Electronic Supplementary Information

Rhodium(III)-Catalyzed Cascade C−H Functionalization/Annulation of Sulfoximines with Iodonium ylides for the Synthesis of Cyclohexanone-1,2-benzothiazines

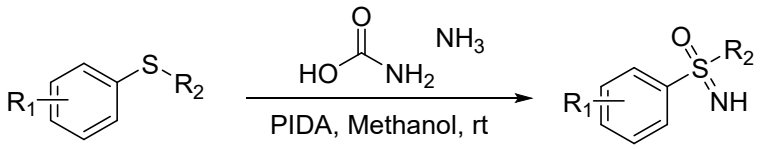
Lu Chen,‡[a] Zhichao Wang,‡[a] Yangyang Wang,[a] Liqiang Hao,[a] Xiaobo Xu,[a] Gaorong Wu,*[a] and Yafei Ji*[a]

[a] Engineering Research Centre of Pharmaceutical Process Chemistry, Ministry of Education; School of Pharmacy,
East China University of Science and Technology,
130 Meilong Road, Shanghai 200237, P. R. China
E-mail: jyf@ecust.edu.cn (Ji).
E-mail: gaorongwu09@163.com (Wu).
‡These authors have equally contributed to this article.

Table of Contents

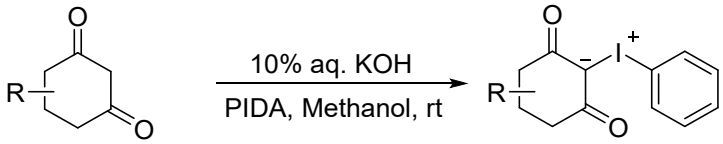
1 General Procedure for Preparation of the Substrates

1.1 Synthesis of substrates 1[1]



To a flask containing a stirrer bar was added successively, sulfide (1 equiv), ammonium carbamate (1.5 equiv) and then MeOH (0.5 M). PIDA (2.1 equiv) was added in one portion and the reaction was stirred at 20 °C for 30 min (open flask to the atmosphere). The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel.

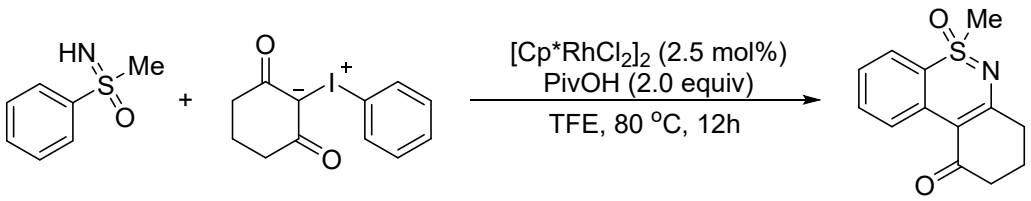
1.2 Synthesis of substrates 2[2]



Taken in a 100 mL round bottom flask fitted with a magnetic stirrer, added solution of cyclic 1,3-dione (1.0 equiv) in 30 mL methanol at room temperature added 20 mL of 10% aqueous solution of KOH followed by addition of diacetoxy iodobenzene (PIDA) (1.2 equiv) in 40 mL methanol. The reaction mixture was stirred for 2 hours at room temperature and then quenched with ice cold water. The resulting white precipitate was filtered and mother solution was extracted with DCM, then washed with water three times, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resultant white solid was mixed with the first crop and the mixture recrystallized from DCM/Hexane. The precipitated compound was obtained and can be directly used further without purification.

2 1.0 mmol scale experiment and derivatization reaction

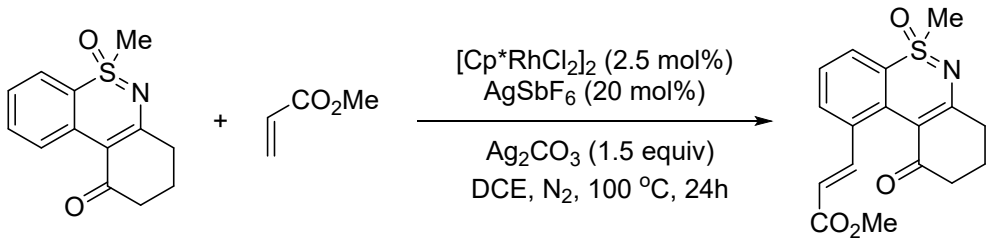
2.1 1.0 mmol scale experiment



1a **2a** **3a**

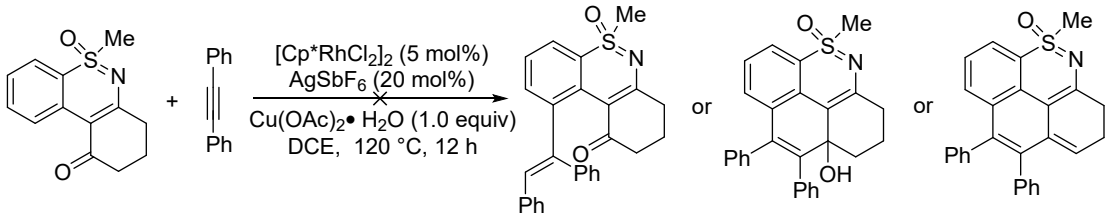
A mixture of substrates sulfoximine **1a** (155.0 mg, 1 mmol), iodonium ylide **2a** (376.8 mg, 1.2 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 2.5 mol%), PivOH (204.3 mg, 2.0 mmol, 2.0 equiv) in TFE (5.0 mL) was charged in a glass sealed-tube and stirred at 80 °C (oil bath) for 12 h. Upon completion of the reaction, water (20 mL) and DCM (10 mL) were added to the mixture, then the aqueous layer was extracted with DCM (10 mL ×3). The combined organic layer was dried over anhydrous Na_2SO_4. Finally, the solution was concentrated in vacuo to provide a crude product, which was further purified via a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1 to 3:1) to supply the desired products **3a** as a white solid (214.9 mg, 87%).

2.2 Derivatization reaction

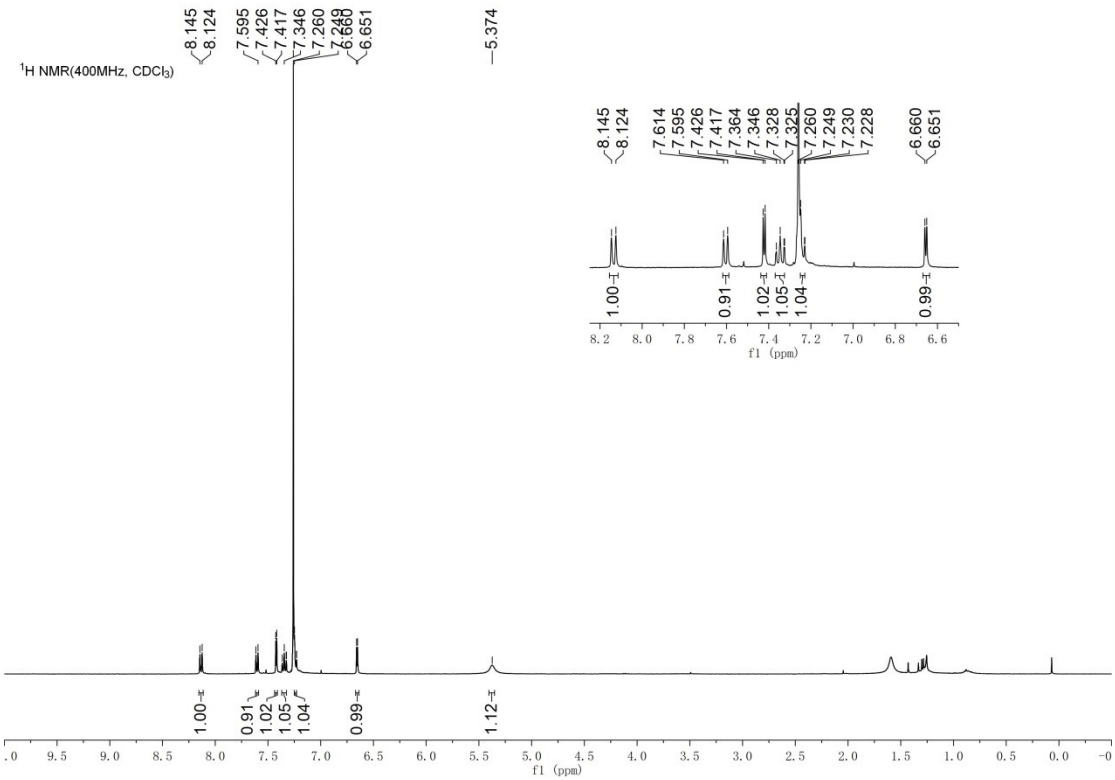


3a **5** **6**

A mixture of **3a** (24.7 mg, 0.1 mmol), methyl acrylate **5** (17.2 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), $AgSbF_6$ (7.1 mg, 20 mol%) and Ag_2CO_3 (41.4 mg, 0.15 mmol, 1.5 equiv) in DCE (1.0 mL) was charged in a schlenk tube and stirred at 100 °C (oil bath) under N_2 for 24 h. Upon completion of the reaction, water (10 mL) and DCM (5 mL) were added to the mixture, then the aqueous layer was extracted with DCM (5 mL ×3). The combined organic layer was dried over anhydrous Na_2SO_4. Finally, the solution was concentrated in vacuo to provide a crude product, which was further purified via a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1 to 1:2) to supply the desired products **6** (28.1 mg, 85%).



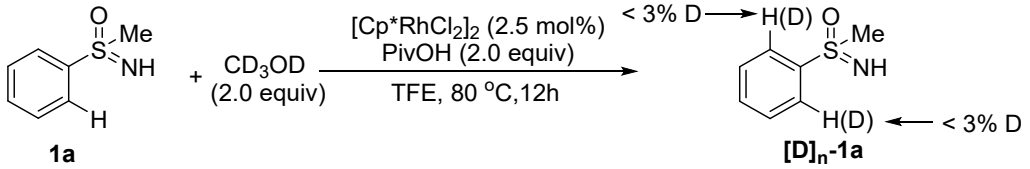
A mixture of **3a** (24.7 mg, 0.1 mmol), diphenylacetylene (21.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), $AgSbF_6$ (7.1 mg, 20 mol%) and $Cu(OAc)_2{\cdot}H_2O$ (19.9 mg, 0.1 mmol, 1.0 equiv) in DCE (1.0 mL) was charged in a glass sealed-tube and stirred at 120 °C (oil bath) for 12 h. Upon completion of the reaction, water (10 mL) and DCM (5 mL) were added to the mixture, then the aqueous layer was extracted with DCM (5 mL ×3). The combined organic layer was dried over anhydrous Na_2SO_4. Finally, the solution was concentrated in vacuo to provide a crude product, which was further purified via a column chromatography on silica gel to supply the major products. The following ^1H NMR analysis showed that it was not the desired product.



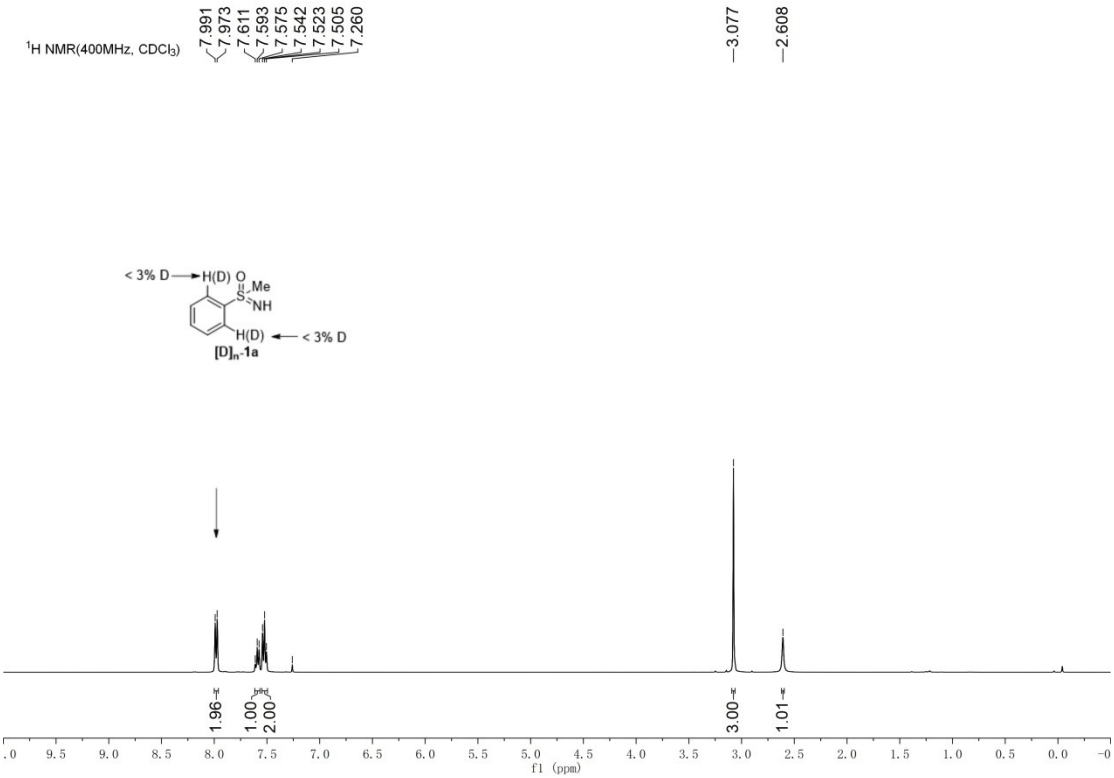
^{1}H NMR spectrum for the major product

3 Control experiments

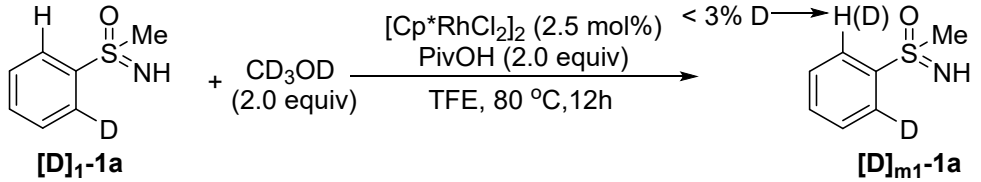
3.1 H/D Exchange reaction



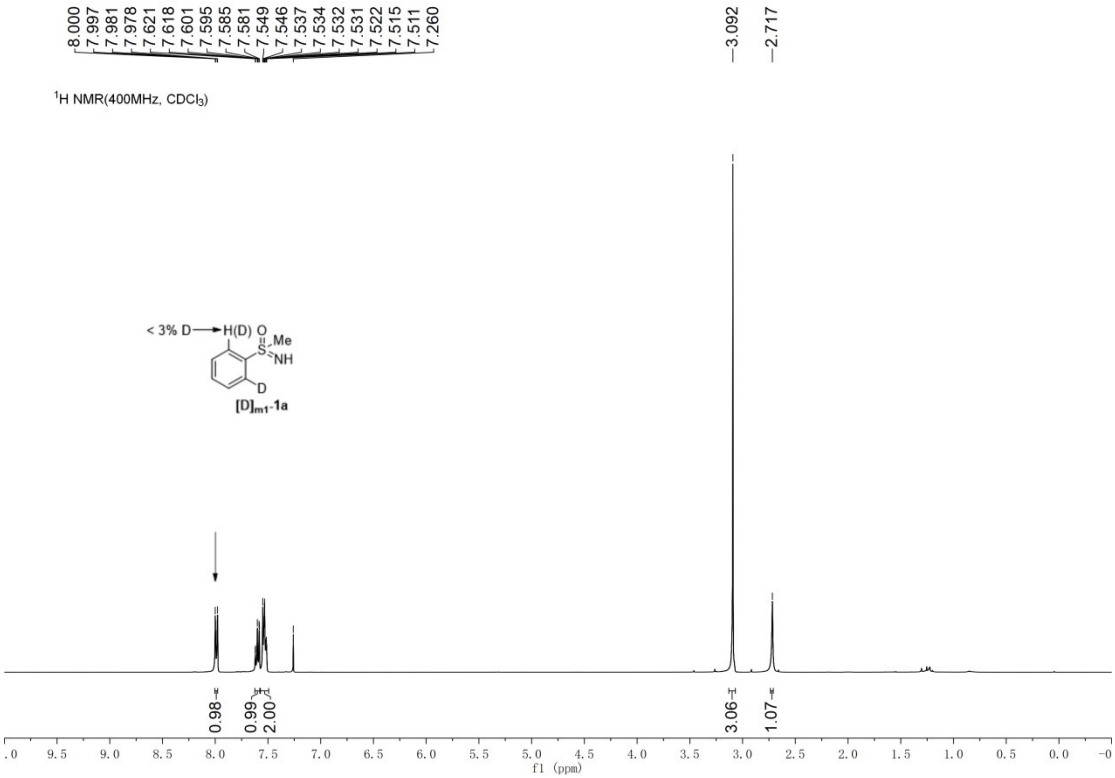
A mixture of sulfoximine **1a** (31.0 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol%) and PivOH (40.9 mg, 0.4 mmol, 2.0 equiv), CD_3OD (14.4 mg, 0.4 mmol, 2.0 equiv) in TFE (2.0 mL) was charged in a glass sealed-tube and the reaction mixture was allowed to stir at 80 °C for 12 h. Upon completion of the reaction, water (10 mL) and DCM (5 mL) were added to the mixture, then the aqueous layer was extracted with DCM (5 mL ×3). The combined organic layer was dried over anhydrous Na_2SO_4. Finally, the solution was concentrated in vacuo to provide a crude product, which was further purified via a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1 to 1:1) to give product **$[D]_n$-1a**. The ^{1}H NMR analysis showed that < 3% hydrogen of the each *ortho*-position of **1a** was deuterated.



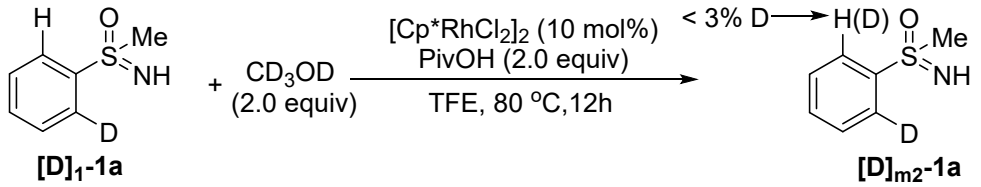
^{1}H NMR spectrum for **[D]$_n$-1a**



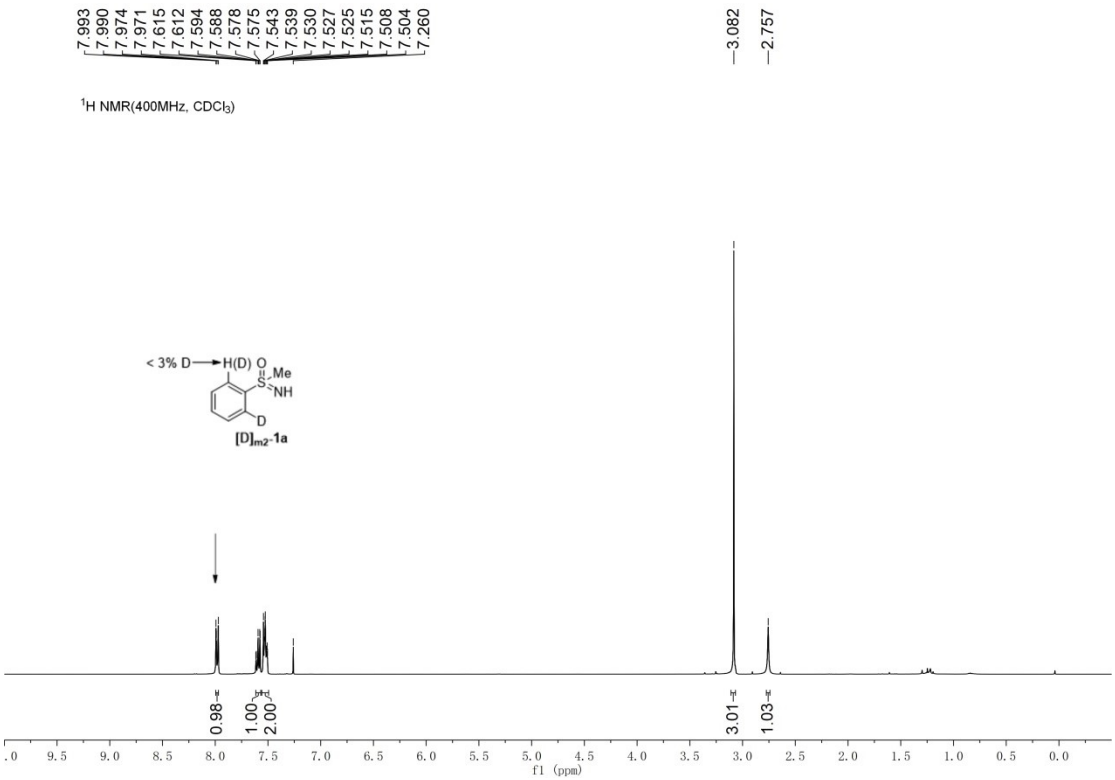
A mixture of sulfoximine **[D]$_1$-1a** (31.2 mg, 0.2 mmol), [Cp*RhCl$_2$]$_2$ (3.1 mg, 2.5 mol%) and PivOH (40.9 mg, 0.4 mmol, 2.0 equiv), CD_3OD (14.4 mg, 0.4 mmol, 2.0 equiv) in TFE (2.0 mL) was charged in a glass sealed-tube and the reaction mixture was allowed to stir at 80 °C for 12 h. Upon completion of the reaction, water (10 mL) and DCM (5 mL) were added to the mixture, then the aqueous layer was extracted with DCM (5 mL ×3). The combined organic layer was dried over anhydrous Na_2SO_4. Finally, the solution was concentrated in vacuo to provide a crude product, which was further purified via a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1 to 1:1) to give product **[D]$_{m1}$-1a**. The ^{1}H NMR analysis showed that < 3% hydrogen of the **[D]$_1$-1a** was deuterated.



^{1}H NMR spectrum for **[D]$_{m1}$-1a**

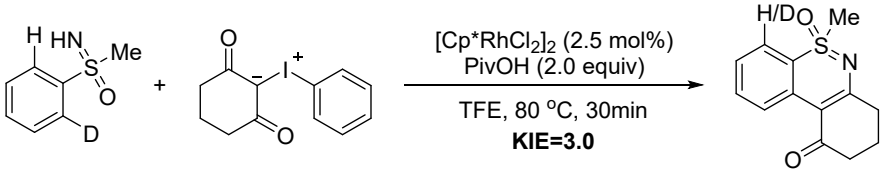


A mixture of sulfoximine **[D]$_1$-1a** (31.2 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (12.4 mg, 10 mol%) and PivOH (40.9 mg, 0.4 mmol, 2.0 equiv), CD_3OD (14.4 mg, 0.4 mmol, 2.0 equiv) in TFE (2.0 mL) was charged in a glass sealed-tube and the reaction mixture was allowed to stir at 80 °C for 12 h. Upon completion of the reaction, water (10 mL) and DCM (5 mL) were added to the mixture, then the aqueous layer was extracted with DCM (5 mL ×3). The combined organic layer was dried over anhydrous Na_2SO_4. Finally, the solution was concentrated in vacuo to provide a crude product, which was further purified via a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1 to 1:1) to give product **[D]$_{m2}$-1a**. The ^{1}H NMR analysis showed that < 3% hydrogen of the **[D]$_1$-1a** was deuterated.



^{1}H NMR spectrum for **[D]$_{m2}$-1a**

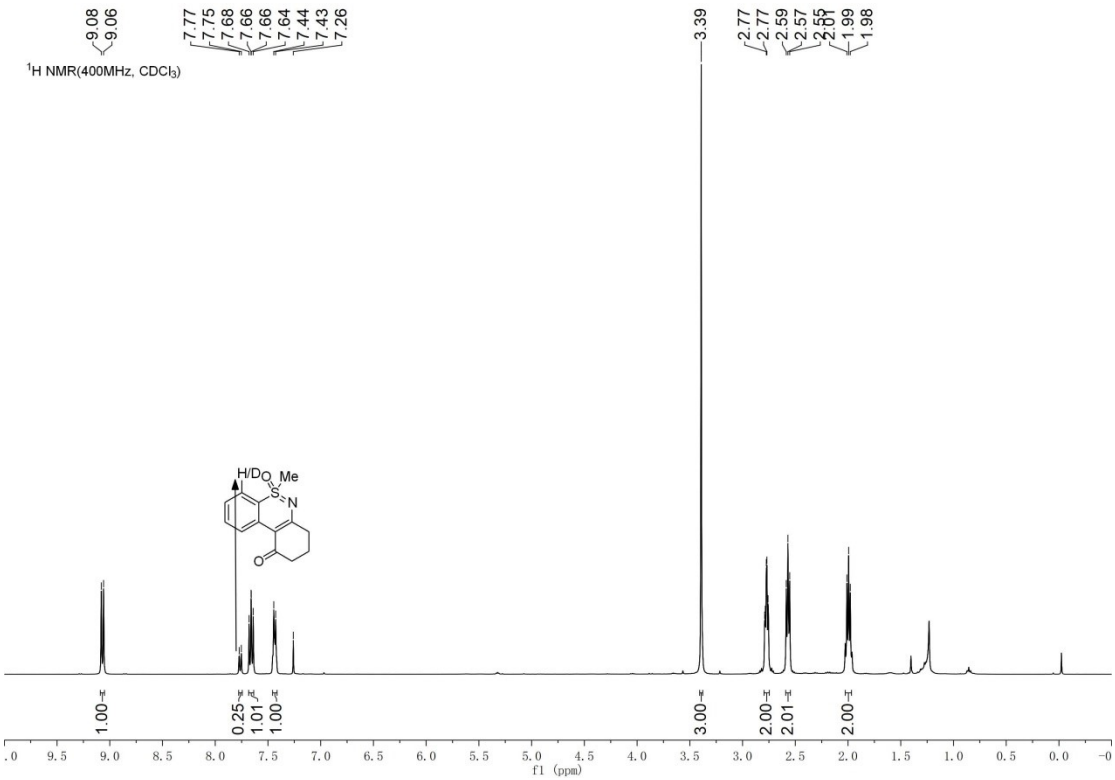
3.2 Intramolecular KIE Experiment



[D]$_1$-1a **2a** **3a+[D]$_1$-3a**

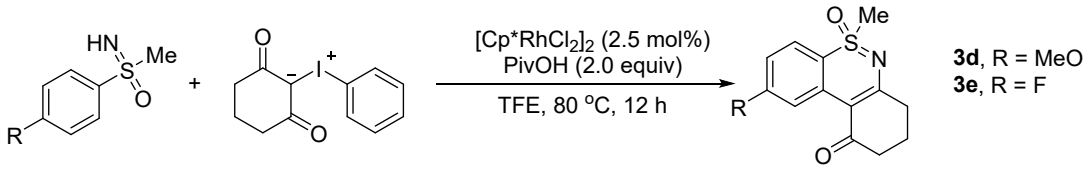
A mixture of substrates **[D]$_1$-1a** (31.2 mg, 0.2 mmol), iodonium ylide **2a** (75.6 mg, 0.24 mmol), [Cp*RhCl$_2$]$_2$ (3.1 mg, 2.5 mol%), PivOH (40.9 mg, 0.4 mmol, 2.0 equiv) in TFE (2.0 mL) was charged in a glass sealed-tube and stirred at 80 ℃ (oil bath) for 30 min. After the reaction, water (10 mL) and DCM (5 mL) were added to the mixture, then the aqueous layer was extracted with DCM (5 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. Finally, the solution was concentrated in vacuo to provide a crude product, which was further purified via a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1 to 3:1) to supply the mixed products **3a** and **[D]$_1$-3a** (13.8 mg, 28%). The product distribution k_H/k_D = 3.0 (0.75/0.25) was analyzed by ^{1}H NMR.

(**3a+[D]$_1$-3a**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.07 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 0.25H), 7.66 (dd, J_1 = 8.3, J_2 = 7.5 Hz, 1H), 7.44 (d, J = 7.0 Hz, 1H), 3.39 (s, 3H), 2.81−2.74 (m, 2H), 2.60−2.53 (m, 2H), 2.03–1.96 (m, 2H).



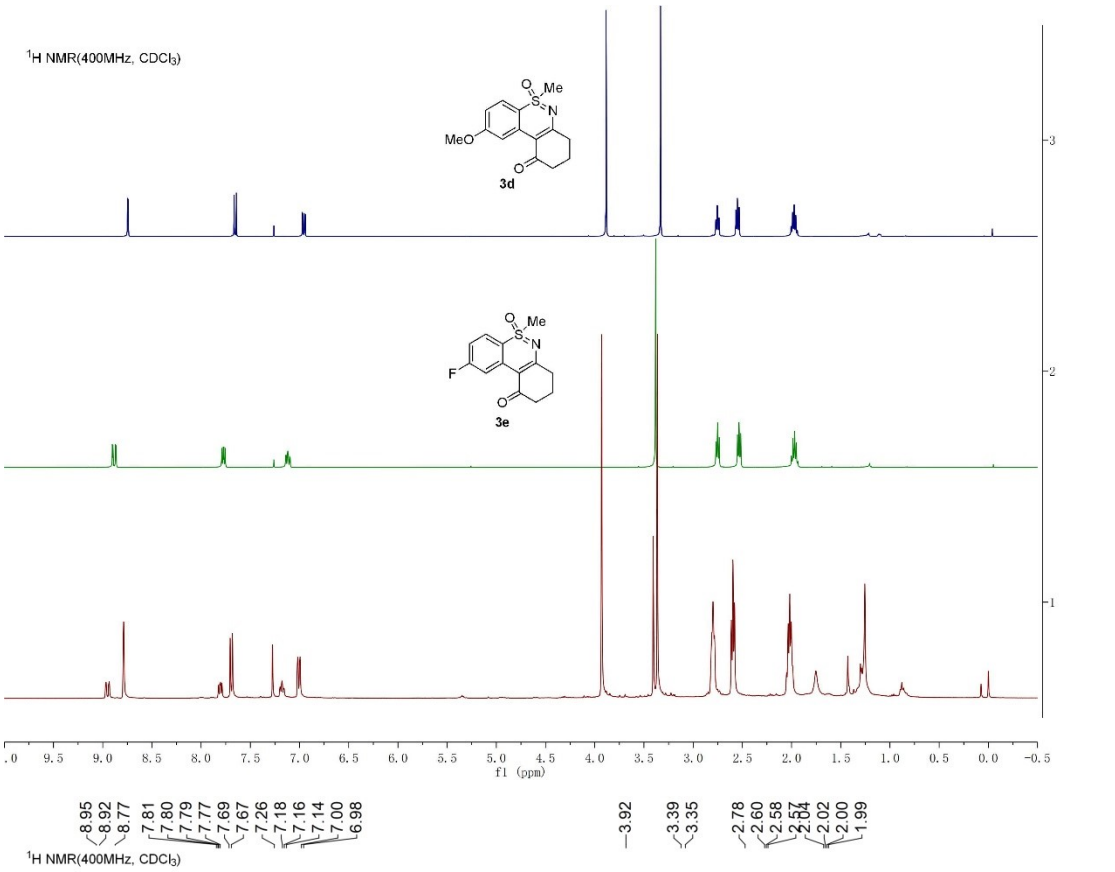
^{1}H NMR spectrum for KIE analysis

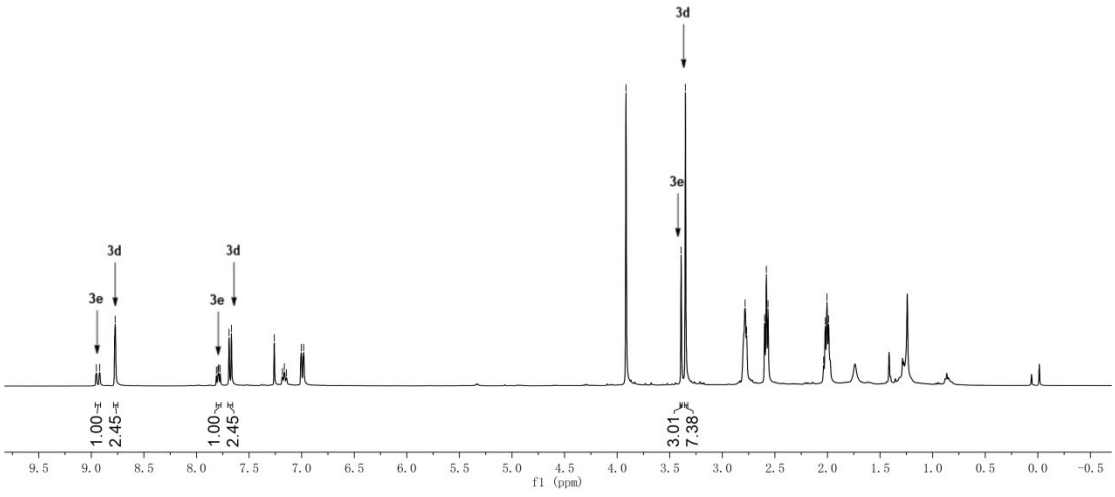
3.3 Competition experiment



1d/1e = 1:1 **2a** (1.2 equiv) **3d/3e=** 2.45/1

A mixture of substrates **1d/1e** (**1d**, 37.1 mg, 0.2 mmol; **1e**, 34.6mg, 0.2 mmol), iodonium ylide **2a** (75.6 mg, 0.24 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol%), PivOH (40.9 mg, 0.4 mmol, 2.0 equiv) in TFE (4.0 mL) was charged in a glass sealed-tube and stirred at 80 ℃ (oil bath) for 30 min. After the reaction, water (10 mL) and DCM (5 mL) were added to the mixture, then the aqueous layer was extracted with DCM (5 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. Finally, the solution was concentrated in vacuo to provide a crude product, which was further purified via a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1 to 2:1) to supply the mixed products **3d** and **3e**. ^{1}H NMR of mixture was presented as red color; ^{1}H NMR of **3d** was presented as blue color; ^{1}H NMR of **3e** was presented as green color.





^{1}H NMR spectrum for competition experiment analysis

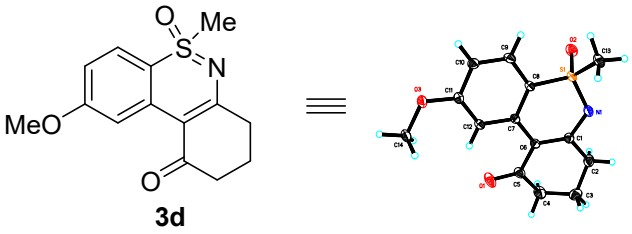
4 Single Crystal Structure of 3d

Sample preparation

20 mg of **3d** was added to a 10 mL glass vial and dissolved in 1 mL DCM and l mL methanol. The glass vial was capped loosely and kept for slow evaporation. After 7 days, single crystal was obtained and then subjected to X-ray diffraction.

Crystal measurement

X-ray diffraction data were recorded on a Bruker D8 Venture single-crystal X-ray diffractometer. Absorption was corrected by semi-empirical from equivalents. The structure was solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 2114921 for compound **3d**.



3d

X-ray structure of **3d**

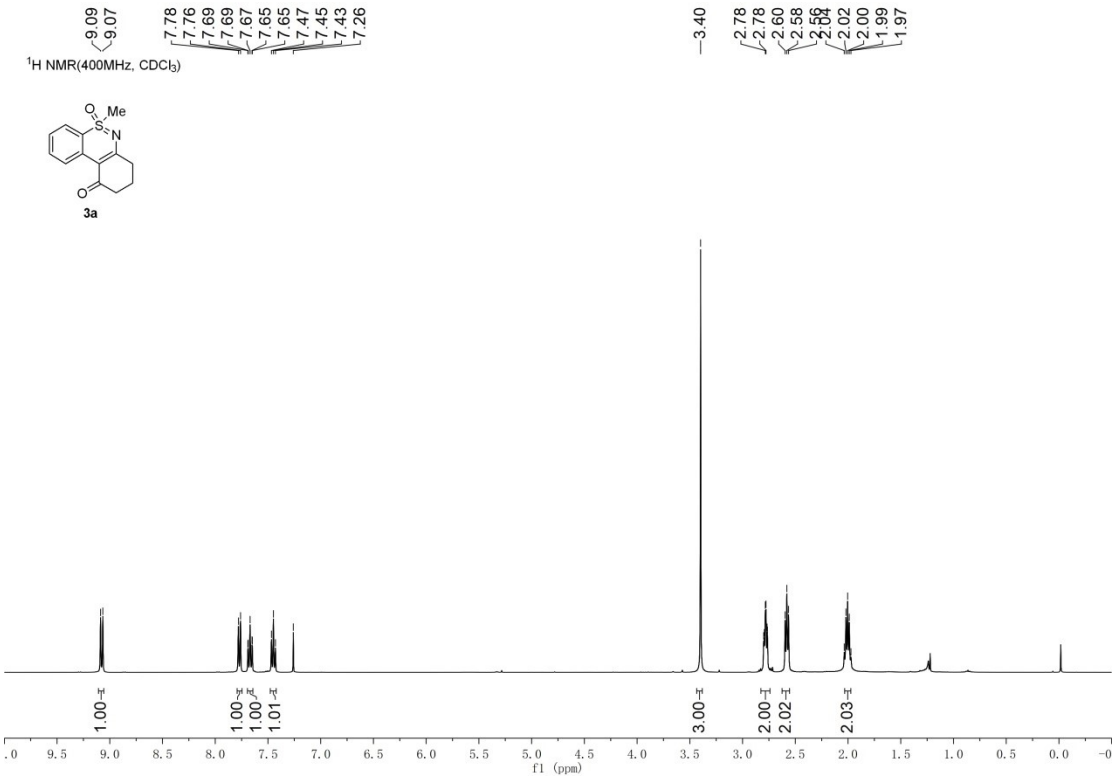
CCDC 2114921

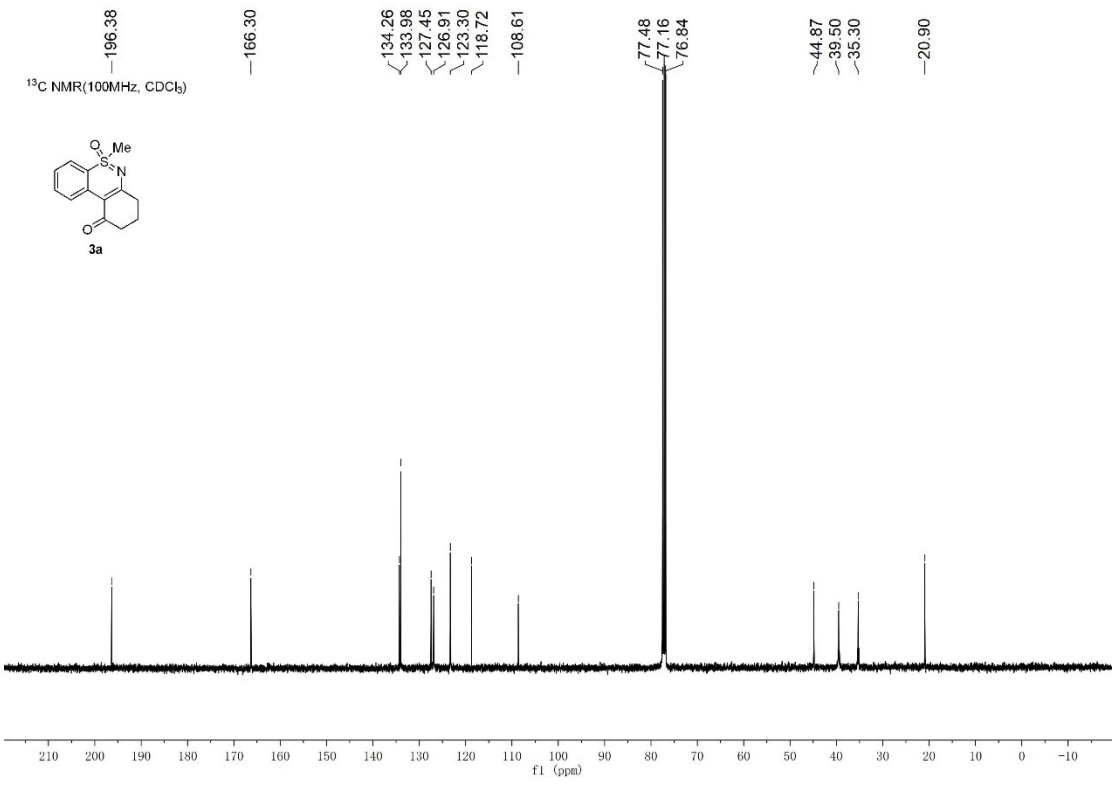
Ellipsoids are drawn at 50% probability level.

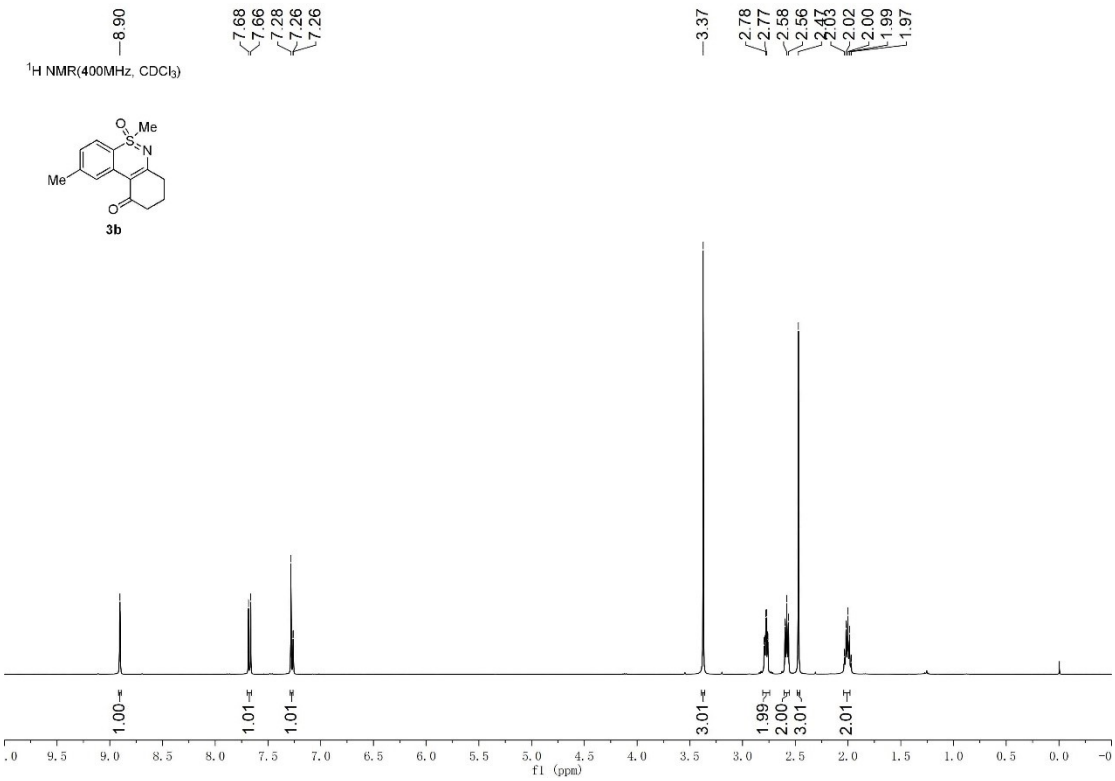
Identification code	d8v21755	
Empirical formula	C14 H15 N O3 S	
Formula weight	277.33	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.3951(5) Å	a= 90°.
	b = 8.7516(4) Å	b= 95.6710(10)°.
	c = 14.2044(6) Å	g = 90°.
Volume	1285.90(10) $Å^3$	
Z	4	
Density (calculated)	1.433 Mg/m^3	
Absorption coefficient	0.255 mm^{-1}	
F(000)	584	
Crystal size	0.200 x 0.160 x 0.120 mm^3	
Theta range for data collection	3.049 to 25.995°.	
Index ranges	-12<=h<=12, -10<=k<=10, -17<=l<=17	

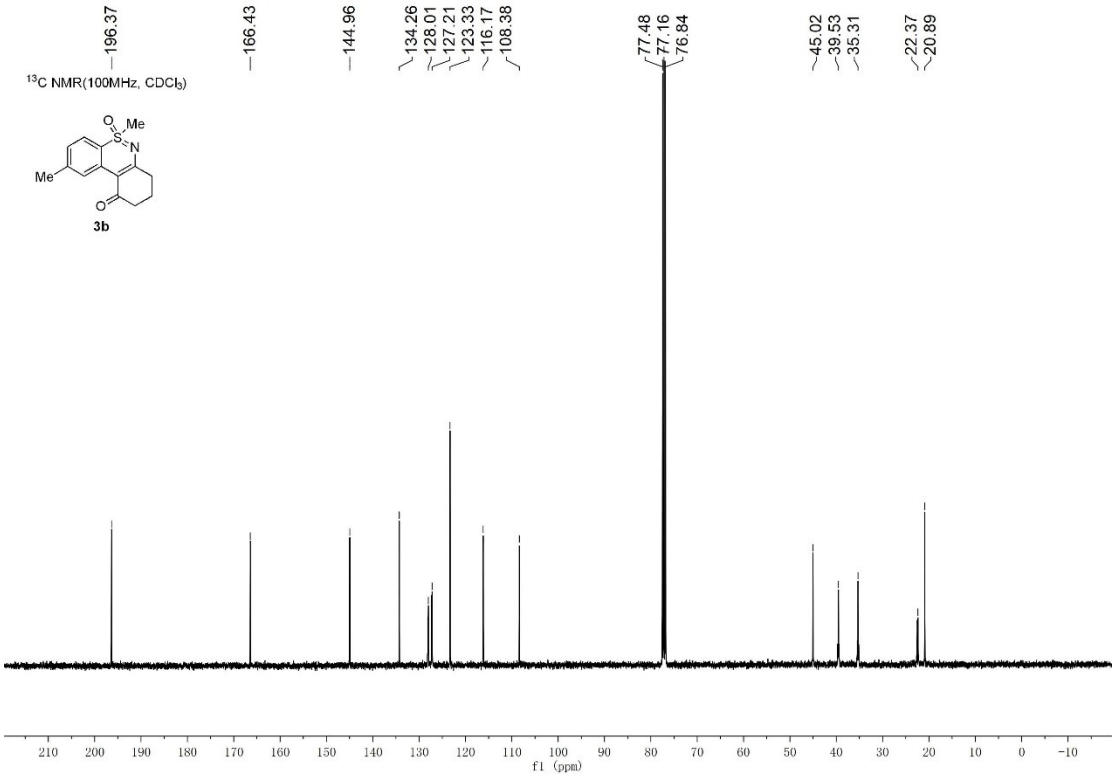
Reflections collected	12404
Independent reflections	2501 [R(int) = 0.0295]
Completeness to theta = 25.242°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6497
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2501 / 0 / 174
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0336, wR2 = 0.0879
R indices (all data)	R1 = 0.0365, wR2 = 0.0900
Extinction coefficient	n/a
Largest diff. peak and hole	0.316 and -0.320 e.$Å^{-3}$

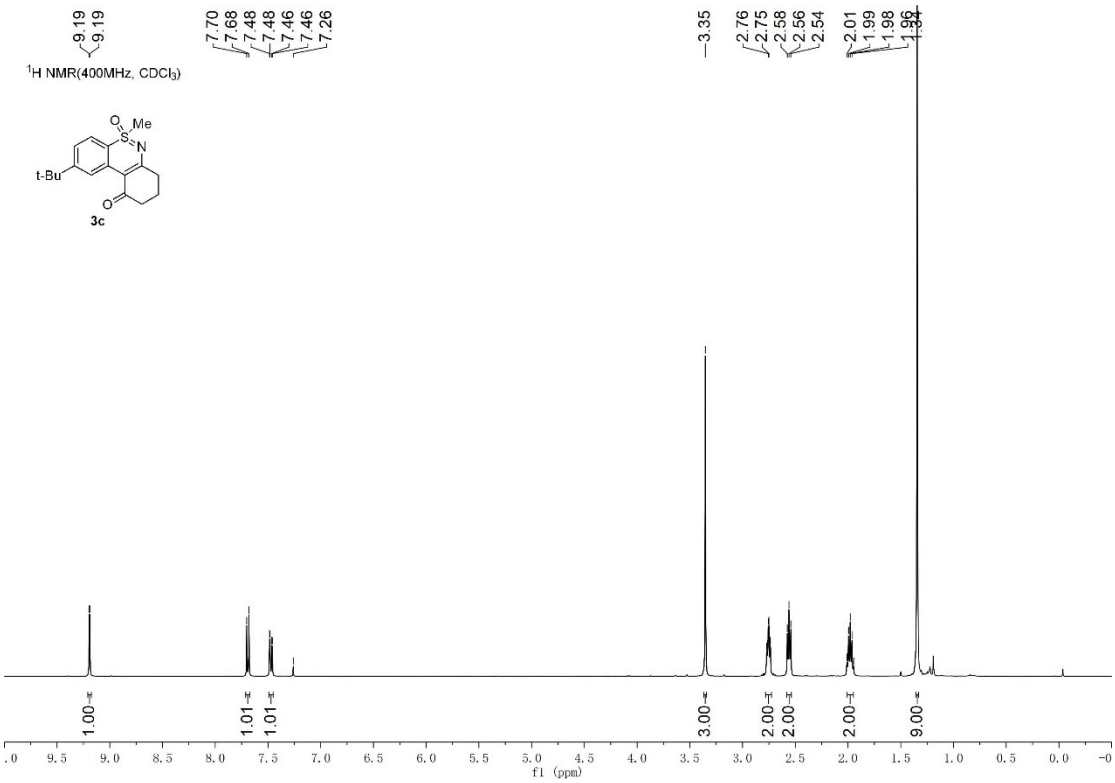
5 ^{1}H and ^{13}C NMR Spectrum for All isolated Products

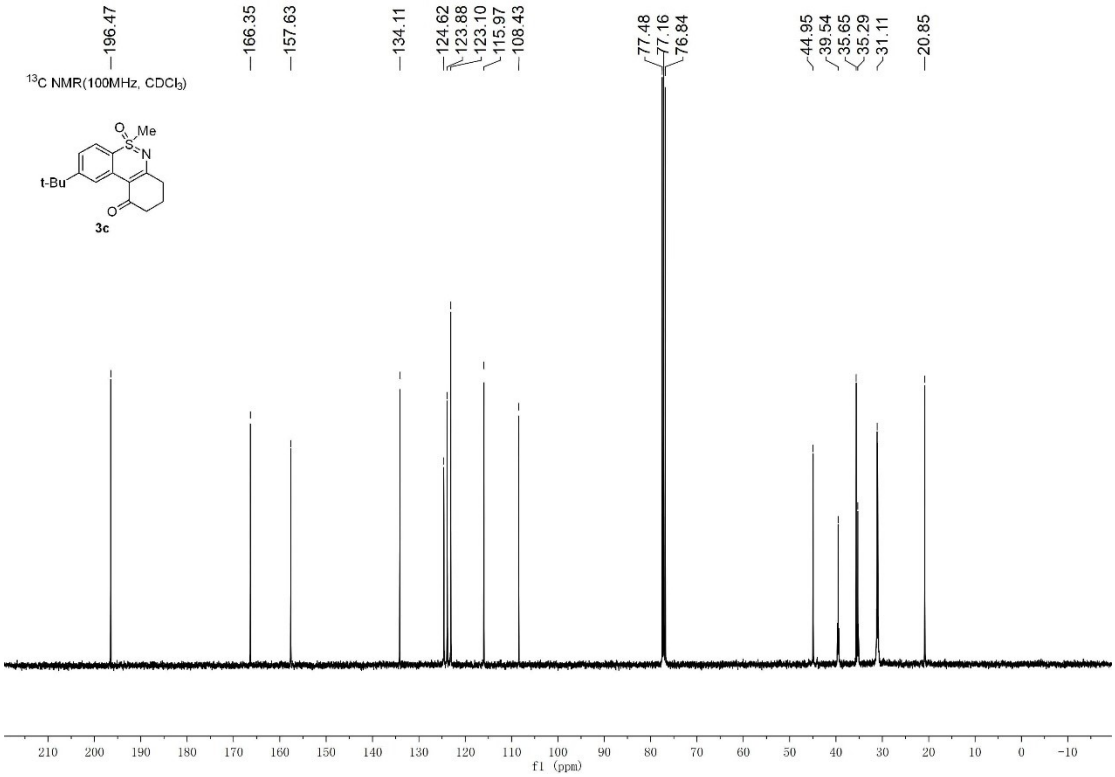


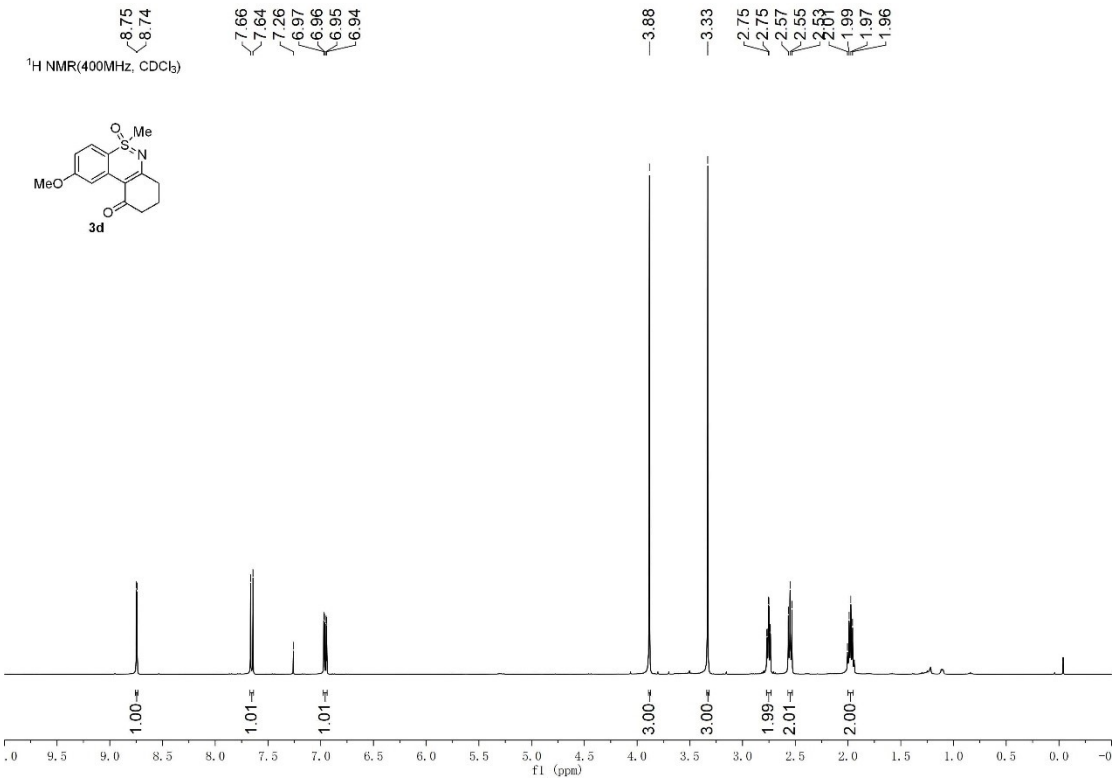


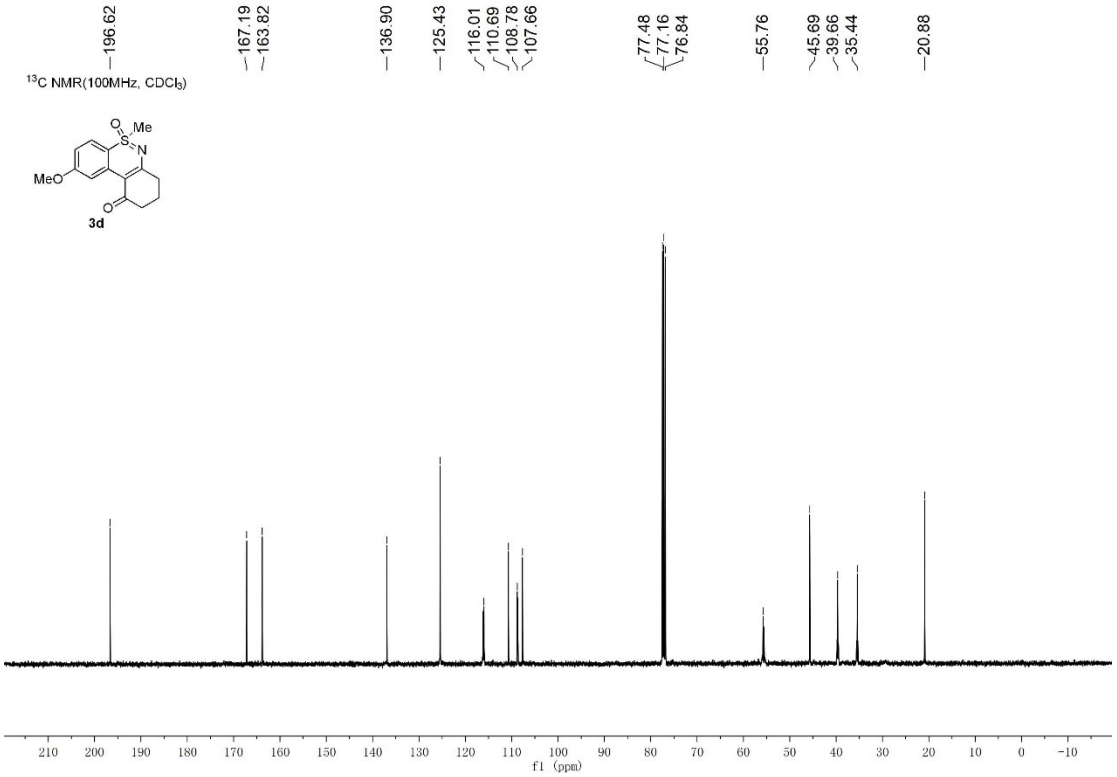

8.90
7.68
7.66
7.28
7.26
7.26
3.37
2.78
2.77
2.58
2.56
2.47
2.03
2.02
2.00
1.99
1.97
1H NMR(400MHz, CDCl3)
Me
S
O
N
Me
O
3b
1.00
1.01
1.01
3.01
1.99
2.00
3.01
2.01
f1 (ppm)

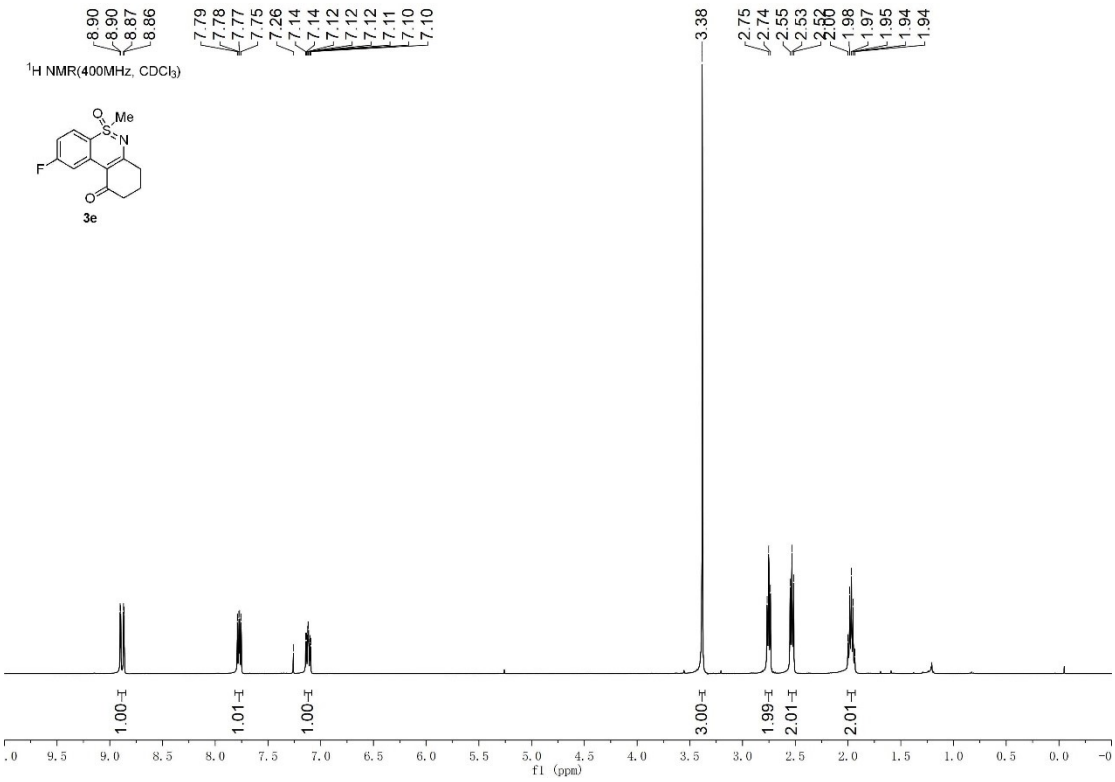

196.37
166.43
144.96
134.26
128.01
127.21
123.33
116.17
108.38
77.48
77.16
76.84
45.02
39.53
35.31
22.37
20.89
13C NMR(100MHz, CDCl3)
Me
S
O
N
Me
O
3b
f1 (ppm)

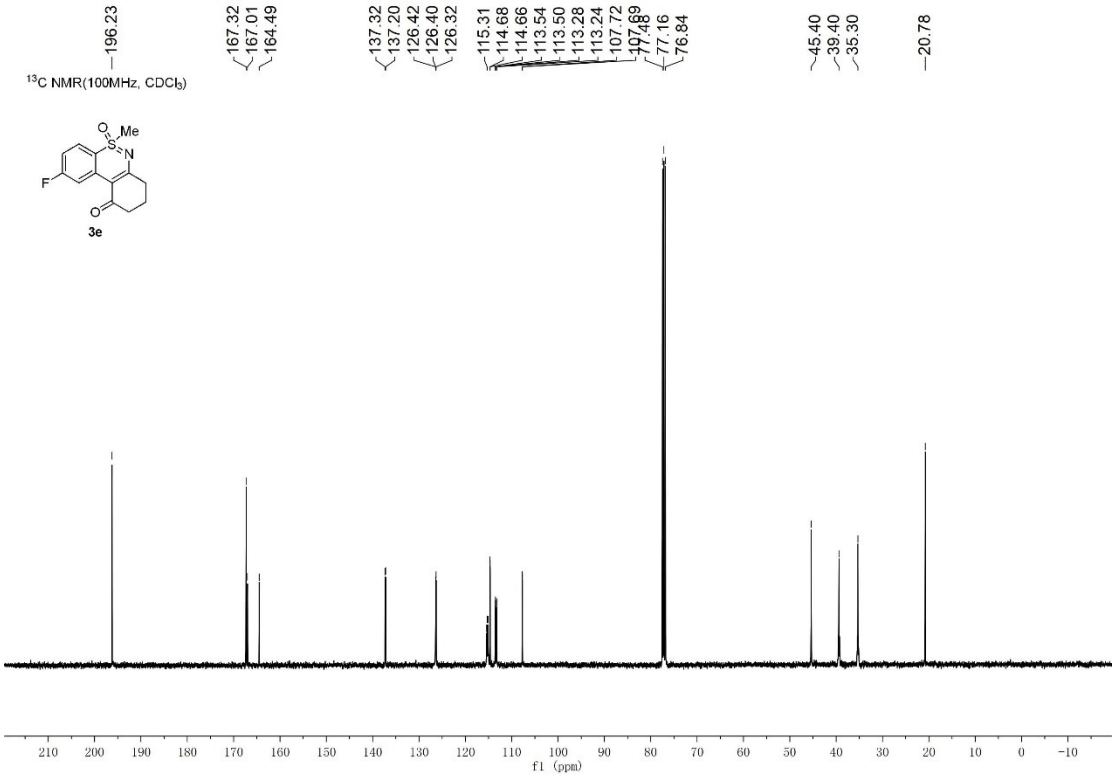

9.19
9.19
7.70
7.68
7.48
7.48
7.46
7.46
7.26
3.35
2.76
2.75
2.58
2.56
2.54
2.01
1.99
1.98
1.96
1.84
1H NMR(400MHz, CDCl3)
Me
O
S
N
t-Bu
O
3c
1.00
1.01
1.01
3.00
2.00
2.00
2.00
9.00
f1 (ppm)

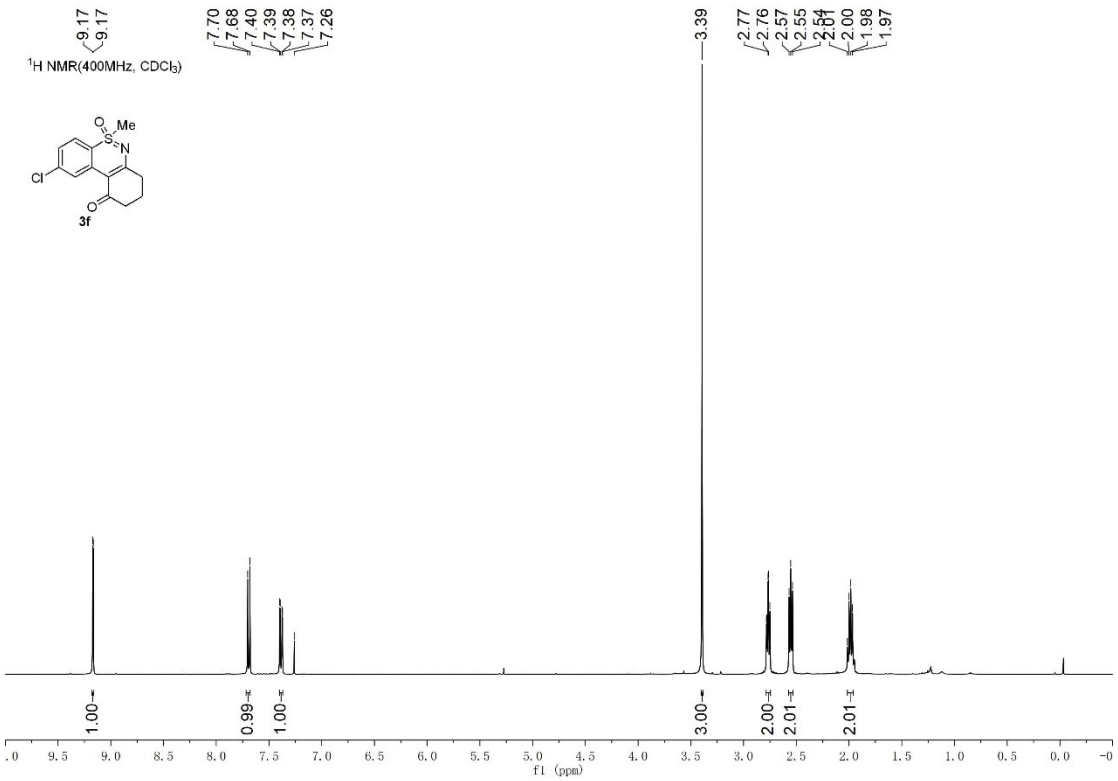

196.47
166.35
157.63
134.11
124.62
123.88
123.10
115.97
108.43
77.48
77.16
76.84
44.95
39.54
35.65
35.29
31.11
20.85
13C NMR(100MHz, CDCl3)
Me
O
S
N
t-Bu
O
3c
f1 (ppm)

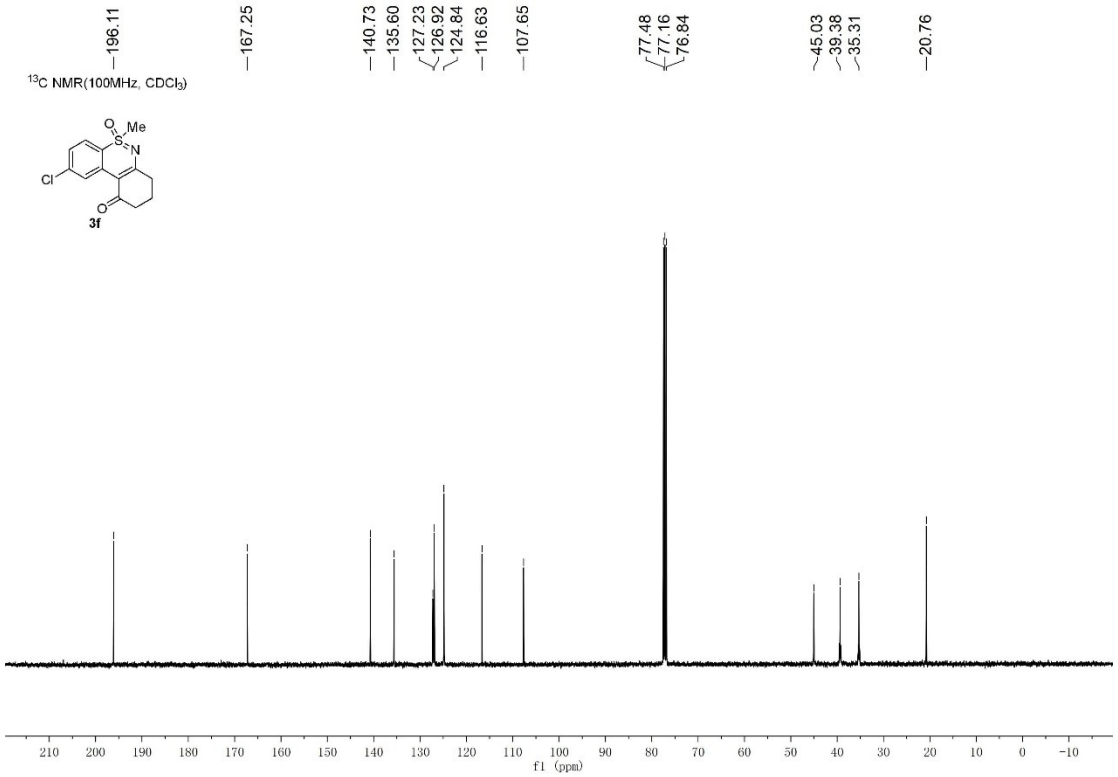

8.75
8.74
7.66
7.64
7.26
6.97
6.96
6.95
6.94
3.88
3.33
2.75
2.75
2.57
2.55
2.53
2.01
1.99
1.97
1.96
1H NMR(400MHz, CDCl3)
Me
O
S
N
MeO
O
3d
1.00
1.01
1.01
3.00
3.00
1.99
2.01
2.00
f1 (ppm)

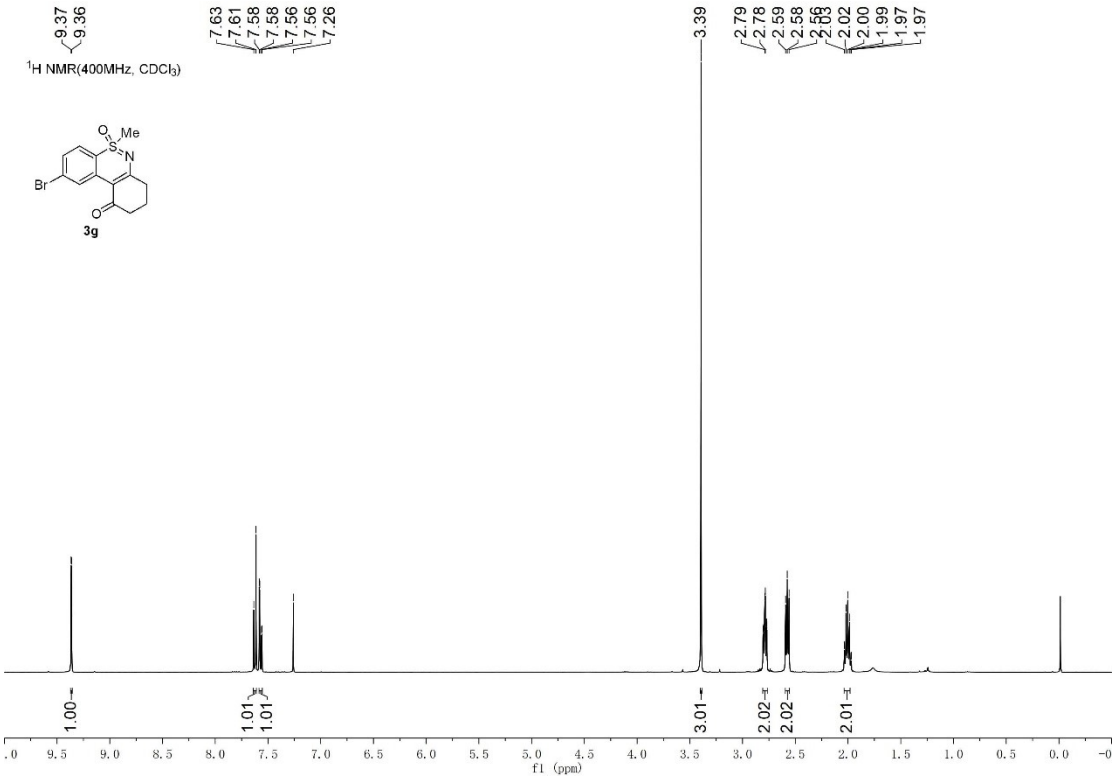

196.62
167.19
163.82
136.90
125.43
116.01
110.69
108.78
107.66
77.48
77.16
76.84
55.76
45.69
39.66
35.44
20.88
13C NMR(100MHz, CDCl3)
Me
O
S
N
MeO
O
3d
f1 (ppm)

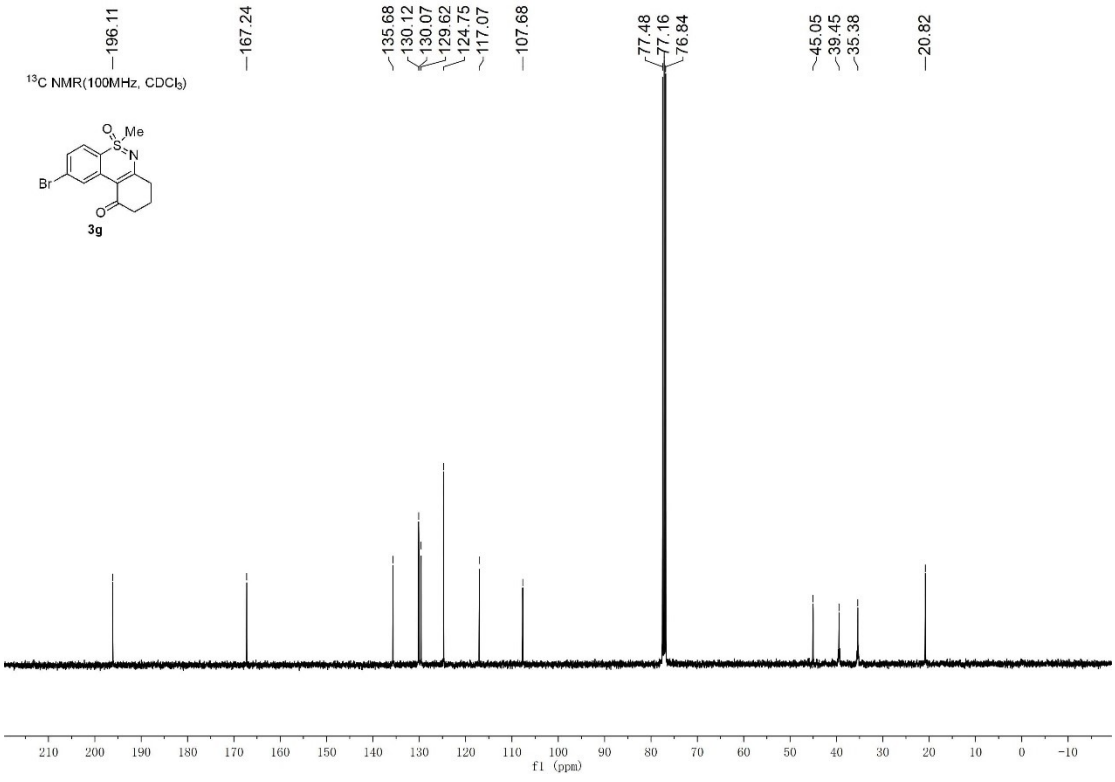

8.90
8.90
8.87
8.86
7.79
7.78
7.77
7.75
7.26
7.14
7.14
7.12
7.12
7.12
7.11
7.10
7.10
3.38
2.75
2.74
2.55
2.53
2.52
2.00
1.98
1.97
1.95
1.94
1.94
1H NMR(400MHz, CDCl3)
Me
O
S
N
F
O
3e
1.00
1.01
1.00
3.00
1.99
2.01
2.01
f1 (ppm)

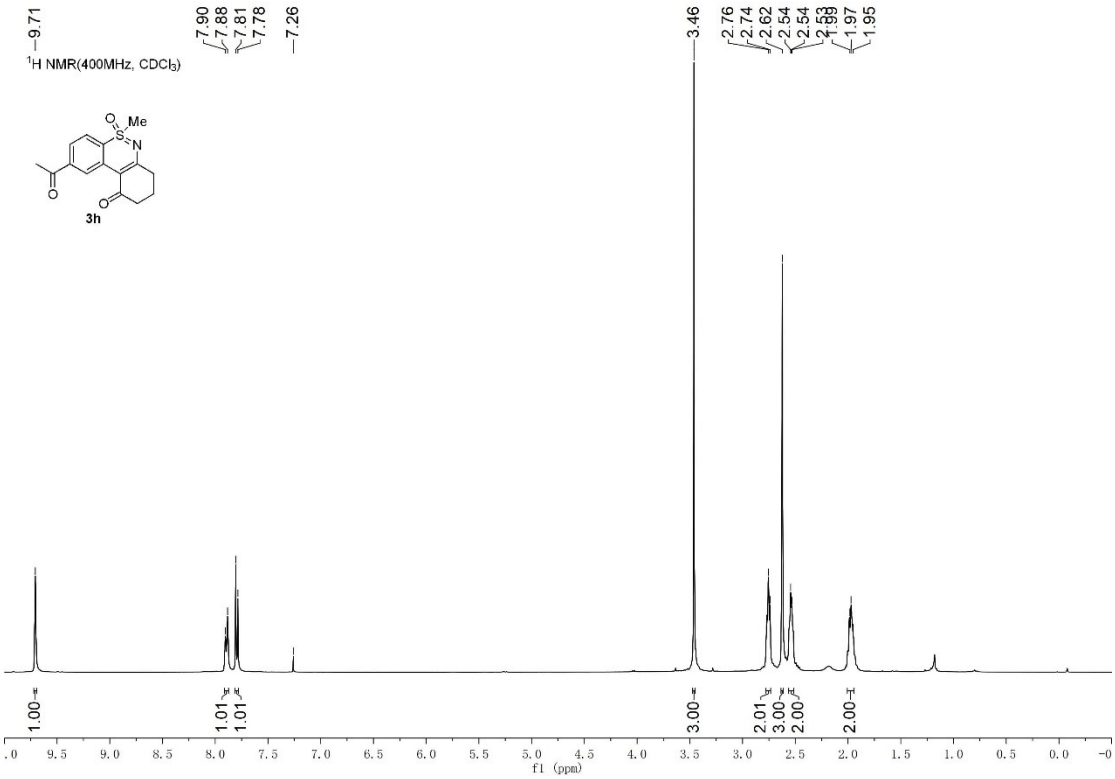

196.23
167.32
167.01
164.49
137.32
137.20
126.42
126.40
126.32
115.31
114.68
114.66
113.54
113.50
113.28
113.24
107.72
107.69
77.48
77.16
76.84
45.40
39.40
35.30
20.78
13C NMR(100MHz, CDCl3)
Me
O
S
N
F
O
3e
f1 (ppm)

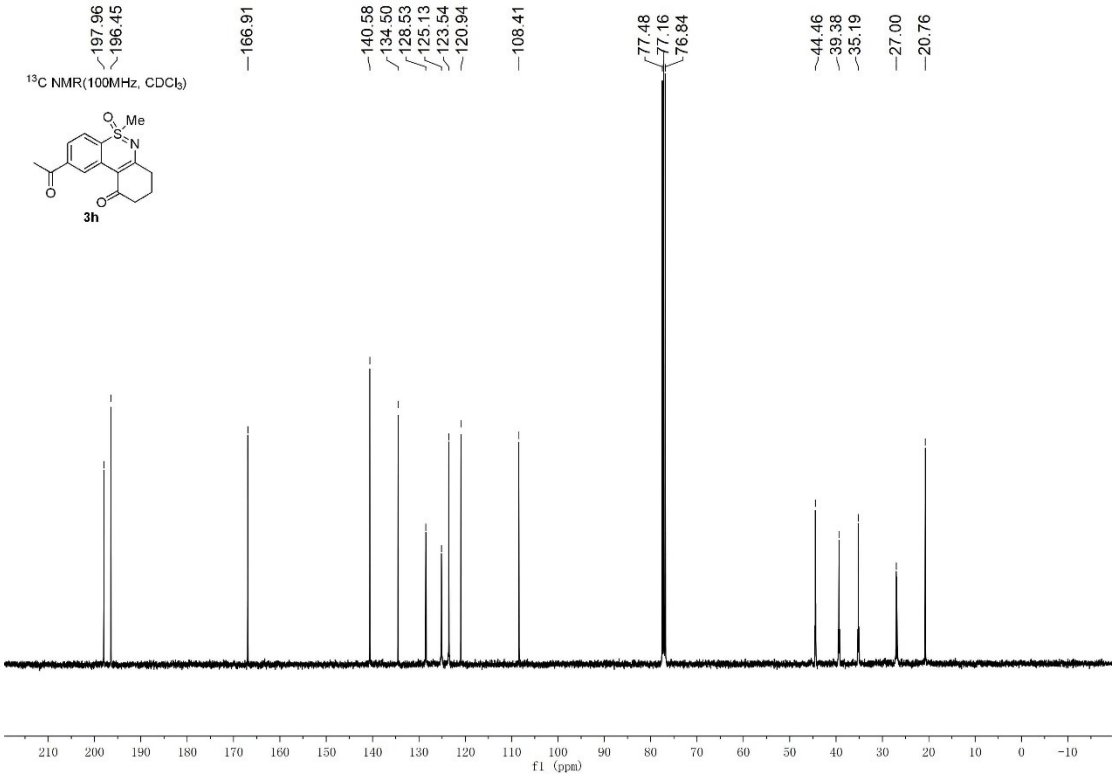

9.17
9.17
7.70
7.68
7.40
7.39
7.38
7.37
7.26
3.39
2.77
2.76
2.57
2.55
2.01
2.00
1.98
1.97
1H NMR(400MHz, CDCl3)
Me
S
N
Cl
O
3f
1.00
0.99
1.00
3.00
2.00
2.01
2.01
f1 (ppm)

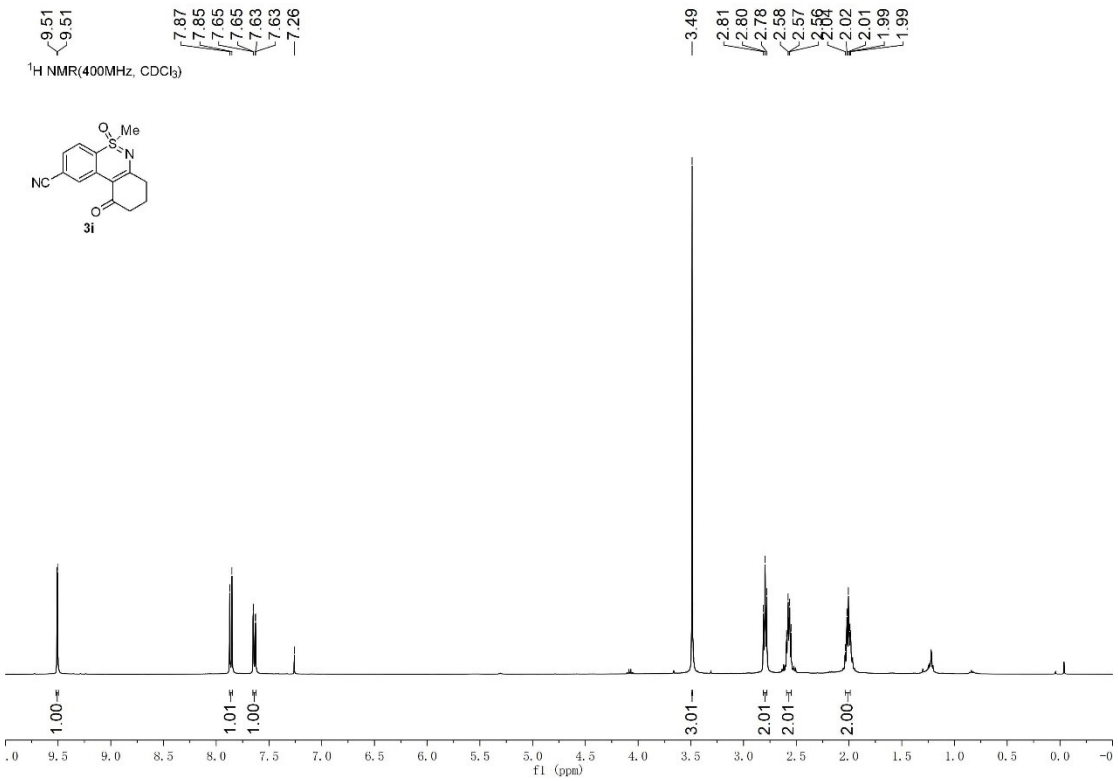

196.11
167.25
140.73
135.60
127.23
126.92
124.84
116.63
107.65
77.48
77.16
76.84
45.03
39.38
35.31
20.76
13C NMR(100MHz, CDCl3)
Me
S
N
Cl
O
3f
f1 (ppm)

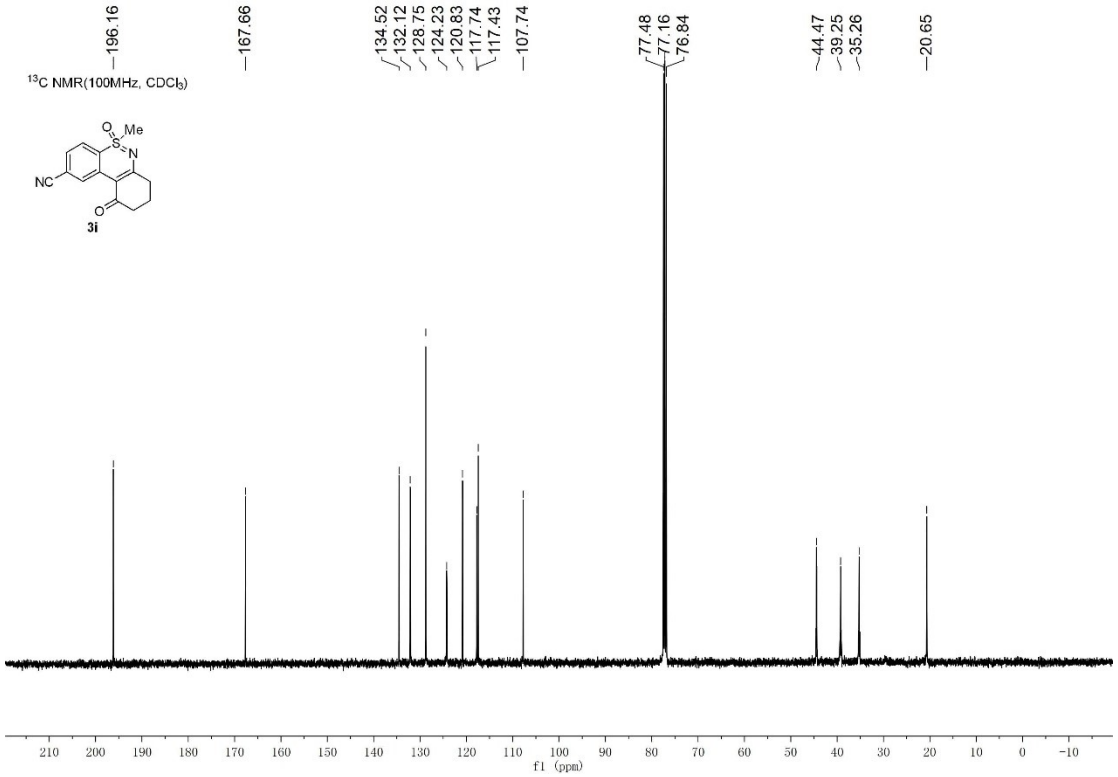

9.37
9.36
7.63
7.61
7.58
7.58
7.56
7.56
7.26
3.39
2.79
2.78
2.59
2.58
2.02
2.00
1.99
1.97
1.97
1H NMR(400MHz, CDCl3)
Me
O
S
N
Br
O
3g
1.00
1.01
1.01
3.01
2.02
2.02
2.01
f1 (ppm)

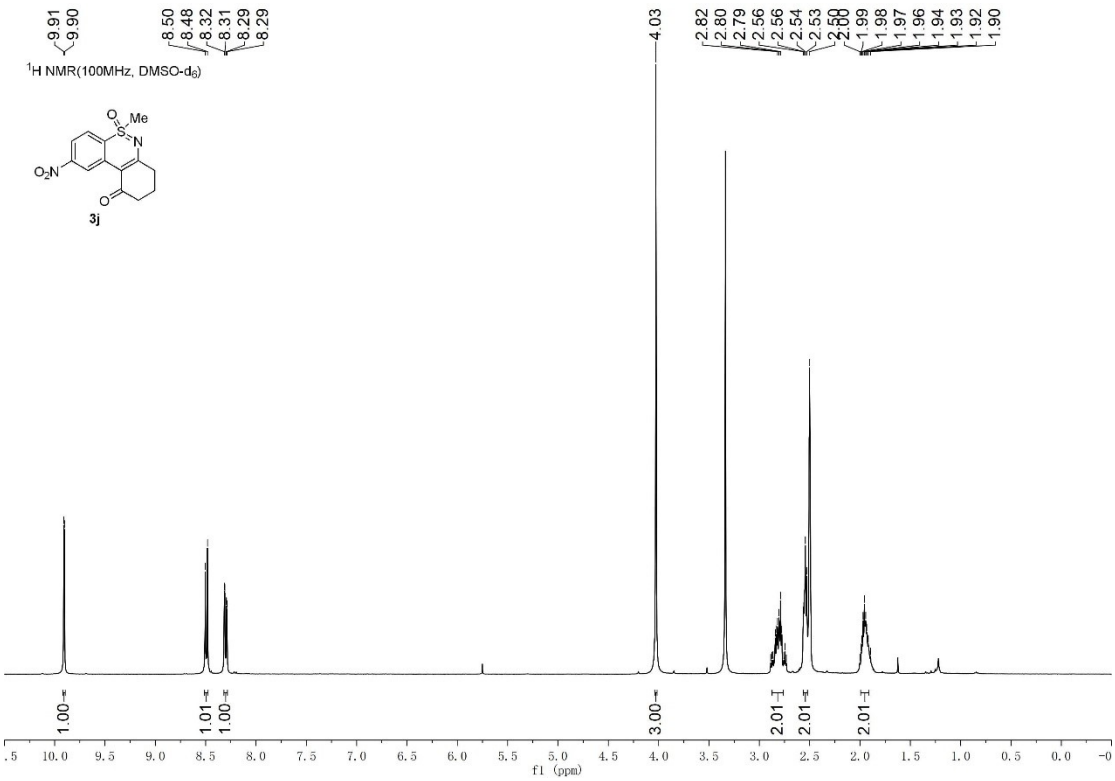

196.11
167.24
135.68
130.12
130.07
129.62
124.75
117.07
107.68
77.48
77.16
76.84
45.05
39.45
35.38
20.82
13C NMR(100MHz, CDCl3)
Me
O
S
N
Br
O
3g
f1 (ppm)

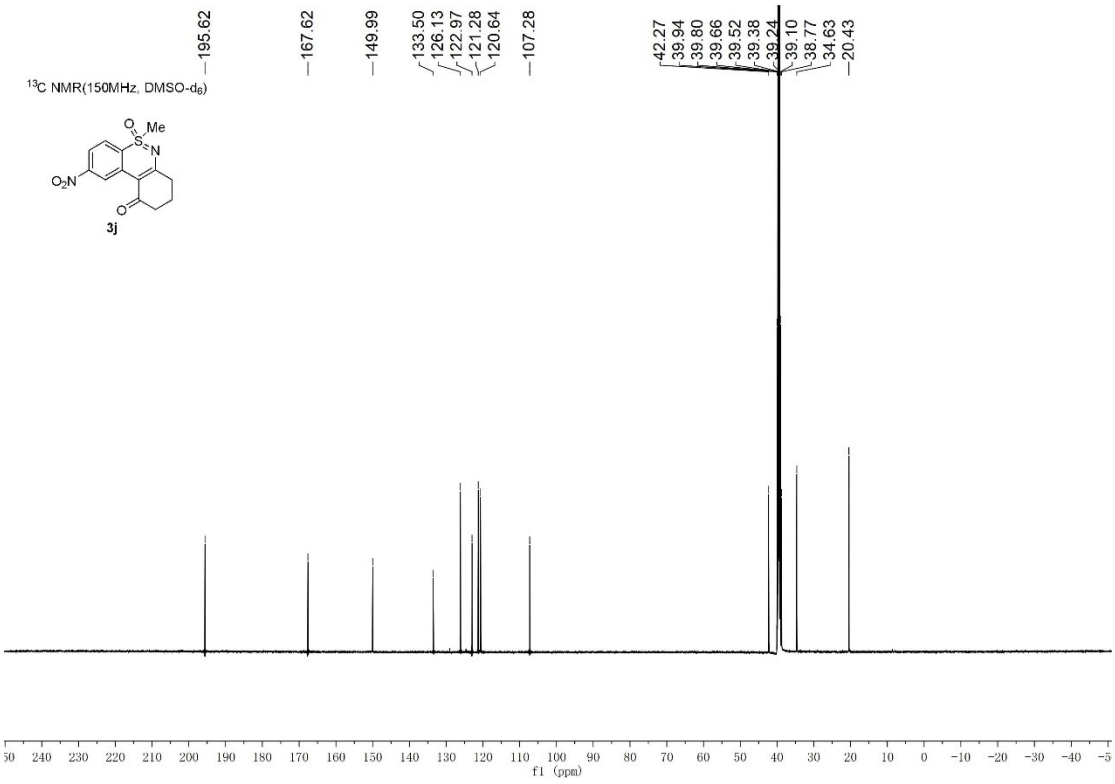

9.71
7.90
7.88
7.81
7.78
7.26
3.46
2.76
2.74
2.62
2.54
2.54
2.53
1.99
1.97
1.95
1H NMR(400MHz, CDCl3)
Me
3h
1.00
1.01
1.01
3.00
2.01
3.00
2.00
2.00
f1 (ppm)

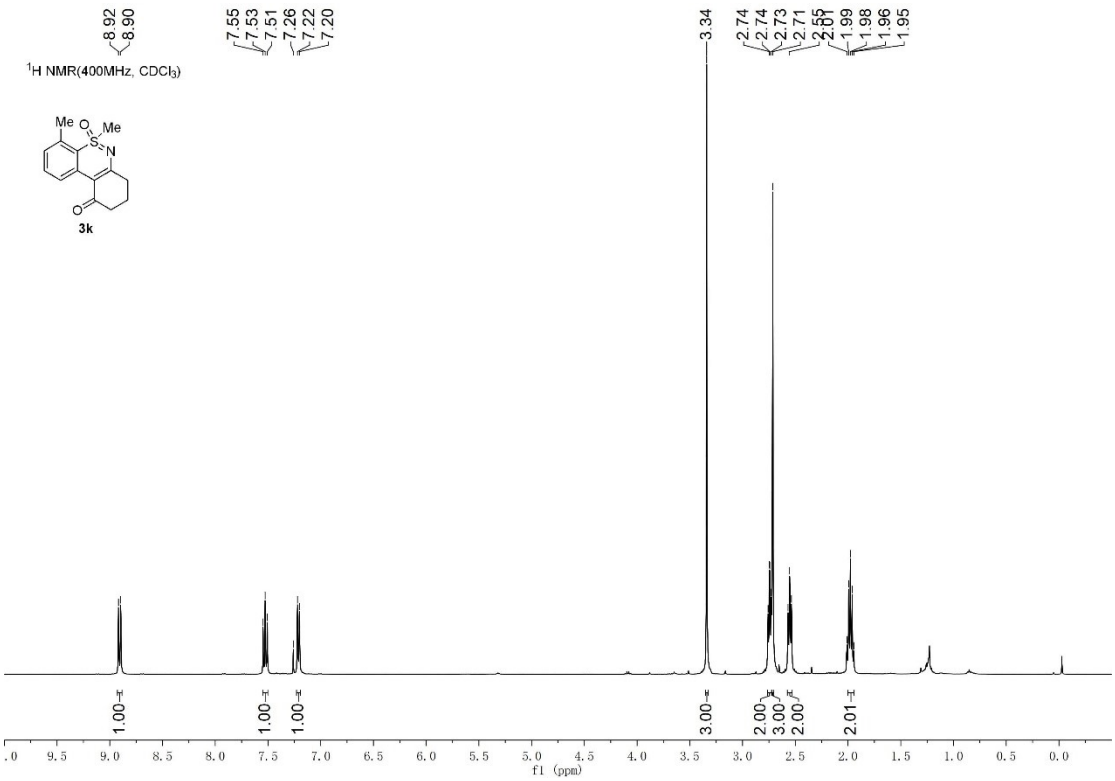

197.96
196.45
166.91
140.58
134.50
128.53
125.13
123.54
120.94
108.41
77.48
77.16
76.84
44.46
39.38
35.19
27.00
20.76
13C NMR(100MHz, CDCl3)
Me
3h
f1 (ppm)

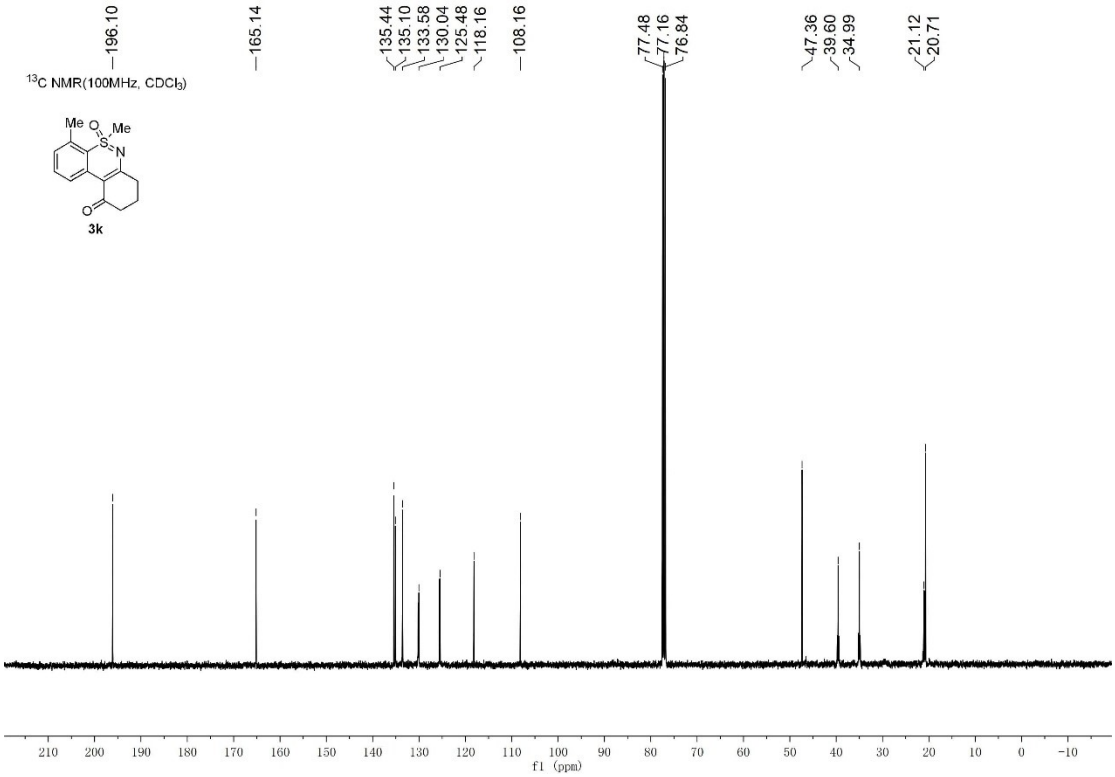

9.51
9.51
7.87
7.85
7.65
7.65
7.63
7.63
7.26
3.49
2.81
2.80
2.78
2.58
2.57
2.02
2.01
1.99
1.99
1H NMR(400MHz, CDCl3)
Me
NC
3i
1.00
1.01
1.00
3.01
2.01
2.01
2.00
f1 (ppm)

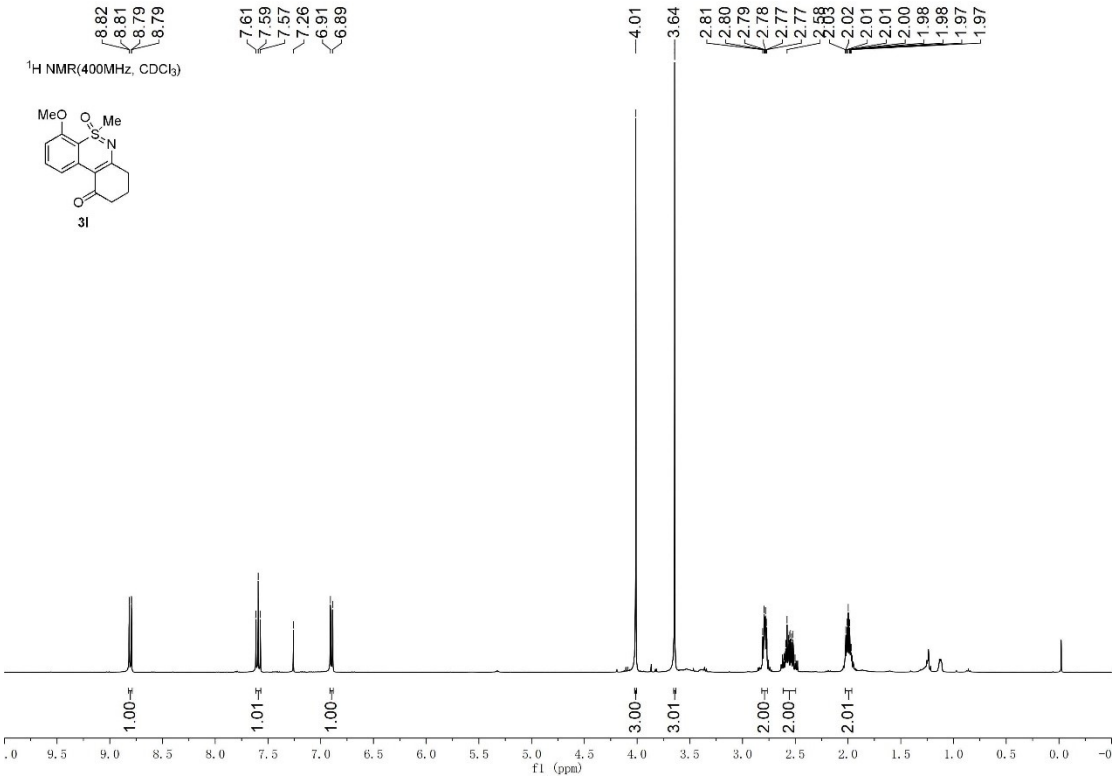

196.16
167.66
134.52
132.12
128.75
124.23
120.83
117.74
117.43
107.74
77.48
77.16
76.84
44.47
39.25
35.26
20.65
13C NMR(100MHz, CDCl3)
Me
NC
3i
f1 (ppm)

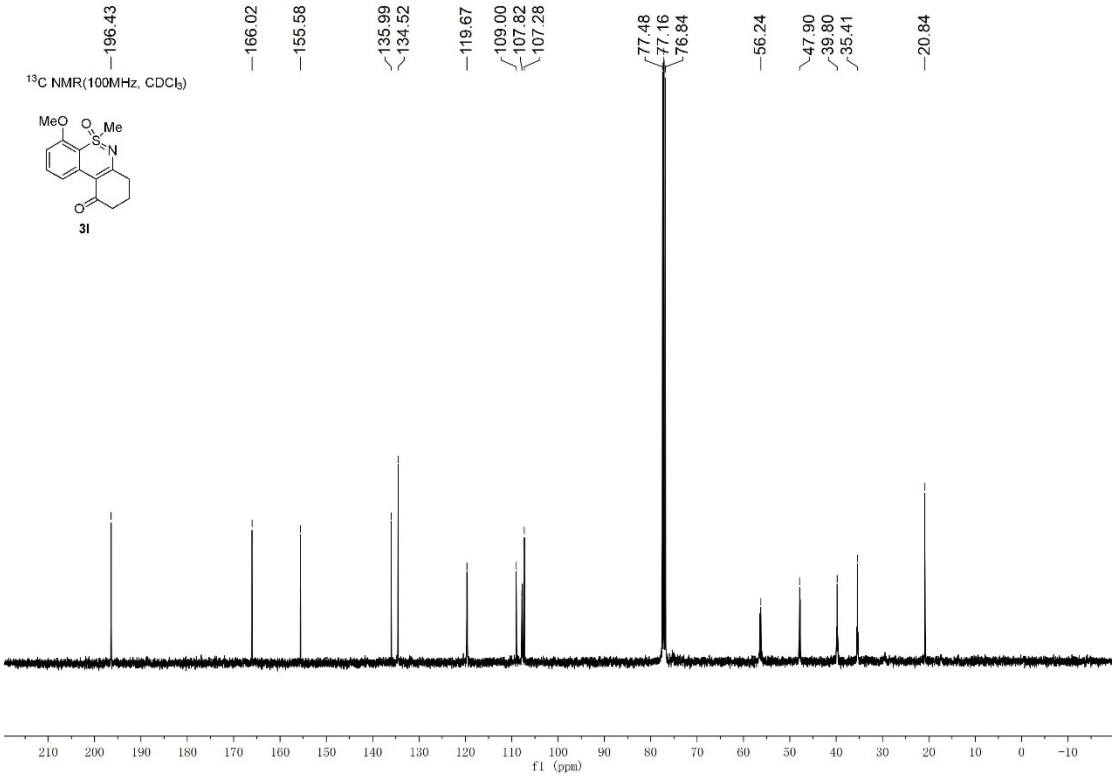

9.91
9.90
8.50
8.48
8.32
8.31
8.29
8.29
4.03
2.82
2.80
2.79
2.56
2.56
2.54
2.53
2.00
1.99
1.98
1.97
1.96
1.94
1.93
1.92
1.90
1H NMR(100MHz, DMSO-d6)
Me
O
S
N
O2N
O
3j
1.00
1.01
1.00
3.00
2.01
2.01
2.01
f1 (ppm)

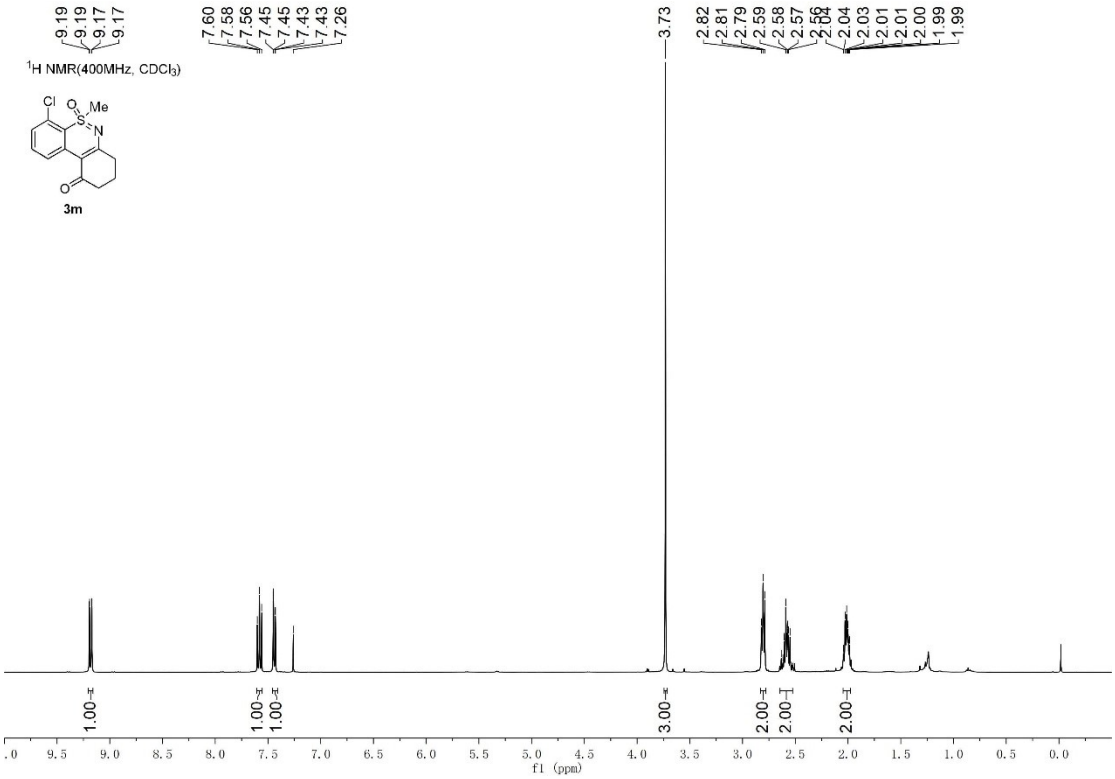

195.62
167.62
149.99
133.50
126.13
122.97
121.28
120.64
107.28
42.27
39.94
39.80
39.66
39.52
39.38
39.24
39.10
38.77
34.63
20.43
13C NMR(150MHz, DMSO-d6)
Me
O
S
N
O2N
O
3j
f1 (ppm)

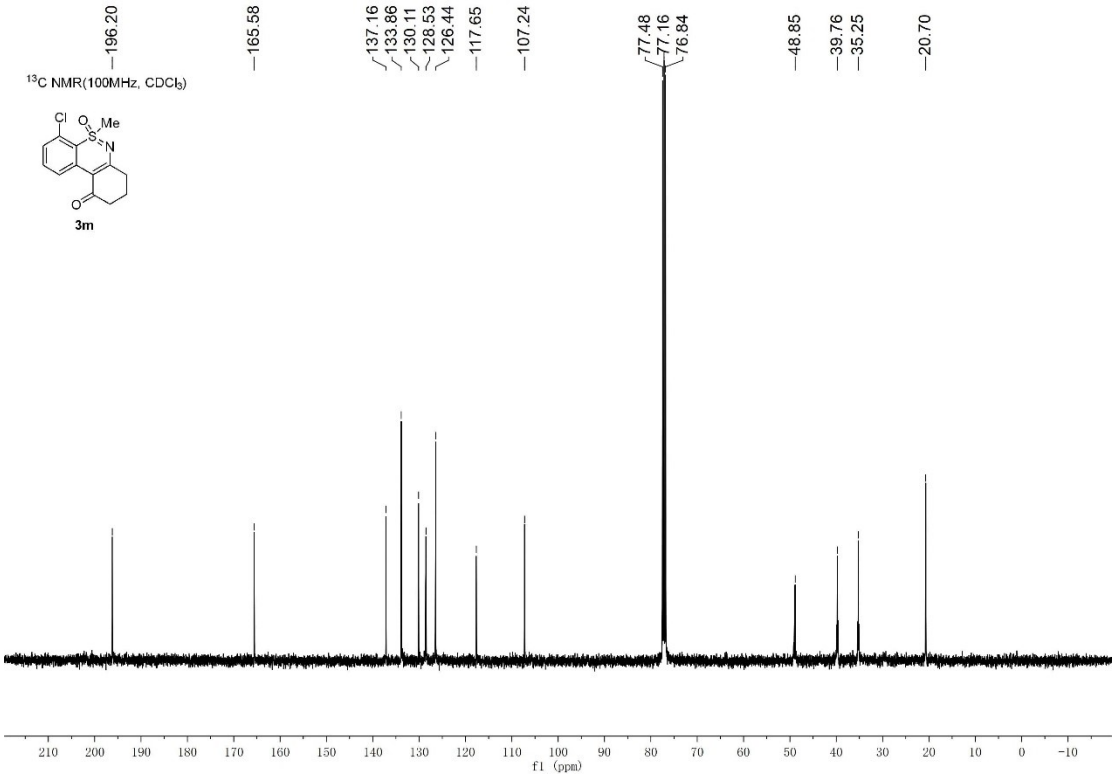

8.92
8.90
7.55
7.53
7.51
7.26
7.22
7.20
3.34
2.74
2.74
2.73
2.71
2.55
2.01
1.99
1.98
1.96
1.95
1H NMR(400MHz, CDCl3)
Me
O
Me
S
N
O
3k
1.00
1.00
1.00
3.00
2.00
3.00
2.00
2.01
f1 (ppm)

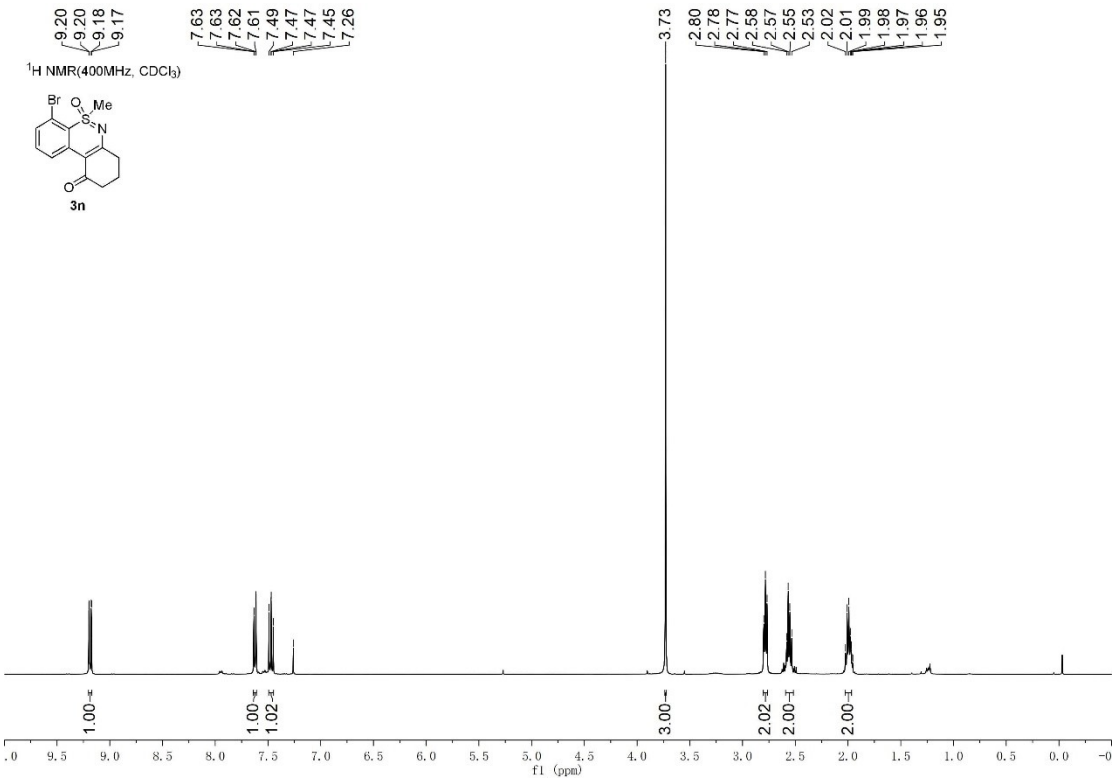

196.10
165.14
135.44
135.10
133.58
130.04
125.48
118.16
108.16
77.48
77.16
76.84
47.36
39.60
34.99
21.12
20.71
13C NMR(100MHz, CDCl3)
Me
O
Me
S
N
O
3k
f1 (ppm)

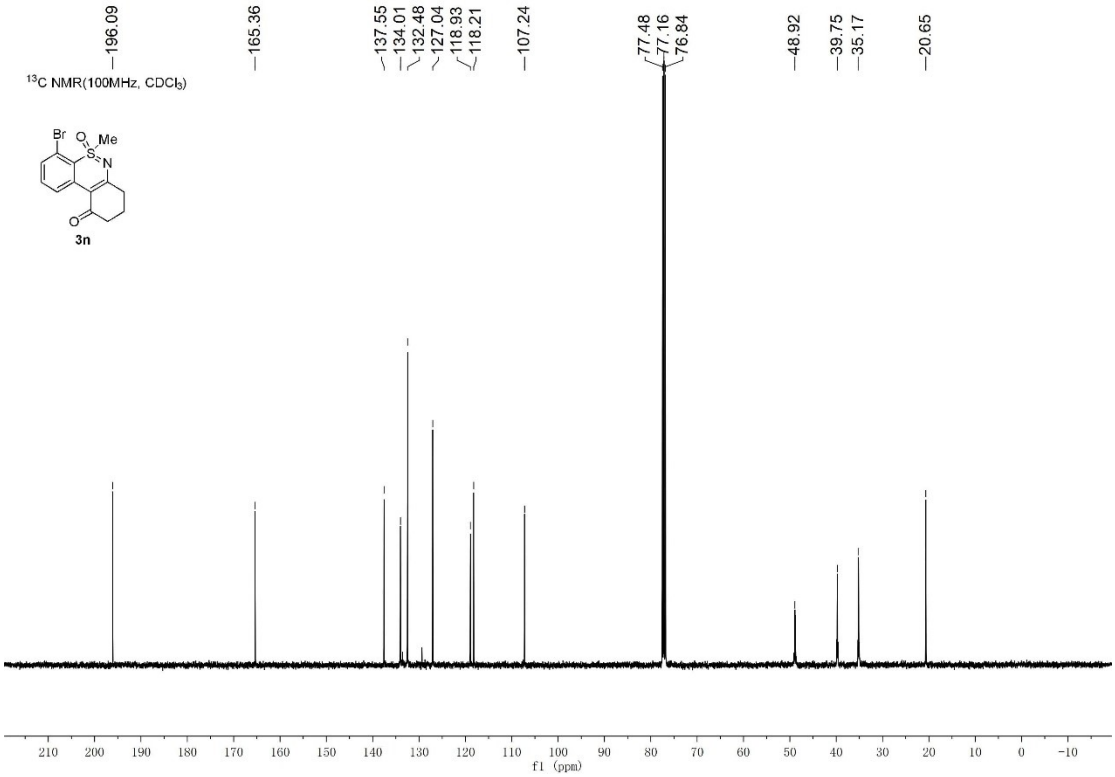

8.82
8.81
8.79
8.79
7.61
7.59
7.57
7.26
6.91
6.89
4.01
3.64
2.81
2.80
2.79
2.78
2.77
2.77
2.03
2.02
2.01
2.01
2.00
1.98
1.98
1.97
1.97
1H NMR(400MHz, CDCl3)
MeO
Me
N
O
3l
1.00
1.01
1.00
3.00
3.01
2.00
2.00
2.01
f1 (ppm)

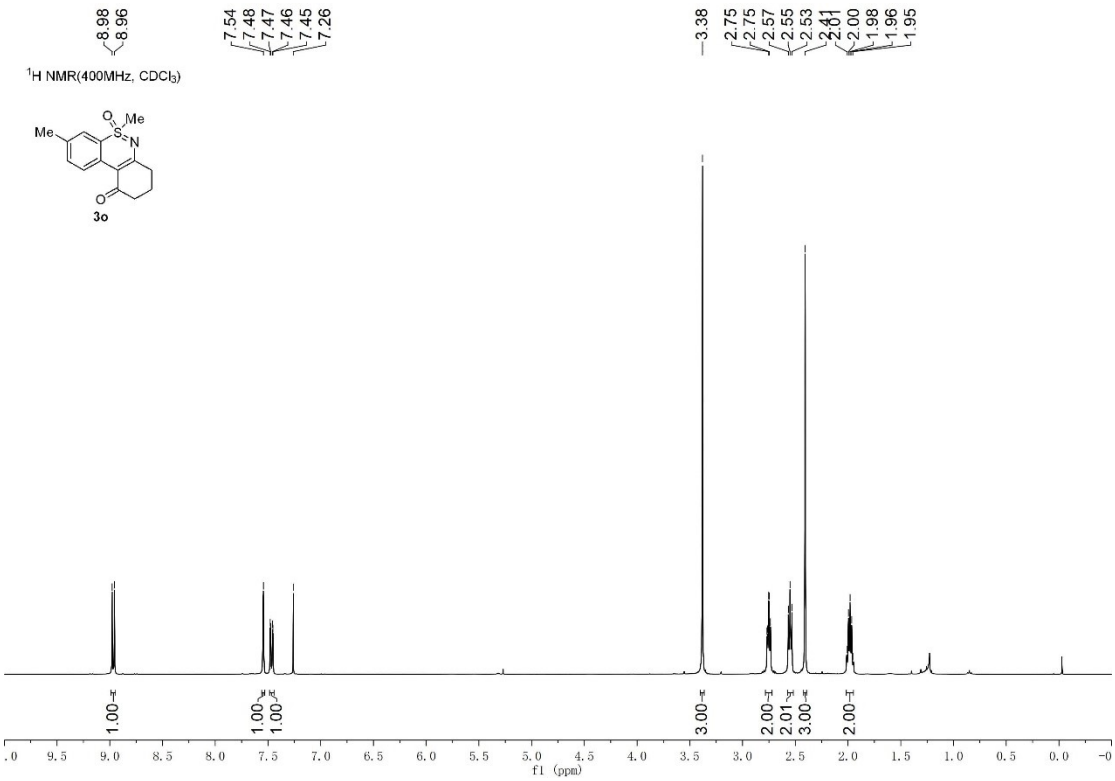

196.43
166.02
155.58
135.99
134.52
119.67
109.00
107.82
107.28
77.48
77.16
76.84
56.24
47.90
39.80
35.41
20.84
13C NMR(100MHz, CDCl3)
MeO
Me
N
O
3l
f1 (ppm)

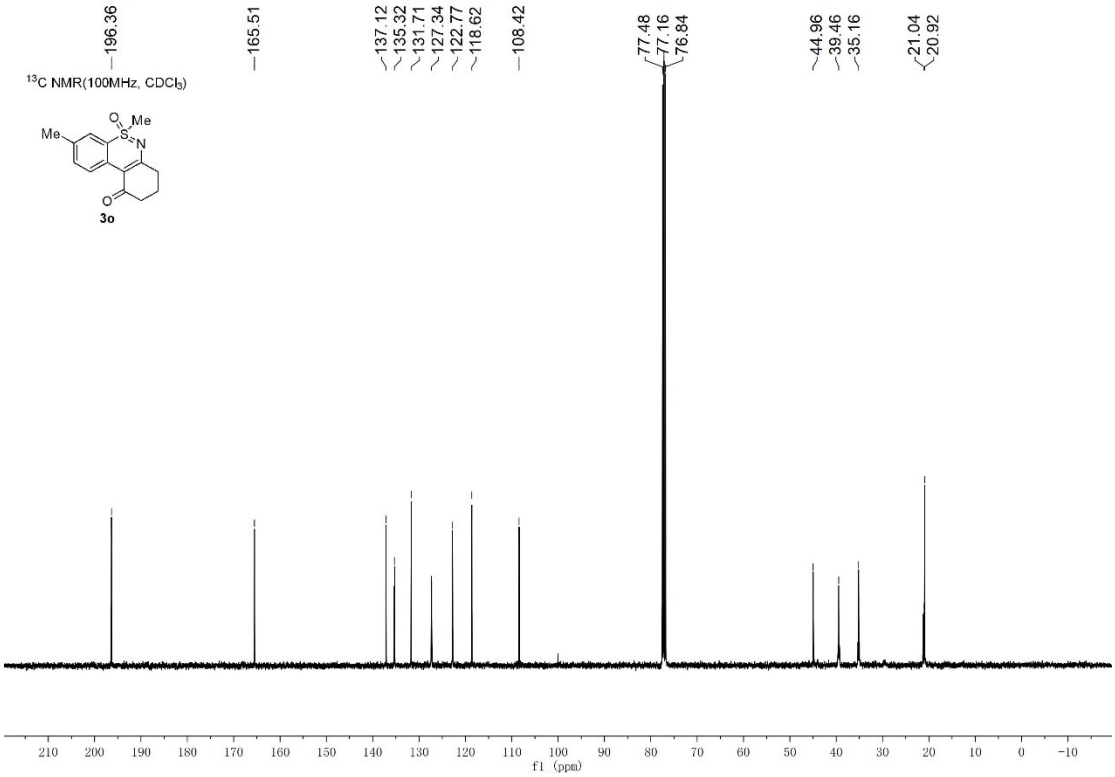

9.19
9.19
9.17
9.17
7.60
7.58
7.56
7.45
7.45
7.43
7.43
7.26
3.73
2.82
2.81
2.79
2.59
2.58
2.57
2.04
2.03
2.01
2.01
2.00
1.99
1.99
1H NMR(400MHz, CDCl3)
Cl
O
Me
S
N
O
3m
1.00
1.00
1.00
3.00
2.00
2.00
2.00
f1 (ppm)

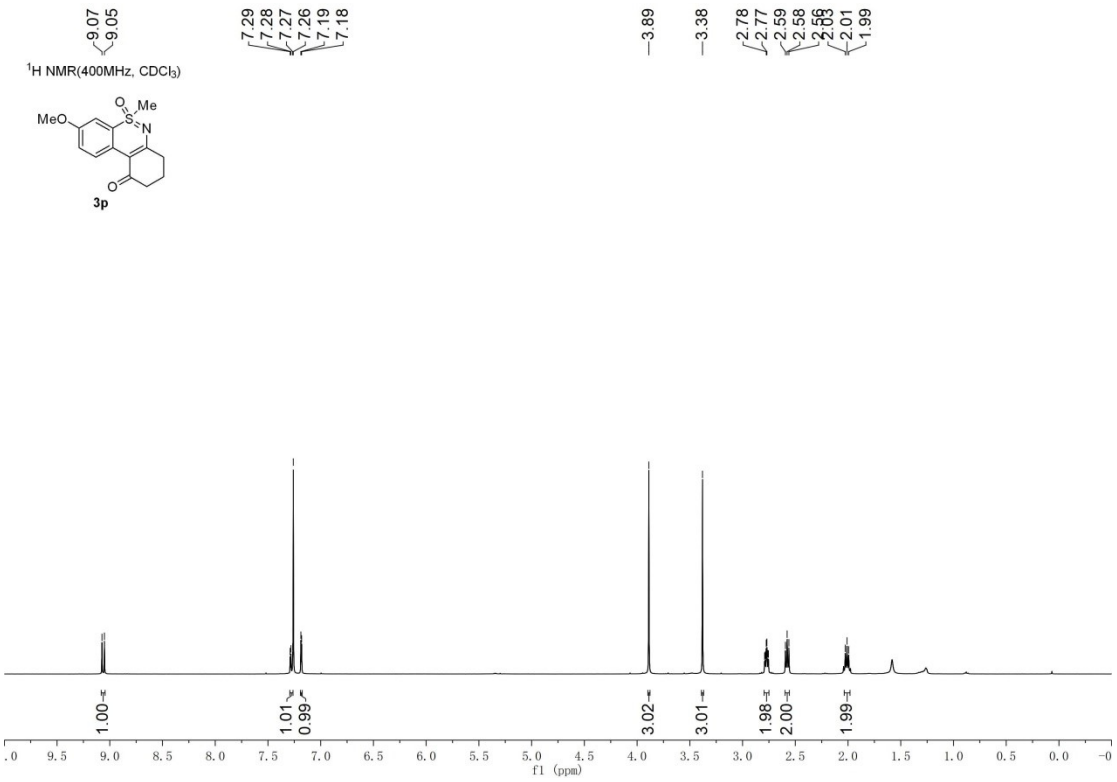

196.20
165.58
137.16
133.86
130.11
128.53
126.44
117.65
107.24
77.48
77.16
76.84
48.85
39.76
35.25
20.70
13C NMR(100MHz, CDCl3)
Cl
O
Me
S
N
O
3m
f1 (ppm)

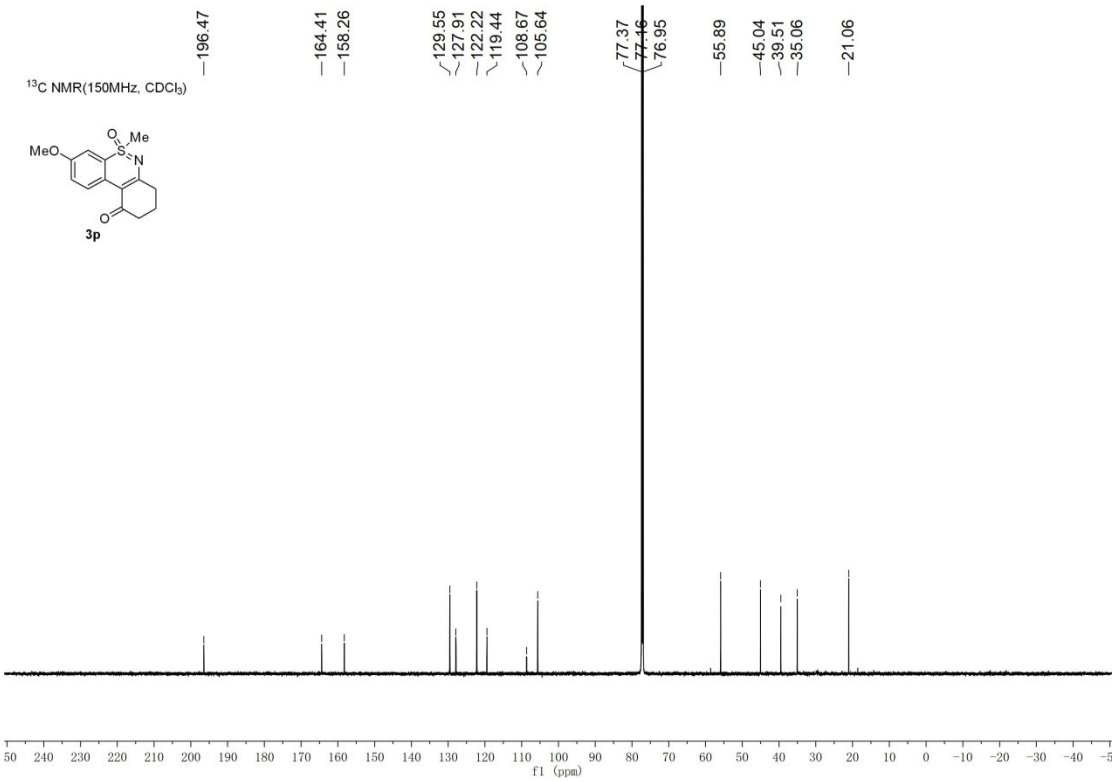

9.20
9.20
9.18
9.17
7.63
7.63
7.62
7.61
7.49
7.47
7.47
7.45
7.26
3.73
2.80
2.78
2.77
2.58
2.57
2.55
2.53
2.02
2.01
1.99
1.98
1.97
1.96
1.95
1H NMR(400MHz, CDCl3)
Br
O
Me
S
N
O
3n
1.00
1.00
1.02
3.00
2.02
2.00
2.00
f1 (ppm)

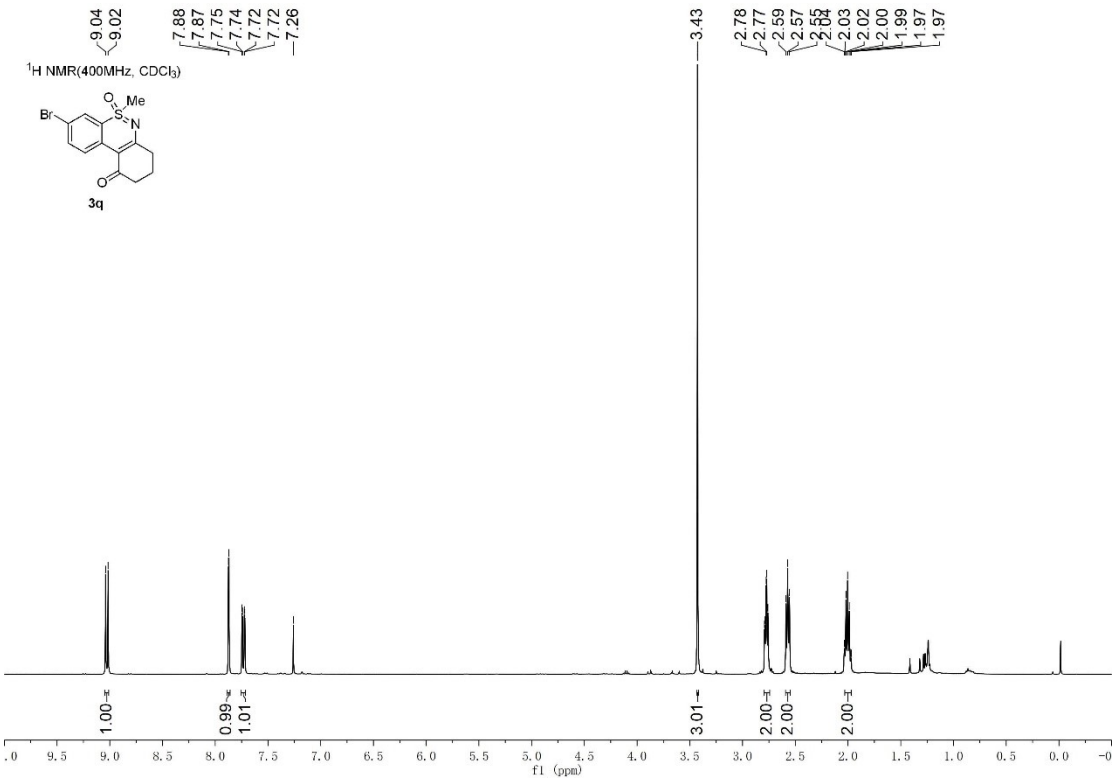

196.09
165.36
137.55
134.01
132.48
127.04
118.93
118.21
107.24
77.48
77.16
76.84
48.92
39.75
35.17
20.65
13C NMR(100MHz, CDCl3)
Br
O
Me
S
N
O
3n
f1 (ppm)

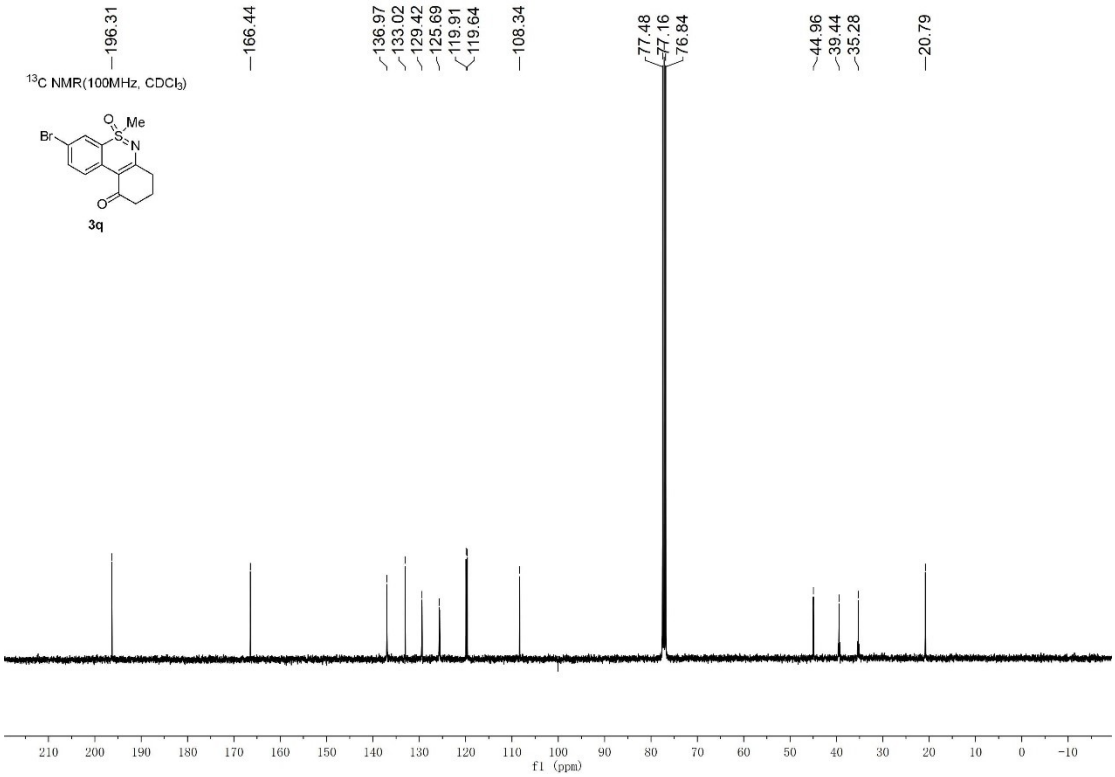

8.98
8.96
7.54
7.48
7.47
7.46
7.45
7.26
3.38
2.75
2.75
2.57
2.55
2.53
2.41
2.00
1.98
1.96
1.95
1H NMR(400MHz, CDCl3)
Me
Me
O
S
N
O
3o
1.00
1.00
1.00
3.00
2.00
2.01
3.00
2.00
f1 (ppm)

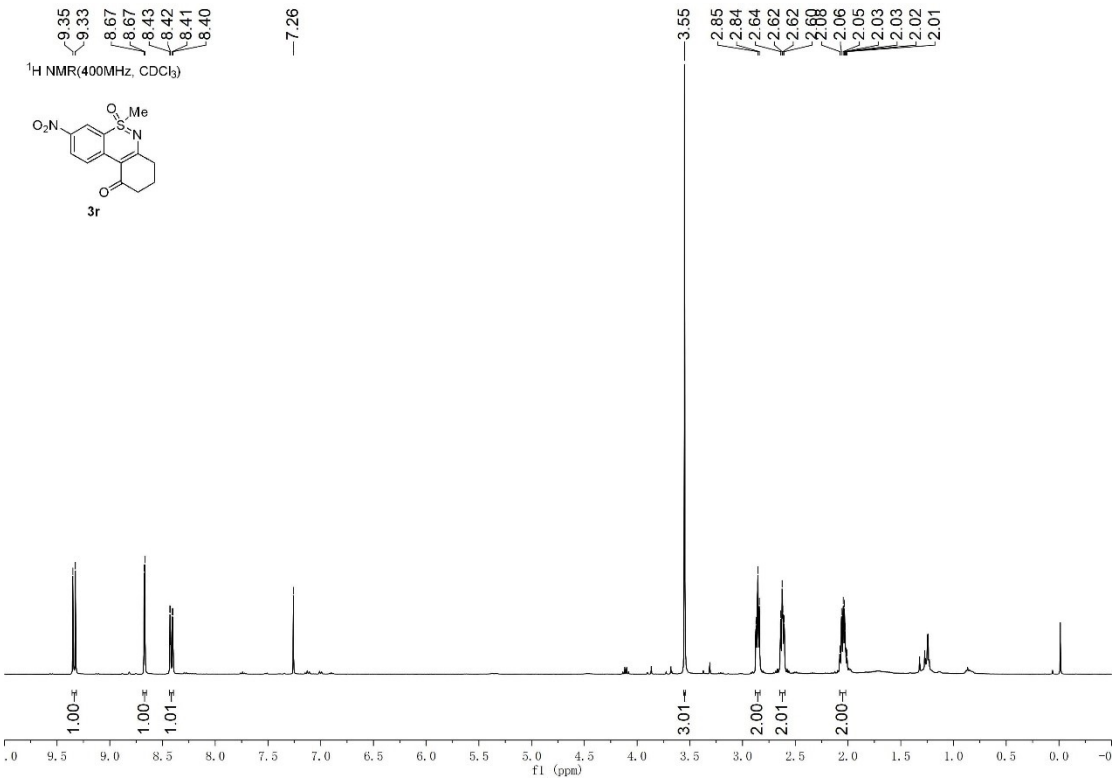

196.36
165.51
137.12
135.32
131.71
127.34
122.77
118.62
108.42
77.48
77.16
76.84
44.96
39.46
35.16
21.04
20.92
13C NMR(100MHz, CDCl3)
Me
Me
O
S
N
O
3o
f1 (ppm)

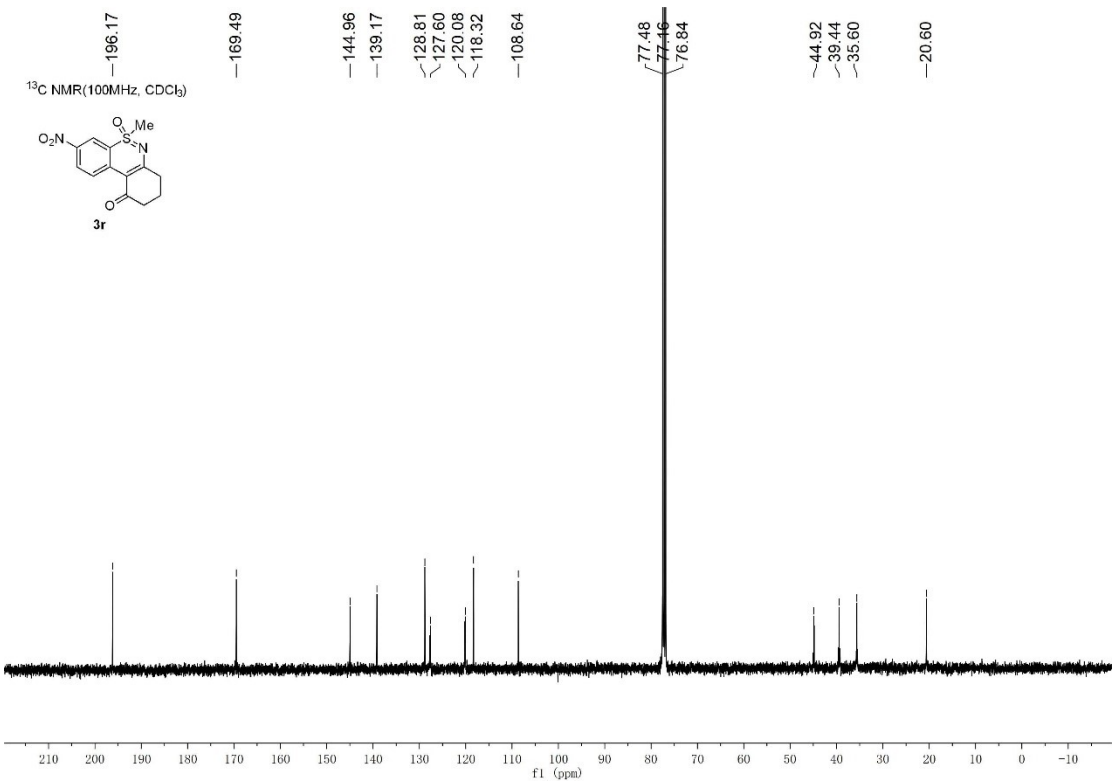

9.07
9.05
7.29
7.28
7.27
7.26
7.19
7.18
3.89
3.38
2.78
2.77
2.59
2.58
2.01
1.99
1H NMR(400MHz, CDCl3)
MeO
Me
O
S
N
O
3p
1.00
1.01
0.99
3.02
3.01
1.98
2.00
1.99
f1 (ppm)

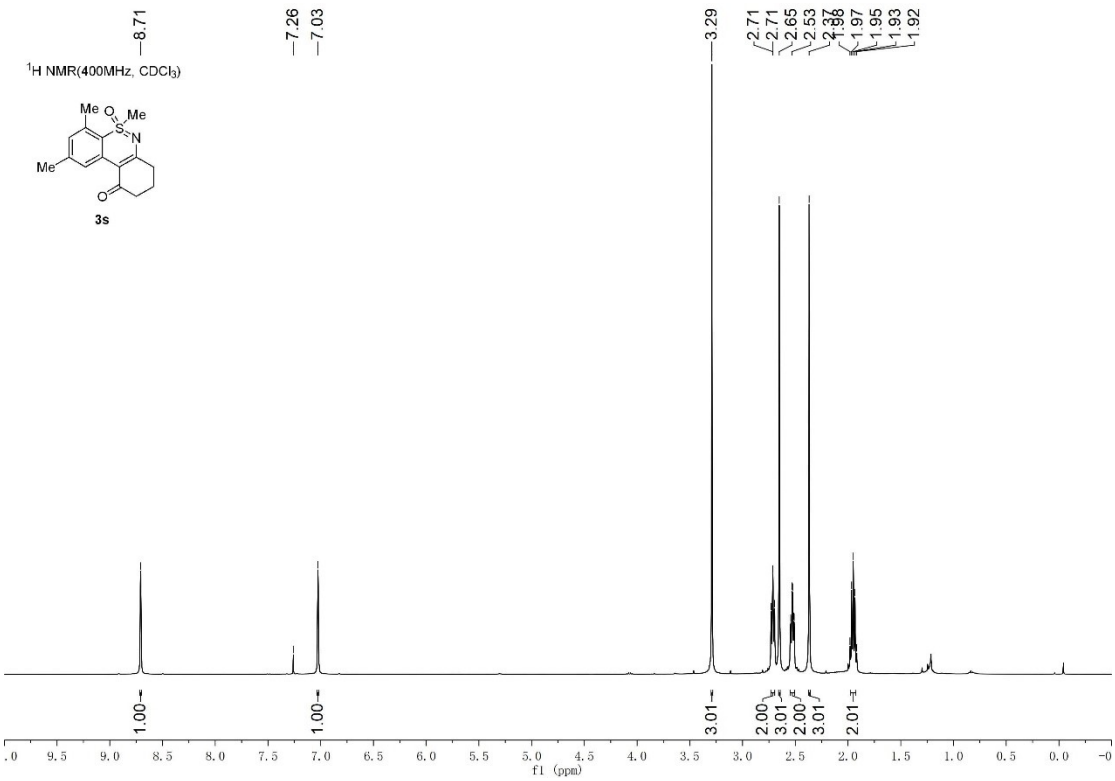

196.47
164.41
158.26
129.55
127.91
122.22
119.44
108.67
105.64
77.37
77.16
76.95
55.89
45.04
39.51
35.06
21.06
13C NMR(150MHz, CDCl3)
MeO
Me
O
S
N
O
3p
f1 (ppm)

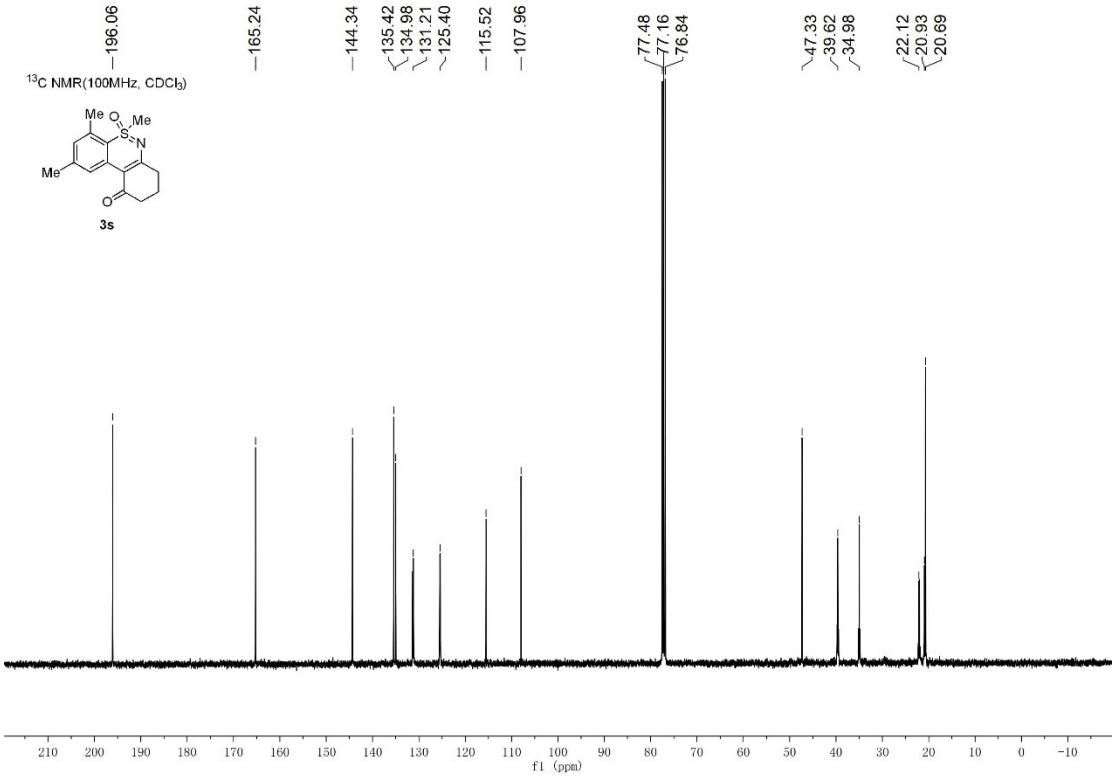

9.04
9.02
7.88
7.87
7.75
7.74
7.72
7.72
7.26
3.43
2.78
2.77
2.59
2.57
2.03
2.02
2.00
1.99
1.97
1.97
1H NMR(400MHz, CDCl3)
Me
Br
3q
1.00
0.99
1.01
3.01
2.00
2.00
2.00
f1 (ppm)

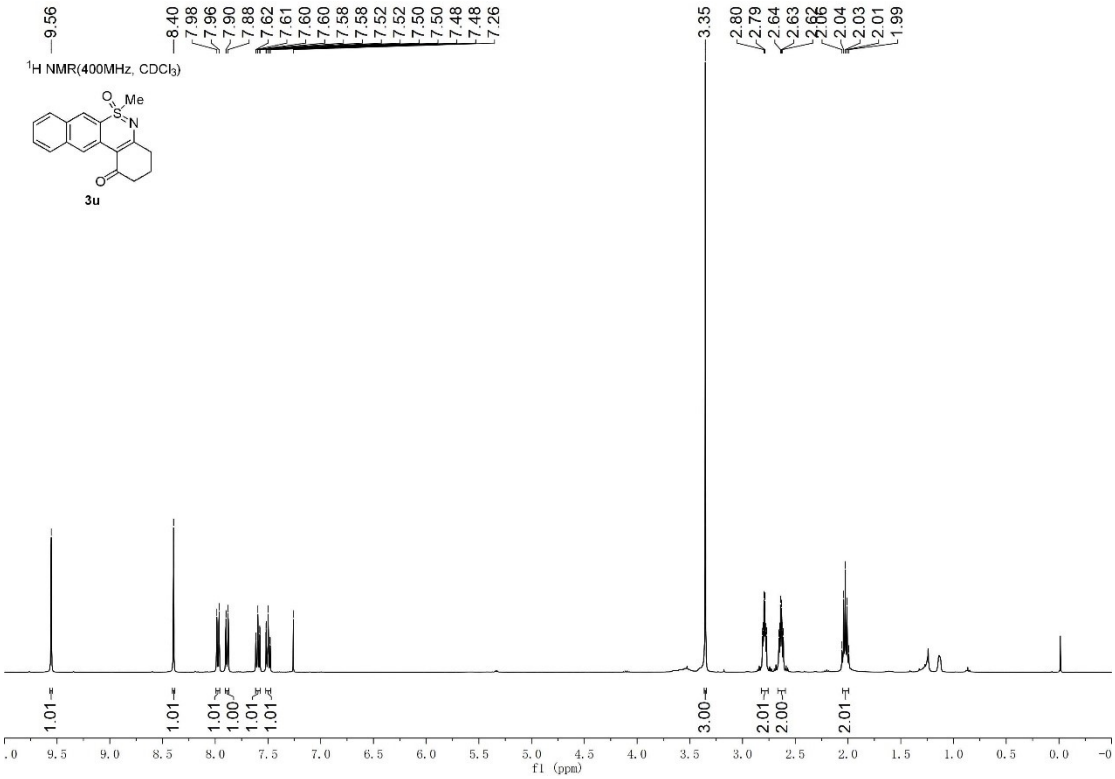

196.31
166.44
136.97
133.02
129.42
125.69
119.91
119.64
108.34
77.48
77.16
76.84
44.96
39.44
35.28
20.79
13C NMR(100MHz, CDCl3)
Me
Br
3q
f1 (ppm)

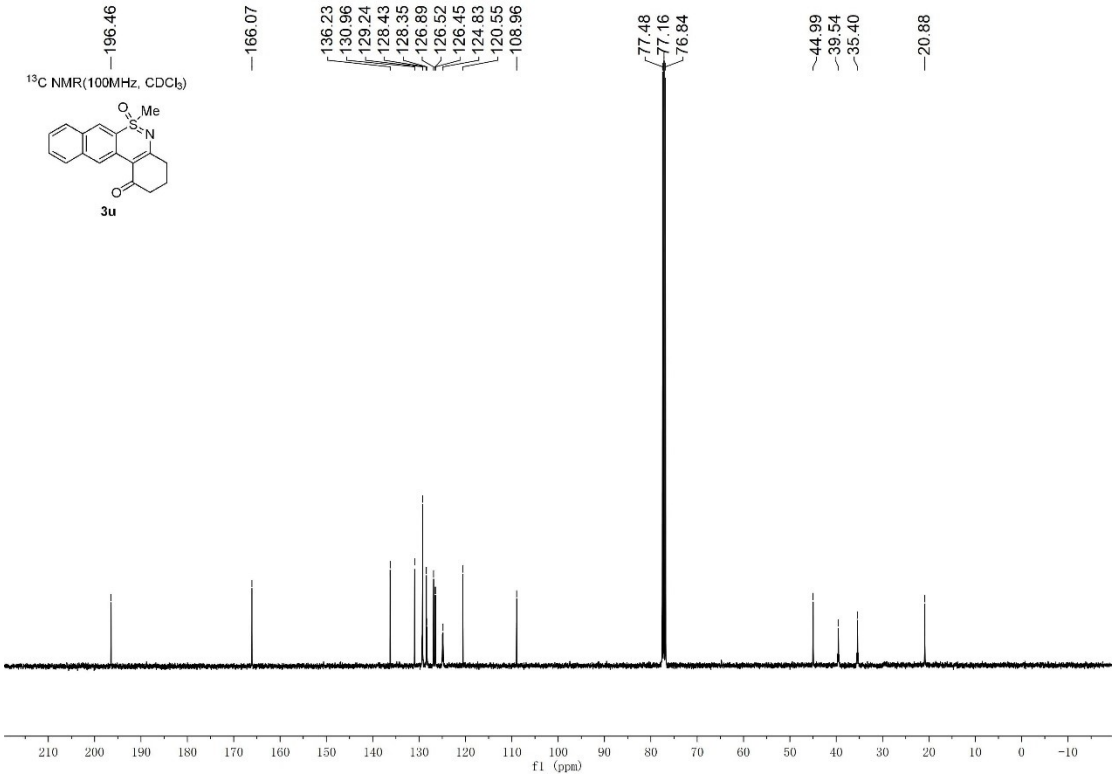

9.35
9.33
8.67
8.67
8.43
8.42
8.41
8.40
7.26
3.55
2.85
2.84
2.64
2.62
2.62
2.60
2.06
2.05
2.03
2.03
2.02
2.01
1H NMR(400MHz, CDCl3)
Me
O2N
3r
1.00
1.00
1.01
3.01
2.00
2.01
2.00
f1 (ppm)

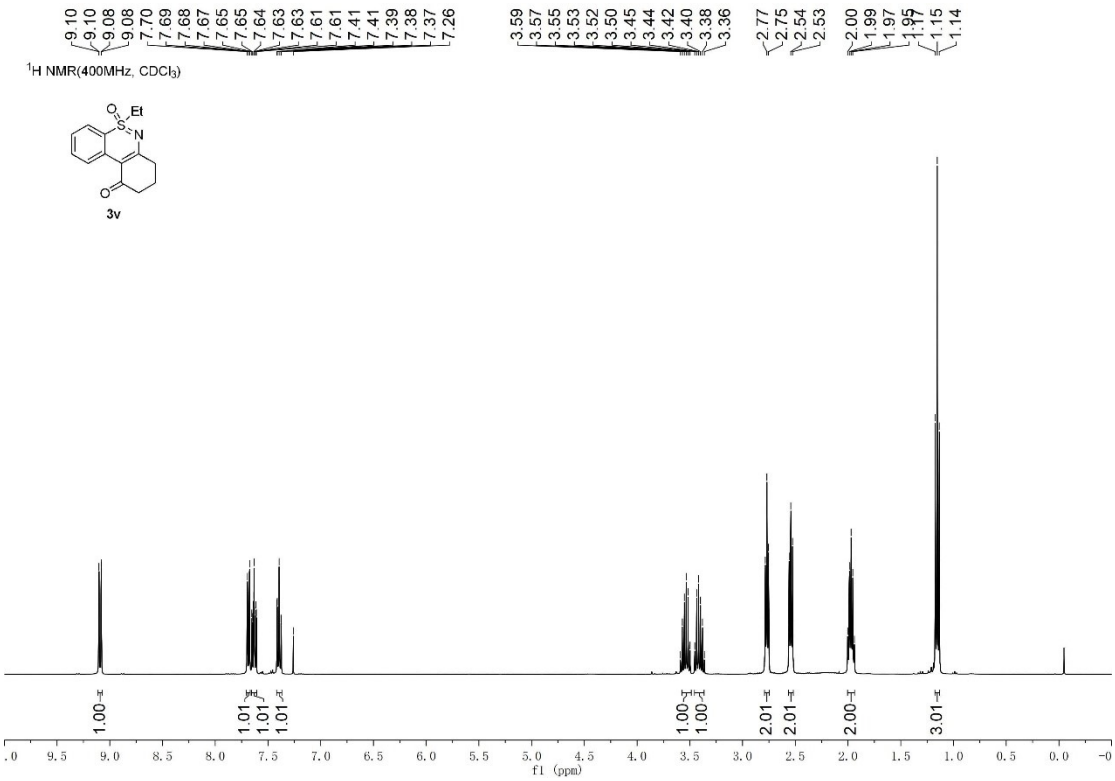

196.17
169.49
144.96
139.17
128.81
127.60
120.08
118.32
108.64
77.48
77.16
76.84
44.92
39.44
35.60
20.60
13C NMR(100MHz, CDCl3)
Me
O2N
3r
f1 (ppm)

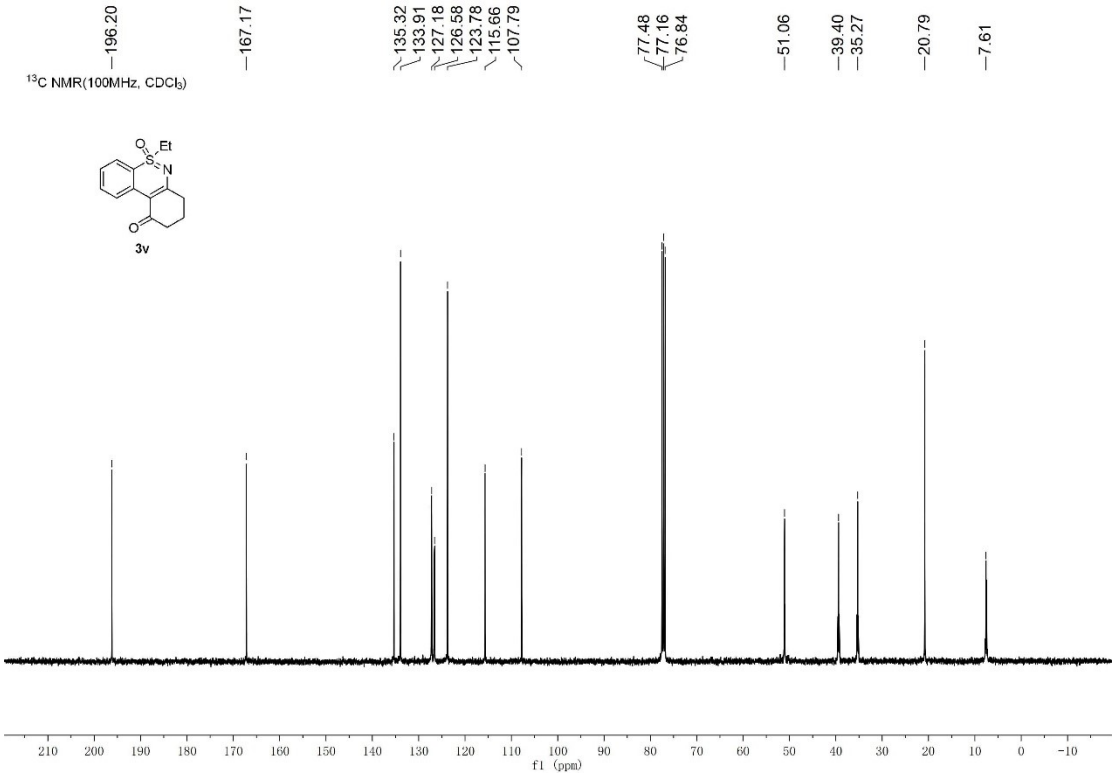

8.71
7.26
7.03
3.29
2.71
2.71
2.65
2.53
2.37
1.97
1.95
1.93
1.92
1H NMR(400MHz, CDCl3)
Me
O
Me
S
N
Me
O
3s
1.00
1.00
3.01
2.00
3.01
2.00
3.01
2.01
f1 (ppm)

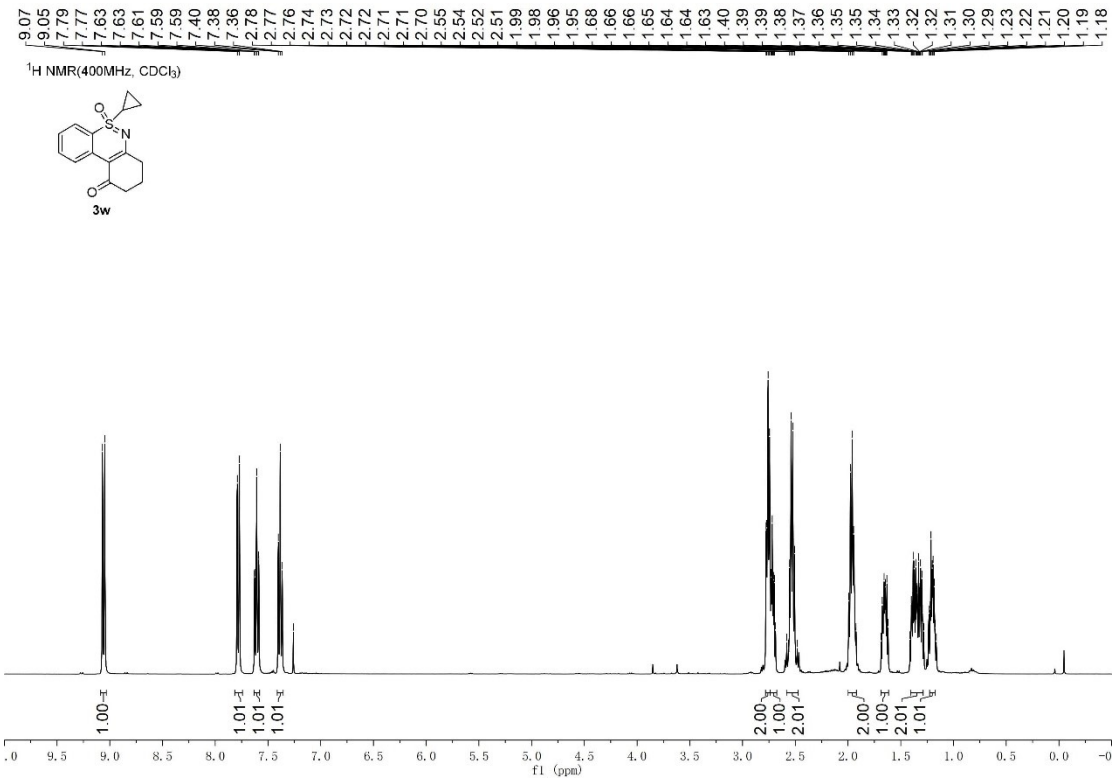

196.06
165.24
144.34
135.42
134.98
131.21
125.40
115.52
107.96
77.48
77.16
76.84
47.33
39.62
34.98
22.12
20.93
20.69
13C NMR(100MHz, CDCl3)
Me
O
Me
S
N
Me
O
3s
f1 (ppm)

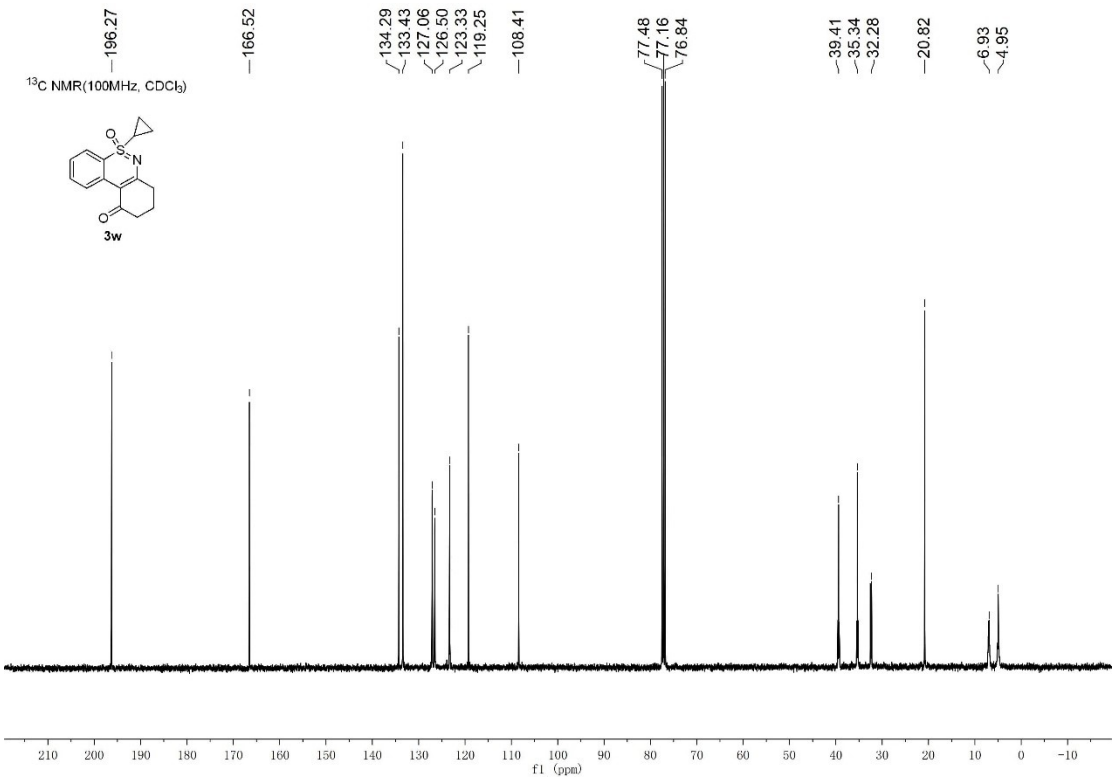

9.56
8.40
7.98
7.96
7.90
7.88
7.62
7.61
7.60
7.60
7.58
7.58
7.52
7.52
7.50
7.50
7.48
7.48
7.26
3.35
2.80
2.79
2.64
2.63
2.62
2.06
2.04
2.03
2.01
1.99
1H NMR(400MHz, CDCl3)
Me
O
S
N
O
3u
1.01
1.01
1.01
1.00
1.01
1.01
3.00
2.01
2.00
2.01
f1 (ppm)

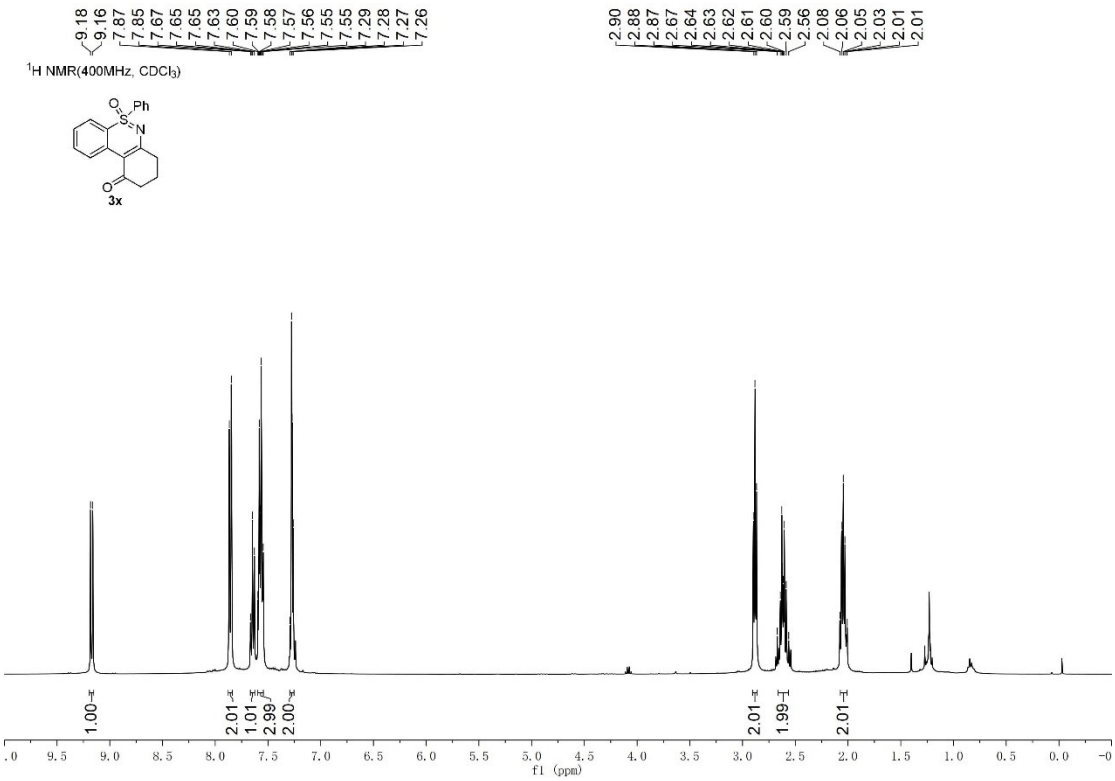

196.46
166.07
136.23
130.96
129.24
128.43
128.35
126.89
126.52
126.45
124.83
120.55
108.96
77.48
77.16
76.84
44.99
39.54
35.40
20.88
13C NMR(100MHz, CDCl3)
Me
O
S
N
O
3u
f1 (ppm)

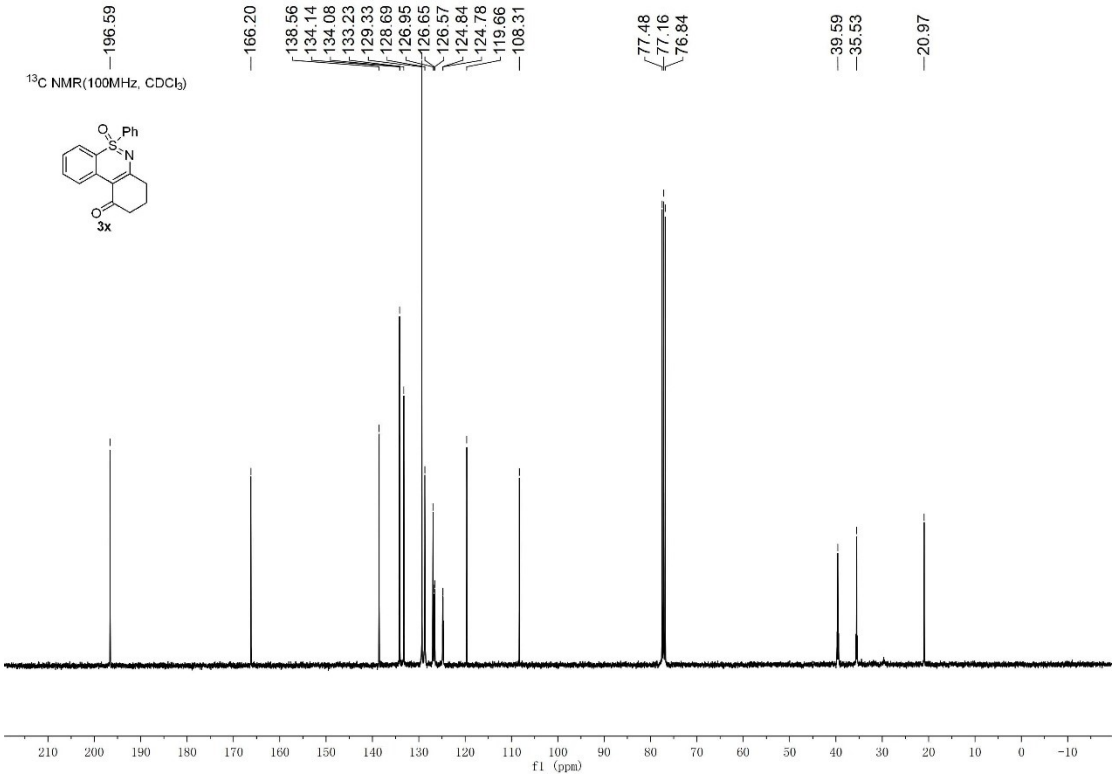

9.10
9.10
9.08
9.08
7.70
7.69
7.68
7.67
7.65
7.65
7.64
7.63
7.63
7.61
7.61
7.41
7.41
7.39
7.38
7.37
7.26
3.59
3.57
3.55
3.53
3.52
3.50
3.45
3.44
3.42
3.40
3.38
3.36
2.77
2.75
2.54
2.53
2.00
1.99
1.97
1.95
1.17
1.15
1.14
1H NMR(400MHz, CDCl3)
Et
O
S
N
O
3v
1.00
1.01
1.01
1.01
1.00
1.00
2.01
2.01
2.00
3.01
f1 (ppm)

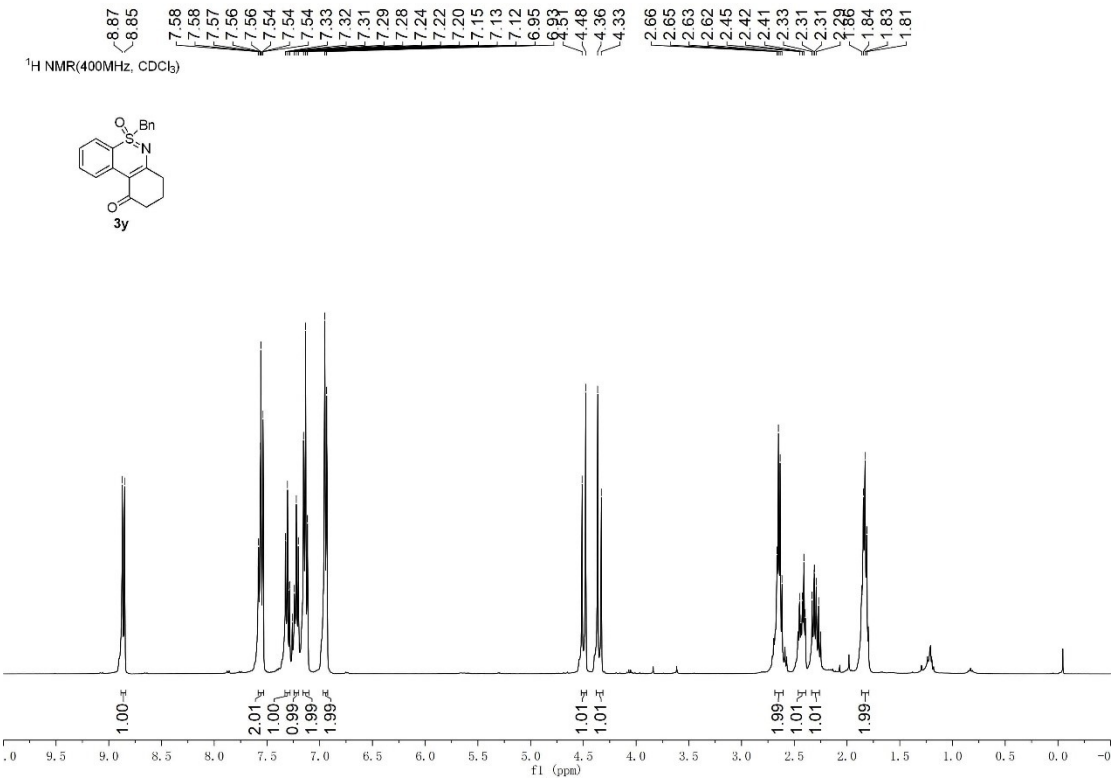

196.20
167.17
135.32
133.91
127.18
126.58
123.78
115.66
107.79
77.48
77.16
76.84
51.06
39.40
35.27
20.79
7.61
13C NMR(100MHz, CDCl3)
Et
O
S
N
O
3v
f1 (ppm)

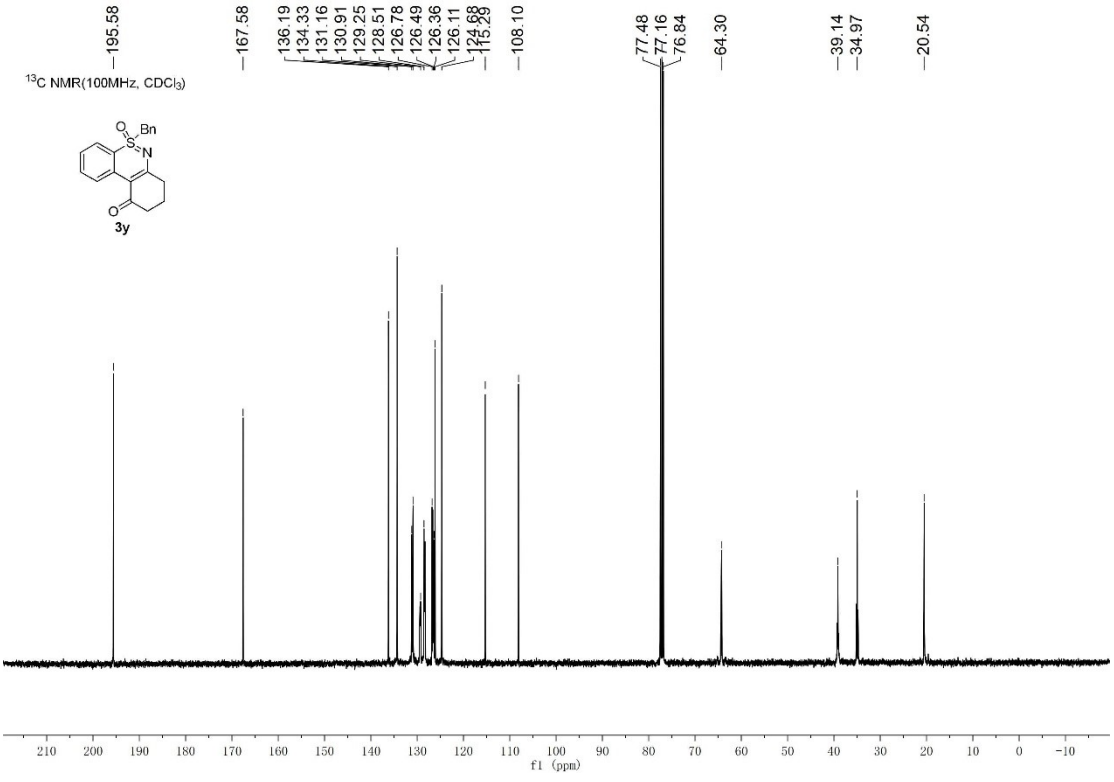

9.07 9.05 7.79 7.77 7.63 7.63 7.61 7.59 7.59 7.40 7.38 7.36 2.78 2.77 2.76 2.74 2.73 2.72 2.72 2.71 2.71 2.70 2.55 2.54 2.52 2.51 1.99 1.98 1.96 1.95 1.68 1.66 1.66 1.65 1.64 1.64 1.63 1.40 1.39 1.39 1.38 1.37 1.36 1.35 1.35 1.34 1.33 1.32 1.32 1.31 1.30 1.29 1.23 1.22 1.21 1.20 1.19 1.18
1H NMR(400MHz, CDCl3)
3w
1.00 1.01 1.01 1.01 2.00 1.00 2.01 2.00 1.00 2.01 1.01
f1 (ppm)

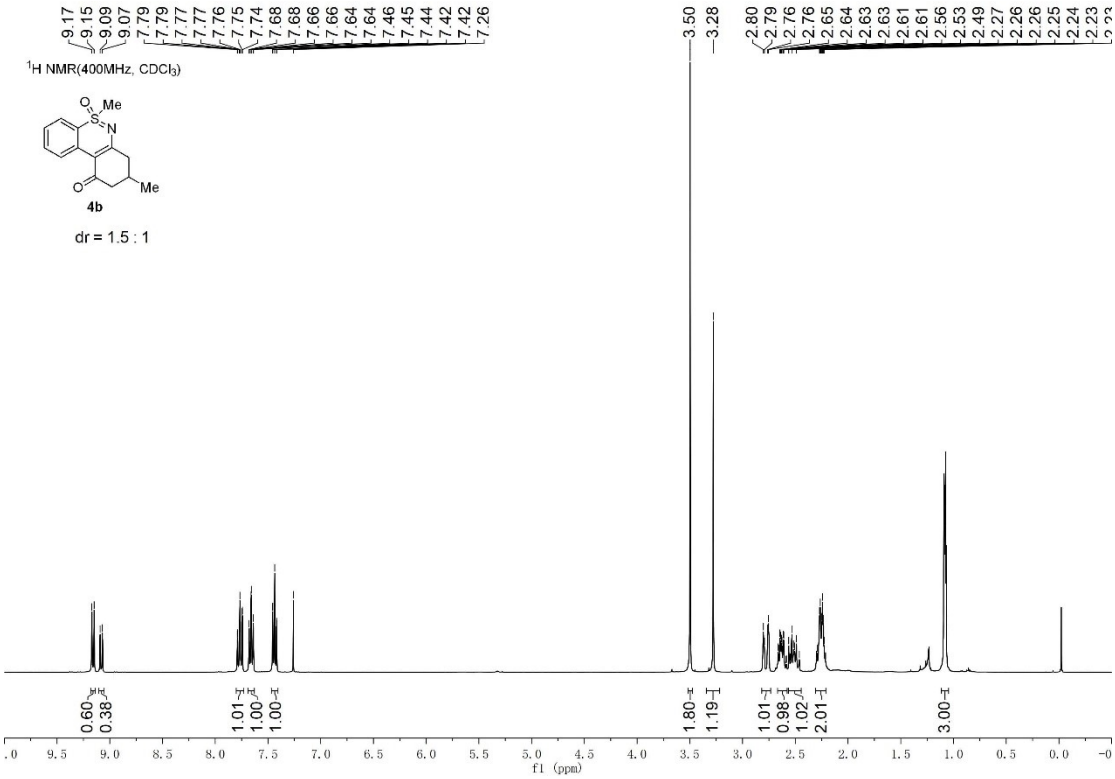

196.27 166.52 134.29 133.43 127.06 126.50 123.33 119.25 108.41 77.48 77.16 76.84 39.41 35.34 32.28 20.82 6.93 4.95
13C NMR(100MHz, CDCl3)
3w
f1 (ppm)

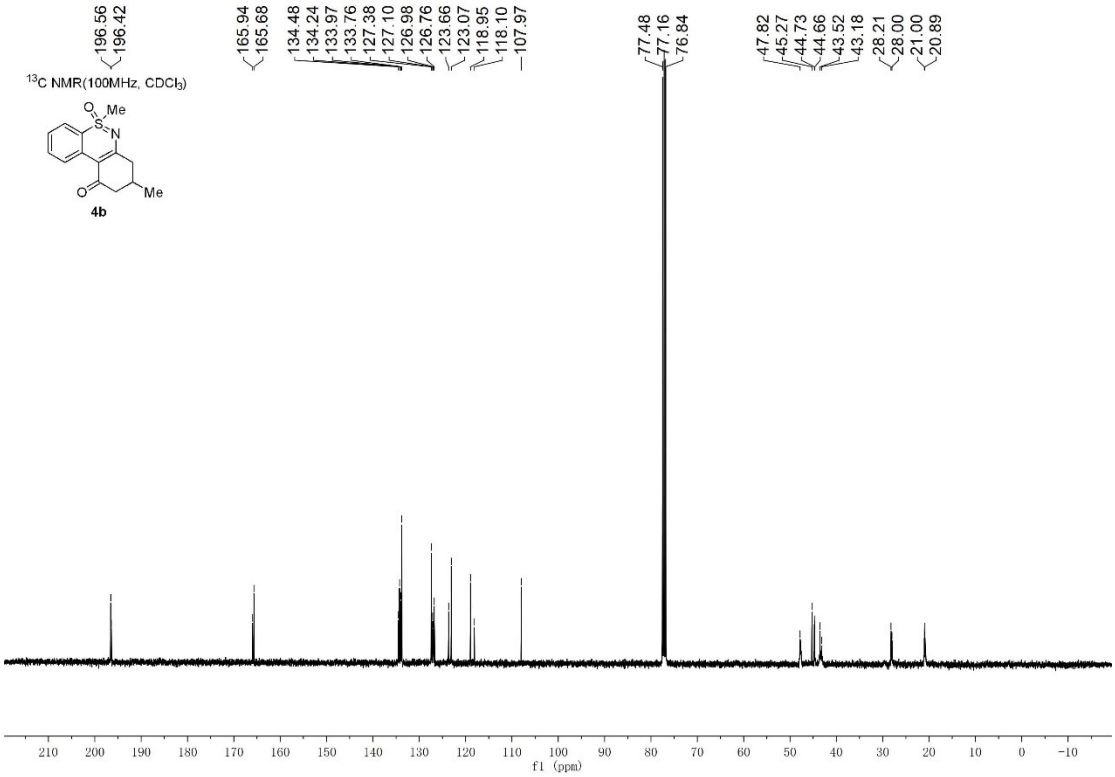

9.18
9.16
7.87
7.85
7.67
7.65
7.65
7.63
7.60
7.59
7.58
7.57
7.56
7.55
7.55
7.29
7.28
7.27
7.26
2.90
2.88
2.87
2.67
2.64
2.63
2.62
2.61
2.60
2.59
2.56
2.08
2.06
2.05
2.03
2.01
2.01
1H NMR(400MHz, CDCl3)
Ph
O
S
N
O
3x
1.00
2.01
1.01
2.99
2.00
2.01
1.99
2.01
f1 (ppm)

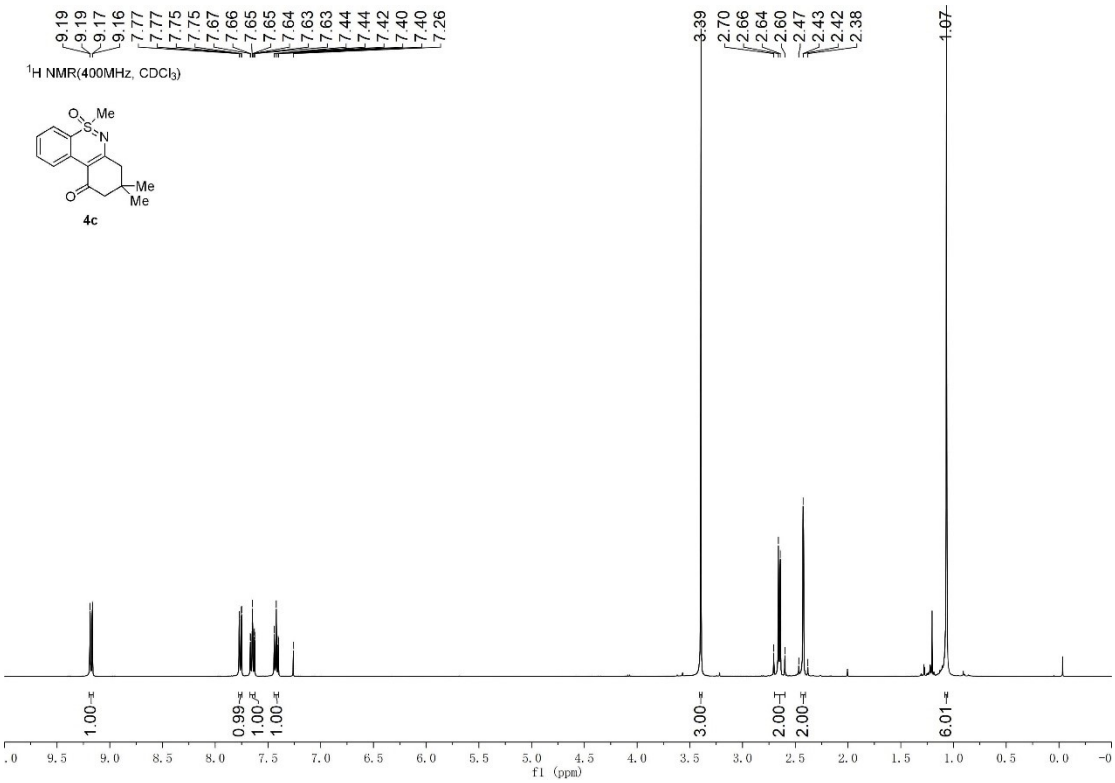

196.59
166.20
138.56
134.14
134.08
133.23
129.33
128.69
126.95
126.65
126.57
124.84
124.78
119.66
108.31
77.48
77.16
76.84
39.59
35.53
20.97
13C NMR(100MHz, CDCl3)
Ph
O
S
N
O
3x
f1 (ppm)

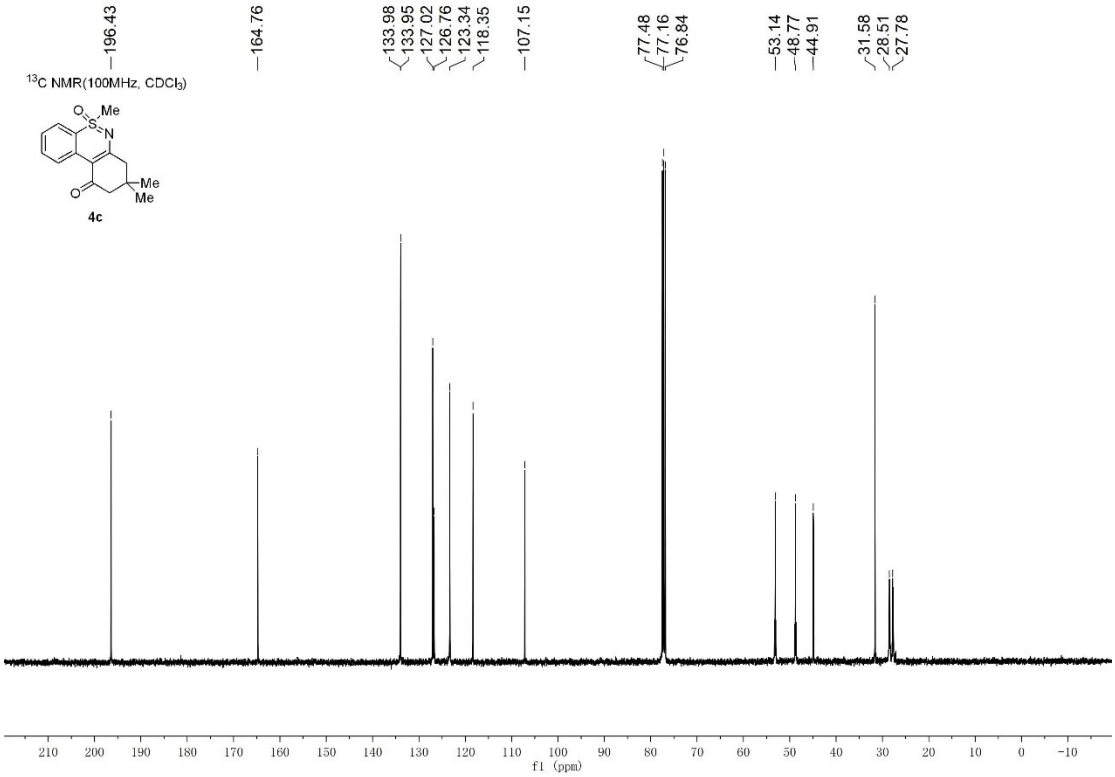

8.87
8.85
7.58
7.58
7.57
7.56
7.56
7.54
7.54
7.54
7.33
7.32
7.31
7.29
7.28
7.24
7.22
7.20
7.15
7.13
7.12
6.95
6.93
4.51
4.48
4.36
4.33
2.66
2.65
2.63
2.62
2.45
2.42
2.41
2.33
2.31
2.31
2.29
1.88
1.84
1.83
1.81
1H NMR(400MHz, CDCl3)
Bn
O
S
N
O
3y
1.00
2.01
1.00
0.99
1.99
1.99
1.01
1.01
1.99
1.01
1.01
1.99
f1 (ppm)

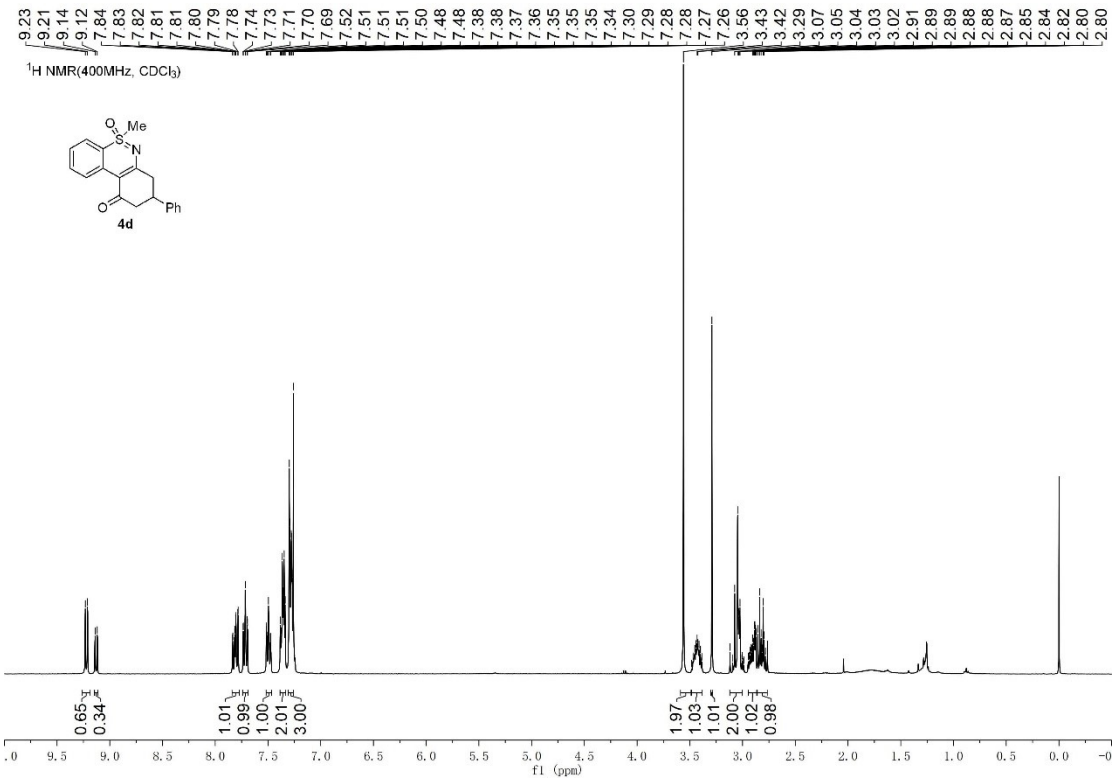

195.58
167.58
136.19
134.33
131.16
130.91
129.25
128.51
126.78
126.49
126.36
126.11
124.68
115.29
108.10
77.48
77.16
76.84
64.30
39.14
34.97
20.54
13C NMR(100MHz, CDCl3)
Bn
O
S
N
O
3y
f1 (ppm)

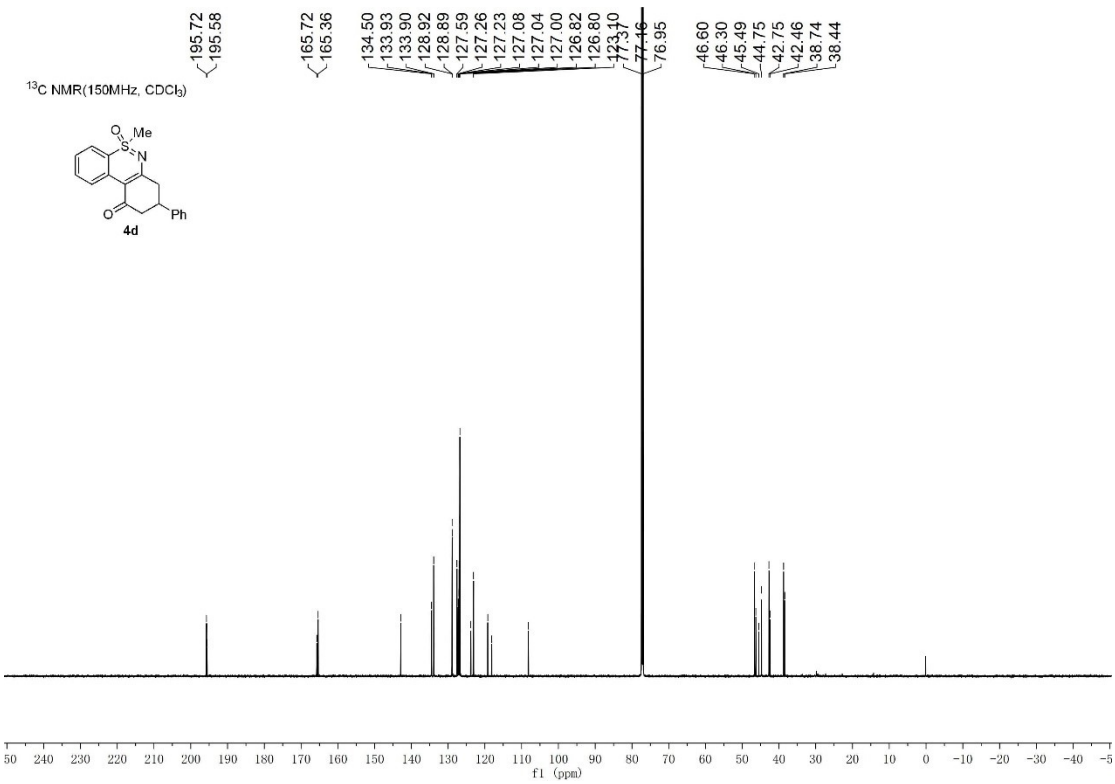

9.17
9.15
9.09
9.07
7.79
7.79
7.77
7.77
7.76
7.75
7.74
7.68
7.68
7.66
7.66
7.64
7.64
7.46
7.45
7.44
7.42
7.42
7.26
3.50
3.28
2.80
2.79
2.76
2.76
2.65
2.64
2.63
2.63
2.61
2.61
2.56
2.53
2.49
2.27
2.26
2.26
2.25
2.24
2.23
1H NMR(400MHz, CDCl3)
Me
N
Me
4b
dr = 1.5 : 1
0.60
0.38
1.01
1.00
1.00
1.80
1.19
1.01
0.98
1.02
2.01
3.00
f1 (ppm)

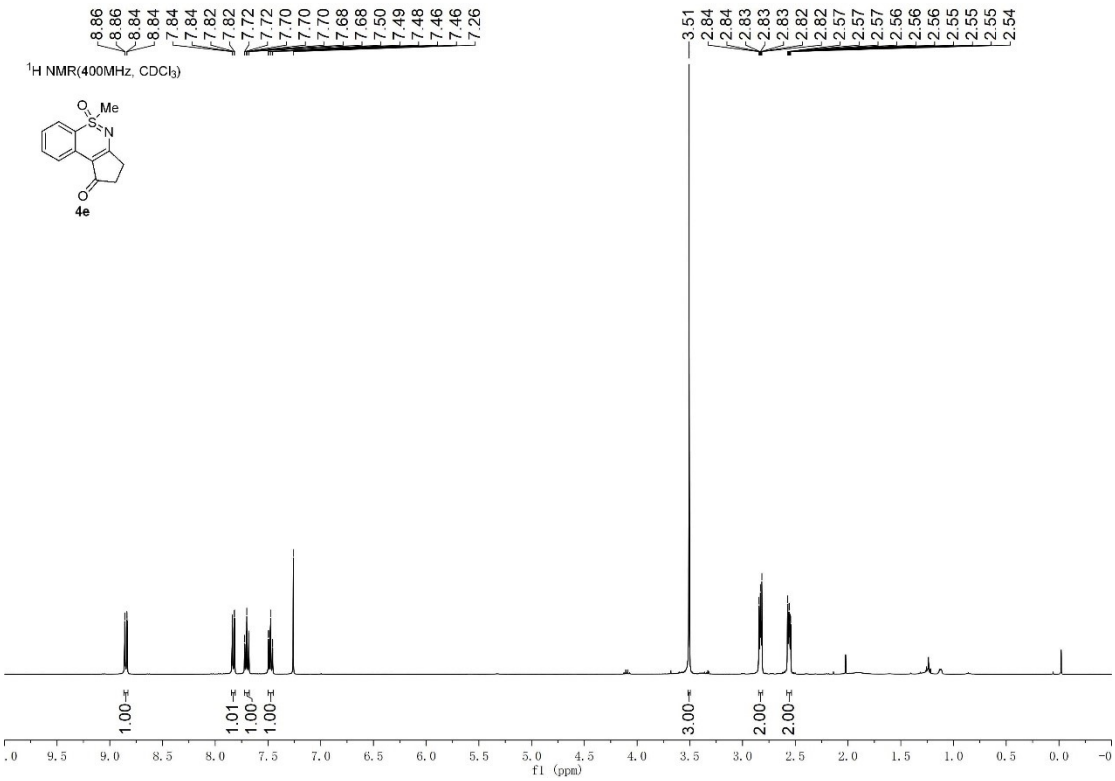

196.56
196.42
165.94
165.68
134.48
134.24
133.97
133.76
127.38
127.10
126.98
126.76
123.66
123.07
118.95
118.10
107.97
77.48
77.16
76.84
47.82
45.27
44.73
44.66
43.52
43.18
28.21
28.00
21.00
20.89
13C NMR(100MHz, CDCl3)
Me
N
Me
4b
f1 (ppm)

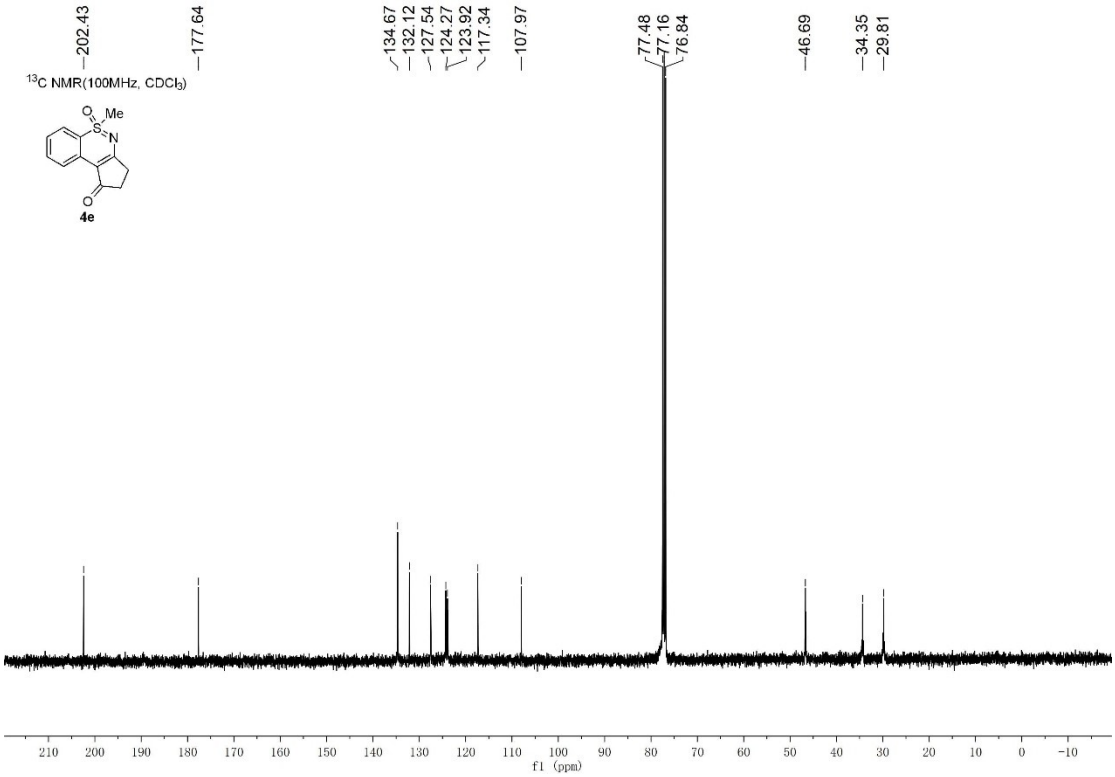

9.19
9.19
9.17
9.16
7.77
7.77
7.75
7.75
7.67
7.66
7.65
7.65
7.64
7.63
7.63
7.44
7.44
7.42
7.40
7.40
7.26
3.39
2.70
2.66
2.64
2.60
2.47
2.43
2.42
2.38
1.07
1H NMR(400MHz, CDCl3)
Me
N
Me
Me
4c
1.00
0.99
1.00
1.00
3.00
2.00
2.00
6.01
f1 (ppm)

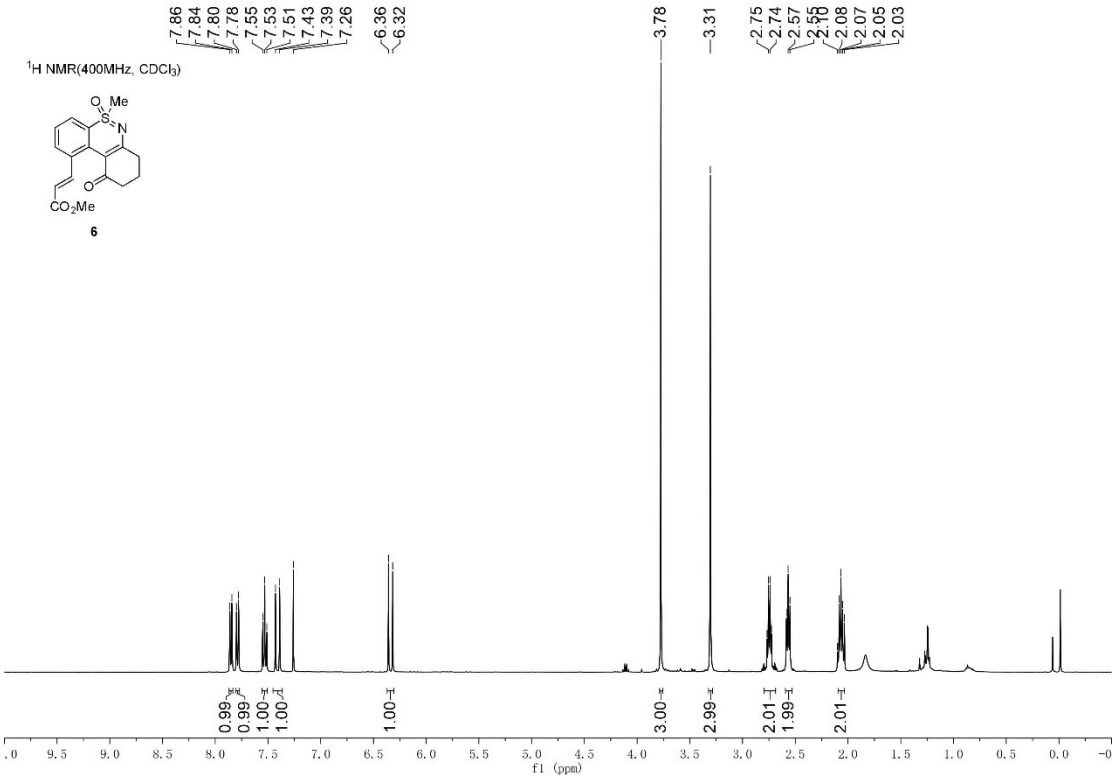

196.43
164.76
133.98
133.95
127.02
126.76
123.34
118.35
107.15
77.48
77.16
76.84
53.14
48.77
44.91
31.58
28.51
27.78
13C NMR(100MHz, CDCl3)
Me
N
Me
Me
4c
f1 (ppm)

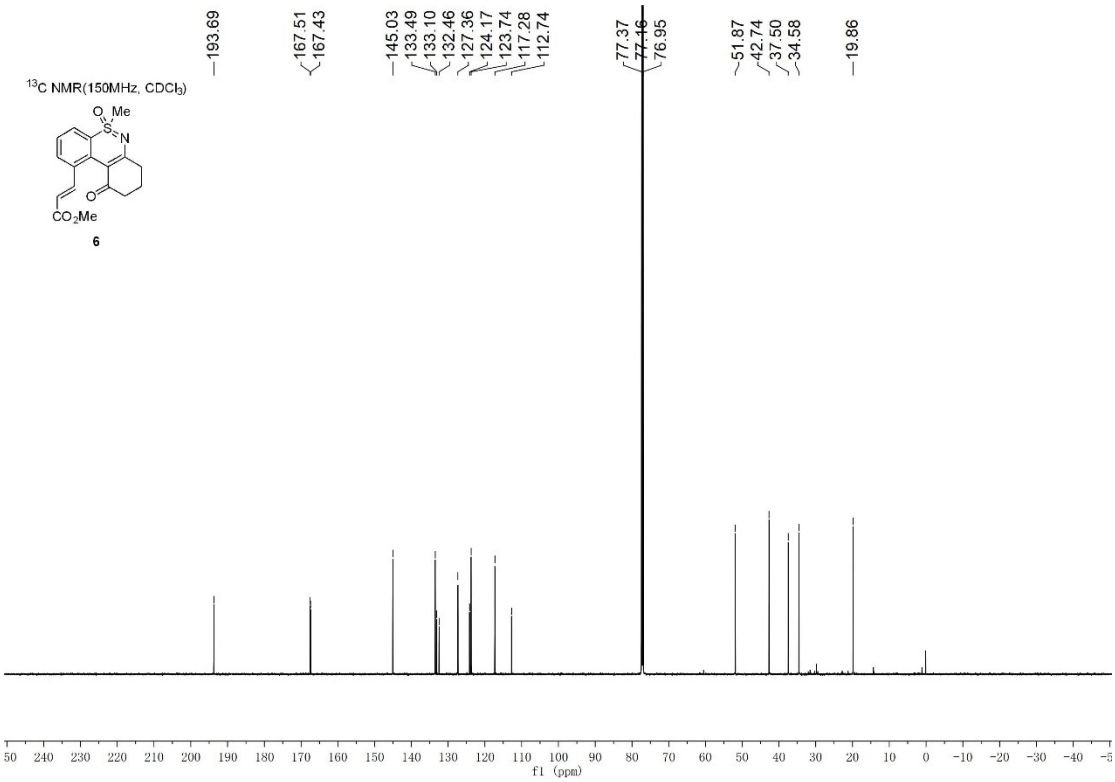

9.23
9.21
9.14
9.12
7.84
7.83
7.82
7.81
7.81
7.80
7.79
7.78
7.74
7.73
7.71
7.70
7.69
7.52
7.51
7.51
7.51
7.50
7.48
7.48
7.38
7.38
7.37
7.36
7.35
7.35
7.35
7.34
7.30
7.29
7.28
7.28
7.27
7.26
3.56
3.43
3.42
3.29
3.07
3.05
3.04
3.03
3.02
2.91
2.89
2.89
2.88
2.88
2.87
2.85
2.84
2.82
2.80
2.80
1H NMR(400MHz, CDCl3)
Me
S
O
N
O
Ph
4d
0.65
0.34
1.01
0.99
1.00
2.01
3.00
1.97
1.03
1.01
2.00
1.02
0.98
f1 (ppm)


195.72
195.58
165.72
165.36
134.50
133.93
133.90
128.92
128.89
127.59
127.26
127.23
127.08
127.04
127.00
126.82
126.80
123.10
77.37
77.16
76.95
46.60
46.30
45.49
44.75
42.75
42.46
38.74
38.44
13C NMR(150MHz, CDCl3)
Me
S
O
N
O
Ph
4d
f1 (ppm)


8.86
8.86
8.84
8.84
7.84
7.84
7.82
7.82
7.72
7.72
7.70
7.70
7.70
7.68
7.68
7.50
7.49
7.48
7.46
7.46
7.26
3.51
2.84
2.84
2.83
2.83
2.83
2.82
2.82
2.57
2.57
2.56
2.56
2.55
2.55
2.54
1H NMR(400MHz, CDCl3)
Me
S
N
O
O
4e
1.00
1.01
1.00
1.00
3.00
2.00
2.00
f1 (ppm)


202.43
177.64
134.67
132.12
127.54
124.27
123.92
117.34
107.97
77.48
77.16
76.84
46.69
34.35
29.81
13C NMR(100MHz, CDCl3)
Me
S
N
O
O
4e
f1 (ppm)


7.86
7.84
7.80
7.78
7.55
7.53
7.51
7.43
7.39
7.26
6.36
6.32
3.78
3.31
2.75
2.74
2.57
2.55
2.10
2.08
2.07
2.05
2.03
1H NMR(400MHz, CDCl3)
Me
O
S
N
O
CO2Me
6
0.99
0.99
1.00
1.00
1.00
3.00
2.99
2.01
1.99
2.01
f1 (ppm)


193.69
167.51
167.43
145.03
133.49
133.10
132.46
127.36
124.17
123.74
117.28
112.74
77.37
77.16
76.95
51.87
42.74
37.50
34.58
19.86
13C NMR(150MHz, CDCl3)
Me
O
S
N
O
CO2Me
6
f1 (ppm)

6 References

[1] J.-F. Lohier, T. Glachet, H. Marzag, A.-C. Gaumont and V. Reboul, *Chem. Commun.,* 2017, **53**, 2064.

[2] R. M. Moriarty, S. Tyagi, D. Ivanov and M. Constantinescu, *J. Am. Chem. Soc.,* 2008, **130**, 7564.