Electronic Supplementary Material (ESI) for ChemComm.

Electrochemical Synthesis of Phosphorylated Azaspiro[4.5]di/trienones through Dearomative Spirocyclization

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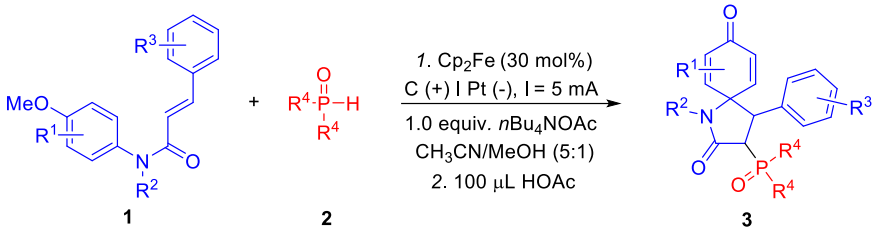
1. General information:

All reactions were carried out under Ar. 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 1H 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. Highresolution mass spectra (HRMS) were recorded with an Thermo Scientific Q Exactive Plus Orbitrap LC-MS/MS System by ESI on a quadrupole mass analyzer. All crystals were grown via a slow evaporation method. Each compound was dissolved in a 2 mL solution of either DCM within a 5 mL brown flask, which was covered with a film at the flask's mouth. Ensure not to seal it too tightly. Allow the solvent to gradually evaporate over the next 2-3 days, resulting in the formation of high-quality crystals. The single-crystal X-ray diffraction data were collected on a Bruker D8 QUEST diffractometer. Electrolysis experiments were performed using a MESTEK power supply (DP3005B). RVC electrode (Reticulated Vitreous Carbon purchased from IKA) was cut into 13 x 6 x 4 mm^3 pieces before use. Carbon Felt was cut into 25 x 5 x 1.5 mm^3 pieces before use, and was connected to electrical feed-through on the Teflon cap of the electrochemical cell via PTFE electrode holder. Saturated calomel electrode (CHI150), platinum wire counter electrode (CHI115) and platinum working electrode (CHI102) were obtained from CH Instruments and Saturated calomel electrode was stored in 3.0 M KCl aqueous solution before use.

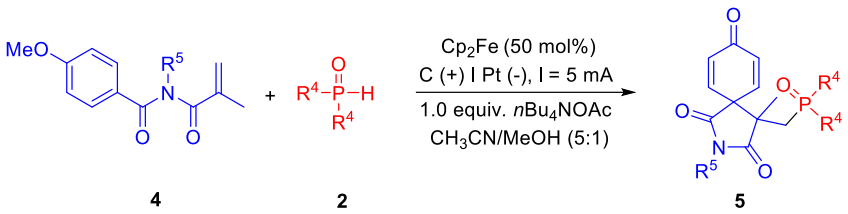
General Procedure A



1 **2** **3**

An oven-dried 10 mL three-necked round-bottomed flask with a magnetic stir bar was charged with **1** (0.2 mmol, 1.0 equiv.), diphenylphosphine oxide **2** (0.4 mmol, 2.0 equiv.), Cp_2Fe (0.06 mmol, 0.3 equiv.) and *n*Bu_4NOAc (0.2 mmol, 1.0 equiv.). The flask was equipped with a carbon plate anode (25 mm x 5 mm x 1.5 mm) and a platinum plate cathode (10 mm x 10 mmx 0.2 mm). The cell was sealed and flushed with Argon for 15 minutes, followed by the addition via syringe of CH_3CN (5.0 mL) and MeOH (1.0 mL). The mixture was charged by constant current (I = 5 mA). The complete consumption of the starting material **1** was checked by TLC (30 % AcOEt/petroleum ether). Once the starting material was fully consumed, the power was cut. Then 0.1 mL of HOAc was added to the mixture, and it was stirred for 1-12 hours at room temperature in air. The reaction solution was concentrated in vacuo and extracted with EtOAc and H_2O (3×10 mL). The combined organic layer was dried over $MgSO_4$, filtered andconcentrated in vacuo. The residue was purified by silica gel column chromatography to give the corresponding products **3**.

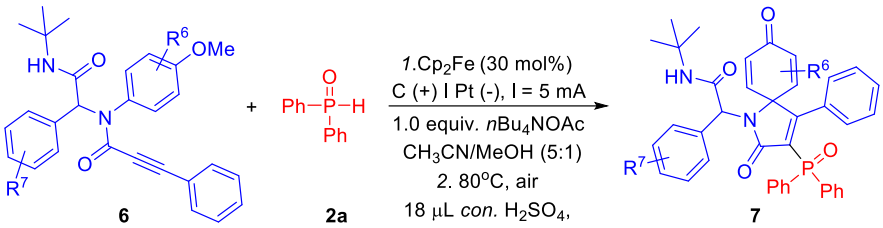
General Procedure B



4 **2** **5**

An oven-dried 10 mL three-necked round-bottomed flask with a magnetic stir bar was charged with **4** (0.2 mmol, 1.0 equiv.), diphenylphosphine oxide **2** (0.4 mmol, 2.0 equiv.), Cp_2Fe (0.10 mmol, 0.5 equiv.) and *n*Bu_4NOAc (0.2 mmol, 1.0 equiv.). The flask was equipped with a carbon plate anode (25 mm x 5 mm x 1.5 mm) and a platinum plate cathode (10 mm x 10 mmx 0.2 mm). The cell was sealed and flushed with Argon for 15 minutes, followed by the addition via syringe of CH_3CN (5.0 mL) and MeOH (1.0 mL). The mixture was charged by constant current (I = 5 mA). The complete consumption of the starting material **4** was checked by TLC (20 % AcOEt/petroleum ether). Once the starting material was fully consumed, the reaction solution was concentrated in vacuo and extracted with EtOAc and H_2O (3×10 mL). The combined organic layer was dried over $MgSO_4$, filtered andconcentrated in vacuo. The residue was purified by silica gel column chromatography to give the corresponding products **5**.

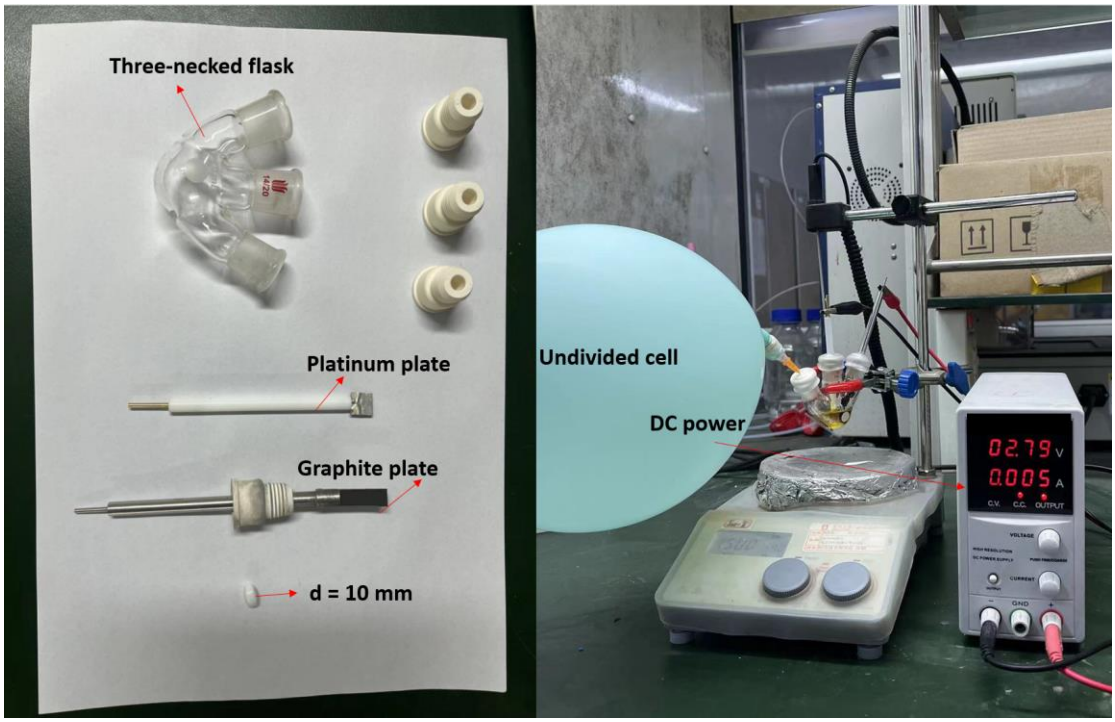
General Procedure C



6 **2a** **7**

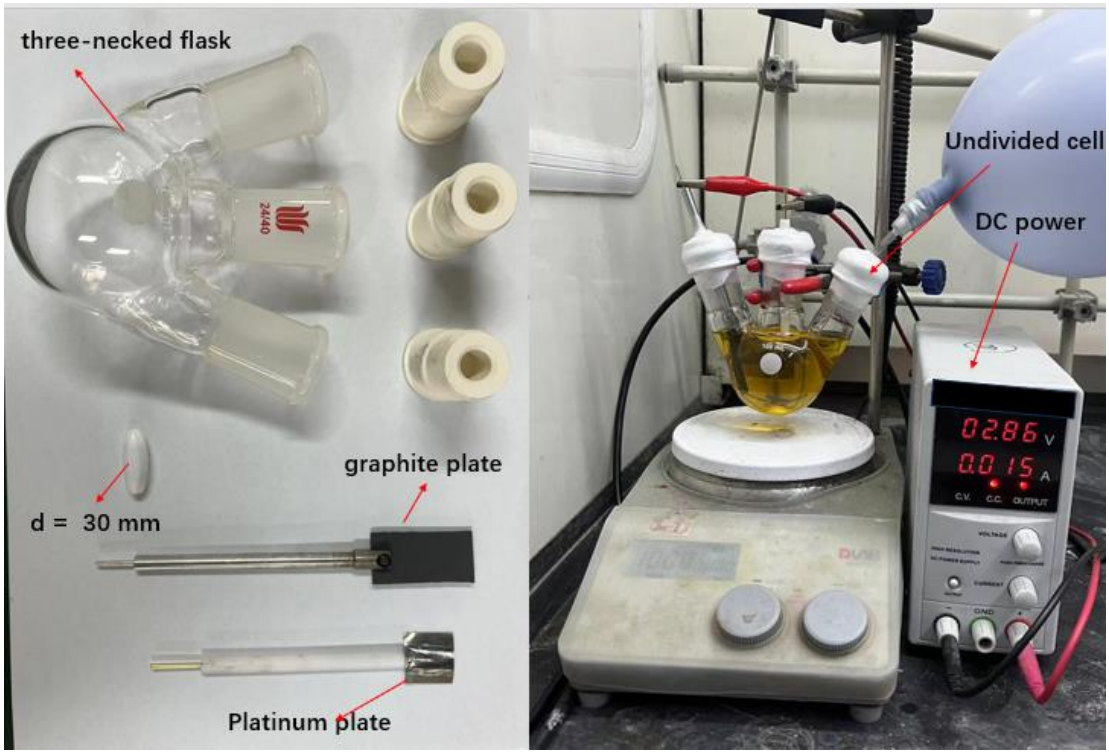
An oven-dried 10 mL three-necked round-bottomed flask with a magnetic stir bar was charged with **6** (0.2 mmol, 1.0 equiv.), diphenylphosphine oxide **2a** (0.4 mmol, 2.0 equiv.), Cp_2Fe (0.06 mmol, 0.3 equiv.) and *n*Bu_4NOAc (0.2 mmol, 1.0 equiv.). The flask was equipped with a carbon plate anode (25 mm x 5 mm x 1.5 mm) and a platinum plate cathode (10 mm x 10 mmx 0.2 mm). The cell was sealed and flushed with Argon for 15 minutes, followed by the addition via syringe of CH_3CN (5.0 mL) and MeOH (1.0 mL). The mixture was charged by constant current (I = 5 mA). Once the starting material was fully consumed, the power was cut. Then 18 μL of *con.* H_2SO_4 was added to the mixture, and it was stirred for 3 hours at 80℃ in air. The reaction solution was concentrated in vacuo and extracted with EtOAc and H_2O (3×10 mL). The combined organic layer was dried over $MgSO_4$, filtered andconcentrated in vacuo. The residue was purified by silica gel column chromatography to give the corresponding products **7**.

The reaction setup:

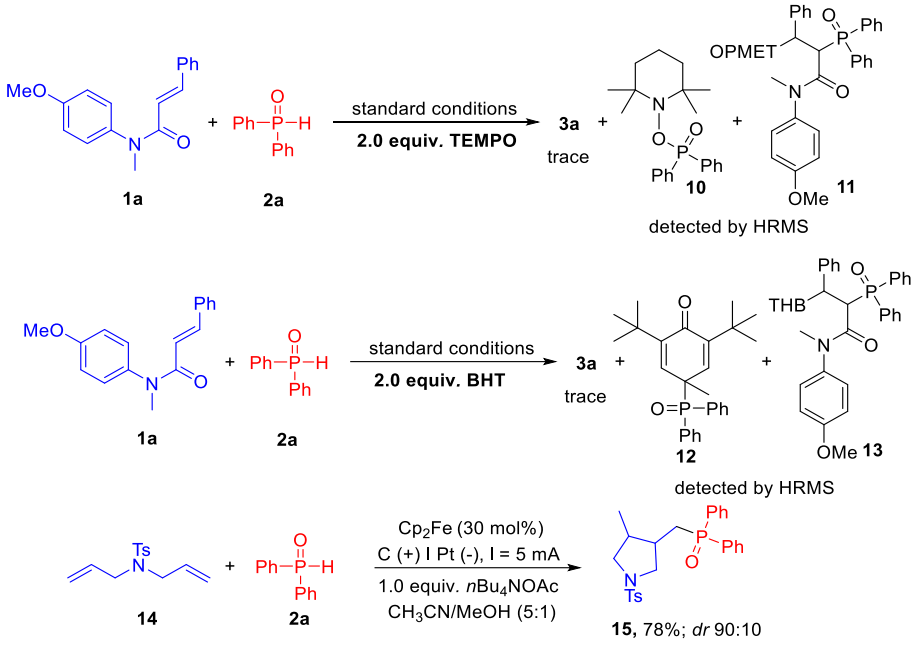


Scale-up experiment: An oven-dried 100 mL three-necked round-bottomed flask with a magnetic stir bar was charged with **1a** (3.4 mmol, 0.9078 g, 1.0 equiv.), diphenylphosphine oxide **2a** (6.8 mmol, 2.0 equiv.), Cp_2Fe (1.02 mmol, 0.3 equiv.) and *n*-Bu_4NOAc (3.4 mmol, 1.0 equiv.). The flask was equipped with a carbon plate anode (40 mm x 20 mm x 1.5 mm) and a platinum plate cathode (20 mm x 20 mm x 1 mm). The cell was sealed and flushed with Argon for 15 minutes, followed by the addition via syringe of CH_3CN (85mL) and MeOH (17 mL). The mixture was charged by constant current (I = 15 mA). The complete consumption of the starting material **1a** was checked by TLC (20 % AcOEt/petroleum ether). The reaction solution was concentrated in vacuo and extracted with EtOAc and H_2O (3x10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography to give the corresponding products **3aa** (1316 mg, 2.71 mmol, 80%).

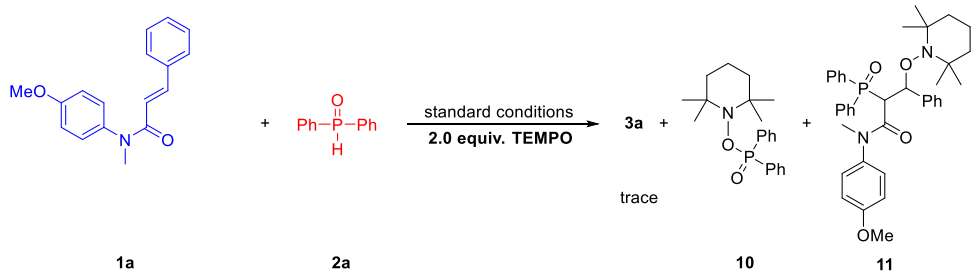
Gram-scale experiment:



2. Control experiments

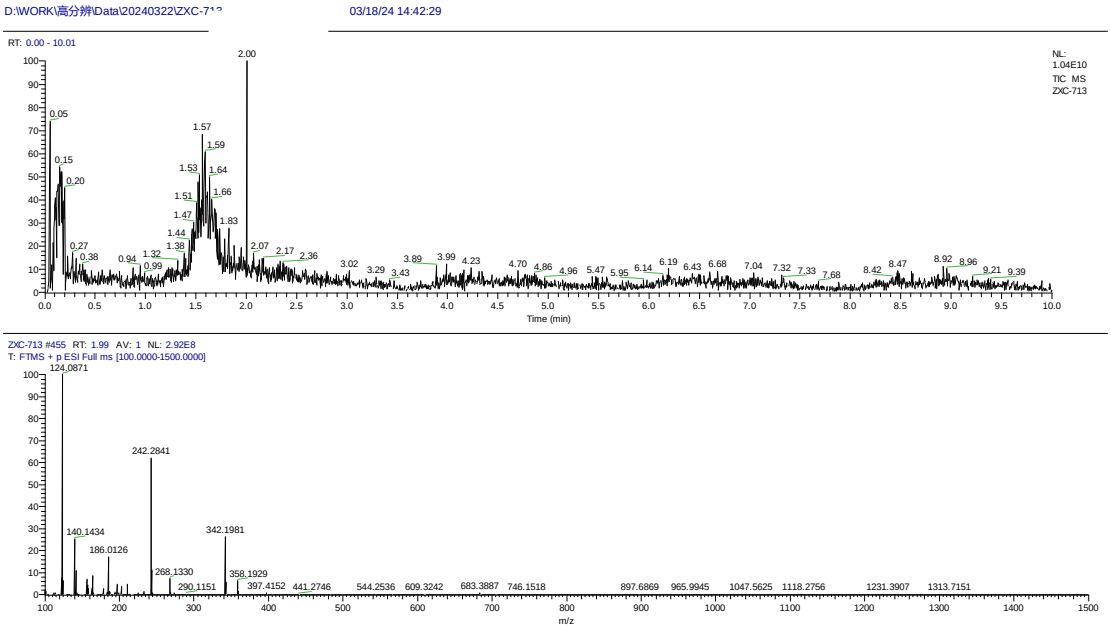


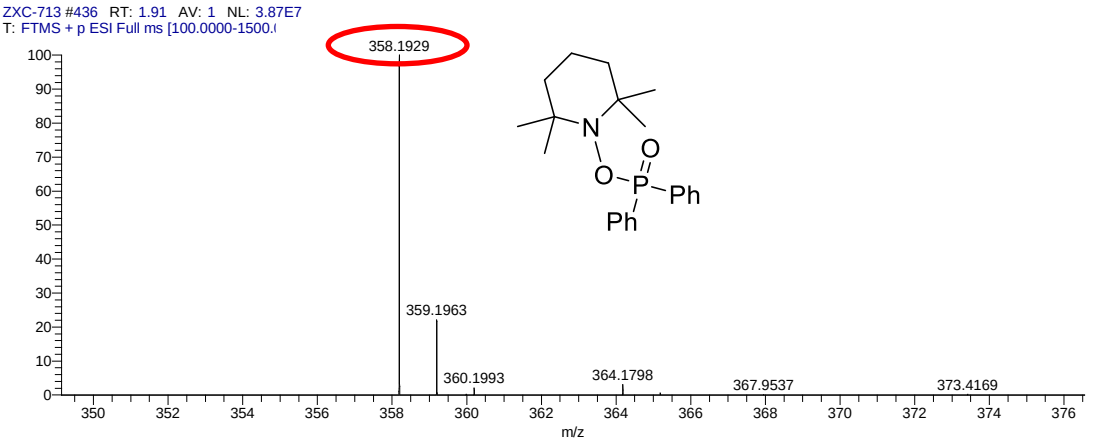
Control experiment 1:



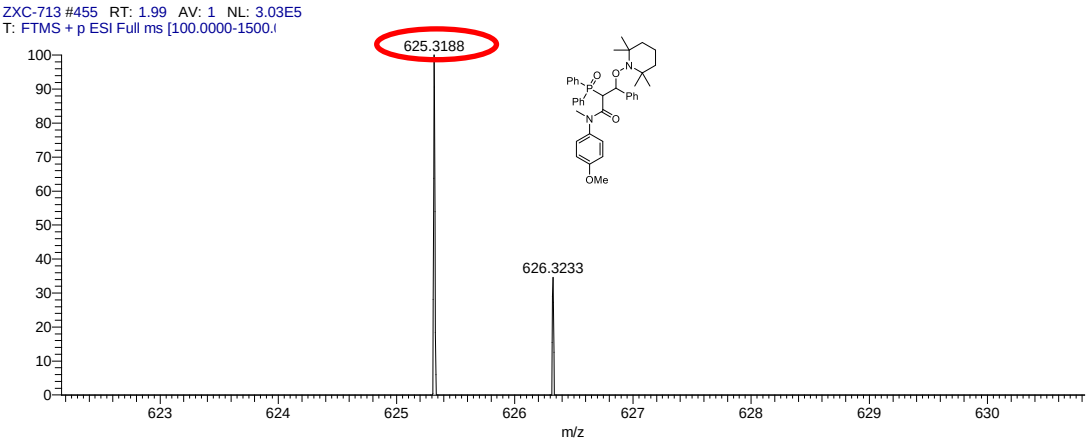
An oven-dried 10 mL three-necked round-bottomed flask with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv.), diphenylphosphine oxide **2a** (0.4 mmol, 2.0 equiv.), Cp_2Fe (0.06 mmol, 0.3 equiv.), TEMPO ((2,2,6,6-Tetramethylpiperidin-1-yl)oxyl, 0.4 mmol, 2.0 equiv.) and *n*-Bu_4NOAc (0.2 mmol, 1.0 equiv.). The flask was equipped with a carbon plate anode (25 mm x 5 mm x 1.5 mm) and a platinum plate cathode (10 mm x 10 mmx 0.2 mm). The cell was sealed and flushed with Argon for 15 minutes, followed by the addition via syringe of CH_3CN (5.0 mL) and MeOH (1.0 mL). The mixture was charged by constant current (I = 5 mA) for 6 hours. After Acetic acid (0.2 mL) was added, and the mixture was allowed to stir for 5 h at room temperature in air. Only trace amount of **3a** was detected, the recovery was 88%. The crude mixture was analyzed by **LC-MS.**

The mixture was checked by LC-MS:



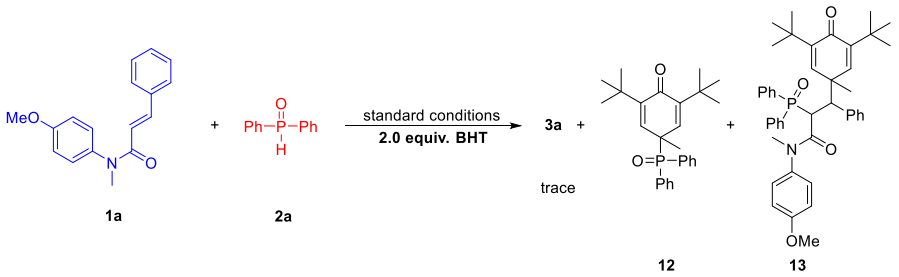


HRMS-ESI: Calcd for $C_{21}H_{29}NO_2P^+$ $[M+H]^+$ 358.1930, found 358.1929



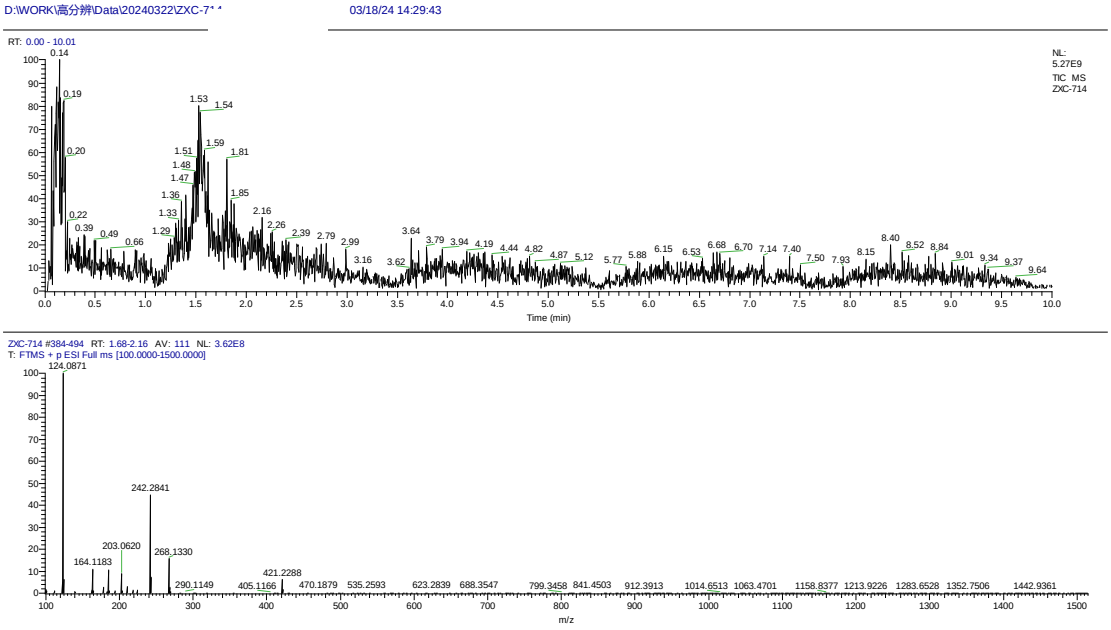
HRMS-ESI: Calcd for $C_{38}H_{46}N_2O_4P^+$ $[M+H]^+$ 625.3190, found 625.3188

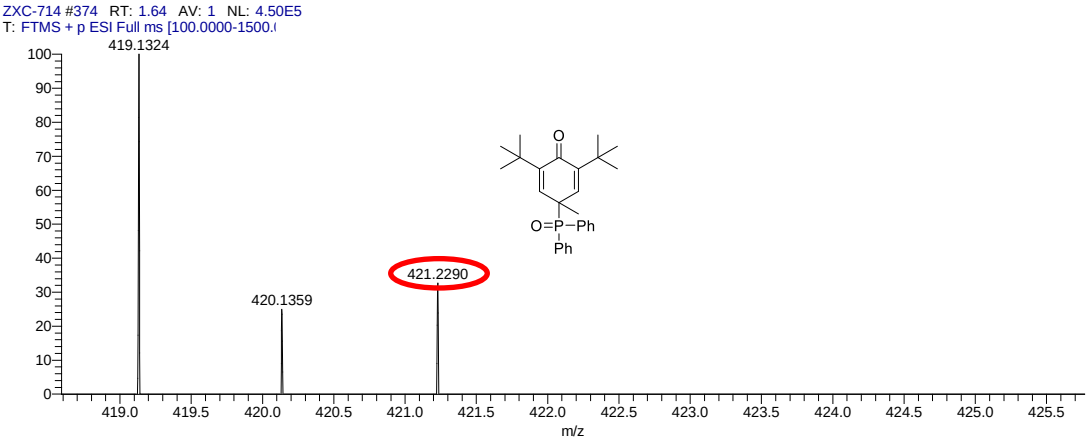
Control experiment 2:



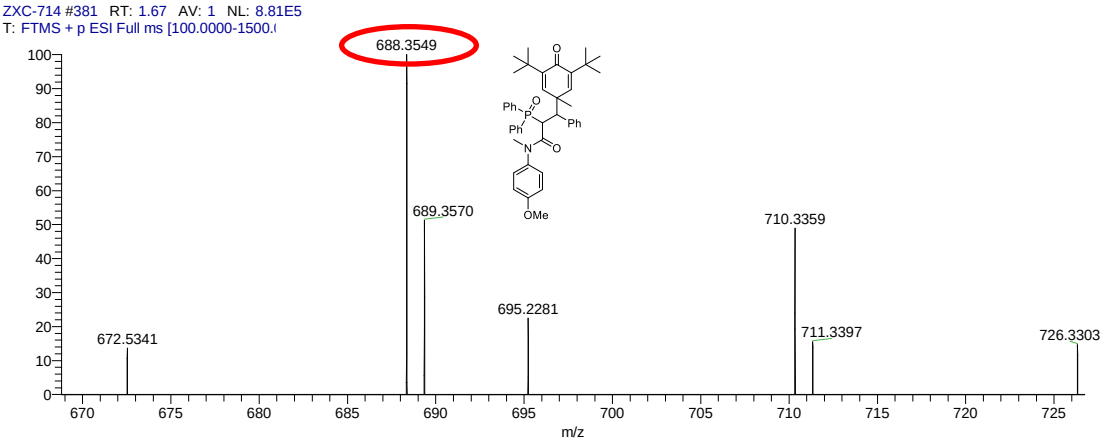
An oven-dried 10 mL three-necked round-bottomed flask with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv.), diphenylphosphine oxide **2a** (0.4 mmol, 2.0 equiv.), Cp_2Fe (0.06 mmol, 0.3 equiv.), BHT (butylated hydroxytoluene, 0.4 mmol, 2.0 equiv.) and *n*-Bu_4NOAc (0.2 mmol, 1.0 equiv.). The flask was equipped with a carbon plate anode (25 mm x 5 mm x 1.5 mm) and a platinum plate cathode (10 mm x 10 mmx 0.2 mm). The cell was sealed and flushed with Argon for 15 minutes, followed by the addition via syringe of CH_3CN (5.0 mL) and MeOH (1.0 mL). The mixture was charged by constant current (I = 5 mA) for 6 hours. After Acetic acid (0.2 mL) was added, and the mixture was allowed to stir for 5 h at room temperature in air. Only trace amount of **3a** was detected, the recovery was 90%. The crude mixture was analyzed by **LC-MS.**

The mixture was checked by LC-MS:



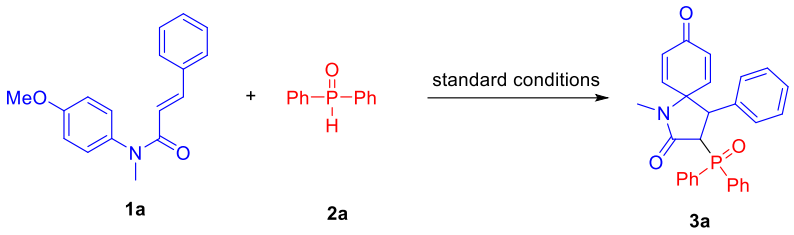


HRMS-ESI: Calcd for $C_{27}H_{34}O_2P^+$ $[M+H]^+$ 421.2291, found 421.2290



HRMS-ESI: Calcd for $C_{44}H_{55}NO_4P^+$ $[M+H]^+$ 688.3550, found 688.3549

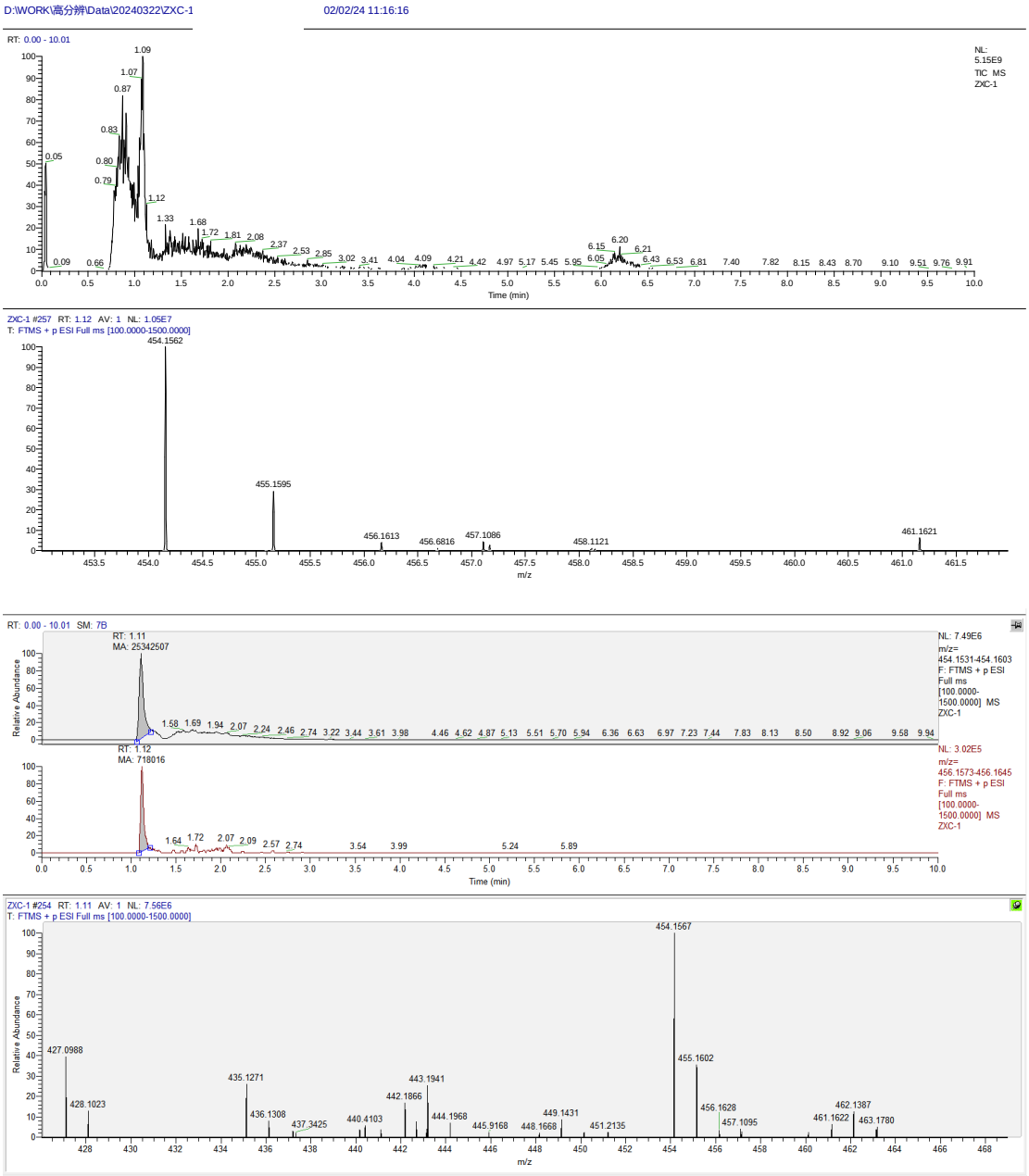
3. ^{18}O-Labeling experiment



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

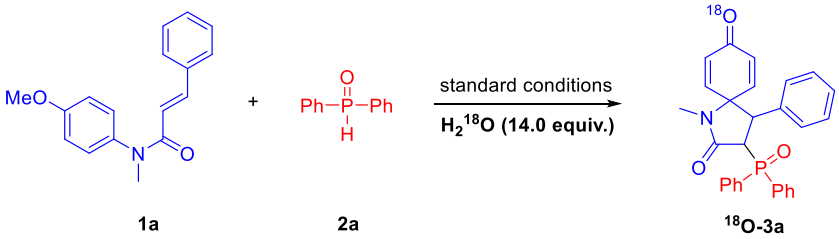
^{16}O-3a: Calcd for $C_{25}H_{28}NO_3P$+[M+H]$^+$ 454.1567, found 454.1562

^{18}O-3a: Calcd for $C_{25}H_{28}N^{18}O_3P$+[M+H]$^+$ 456.1609, found 456.1613.



#	m/z	Intensity	Relative Intensity(%)
^{16}O-3a	**454.1568**	**25342507**	**100**
^{18}O-3a	**456.1610**	**718016**	**2.84**

(2) In presence of 50 μL H_2O (14 equiv. of $H_2{}^{18}O$)

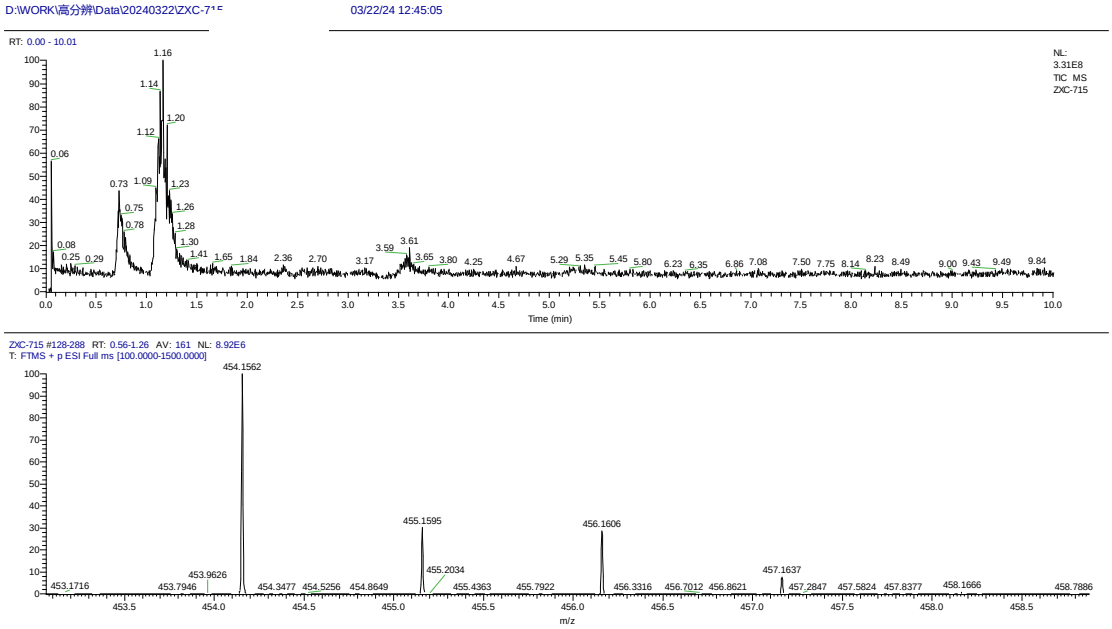


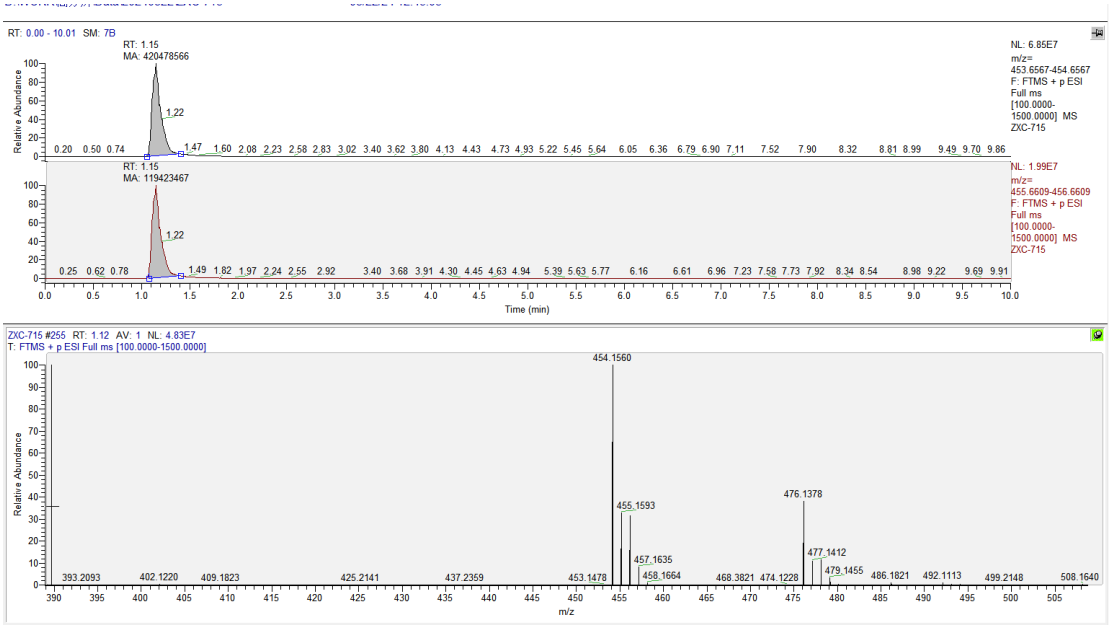
1a **2a** **^{18}O-3a**

The reaction was performed under in presence of 50 μL $H_2{}^{18}O$ and the residue was purified by silica gel column chromatography.

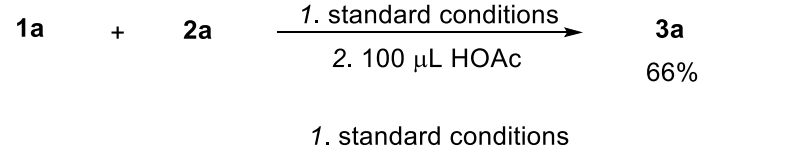
^{16}O-3a: Calcd for $C_{25}H_{28}NO_3P$+[M+H]$^+$ 454.1567, found 454.1562

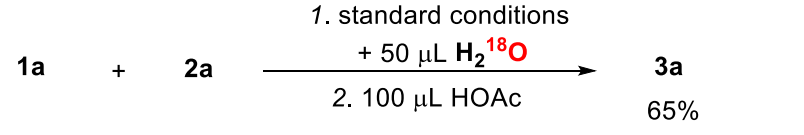
^{18}O-3a: Calcd for $C_{25}H_{28}N^{18}O_3P$+[M+H]$^+$ 456.1609, found 456.1606.





#	m/z	Intensity	Relative Intensity(%)
^{16}O-3a	**454.1568**	**420478566**	**100**
^{18}O-3a	**456.1610**	**119423467**	**28.4**

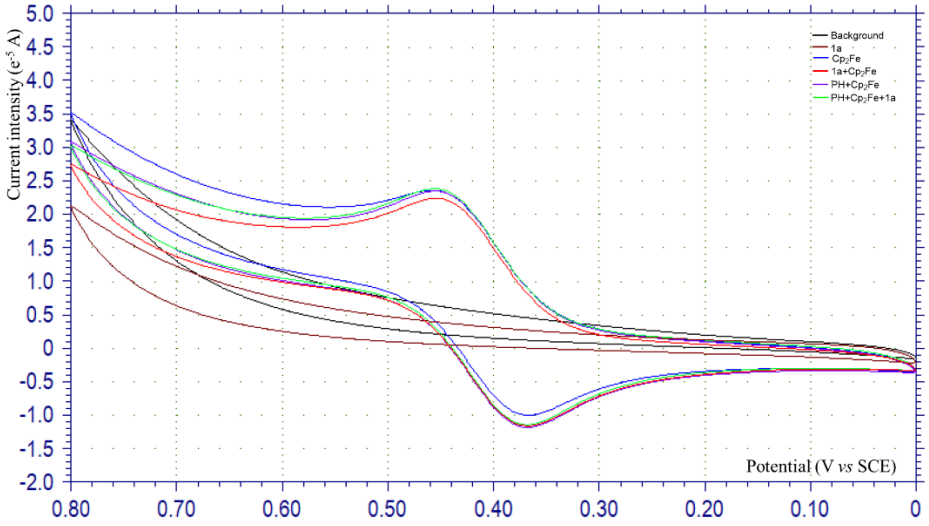




	Relative intensity (%) (detected by HRMS)	
	^{16}O-3a	^{18}O-3a
reaction without $H_2{}^{18}O$	100	2.8
reaction with $H_2{}^{18}O$	100	28.4

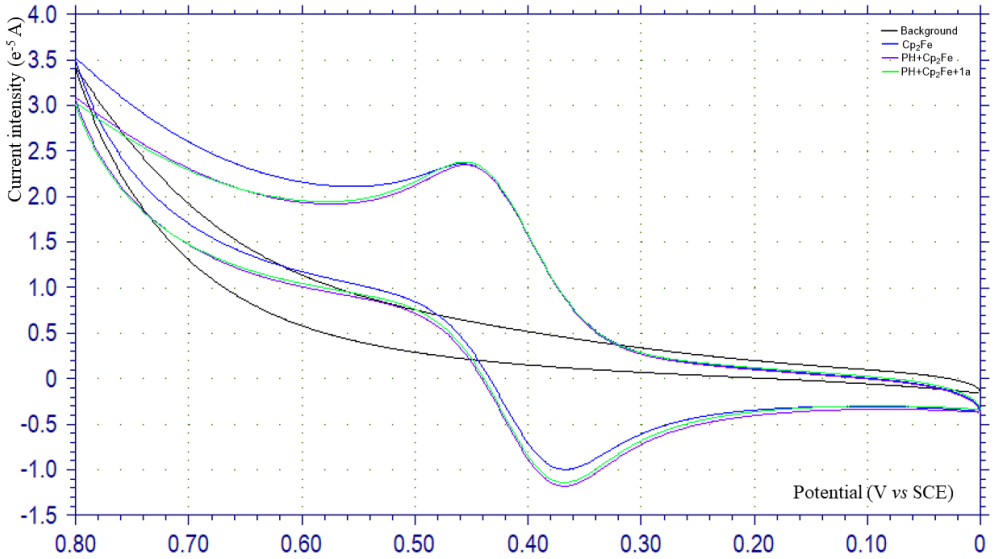
4. Cyclic voltammetry

Cyclic voltammetry was performed with CHI760E Electrochemical Workstation using the cyclic voltammetry mode. A platinum disc (diameter 3 mm) working electrode, a platinum wire counter electrode and a reference electrode (saturated calomel electrode (in a 3.0 M KCl aqueous solution) were used at a scan rate of 100 mV/s. All electrodes are purchased from CH Instruments. The experiments were conducted in a 25 mL four neck vial without stirring in CH_3CN/MeOH (17 mL/3 mL) with *n*Bu_4NOAc (0.1 M) as electrolyte under Ar. The working electrode was polished by a commercially available polishing pad and alumina (Al_2O_3) (purchased from CH Instruments), and sonicated in deionized water before data collection. The solution of interest was sparged with Argon for 5 minutes.



Note: background: 0.1 M *n*-Bu_4NOAc in CH_3CN+MeOH under Ar; Cp_2Fe (1.5 mM); diphenylphosphine oxide **2a** (8.0 mM); **1a** (4.0 mM).

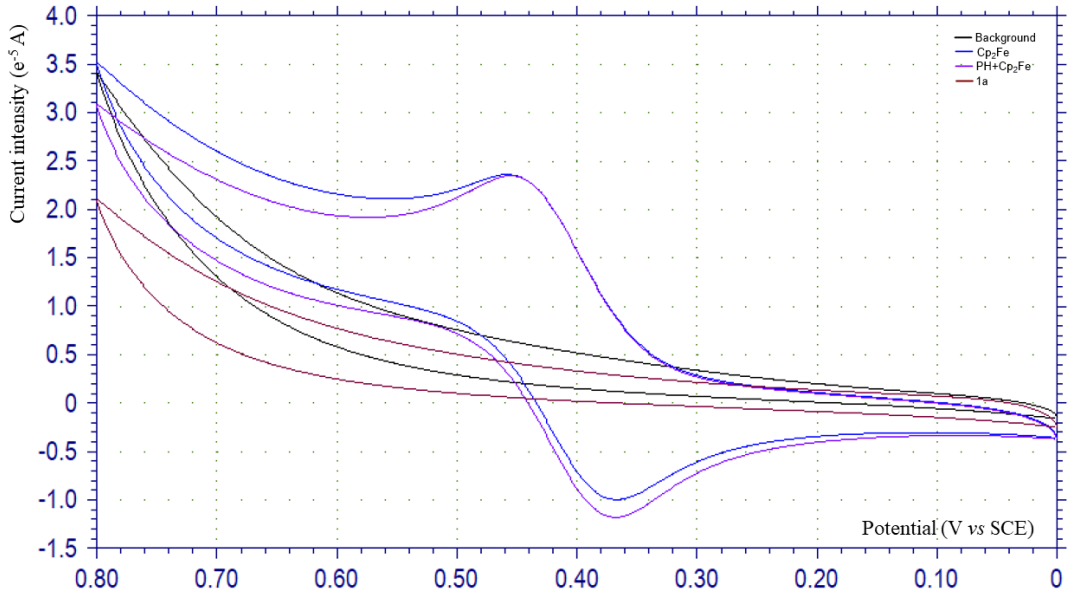
Figure S1: *Cyclic voltammetry of Cp_2Fe,* ***1a****, and* ***2a*** *in the [0V, +0.8V] range*



Note: background: 0.1 M *n*-Bu_4NOAc in CH_3CN+MeOH under Ar; Cp_2Fe (1.5 mM); diphenylphosphine oxide **2a** (8.0 mM) + Cp_2Fe (1.5 mM); **2a** (8.0 mM) + Cp_2Fe (1.5 mM) + **1a** (4.0 mM).

Figure S2: *Cyclic voltammetry of Cp_2Fe, Cp_2Fe +* ***2a****, and* ***2a*** *+ Cp_2Fe +* ***1a*** *in the [0V,*

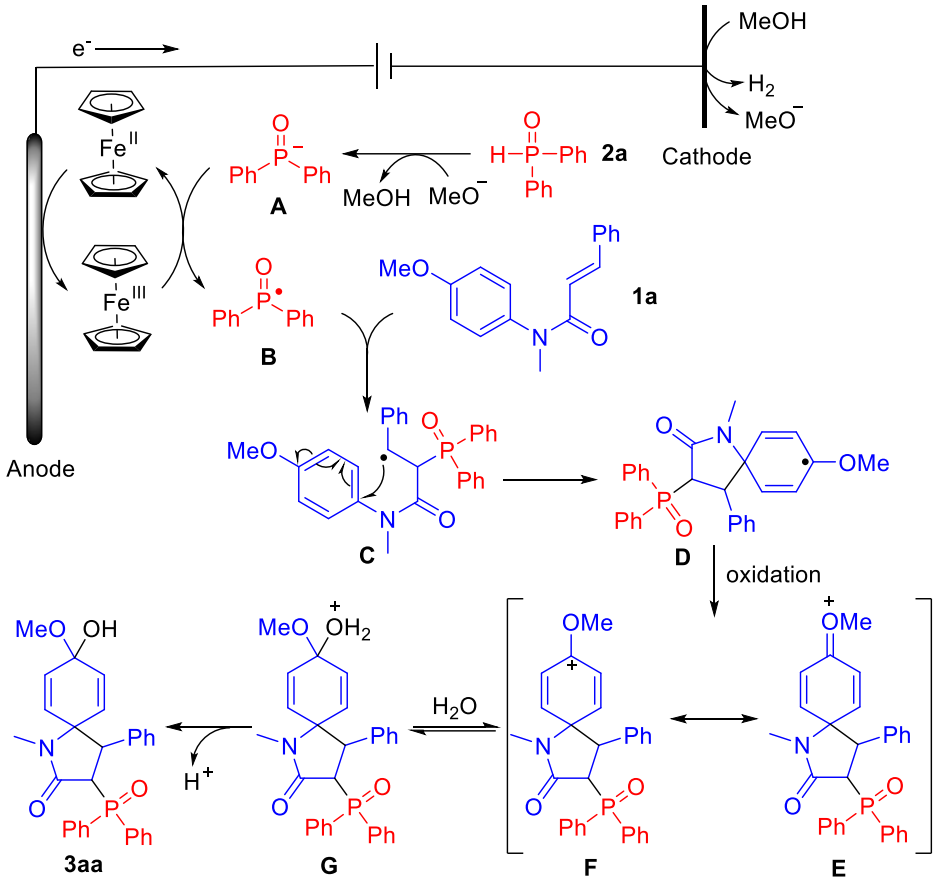
+0.8V] range



Note: background: 0.1 M *n*-Bu_4NOAc in CH_3CN+MeOH under Ar; Cp_2Fe (1.5 mM); diphenylphosphine oxide **2a** (8.0 mM); **1a** (4.0 mM).

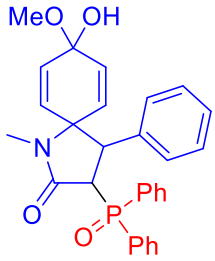
Figure S3: *Cyclic voltammetry of Cp_2Fe,* ***1a****, and* ***2a*** **+** *Cp_2Fe in the [0V, +0.8V]*

5. Mechanistic proposal



6. Spectral data

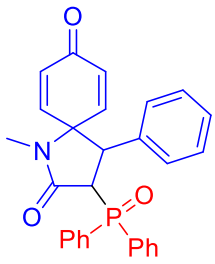
3-(diphenylphosphoryl)-8-hydroxy-8-methoxy-1-methyl-4-phenyl-1-azaspiro[4.5]deca-6,9-dien-2-one (3aa)



Compound **3aa** was prepared from (E)-*N*-(4-methoxyphenyl)-*N*-methyl-3-phenylacrylamide **1a** (53.4 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.04 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **3aa** (88.0 mg, 0.180 mmol, 90%, *dr* = 50:50) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.94-7.88 (m, 2H), 7.54 (dd, *J* = 11.6 Hz, *J* = 8.0 Hz, 2H), 7.51-7.42 (m, 3.5H), 7.31-7.23 (m, 2H), 7.21-7.05 (m, 5H), 6.84-6.80 (m, 2H), 6.30 (dd, *J* = 10.3 Hz, *J* = 3.0 Hz, 0.5H), 6.29 (dd, *J* = 10.0 Hz, *J* = 1.9 Hz, 0.5H), 6.23 (dd, *J* = 10.4 Hz, *J* = 2.5 Hz, 0.5H), 6.00 (dd, *J* = 10.2 Hz, *J* = 2.5 Hz, 0.5H), 5.91 (dd, *J* =10.1 Hz, *J* = 1.9 Hz, 0.5H), 5.69 (dd, *J* = 10.5 Hz, *J* = 2.5 Hz, 0.5H), 5.54 (dd, *J* = 10.5 Hz, *J* = 2.5 Hz, 0.5H), 4.04 (dd, *J* = 8.8 Hz, *J* = 7.8 Hz, 0.5H), 3.97 (dd, *J* = 9.3 Hz, *J* = 8.5 Hz, 0.5H), 3.83 (dd, *J* = 17.8 Hz, *J* = 7.1 Hz, 0.5H), 3.74 (dd, *J* = 17.8 Hz, *J* = 7.9 Hz, 0.5H), 3.19 (s, 1.5H), 2.69 (s, 1.5H), 2.68 (s, 1.5H), 2.62 (s, 1.5H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.1, 169.0 (d, *J* = 3.6 Hz), 168.7 (d, *J* = 3.5 Hz), 149.9, 147.2, 137.2 (d, *J* = 3.8 Hz), 136.9 (d, *J* = 4.4 Hz), 134.9, 132.29, 132.20 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 2.7 Hz), 131.68, 131.65 (d, *J* = 9.2 Hz), 131.61 (d, *J* = 9.8 Hz), 131.3 (d, *J* = 103.1 Hz), 131.14 (d, *J* = 9.6 Hz), 131.11, 131.09 (d, *J* = 101.1 Hz), 131.04 (d, *J* = 9.4 Hz), 130.77 (d, *J* = 103.7 Hz), 130.73 (d, *J* = 103.7 Hz, overlapped), 130.5, 130.2, 129.6, 128.7, 128.59, 128.53, 128.43, 128.40 (d, *J* = 11.9 Hz), 128.3 (d, *J* = 12.2 Hz), 128.2 (d, *J* = 11.8 Hz), 128.16, 128.14 (d, *J* = 12.4 Hz), 92.2, 64.3 (d, *J* = 4.8 Hz), 63.5 (d, *J* = 6.2 Hz), 49.6, 49.5, 48.8 (d, *J* = 66.0 Hz), 48.7 (d, *J* = 67.2 Hz), 48.6, 27.2, 26.7.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 31.1, 30.7
HRMS-ESI: Calcd for $C_{29}H_{29}NO_4P^+$ $[M+H]^+$ 486.1828, found 486.1827.

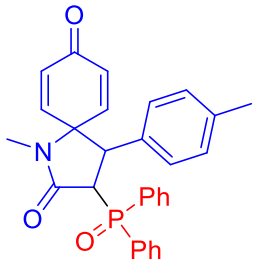
3-(diphenylphosphoryl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3a)



Compound **3a** was prepared from (E)-*N*-(4-methoxyphenyl)-*N*-methyl-3-phenylacrylamide **1a** (53.4 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.04 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.2 mL) was added, and the mixture was allowed to stir for 5 h at room temperature in air. Purified by silica gel column chromatography to give **3a** (60.0 mg, 0.132 mmol, 66%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.92 (dd, *J* = 12.5 Hz, *J* = 7.8 Hz, 2H), 7.60-7.46 (m, 5H), 7.34 (t, *J* = 6.9 Hz, 1H), 7.28 (d, *J* = 10.3 Hz, 1H), 7.25-7.18 (m, 2H), 7.17-7.10 (m, 3H), 6.83 (d, *J* = 5.7 Hz, 2H), 6.31 (t, *J* = 8.2 Hz, 2H), 5.94 (d, *J* = 10.1 Hz, 1H), 4.03 (dd, *J* = 9.5 Hz, *J* = 7.5 Hz, 1H), 3.84 (dd, *J* = 17.8 Hz, *J* = 6.7 Hz, 1H), 2.70 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.2, 169.1 (d, *J* = 3.4 Hz), 150.1, 147.3, 137.0 (d, *J* = 4.7 Hz), 132.3 (d, *J* = 2.3 Hz), 132.1 (d, *J* = 2.3 Hz), 131.7 (d, *J* = 9.8 Hz), 131.2, 131.1 (d, *J* = 9.5 Hz), 130.78 (d, *J* = 104.0 Hz), 130.77 (d, *J* = 102.4 Hz), 130.6, 128.8, 128.6 (d, *J* = 12.1 Hz), 128.5 (d, *J* = 11.3 Hz), 128.1, 128.0, 64.4 (d, *J* = 4.8 Hz), 49.0 (d, *J* = 66.8 Hz), 48.7, 27.3.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 31.2
HRMS-ESI: Calcd for $C_{28}H_{25}NO_3P^+$ $[M+H]^+$454.1567, found 454.1568.

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



Compound **3b** was prepared from (E)-*N*-(4-methoxyphenyl)-*N*-methyl-3-(*p*-tolyl)acrylamide **1b** (56.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.19 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3b** (57.0 mg, 0.122 mmol, 61%, *dr* = 95:5) as white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.91(dd, *J* = 12.1 Hz, *J* = 7.8 Hz, 2H), 7.58 (dd, *J* =

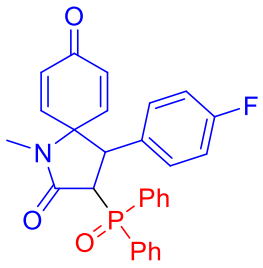
11.3 Hz, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.49 (td, *J* = 7.4 Hz, *J* = 2.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.32 (dd, *J* = 9.9 Hz, *J* = 2.8 Hz, 1H), 7.24 (dd, *J* = 7.2 Hz, *J* = 2.5 Hz, 2H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 2H), 6.34-6.27 (m, 2H), 5.97 (d, *J* = 10.3 Hz, 1H), 3.99 (dd, *J* = 9.1 Hz, *J* = 7.2 Hz, 1H), 3.80 (dd, *J* = 18.0 Hz, *J* = 6.5 Hz, 1H), 2.71 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.3, 169.2 (d, *J* = 3.7 Hz), 150.3, 147.5, 138.0, 134.3 (d, *J* = 5.0 Hz), 132.3 (d, *J* = 2.7 Hz), 132.0 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 9.6 Hz), 131.2, 131.1, 130.9 (d, *J* = 101.6 Hz), 130.8 (d, *J* = 103.1 Hz), 130.4, 129.5, 128.6 (d, *J* = 12.4 Hz), 128.5 (d, *J* = 11.9 Hz), 127.8, 64.5 (d, *J* = 4.5 Hz), 49.4 (d, *J* = 65.7 Hz), 48.4, 27.3, 21.1.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 31.3

HRMS-ESI: Calcd for $C_{29}H_{27}NO_3P^+$ $[M+H]^+$468.1723, found 468.1724

3-(diphenylphosphoryl)-4-(4-fluorophenyl)-1-methyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3c)



Compound **3c** was prepared from (E)-3-(4-fluorophenyl)-*N*-(4-methoxyphenyl)-*N*-methylacrylamide **1c** (57.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.50 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3c** (65.0 mg, 0.138 mmol, 69%, *dr* = 95:5) as brown solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.92 (dd, *J* = 12.8 Hz, *J* = 8.4 Hz, 2H), 7.59-7.47 (m, 5H), 7.34 (t, *J* = 6.3 Hz, 1H), 7.24-7.19 (m, 2H), 7.16 (d, *J* = 9.4 Hz, 1H), 6.84-6.76 (m, 4H), 6.33-6.28 (m, 2H), 5.97 (d, *J* = 9.4 Hz, 1H), 3.99 (dd, *J* = 10.3 Hz, *J* = 6.8 Hz, 1H), 3.87 (dd, *J* = 17.2 Hz, *J* = 6.8 Hz, 1H), 2.69 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.9, 168.8 (d, *J* = 3.5 Hz), 162.1 (d, *J* = 247.0 Hz), 149.5, 146.9, 132.3 (d, *J* = 2.1 Hz), 132.15 (d, *J* = 2.3 Hz), 132.12 (d, *J* = 2.3 Hz), 131.6 (d, *J* = 9.5 Hz), 131.4, 131.1, 131.0, 130.5 (d, *J* = 102.4 Hz), 130.4 (d, *J* = 104.0 Hz), 129.6 (d, *J* = 8.1 Hz), 128.5 (d, *J* = 12.6 Hz), 128.4 (d, *J* = 12.2 Hz), 115.6 (d, *J* = 21.4 Hz), 64.6 (d, *J* = 5.7 Hz), 48.4 (d, *J* = 67.6 Hz), 48.0, 27.3.

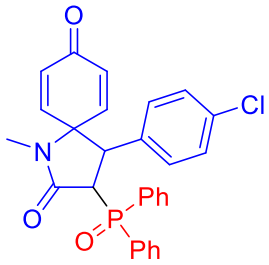
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.8.

^{19}F NMR (470 MHz, $CDCl_3$, 300K): δ (ppm) -113.3

HRMS-ESI: Calcd for $C_{28}H_{24}FNO_3P^+$ $[M+H]^+$472.1473, found 472.1471

4-(4-chlorophenyl)-3-(diphenylphosphoryl)-1-methyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione

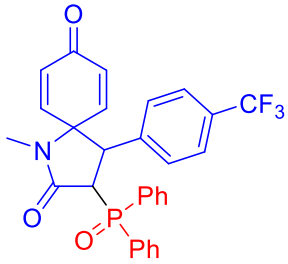
(3d)



Compound **3d** was prepared from (E)-3-(4-chlorophenyl)-*N*-(4-methoxyphenyl)-*N*-methylacrylamide **1d** (60.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.19 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 1 h at room temperature in air. Purified by silica gel column chromatography to give **3d** (61.0 mg, 0.120 mmol, 60%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.95-7.89 (m, 2H), 7.59-7.52 (m, 3H), 7.49 (td, *J* = 7.5 Hz, *J* = 2.9 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.23 (td, *J* = 7.5 Hz, *J* = 2.9 Hz, 2H), 7.17 (dd, *J* = 10.0 Hz, *J* = 3.0 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.34-6.29 (m, 2H), 5.98 (dd, *J* = 10.2 Hz, *J* = 1.8 Hz, 1H), 3.98 (dd, *J* = 8.8 Hz, *J* = 8.1 Hz, 1H), 3.84 (dd, *J* = 17.3 Hz, *J* = 7.8 Hz, 1H), 2.68 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.9, 168.8 (d, *J* = 3.9 Hz), 149.5, 146.7, 135.2 (d, *J* = 4.0 Hz), 134.0, 132.3 (d, *J* = 2.4 Hz), 132.1 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 9.7 Hz), 131.5, 131.1 (d, *J* = 9.5 Hz), 130.9, 130.7 (d, *J* = 104.2 Hz), 130.6 (d, *J* = 104.2 Hz), 129.3, 128.9, 128.6 (d, *J* = 6.0 Hz), 128.5 (d, *J* = 5.4 Hz), 64.4 (d, *J* = 5.5 Hz), 48.6 (d, *J* = 66.0 Hz), 48.2, 27.3.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.7
HRMS-ESI: Calcd for $C_{28}H_{24}ClNO_3P^+$ $[M+H]^+$488.1177, found 488.1176

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

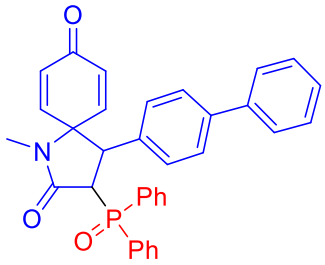


Compound **3e** was prepared from (E)-*N*-(4-methoxyphenyl)-*N*-methyl-3-(4-(trifluoromethyl)phenyl)acrylamide **1e** (67.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.97 F/mol) (**General Procedure A**). The

consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3e** (62.0 mg, 0.118 mmol, 59%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.94 (dd, *J* =11.9 Hz, *J* = 7.6 Hz, 2H), 7.58-7.52 (m, 3H), 7.49 (td, *J* = 7.6 Hz, *J* = 2.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.18 (td, *J* = 7.30 Hz, *J* = 2.6 Hz, 2H), 7.13 (dd, *J* = 10.2 Hz, *J* = 2.9 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.36 (dd, *J* = 10.3 Hz, *J* = 3.0 Hz, 1H), 6.33 (dd, *J* = 10.1 Hz, *J* = 1.5 Hz, 1H), 5.98 (dd, *J* = 10.2 Hz, *J* = 1.5 Hz, 1H), 4.06 (dd, *J* = 9.5 Hz, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 16.9 Hz, *J* = 8.3 Hz, 1H), 2.69 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.7, 168.7 (d, *J* = 3.6 Hz), 149.2, 146.3, 140.3, 132.5 (d, *J* = 2.5 Hz), 132.2 (d, *J* = 2.5 Hz), 131.77, 131.73 (d, *J* = 9.5 Hz), 131.3, 131.1 (d, *J* = 9.5 Hz), 130.6 (d, *J* = 102.0 Hz), 130.3 (d, *J* = 104.2 Hz), 130.2 (q, *J* = 33.2 Hz), 128.66 (d, *J* = 12.3 Hz), 128.61, 128.5 (d, *J* = 12.3 Hz), 125.6 (q, *J* = 3.5 Hz), 123.6 (q, *J* = 272.3 Hz), 64.4 (d, *J* = 5.9 Hz), 48.6, 48.3 (d, *J* = 67.3 Hz), 27.3.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.4
^{19}F NMR (470 MHz, $CDCl_3$, 300K): δ (ppm) -62.8
HRMS-ESI: Calcd for $C_{29}H_{24}F_3NO_3P^+$ $[M+H]^+$522.1441, found 522.1443

4-([1,1'-biphenyl]-4-yl)-3-(diphenylphosphoryl)-1-methyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3f)

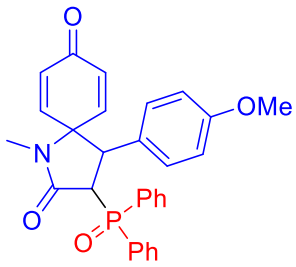


Compound **3f** was prepared from (E)-3-([1,1'-biphenyl]-4-yl)-*N*-(4-methoxyphenyl)-*N*-methylacrylamide **1f** (68.6 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (3.73 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (30% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3f** (54.0 mg, 0.112 mmol, 56%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.94 (dd, *J* = 11.8 Hz, *J* = 7.5 Hz, 2H), 7.60 (dd, *J* = 11.7 Hz, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 6.6 Hz, 1H), 7.53-7.48 (m, 4H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.37-7.32 (m, 4H), 7.29 (dd, *J* = 10.1 Hz, *J* = 2.9 Hz, 1H), 7.23 (td, *J* = 7.8 Hz, *J* = 2.3 Hz, 2H), 6.90 (d, d, *J* = 7.7 Hz, 2H), 6.39 (dd, *J* = 10.4 Hz, *J* = 3.0 Hz, 1H), 6.35 (dd, *J* = 10.1 Hz, *J* = 1.5 Hz, 1H), 6.00 (dd, *J* = 10.0 Hz, *J* =1.3 Hz, 1H), 4.06 (dd, *J* = 8.9 Hz, *J* = 8.1 Hz, 1H), 3.91 (dd, *J* = 17.6 Hz, *J* = 7.3 Hz, 1H), 2.73 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.2, 169.1 (d, *J* = 3.3 Hz), 150.0, 147.2, 140.9, 140.1, 135.9 (d, *J* = 4.4 Hz), 132.4 (d, *J* = 2.6 Hz), 132.1 (d, *J* = 2.6 Hz), 131.7 (d, *J* = 9.2 Hz), 131.4, 131.2 (d, *J* = 9.3 Hz), 131.1, 130.7, 130.3 (d, *J* = 5.1 Hz), 128.9, 128.6 (d, *J* = 12.5 Hz), 128.58 (d, *J* = 12.4 Hz), 128.54, 127.7, 127.4, 127.0, 64.5 (d, *J* = 5.0 Hz), 49.1 (d, *J* = 66.6 Hz), 48.5, 27.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 31.2
HRMS-ESI: Calcd for $C_{34}H_{29}NO_3P^+$ $[M+H]^+$530.1880, found 530.1883

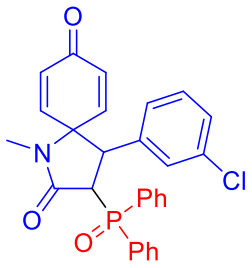
3-(diphenylphosphoryl)-4-(4-methoxyphenyl)-1-methyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3g)



Compound **3g** was prepared from (E)-*N*,3-bis(4-methoxyphenyl)-*N*-methylacrylamide **1g** (59.4 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.43 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3g** (40.0 mg, 0.082 mmol, 41%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.91 (dd, *J* = 11.9 Hz, *J* = 7.4 Hz, 2H), 7.60-7.53 (m, 3H), 7.50 (td, *J* = 7.4 Hz, *J* = 2.4 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.30-7.26 (m, 3H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 2H), 6.31 (td, *J* = 10.1 Hz, *J* = 1.8 Hz, 2H), 5.98 (dd, *J* = 10.2 Hz, *J* = 1.7 Hz, 1H), 3.96 (dd, *J* = 8.9 Hz, *J* = 7.2 Hz, 1H), 3.80 (dd, *J* = 18.0 Hz, *J* = 6.9 Hz, 1H), 3.74 (s, 3H), 2.70 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.3, 169.2 (d, *J* = 3.6 Hz), 159.3, 150.3, 147.6, 132.3 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 9.4 Hz), 131.2, 131.1 (d, *J* = 9.4 Hz), 130.9 (d, *J* = 101.8 Hz), 130.8 (d, *J* = 103.3 Hz), 130.5, 129.2 (d, *J* = 4.7 Hz), 129.1, 128.6 (d, *J* = 12.3 Hz), 128.5 (d, *J* = 11.8 Hz), 114.2, 64.7 (d, *J* = 4.8 Hz), 55.3, 49.4 (d, *J* = 66.0 Hz), 48.1, 27.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 31.3
HRMS-ESI: Calcd for $C_{29}H_{27}NO_4P^+$ $[M+H]^+$484.1672, found 484.1670

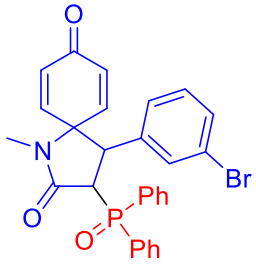
4-(3-chlorophenyl)-3-(diphenylphosphoryl)-1-methyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3h)



Compound **3h** was prepared from (E)-3-(3-chlorophenyl)-*N*-(4-methoxyphenyl)-*N*-methylacrylamide **1h** (60.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (3.26 F/mol) **(General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3h** (75.0 mg, 0.154 mmol, 77%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.94 (dd, *J* = 12.4 Hz, *J* = 7.4 Hz, 2H), 7.59-7.52 (m, 3H), 7.49 (td, *J* =7.5 Hz, *J* = 2.7 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.22 (td, *J* = 7.9 Hz, *J* = 2.7 Hz, 2H), 7.14 (dd, *J* = 9.9 Hz, *J* = 2.7 Hz, 1H), 7.09 (dd, *J* = 7.7 Hz, *J* = 1.0 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.79 (s, 1H), 6.71 (d, *J* = 7.1 Hz, 1H), 6.37 (dd, *J* = 10.5 Hz, *J* = 2.6 Hz, 1H), 6.32 (dd, *J* = 10.0 Hz, *J* = 1.7 Hz, 1H), 5.98 (dd, *J* = 10.2 Hz, *J* = 1.7 Hz, 1H), 4.01 (dd, *J* = 9.2 Hz, *J* = 8.3 Hz, 1H), 3.89 (dd, *J* = 17.1 Hz, *J* = 7.9 Hz, 1H), 2.68 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.9, 168.7 (d, *J* = 3.4 Hz), 149.3, 146.6, 138.4 (d, *J* = 2.6 Hz), 134.5, 132.4 (d, *J* = 2.6 Hz), 132.2 (d, *J* = 2.4 Hz), 131.7, 131.6 (d, *J* = 9.4 Hz), 131.1 (d, *J* = 2.0 Hz), 131.0, 130.5 (d, *J* = 102.0 Hz), 130.4 (d, *J* = 103.9 Hz), 129.9, 128.6, 128.5 (d, *J* = 6.0 Hz), 128.3 (d, *J* = 11.0 Hz), 128.0, 126.4, 64.3 (d, *J* = 5.7 Hz), 48.4, 48.3 (d, *J* = 66.6 Hz), 27.3.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.6
HRMS-ESI: Calcd for $C_{28}H_{24}ClNO_3P^+$ $[M+H]^+$488.1177, found 488.1174

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

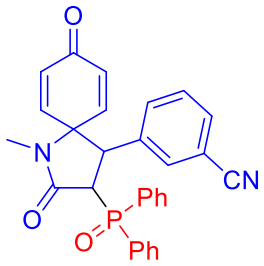


Compound **3i** was prepared from (E)-3-(3-bromophenyl)-*N*-(4-methoxyphenyl)-*N*-methylacrylamide **1i** (69.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.97 F/mol) (**General Procedure A**). The consumption of

the starting material was checked by TLC (30% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3i** (56 mg, 0.104 mmol, 52%, *dr* = 95:5) as brown solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.94 (dd, *J* = 12.4 Hz, *J* = 7.3 Hz, 2H), 7.59-7.53 (m, 3H), 7.50 (td, *J* = 7.6 Hz, *J* = 2.9 Hz, 2H), 7.35 (t, *J* =7.3 Hz, 1H), 7.25-7.21 (m, 2H), 7.16 (dd, *J* = 10.1 Hz, *J* = 2.9 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.92 (s, 1H), 6.76 (d, *J* = 7.3 Hz, 1H), 6.36 (dd, *J* = 10.3 Hz, *J* = 2.8 Hz, 1H), 6.33 (dd, *J* = 10.1 Hz, *J* = 1.8 Hz, 1H), 6.01 (dd, *J* = 10.3 Hz, *J* = 1.8 Hz, 1H), 3.97 (dd, *J* = 9.2 Hz, *J* = 8.1 Hz, 1H), 3.83 (dd, *J* = 17.4 Hz, *J* = 7.8 Hz, 1H), 2.70 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.9, 168.7 (d, *J* = 3.8 Hz), 149.4, 146.8, 138.7 (d, *J* = 3.5 Hz), 132.5 (d, *J* = 2.5 Hz), 132.3 (d, *J* = 2.5 Hz), 131.76 (d, *J* = 9.5 Hz), 131.70, 131.3, 131.2, 131.1 (d, *J* = 9.6 Hz), 130.9, 130.5 (d, *J* = 102.2 Hz), 130.4 (d, *J* = 104.3 Hz), 130.2, 128.6 (d, *J* = 12.4 Hz), 128.5 (d, *J* = 11.6 Hz), 126.9, 122.8, 64.4 (d, *J* = 5.6 Hz), 48.48 (d, *J* = 67.1 Hz), 48.42, 27.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.7
HRMS-ESI: Calcd for $C_{28}H_{24}BrNO_3P^+$ $[M+H]^+$532.0671, found 532.0673

3-(3-(diphenylphosphoryl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-6,9-dien-4-yl)benzonitrile (3j)

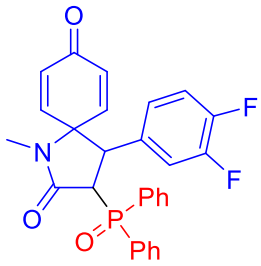


Compound **3j** was prepared from (E)-3-(3-cyanophenyl)-*N*-(4-methoxyphenyl)-*N*-methylacrylamide **1j** (58.4 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (6.06 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (30% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3j** (54.0 mg, 0.112 mmol, 56%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.96 (dd, *J* = 12.0 Hz, *J* = 8.0 Hz, 2H), 7.59-7.53 (m, 3H), 7.49 (t, *J* = 5.0 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.22-7.14 (m, 4H), 7.09 (d, *J* = 7.1 Hz, 1H), 7.01 (d, *J* = 10.4 Hz, 1H), 6.44 (d, *J* = 9.9 Hz, 1H), 6.33 (d, *J* = 9.9 Hz, 1H), 5.96 (d, *J* = 9.9 Hz, 1H), 4.14 (dd, *J* = 9.7 Hz, *J* = 8.9 Hz, 1H), 3.98 (dd, *J* = 16.1 Hz, *J* = 9.6 Hz, 1H), 2.67 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.6, 168.4 (d, *J* = 3.2 Hz), 148.6, 146.0, 137.1, 132.8, 132.5 (d, *J* = 2.4 Hz), 132.2 (d, *J* = 2.3 Hz), 131.98, 131.94, 131.7 (d, *J* = 9.5 Hz), 131.59,

131.55, 131.1 (d, J = 9.5 Hz), 130.5 (d, J = 102.1 Hz), 130.1 (d, J = 104.8 Hz), 129.3, 128.6 (d, J = 12.4 Hz), 128.5 (d, J = 12.0 Hz), 118.1, 112.6, 64.6 (d, J = 7.0 Hz), 48.4, 47.1 (d, J = 68.8 Hz), 27.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.1
HRMS-ESI: Calcd for $C_{29}H_{24}N_2O_3P^+$ $[M+H]^+$479.1519, found 479.1520

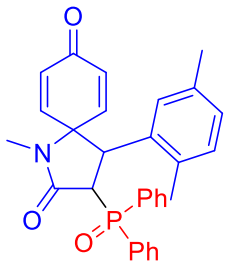
4-(3,4-difluorophenyl)-3-(diphenylphosphoryl)-1-methyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3k)



Compound **3k** was prepared from (E)-3-(3,4-difluorophenyl)-*N*-(4-methoxyphenyl)-*N*-methylacrylamide **1k** (60.6 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (6.14 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (30% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3k** (63.0 mg, 0.144 mmol, 72%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.94 (dd, J = 12.5 Hz, J = 8.0 Hz, 2H), 7.58 (dd, J = 11.8 Hz, J = 7.8 Hz, 2H), 7.54 (d, J = 7.0 Hz, 1H), 7.49 (td, J = 7.3 Hz, J = 1.7 Hz, 2H), 7.35 (t, J = 7.1 Hz, 1H), 7.23 (td, J = 7.6 Hz, J = 1.7 Hz, 2H), 7.06 (d, J = 10.0 Hz, 1H), 6.87 (q, J = 8.2 Hz, 1H), 6.69 (dd, J = 11.1 Hz, J = 9.7 Hz, 1H), 6.57 (d, J = 9.0 Hz, 1H), 6.38 (d, J = 9.1 Hz, 1H), 6.32 (d, J = 10.0 Hz, 1H), 6.00 (d, J = 9.7 Hz, 1H), 4.01 (dd, J = 9.5 Hz, J = 8.2 Hz, 1H), 3.87 (dd, J = 16.8 Hz, J = 8.3 Hz, 1H), 2.67 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.8, 168.5 (d, J = 3.5 Hz), 149.9 (dd, J = 250.1 Hz, J = 12.9 Hz), 149.7 (dd, J = 251.0 Hz, J = 13.0 Hz), 149.1, 146.4, 133.1 (d, J = 3.2 Hz), 132.4 (d, J = 2.5 Hz), 132.2 (d, J = 2.5 Hz), 131.75, 131.74 (d, J = 9.4 Hz), 131.4, 131.1 (d, J = 9.4 Hz), 130.7 (d, J = 104.1 Hz), 130.2 (d, J = 104.4 Hz), 128.6 (d, J = 12.5 Hz), 128.5 (d, J = 11.9 Hz), 124.4 (d, J = 2.4 Hz), 117.5 (d, J = 17.5 Hz), 117.0 (d, J = 18.0 Hz), 64.5 (d, J = 6.1 Hz), 48.1 (d, J = 67.3 Hz), 48.0, 27.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.4
^{19}F NMR (470 MHz, $CDCl_3$, 300K): δ (ppm) -136.0 (d, J = 21.4 Hz); -137.5 (d, J = 21.1 Hz)
HRMS-ESI: Calcd for $C_{28}H_{23}F_2NO_3P^+$ $[M+H]^+$490.1378, found 490.1379

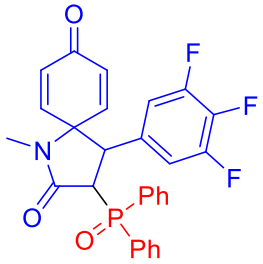
4-(2,5-dimethylphenyl)-3-(diphenylphosphoryl)-1-methyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3l)



Compound **3l** was prepared from (E)-3-(2,5-dimethylphenyl)-*N*-(4-methoxyphenyl)-*N*-methylacrylamide **1l** (59.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (12.28 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (30% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3l** (50.0 mg, 0.104 mmol, 52%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.92-7.86 (m, 2H), 7.69 (dd, *J* = 10.2 Hz, *J* = 3.1 Hz, 1H), 7.62-7.57 (m, 2H), 7.54 (dd, *J* = 7.2 Hz, *J* = 1.5 Hz, 1H), 7.51-7.44 (m, 3H), 7.32 (td, *J* = 7.6 Hz, *J* = 3.0 Hz, 2H), 6.97 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.32 (dd, *J* = 10.2 Hz, *J* = 2.0 Hz, 1H), 6.16 (dd, *J* = 10.1 Hz, *J* = 3.0 Hz, 1H), 5.97 (dd, *J* = 10.4 Hz, *J* = 1.9 Hz, 1H), 4.04 (dd, *J* = 19.4 Hz, *J* = 4.0 Hz, 1H), 3.96 (dd, *J* = 9.2 Hz, *J* = 3.8 Hz, 1H), 2.73 (s, 3H), 2.33 (s, 3H), 1.50 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.3, 169.4 (d, *J* = 3.8 Hz), 151.7, 147.9, 137.7 (d, *J* = 6.9 Hz), 136.4, 133.6, 132.4 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 9.5 Hz), 131.32 (d, *J* = 103.1 Hz), 131.30 (d, *J* = 104.1 Hz), 131.0 (d, *J* = 103.5 Hz), 130.99 (d, *J* = 9.1 Hz), 130.90, 130.8, 129.3, 128.93 (d, *J* = 11.5 Hz), 128.92, 128.6 (d, *J* = 12.5 Hz), 127.0, 63.3, 51.6 (d, *J* = 63.8 Hz), 43.2, 27.1, 21.3, 19.2.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 32.7
HRMS-ESI: Calcd for $C_{30}H_{29}NO_3P^+$ $[M+H]^+$482.1879, found 482.1877

3-(diphenylphosphoryl)-1-methyl-4-(3,4,5-trifluorophenyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3m)

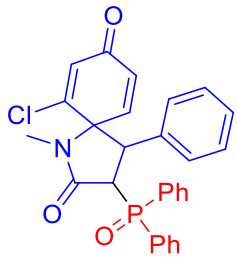


Compound **3m** was prepared from (E)-*N*-(4-methoxyphenyl)-*N*-methyl-3-(3,4,5-trifluorophenyl)acrylamide **1m** (64.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.04 F/mol) (**General Procedure A**). The consumption of

the starting material was checked by TLC (30% EtOAc/petroleum ether), followed by aqueous work-up, After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 1 h at room temperature in air. Purified by silica gel column chromatography to give **3m** (82.0 mg, 0.160 mmol, 80%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.96 (dd, *J* = 12.0 Hz, *J* = 7.7 Hz, 2H), 7.61 (dd, *J* = 11.9 Hz, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.49 (td, *J* = 7.8 Hz, *J* = 2.7 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.29-7.25 (m, 2H), 6.97 (dd, *J* = 10.4 Hz, *J* = 2.6 Hz, 1H), 6.52 (t, *J* = 6.9 Hz, 2H), 6.45 (dd, *J* = 10.3 Hz, *J* = 2.4 Hz, 1H), 6.34 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 6.03 (dd, *J* = 10.3 Hz, *J* = 1.2 Hz, 1H), 4.07 (dd, *J* = 10.5 Hz, *J* = 8.8 Hz, 1H), 3.85 (dd, *J* = 16.6 Hz, *J* = 9.4 Hz, 1H), 2.66 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.6, 168.3 (d, *J* = 2.9 Hz), 150.7 (ddd, *J* = 251.1 Hz, *J* = 10.5 Hz, *J* = 4.0 Hz), 148.5, 145.9, 139.2 (ddd, *J* = 253.5 Hz, *J* = 17.3 Hz, *J* = 15.3 Hz), 132.5 (d, *J* = 2.5 Hz), 132.3 (d, *J* = 2.4 Hz), 132.1, 132.0, 131.9, 131.7 (d, *J* = 9.6 Hz), 131.1 (d, *J* = 9.6 Hz), 130.7 (d, *J* = 101.9 Hz), 130.1 (d, *J* = 104.5 Hz), 128.7 (d, *J* = 12.6 Hz), 128.5 (d, *J* = 12.0 Hz), 112.6 (dd, *J* = 16.5 Hz, *J* = 4.9 Hz), 64.5 (d, *J* = 7.0 Hz), 48.2, 47.6 (d, *J* = 67.7 Hz), 27.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.1
^{19}F NMR (470 MHz, $CDCl_3$, 300K): δ (ppm) -132.6 (d, *J* = 20.6 Hz), -159.7 (t, *J* = 20.3 Hz)
HRMS-ESI: Calcd for $C_{28}H_{22}F_3NO_3P^+$ $[M+H]^+$508.1284, found 508.1286

6-chloro-3-(diphenylphosphoryl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3n)



Compound **3n** was prepared from *N*-(2-chloro-4-methoxyphenyl)-*N*-methylcinnamamide **1n** (60.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.20 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 1 h at room temperature in air. Purified by silica gel column chromatography to give **3n** (50.6 mg, 0.104 mmol, 52%, *dr* = 85:15) as yellow solid.

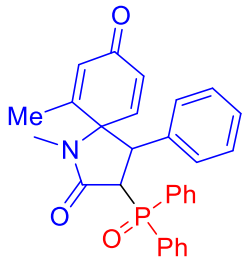
^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.96 (dd, *J* = 11.4 Hz, *J* = 7.9 Hz, 2H), 7.76 (dd, *J* = 11.8 Hz, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 6.7 Hz, 1H), 7.53-7.48 (m, 2H), 7.32 (t, *J* = 6.5 Hz, 1H), 7.26-7.21 (m, 2H), 7.13-7.05 (m, 3H), 6.89 (s, 1H), 6.88 (s, 1H), 6.58 (s, 1H), 6.50 (d, *J* = 9.7 Hz, 1H), 5.93 (d, *J* = 9.7 Hz, 1H), 4.46 (dd, *J* = 15.6 Hz, *J* = 11.7 Hz, 1H), 4.22 (dd, *J* = 12.5 Hz, *J* = 11.1 Hz, 1H), 2.63 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 182.5, 169.3, 153.6, 146.5, 133.5, 132.8, 132.4 (d, *J*

= 2.4 Hz), 132.2 (d, *J* = 9.5 Hz), 132.0 (d, *J* = 2.2 Hz), 131.4 (d, *J* = 9.6 Hz), 131.1 (d, *J* = 102.7 Hz), 130.3, 130.1 (d, *J* = 102.9 Hz), 128.6, 128.5 (d, *J* = 12.2 Hz), 128.3, 128.2 (d, *J* = 12.2 Hz), 127.8, 69.4 (d, *J* = 8.8 Hz), 47.9, 45.6 (d, *J* = 70.2 Hz), 27.1.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 29.7

HRMS-ESI: Calcd for $C_{28}H_{24}ClNO_3P^+$ $[M+H]^+$488.1177, found 188.1175

3-(diphenylphosphoryl)-1,6-dimethyl-4-phenyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3o)



Compound **3o** was prepared from *N*-(4-methoxy-2-methylphenyl)-*N*-methylcinnamamide **1o (**56.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (9.79 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 1 h at room temperature in air. Purified by silica gel column chromatography to give **3o** (44.8 mg, 0.096 mmol, 48%, *dr* = 85:15) as yellow solid.

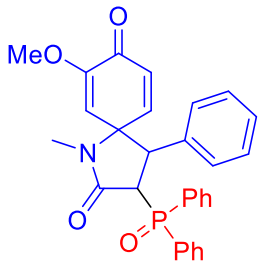
^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.98 (dd, *J* = 12.2 Hz, *J* = 7.6 Hz, 2H), 7.64-7.50 (m, 5H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.16-7.09 (m, 2H), 7.07-6.99 (m, 3H), 6.86 (d, *J* = 8.3 Hz, 0.3H), 6.84 (d, *J* = 10.2 Hz, 0.15H), 6.74 (d, *J* = 7.0 Hz, 1.7H), 6.44 (d, *J* = 10.1 Hz, 0.85H), 6.36 (d, *J* = 9.7 Hz, 0.15H), 6.23 (s, 0.85H), 5.85 (d, *J* = 9.8 Hz, 0.85H), 5.79 (s, 0.15H), 4.23-4.14 (m, 1H), 4.12-4.04 (m, 1H), 2.64 (s, 0.45H), 2.60 (s, 2.55H), 2.08 (s, 2.55H), 1.66 (s, 0.45H).

^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.6 (minor), 184.3, 169.6 (d, *J* = 3.1 Hz), 169.5 (d, *J* = 3.1 Hz, minor), 156.6, 156.0 (minor), 150.6 (minor), 147.8, 134.5, 133.4 (minor), 132.48 (d, *J* = 2.6 Hz, minor), 132.40 (d, *J* = 2.6 Hz), 132.06 (minor), 132.02 (d, *J* = 9.4 Hz, minor), 131.92 (d, *J* = 3.1 Hz), 131.90 (d, *J* = 9.1 Hz), 131.5 (minor), 131.43, 131.40 (d, *J* = 9.4 Hz, minor), 131.2 (d, *J* = 9.6 Hz), 130.8 (minor), 130.7, 130.6 (d, *J* = 101.9 Hz), 130.5 (d, *J* = 102.1 Hz), 130.1 (d, *J* = 103.1 Hz, minor), 129.5 (d, *J* = 101.1 Hz, minor), 128.6 (d, *J* = 12.1 Hz), 128.4, 128.3 (minor), 128.27 (d, *J* = 11.8 Hz, minor), 128.22 (d, *J* = 11.8 Hz), 127.99 (minor, overlapped), 127.97, 127.94 (minor, overlapped), 127.93, 127.2 (minor), 69.2 (d, *J* = 7.2 Hz, minor), 68.1 (d, *J* = 8.0 Hz), 47.6 (minor), 46.7, 46.0 (d, *J* = 69.7 Hz), 45.4 (d, *J* = 68.8 Hz, minor), 27.9 (minor), 27.5, 20.1 (minor), 18.3.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.77 (minor), 30.70

HRMS-ESI: Calcd for $C_{29}H_{27}NO_3P^+$ $[M+H]^+$468.1723, found 468.1724

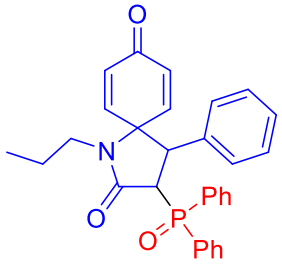
3-(diphenylphosphoryl)-7-methoxy-1-methyl-4-phenyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3p)



Compound **3p** was prepared from *N*-(3,4-dimethoxyphenyl)-*N*-methylcinnamamide **1p** (59.4 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (5.83 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 2 h at room temperature in air. Purified by silica gel column chromatography to give **3p** (48.3 mg, 0.100 mmol, 50%, *dr* = 50:50) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.96-7.87 (m, 2H), 7.60-7.51 (m, 3H), 7.48 (td, *J* = 7.4 Hz, *J* = 2.9 Hz, 2H), 7.38-7.31 (m, 1.5H), 7.25-7.19 (m, 2H), 7.16-7.07 (m, 3H), 6.86-6.79 (m, 2H), 6.38 (d, *J* = 2.7 Hz, 0.5H), 6.32-6.27 (m, 1H), 5.94 (d, *J* = 10.0 Hz, 0.5H), 5.05 (d, *J* = 2.4 Hz, 0.5H), 4.07-3.98 (m, 1H), 3.86 (dd, *J* = 6.7 Hz, *J* = 4.3 Hz, 0.5H), 3.83 (dd, *J* = 6.8 Hz, *J* = 3.9 Hz, 0.5H), 3.76 (s, 1.5H), 3.16 (s, 1.5H), 2.69 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 179.8, 179.7, 168.9 (d, *J* = 4.3 Hz), 168.8 (d, *J* = 3.8 Hz), 151.8, 151.4, 150.9, 148.0, 138.1 (d, *J* = 5.3 Hz), 137.4 (d, *J* = 4.3 Hz), 132.31 (d, *J* = 3.0 Hz), 132.30 (d, *J* = 3.0 Hz, overlapped), 132.13 (d, *J* = 3.0 Hz), 132.12 (d, *J* = 3.0 Hz, overlapped), 131.66 (d, *J* = 9.7 Hz), 131.63 (d, *J* = 9.7 Hz), 131.08 (d, *J* = 9.7 Hz), 131.04 (d, *J* = 9.7 Hz), 130.8 (d, *J* = 103.8 Hz), 130.75 (d, *J* = 102.3 Hz), 130.74 (d, *J* = 102.3 Hz, overlapped), 130.70 (d, *J* = 103.9 Hz), 130.3, 129.4, 128.8, 128.79 (overlapped), 128.59 (d, *J* = 12.0 Hz), 128.57 (d, *J* = 12.0 Hz), 128.55 (d, *J* = 12.0 Hz, overlapped), 128.54 (d, *J* = 12.0 Hz), 128.11, 128.10 (overlapped), 127.9, 127.8, 117.3, 114.3, 66.24 (d, *J* = 6.4 Hz), 66.20 (d, *J* = 6.5 Hz), 55.7, 54.7, 50.3, 49.4 (d, *J* = 16.5 Hz), 48.9 (d, *J* = 16.5 Hz), 48.7, 27.1, 27.0.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 31.6, 31.5
HRMS-ESI: Calcd for $C_{29}H_{27}NO_4P^+$ $[M+H]^+$484.1672, found 484.1673

3-(diphenylphosphoryl)-4-phenyl-1-propyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3q)

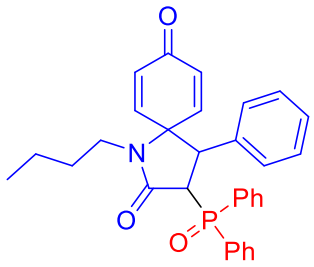


Compound **3q** was prepared from *N*-(4-methoxyphenyl)-*N*-propylcinnamamide **1q** (59.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (7.15

F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 1.5 h at room temperature in air. Purified by silica gel column chromatography to give **3q** (32.7 mg, 0.068 mmol, 34%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.93-7.87 (m, 2H), 7.64-7.58 (m, 2H), 7.54 (td, *J* = 7.4 Hz, *J* = 1.4 Hz, 1H), 7.50-7.46 (m, 2H), 7.40-7.34 (m, 2H), 7.26 (td, *J* = 7.4 Hz, *J* = 3.0 Hz, 2H), 7.19-7.13 (m, 3H), 6.88-6.83 (m, 2H), 6.31 (dd, *J* = 10.1 Hz, *J* = 3.0 Hz, 1H), 6.28 (dd, *J* = 10.0 Hz, *J* = 2.0 Hz, 1H), 5.92 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 4.01 (dd, *J* = 9.5 Hz, *J* = 6.6 Hz, 1H), 3.81 (dd, *J* = 17.8 Hz, *J* = 6.7 Hz, 1H), 3.12-3.04 (m, 1H), 3.02-2.95 (m, 1H), 1.56-1.43 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.4, 169.4 (d, *J* = 3.5 Hz), 150.8, 147.9, 137.5 (d, *J* = 4.7 Hz), 132.3 (d, *J* = 2.6 Hz), 132.1 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 9.7 Hz), 131.1 (d, *J* = 9.5 Hz), 131.0 (d, *J* = 101.9 Hz), 130.8 (d, *J* = 103.4 Hz), 130.6, 129.7, 128.9, 128.61 (d, *J* = 11.9 Hz), 128.60 (d, *J* = 11.9 Hz), 128.2, 128.0, 64.7 (d, *J* = 4.7 Hz), 49.4 (d, *J* = 65.9 Hz), 49.1, 44.1, 22.8, 11.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 31.1
HRMS-ESI: Calcd for $C_{30}H_{29}NO_3P^+$ $[M+H]^+$482.1879, found 482.1877

1-butyl-3-(diphenylphosphoryl)-4-phenyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3r)



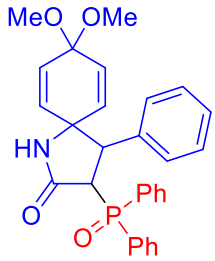
Compound **3r** was prepared from *N*-butyl-*N*-(4-methoxyphenyl)cinnamamide **1r** (61.8 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (9.79 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 12 h at room temperature in air. Purified by silica gel column chromatography to give **3r** (44.5 mg, 0.090 mmol, 45%, *dr* = 95:5) as yellow solid.
^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.90 (dd, *J* = 12.2 Hz, *J* = 8.1 Hz, 2H), 7.61 (dd, *J* = 12.4 Hz, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.48 (td, *J* = 7.4 Hz, *J* = 2.8 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.34 (dd, *J* = 10.1 Hz, *J* = 3.1 Hz, 1H), 7.29-7.25 (m, 2H), 7.18-7.13 (m, 3H), 6.88-6.84 (m, 2H), 6.31 (dd, *J* = 10.3 Hz, *J* = 2.9 Hz, 1H), 6.28 (dd, *J* = 10.1 Hz, *J* = 1.9 Hz, 1H), 5.92 (dd, *J* = 10.3 Hz, *J* = 1.7 Hz, 1H), 4.01 (dd, *J* = 9.6 Hz, *J* = 6.7 Hz, 1H), 3.82 (dd, *J* = 17.9 Hz, *J* = 6.7 Hz, 1H), 3.14-3.07 (m, 1H), 3.04-2.97 (m, 1H), 1.50-1.37 (m, 2H), 1.26-1.18 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.5, 169.4 (d, *J* = 3.5 Hz), 150.8, 147.9, 137.4 (d, *J* = 4.8 Hz), 132.3 (d, *J* = 2.5 Hz), 132.2 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 9.7 Hz), 131.2 (d, *J* = 9.6 Hz), 130.9 (d, *J* = 102.1 Hz), 130.8 (d, *J* = 103.4 Hz), 130.6, 129.7, 128.9, 128.6 (d, *J* = 12.0 Hz), 128.6

(d, *J* = 12.0 Hz, overlapped), 128.2, 127.9, 64.8 (d, *J* = 4.7 Hz), 49.3 (d, *J* = 65.4 Hz), 49.0, 42.4, 31.6, 20.2, 13.8.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 31.1

HRMS-ESI: Calcd for $C_{31}H_{31}NO_3P^+$ $[M+H]^+$496.2036, found 496.2037

3-(diphenylphosphoryl)-8,8-dimethoxy-4-phenyl-1-azaspiro[4.5]deca-6,9-dien-2-one (3s)



Compound **3s** was prepared from *N*-(4-methoxyphenyl)cinnamamide **1s** (50.6 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (5.36 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **3s** (50.0 mg, 0.102 mmol, 51%, *dr* = 95:5) as white solid.

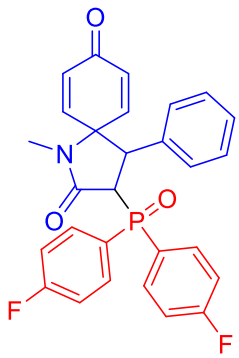
^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 8.77 (br, 1H), 7.88 (dd, *J* = 11.7 Hz, *J* = 8.5 Hz, 2H), 7.78 (dd, *J* = 11.7 Hz, *J* = 8.9 Hz, 2H), 7.51-7.36 (m, 6H), 7.23-7.17 (m, 5H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 7.5 Hz, 2H), 4.95 (s, 1H), 3.83 (s, 1H), 3.75 (s, 3H), 3.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 164.3, 156.6, 138.1 (d, *J* = 7.4 Hz), 132.1, 131.8 (d, *J* = 103.4 Hz), 131.45 (d, *J* = 9.0 Hz), 131.40, 131.39 (d, *J* = 9.0 Hz), 130.0 (d, *J* = 103.2 Hz), 128.77 (d, *J* = 10.3 Hz), 128.73, 128.6 (d, *J* = 11.1 Hz), 128.4, 126.8, 122.4, 114.0, 80.5, 57.79, 57.73 (d, *J* = 57.3 Hz), 55.5.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 29.2

HRMS-ESI: Calcd for $C_{29}H_{29}NO_4P^+$ $[M+H]^+$486.1828, found 496.1829

3-(bis(4-fluorophenyl)phosphoryl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3t)

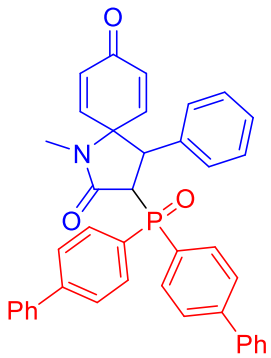


Compound **3t** was prepared from *N*-(4-methoxyphenyl)-*N*-methylcinnamamide **3t** (53.4 mg, 0.2

mmol), bis(4-fluorophenyl)phosphine oxide (95.4 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (**General Procedure A**). The consumption of the starting material was checked by TLC (4.66 F/mol) (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.2 mL) was added, and the mixture was allowed to stir for 5 h at room temperature in air. Purified by silica gel column chromatography to give **3t** (72.3 mg, 0.148 mmol, 74%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.94-7.87 (m, 2H), 7.57-7.51 (m, 2H), 7.22-7.11 (m, 6H), 6.90 (td, *J* = 8.6 Hz, *J* = 2.1 Hz, 2H), 6.83 (d, *J* = 6.9 Hz, 2H), 6.35-6.31 (m, 2H), 5.96 (dd, *J* = 10.3 Hz, *J* = 1.9 Hz, 1H), 3.97 (dd, *J* = 8.7 Hz, *J* = 8.2 Hz, 1H), 3.84 (dd, *J* = 17.0 Hz, *J* = 7.6 Hz, 1H), 2.71 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.1, 168.8 (d, *J* = 3.5 Hz), 165.5 (dd, *J* = 254.2 Hz, *J* = 2.7 Hz), 165.1 (dd, *J* = 254.2 Hz, *J* = 2.8 Hz), 149.5, 146.8, 136.4 (d, *J* = 3.8 Hz), 134.3 (dd, *J* = 12.0 Hz, *J* = 9.1 Hz), 133.7 (dd, *J* = 12.0 Hz. *J* = 9.0 Hz), 131.4, 131.0, 128.9, 128.4, 128.0, 126.5 (dd, *J* = 107.9 Hz, *J* = 3.5 Hz), 126.4 (dd, *J* = 105.9 Hz, *J* = 3.8 Hz), 116.1 (dd, *J* = 21.0 Hz, *J* = 13.8 Hz), 116.0 (dd, *J* = 21.6 Hz, *J* = 13.0 Hz), 64.6 (d, *J* = 5.7 Hz), 48.9 (d, *J* = 68.2 Hz), 48.7, 27.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 29.9
^{19}F NMR (470 MHz, $CDCl_3$, 300K): δ (ppm) -105.7, -105.8
HRMS-ESI: Calcd for $C_{28}H_{23}F_2NO_3P^+$ $[M+H]^+$490.1378, found 490.1376

3-(di([1,1'-biphenyl]-4-yl)phosphoryl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3u)



Compound **3u** was prepared from (E)-*N*-(4-methoxyphenyl)-*N*-methyl-3-phenylacrylamide **1u** (53.4 mg, 0.2 mmol), di([1,1'-biphenyl]-4-yl)phosphine oxide (141.6 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.35 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.3 mL) was added, and the mixture was allowed to stir for overnight at room temperature in air. Purified by silica gel column chromatography to give **3u** (86.0 mg, 0.142 mmol, 71%, *dr* = 95:5) as brown solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 8.07 (dd, *J* = 12.2 Hz, *J* = 8.2 Hz, 2H), 7.74 (dd, *J* = 8.6 Hz, *J* = 2.5 Hz, 2H), 7.63 (dd, *J* = 12.2 Hz, *J* = 8.3 Hz, 2H), 7.60 (s, 1H), 7.59 (s, 1H), 7.46-7.34 (m, 10H), 7.28 (dd, *J* = 10.1 Hz, *J* = 3.0 Hz, 1H), 7.15-7.06 (m, 3H), 6.87 (d, *J* = 6.9 Hz, 2H), 6.41

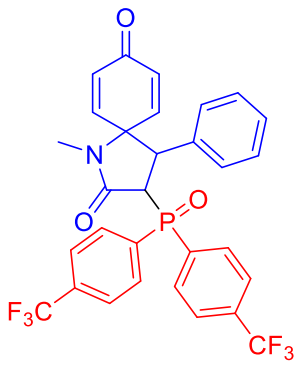
(dd, J = 10.4 Hz, J = 3.1 Hz, 1H), 6.35 (dd, J = 10.1 Hz, J = 1.8 Hz, 1H), 5.97 (dd, J = 10.3 Hz, J = 1.8 Hz, 1H), 4.17 (dd, J = 9.3 Hz, J = 8.1 Hz, 1H), 3.95 (dd, J = 17.6 Hz, J = 7.9 Hz, 1H), 2.74 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.1, 169.1 (d, J = 3.8 Hz), 149.7, 147.1, 144.9 (d, J = 2.9 Hz), 144.7 (d, J = 2.9 Hz), 139.8, 139.6, 136.4 (d, J = 3.5 Hz), 132.1 (d, J = 9.5 Hz), 131.5 (d, J = 10.1 Hz), 131.2, 130.8, 129.3 (d, J = 106.8 Hz), 129.0 (d, J = 102.7 Hz), 128.94, 128.92, 128.6, 128.2, 128.1, 128.0 (d, J = 13.1 Hz), 127.3, 127.2, 127.17, 127.11, 127.0 (d, J = 12.2 Hz), 64.6 (d, J = 5.9 Hz), 48.7, 48.6 (d, J = 67.0 Hz), 27.3.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 31.2

HRMS-ESI: Calcd for $C_{40}H_{33}NO_3P^+$ $[M+H]^+$606.2192, found 606.2191

3-(bis(4-(trifluoromethyl)phenyl)phosphoryl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3v)



Compound **3v** was prepared from (E)-*N*-(4-methoxyphenyl)-*N*-methyl-3-phenylacrylamide **1v** (53.4 mg, 0.2 mmol), bis(4-(trifluoromethyl)phenyl)phosphine oxide (135.2 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.89 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.2 mL) was added, and the mixture was allowed to stir for 3 h at room temperature in air. Purified by silica gel column chromatography to give **3v** (88.0 mg, 0.148 mmol, 74%, *dr* = 95:5) as brown solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 8.08 (dd, J = 12.2 Hz, J = 8.2 Hz, 2H), 7.74 (dd, J = 8.6 Hz, J = 1.9 Hz, 2H), 7.61 (dd, J = 11.9 Hz, J = 8.1 Hz, 2H), 7.36 (dd, J = 8.7 Hz, J = 1.7 Hz, 2H), 7.12-7.02 (m, 4H), 6.77 (d, J = 7.6 Hz, 2H), 6.44 (dd, J = 10.4 Hz, J = 3.1 Hz, 1H), 6.32 (dd, J = 9.9 Hz, J = 1.7 Hz, 1H), 5.96 (dd, J = 10.3 Hz, J = 1.8 Hz, 1H), 4.13 (dd, J = 10.1 Hz, J = 8.5 Hz, 1H), 3.89 (dd, J = 17.3 Hz, J = 9.2 Hz, 1H), 2.70 (s, 3H).

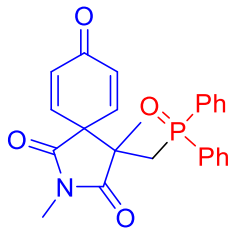
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.8, 168.2 (d, J = 3.9 Hz), 148.7, 146.3, 134.9 (d, J = 2.6 Hz), 134.4 (d, J = 102.9 Hz), 134.2 (q, J = 31.7 Hz), 134.1 (d, J = 99.6 Hz), 133.9 (q, J = 31.7 Hz), 132.1 (d, J =10.1 Hz), 131.6, 131.58, 131.57 (d, J = 9.0 Hz), 127.1, 128.4, 128.0, 125.5 (dq, J = 12.2 Hz, J = 3.5 Hz), 125.2 (dq, J = 12.0 Hz, J = 3.5 Hz), 123.5 (q, J = 273.3 Hz), 123.2 (q, J = 273.2 Hz), 64.9 (d, J = 7.1 Hz), 48.6, 47.5 (d, J = 71.0 Hz), 27.4.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 28.8

^{19}F NMR (470 MHz, $CDCl_3$, 300K): δ (ppm) -63.2, -63.5

HRMS-ESI: Calcd for $C_{30}H_{23}F_6NO_3P^+$ $[M+H]^+$590.1314, found 590.1313

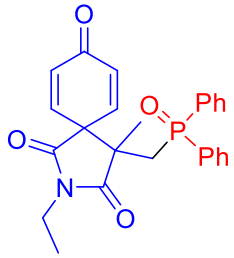
4-((diphenylphosphoryl)methyl)-2,4-dimethyl-2-azaspiro[4.5]deca-6,9-diene-1,3,8-trione (5a)



Compound **5a** was prepared from *N*-methacryloyl-4-methoxy-*N*-methylbenzamide **4a** (46.6 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (18.6 mg, 0.10 mmol), the solution was charged in constant current mode (3.42 F/mol) (**General Procedure B**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **5a** (57.0 mg, 0.136 mmol, 68%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.74-7.65 (m, 4H), 7.51 (td, *J* = 7.4 Hz, *J* = 1.2 Hz, 2H), 7.48-7.42 (m, 4H), 7.24 (dd, *J* = 10.2 Hz, *J* = 3.1 Hz, 1H), 6.69 (dd, *J* = 10.2 Hz, *J* = 3.0 Hz, 1H), 6.46 (dd, *J* = 10.3 Hz, *J* = 1.8 Hz, 1H), 6.30 (dd, *J* = 10.3 Hz, *J* = 1.6 Hz, 1H), 2.86 (dd, *J* = 16.5 Hz, *J* = 11.6 Hz, 1H), 2.80 (s, 3H), 2.66 (dd, *J* = 16.2 Hz, *J* = 9.5 Hz, 1H), 1.49 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.2, 178.5 (d, *J* = 8.1 Hz), 172.4, 143.0, 142.7, 134.0 (d, *J* = 101.3 Hz), 133.4, 132.6, 132.4 (d, *J* = 100.8 Hz), 132.3 (d, *J* = 2.6 Hz), 132.1 (d, *J* = 2.6 Hz), 130.8 (d, *J* = 9.6 Hz), 130.3 (d, *J* = 9.1 Hz), 129.0 (d, *J* = 11.7 Hz), 128.8 (d, *J* = 12.0 Hz), 57.8, 52.9 (d, *J* = 4.1 Hz), 35.6 (d, *J* = 67.7 Hz), 25.9, 24.0 (d, *J* = 8.4 Hz).
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 25.7
HRMS-ESI: Calcd for $C_{24}H_{23}NO_4P^+$ $[M+H]^+$420.1359, found 420.1360

4-((diphenylphosphoryl)methyl)-2-ethyl-4-methyl-2-azaspiro[4.5]deca-6,9-diene-1,3,8-trione (5b)



Compound **5b** was prepared from *N*-ethyl-*N*-methacryloyl-4-methoxybenzamide **4b** (49.4 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (18.6 mg, 0.10 mmol), the solution was charged in constant current mode (5.28 F/mol) (**General Procedure B**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **5b** (39.0 mg, 0.090 mmol, 45%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.74-7.69 (m, 2H), 7.67-7.62 (m, 2H), 7.52-7.39 (m, 6H), 7.05 (dd, *J* = 10.1 Hz, *J* = 3.1 Hz, 1H), 6.72 (dd, *J* = 10.4 Hz, *J* = 3.1 Hz, 1H), 6.47 (dd, *J* =

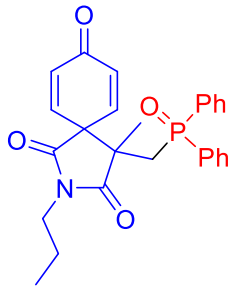
10.2 Hz, *J* = 1.6 Hz, 1H), 6.23 (dd, *J* = 10.2 Hz, *J* = 1.6 Hz, 1H), 3.51-3.42 (m, 1H), 3.32-3.22 (m, 1H), 2.90 (dd, *J* = 16.1 Hz, *J* = 11.7 Hz, 1H), 2.62 (dd, *J* = 16.1 Hz, *J* = 9.3 Hz, 1H), 1.52 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.2, 178.6 (d, *J* = 9.9 Hz), 172.0, 142.9, 142.2, 134.2 (d, *J* = 100.4 Hz), 133.1, 133.0, 132.8 (d, *J* = 100.8 Hz), 132.2 (d, *J* = 2.6 Hz), 132.0 (d, *J* = 2.6 Hz), 130.7 (d, *J* = 9.2 Hz), 130.3 (d, *J* = 9.2 Hz), 128.9 (d, *J* = 11.9 Hz), 128.8 (d, *J* = 12.1 Hz), 58.0, 52.9 (d, *J* = 4.4 Hz), 34.9, 34.7 (d, *J* = 69.2 Hz), 24.1 (d, *J* = 7.6 Hz), 12.6.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 25.7

HRMS-ESI: Calcd for $C_{25}H_{25}NO_4P^+$ $[M+H]^+$434.1515, found 434.1514

4-((diphenylphosphoryl)methyl)-4-methyl-2-propyl-2-azaspiro[4.5]deca-6,9-diene-1,3,8-trione (5c)



Compound **5c** was prepared from *N*-methacryloyl-4-methoxy-*N*-propylbenzamide **4c** (52.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (18.6 mg, 0.10 mmol), the solution was charged in constant current mode (5.05 F/mol) (**General Procedure B**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **5c** (70.6 mg, 0.158 mmol, 79%) as yellow oil.

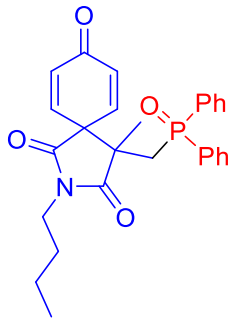
^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.73-7.69 (m, 2H), 7.66-7.61 (m, 2H), 7.50-7.38 (m, 6H), 7.01 (dd, *J* = 10.1 Hz, *J* = 3.0 Hz, 1H), 6.74 (dd, *J* = 10.1 Hz, *J* = 1.7 Hz, 1H), 6.47 (dd, *J* = 10.3 Hz, *J* = 1.7 Hz, 1H), 6.21 (dd, *J* = 10.2 Hz, *J* = 2.1 Hz, 1H), 3.41-3.33 (m, 1H), 3.24-3.16 (m, 1H), 2.91 (dd, *J* = 15.9 Hz, *J* = 11.5 Hz, 1H), 2.61 (dd, *J* = 15.8 Hz, *J* = 9.8 Hz, 1H), 1.57-1.49 (m, 5H), 0.83 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.2, 178.9 (d, *J* = 10.0 Hz), 172.2, 142.9, 142.2, 134.2 (d, *J* = 99.8 Hz), 133.03, 133.01, 133.0 (d, *J* = 100.7 Hz), 132.1 (d, *J* = 2.5 Hz), 132.0 (d, *J* = 2.5 Hz), 130.7 (d, *J* = 9.6 Hz), 130.3 (d, *J* = 9.3 Hz), 128.9 (d, *J* = 11.7 Hz), 128.7 (d, *J* = 11.8 Hz), 58.1, 52.9 (d, *J* = 3.9 Hz), 41.5, 34.5 (d, *J* = 70.4 Hz), 24.3 (d, *J* = 7.1 Hz), 20.8, 11.2.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 25.8

HRMS-ESI: Calcd for $C_{26}H_{27}NO_4P^+$ $[M+H]^+$448.1672, found 448.1673

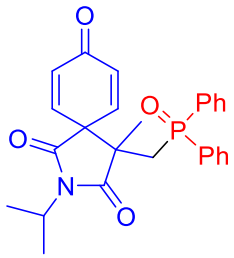
2-butyl-4-((diphenylphosphoryl)methyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-1,3,8-trione (5d)



Compound **5d** was prepared from *N*-butyl-*N*-methacryloyl-4-methoxybenzamide **4d** (55.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (18.6 mg, 0.10 mmol), the solution was charged in constant current mode (5.90 F/mol) (**General Procedure B**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **5d** (77.5 mg, 0.168 mmol, 84%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.72 (dd, *J* = 11.3 Hz, *J* = 7.7 Hz, 2H), 7.64 (dd, *J* = 11.9 Hz, *J* = 7.7 Hz, 2H), 7.51-7.40 (m, 6H), 7.00 (dd, *J* = 10.3 Hz, *J* = 2.4 Hz, 1H), 6.74 (dd, *J* = 10.3 Hz, *J* = 2.7 Hz, 1H), 6.49 (dd, *J* = 10.3 Hz, *J* = 1.0 Hz, 1H), 6.24 (dd, *J* = 10.3 Hz, *J* = 0.9 Hz, 1H), 3.44-3.37 (m, 1H), 3.26-3.18 (m, 1H), 2.92 (dd, *J* = 16.1 Hz, *J* = 11.7 Hz, 1H), 2.61 (dd, *J* = 16.2 Hz, *J* = 9.5 Hz, 1H), 1.53 (s, 3H), 1.51-1.44 (m, 2H), 1.28-1.20 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.2, 178.8 (d, *J* = 10.2 Hz), 172.2, 142.9, 142.2, 134.1 (d, *J* = 100.5 Hz), 130.08, 130.02, 132.8 (d, *J* = 100.5 Hz), 132.1 (d, *J* = 2.5 Hz), 132.0 (d, *J* = 2.5 Hz), 130.7 (d, *J* = 9.3 Hz), 130.3 (d, *J* = 9.1 Hz), 128.9 (d, *J* = 11.9 Hz), 128.8 (d, *J* = 11.9 Hz), 58.1, 52.9 (d, *J* = 4.0 Hz), 39.7, 34.4 (d, *J* = 69.8 Hz), 29.4, 24.1 (d, *J* = 7.2 Hz), 20.0, 13.5.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 25.9.
HRMS-ESI: Calcd for $C_{27}H_{29}NO_4P^+$ $[M+H]^+$462.1828, found 462.1829

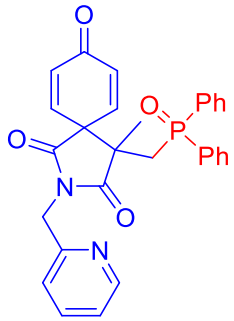
4-((diphenylphosphoryl)methyl)-2-isopropyl-4-methyl-2-azaspiro[4.5]deca-6,9-diene-1,3,8-trione (5e)



Compound **5e** was prepared from *N*-isopropyl-*N*-methacryloyl-4-methoxybenzamide **4e** (52.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (18.6 mg, 0.10 mmol), the solution was charged in constant current mode (7.00 F/mol) (**General Procedure B**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **5e** (74.2 mg, 0.166 mmol, 83%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.74 (dd, *J* = 10.4 Hz, *J* = 7.3 Hz, 2H), 7.62 (dd, *J* = 12.0 Hz, *J* = 7.7 Hz, 2H), 7.53-7.45 (m, 4H), 7.43-7.37 (m, 2H), 6.83 (d, *J* = 9.9 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 6.51 (d, *J* = 9.9 Hz, 1H), 6.15 (d, *J* = 8.5 Hz, 1H), 4.33-4.28 (m, 1H), 2.98 (dd, *J* = 17.0 Hz, *J* = 11.3 Hz, 1H), 2.58 (dd, *J* = 16.5 Hz, *J* = 10.0 Hz, 1H), 1.59 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.2, 179.2 (d, *J* = 12.3 Hz), 172.0, 142.8, 141.8, 134.4 (d, *J* = 97.5 Hz), 133.4, 132.9, 132.4, 132.0, 131.5 (d, *J* = 103.5 Hz), 130.7 (d, *J* = 9.2 Hz), 130.4 (d, *J* = 8.9 Hz), 129.0 (d, *J* = 11.1 Hz), 128.9 (d, *J* = 11.3 Hz), 58.4, 52.9, 45.3, 24.3 (d, *J* = 4.7 Hz), 19.4, 18.7.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 26.1.
HRMS-ESI: Calcd for $C_{26}H_{27}NO_4P^+$ $[M+H]^+$448.1672, found. 448.1673

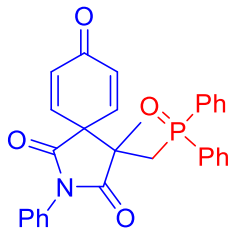
4-((diphenylphosphoryl)methyl)-4-methyl-2-(pyridin-2-ylmethyl)-2-azaspiro[4.5]deca-6,9-diene-1,3,8-trione (5f)



Compound **5f** was prepared from *N*-methacryloyl-4-methoxy-*N*-(pyridin-2-ylmethyl)benzamide **4f** (62.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (18.6 mg, 0.10 mmol), the solution was charged in constant current mode (5.60 F/mol) (**General Procedure B**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **5f** (60.5 mg, 0.122 mmol, 61%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 8.42 (d, *J* = 4.9 Hz, 1H), 7.75 (dd, *J* = 11.4 Hz, *J* = 7.8 Hz, 2H), 7.69 (dd, *J* = 11.7 Hz, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 6.8 Hz, 2H), 7.49-7.43 (m, 4H), 7.27 (s, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 5.4 Hz, 1H), 6.97 (dd, *J* = 10.4, *J* = 2.1 Hz, 1H), 6.49 (d, *J* = 10.2 Hz, 1H), 6.31 (d, *J* = 9.9 Hz, 1H), 4.70 (d, *J* = 15.6 Hz, 1H), 4.45 (d, *J* = 15.6 Hz, 1H), 2.98 (dd, *J* = 16.7 Hz, *J* = 12.0 Hz, 1H), 2.68 (dd, *J* = 16.3 Hz, *J* = 9.7 Hz, 1H), 1.60 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.5, 178.6 (d, *J* = 10.2 Hz), 172.2, 153.4, 149.5, 143.2, 142.8, 136.8, 134.2 (d, *J* = 100.1 Hz), 133.3, 132.9 (d, *J* = 100.2 Hz), 133.8, 132.2 (d, *J* = 2.5 Hz), 132.1 (d, *J* = 2.2 Hz), 130.8 (d, *J* = 9.4 Hz), 130.4 (d, *J* = 9.1 Hz), 128.9 (d, *J* = 12.2 Hz), 128.8 (d, *J* = 12.4 Hz), 122.8, 121.9, 58.3, 53.2 (d, *J* = 3.7 Hz), 43.6, 34.8 (d, *J* = 70.0 Hz), 23.9 (d, *J* =7.3 Hz).
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 25.8
HRMS-ESI: Calcd for $C_{29}H_{26}N_2O_4P^+$ $[M+H]^+$497.1624, found.497.1627

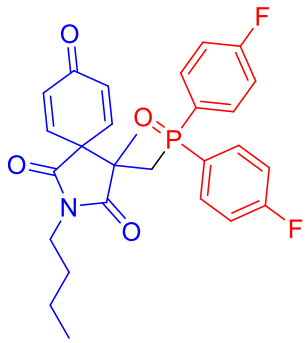
4-((diphenylphosphoryl)methyl)-4-methyl-2-phenyl-2-azaspiro[4.5]deca-6,9-diene-1,3,8-trione (5g)



Compound **5g** was prepared from *N*-methacryloyl-4-methoxy-*N*-phenylbenzamide **4g** (59.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (18.6 mg, 0.10 mmol), the solution was charged in constant current mode (5.60 F/mol) (**General Procedure B**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **5g** (37.5 mg, 0.078 mmol, 39%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.79-7.74 (m, 2H), 7.69-7.64 (m, 2H), 7.54 (td, *J* = 7.1 Hz, *J* = 1.3 Hz, 1H), 7.51-7.46 (m, 3H), 7.45-7.36 (m, 5H), 7.26 (s, 1H), 7.25 (s, 1H), 7.16 (dd, *J* = 10.1 Hz, *J* = 3.1 Hz, 1H), 6.91 (dd, *J* = 10.3 Hz, *J* = 1.7 Hz, 1H), 6.54 (dd, *J* = 10.2 Hz, *J* = 1.7 Hz, 1H), 6.26 (dd, *J* = 10.1 Hz, *J* = 1.7 Hz, 1H), 3.00 (dd, *J* = 15.9 Hz, *J* = 11.4 Hz, 1H), 2.73 (dd, *J* = 15.9 Hz, *J* = 9.7 Hz, 1H), 1.70 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.1, 178.0 (d, *J* = 9.8 Hz), 171.4, 142.7, 142.0, 134.2 (d, *J* = 100.4 Hz), 133.4, 133.3, 133.1 (d, *J* = 101.8 Hz), 132.3 (d, *J* = 2.6 Hz), 132.2 (d, *J* = 2.6 Hz), 131.7, 130.9 (d, *J* = 9.2 Hz), 130.5 (d, *J* = 9.2 Hz), 129.3, 129.1 (d, *J* = 11.7 Hz), 129.0, 128.9 (d, *J* = 12.4 Hz), 128.0, 58.2, 53.1 (d, *J* = 3.7 Hz). 34.8 (d, *J* = 68.6 Hz), 24.5 (d, *J* = 7.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 26.4
HRMS-ESI: Calcd for $C_{29}H_{25}NO_4P^+$ $[M+H]^+$482.1515, found 482.1517

4-((bis(4-fluorophenyl)phosphoryl)methyl)-2-butyl-4-methyl-2-azaspiro[4.5]deca-6,9-diene-1,3,8-trione (5h)

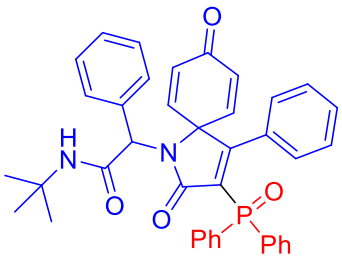


Compound **5h** was prepared from *N*-butyl-*N*-methacryloyl-4-methoxybenzamide **4h** (55.0 mg, 0.2 mmol), bis(4-fluorophenyl)phosphine oxide (95.2 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (18.6 mg, 0.10 mmol), the solution was charged in constant current mode (4.12 F/mol) (**General Procedure B**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column

chromatography to give **5h** (69.5 mg, 0.140 mmol, 70%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.75-7.68 (m, 2H), 7.67-7.60 (m, 2H), 7.17 (td, *J* = 8.8 Hz, *J* = 2.0 Hz, 2H), 7.13 (td, *J* = 8.8 Hz, *J* = 2.0 Hz, 2H), 6.99 (dd, *J* = 10.2 Hz, *J* = 3.1 Hz, 1H), 6.76 (dd, *J* = 10.2 Hz, *J* = 3.1 Hz, 1H), 6.52 (dd, *J* = 10.3 Hz, *J* = 1.7 Hz, 1H), 6.29 (dd, *J* = 10.0 Hz, *J* = 1.8 Hz, 1H), 3.48-3.40 (m, 1H), 3.32-3.25 (m, 1H), 2.88 (dd, *J* = 15.9 Hz, *J* = 11.4 Hz, 1H), 2.56 (dd, *J* =15.9 Hz, *J* = 10.2 Hz, 1H), 1.56-1.46 (m, 5H), 1.29-1.24 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.1, 178.8 (d, *J* = 10.6 Hz), 172.2, 165.2 (dd, *J* = 254.6 Hz, *J* = 3.1 Hz), 165.1 (dd, *J* = 254.3 Hz, *J* = 3.1 Hz), 142.8, 142.1, 133.3, 133.2, 133.1 (dd, *J* = 44.9 Hz, *J* = 8.9 Hz), 133.0 (dd, *J* = 44.9 Hz, *J* = 8.9 Hz), 129.9 (dd, *J* = 103.6 Hz, *J* = 3.4 Hz), 128.9 (dd, *J* = 104.4 Hz, *J* = 3.4 Hz), 116.5 (dd, *J* = 16.9 Hz, *J* = 12.7 Hz), 116.4 (dd, *J* = 17.1 Hz, *J* = 13.2 Hz), 58.1, 53.0 (d, *J* = 3.9 Hz), 39.8, 34.7 (d, *J* = 71.3 Hz), 29.5, 24.4 (d, *J* = 7.2 Hz), 20.0, 13.6.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 25.0
^{19}F NMR (470 MHz, $CDCl_3$, 300K): δ (ppm) -105.7, -105.9
HRMS-ESI: Calcd for $C_{27}H_{27}F_2NO_4P^+$ $[M+H]^+$498.1640, found 498.1642

***N*-(*tert*-butyl)-2-(3-(diphenylphosphoryl)-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)-2-phenylacetamide (7a)**



Compound **7a** was prepared from *N*-(2-(tert-butylamino)-2-oxo-1-phenylethyl)-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **6a** (88.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (6.53 F/mol) (**General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Concentrated sulfuric acid (0.018 mL) was added, and the mixture was allowed to stir for 3h at 80℃ in air. Purified by silica gel column chromatography to give **7a** (68.0 mg, 0.108 mmol, 54%) as yellow solid.

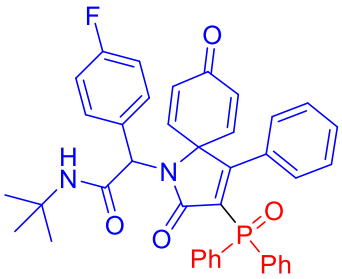
^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.78 (dd, *J* = 13.1 Hz, *J* = 7.4 Hz, 2H), 7.66 (dd, *J* = 13.1 Hz, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.41-7.35 (m, 3H), 7.35 (s, 1H) 7.33 (s, 1H), 7.30-7.26 (m, 5H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.3 Hz, 2H), 6.94 (d, *J* = 7.4 Hz, 2H), 6.68 (t, *J* = 9.2 Hz, 2H), 6.13 (t, *J* = 10.0 Hz, 2H), 5.59 (s, 1H), 4.91 (s, 1H), 1.22 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.9, 169.8 (d, *J* = 4.7 Hz), 168.8 (d, *J* = 13.6 Hz), 167.4, 144.07, 144.00, 134.6, 132.7, 132.4, 131.9, 131.87, 131.83 (d, *J* = 110.5 Hz), 131.75 (d, *J* = 10.5 Hz), 131.72 (d, *J* = 110.5 Hz), 131.6 (d, *J* = 10.3 Hz), 131.4 (d, *J* = 100.0 Hz), 129.8, 129.4,

129.2, 128.9, 128.4 (d, J = 12.5 Hz), 128.3, 128.2 (d, J = 12.8 Hz), 127.6, 70.9 (d, J = 10.1 Hz), 62.7, 51.9, 28.4.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 18.2

HRMS-ESI: Calcd for $C_{39}H_{36}N_2O_4P^+$ $[M+H]^+$627.2407, found 627.2410

***N*-(*tert*-butyl)-2-(3-(diphenylphosphoryl)-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)-2-(4-fluorophenyl)acetamide (7b)**



Compound **7b** was prepared from *N*-(2-(tert-butylamino)-1-(4-fluorophenyl)-2-oxoethyl)-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **6b** (91.6 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (7.15 F/mol) (**General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Concentrated sulfuric acid (0.018 mL) was added, and the mixture was allowed to stir for 3h at 80℃ in air. Purified by silica gel column chromatography to give **7b** (90.0 mg, 0.140 mmol, 70%) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.77 (dd, J = 12.7 Hz, J = 7.6 Hz, 2H), 7.63 (dd, J = 13.0 Hz, J = 7.6 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 7.42-7.33 (m, 5H), 7.27-7.23 (m, 2H), 7.14 (t, J = 7.5 Hz, 1H), 7.03 (t, J = 7.3 Hz, 2H), 6.99-6.92 (m, 4H), 6.75 (d, J = 9.2 Hz, 1H), 6.61 (d, J = 9.8 Hz, 1H), 6.23 (d, J = 9.7 Hz, 1H), 6.14 (d, J = 9.7 Hz, 1H), 5.61 (s, 1H), 4.83 (s, 1H), 1.22 (s, 9H).

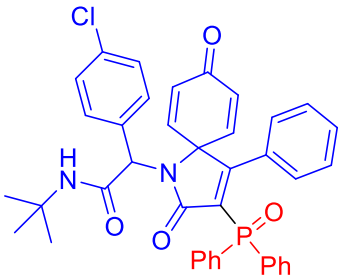
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.7, 169.7 (d, J = 4.0 Hz), 168.8 (d, J = 13.4 Hz), 167.2, 163.0 (d, J = 250.7 Hz), 143.94, 143.90, 133.0, 132.5, 132.0 (d, J = 2.5 Hz), 131.9 (d, J = 2.5 Hz), 131.69 (d, J = 10.3 Hz), 131.68 (d, J = 110.4 Hz), 131.57 (d, J = 110.5 Hz), 131.53 (d, J = 10.1 Hz), 131.3 (d, J = 8.3 Hz), 130.9, 130.7 (d, J = 3.3 Hz), 129.8, 129.7 (d, J = 2.4 Hz), 128.4 (d, J = 12.7 Hz), 128.3, 128.2 (d, J = 12.7 Hz), 127.6, 116.0 (d, J = 21.6 Hz), 70.9 (d, J = 11.1 Hz), 62.0, 52.0, 28.4.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 17.9

^{19}F NMR (470 MHz, $CDCl_3$, 300K): δ (ppm) -111.6

HRMS-ESI: Calcd for $C_{39}H_{35}FN_2O_4P^+$ $[M+H]^+$645.2313, found 645.2316

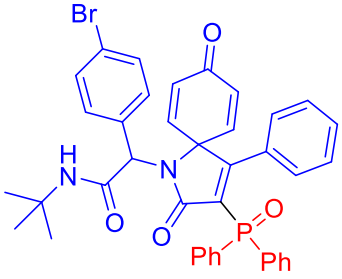
***N*-(*tert*-butyl)-2-(4-chlorophenyl)-2-(3-(diphenylphosphoryl)-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetamide (7c)**



Compound **7c** was prepared from *N*-(2-(tert-butylamino)-1-(4-chlorophenyl)-2-oxoethyl)-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **6c** (94.8mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (4.97 F/mol) (**General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Concentrated sulfuric acid (0.018 mL) was added, and the mixture was allowed to stir for 3h at 80℃ in air. Purified by silica gel column chromatography to give **7c** (88.4 mg, 0.134 mmol, 67%) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.77 (d, *J* = 12.8 Hz, *J* = 7.5 Hz, 2H), 7.64 (dd, *J* = 12.8 Hz, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.0 Hz, 1H), 7.40 (td, *J* = 7.7 Hz, *J* = 2.5 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.28-7.24 (m, 4H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.78 (dd, *J* = 10.1 Hz, *J* = 2.3 Hz, 1H), 6.59 (dd, *J* =10.0 Hz, *J* = 2.3 Hz, 1H), 6.28 (d, *J* = 10.0 Hz, 1H), 6.15 (dd, *J* = 10.0 Hz, *J* = 1.1 Hz, 1H), 5.74 (s, 1H), 4.81 (s, 1H), 1.22 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.5, 169.6 (d, *J* = 4.6 Hz), 168.7 (d, *J* = 13.5 Hz), 166.9, 143.69, 143.67, 135.0, 133.2, 133.0, 132.5, 131.9 (d, *J* = 2.2 Hz), 131.8 (d, *J* = 2.4 Hz), 131.55 (d, *J* = 10.2 Hz), 131.54 (d, *J* = 110.5 Hz), 131.41 (d, *J* = 109.8 Hz), 131.40 (d, *J* = 10 Hz), 131.2 (d, *J* = 100.2 Hz), 130.8, 129.8, 129.6 (d, *J* = 2.3 Hz), 129.0, 128.3 (d, *J* = 13.1 Hz), 128.2, 128.17 (d, *J* = 12.6 Hz), 127.6, 70.8 (d, *J* = 10.7 Hz), 62.0, 51.8, 28.3.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 17.9.
HRMS-ESI: Calcd for $C_{39}H_{35}ClN_2O_4P^+$ $[M+H]^+$661.2017, found 661.2016

2-(4-bromophenyl)-*N*-*(tert*-butyl)-2-(3-(diphenylphosphoryl)-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetamide (7d)

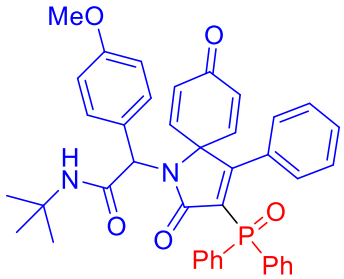


Compound **7d** was prepared from *N*-(1-(4-bromophenyl)-2-(tert-butylamino)-2-oxoethyl)-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **6d** (94.8mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (6.53 F/mol) (**General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed

by aqueous work-up. After Concentrated sulfuric acid (0.018 mL) was added, and the mixture was allowed to stir for 3h at 80℃ in air. Purified by silica gel column chromatography to give **7d** (84.6 mg, 0.120 mmol, 60%) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.76 (dd, *J* = 13.1 Hz, *J* = 7.5 Hz, 2H), 7.62 (dd, *J* = 13.1 Hz, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.40-7.37 (m, 4H), 7.34 (t, *J* = 7.1 Hz, 1H), 7.26-7.21 (m, 4H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 9.2 Hz, 1H), 6.55 (d, *J* = 9.1 Hz, 1H), 6.27 (d, *J* = 10.1 Hz, 1H), 6.14 (d, *J* = 9.7 Hz, 1H), 5.72 (s, 1H), 4.76 (s, 1H), 1.20 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.6, 169.6 (d, *J* = 4.3 Hz), 168.8 (d, *J* = 13.6 Hz), 166.8, 143.7, 143.6, 133.8, 133.2, 132.6, 132.0, 131.9 (d, *J* = 2.3 Hz), 131.8 (d, *J* = 2.1 Hz), 131.6 (d, *J* = 10.3 Hz), 131.5 (d, *J* = 110.4 Hz), 131.45 (d, *J* = 10.2 Hz), 131.44 (d, *J* = 110.1 Hz), 131.3 (d, *J* = 100.8 Hz), 130.8, 129.8, 129.6 (d, *J* = 2.4 Hz), 128.4 (d, *J* = 12.7 Hz), 128.26, 128.21 (d, *J* = 11.9 Hz), 127.6, 123.3, 70.9 (d, *J* = 10.6 Hz), 62.2, 51.9, 28.3.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 17.9
HRMS-ESI: Calcd for $C_{39}H_{35}BrN_2O_4P^+$ $[M+H]^+$705.1512, found 705.1509

***N*-(*tert*-butyl)-2-(3-(diphenylphosphoryl)-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)-2-(4-methoxyphenyl)acetamide (7e)**



Compound **7e** was prepared from *N*-(2-(tert-butylamino)-1-(4-methoxyphenyl)-2-oxoethyl)-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **6e** (94.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (8.24 F/mol) (**General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Concentrated sulfuric acid (0.018 mL) was added, and the mixture was allowed to stir for 3h at 80℃ in air. Purified by silica gel column chromatography to give **7e** (43.3 mg, 0.066 mmol, 33%) as yellow solid.

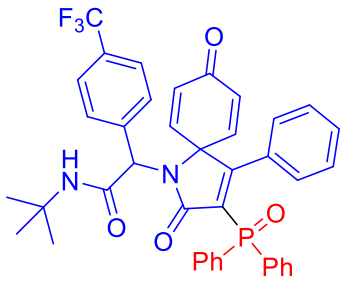
^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.76 (dd, *J* = 12.7 Hz, *J* = 7.3 Hz, 2H), 7.64 (dd, *J* = 12.7 Hz, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 6.9 Hz, 1H), 7.39-7.34 (m, 3H), 7.27-7.23 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 2H), 6.67 (dd, *J* = 17.5 Hz, *J* = 9.8 Hz, 2H), 6.12 (d, *J* = 10.0 Hz, 2H), 5.55 (s, 1H), 4.88 (s, 1H), 3.75 (s, 3H), 1.22 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.9, 169.6 (d, *J* = 5.7 Hz), 168.7 (d, *J* = 13.9 Hz), 167.6, 160.2, 144.3, 144.0, 132.29, 132.22, 131.9 (d, *J* = 2.3 Hz), 131.8 (d, *J* = 2.6 Hz), 131.7 (d, *J* = 110.2 Hz), 131.69 (d, *J* = 10.2 Hz), 131.63 (d, *J* = 110.2 Hz), 131.5 (d, *J* = 10.5 Hz), 131.1, 130.9, 129.8 (d, *J* = 2.4 Hz) 129.7, 128.4 (d, *J* = 12.6 Hz), 128.3, 128.2 (d, *J* = 12.8 Hz), 127.5, 126.5,

114.1, 70.8 (d, J = 10.1 Hz), 61.9, 55.4, 51.8, 28.4.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 18.1

HRMS-ESI: Calcd for $C_{40}H_{38}N_2O_4P^+$ $[M+H]^+$657.2512, found 657.2510

***N*-(*tert*-butyl)-2-(3-(diphenylphosphoryl)-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)-2-(4-(trifluoromethyl)phenyl)acetamide (7f)**



Compound **7f** was prepared from *N*-(2-(tert-butylamino)-2-oxo-1-(4-(trifluoromethyl)phenyl)ethyl)-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **6f** (101.6 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (7.77 F/mol) **(General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Concentrated sulfuric acid (0.018 mL) was added, and the mixture was allowed to stir for 3 h at 80℃ in air. Purified by silica gel column chromatography to give **7f** (50.0 mg, 0.072 mmol, 36%) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.80 (dd, J = 12.6 Hz, J = 7.3 Hz, 2H), 7.63 (dd, J = 13.5 Hz, J = 7.3 Hz, 2H), 7.57-7.47 (m, 5H), 7.42 (td, J = 7.7 Hz, J = 2.8 Hz, 2H), 7.36 (td, J = 7.7 Hz, J = 1.0 Hz, 1H), 7.27 (d, J = 3.0 Hz, 1H), 7.24 (d, J = 2.8 Hz, 1H), 7.14 (t, J = 7.3 Hz, 1H), 7.06 (t, J = 7.7 Hz, 2H), 6.99 (d, J = 7.5 Hz, 2H), 6.82 (dd, J = 10.1 Hz, J = 3.1 Hz, 1H), 6.51 (dd, J = 9.9 Hz, J = 2.8 Hz, 1H), 6.36 (dd, J = 9.4 Hz, J = 0.7 Hz, 1H), 6.18 (dd, J = 10.0 Hz, J = 1.5 Hz, 1H), 5.75 (s, 1H), 4.81 (s, 1H), 1.21 (s, 9H).

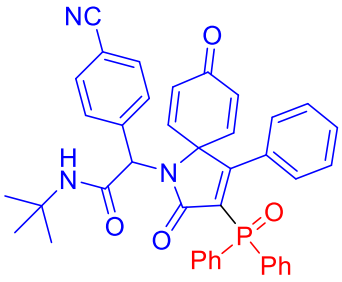
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.5, 169.9 (d, J = 4.9 Hz), 169.1 (d, J = 13.5 Hz), 166.7, 143.4, 143.3, 138.9, 133.7, 133.1, 132.1 (d, J = 2.7 Hz), 131.9 (d, J = 2.7 Hz), 131.7 (d, J = 10.5 Hz), 131.68 (d, J = 110.8 Hz), 131.54 (d, J = 10.5 Hz), 131.51 (d, J = 110.8 Hz), 131.4, 131.1, 130.1, 129.7 (d, J = 3.1 Hz), 129.2, 128.5 (d, J = 13.0 Hz), 128.34 (d, J = 11.5 Hz), 128.30, 127.8, 126.0 (q, J = 3.7 Hz), 123.8 (q, J = 272.2 Hz), 71.1 (d, J = 10.1 Hz), 62.8, 52.1, 28.4.

^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 17.8

^{19}F NMR (470 MHz, $CDCl_3$, 300K): δ (ppm) -62.8

HRMS-ESI: Calcd for $C_{40}H_{35}F_3N_2O_4P^+$ $[M+H]^+$695.2281, found 695.2282

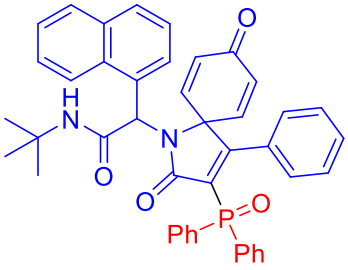
***N*-(*tert*-butyl)-2-(4-cyanophenyl)-2-(3-(diphenylphosphoryl)-2,8-dioxo-4-phenyl-1 azaspiro[4.5]deca-3,6,9-trien-1-yl)acetamide (7g)**



Compound **7g** was prepared from *N*-(2-(tert-butylamino)-1-(4-cyanophenyl)-2-oxoethyl)-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **6g** (93.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (6.61 F/mol) (**General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After concentrated sulfuric acid (0.018 mL) was added, and the mixture was allowed to stir for 3h at 80℃ in air. Purified by silica gel column chromatography to give **7g** (60.0 mg, 0.086 mmol, 43%) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.79-7.74 (m, 2H), 7.62-7.57 (m, 4H), 7.51-7.46 (m, 3H), 7.41 (td, *J* = 7.2 Hz, *J* = 2.9 Hz, 2H), 7.35 (td, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H), 7.24 (td, *J* = 7.8 Hz, *J* = 3.0 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.80 (dd, *J* = 10.1 Hz, *J* = 3.0 Hz, 1H), 6.51 (dd, *J* = 10.0 Hz, *J* = 3.0 Hz, 1H), 6.37 (dd, *J* = 10.0 Hz, *J* = 1.6 Hz, 1H), 6.18 (dd, *J* = 10.1 Hz, *J* = 1.6 Hz, 1H), 5.90 (s, 1H), 4.80 (s, 1H), 1.20 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.3, 169.8 (d, *J* = 4.6 Hz), 169.1 (d, *J* = 13.4 Hz), 166.4, 143.2, 143.0, 140.0, 133.7, 133.2, 132.6, 132.1 (d, *J* = 2.2 Hz), 131.9 (d, *J* = 2.2 Hz), 131.58 (d, *J* = 10.2 Hz), 131.50 (d, *J* = 110.7 Hz), 131.4 (d, *J* = 10.3 Hz), 131.32 (d, *J* = 100.7 Hz), 131.31 (d, *J* = 110.1 Hz), 130.1, 129.5 (d, *J* = 2.2 Hz), 129.4, 128.5 (d, *J* = 12.7 Hz), 128.3 (d, *J* = 12.8 Hz), 128.2, 127.8, 118.1, 121.9, 71.0 (d, *J* = 10.6 Hz), 62.8, 52.1, 28.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 17.7
HRMS-ESI: Calcd for $C_{40}H_{35}N_3O_4P^+$ $[M+H]^+$652.2359, found 652.2362

***N*-(*tert*-butyl)-2-(3-(diphenylphosphoryl)-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)-2-(naphthalen-1-yl)acetamide (7h)**

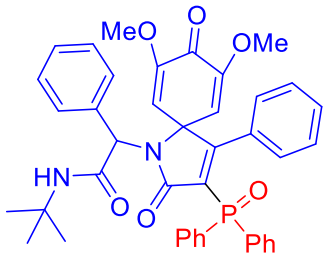


Compound **7h** was prepared from *N*-(2-(tert-butylamino)-1-(naphthalen-2-yl)-2-oxoethyl)-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **6h** (98.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (7.00 F/mol) (**General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After concentrated sulfuric acid (0.018 mL) was added, and the mixture was

allowed to stir for 3h at 80℃ in air. Purified by silica gel column chromatography to give **7h** (75.0mg, 0.110 mmol, 55%) as yellow solid.

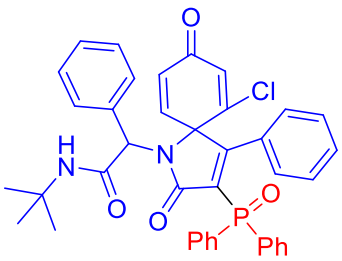
^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.86-7.63 (m, 8H), 7.57-7.27 (m, 7H), 7.18-6.91 (m, 6H), 6.80 (d, *J* = 5.6 Hz, 1H), 6.60 (d, *J* = 5.5 Hz, 1H), 6.16 (d, *J* = 7.5 Hz, 1H), 6.10 (d, *J* = 7.4 Hz, 1H), 5.59 (s, 1H), 4.97 (s, 1H), 1.20 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 183.6, 169.7, 168.8 (d, *J* = 6.9 Hz), 167.2, 143.9 (d, *J* = 3.1 Hz), 133.1, 132.9 (d, *J* = 2.6 Hz), 132.4, 132.1, 131.9, 131.7, 131.69, 131.63 (overlapped), 131.55, 131.50 (overlapped), 129.78 (overlapped), 129.75, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 127.7, 127.5, 127.0, 126.7, 126.3, 70.9 (d, *J* = 6.8 Hz), 62.9, 51.9, 28.3.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 18.0
HRMS-ESI: Calcd for $C_{43}H_{37}N_2O_4P^+$ $[M+H]^+$677.2563, found 677.2567

***N*-(*tert*-butyl)-2-(3-(diphenylphosphoryl)-7,9-dimethoxy-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)-2-phenylacetamide (7i)**



Compound **7i** was prepared from *N*-(2-(tert-butylamino)-2-oxo-1-phenylethyl)-3-phenyl-*N*-(3,4,5-trimethoxyphenyl)propiolamide **6i** (100.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (8.40 F/mol) (**General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After concentrated sulfuric acid (0.018 mL) was added, and the mixture was allowed to stir for 3h at 80℃ in air. Purified by silica gel column chromatography to give **7i** (56.2 mg, 0.082 mmol, 41%) as yellow solid.
^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.80 (dd, *J* = 12.2 Hz, *J* = 7.5 Hz, 2H), 7.68 (dd, *J* = 12.5 Hz, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.0 Hz, 1H), 7.39 (td, *J* = 7.1 Hz, *J* = 2.0 Hz, 3H), 7.35 (d, *J* = 6.3 Hz, 2H), 7.29-7.26 (m, 5H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.4 Hz, 2H), 5.60 (d, *J* = 6.8 Hz, 2H), 5.51 (s, 1H), 4.91 (s, 1H), 3.60 (s, 3H), 3.38 (s, 3H), 1.23 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 175.1, 172.2 (d, *J* = 4.2 Hz), 168.1 (d, *J* = 13.5 Hz), 167.4, 153.1, 152.5, 135.0, 132.0 (d, *J* = 110.0 Hz), 131.9 (d, *J* = 110.0 Hz), 131.8 (d, *J* = 2.5 Hz), 131.78 (d, *J* = 2.5 Hz), 131.70 (d, *J* = 10.7 Hz), 131.5 (d, *J* = 10.5 Hz), 130.1 (d, *J* = 2.8 Hz), 129.8 (d, *J* = 101.9 Hz), 129.6, 129.4, 129.1, 128.9, 128.4 (d, *J* = 12.8 Hz), 128.2 (d, *J* = 12.8 Hz), 128.1, 127.6, 111.6, 111.4, 70.7 (d, *J* = 10.9 Hz), 62.1, 55.9, 55.7, 51.8, 28.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 18.0
HRMS-ESI: Calcd for $C_{41}H_{40}N_2O_6P^+$ $[M+H]^+$687.2618, found 687.2617

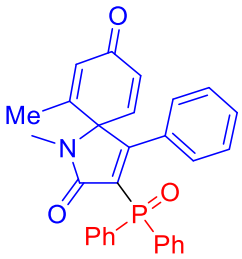
***N*-(*tert*-butyl)-2-(6-chloro-3-(diphenylphosphoryl)-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)-2-phenylacetamide (7j)**



Compound **7j** was prepared from *N*-(2-(tert-butylamino)-2-oxo-1-phenylethyl)-*N*-(2-chloro-4-methoxyphenyl)-3-phenylpropiolamide **6j** (94.8 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (10.26 F/mol) (**General Procedure C**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Concentrated sulfuric acid (0.018 mL) was added, and the mixture was allowed to stir for 3 h at 80℃ in air. Purified by silica gel column chromatography to give **6j** (56.7 mg, 0.086 mmol, 43%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.85-7.80 (m, 2H), 7.69-7.66 (m, 2H), 7.51 (td, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 7.45-7.37 (m, 3H), 7.32-7.26 (m, 5H), 7.22-7.16 (m, 3H), 7.14-7.06 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.17 (dd, *J* = 10.0 Hz, *J* = 1.6 Hz, 1H), 6.07 (d, *J* = 1.5 Hz, 1H), 6.00 (s, 1H), 5.25 (s, 1H), 1.26 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 182.6, 169.6 (d, *J* = 13.5 Hz), 168.6 (d, *J* = 4.9 Hz), 167.6, 148.9, 143.5, 132.91, 132.90 (d, *J* = 99.8 Hz), 132.56, 132.52 (d, *J* = 109.8 Hz), 132.2 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 2.7 Hz), 131.82, 131.80 (d, *J* = 109.2 Hz), 131.7 (d, *J* = 10.3 Hz), 131.6 (d, *J* = 10.3 Hz), 131.53 (d, *J* = 110.8 Hz), 131.51, 130.17, 130.13, 129.5, 128.9 (d, *J* = 2.5 Hz), 128.5 (d, *J* = 12.9 Hz), 128.36 (d, *J* = 13.1 Hz), 128.30, 1281, 127.8, 73.5 (d, *J* = 10.6 Hz), 62.9, 51.9, 28.5.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 17.9
HRMS-ESI: Calcd for $C_{39}H_{35}ClN_2O_4P^+$ $[M+H]^+$661.2017, found 661.2018

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

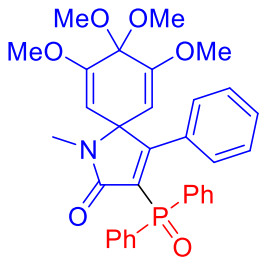


Compound **9a** was prepared from *N*-(4-methoxy-2-methylphenyl)-*N*-methyl-3-phenylpropiolamide **8a** (55.8 mg, 0.2 mmol), diphenylphosphine oxide (121.2 mg, 0.6 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (11.04 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up. After Acetic acid (0.1 mL) was added, and the mixture was allowed to stir for 1h at room temperature in air. Purified

by silica gel column chromatography to give **9a** (80.0 mg, 0.172 mmol, 86%, *dr* = 95:5) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.82-7.74 (m, 4H), 7.51-7.46 (m, 2H), 7.43-7.38 (m, 4H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.45 (dd, *J* = 18.0 Hz, *J* = 9.8 Hz, 2H), 6.31 (s, 1H), 2.73 (s, 3H), 1.79 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 184.4, 169.2 (d, *J* = 4.6 Hz), 168.8 (d, *J* = 14.6 Hz), 151.9, 144.0, 133.3, 132.6, 132.21, 132.20, 131.9 (d, *J* = 110.1 Hz), 131.8 (d, *J* = 110.0 Hz), 131.7 (d, *J* = 10.7 Hz), 131.6 (d, *J* = 109.7 Hz), 131.5 (d, *J* = 10.7 Hz), 130.4, 130.0 (d, *J* = 2.5 Hz), 128.5 (d, *J* = 12.7 Hz), 128.4 (d, *J* = 12.9 Hz), 128.1, 127.9, 71.9 (d, *J* = 10.3 Hz), 25.8, 17.9.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 18.4
HRMS-ESI: Calcd for $C_{29}H_{25}NO_3P^+$ $[M+H]^+$466.1566, found 466.1564

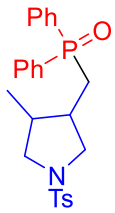
3-(diphenylphosphoryl)-7,8,8,9-tetramethoxy-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-2-one (9b)



Compound **9b** was prepared from *N*-methyl-3-phenyl-*N*-(3,4,5-trimethoxyphenyl)propiolamide **8b** (65.0 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (11.34 F/mol) **(General Procedure A)**. The consumption of the starting material was checked by TLC (20% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography to give **9b** (76.8 mg, 0.138 mmol, 69%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.76 (dd, *J* = 12.5 Hz, *J* = 7.0 Hz, 4H), 7.44 (t, *J* = 6.3 Hz, 2H), 7.40-7.35 (m, 4H), 7.14 (t, *J* = 7.0 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 2H), 6.98 (d, *J* = 6.0 Hz, 2H), 4.65 (s, 2H), 3.62 (s, 6H), 3.27 (s, 3H), 2.78 (s, 3H), 2.26 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 174.4 (d, *J* = 3.4 Hz), 167.1 (d, *J* = 14.3 Hz), 155.7, 132.5, 131.8 (d, *J* = 2.2 Hz), 131.69, 131.60, 131.4 (d, *J* = 2.6 Hz), 129.2 (d, *J* = 108.5 Hz), 128.7, 128.5, 128.4 (d, *J* = 110.4 Hz), 128.39, 128.30, 128.2, 128.07 (d, *J* = 110.4 Hz), 128.01, 127.2, 98.9, 94.9, 69.7, (d, *J* = 11.5 Hz), 55.6, 52.4, 51.1, 25.3.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 18.4
HRMS-ESI: Calcd for $C_{32}H_{33}NO_6P^+$ $[M+H]^+$558.2040, found 558.2041

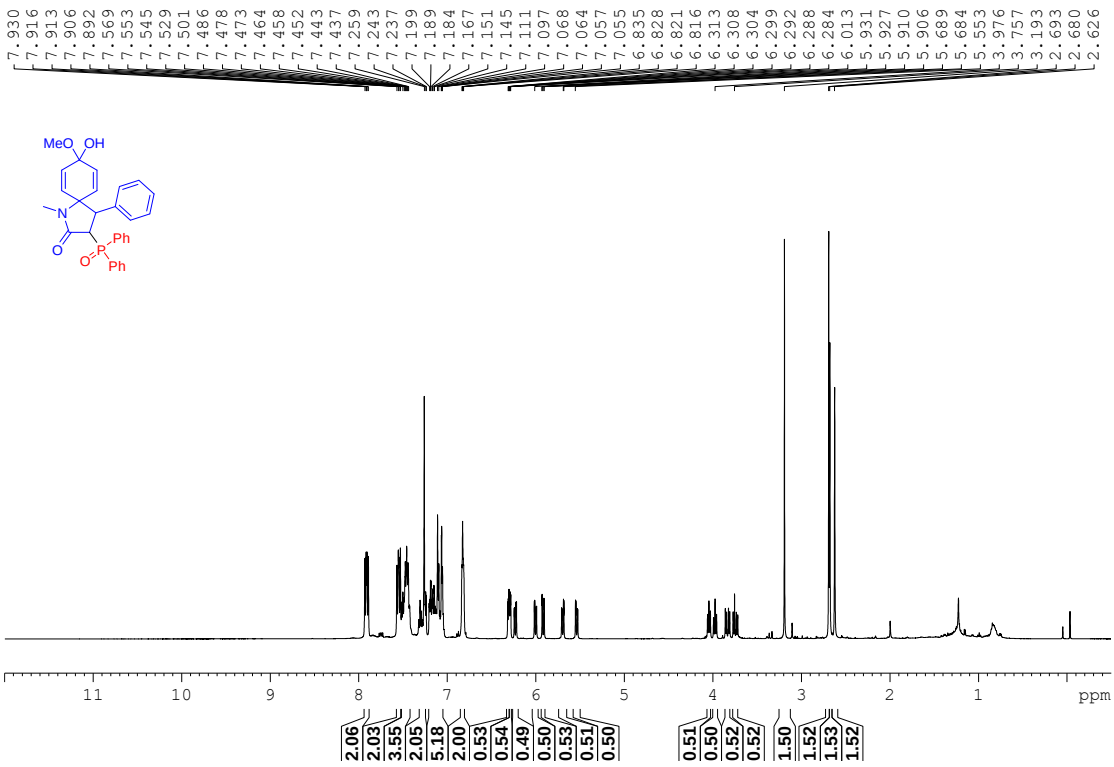
((4-methyl-1-tosylpyrrolidin-3-yl)methyl)diphenylphosphine oxide (**15**)



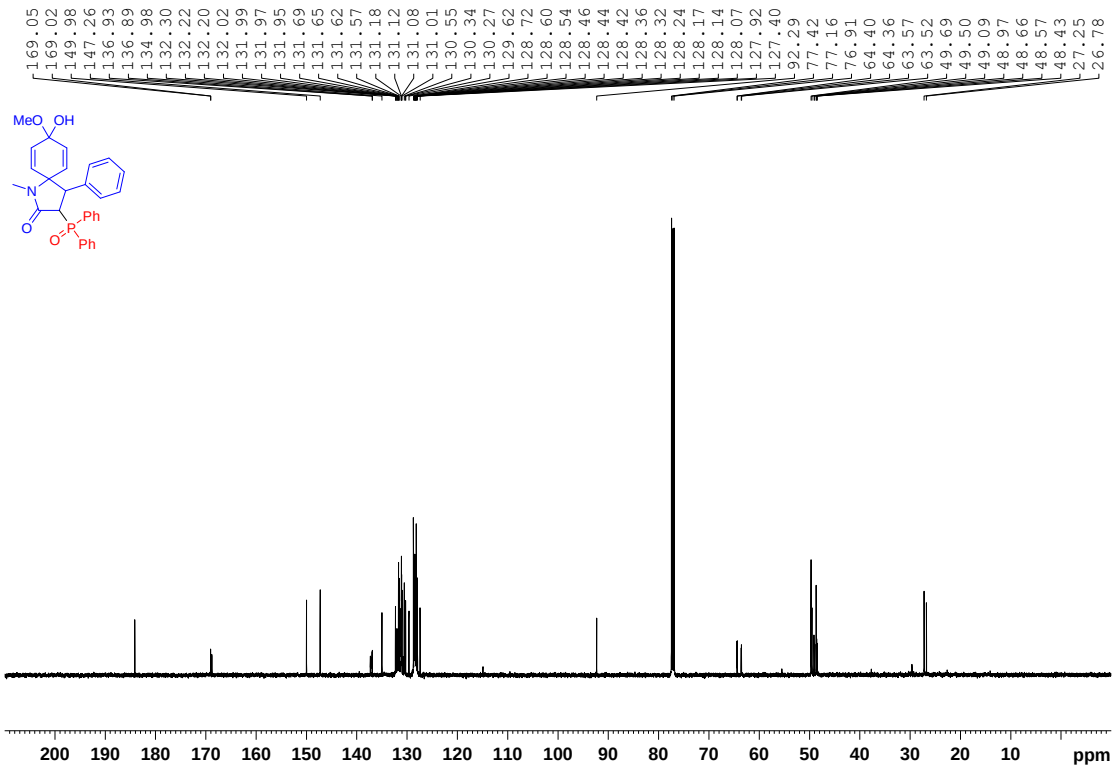
Compound **15** was prepared from *N,N*-diallyl-4-methylbenzenesulfonamide **14** (50.2 mg, 0.2 mmol), diphenylphosphine oxide (80.8 mg, 0.4 mmol), tetrabutylammonium acetate (60.3 mg, 0.2 mmol), ferrocene (11.1 mg, 0.06 mmol), the solution was charged in constant current mode (2.77 F/mol) (**General Procedure A**). The consumption of the starting material was checked by TLC (10% EtOAc/petroleum ether), followed by aqueous work-up, purified by silica gel column chromatography using EtOAc/petroleum ether as the eluent to give **15** (70.6 mg, 0.156 mmol, 78%, *dr* = 90 :10) as white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ (ppm) 7.71-7.65 (m, 4H), 7.63-7.58 (m, 2H), 7.56-7.43 (m, 6H), 7.27-7.25 (m, 2H), 3.46 (dd, *J* = 9.8 Hz, *J* = 6.7 Hz, 0.2H), 3.40 (dd, *J* = 10.6 Hz, *J* = 6.8 Hz, 0.2H), 3.27 (dd, *J* = 10.0 Hz, *J* = 7.2 Hz, 0.9H), 3.24 (dd, *J* = 9.5 Hz, *J* = 6.7 Hz, 0.9H), 3.00 (dd, *J* = 7.7 Hz, *J* = 4.0 Hz, 0.9H), 2.99 (dd, *J* = 7.9 Hz, *J* = 3.4 Hz, 0.9H), 2.84 (dd, *J* = 10.7 Hz, *J* = 8.1 Hz, 0.2H), 2.67 (dd, *J* = 9.7 Hz, *J* = 8.3 Hz, 0.2H), 2.41-2.32 (m, 3.9H), 2.26-2.16 (m, 1.8H), 2.04-1.98 (m, 0.9H), 0.87 (d, *J* = 6.0 Hz, 0.3H), 0.75 (d, *J* = 7.0 Hz, 2.7H).
^{13}C NMR (125 MHz, $CDCl_3$, 300K): δ (ppm) 143.45 (minor), 143.42, 133.9, 133.7 (minor), 133.2 (d, *J* = 1.7 Hz, minor), 133.0 (d, *J* = 98.5 Hz), 132.7 (d, *J* = 99.0 Hz), 132.5 (d, *J* = 2.6 Hz, minor), 132.1 (d, *J* = 2.6 Hz), 132.0 (d, *J* = 2.4 Hz), 130.8 (d, *J* = 1.2 Hz), 130.7 (minor), 130.7 (d, *J* = 1.4 Hz), 130.7 (minor, overlapped), 129.7, 129.7 (minor, overlapped), 128.95 (d, *J* = 3.4 Hz), 128.94 (minor, overlapped), 128.86 (d, *J* = 3.5 Hz), 128.85 (minor, overlapped), 127.6 (minor), 127.5, 54.2, 53.8 (minor), 53.6 (d, *J* = 3.3 Hz, minor), 51.6 (d, *J* = 6.0 Hz), 40.4 (d, *J* = 12.4 Hz, minor), 39.8 (d, *J* = 3.7 Hz, minor), 36.3 (d, *J* = 9.5 Hz), 35.9 (d, *J* = 3.3 Hz), 32.4 (d, *J* = 70.0 Hz, minor), 28.3 (d, *J* = 73.2 Hz), 21.65 (minor), 21.63, 15.9 (minor), 13.4.
^{31}P NMR (162 MHz, $CDCl_3$, 300K): δ (ppm) 30.2, 29.7
HRMS-ESI: Calcd for $C_{25}H_{29}NO_3PS^+$ $[M+H]^+$454.1601, found 454.1599.

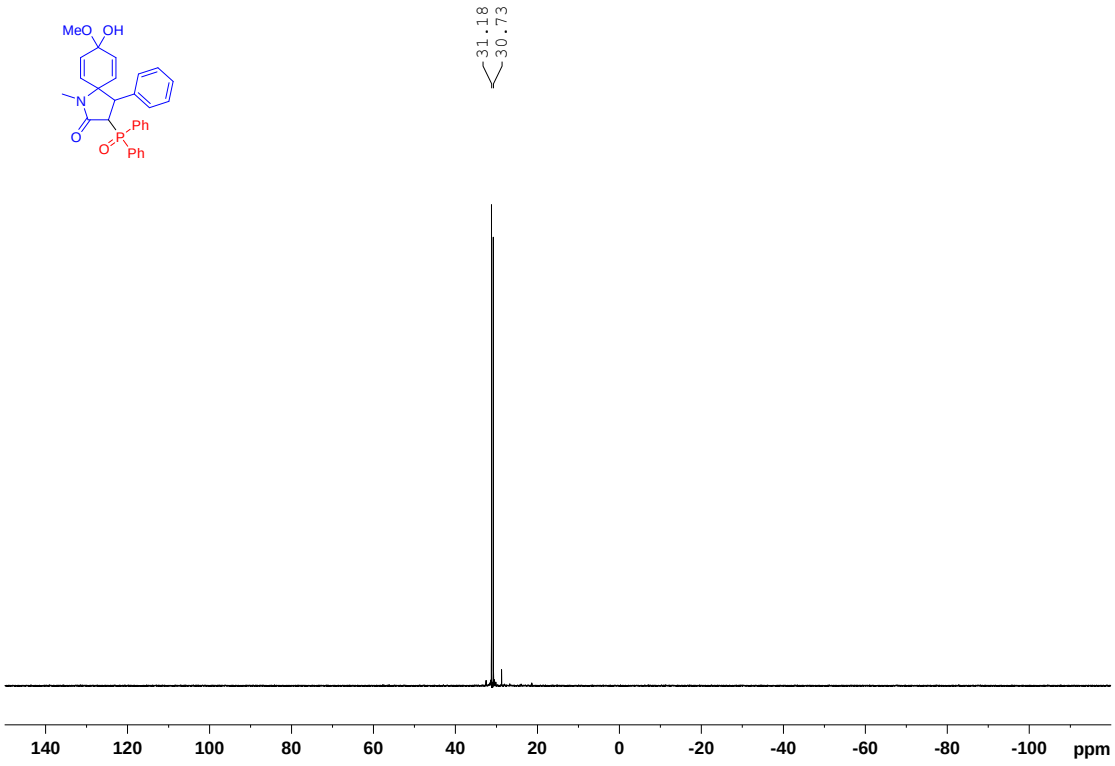
^{1}H NMR (500 MHz, $CDCl_3$, 300K):**3aa**



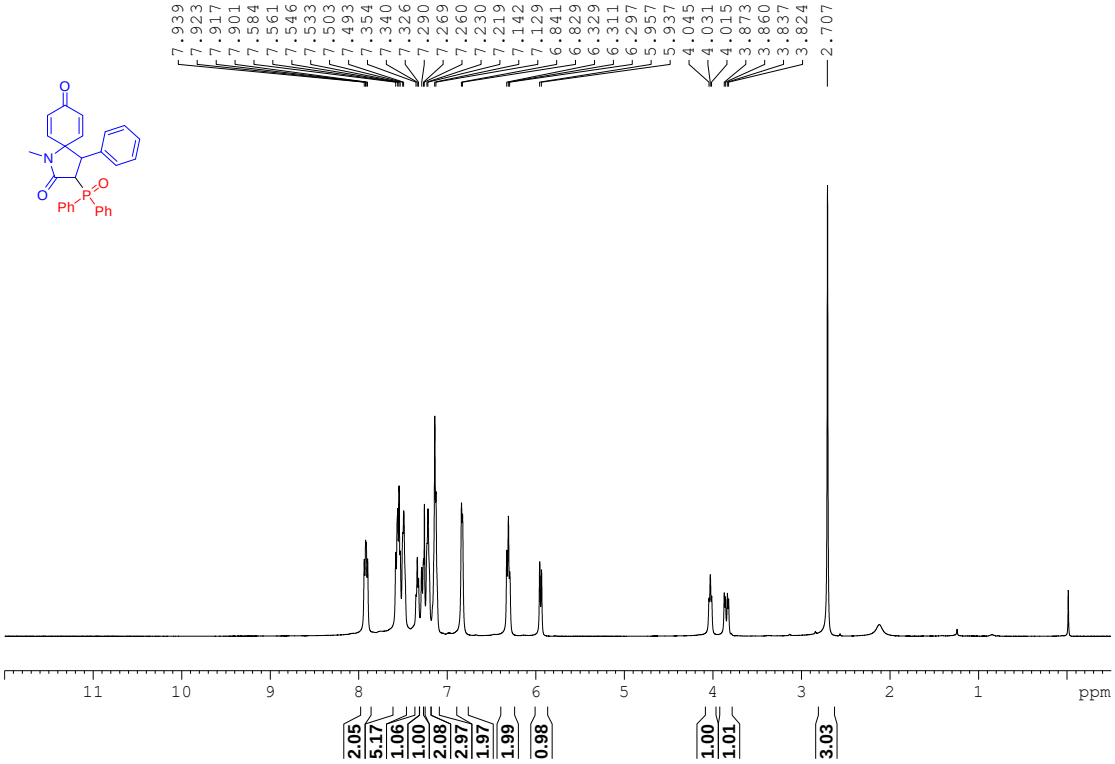
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3aa**



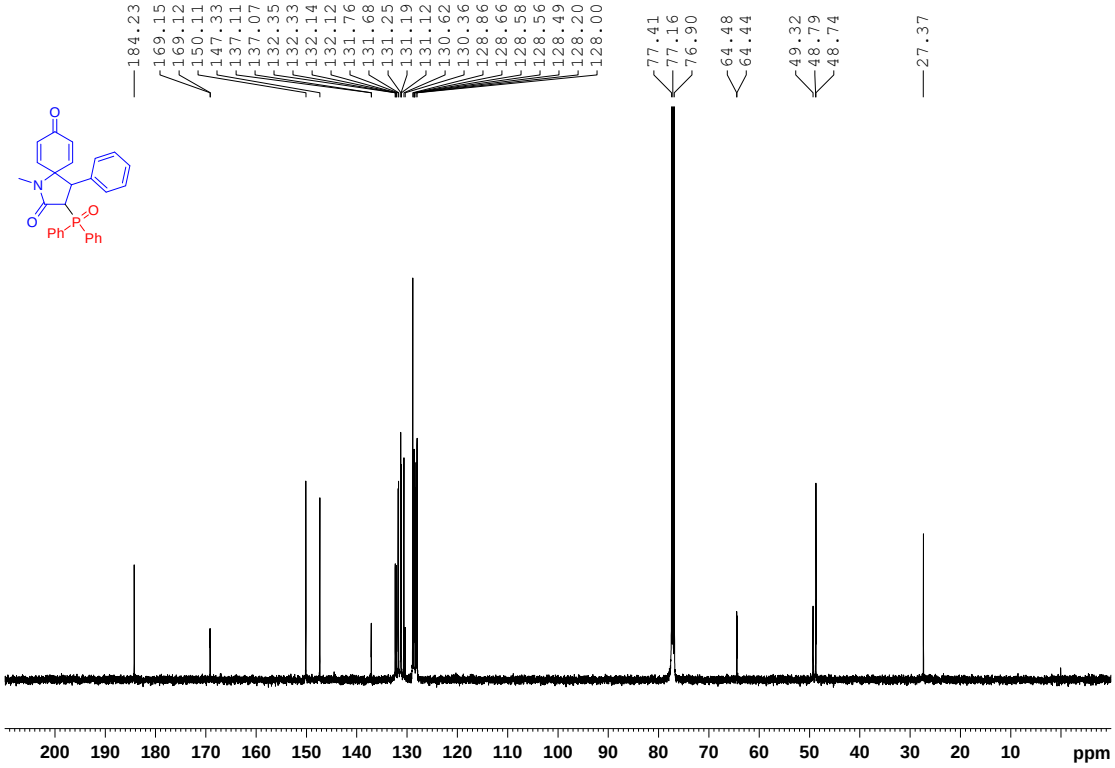
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3aa**



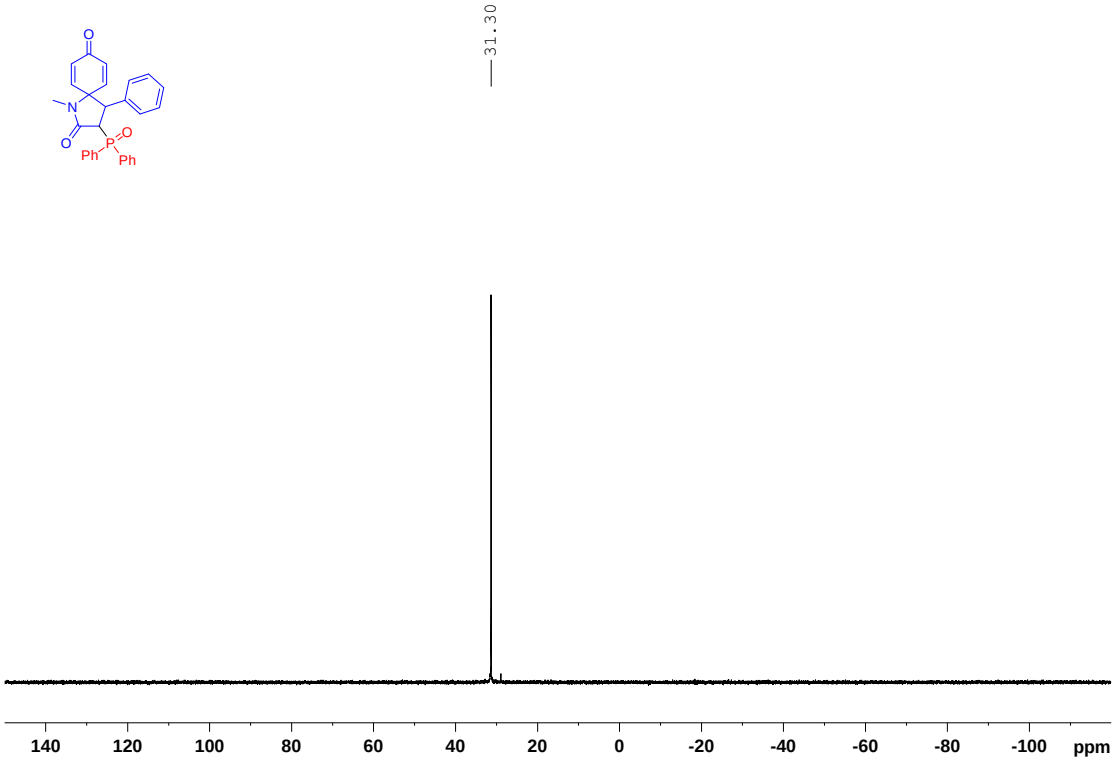
^{1}H NMR (500 MHz, $CDCl_3$, 300K):**3a**



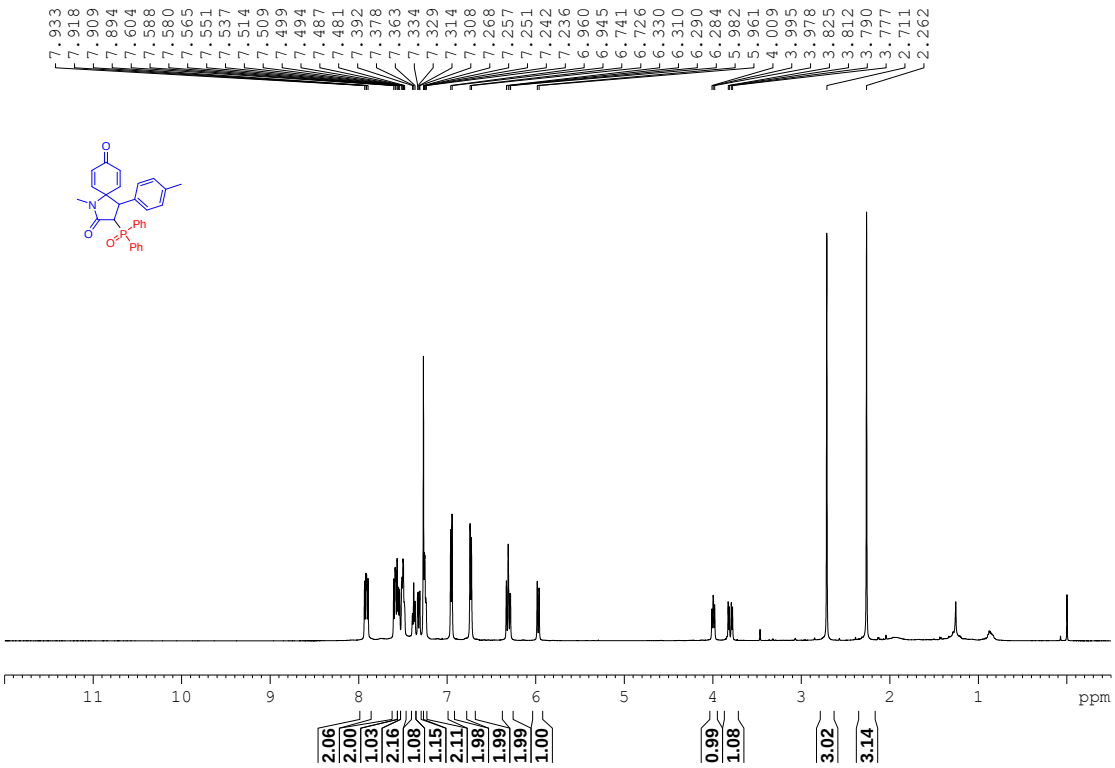
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3a**



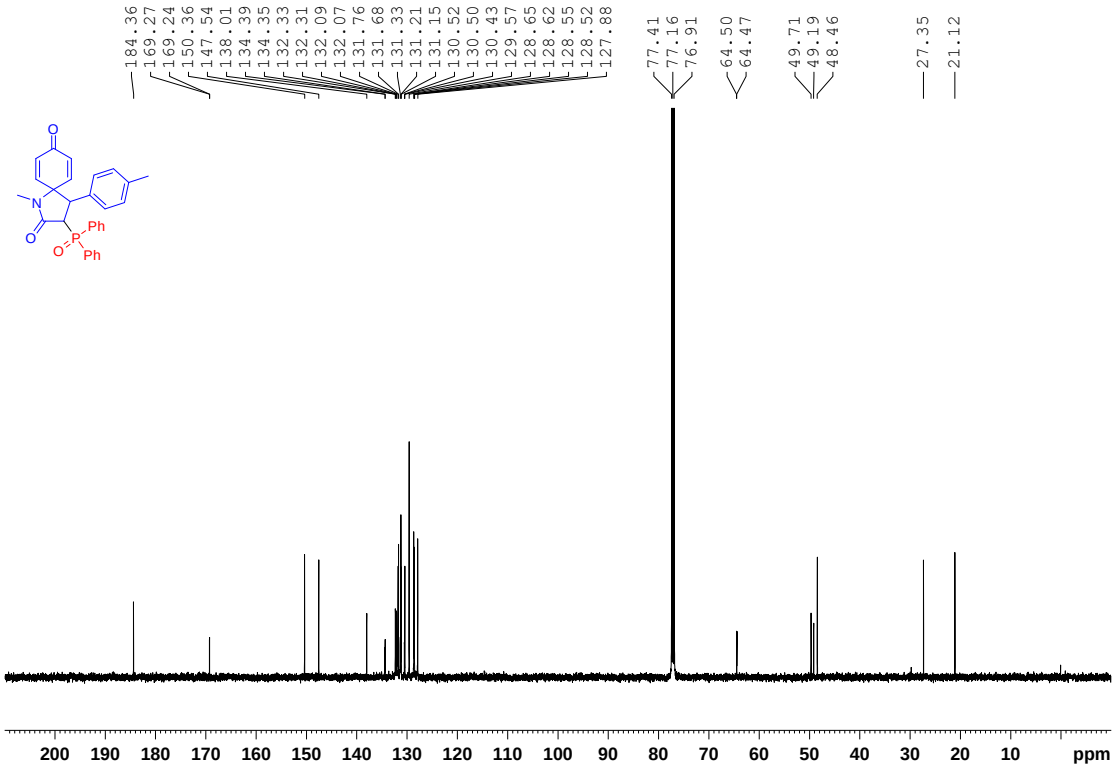
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3a**



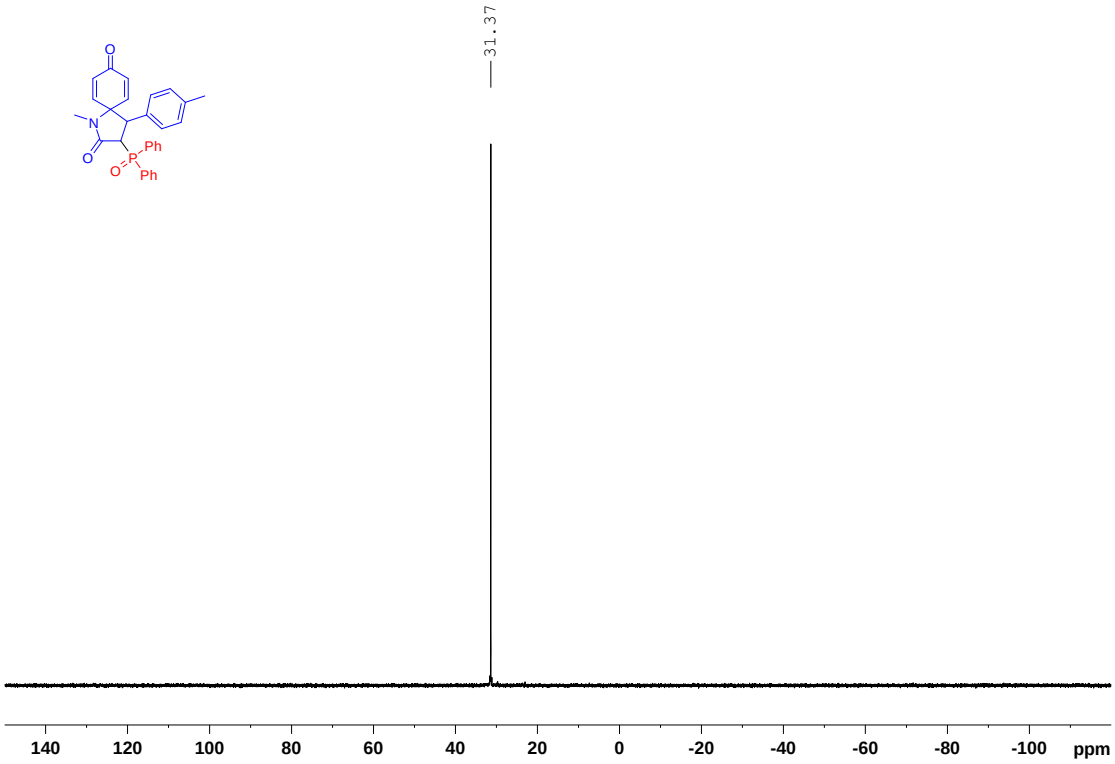
^{1}H NMR (500 MHz, $CDCl_3$, 300K):**3b**



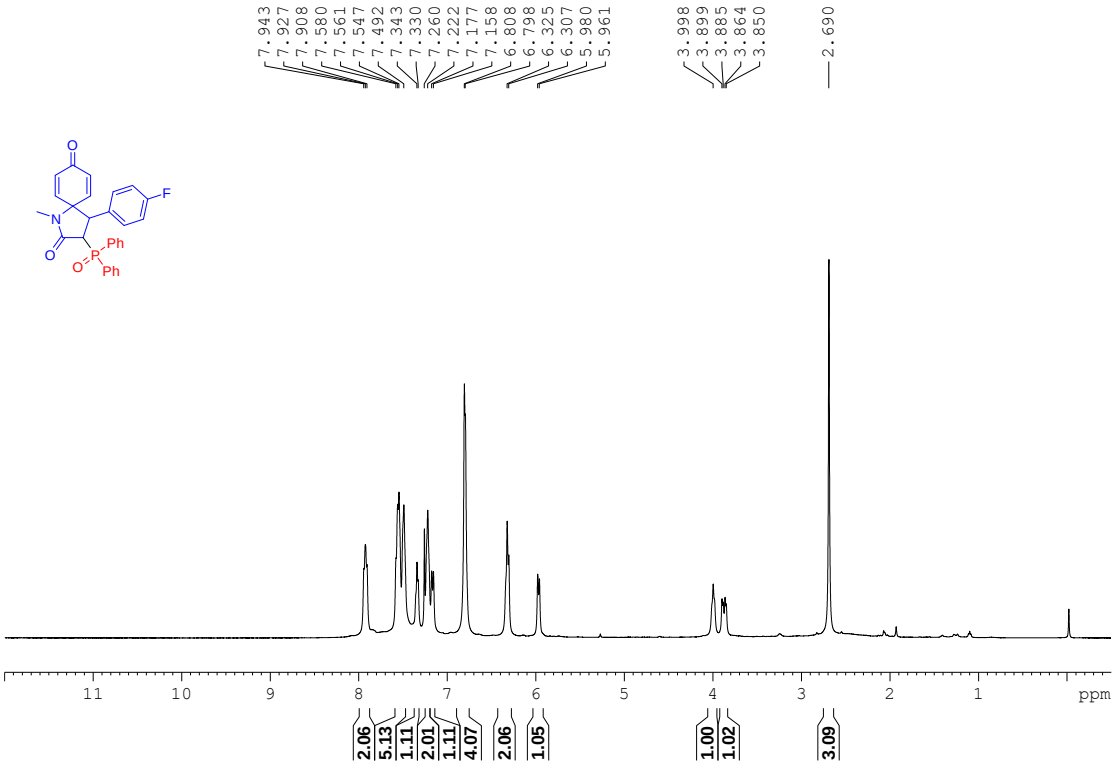
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3b**



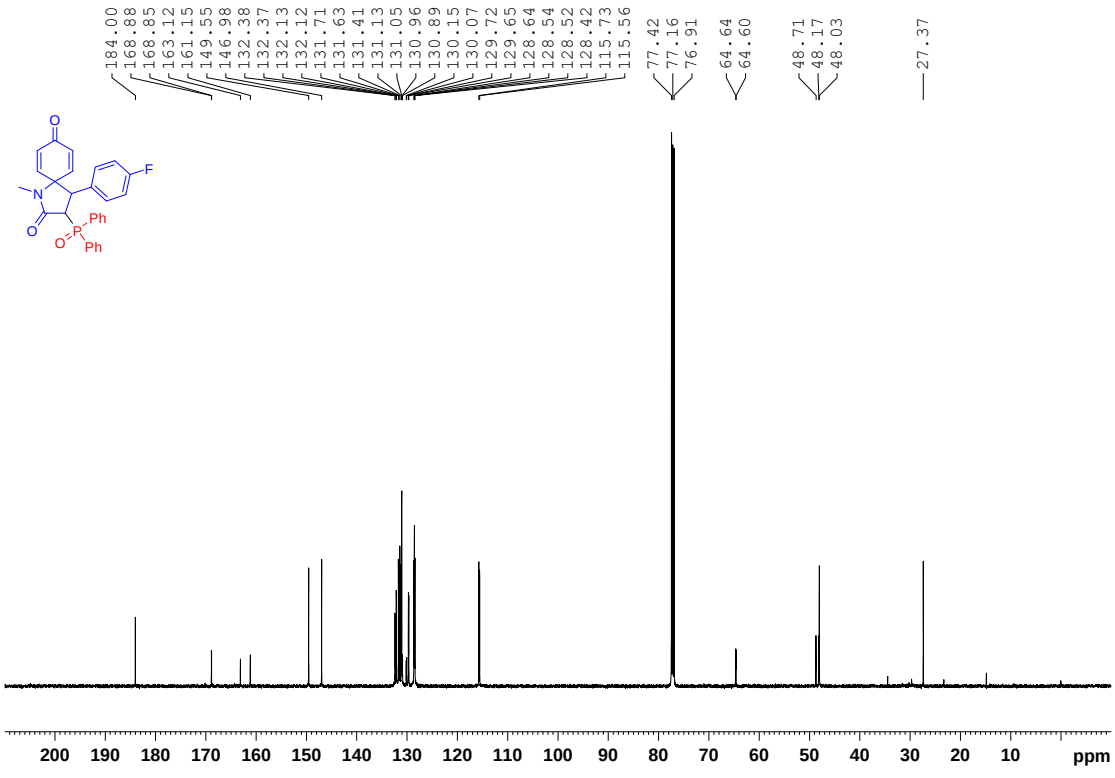
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3b**



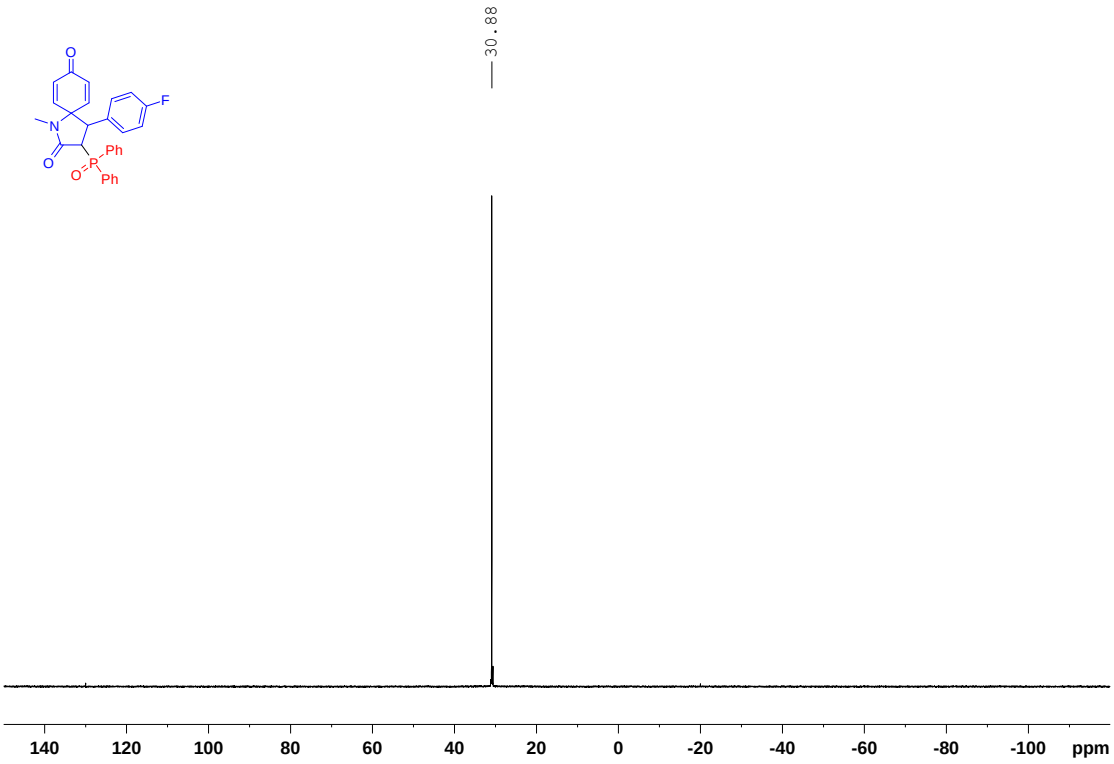
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3c**



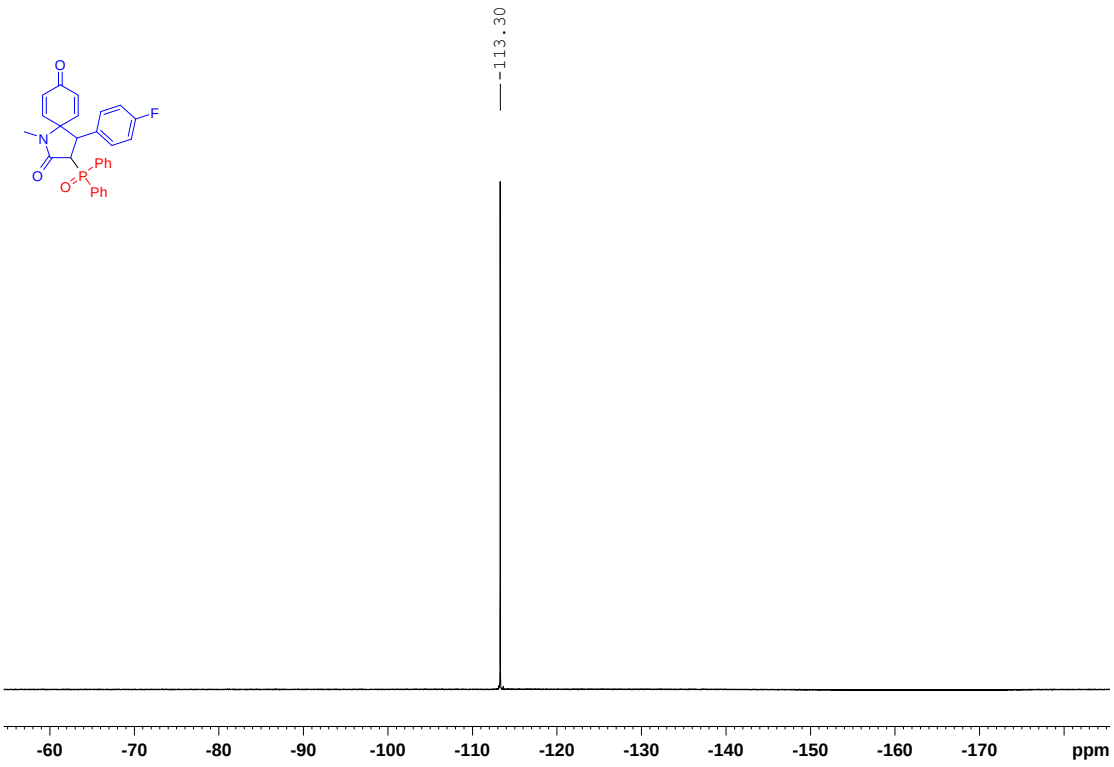
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3c**



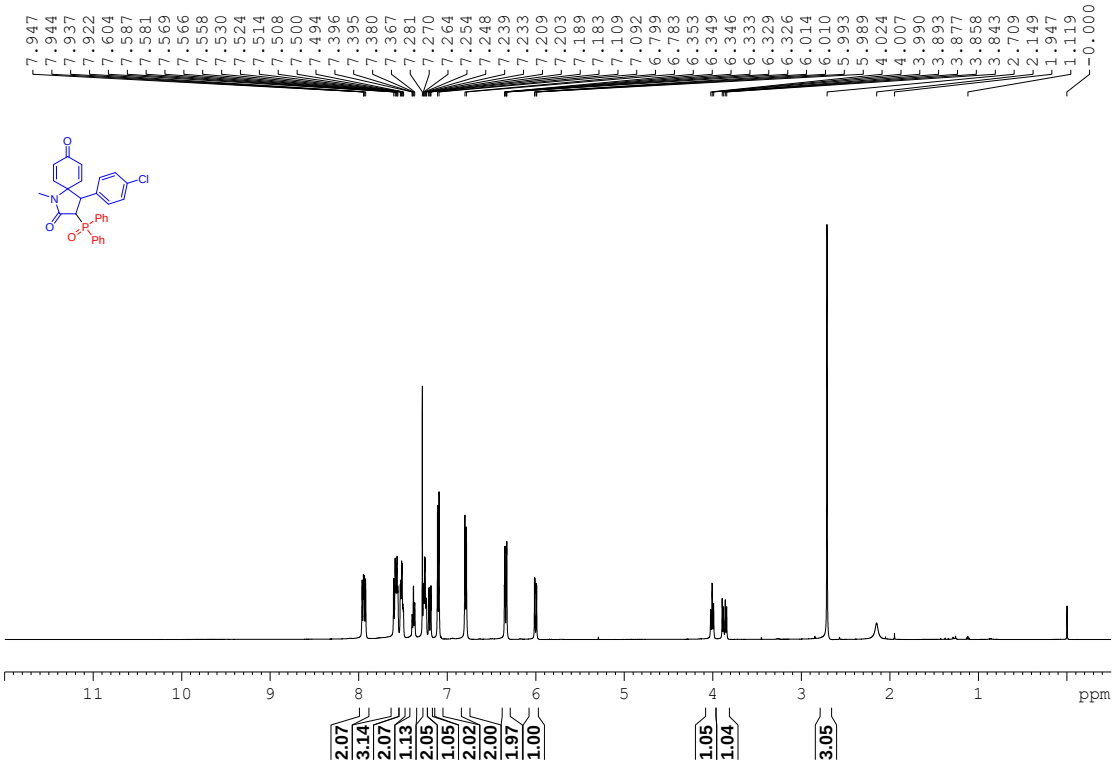
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3c**



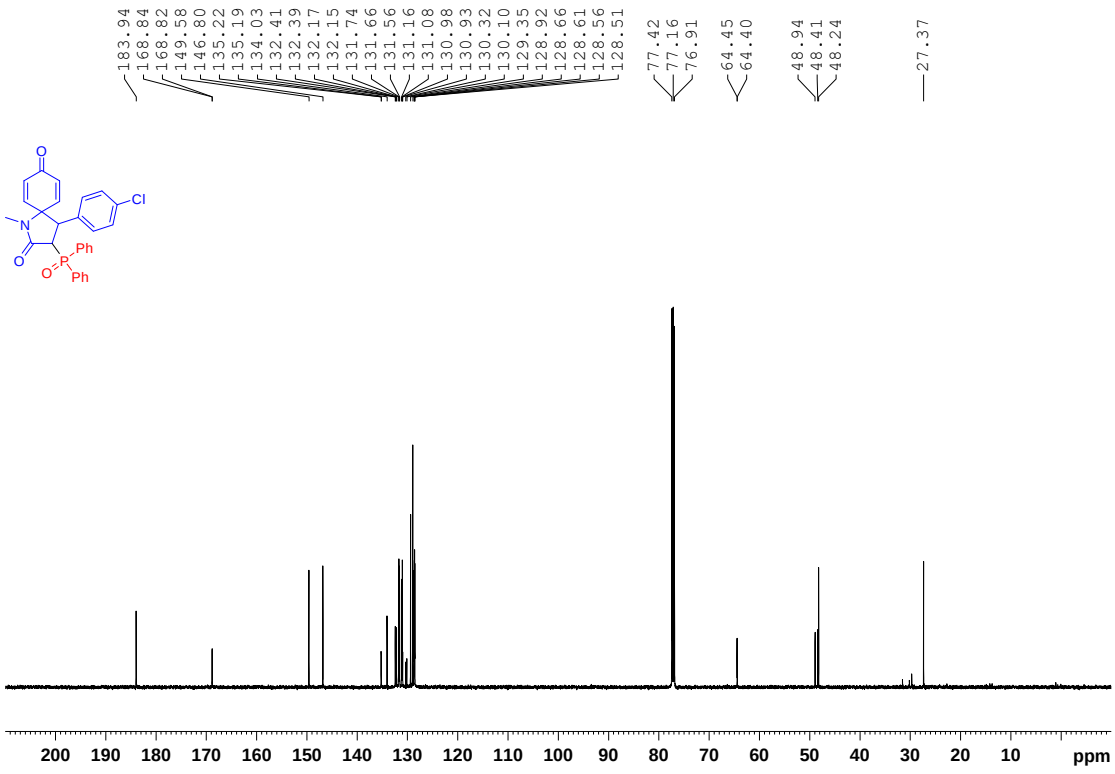
^{19}F NMR (470 MHz, $CDCl_3$, 300K): **3c**



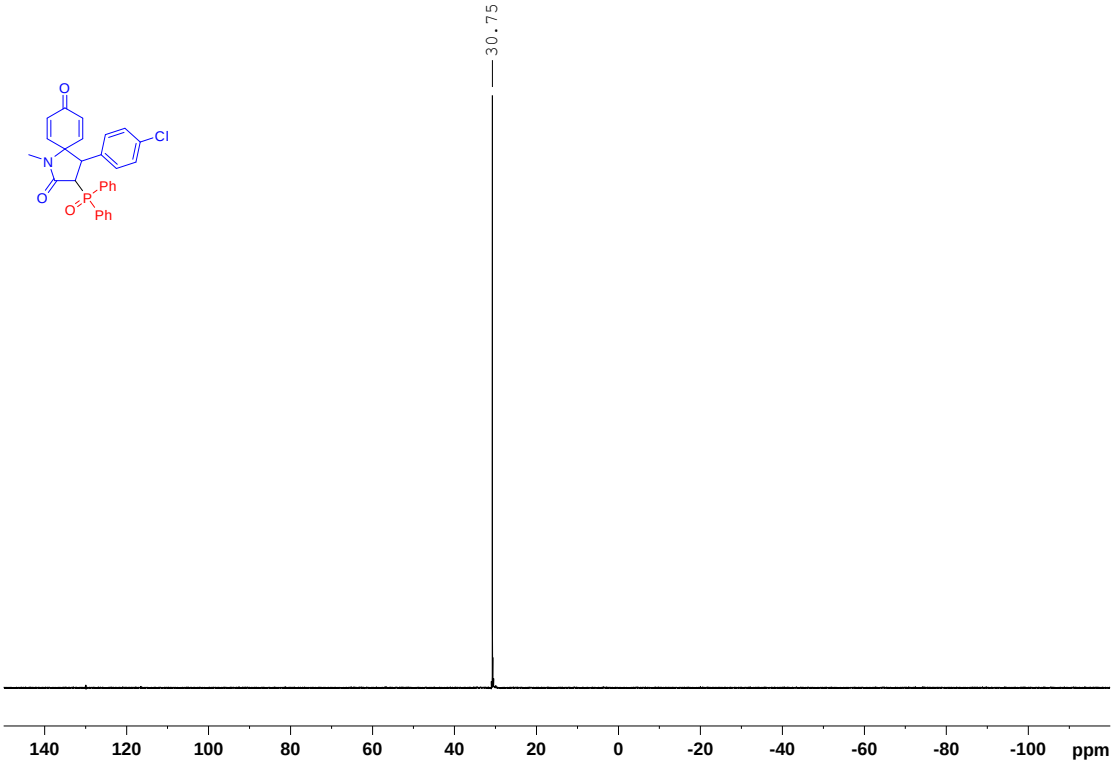
^{1}H NMR (500 MHz, $CDCl_3$, 300K):**3d**



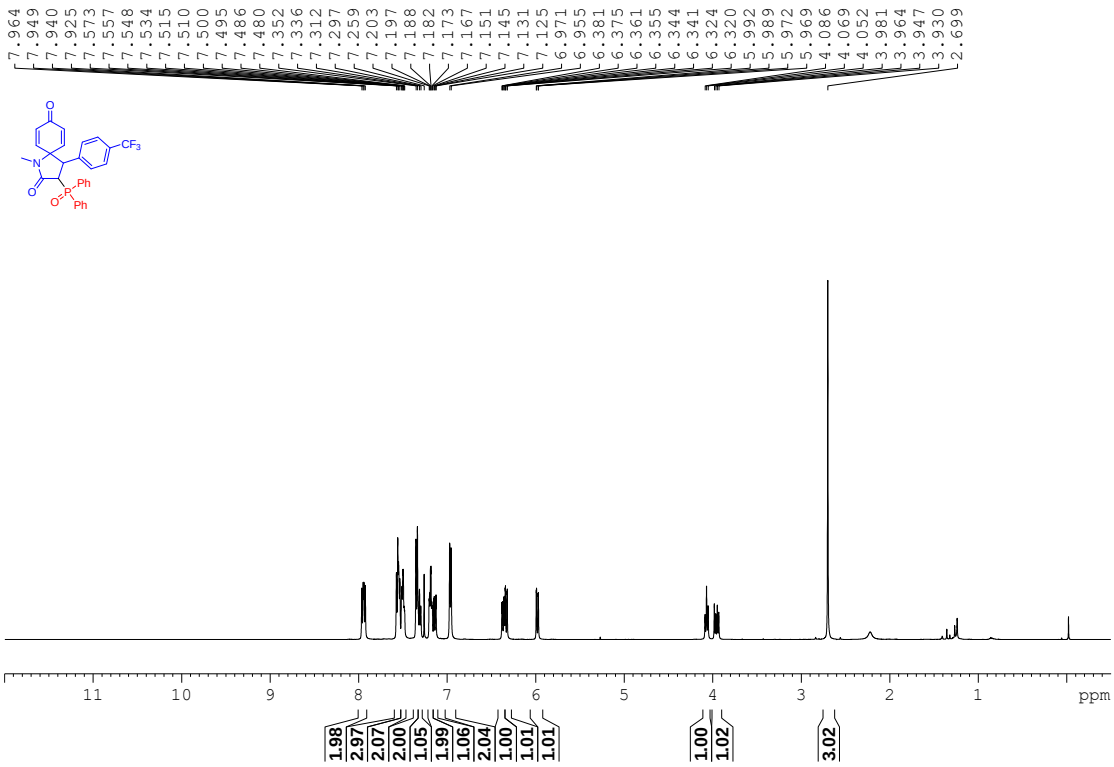
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3d**



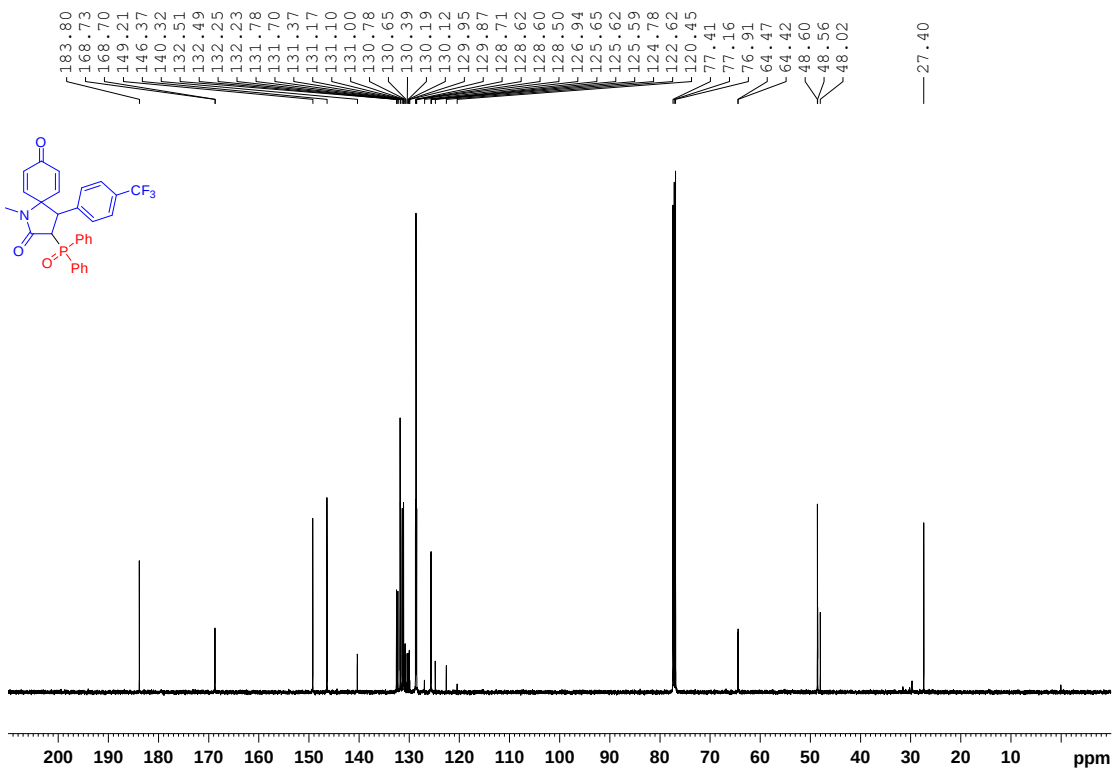
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3d**



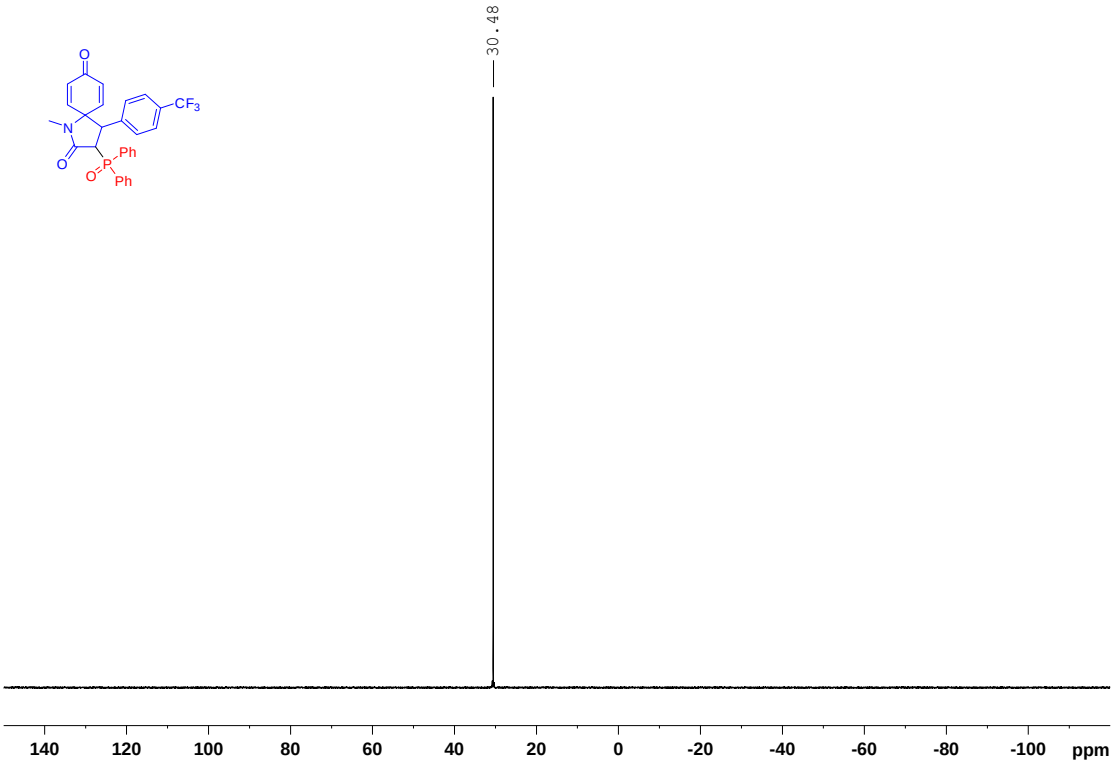
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3e**



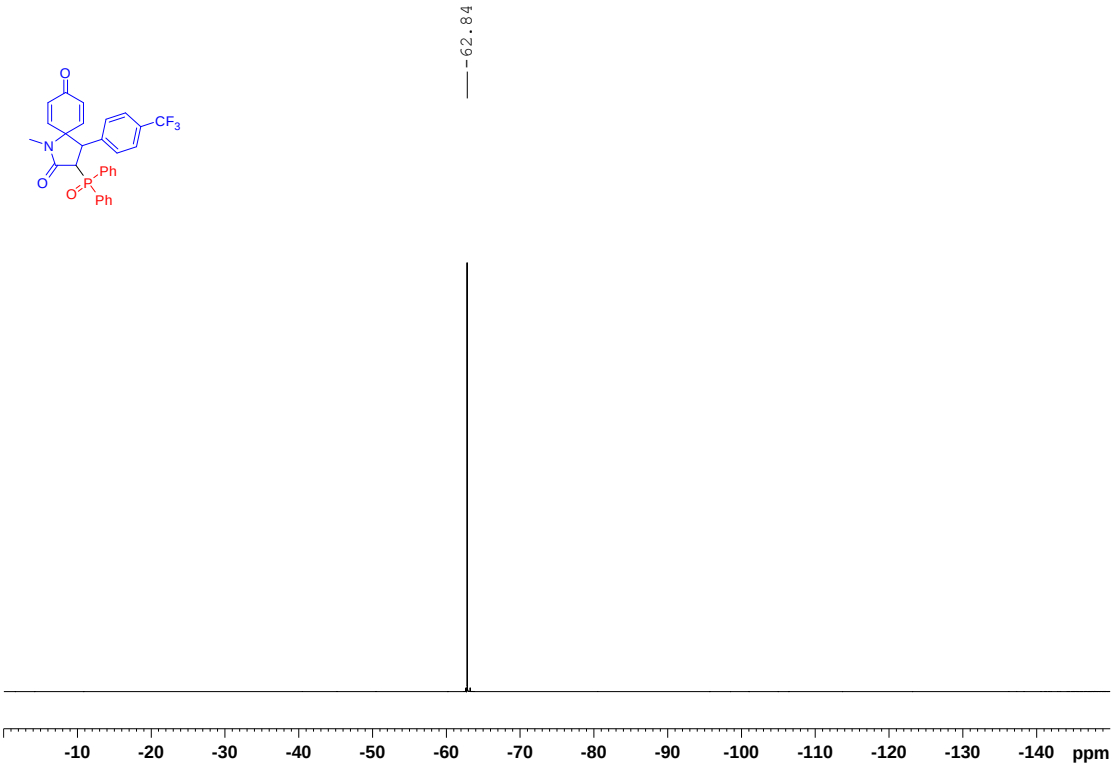
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3e**



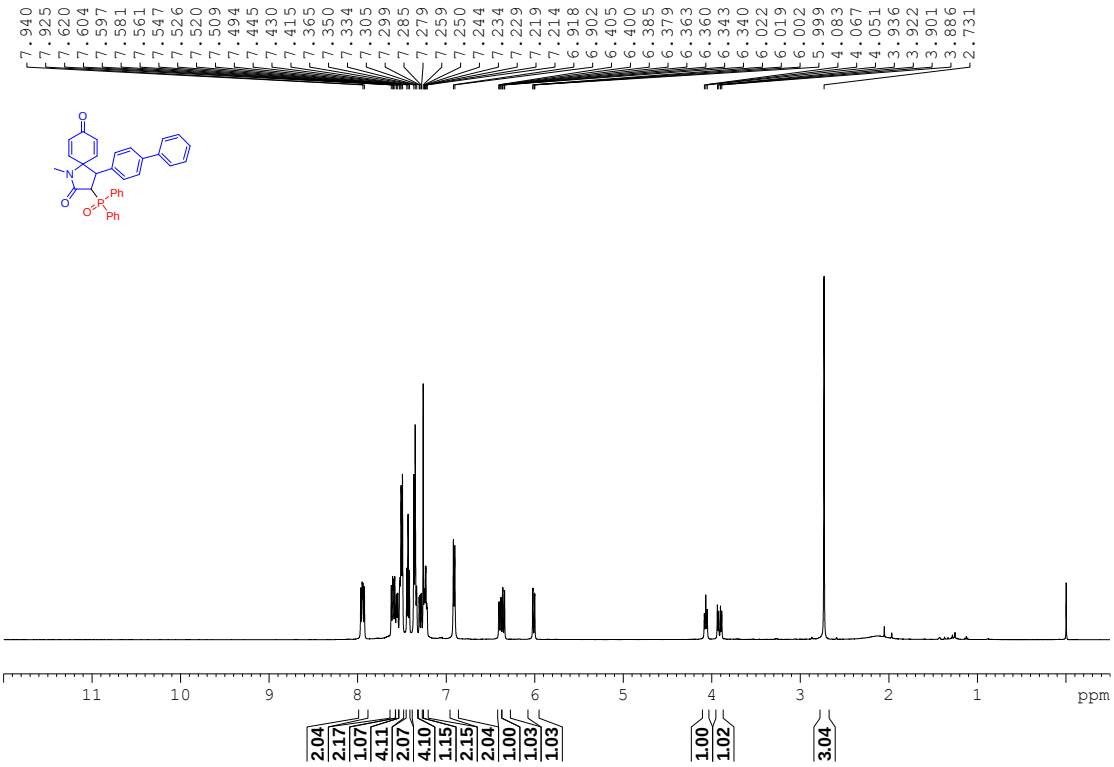
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3e**



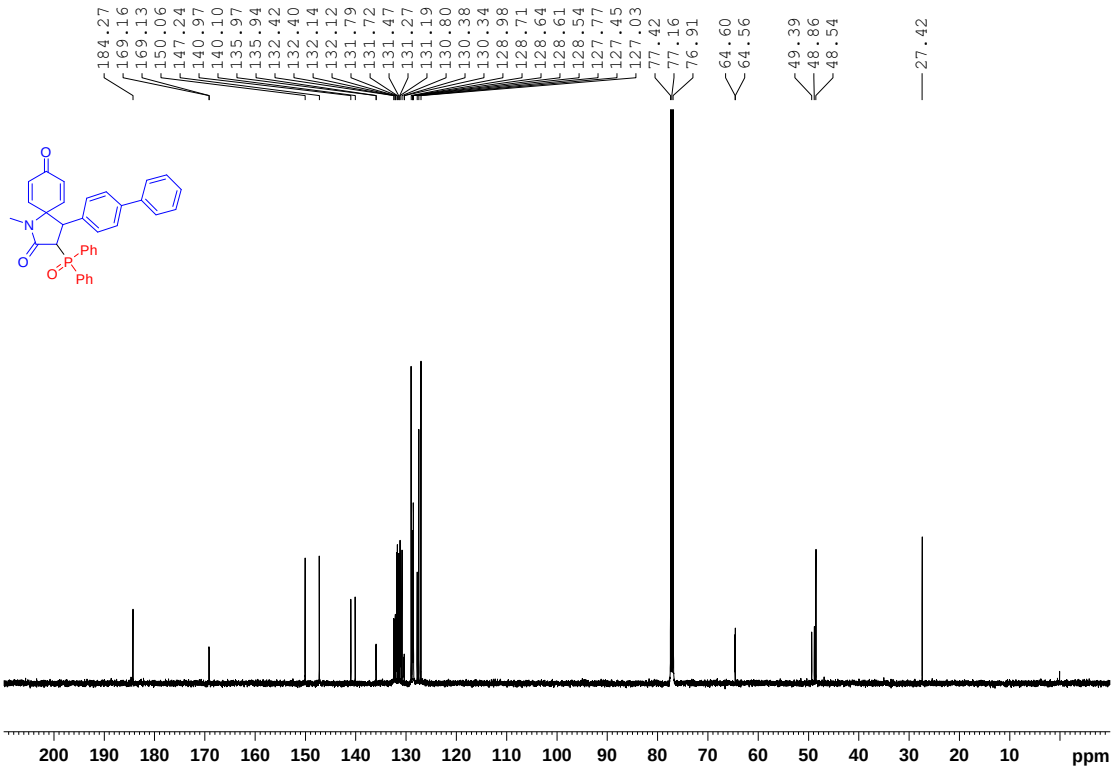
^{19}F NMR (470 MHz, $CDCl_3$, 300K): **3e**



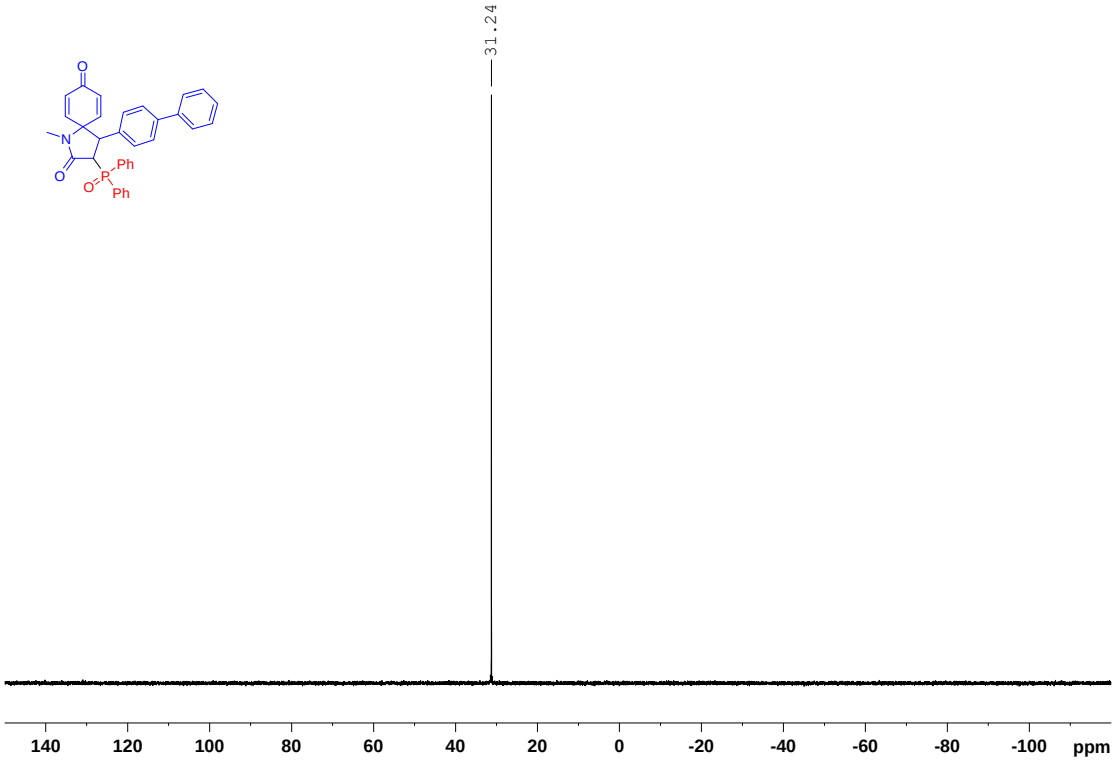
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3f**



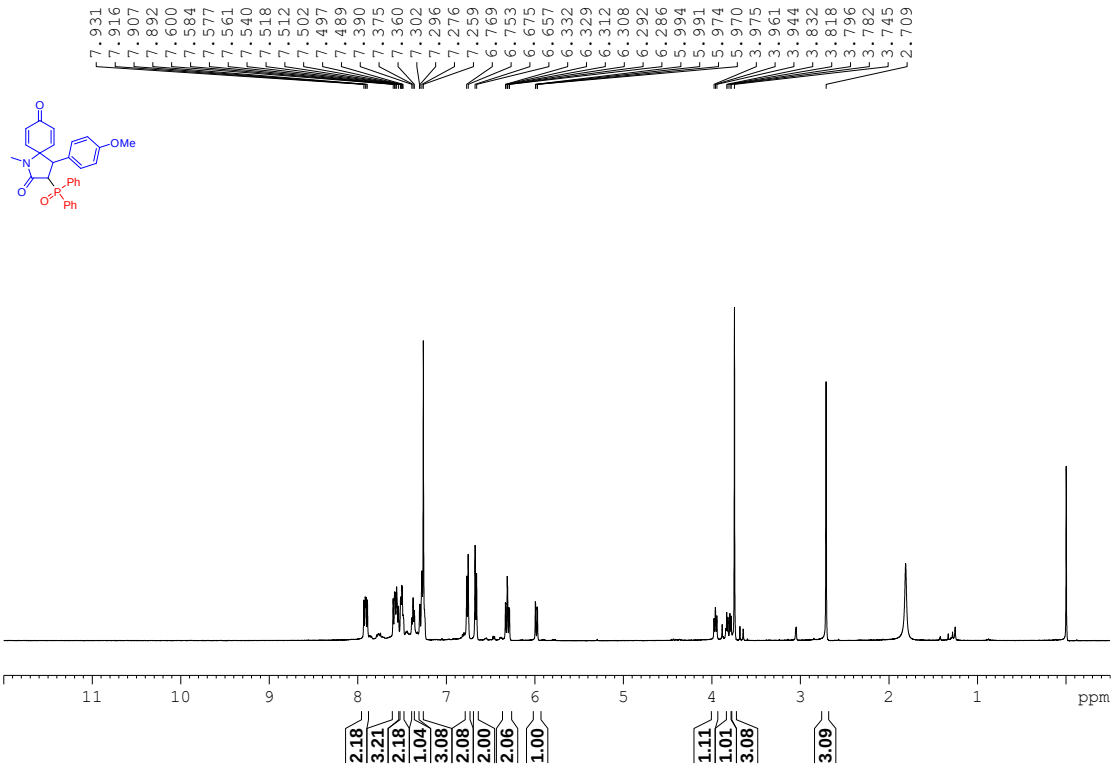
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3f**



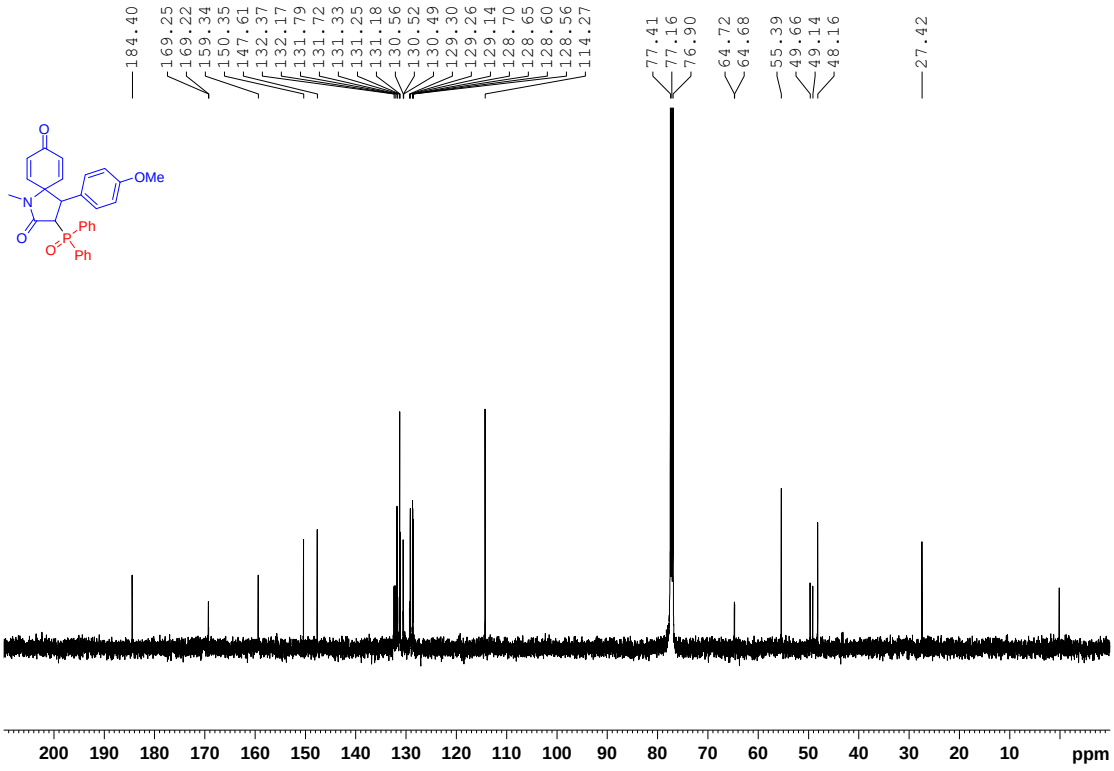
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3f**



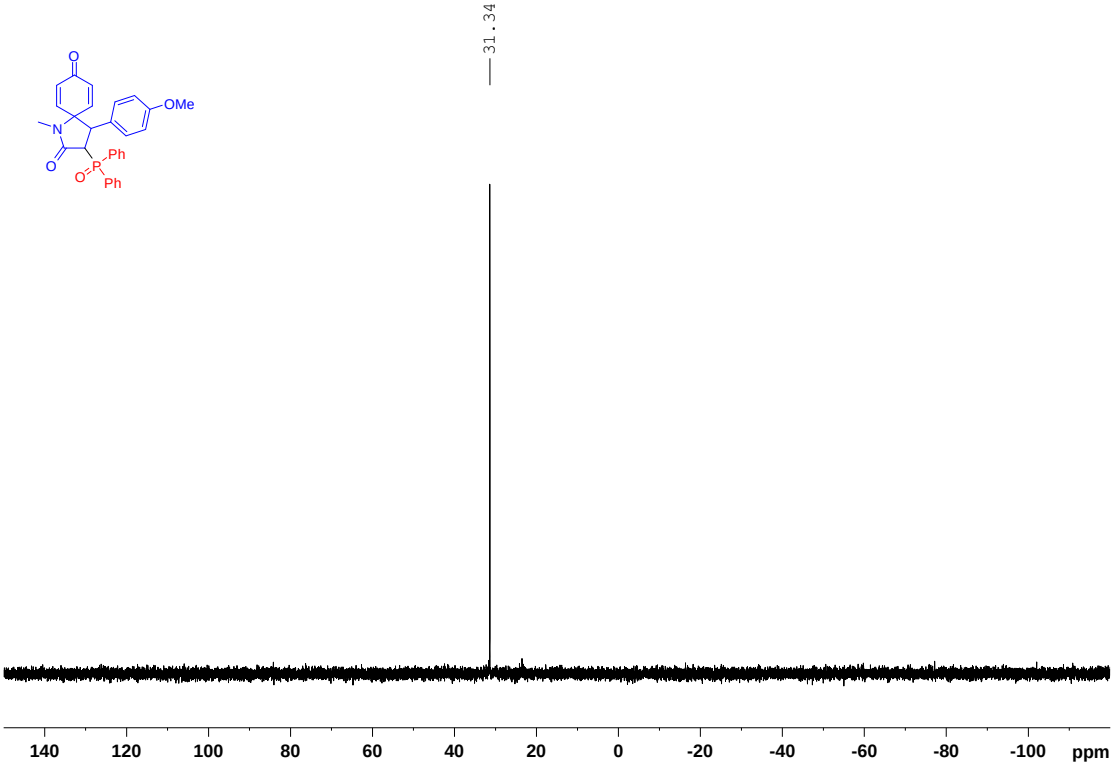
^{1}H NMR (500 MHz, $CDCl_3$, 300K):**3g**



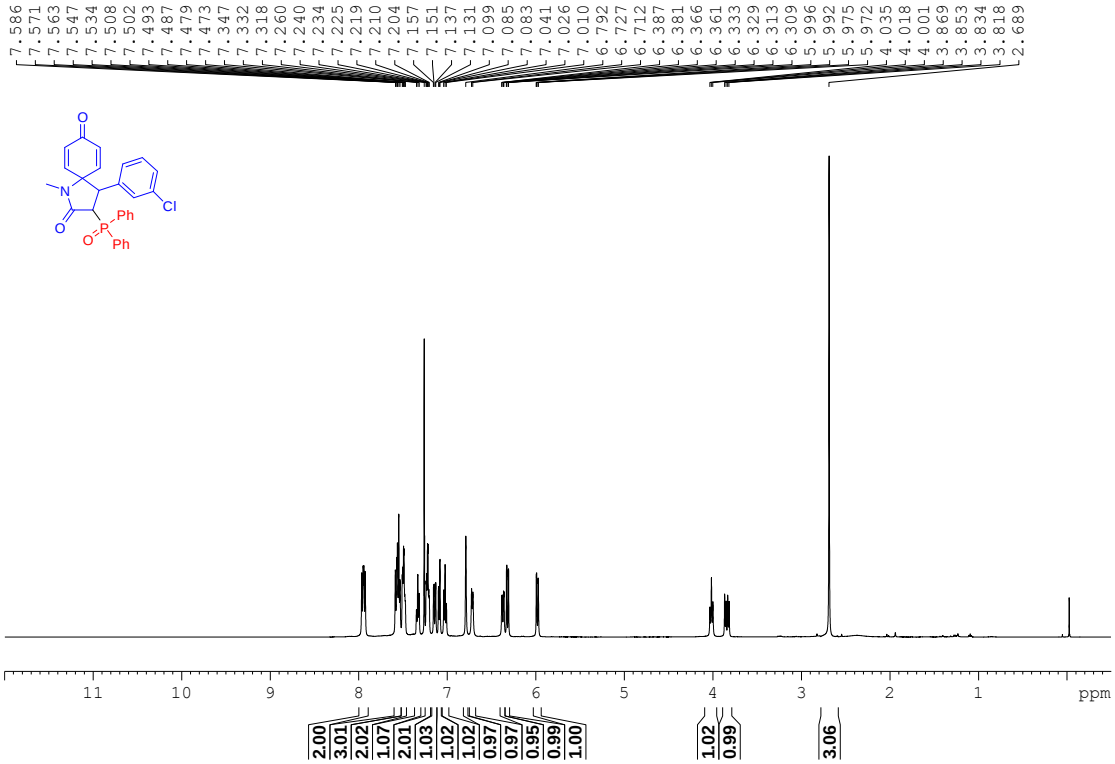
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3g**



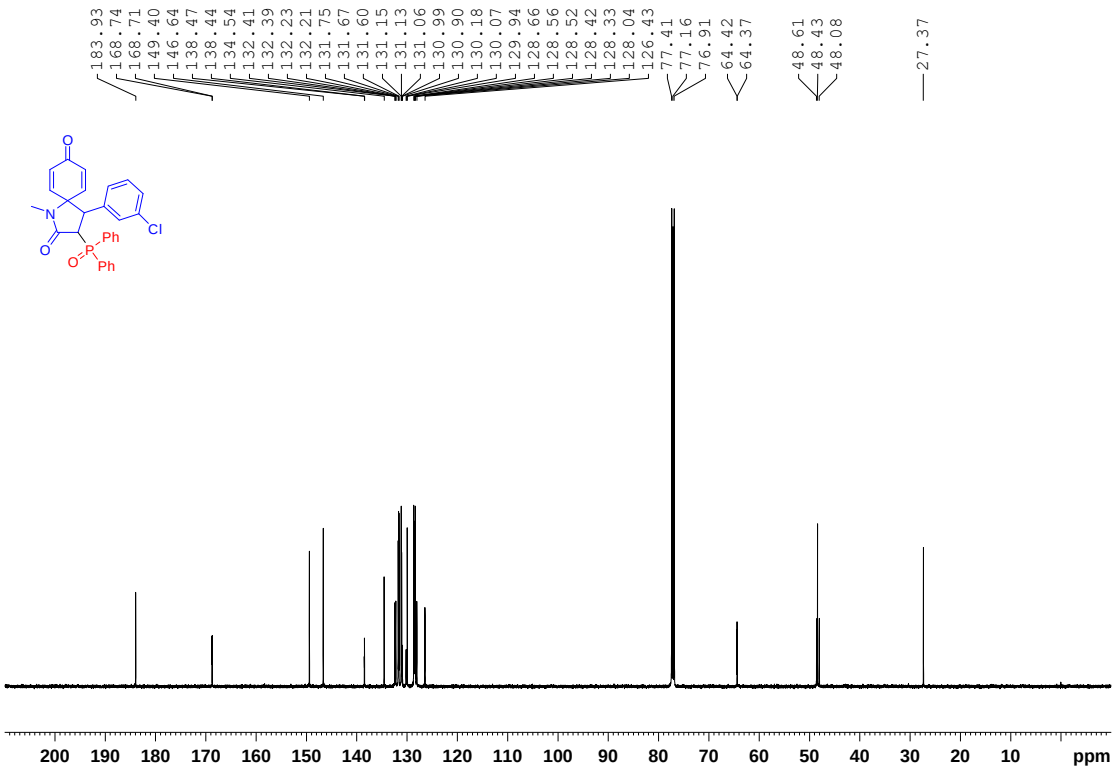
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3g**



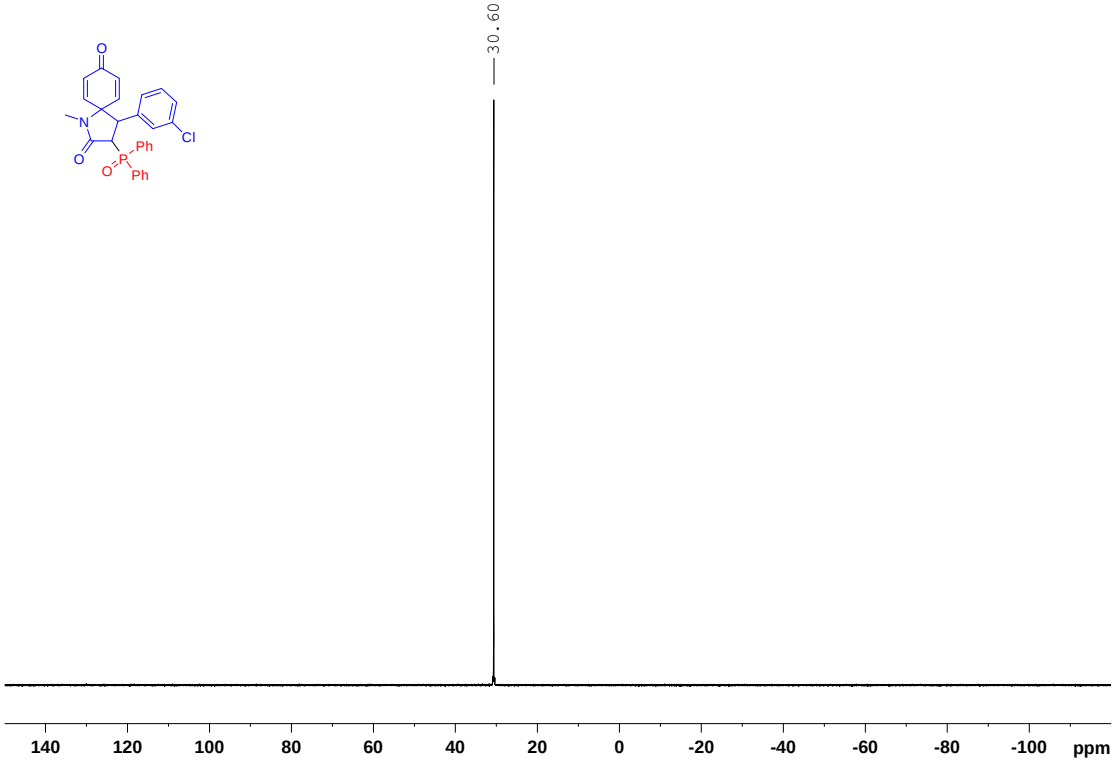
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3h**



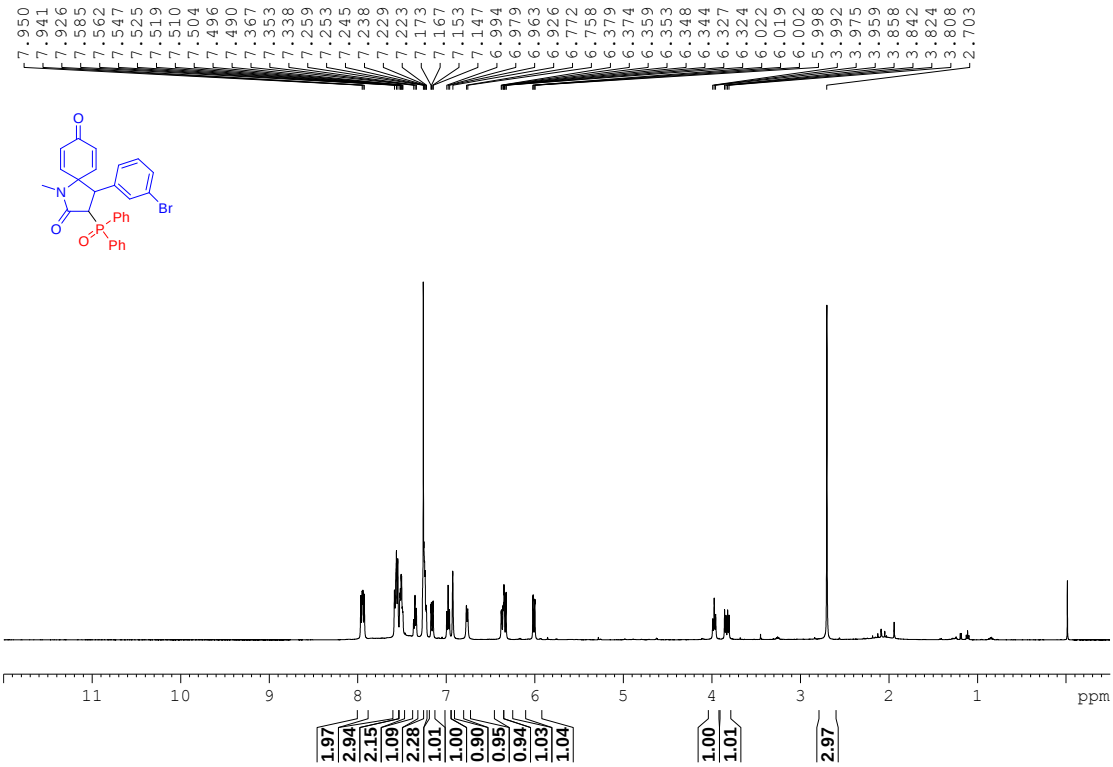
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3h**



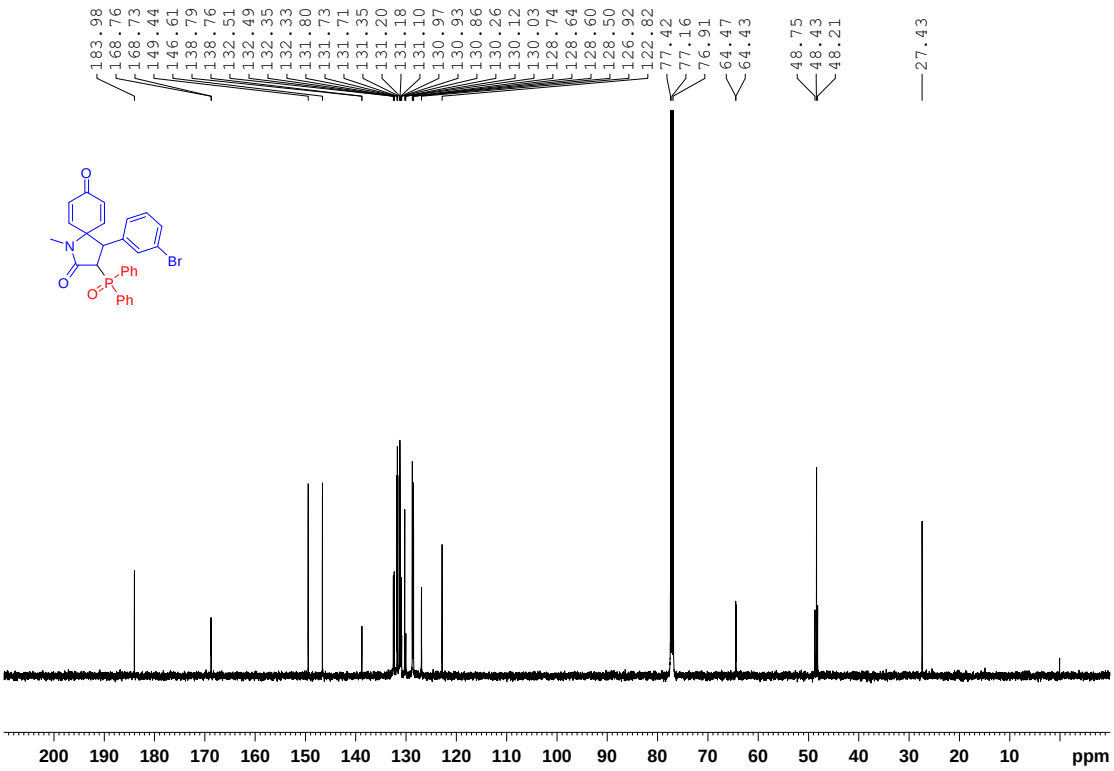
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3h**



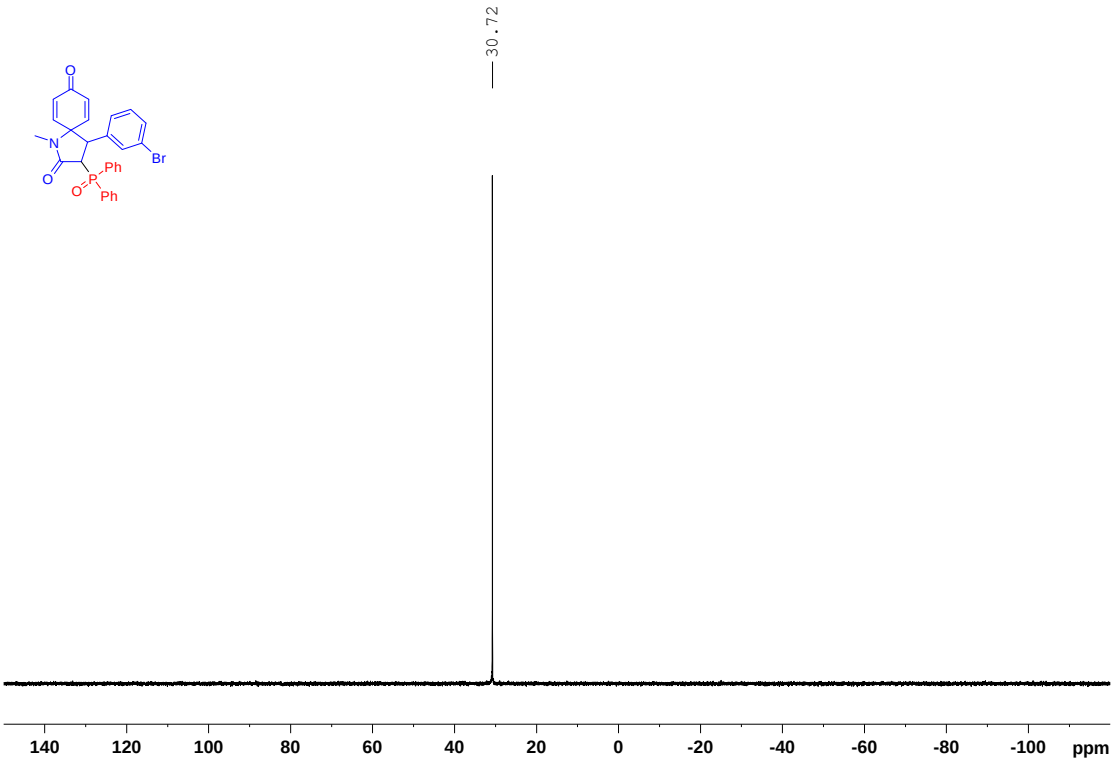
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3i**



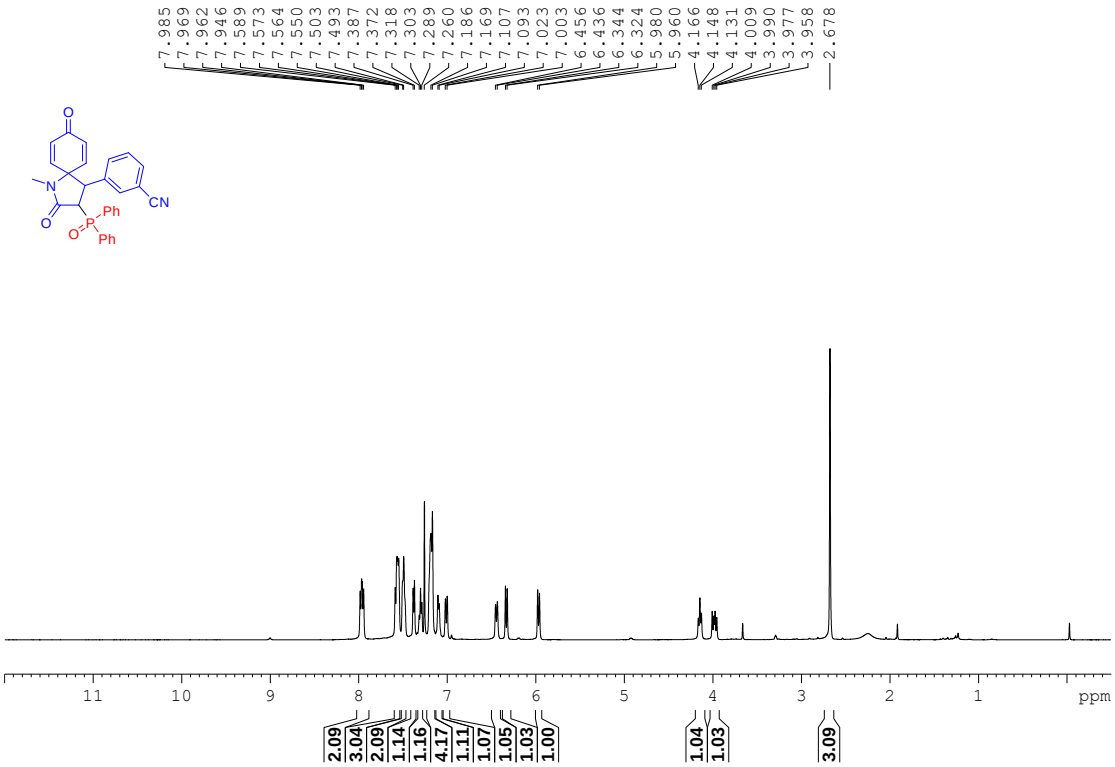
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3i**



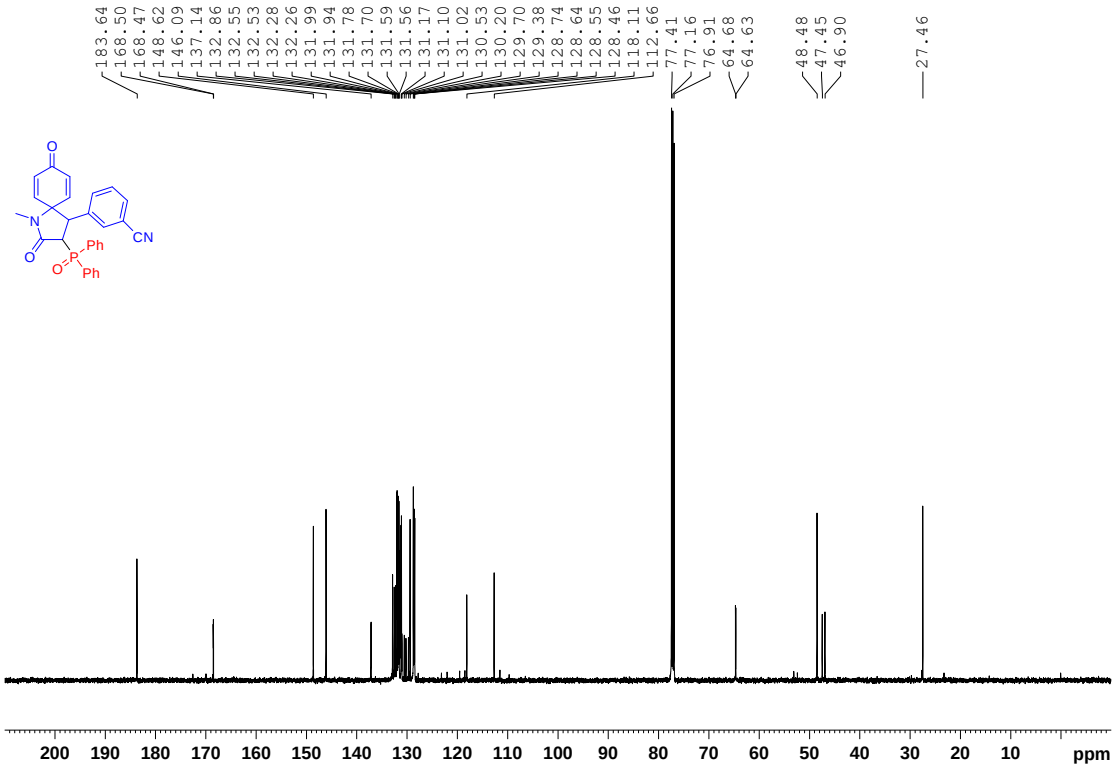
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3i**



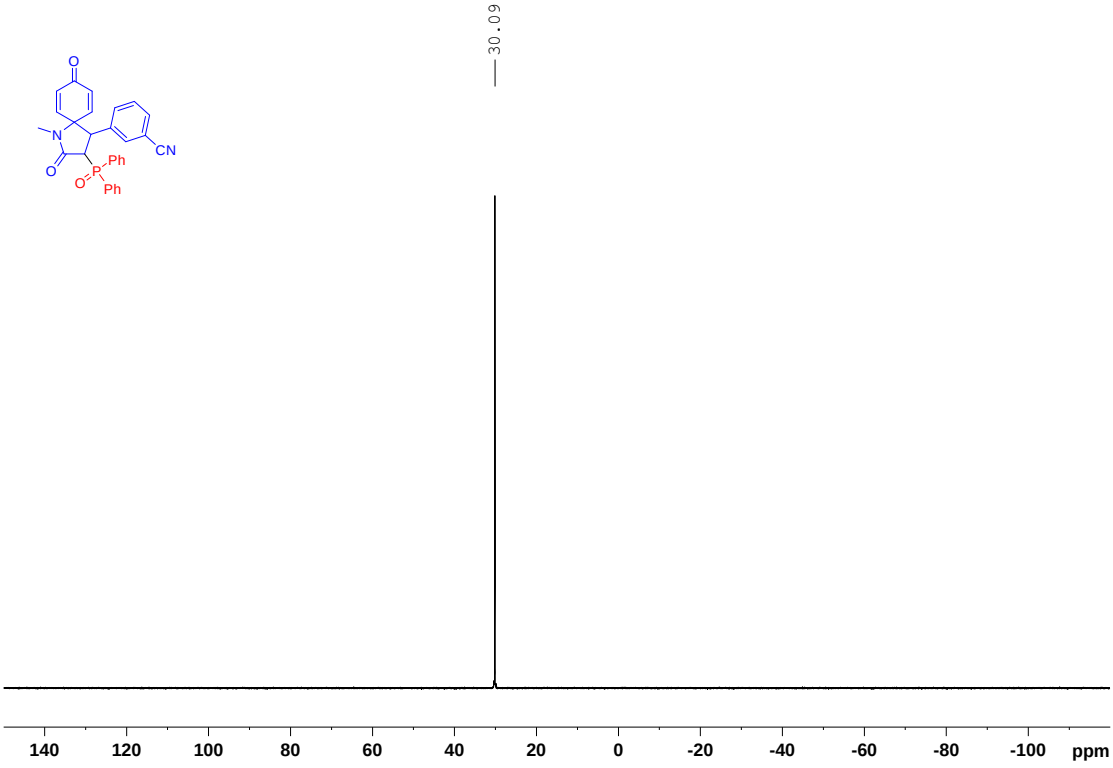
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3j**



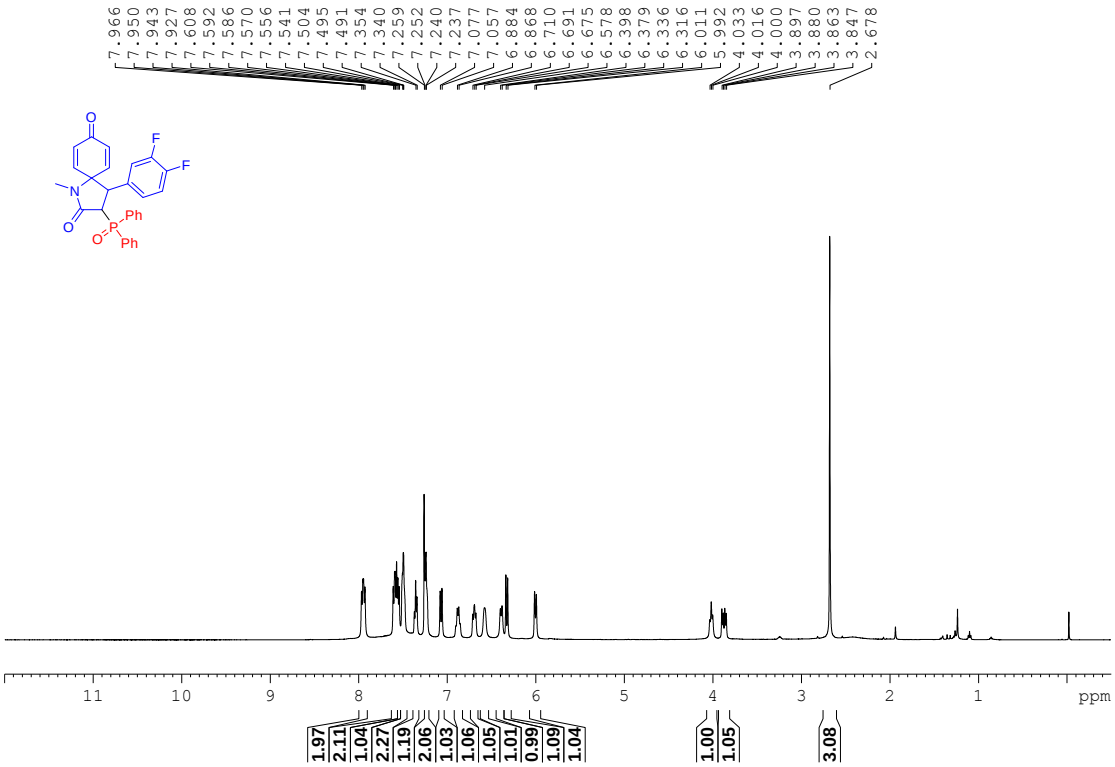
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3j**



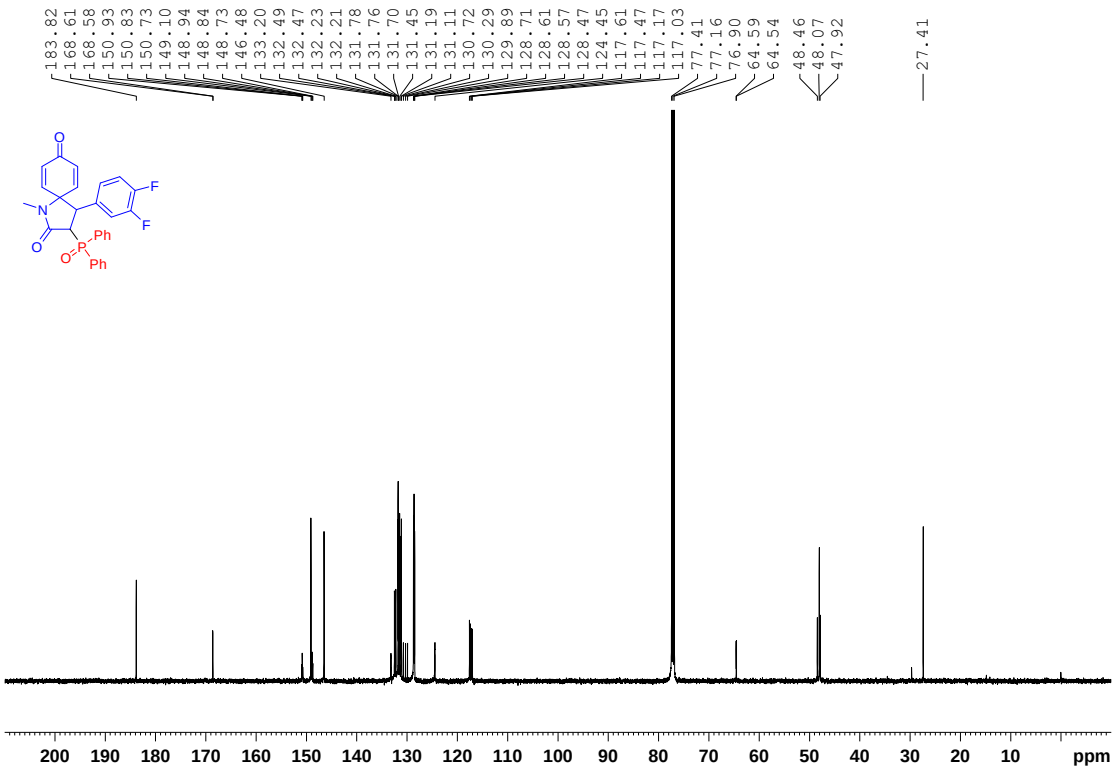
^{31}P NMR (162 MHz, $CDCl_3$, 300K):**3j**



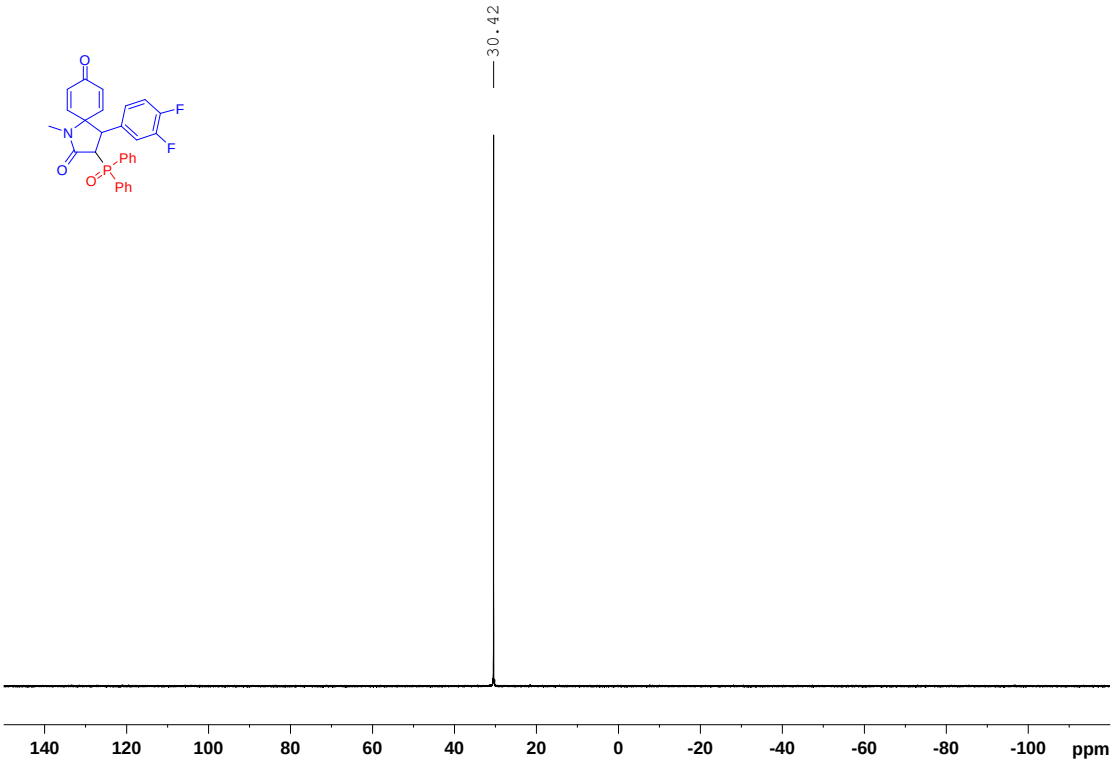
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3k**



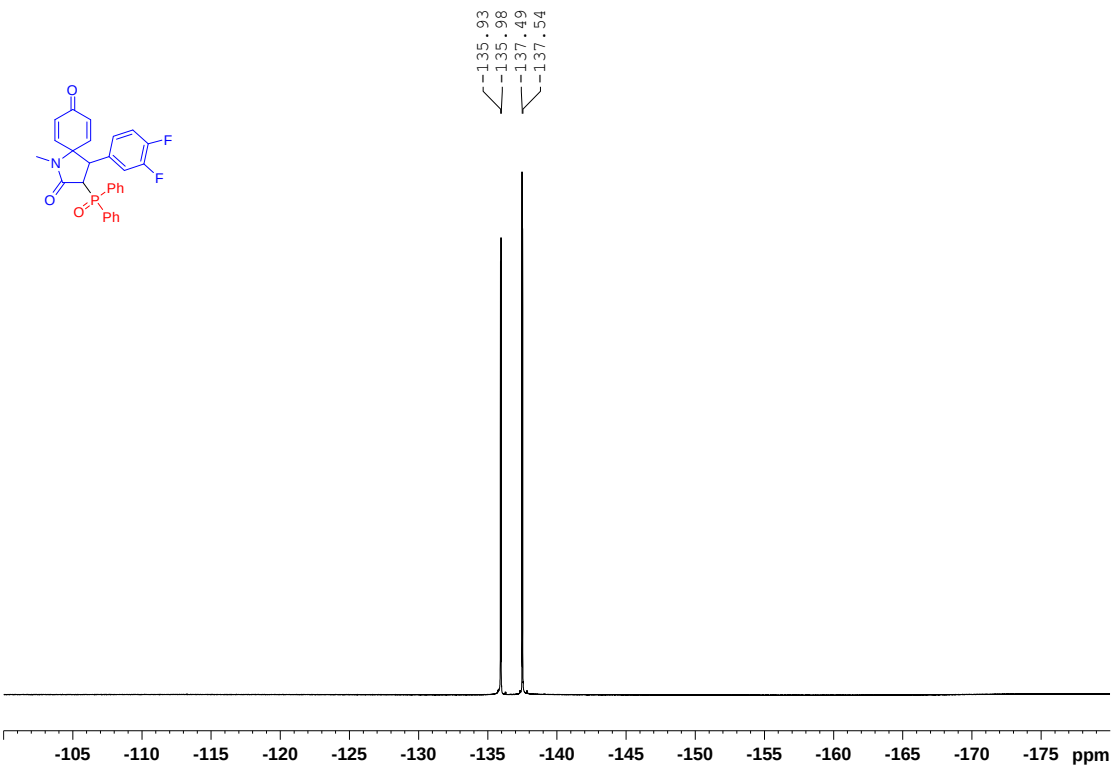
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3k**



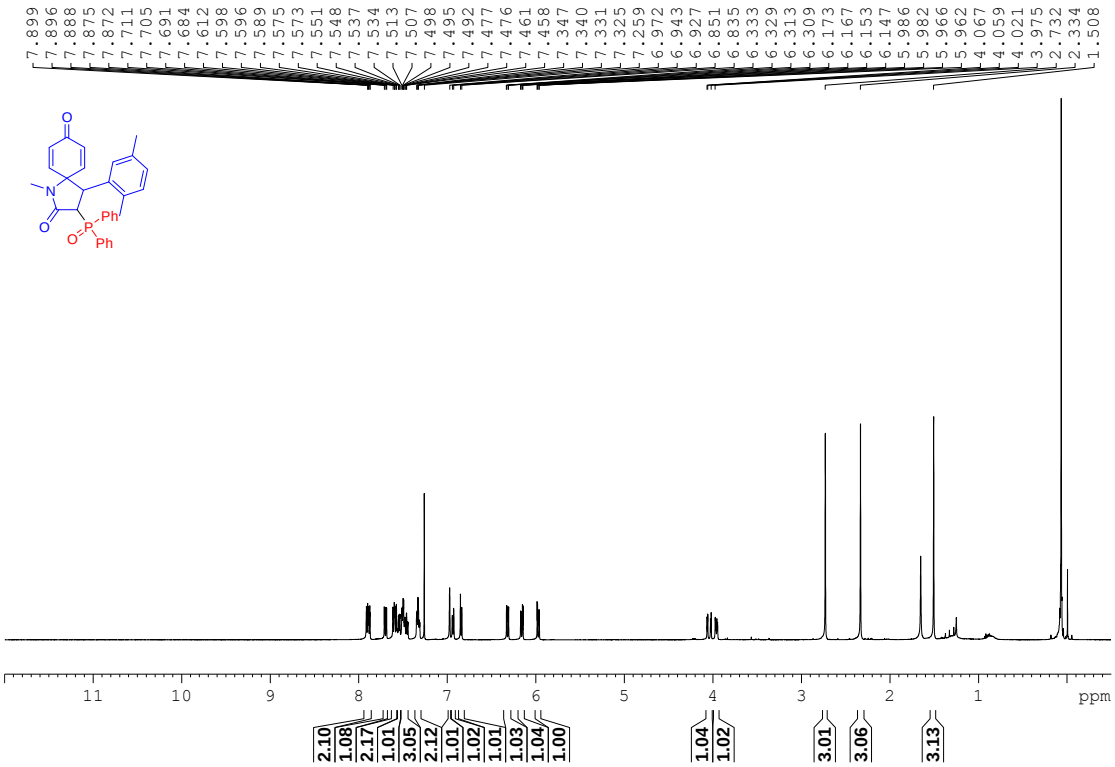
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3k**



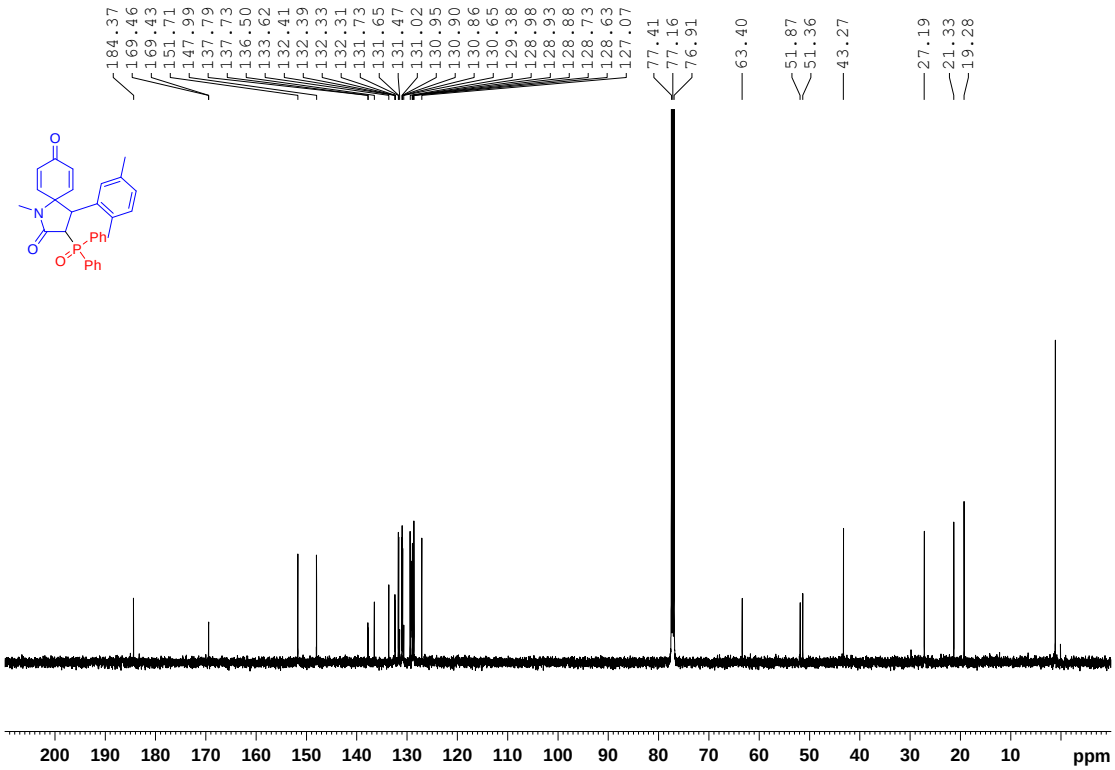
^{19}F NMR (470 MHz, $CDCl_3$, 300K): **3k**



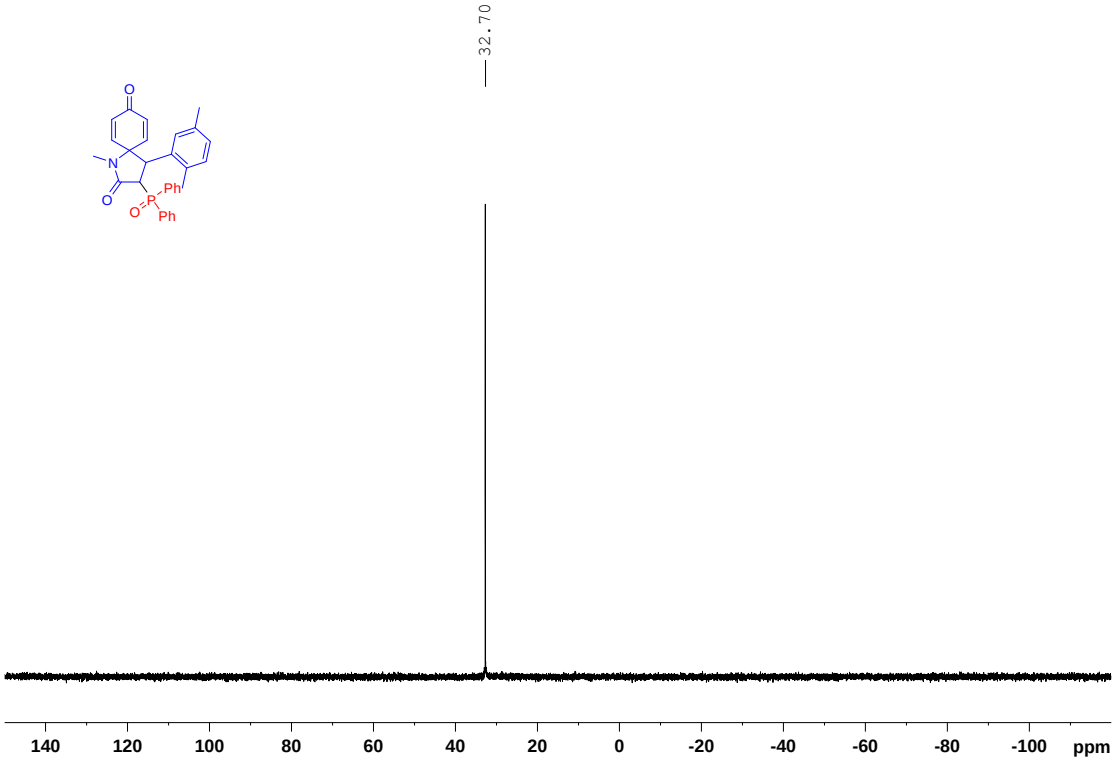
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3l**



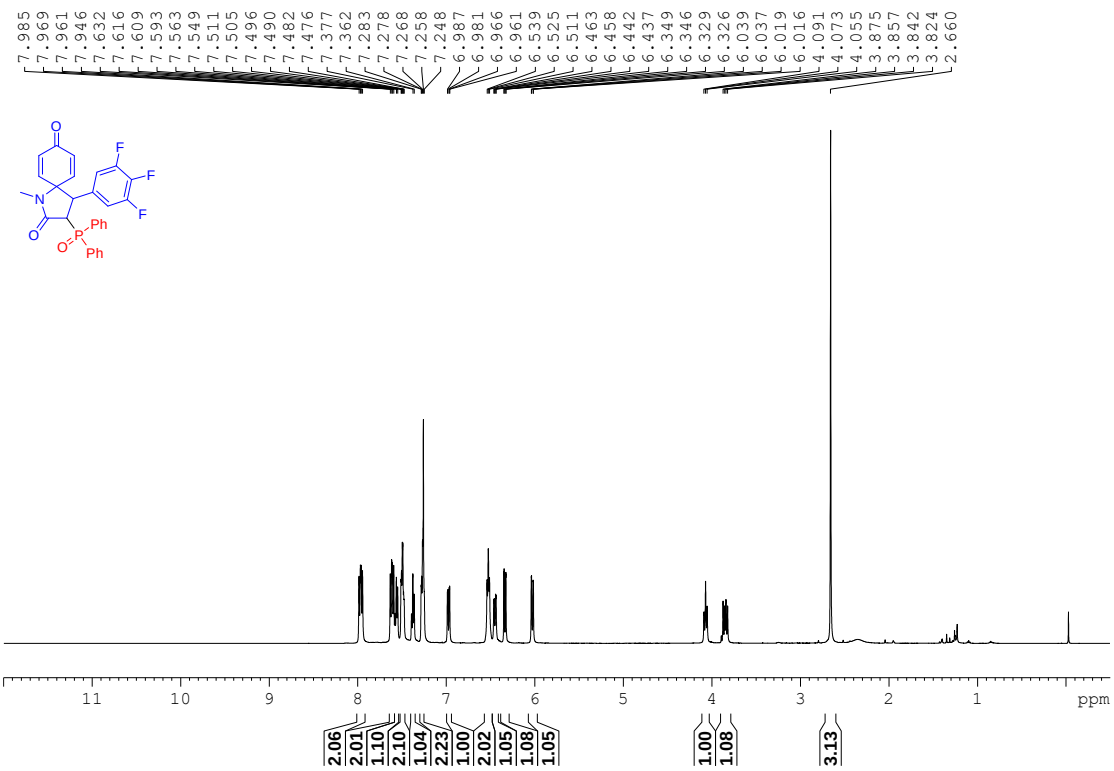
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3l**



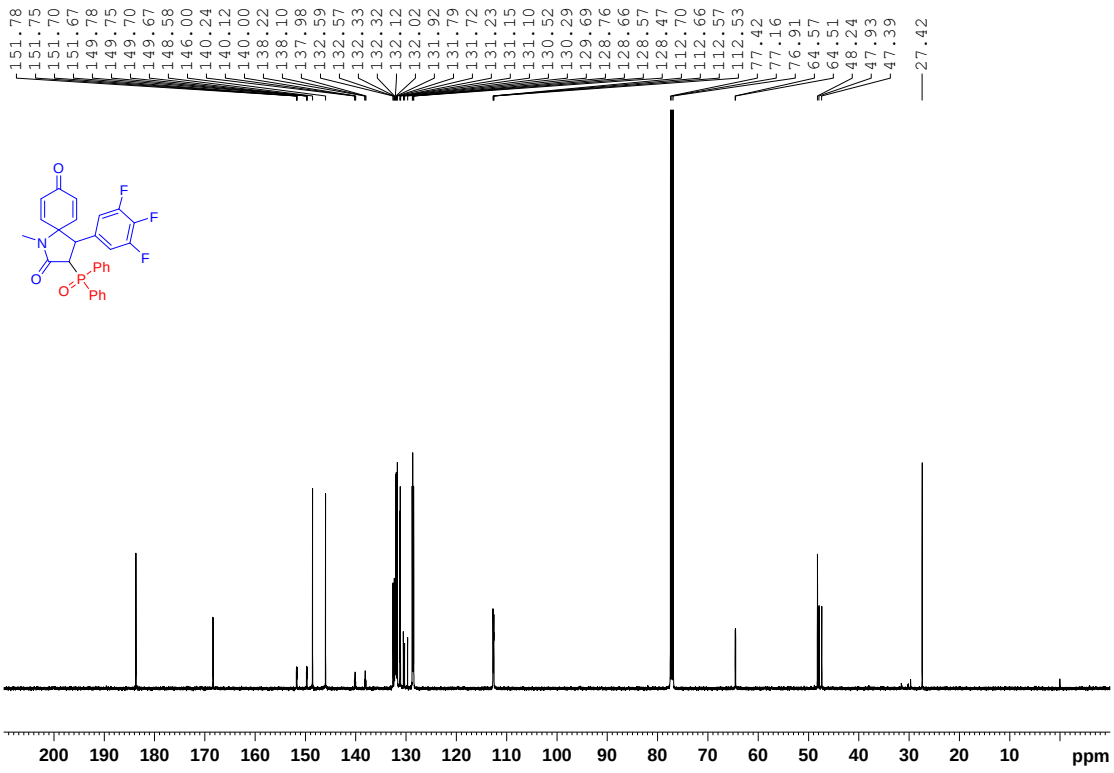
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3l**



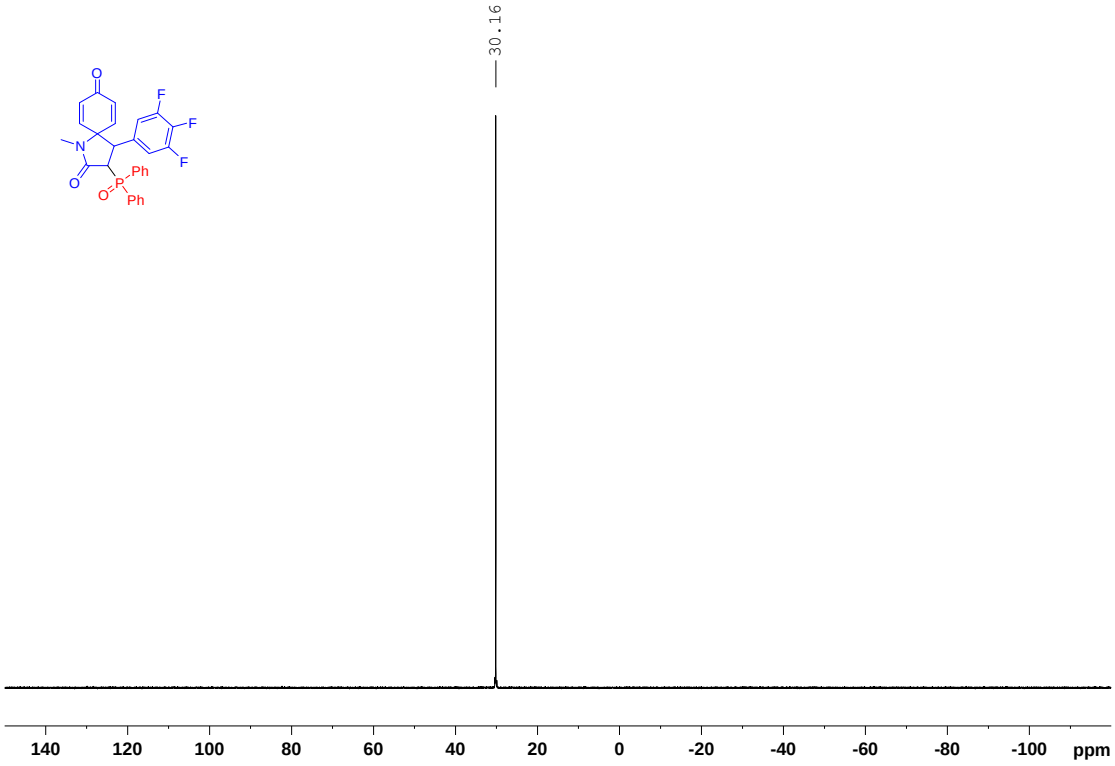
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3m**



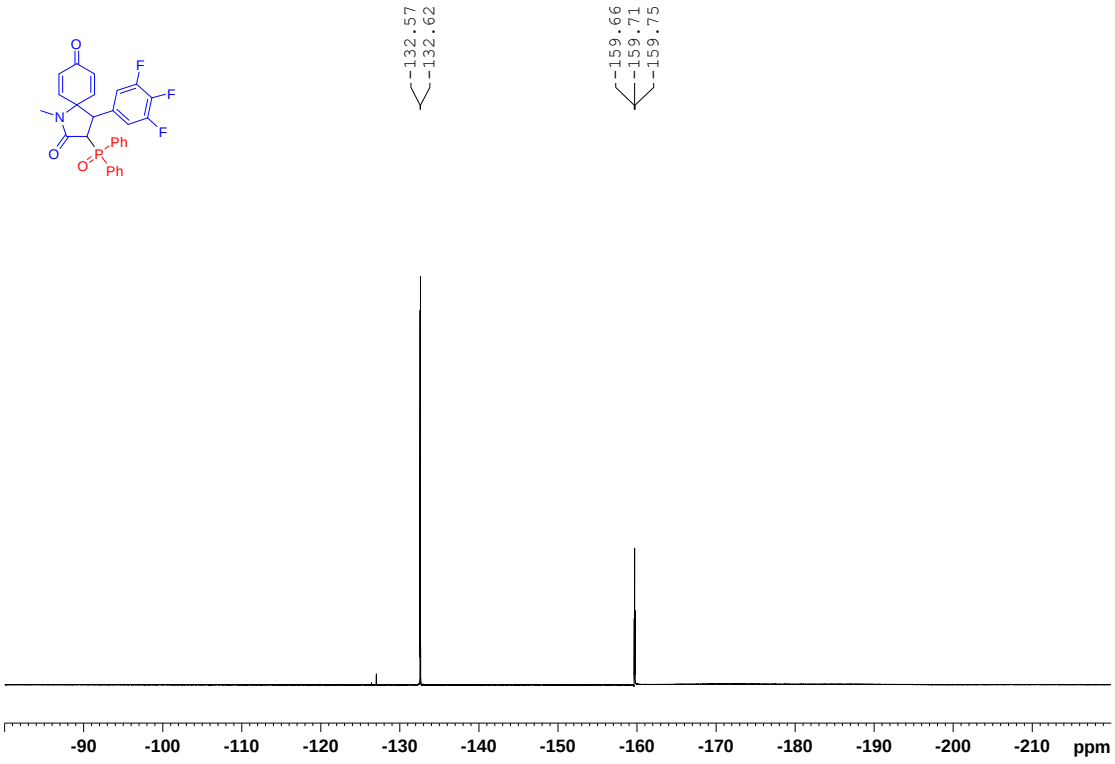
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3m**



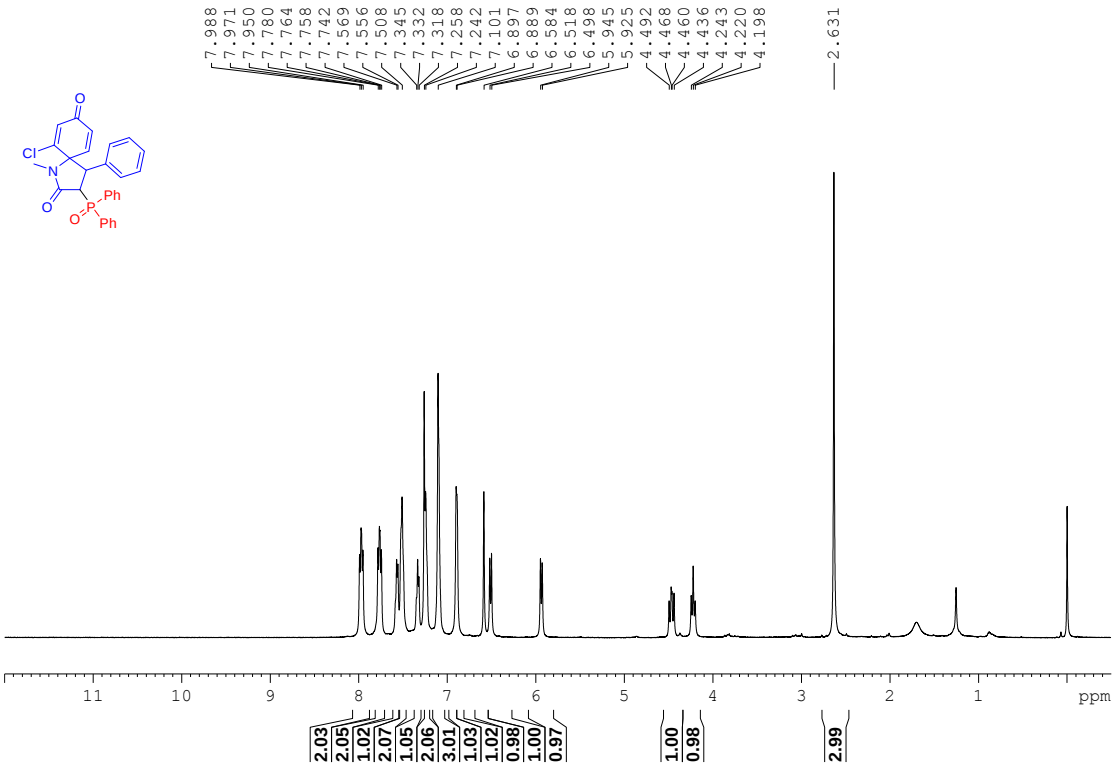
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3m**



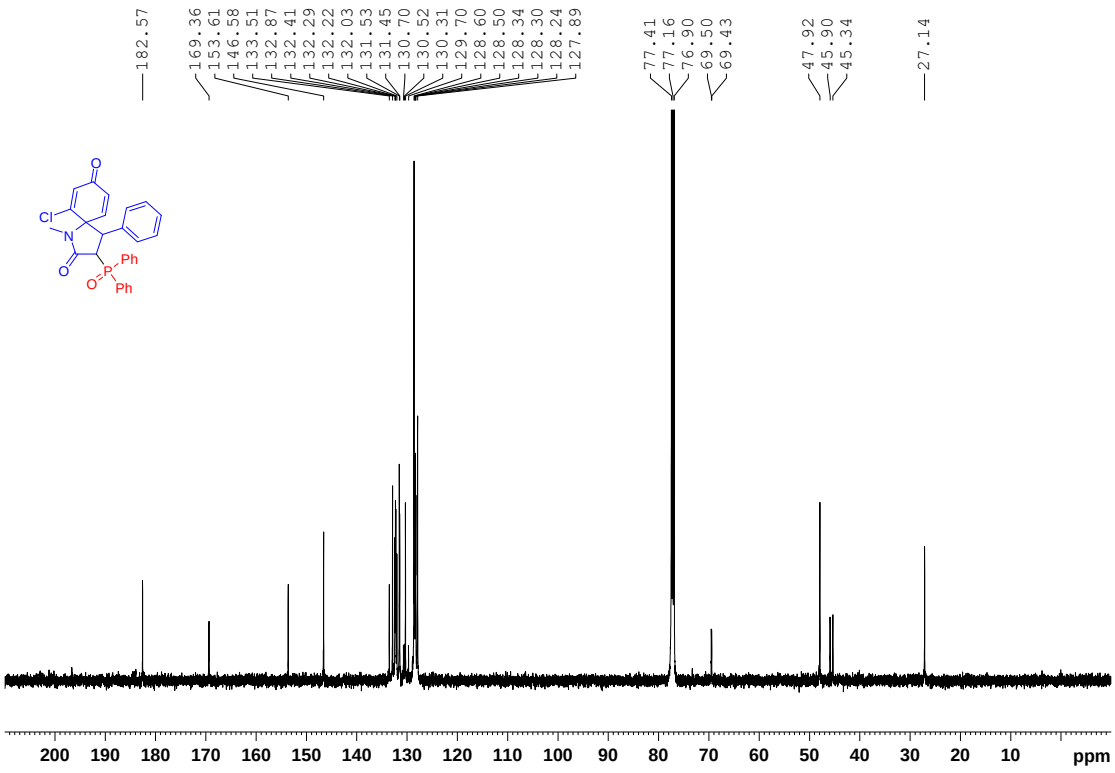
^{19}F NMR (470 MHz, $CDCl_3$, 300K): **3m**



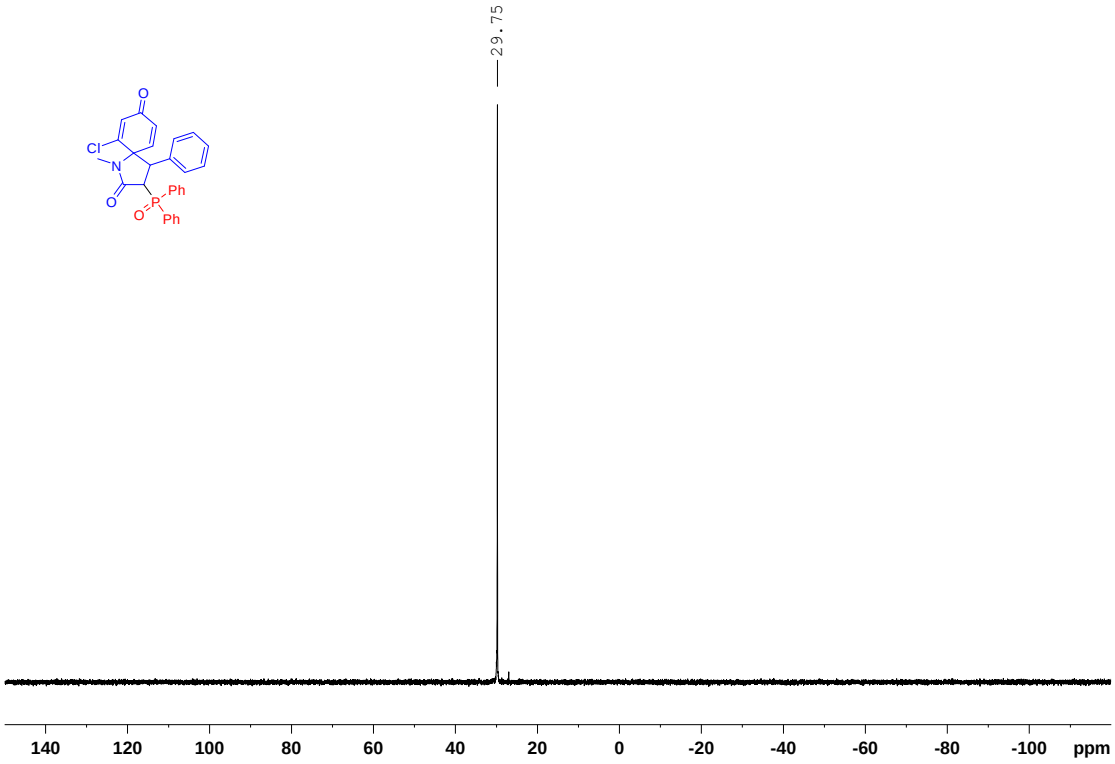
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3n**



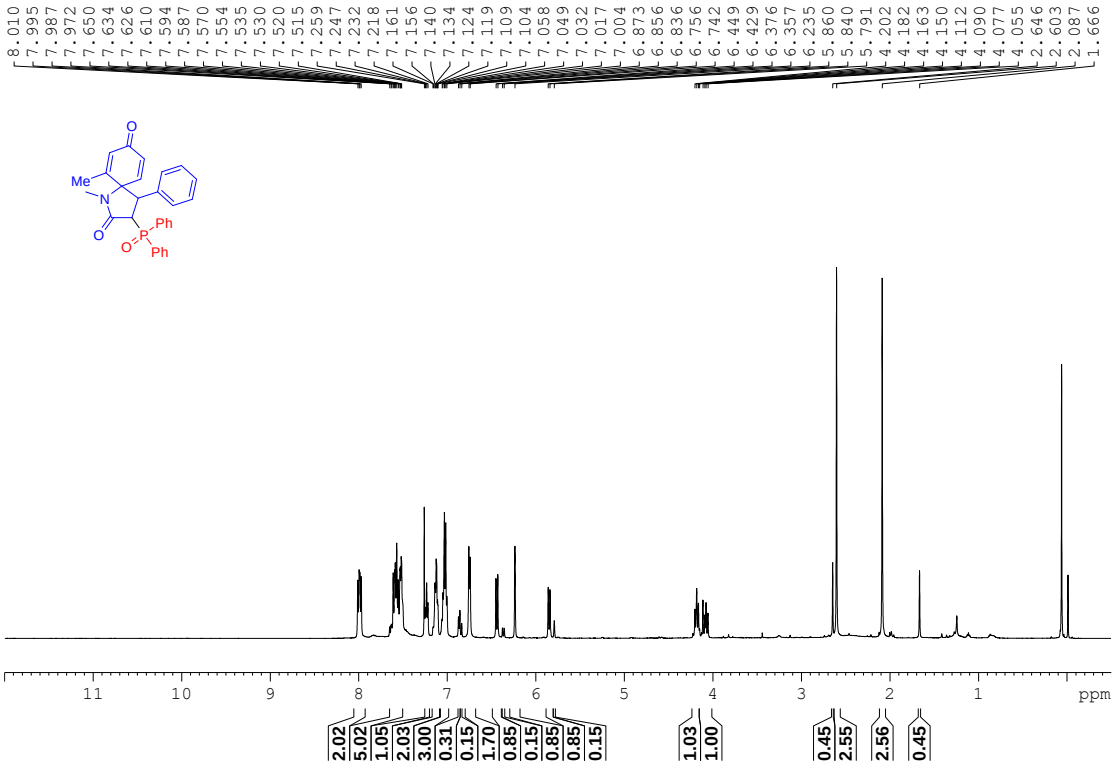
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3n**



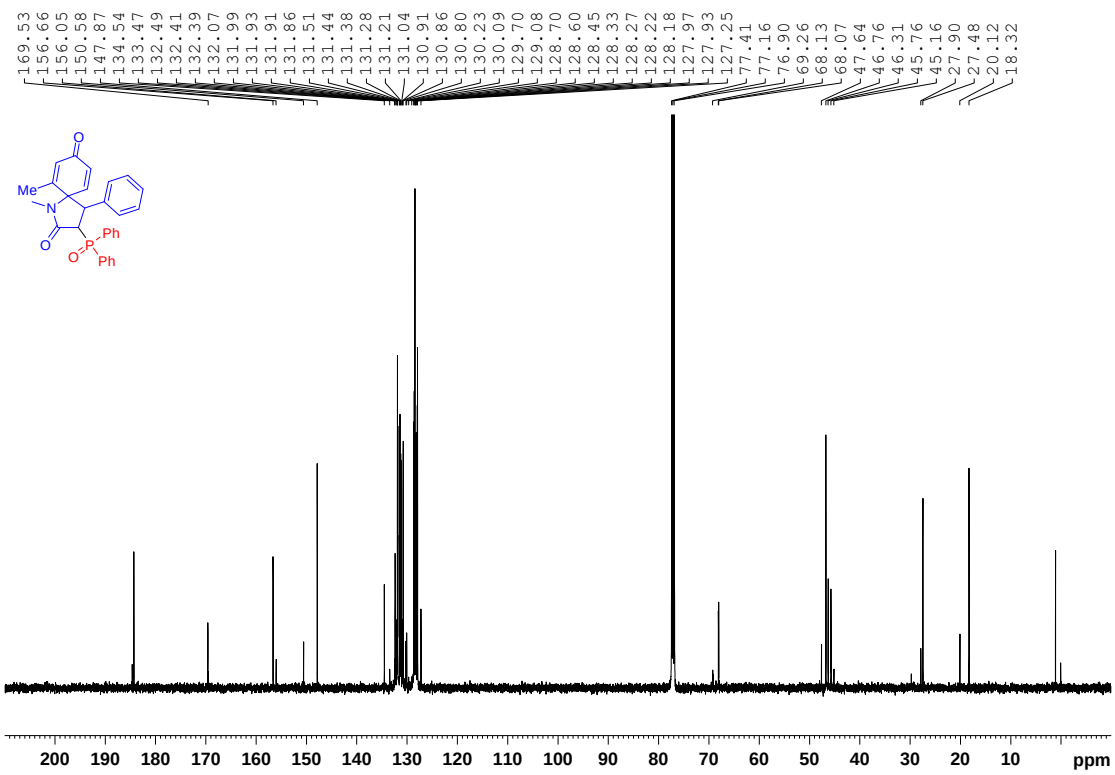
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3n**



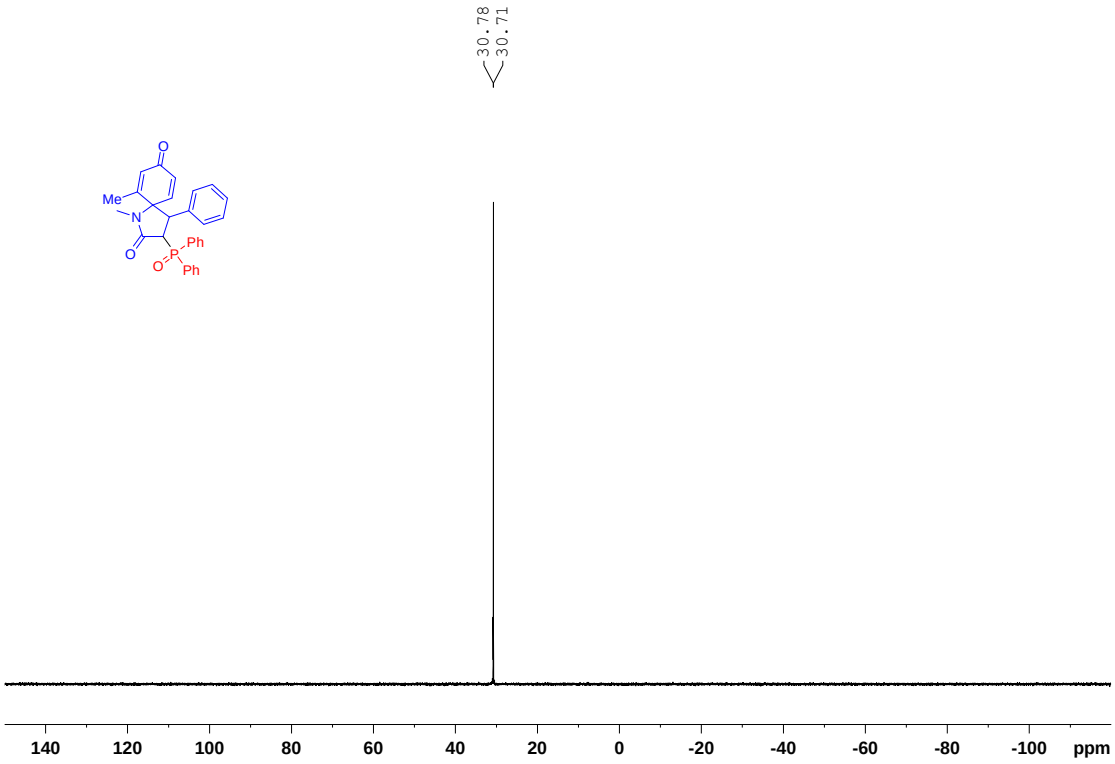
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3o**



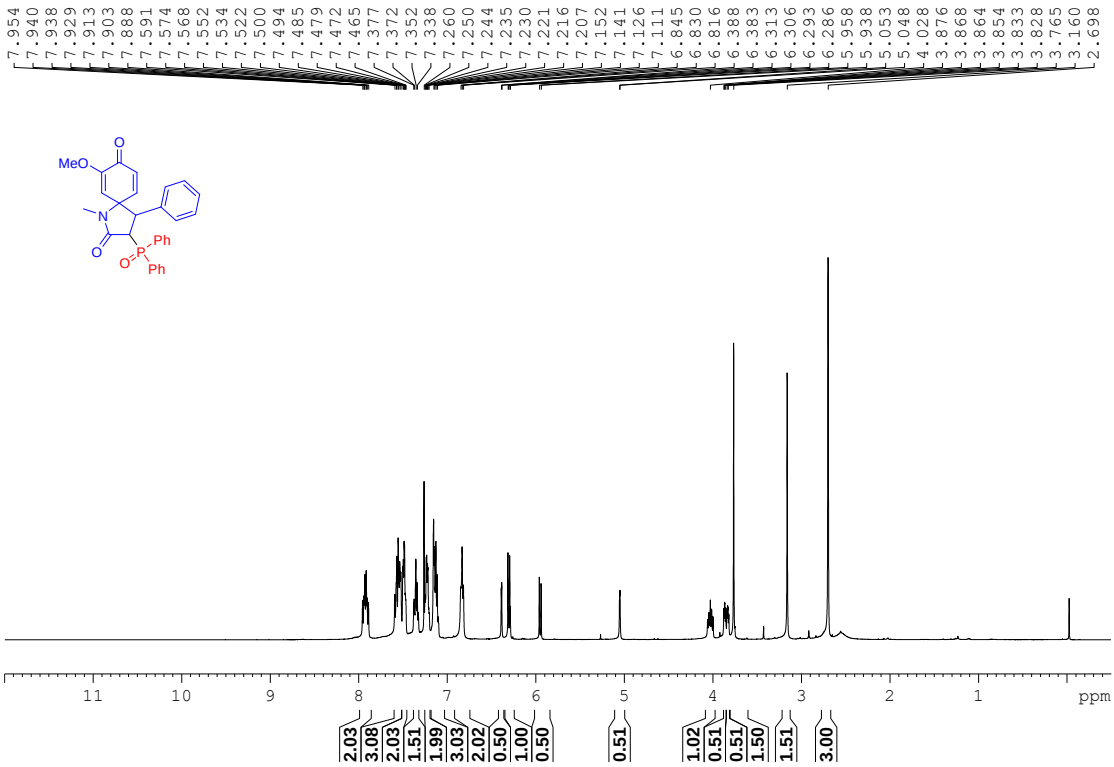
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3o**



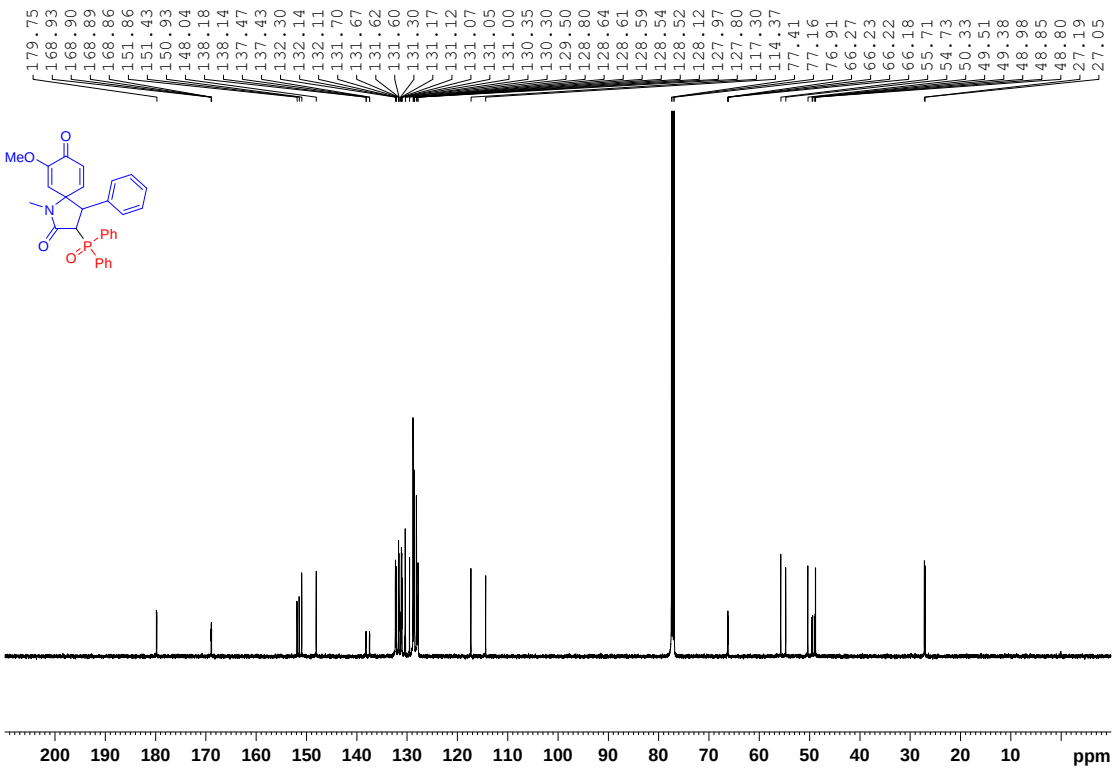
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3o**



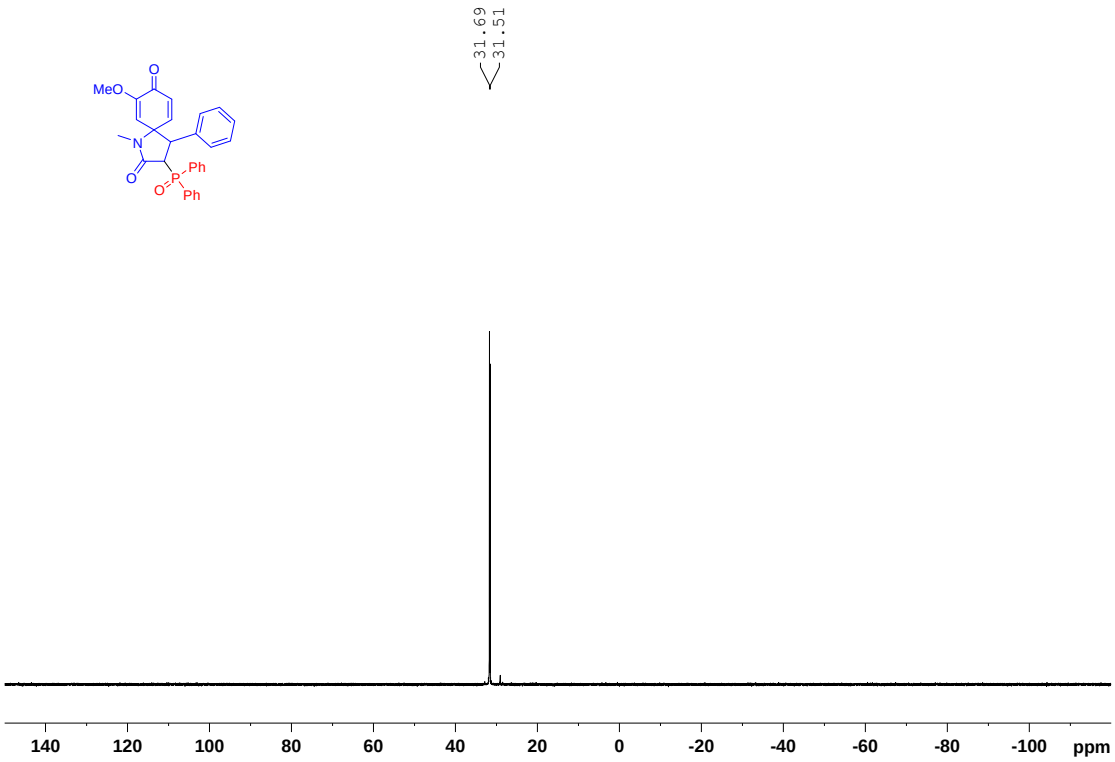
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3p**



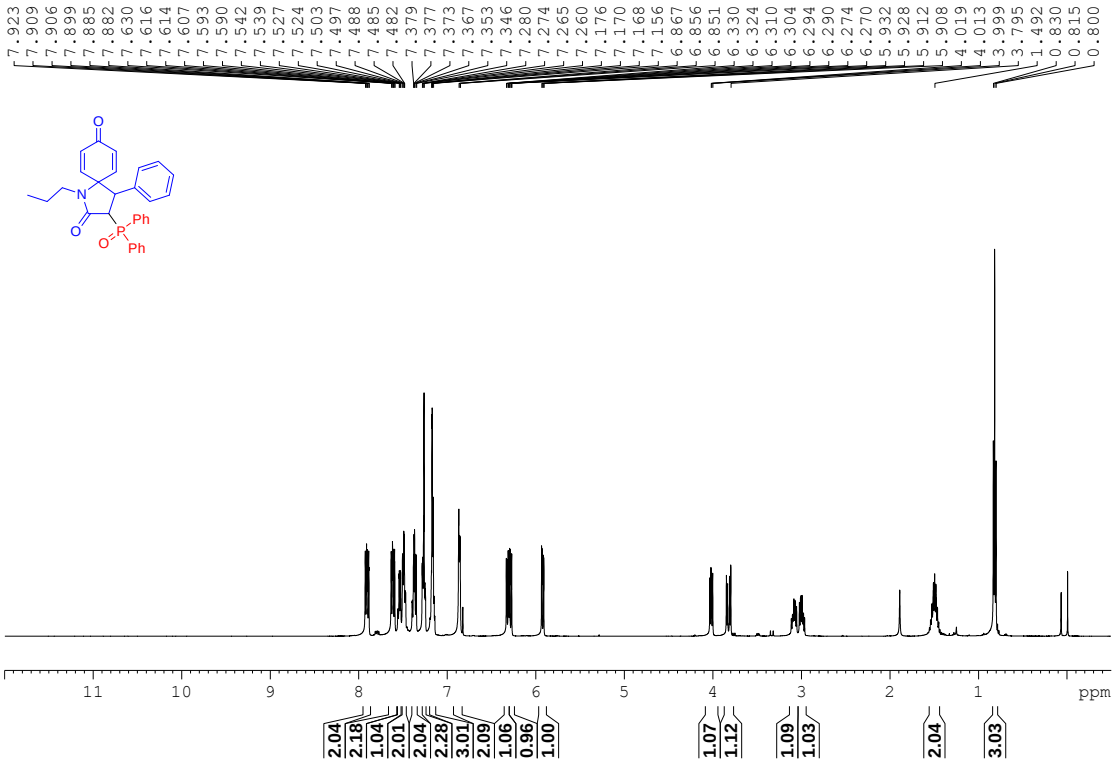
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3p**



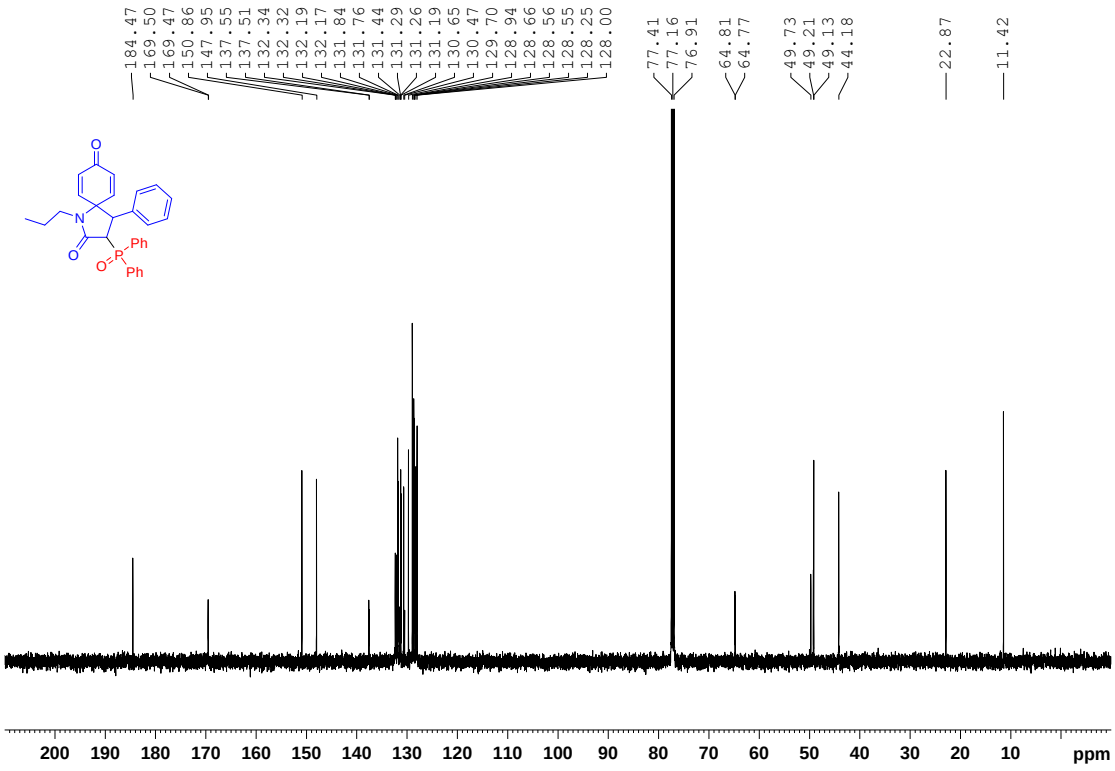
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3p**



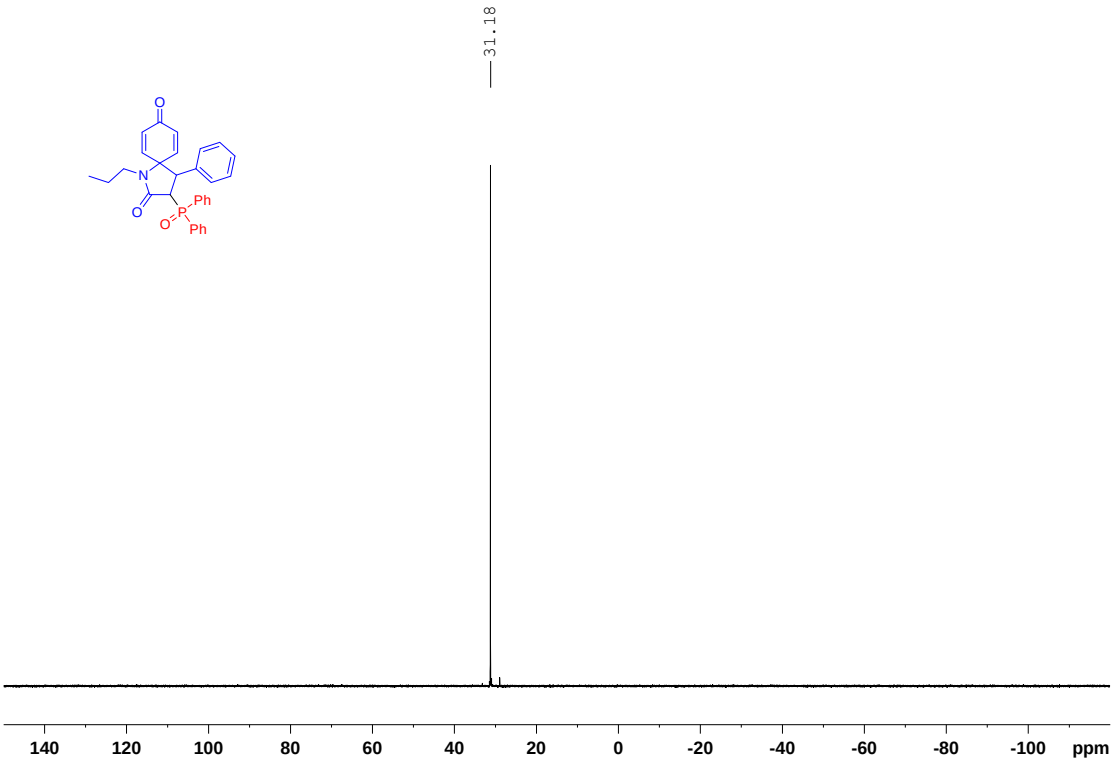
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3q**



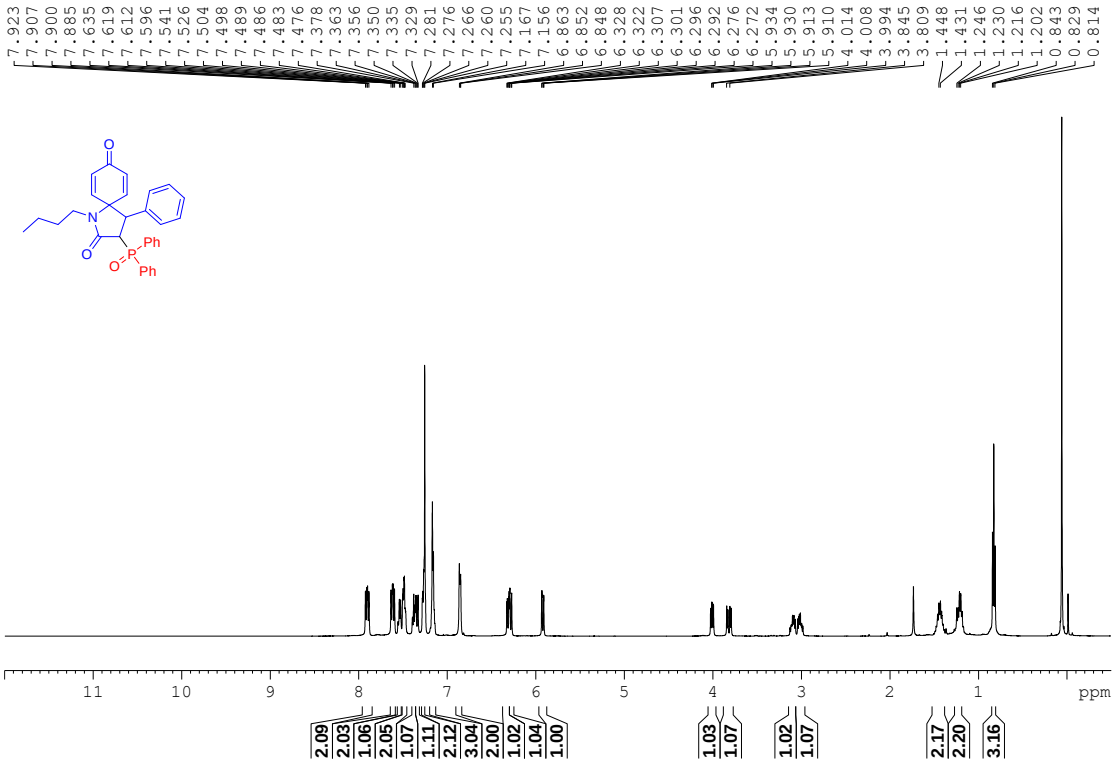
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3q**



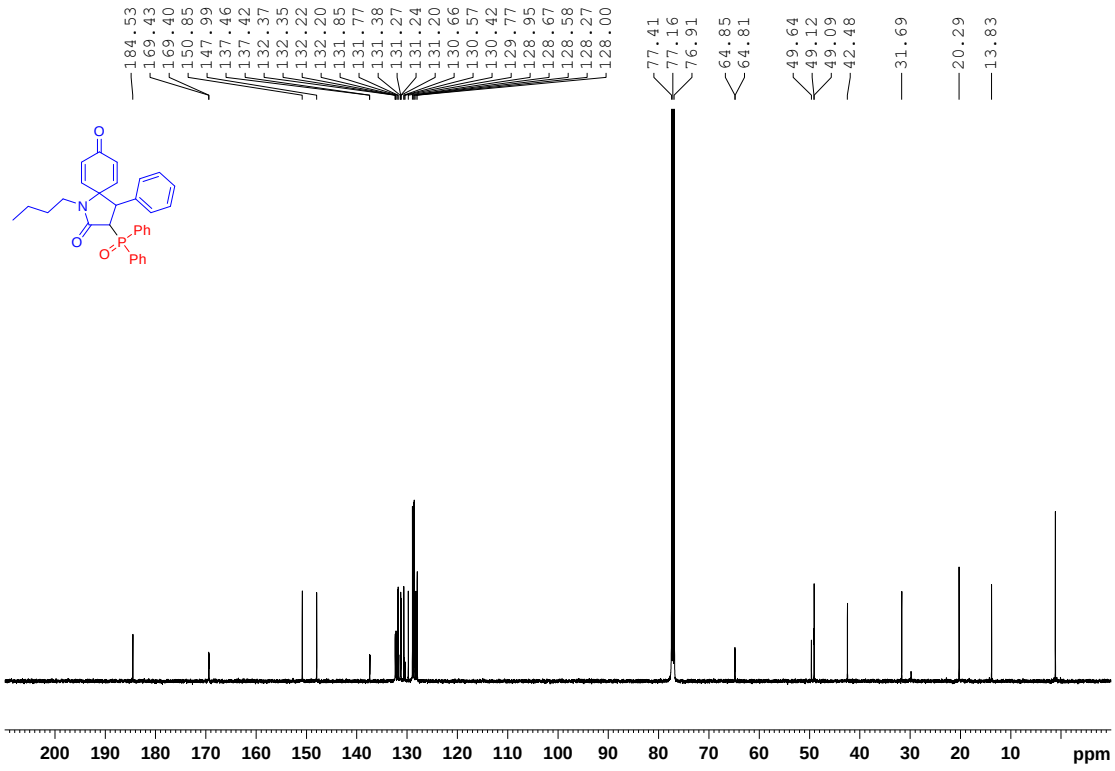
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3q**



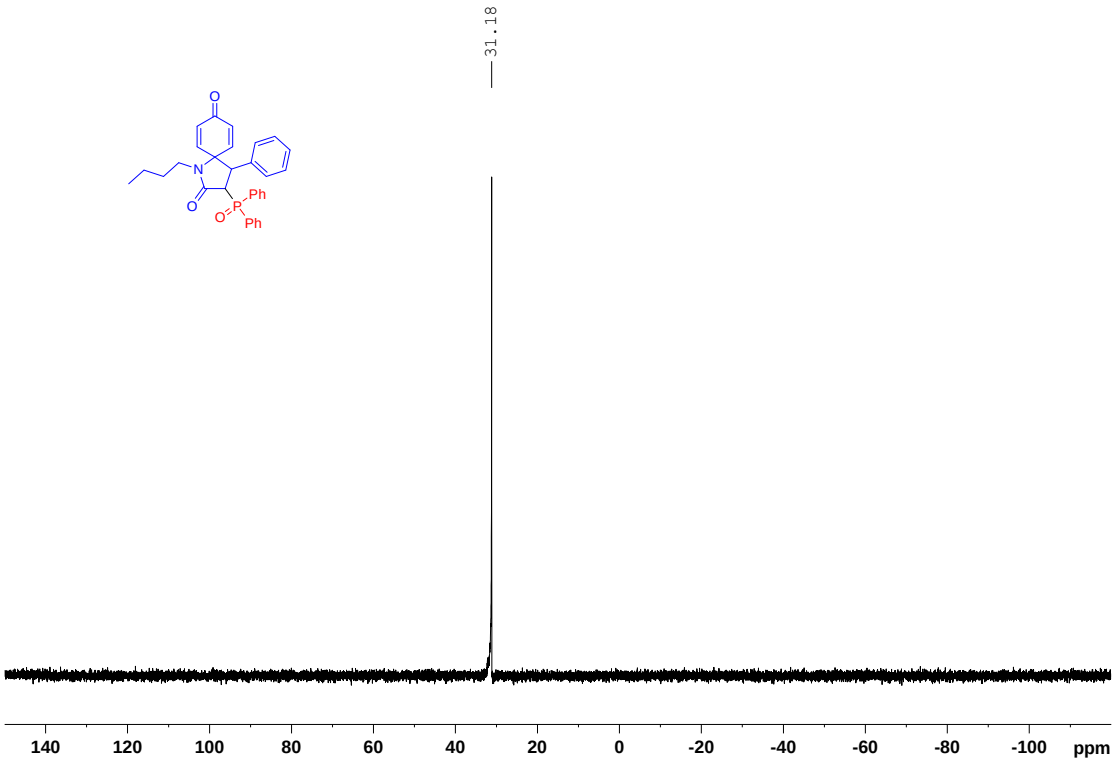
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3r**



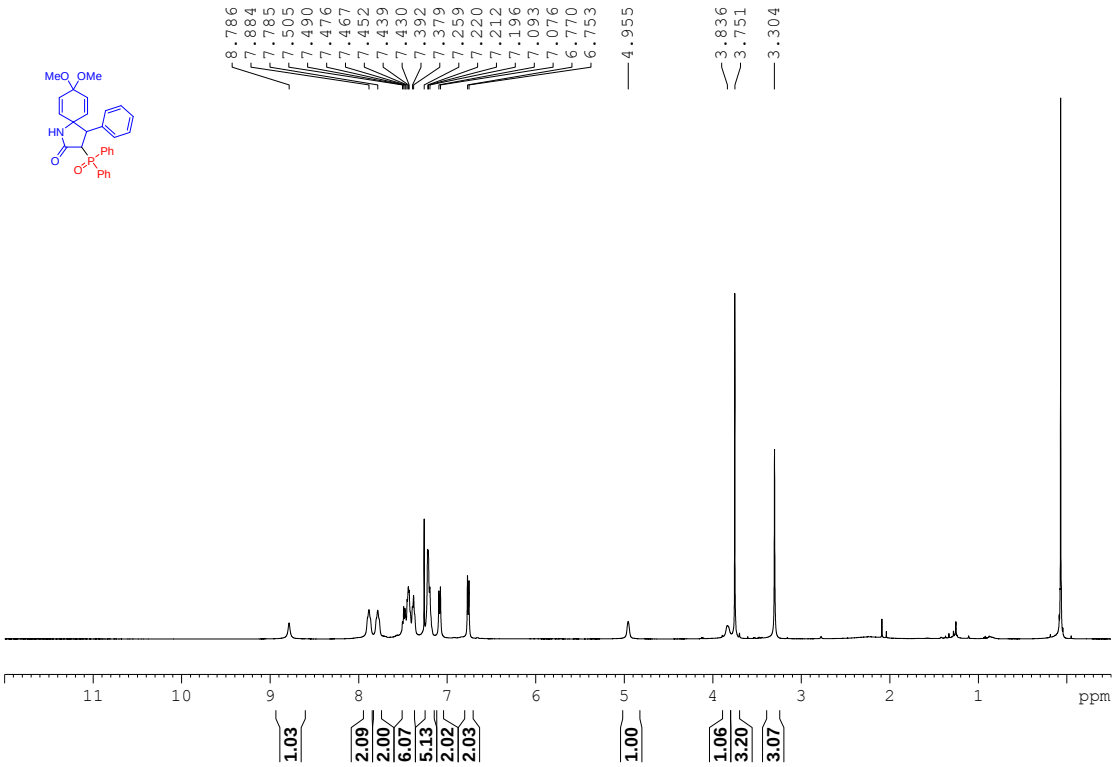
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3r**



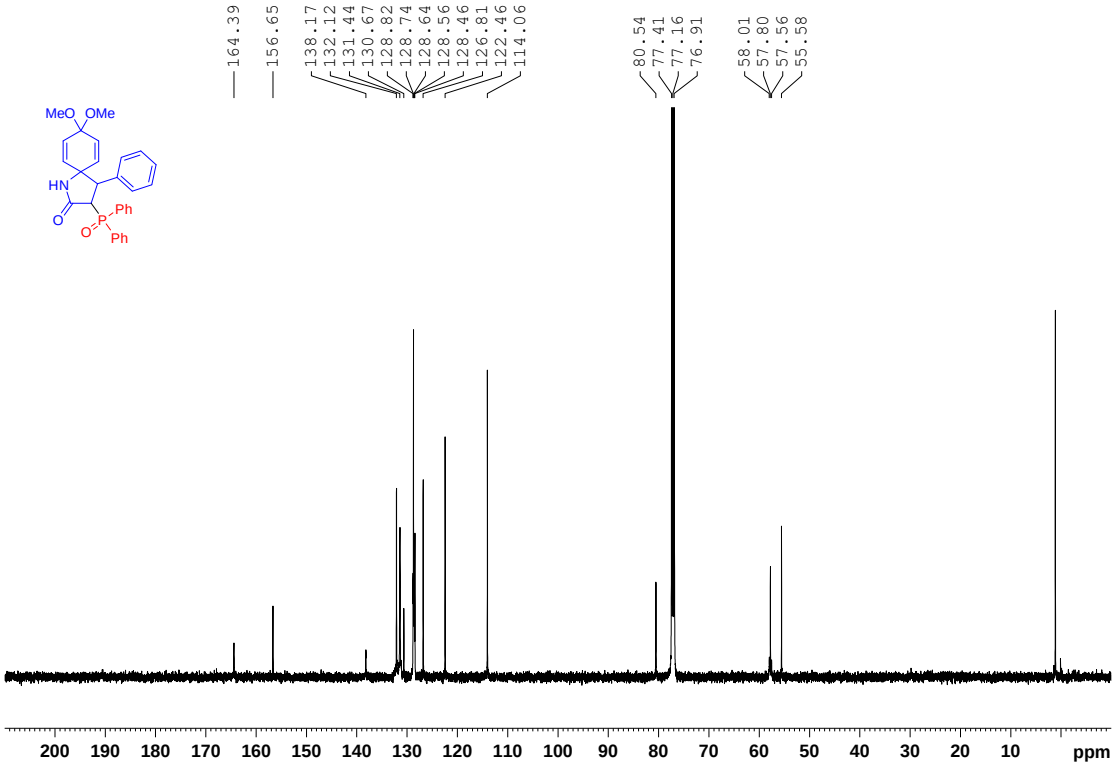
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3r**



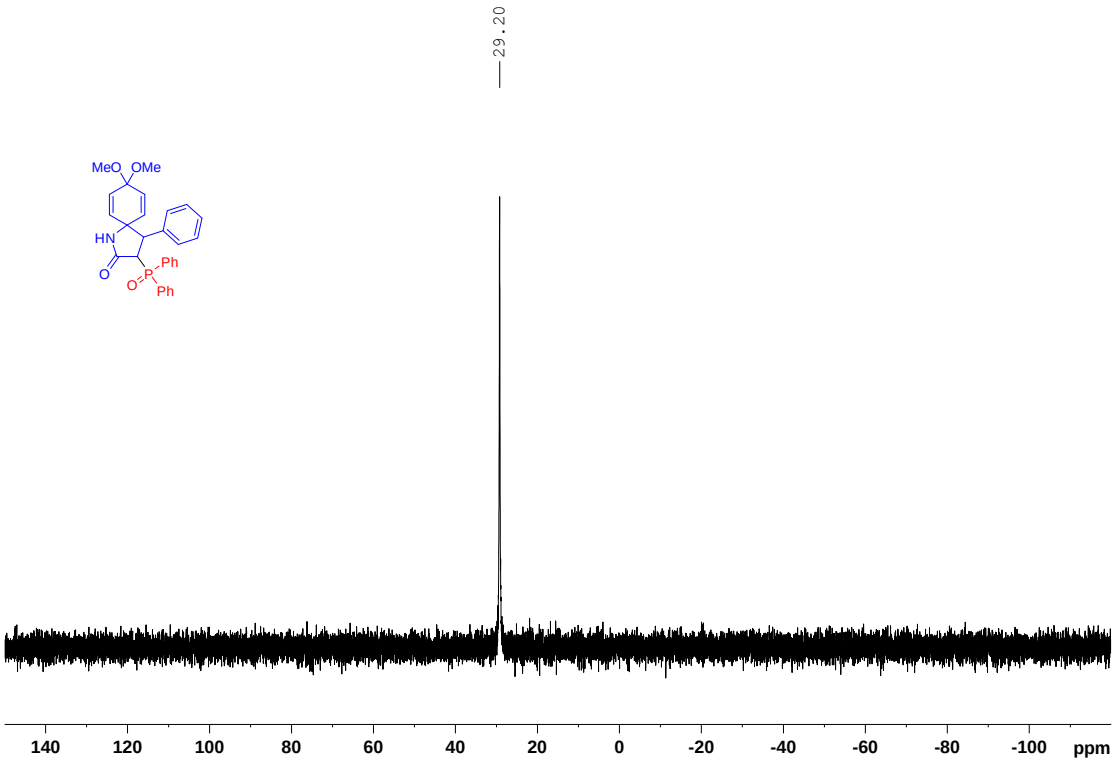
^{1}H NMR (500 MHz, $CDCl_3$, 300K):**3s**



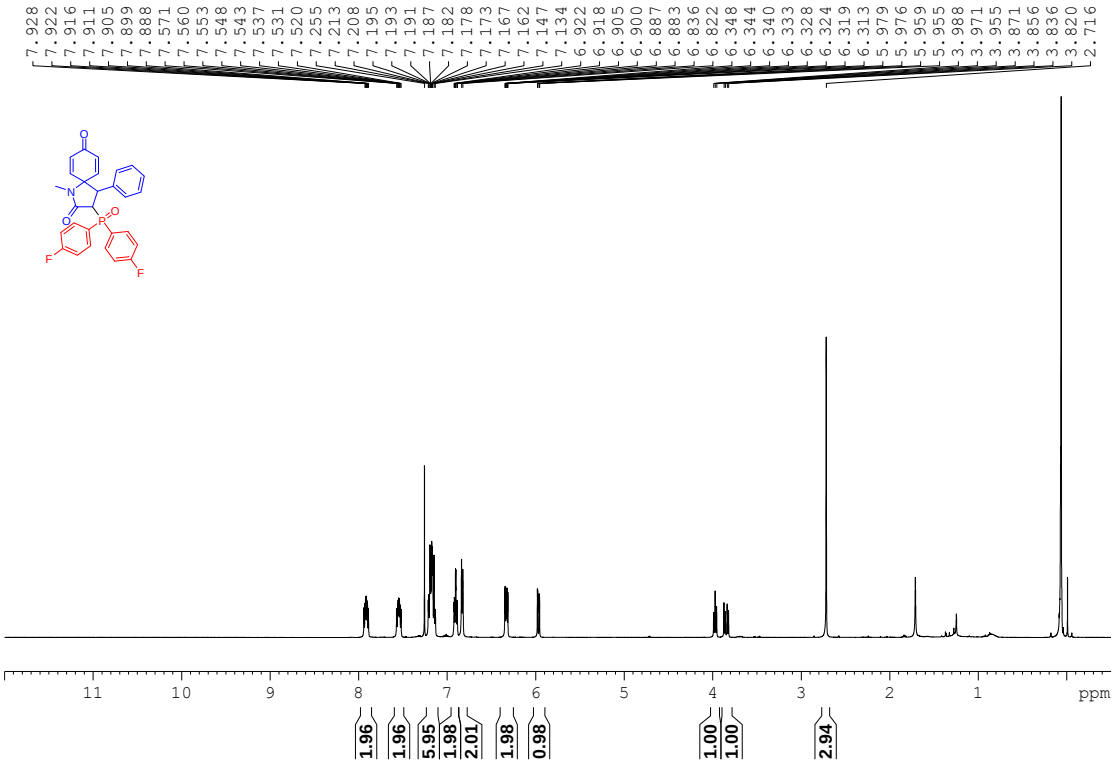
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3s**



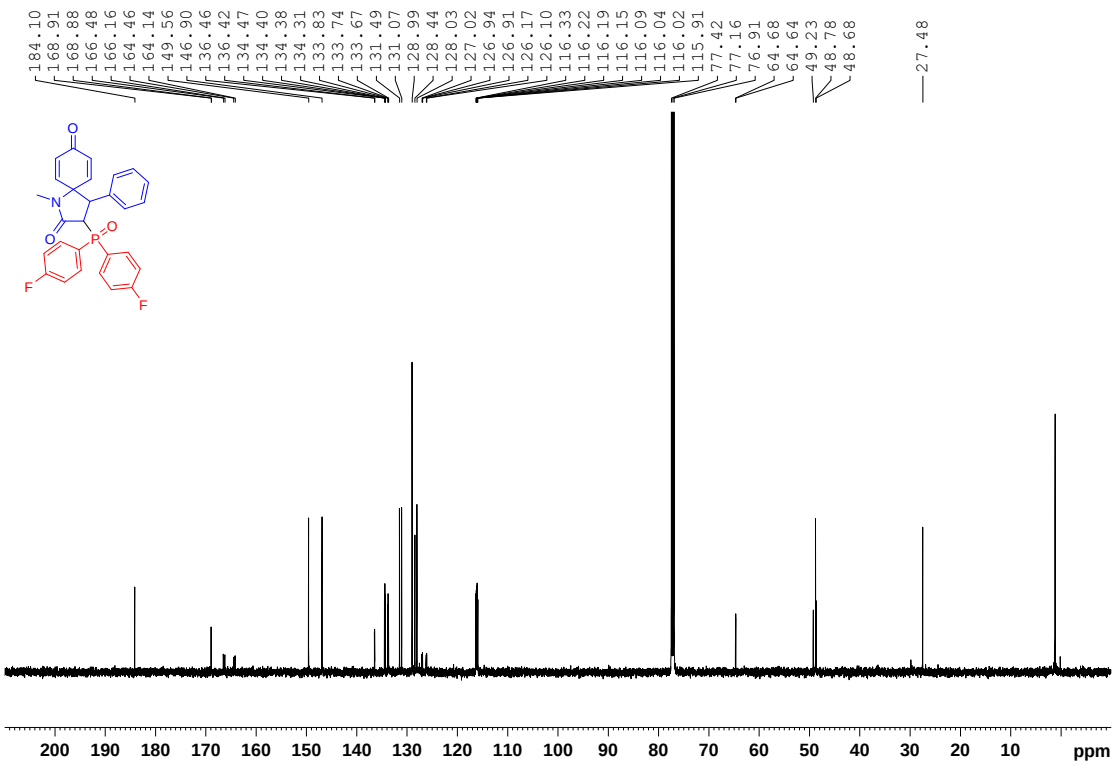
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3s**



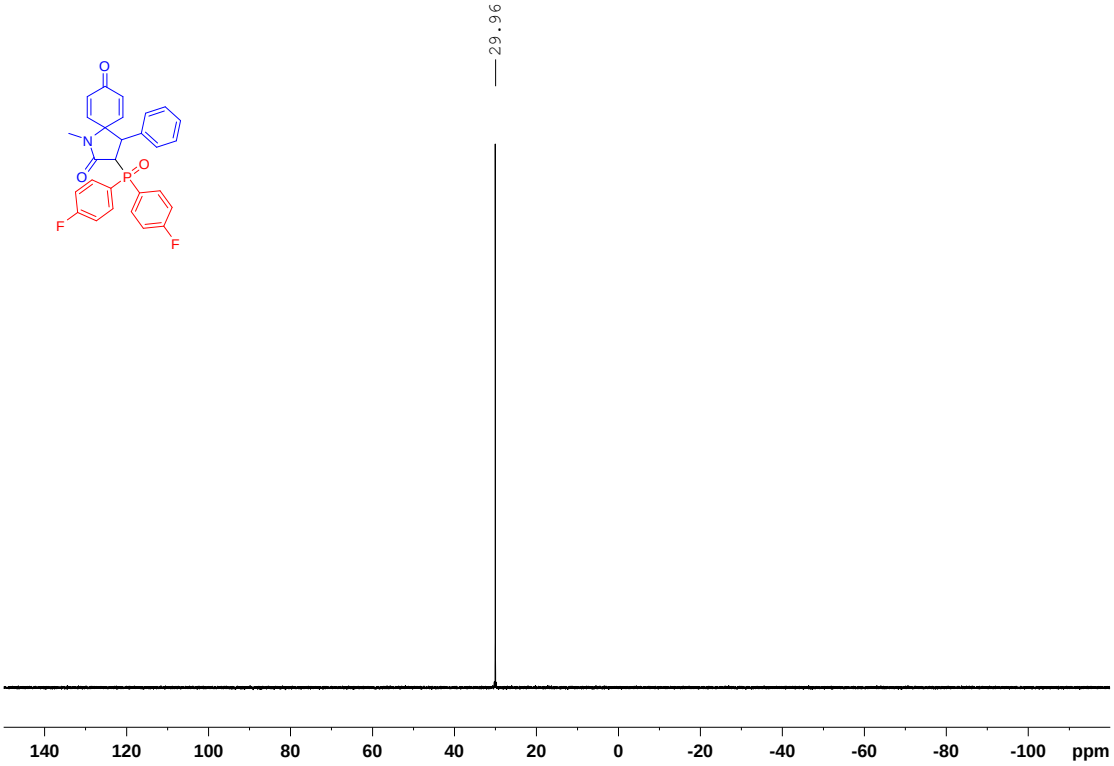
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3t**



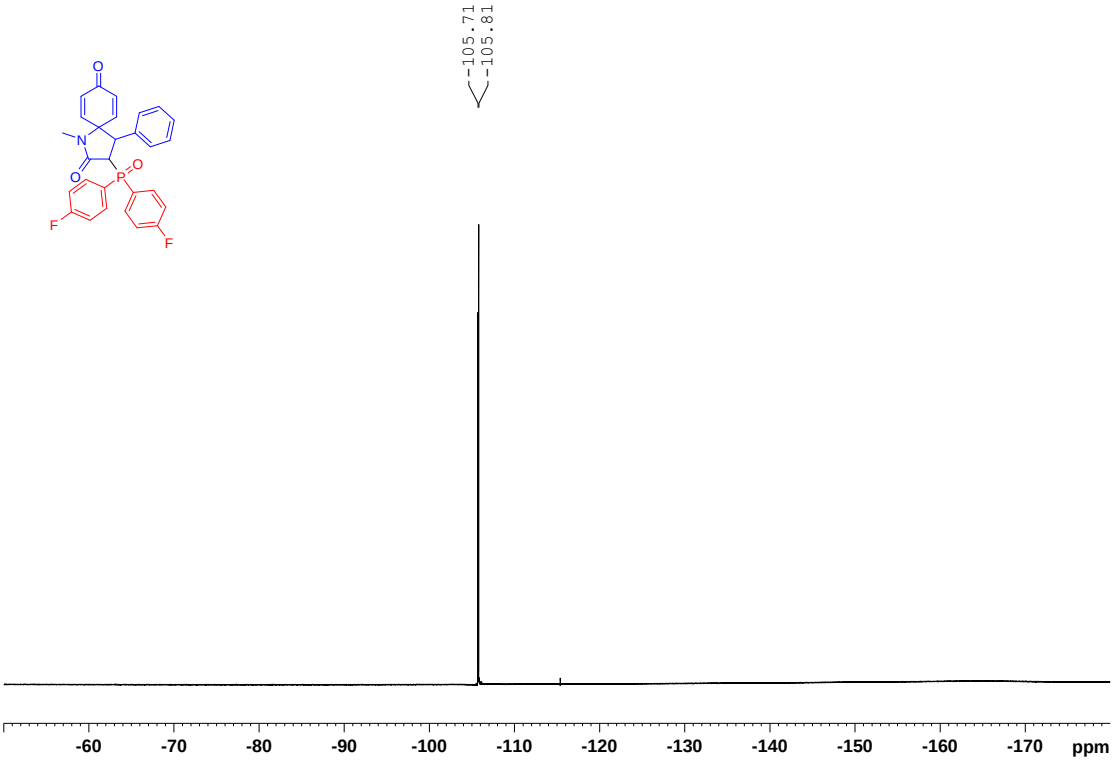
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3t**



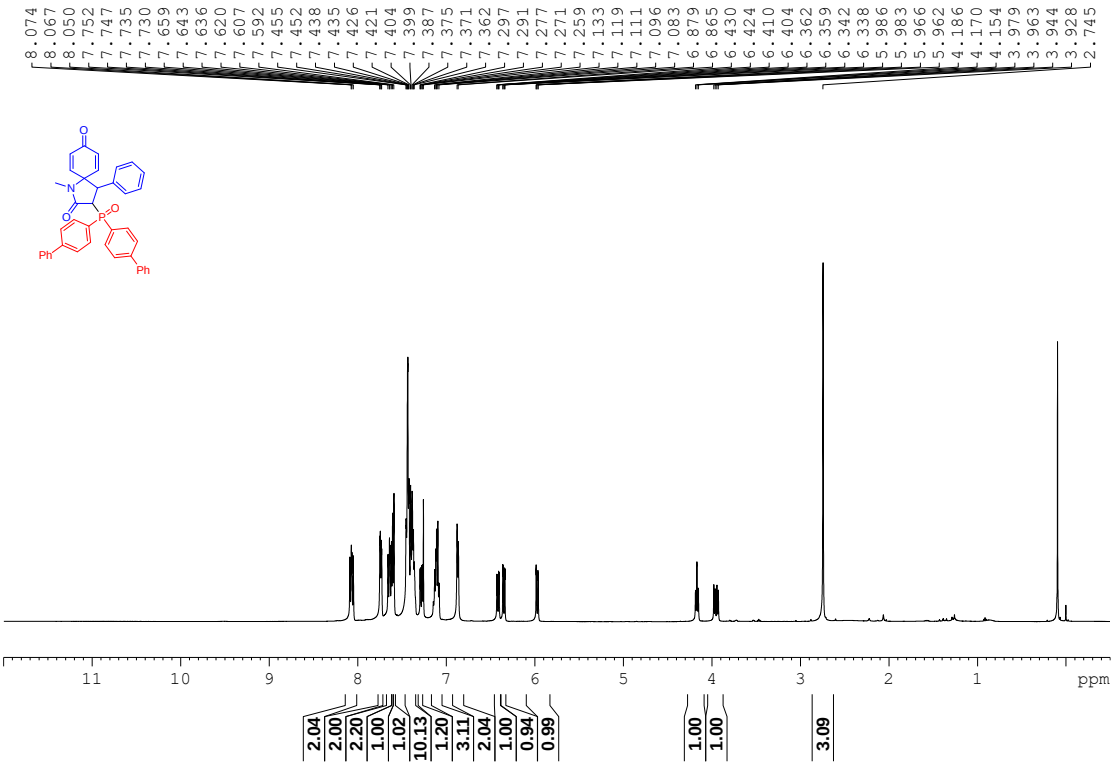
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3t**



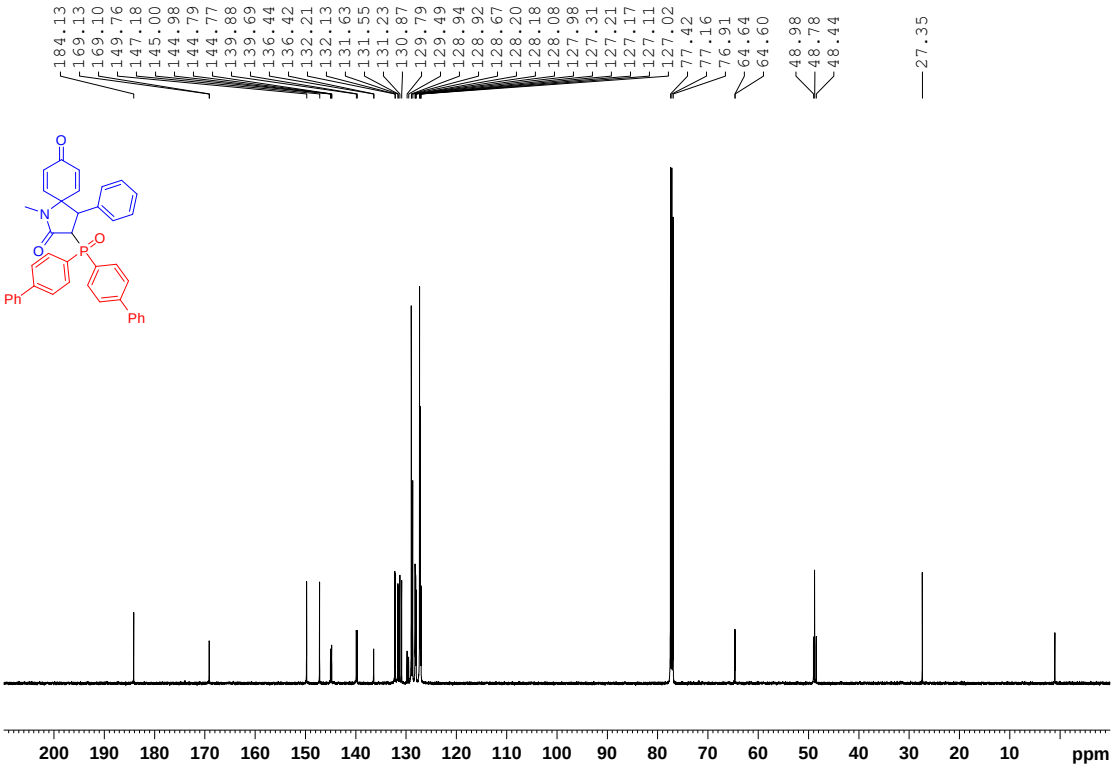
^{19}F NMR (470 MHz, $CDCl_3$, 300K): **3t**



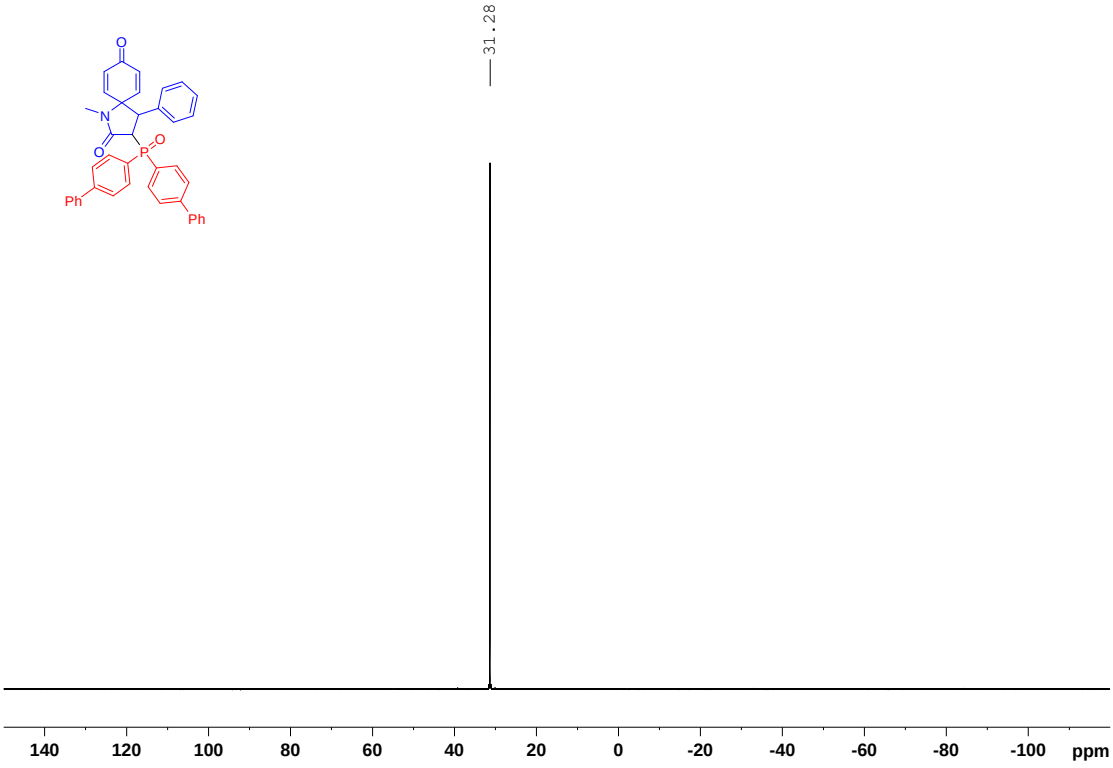
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3u**



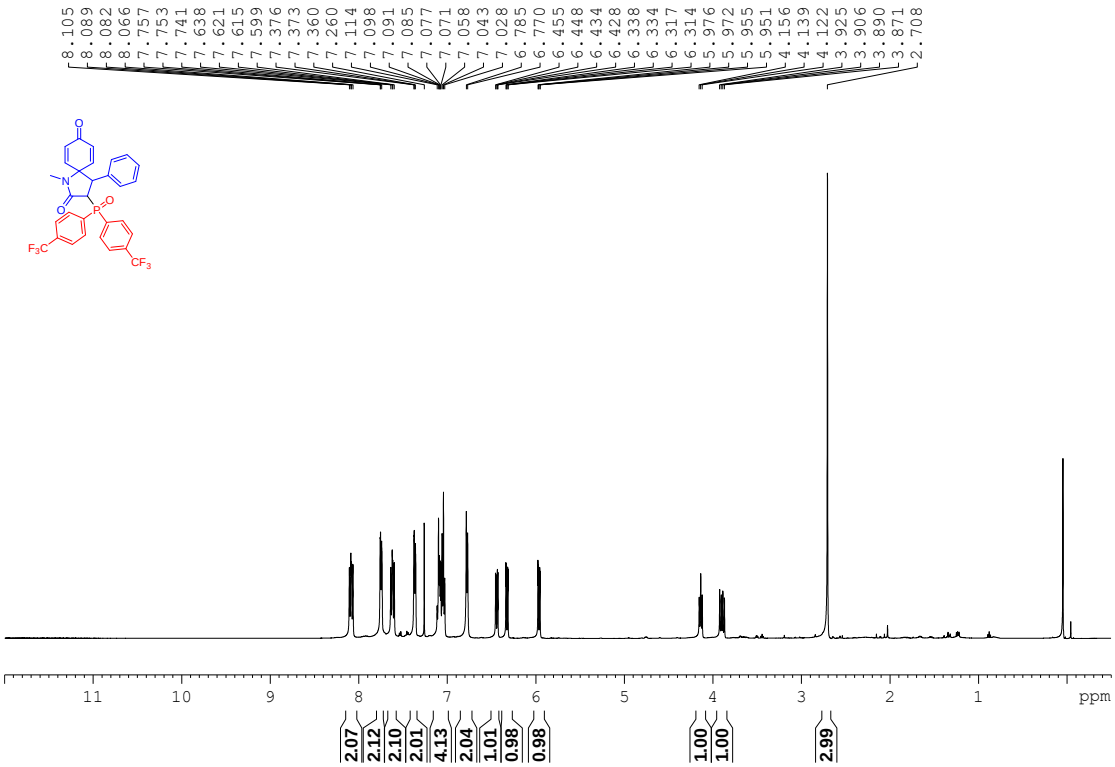
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3u**



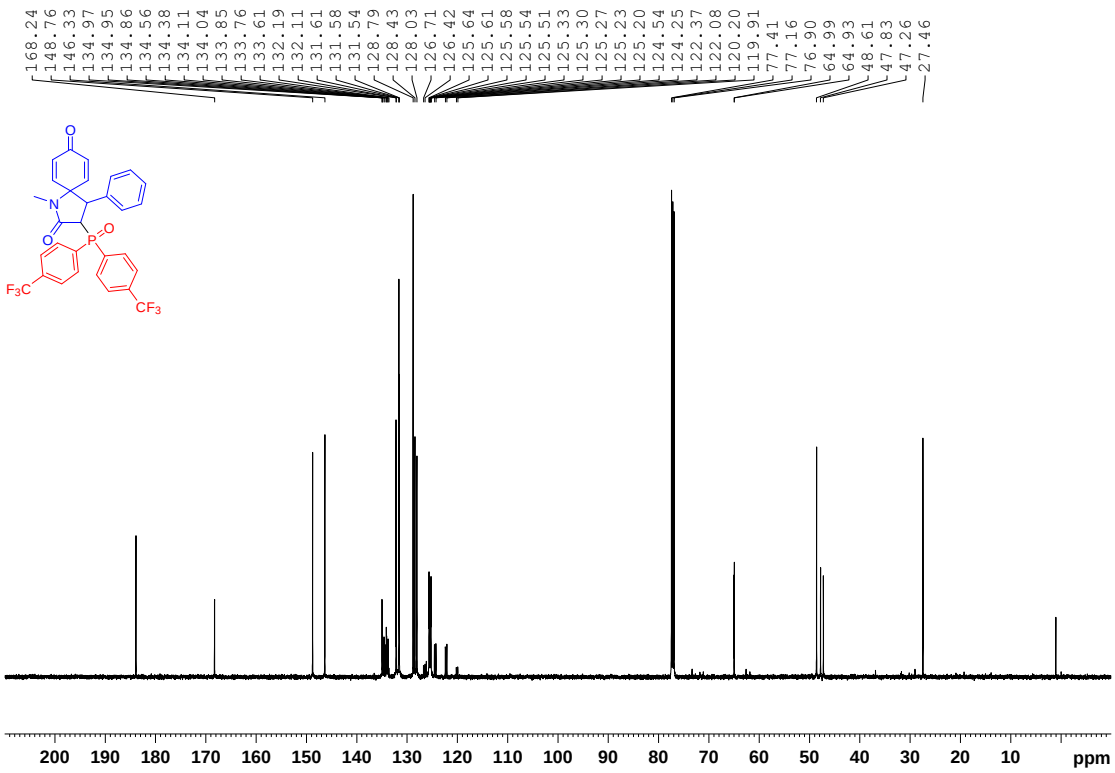
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3u**



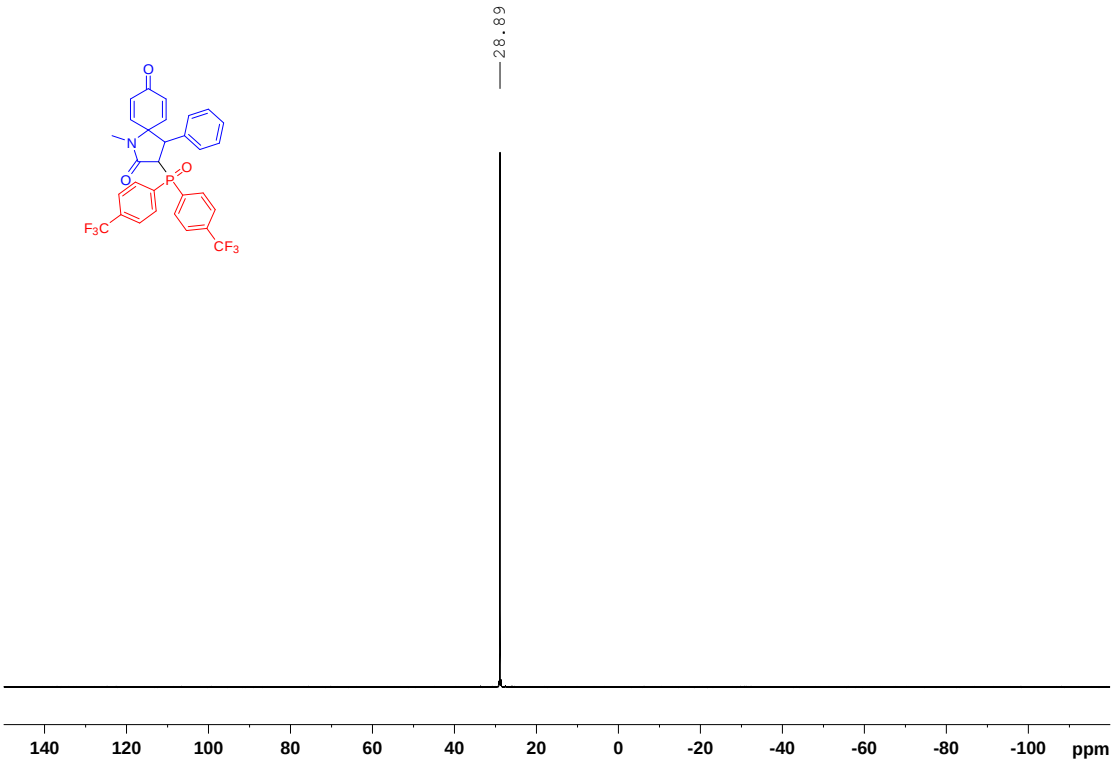
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **3v**



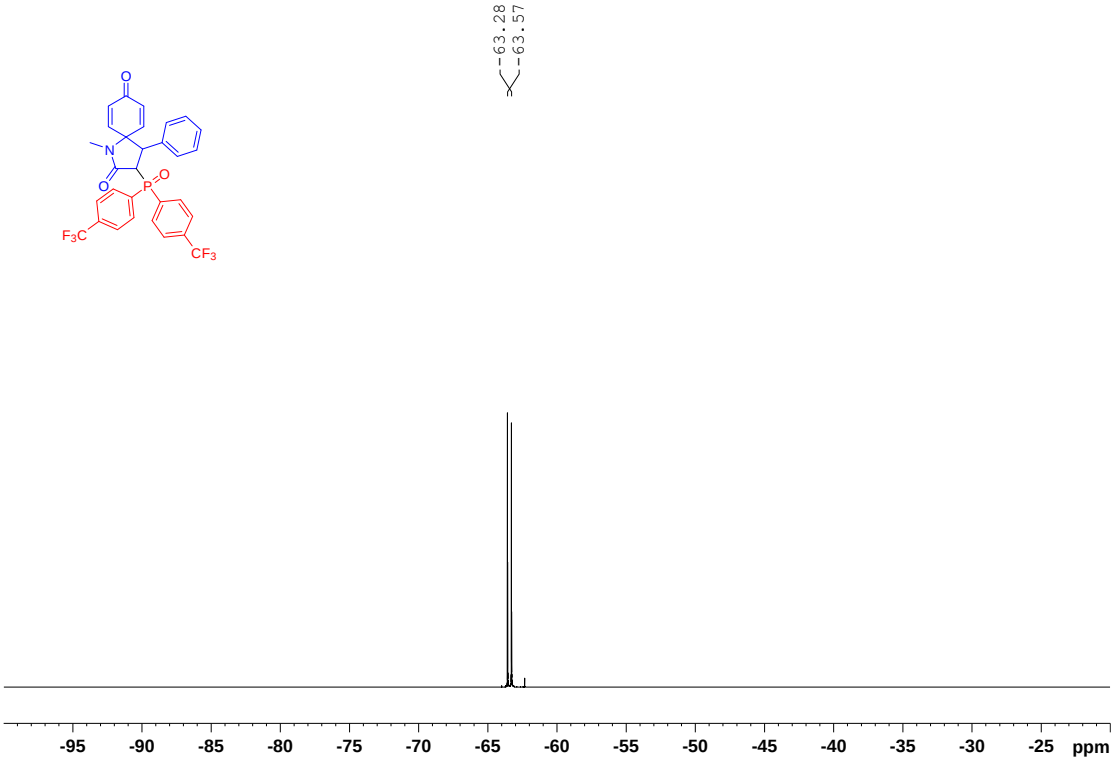
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **3v**



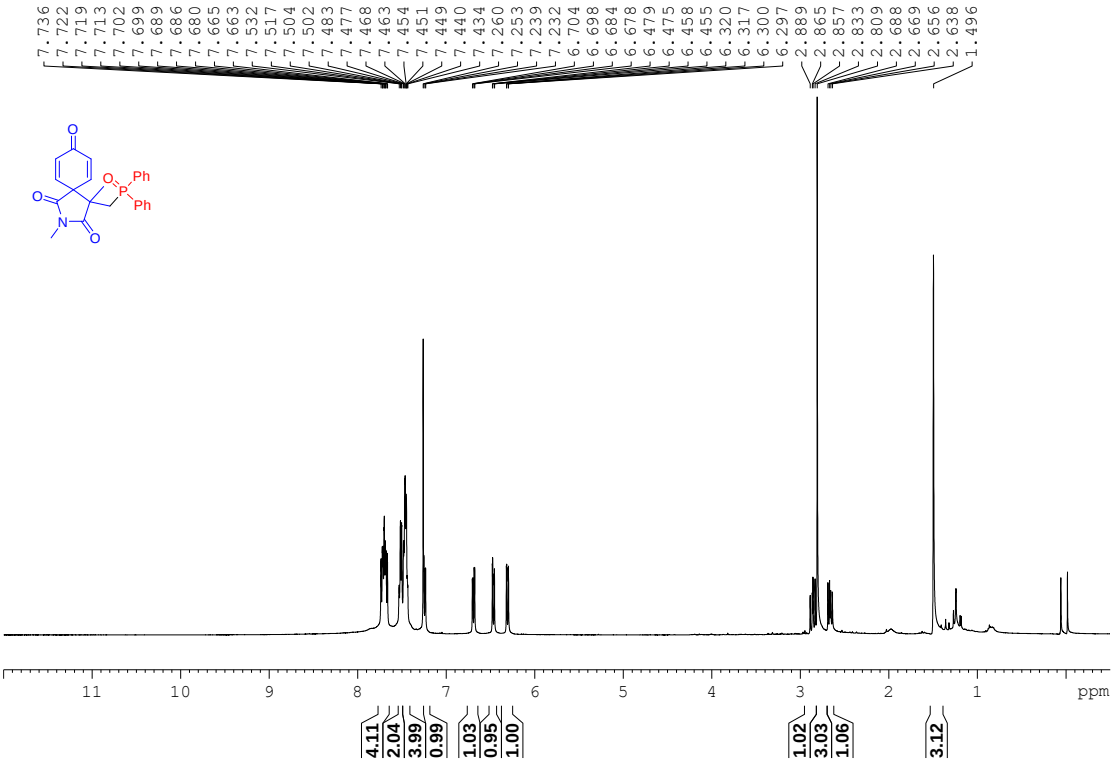
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **3v**



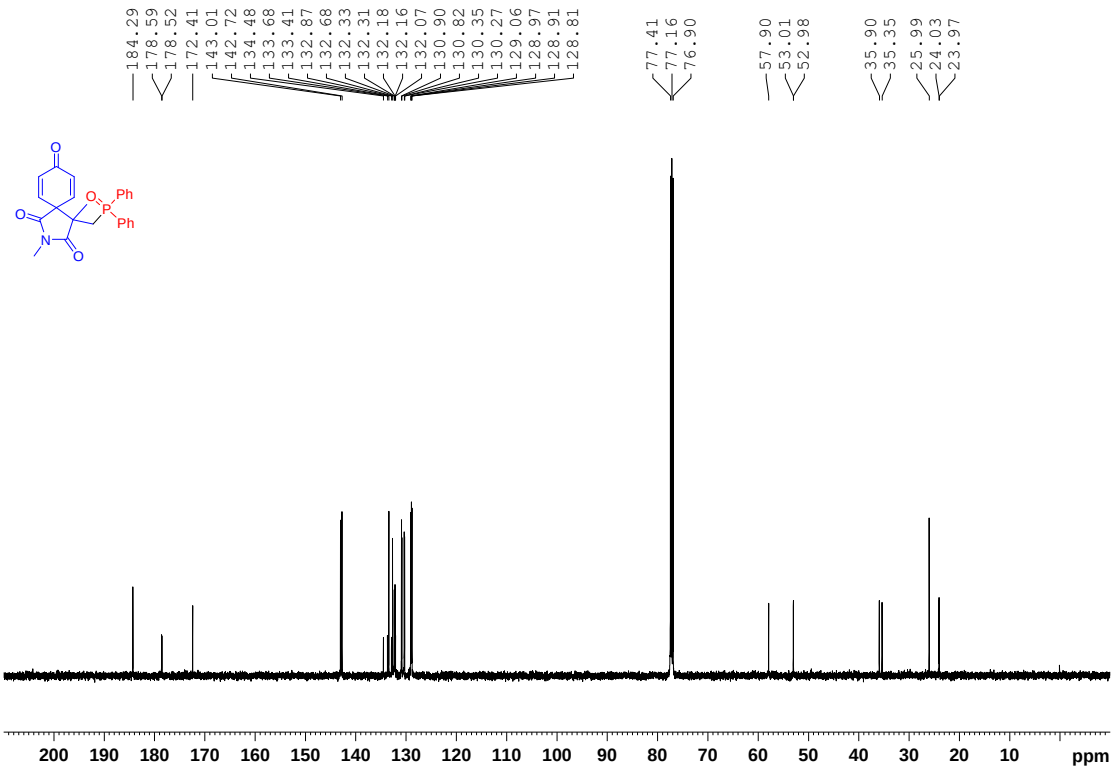
^{19}F NMR (470 MHz, $CDCl_3$, 300K): **3v**



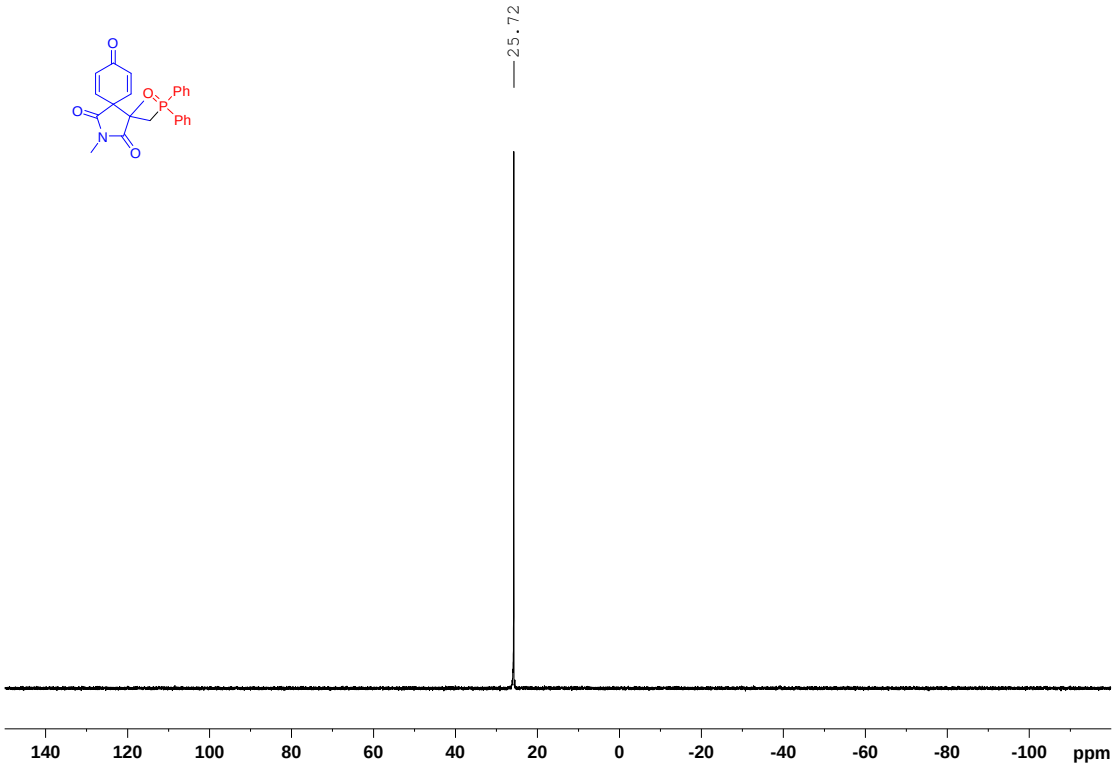
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **5a**



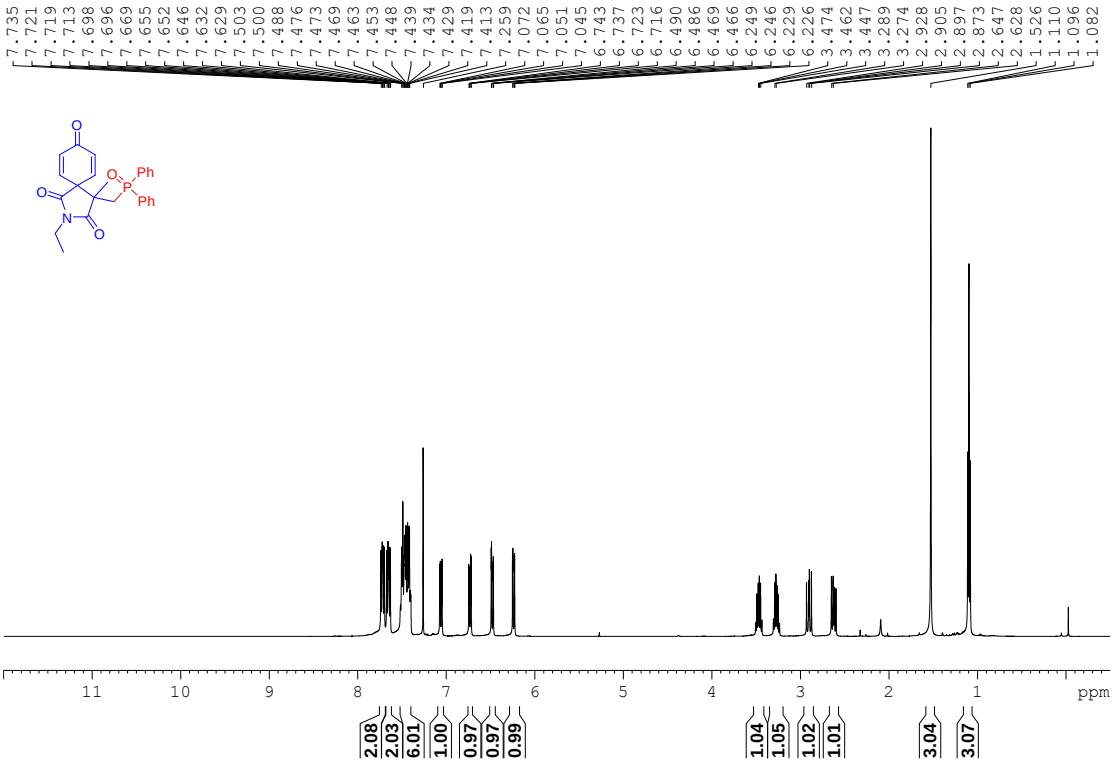
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **5a**



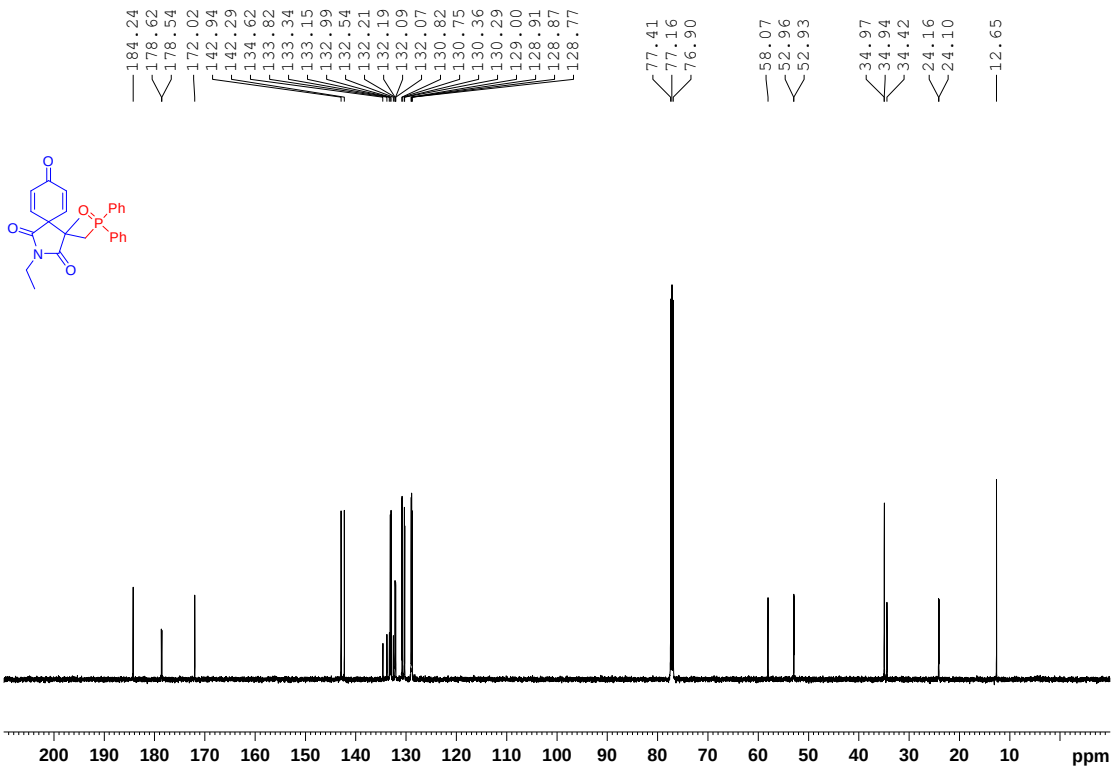
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **5a**



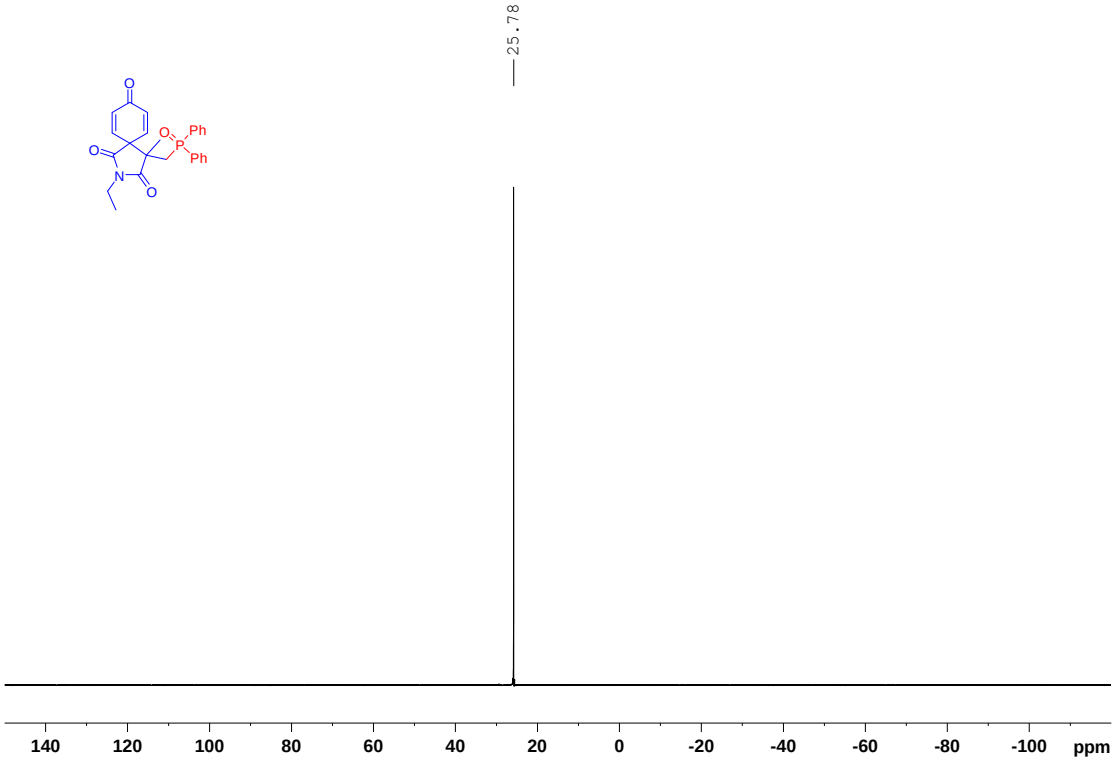
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **5b**



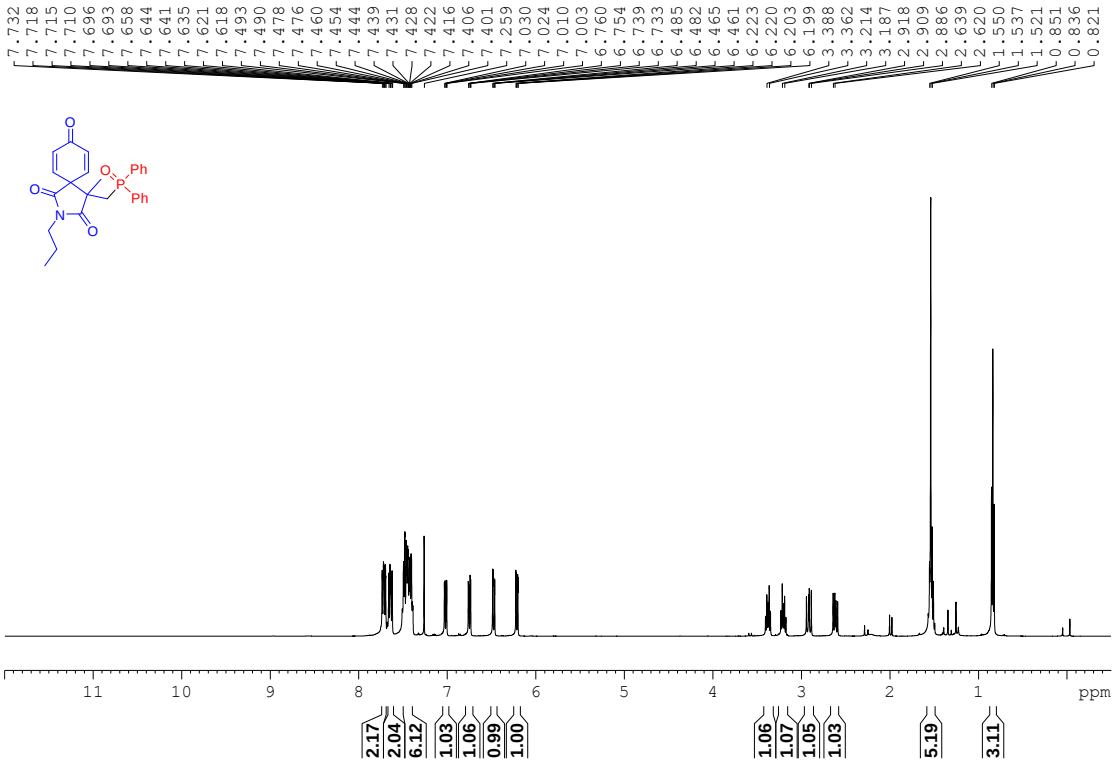
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **5b**



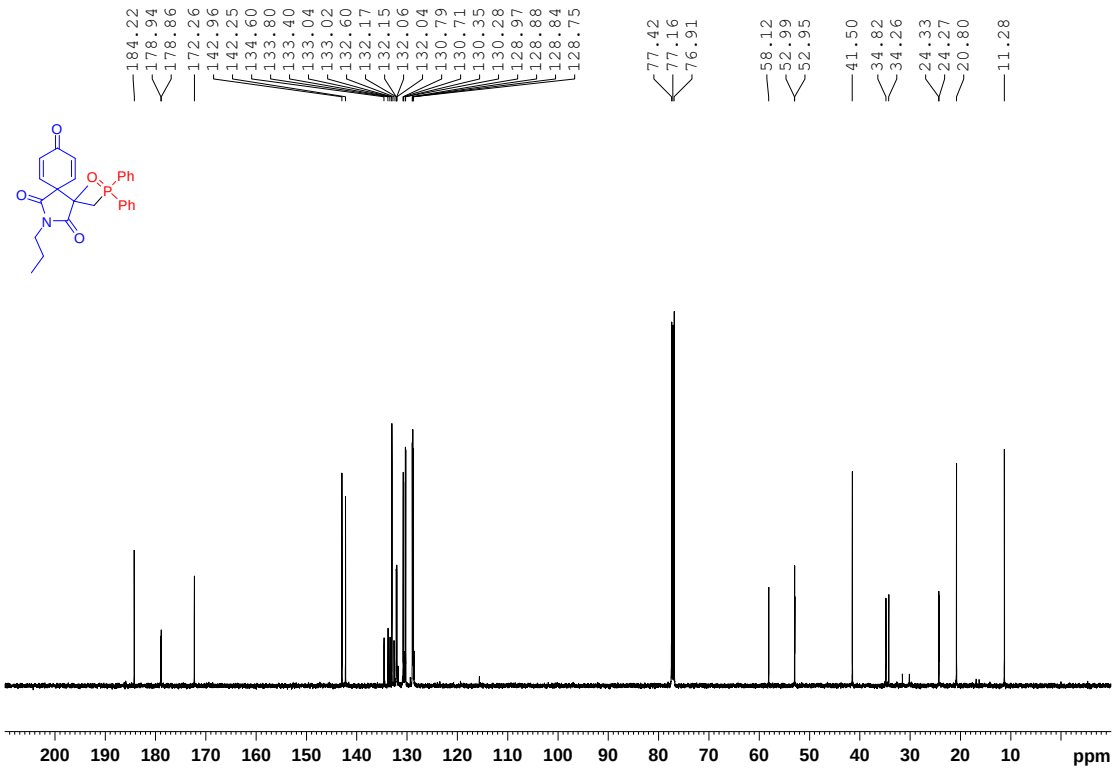
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **5b**



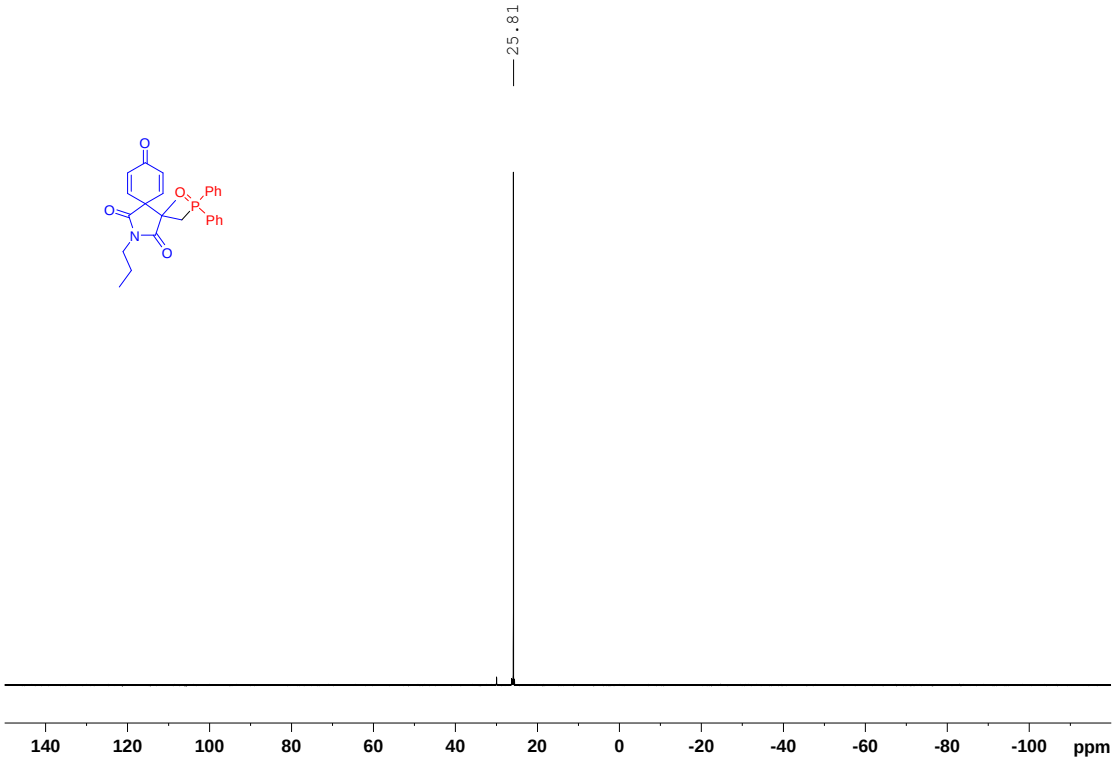
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **5c**



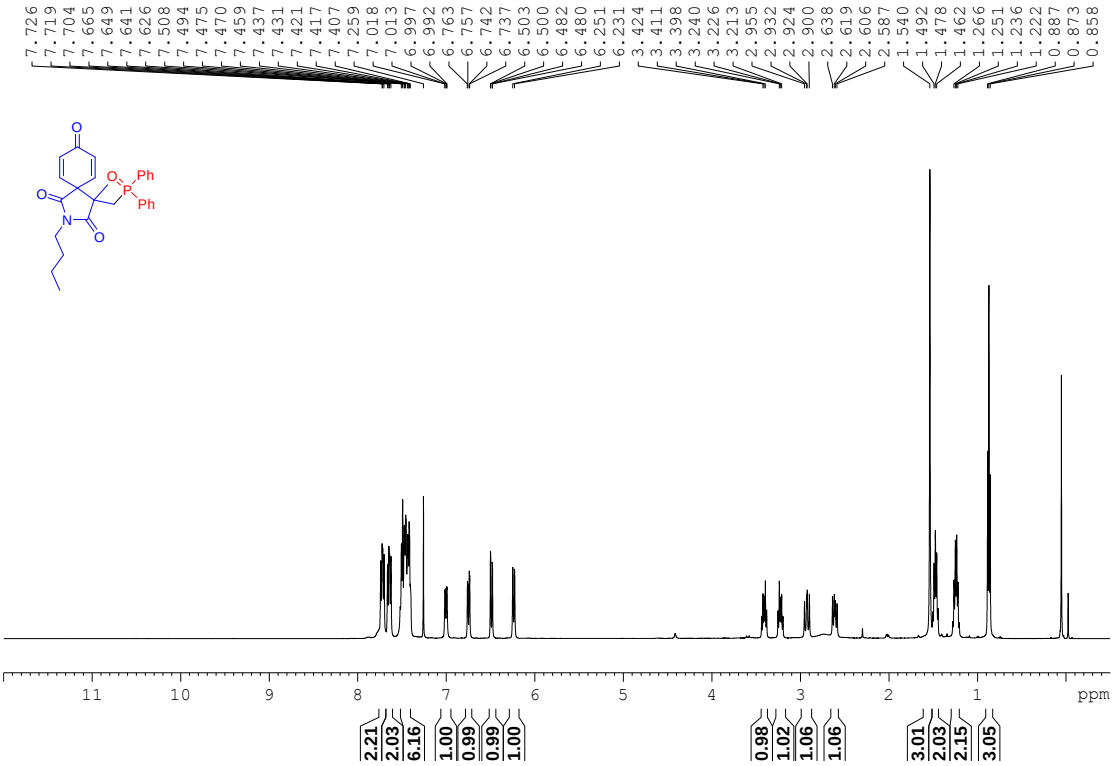
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **5c**



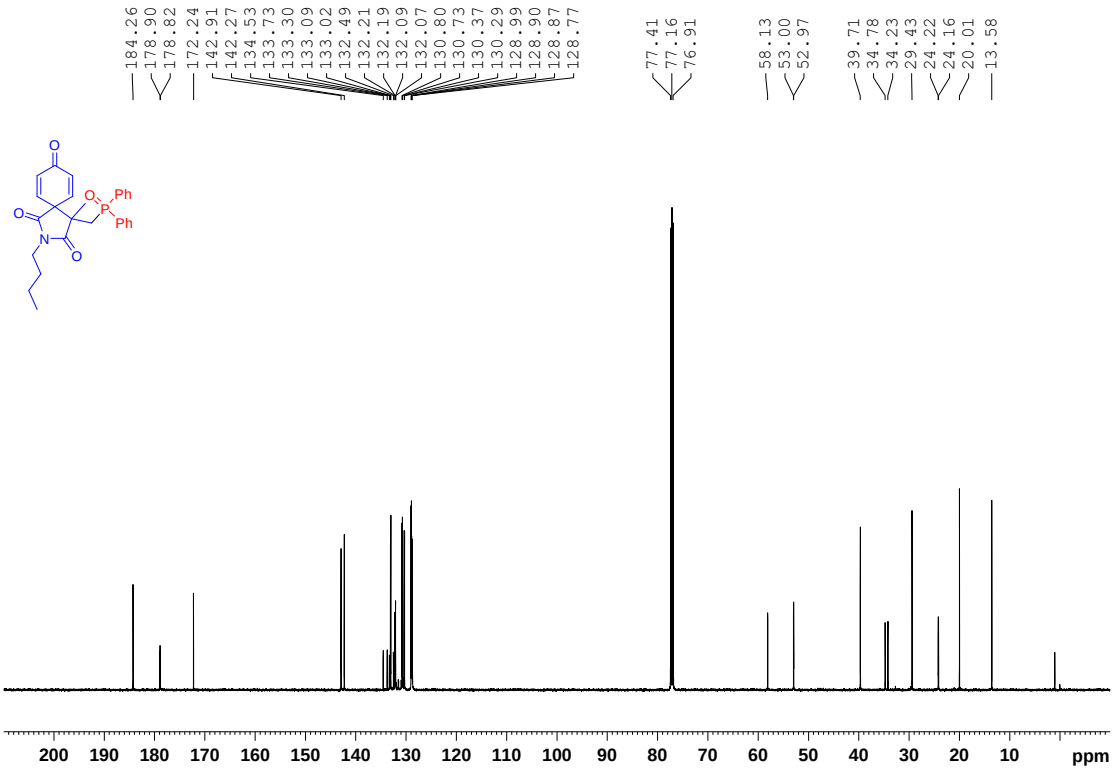
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **5c**



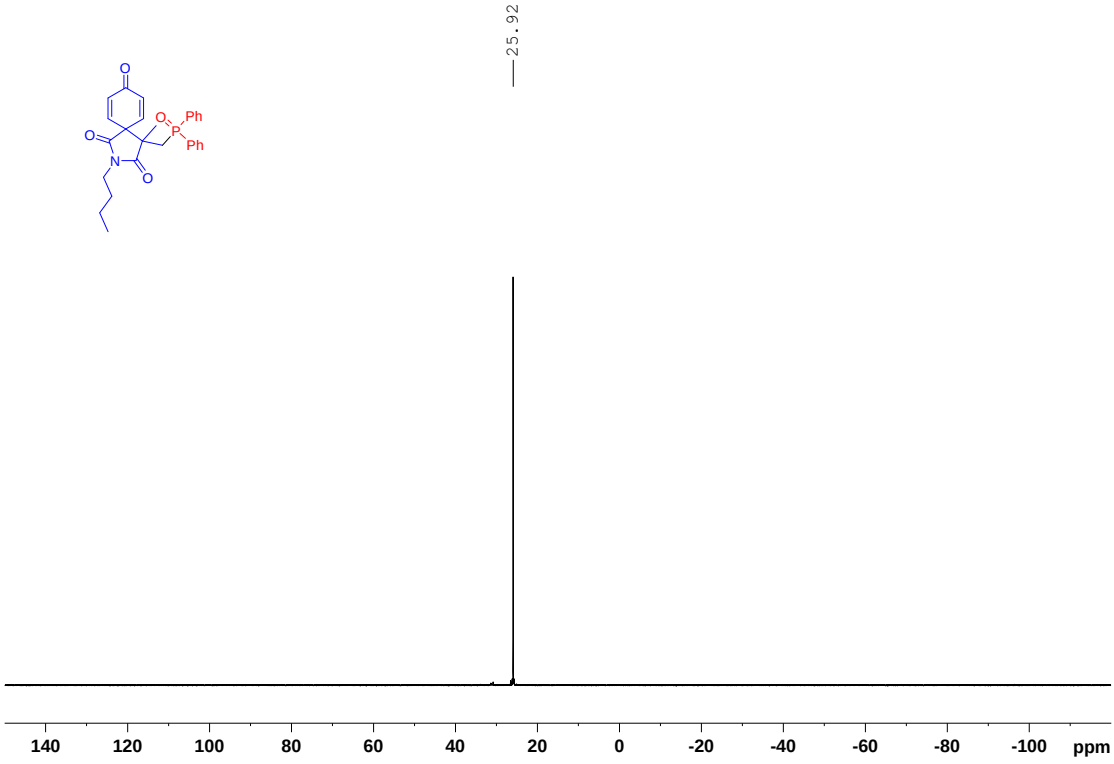
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **5d**



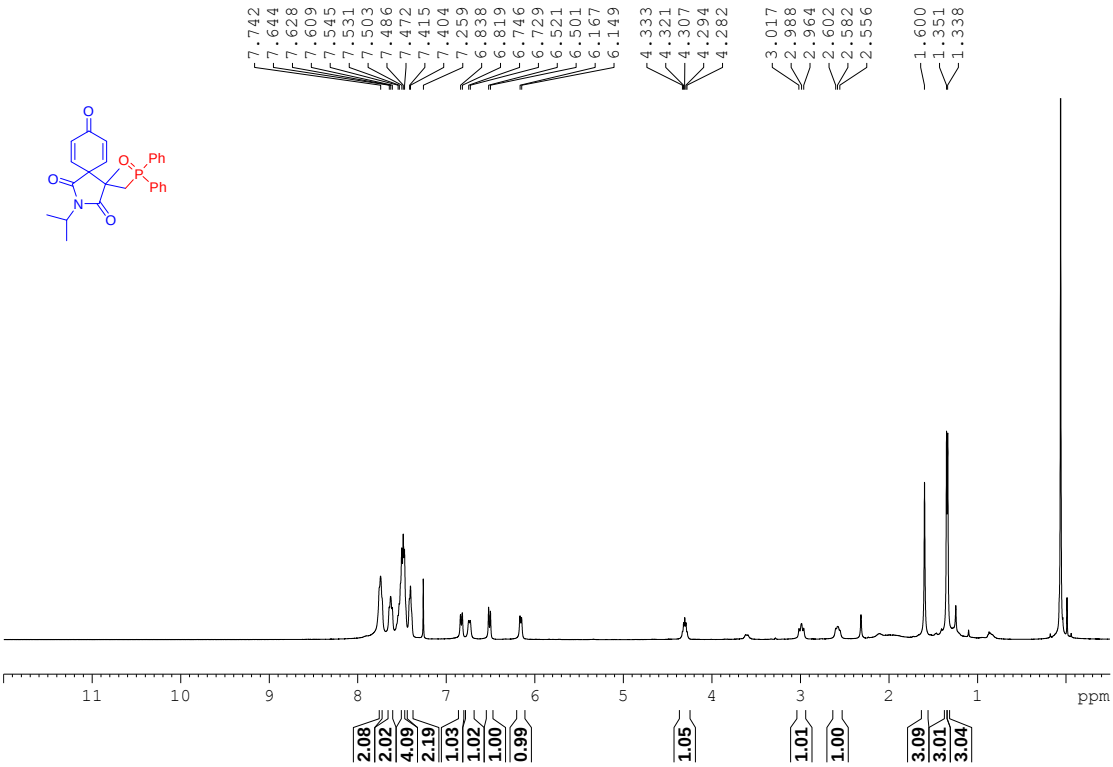
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **5d**



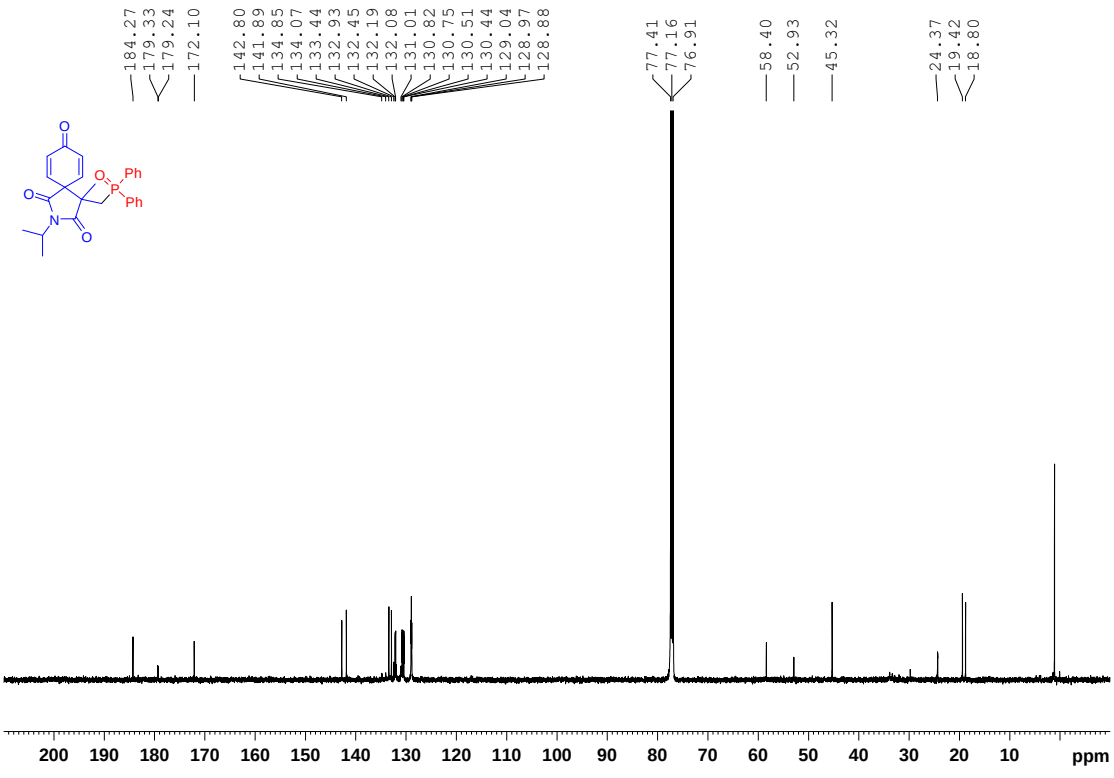
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **5d**



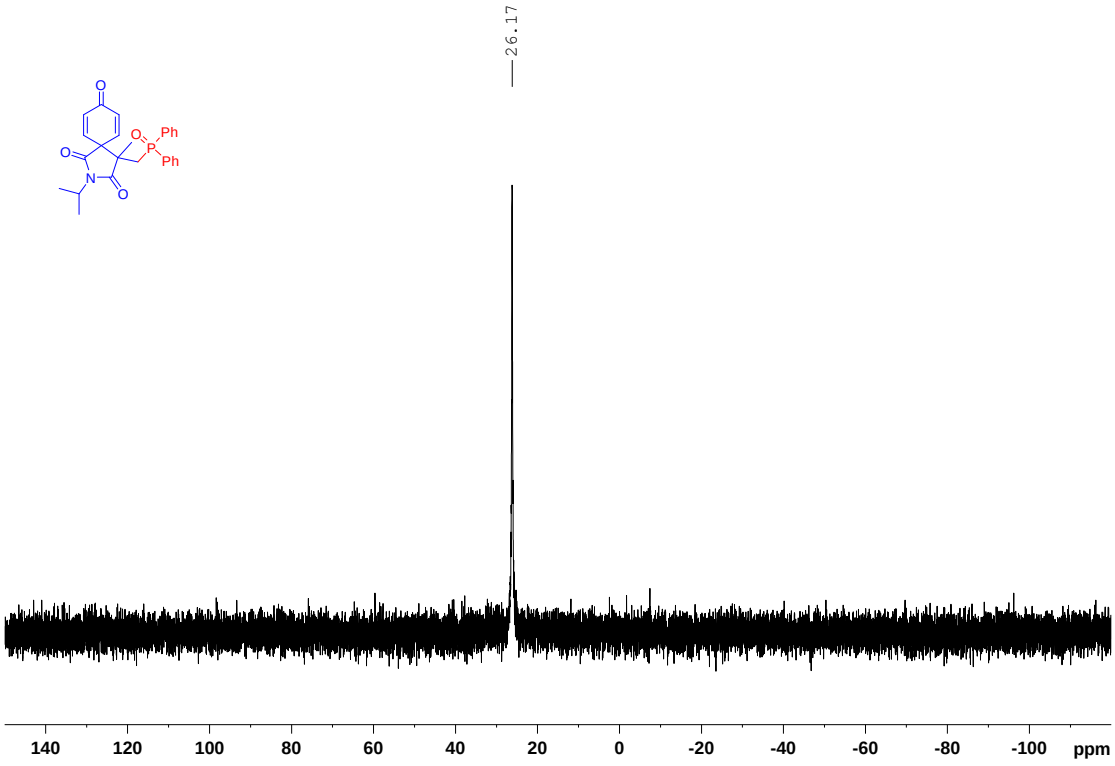
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **5e**



^{13}C NMR (125 MHz, $CDCl_3$, 300K): **5e**



^{31}P NMR (162 MHz, $CDCl_3$, 300K): **5e**



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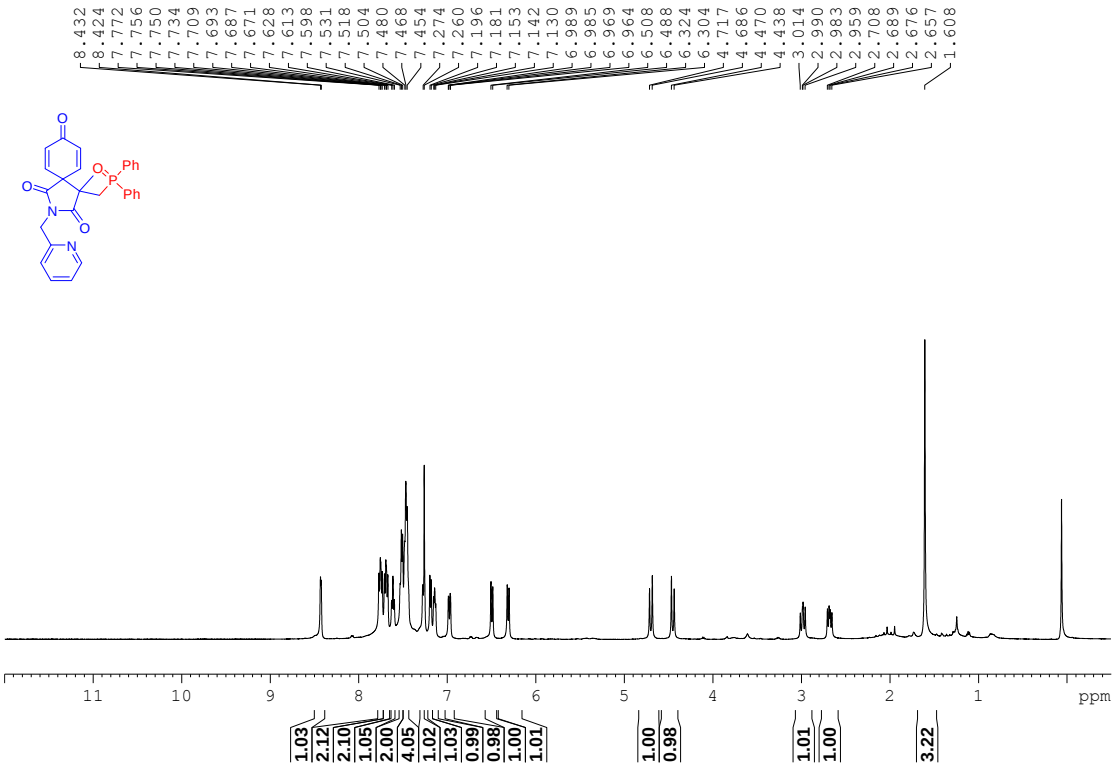
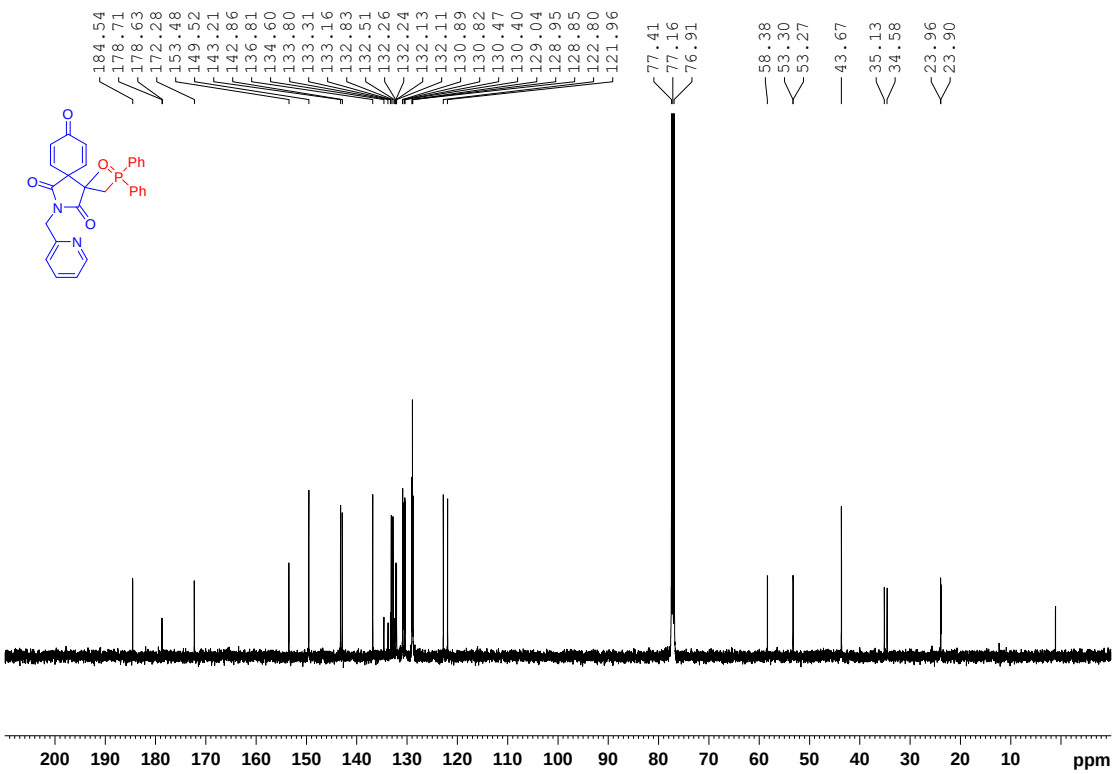
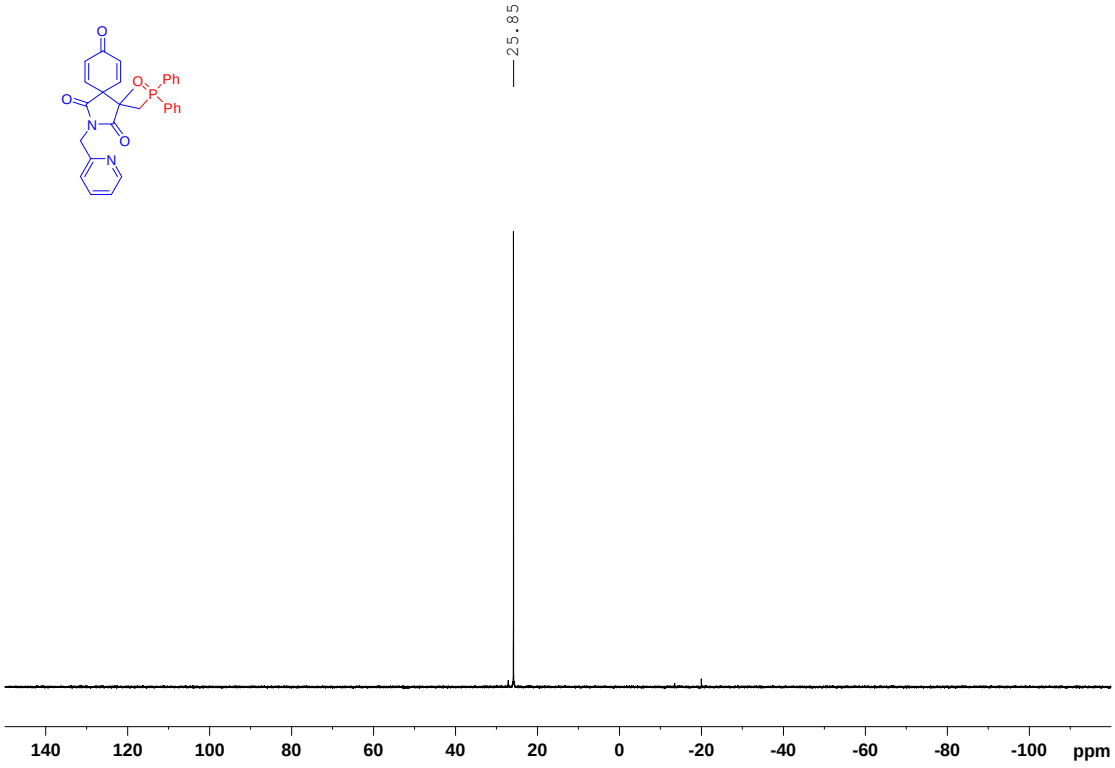


^{13}C NMR (125 MHz, $CDCl_3$, 300K): **5f**



^{31}P NMR (162 MHz, $CDCl_3$, 300K): **5f**



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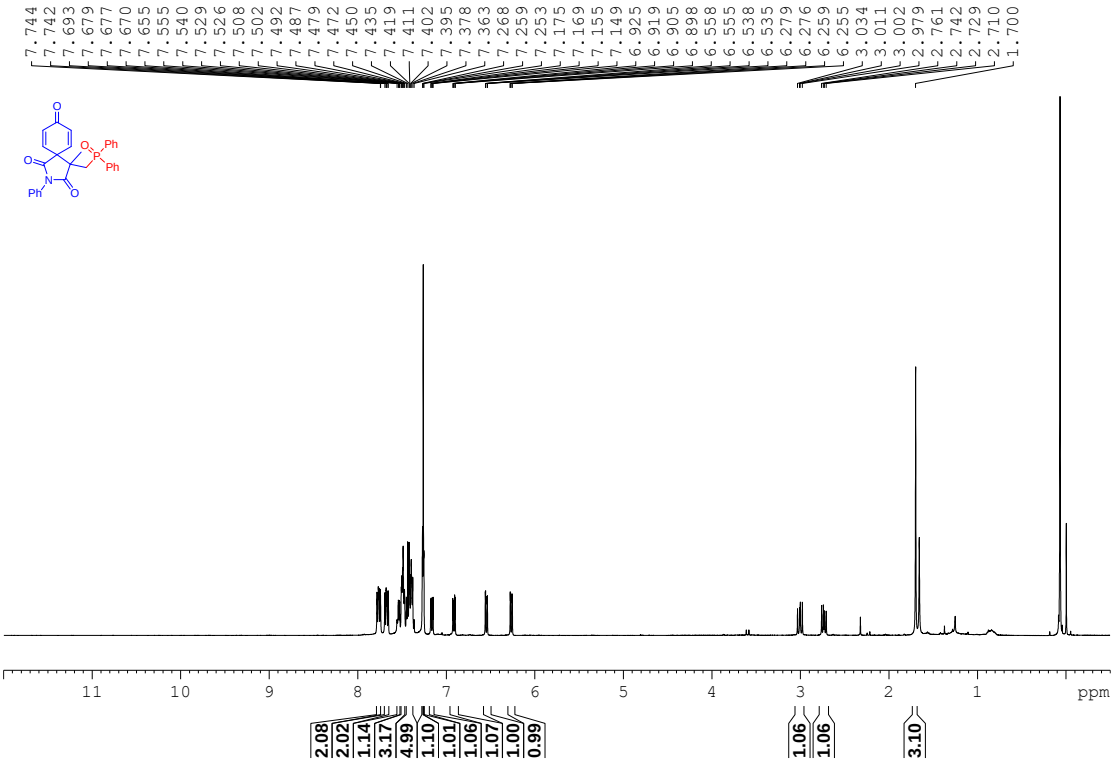
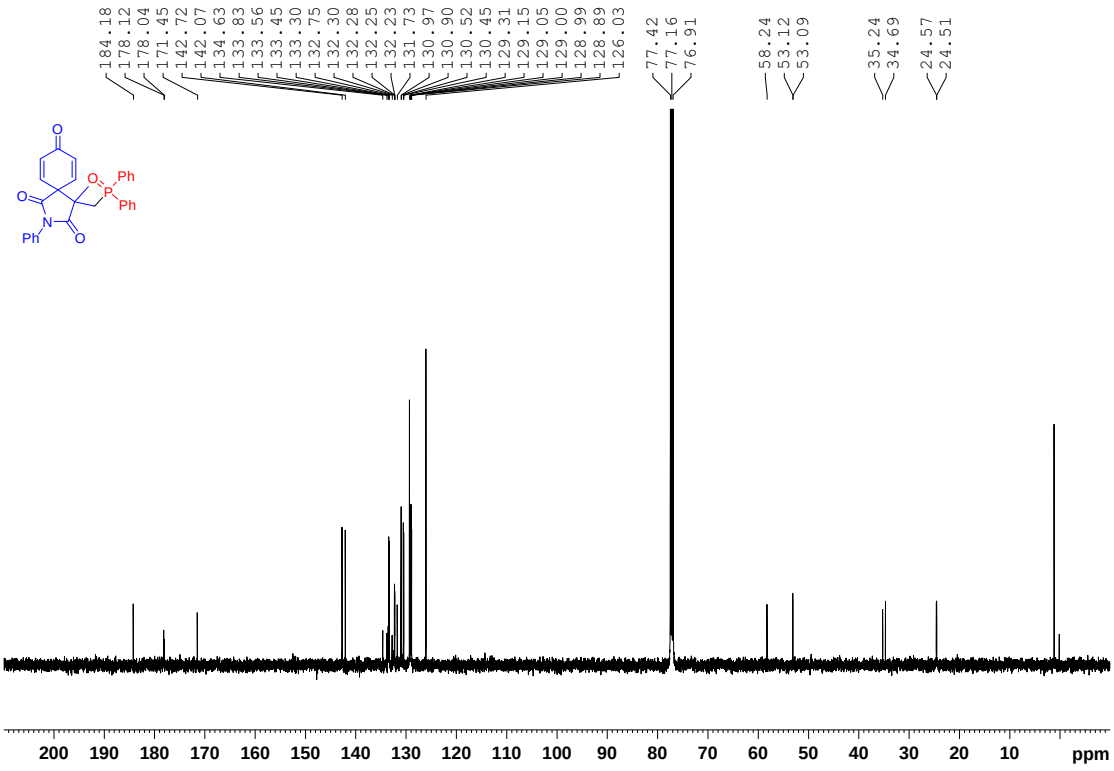
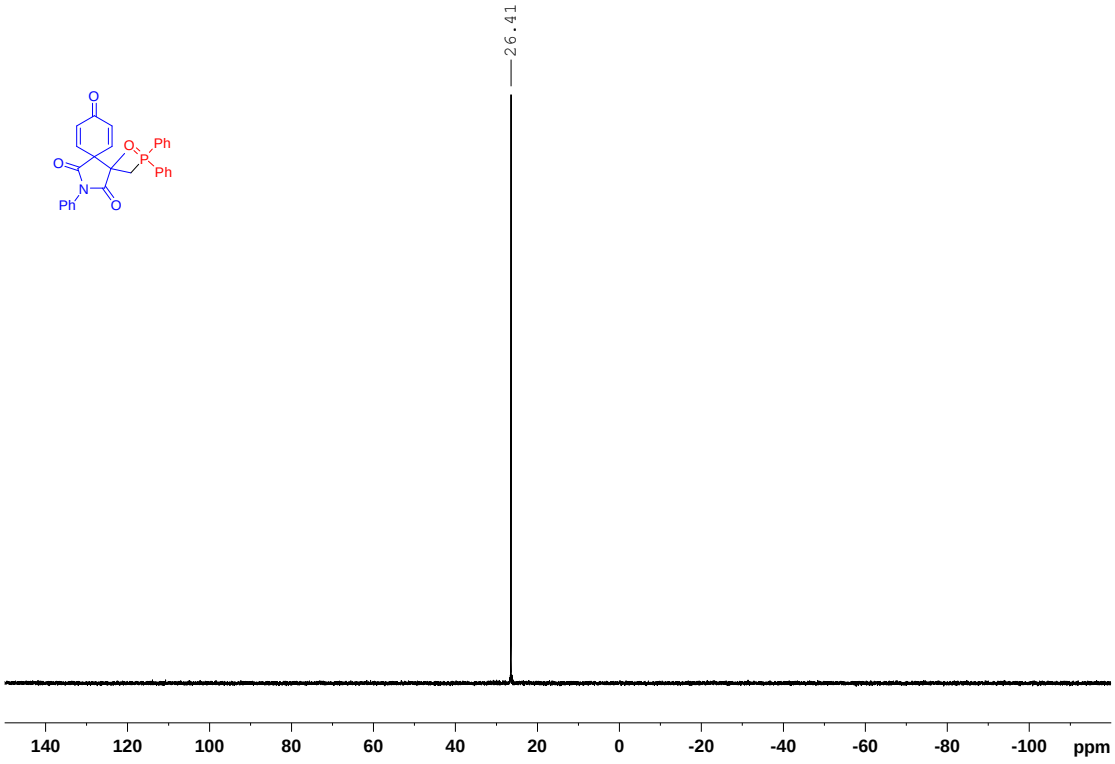


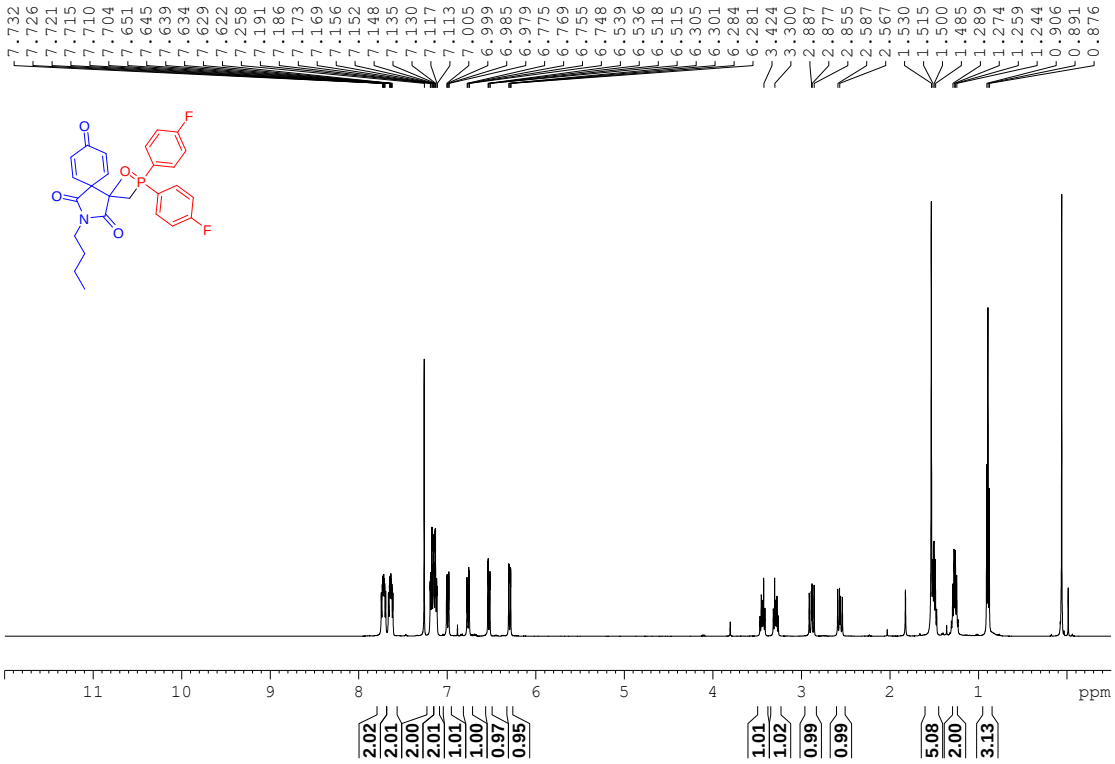
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **5g**



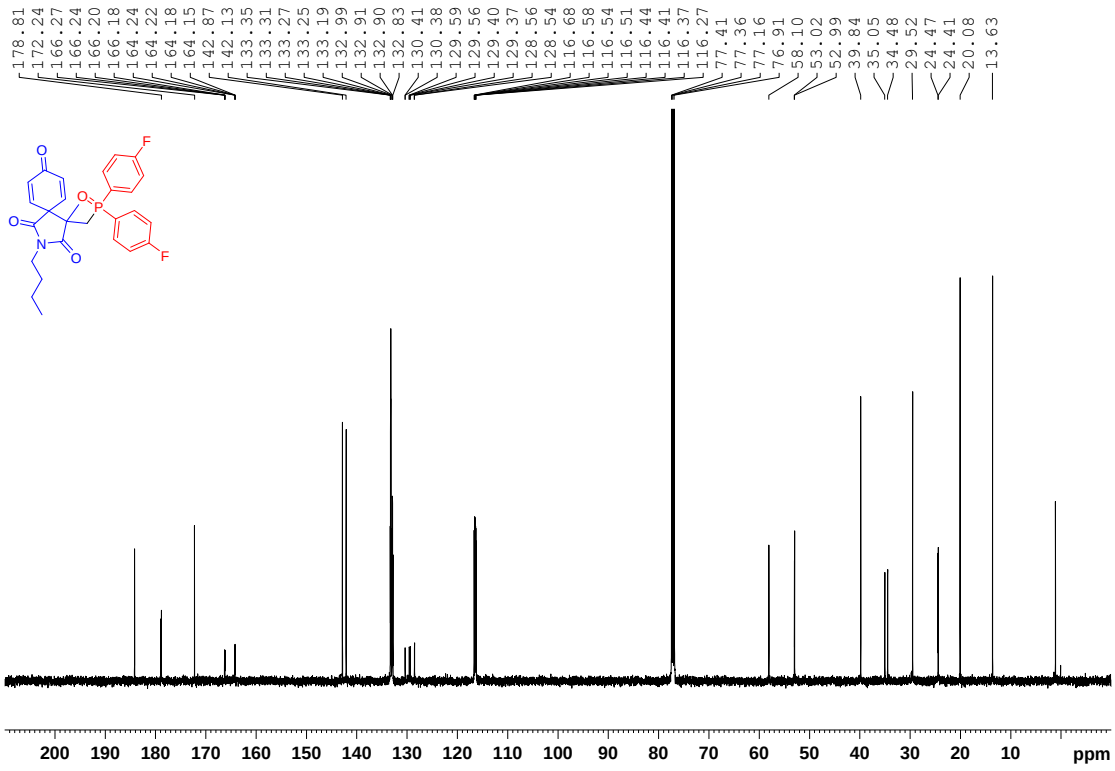
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **5g**



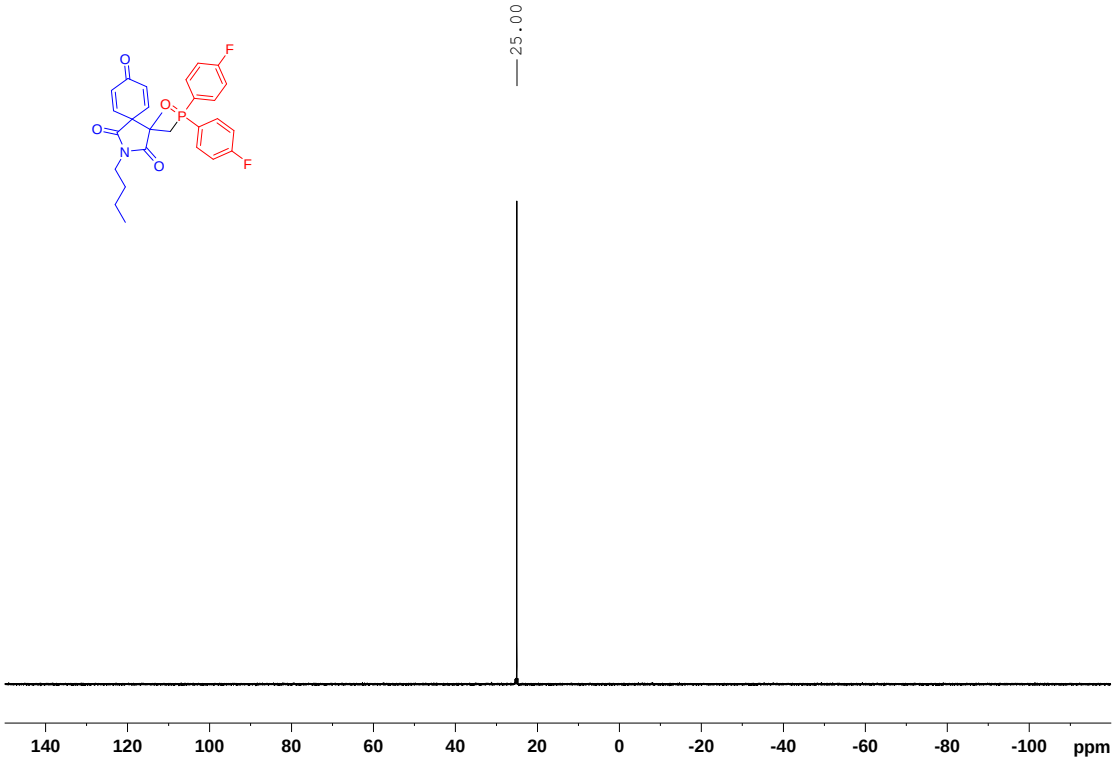
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **5h**



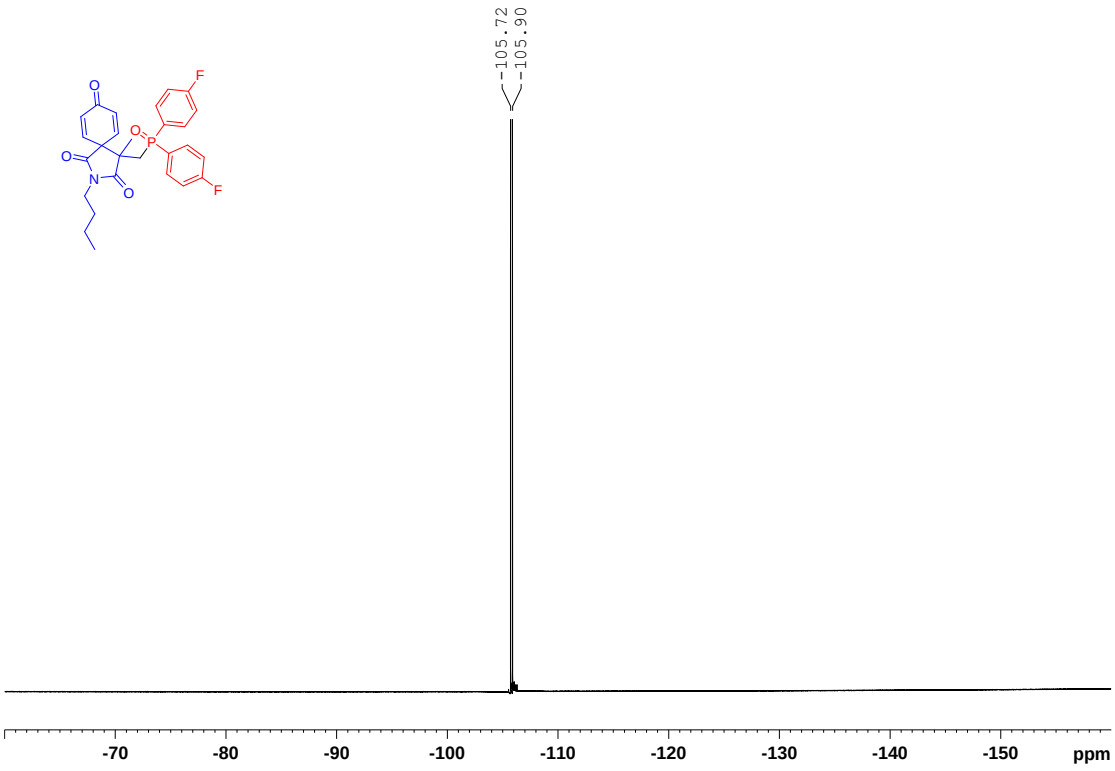
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **5h**



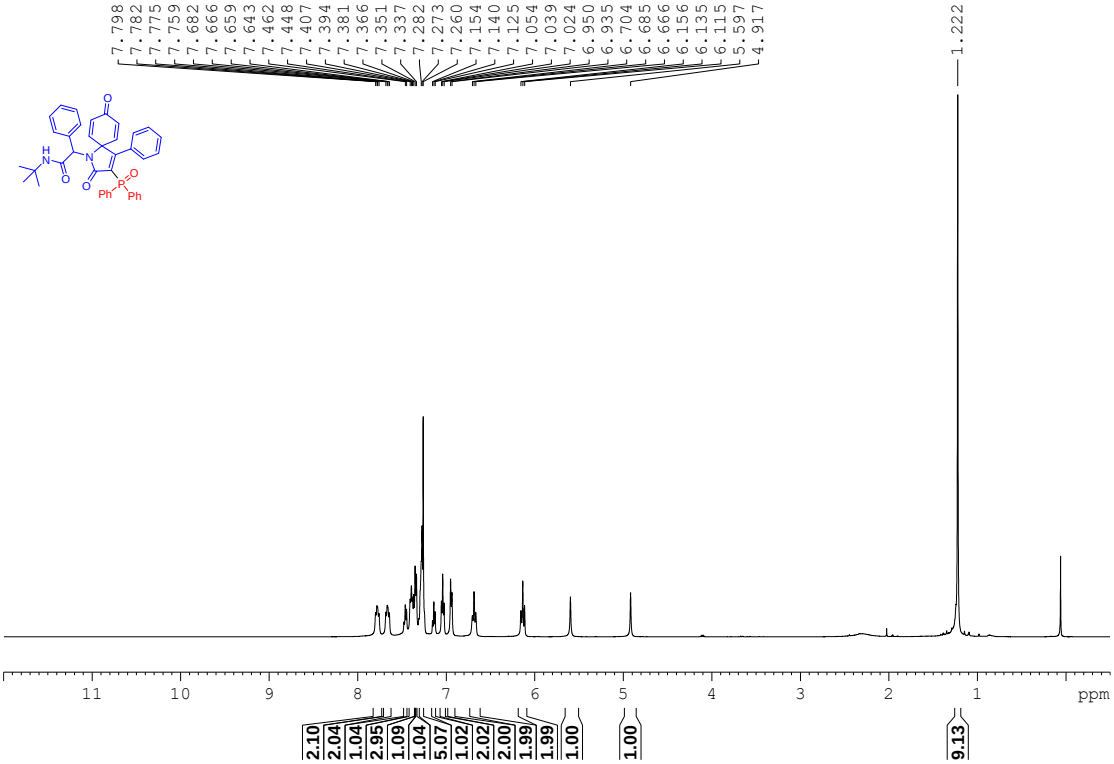
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **5h**



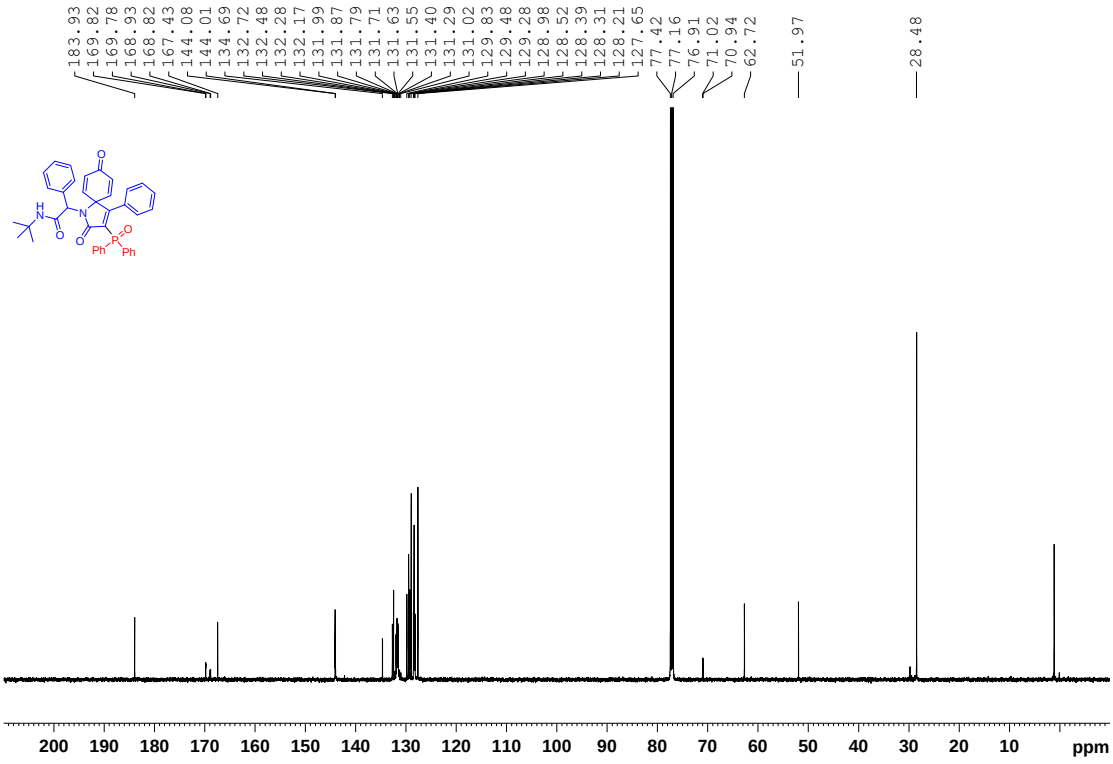
^{19}F NMR (470 MHz, $CDCl_3$, 300K): **5h**



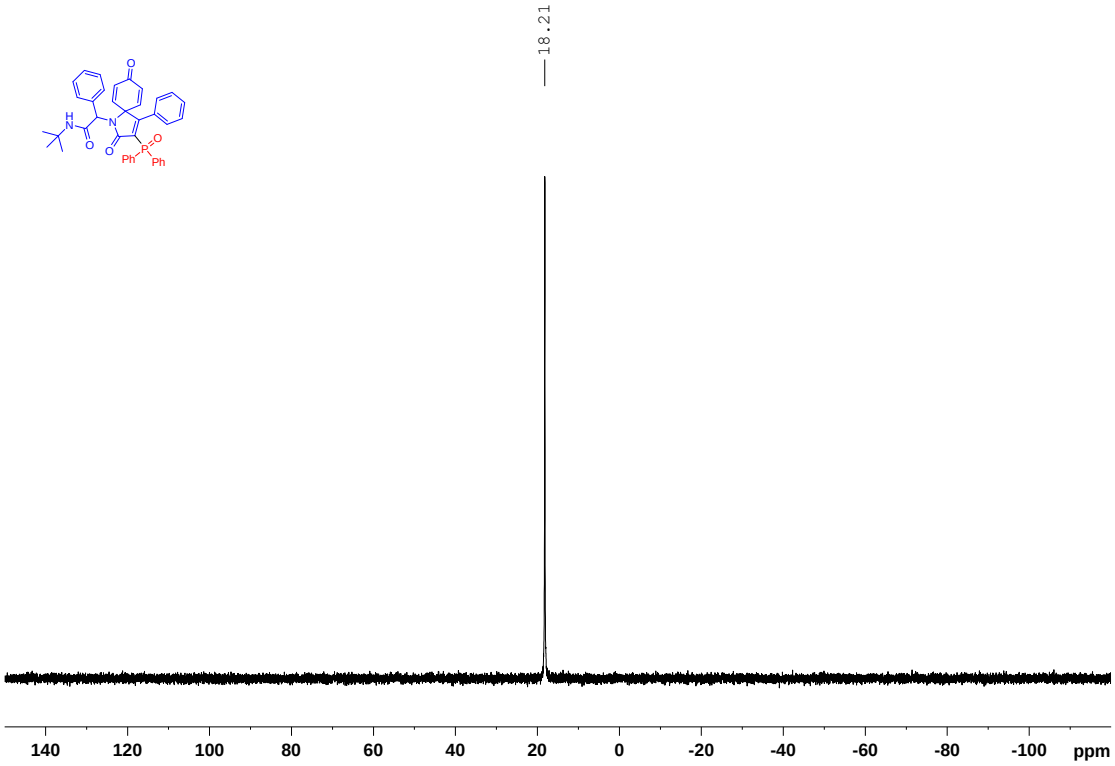
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **7a**



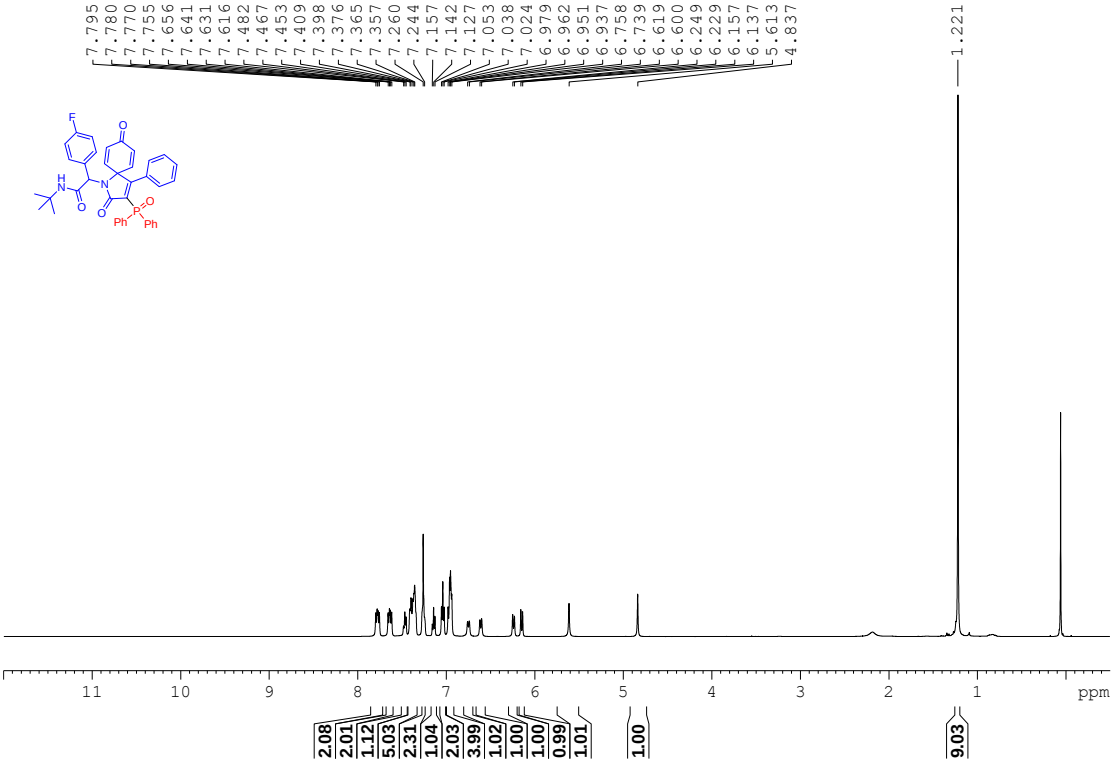
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7a**



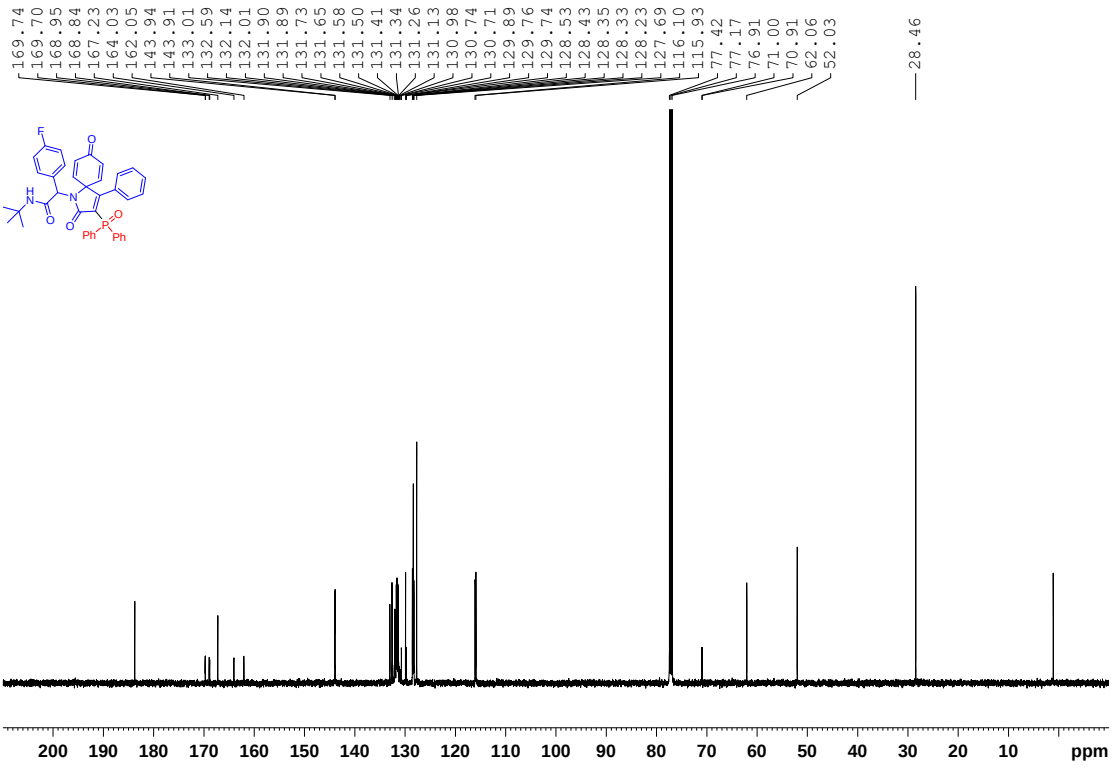
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7a**



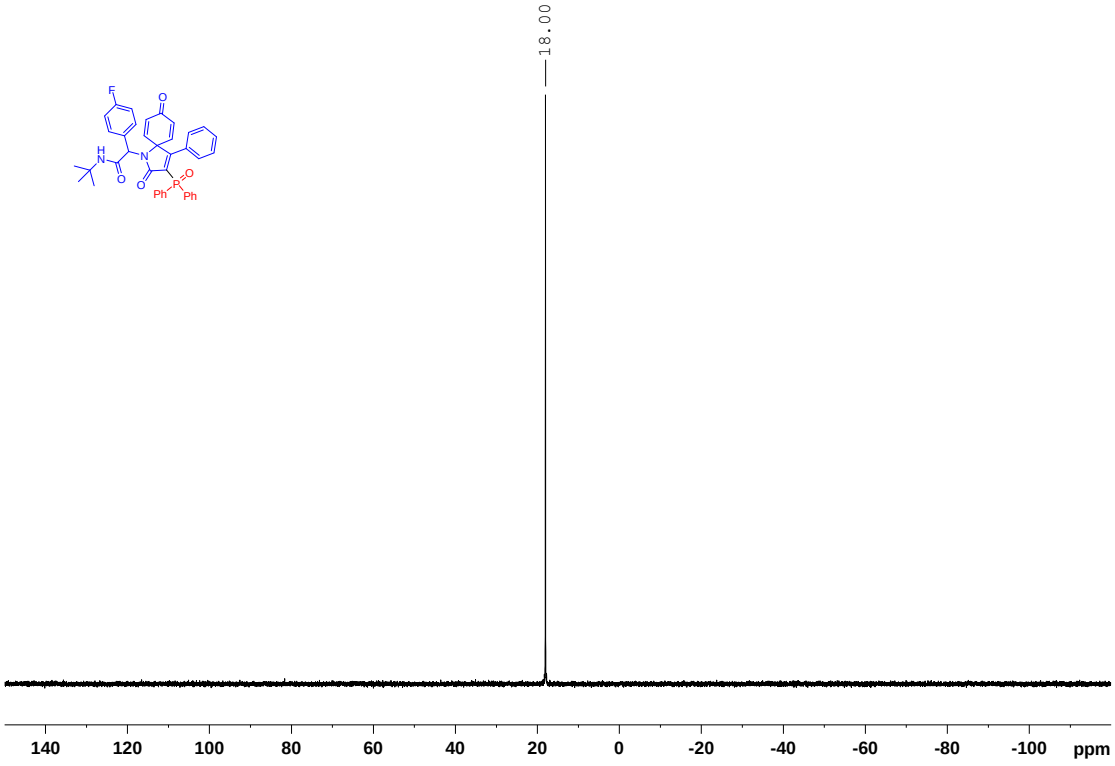
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **7b**



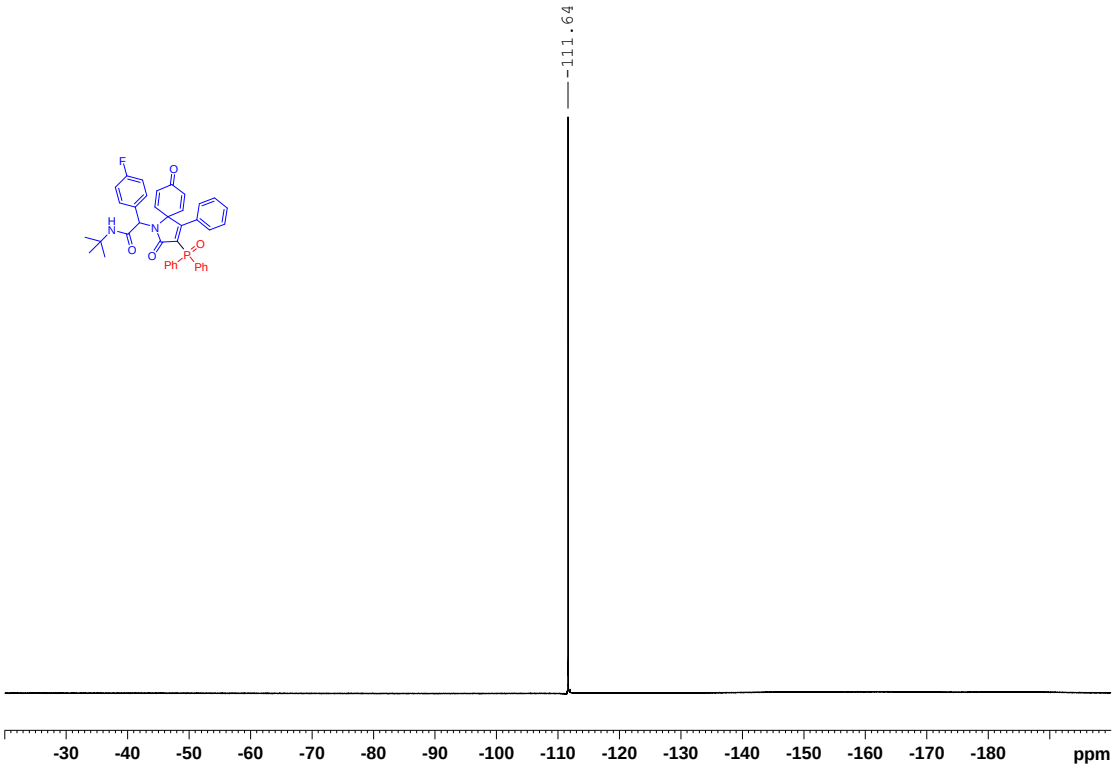
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7b**



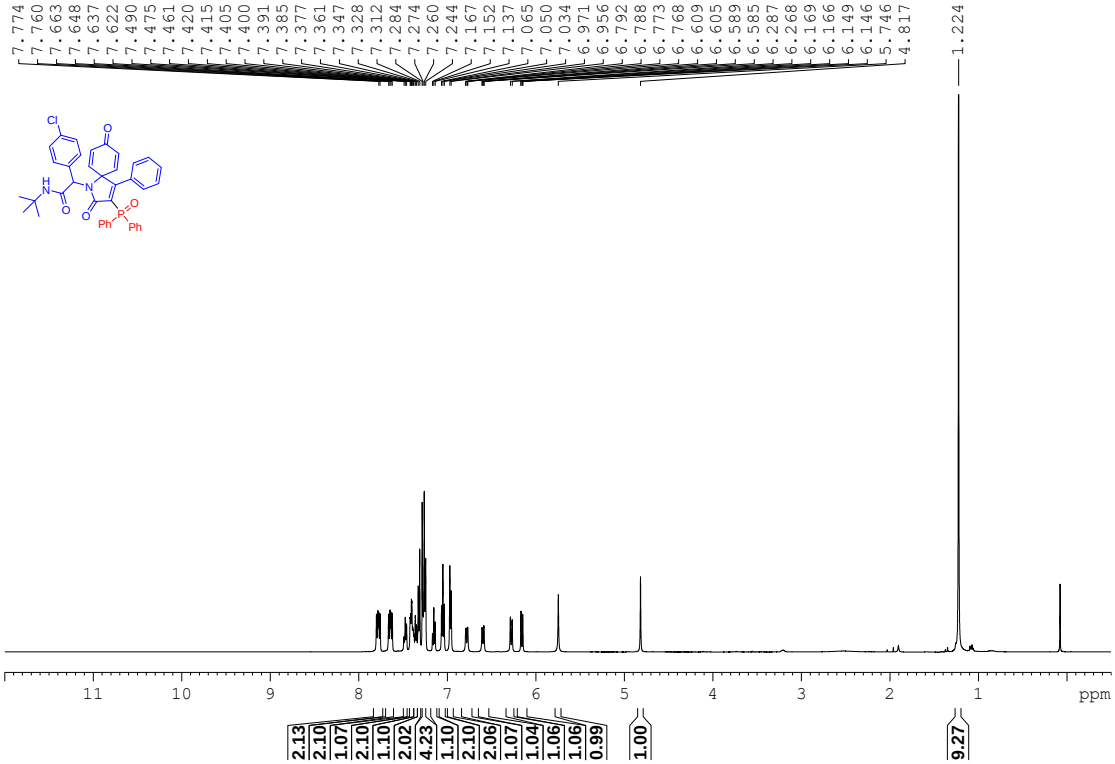
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7b**



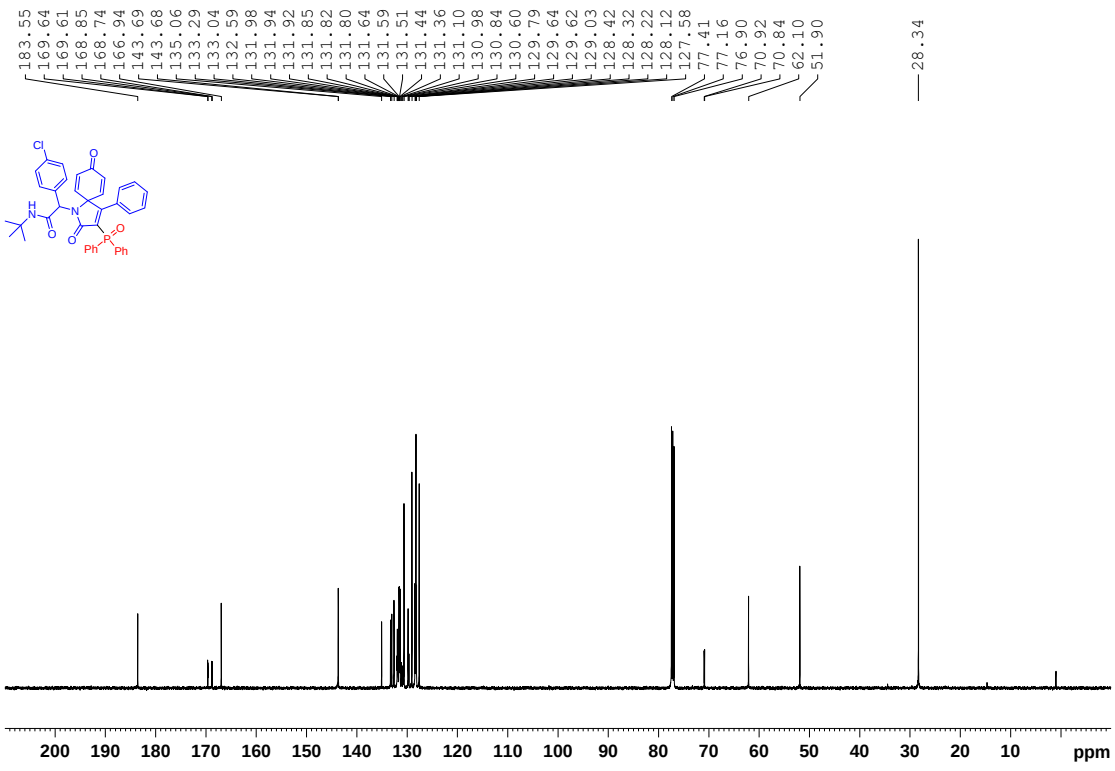
^{19}F NMR (470 MHz, $CDCl_3$, 300K): **7b**



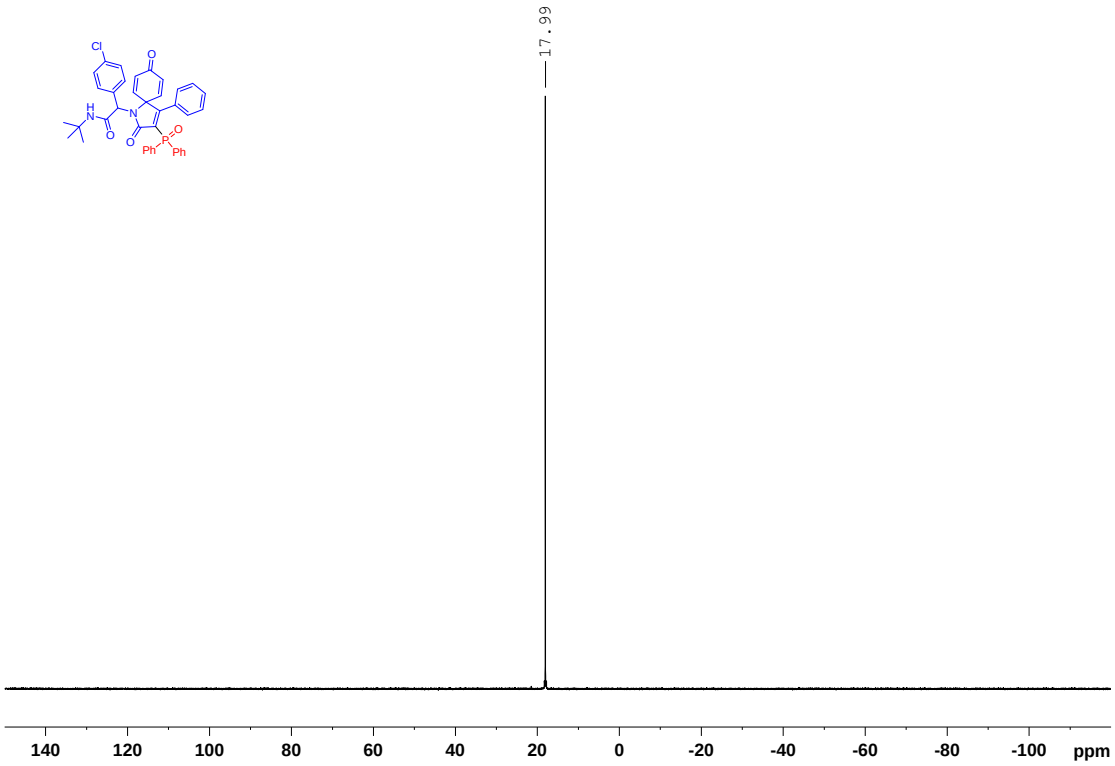
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **7c**



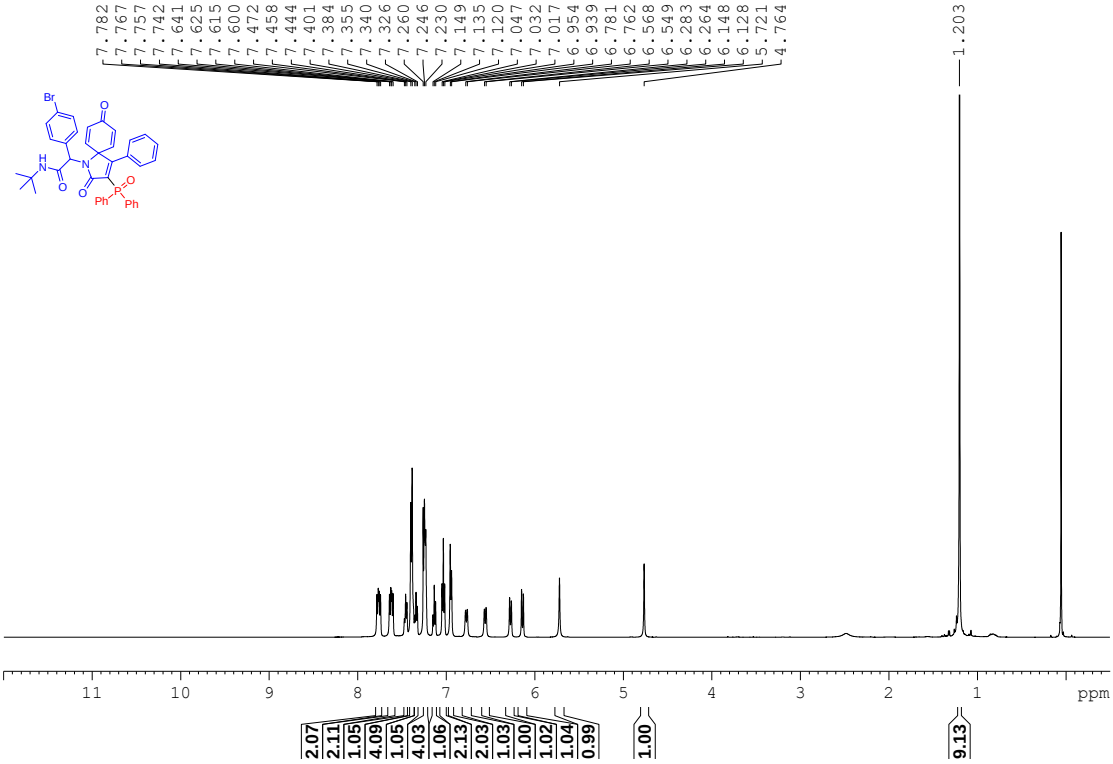
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7c**



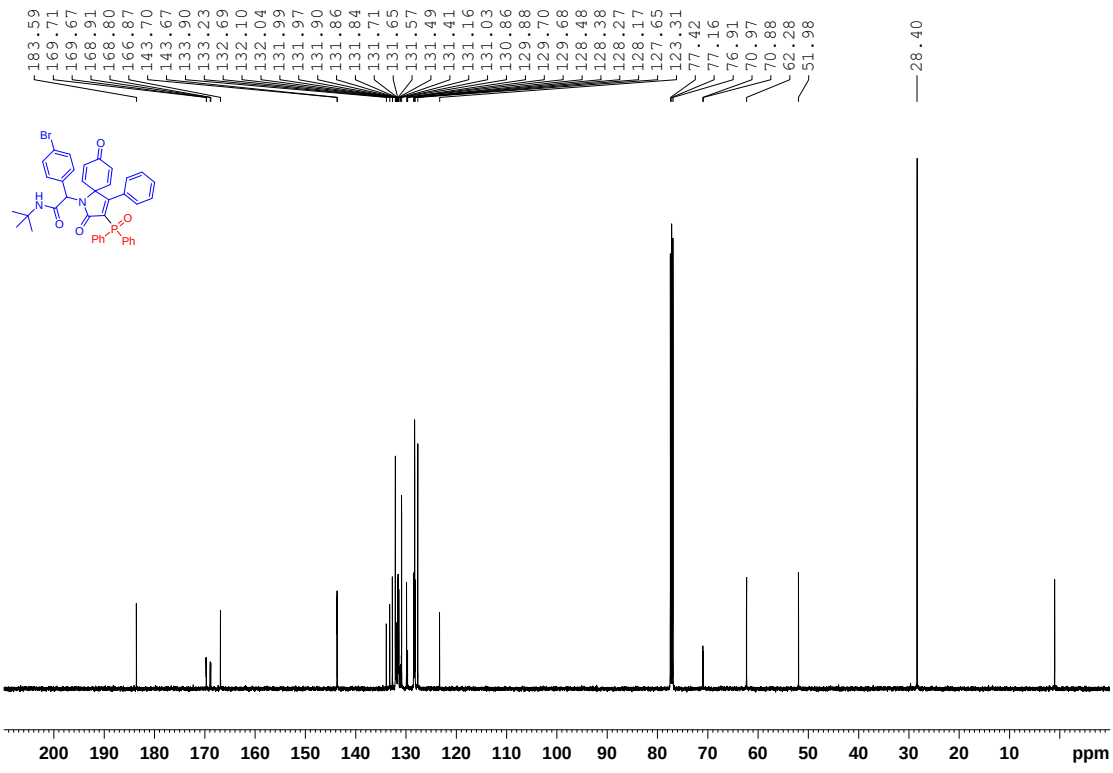
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7c**



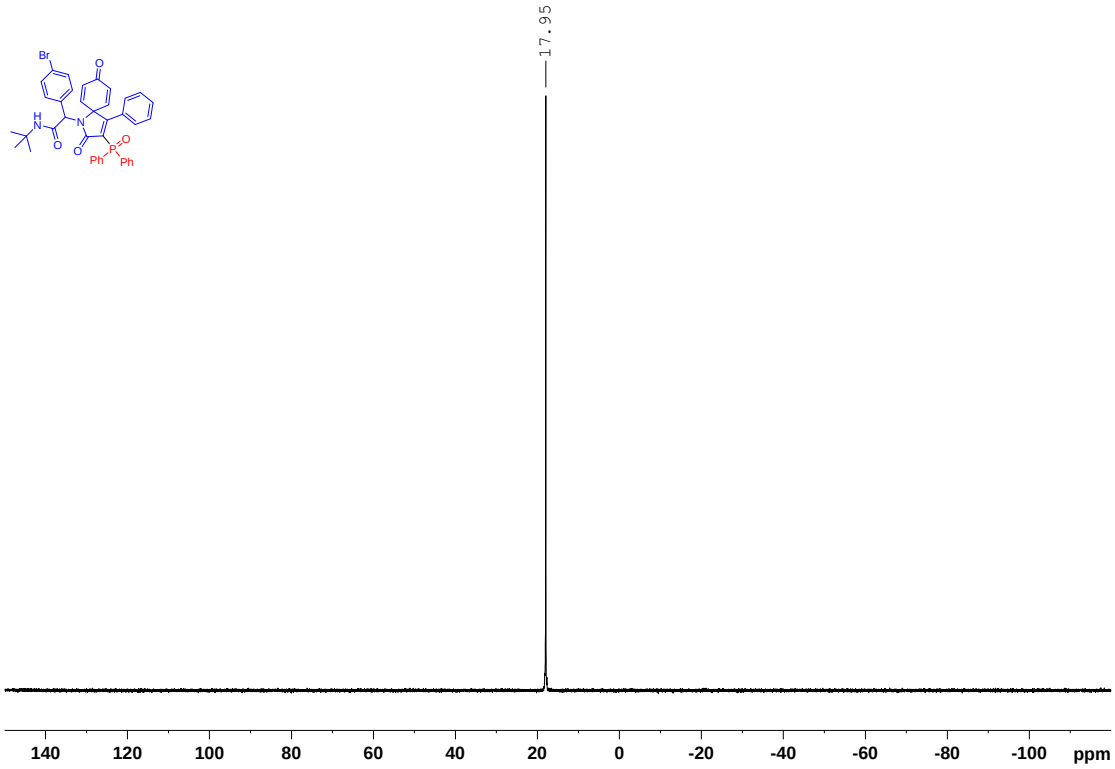
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **7d**



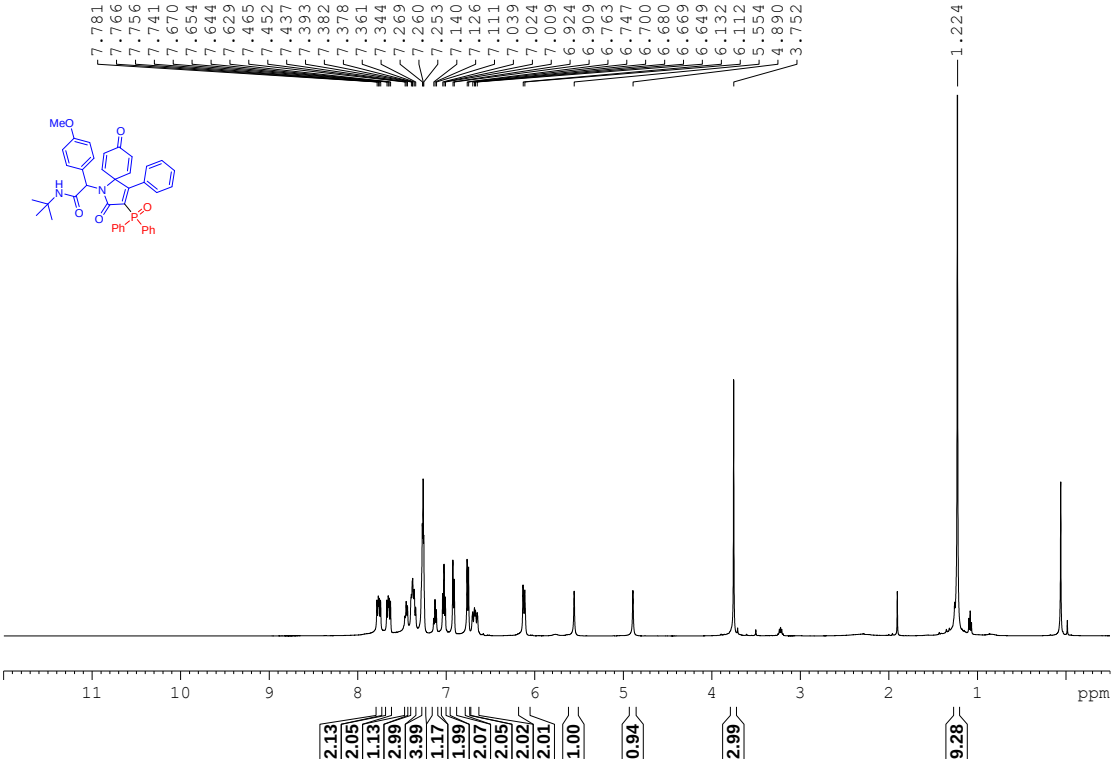
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7d**



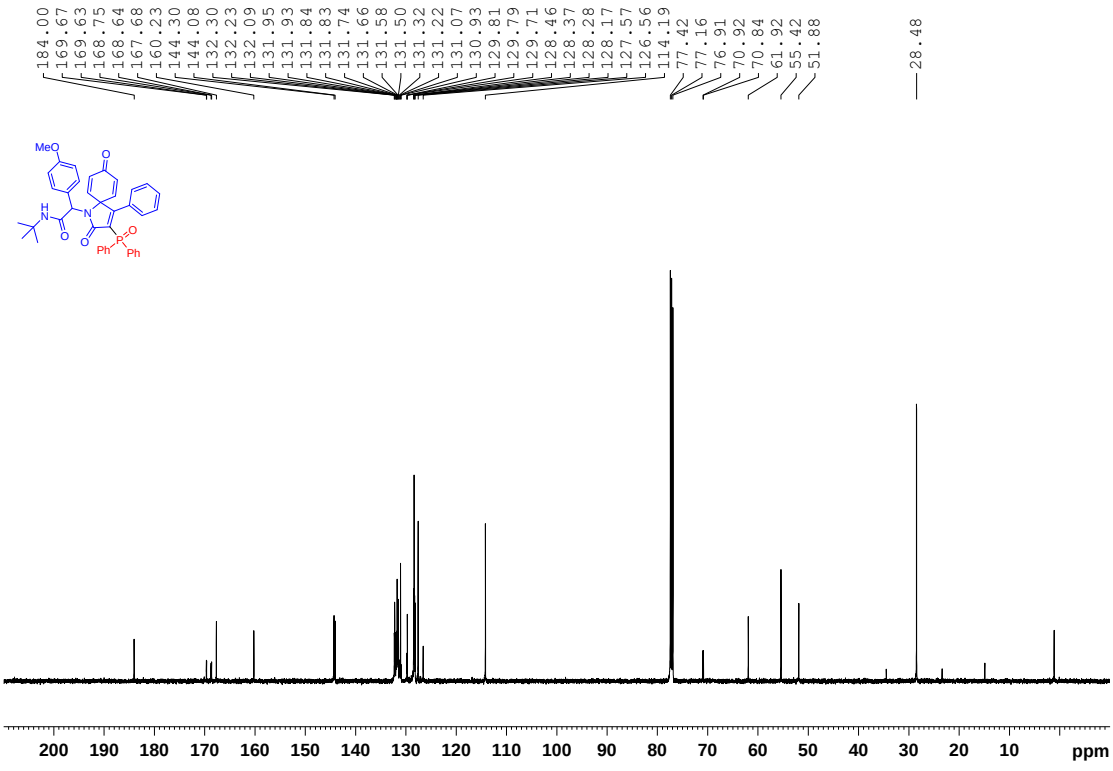
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7d**



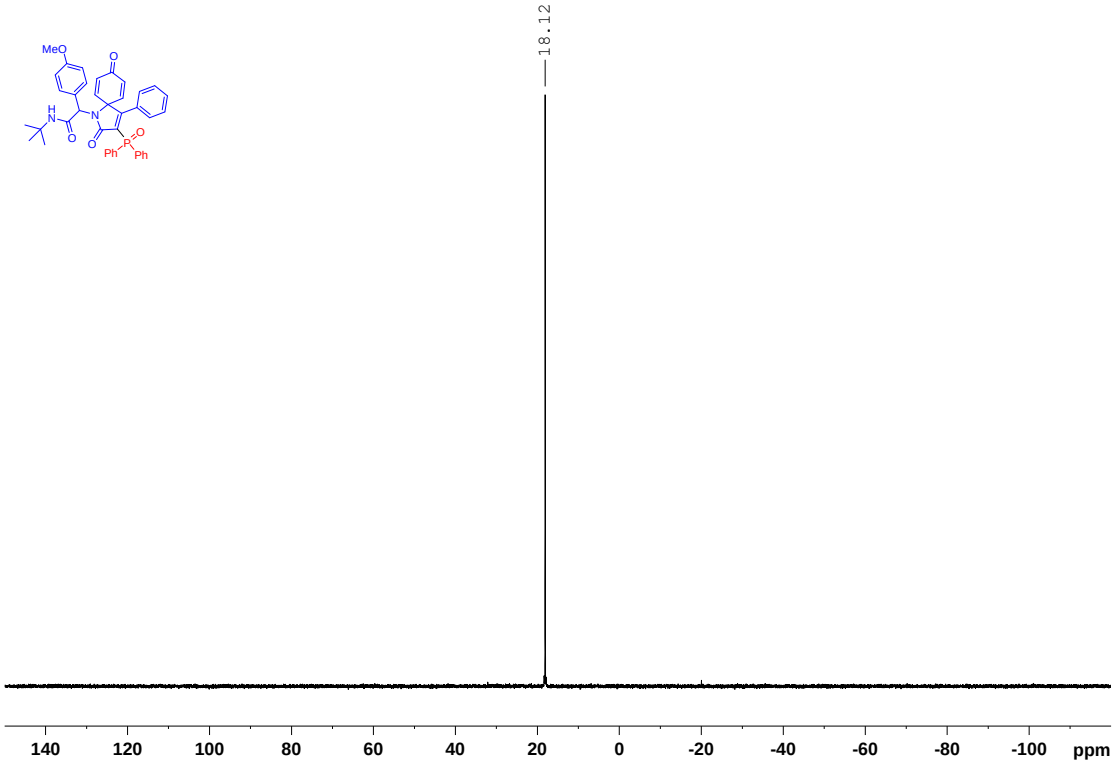
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **7e**



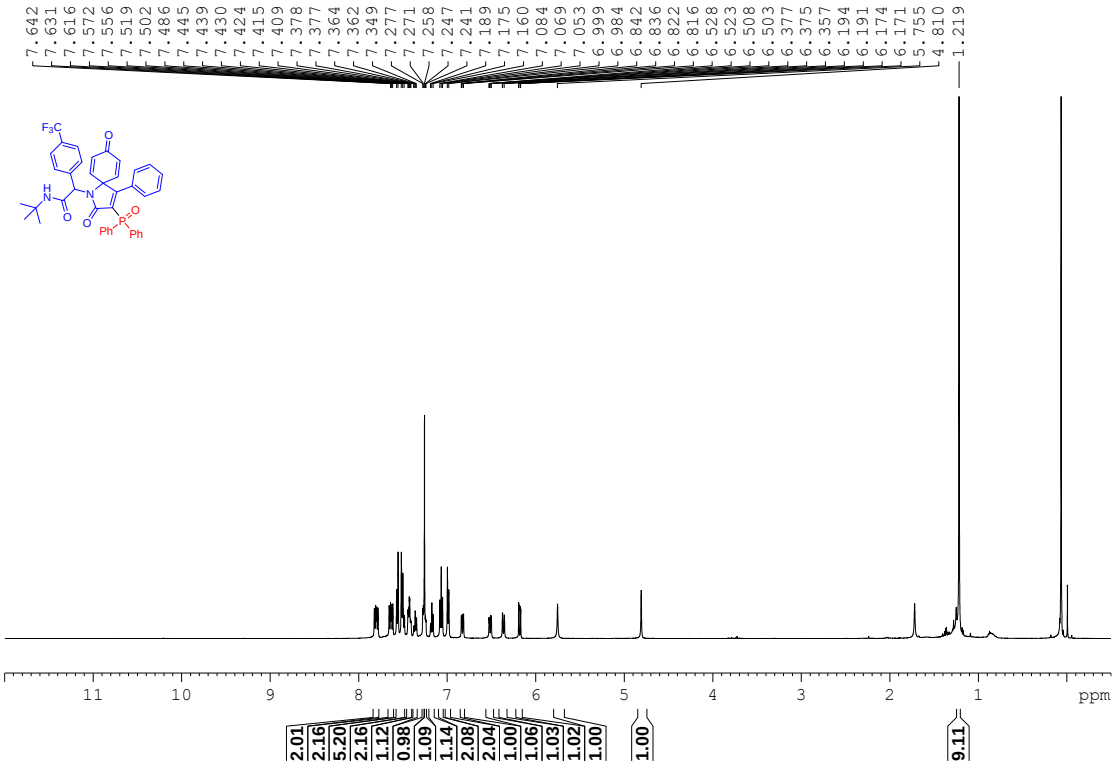
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7e**



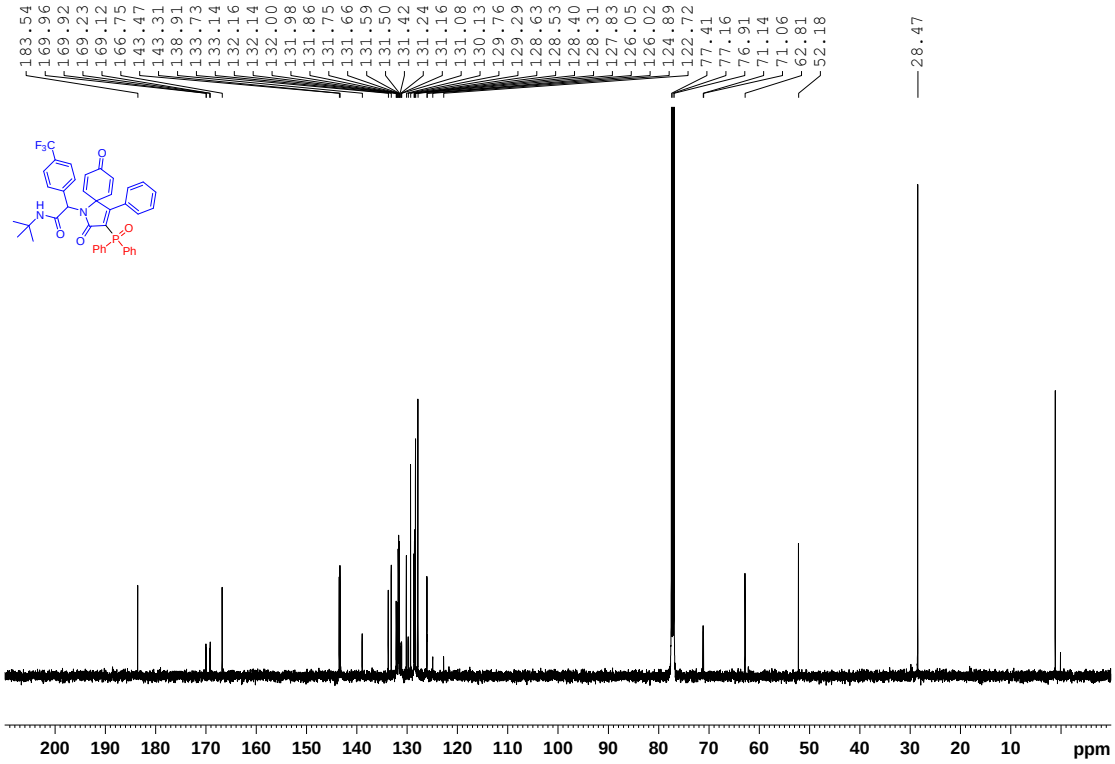
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7e**



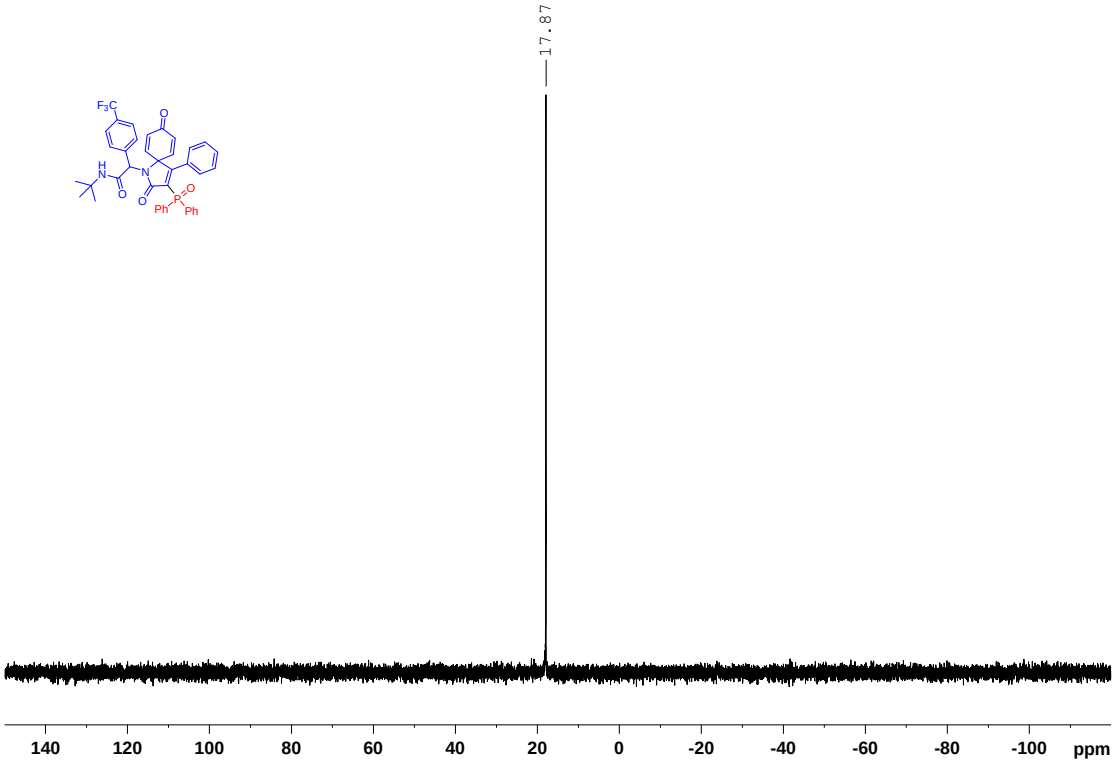
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **7f**



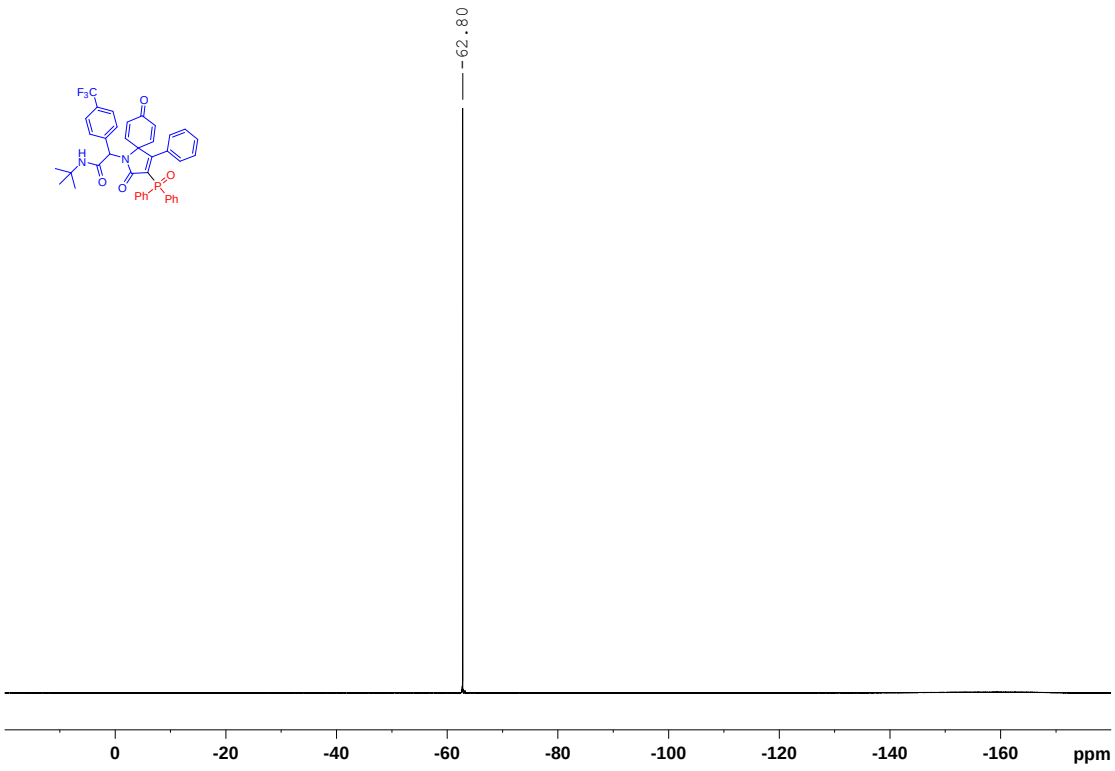
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7f**



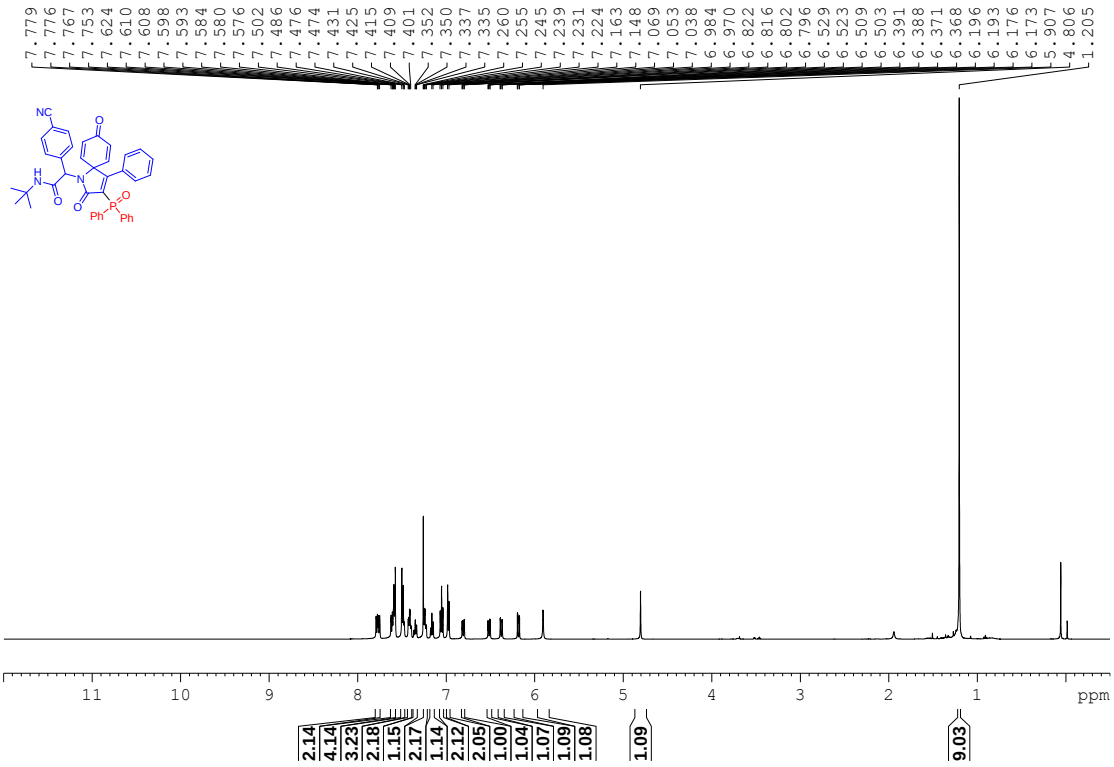
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7f**



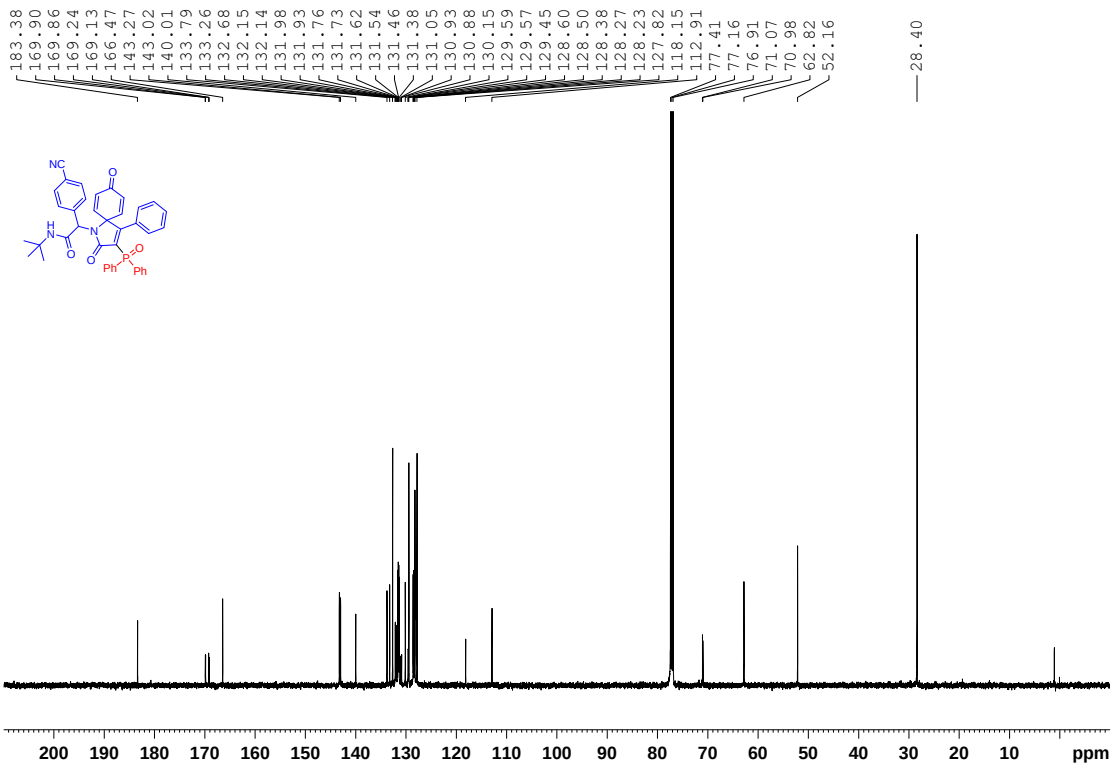
^{19}F NMR (470 MHz, $CDCl_3$, 300K): **7f**



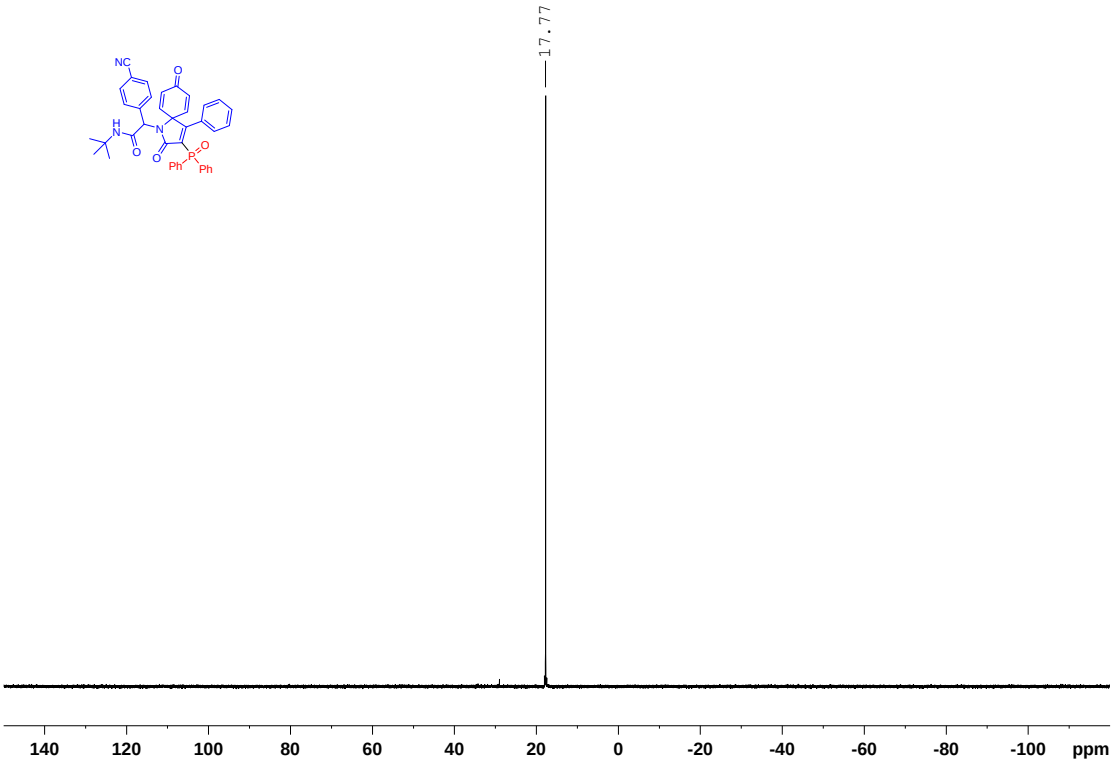
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **7g**



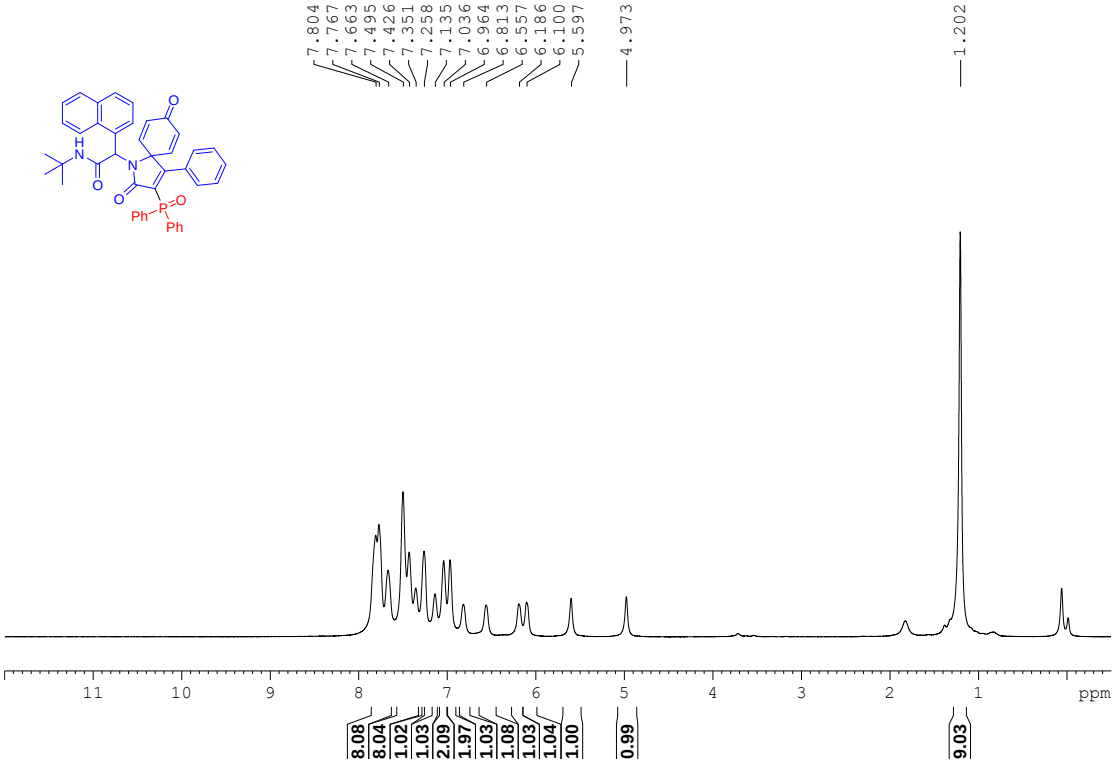
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7g**



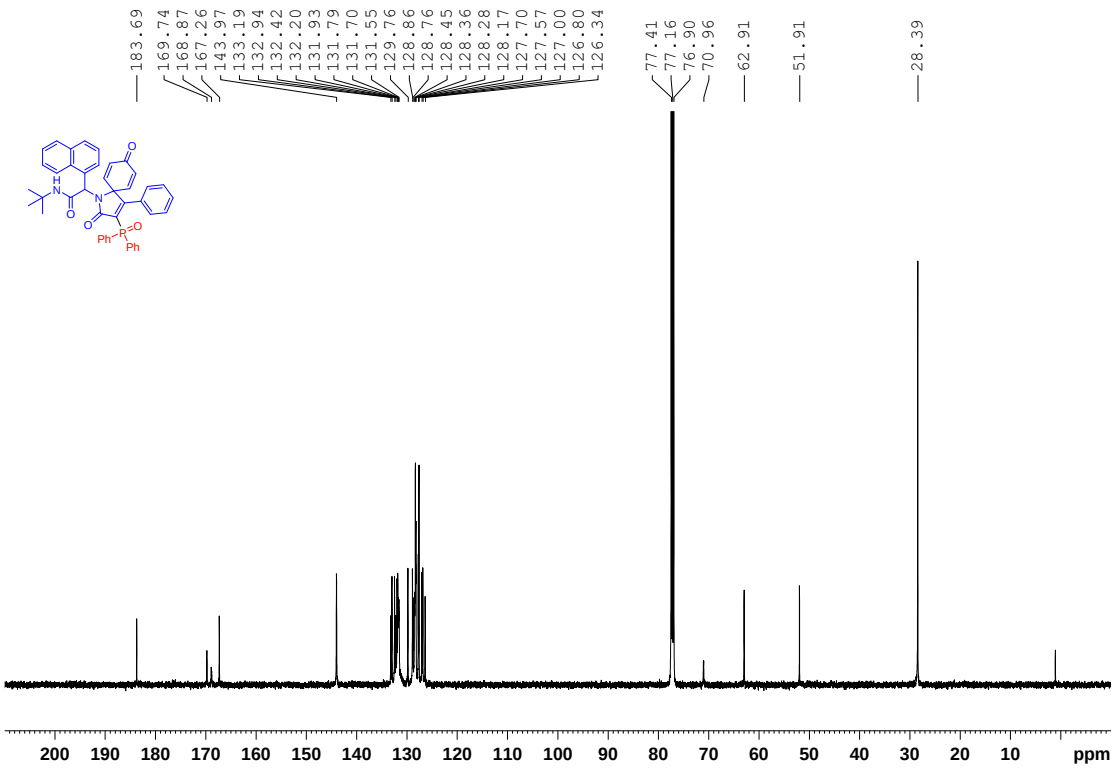
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7g**



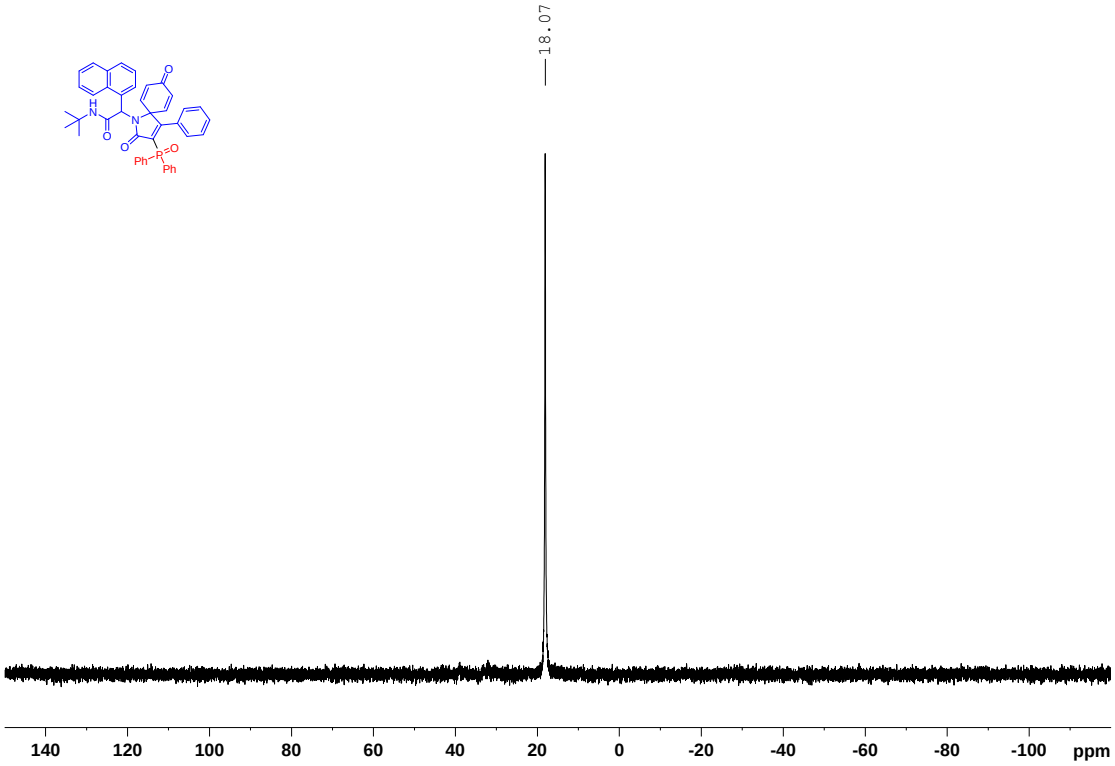
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **7h**



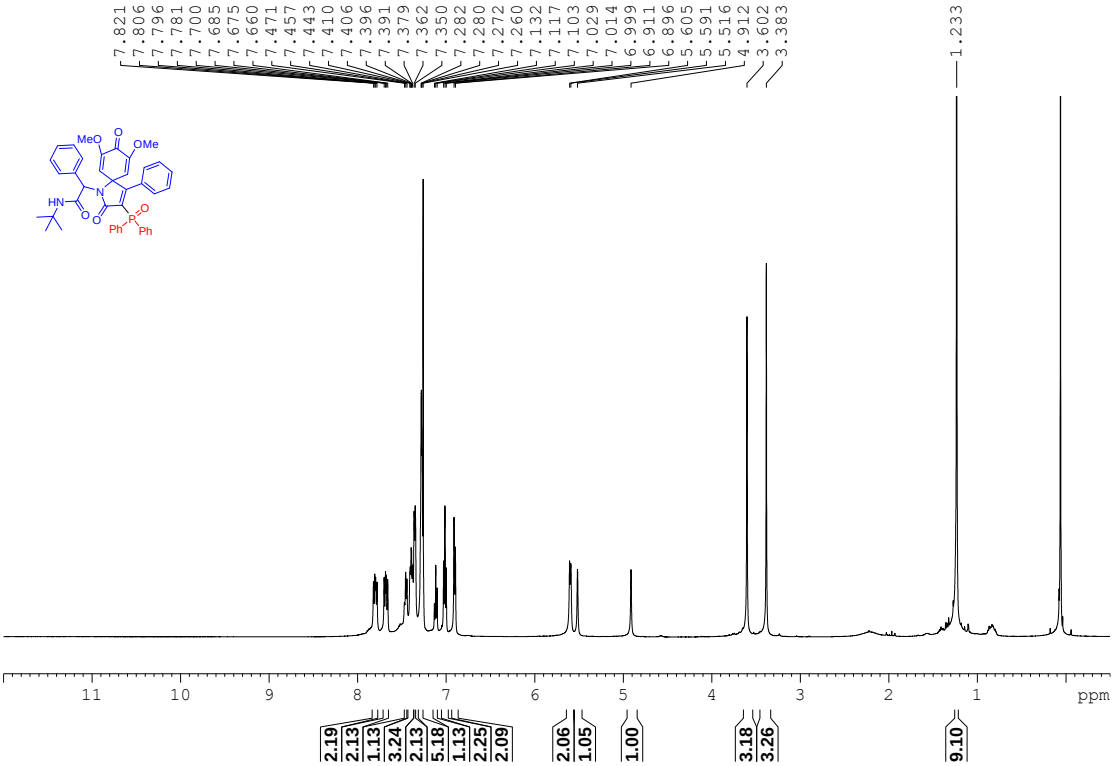
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7h**



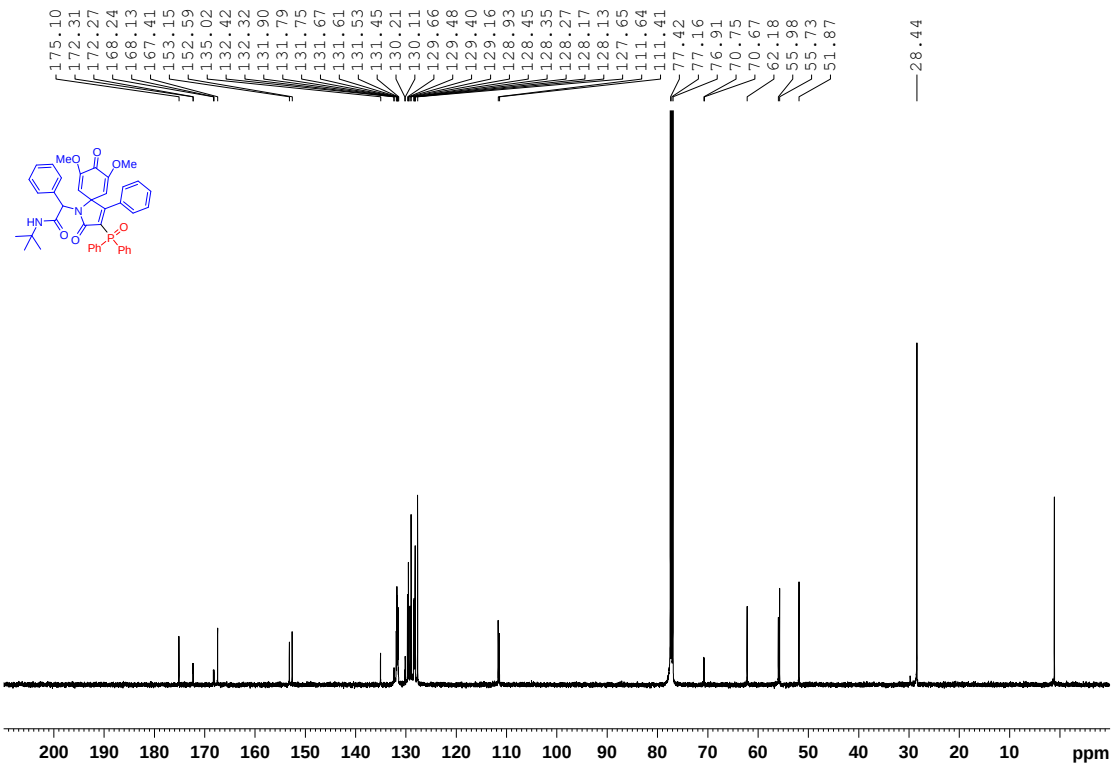
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7h**



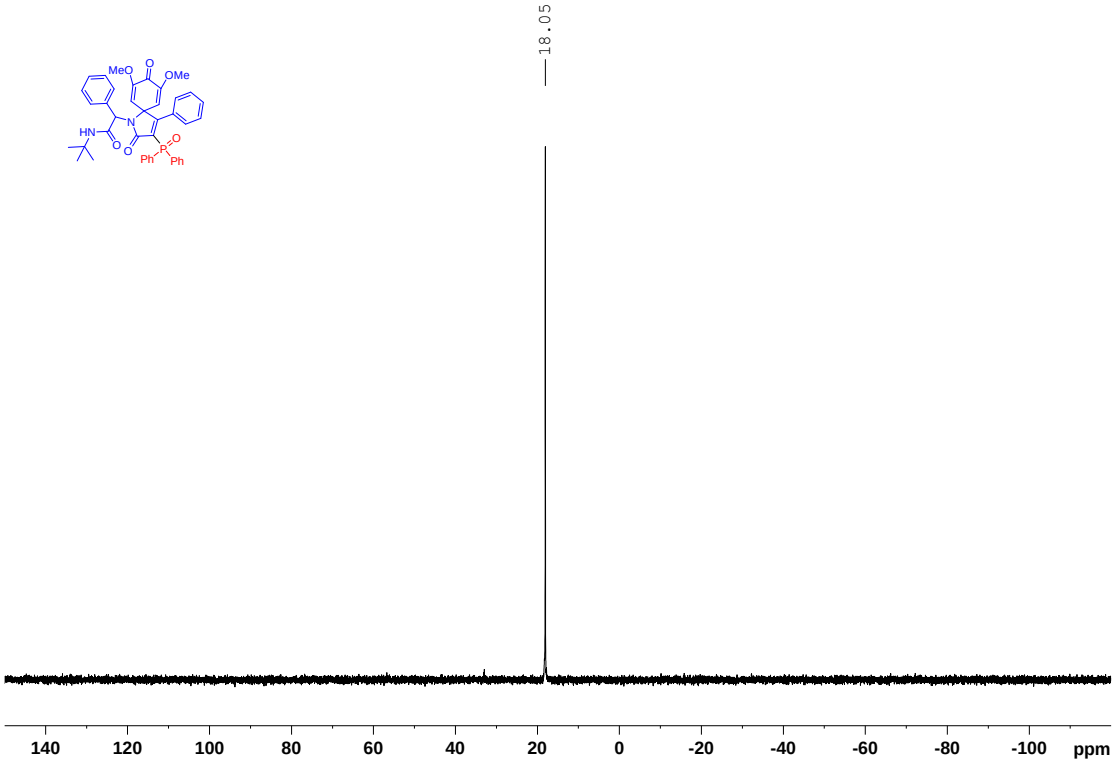
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **7i**



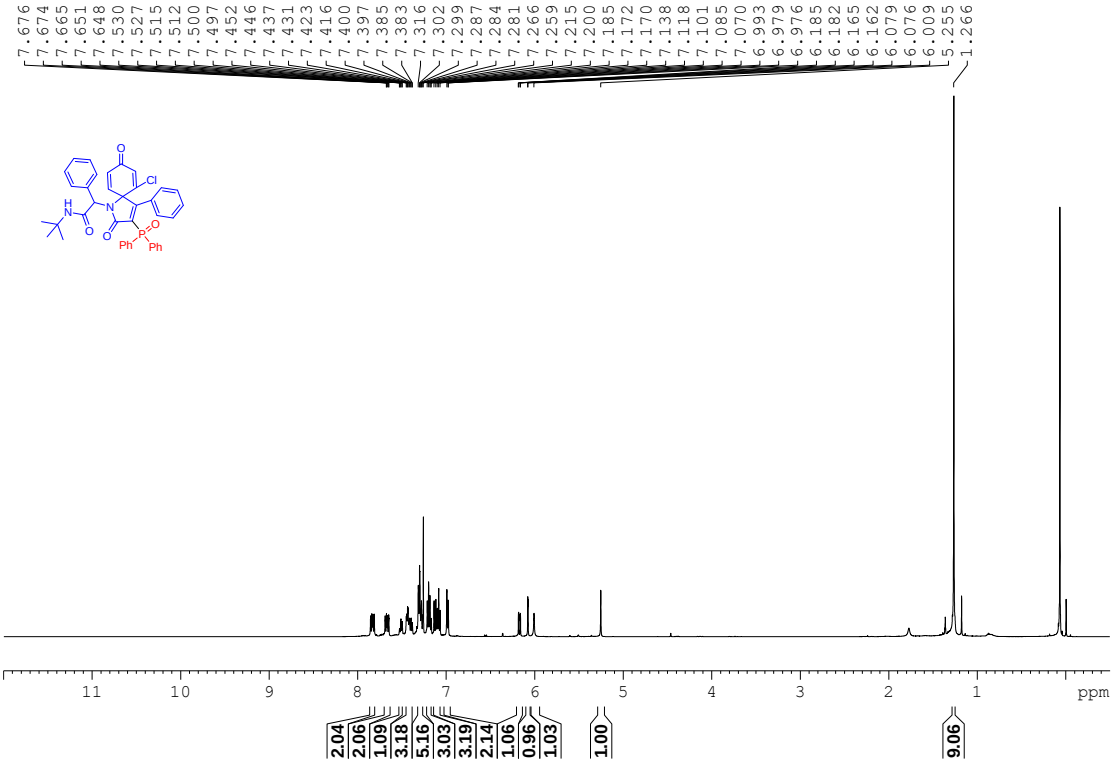
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7i**



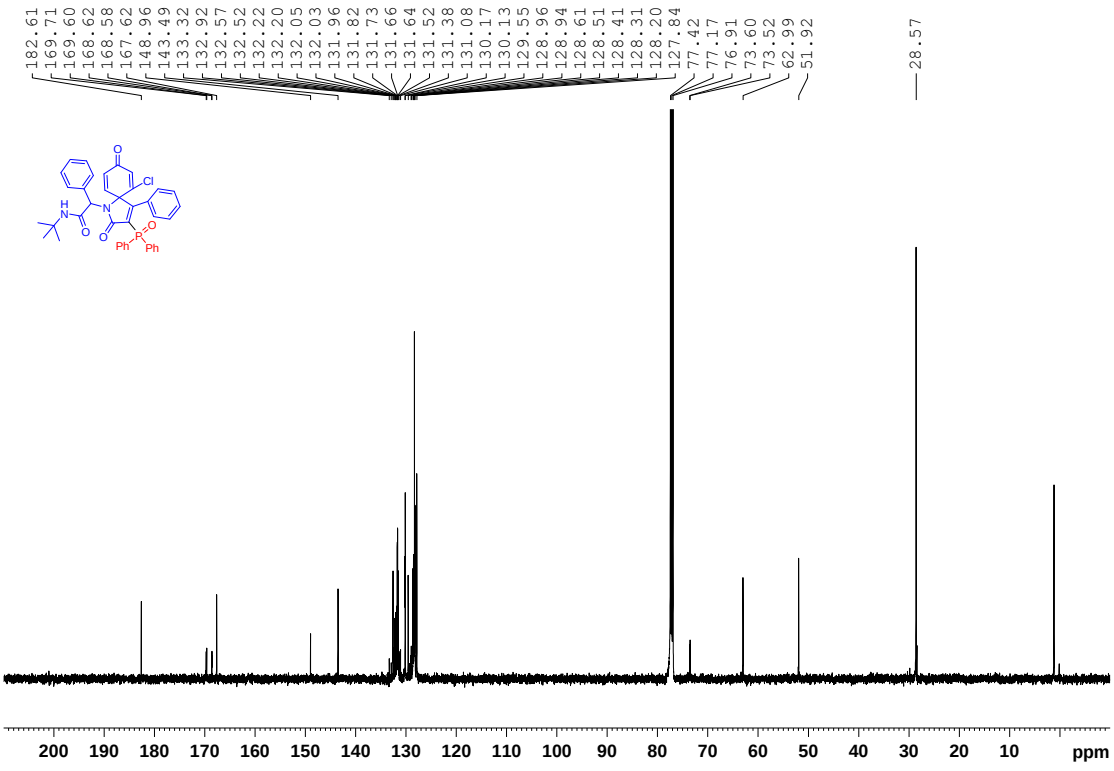
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7i**



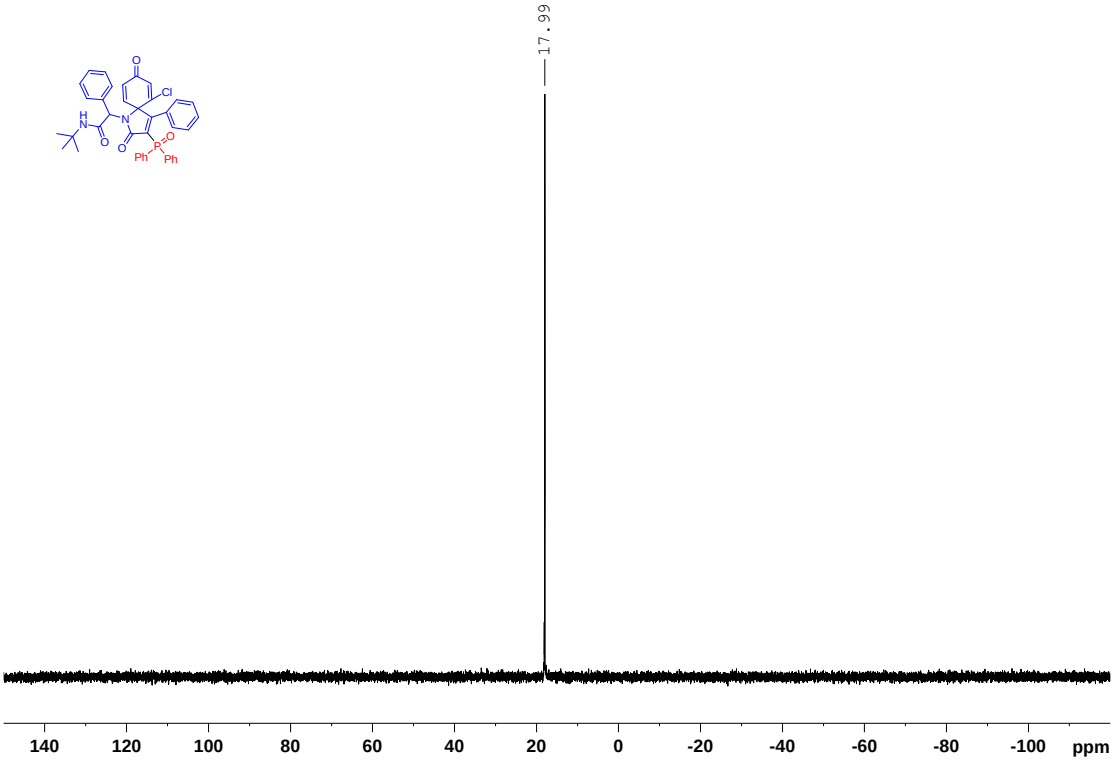
^{1}H NMR (500 MHz, $CDCl_3$, 300K):**7j**



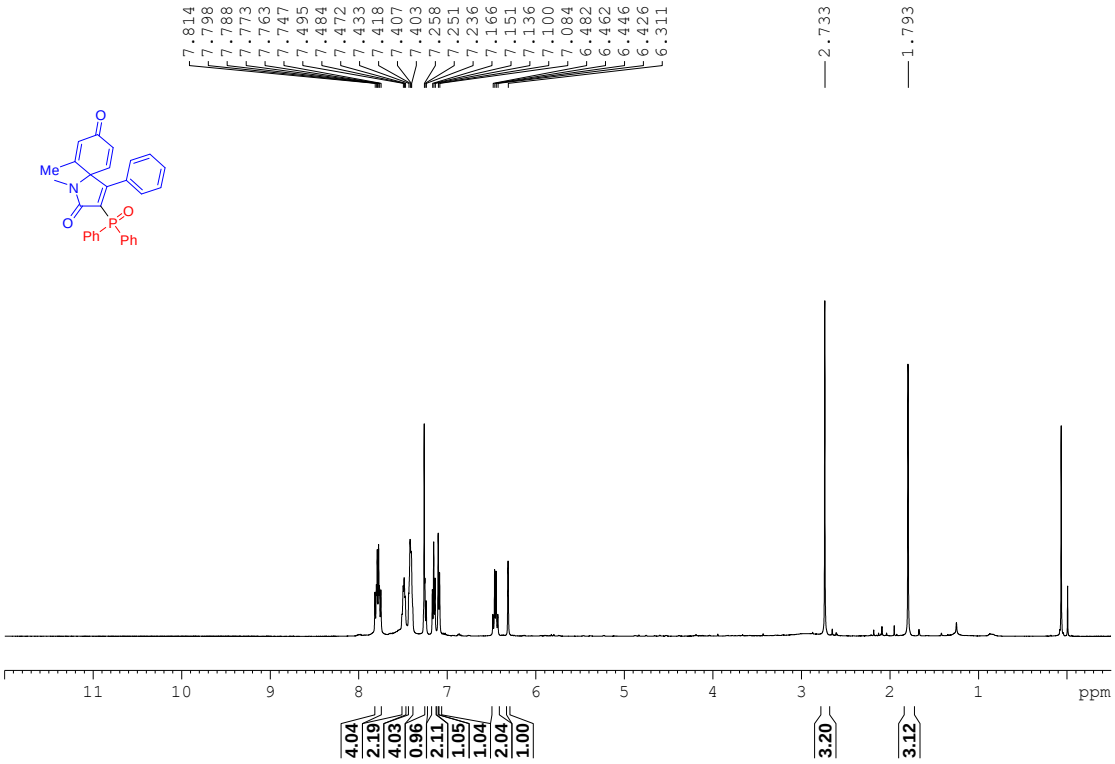
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **7j**



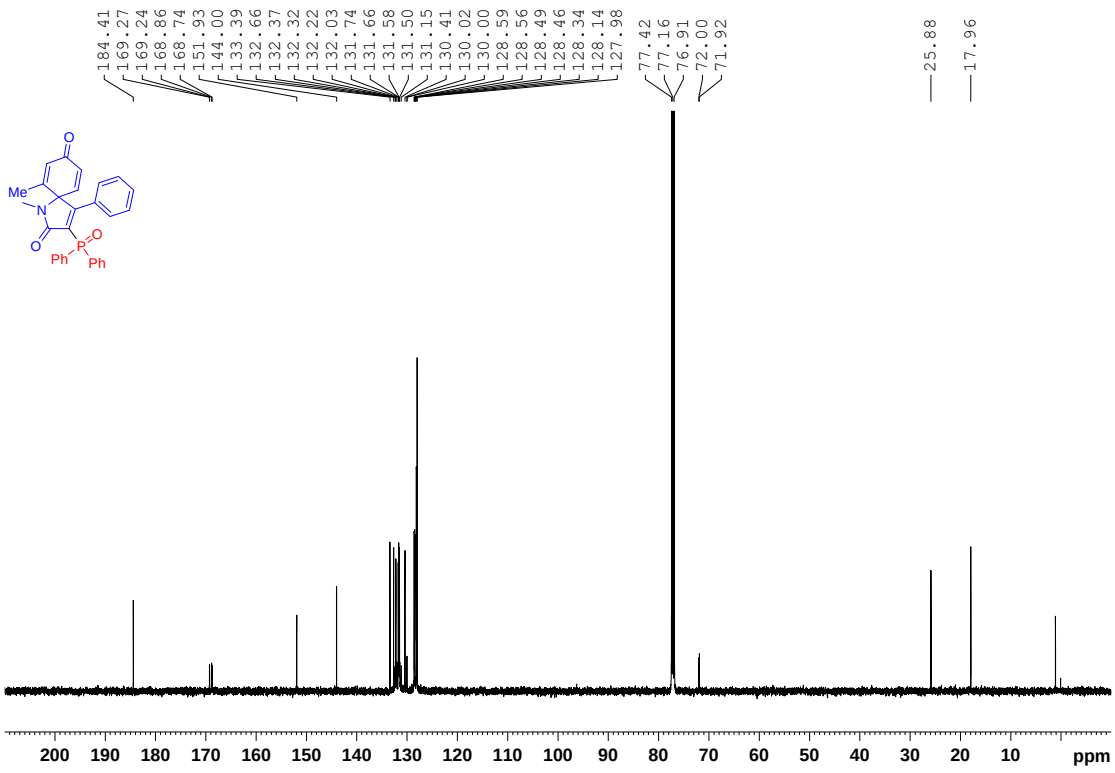
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **7j**



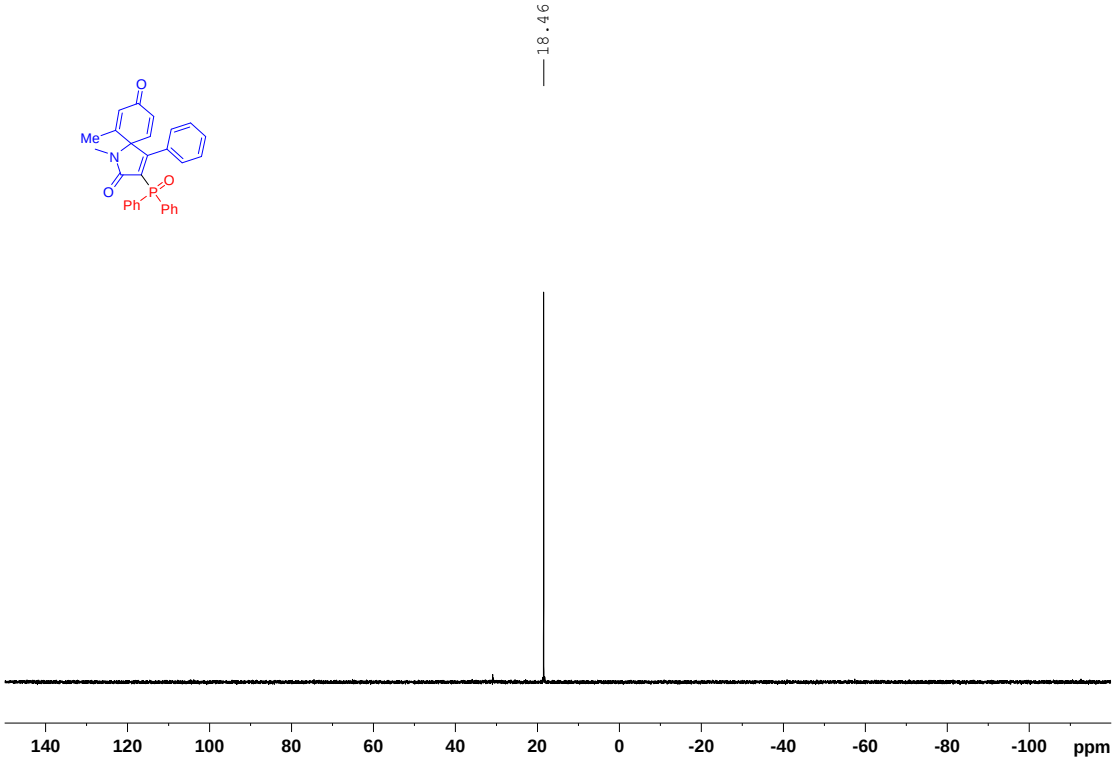
^{1}H NMR (500 MHz, $CDCl_3$, 300K):**9a**



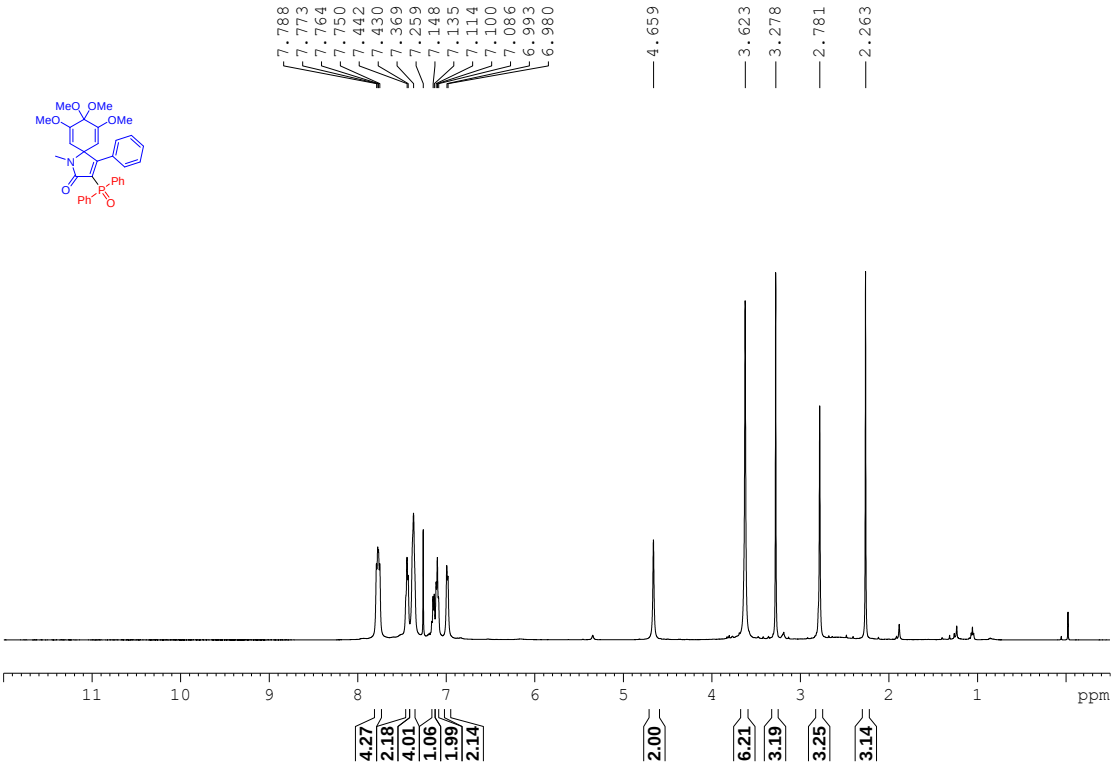
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **9a**



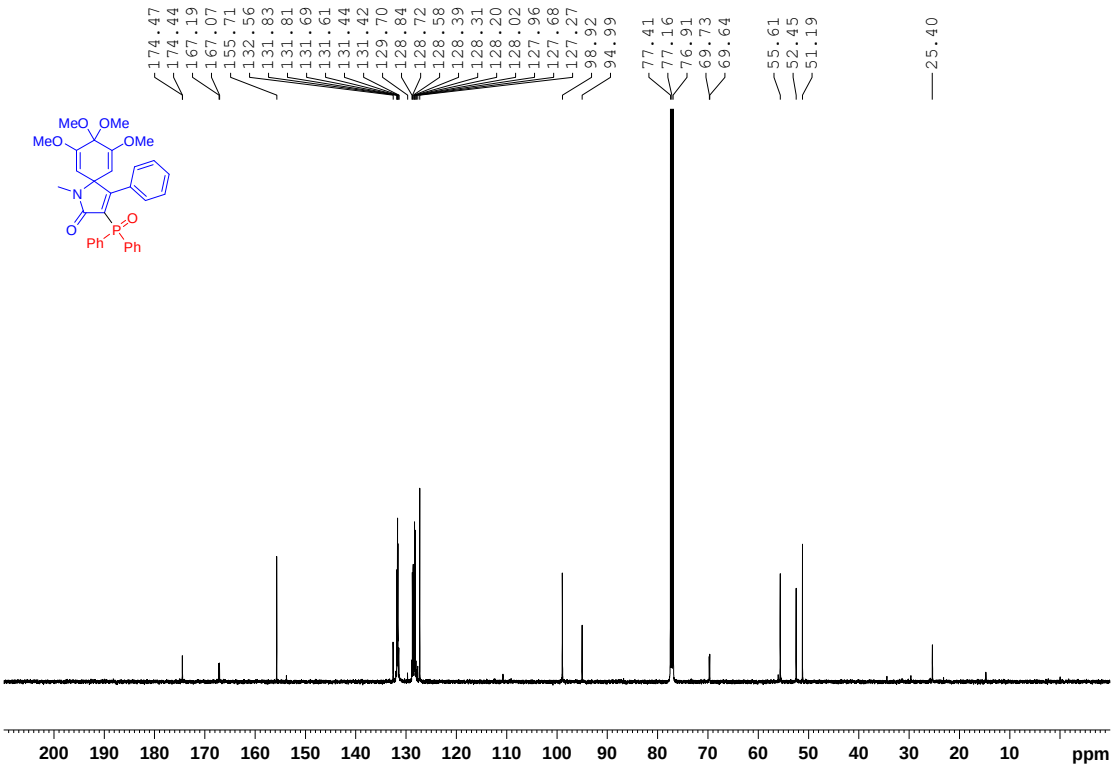
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **9a**



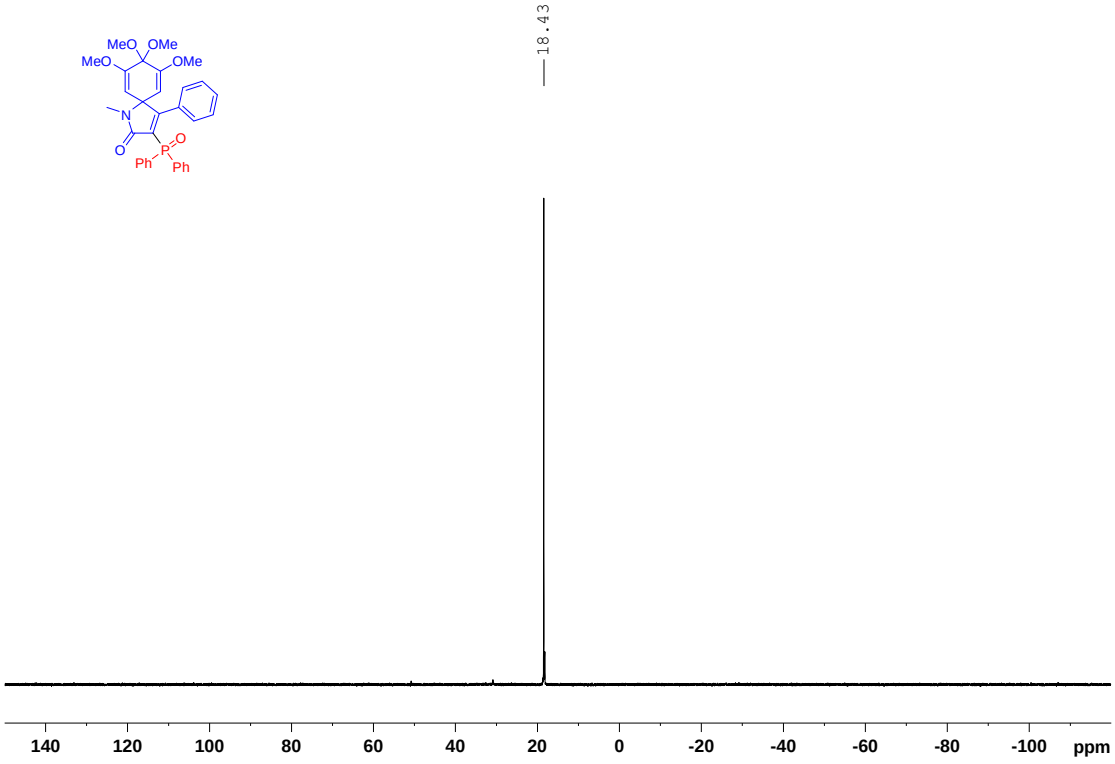
^{1}H NMR (500 MHz, $CDCl_3$, 300K): **9b**



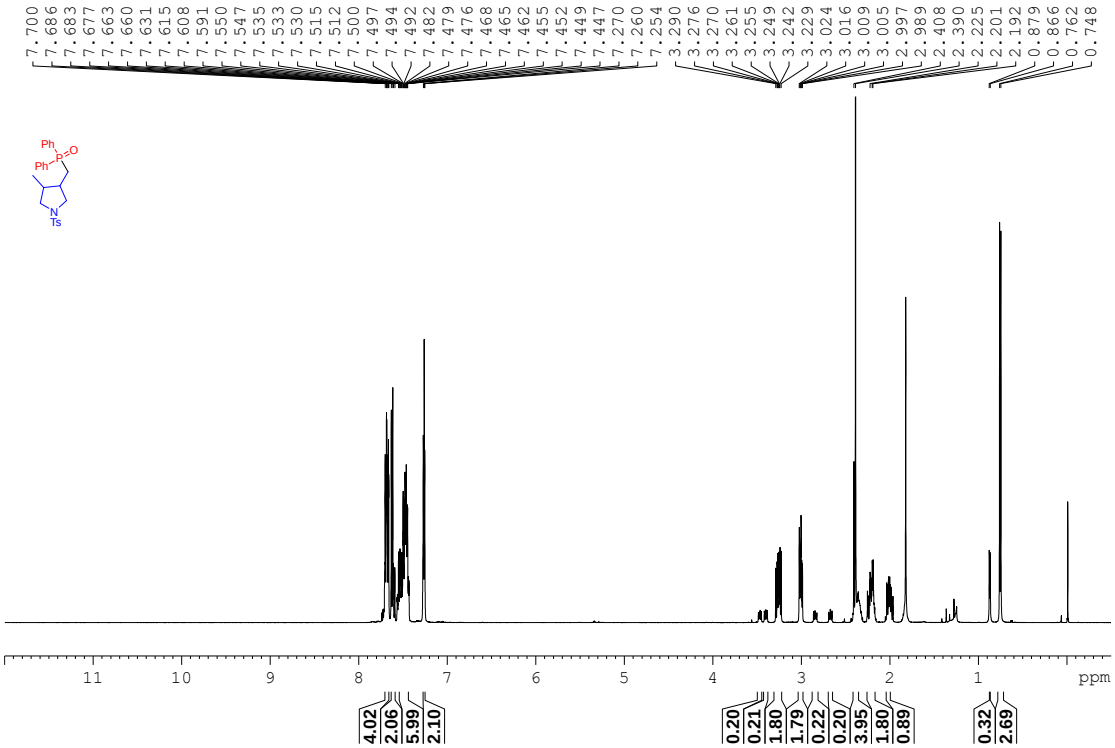
^{13}C NMR (125 MHz, $CDCl_3$, 300K): **9b**



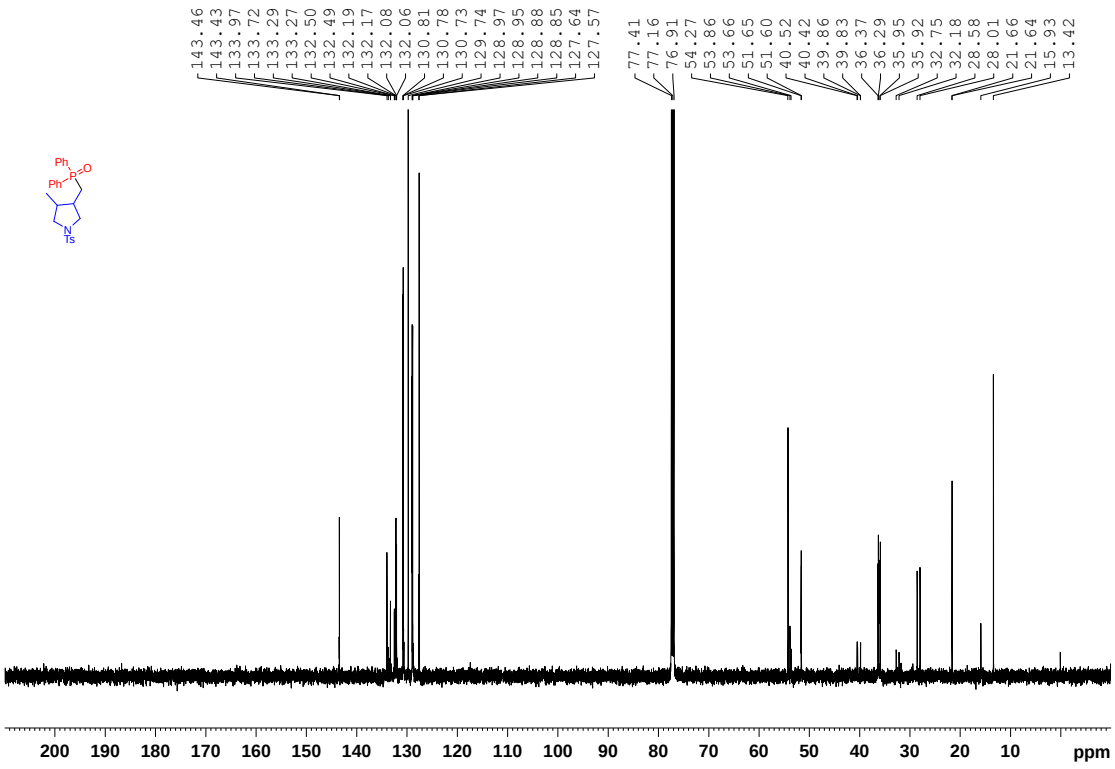
^{31}P NMR (162 MHz, $CDCl_3$, 300K): **9b**



^{1}H NMR (500 MHz, $CDCl_3$, 300K):



^{13}C NMR (125 MHz, $CDCl_3$, 300K):



^{31}P NMR (162 MHz, $CDCl_3$, 300K):