Supporting Information

TBN-triggered, manipulable annulations of *o*-hydroxyarylenaminones for divergent syntheses of oximinochromanones and oximinocoumaranones

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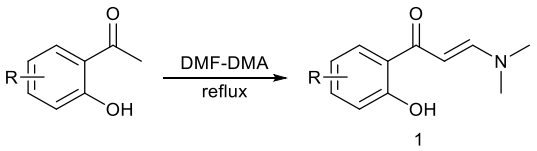
Table of Contents

1. General Information

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were reported in *ppm* relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh).

2. General Procedure for the Synthesis of Compounds 1



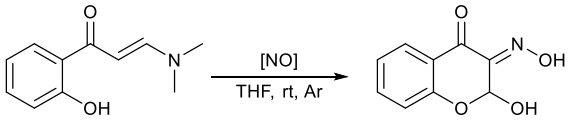
1

Hydroxyarylenaminones **1** were prepared by treatment of the corresponding unsubstituted or substituted *o*-hydroxyacetophenones with *N,N*-dimethylformamide dimethyl acetal (DMF-DMA), according to a reported protocol. [1]

3. Detailed Optimization of Reaction Conditions

3.1 Optimization of the reaction condition for products 2

Table S1. Optimization of nitroso reagent [a]

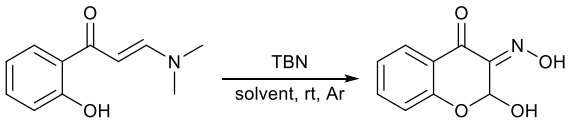


1a **2a**

Entry	[NO]	Yield (%) [b]
1	***tert*-butyl nitrite (TBN)**	**61**
2	butyl nitrite	54
3	*iso*-butyl nitrite	50
4	$NaNO_2$	NR
5	$AgNO_2$	NR

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), THF (1 mL), [NO] (3.0 equiv.), room temperature, 24 h, Ar. [b] Yield of the isolated product.

Table S2. Optimization of solvent[a]



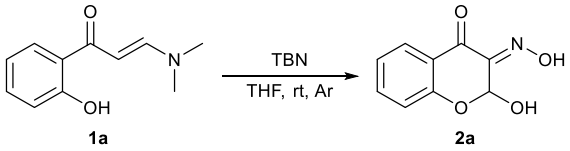
1a **2a**

Entry	Solvent	Yield (%) [b]
1	CH_2Cl_2	46
2	**THF**	**61**
3[c]	THF	60
4[d]	THF	47
5	EtOAc	58
6	1,4-dioxane	57
7	acetone	52
8	MeCN	40
9	DMF	38
10	MeOH	ND

11	DMSO	ND

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), solvent (1 mL), TBN (3.0 equiv.), room temperature, 24 h, Ar. [b] Yield of the isolated product. [c] Add 3.0 equiv. H_2O. [d] Add 30.0 equiv. H_2O.

Table S3. Optimization of additive[a]

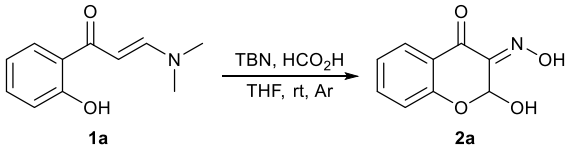


1a **2a**

Entry	Additive	Yield (%) [b]
1	K_2CO_3	NR
2	Et_3N	trace
3	K_2HPO_4	trace
4	NaOAc	trace
5	AcOH	57
6	**HCO_2H**	**78**
7	$PhCO_2H$	64
8	CF_3CO_2H	59
9	Ac_2O	ND
10	36% HCl	ND

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), THF (1 mL), TBN (3.0 equiv.), additive (2.0 equiv.), room temperature, 24 h, Ar. [b] Yield of the isolated product.

Table S4. Optimization of molar ratio of acid [a]

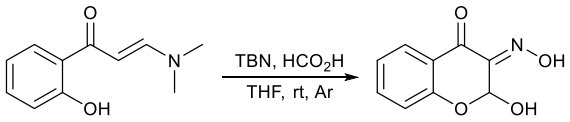


1a **2a**

Entry	HCO_2H (μL)	Yield (%) [b]
1	**4 (0.5 equiv.)**	**83**
2	8 (1.0 equiv.)	83
3	16 (2.0 equiv.)	78
4	24 (3.0 equiv.)	66

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), THF (1 mL), TBN (3.0 equiv.), HCO_2H, room temperature, 24 h, Ar. [b] Yield of the isolated product.

Table S5. Optimization of molar ratio of TBN [a]



1a 2a

Entry	TBN (μL)	Yield (%) [b]
1	35 (1.5 equiv.)	incomplete
2	48 (2.0 equiv.)	incomplete (65)
3	60 (2.5 equiv.)	73
4	**71 (3.0 equiv.)**	**83**

[a] Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), THF (1 ml), TBN, HCO_2H (0.5 equiv.), room temperature, 24 h, Ar. [b] Yield of the isolated product.

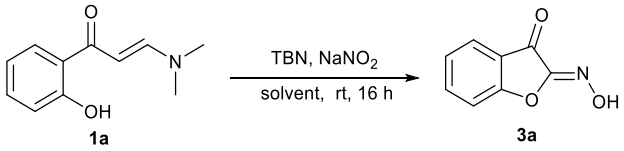
Table S6. Optimization of solvent volume [a]

Entry	THF (mL)	Yield (%) [b]
1	0.5	incomplete
2	**1.0**	**83**
3	2.0	75

[a] Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), THF, TBN (3.0 equiv.), HCO_2H (0.5 equiv.), room temperature, 24 h, Ar. [b] Yield of the isolated product.

3.2 The reaction condition optimization for Products 3

Table S1. Optimization of solvent[a]

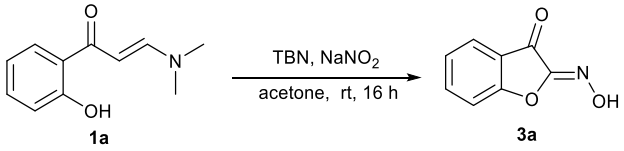


1a 3a

Entry	solvent	Yield (%) [b]
1	toluene	ND
2	EtOAc	83
3	MeCN	85
4	acetone	90
5	MeOH	ND
6	EtOH	trace
7	THF	88

[a] Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), solvent (1 mL), TBN (3.0 equiv.), $NaNO_2$ (2.0 equiv.), room temperature, 16 h, air. [b] Yield of the isolated product.

Table S2. Optimization of molar ratio of $NaNO_2$[a]



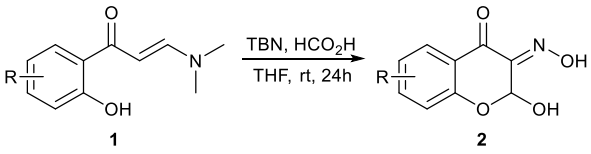
1a 3a

Entry	molar ratio	Yield (%) [b]
1	1.0:0.5	incomplete
2	1.0:1.0	83
3	**1.0:2.0**	**90**

[a] Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), acetone (1 mL), TBN (3.0 equiv.), $NaNO_2$, room temperature, 16 h, air. [b] Yield of the isolated product.

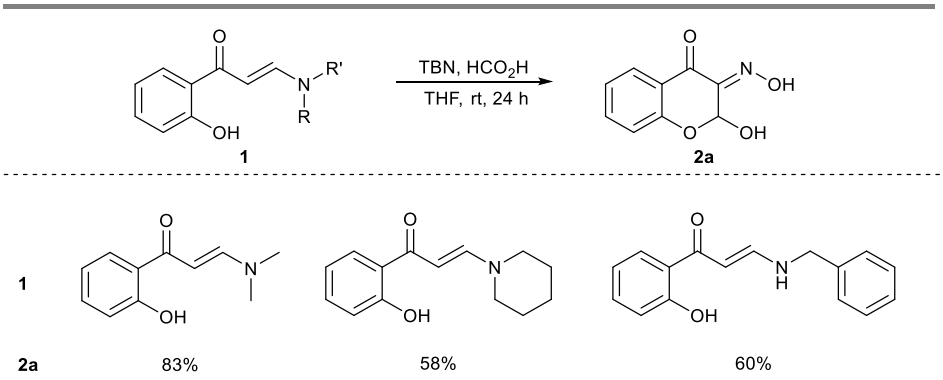
4. General Procedure for the Preparation of Products 2 and 3

4.1 Procedure for the preparation of compounds 2

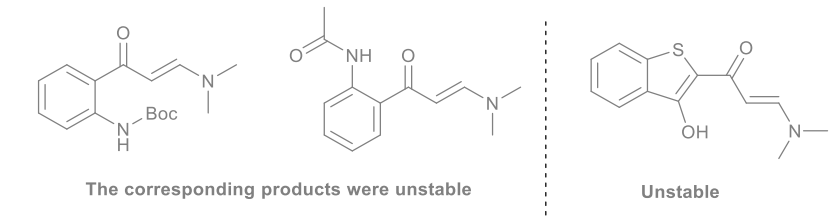


To a 15 mL Schlenk flask equipped with a magnetic stirring bar, compounds **1** (0.2 mmol, 1.0 equiv.) TBN (98.5%, 0.6 mmol, 3.0 equiv.), HCO_2H (0.1 mmol, 0.5 equiv.) and THF (1 mL) were added. The vessel was evacuated and quickly backfilled with Ar three times. The tube was screw-capped and stirred at room temperature under Ar atmosphere for 24 h, and the reaction was monitored by thin layer chromatography analysis. Thereafter, the solvent was then evaporated and the resulting residue was purified by column chromatography to afford pure products **2**.

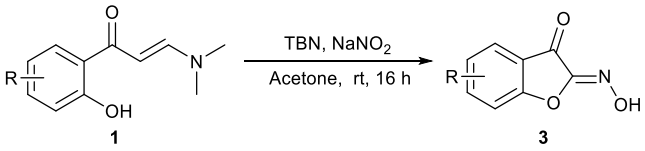
Scheme S1 Evaluation of amino substituents of starting materials 1



Scheme S2 Unsuccessful substrates

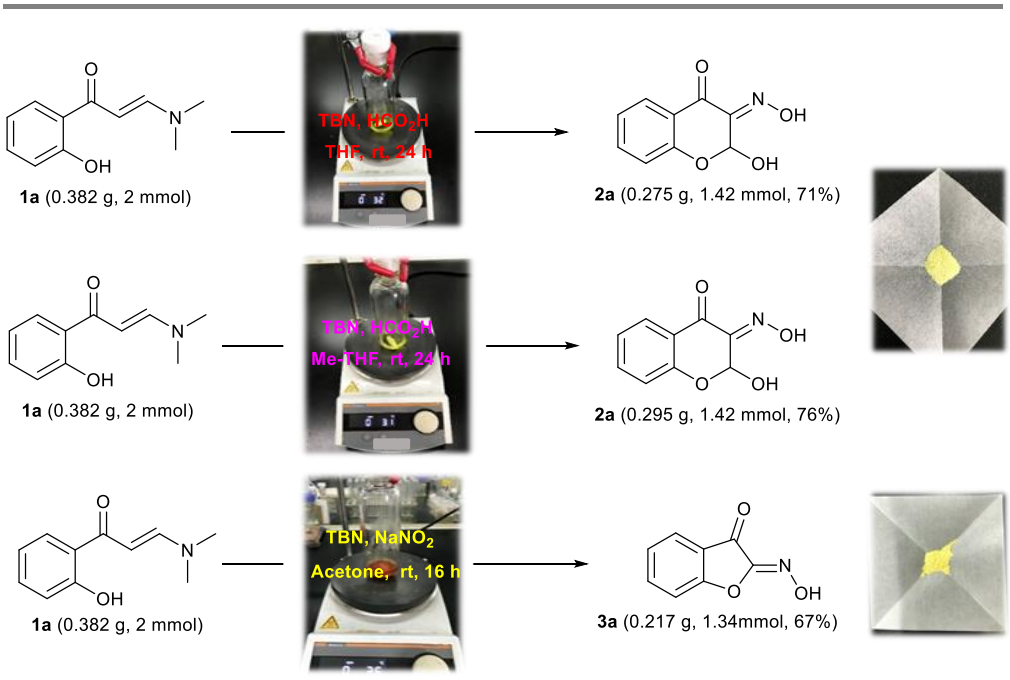


4.2 Procedure for the preparation of products 3



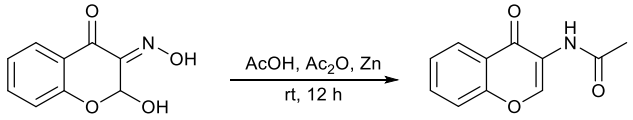
To a 15 mL Schlenk flask equipped with a magnetic stirring bar, compounds **1** (0.2 mmol, 1.0 equiv.) TBN (98.5%, 0.6 mmol, 3.0 equiv.), $NaNO_2$ (0.4 mmol, 2.0 equiv.) and acetone (1 mL) were added. The tube was screw-capped and stirred at room temperature under air atmosphere for 16 h, and the reaction was monitored by thin layer chromatography analysis. The solvent was then evaporated and the resulting residue was purified by column chromatography to afford pure products **3**.

4.3 Scale-up reaction



5. General Procedure for the Synthesis of 4a-8a

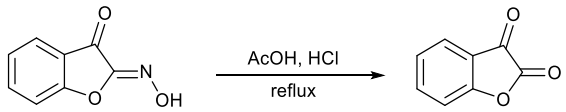
5.1 General procedure for the synthesis of 4a using 2a as starting material



2a **4a**

To the above compounds **2a** (0.2 mmol) were successively added AcOH (1 mL), Ac_2O (0.7 mL) and Zn powder (3.0 equiv.). The resulting slurry was stirred at room temperature for 12 h, and monitored by thin layer chromatography analysis. The mixture was then extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography to yield the title compound (61% yield). [2]

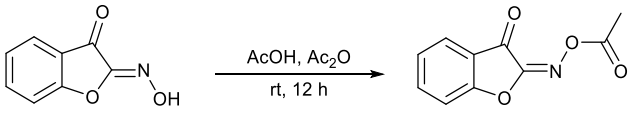
5.2 General procedure for the synthesis of 5a using 3a as starting material



3a **5a**

To the above compounds **3a** (0.2 mmol) were successively added AcOH (1 mL) and HCl (0.6 mL). The resulting slurry was heated to reflux, and monitored by thin layer chromatography analysis. The mixture was thencooled to room temperature, extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography to yield the title compound (39% yield).[3]

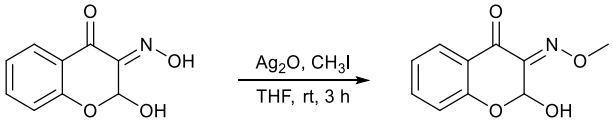
5.2 General procedure for the synthesis of 6a using 3a as starting material



3a **6a**

To the above compounds **3a** (0.2 mmol) were successively added AcOH (1 mL) and Ac_2O (0.7 mL). The resulting slurry was stirred at room temperature for 12 h, and monitored by thin layer chromatography analysis. The mixture was then extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography to yield the title compound (80% yield).

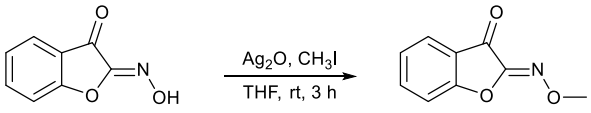
5.3 General procedure for the synthesis of 7a using 2a as starting material



2a **7a**

To a suspension of compounds **2a** (0.2 mmol, 1.0 equiv.) and Ag_2O (0.55 equiv.) in 1 mL THF, methyliodide (1.20 equiv.) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 3 hours, and monitored by thin layer chromatography analysis. The solvent was removed under reduced pressure and the crude product was further purified by silica gel column chromatography to yield the title compound (95% yield). [4]

5.4 General procedure for the synthesis of 8a using 3a as starting material

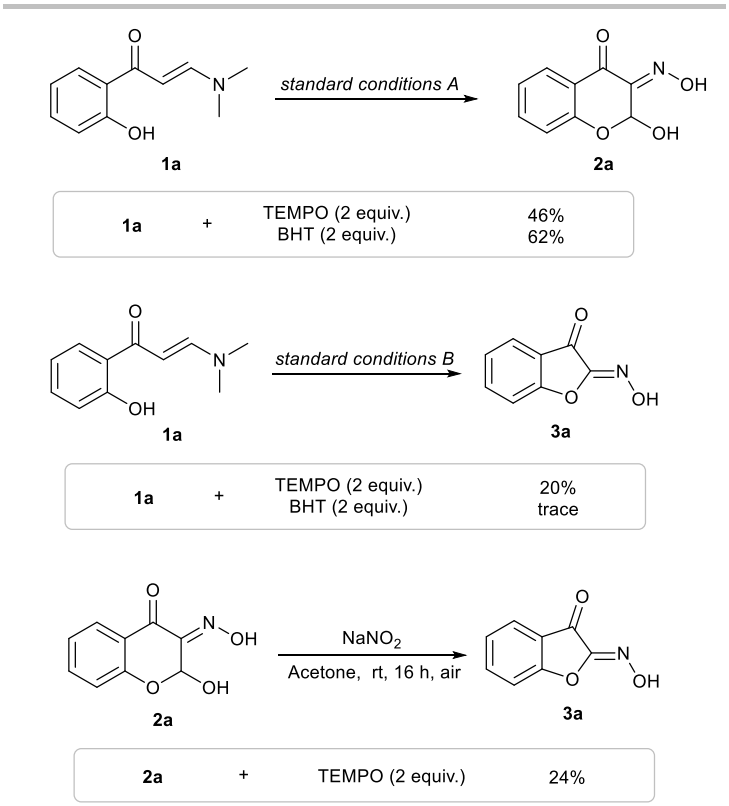


3a **8a**

To a suspension of compounds **3a** (0.2 mmol, 1.0 equiv.) and Ag_2O (0.55 equiv.) in 1 mL THF, methyliodide (1.20 equiv.) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 3 hours, and monitored by thin layer chromatography analysis. The solvent was removed under reduced pressure and the crude product was further purified by silica gel column chromatography to yield the title compound (63% yield). [4]

6. Mechanistic Studies

Trapping Experiment



Monitoring the reaction mixture by HRMS

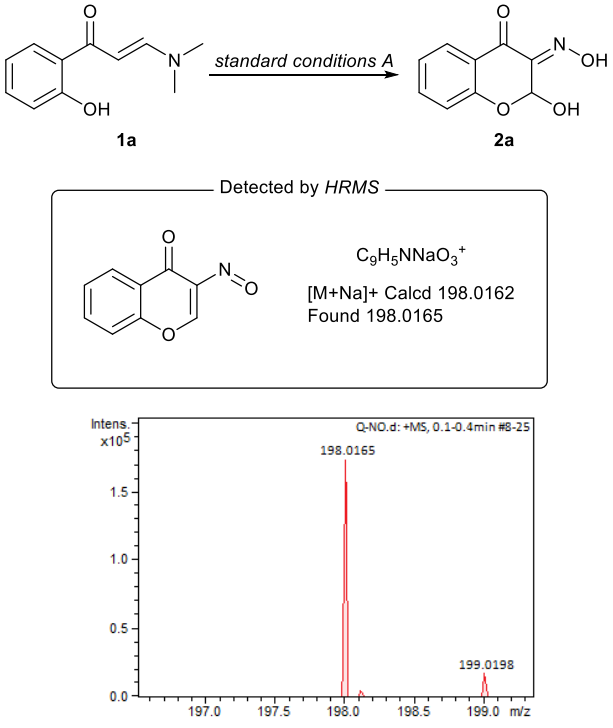


Figure S1 ESI-MS of the intermediate **C** (3-nitroso-chromone)

Labelling Experiment by Adding H_2O^{18}

Standard reaction was set up with using labelled H_2O^{18}. As detected by ESI-MS (Figure S1), the desired labelled O^{18} product **2a'** was obtained.

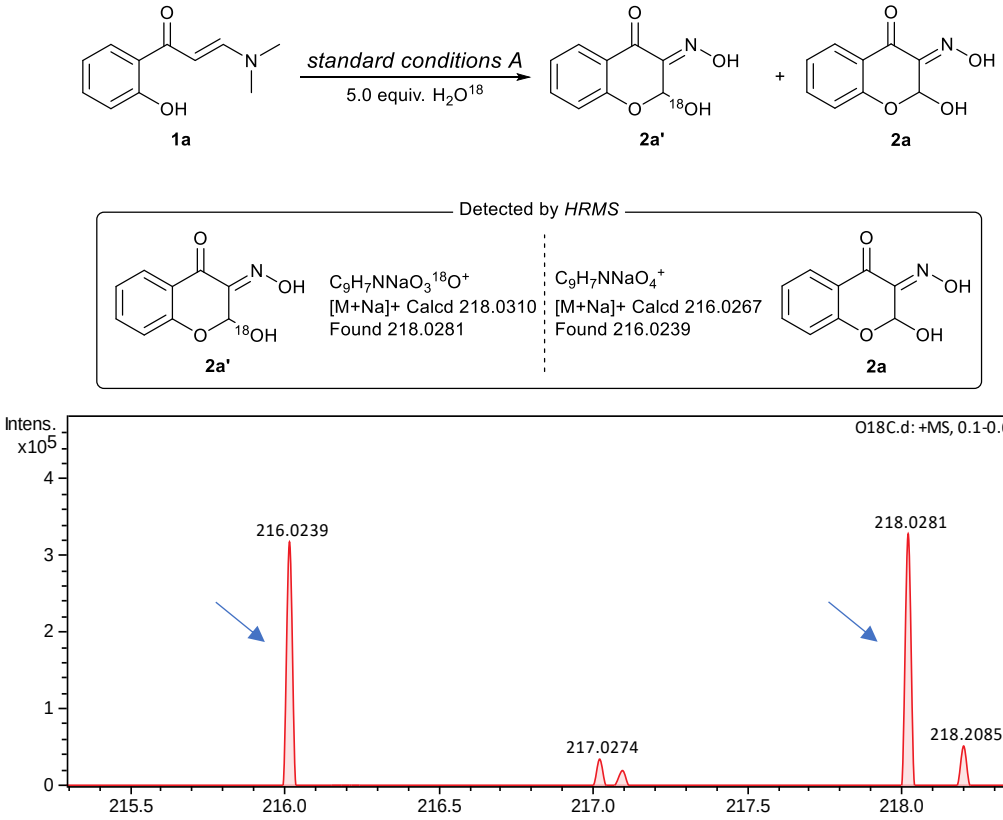
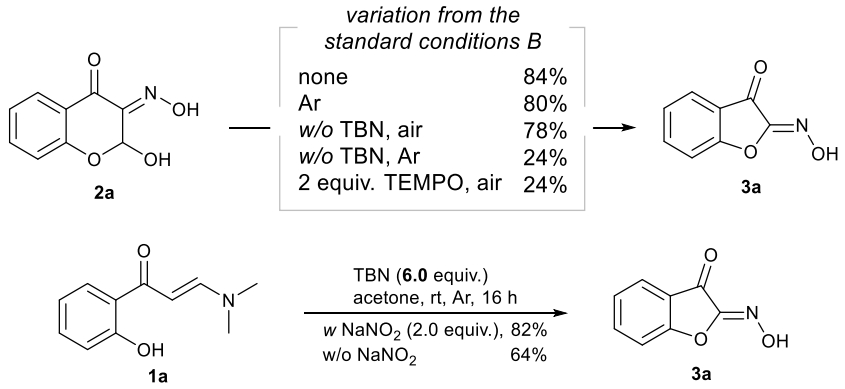


Figure S2 ESI-MS of the labelled O^{18} product

Other mechanism experiments were performed as follows:



References

[1] (a) M. O. Akram, S. Bera and N. T. Patil, *Chem. Commun.*, 2016, **52**, 12306-12309; (b) K. S. Levchenko, I. S. Semenova, V. N. Yarovenko, P. S. Shmelin and M. M. Krayushkin, *Tetrahedron Lett.*, 2012, **53**, 3630-3632.

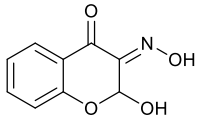
[2] A. E. Cotman, M. Lozinsek, B. Wang, M. Stephan and B. Mohar, *Org. Lett.*, 2019, **21**, 3644-3648.

[3] L. I. Smith and R. R. Holmes, *J. Am. Chem. Soc.*, 1951, **73**, 4294-4297.

[4] M. Schlegel and C. Schneider, *Org. Lett.*, 2018, **20**, 3119-3123.

7. Characterization Data (In most cases, the signal for the two OH was unobserved in ^{1}H NMR.)

7.1 Characterization Data of Products 2



2a, 31.8 mg, (PE/EA = 100:45), yellow solid, yield: 82%;

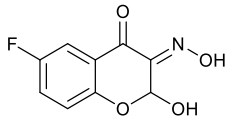
m.p.: 144 – 146 °C;

IR (neat) ν 3313, 2848, 1677, 1461, 1207, 1058, 741 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.93 (dd, J = 7.9, 1.8 Hz, 1H), 7.60 (ddd, J = 8.7, 7.2, 1.8 Hz, 1H), 7.13 (ddd, J = 8.0, 7.3, 1.1 Hz, 1H), 7.04 (dd, J = 8.3, 1.1 Hz, 1H), 6.72 (s, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.66, 158.45, 149.53, 136.83, 126.72, 122.10, 121.83, 119.01, 88.11;

HRMS (ESI): $C_9H_7NNaO_4^+$ $[M+Na]^+$ Calcd 216.0267, Found 216.0271.



2b, 36.5 mg, (PE/EA = 100:40), yellow solid, yield: 87%;

m.p.: 145 – 147 °C;

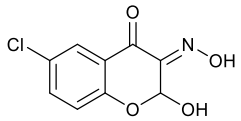
IR (neat) ν 3228, 1676, 1478, 1259, 1259, 725 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.59 (dd, J = 8.3, 3.2 Hz, 1H), 7.40 (td, J = 8.7, 3.2 Hz, 1H), 7.09 (dd, J = 9.1, 4.2 Hz, 1H), 6.71 (s, 1H);

^{19}F{^{1}H} NMR (376 MHz, Methanol-d_4) δ -122.78;

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 177.80 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 157.83 (d, $^1J_{C\text{-}F}$ = 241.1 Hz), 154.65 (d, $^4J_{C\text{-}F}$ = 1.9 Hz), 149.10, 123.87 (d, $^2J_{C\text{-}F}$ = 24.7 Hz), 122.47 (d, $^3J_{C\text{-}F}$ = 6.9 Hz), 121.00 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 111.40 (d, $^2J_{C\text{-}F}$ = 24.1 Hz), 88.24;

HRMS (ESI): $C_9H_6FNNaO_4^+$ $[M+Na]^+$ Calcd 234.0173, Found 234.0153.



2c, 29.1 mg, (PE/EA = 100:40), yellow solid, yield: 64%;

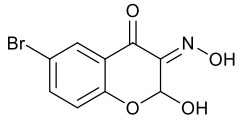
m.p.: 141 – 143 °C;

IR (neat) ν 3367, 2853, 1678, 1464, 1211, 1065 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.86 (d, J = 2.7 Hz, 1H), 7.58 (dd, J = 8.8, 2.8 Hz, 1H), 7.06 (d, J = 8.8 Hz, 1H), 6.72 (s, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 177.51, 156.96, 149.00, 136.29, 127.45, 125.76, 122.75, 121.00, 88.39;

HRMS (ESI): $C_9H_6ClNNaO_4^+$ $[M+Na]^+$ Calcd 249.9878, Found $[M+Na]^+$ 249.9851, $[M+2+Na]^+$ 251.9827 (100%: 34.1%).



2d, 45.4 mg, (PE/EA = 100:40), yellow solid, yield: 83%;

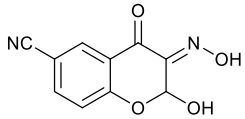
m.p.: 150 – 152 °C;

IR (neat) ν 3336, 2723, 1678, 1460, 1271, 1067, 661 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.88 (d, J = 2.6 Hz, 1H), 7.58 (dd, J = 8.8, 2.6 Hz, 1H), 6.88 (d, J = 8.8 Hz, 1H), 6.60 (s, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 177.39, 157.40, 148.96, 139.15, 128.94, 123.21, 121.31, 114.43, 88.40;

HRMS (ESI): $C_9H_6BrNNaO_4^+$ $[M+Na]^+$ Calcd 293.9372, Found $[M+Na]^+$ 293.9337, $[M+2+Na]^+$ 295.9315 (100%: 98.8%).



2e, 33.0 mg, (PE/EA = 100:40), yellow solid, yield: 76%;

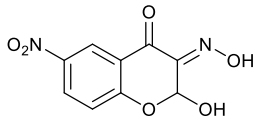
m.p.: 157 – 159 °C;

IR (neat) ν 3341, 2757, 2227, 1673, 1483, 1210, 1074 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.16 (d, J = 2.2 Hz, 1H), 7.80 (dd, J = 8.7, 2.2 Hz, 1H), 7.10 (d, J = 8.6 Hz, 1H), 6.67 (s, 1H).

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 176.84, 161.18, 148.56, 138.95, 131.74, 122.23, 120.68, 117.42, 105.85, 89.08.

HRMS (ESI): $C_{10}H_6N_2NaO_4^+$ $[M+Na]^+$ Calcd 241.0220, Found 241.0188.



2f, 29.9 mg, (PE/EA = 100:40), light gray solid, yield: 63%;

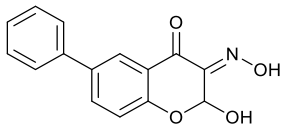
m.p.: 150 – 152 °C;

IR (neat) ν 3383, 2848, 2503, 1682, 1343, 1065, 740 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.75 (d, J = 2.9 Hz, 1H), 8.45 (dd, J = 9.0, 2.9 Hz, 1H), 7.25 (d, J = 9.1 Hz, 1H), 6.81 (s, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 176.96, 162.47, 148.37, 142.75, 130.59, 122.67, 121.46, 120.45, 89.28;

HRMS (ESI): $C_9H_6N_2NaO_6^+$ $[M+Na]^+$ Calcd 261.0118, Found 261.0087.



2g, 36.0 mg, (PE/EA = 100:60), yellow solid, yield: 67%;

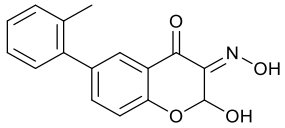
m.p.: 172 – 174 °C;

IR (neat) ν 3256, 2468, 1681, 1475, 1214, 1021, 757 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.03 (d, J = 2.4 Hz, 1H), 7.76 (dd, J = 8.6, 2.5 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.20 (m, 1H), 7.01 (d, J = 8.6 Hz, 1H), 6.63 (s, 1H);

^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4) δ 178.62, 157.85, 149.51, 139.25, 135.46, 135.31, 128.63, 127.19, 126.24, 124.44, 121.90, 119.59, 88.24;

HRMS (ESI): $C_{15}H_{11}NNaO_4^+$ $[M+Na]^+$ Calcd 292.0580, Found 292.0548.



2h, 31.1 mg, (PE/EA = 100:60), yellow solid, yield: 55%;

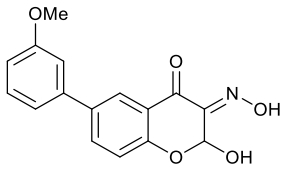
m.p.: 176 – 178 °C;

IR (neat) ν 3250, 2408, 1686, 1474, 1198, 1062, 732 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.73 (d, J = 2.3 Hz, 1H), 7.45 (dd, J = 8.5, 2.3 Hz, 1H), 7.19 – 7.06 (m, 4H), 7.00 (d, J = 8.5 Hz, 1H), 6.64 (s, 1H), 2.14 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.61, 157.44, 149.53, 140.06, 137.69, 136.28, 134.98, 130.11, 129.23, 127.38, 126.74, 125.70, 121.44, 118.88, 88.23, 19.14;

HRMS (ESI): $C_{16}H_{13}NNaO_4^+$ $[M+Na]^+$ Calcd 306.0737, Found 306.0700.



2i, 42.9 mg, (PE/EA = 100:40), yellow solid, yield: 72%;

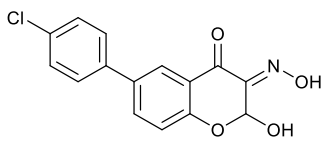
m.p.: 166 – 168 °C;

IR (neat) ν 3165, 1668, 1426, 1255, 1054, 735 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.00 (d, J = 2.4 Hz, 1H), 7.74 (dd, J = 8.6, 2.5 Hz, 1H), 7.22 (t, J = 7.9 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 7.02 – 6.97 (m, 2H), 6.79 (dd, J = 8.3, 2.5 Hz, 1H), 6.63 (s, 1H), 3.73 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.62, 160.29, 157.91, 149.50, 140.66, 135.36, 135.31, 129.66, 124.48, 121.83, 119.53, 118.66, 112.65, 111.91, 88.25, 54.39;

HRMS (ESI): $C_{16}H_{13}NNaO_5^+$ $[M+Na]^+$ Calcd 322.0686, Found 322.0658.



2j, 34.5 mg, (PE/EA = 100:40), yellow solid, yield: 57%;

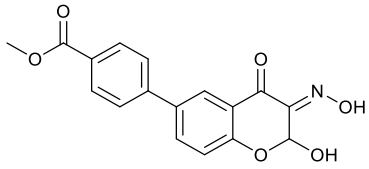
m.p.: 172 – 174 °C;

IR (neat) ν 3264, 1682, 1472, 1261, 1063, 992 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.98 (d, J = 2.5 Hz, 1H), 7.71 (dd, J = 8.6, 2.5 Hz, 1H), 7.44 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.6 Hz, 1H), 6.62 (s, 1H);

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 178.48, 158.03, 149.42, 137.84, 135.07, 133.99, 133.24, 128.69, 127.72, 124.43, 121.91, 119.72, 88.29;

HRMS (ESI): $C_{15}H_{10}ClNNaO_4^+$ $[M+Na]^+$ Calcd 326.0191, Found $[M+Na]^+$ 326.0154, $[M+2+Na]^+$ 328.0128 (100%: 34.8%).



2k, 45.5 mg, (PE/EA = 100:70), yellow solid, yield: 70%;

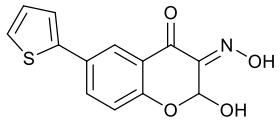
m.p.: 173 – 175 °C;

IR (neat) ν 3269, 2444, 1682, 1432, 1291, 1015, 718 cm^{-1};

^1H NMR (400 MHz, Methanol-d_4) δ 8.05 (d, J = 2.4 Hz, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.78 (dd, J = 8.6, 2.4 Hz, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.6 Hz, 1H), 6.63 (s, 1H), 3.80 (s, 3H);

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 178.41, 166.93, 158.48, 149.37, 143.83, 135.29, 133.96, 129.85, 128.87, 126.31, 124.91, 122.00, 119.85, 88.36, 51.26;

HRMS (ESI): $C_{17}H_{13}NNaO_6^+$ $[M+Na]^+$ Calcd 350.0635, Found 350.0592.



2l, 25.8 mg, (PE/EA = 100:40), dark orange solid, yield: 47%;

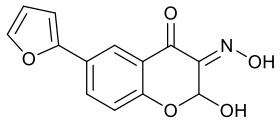
m.p.: 161 – 163 °C;

IR (neat) ν 3268, 2434, 1680, 1440, 1293, 1061, 712 cm^{-1};

^1H NMR (400 MHz, Methanol-d_4) δ 8.01 (d, J = 2.4 Hz, 1H), 7.76 (dd, J = 8.6, 2.4 Hz, 1H), 7.27 – 7.25 (m, 2H), 7.25 (s, 1H), 7.01 – 6.94 (m, 2H), 6.62 (s, 1H);

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 178.37, 157.71, 149.39, 142.26, 133.97, 129.12, 127.87, 124.65, 123.10, 123.00, 121.90, 119.76, 88.30;

HRMS (ESI): $C_{13}H_9NNaO_4S^+$ $[M+Na]^+$ Calcd 298.0144, Found 298.0113.



2m, 34.7 mg, (PE/EA = 100:40), dark orange solid, yield: 67%;

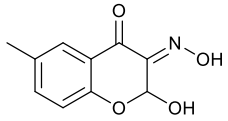
m.p.: 166 – 168 °C;

IR (neat) ν 3165, 1668, 1426, 1255, 1054, 735 cm^{-1};

^1H NMR (400 MHz, Methanol-d_4) δ 8.07 (d, J = 2.3 Hz, 1H), 7.79 (dd, J = 8.6, 2.3 Hz, 1H), 7.44 (d, J = 1.8 Hz, 1H), 6.96 (d, J = 8.7 Hz, 1H), 6.63 (d, J = 3.4 Hz, 1H), 6.61 (s, 1H), 6.39 (dd, J = 3.3, 1.8 Hz, 1H);

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 178.39, 157.57, 152.39, 149.42, 142.21, 132.02, 125.72, 121.83, 121.18, 119.58, 111.42, 104.76, 88.28;

HRMS (ESI): $C_{13}H_9NNaO_5^+$ $[M+Na]^+$ Calcd 282.0373, Found 282.0347.



2n, 26.0 mg, (PE/EA = 100:40), yellow solid, yield: 63%;

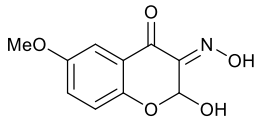
m.p.: 139 – 141 °C;

IR (neat) ν 3347, 3029, 2861, 1681, 1485, 1204, 999 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.60 (d, J = 2.3 Hz, 1H), 7.31 (dd, J = 8.4, 2.3 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.56 (s, 1H), 2.22 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.69, 156.51, 149.65, 137.78, 131.85, 126.23, 121.47, 118.84, 87.95, 19.06;

HRMS (ESI): $C_{10}H_9NNaO_4^+$ $[M+Na]^+$ Calcd 230.0424, Found 230.0396.



2o, 20.8 mg, (PE/EA = 100:40), orange solid, yield: 47%;

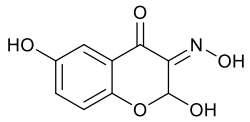
m.p.: 98 – 100 °C;

IR (neat) ν 3219, 2920, 1674, 1484, 1269, 1027, 716 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.26 (d, J = 3.2 Hz, 1H), 7.10 (dd, J = 9.0, 3.2 Hz, 1H), 6.87 (d, J = 9.0 Hz, 1H), 6.55 (s, 1H), 3.71 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.45, 154.96, 152.92, 149.59, 125.28, 121.82, 120.28, 107.58, 87.95, 54.86;

HRMS (ESI): $C_{10}H_9NNaO_5^+$ $[M+Na]^+$ Calcd 246.0373, Found 246.0334.



2p, 3.5 mg, (PE/EA = 100:70), dark orange solid, yield: 8%;

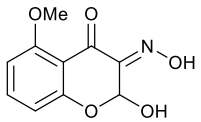
m.p.: 177 – 179 °C;

IR (neat) ν 3177, 1690, 1587, 1460, 1220, 1037 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.28 (d, J = 3.1 Hz, 1H), 7.10 (dd, J = 8.9, 3.1 Hz, 1H), 6.92 (d, J = 8.9 Hz, 1H), 6.64 (s, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.60, 152.39, 151.86, 149.74, 125.14, 122.13, 119.98, 110.36, 87.81;

HRMS (ESI): $C_9H_7NNaO_5^+$ $[M+Na]^+$ Calcd 232.0216, Found 232.0185.



2q, 24.8 mg, (PE/EA = 100:70), yellow solid, yield: 56%;

m.p.: 160 – 162 °C;

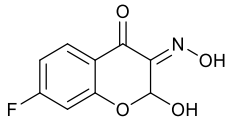
IR (neat) ν 3201, 2844, 1598, 1462, 1234, 1086, 765cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.41 (t, J = 8.4 Hz, 1H), 6.65 (d, J = 8.5 Hz, 1H), 6.52 (d, J = 8.3

Hz, 1H), 6.49 (s, 1H), 3.79 (s, 3H);

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 177.23, 161.32, 159.88, 150.18, 137.15, 112.16, 111.15, 105.24, 87.69, 55.20;

HRMS (ESI): $C_{10}H_9NNaO_5^+$ $[M+Na]^+$ Calcd 246.0373, Found 246.0341.



2r, 20.8 mg, (PE/EA = 100:40), yellow solid, yield: 49%;

m.p.: 145 – 147 °C;

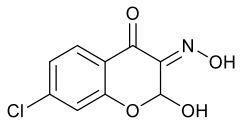
IR (neat) ν 2917, 2848, 1677, 1585, 1232, 1000, 765 cm^{-1};

^1H NMR (400 MHz, Methanol-d_4) δ 7.89 (dd, J = 8.8, 6.5 Hz, 1H), 6.80 (td, J = 8.6, 2.4 Hz, 1H), 6.69 (dd, J = 9.9, 2.4 Hz, 1H), 6.61 (s, 1H);

$^{19}F\{^1H\}$ NMR (376 MHz, Methanol-d_4) δ -101.51;

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 177.31, 168.15 (d, $^1J_{C\text{-}F}$ = 256.2 Hz), 160.43 (d, $^3J_{C\text{-}F}$ = 13.9 Hz), 149.04, 129.60 (d, $^3J_{C\text{-}F}$ J = 11.6 Hz), 118.89 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 110.13 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 105.64 (d, $^2J_{C\text{-}F}$ = 24.9 Hz), 88.70;

HRMS (ESI): $C_9H_6FNNaO_4^+$ $[M+Na]^+$ Calcd 234.0173, Found 234.0158.



2s, 32.9 mg, (PE/EA = 100:40), white solid, yield: 72%;

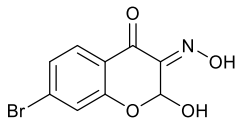
m.p.: 147 – 149 °C;

IR (neat) ν 3378, 2768, 1677, 1423, 1198, 1063, 762 cm^{-1};

^1H NMR (400 MHz, Methanol-d_4) δ 7.79 (d, J = 8.5 Hz, 1H), 7.03 (dd, J = 8.4, 1.9 Hz, 1H), 6.98 (d, J = 1.8 Hz, 1H), 6.61 (s, 1H);

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 177.64, 158.91, 149.06, 142.39, 128.21, 122.66, 120.61, 118.98, 88.70;

HRMS (ESI): $C_9H_6ClNNaO_4^+$ $[M+Na]^+$ Calcd 249.9878, Found $[M+Na]^+$ 249.9844, $[M+2+Na]^+$ 251.9821 (100%: 33.3%).



2t, 30.2 mg, (PE/EA = 100:40), yellow solid, yield: 56%;

m.p.: 168 – 170 °C;

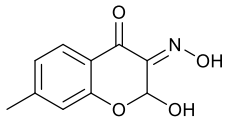
IR (neat) ν 3079, 2350, 1691, 1418, 1191, 1004 cm^{-1};

^1H NMR (400 MHz, Methanol-d_4) δ 7.71 (d, J = 8.4 Hz, 1H), 7.20 (dd, J = 8.4, 1.8 Hz, 1H), 7.16 (d, J = 1.8 Hz, 1H), 6.61 (s, 1H);

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 177.81, 158.70, 149.09, 130.86, 128.14, 125.58, 122.07, 120.95, 88.72;

HRMS (ESI): $C_9H_6BrNNaO_4^+$ $[M+Na]^+$ Calcd 293.9372, Found $[M+Na]^+$ 293.9338, $[M+2+Na]^+$

295.9322 (100%: 97.8%).



2u, 25.1 mg, (PE/EA = 100:40), yellow solid, yield: 61%;

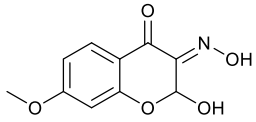
m.p.: 150 – 152 °C;

IR (neat) ν 3220, 2918, 2401, 1669, 1614, 1225, 1015 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.82 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 6.87 (s, 1H), 6.69 (s, 1H), 2.39 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.28, 158.56, 149.57, 148.98, 126.66, 123.33, 119.56, 118.96, 88.05, 20.58;

HRMS (ESI): $C_{10}H_9NNaO_4^+$ $[M+Na]^+$ Calcd 230.0424, Found 230.0401.



2v, 30.3 mg, (PE/EA = 100:70), yellow solid, yield: 68%;

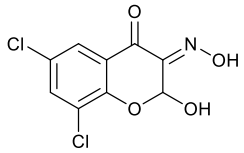
m.p.: 163 – 165 °C;

IR (neat) ν 3586, 3437, 2783, 1670, 1236, 765 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.76 (d, J = 8.9 Hz, 1H), 6.59 (dd, J = 8.9, 2.4 Hz, 1H), 6.57 (s, 1H), 6.42 (d, J = 2.4 Hz, 1H), 3.76 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 177.25, 167.43, 160.84, 149.46, 128.65, 115.45, 110.39, 102.08, 88.28, 55.05.

HRMS (ESI): $C_{10}H_9NNaO_5^+$ $[M+Na]^+$ Calcd 246.0373, Found 246.0356.



2w, 44.1 mg, (PE/EA = 100:30), yellow solid, yield: 85%;

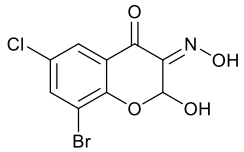
m.p.: 141 – 143 °C;

IR (neat) ν 3212, 1690, 1456, 1247, 1074, 789 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.82 (d, J = 2.6 Hz, 1H), 7.75 (d, J = 2.6 Hz, 1H), 6.83 (s, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 176.75, 152.73, 148.46, 135.60, 127.13, 125.16, 124.71, 123.69, 89.15;

HRMS (ESI): $C_9H_5Cl_2NNaO_4^+$ $[M+Na]^+$ Calcd 283.9488, Found $[M+Na]^+$ 283.9450, $[M+2+Na]^+$ 285.9421, $[M+4+Na]^+$ 287.9402 (100%: 64.4%: 10.4%).



2x, 48.4 mg, (PE/EA = 100:30), yellow solid, yield: 79%;

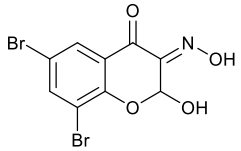
m.p.: 155 – 157 °C;

IR (neat) ν 3214, 2875, 1687, 1442, 1202, 1057, 676 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.90 (d, J = 2.6 Hz, 1H), 7.86 (d, J = 2.6 Hz, 1H), 6.82 (s, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 176.77, 153.69, 148.37, 138.59, 127.54, 125.41, 123.48, 113.79, 89.16;

HRMS (ESI): $C_9H_5BrClNNaO_4^+$ $[M+Na]^+$ Calcd 327.8983, Found $[M+Na]^+$ 327.8943, $[M+2+Na]^+$ 329.8920, $[M+4+Na]^+$ 331.8900 (100%: 130.7%: 32.9%).



2y, 44.1 mg, (PE/EA = 100:30), yellow solid, yield: 63%;

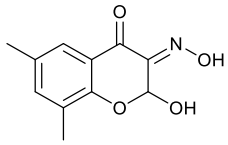
m.p.: 121 – 123 °C;

IR (neat) ν 3065, 1676, 1440, 1236, 1075 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.91 (d, J = 2.4 Hz, 1H), 7.88 (d, J = 2.4 Hz, 1H), 6.71 (s, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 176.67, 154.10, 148.34, 141.22, 128.53, 123.96, 114.21, 114.05, 89.16;

HRMS (ESI): $C_9H_5BrNNaO_4^+$ $[M+Na]^+$ Calcd 371.8478, Found $[M+Na]^+$ 371.8444, $[M+2+Na]^+$ 373.8432, $[M+4+Na]^+$ 375.8455 (100%: 196.6%: 96.4%).



2z, 38.9 mg, (PE/EA = 100:40), yellow solid, yield: 88%;

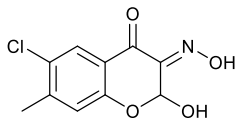
m.p.: 138 – 140 °C;

IR (neat) ν 3381, 1672, 1476, 1192, 1057, 723 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.55 (d, J = 2.2 Hz, 1H), 7.30 (d, J = 2.2 Hz, 1H), 6.72 (s, 1H), 2.29 (s, 3H), 2.23 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 179.01, 154.59, 149.67, 138.69, 131.22, 128.15, 123.86, 121.22, 87.78, 19.08, 14.32;

HRMS (ESI): $C_{11}H_{11}NNaO_4^+$ $[M+Na]^+$ Calcd 244.0580, Found 244.0550.



2aa, 32.0 mg, (PE/EA = 100:40), yellow solid, yield: 66%;

m.p.: 166 – 168 °C;

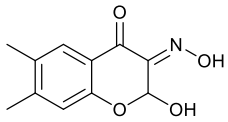
IR (neat) ν 2499, 1673, 1407, 1230, 1027, 661 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.70 (s, 1H), 6.87 (s, 1H), 6.57 (s, 1H), 2.28 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 177.30, 156.83, 149.06, 146.01, 127.99, 126.17, 121.23, 120.89, 88.33, 19.44;

HRMS (ESI): $C_{10}H_8ClNNaO_4^+$ $[M+Na]^+$ Calcd 264.0034, Found $[M+Na]^+$ 264.0006, $[M+2+Na]^+$

265.9980 (100%: 33.4%).



2ab, 32.1 mg, (PE/EA = 100:40), yellow solid, yield: 73%;

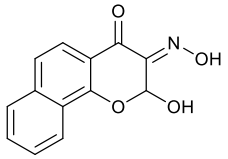
m.p.: 155 – 157 °C;

IR (neat) ν3443, 2519, 1665, 1468, 1241, 1037, 751 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.52 (s, 1H), 6.70 (s, 1H), 6.54 (s, 1H), 2.18 (s, 3H), 2.13 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.32, 156.86, 149.70, 147.92, 130.97, 126.61, 119.56, 119.43, 87.93, 19.17, 17.48;

HRMS (ESI): $C_{11}H_{11}NNaO_4^+$ $[M+Na]^+$ Calcd 244.0580, Found 244.0552.



2ac, 26.5 mg, (PE/EA = 100:40), orange solid, yield: 55%;

m.p.: 151 – 153 °C;

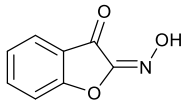
IR (neat) ν 3218, 2414, 1663, 1510, 1258, 1059, 748 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.24 (d, J = 8.4 Hz, 1H), 7.78 – 7.45 (m, 2H), 7.57 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.47 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 6.84 (s, 1H);

^{13}{^{1}H}C NMR (100 MHz, Methanol-d_4) δ 178.17, 157.04, 149.34, 138.03, 129.95, 127.66, 126.30, 125.39, 123.42, 121.77, 120.90, 116.17, 88.91;

HRMS (ESI): $C_{13}H_9NNaO_4^+$ $[M+Na]^+$ Calcd 266.0424, Found 266.0396.

7.2 Characterization Data of Products 3



3a, 29.3 mg, (PE/EA = 100:25), yellow solid, yield: 90%;

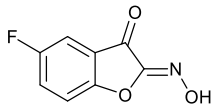
m.p.: 155 – 157 °C;

IR (neat) ν 3271, 3101, 2906, 1718, 1241, 1021, 753 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.81 (ddd, J = 8.6, 7.3, 1.5 Hz, 1H), 7.77 (dd, J = 7.7, 1.4 Hz, 1H), 7.38 (d, J = 8.3 Hz, 1H), 7.34 (td, J = 7.6, 0.8 Hz, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 180.21, 164.48, 147.07, 138.57, 124.26, 124.05, 121.26, 112.78;

HRMS (ESI): $C_8H_5NNaO_3^+$ $[M+Na]^+$ Calcd 186.0162, Found 186.0168.



3b, 33.4 mg, (PE/EA = 100:25), yellow solid, yield: 92%;

m.p.: 191 – 193 °C;

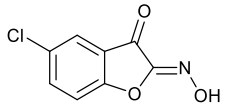
IR (neat) ν 3286, 3070, 1719, 1273, 1022, 776 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.47 (td, J = 8.9, 2.8 Hz, 1H), 7.37 (dd, J = 6.7, 2.8 Hz, 1H), 7.29 (dd, J = 9.0, 3.6 Hz, 1H);

^{19}F{^{1}H} NMR (376 MHz, Methanol-d_4) δ -119.79;

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 179.55 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 160.53 (d, J = 1.1 Hz), 159.23 (d, $^{1}J_{C\text{-}F}$ = 244.0 Hz), 147.52 , 125.48 (d, $^{2}J_{C\text{-}F}$ = 26.1 Hz), 122.00 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 114.51 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 109.59 (d, $^{2}J_{C\text{-}F}$ = 25.1 Hz);

HRMS (ESI): $C_8H_4FNNaO_3^+$ $[M+Na]^+$ Calcd 204.0067, Found 204.0063.



3c, 35.3 mg, (PE/EA = 100:25), yellow solid, yield: 89%;

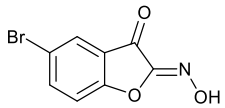
m.p.: 195 – 197 °C;

IR (neat) ν 3294, 1713, 1455, 1268, 1023, 716 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.52 (s, 1H), 7.86 (dd, J = 8.7, 2.4 Hz, 1H), 7.83 (d, J = 2.1 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 178.85, 162.51, 147.26, 138.48, 129.17, 124.23, 123.13, 115.72;

HRMS (ESI): $C_8H_4ClNNaO_3^+$ $[M+Na]^+$ Calcd 219.9772, Found $[M+Na]^+$ 219.9765, $[M+2+Na]^+$ 221.9733 (100%: 34.7%).



3d, 47.0 mg, (PE/EA = 100:80), yellow solid, yield: 97%;

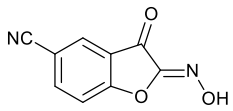
m.p.: 160 – 162 °C;

IR (neat) ν 3093, 2868, 1723, 1445, 1267, 1030 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.83 – 7.77 (m, 2H), 7.23 (d, J = 8.5 Hz, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.77, 163.15, 146.88, 140.79, 126.60, 123.01, 116.67, 114.91;

HRMS (ESI): $C_8H_4BrNNaO_3^+$ $[M+Na]^+$ Calcd 263.9267, Found $[M+Na]^+$ 263.9242, $[M+2+Na]^+$ 265.9214 (100%: 99.9%).



3e, 37.0 mg, (PE/EA = 100:80), light gray solid, yield: 98%;

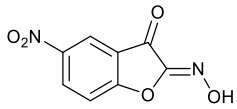
m.p.: 227 – 229 °C;

IR (neat) ν 3271, 3096, 2247, 1730, 1282, 1017, 744 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H), 8.35 (d, J = 1.8 Hz, 1H), 8.25 (dd, J = 8.6, 1.9 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 178.42, 165.70, 146.75, 142.24, 129.89, 122.75, 118.22, 115.29, 107.76;

HRMS (ESI): $C_9H_4N_2NaO_3^+$ $[M+Na]^+$ Calcd 211.0114, Found 211.0109.



3f, 31.8 mg, (PE/EA = 100:25), light gray solid, yield: 76%;

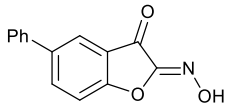
m.p.: 163 – 165 °C;

IR (neat) ν 3248, 1721, 1598, 1342, 1258, 1040, 745 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.68 (dd, J = 9.0, 2.5 Hz, 1H), 8.62 (d, J = 2.5 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.37, 166.82, 146.88, 144.61, 132.87, 121.86, 120.04, 113.96;

HRMS (ESI): $C_8H_4N_2NaO_5^+$ $[M+Na]^+$ Calcd 231.0012, Found 230.9996.



3g, 31.5 mg, (PE/EA = 100:25), yellow solid, yield: 66%;

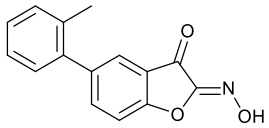
m.p.: 161 – 163 °C;

IR (neat) ν 3055, 1724, 1610, 1261, 1027, 756 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.48 (s, 1H), 8.13 (dd, J = 8.6, 2.1 Hz, 1H), 7.98 (d, J = 2.1 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.57 (d, J = 8.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.44 – 7.37 (m, 1H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.81, 163.52, 147.46, 138.82, 137.73, 137.24, 129.53, 128.32, 127.26, 122.30, 122.22, 114.19;

HRMS (ESI): $C_{14}H_9NNaO_3^+$ $[M+Na]^+$ Calcd 262.0475, Found 262.0463.



3h, 29.6 mg, (PE/EA = 100:25), yellow solid, yield: 58%;

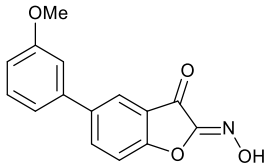
m.p.: 150 – 152 °C;

IR (neat) ν 3294, 1720, 1474, 1258, 1024, 728 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.46 (s, 1H), 7.80 (dd, J = 8.5, 2.0 Hz, 1H), 7.66 (d, J = 2.0 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.35 – 7.22 (m, 4H), 2.24 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.79, 163.14, 147.41, 140.04, 139.82, 138.05, 135.39, 130.96, 130.08, 128.33, 126.60, 124.52, 121.65, 113.57, 20.52;

HRMS (ESI): $C_{15}H_{11}NNaO_3^+$ $[M+Na]^+$ Calcd 276.0631, Found 276.0623.



3i, 46.7 mg, (PE/EA = 100:25), yellow solid, yield: 87%;

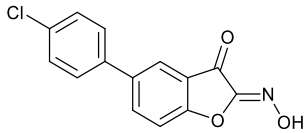
m.p.: 110 – 112 °C;

IR (neat) ν 3261, 1725, 1468, 1272, 1022, 773 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.48 (s, 1H), 8.13 (dd, J = 8.7, 2.1 Hz, 1H), 7.99 (d, J = 2.2 Hz, 1H), 7.55 (d, J = 8.6 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.26 (d, J = 7.7 Hz, 1H), 7.23 (t, J = 2.1 Hz, 1H), 6.96 (dd, J = 8.2, 2.5 Hz, 1H), 3.84 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.80, 163.58, 160.29, 147.46, 140.30, 137.85, 137.13, 130.57, 122.48, 122.15, 119.53, 114.14, 114.09, 112.60, 55.66;

HRMS (ESI): $C_{15}H_{11}NNaO_4^+$ $[M+Na]^+$ Calcd 292.0580, Found 292.0575.



3j, 51.1 mg, (PE/EA = 100:25), yellow solid, yield: 93%;

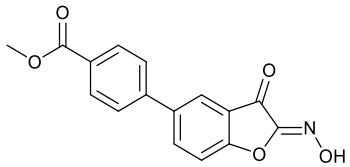
m.p.: 195 – 197 °C;

IR (neat) ν 3205, 1716, 1470, 1286 1026, 755 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.49 (s, 1H), 8.12 (dd, J = 8.6, 2.2 Hz, 1H), 7.99 (d, J = 2.2 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.7 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H)；

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.70, 163.63, 147.40, 137.60, 135.85, 133.25, 129.40, 129.05, 122.42, 122.25, 114.25；

HRMS (ESI): $C_{14}H_8ClNNaO_3^+$ $[M+Na]^+$ Calcd 296.0085, Found $[M+Na]^+$ 296.0070, $[M+2+Na]^+$ 298.0046 (100%: 35.0%).



3k, 30.3 mg, (PE/EA = 100:80), yellow solid, yield: 51%;

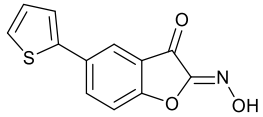
m.p.: 205 – 207 °C;

IR (neat) ν 3227, 1735, 1680, 1262, 1004, 744 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.49 (s, 1H), 8.21 (dd, J = 8.6, 2.2 Hz, 1H), 8.08 (d, J = 2.1 Hz, 1H), 8.04 (d, J = 8.1 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.6 Hz, 1H), 3.88 (s, 3H)；

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.69, 166.43, 163.97, 147.40, 143.27, 137.89, 135.80, 130.31, 129.25, 127.58, 122.89, 122.39, 114.40, 52.68；

HRMS (ESI): $C_{16}H_{11}NNaO_5^+$ $[M+Na]^+$ Calcd 320.0529, Found 320.0512.



3l, 22.2 mg, (PE/EA = 100:25), dark orange solid, yield: 45%;

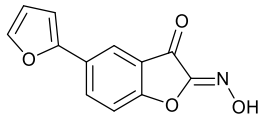
m.p.: 175 – 177 °C;

IR (neat) ν 3266, 1727, 1613, 1281, 1023, 692 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 8.10 (dd, J = 8.7, 2.2 Hz, 1H), 7.96 (d, J = 2.1 Hz, 1H), 7.63 (d, J = 3.7 Hz, 1H), 7.59 (d, J = 5.1 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.16 (t, J = 4.5 Hz, 1H)；

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.65, 163.19, 147.38, 141.77, 136.26, 130.98, 129.18, 126.78, 125.19, 122.34, 120.65, 114.49；

HRMS (ESI): $C_{12}H_7NNaO_3S^+$ $[M+Na]^+$ Calcd 268.0039, Found 268.0033.



3m, 15.4 mg, (PE/EA = 100:25), dark orange solid, yield: 34%;

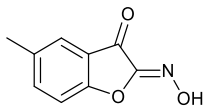
m.p.: 188 – 190 °C;

IR (neat) ν 3248, 1726, 1505, 1299, 1039, 729 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.00 (dd, J = 8.7, 1.6 Hz, 1H), 7.88 (d, J = 1.9 Hz, 1H), 7.48 (d, J = 1.8 Hz, 1H), 7.29 (d, J = 8.7 Hz, 1H), 6.73 (d, J = 3.4 Hz, 1H), 6.43 (dd, J = 3.4, 1.7 Hz, 1H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 179.98, 163.38, 151.88, 147.23, 142.72, 133.83, 127.96, 121.64, 118.31, 113.25, 111.58, 105.68;

HRMS (ESI): $C_{12}H_7NNaO_4^+$ $[M+Na]^+$ Calcd 252.0267, Found 252.0260.



3n, 19.2 mg, (PE/EA = 100:25), yellow solid, yield: 54%;

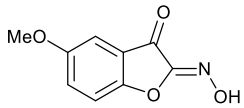
m.p.: 176 – 178 °C;

IR (neat) ν 3261, 1707, 1488, 1288, 1024, 773 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.36 (s, 1H), 7.64 (dd, J = 8.4, 2.0 Hz, 1H), 7.56 (s, 1H), 7.37 (d, J = 8.4 Hz, 1H), 2.36 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.90, 162.48, 147.48, 140.05, 134.52, 124.34, 121.51, 113.34, 20.60;

HRMS (ESI): $C_9H_7NNaO_3^+$ $[M+Na]^+$ Calcd 200.0318, Found 200.0309.



3o, 6.9 mg, (PE/EA = 100:25), light orange solid, yield: 18%;

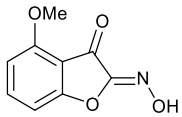
m.p.: 166 – 168 °C;

IR (neat) ν 3231, 2410, 1712, 1488, 1288, 1016 774 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.40 (dd, J = 9.0, 2.8 Hz, 1H), 7.30 (d, J = 9.0 Hz, 1H), 7.24 (d, J = 2.8 Hz, 1H), 3.86 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 180.39, 159.38, 156.91, 147.86, 126.96, 121.43, 113.74, 105.36, 55.18;

HRMS (ESI): $C_9H_7NNaO_4^+$ $[M+Na]^+$ Calcd 216.0267, Found 216.0253.



3q, 18.8 mg, (PE/EA = 100:40), yellow solid, yield: 49%;

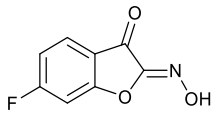
m.p.: 175 – 177 °C;

IR (neat) ν 3247, 1727, 1595, 1256, 1011, 766 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.21 (s, 1H), 7.75 (t, J = 8.3 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 3.93 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 176.75, 164.54, 158.37, 146.98, 140.93, 110.57, 107.65, 104.89, 56.79;

HRMS (ESI): $C_9H_7NNaO_4^+$ $[M+Na]^+$ Calcd 216.0267, Found 216.0258.



3r, 28.3 mg, (PE/EA = 100:25), light gray solid, yield: 78%;

m.p.: 172 – 174 °C;

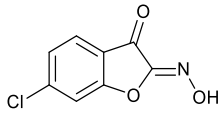
IR (neat) ν 3249, 3107, 2890, 1707, 1273, 862 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.71 (dd, J = 8.6, 5.6 Hz, 1H), 7.08 (dd, J = 8.8, 2.2 Hz, 1H), 6.98 (td, J = 8.9, 2.2 Hz, 1H);

^{19}F{^{1}H} NMR (376 MHz, Methanol-d_4) δ -96.72;

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 178.42, 169.01 (d, $^1J_{C\text{-}F}$ = 258.5 Hz), 165.86 (d, $^3J_{C\text{-}F}$ = 15.0 Hz), 146.98 , 126.53 (d, $^3J_{C\text{-}F}$ = 12.0 Hz), 118.10 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 112.38 (d, $^2J_{C\text{-}F}$ = 24.4 Hz), 100.82 (d, $^2J_{C\text{-}F}$ = 27.4 Hz);

HRMS (ESI): $C_8H_4FNNaO_3^+$ $[M+Na]^+$ Calcd 204.0067, Found 204.0067.



3s, 27.4 mg, (PE/EA = 100:25), light gray solid, yield: 70%;

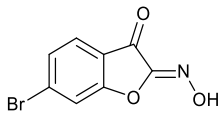
m.p.: 198 – 200 °C;

IR (neat) ν 3260, 3092, 1725, 1265, 1012, 772 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.51 (s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 1.7 Hz, 1H), 7.38 (dd, J = 8.2, 1.7 Hz, 1H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 178.66, 164.35, 147.01, 143.06, 126.19, 125.45, 120.77, 114.29;

HRMS (ESI): $C_8H_4ClNNaO_3^+$ $[M+Na]^+$ Calcd 219.9772, Found $[M+Na]^+$ 219.9761, $[M+2+Na]^+$ 221.9733 (100%: 33.4%).



3t, 40.9 mg, (PE/EA = 100:80), yellow solid, yield: 85%;

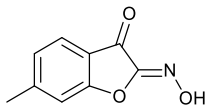
m.p.: 199 – 201 °C;

IR (neat) ν 3278, 1724, 1587, 1225, 1006, 771cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.52 (s, 1H), 7.86 (d, J = 1.6 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.52 (dd, J = 8.2, 1.6 Hz, 1H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 178.86, 164.20, 146.90, 132.14, 128.28, 126.18, 121.05, 117.13;

HRMS (ESI): $C_8H_4BrNNaO_3^+$ $[M+Na]^+$ Calcd 263.9267, Found $[M+Na]^+$ 263.9253, $[M+2+Na]^+$ 265.9237 (100%: 98.4%).



3u, 29.6 mg, (PE/EA = 100:25), light gray solid, yield: 84%;

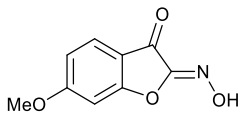
m.p.: 167 – 169 °C;

IR (neat) ν 3219, 1733, 1260, 1021, 773 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.60 (d, J = 7.9 Hz, 1H), 7.16 – 7.13 (m, 2H), 2.50 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 179.68, 164.91, 151.57, 147.37, 125.50, 123.75, 118.85, 112.82, 21.31;

HRMS (ESI): $C_9H_7NNaO_3^+$ $[M+Na]^+$ Calcd 200.0318, Found 200.0320.



3v, 31.1 mg, (PE/EA = 100:30), yellow solid, yield: 81%;

m.p.: 162 – 164 °C;

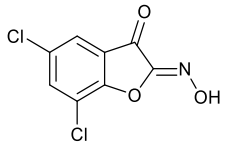
IR (neat) ν 3075, 2890, 1703, 1282, 1004, 771 cm^{-1};

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.65 (d, J = 8.6 Hz, 1H), 6.88 (d, J = 2.1 Hz, 1H), 6.85 (dd, J = 8.6,

2.2 Hz, 1H), 3.96 (s, 3H);

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 178.34, 169.15, 167.12, 147.64, 125.54, 114.20, 112.73, 96.67, 55.63;

HRMS (ESI): $C_9H_7NNaO_4^+$ $[M+Na]^+$ Calcd 216.0267, Found 216.0264.



3w, 36.3 mg, (PE/EA = 100:25), yellow solid, yield: 72%;

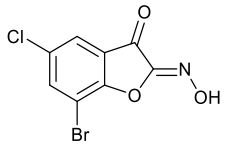
m.p.: 171 – 173 °C;

IR (neat) ν 3261, 3066, 1719, 1460, 1260, 1031, 714 cm^{-1};

^1H NMR (400 MHz, DMSO-d_6) δ 12.71 (s, 1H), 8.12 (d, J = 2.1 Hz, 1H), 7.84 (d, J = 2.1 Hz, 1H);

$^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 178.15, 158.43, 146.65, 137.21, 129.37, 124.68, 123.20, 118.81;

HRMS (ESI): $C_8H_3Cl_2NNaO_3^+$ $[M+Na]^+$ Calcd 253.9382, Found $[M+Na]^+$ 253.9370, $[M+2+Na]^+$ 255.9340, $[M+4+Na]^+$ 257.9323 (100%: 20.8%: 9.0%).



3x, 39.9 mg, (PE/EA = 100:25), yellow solid, yield: 72%;

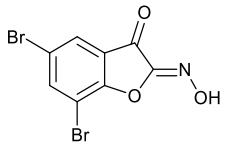
m.p.: 172 – 174 °C;

IR (neat) ν 3239, 3062, 2890, 1722, 1260, 1023, 729 cm^{-1};

^1H NMR (400 MHz, DMSO-d_6) δ 12.71 (s, 1H), 8.20 (d, J = 2.2 Hz, 1H), 7.85 (d, J = 2.1 Hz, 1H;

$^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 178.40, 159.86, 146.75, 139.83, 129.66, 124.42, 123.58, 106.87;

HRMS (ESI): $C_8H_3BrClNNaO_3^+$ $[M+Na]^+$ Calcd 297.8877, Found $[M+Na]^+$ 297.8828, $[M+2+Na]^+$ 299.8803, $[M+4+Na]^+$ 301.8779 (100%: 135.3%: 6.1%).



3y, 42.2 mg, (PE/EA = 100:25), yellow solid, yield: 66%;

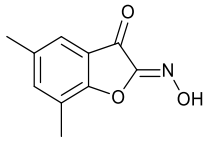
m.p.: 176 – 178 °C;

IR (neat) ν 3061, 2439, 1717, 1262, 1023, 710 cm^{-1};

^1H NMR (400 MHz, Methanol-d_4) δ 8.04 (d, J = 1.9 Hz, 1H), 7.77 (d, J = 1.9 Hz, 1H);

$^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ 178.12, 160.45, 146.31, 142.38, 125.74, 124.14, 116.83, 106.83;

HRMS (ESI): $C_8H_3Br_2NNaO_3^+$ $[M+Na]^+$ Calcd 341.8372, Found $[M+Na]^+$ 341.8327, $[M+2+Na]^+$ 343.8303, $[M+4+Na]^+$ 345.8322 (100%: 187.3%: 79.1%).



3z, 30.5 mg, (PE/EA = 100:25), yellow solid, yield: 80%;

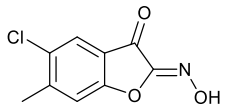
m.p.: 186 – 188 °C;

IR (neat) ν 3476, 2865, 1712, 1608, 1264, 1017, 776 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.37 (s, 1H), 7.48 (s, 1H), 7.35 (s, 1H), 2.32 (s, 3H), 2.29 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 180.20, 161.11, 147.51, 140.89, 134.19, 122.84, 121.60, 121.12, 20.57, 14.13;

HRMS (ESI): $C_{10}H_9NNaO_3^+$ $[M+Na]^+$ Calcd 214.0475, Found 214.0470.



3aa, 28.3 mg, (PE/EA = 100:80), yellow solid, yield: 67%;

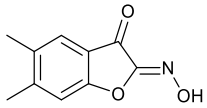
m.p.: 224 – 226 °C;

IR (neat) ν 3235, 1721, 1454, 1271, 1035, 758 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.46 (s, 1H), 7.80 (s, 1H), 7.55 (s, 1H), 2.46 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 178.44, 162.58, 147.96, 147.33, 129.83, 124.39, 120.95, 115.97, 21.73;

HRMS (ESI): $C_9H_6ClNNaO_3^+$ $[M+Na]^+$ Calcd 233.9928, Found $[M+Na]^+$ 233.9915, $[M+2+Na]^+$ 235.9888 (100%: 32.3%).



3ab, 18.3 mg, (PE/EA = 100:25), yellow solid, yield: 48%;

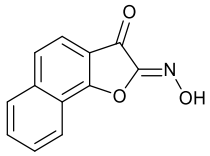
m.p.: 205 – 207 °C;

IR (neat) ν 3066, 2880, 1714, 1613, 1280, 1014, 770 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.29 (s, 1H), 7.50 (s, 1H), 7.28 (s, 1H), 2.36 (s, 3H), 2.26 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.31, 163.08, 150.38, 147.53, 133.75, 124.42, 119.31, 113.90, 21.45, 19.22;

HRMS (ESI): $C_{10}H_9NNaO_3^+$ $[M+Na]^+$ Calcd 214.0475, Found 214.0464.



3ac, 19.4 mg, (PE/EA = 100:25), dark orange solid, yield: 46%;

m.p.: 183 – 185 °C;

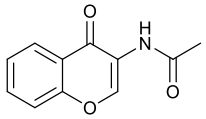
IR (neat) ν 3222, 1700, 1621, 1278, 1014, 744 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H), 8.22 (dd, J = 8.1, 1.2 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.82 – 7.75 (m, 2H), 7.66 (d, J = 8.5 Hz, 1H);

$^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 179.30, 163.97, 147.23, 138.79, 131.76, 129.40, 128.51, 124.99, 121.80, 120.12, 118.80, 116.98;

HRMS (ESI): $C_{12}H_7NNaO_3^+$ $[M+Na]^+$ Calcd 236.0318, Found 236.0312.

7.3 Characterization Data of Products 4a-8a



4a, 24.7 mg, (PE/EA = 100:15), light yellow solid, yield: 61%;

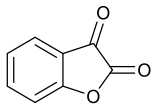
m.p.: 140 – 142 °C;

IR (neat) ν 3288, 3131, 3047, 1675, 1461, 1244, 760 cm^{-1};

^1H NMR (400 MHz, Chloroform-*d*) δ 9.39 (s, 1H), 8.26 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.08 (*br* s, 1H), 7.70 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.52 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.42 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 2.24 (s, 3H);

$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 171.81, 168.73, 155.79, 145.06, 133.90, 125.86, 124.83, 124.53, 121.96, 118.50, 24.06;

HRMS (ESI): $C_{11}H_9NNaO_3^+$ $[M+Na]^+$ Calcd 226.0475, Found 226.0446.

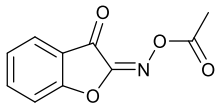


5a, 11.4 mg, (PE/EA = 100:5), light yellow solid, yield: 39%;

m.p.: 146 – 148°C[3];

^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.85, 154.89, 141.42, 133.94, 127.85, 124.97, 116.99, 111.53.



6a, 32.8 mg, (PE/EA = 100:20), yellow solid, yield: 80%;

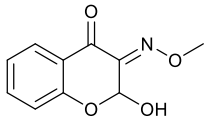
m.p.: 170 – 172 °C;

IR (neat) ν 1782, 1729, 1665, 1592, 1305, 1203, 750 cm^{-1};

^1H NMR (400 MHz, DMSO-d_6) δ 7.88 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.37 (m, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 179.89, 167.54, 164.42, 149.44, 139.83, 125.86, 125.35, 121.16, 113.69, 19.58.

HRMS (ESI): $C_{10}H_7NNaO_4^+$ $[M+Na]^+$ Calcd 228.0267, Found 228.0258.



7a, 39.2 mg, (PE/EA = 100:20), green yellow solid, yield: 95%;

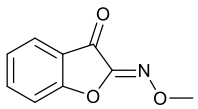
m.p.: 115 – 117 °C;

IR (neat) ν 3315, 2945, 1670, 1604, 1205, 1085, 749 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.8, 7.3, 1.8 Hz, 1H), 7.02 (ddd, *J* = 8.0, 7.3, 1.1 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.61 (s, 1H), 4.74 (*br* s, 1H), 4.09 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 176.17, 156.79, 147.33, 136.16, 126.74, 121.79, 120.83, 118.08, 87.36, 63.48;

HRMS (ESI): $C_{10}H_9NNaO_4^+$ $[M+Na]^+$ Calcd 230.0424, Found 230.0396.



8a, 22.3 mg, (PE/EA = 100:7), light yellow solid, yield: 63%;

m.p.: 103 – 105 °C;

IR (neat) ν 2946, 1717, 1591, 1299, 1028, 757 cm^{-1};

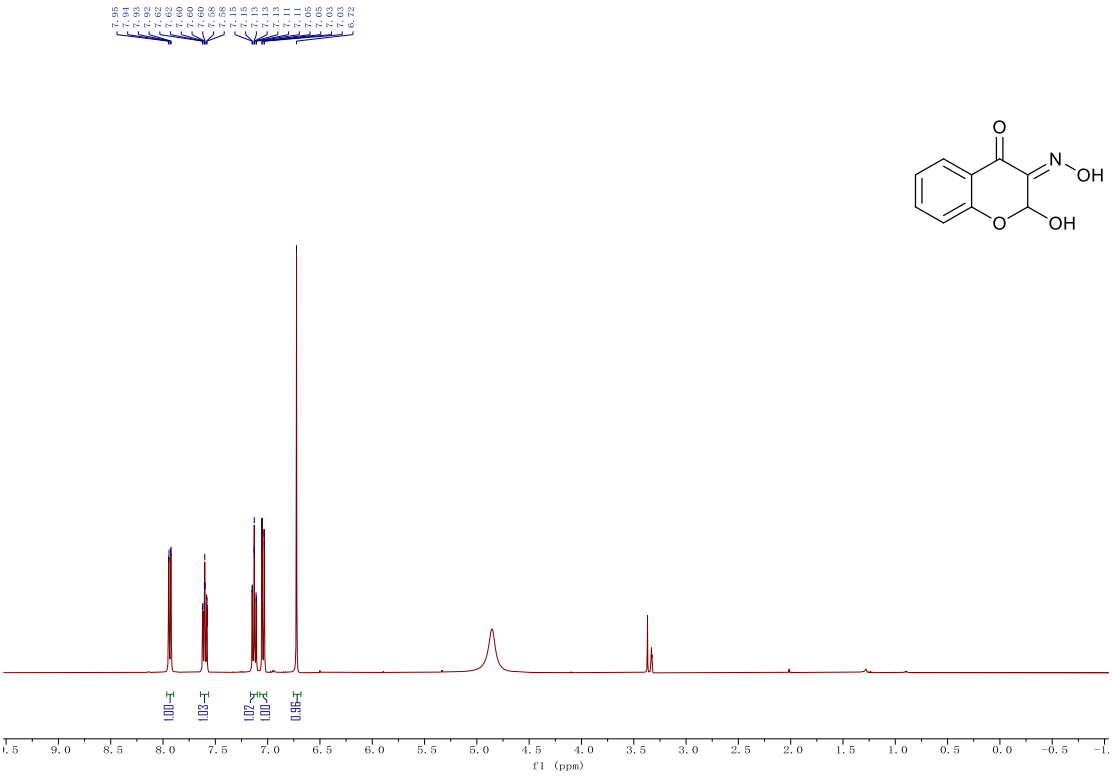
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.64 (ddd, *J* = 8.7, 7.5, 1.5 Hz, 1H), 7.25 – 7.19 (m, 2H), 4.10 (s, 3H);

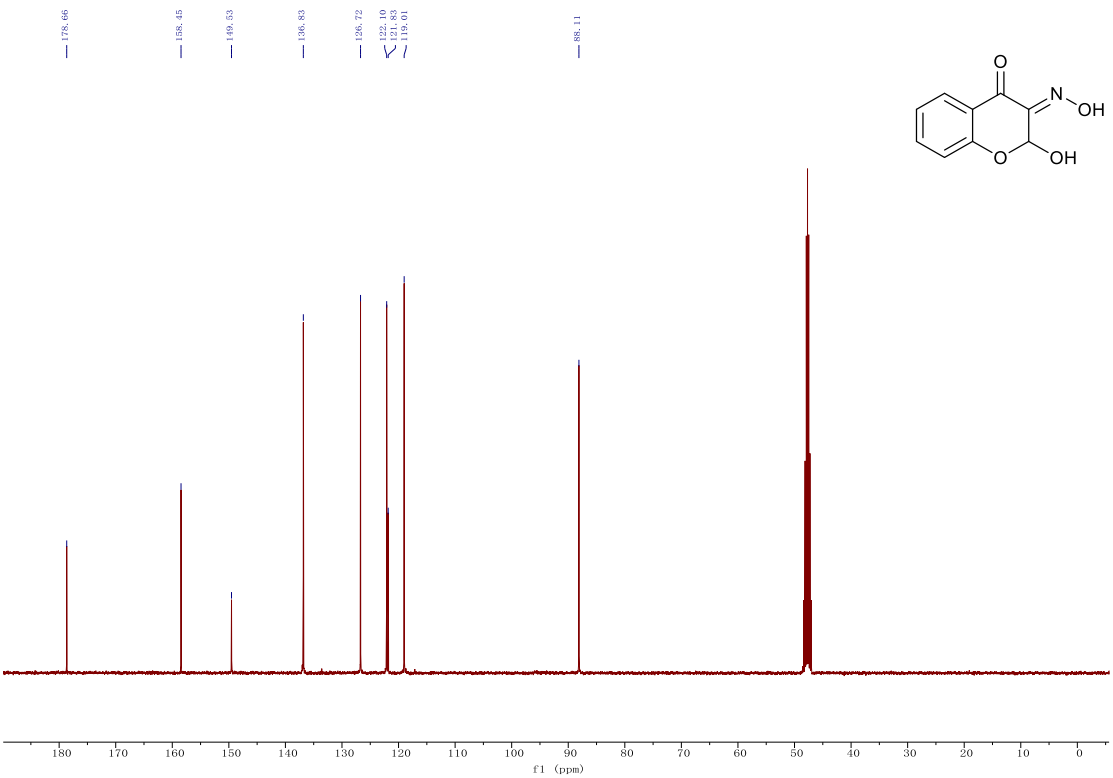
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 178.38, 163.45, 144.68, 137.62, 124.00, 123.77, 120.14, 112.17, 63.82;

HRMS (ESI): $C_9H_7NNaO_3^+$ $[M+Na]^+$ Calcd 200.0318, Found 200.0312.

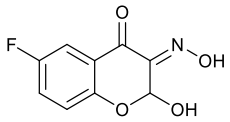
7.3 Copies of NMR Spectra

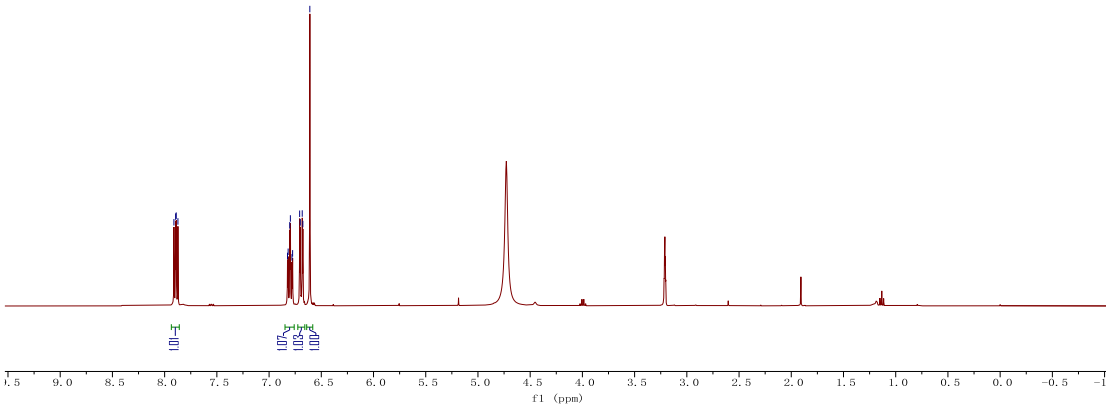
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2a

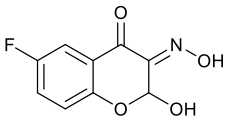


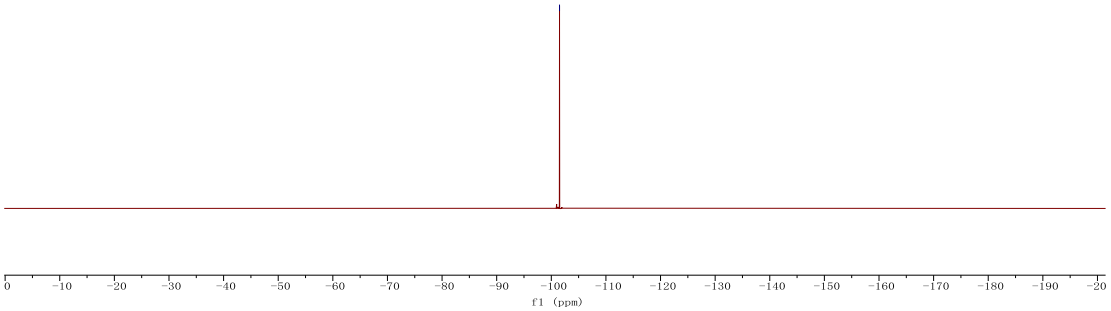


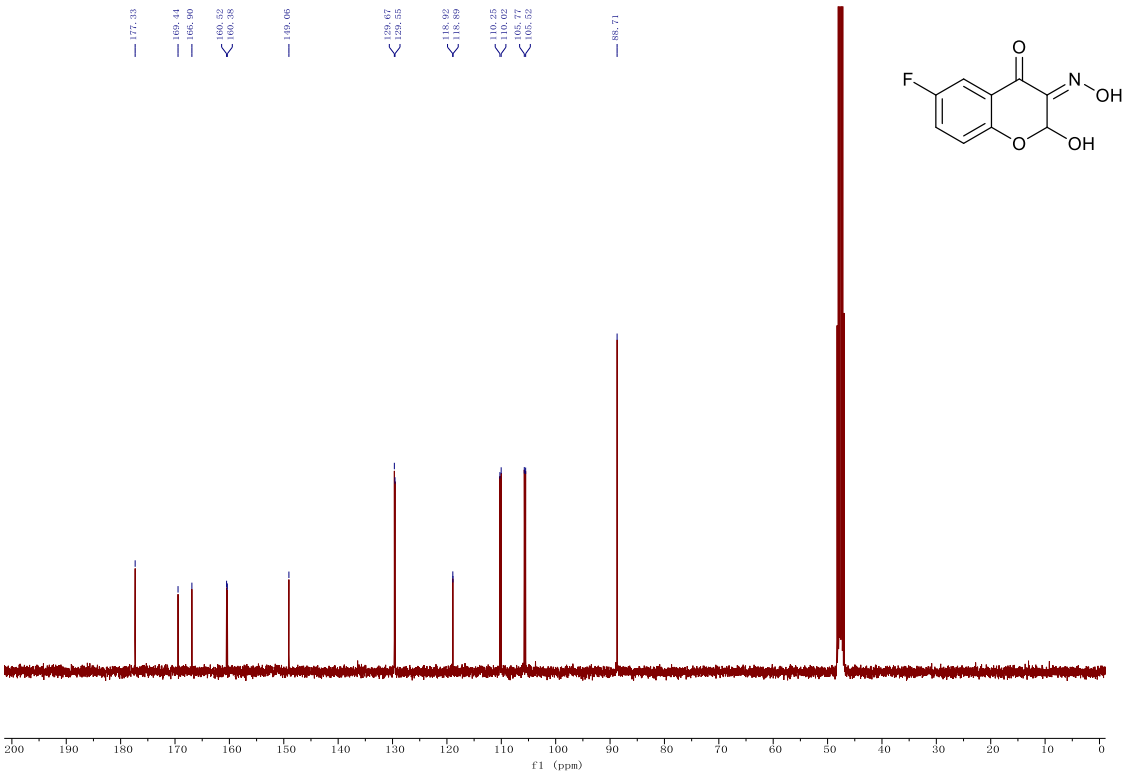
^{1}H NMR (400 MHz, CD_3OD), ^{19}F NMR (376 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2b







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129.55
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105.52
88.71
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OH
O
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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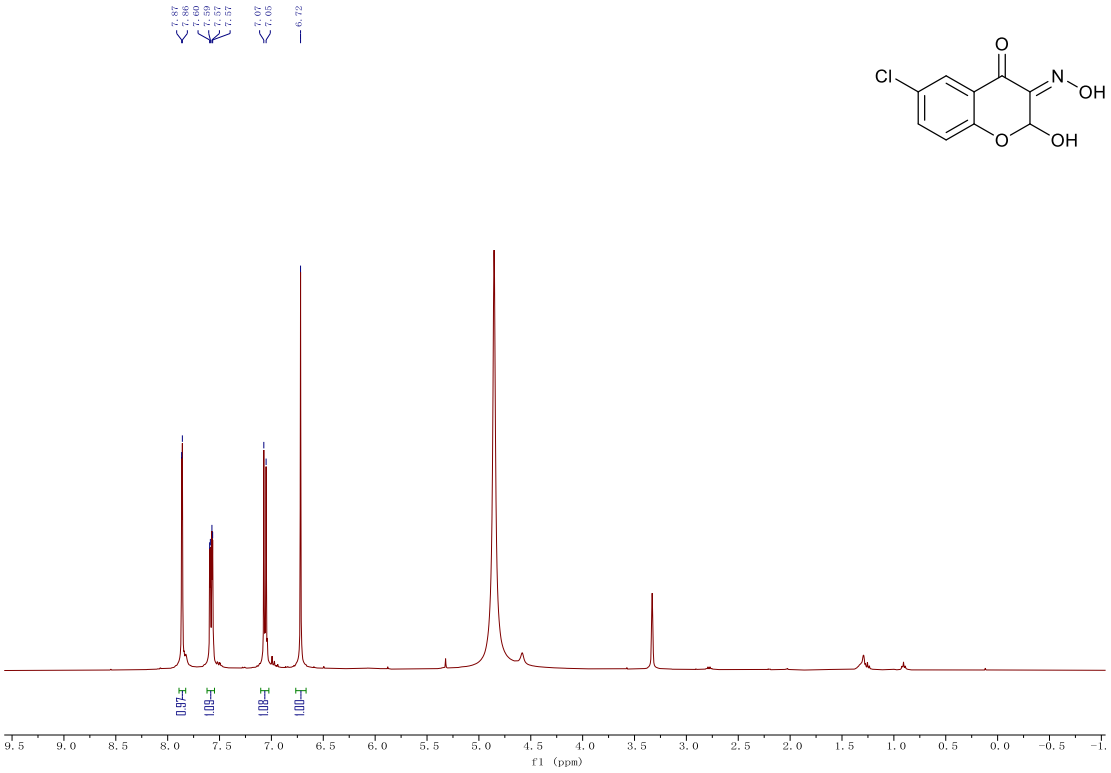
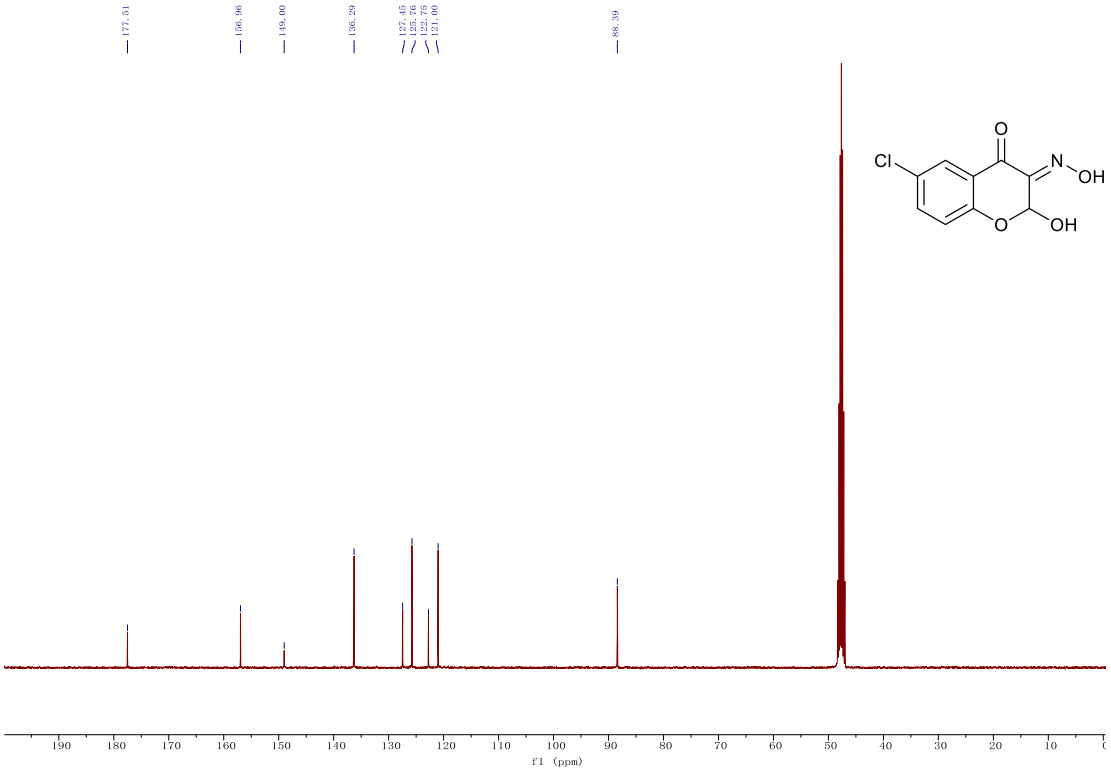
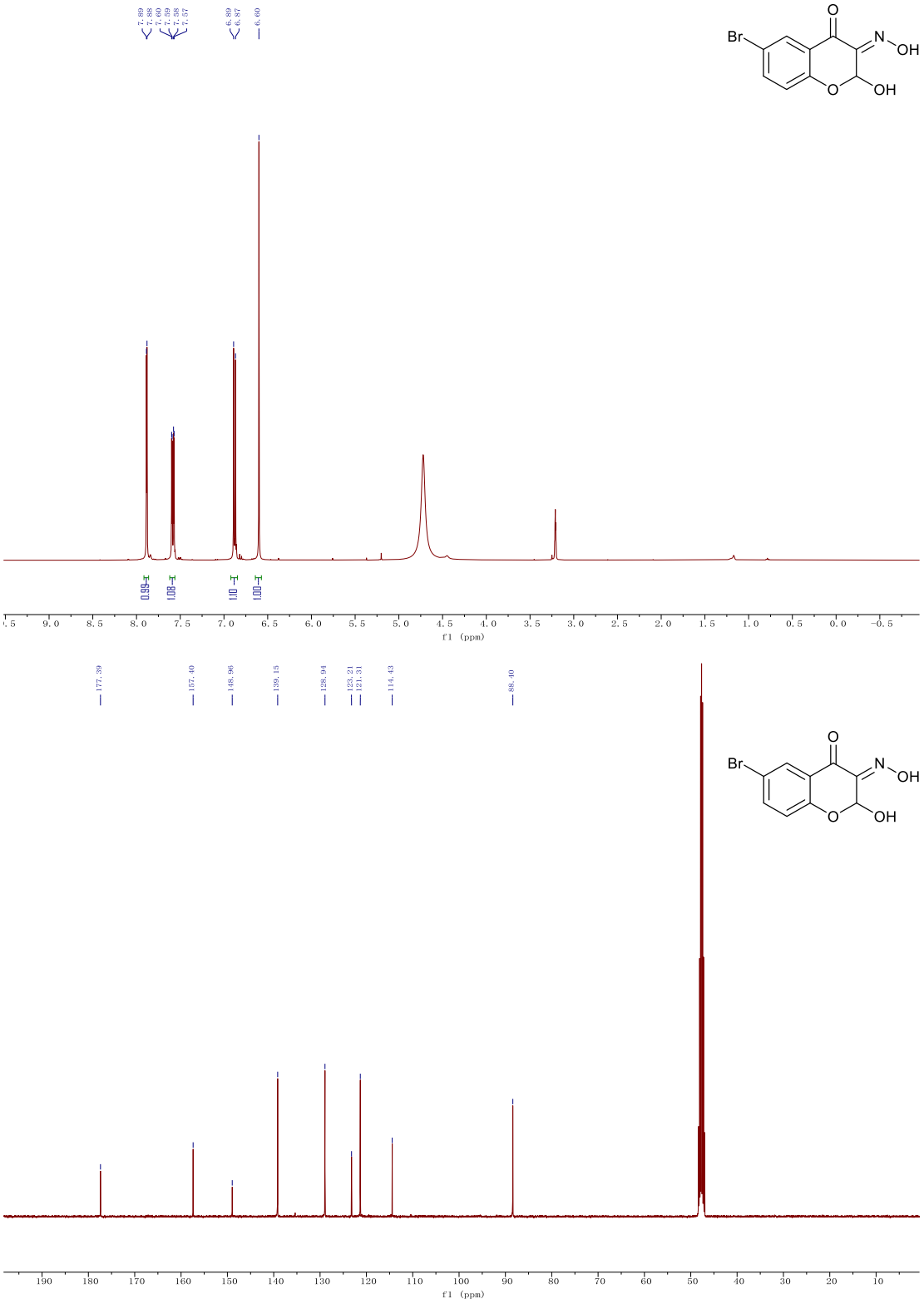
40
30
20
10
0
f1 (ppm)

^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2c

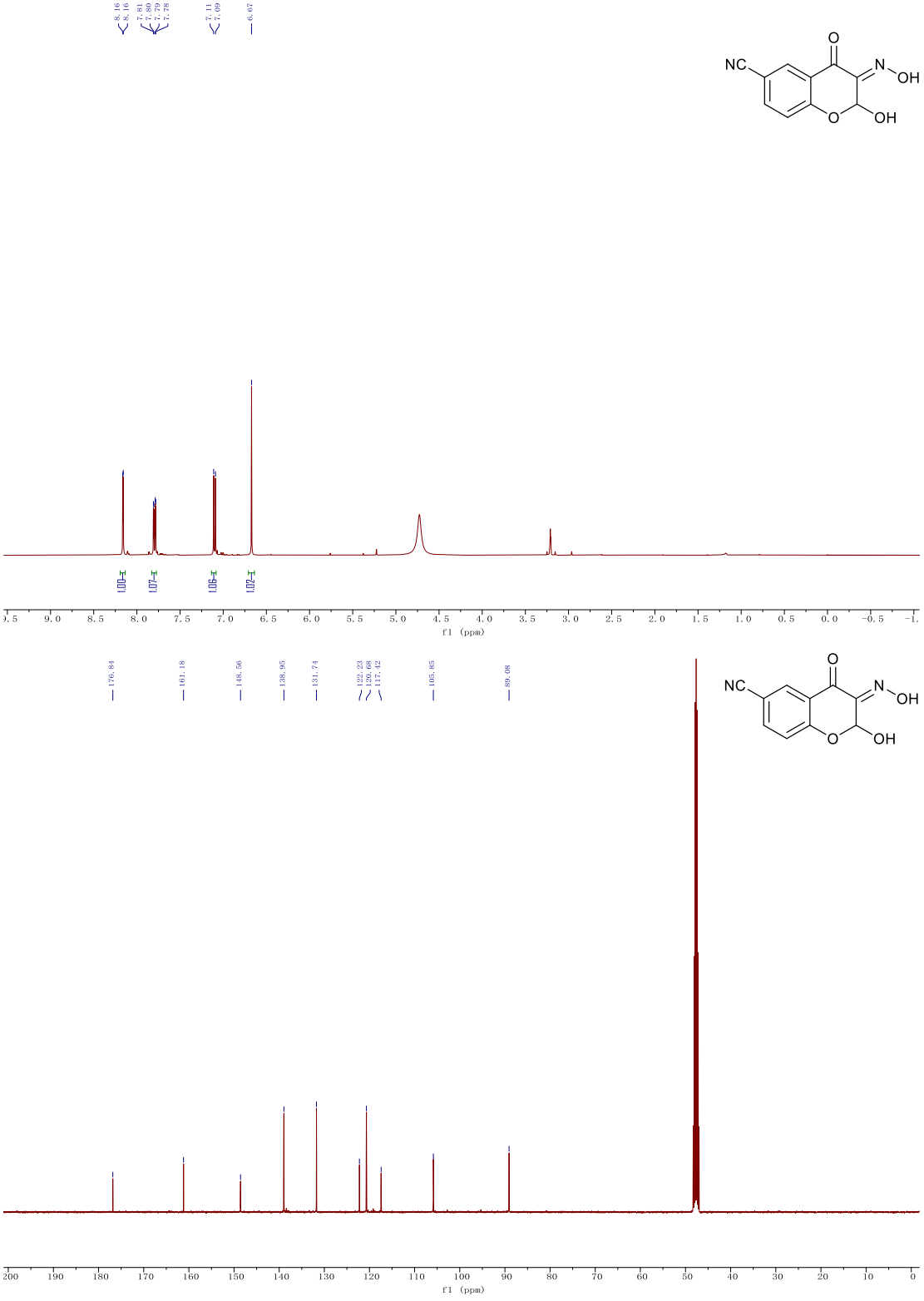




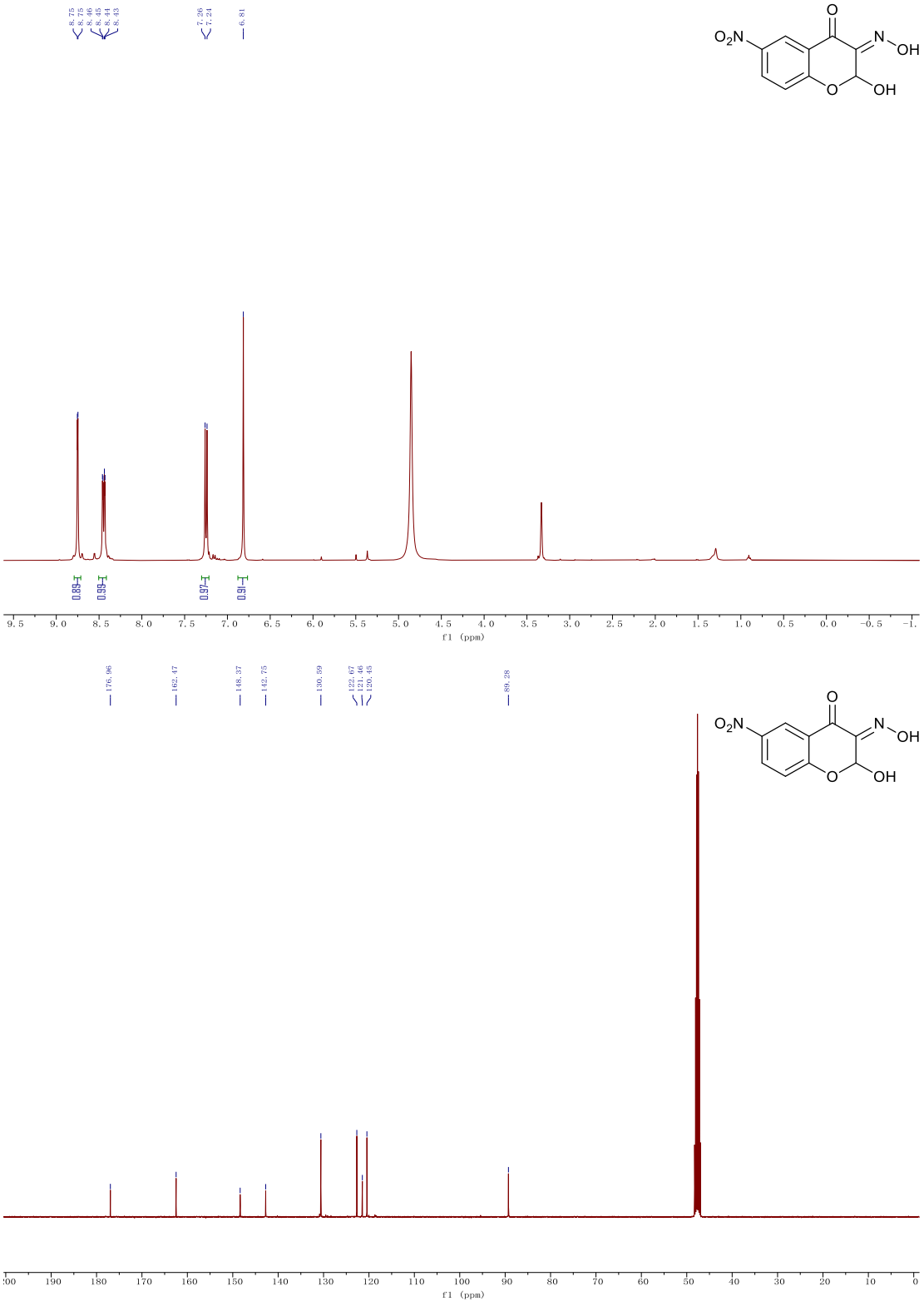
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2d



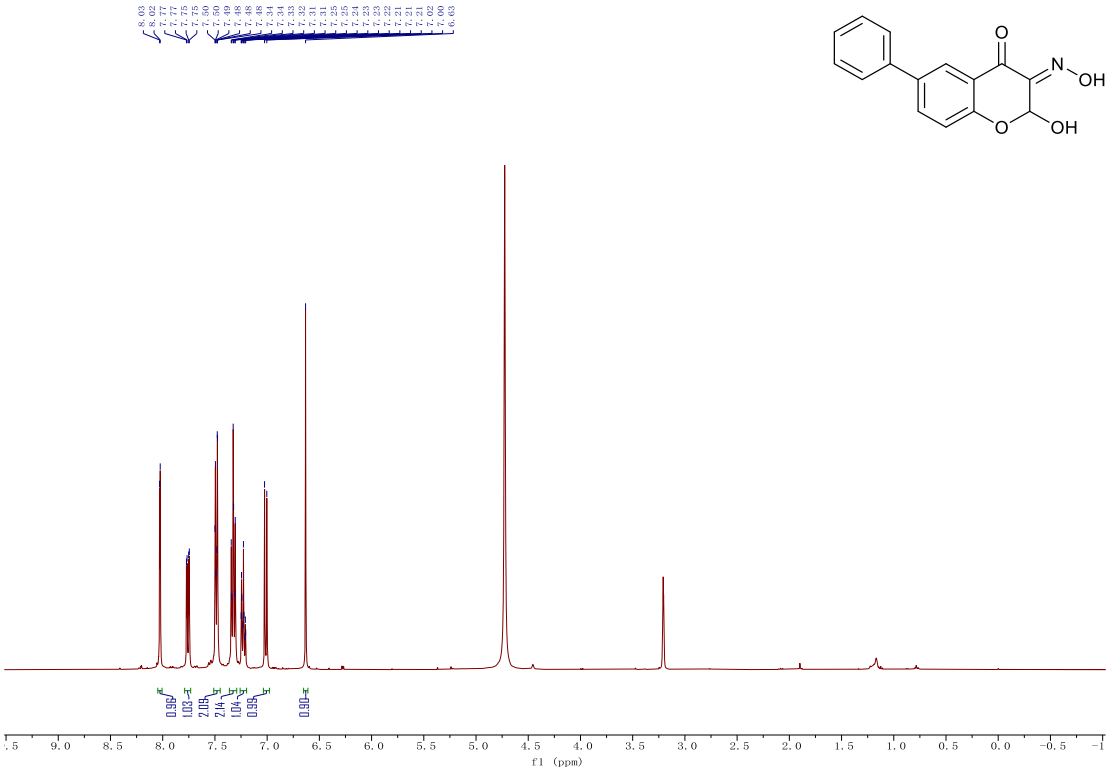
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2e

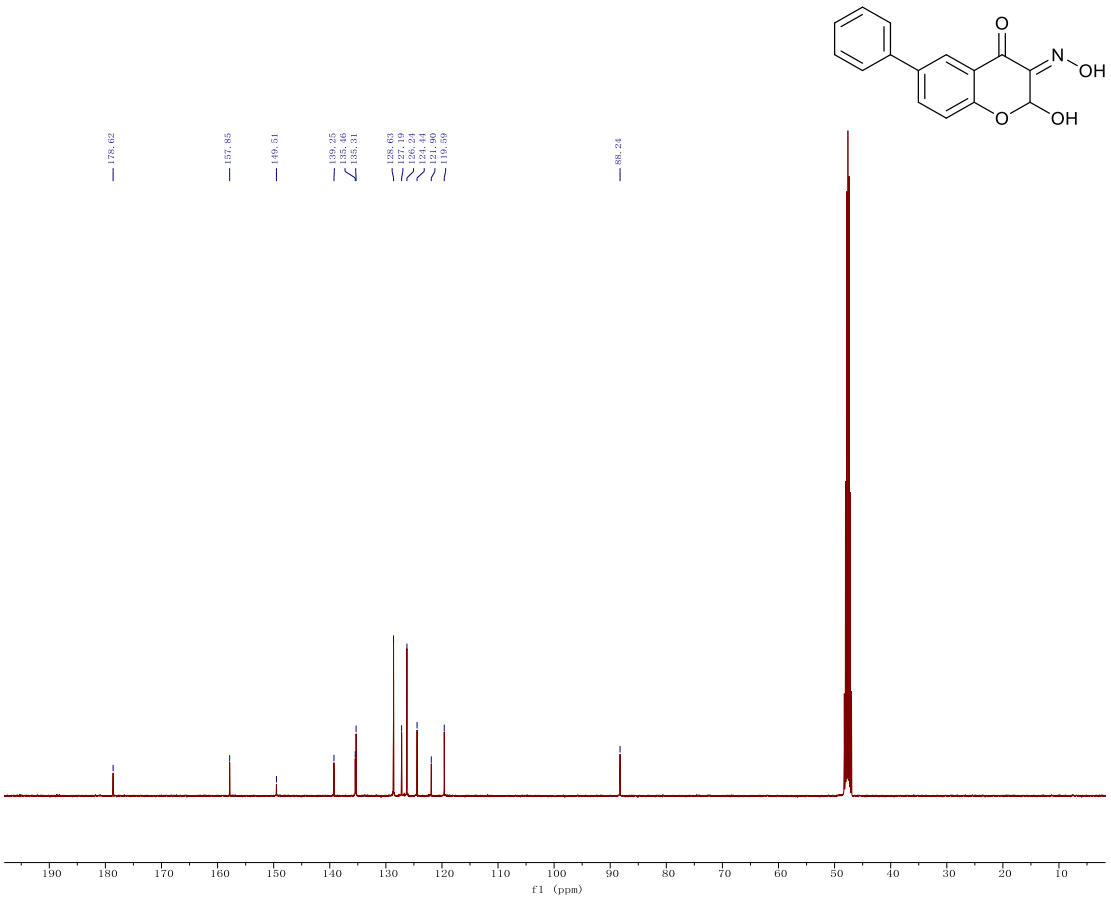


^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2f

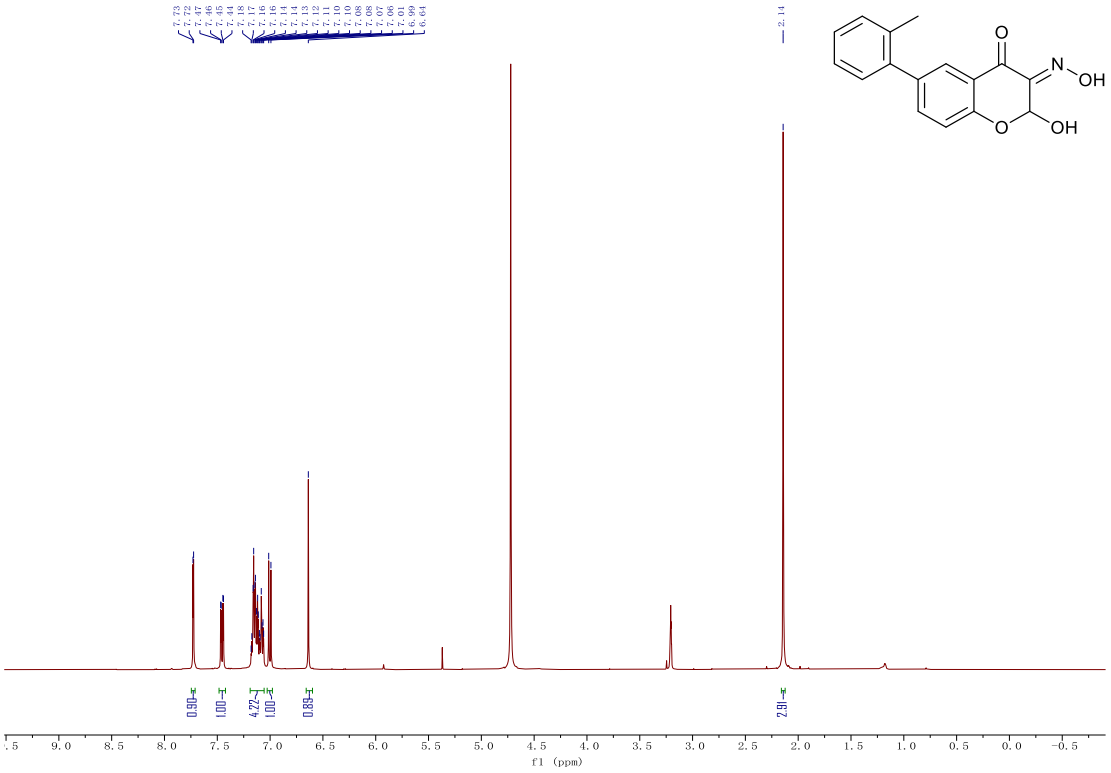


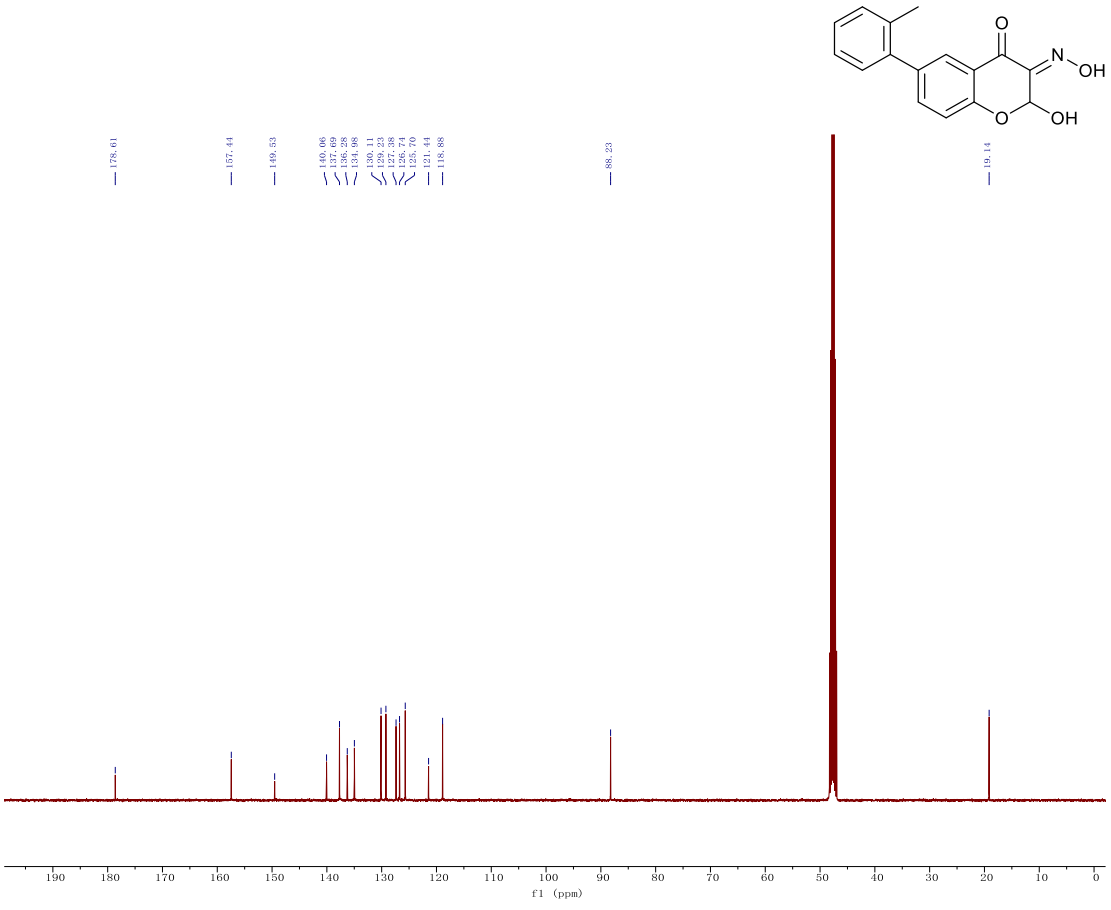
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2g



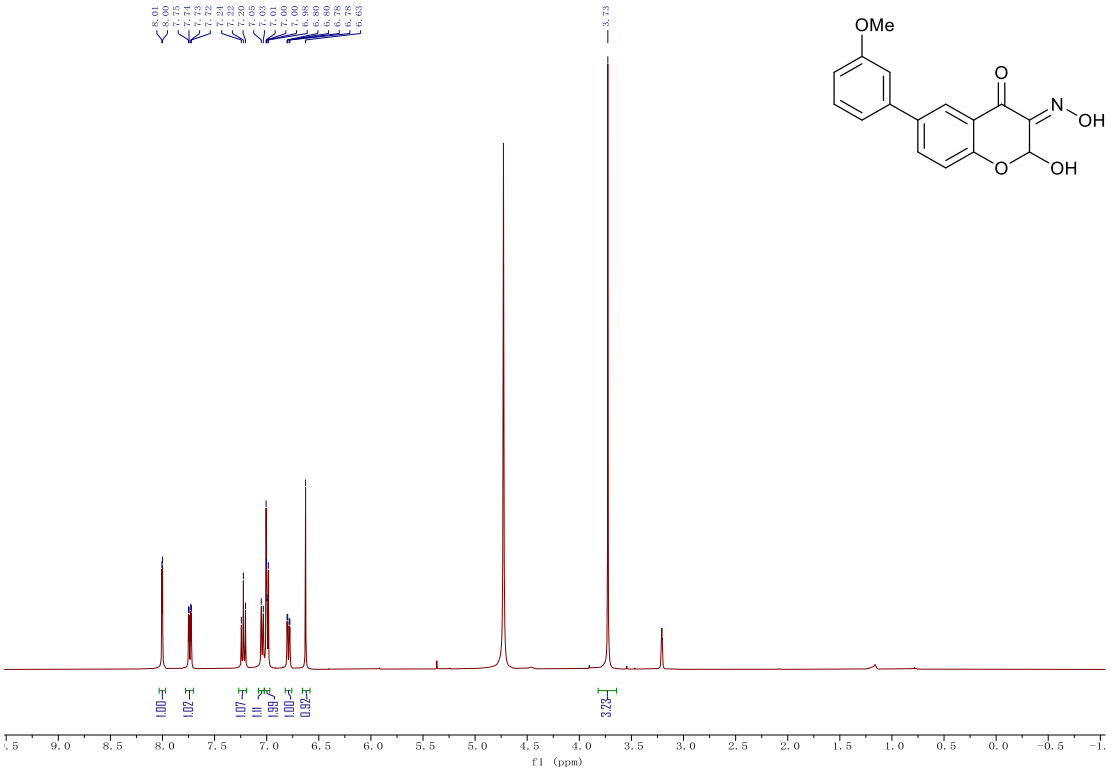


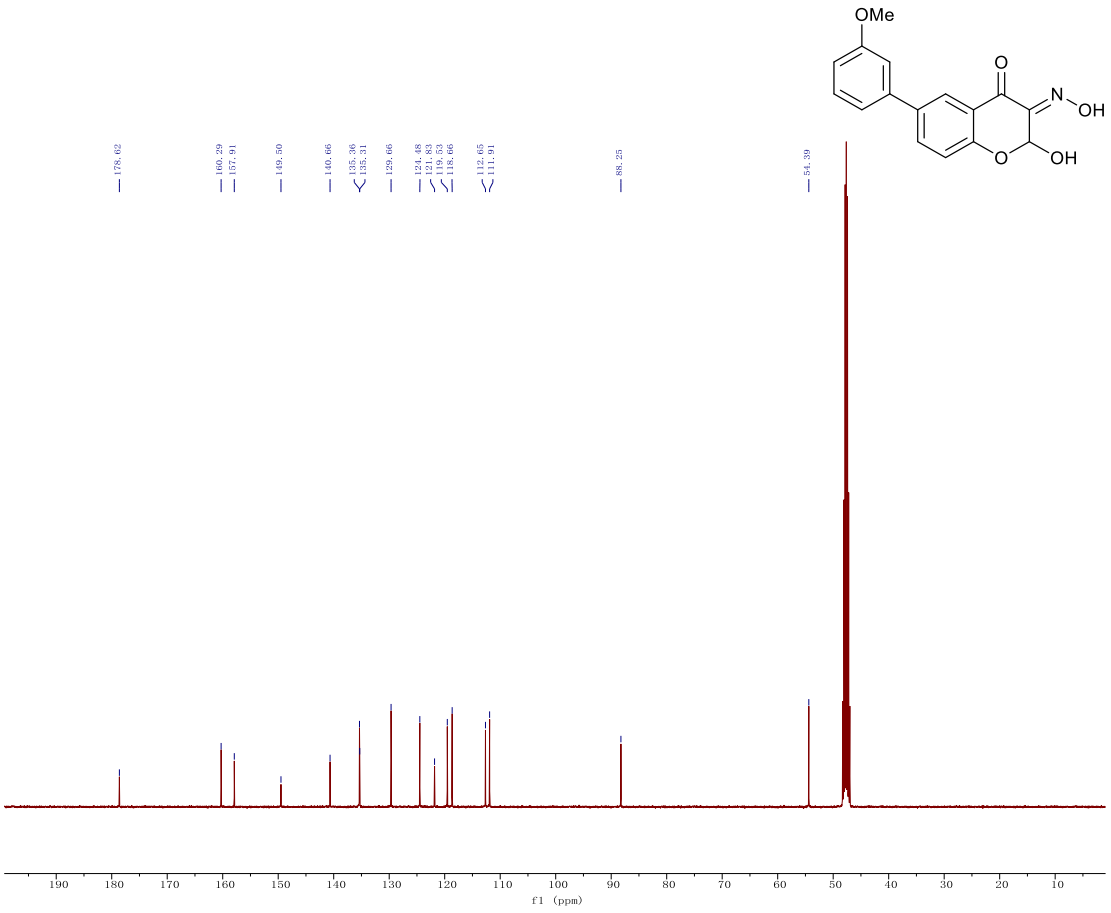
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2h



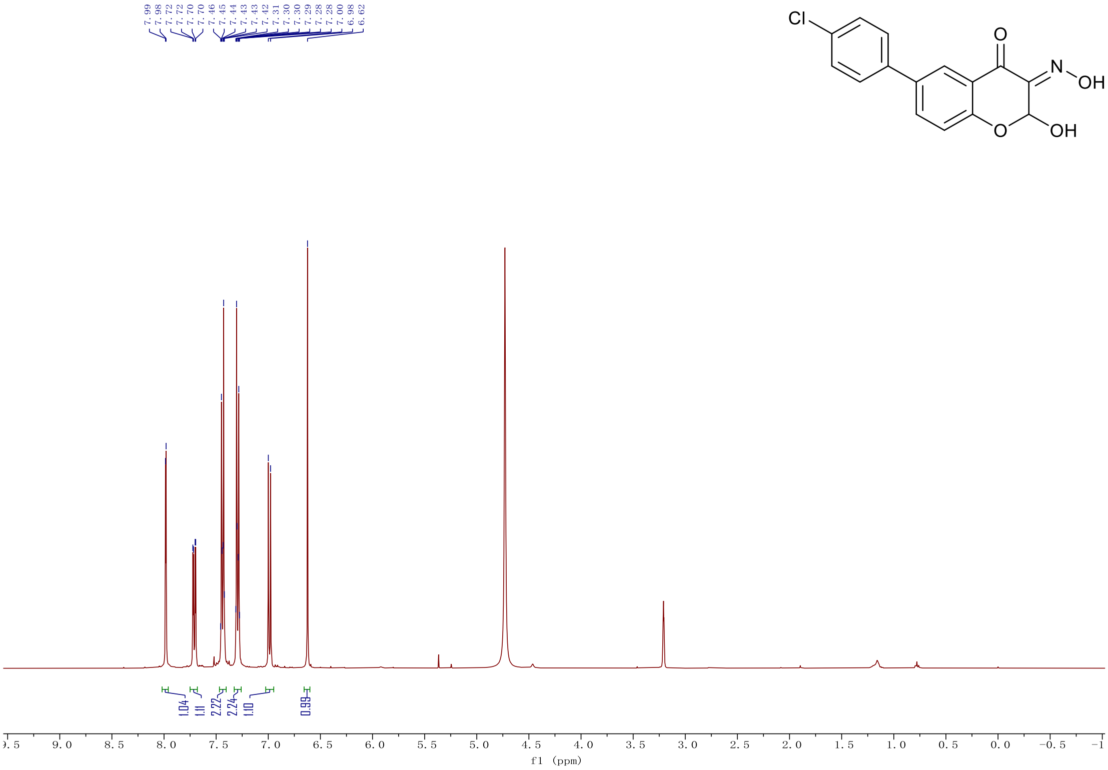


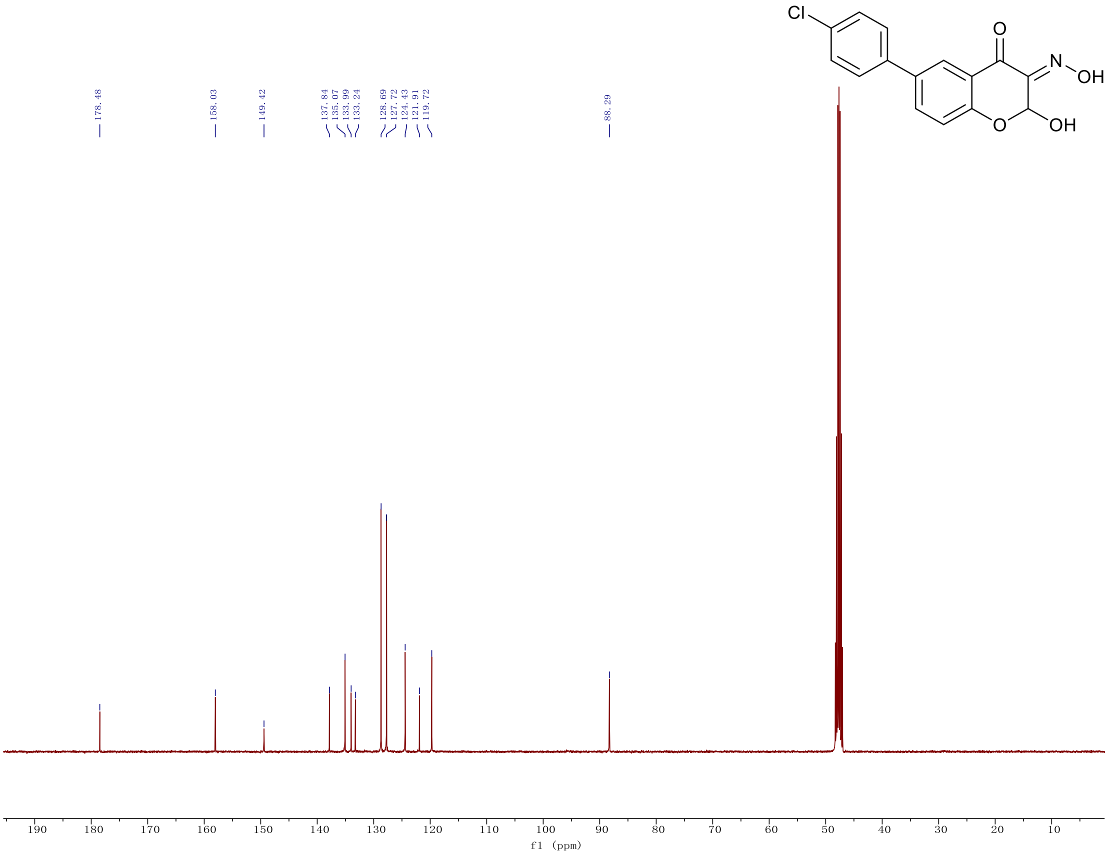
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2i



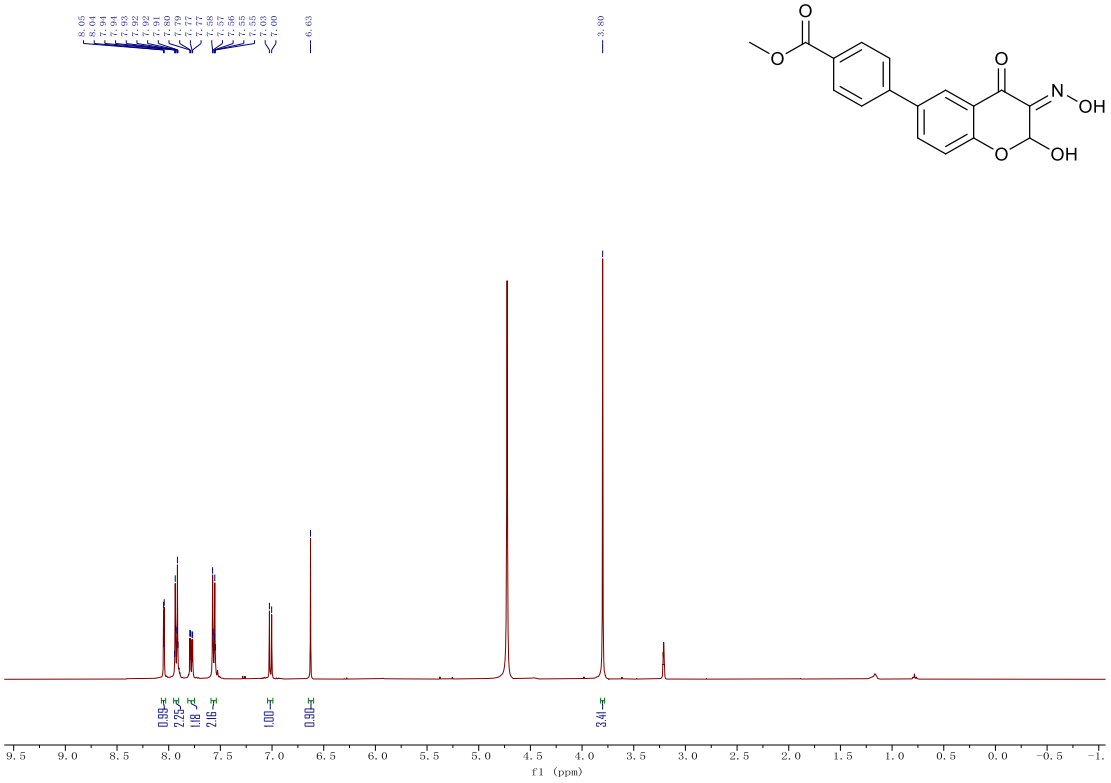


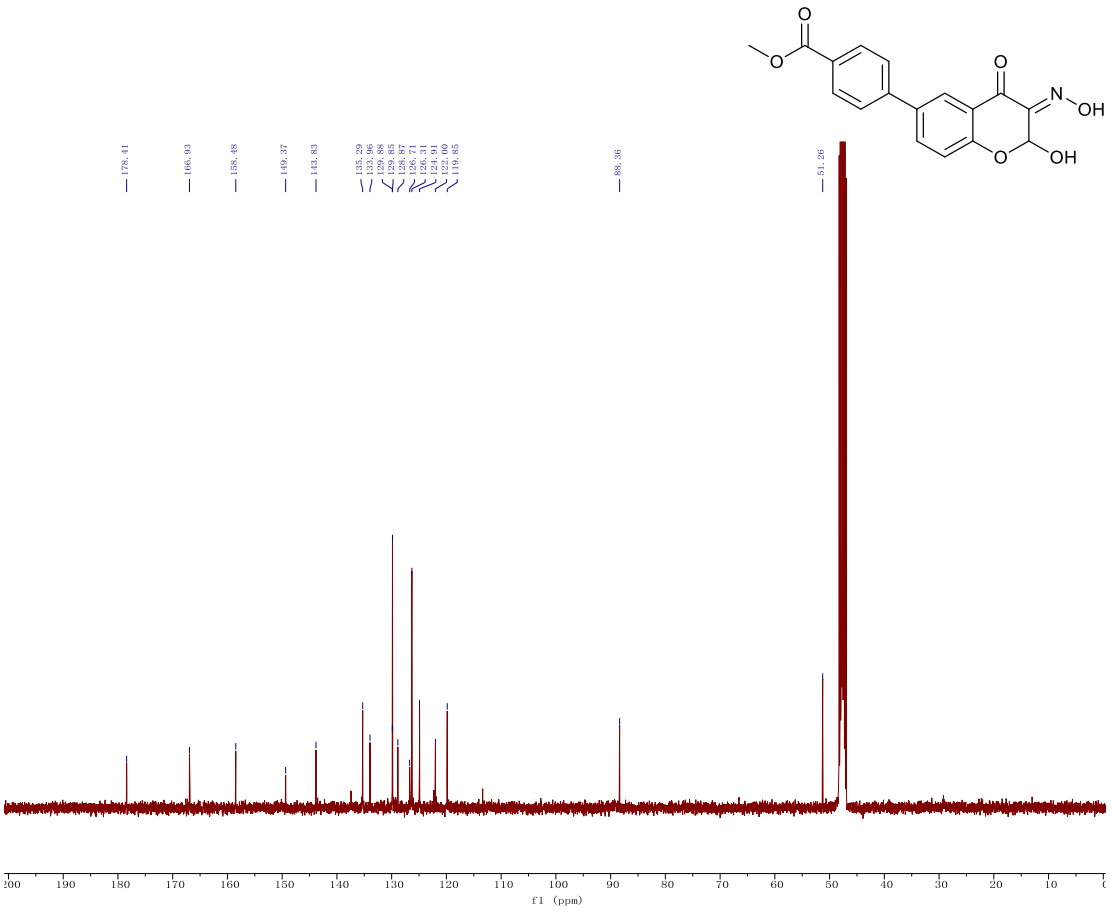
[1]H NMR (400 MHz, CD_3OD), and [13]C NMR (100 MHz, CD_3OD) spectrum of product 2j



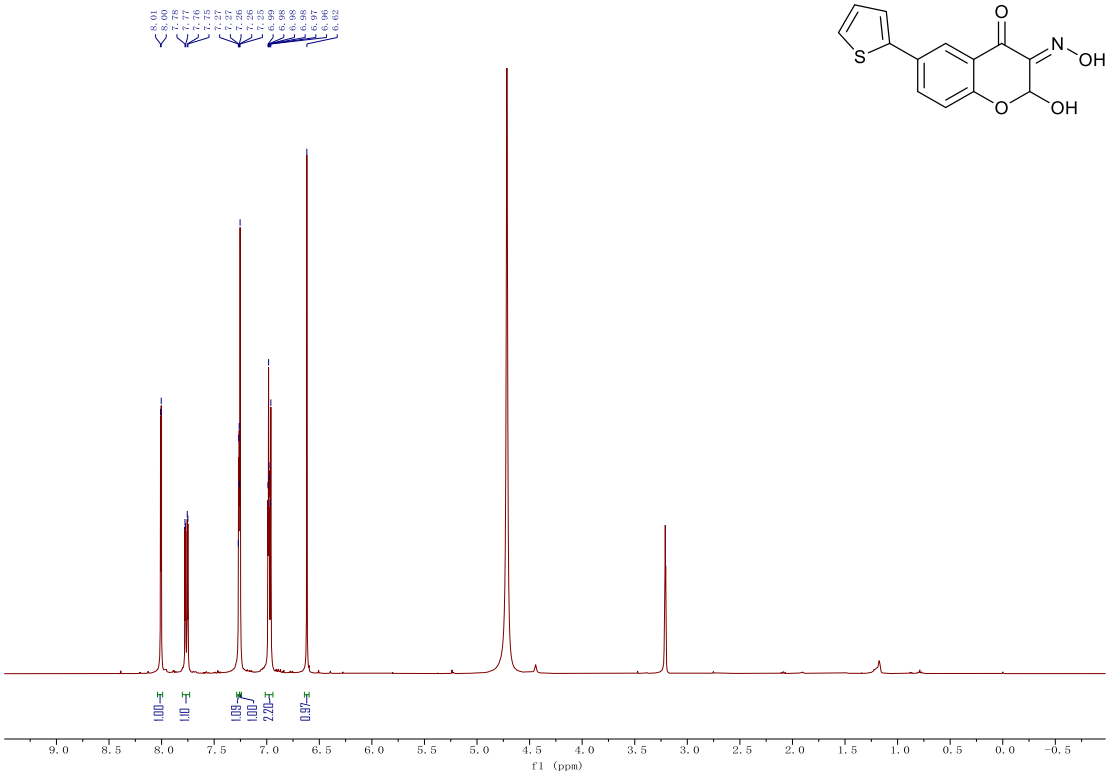


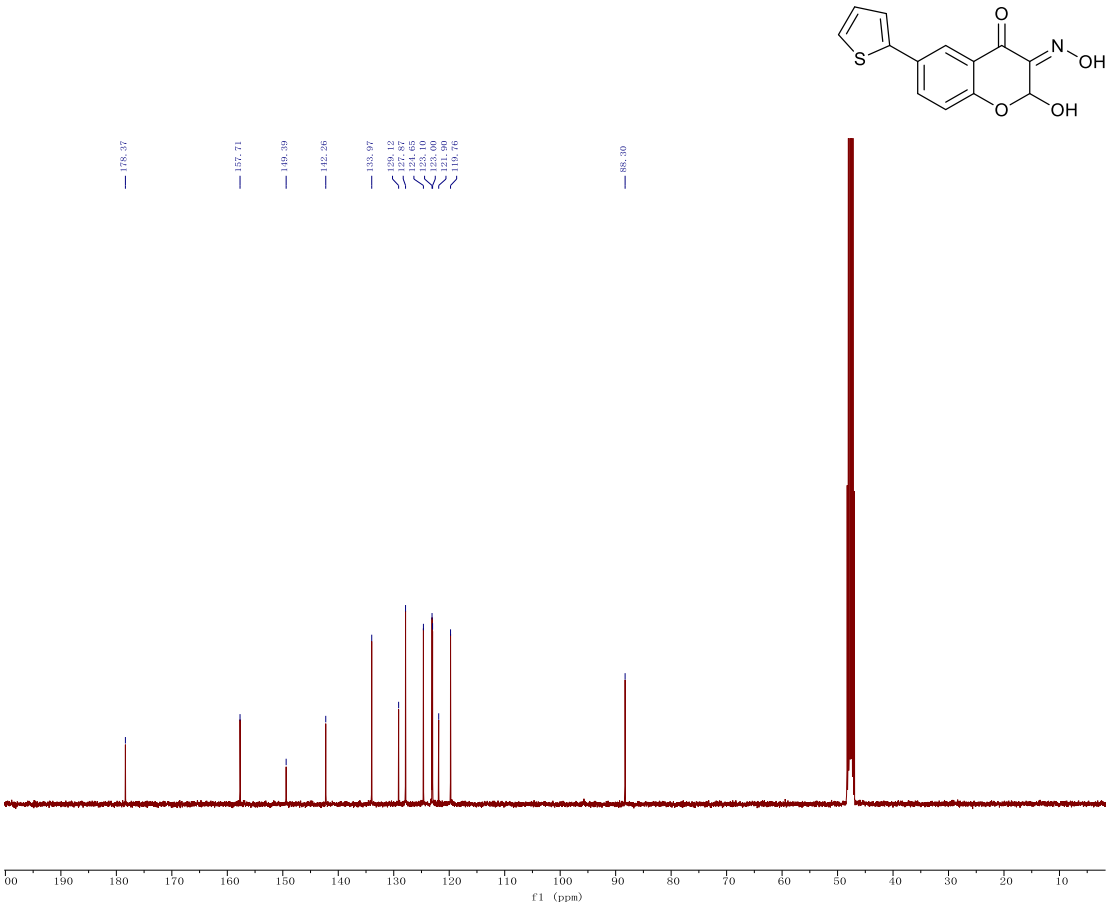
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2k



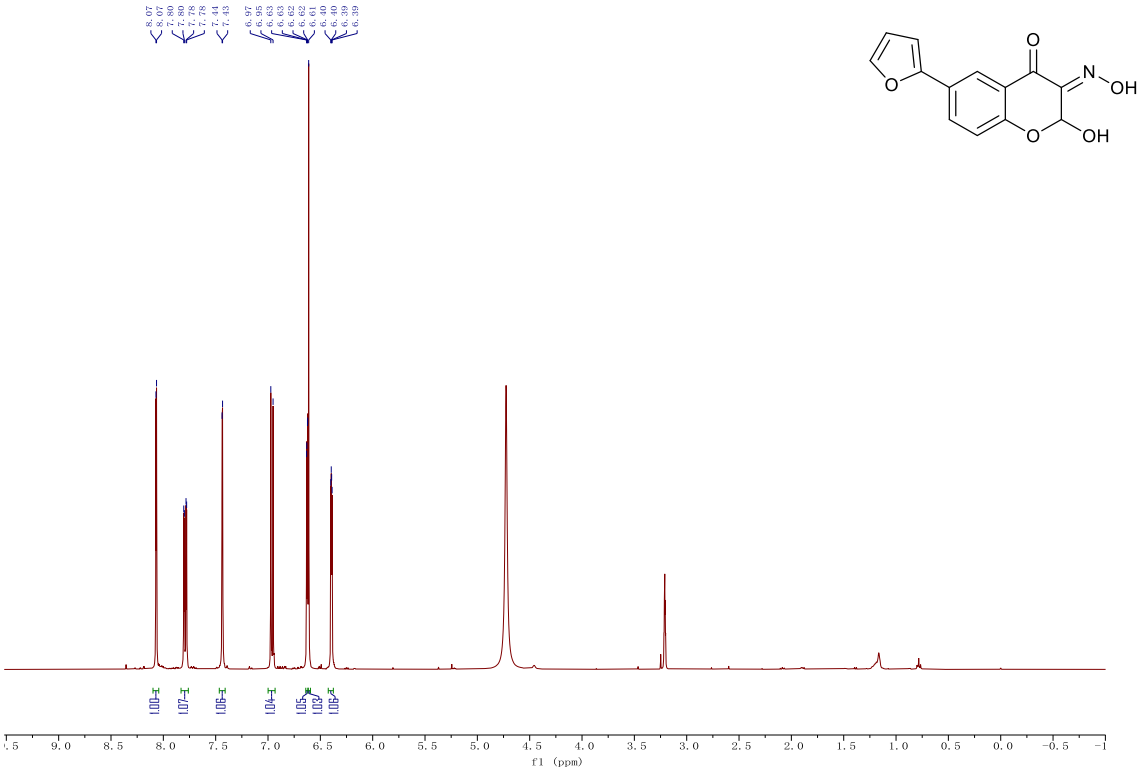


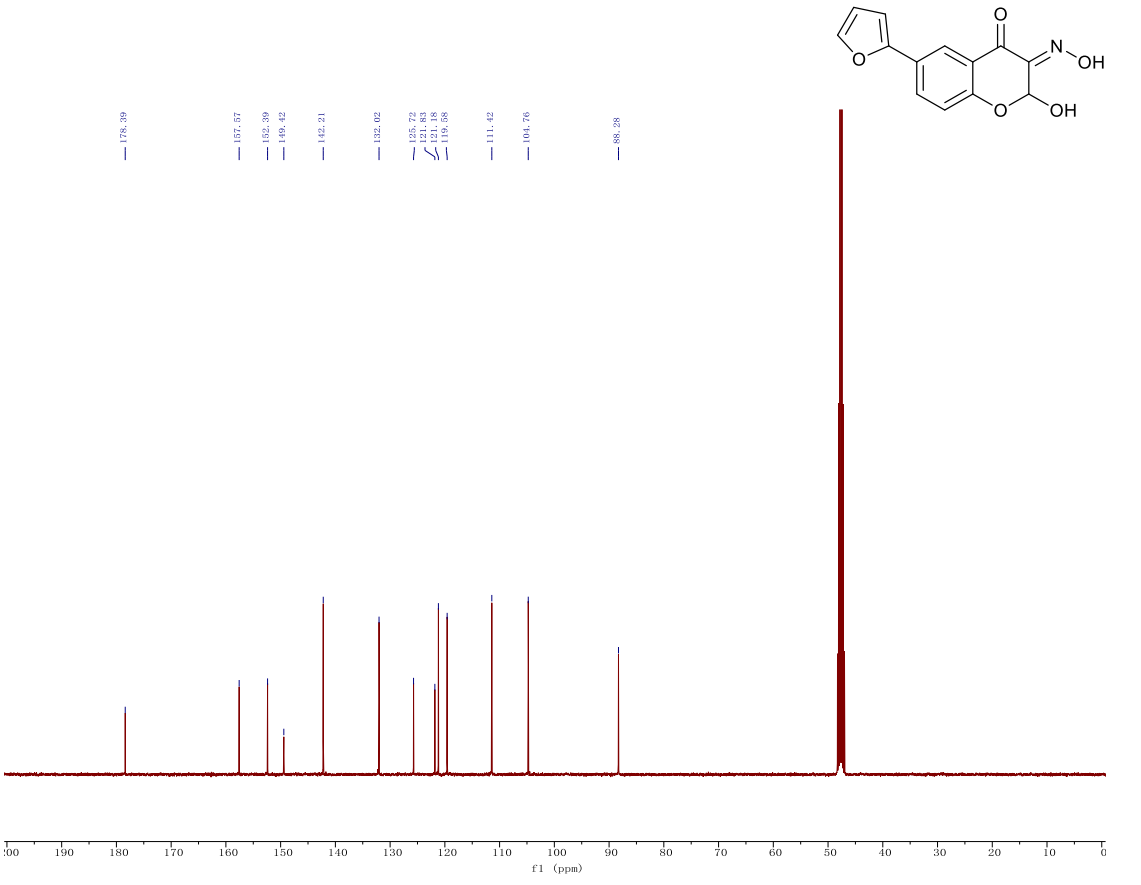
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2l



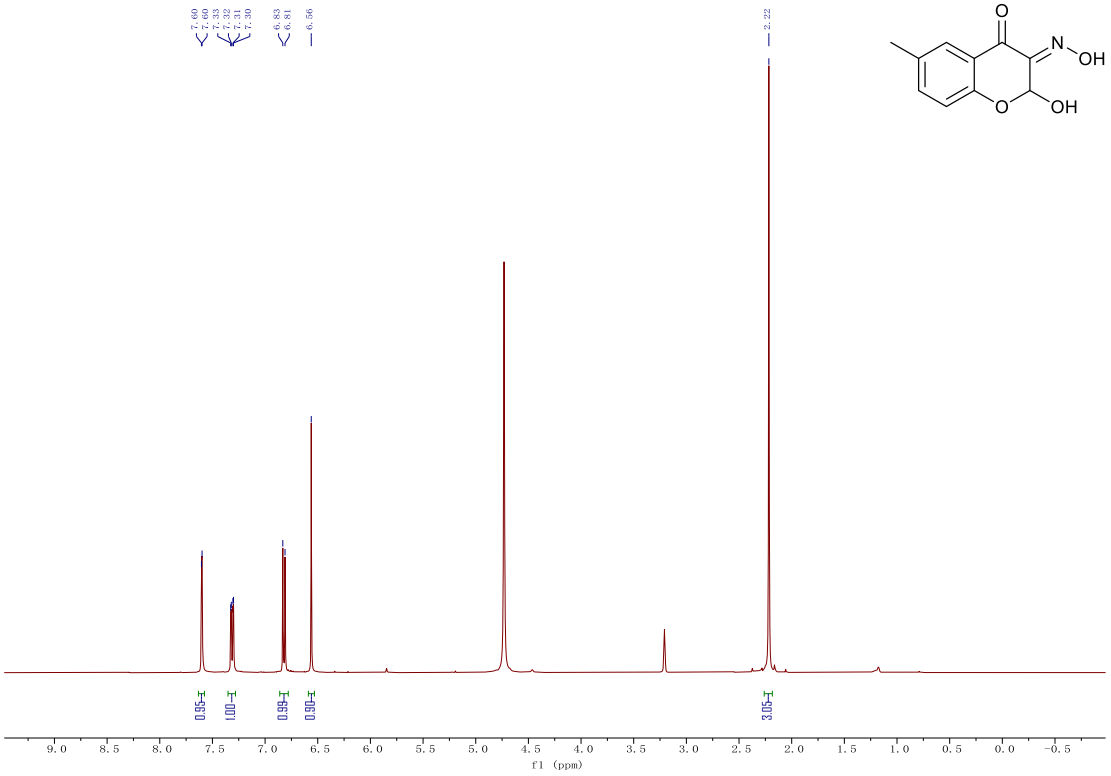


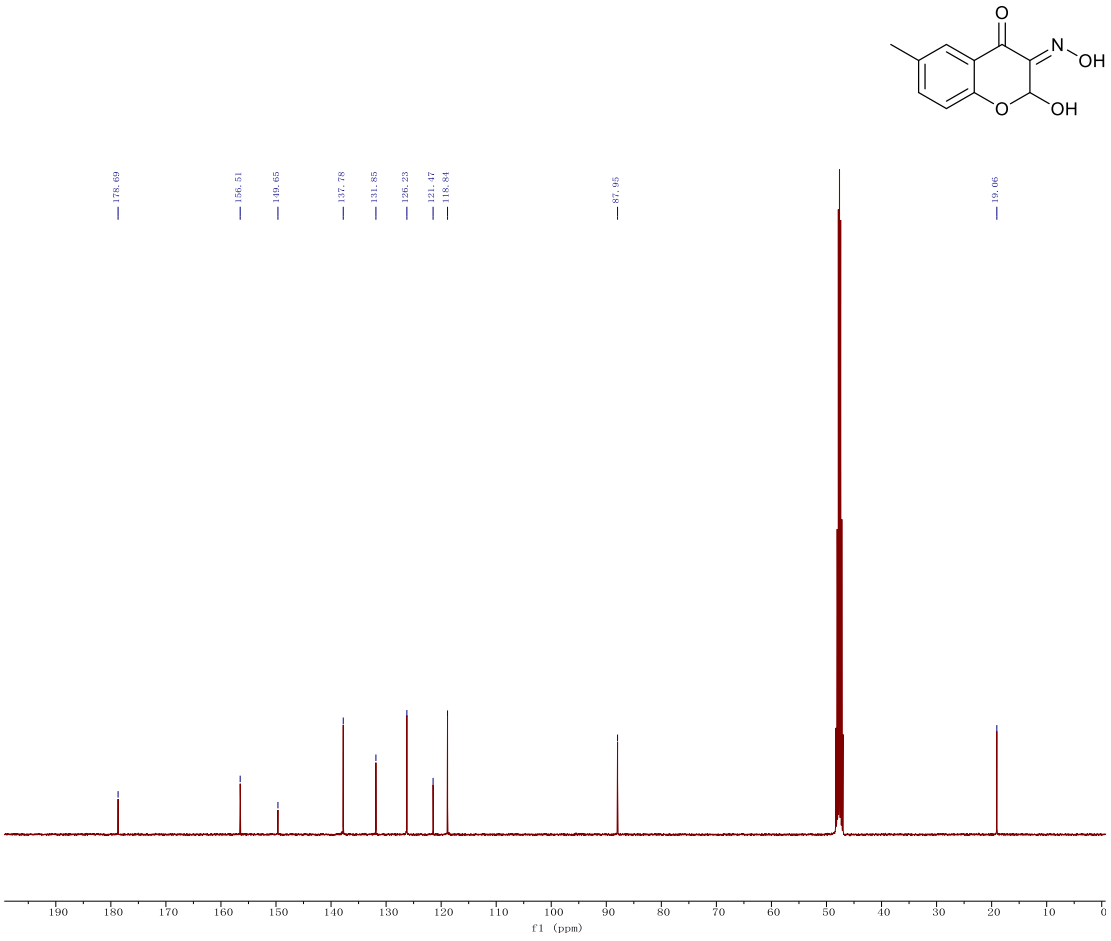
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2m



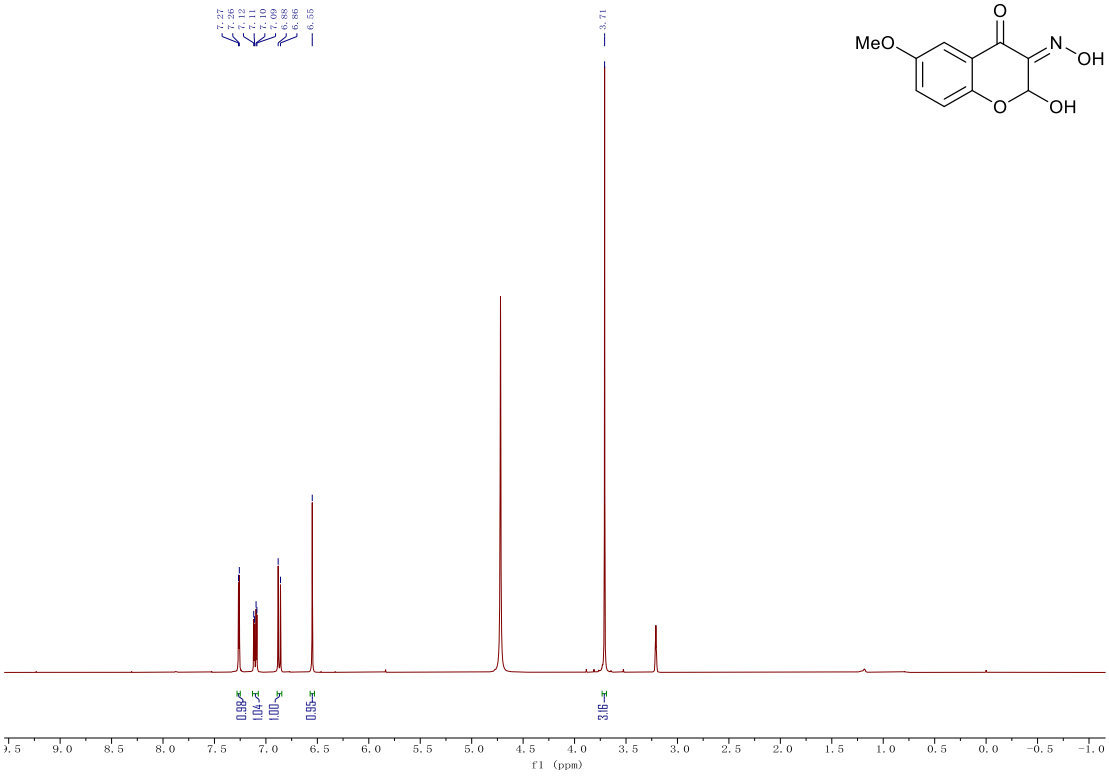


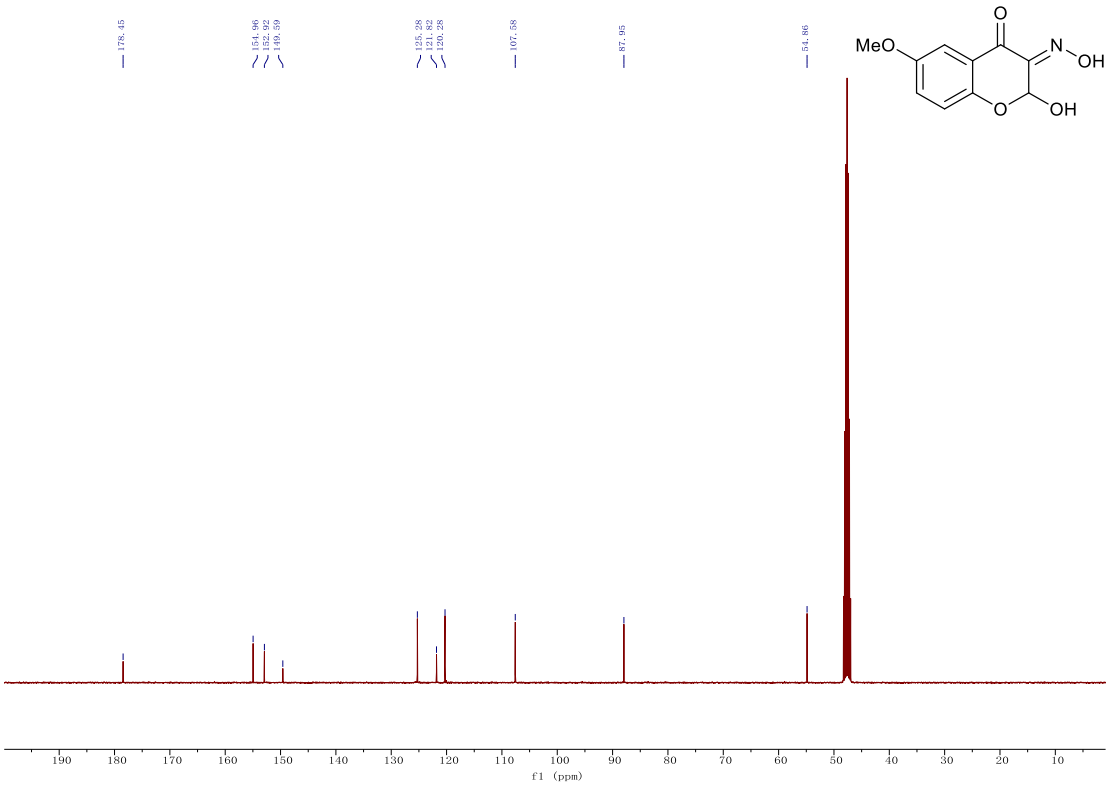
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2n



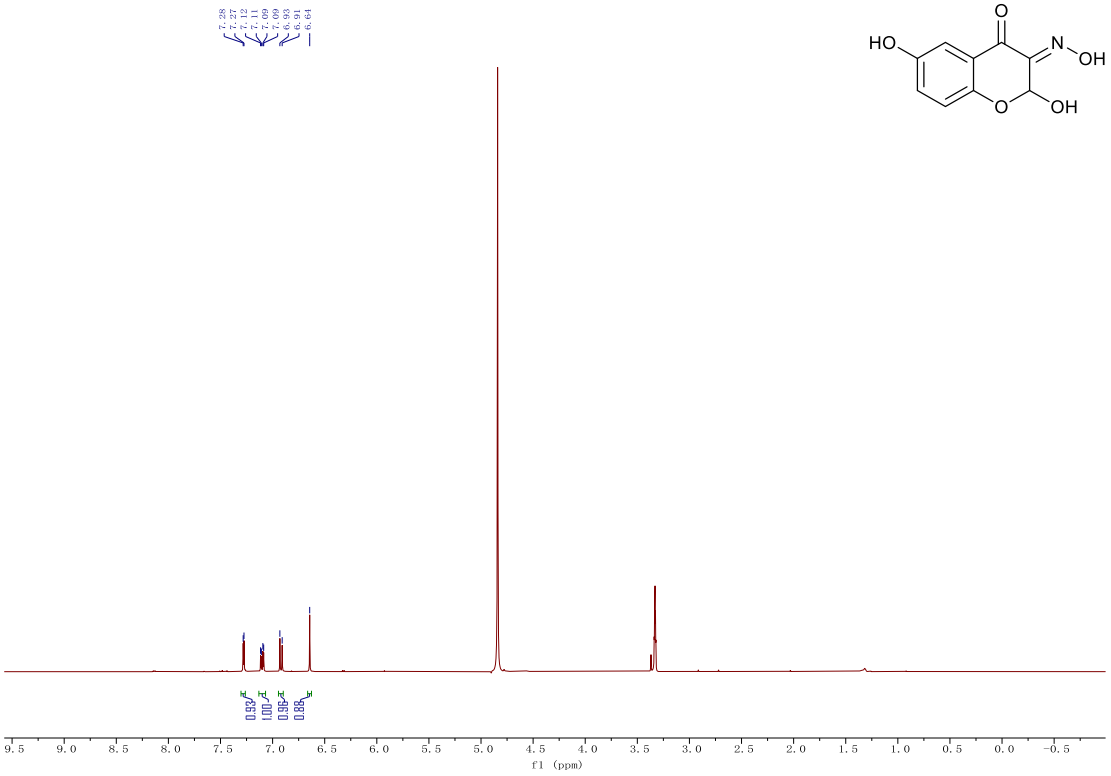


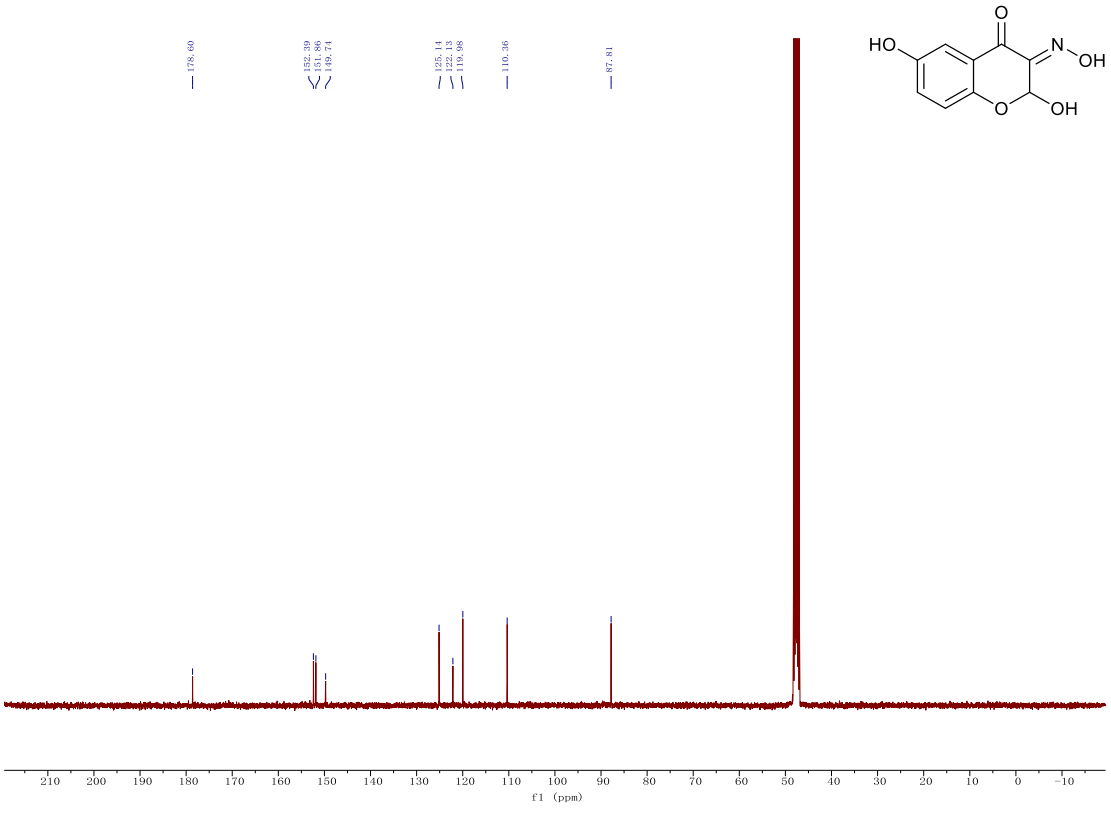
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2o



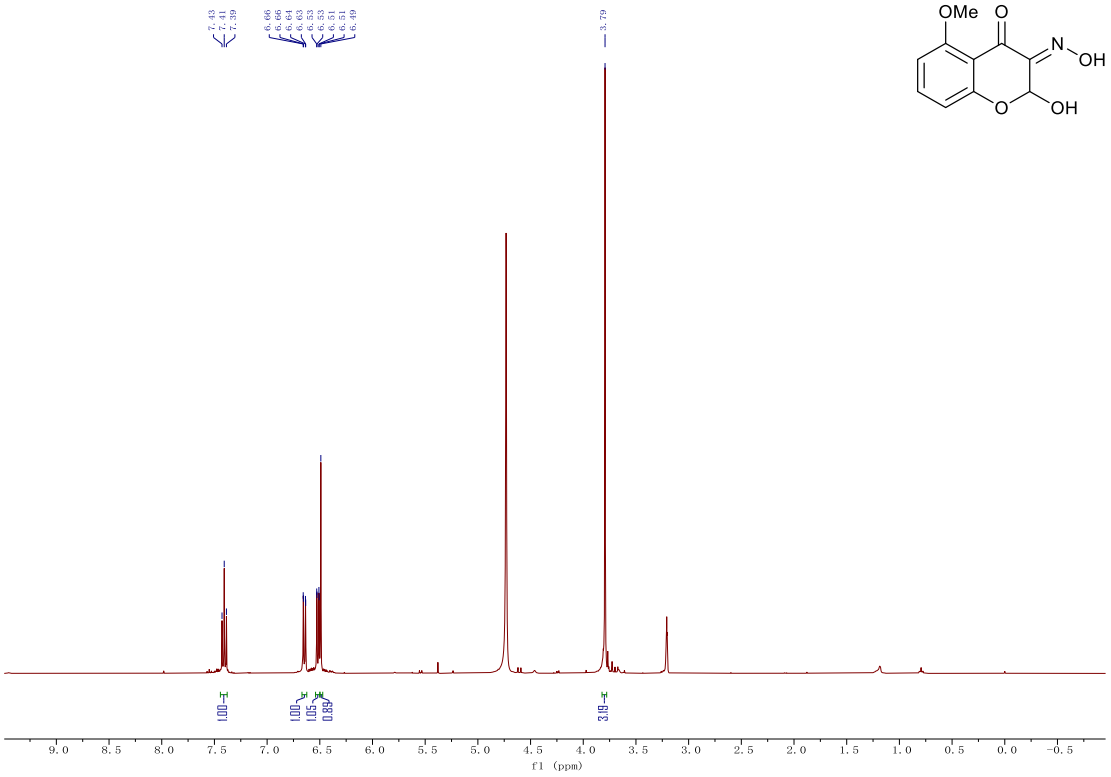


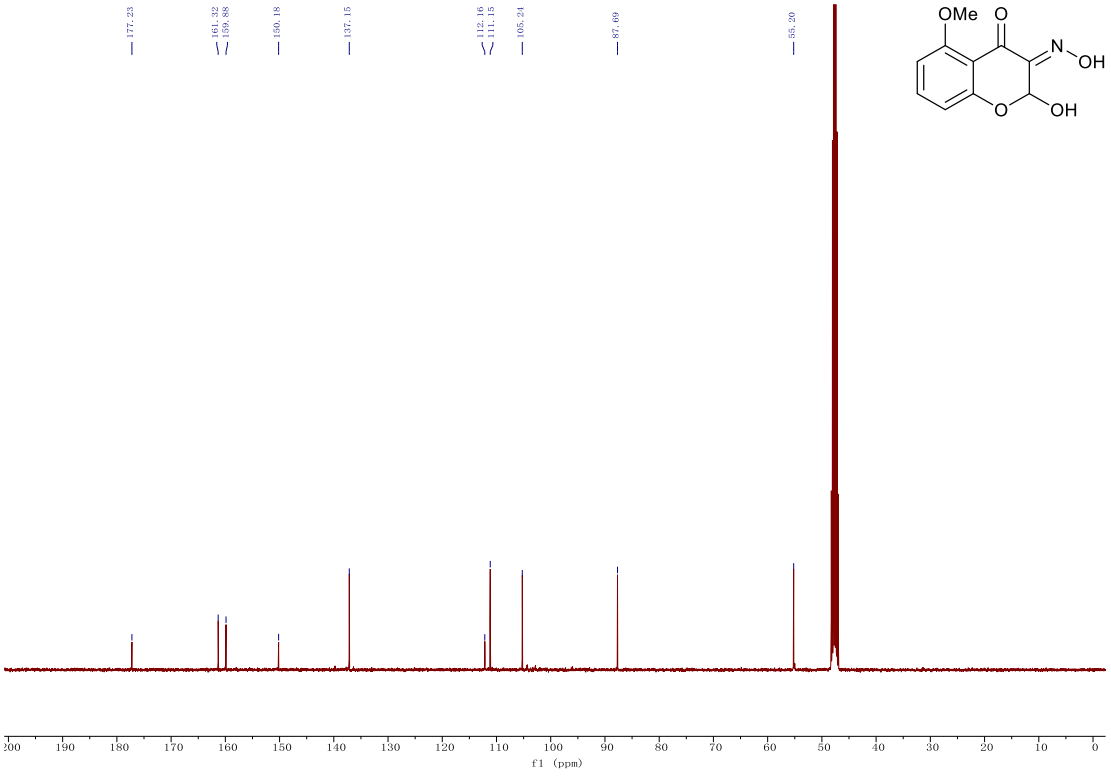
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2p



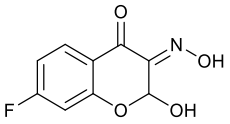


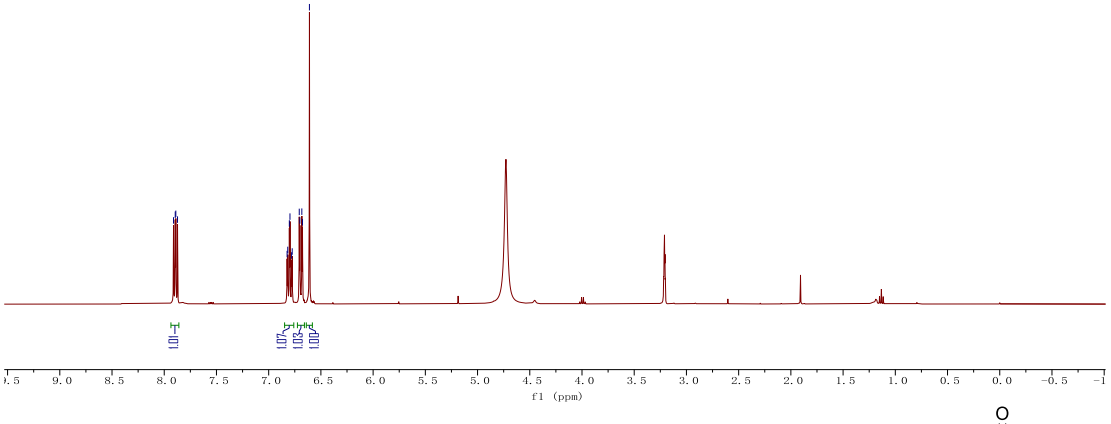
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2q

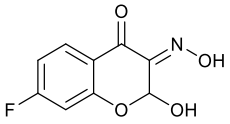


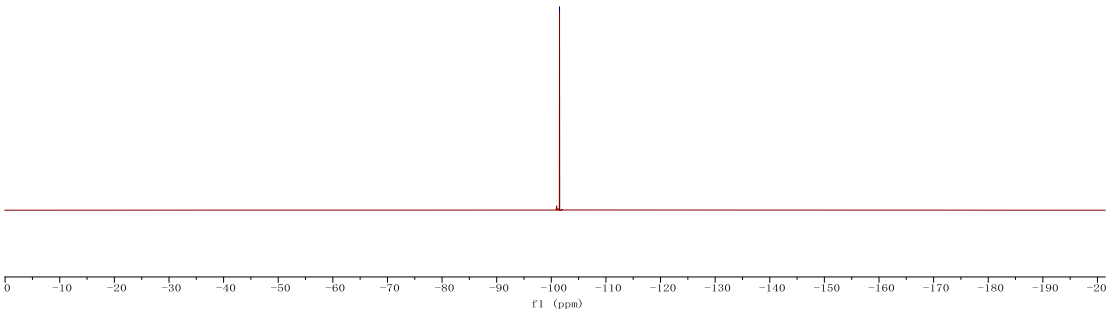


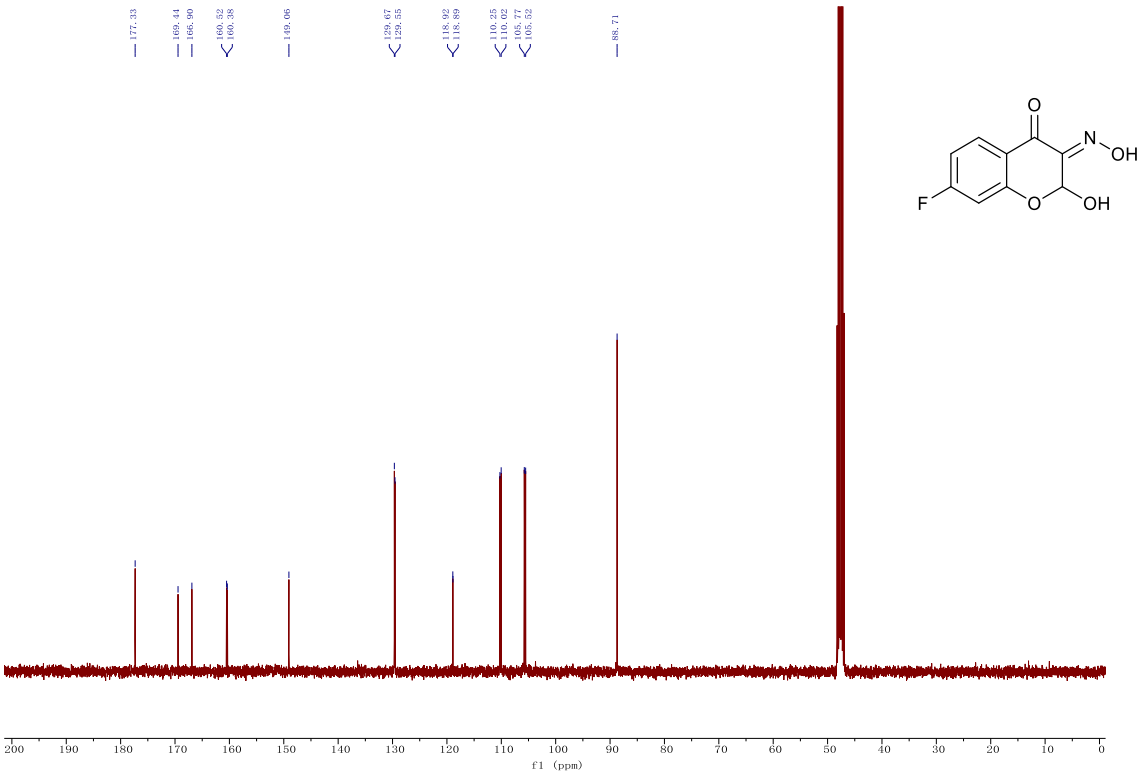
^{1}H NMR (400 MHz, CD_3OD), ^{19}F NMR (376 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2r







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170
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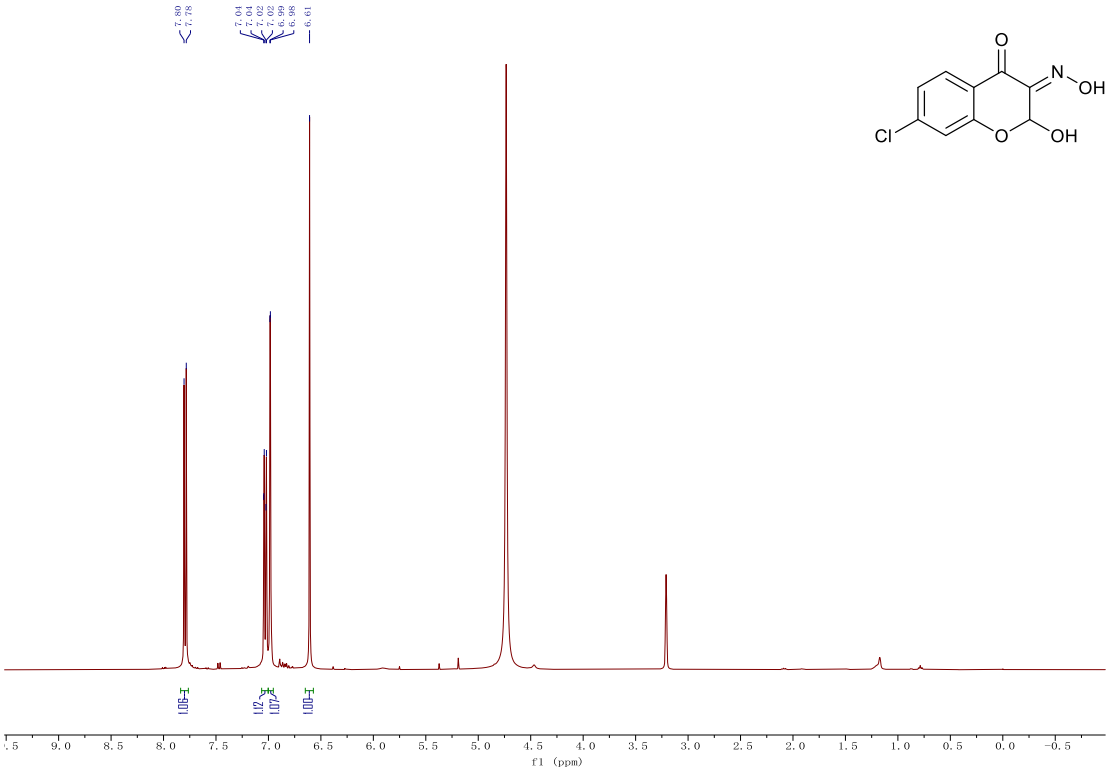
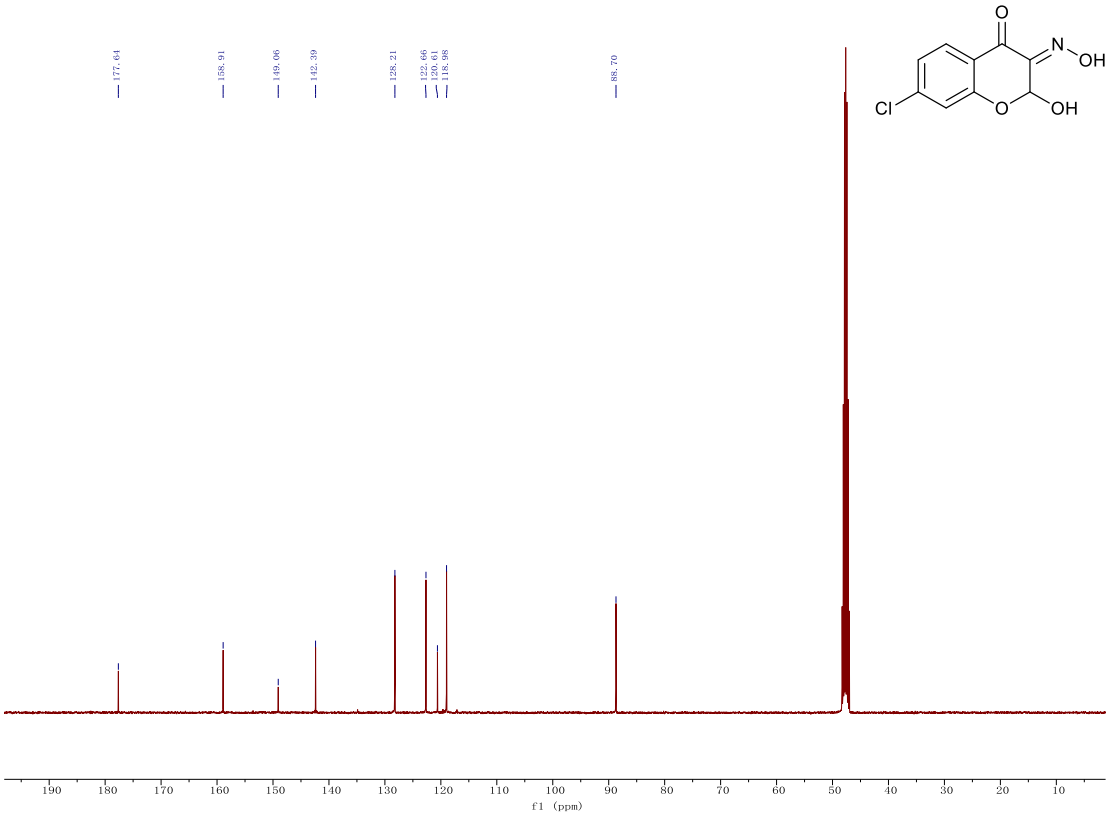
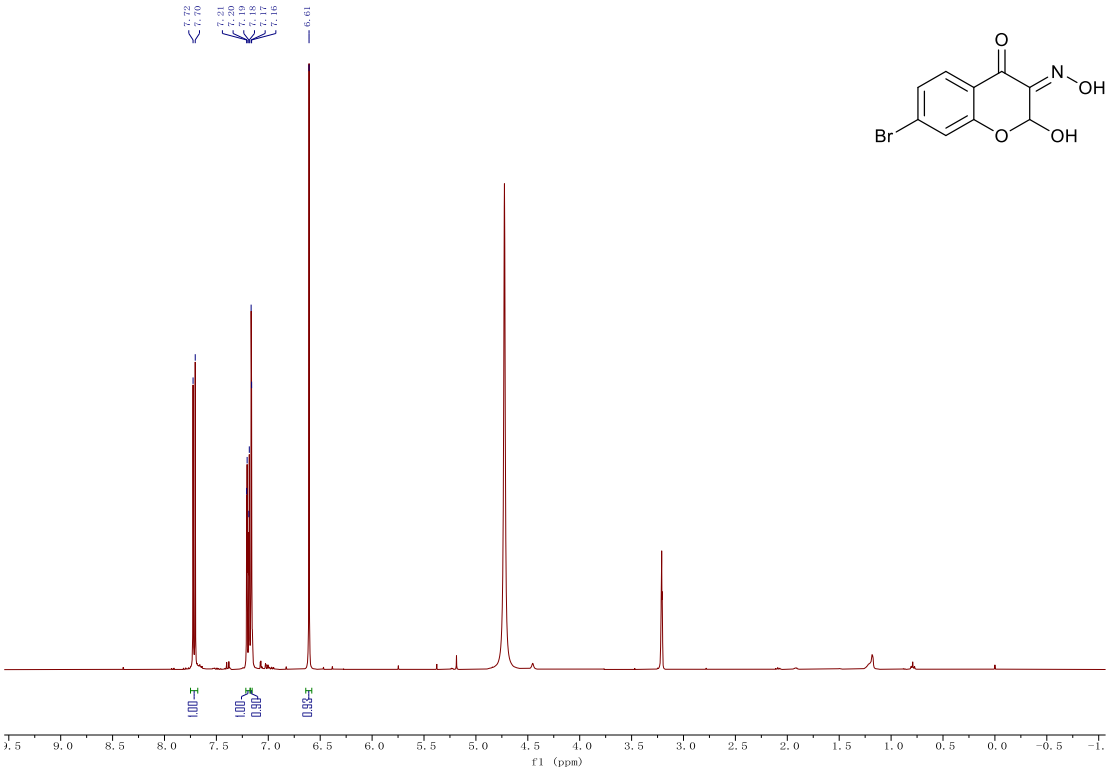
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

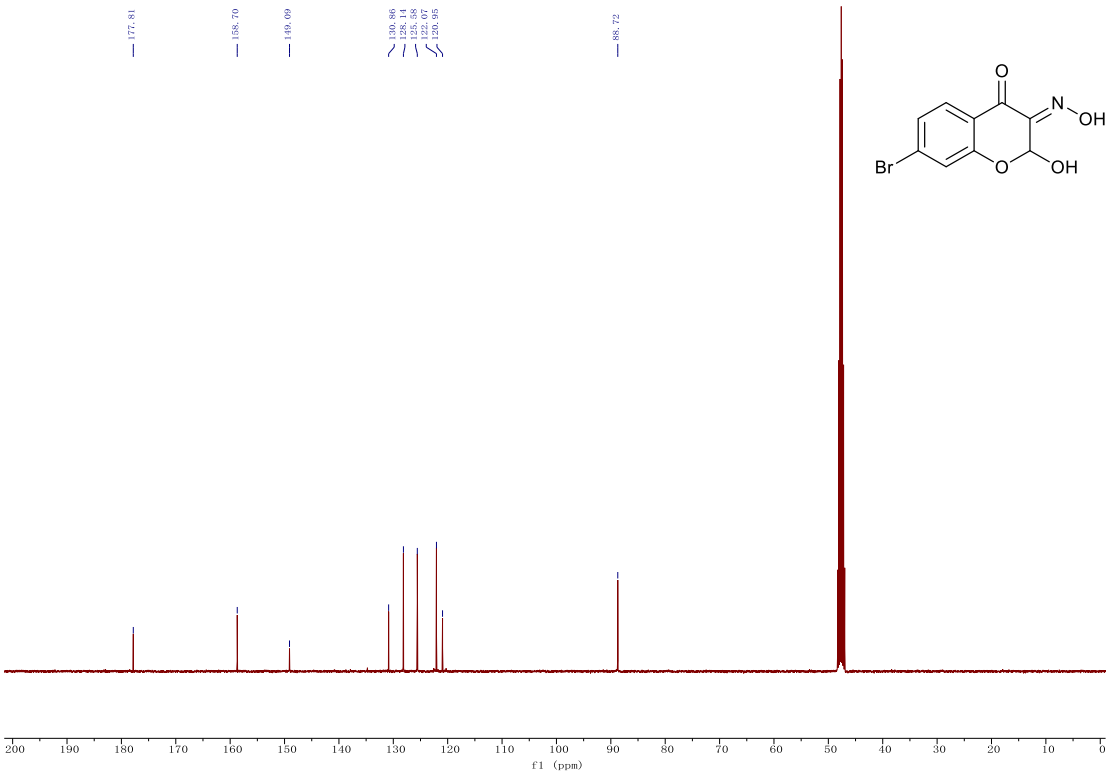
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2s



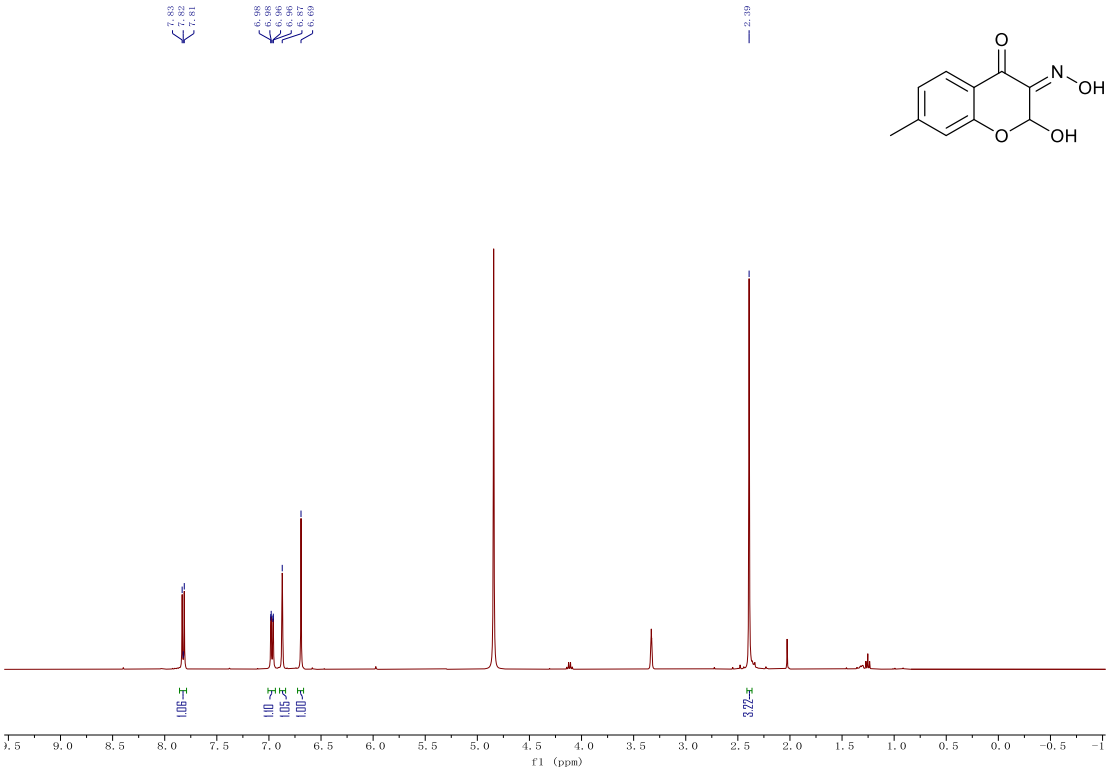


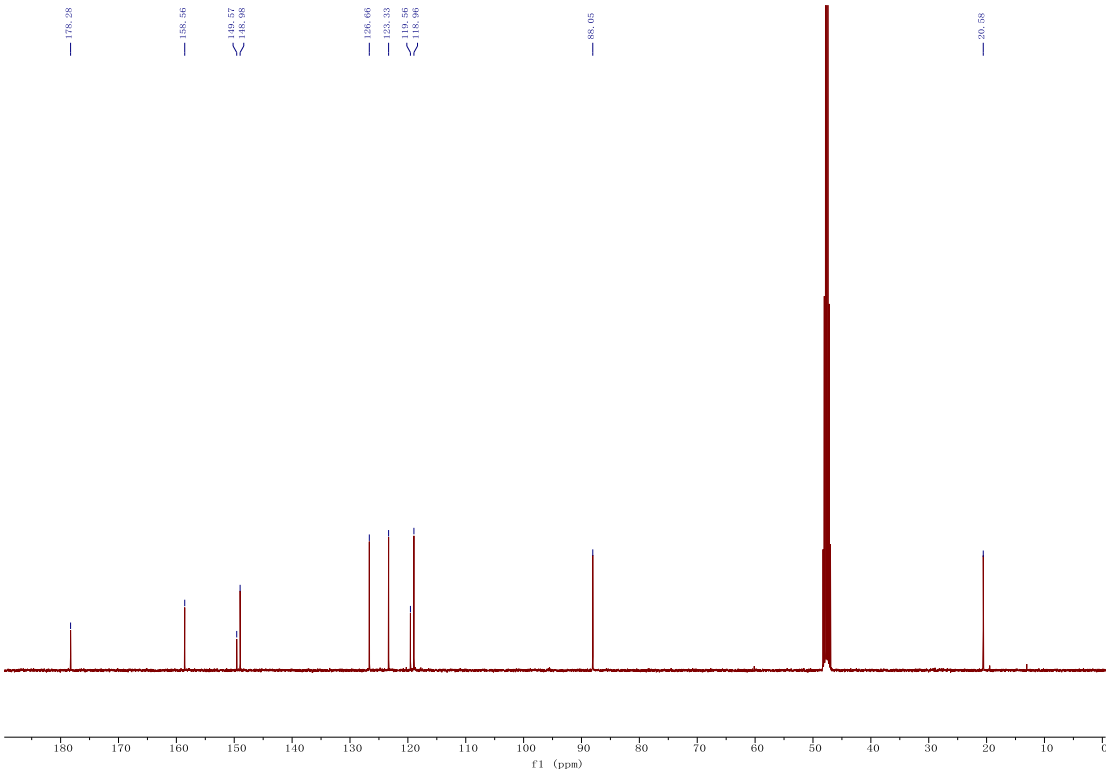
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2t



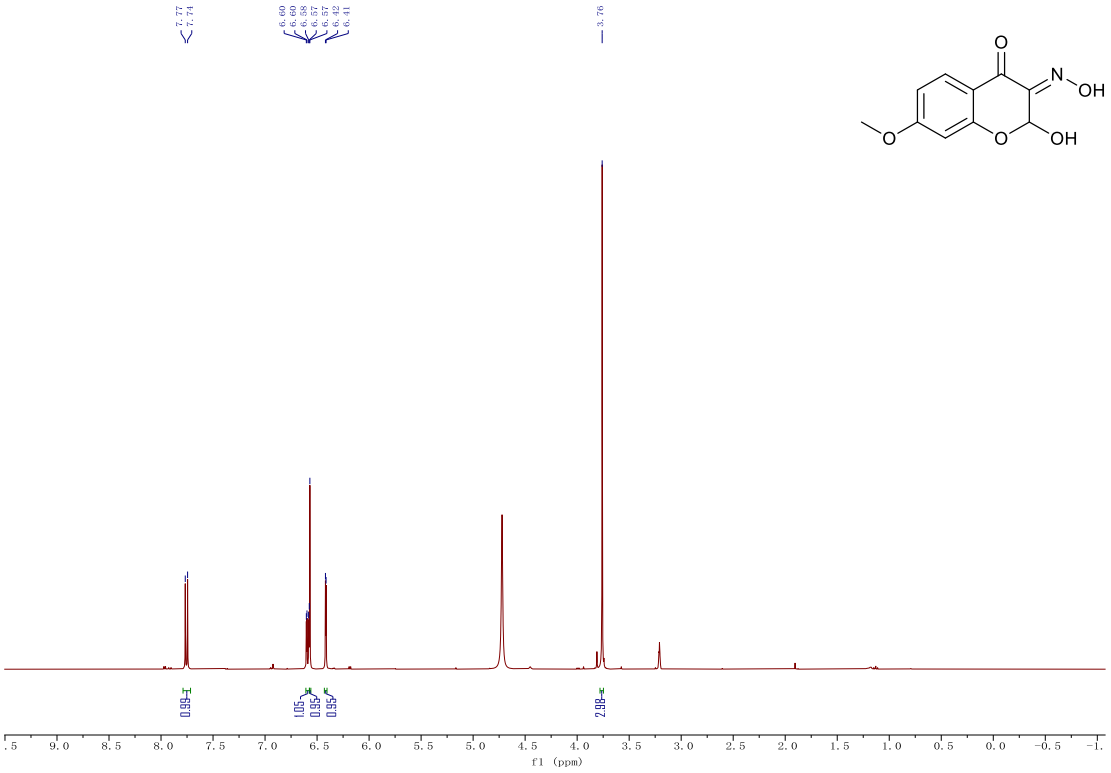


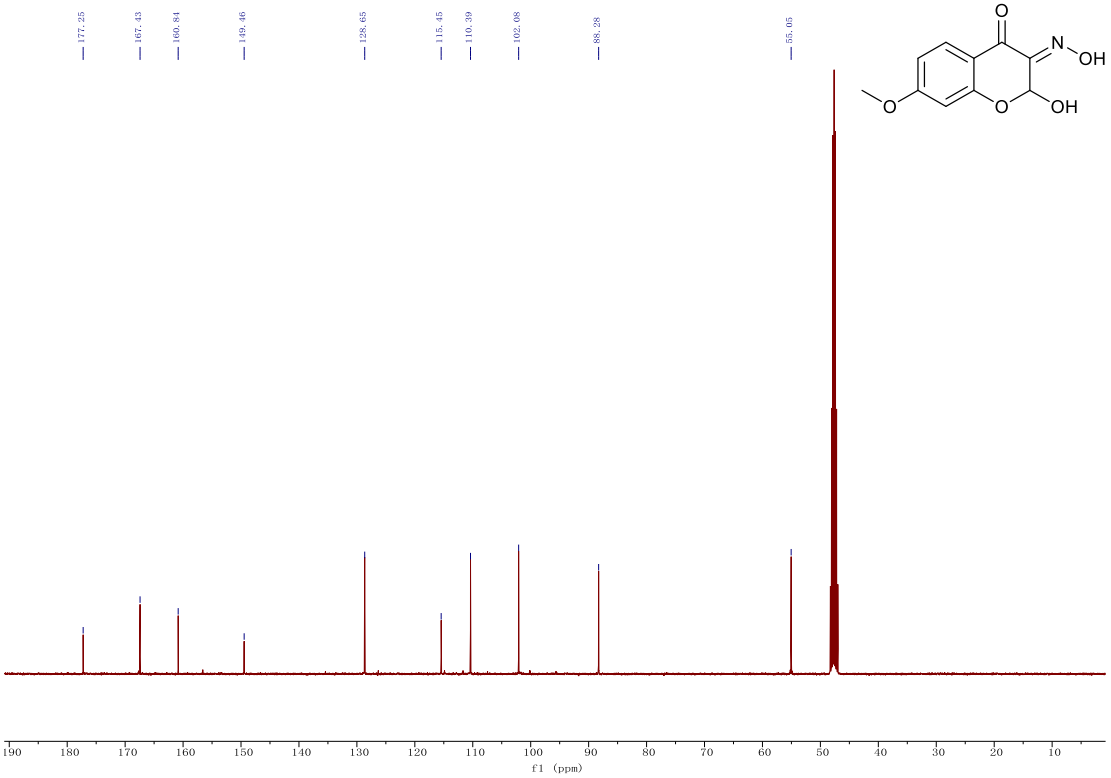
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2u



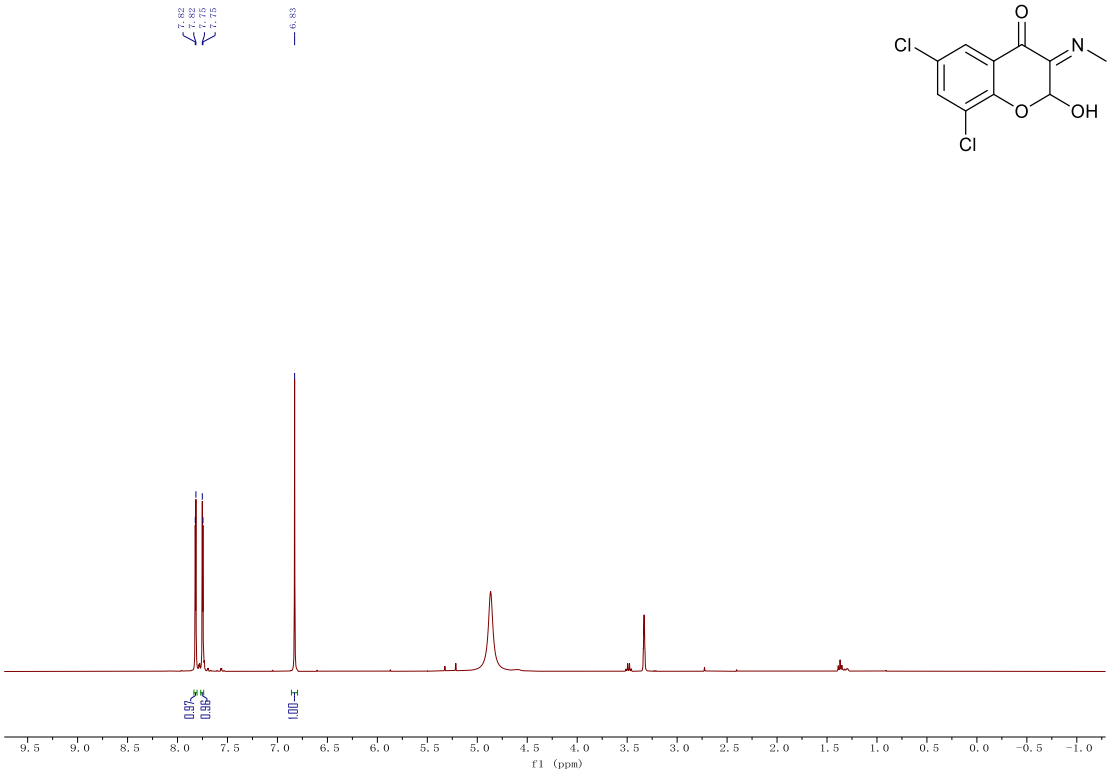


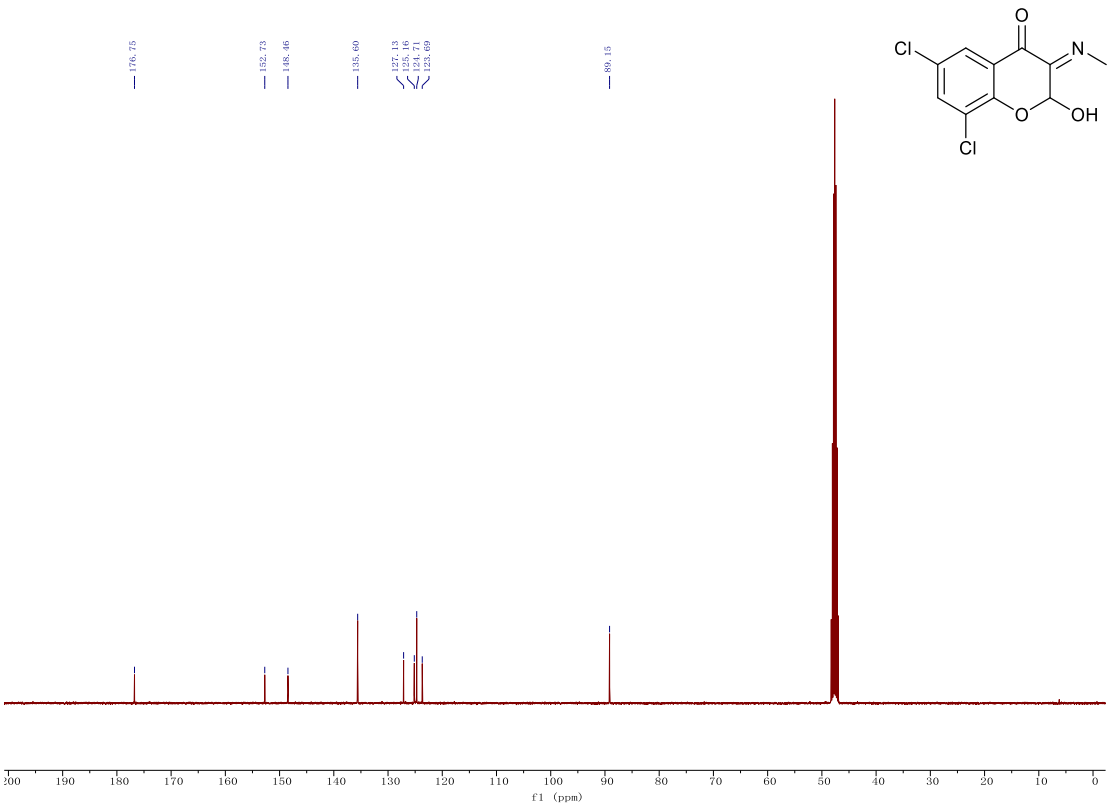
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2v



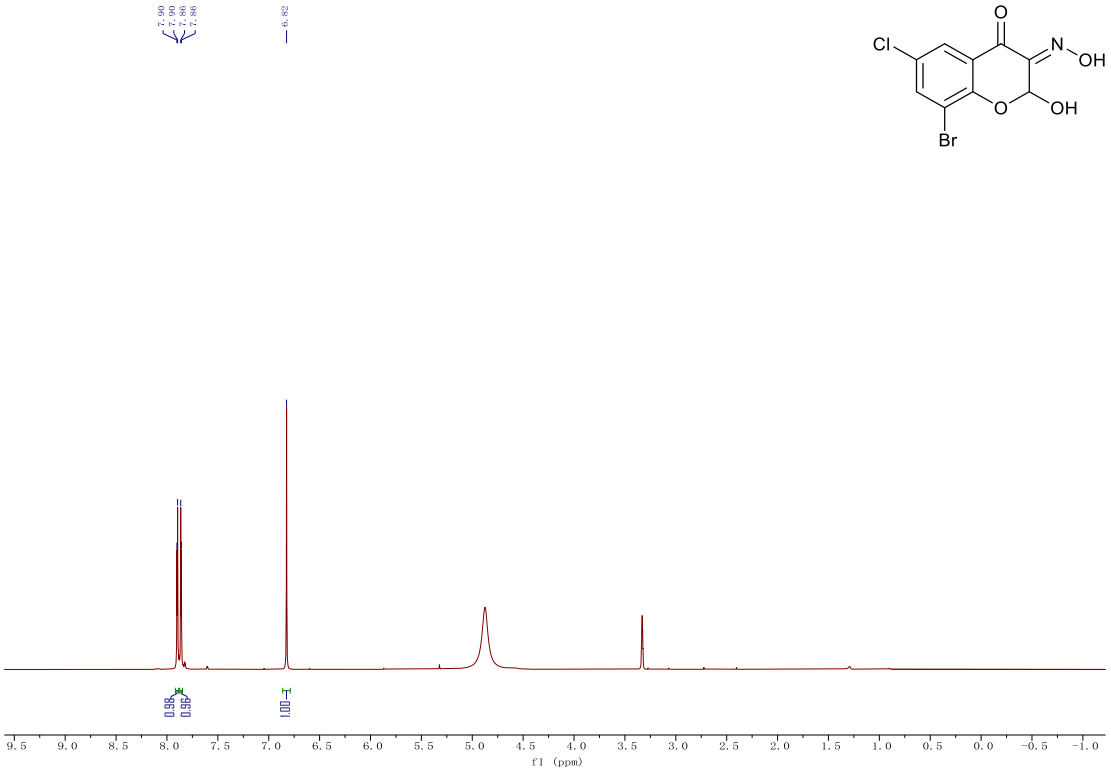


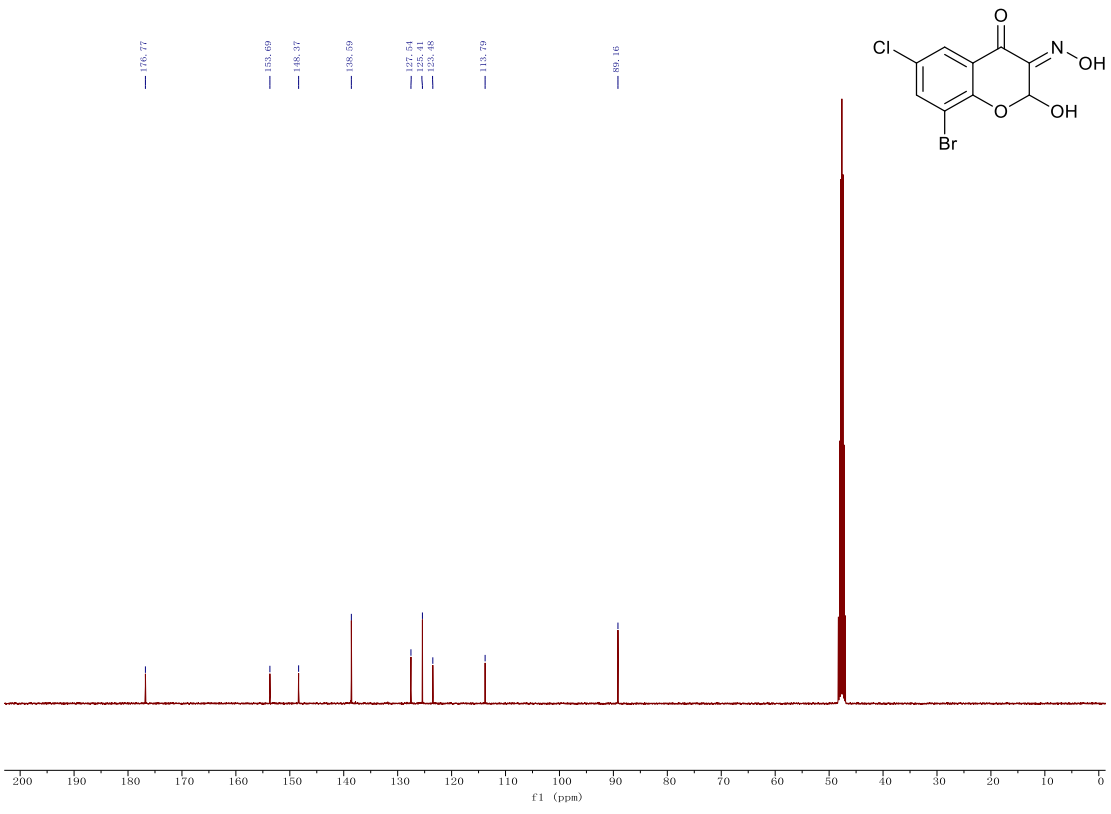
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2w



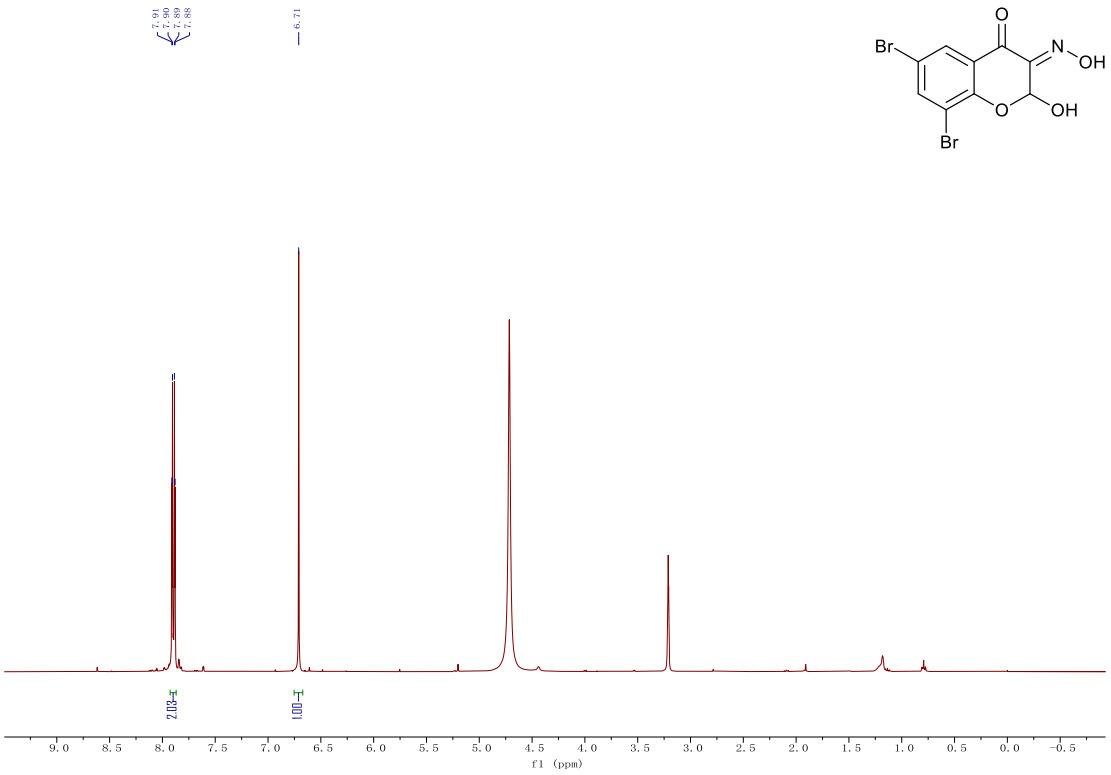


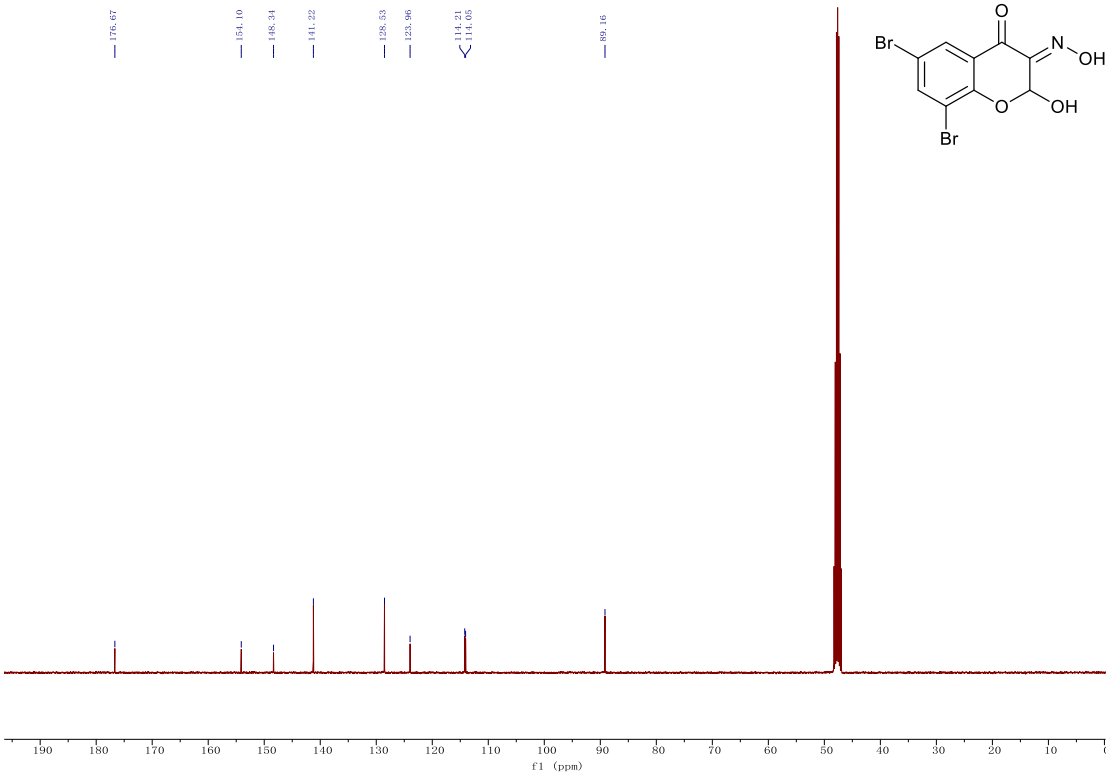
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2x



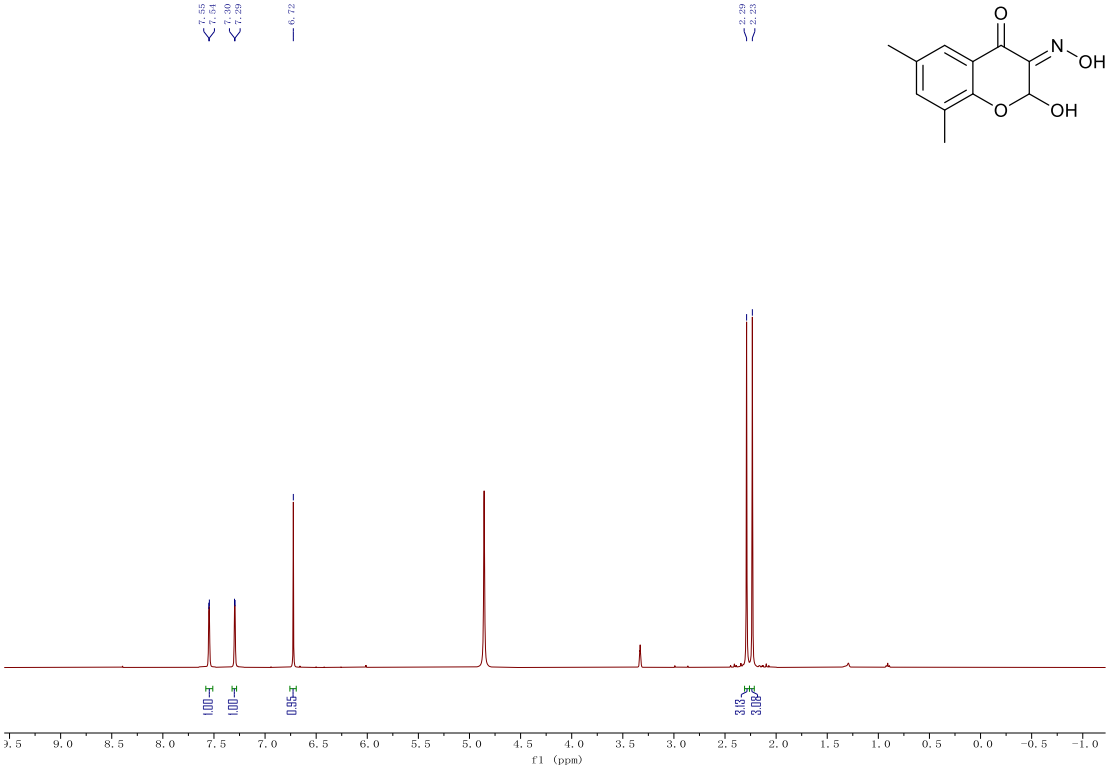


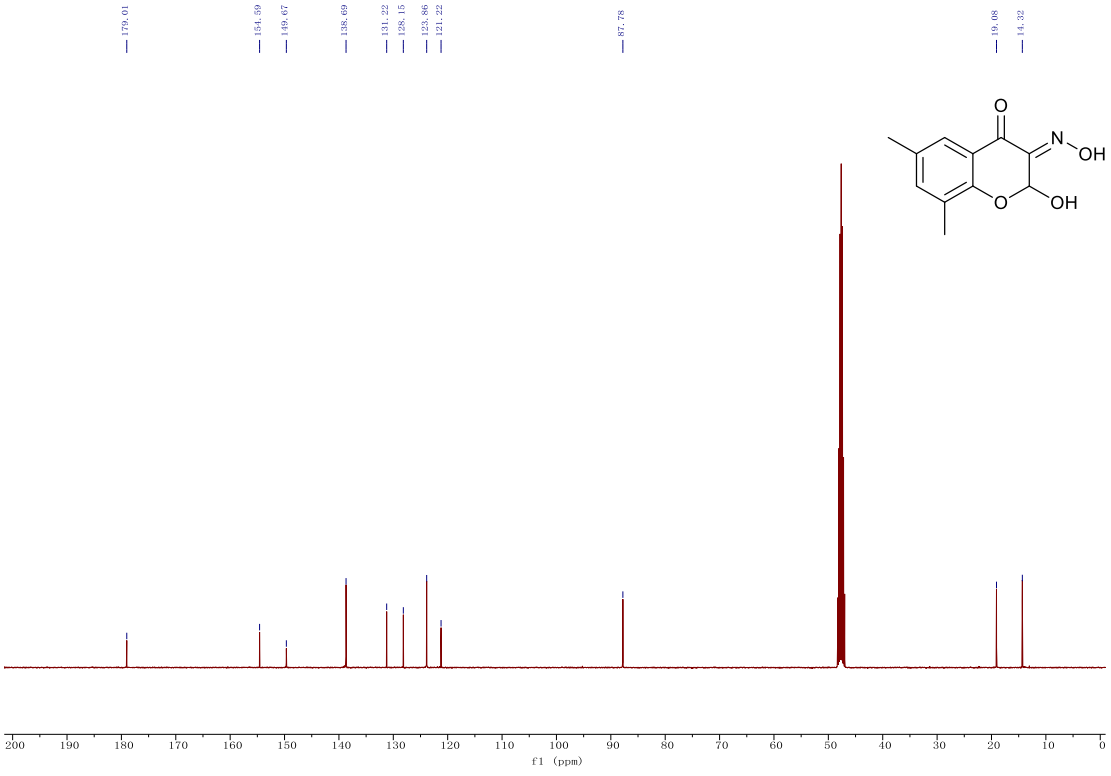
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2y



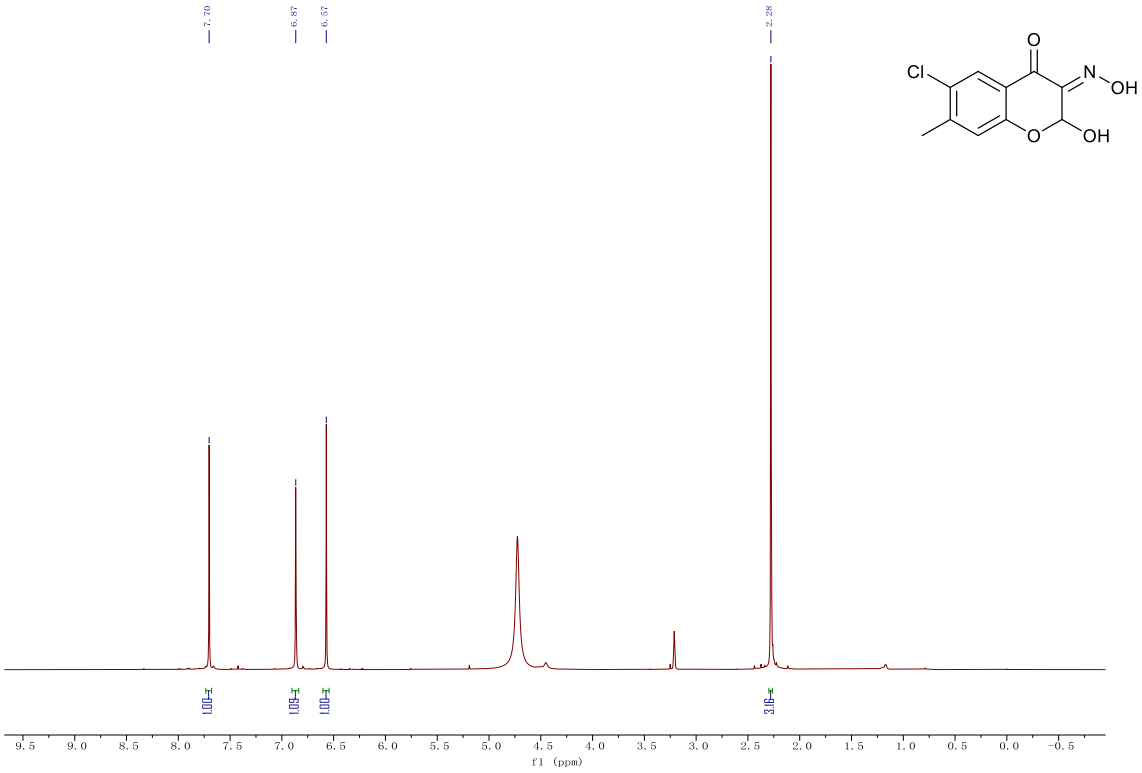


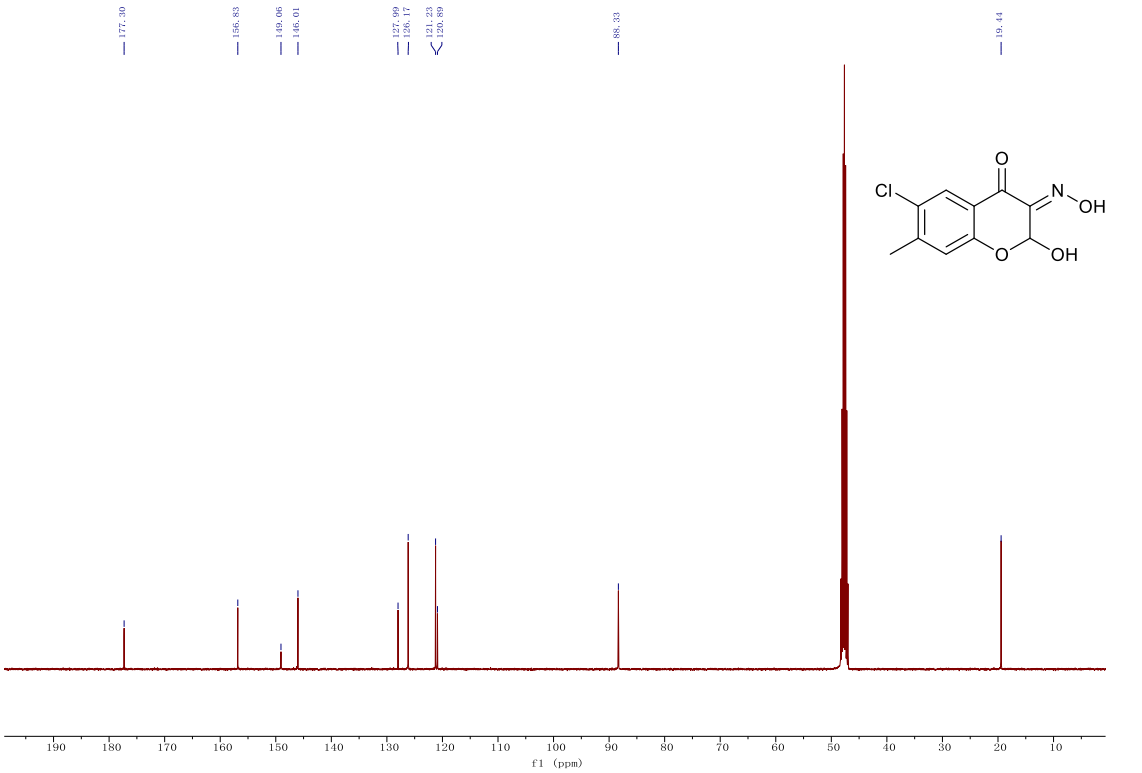
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2z



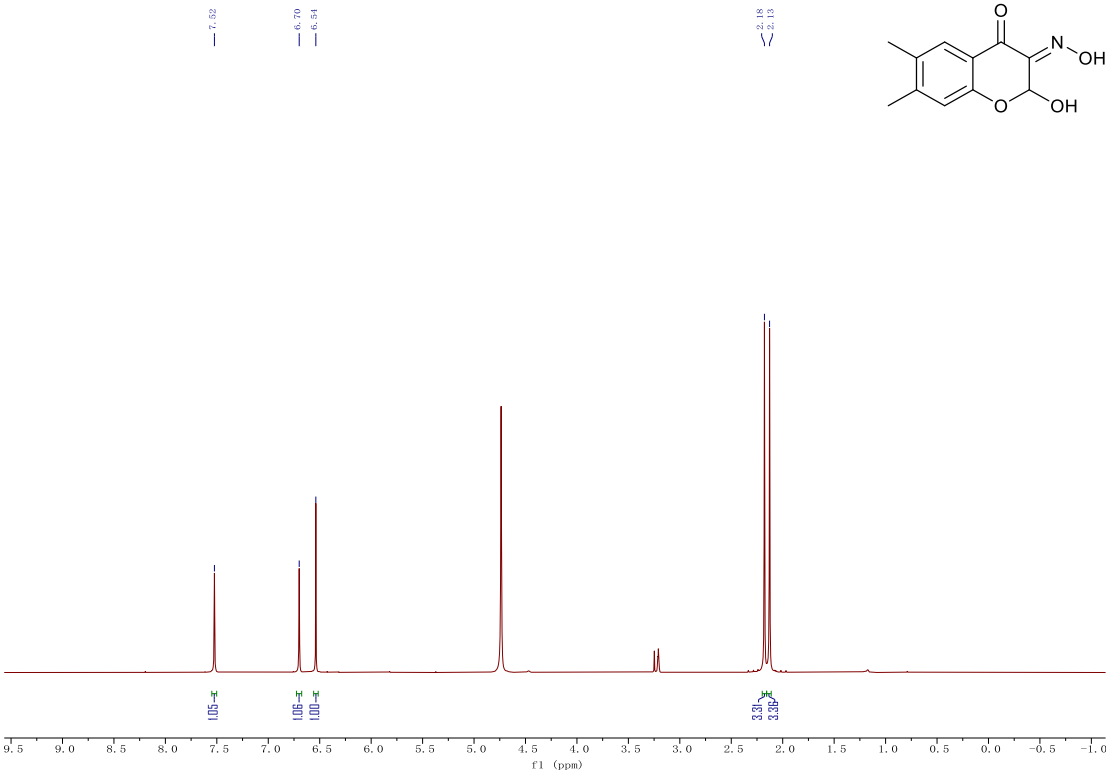


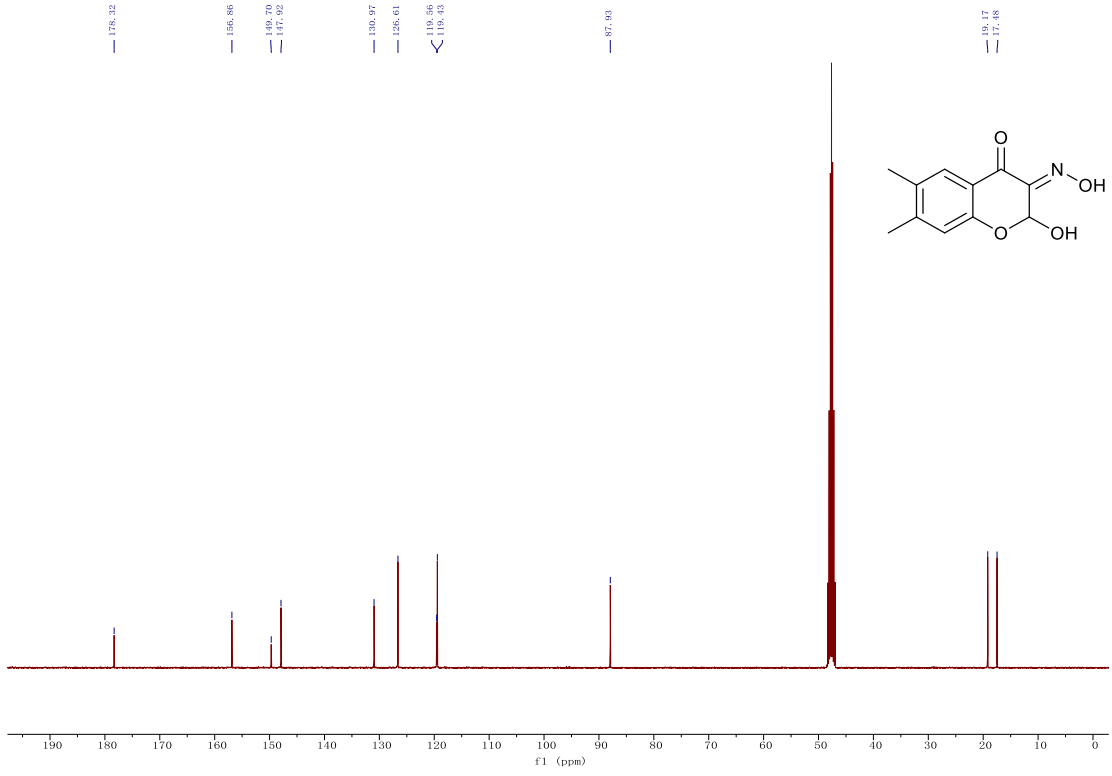
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2aa



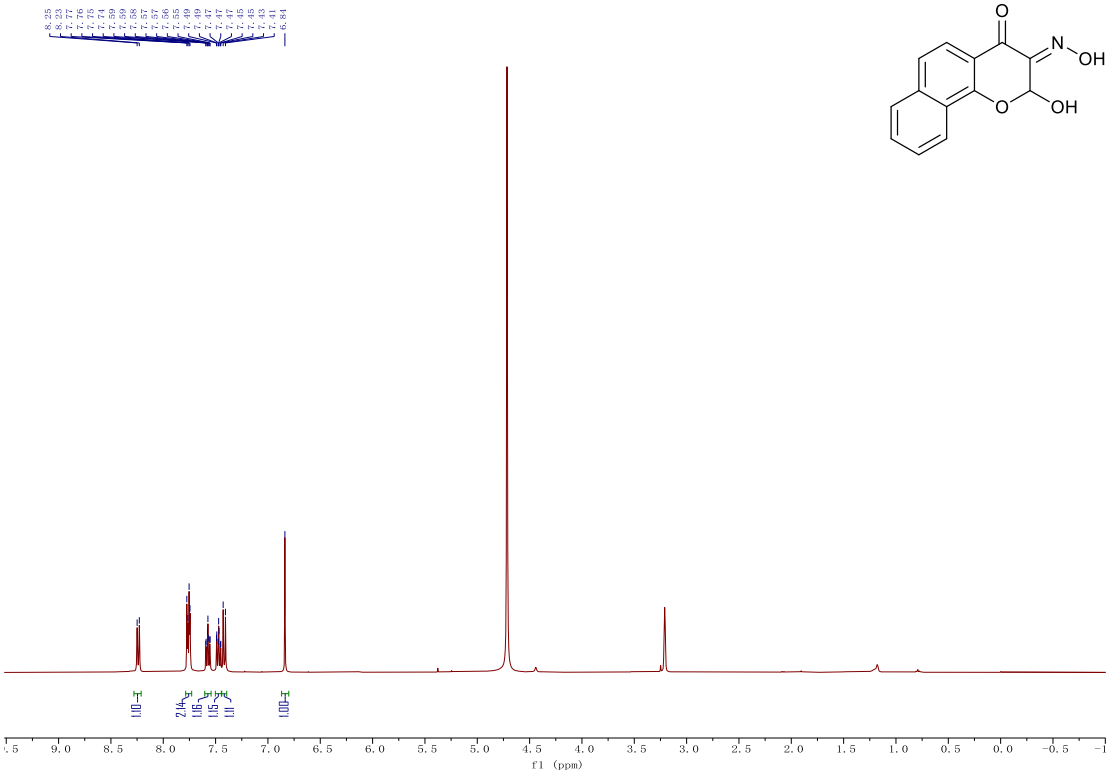


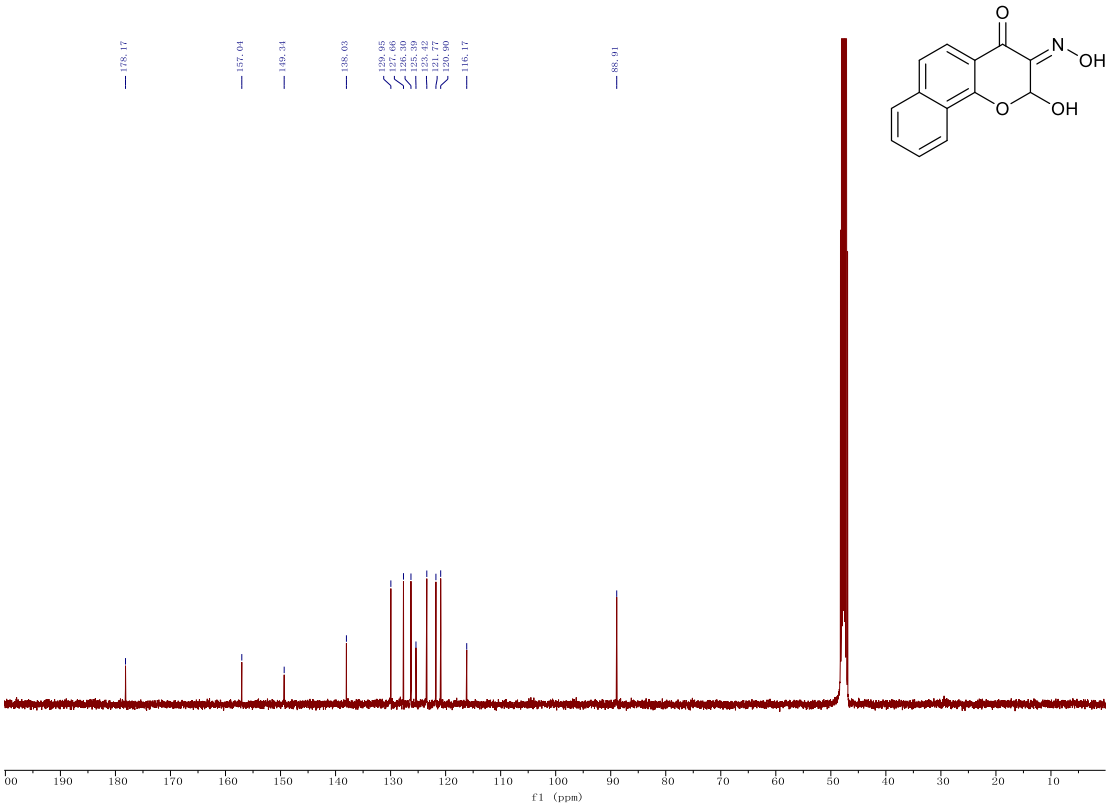
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2ab



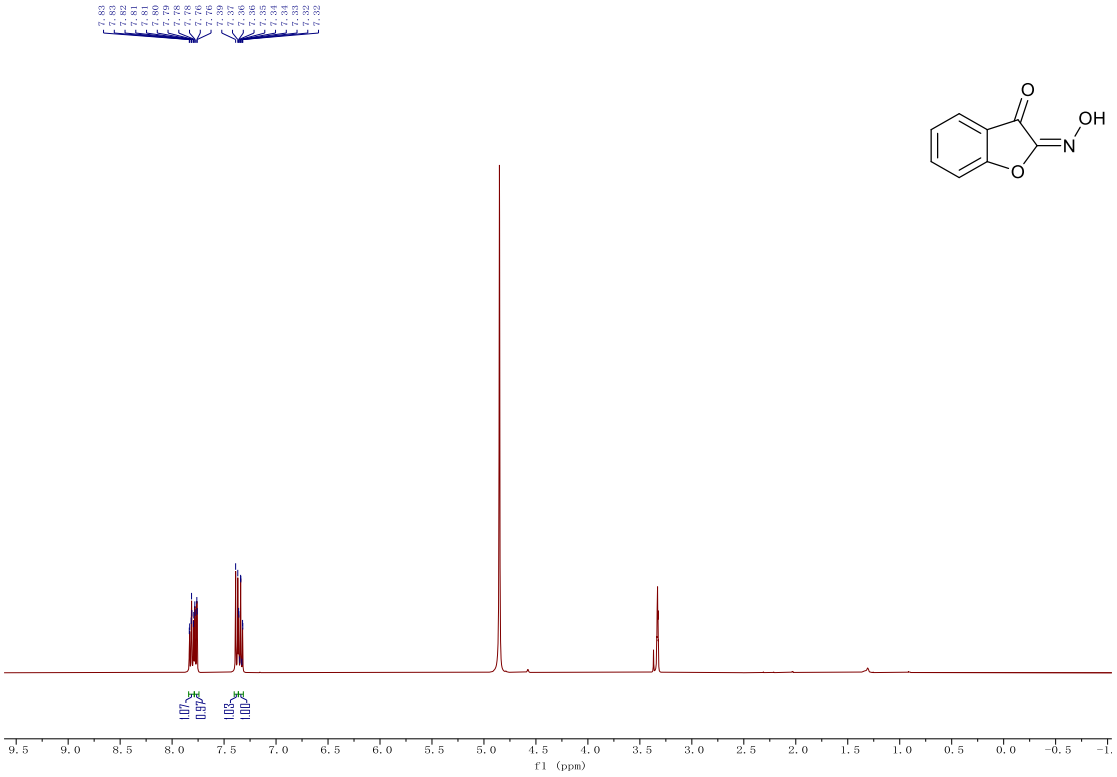


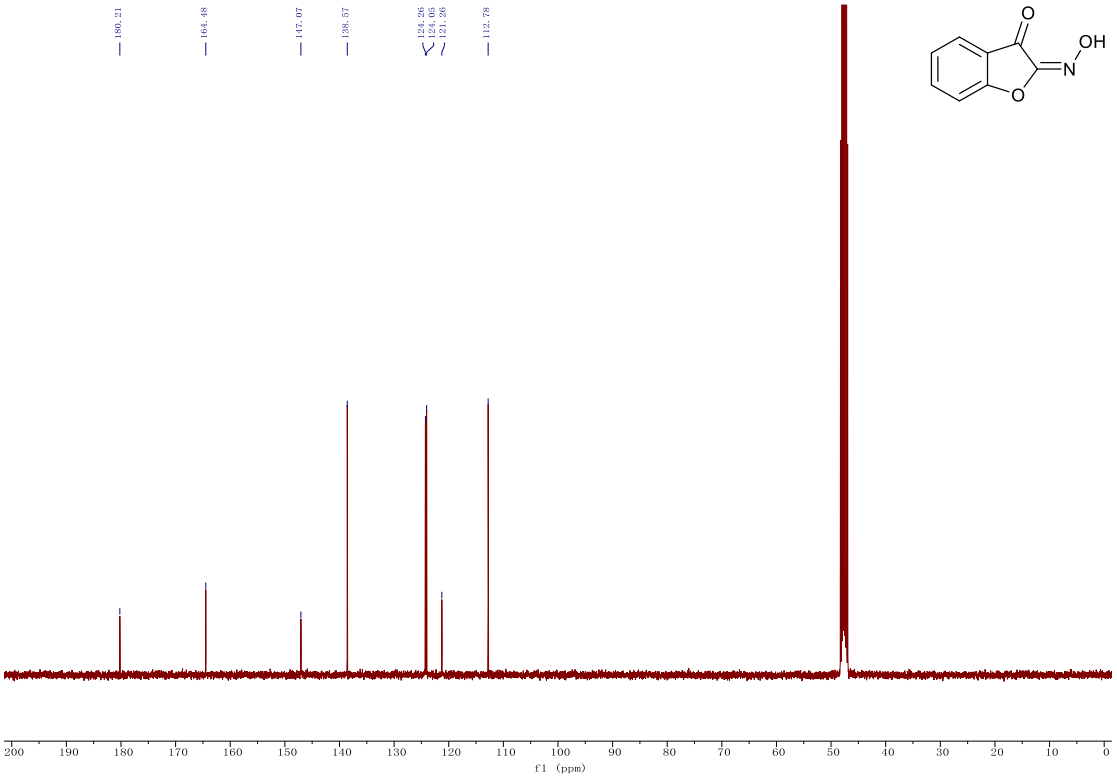
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 2ac



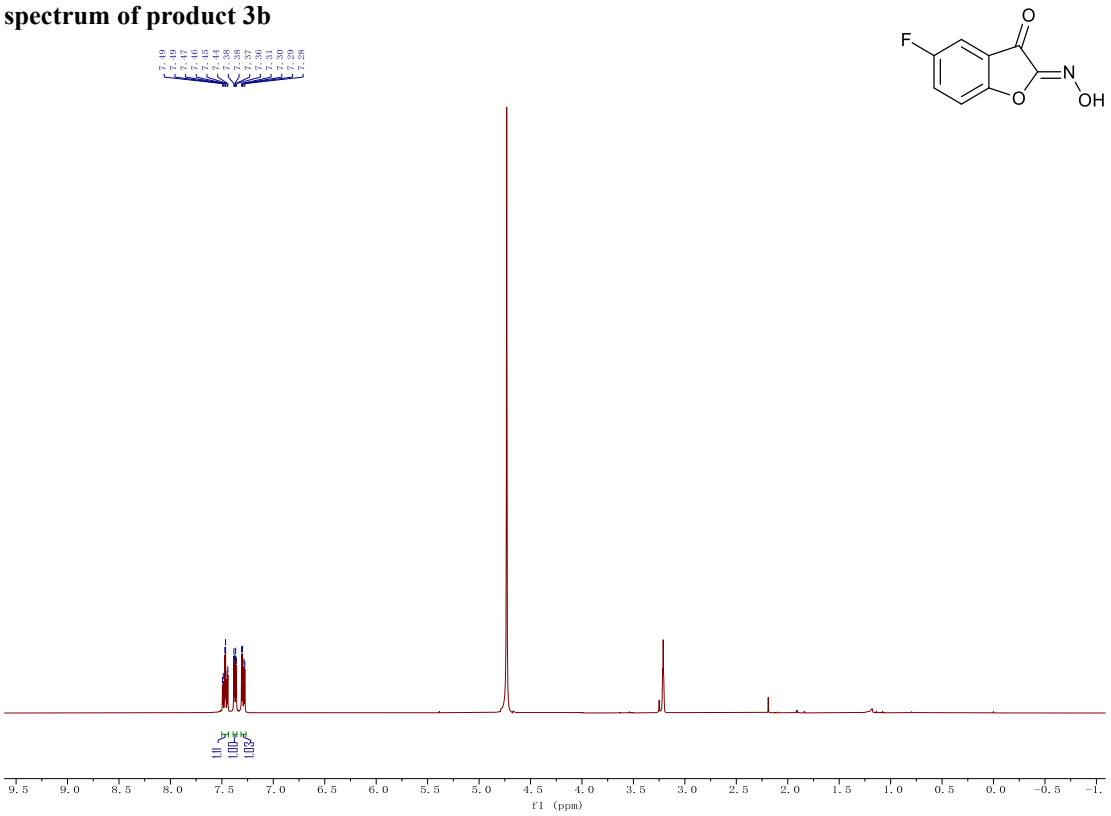


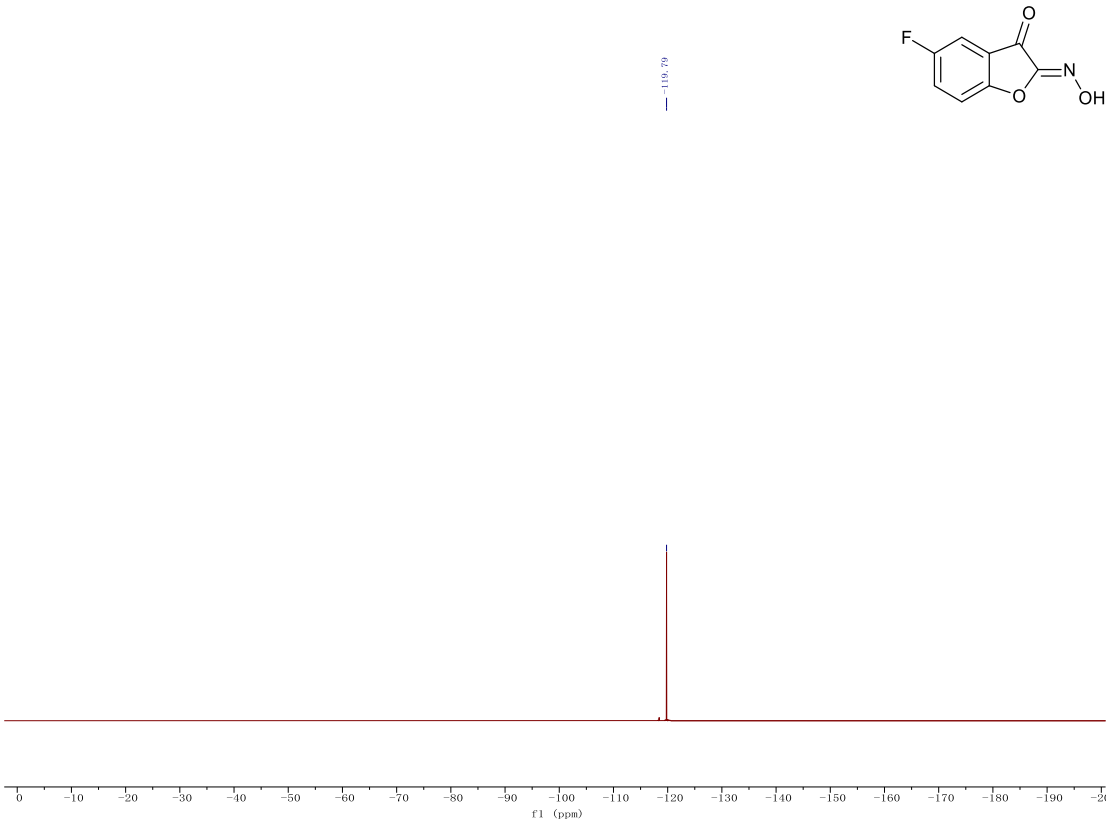
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 3a

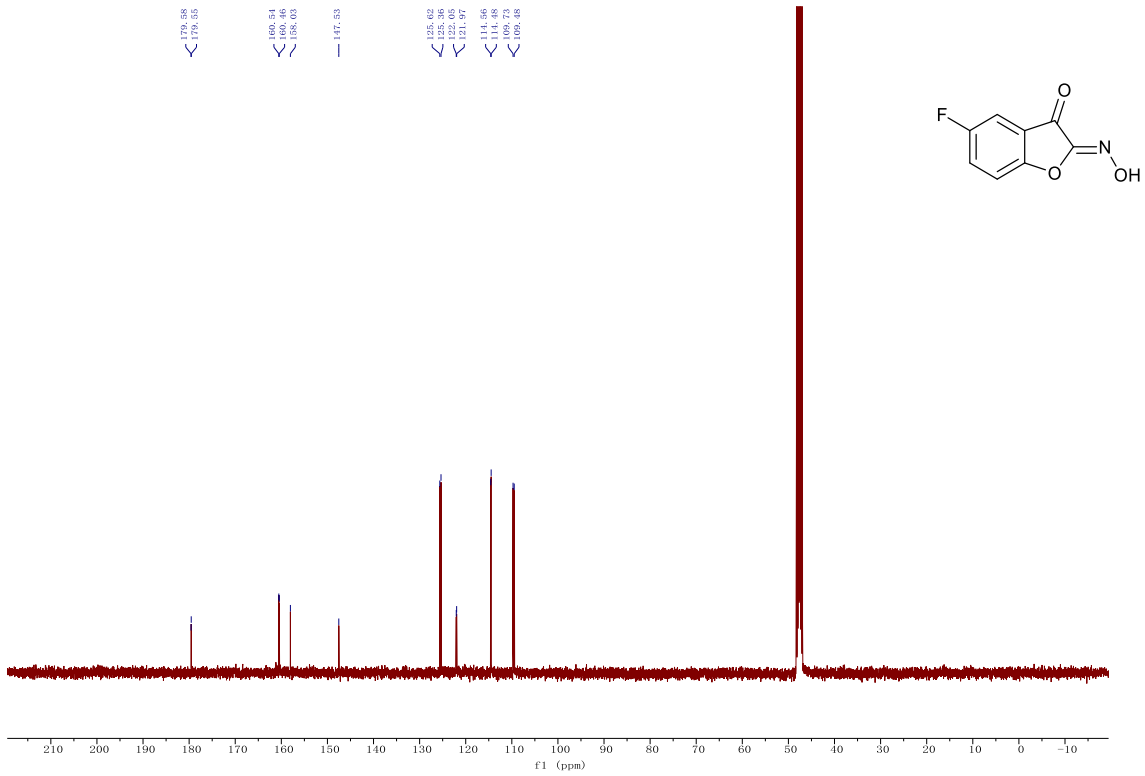




^{1}H NMR (400 MHz, CD_3OD), ^{19}F NMR (376 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 3b



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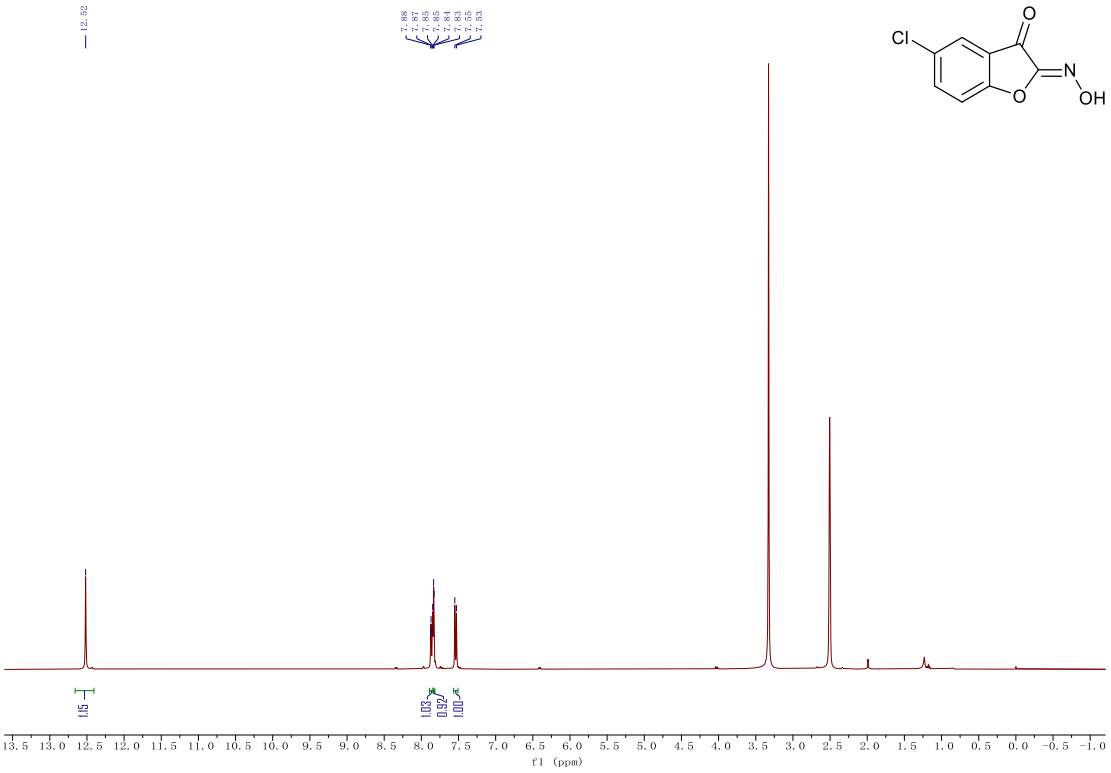
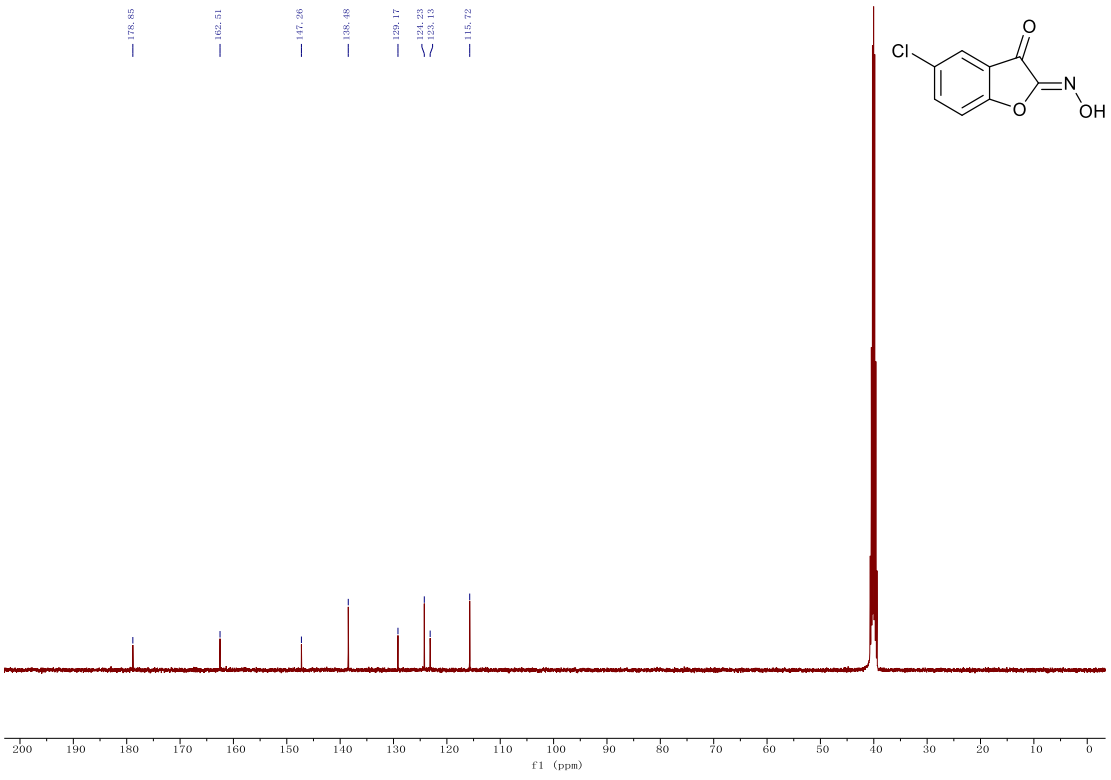
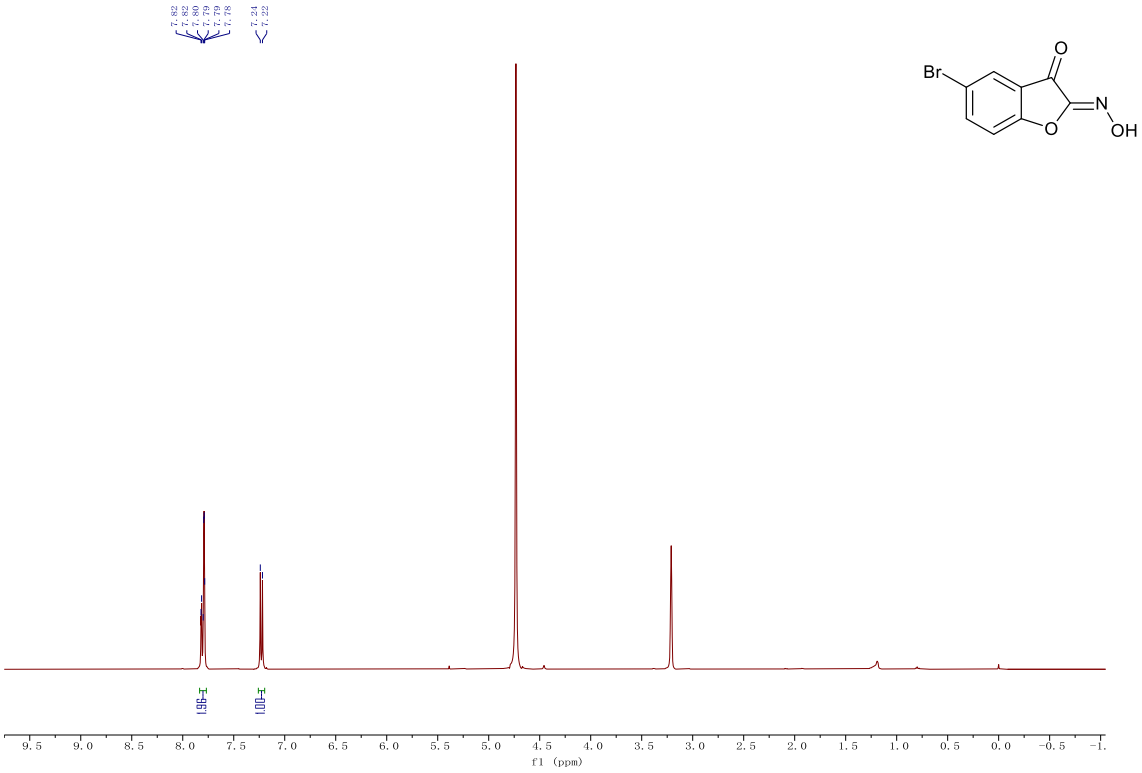
121.97
111.56
111.48
109.73
109.48
F
O
N
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

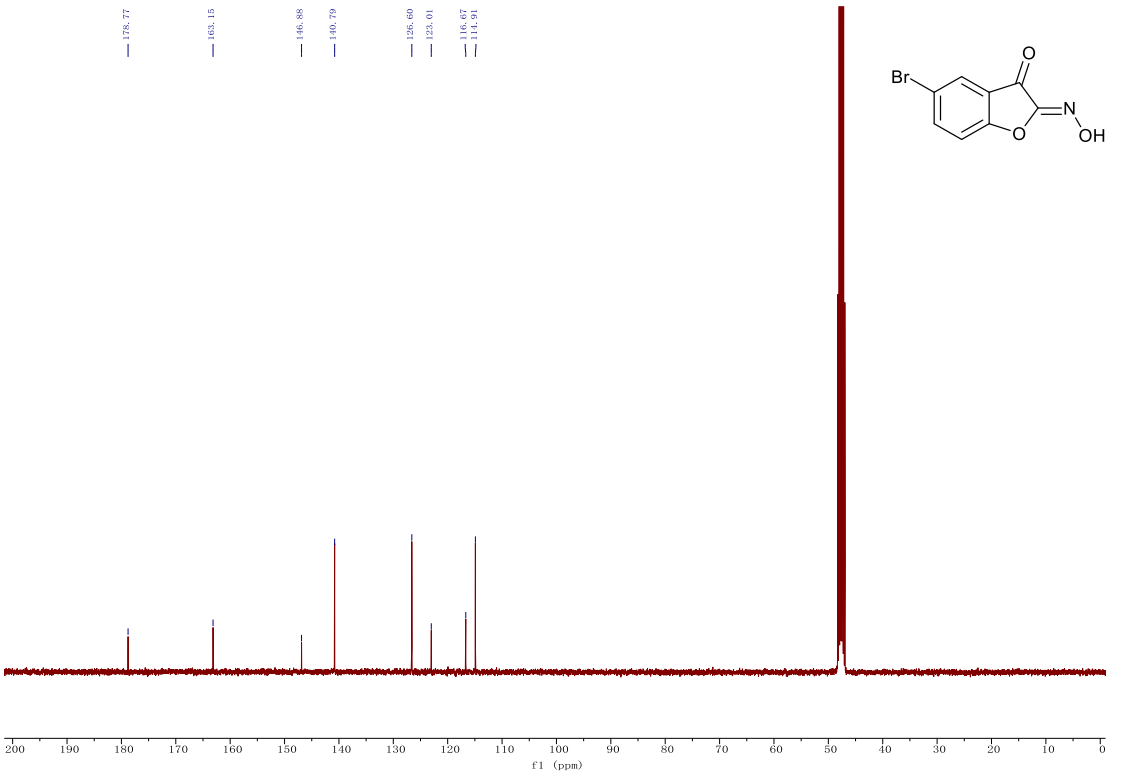
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3c



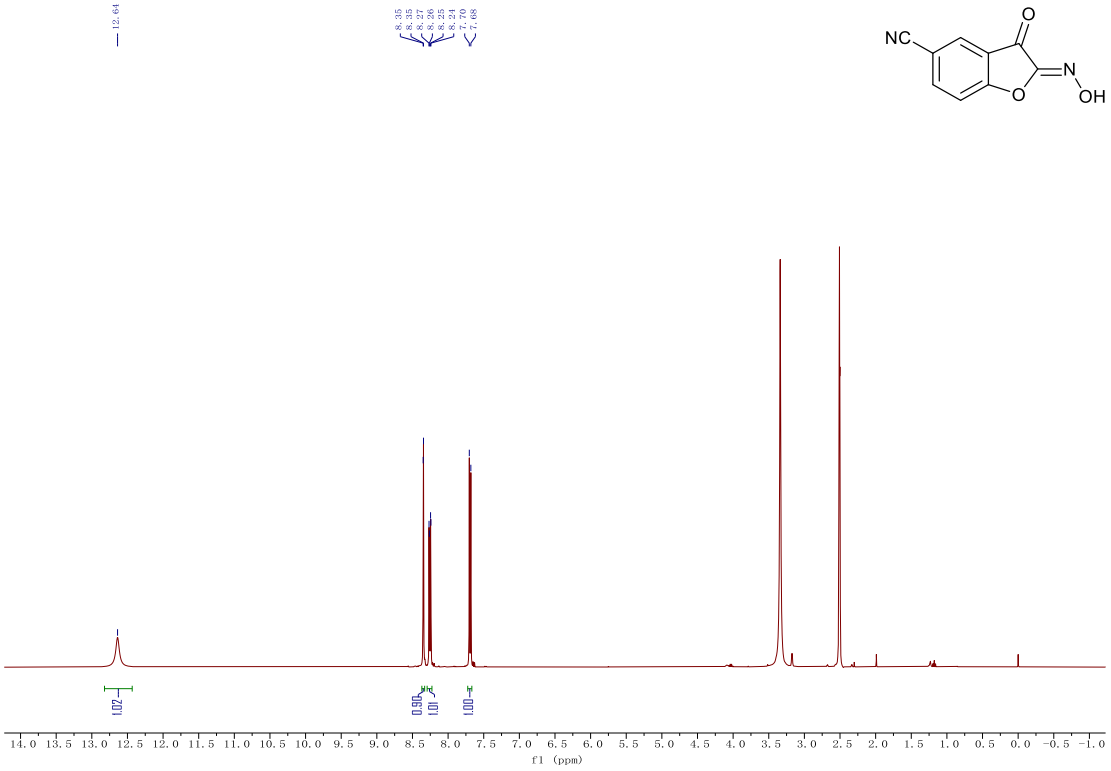


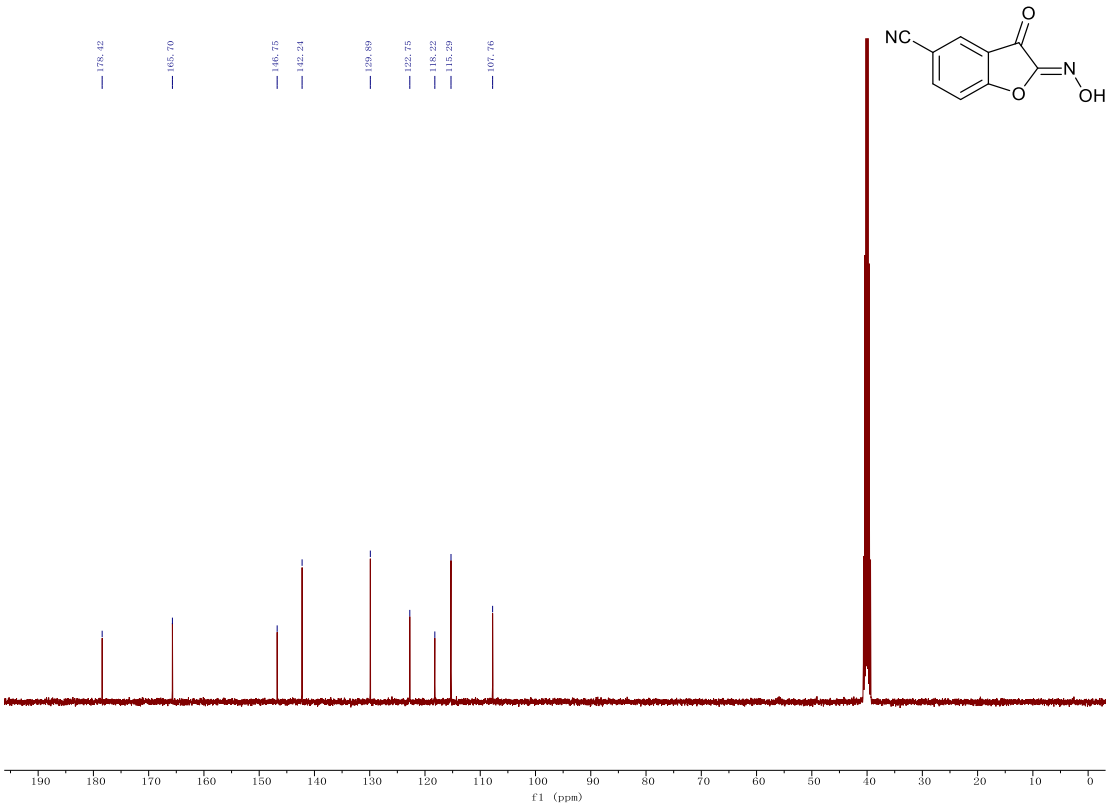
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 3d



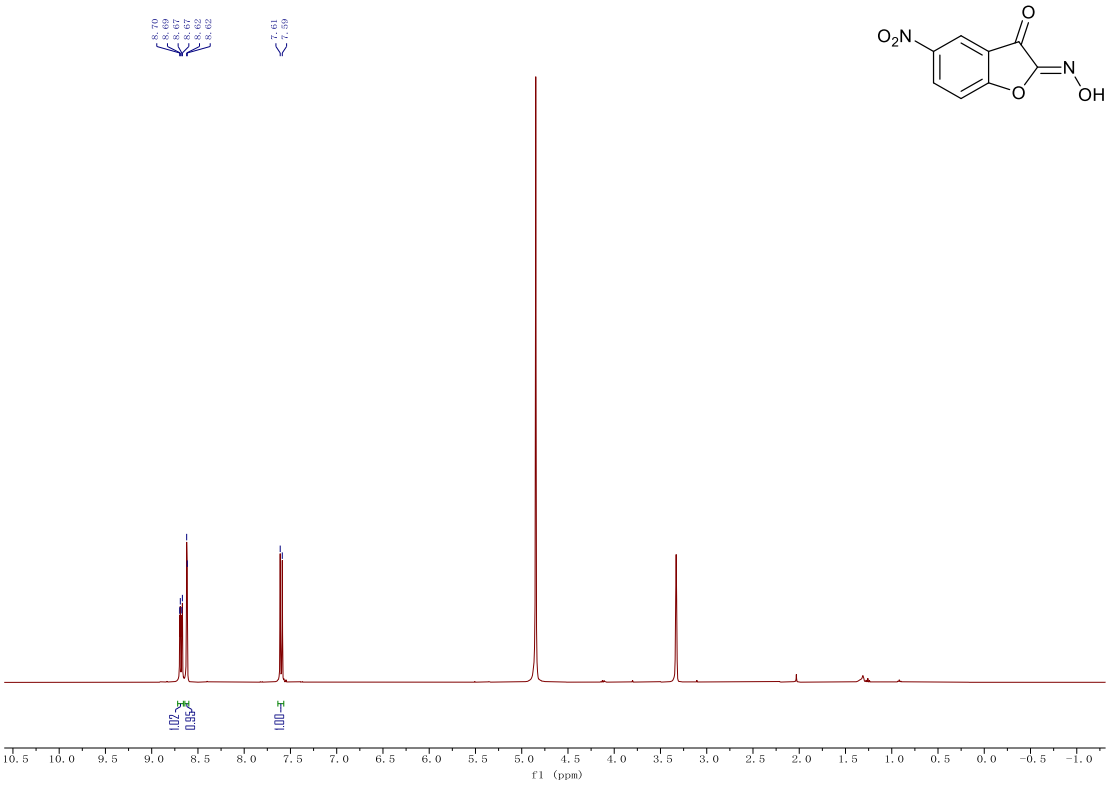


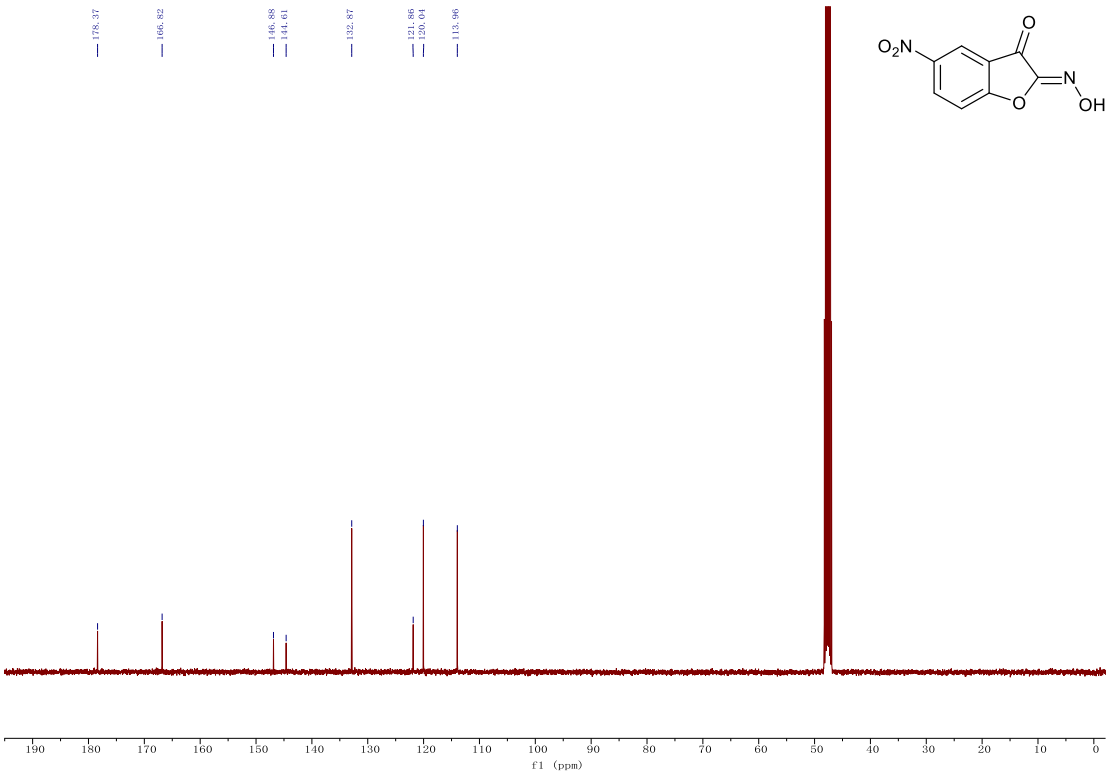
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3e



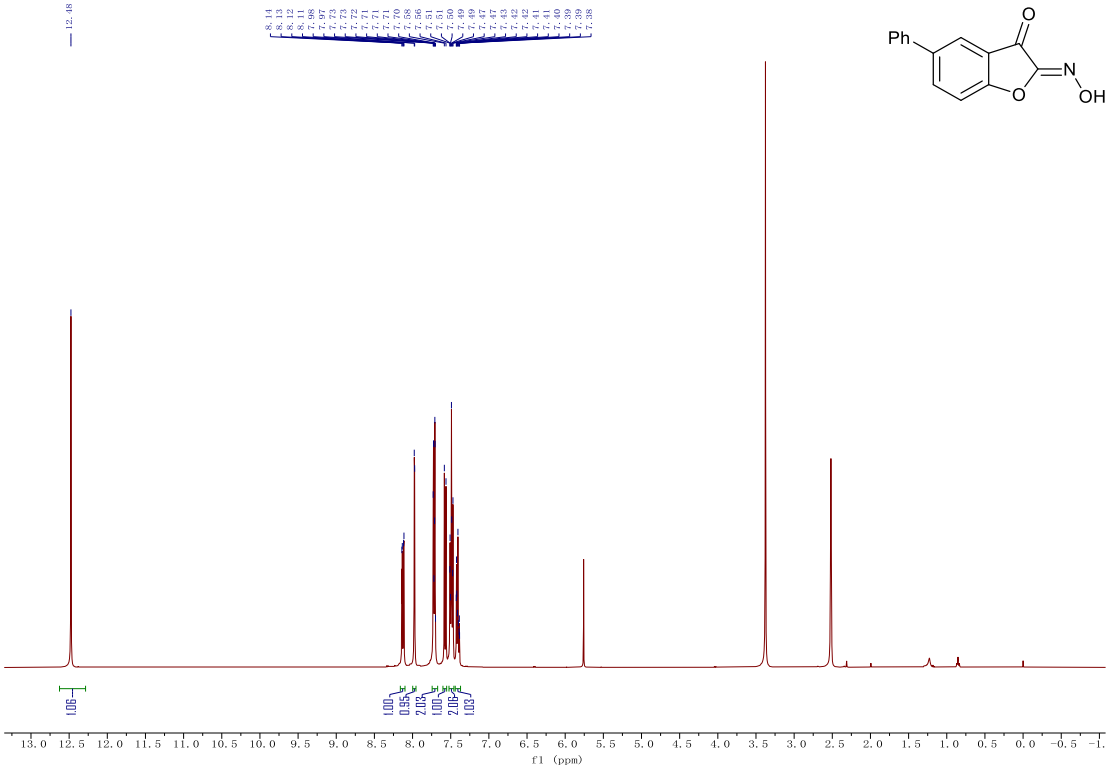


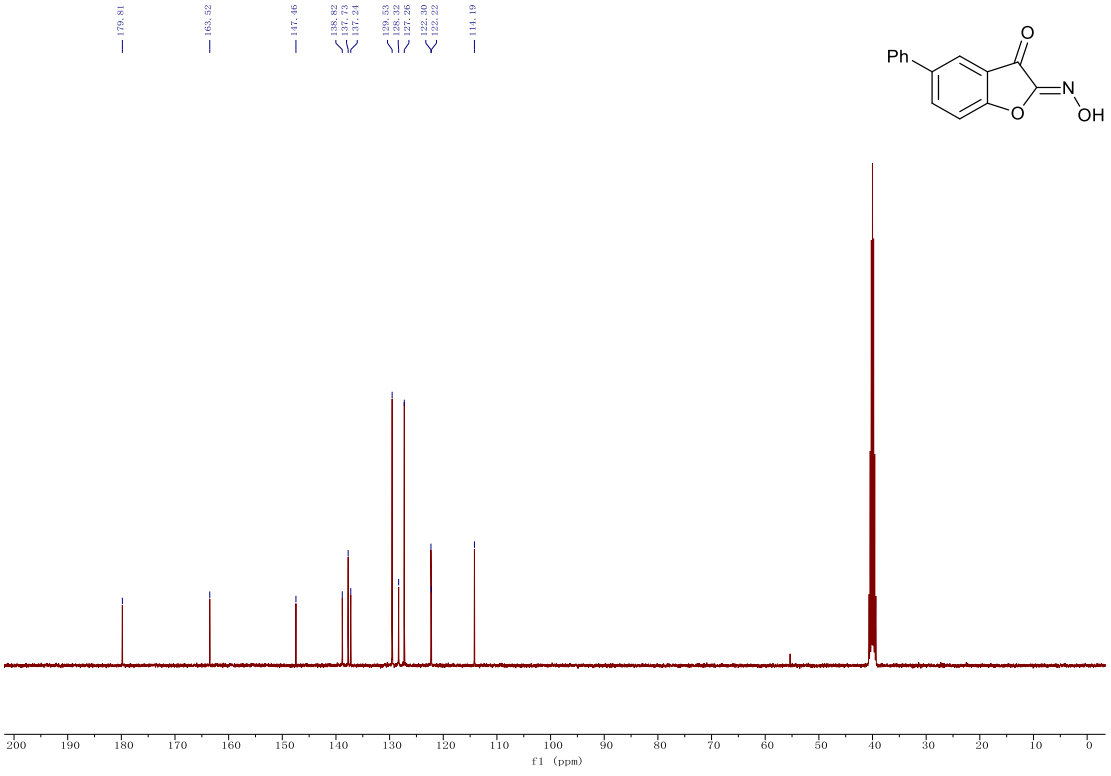
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 3f



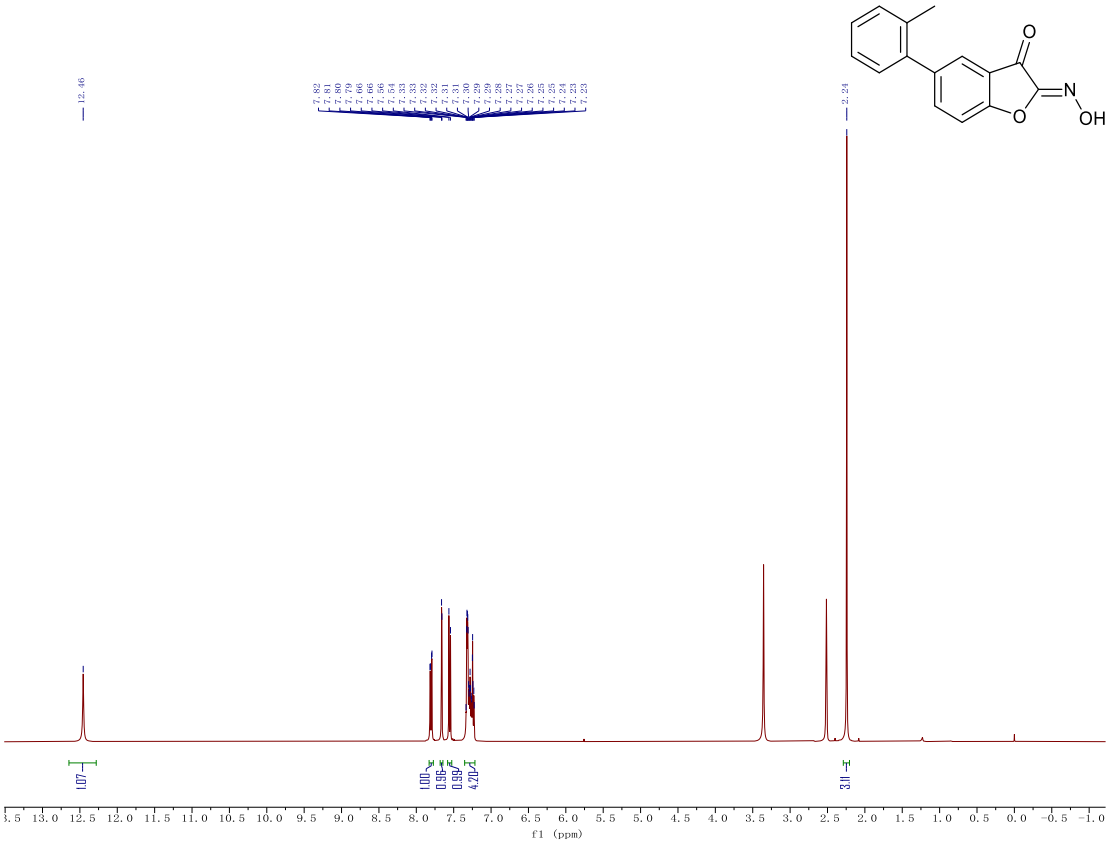


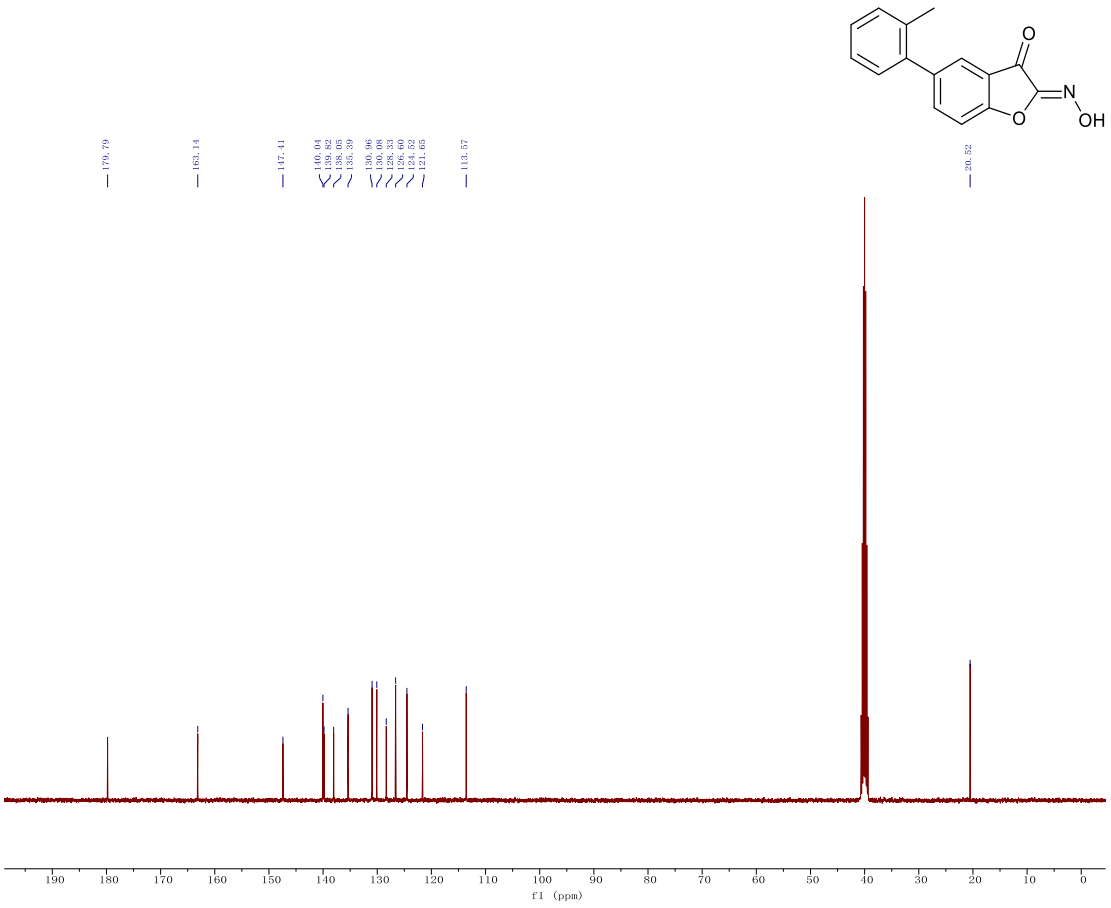
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3g



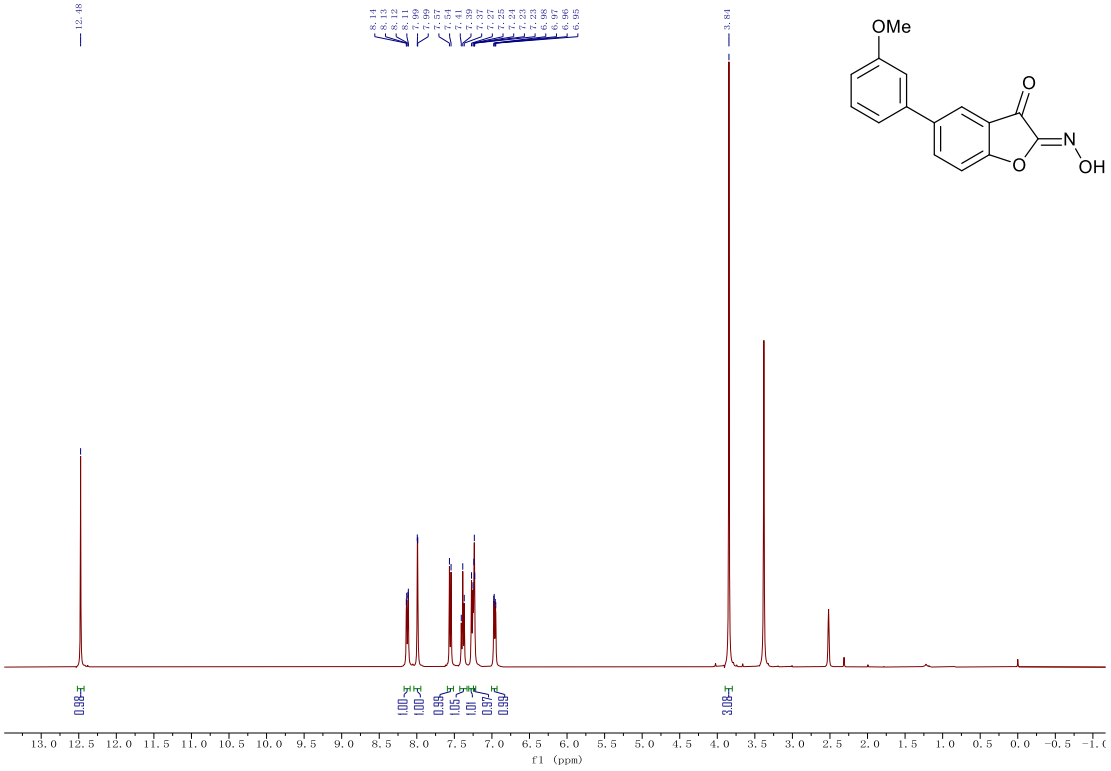


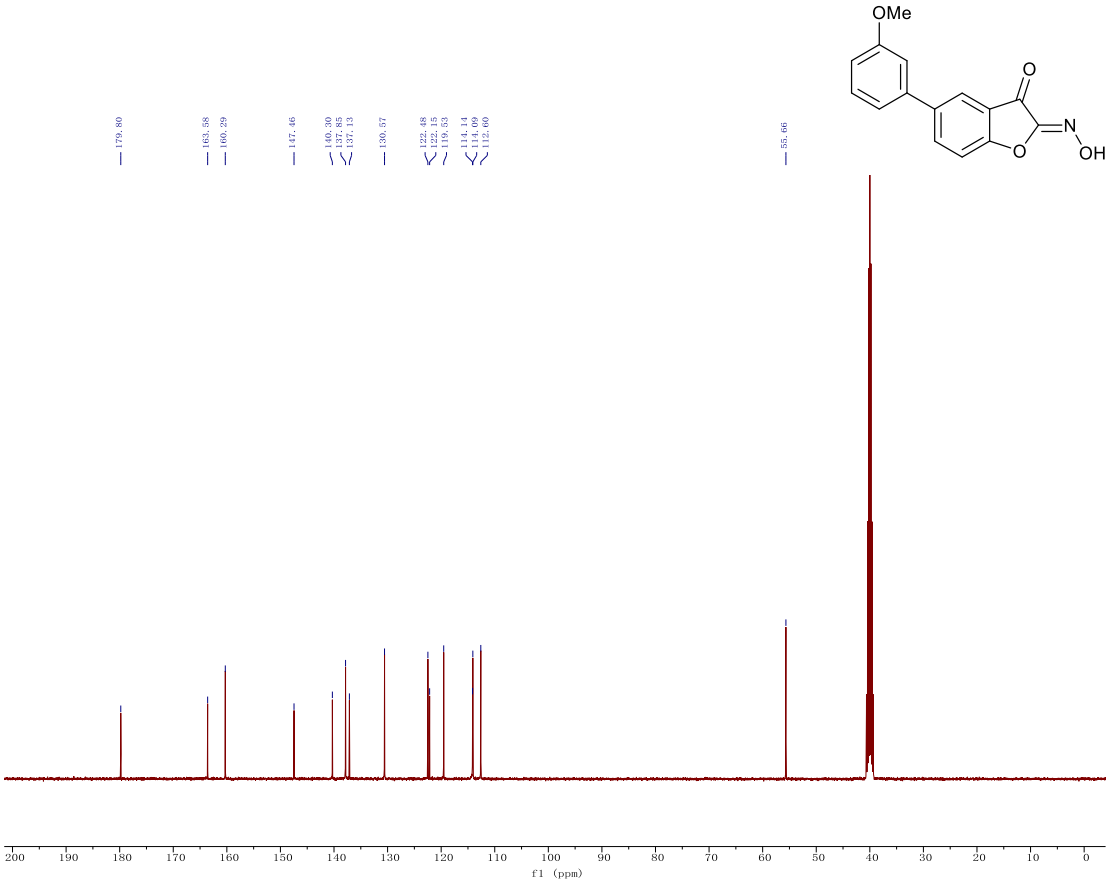
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3h



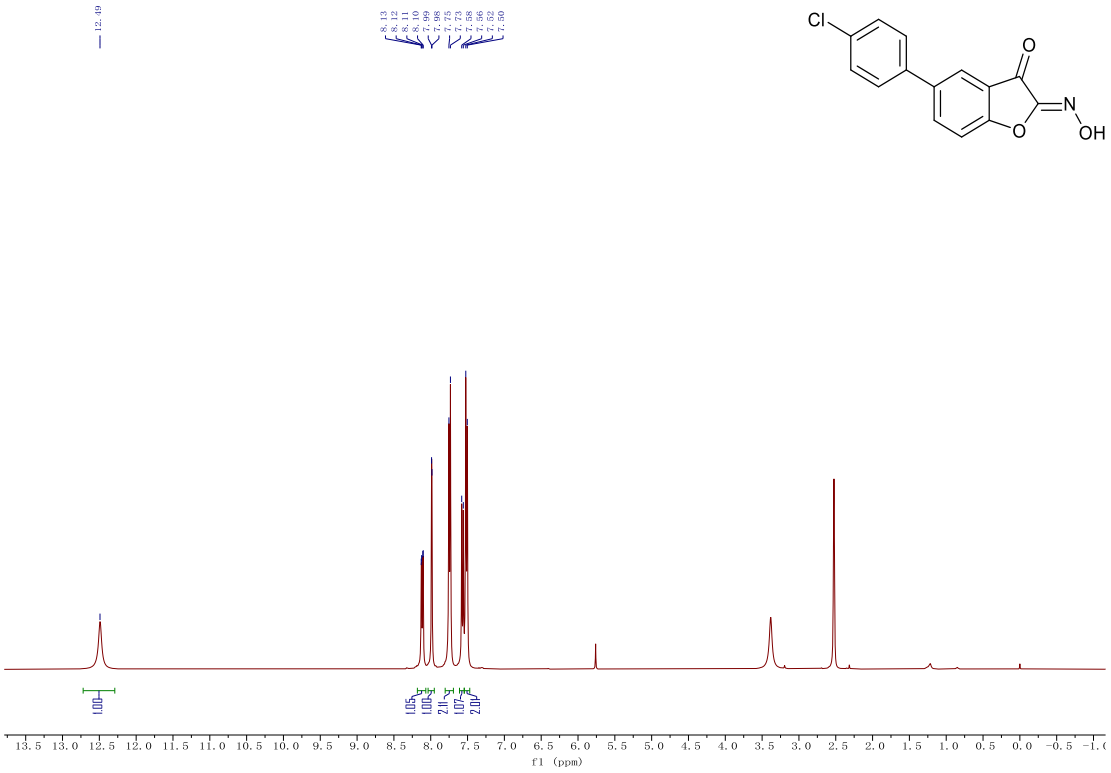


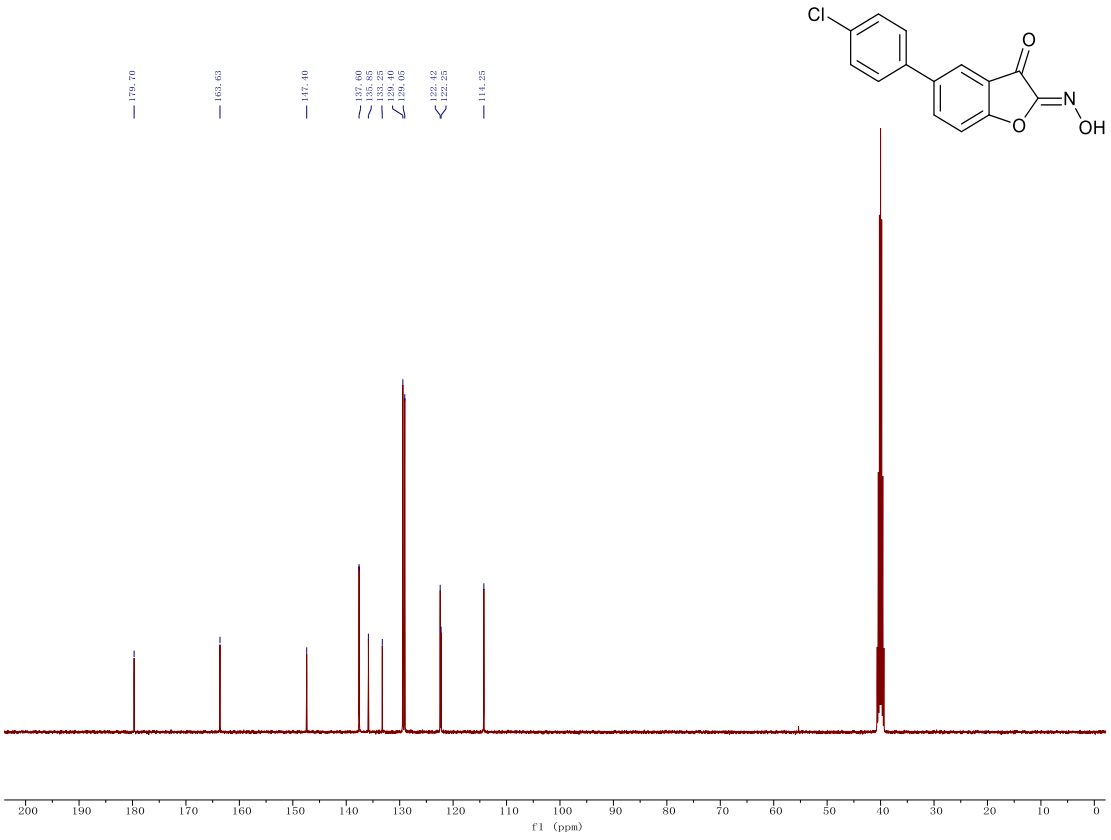
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3i



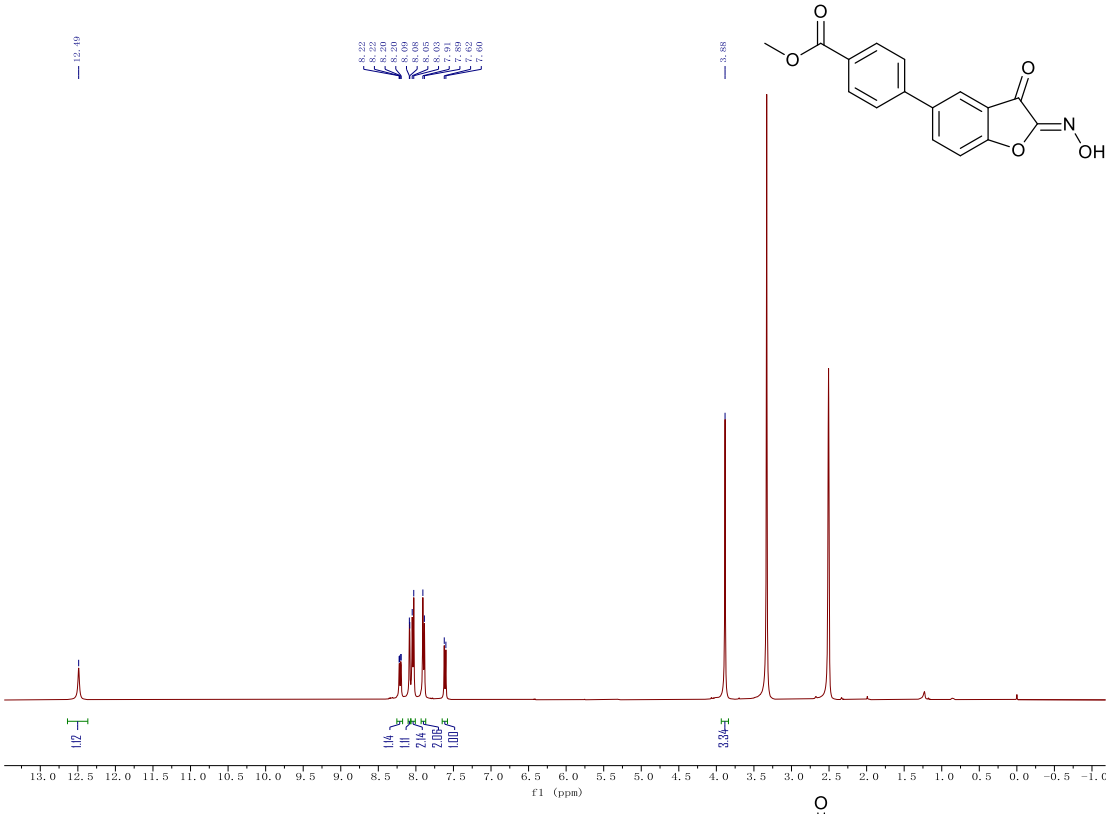


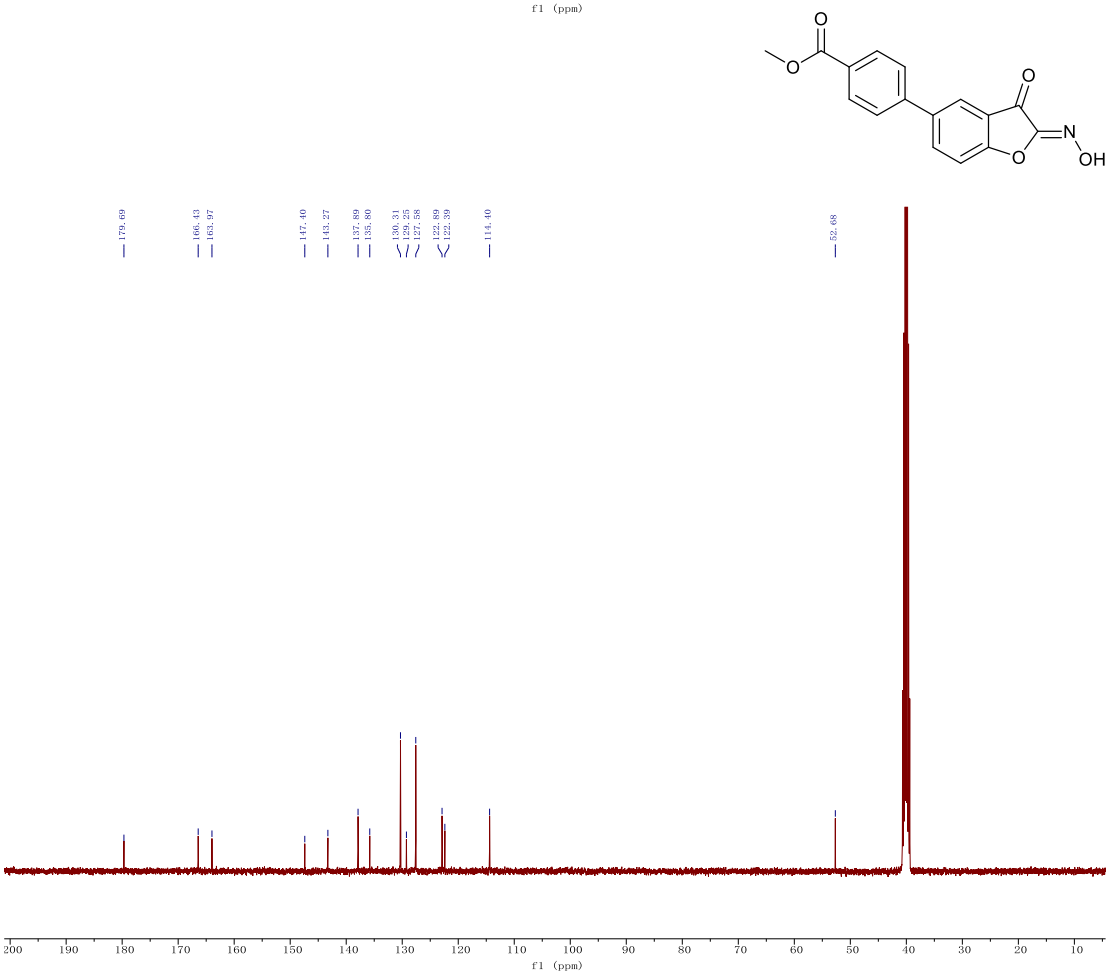
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3j



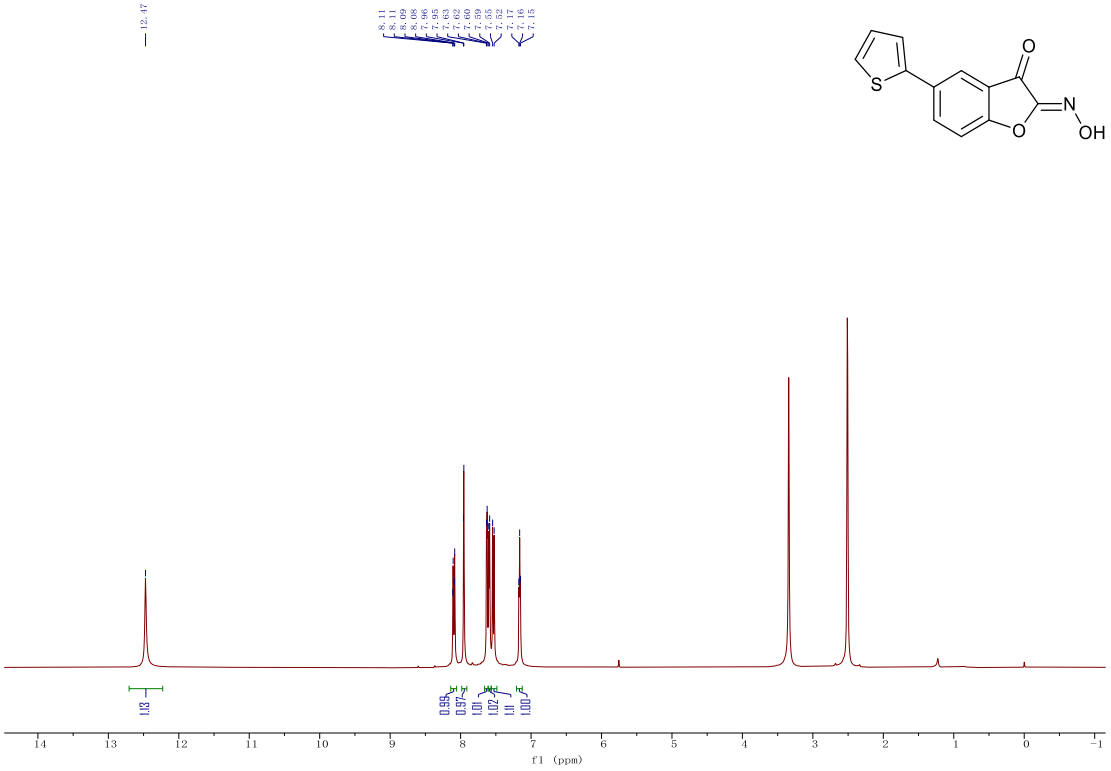


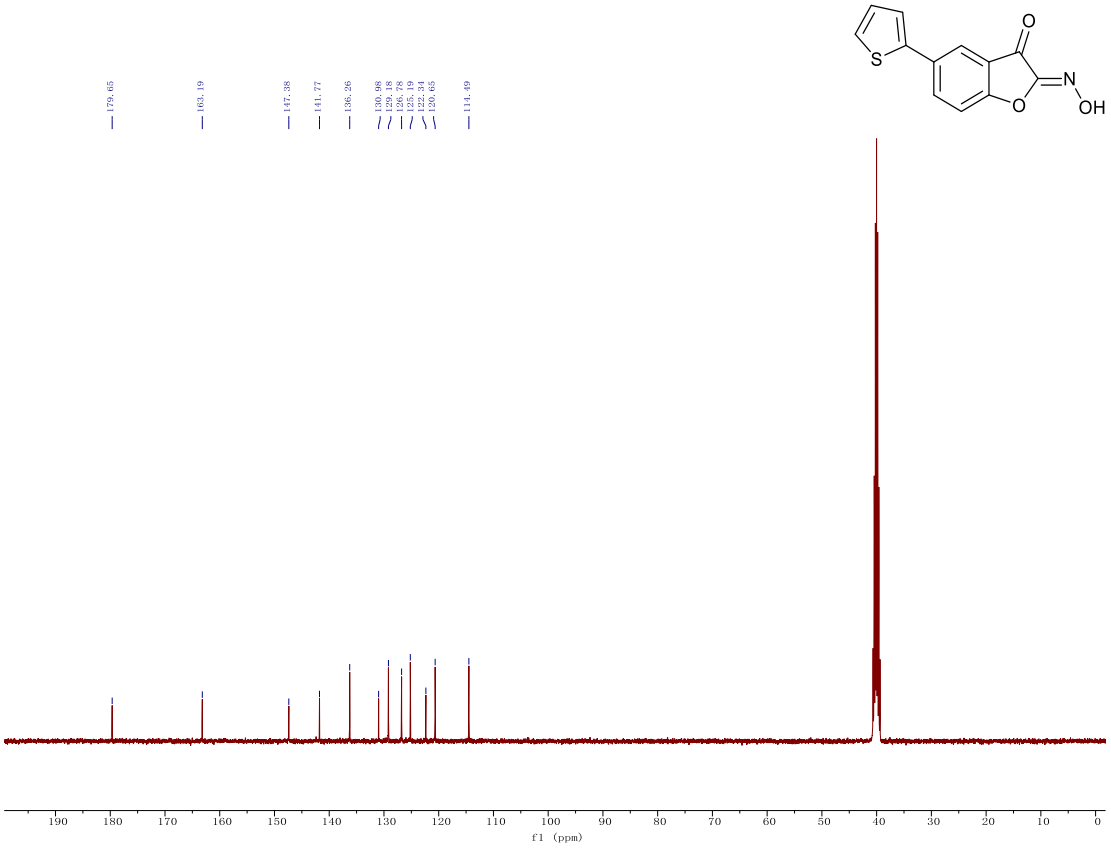
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3k



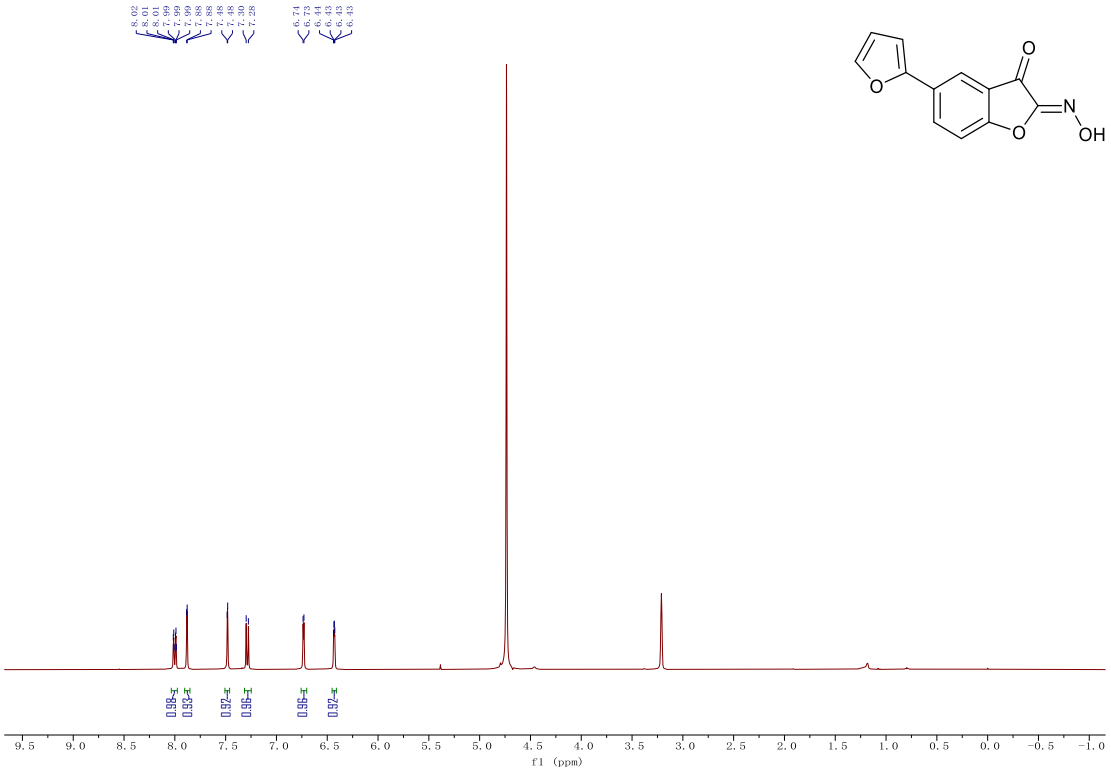


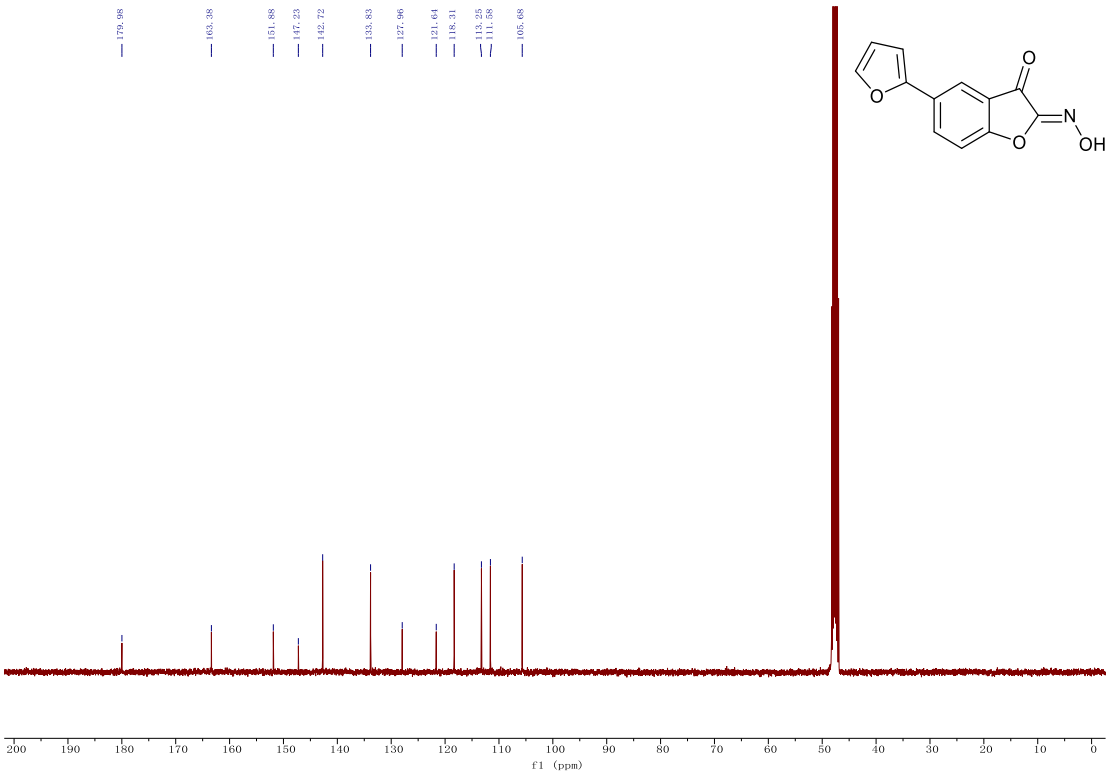
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3l



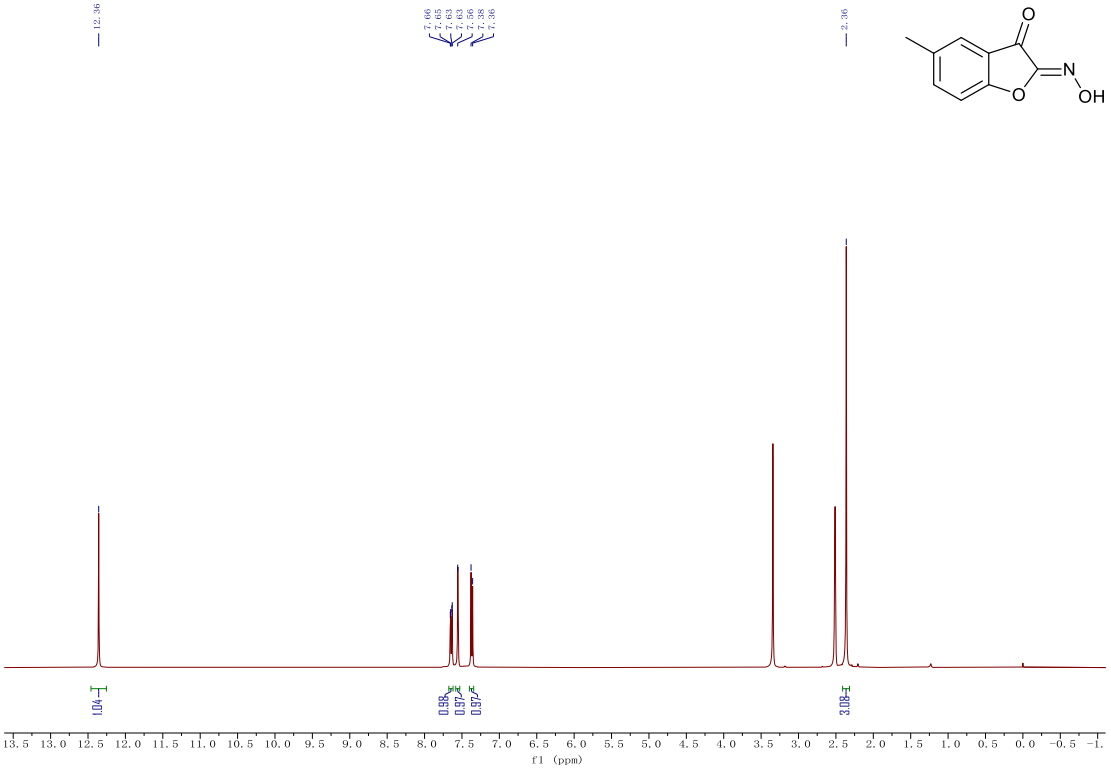


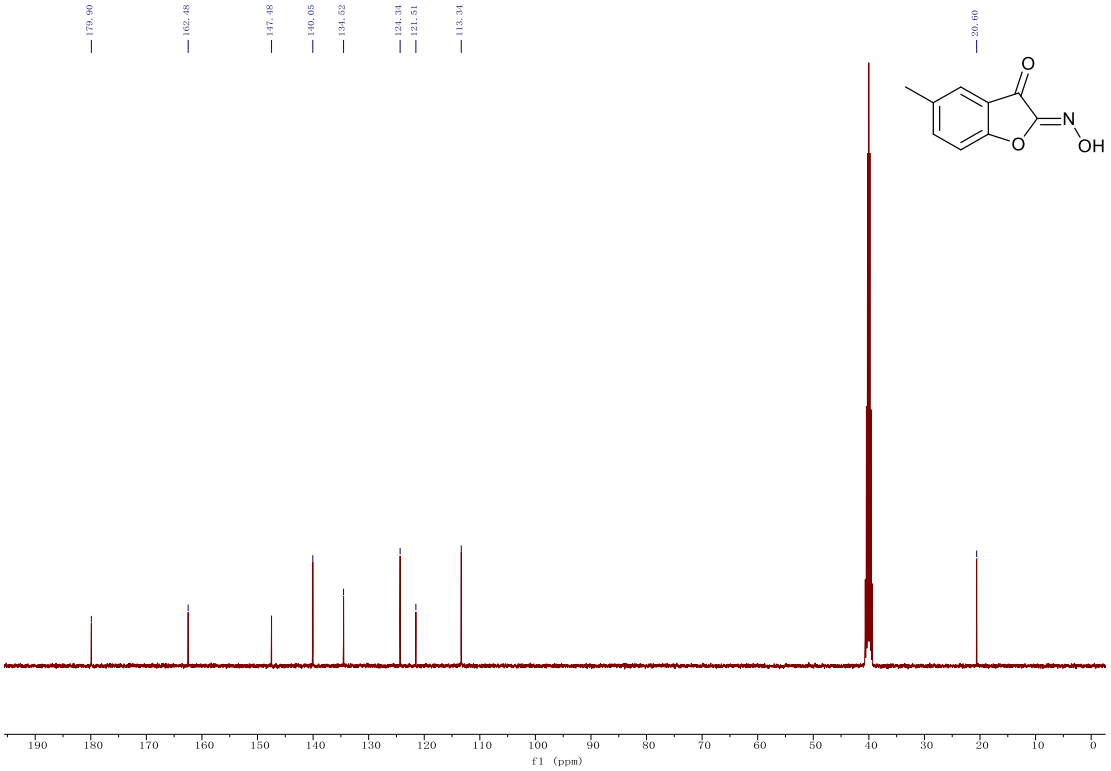
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 3m



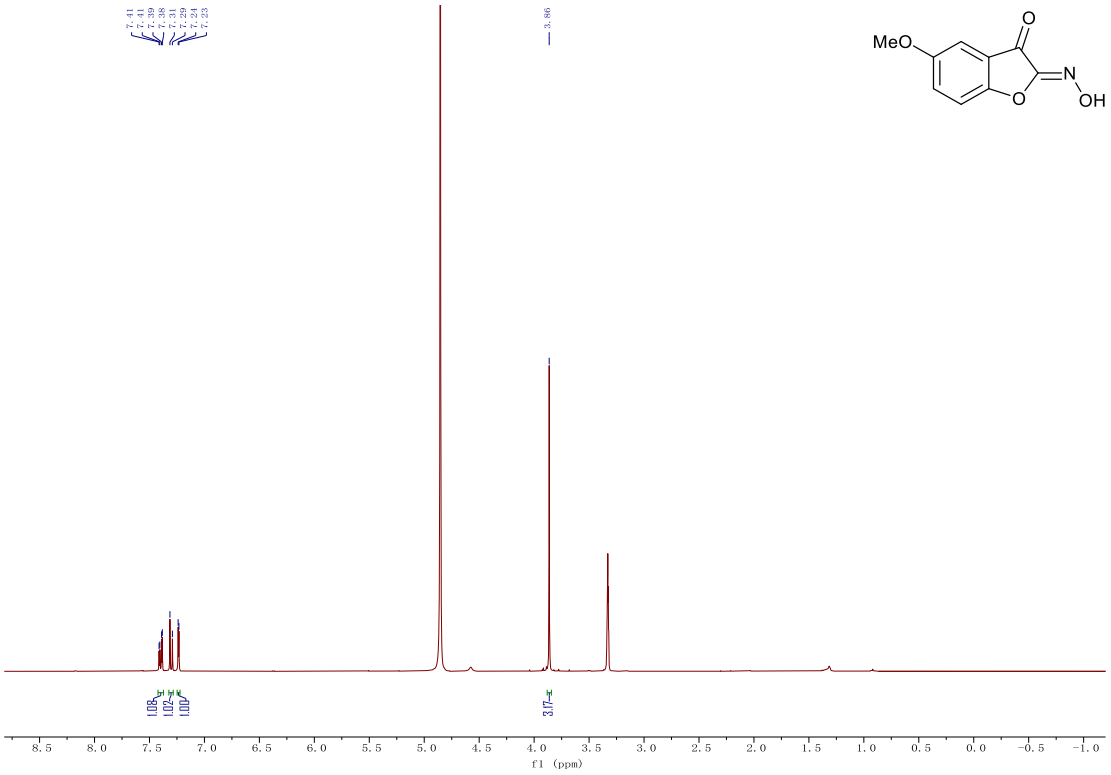


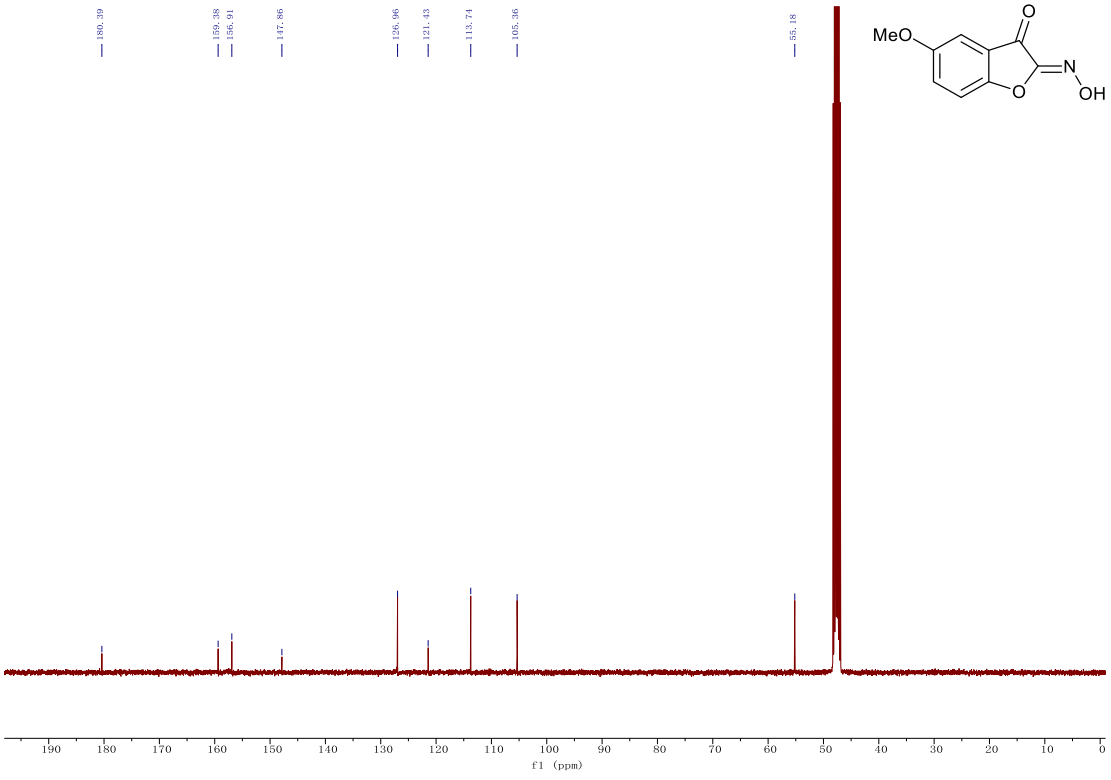
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3n



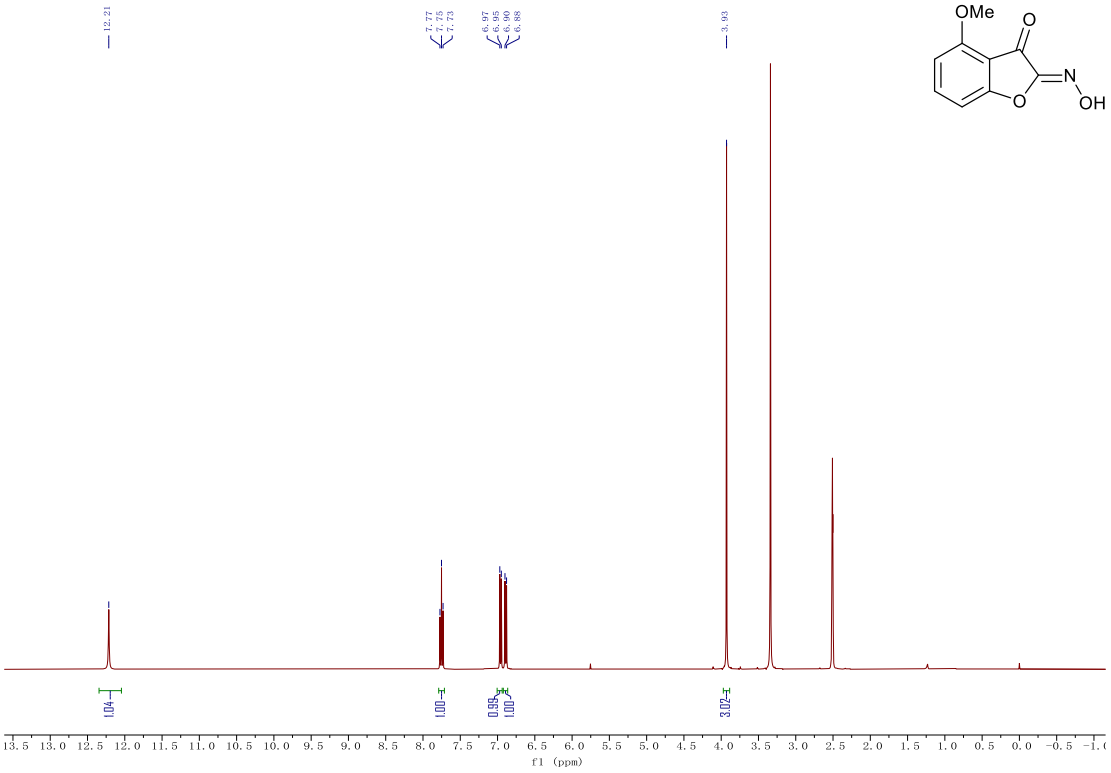


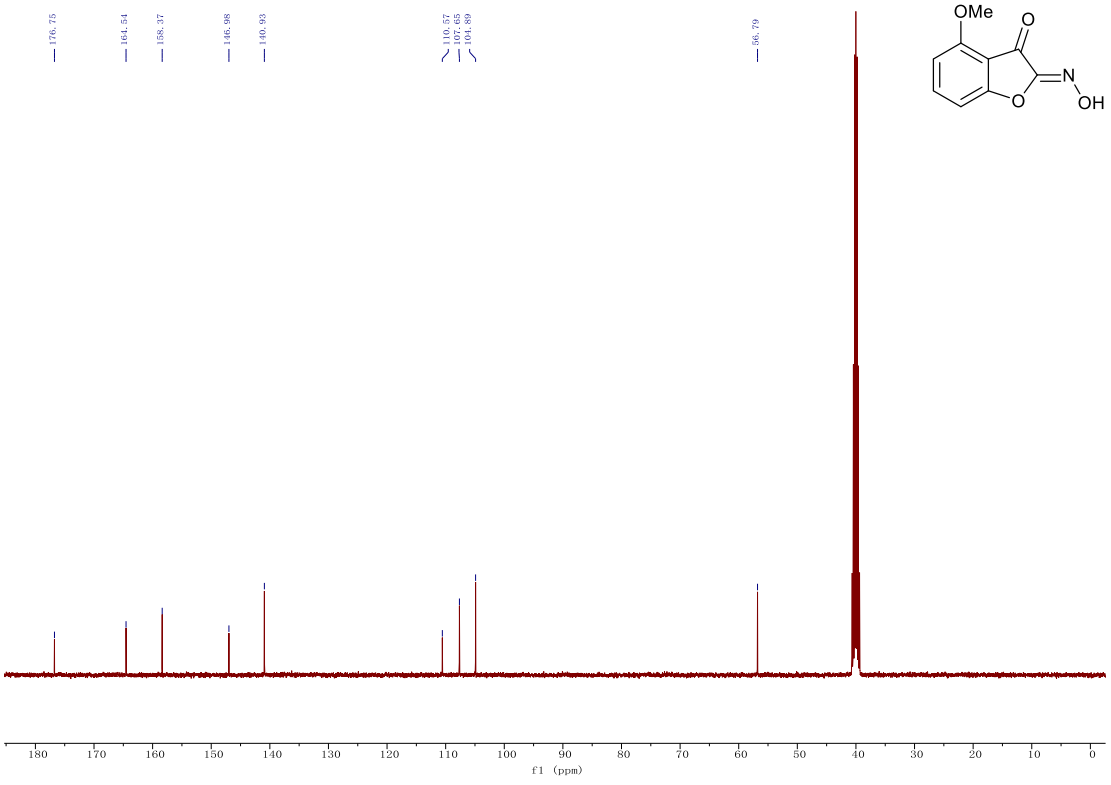
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 3o



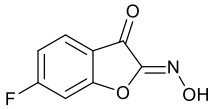


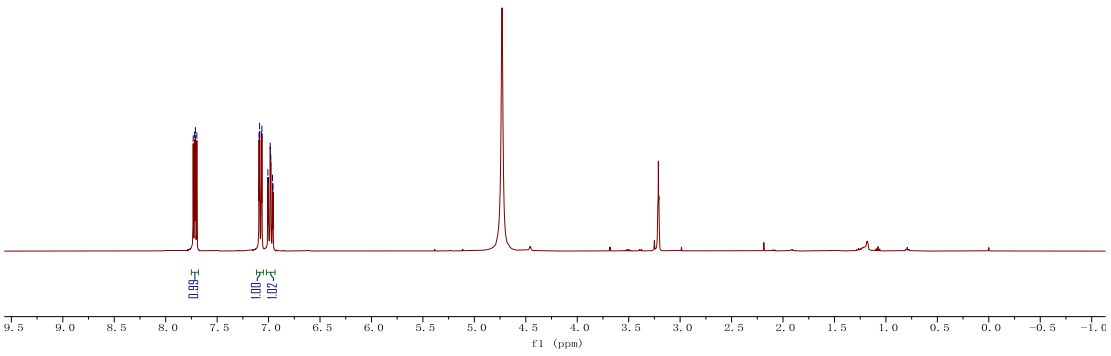
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3q

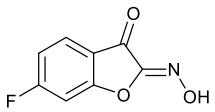


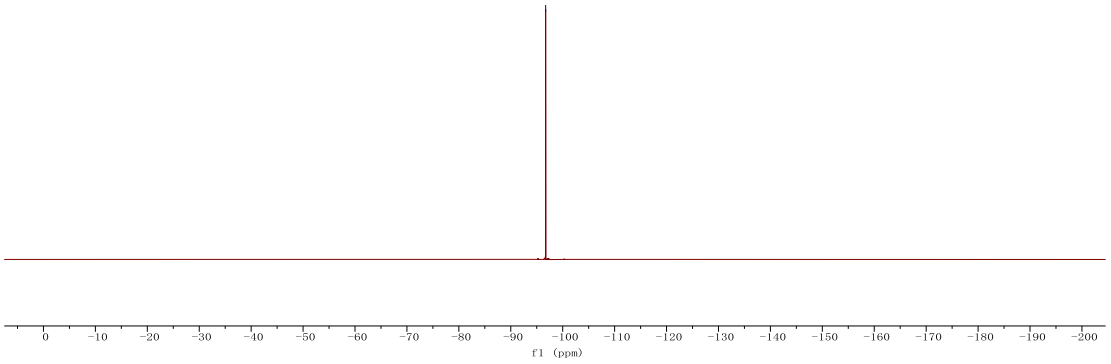


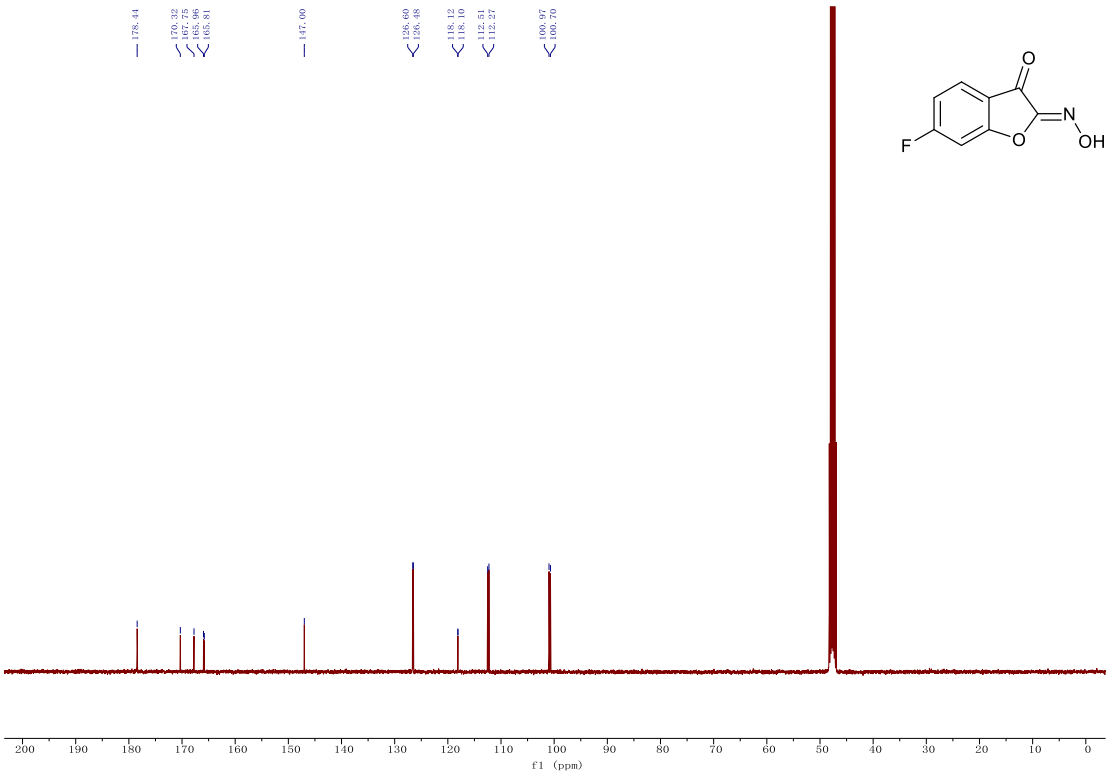
^{1}H NMR (400 MHz, CD_3OD), ^{19}F NMR (376 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 3r







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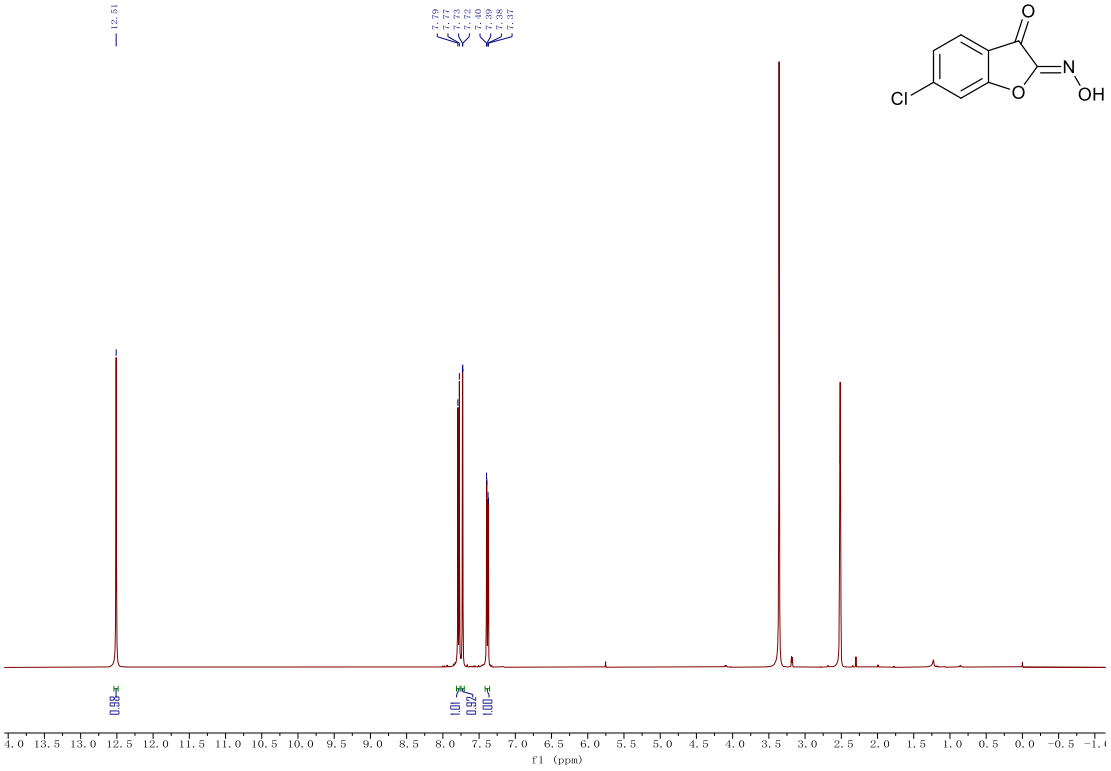
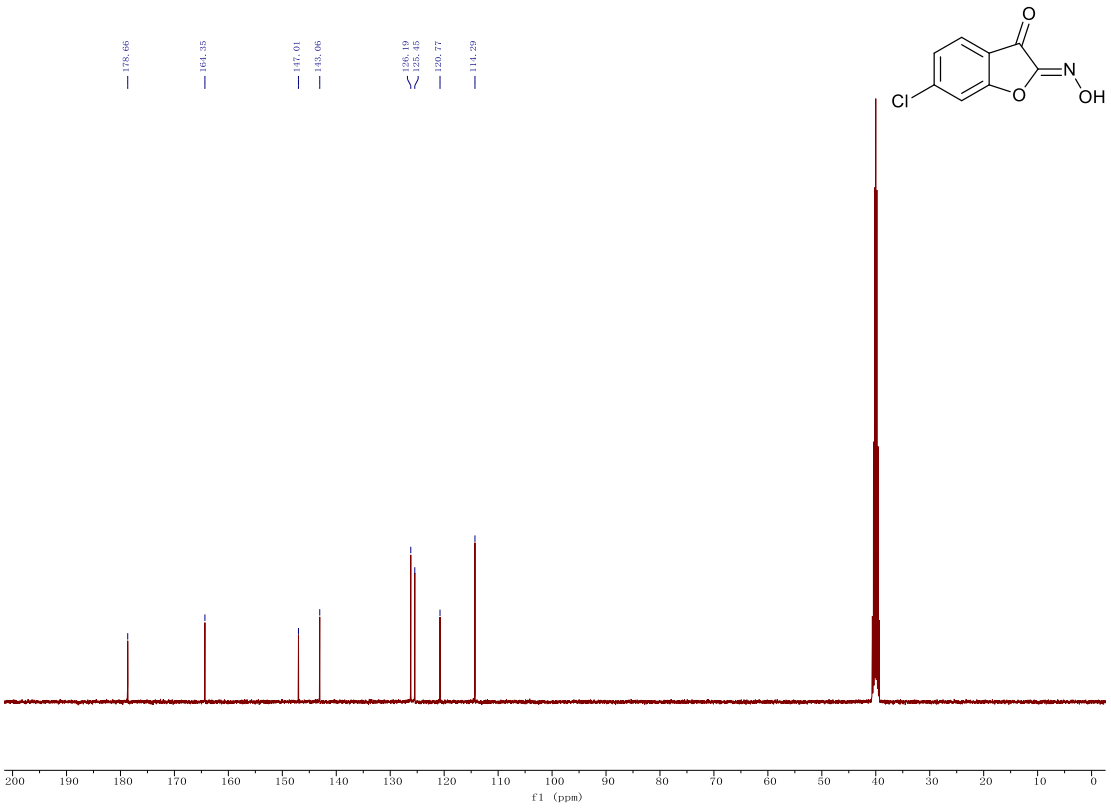
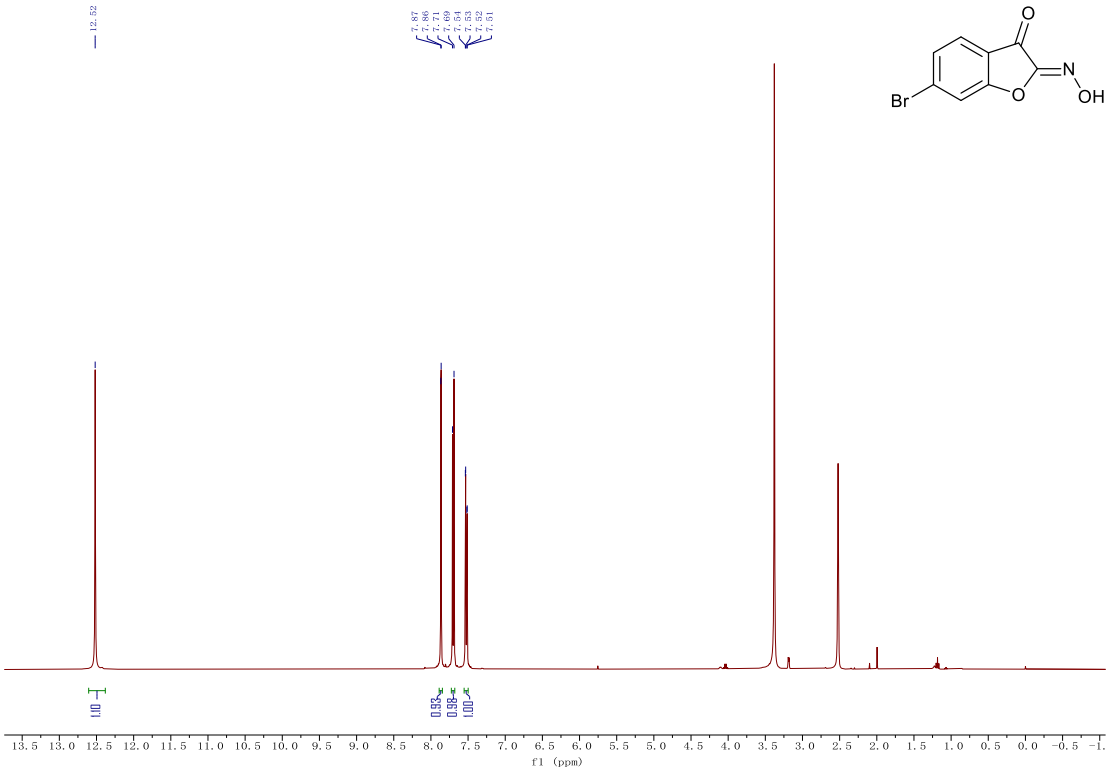
N
OH
O
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

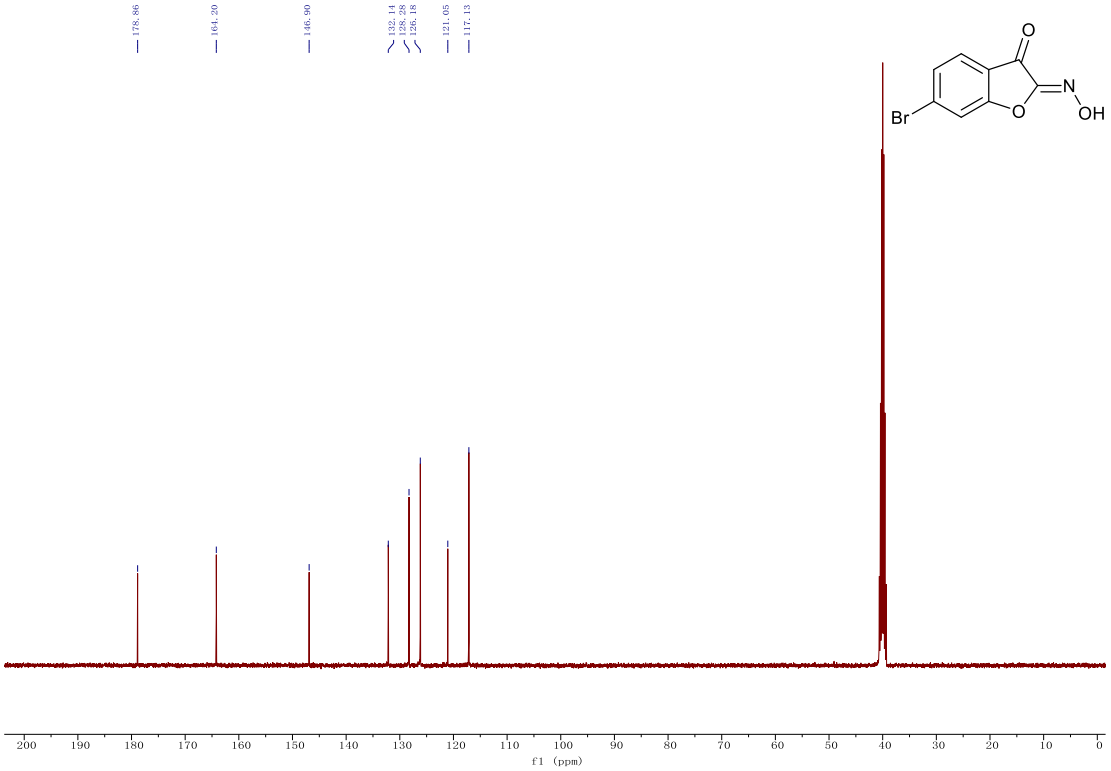
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3s



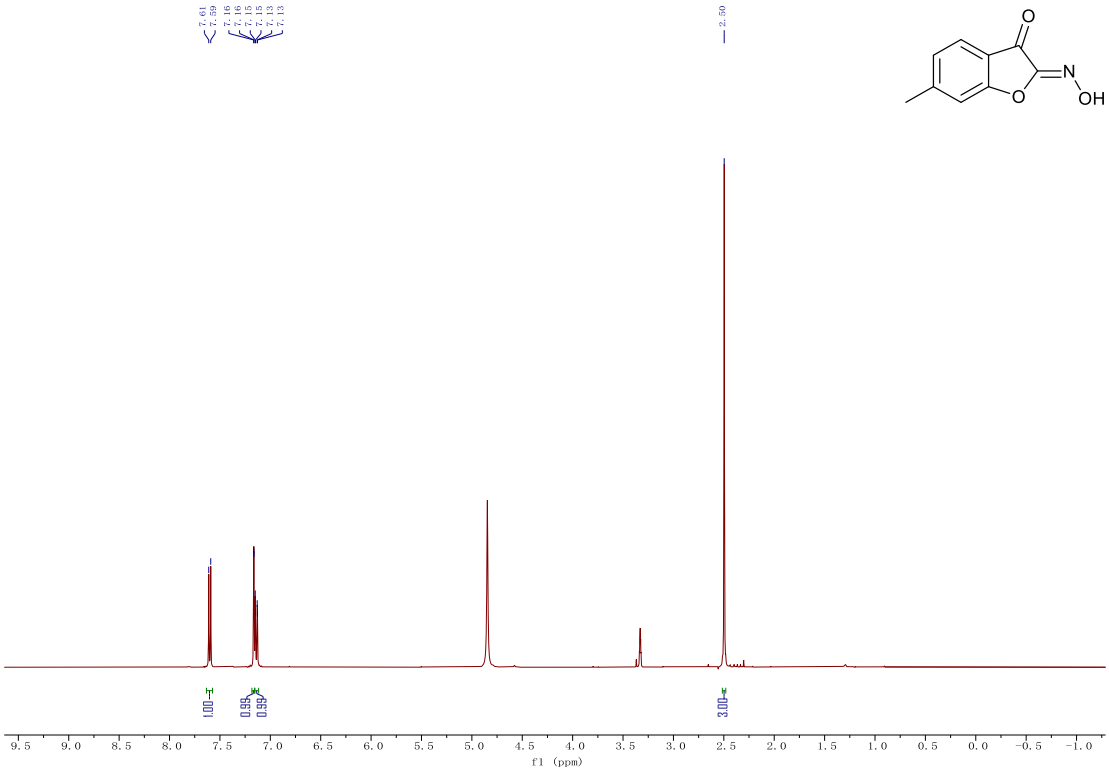


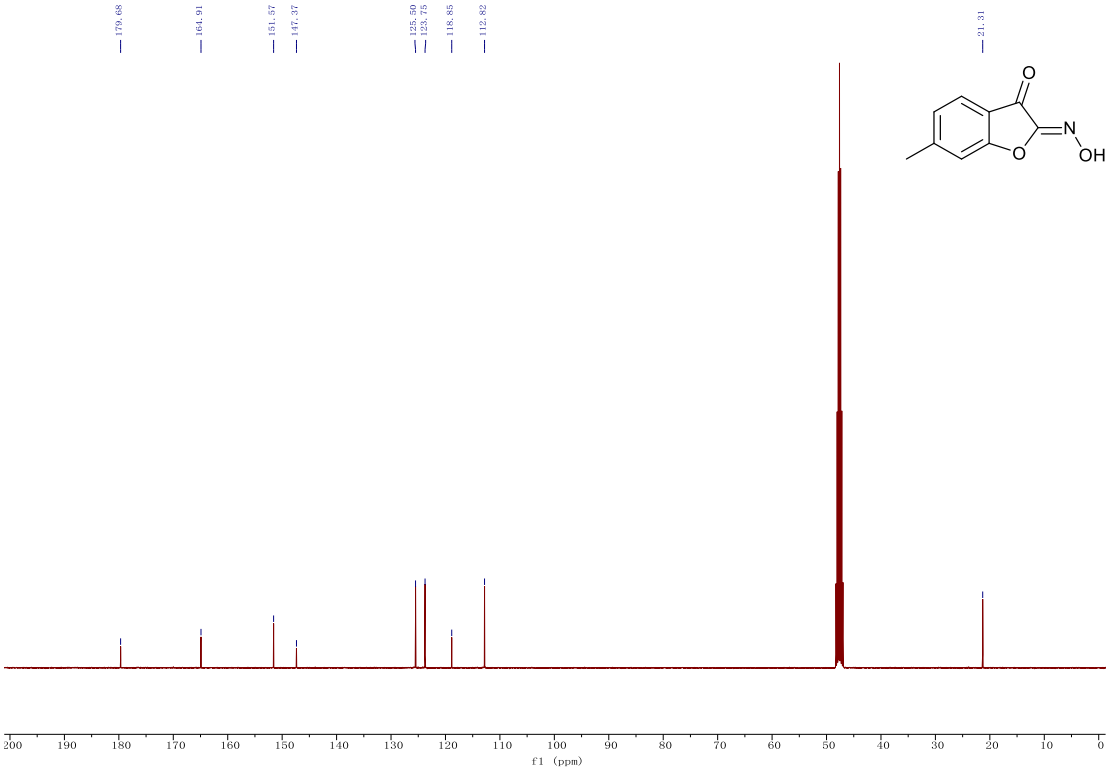
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3t



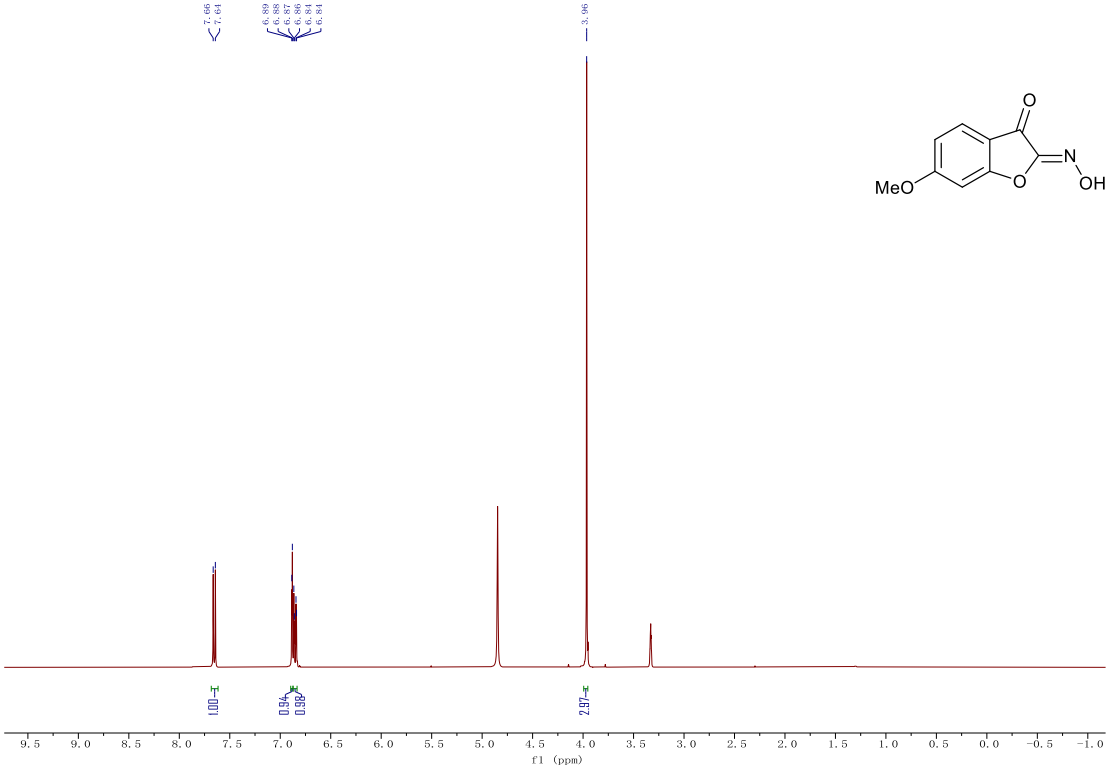


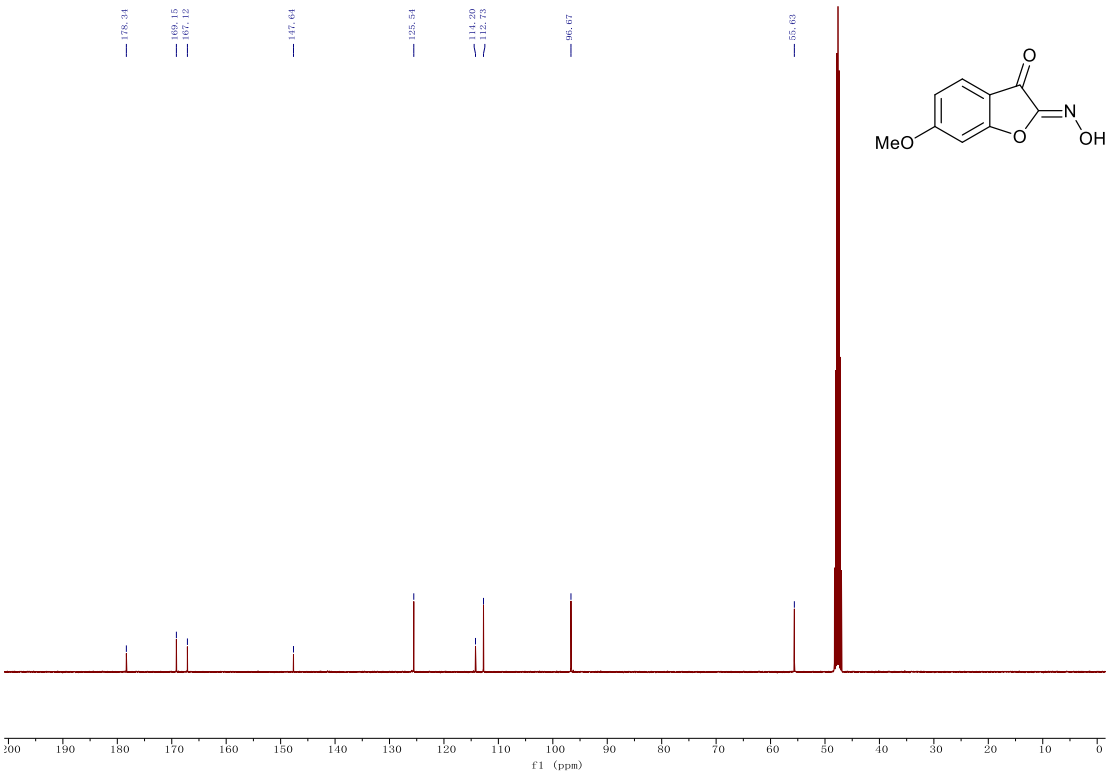
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 3u



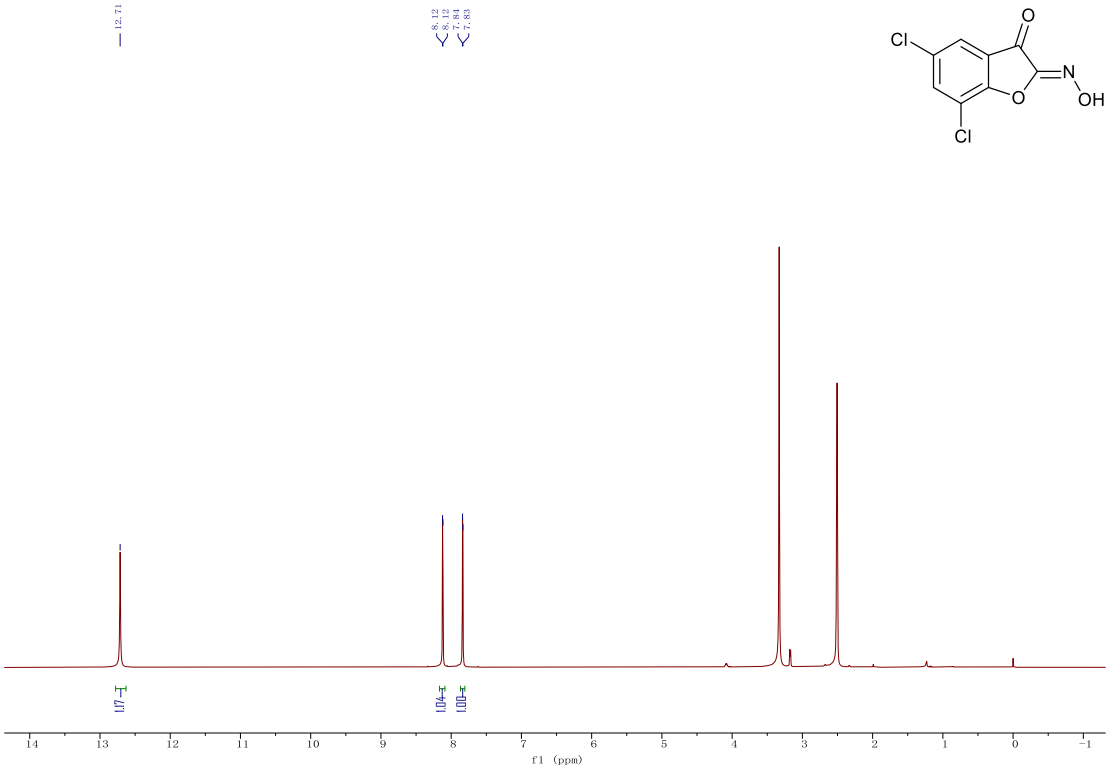


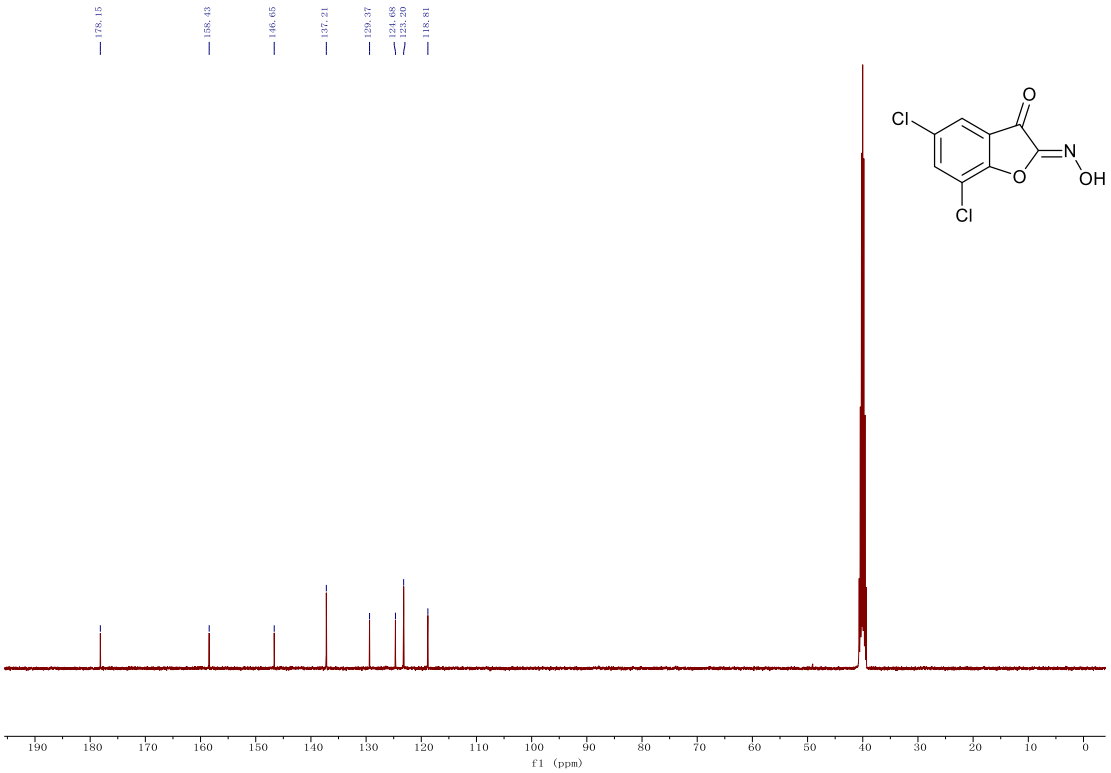
^{1}H NMR (400 MHz, CD_3OD), and ^{13}C NMR (100 MHz, CD_3OD) spectrum of product 3v



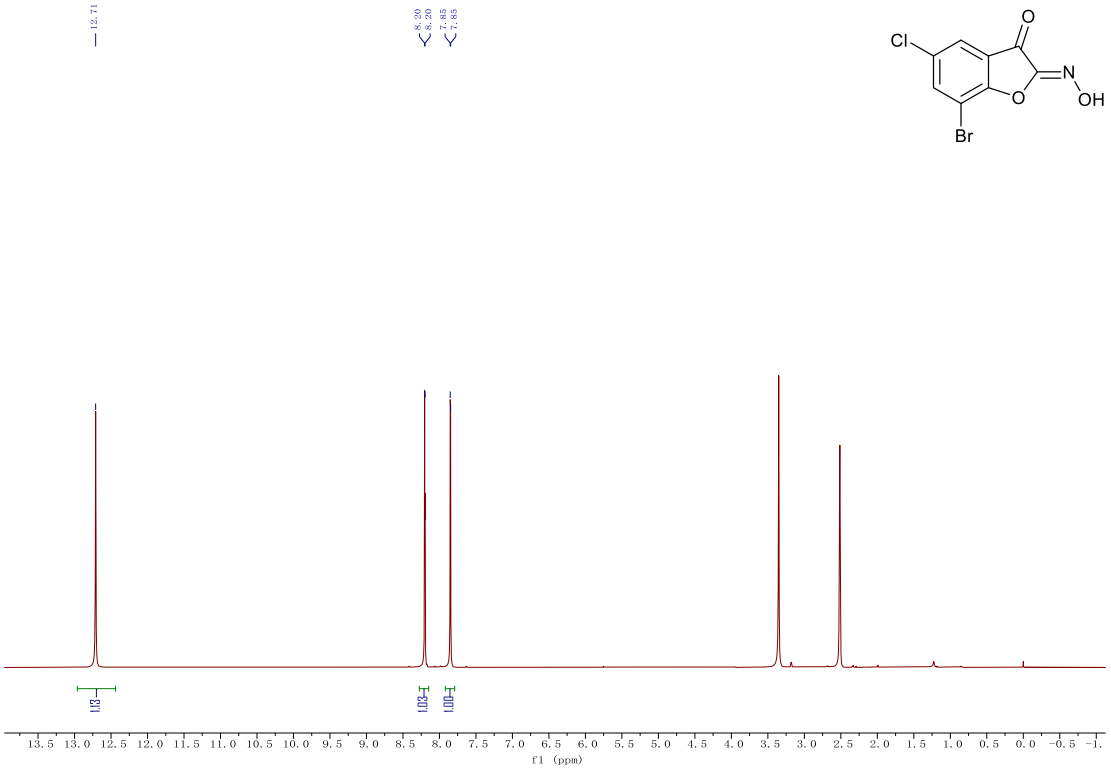


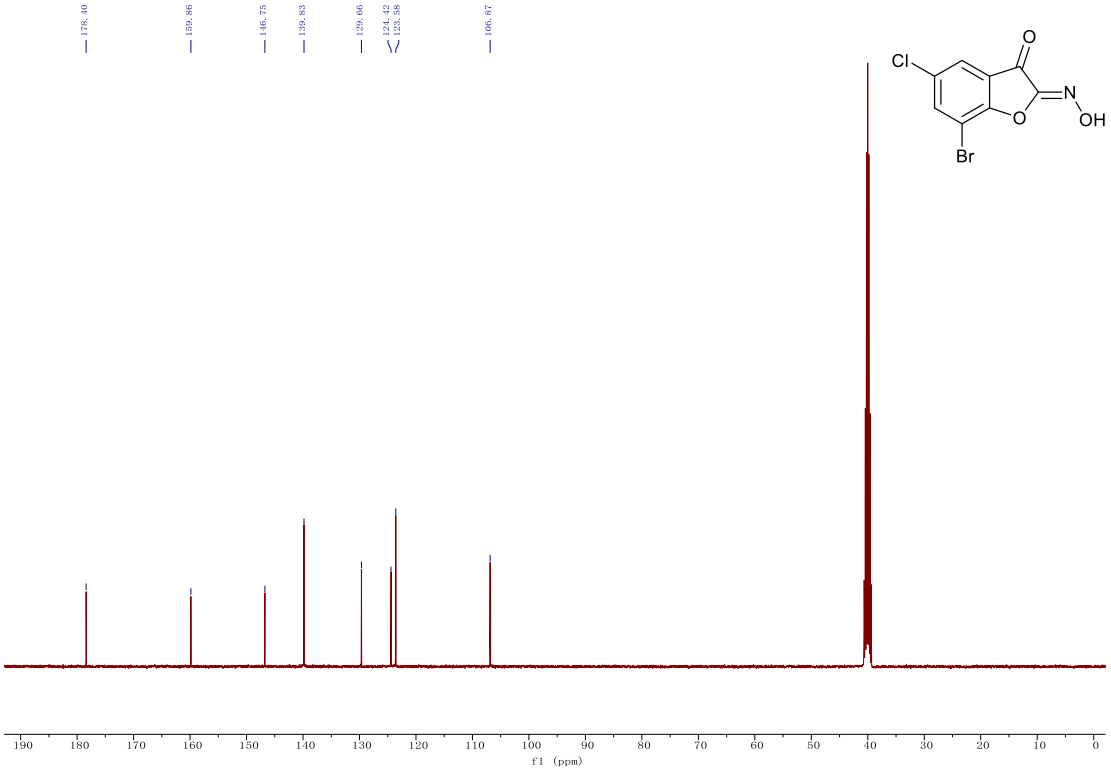
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3w



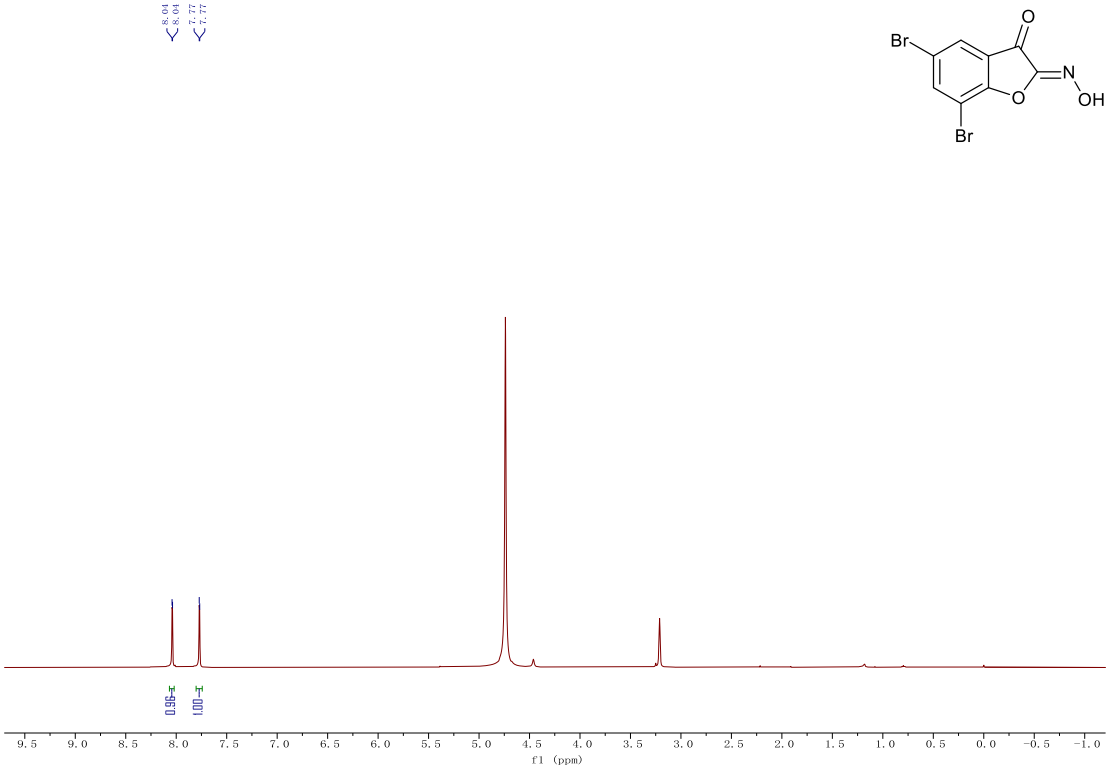


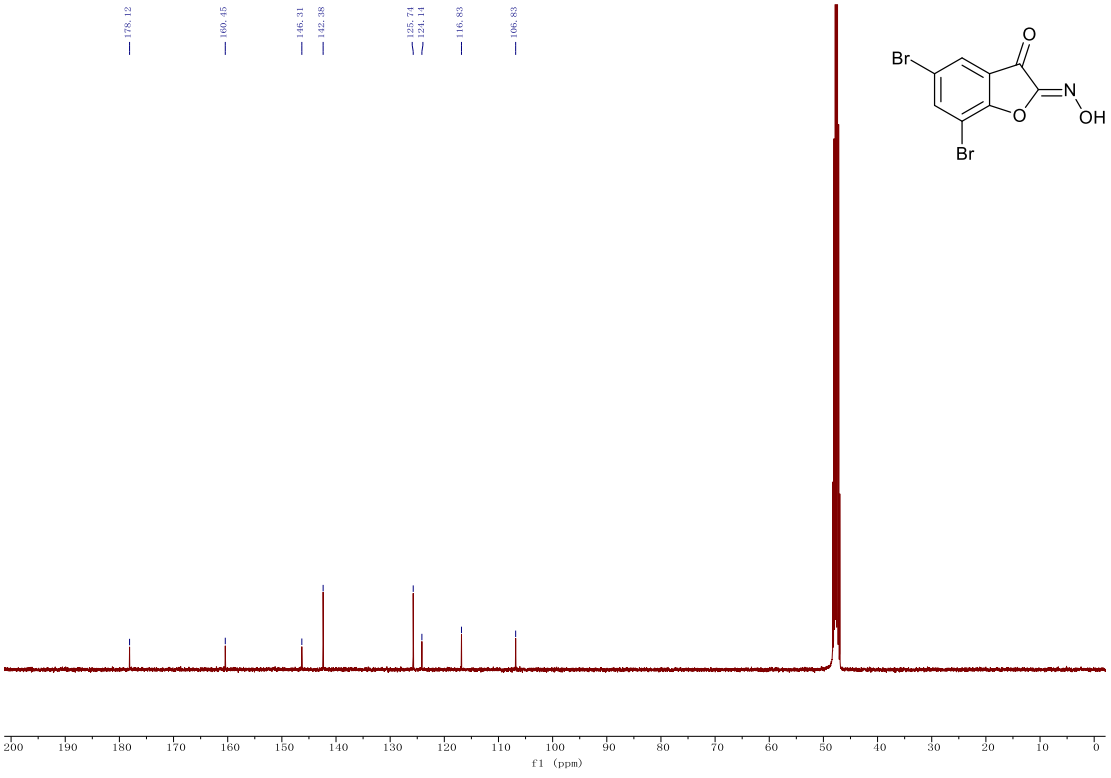
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3x



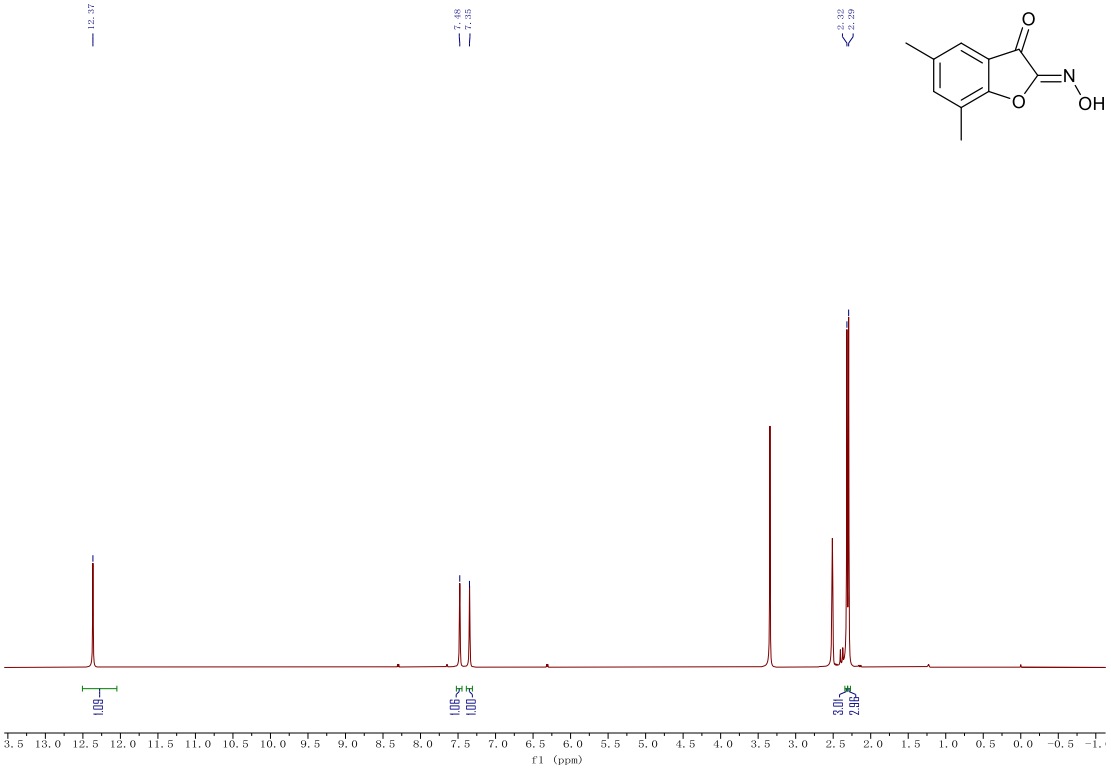


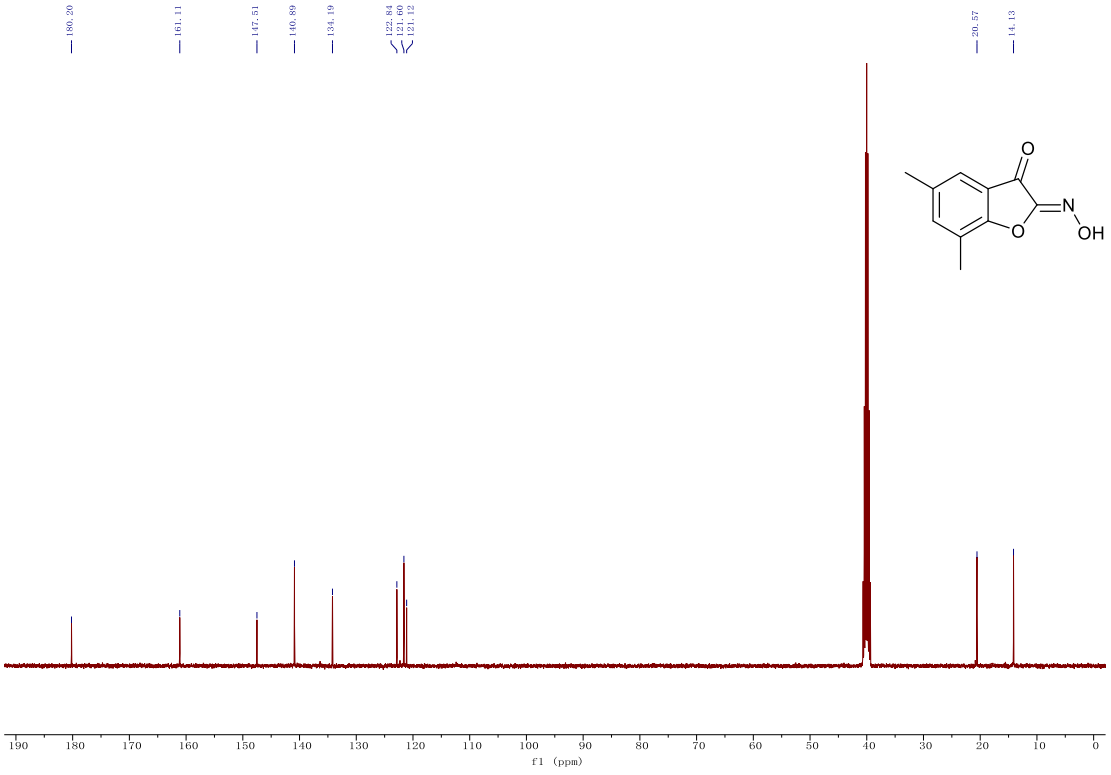
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3y



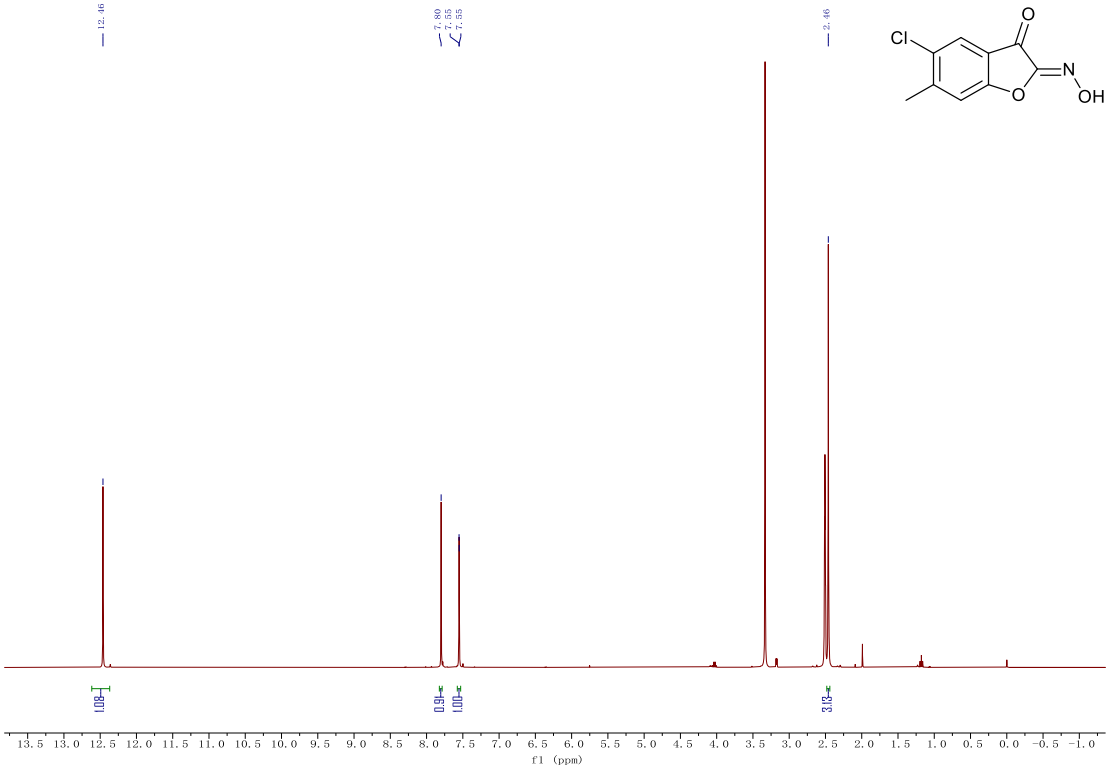


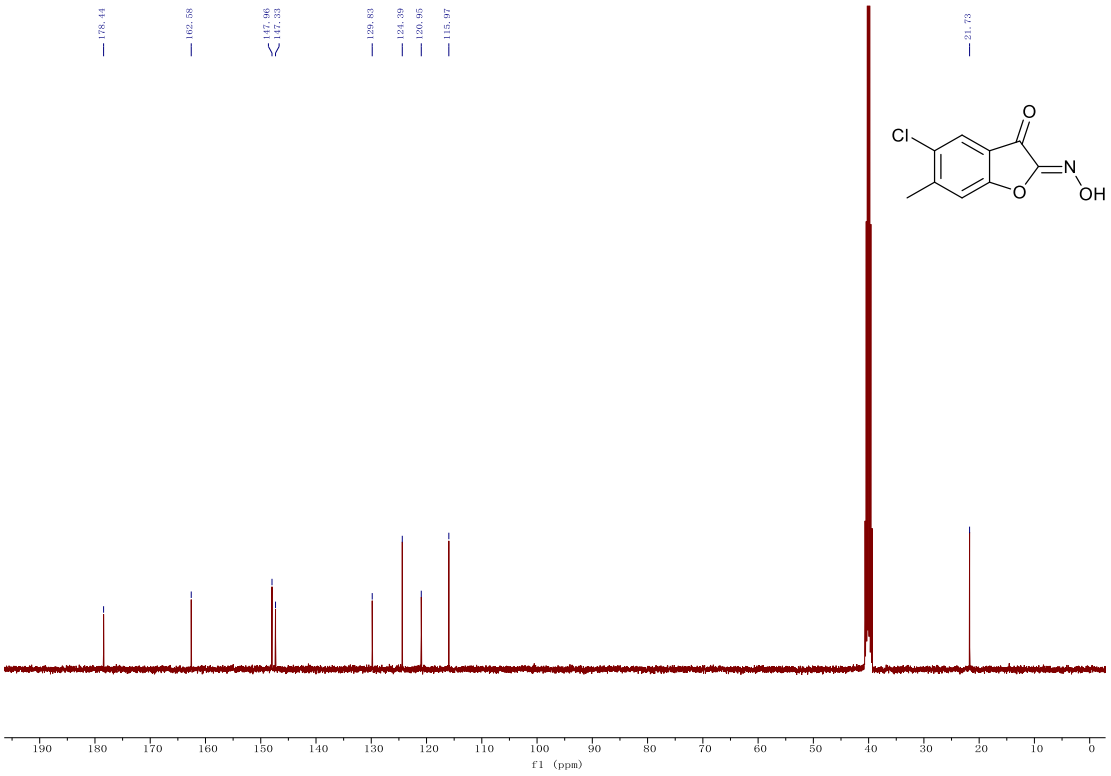
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3z



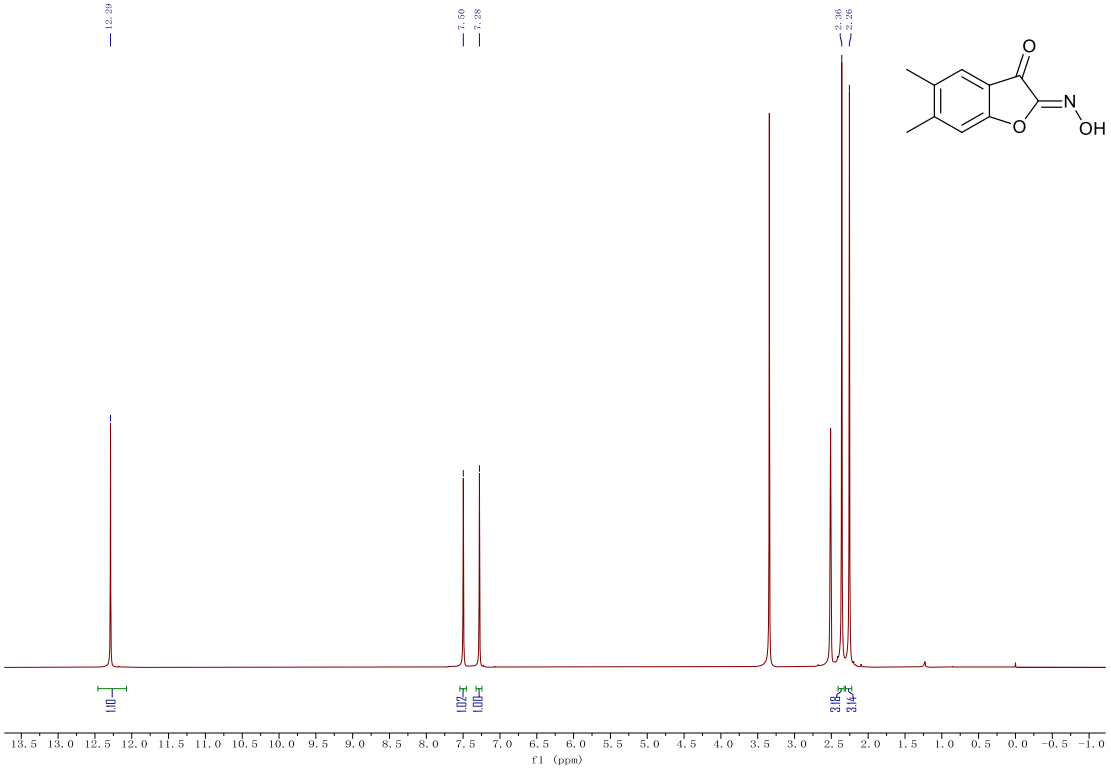


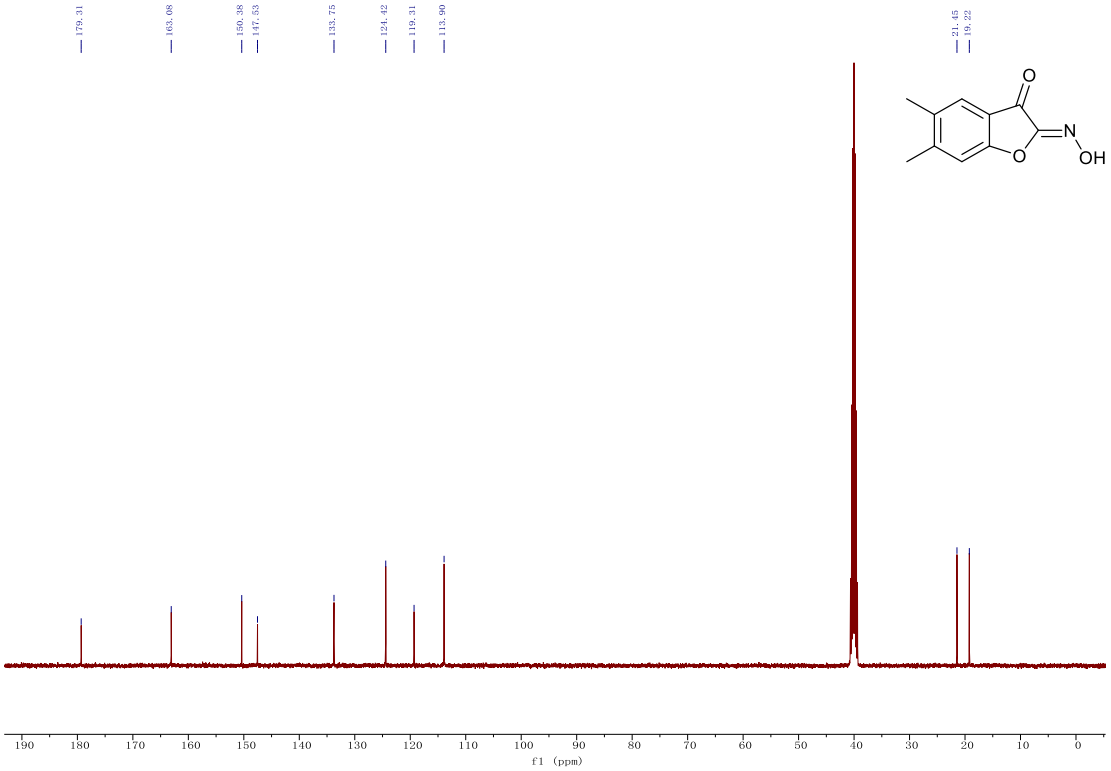
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3aa



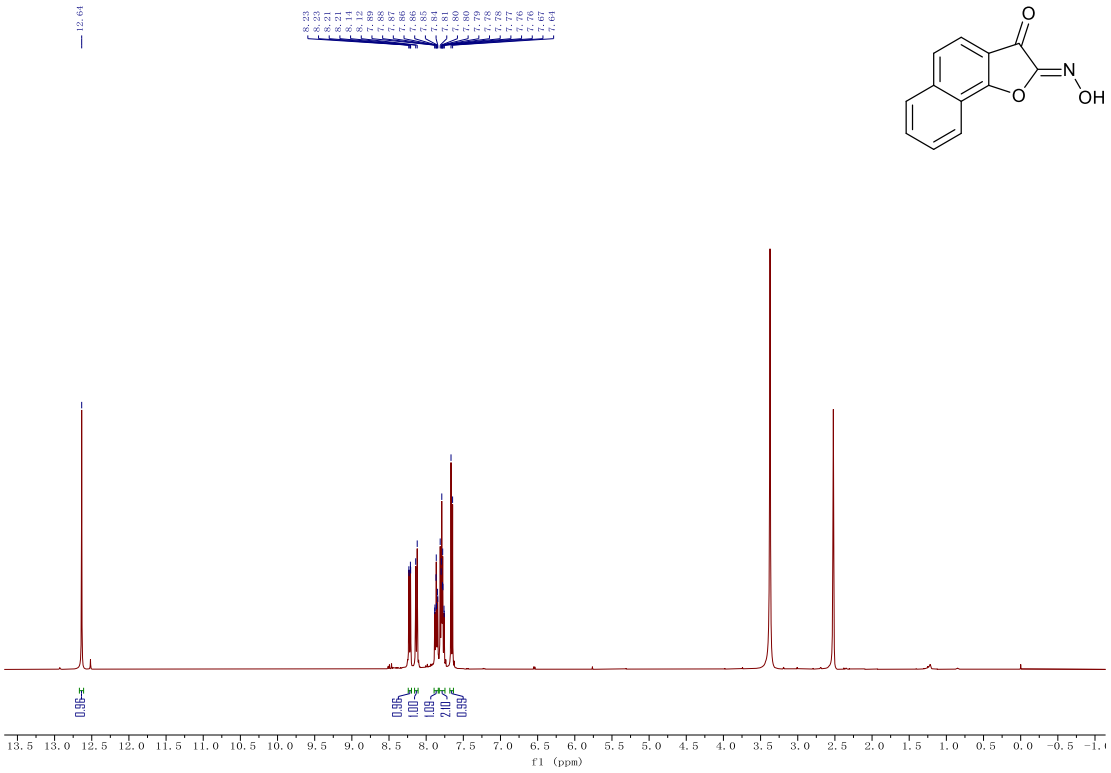


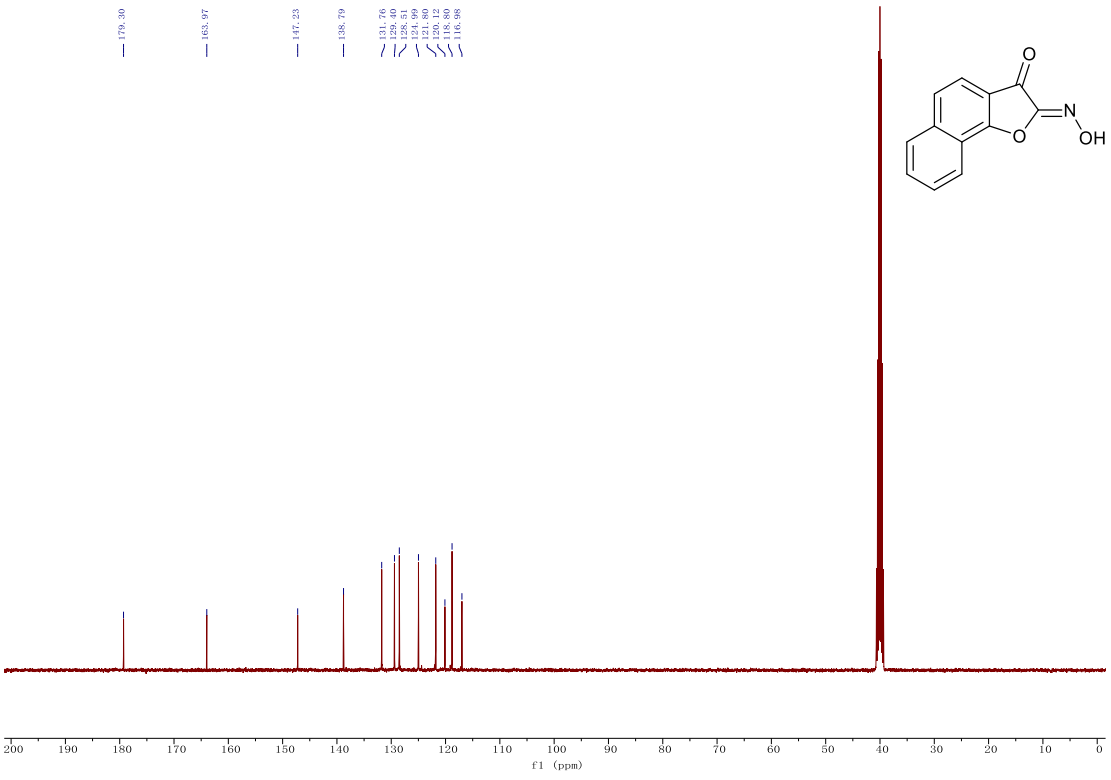
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3ab



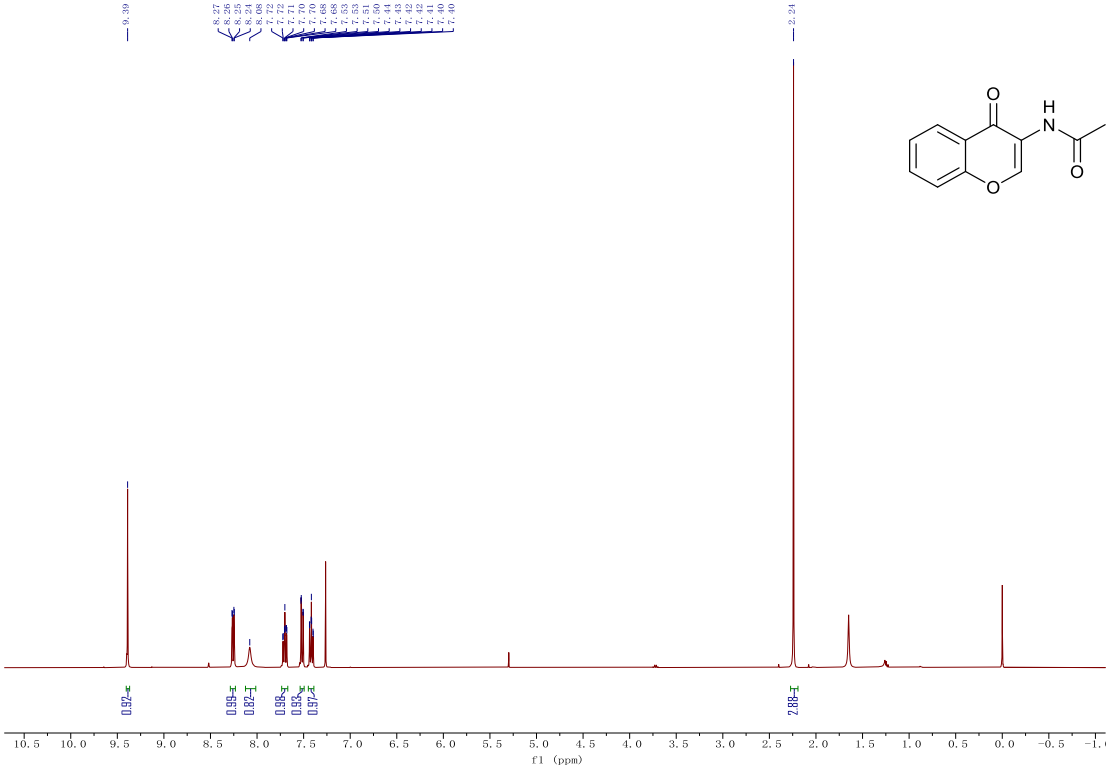


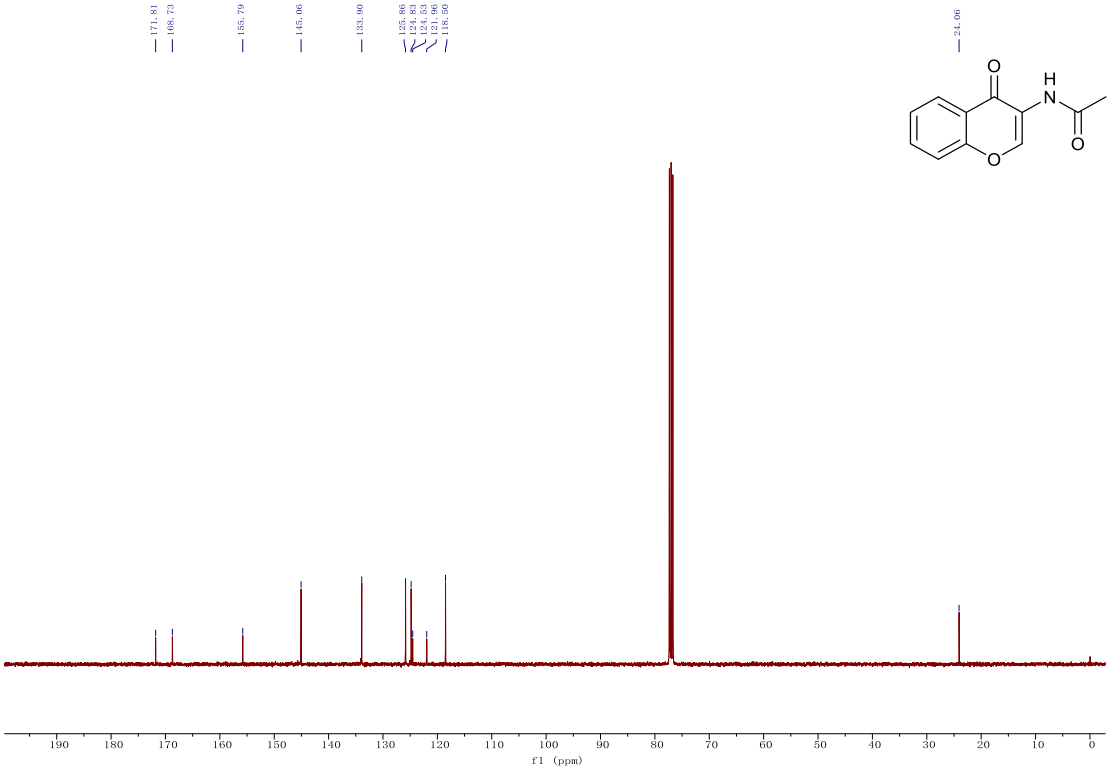
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 3ac



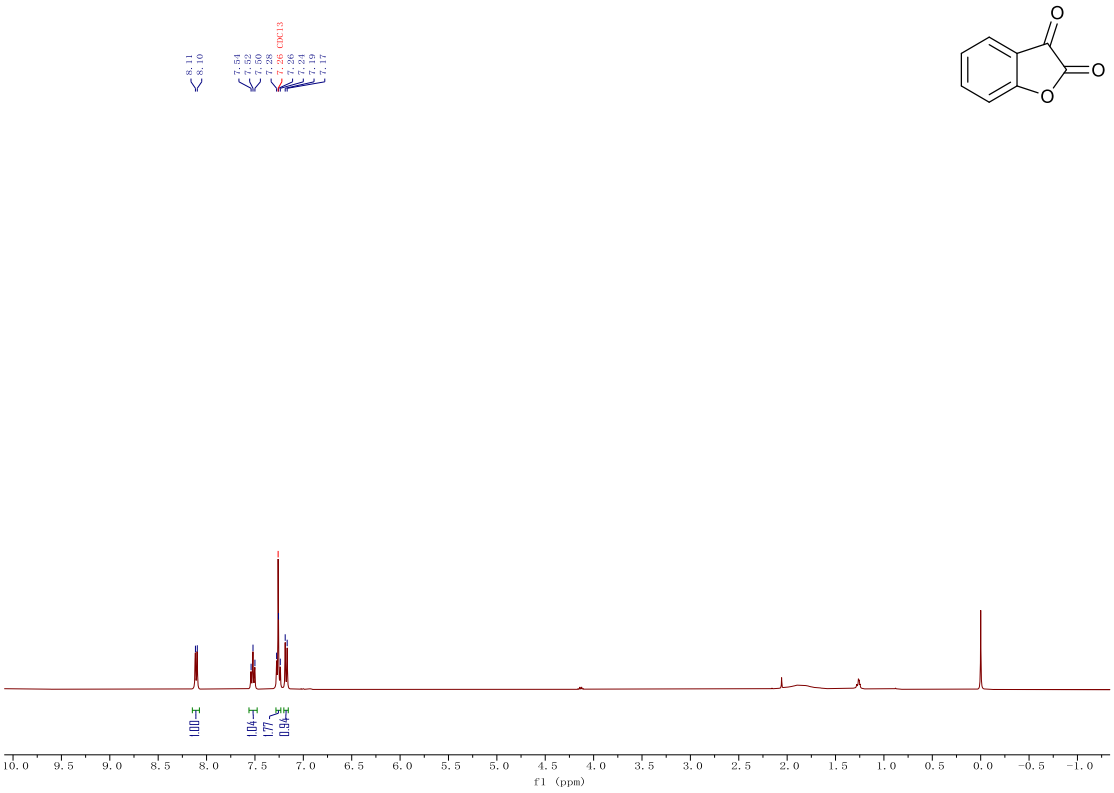


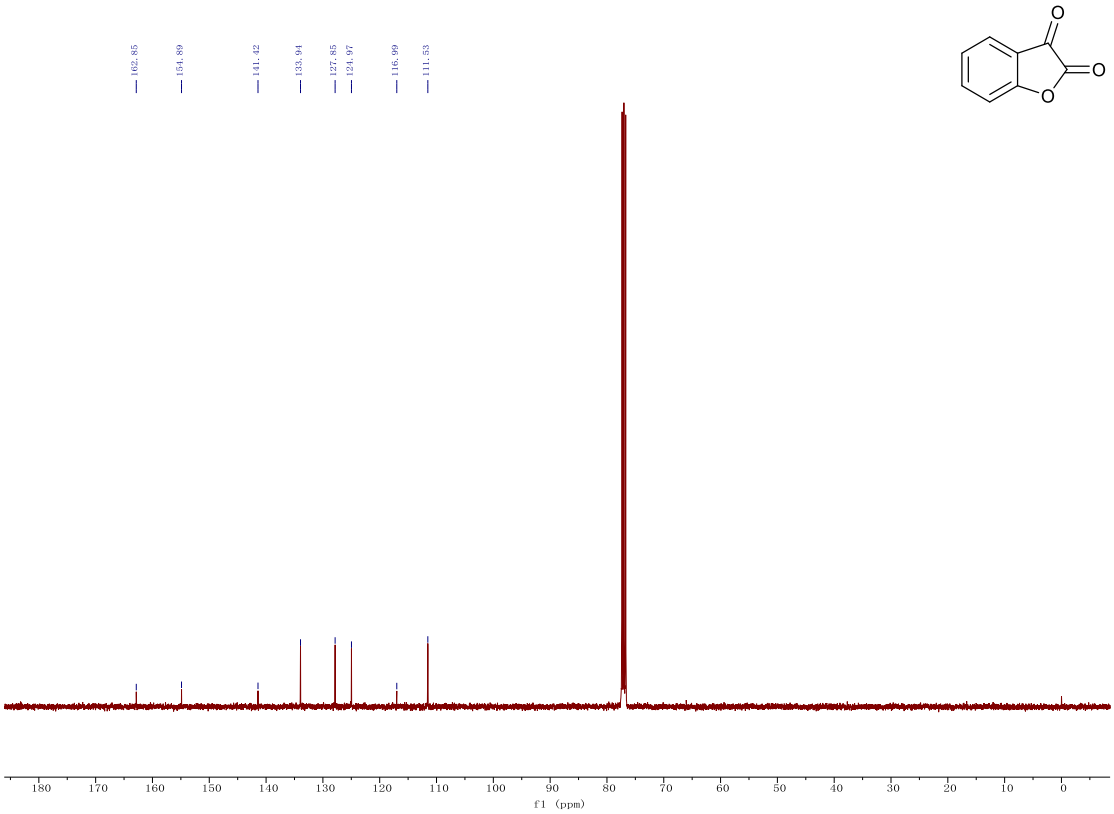
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4a



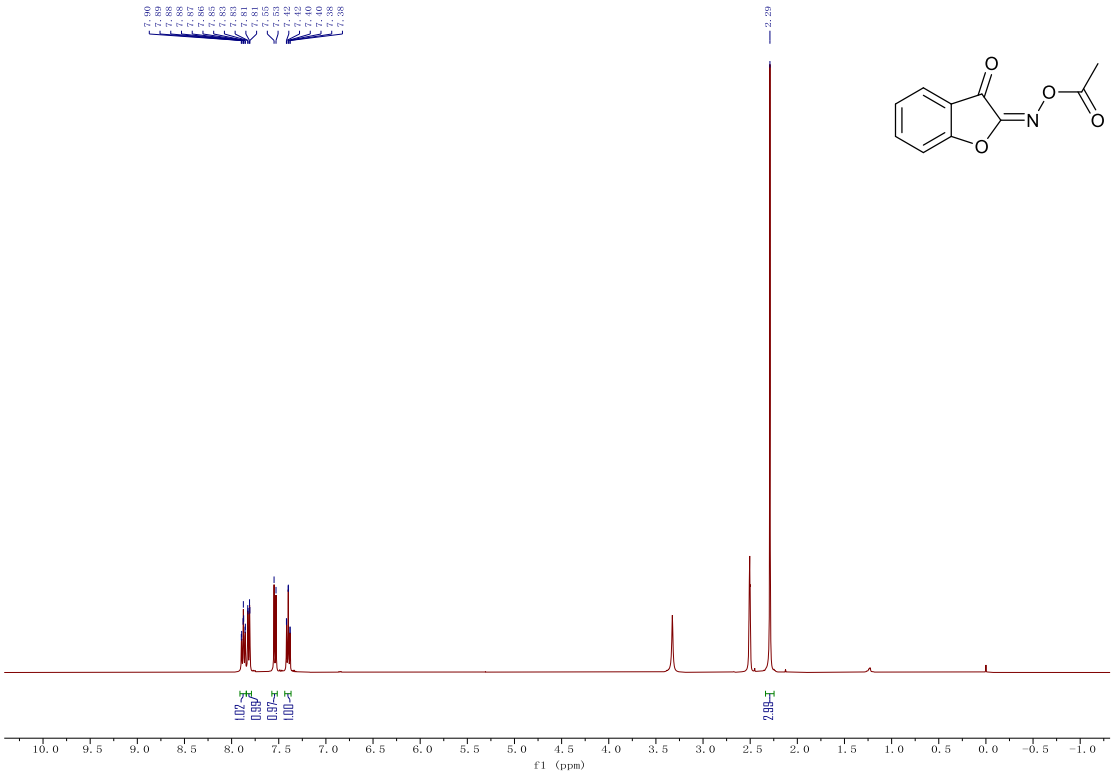


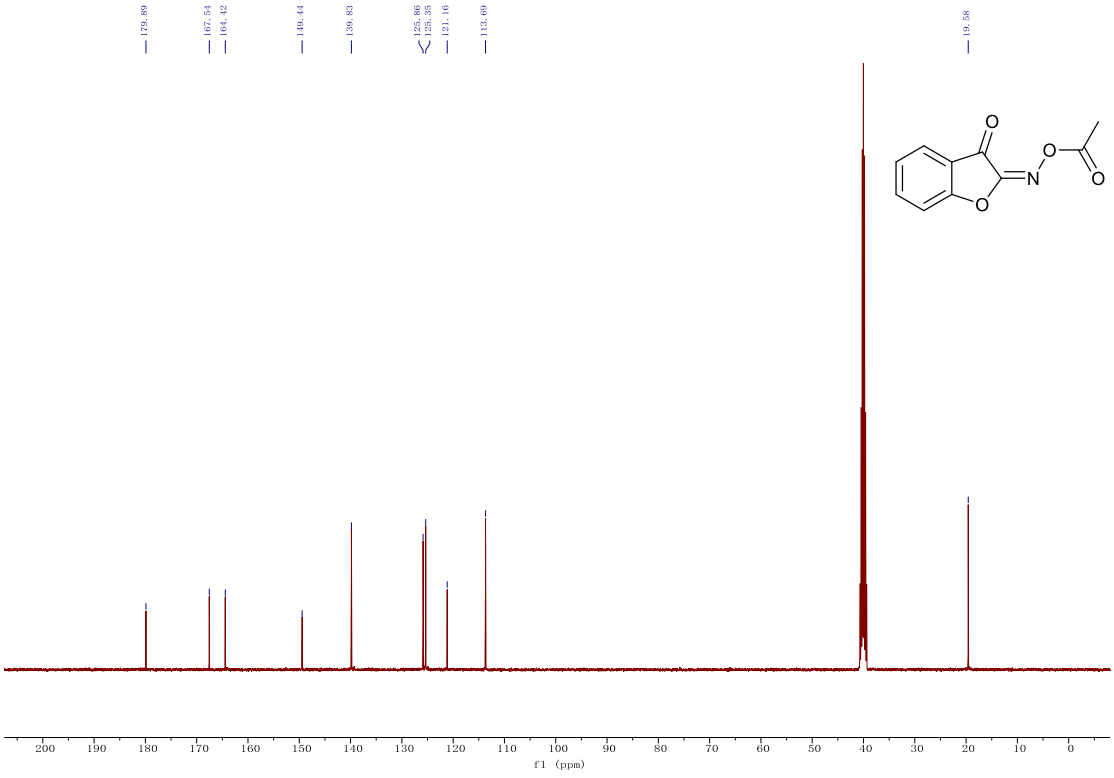
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 5a



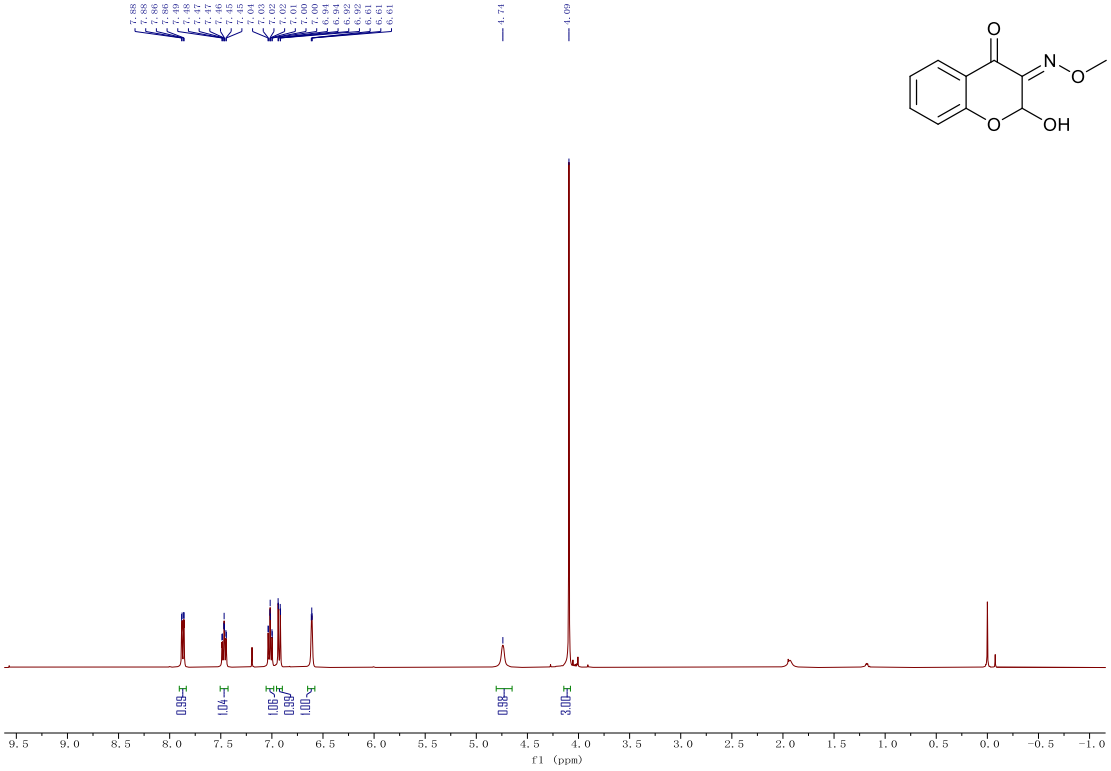


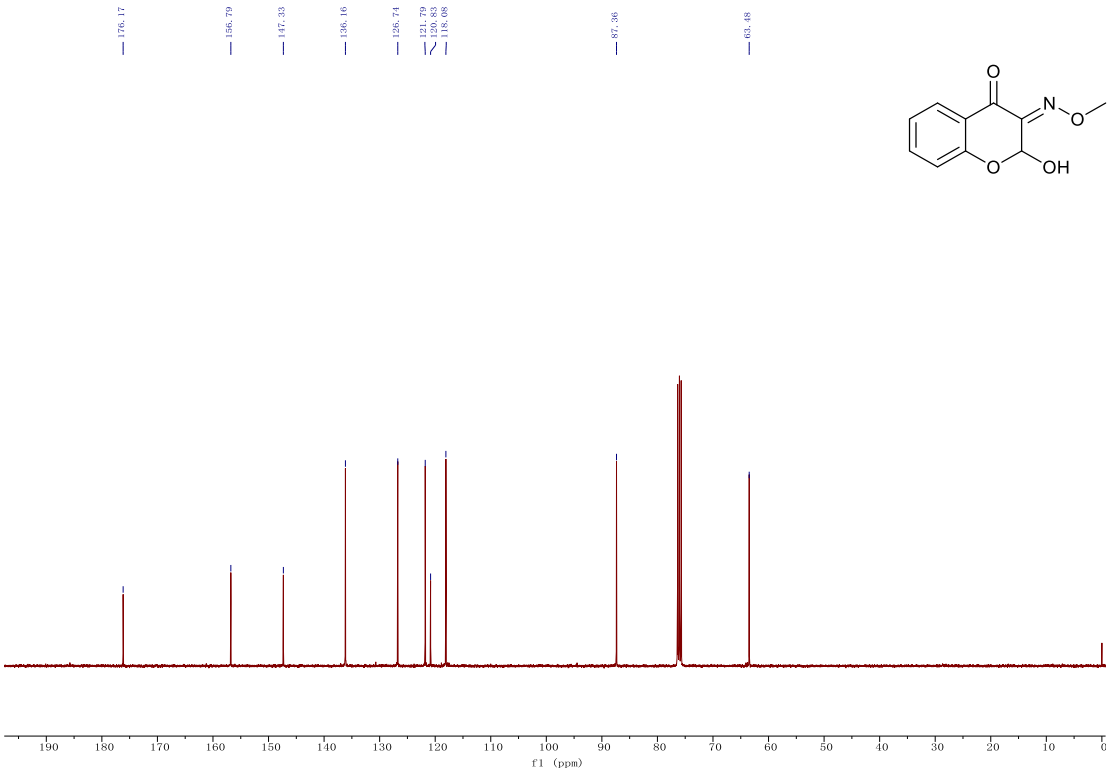
^{1}H NMR (400 MHz, DMSO), and ^{13}C NMR (100 MHz, DMSO) spectrum of product 6a



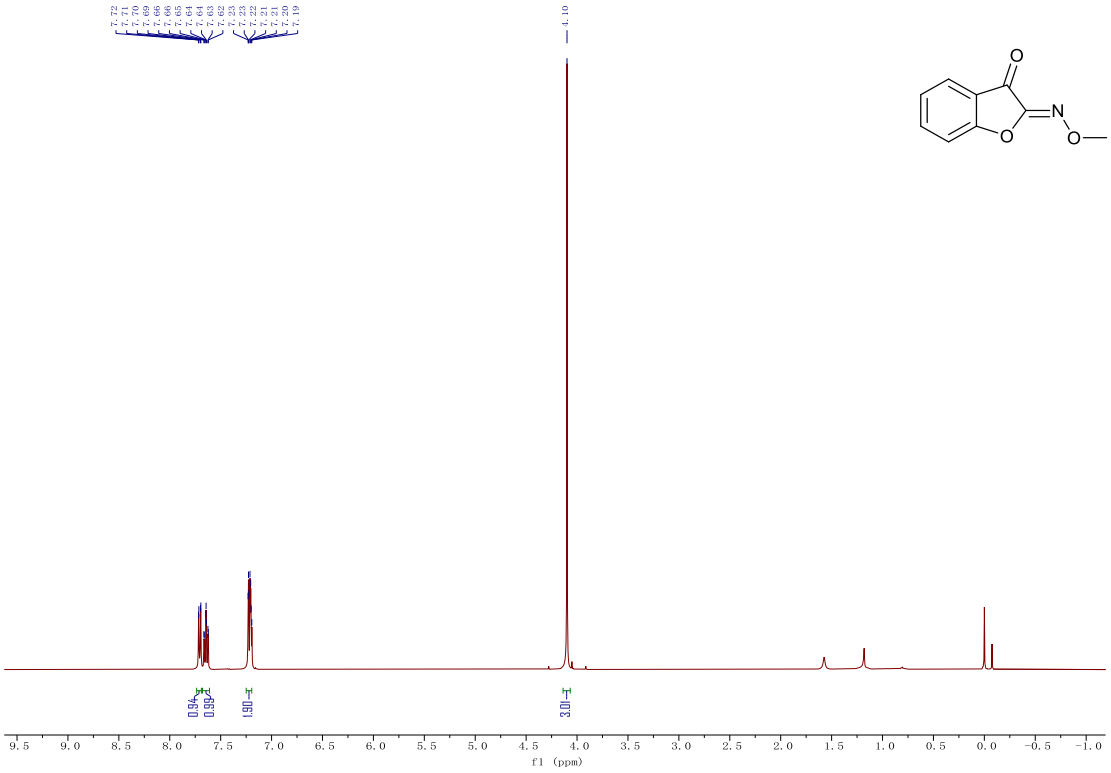


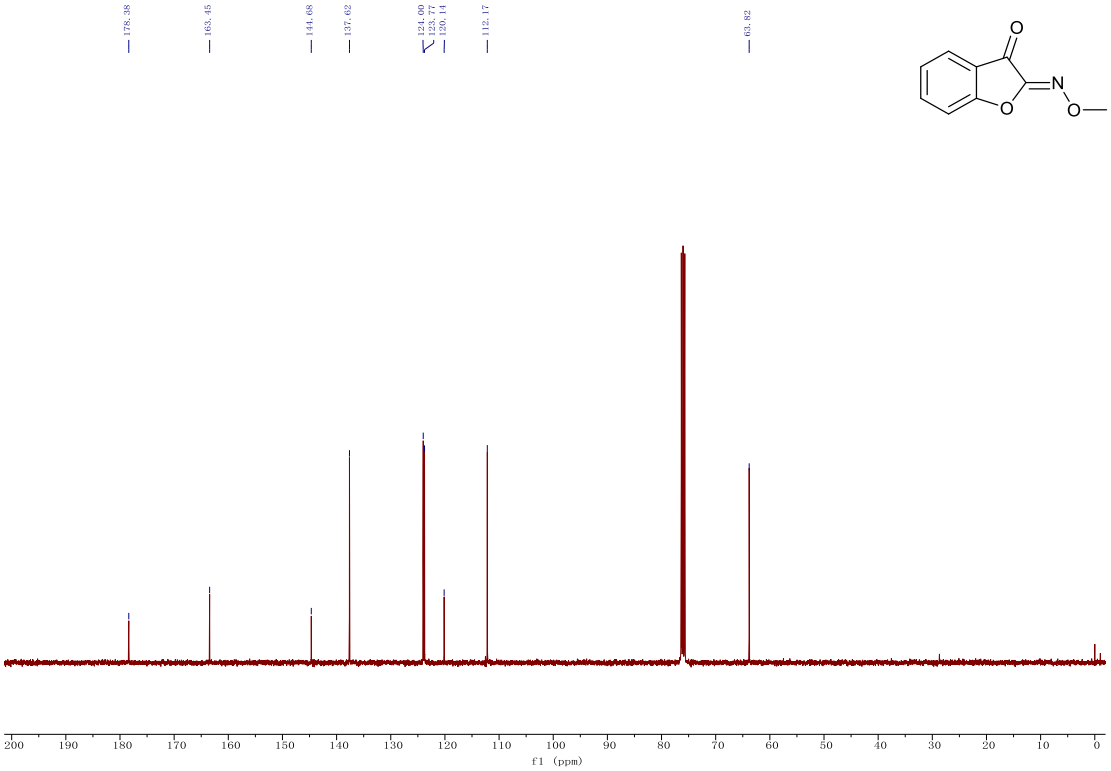
^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 7a





^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 8a





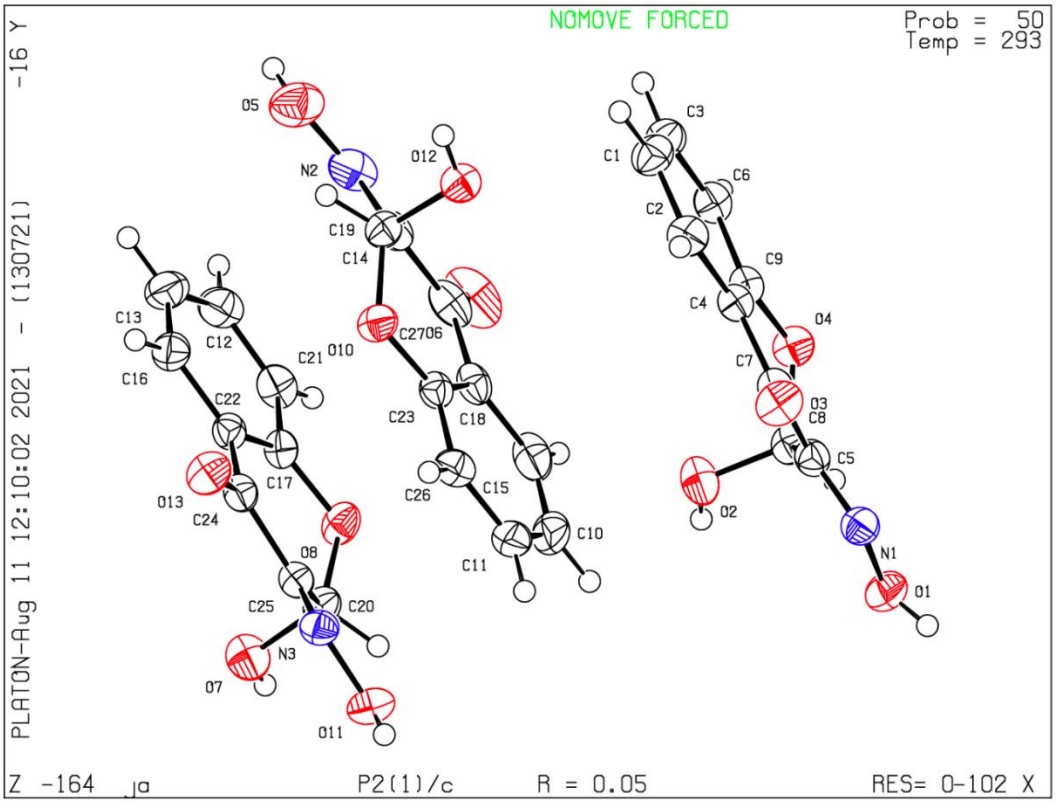
8. X-ray Crystallographic Data of Compound 3a

Crystal of compound 2a was prepared in a solvent mixture of EtOAc and *n*-hexane (v/v = 1/1). 2a (20.0 mg) was firstly dissolved in EtOAc (~1 mL) in a vial, then *n*-hexane (~1 mL) was added dropwise to it. The vial was not fully screwed down and the sample was carefully setting in room temperature. The crystal was obtained in about 72 h.

All the measurements were performed on a BRUKER Single Crystal X-Ray Diffractometer, Germany (model of the instrument –AXS D8 Quest System).

Specification: D8 QUEST, Photon 100 CMOS Detector, Horizontal Goniometer, Fixed Chi stage, Goniometer head manual, Ceramic Tube KFF Mo-2K-90c, two pinhole collimator (0.3/17 mrad, 0.6/17 mrad), Head turned by 90°, APEX2 w.SHELXTL S/W, Video microscope SCD, Cryostream700 plus extended range low Temperature.

X-Ray crystallographic analysis of 3-oximinochroman-4-one **3a** (CCDC 2110236) showing the thermal ellipsoids at 50% probability level.



Bond precision: C-C = 0.0024 A Wavelength=0.71073

Cell: a=16.265(3) b=12.684(2) c=12.3063(18)
alpha=90 beta=100.784(6) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2494.0(7)	2494.1(7)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C9 H7 N O4	?
Sum formula	C9 H7 N O4	C2.16 H1.68 N0.24 O0.96
Mr	193.16	46.36
Dx,g cm-3	1.543	1.543
Z	12	50
Mu (mm-1)	0.124	0.124
F000	1200.0	1200.0
F000'	1200.75	
h,k,lmax	21,16,16	21,16,16
Nref	6217	6191
Tmin,Tmax	0.971,0.976	
Tmin'	0.963	

Correction method= Not given

Data completeness= 0.996 Theta(max)= 28.320

R(reflections)= 0.0456(5064) wR2(reflections)= 0.1292(6191)

S = 1.055 Npar= 379