Supplementary Information

Silver-catalyzed direct spirocyclization of alkynes with thiophenols: a simple and facile approach to 3-thioazaspiro[4,5]trienones

Huanhuan Cui, Wei Wei,* Daoshan Yang, Jimei Zhang, Zhihong Xu,

Jiangwei Wen, HuaWang*[a]

The Key Laboratory of Life-Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China

*****Phone:+86 537 4458317; Fax:+86 537 4458317.

. E-mail: weiweiqfnu@163.com, huawang_qfnu@126.com

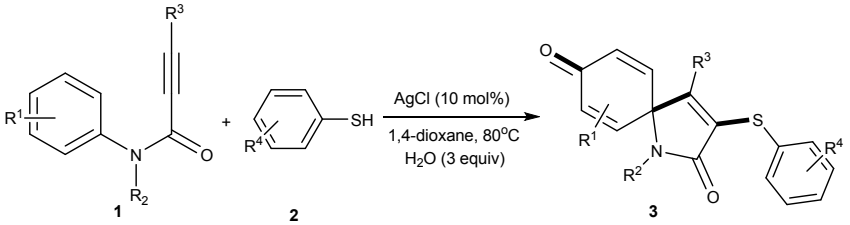
Contents

1.General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ with TMS as internal standard (400 MHz ^{1}H and 100 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq) and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). In a few cases the number of signals in the ^{13}C NMR spectrum is than due, which may be caused by the superimposition of signals. HRMS data were obtained by ESI on a TOF mass analyzer. Column chromatography was performed on silica gel (200-300 mesh). All N-

arylpropiolamides **1** were synthesized according to the known procedures.[1]

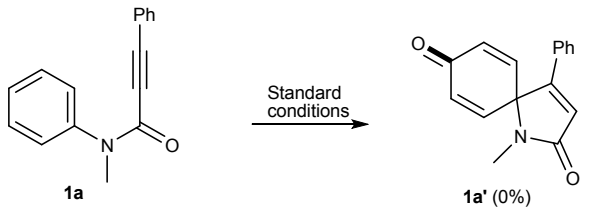
2. General procedure for silver-catalyzed spirocyclization of alkynes with thiophenols leading to 3-thioazaspiro[4,5]trienones.



To a mixture of N-arylpropiolamides **1** (0.25 mmol), thiophenols **2** (0.5 mmol), AgCl (10 mol%), and H_2O (0.75 mmol) in a 25 mL round-bottomed flack at room temperature, was added the 1,4-dioxane (2 mL). The reaction vessel was allowed to stir at 80^{o}C for 8-24h. After the reaction, the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3**.

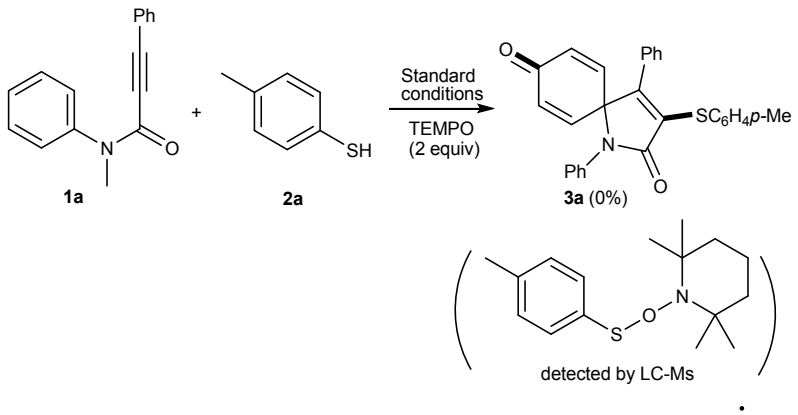
3. Preliminary mechanistic studies.

(1) The reaction of N-Arylpropiolamide **1a** under standard conditions



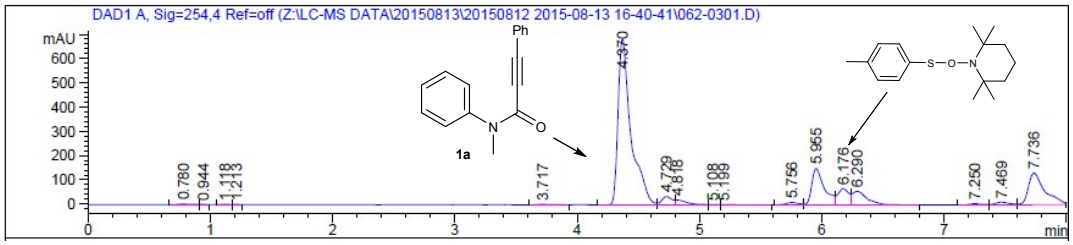
To a mixture of N-Arylpropiolamide **1a** (0.25 mmol), AgCl (10 mol%), H_2O (0.75 mmol) in a 25 mL round-bottomed flack at room temperature, was added the 1,4-dioxane (2 mL). The reaction vessel was allowed to stir at 80°C for 12h. After the reaction, the solution was concentrated in vacuum, no desired product **1a'** was detected.

(2) The reaction of **1a** and **2a** with TEMPO under the standard conditions**.**



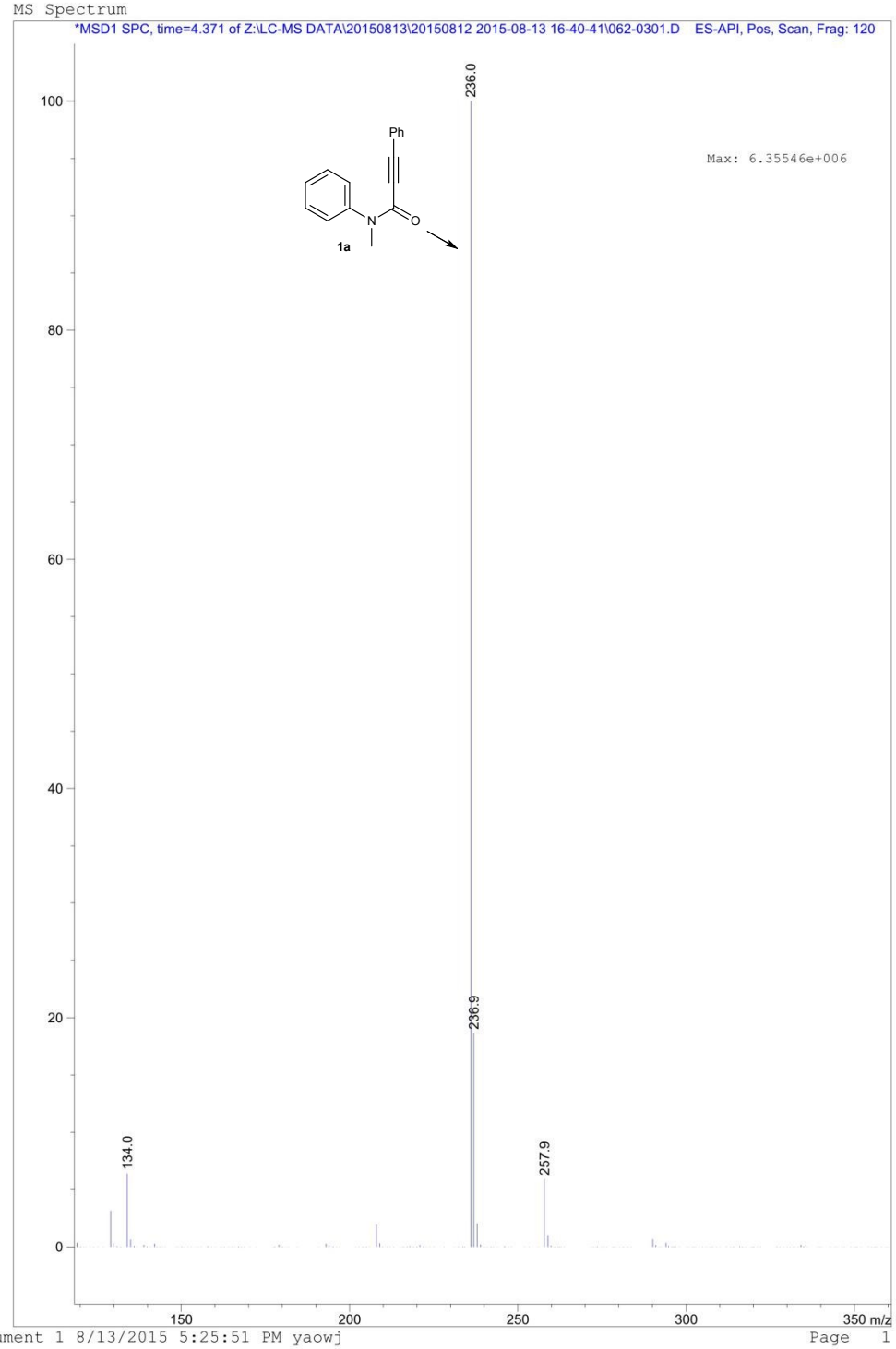
To a mixture of **1a** (0.25 mmol), **2a** (0.5 mmol), AgCl (10 mol%), H_2O (0.75mmol) and TEMPO (0.5 mmol) in a 25 mL round-bottomed flack at room temperature, was added the 1,4-dioxane (2 mL). The reaction vessel was allowed to stir at 80°C for 12 h. After the reaction, the solution was concentrated in vacuum, the TEMPO-trapped complex (*p*-MePhS-Tempo) was detected by LC-MS analysis and none of the desired product **3a** was detected.

```
Data File Z:\LC-MS DATA\20150813\20150812 2015-08-13 16-40-41\062-0301.D
Sample Name: CHH-8-9-2
    ======================================================================
    Acq. Operator   : yaowj                          Seq. Line :   3
    Acq. Instrument : Instrument 1                    Location : Vial 62
    Injection Date  : 8/13/2015 5:03:45 PM                 Inj :   1
                                                    Inj Volume : 2.000 µl
    Different Inj Volume from Sequence !     Actual Inj Volume : 10.000 µl
    Acq. Method     : Z:\LC-MS DATA\20150813\20150812 2015-08-13 16-40-41\SH-METHOD.M
    Last changed    : 7/31/2015 9:26:57 AM by ZXE
    Analysis Method : D:\METHOD\WYKM.M
    Last changed    : 8/13/2015 3:43:44 PM by yaowj
                      (modified after loading)

    Sample-related custom fields:

    Name                          |Value
    ------------------------------|---------------------------------------
    ======================================================================
```



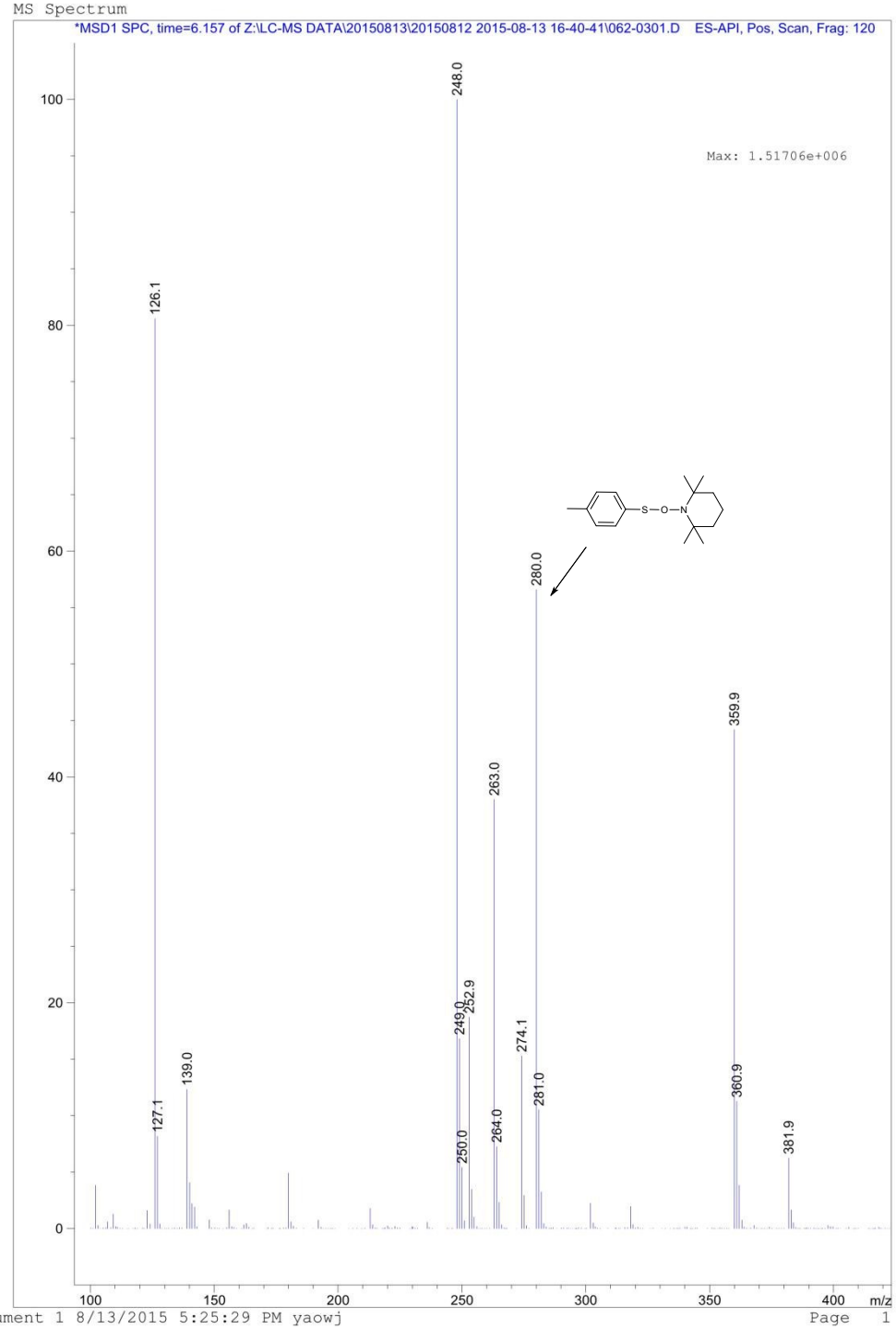
Print of window 80: MS Spectrum

MS Spectrum

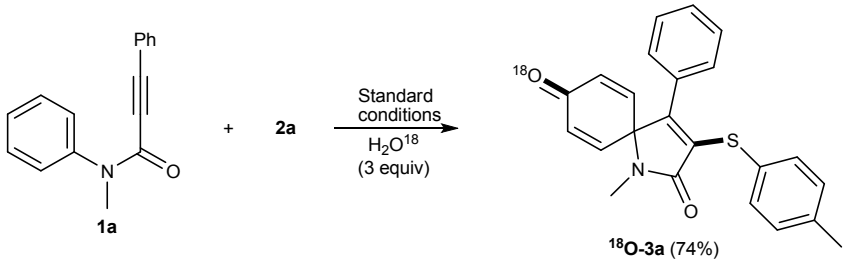


Print of window 80: MS Spectrum

MS Spectrum



(3) Labeling experiment.



To a mixture of N-arylpropiolamide **1a** (0.25 mmol), 4-methylbenzenethiol **2a** (0.5 mmol), AgCl (10 mol%), and $H_2{}^{18}O$ (0.75 mmol) in a 25 mL round-bottomed flack at room temperature, was added the 1,4-dioxane (2 mL). The reaction vessel was allowed to stir at 80°C for 12 h. After the reaction, the solution was concentrated in vacuum, The residue was purified by flash column chromatography to give the corresponding labeling product in 74% yield.

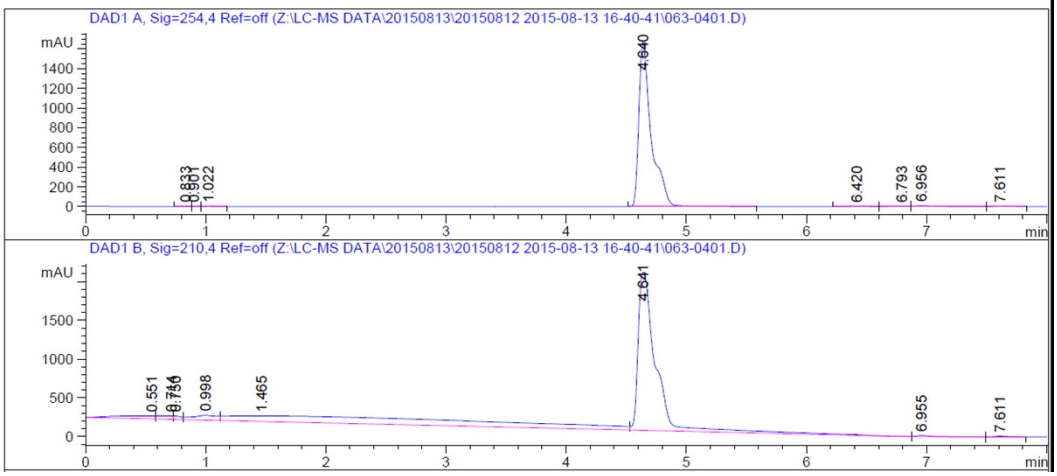
The LC-MS spectrum of product was listed as bellow.

Data File Z:\LC-MS DATA\20150813\20150812 2015-08-13 16-40-41\063-0401.D
Sample Name: CHH-8-3-3

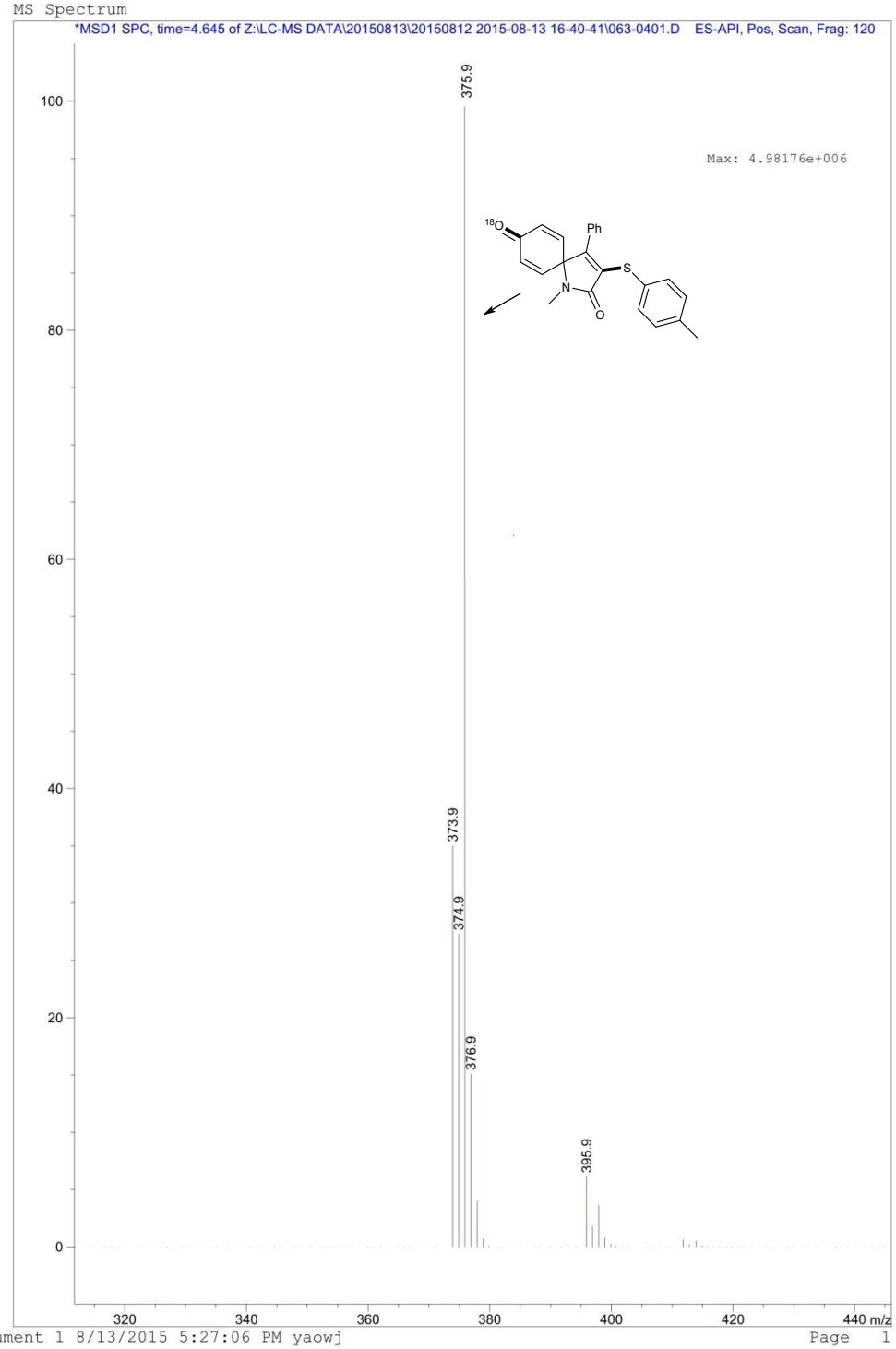
Acq. Operator	: yaowj	Seq. Line	: 4
Acq. Instrument	: Instrument 1	Location	: Vial 63
Injection Date	: 8/13/2015 5:13:57 PM	Inj	: 1
		Inj Volume	: 2.000 µl
Acq. Method	: Z:\LC-MS DATA\20150813\20150812 2015-08-13 16-40-41\SH-METHOD.M		
Last changed	: 7/31/2015 9:26:57 AM by ZXE		
Analysis Method	: D:\METHOD\WYKM.M		
Last changed	: 8/13/2015 3:43:44 PM by yaowj (modified after loading)		

Sample-related custom fields:

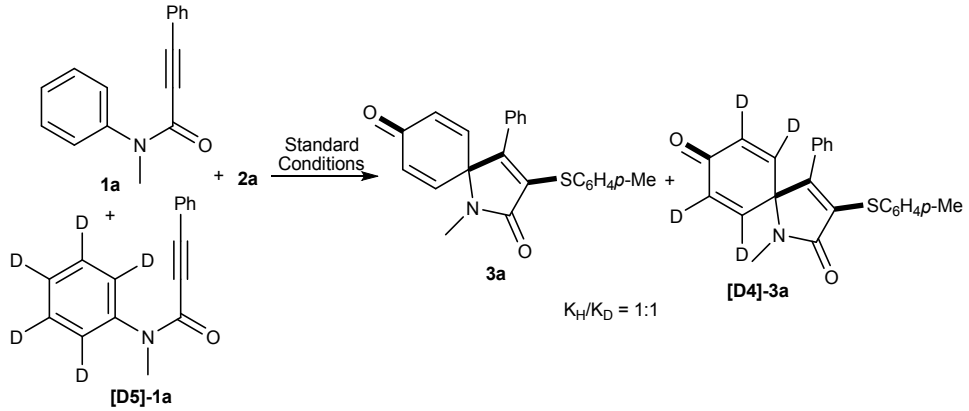
Name	Value



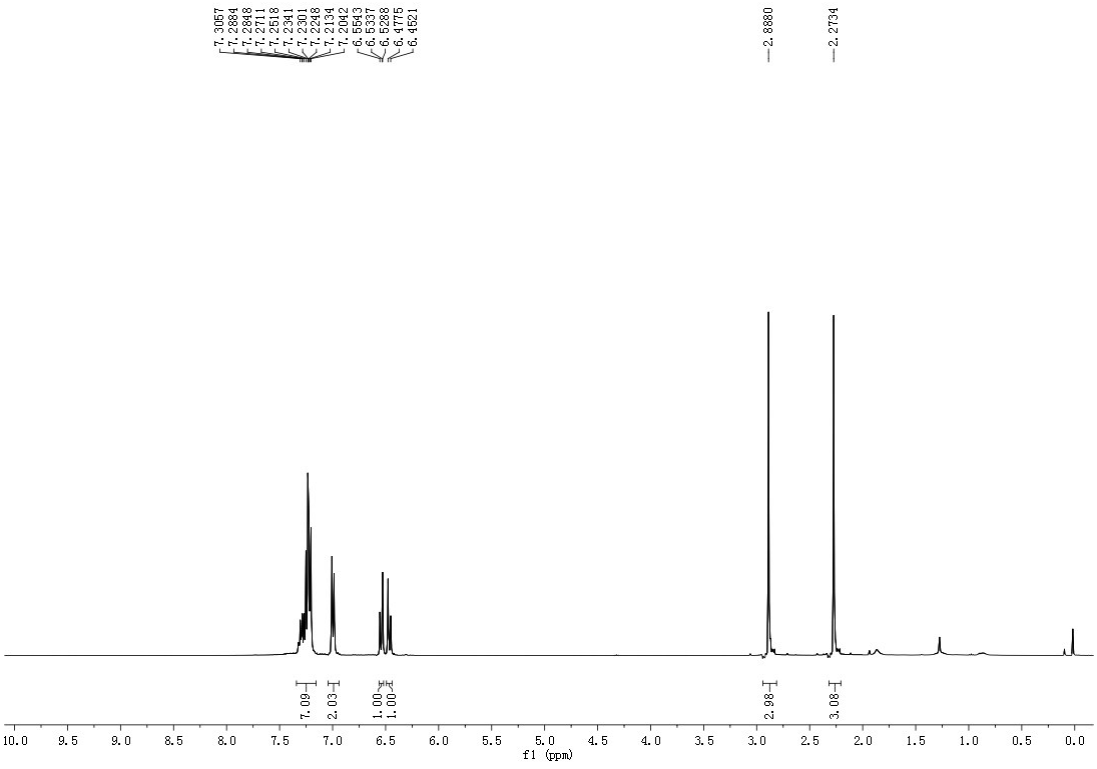
MS Spectrum


*MSD1 SPC, time=4.645 of Z:\LC-MS DATA\20150813\20150812 2015-08-13 16-40-41\063-0401.D ES-API, Pos, Scan, Frag: 120
Max: 4.98176e+006
375.9
373.9
374.9
376.9
395.9
18O
Ph
S
N
O
100
80
60
40
20
0
320
340
360
380
400
420
440 m/z

(4) Intermolecular KIE experiment.



To a mixture of **1a** (0.25 mmol), **[D5]-1a** (0.25 mmol), 4-methylbenzenethiol **2a** (0.5 mmol), AgCl (10 mol%), and H_2O (0.75 mmol) in a 25 mL round-bottomed flack at room temperature, was added the 1,4-dioxane (2 mL). The reaction vessel was allowed to stir at 80^{o}C for 12 h. After the reaction, the solution was concentrated in vacuum, The residue was purified by flash column chromatography to afford the products **3a** and **[D4]-3a**. The products were under ^{1}H-NMR analysis.

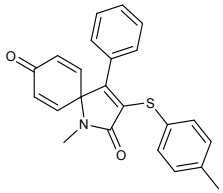


^{1}H NMR spectra of the mixture of compound **3a** and **[D4]-3a.**

4. Reference

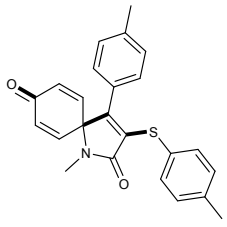
[1] (*a*) T. P. Appel, N. A. M. Yehia, U. Baumeister, H. Hartung, R. Kluge, D. Ströhl, and E. Fanghänel, *Eur. J. Org. Chem.,* 2003, 47; (*b*) X.Zhang and R. C. Larock, *J. Am. Chem. Soc.,* 2005, **127**, 12230; (*c*) B.-X. Tang, D.-J. Tang, S. Tang, Q.-F. Yu, T.-H. Zhang, Y. Liang, P. Zhong and J.-h. Li, *Org. Lett.,* 2008, **10**, 1063; (*d*) Q.-F. Yu, Y.-H. Zhang, Q. Yin, B.-X. Tang, R.-Y. Tang, P. Zhong and J.-H. Li, *J. Org. Chem.,* 2008, **73**, 3658; (*e*) S. Tang, P. Peng, S.-F. Pi, Y. Liang, N.-X. Wang and J.-H. Li, *Org. Lett.* 2008, **10**, 1179; (*f*) J. Wen, W. Wei, S. Xue, D. Yang, Y. Lou, C. Gao and H. Wang, *J. Org. Chem.* 2015, **80**, 4966.

5. Characterization data of products (3a-3s)



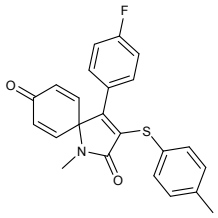
1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3a** was obtained in 76% yield according to the general procedure (12 h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.68 (d, J = 8.2 Hz, 2H), 7.49-7.45 (m, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.34-7.28 (m, 4H), 6.53-6.44 (m, 4H), 2.83 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.4, 164.6, 159.2, 143.3, 143.2, 141.9, 139.4, 138.0, 134.0, 133.9, 130.7, 129.9, 128.7, 128.5, 125.2, 68.0, 25.9, 21.5; HRMS calc. for $C_{23}H_{19}O_2NSNa$ $(M+Na)^+$, 396.1034; found, 396.1036.



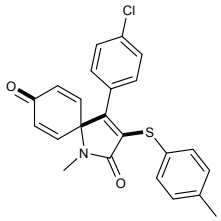
1-methyl-4-p-tolyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3b** was obtained in 64% yield according to the general procedure (14 h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.30 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.56-6.49 (m, 4H), 3.80 (s, 3H), 2.88 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 184.1, 167.9, 160.7, 152.2, 145.7, 137.5, 133.0, 131.1, 130.9, 129.7, 129.7, 128.3, 123.1, 113.8, 67.5, 55.3, 26.1, 21.1; HRMS calc. for $C_{24}H_{21}O_2NSNa$ $(M+Na)^+$, 410.1191; found, 410.1197.



4-(4-fluorophenyl)-1-methyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

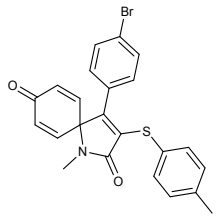
Compound **3c** was obtained in 58% yield according to the general procedure (14 h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.21-7.18 (m, 4H), 6.99 (d, J = 8.0 Hz, 2H), 6.94-6.90 (m, 2H), 6.54-6.46 (m, 4H), 2.90 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.6, 163.1 (d, J = 249.4 Hz), 149.7, 145.2, 138.1, 133.3, 133.2, 131.9, 130.3 (d, J = 8.4 Hz), 129.7, 127.2, 126.7 (d, J = 3.5 Hz), 115.5 (d, J = 21.7 Hz), 67.7, 26.3, 21.1; HRMS calc. for $C_{23}H_{18}O_2NSFNa$ $(M+Na)^+$, 414.0940; found, 414.0944.



4-(4-chlorophenyl)-1-methyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

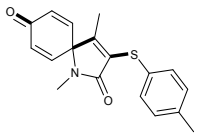
Compound **3d** was obtained in 65% yield according to the general procedure (14 h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.20-7.18 (m, 4H), 7.10 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 6.53-6.46 (m, 4H), 2.90 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.7, 167.5, 148.8, 145.1, 138.3, 135.5, 133.8, 133.3, 132.2,

129.7, 129.6, 129.0, 128.5, 126.8, 123.8, 67.7, 26.3, 21.1; HRMS calc. for $C_{23}H_{18}O_2NClSNa$ $(M+Na)^+$, 430.0644; found, 430.0645.



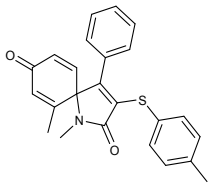
4-(4-bromophenyl)-1-methyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3e** was obtained in 60 % yield according to the general procedure (14 h). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.34 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.03-6.97 (m, 4H), 6.52-6.45 (m, 4H), 2.90 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.7, 167.5, 148.6, 145.0, 138.4, 133.9, 133.3, 132.3, 131.4, 130.0, 129.8, 129.7, 129.5, 128.8, 126.6, 123.8, 67.6, 26.3, 21.1; HRMS calc. for $C_{23}H_{18}O_2NBrSNa$ $(M+Na)^+$, 474.0139; found, 474.0142.



1,4-dimethyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

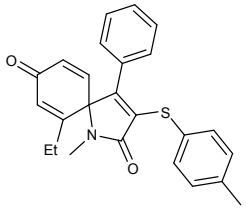
Compound **3f** was obtained in 32% yield according to the general procedure (14 h). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.31 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.57 (d, J = 10.0 Hz, 2H), 6.36 (d, J = 10.0 Hz, 2H), 2.89 (s, 3H), 2.33 (s, 3H), 1.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 184.0, 168.2, 153.5, 145.6, 138.2, 133.4, 131.4, 131.1, 130.9, 129.9, 68.1, 26.6, 21.1, 11.8; HRMS calc. for $C_{18}H_{17}O_2NSNa$ $(M+Na)^+$, 334.0878; found, 334.0879.



1,6-dimethyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

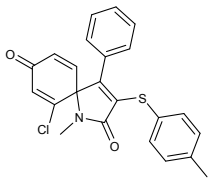
Compound **3g** was obtained in 68% yield according to the general procedure (14 h). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.34-7.31 (m, 1H), 7.30-7.27 (m, 4H), 7.23 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 7.9 Hz, 2H), 6.49 (s, 2H), 6.37 (s, 1H), 2.80 (s, 3H), 2.29 (s,

3H), 1.78 (d, J = 1.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 184.7, 168.1, 153.5, 152.1, 145.5, 137.8, 133.0, 132.6, 132.0, 131.5, 130.6, 129.7, 128.4, 128.1, 127.9, 69.7, 25.8, 21.1, 17.8; HRMS calc. for $C_{24}H_{21}O_2NSNa$ $(M+Na)^+$, 410.1191; found, 410.1193.



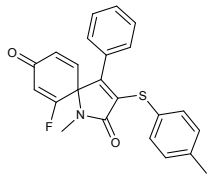
6-ethyl-1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3h** was obtained in 61% yield according to the general procedure (14 h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.34-7.30 (m, 1H), 7.29-7.26 (m, 4H), 7.23 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.52-6.46 (m, 2H), 6.41 (d, J = 1.4 Hz, 1H), 2.78 (s, 3H), 2.29 (s, 3H), 2.04-1.98 (m, 2H), 1.11 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 184.9, 168.2, 158.7, 152.4, 145.8, 137.8, 132.8, 132.3, 131.5, 130.6, 129.7, 129.4, 128.4, 128.1, 127.9, 69.9, 25.9, 22.7, 21.1, 10.4; HRMS calc. for $C_{25}H_{23}O_2NSNa$ $(M+Na)^+$, 424.1347; found, 424.1343.



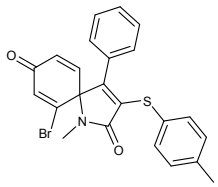
6-chloro-1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3i** was obtained in 50% yield according to the general procedure (12h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.34-7.30 (m, 1H), 7.29-7.24 (m, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.18 (q, J_1 = 1.0 Hz，J_2 = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.68 (d, J = 1.6 Hz, 1H), 6.59 (d, J = 9.9 Hz, 1H), 6.47 (dd, J_1 = 1.6 Hz, J_2 = 9.8 Hz, 1H), 2.85 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 182.9, 167.9, 151.1, 149.9, 144.6, 137.8, 134.6, 132.9, 132.0, 131.7, 130.0, 129.7 (d, J = 3.8 Hz), 128.4, 128.1, 127.5, 70.8, 25.9, 21.1; HRMS calc. for $C_{23}H_{18}O_2NSClNa$ $(M+Na)^+$, 430.0644; found, 430.0645.



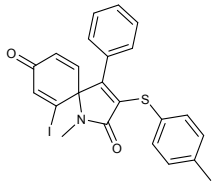
6-fluoro-1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3j** was obtained in 61% yield according to the general procedure (12 h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.35-7.31 (m, 1H), 7.29-7.25 (m, 3H), 7.12-7.15 (m, 4H), 7.00 (d, J = 7.9 Hz, 2H), 6.43-6.41 (m, 2H), 6.19 (d, J = 12.1 Hz, 1H), 2.90 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 185.9 (d, J = 15.1 Hz), 170.9, 168.0, 148.7, 141.5 (d, J = 3.2 Hz), 137.9, 134.4, 132.2, 131.8, 129.7, 129.6, 128.6 (d, J = 276.7 Hz), 128.4, 128.1, 113.9 (d, J = 9.0 Hz), 68.3 (d, J = 23.3 Hz), 26.1, 21.1; HRMS calc. for $C_{23}H_{18}O_2NSFNa$ $(M+Na)^+$, 414.0940; found, 414.0943.



6-bromo-1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

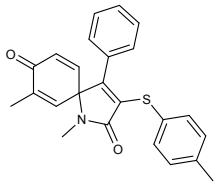
Compound **3k** was obtained in 52% yield according to the general procedure (14 h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.35-7.31(m, 1H), 7.29-7.25 (m, 3H), 7.24-7.20 (m, 3H), 7.00 (d, J = 7.9 Hz, 2H), 6.93 (d, J = 1.6 Hz, 1H), 6.67 (d, J = 9.8 Hz, 1H), 6.50 (dd, J_1 = 1.6 Hz, J_2 = 9.8 Hz, 1H), 2.85 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 182.2, 167.8, 150.1, 144.9, 144.3, 137.8, 137.1, 134.6, 131.9, 131.8, 130.0, 129.7, 128.4, 128.2, 127.5, 71.3, 25.9, 21.1; HRMS calc. for $C_{23}H_{18}O_2NSBrNa$ $(M+Na)^+$, 474.0139; found, 474.0139.



6-iodo-1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

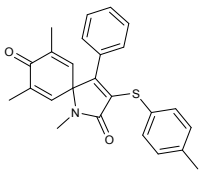
Compound **3l** was obtained in 61% yield according to the general procedure (24h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.35-7.31 (m, 1H), 7.30-7.27 (m, 4H), 7.25-7.23 (m,

3H), 7.00 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 9.8 Hz, 1H), 6.55 (dd, J_1 = 1.6 Hz, J_2 = 9.8 Hz, 1H), 2.84 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 181.0, 167.5, 150.4, 144.9, 144.5, 137.9, 134.7, 132.0, 131.9, 130.0, 129.7, 129.6, 128.3, 127.3, 125.5, 72.1, 25.9, 21.1; HRMS calc. for $C_{23}H_{18}O_2NSINa$ $(M+Na)^+$, 522.0001; found, 522.0003.



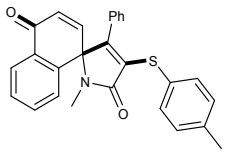
1,7-dimethyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3m** was obtained in 71% yield according to the general procedure (8 h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.32-7.29 (m, 1H), 7.27-7.23 (m, 3H), 7.21-7.19 (m, 3H), 7.01 (d, J = 8.0 Hz, 2H), 6.49 (dd, J_1 = 2.9 Hz, J_2 = 9.8 Hz, 1H), 6.44 (d, J = 9.8 Hz, 1H), 6.31-6.30 (m, 1H), 2.87 (s, 3H), 2.28 (s, 3H), 1.94 (d, J = 1.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 184.8, 167.7, 152.7, 145.1, 140.3, 140.0, 137.7, 132.9, 132.2, 131.6, 130.9, 129.7, 129.4, 128.2, 128.0, 68.2, 26.2, 21.1, 15.8; HRMS calc. for $C_{24}H_{21}O_2NSNa$ $(M+Na)^+$, 410.1191; found, 410.1192.



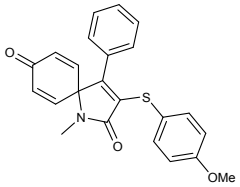
1,7,9-trimethyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3n** was obtained in 77% yield according to the general procedure (12 h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.31-7.27 (m, 1H), 7.26-7.21 (m, 4H), 7.19-7.16 (m, 2H), 7.01 (d, J = 7.9 Hz, 2H), 6.27 (s, 2H), 2.85 (s, 3H), 2.28 (s. 3H), 1.92 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 185.5, 167.7, 153.7, 139.9, 139.8, 137.5, 131.7, 131.4, 131.1, 129.7, 129.3, 128.4, 128.2, 128.1, 68.1, 26.2, 21.1, 16.1; HRMS calc. for $C_{25}H_{23}O_2NSNa$ $(M+Na)^+$, 424.1347; found, 424.1350.



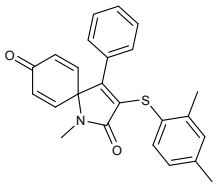
1'-methyl-3'-phenyl-4'-(p-tolylthio)-4H-spiro[naphthalene-1,2'-pyrrole]-4,5'(1'H)-dione

Compound **3o** was obtained in 60% yield according to the general procedure (13.5h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.16 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.66 (dt, J_1 = 1.4 Hz, J_2 = 7.6 Hz, 1H), 7.54 (dt, J_1 = 1.1 Hz, J_2 = 7.8 Hz, 1H), 7.27 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 7.9 Hz, 1H), 7.19 (t, J = 7.4 Hz, 1H), 7.11-7.07 (m, 2H), 7.03 (d, J = 7.9 Hz, 2H), 6.75-6.73 (m, 2H), 6.59 (d, J = 1.0 Hz, 2H), 2.74 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.1, 168.3, 155.8, 145.5, 137.7, 137.5, 133.8, 132.8, 132.7, 131.6, 130.7, 129.7, 129.4, 129.3, 128.3, 128.2, 128.1, 127.5, 125.9, 68.7, 26.0, 21.1; HRMS calc. for $C_{26}H_{19}O_2NSNa$ $(M+Na)^+$, 432.1034; found, 432.1035.



3-(4-methoxyphenylthio)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

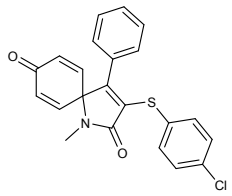
Compound **3p** was obtained in 73% yield according to the general procedure (16h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.32-7.27 (m, 3H), 7.25-7.22 (m, 2H), 7.18-7.16 (m, 2H), 6.71 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 10.2 Hz, 2H), 6.44 (d, J = 10.2 Hz, 2H), 3.76 (s, 3H), 2.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 184.0, 167.9, 159.8, 150.3, 145.3, 134.5, 133.5, 133.1, 130.7, 129.4, 128.3, 128.2, 121.1, 114.5, 67.7, 55.3, 26.3; HRMS calc. for $C_{23}H_{19}O_3NSNa$ $(M+Na)^+$, 412.0983; found, 412.0985.



3-(2,4-dimethylphenylthio)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

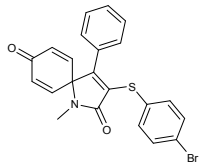
Compound **3q** was obtained in 45% yield according to the general procedure (21.5h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.28-7.25 (m, 1H), 7.23-7.19 (m, 2H), 7.18-7.14 (m, 3H), 6.87 (s, 1H), 6.82 (d, J = 7.9 Hz, 1H), 6.54-6.44 (m, 4H), 2.90 (s, 3H), 2.31 (s, 3H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 184.0, 167.7, 149.9, 145.4, 140.0, 138.4, 133.2, 133.1, 133.0, 131.2, 130.6, 129.2, 128.1, 128.0, 127.2, 126.3,

67.8, 26.3, 21.0, 20.8; HRMS calc. for $C_{24}H_{21}O_2NSNa$ $(M+Na)^+$, 410.1191; found, 410.1194.



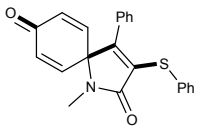
3-(4-chlorophenylthio)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3r** was obtained in 60% yield according to the general procedure (16h). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.37-7.33 (m, 1H), 7.30-7.26 (m, 3H), 7.24-7.20 (m, 3H), 7.16 (d, J = 8.6 Hz, 2H), 6.55-6.47 (m, 4H), 2.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.4, 152.9, 144.9, 133.9, 133.3, 132.7, 132.0, 130.5, 130.0, 129.8, 129.1, 128.4, 128.1, 67.8, 26.3; HRMS calc. for $C_{22}H_{16}O_2NSClNa$ $(M+Na)^+$, 416.0488; found, 416.0488.



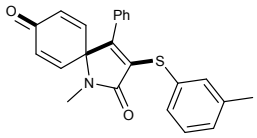
3-(4-bromophenylthio)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound **3s** was obtained in 76% yield according to the general procedure (16 h). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.37-7.27 (m, 5H), 7.23-7.17 (m, 4H), 6.51 (dd, J_1 = 10.3 Hz, J_2 = 19.8 Hz, 4H), 2.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.4, 153.1, 144.8, 133.3, 132.8, 132.0, 131.8, 130.7, 130.5, 129.8, 128.4, 128.1, 121.9, 67.8, 26.3; HRMS calc. for $C_{22}H_{16}O_2NSBrNa$ $(M+Na)^+$, 459.9983; found, 459.9984.

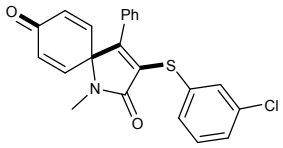


Compound **3t** was obtained in 63% yield according to the general procedure (16 h). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.33-7.25 (m, 7H), 7.22-7.19 (m, 3H), 6.57-6.54 (m, 2H), 6.51-6.48 (m, 2H), 2.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.9, 167.7, 152.8, 145.1, 133.2, 132.3, 132.0, 131.7, 130.7, 129.7, 128.9, 128.3, 128.1,

127.5, 67.8, 26.3; HRMS calc. for $C_{22}H_{17}O_2NSNa$ $(M+Na)^+$, 382.0878; found, 382.0875.

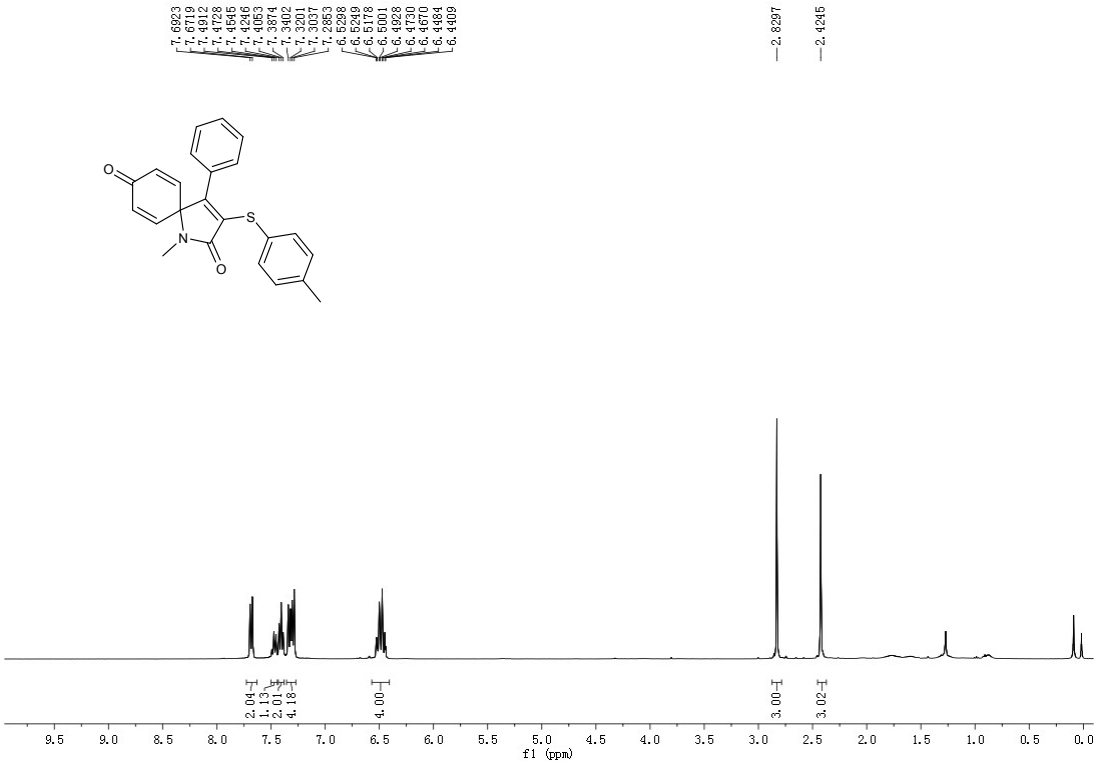


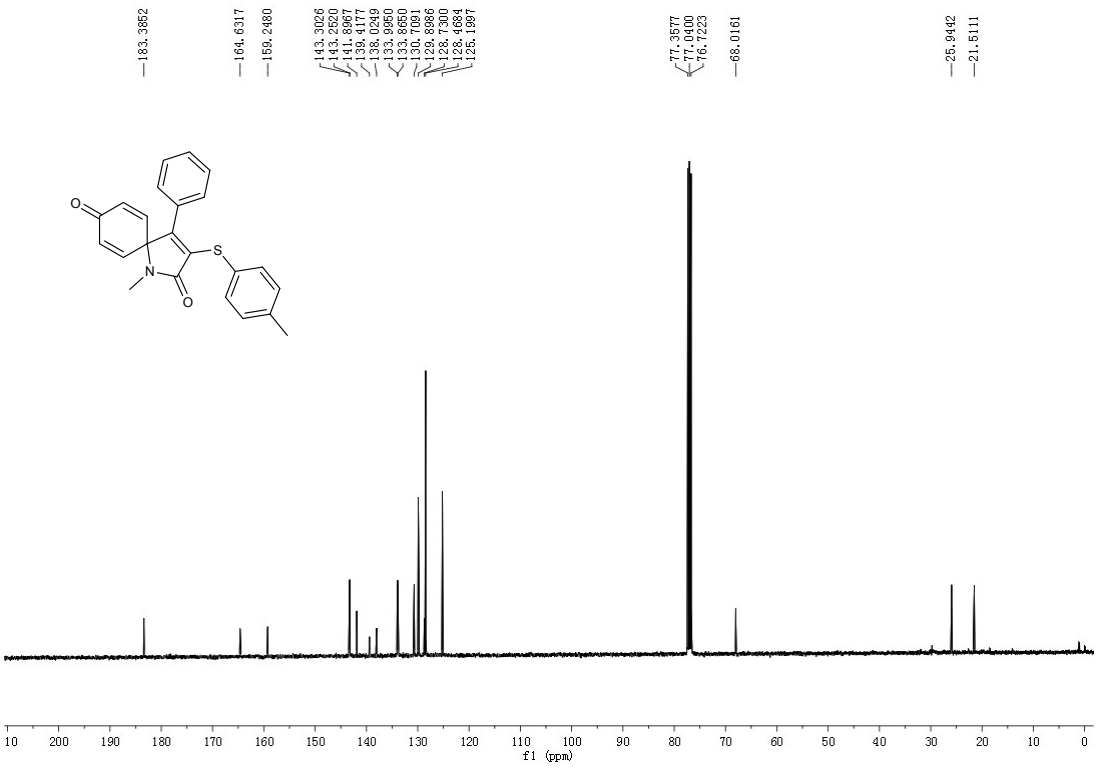
Compound **3u** was obtained in 72% yield according to the general procedure (16 h). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.29-7.21 (m, 5H), 7.11-7.06 (m, 3H), 6.98-6.96 (m, 1H), 6.57-6.53 (m, 2H), 6.50-6.47 (m, 2H), 2.91 (s, 3H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.9, 167.7, 152.1, 145.2, 138.6, 133.1, 132.5, 132.0, 131.1, 130.7, 129.5, 128.7, 128.5, 128.2, 128.1, 67.8, 26.3, 21.2; HRMS calc. for $C_{23}H_{19}O_2NSNa$ $(M+Na)^+$, 396.1034; found, 396.1036.

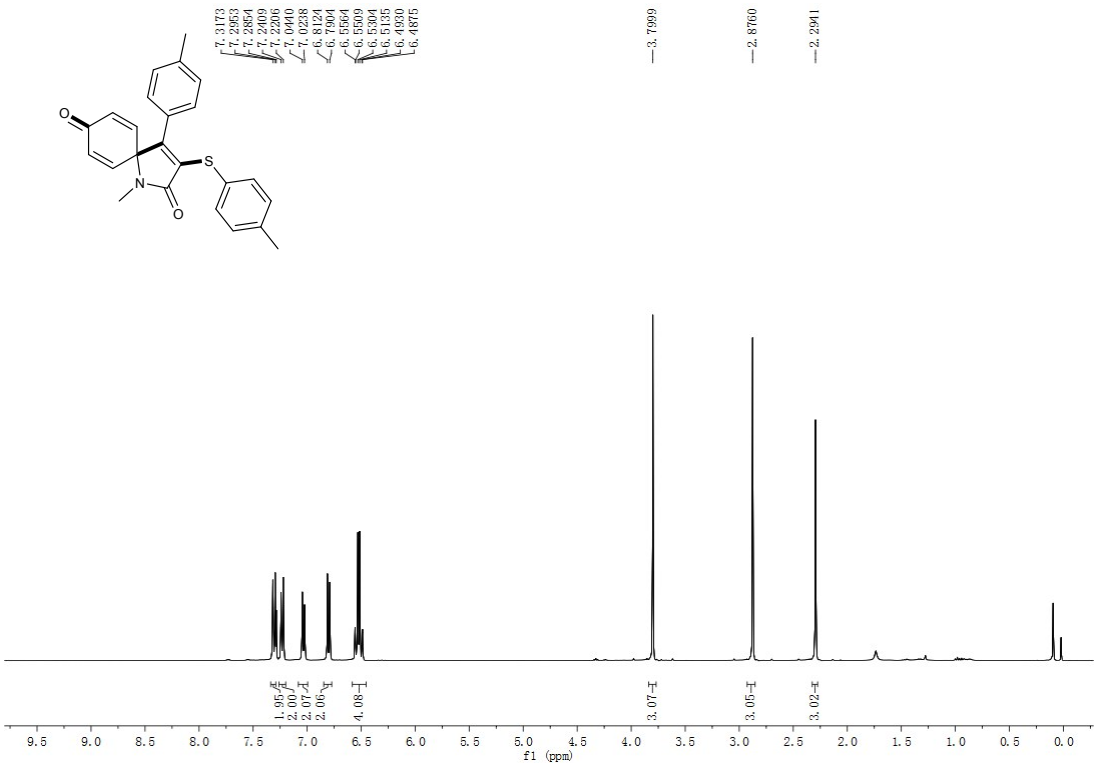


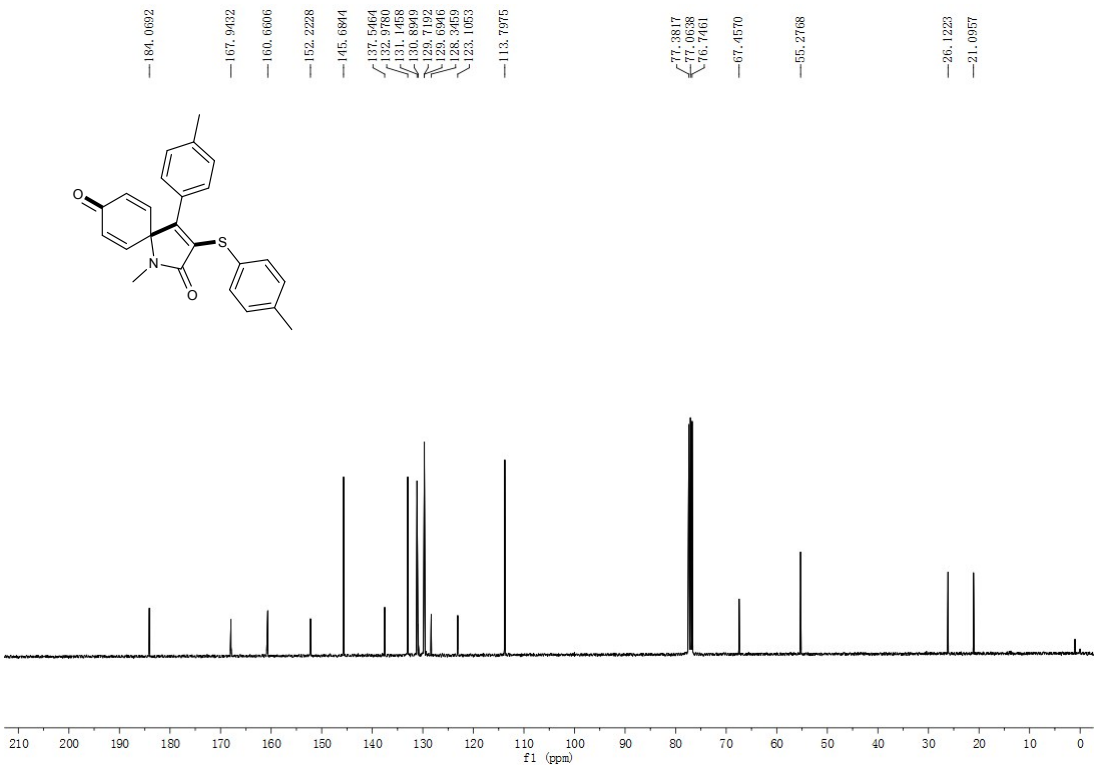
Compound **3v** was obtained in 60% yield according to the general procedure (16 h). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.35-7.30 (m, 3H), 7.24-7.18 (m, 4H), 7.17-7.11(m, 2H), 6.57-6.54 (m, 2H), 6.52-6.49 (m, 2H), 2.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.4, 153.4, 144.8, 134.6, 133.5, 133.3, 131.5, 130.7, 130.4, 129.9, 129.0, 128.4, 128.0, 127.7, 67.9, 26.3; HRMS calc. for $C_{22}H_{16}O_2NSClNa$ $(M+Na)^+$, 416.0488; found, 416.0489.

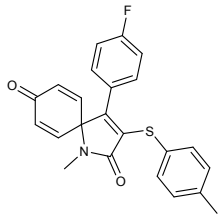
6.Copies of NMR spectra for 3a−3v



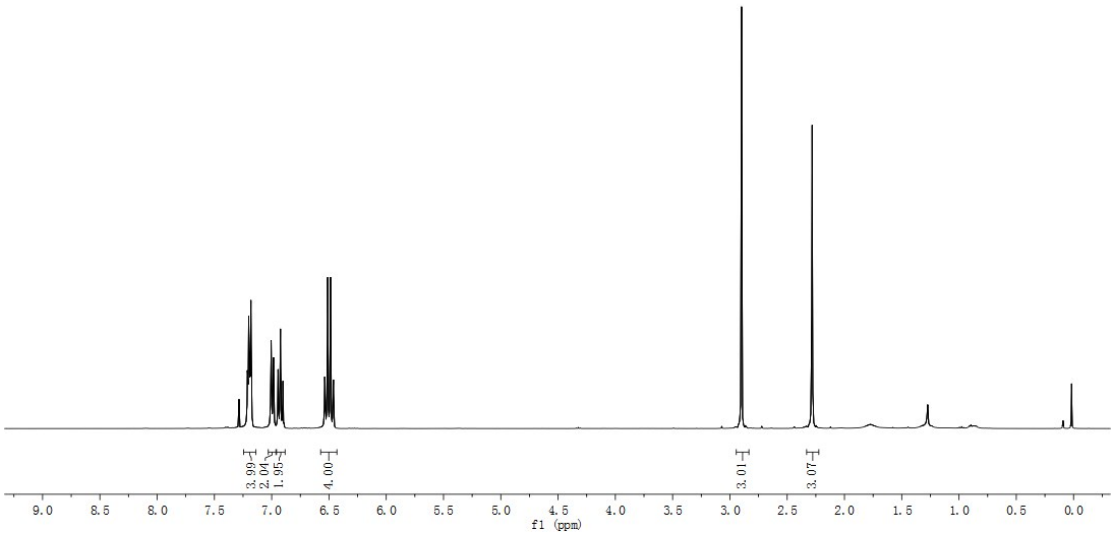


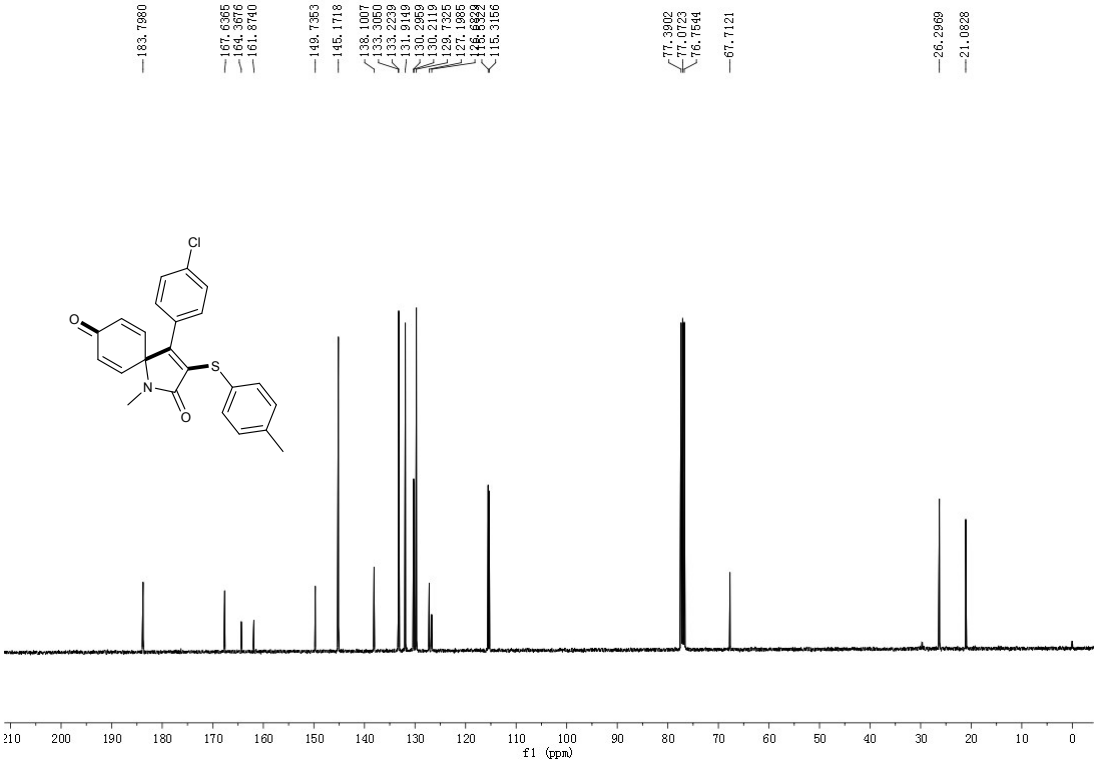

7.3173
7.2953
7.2854
7.2809
7.2206
7.0440
7.0238
6.8124
6.7904
6.5564
6.5509
6.5304
6.5135
6.4930
6.4875
3.7999
2.8760
2.2941
O
S
N
O
1.95
2.00
2.07
2.06
4.08
3.07
3.05
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

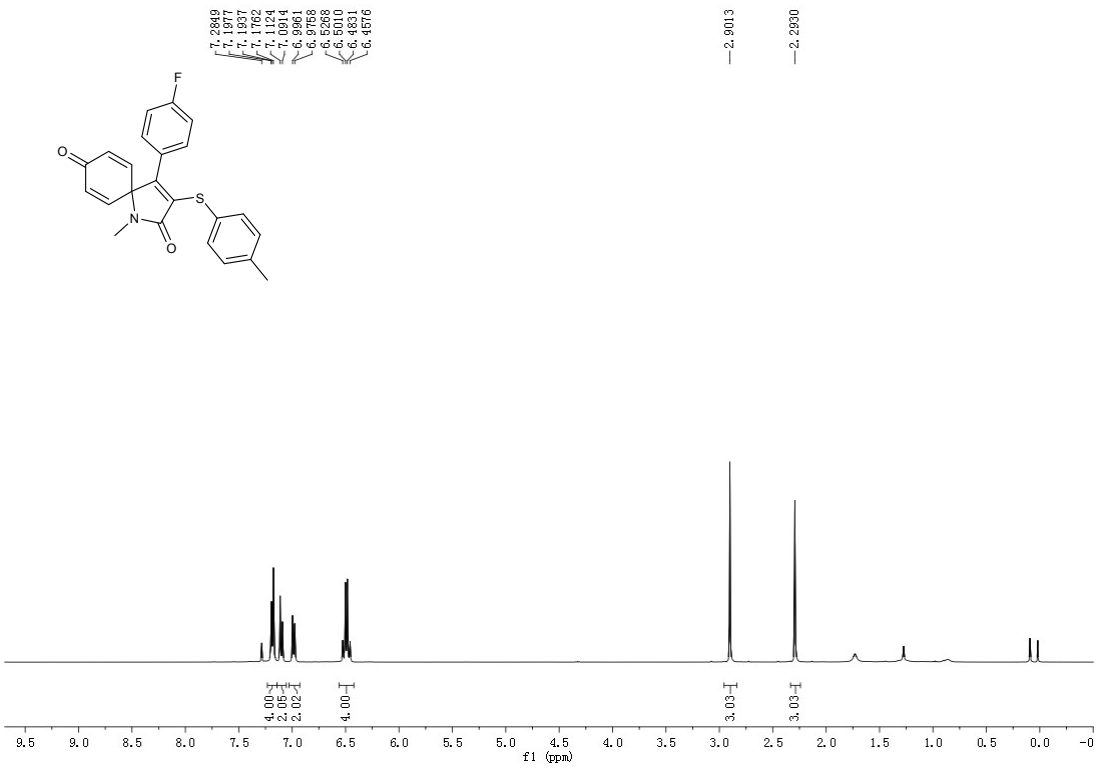

184.0692
167.9432
160.6606
152.2228
145.6844
137.5464
132.9780
131.1458
130.8949
129.7192
129.6946
128.3459
123.1053
113.7975
77.3817
77.0638
76.7461
67.4570
55.2768
26.1223
21.0957
O
S
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

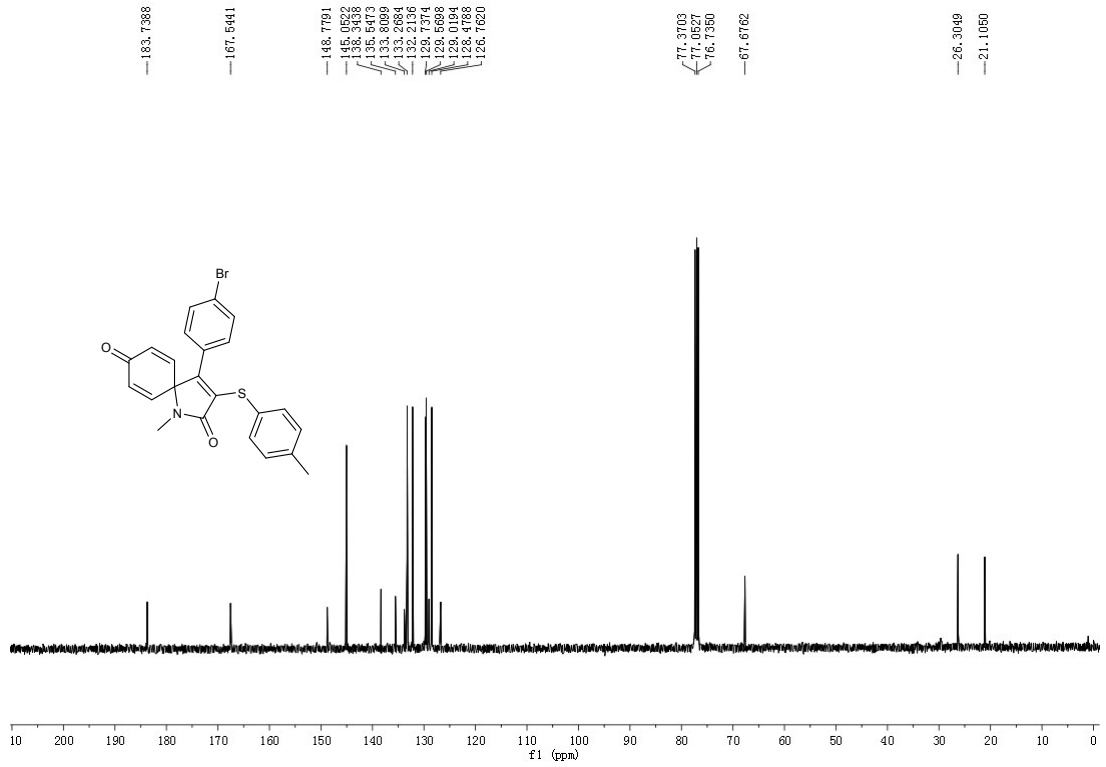

F
O
S
N
O

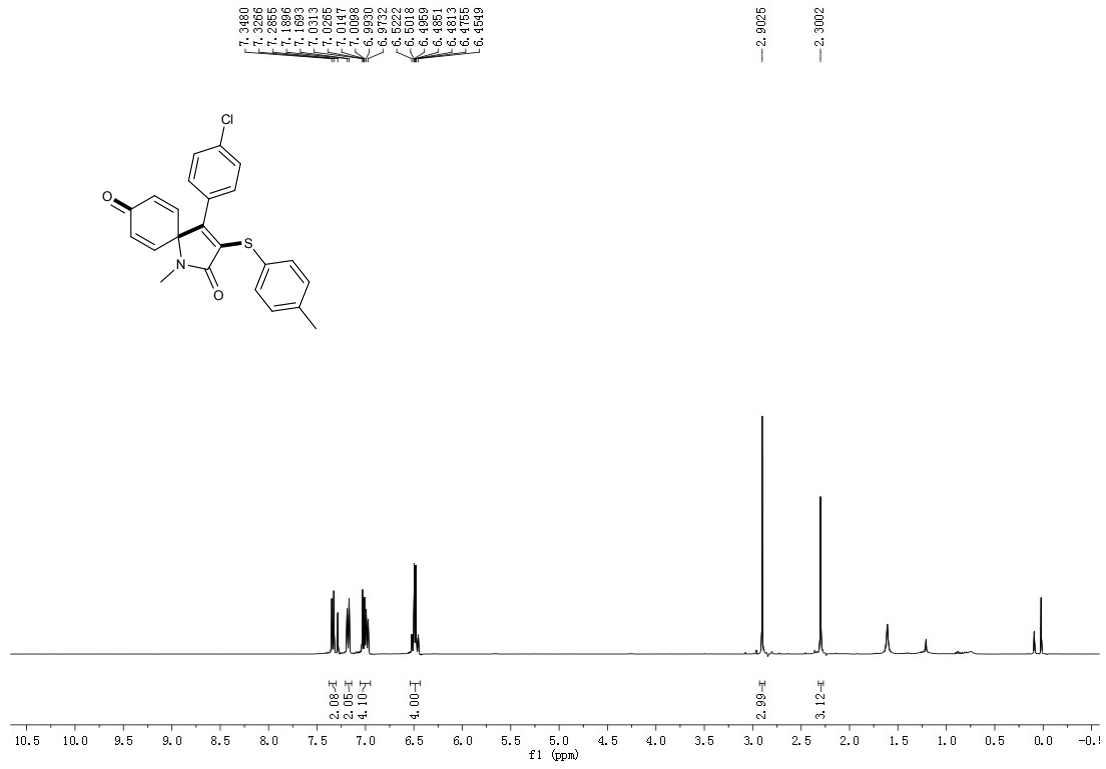

7.2853
7.2121
7.2066
7.2008
7.1900
7.1813
7.1773
7.0942
6.9943
6.9848
6.9596
6.9223
6.9066
6.5916
6.5969
6.5316
6.5110
6.4867
6.4661
6.4609
2.8985
2.2820

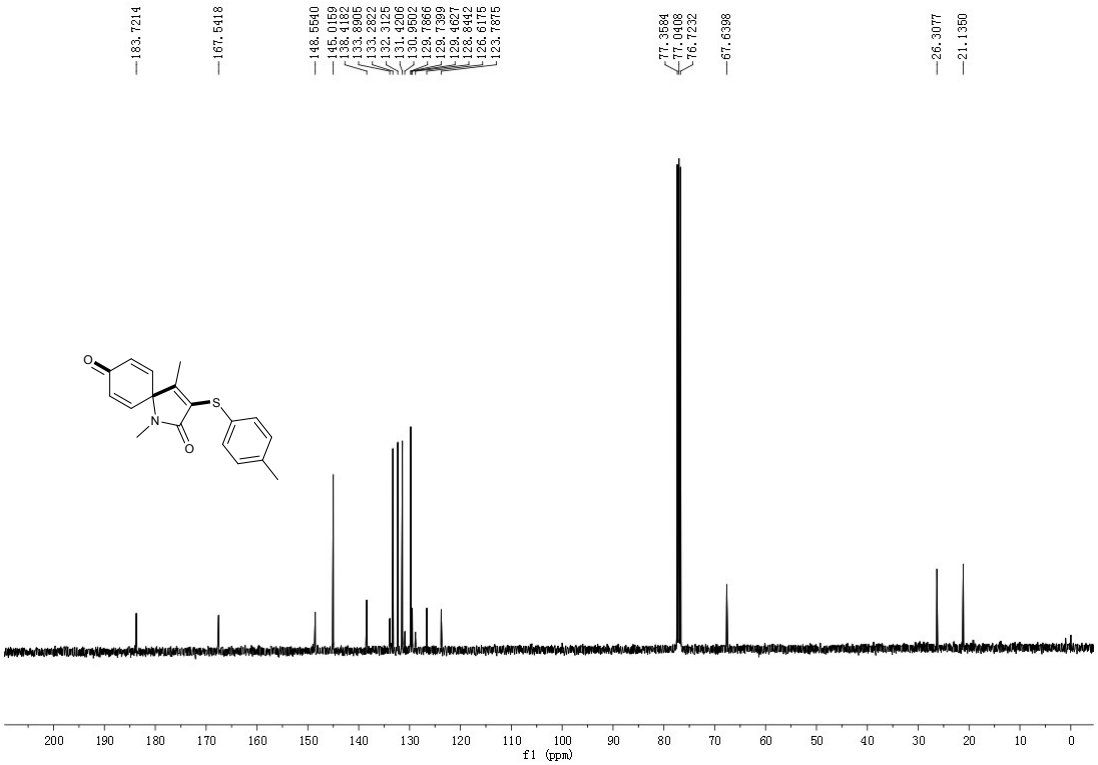

3.99
2.04
1.95
4.00
3.01
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

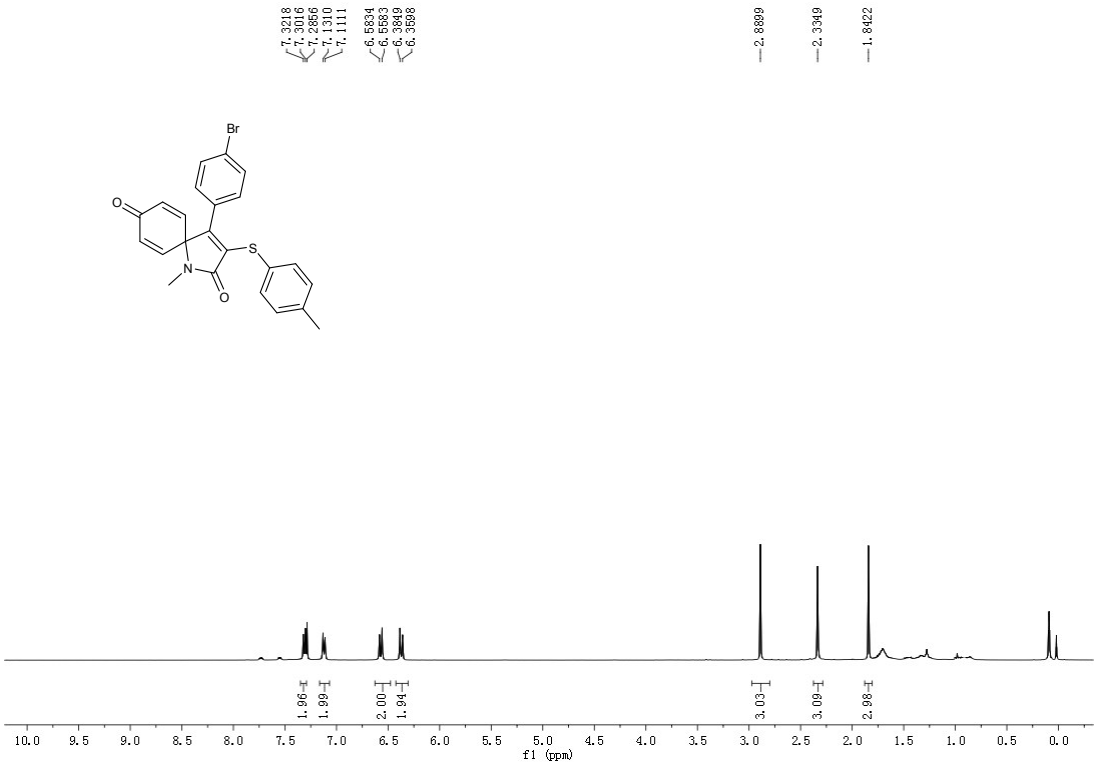

183.7980
167.6365
164.3676
161.8740
149.7353
145.1718
138.1007
133.3050
133.2239
131.9149
130.2959
130.2119
129.7325
127.1985
126.6829
126.6322
115.3156
77.3902
77.0723
76.7544
67.7121
26.2969
21.0828
Cl
O
S
N
O
f1 (ppm)

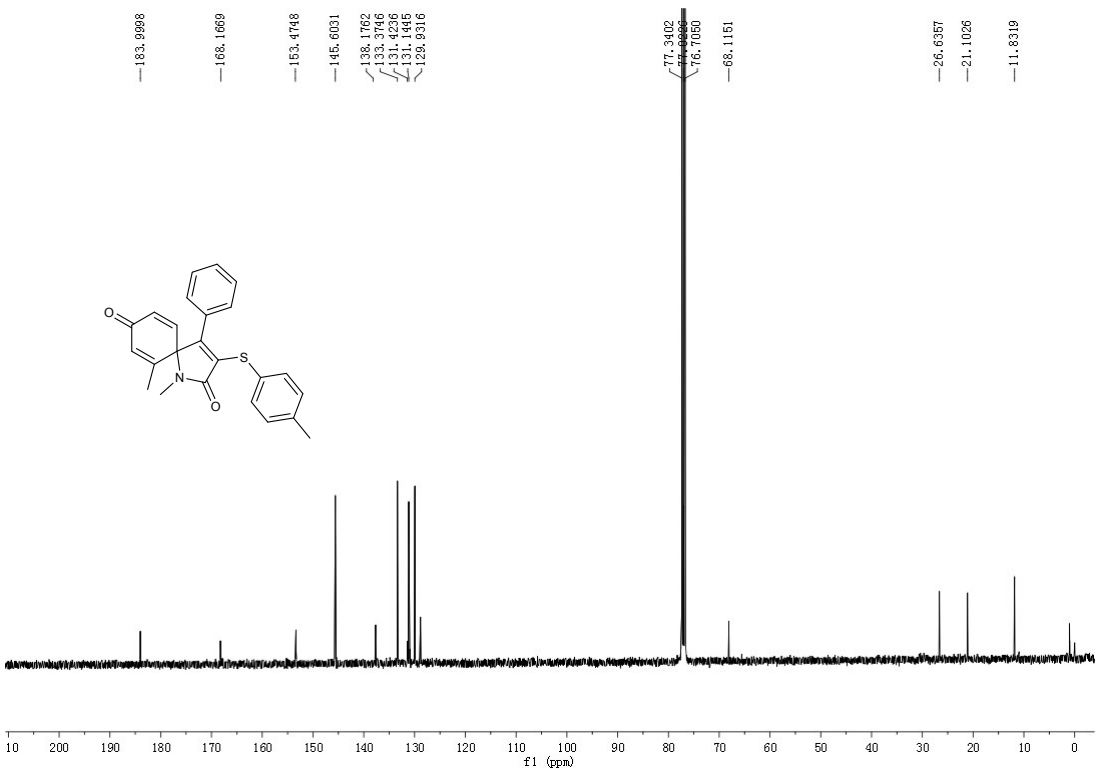

7.2849
7.1977
7.1937
7.1762
7.1124
7.0914
6.9961
6.9758
6.6288
6.6010
6.4831
6.4576
2.9013
2.2930
F
O
S
N
O
4.00
2.05
2.02
4.00
3.03
3.03
f1 (ppm)

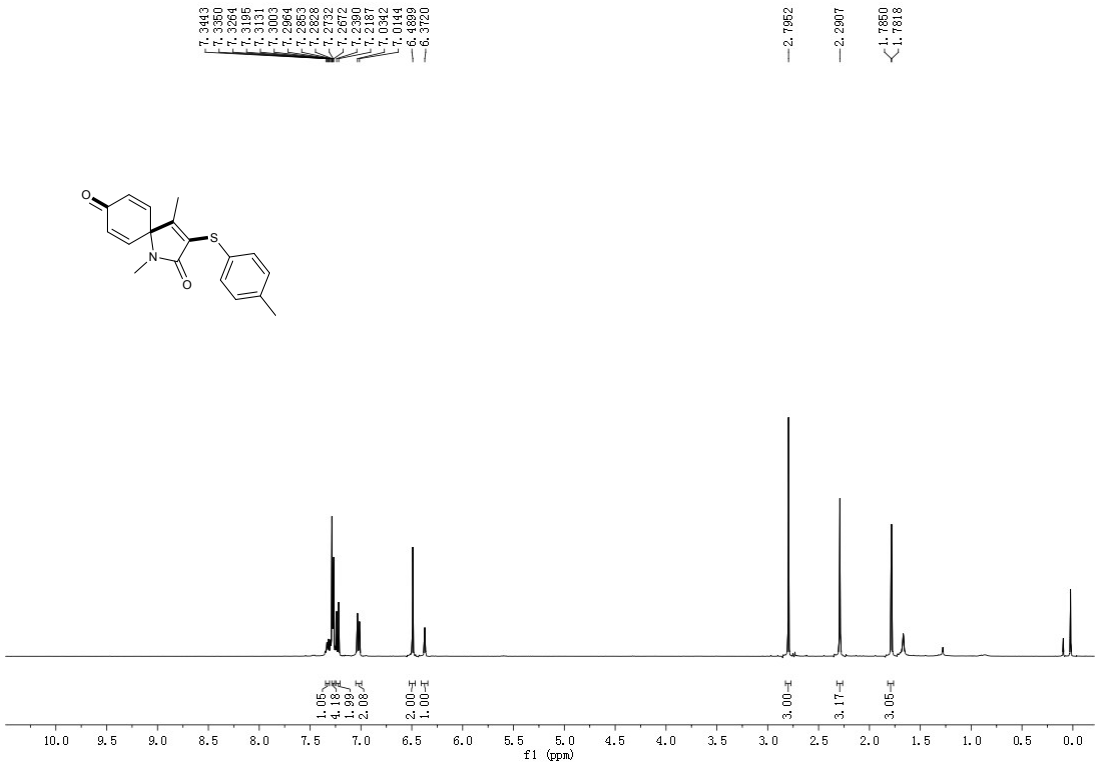

183.7388
167.5441
148.7791
145.0522
138.9438
135.5473
133.8099
133.2684
132.2136
129.7374
129.5698
129.0194
128.4788
126.7620
77.3703
77.0527
76.7360
67.6762
26.3049
21.1050
Br
O
N
S
O
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

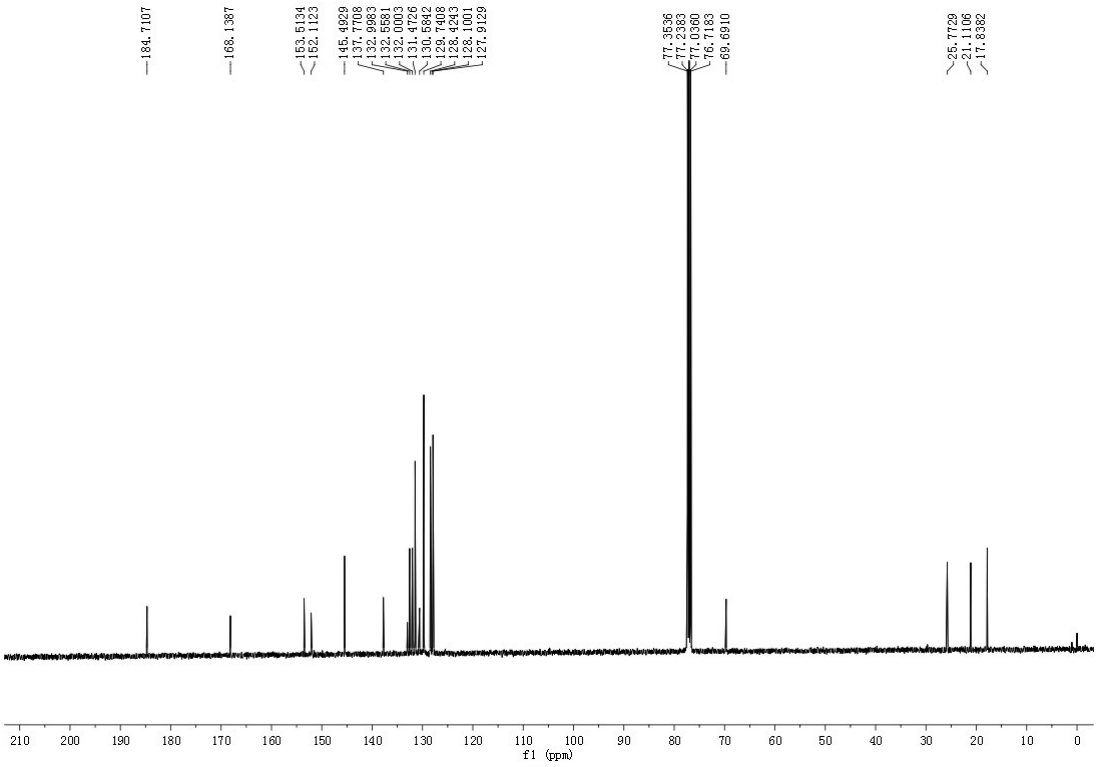

7.3480
7.3266
7.2855
7.1896
7.1693
7.1313
7.1265
7.0147
7.0098
6.9930
6.9732
6.5222
6.5018
6.4959
6.4851
6.4813
6.4755
6.4549
2.9025
2.3002
Cl
O
N
S
O
2.08
2.05
4.10
4.00
2.99
3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

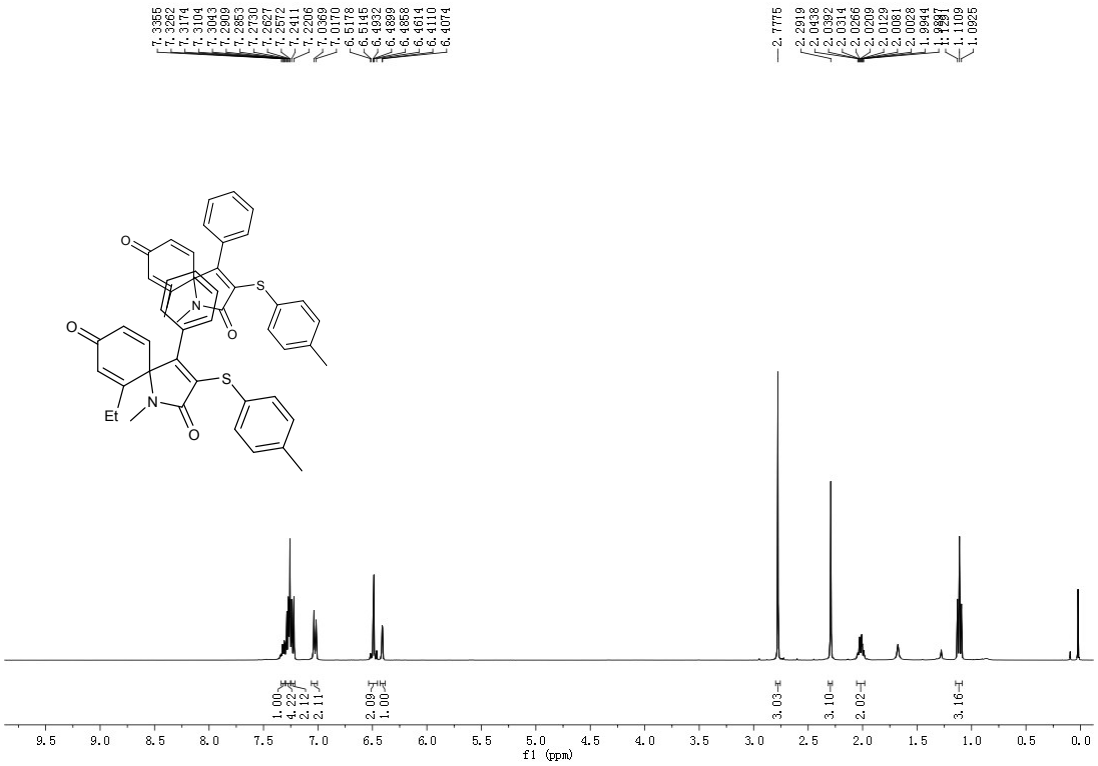

183.7214
167.5418
148.5540
145.0159
138.4182
133.8905
133.2822
132.3125
131.4206
130.9502
129.7866
129.7399
129.4627
128.8442
126.6175
123.7875
77.3684
77.0408
76.7232
67.6398
26.3077
21.1360
O
S
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

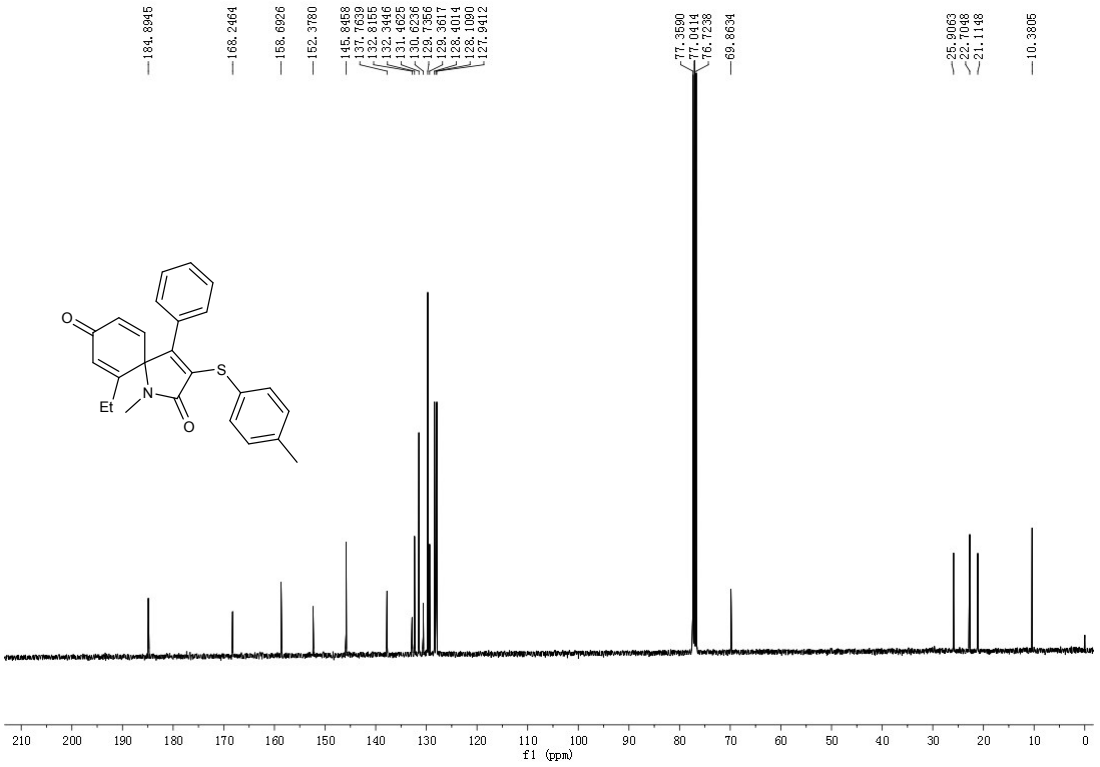

7.3218
7.3016
7.2866
7.1310
7.1111
6.5834
6.5583
6.3849
6.3598
2.8899
2.3349
1.8422
Br
O
S
N
O
1.96
1.99
2.00
1.94
3.03
3.09
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

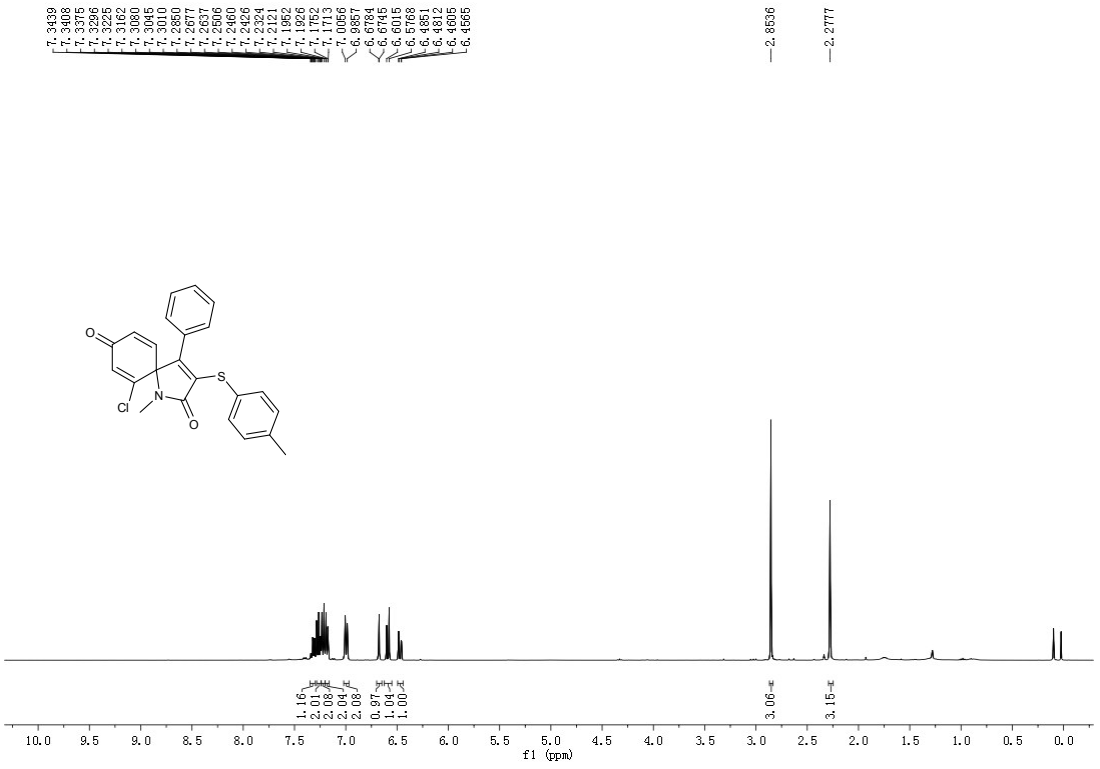

183.9998
168.1669
153.4748
145.6031
138.1762
133.3746
131.4236
131.1445
129.9316
77.3402
77.0986
76.7050
68.1151
26.6357
21.1026
11.8319
O
N
O
S
f1 (ppm)

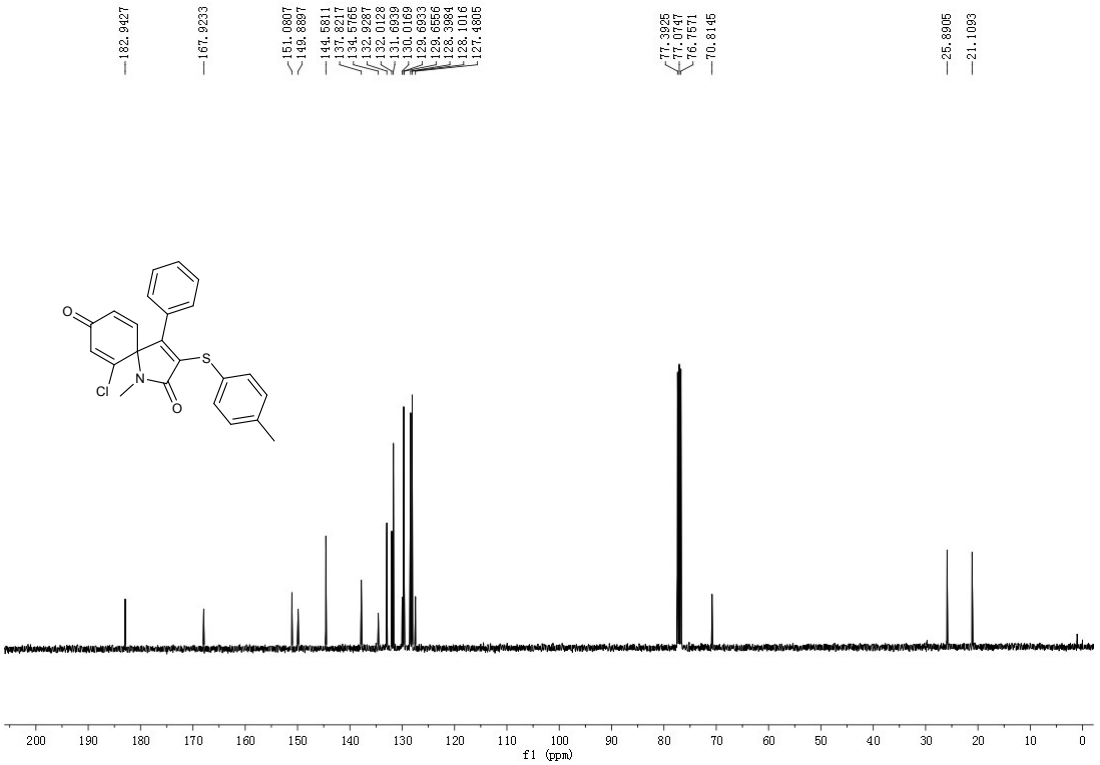

7.3443
7.3350
7.3264
7.3195
7.3131
7.3003
7.2964
7.2853
7.2828
7.2732
7.2672
7.2390
7.2187
7.0342
7.0144
6.4899
6.3720
2.7952
2.2907
1.7850
1.7818
O
N
O
S
1.05
4.18
1.99
2.08
2.00
1.00
3.00
3.17
3.05
f1 (ppm)

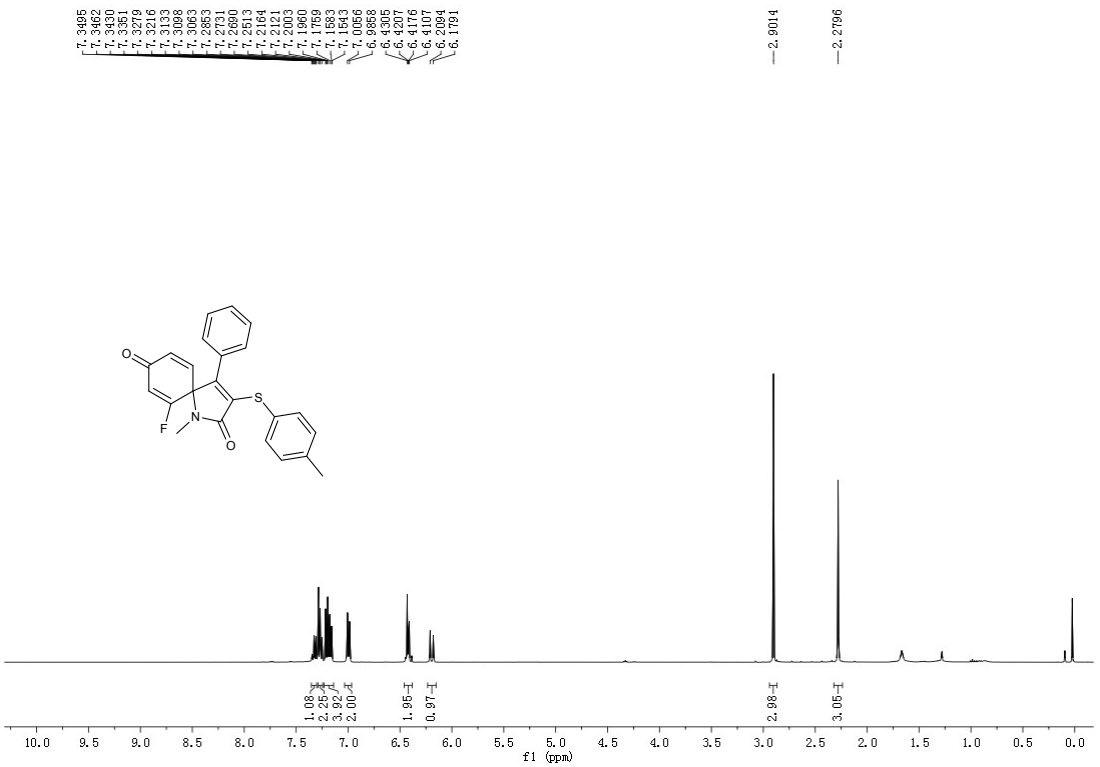

184.7107
168.1387
153.5134
152.1123
145.4929
137.7708
132.9983
132.5581
132.0003
131.4726
130.5842
129.7408
128.4243
128.1001
127.9129
77.3536
77.2383
77.0360
76.7183
69.6910
25.7729
21.1106
17.8382
f1 (ppm)

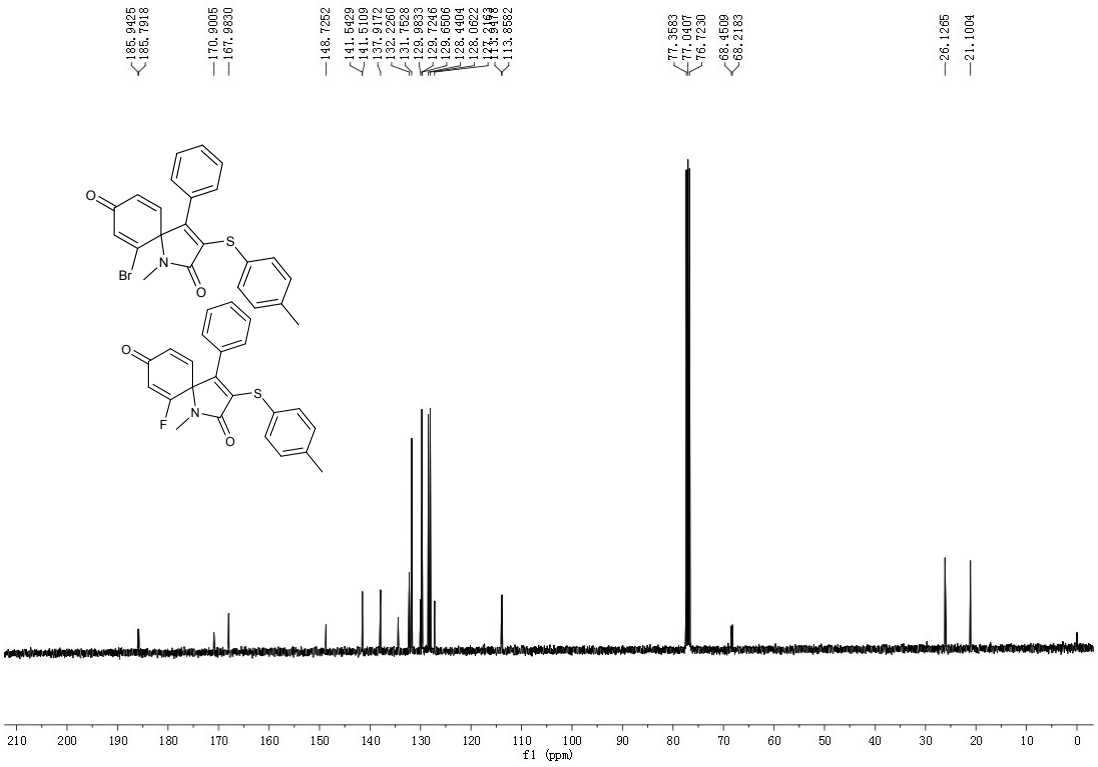

7.3955
7.3692
7.3504
7.3304
7.3043
7.2909
7.2853
7.2730
7.2627
7.2572
7.2411
7.2206
7.0369
7.0170
6.5178
6.5145
6.4932
6.4899
6.4858
6.4614
6.4110
6.4074
2.7775
2.2919
2.0438
2.0292
2.0314
2.0266
2.0209
2.0129
2.0081
2.0028
1.9944
1.1109
1.0925
O
O
N
O
S
S
N
Et
O
1.00
4.22
2.12
2.11
2.09
1.00
3.03
3.10
2.02
3.16
f1 (ppm)

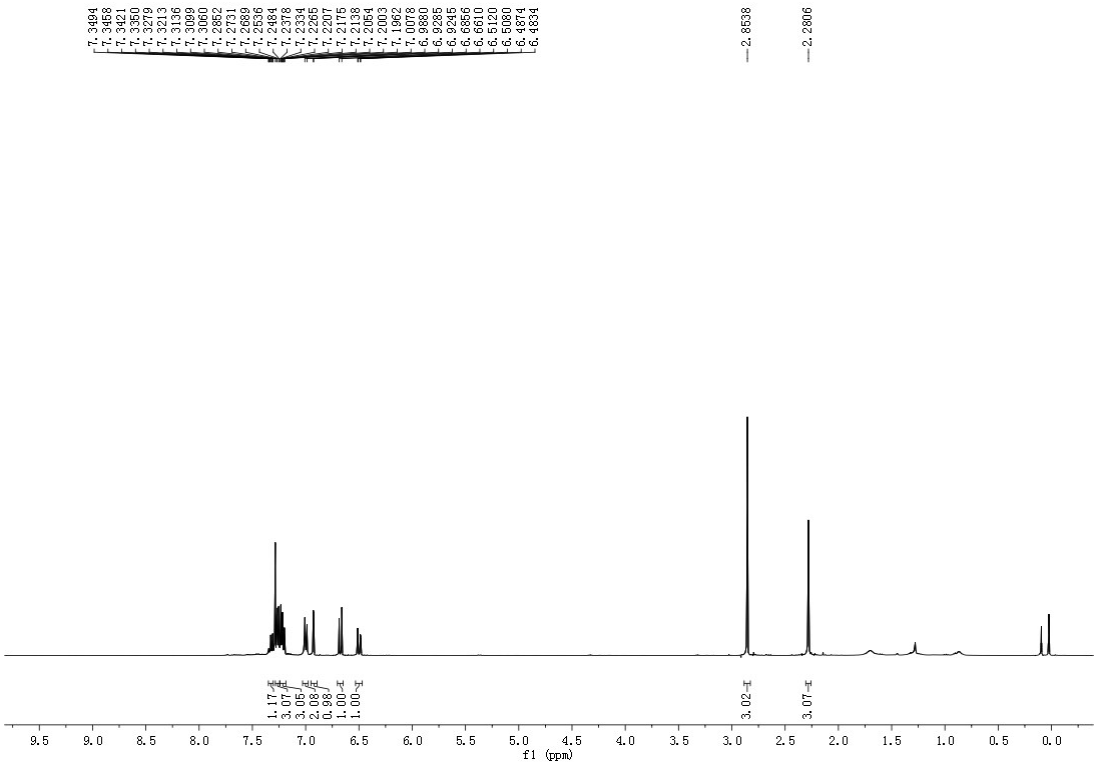

184.8945
168.2464
158.6926
152.3780
145.8458
137.7639
132.8155
132.3446
131.4625
130.6236
129.7356
129.3617
128.4014
128.1090
127.9412
77.3590
77.0414
76.7238
69.8634
25.9063
22.7048
21.1148
10.3805
O
Et
N
O
S
f1 (ppm)

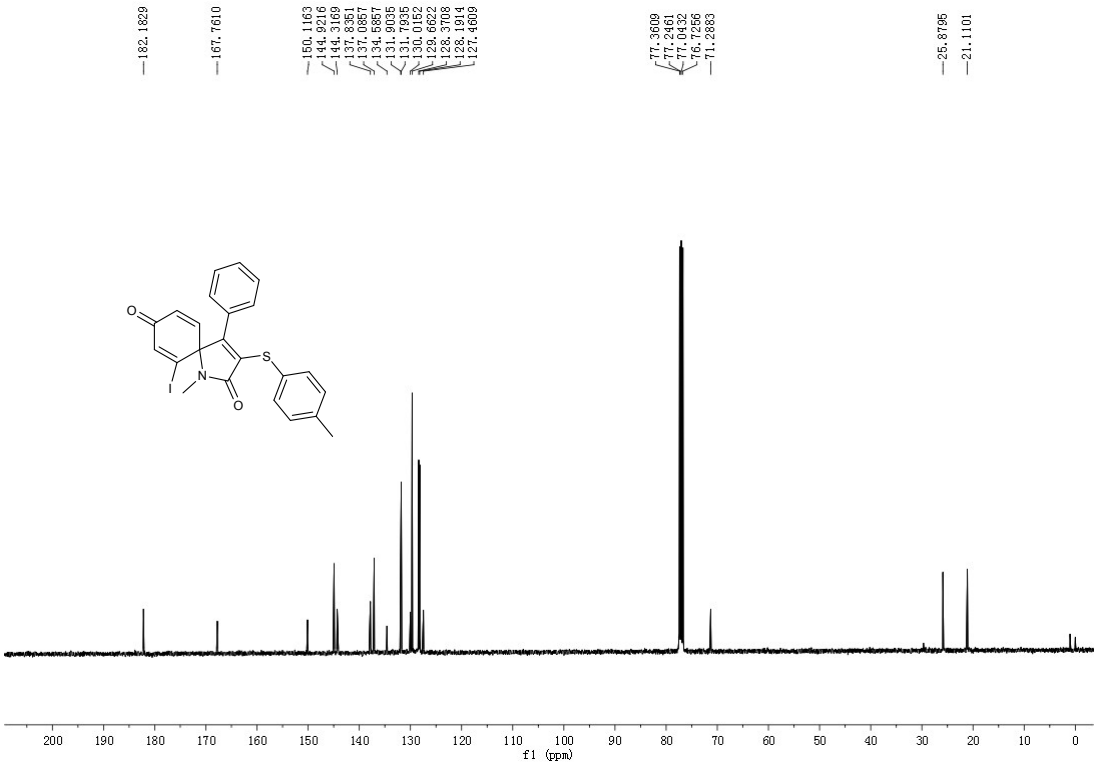

7.3439
7.3408
7.3375
7.3296
7.3225
7.3162
7.3080
7.3045
7.3010
7.2850
7.2677
7.2637
7.2506
7.2460
7.2426
7.2324
7.2121
7.1962
7.1926
7.1762
7.1713
7.0056
6.9857
6.6784
6.6745
6.6015
6.5768
6.4861
6.4812
6.4605
6.4565
2.8536
2.2777
1.16
2.01
2.08
2.04
2.08
0.97
1.04
1.00
3.06
3.15
O
Cl
N
O
S
f1 (ppm)

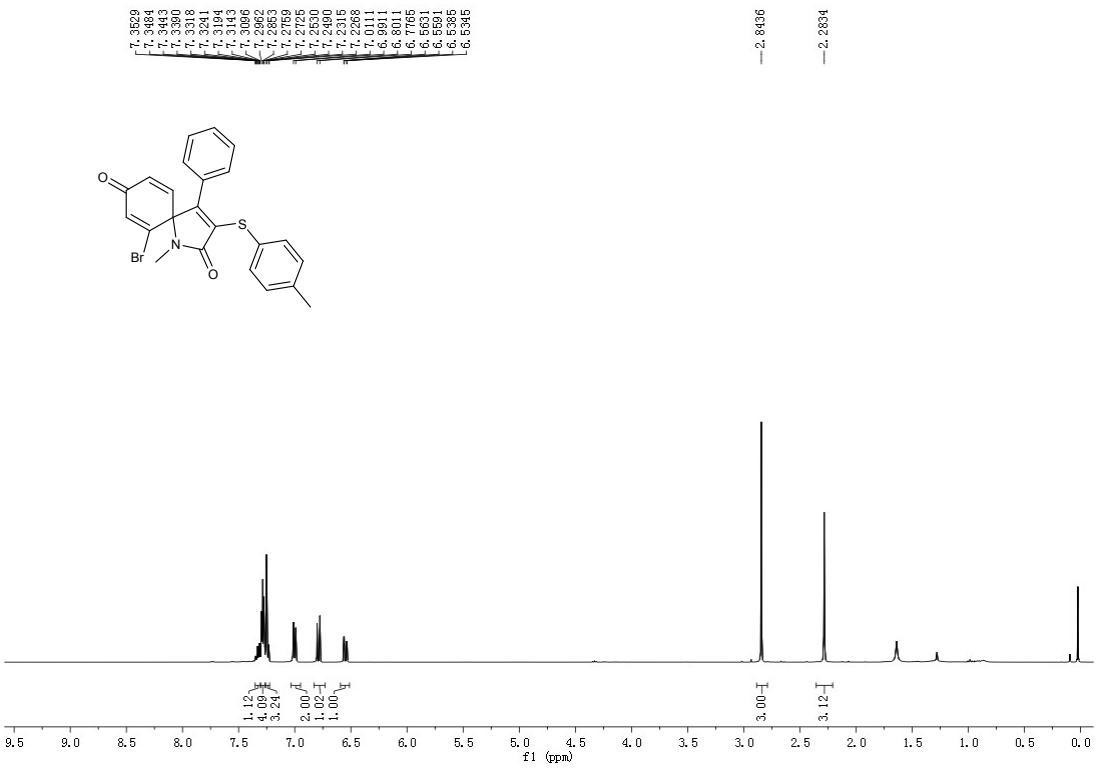

182.9427
167.9233
151.0807
149.8897
144.5811
137.8217
134.5565
132.9287
132.0128
131.6939
130.6169
129.6933
129.6556
128.3884
128.1016
127.4805
77.3925
77.0747
76.7571
70.8145
25.8905
21.1093
O
Cl
N
O
S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

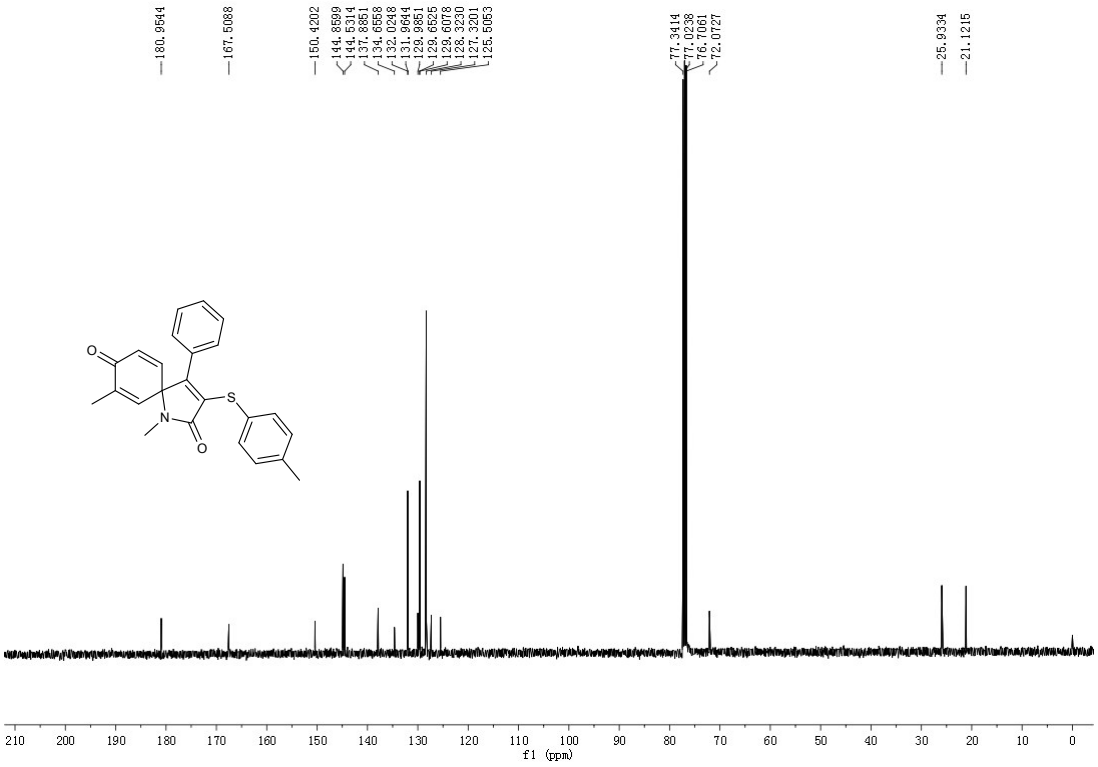

7.3495
7.3462
7.3430
7.3351
7.3279
7.3216
7.3133
7.3098
7.3063
7.2853
7.2731
7.2690
7.2513
7.2164
7.2121
7.2003
7.1960
7.1759
7.1583
7.1543
7.0056
6.9858
6.4305
6.4207
6.4176
6.4107
6.2094
6.1791
2.9014
2.2796
O
F
N
O
S
1.08
2.25
3.02
2.00
1.95
0.97
2.98
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

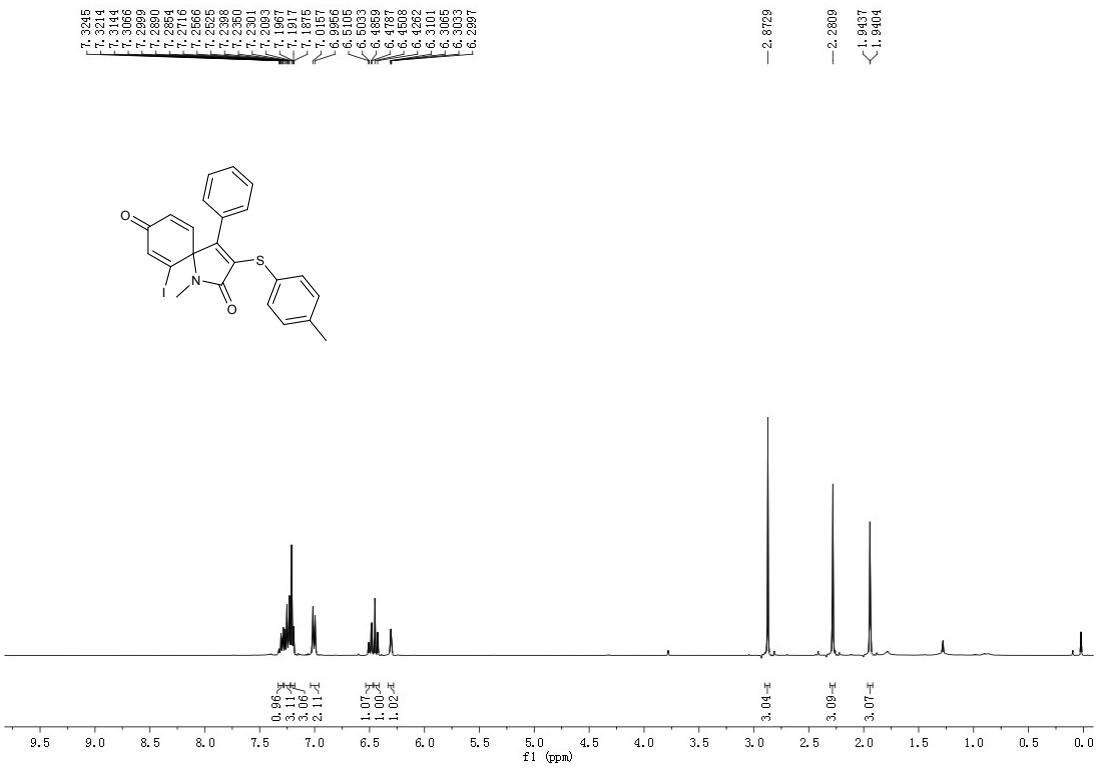

185.9425
185.7918
170.9005
167.9830
148.7252
141.5429
141.5109
137.9172
132.2260
131.7528
129.9833
129.7246
129.6506
128.4404
128.0622
113.8862
77.3583
77.0407
76.7230
68.4509
68.2183
26.1265
21.1004
O
Br
N
O
S
O
F
f1 (ppm)

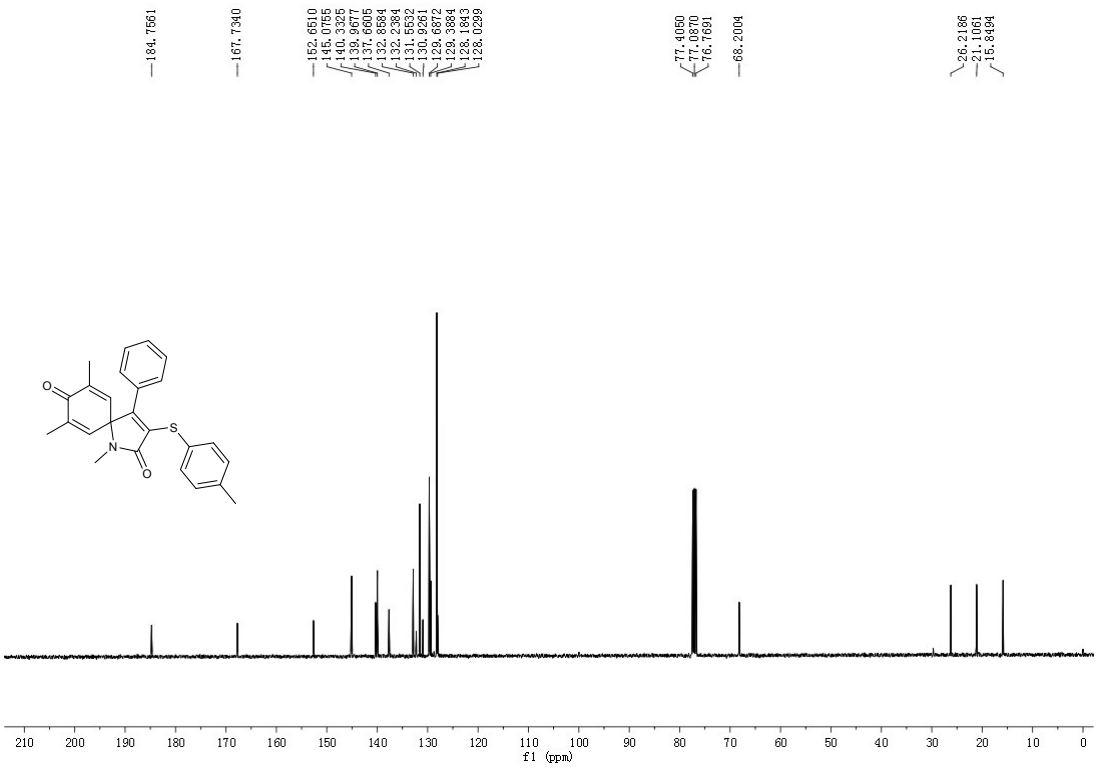

7.3494
7.3458
7.3421
7.3350
7.3279
7.3213
7.3136
7.3099
7.3060
7.2852
7.2731
7.2689
7.2636
7.2484
7.2378
7.2334
7.2265
7.2207
7.2175
7.2138
7.2064
7.2003
7.1962
7.0078
6.9880
6.9285
6.9245
6.6856
6.6610
6.5120
6.5080
6.4874
6.4634
2.8538
2.2806
1.17
3.07
3.05
2.08
0.98
1.00
1.00
3.02
3.07
f1 (ppm)

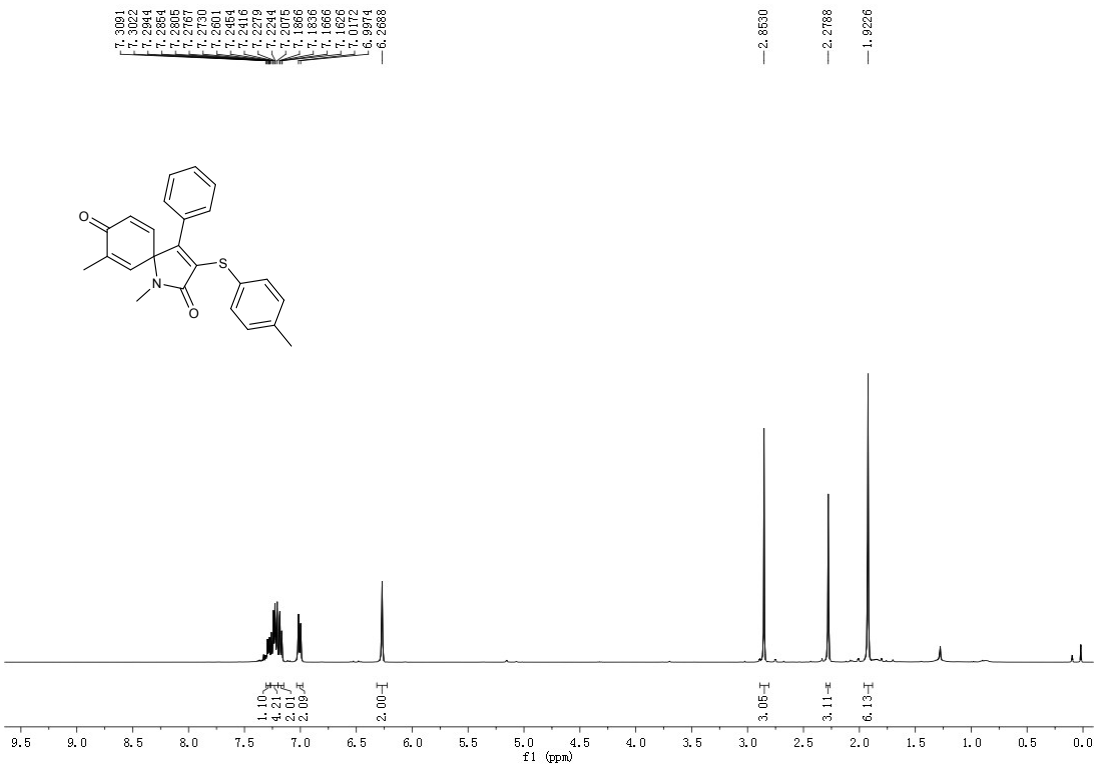

182.1829
167.7610
150.1163
144.9216
144.3169
137.8351
137.0857
134.5857
131.9035
131.7935
130.0152
129.6622
128.3708
128.1914
127.4609
77.3609
77.2461
77.0432
76.7256
71.2883
25.8795
21.1101
O
N
I
O
S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

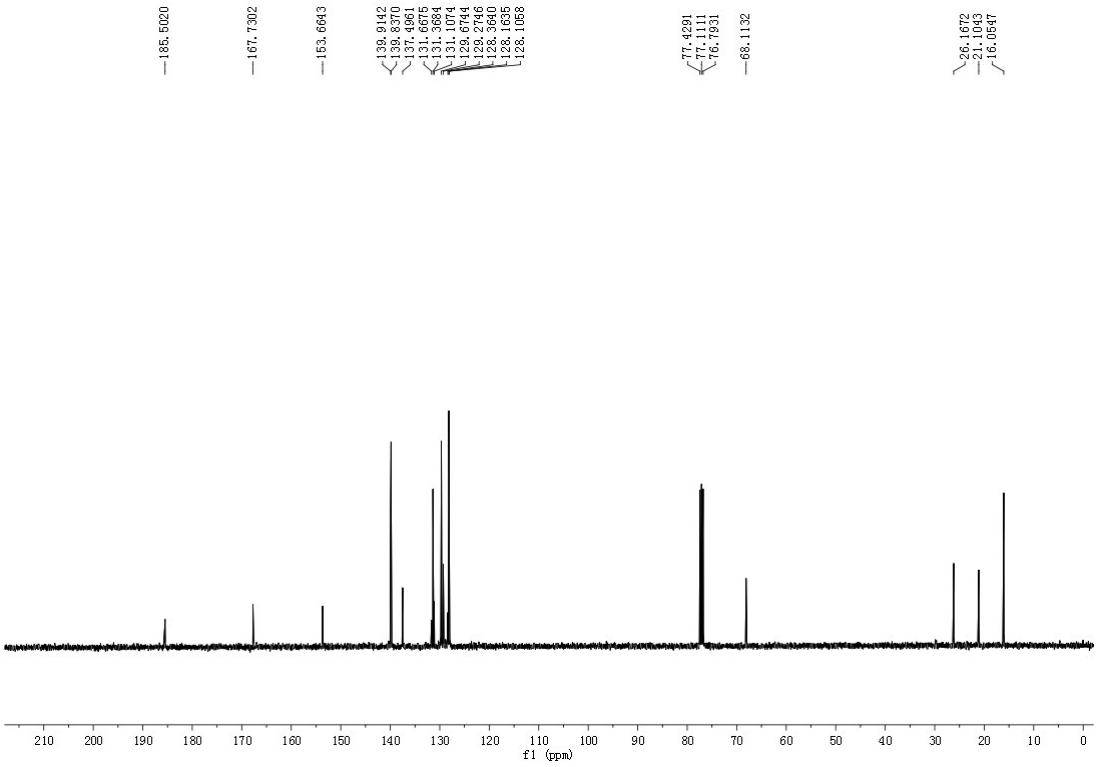

7.3629
7.3484
7.3443
7.3390
7.3318
7.3241
7.3194
7.3143
7.3096
7.2962
7.2863
7.2759
7.2725
7.2630
7.2490
7.2315
7.2268
7.0111
6.9911
6.8011
6.7765
6.5631
6.5581
6.5385
6.5345
2.8436
2.2834
O
N
Br
O
S
1.12
4.09
3.24
2.00
1.02
1.00
3.00
3.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

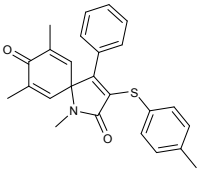

180.9644
167.5088
150.4202
144.8599
144.5314
137.8851
134.6558
132.0248
131.9644
129.9851
129.6525
129.6078
128.3230
127.3201
125.5053
77.3414
77.0238
76.7061
72.0727
25.9334
21.1215
O
O
N
S
O
f1 (ppm)

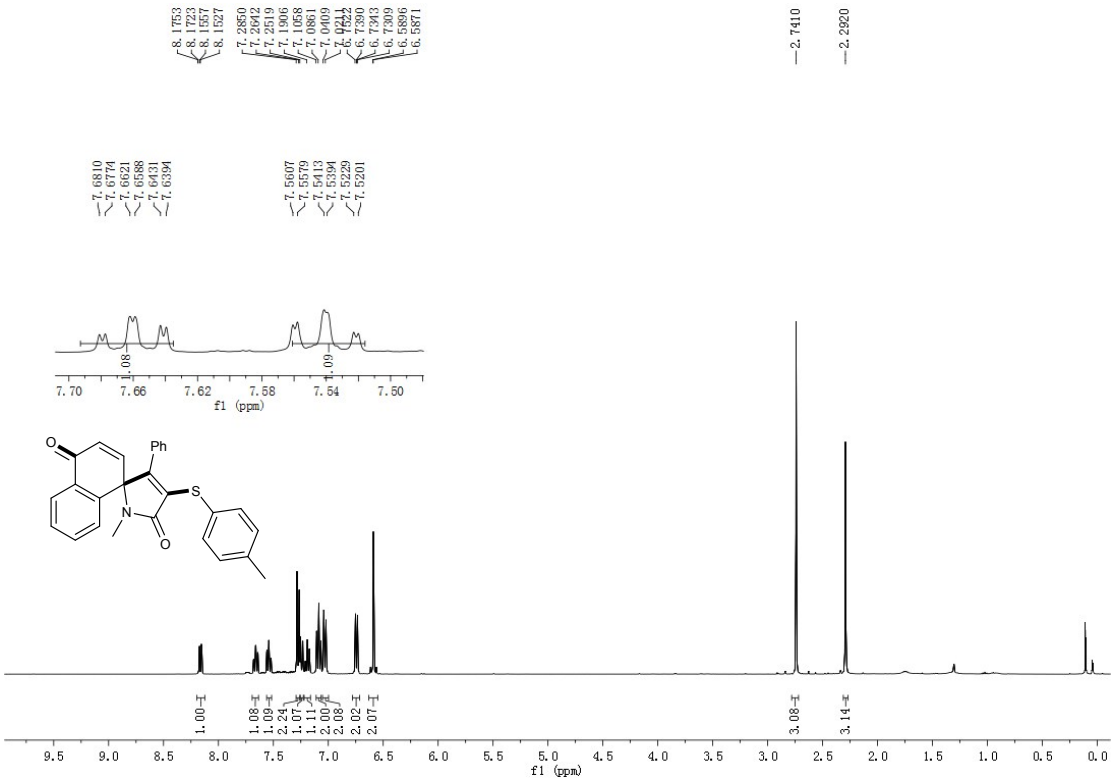

7.3245
7.3214
7.3144
7.3066
7.2999
7.2890
7.2854
7.2716
7.2566
7.2525
7.2398
7.2350
7.2301
7.2093
7.1967
7.1917
7.1875
7.0157
6.9956
6.5105
6.5033
6.4859
6.4787
6.4508
6.4262
6.3101
6.3065
6.3033
6.2997
2.8729
2.2809
1.9437
1.9404
O
I
N
S
O
0.96
3.11
3.06
2.11
1.07
1.00
1.02
3.04
3.09
3.07
f1 (ppm)

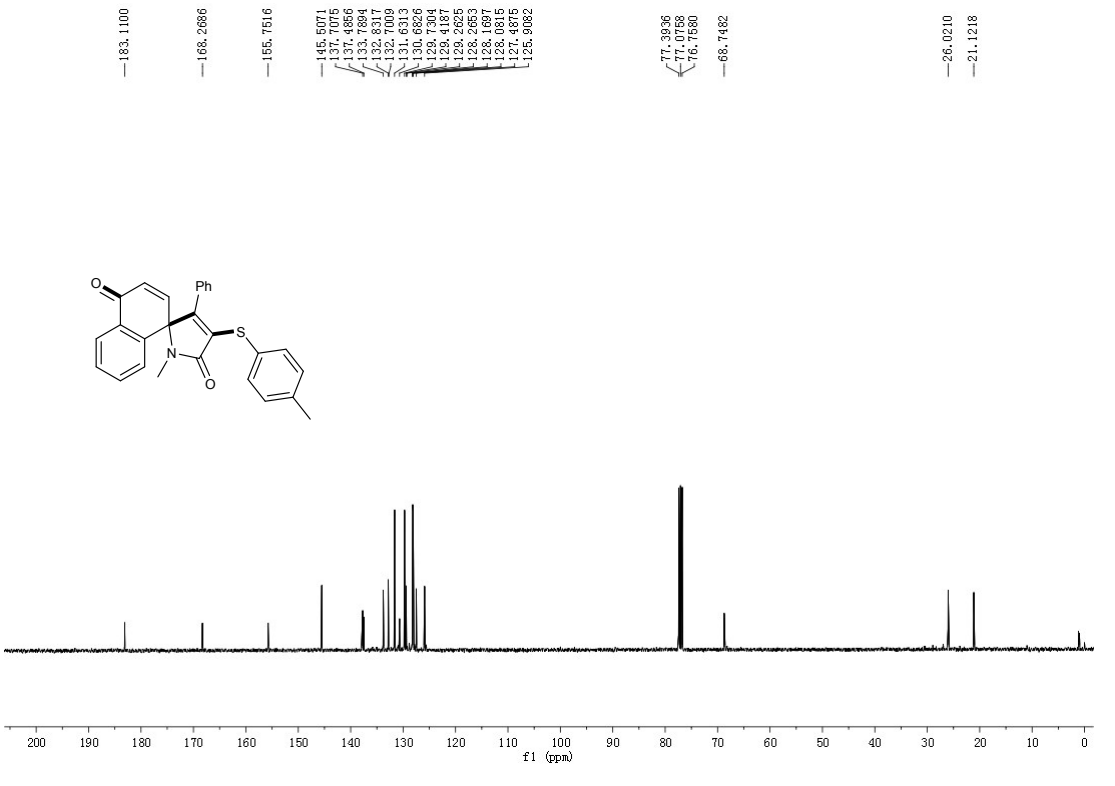

184.7561
167.7340
152.6510
145.0755
140.3325
139.9677
137.6605
132.8684
132.2384
131.6532
130.9261
129.6872
129.3884
128.1843
126.0299
77.4050
77.0870
76.7691
68.2004
26.2186
21.1061
15.8494
O
S
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

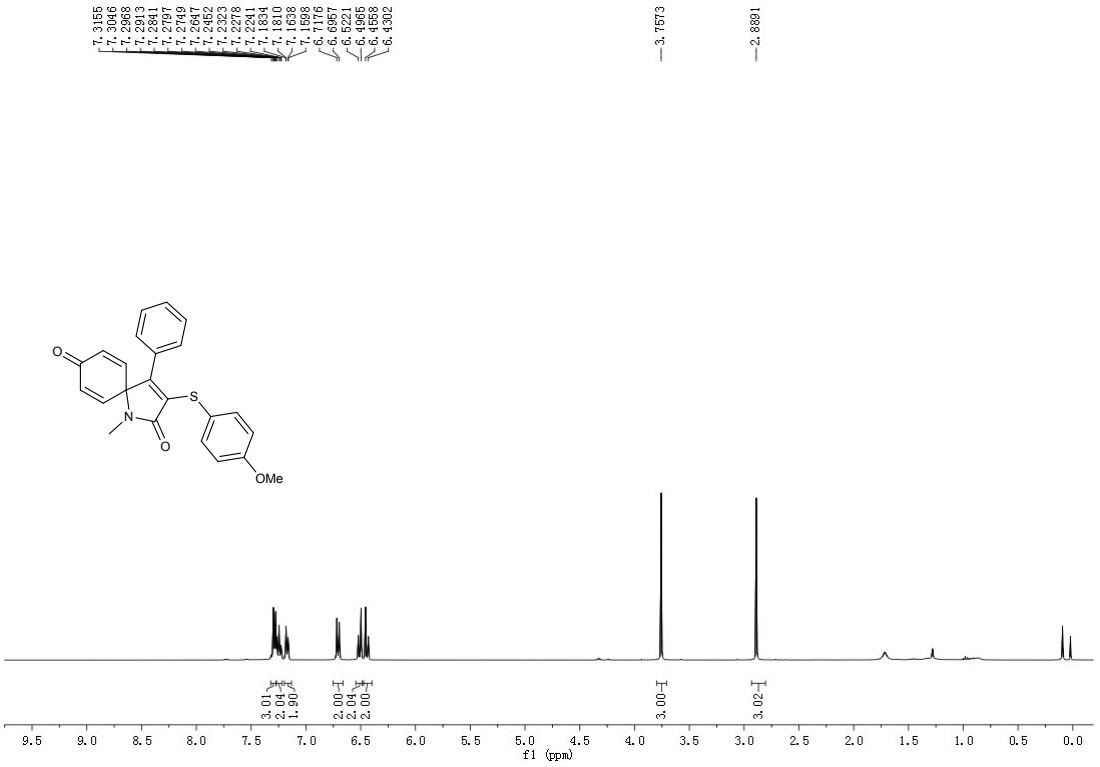

7.3091
7.3022
7.2944
7.2854
7.2805
7.2767
7.2730
7.2601
7.2454
7.2416
7.2279
7.2244
7.2075
7.1866
7.1836
7.1666
7.1626
7.0172
6.9974
6.2688
2.8530
2.2788
1.9226
O
S
N
O
1.10
4.21
2.01
2.09
2.00
3.05
3.11
6.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

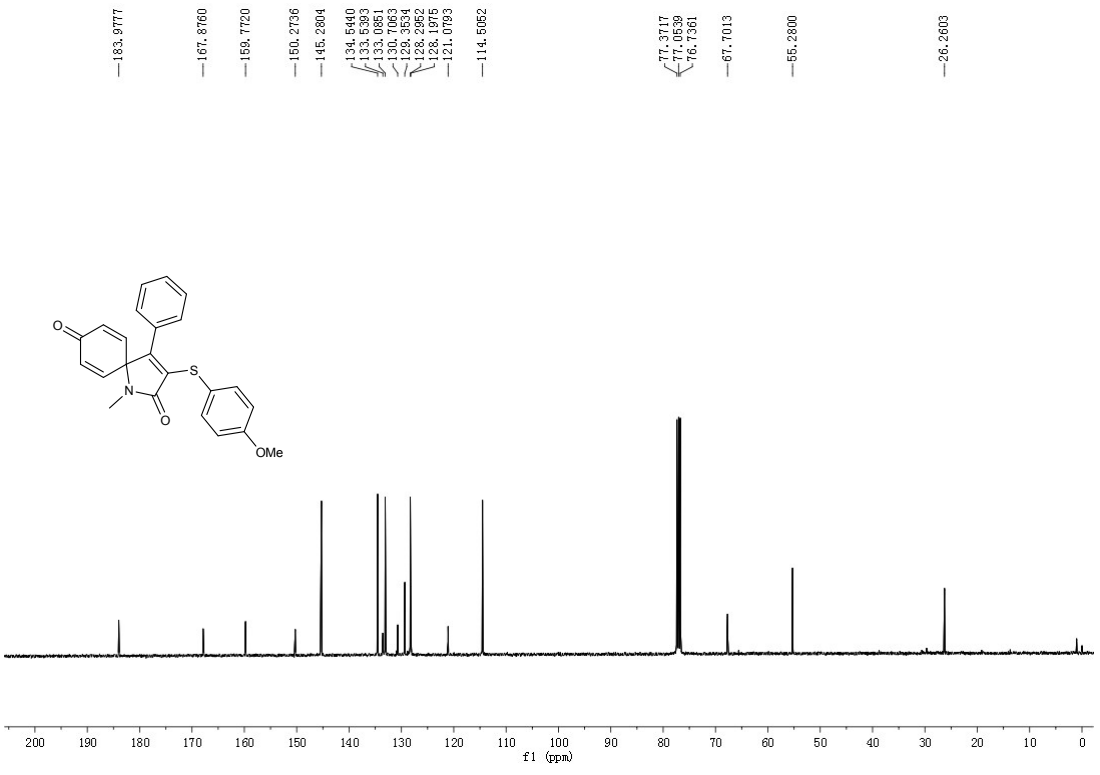

185.5020
167.7302
153.6643
139.9142
139.6370
137.4961
131.6675
131.3684
131.1074
129.6544
128.7746
128.3640
128.1635
128.1058
77.4291
77.1111
76.7931
68.1132
26.1672
21.1043
16.0547
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

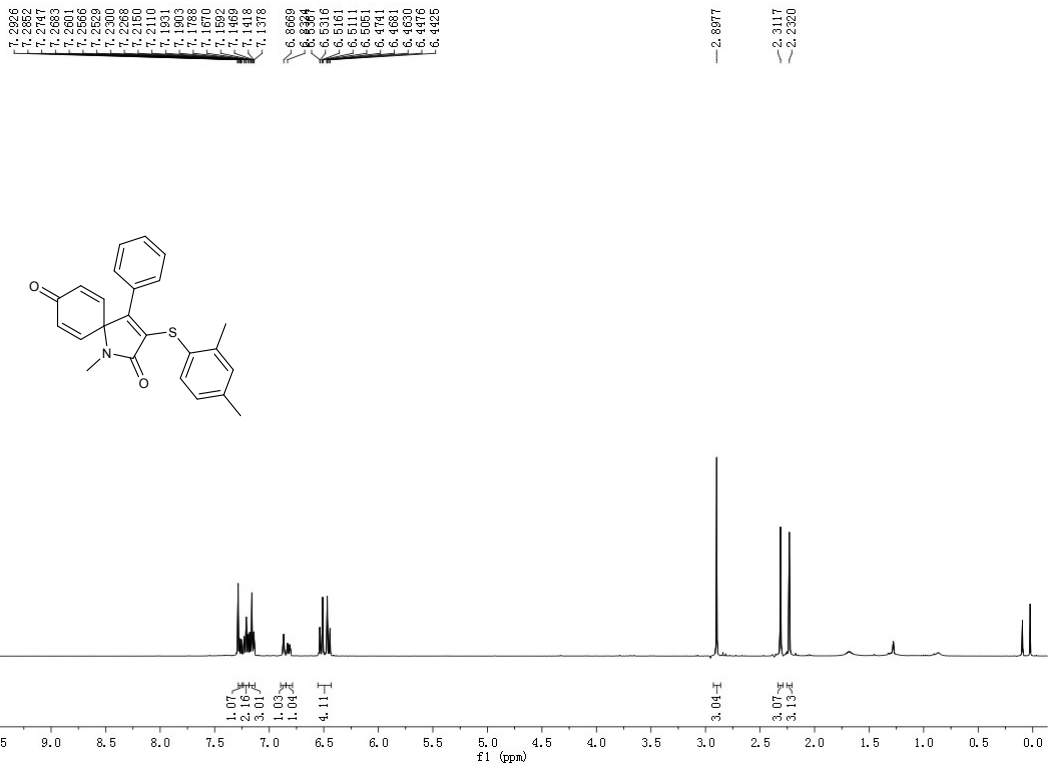

O
N
O
S

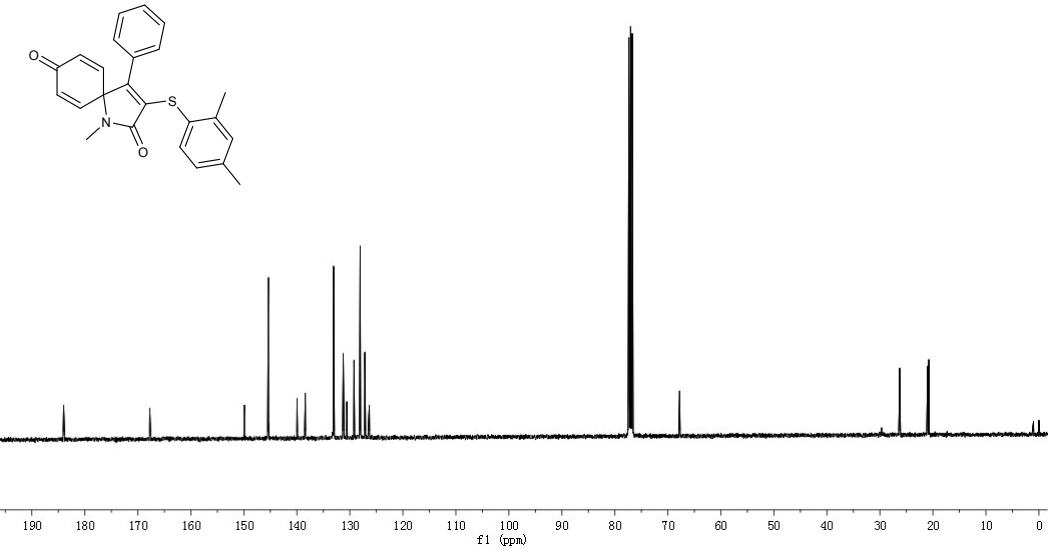

8.1753
8.1723
8.1557
8.1527
7.2850
7.2642
7.2519
7.1906
7.1058
7.0861
7.0409
6.7622
6.7390
6.7343
6.7309
6.5896
6.5871
2.7410
2.2920
7.6810
7.6774
7.6621
7.6588
7.6431
7.6394
7.5607
7.5579
7.5413
7.5394
7.5229
7.5201
1.08
1.09
7.70
7.66
7.62
7.58
7.54
7.50
f1 (ppm)
Ph
O
N
S
O
1.00
1.08
1.09
2.24
1.07
1.11
2.08
2.02
2.07
3.08
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

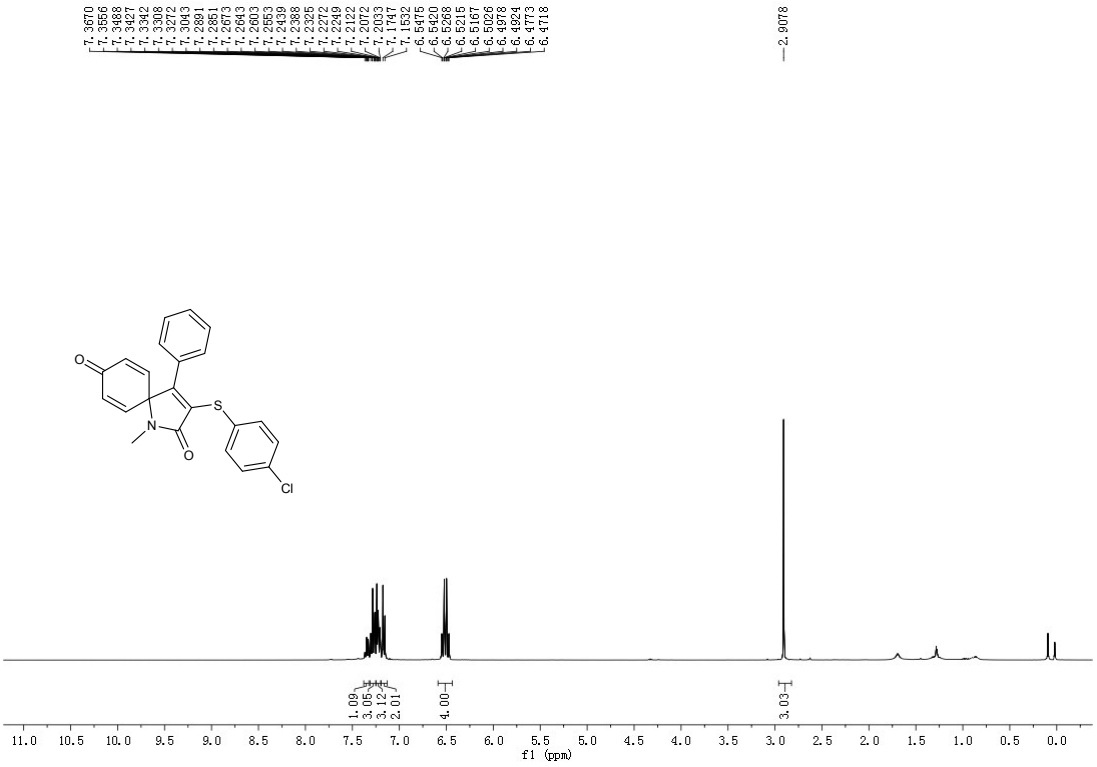

183.1100
168.2686
155.7516
145.5071
137.7075
137.4856
133.7894
132.8317
132.7009
131.6313
130.6826
129.7304
129.4187
129.2625
128.2653
128.1697
128.0815
127.4875
125.9082
77.3936
77.0758
76.7580
68.7482
26.0210
21.1218
O
Ph
N
S
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

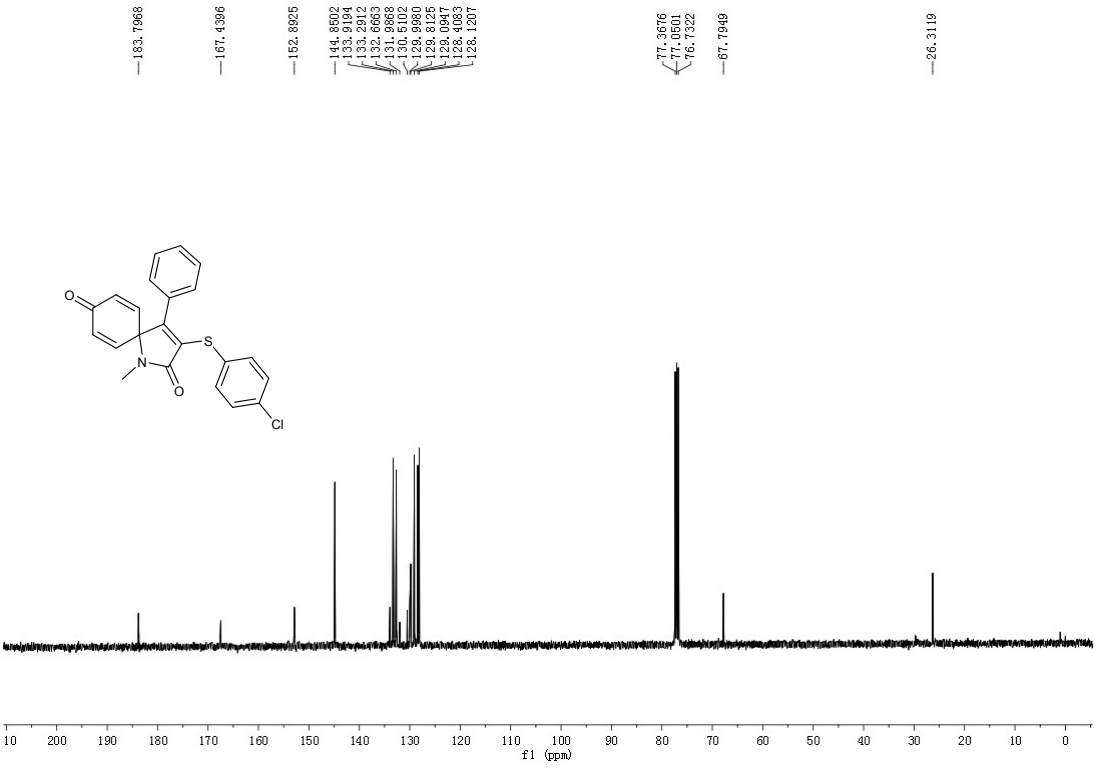

7.3155
7.3046
7.2968
7.2913
7.2841
7.2797
7.2749
7.2647
7.2452
7.2323
7.2278
7.2241
7.1834
7.1810
7.1638
7.1598
6.7176
6.6957
6.5221
6.4965
6.4558
6.4302
3.7573
2.8891
O
N
O
S
OMe
3.01
2.04
1.90
2.00
2.04
2.00
3.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

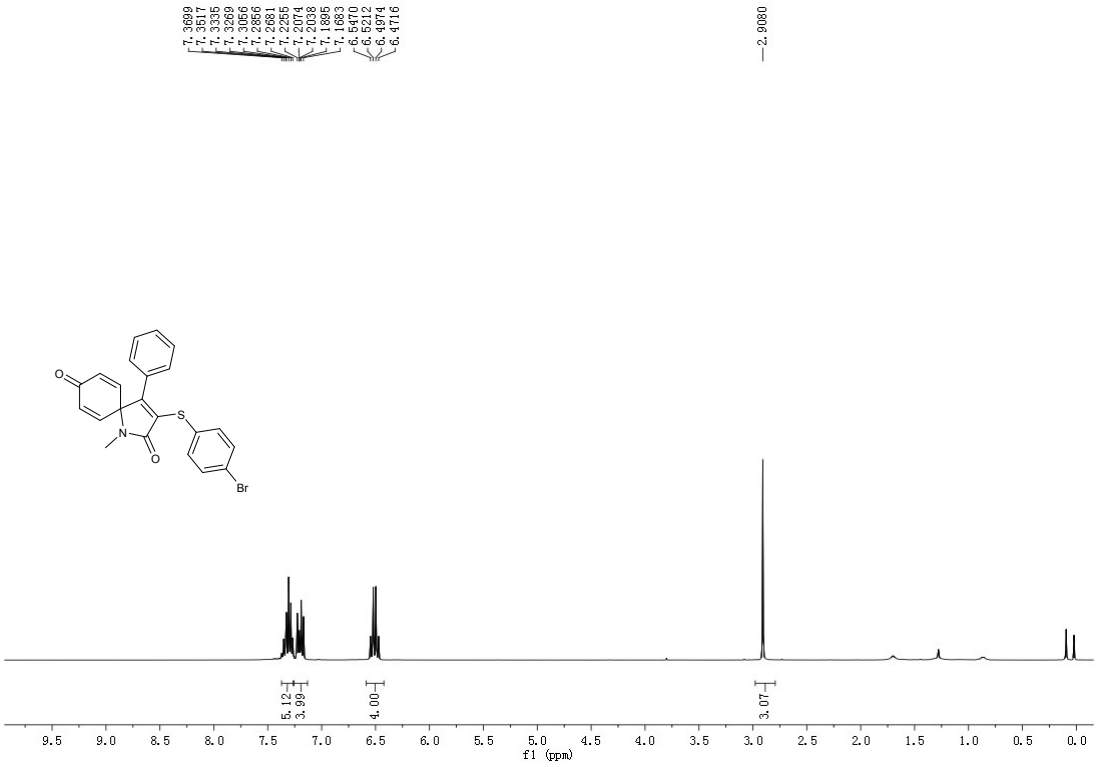

183.9777
167.8760
159.7720
150.2736
145.2804
134.5440
133.5393
133.0851
130.7063
128.3534
128.2952
128.1975
121.0793
114.5052
77.3717
77.0539
76.7361
67.7013
55.2800
26.2603
O
N
O
S
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

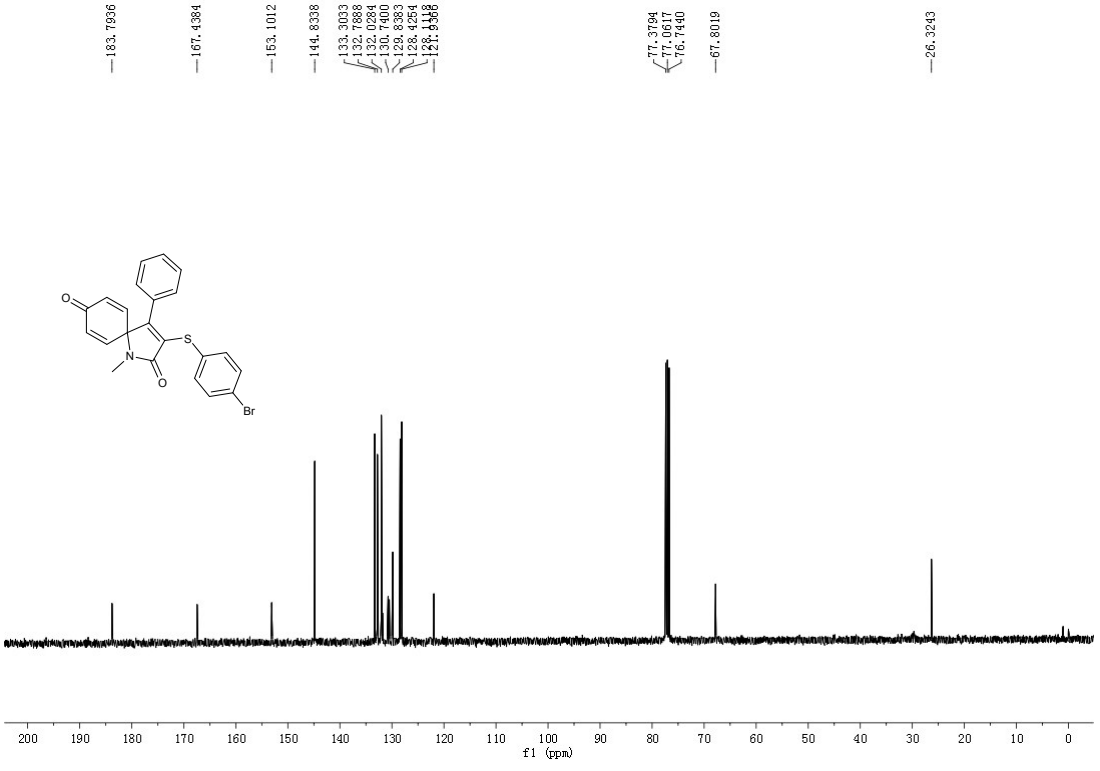

7.2926
7.2852
7.2747
7.2683
7.2601
7.2566
7.2529
7.2300
7.2268
7.2155
7.2110
7.1931
7.1903
7.1788
7.1670
7.1592
7.1469
7.1418
7.1378
6.8669
6.8324
6.5316
6.5161
6.5111
6.5061
6.4741
6.4681
6.4630
6.4476
6.4425
2.8977
2.3117
2.2320
1.07
2.16
3.01
1.03
1.04
4.11
3.04
3.07
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


183.9984
167.7487
149.9072
138.4110
133.2234
133.0707
132.9980
131.2496
130.5622
129.2103
128.0776
128.0594
127.1685
126.3281
77.3559
77.0383
76.7206
67.7836
26.2746
20.9872
20.7544
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.3670
7.3656
7.3488
7.3427
7.3342
7.3308
7.3272
7.3043
7.2891
7.2851
7.2673
7.2643
7.2603
7.2553
7.2439
7.2388
7.2325
7.2272
7.2249
7.2122
7.2072
7.2033
7.1747
7.1532
6.5475
6.5420
6.5268
6.5215
6.5167
6.5026
6.4978
6.4924
6.4773
6.4718
2.9078
O
S
N
O
Cl
1.09
3.05
3.12
2.01
4.00
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


183.7968
167.4396
152.8925
144.8502
133.9194
133.2912
132.6663
131.9866
130.5102
129.9980
129.8125
129.0947
128.4083
128.1207
77.3676
77.0501
76.7322
67.7949
26.3119
O
S
N
O
Cl
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

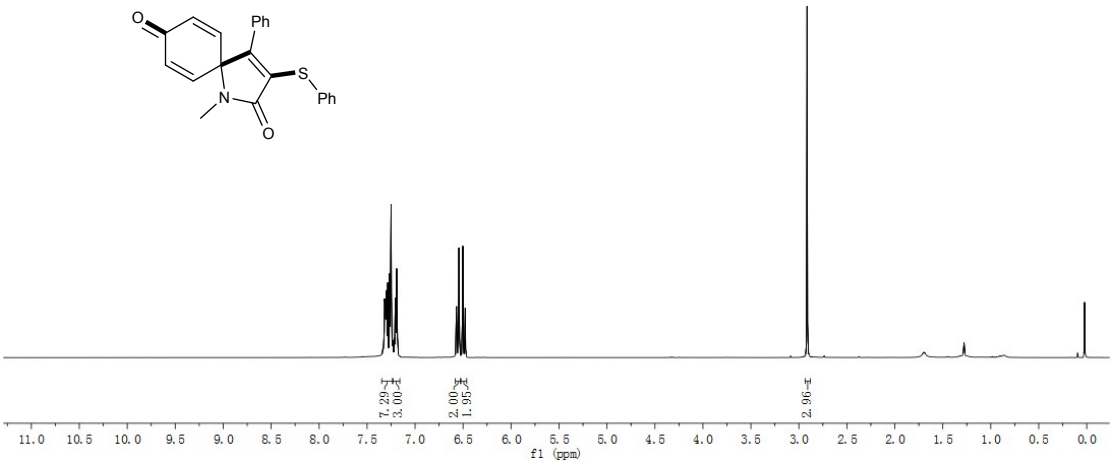

7.3699
7.3617
7.3335
7.3269
7.3056
7.2866
7.2681
7.2255
7.2074
7.2038
7.1895
7.1683
6.5470
6.5212
6.4974
6.4716
2.9080
O
N
O
S
Br
5.12
3.99
4.00
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


183.7936
167.4384
153.1012
144.8338
133.3033
132.7888
132.0284
130.7400
129.8383
128.4254
128.0118
121.9308
77.3794
77.0617
76.7440
67.8019
26.3243
O
N
O
S
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

CH-9-13-1

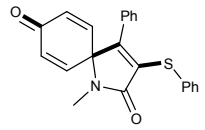

7.3281
7.3182
7.3099
7.3028
7.2986
7.2943
7.2851
7.2712
7.2657
7.2555
7.2500
7.2347
7.2283
7.2157
7.2055
7.2001
7.1924
7.1873
6.5687
6.5478
6.5431
6.5377
6.5084
6.5026
6.4981
6.4771


2.9141


O
Ph
S
Ph
N
O
7.29-7
3.00-7
2.00-2
1.95-2
2.96-3
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

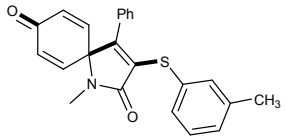
CH-9-13-1

183.8905
167.6767
152.8002
145.1193
133.1905
132.2636
131.6952
131.0487
130.6929
129.6761
128.9253
128.3169
128.1145
127.5135
77.3635
77.0459
76.7281
67.7508
26.2929

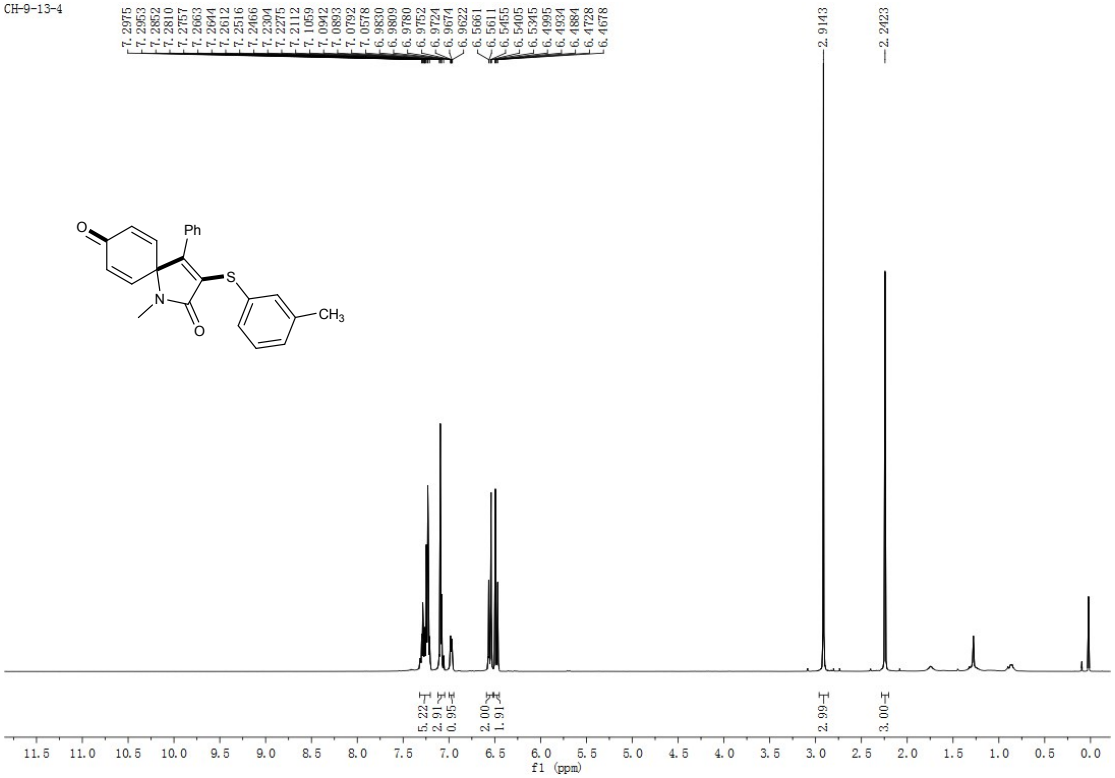


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

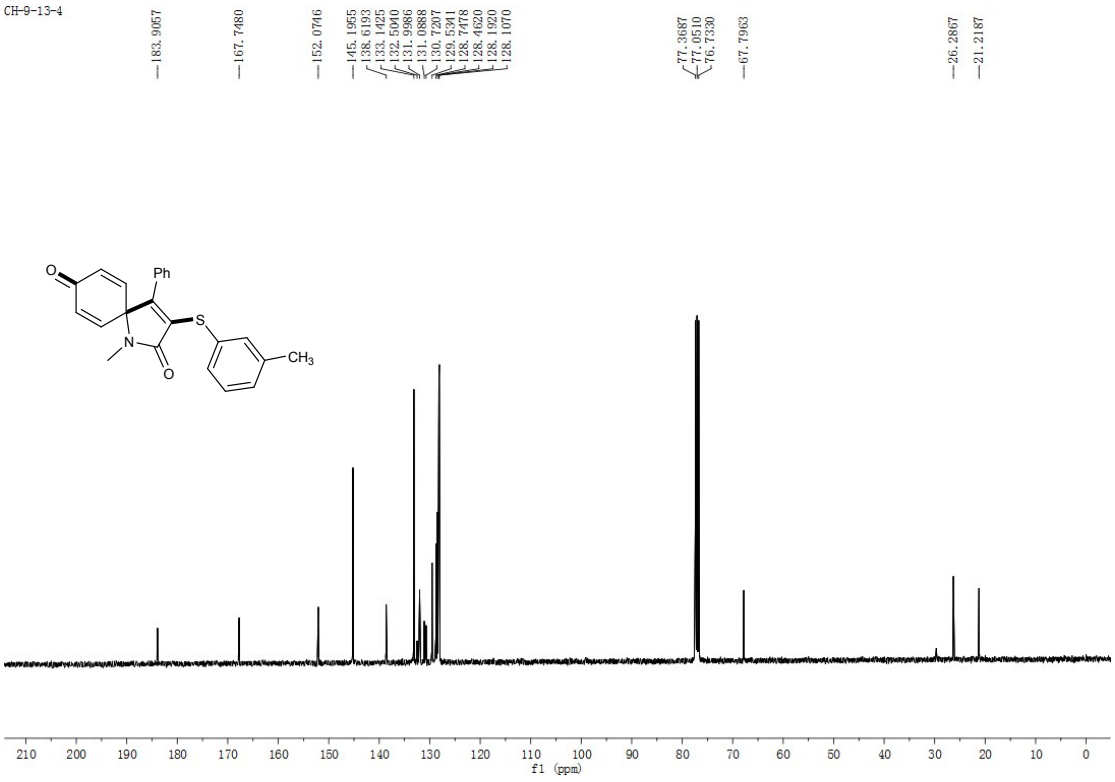
f1 (ppm)

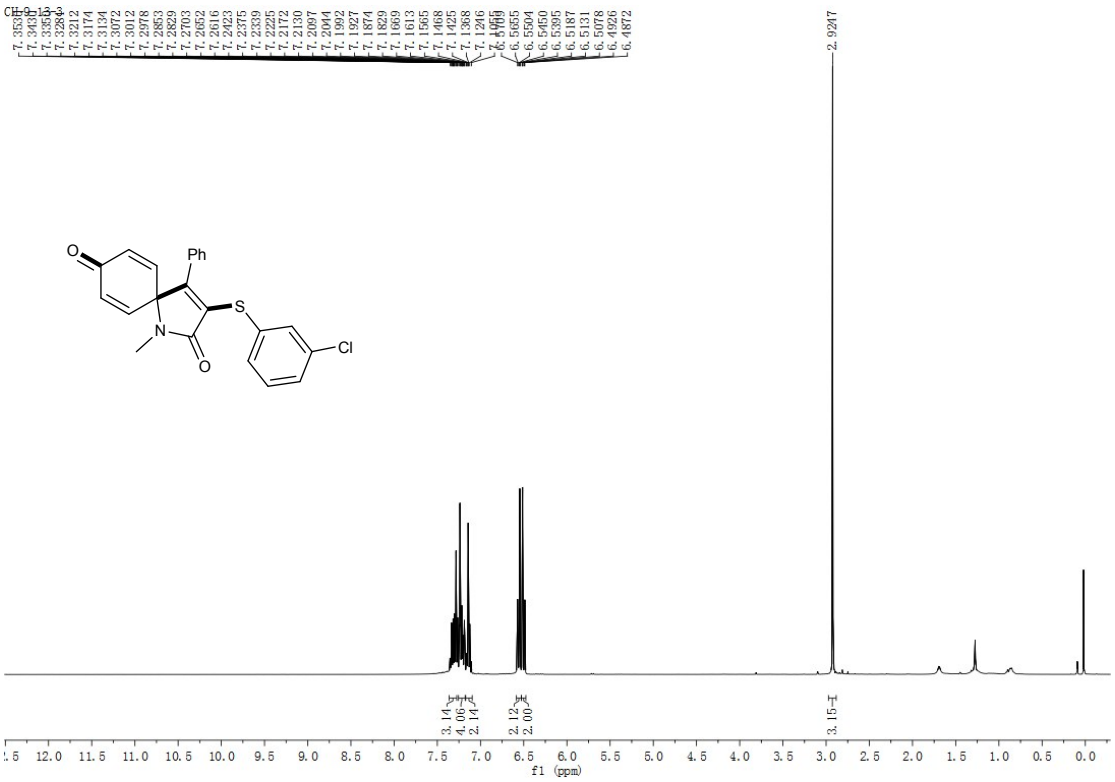


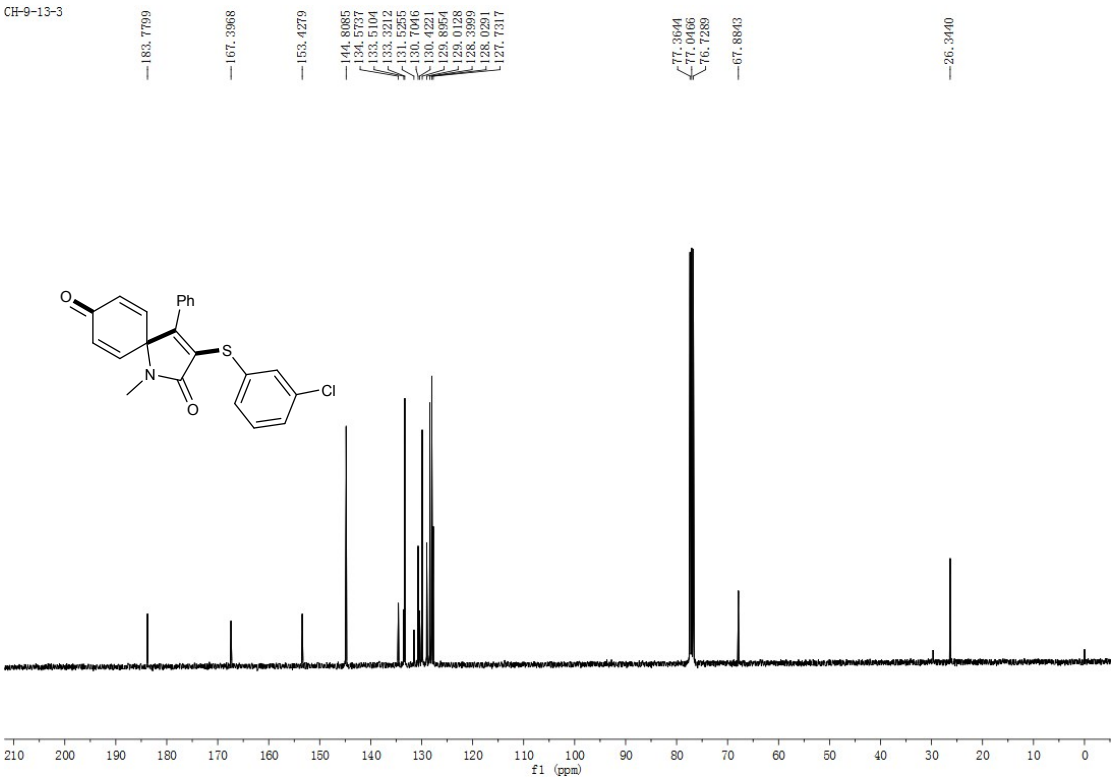
CH-9-13-4



CH-9-13-4




CH-9-13-3
O
Ph
S
N
O
Cl
2.9247
3.14
4.06
2.14
2.12
2.00
3.15
f1 (ppm)


CH-9-13-3
183.7799
167.3968
153.4279
144.8085
134.5737
133.5104
133.3212
131.5255
130.7046
130.4221
129.8954
129.0128
128.3999
128.0291
127.7317
77.3644
77.0466
76.7289
67.8843
26.3440
O
Ph
S
N
O
Cl
f1 (ppm)