.31
39.10
38.89
13.81
O
O
HO
N–O
O
Cl
13C NMR (100.6 MHz, DMSO-d6)
(ppm)



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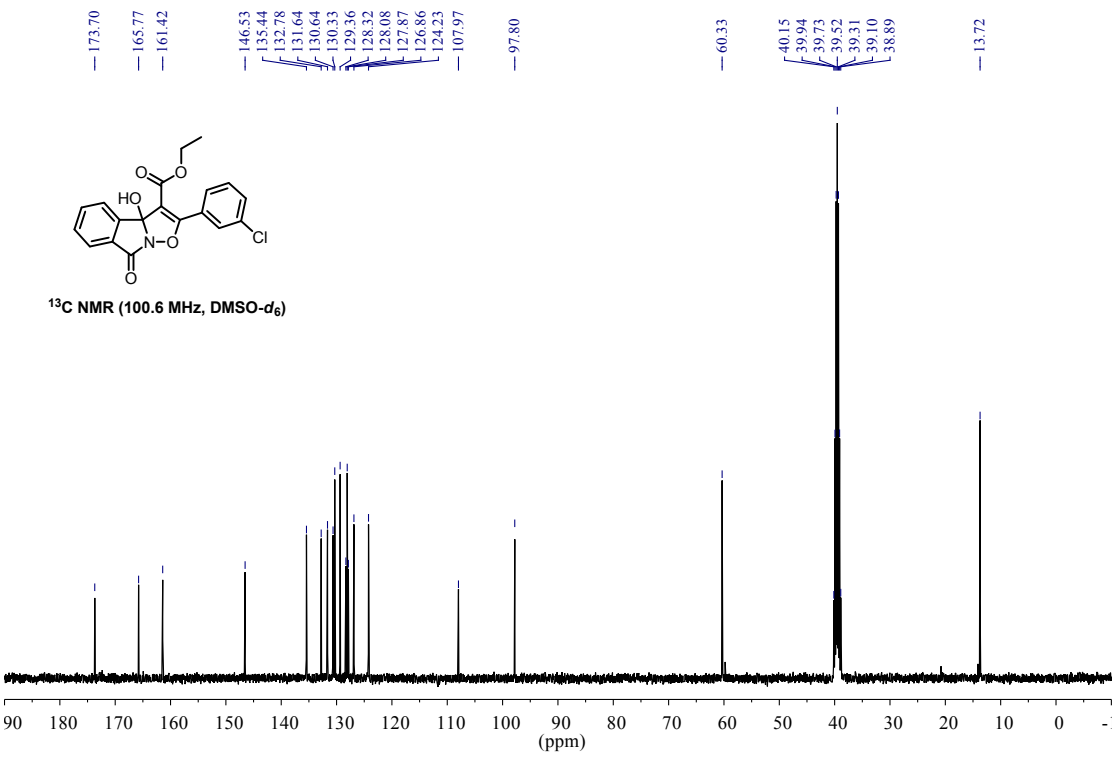

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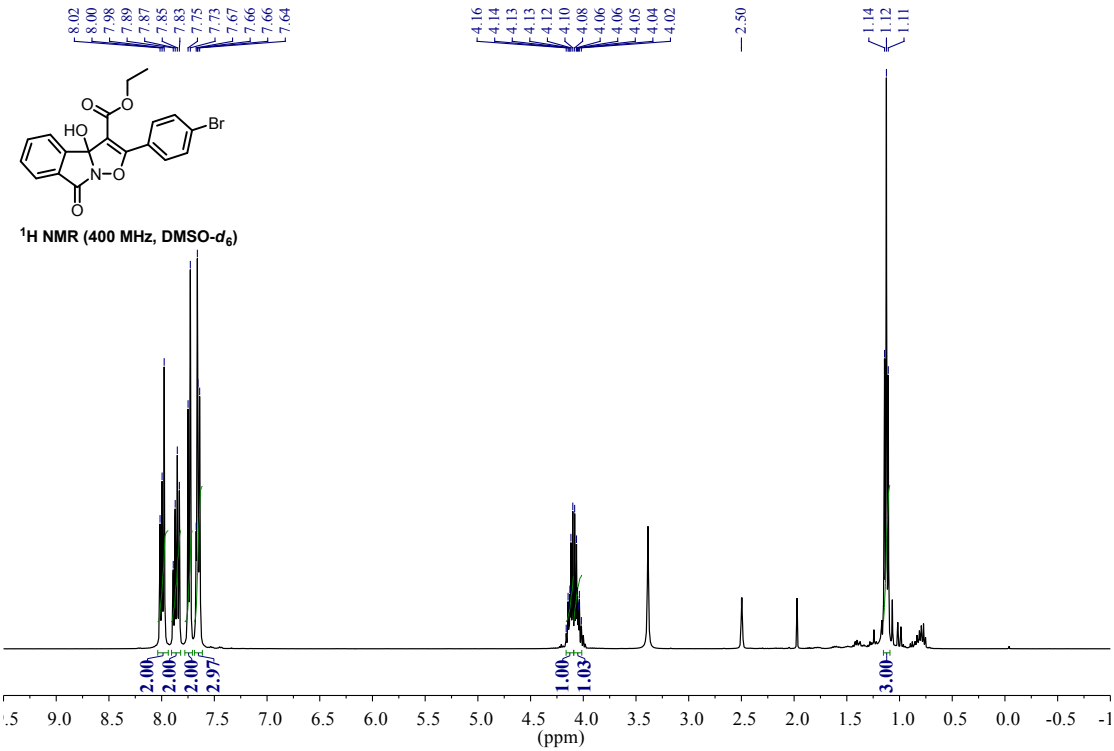
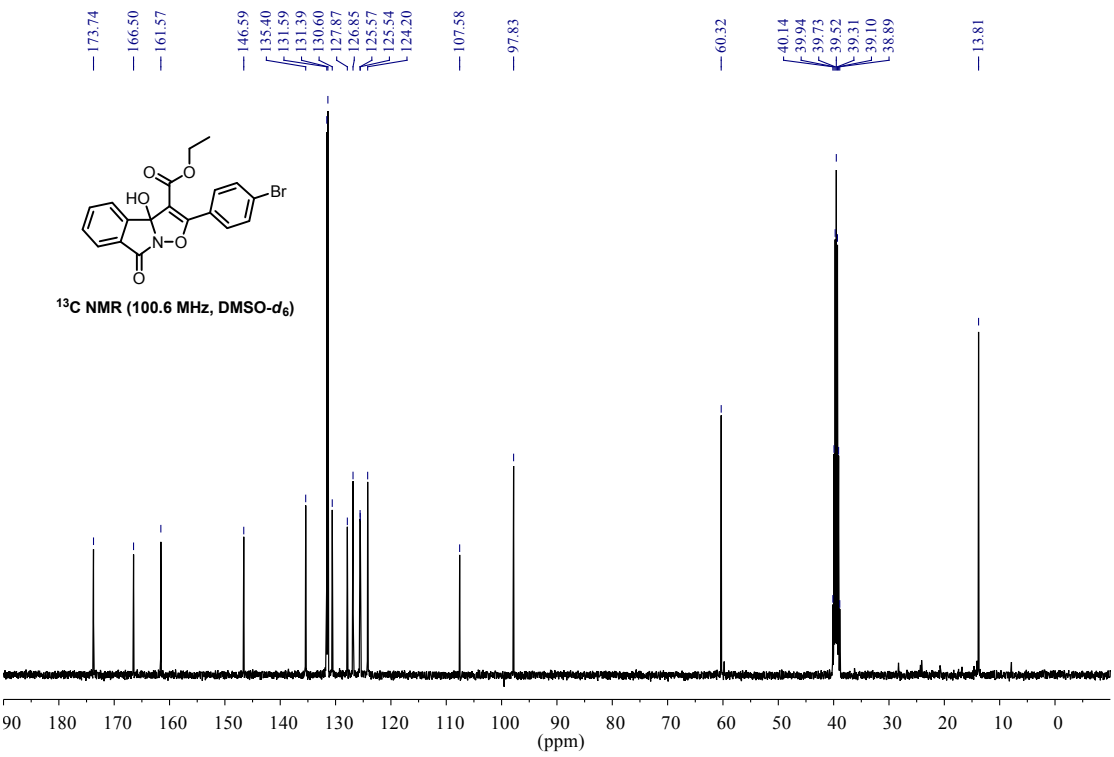


^{1}H NMR (400 MHz, DMSO-d_6)



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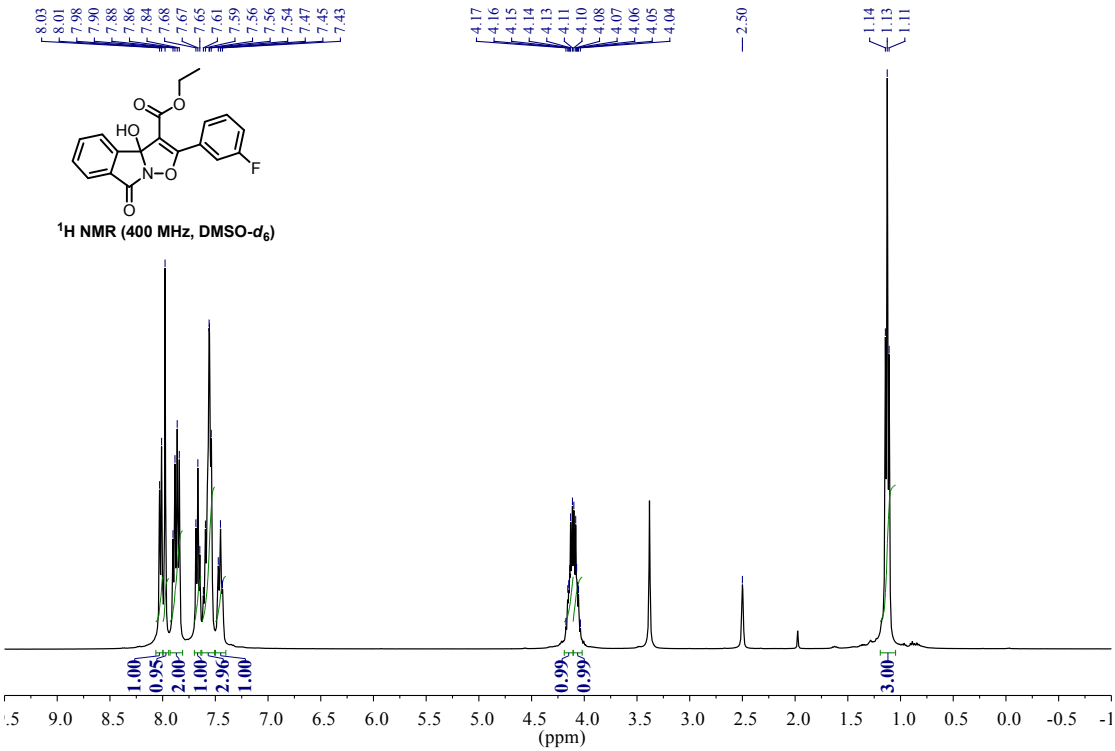

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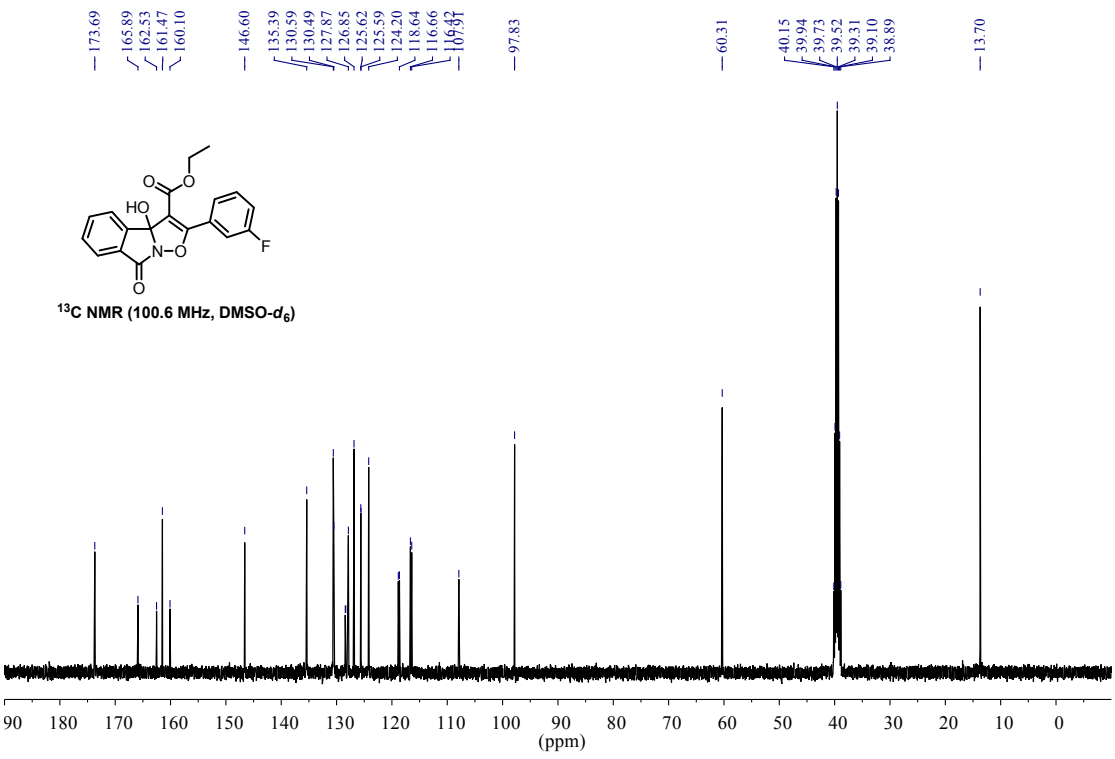

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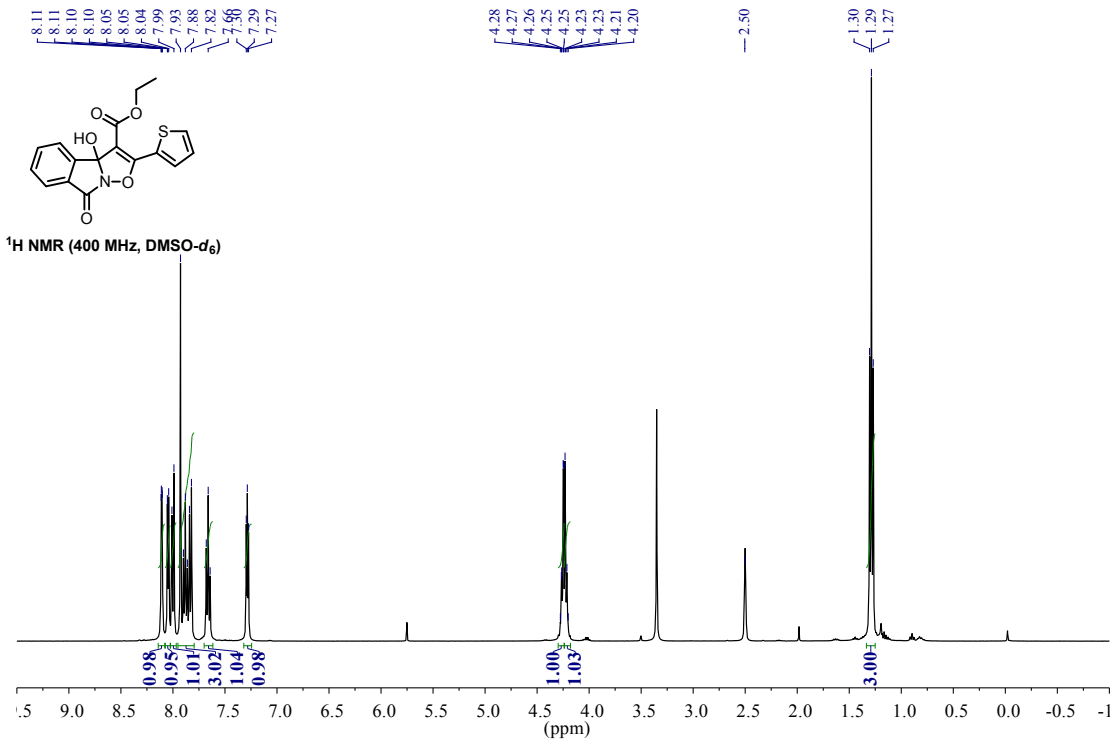

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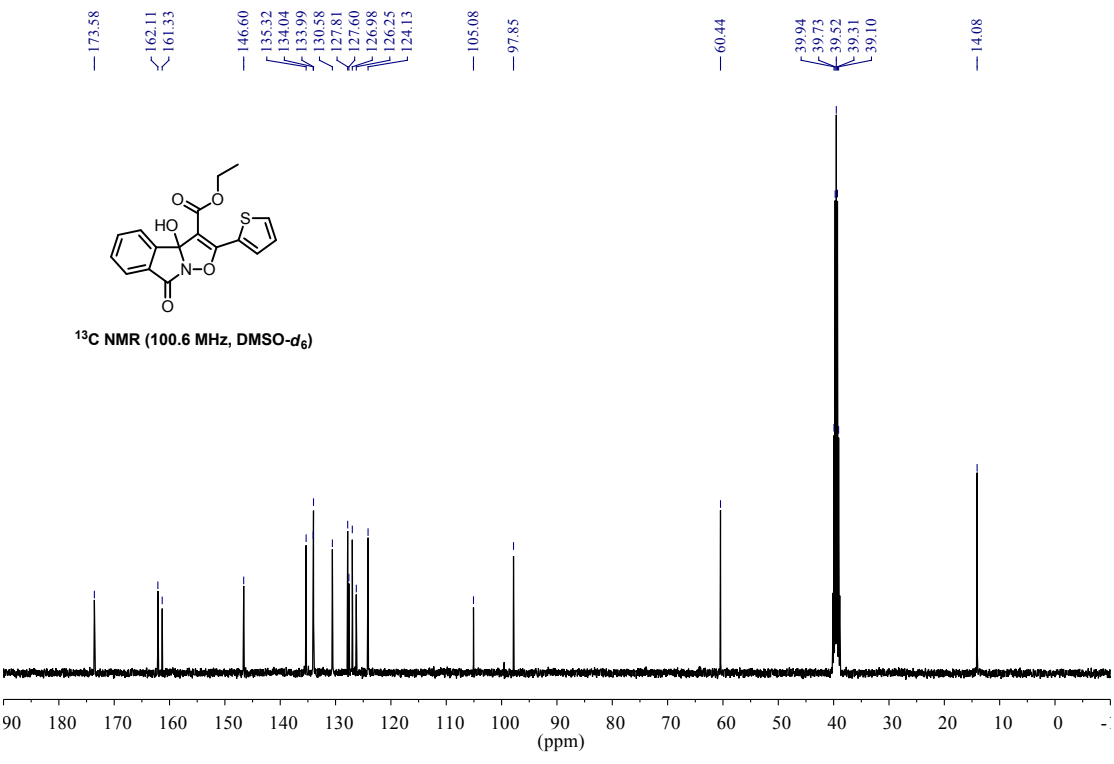
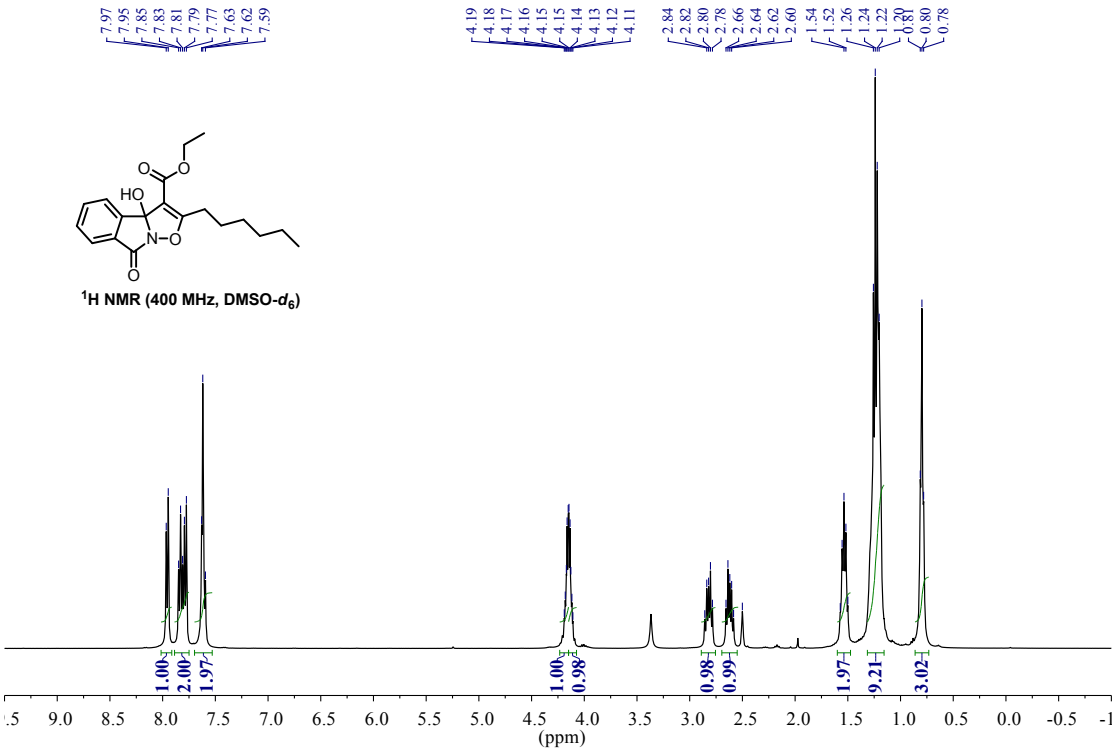


^{13}C NMR (100.6 MHz, DMSO-d_6)



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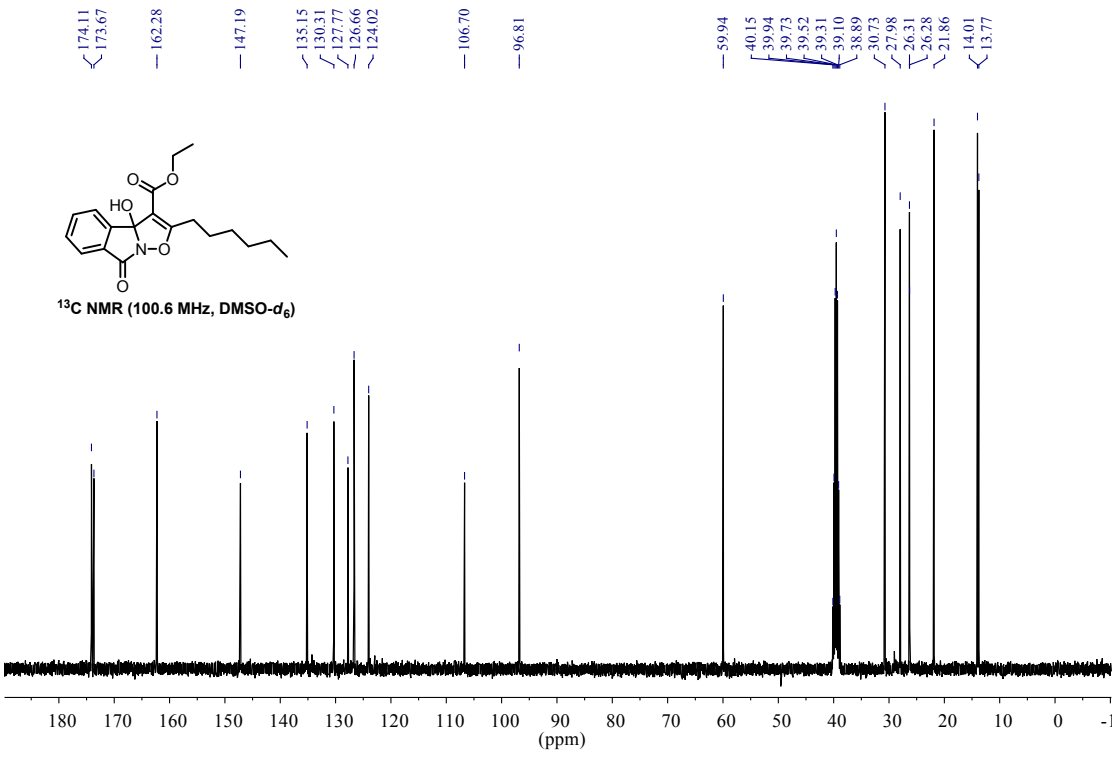
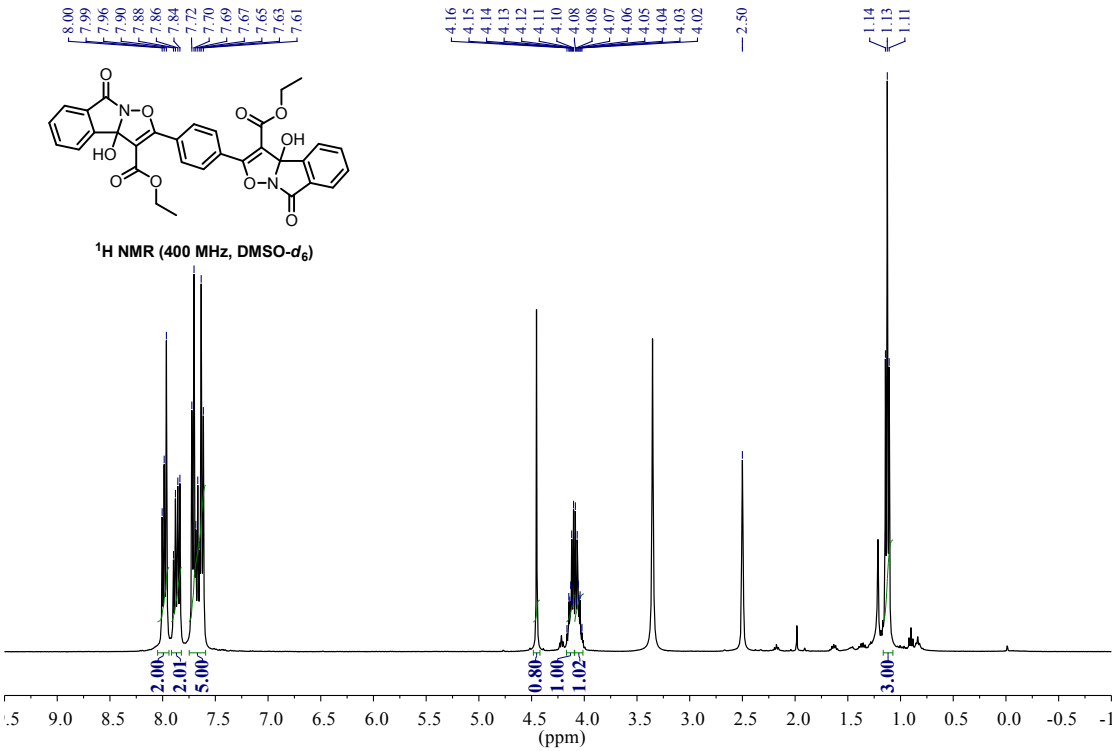


^{13}C NMR (100.6 MHz, DMSO-d_6)



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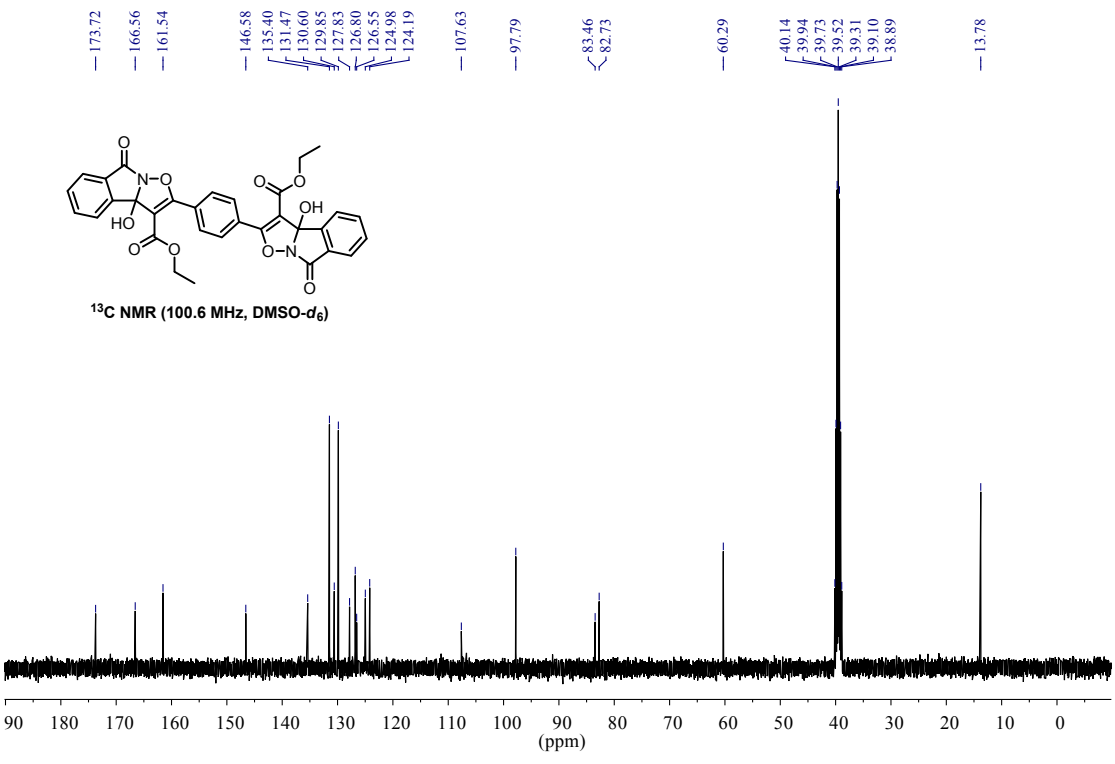
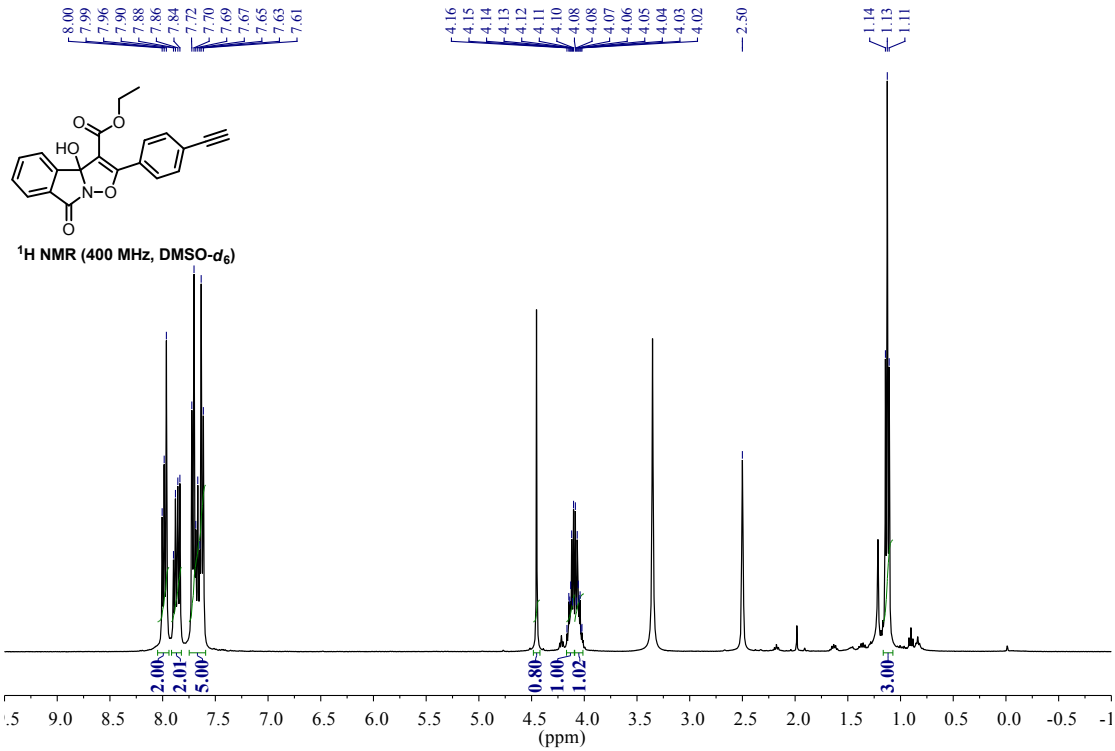


^{13}C NMR (100.6 MHz, DMSO-d_6)



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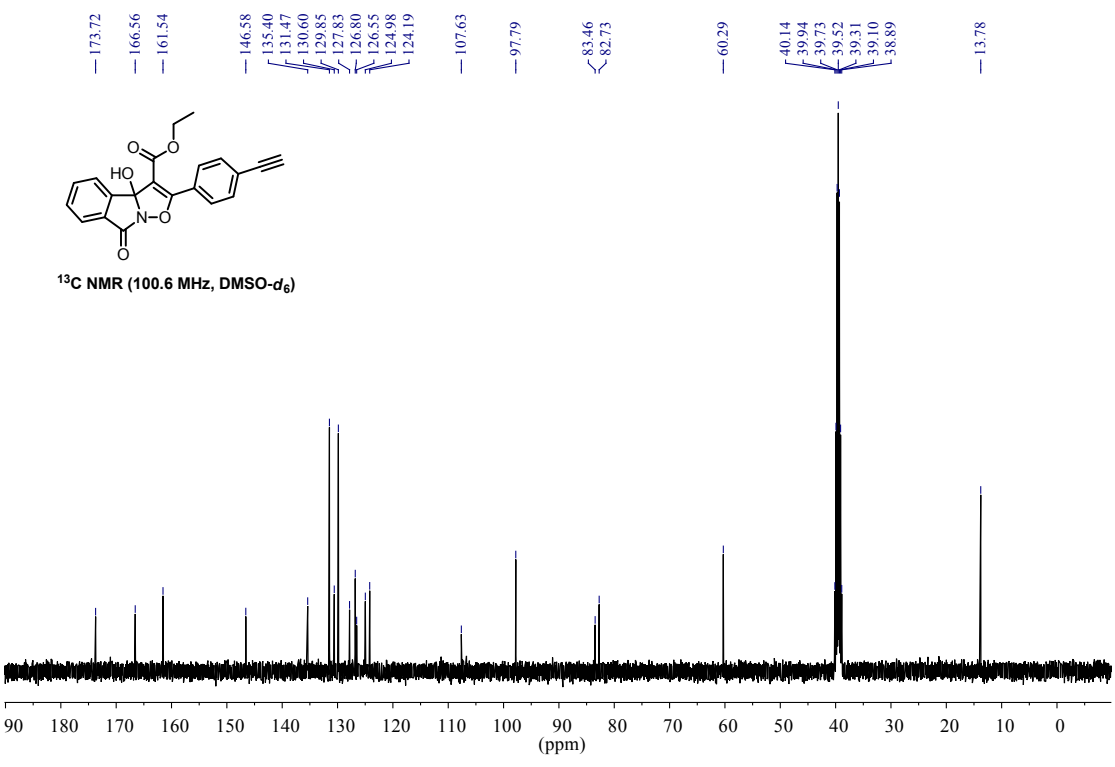

^{13}C NMR (100.6 MHz, DMSO-d_6)