

Supporting Information

Visible-light-promoted one-pot synthesis of sulfonated spiro[4,5]trienones from propiolamides, anilines and sulfur dioxide under transition-metal-free conditions

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List of Contents

1. General Information	S1
2. Experimental Section	S1
2.1 General procedure for the synthesis of propioamides (1):	S1
2.2 Typical Experimental Procedure for the Synthesis of Sulfonated Spiro[4,5]trienones	S1-S2
2.3 Table S1: Screening the optimal conditions	S2-S3
2.4 The O¹⁸-Labelled Control Experiment	S3-S4
3. Analytical data	S5-S16
4. Reference	S17
5. ¹H and ¹³C spectra	S18-S64

1. General Information

All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All reagents and solvents were commercially available and used without any further purification unless specified. Proton (¹H NMR) and carbon (¹³C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ¹H NMR: TMS = 0.00 ppm, for ¹³C NMR: CDCl₃ = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. Analytical TLC was performed on precoated silica gel plates. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experiment Section

2.1 General procedure for the synthesis of alkynoates (1):

All propioamides (**1**) were synthesized according to the known methods.¹⁻³

2.2 Typical Experimental Procedure for the Synthesis of Sulfonated Spiro[4,5]trienones



To a Schlenk tube were added **1** (0.2 mmol), **2** (0.4 mmol, 2 equiv), DABSO (0.3 mmol, 1.5 equiv), Eosin Y (10 mol%), ^tBuONO (0.4 mmol, 2 equiv), H₂O (0.8 mmol, 4 equiv), CH₃CN (2 mL). Then the mixture was stirred at 70 °C (oil bath temperature) in argon atmosphere (1 atm) under 5 W blue LED light for 24 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3×10 mL). The combined organic extracts were dried

over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 2 : 1 to 1 : 2) to afford the desired products **3**.

2.3 Table S1: Screening the optimal conditions

To identify the best reaction conditions, we began to investigate the sulfonylation/*ipso*-cyclization of *N*-(*p*-methoxyaryl)propiolamide (**1a**, 0.2 mmol) with 4-methoxyaniline (**2a**, 2 equiv) in the presence of DABSO (1.5 equiv), Eosin Y (10 mol%), $^t\text{BuONO}$ (2 equiv) and H_2O (4 equiv) at 70 °C in acetonitrile (2 mL) irradiation with a 5 W blue LED light source for 24 h (Table S1). To our surprise, the product **3aa** could be obtained in 89% yield (entry 1). Conducting the reaction without Eosin Y and additional light could also give the target product in 45% yield (entry 2). The reaction yield increased when the reaction was irradiated by a 5 W blue LED light under no Eosin Y conditions (entry 3). These results suggested that light only promoted the sulfonylation/*ipso*-cyclization reaction. Two other photocatalysts, including $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and $\text{Ir}(\text{ppy})_3$, were investigated (entries 4-5). The results indicated that they were inferior to Eosin Y. Using 3 W blue LED light, 12 W blue LED light or 36 W compact fluorescent light instead of 5 W bule LED light could not deliver higher reaction yields (entries 6-8). Subsequently, several kinds of other solvents, including DMF, DMSO, DCE, and THF, were tested. None of them afforded higher yields than that of CH_3CN (entries 9-12). Next, the amount of H_2O was investigated and the addition of 4 equiv of H_2O to the reaction afforded the highest reaction yields (entries 13-14). Decreasing the temperature to 50 °C or increasing the temperature to 90 °C did not give satisfactory reaction yields (entries 15-16). A longer reaction time (36 h) furnished the desired product in a similar yield (entry 17). However, 1 gram (3.77 mmol) of substrate **1a** could also construct the 3-sulfonyl-spiro[4,5]decatrienone **3aa** in good yield (entry 18).

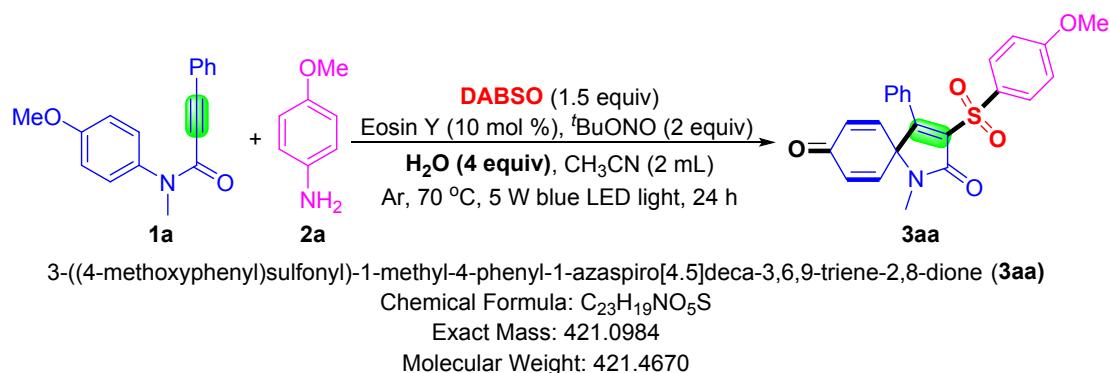
Table S1. Screening of optimal reaction conditions^a



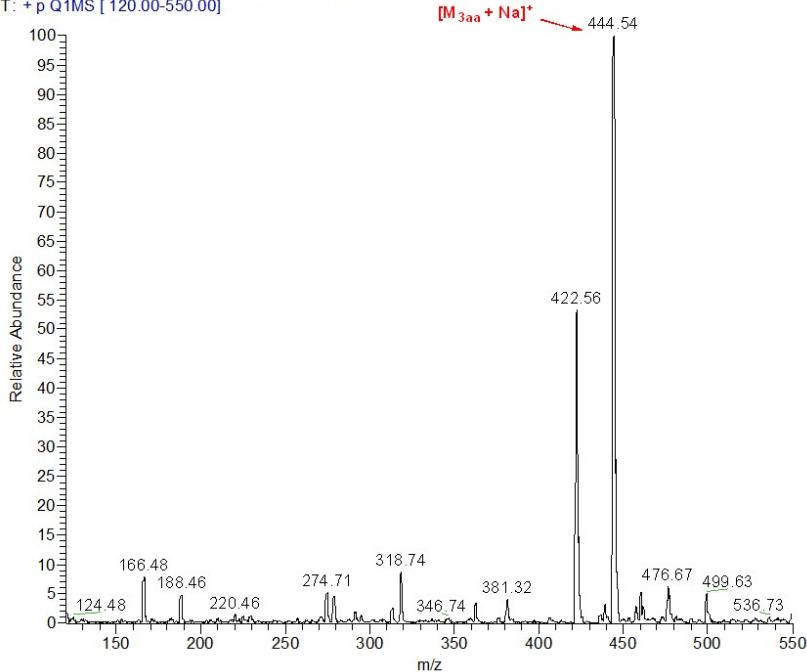
entry	variation from the standard conditions	yield (%) ^b
1	none	89
2 ^c	without Eosin Y and additional light	45
3	without Eosin Y	64
4	Ru(bpy) ₃ Cl ₂ instead of Eosin Y	76
5	Ir(ppy) ₃ (5 mol %) instead of Eosin Y	70
6	3 W blue LED light instead of 5 W blue LED light	75
7	12 W blue LED light instead of 5 W blue LED light	84
8	36 W compact fluorescent light instead of 5 W blue LED light	78
9 ^c	DMF instead of CH ₃ CN	40
10 ^c	DMSO instead of CH ₃ CN	34
11	DCE instead of CH ₃ CN	65
12	THF instead of CH ₃ CN	71
13 ^c	6 equiv of H ₂ O	83
14	2 equiv of H ₂ O	74
15 ^c	at 50 °C	57
16	at 90 °C	77
17	for 36 h	87
18 ^d	none	73

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), DABSO (0.3 mmol, 1.5 equiv), Eosin Y (10 mol %), TBN (0.4 mmol, 2 equiv), H₂O (4 equiv), CH₃CN (2 mL), at 70 °C under an argon atmosphere and 5 W blue LED irradiation for 24 h. ^b Isolated yield. ^c The rest of substrate **1a** was recovered. ^d **1a** (1.0 g, 3.77 mmol) and CH₃CN (20 mL) for 60 h.

2.4 The O¹⁸-Labelled Control Experiment



zqs1 #215-275 RT: 2.31-2.91 AV: 61 NL: 6.98E7
T: + p Q1MS [120.00-550.00]

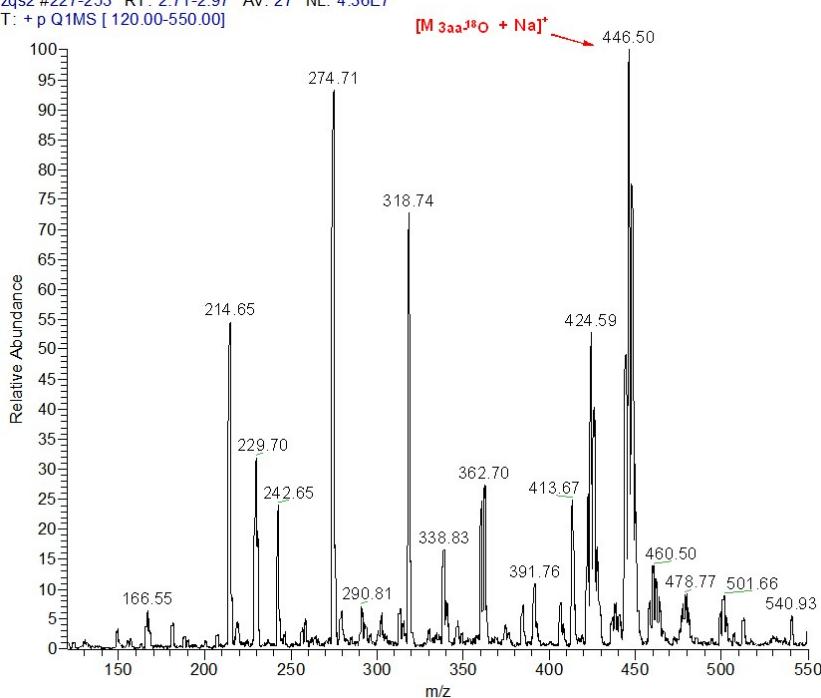


Chemical Formula: C₂₃H₁₉NO₄¹⁸OS

Exact Mass: 423.1026

Molecular Weight: 423.4672

zqs2 #227-253 RT: 2.71-2.97 AV: 27 NL: 4.36E7
T: + p Q1MS [120.00-550.00]



3. Analytical data

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

(3aa): yield: 75.0 mg, 89%; yellow solid; mp 216-218 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.97 (d, *J* = 8.8 Hz, 2H), 7.45-7.41 (m, 1H), 7.39-7.35 (m, 2H), 7.15-7.13 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.47-6.41 (m, 4H), 3.87 (s, 3H), 2.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.1, 164.3, 163.6, 160.9, 142.3 (2C), 136.9, 134.2 (2C), 131.5, 130.3, 130.2, 128.6, 127.9, 127.7, 114.2, 68.1, 55.7, 26.3; HRMS (ESI-TOF) *m/z*: C₂₃H₂₀NO₅S (M + H)⁺ calcd for 422.1057, found 422.1062.

1-Benzyl-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

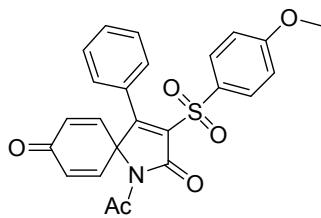
(3ba): yield: 82.5 mg, 83%; red solid; mp 224-225 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.99 (d, *J* = 9.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27-7.24 (m, 3H), 7.18-7.16 (m, 2H), 7.06-7.00 (m, 4H), 6.26-6.18 (m, 4H), 4.48 (s, 2H), 3.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.3, 164.3, 163.8, 161.2, 142.6 (2C), 136.9, 136.4, 133.3 (2C), 131.5, 130.4, 130.1, 129.0, 128.6, 128.3, 128.1, 127.8, 127.8, 114.3, 68.4, 55.7, 45.1; HRMS (ESI-TOF) *m/z*: C₂₉H₂₄NO₅S (M + H)⁺ calcd for 498.1370, found 498.1375.

1-(2-Iodobenzyl)-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ca):

dione (3ca): yield: 94.7 mg, 76%; red solid; mp 203-204 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.00-7.97 (m, 2H), 7.74-7.71 (m, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.34-7.29 (m, 3H), 7.25-7.24 (m, 1H), 7.09-7.06 (m, 2H), 7.02-7.00 (m, 2H), 6.94-6.93 (m, 1H), 6.25-6.16 (m, 4H), 4.63. (s, 2H), 3.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.3, 164.3, 163.8, 161.5, 141.7 (2C), 139.5, 138.7, 136.6, 133.6 (2C), 131.5, 130.4, 130.3, 130.1, 129.8, 128.7, 128.3, 127.8, 127.7, 114.3, 99.5, 68.3, 55.7, 49.2; HRMS (ESI-TOF) *m/z*: C₂₉H₂₃¹²⁷INO₅S (M + H)⁺ calcd for 624.0336, found 624.0342.

1-Acetyl-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ea):

yield: 62.0 mg, 69%; red solid; mp 143-144 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.88 (d, *J* = 8.8 Hz, 2H), 7.44-7.41 (m, 1H), 7.37-7.33 (m, 2H), 7.03-6.98 (m, 4H), 6.50 (d, *J* = 10.0 Hz, 2H),



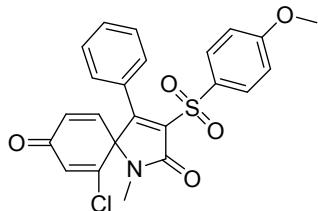
6.22 (d, $J = 10.0$ Hz, 2H), 3.88 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 183.1, 168.6, 164.5, 163.9, 162.5, 141.7 (2C), 136.5, 133.0 (2C), 131.4, 130.2, 129.9, 128.0, 127.5, 126.9, 114.4, 67.9, 55.7, 25.6; HRMS (ESI-TOF) m/z : $\text{C}_{24}\text{H}_{20}\text{NO}_6\text{S}$ ($M + \text{H}$) $^+$ calcd for 450.1006, found 450.1011.

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

(3fa): yield: 64.4 mg, 74%; red solid; mp 194-195 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ :

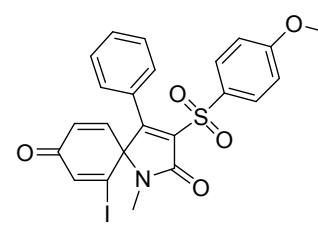
7.96 (d, $J = 9.2$ Hz, 2H), 7.44-7.42 (m, 1H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.17-7.14 (m, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 6.45-6.37 (m, 2H), 6.31-6.30 (m, 1H), 3.88 (s, 3H), 2.74 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 183.8, 164.2, 164.1, 161.1, 150.7, 142.4, 137.4, 133.8, 132.8, 131.4, 130.5, 130.4, 128.3, 128.0, 127.7, 114.2, 70.4, 55.6, 25.9, 17.6; HRMS (ESI-TOF) m/z : $\text{C}_{24}\text{H}_{22}\text{NO}_5\text{S}$ ($M + \text{H}$) $^+$ calcd for 436.1213, found 436.1219.

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



(3ga): yield: 63.7 mg, 70%; red solid; mp 190-191 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.97-7.94 (m, 2H), 7.44-7.37 (m, 3H), 7.13-7.11 (m, 2H), 7.03-6.98 (m, 2H), 6.69-6.68 (m, 1H), 6.51-6.50 (m, 2H), 3.88 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.3, 164.3, 163.3, 159.9, 143.1, 138.2, 137.5, 137.2, 133.1, 131.5, 130.3, 130.1, 128.1, 128.0, 127.7, 114.3, 69.8, 55.7, 26.5; HRMS (ESI-TOF) m/z : $\text{C}_{23}\text{H}_{19}^{35}\text{ClNO}_5\text{S}$ ($M + \text{H}$) $^+$ calcd for 456.0667, found 456.0672.

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



(3ha): yield: 68.9 mg, 63%; red oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.96 (d, $J = 9.2$ Hz, 2H), 7.44-7.37 (m, 3H), 7.25-7.24 (m, 1H), 7.12-7.09 (m, 2H), 6.01-6.99 (m, 2H), 6.53-6.49 (m, 2H), 3.88 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 177.1, 164.4, 163.4, 159.5, 150.1, 143.1, 137.1, 131.6, 131.0, 130.3, 130.1, 128.1, 128.0, 127.7, 114.3, 109.3, 71.3, 55.7, 26.6; HRMS (ESI-TOF) m/z : $\text{C}_{23}\text{H}_{19}^{127}\text{INO}_5\text{S}$ ($M + \text{H}$) $^+$ calcd for 548.0023, found 548.0029.

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

(3ia): yield: 67.7 mg, 75%; red solid; mp 257-258 °C (uncorrected); ^1H NMR (400 MHz,

CDCl_3 δ : 8.00-7.97 (m, 2H), 7.42-7.40 (m, 1H), 7.38-7.34 (m, 2H), 7.13-7.11 (m, 2H), 7.01-6.99 (m, 2H), 6.47-6.41 (m, 2H), 5.30 (s, 1H), 3.88 (s, 3H), 3.66 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 178.7, 164.2, 163.3, 162.0, 154.4, 143.0, 136.3, 133.6, 131.6, 130.4, 130.1, 128.7, 127.8, 127.6, 114.2, 108.6, 69.6, 55.7, 55.6, 26.1; HRMS (ESI-TOF) m/z : C₂₄H₂₂NO₆S (M + H)⁺ calcd for 452.1162, found 452.1168.

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

dione (3ja): yield: 65.5 mg, 72%; red oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.95 (d, J = 8.8 Hz, 2H), 7.44-7.36 (m, 3H), 7.13-7.11 (m, 2H), 6.99 (d, J = 9.2 Hz, 2H), 6.69 (s, 1H), 6.51-6.48 (m, 2H), 3.87 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.3, 164.3, 163.3, 159.9, 143.1, 138.2, 137.4, 137.2, 133.1, 131.5, 130.3, 130.1, 128.1, 128.0, 127.7, 114.3, 69.8, 55.7, 26.5; HRMS (ESI-TOF) m/z : C₂₃H₁₉³⁵ClNO₅S (M + H)⁺ calcd for 456.0667, found 456.0672.

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

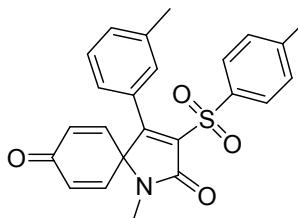
dione (3ka): yield: 53.9 mg, 60%; red solid; mp 230-231 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.94-7.92 (m, 2H), 7.36-7.34 (m, 2H), 7.15-7.13 (m, 1H), 6.99-6.97 (m, 2H), 6.76 (d, J = 7.6 Hz, 1H), 6.53-6.50 (m, 1H), 6.45-6.44 (m, 2H), 6.34 (d, J = 10.0 Hz, 1H), 3.87 (s, 3H), 2.85 (s, 3H), 2.72-2.62 (m, 1H), 2.45-2.36 (m, 1H), 1.28 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 183.0, 164.3, 163.5, 161.0, 142.6, 142.5, 141.7, 138.0, 134.3, 133.7, 131.5, 130.2, 129.9, 127.8, 127.1, 127.0, 124.5, 114.1, 69.2, 55.6, 26.5, 26.3, 14.3; HRMS (ESI-TOF) m/z : C₂₅H₂₄NO₅S (M + H)⁺ calcd for 450.1370, found 450.1375.

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

(3la): yield: 58.3 mg, 67%; red solid; mp 240-241 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.94 (d, J = 8.8 Hz, 2H), 7.29-7.27 (m, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.15 (t, J = 6.8 Hz, 1H), 6.99-6.97 (m, 2H), 6.79 (d, J = 7.6 Hz, 1H), 6.52-6.51 (m, 1H), 6.47-6.46 (m, 2H), 6.35-6.32 (m, 1H), 3.87 (s, 3H), 2.86 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 183.0, 164.3, 163.5, 160.7, 142.4, 142.2, 135.9, 134.4, 133.7, 131.6, 130.3, 130.2, 129.7, 127.6, 127.2, 124.6,

114.2, 69.4, 55.6, 26.5, 20.8; HRMS (ESI-TOF) m/z : C₂₄H₂₂NO₅S (M + H)⁺ calcd for 436.1213, found 436.1219.

3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(*m*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

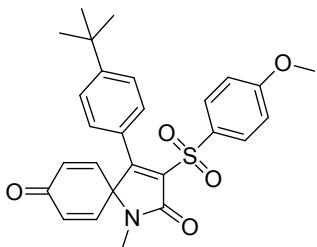


(3ma): yield: 60.9 mg, 70%; yellow solid; mp 115-116 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.96 (d, J = 8.8 Hz, 2H), 7.28-7.21 (m, 2H), 6.99 (d, J = 8.8 Hz, 2H), 6.94-6.91 (m, 2H), 6.44 (s, 4H), 3.87 (s, 3H), 2.82 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.2, 164.2, 163.7, 161.1, 142.4 (2C), 137.5, 136.7, 134.1 (2C), 131.5, 131.0, 130.4, 128.5, 128.3, 127.7, 124.7, 114.2, 68.1, 55.6, 26.2, 21.3; HRMS (ESI-TOF) m/z : C₂₄H₂₂NO₅S (M + H)⁺ calcd for 436.1213, found 436.1219.

4-(3,5-Dimethylphenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3na): yield: 74.6 mg, 83%; red solid; mp 206-207 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (d, J = 9.2 Hz, 2H), 7.02 (s, 1H), 6.98 (d, J = 8.8 Hz, 2H), 6.70 (s, 2H), 6.43 (s, 4H), 3.87 (s, 3H), 2.82 (s, 3H), 2.29 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.2, 164.1, 163.7, 161.3, 142.5 (2C), 137.3, 136.5, 133.9 (2C), 131.9, 131.4, 130.5, 128.4, 125.3, 114.1, 68.0, 55.6, 26.2, 21.2; HRMS (ESI-TOF) m/z : C₂₅H₂₄NO₅S (M + H)⁺ calcd for 450.1370, found 450.1375.

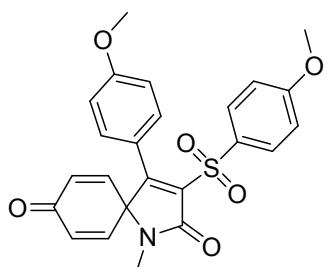
3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(*p*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3oa): yield: 74.8 mg, 86%; red solid; mp 198-199 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.97 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 6.99 (m, 2H), 6.45-6.44 (m, 4H), 3.87 (s, 3H), 2.82 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.2, 164.2, 163.7, 161.2, 142.5 (2C), 140.5, 136.5, 134.1 (2C), 131.5, 130.4, 128.6, 127.7, 125.6, 114.2, 68.1, 55.6, 26.2, 21.4; HRMS (ESI-TOF) m/z : C₂₄H₂₂NO₅S (M + H)⁺ calcd for 436.1213, found 436.1219.

4-(*tert*-Butyl)phenyl-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3pa): yield: 84.0 mg, 88%; red solid; mp 215-216 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.96 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.48-6.42 (m, 4H), 3.86 (s, 3H), 2.80 (s, 3H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ:



183.3, 164.1, 163.7, 161.1, 153.4, 142.5 (2C), 136.3, 134.0 (2C), 131.4, 130.4, 127.6, 125.6, 124.7, 114.1, 67.9, 55.6, 34.7, 31.0, 26.1; HRMS (ESI-TOF) *m/z*: C₂₇H₂₈NO₅S (M + H)⁺ calcd for 478.1683, found 478.1688.

4-(4-Methoxyphenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-

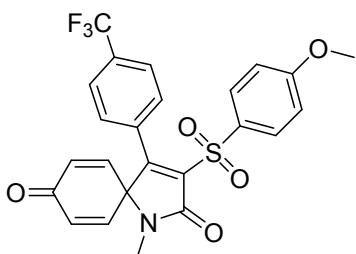


2,8-dione (3qa): yield: 76.7 mg, 85%; yellow solid; mp 218-219 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.98 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 9.2 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.48-6.42 (m, 4H), 3.87 (s, 3H), 3.81 (s, 3H), 2.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.2, 164.1, 163.8, 161.1, 160.8, 142.7 (2C), 135.9, 134.0 (2C), 131.5, 130.4, 129.6, 120.6, 114.1, 113.4, 68.0, 55.6, 55.2, 26.1; HRMS (ESI-TOF) *m/z*: C₂₄H₂₂NO₆S (M + H)⁺ calcd for 452.1162, found 452.1168.

4-(4-Fluorophenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ra): yield: 68.5 mg, 78%; red solid; mp 94-95 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.97 (d, *J* = 9.2 Hz, 2H), 7.20-7.17 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 2H), 7.06-7.00 (m, 2H), 6.49-6.43 (m, 4H), 3.89 (s, 3H), 2.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.0, 164.4, 163.6 (d, *J* = 250.1 Hz, 1C), 163.4, 159.7, 142.2 (2C), 137.4, 134.3 (2C), 131.6, 130.1, 130.0, 124.5 (d, *J* = 3.6 Hz, 1C), 115.3 (d, *J* = 2.2 Hz, 1C), 114.3, 68.1, 55.7, 26.3; ¹⁹F NMR (282 MHz, CDCl₃) δ: -109.2 (s, 1F); HRMS (ESI-TOF) *m/z*: C₂₃H₁₉¹⁹FNO₅S (M + H)⁺ calcd for 440.0962, found 440.0968.

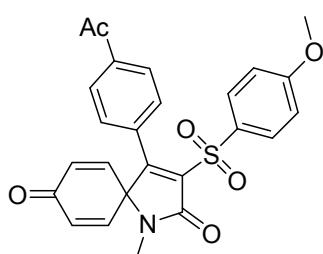
4-(4-Chlorophenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3sa): yield: 72.8 mg, 80%; red solid; mp 120-121 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (d, *J* = 9.2 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 9.2 Hz, 2H), 6.45 (s, 4H), 3.88 (s, 3H), 2.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 182.9, 164.4, 163.3, 159.3, 142.1 (2C), 137.4, 136.5, 134.3 (2C), 131.5, 130.0, 129.2, 128.3, 126.9, 114.3, 68.0, 55.6, 26.3; HRMS (ESI-TOF) *m/z*: C₂₃H₁₉³⁵ClNO₅S (M + H)⁺ calcd for 456.0667, found 456.0672.

3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(4-(trifluoromethyl)phenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ta):



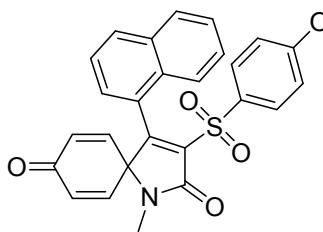
3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(4-(trifluoromethyl)phenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ta): yield: 72.4 mg, 74%; yellow solid; mp 185-186 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.29-7.27 (m, 2H), 7.00 (d, *J* = 9.2 Hz, 2H), 6.51-6.44 (m, 4H), 3.88 (s, 3H), 2.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 182.7, 164.5, 163.2, 158.7, 141.8 (2C), 138.1, 134.5, 132.3 (2C), 132.0 (q, *J* = 32.8 Hz, 1C), 131.6, 129.8, 128.4, 124.9 (q, *J* = 3.7 Hz, 1C), 123.5 (q, *J* = 271.0 Hz, 1C), 114.4, 68.0, 55.7, 26.4; ¹⁹F NMR (282 MHz, CDCl₃) δ: -62.9 (s, 3F); HRMS (ESI-TOF) *m/z*: C₂₄H₁₉¹⁹F₃NO₅S (M + H)⁺ calcd for 490.0931, found 490.0936.

4-(4-Acetylphenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-



4-(4-Acetylphenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ua): yield: 69.5 mg, 75%; white solid; mp 239-240 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.99-7.96 (m, 4H), 7.27-7.24 (m, 2H), 7.03-7.01 (m, 2H), 6.45 (s, 4H), 3.89 (s, 3H), 2.85 (s, 3H), 2.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 197.0, 182.8, 164.6, 163.3, 159.4, 141.9 (2C), 138.0, 137.9, 134.5 (2C), 133.3, 131.7, 129.9, 128.2, 127.8, 114.4, 68.0, 55.7, 26.6, 26.4; HRMS (ESI-TOF) *m/z*: C₂₅H₂₂NO₆S (M + H)⁺ calcd for 464.1162, found 464.1168.

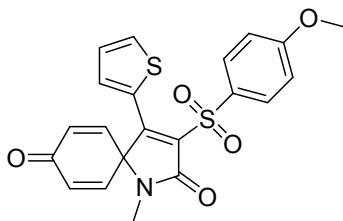
3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(naphthalen-1-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-



3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(naphthalen-1-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3va): yield: 57.5 mg, 61%; red solid; mp 136-137 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.88-7.75 (m, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 6.8 Hz, 1H), 7.42-7.40 (m, 3H), 7.10-7.09 (m, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.60-6.59 (m, 1H), 6.54-6.48 (m, 2H), 6.04-6.01 (m, 1H), 3.85 (s, 3H), 2.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 182.9, 164.3, 163.6, 159.0, 142.4, 142.3, 139.4, 134.6, 133.6, 133.0, 131.9, 130.5, 130.3, 129.6, 129.0, 126.8, 126.3, 126.1, 125.8, 124.7, 124.1, 113.9, 69.4, 55.7, 26.6; HRMS (ESI-TOF) *m/z*: C₂₇H₂₂NO₅S (M + H)⁺ calcd for 472.1213, found 472.1219.

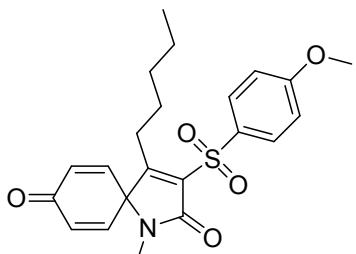
3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-

dione (3wa): yield: 52.1 mg, 61%; yellow solid; mp 218-219 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.05 (d, *J* = 8.8 Hz, 2H), 7.67-7.66 (m, 1H), 7.58-7.56 (m, 1H), 7.15-7.13 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 10.4 Hz, 2H), 6.43 (d, *J* = 10.0 Hz, 2H), 3.89 (s, 3H), 2.77 (s, 3H); ¹³C



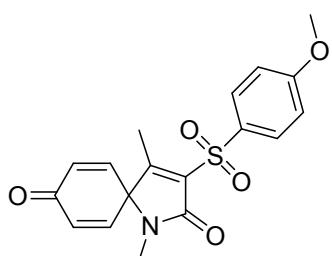
¹H NMR (100 MHz, CDCl₃) δ: 183.4, 164.3, 163.7, 153.0, 142.7 (2C), 134.6 (2C), 134.5, 134.1, 131.7, 131.5, 130.2, 127.9, 127.7, 114.1, 67.1, 55.6, 25.9; HRMS (ESI-TOF) *m/z*: C₂₁H₁₈NO₅S₂ (M + H)⁺ calcd for 428.0621, found 428.0626.

3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-pentyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3xa):



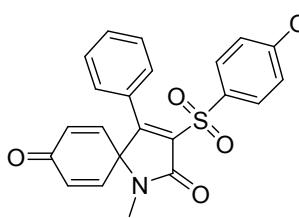
yield: 54.0 mg, 65%; red solid; mp 127-128 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.08 (d, *J* = 9.2 Hz, 2H), 7.02 (d, *J* = 9.2 Hz, 2H), 6.60 (d, *J* = 10.0 Hz, 2H), 6.32 (d, *J* = 10.0 Hz, 2H), 3.89 (s, 3H), 2.76 (s, 3H), 2.58-2.54 (m, 2H), 1.62-1.58 (m, 2H), 1.39-1.26 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.5, 164.8, 164.3, 164.1, 143.3 (2C), 135.4, 134.1 (2C), 131.5, 130.5, 114.2, 68.2, 55.7, 32.2, 31.0, 26.6, 26.2, 22.0, 13.8; HRMS (ESI-TOF) *m/z*: C₂₂H₂₆NO₅S (M + H)⁺ calcd for 416.1526, found 416.1532.

3-((4-Methoxyphenyl)sulfonyl)-1,4-dimethyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ya):



yield: 39.5 mg, 55%; red solid; mp 170-171 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.06 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 10.0 Hz, 2H), 6.30 (d, *J* = 10.0 Hz, 2H), 3.89 (s, 3H), 2.78 (s, 3H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.3, 164.3, 163.9, 160.5, 143.4 (2C), 135.7, 134.4 (2C), 131.3, 130.6, 114.3, 68.1, 55.7, 26.2, 12.0; HRMS (ESI-TOF) *m/z*: C₁₈H₁₈NO₅S (M + H)⁺ calcd for 360.0900, found 360.0906.

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



yield: 79.2 mg, 91%; yellow solid; mp 207-208 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (d, *J* = 8.8 Hz, 2H), 7.44-7.34 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.47-6.41 (m, 4H), 4.12-4.07 (m, 2H), 2.83 (s, 3H), 1.44 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.1, 163.7, 163.6, 160.8, 142.3 (2C), 137.0, 134.2 (2C), 131.5, 130.1, 130.0, 128.6, 127.8, 127.7, 114.6, 68.1, 64.0, 26.2, 14.5; HRMS (ESI-TOF) *m/z*: C₂₄H₂₂NO₅S (M + H)⁺ calcd for 436.1213, found 436.1219.

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

(3ac): yield: 85.0 mg, 88%; yellow solid; mp 100-101 °C (uncorrected);
¹H NMR (400 MHz, CDCl₃) δ: 7.99-7.97 (m, 2H), 7.44-7.37 (m, 5H),
7.27-7.25 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.10-7.07 (m, 2H), 7.04-7.02
(m, 2H), 6.45 (s, 4H), 2.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.1,
163.2, 161.3, 154.5, 142.2 (2C), 134.3 (2C), 132.1, 131.7, 130.3, 130.2 (2C), 128.6, 127.9 (2C), 127.8,
125.3, 120.6, 117.1, 68.2, 26.3; HRMS (ESI-TOF) *m/z*: C₂₈H₂₂NO₅S (M + H)⁺ calcd for 484.1213,
found 484.1219.

1-Methyl-4-phenyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ad): yield: 64.8 mg, 80%;

yellow solid; mp 284-285 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.93 (d, *J* = 8.4 Hz, 2H), 7.46-7.42 (m, 1H), 7.40-7.33 (m, 4H), 7.16-7.14 (m, 2H), 6.44 (s, 4H), 2.83 (s, 3H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.1, 163.6, 161.5, 145.6, 142.2 (2C), 136.8, 136.1, 134.3 (2C), 130.3, 129.7, 129.3, 128.5, 127.9, 127.8, 68.2, 26.3, 21.8; HRMS (ESI-TOF) *m/z*: C₂₃H₂₀NO₄S (M + H)⁺ calcd for 406.1108, found 406.1113.

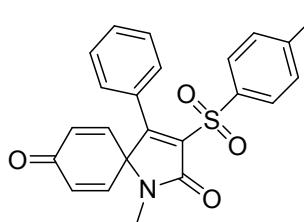
3-((4-(*tert*-Butyl)phenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

(3ae): yield: 68.0 mg, 76%; yellow solid; mp 263-264 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.44-7.41 (m, 1H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.49-6.42 (m, 4H), 2.84 (s, 3H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.1, 163.5, 161.5, 158.2, 142.3 (2C), 136.8, 136.0, 134.2 (2C), 130.2, 128.9, 128.5, 127.8, 127.7, 126.1, 68.2, 35.3, 30.9, 26.3; HRMS (ESI-TOF) *m/z*: C₂₆H₂₆NO₄S (M + H)⁺ calcd for 448.1577, found 448.1583.

1-Methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3af): yield: 66.5

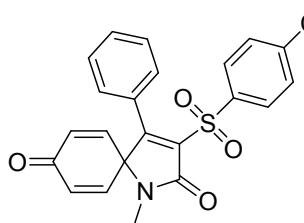
mg, 85%; yellow solid; mp 207-208 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.06-8.03 (m, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.57-7.53 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.40-7.36 (m, 2H), 7.16-7.14 (m, 2H), 6.45 (s, 4H), 2.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.0, 163.4, 162.1, 142.2 (2C), 139.1, 136.6, 134.3 (2C), 134.3, 130.3, 129.1, 129.0, 128.4, 127.9, 127.7, 68.2, 26.3; HRMS (ESI-TOF) *m/z*: C₂₂H₁₈NO₄S (M + H)⁺ calcd for 392.0951, found 392.0957.

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



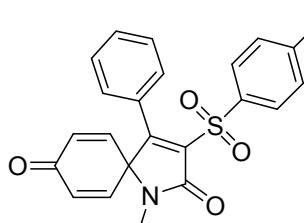
yield: 67.9 mg, 83%; yellow solid; mp 206-207 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.09-8.06 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.49-6.43 (m, 4H), 2.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.0, 166.3 (d, *J* = 256.1 Hz, 1C), 163.4, 162.1, 142.1, 136.5, 135.0 (d, *J* = 2.9 Hz, 1C), 134.4 (2C), 132.3, 132.2, 130.5, 128.4, 128.0, 127.1, 116.4 (d, *J* = 22.5 Hz, 1C), 68.3, 26.3; ¹⁹F NMR (282 MHz, CDCl₃) δ: -102.1 (s, 1F); HRMS (ESI-TOF) *m/z*: C₂₂H₁₇¹⁹FNO₄S (M + H)⁺ calcd for 410.0857, found 410.0862.

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



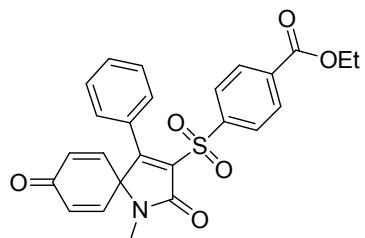
yield: 68.0 mg, 80%; yellow solid; mp 259-260 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.98 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.45 (s, 4H), 2.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 182.9, 163.3, 162.4, 141.9 (2C), 141.2, 137.4, 136.2, 134.4 (2C), 130.7, 130.4, 129.4, 128.3, 128.0, 127.7, 68.3, 26.3; HRMS (ESI-TOF) *m/z*: C₂₂H₁₇³⁵ClNO₄S (M + H)⁺ calcd for 426.0561, found 426.0567.

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



yield: 70.3 mg, 75%; white solid; mp 232-233 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.92-7.89 (m, 2H), 7.69-7.67 (m, 2H), 7.45-7.43 (m, 1H), 7.41-7.36 (m, 2H), 7.15-7.13 (m, 2H), 6.45 (s, 4H), 2.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 182.9, 163.3, 162.4, 141.9 (2C), 137.9, 136.2, 134.4 (2C), 132.3, 130.7, 130.5, 130.0, 128.3, 128.0, 127.7, 68.3, 26.3; HRMS (ESI-TOF) *m/z*: C₂₂H₁₇⁷⁹BrNO₄S (M + H)⁺ calcd for 470.0056, found 470.0062.

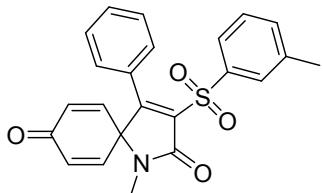
Ethyl 4-((1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)sulfonyl)benzoate (3aj):



yield: 65.8 mg, 71%; red solid; mp 200-201 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.20 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.48-7.45 (m, 1H), 7.41-7.37 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.48-6.42 (m, 4H), 4.45-4.39 (m, 2H), 2.83 (s, 3H), 1.41 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz,

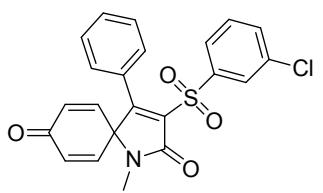
CDCl_3 δ : 182.9, 164.9, 163.2, 162.9, 142.6, 141.9 (2C), 136.1, 135.6, 134.4 (2C), 130.6, 130.1, 129.2, 128.2, 128.0, 127.7, 68.3, 61.8, 26.3, 14.2; HRMS (ESI-TOF) m/z : $\text{C}_{25}\text{H}_{22}\text{NO}_5\text{S}$ ($\text{M} + \text{H}$) $^+$ calcd for 464.1162, found 464.1168.

1-Methyl-4-phenyl-3-(m-tolylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ak): yield:



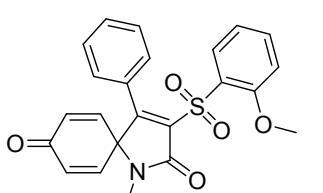
61.6 mg, 76%; yellow solid, mp 230-231 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.84-7.82 (m, 2H), 7.47-7.43 (m, 3H), 7.40-7.36 (m, 2H), 7.1-7.13 (m, 2H), 6.45 (s, 4H), 2.84 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 183.1, 163.5, 161.9, 142.2 (2C), 139.3, 139.0, 136.7, 135.2, 134.3 (2C), 130.4, 129.4, 128.9, 128.5, 127.9, 127.8, 126.3, 68.2, 26.4, 21.4; HRMS (ESI-TOF) m/z : $\text{C}_{23}\text{H}_{20}\text{NO}_4\text{S}$ ($\text{M} + \text{H}$) $^+$ calcd for 406.1108, found 406.1113.

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



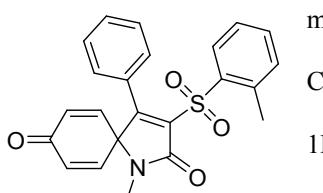
yield: 61.2 mg, 72%; yellow solid; mp 228-229 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.97-7.95 (m, 2H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.51-7.44 (m, 2H), 7.40-7.37 (m, 2H), 7.17-7.14 (m, 2H), 6.49-6.46 (m, 4H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 182.9, 163.2, 162.8, 141.9, 140.7, 136.0, 135.1, 134.4, 134.4, 134.4, 130.5, 130.3, 129.0, 128.2, 128.0, 127.7, 127.7, 127.4, 68.3, 26.3; HRMS (ESI-TOF) m/z : $\text{C}_{22}\text{H}_{17}\text{ClNO}_4\text{S}$ ($\text{M} + \text{H}$) $^+$ calcd for 426.0561, found 426.0567.

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



(3am): yield: 62.3 mg, 74%; yellow solid; mp 119-120 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (d, $J = 8.0$ Hz, 1H), 7.57-7.56 (m, 1H), 7.38 (d, $J = 7.2$ Hz, 1H), 7.34-7.30 (m, 2H), 7.25-7.23 (m, 2H), 7.12-7.10 (m, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 6.47 (s, 4H), 3.87 (s, 3H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 183.2, 163.5, 161.1, 157.3, 142.7 (2C), 136.0, 135.8, 134.1 (2C), 131.1, 130.3, 128.4, 128.1, 127.7, 127.0, 120.8, 112.2, 67.9, 56.2, 26.1; HRMS (ESI-TOF) m/z : $\text{C}_{23}\text{H}_{20}\text{NO}_5\text{S}$ ($\text{M} + \text{H}$) $^+$ calcd for 422.1057, found 422.1062.

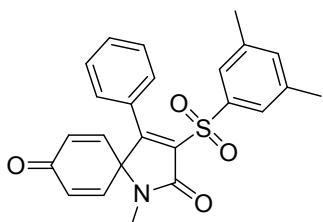
1-Methyl-4-phenyl-3-(o-tolylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3an): yield: 56.7



mg, 70%; yellow solid; mp 207-208 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 8.11 (d, $J = 8.0$ Hz, 1H), 7.50-7.48 (m, 1H), 7.41 (d, $J = 7.2$ Hz, 1H), 7.36-7.33 (m, 3H), 7.24-7.21 (m, 3H), 6.47 (s, 4H), 2.81 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 183.0, 163.2, 161.8, 142.3 (2C),

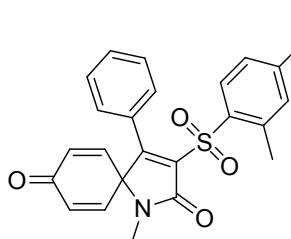
138.0, 136.7, 135.8, 134.2 (2C), 134.2, 132.2, 131.2, 130.5, 128.1, 128.1, 127.9, 126.3, 68.0, 26.2, 20.0; HRMS (ESI-TOF) m/z : C₂₃H₂₀NO₄S (M + H)⁺ calcd for 406.1108, found 406.1113.

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



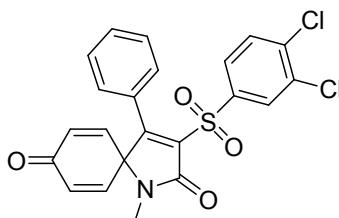
(3ao): yield: 64.5 mg, 77%; yellow solid; mp 211-212 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.77-7.73 (m, 2H), 7.43-7.41 (m, 1H), 7.39-7.34 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 7.15-7.13 (m, 2H), 6.47-6.41 (m, 4H), 2.83 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.1, 163.5, 161.3, 144.2, 142.3, 137.8, 136.9, 136.2, 134.2, 130.2, 130.2, 129.8, 128.6, 127.8, 127.8, 126.7, 68.2, 26.3, 20.1; HRMS (ESI-TOF) m/z : C₂₄H₂₂NO₄S (M + H)⁺ calcd for 420.1264, found 420.1270.

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



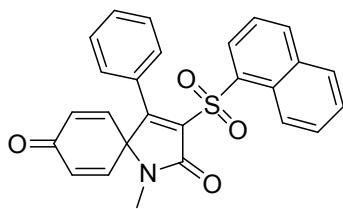
(3ap): yield: 66.1 mg, 76%; red solid; mp 265-266 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.09 (d, J = 8.8 Hz, 1H), 7.44-7.40 (m, 1H), 7.37-7.33 (m, 2H), 7.23-7.21 (m, 2H), 6.85-6.83 (m, 1H), 6.71 (s, 1H), 6.50-6.43 (s, 4H), 3.84 (s, 3H), 2.81 (s, 3H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.1, 163.9, 163.5, 161.0, 142.5 (2C), 140.6, 136.3, 134.3 (2C), 134.2, 130.5, 128.4, 128.3, 128.2, 127.9, 117.8, 110.9, 68.0, 55.5, 26.2, 20.4; HRMS (ESI-TOF) m/z : C₂₄H₂₂NO₅S (M + H)⁺ calcd for 436.1213, found 436.1219.

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



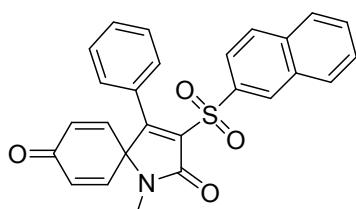
(3aq): yield: 62.4 mg, 68%; red solid; mp 217-218 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.07 (s, 1H), 7.91-7.88 (m, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.16-7.14 (m, 2H), 6.50-6.44 (m, 4H), 2.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 182.9, 163.1, 162.9, 141.8 (2C), 139.5, 138.5, 135.8, 134.4 (2C), 133.6, 131.0, 131.0, 130.5, 128.4, 128.1, 128.0, 127.7, 68.3, 26.3; HRMS (ESI-TOF) m/z : C₂₂H₁₆³⁵Cl₂NO₄S (M + H)⁺ calcd for 460.0172, found 460.0177.

1-Methyl-3-(naphthalen-1-ylsulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ar): yield: 62.6 mg, 71%; red solid; mp 104-105 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.44 (d, J = 8.4 Hz, 1H), 8.29-8.27 (m, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.94-7.91 (m, 1H), 7.59-7.55 (m, 3H), 7.43 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.20-7.17 (m, 2H), 6.42 (d, J = 10.0 Hz, 2H), 6.33 (d, J =



10.0 Hz, 2H), 2.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.1, 163.2, 162.0, 142.3 (2C), 135.9, 135.7, 134.2 (2C), 133.8, 133.1, 132.4, 130.6, 129.3, 128.6, 128.3, 128.2, 128.1, 127.9, 126.7, 124.5, 123.4, 67.9, 26.2; HRMS (ESI-TOF) *m/z*: C₂₆H₂₀NO₄S (M + H)⁺ calcd for 442.1108, found 442.1113.

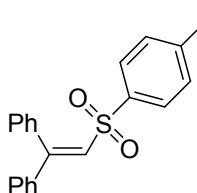
1-Methyl-3-(naphthalen-2-ylsulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3as):



yield: 65.3 mg, 74%; white solid; mp 284-285 °C ¹H NMR (400 MHz, CDCl₃) δ: 8.63 (s, 1H), 8.02-7.98 (m, 3H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.69-7.62 (m, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.44 (s, 4H), 2.82 (s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ: 183.0, 163.5, 162.0, 142.2 (2C), 136.7, 135.9, 135.6, 134.3 (2C), 132.0, 131.6, 130.4, 129.8, 129.6, 129.2, 128.5, 127.9, 127.9, 127.8, 127.6, 123.4, 68.3, 26.3; HRMS (ESI-TOF) *m/z*: C₂₆H₂₀NO₄S (M + H)⁺ calcd for 442.1108, found 442.1113.

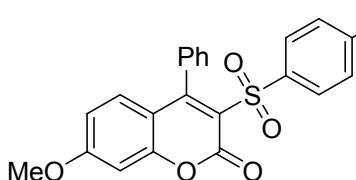
(2-((4-Methoxyphenyl)sulfonyl)ethene-1,1-diyl)dibenzene (4): yield: 39.9 mg, 57%; white solid; mp



84-85 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.49 (d, *J* = 9.2 Hz, 2H), 7.36-7.26 (m, 6H), 7.21-7.18 (m, 2H), 7.11-7.08 (m, 2H), 7.01 (s, 1H), 6.80 (d, *J* = 9.2 Hz, 2H), 3.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 163.0, 154.1, 139.0, 135.4, 132.9, 130.1, 129.7, 129.6, 129.2, 128.7, 128.4, 128.0,

127.7, 113.8, 55.5; HRMS (ESI-TOF) *m/z*: C₂₁H₁₉O₃S (M + H)⁺ calcd for 351.1049, found 351.1055.

7-Methoxy-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (6): yield: 67.5 mg, 80%;



yellow oli; ¹H NMR (400 MHz, CDCl₃) δ: 7.93 (d, *J* = 8.8 Hz, 2H), 7.56-7.55 (m, 3H), 7.32-7.30 (m, 2H), 6.96-6.93 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.78 (s, 1H), 6.74-6.71 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 165.0, 163.6, 158.9, 156.1, 155.9, 133.1, 131.9, 131.4, 131.1, 128.9, 128.0, 127.3, 122.7,

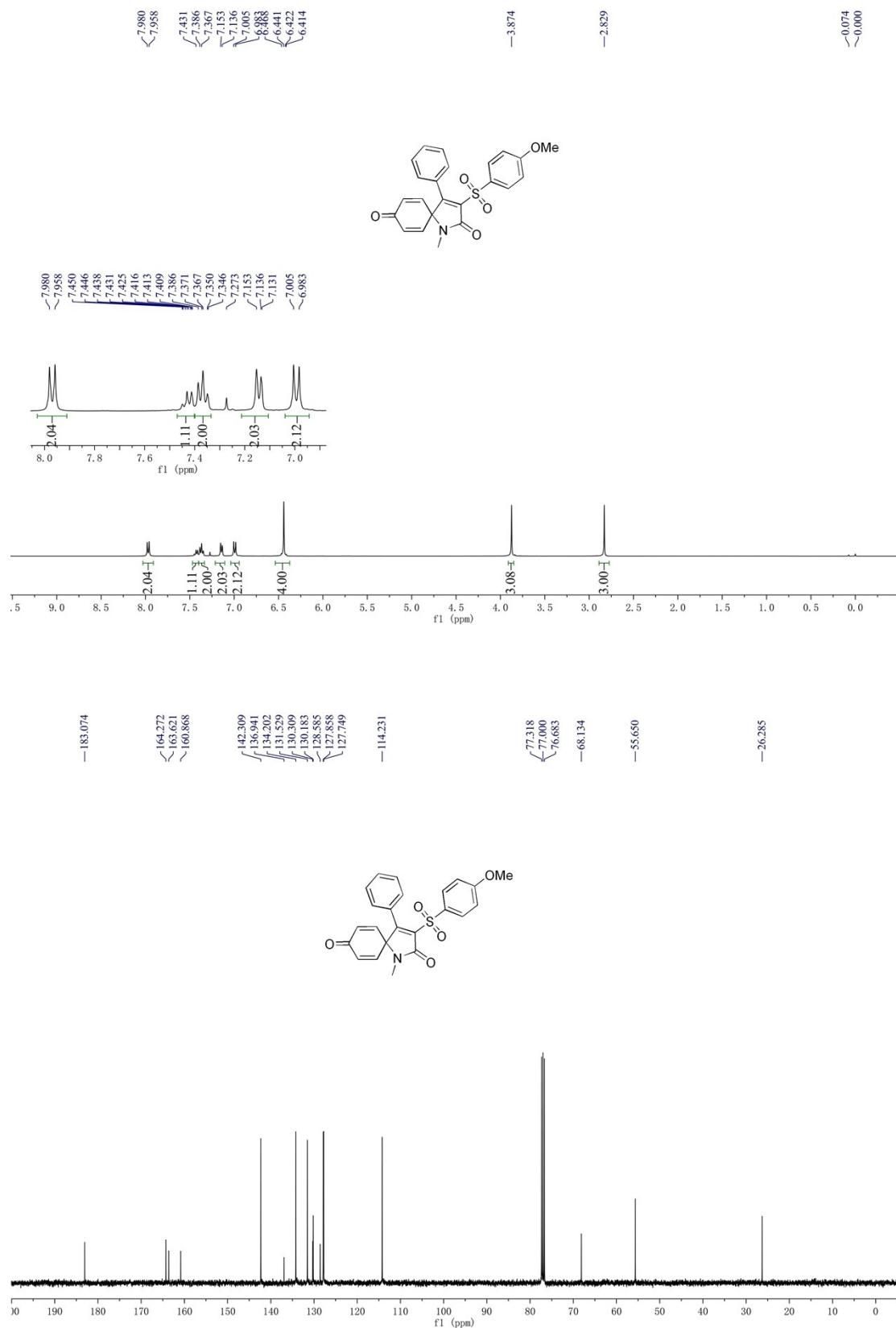
113.7, 113.6, 113.4, 100.1, 56.0, 55.6; HRMS (ESI-TOF) *m/z*: C₂₃H₁₉O₆S (M + H)⁺ calcd for 423.0897, found 423.0902.

4. Reference

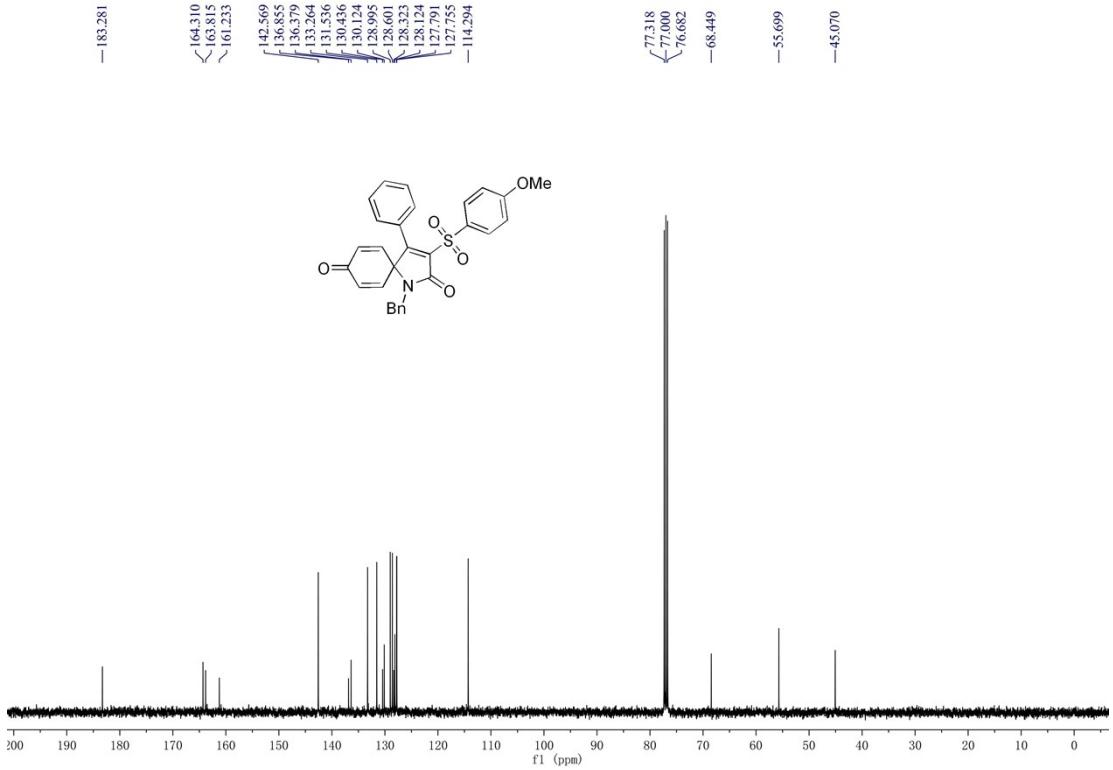
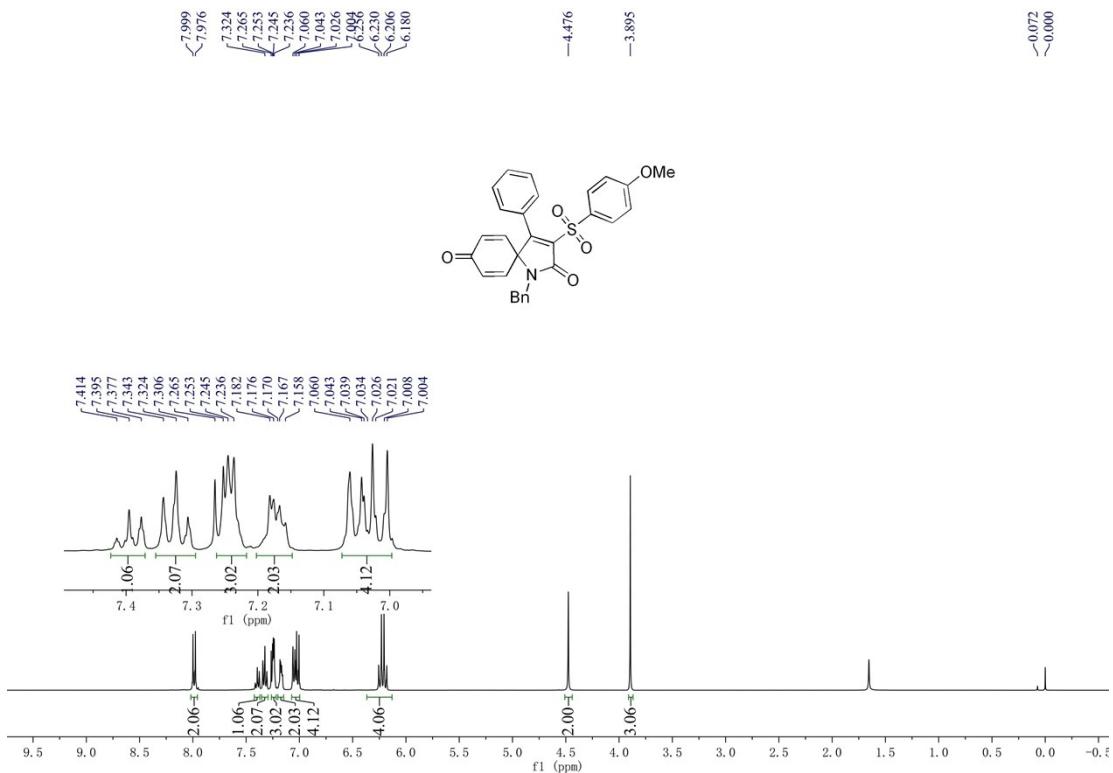
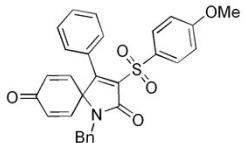
- [1] S. Tang, P. Peng, S.-F. Pi, Y. Liang, N.-X. Wang and J.-H. Li, *Org. Lett.*, 2008, **10**, 1179.
- [2] Q.-F. Yu, Y.-H. Zhang, Q. Yin, B.-X. Tang, R.-Y. Tang, P. Zhang and J.-H. Li, *J. Org. Chem.*; 2008, **7**, 3658.
- [3] Y. Liu, Q.-L. Wang, C.-S. Zhou, B.-Q. Xiong, P.-L. Zhang, C.-A. Yang and K.-W. Tang, *J. Org. Chem.*; 2018, **83**, 2210.

(5) Spectra

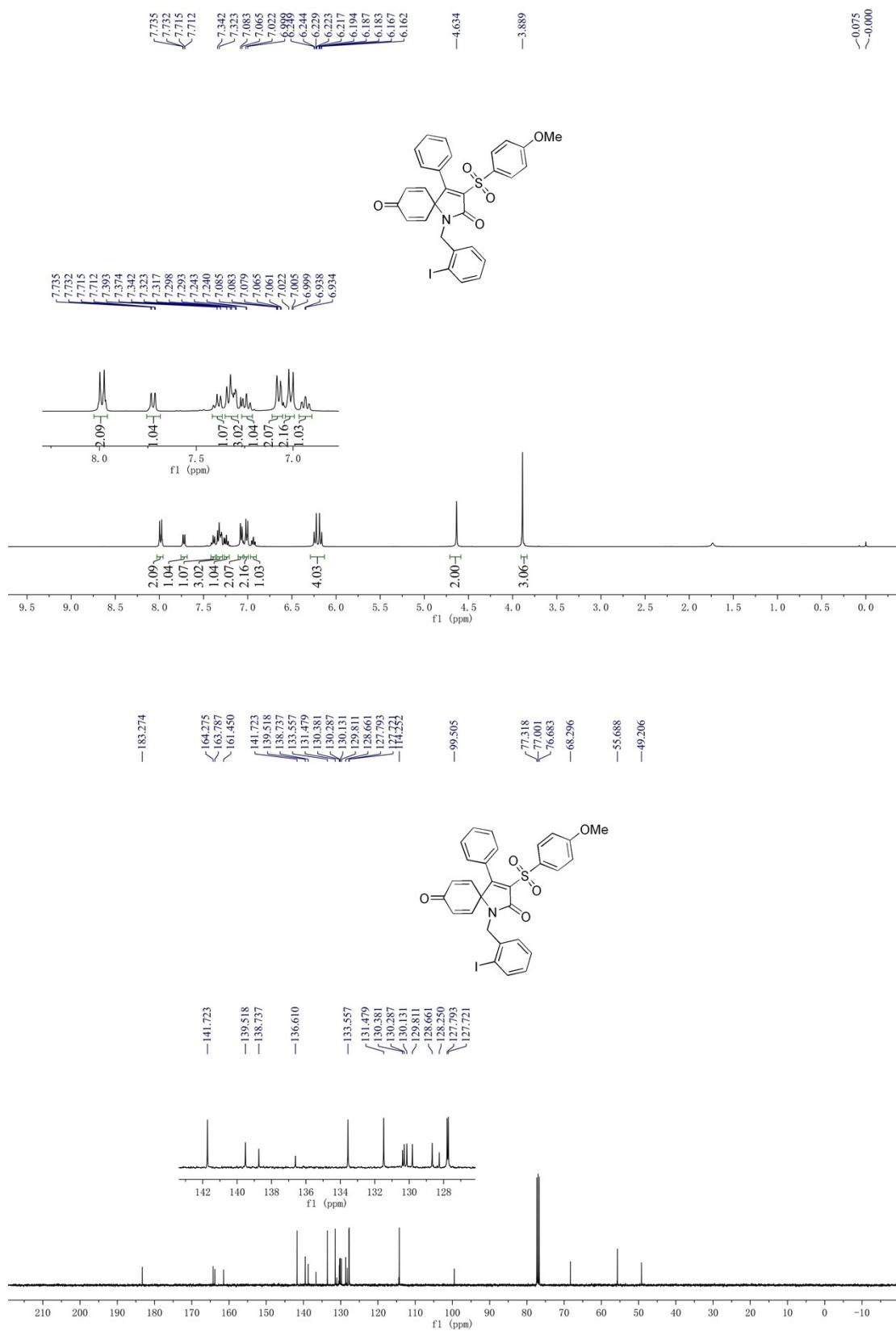
3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3aa)



1-Benzyl-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ba)



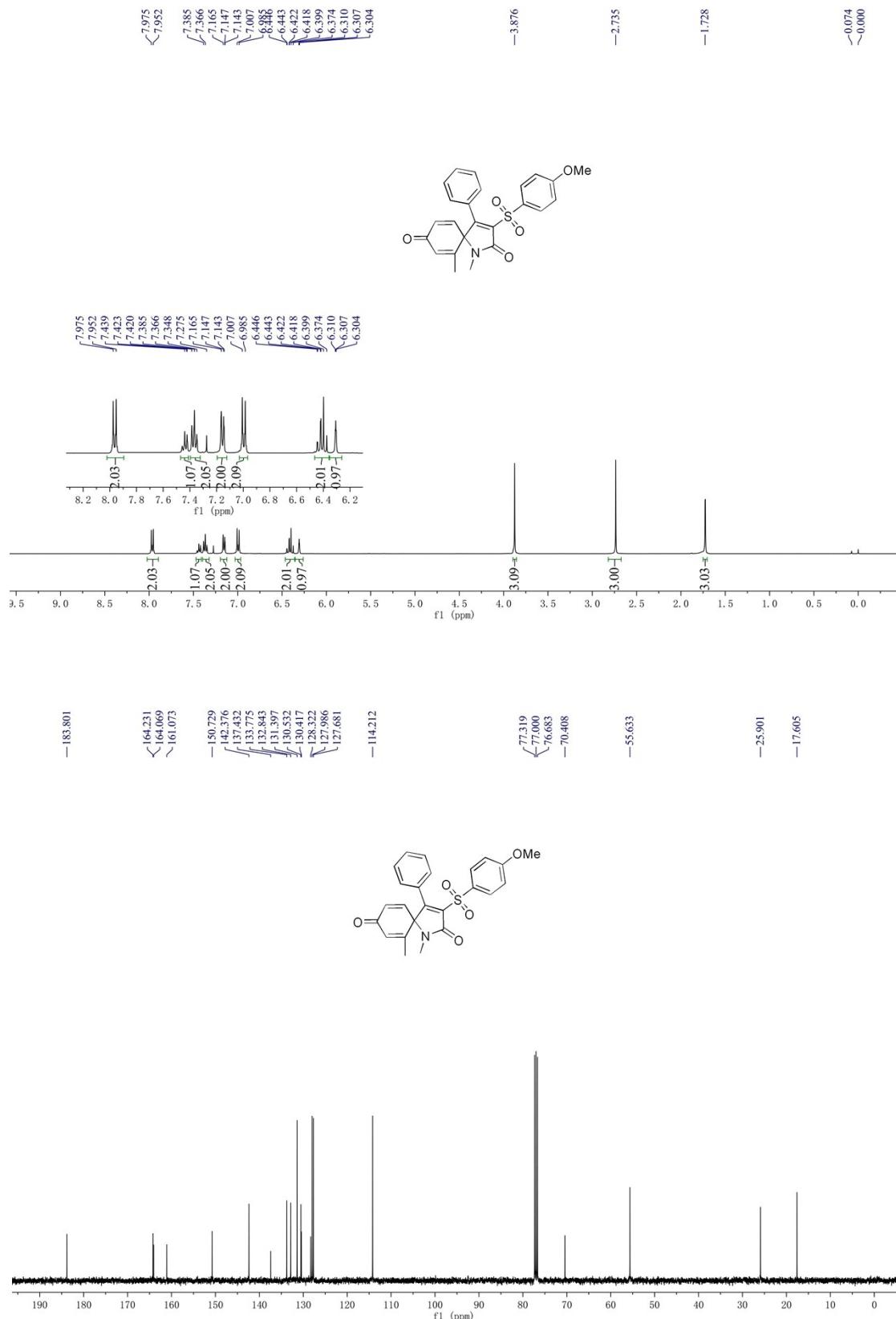
1-(2-Iodobenzyl)-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ca)



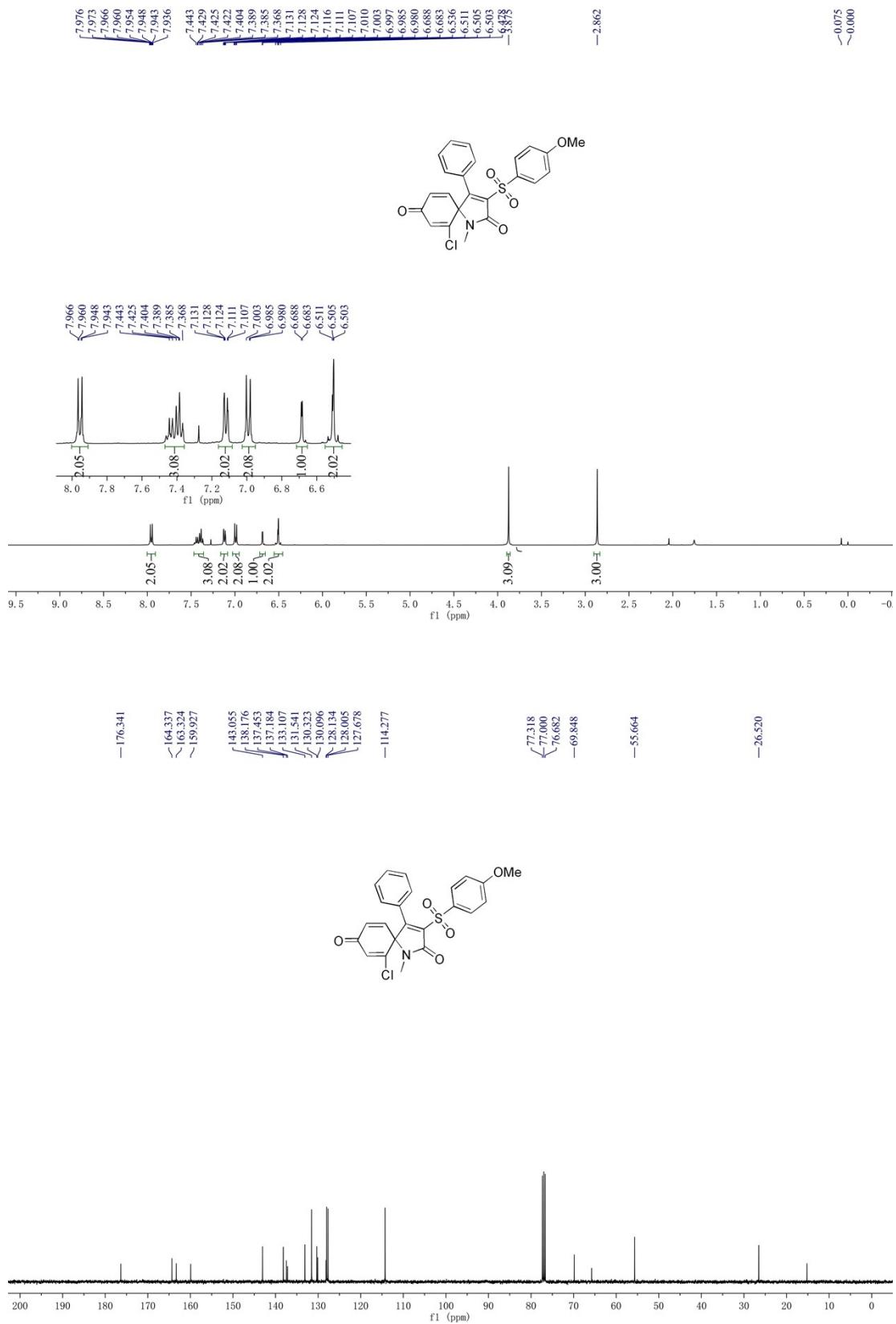
1-Acetyl-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ea)



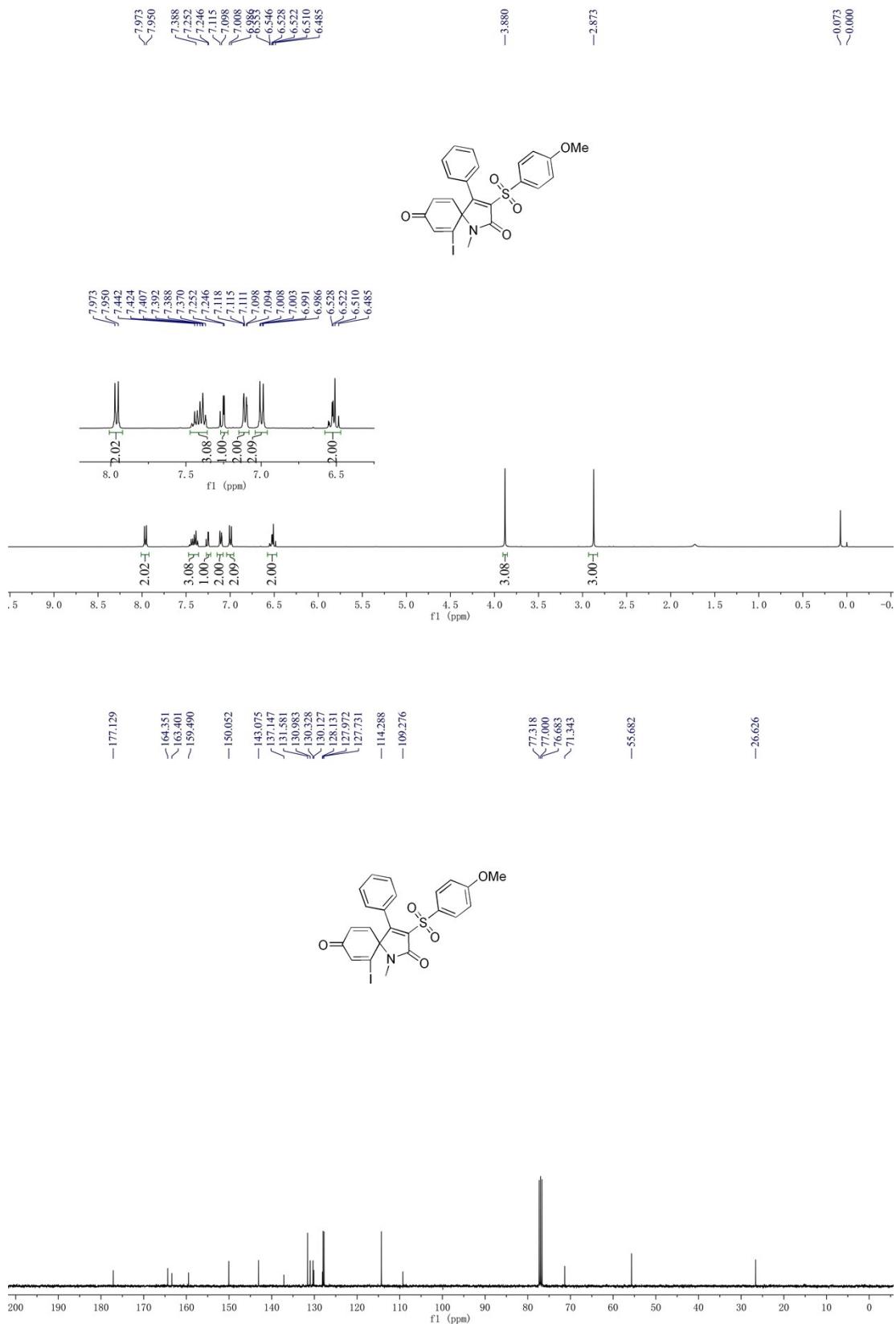
3-((4-Methoxyphenyl)sulfonyl)-1,6-dimethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3fa)



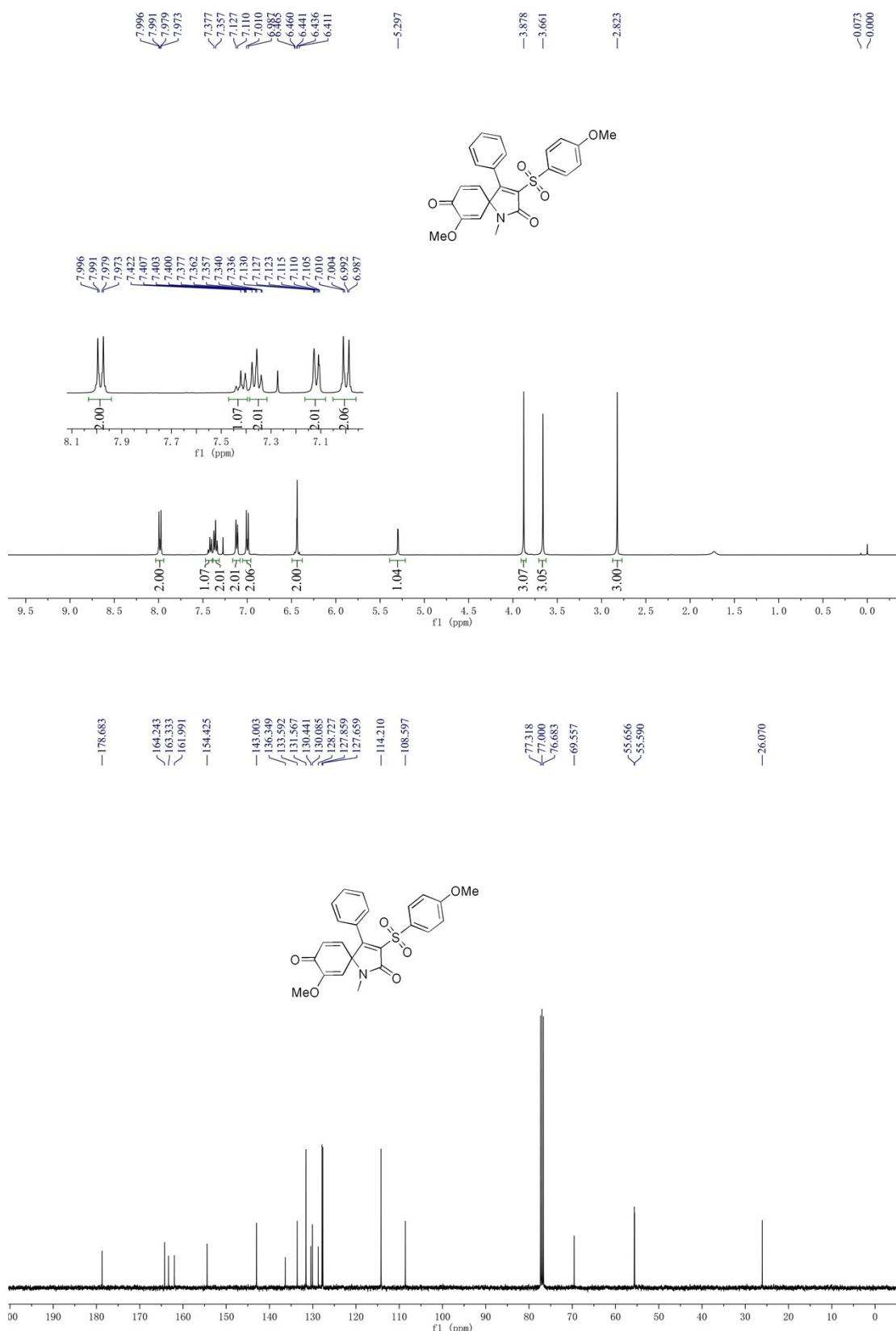
6-Chloro-3-((4-methoxyphenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ga)



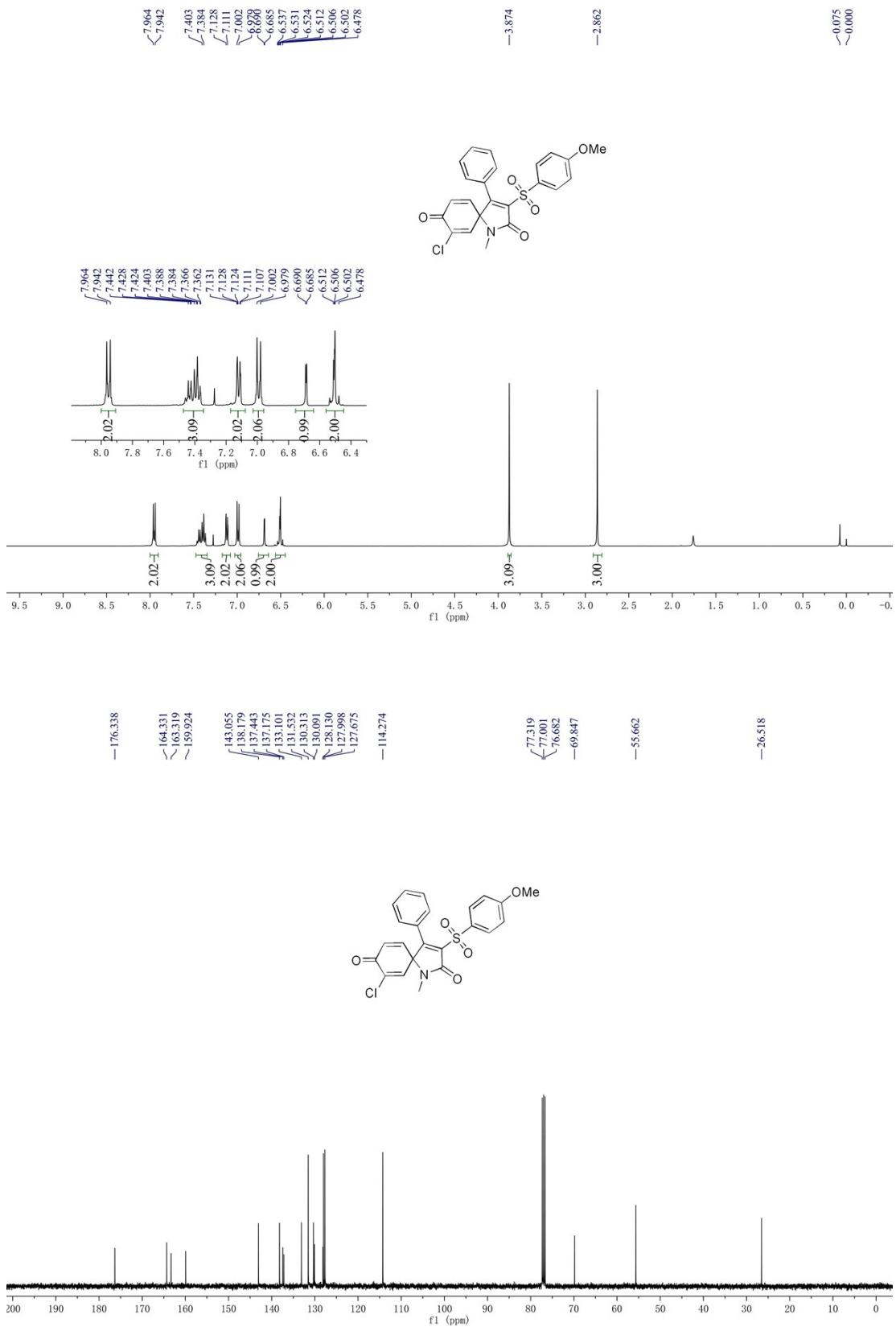
6-Iodo-3-((4-methoxyphenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ha)



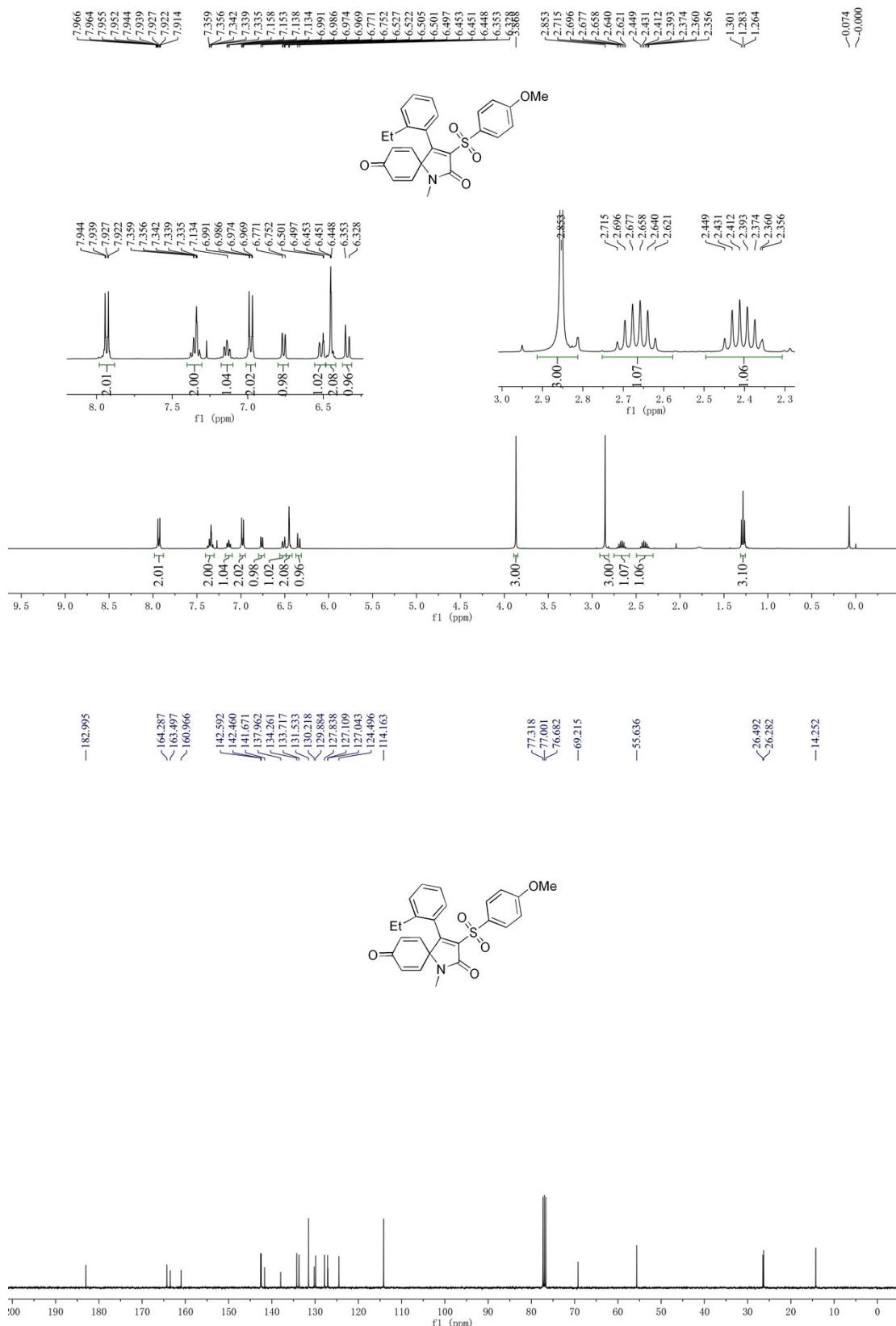
7-Methoxy-3-(((4-methoxyphenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ia)



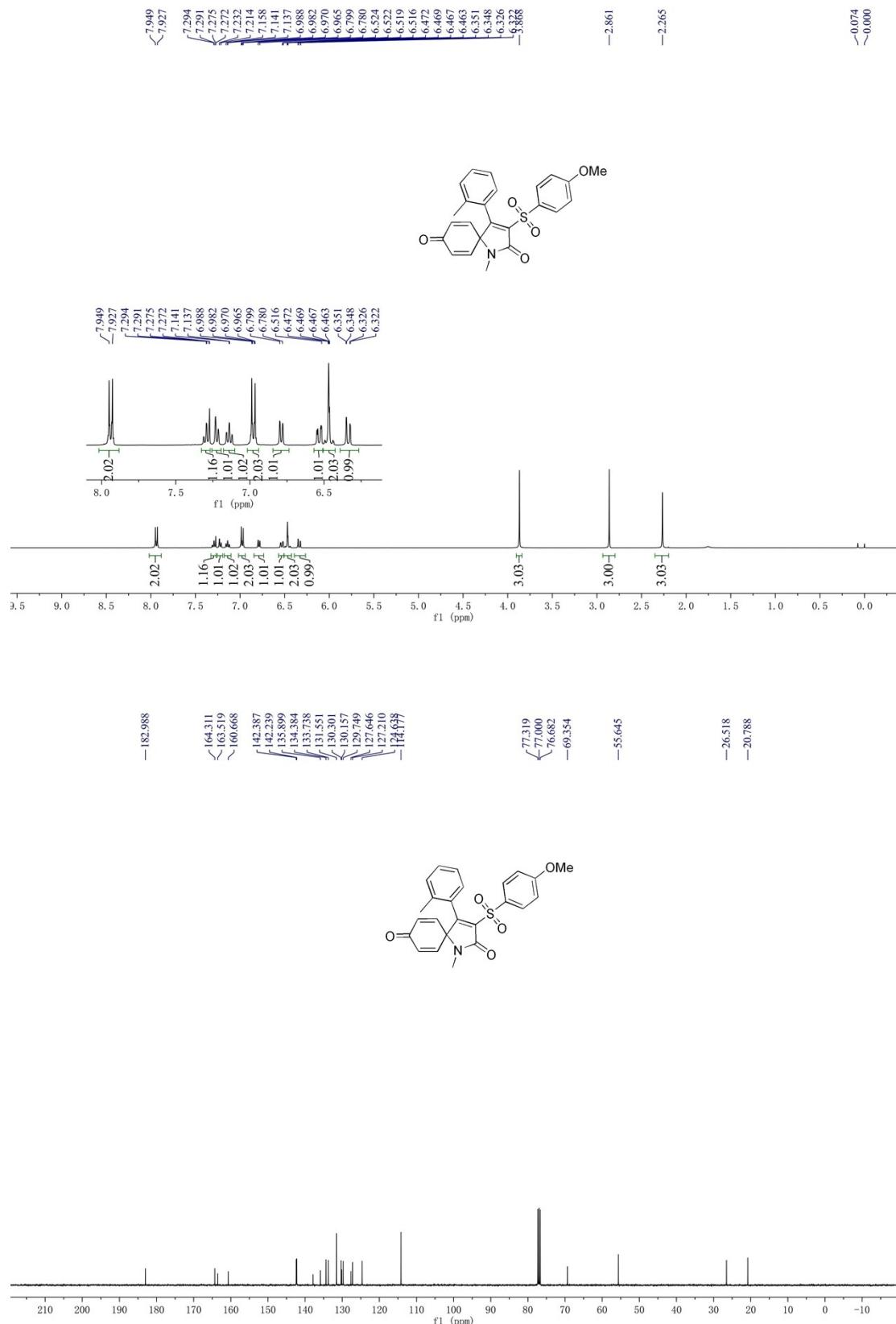
7-Chloro-3-((4-methoxyphenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ja)



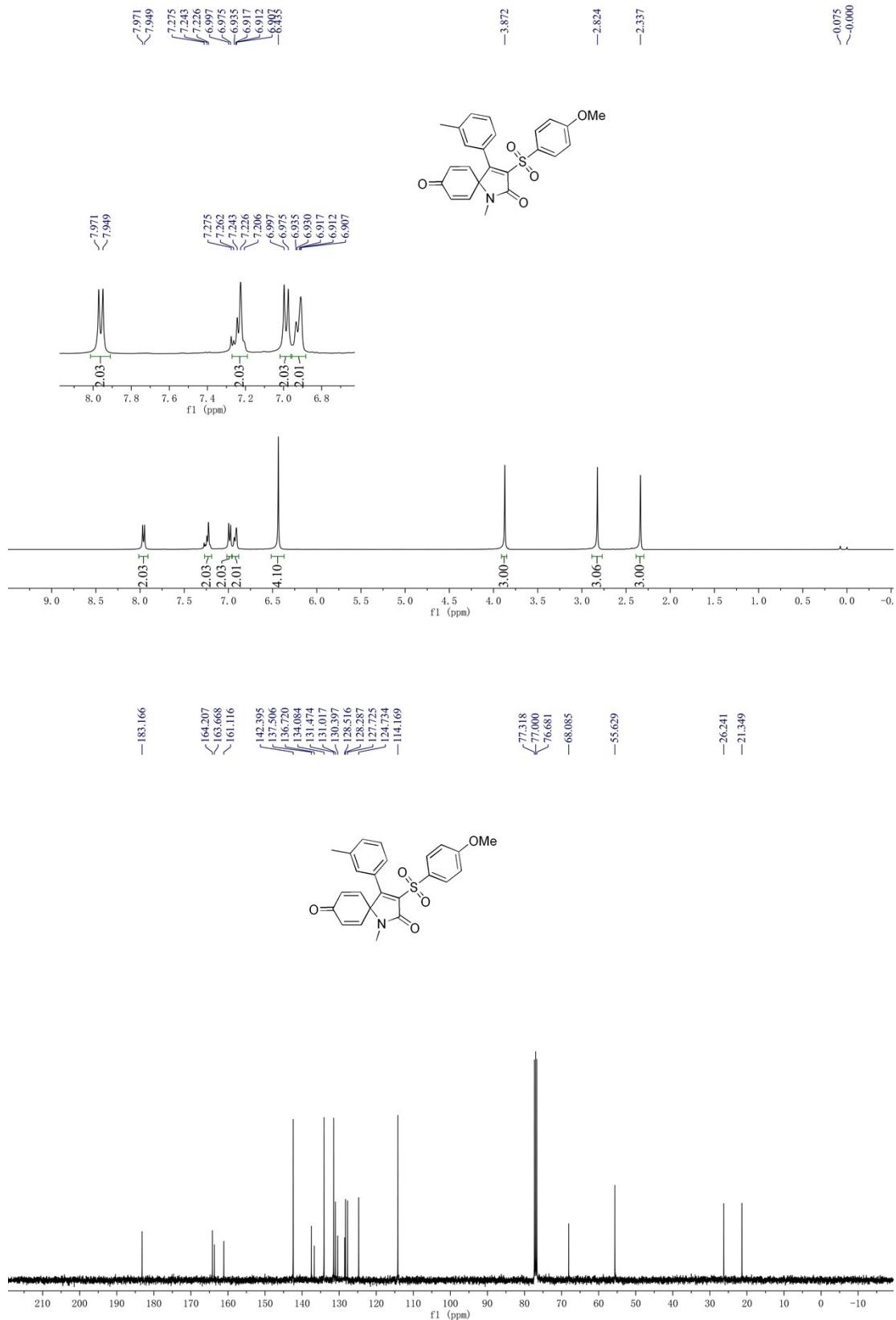
4-(2-Ethylphenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ka)



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

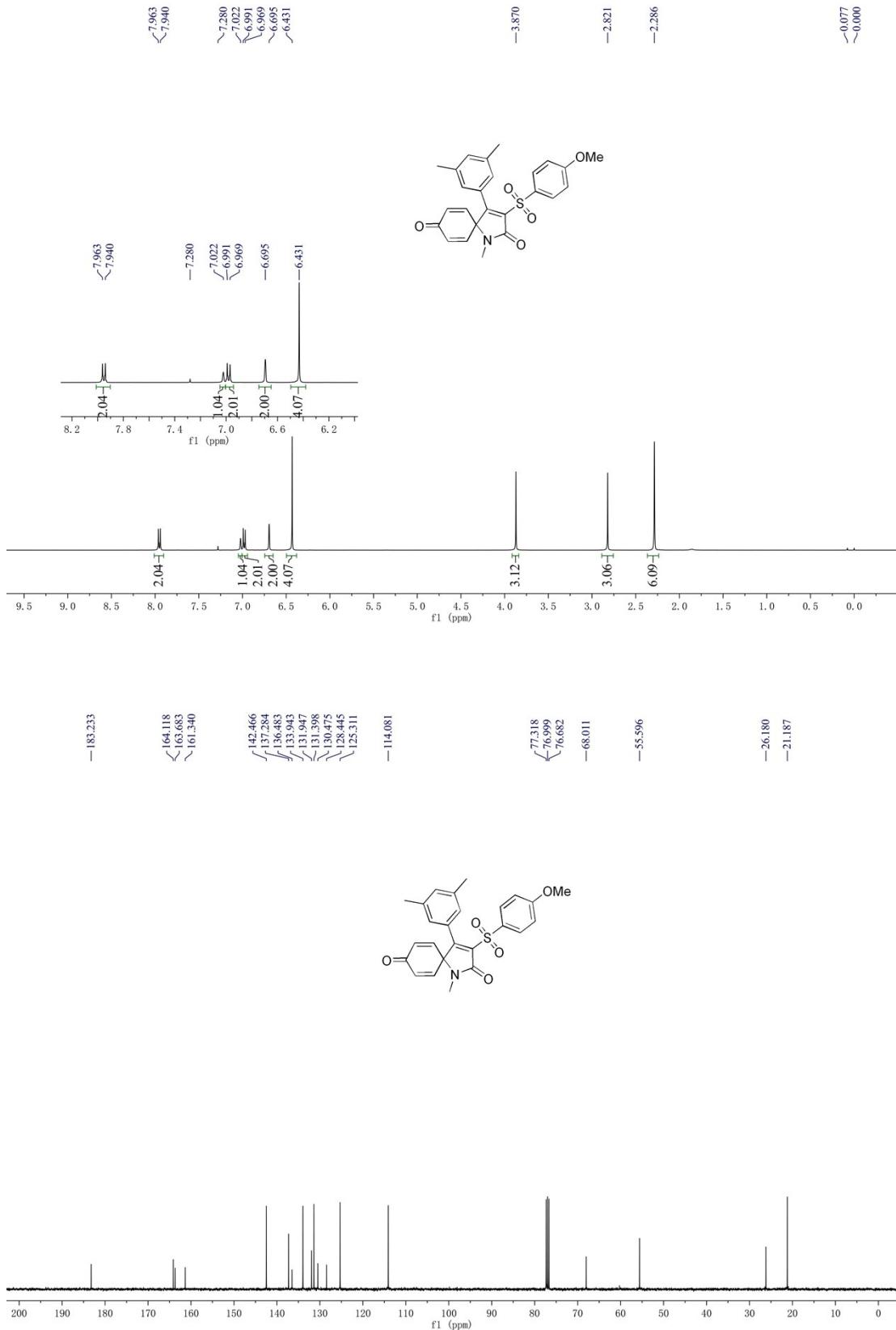


3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(*m*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ma)

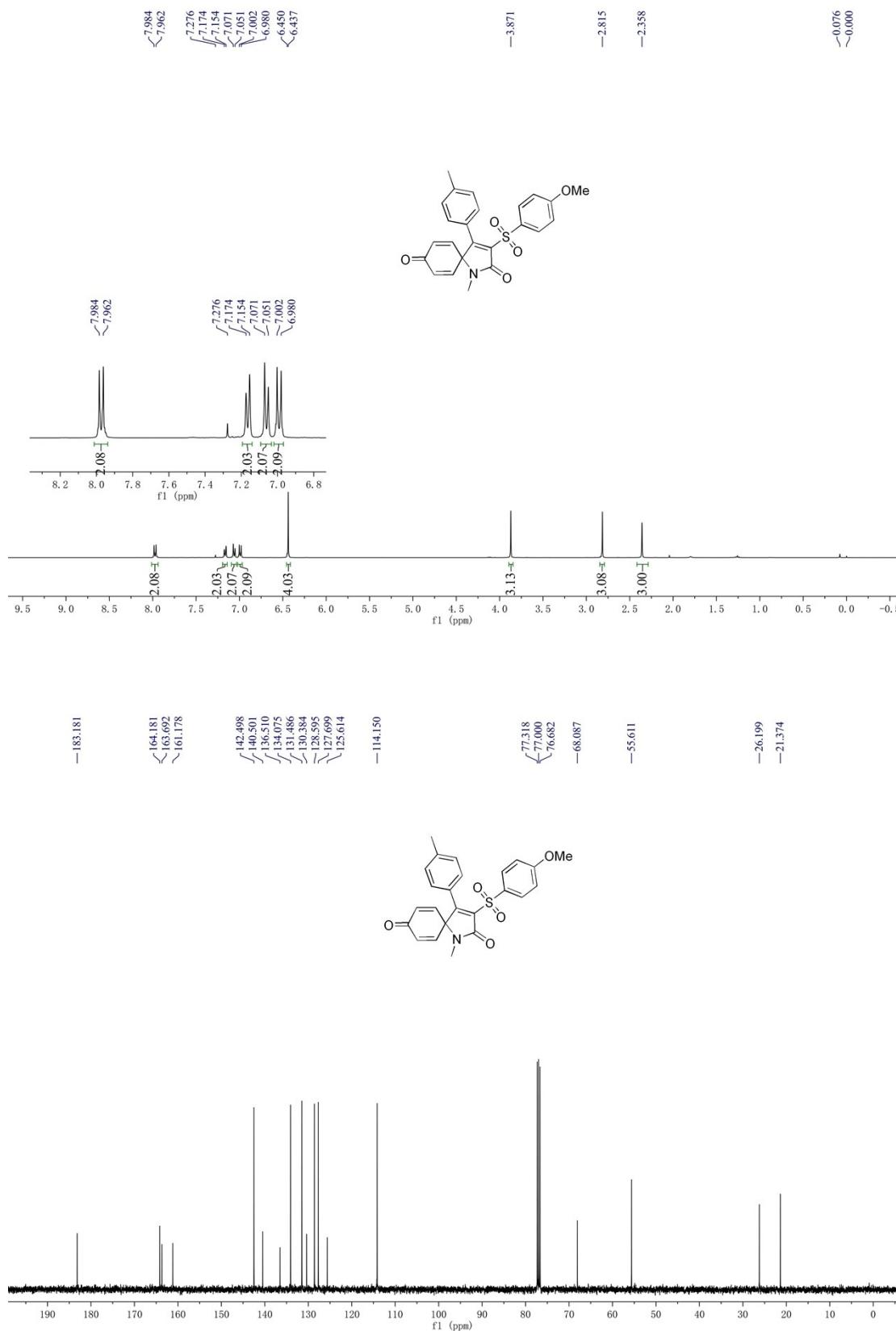


4-(3,5-Dimethylphenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

(3na)

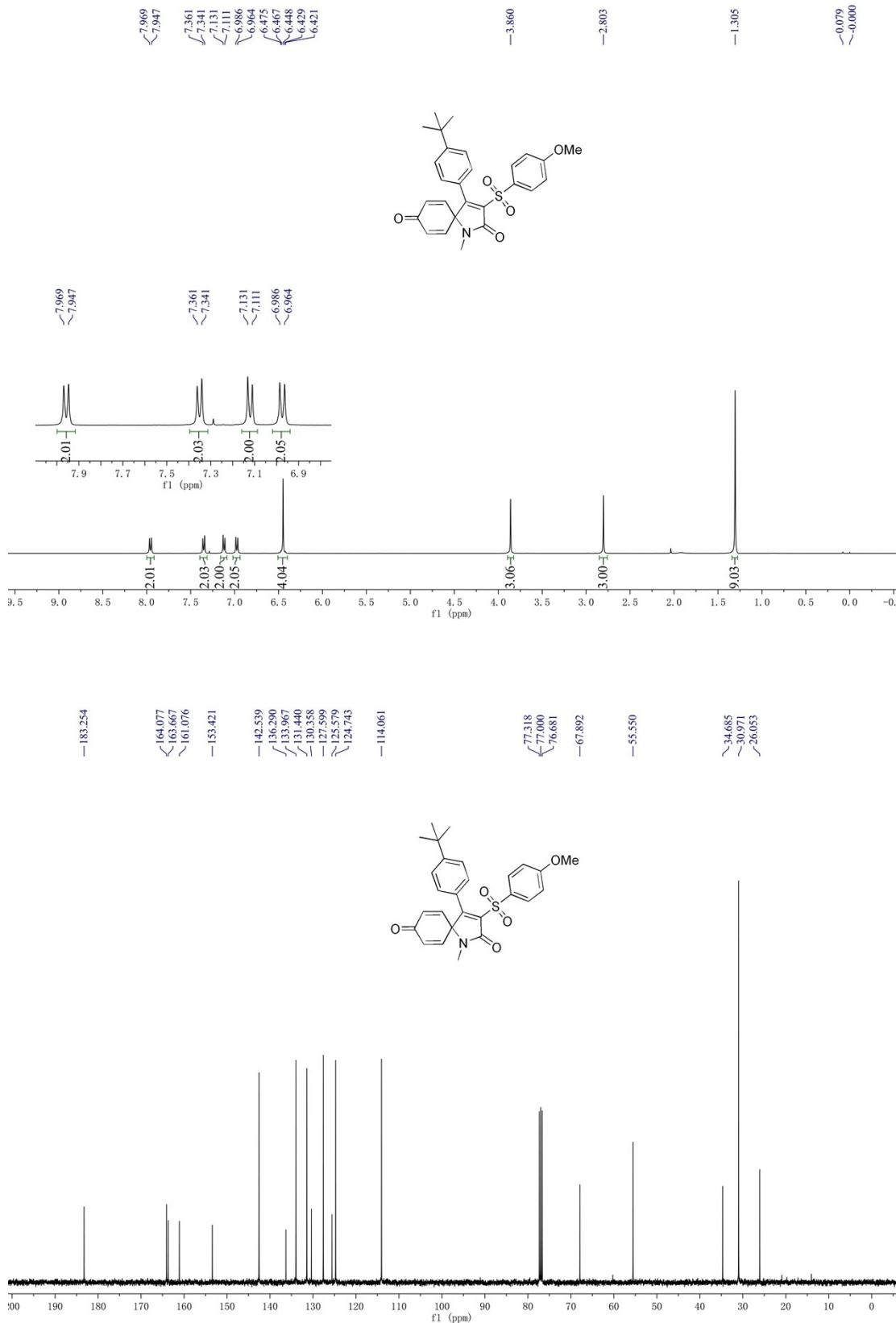


3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(*p*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3oa)



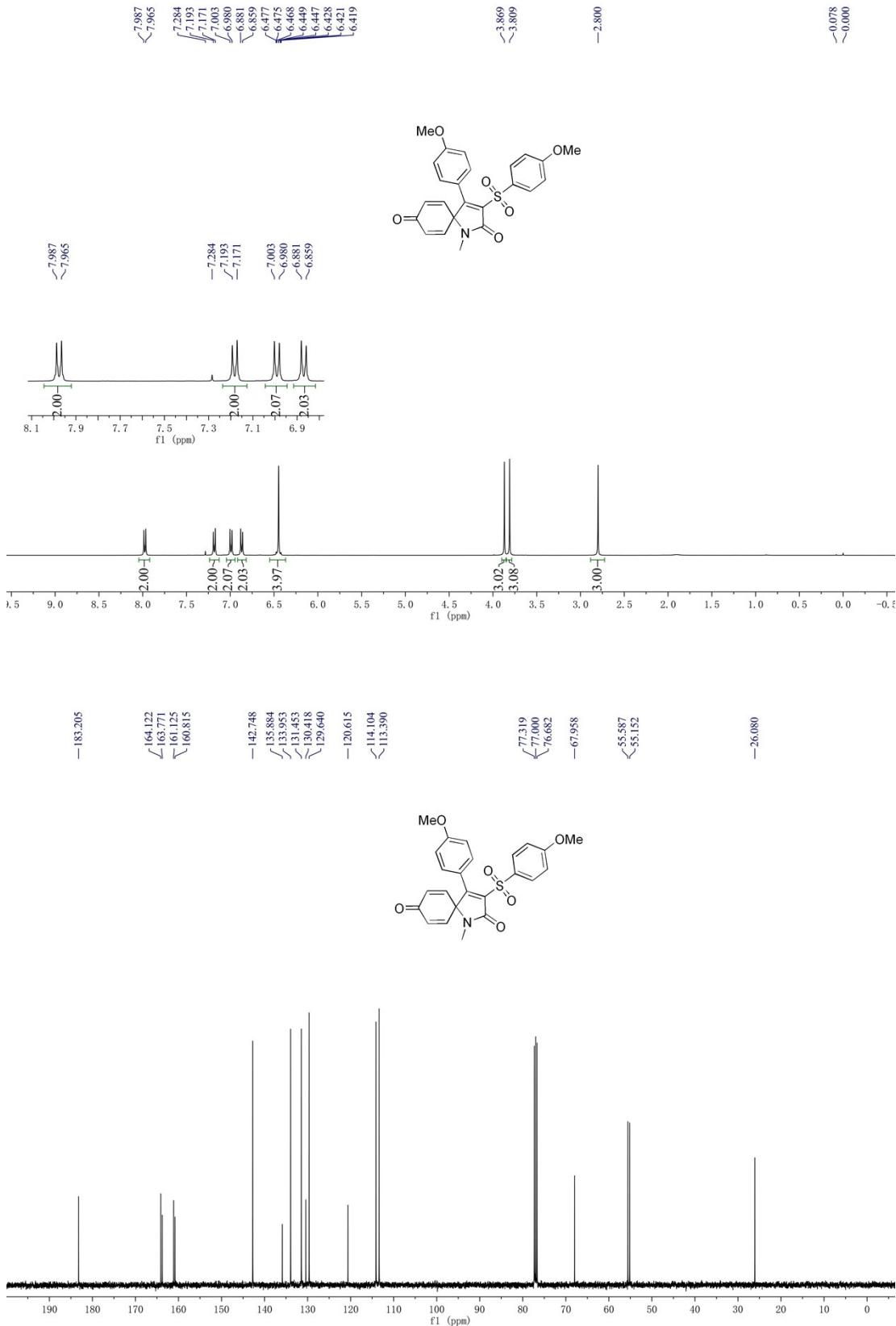
4-(4-(*tert*-Butyl)phenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

(3pa)

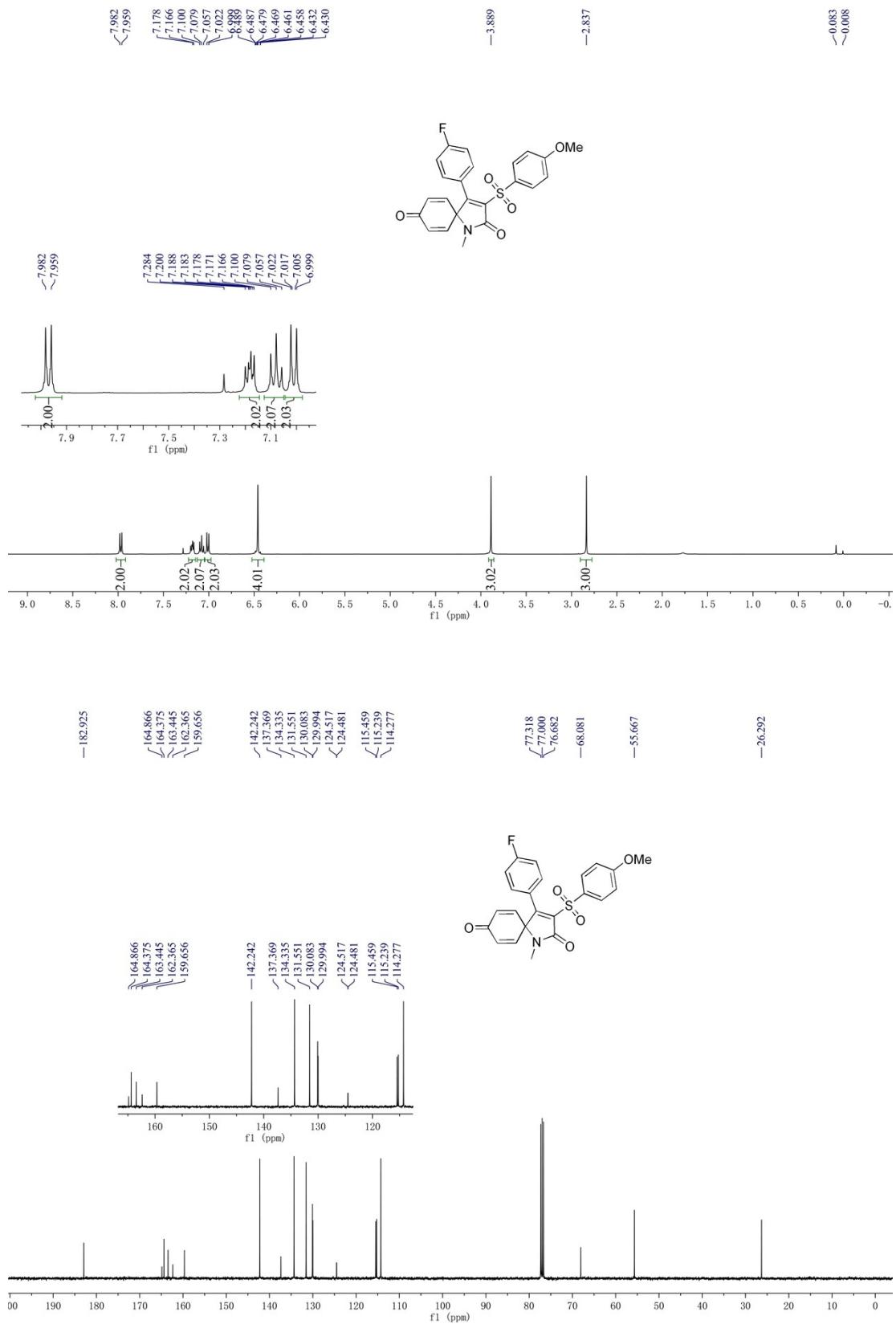


4-(4-Methoxyphenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

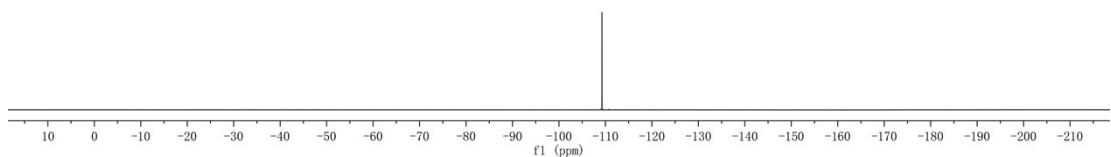
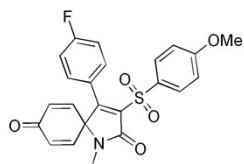
(3qa)



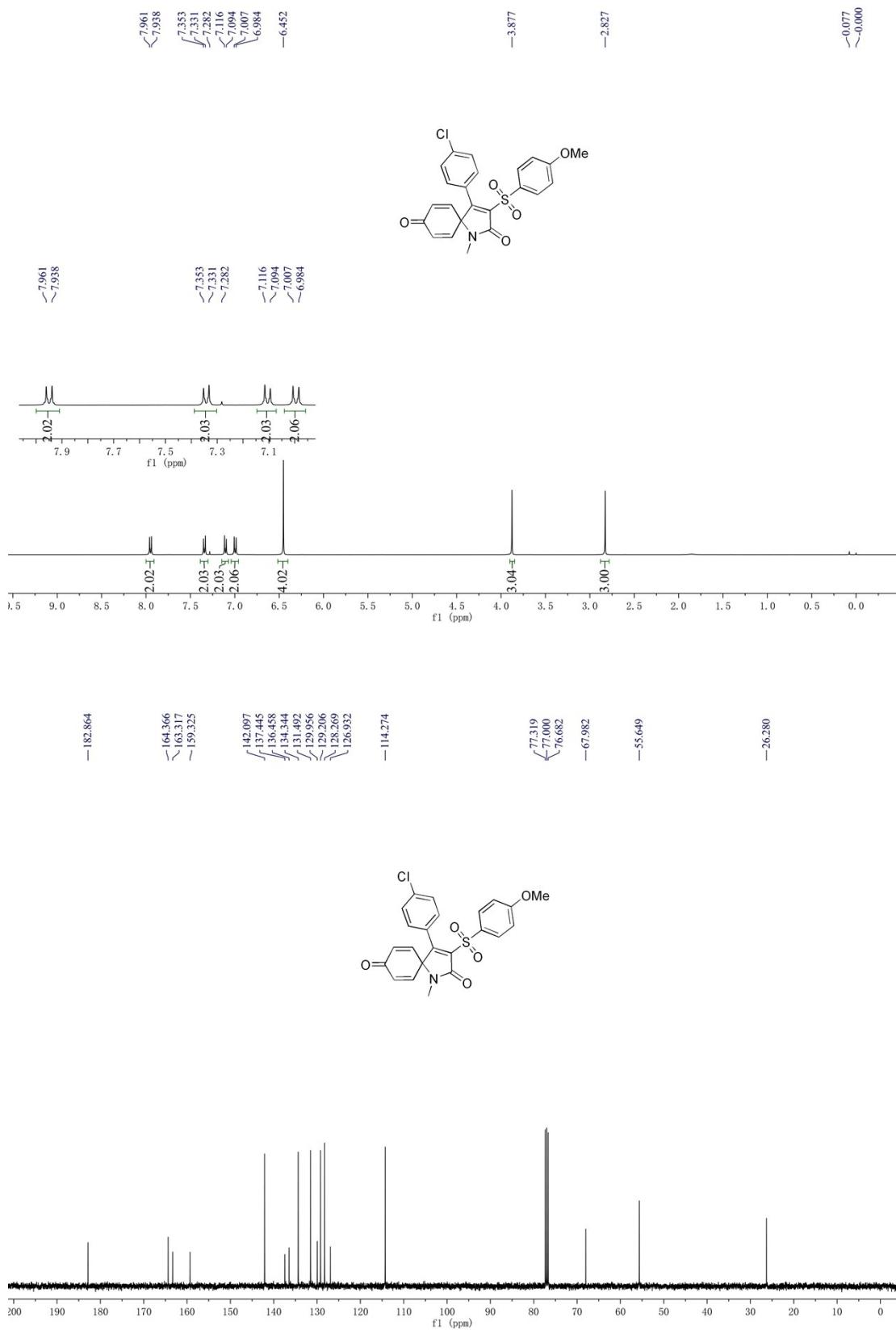
4-(4-Fluorophenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ra)



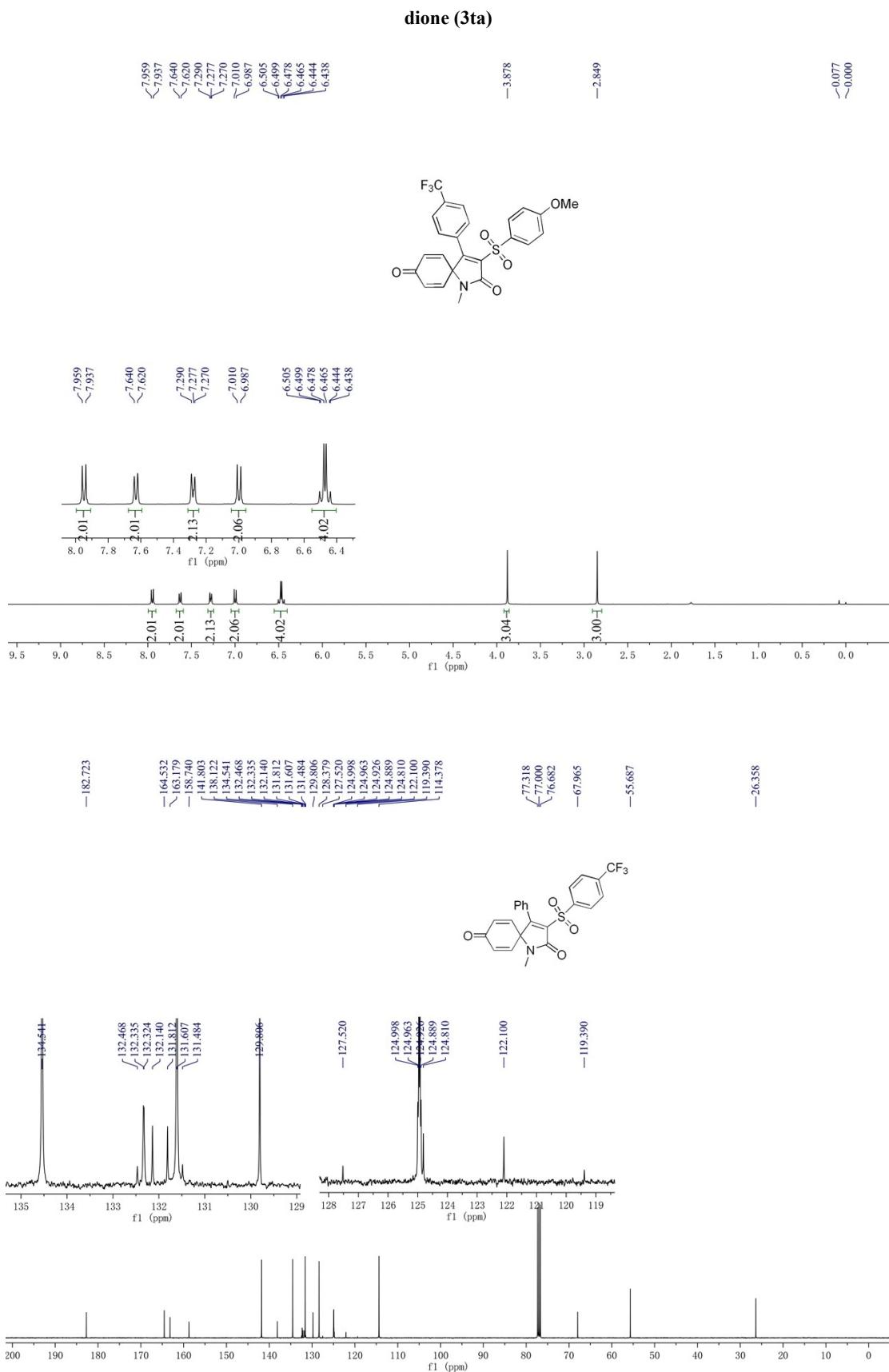
-109.249



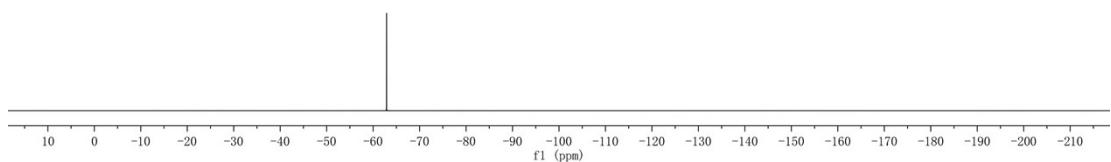
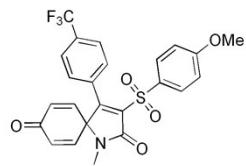
4-(4-Chlorophenyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3sa)



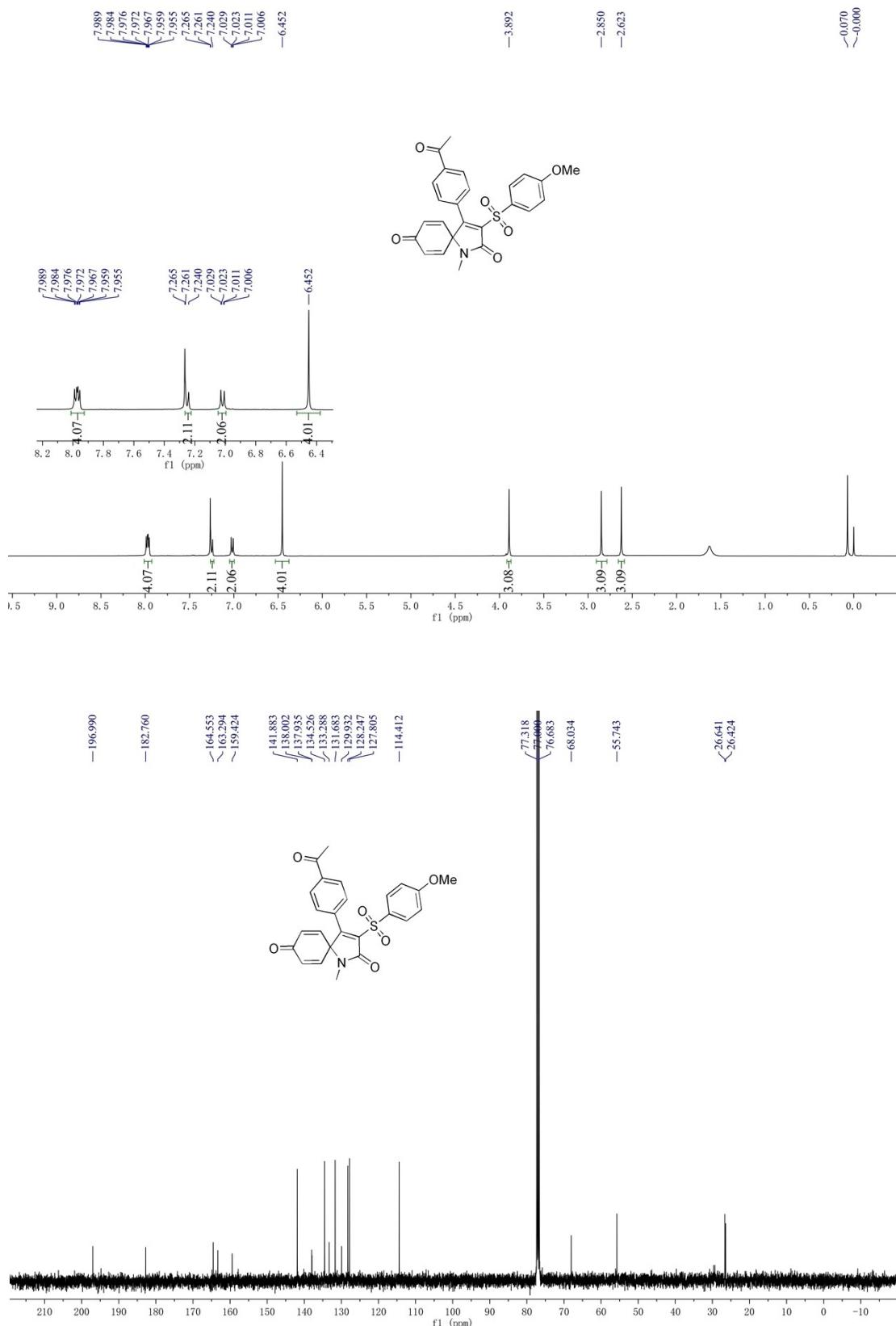
3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(4-(trifluoromethyl)phenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ta)



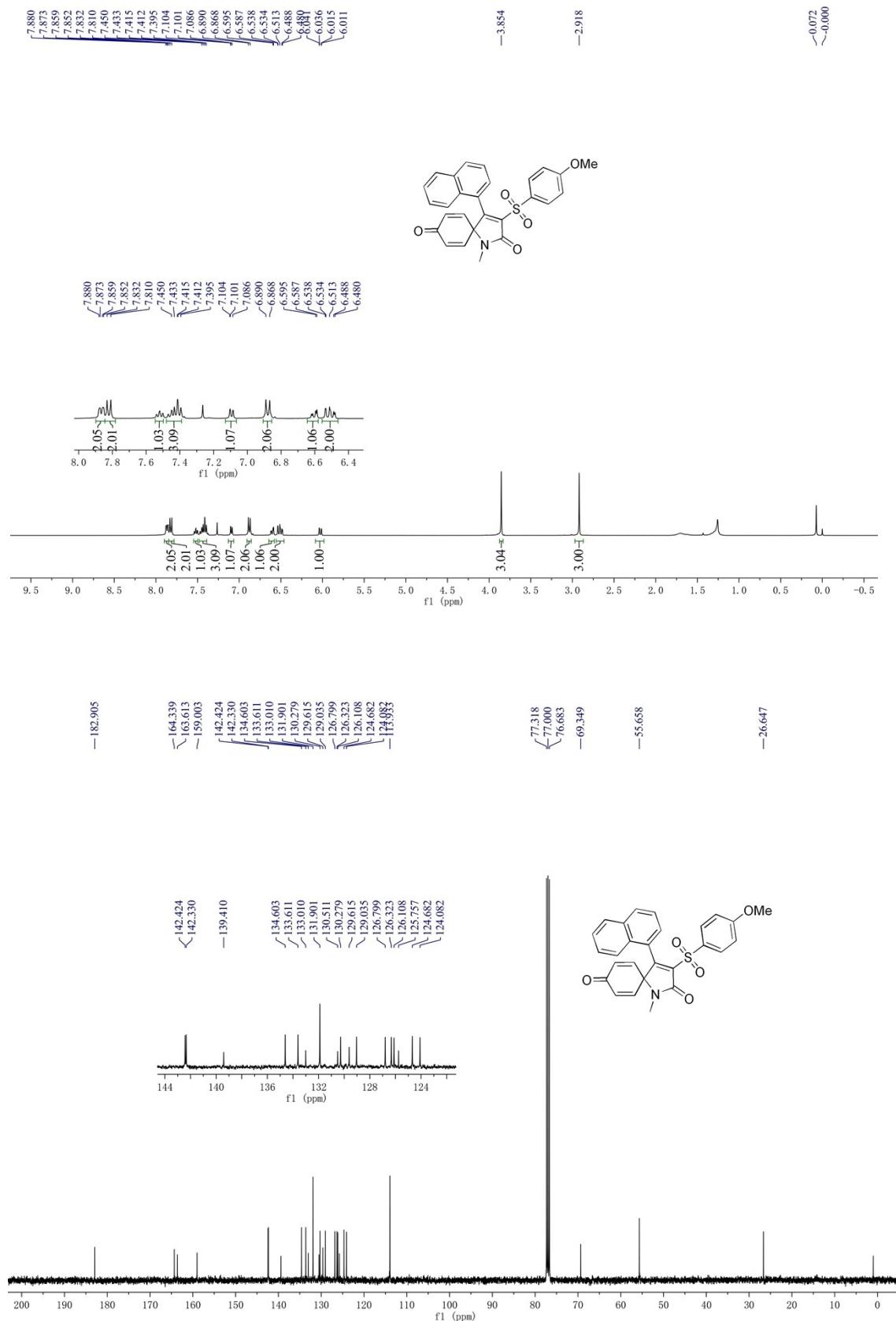
—62.898



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



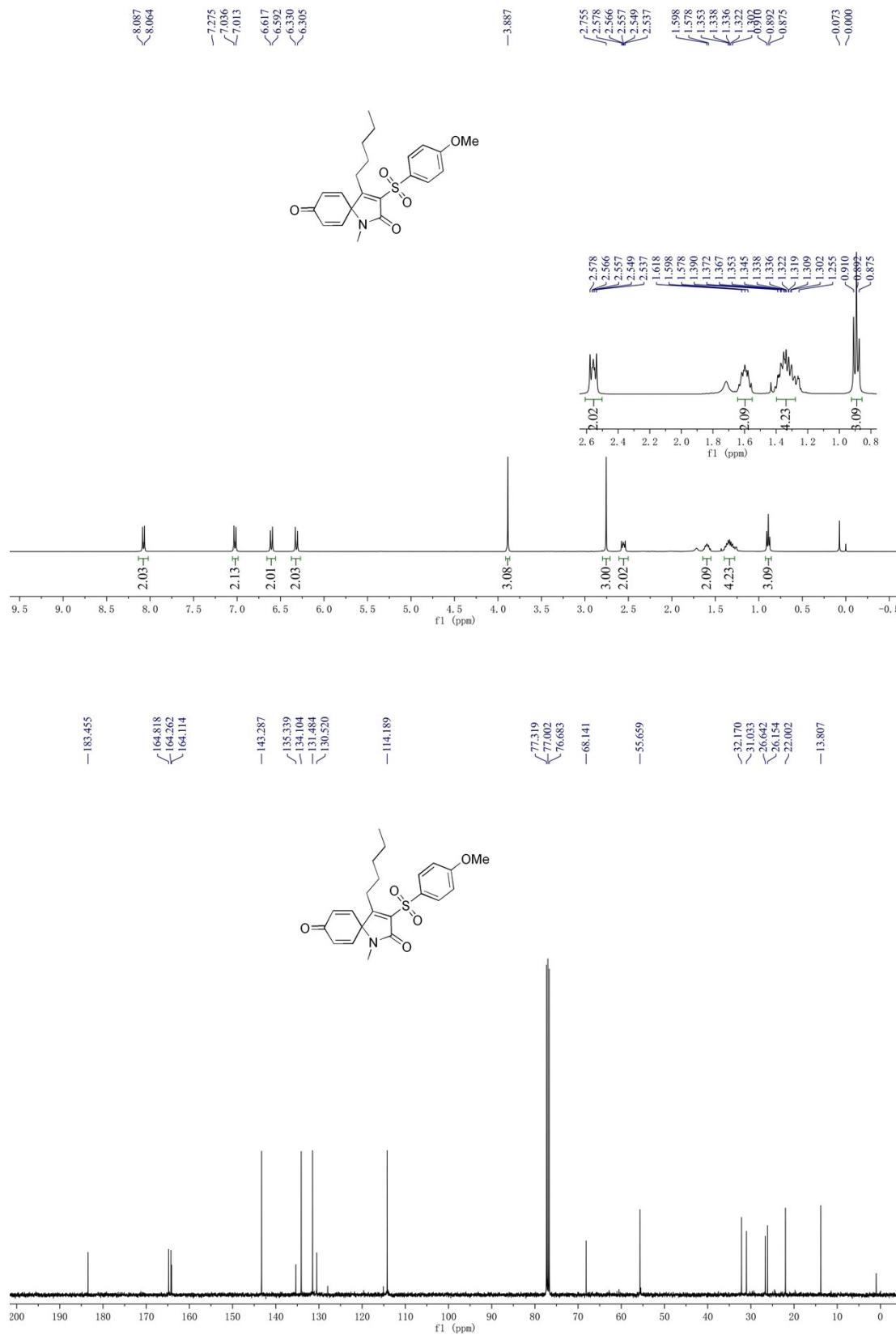
3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(naphthalen-1-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3va)



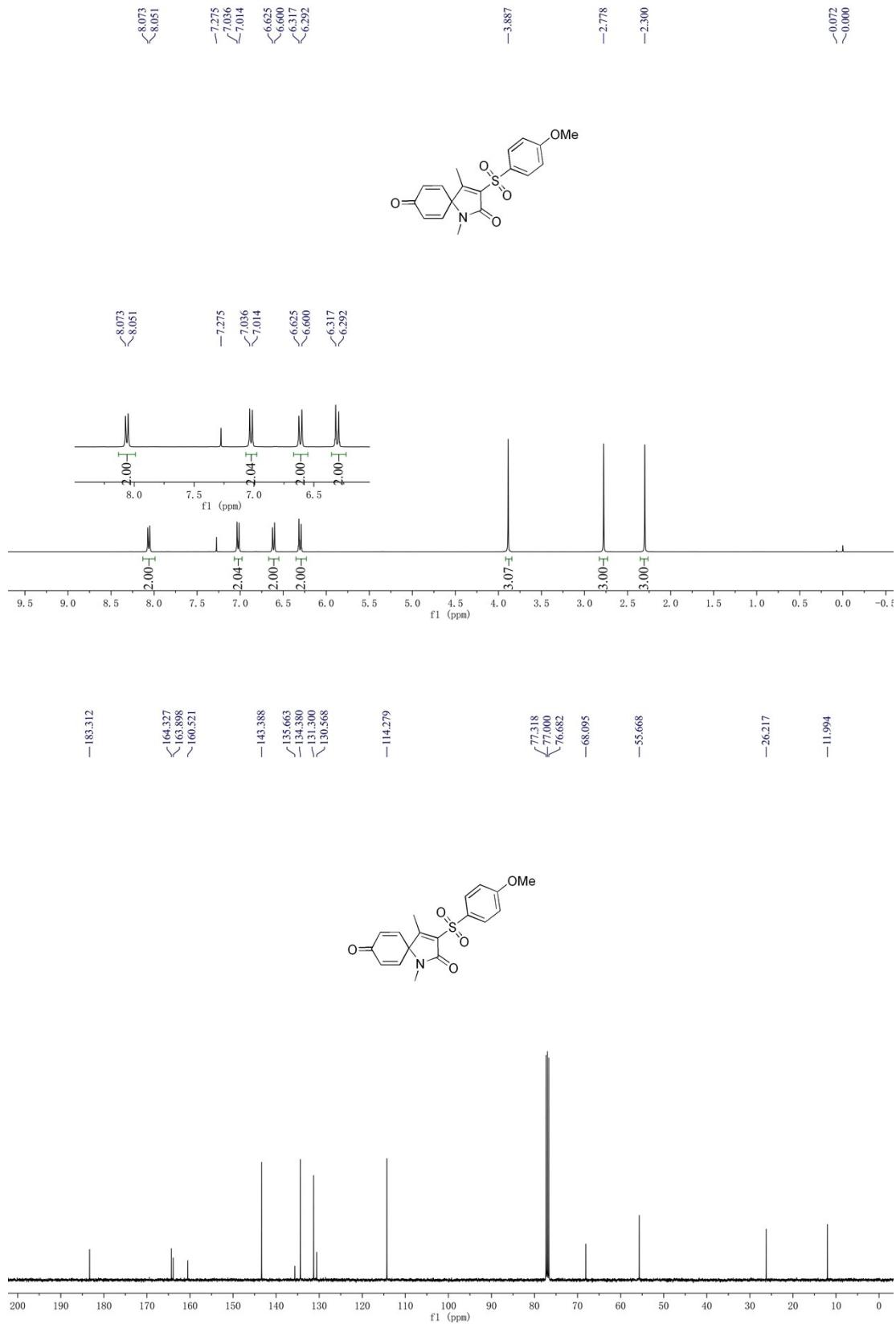
3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3wa)



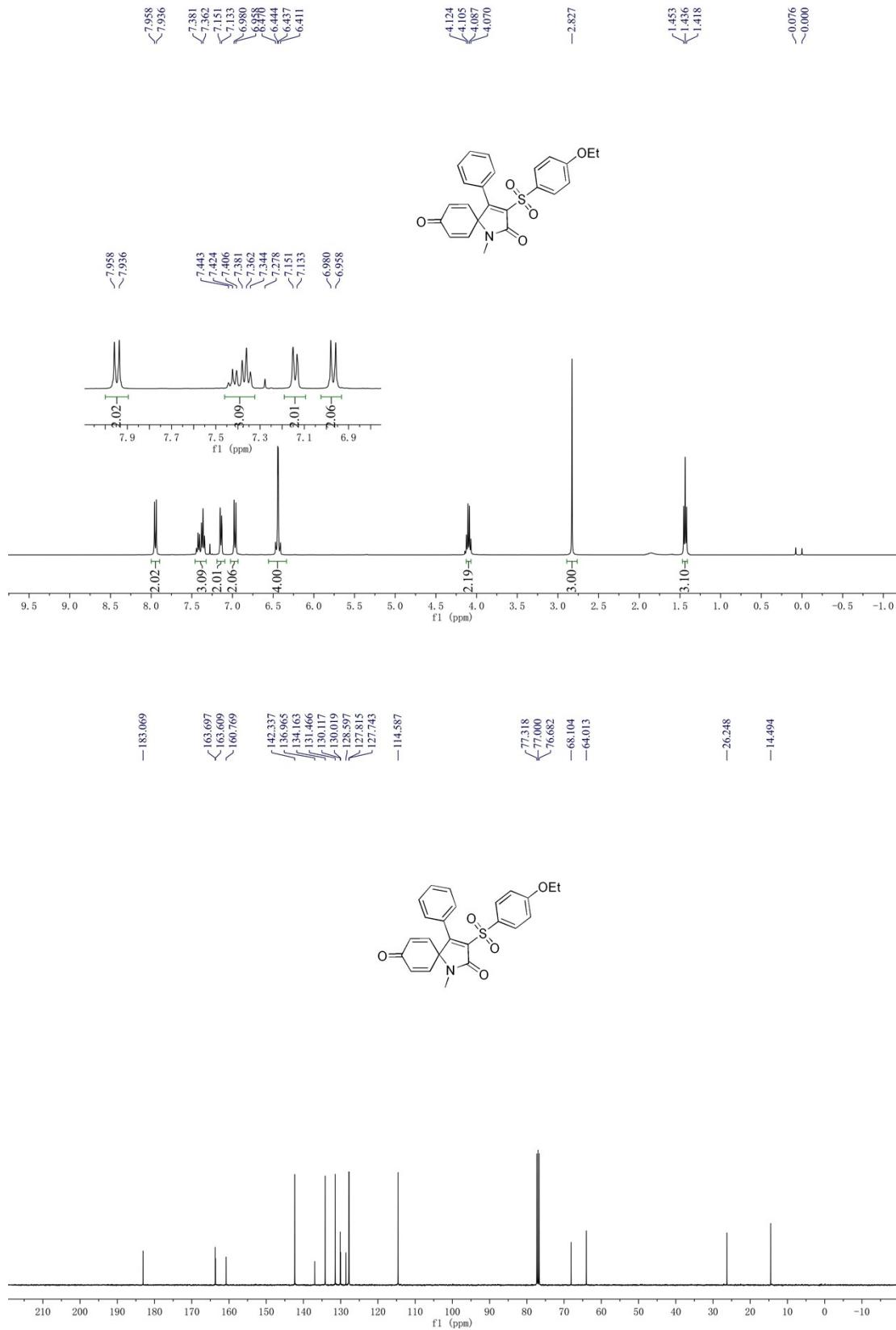
3-((4-Methoxyphenyl)sulfonyl)-1-methyl-4-pentyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3xa)



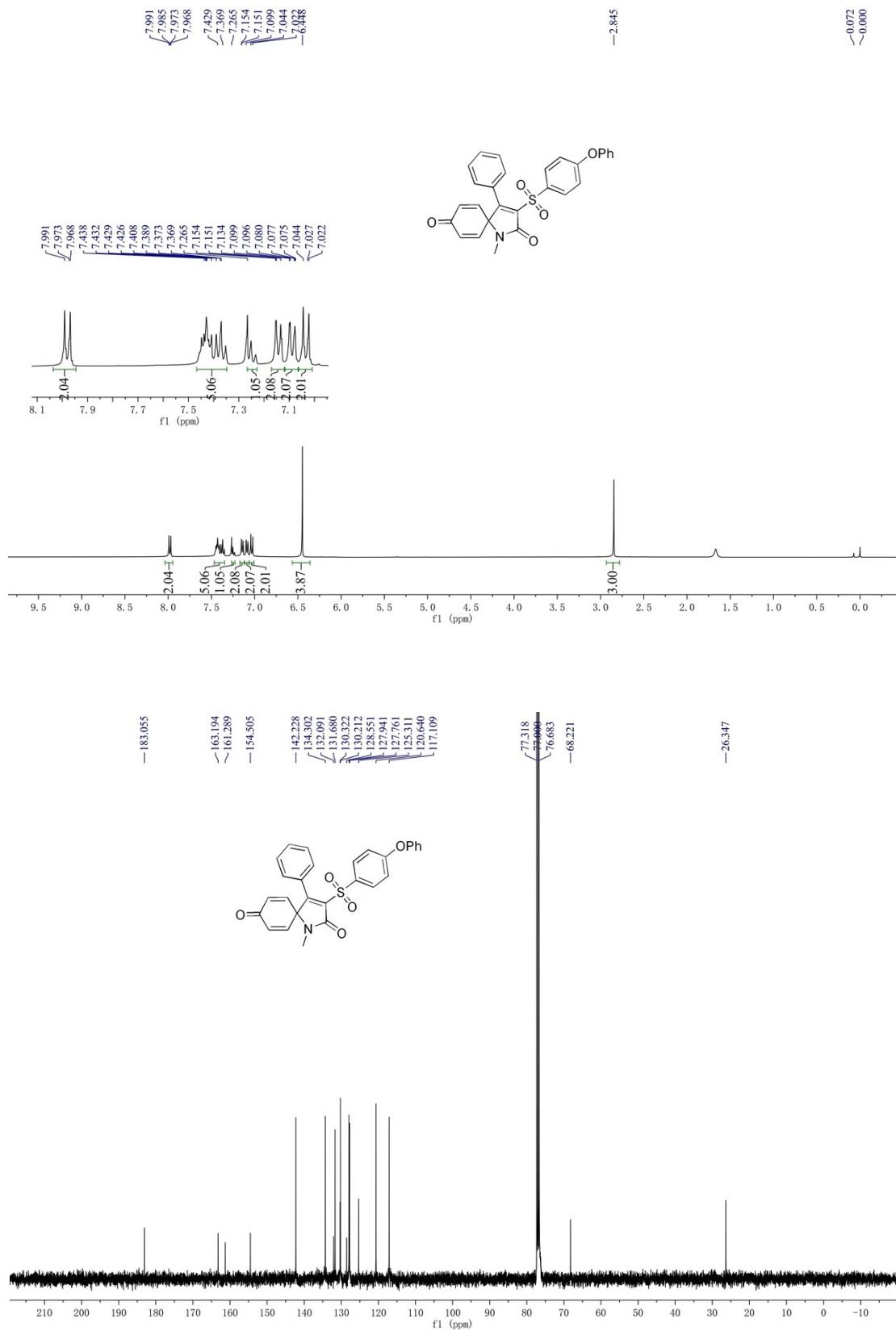
3-((4-Methoxyphenyl)sulfonyl)-1,4-dimethyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ya)



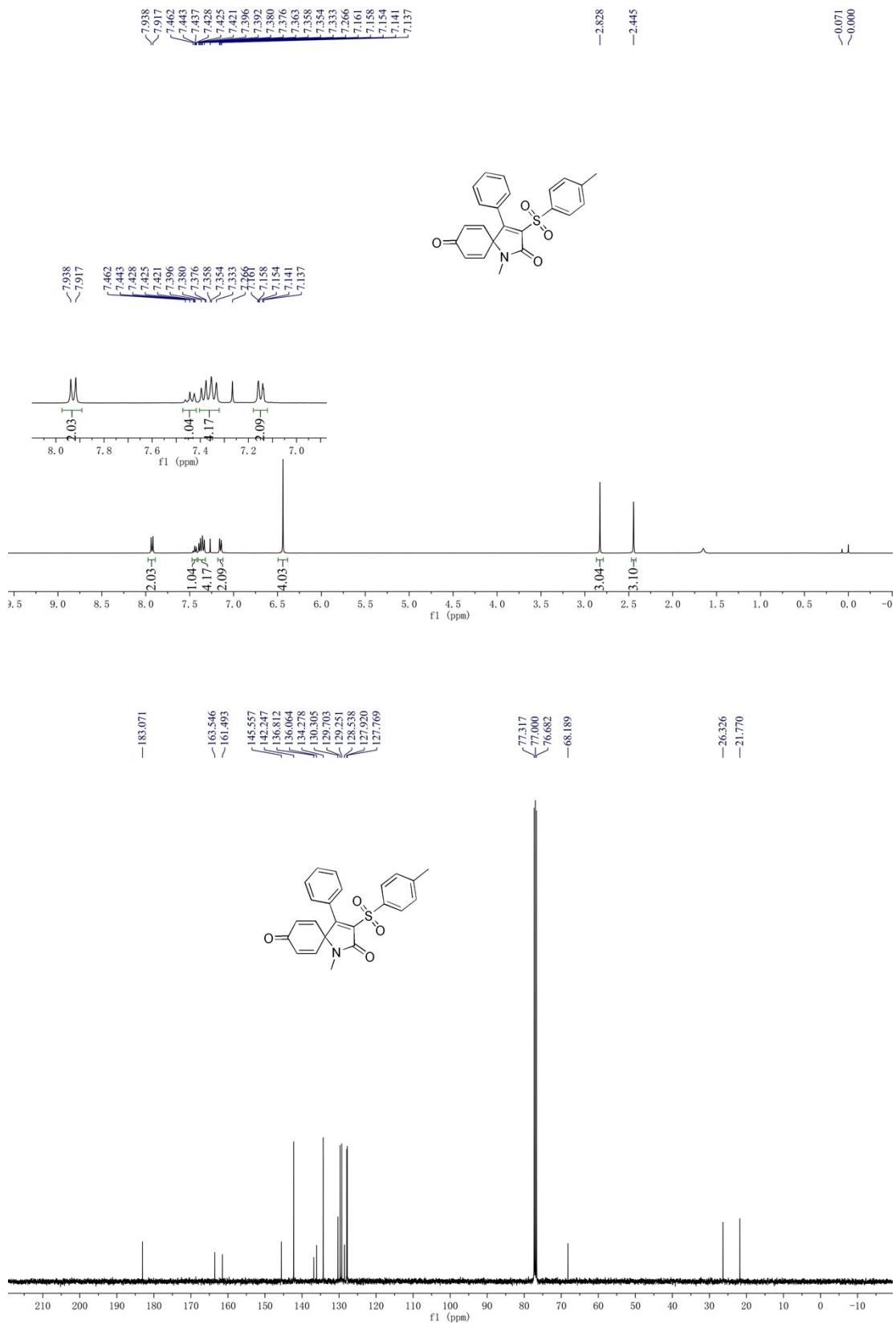
3-((4-Ethoxyphenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ab)



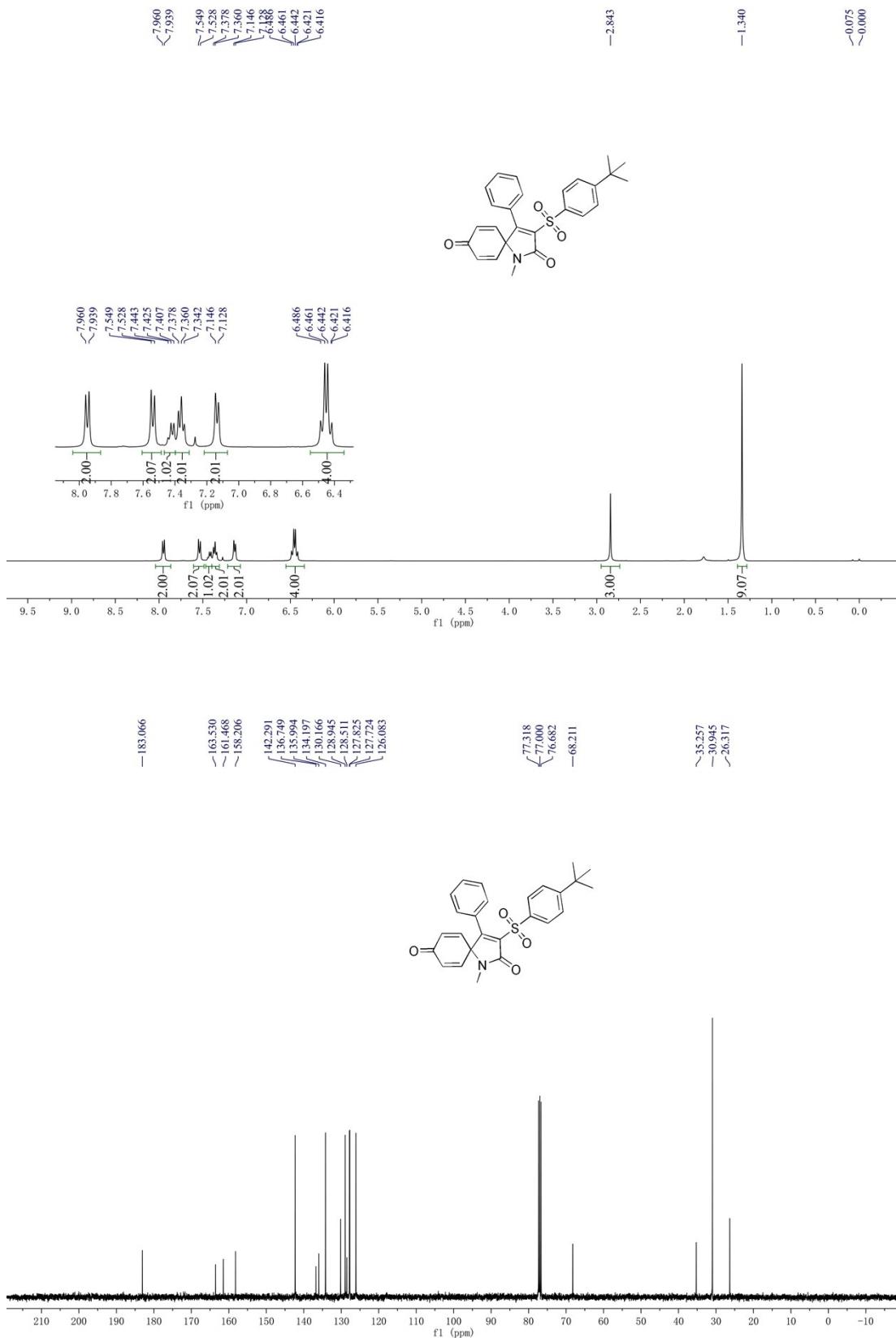
1-Methyl-3-((4-phenoxyphenyl)sulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ac)



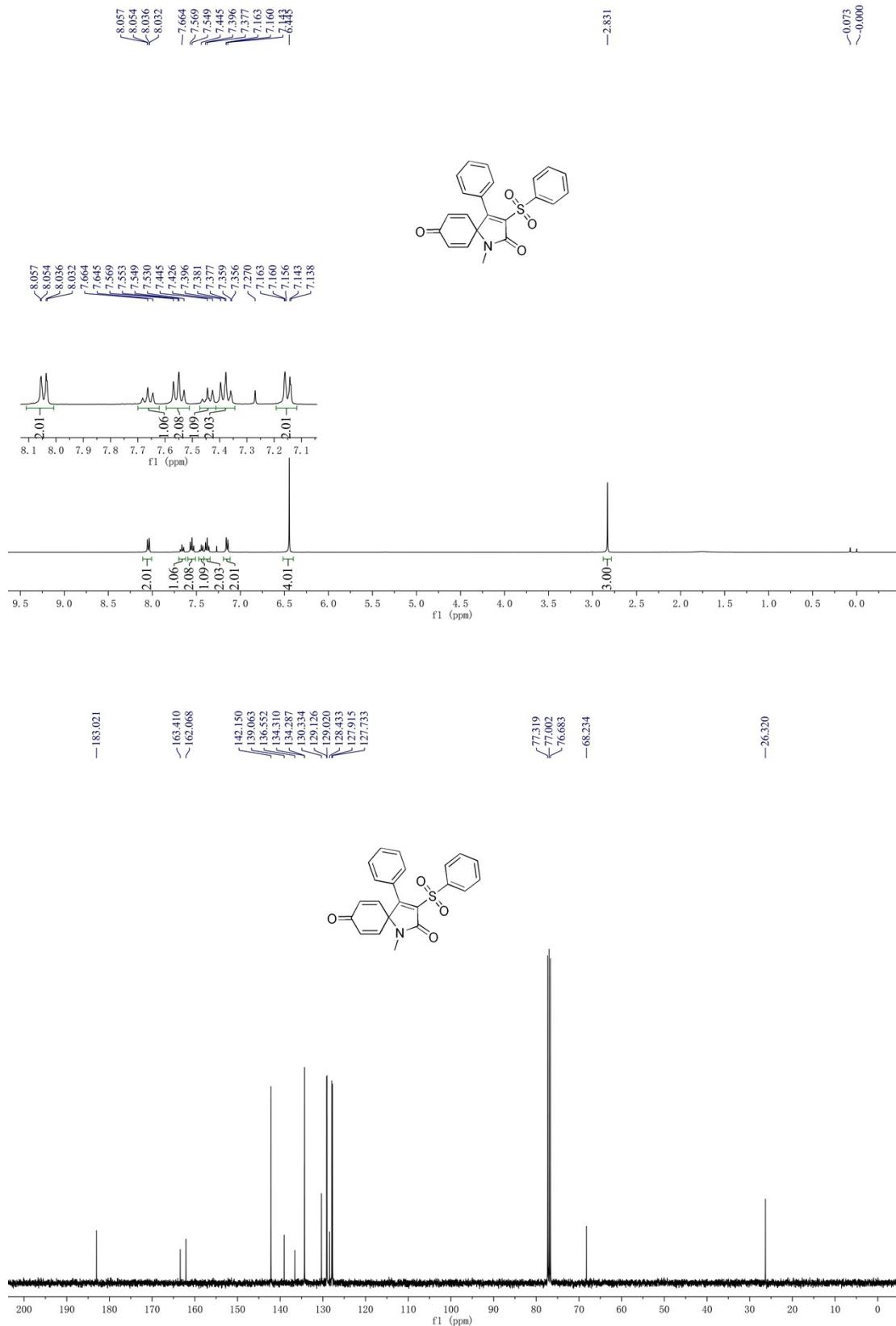
1-Methyl-4-phenyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ad)



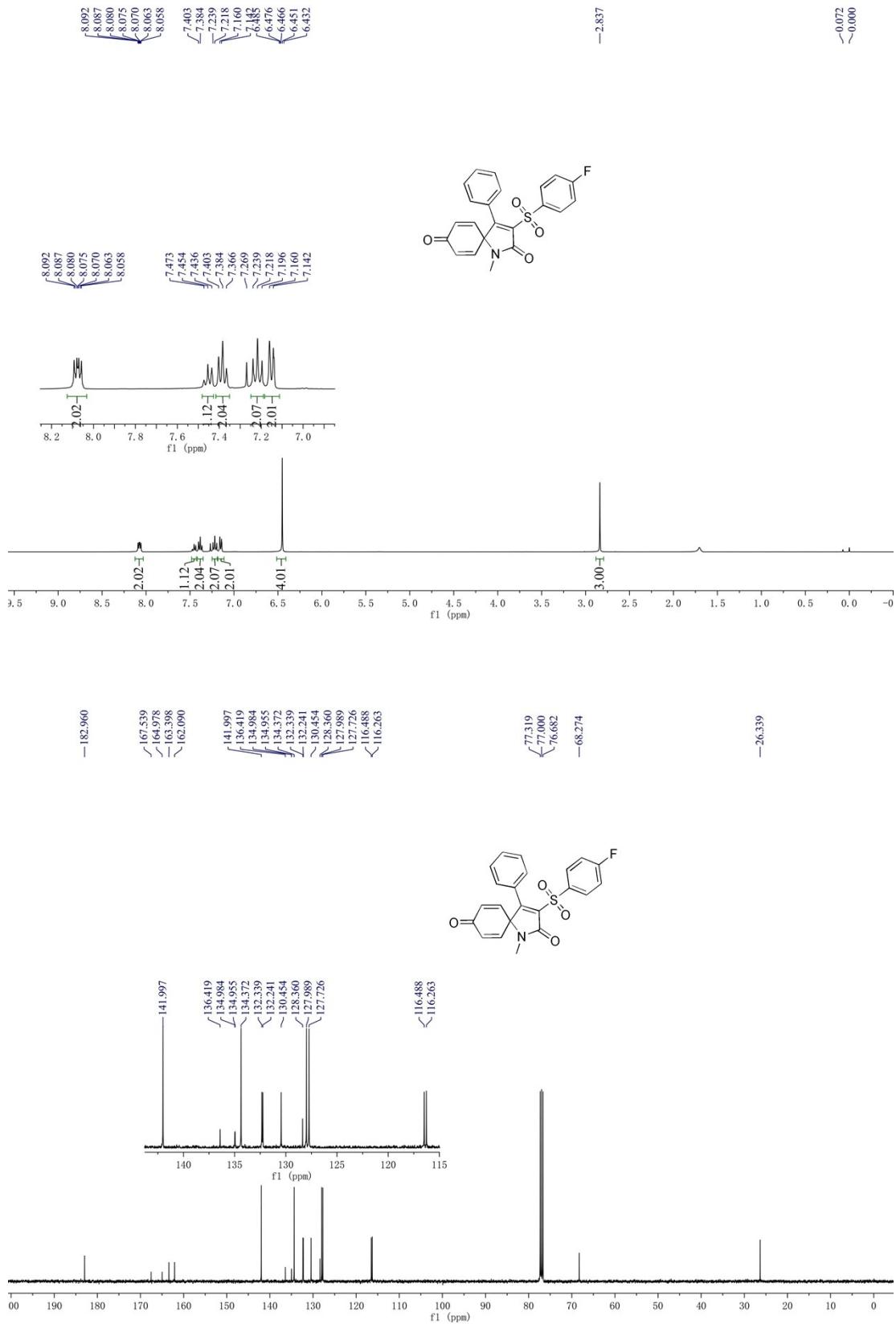
3-((4-(*tert*-Butyl)phenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ae)

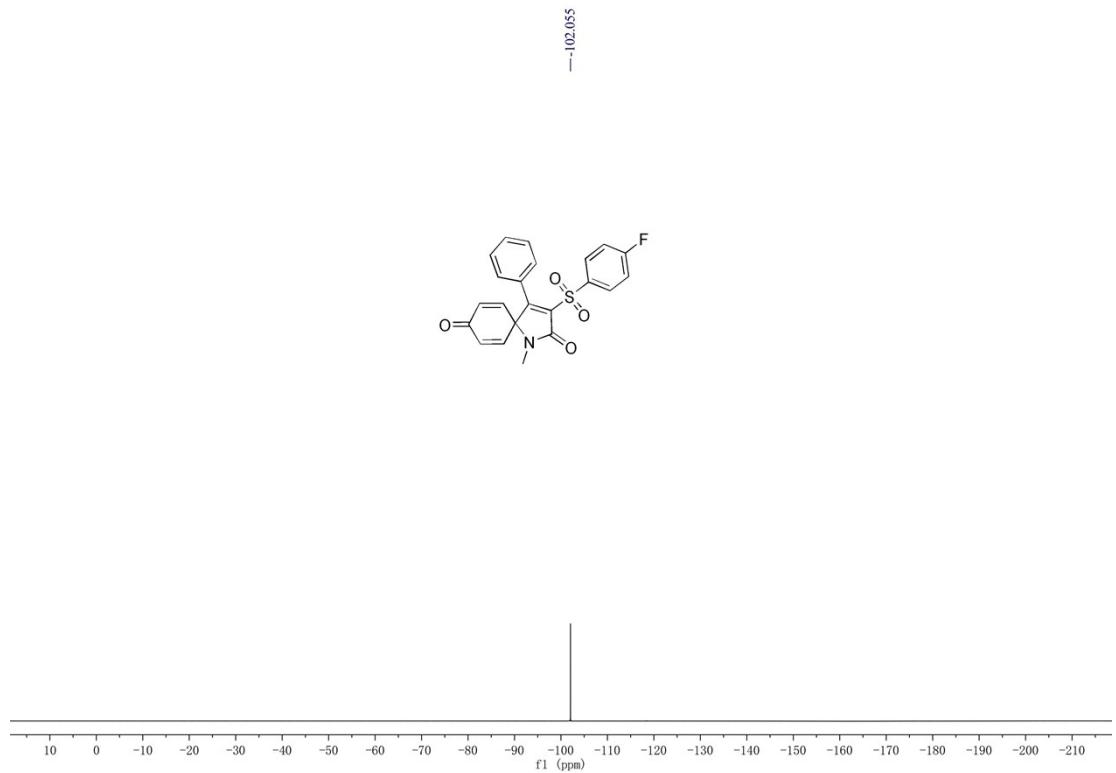


1-Methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3af)

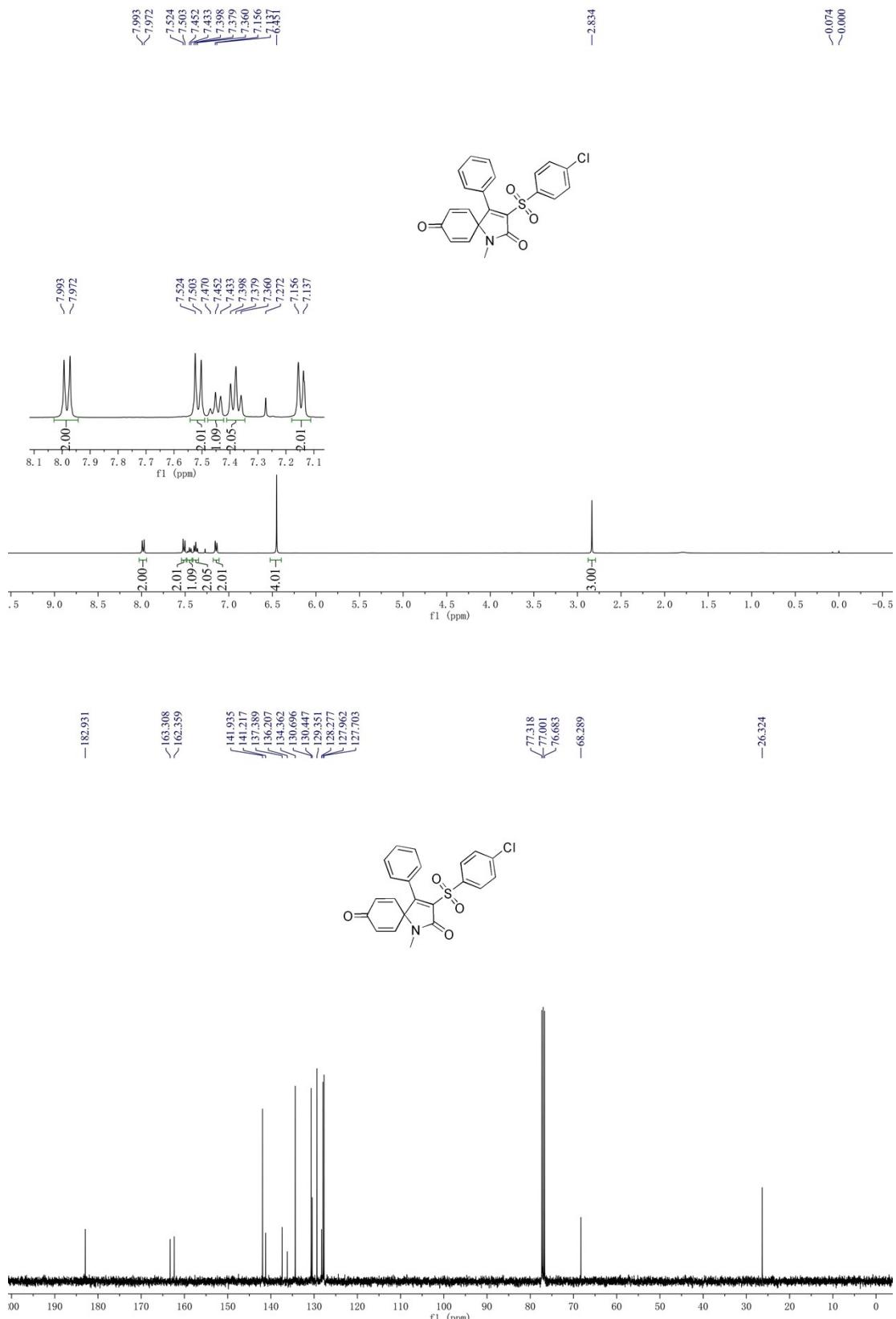


3-((4-Fluorophenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ag)

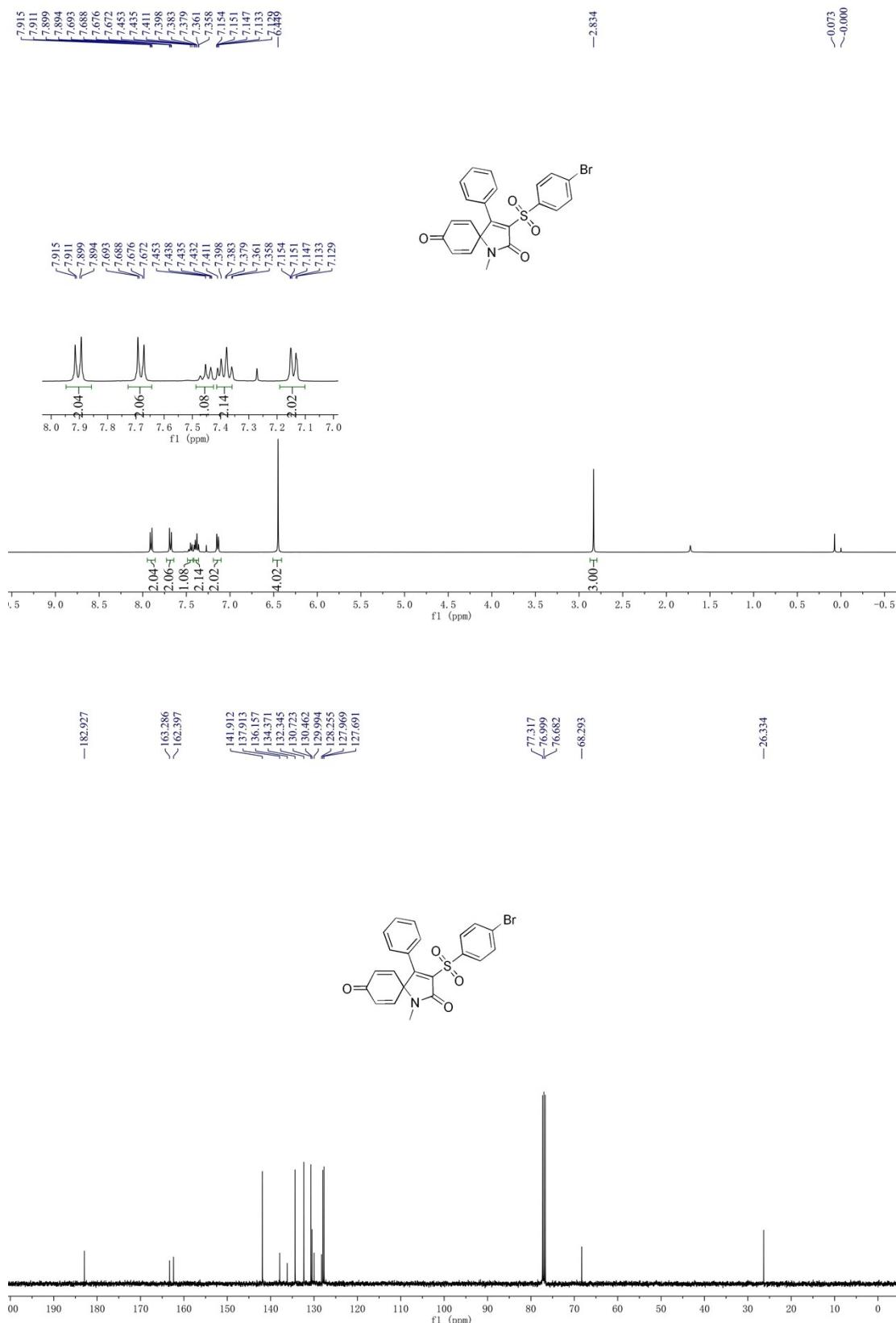




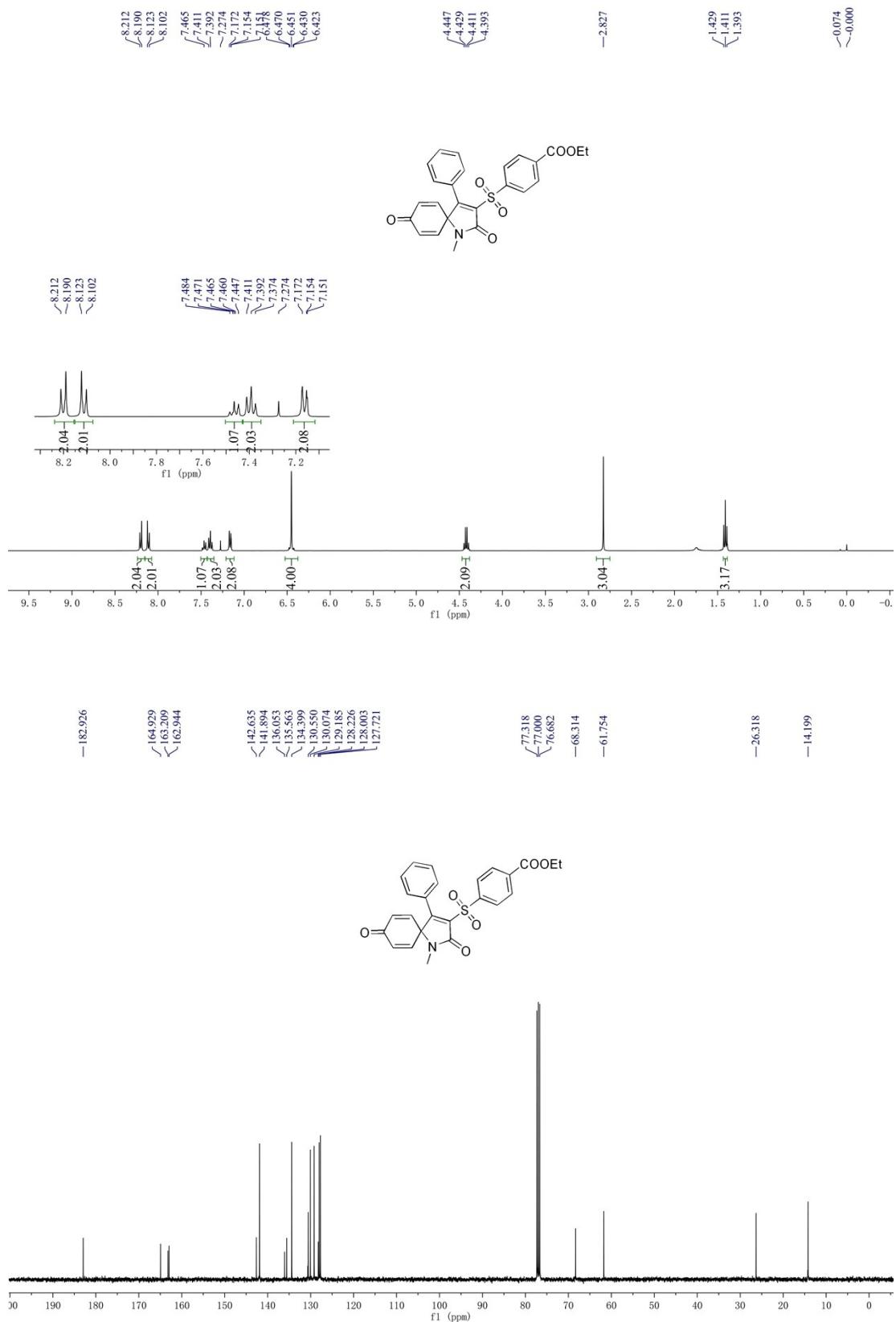
3-((4-Chlorophenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ah)



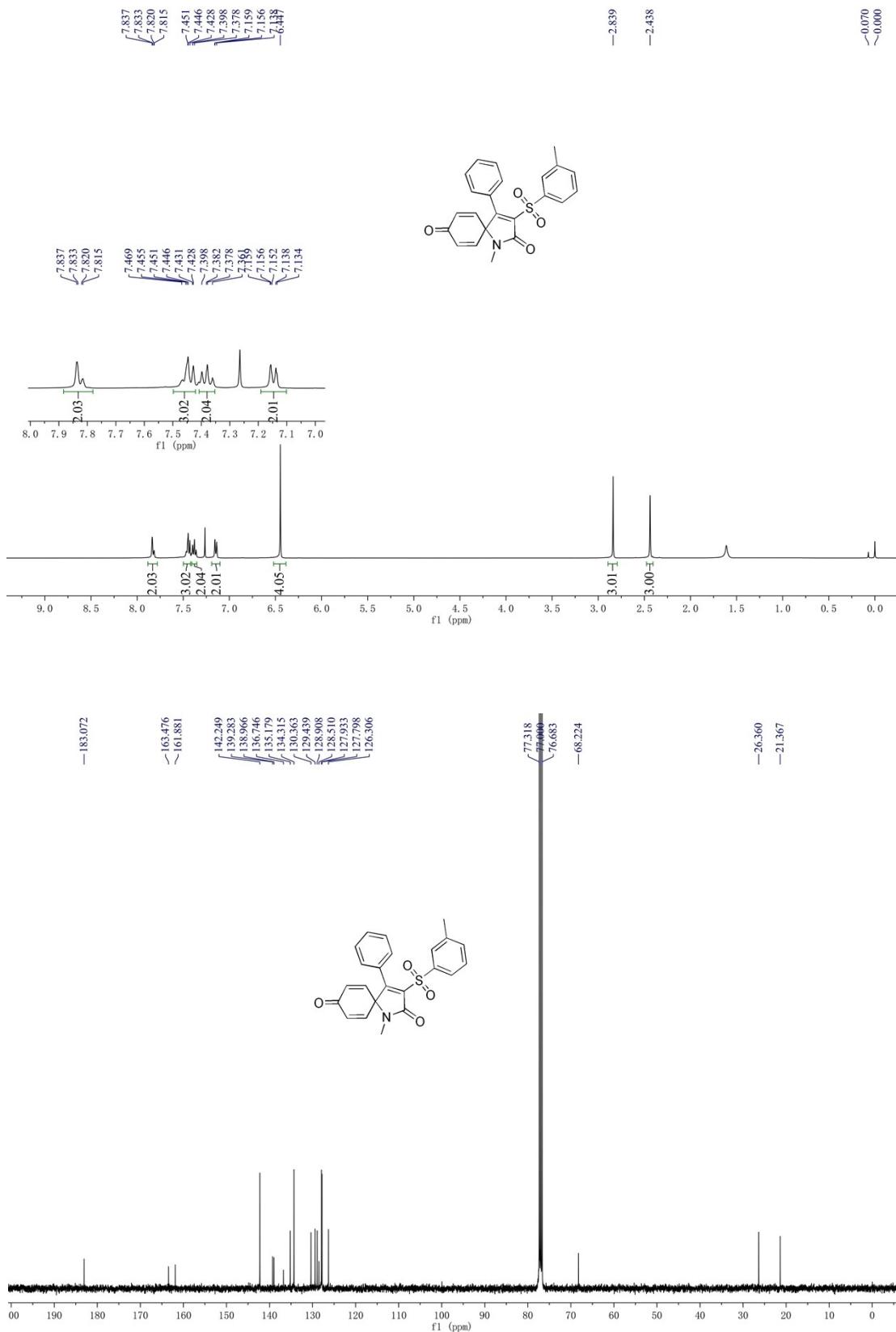
3-((4-Bromophenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ai)



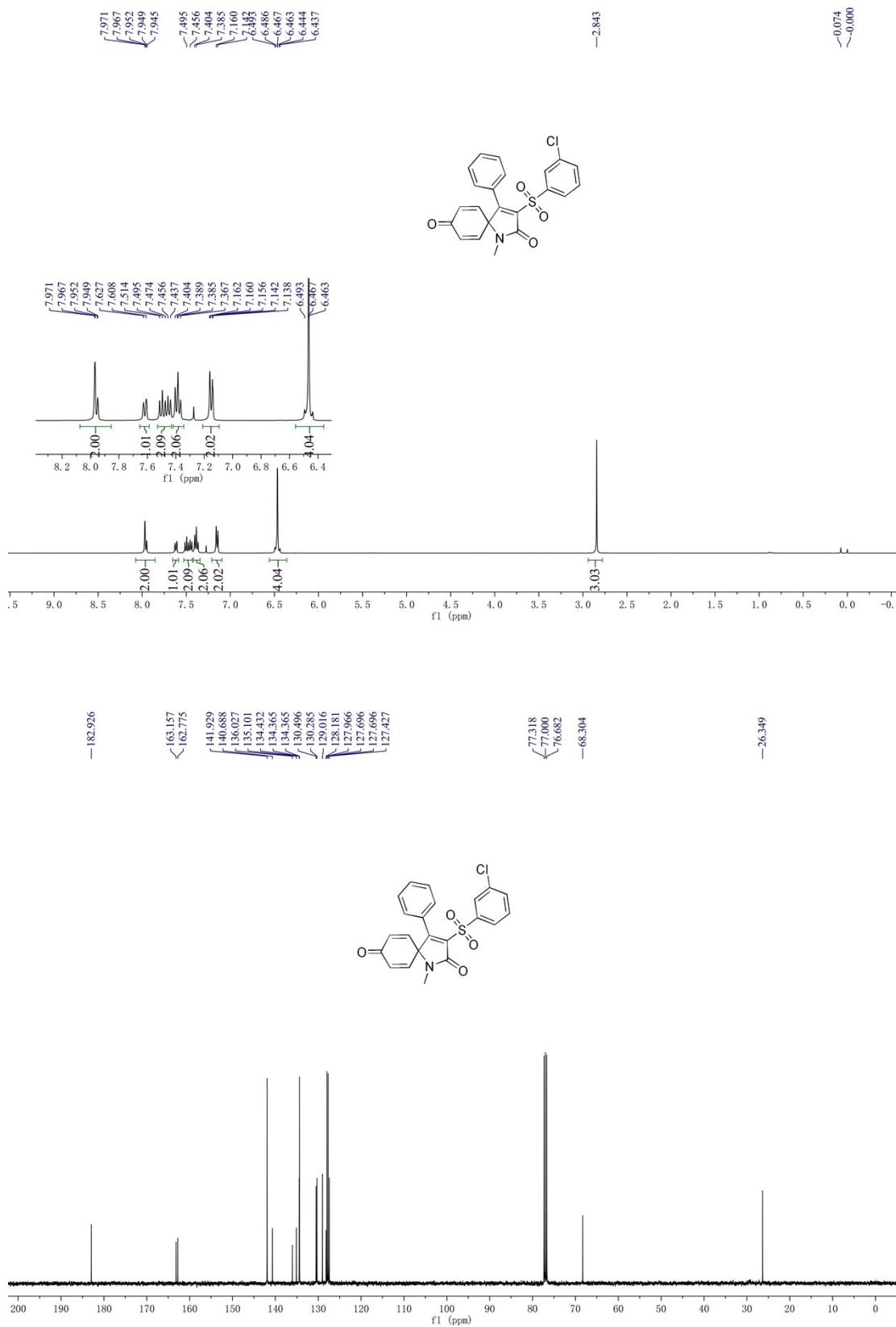
Ethyl 4-((1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)sulfonyl)benzoate (3aj)



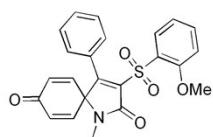
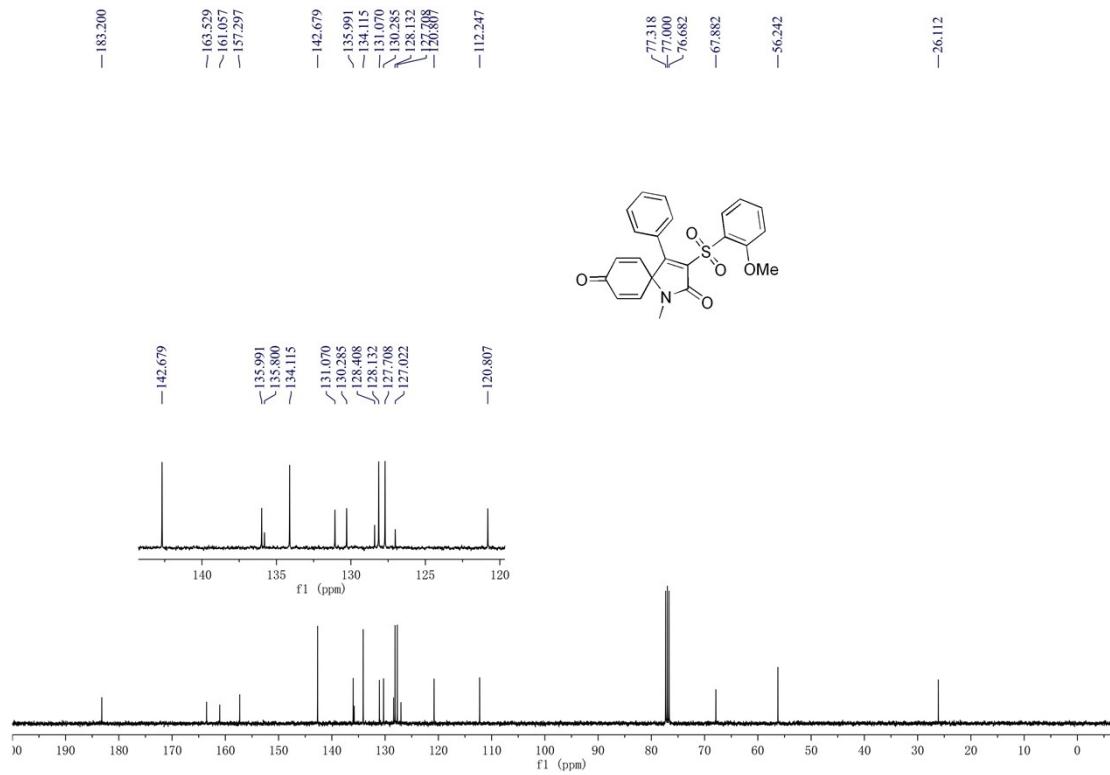
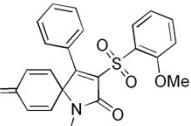
1-Methyl-4-phenyl-3-(m-tolylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ak)



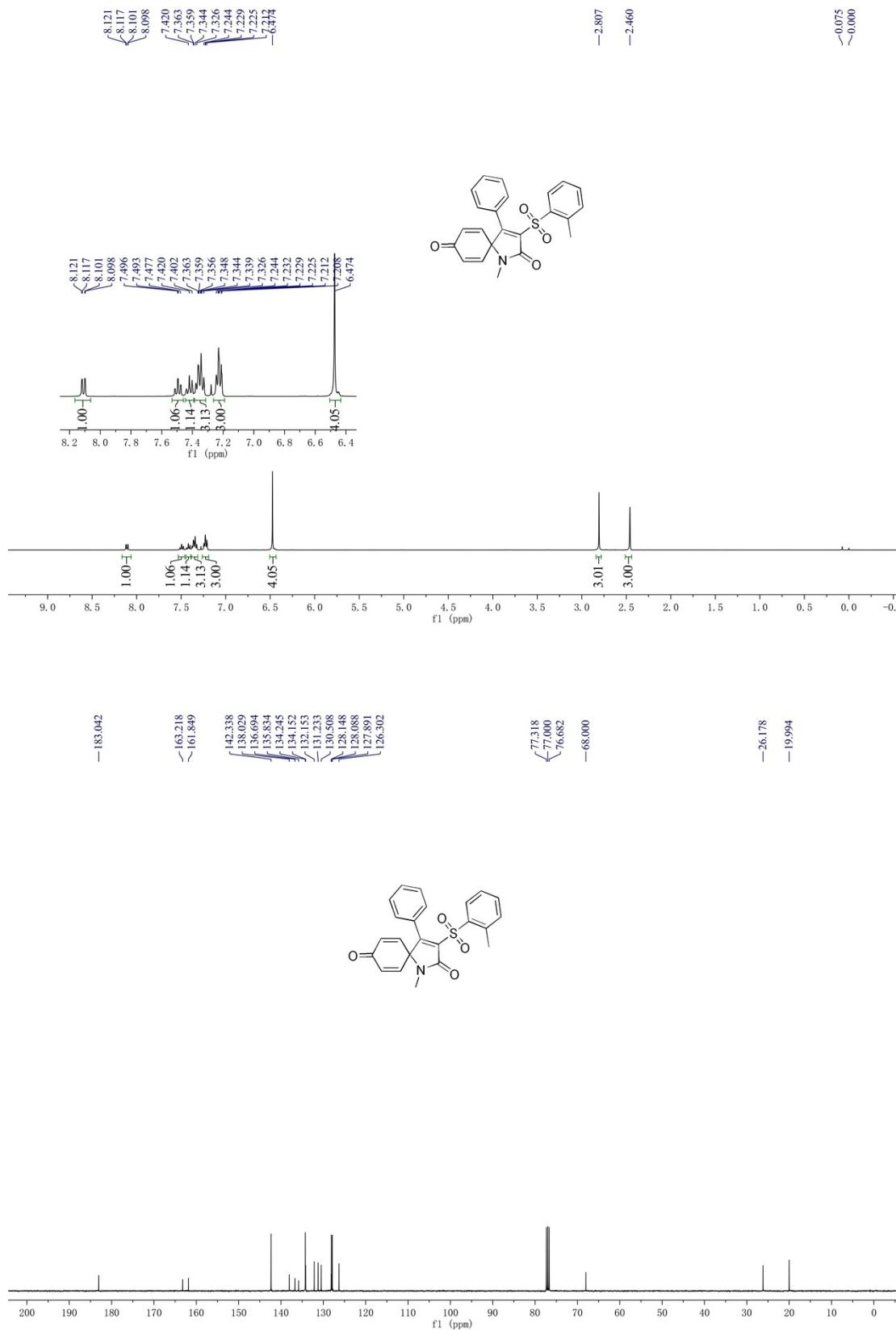
3-((3-Chlorophenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3al)



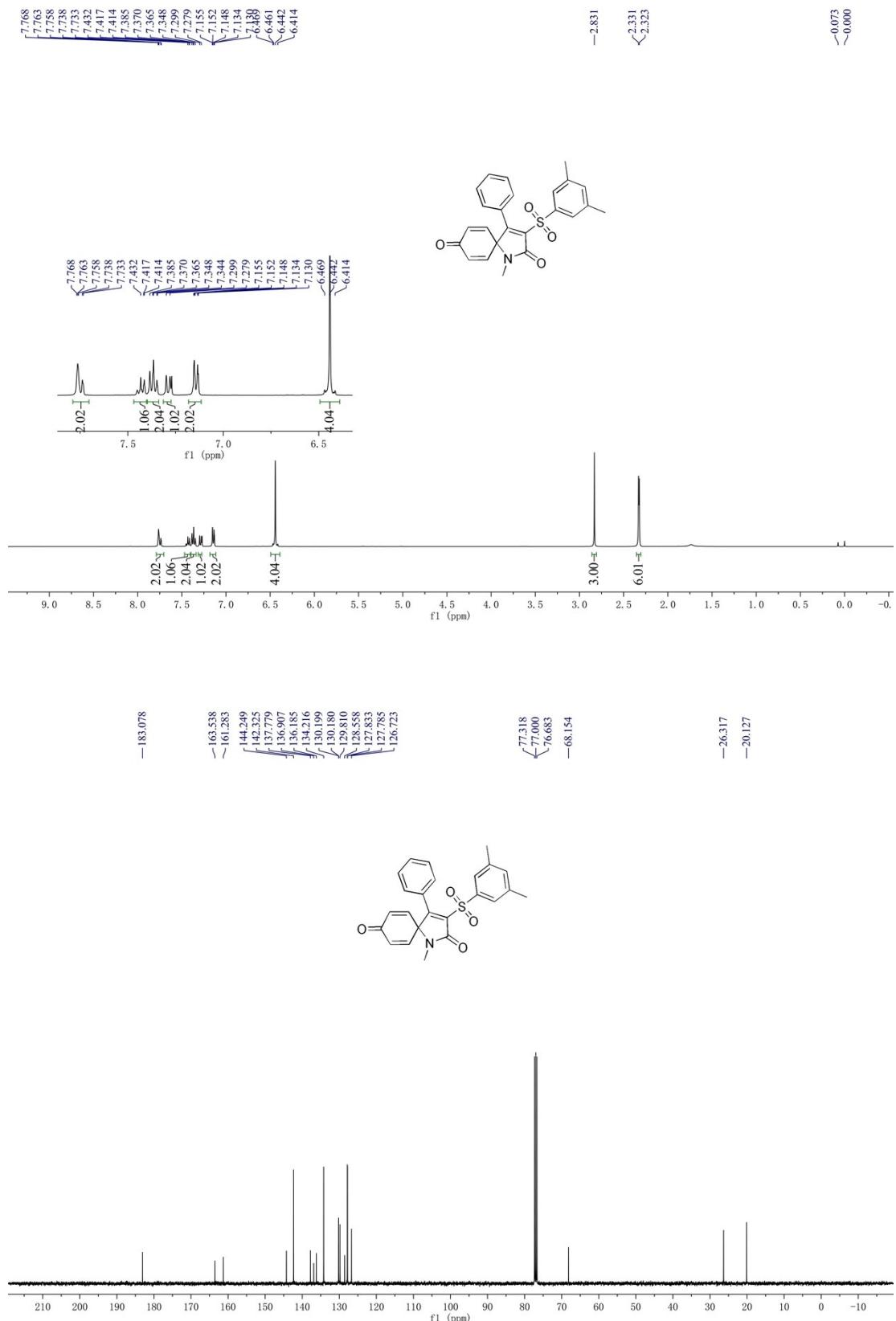
3-((2-Methoxyphenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3am)



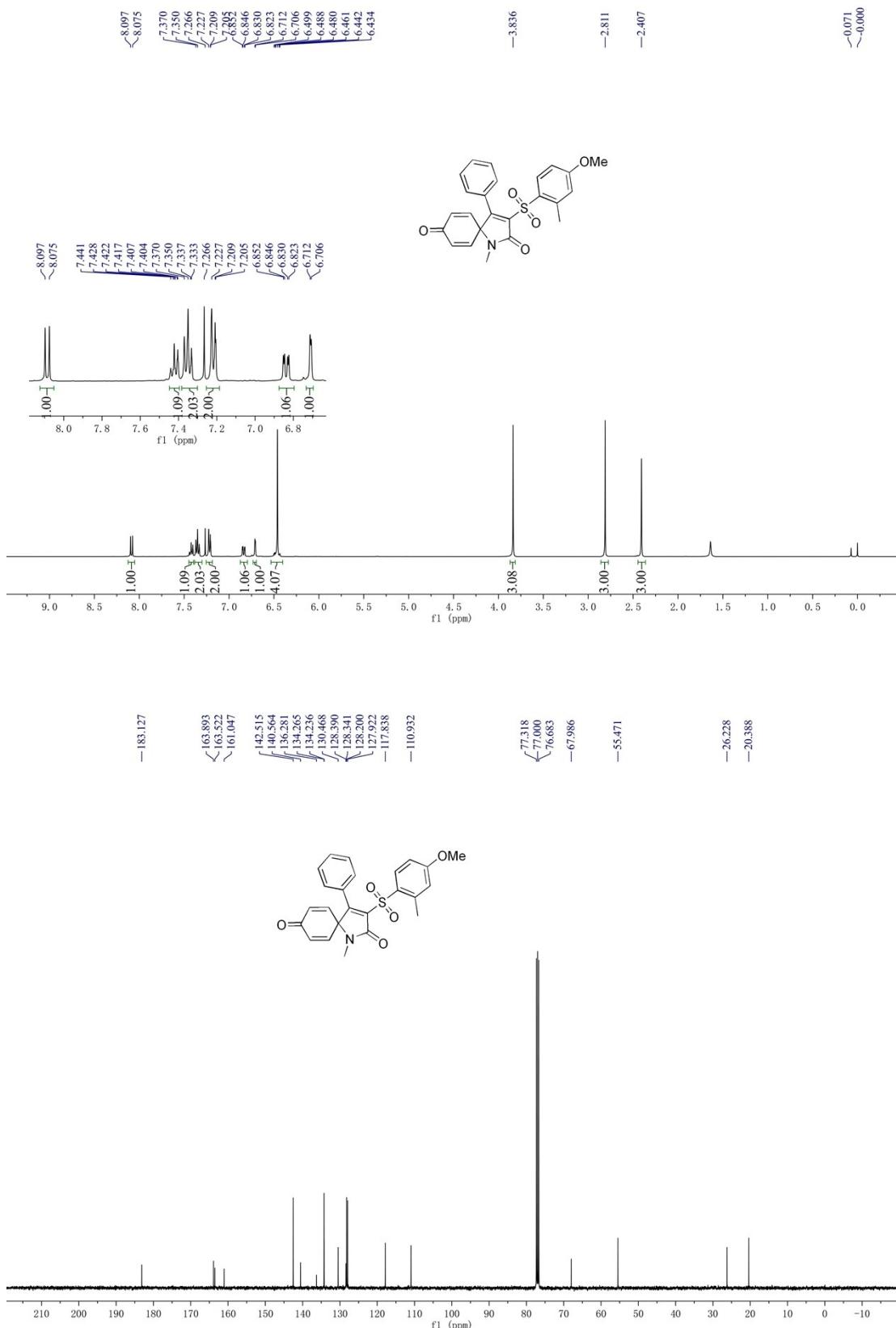
1-Methyl-4-phenyl-3-(*o*-tolylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3an)



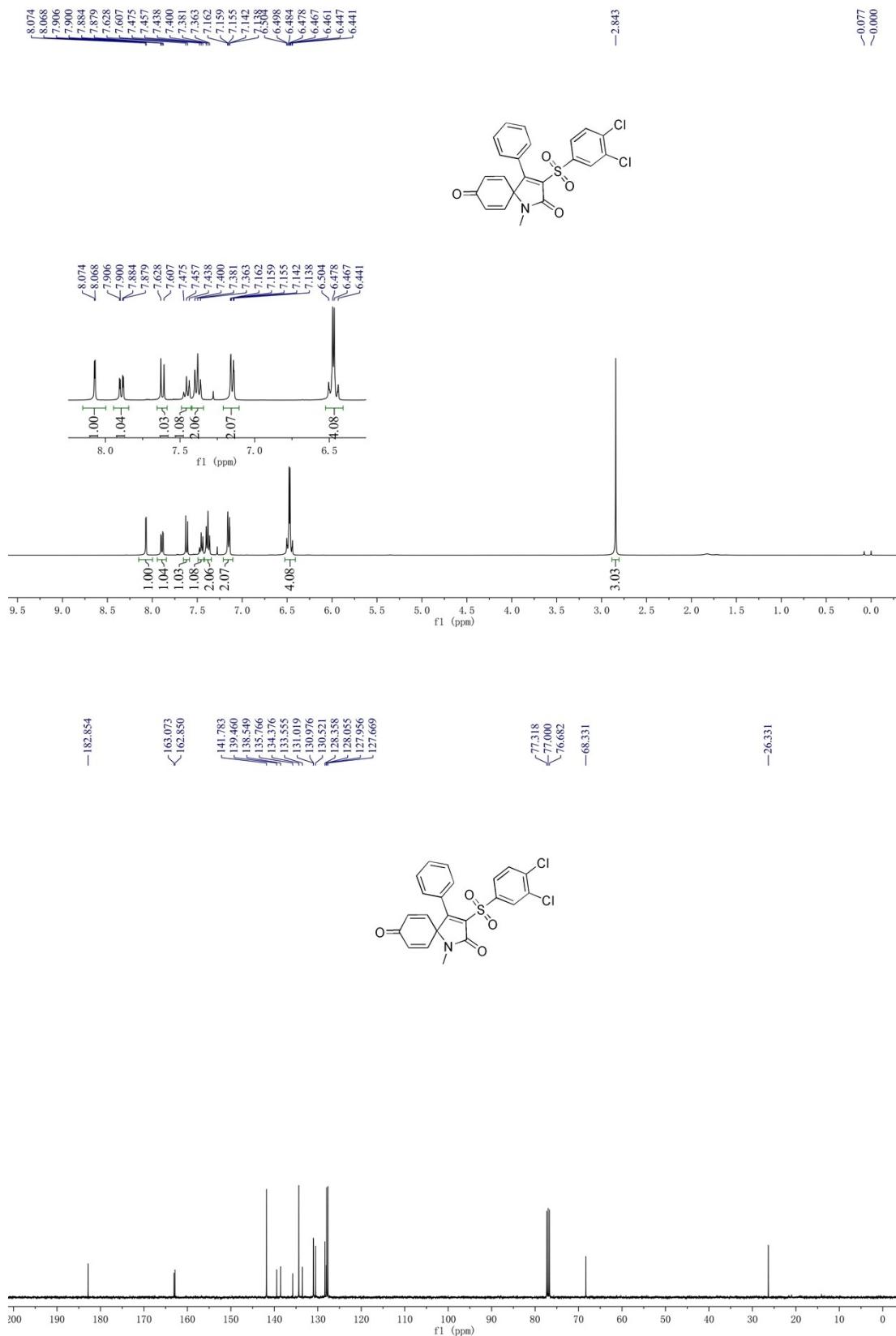
3-((3,5-Dimethylphenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ao)



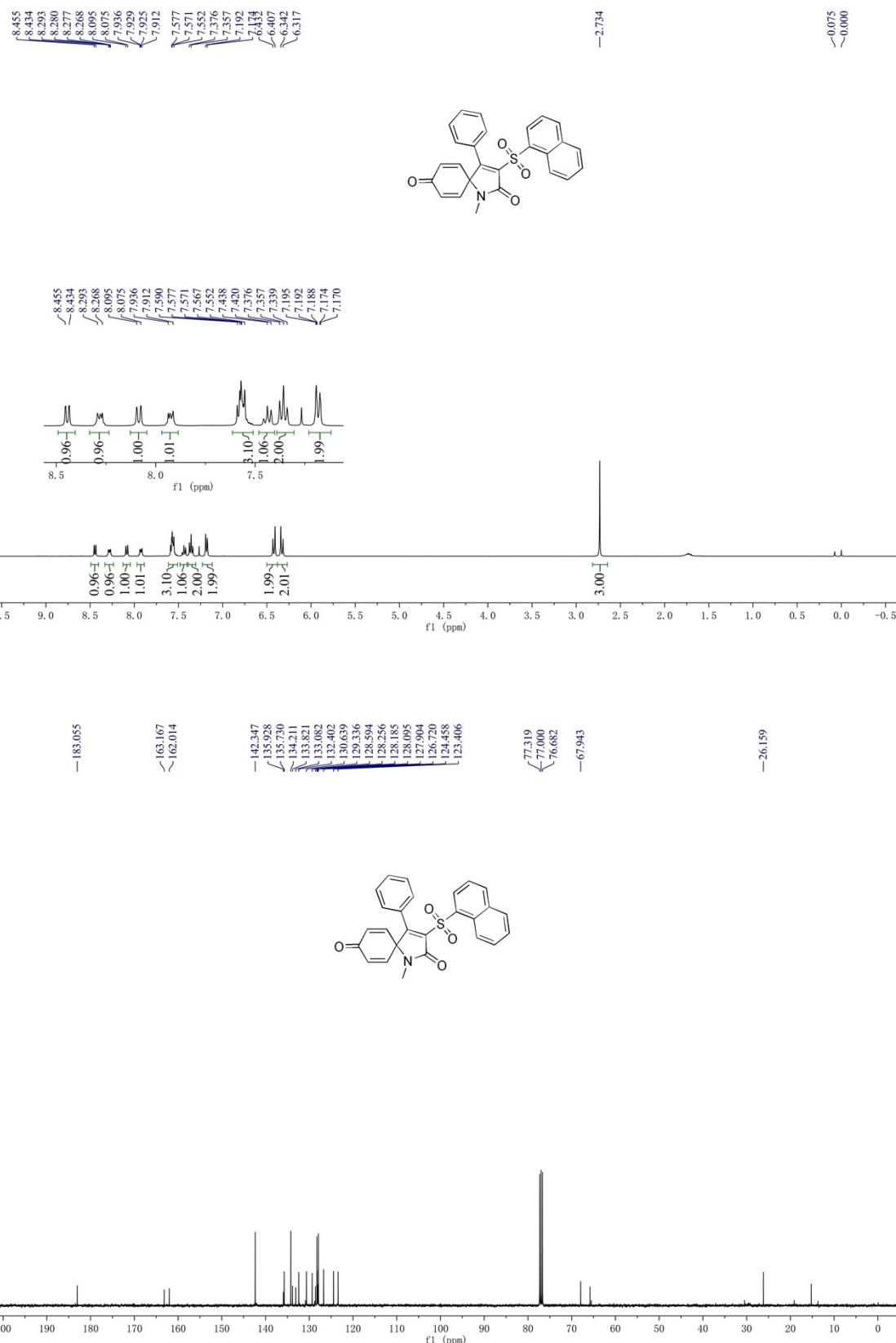
3-((4-Methoxyphenyl)sulfonyl)-1,6-dimethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ap)



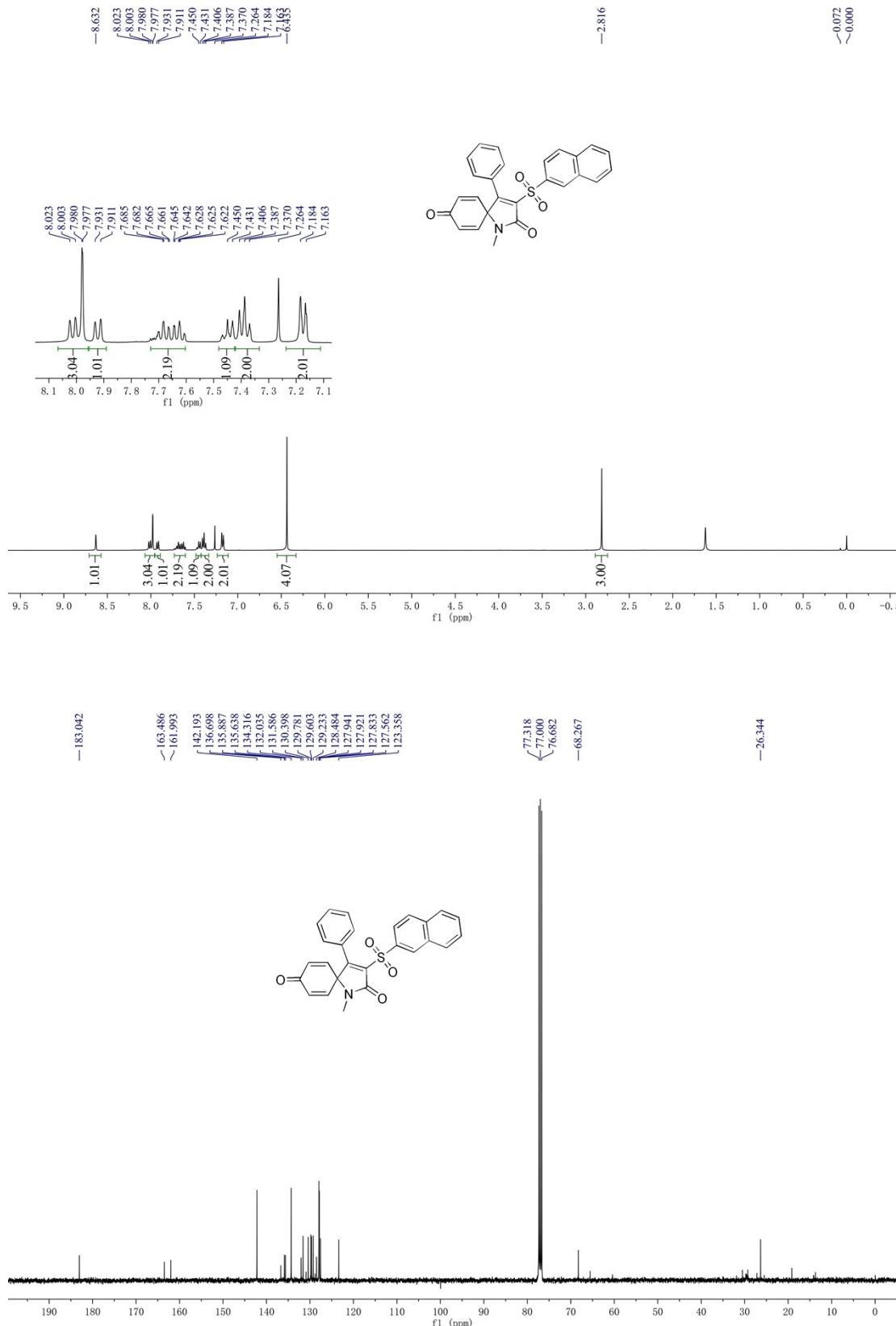
3-((3,4-Dichlorophenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3aq)



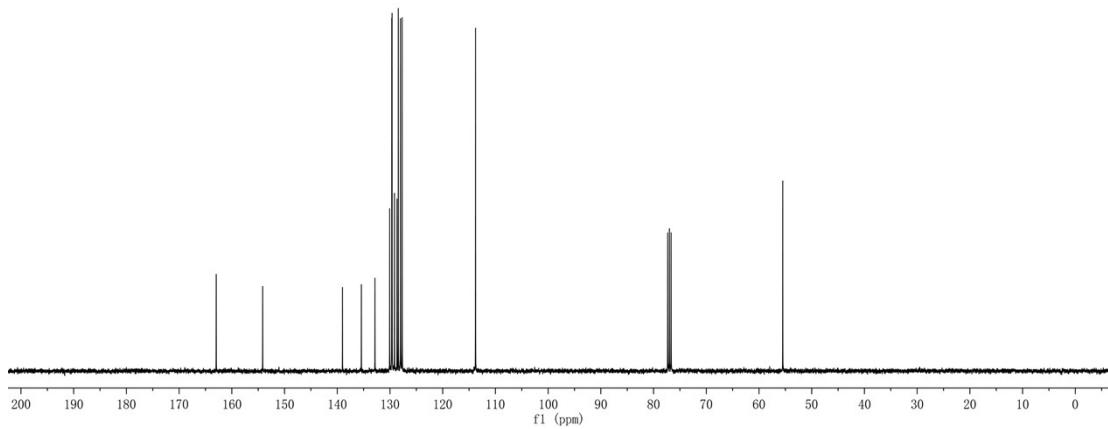
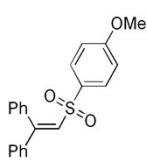
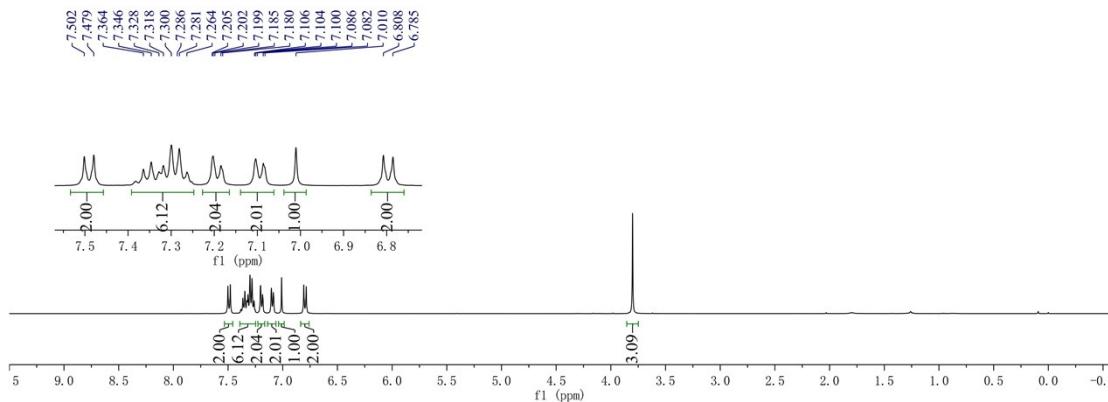
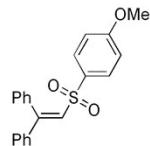
1-Methyl-3-(naphthalen-1-ylsulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ar)



1-Methyl-3-(naphthalen-2-ylsulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3as)



(2-((4-Methoxyphenyl)sulfonyl)ethene-1,1-diyl)dibenzene (4)



7-methoxy-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (6)

