Radical-induced Denitration of *N*-(*p*-nitrophenyl)propiolamides Coupled With Dearomatization: Access to Phosphonylated/Trifluoromethylated Azaspiro[4.5]-trienones

Kangdong Mo,[a] Xiaocong Zhou,[a] Ju Wu,[*,a,b] and Yufen Zhao[*,a,b]

[a]*Institute of Drug Discovery Technology, Ningbo University, Ningbo, Zhejiang, China*

E-mail: wuju@nbu.edu.cn, wuduanyazhici@163.com

[b]*Qian Xuesen Collaborative Research Center of Astrochemistry and Space Life Sciences, Ningbo University, Ningbo, Zhejiang, China*

E-mail: zhaoyufen@nbu.edu.cn

Table of Contents

1. General information: 2

2. Optimization of Reaction B 3

3. Reaction in the presence of 3.0 equiv TEMPO 4

4. ^{18}O-Labeling Experiment 7

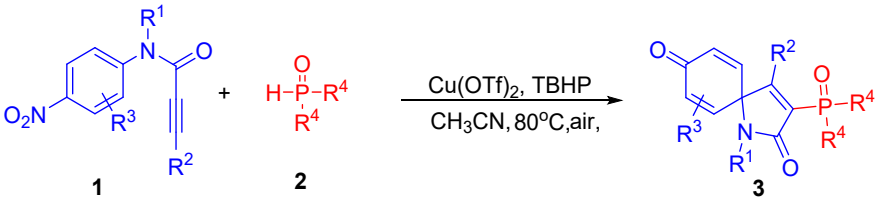
5. Spectral Data 9

6. ^{1}H and ^{13}C NMR spectra 27

1. General information:

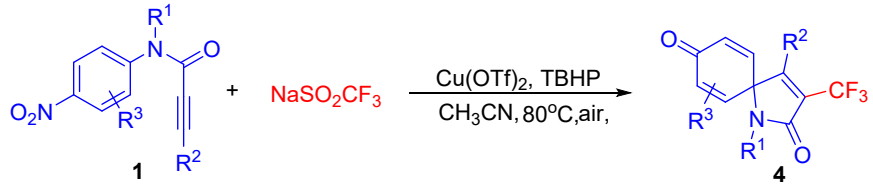
All reactions were carried out under air. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were measured on Bruker AVIII 500M spectrometers with $CDCl_3$ as solvent and the residual protonated solvent as internal standard or 85% H_3PO_4 as external standard for ^{31}P NMR (202 MHz). Chemical shifts were reported in units (ppm) by assigning the residual protonated solvent of $CDCl_3$ resonance in the ^{1}H spectrum as 7.26 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.16 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Chemical shifts of common trace ^{1}H NMR impurities (ppm): H_2O: 1.56, $CHCl_3$: 7.26. Column chromatography was performed on silica gel 300-400 mesh. The unknown products were further characterized by HRMS-ESI.

General experimental procedure A:



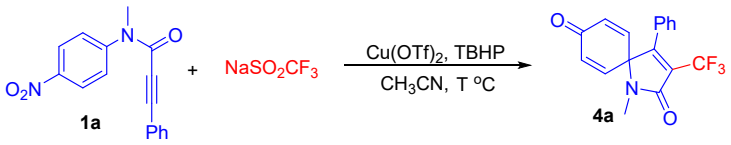
An oven-dried Schlenk tube with a magnetic stir bar was charged with **1** (0.20 mmol, 1.0 equiv) and $Cu(OTf)_2$ (0.02 mmol, 0.1 equiv), then **2** (0.60 mmol, 3.0 equiv) and 2.0 mL CH_3CN were added into the tube, the mixture was stirred under air at 80 °C for 2 min. TBHP (70% aqueous solution, 0.6 mmol, 3 equiv) was sequentially added to the mixture. The consumption of the starting material **1** was checked by TLC (20% to 30% AcOEt/petroleum ether). The reaction solution was concentrated in *vacuo* and then added 15 mL saturated sodium bicarbonate solution and extracted with EtOAc (3×10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography using 50% to 80% AcOEt/petroleum ether as the eluent to give the corresponding products.

General experimental procedure B:



An oven-dried Schlenk tube with a magnetic stir bar was charged with **1** (0.20 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (1.0 mmol, 5 equiv) and $Cu(OTf)_2$ (0.02 mmol, 0.1 equiv), then 2.0 mL CH_3CN was added into the tube, the mixture was stirred under air at 80 °C for 2 min. TBHP (70% aqueous solution, 1.6 mmol, 8 equiv) was sequentially added to the mixture. The complete consumption of the starting material **1** was checked by TLC (10% to 25% AcOEt/petroleum ether). The reaction solution was concentrated in *vacuo* and then added 15 mL saturated sodium bicarbonate solution and extracted with EtOAc (3×10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography using 10% to 25% AcOEt/petroleum ether as the eluent to give the corresponding products.

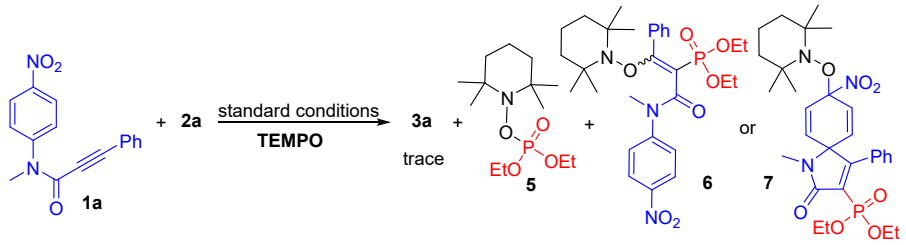
2. Optimization of Reaction B[a]



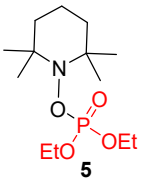
entry	$NaSO_2CF_3$ (equiv)	TBHP (equiv)	T (°C)	Solvent	Additives	Conversion %	Yield (%)[b]
1	2.0	3.0	60	CH_3CN (2.0 mL)	—	40	16
2	2.0	3.0	60	CH_3CN/H_2O (1.8 mL/0.2 mL)	—	43	18
3[c]	2.0	3.0	60	CH_3CN (2.0 mL)	—	41	17
4	2.0	3.0	rt	CH_3CN (2.0 mL)	—	0	nr
5	2.0	3.0	60	CH_3CN (2.0 mL)	NaOH (2.0 equv)	45	18
6	2.0	3.0	60	CH_3CN (2.0 mL)	NaOAc (2.0 equv)	37	22
7[d]	1.0	3.0	60	CH_3CN (2.0 mL)	—	35	< 10
8	2.0	3.0	80	CH_3CN (2.0 mL)	—	57	37
9	2.0	3.0	100	CH_3CN (2.0 mL)	—	55	30
10[e]	2.0	DTBP	80	CH_3CN (2.0 mL)	—	20	< 10
11[f]	2.0	3.0	80	CH_3CN (2.0 mL)	—	43	31
12[g]	2.0	3.0	80	CH_3CN (2.0 mL)	—	65	34
13[h]	2.0	3.0	80	CH_3CN (2.0 mL)	—	70	36
14[i]	2.0	3.0	80	CH_3CN (2.0 mL)	—	68	39
15[i]	2.0	5.0	80	CH_3CN (2.0 mL)	—	77	44
16[i]	2.0	8.0	80	CH_3CN (2.0 mL)	—	>80	47
17[i]	4.0	8.0	80	CH_3CN (2.0 mL)	—	>80	52
18[i]	5.0	8.0	80	CH_3CN (2.0 mL)	—	>80	56
19[g,i]	2.5	7.0	60	CH_3CN/H_2O (1.0 mL/0.5 mL)	MnO_2 (3.0 equv) NaOAc (2.0 equv)	>80	28

[a]Reaction conditions: **1a** (0.2 mmol), $NaSO_2CF_3$ and $Cu(OTf)_2$ (10 mol%) in solvent (2.0 mL) was stirred for 16 h under Ar. [b]Yields of isolated products. [c]3.0 equiv of TBHP (5.0 M in decane solution) was used. [d]2 equiv of **1a** was added. [e]3.0 equiv of DTBP was used. [f]$FeCl_3$ (10 mol%) was used instead of $Cu(OTf)_2$. [g]CuI (10 mol%) was used instead of $Cu(OTf)_2$. [h]$Cu(OAc)_2 \cdot H_2O$ (10 mol%) was used instead of $Cu(OTf)_2$. [i] under air.

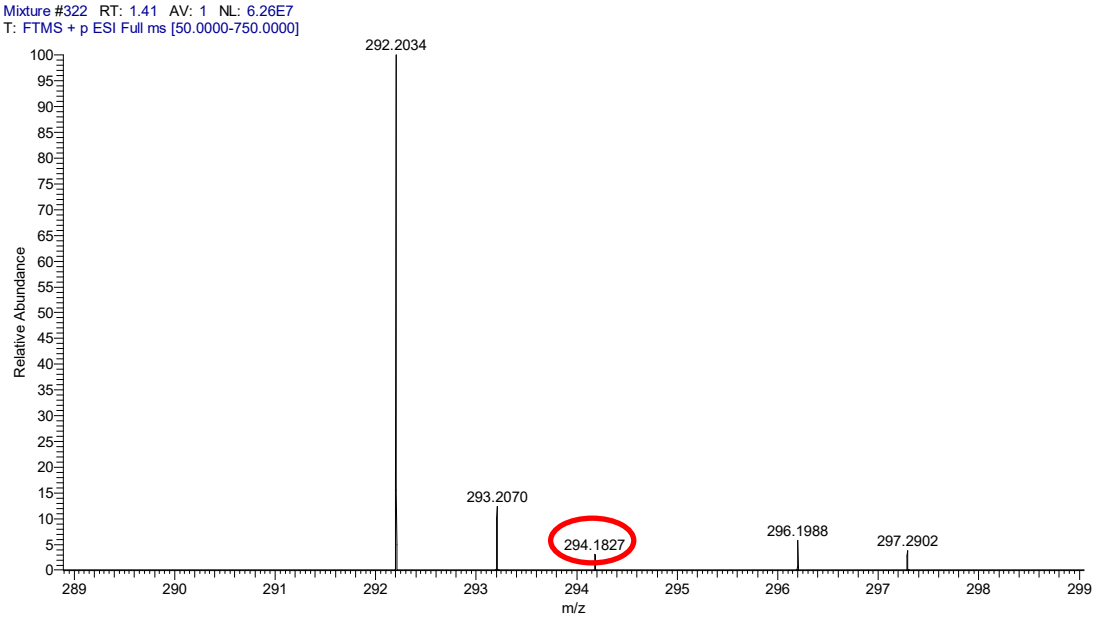
3. Reaction in the presence of 3.0 equiv TEMPO

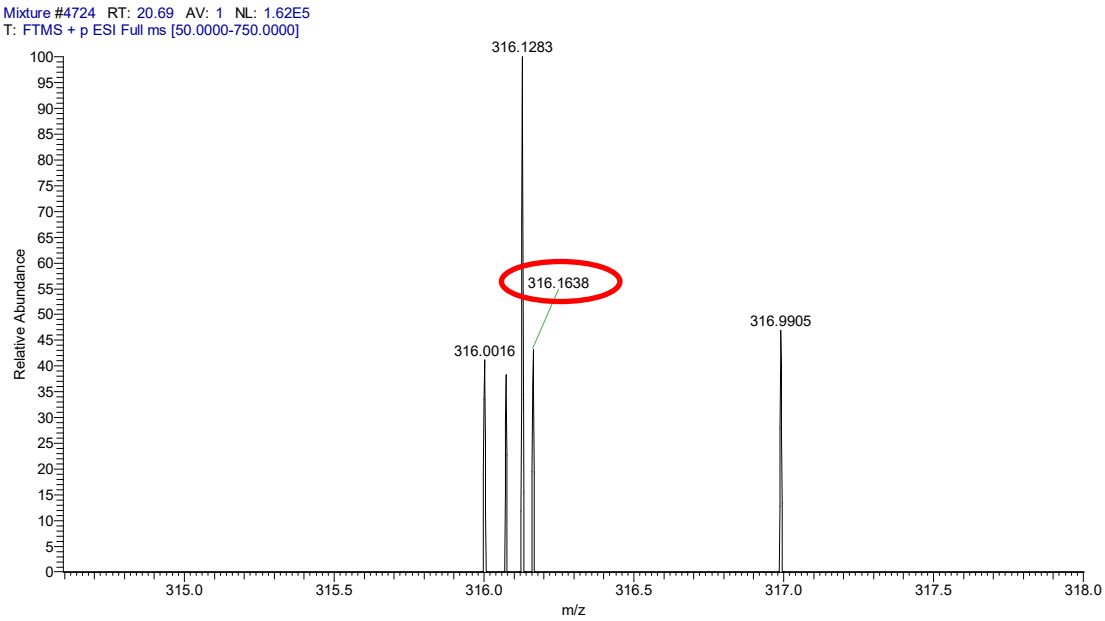


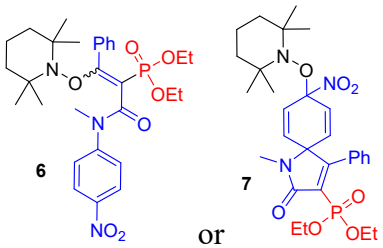
An oven-dried Schlenk tube with a magnetic stir bar was charged with **1a** (0.20 mmol, 1.0 equiv), $Cu(OTf)_2$ (0.02 mmol, 0.1 equiv), and TEMPO (2,2,6,6-tetramethylpiperidine oxide) (0.60 mmol, 3.0 equiv), then **2a** (0.60 mmol, 3.0 equiv) and 2.0 mL CH_3CN were added into the tube, the mixture was stirred under air at 80 °C for 2 min. TBHP (70% aqueous solution, 0.6 mmol, 3 equiv) was sequentially added to the mixture. The reaction was run for 3 hours at 80 °C, the reaction solution was concentrated in *vacuo* and then added 15 mL saturated sodium bicarbonate solution and extracted with EtOAc (3×10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was analyzed by HRMS.



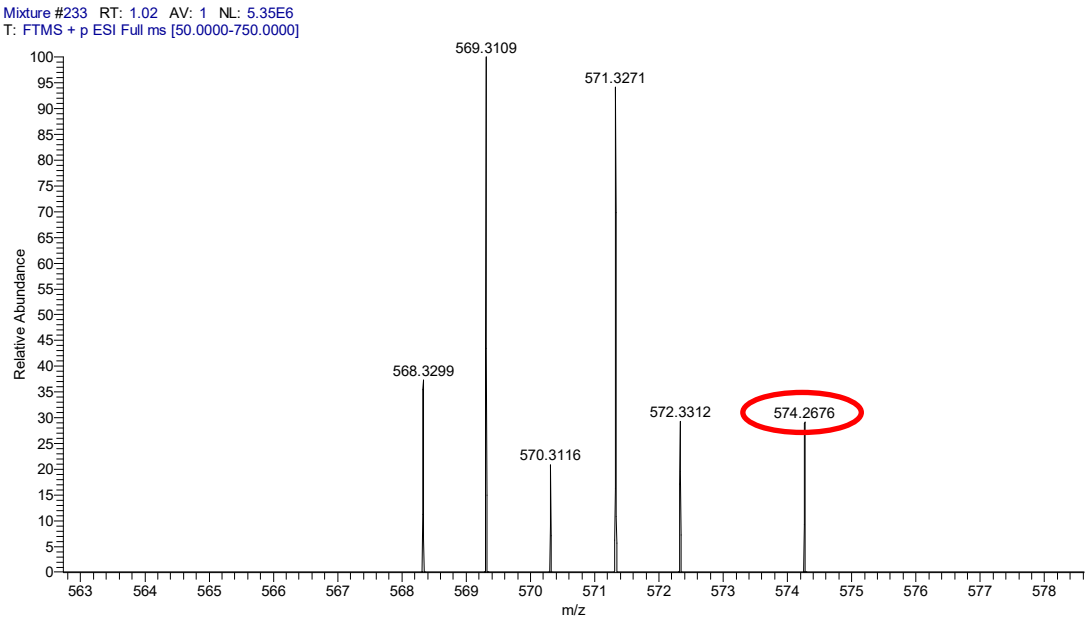
Compound 5: Calcd for $C_{13}H_{29}NO_4P^+$ $[M+H]^+$ 294.1829, found 294.1827.
Calcd for $C_{13}H_{28}NNaO_4P^+$ $[M+Na]^+$ 316.1648, found 316.1638.

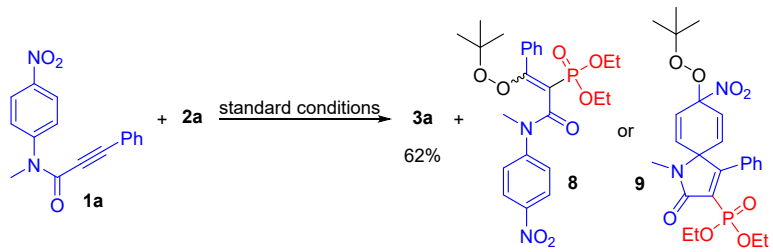




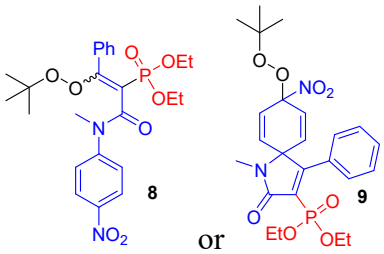


Compound 6 or 7: Calcd for $C_{29}H_{41}N_3O_7P^+$ $[M+H]^+$ 574.2677, found 574.2676.



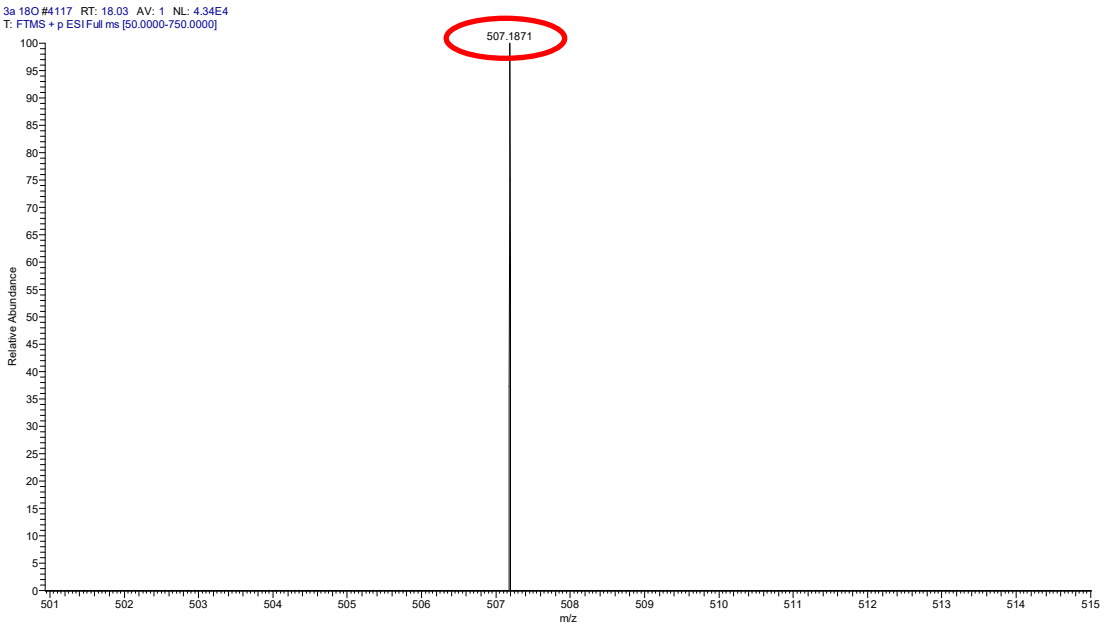


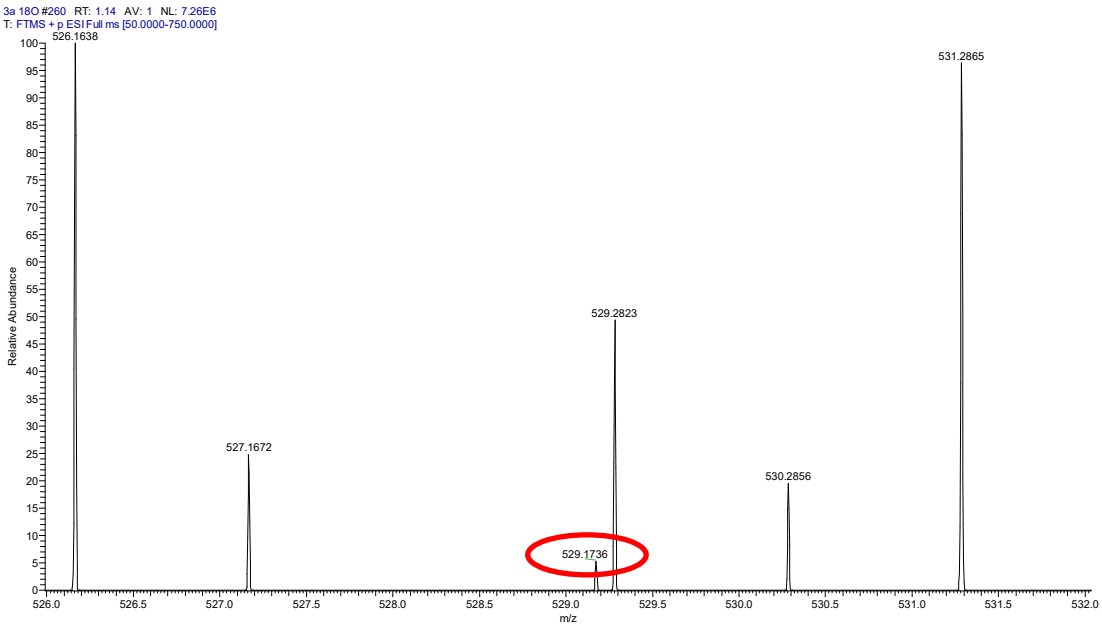
An oven-dried Schlenk tube with a magnetic stir bar was charged with **1a** (0.20 mmol, 1.0 equiv) and $Cu(OTf)_2$ (0.02 mmol, 0.1 equiv), then **2a** (0.60 mmol, 3.0 equiv) and 2.0 mL CH_3CN were added into the tube, the mixture was stirred under air at 80 °C for 2 min. TBHP (70% aqueous solution, 0.6 mmol, 3 equiv) was sequentially added to the mixture. The reaction was run for 3 hours at 80 °C, the reaction solution was concentrated in *vacuo* and then added 15 mL saturated sodium bicarbonate solution and extracted with EtOAc (3×10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was analyzed by HRMS.



Compound 8 or 9: Calcd. for $C_{24}H_{32}N_2O_8P^+$ $[M+H]^+$ 507.1891, found 507.1871.

Calcd. for $C_{24}H_{31}N_2NaO_8P^+$ $[M+Na]^+$ 529.1710, found 529.1736.



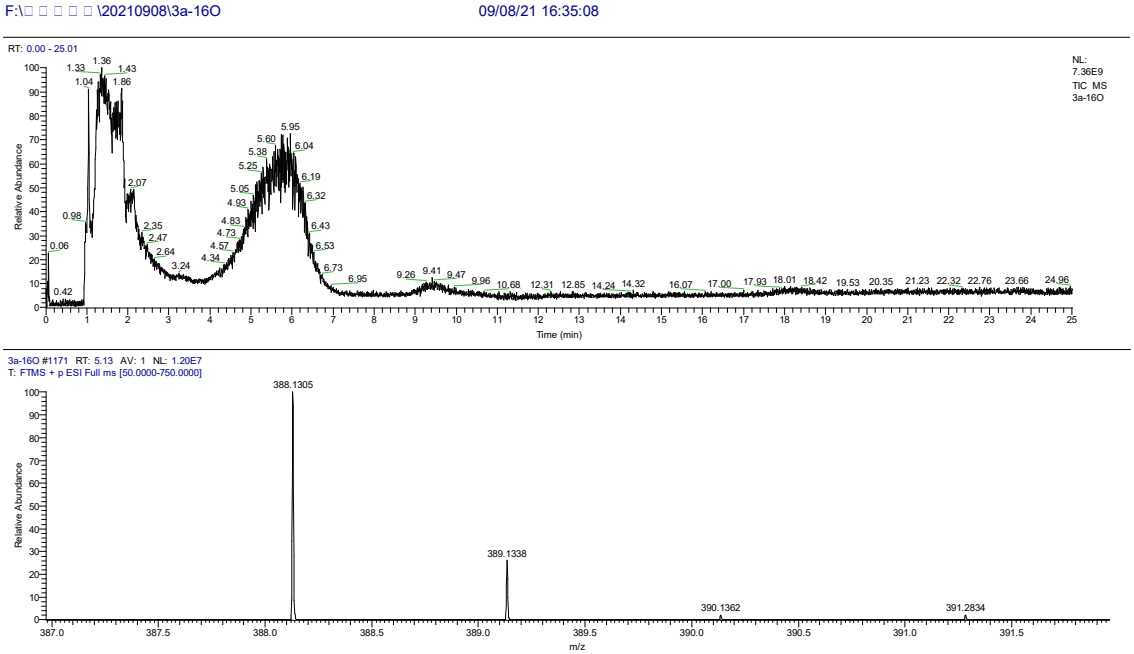


4. ^{18}O-Labeling Experiment

(1) Standard contitions: The reaction was performed under the optimized conditions and the residue was purified by silica gel column chromatography.

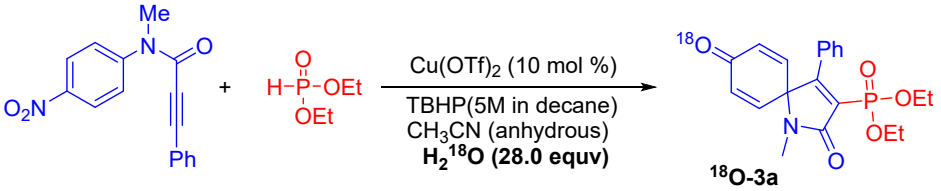
^{16}O-3a: Calcd for $C_{20}H_{23}NO_4{}^{16}OP^+$ $[M+H]^+$ 388.1308, found 388.1305.

^{18}O-3a: Calcd for $C_{20}H_{23}NO_4{}^{18}OP^+$ $[M+H]^+$ 390.1351, found 390.1362.



	m/z	Intensity	Relative Intensity (%)
1, ^{16}O-3a	**388.1305**	**12488403.0**	**100**
2	389.1338	3232801.0	25.89
3, ^{18}O-3a	**390.1362**	**257062.6**	**2.06**
4	391.2834	257878.5	2.06

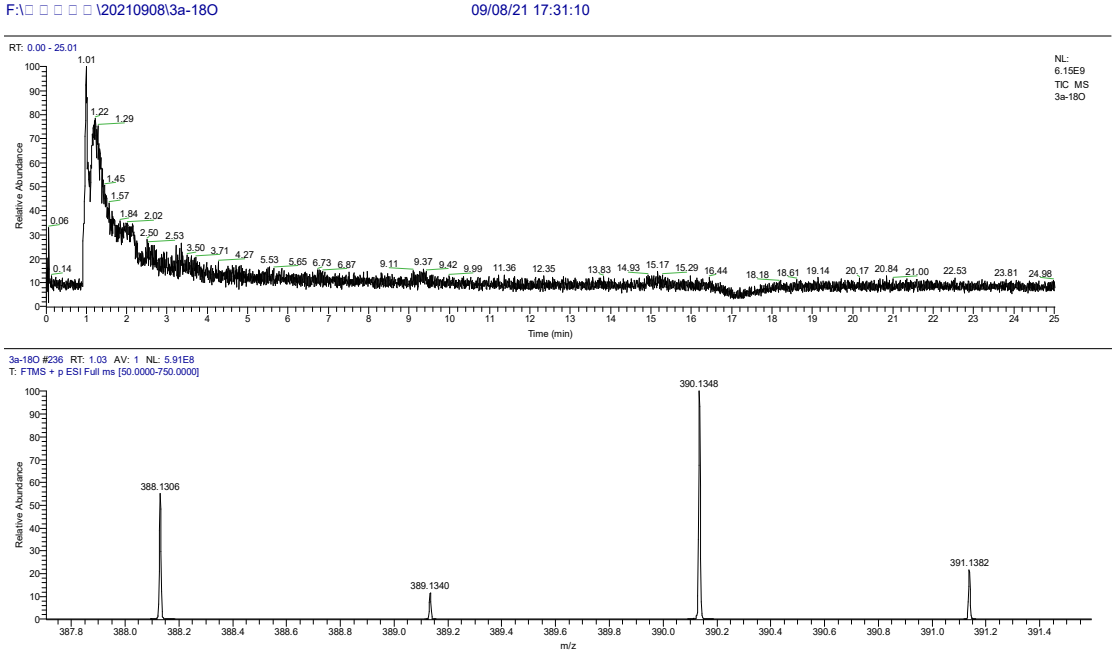
(2) In presence of 0.1mL $H_2{}^{18}O$ (28 equivalents of $H_2{}^{18}O$)



The reaction was performed under in presence of 0.1 mL $H_2{}^{18}O$ (28 equivalents of $H_2{}^{18}O$) and the residue was purified by silica gel column chromatography.

^{16}O-3a: Calcd for $C_{20}H_{23}NO_4{}^{16}OP^+$ $[M+H]^+$ 388.1308, found 388.1306

^{18}O-3a: Calcd for $C_{20}H_{23}NO_4{}^{18}OP^+$ $[M+H]^+$ 390.1351, found 390.1348

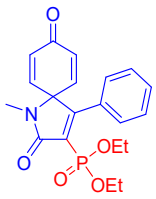


#	m/z	Intensity	Relative Intensity (%)
1, ^{16}O-3a	**388.1306**	**332918720.0**	**100**
2	389.1340	72485768.0	21.77
3, ^{18}O-3a	**390.1348**	**613377408.0**	**184.24**
4	391.1382	134088744.0	40.28

There is a significant increase in terms of the amount of ^{18}O-labeled product when $H_2{}^{18}O$ was added.

5. Spectral Data

Diethyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3a)



Compound **3a** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1a** (58 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3a** (48 mg, 0.124 mmol, 62%) as colorless solid.

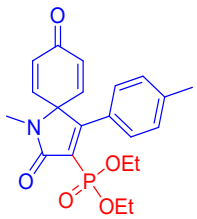
***Note*:** Compound **3a** was prepared from *N*-methyl-*N*,3-diphenylpropiolamide **1w** (47 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3a** (19 mg, 0.05 mmol, 25%) as colorless solid.

Compound **3a** was prepared from *N*-(4-fluorophenyl)-*N*-methyl-3-phenylpropiolamide **1x** (50.6 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3a** (25 mg, 0.064 mmol, 32%) as colorless solid.

Compound **3a** was prepared from *N*-(4-methoxyphenyl)-*N*-methyl-3-phenylpropiolamide **1y** (53 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3a** (17 mg, 0.044 mmol, 22%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.37-7.33 (m, 1H), 7.32-7.27 (m, 2H), 7.22 (d, *J* = 7.3 Hz, 2H), 6.49 (d, *J* = 10.2 Hz, 2H), 6.42 (d, *J* = 10.2 Hz, 2H), 4.11-3.95 (m, 4H), 2.86 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.6, 167.8 (d, *J* = 17.8 Hz), 165.5 (d, *J* = 7.8 Hz), 143.7, 133.8, 131.0 (d, *J* = 3.5 Hz), 130.0, 128.8 (d, *J* = 202.2 Hz), 128.03, 128.00, 69.4 (d, *J* = 15.7 Hz), 63.0 (d, *J* = 6.1 Hz), 26.2, 16.1 (d, *J* = 6.6 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.5
HRMS-ESI: Calcd. for $C_{20}H_{23}NO_5P^+$ $[M+H]^+$ 388.1308, found 388.1293.

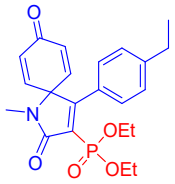
Diethyl (1-methyl-2,8-dioxo-4-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3b)



Compound **3b** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-(p-tolyl)propiolamide **1b** (58.8 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3b** (48 mg, 0.120 mmol, 60%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.10 (t, *J* = 8.8 Hz, 4H), 6.48 (d, *J* = 10.0 Hz, 2H), 6.42 (d, *J* = 10.0 Hz, 2H), 4.12-3.98 (m, 4H), 2.85 (s, 3H), 2.31 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.8, 168.0 (d, *J* = 17.5 Hz), 166.0 (d, *J* = 8.3 Hz), 143.9, 140.4, 133.7, 128.8, 128.2 (d, *J* = 202.3 Hz), 128.06, 128.00, 69.4 (d, *J* = 15.7 Hz), 63.0 (d, *J* = 6.1 Hz), 26.1, 21.4, 16.1 (d, *J* = 6.5 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.7
HRMS-ESI: Calcd. for $C_{21}H_{25}NO_5P^+$ $[M+H]^+$ 402.1465, found 402.1455.

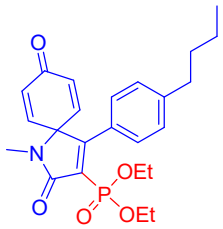
Diethyl(4-(4-ethylphenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3c)



Compound **3c** was prepared from 3-(4-ethylphenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1c** (61.9 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3c** (54 mg, 0.130 mmol, 65%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.16-7.12 (m, 4H), 6.49 (d, *J* = 9.5 Hz, 2H), 6.44 (d, *J* = 9.8 Hz, 2H), 4.11-3.99 (m, 4H), 2.86 (s, 3H), 2.62 (q, *J* = 7.7 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.8, 168.0 (d, *J* = 18.0 Hz), 165.9 (d, *J* = 8.0 Hz), 146.7, 144.0, 133.8, 128.35 (d, *J* = 202.2 Hz), 128.33 (d, *J* = 3.3 Hz), 128.1, 127.6, 69.4 (d, *J* = 15.6 Hz), 63.0 (d, *J* = 5.8 Hz), 28.8, 26.2, 16.2 (d, *J* = 6.6 Hz), 15.3.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.7
HRMS-ESI: Calcd. for $C_{22}H_{27}NO_5P^+$ $[M+H]^+$ 416.1621, found 416.1620.

Diethyl(4-(4-butylphenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3d)

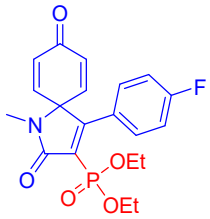


Compound **3d** was prepared from 3-(4-butylphenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1d**

(67.2 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3d** (54 mg, 0.122 mmol, 61%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.13 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.48 (d, *J* = 10.2 Hz, 2H), 6.42 (d, *J* = 10.2 Hz, 2H), 4.10-3.95 (m, 4H), 2.84 (s, 3H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.56-1.50 (m, 2H), 1.32-1.26 (m, 2H), 1.08 (t, *J* = 7.0 Hz, 6H), 0.88 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.8, 168.0 (d, *J* = 17.5 Hz), 165.9 (d, *J* = 8.2 Hz), 145.4, 143.9, 133.7, 128.3 (d, *J* = 3.4 Hz), 128.2 (d, *J* = 202.3 Hz), 128.1, 128.0, 69.3 (d, *J* = 15.8 Hz), 63.0 (d, *J* = 6.0 Hz), 35.5, 33.3, 26.1, 22.4, 16.1 (d, *J* = 7.1 Hz), 14.0.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.8
HRMS-ESI: Calcd. for $C_{24}H_{31}NO_5P^+$ $[M+H]^+$ 444.1934, found 444.1929.

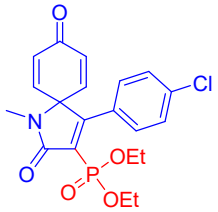
Diethyl(4-(4-fluorophenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3e)



Compound **3e** was prepared from 3-(4-fluorophenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1e** (59.6 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3e** (42 mg, 0.104 mmol, 52%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.25-7.22 (m, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.48 (d, *J* = 10.5 Hz, 2H), 6.45 (d, *J* = 10.4 Hz, 2H), 4.13-4.03 (m, 4H), 2.87 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.5, 167.7 (d, *J* = 17.4 Hz), 164.4 (d, *J* = 7.9 Hz), 163.7 (d, *J* = 250.2 Hz), 143.6, 134.0, 130.3 (d, *J* = 8.3 Hz), 129.3 (d, *J* = 202.2 Hz), 127.0 (t, *J* = 3.2 Hz), 115.4 (d, *J* = 21.8 Hz), 69.4 (d, *J* = 15.5 Hz), 63.2 (d, *J* = 6.2 Hz), 26.2, 16.2 (d, *J* = 6.6 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.3
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -109.8
HRMS-ESI: Calcd. for $C_{20}H_{22}FNO_5P^+$ $[M+H]^+$ 406.1214, found 406.1210.

Diethyl(4-(4-chlorophenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3f)

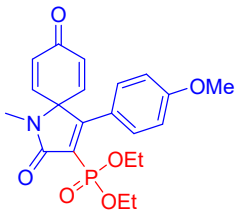


Compound **3f** was prepared from 3-(4-chlorophenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1f** (62.8 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3f** (45 mg, 0.106 mmol, 53%) as white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.30 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.45 (d, *J* = 10.4 Hz, 2H), 6.44 (d, *J* = 10.4 Hz, 2H), 4.14-4.02 (m, 4H), 2.86 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.4, 167.6 (d, *J* = 17.4 Hz), 164.3 (d, *J* = 8.0 Hz), 143.5, 136.5, 134.0, 129.5, 129.41 (d, *J* = 202.3 Hz), 129.40 (d, *J* = 3.5 Hz), 128.4, 69.3 (d, *J* = 15.5 Hz), 63.2 (d, *J* = 6.2 Hz), 26.3, 16.2 (d, *J* = 6.6 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.1
HRMS-ESI: Calcd. for $C_{20}H_{22}ClNO_5P^+$ $[M+H]^+$ 422.0919, found 422.0911.

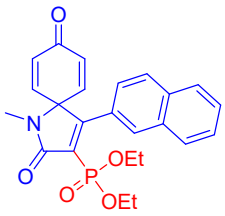
Diethyl(4-(4-methoxyphenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3g)



Compound **3g** was prepared from 3-(4-methoxyphenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1g** (62 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3g** (50 mg, 0.120 mmol, 60%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.24 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.48 (d, *J* = 10.5 Hz, 2H), 6.44 (d, *J* = 10.4 Hz, 2H), 4.13-4.02 (m, 4H), 3.78 (s, 3H), 2.83 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.8, 168.1 (d, *J* = 17.6 Hz), 165.6 (d, *J* = 8.2 Hz), 161.2, 144.2, 133.6, 129.8, 127.4 (d, *J* = 202.4 Hz), 123.3 (d, *J* = 3.5 Hz), 113.6, 69.2 (d, *J* = 15.7 Hz), 63.0 (d, *J* = 6.2 Hz), 55.4, 26.1, 16.3 (d, *J* = 6.6 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 8.0
HRMS-ESI: Calcd. for $C_{21}H_{25}NO_6P^+$ $[M+H]^+$ 418.1414, found 418.1408.

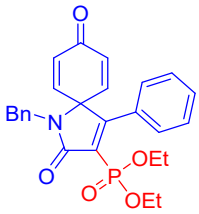
Diethyl(1-methyl-4-(naphthalen-2-yl)-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3h)



Compound **3h** was prepared from *N*-methyl-3-(naphthalen-2-yl)-*N*-(4-nitrophenyl)propiolamide **1h** (66 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3h** (45 mg, 0.102 mmol, 51%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.82-7.74 (m, 4H), 7.53-7.48 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 6.58 (d, *J* = 9.9 Hz, 2H), 6.44 (d, *J* = 9.7 Hz, 2H), 4.10-3.94 (m, 4H), 2.90 (s, 3H), 1.00 (t, *J* = 6.9 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.6, 168.1 (d, *J* = 17.5 Hz), 165.6 (d, *J* = 7.1 Hz), 143.8, 133.9, 133.6, 132.3, 129.0 (d, *J* = 203.2 Hz), 128.6, 128,5, 128.1, 127.83, 127.81, 127.6, 127.0, 125.1, 69.5 (d, *J* = 15.2 Hz), 63.1 (d, *J* = 5.3 Hz), 26.2, 16.1 (d, *J* = 6.0 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.6
HRMS-ESI: Calcd. for $C_{24}H_{25}NO_5P^+$ $[M+H]^+$ 438.1465, found 438.1458.

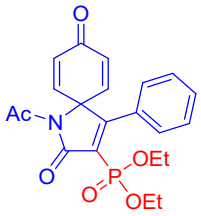
Diethyl (1-benzyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3i)



Compound **3i** was prepared from *N*-benzyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1i** (71.2 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3i** (50 mg, 0.108 mmol, 54%) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.32 (t, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 3H), 7.23-7.19 (m, 4H), 7.10 (dd, *J* = 7.7 Hz, *J* = 1.3 Hz, 2H), 6.30 (d, *J* = 10.0 Hz, 2H), 6.18 (d, *J* = 10.0 Hz, 2H), 4.51 (s, 2H), 4.12-4.05 (m, 2H), 4.04-3.96 (m, 2H), 1.08 (t, *J* = 6.9 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.8, 168.0 (d, *J* = 17.7 Hz), 165.7 (d, *J* = 7.9 Hz), 143.9, 137.1, 132.9, 130.7 (d, *J* = 3.4 Hz), 129.9, 129.0, 128.7 (d, *J* = 203.4 Hz), 128.6, 128.06, 128.03, 127.9, 69.7 (d, *J* = 15.6 Hz), 63.0 (d, *J* = 6.0 Hz), 44.9, 16.1 (d, *J* = 6.6 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.5
HRMS-ESI: Calcd. for $C_{26}H_{27}NO_5P^+$ $[M+H]^+$ 464.1621, found 464.1615.

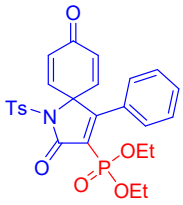
Diethyl (1-acetyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3j)



Compound **3j** was prepared from *N*-acetyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1j** (61.6 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3j** (47 mg, 0.114 mmol, 57%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.38 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.10 (dd, *J* = 7.6 Hz, *J* = 1.3 Hz, 2H), 6.54 (d, *J* = 10.1 Hz, 2H), 6.34 (d, *J* = 10.0 Hz, 2H), 4.11-4.03 (m, 2H), 3.98-3.90 (m, 2H), 2.61 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.7, 169.1, 168.5 (d, *J* = 7.2 Hz), 166.7 (d, *J* = 18.7 Hz), 142.8, 132.9, 130.3, 129.5 (d, *J* = 2.9 Hz), 129.0 (d, *J* = 202.3 Hz), 128.4, 127.8, 69.4 (d, *J* = 14.2 Hz), 63.2 (d, *J* = 6.0 Hz), 25.8, 16.2 (d, *J* = 6.7 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 5.8
HRMS-ESI: Calcd. for $C_{21}H_{23}NO_6P^+$ $[M+H]^+$ 416.1258, found 416.1252.

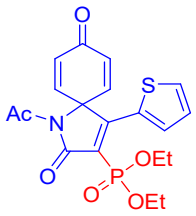
Diethyl (2,8-dioxo-4-phenyl-1-tosyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3k)



Compound **3k** was prepared from *N*-(4-nitrophenyl)-3-phenyl-*N*-tosylpropiolamide **1k** (84 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3k** (56 mg, 0.106 mmol, 53%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.97 (d, *J* = 8.0 Hz, 2H), 7.37-7.33 (m, 3H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 9.8 Hz, 2H), 6.39 (d, *J* = 9.8 Hz, 2H), 4.05-3.97 (m, 2H), 3.92-3.85 (m, 2H), 2.46 (s, 3H), 1.03 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.5, 168.1 (d, *J* = 8.0 Hz), 165.1 (d, *J* = 19.3 Hz), 146.1, 142.1, 135.4, 132.9, 130.3, 130.0, 129.5 (d, *J* = 3.1 Hz), 128.8, 128.3 (d, *J* = 203.4 Hz), 128.2, 127.9, 70.8 (d, *J* = 14.0 Hz), 63.4 (d, *J* = 6.4 Hz), 21.9, 16.1 (d, *J* = 6.6 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 5.4
HRMS-ESI: Calcd. for $C_{26}H_{27}NO_7PS^+$ $[M+H]^+$ 528.1240, found 528.1229.

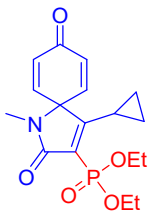
Diethyl(1-acetyl-2,8-dioxo-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3l)



Compound **3l** was prepared from *N*-acetyl-*N*-(4-nitrophenyl)-3-(thiophen-2-yl)propiolamide **1l** (62.8 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3l** (42 mg, 0.100 mmol, 50%) as white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.56 (dd, *J* = 3.6 Hz, *J* = 1.0 Hz, 1H), 7.51 (dd, *J* = 5.0 Hz, *J* = 0.8 Hz, 1H), 7.09 (dd, *J* = 5.1 Hz, *J* = 3.8 Hz, 1H), 6.49 (s, 4H), 4.19-4.06 (m, 4H), 2.58 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 184.2, 169.0, 166.5 (d, *J* = 18.2 Hz), 161.7 (d, *J* = 6.6 Hz), 142.5, 134.3, 133.7, 131.7, 129.1 (d, *J* = 3.6 Hz), 127.6, 125.9 (d, *J* = 203.2 Hz), 68.0 (d, *J* = 13.6 Hz), 63.6 (d, *J* = 6.2 Hz), 26.0, 16.3 (d, *J* = 6.7 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 6.3
HRMS-ESI: Calcd. for $C_{19}H_{21}NO_6PS^+$ $[M+H]^+$ 422.0822, found 422.0822.

Diethyl(4-cyclopropyl-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3n)

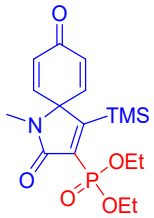


Compound **3n** was prepared from 3-cyclopropyl-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1n** (48.8 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 6 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3n** (34 mg, 0.096 mmol, 48%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.53 (d, *J* = 8.3 Hz, 2H), 6.41 (d, *J* = 8.3 Hz, 2H), 4.27-4.21 (m, 4H), 2.70 (s, 3H), 2.47-2.41 (m, 1H), 1.38 (t, *J* = 7.1 Hz, 6H), 1.18-1.15 (m, 2H), 1.06-1.01 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.9, 172.9 (d, *J* = 11.8 Hz), 168.1 (d, *J* = 16.4 Hz), 144.7, 132.9, 125.0 (d, *J* = 200.6 Hz), 67.4 (d, *J* = 16.4 Hz), 63.1 (d, *J* = 6.2 Hz), 25.2, 16.5 (d, *J* = 6.4 Hz), 12.8 (d, *J* = 2.9 Hz), 11.0.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 8.9
HRMS-ESI: Calcd. for $C_{17}H_{23}NO_5P^+$ $[M+H]^+$ 352.1308, found 352.1305.

Diethyl(1-methyl-2,8-dioxo-4-(trimethylsilyl)-1-azaspiro[4.5]deca-3,6,9-trien-3-

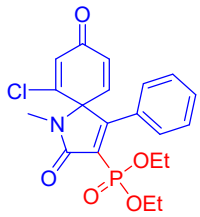
yl)phosphonate (3o)



Compound **3o** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-(trimethylsilyl)propiolamide **1o** (55.2 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 6 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 50% to 70% AcOEt/petroleum ether as the eluent to give **3o** (36 mg, 0.094 mmol, 47%) as yellow foam.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.56 (d, *J* = 10.0 Hz, 2H), 6.29 (d, *J* = 10.0 Hz, 2H), 4.29-4.19 (m, 4H), 2.73 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 6H), 0.30 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 184.1, 173.0 (d, *J* = 19.5 Hz), 168.1 (d, *J* = 19.6 Hz), 144.1, 141.3 (d, *J* = 200.2 Hz), 133.5, 70.3 (d, *J* = 20.5 Hz), 63.1 (d, *J* = 5.8 Hz), 25.5, 16.6 (d, *J* = 6.1 Hz), 0.7.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 8.8
HRMS-ESI: Calcd. for $C_{17}H_{27}NO_5PSi^+$ $[M+H]^+$ 384.1391, found 384.1387.

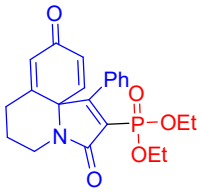
Diethyl(6-chloro-1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3p)



Compound **3p** was prepared from *N*-(2-chloro-4-nitrophenyl)-*N*-methyl-3-phenylpropiolamide **1p** (62.8 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3p** (45 mg, 0.106 mmol, 53%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.39 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 1.6 Hz, 1H), 6.57 (d, *J* = 9.9 Hz, 1H), 6.45 (d, *J* = 9.9 Hz, 1H), 4.16-3.92 (m, 4H), 2.84 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 182.6, 168.1 (d, *J* = 17.3 Hz), 164.1 (d, *J* = 8.4 Hz), 149.6, 143.0, 133.3, 132.8, 130.37, 130.32 (d, *J* = 201.2 Hz), 130.22 (d, *J* = 3.7 Hz), 128.2, 127.9, 72.5 (d, *J* = 15.6 Hz), 63.2 (d, *J* = 5.8 Hz), 62.9 (d, *J* = 6.2 Hz), 25.8, 16.3 (d, *J* = 6.6 Hz), 16.1 (d, *J* = 6.5 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 6.6
HRMS-ESI: Calcd. for $C_{20}H_{22}ClNO_5P^+$ $[M+H]^+$ 422.0919, found 422.0911.

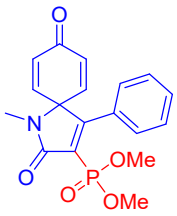
Diethyl (3,9-dioxo-1-phenyl-5,6,7,9-tetrahydro-3H-pyrrolo[2,1-j]quinolin-2-yl)phosphonate (3q)



Compound **3q** was prepared from 1-(6-nitro-3,4-dihydroquinolin-1(2H)-yl)-3-phenylprop-2-yn-1-one **1q** (61.2 mg, 0.2 mmol), diethyl phosphonate **2a** (82.8 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3q** (36 mg, 0.088 mmol, 44%) as white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.33 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.01 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 2H), 6.56 (d, *J* = 9.7 Hz, 1H), 6.27 (t, *J* = 1.3 Hz, 1H), 6.22 (dd, *J* = 9.9 Hz, *J* = 1.5 Hz, 1H), 4.19 (dd, *J* = 13.8 Hz, *J* = 8.7 Hz, 1H), 4.11-3.93 (m, 4H), 2.81-2.75 (m, 1H), 2.53-2.42 (m, 2H), 2.10-2.04 (m, 1H), 1.87-1.79 (m, 1H), 1.11-1.06 (m, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 184.1, 171.8 (d, *J* = 17.7 Hz), 167.0 (d, *J* = 8.5 Hz), 157.2, 145.0, 132.8, 130.1 (d, *J* = 3.1 Hz), 129.7,129.3, 129.25 (d, *J* = 200.3 Hz), 128.2, 127.6, 73.3 (d, *J* = 15.6 Hz), 63.0 (d, *J* = 6.0 Hz), 62.8 (d, *J* = 6.0 Hz), 36.5, 26.8, 26.3, 16.1 (d, *J* = 6.9 Hz), 16.0 (d, *J* = 6.5 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.3
HRMS-ESI: Calcd. for $C_{22}H_{25}NO_5P^+$ $[M+H]^+$ 414.1465, found 414.1454.

Dimethyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3r)

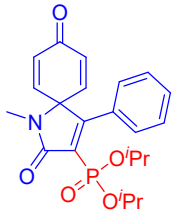


Compound **3r** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1a** (58 mg, 0.2 mmol), diethyl phosphonate **2r** (66 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3r** (32 mg, 0.092 mmol, 46%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.37 (t, *J* = 7.3 Hz, 1H), 7.31(t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.3 Hz, 2H), 6.50 (d, *J* = 10.2 Hz, 2H), 6.43 (d, *J* = 10.2 Hz, 2H), 3.62 (s, 3H), 3.60 (s, 3H), 2.96 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.5, 167.7 (d, *J* = 17.6 Hz), 166.2 (d, *J* = 8.3 Hz), 143.5, 133.9, 130.7 (d, *J* = 3.5 Hz), 130.2, 128.4 (d, *J* = 203.2 Hz), 128.1, 127.9, 69.5 (d, *J* = 15.7 Hz), 53.4 (d, *J* = 5.8 Hz), 26.2.

^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 10.2
HRMS-ESI: Calcd. for $C_{18}H_{19}NO_5P^+$ $[M+H]^+$ 360.0995, found 360.0994.

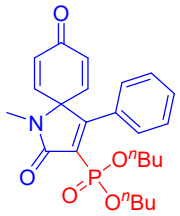
Diisopropyl(1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3s)



Compound **3s** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1a** (58 mg, 0.2 mmol), diisopropyl phosphonate **2s** (99.7 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3s** (50 mg, 0.120 mmol, 60%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.35 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.49 (d, *J* = 10.0 Hz, 2H), 6.42 (d, *J* = 10.0 Hz, 2H), 4.81-4.75 (m, 2H), 2.87 (s, 3H), 1.21 (d, *J* = 6.1 Hz, 6H), 1.08 (d, *J* = 6.1 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.8, 167.9 (d, *J* = 18.0 Hz), 165.0 (d, *J* = 7.6 Hz), 144.0, 133.8, 131.4 (d, *J* = 3.3 Hz), 129.9, 129.6 (d, *J* = 204.2 Hz), 128.2, 128.0, 72.1 (d, *J* = 6.2 Hz), 69.4 (d, *J* = 15.3 Hz), 26.2, 24.3 (d, *J* = 3.3 Hz), 23.6 (d, *J* = 6.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 5.3
HRMS-ESI: Calcd. for $C_{22}H_{27}NO_5P^+$ $[M+H]^+$ 416.1621, found 416.1617.

Dibutyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3t)

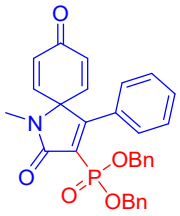


Compound **3t** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1a** (58 mg, 0.2 mmol), dibutyl phosphonate **2t** (116.4 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3t** (52 mg, 0.118 mmol, 59%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.36 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 6.49 (d, *J* = 10.2 Hz, 2H), 6.42 (d, *J* = 10.1 Hz, 2H), 4.05-3.99 (m, 2H), 3.96-3.89 (m, 2H), 2.86 (s, 3H), 1.43-1.37 (m, 4H), 1.24-1.17 (m, 4H), 0.82 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.7, 167.9 (d, *J* = 17.4 Hz), 165.3 (d, *J* = 7.8 Hz), 143.8, 133.8, 131.1 (d, *J* = 3.5 Hz), 130.0, 129.8 (d, *J* = 208.2 Hz), 129.7, 128.1, 69.5 (d, *J* = 15.5 Hz), 66.8 (d, *J* = 6.5 Hz), 32.4 (d, *J* = 6.4 Hz), 26.2, 18.7, 13.7.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 7.7

HRMS-ESI: Calcd. for $C_{24}H_{31}NO_5P^+$ $[M+H]^+$ 444.1934, found 444.1928.

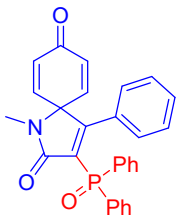
Dibenzyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3u)



Compound **3u** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1a** (58 mg, 0.2 mmol), dibenzyl phosphonate **2u** (157.2 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **3u** (68 mg, 0.132 mmol, 66%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.33-7.23 (m, 9H), 7.16-7.13 (m, 6H), 6.43-6.38 (m, 4H), 5.04 (dd, *J* = 12.0 Hz, *J* = 8.5 Hz, 2H), 4.91 (dd, *J* = 11.7 Hz, *J* = 9.0 Hz, 2H), 2.86 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.6, 167.8 (d, *J* = 17.8 Hz), 166.0 (d, *J* = 8.3 Hz), 143.6, 136.0 (d, *J* = 6.4 Hz), 133.8, 130.8 (d, *J* = 3.5 Hz), 130.2, 128.8, 128.6 (d, *J* = 202.4 Hz), 128.5, 128.2, 128.1, 128.0, 69.5 (d, *J* = 16.1 Hz), 68.5 (d, *J* = 6.0 Hz), 26.2.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 8.3
HRMS-ESI: Calcd. for $C_{30}H_{27}NO_5P^+$ $[M+H]^+$ 512.1621, found 512.1615.

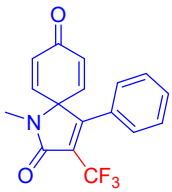
3-(Diphenylphosphoryl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3v)



Compound **3v** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1a** (58 mg, 0.2 mmol), diphenylphosphine oxide **2v** (121.2 mg, 0.6 mmol), the solution was stirred for 3 hours at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 50% to 70% AcOEt/petroleum ether as the eluent to give **3v** (40 mg, 0.088 mmol, 44%) as white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.78 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.48 (td, *J* = 7.4 Hz, *J* = 1.3 Hz, 2H), 7.39 (td, *J* = 7.8 Hz, *J* = 3.0 Hz, 4H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.51 (d, *J* = 10.0 Hz, 2H), 6.42 (d, *J* = 10.0 Hz, 2H), 2.83 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.6, 168.9 (d, *J* = 4.6 Hz), 168.3 (d, *J* = 14.3 Hz), 143.8, 133.8, 132.18, 132.16, 131.7, 131.62, 131.61 (d, *J* = 110.2 Hz), 131.4 (d, *J* = 100.2Hz), 130.21, 130.19, 130.0, 128.5, 128.4, 128.2, 127.8, 69.8 (d, *J* = 10.7 Hz), 26.3.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 18.4.
HRMS-ESI: Calcd. for $C_{28}H_{23}NO_3P^+$ $[M+H]^+$ 452.1410, found 452.1405.

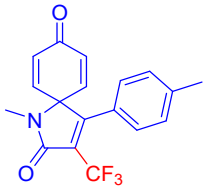
1-Methyl-4-phenyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4a)



Compound **4a** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1a** (58 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4a** (36 mg, 0.112 mmol, 56%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.38 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 2H), 6.52 (d, *J* = 10.2 Hz, 2H), 6.44 (d, *J* = 10.2 Hz, 2H), 2.88 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.3, 164.6, 159.6 (q, *J* = 3.6 Hz), 142.7, 134.2, 130.4, 128.8, 128.3, 127.6, 126.5 (q, *J* = 33.6 Hz), 120.4 (q, *J* = 270.2 Hz), 68.0, 26.2.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.7
HRMS-ESI: Calcd. for $C_{17}H_{13}F_3NO_2^+$ $[M+H]^+$ 320.0893, found 320.0889.

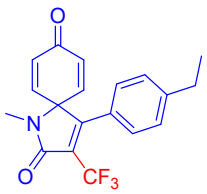
1-Methyl-4-(p-tolyl)-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4b)



Compound **4b** was prepared from 3-(4-fluorophenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1b** (58.8 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4b** (31 mg, 0.094 mmol, 47%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.14 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 10.5 Hz, 2H), 6.46 (d, *J* = 10.4 Hz, 2H), 2.89 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.5, 164.8, 159.8 (q, *J* = 3.4 Hz), 143.0, 140.9, 134.2, 129.2, 127.6, 126.2 (q, *J* = 33.9 Hz), 126.0, 120.6 (q, *J* = 272.0 Hz), 68.0, 26.3, 21.5.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.6
HRMS-ESI: Calcd. for $C_{18}H_{15}F_3NO_2^+$ $[M+H]^+$ 334.1049, found 334.1043.

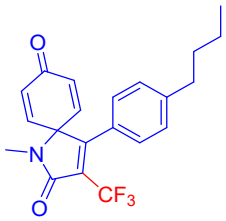
4-(4-Ethylphenyl)-1-methyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4c)



Compound **4c** was prepared from 3-(4-ethylphenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1c** (62 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4c** (32 mg, 0.092 mmol, 46%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.16 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.50 (d, *J* = 10.8 Hz, 2H), 6.47 (d, *J* = 10.5 Hz, 2H), 2.90 (s, 3H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.5, 164.9, 159.9 (q, *J* = 3.0 Hz), 147.0, 143.0, 134.2, 128.0, 127.6, 126.22 (q, *J* = 33.4 Hz), 126.19, 120.6 (q, *J* = 272.6 Hz), 68.0, 28.7, 26.3, 15.0.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.6
HRMS-ESI: Calcd. for $C_{19}H_{17}F_3NO_2^+$ $[M+H]^+$ 348.1206, found 348.1202.

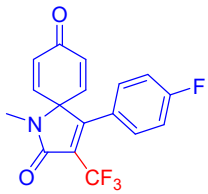
4-(4-Butylphenyl)-1-methyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4d)



Compound **4d** was prepared from 3-(4-butylphenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1d** (67.2 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 20 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4d** (33 mg, 0.088 mmol, 44%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.14 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 11.0 Hz, 2H), 6.47 (d, *J* = 10.6 Hz, 2H), 2.89 (s, 3H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.60-1.54 (m, 2H), 1.35-1.30 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.5, 164.9, 159.9 (q, *J* = 3.4 Hz), 145.8, 143.0, 134.2, 128.5, 127.6, 126.20 (q, *J* = 33.4 Hz), 126.05, 120.5 (q, *J* = 273.3 Hz), 68.0, 35.5, 33.2, 26.2, 22.5, 14.0.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.6
HRMS-ESI: Calcd. for $C_{21}H_{21}F_3NO_2^+$ $[M+H]^+$ 376.1519, found 376.1510.

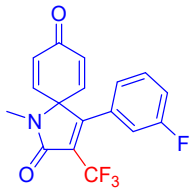
4-(4-Fluorophenyl)-1-methyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4e)



Compound **4e** was prepared from 3-(4-fluorophenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1e** (59.6 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4e** (31 mg, 0.092 mmol, 46%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.13 (dd, *J* = 8.6 Hz, *J* = 5.2 Hz, 2H), 7.06 (t, *J* = 8.5 Hz, 2H), 6.49 (t, *J* = 10.5 Hz, 4H), 2.91 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.1, 164.9, 163.7 (d, *J* = 252.4 Hz), 158.5 (q, *J* = 3.5 Hz), 142.6, 134.5, 129.9 (d, *J* = 9.2 Hz), 127.2 (q, *J* = 33.6 Hz), 124.9 (d, *J* = 3.6 Hz), 120.4 (q, *J* = 272.8 Hz), 116.0 (d, *J* = 22.1 Hz), 68.0, 26.4.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.7, -108.9
HRMS-ESI: Calcd. for $C_{17}H_{12}F_4NO_2^+$ $[M+H]^+$ 338.0799, found 338.0792.

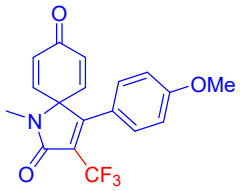
4-(3-Fluorophenyl)-1-methyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4f)



Compound **4f** was prepared from 3-(3-fluorophenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1ff** (59.6 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4f** (37 mg, 0.110 mmol, 55%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.37-7.32 (m, 1H), 7.13 (td, *J* = 8.5 Hz, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.83 (dt, *J* = 8.9 Hz, *J* = 1.9 Hz, 1H), 6.50 (s, 4H), 2.92 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.1, 164.3, 162.1 (d, *J* = 253.2 Hz), 157.9, 142.3, 134.6, 130.7 (d, *J* = 8.0 Hz), 130.4 (d, *J* = 8.5 Hz), 127.4 (d, *J* = 34.9 Hz), 123.6, 120.3 (q, *J* = 270.0 Hz), 117.7 (d, *J* = 20.6 Hz), 115.1 (d, *J* = 22.6 Hz), 67.9, 26.4.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.8, -111.0
HRMS-ESI: Calcd. for $C_{17}H_{12}F_4NO_2^+$ $[M+H]^+$ 338.0799, found 338.0798.

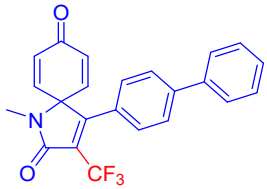
4-(4-Methoxyphenyl)-1-methyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4g)



Compound **4g** was prepared from 3-(4-methoxyphenyl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1g** (62 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4g** (35 mg, 0.1 mmol, 50%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.11 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 10.6 Hz, 2H), 6.48 (d, *J* = 10.8 Hz, 2H), 3.80 (s, 3H), 2.89 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.5, 165.0, 161.4, 159.5 (q, *J* = 3.2 Hz), 143.2, 134.2, 129.3, 125.8 (q, *J* = 34.0 Hz), 121.1, 120.6 (q, *J* = 273.2 Hz), 114.1, 67.9, 55.5, 26.2.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.5
HRMS-ESI: Calcd. for $C_{18}H_{15}F_3NO_3^+$ $[M+H]^+$ 350.0999, found 350.0992.

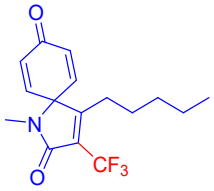
4-([1,1'-Biphenyl]-4-yl)-1-methyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4h)



Compound **4h** was prepared from 3-([1,1'-biphenyl]-4-yl)-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1hh** (71.2 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4h** (36 mg, 0.090 mmol, 45%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.58-7.55 (m, 4H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.52 (s, 4H), 2.92 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.4, 164.7, 159.3 (q, *J* = 3.5 Hz), 143.5, 142.8, 139.7, 134.4, 129.1, 128.3, 128.2, 127.8, 127.3, 127.1, 126.6 (d, *J* = 33.9 Hz), 120.6 (q, *J* = 273.7 Hz), 68.0, 26.3.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.5
HRMS-ESI: Calcd. for $C_{23}H_{17}F_3NO_2^+$ $[M+H]^+$ 396.1206, found 396.1206.

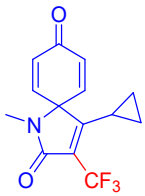
1-Methyl-4-pentyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4i)



Compound **4i** was prepared from *N*-methyl-*N*-(4-nitrophenyl)oct-2-ynamide **1ii** (54.8 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4i** (29 mg, 0.092 mmol, 46%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.61 (d, *J* = 10.0 Hz, 2H), 6.36 (d, *J* = 10.0 Hz, 2H), 2.85 (s, 3H), 2.24 (t, *J* = 8.0 Hz, 2H), 1.46-1.40 (m, 2H), 1.30-1.23 (m, 4H), 0.86 (t, *J* = 6.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.6, 165.2 (d, *J* = 1.8 Hz), 161.8 (q, *J* = 3.3 Hz), 143.6, 134.2, 125.7 (q, *J* = 34.2 Hz), 121.2 (q, *J* = 267.3 Hz), 68.0, 32.0, 30.3, 26.5, 26.2, 22.0, 13.8.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -61.8
HRMS-ESI: Calcd. for $C_{16}H_{19}F_3NO_2^+$ $[M+H]^+$ 314.1362, found 314.1362.

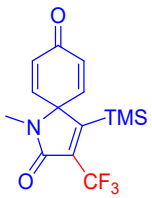
4-Cyclopropyl-1-methyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4j)



Compound **4j** was prepared from 3-cyclopropyl-*N*-methyl-*N*-(4-nitrophenyl)propiolamide **1n** (48.8 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4j** (23 mg, 0.082 mmol, 41%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.58 (d, *J* = 10.1 Hz, 2H), 6.41 (d, *J* = 10.0 Hz, 2H), 2.75 (s, 3H), 1.79-1.69 (m, 1H), 1.05-0.97 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.7, 165.1, 163.3 (q, *J* = 3.3 Hz), 144.0, 133.5, 124.7 (q, *J* = 33.4 Hz), 121.3 (q, *J* = 272.6 Hz), 66.6, 25.4, 10.5, 9.71, 9.69.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -59.6
HRMS-ESI: Calcd. for $C_{14}H_{13}F_3NO_2^+$ $[M+H]^+$ 284.0893, found 284.0892.

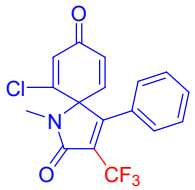
1-Methyl-3-(trifluoromethyl)-4-(trimethylsilyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4k)



Compound **4k** was prepared from *N*-methyl-*N*-(4-nitrophenyl)-3-(trimethylsilyl)propiolamide **1o** (55.2 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4k** (22 mg, 0.070 mmol, 35%) as brown oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.58 (d, *J* = 10.0 Hz, 2H), 6.30 (d, *J* = 10.0 Hz, 2H), 2.76 (s, 3H), 0.23 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.7, 164.9, 162.6 (q, *J* = 3.5 Hz), 143.3, 139.1 (q, *J* = 34.1 Hz), 133.8, 121.3 (q, *J* = 267.5 Hz), 68.4, 25.6, 0.004 (q, *J* = 2.2 Hz).
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.2
HRMS-ESI: Calcd. for $C_{14}H_{17}F_3NO_2Si^+$ $[M+H]^+$ 316.0975, found 316.0971.

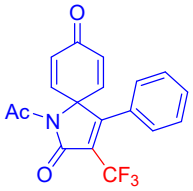
6-Chloro-1-methyl-4-phenyl-3-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (4l)



Compound **4l** was prepared from *N*-(2-chloro-4-nitrophenyl)-*N*-methyl-3-phenylpropiolamide **1p** (62.8 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 70% to 80% AcOEt/petroleum ether as the eluent to give **4l** (38 mg, 0.106 mmol, 53%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 1.4 Hz, 1H), 6.59 (d, *J* = 9.9 Hz, 1H), 6.51 (dd, *J* = 9.9 Hz, *J* = 1.3 Hz, 1H), 2.87 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 182.3, 164.9 (d, *J* = 1.8 Hz), 158.1 (q, *J* = 3.6 Hz), 148.8, 141.9, 133.6, 133.3, 130.7, 128.5, 128.2 (q, *J* = 34.3 Hz), 128.0, 127.5, 120.2 (q, *J* = 273.1 Hz), 71.2, 26.0.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.8
HRMS-ESI: Calcd. for $C_{17}H_{12}ClF_3NO_2^+$ $[M+H]^+$ 354.0503, found 354.0499.

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

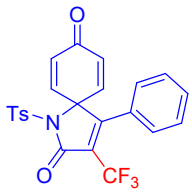


Compound **4m** was prepared from *N*-acetyl-*N*-(4-nitrophenyl)-3-phenylpropiolamide **1j** (61.6 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using

20% to 30% AcOEt/petroleum ether as the eluent to give **4m** (29 mg, 0.084 mmol, 42%) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.04 (dd, *J* = 8.1 Hz, *J* = 1.2 Hz, 2H), 6.54 (dd, *J* = 9.8 Hz, *J* = 2.4 Hz, 2H), 6.39 (dd, *J* = 9.9 Hz, *J* = 2.9 Hz, 2H), 2.64 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.4, 168.8, 163.4 (d, *J* = 1.7 Hz), 163.2 (q, *J* = 2.7 Hz), 141.8, 133.3, 130.8, 128.2, 127.9, 127.2, 126.2 (q, *J* = 34.3 Hz), 119.7 (q, *J* = 273.2 Hz), 67.9, 25.9.
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -60.8
HRMS-ESI: Calcd. for $C_{18}H_{13}F_3NO_3^+$ $[M+H]^+$ 348.0842, found 348.0838.

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

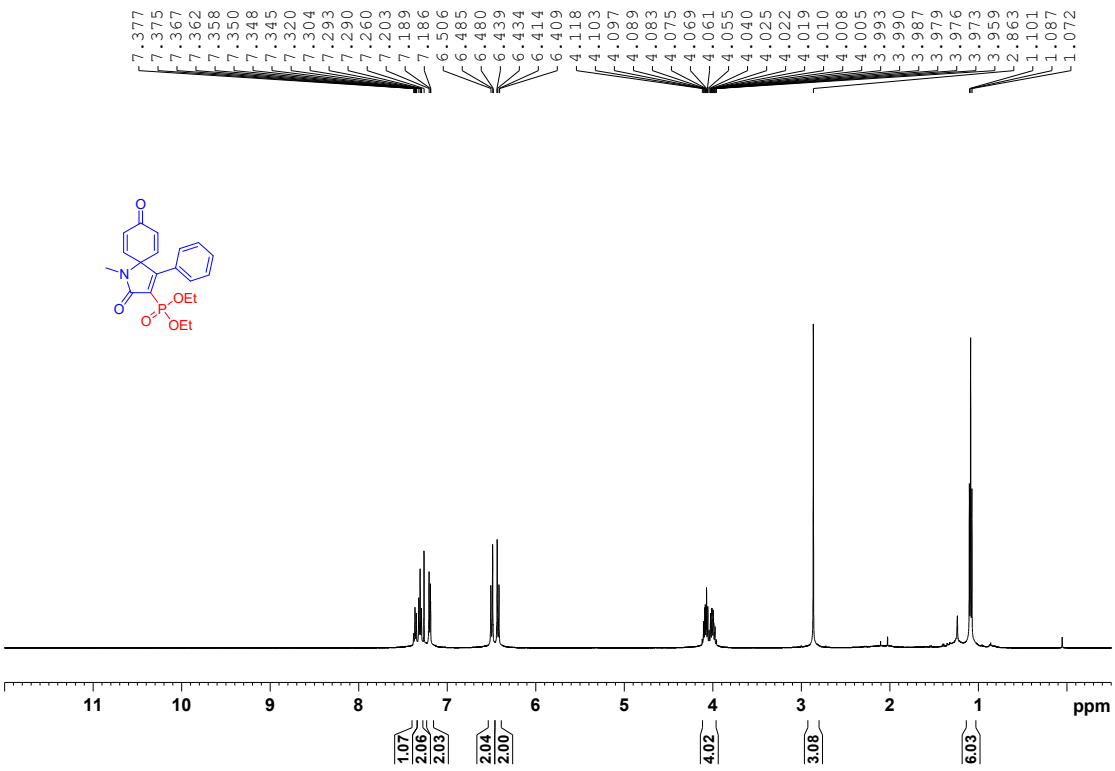


Compound **4n** was prepared from *N*-(4-nitrophenyl)-3-phenyl-*N*-tosylpropiolamide **1k** (84 mg, 0.2 mmol), sodium trifluoromethanesulfinate (155 mg, 1.0 mmol), the solution was stirred for 40 minutes at 80 °C, followed by aqueous work-up, purified by silica gel column chromatography using 20% to 30% AcOEt/petroleum ether as the eluent to give **4n** (43 mg, 0.094 mmol, 47%) as colorless solid.

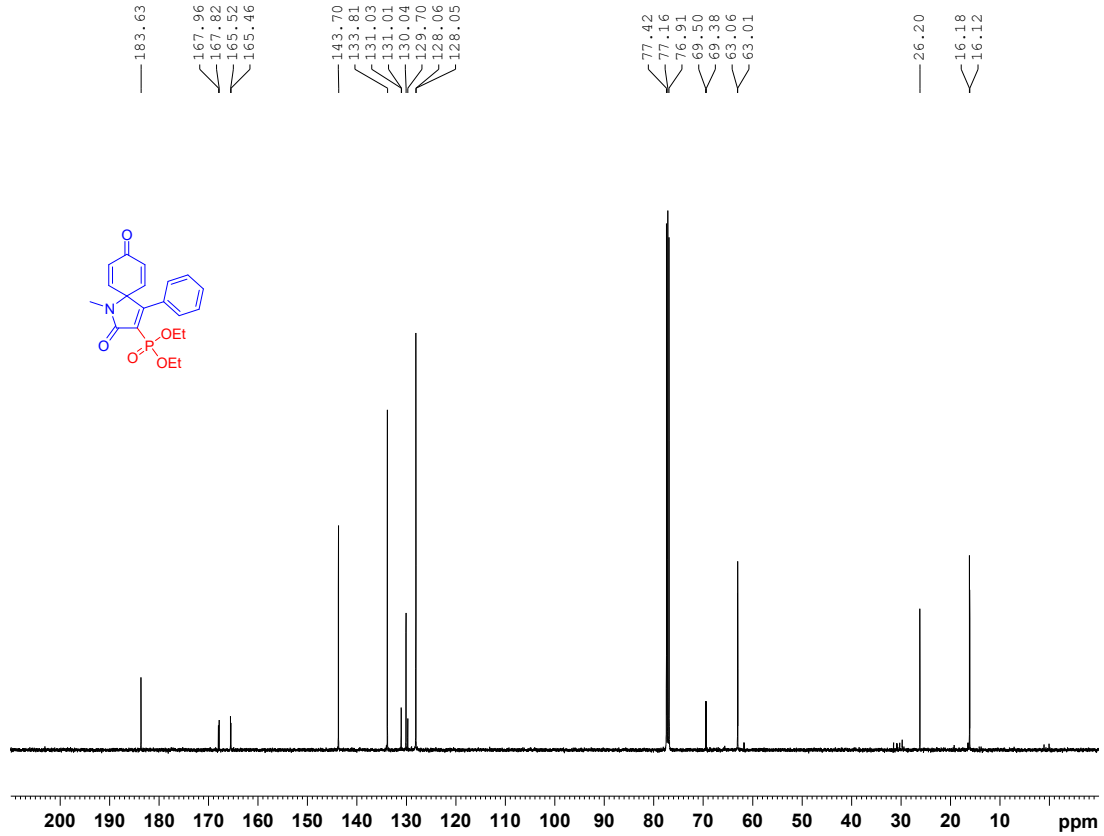
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.01 (d, *J* = 8.3 Hz, 2H), 7.44-7.38 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 2H), 6.66 (d, *J* = 9.9 Hz, 2H), 6.45 (d, *J* = 9.9 Hz, 2H), 2.48 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 183.2, 163.0 (q, *J* = 2.8 Hz), 162.0, 146.5, 141.2, 135.1, 133.5, 130.9, 130.1, 128.9, 128.3, 127.8, 127.2, 125.7 (d, *J* = 34.8 Hz), 119.7 (q, *J* = 272.6 Hz), 69.5, 21.9.
^{19}F NMR (162 MHz, $CDCl_3$): δ (ppm) -60.5
HRMS-ESI: Calcd. for $C_{23}H_{17}F_3NO_4S^+$ $[M+H]^+$ 460.0825, found 460.0815.

6. ^{1}H and ^{13}C NMR spectra

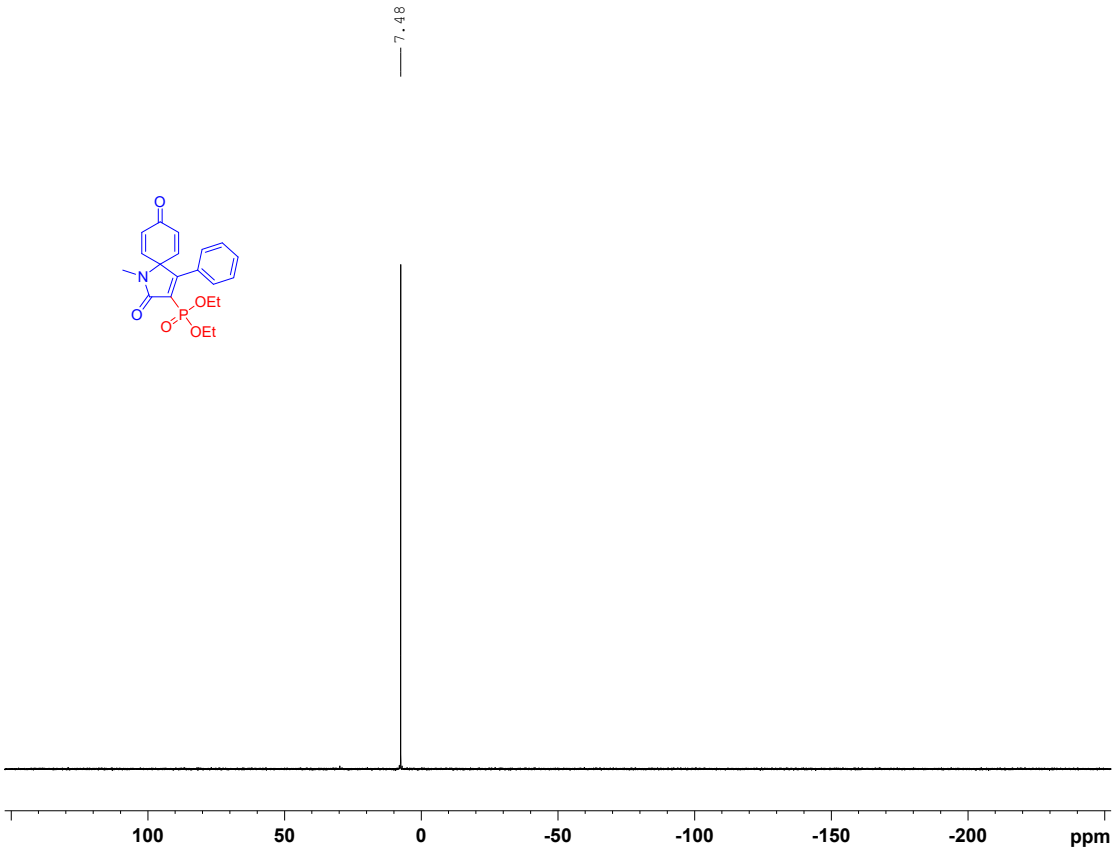
^{1}H NMR ($CDCl_3$, 300 K), **3a**



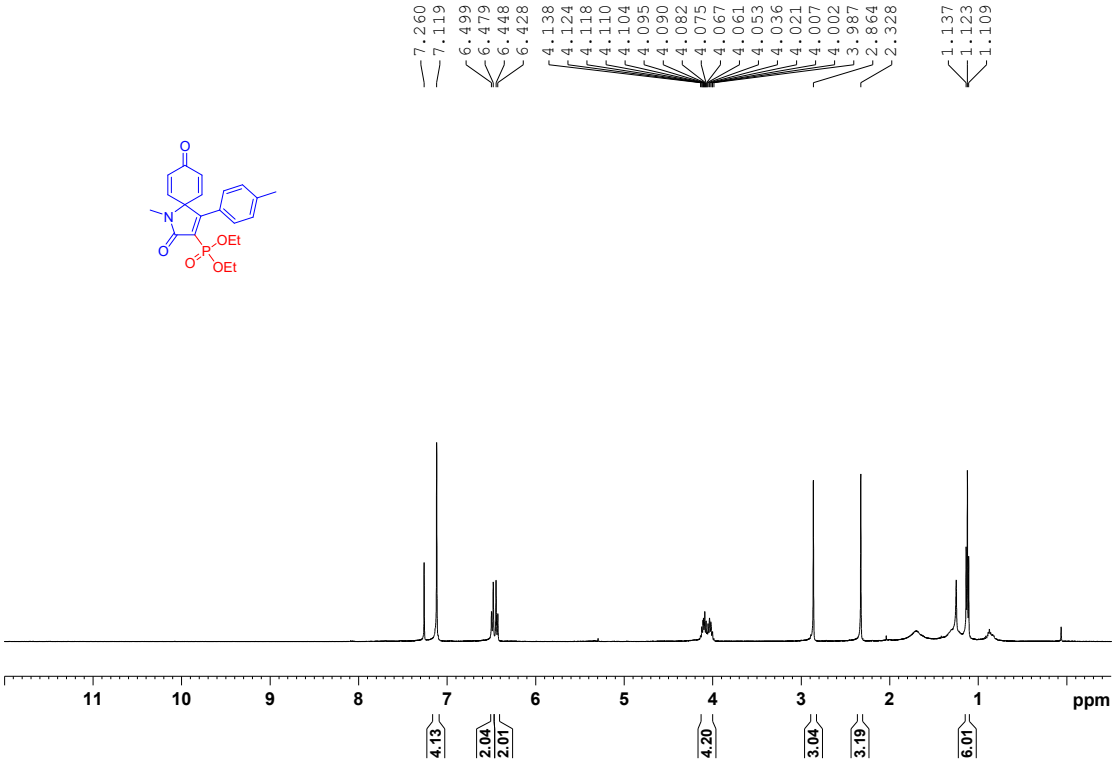
^{13}C NMR ($CDCl_3$, 300 K), **3a**



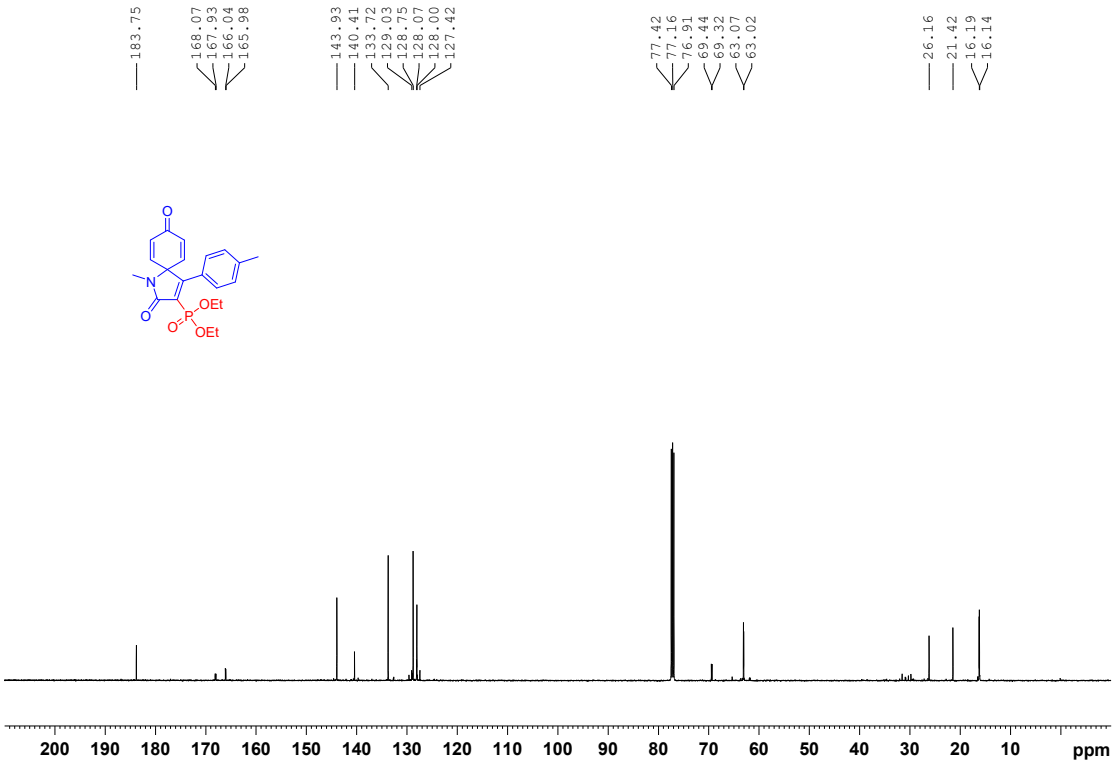
^{31}P NMR (CDCl$_3$, 300 K) **3a**



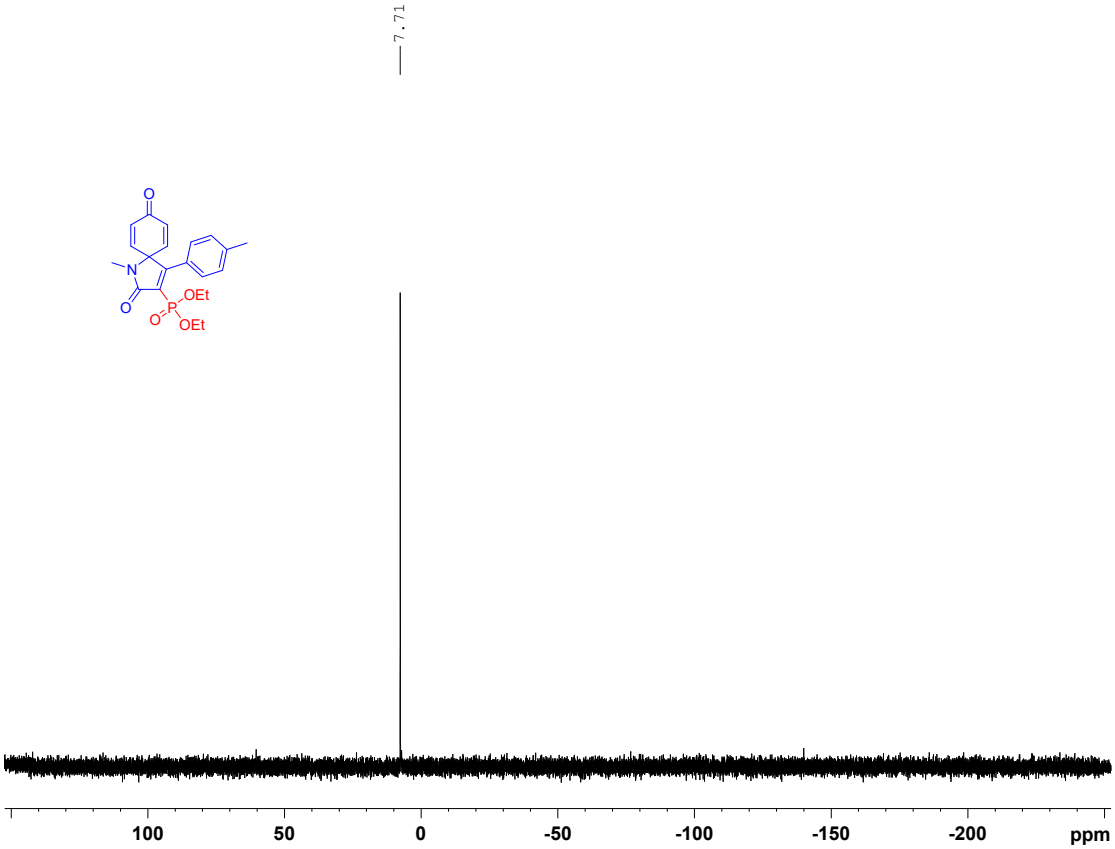
^{1}H NMR (CDCl$_3$, 300 K), **3b**



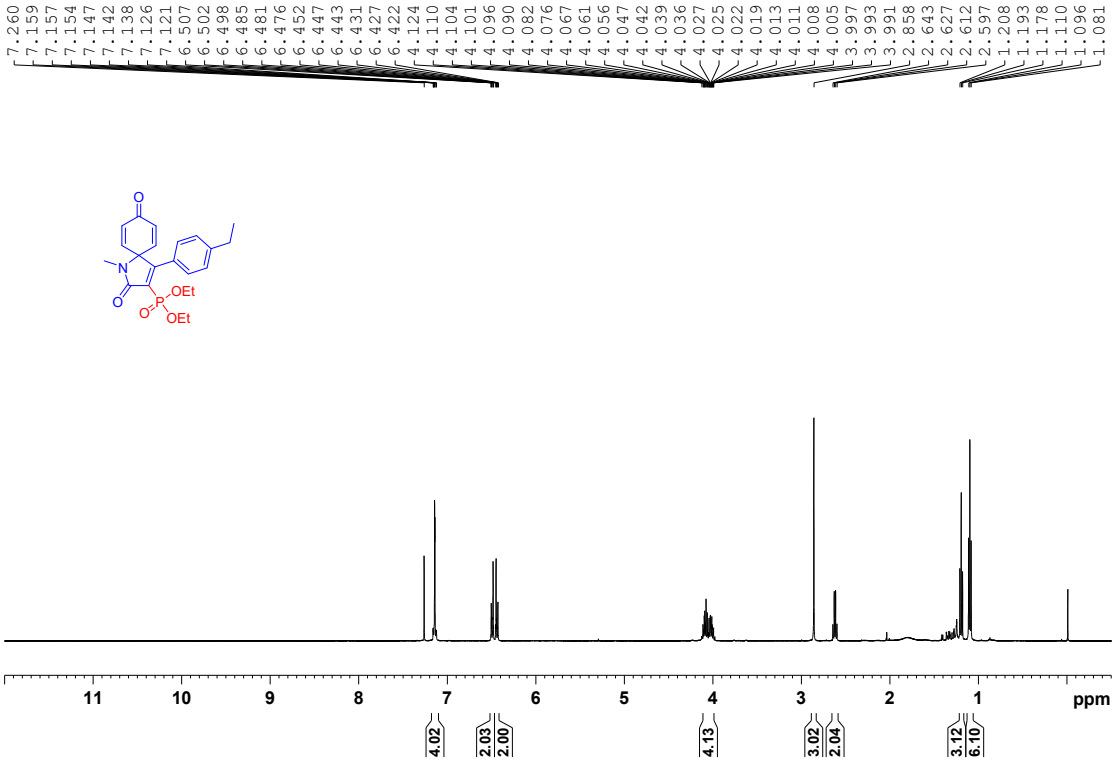
^{13}C NMR (CDCl$_3$, 300 K), **3b**



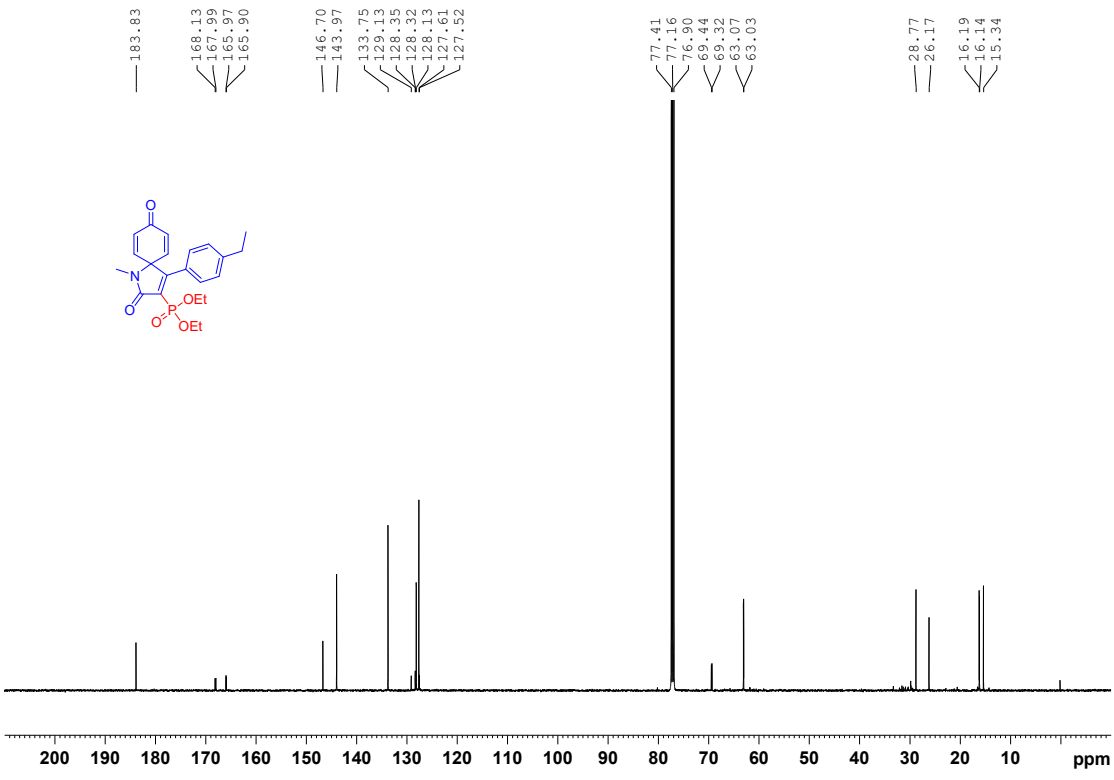
^{31}P NMR (CDCl$_3$, 300 K) **3b**



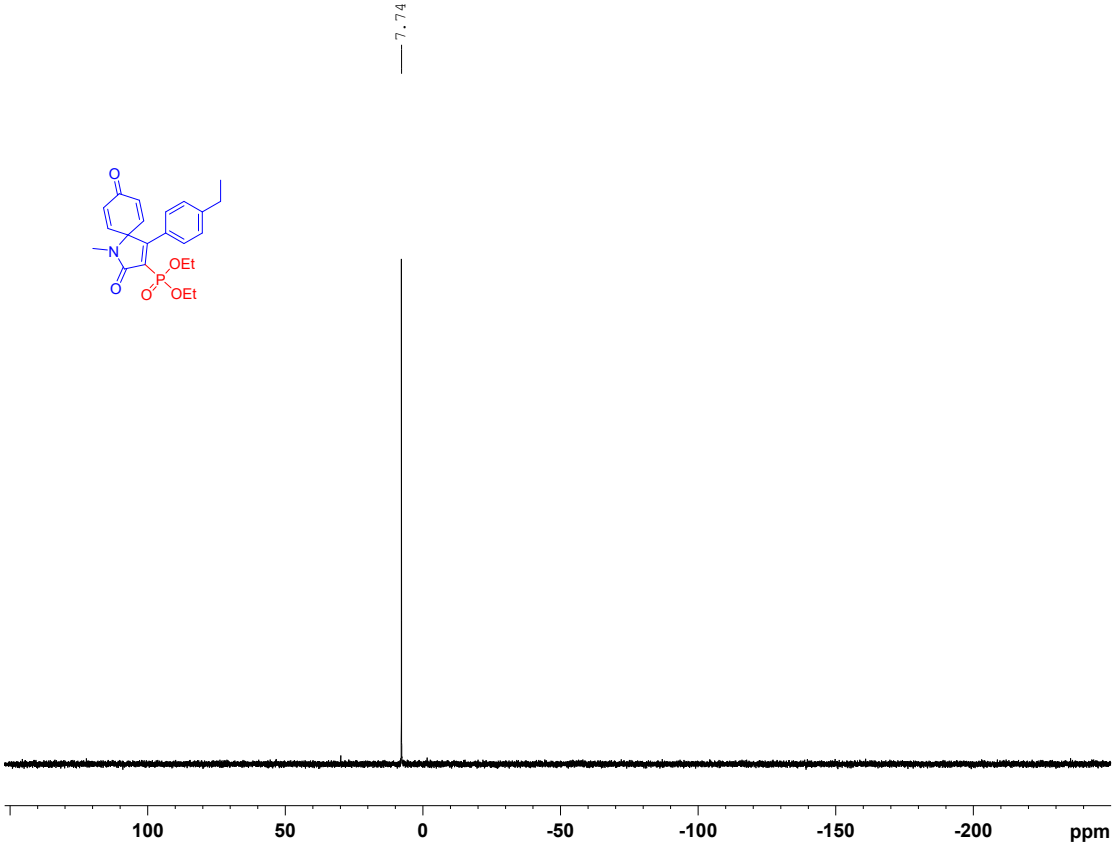
^{1}H NMR (CDCl$_3$, 300 K), **3c**



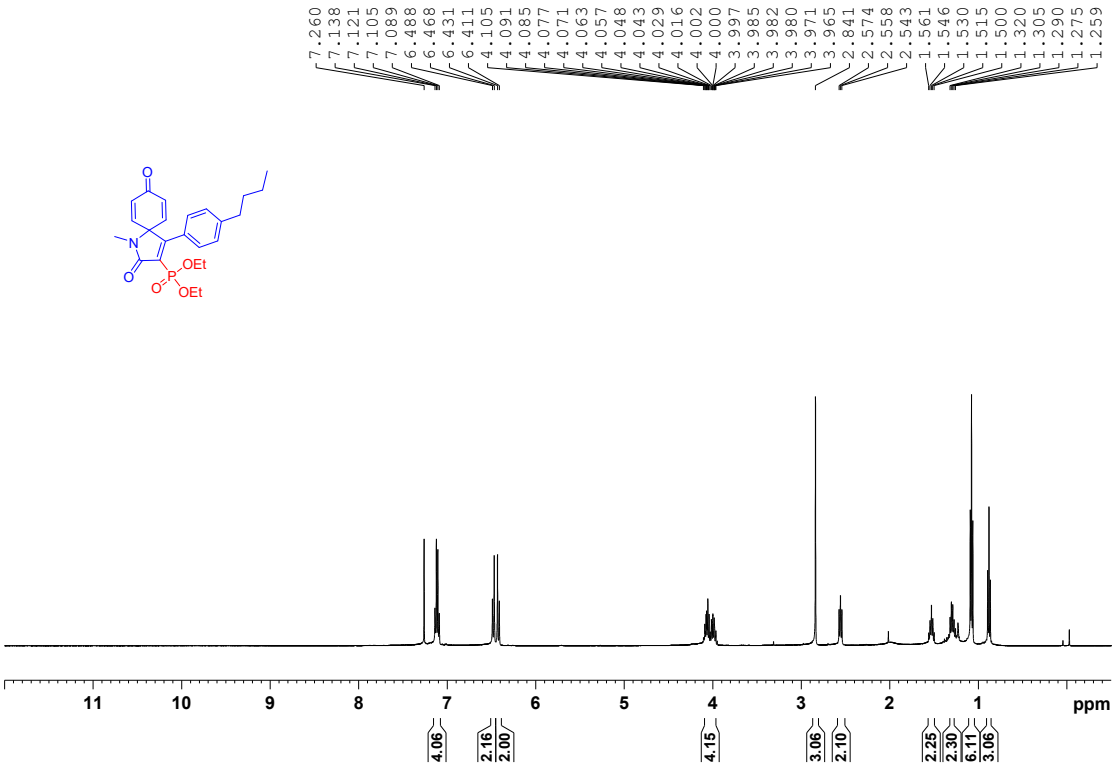
^{13}C NMR (CDCl$_3$, 300 K), **3c**



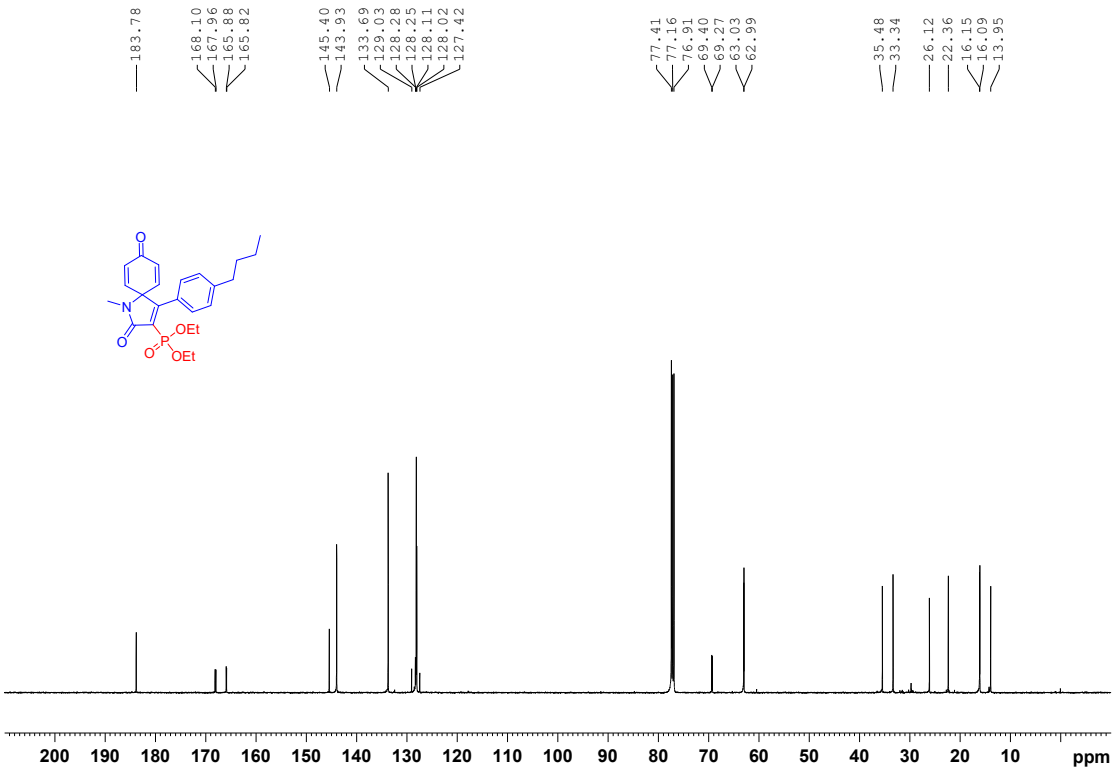
^{31}P NMR (CDCl$_3$, 300 K) **3c**



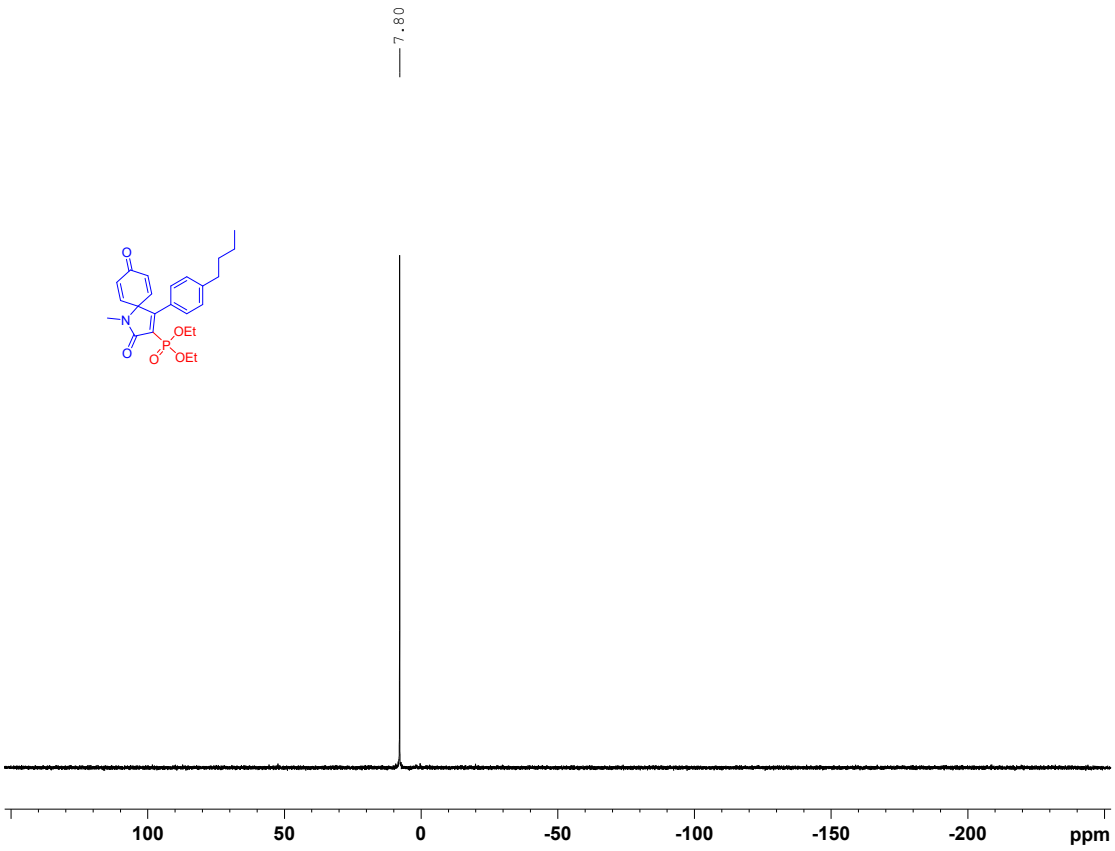
^{1}H NMR (CDCl$_3$, 300 K), **3d**



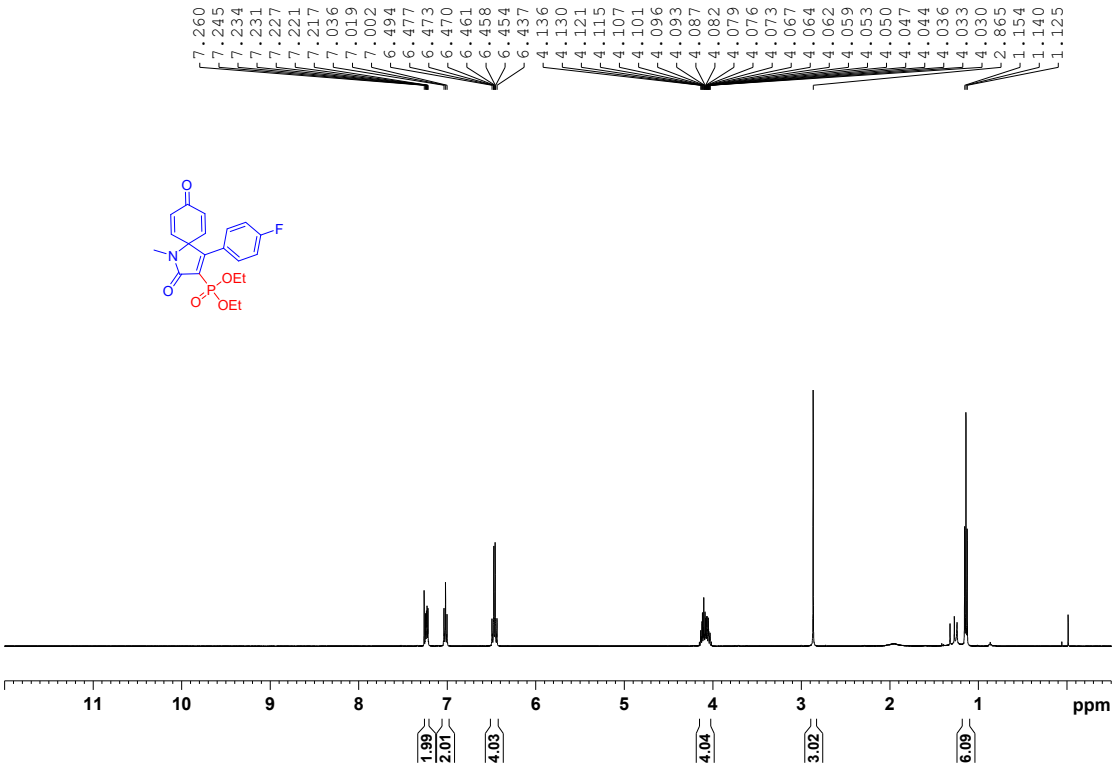
^{13}C NMR (CDCl$_3$, 300 K), **3d**



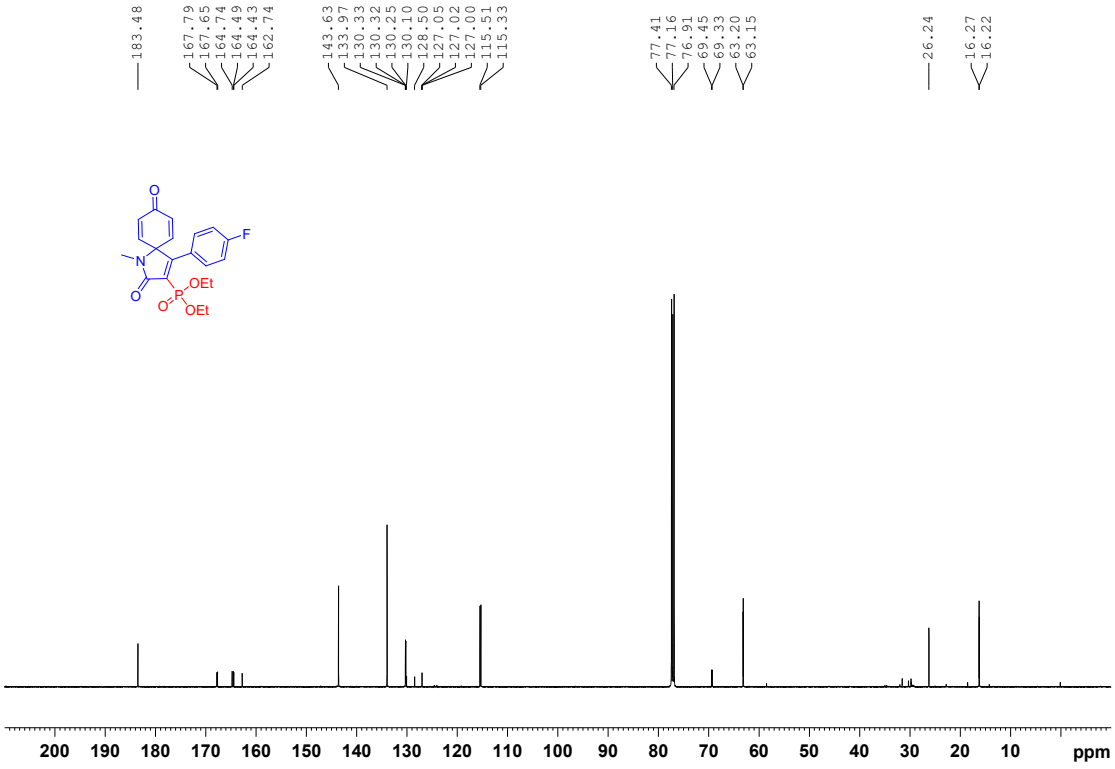
^{31}P NMR (CDCl$_3$, 300 K) **3d**



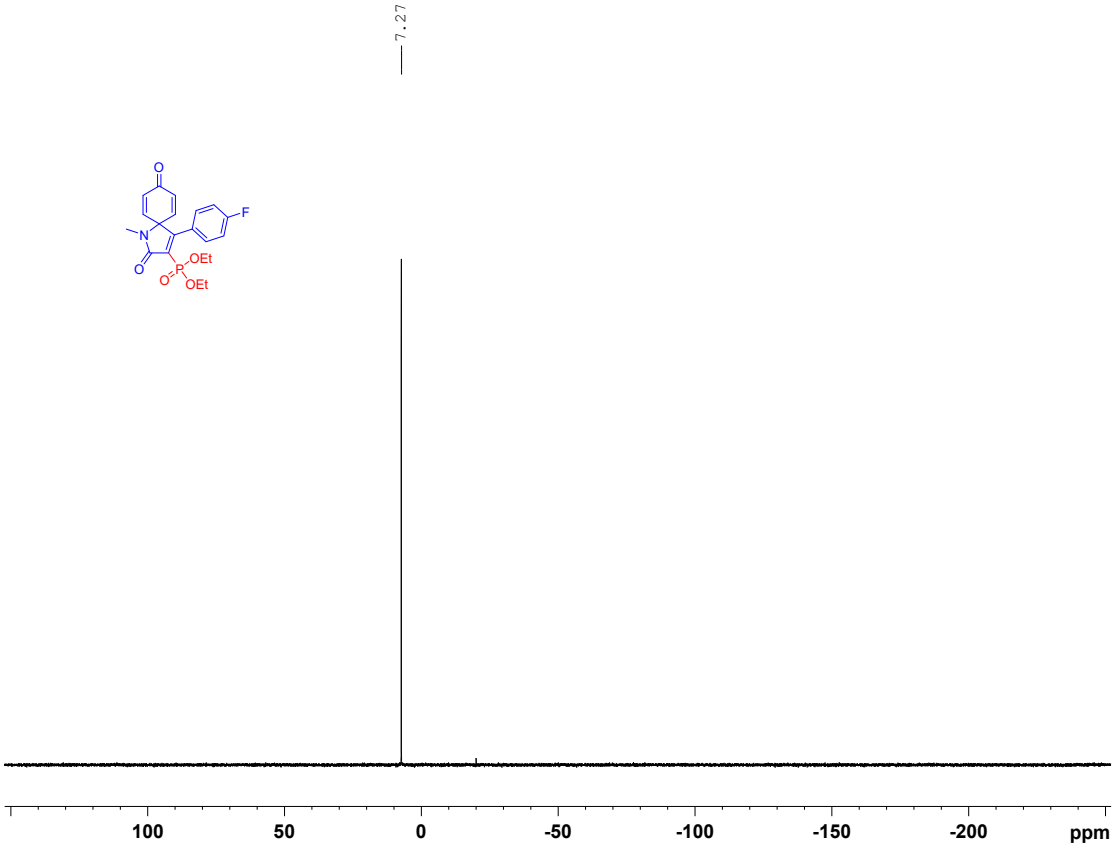
^{1}H NMR (CDCl$_3$, 300 K), **3e**



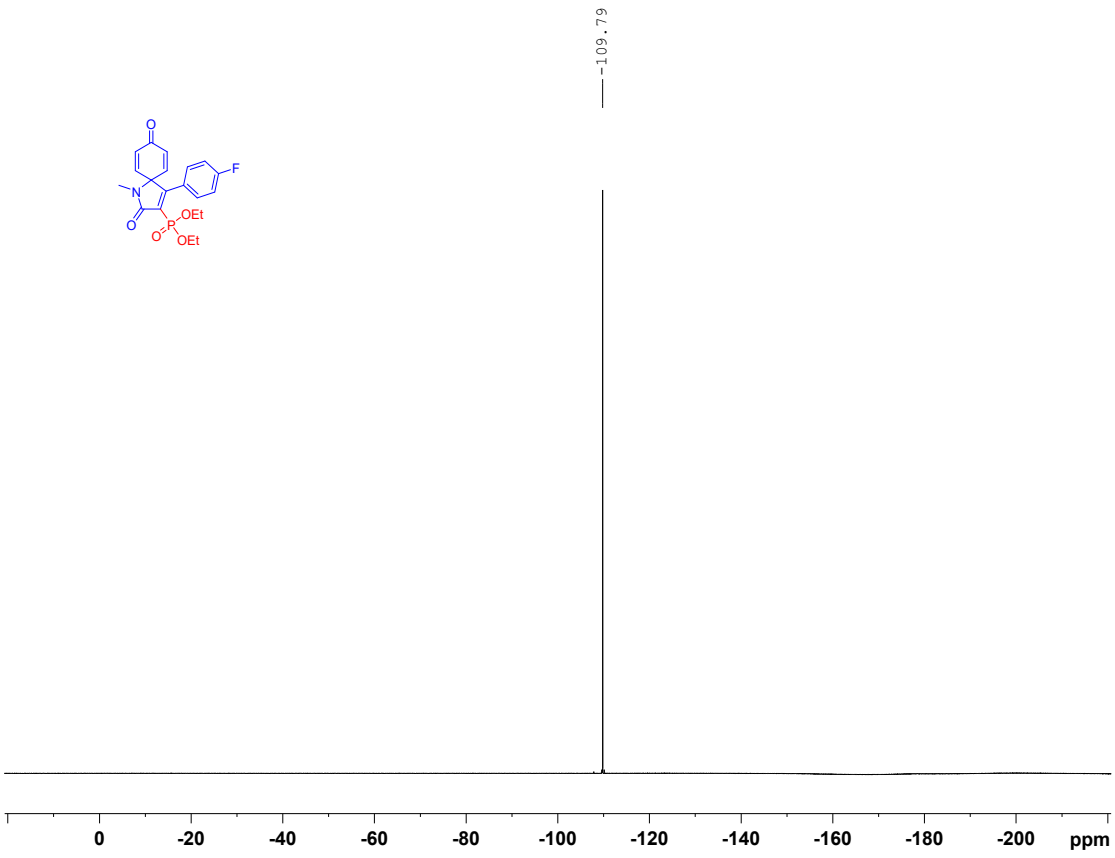
^{13}C NMR (CDCl$_3$, 300 K), **3e**



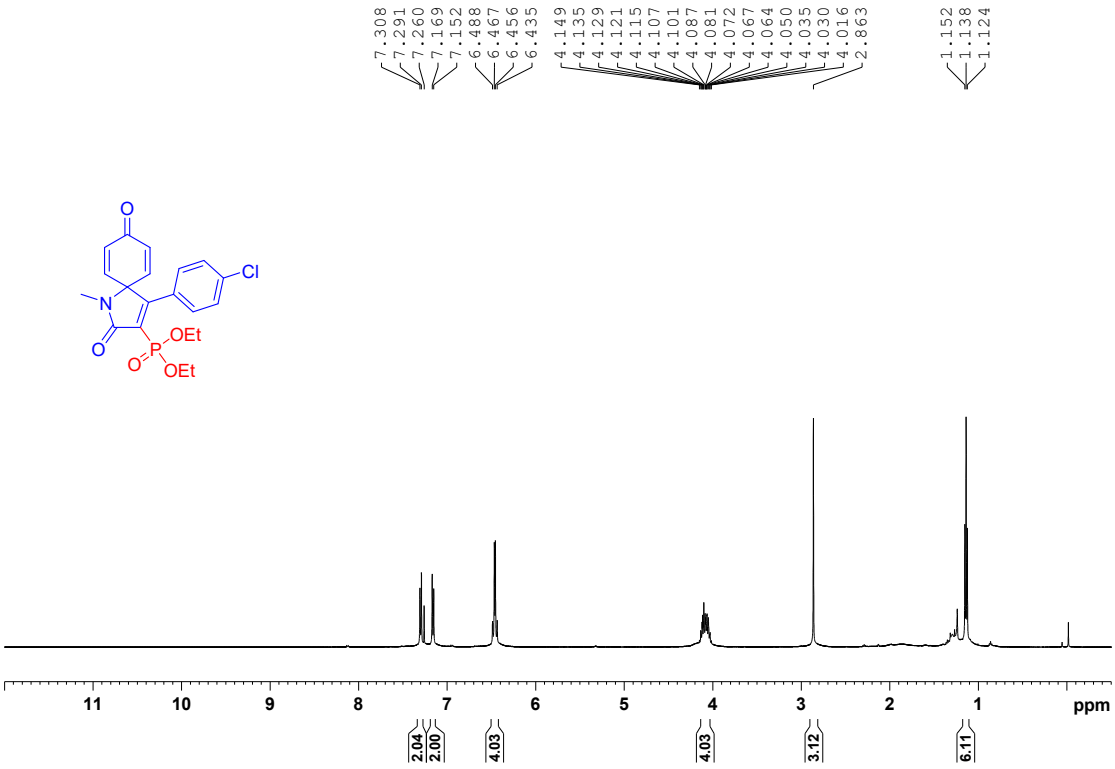
^{31}P NMR (CDCl$_3$, 300 K) **3e**



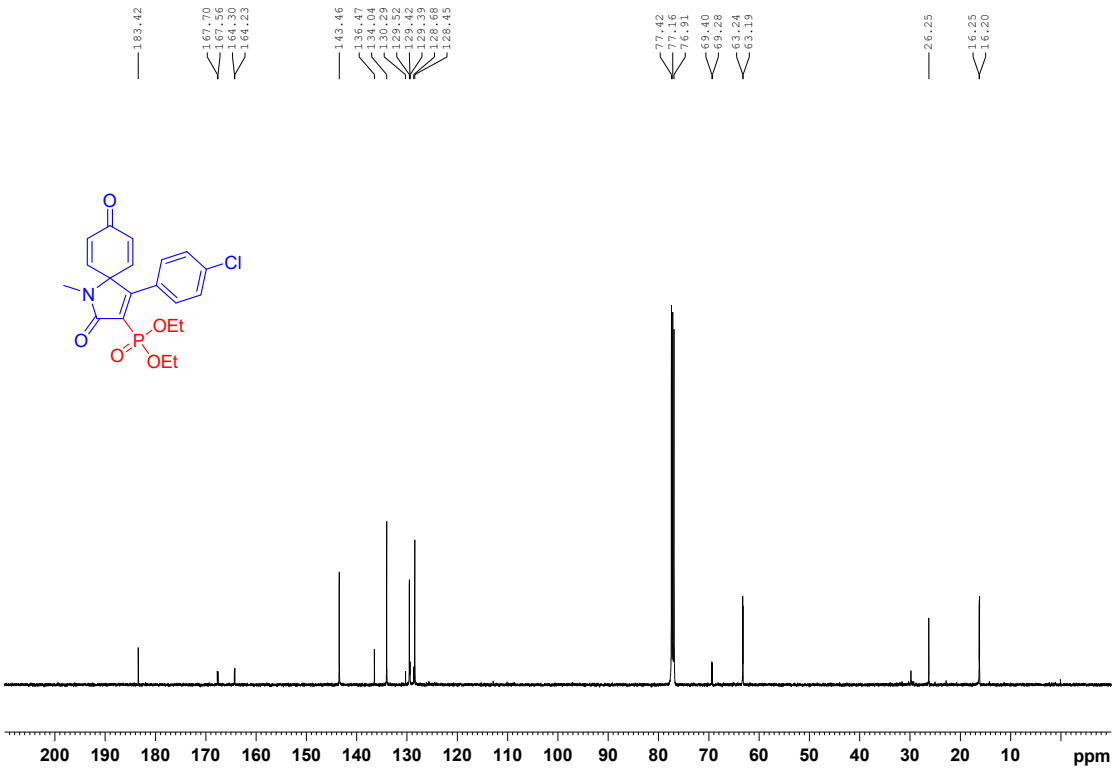
^{19}F NMR (CDCl$_3$, 300 K) **3e**



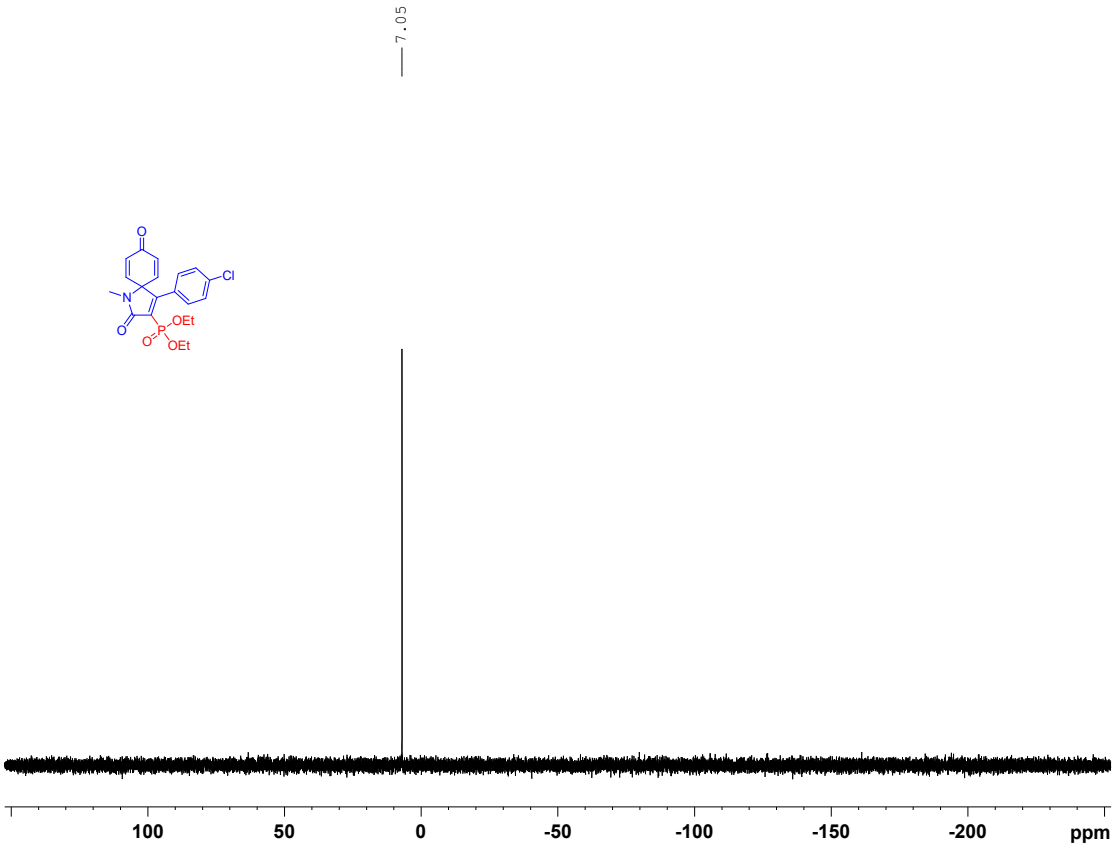
^{1}H NMR (CDCl$_3$, 300 K), **3f**



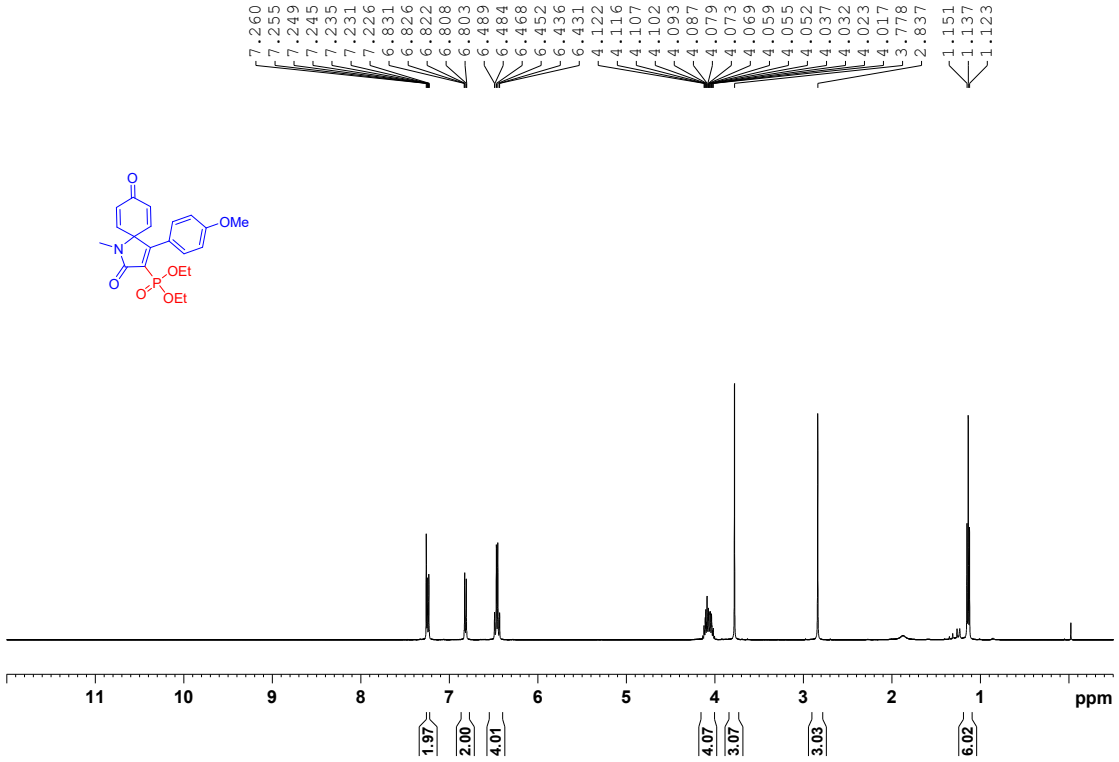
^{13}C NMR (CDCl$_3$, 300 K), **3f**



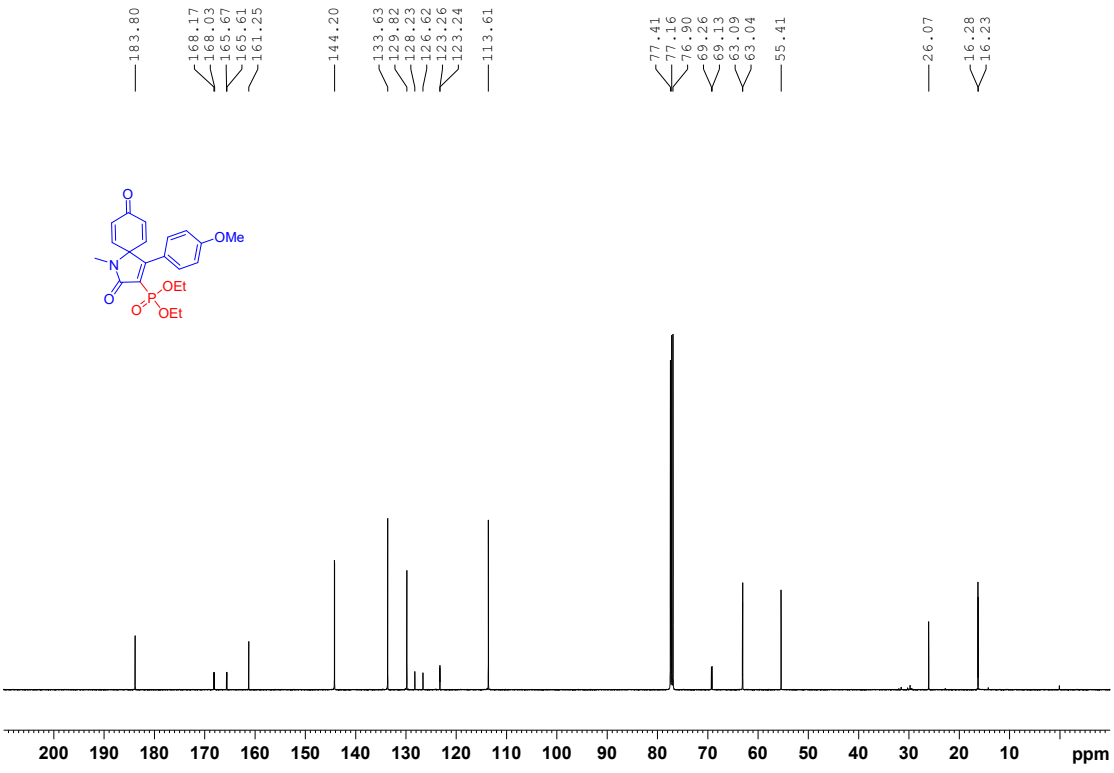
^{31}P NMR (CDCl$_3$, 300 K) **3f**



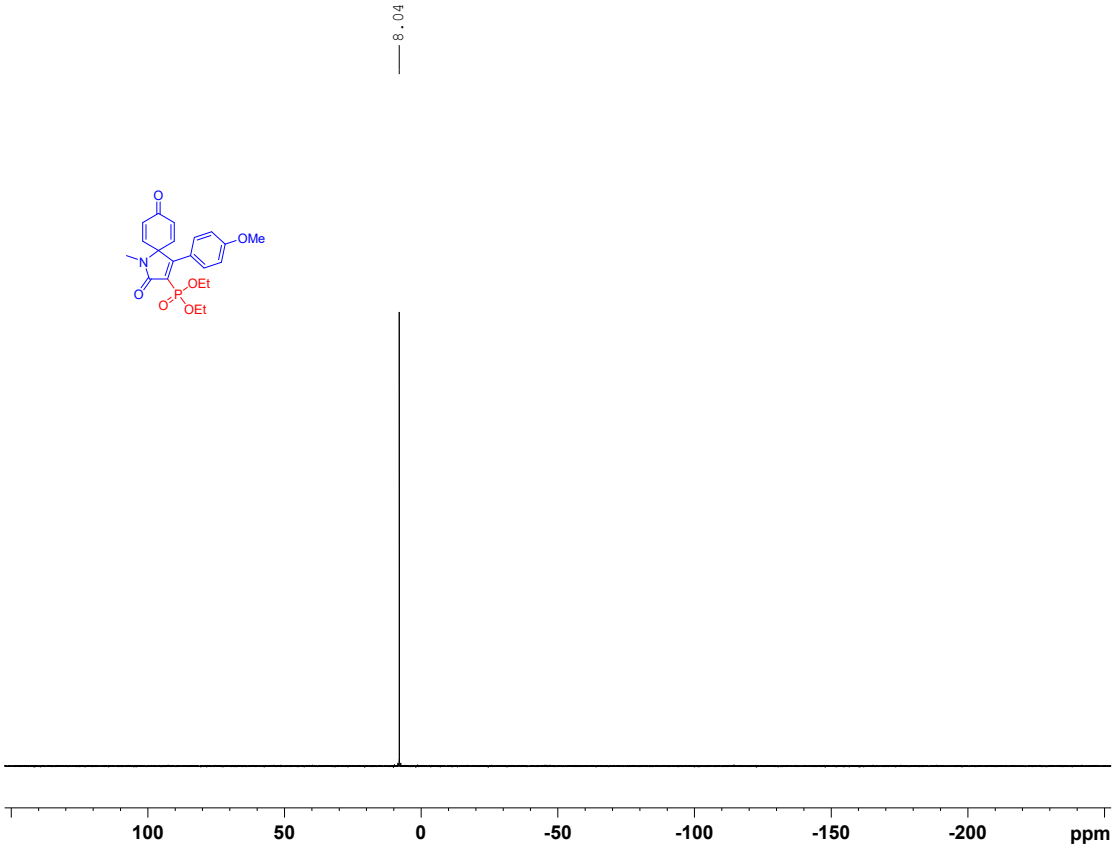
^{1}H NMR (CDCl$_3$, 300 K), **3g**



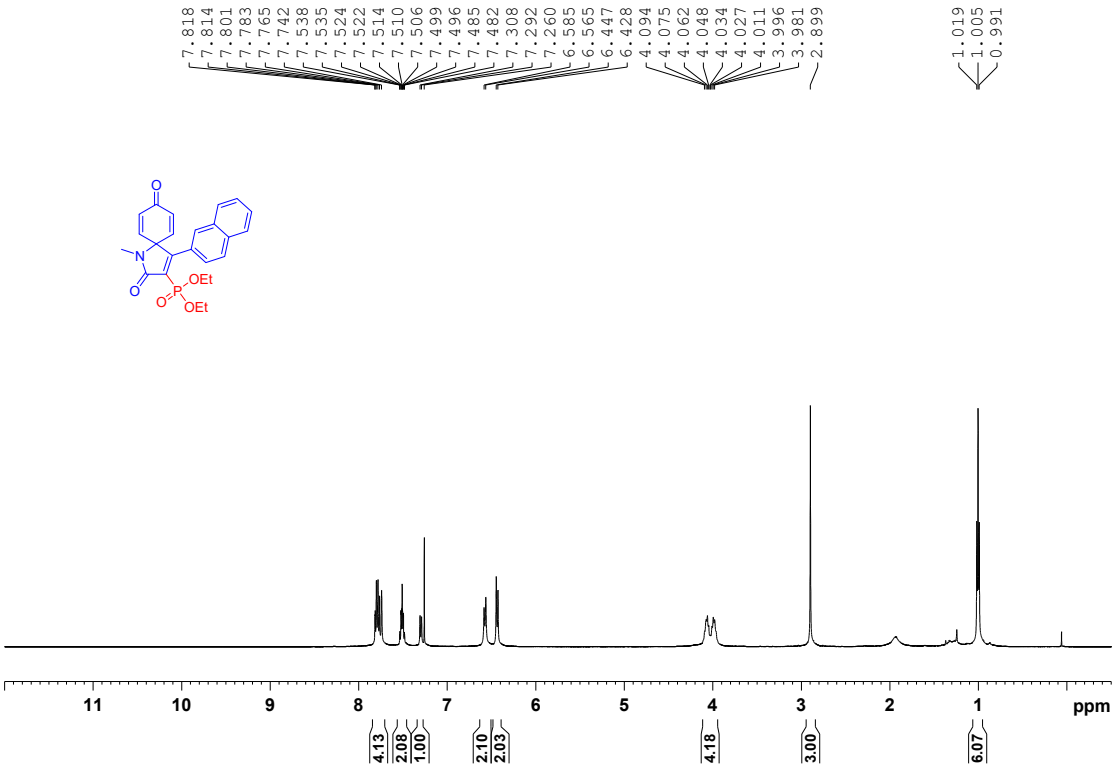
^{13}C NMR (CDCl$_3$, 300 K), **3g**



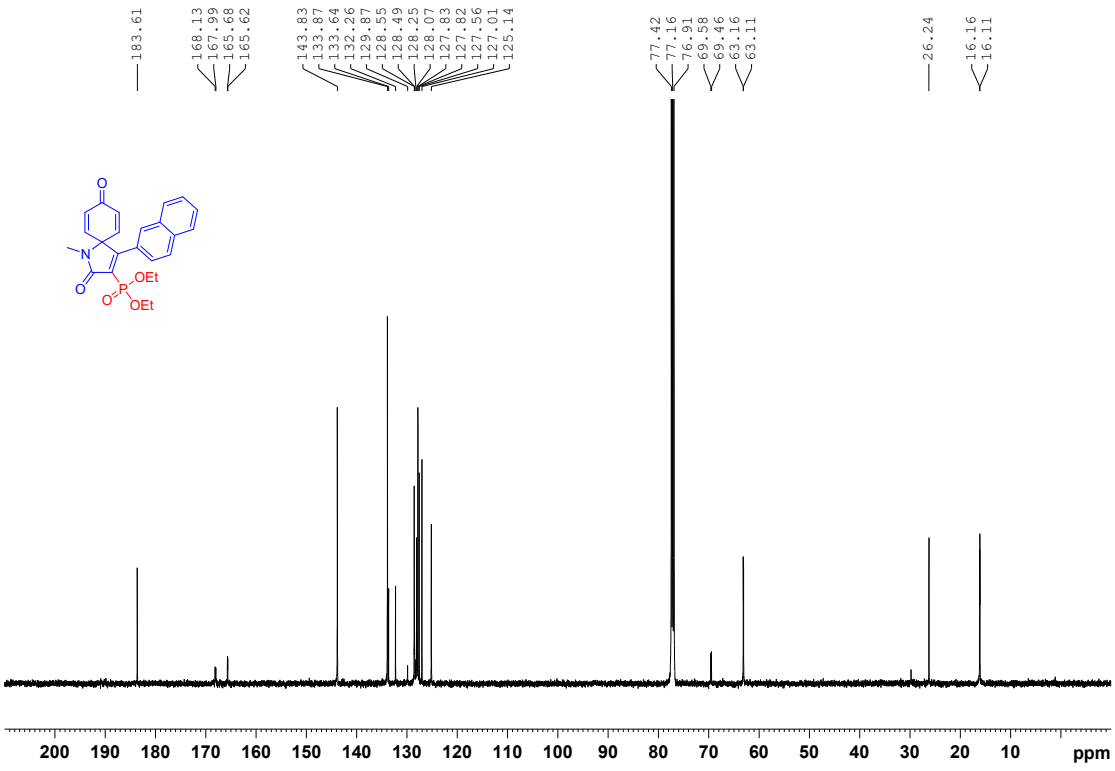
^{31}P NMR (CDCl$_3$, 300 K) **3g**



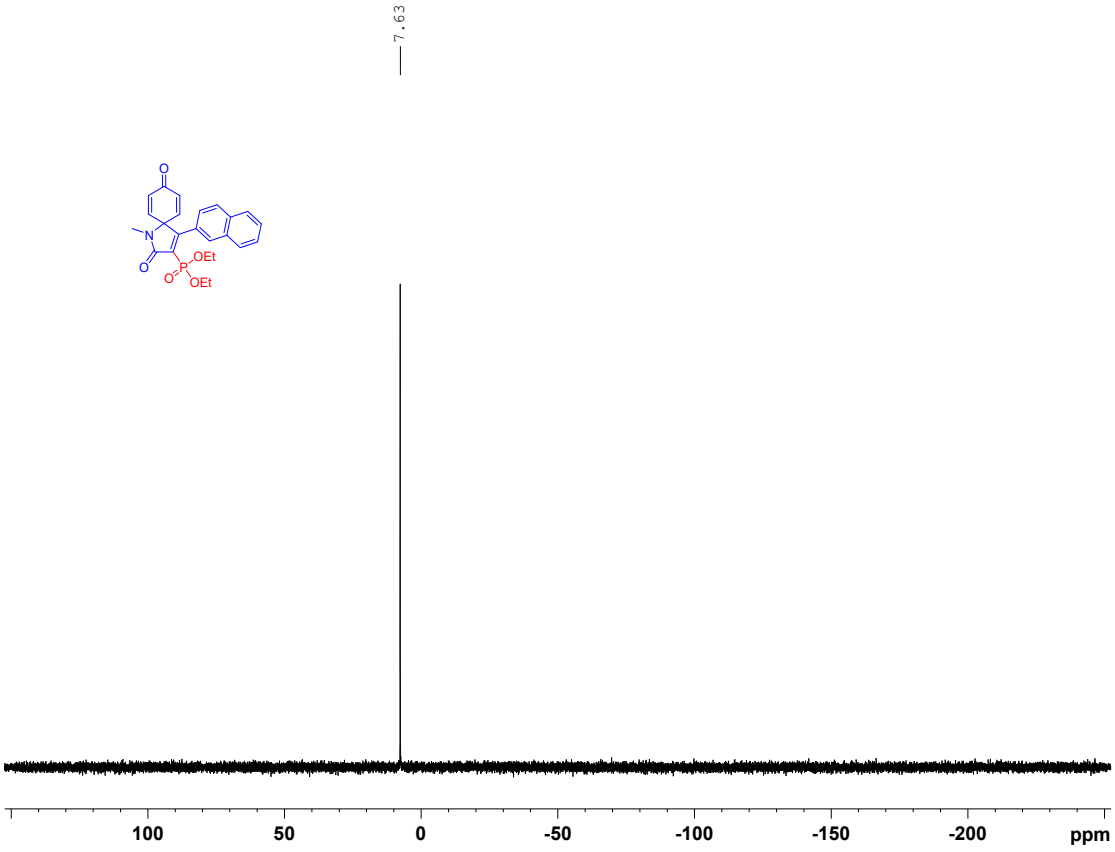
^{1}H NMR (CDCl$_3$, 300 K), **3h**



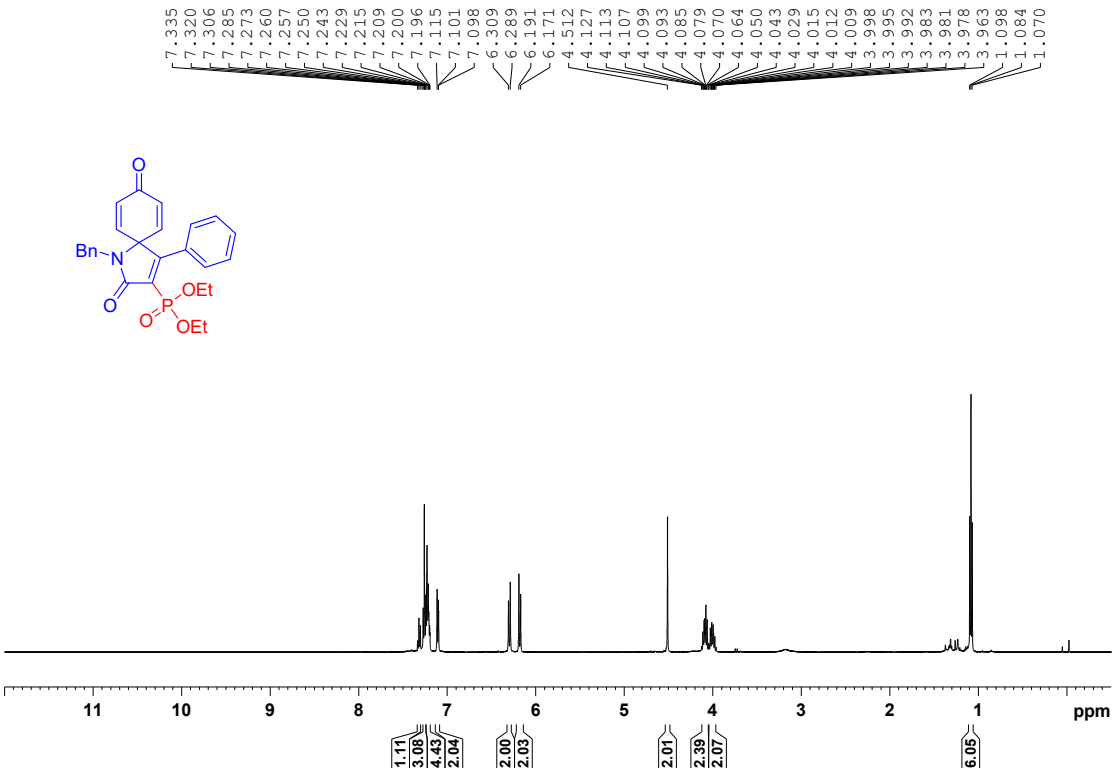
^{13}C NMR (CDCl$_3$, 300 K), **3h**



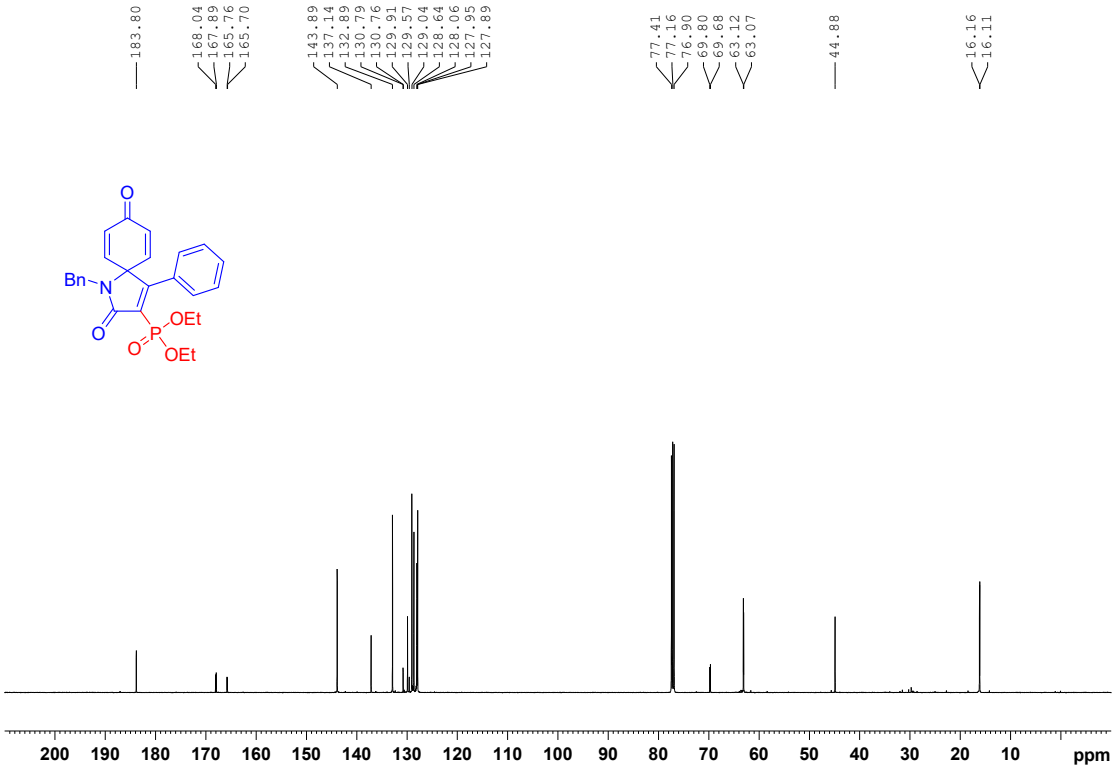
^{31}P NMR (CDCl$_3$, 300 K) **3h**



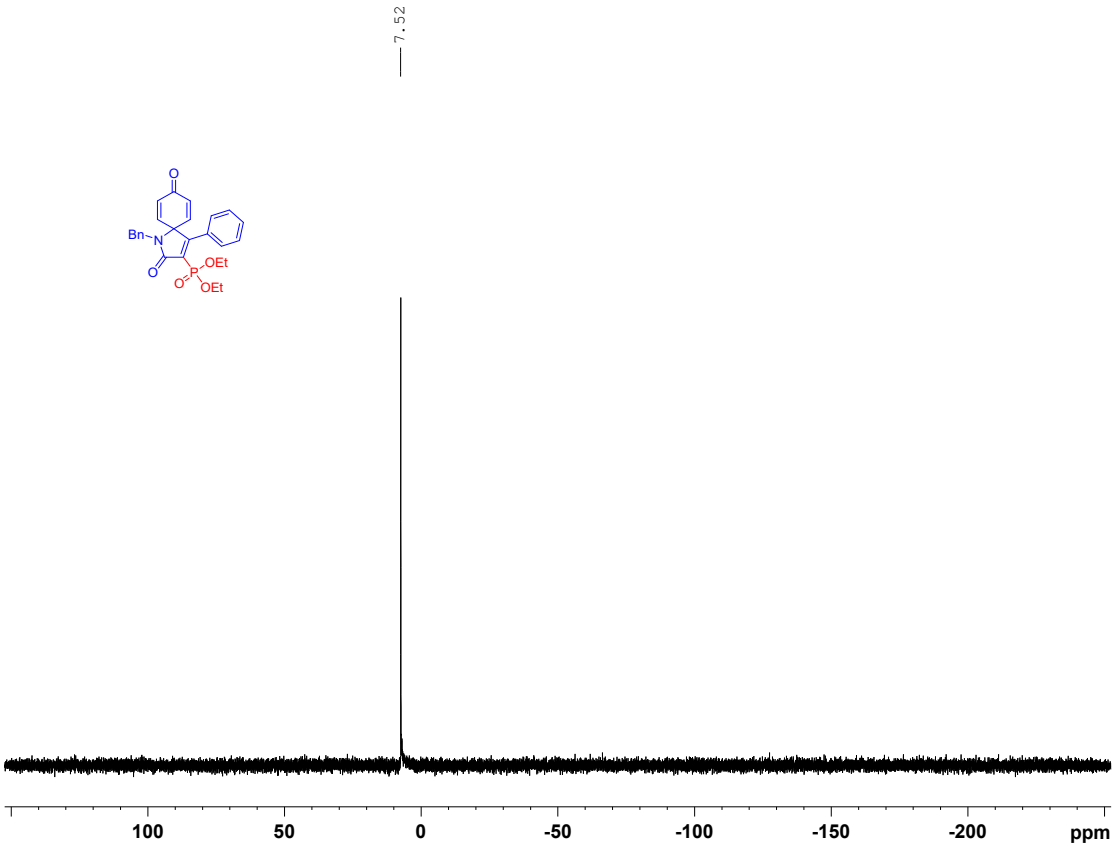
^{1}H NMR (CDCl$_3$, 300 K), **3i**



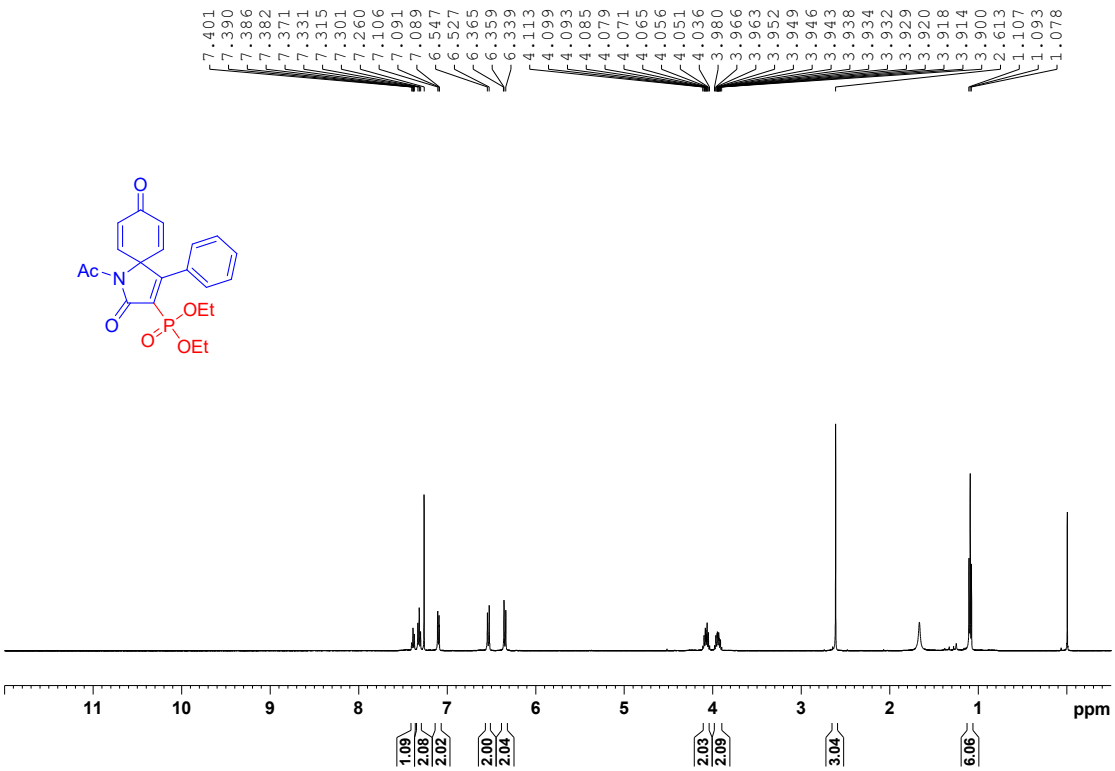
^{13}C NMR (CDCl$_3$, 300 K), **3i**



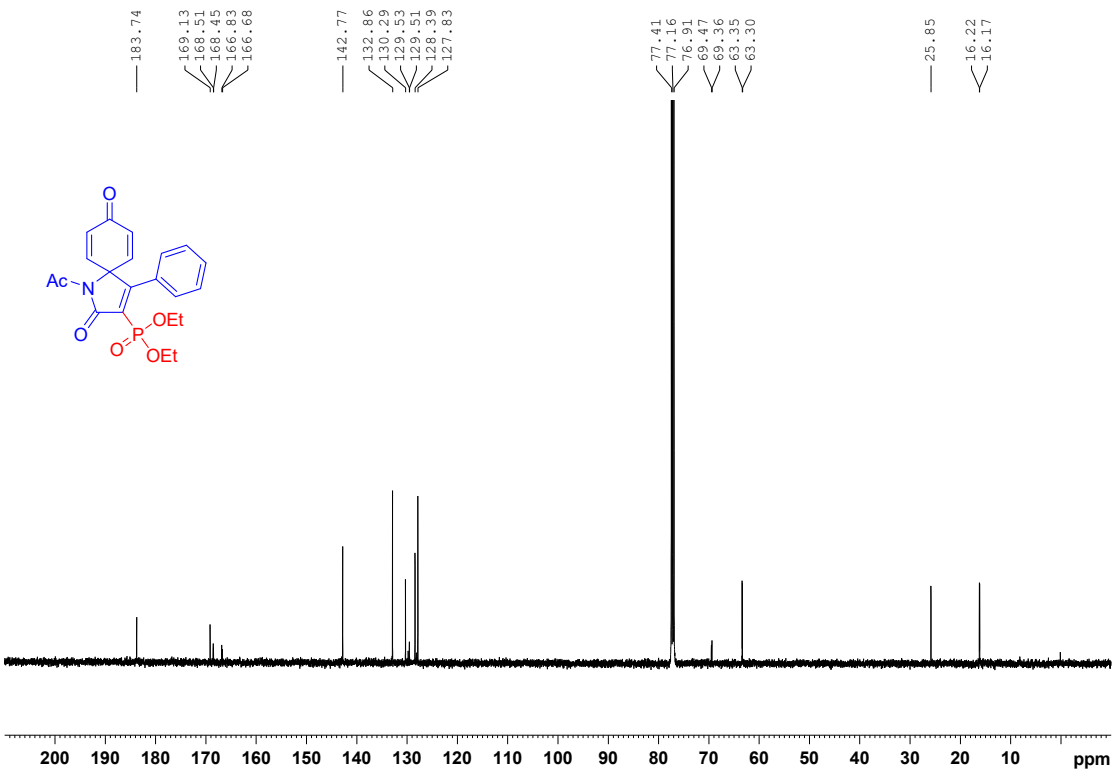
^{31}P NMR (CDCl$_3$, 300 K) **3i**



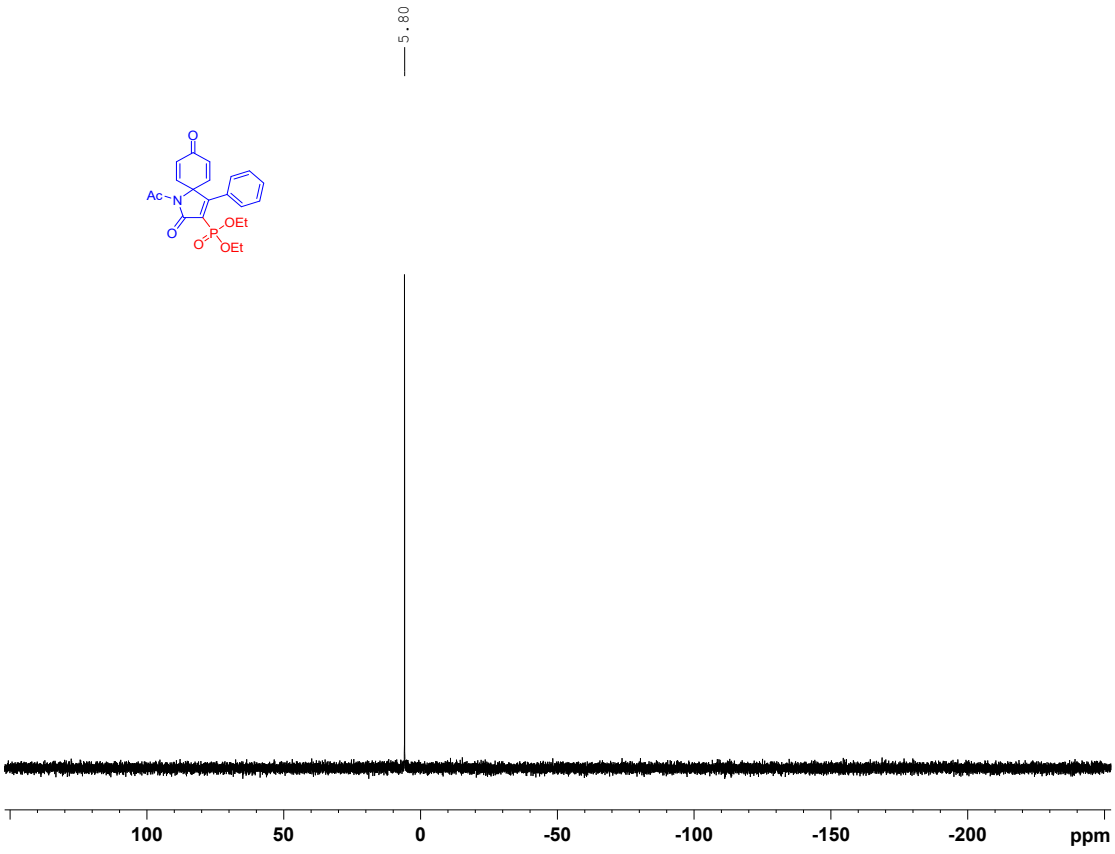
^{1}H NMR (CDCl$_3$, 300 K), **3j**



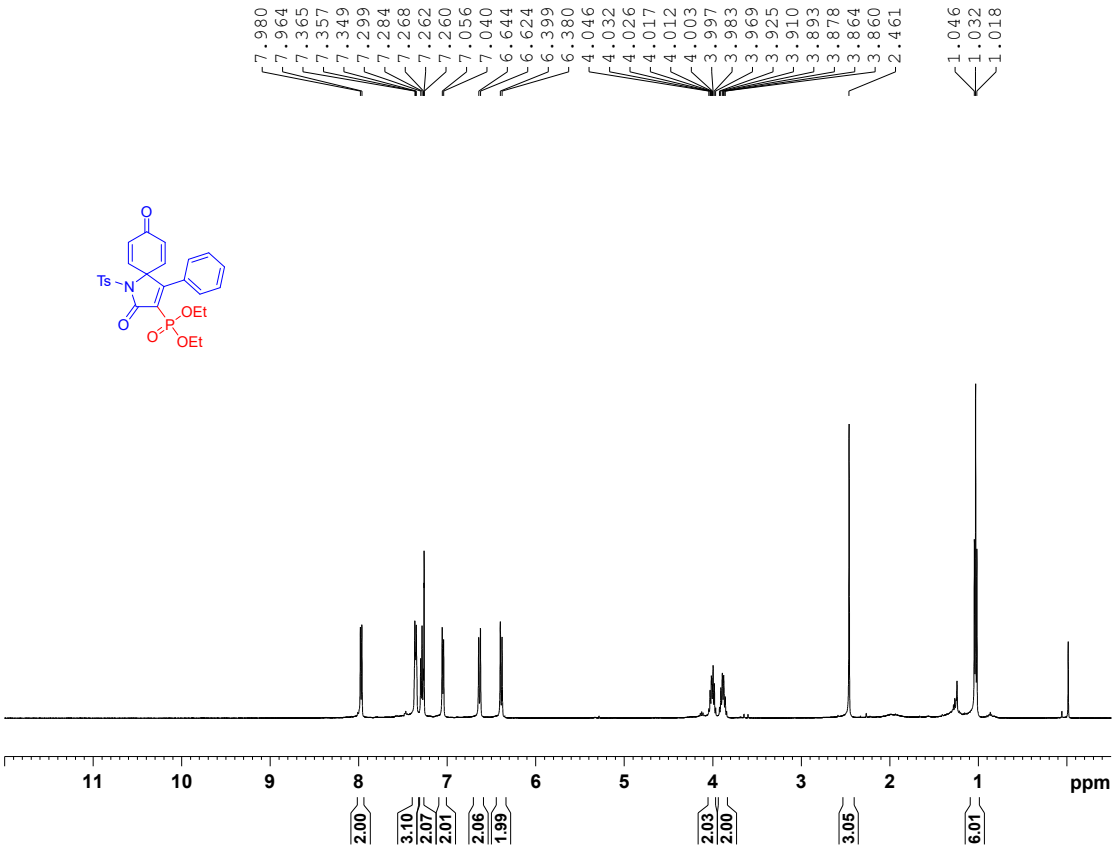
^{13}C NMR (CDCl$_3$, 300 K), **3j**



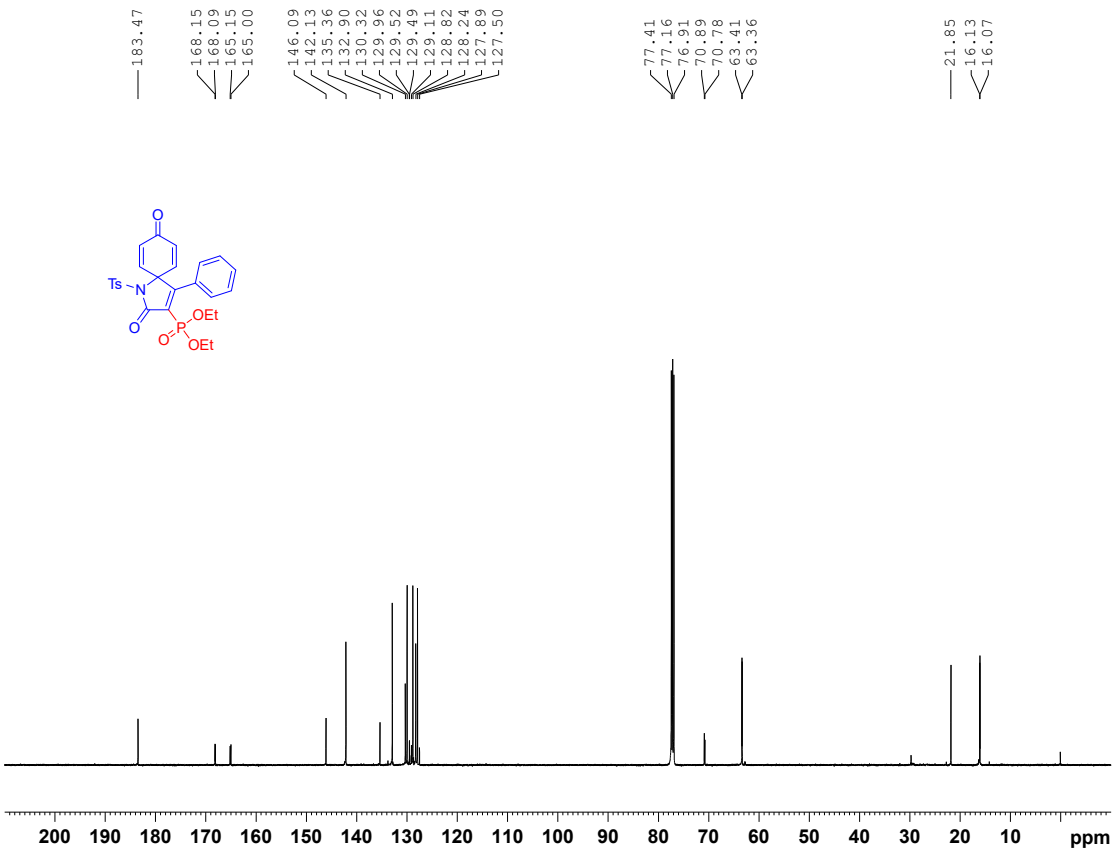
^{31}P NMR (CDCl$_3$, 300 K) **3j**



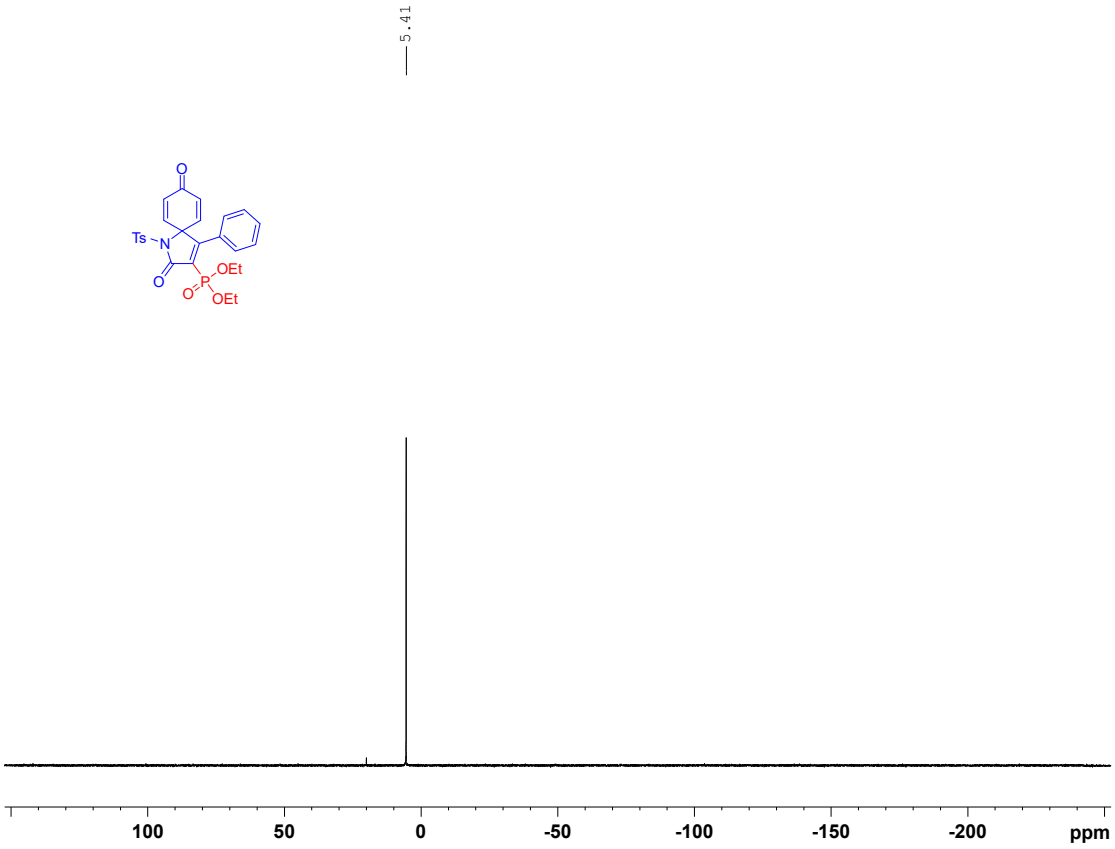
^{1}H NMR (CDCl$_3$, 300 K), **3k**



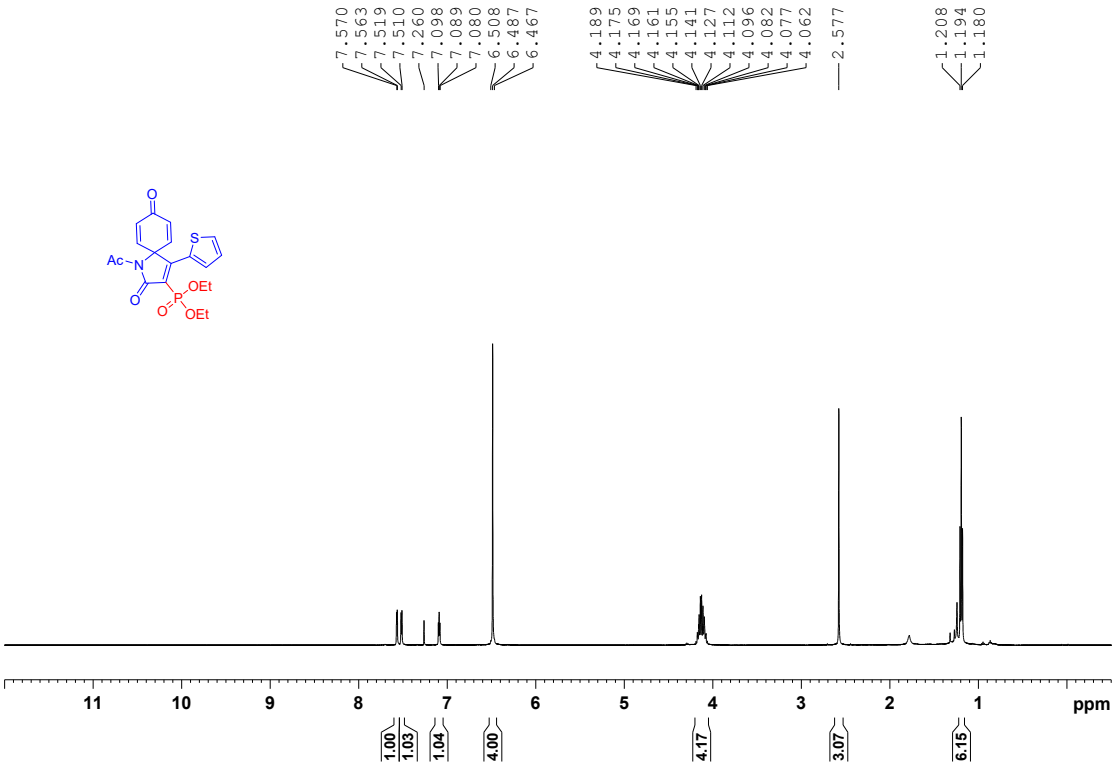
^{13}C NMR (CDCl$_3$, 300 K), **3k**



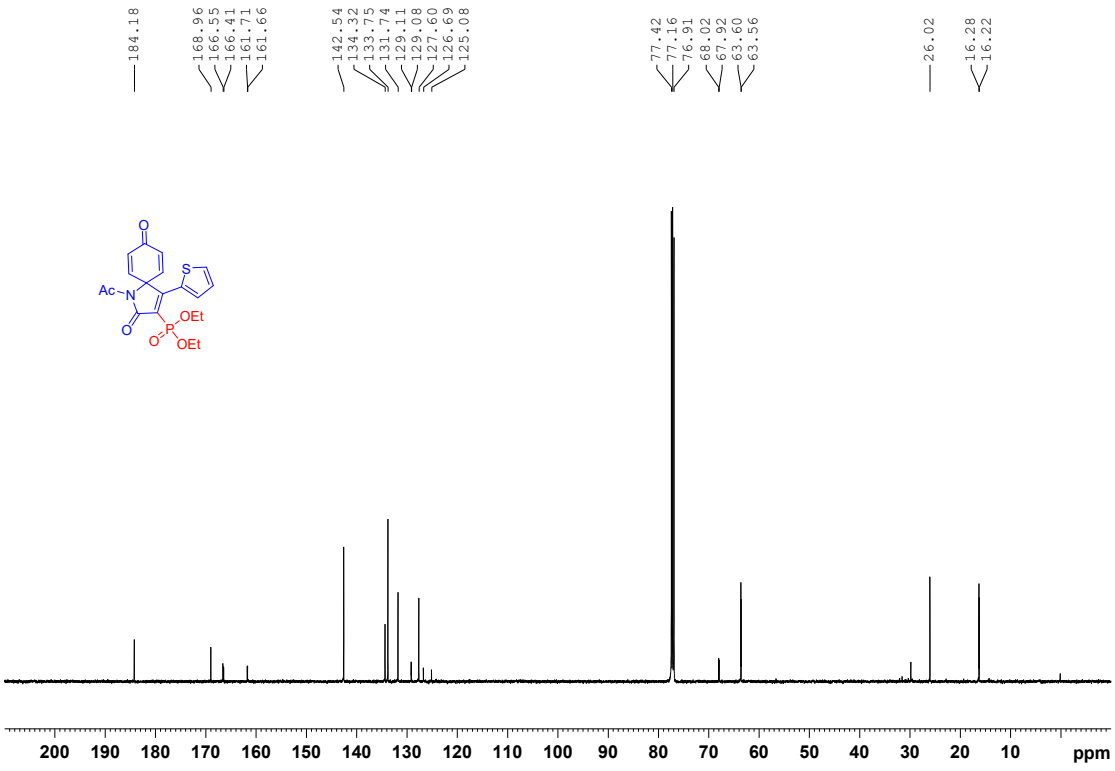
^{31}P NMR (CDCl$_3$, 300 K), **3k**



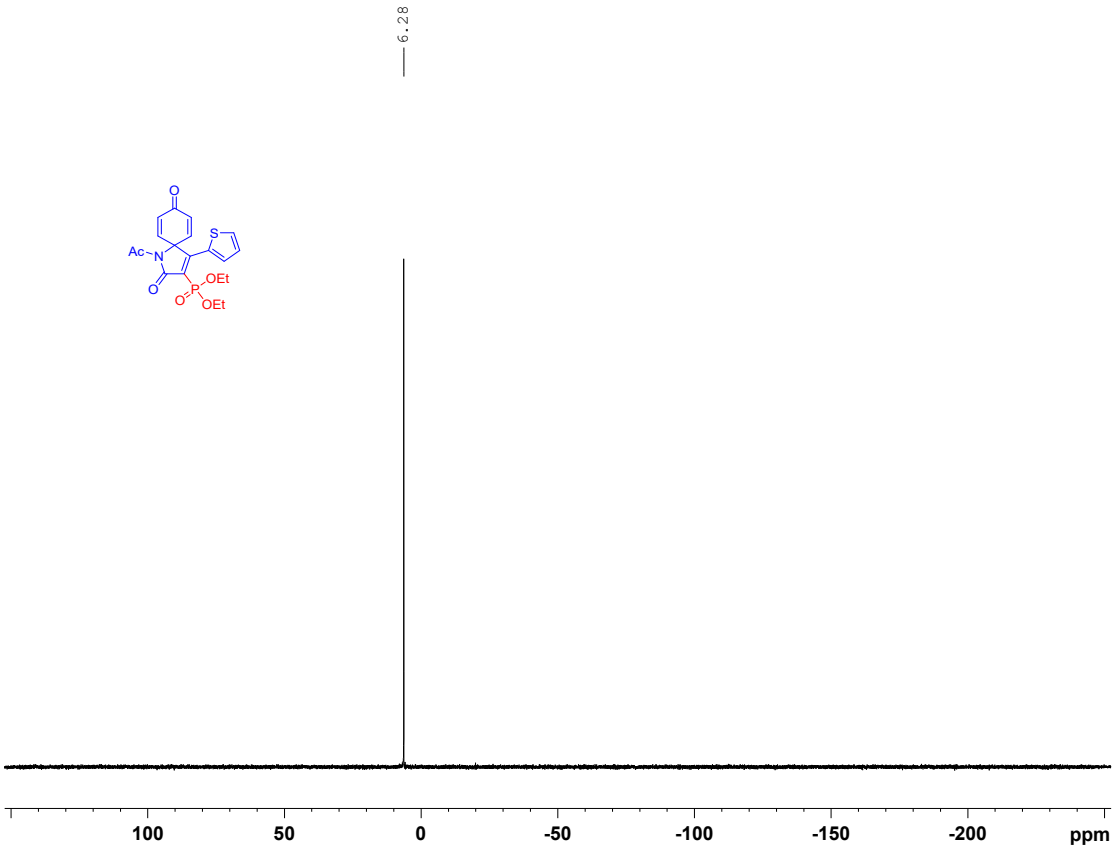
^{1}H NMR (CDCl$_3$, 300 K), **3l**



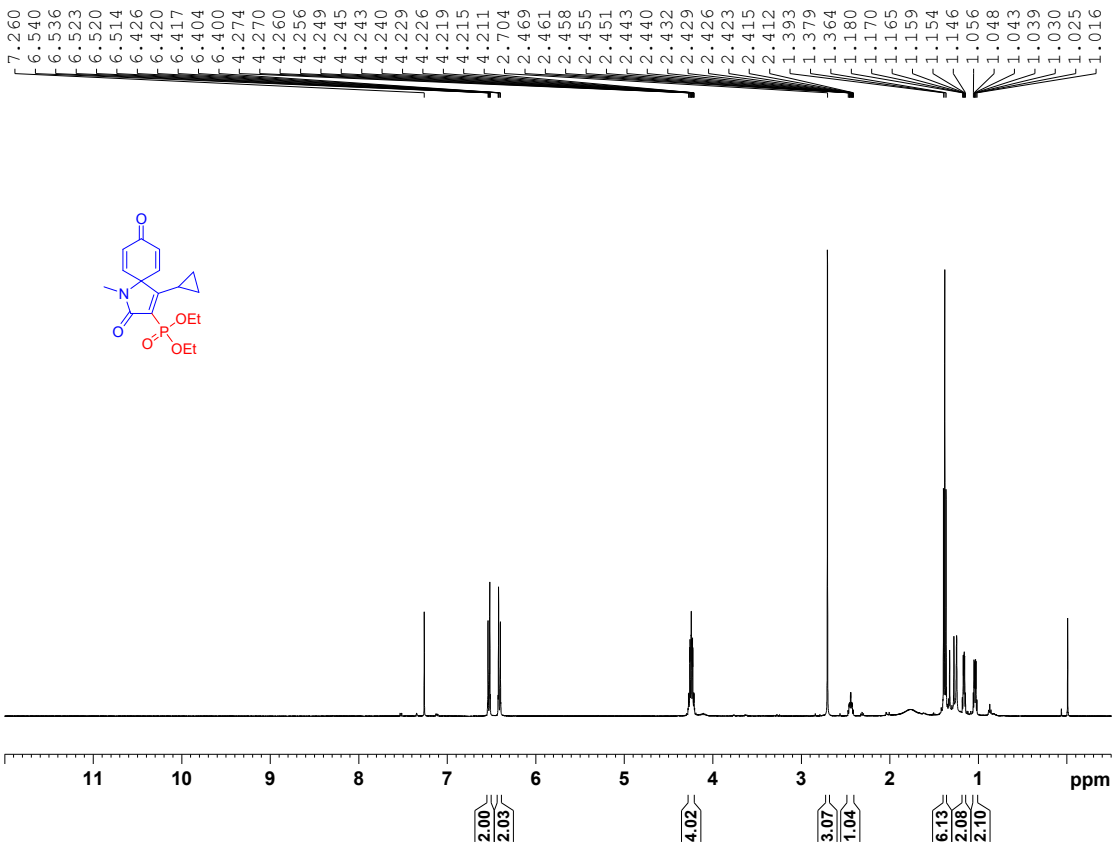
^{13}C NMR (CDCl$_3$, 300 K), **3l**



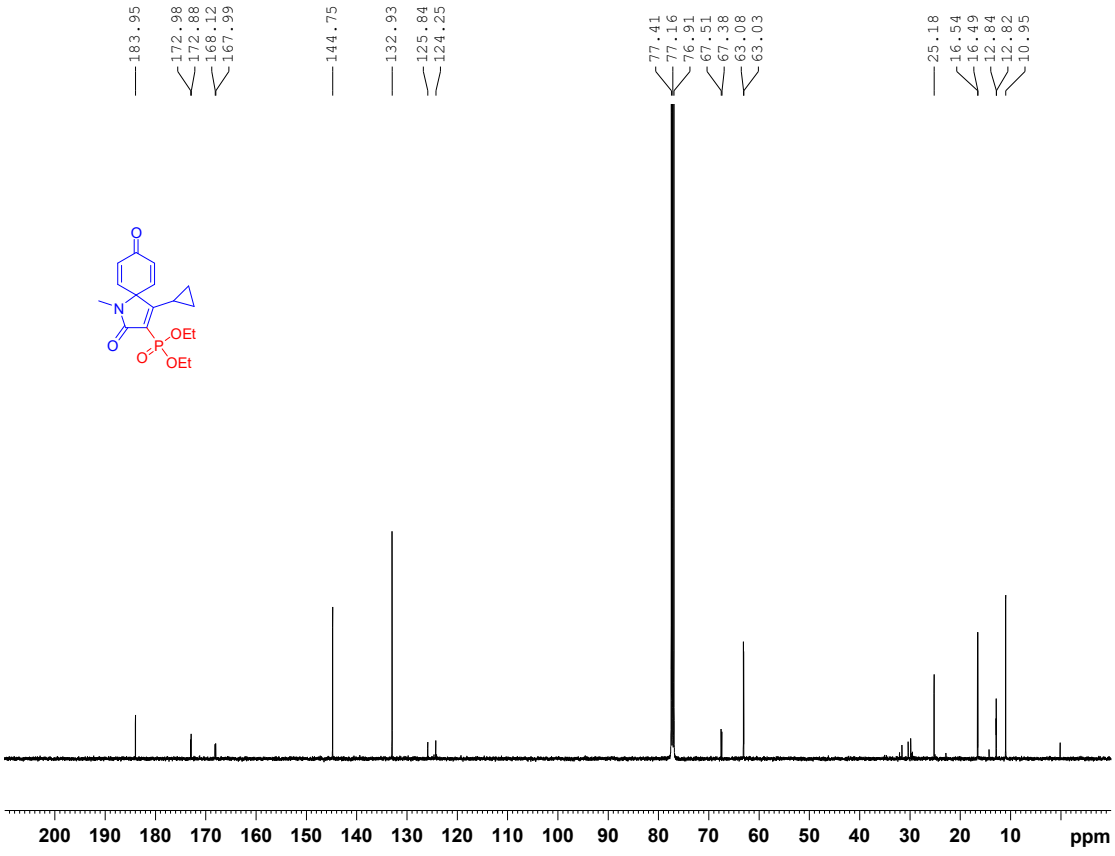
^{31}P NMR (CDCl$_3$, 300 K) **3l**



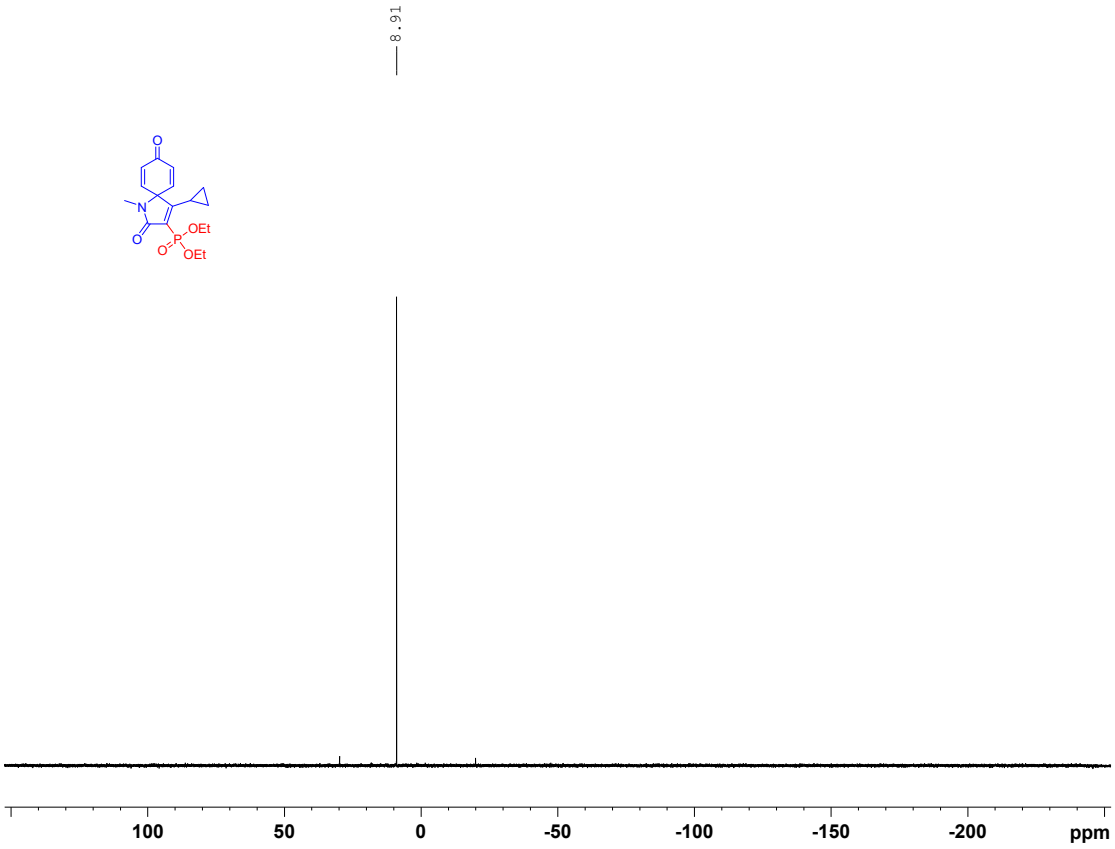
^{1}H NMR (CDCl$_3$, 300 K), **3n**



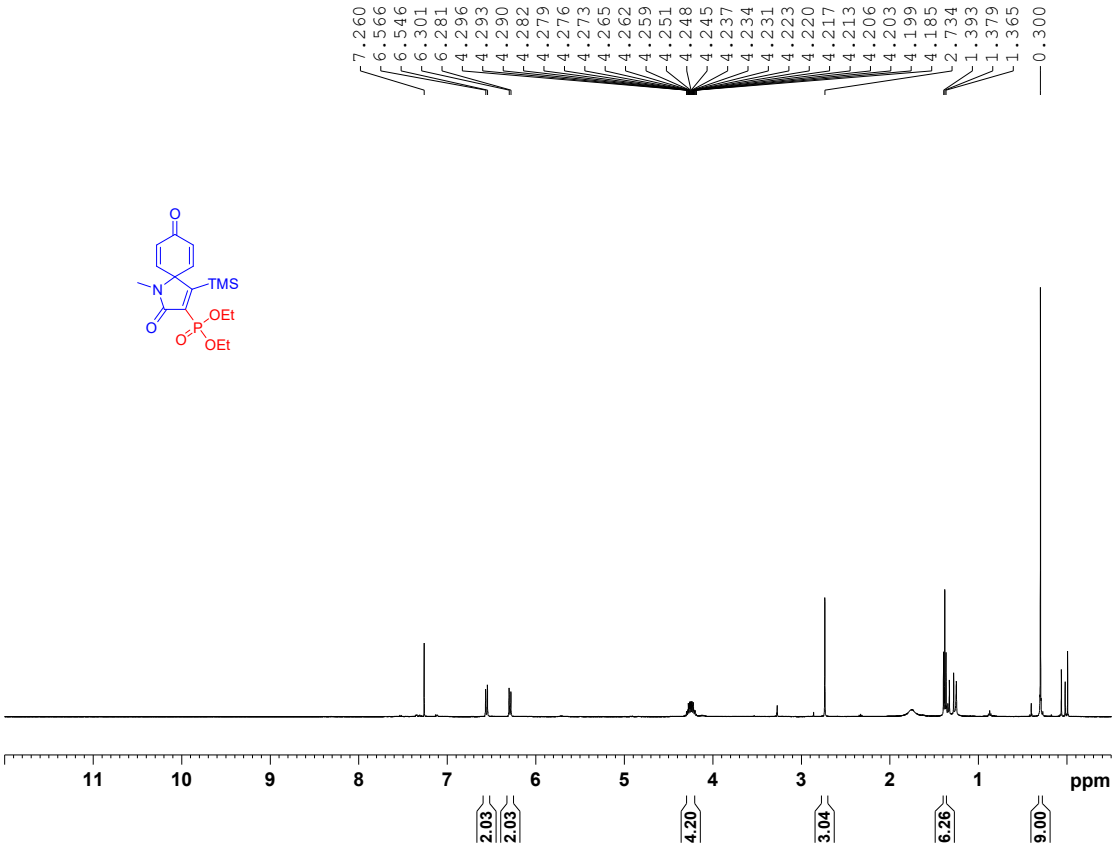
^{13}C NMR (CDCl$_3$, 300 K), **3n**



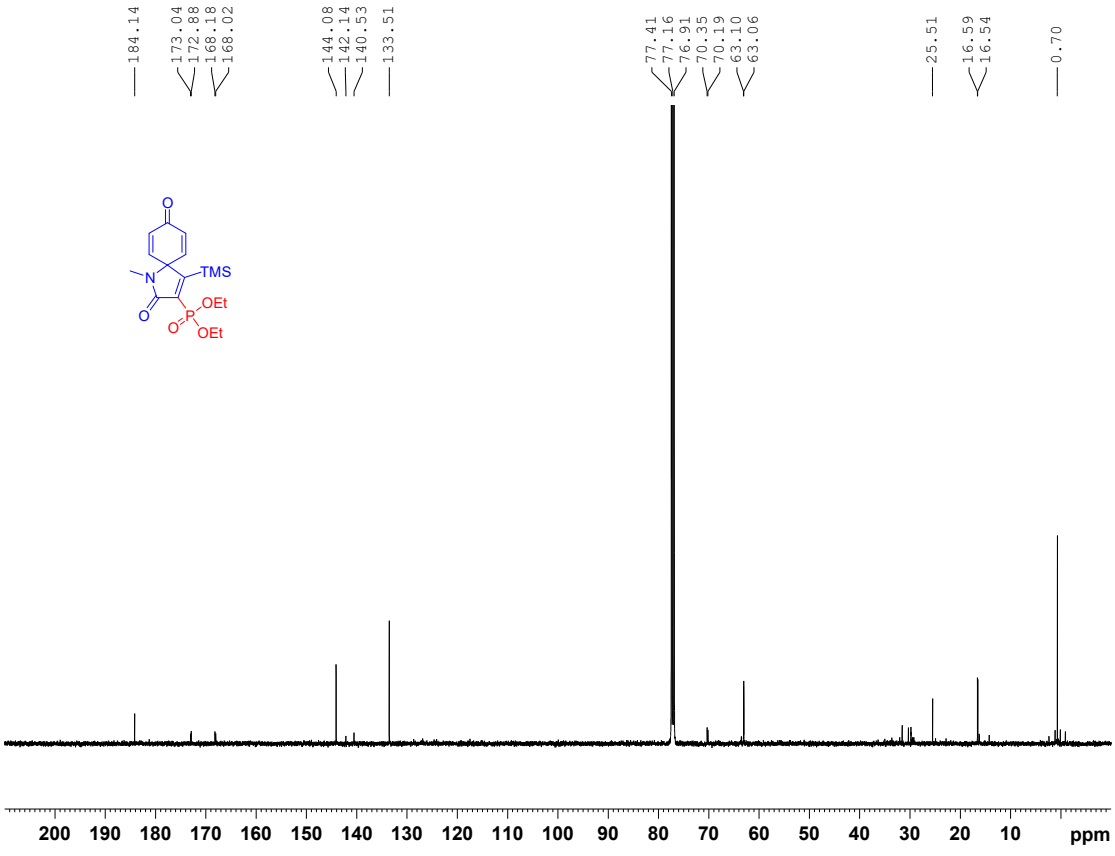
^{31}P NMR (CDCl$_3$, 300 K) **3n**



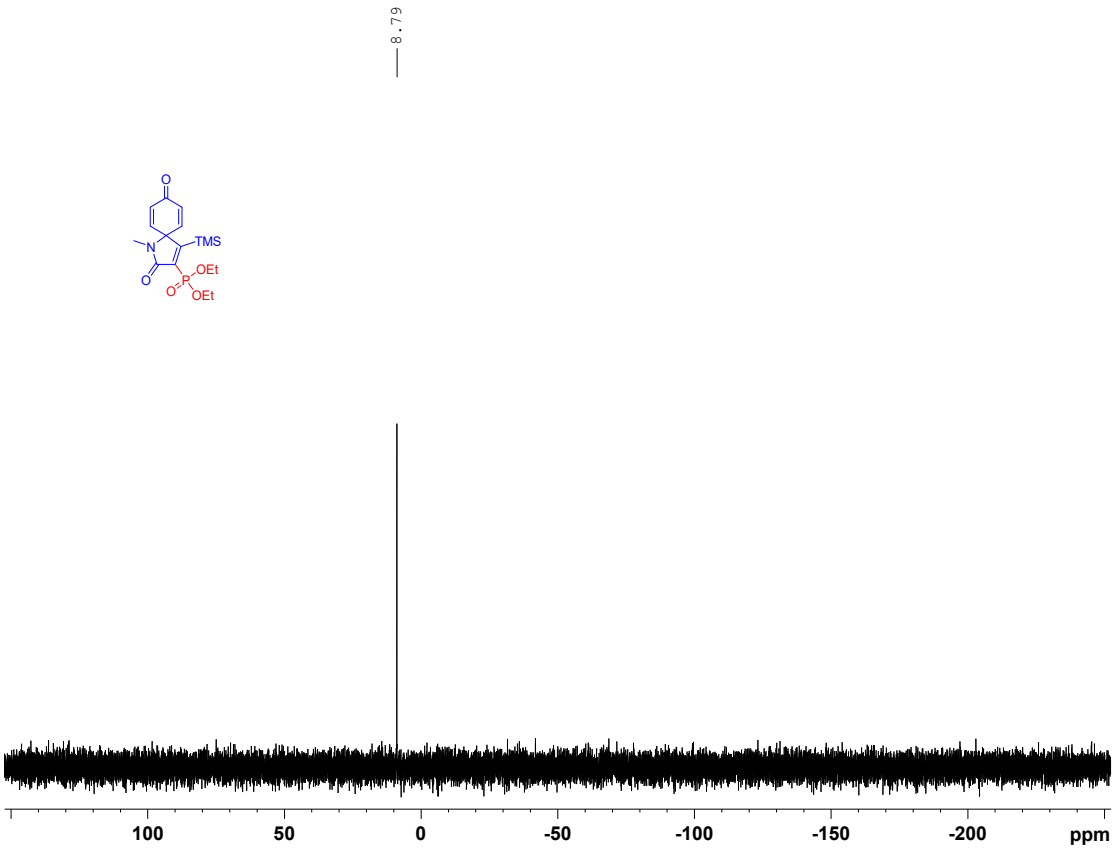
^{1}H NMR (CDCl$_3$, 300 K), **3o**



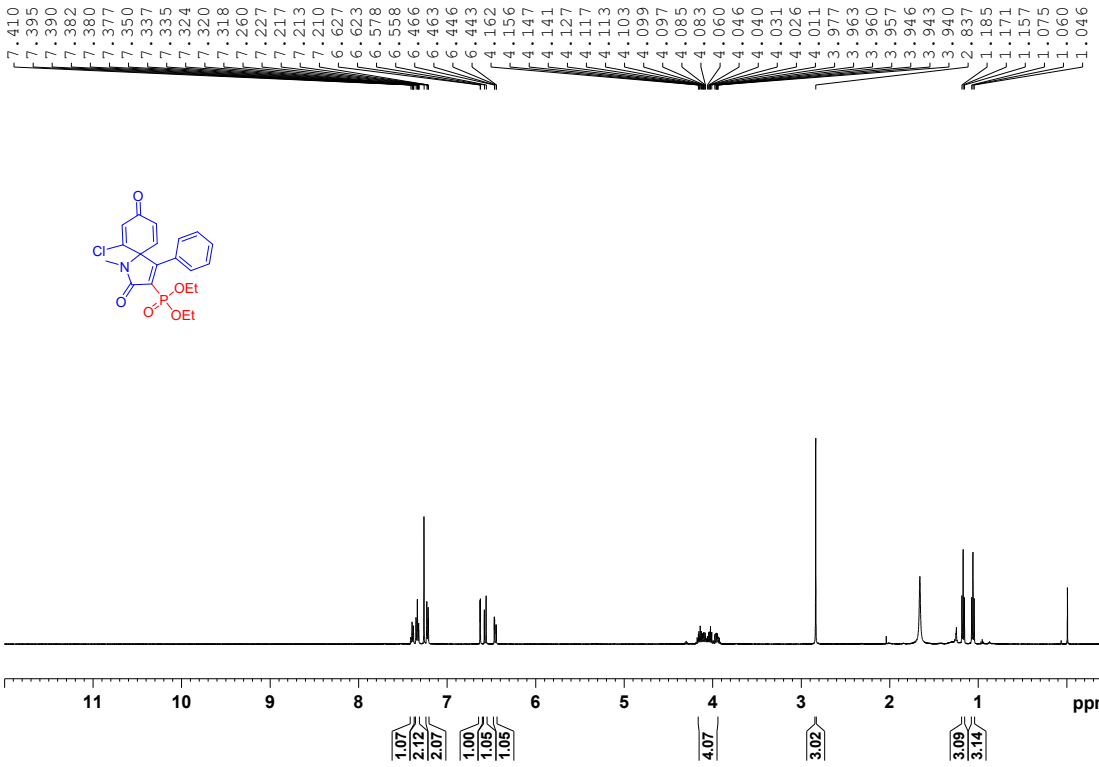
^{13}C NMR (CDCl$_3$, 300 K), **3o**



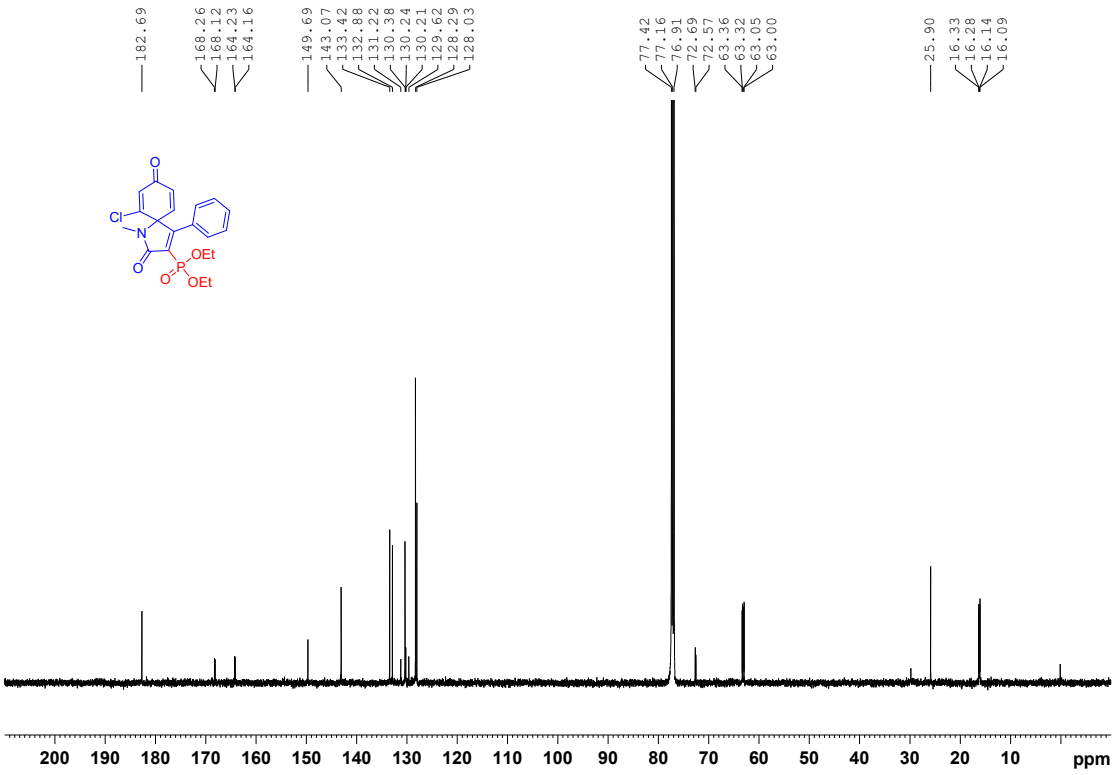
^{31}P NMR (CDCl$_3$, 300 K) **3o**



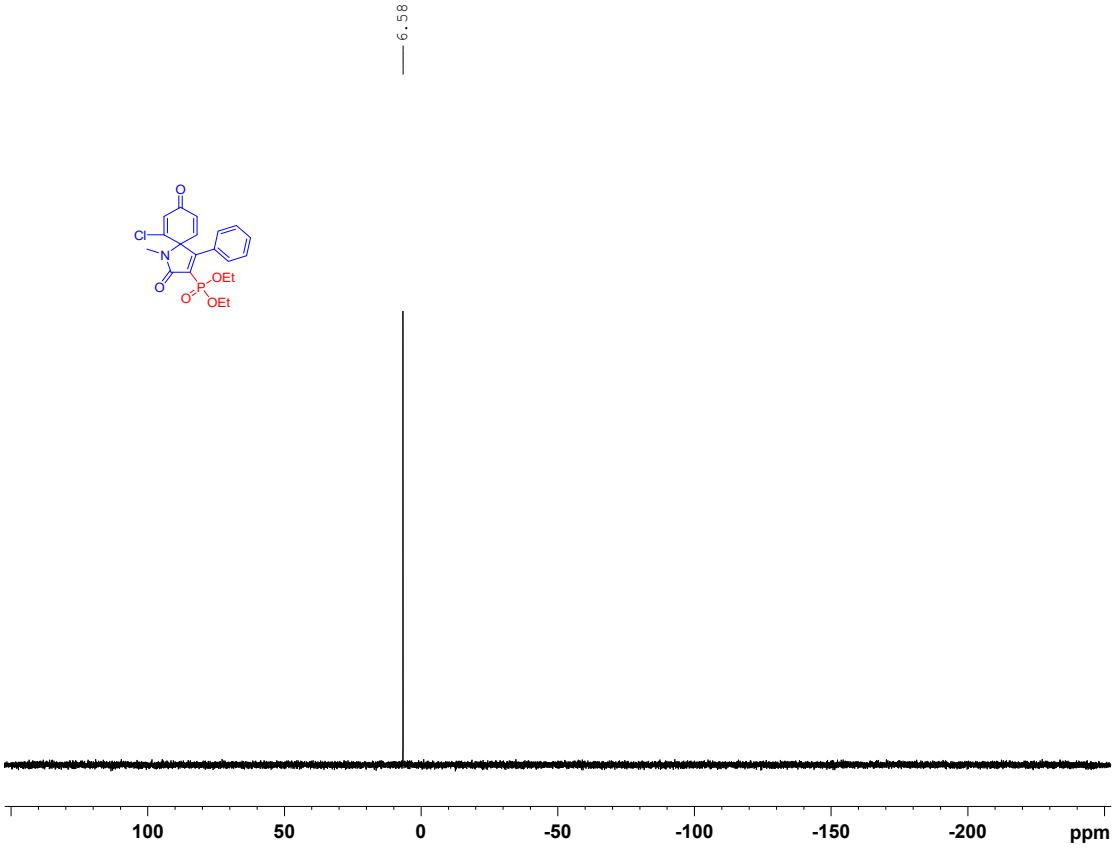
^{1}H NMR (CDCl$_3$, 300 K), **3p**



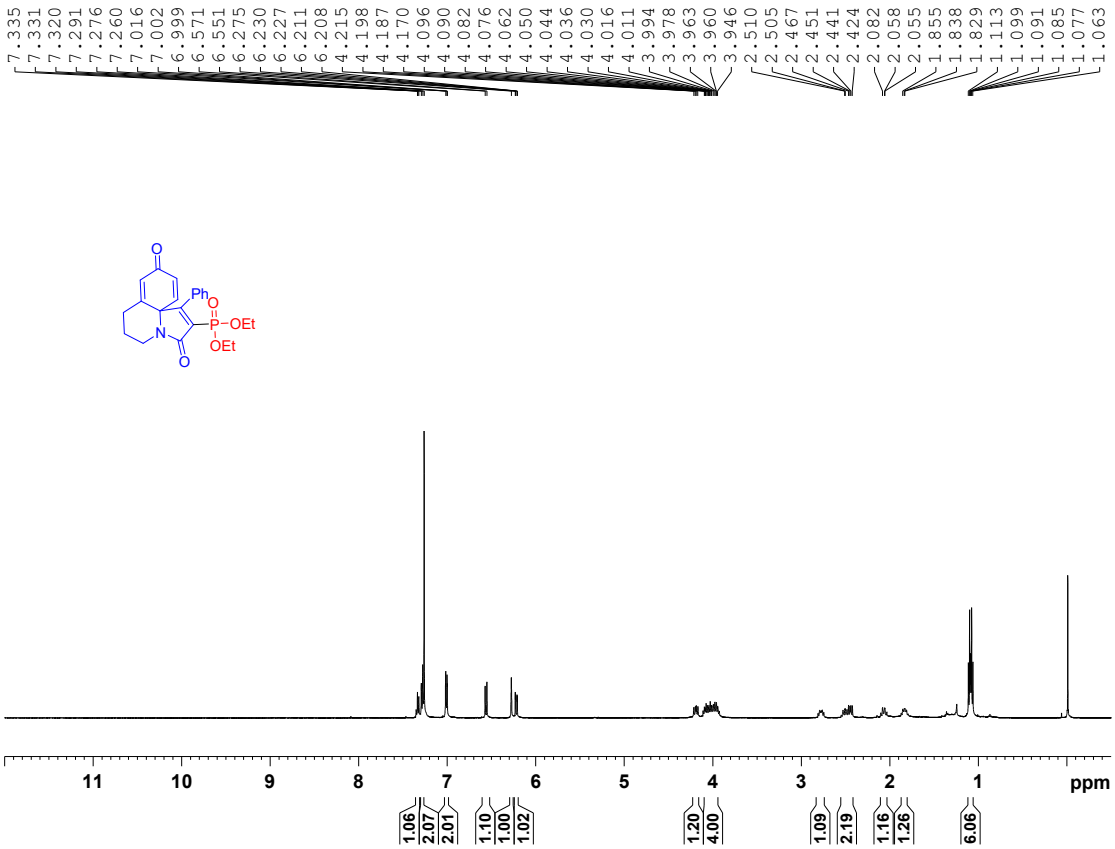
^{13}C NMR (CDCl$_3$, 300 K), **3p**



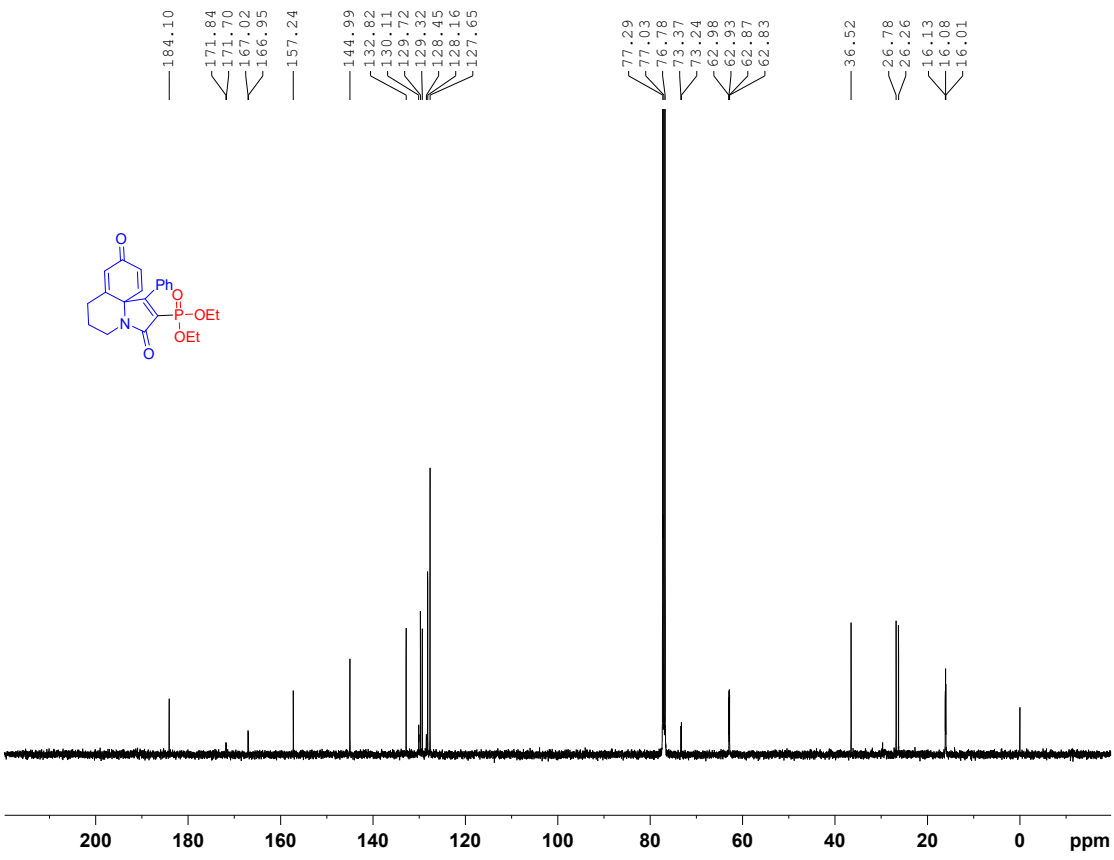
^{31}P NMR (CDCl$_3$, 300 K) **3p**



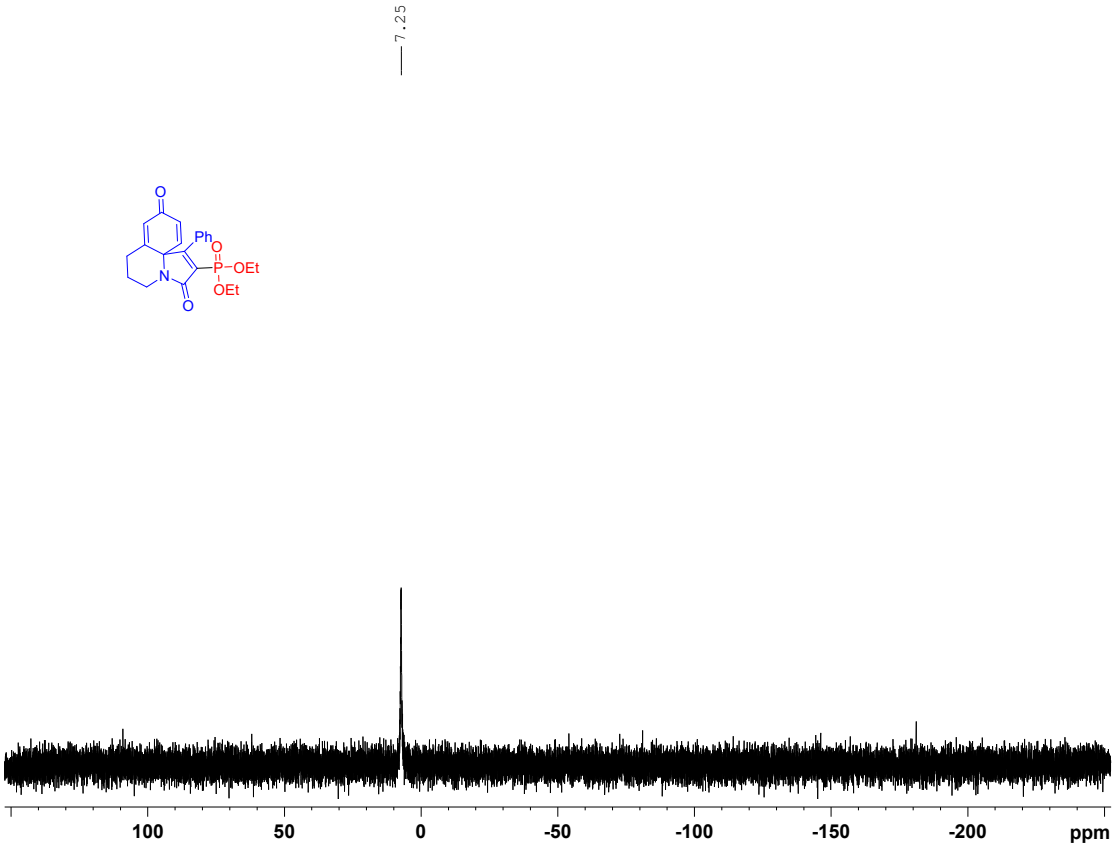
^{1}H NMR (CDCl$_3$, 300 K), **3q**



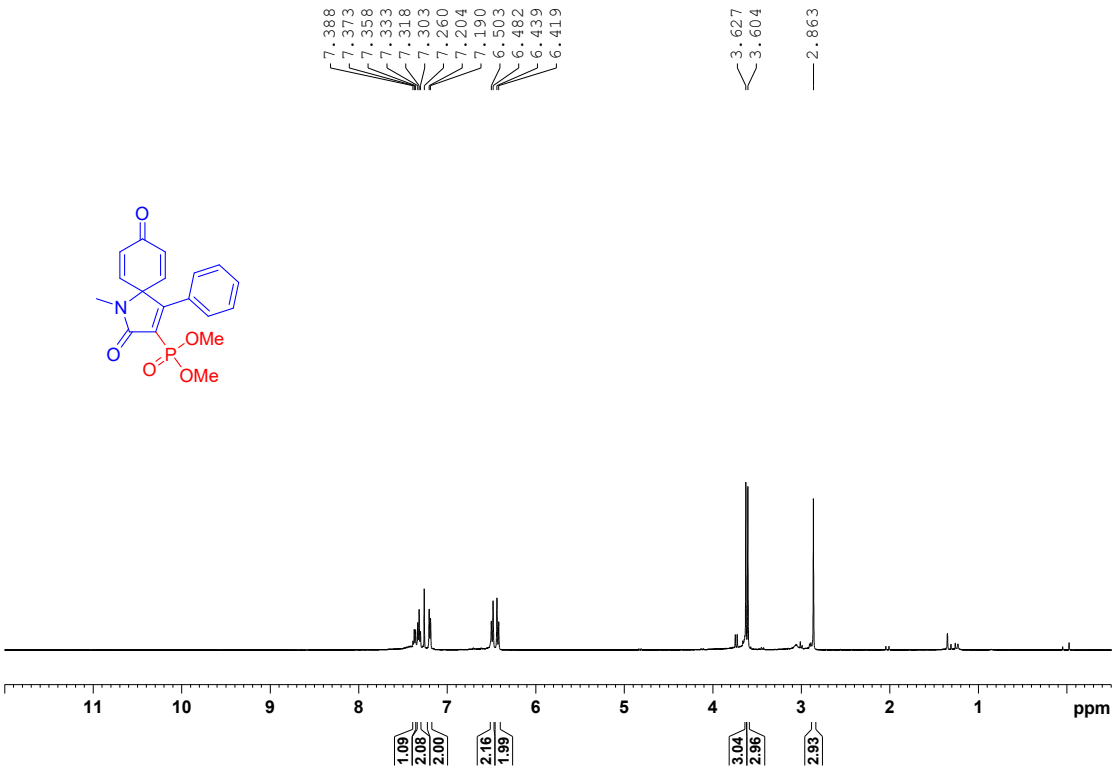
^{13}C NMR (CDCl$_3$, 300 K), **3q**



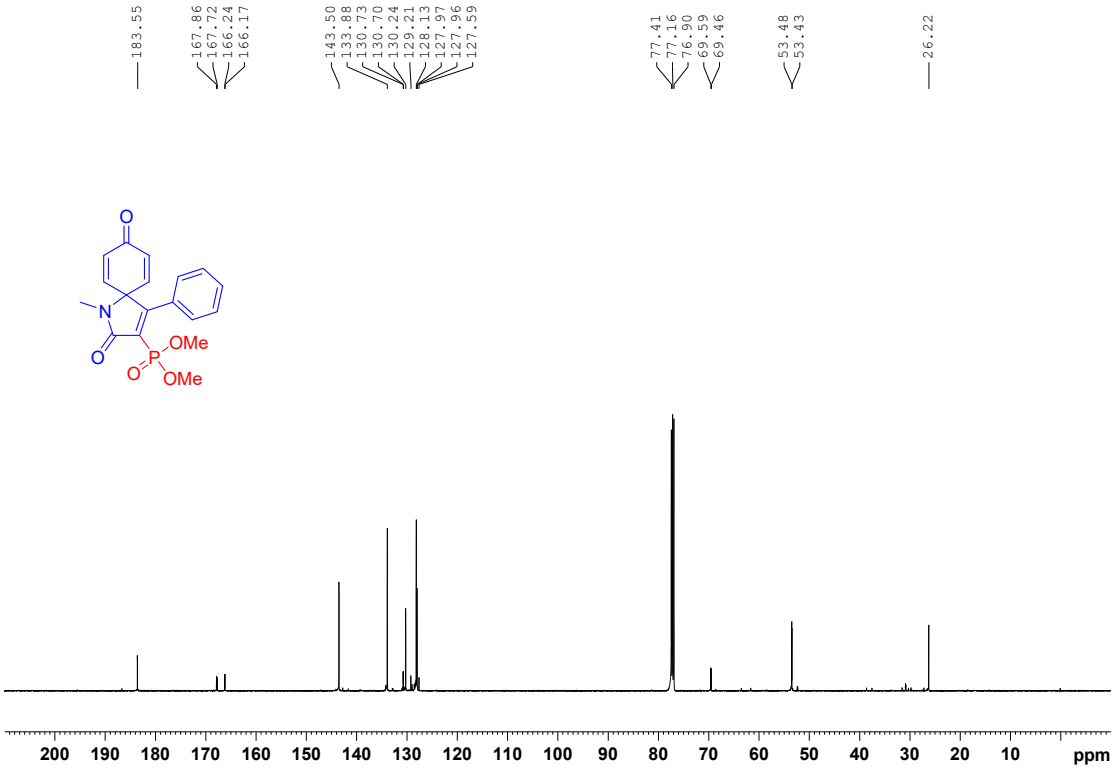
^{31}P NMR (CDCl$_3$, 300 K), **3q**



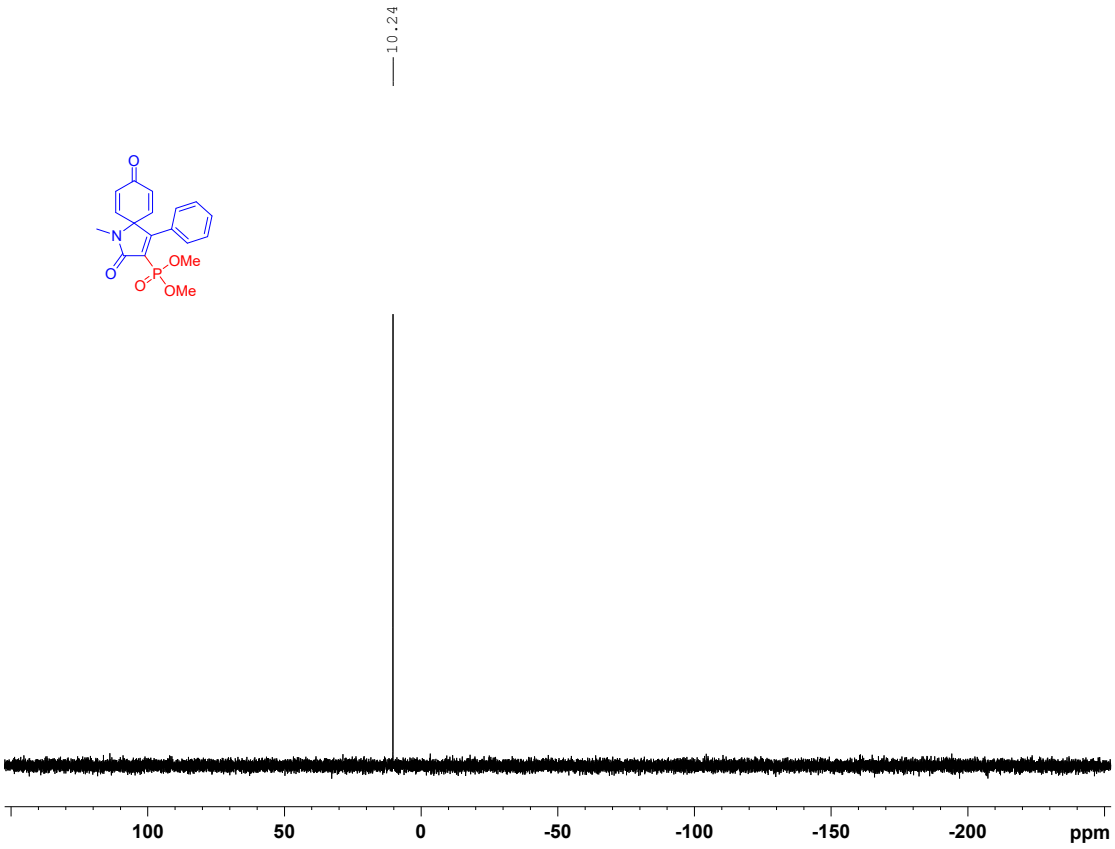
^{1}H NMR (CDCl$_3$, 300 K), **3r**



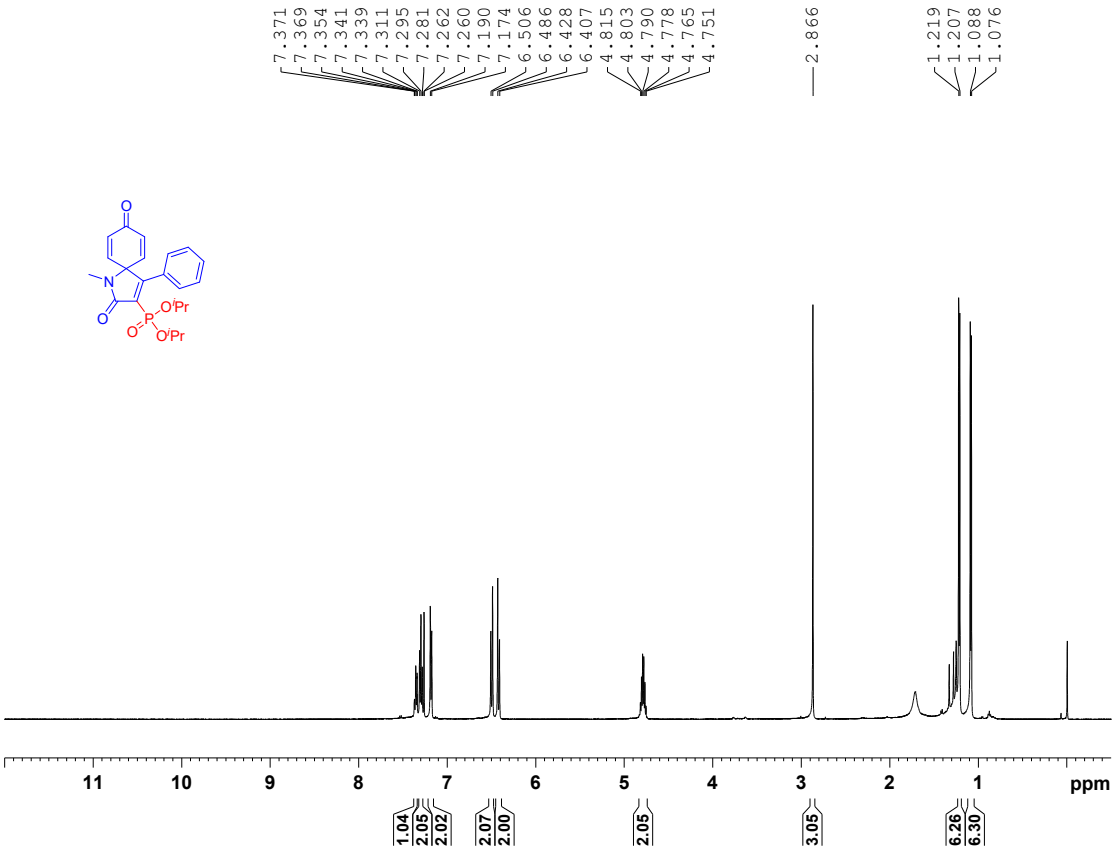
^{13}C NMR (CDCl$_3$, 300 K), **3r**



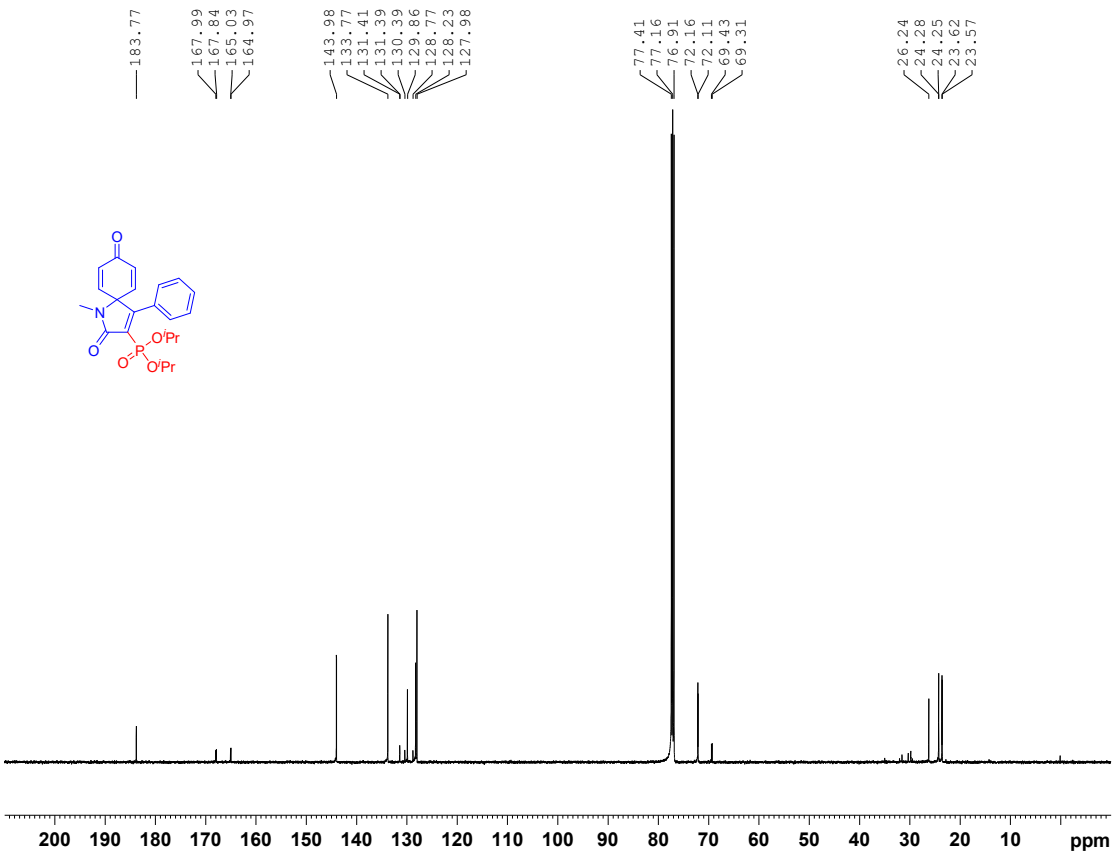
^{31}P NMR (CDCl$_3$, 300 K) **3r**



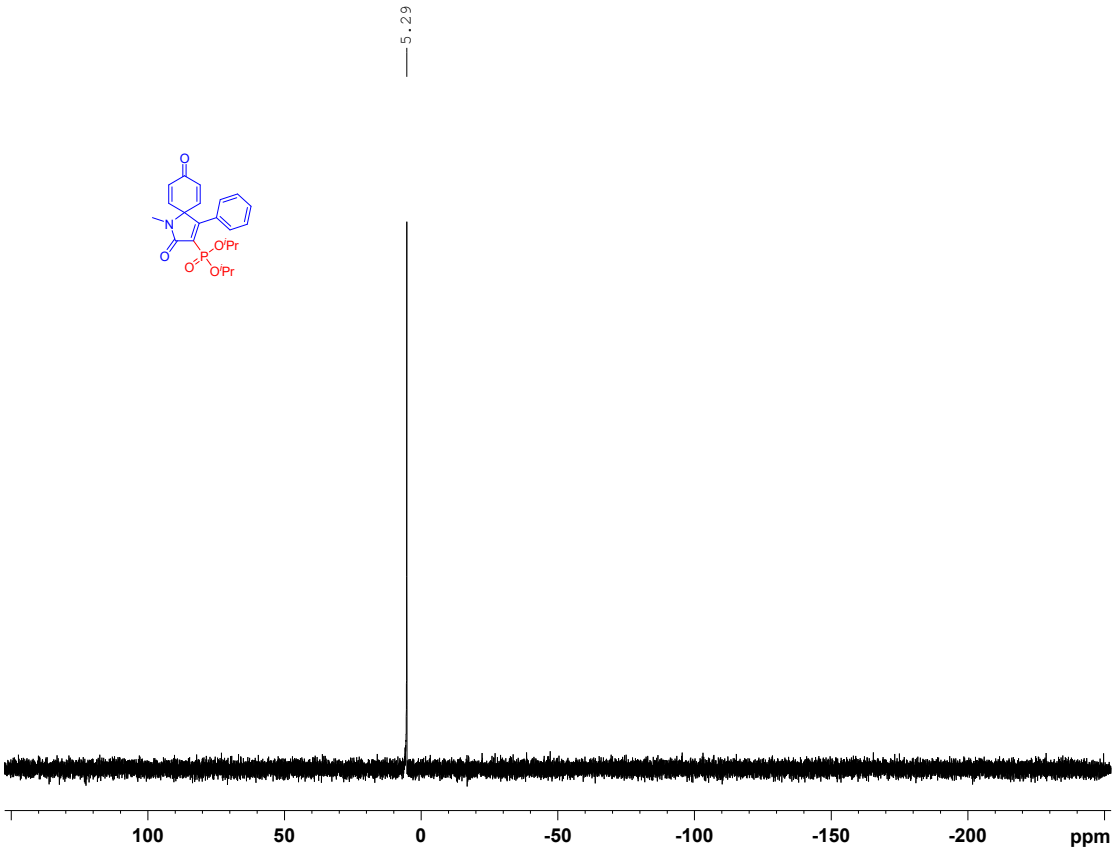
^{1}H NMR (CDCl$_3$, 300 K), **3s**



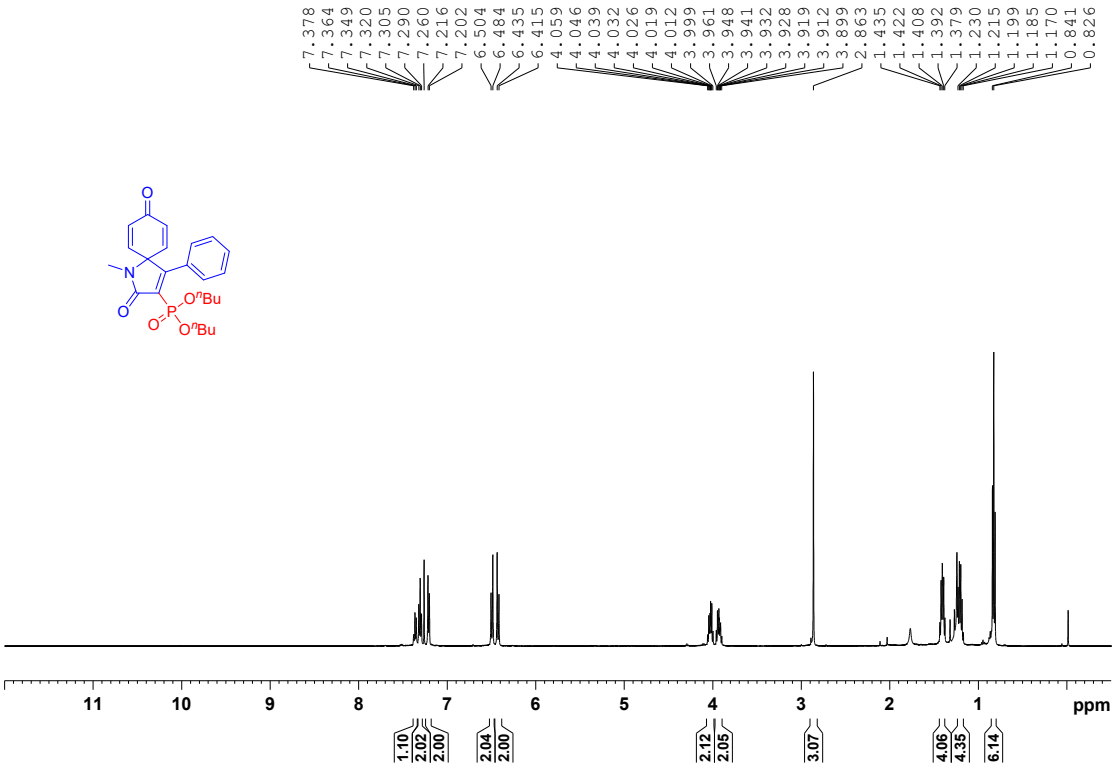
^{13}C NMR (CDCl$_3$, 300 K), **3s**



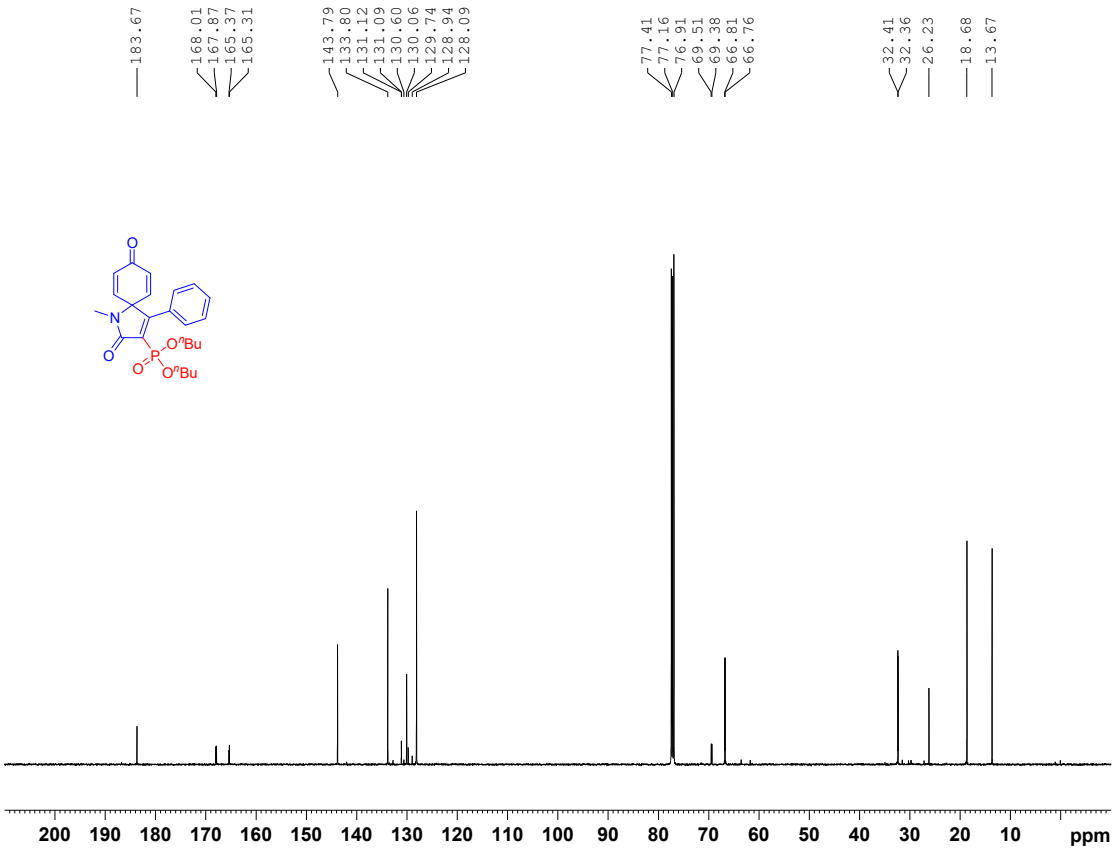
^{31}P NMR (CDCl$_3$, 300 K) **3s**



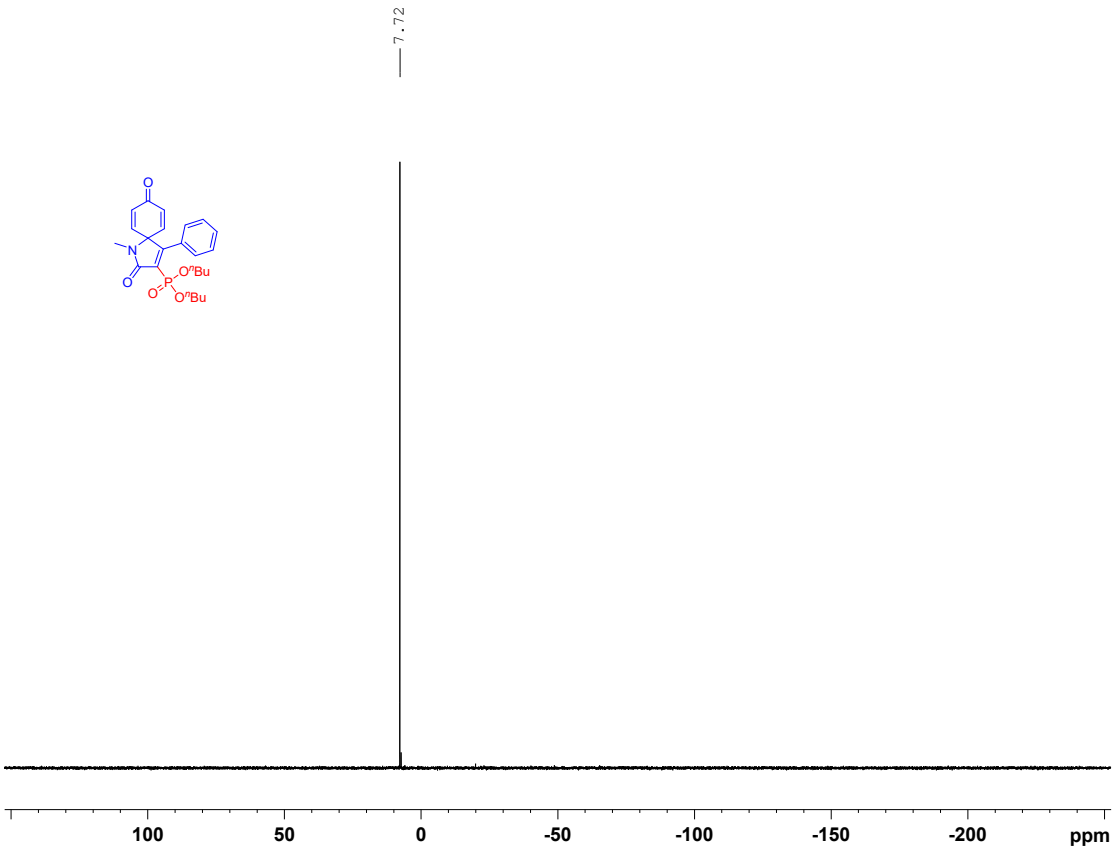
^{1}H NMR (CDCl$_3$, 300 K), **3t**



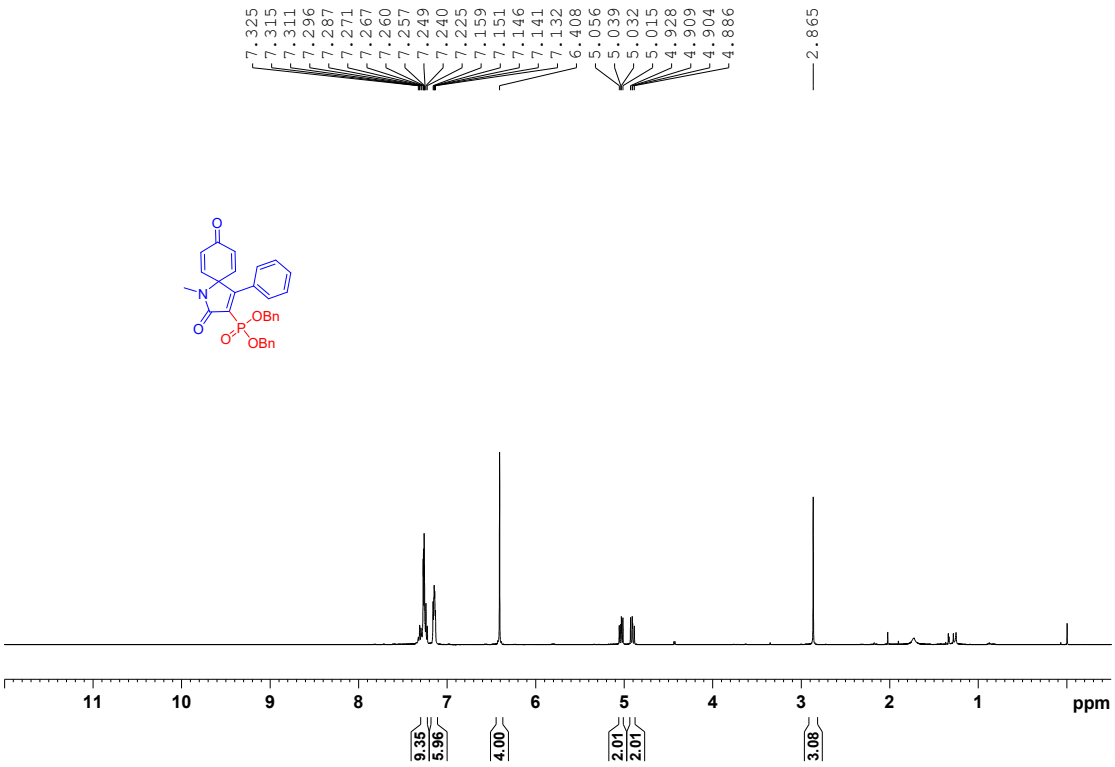
^{13}C NMR (CDCl$_3$, 300 K), **3t**



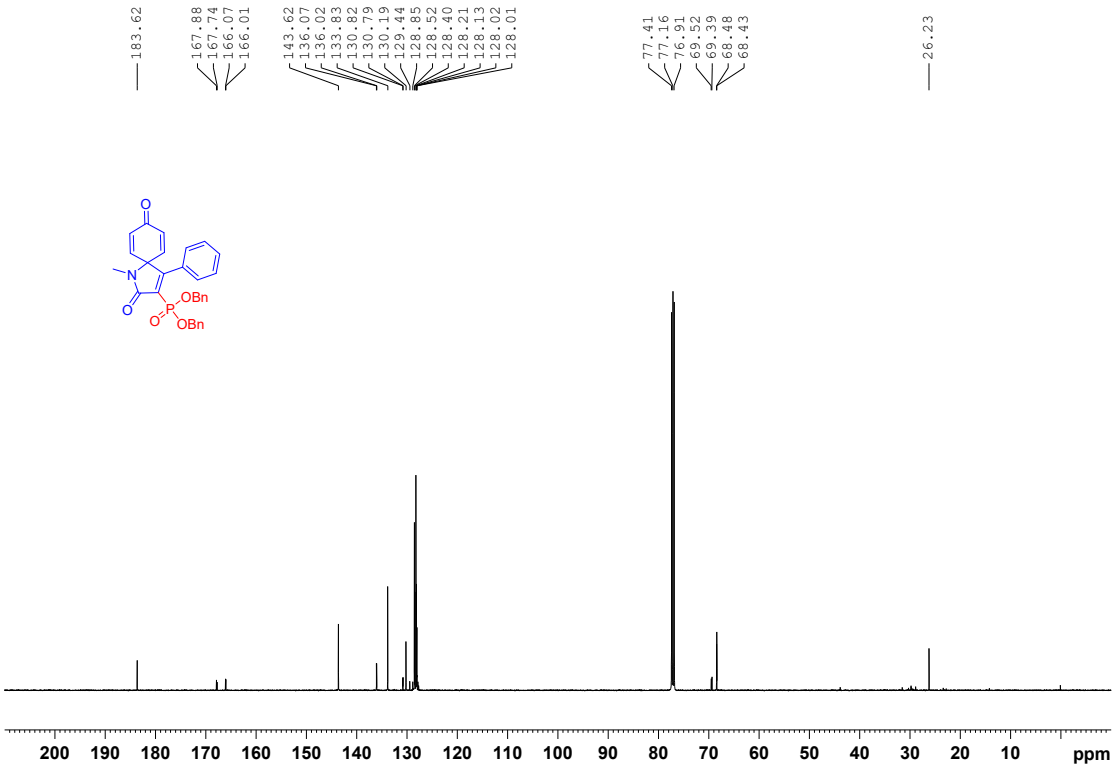
^{31}P NMR (CDCl$_3$, 300 K) **3t**



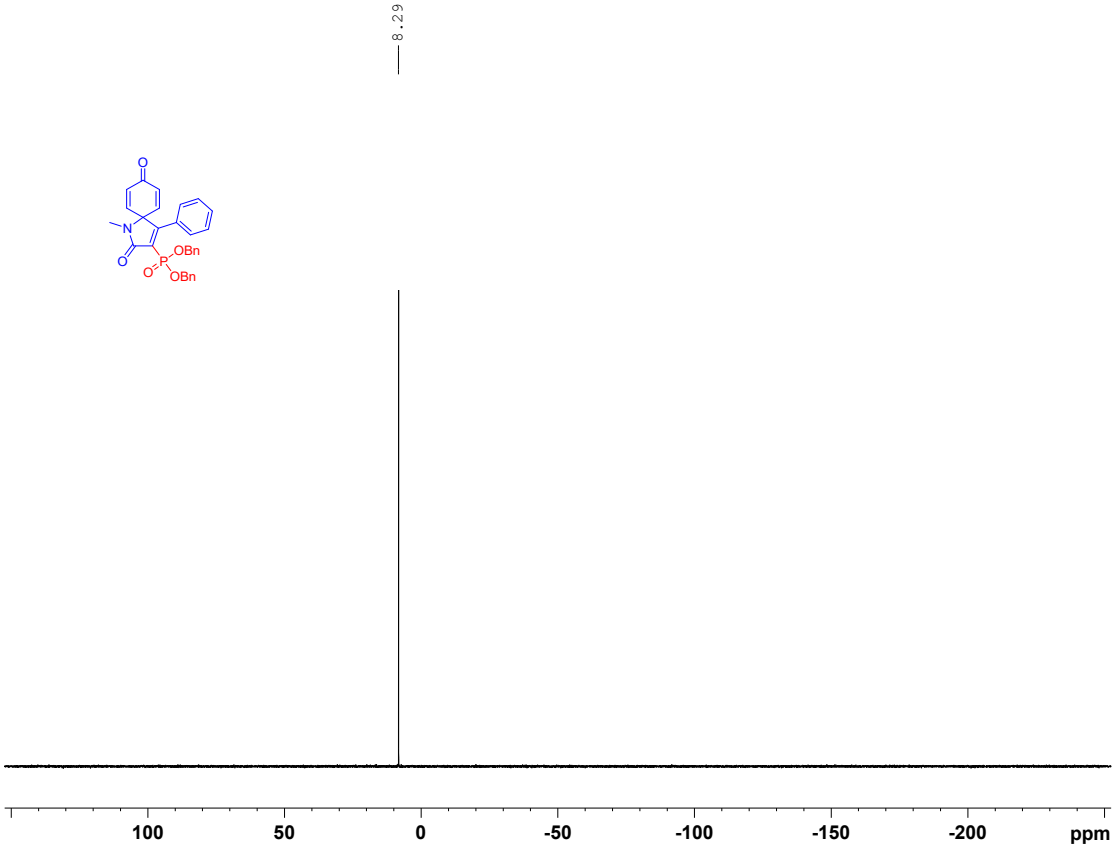
^{1}H NMR (CDCl$_3$, 300 K), **3u**



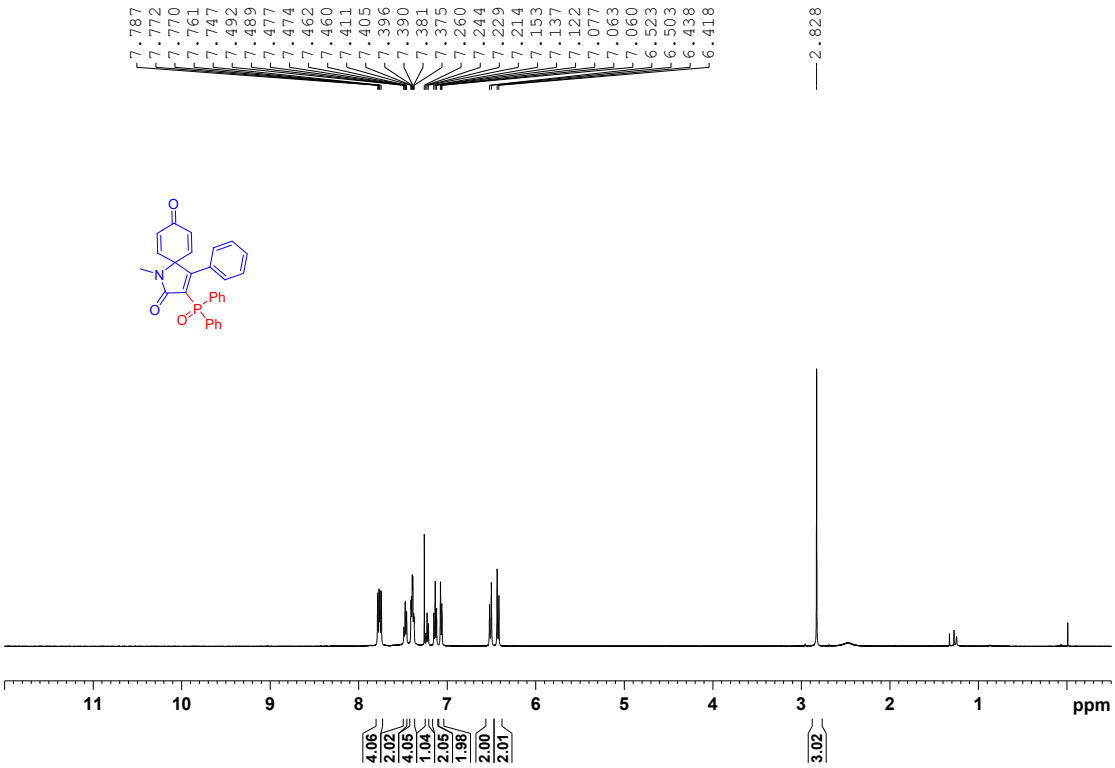
^{13}C NMR (CDCl$_3$, 300 K), **3u**



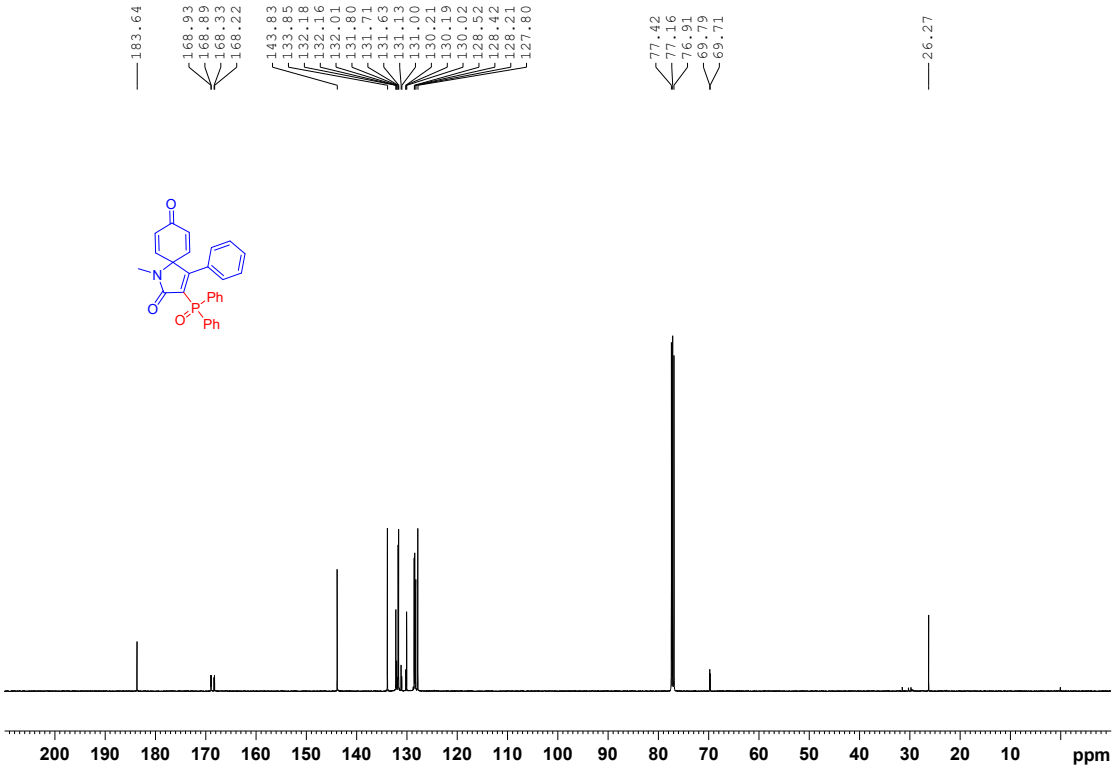
^{31}P NMR (CDCl$_3$, 300 K) **3u**



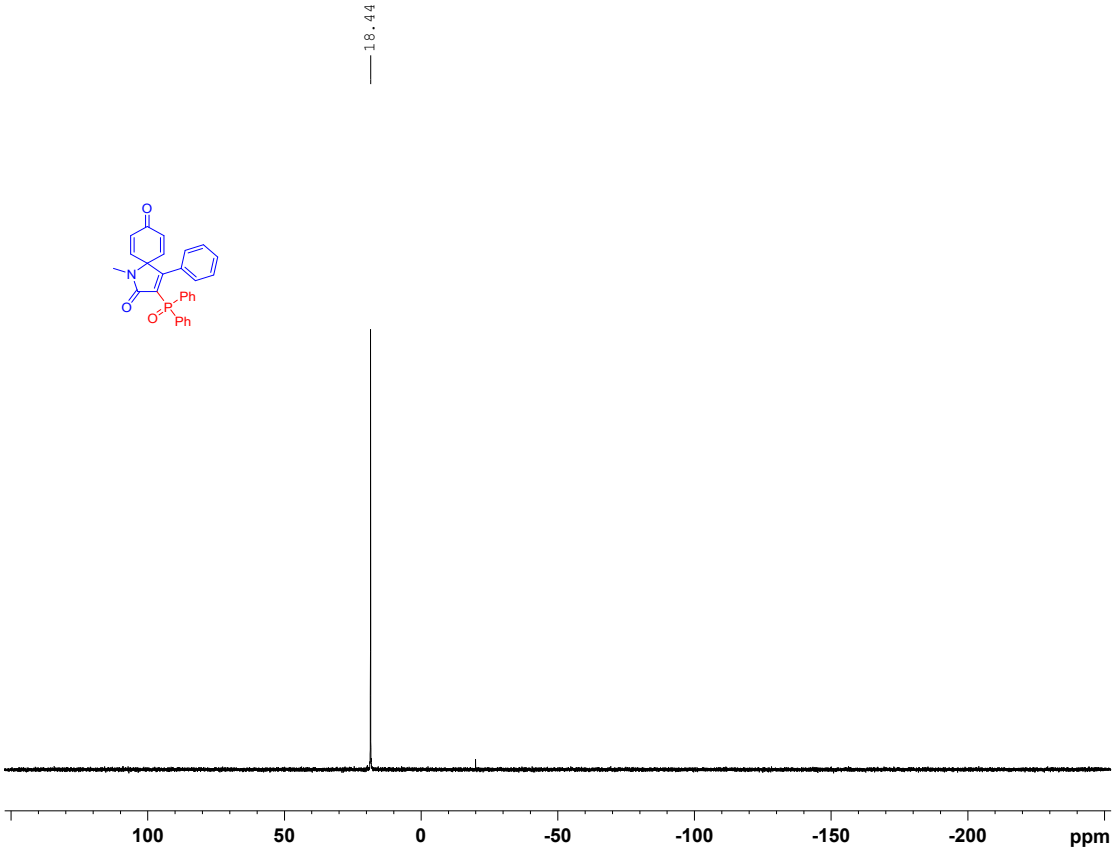
^{1}H NMR (CDCl$_3$, 300 K), **3v**



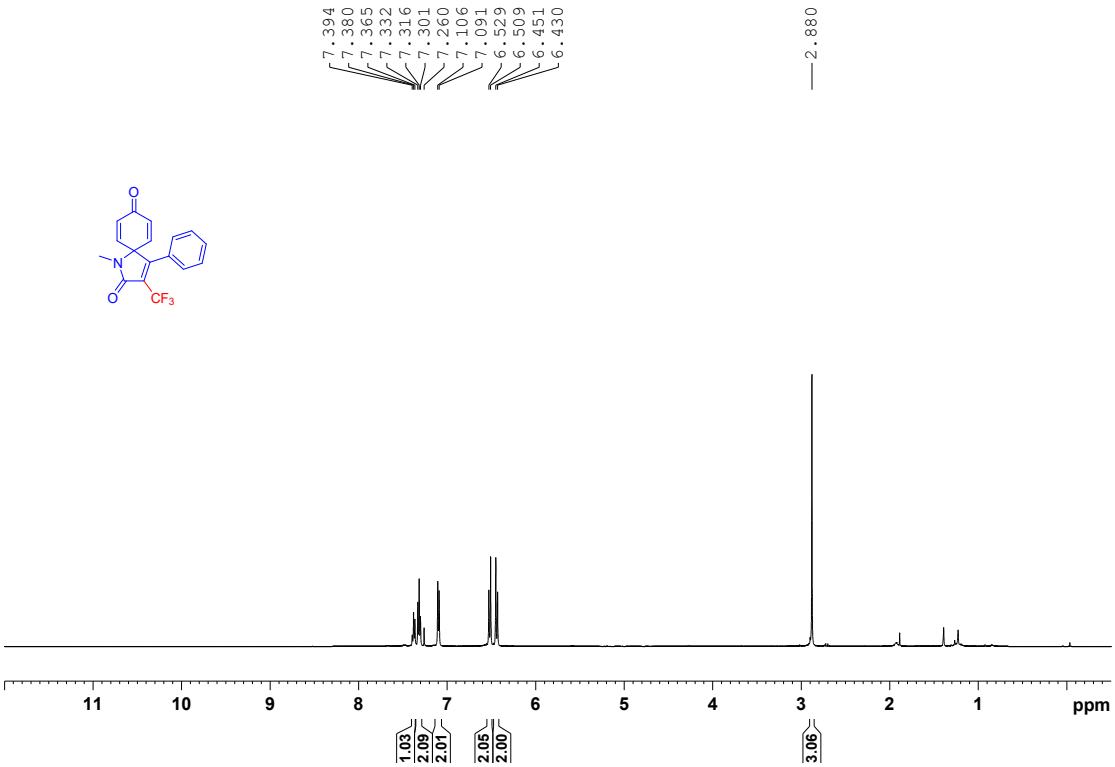
^{13}C NMR (CDCl$_3$, 300 K), **3v**



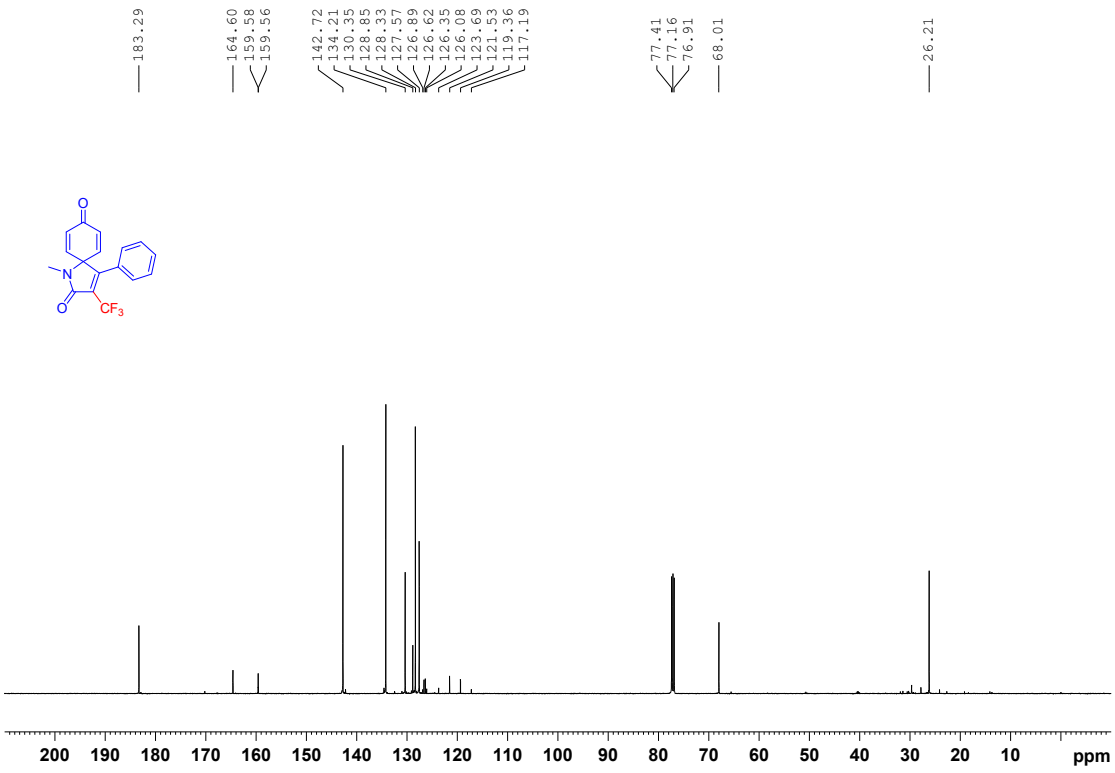
^{31}P NMR (CDCl$_3$, 300 K) **3v**



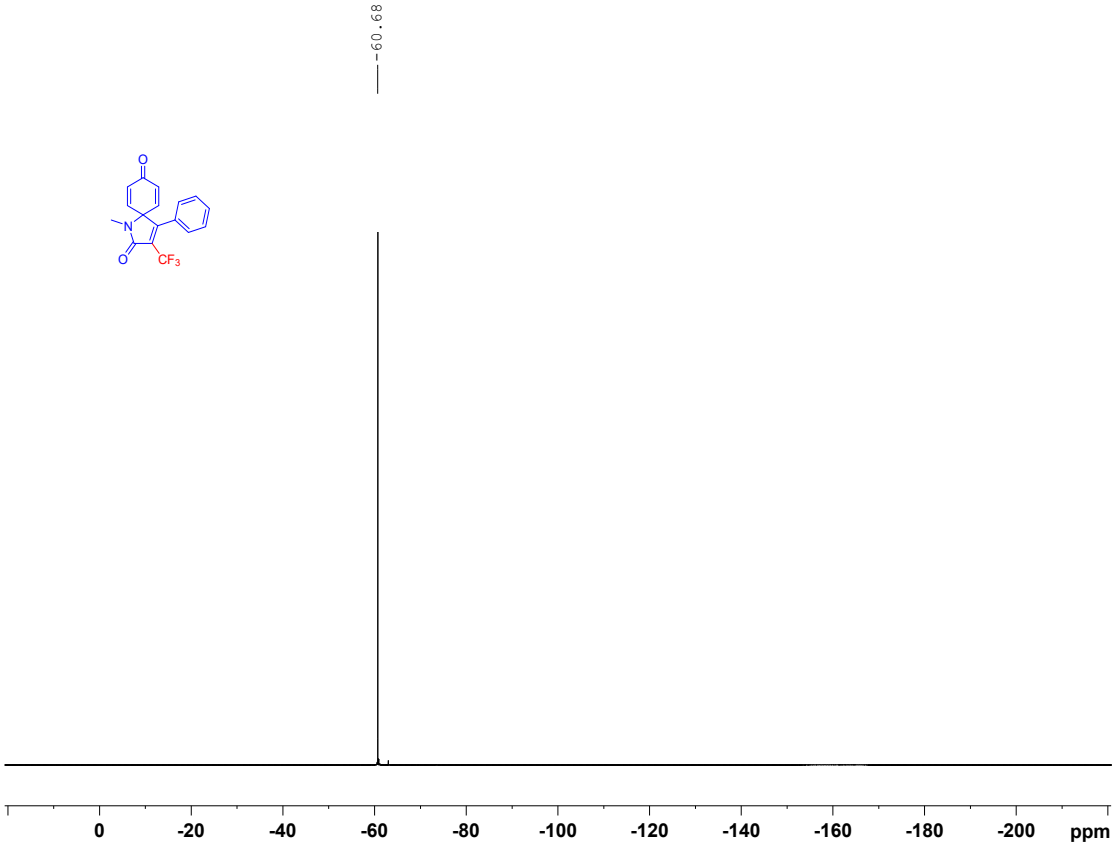
^{1}H NMR (CDCl$_3$, 300 K), **4a**



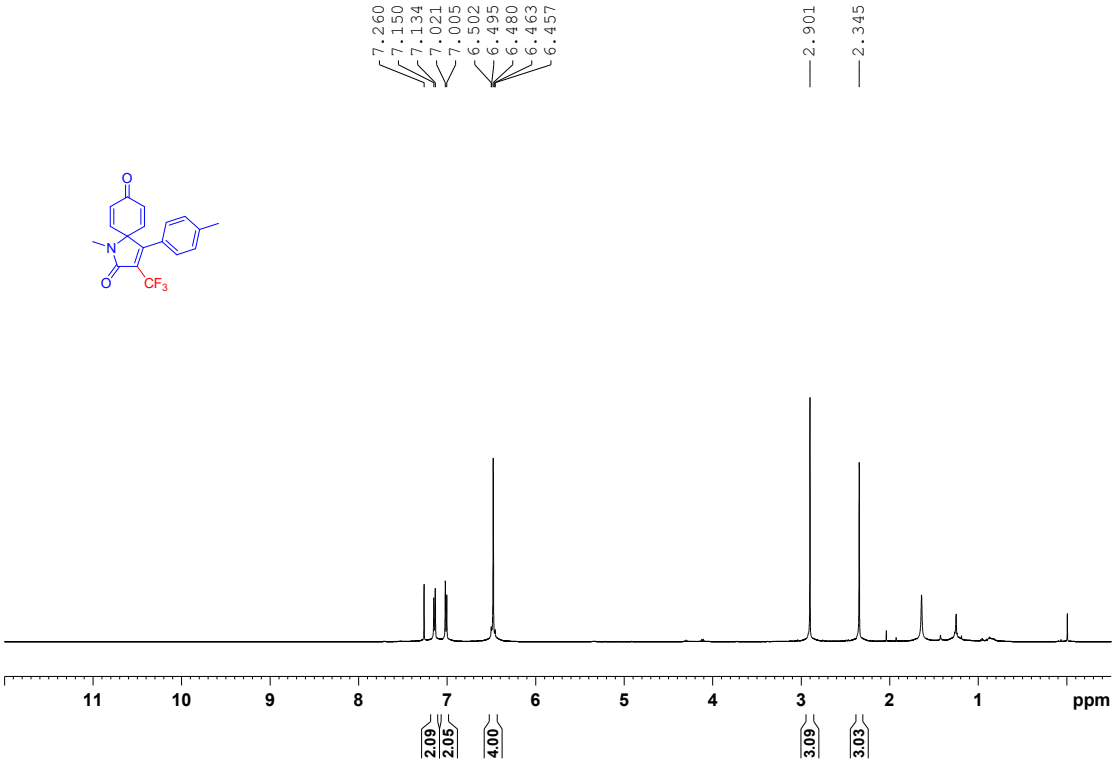
^{13}C NMR (CDCl$_3$, 300 K), **4a**



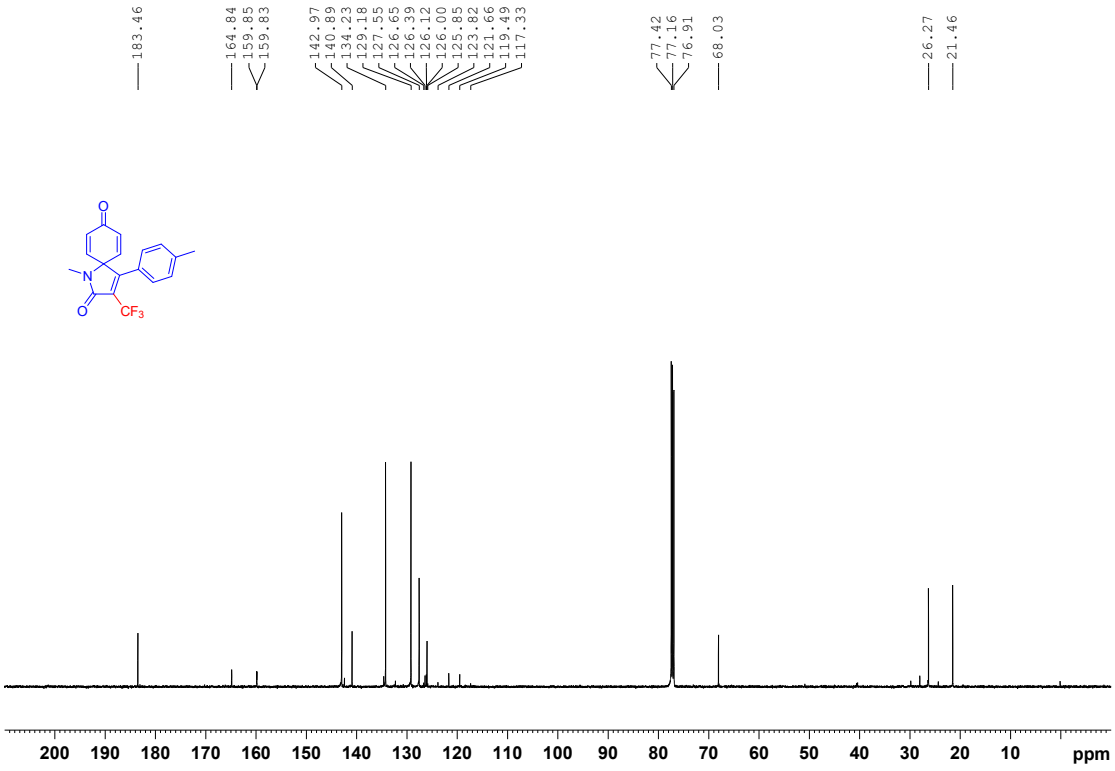
^{19}F NMR (CDCl$_3$, 300 K) **4a**



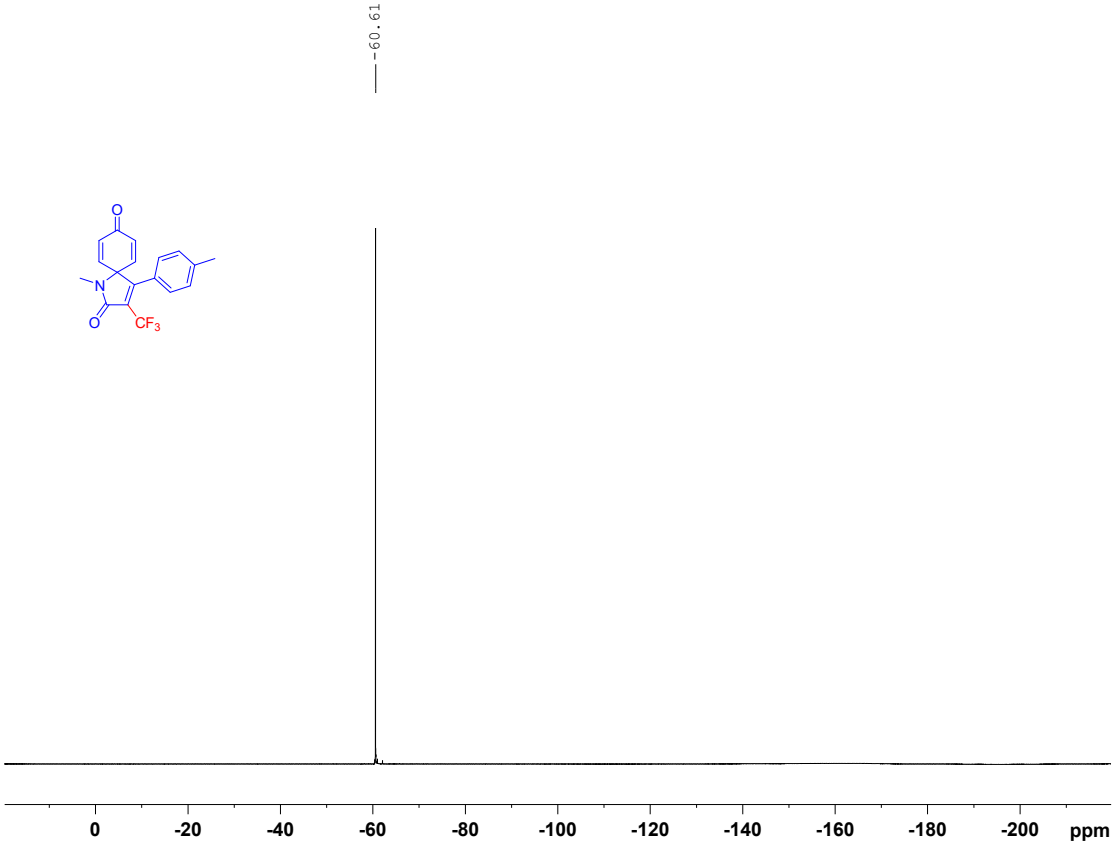
^{1}H NMR (CDCl$_3$, 300 K), **4b**



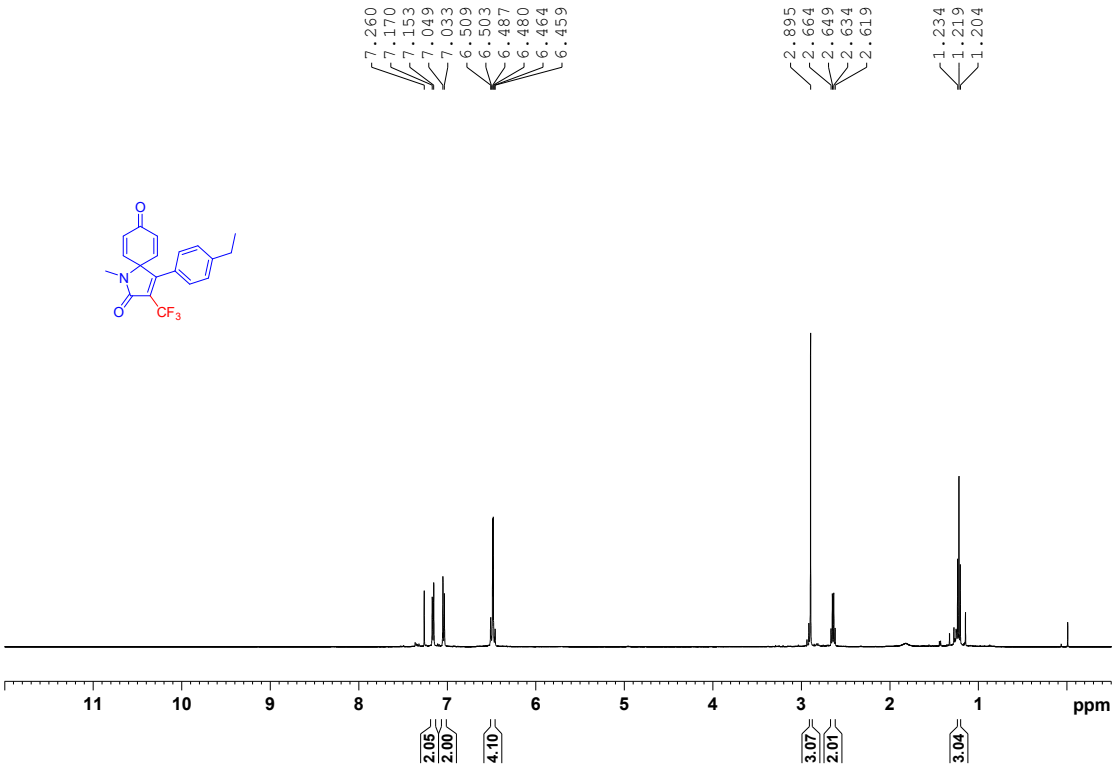
^{13}C NMR (CDCl$_3$, 300 K), **4b**



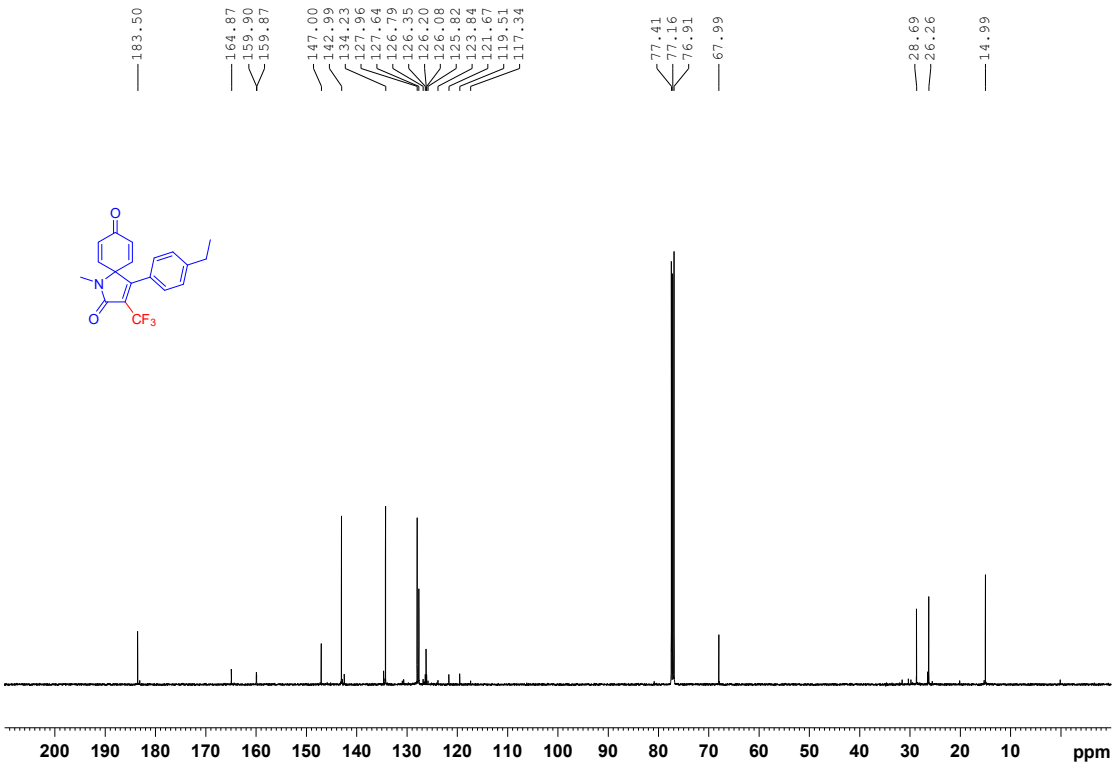
^{19}F NMR (CDCl$_3$, 300 K) **4b**



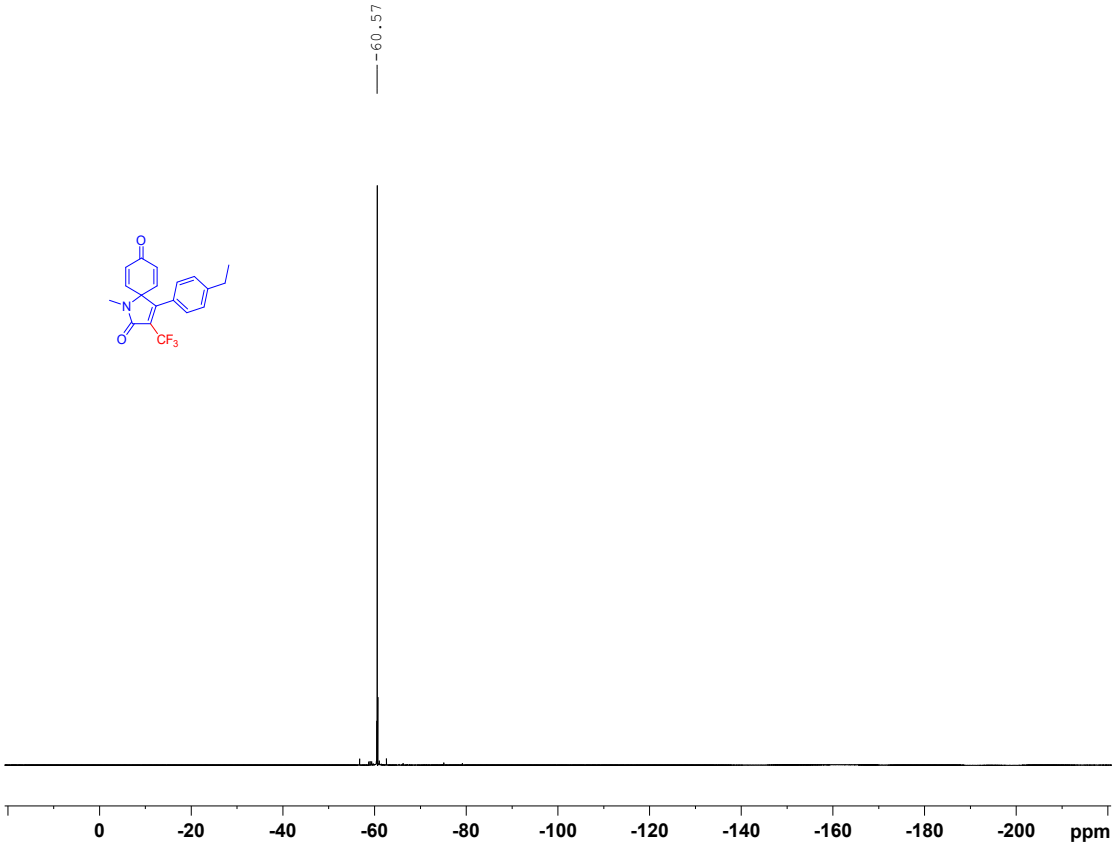
^{1}H NMR (CDCl$_3$, 300 K), **4c**



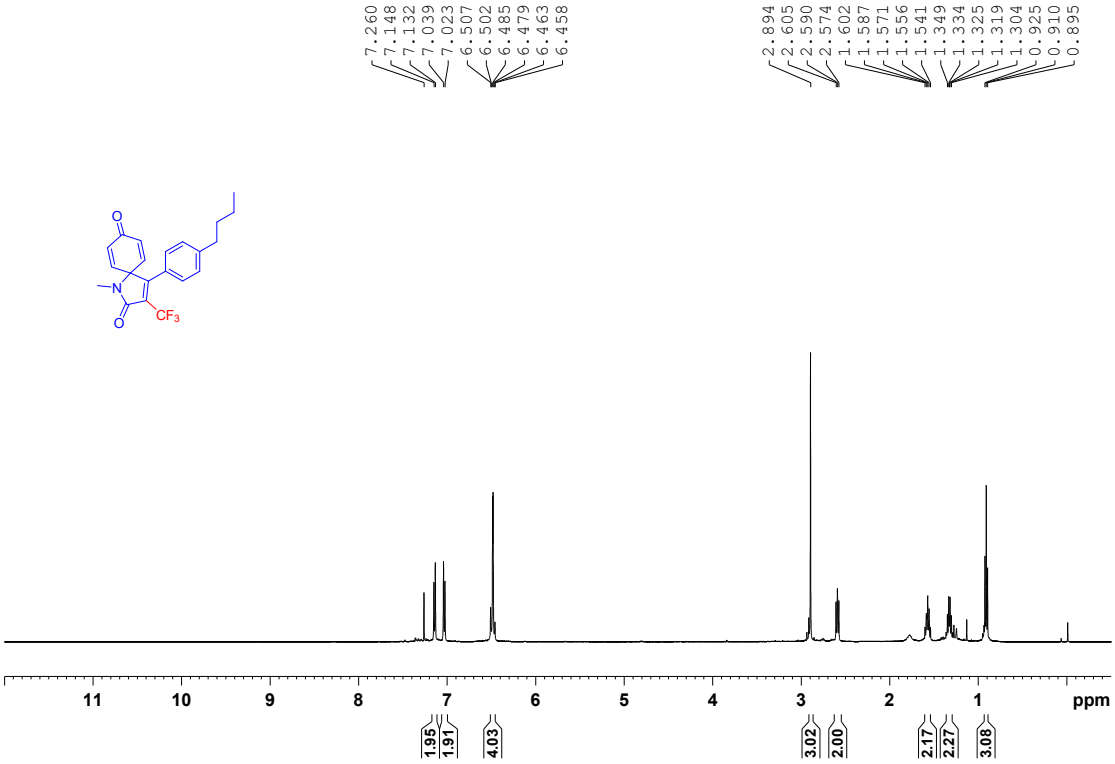
^{13}C NMR (CDCl$_3$, 300 K), **4c**



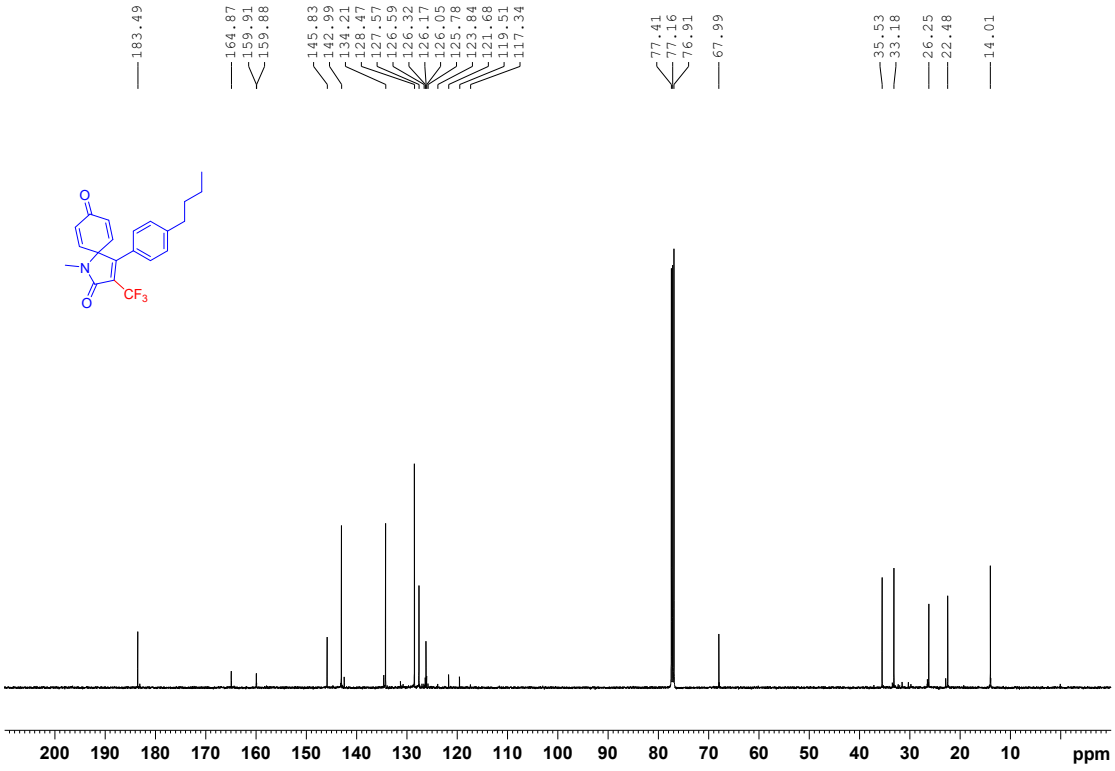
^{19}F NMR (CDCl$_3$, 300 K) **4c**



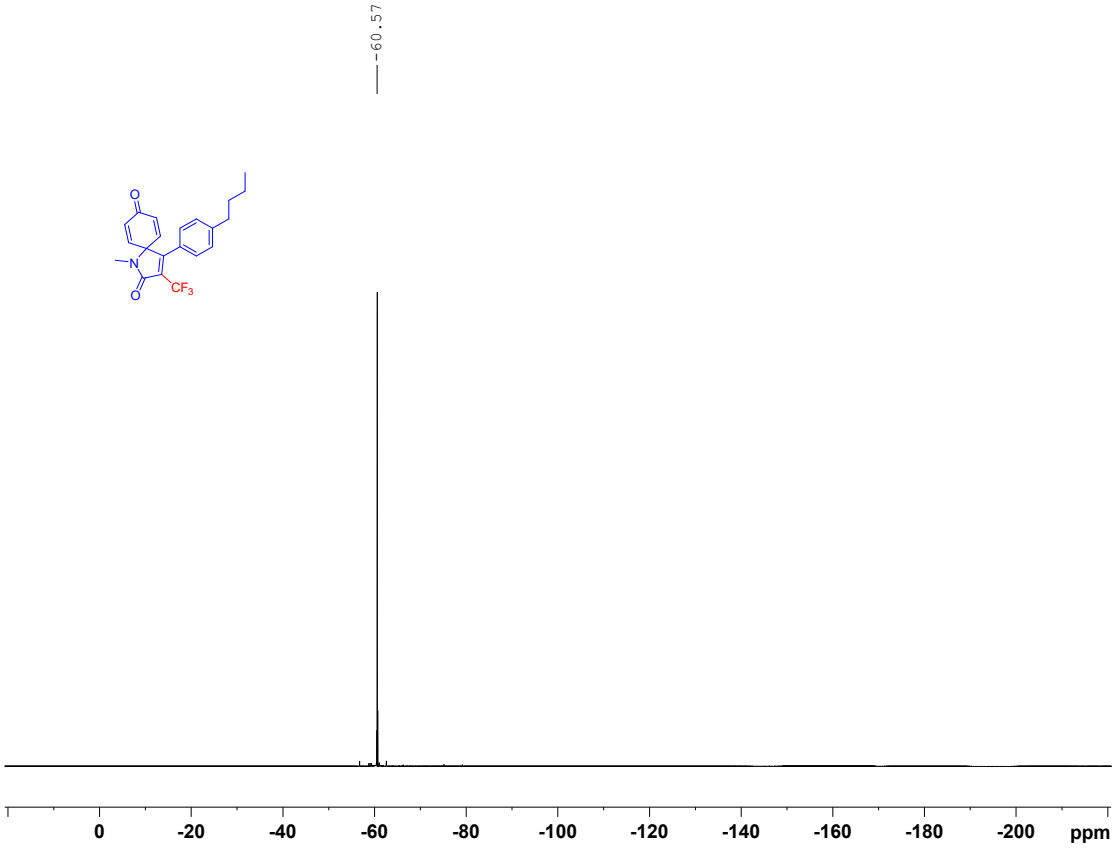
^{1}H NMR (CDCl$_3$, 300 K), **4d**



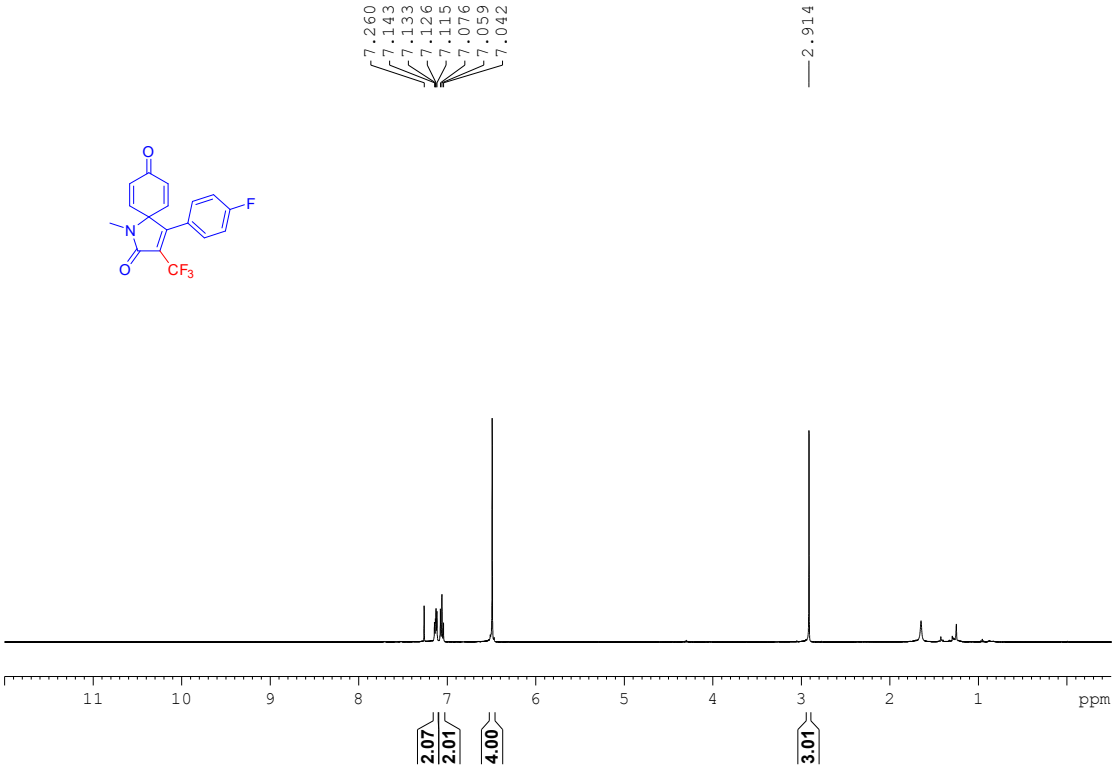
^{13}C NMR (CDCl$_3$, 300 K), **4d**



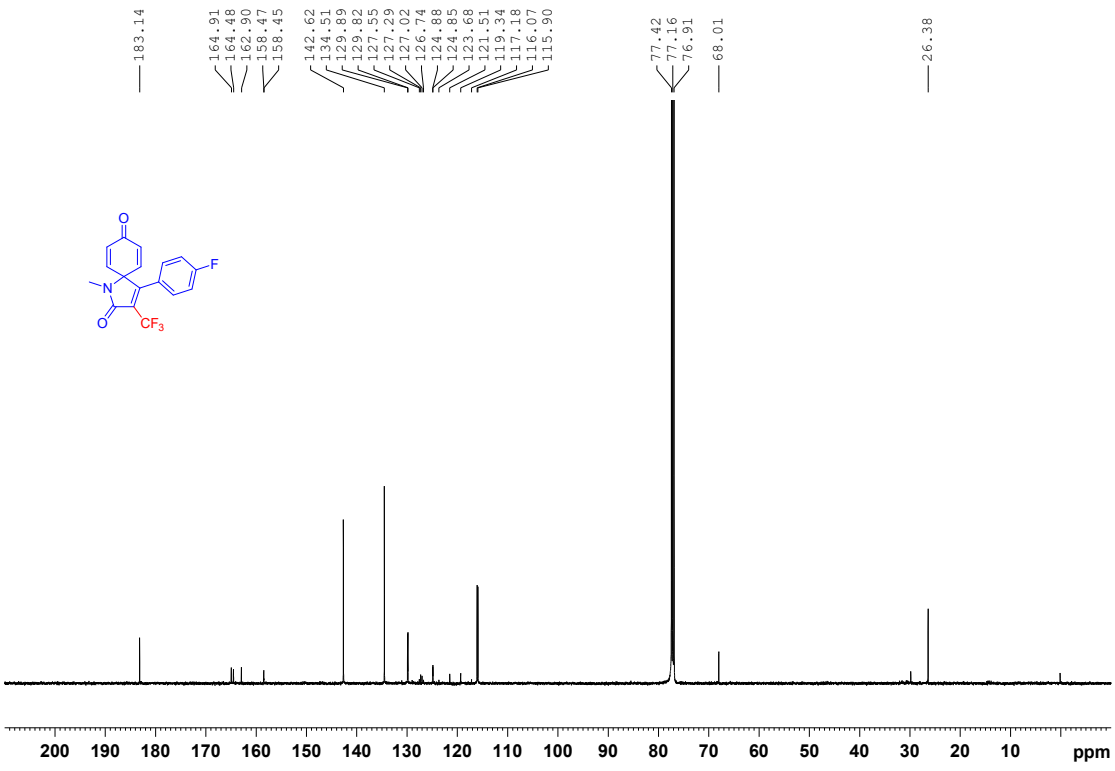
^{19}F NMR (CDCl$_3$, 300 K) **4d**



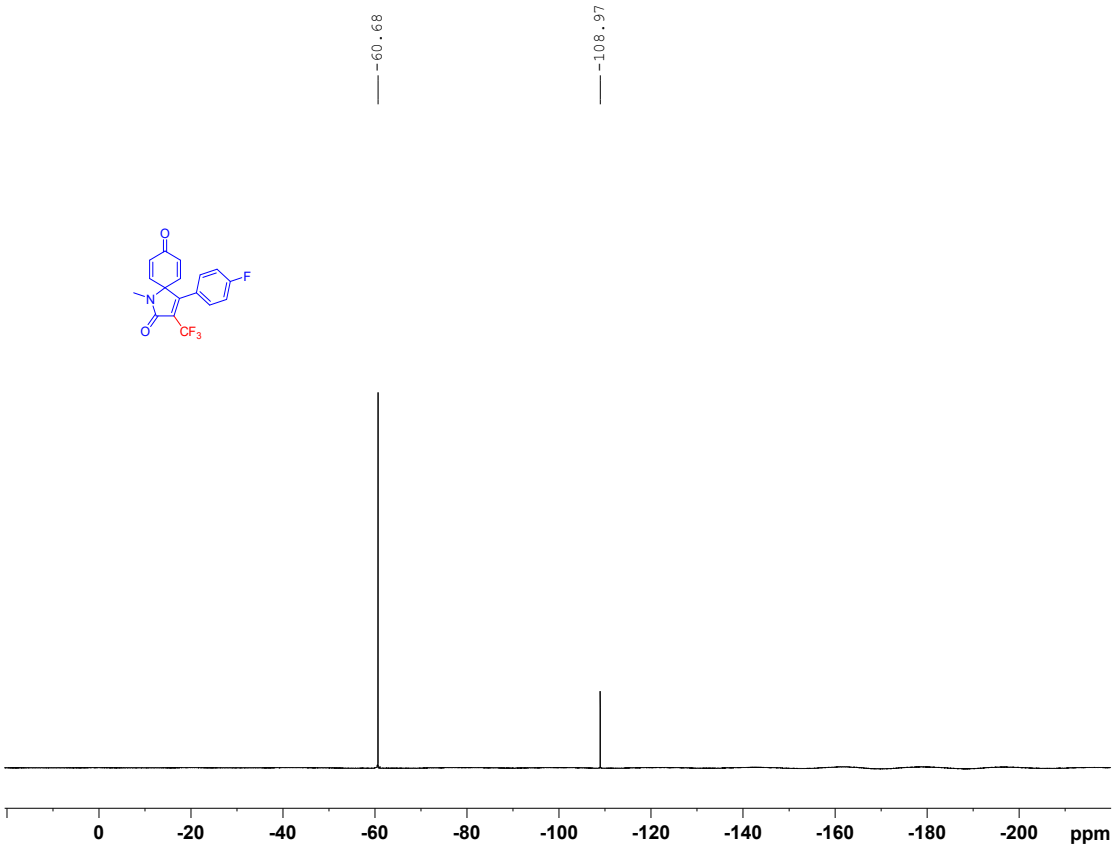
^{1}H NMR (CDCl$_3$, 300 K), **4e**



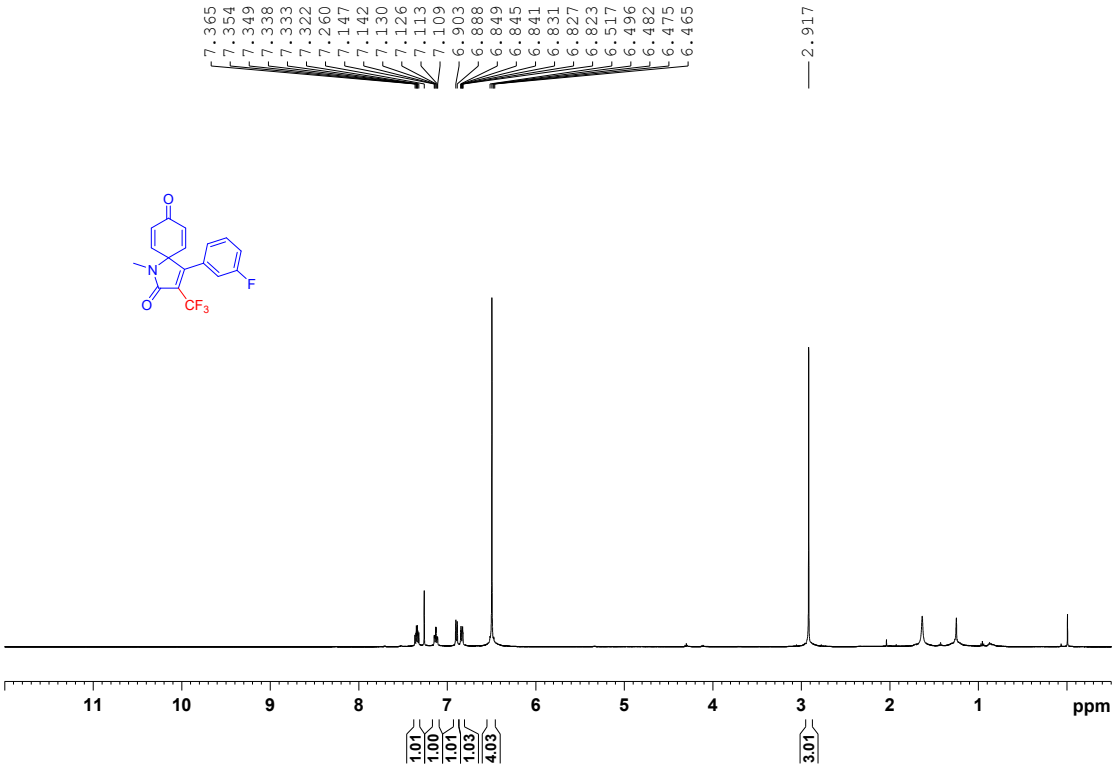
^{13}C NMR (CDCl$_3$, 300 K), **4e**



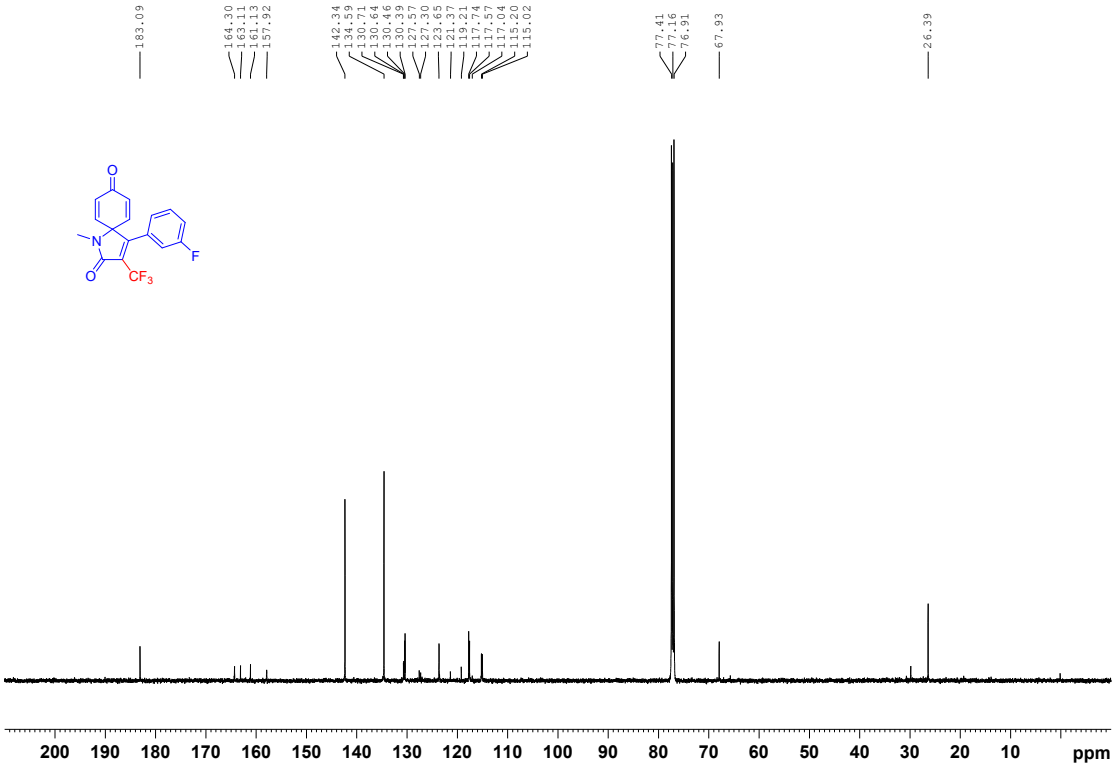
^{19}F NMR ($CDCl_3$, 300 K) **4e**



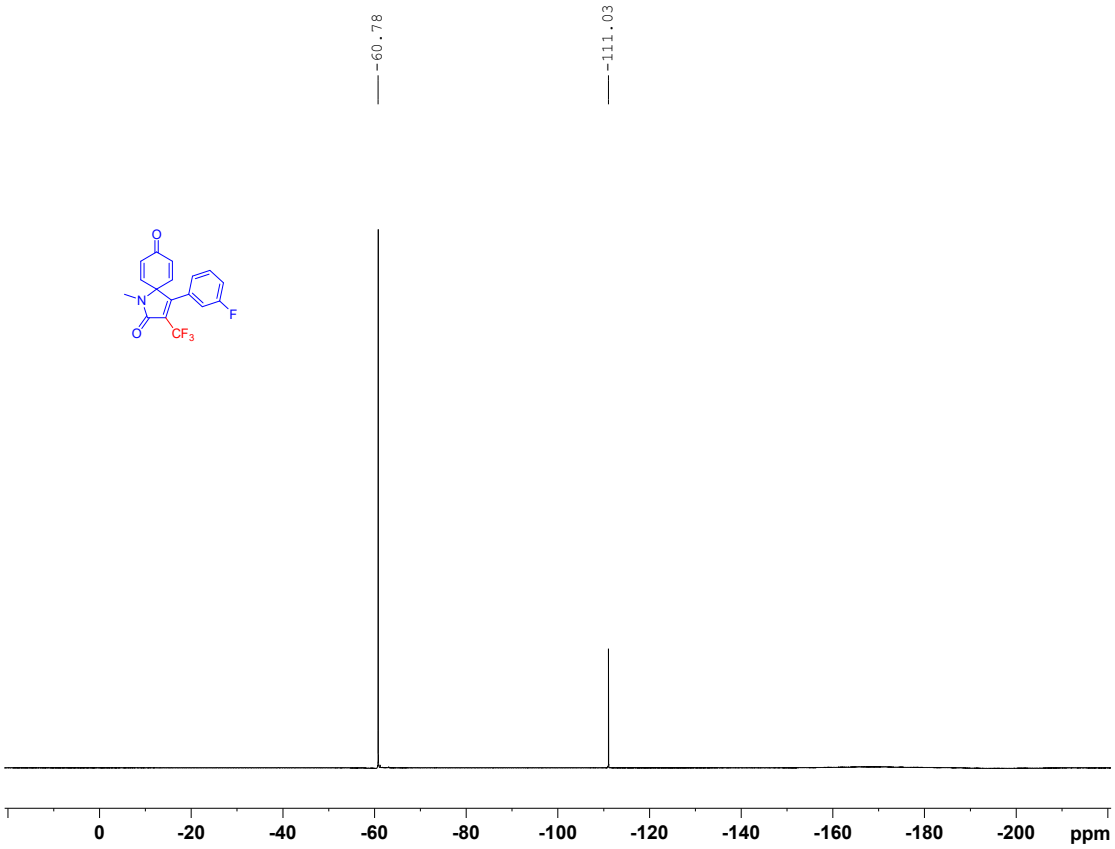
^{1}H NMR (CDCl$_3$, 300 K), **4f**



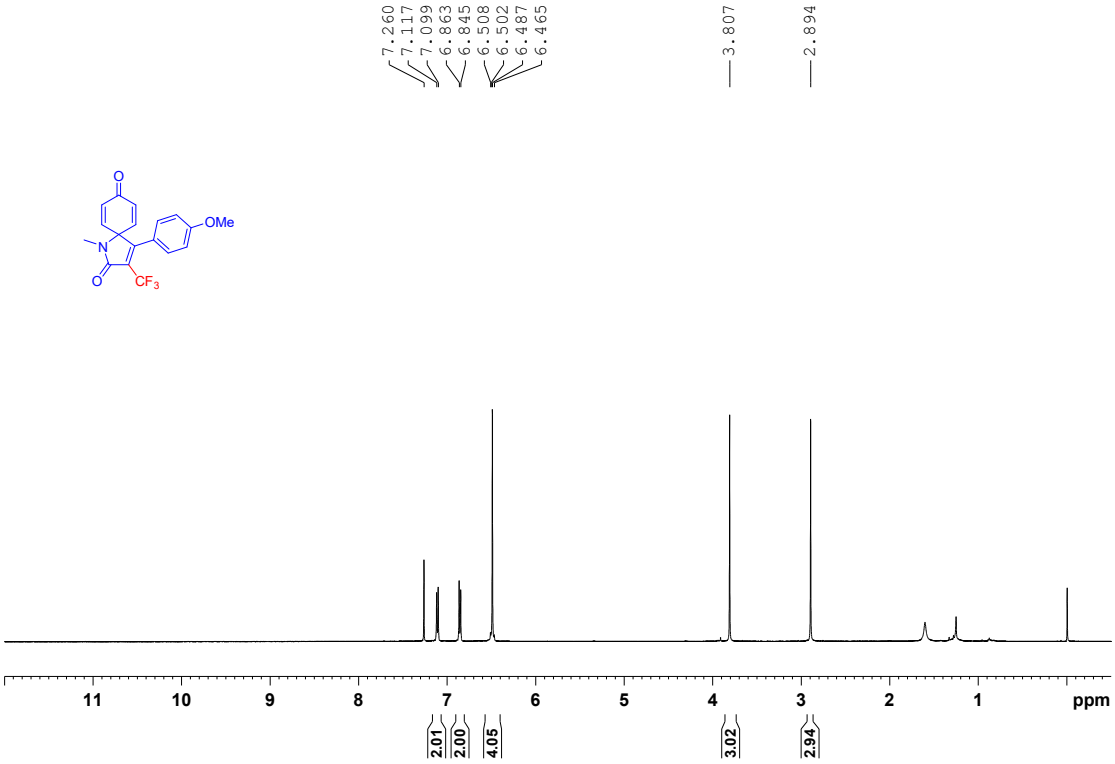
^{13}C NMR (CDCl$_3$, 300 K), **4f**



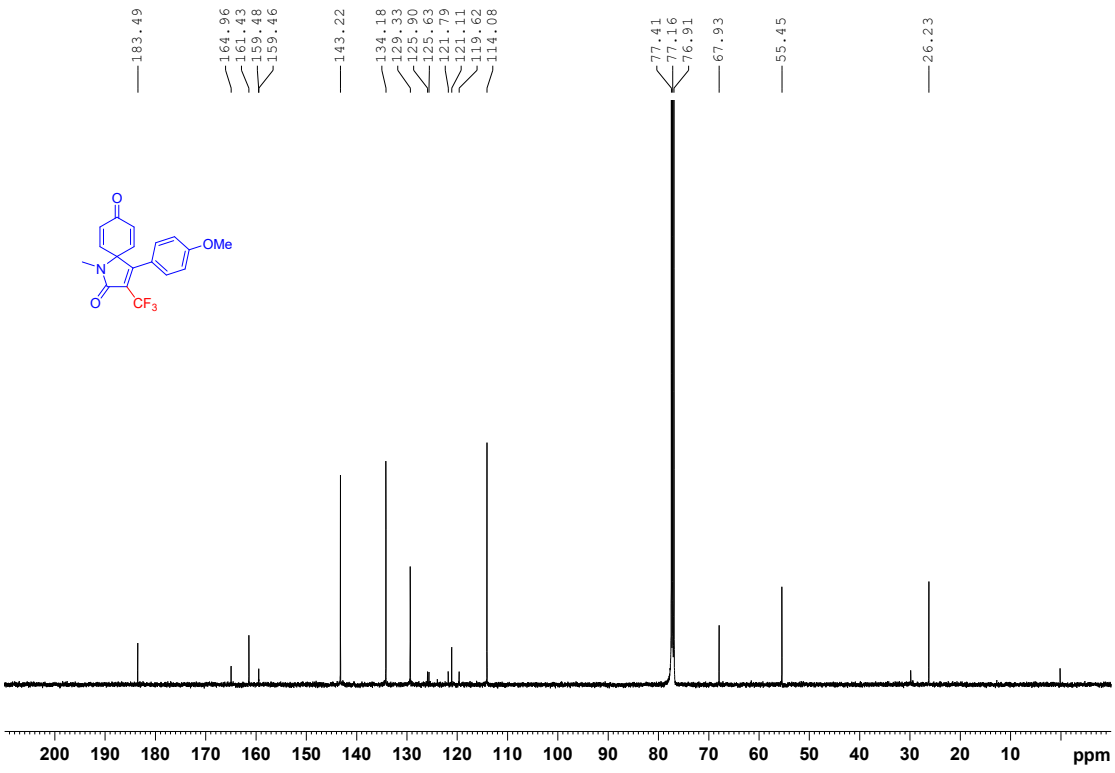
^{19}F NMR ($CDCl_3$, 300 K) **4f**



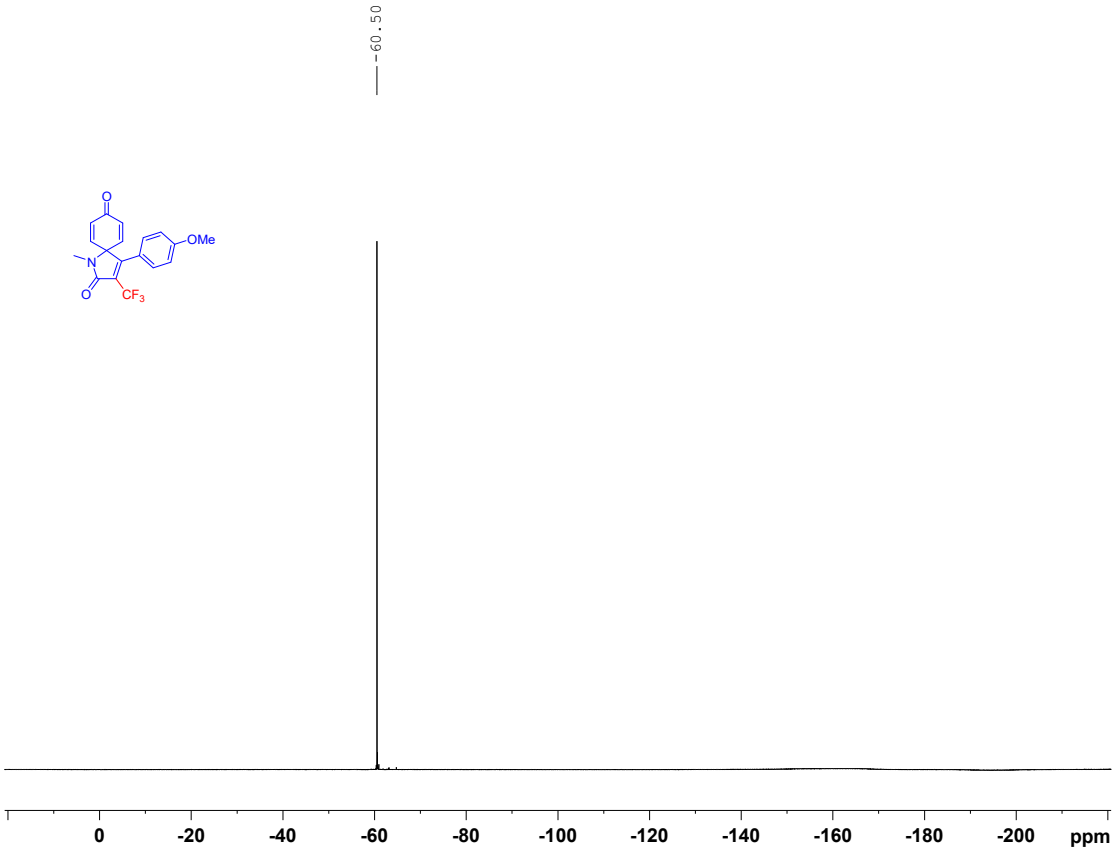
^{1}H NMR (CDCl$_3$, 300 K), **4g**



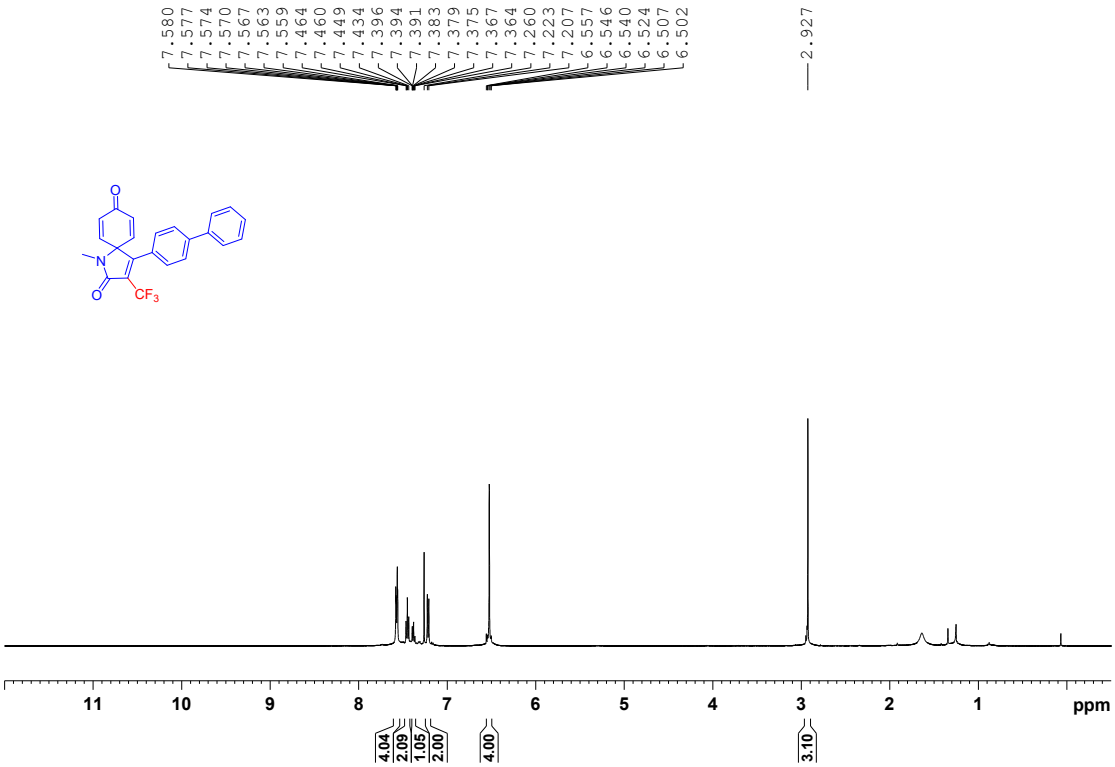
^{13}C NMR (CDCl$_3$, 300 K), **4g**



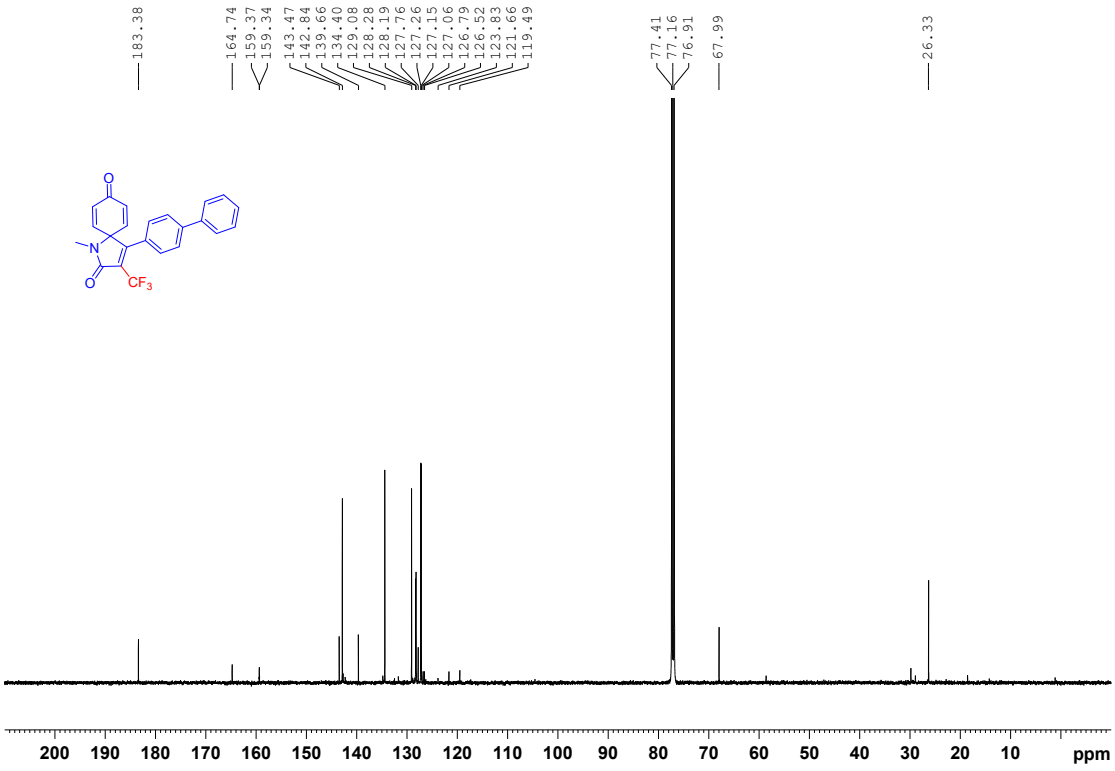
^{19}F NMR (CDCl$_3$, 300 K) **4g**



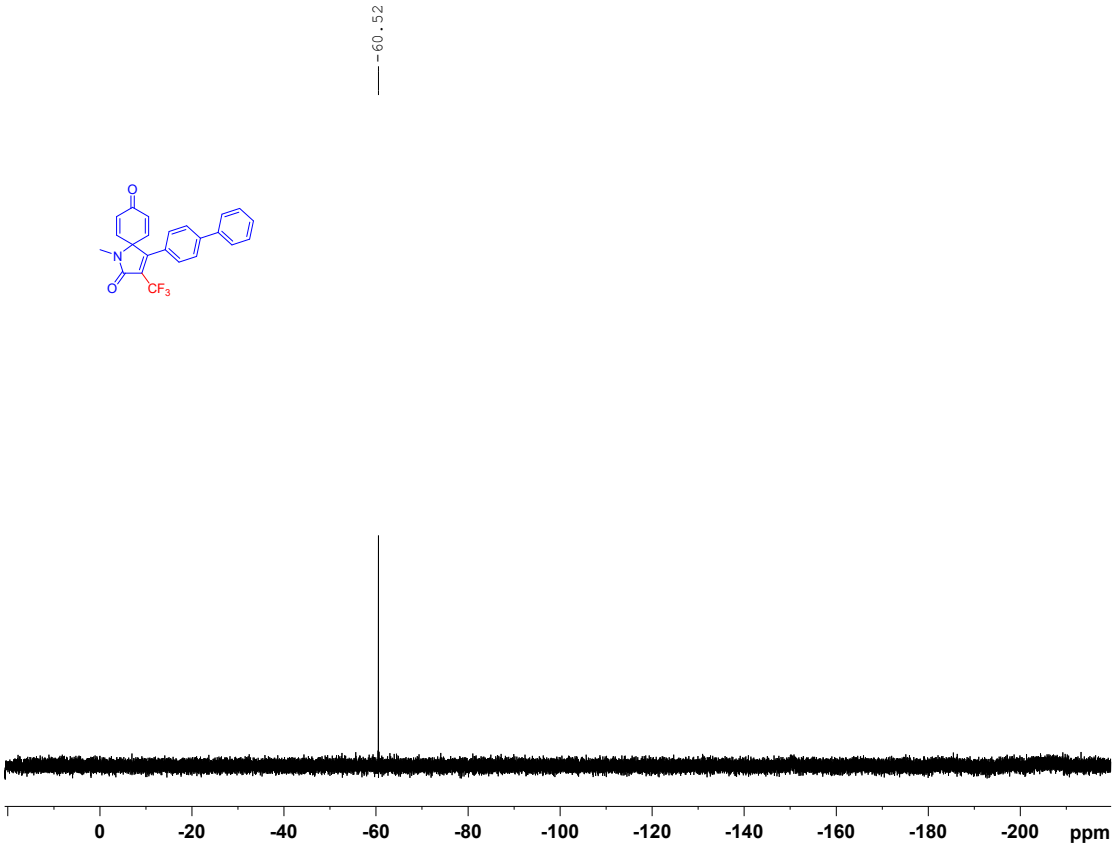
^{1}H NMR (CDCl$_3$, 300 K), **4h**



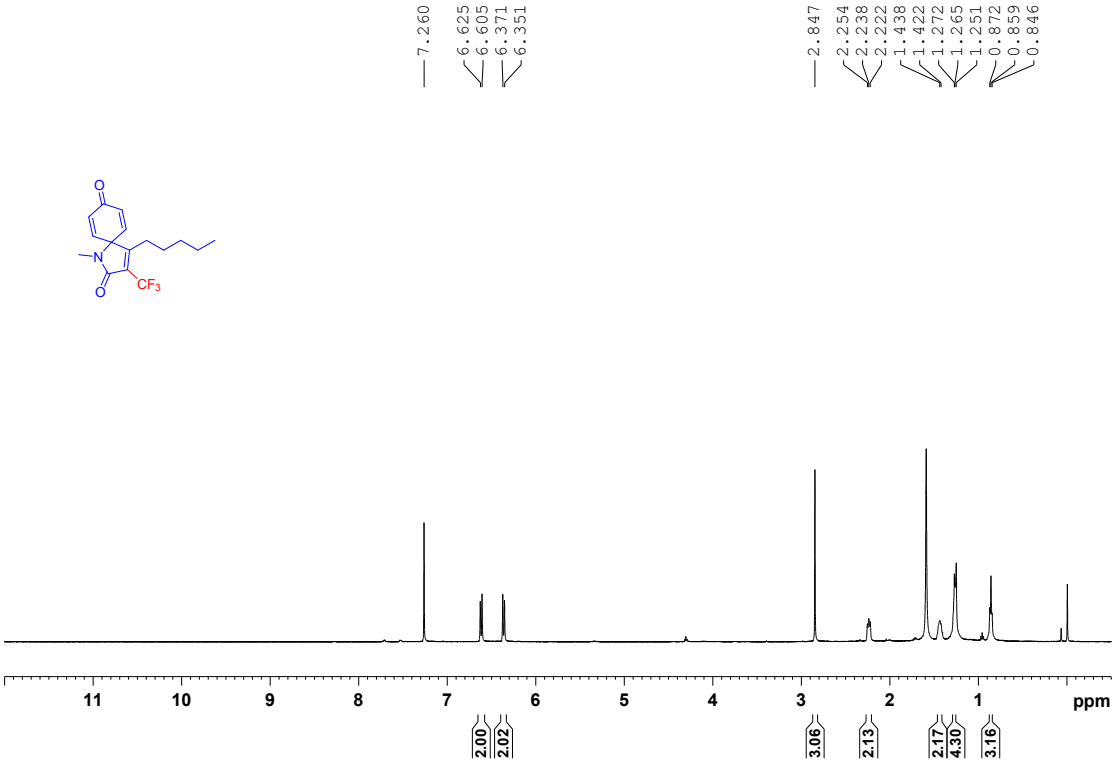
^{13}C NMR (CDCl$_3$, 300 K), **4h**



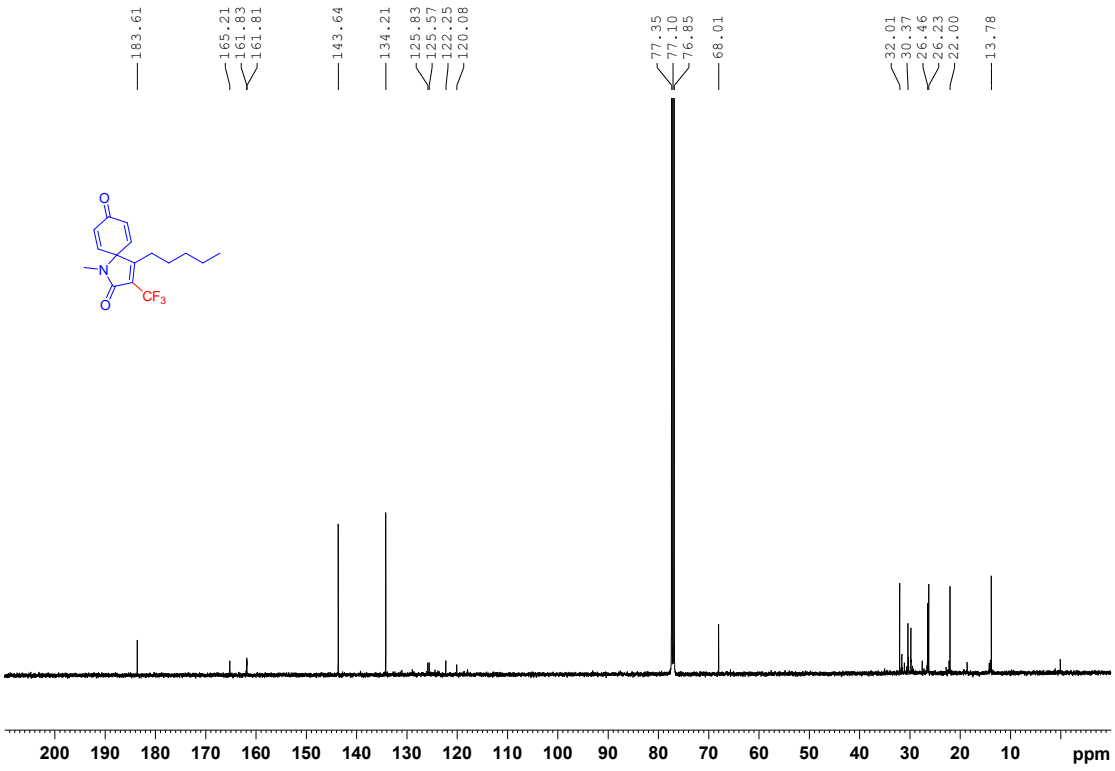
^{19}F NMR (CDCl$_3$, 300 K) **4h**



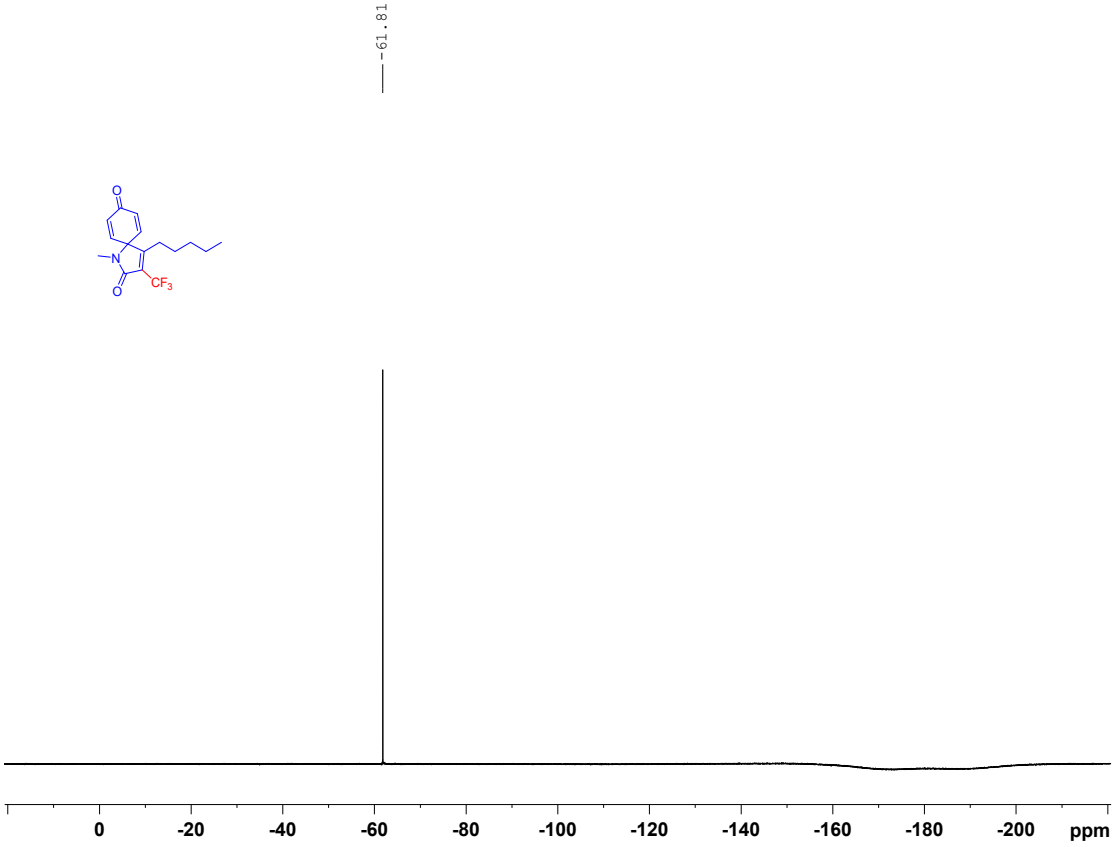
^{1}H NMR (CDCl$_3$, 300 K), **4i**



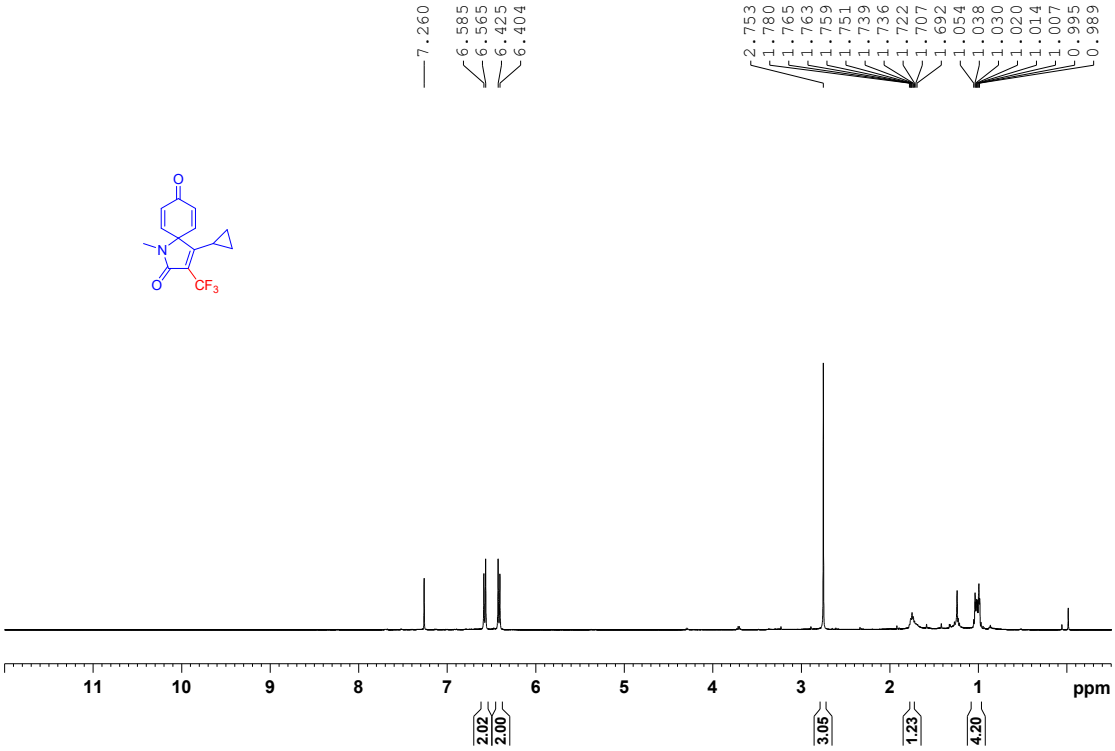
^{13}C NMR (CDCl$_3$, 300 K), **4i**



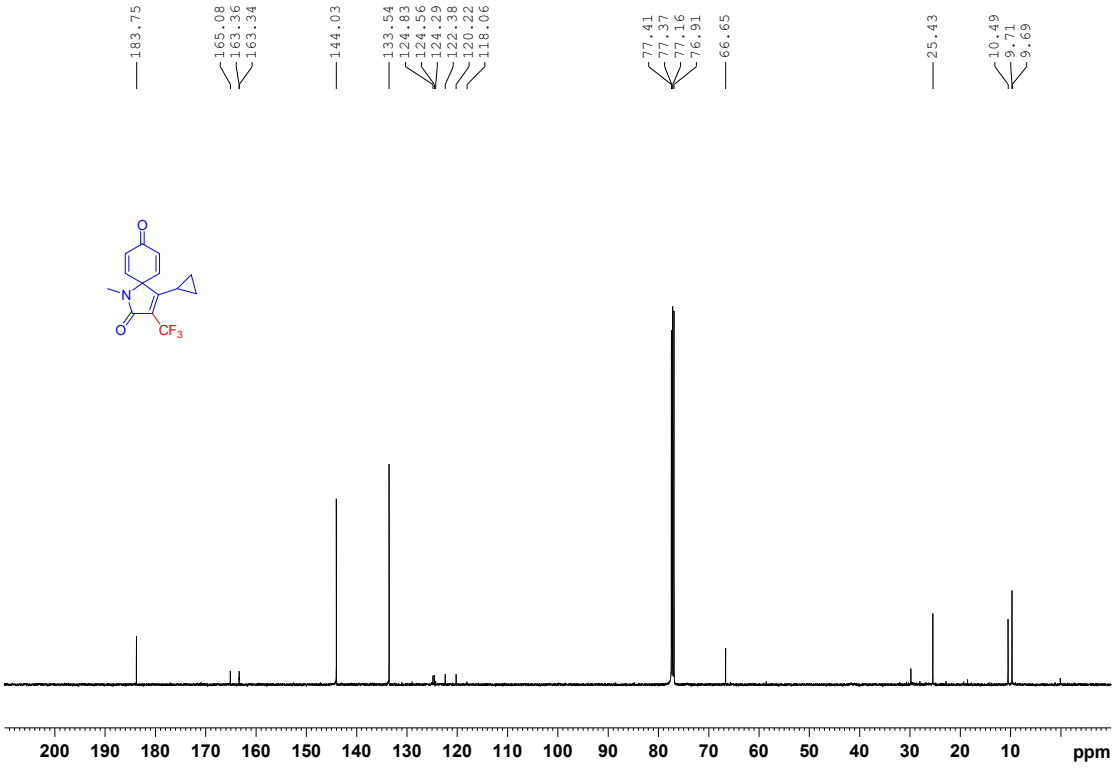
^{19}F NMR ($CDCl_3$, 300 K) **4i**



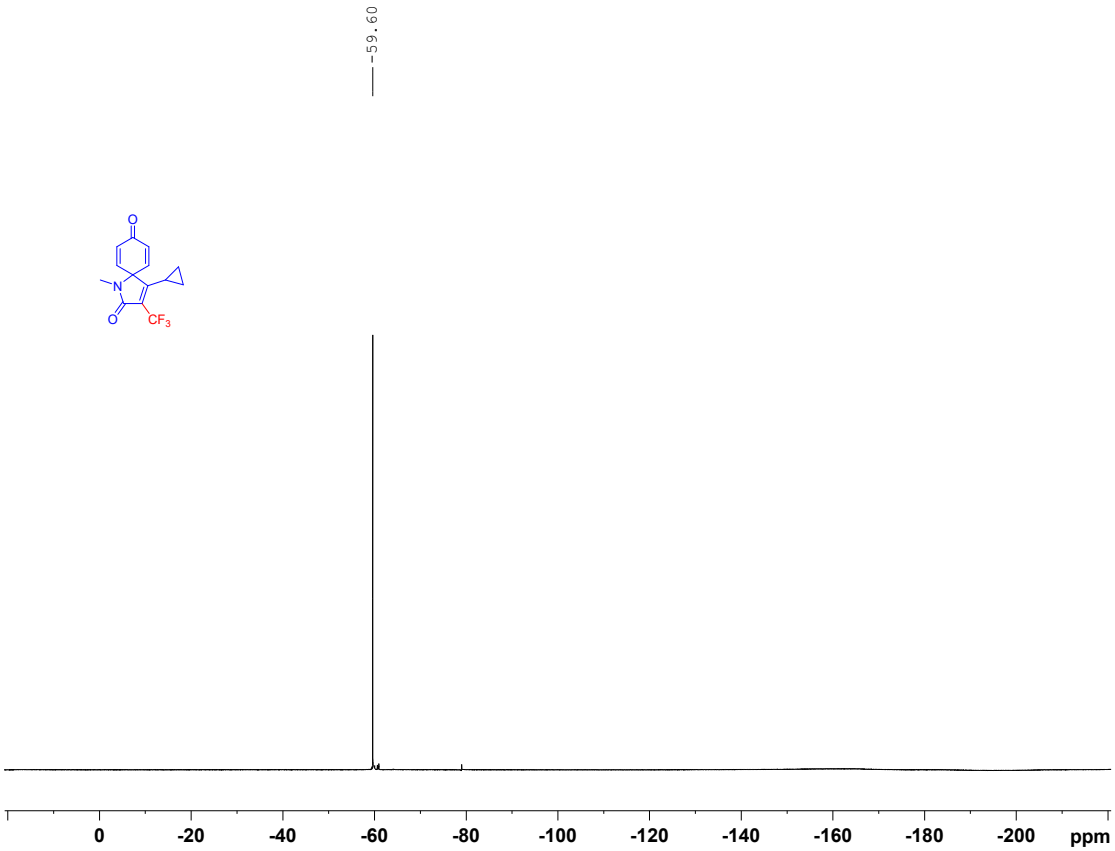
^{1}H NMR (CDCl$_3$, 300 K), **4j**



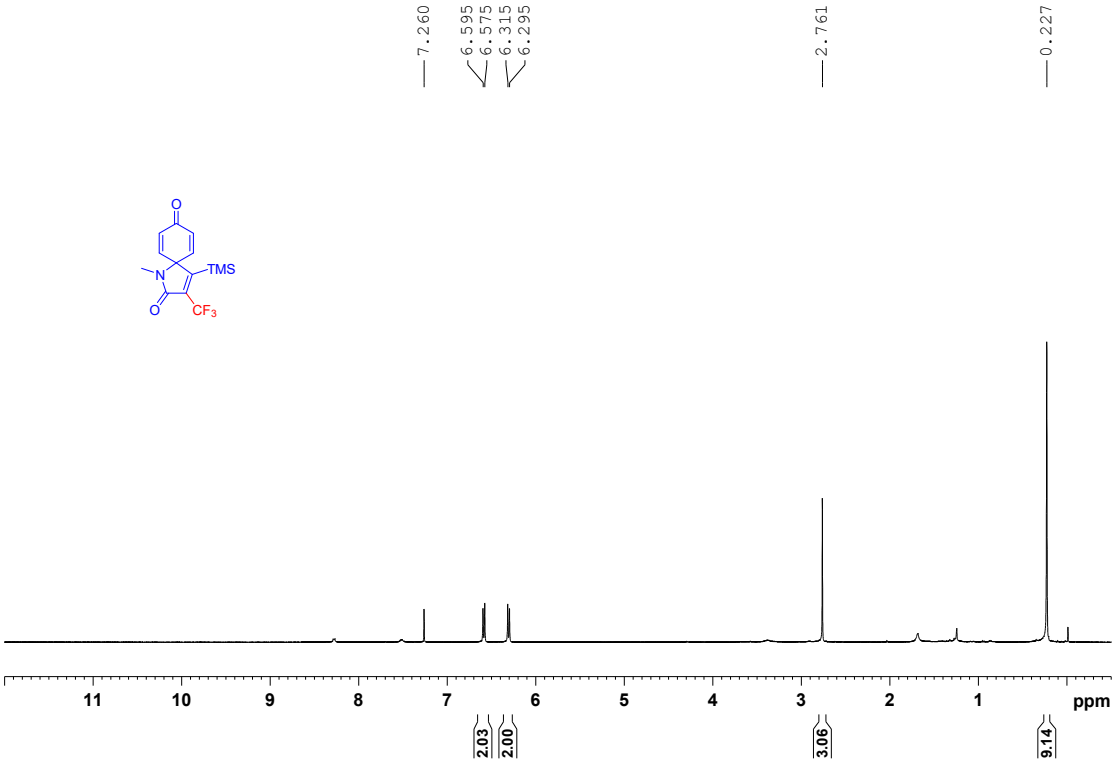
^{13}C NMR (CDCl$_3$, 300 K), **4j**



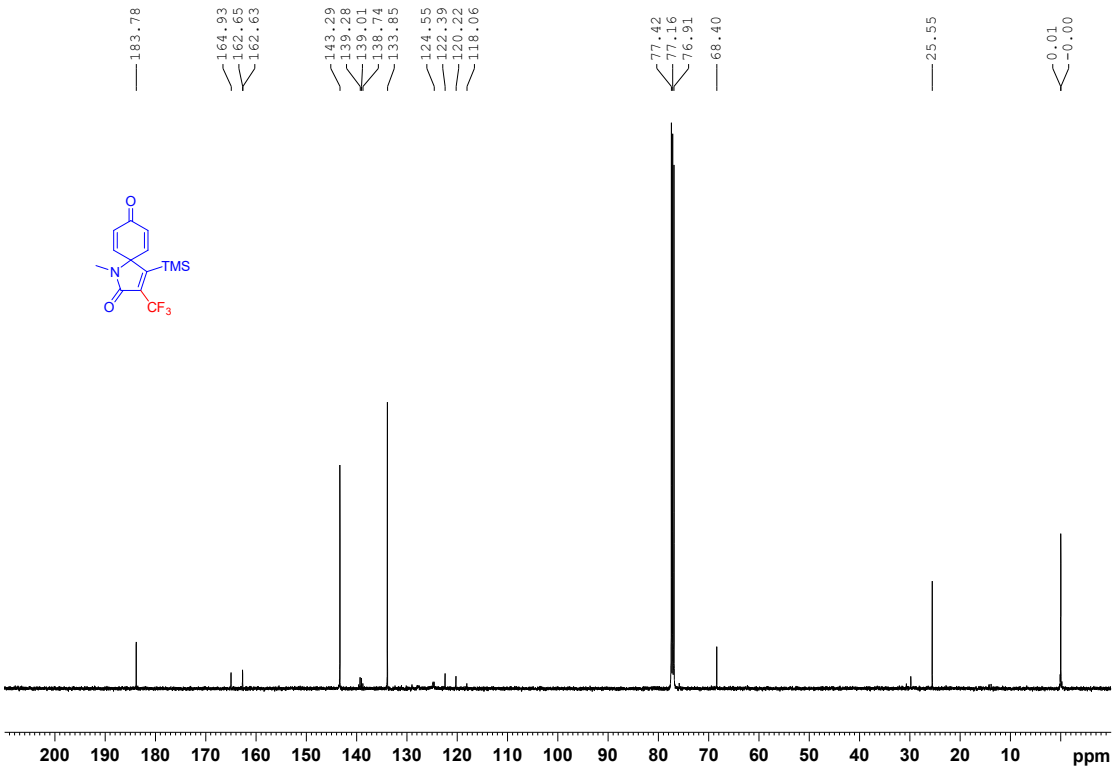
^{19}F NMR ($CDCl_3$, 300 K) **4j**



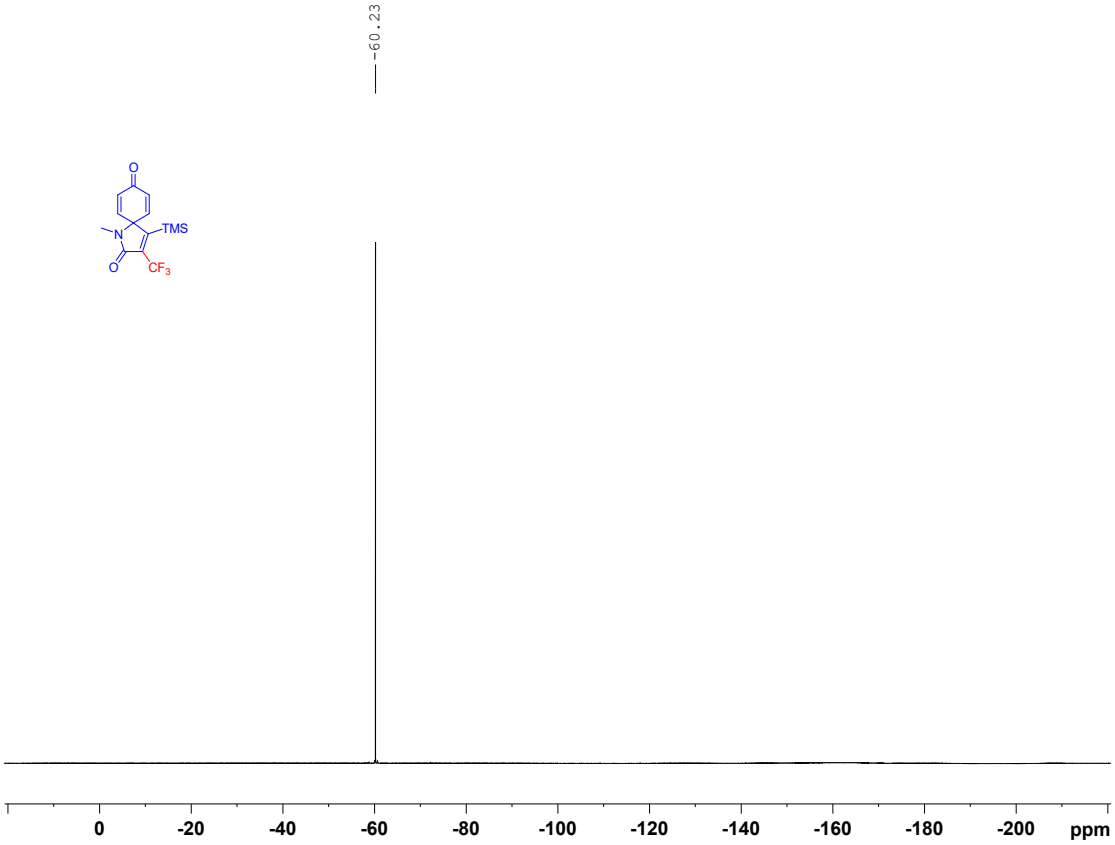
^{1}H NMR (CDCl$_3$, 300 K), **4k**



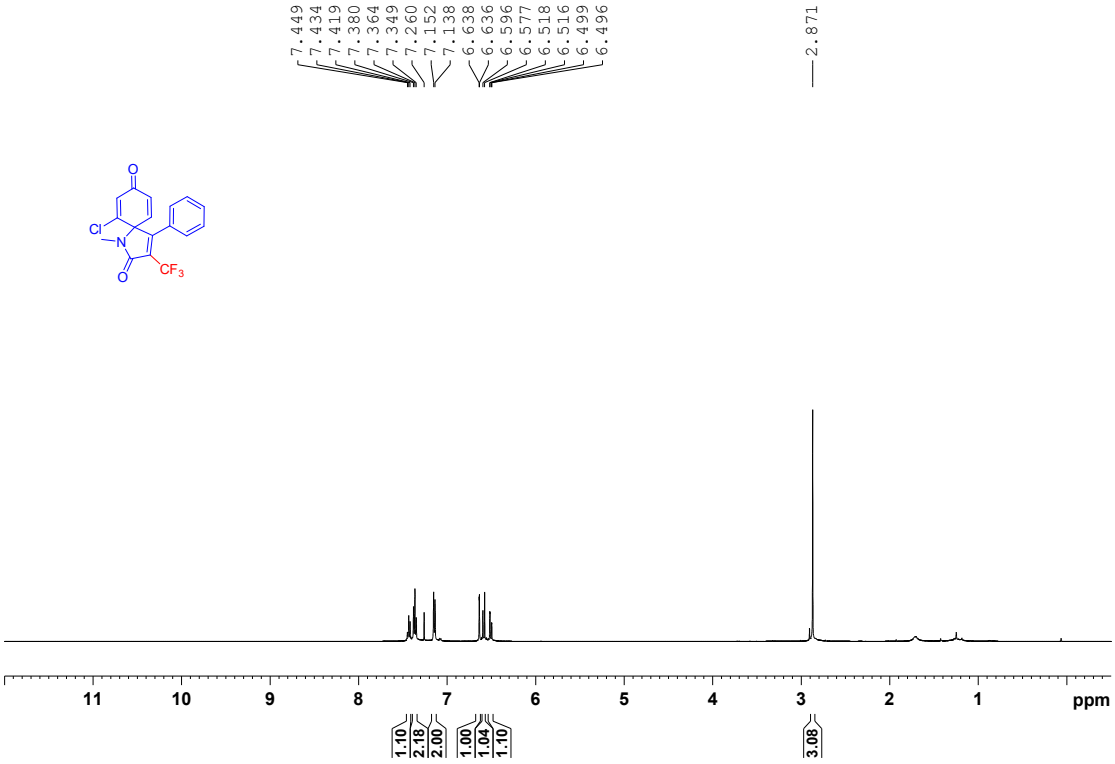
^{13}C NMR (CDCl$_3$, 300 K), **4k**



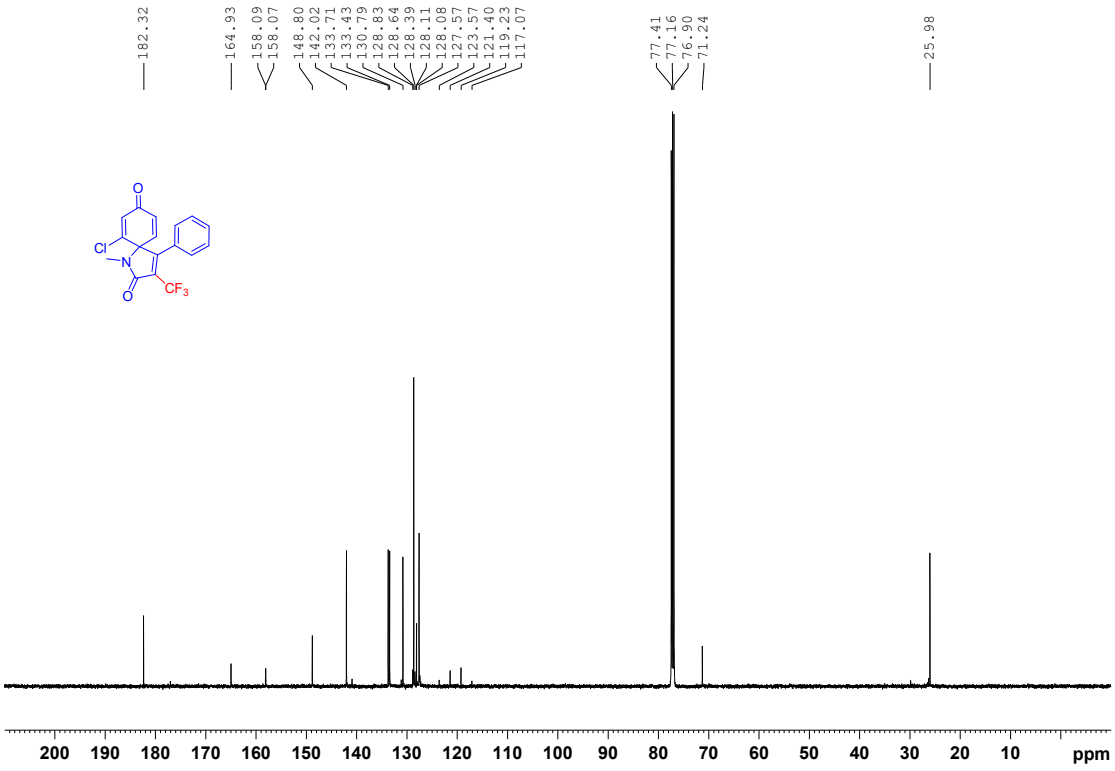
^{19}F NMR (CDCl$_3$, 300 K) **4k**



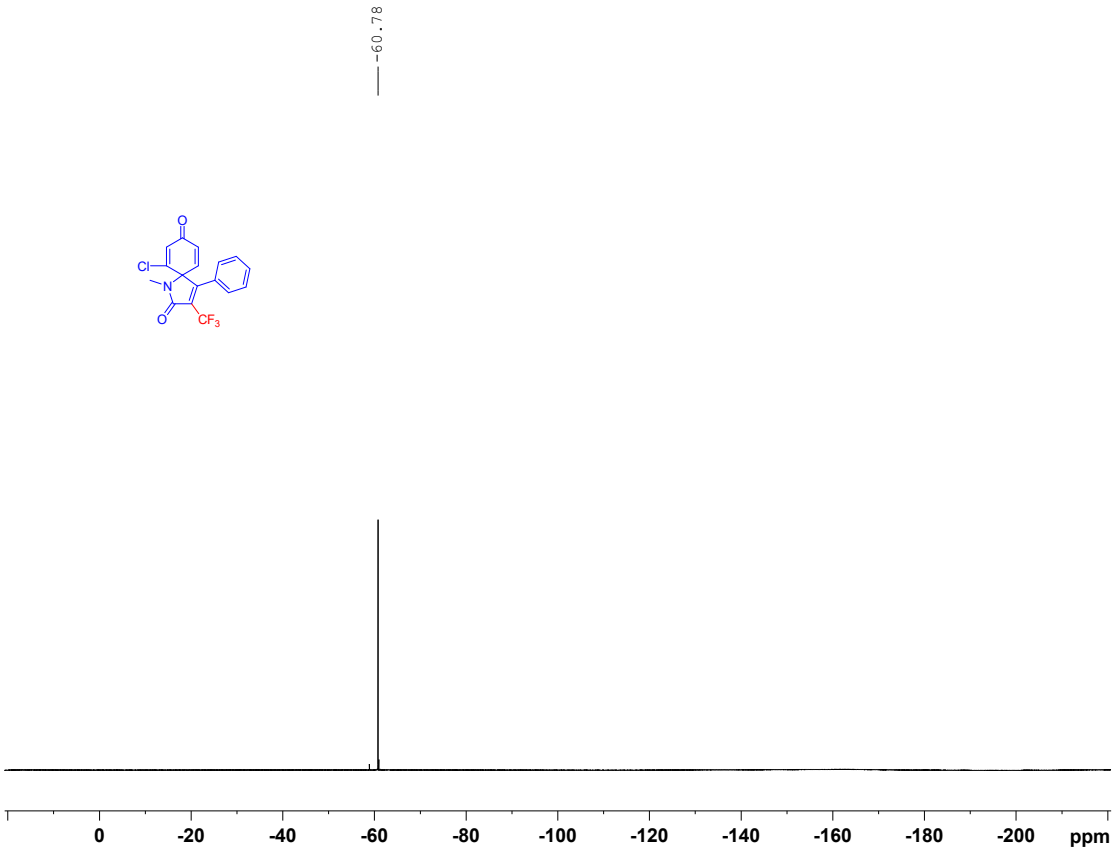
^{1}H NMR (CDCl$_3$, 300 K), **4l**



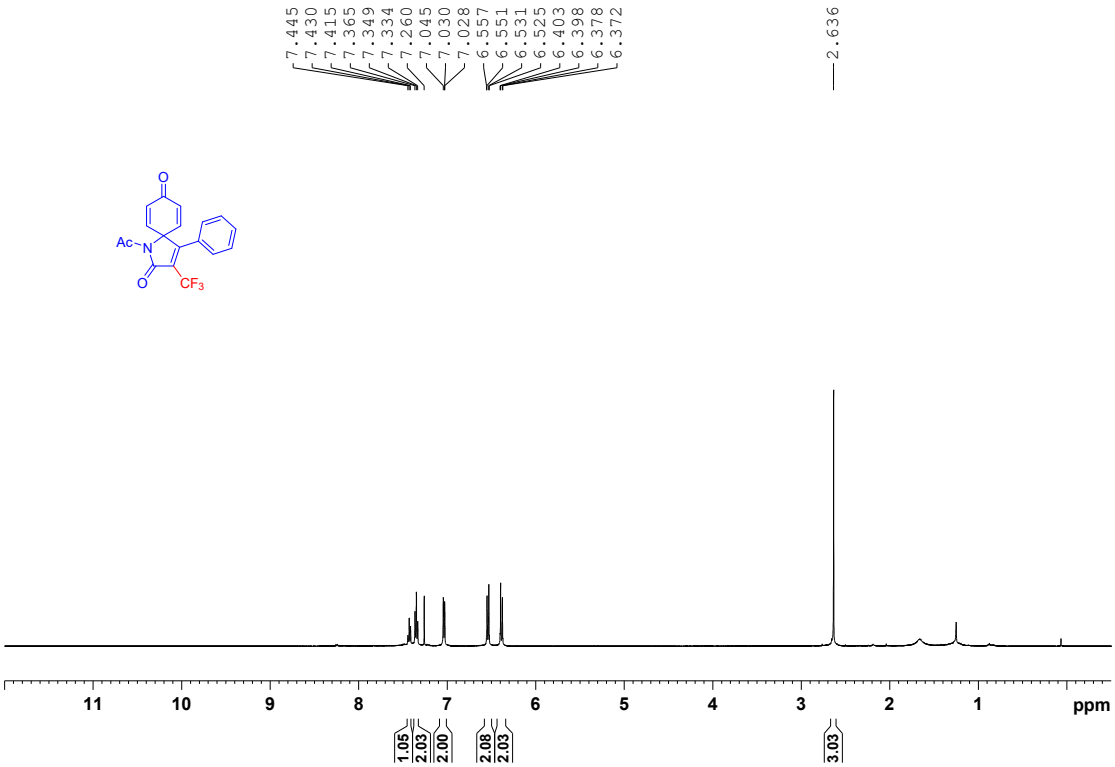
^{13}C NMR (CDCl$_3$, 300 K), **4l**



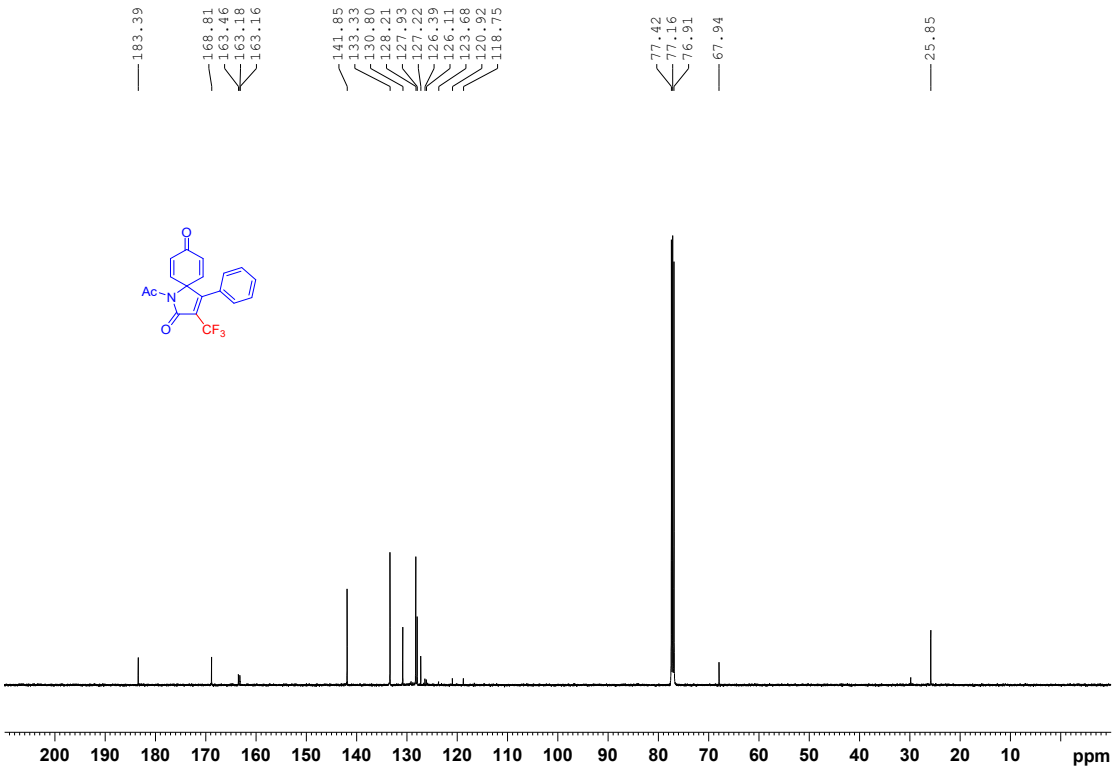
^{19}F NMR (CDCl$_3$, 300 K) **4l**



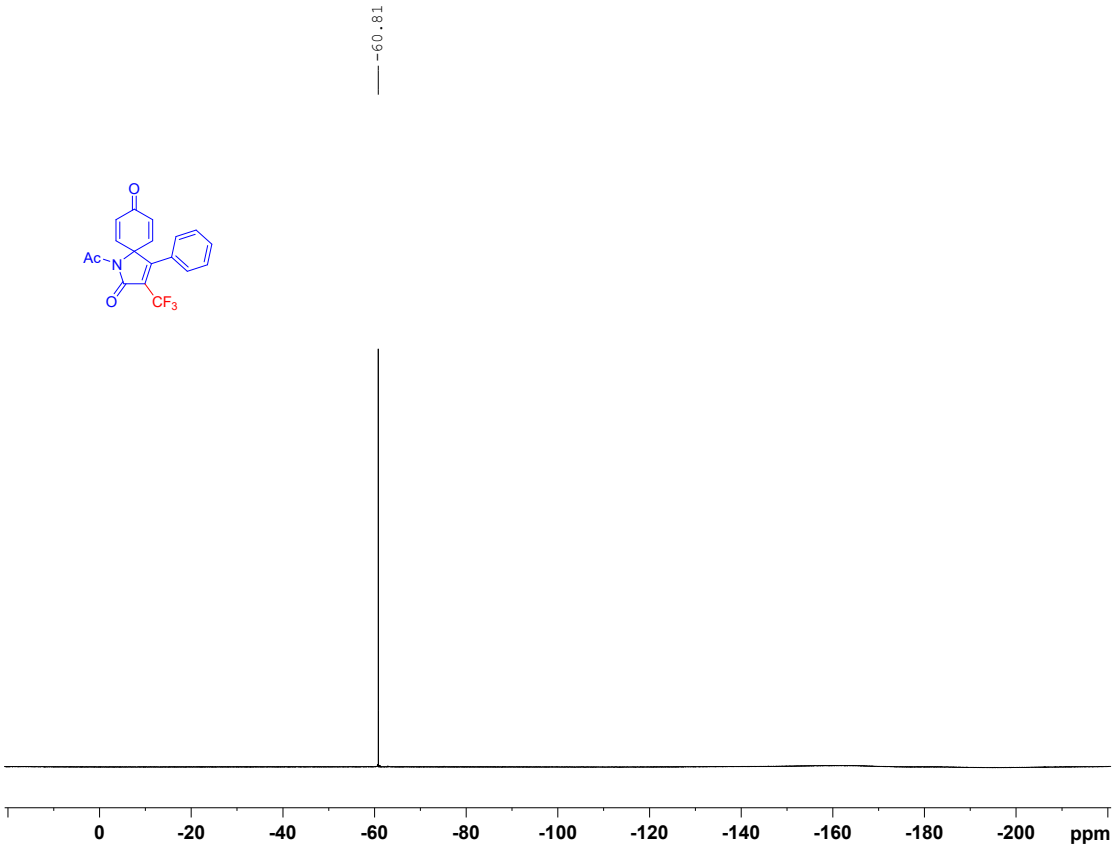
^{1}H NMR (CDCl$_3$, 300 K), **4m**



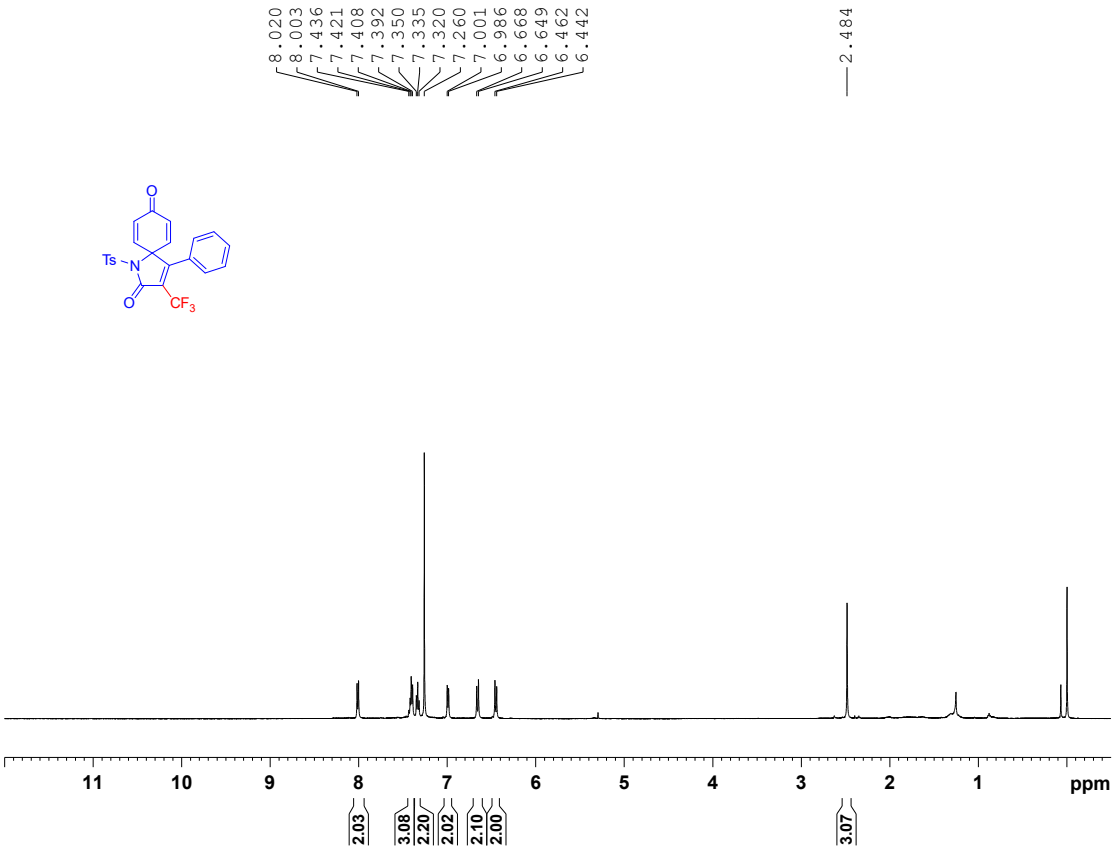
^{13}C NMR (CDCl$_3$, 300 K), **4m**



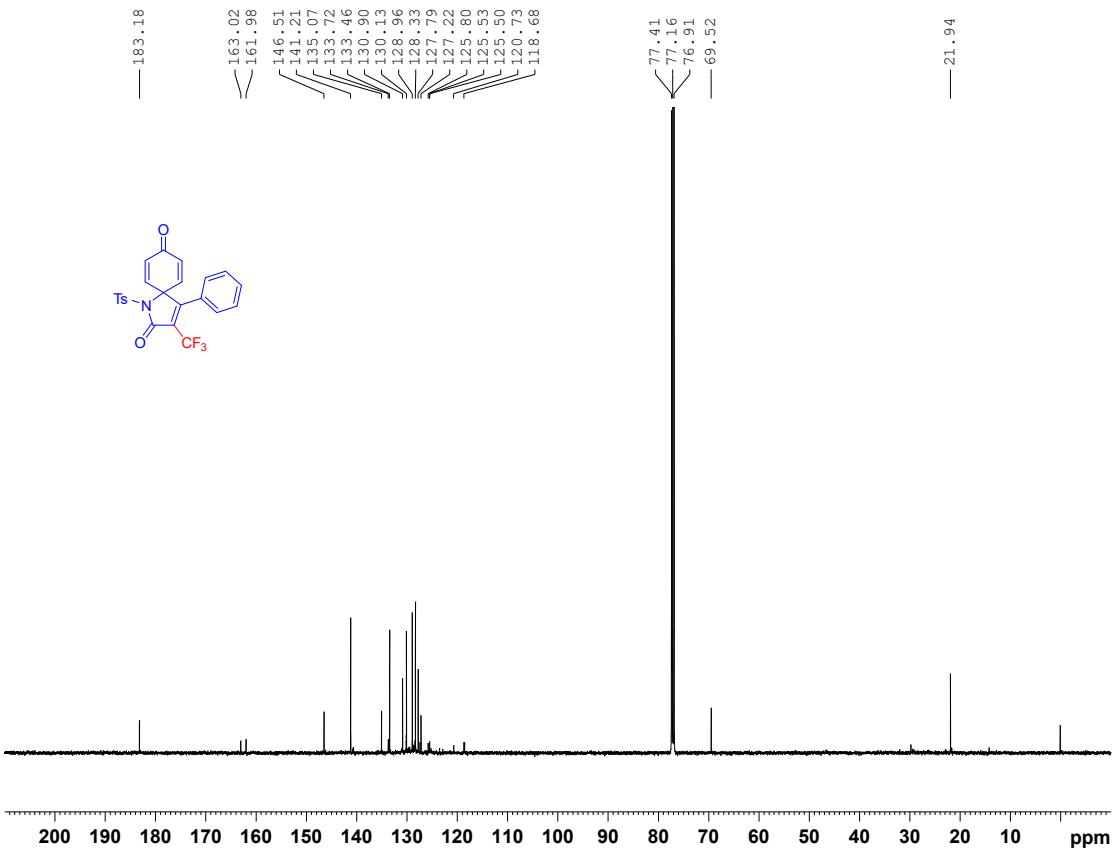
^{19}F NMR (CDCl$_3$, 300 K) **4m**



^{1}H NMR (CDCl$_3$, 300 K), **4n**



^{13}C NMR (CDCl$_3$, 300 K), **4n**



^{19}F NMR (CDCl$_3$, 300 K) **4n**