$ZnBr_2$-Mediated Oxidative *Spiro*-Bromocyclization of Propiolamide for the Synthesis of 3-Bromo-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Yicheng He and Guanyinsheng Qiu*

College of Biological, Chemical Science and Engineering, Jiaxing University, 118 Jiahang Road, Jiaxing 314001, China. Email: 11110220028@fudan.edu.cn

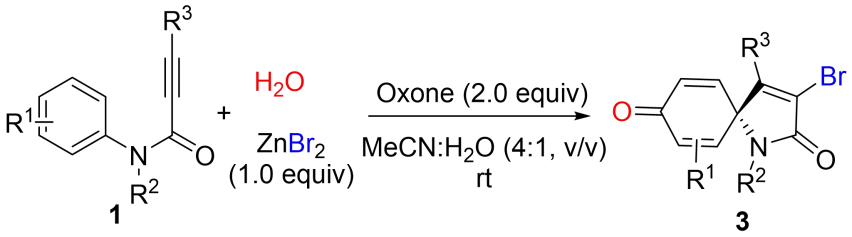
Supporting Information

1. General experimental methods.
2. General experimental procedure and characterization data.
3. Check CIF report of the Crystal (Compound **3a**)
4. ^{1}H and ^{13}C NMR spectra of compound **3**.

General experimental methods:

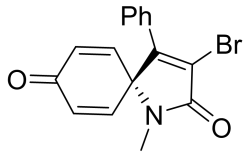
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

General experimental procedure for $ZnBr_2$-Mediated Oxidative *Spiro*-Bromocyclization of Propiolamide.



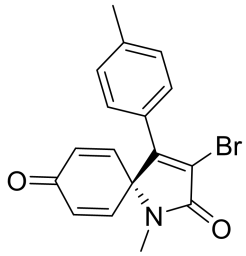
N-arylpropolamide **1** (0.2 mmol), $ZnBr_2$ (1.0 equiv) and Oxone (2.0 equiv) was added to a test tube, and then co-solvent MeCN:H_2O (2.0 mL, 4:1, v/v) was added. The mixture was stirred at room temperature. After completion of reaction as indicated by TLC (overnight), the mixture was filtrated and separated. The organic layer was dried by Na_2SO_4. Evaporation of the solvent and flash column chromatograph provided the desired product **3**.

The final products **6** and **8** were also synthesized according to the above procedure.



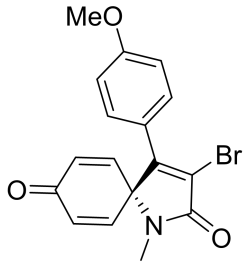
3-bromo-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3a**)[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 5H), 6.52 (d, *J* = 10.1 Hz, 2H), 6.47 (d, *J* = 10.1 Hz, 2H), 2.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7, 165.7, 151.3, 144.1, 133.4, 130.2, 130.1, 128.7, 127.7, 119.8, 68.3, 26.6; HRMS (ESI) calcd for $C_{16}H_{13}BrNO_2^+$: 330.0124 ($M + H^+$), found: 330.0124.



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

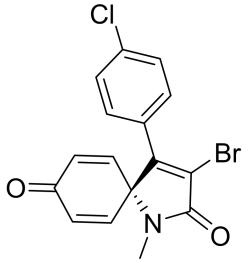
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 10.5 Hz, 2H), 6.46 (d, *J* = 10.4 Hz, 2H), 2.91 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7, 165.9, 151.2, 144.3, 140.6, 133.3, 129.4, 127.6, 127.2, 119.2, 68.3, 26.6, 21.4; HRMS (ESI) calcd for $C_{17}H_{15}BrNO_2^+$: 344.0281 ($M + H^+$), found: 344.0271.



3-bromo-4-(4-methoxyphenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3c**)[1]

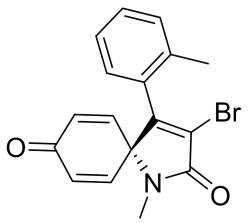
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.52-6.51 (m, 4H), 3.81 (s, 3H), 2.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.8,

166.0, 161.0, 150.5, 144.6, 133.2, 129.2, 122.3, 118.2, 114.1, 68.1, 55.3, 26.5; HRMS (ESI) calcd for $C_{17}H_{15}BrNO_3^+$: 360.0230 ($M + H^+$), found: 360.0229.



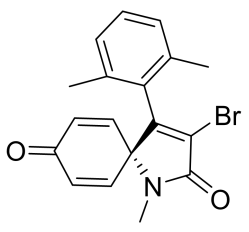
3-bromo-4-(4-chlorophenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3d**)

^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 4H), 6.51-6.50 (m, 4H), 2.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.4, 165.5, 150.0, 143.9, 136.5, 133.6, 129.1, 129.0, 128.5, 68.1, 26.6; HRMS (ESI) calcd for $C_{16}H_{12}BrClNO_2^+$: 363.9734 ($M + H^+$), found: 363.9730.



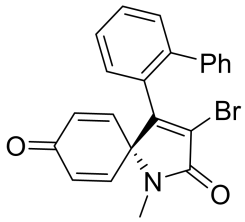
3-bromo-1-methyl-4-(*o*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3e**)

^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 2H), 7.13-7.09 (m, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.60 (d, J = 10.0 Hz, 1H), 6.52-6.46 (m, 2H), 6.29 (d, J = 10.0 Hz, 1H), 2.93 (d, J = 1.2 Hz, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.4, 165.5, 152.5, 143.5, 143.3, 136.0, 133.8, 133.2, 130.7, 129.8, 128.7, 125.4, 122.0, 69.8, 27.2, 19.9; HRMS (ESI) calcd for $C_{17}H_{15}BrNO_2^+$: 344.0281 ($M + H^+$), found: 344.0285.



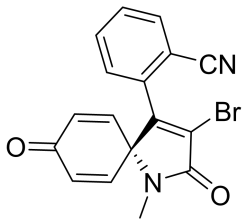
3-bromo-4-(2,6-dimethylphenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 9.6 Hz, 2H), 6.35 (d, *J* = 9.6 Hz, 2H), 2.99 (s, 3H), 2.13 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.5, 165.5, 153.6, 144.4, 136.0, 132.7, 129.4, 128.3, 128.1, 122.7, 71.2, 27.3, 21.0; HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2^+$: 358.0437 (M + H^+), found: 358.0438.



4-([1,1'-biphenyl]-2-yl)-3-bromo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3g**)

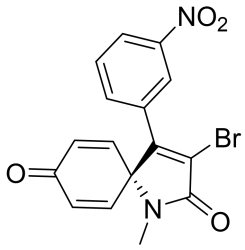
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 1H), 7.36-7.33 (m, 5H), 7.23-7.21 (m, 2H), 6.99-6.96 (m, 1H), 6.32 (d, *J* = 10.0 Hz, 1H), 6.22 (d, *J* = 10.0 Hz, 1H), 5.83 (dd, *J* = 10.0, 1.7 Hz, 1H), 4.99 (dd, *J* = 10.0, 2.8 Hz, 1H), 2.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.6, 165.4, 154.8, 144.1, 143.1, 141.0, 140.5, 132.9, 130.7, 130.1, 129.6, 128.7, 128.3, 128.0, 127.3, 123.8, 69.1, 26.8; HRMS (ESI) calcd for $C_{22}H_{17}BrNO_2^+$: 406.0437 (M + H^+), found: 406.0440.



2-(3-bromo-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-4-yl)benzonitrile (**3h**)

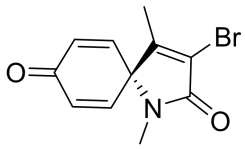
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 1H), 7.59-7.51 (m, 2H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.67-6.61 (m, 2H), 6.49-6.37 (m, 2H), 2.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.2, 164.7, 148.5, 143.3, 142.5, 133.5, 133.4, 132.7, 130.3, 129.2, 124.5,

117.0, 112.8, 69.4, 27.2; HRMS (ESI) calcd for $C_{17}H_{12}BrN_2O_2^+$: 355.0077 (M + H^+), found: 355.0010.



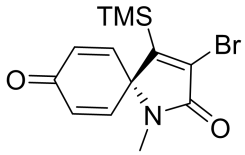
3-bromo-1-methyl-4-(3-nitrophenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3i**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.25 (m, 2H), 7.71-7.68 (m, 1H), 7.60-7.58 (m, 1H), 6.51-6.55 (m, 4H), 2.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.0, 164.9, 148.6, 148.1, 143.3, 134.0, 133.6, 131.7, 130.1, 124.9, 123.1, 122.2, 68.2, 26.8; HRMS (ESI) calcd for $C_{16}H_{12}BrN_2O_4^+$: 374.9975 (M + H^+), found: 374.9985.



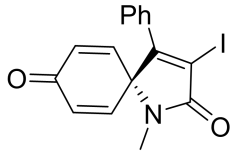
3-bromo-1,4-dimethyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3j**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (d, *J* = 9.7 Hz, 2H), 6.32 (d, *J* = 9.7 Hz, 2H), , 2.81 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7, 165.8, 149.8, 144.6, 133.4, 118.9, 68.4, 26.9, 12.4; HRMS (ESI) calcd for $C_{11}H_{11}BrNO_2^+$: 267.9968 (M + H^+), found: 267.9972.



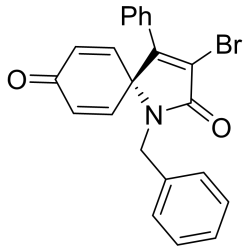
3-bromo-1-methyl-4-(trimethylsilyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3k**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, *J* = 9.6 Hz, 2H), 6.31 (d, *J* = 9.6 Hz, 2H), , 2.83 (s, 3H), 0.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.9, 165.7, 152.4, 144.5, 133.2, 132.9, 69.4, 26.4, -1.2; HRMS (ESI) calcd for $C_{13}H_{17}BrNO_2Si^+$: 326.0206 (M + H^+), found: 326.0208.



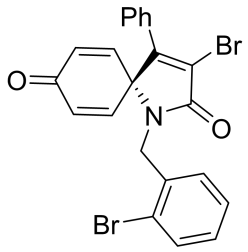
3-iodo-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3l**)[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.34(m, 3H), 7.29-7.27 (m, 2H), 6.51 (d, *J* = 10.0 Hz, 2H), 6.46 (d, *J* = 10.6 Hz, 2H), 2.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7, 167.4, 157.9, 144.0, 133.3, 131.8, 130.1, 128.7, 127.7, 98.2, 70.3, 27.0



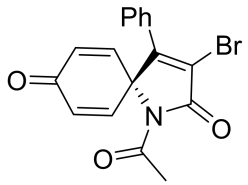
1-benzyl-3-bromo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3n**)[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21(m, 10H), 6.33 (d, *J* = 10.2 Hz, 2H), 6.22 (d, *J* = 10.7 Hz, 2H), 4.54 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.9, 165.9, 151.8, 144.2, 137.0, 132.6, 130.1, 128.9, 128.6, 128.5, 128.0, 127.8, 119.8, 68.8, 45.4; HRMS (ESI) calcd for $C_{22}H_{17}BrNO_2^+$: 406.0437 (M + H^+), found: 406.0439.



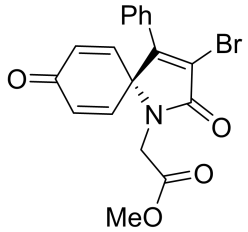
3-bromo-1-(2-bromobenzyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3o**)[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.10 (m, 9H), 6.29-6.26 (m, 4H), 4.76 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.8, 165.9, 152.2, 143.3, 136.2, 132.8, 130.7, 130.2, 129.9, 129.7, 128.6, 127.8, 124.0, 119.5, 68.6, 44.7; HRMS (ESI) calcd for $C_{22}H_{16}Br_2NO_2^+$: 483.9542 (M + H^+), found: 483.9541



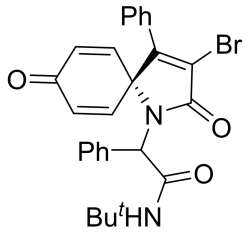
1-acetyl-3-bromo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3p**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.35 (m, 3H), 7.23-7.17 (m, 2H), 6.56 (d, *J* = 10.1 Hz, 2H), 6.40 (d, *J* = 10.6 Hz, 2H), 2.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.69, 168.50, 164.41, 156.22, 142.81, 132.49, 130.53, 128.57, 128.11, 119.15, 68.49, 25.59; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{13}BrNO_3^+$: 358.0079; found: 358.0072.



methyl 2-(3-bromo-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetate (**3q**)

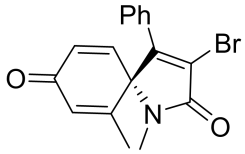
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 5H), 6.65 (d, *J* = 9.7 Hz, 2H), 6.42 (d, J = 9.7 Hz, 2H), 4.03 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7, 168.5, 165.8, 152.6, 143.4, 133.1, 130.4, 128.8, 127.7, 119.3, 105.0, 68.3, 52.6, 41.7; HRMS (ESI) calcd for $C_{18}H_{15}BrNO_4^+$: 388.0179 ($M + H^+$), found: 388.0161



2-(3-bromo-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)-N-(tert-butyl)-2-phenylacetamide (**3r**)

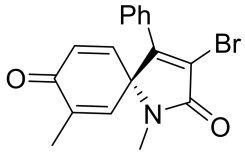
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.22 (m, 10H), 6.72 (dd, *J* = 10.0, 2.8 Hz, 1H), 6.49 (dd, *J* = 10.0, 2.9 1H), 6.25 (d, *J* = 10.0 Hz, 1H), 6.21 (d, *J* = 10.0 Hz, 1H), 5.49

(s, 1H), 4.79 (s, 1H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.0, 166.6, 165.7, 152.4, 144.3, 144.1, 135.2, 132.5, 132.3, 130.1, 129.4, 129.3, 129.1, 128.6, 127.8, 120.0, 69.6, 62.8, 52.0, 28.5; HRMS (ESI) calcd for $C_{27}H_{26}BrN_2O_3^+$: 505.1121 (M + H^+), found: 505.1116



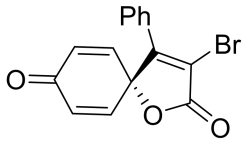
3-bromo-1,6-dimethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3s)**[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (m, 5H), 6.49-6.45 (m, 2H), 6.36 (s, 1H), 2.84 (s, 3H), 1.74 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4, 166.2, 152.6, 151.2, 144.4, 132.9, 132.2, 130.4, 129.9, 128.9, 127.5, 119.7, 70.4, 26.2, 17.7; HRMS (ESI) calcd for $C_{17}H_{15}BrNO_2^+$: 344.0281 (M + H^+), found: 344.0289



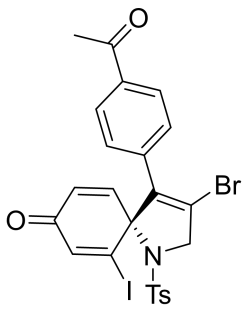
3-bromo-1,7-dimethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3t**) [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 5H), 6.46-6.45 (m, 2H), 6.28 (s, 1H), 2.91 (s, 3H), 1.92 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 165.8, 151.7, 143.9, 140.7, 138.8, 133.2, 130.3, 130.1, 128.7, 127.7, 119.4, 68.8, 26.5, 15.9; HRMS (ESI) calcd for $C_{17}H_{15}BrNO_2^+$: 344.0281 (M + H^+), found: 344.0280



3-bromo-4-phenyl-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6**)[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.41(m, 5H), 6.67 (d, *J* = 10.1 Hz, 2H), 6.42 (d, *J* = 10.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.5, 166.9, 159.8, 141.7, 132.2, 131.4, 129.0, 128.6, 127.4, 112.3, 83.0; HRMS (ESI) calcd for $C_{15}H_{10}BrO_3^+$: 316.9808 (M + H^+), found: 316.9818



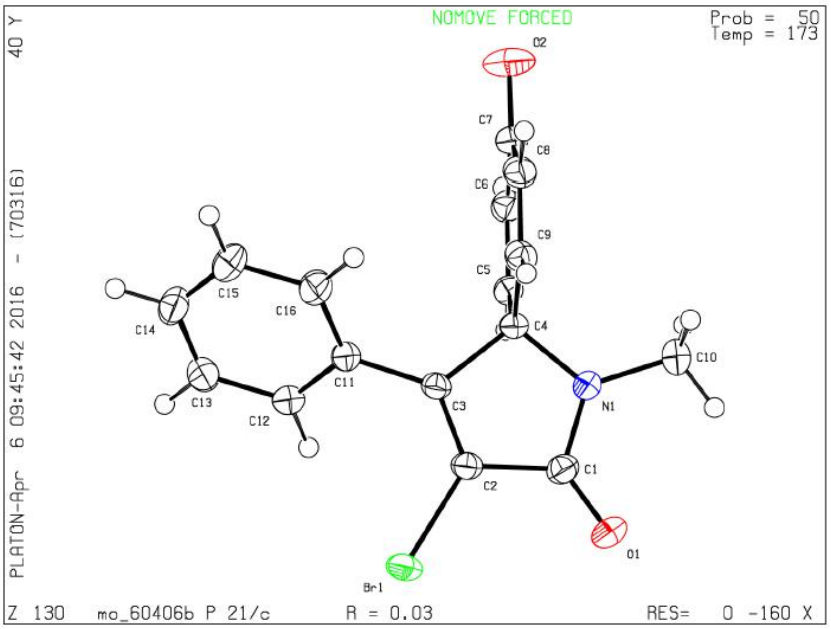
4-(4-acetylphenyl)-3-bromo-6-iodo-1-tosyl-1-azaspiro[4.5]deca-3,6,9-trien-8-one (**8**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.95-6.89 (m, 2H), 6.30 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.60-4.51 (m, 2H), 2.55 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 181.0, 144.9, 144.7, 141.6, 137.6, 137.0, 136.0, 134.1, 129.9, 129.1, 128.3, 127.8, 119.4, 59.3, 26.6, 21.6; HRMS (ESI) calcd for $C_{24}H_{20}BrINO_4S^+$: 623.9336 (M + H^+), found: 623.9348

Reference:

1. (a) B.-X. Tang, Y.-H. Zhang, R.-J. Song, D.-J. Tang, G.-B. Deng, Z.-Q. Wang, Y.-X. Xie, Y.-Z. Xia and J.-H. Li, *J. Org. Chem.*, 2012, **77**, 2837 (b) B.-X. Tang, D.-J. Tang, S. Tang, Q.-F. Yu, Y.-H. Zhang, Y. Liang, P. Zhong and J.-H. Li, *Org. Lett.*, 2008, **10**, 1063

Crystal data of Compound 3a:

Datablock mo_60406b - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_60406b

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_60406b

```
Bond precision:  C-C = 0.0031 A          Wavelength=0.71073

Cell:            a=8.4178(12)    b=14.517(2)         c=11.7373(17)
                 alpha=90        beta=104.665(2)     gamma=90
Temperature:     173 K

                 Calculated                Reported
Volume           1387.6(3)                 1387.6(3)
Space group      P 21/c                    P 21/c
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C16 H12 Br N O2           ?
Sum formula      C16 H12 Br N O2           C16 H12 Br N O2
Mr               330.17                    330.18
Dx,g cm-3        1.581                     1.581
Z                4                         4
Mu (mm-1)        2.962                     2.962
F000             664.0                     664.0
F000'            663.13
h,k,lmax         10,18,15                  10,18,15
Nref             3186                      3169
Tmin,Tmax        0.496,0.587               0.558,0.746
Tmin'            0.432

Correction method= # Reported T Limits: Tmin=0.558 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.995          Theta(max)= 27.525

R(reflections)= 0.0259( 2703)     wR2(reflections)= 0.0789( 3169)

S = 1.115                 Npar= 182
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

```
PLAT934_ALERT_3_B Number of (Iobs-Icalc)/SigmaW > 10 Outliers ....          4 Check
```

Alert level C

```
PLAT434_ALERT_2_C Short Inter HL..HL Contact Br1    ..  Br1     ..       3.34 Ang.
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.600         13 Report
```

Alert level G

```
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          4 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density          13 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   2 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

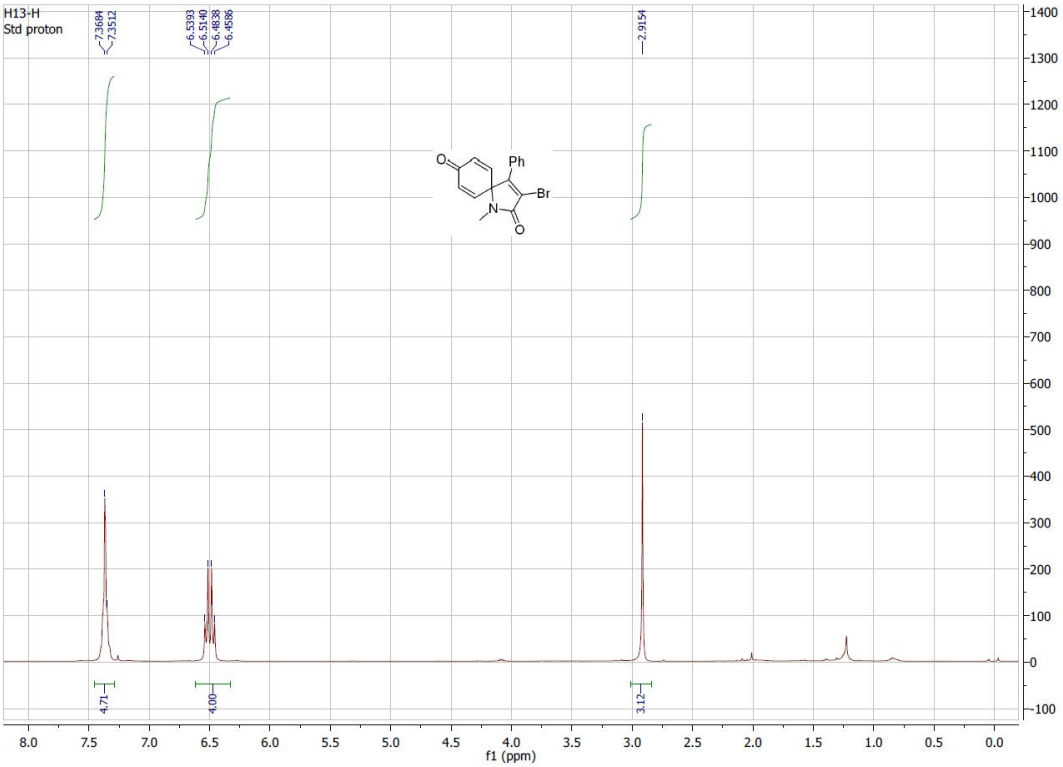
Publication of your CIF in IUCr journals

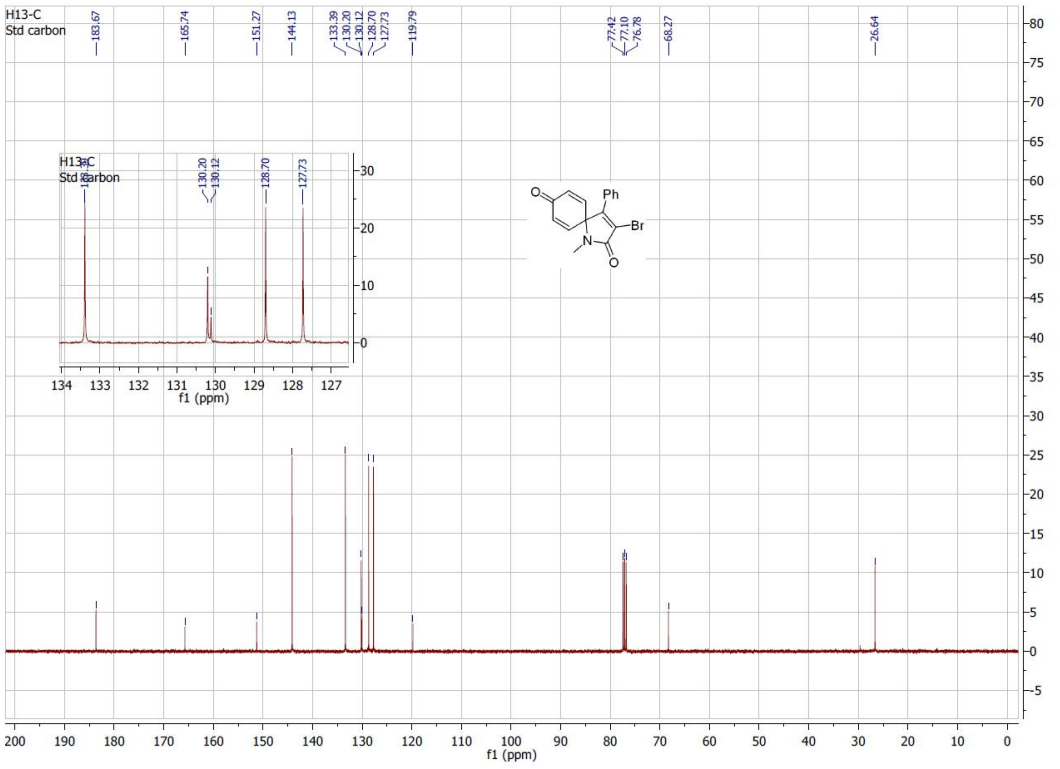
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

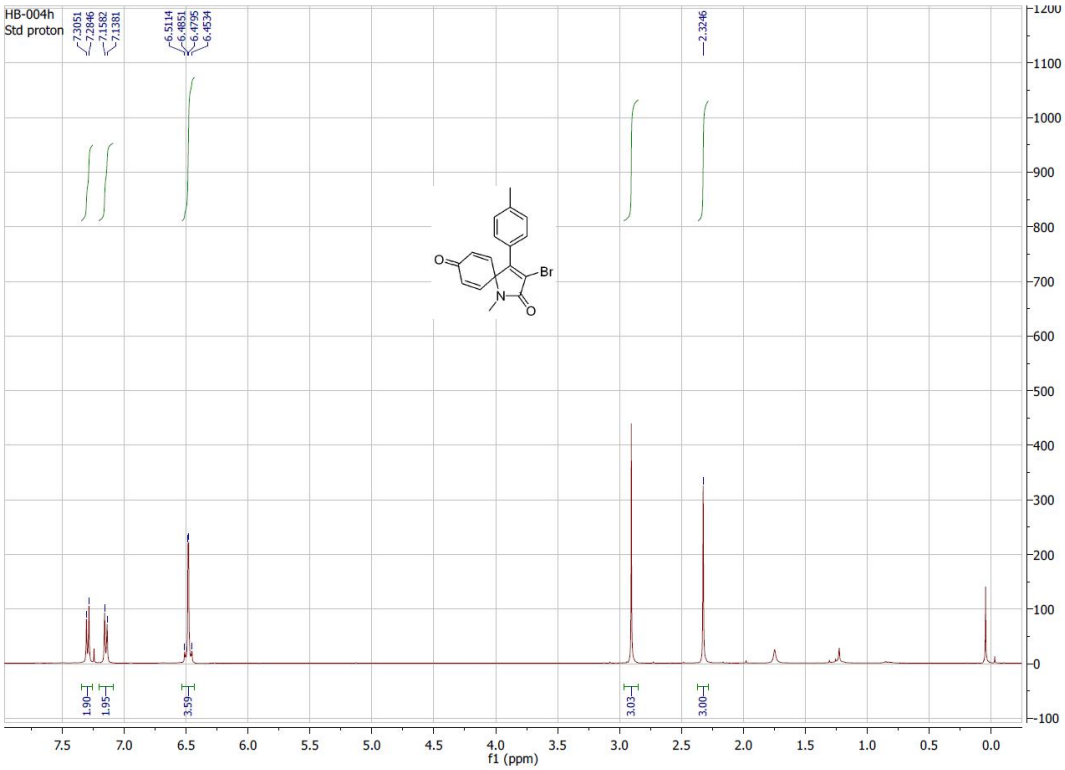
Publication of your CIF in other journals

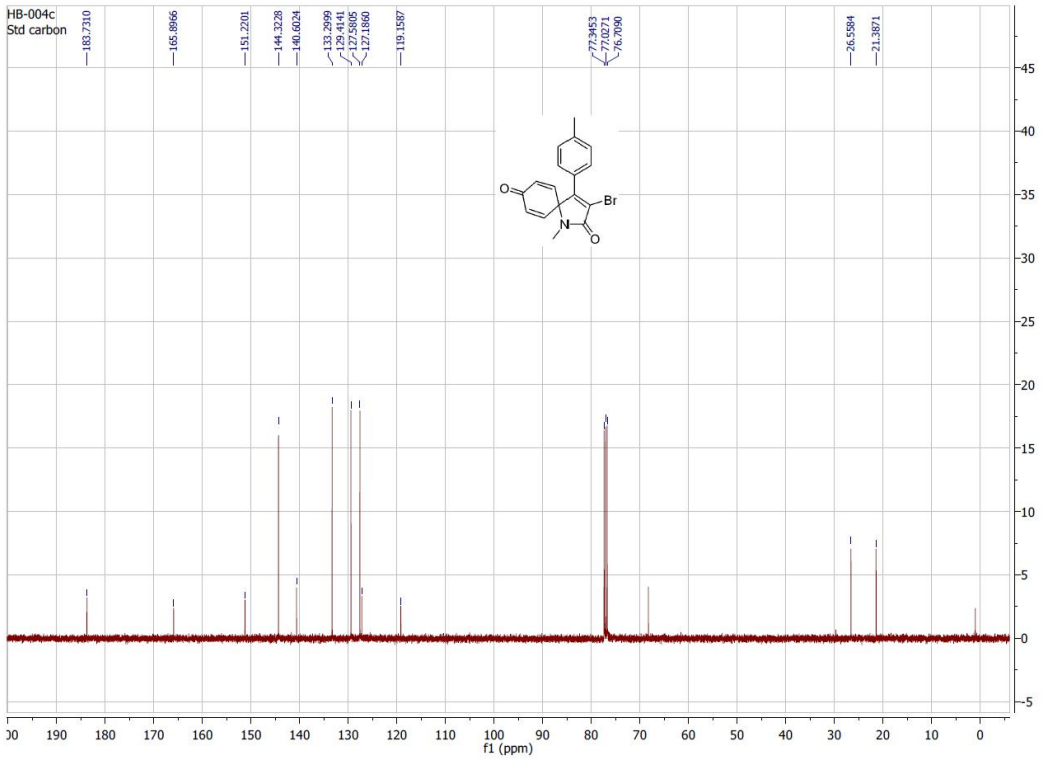
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

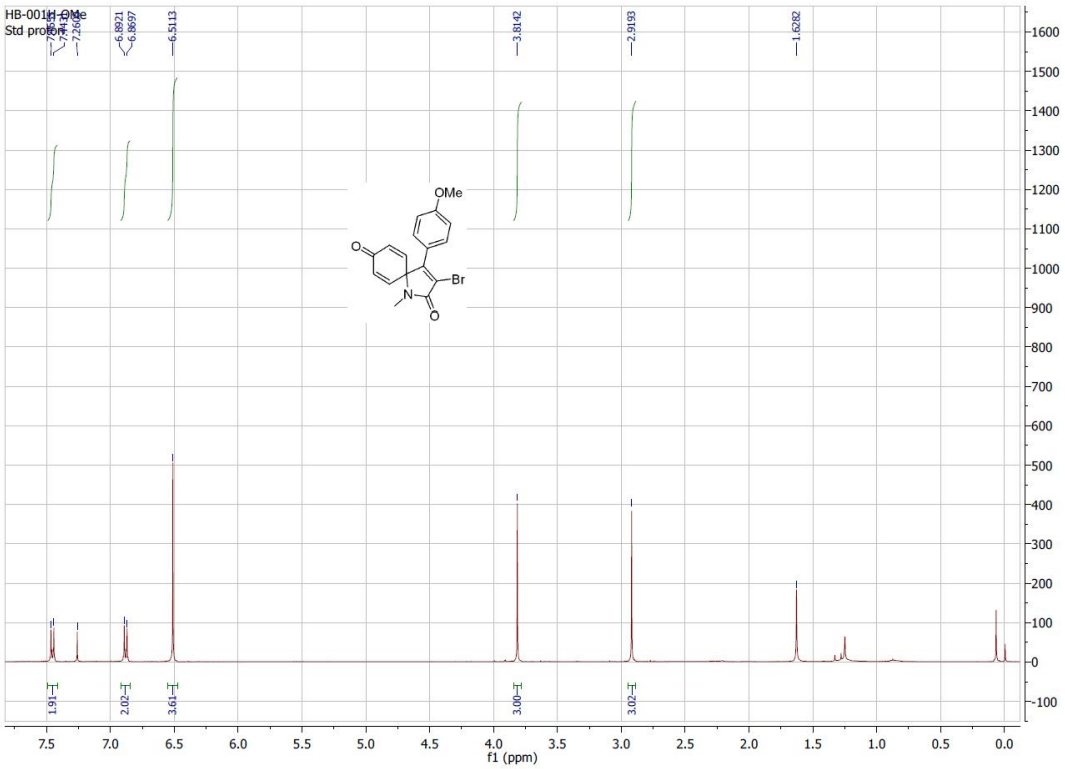
PLATON version of 30/03/2016; check.def file version of 30/03/2016

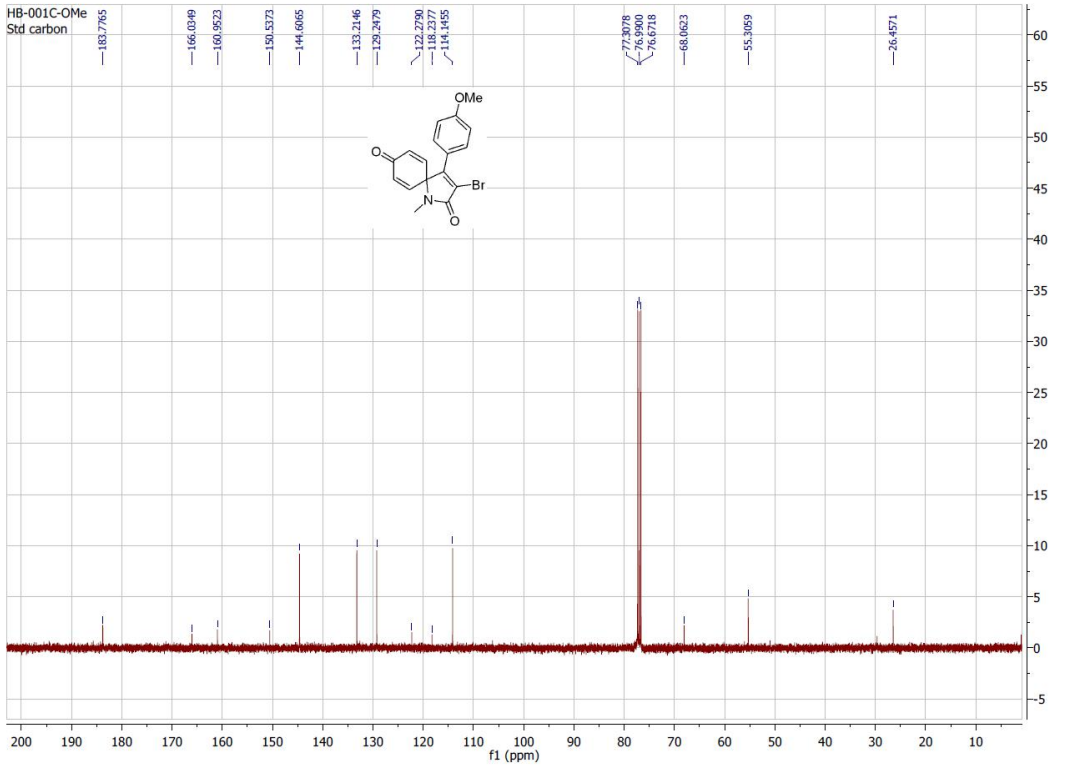

H13-H
Std proton
7.3684
7.3512
6.5393
6.5140
6.4938
6.4586
2.9154
Ph
Br
N
O
4.71
4.00
3.12
f1 (ppm)

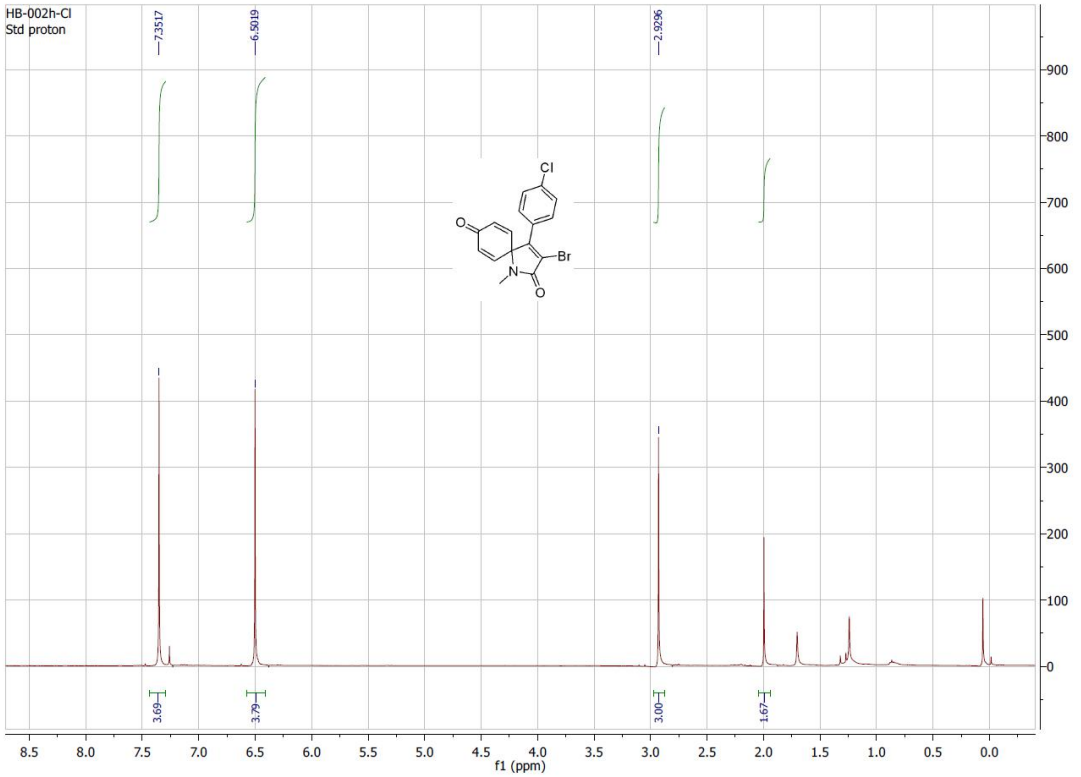

H13-C
Std carbon
183.67
165.74
151.27
144.13
133.39
130.20
130.12
128.70
127.73
119.79
77.42
77.10
76.78
68.27
26.64
H13-C
Std carbon
Ph
Br
N
O
f1 (ppm)

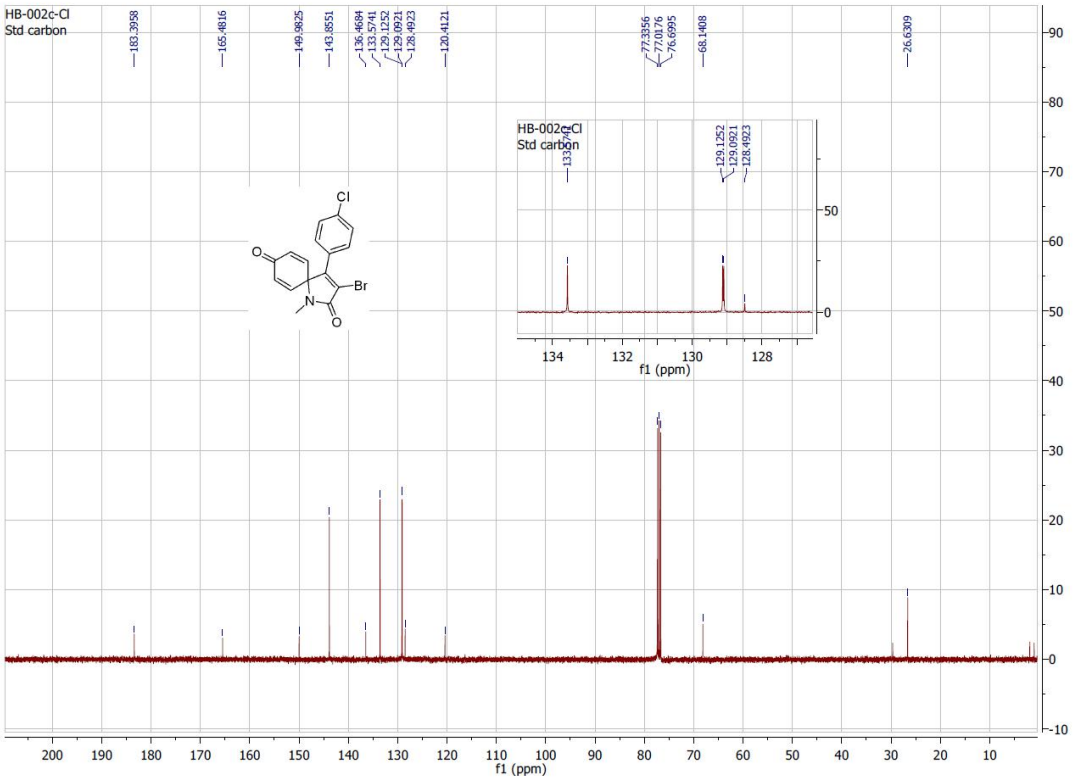

HB-004h
Std proton
7.3051
7.2846
7.1582
7.1381
6.5114
6.4851
6.4795
6.4534
2.3246
1.90
1.95
3.59
3.03
3.00
f1 (ppm)

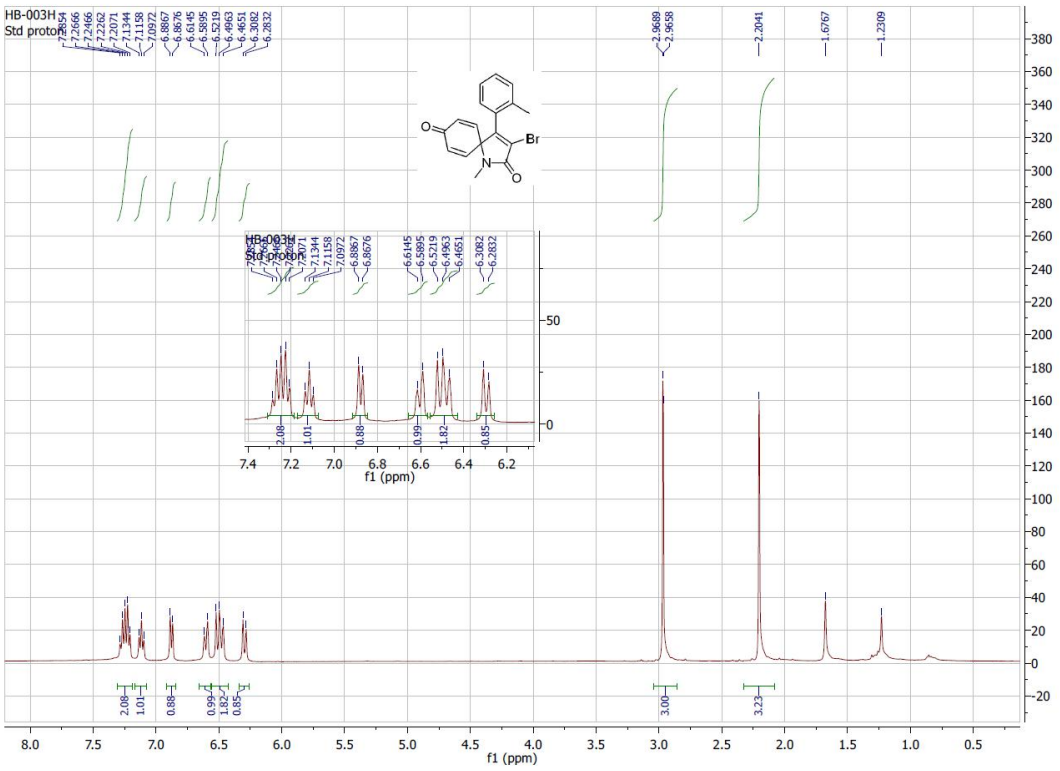

HB-004c
Std carbon
183.7310
165.8966
151.2201
144.3228
140.6024
133.2999
129.4141
127.5865
127.1060
119.1587
77.3453
77.0271
76.7090
26.5584
21.3871
f1 (ppm)

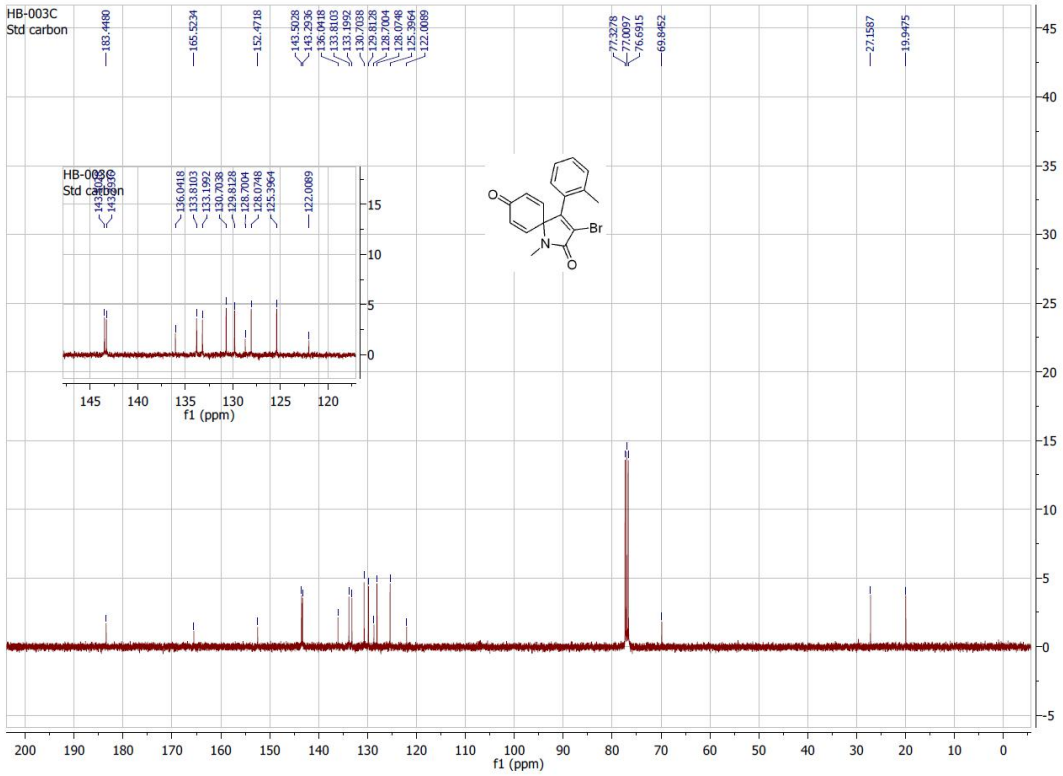

HB-001H-OMe
Std proton
7.6343
7.4117
7.2664
6.8921
6.8697
6.5113
3.8142
2.9193
1.6282
OMe
O
Br
N
O
1.91
2.02
3.61
3.00
3.02
f1 (ppm)

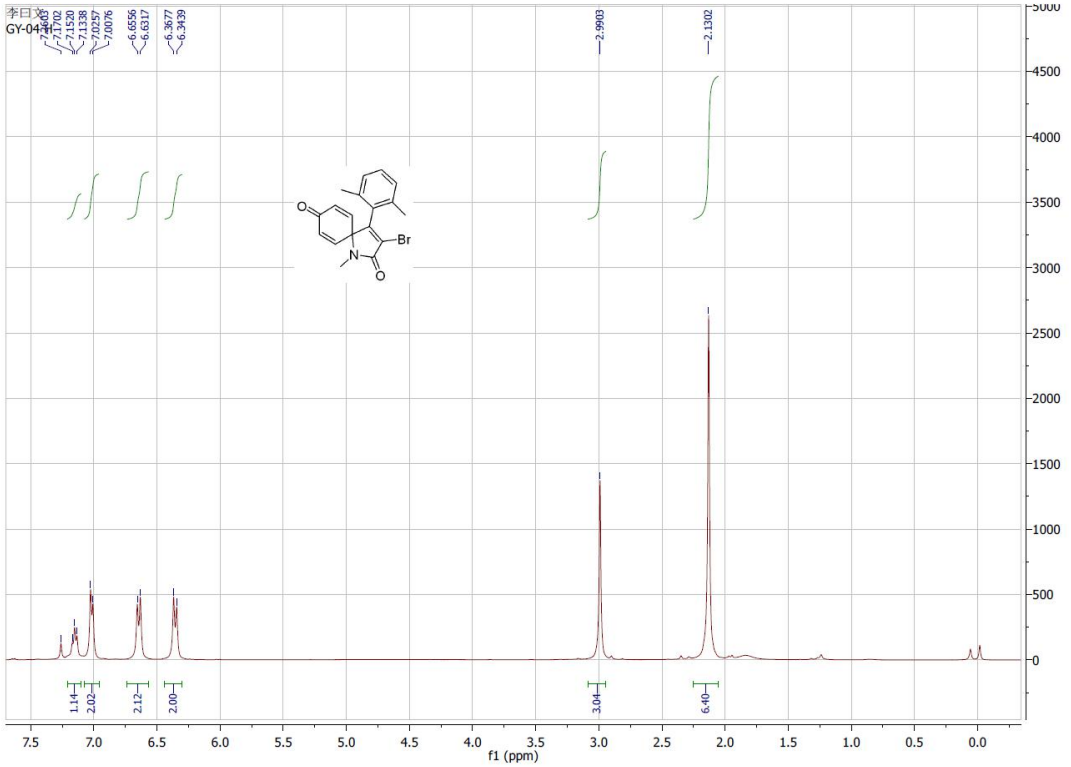

HB-001C-OMe
Std carbon
183.7765
166.0349
160.9523
150.5373
144.6065
133.2146
129.2479
122.2790
118.2377
114.1455
77.3078
76.9900
76.6718
68.0623
55.3059
26.4571
OMe
O
Br
N
O
f1 (ppm)

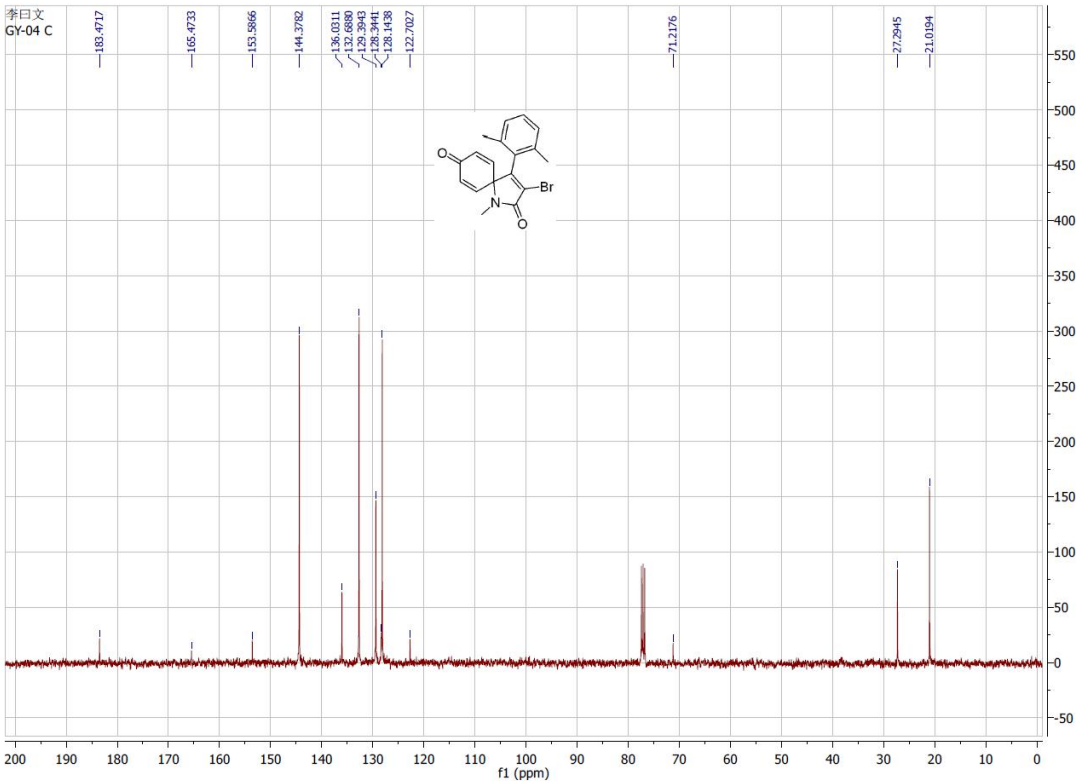

HB-002h-Cl
Std proton
7.3517
6.5019
2.9296
3.69
3.79
3.00
1.67
f1 (ppm)

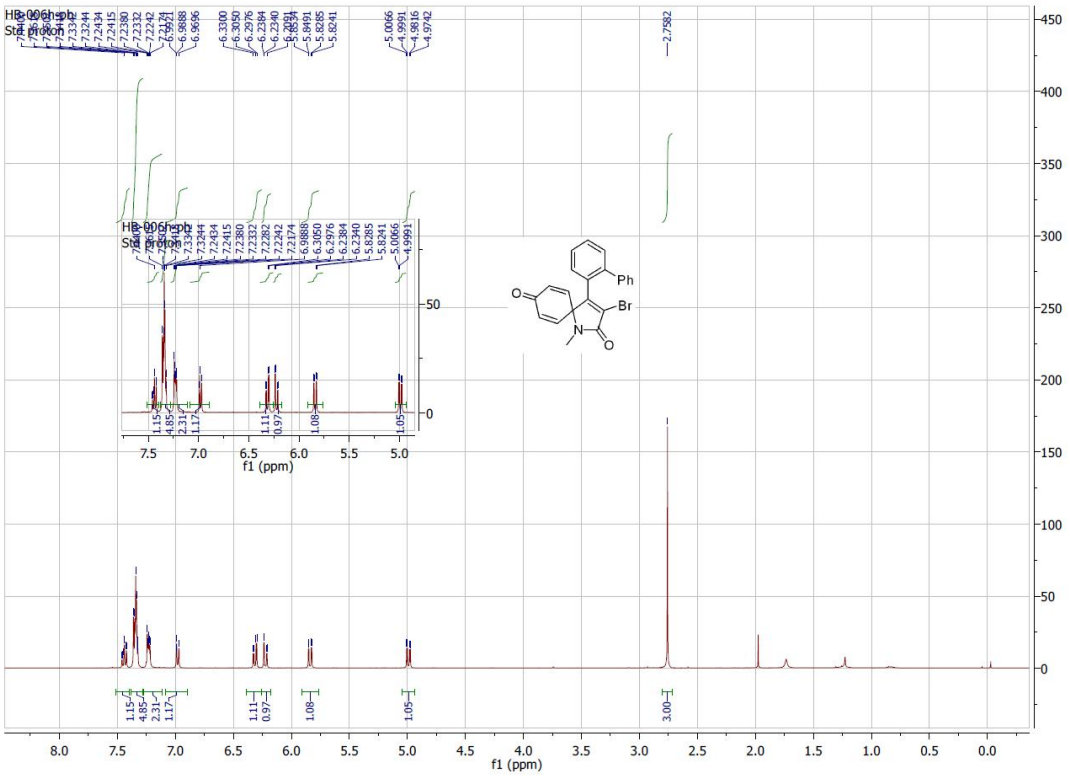

HB-002c-Cl
Std carbon
183.3958
165.4816
149.9825
143.8551
136.4684
133.5741
129.1252
129.0921
128.4923
120.4121
77.3356
77.0176
76.6995
68.1408
26.6309
HB-002c-Cl
Std carbon
f1 (ppm)

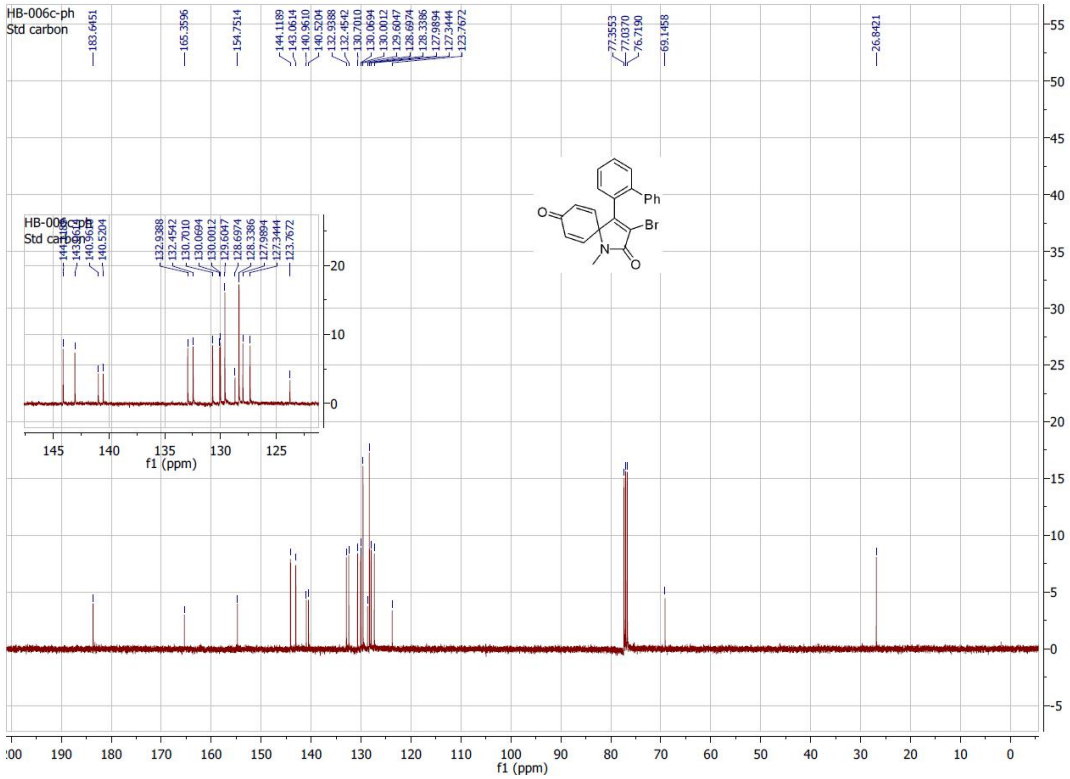

HB-003H
Std proton
f1 (ppm)

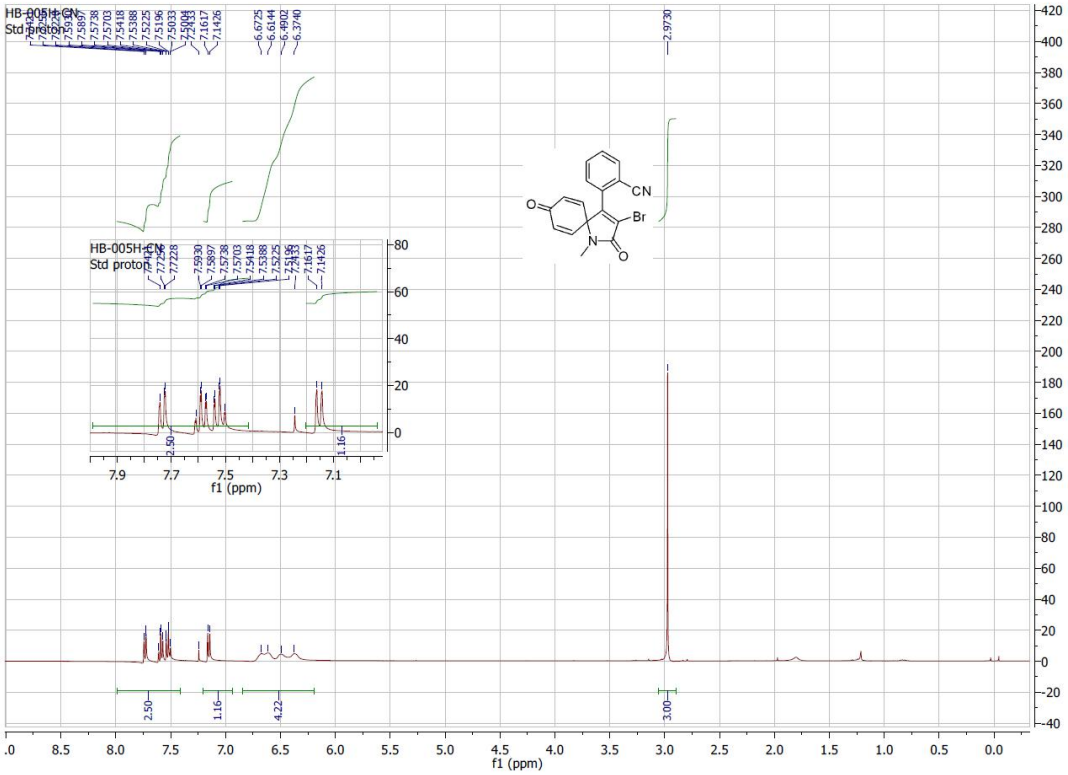

HB-003C
Std carbon
f1 (ppm)

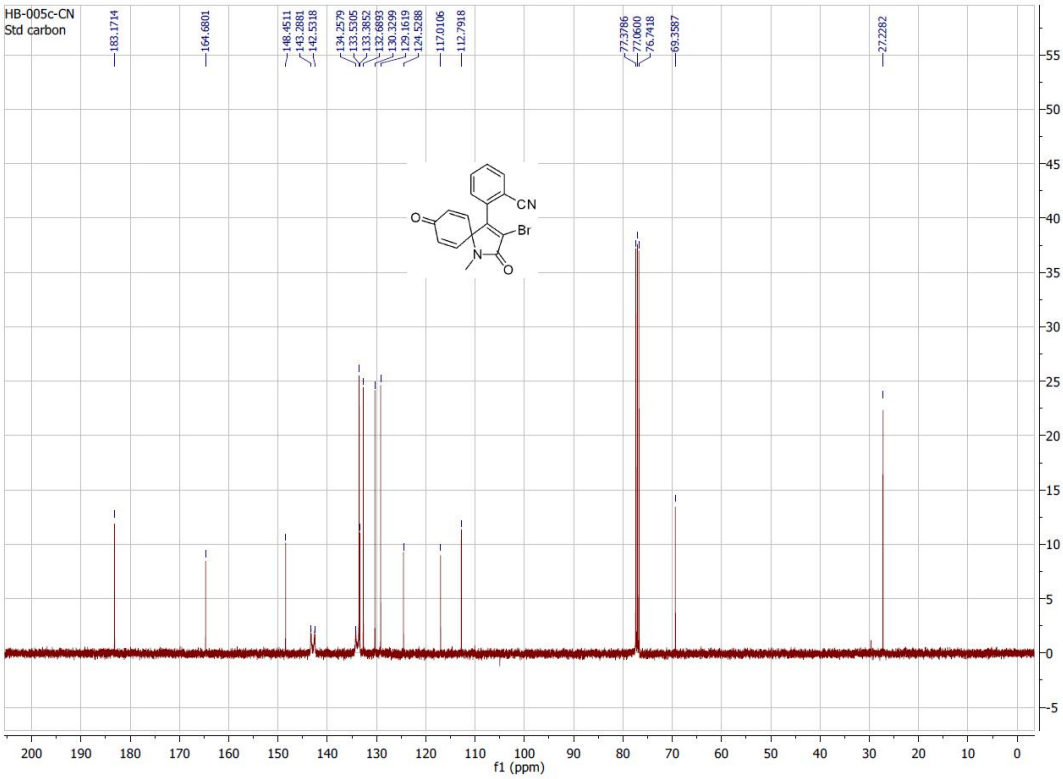

李曰文
GY-04-H
7.2403
7.1702
7.1530
7.1338
7.0257
7.0076
6.6556
6.6317
6.3677
6.3439
2.9903
2.1302
Br
O
N
O
1.14
2.02
2.12
2.00
3.04
6.40
f1 (ppm)

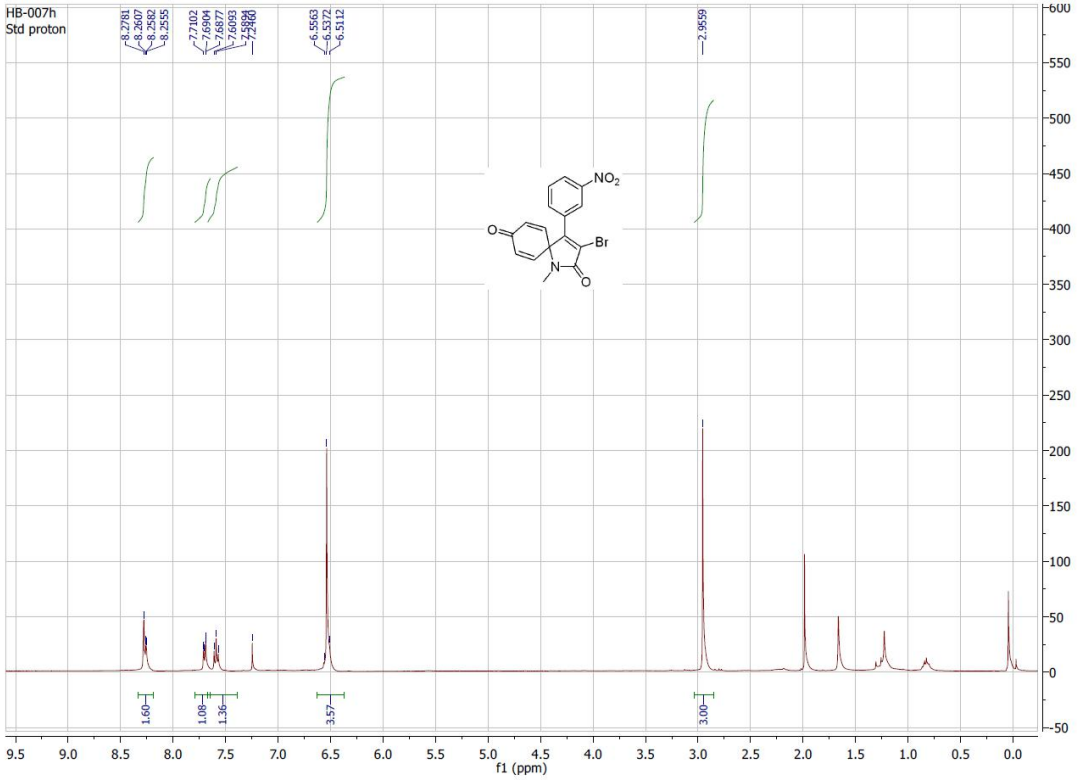

李曰文
GY-04 C
183.4717
165.4733
153.5866
144.3782
136.0311
132.6880
129.5943
128.5441
126.1438
122.7027
71.2176
27.2945
21.0194
Br
O
N
O
f1 (ppm)

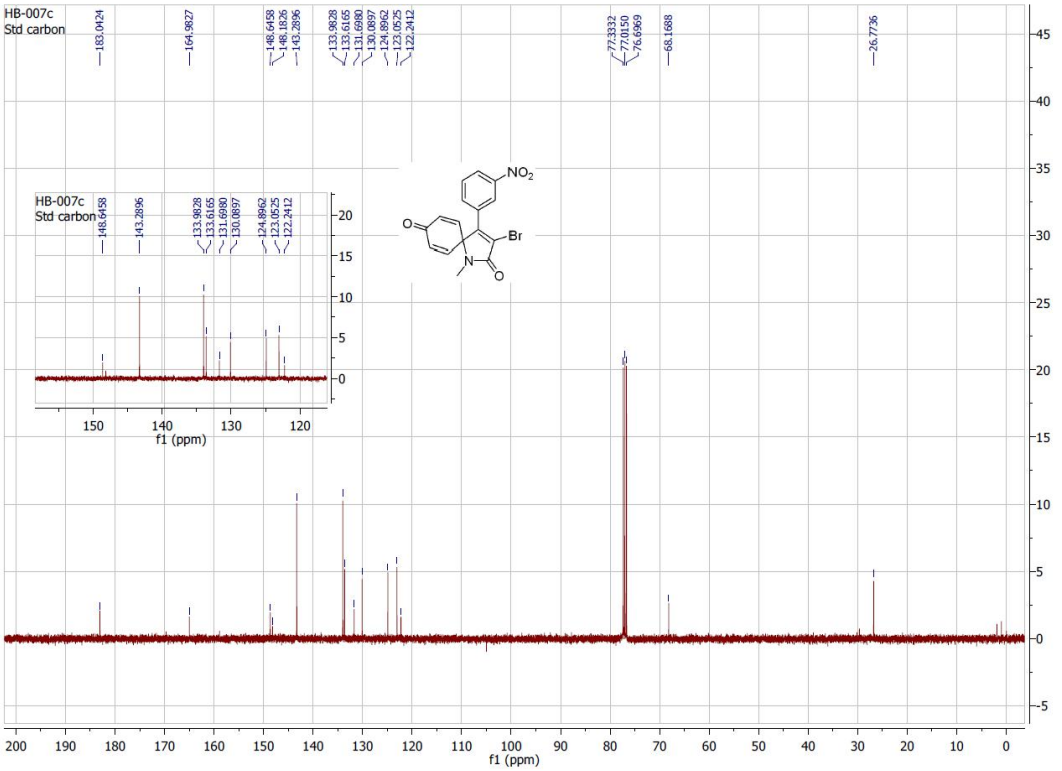

HB-006h-ph
Std proton
Ph
Br
O
N
O
f1 (ppm)

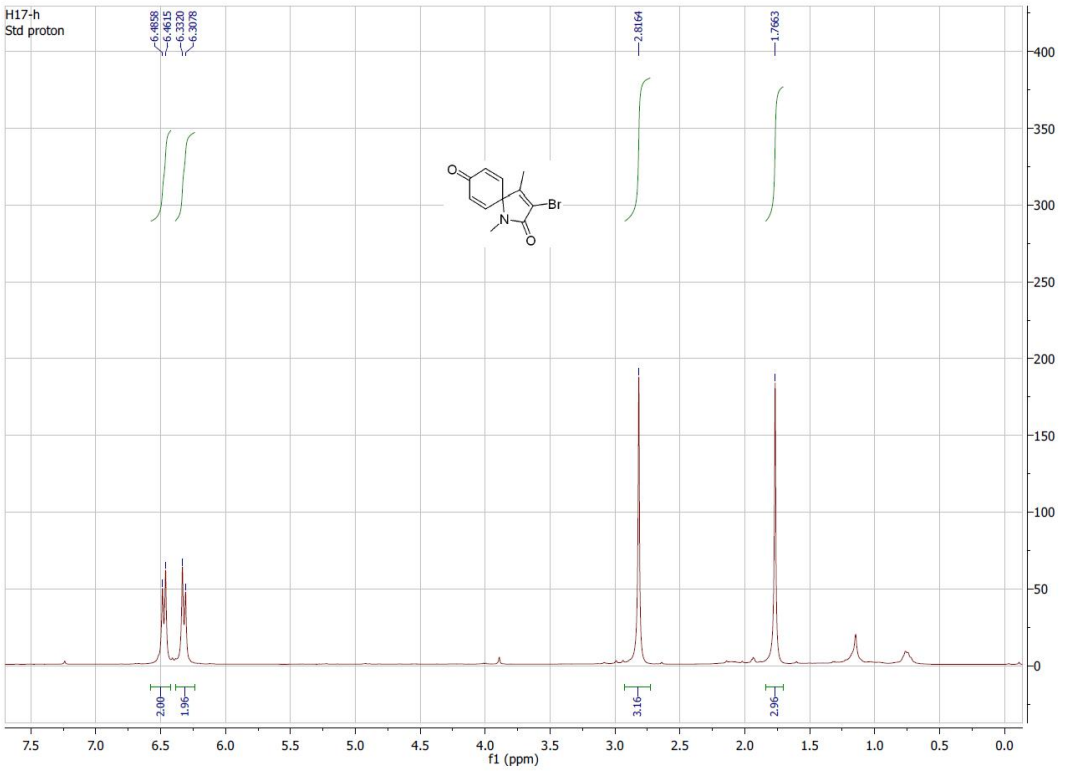

HB-006c-ph
Std carbon
Ph
Br
O
N
O
f1 (ppm)

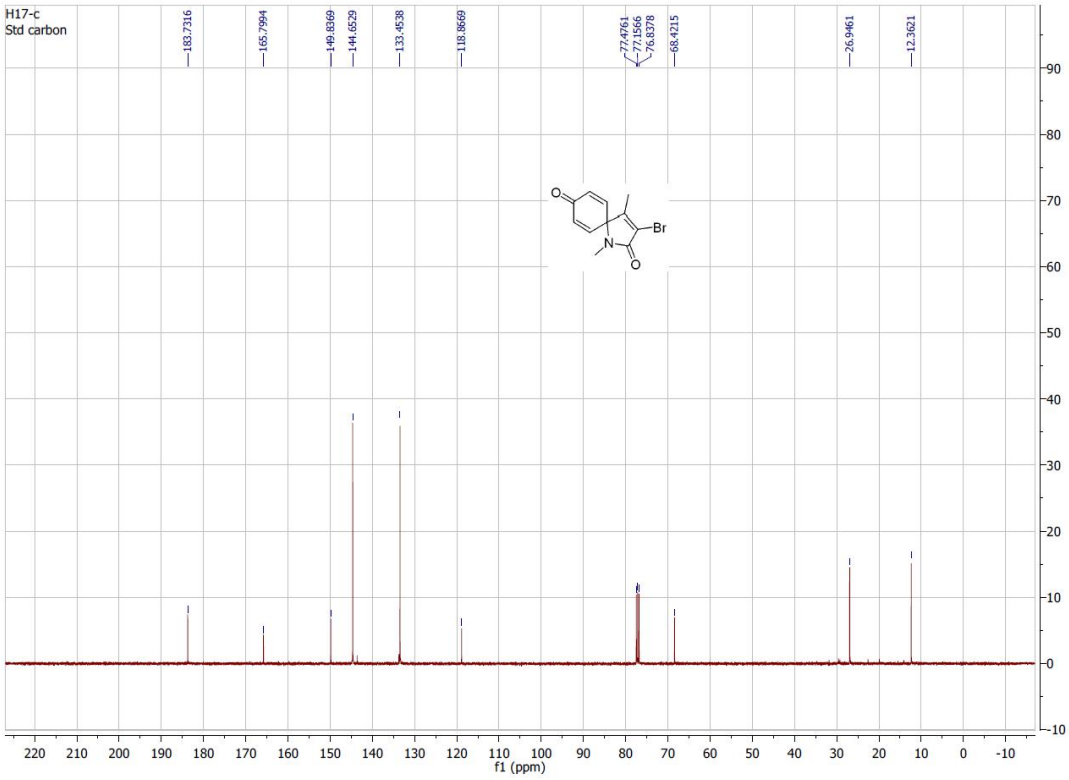

HB-005H-CN
Std proton
f1 (ppm)

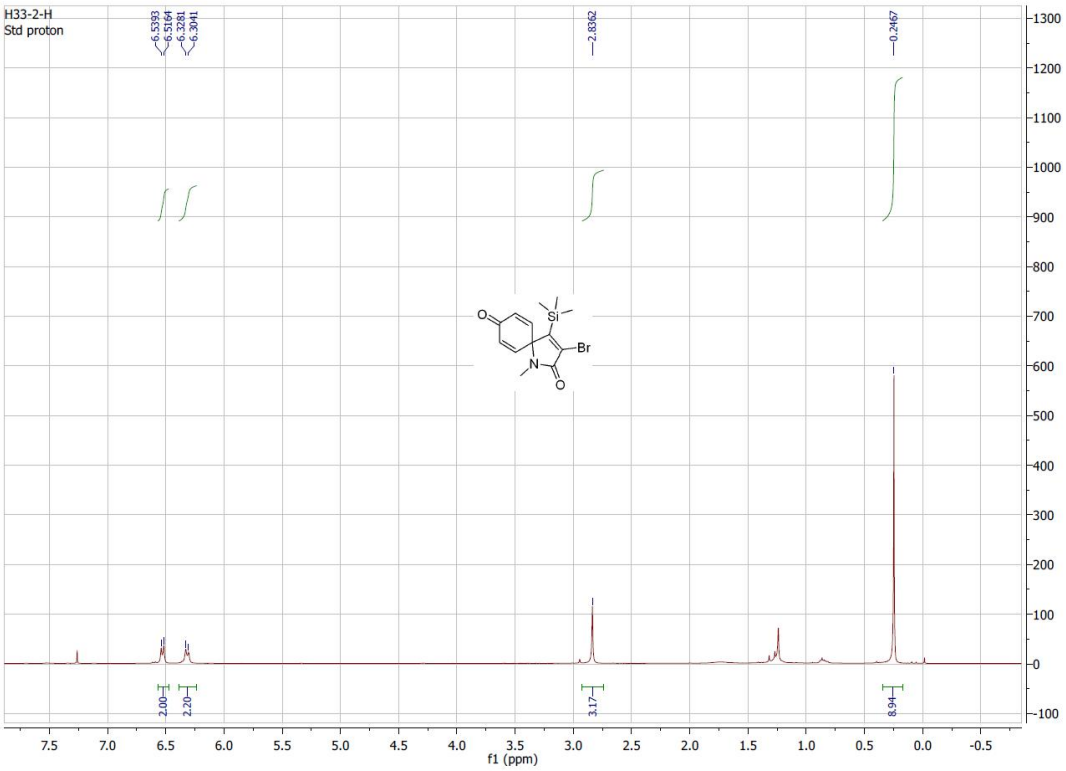

HB-005c-CN
Std carbon
f1 (ppm)

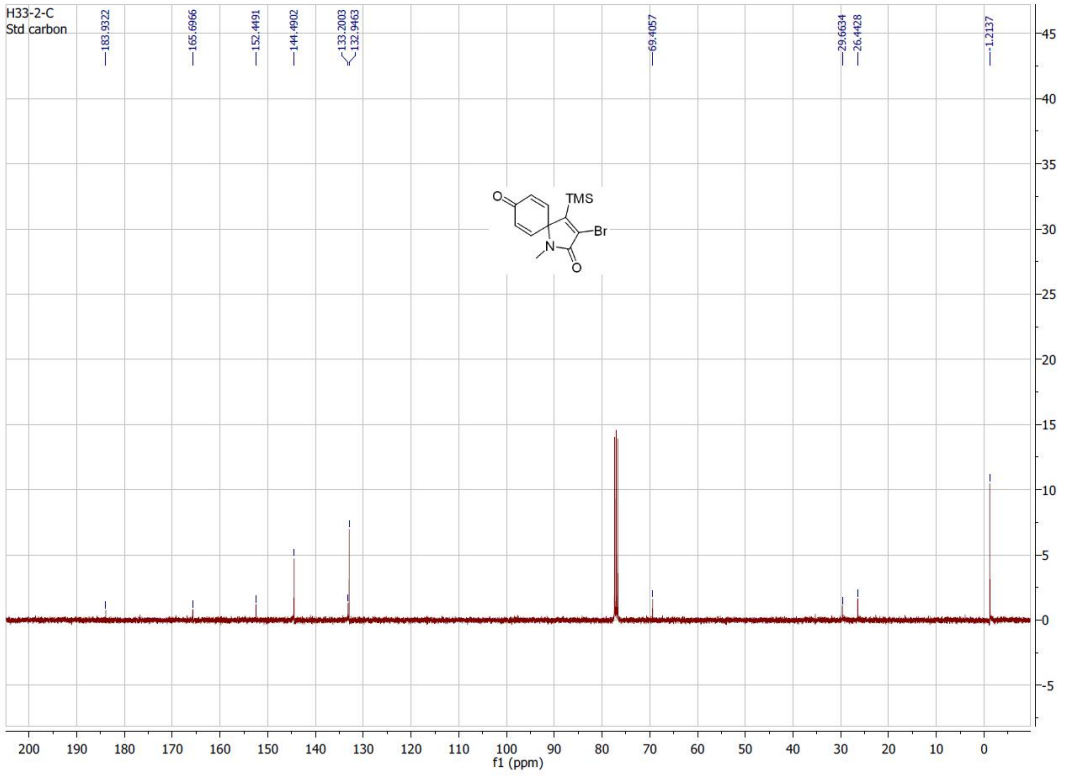

HB-007h
Std proton
8.2781
8.2607
8.2582
8.2555
7.7102
7.6904
7.6877
7.6093
6.5563
6.5372
6.5112
2.9559
1.60
1.08
1.36
3.57
3.00
f1 (ppm)

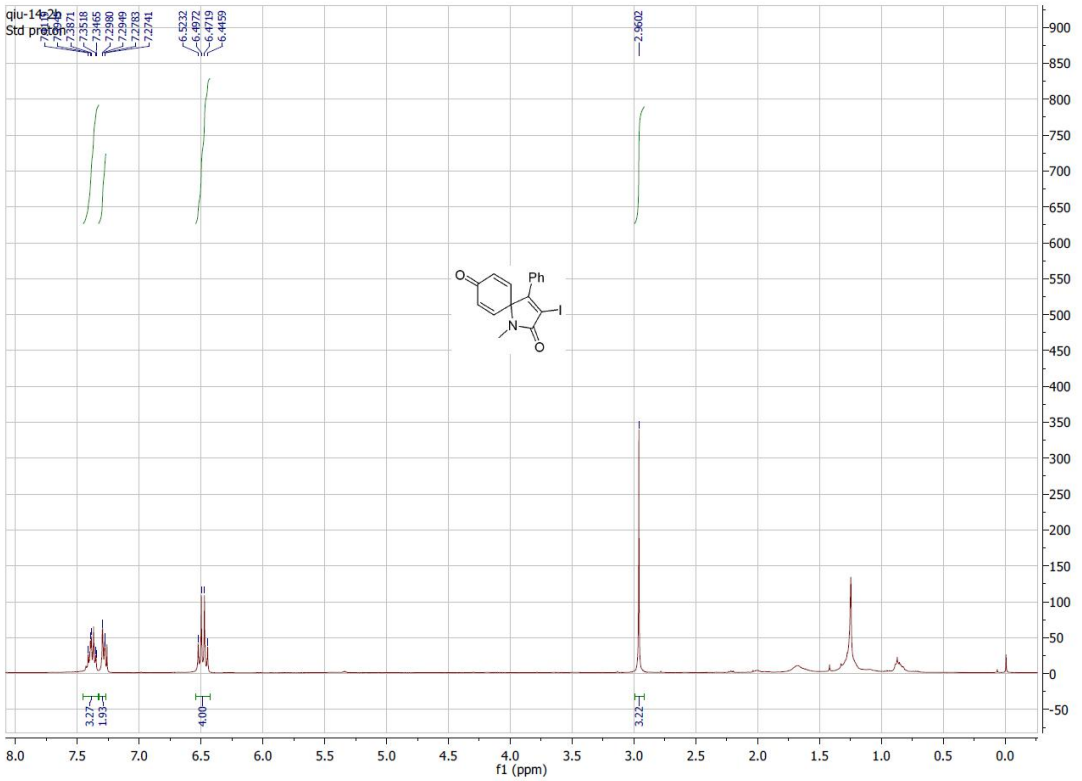

HB-007c
Std carbon
183.0424
164.9827
148.6458
148.1826
143.2896
133.9828
133.6165
131.6980
130.0897
124.8962
123.0525
122.2412
77.3332
77.0150
76.6969
68.1688
26.7736
HB-007c
Std carbon
f1 (ppm)
f1 (ppm)

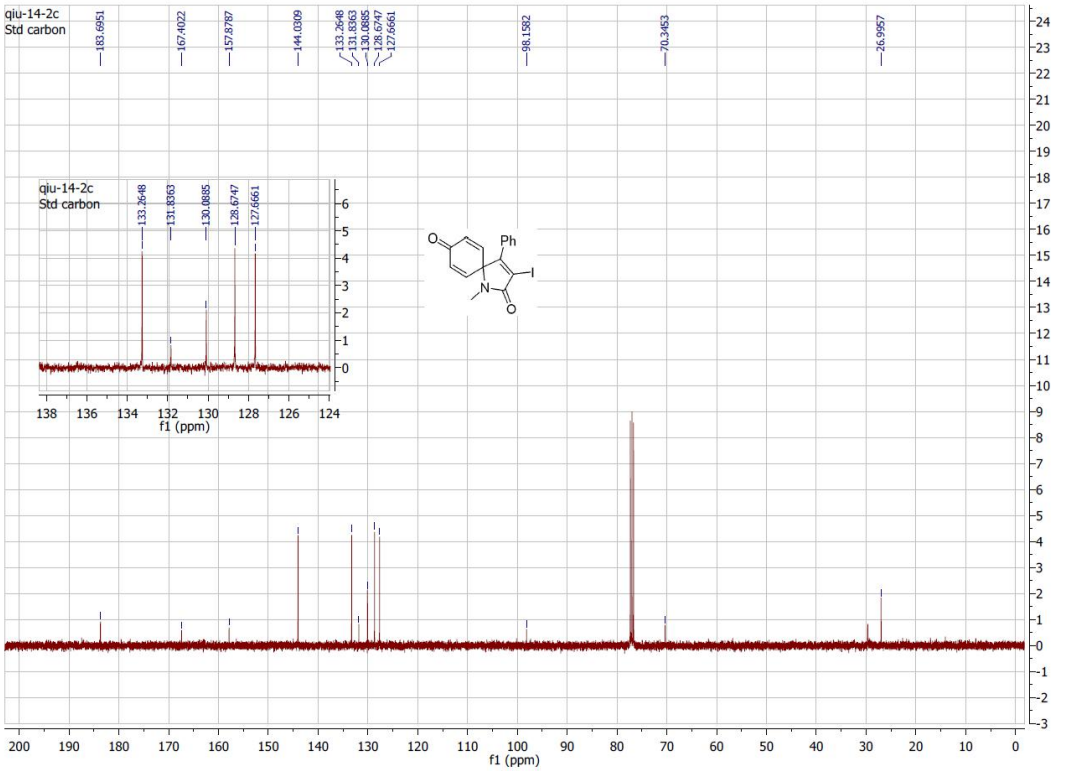

H17-h
Std proton
6.4858
6.4615
6.3320
6.3078
2.8164
1.7663
Br
O
N
O
2.00
1.96
3.16
2.96
f1 (ppm)

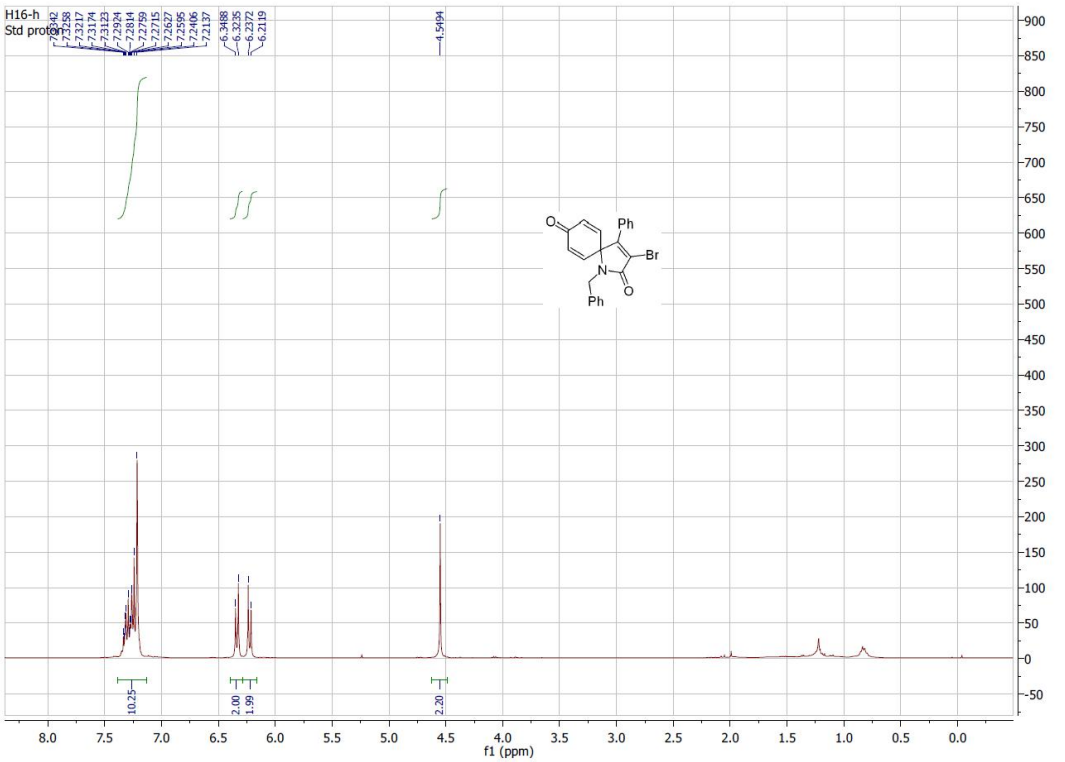

H17-c
Std carbon
183.7316
165.7994
149.8369
144.6529
133.4538
118.8669
77.4761
77.1566
76.8378
68.4215
26.9461
12.3621
Br
O
N
O
f1 (ppm)

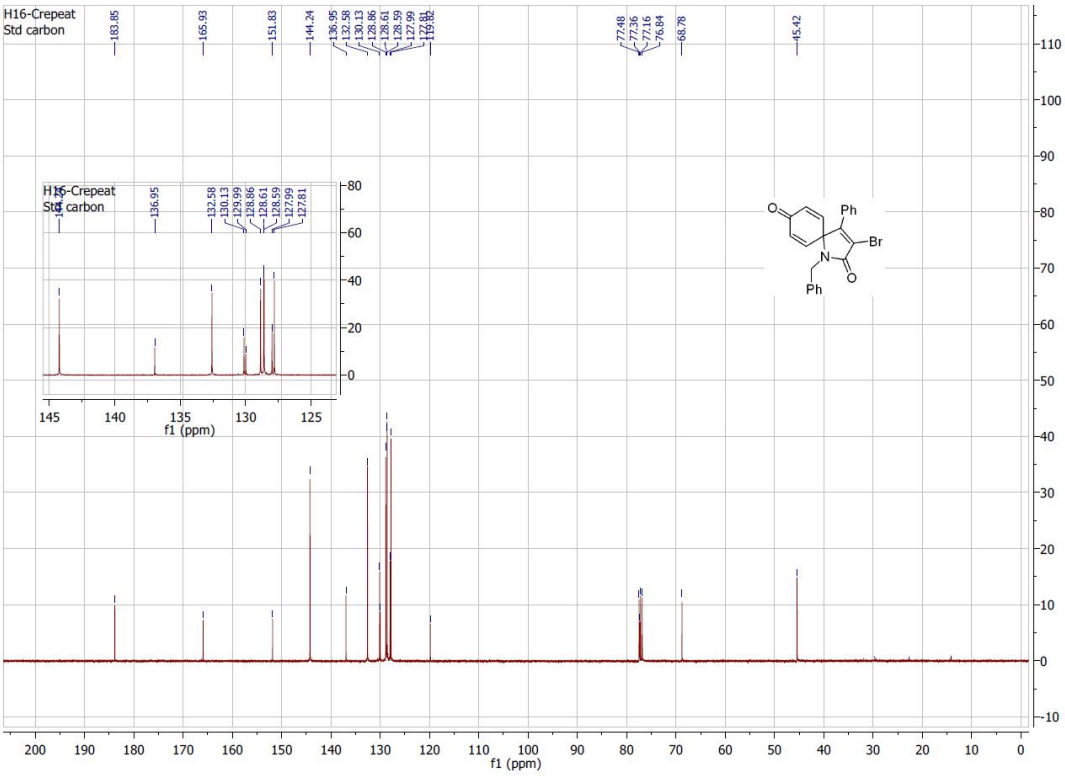

H33-2-H
Std proton
6.5393
6.5164
6.3281
6.3041
2.8362
0.2467
Si
Br
N
O
2.00
2.20
3.17
8.94
f1 (ppm)

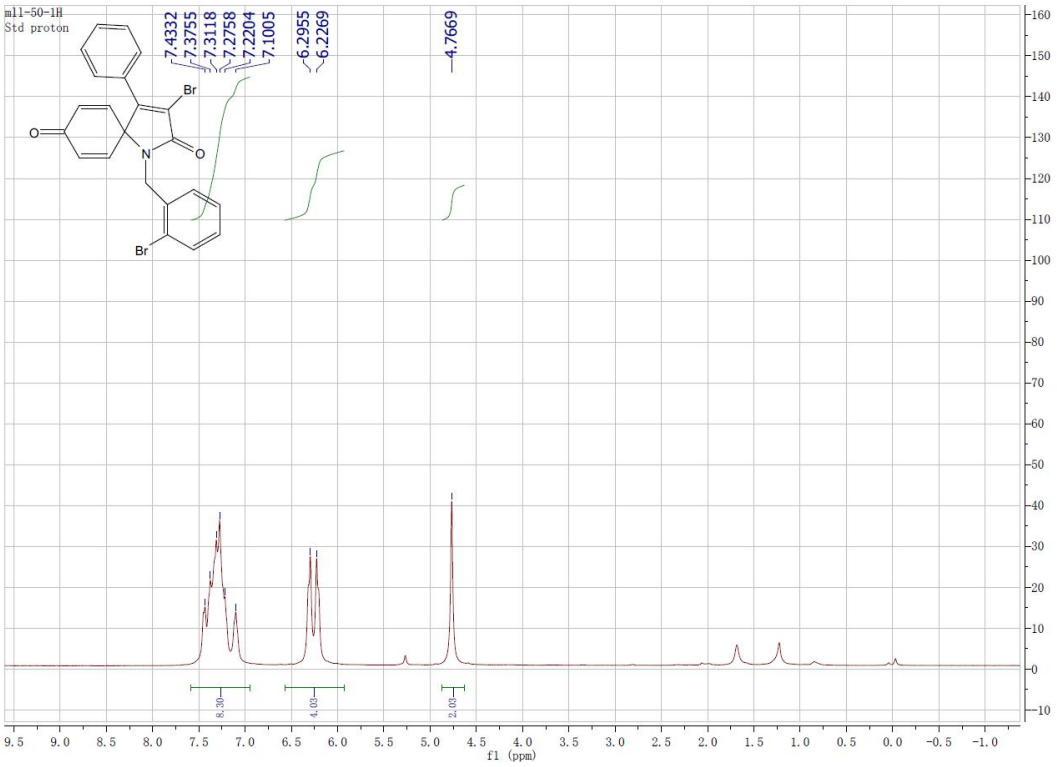

H33-2-C
Std carbon
183.9322
165.6966
152.4491
144.4902
133.2003
132.9463
69.4057
29.6634
26.4428
1.2137
TMS
Br
N
O
f1 (ppm)

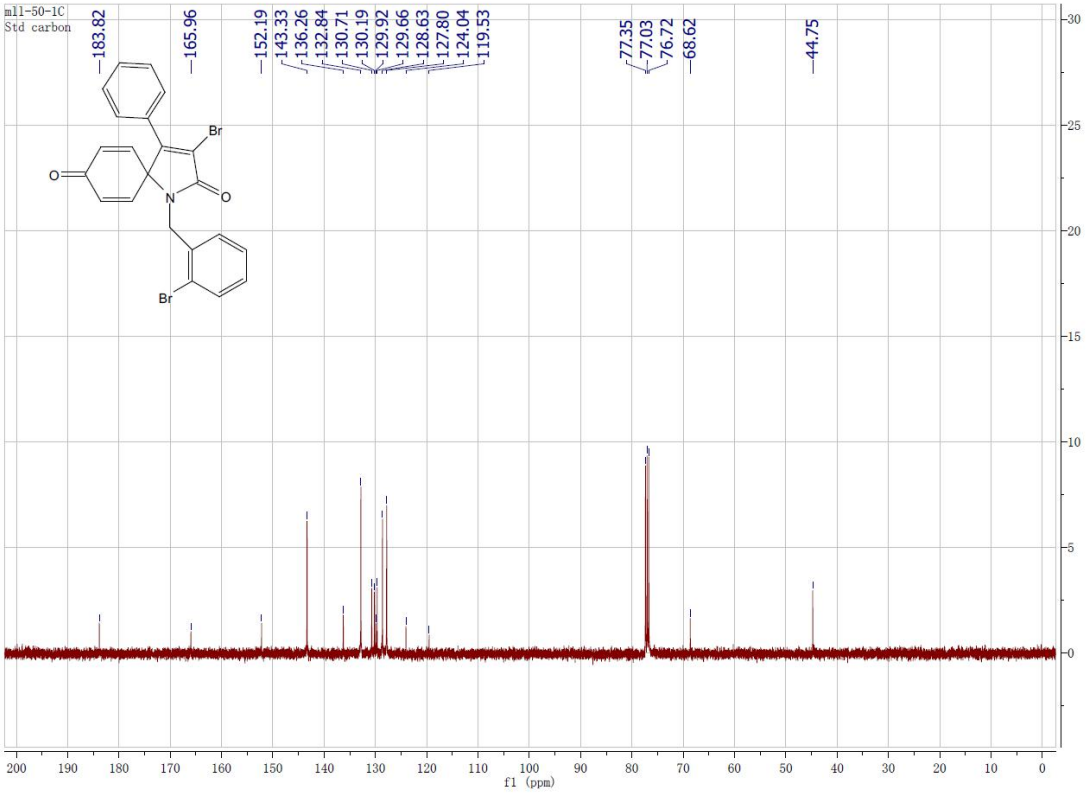

qiu-14-2b
Std proton
7.3671
7.3518
7.3465
7.2980
7.2949
7.2783
7.2741
6.5232
6.4972
6.4719
6.4459
2.9602
Ph
I
O
N
O
3.27
1.93
4.00
3.22
f1 (ppm)

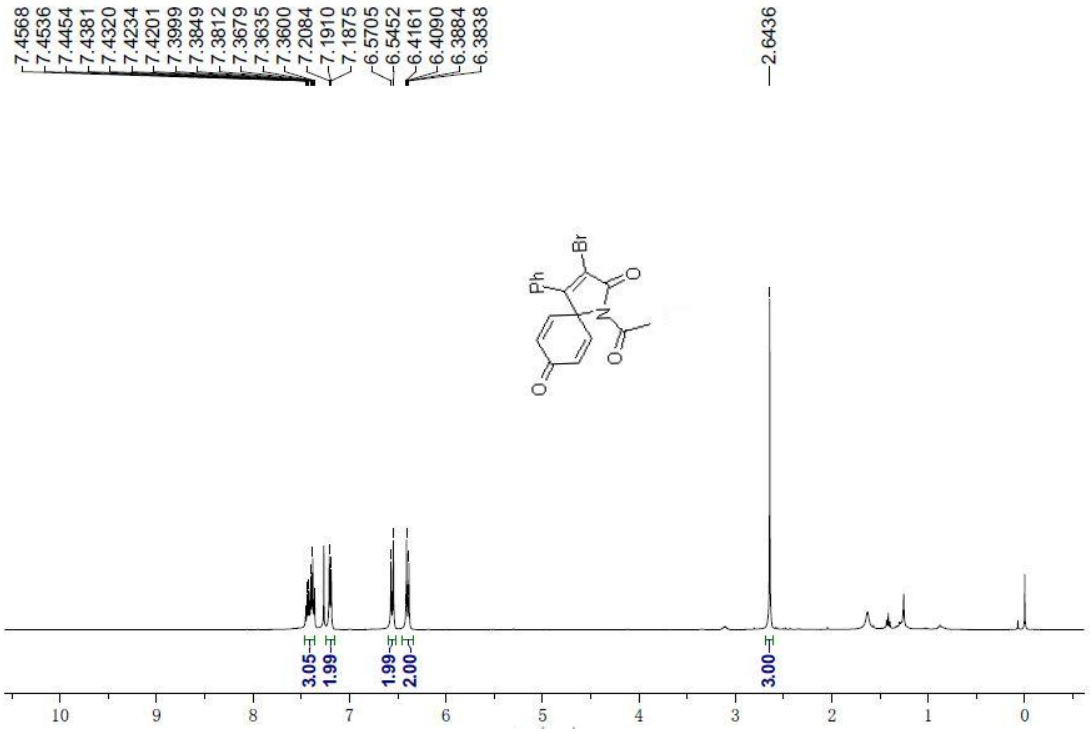

qiu-14-2c
Std carbon
183.6951
167.4022
157.8787
144.0309
133.2648
131.8363
130.0885
128.6747
127.6661
98.1582
70.3453
26.9957
qiu-14-2c
Std carbon
133.2648
131.8363
130.0885
128.6747
127.6661
f1 (ppm)
Ph
I
O
N
O
f1 (ppm)

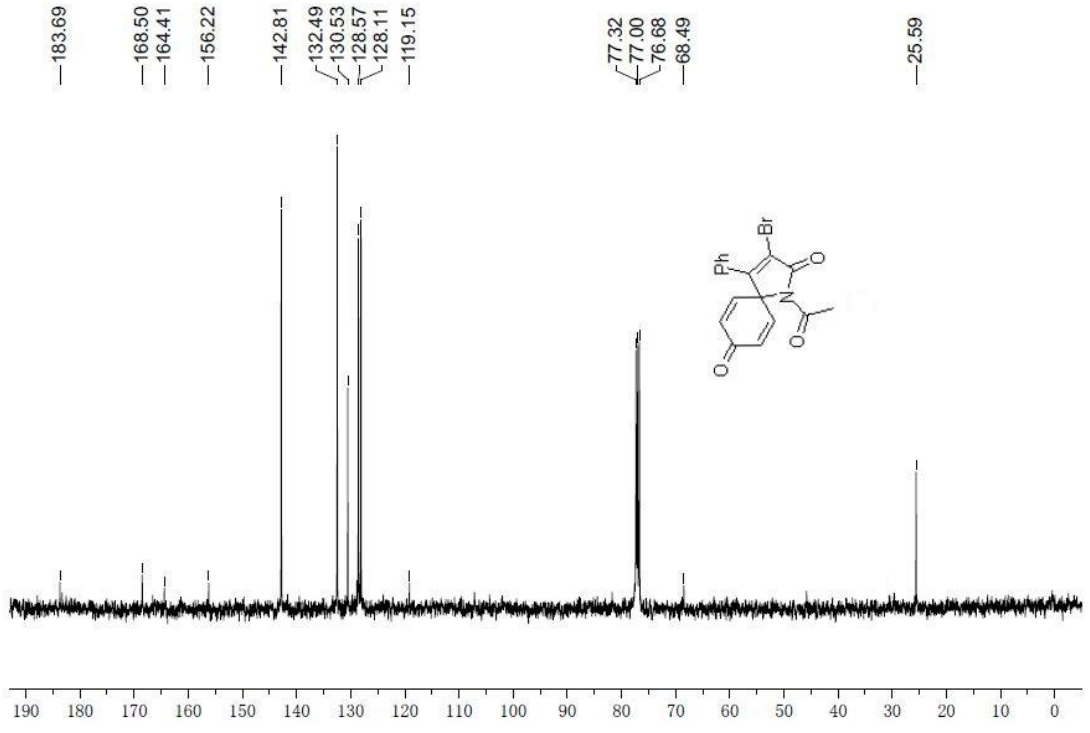

H16-h
Std proton
7.7342
7.7258
7.3217
7.3174
7.3123
7.2984
7.2814
7.2759
7.2715
7.2627
7.2595
7.2406
7.2137
6.3488
6.3235
6.2372
6.2119
4.5494
O
Ph
Br
N
O
Ph
10.25
2.00
1.99
2.20
f1 (ppm)

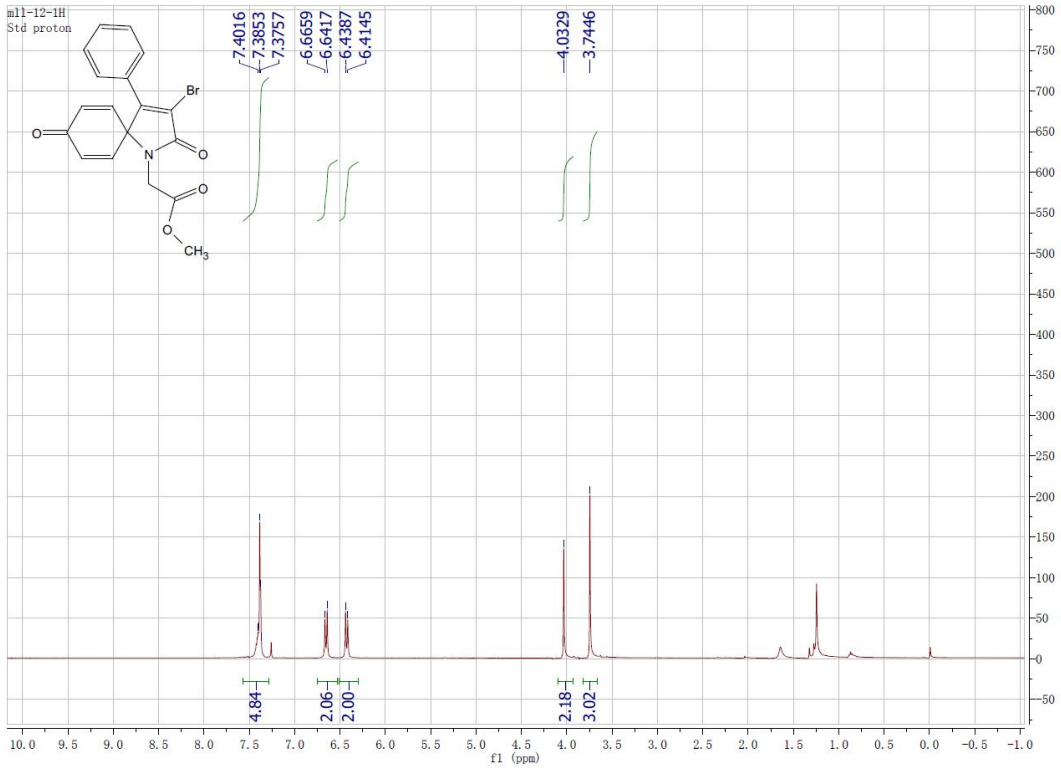

H16-Crepeat
Std carbon
183.85
165.93
151.83
144.24
136.95
132.58
130.13
129.99
128.86
128.61
128.59
127.99
127.81
77.48
77.36
77.16
76.84
68.78
45.42
O
Ph
Br
N
O
Ph
f1 (ppm)

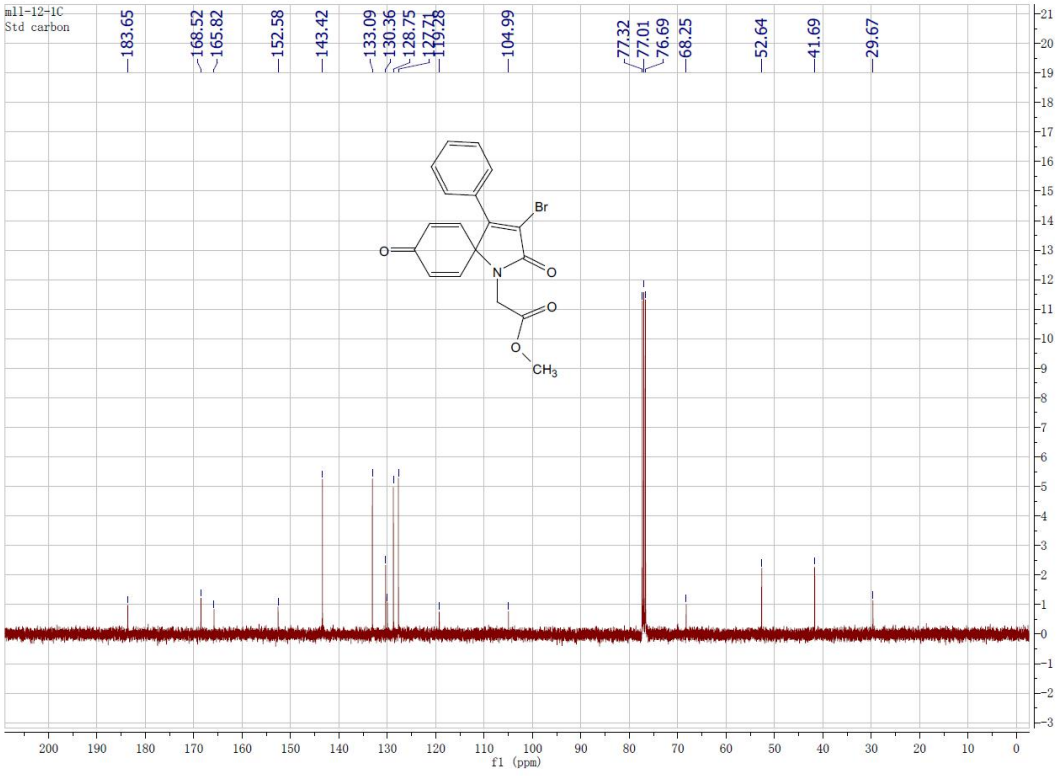

ml1-50-1H
Std proton
7.4332
7.3755
7.3118
7.2758
7.2204
7.1005
6.2955
6.2269
4.7669
Br
O
N
O
Br
8.30
4.03
2.00
f1 (ppm)

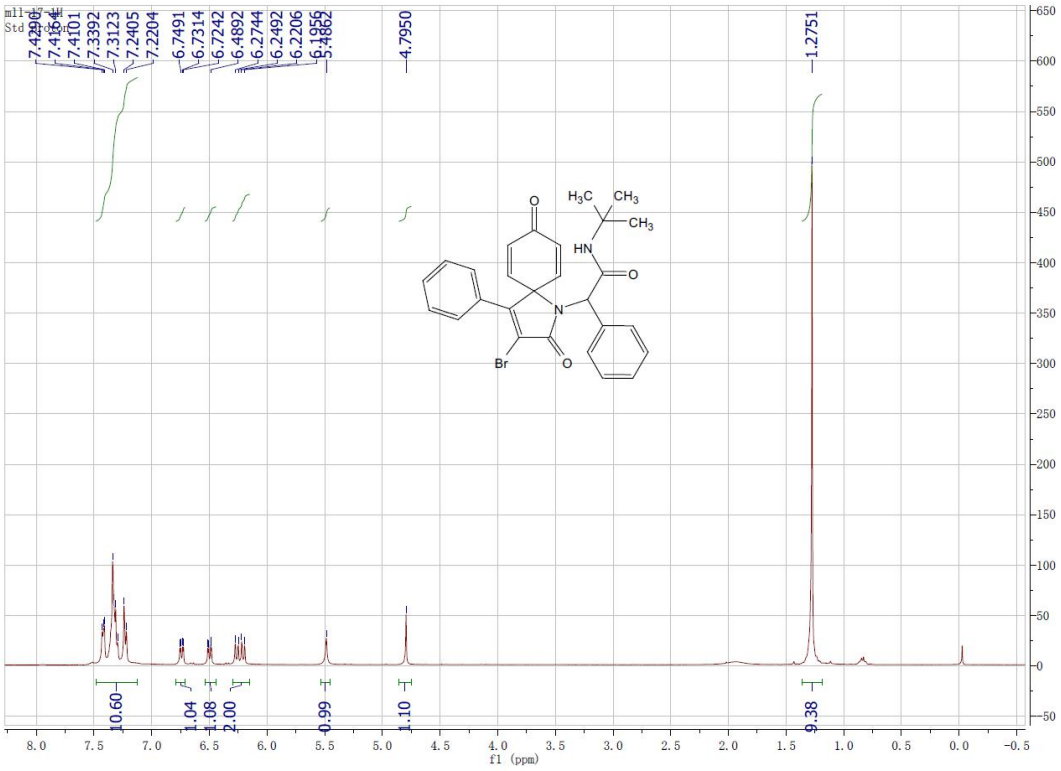

ml1-50-1C
Std carbon
183.82
165.96
152.19
143.33
136.26
132.84
130.71
130.19
129.92
129.66
128.63
127.80
124.04
119.53
77.35
77.03
76.72
68.62
44.75
Br
O
N
O
Br
f1 (ppm)

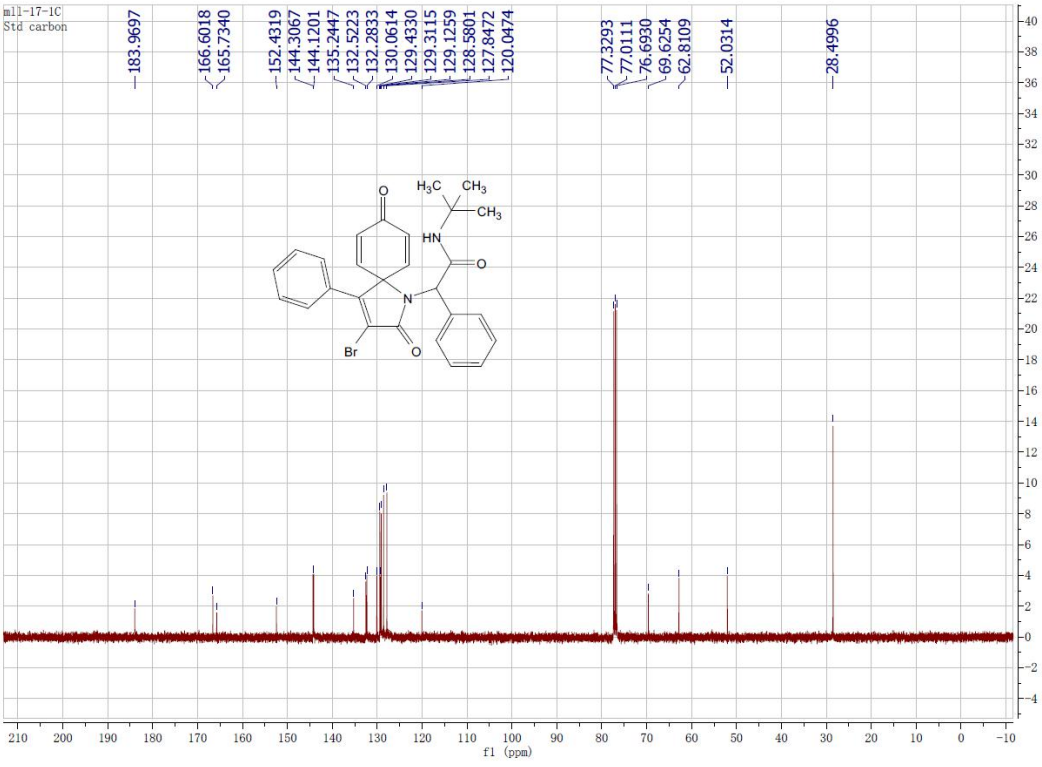

7.4568
7.4536
7.4454
7.4381
7.4320
7.4234
7.4201
7.3999
7.3849
7.3812
7.3679
7.3635
7.3600
7.2084
7.1910
7.1875
6.5705
6.5452
6.4161
6.4090
6.3884
6.3838
2.6436
Br
Ph
O
N
O
O
3.05
1.99
1.99
2.00
3.00
10
9
8
7
6
5
4
3
2
1
0

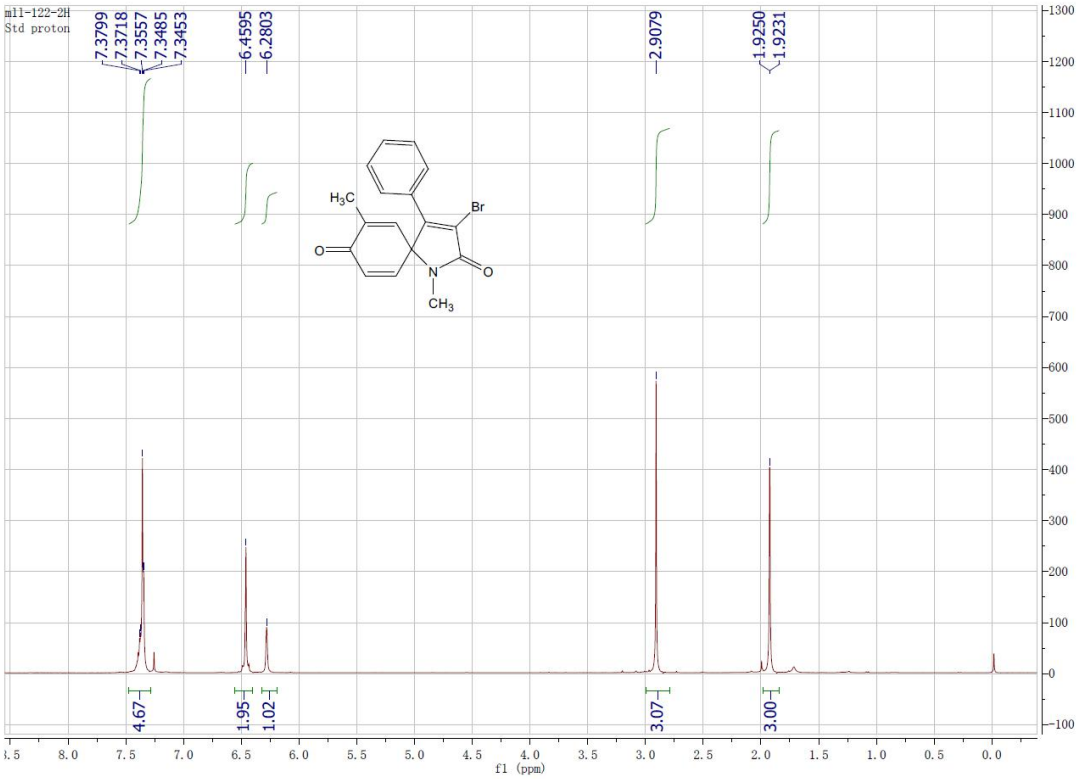

183.69
168.50
164.41
156.22
142.81
132.49
130.53
128.57
128.11
119.15
77.32
77.00
76.68
68.49
25.59
Br
Ph
O
N
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

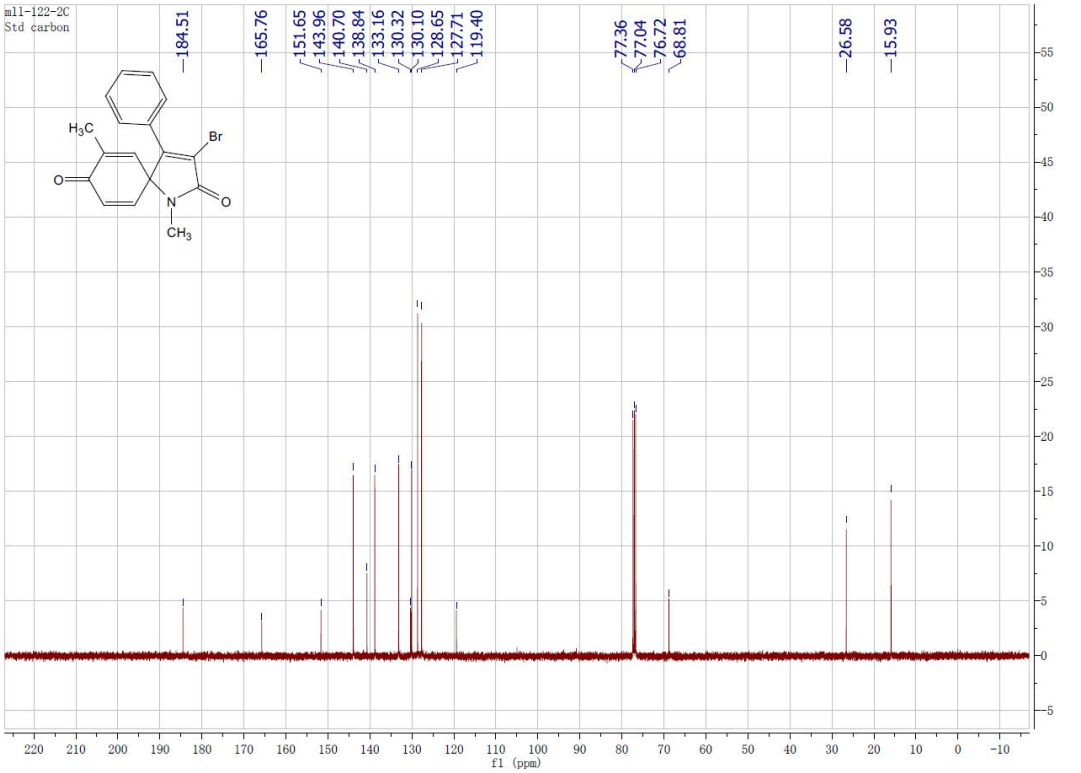

m11-12-1H
Std proton
7.4016
7.3853
7.3757
6.6659
6.6417
6.4387
6.4145
4.0329
3.7446
Br
O
O
N
O
O
O
CH3
4.84
2.06
2.00
2.18
3.02
f1 (ppm)

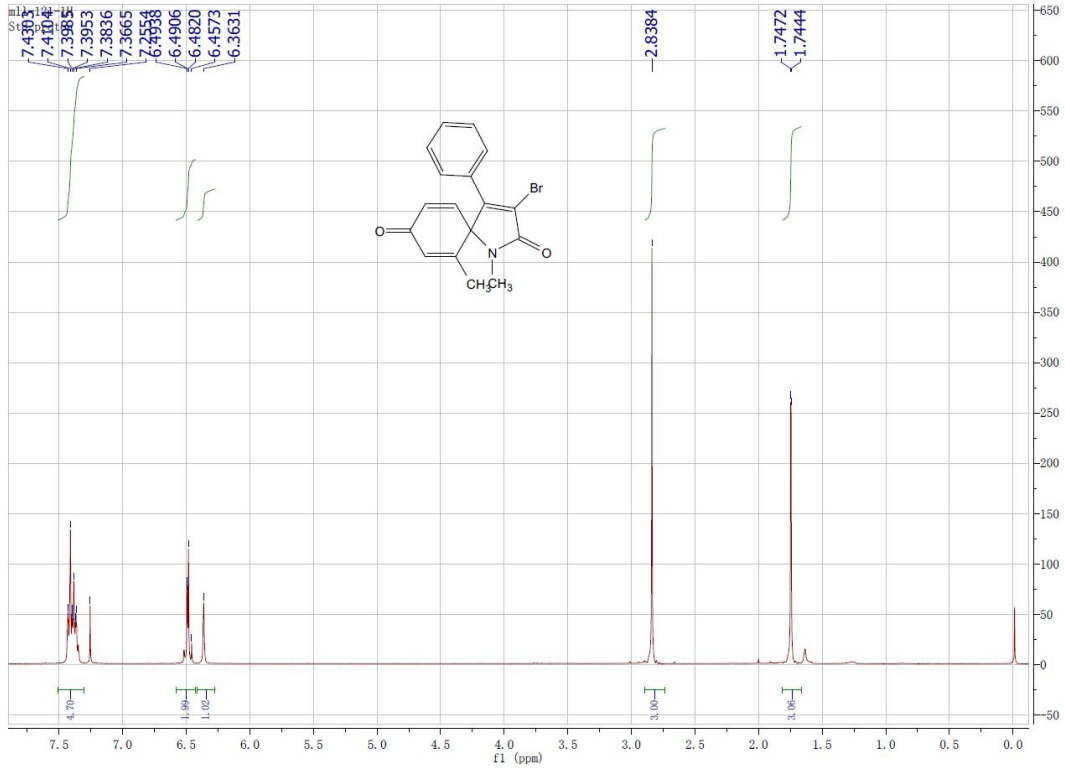

m11-12-1C
Std carbon
183.65
168.52
165.82
152.58
143.42
133.09
130.36
128.75
127.71
119.28
104.99
77.32
77.01
76.69
68.25
52.64
41.69
29.67
Br
O
O
N
O
O
O
CH3
f1 (ppm)

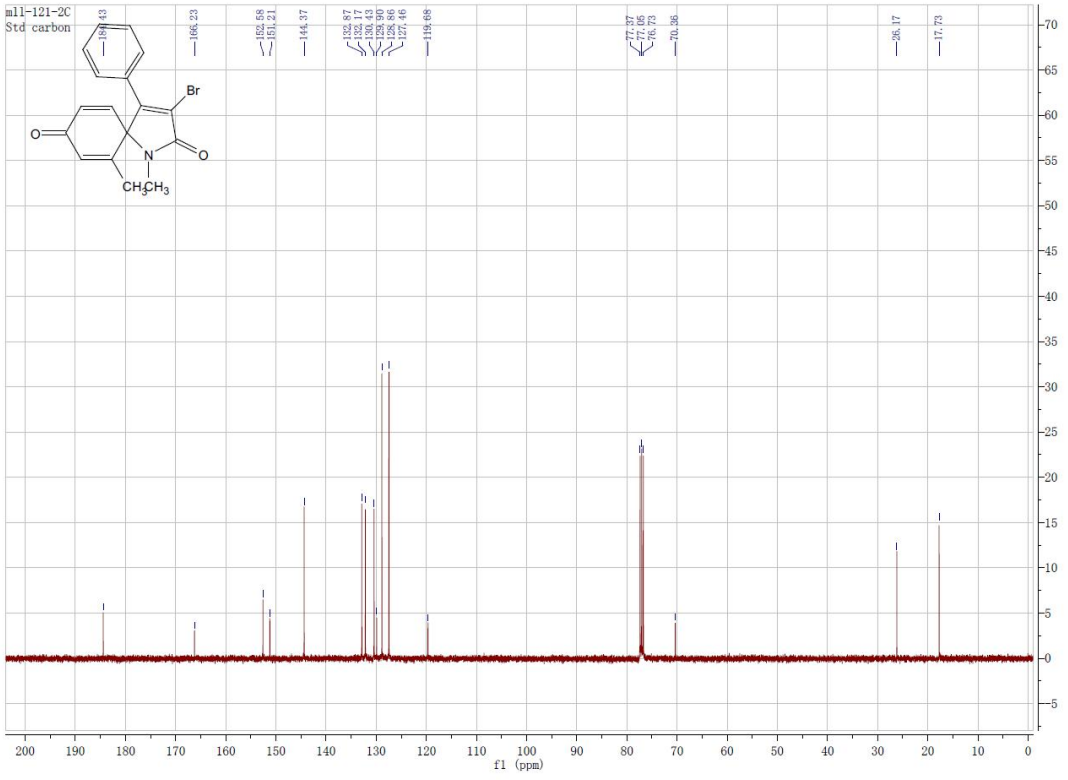

7.4290
7.4164
7.4101
7.3392
7.3123
7.2405
7.2204
6.7491
6.7314
6.7242
6.4892
6.2744
6.2492
6.2206
6.1956
5.4862
4.7950
1.2751
10.60
1.04
1.08
2.00
0.99
1.10
9.38
f1 (ppm)

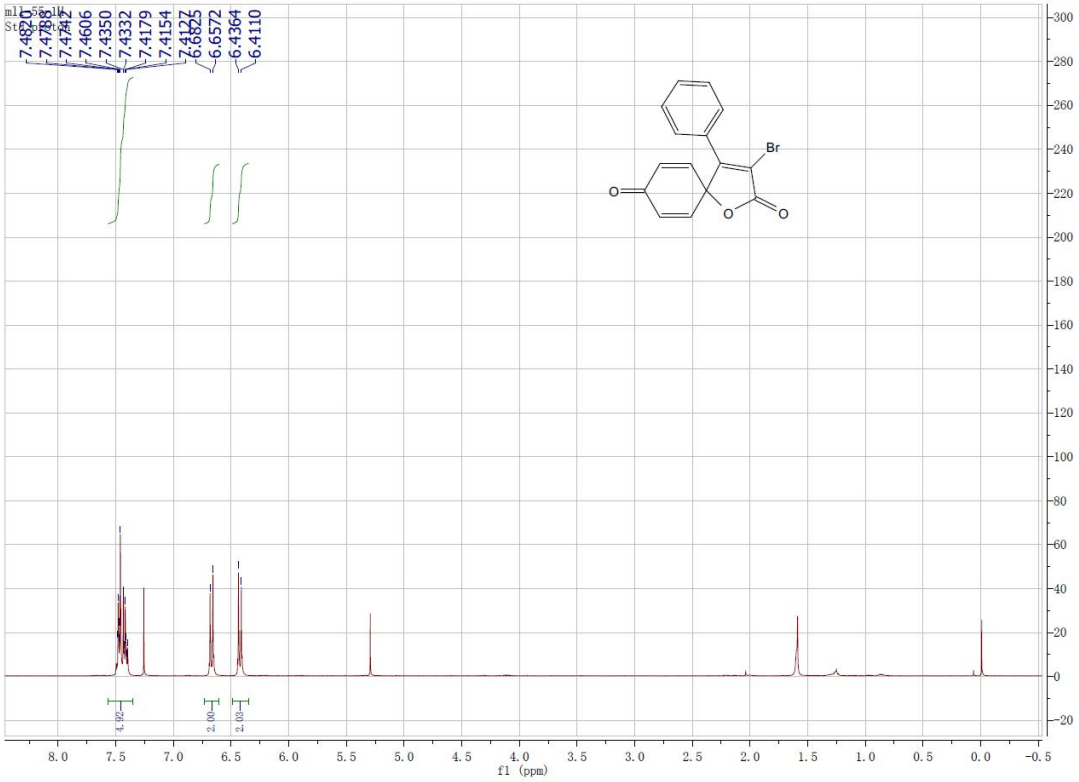

mll-17-1C
Std carbon
183.9697
166.6018
165.7340
152.4319
144.3067
144.1201
135.2447
132.5223
132.2833
130.0614
129.4330
129.3115
129.1259
128.5801
127.8472
120.0474
77.3293
77.0111
76.6930
69.6254
62.8109
52.0314
28.4996
f1 (ppm)

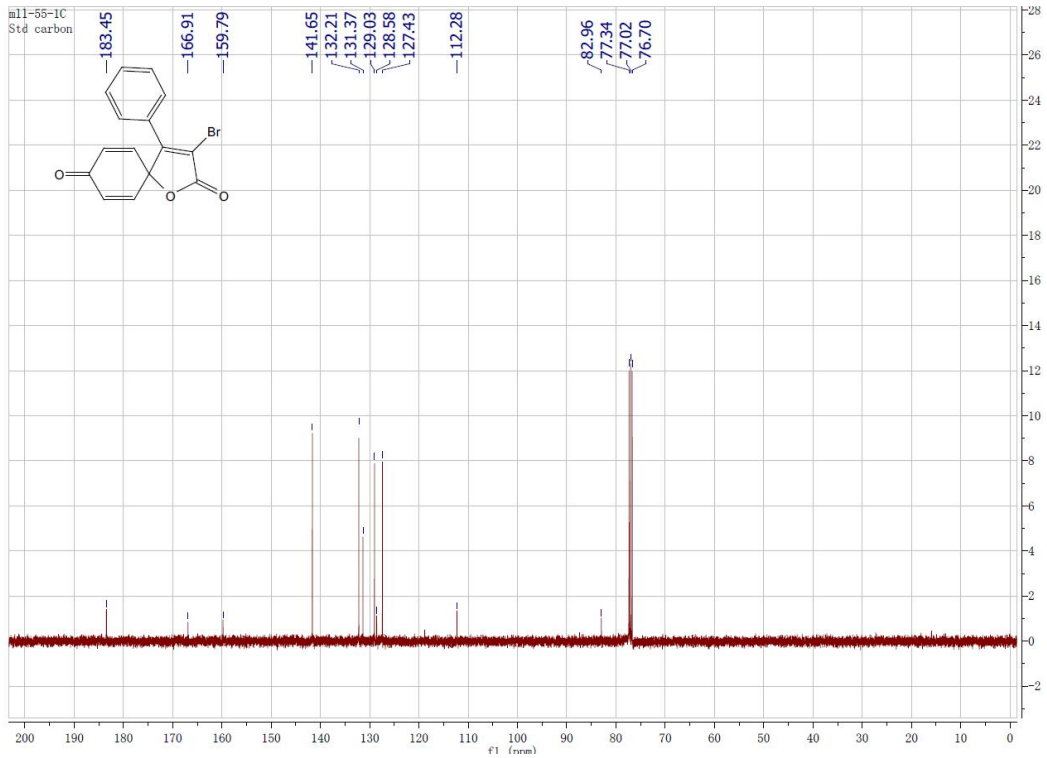

ml1-122-2H
Std proton
7.3799
7.3718
7.3557
7.3485
7.3453
6.4595
6.2803
2.9079
1.9250
1.9231
4.67
1.95
1.02
3.07
3.00
f1 (ppm)

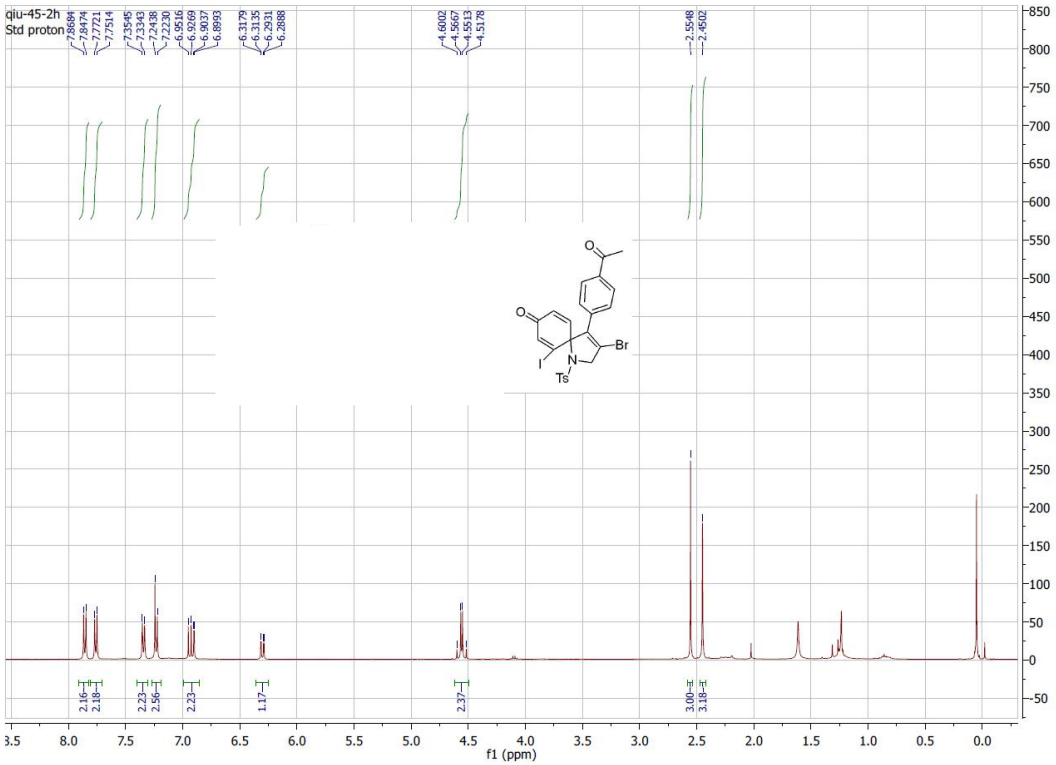

ml1-122-2C
Std carbon
184.51
165.76
151.65
143.96
140.70
138.84
133.16
130.32
130.10
128.65
127.71
119.40
77.36
77.04
76.72
68.81
26.58
15.93
f1 (ppm)

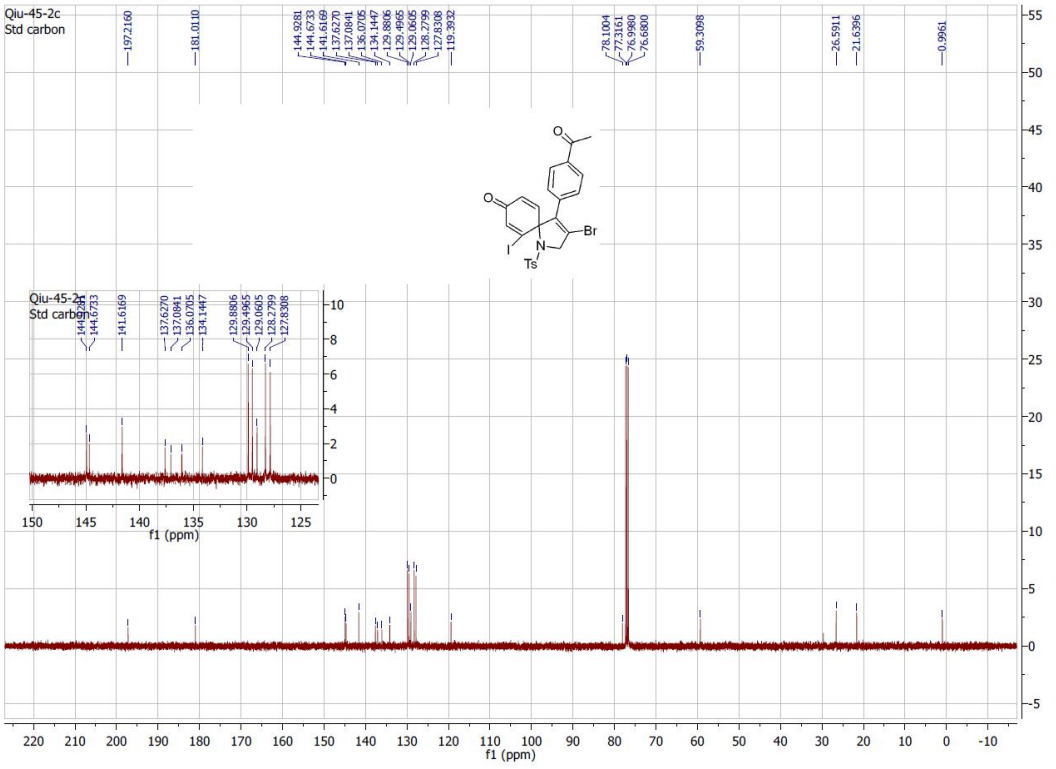

7.4303
7.4014
7.3985
7.3953
7.3836
7.3665
7.2554
6.4906
6.4820
6.4573
6.3631
2.8384
1.7472
1.7444
Br
O
O
N
CH3CH3
4.70
1.99
1.02
3.00
3.06
f1 (ppm)


ml1-121-2C
Std carbon
184.43
166.23
152.58
151.21
144.37
132.87
132.17
130.43
129.90
128.86
127.46
119.68
77.37
77.05
76.73
70.36
26.17
17.73
Br
O
O
N
CH3CH3
f1 (ppm)


7.4820
7.4788
7.4742
7.4606
7.4350
7.4332
7.4179
7.4154
7.4122
6.6825
6.6572
6.4364
6.4110
Br
O
O
O
4.02
2.00
2.03
f1 (ppm)


ml1-55-1C
Std carbon
183.45
166.91
159.79
141.65
132.21
131.37
129.03
128.58
127.43
112.28
82.96
77.34
77.02
76.70
Br
O
O
O
f1 (ppm)


qiu-45-2h
Std proton
f1 (ppm)


Qiu-45-2c
Std carbon
Qiu-45-2c
Std carbon
f1 (ppm)
f1 (ppm)