Supporting Information for

Photo-Mediated Synthesis of Halogenated Spiro[4,5]trienones of N-Aryl Alkynamides with $PhI(OCOCF_3)_2$ and KBr/KCl

Tong Liu, Yaming Li *, Linlin Jiang, Jiaao Wang, Kun Jin, Rong Zhang and Chunying Duan *
State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, P.R. China
ymli@dlut.edu.cn, cyduan@dlut.edu.cn.

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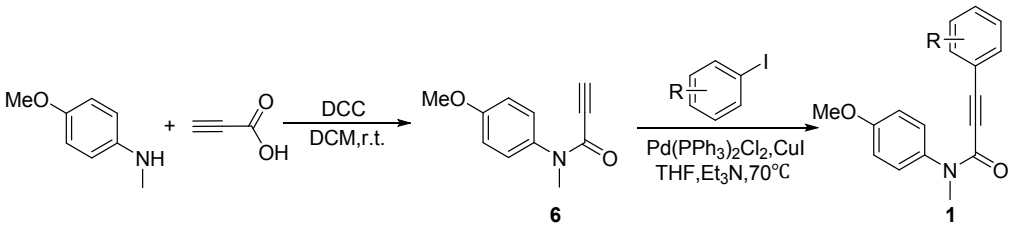
1. General Methods

All reagents unless otherwise noted were obtained from commercial sources and used without further purification. Phenyliodine bis(trifluoroacetate) (PIFA) (98.0%) were used without any purification. The photochemical reactor used the CEL-HXUV300 xenon lamp of Beijing Zhongjiao Jinyuan Company as the light source. The maximum wavelength of the blue LED is 450nm. There is 3.0 cm distance between the reactor and the light source. Reactions were monitored by thin-layer chromatography (TLC) on silica gel plates and visualization of the plates was performed under UV light (254 nm and 365nm). Further flash column chromatography was performed on silica gel (200-300 mesh). NMR spectra (^{1}H and ^{13}C) were obtained using Bruker 400/500/600 MHz instruments, using TMS (Me_4Si) as an internal standard. Chemical shifts (δ) and coupling constant (J) are reported in units of ppm and Hz, respectively. The following abbreviations are used to set multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, q = quartet, tq = triplet of quartets, qt = quartet of triplets, and m = multiplet. High-resolution mass spectrometry data were recorded on a high-resolution mass spectrometer in the ESI mode.

2. Experiment Section

2.1 General Procedure for the Synthesis of *N*-(*p*-Methoxyaryl)propiolamides (1).



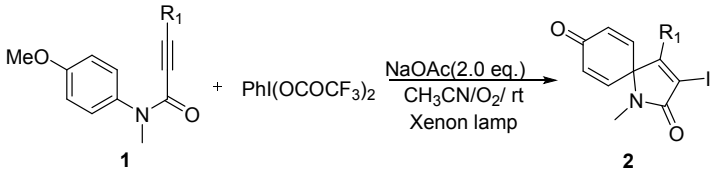
Step 1: Preparation of intermediates **6**

To a solution of 4-methoxy-*N*-methylaniline (10.0 mmol, 1.0 eq.) in CH_2Cl_2 (28 mL) was added propiolic acid (11.0 mmol, 1.1 equiv) at 0℃, then DCC (15.0 mmol, 1.5 equiv) in CH_2Cl_2 (4 mL) was added dropwise. The resulting mixture was stirred at room temperature until the TLC indicated that the total consumption of the substituted aniline. After the reaction was finished, the residue was extracted with CH_2Cl_2 (100 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to remove the solvent. The given residue was purified by flash chromatography using a mixture of EtOAc and PE as eluent to give the products **6**.

Step 2: Preparation of substrates **1**.

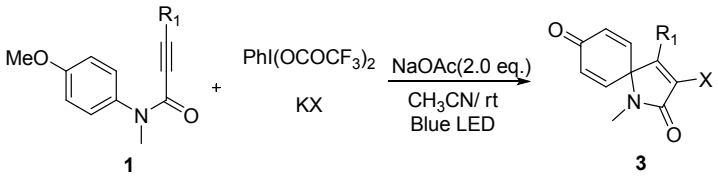
To a solution of the alkyne compound **6** (2 mmol) and the substituted aryliodide (1.5 mmol) in Et_3N (12.5 mL) and THF (12.5 mL), under an argon atmosphere $PdCl_2(PPh_3)_2$ (0.1 mmol) and CuI (0.15 mmol) was added. The reaction mixture was heated to 70℃. The resulting mixture was kept at the same temperature until the TLC indicated that the total consumption of the substituted aryliodide, and then resulting mixture was cooled to room temperature. Then the residue was extracted with EtOAc (20 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to remove the solvent. The given residue was purified by flash chromatography using a mixture of EtOAc and PE as eluent to provide the substrates **1**.

2.2 Typical Experimental Procedure for the Photo-Mediated Synthesis of 3-iodo spiro[4,5]trienones from *N*-Arylpropiolamides with PIFA:



To a Schlenk tube were added **1** (0.2 mmol), PIFA (0.4 mmol, 2.0 equiv), NaOAc (0.4 mmol, 2.0 equiv) and CH_3CN (2 mL). Then the tube was evacuated and backfilled with oxygen for three times. The tube around condensate water was stirred at room temperature with the irradiation of Xenon lamp for 18 h. After the reaction was finished, the reaction mixture was washed with brine, and the aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (EtOAc/PE) to afford the desired product **2**.

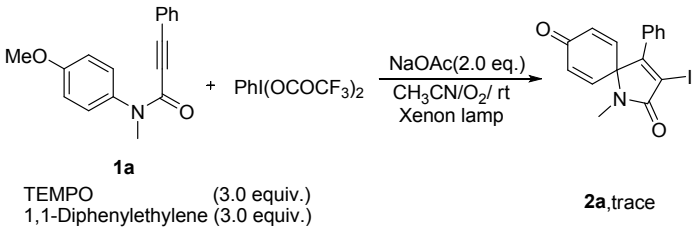
2.3 Typical Experimental Procedure for the Photo-Mediated Synthesis of 3-bromo spiro[4,5]trienones or 3-chloro spiro[4,5]trienones from *N*-Arylpropiolamides with PIFA and KBr or KCl:



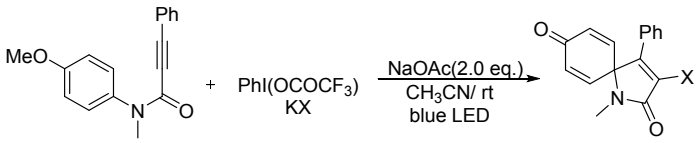
To a Schlenk tube were added **1** (0.2 mmol), PIFA (0.4 mmol, 2.0 equiv), KBr/KCl (0.3 mmol, 1.5 equiv), NaOAc (0.4 mmol, 2.0 equiv) and CH_3CN (2 mL). The tube was allowed to stir at room temperature under the irradiation of 15W blue LED for 2 h. After the reaction was finished, the reaction mixture was washed with brine, and the aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (EtOAc/PE) to afford the desired product **3**.

3. Mechanism Study

3.1 Radical trapping experiment



To a Schlenk tube were added **1a** (0.2 mmol), PIFA (0.4 mmol, 2.0 equiv), NaOAc (0.4 mmol, 2.0 equiv), TEMPO/ 1,1-diphenylethylene (0.6 mmol, 3.0 equiv) and CH_3CN (2 mL). Then the tube was evacuated and backfilled with oxygen for three times. The tube around condensate water was stirred at room temperature with the irradiation of Xenon lamp for 18 h. No desired product **2a** was detected.



1a

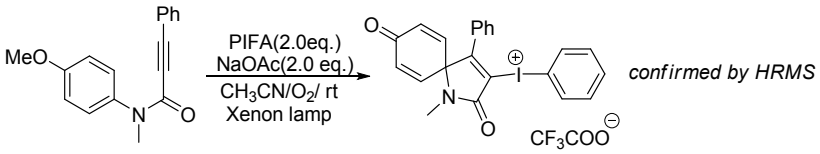
TEMPO (3.0 equiv.)
1,1-Diphenylethylene (3.0 equiv.)

3a, X=Br, trace **3b**, X=Cl, trace
3a, X=Br, 42% **3b**, X=Cl, 13%

To a Schlenk tube were added **1** (0.2 mmol), PIFA (0.4 mmol, 2.0 equiv), KBr/KCl (0.3 mmol, 1.5 equiv), NaOAc (0.4 mmol, 2.0 equiv), TEMPO (0.6 mmol, 3.0 equiv) and CH_3CN (2 mL). The tube was allowed to stir at room temperature under the irradiation of 15W blue LED for 2 h. No desired product **3a**/**3b** was detected. When TEMPO was instead by 1,1-diphenylethylene, the yields of **3a** and **3b** were 42% and 13%.

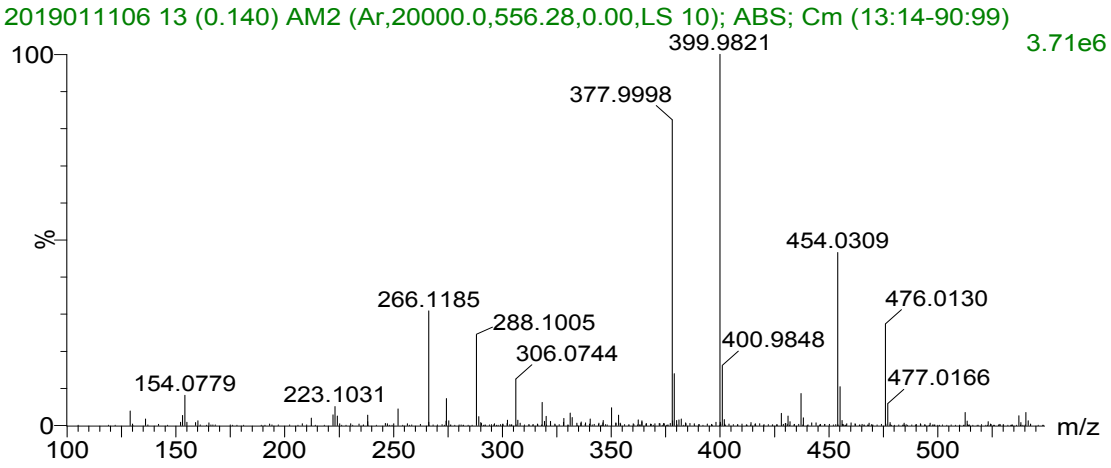
3.2 Detection of intermediates

In order to verify the proposed mechanisms, we carried out additional experiments, managing to isolate and characterize the diaryliodonium trifluoroacetate intermediate. Substrate **1** (1.0 equiv) was treated with 2.0 equiv of PIFA and 2.0 equiv of NaOAc in CH_3CN at room temperature for 18 h. Then the reaction solvent was removed under vacuum and the residue was then taken up by acetonitrile and the HRMS analysis undoubtedly confirmed the existence of diaryliodonium trifluoroacetates in the reaction mixture.



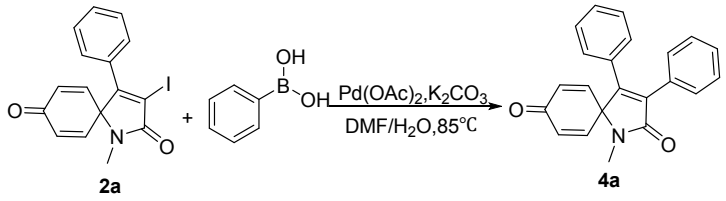
1 **7**

HRMS (ESI) calcd for $C_{22}H_{17}INO_2^+$ [M - CF_3COO^-]$^+$ 454.0298, found 454.0309.

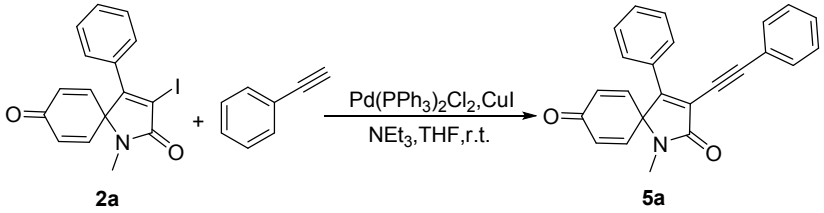


The detection of **7** provided the proposed reaction pathway.

4. Post-functionalization.



To a solution of compound **2a** (0.2 mmol,0.274 mmol), $Pd(OAc)_2$ (0.1 equiv, 0.02 mmol) in DMF (4 mL)and water (1 mL) was added phenylboronic acid (2 equiv, 0.4 mmol) and K_2CO_3 (2 equiv, 0.4 mmol) and the mixture was stirred under reflux at 85℃. The reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was washed with brine, and the aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (EtOAc/PE) to afford the desired product **4a**.



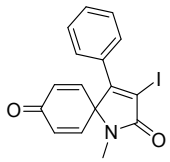
To a solution of the compound **2a** (0.2 mmol) and phenylacetylene (0.3 mmol) in NEt_3 (1.5 mL) and THF (1.5 mL)was added$PdCl_2(PPh_3)_2$ (7.02 mg, 0.01 mmol) and CuI (2.85 mg, 0.015 mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature. The reaction progress was monitored by TLC. After completion of the reaction, the residue was extracted with EtOAc (10 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to remove the solvent. The given residue was purified by flash chromatography using a mixture of EtOAc and PE as eluent to provide the substrates **5a**.

5. Reference

1. L. J. Wang, A. Q. Wang, Y. Xia, X. X. Wu, X. Y. Liu, Y. M. Liang, Silver-catalyzed carbon - Phosphorus functionalization of *N*-(*p*-methoxyaryl)propiolamides coupled with dearomatization: Access to phosphorylated aza-decenones. *Chem. Commun.*, 2014, **50**, 13998-14001.

6. Characterization data of products.

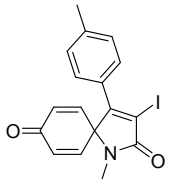
3-Iodo-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2a)



2a

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), R_f = 0.43, 70.1 mg, 93%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.1 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 6.9 Hz, 2H), 6.51 (d, *J* = 10.4 Hz, 2H), 6.46 (d, *J* = 10.3 Hz, 2H), 2.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.67, 167.42, 157.94, 144.04, 133.30, 131.91, 130.12, 128.70, 127.71, 98.18, 70.39, 26.99. HRMS (ESI) *m/z* $C_{16}H_{12}INO_2Na$ $[M + Na]^+$ calcd for 399.9810, found 399.9812.

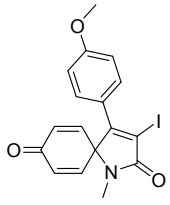
3-Iodo-1-methyl-4-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2b)



2b

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 66.5 mg, 85%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.52 (d, J = 9.9 Hz, 2H), 6.46 (d, J = 9.9 Hz, 2H), 2.95 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.83, 167.52, 157.89, 144.32, 140.39, 133.20, 129.40, 128.92, 127.58, 97.58, 70.35, 26.99, 21.42. HRMS (ESI) *m/z* $C_{17}H_{14}INO_2Na$ $[M + Na]^+$ calcd for 413.9967, found 413.9972.

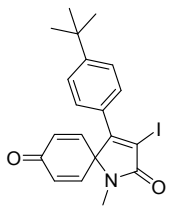
3-Iodo-1-methyl-4-(4-methoxyphenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2c)



2c

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 62.7 mg, 77%;
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 6.48 – 6.37 (m, 4H), 3.75 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 183.86, 167.65, 160.91, 157.22, 144.55, 133.15, 129.22, 123.93, 114.13, 96.81, 70.23, 55.32, 26.91. HRMS (ESI) *m/z* $C_{17}H_{14}INO_3Na$ $[M + Na]^+$ calcd for 429.9916, found 429.9919.

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

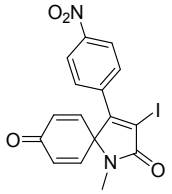


2d

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 75.4 mg, 87%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.50 (q, *J* = 10.3 Hz,

4H), 2.95 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.95, 167.59, 157.54, 153.44, 144.46, 133.16, 128.79, 127.35, 125.62, 97.31, 70.19, 34.86, 31.10, 26.87. HRMS (ESI) *m/z* $C_{20}H_{20}INO_2Na$ $[M + Na]^+$ calcd for 456.0436, found 456.0432.

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

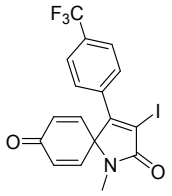


2e

Yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 54.9 mg, 65%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 6.53 (q, *J* = 10.4 Hz, 4H), 3.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.12, 166.75, 155.73, 148.52, 133.81, 133.28, 129.11, 124.04, 123.74, 100.73, 70.30, 27.14. HRMS (ESI) *m/z* $C_{16}H_{11}IN_2O_4Na$ $[M + Na]^+$ calcd for 444.9661, found 444.9664.

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

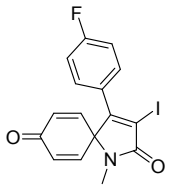


2f

Light yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 58.7 mg, 66%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 6.54 – 6.47 (m, 4H), 2.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.28, 166.94, 156.47, 143.48, 135.52, 133.63, 132.03 (q, J = 33.0 Hz), 128.31, 125.81 (q, J = 3.7 Hz), 123.53 (dd, J = 545.1, 272.5 Hz), 99.83, 70.29, 27.05. HRMS (ESI) *m/z* $C_{17}H_{11}F_3INO_2Na$ $[M + Na]^+$ calcd for 467.9684, found 467.9682.

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

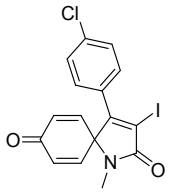


2g

Light yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 56.9 mg, 72%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.43 (d, *J* = 10.6 Hz, 2H), 6.41 (d, *J* = 10.7 Hz, 2H), 2.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.50, 167.23, 163.47 (d, *J* = 251.8 Hz), 156.84, 143.96, 133.41, 129.88 (d, *J* = 8.5 Hz), 127.87 (d, *J* = 3.5 Hz), 116.04 (d, *J* = 21.9 Hz), 98.68, 70.29, 26.69. HRMS (ESI) *m/z* $C_{16}H_{11}FINO_2Na$ $[M + Na]^+$ calcd for 417.9716, found 417.9718.

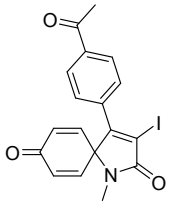
4-(4-Chlorophenyl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2h)



2h

Light yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 60.8 mg, 74%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.51 (q, *J* = 10.2 Hz, 4H), 2.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.54, 167.21, 156.68, 143.87, 136.34, 133.47, 131.47, 130.24, 129.13, 98.91, 70.29, 27.07. HRMS (ESI) *m/z* $C_{16}H_{11}ClINO_2Na$ $[M + Na]^+$ calcd for 433.9421, found 433.9425.

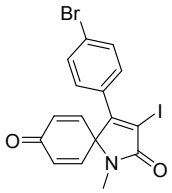
3-Iodo-1-methyl-4-(4-acetylphenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2i)



2i

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), R_f = 0.34, 62.0 mg, 74%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 10.2 Hz, 2H), 6.56 – 6.44 (m, 4H), 2.98 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.01, 183.37, 167.04, 156.89, 143.63, 138.02, 136.40, 133.53, 128.59, 128.16, 99.43, 77.28, 27.06, 26.61. HRMS (ESI) *m/z* $C_{18}H_{14}INO_3Na$ $[M + Na]^+$ calcd for 441.9916, found 441.9915.

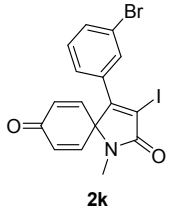
4-(4-Bromophenyl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2j)



2j

Light yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 75.5 mg, 83%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.44 – 6.36 (m, 4H), 2.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.44, 167.14, 156.75, 143.50, 133.48, 132.09, 130.77, 129.32, 124.67, 98.90, 70.01, 27.03. HRMS (ESI) *m/z* $C_{16}H_{11}BrINO_2Na$ $[M + Na]^+$ calcd for 477.8916, found 477.8912.

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

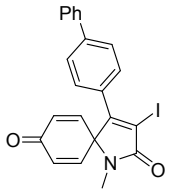


2k

Light yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 72.8 mg, 80%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.9 Hz, 1H), 7.44 (s, 1H), 7.28 – 7.23 (m, 1H), 7.21 (d, J = 7.7 Hz, 1H), 6.51 (d, J = 10.4 Hz, 4H), 2.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.47, 167.06,

156.32, 143.63, 133.84, 133.57, 133.15, 130.76, 130.33, 126.29, 122.70, 99.48, 70.31, 27.07. HRMS (ESI) *m/z* $C_{16}H_{11}BrINO_2Na$ $[M + Na]^+$ calcd for 477.8916, found 477.8910.

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

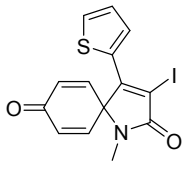


2m

Light yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 67.9 mg, 75%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 4H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 9.9 Hz, 2H), 6.50 (d, *J* = 10.3 Hz, 2H), 2.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.78, 167.48, 157.37, 145.88, 144.23, 142.94, 139.76, 133.34, 130.65, 128.95, 128.16, 127.33, 127.11, 98.04, 70.31, 26.98. HRMS (ESI) *m/z* $C_{22}H_{16}INO_2Na$ $[M + Na]^+$ calcd for 476.0123, found 476.0121.

3-Iodo-1-methyl-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2n)

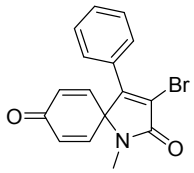


2n

Light yellow solid, Eluent: petroleum ether/ethyl acetate(2:1), 42.9 mg, 56%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 3.7 Hz, 1H), 7.53 (d, *J* = 5.0 Hz, 1H), 7.12 – 7.08 (t, 1H), 6.61 (d, *J* = 10.1 Hz, 2H), 6.55 (d, *J* = 10.2 Hz, 2H), 2.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.96, 167.61, 149.60, 145.16, 133.26, 132.70, 129.74, 129.47, 127.55, 93.53, 69.17, 26.37. HRMS (ESI) *m/z* $C_{14}H_{10}INO_2SNa$ $[M + Na]^+$ calcd for 405.9375, found 405.9378.

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

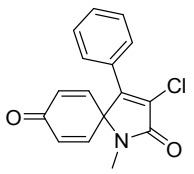


3a

White solid, Eluent: petroleum ether/ethyl acetate (2:1), R_f = 0.47, 59.22 mg, 90%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 6.47 – 6.41 (m, 4H), 2.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.63, 165.79, 151.32, 144.11, 133.44, 130.25, 130.20, 128.74, 127.77, 119.90, 68.32, 26.62. HRMS (ESI) *m/z* $C_{16}H_{12}BrNO_2Na$ $[M + Na]^+$ calcd for 351.9949 , found 351.9962.

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



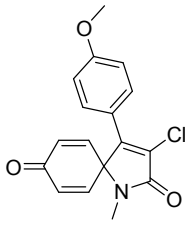
3b

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), R_f = 0.40, 43.33 mg, 76%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.45 – 7.35 (m, 3H), 6.52 (s, 4H), 2.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.67, 165.20, 147.30, 144.42, 133.49, 130.36, 129.31, 128.83, 128.51,

127.79, 66.55, 26.35. HRMS (ESI) *m/z* $C_{16}H_{12}ClNO_2Na$ [M + Na]$^+$ calcd for 308.0454 , found 308.0453.

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

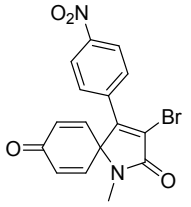


3c

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 46.63 mg, 74%

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 6.4 Hz, 2H), 6.53 (q, *J* = 9.6 Hz, 4H), 3.82 (s, 3H), 2.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 183.86, 165.49, 161.05, 157.23, 144.97, 133.27, 129.34, 126.73, 121.59, 114.27, 66.30, 55.36, 26.17. HRMS (ESI) *m/z* $C_{17}H_{14}ClNO_3Na$ [M + Na]$^+$ calcd for 338.0560 , found 338.0572

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

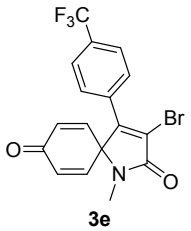


3d

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 59.84 mg, 80%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.50 – 6.43 (m, 4H), 2.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.00, 164.96, 149.02, 148.58, 143.25, 136.47, 133.98, 129.09, 124.03, 122.49, 68.17, 26.79. HRMS (ESI) *m/z* $C_{16}H_{11}BrN_2O_4Na$ [M + Na]$^+$ calcd for 396.9800 , found 396.9812.

3-Bromo-1-methyl-4-(4-trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione(3e)

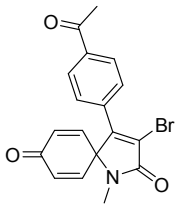


3e

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 65.90mg, 83%;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 6.46 (s, 4H), 2.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.27, 165.29, 149.83, 143.54, 132.13 (q, *J* = 33.0 Hz), 131.96, 131.64, 128.34, 125.84 (q, *J* = 3.7 Hz), 123.51 (q, *J* = 272.5 Hz), 124.86, 68.21, 26.73. HRMS (ESI) *m/z* $C_{17}H_{11}BrF_3NO_2Na$ [M + Na]$^+$ calcd for 419.9823 , found 419.9807.

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

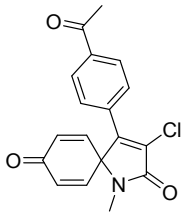


3f

White solid, Eluent: petroleum ether/ethyl acetate (2:1), 59.36 mg, 80%;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.47 – 6.43 (m, 4H), 2.89 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.97, 183.31, 165.37, 150.24, 143.67, 138.11, 134.63, 133.70, 128.60, 128.19, 121.26, 68.25, 26.72, 26.61. HRMS (ESI) *m/z* $C_{18}H_{14}BrNO_3Na$ $[M + Na]^+$ calcd for 394.0055 , found 394.0057.

3-Chloro-1-methyl-4-(4-acetylphenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3g)

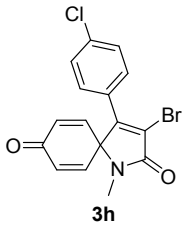


3g

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 47.75 mg, 73%;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, J = 7.9 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H), 6.49 – 6.44 (m, 4H), 2.88 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.01, 183.38, 164.73, 146.16, 143.98, 138.09, 133.75, 133.68, 129.93, 128.66, 128.18, 66.47, 26.67, 26.47. HRMS (ESI) *m/z* $C_{18}H_{14}ClNO_3Na$ $[M + Na]^+$ calcd for 350.0560, found 350.0572.

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

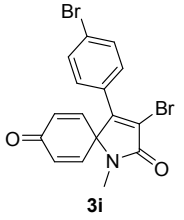


3h

White solid, Eluent: petroleum ether/ethyl acetate (2:1), 52.27 mg, 72%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 4H), 6.53 – 6.47 (m, 4H), 2.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.38, 165.51, 150.03, 143.86, 136.55, 133.62, 129.17, 129.12, 128.55, 120.49, 68.18, 26.63. HRMS (ESI) *m/z* $C_{16}H_{11}BrClNO_2Na$ $[M + Na]^+$ calcd for 385.9559, found 385.9562.

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



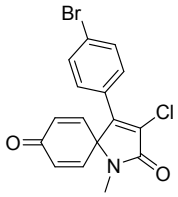
3i

White solid, Eluent: petroleum ether/ethyl acetate (2:1), 63.79 mg, 78%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.48 – 6.40 (m, 4H), 2.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.36, 165.50, 150.08, 143.83, 133.64, 132.14, 129.30,

129.03, 124.85, 120.50, 68.13, 26.64. HRMS (ESI) *m/z* $C_{16}H_{11}Br_2NO_2Na$ $[M + Na]^+$ calcd for 431.9034, found 431.9029.

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

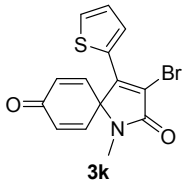


3j

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 50.82 mg, 70%;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 10.1 Hz, 2H), 6.43 (d, *J* = 10.1 Hz, 2H), 2.85 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 183.40, 164.86, 146.08, 144.14, 133.66, 132.19, 129.31, 129.02, 128.15, 124.93, 66.37, 26.36. HRMS (ESI) *m/z* $C_{16}H_{11}BrClNO_2Na$ $[M + Na]^+$ calcd for 385.9959, found 385.9964.

3-Bromo-1-methyl-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3k)

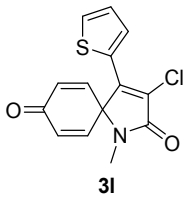


3k

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 41.54 mg, 62%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 3.2 Hz, 1H), 7.55 (d, *J* = 4.8 Hz, 1H), 7.09 (t, *J* = 4.2 Hz, 1H), 6.63 (d, *J* = 9.8 Hz, 2H), 6.55 (d, *J* = 9.8 Hz, 2H), 2.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.87, 165.76, 145.10, 143.69, 133.41, 131.80, 129.88, 129.64, 127.53, 115.72, 66.91, 26.03. HRMS (ESI) *m/z* $C_{14}H_{10}BrNO_2SNa$ $[M + Na]^+$ calcd for 357.9513, found 357.9516.

3-Chloro-1-methyl-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3l)

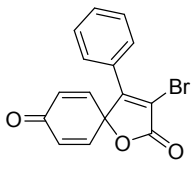


3l

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 31.42 mg, 54%;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.2, 3.9 Hz, 1H), 7.02 (d, *J* = 3.6 Hz, 1H), 6.57 (d, *J* = 9.1 Hz, 1H), 6.48 (d, *J* = 9.2 Hz, 4H), 2.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 183.88, 165.06, 145.21, 140.35, 133.50, 131.15, 130.04, 129.42, 127.56, 124.42, 65.20, 25.89. HRMS (ESI) *m/z* $C_{14}H_{10}ClNO_2SNa$ $[M + Na]^+$ calcd for 314.0018, found 314.0024.

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



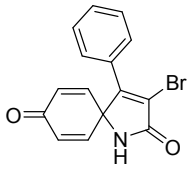
3m

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 35.38 mg, 56%;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 3H), 7.35 (t, *J* = 7.4 Hz, 2H), 6.61 (d, *J* = 9.3 Hz, 2H), 6.36 (d, *J* = 9.3 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 183.42, 166.87, 159.82, 141.66, 132.23,

131.37, 129.04, 128.64, 127.45, 112.32, 82.98. HRMS (ESI) *m/z* $C_{15}H_9BrO_3Na$ [M + Na]$^+$ calcd for 338.9633 , found 338.9642.

3-Phenyl-3-bromo-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione(3n)

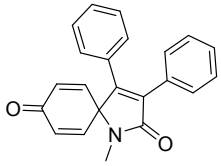


3n

Yellow solid, Eluent: petroleum ether/ethyl acetate (2:1), 32.76 mg, 52%;

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.11 (s, 1H), 7.21 – 7.06 (m, 5H), 6.72 (d, J = 9.9 Hz, 2H), 6.03 (d, J = 9.9 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 184.13, 166.74, 153.36, 146.48, 130.59, 130.27, 129.67, 128.41, 127.77, 119.95, 64.27. HRMS (ESI) *m/z* $C_{15}H_{10}BrNO_2Na$ [M + Na]$^+$ calcd for 337.9793, found 337.9791.

1-Methyl-3, 4-diphenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione(4a)

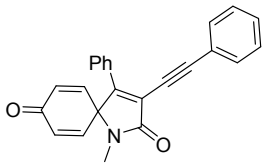


4a

White solid, Eluent: petroleum ether/ethyl acetate (5:1), 58.8 mg, 90%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 4.9 Hz, 2H), 7.31 – 7.21 (m, 6H), 7.12 (d, J = 7.5 Hz, 2H), 6.60 (d, J = 9.7 Hz, 2H), 6.48 (d, J = 9.7 Hz, 2H), 2.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.15, 169.61, 149.75, 145.71, 135.45, 133.20, 131.84, 130.57, 129.49, 129.28, 128.66(2C), 128.41, 128.21, 67.03, 26.19. HRMS (ESI) *m/z* $C_{22}H_{17}NO_2Na$ [M + Na]$^+$ calcd for 350.1157, found 350.1153.

1-Methyl-4-phenyl-3-(phenylethynyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (5a)



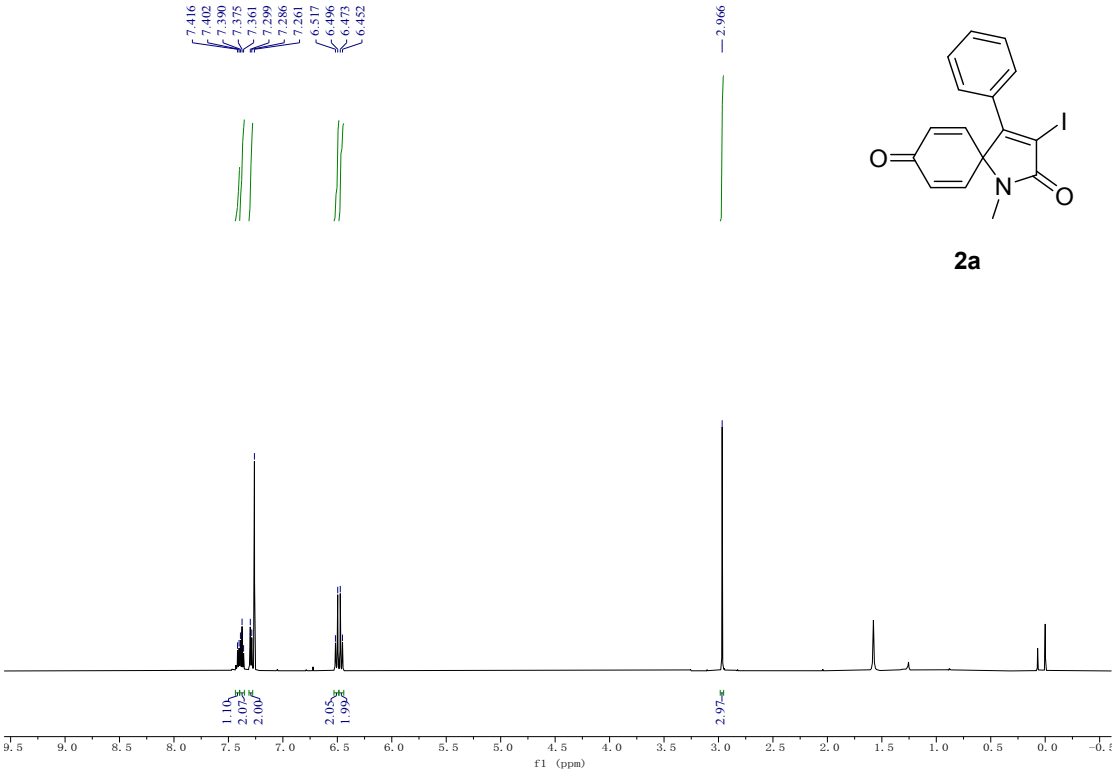
5a

White solid, Eluent: petroleum ether/ethyl acetate(10:1), 58.3 mg, 83%;

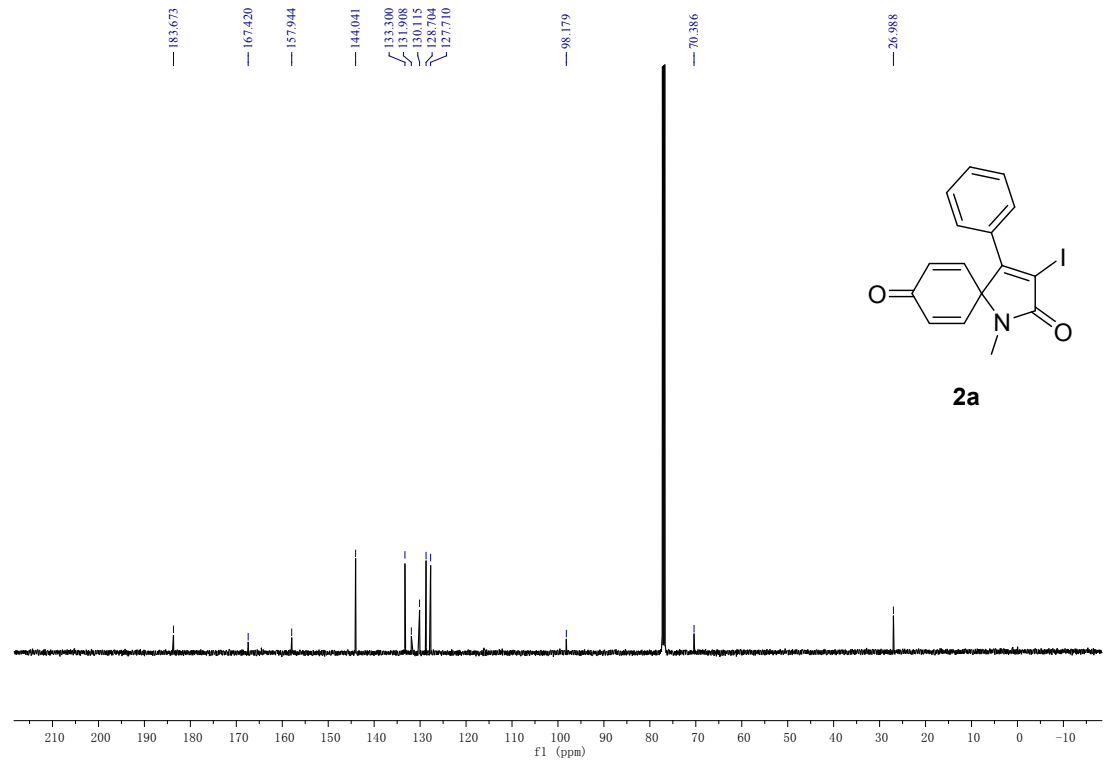
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 6.8 Hz, 2H), 7.54 (d, *J* = 6.1 Hz, 2H), 7.43 – 7.34 (m, 6H), 6.58 (s, 4H), 2.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.03, 167.57, 153.54, 145.80, 132.95, 132.09, 131.23, 130.69, 129.33, 128.74, 128.43, 127.58, 122.19, 119.86, 100.42, 81.63, 66.16, 25.72. HRMS (ESI) *m/z* $C_{24}H_{17}NO_2Na$ [M + Na]$^+$ calcd for 374.1157, found 374.1152.

7. Copies of NMR spectra for products.

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

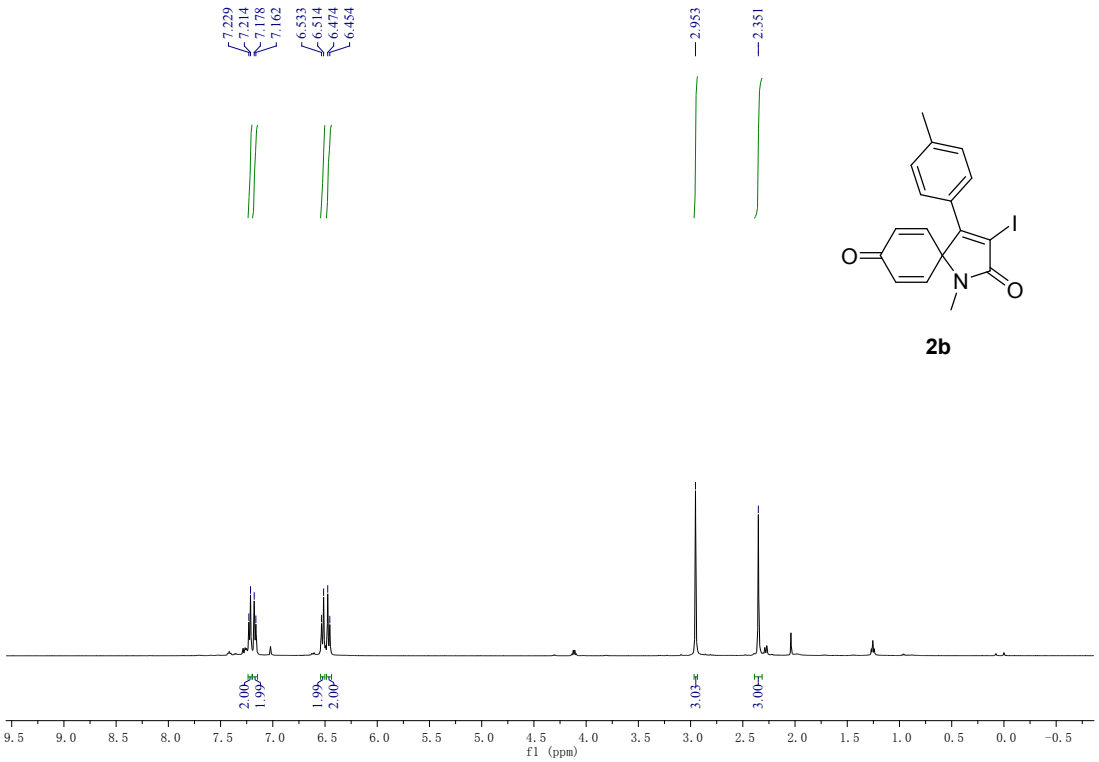


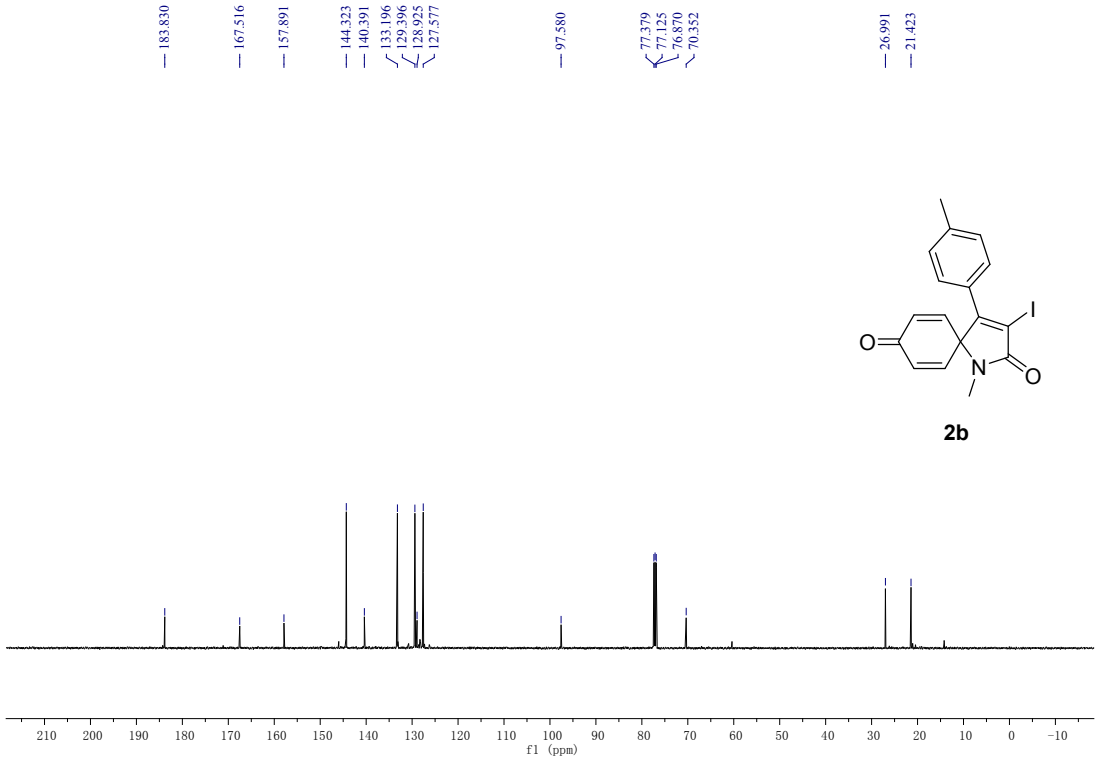
2a



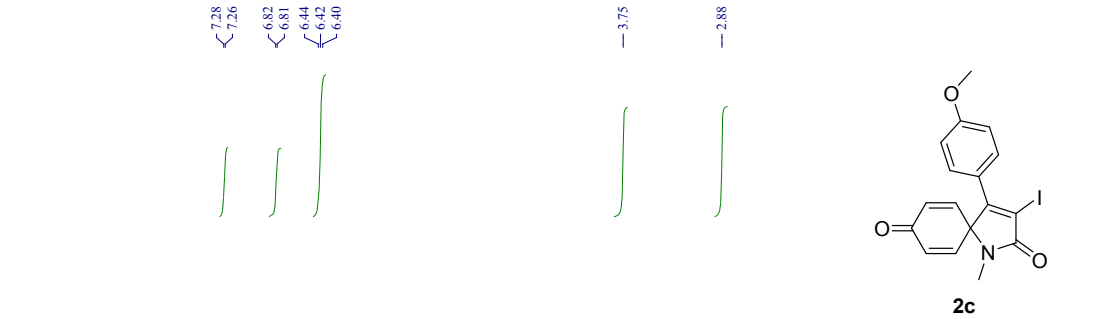
2a

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

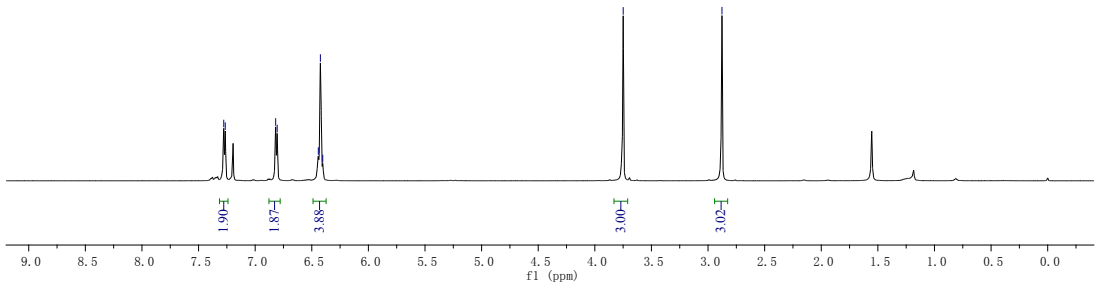


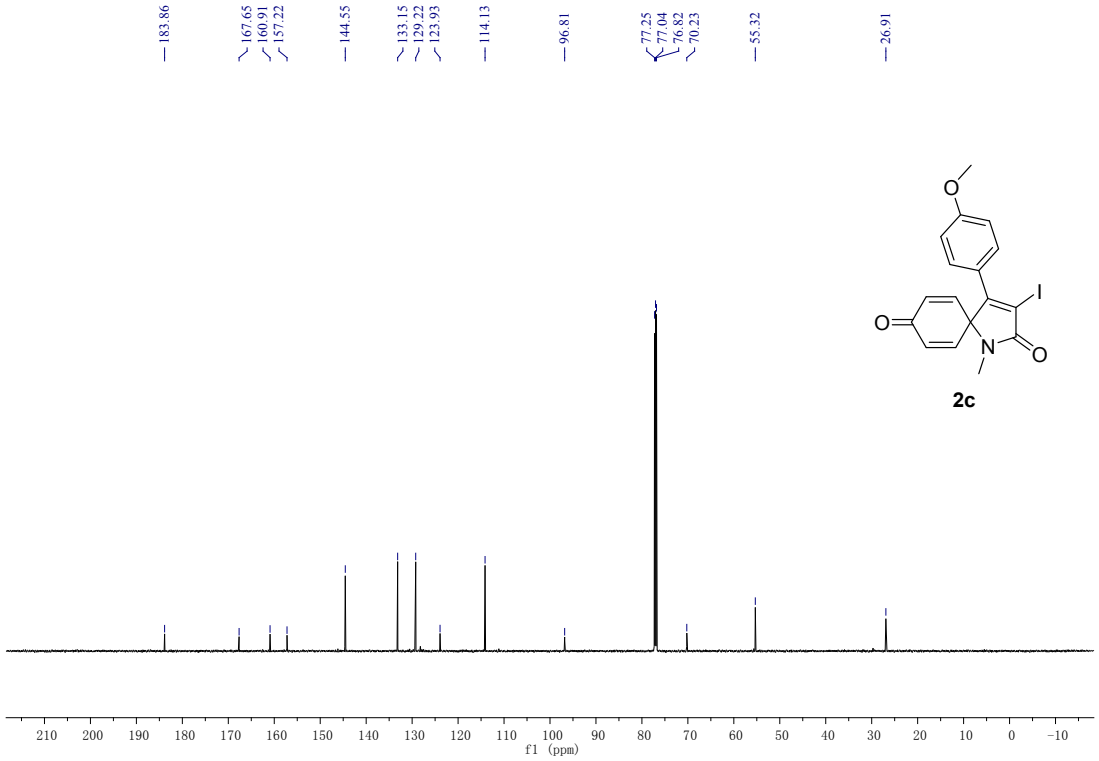


3-Iodo-1-methyl-4-(4-methoxyphenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2c)



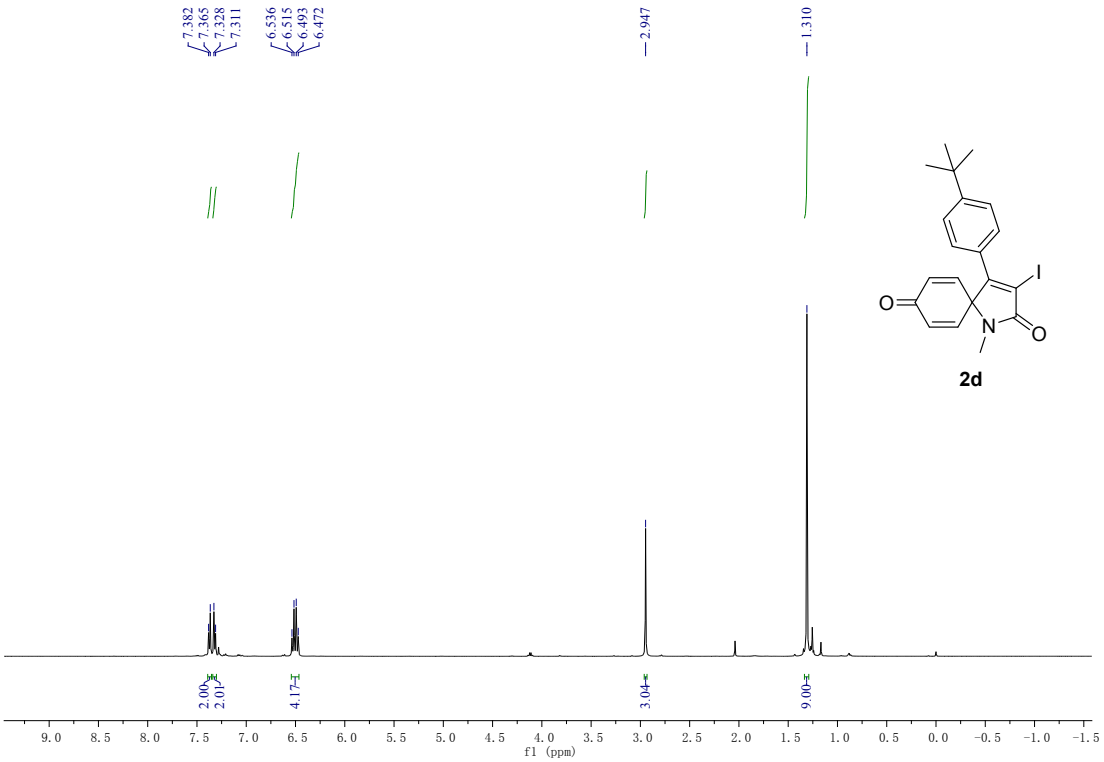
2c



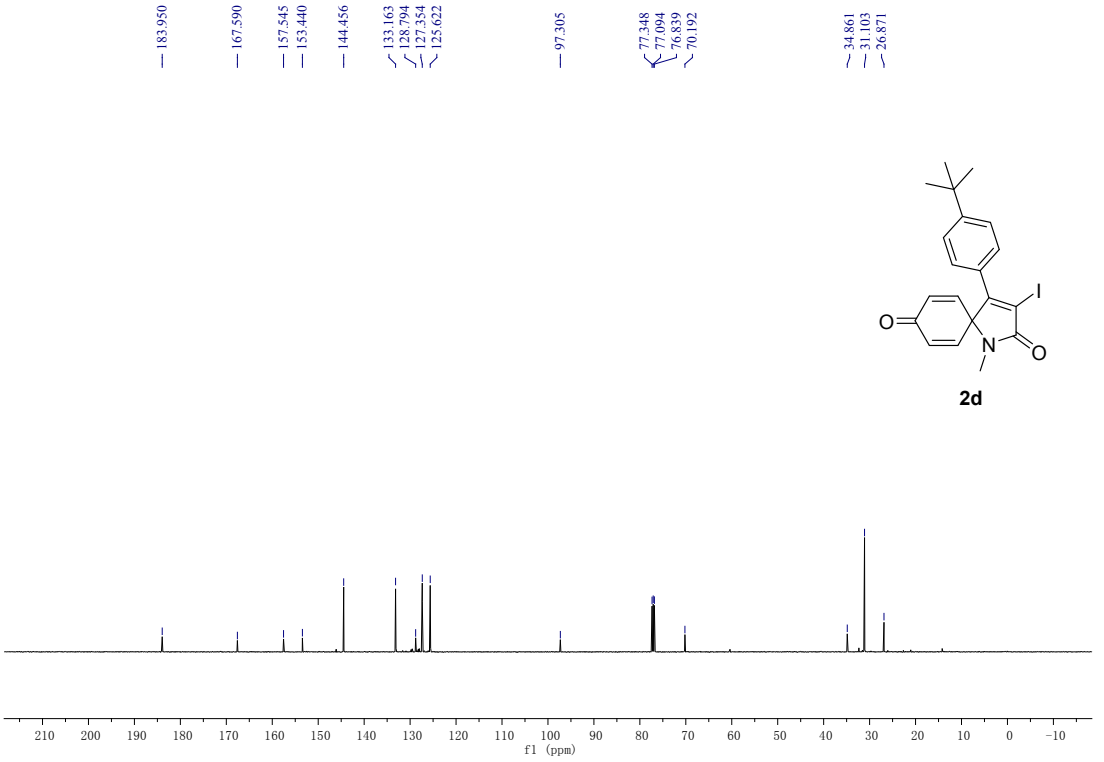


2c

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

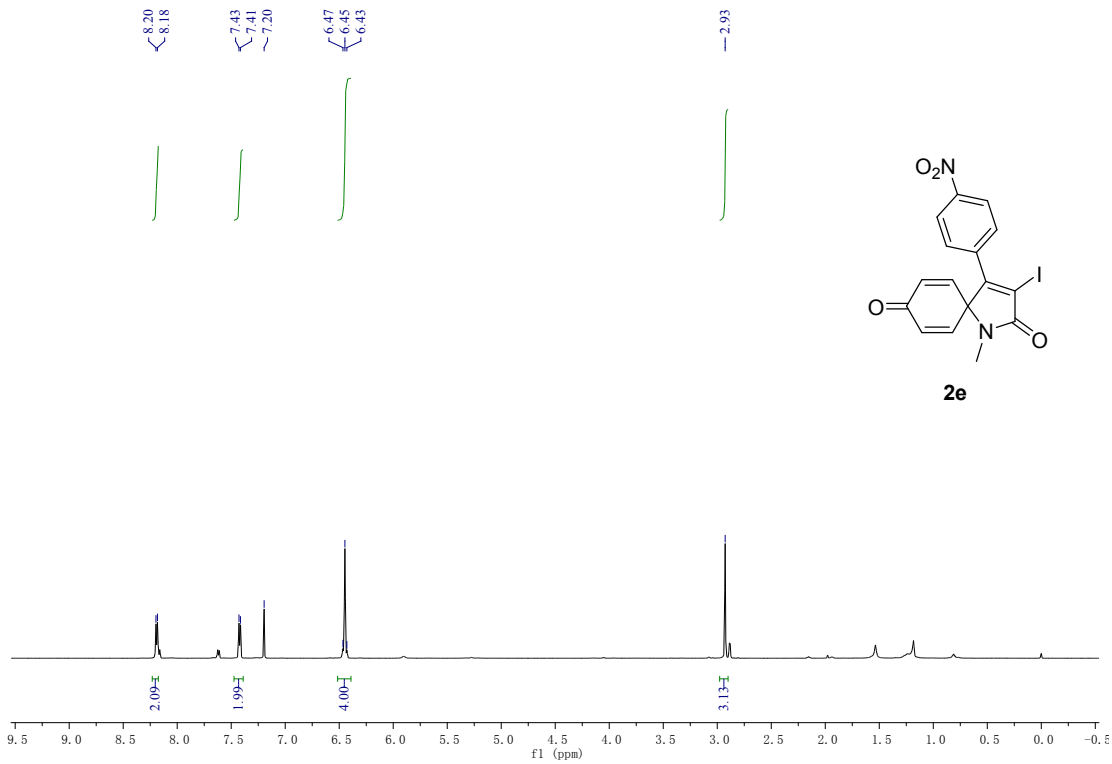


2d

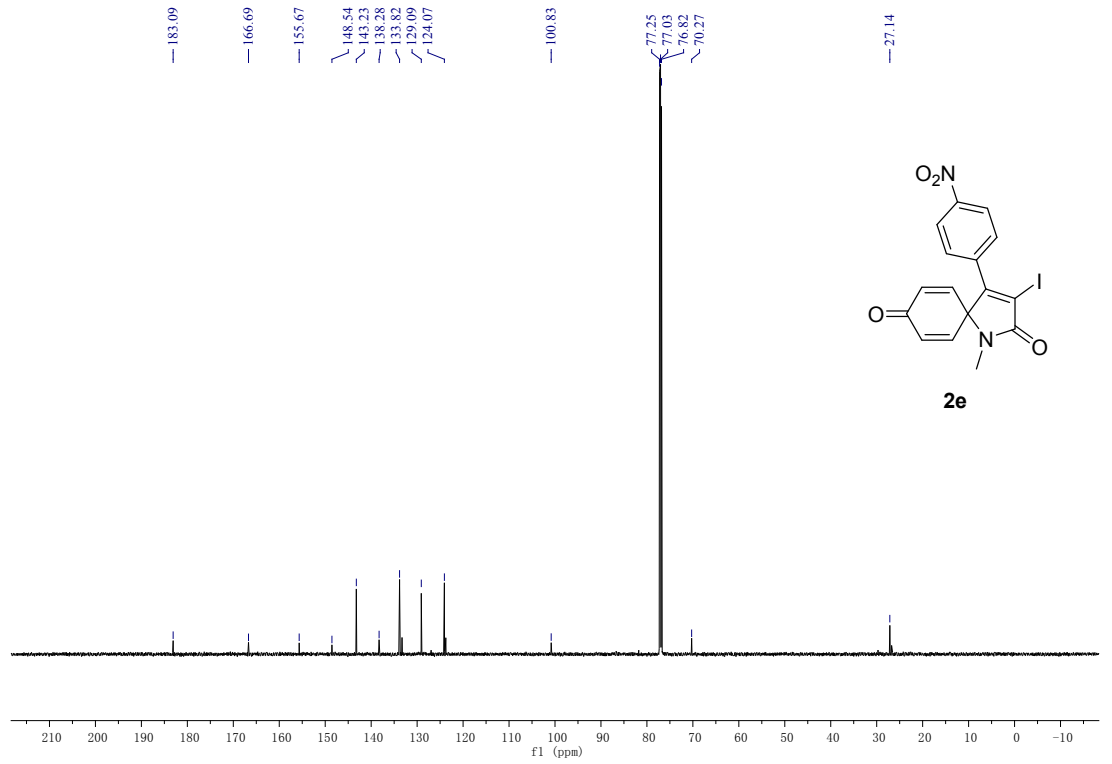


2d

3-Iodo-1-methyl-4-(4- *t*-Butyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2e)

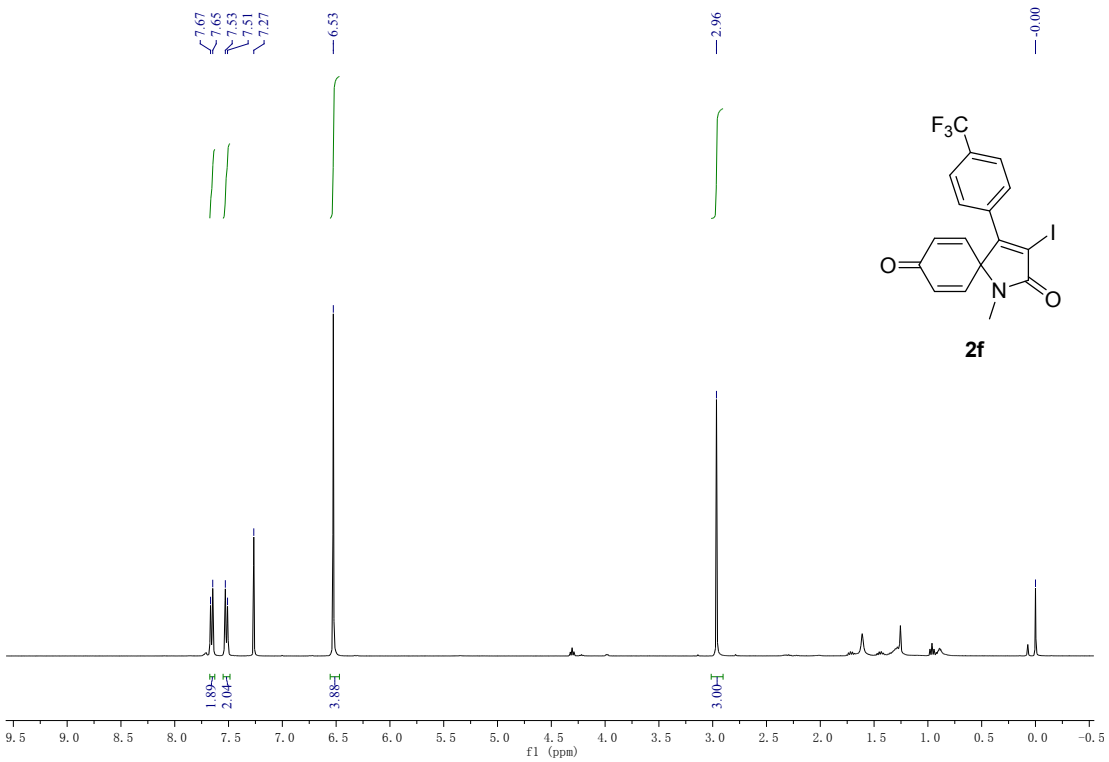


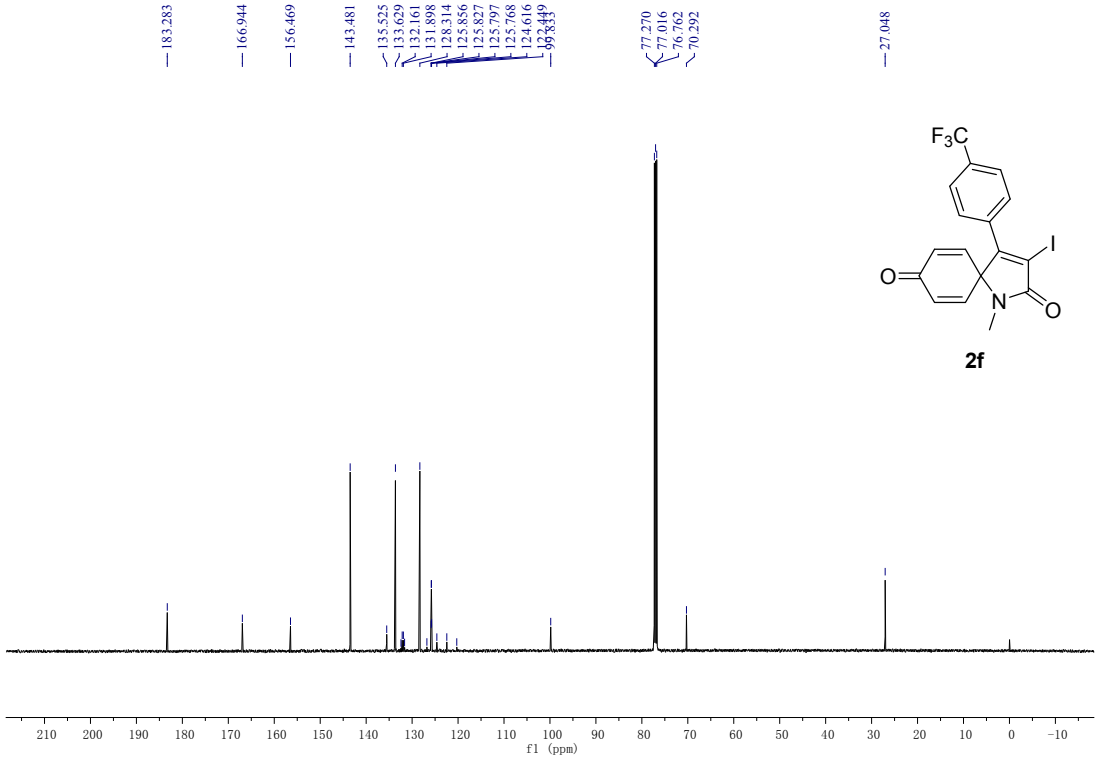
2e



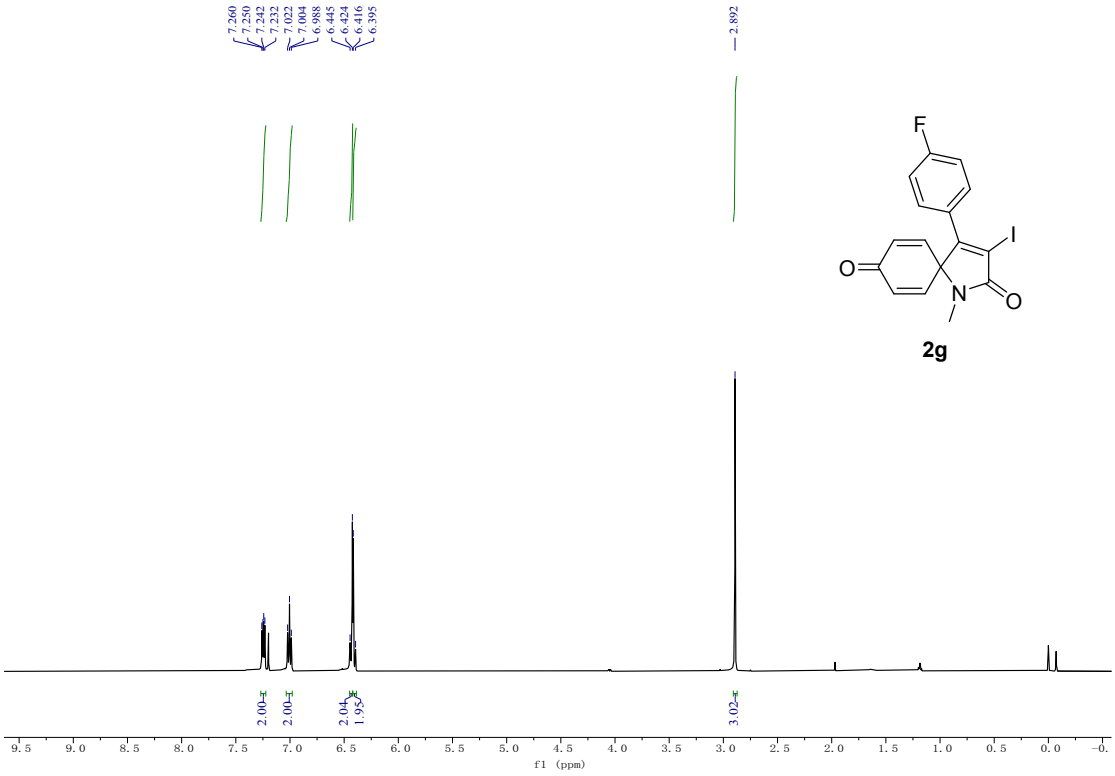
2e

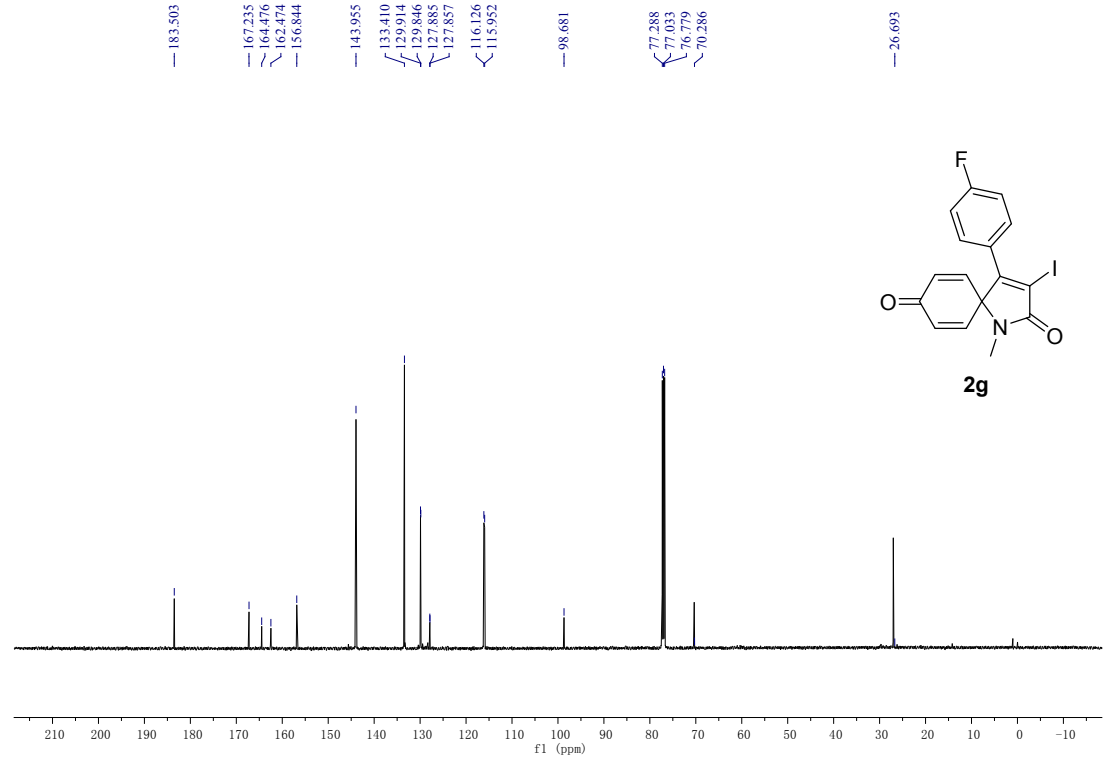
3-Iodo-1-methyl-4-(4-trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2f)



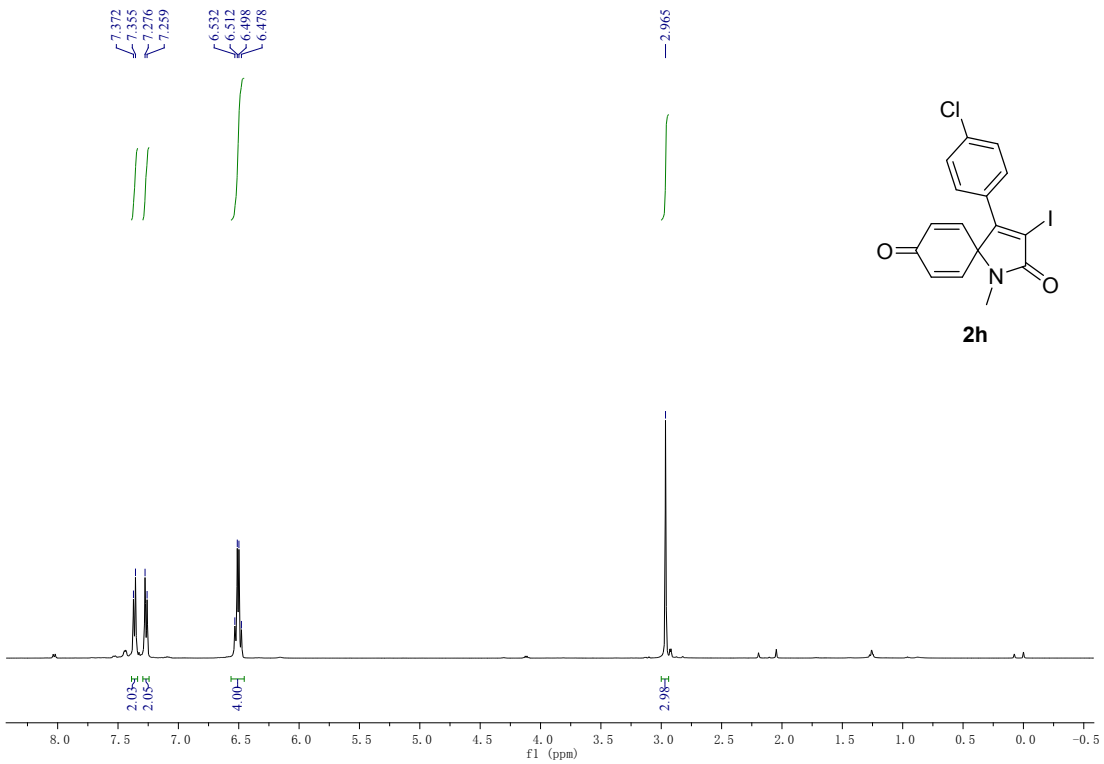


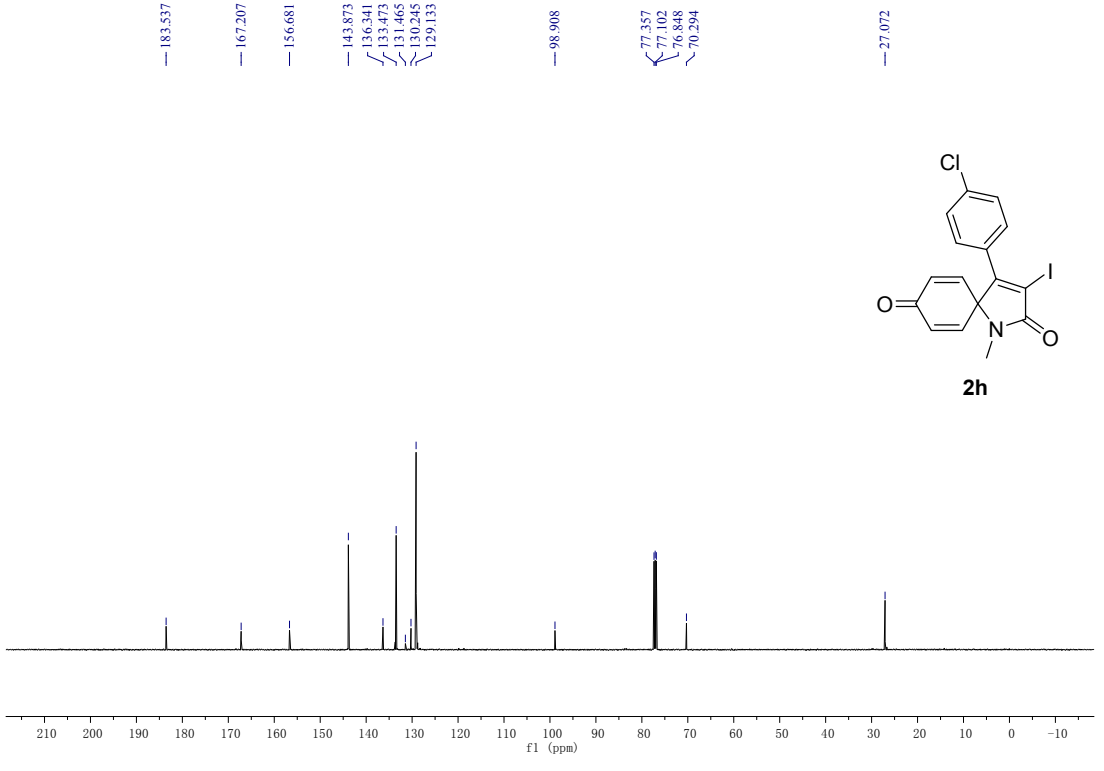
4-(4-Fluorophenyl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2g)



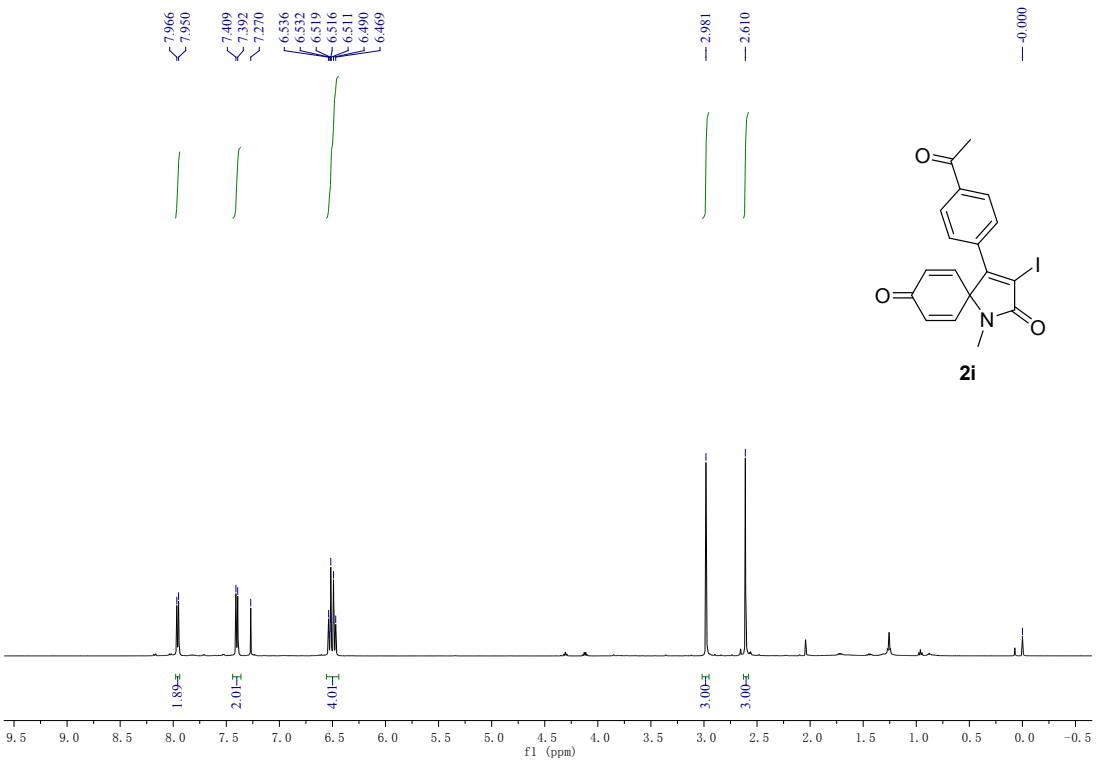


4-(4-Chlorophenyl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2h)

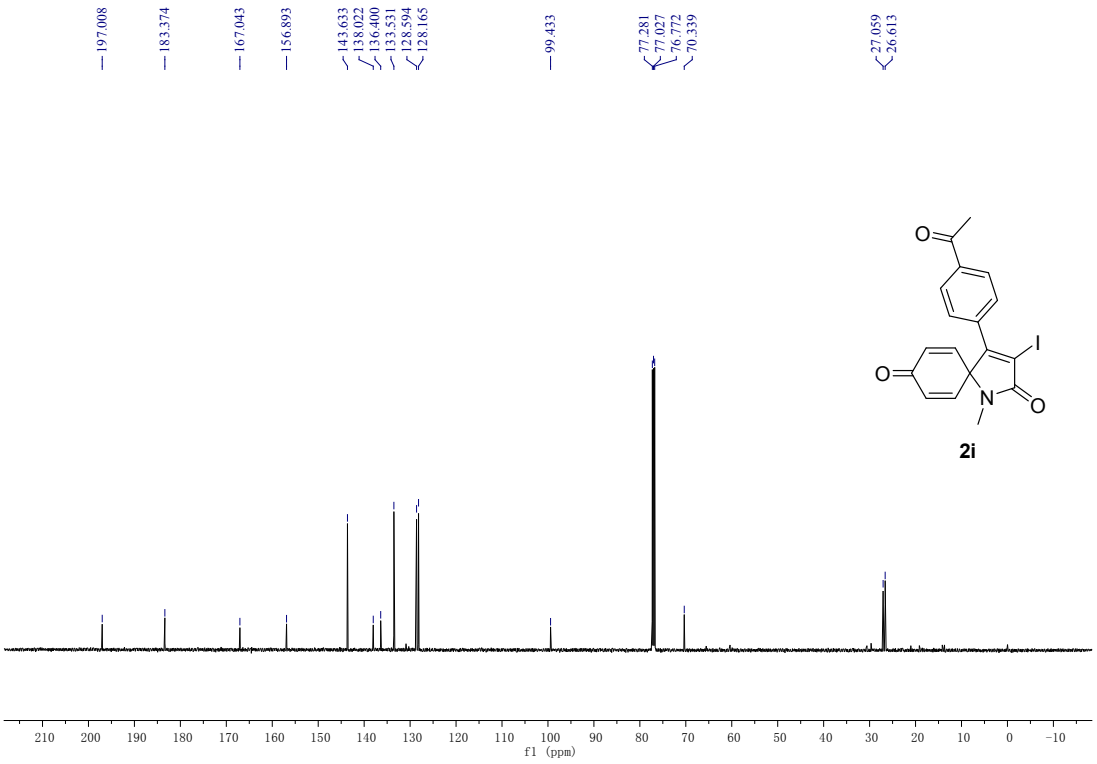




3-Iodo-1-methyl-4-(4-acetylphenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2i)

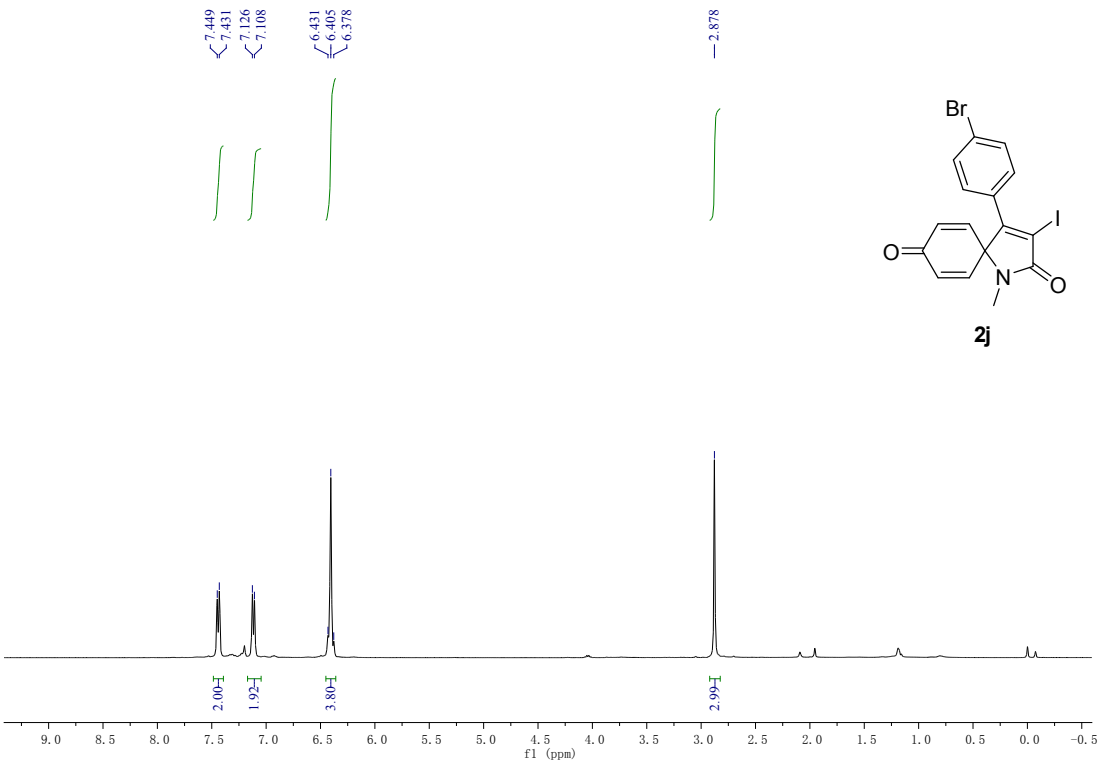


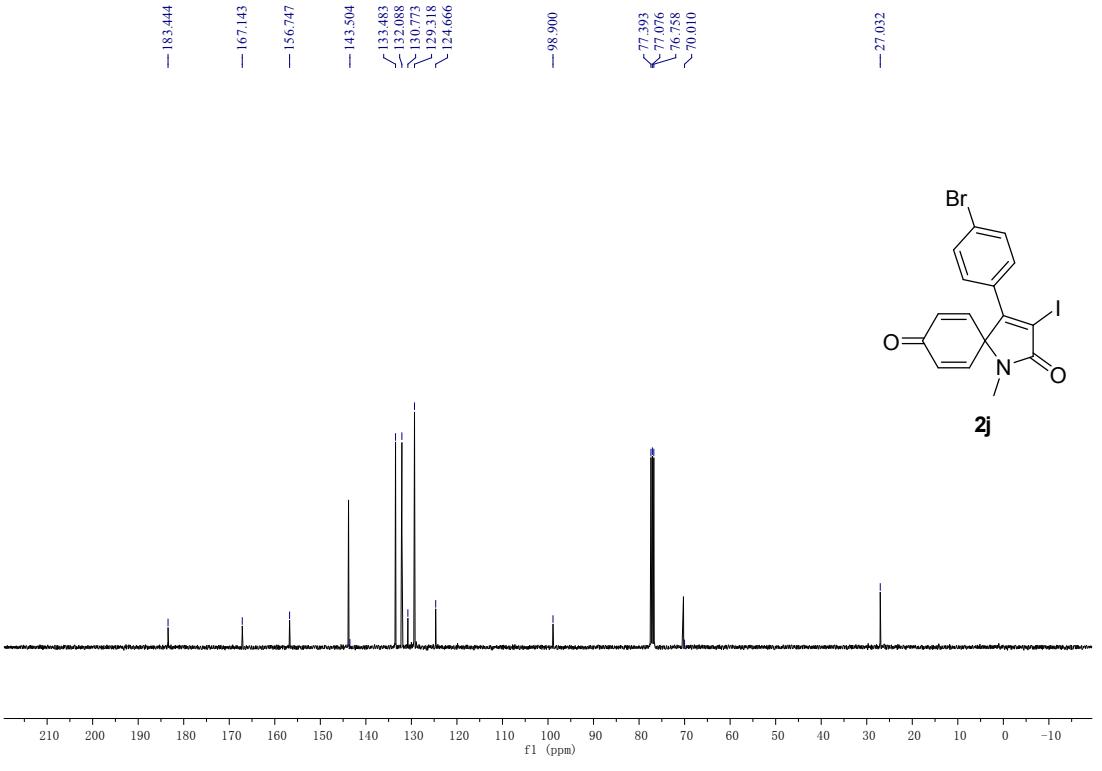
2i



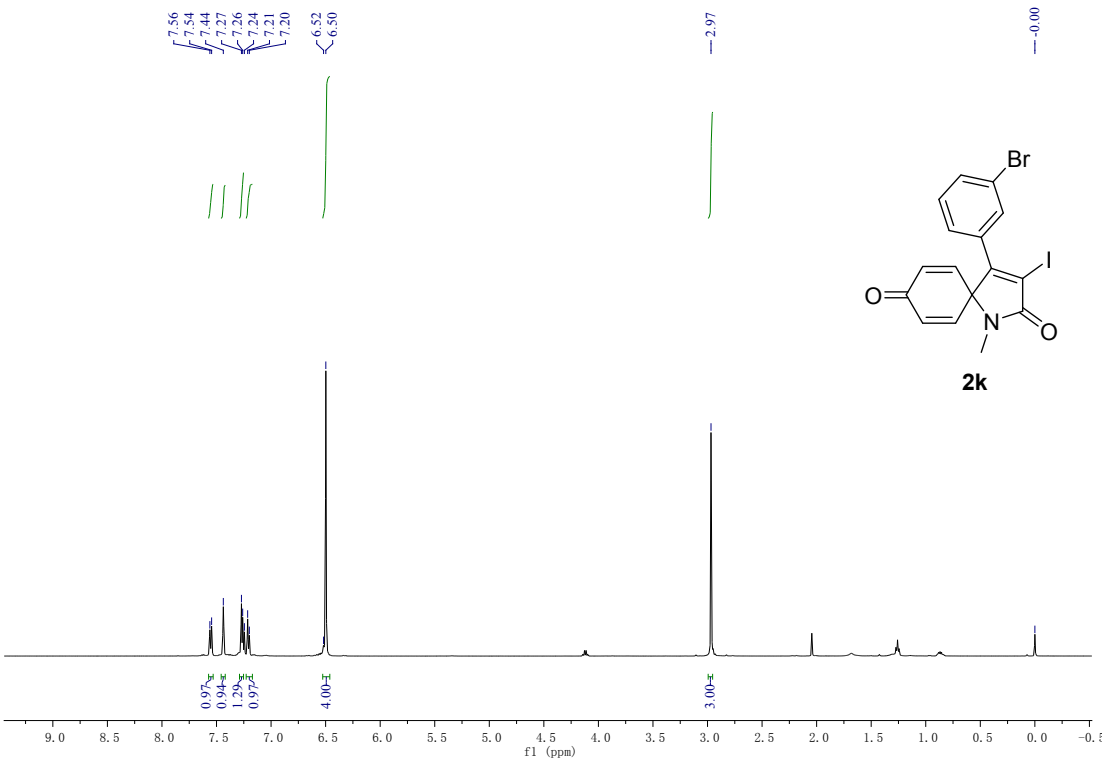
2i

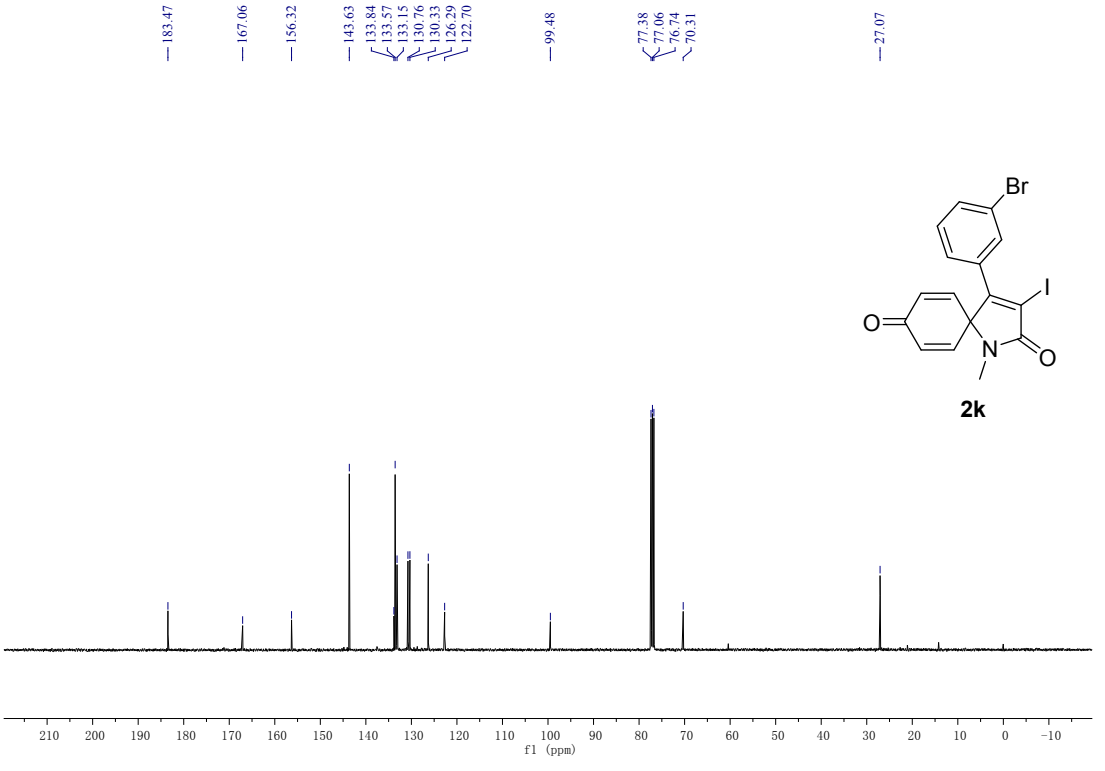
4-(4-Bromophenyl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2j)



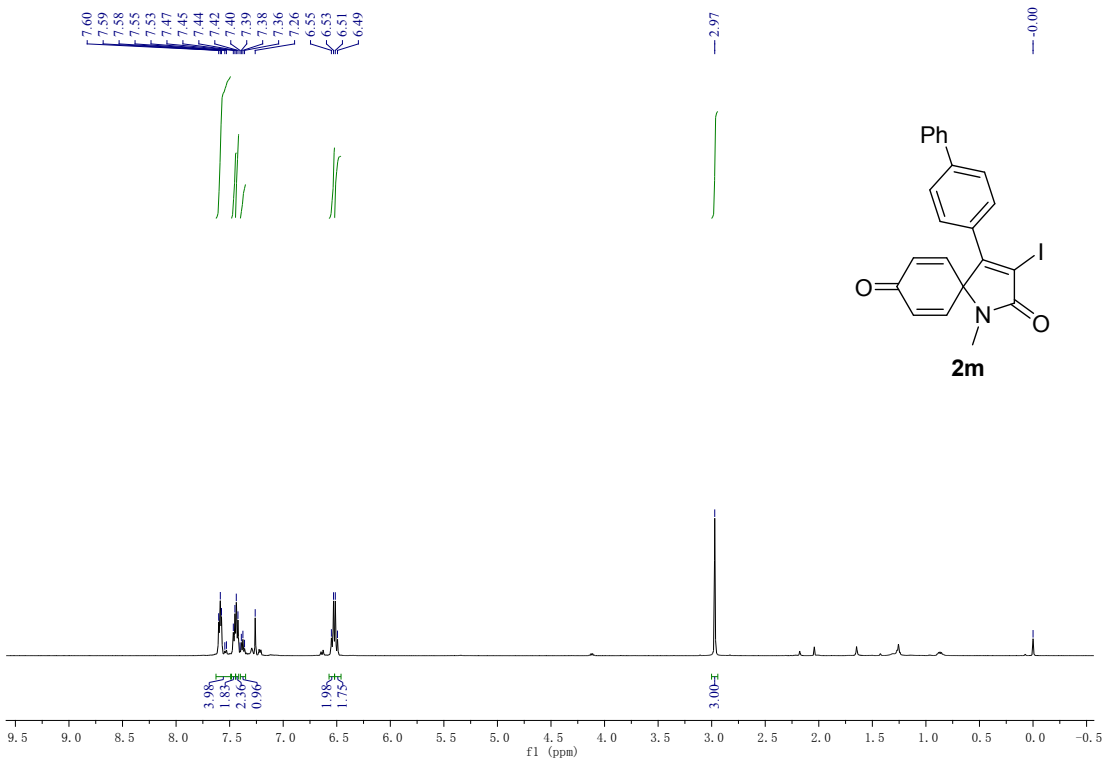


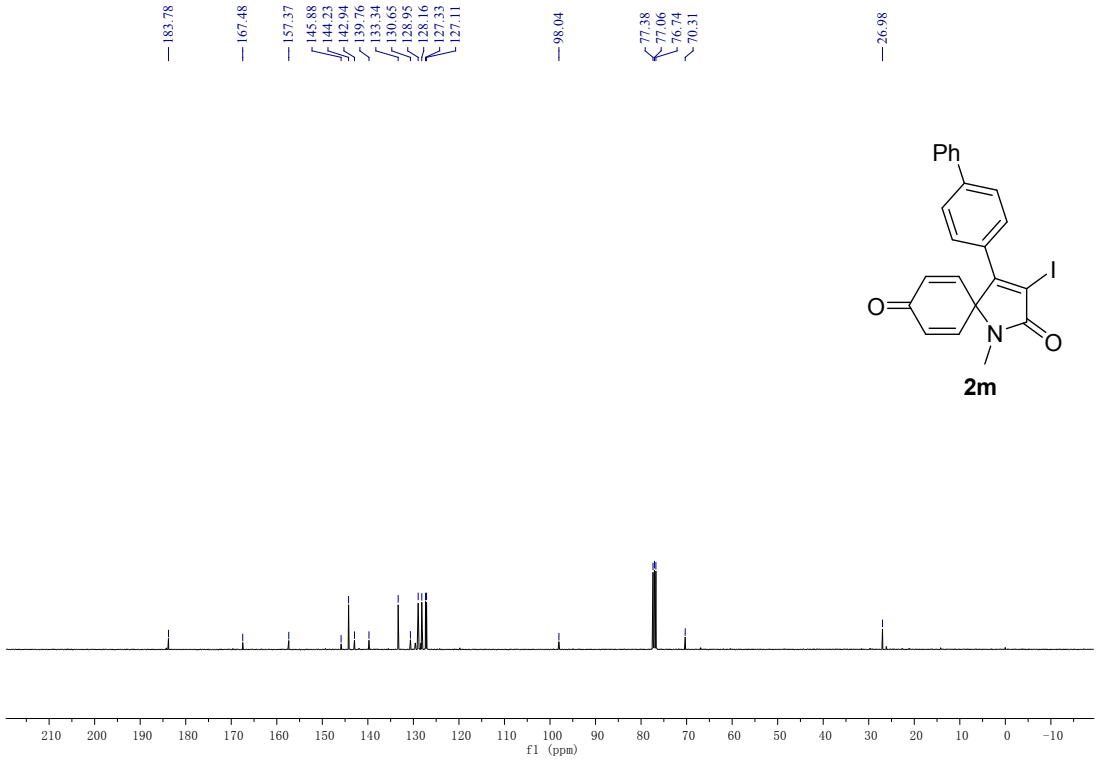
4-(3-Bromophenyl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2k)



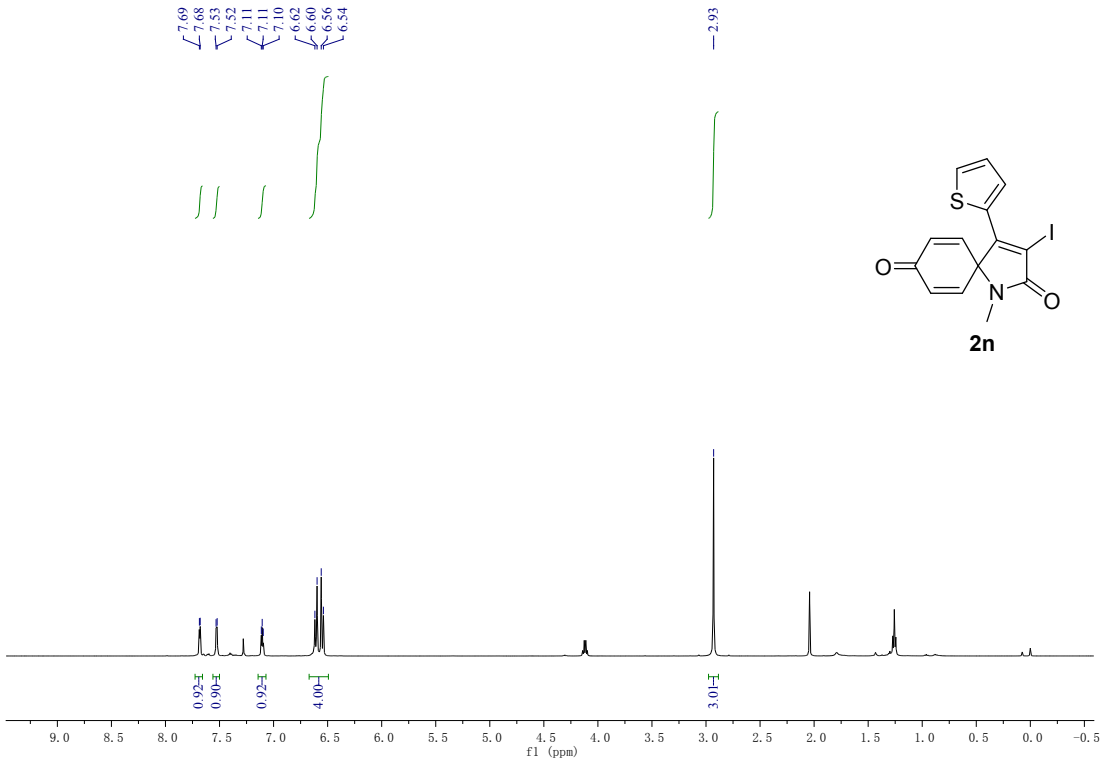


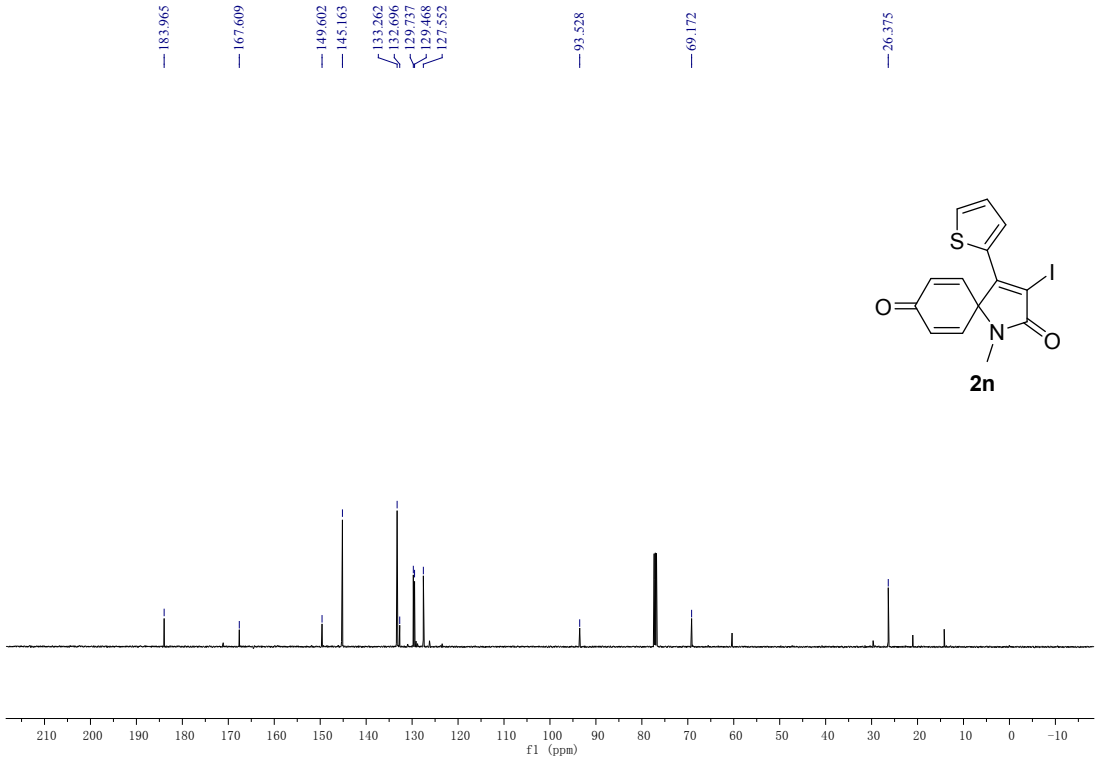
3-Iodo-1-methyl-4-([1,1'-biphenyl]-4-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2m)



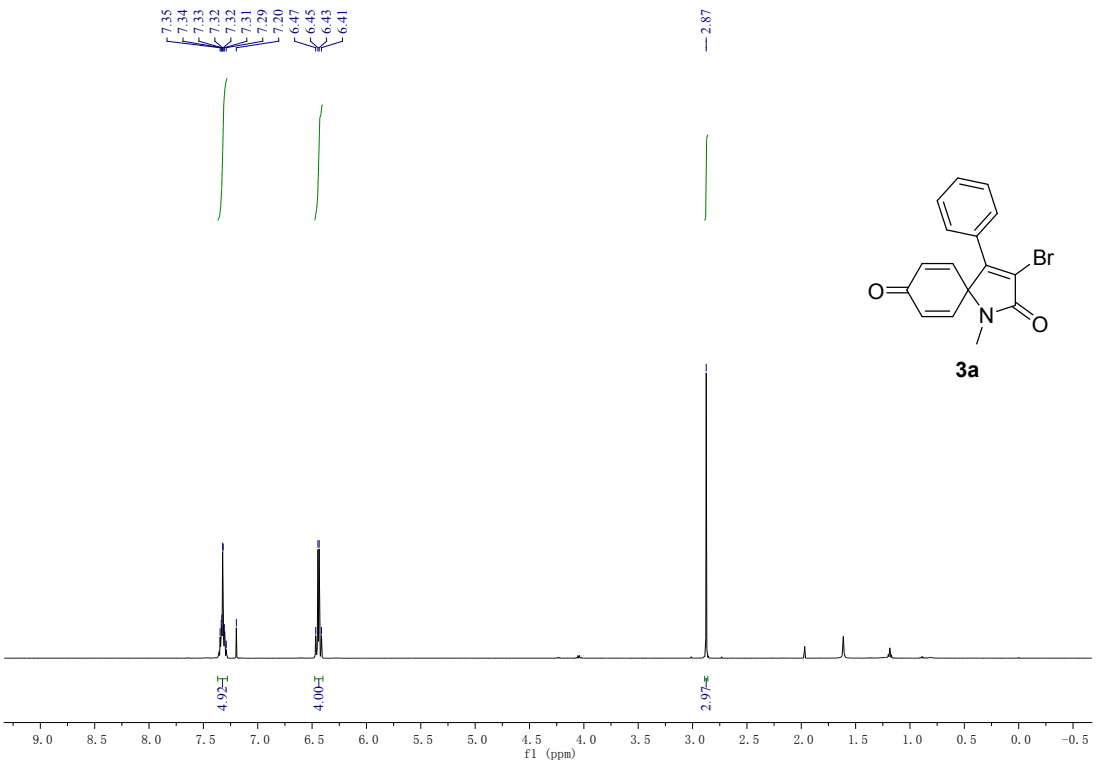


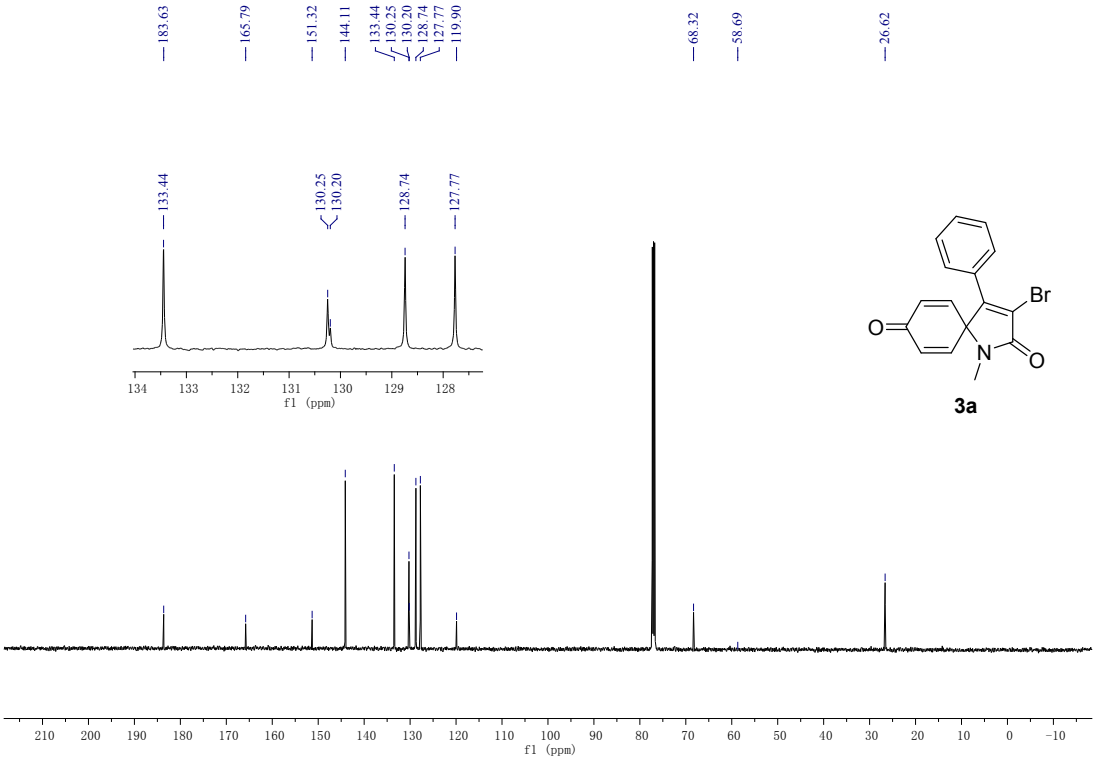
3-Iodo-1-methyl -4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (2n)



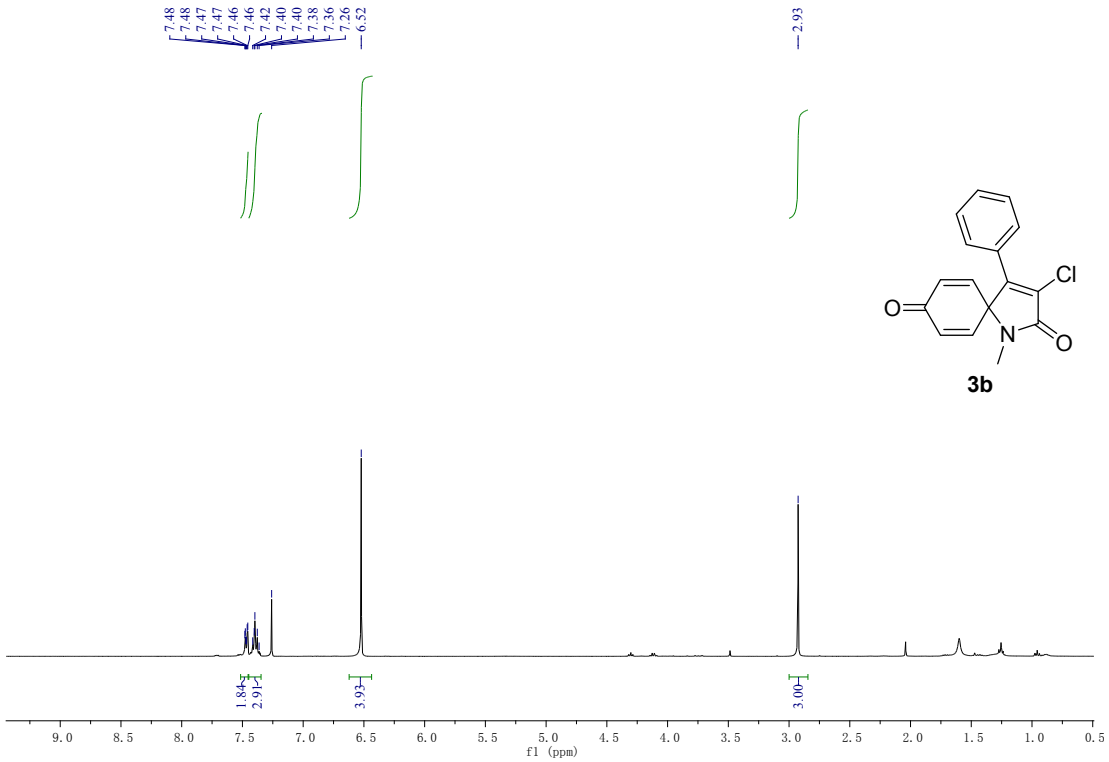


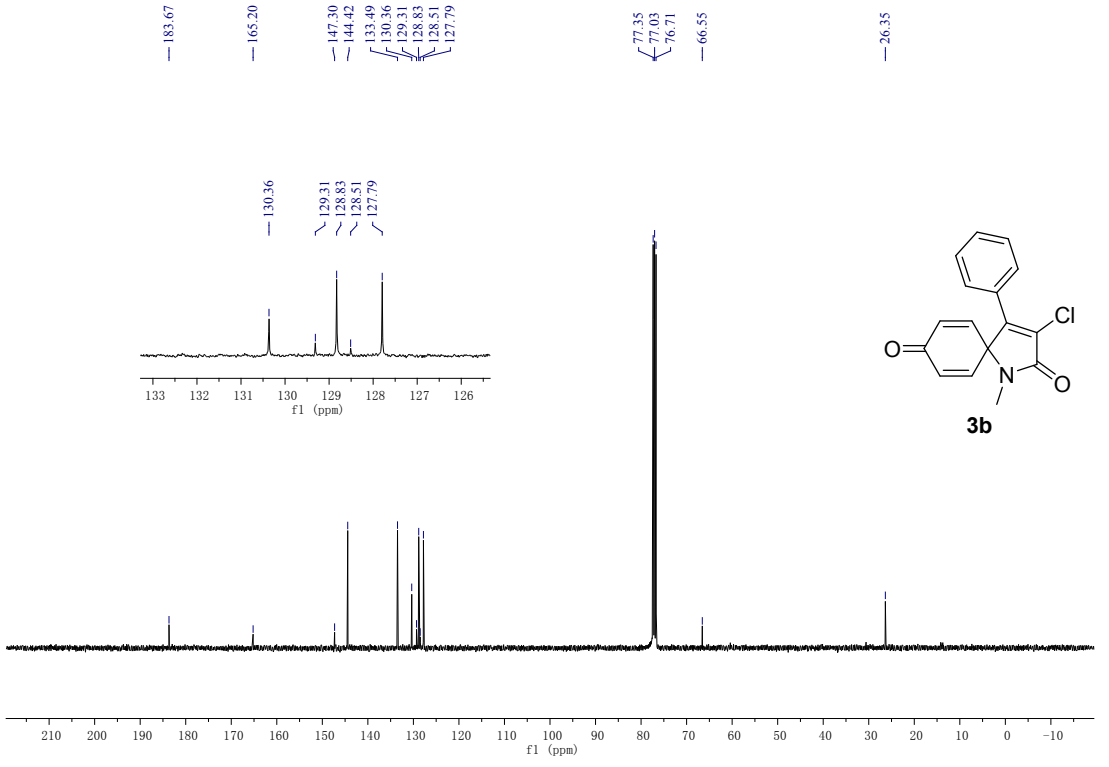
3-Bromo-1-methyl-4-phenyl-1-azaspiro[4.5] deca-3,6,9-triene-2,8-dione (3a)



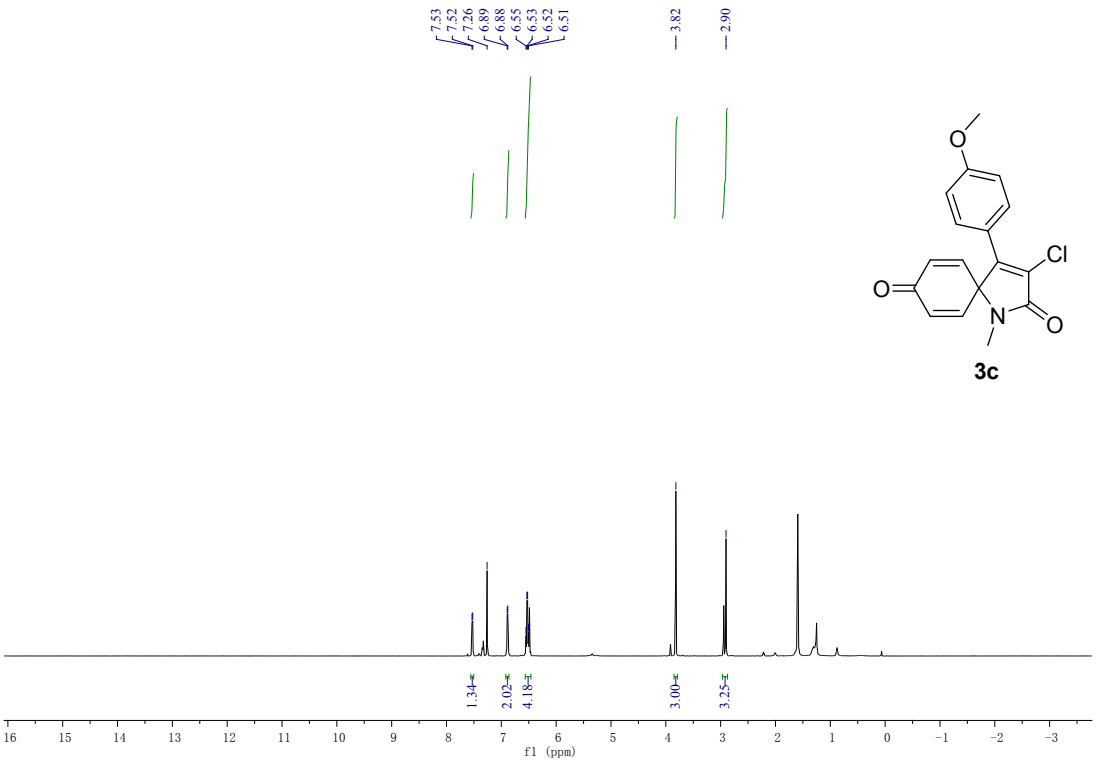


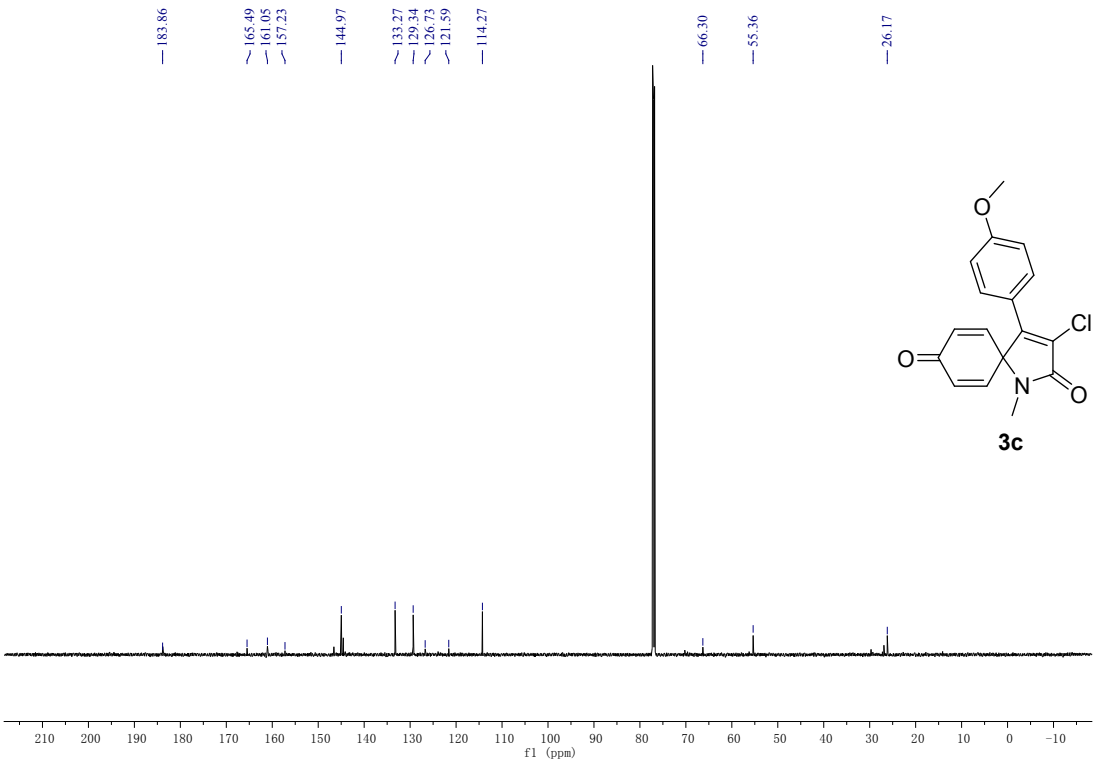
3-Chloro-1-methyl-4-phenyl-1-azaspiro[4.5] deca-3,6,9-triene-2,8-dione (3b)



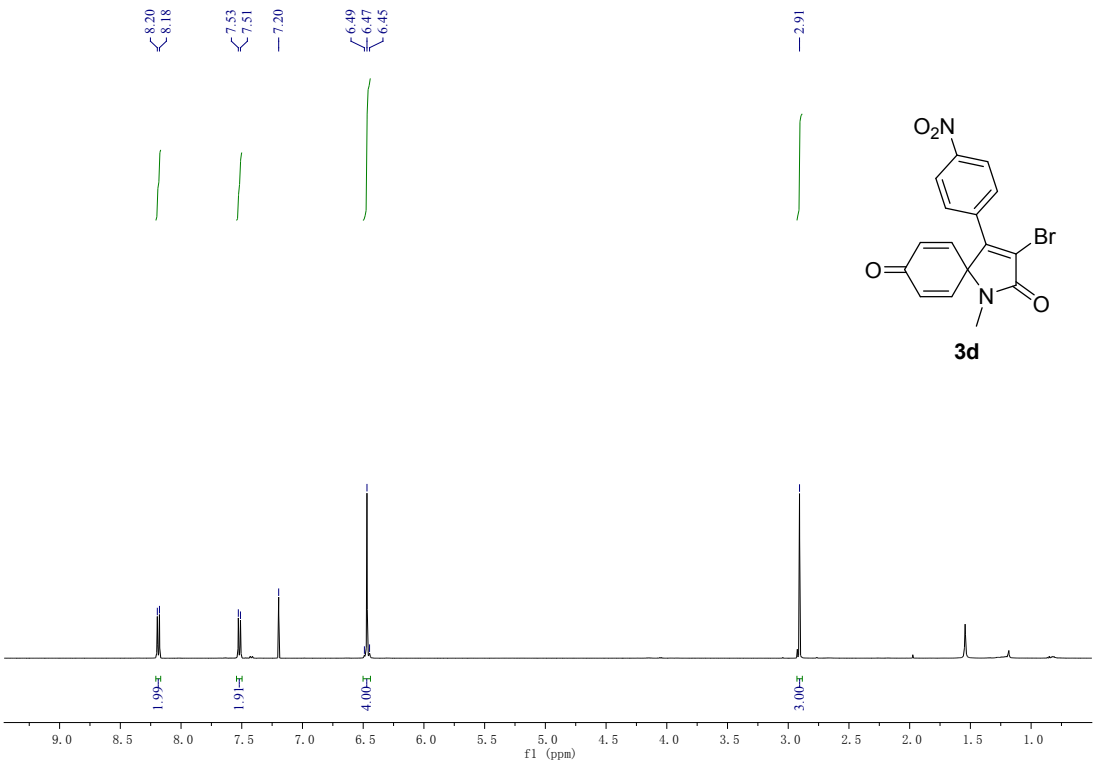


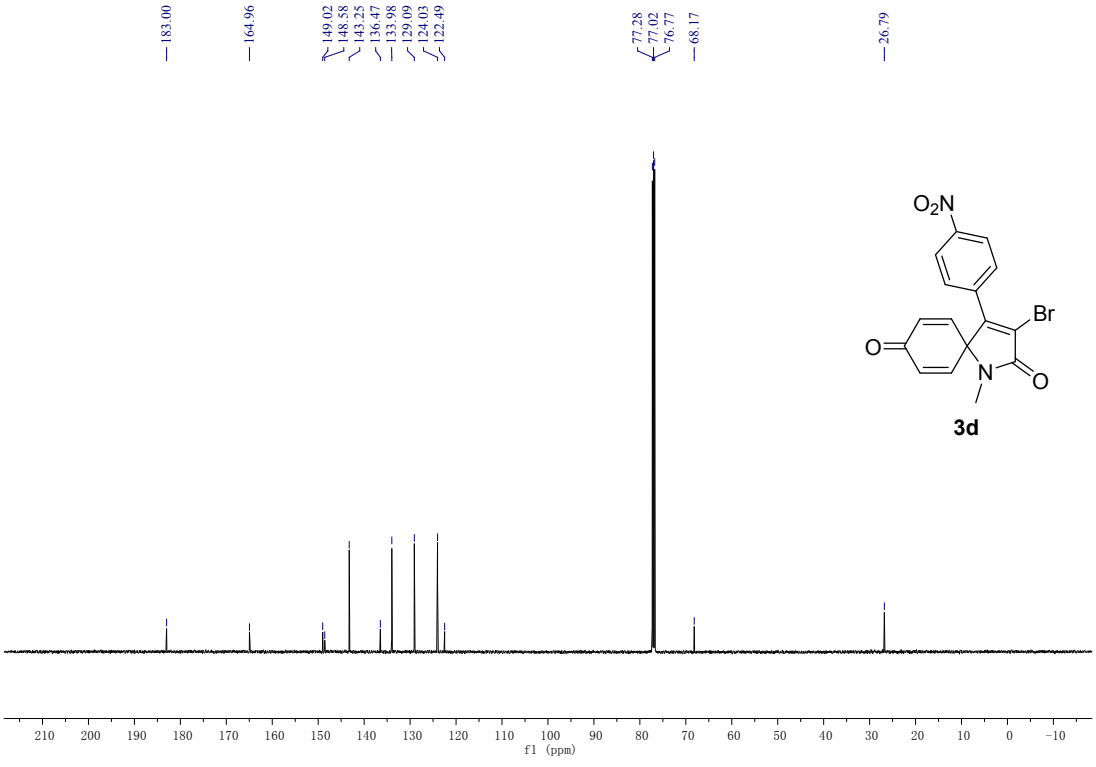
3-Chloro-1-methyl-4-(4-methoxyphenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3c)



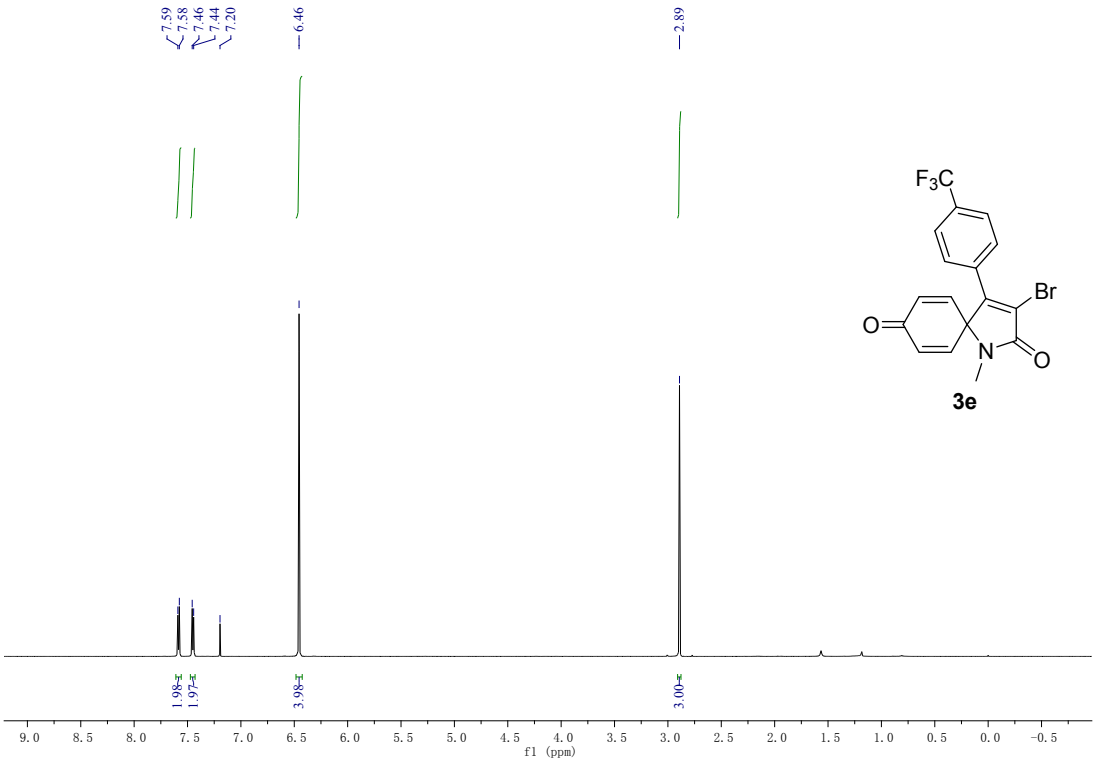


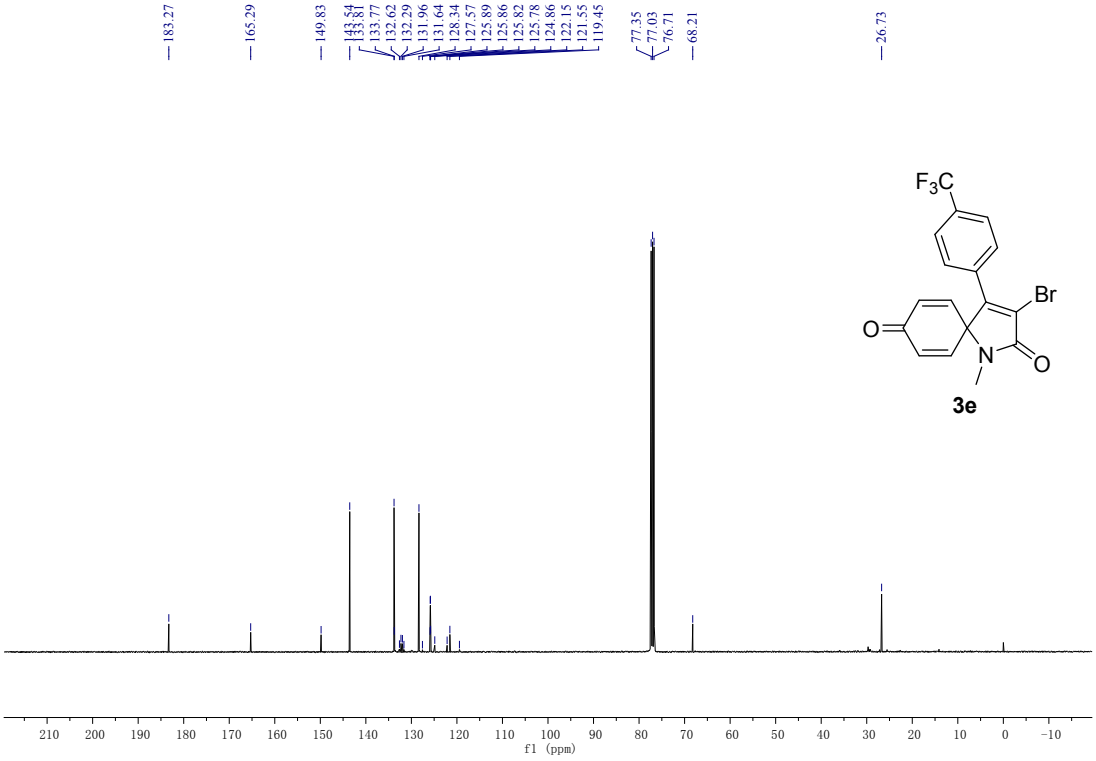
3-Brom-1-methyl-4-(4-nitrophenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3d)



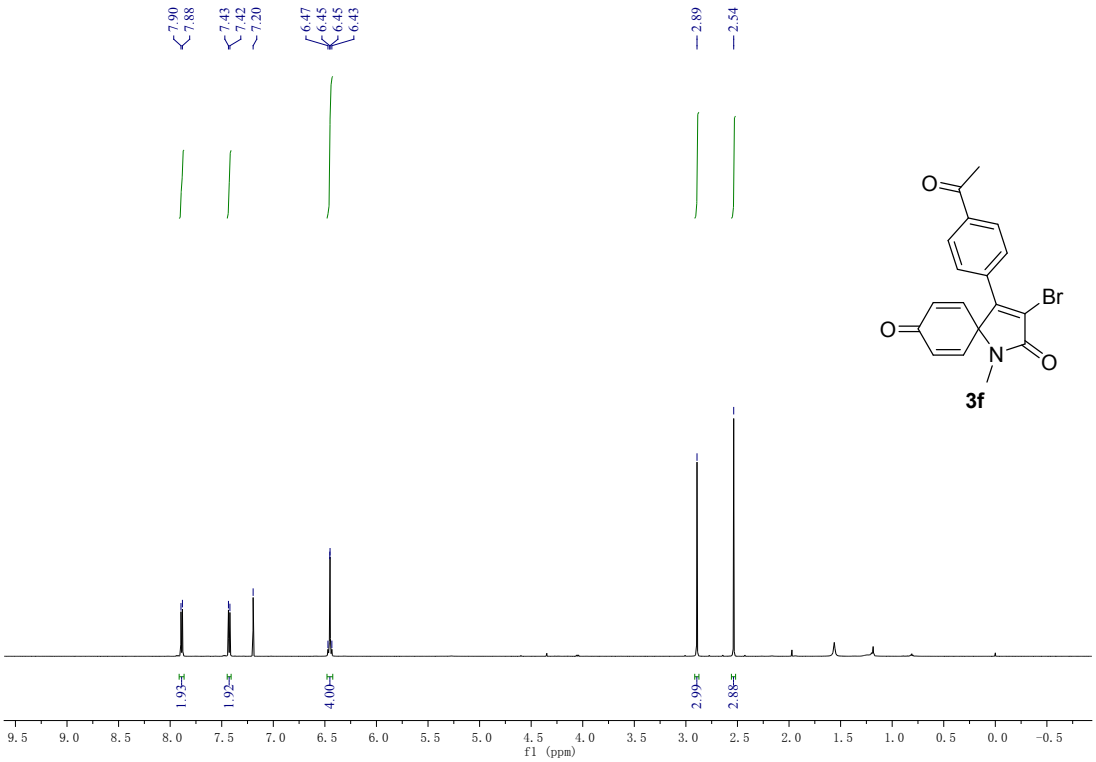


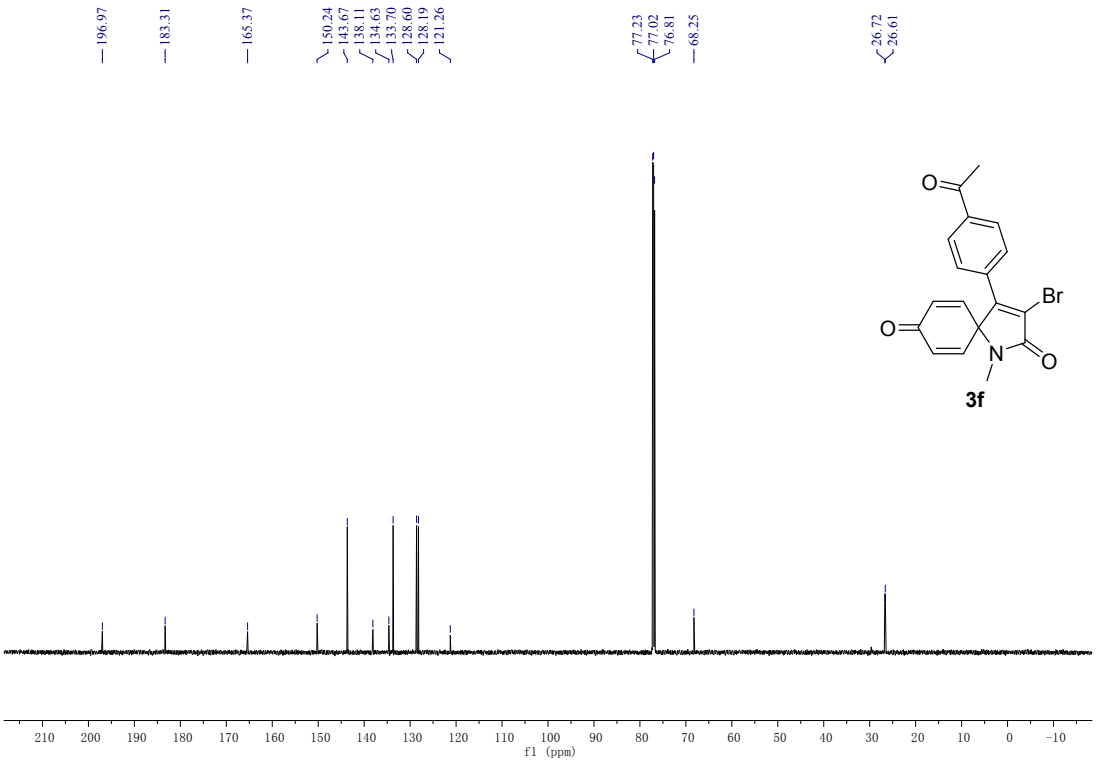
3-Brom-1-methyl-4-(4-trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione(3e)



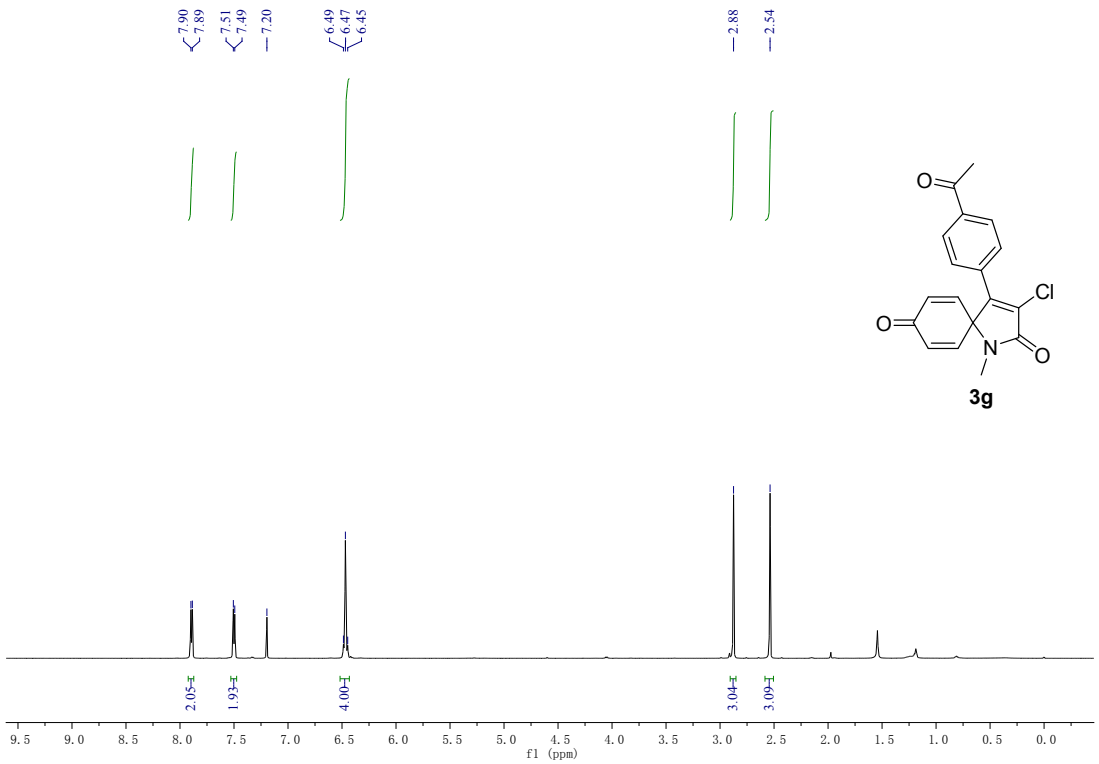


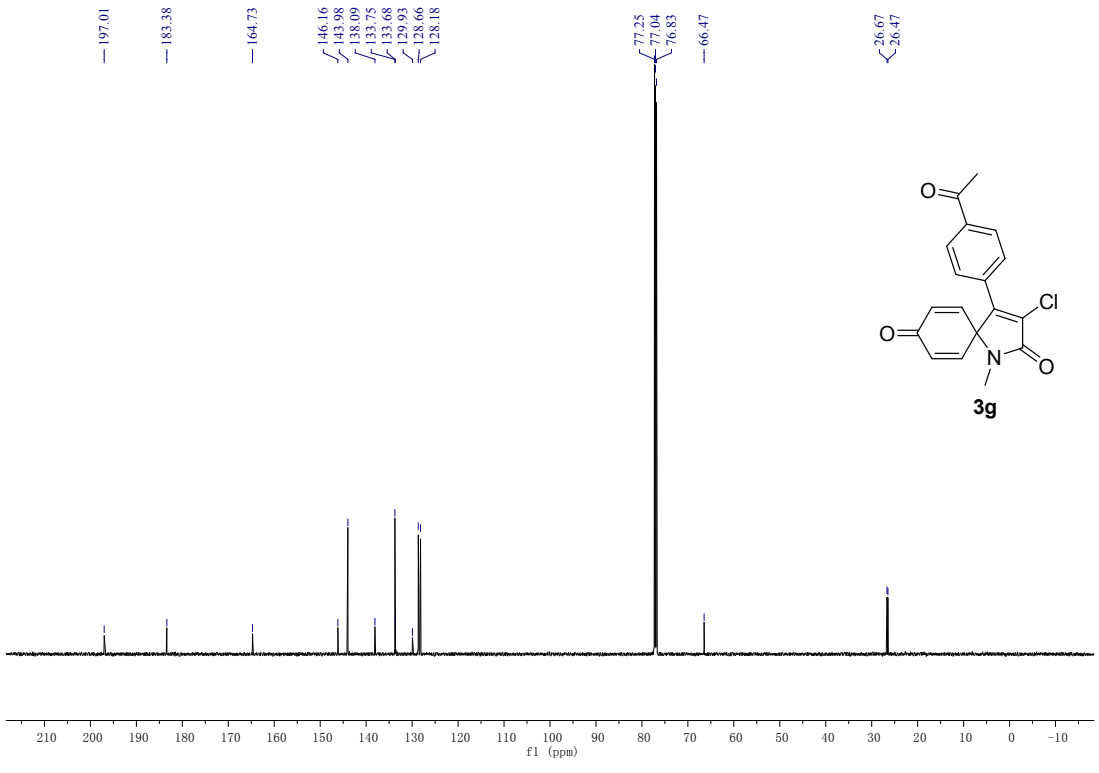
3-Brom-1-methyl-4-(4-acetylphenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3f)



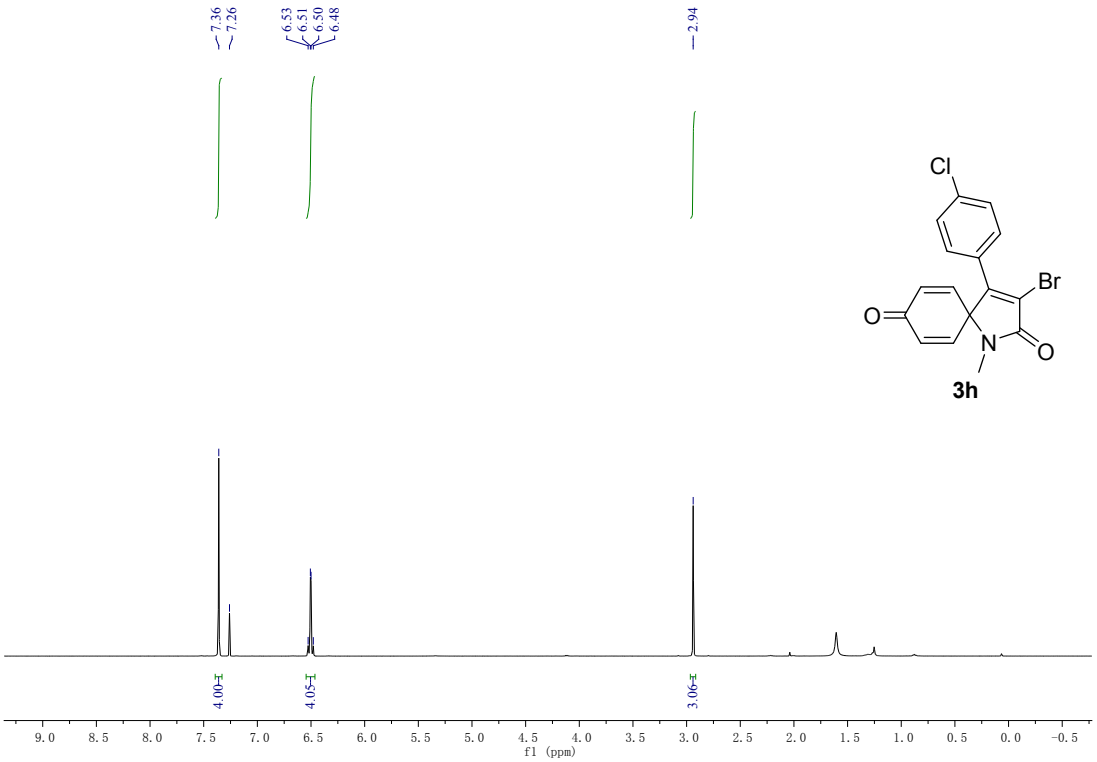


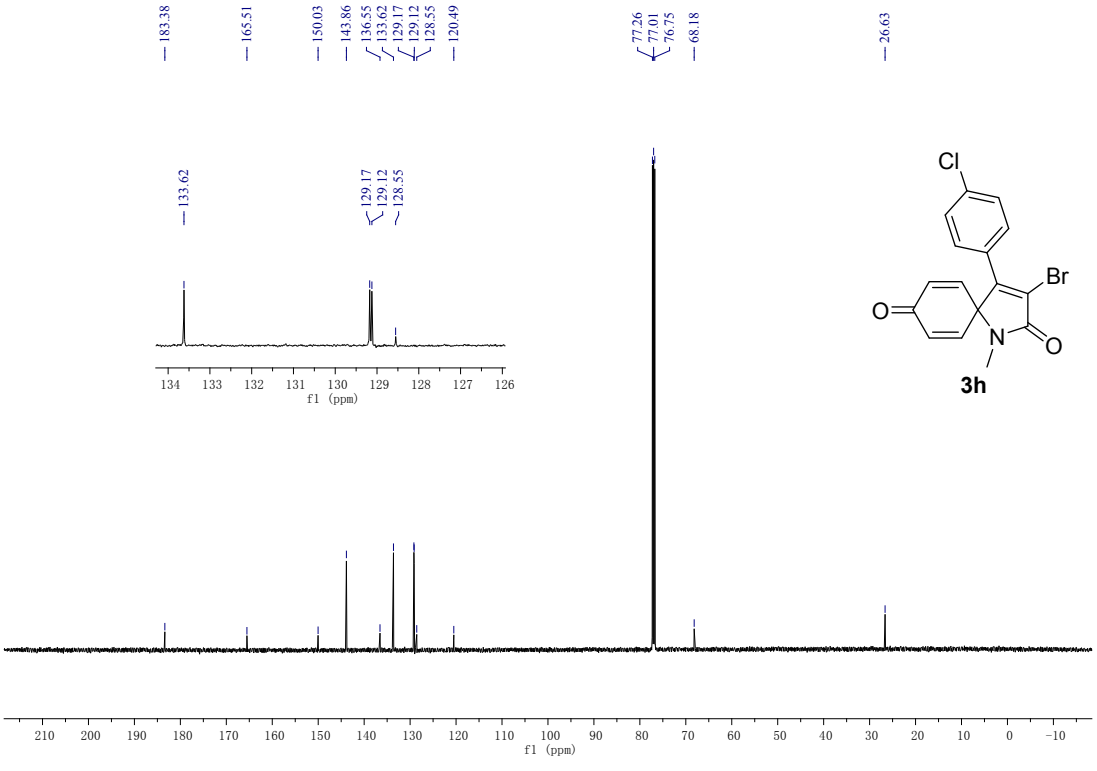
3-Chloro-1-methyl-4-(4-acetylphenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3g)



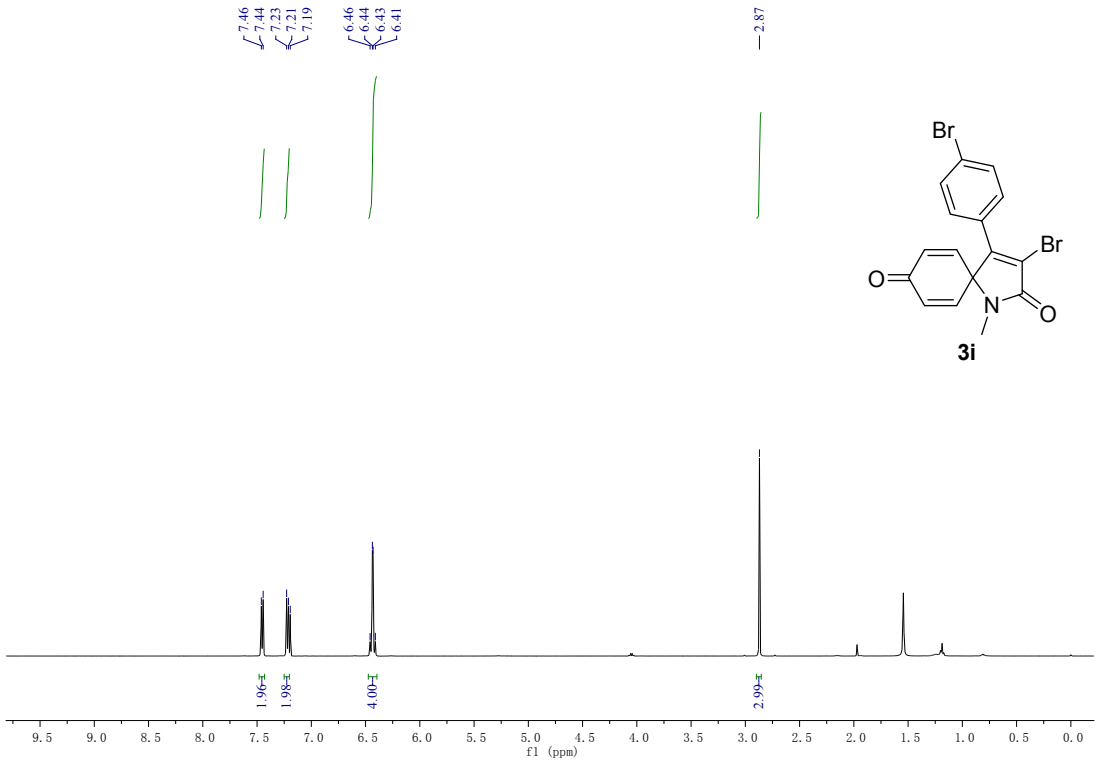


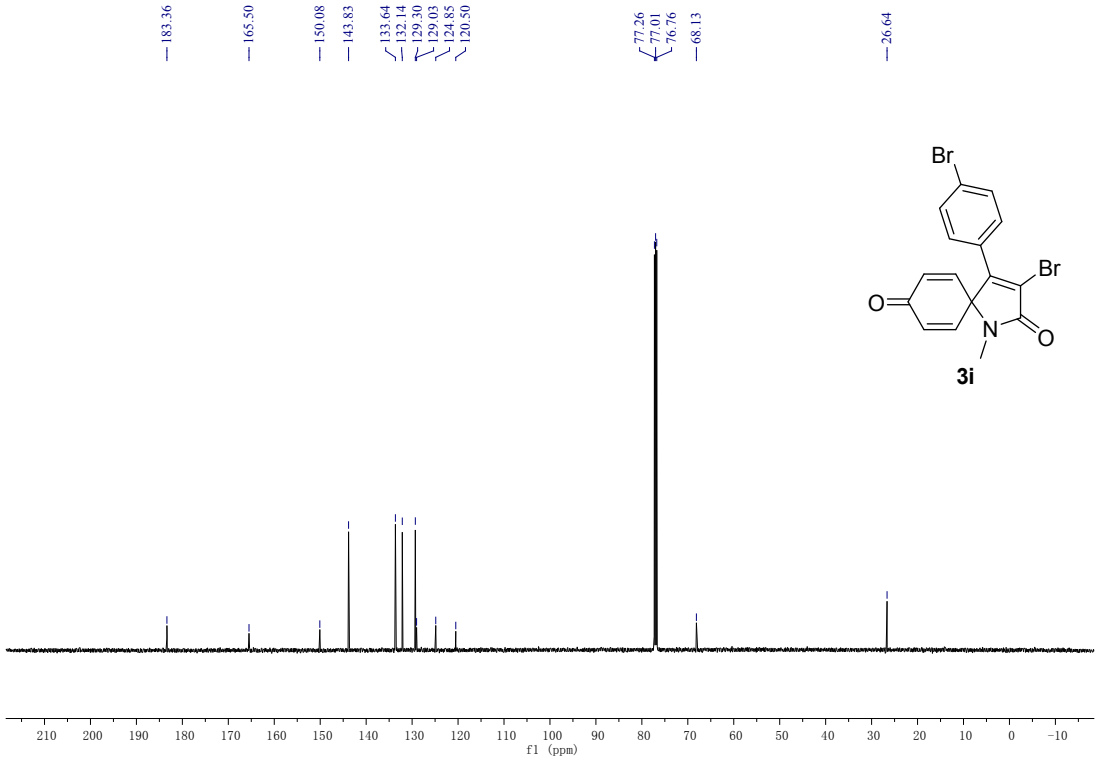
4-(4-Chlorophenyl)-3-bromo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3h)



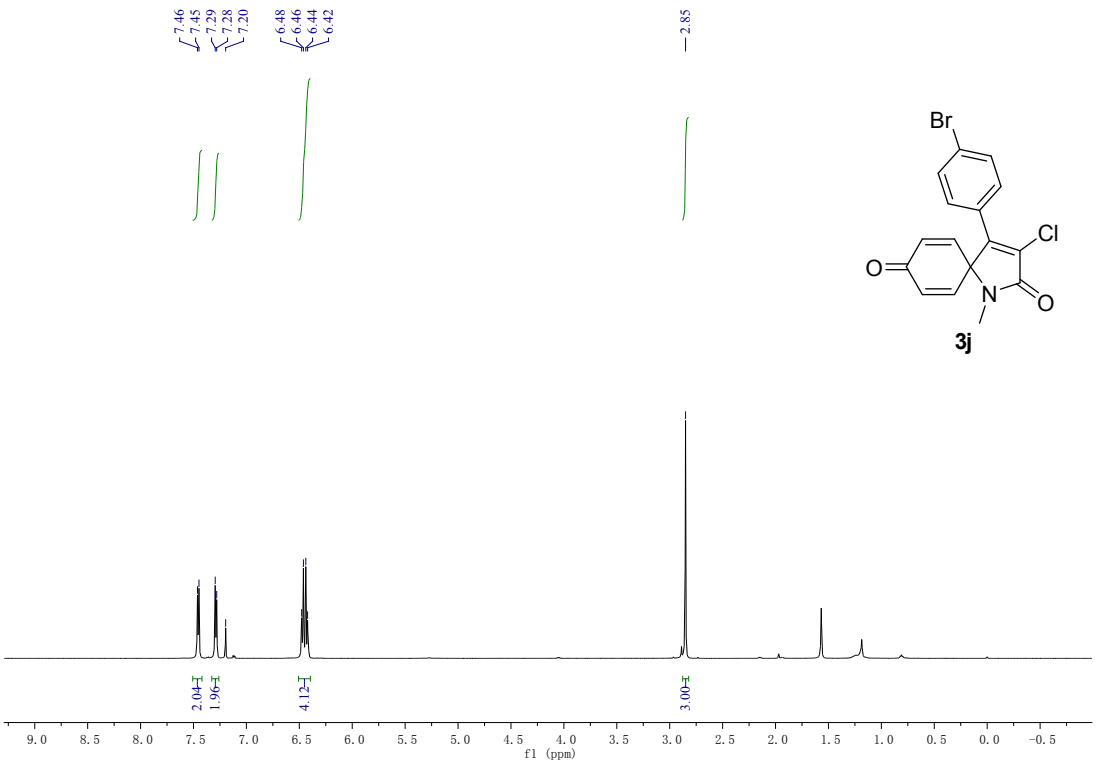


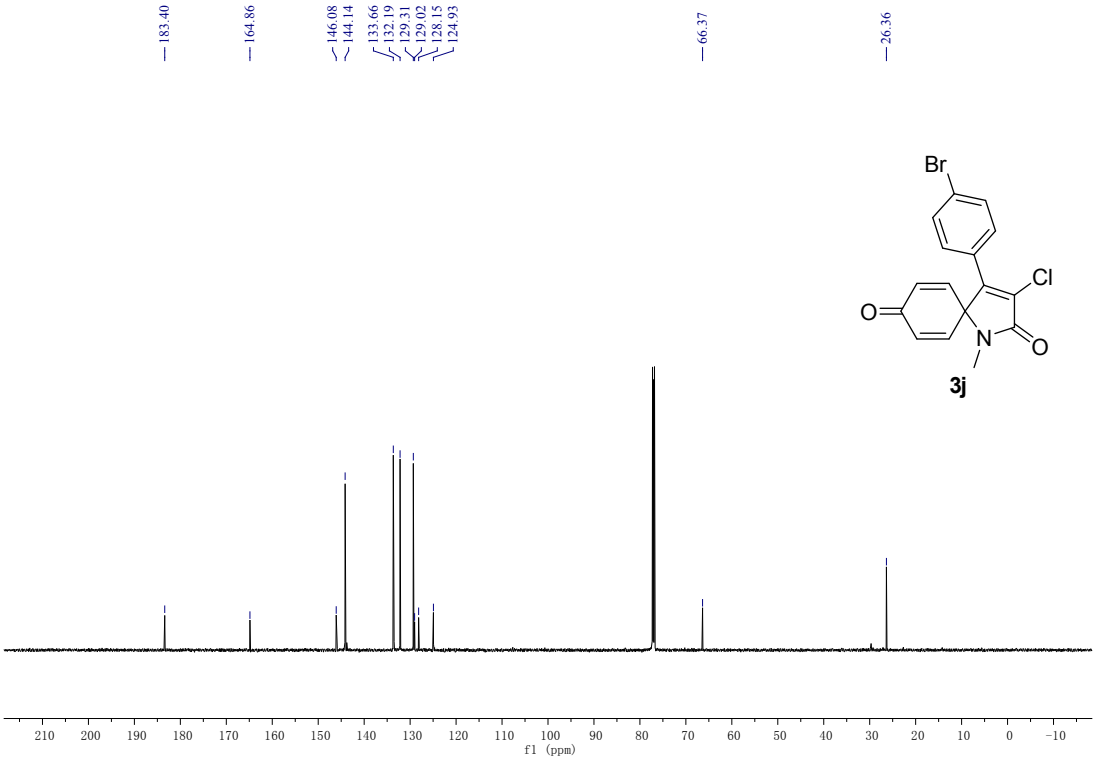
4-(4-bromophenyl)-3- bromo -1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3i)



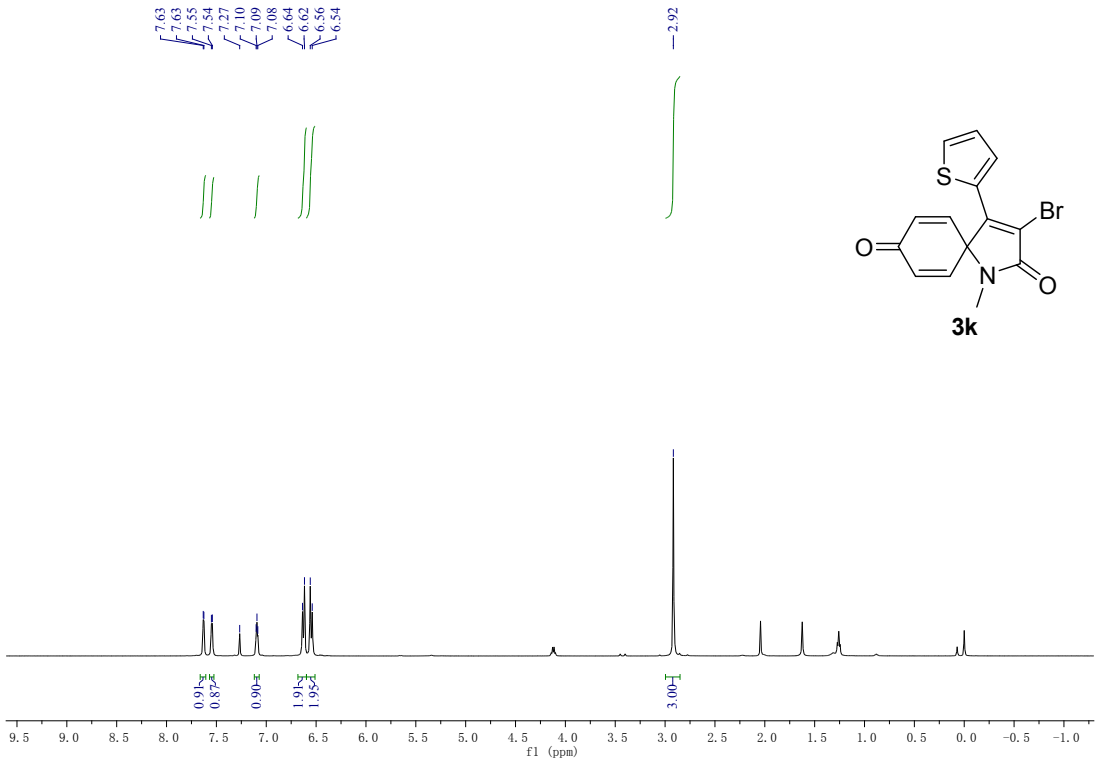


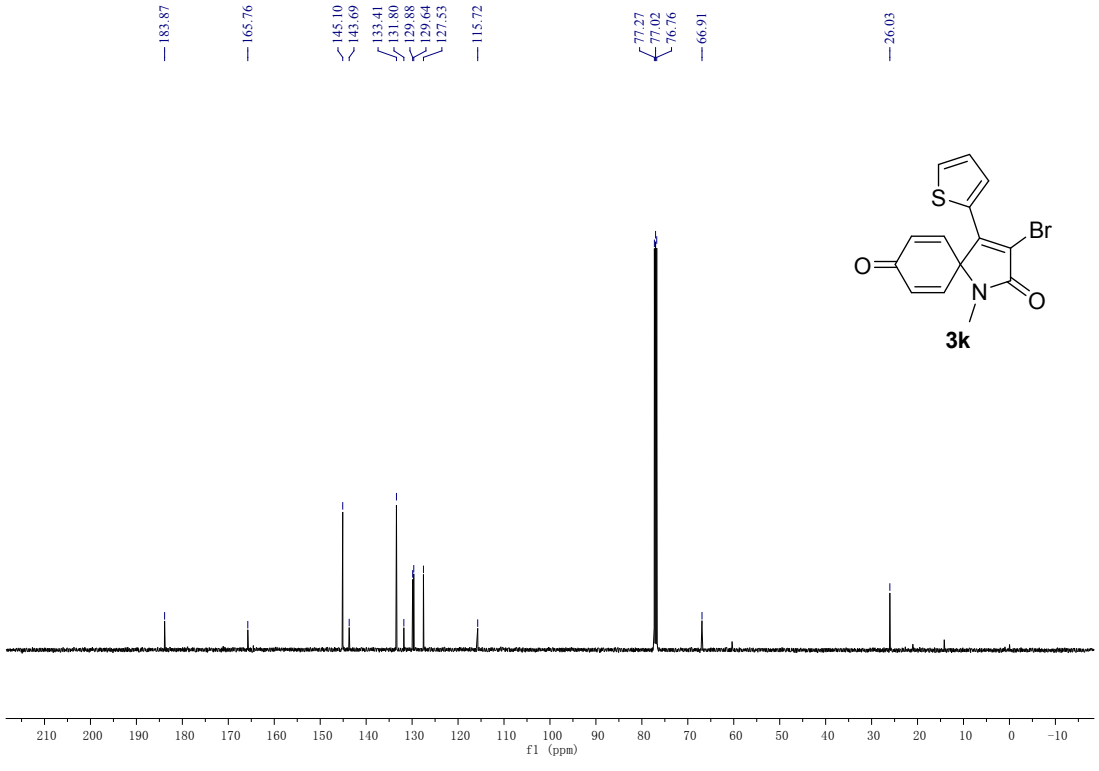
4-(4-bromophenyl)-3-chloro-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3j)



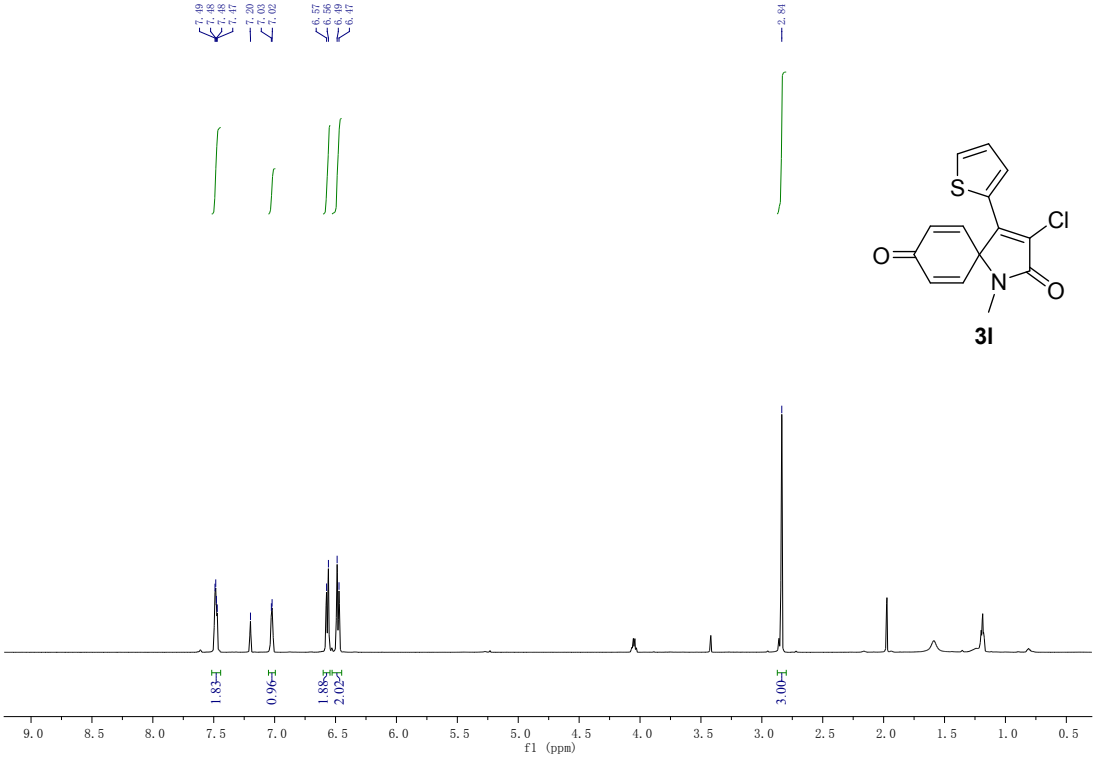


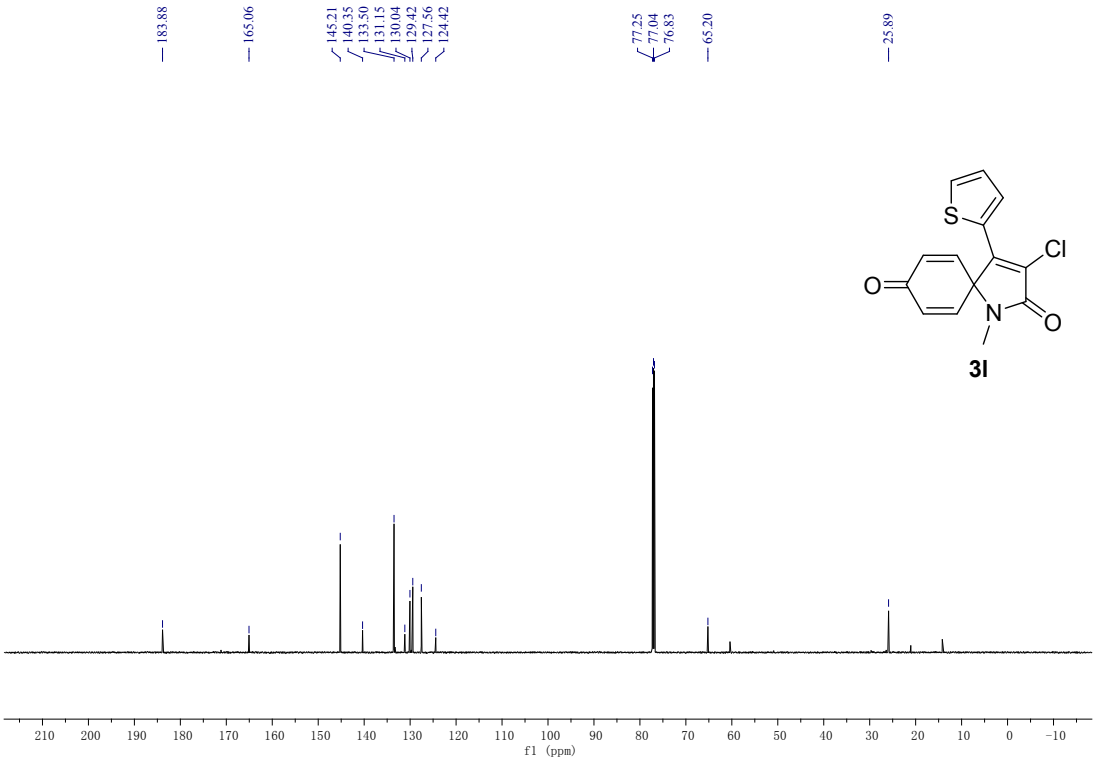
3-bromo-1-methyl-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3k)



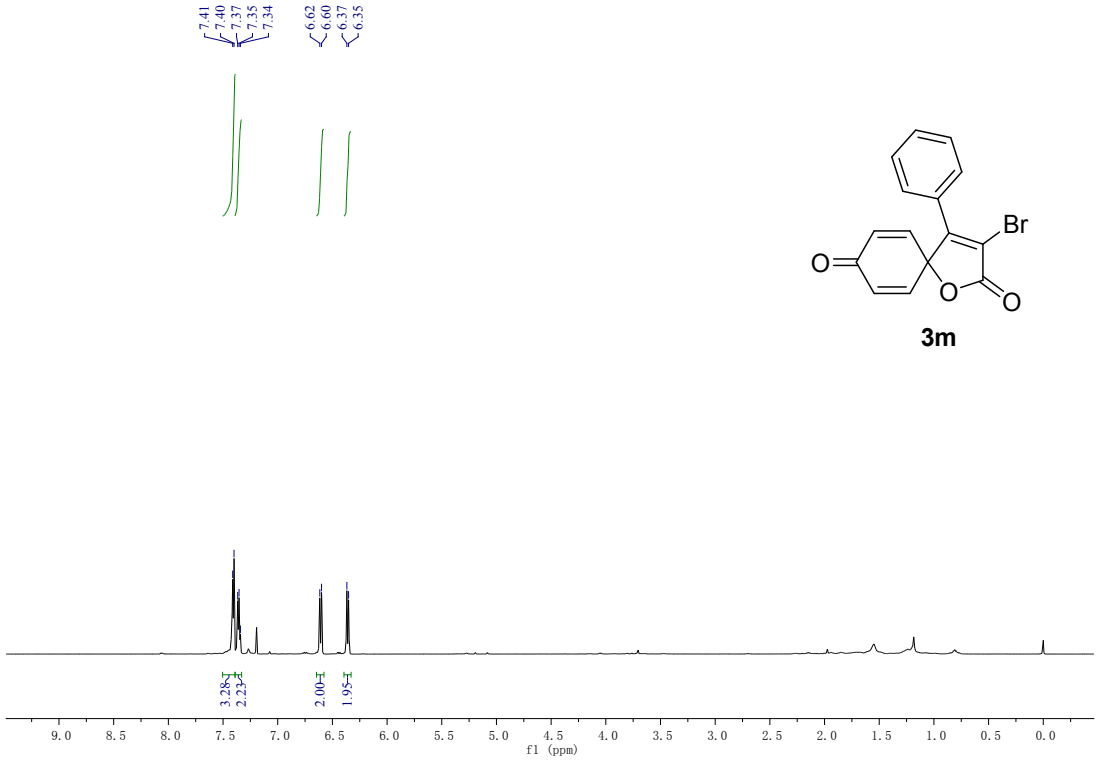


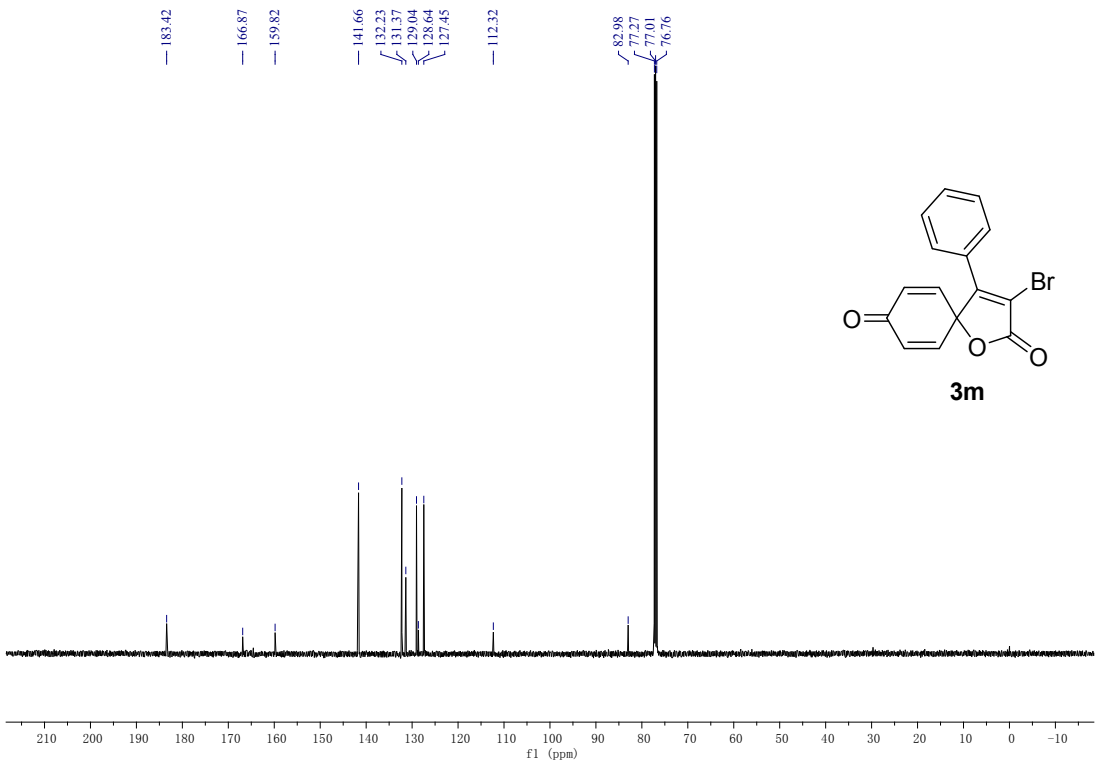
3-Chloro-1-methyl-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3l)



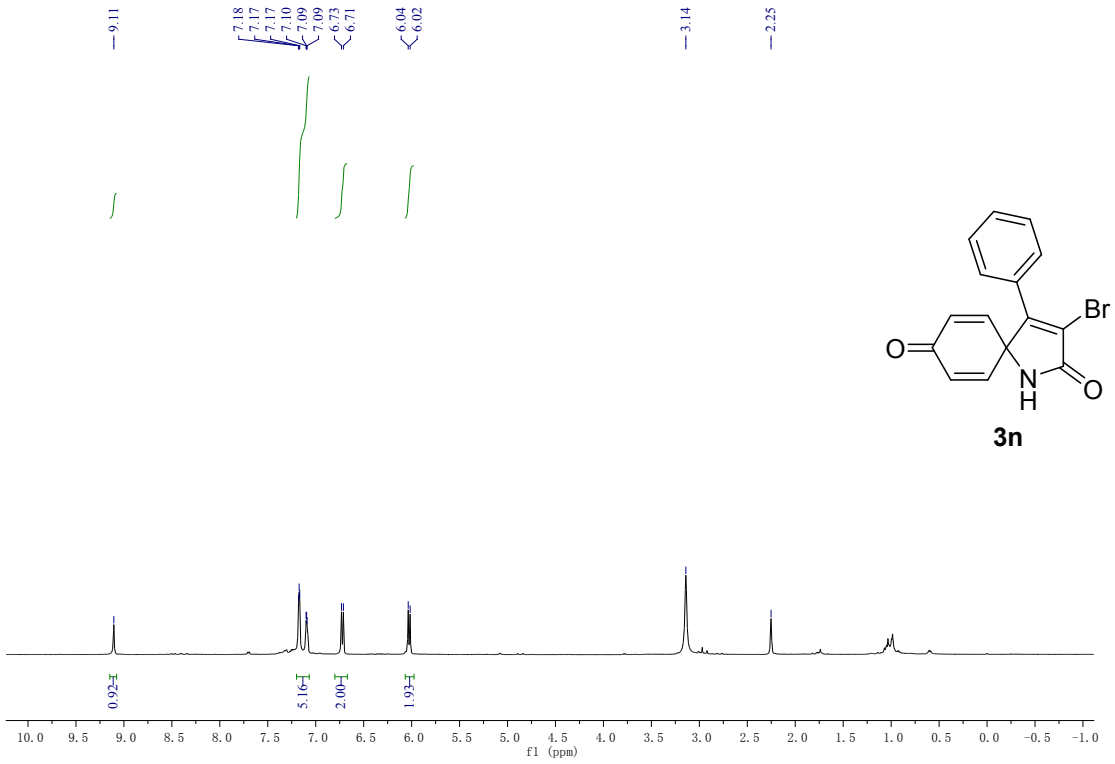


3-Bromo-4-phenyl-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione(3m)

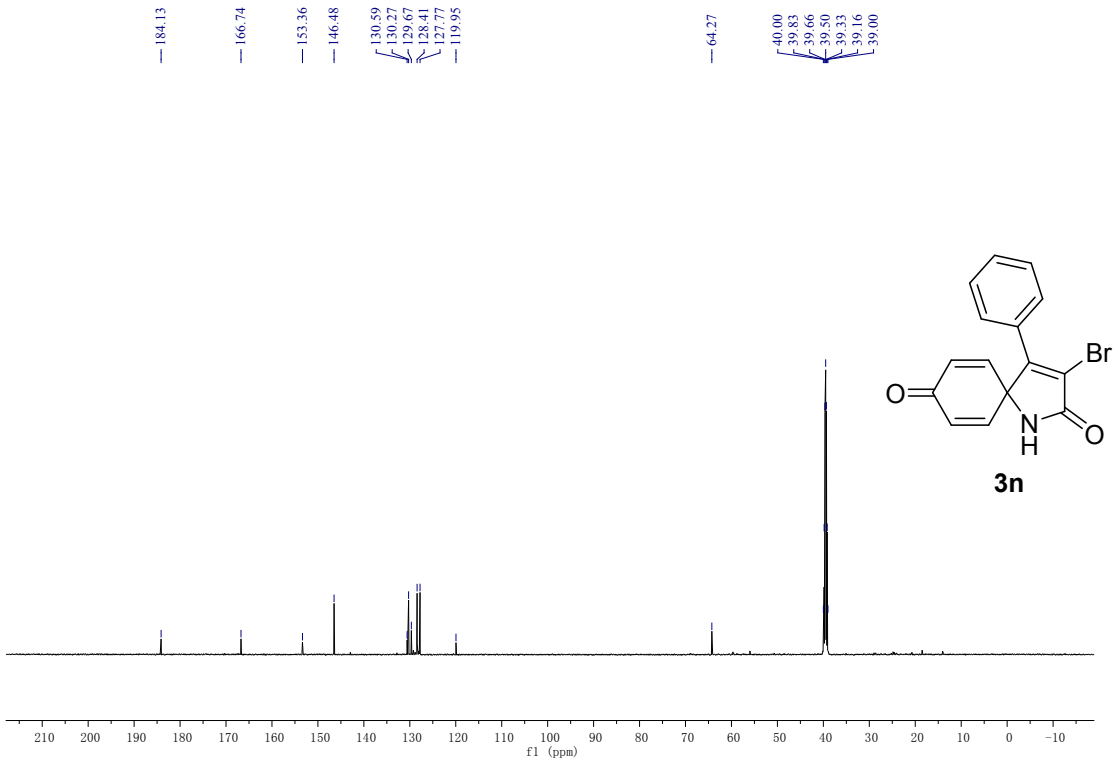




3-phenyl-3-brom-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione(3n)

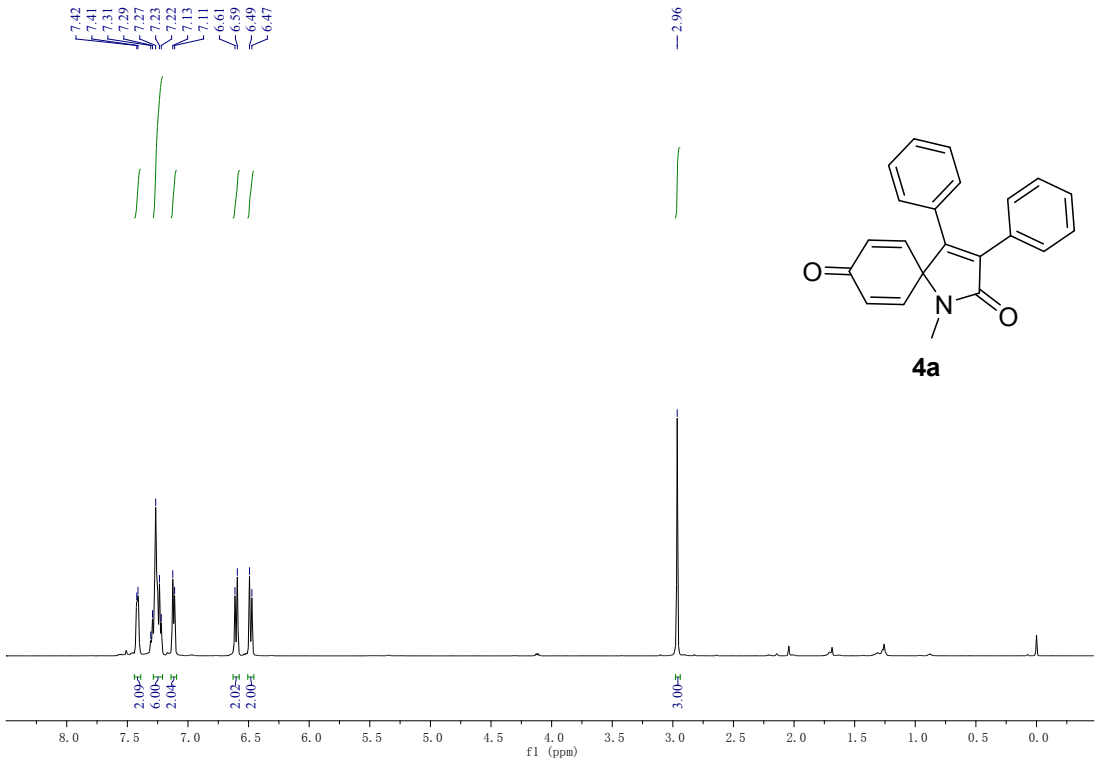


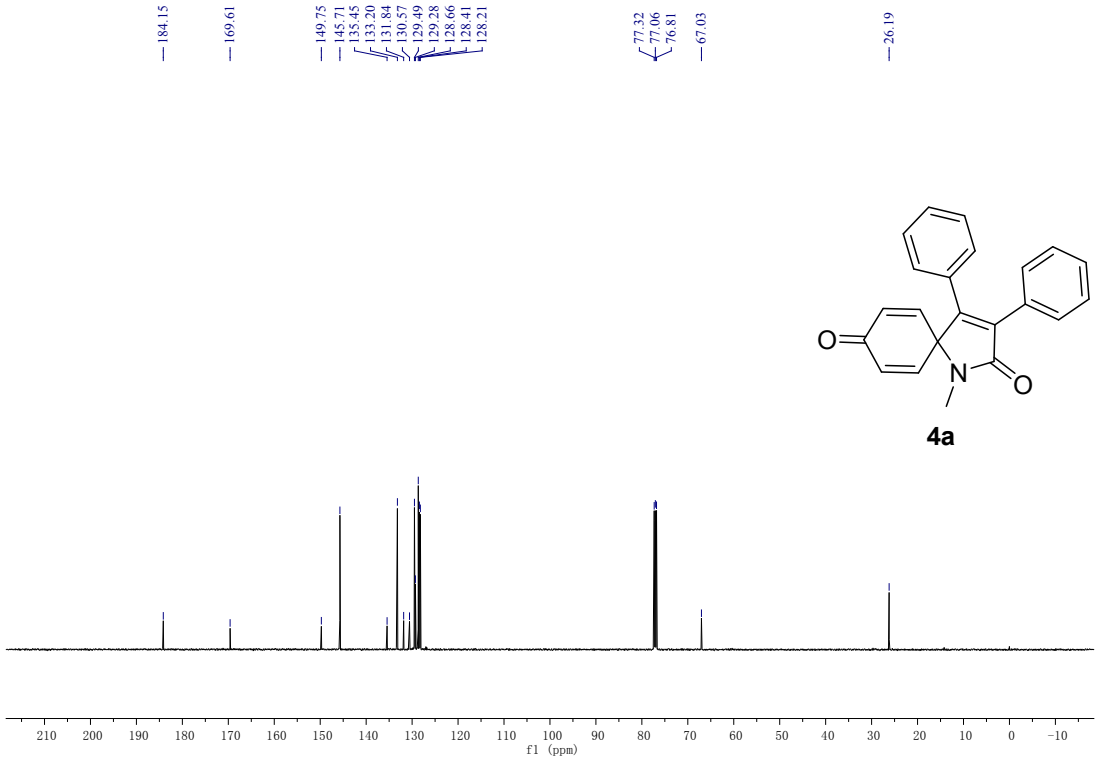
3n



3n

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





1-methyl-4-phenyl-3-(phenylethynyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (5a)