Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Gold-Catalysed Synthesis of Phosphonate-Substituted Oxetan-3-ones – An easy Access to Highly Strained HWE Reagents

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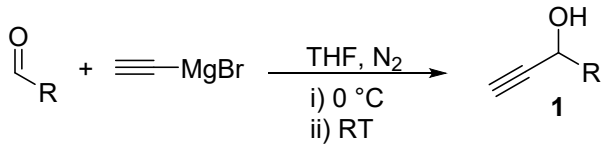
1. General Information:

All commercially available chemicals and deuterated solvents were purchased and used without further purifications. Solvent purification system MB SPS-800-Benchtop was used for dry solvents. The NMR spectra, were recorded at room temperature on Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz), Bruker Avance III 600 (600 MHz) or Fourier 300 (300 MHz) spectrometeres. Chemical shifts δ are quoted in parts per million (ppm) and coupling constants J in hertz (Hz) and the spectra are calibrated relative to the deuterated solvents, namely $CDCl_3$ (7.26 ppm; 77.16 ppm). The signal multiplicity is abbreviates as : s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), m (multiplet), as well as their combinations; for the All the ^{13}C NMR spectra are ^{1}H-decoupled and in some cases also ^{31}P-decoupled. All spectra were integrated and processed using TopSpin 3.5 software. were determined in the chemistry department of the University Heidelberg under the direction of Dr. J. Gross. EI+ -mass spectra (MS and HRMS) were measured on a JOEL JMS-700 spectrometer. Silica gel 60 (0.04 – 0.063 mm / 230 – 400 mesh ASTM) purchased from Macherey-Nagel was used as stationary phase for flash column chromatography. As eluents the respectively mentioned proportions of petroleum ether (PE) and ethyl acetate (EA) were used. Analytical Thin Layer Chromatography (TLC) was carried out on precoated Macherey-Nagel POLYGRAM® SIL G/UV254 or Merck TLC Silical Gel 60 F254 aluminium sheets and detection was accomplished using UV-light.

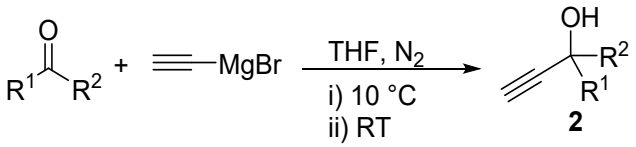
2. General Procedures:

2.1 Synthesis of Secondary Propargyl Alcohols (GP-A)



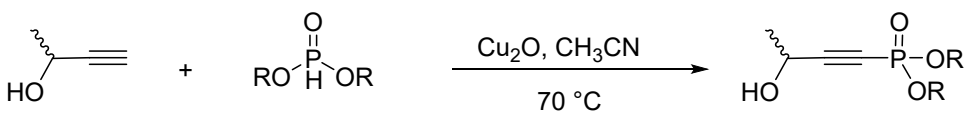
A solution of the corresponding aldehyde in THF (15 mmol, 0.5 M) was added to the solution of ethynylmagnesium bromide in THF (18 mmol, 0.5 M) at 0 °C under N_2, the reaction mixture was stirred for another 2-3 hours at room temperature and upon completion quenched with addition of aqueous saturated solution of NH_4Cl. The mixture was extracted using Et_2O, the combined organic layers were dried using sodium sulphate and the solvent was removed under reduced pressure. The residue was further purified by silica gel column chromatography using a mixture of hexane/ethyl acetate = 4/1 as eluent to get the desired propargylic alcohols as oils.[1]

2.2 Synthesis of Tertiary Propargyl Alcohols (GP-B)



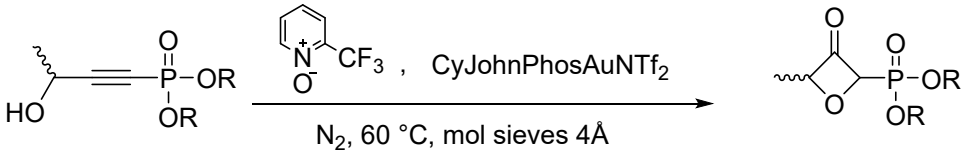
To a solution of ethynylmagnesium bromide in THF (36 mmol, 0.5 M) at -10 °C, a solution of the respective ketone in THF (30.5 mmol, 0.5 M) was added, the reaction was stirred at this temperature for another 10-20 minutes after which it was let warm to room temperature and stirred for another 2 hours. On completion the reaction was quenched using saturated aqueous NH_4Cl solution, extracted using ether, the combined organic layers dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was further purified by silica gel column chromatography using a mixture of hexane/ethyl acetate = 4/1 as eluent to get the desired propargylic alcohols as oils.[2]

2.3 Synthesis of Alkynyl Phosphonates (GP-C)



All the above synthesised alkynols (0.5 mmol), were coupled with diethylphosphite (0.7 mmol) at 70 °C in acetonitrile (2 mL) using Cu_2O (14 mol%) as a catalyst, the completion of reaction was monitored by a change in the reaction mixture colour from red to pale green/ yellow and when not obvious using TLC. The solvent was removed under reduced pressure followed by purification by flash silica gel chromatography using hexane/ethyl acetate mixture as eluent to obtain the desired alkynyl phosphonates.[3]

2.4 Au catalysed Reactions (GP-D)

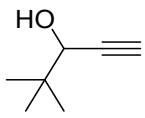


For the Au catalysed reaction, under N_2 and using 4 Å molecular sieves, to a solution of 1 equivalent of the substrate (30 mg, 0.3 mmol), 2 equivalents of 2-trifluoromethylpyridine *N*-oxide (0.6 mmol) in DCE (2.81 mL) and $CyJohnPhosAuNTf_2$ (5 mol%) was added as catalyst. The reaction was stirred for 24 hours at 60 °C, the completion of reaction was monitored by TLC. The solvent was removed under reduced pressure and the resulting residue purified by silica gel column chromatography using hexane/ethyl acetate to get the products.

2.5 Procedure for application as HWE reagents (GP-E)

Synthesised according to the reported procedure,[4] using 0.2 mmol (55.8 mg) of dimethyl(3-oxo-4-phenethyloxetan-2-yl)phosphonate **4e**, 0.3 mmol (0.2 mL) of LDA and 0.3 mmol (30 μL) of benzaldehyde. The configuration is determined based on ppm shift values of the olefinic proton, higher ppm values indicate *E*-isomer while lower ppm value is observed for the *Z*-isomer, also reported for similar compounds.[5]

4,4-Dimethylpent-1-yn-3-ol:

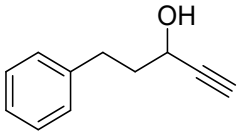


Synthesised according to GP-**A**, using 11.6 mmol (1.3 mL) of pivalaldehyde and 13.9 mmol (27.9 mL) of ethynylmagnesium bromide as a colorless liquid (845 mg, 65 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.01 (bs, 1H), 3.76-3.72 (m, 1H), 2.45-2.44 (d, *J* = 3.0 Hz, 1H), 1.00 (s, 9H).

Consistent with reported data.[6]

5-Phenylpent-1-yn-3-ol:

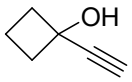


Synthesised according to GP-**A**, using 11.2 mmol (1.47 mL) of 3-phenylpropanal and 13.4 mmol (26.8 mL) of ethynylmagnesium bromide as a pale-yellow liquid (1.78 g, 99 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35-7.20 (m, 5H), 4.40-4.39 (d, *J* = 3.0 Hz, 1H), 2.86-2.81 (t, *J* = 6.0 Hz, 2H), 2.54-2.53 (d, *J* = 3.0 Hz, 1H), 2.11-2.02 (m, 2H).

Consistent with reported data.[7]

1-Ethynylcyclobutan-1-ol:

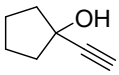


Synthesised according to GP-**B**, using 14.3 mmol (1.0 mL) of cyclobutanone and 17.1 mmol (34.2 mL) of ethynylmagnesium bromide as a colorless liquid (955 mg, 70 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76-3.72 (d, *J* = 6.0 Hz, 1H), 2.48-2.39 (m, 2H), 2.31-2.20 (m, 2H), 1.87-1.84 (m, 2H).

Consistent with reported data.[8]

1-Ethynylcyclopentan-1-ol:

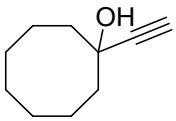


Synthesised according to GP-**B**, using 11.9 mmol (1. 0 mL) of cyclopentanone and 14.3 mmol (28.5 mL) of ethynylmagnesium bromide as a dark orange liquid (688 mg, 52 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77-3.17 (d, *J* = 9.0 Hz, 1H), 2.48 (s, 1H), 2.00-1.89 (m, 4H), 1.87-1.69 (m, 4H).

Consistent with reported data.[8]

1-Ethynylcyclooctan-1-ol:

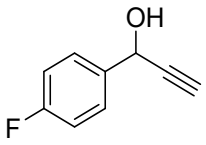


Synthesised according to GP-**B**, using 7.9 mmol (1.0 mL) of cyclooctanone and 9.5 mmol (19.0 mL) of ethynylmagnesium bromide as a pale-yellow liquid (893 mg, 74 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41-2.37 (d, *J* = 3.0 Hz, 1H), 2.01-1.78 (m, 4H), 1.63-1.24 (m, 10H).

Consistent with reported data.[9]

1-(4-fluorophenyl)prop-2-yn-1-ol:

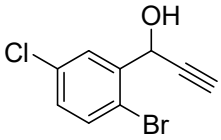


Synthesised according to GP-**A**, using 7.5 mmol of 4-fluorobenzaldehyde (0.8 mL) and 9.0 mmol (18.0 mL) of ethynylmagnesium bromide as an orange liquid (923 mg, 82 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (dddd, *J* = 8.5, 5.5, 2.7, 1.6 Hz, 2H), 7.12 - 7.03 (m, 2H), 5.44 (d, *J* = 3.9 Hz, 1H), 2.68 (d, *J* = 2.2 Hz, 1H).

Consistent with reported data.[10]

1-(2-Bromo-5-chlorophenyl)prop-2-yn-1-ol:

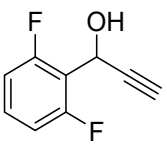


Synthesised according to GP-**A**, using 7.5 mmol (1.6 g) of 2-bromo-5-chlorobenzaldehyde and 9.00 mmol (18.0 mL) of ethynylmagnesium bromide as a beige solid (1.46 g, 79 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 2.6 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.19 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.73 (d, *J* = 2.2 Hz, 1H), 2.68 (d, *J* = 2.2 Hz, 1H).

Consistent with reported data.[11]

1-(2,6-Difluorophenyl)prop-2-yn-1-ol:

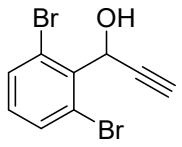


Synthesised according to GP-**A**, using 7.5 mmol (0.9 mL) of 2,6-difluorobenzaldehyde and 9.0 mmol (18.0 mL) of ethynylmagnesium bromide as a beige solid (723 mg, 57 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 2.6 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.19 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.73 (d, *J* = 2.2 Hz, 1H), 2.68 (d, *J* = 2.2 Hz, 1H).

Consistent with reported data.[12]

1-(2,6-Dibromophenyl)prop-2-yn-1-ol:

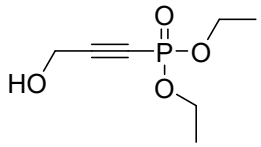


Synthesised according to GP-**A**, using 7.5 mmol (1.65 g) of 2,6-dibromobenzaldehyde and 9.0 mmol (18.0 mL) of ethynylmagnesium bromide as a beige solid (1.35 g, 82 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.1 Hz, 2H), 7.04 (t, *J* = 8.0 Hz, 1H), 2.64 (d, *J* = 2.5 Hz, 1H).

Consistent with reported data.[13]

Diethyl (3-hydroxyprop-1-yn-1-yl)phosphonate (1a):

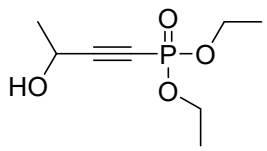


Synthesised according to GP-**C**, using 28.5 mmol (2.1 mL) of prop-2-yn-1-ol 40.0 mmol (6.5 mL) of diethylphosphite and 4.0 mmol (572 mg) of Cu_2O as an orange oil (1.40 g, 30 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.36 (d, *J* = 3.9 Hz, 2H), 4.17 (dq, *J* = 8.6, 7.1 Hz, 4H), 3.39 (s, 1H), 1.37 (td, *J* = 7.1, 0.8 Hz, 6H).

Consistent with reported data. [3]

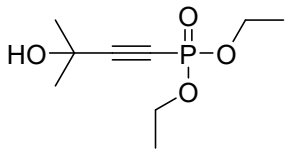
Diethyl (3-hydroxybut-1-yn-1-yl)phosphonate (1b):



Synthesised according to GP-**C**, using 44.6 mmol (2.8 mL) of but-3-yn-2-ol, 62.4 mmol (8.1 mL) of diethylphosphite and 6.2 mmol (893 mg) of Cu_2O as a pale-yellow oil (4.3 g, 50 %).

R_f = 0.18 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.88 (d, *J* = 6.3 Hz, 1H), 4.58 (qd, *J* = 6.8, 3.3 Hz, 1H), 4.14 (p, *J* = 7.2 Hz, 4H), 1.48 (d, *J* = 6.7 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 103.55 (d, *J* = 49.5 Hz), 73.61, 71.64, 63.57 (dd, *J* = 5.6, 2.6 Hz), 57.83 (d, *J* = 4.1 Hz), 23.22, 16.12 (d, *J* = 7.0 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 103.55, 72.63, 63.57, 57.83, 23.23, 16.13; ^{31}P NMR (122 MHz, $CDCl_3$): δ = -6.56; IR (film): n = 3359, 2987, 2936, 2909, 2204, 1478, 1245, 1165, 1123, 964, 799 cm $^{-1}$; HR-MS (EI): m/z = 207.07721, calcd. for $C_8H_{15}O_4P$ [M^++H]: 207.07807.s

Diethyl (3-hydroxy-3-methylbut-1-yn-1-yl)phosphonate (1c):

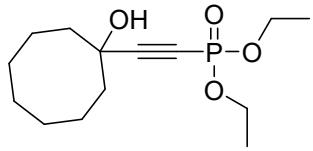


Synthesised according to GP-**C**, using 53.1 mmol (3.5 mL) of 2-methylbut-3-yn-2-ol, 75.0 mmol (9.7 mL) of diethylphosphite and 7.5 mmol (1.1 g) of Cu_2O as a yellow oil (3.1 g, 30%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.40 (s, 1H), 4.06 (dd, *J* = 8.3, 6.8 Hz, 4H), 1.39 (d, *J* = 6.6 Hz, 6H), 1.27 (t, *J* = 7.1 Hz, 6H).

Consistent with reported data. [3]

Diethyl ((1-hydroxycyclooctyl)ethynyl)phosphonate (1d):

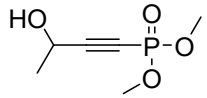


Synthesised according to GP-**C**, using 1.3 mmol (200 mg) of 1-ethynylcyclooctan-1-ol, 1.8 mmol (0.2 mL) of diethylphosphite and 1.8 mmol (26 mg) of Cu_2O as a yellow oil (246 mg, 65%).

R_f = 0.28 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.15 (dq, *J* = 8.8, 7.0 Hz, 4H), 3.03 (s, 1H), 2.09-1.86 (m, 4H), 1.73-1.43 (m, 10H), 1.36 (td, *J* = 7.1, 0.7 Hz, 6H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 4.19-4.11 (m, 4H), 3.02 (s, 1H), 2.09-1.86 (m, 4H), 1.70-1.43 (m, 12H),

1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 105.62 (d, *J* = 48.8 Hz), 73.42, 71.32 (d, *J* = 3.8 Hz), 63.39 (d, *J* = 5.3 Hz), 37.31, 27.85, 24.43, 21.82, 16.20 (d, *J* = 6.9 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 105.65, 72.43, 71.31, 63.39, 37.31, 27.85, 24.44, 21.83, 16.20; ^{31}P NMR (122 MHz, $CDCl_3$): δ = -6.42; HR-MS (EI): m/z = 288.14776, calcd. for $C_{14}H_{25}O_4P$: 288.14850.

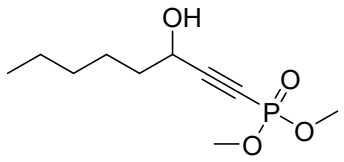
Dimethyl (3-hydroxybut-1-yn-1-yl)phosphonate (3a):



Synthesised according to GP-**C**, using 7.1 mmol (0.6 mL) of but-3-yn-2-ol, 10.0 mmol (0.9 mL) of dimethylphosphite and 1.0 mmol (142 mg) of Cu_2O as an orange oil (466 mg, 37%).

R_f = 0.12 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.77 (s, 1H), 4.60-4.52 (qd, *J* = 6.8, 3.3 Hz, 1H), 3.74 (d, *J* = 12.4 Hz, 6H), 1.46-1.44 (d, *J* = 6.6 Hz, 3H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 4.76 (s, 1H), 4.59-4.52 (q, *J* = 6.8 Hz, 1H), 3.77 (s, 6H), 1.46-1.44 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 104.44 (d, *J* = 49.8 Hz), 71.19 (d, *J* = 300.7 Hz), 57.79 (d, *J* = 4.2 Hz), 53.68 (d, *J* = 3.4 Hz), 23.22 (d, *J* = 1.4 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 104.44, 71.19, 57.79, 53.68 (d, *J* = 2.7 Hz), 23.22; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -3.32; IR (film): n = 3369, 2987, 2203, 1451, 1240, 1184, 1118, 951, 780 cm $^{-1}$; HR-MS (EI): m/z = 179.04677, calcd. for $C_6H_{11}O_4P$ [M^++H]: 179.04703.

Dimethyl (3-hydroxyoct-1-yn-1-yl)phosphonate (3b):

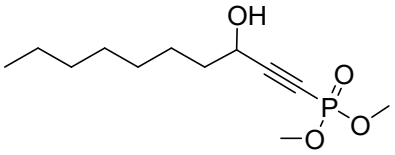


Synthesised according to GP-*C*, using 4.0 mmol (500 mg) of 1-octyne-3-ol, 5.5 mmol (0.5 mL) of dimethylphosphite and 0.6 mmol (79 mg) of Cu_2O, as pale-yellow liquid (678 mg, 73%).

R_f = 0.32 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.45 (td, *J* = 6.7, 3.4 Hz, 1H), 3.88 - 3.75 (d, 6H), 3.49 (s, 1H), 1.82-1.70 (m, 2H), 1.51-1.41 (m, 2H), 1.31 (m, *J* = 7.1, 4.9, 2.6 Hz, 4H), 0.93 - 0.85 (m, 3H); ^{1}H{^{31}P} NMR (500 MHz, $CDCl_3$): δ = 4.45 (t, *J* = 6.7 Hz, 1H), 3.79 (s, *J* = 0.6 Hz, 6H), 3.49 (s, 1H), 1.83 - 1.69 (m, 2H), 1.53-1.40 (m, 2H), 1.39-1.27 (m, 4H), 0.96-0.83 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 104.26 (dd, *J* = 49.9, 3.4 Hz), 71.38 (dt, *J* = 301.0, 5.7 Hz), 61.63, 53.51, 36.56, 31.25, 24.66, 22.40, 13.86; ^{13}C{^{31}P} NMR (151 MHz,

$CDCl_3$): δ = 104.27 (d, *J* = 3.6 Hz), 71.40 (d, *J* = 4.7 Hz), 61.63 (d, *J* = 2.8 Hz), 36.57, 31.25, 24.67, 22.41, 13.87; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -3.58; IR (film): n = 3364, 2956, 2932, 2859, 2201, 1460, 1257, 1127, 1032, 924, 798 cm $^{-1}$; HR-MS (EI): m/z = 235.10888, calcd. for $C_{10}H_{19}O_4P$ [M^++H]: 235.10937.

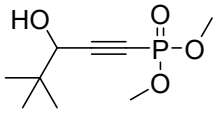
Dimethyl (3-hydroxydec-1-yn-1-yl)phosphonate (3c):



Synthesised according to GP-**C**, using 3.2 mmol (500 mg) of dec-1-yn-3-ol, 4.5 mmol (0.4 mL) of dimethylphosphite and 0.5 mmol (65 mg) of Cu_2O, as pale-yellow oil (561 mg, 66 %).

R_f = 0.32 (PE:EA-1:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 4.45-4.45 (td, *J* = 6.7, 3.3 Hz, 1H), 3.79 (d, *J* = 12.3 Hz, 6H), 3.16 (s, 1H), 1.84-1.68 (m, 2H), 1.53-1.19 (m, 10H), 0.96-0.76 (m, 3H); $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ = 4.45 (t, *J* = 6.7 Hz, 1H), 3.79 (s, 6H), 3.15 (s, 1H), 1.84-1.64 (m, 2H), 1.52-1.20 (m, 10H), 0.93-0.74 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 104.23 (d, *J* = 49.8 Hz), 71.61 (d, *J* = 301.0 Hz), 61.78 (d, *J* = 4.0 Hz), 53.58 (dd, *J* = 5.6, 3.5 Hz), 36.69 (d, *J* = 1.5 Hz), 31.75, 29.14, 25.08, 22.61, 14.06; $^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$): δ = 104.22, 71.60, 61.78, 53.59, 36.69, 31.75, 29.14, 25.08, 22.61, 14.07; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -3.58; IR (film): n = 3361, 2954, 2927, 2856, 2201, 1460, 1260, 1128, 1034, 943, 792 cm $^{-1}$; HR-MS (EI): m/z = 263.14157, calcd. for $C_{12}H_{23}O_4P$ [M^++H]: 263.14304.

Dimethyl (3-hydroxy-4,4-dimethylpent-1-yn-1-yl)phosphonate (3d):

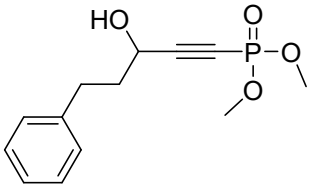


Synthesised according to GP-**C**, using 4.5 mmol (500 mg) of 4,4-dimethylpent-1-yn-3-ol, 6.2 mmol (0.6 mL) of dimethylphosphite and 0.6 mmol (89 mg) of Cu_2O, as pale-yellow oil (552 mg, 56%).

R_f = 0.37 (PE:EA-1:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 4.12 (d, *J* = 3.5 Hz, 1H), 3.85 (d, *J* = 12.3 Hz, 1H), 3.79 (dd, *J* = 12.3, 1.0 Hz, 6H), 2.81 (s, 1H), 1.23 (s, 1H), 1.02 (s, 8H); $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ = 4.12 (s, 1H), 3.79 (d, *J* = 1.0 Hz, 6H), 2.81 (s, 1H), 1.23 (s, 1H), 1.02 (s, 8H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 103.18 (dd, *J* = 50.2, 3.9 Hz), 72.70

(d, *J* = 301.8 Hz), 70.63 (d, *J* = 3.9 Hz), 53.53, 35.81, 25.31; $^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$): δ = 103.17 (d, *J* = 3.9 Hz), 72.70, 70.64 (d, *J* = 3.1 Hz), 53.54 (d, *J* = 4.9 Hz), 35.82, 25.32; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -3.70; IR (film): n = 3366, 2959, 2909, 2871, 2200, 1479, 1463, 1268, 1186, 1070, 936, 795 cm $^{-1}$; HR-MS (EI): m/z = 221.09409, calcd. for $C_9H_{17}O_4P$ $[M^+ + H]$: 221.09372.

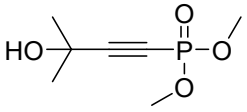
Dimethyl (3-hydroxy-5-phenylpent-1-yn-1-yl)phosphonate (3e):



Synthesised according to GP-**C**, using 3.1 mmol (500 mg) of 5-phenylpent-1-yn-3-ol, 4.4 mmol (0.4 mL) of dimethylphosphite and 0.4 mmol (62 mg) of Cu_2O, as pale-yellow oil (686 mg, 82%).

R_f = 0.19 (PE:EA-1:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.38-7.28 (m, 2H), 7.26-7.18 (m, 3H), 4.48 (ddd, *J* = 7.3, 6.1, 3.4 Hz, 1H), 3.92 (s, 1H), 3.82 (dd, *J* = 12.3, 0.9 Hz, 6H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.2-1.94 (m, 2H); $^1H\{^{31}P\}$ (300 MHz, $CDCl_3$): δ = 7.38-7.27 (m, 2H), 7.27-7.18 (m, 3H), 4.48 (dd, *J* = 7.4, 6.1 Hz, 1H), 3.92 (s, 1H), 3.82 (d, *J* = 1.0 Hz, 6H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.38 - 2.00 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.84 (d, *J* = 2.6 Hz), 128.57, 126.23, 103.74 (d, *J* = 51.2 Hz), 72.14 (dd, *J* = 300.2, 8.8 Hz), 61.03, 53.69 (dd, *J* = 5.8, 3.1 Hz), 38.28 (d, *J* = 1.4 Hz), 31.29; $^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$): δ = 140.83 (d, *J* = 2.3 Hz), 128.57 (d, *J* = 2.3 Hz), 126.22, 103.70 (d, *J* = 10.7 Hz), 72.17 (d, *J* = 8.9 Hz), 61.03 (d, *J* = 3.8 Hz), 53.70 (d, *J* = 3.3 Hz), 38.29, 31.29; ^{31}P NMR (121 MHz, $CDCl_3$): δ = - 3.15; IR (film): n = 3353, 3027, 2954, 2854, 2201, 1495, 1455, 1254, 1028, 1183, 928, 789 cm $^{-1}$; HR-MS (EI): m/z = 269.09356, calcd. for $C_{13}H_{18}O_4P$ $[M^+ + H]$: 269.09372.

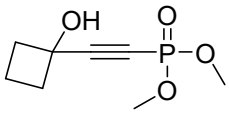
Dimethyl (3-hydroxy-3-methylbut-1-yn-1-yl)phosphonate (3f):



Synthesised according to GP-**C**, using 5.9 mmol (0.6 mL) of 2-methylbut-3-yn-2-ol, 8.3 mmol (0.8 mL) of dimethylphosphite and 0.8 mmol (119 mg) of Cu_2O, as yellow oil (593 mg, 52%).

R_f = 0.24 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.45 (s, 1H), 3.71 (dd, *J* = 12.2, 1.6 Hz, 6H), 1.48 (d, *J* = 4.5 Hz, 6H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 4.45 (s, 1H), 3.71 (d, *J* = 1.7 Hz, 6H), 1.48 (d, *J* = 1.8 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 107.15 (d, *J* = 48.6 Hz), 69.23 (d, *J* = 301.2 Hz), 64.57, 53.54 (d, *J* = 5.6 Hz), 30.41; ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 107.18 (d, *J* = 3.2 Hz), 69.17 (d, *J* = 2.8 Hz), 64.55 (d, *J* = 3.7 Hz), 53.53, 30.40; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -2.85; IR (film): n = 3363, 2985, 2956, 2854, 2202, 1457, 1404, 1377, 1247, 1172, 1019, 819, 765 cm $^{-1}$; HR-MS (EI): m/z = 193.06144, calcd. for $C_7H_{13}O_4P$ [M^++H]: 193.06242.

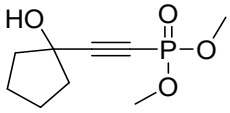
Dimethyl ((1-hydroxycyclobutyl)ethynyl)phosphonate (3g):



Synthesised according to GP-**C**, using 5.2 mmol (500 mg) of 1-ethynylcyclobutan-1-ol, 7.3 mmol (0.7 mL) of dimethylphosphite and 0.7 mmol (104 mg) of Cu_2O, as pale-yellow oil (425 mg, 40%).

R_f = 0.24 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (d, *J* = 12.3 Hz, 6H), 2.77 (s, 1H), 2.58-2.44 (m, 2H), 2.40-2.24 (m, 2H), 2.01-1.77 (m, 2H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 1H), 2.77 (s, 1H), 2.58-2.43 (m, 2H), 2.40-2.23 (m, 2H), 2.01-1.75 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 105.35 (d, *J* = 49.4 Hz), 71.27 (d, *J* = 300.7 Hz), 67.49 (d, *J* = 4.1 Hz), 53.66 (d, *J* = 5.6 Hz), 37.80, 13.14; ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 105.35, 71.26, 67.49, 53.66, 37.81, 13.15; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -2.95; IR (film): n = 3334, 2994, 2954, 2854, 2198, 1450, 1423, 1254, 1167, 1021, 970, 796 cm $^{-1}$; HR-MS (EI): m/z = 205.06182, calcd. for $C_8H_{13}O_4P$ [M^++H]: 205.06242.

Dimethyl ((1-hydroxycyclopentyl)ethynyl)phosphonate (3h):

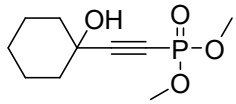


Synthesised according to GP-**C**, using 4.5 mmol (500 mg) of 1-ethynylcyclopentan-1-ol, 6.4 mmol (0.6 mL) of dimethylphosphite and 0.6 mmol (91 mg) of Cu_2O, as pale-yellow oil (495 mg, 50%).

R_f = 0.27 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (d, *J* = 12.3 Hz, 6H), 2.08-1.91 (m, 4H), 1.91-1.66 (m, 4H); ^{1}H{^{31}P} NMR (500 MHz, $CDCl_3$): δ = 3.78 (s, 6H), 2.06-1.93 (m,

4H), 1.93-1.63 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 106.23 (d, *J* = 49.8 Hz), 73.88 (d, *J* = 4.1 Hz), 70.59 (d, *J* = 301.7 Hz), 53.59 (d, *J* = 5.7 Hz), 42.15, 23.65; ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 106.23, 73.88, 70.58, 53.59, 42.16, 23.66; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -2.72; IR (film): n = 3358, 2955, 2874, 2854, 2189, 1449, 1410, 1248, 1184, 1024, 918, 822 cm $^{-1}$; HR-MS (EI): m/z = 219.07530, calcd. for $C_9H_{15}O_4P$ [M^++H]: 219.07807.

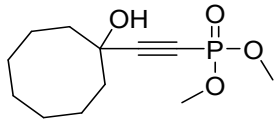
Dimethyl ((1-hydroxycyclohexyl)ethynyl)phosphonate (3i):



Synthesised according to GP-**C**, using 4.0 mmol (500 mg) of 1-ethynylcyclohexan-1-ol, 5.6 mmol (0.5 mL) of dimethylphosphite and 0.6 mmol (81 mg) of Cu_2O as pale-yellow oil (449 mg, 48%).

R_f = 0.29 (PE:EA-1:1); ^{1}H (600 MHz, $CDCl_3$): δ = 3.79 (d, *J* = 12.4 Hz, 6H), 2.00-1.47 (m, 10H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 6H), 2.07-1.20 (m, 10H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 105.91 (d, *J* = 48.7 Hz), 71.93 (d, *J* = 299.2 Hz), 68.58 (d, *J* = 3.9 Hz), 53.59 (d, *J* = 5.5 Hz), 39.04, 24.99, 22.99; ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 105.91, 71.93, 68.58, 53.59, 39.05, 24.99, 23.00; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -2.83; IR (film): n = 3361, 2935, 2857, 2190, 2190, 1448, 1254, 1184, 1033, 974, 802 cm $^{-1}$; HR-MS (EI): m/z = 232.08502, calcd. for $C_{10}H_{17}O_4P$: 232.08502.

Dimethyl ((1-hydroxycyclooctyl)ethynyl)phosphonate (3j):

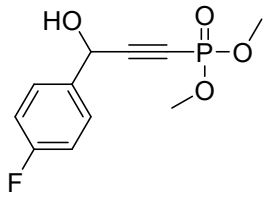


Synthesised according to GP-**C**, using 3.3 mmol (500 mg) of 1-ethynylcyclooctan-1-ol and 4.6 mmol (0.4 mL) of dimethylphosphite and 0.5 mmol (66 mg) of Cu_2O, as pale-yellow oil (444 mg, 52%).

R_f = 0.3 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (d, *J* = 12.3 Hz, 6H), 3.05 (s, 1H), 2.01 (dddd, *J* = 17.1, 10.0, 7.9, 2.7 Hz, 4H), 1.77-1.46 (m, 10H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ 3.78 (s, 6H), 3.02 (s, 1H), 2.08-1.90 (m, 4H), 1.71-1.43 (m, 10H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 106.65 (d, *J* = 48.6 Hz), 71.97(d, *J* = 48.6 Hz), 71.37 (d, *J* = 299.0 Hz), 53.59 (d, *J* = 5.5 Hz), 37.30, 27.83, 24.42, 21.82; ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ =

106.67 (d, *J* = 2.8 Hz), 71.36, 70.96, 53.59, 37.29, 27.84, 24.42, 21.82; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -2.75; IR (film): n = 3353, 2926, 2854, 2193, 1446, 1440, 1240, 1184, 1026, 919, 806 cm $^{-1}$; HR-MS (EI): m/z = 261.12576, calcd. for $C_{12}H_{21}O_4P$ [M^++H]: 261.12502.

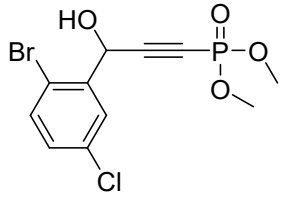
Dimethyl (3-(4-fluorophenyl)-3-hydroxyprop-1-yn-1-yl)phosphonate (3k):



Synthesised according to GP-**C**, using 3.3 mmol (500 mg) of 1-(4-fluorophenyl)prop-2-yn-1-ol, 4.7 mmol (0.4 mL) of dimethylphosphite and 0.5 mmol (67 mg) of Cu_2O, as orange oil (542 mg, 63%).

R_f = 0.2 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29-8.04 (m, 1H), 7.51-7.44 (m, 1H), 7.23-7.15 (m, 1H), 7.08-7.00 (m, 1H), 5.52 (d, J = 3.6 Hz, 1H), 3.89 (d, J = 12.3 Hz, 2H), 3.76 (dd, J = 12.3, 1.3 Hz, 4H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 8.21-8.09 (m, 1H), 7.53-7.42 (m, 1H), 7.19 (t, *J* = 8.5 Hz, 1H), 7.08-6.99 (m, 1H), 3.93-3.85 (m, 2H), 3.76 (d, *J* = 1.4 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.28 (d, *J* = 4.7 Hz), 167.26 (d, *J* = 259.4 Hz), 162.89 (d, *J* = 247.6 Hz), 134.81, 132.82, 132.05 (d, *J* = 2.7 Hz), 128.59 (d, *J* = 8.7 Hz), 116.62, 115.66, 101.95 (d, *J* = 49.5 Hz), 92.07 (d, *J* = 44.2 Hz), 80.00, 73.71 (d, *J* = 299.8 Hz), 63.42 (d, *J* = 4.2 Hz), 54.28 (d, *J* = 5.6 Hz), 53.79 (d, *J* = 5.6 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 174.27, 167.25 (d, *J* = 259.4 Hz), 162.88 (d, *J* = 247.4 Hz), 134.72 (d, *J* = 3.4 Hz), 132.78 (d, *J* = 9.8 Hz), 128.58 (d, *J* = 8.4 Hz), 116.54 (d, *J* = 22.3 Hz), 115.73 (d, *J* = 21.9 Hz), 101.96, 92.07, 79.06, 73.70, 63.42, 54.28, 53.80; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -3.97; IR (film): n = 3316, 3075, 3006, 2957, 2203, 1507, 1458, 1224, 1186, 1028, 840, 793 cm $^{-1}$; HR-MS (EI): m/z = 258.04339, calcd. for $C_{11}H_{12}O_4FP$: 258.04518.

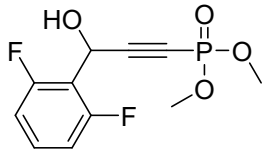
Dimethyl (3-(2-bromo-5-chlorophenyl)-3-hydroxyprop-1-yn-1-yl)phosphonate (3l):



Synthesised according to GP-**C**, using 2.0 mmol (500 mg) of 1-(2-bromo-5-chlorophenyl)prop-2-yn-1-ol, 2.4 mmol (0.2 mL) of dimethylphosphite and 0.3 mmol (41 mg) of Cu_2O, as beige solid (547 mg, 76%).

R_f= 0.27 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 2.6 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.19 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.78 (d, *J* = 3.5 Hz, 1H), 3.80 (dd, *J* = 12.4, 5.9 Hz, 6H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 2.6 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.19 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.78 (s, 1H), 3.80 (d, *J* = 5.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.67, 134.12, 130.27, 128.49, 119.90, 100.15 (d, *J* = 49.8 Hz), 73.59 (d, *J* = 298.3 Hz), 63.27, 53.93 (d, *J* = 5.4 Hz); ^{13}C{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 139.66, 134.12, 130.26, 128.49, 119.89, 100.15, 73.59, 63.29, 53.93; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -4.21; IR (film): n = 3313, 3097, 2956, 2853, 2197, 1456, 1430, 1254, 1184, 1063, 902, 847, 742, 671 cm $^{-1}$; HR-MS (EI): m/z = 351.92513, calcd. for $C_{11}H_{11}O_4PClBr$: 351.92614.

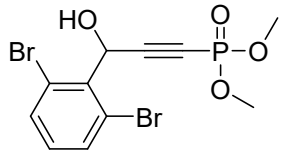
Dimethyl (3-(2,6-difluorophenyl)-3-hydroxyprop-1-yn-1-yl)phosphonate (3m):



Synthesised according to GP-**C**, using 3.0 mmol (500 mg) of 1-(2,6-difluorophenyl)prop-2-yn-1-ol, 4.2 mmol (0.4 mL) of dimethylphosphite and 0.4 mmol (60 mg) of Cu_2O, as orange oil (476 mg, 58%).

R_f= 0.21 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38-7.28 (m, 1H), 6.97-6.88 (m, 2H), 5.87 (dt, *J* = 3.9, 1.6 Hz, 1H), 3.78 (dd, *J* = 12.4, 6.1 Hz, 6H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 1H), 6.92 (t, *J* = 8.2 Hz, 2H), 5.87 (t, *J* = 1.6 Hz, 1H), 3.86 (s, 1H), 3.78 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.76 (dd, *J* = 251.7, 7.1 Hz), 131.10, 115.41, 112.07 (d, *J* = 25.5 Hz), 99.71 (d, *J* = 49.8 Hz), 72.88 (d, *J* = 297.6 Hz), 54.49 (q, *J* = 4.9 Hz), 53.77 (t, *J* = 6.3 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 160.75 (dd, *J* = 251.8, 7.0 Hz), 131.09, 115.40, 112.07 (d, *J* = 25.6 Hz), 99.70, 72.88, 54.49 (t, *J* = 5.2 Hz), 53.78 (d, *J* = 7.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = -4.09; IR (film): n = 3312, 2958, 2855, 2209, 1474, 1261, 1192, 1066, 999, 847, 791 cm $^{-1}$; HR-MS (EI): m/z = 276.03494, calcd. for $C_{11}H_{11}O_4F_2P$: 276.03575.

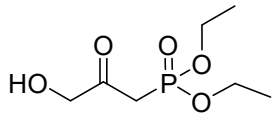
Dimethyl (3-(2,6-dibromophenyl)-3-hydroxyprop-1-yn-1-yl)phosphonate (3n):



Synthesised according to GP-**C**, using 1.7 mmol (500 mg) of 1-(2,6-dibromophenyl)prop-2-yn-1-ol, 2.4 mmol (0.2 mL) of dimethylphosphite and 0.2 mmol (35 mg) of Cu_2O, as yellow solid (446 mg, 65%).

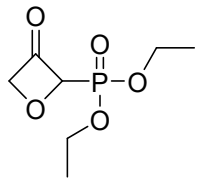
R_f = 0.36 (PE:EA-1:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 4.0 Hz, 1H), 3.79 (dd, *J* = 12.3, 2.9 Hz, 6H), 3.60 (s, 1H); $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.0 Hz, 2H), 7.07 (t, J = 8.0 Hz, 1H), 6.36 (s, 1H), 3.79 (d, J = 2.5 Hz, 6H), 3.74 - 3.64 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 135.92, 133.60, 131.43, 124.21, 98.00 (d, *J* = 48.8 Hz), 75.18 (d, *J* = 296.0 Hz), 65.29 (d, *J* = 4.2 Hz), 53.76 (d, *J* = 5.6 Hz); $^{13}C\{^{31}P\}$ (151 MHz, $CDCl_3$): δ = 135.90, 133.59, 131.42, 124.21, 98.01, 75.16, 65.29, 53.76); ^{31}P NMR (121 MHz, $CDCl_3$): δ = -3.94; IR (film): n = 3289, 3069, 2954, 2852, 2200, 1433, 1258, 1182, 1034, 842, 796, 697, 639 cm^{-1}; HR-MS (EI): m/z = 395.87604, calcd. for $C_{11}H_{11}O_4PBr_2$: 395.87562.

Diethyl (3-hydroxy-2-oxopropyl)phosphonate (hydration product 2aa):



^1H NMR (301 MHz, Chloroform-*d*) δ 4.32 (s, 2H), 4.14 (dd, *J* = 8.0, 6.7 Hz, 4H), 3.84 (d, *J* = 1.2 Hz, 1H), 3.18 (d, *J* = 22.9 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 6H).

Diethyl (3-oxooxetan-2-yl)phosphonate (2a):

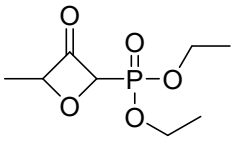


Synthesised according to the GP-**D**, using 0.3 mmol (60 mg) of **1a**, 0.6 mmol (102 mg) of the *N*-oxide **6** and 5 mol% of $CyJohnPhosAuNtF_2$, *as* a colorless oil. (35 mg, 54%).

R_f = 0.44 (PE:EA-1:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 5.78 (ddd, *J* = 7.3, 4.3, 1.0 Hz, 1H), 5.64-5.39 (m, 2H), 4.33-4.13 (m, 4H), 1.36 (td, *J* = 7.1, 2.8 Hz, 6H). $^1H\{^{31}P\}$ (300 MHz, $CDCl_3$): δ = 5.72 (dd, *J* = 4.3, 1.0 Hz, 1H), 5.58-5.36 (m, 2H), 4.24-4.11 (m, 4H), 1.31 (td, *J*

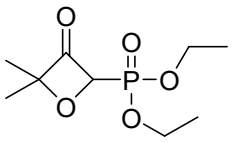
= 7.1, 2.8 Hz, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.31 (d, *J* = 5.8 Hz), 100.07, 98.03, 93.88 (d, *J* = 7.4 Hz), 66.15-62.54 (m), 16.53 (d, *J* = 5.6 Hz); ^{31}P NMR (122 MHz, $CDCl_3$): δ = 10.62; IR (film): n = 2988, 2934, 2916, 1829, 1395, 1197, 1166, 1021, 951, 793 cm $^{-1}$; HR-MS (EI): m/z = 209.05854, calcd. for $C_7H_{13}O_5P$ $[M^+ + H]$: 209.05971.

Diethyl (4-methyl-3-oxooxetan-2-yl)phosphonate (2b):



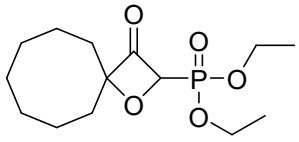
Synthesised according to the GP-**D**, using 0.3 mmol (60 mg) of **1b**, 0.6 mmol (95 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2, mixture obtained. See NMR below.

Diethyl (4,4-dimethyl-3-oxooxetan-2-yl)phosphonate (2c):



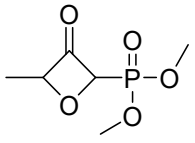
Synthesised according to the GP-**D**, using 0.3 mmol (60 mg) of **1c**, 0.6 mmol (89 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2, mixture obtained. See NMR below.

Diethyl (3-oxo-1-oxaspiro[3.7]undecan-2-yl)phosphonate (2d):



Synthesised according to the GP-**D**, using 0.3 mmol (60 mg) of **1d**, 0.6 mmol (68 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2, mixture obtained. See NMR below.

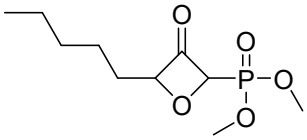
Dimethyl (4-methyl-3-oxooxetan-2-yl)phosphonate (4a):



Synthesised according to the GP-**D**, using 0.3 mmol (60 mg) of **3a**, 0.6 mmol (110 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2, as a colorless oil. (44 mg, 67%).

R_f = 0.52 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.87-5.64 (m, 2H), 3.87 (dd, *J* = 10.9, 2.6 Hz, 6H), 1.67-1.50 (m, 3H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 5.87-5.64 (m, 2H), 3.93-3.85 (m, 6H), 1.65-1.53 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.48 (dd, J = 36.4, 5.8 Hz), 102.87 - 101.54 (m), 94.82 (d, J = 155.0 Hz), 55.77 - 51.25 (m), 16.46 (d, J = 10.6 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 196.46 (d, J = 36.7 Hz), 102.37 (d, J = 53.6 Hz), 94.82, 57.01-50.90 (m), 16.47 (d, J = 11.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): (dr = 1.09:1) δ = 13.96, 13.08; IR (film): n = 2964, 2935, 2859, 1824, 1451, 1221, 1026, 975, 828, 782 cm $^{-1}$; HR-MS (EI): m/z = 195.04268, calcd. for $C_6H_{12}O_5P$ [M^++H]: 195.04169.

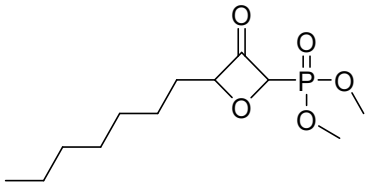
Dimethyl (3-oxo-4-pentyloxetan-2-yl)phosphonate (4b):



Synthesised according to the GP-**D**, using 0.2 mmol (60 mg) of **3a**, 0.5 mmol (84 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2 as a pale-yellow oil. (34 mg, 53%)

R_f = 0.51 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.73-5.47 (m, 2H), 3.84 (ddd, *J* = 11.0, 2.8, 1.7 Hz, 6H), 2.12 - 1.76 (m, 2H), 1.53 - 1.22 (m, 6H), 0.87 (m, 3H); ^{1}H{^{31}P} (300 MHz, $CDCl_3$): δ = 5.73 - 5.51 (m, 2H), 3.88 - 3.82 (m, 6H), 2.10 - 1.78 (m, 2H), 1.57 - 1.24 (m, 6H), 0.89 - 0.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.43, 106.07, 95.72, 93.68, 53.98, 31.45, 23.78, 22.44, 13.97; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.01, 13.08; IR (film): n = 3427, 2959, 2855, 2192, 1819, 1453, 1353, 1228, 1189, 1033, 845, 617 cm $^{-1}$; HR-MS (EI): m/z = 250.09732, calcd. for $C_{10}H_{19}O_5P$: 250.09646.

Dimethyl (4-heptyl-3-oxooxetan-2-yl)phosphonate (4c):

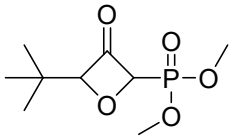


Synthesised according to the GP-**D**, using 0.2 mmol (60 mg) of **3a**, 0.5 mmol (75 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2 as a pale-yellow oil. (29 mg, 46%)

R_f= 0.51 (PE:EA-1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.79-5.43 (m, 2H), 3.96-3.80 (m, 6H), 2.09-1.76 (m, 2H), 1.51-1.27 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 5H); ^{13}C NMR (76 MHz, $CDCl_3$): δ = 196.46, 106.05 (d, *J* = 6.3 Hz), 94.72 (d, *J* = 154.8 Hz), 53.96 (d, *J* = 4.1 Hz), 31.75, 29.07,

24.46, 22.69, 14.15; $^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$): δ = 196.56 (d, *J* = 2.5 Hz), 106.08, 94.70, 54.04 (d, *J* = 6.9 Hz), 31.78, 31.05 (d, *J* = 12.8 Hz), 29.83, 29.10, 22.72, 14.19; ^{31}P NMR (243 MHz, $CDCl_3$): δ = 14.62, 14.31, 13.38; IR (film): n = 2958, 2930, 2858, 1799, 1462, 1250, 1046, 847, 791 cm^{-1}; HR-MS (EI): m/z = 277.11837 (100 %), calcd. for $C_{12}H_{23}O_5P$ $[M^+-H]$: 277.11994.

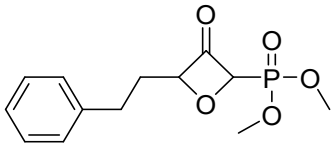
Dimethyl (4-(tert-butyl)-3-oxooxetan-2-yl)phosphonate (4d):



Synthesised according to the GP-**D**, using 0.2 mmol (60 mg) of **3a**, 0.5 mmol (89 mg) of the *N*-oxide **6** and 5 mol% of $CyJohnPhosAuNtF_2$ as a pale-yellow oil. (25 mg, 39%)

R_f = 0.59 (PE:EA-1:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 5.66 (dd, *J* = 9.1, 2.1 Hz, 0.4H), 5.50 (dd, *J* = 7.3, 4.4 Hz, 1H), 5.31 (dd, *J* = 4.5, 3.0 Hz, 1H), 5.27 (dd, *J* = 7.5, 2.0 Hz, 0.4H), 3.87 (dd, *J* = 11.0, 2.4 Hz, 6H), 1.02 (s, 9H); $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ = 5.66 (d, *J* = 2.0 Hz, 0.4H), 5.50 (d, *J* = 4.4 Hz, 1H), 5.31 (d, *J* = 4.4 Hz, 1H), 5.27 (d, *J* = 2.0 Hz, 0.4H), 3.87 (d, *J* = 2.4 Hz, 6H), 1.02 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.16 (d, *J* = 4.9 Hz), 113.18 (d, *J* = 6.9 Hz), 94.53 (d, *J* = 154.7 Hz), 54.12 - 54.01 (m), 34.95 (d, *J* = 3.4 Hz), 24.66; $^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$): δ = 196.15, 113.17, 94.53, 54.10 (d, *J* = 2.7 Hz), 34.96, 24.67; ^{31}P NMR (121 MHz, $CDCl_3$): (dr = 1.09:1) δ = 13.96, 13.08; IR (film): n = 2964, 2935, 2859, 1824, 1451, 1221, 1026, 975, 828, 782 cm^{-1}; HR-MS (EI): m/z = 236.07915, calcd. for $C_9H_{17}O_5P$: 236.08081.

Dimethyl (3-oxo-4-phenethyloxetan-2-yl)phosphonate (4e):

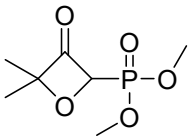


Synthesised according to the GP-**D**, using 0.2 mmol (60 mg) of **3a**, 0.5 mmol (73 mg) of the *N*-oxide **6** and 5 mol% of $CyJohnPhosAuNtF_2$ as a pale-yellow oil (56 mg, 88%).

R_f = 0.6 (PE:EA-1:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30 (ddt, *J* = 7.2, 6.1, 1.2 Hz, 2H), 7.24-7.18 (m, 3H), 5.78-5.65 (m, 1H), 5.54 (dddd, *J* = 8.9, 7.2, 5.8, 1.2 Hz, 1H), 3.88 (dd, *J* = 11.0, 1.6 Hz, 6H), 2.81 (td, *J* = 8.0, 7.0, 5.1 Hz, 2H), 2.46-2.10 (m, 2H); $^1H\{^{31}P\}$ (300 MHz,

$CDCl_3$): δ = 7.30 (ddt, *J* = 7.1, 6.0, 1.2 Hz, 2H), 7.20 (ddd, *J* = 7.9, 2.5, 1.4 Hz, 3H), 5.75-5.66 (d, 1.6H), 5.54 (ddd, *J* = 9.1, 5.8, 1.2 Hz, 0.4H), 3.89 - 3.87 (m, 6H), 2.81 (td, *J* = 8.0, 7.0, 5.1 Hz, 2H), 2.48-2.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.15 (d, *J* = 15.5 Hz), 140.08, 128.70, 126.51, 104.79, 94.83 (dd, *J* = 154.6, 17.2 Hz), 56.47-51.83 (m), 32.62 (d, *J* = 1.7 Hz), 32.32, 30.23 (d, *J* = 13.9 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 196.25 (d, J = 33.2 Hz), 140.08, 128.67 (d, J = 13.8 Hz), 126.50 (d, J = 11.0 Hz), 104.86, 94.94, 54.07, 32.50 (d, J = 45.0 Hz), 30.25 (d, J = 27.3 Hz), 22.80, 14.24; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 13.81, 13.02; dr = 1.1:1 IR (film): n = 3062, 3028, 2931, 2858, 11823, 1731, 1354, 1255, 1199, 1059, 843, 753, 702 cm $^{-1}$; HR-MS (EI): m/z = 284.08004, calcd. for $C_{13}H_{17}O_5P$: 284.08081.

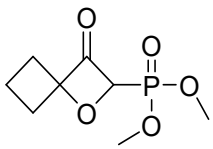
Dimethyl (4,4-dimethyl-3-oxooxetan-2-yl)phosphonate (4f):



Synthesised according to the GP-**D**, using 0.3 mmol (60 mg) of **3a**, 0.6 mmol (102 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF$_2$ as a colorless oil (53 mg, 82%).

R_f = 0.53 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.66 (d, *J* = 8.4 Hz, 1H), 3.84 (dd, *J* = 11.0, 0.6 Hz, 6H), 1.60 (s, 3H), 1.52 (s, 3H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 5.66 (s, 1H), 3.84 (s, 4H), 1.60 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 199.30 (d, J = 5.7 Hz), 109.73 (d, J = 8.1 Hz), 91.56 (d, J = 156.0 Hz), 53.93 (dd, J = 21.5, 6.4 Hz), 29.83, 22.94 (d, J = 35.2 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 199.28, 109.73, 91.55, 53.93 (d, J = 21.4 Hz), 29.84, 22.72; ^{31}P NMR (121 MHz, $CDCl_3$): (dr = 1.09:1) δ = 13.96, 13.08; IR (film): n = 2964, 2935, 2859, 1824, 1451, 1221, 1026, 975, 828, 782 cm $^{-1}$; HR-MS (EI): m/z = 195.04268 calcd. for $C_6H_{12}O_5P$ [M^++H]: 195.04169.

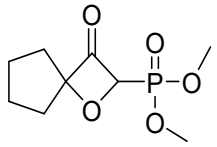
Dimethyl (3-oxo-1-oxaspiro[3.3]heptan-2-yl)phosphonate (4g):



Synthesised according to the GP-**D**, using 0.3 mmol (60 mg) of **3a**, 0.6 mmol (96 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF$_2$ as a colorless oil. (27 mg, 42%)

R_f = 0.59 (PE:EA-1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.58 (d, *J* = 6.1 Hz, 1H), 3.85 (dd, *J* = 11.0, 9.9 Hz, 6H), 2.70-2.57 (m, 2H), 2.57-2.42 (m, 2H), 1.82-1.65 (m, 2H); ^{1}H{^{31}P} (300 MHz, $CDCl_3$): δ = 5.58 (s, 1H), 3.85 (d, *J* = 4.8 Hz, 6H), 2.73 - 2.38 (m, 4H), 1.86 - 1.68 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 198.15 (d, *J* = 5.5 Hz), 108.60 (d, *J* = 6.9 Hz), 92.65 (d, *J* = 154.9 Hz), 54.03 (dd, *J* = 27.2, 6.7 Hz), 34.14, 33.44, 11.87; ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 198.14, 108.59, 92.65, 54.03 (d, *J* = 27.4 Hz), 34.14, 33.45, 11.88; ^{31}P NMR (151 MHz, $CDCl_3$): δ = 14.05; IR (film): n = 3461, 2959, 2933, 2861, 1798, 1731, 1460, 1355, 1191, 1041, 848, 788 cm $^{-1}$; HR-MS (EI): m/z = 221.05648, calcd. for $C_8H_{14}O_5P$ [M^++H]: 221.05734.

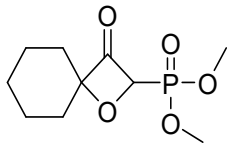
Dimethyl (3-oxo-1-oxaspiro[3.4]octan-2-yl)phosphonate (4h):



Synthesised according to the GP-**D**, using 0.2 mmol (60 mg) of **3a**, 0.5 mmol (90 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2 as a colorless oil. (36 mg, 56%).

R_f = 0.58 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.58 (d, J = 7.2 Hz, 1H), 3.85 (dd, J = 10.9, 3.1 Hz, 6H), 2.35-2.08 (m, 4H), 1.84-1.48 (m, 4H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 5.58 (s, 1H), 3.85 (d, J = 3.1 Hz, 6H), 2.33-2.07 (m, 4H), 1.88 - 1.56 (m, 4H); ^{13}C NMR (151MHz, $CDCl_3$): δ = 200.66 (d, J = 5.7 Hz), 118.54 (d, J = 7.5 Hz), 91.82 (d, J = 155.5 Hz), 54.34 - 53.51 (m), 36.73, 36.41, 24.92 (d, J = 2.9 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 200.63, 118.53, 91.81, 53.97 (d, J = 3.8 Hz), 36.73, 36.41, 24.92 (d, J = 3.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.12; IR (film): n = 2961, 2902, 2856, 2206, 1829, 1744, 1455, 1353, 1136, 1036, 827, 759 cm $^{-1}$; HR-MS (EI): m/z = 235.09822, calcd. for $C_9H_{15}O_5P$ [M^++H]: 235.09649.

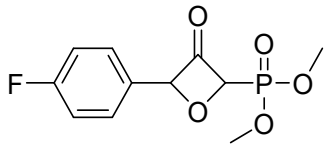
Dimethyl (3-oxo-1-oxaspiro[3.5]nonan-2-yl)phosphonate (4i):



Synthesised according to the GP-**D**, using 0.2 mmol (60 mg) of **3a**, 0.5 mmol (84 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2 as a pale-yellow oil. (33 mg, 52%)

R_f = 0.56 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.61 (d, J = 8.3 Hz, 1H), 3.87 (d, J = 10.9 Hz, 6H), 2.48-1.32 (m, 10H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 5.61 (s, 1H), 3.86 (s, 6H), 2.40-1.43 (m, 10H); ^{13}C NMR (MHz, $CDCl_3$): δ = 199.40, 111.80 (d, J = 7.8 Hz), 90.53 (d, J = 155.8 Hz), 56.28 - 52.13 (m), 32.63 (d, J = 2.4 Hz), 31.89, 24.72, 22.12 (d, J = 4.6 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 199.49, 111.80, 90.64, 53.88, 32.08, 29.85, 29.52, 22.85, 14.28; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.16; IR (film): n = 2928, 2851, 1738, 1463, 1371, 1240, 1154, 1038, 991, 719 cm $^{-1}$; HR-MS (EI): m/z = 249.08874, calcd. for $C_{10}H_{17}O_5P$ [M^++H]: 249.08864.

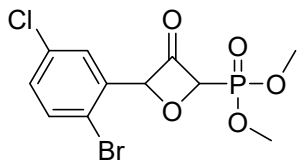
Dimethyl (4-(4-fluorophenyl)-3-oxooxetan-2-yl)phosphonate (4k):



Synthesised according to the GP-**D**, using 0.2 mmol (60 mg) of **3a**, 0.5 mmol (76 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2 as a yellow oil. (45 mg, 70%)

R_f = 0.48 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (ddd, *J* = 9.0, 5.3, 0.6 Hz, 1H), 7.34 (ddd, *J* = 8.9, 5.2, 0.7 Hz, 2H), 7.10 (t, *J* = 8.7 Hz, 3H), 6.57 (t, *J* = 4.0 Hz, 1H), 6.49 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.93 (dd, *J* = 8.3, 1.7 Hz, 1H), 5.84 (dd, *J* = 7.4, 4.4 Hz, 1H), 3.92 (dd, *J* = 11.0, 1.1 Hz, 6H), 3.81 (dd, *J* = 11.1, 0.8 Hz, 4H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 7.56 - 7.49 (m, 2H), 7.34 (dddd, *J* = 8.2, 5.3, 2.6, 1.5 Hz, 2H), 7.10 (t, *J* = 8.7 Hz, 3H), 6.57 (dd, *J* = 4.5, 0.8 Hz, 1H), 6.48 (dd, *J* = 1.7, 0.8 Hz, 1H), 5.93 (d, *J* = 1.7 Hz, 1H), 5.84 (d, *J* = 4.4 Hz, 1H), 3.92 (d, *J* = 1.1 Hz, 6H), 3.81 (d, *J* = 0.8 Hz, 5H); ^{31}P NMR (121 MHz, $CDCl_3$): (dr = 1.3:1) δ = 13.62, 12.25.; IR (film): n = 2960, 2923, 2855, 1823, 1604, 1509, 1451, 1185, 1026, 959, 822, 776 cm $^{-1}$; HR-MS (EI): m/z = 275.04784, calcd. for $C_{11}H_{12}O_5FP$ [M^++H]: 275.04791.

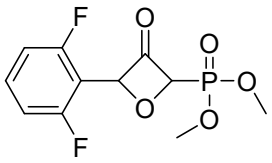
Dimethyl (4-(2-bromo-5-chlorophenyl)-3-oxooxetan-2-yl)phosphonate (4l):



Synthesised according to the GP-**D**, using 0.2 mmol (60 mg) of **3a**, 0.3 mmol (55 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF_2 as a yellow oil. (40 mg, 63%)

R_f = 0.47 (PE:EA-1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, J = 2.6 Hz, 1H), 7.58-7.48 (m, 2H), 7.22 (dd, J = 8.5, 2.6 Hz, 2H), 6.91-6.86 (m, 1H), 5.98 (dd, J = 7.9, 1.6 Hz, 1H), 5.88 (dd, J = 7.5, 4.3 Hz, 1H), 3.95 (d, J = 10.9 Hz, 6H), 3.86 (dd, J = 11.1, 8.0 Hz, 5H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, J = 2.7 Hz, 1H), 7.60-7.46 (m, 2H), 7.22 (dd, J = 8.5, 2.6 Hz, 2H), 6.92 - 6.84 (m, 1H), 5.98 (d, J = 1.6 Hz, 1H), 5.88 (d, J = 4.4 Hz, 1H), 3.95 (s, 6H), 3.86 (d, J = 7.9 Hz, 5H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 190.39 (d, J = 7.7 Hz), 190.11 (d, J = 4.2 Hz), 134.51, 134.33, 134.09, 134.03, 130.72 (d, J = 16.7 Hz), 128.80, 127.62, 118.70, 104.48 (d, J = 6.3 Hz), 104.22 (d, J = 10.4 Hz), 96.60 (d, J = 155.4 Hz), 96.29, 95.26, 54.36 (dd, J = 13.1, 6.4 Hz), 53.98 (dd, J = 13.5, 6.6 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 190.38, 190.10, 134.51, 134.28, 134.10, 134.03, 130.77, 130.66, 128.79, 127.62, 118.69, 104.48, 104.22, 96.60, 95.78, 54.37 (d, J = 12.8 Hz), 53.99 (d, J = 13.2 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): (dr = 1.2:1) δ = 13.22, 11.92; IR (film): n = 2961, 2902,2856, 1829, 1744, 1455, 1353, 1136, 1036, 827, 759 cm $^{-1}$; HR-MS (EI): m/z = 368.92961, calcd. for $C_{11}H_{11}BrClO_5P$ [M^++H]: 368.92888.

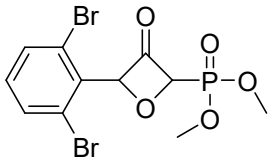
Dimethyl (4-(2,6-difluorophenyl)-3-oxooxetan-2-yl)phosphonate (4m):



Synthesised according to the GP-**D**, using 0.2 mmol (60 mg) of **3a**, 0.4 mmol (71 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF$_2$ as a yellow oil. (42 mg, 66%)

R_f = 0.47 (PE:EA-1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (m, J = 8.4, 6.5 Hz, 1H), 6.95 (dd, J = 9.8, 6.6 Hz, 2H), 6.82 (t, J = 4.1 Hz, 1H), 5.98 (dd, J = 6.6, 4.3 Hz, 1H), 3.92 (dd, J = 11.0, 1.2 Hz, 6H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = δ 7.41 (m, *J* = 8.5, 6.5 Hz, 1H), 7.10 - 6.88 (m, 2H), 6.82 (d, *J* = 4.3 Hz, 1H), 6.01 - 5.88 (m, 1H), 3.92 (d, *J* = 0.5 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 192.74 (d, *J* = 3.8 Hz), 162.44 (d, *J* = 6.8 Hz), 160.77 (d, *J* = 6.9 Hz), 133.14, 111.99 (dd, *J* = 21.4, 4.0 Hz), 110.60 (t, *J* = 17.7 Hz), 96.11 (d, *J* = 154.9 Hz), 94.96 (d, *J* = 6.2 Hz), 54.25 (dd, *J* = 21.2, 6.6 Hz); ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 192.72, 162.43 (d, *J* = 6.9 Hz), 160.75 (d, *J* = 6.9 Hz), 133.13, 111.98 (dd, *J* = 21.4, 4.1 Hz), 110.59 (t, *J* = 17.7 Hz), 96.10, 94.96, 54.25 (d, *J* = 21.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): (dr = 10:1) δ = 13.83, 11.10; IR (film): n = 3070, 2962, 2858, 1832, 1628, 1592, 1474, 1267, 1191, 1056, 940, 830 cm $^{-1}$; HR-MS (EI): m/z = 293.03750 (11.9 %), calcd. for $C_{11}H_{11}O_5F_2P$ [M^++H]: 293.03849.

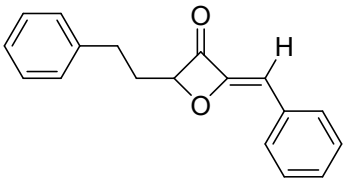
Dimethyl (4-(2,6-dibromophenyl)-3-oxooxetan-2-yl)phosphonate (4n):



Synthesised according to the GP-**D**, using 0.15 mmol (60 mg) of **3a**, 0.3 mmol (49 mg) of the *N*-oxide **6** and 5 mol% of CyJohnPhosAuNtF$_2$ as a yellow oil. (36 mg, 58%)

R_f= 0.49 (PE:EA-1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.1 Hz, 2H), 7.29 (t, J = 4.7 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H), 6.06 (dd, J = 6.5, 4.5 Hz, 1H), 3.94 (dd, J = 10.9, 6.8 Hz, 6H); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 4.5 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H), 6.06 (d, J = 4.4 Hz, 1H), 3.94 (d, J = 3.4 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 192.10, 133.29, 132.96, 126.75, 104.92 (d, *J* = 4.2 Hz), 96.41 (d, *J* = 154.5 Hz), 54.30; ^{13}C{^{31}P} NMR (151 MHz, $CDCl_3$): δ = 192.08, 133.29, 132.96, 131.65, 126.75, 104.92, 96.41, 54.30 (d, *J* = 6.4 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.60; IR (film): n = 3079, 2959, 2923, 2855, 1825, 1571, 1522, 1433, 1261, 1031, 940, 829, 780, 717 cm $^{-1}$; HR-MS (EI): m/z = 412.87723, calcd. for $C_{11}H_{11}O_5PBr_2$ [M^++H]: 412.87836.

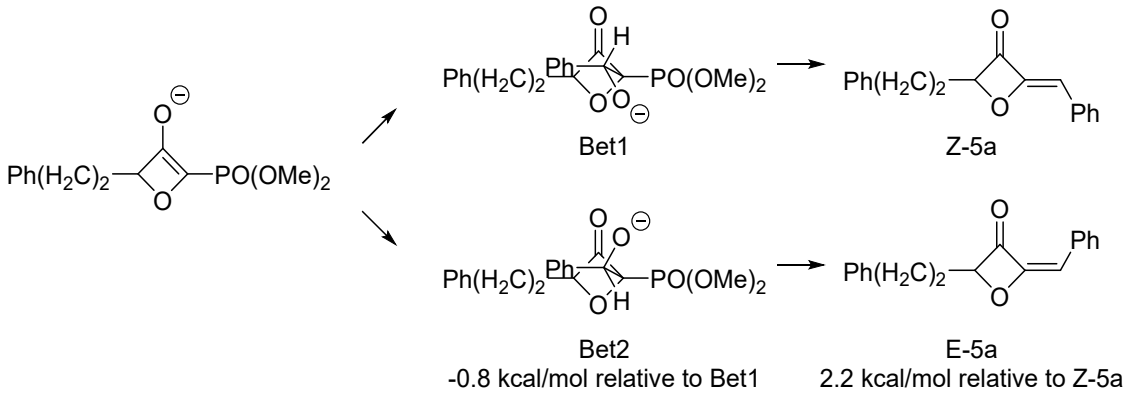
2-Benzylidene-4-phenethyloxetan-3-one (5a)



Synthesised according to the GP-**E**, as a colorless oil. (26 mg, 95%)

R_f= 0.62 (PE:EA-10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 - 7.64 (m, 2H), 7.51 - 7.42 (m, 7H), 6.03 (s, 0.2H), 5.99 (s, 0.8), 5.67 - 5.49 (m, 0.4H), 5.32 (dd, *J* = 7.4, 6.0 Hz, 1H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.32 - 2.14 (m, 2H), E/Z = 1:5;^{13}C NMR (101 MHz, $CDCl_3$): δ = 189.48, 161.85, 140.27, 133.06, 130.06, 128.90, 128.77, 128.67, 128.62, 128.41, 126.55, 110.53, 97.32, 32.18, 30.41; IR (film): n = 3064, 3029, 2929, 2872, 1687, 1454, 1290, 1177, 1071, 933, 748, 704 cm $^{-1}$; HR-MS (EI): m/z = 264.11173, calcd. for $C_{18}H_{16}O_2$: 264.11448.

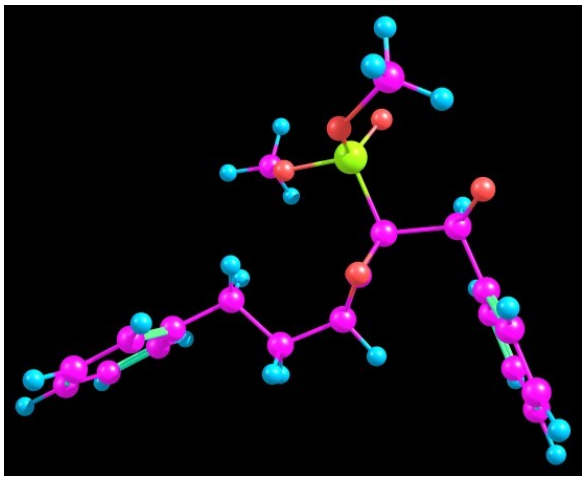
3. Quantum chemical Calculations



We used the orca 4.2.1 program package[14] to calculate the relative energy and geometry of the intermediate betaines Bet1 and Bet2 and their reaction products Z-5a and E-5a. We employed the wB97X-D3[15] functional in combination with the RIJCOSX Approximation and the def2-TZVP[16] basis set to optimize the geometries and calculate relative energies.

Geometrys:

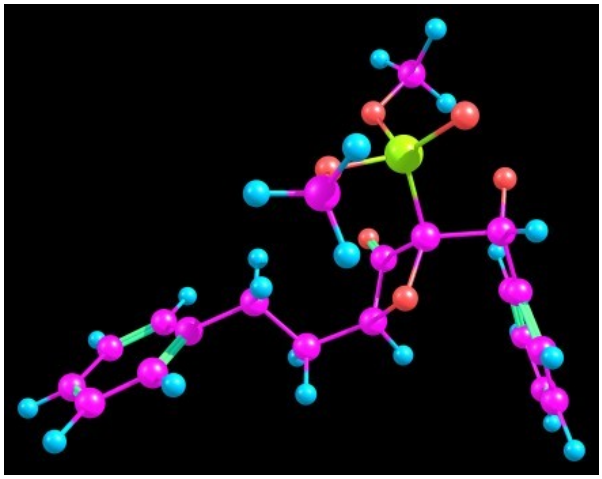
Bet1: -1568.38338629384 E_h



C	5.215498	-1.970143	-3.125996
C	4.164459	-1.442615	-4.085379
O	4.509980	-0.101633	-3.664102
C	5.358316	-0.563404	-2.580290
H	3.164364	-1.701824	-3.717024
C	4.245698	-1.712041	-5.570176
H	3.499286	-1.082943	-6.064425
H	3.929303	-2.748154	-5.725269
C	5.618187	-1.484572	-6.202320
H	5.941003	-0.460939	-6.008579
H	6.349200	-2.143768	-5.727837
C	5.597507	-1.747162	-7.684527
C	5.287881	-0.730337	-8.584828
C	5.853184	-3.021233	-8.186325
C	5.233584	-0.978471	-9.949479
C	5.800777	-3.274940	-9.550037
C	5.489873	-2.253076	-10.437231
H	5.091080	0.269169	-8.210534

H	6.100547	-3.823575	-7.498410
H	4.994269	-0.172782	-10.634144
H	6.006780	-4.272582	-9.920762
H	5.451455	-2.447794	-11.502642
O	5.714965	-3.036288	-2.905663
C	4.755163	-0.302034	-1.143349
H	5.426181	-0.913483	-0.495716
C	3.375421	-0.962364	-1.055815
C	2.240599	-0.228262	-1.383689
C	3.220808	-2.287456	-0.660442
C	0.981891	-0.810309	-1.343239
C	1.962652	-2.875729	-0.612808
C	0.838349	-2.139494	-0.960662
H	2.372147	0.809044	-1.666136
H	4.096633	-2.866914	-0.384533
H	0.107004	-0.226450	-1.608070
H	1.860204	-3.908432	-0.298251
H	-0.144995	-2.594503	-0.924271
O	4.758020	1.007875	-0.877350
P	7.028742	0.190414	-2.656753
O	7.666953	-0.379746	-3.999129
C	8.598268	-1.465920	-3.972702
H	9.441405	-1.228879	-3.324950
H	8.117875	-2.382212	-3.627276
H	8.943806	-1.598059	-4.995743
O	6.855396	1.684353	-3.117779
C	6.816828	2.776834	-2.180696
H	6.099845	2.541411	-1.394879
H	7.815178	2.938842	-1.773650
H	6.504449	3.649064	-2.750667
O	7.842723	-0.064616	-1.457822

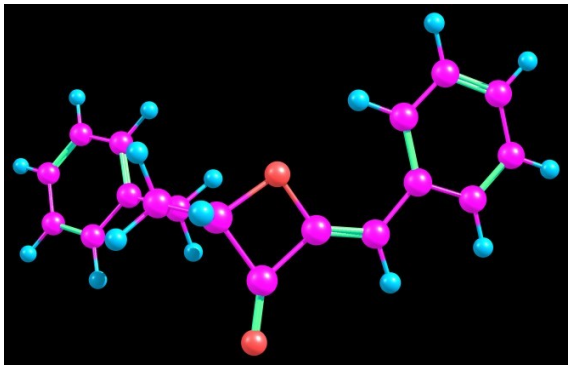
Bet2: -1568.38462376265 E_h



C	5.222677	-1.977310	-3.264196
C	4.118116	-1.304662	-4.061806
O	4.518783	-0.039411	-3.480087
C	5.437370	-0.664574	-2.540787
H	3.137642	-1.600553	-3.670051
C	4.108033	-1.381606	-5.570793
H	3.321536	-0.719027	-5.944026
H	3.801995	-2.400758	-5.827826
C	5.434141	-1.049162	-6.253682
H	5.713639	-0.024555	-6.011988
H	6.224841	-1.693613	-5.861097
C	5.343892	-1.211505	-7.747738
C	4.928602	-0.154512	-8.554386
C	5.636394	-2.431457	-8.352860
C	4.806965	-0.310563	-9.928299
C	5.517635	-2.592891	-9.726401
C	5.101003	-1.532029	-10.519560
H	4.700962	0.804330	-8.099369

H	5.965344	-3.263953	-7.739099
H	4.485138	0.525232	-10.539078
H	5.754106	-3.549283	-10.178615
H	5.010050	-1.655177	-11.592429
O	5.697083	-3.074194	-3.245603
C	4.977503	-0.703521	-1.035044
H	4.868551	0.376679	-0.784786
C	3.568658	-1.290124	-0.926917
C	2.436492	-0.510915	-1.148574
C	3.402394	-2.632237	-0.605696
C	1.165586	-1.065051	-1.073074
C	2.134479	-3.192695	-0.527571
C	1.010645	-2.411182	-0.765302
H	2.555063	0.541168	-1.386659
H	4.292411	-3.220662	-0.415755
H	0.293581	-0.444665	-1.248760
H	2.021084	-4.242022	-0.277899
H	0.019458	-2.845761	-0.702164
O	5.927341	-1.349261	-0.349186
P	7.117756	0.083873	-2.566312
O	8.177843	-1.079902	-2.569519
C	8.731358	-1.641850	-1.368893
H	9.286837	-0.875207	-0.827555
H	7.922539	-2.027204	-0.751420
H	9.408451	-2.429146	-1.692577
O	7.322358	0.535942	-4.079392
C	6.914290	1.839421	-4.502975
H	5.826758	1.920861	-4.490725
H	7.349676	2.602495	-3.858141
H	7.282477	1.964967	-5.519362
O	7.312043	1.180679	-1.603660

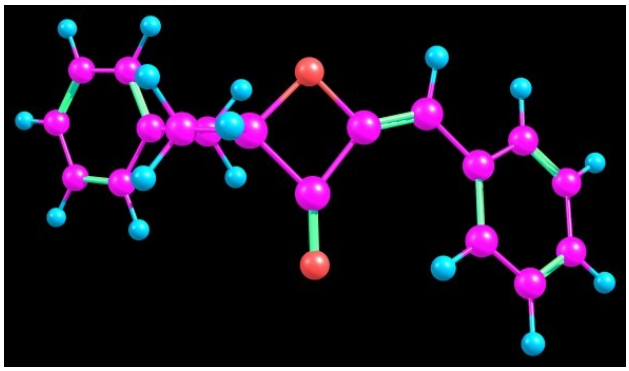
Z-5a: -846.036828268486 E_h



C	-1.428545	-1.766590	-1.516474
C	-0.688475	-2.720392	-0.584792
O	-1.543476	-2.232205	0.495806
C	-2.257593	-1.384503	-0.336569
H	0.348607	-2.426687	-0.409932
C	-0.819098	-4.203558	-0.844624
H	-0.362873	-4.740433	-0.008498
H	-0.217924	-4.431016	-1.730056
C	-2.260893	-4.679520	-1.045659
H	-2.853187	-4.414837	-0.167161
H	-2.706300	-4.164691	-1.901943
C	-2.323460	-6.167536	-1.269724
C	-2.412490	-7.044270	-0.191517
C	-2.251399	-6.699010	-2.554531
C	-2.426400	-8.417754	-0.390021
C	-2.265821	-8.072063	-2.758380
C	-2.352470	-8.936532	-1.675548
H	-2.475571	-6.645213	0.815784
H	-2.186402	-6.029057	-3.405922
H	-2.499247	-9.084479	0.461454
H	-2.211554	-8.467323	-3.766198
H	-2.366334	-10.008637	-1.832491
O	-1.353218	-1.487516	-2.677354

C	-3.317541	-0.657616	0.012008
H	-3.636259	-0.755850	1.046281
C	-4.116404	0.230723	-0.831750
C	-3.729052	0.626320	-2.115608
C	-5.327494	0.708458	-0.322973
C	-4.537078	1.463928	-2.865722
C	-6.135739	1.543968	-1.077193
C	-5.742888	1.926029	-2.352373
H	-2.793036	0.276360	-2.531141
H	-5.638099	0.414447	0.673673
H	-4.220342	1.761043	-3.858481
H	-7.072993	1.899159	-0.665567
H	-6.370600	2.582628	-2.942904

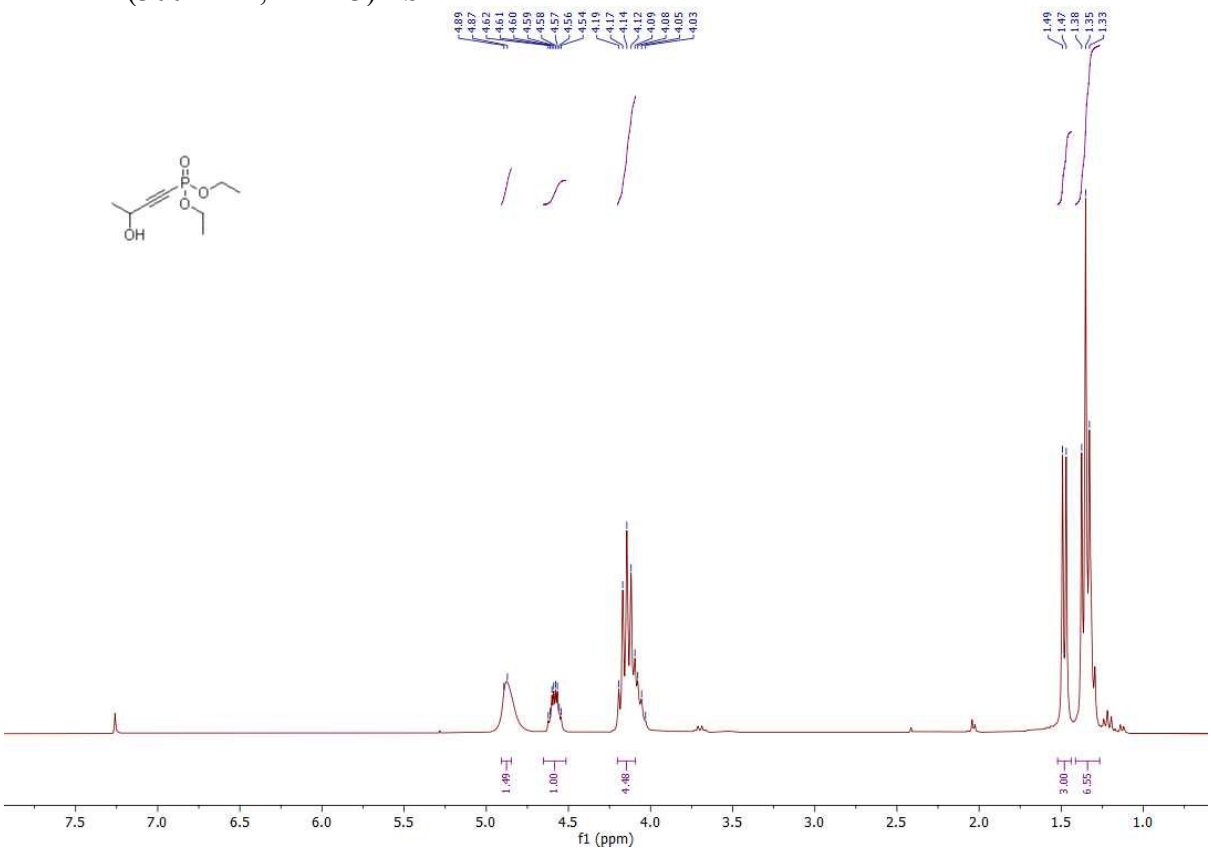
E-5a -846.033395849972 E_h



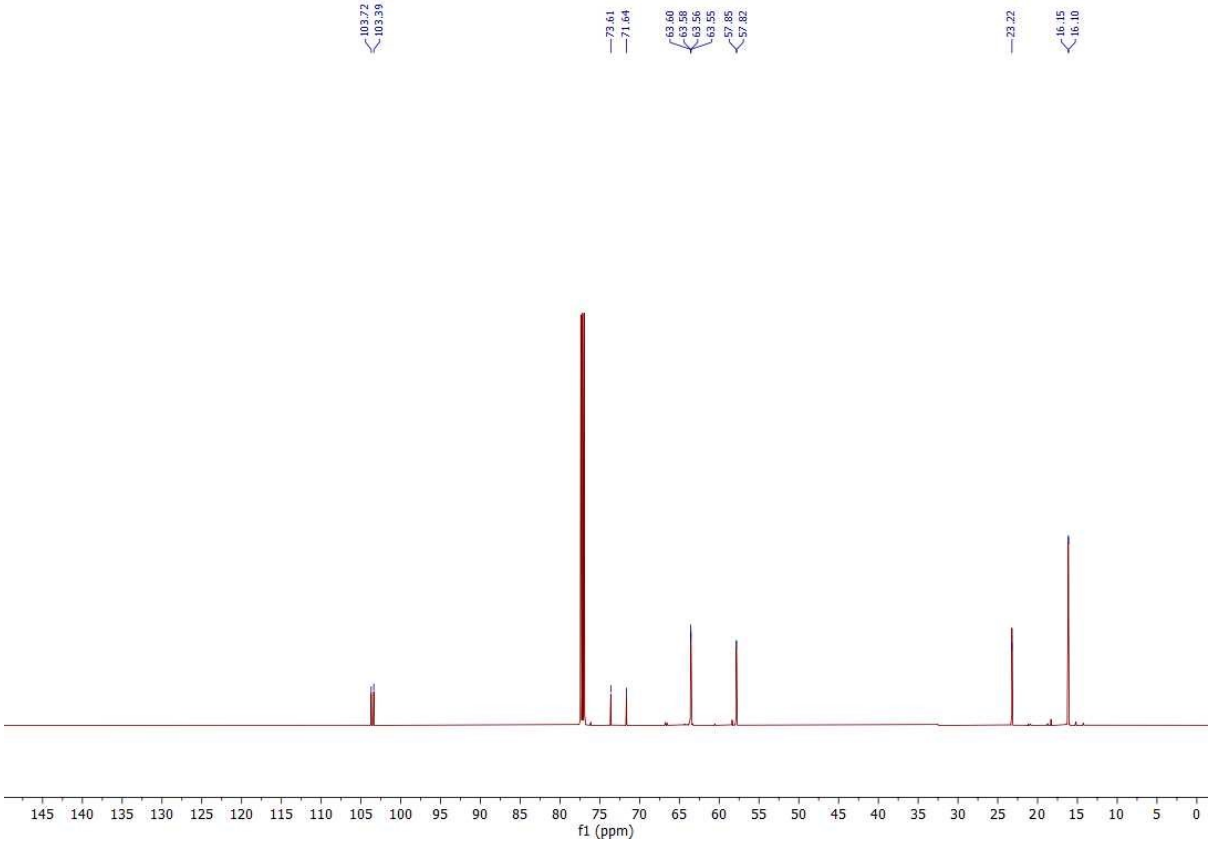
C	-1.658459	-1.780271	-1.428416
C	-0.844706	-2.728115	-0.544773
O	-1.694646	-2.300050	0.574923
C	-2.430338	-1.436697	-0.210918
H	0.178878	-2.383828	-0.384289
C	-0.902483	-4.209530	-0.828764
H	-0.431017	-4.737474	0.004850
H	-0.277355	-4.391753	-1.708046
C	-2.314501	-4.754660	-1.061955
H	-2.935466	-4.535845	-0.190416
H	-2.769653	-4.249593	-1.918870
C	-2.292004	-6.240476	-1.309703
C	-2.414325	-7.139625	-0.253738
C	-2.100834	-6.744173	-2.593314
C	-2.339240	-8.508383	-0.472058
C	-2.025577	-8.111926	-2.816956
C	-2.142289	-8.999249	-1.755319
H	-2.570976	-6.762414	0.751724
H	-2.009719	-6.056364	-3.428021
H	-2.438102	-9.193133	0.362340
H	-1.877870	-8.486049	-3.823540
H	-2.084223	-10.067500	-1.927921
O	-1.661428	-1.473761	-2.584314
C	-3.442464	-0.621708	0.075373
H	-3.814460	-0.059685	-0.775146
C	-4.090874	-0.388373	1.362804
C	-3.734013	-1.072989	2.530278
C	-5.109655	0.566981	1.431284
C	-4.377912	-0.797882	3.726289
C	-5.750295	0.839513	2.628243
C	-5.384288	0.158003	3.781663
H	-2.952727	-1.821251	2.502103
H	-5.396583	1.099977	0.531416
H	-4.091534	-1.334614	4.622956
H	-6.536043	1.584916	2.661410
H	-5.883099	0.369233	4.720031

4. ^{1}H, ^{13}C, ^{31}P, $^{1}H\{^{31}P\}$ and $^{13}C\{^{31}P\}$ NMR Spectra

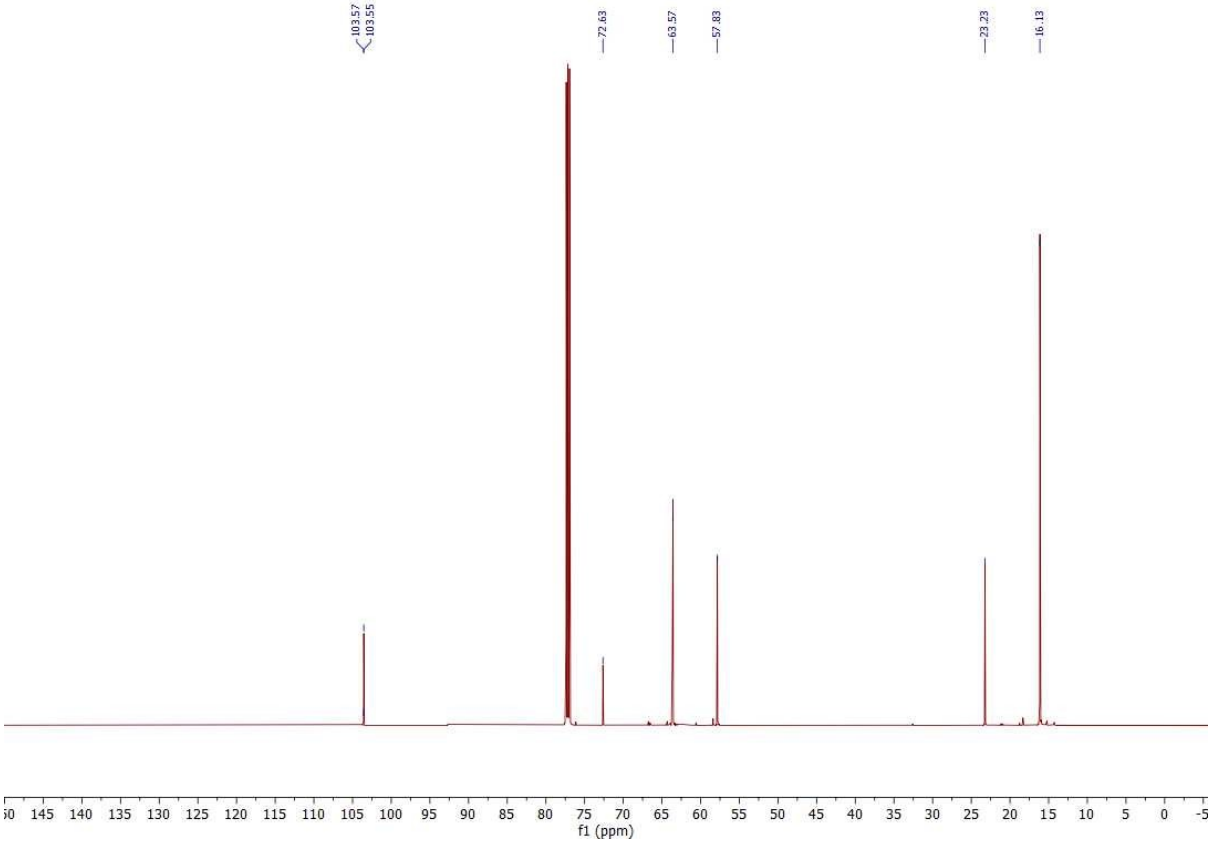
^{1}H NMR (300 MHz, CDCl3)-**1b**



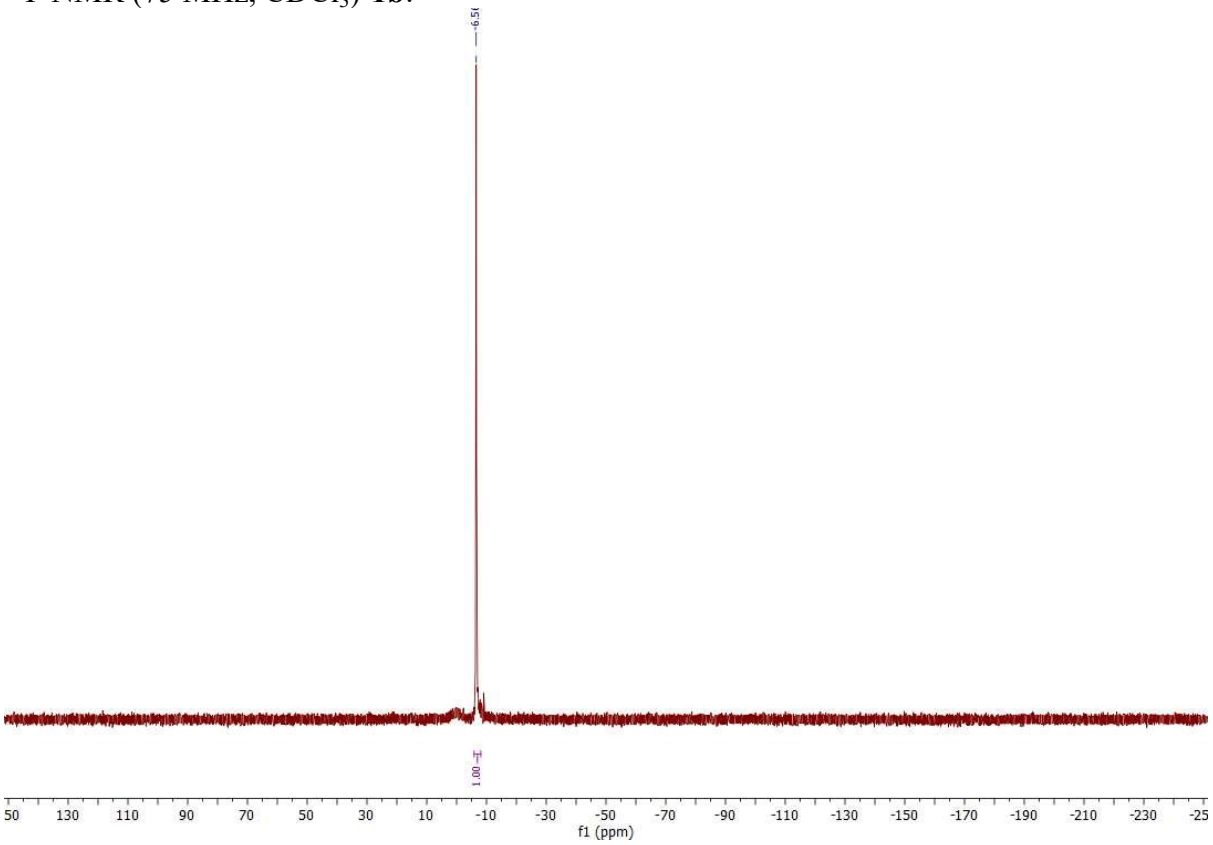
^{13}C NMR (151 MHz, $CDCl_3$)-**1b**:



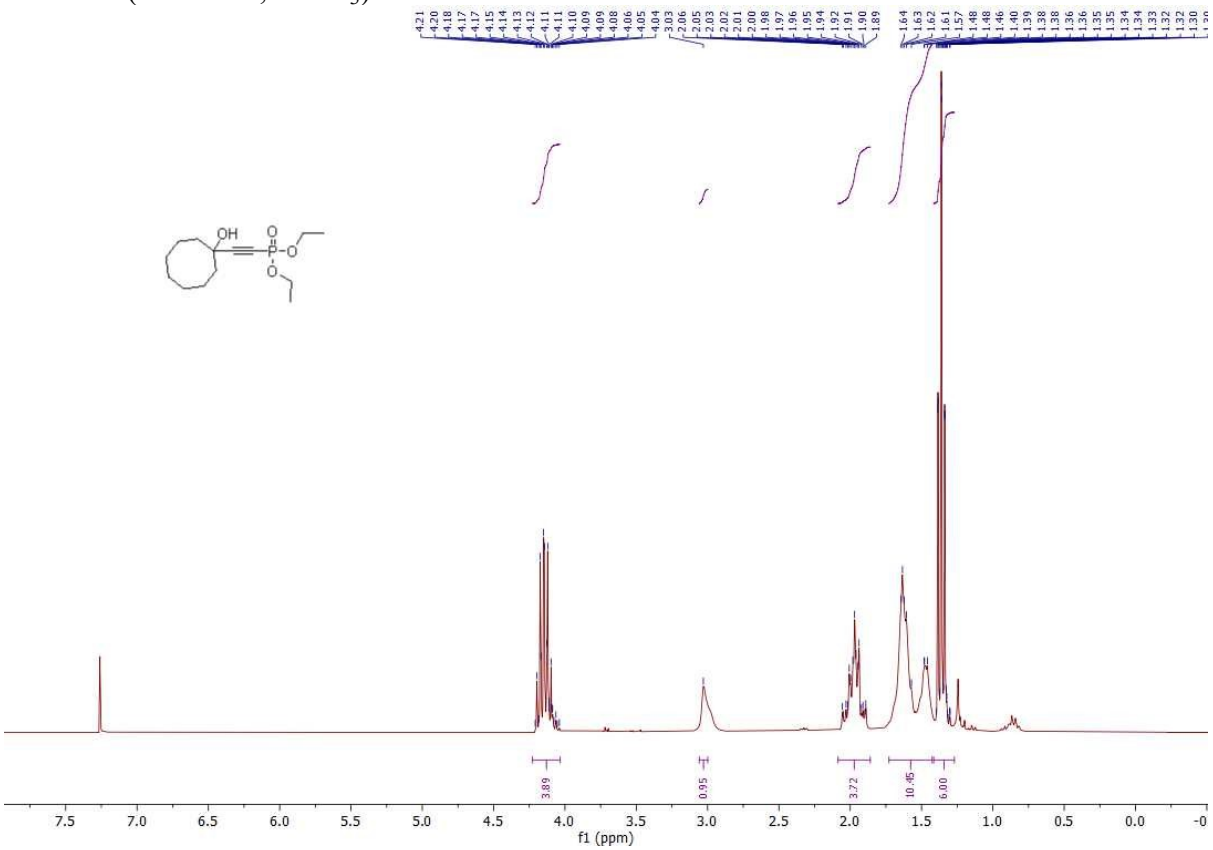
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**1b**:



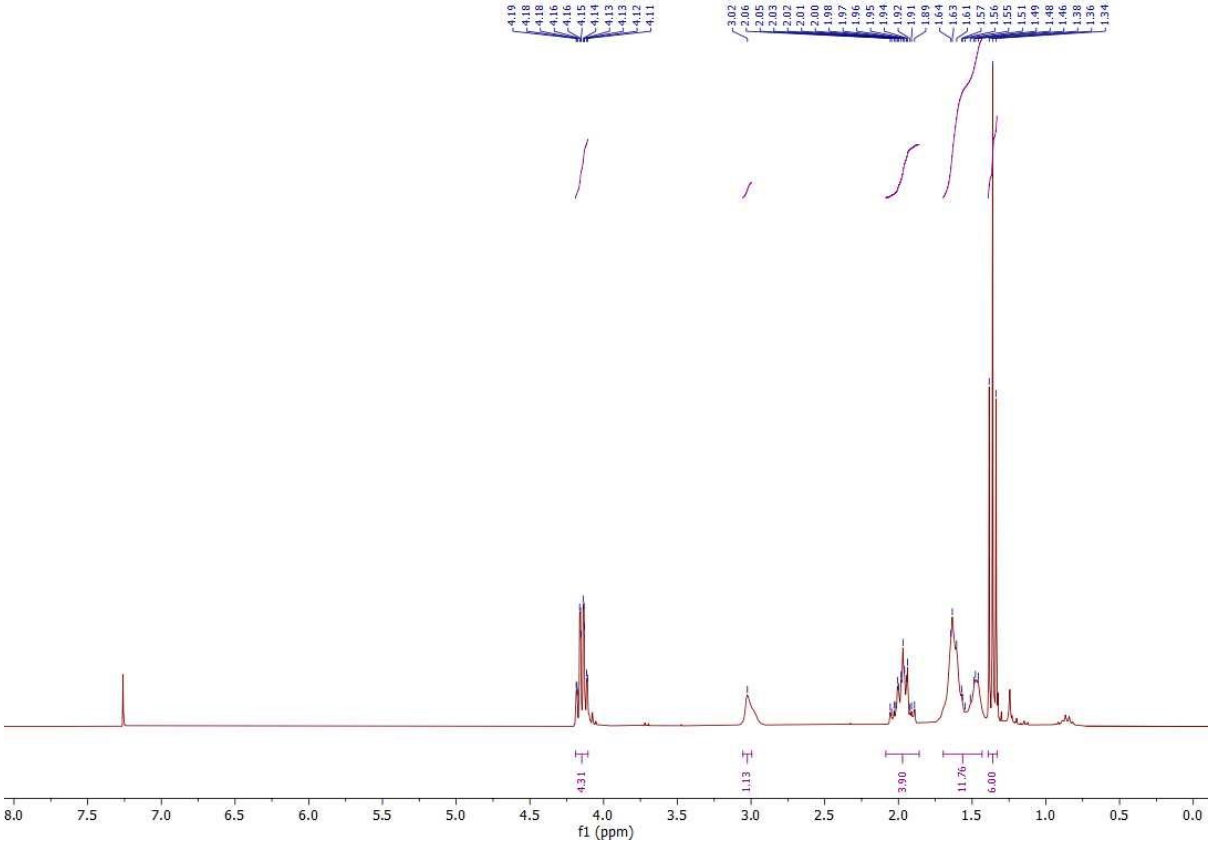
^{31}P NMR (75 MHz, $CDCl_3$)-**1b**:



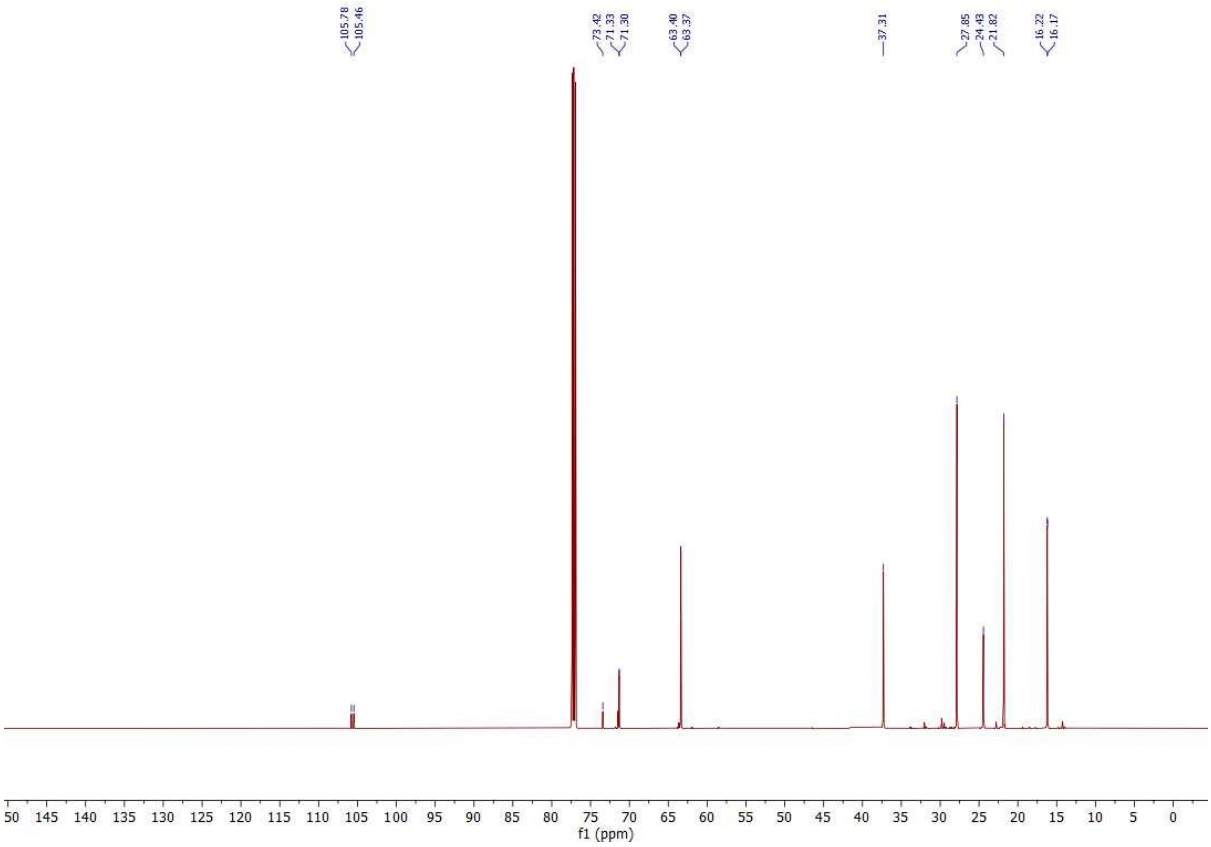
^{1}H NMR (300 MHz, $CDCl_3$)-**1d**:



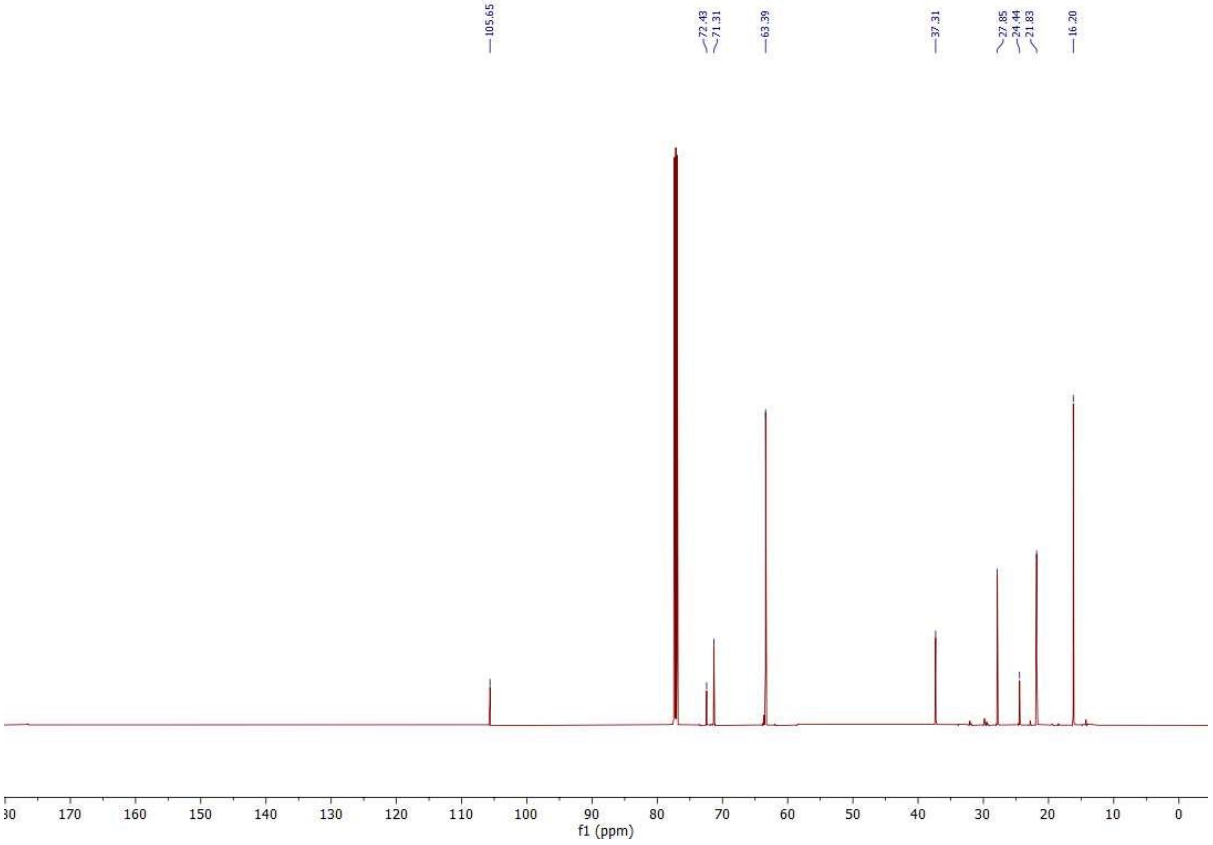
^{1}H $\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**1d**:



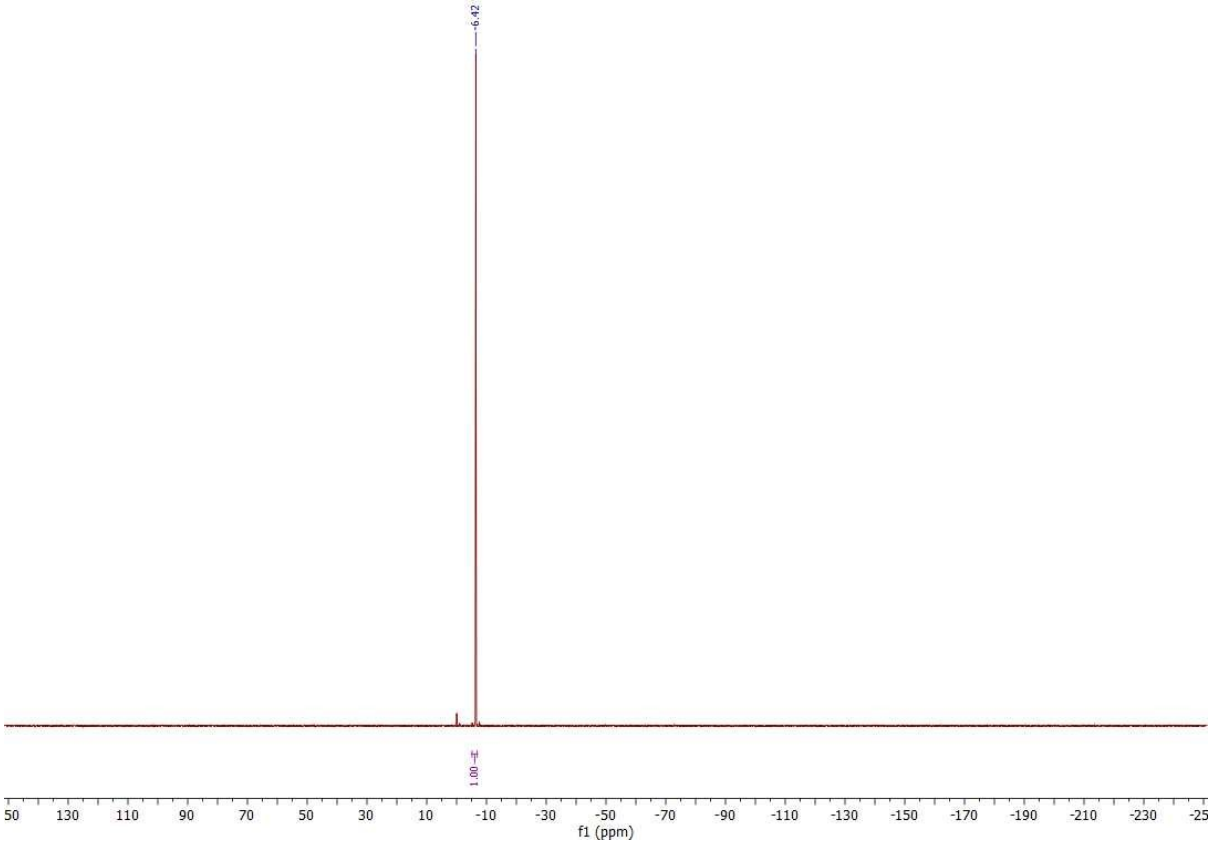
^{13}C NMR (151 MHz, $CDCl_3$)-**1d**:



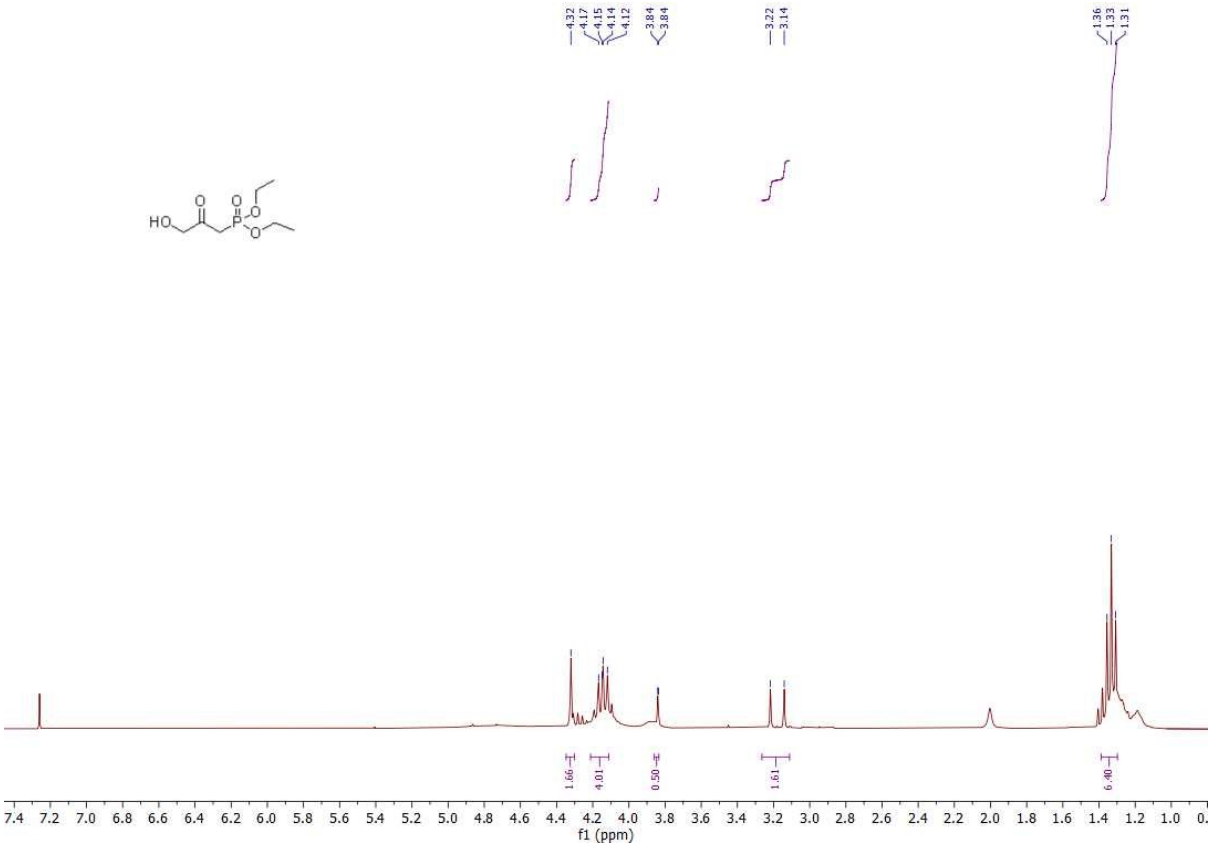
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**1d**:



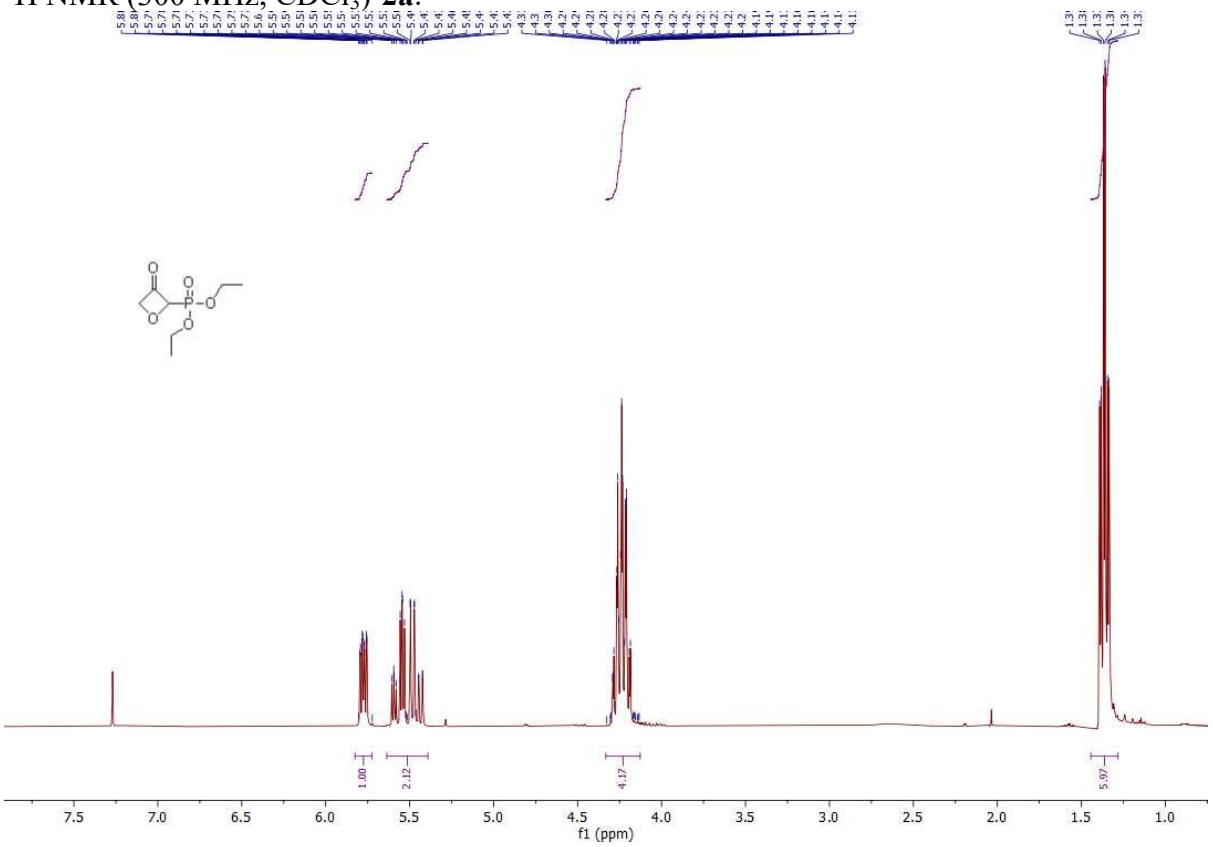
^{31}P NMR (75 MHz, $CDCl_3$)-**1d**:



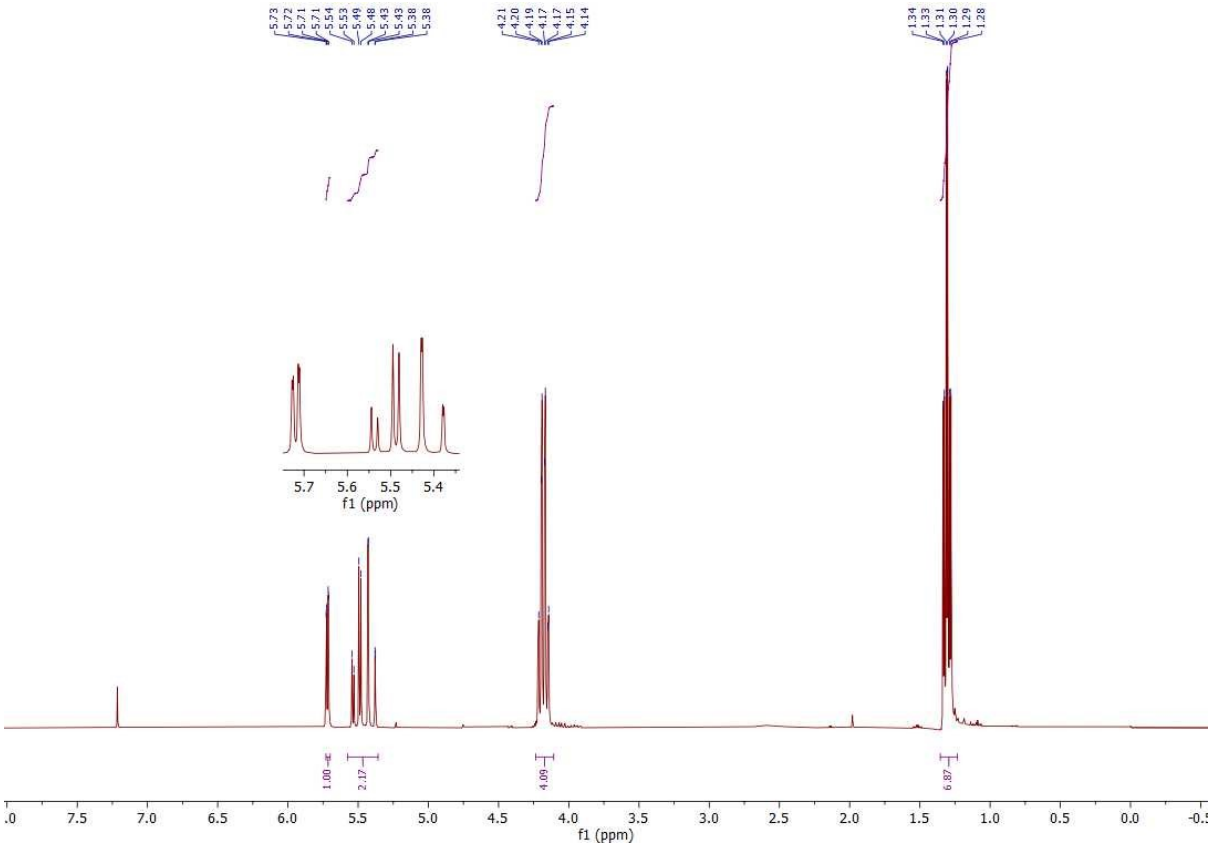
^{1}H NMR (300 MHz, $CDCl_3$)-**2aa**:



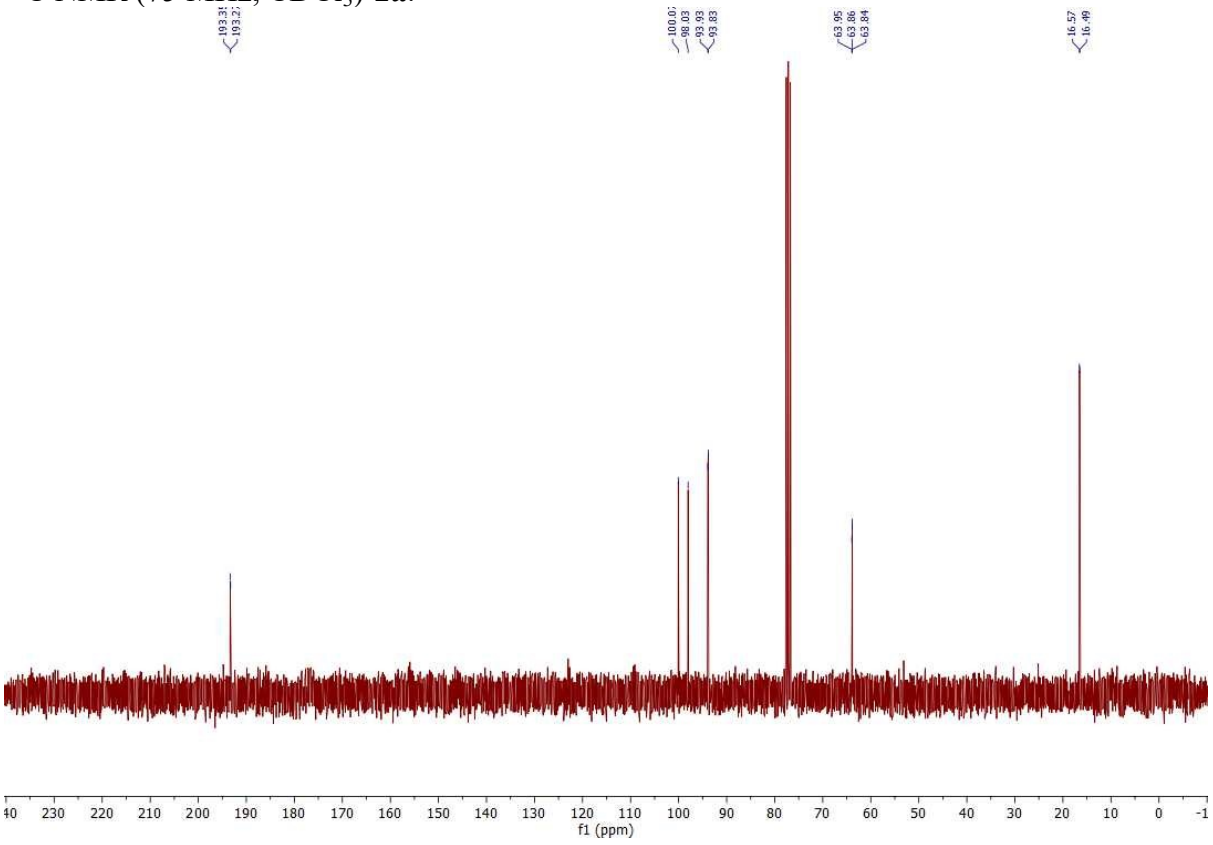
^{1}H NMR (300 MHz, $CDCl_3$)-**2a**:



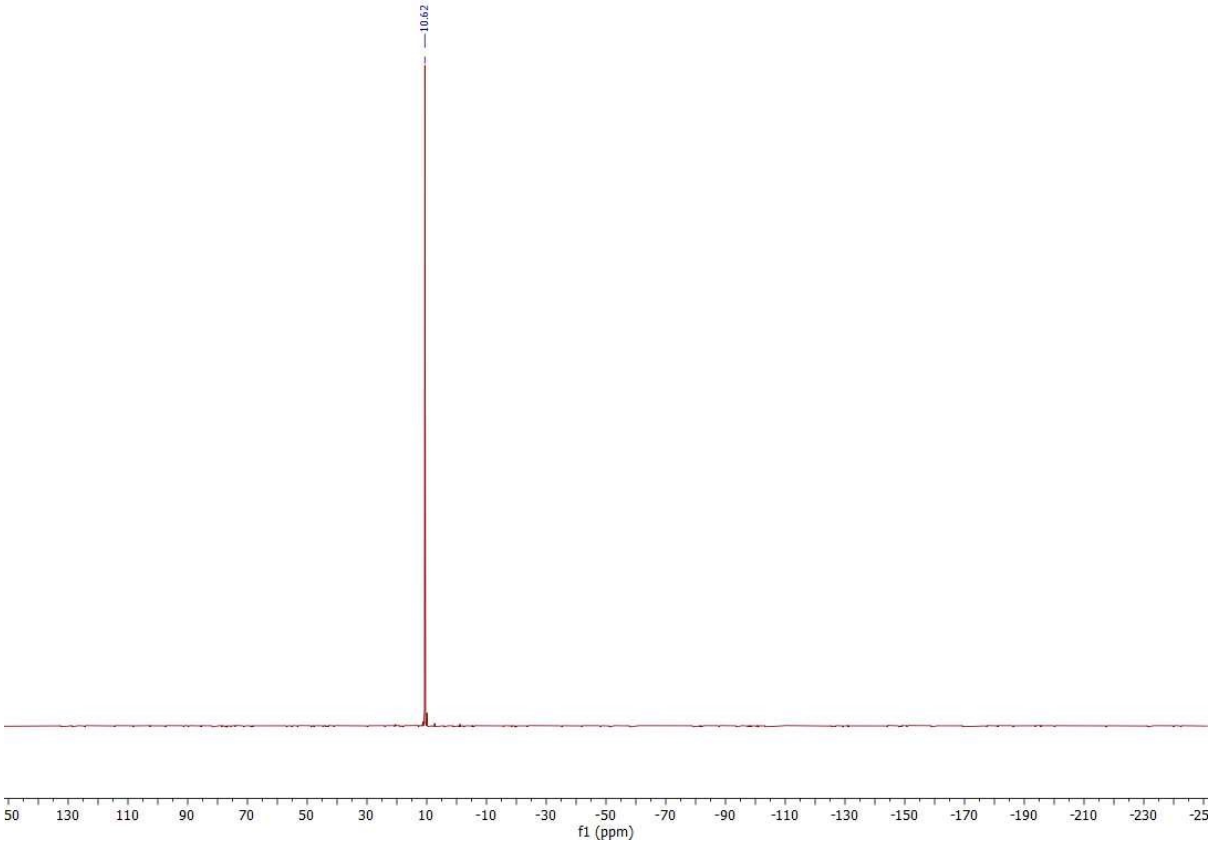
^{1}H {^{31}P} NMR (300 MHz, $CDCl_3$)-**2a**:



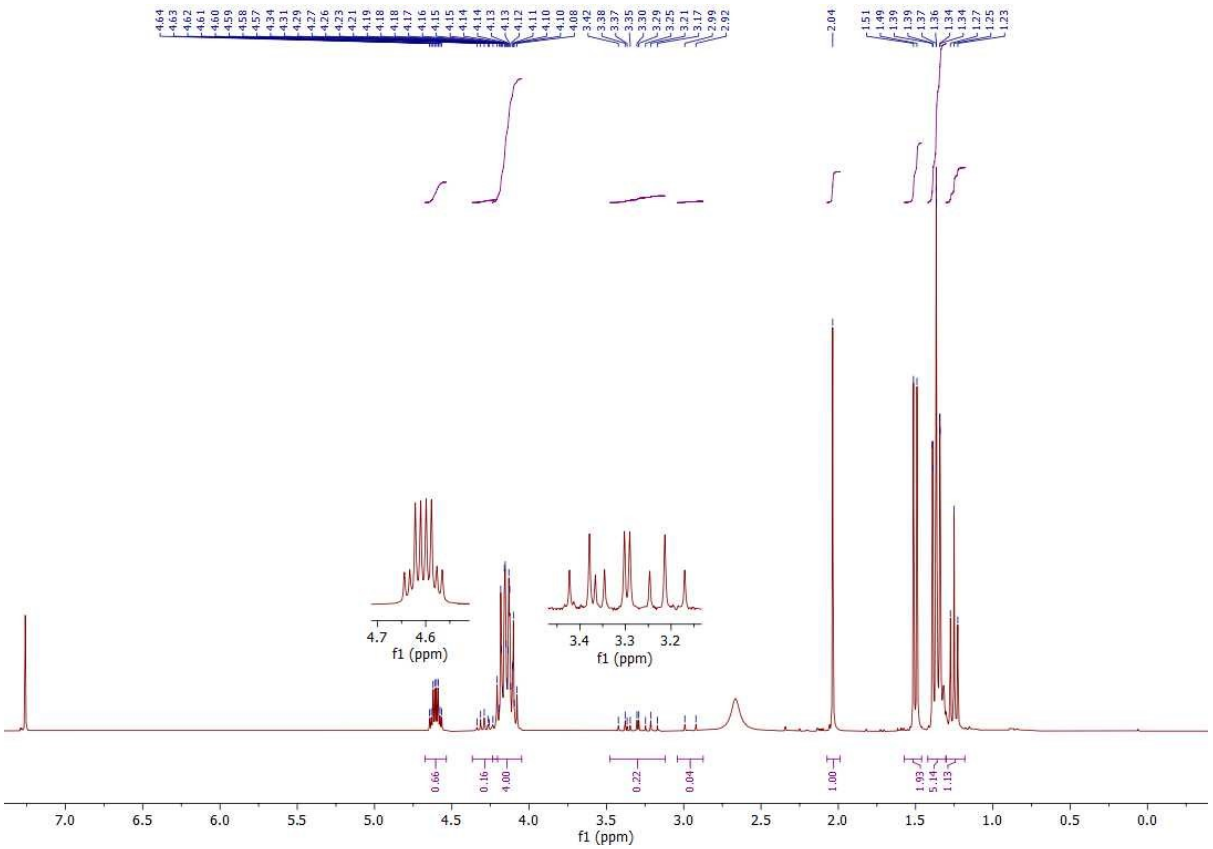
^{13}C NMR (75 MHz, $CDCl_3$)-**2a**:



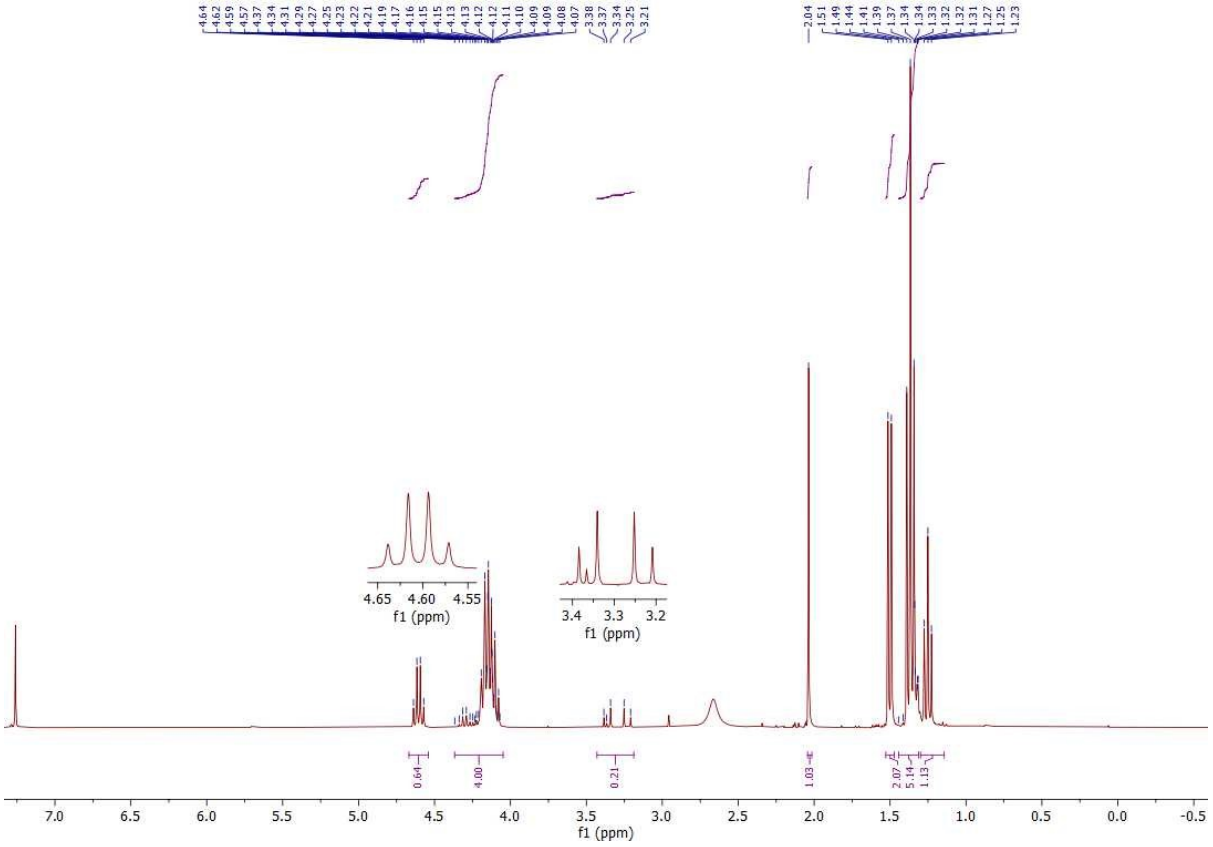
^{31}P NMR (75 MHz, $CDCl_3$)-**2a**:



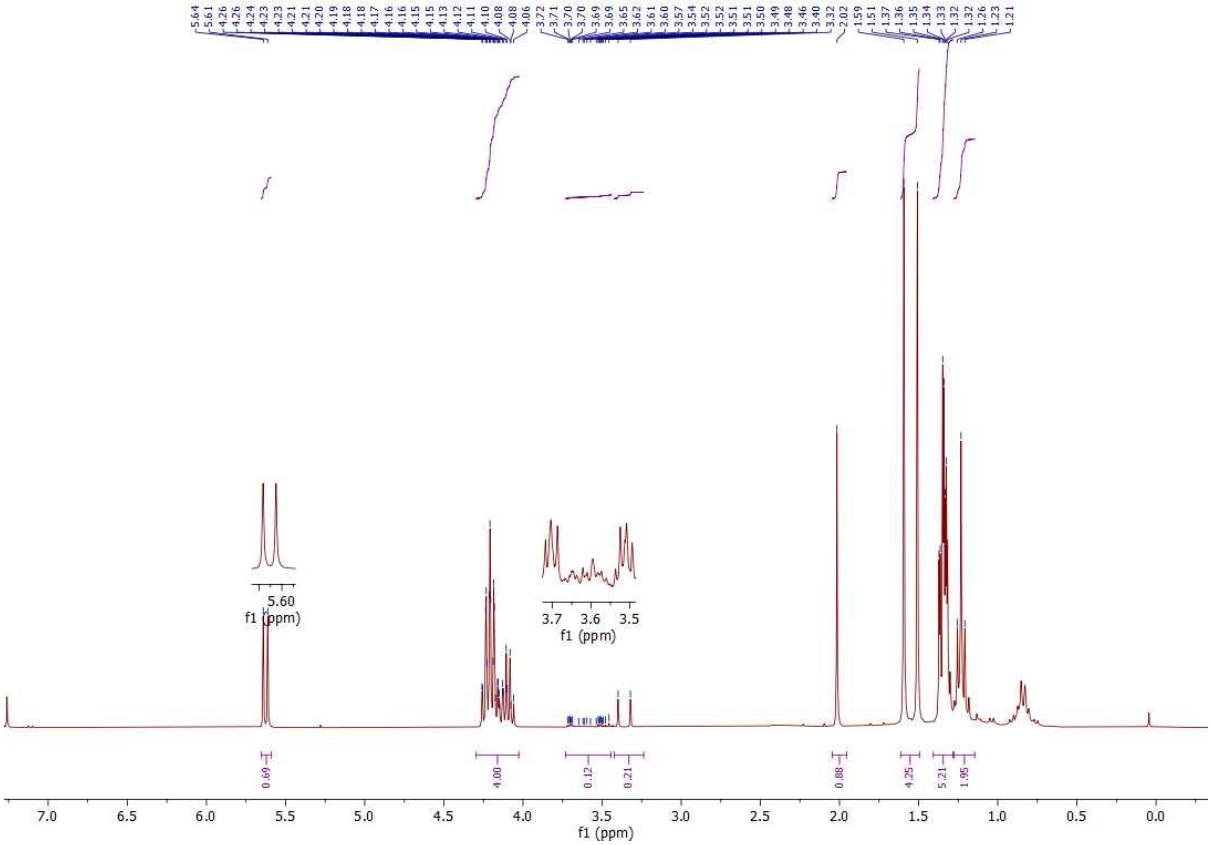
^{1}H NMR (300 MHz, $CDCl_3$)-**2b** mixture:



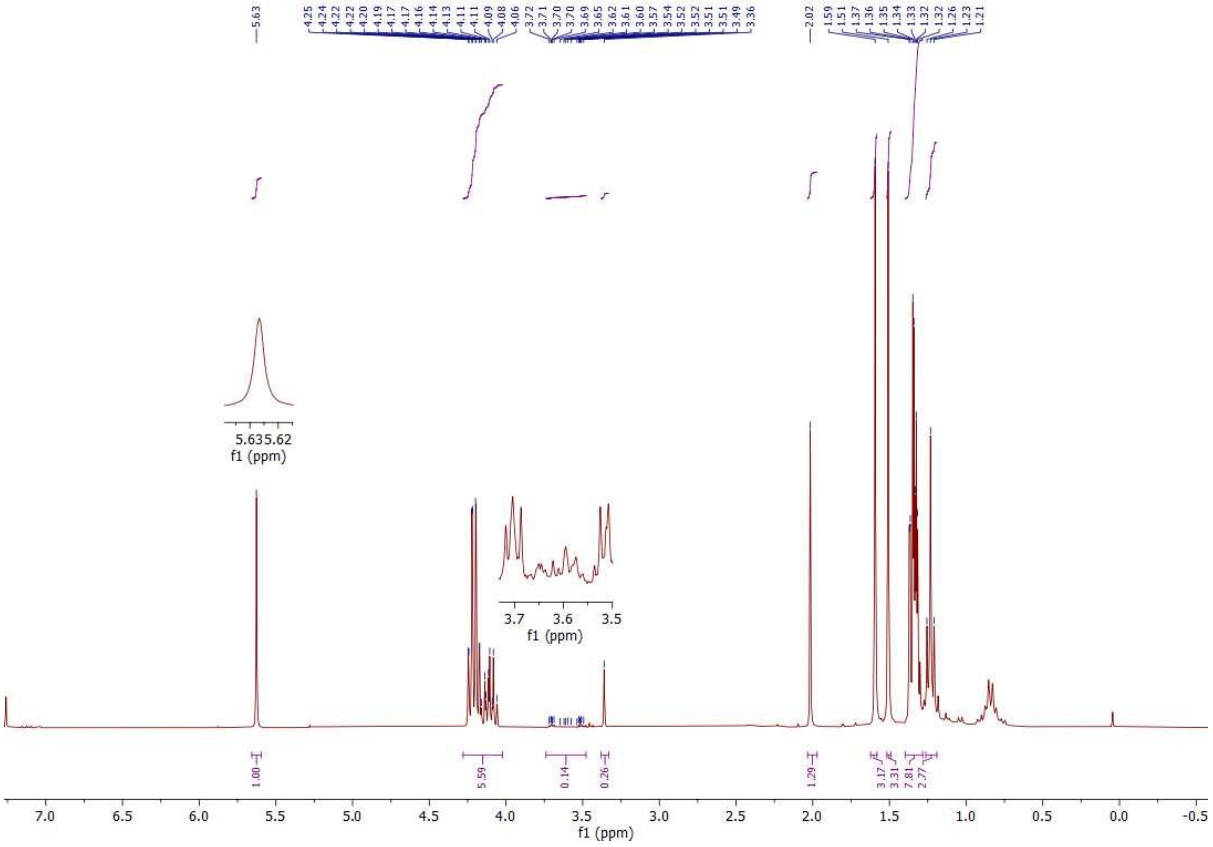
^{1}H NMR (300 MHz, $CDCl_3$)-**2b** mixture:



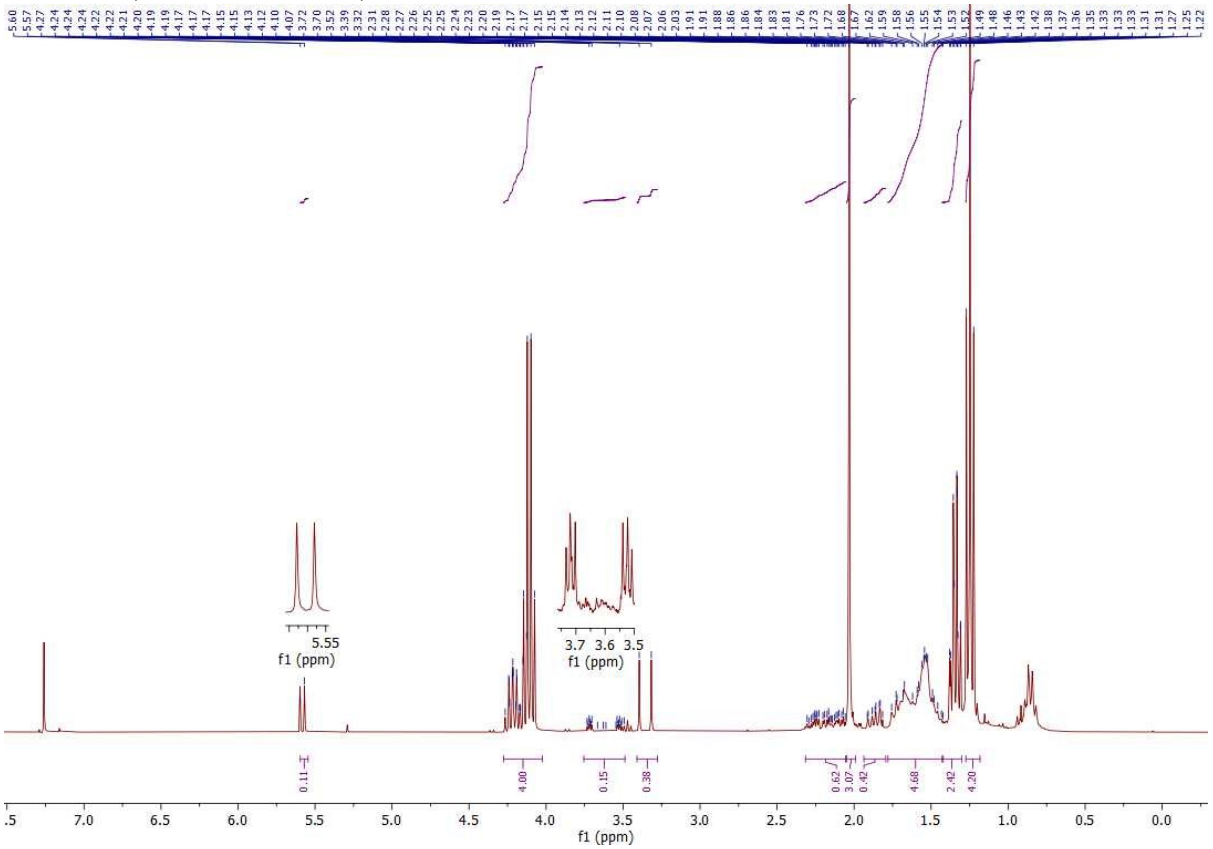
^{1}H NMR (300 MHz, $CDCl_3$)-**2c** mixture:



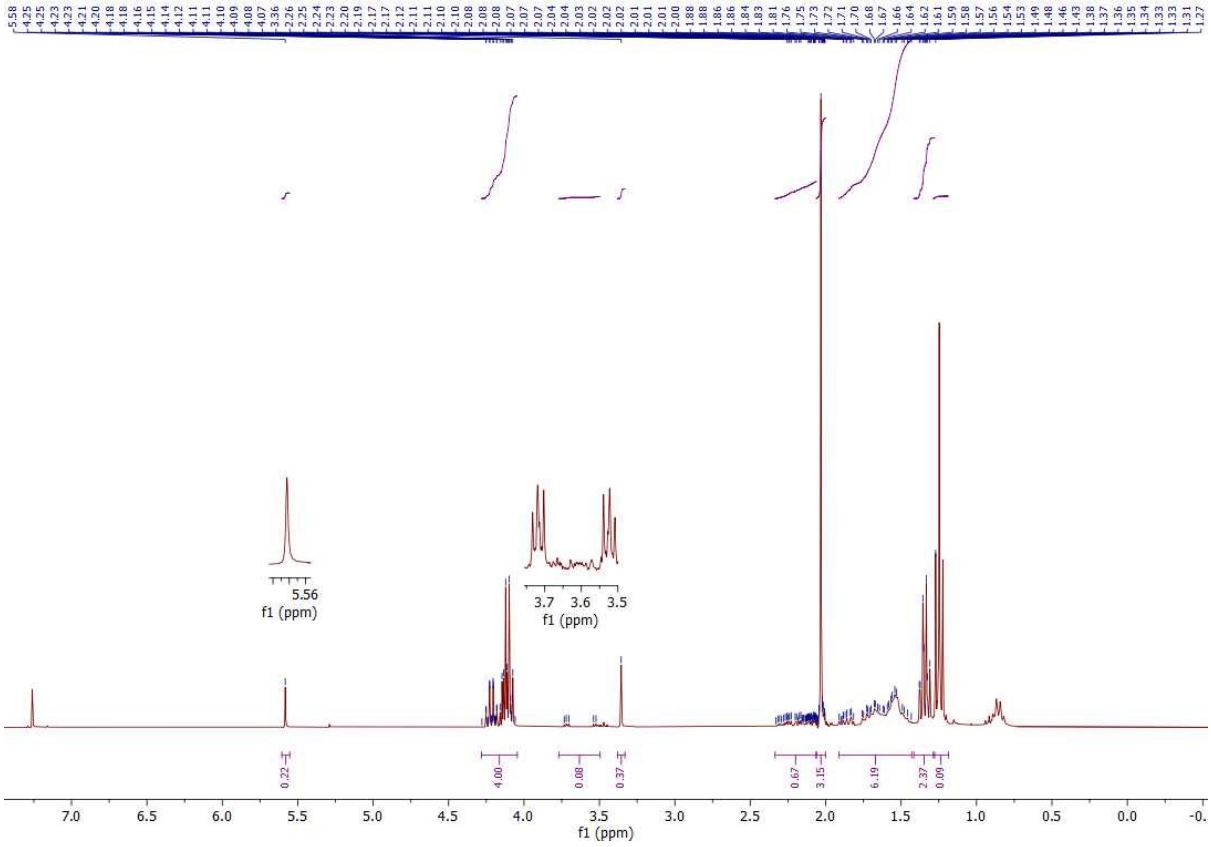
^{1}H $\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**2c** mixture:



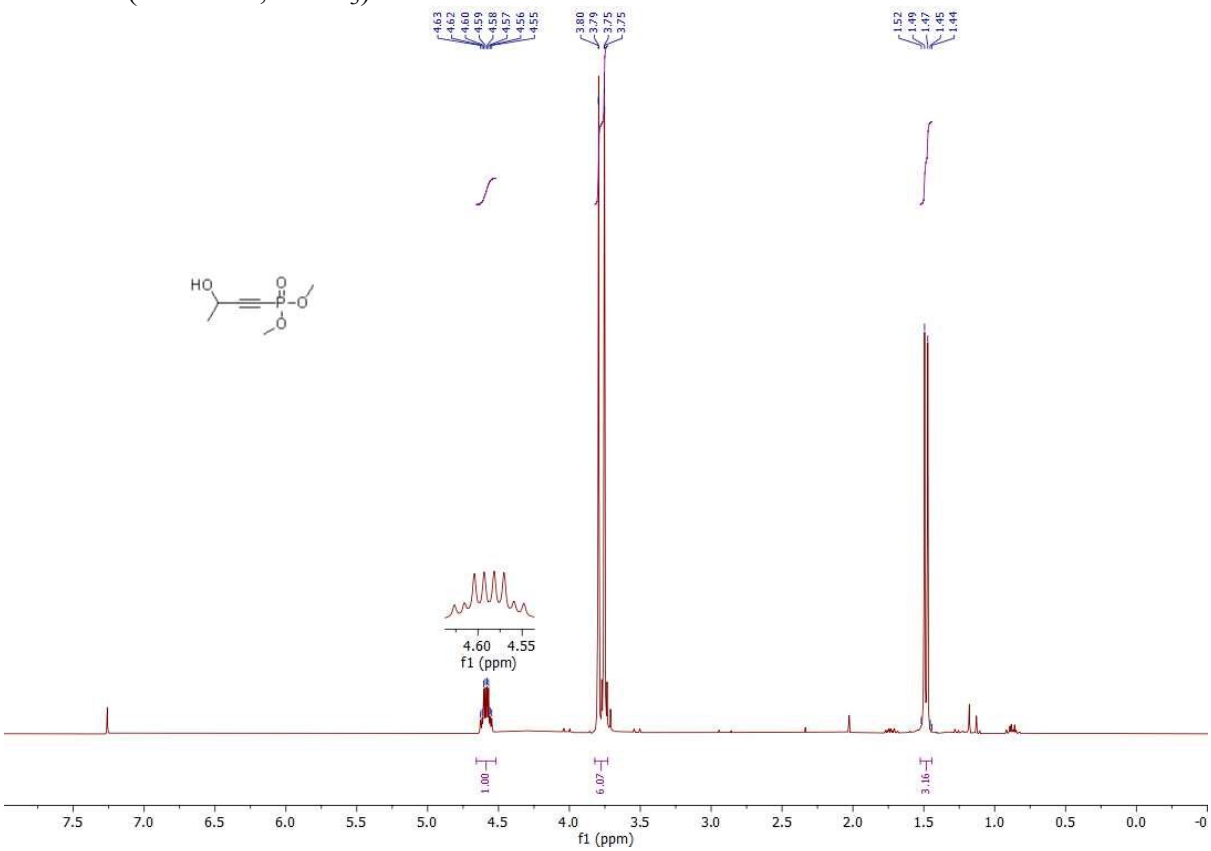
^{1}H NMR (300 MHz, $CDCl_3$)-**2d** mixture:



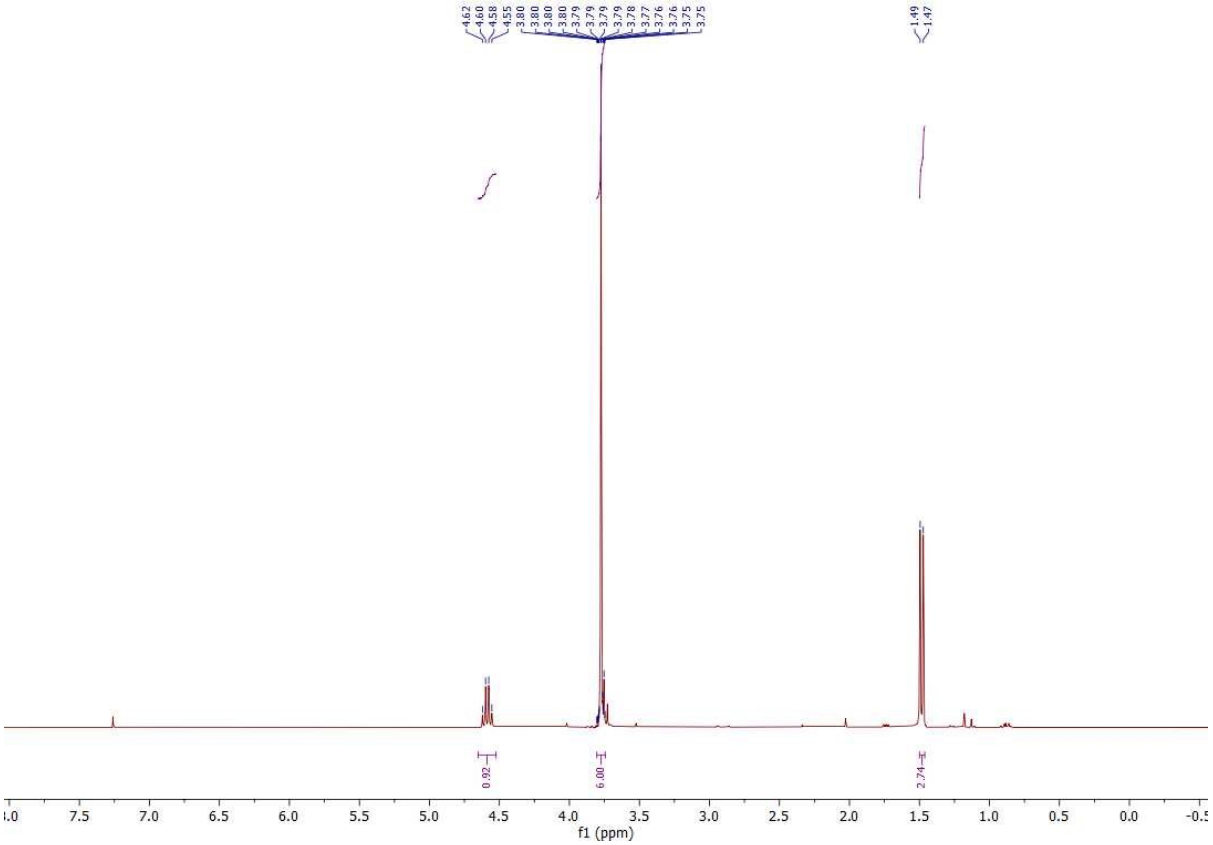
^{1}H $\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**2d** mixture:



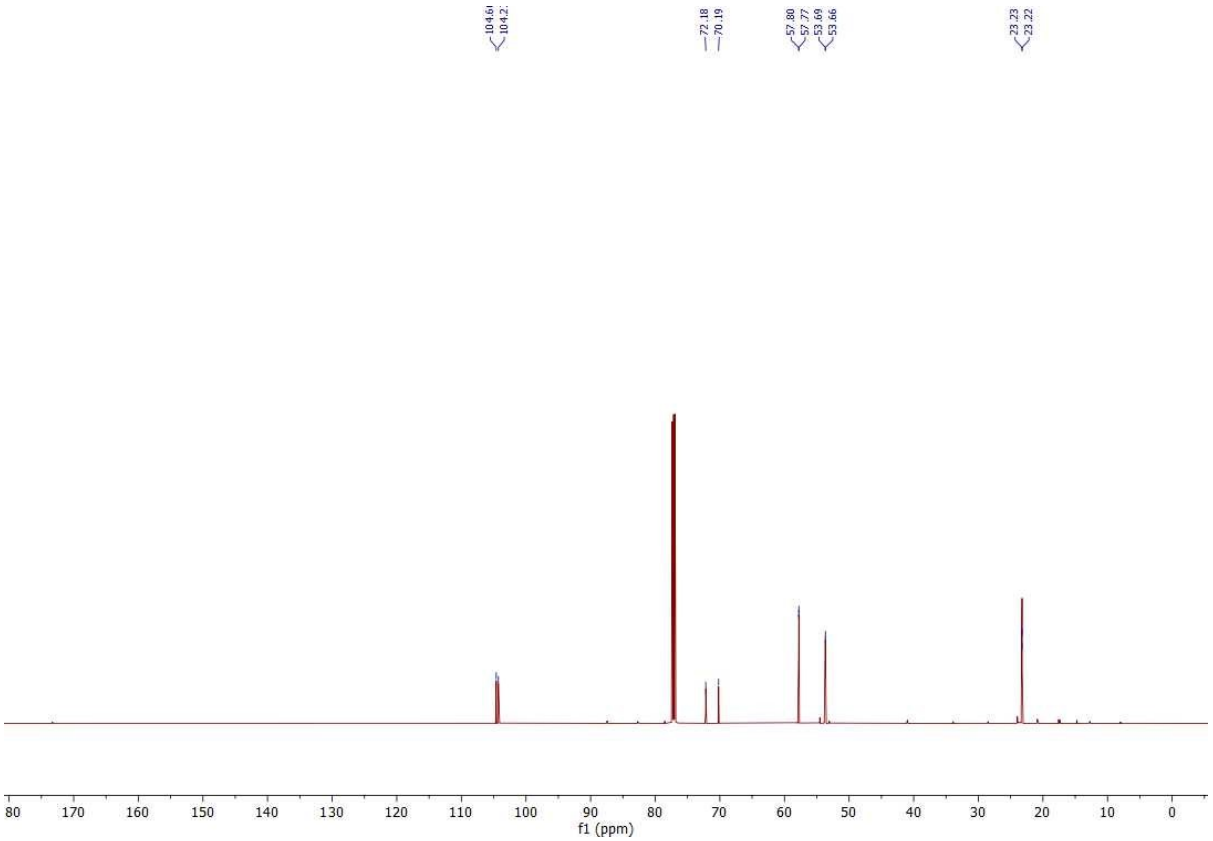
^{1}H NMR (300 MHz, $CDCl_3$)-**3a**:



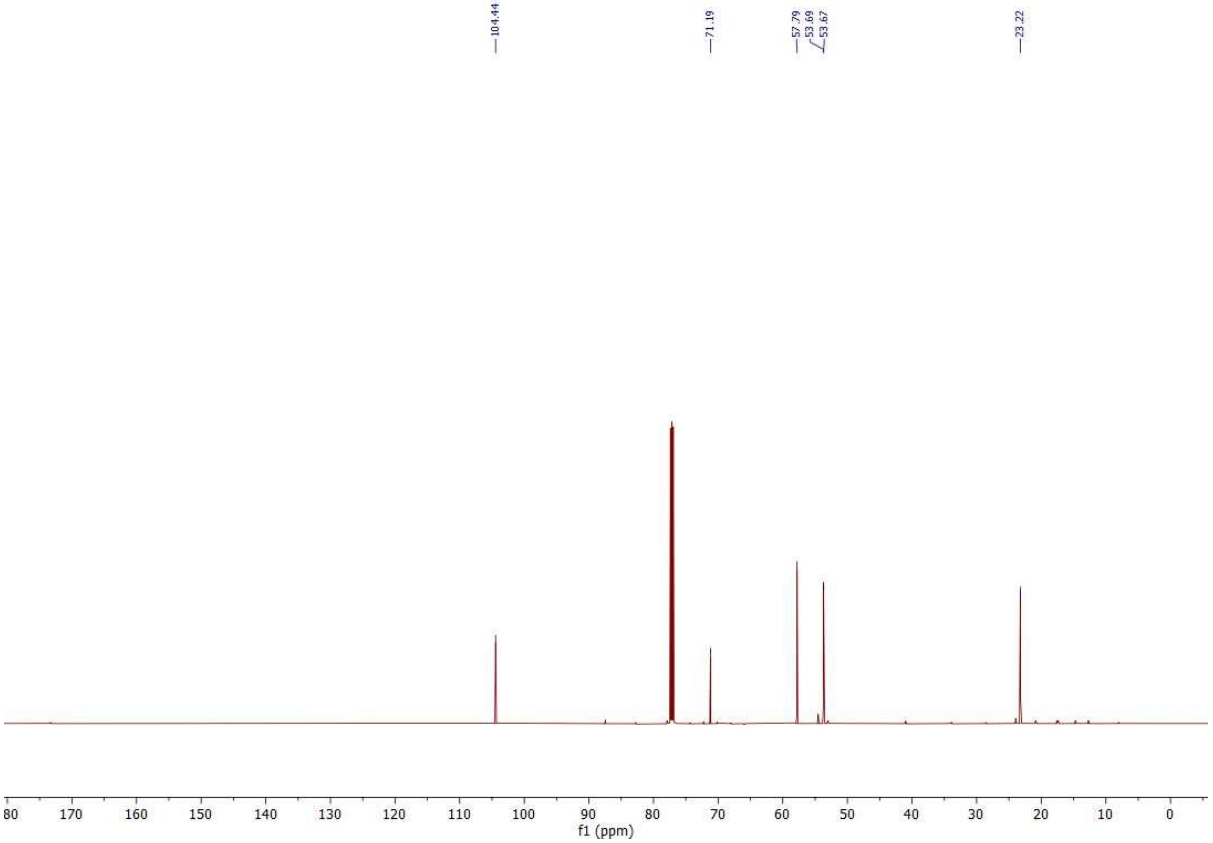
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**3a**:



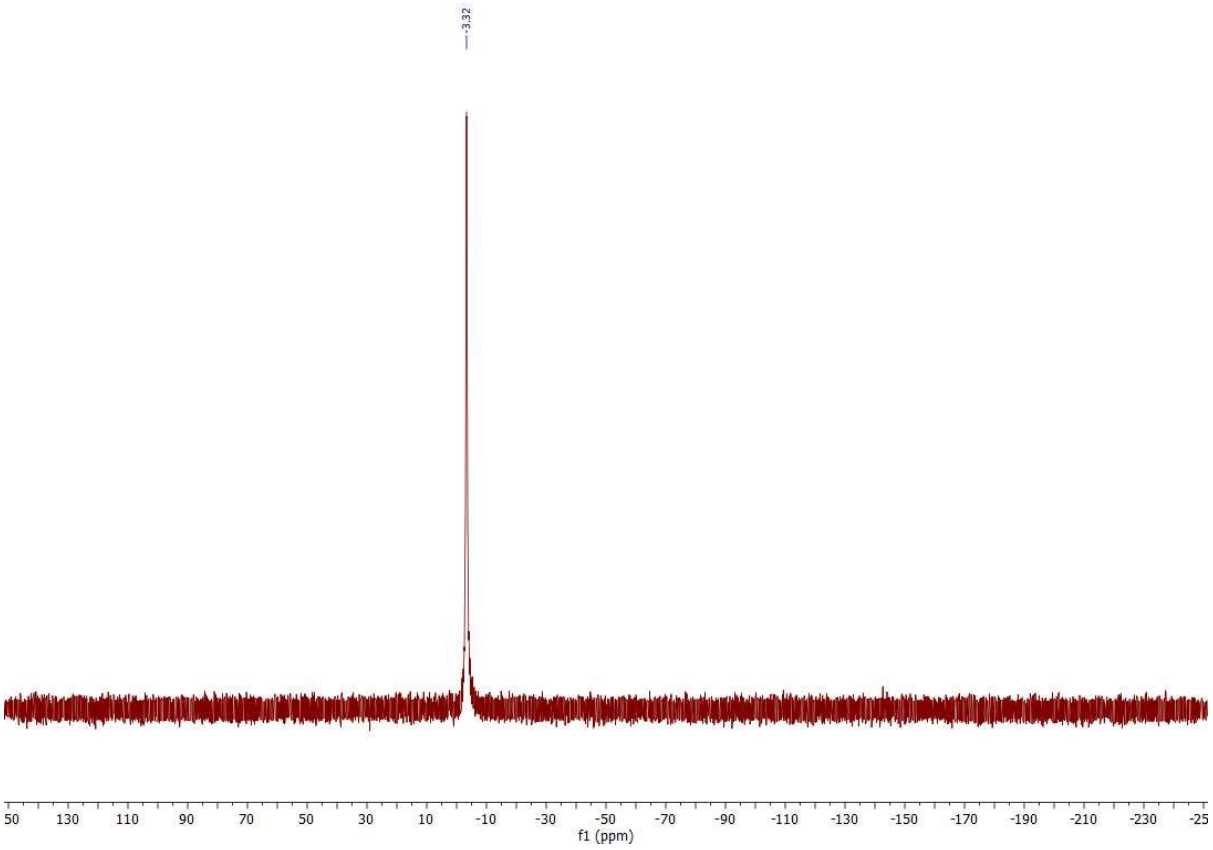
^{13}C NMR (151 MHz, $CDCl_3$)-**3a**:



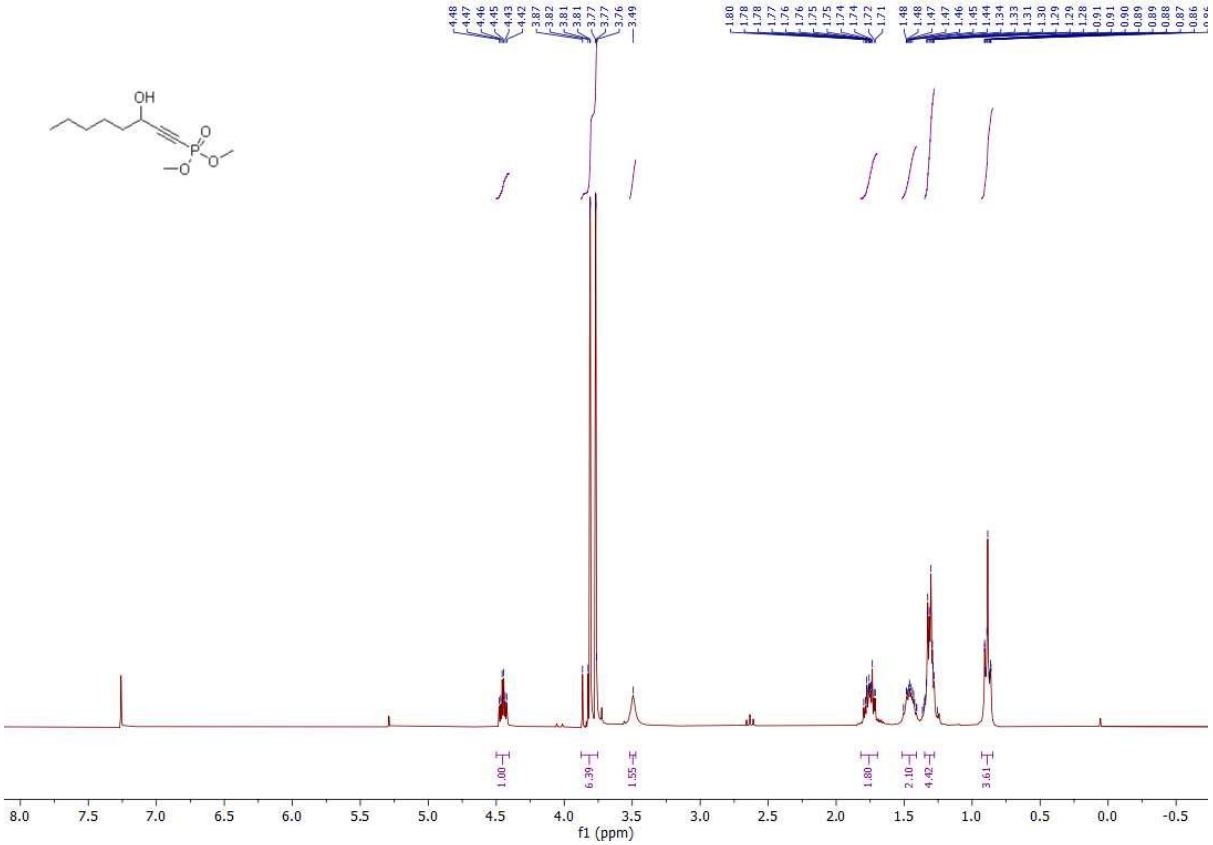
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3a**:



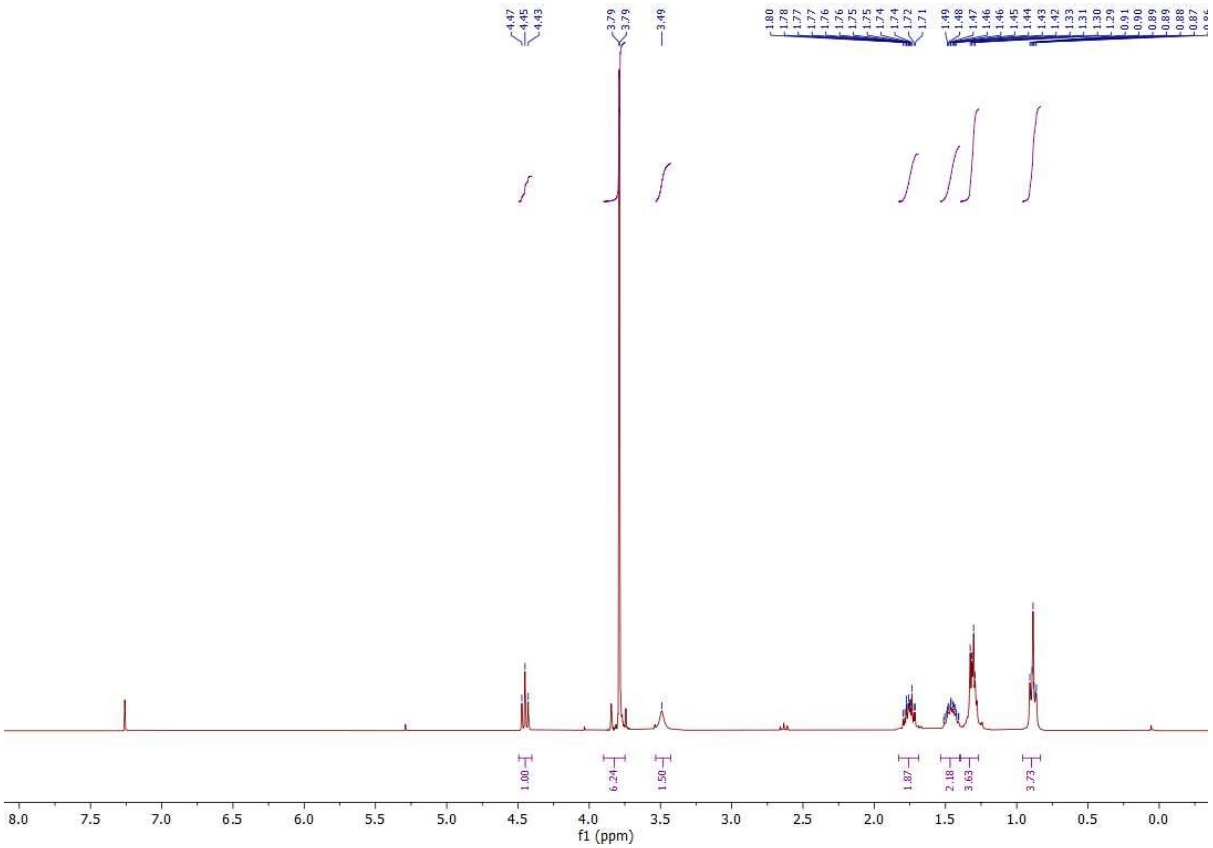
^{31}P NMR (121 MHz, $CDCl_3$)-**3a**:



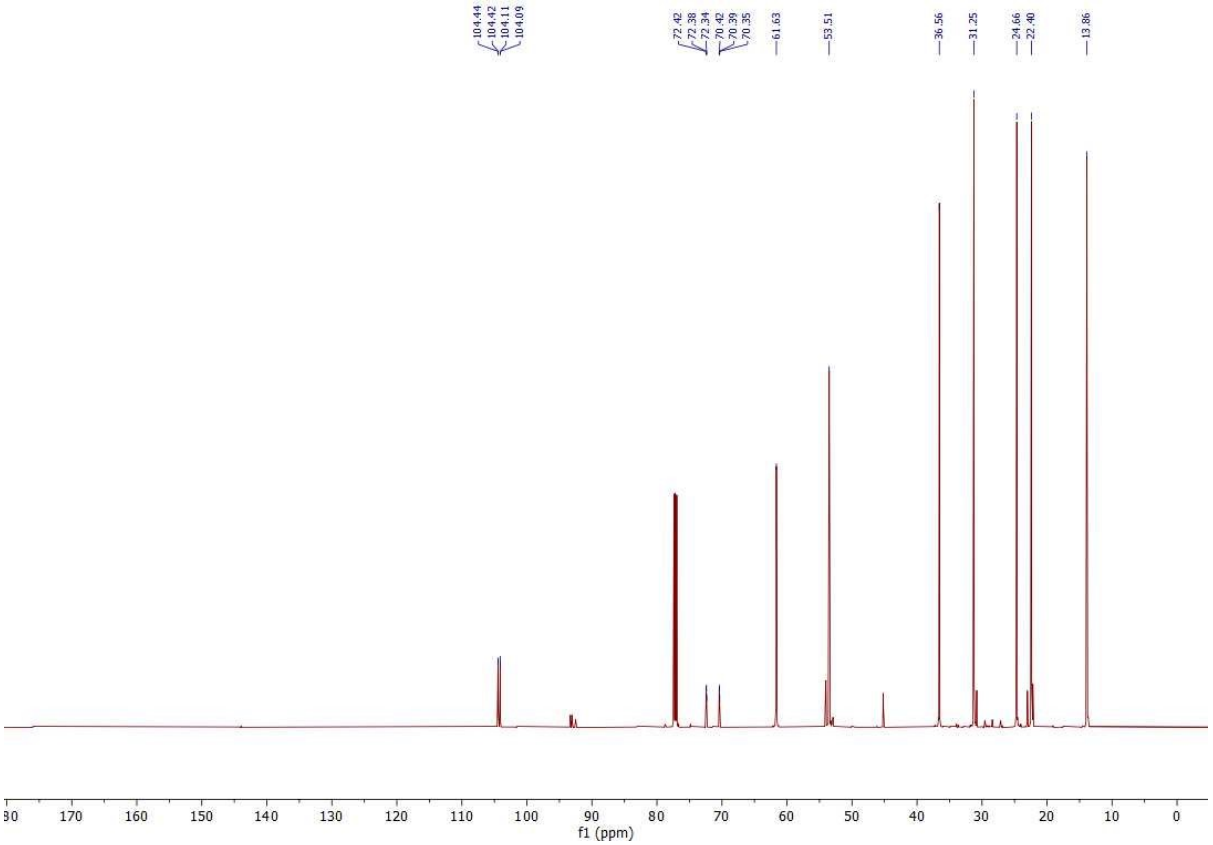
^{1}H NMR (300 MHz, $CDCl_3$)-**3b**:



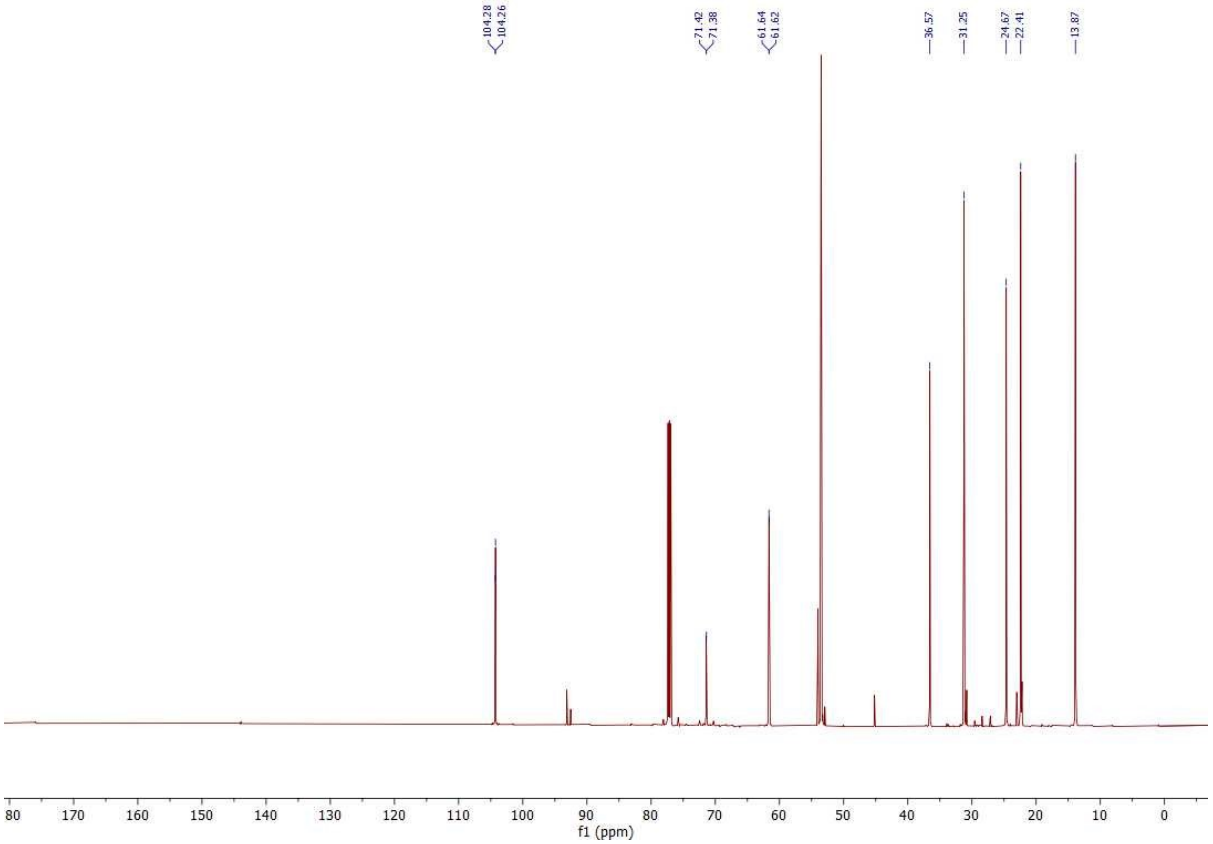
^{1}H{^{31}P} NMR (500 MHz, $CDCl_3$)-**3b**:



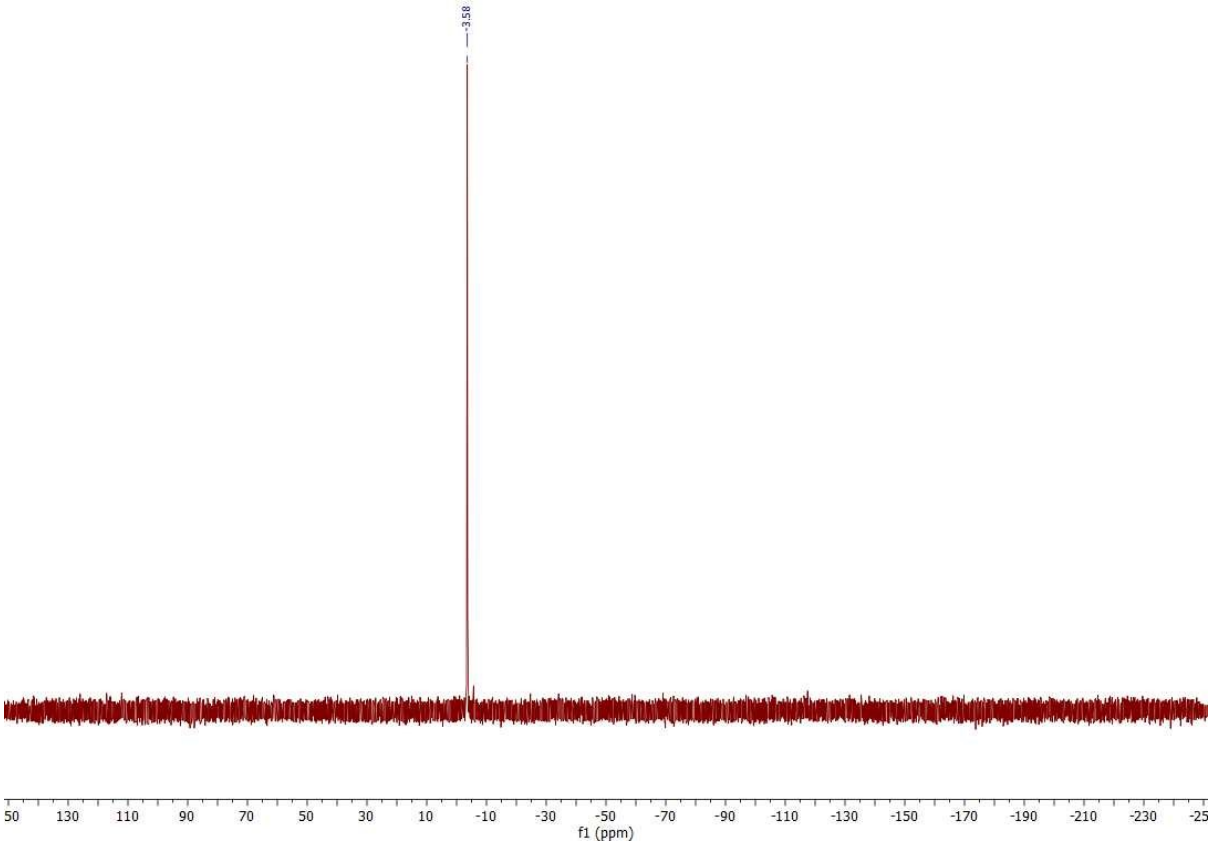
^{13}C NMR (151 MHz, $CDCl_3$)-**3b**:



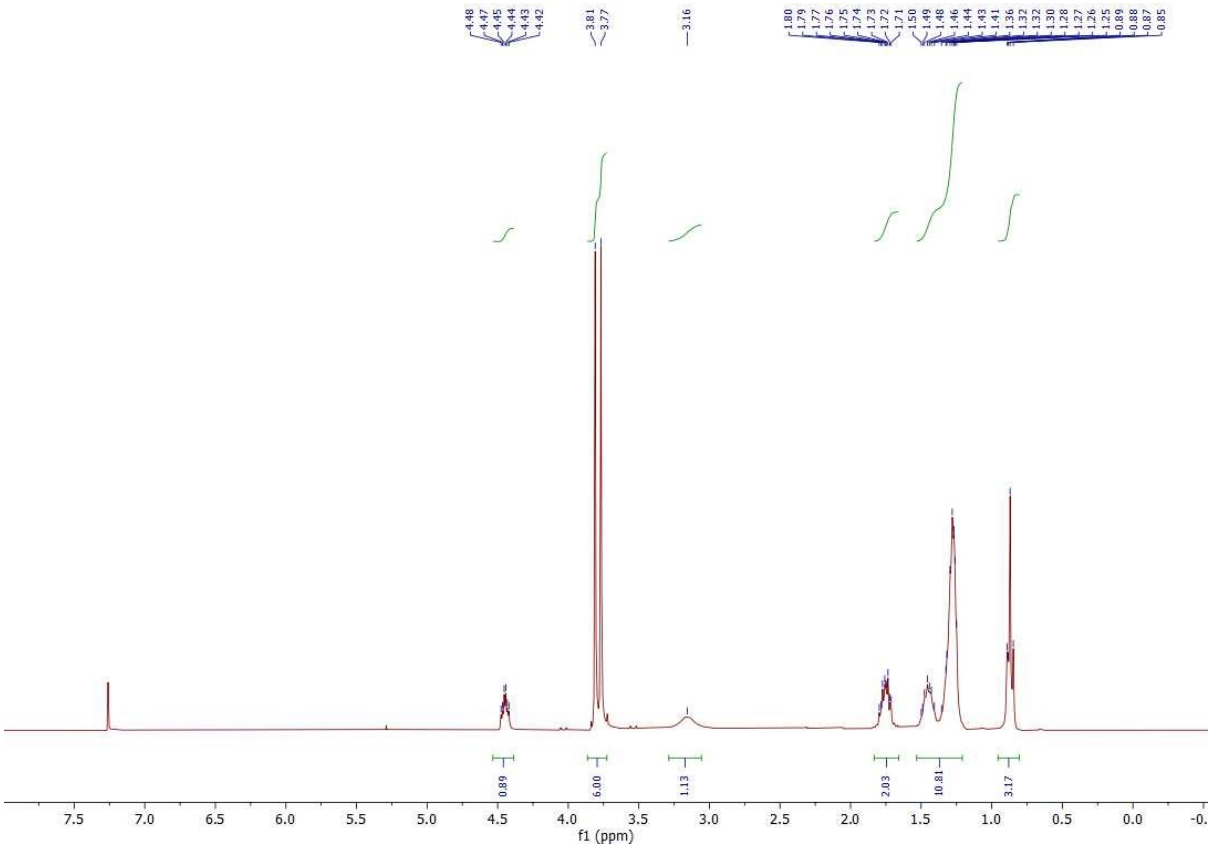
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3b**:



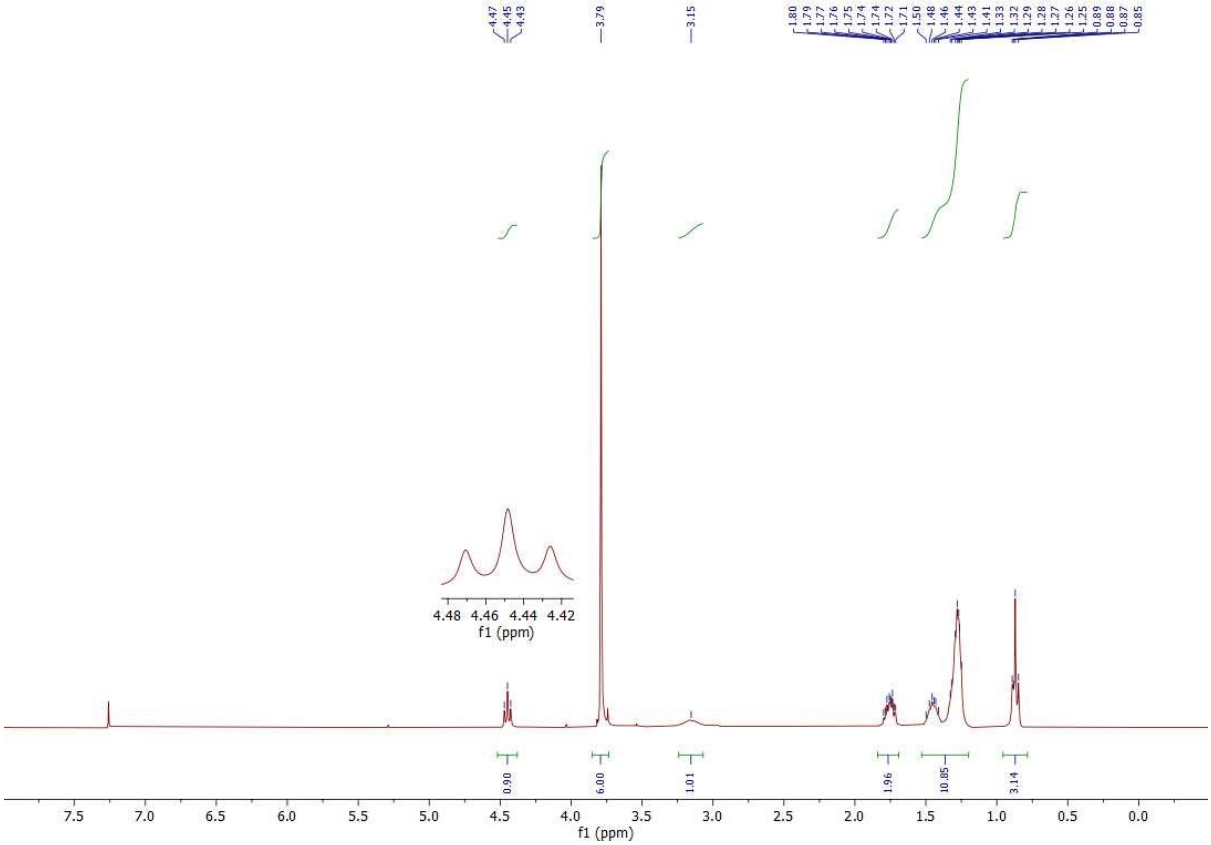
^{31}P NMR (121 MHz, $CDCl_3$)-**3b**:



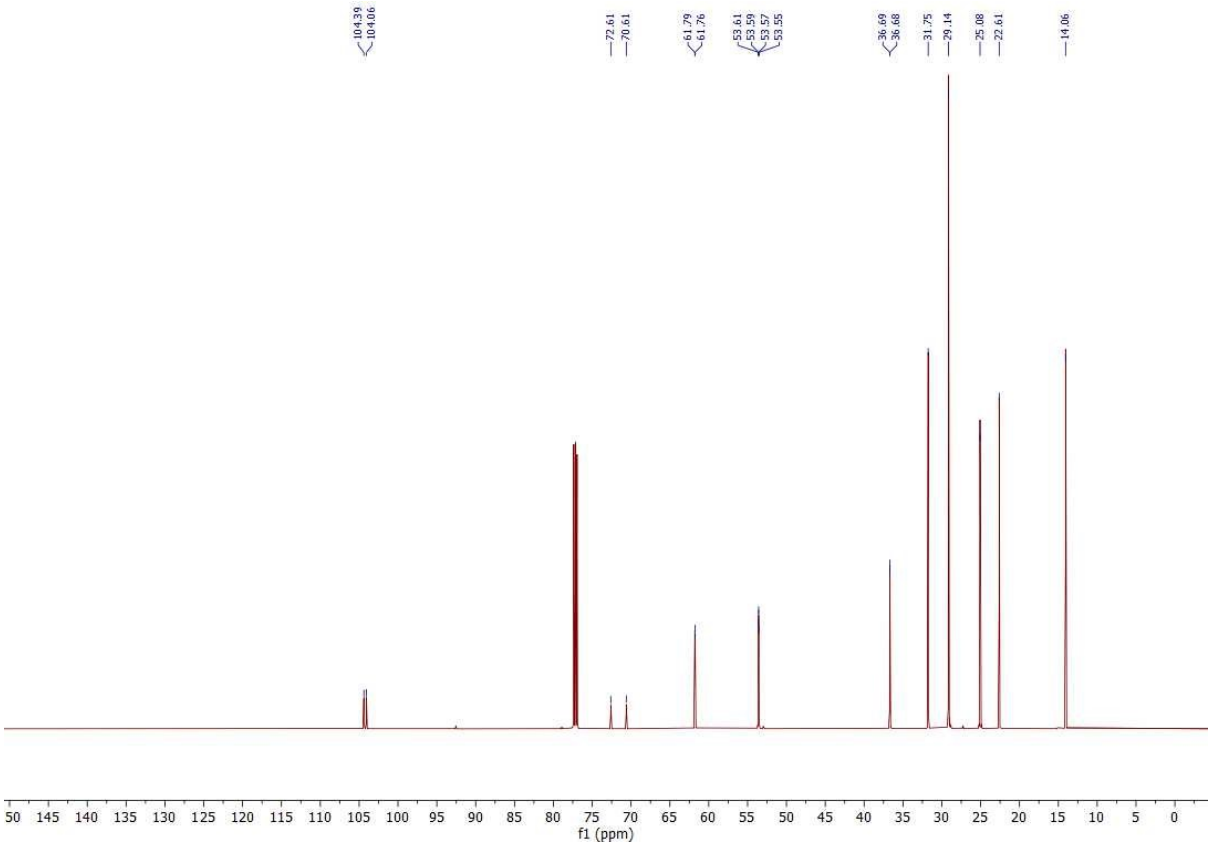
^{1}H NMR (300 MHz, $CDCl_3$)-**3c**:



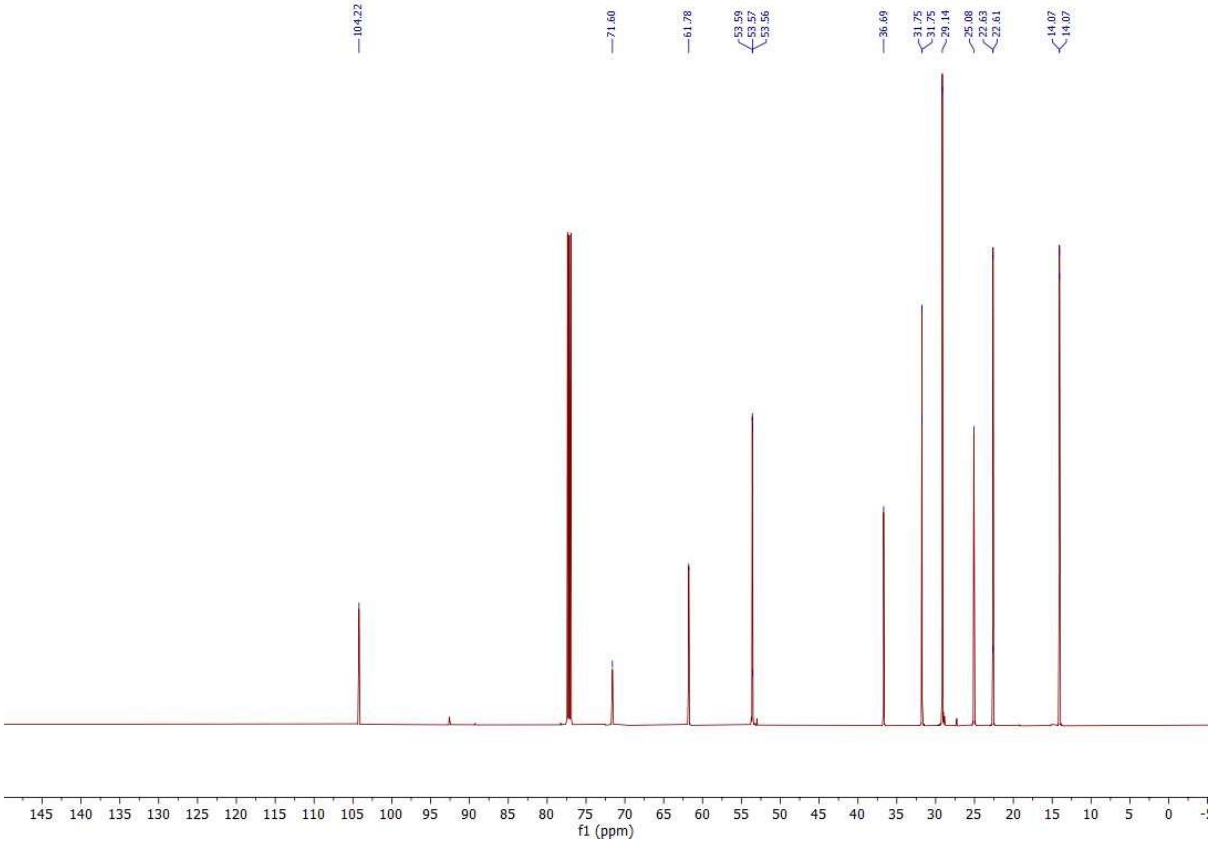
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**3c**:



^{13}C NMR (151 MHz, $CDCl_3$)-**3c**:

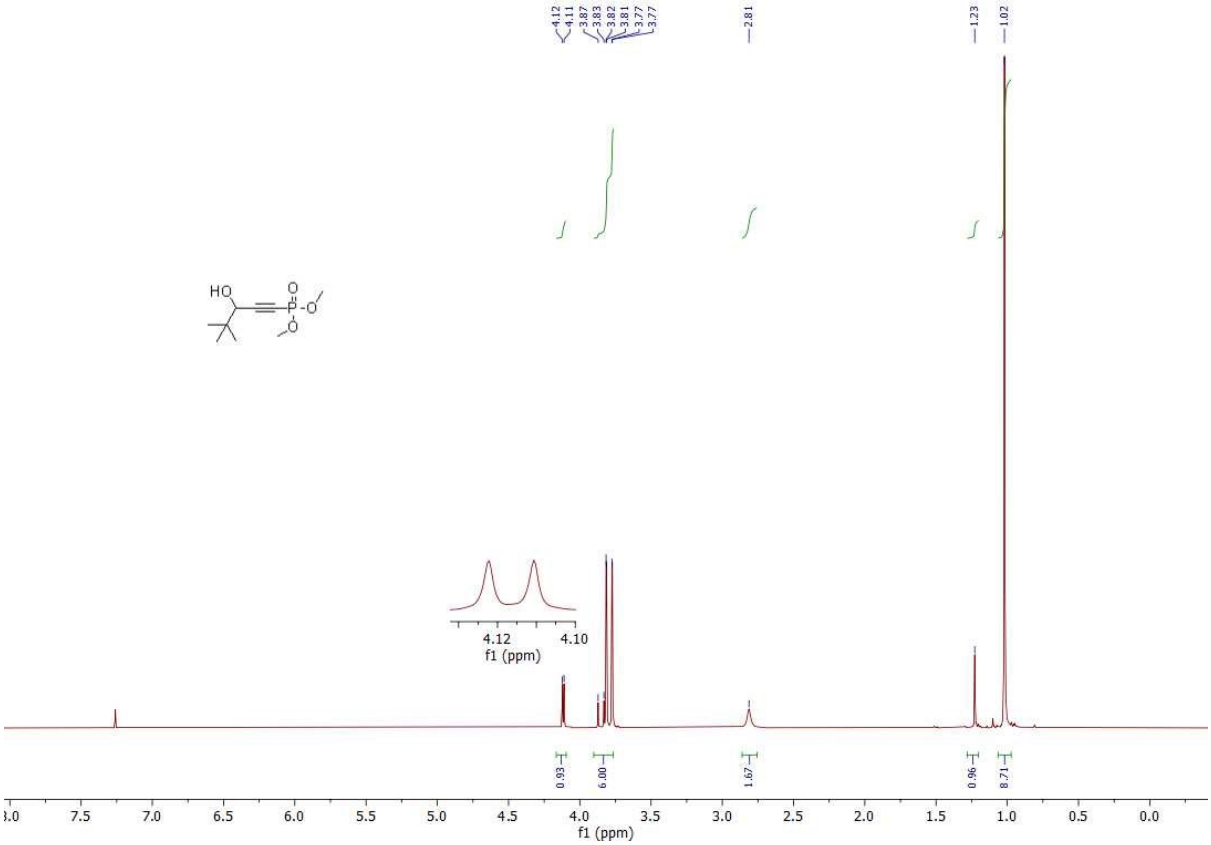


$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3c**:

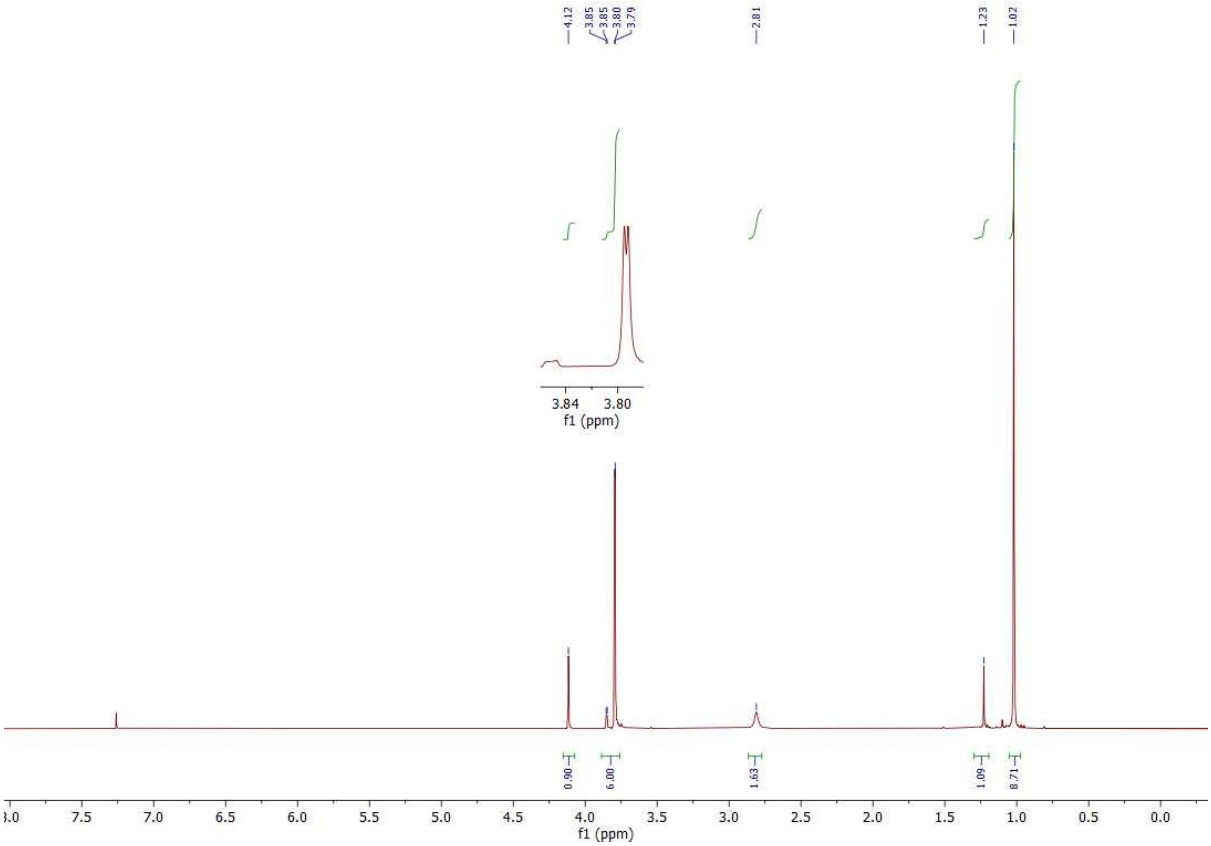


^{31}P NMR (121 MHz, $CDCl_3$)-**3c**:

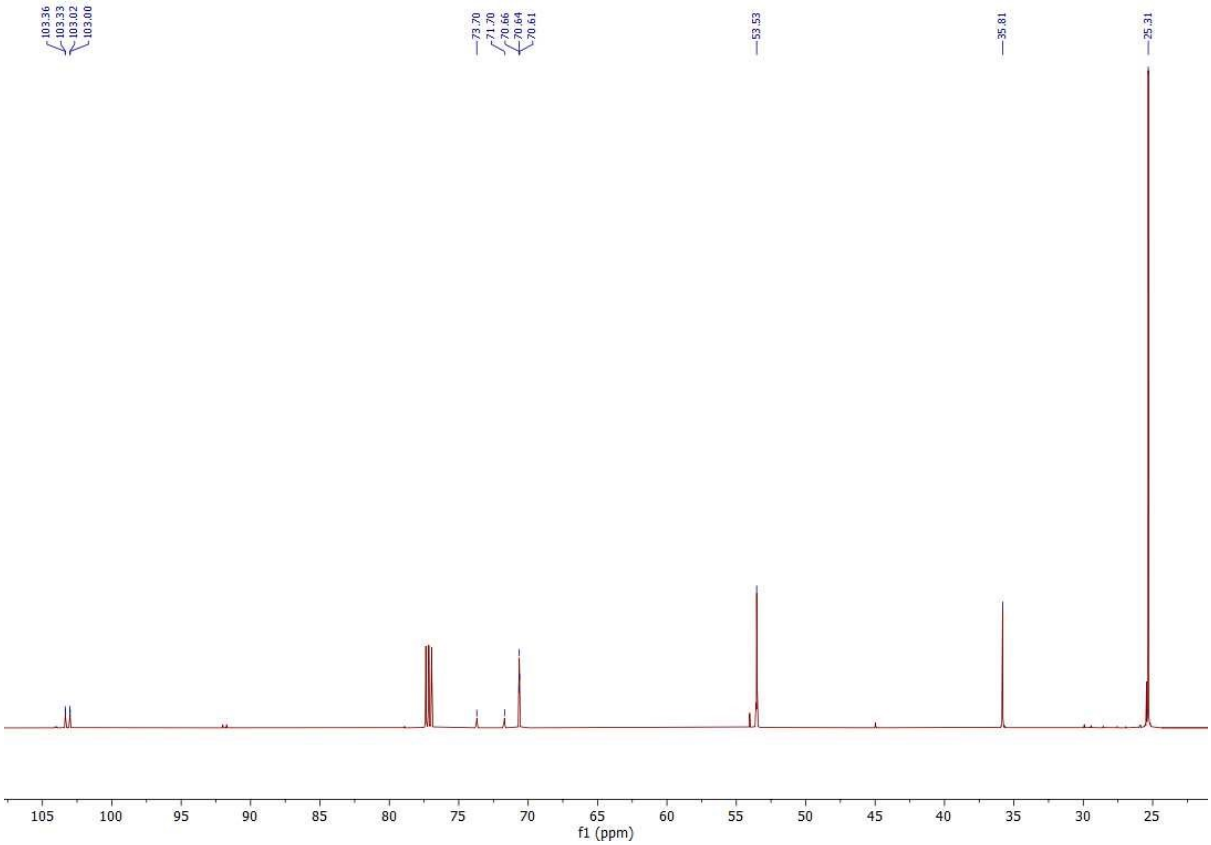
^{1}H NMR (300 MHz, $CDCl_3$)-**3d**:



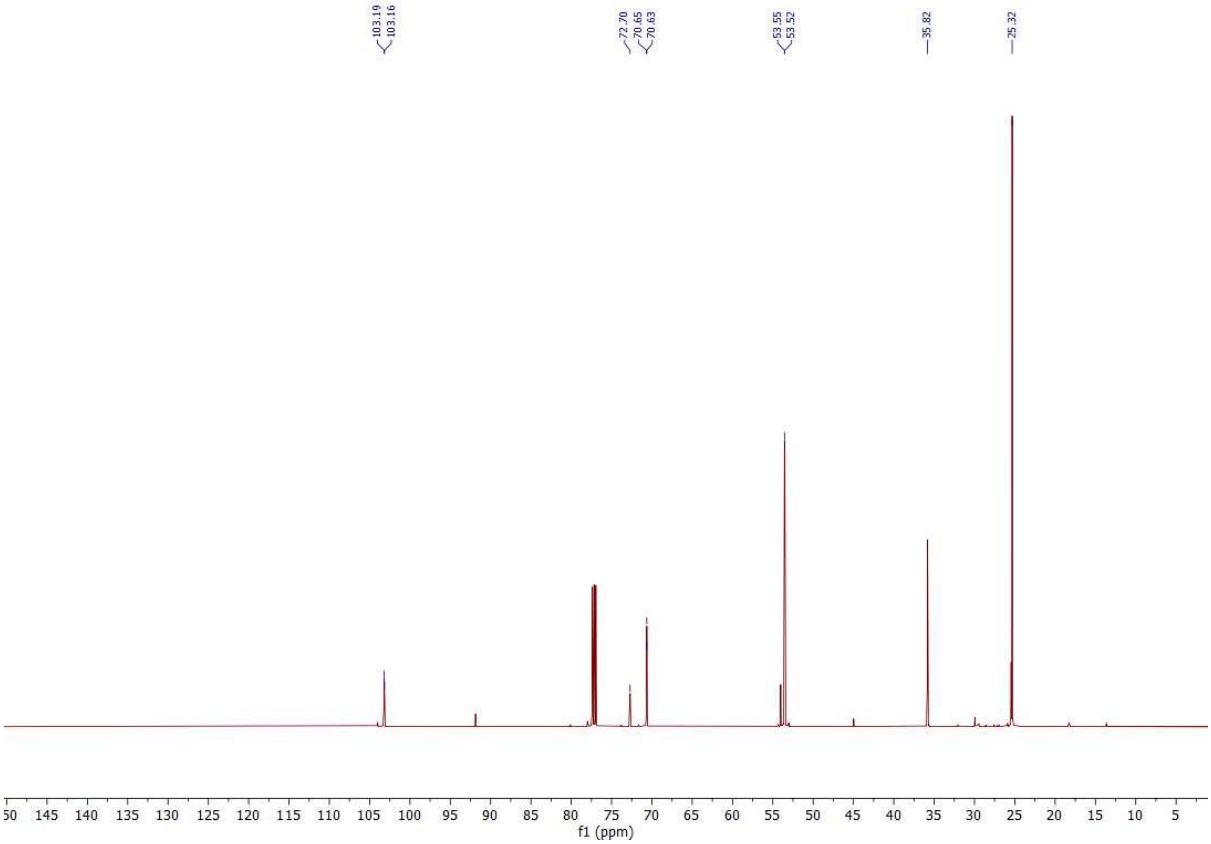
^{1}H{^{31}P} NMR ^{1}H NMR (300 MHz, $CDCl_3$)-**3d**:



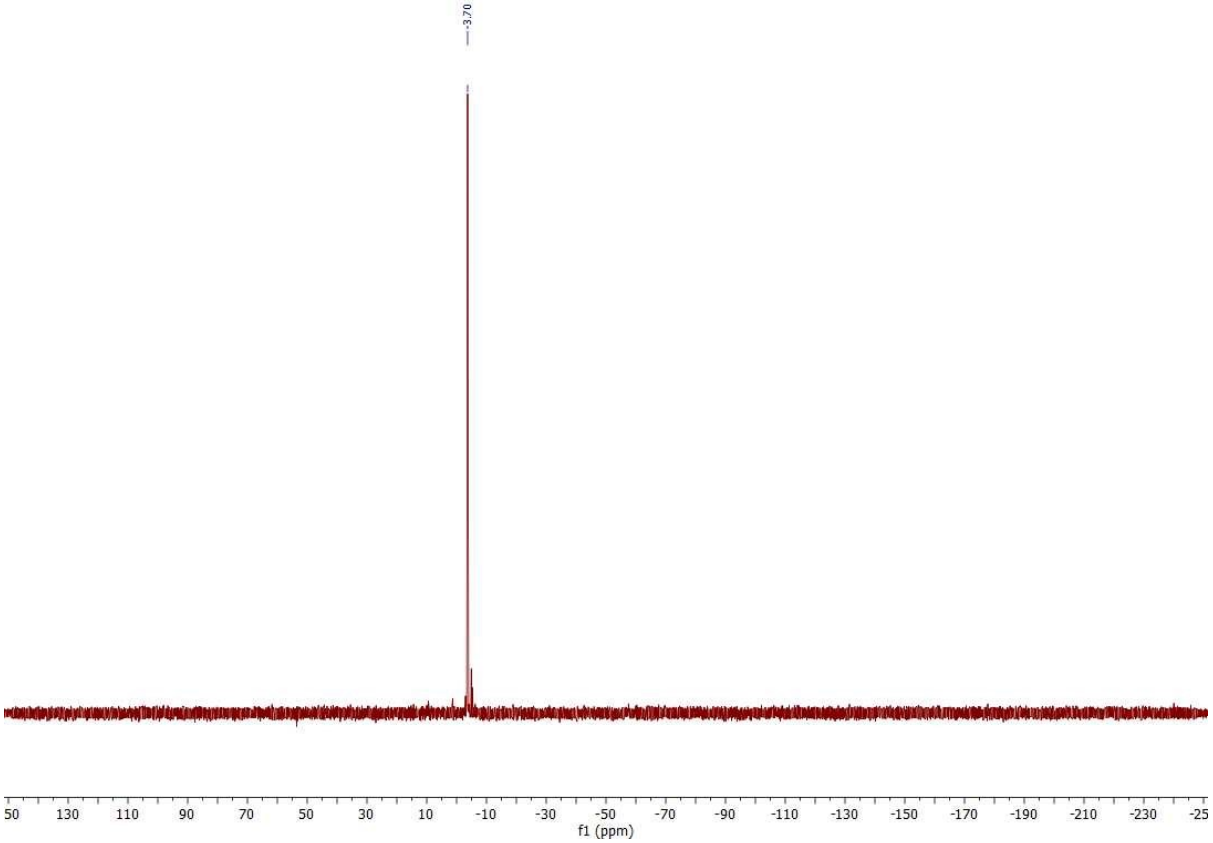
^{13}C NMR (151 MHz, $CDCl_3$)-**3d**:



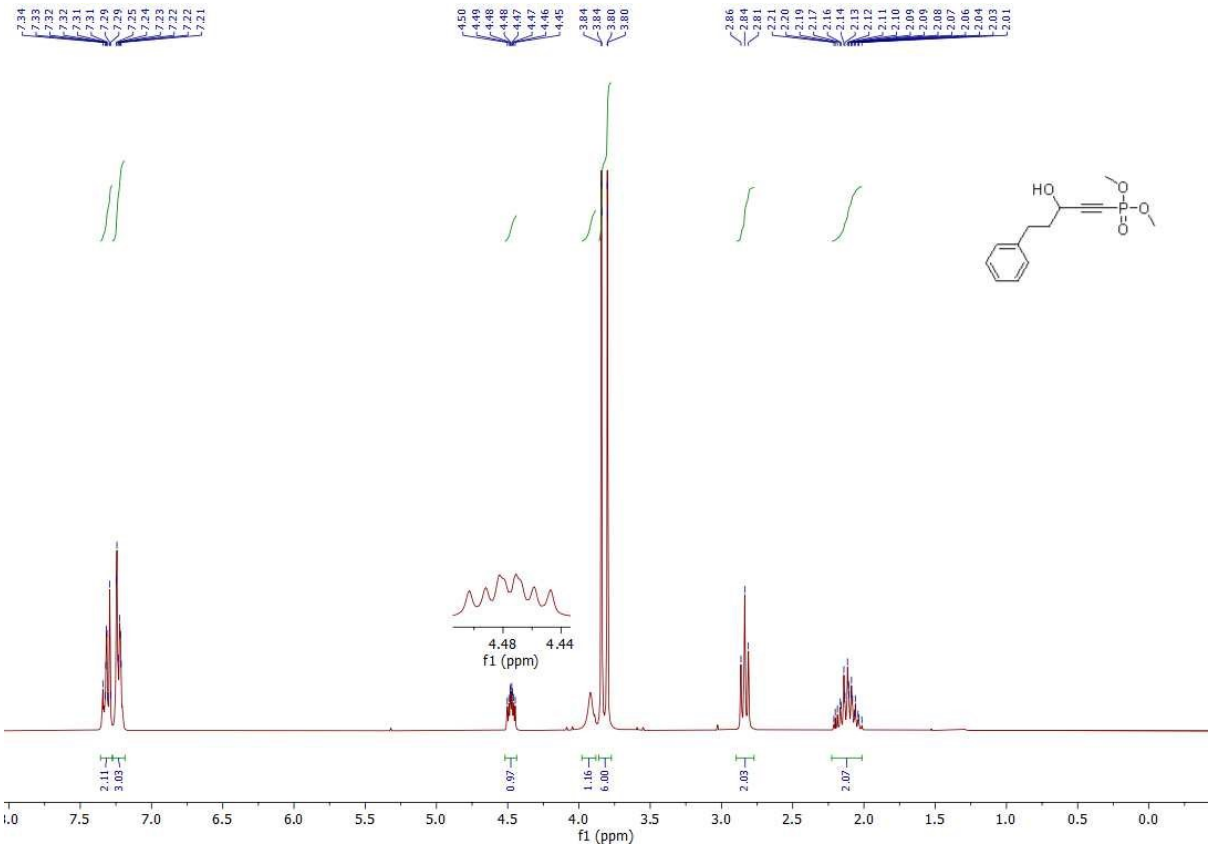
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3d**:



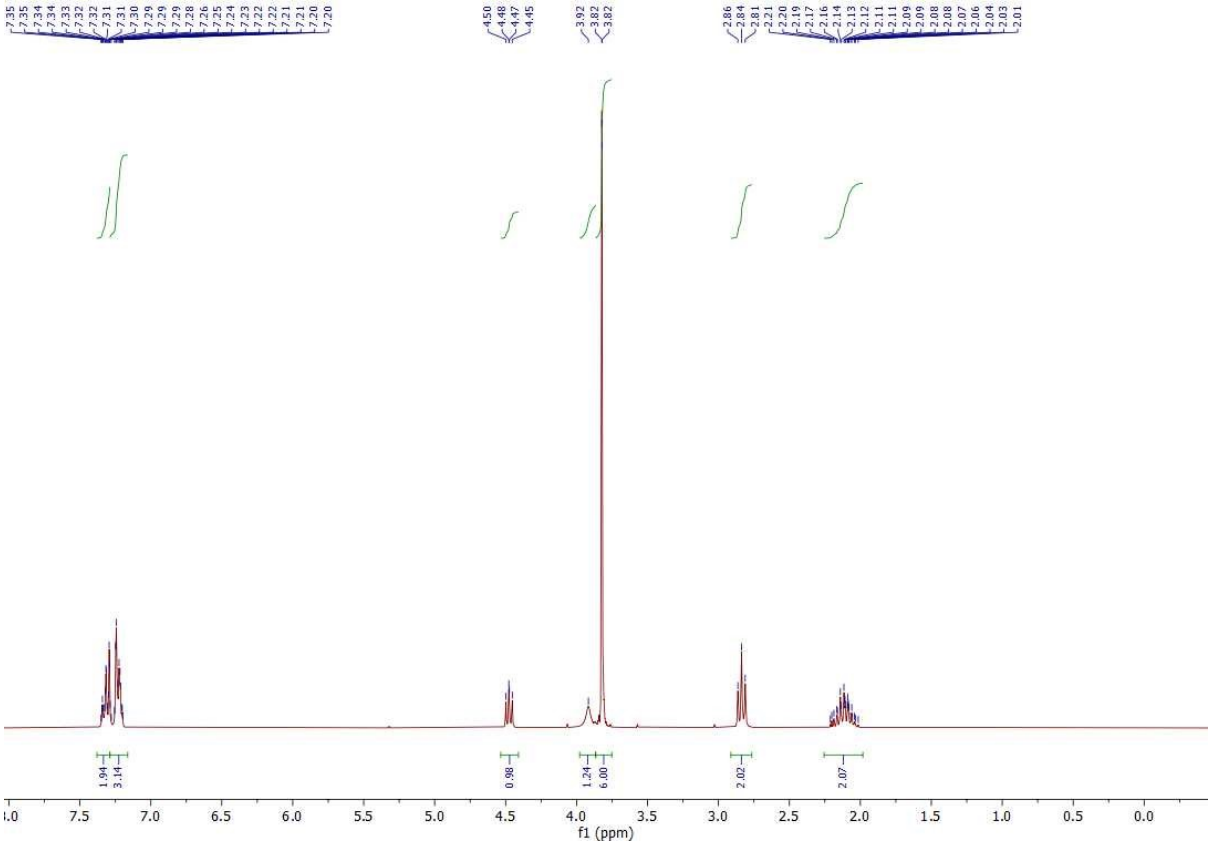
^{31}P NMR (121 MHz, $CDCl_3$)-**3d**:



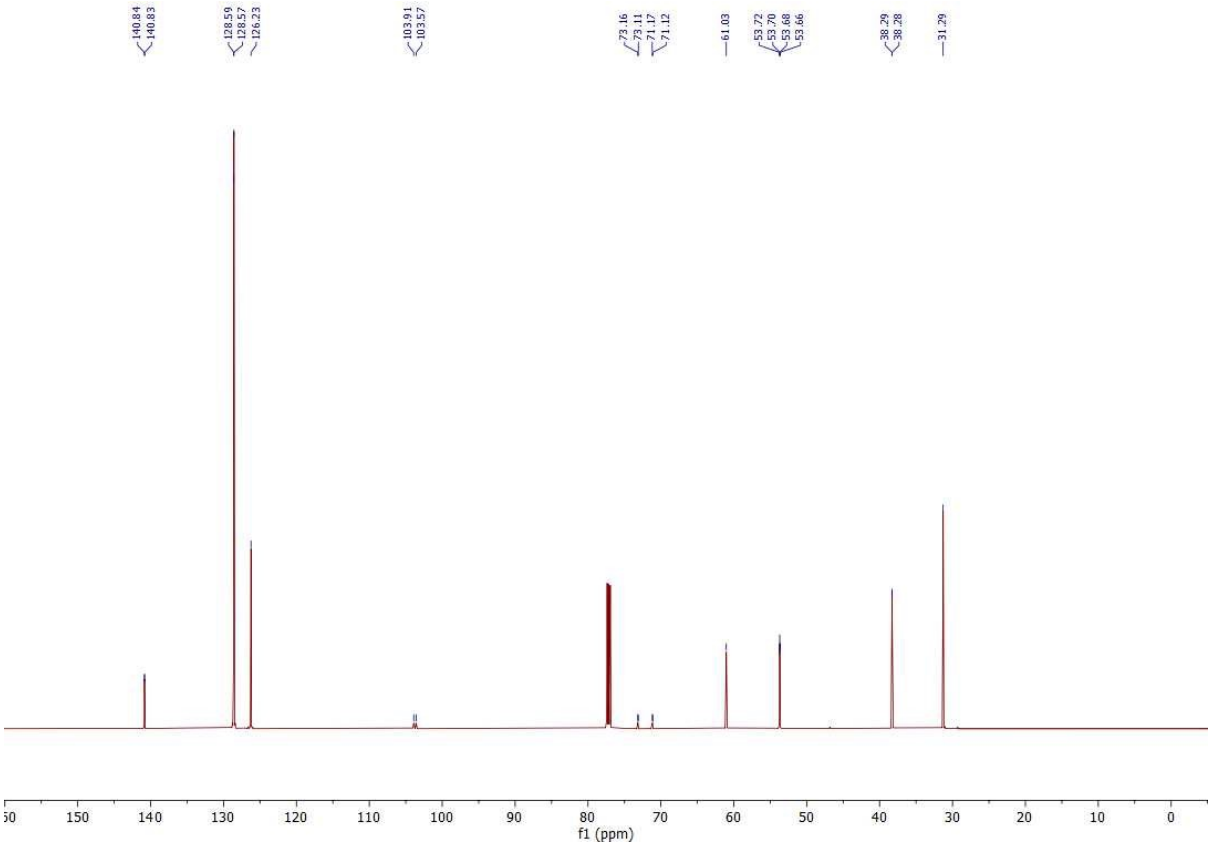
^{1}H NMR (300 MHz, $CDCl_3$)-**3e**:



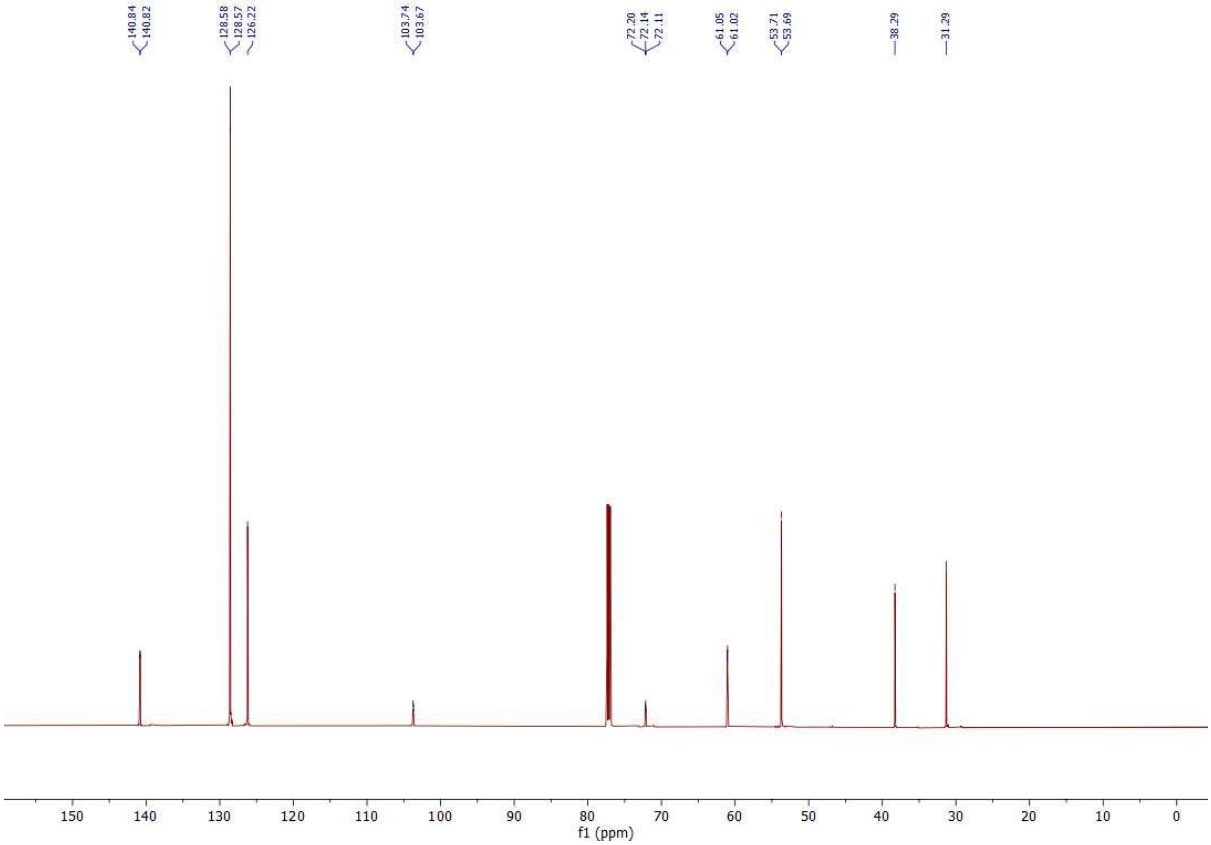
$^{1}H\{^{31}P\}$ (300 MHz, $CDCl_3$)-**3e**:



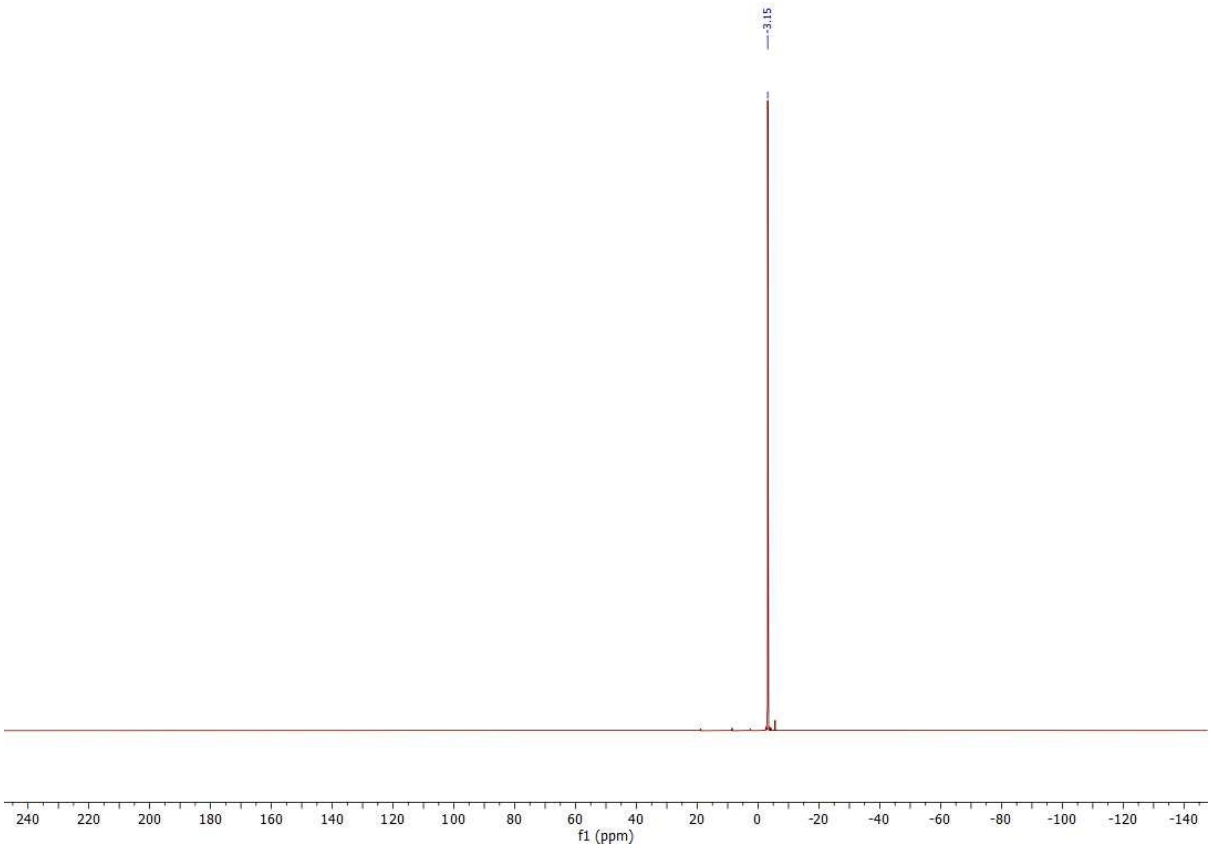
^{13}C NMR (151 MHz, $CDCl_3$)-**3e**:



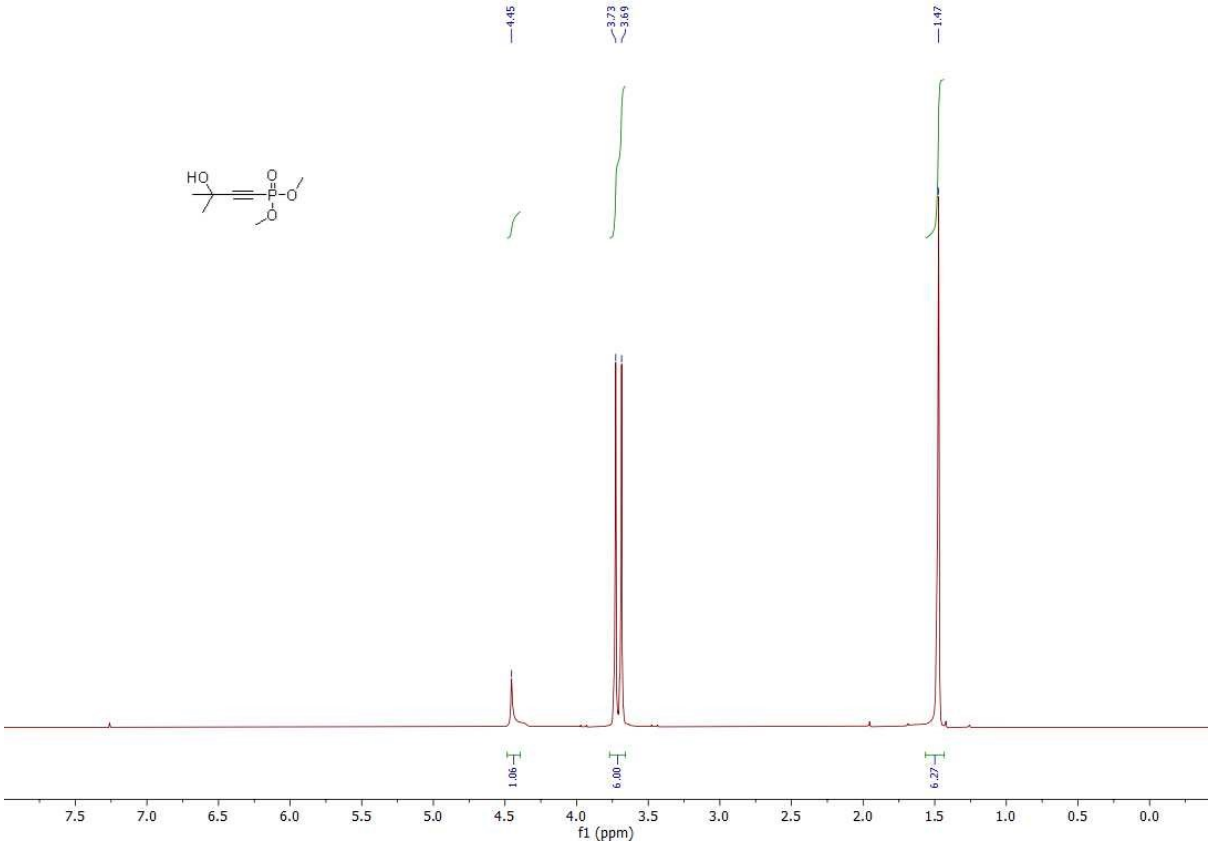
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3e**:



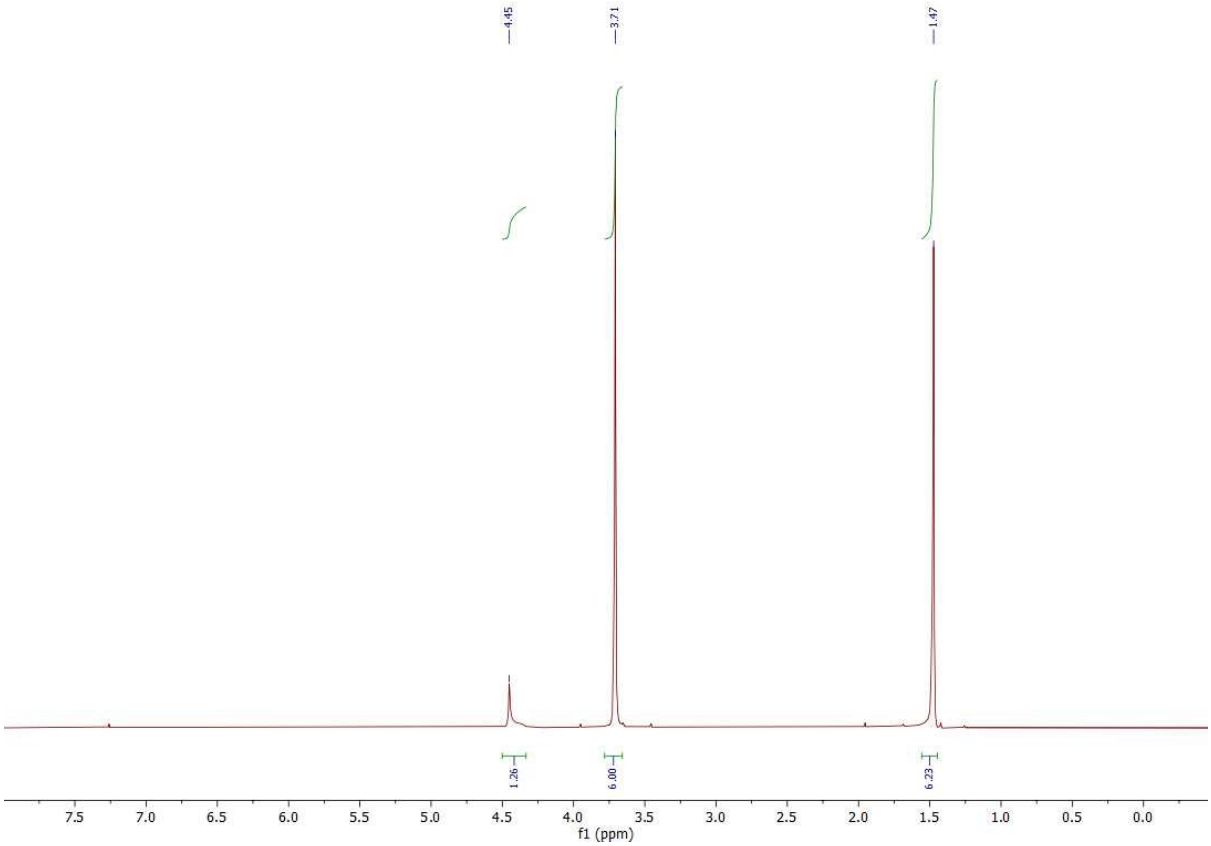
^{31}P NMR (121 MHz, $CDCl_3$)-**3e**:



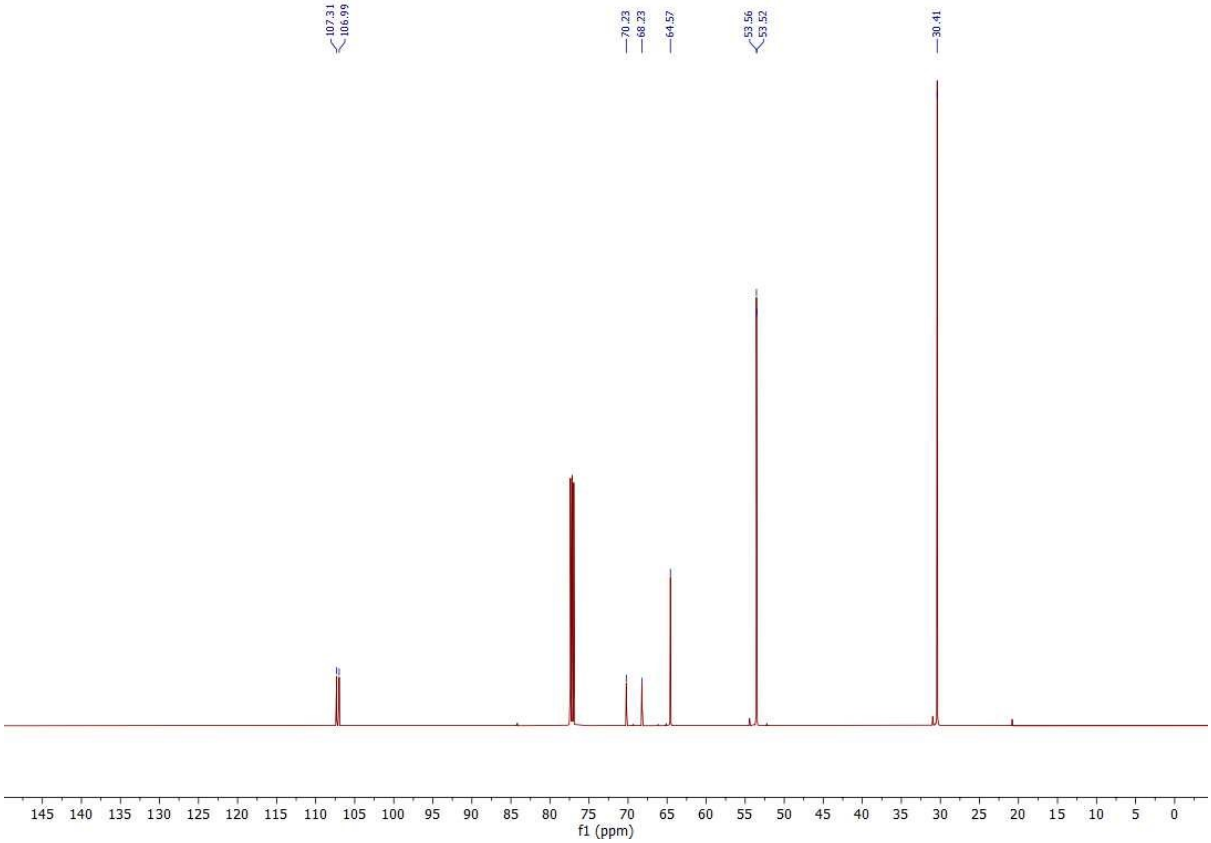
^{1}H NMR (300 MHz, $CDCl_3$)-**3f**:



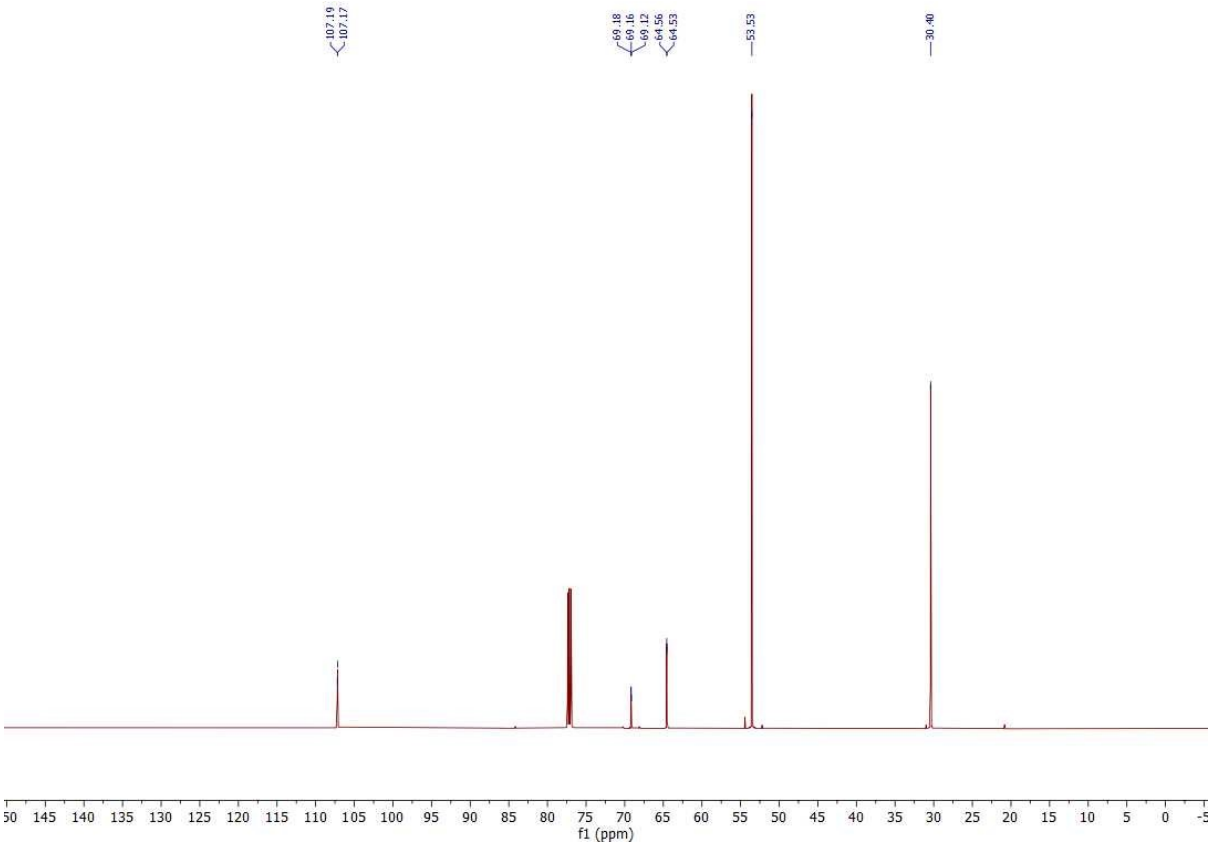
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**3f**:



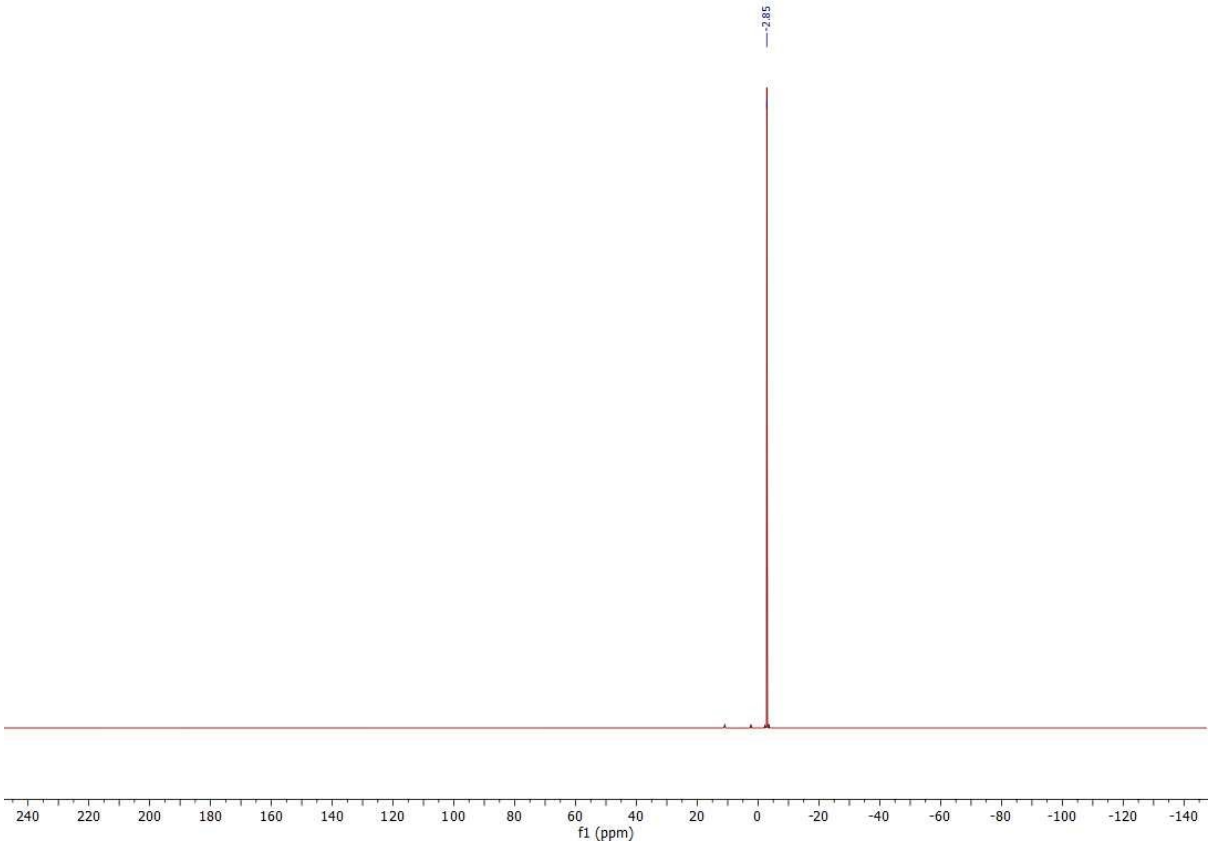
^{13}C NMR (151 MHz, $CDCl_3$)-**3f**:



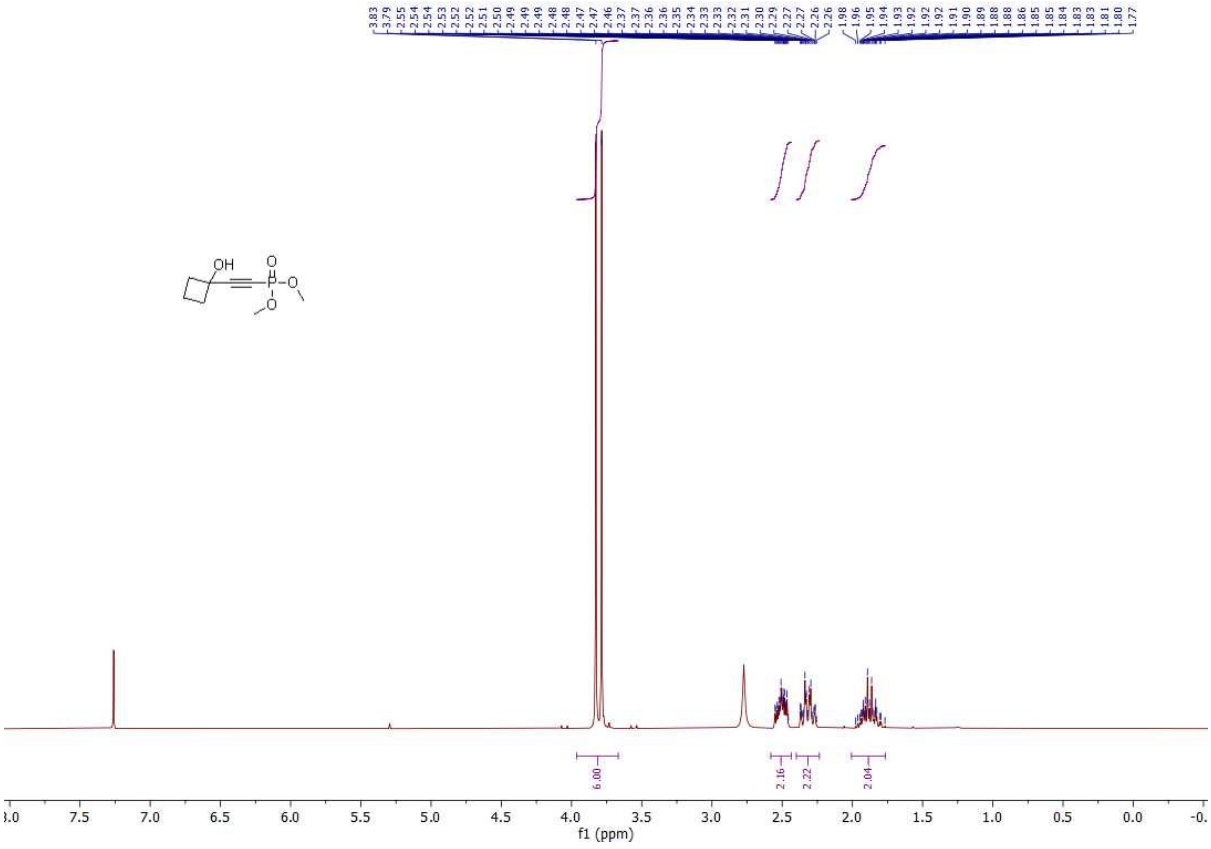
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3f**:



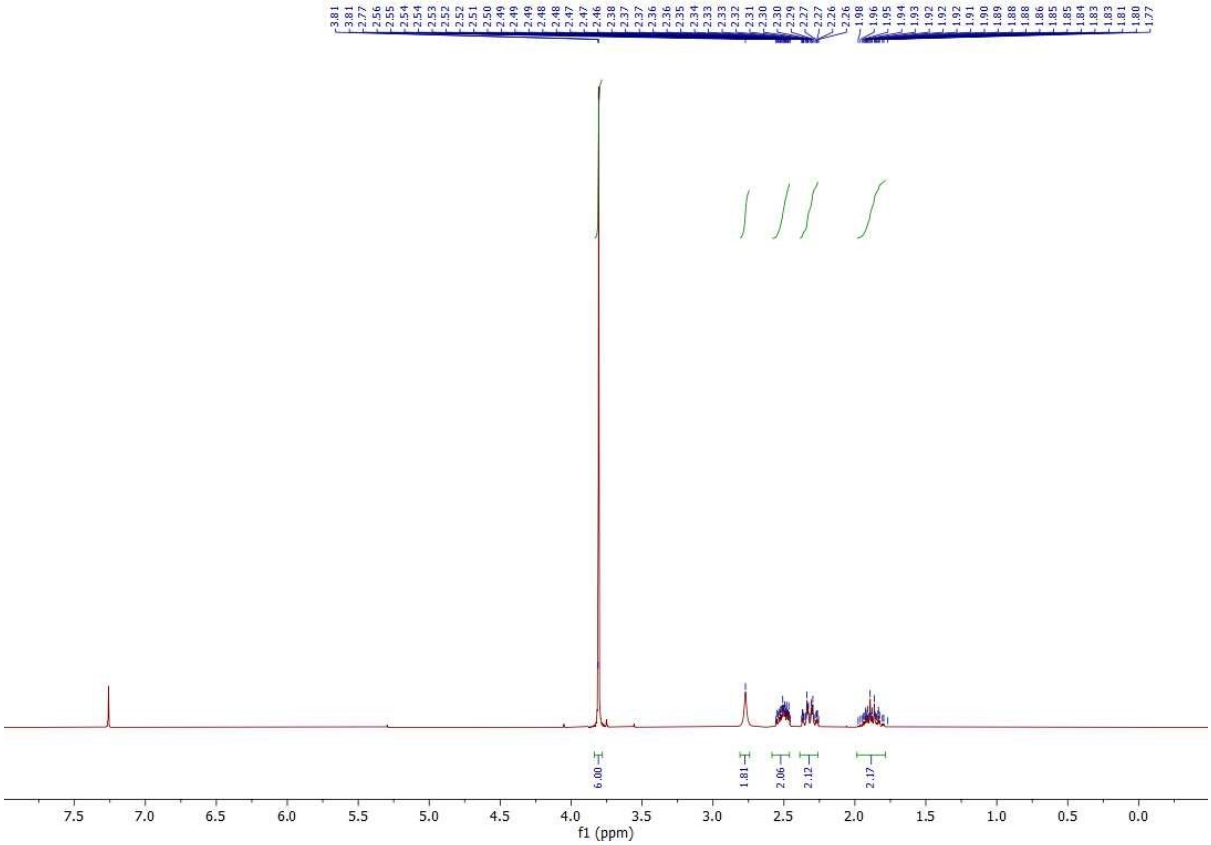
^{31}P NMR (121 MHz, $CDCl_3$)-**3f**:



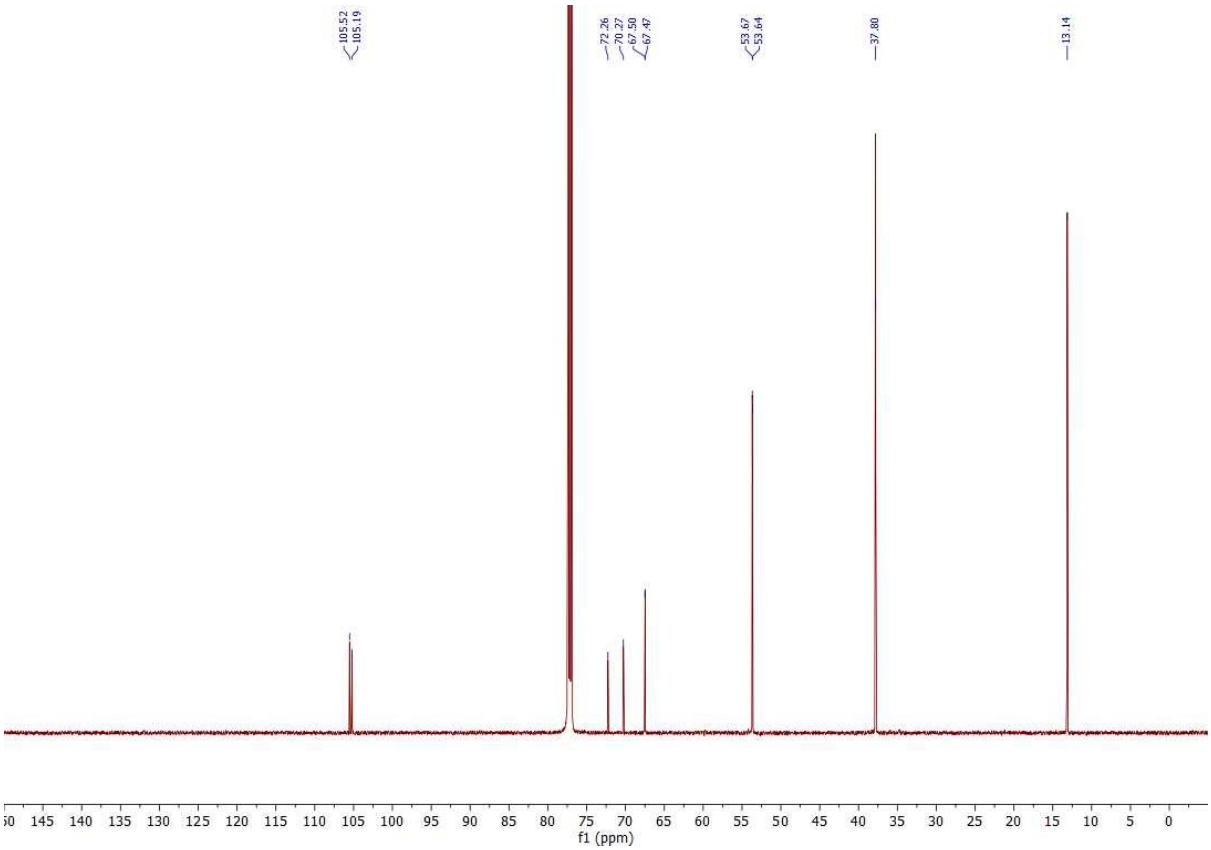
^{1}H NMR (300 MHz, $CDCl_3$)-**3g**:



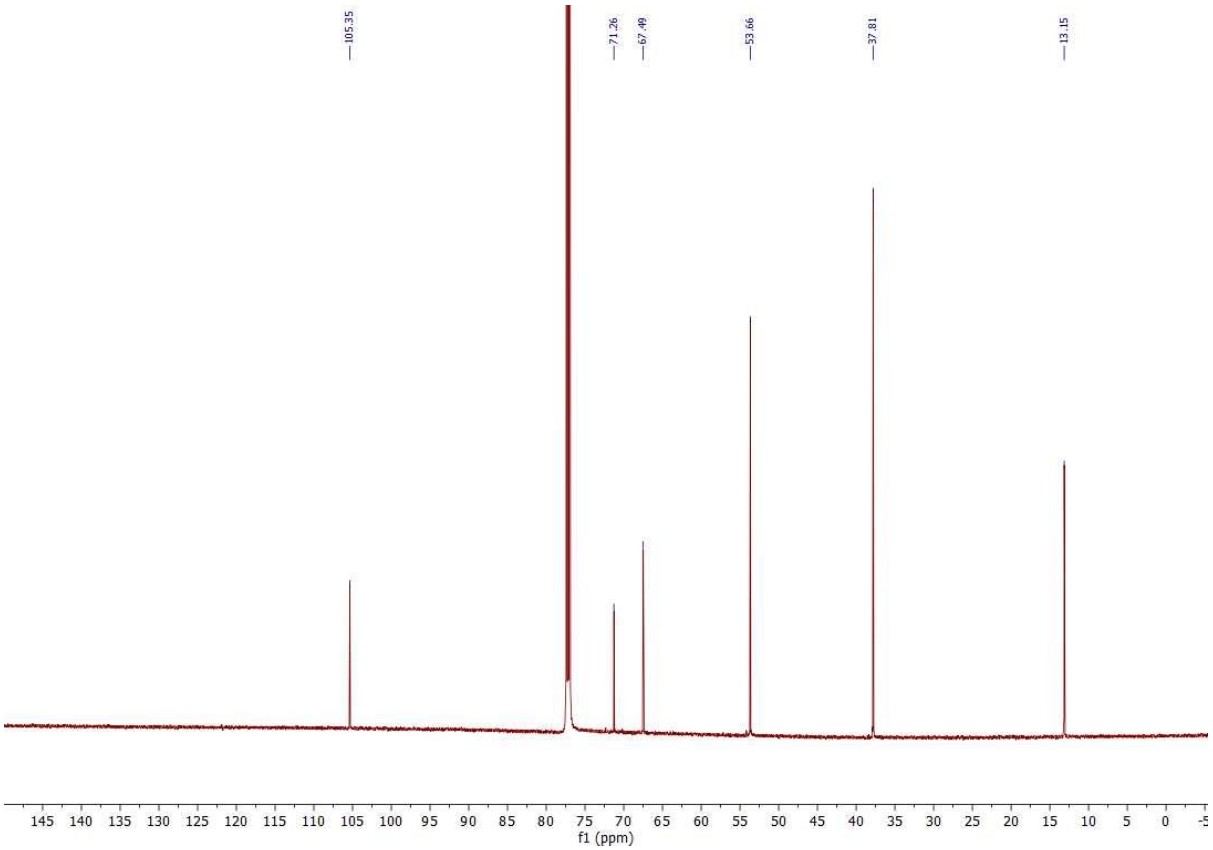
$^{1}H\{^{31}P\}$ ^{1}H NMR (300 MHz, $CDCl_3$)-**3g**:



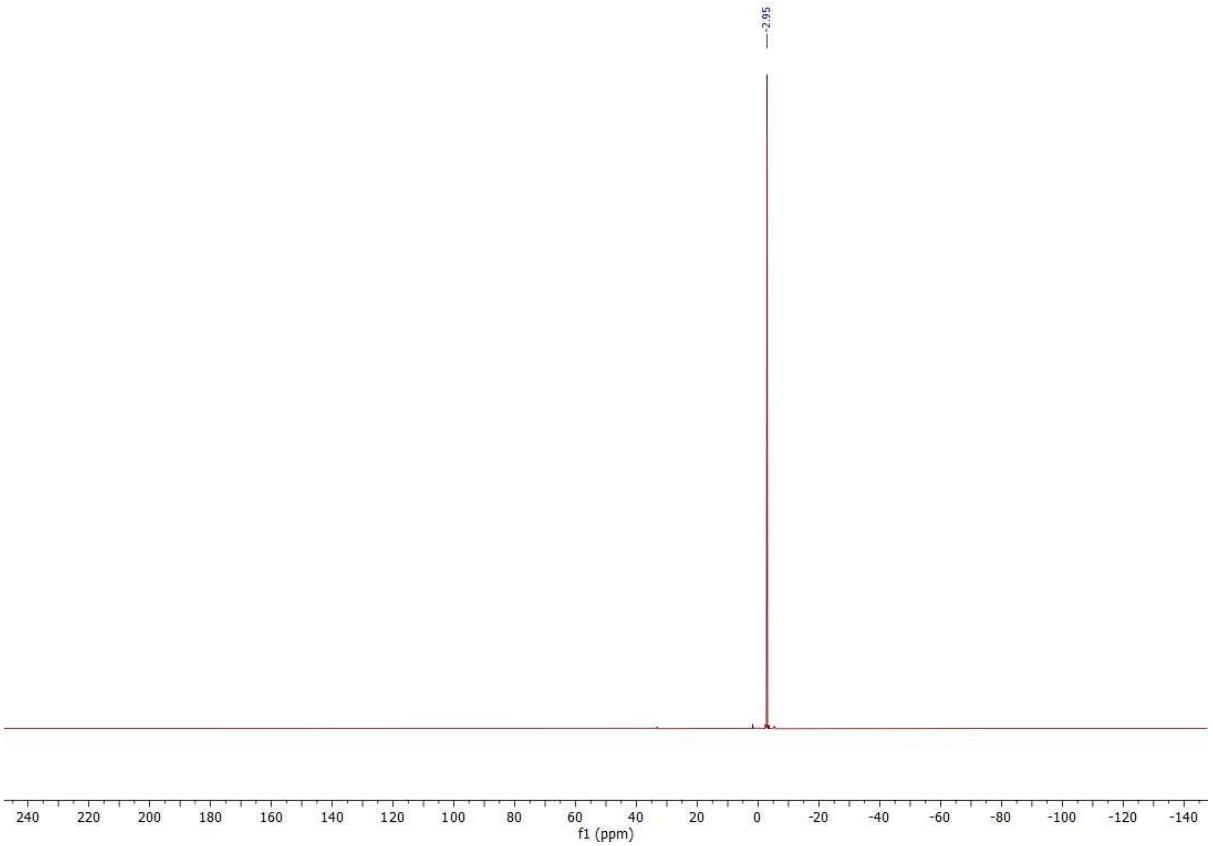
^{13}C NMR (151 MHz, $CDCl_3$)-**3g**:



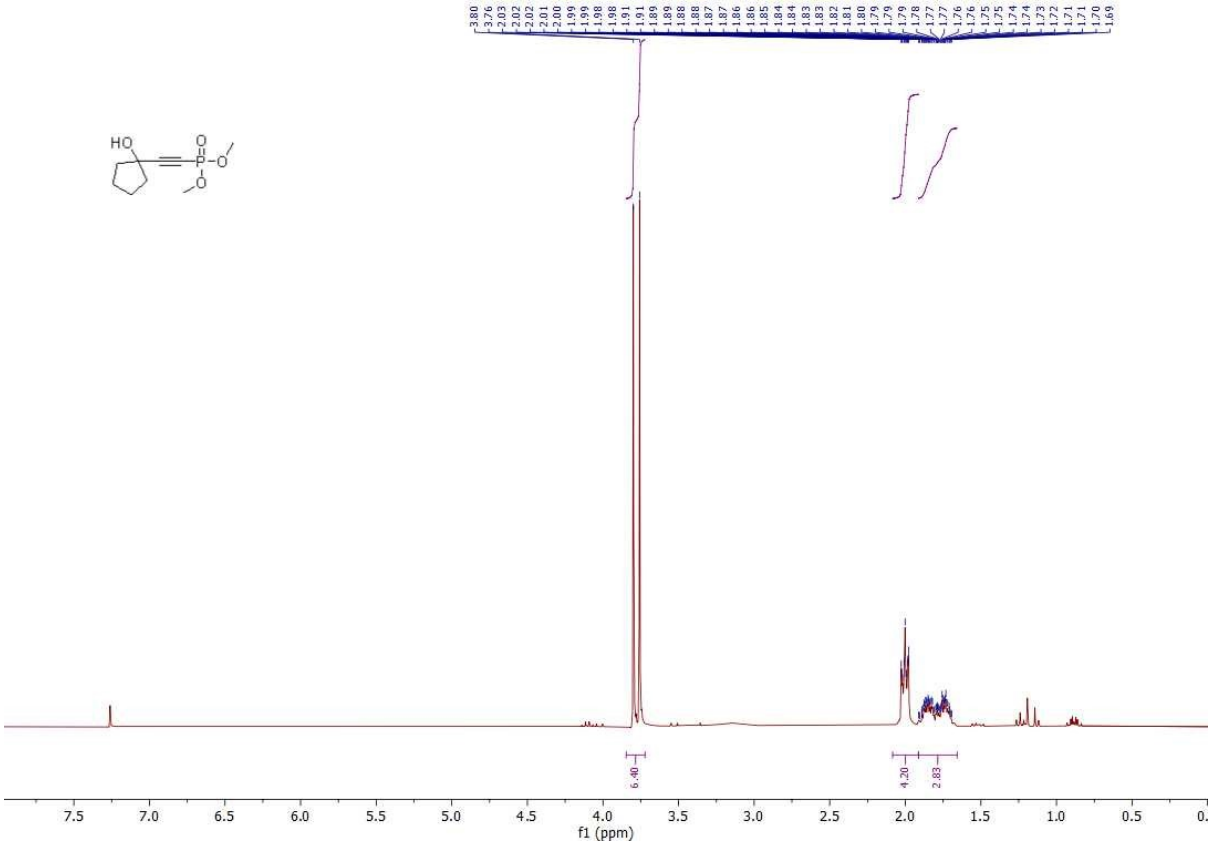
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3g**:



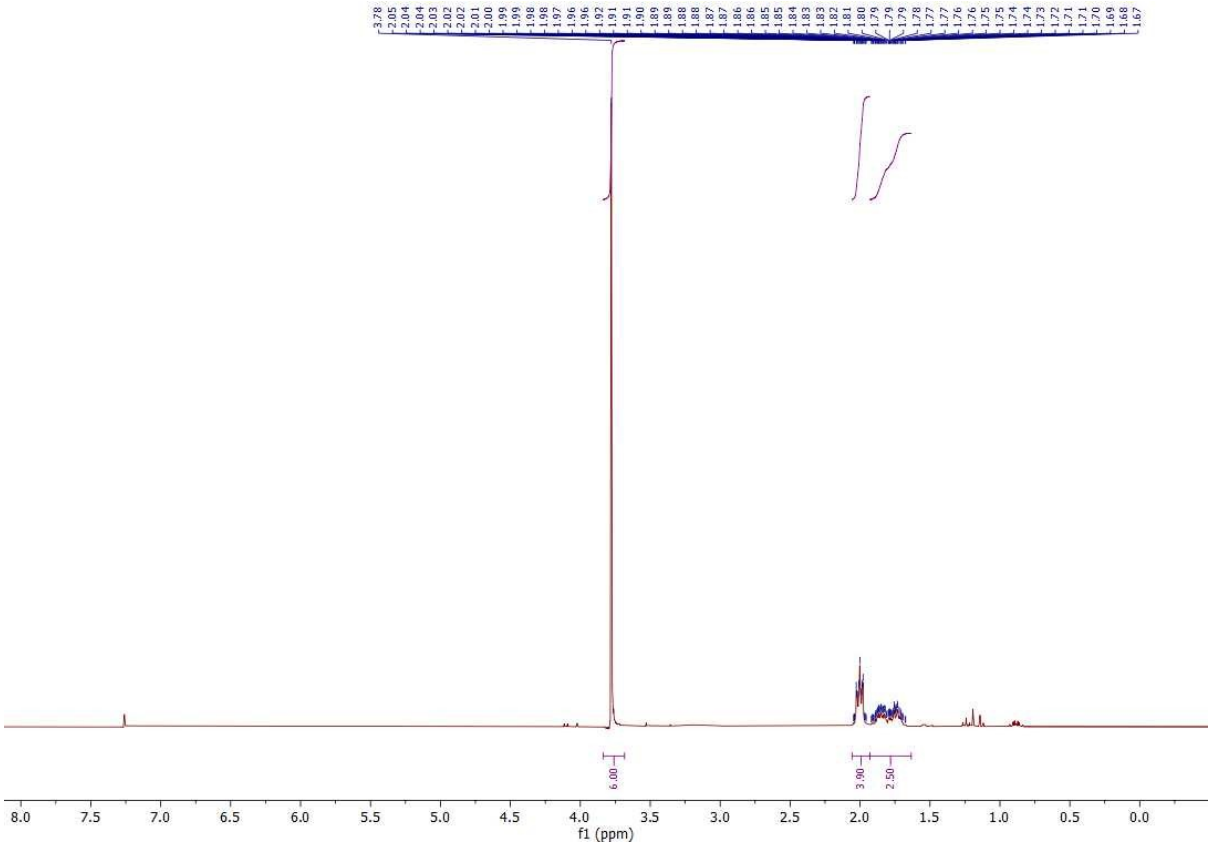
^{31}P NMR (121 MHz, $CDCl_3$)-**3g**:



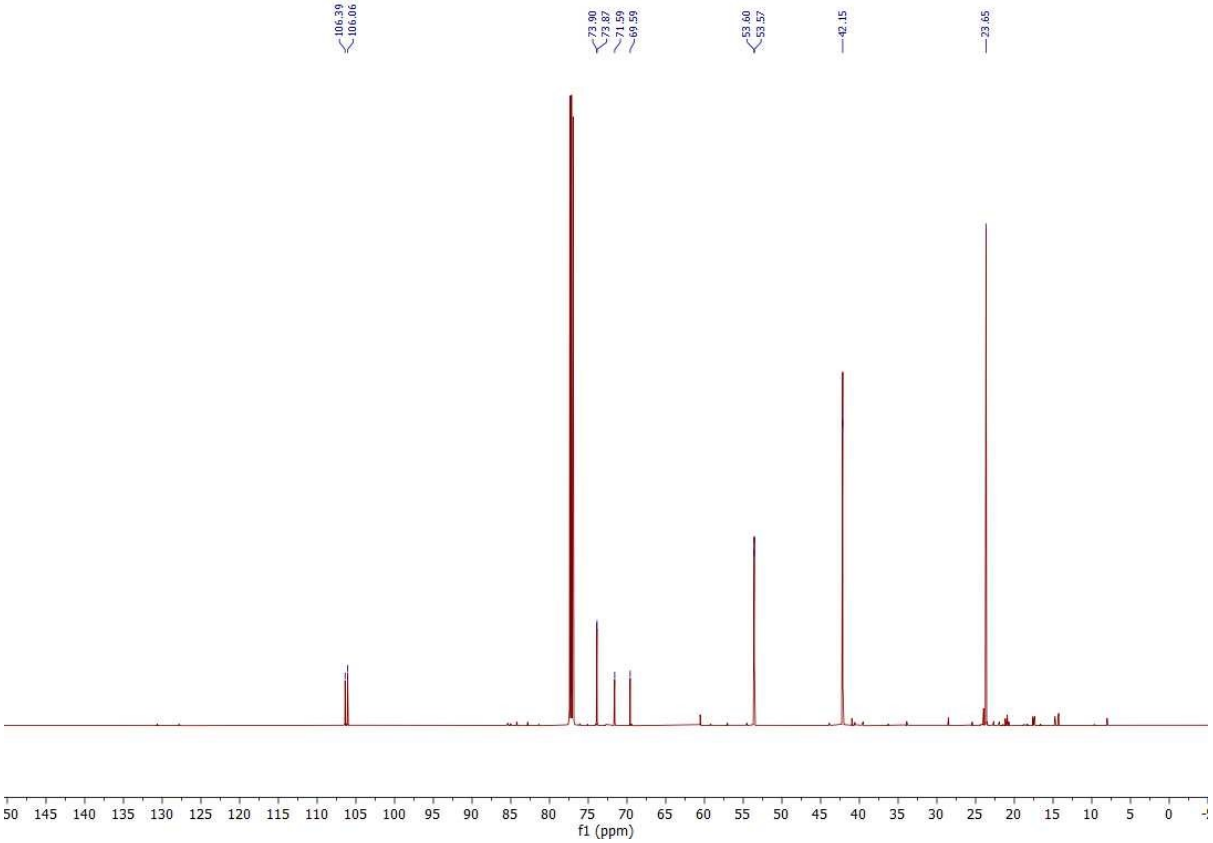
^{1}H NMR (300 MHz, $CDCl_3$)-**3h**:



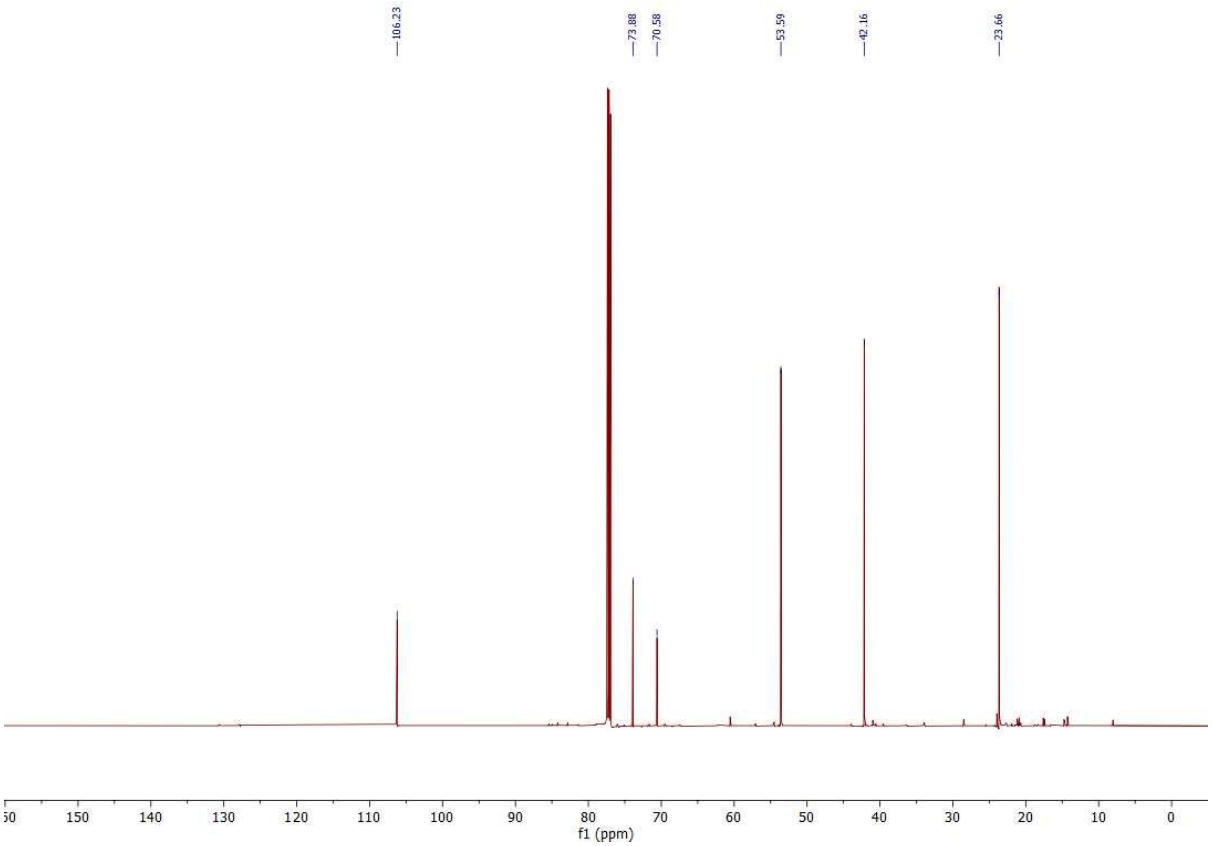
$^{1}H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$)-**3h**:



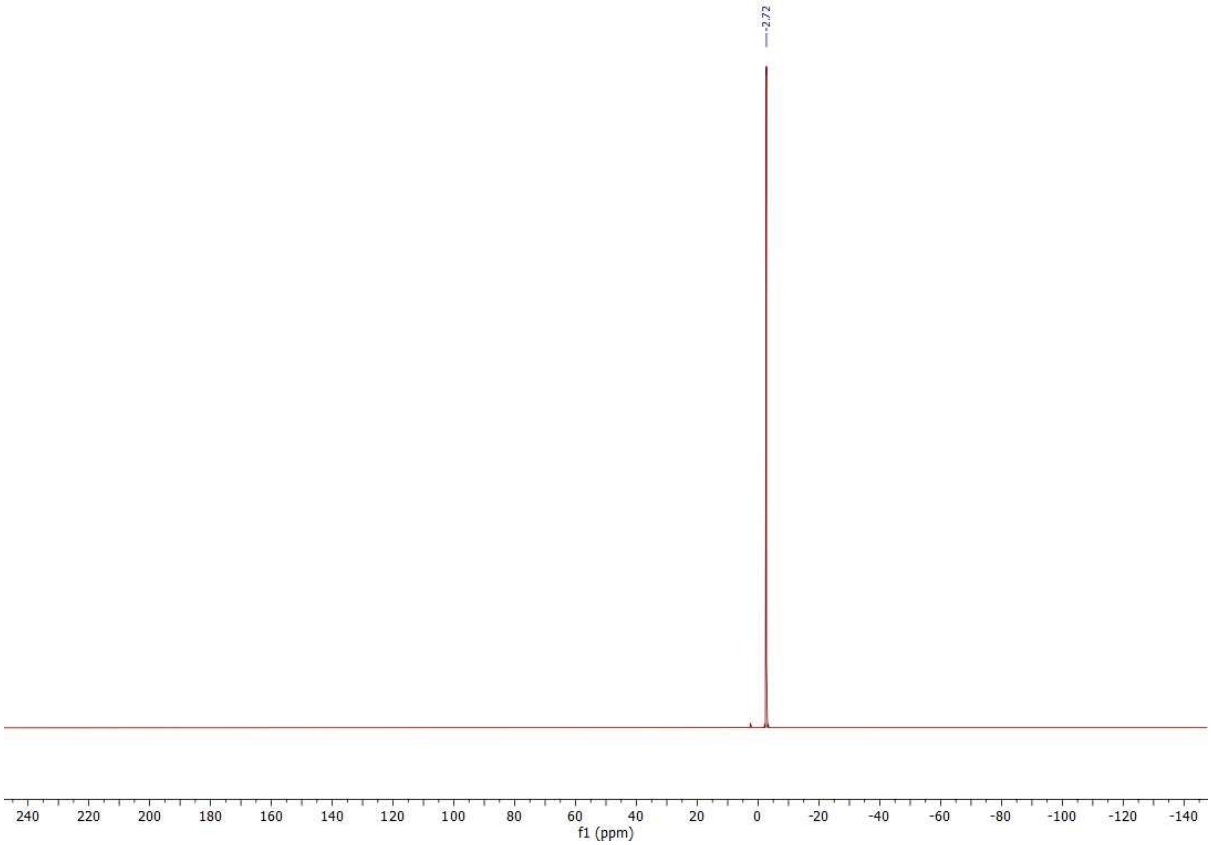
^{13}C NMR (151 MHz, $CDCl_3$)-**3h**:



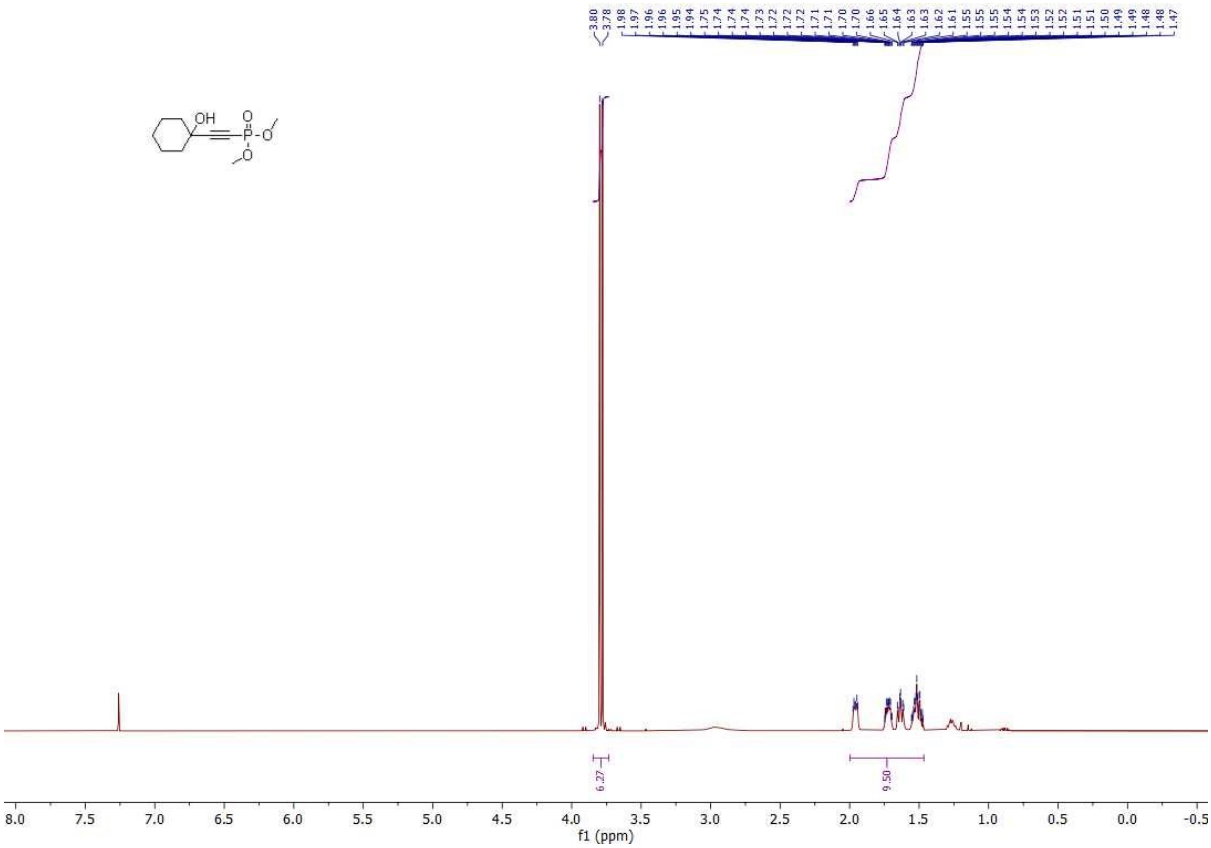
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3h**:



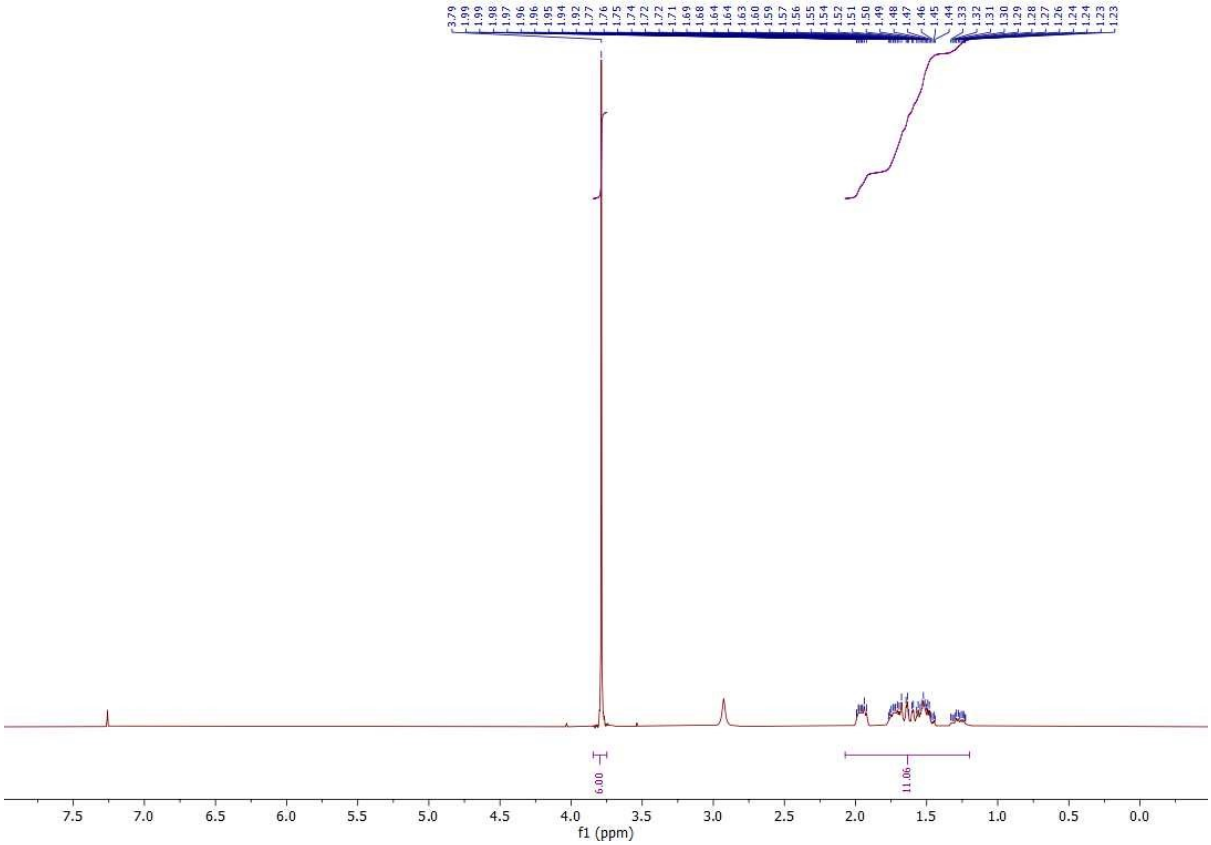
^{31}P NMR (121 MHz, $CDCl_3$)-**3h**:



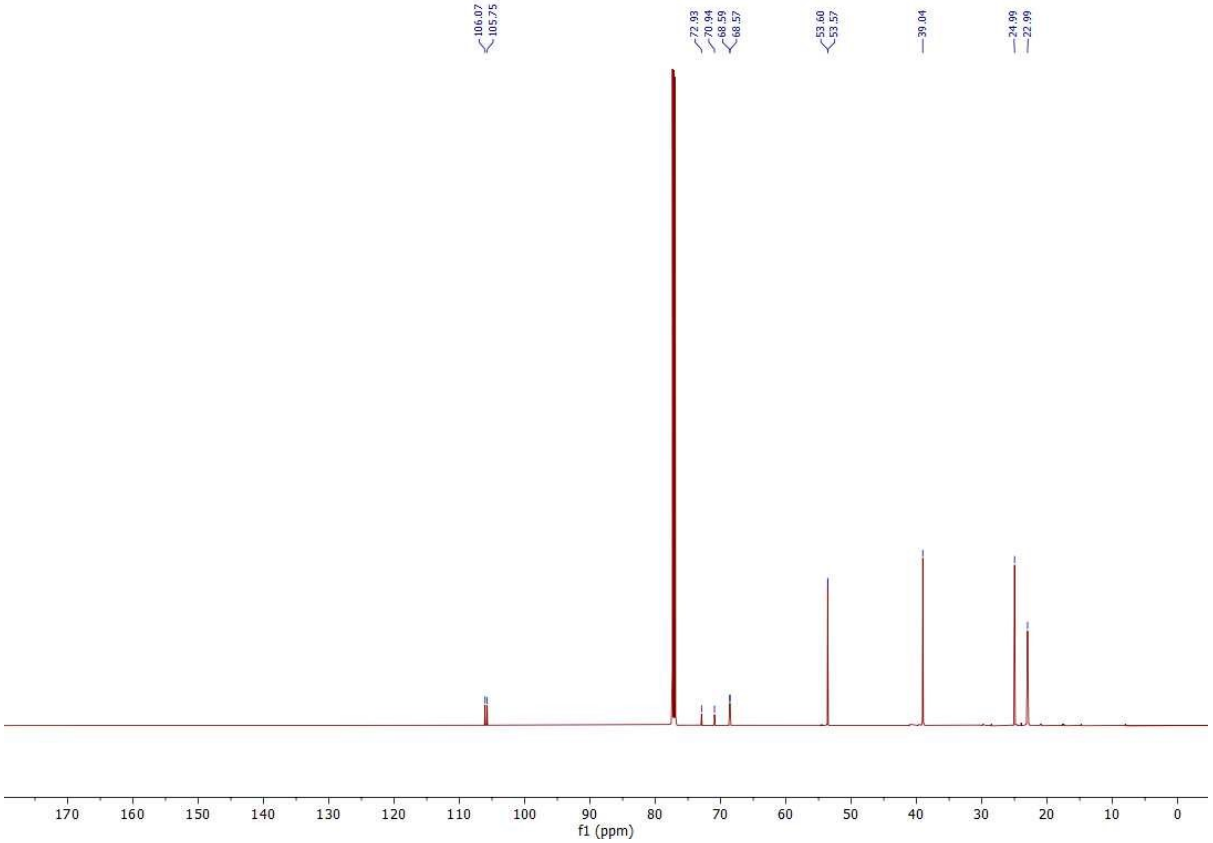
^{1}H (600 MHz, $CDCl_3$)-**3i**:



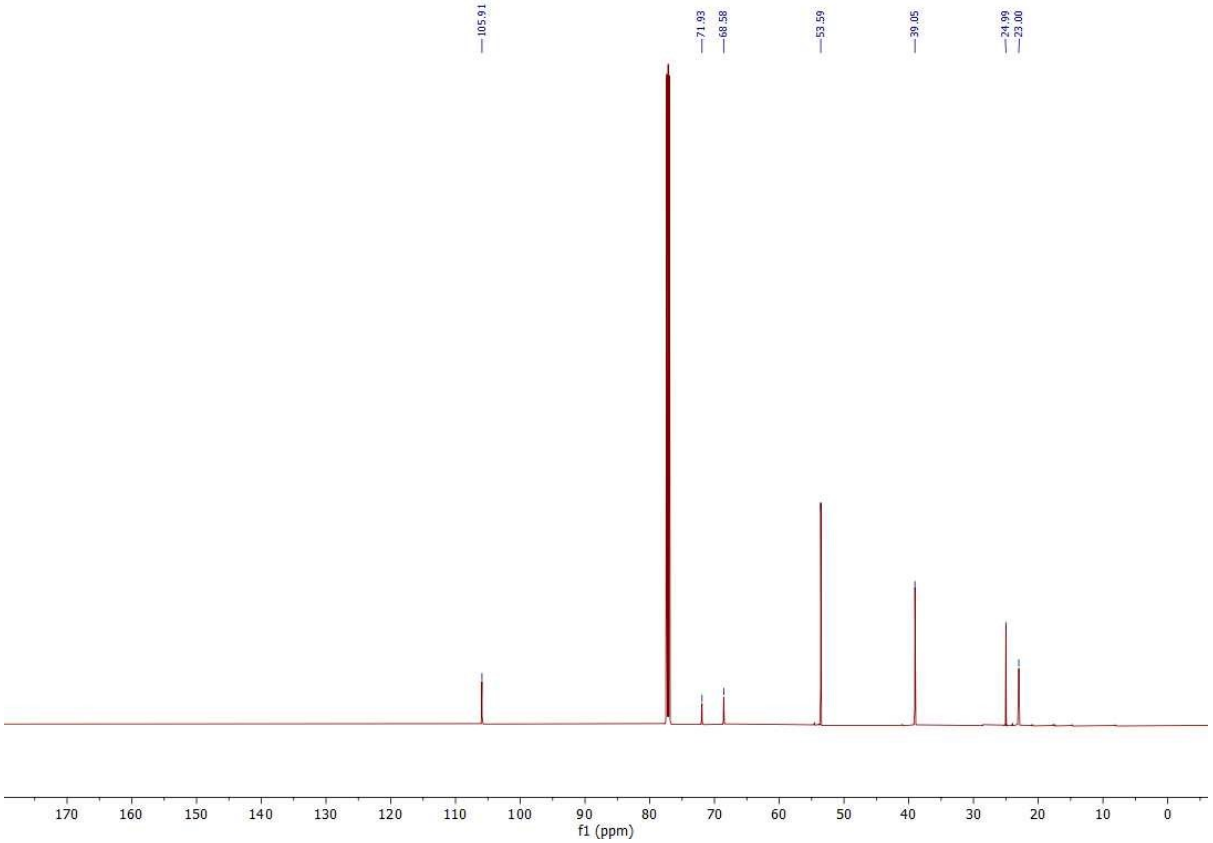
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**3i**:



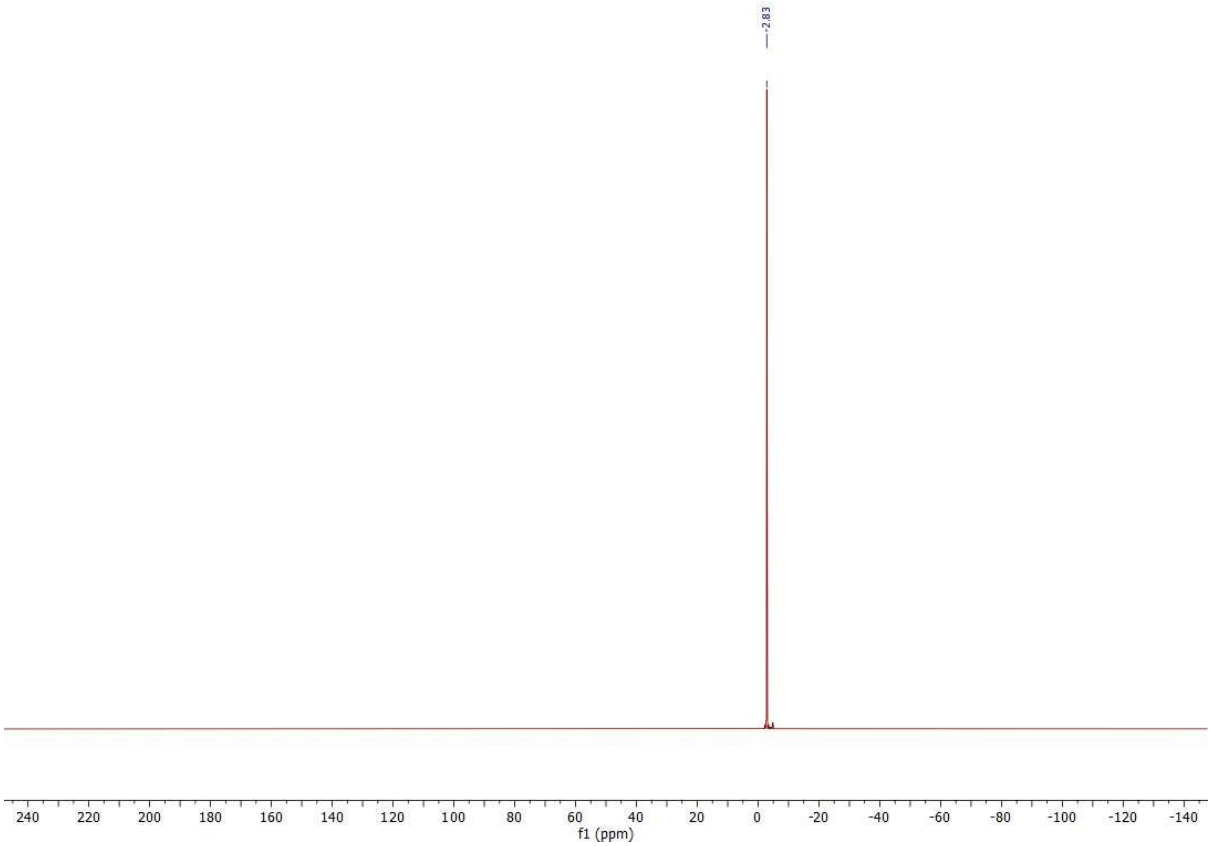
^{13}C NMR (151 MHz, $CDCl_3$)-**3i**:



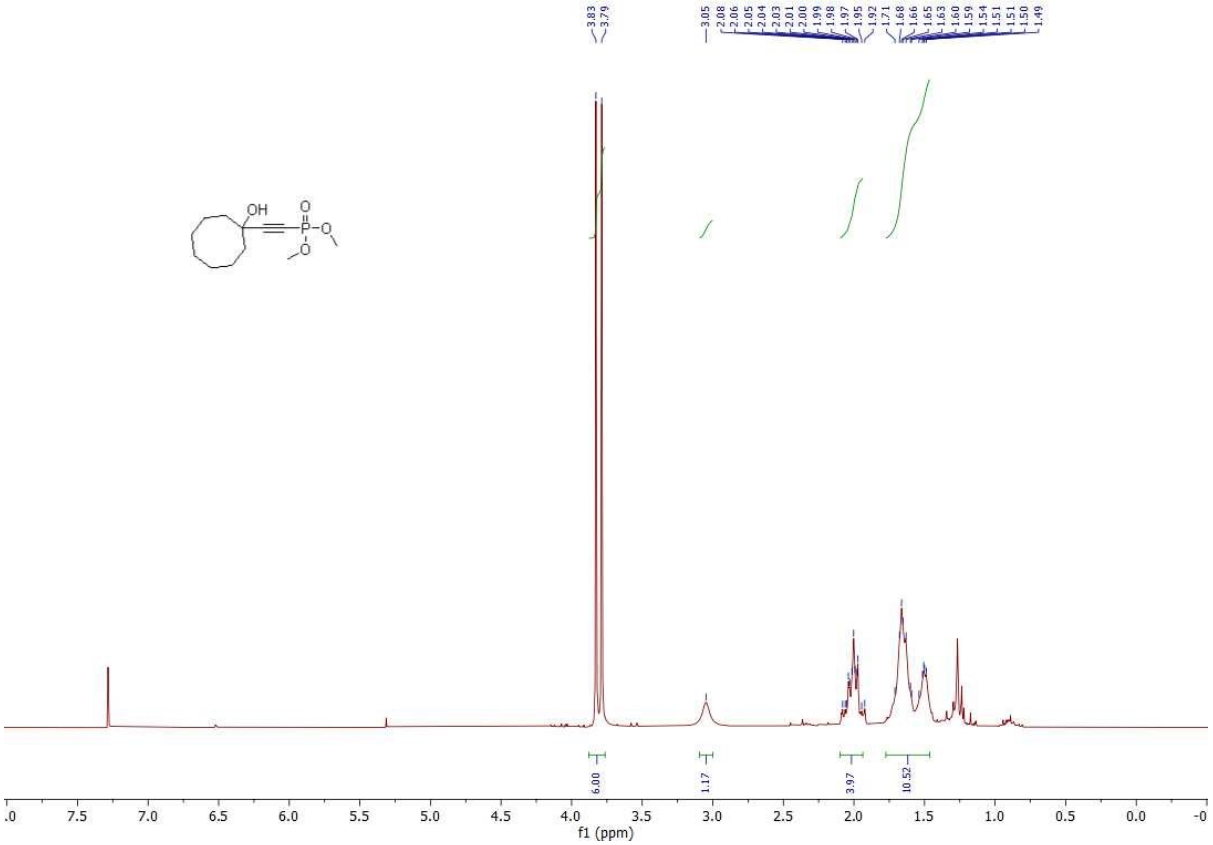
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3i**:



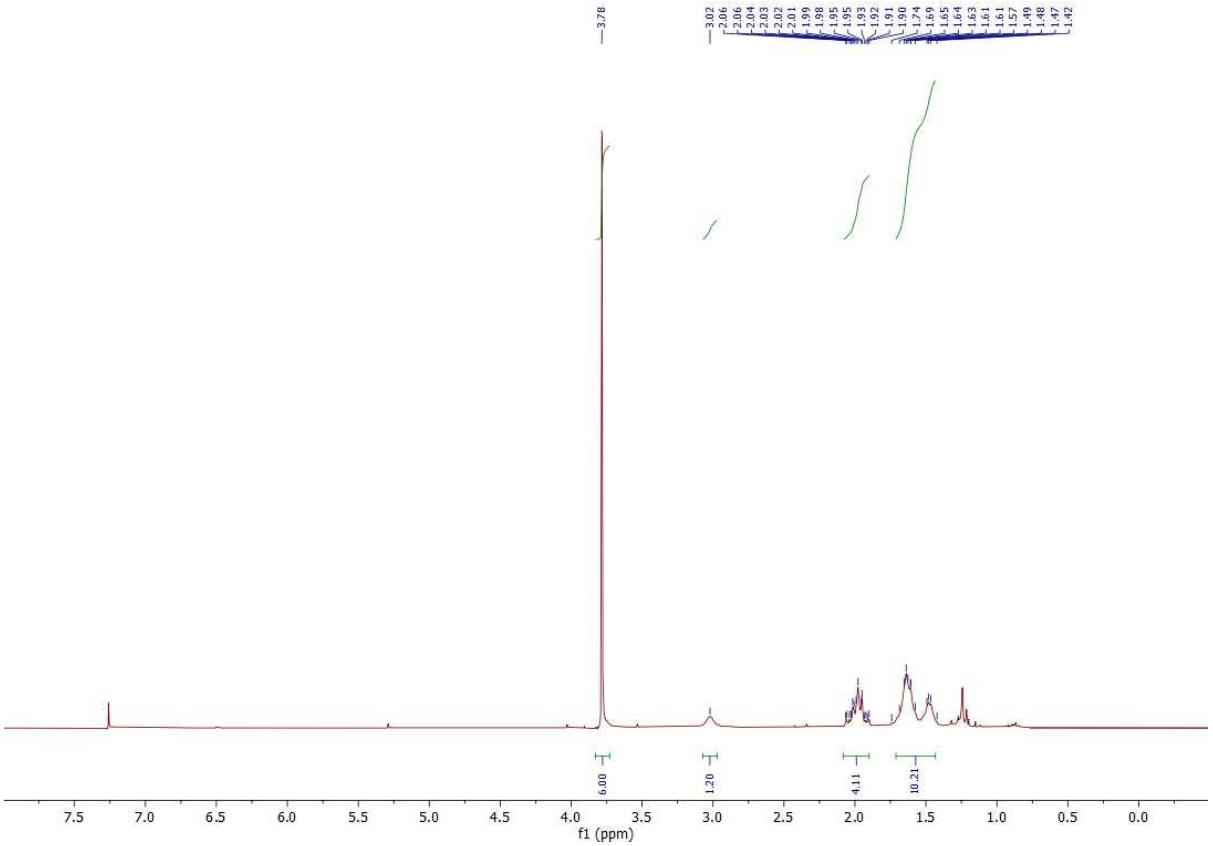
^{31}P NMR (121 MHz, $CDCl_3$)-**3i**:



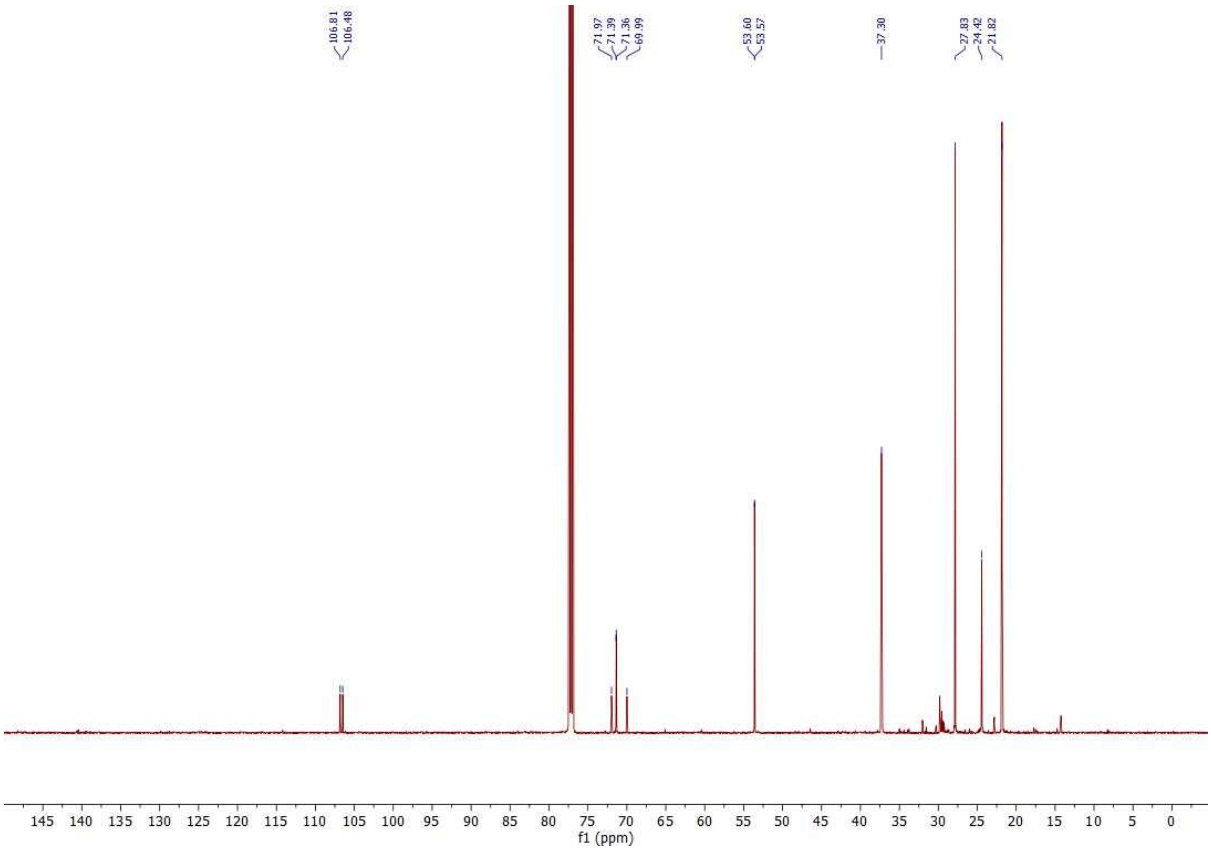
^{1}H NMR (300 MHz, $CDCl_3$)-**3j**:



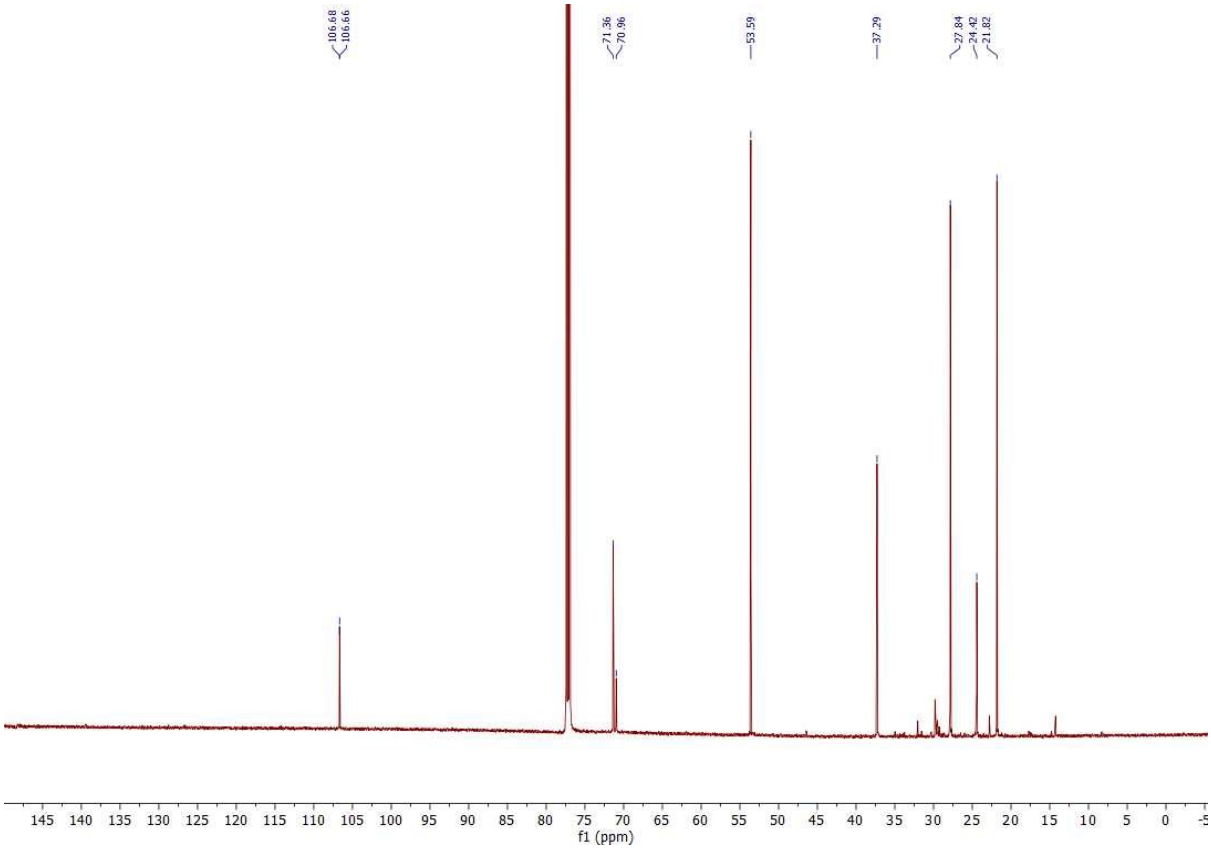
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**3j**:



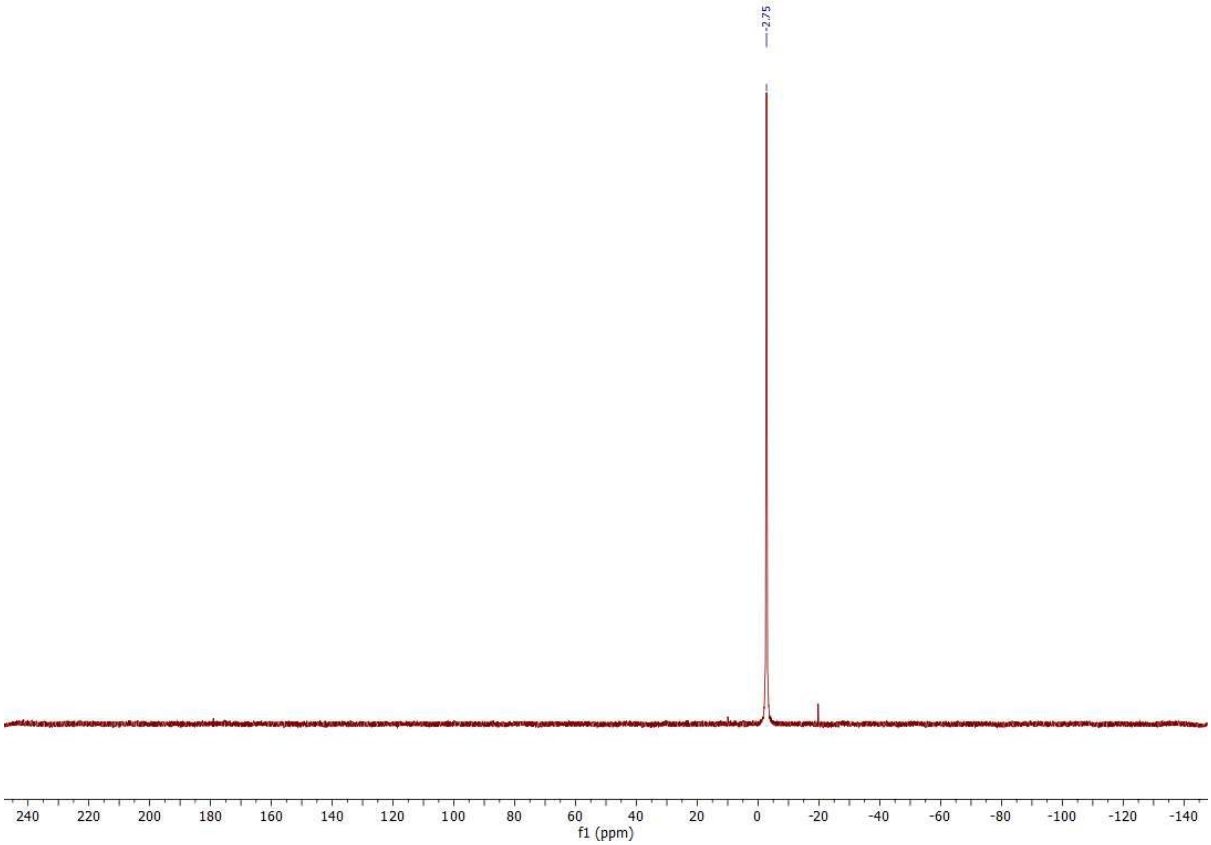
^{13}C NMR (151 MHz, $CDCl_3$)-**3j**:



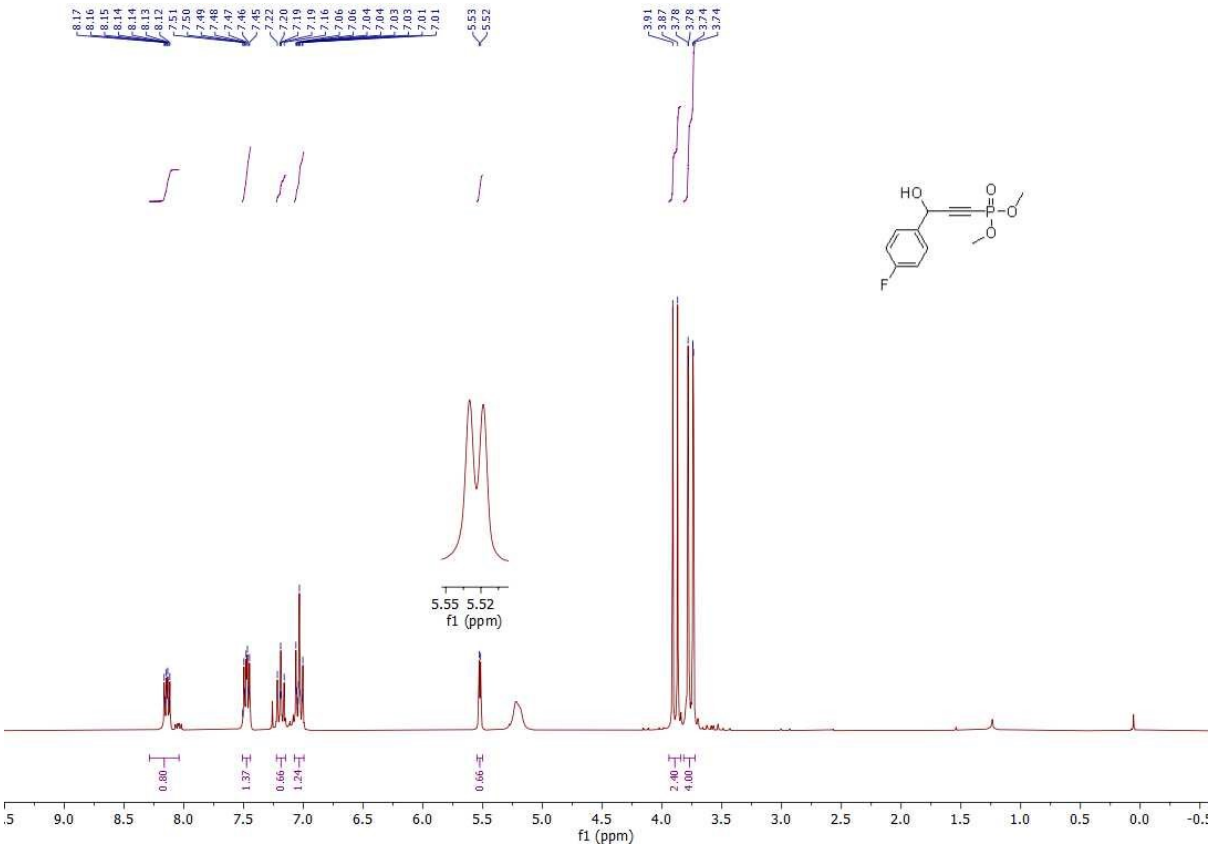
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3j**:



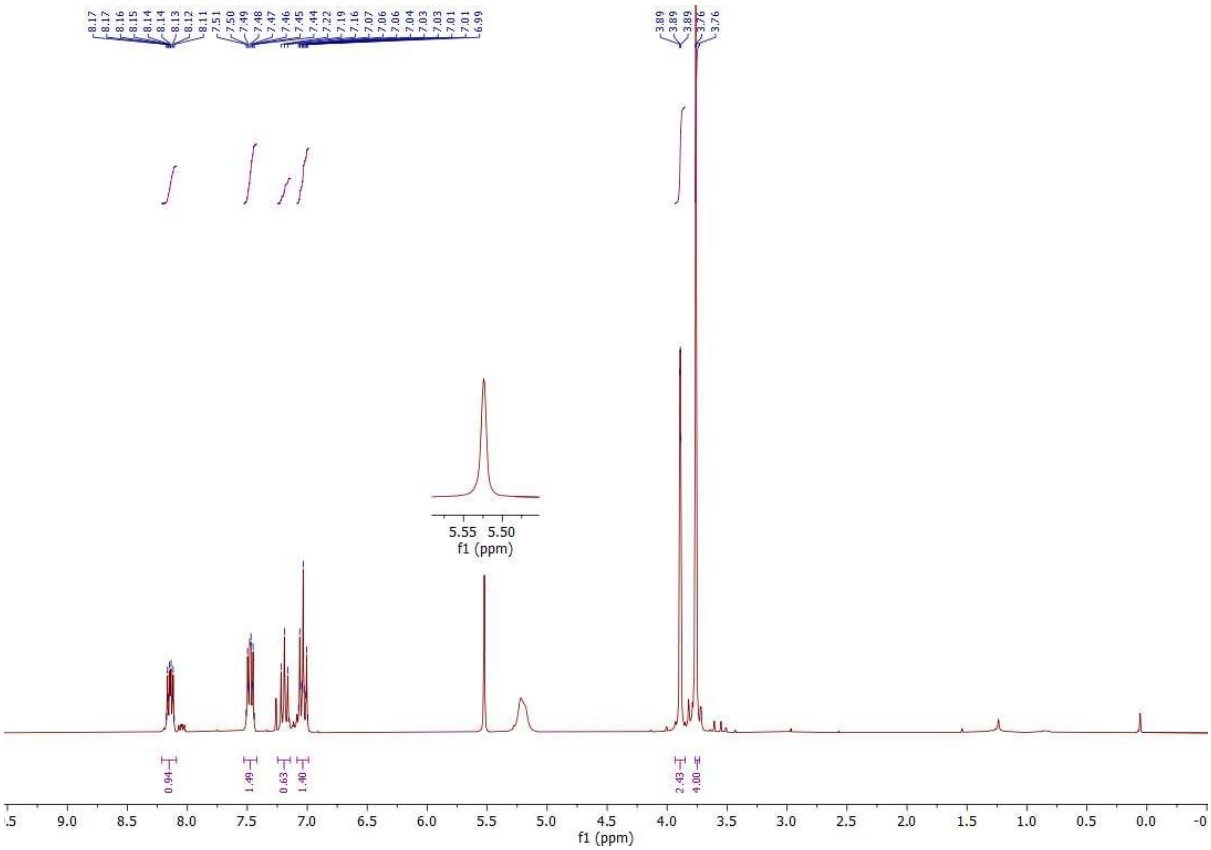
^{31}P NMR (121 MHz, $CDCl_3$)-**3j**:



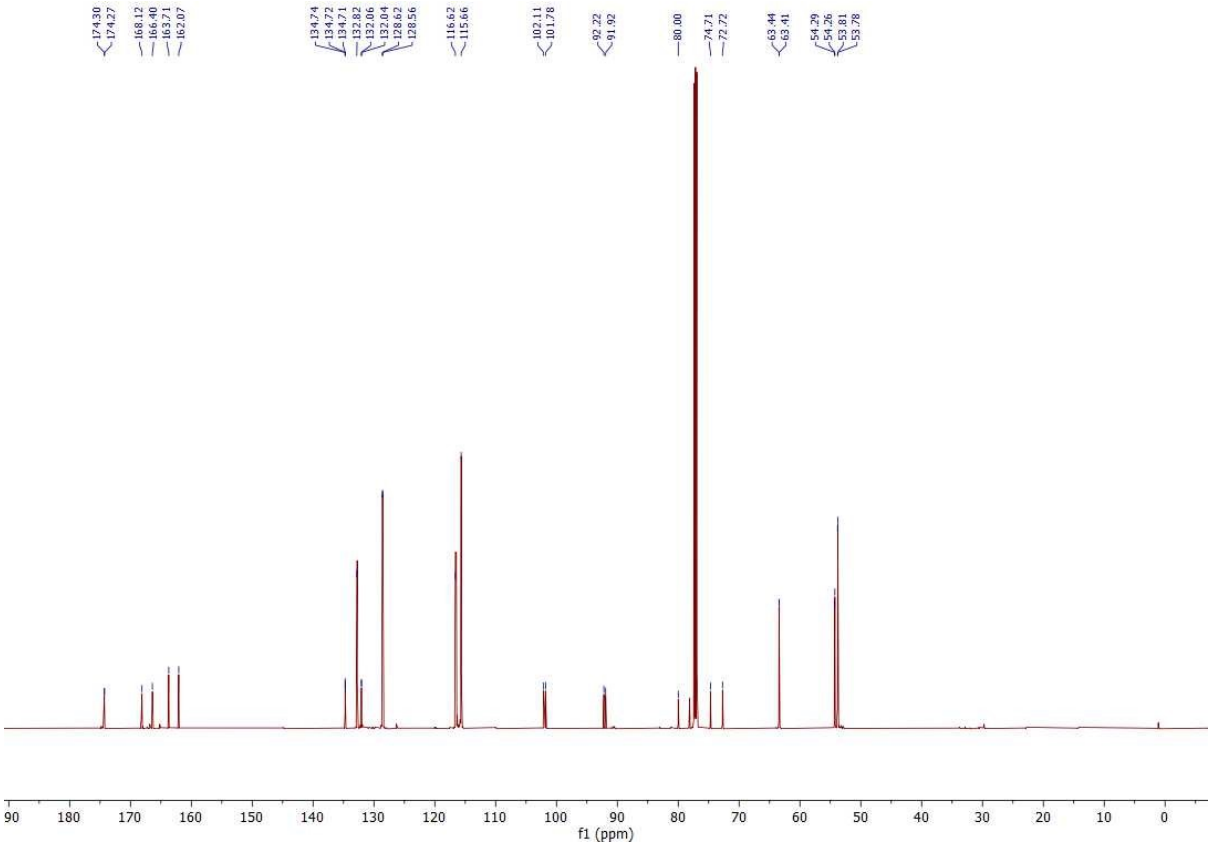
^{1}H NMR (300 MHz, $CDCl_3$)-**3k**:



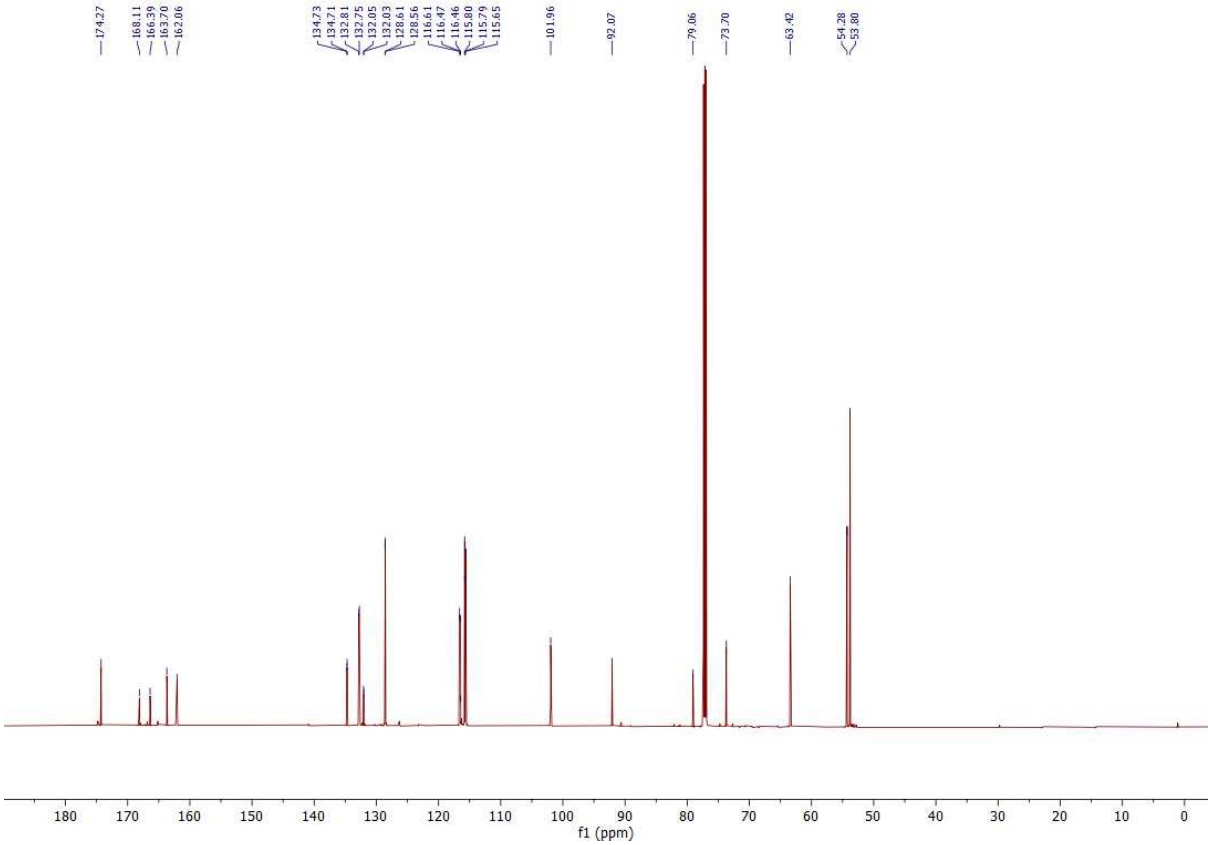
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**3k**:



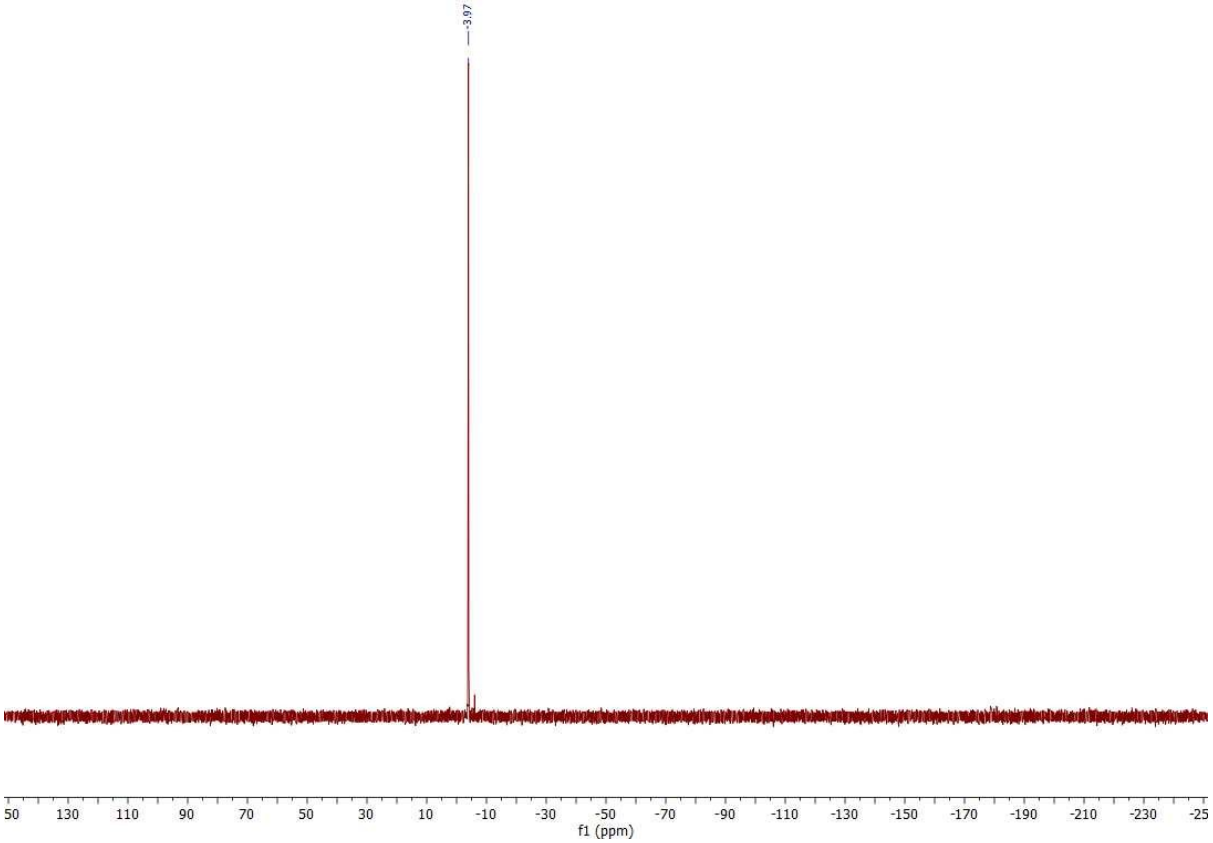
^{13}C NMR (151 MHz, $CDCl_3$)-**3k**:



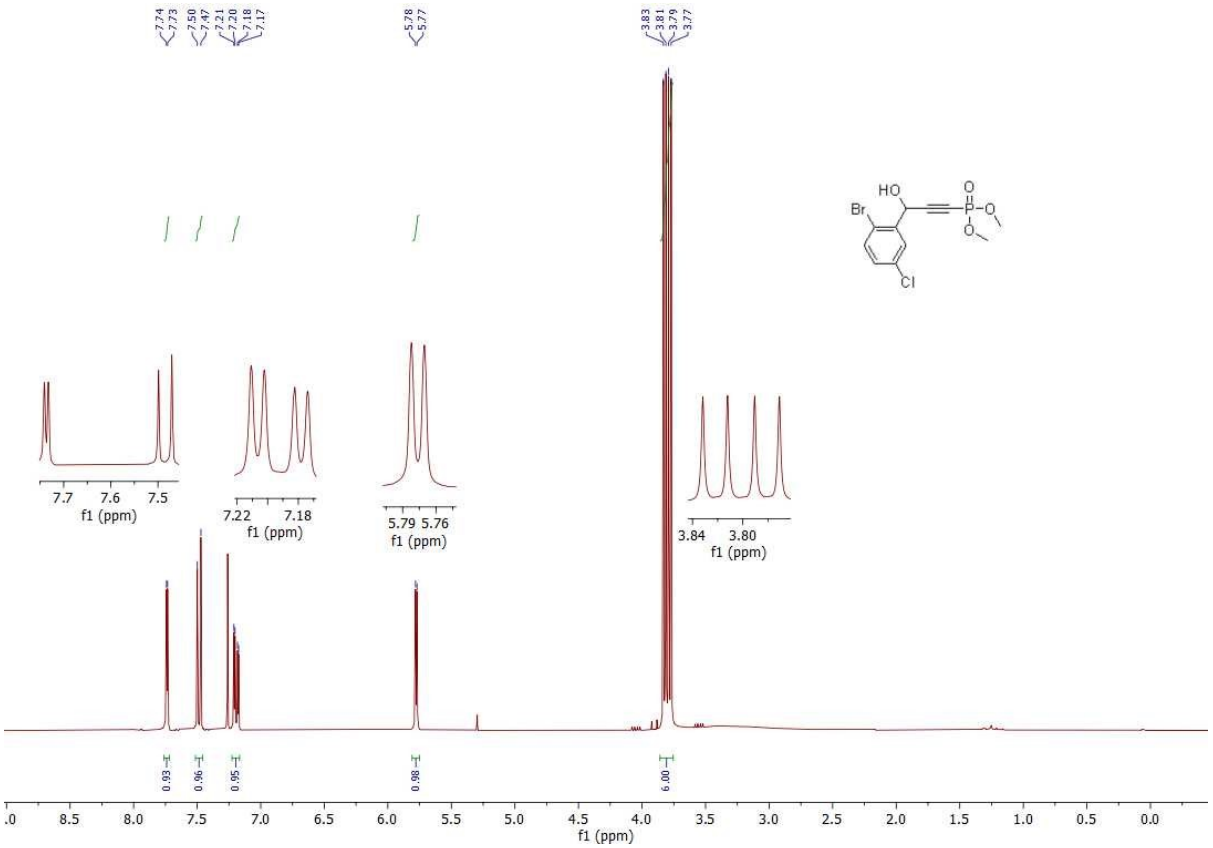
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3k**:



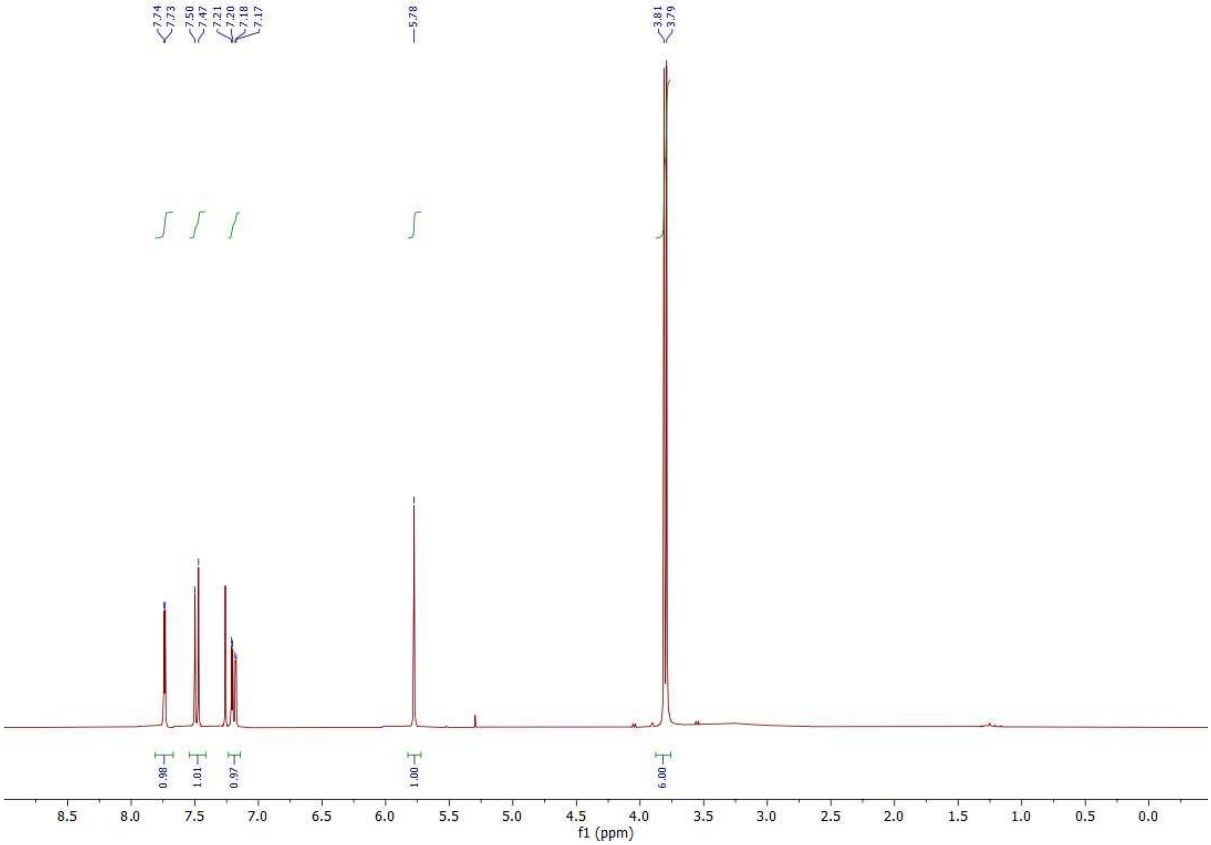
^{31}P NMR (121 MHz, $CDCl_3$)-**3k**:



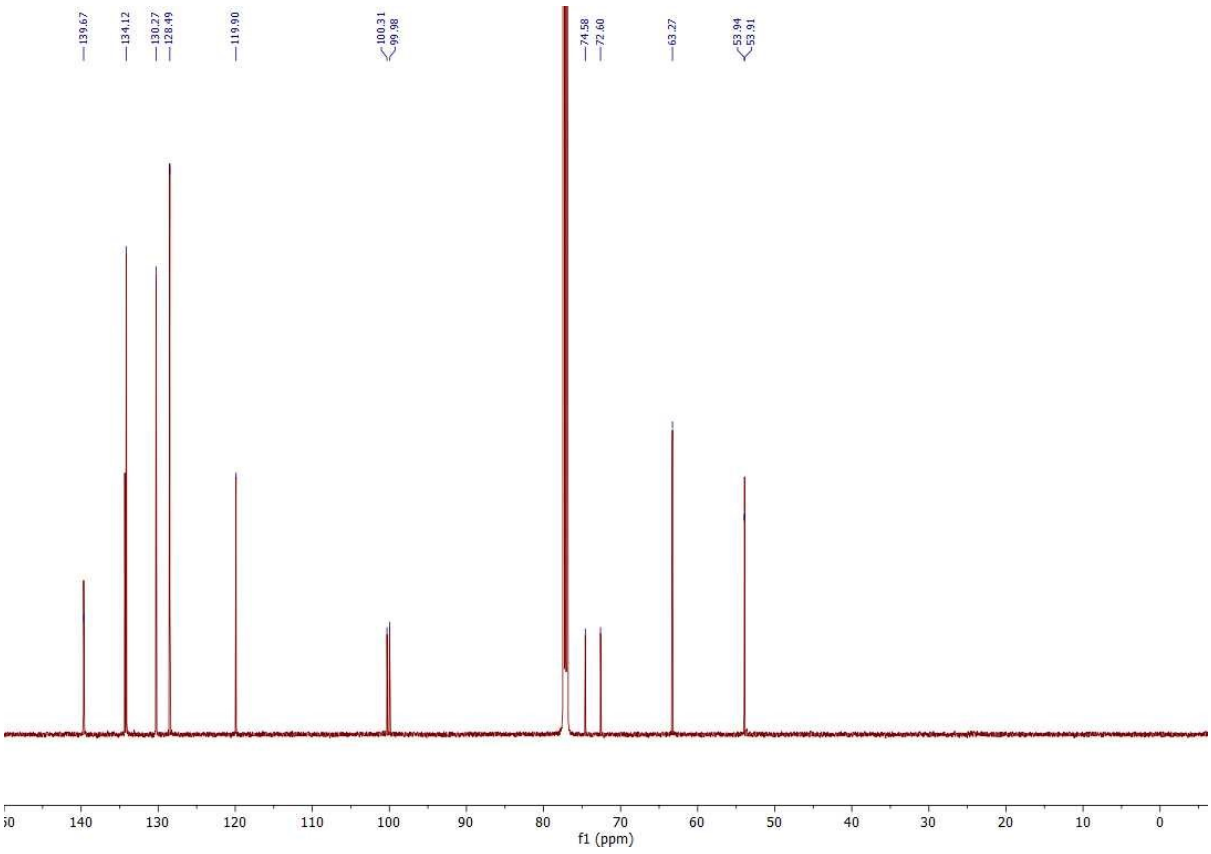
^{1}H NMR (300 MHz, $CDCl_3$)-**3l**:



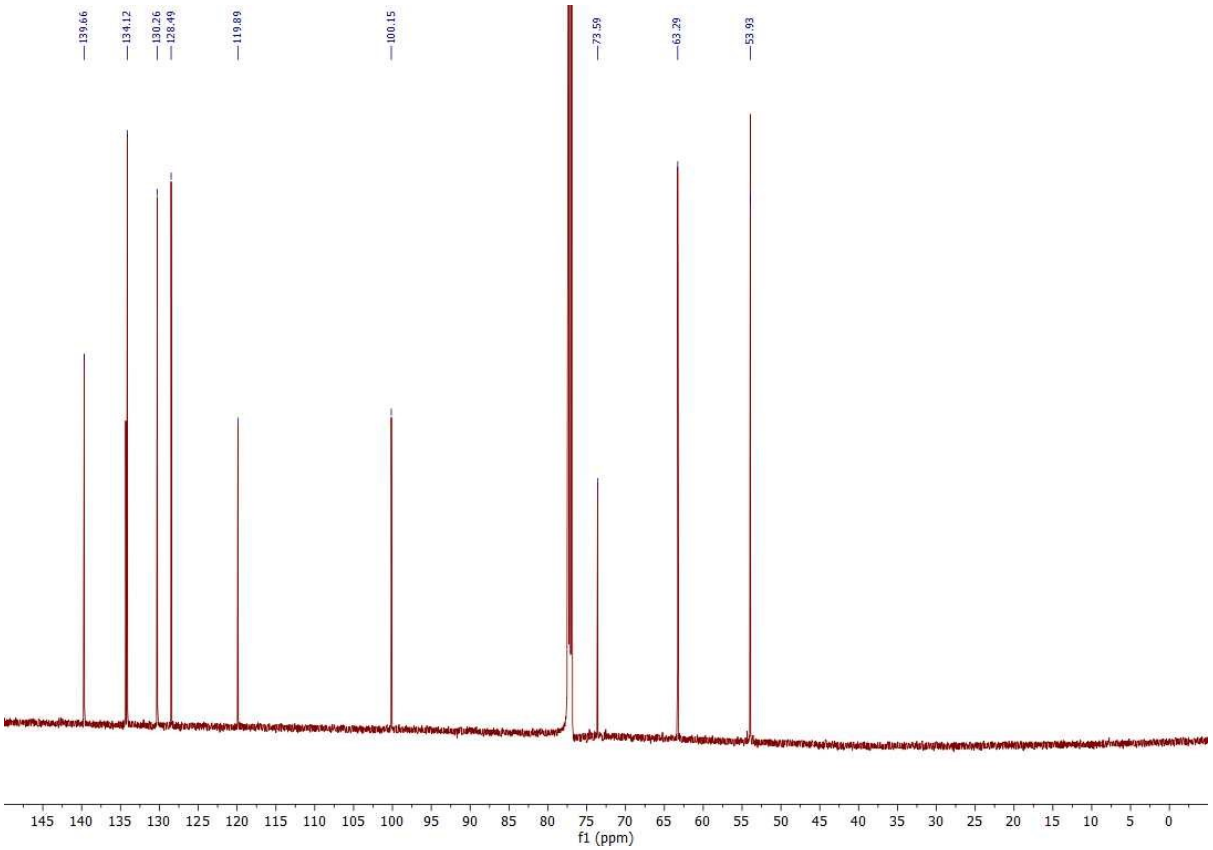
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**3l**:



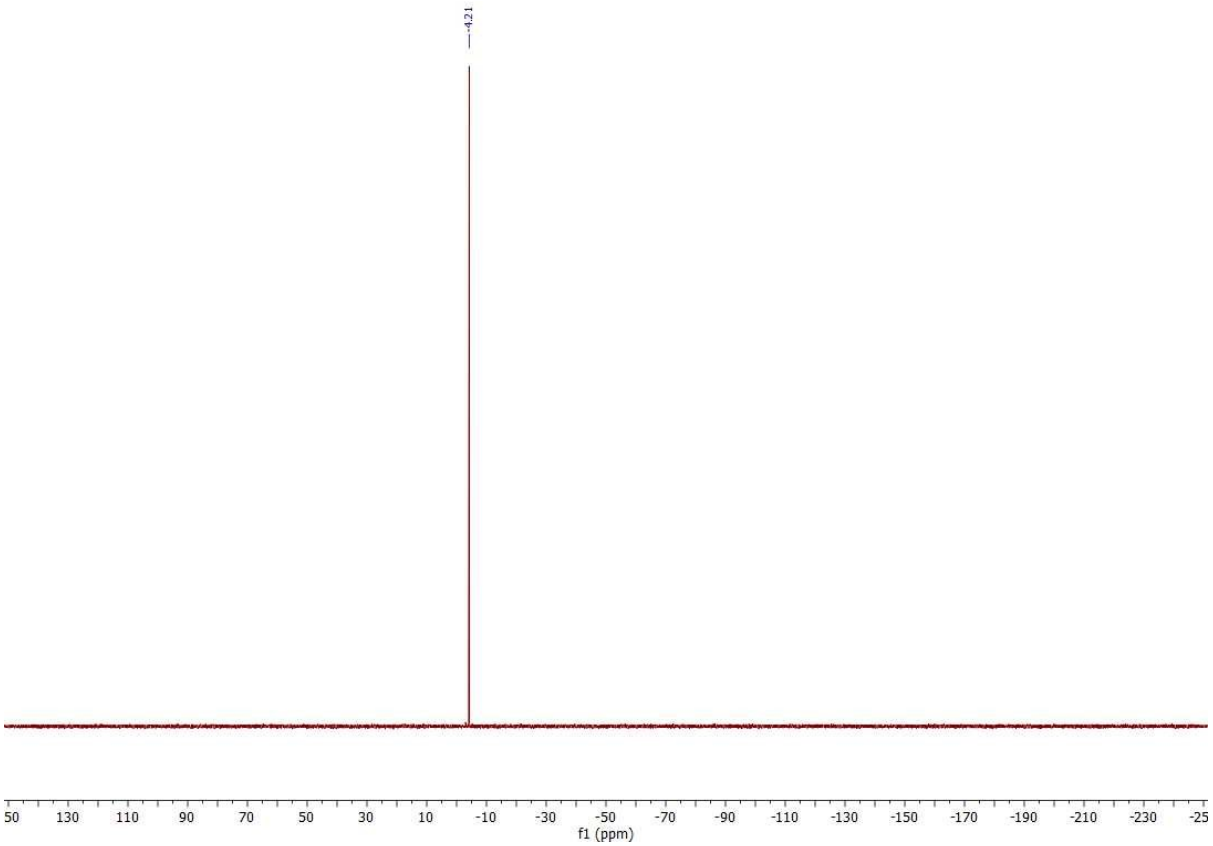
^{13}C NMR (151 MHz, $CDCl_3$)-**3l**:



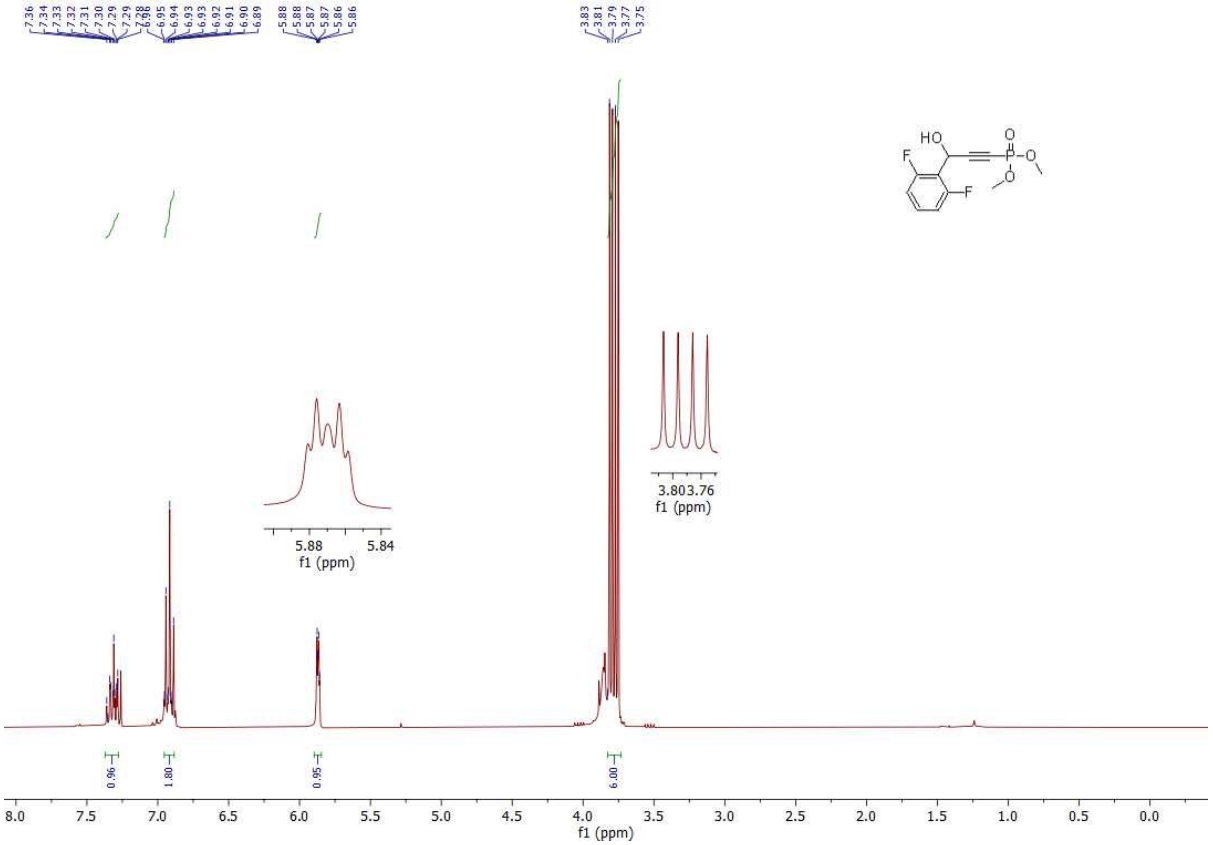
$^{13}C\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**3l**:



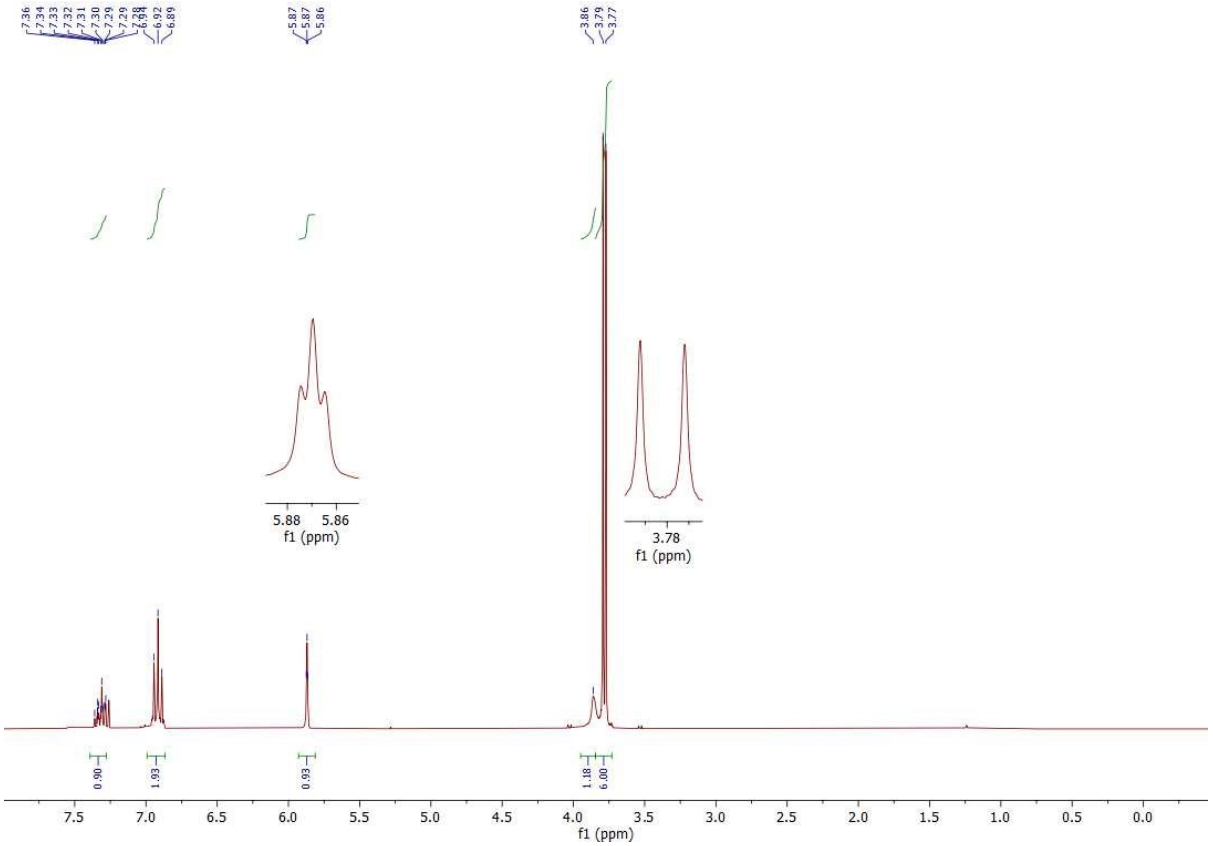
^{31}P NMR (121 MHz, $CDCl_3$)-**3l**:



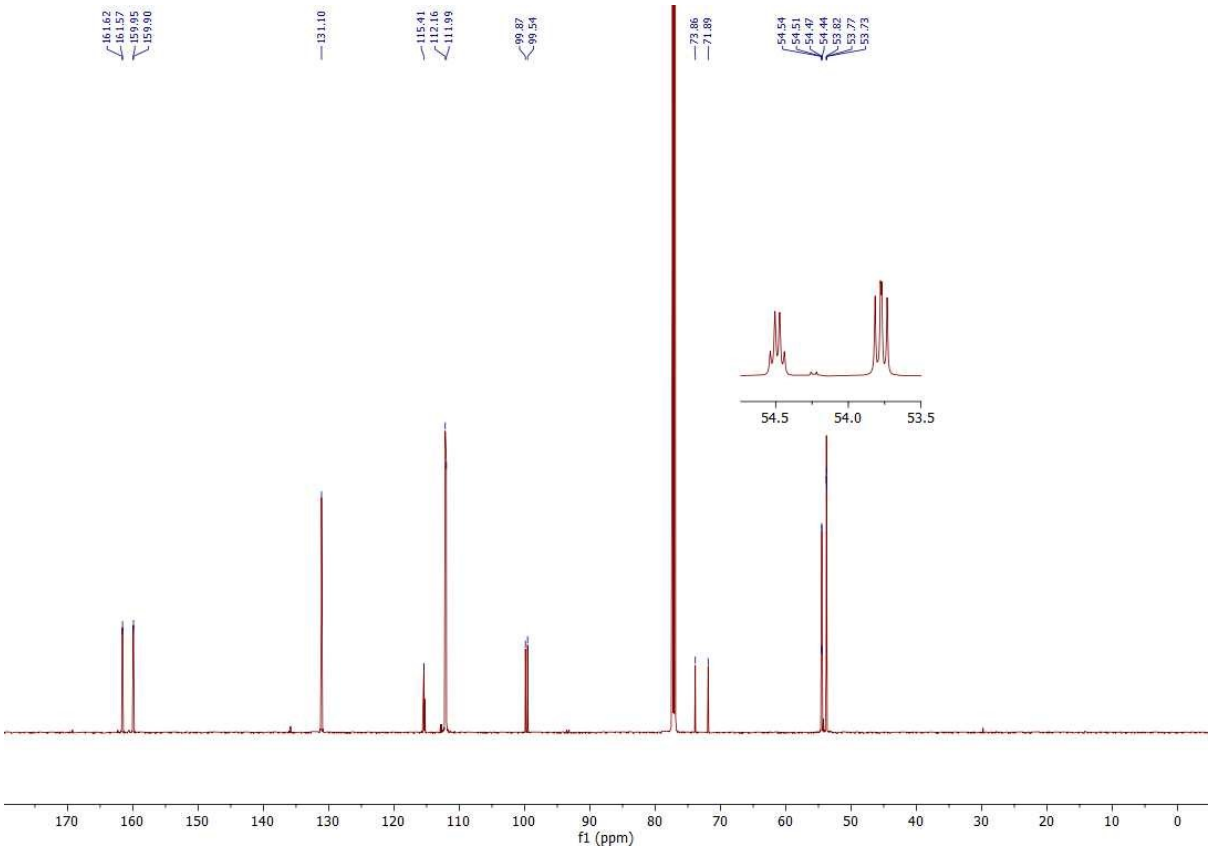
^{1}H NMR (300 MHz, $CDCl_3$)-**3m**:



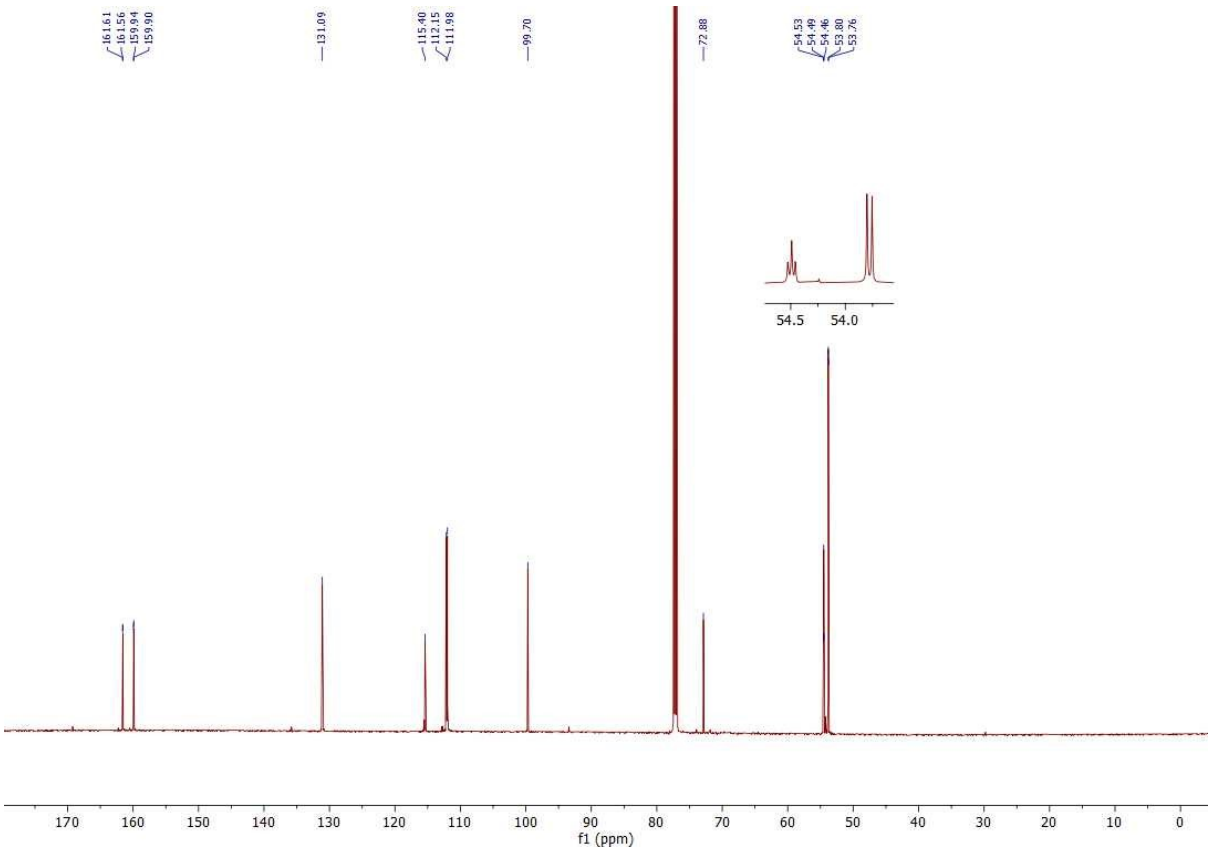
^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$)-**3m**:



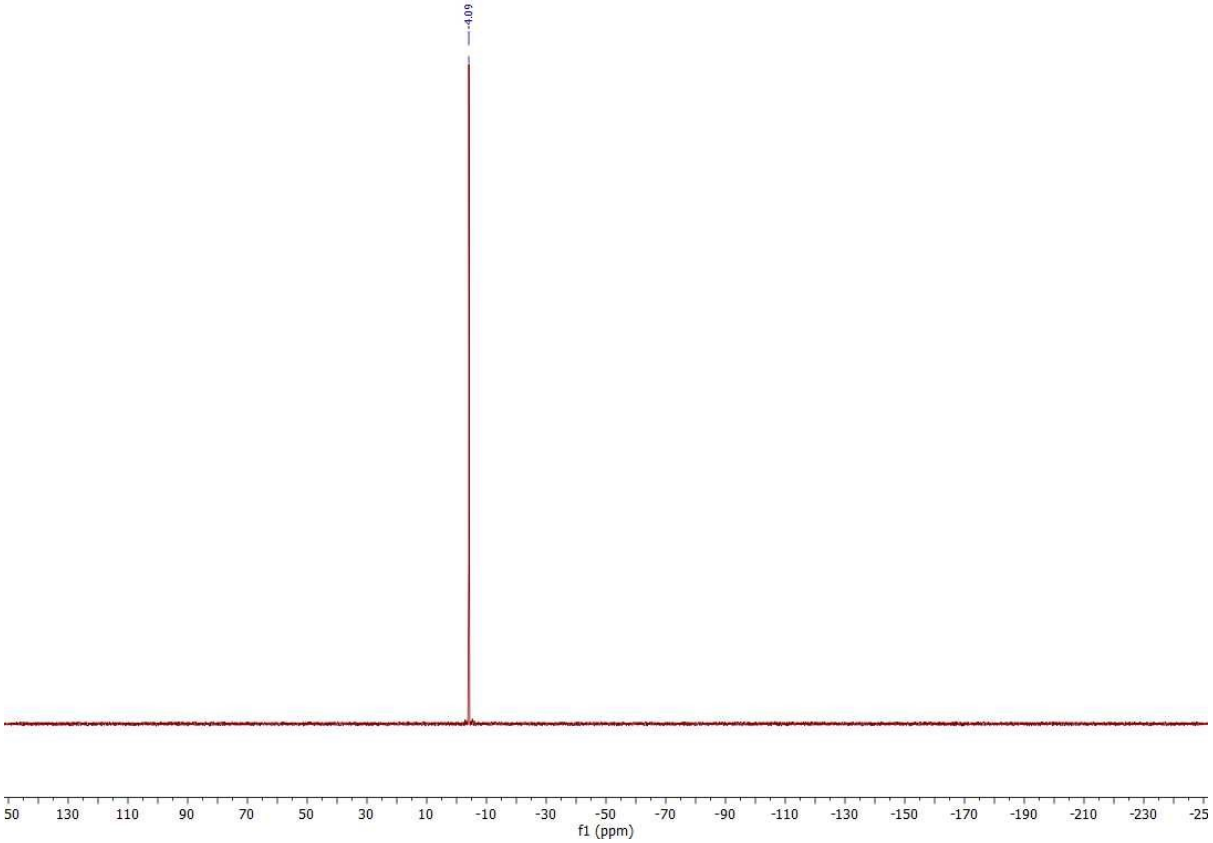
^{13}C NMR (151 MHz, $CDCl_3$)-**3m**:



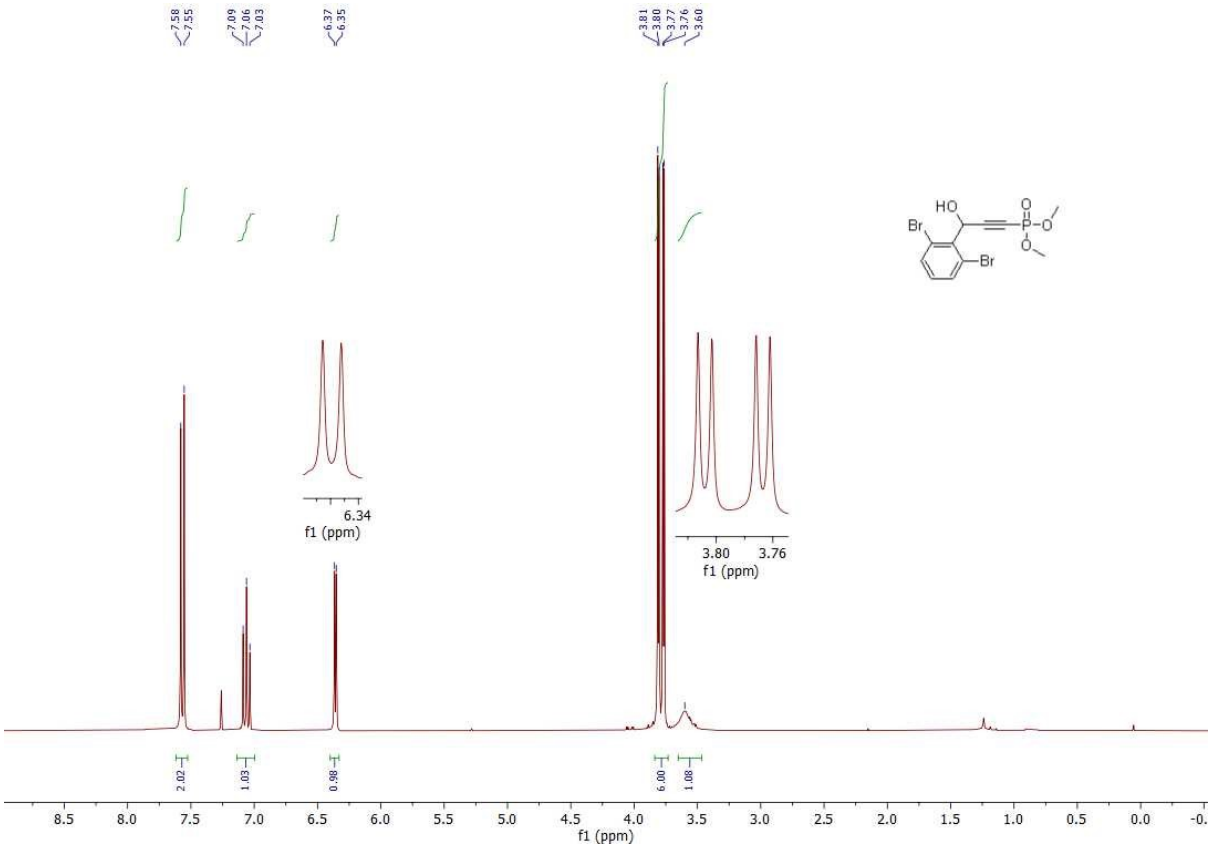
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**3m**:



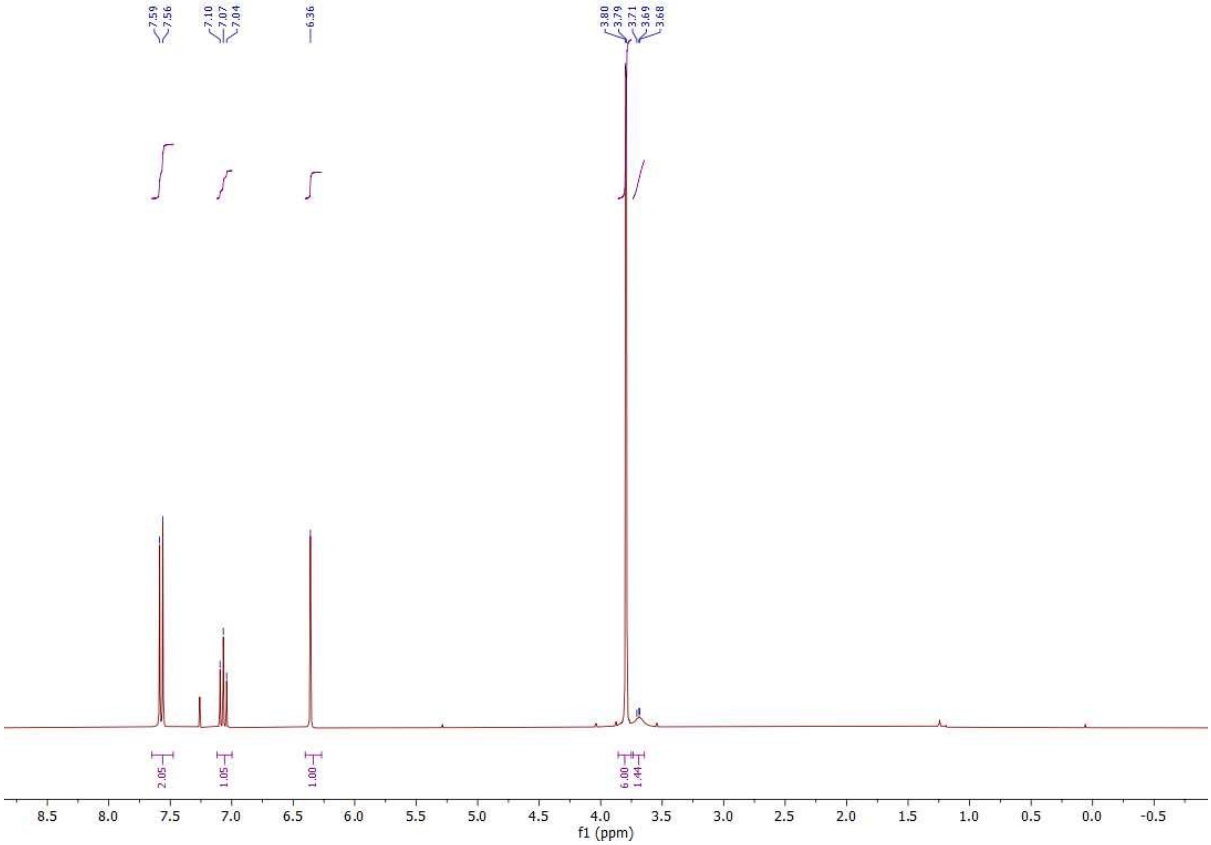
^{31}P NMR (121 MHz, $CDCl_3$)-**3m**:



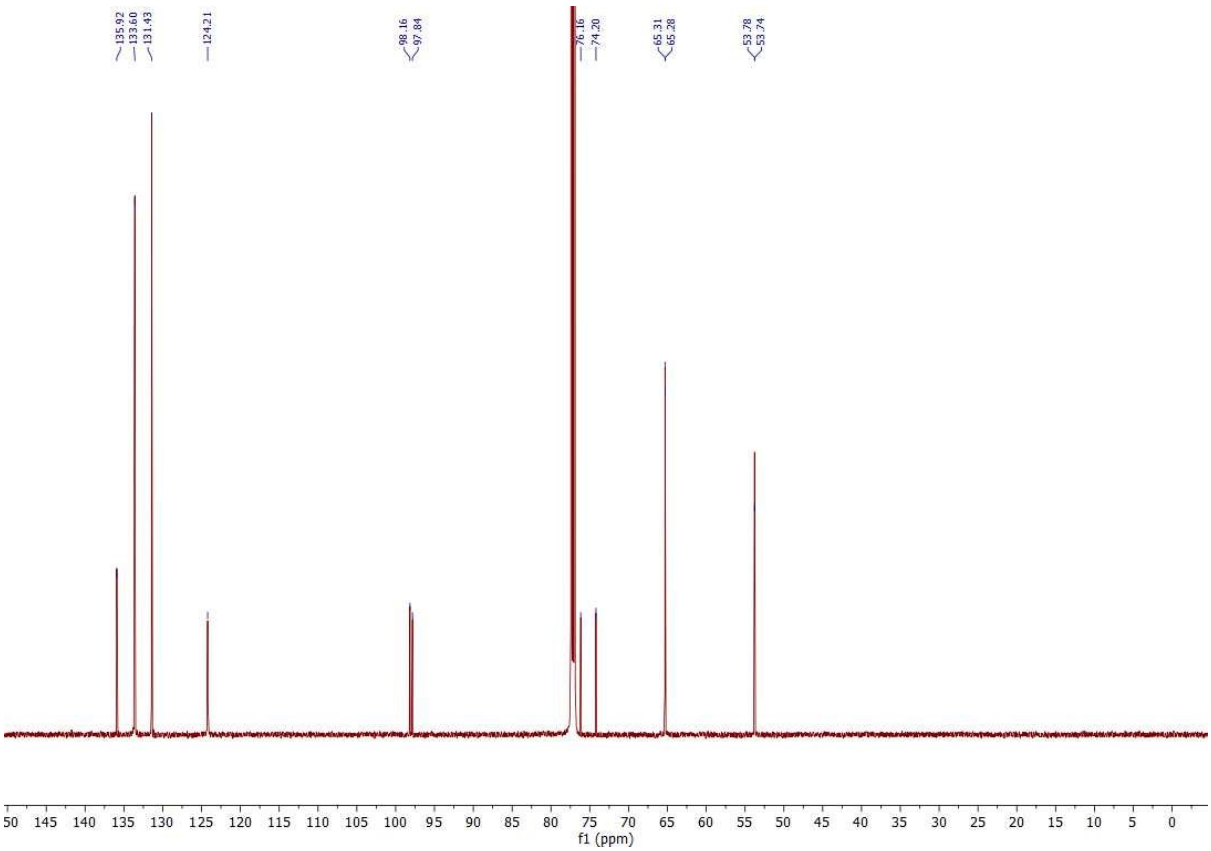
^{1}H NMR (300 MHz, $CDCl_3$)-**3n**:



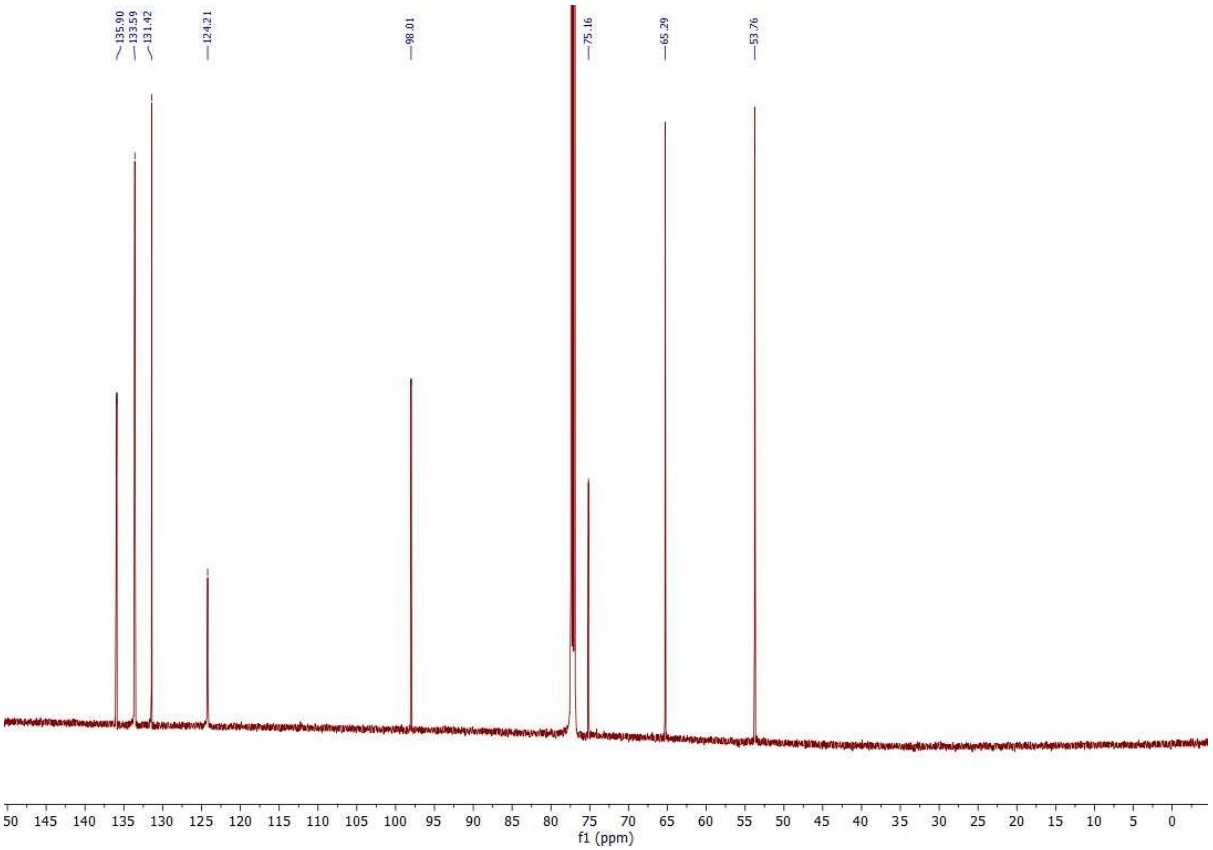
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**3n**:



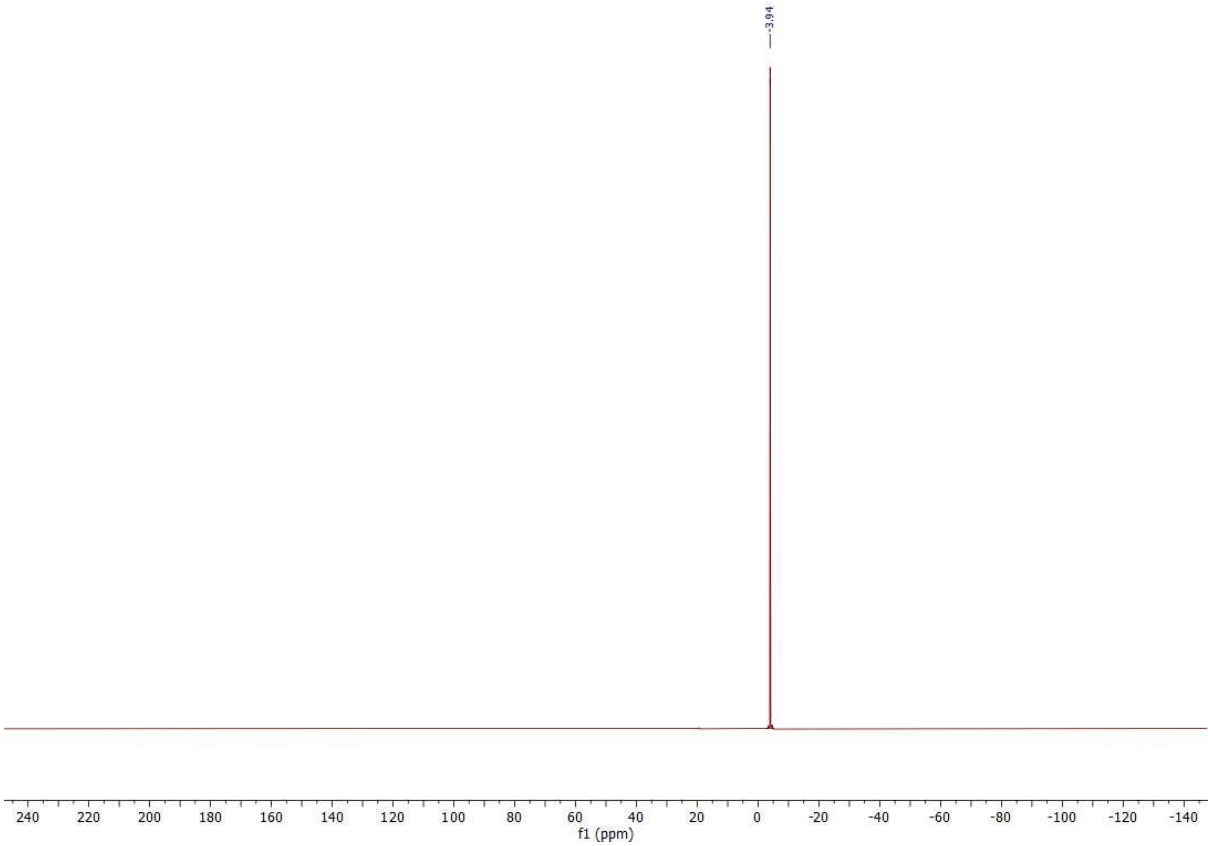
^{13}C NMR (151 MHz, $CDCl_3$)-**3n**:



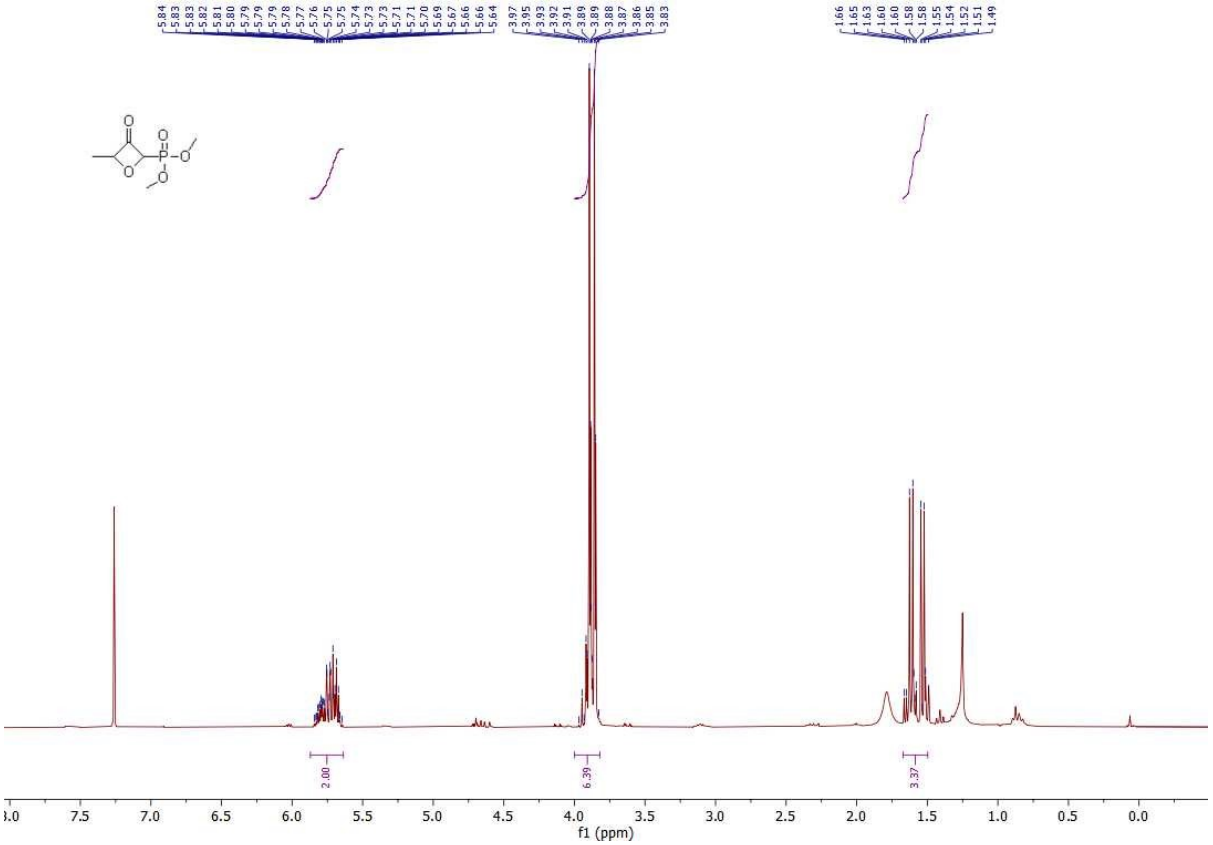
$^{13}C\{^{31}P\}$ (151 MHz, $CDCl_3$)-**3n**:



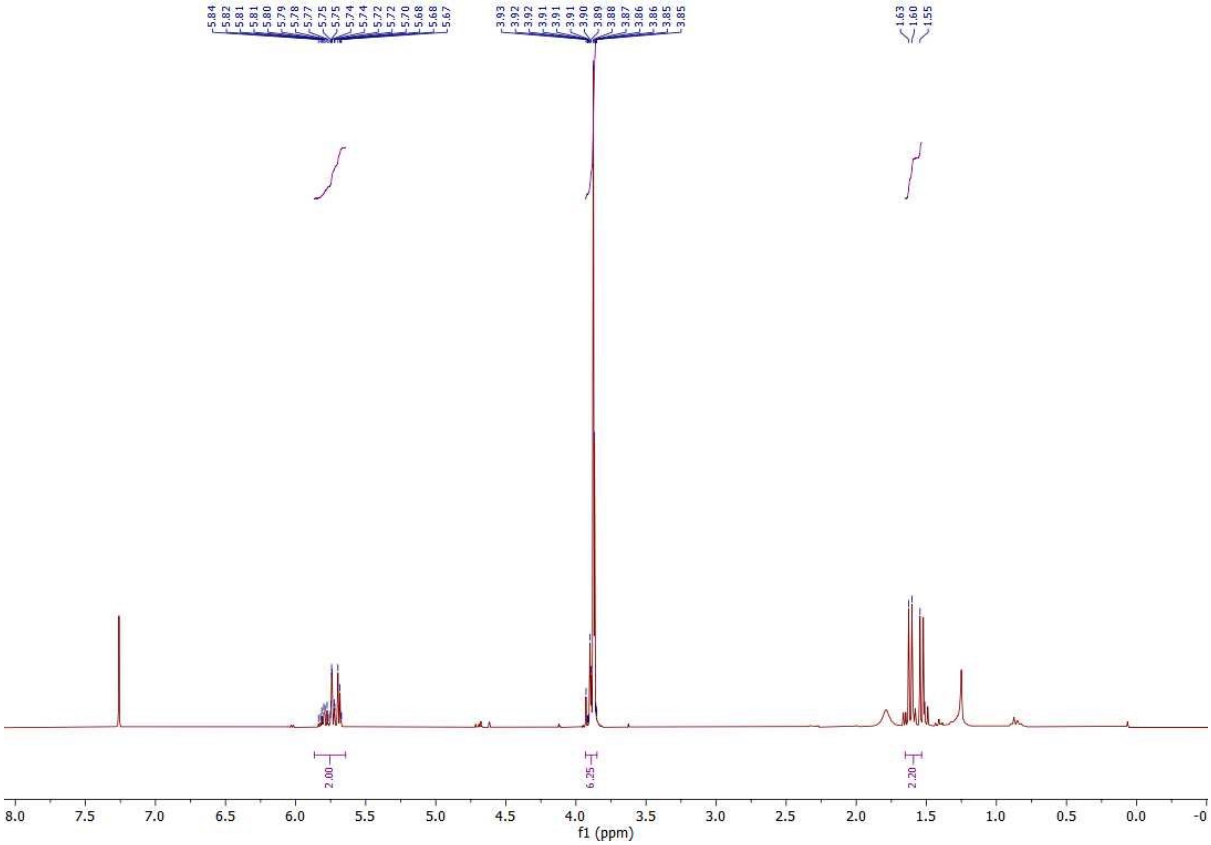
^{31}P NMR (121 MHz, $CDCl_3$)-**3n**:



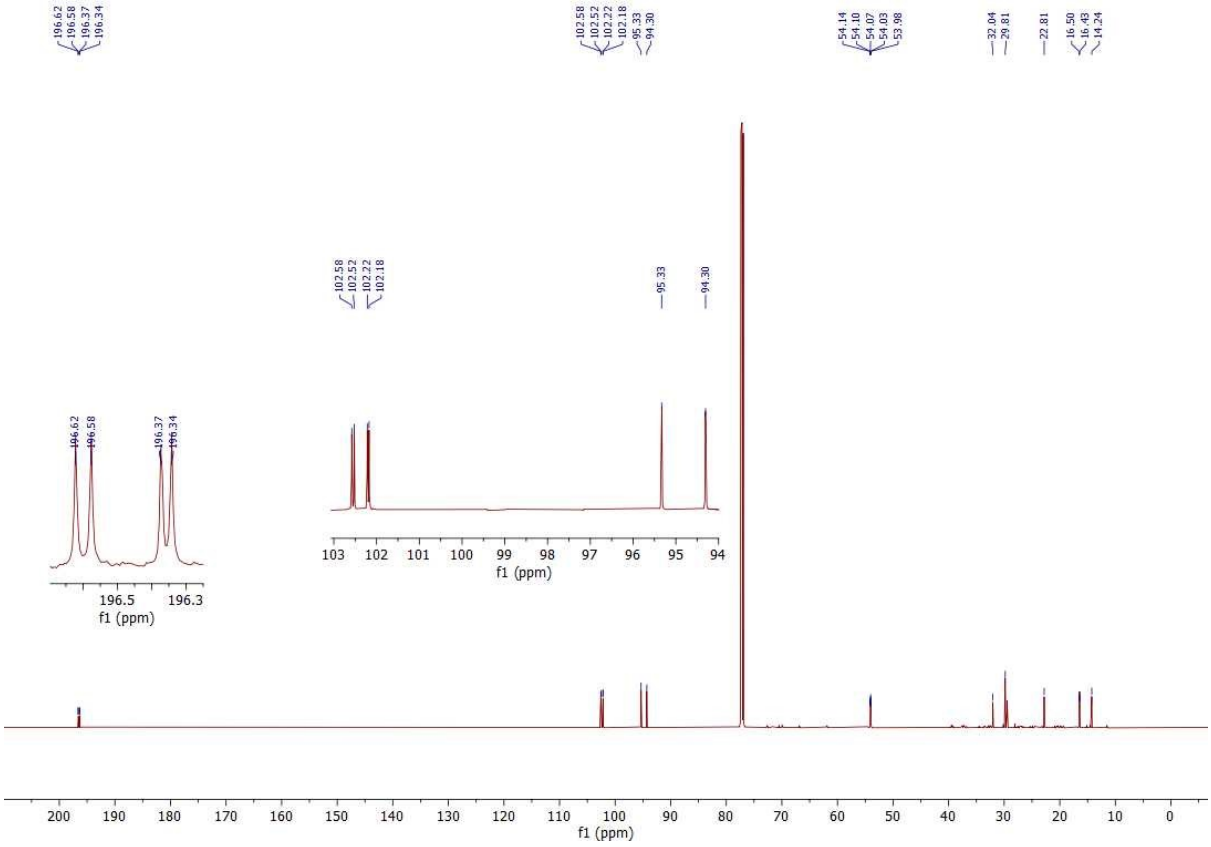
^{1}H NMR (300 MHz, $CDCl_3$)-**4a**:



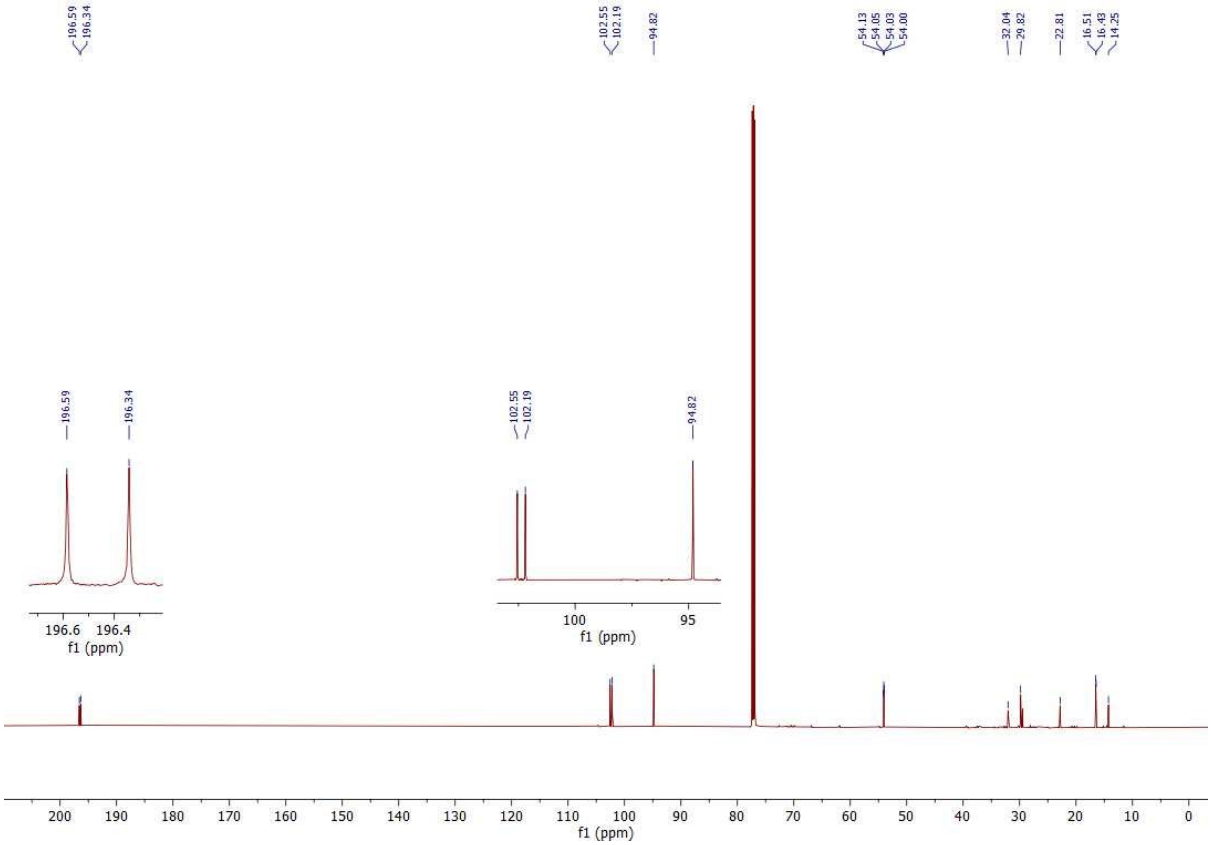
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**4a**:



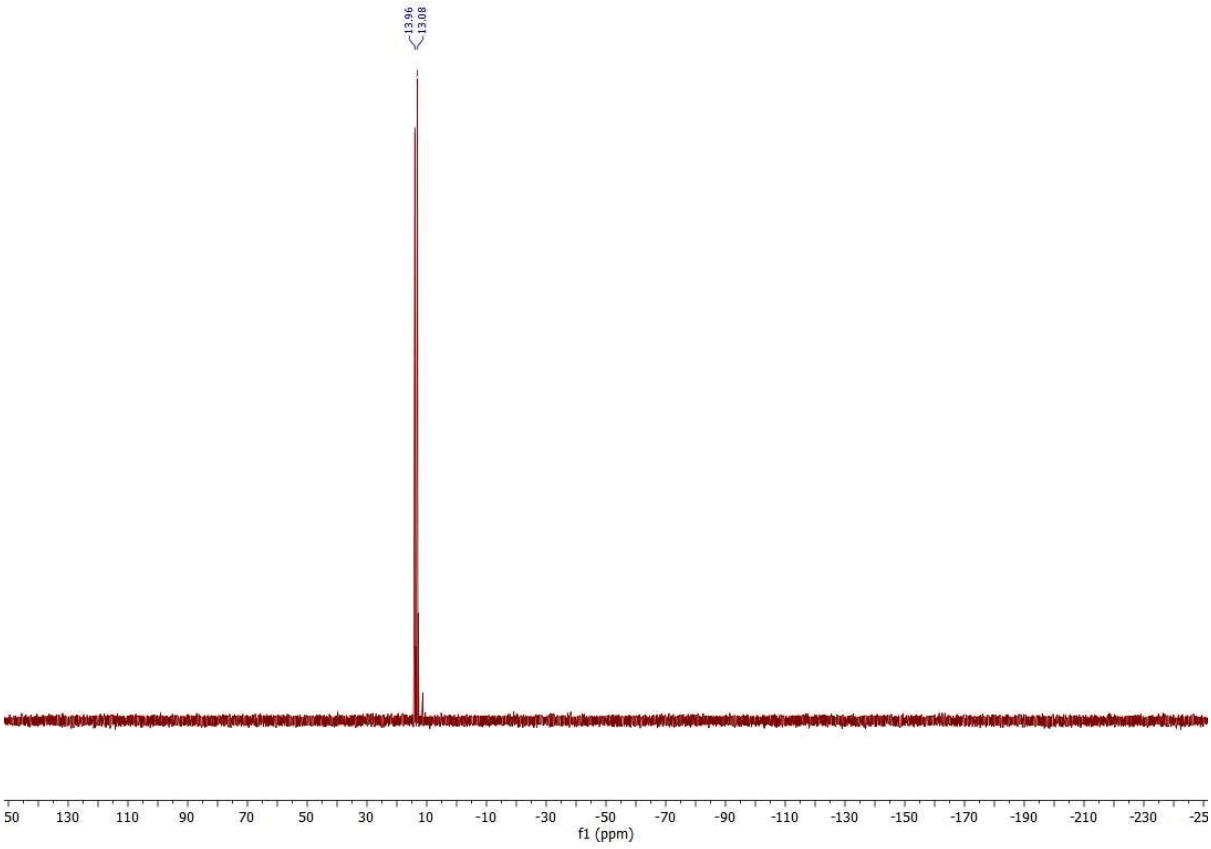
^{13}C NMR (151 MHz, $CDCl_3$)-**4a**:



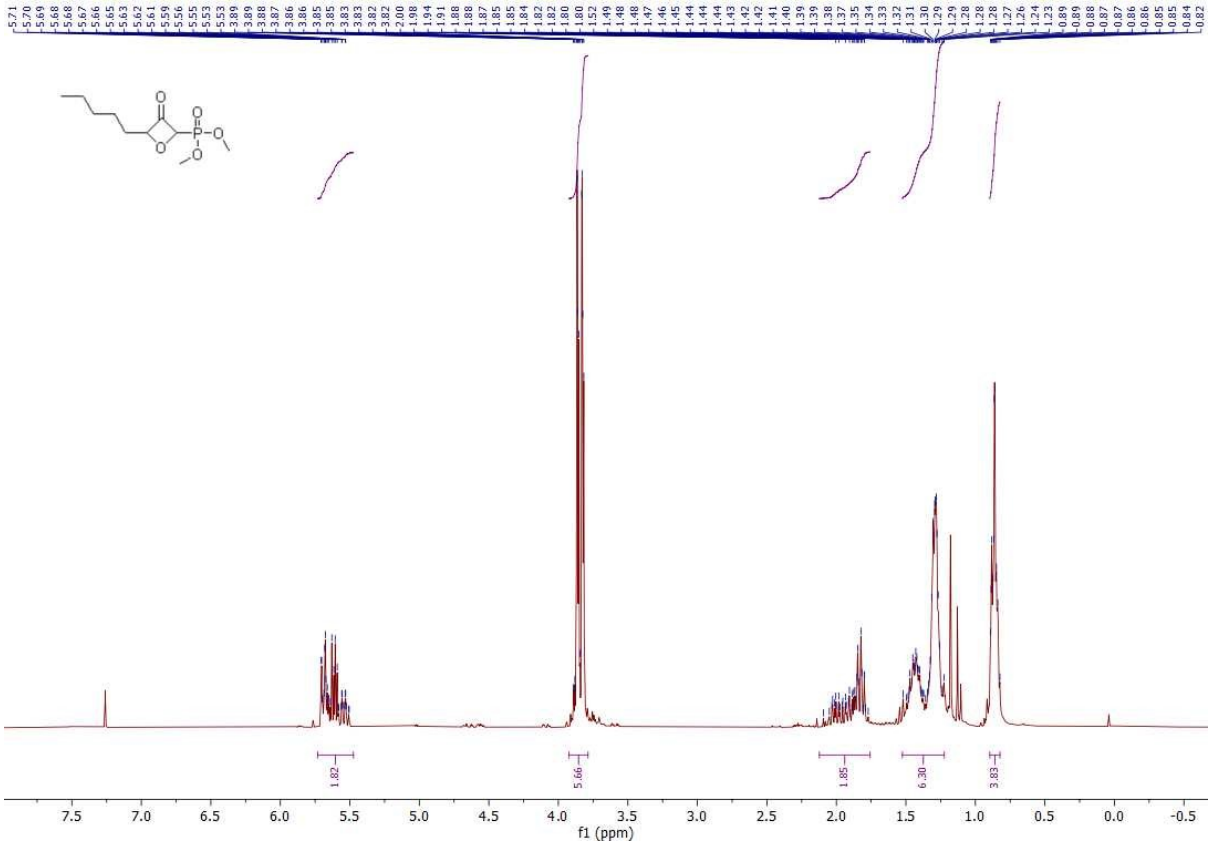
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4a**:



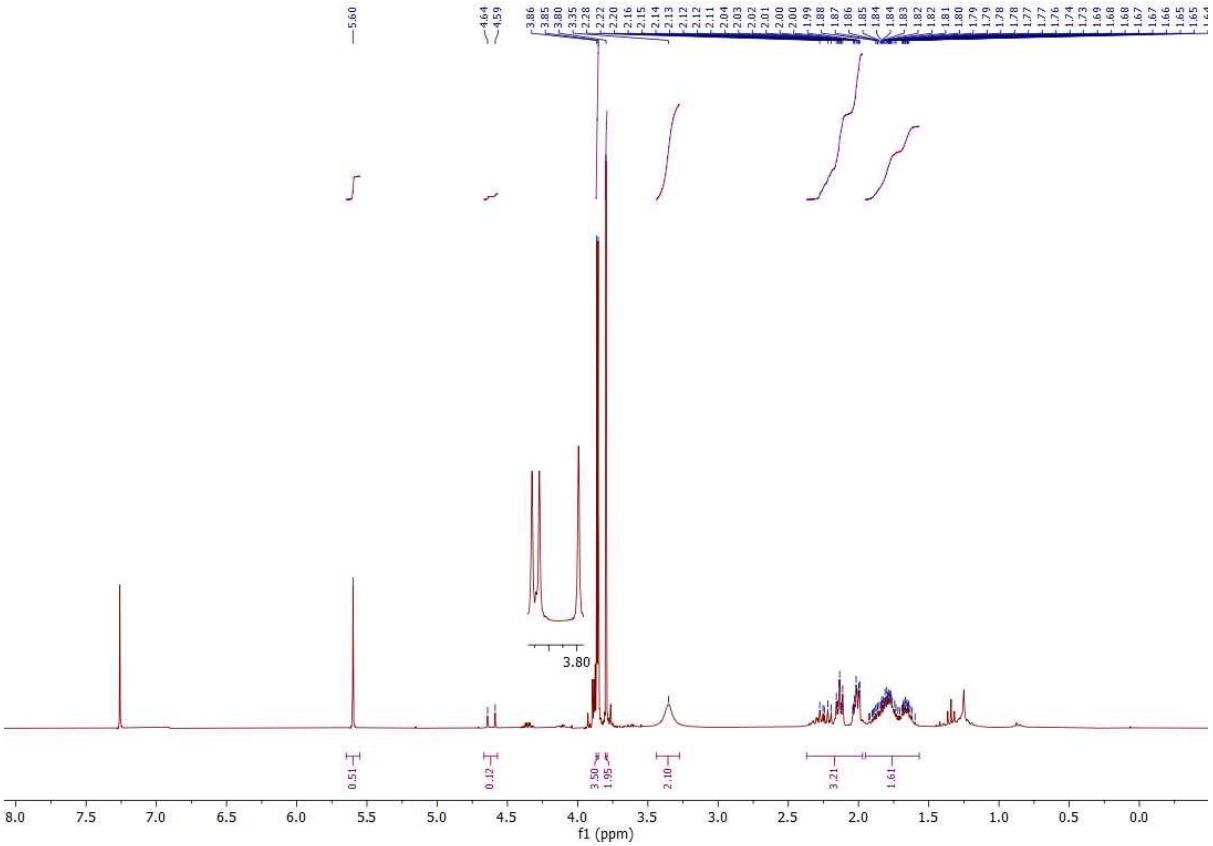
^{31}P NMR (121 MHz, $CDCl_3$)-**4a**:



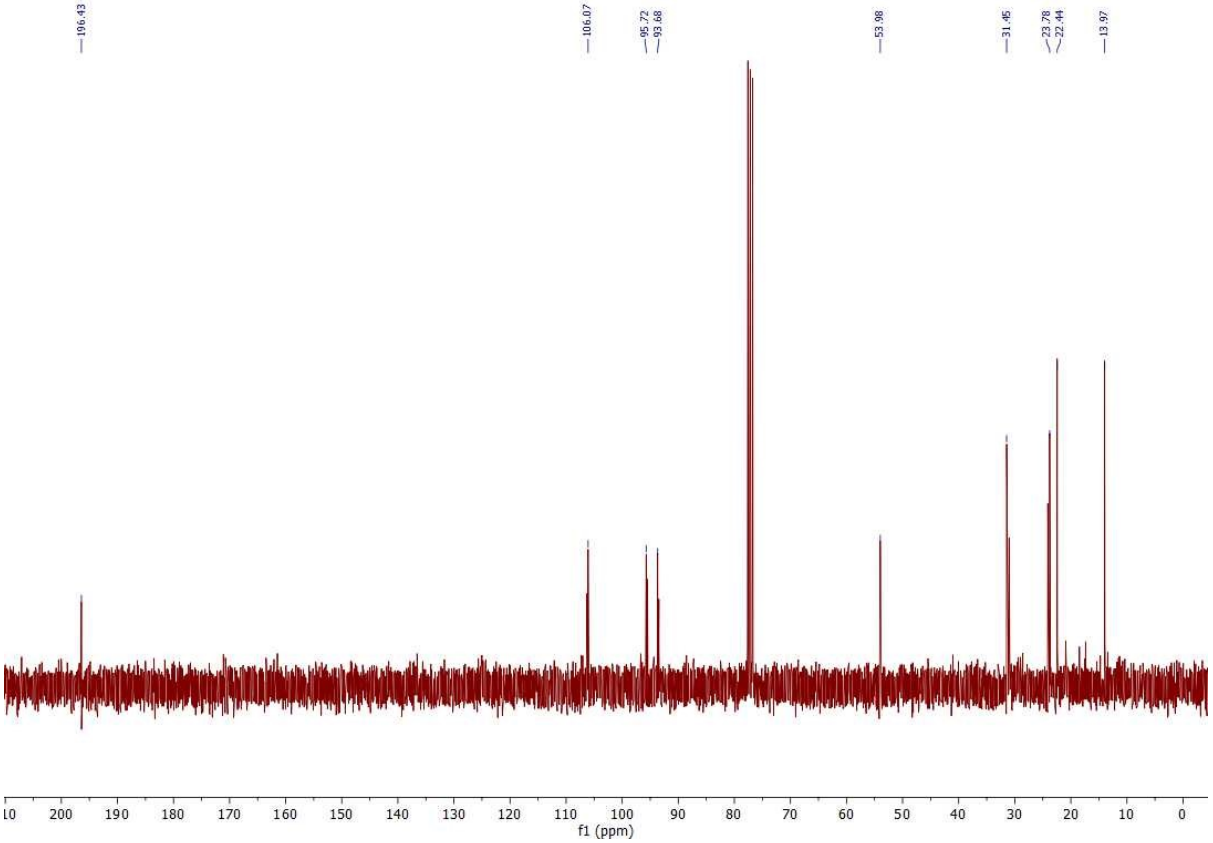
^{1}H NMR (300 MHz, $CDCl_3$)-**4b**:



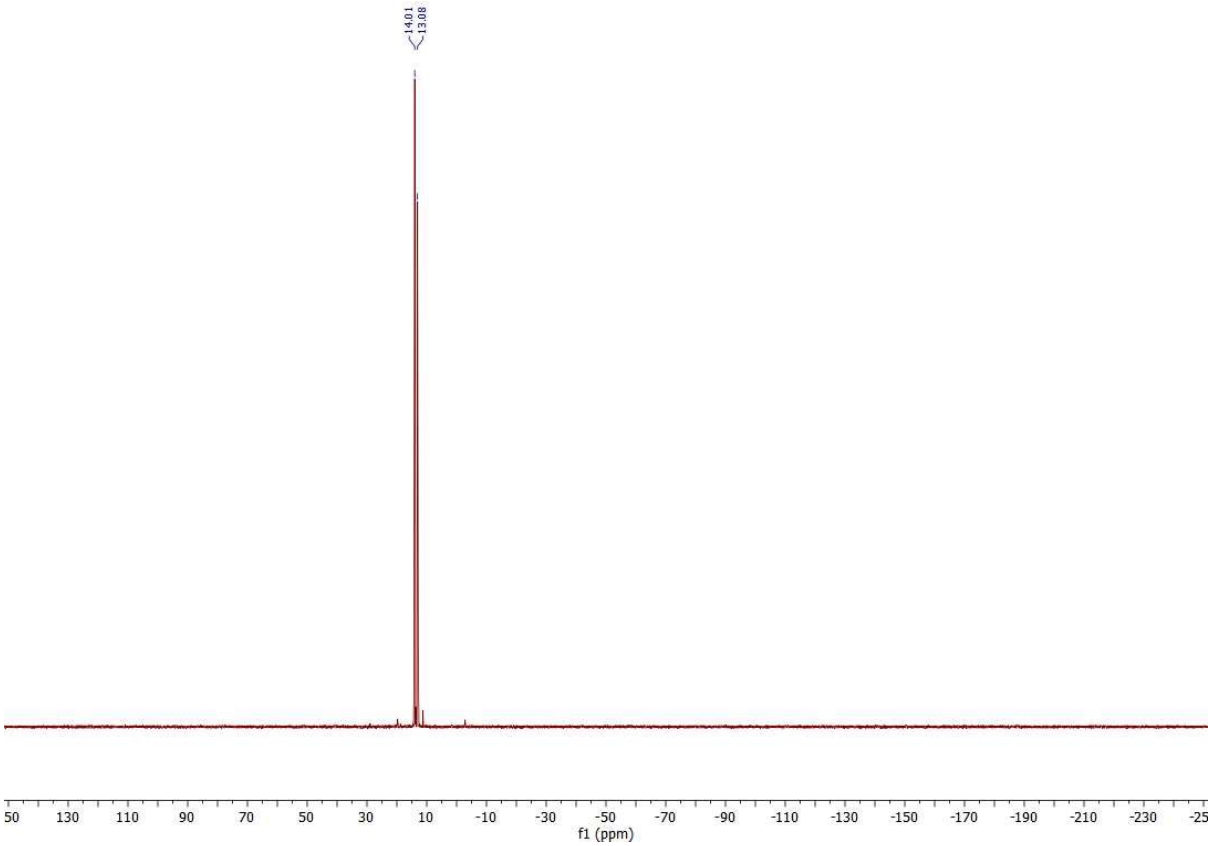
$^{1}H\{^{31}P\}$ (300 MHz, $CDCl_3$)-**4b**:



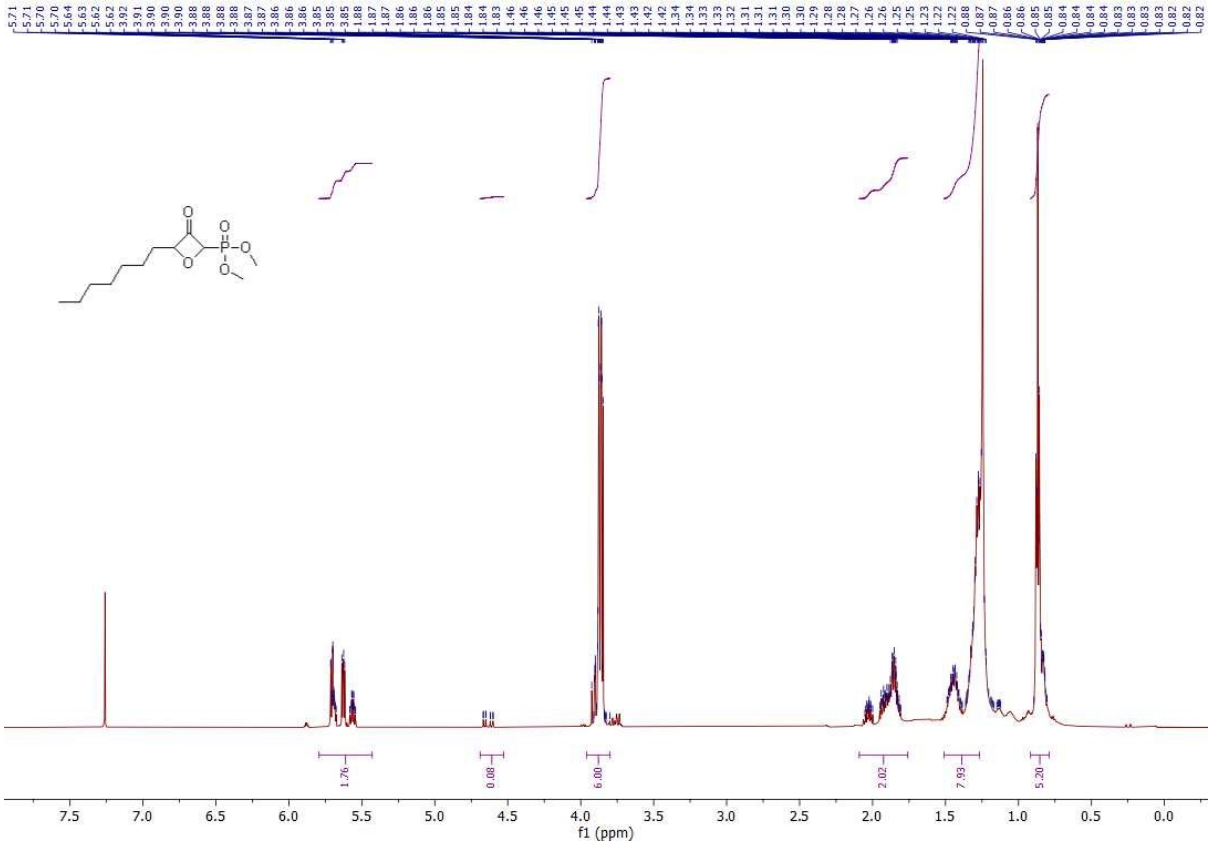
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4b**:



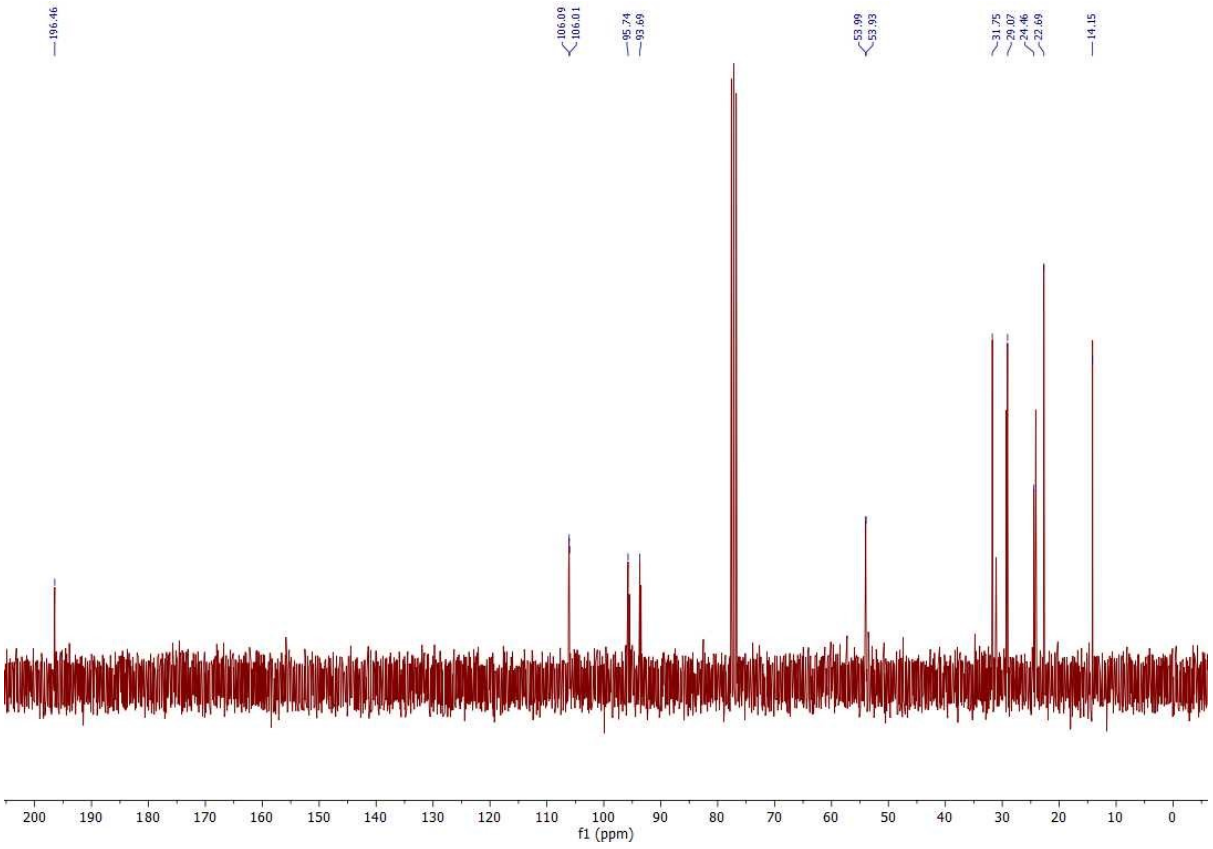
^{31}P NMR (121 MHz, $CDCl_3$)-**4b**:



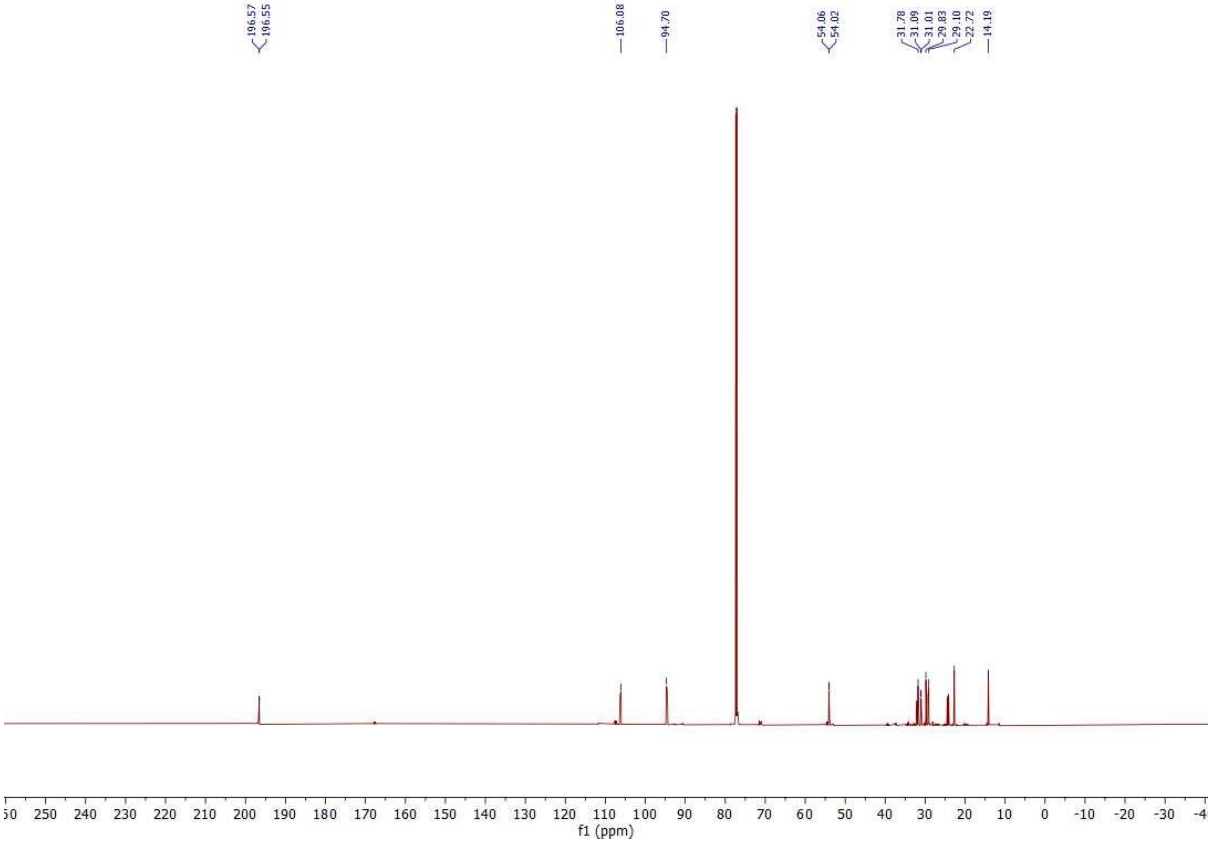
^{1}H NMR (300 MHz, $CDCl_3$)-**4c**:



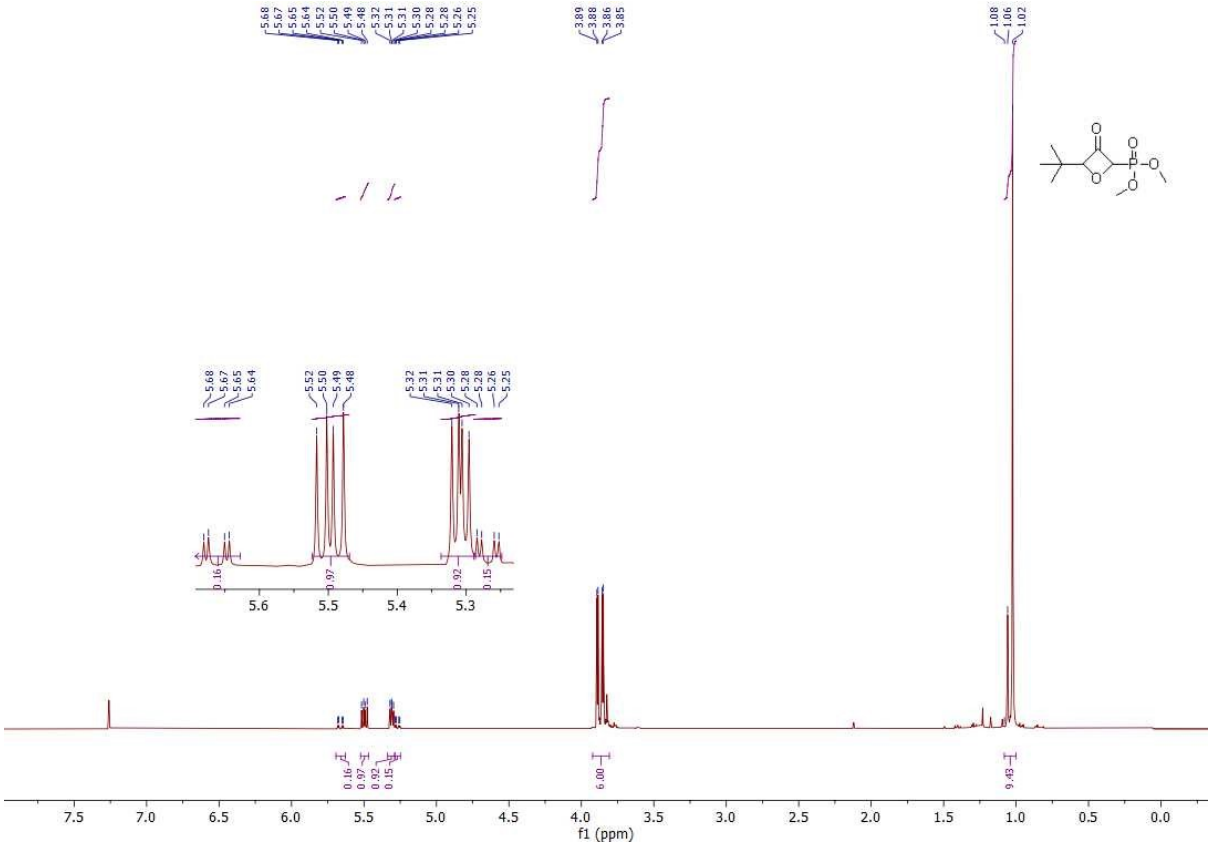
^{13}C NMR (75 MHz, $CDCl_3$)-**4c**:



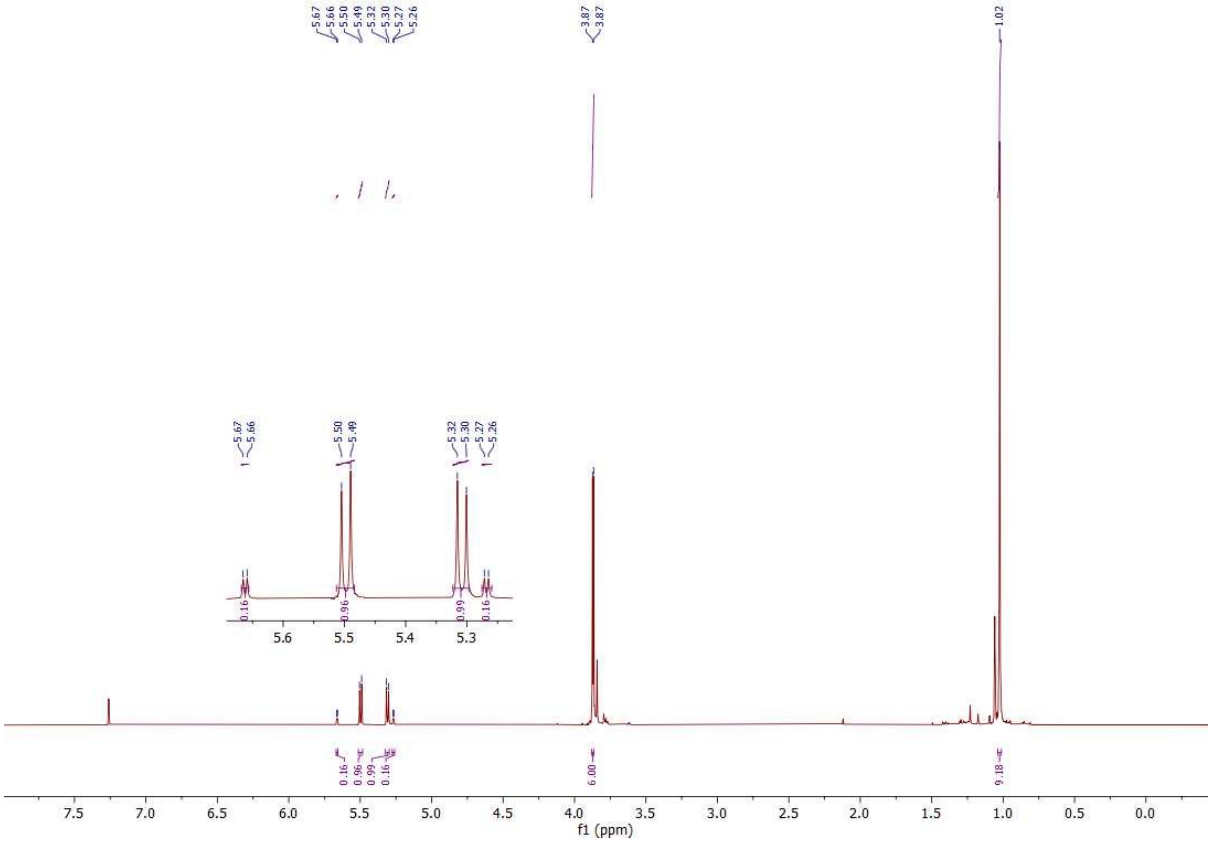
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4c**:



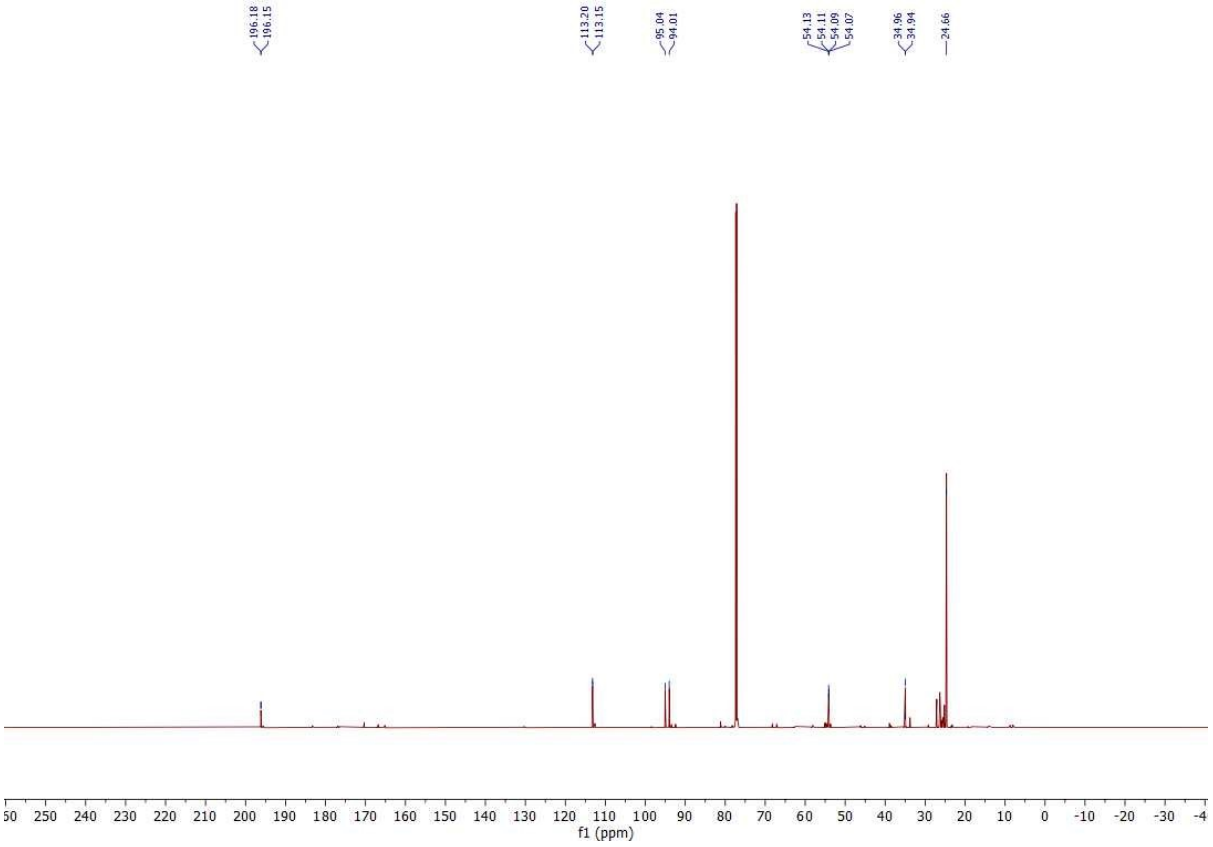
^{1}H NMR (300 MHz, $CDCl_3$)-**4d**:



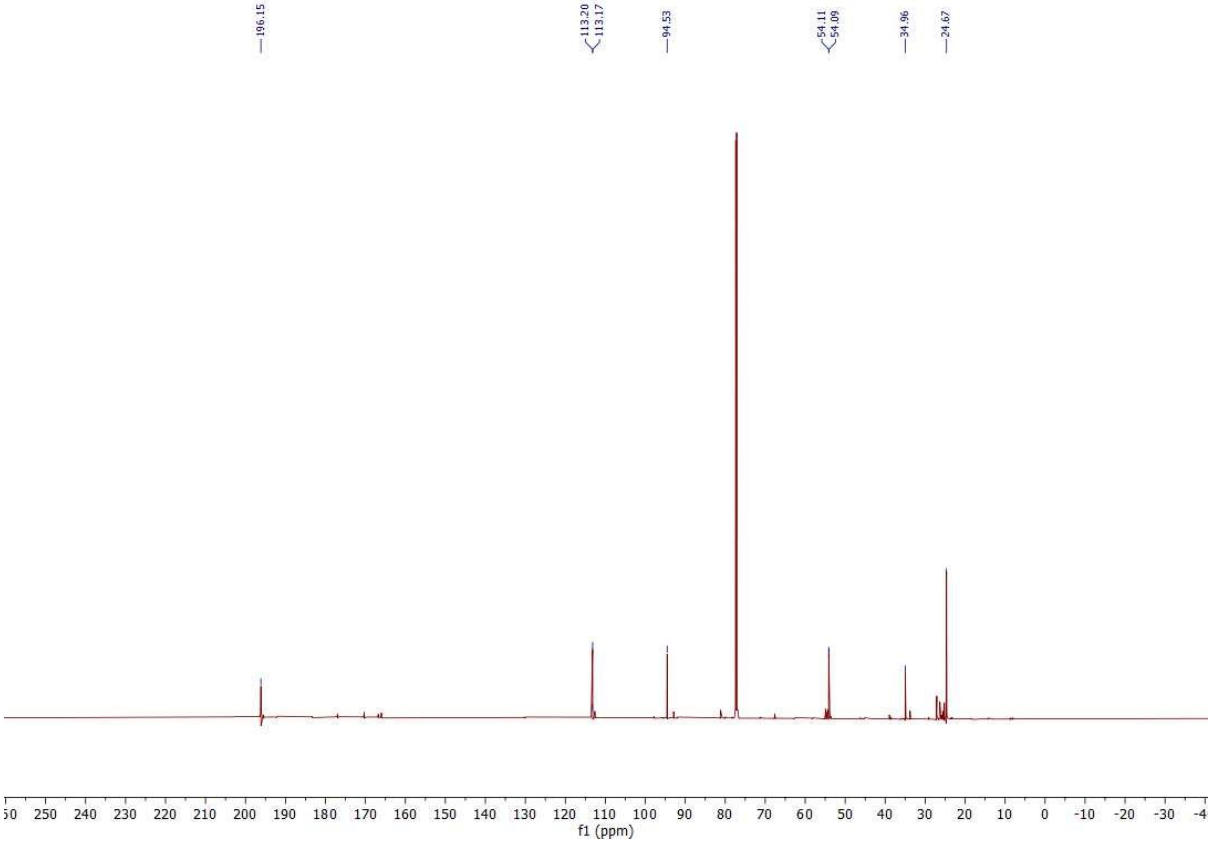
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**4d**:



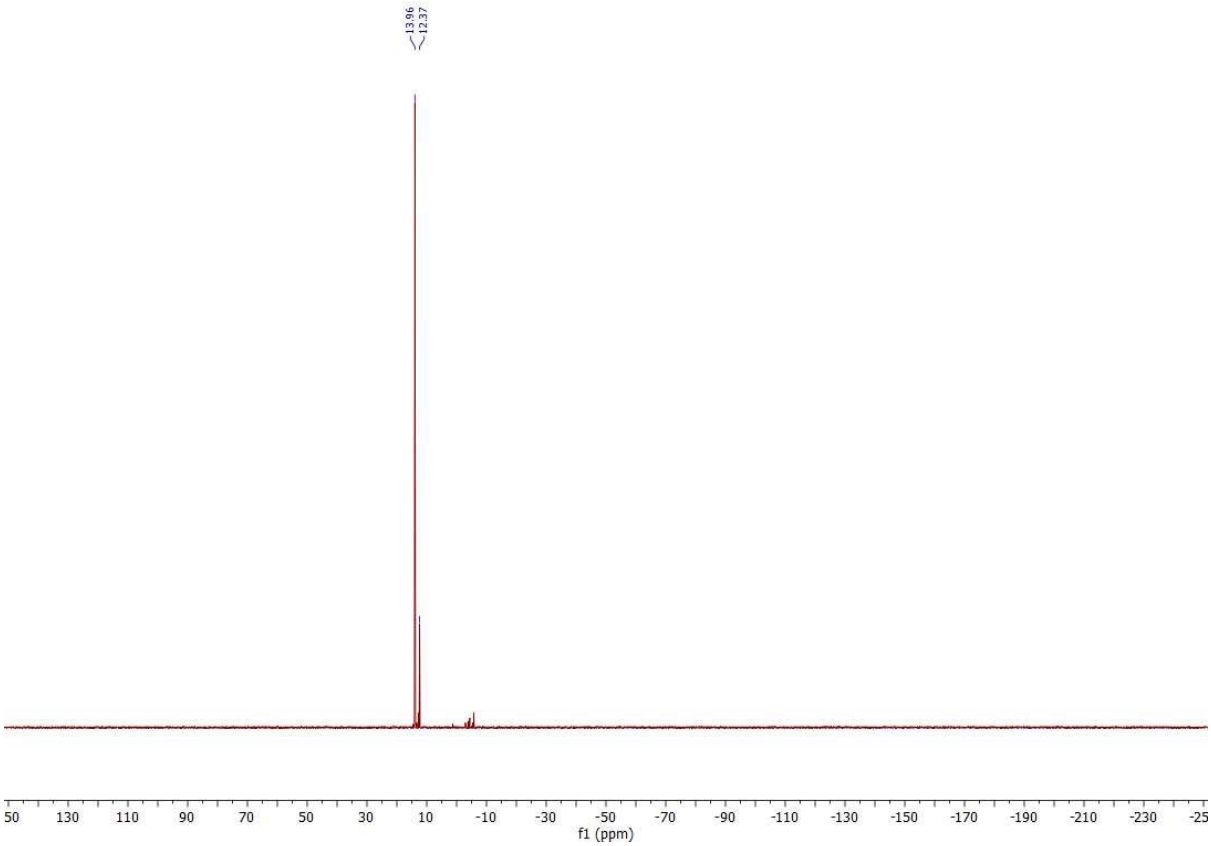
^{13}C NMR (151 MHz, $CDCl_3$)-**4d**:



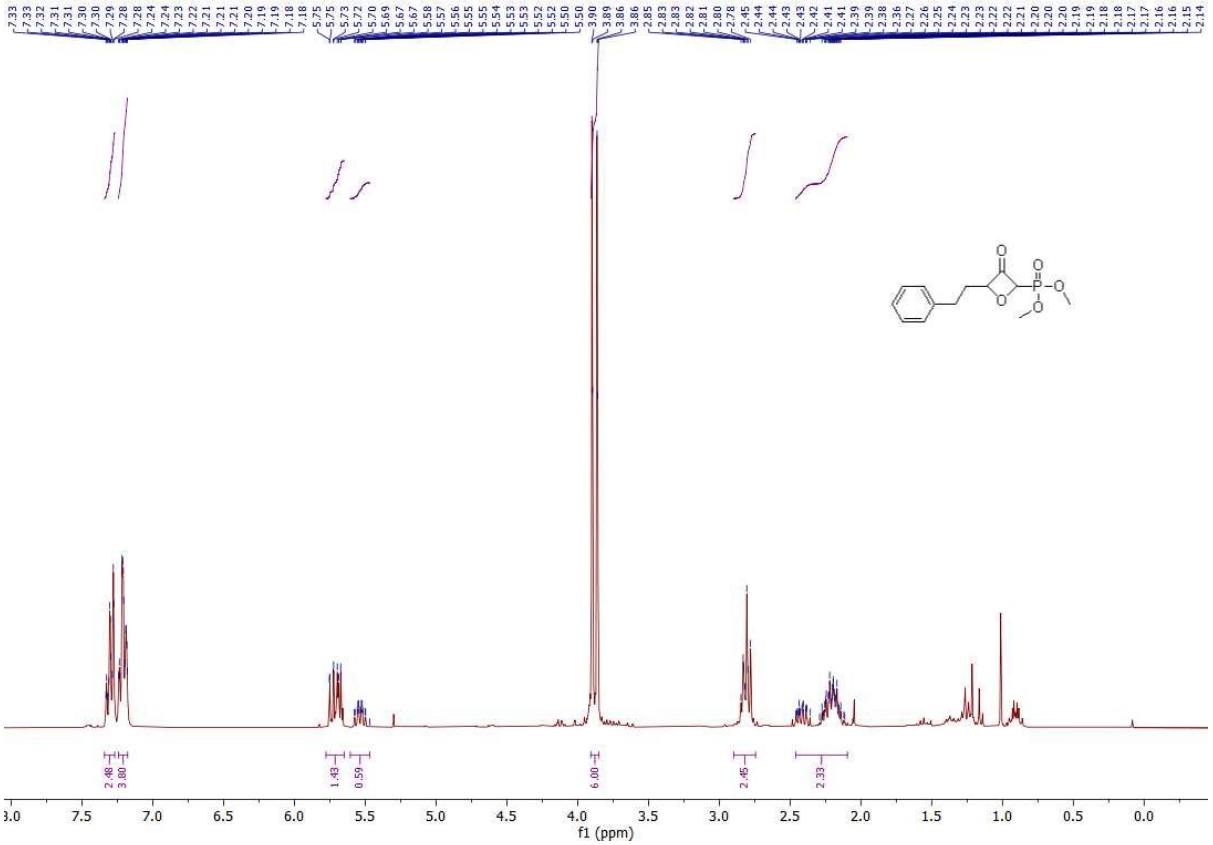
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4d**:



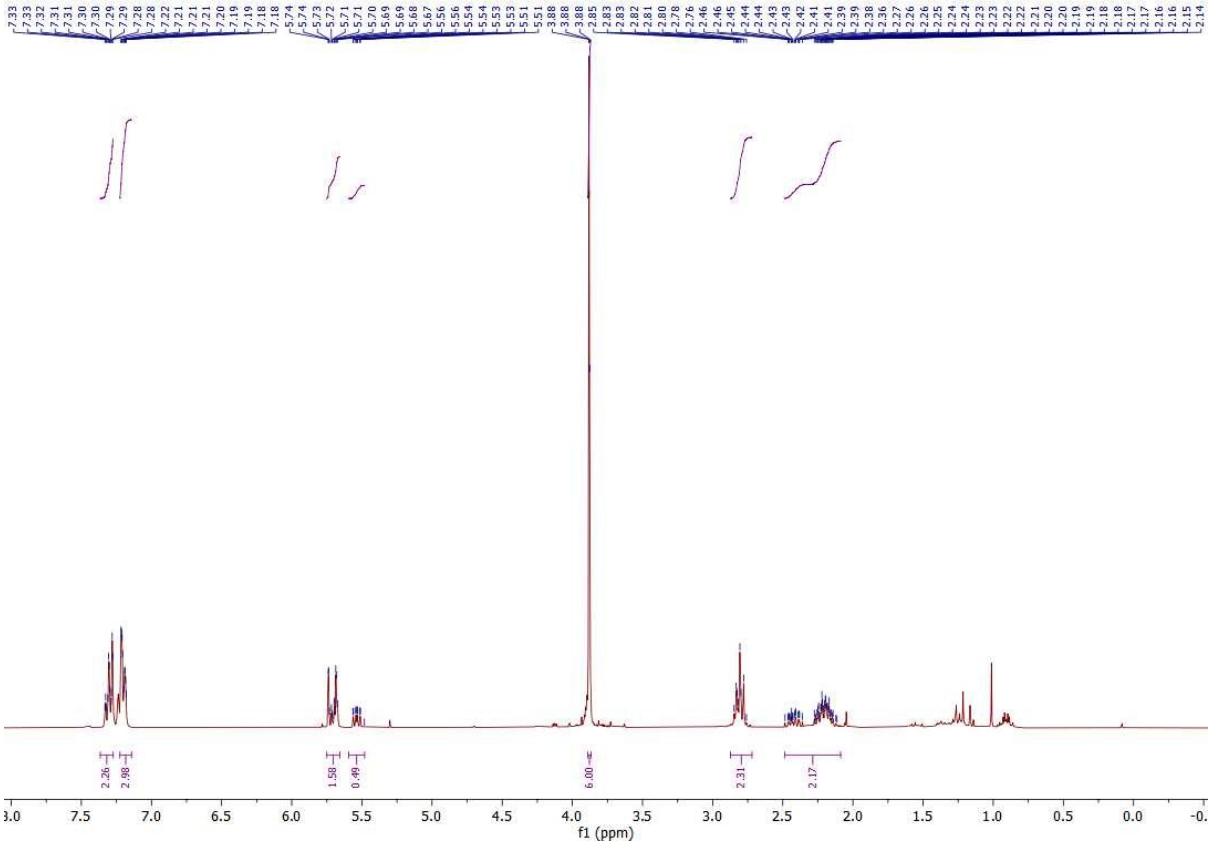
^{31}P NMR (121 MHz, $CDCl_3$)-**4d**:



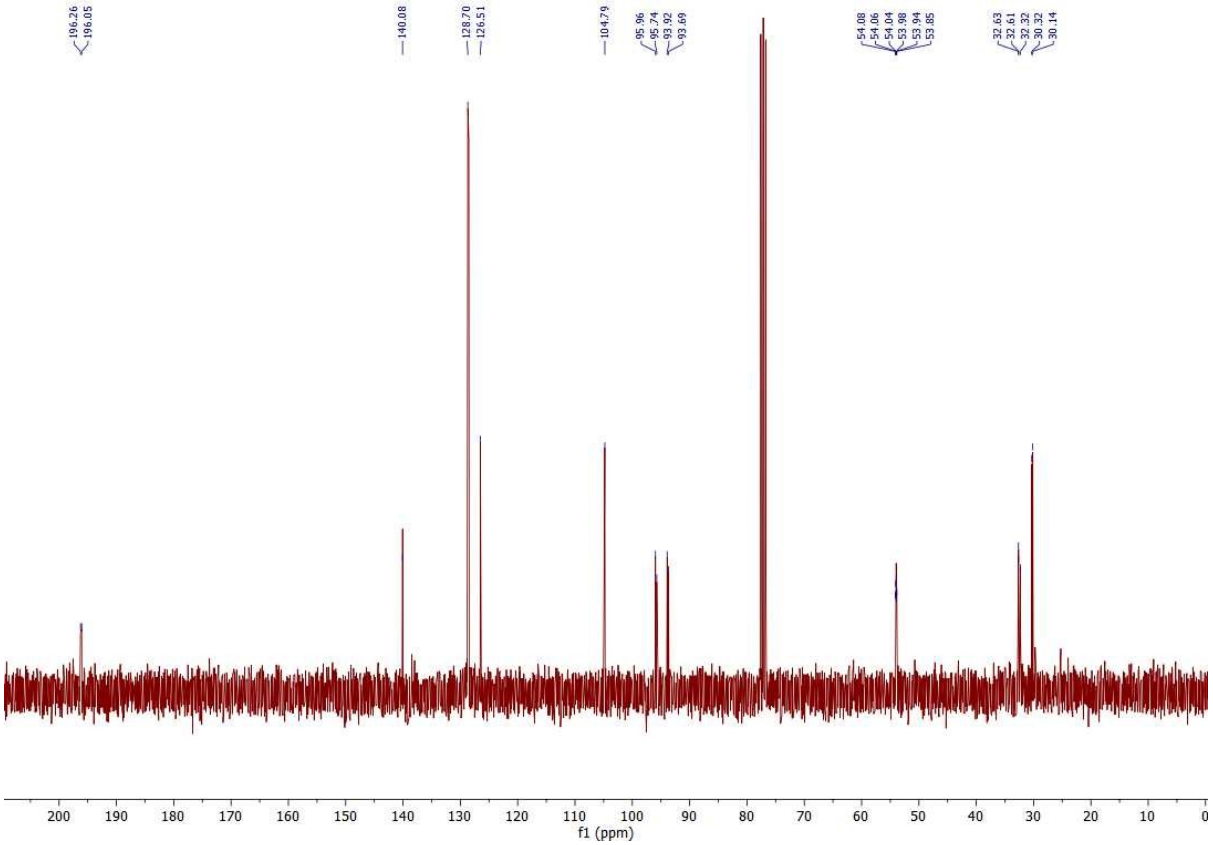
^{1}H NMR (300 MHz, $CDCl_3$)-**4e**:



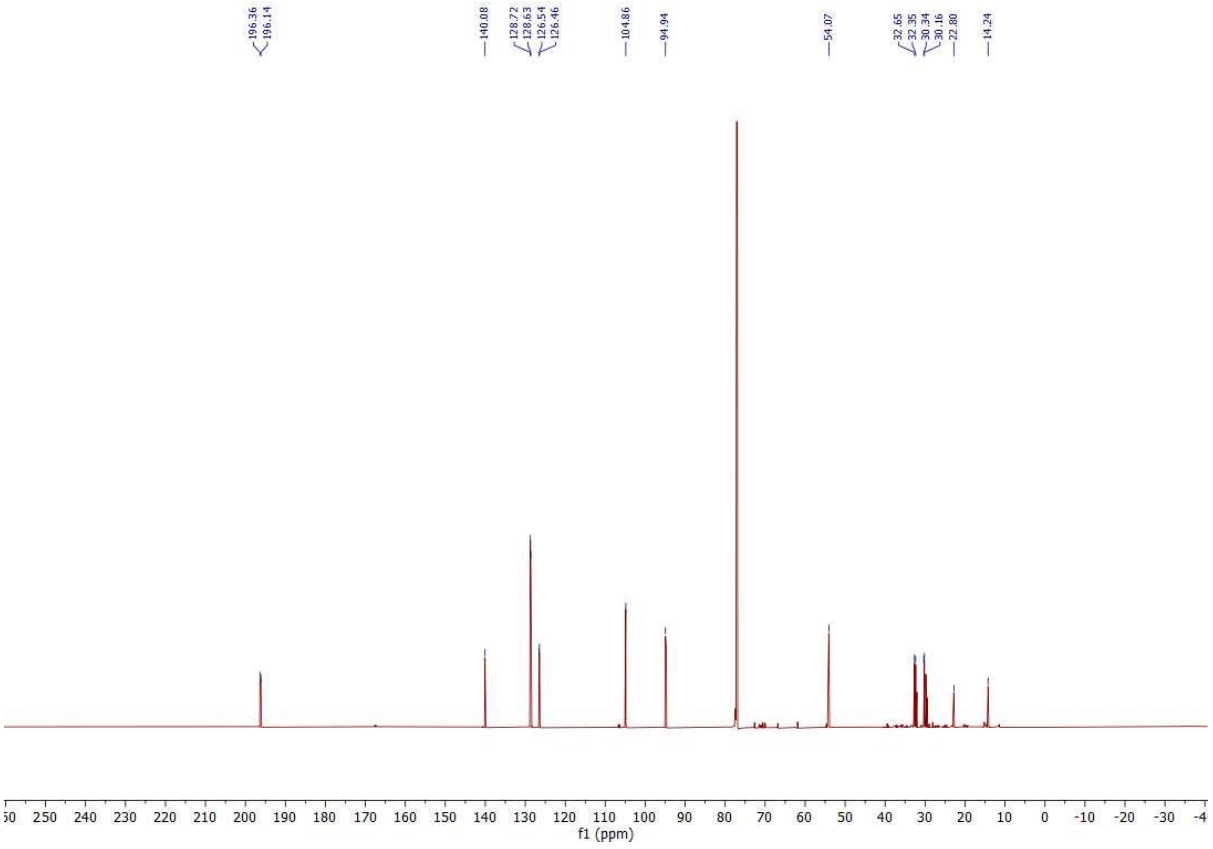
$^{1}H\{^{31}P\}$ (300 MHz, $CDCl_3$)-**4e**:



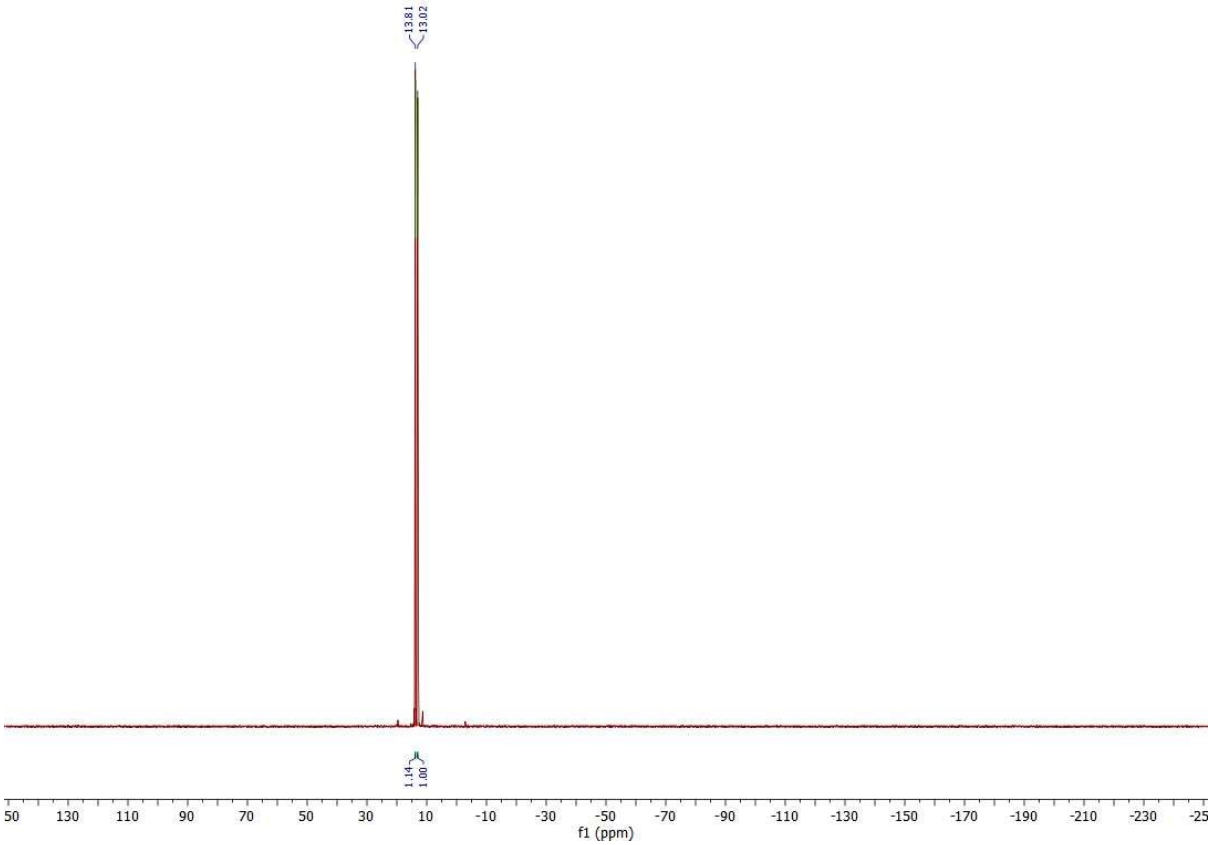
^{13}C NMR (75 MHz, $CDCl_3$)-**4e**:



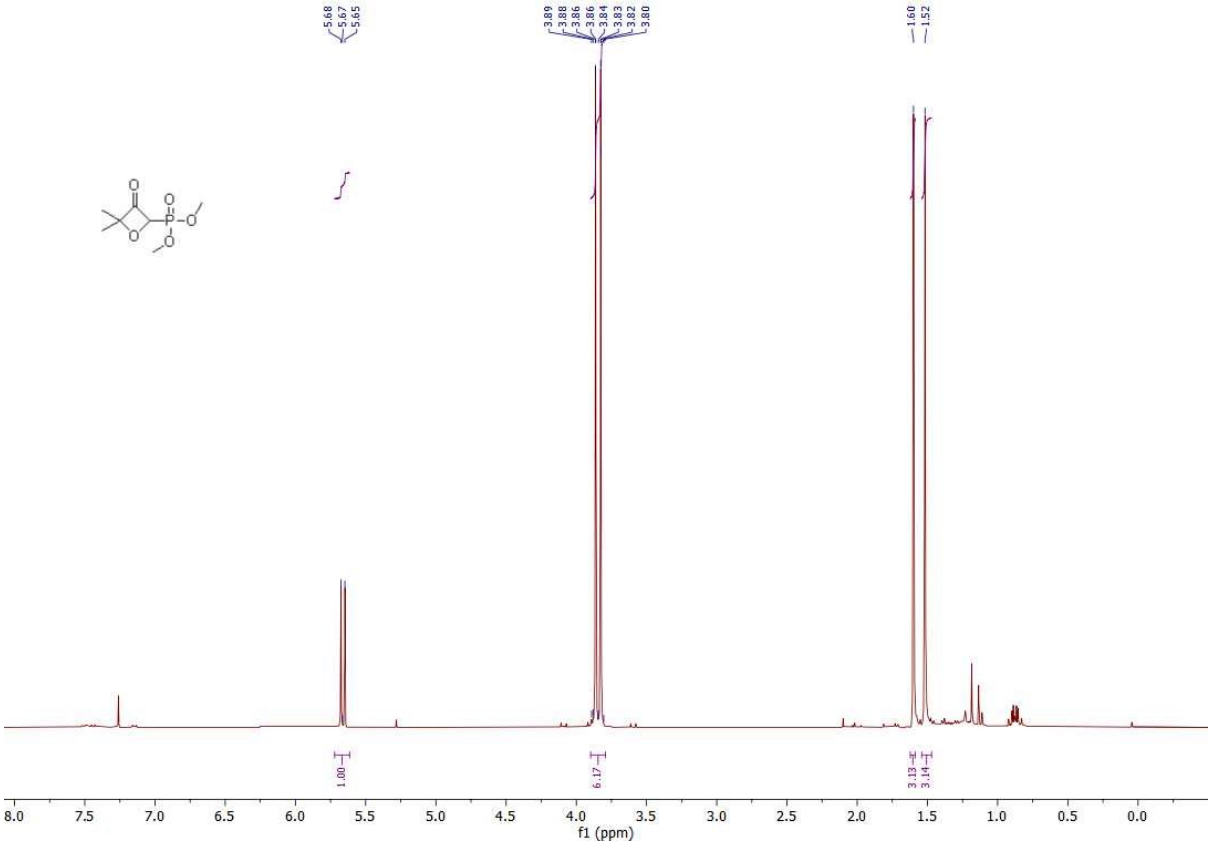
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4e**:



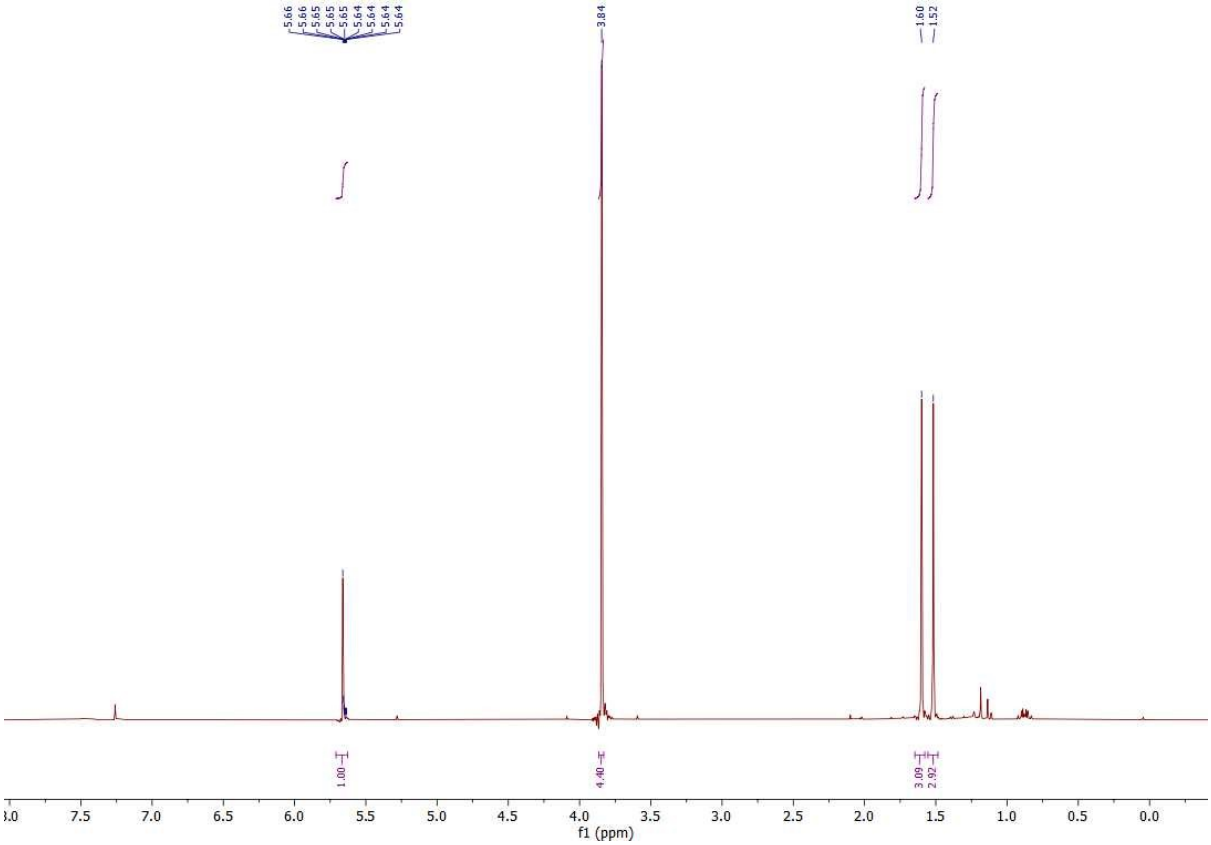
^{31}P NMR (121 MHz, $CDCl_3$)-**4e**:



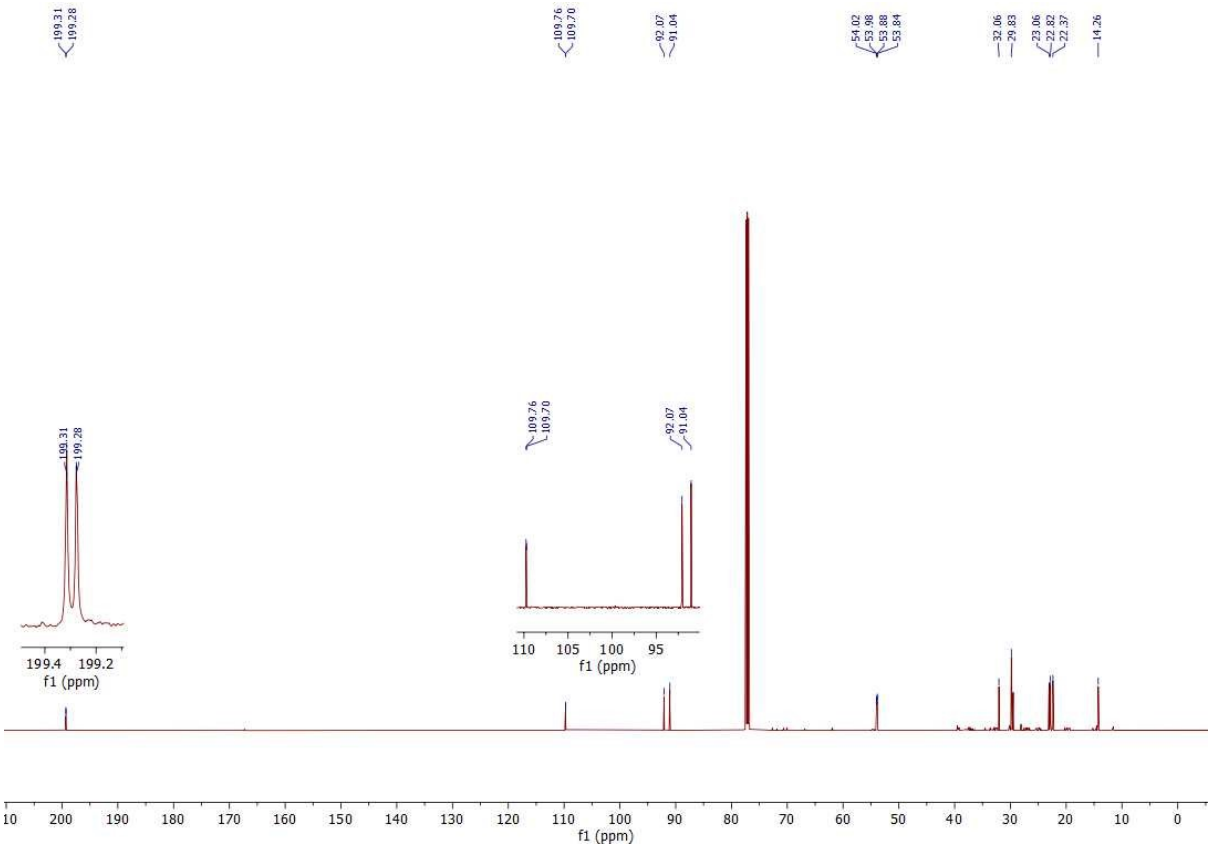
^{1}H NMR (300 MHz, $CDCl_3$)-**4f**:



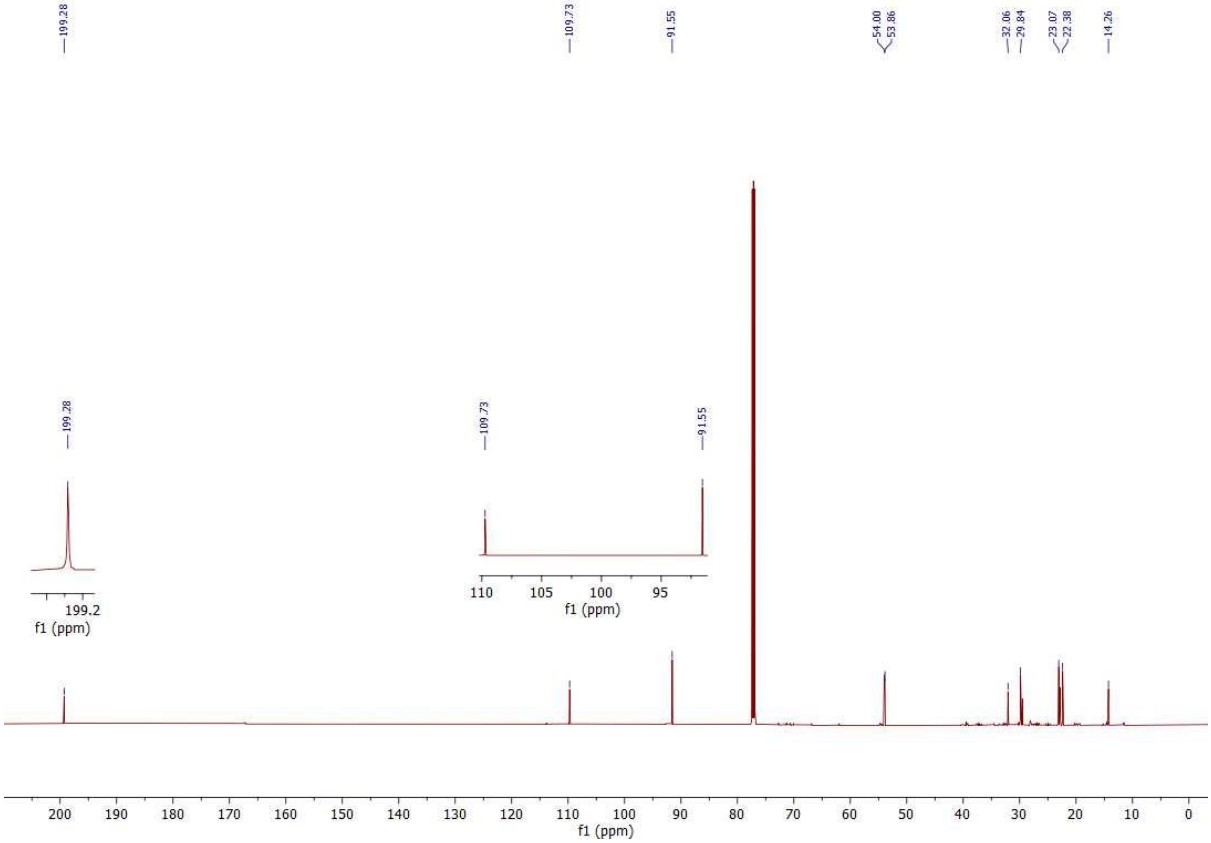
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**4f**:



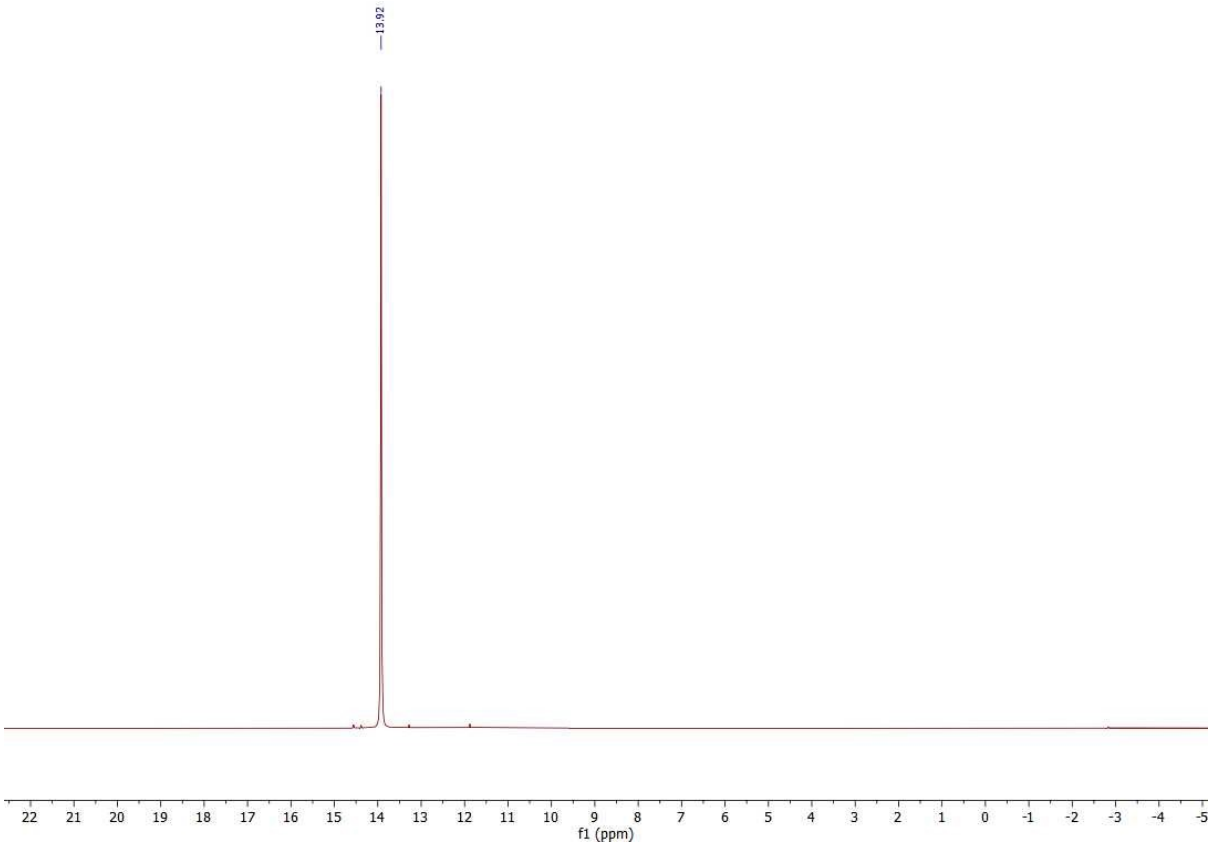
^{13}C NMR (151 MHz, $CDCl_3$)-**4f**:



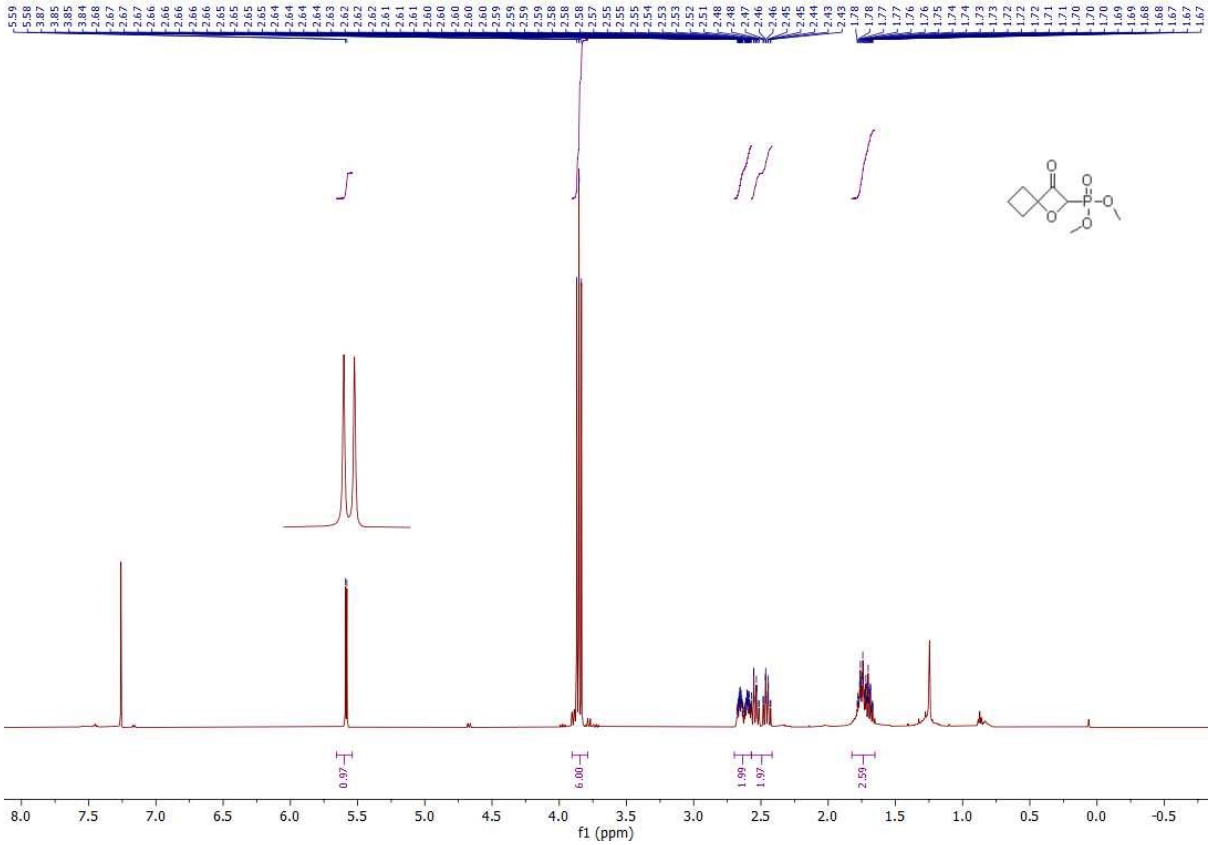
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4f**:



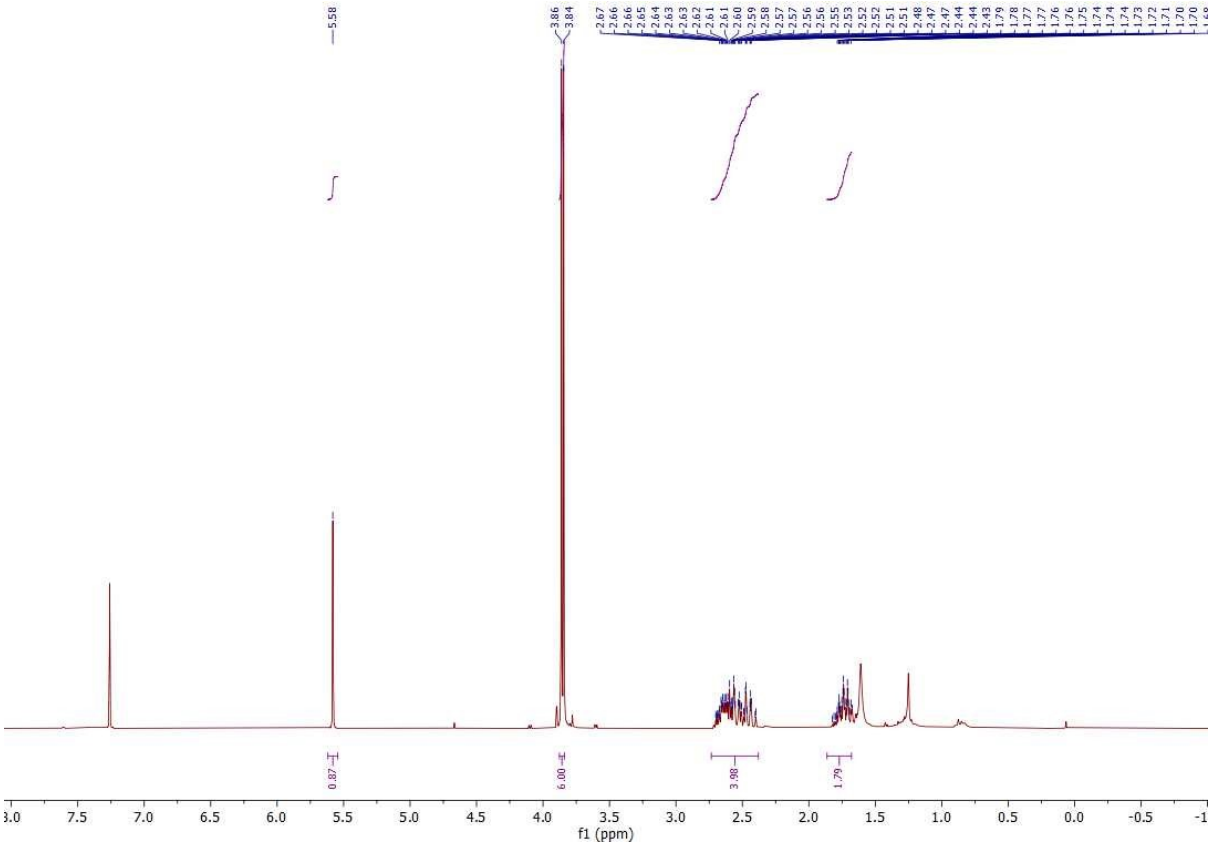
^{31}P NMR (121 MHz, $CDCl_3$)-**4f**:



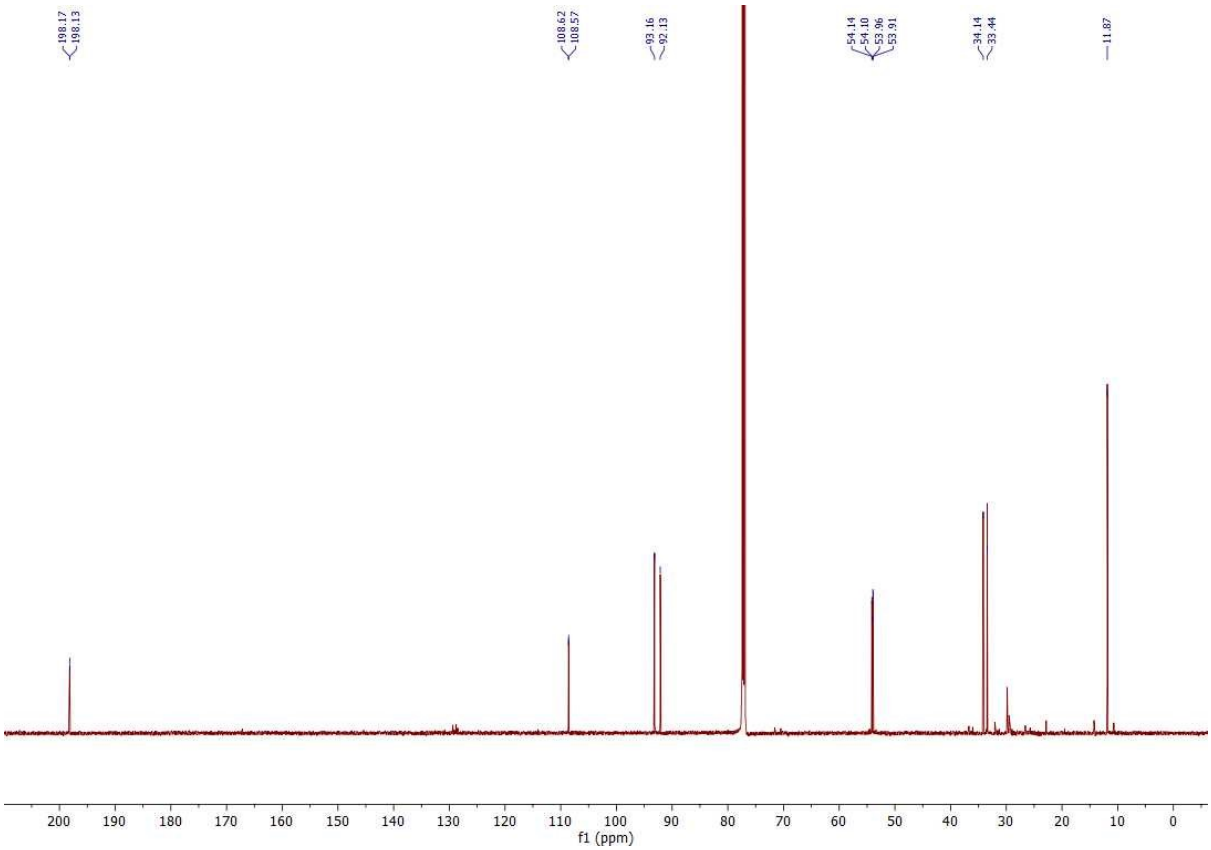
^{1}H NMR (600 MHz, $CDCl_3$)-**4g**:



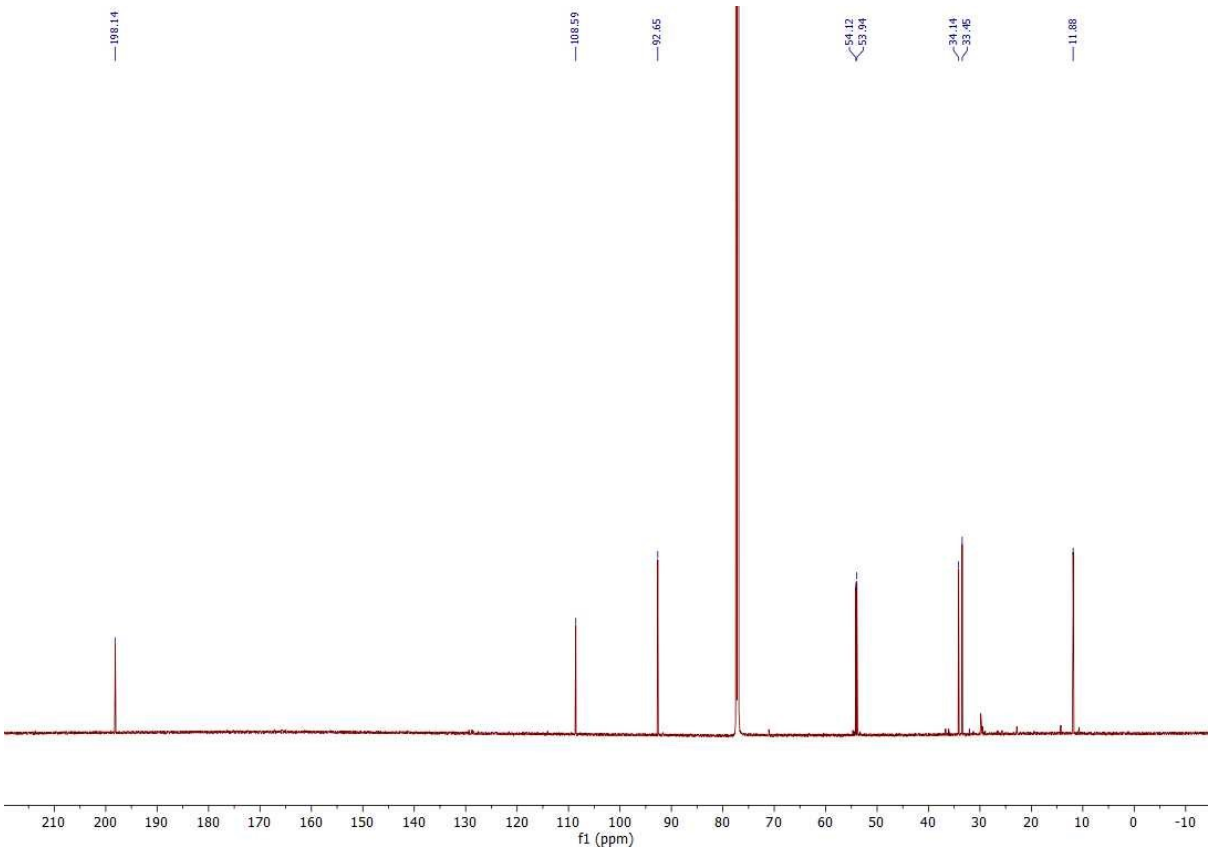
$^{1}H\{^{31}P\}$ (300 MHz, $CDCl_3$)-**4g**:



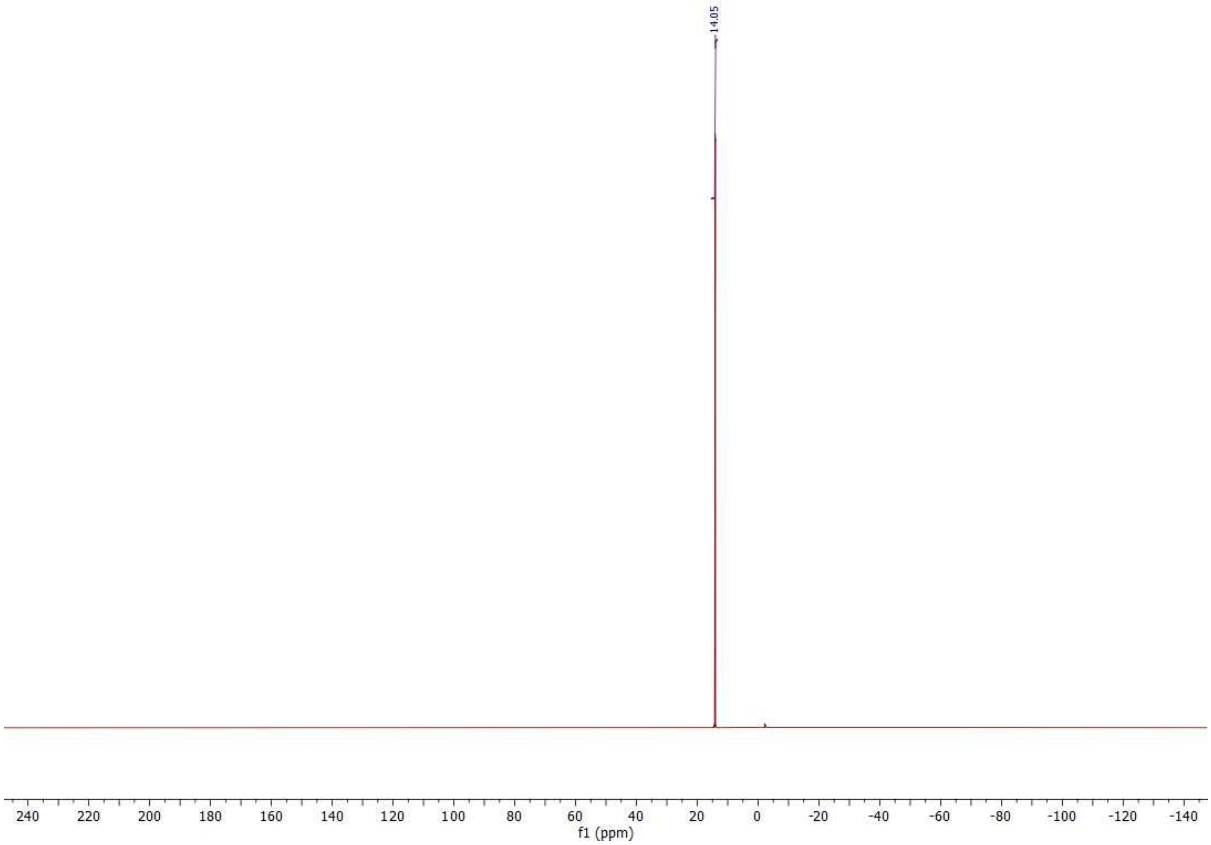
^{13}C NMR (151 MHz, $CDCl_3$)-**4g**:



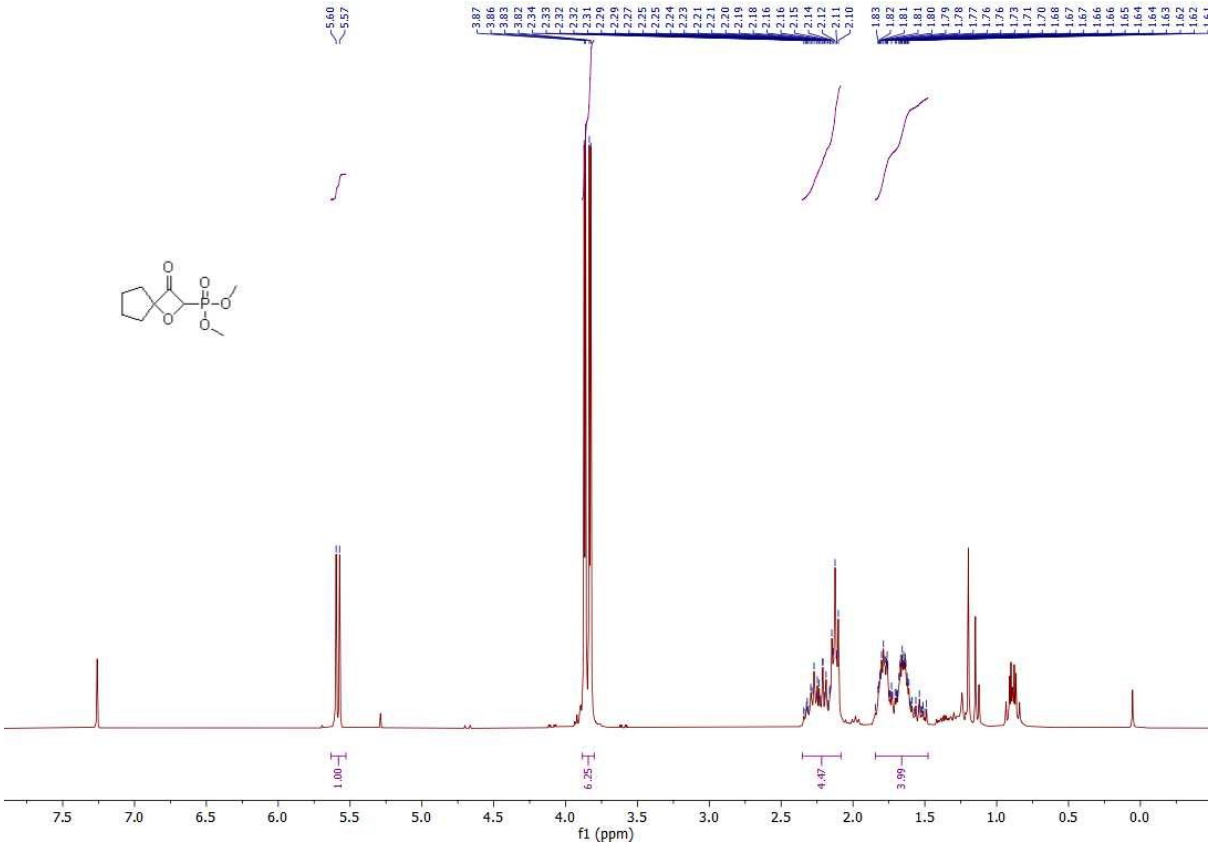
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4g**:



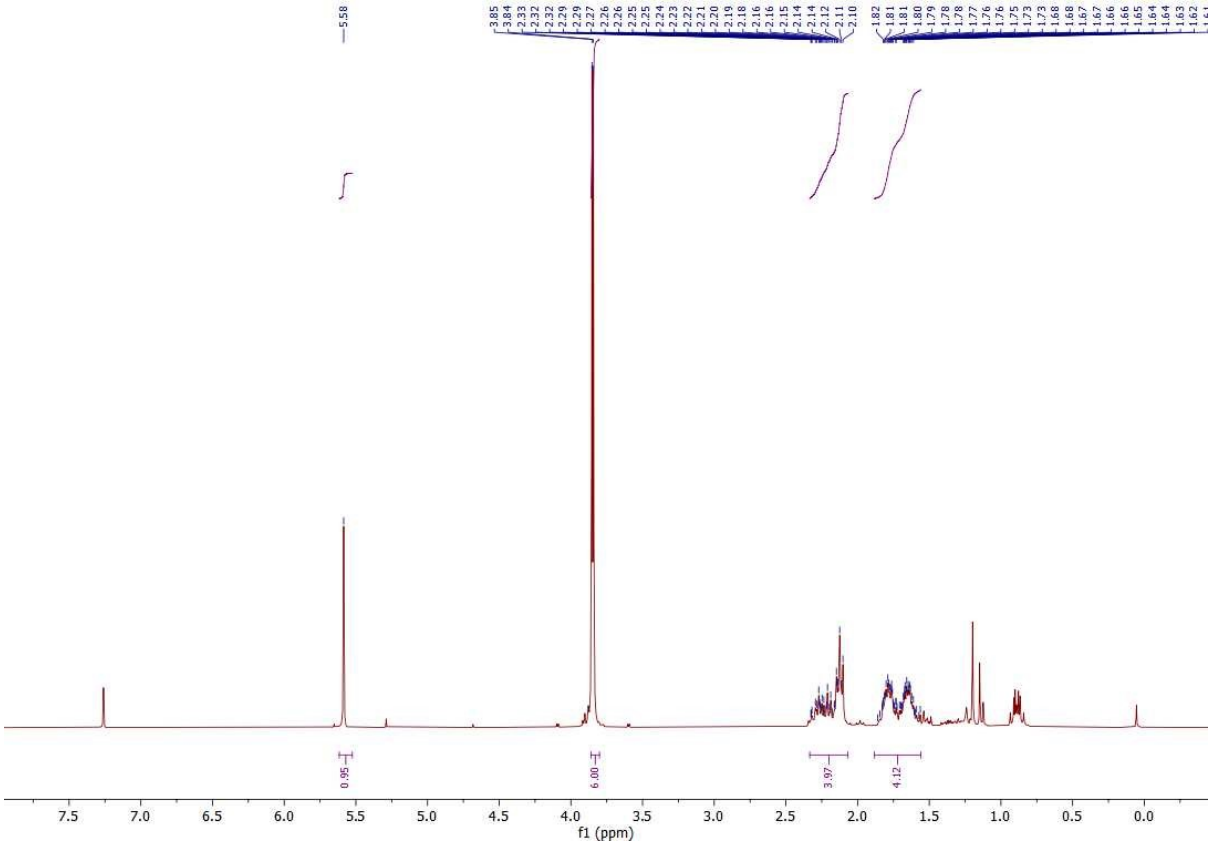
^{31}P NMR (151 MHz, $CDCl_3$)-**4g**:



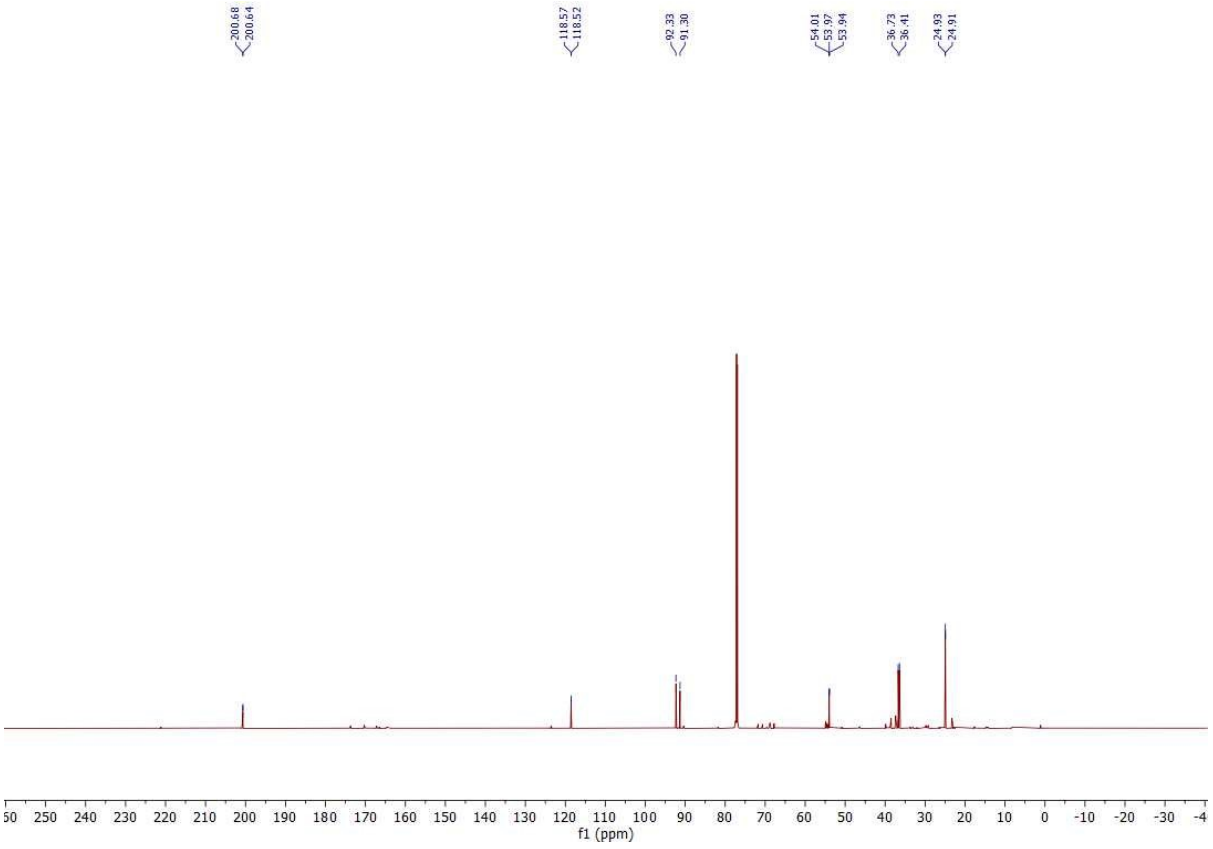
^{1}H NMR (300 MHz, $CDCl_3$)-**4h**:



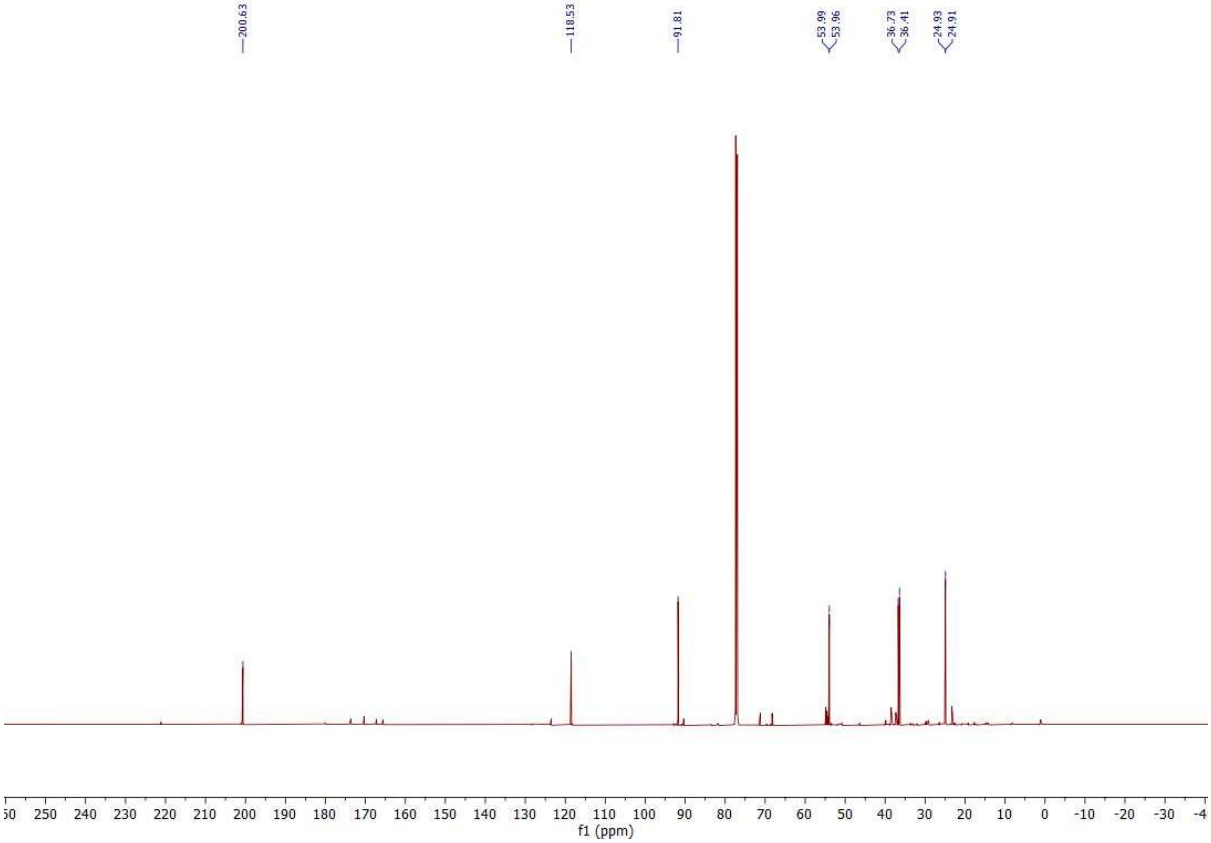
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**4h**:



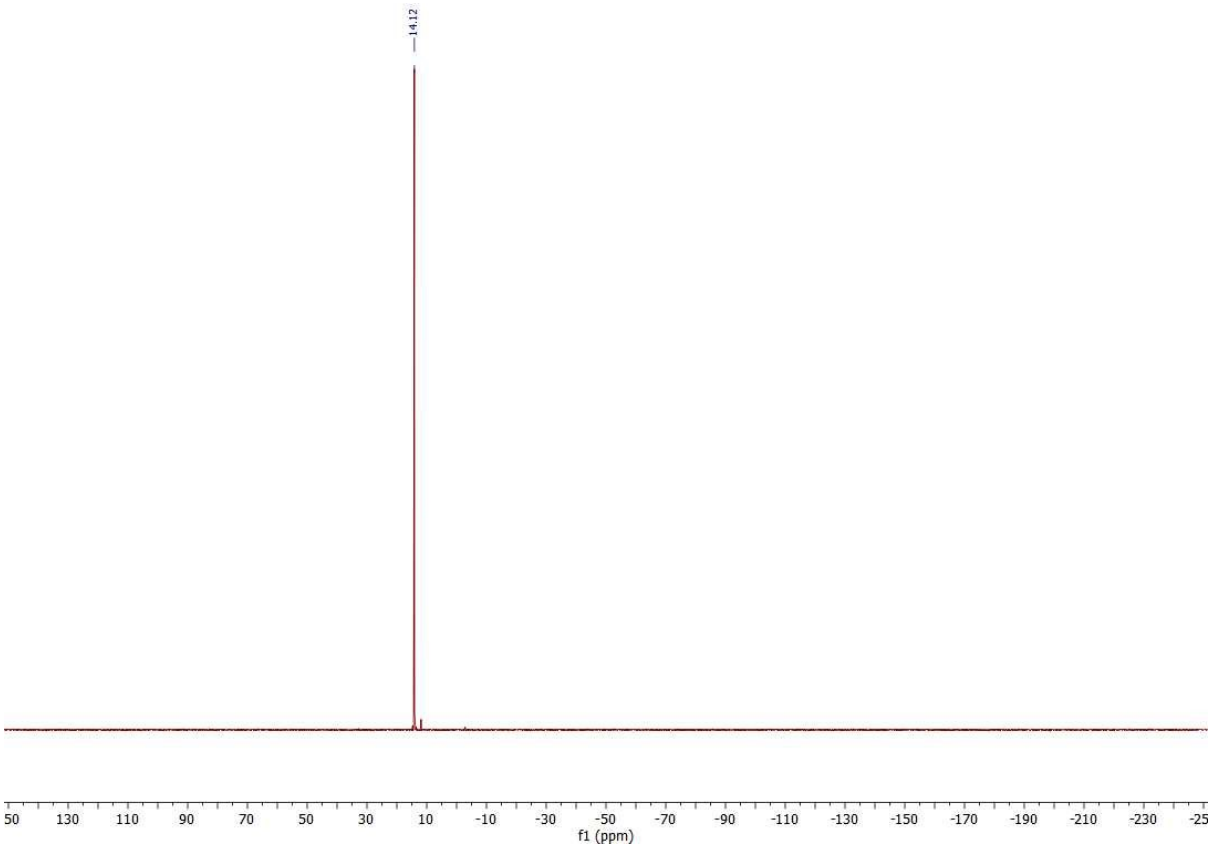
^{13}C NMR (151MHz, $CDCl_3$)-**4h**:



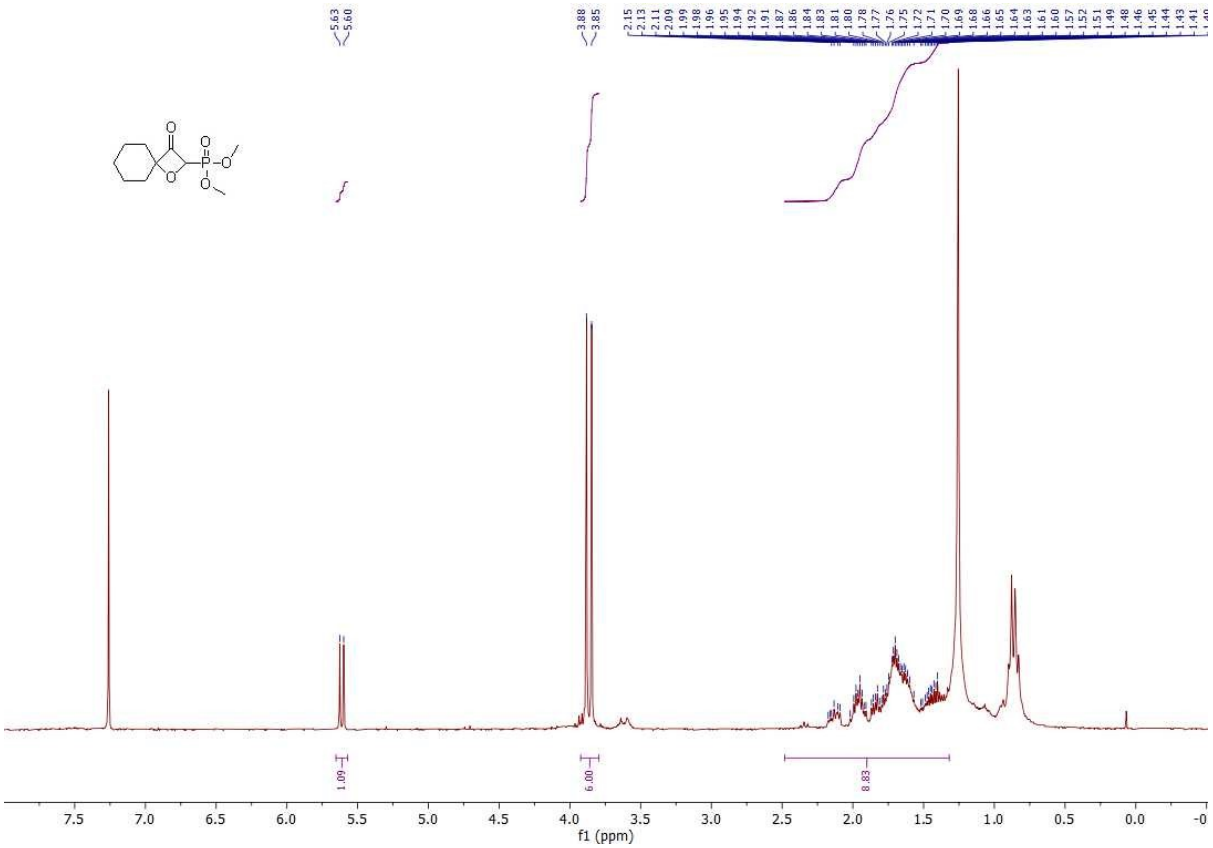
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4h**:



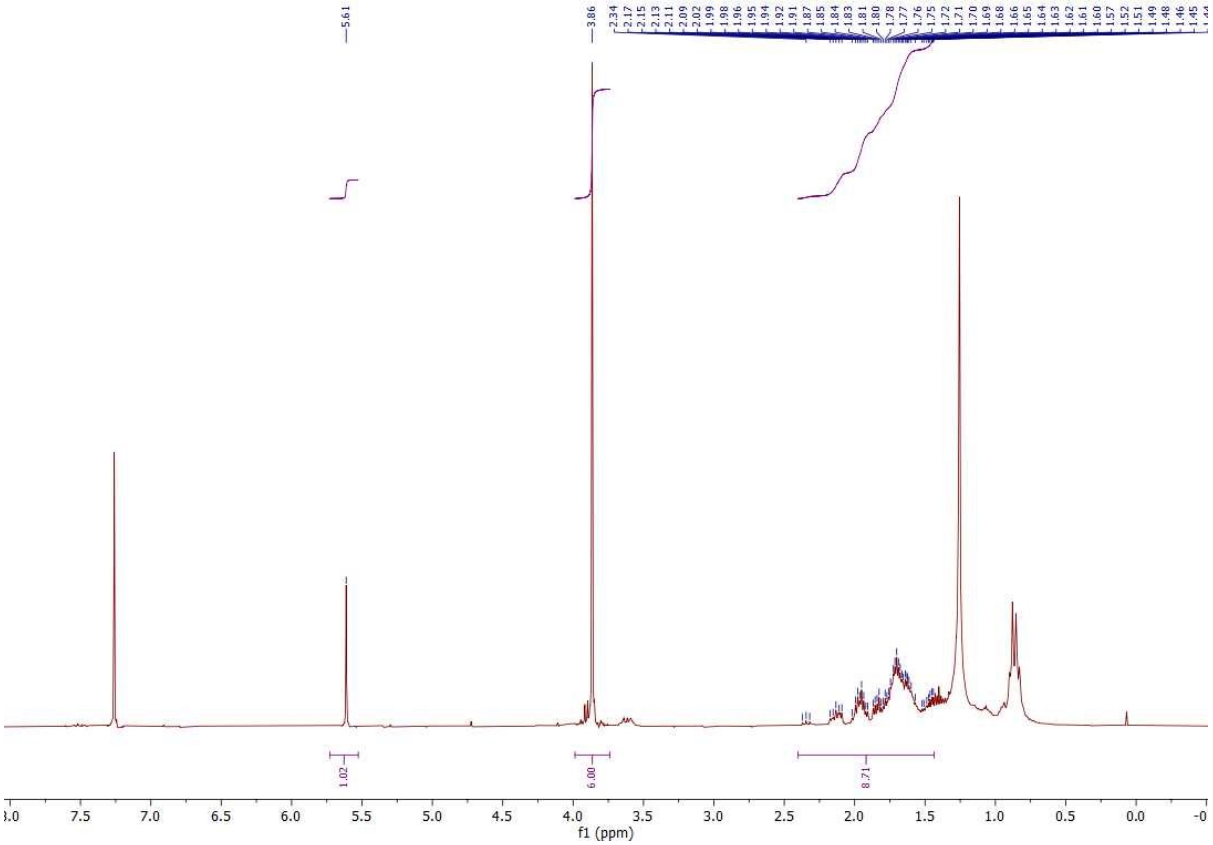
^{31}P NMR (121 MHz, $CDCl_3$)-**4h**:



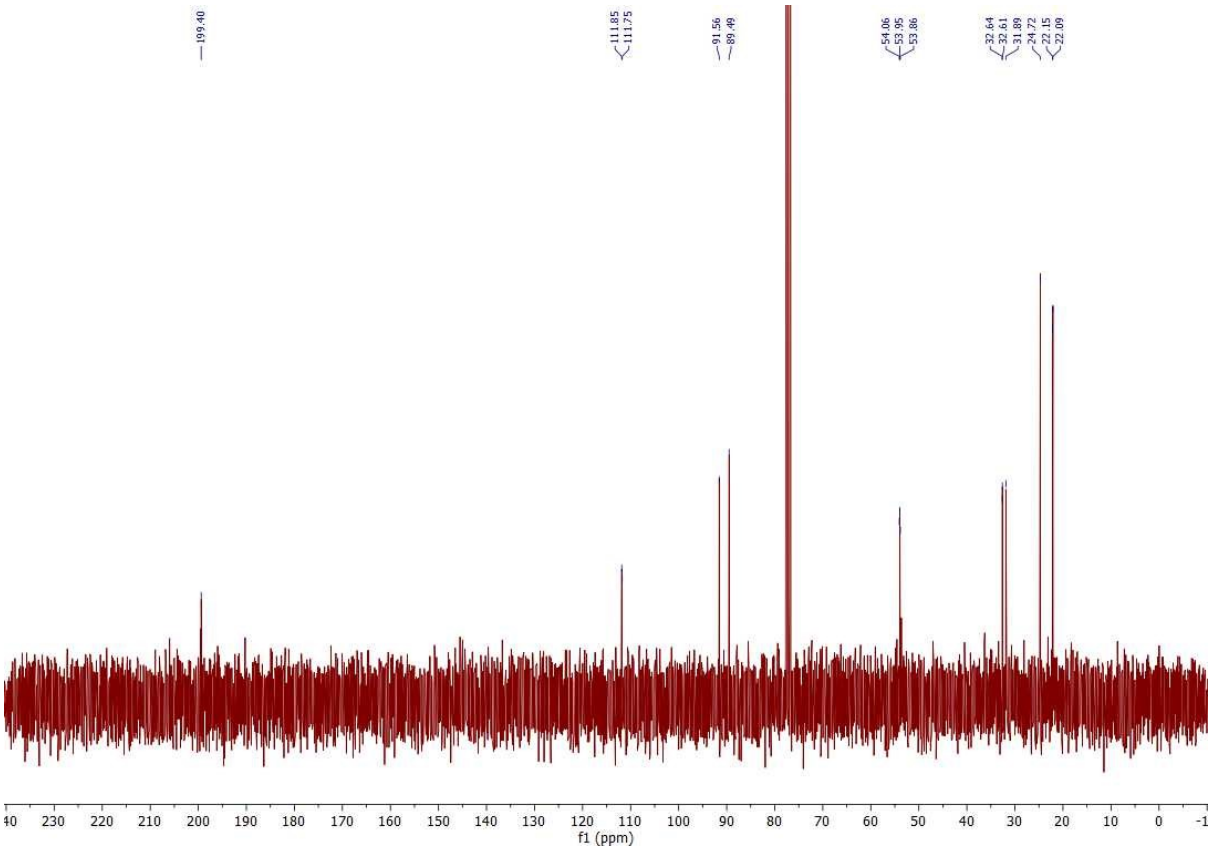
^{1}H NMR (300 MHz, $CDCl_3$)-**4i**:



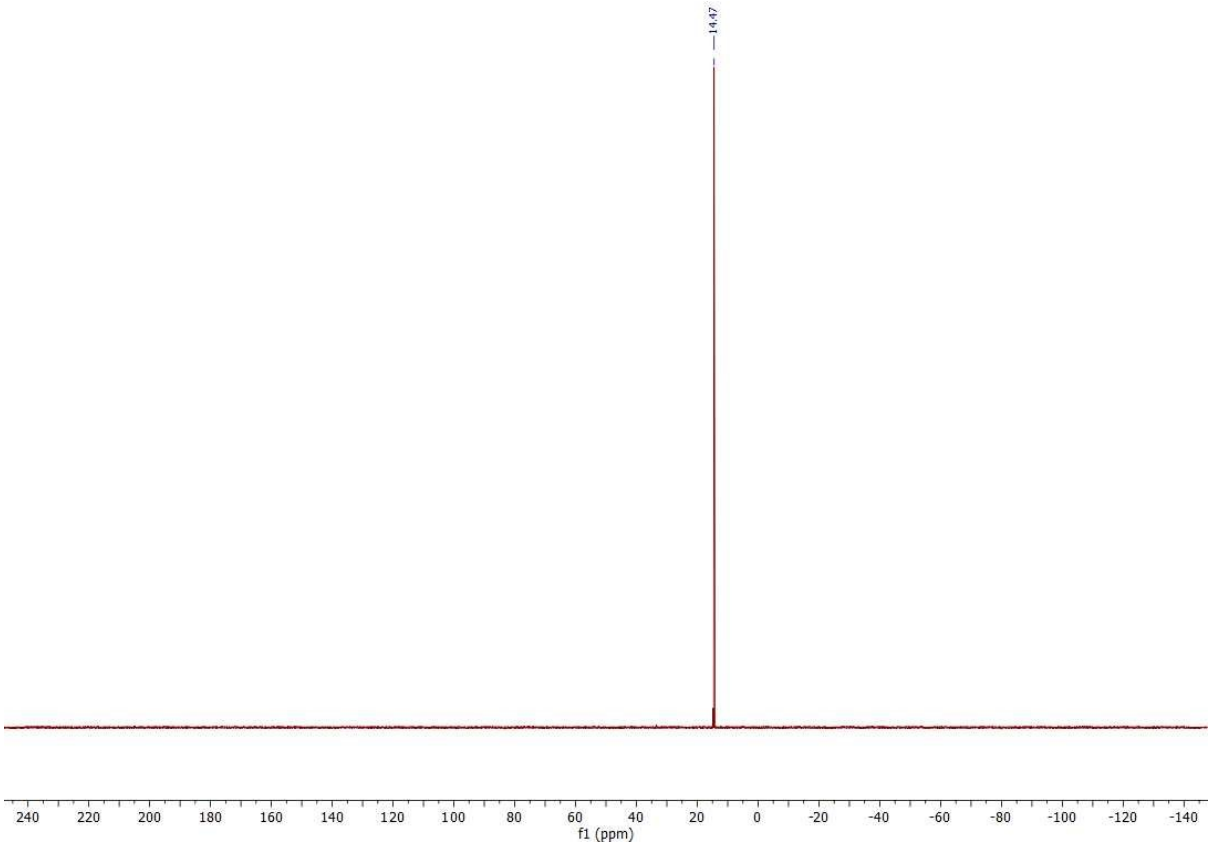
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**4i**:



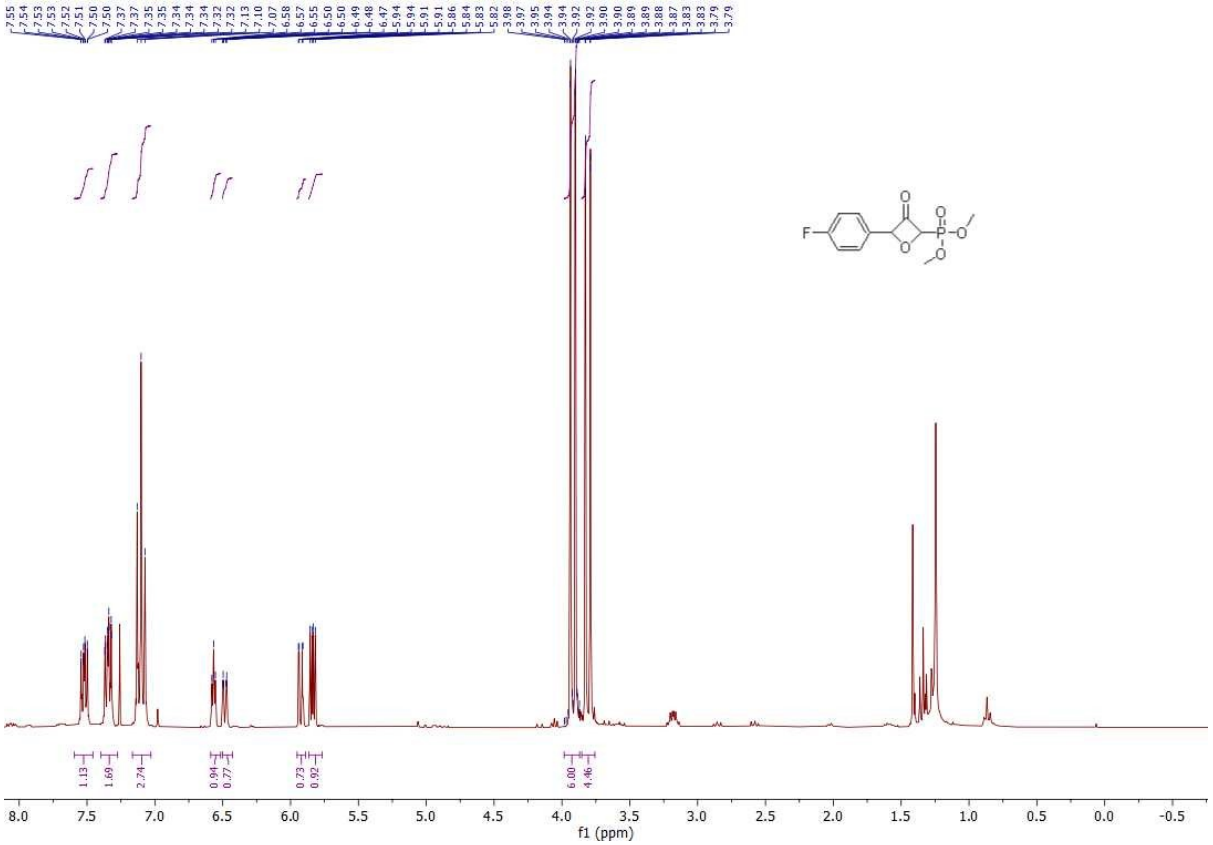
^{13}C NMR (MHz, $CDCl_3$)-**4i**:



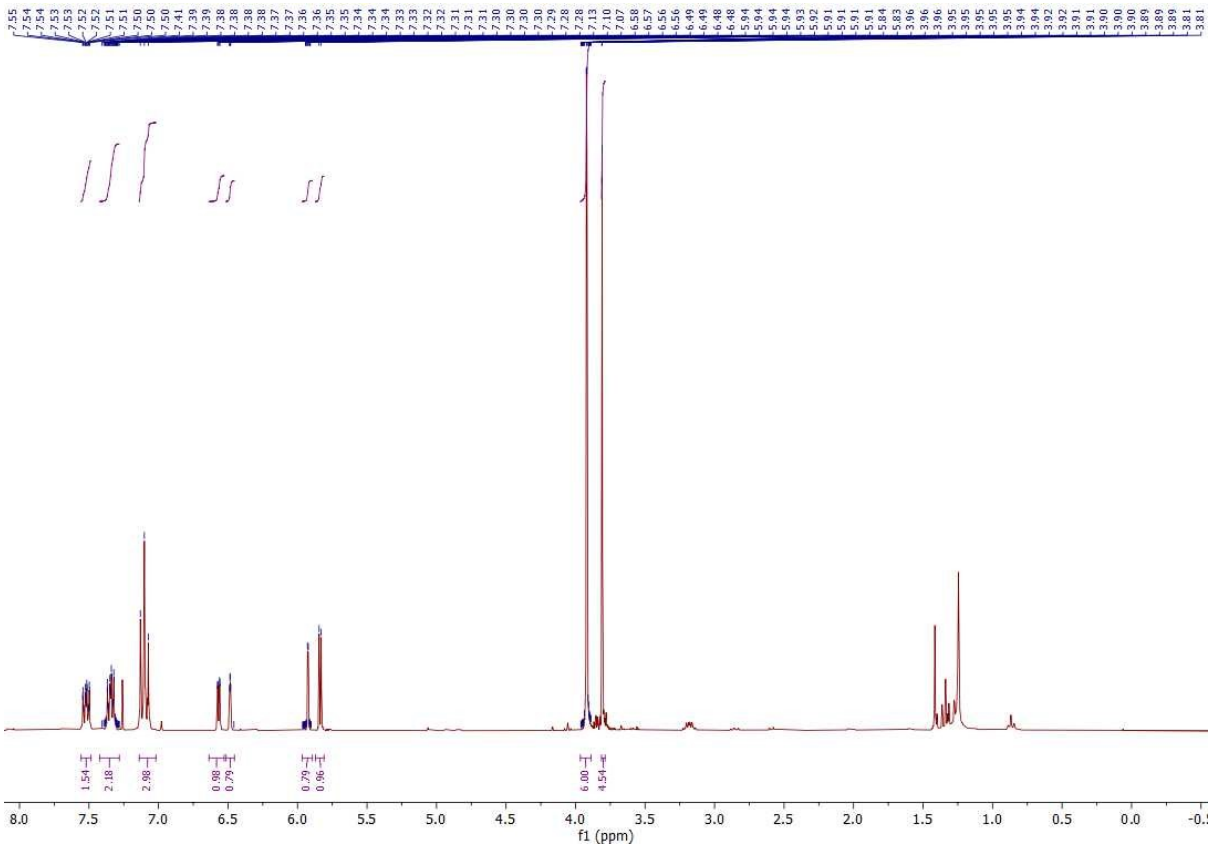
^{31}P NMR (121 MHz, $CDCl_3$)-**4i**:



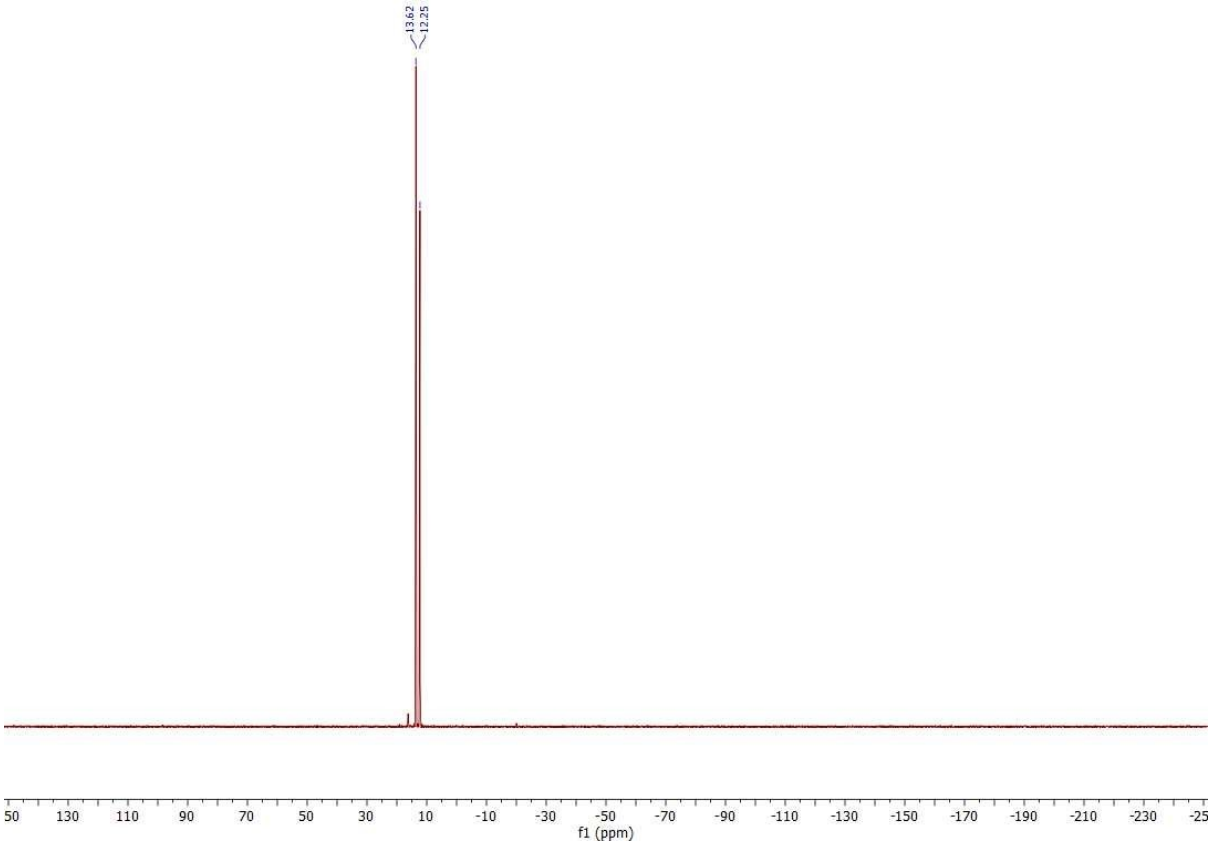
^{1}H NMR (300 MHz, $CDCl_3$)-**4k**:



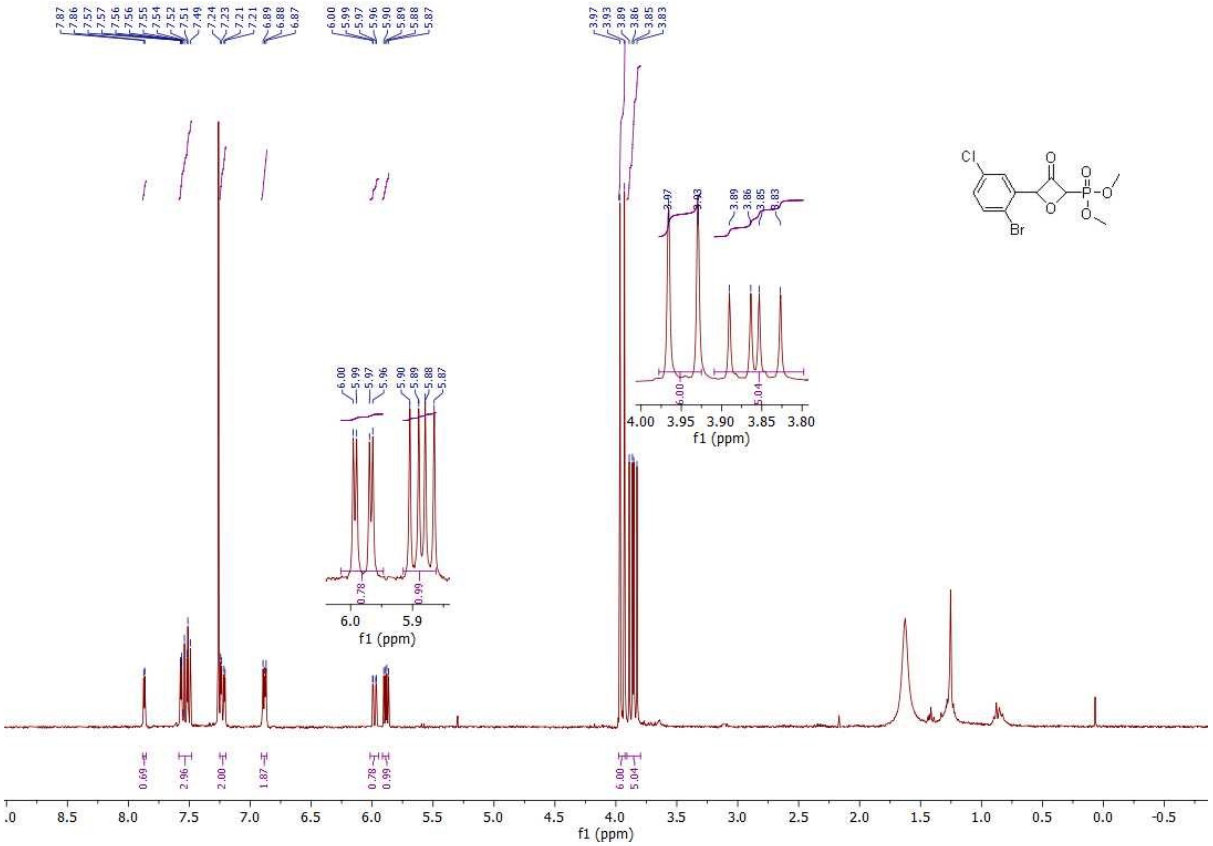
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**4k**:



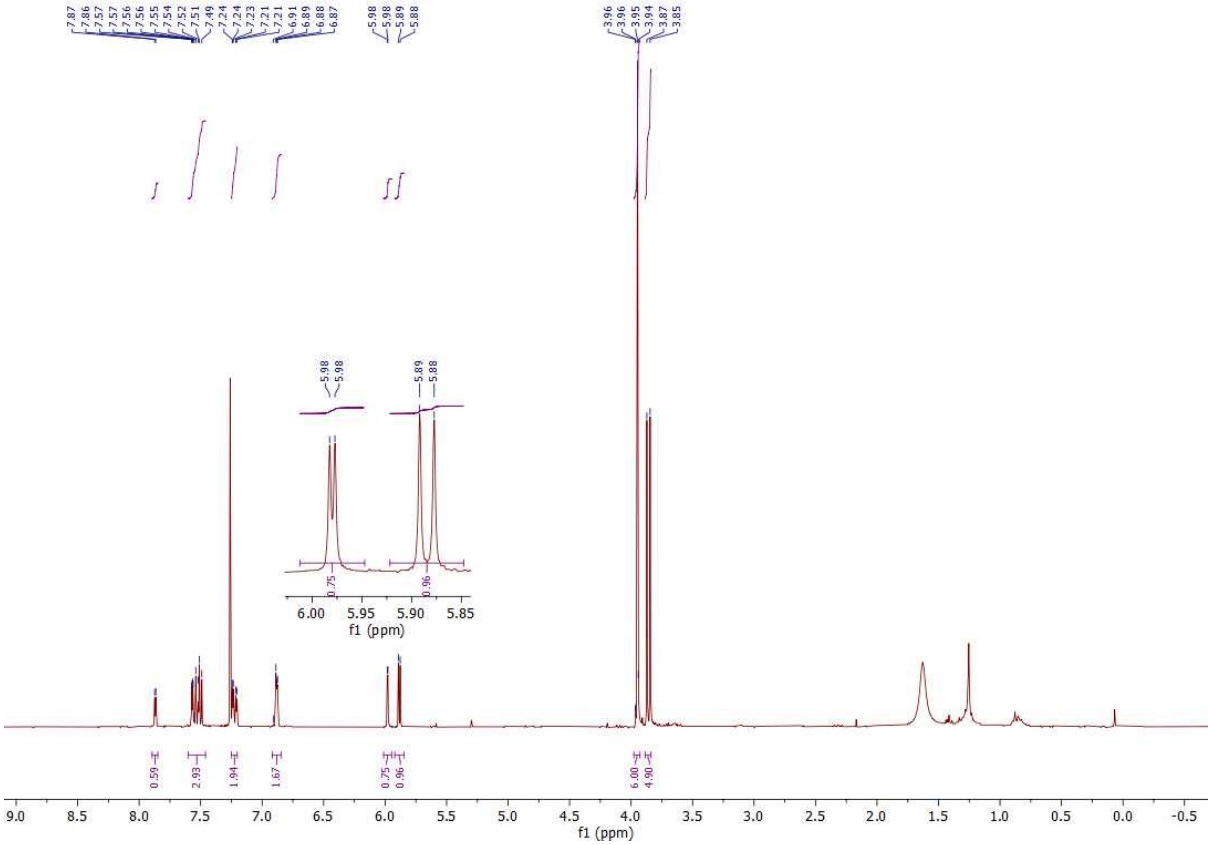
^{31}P NMR (121 MHz, $CDCl_3$)-**4k**:



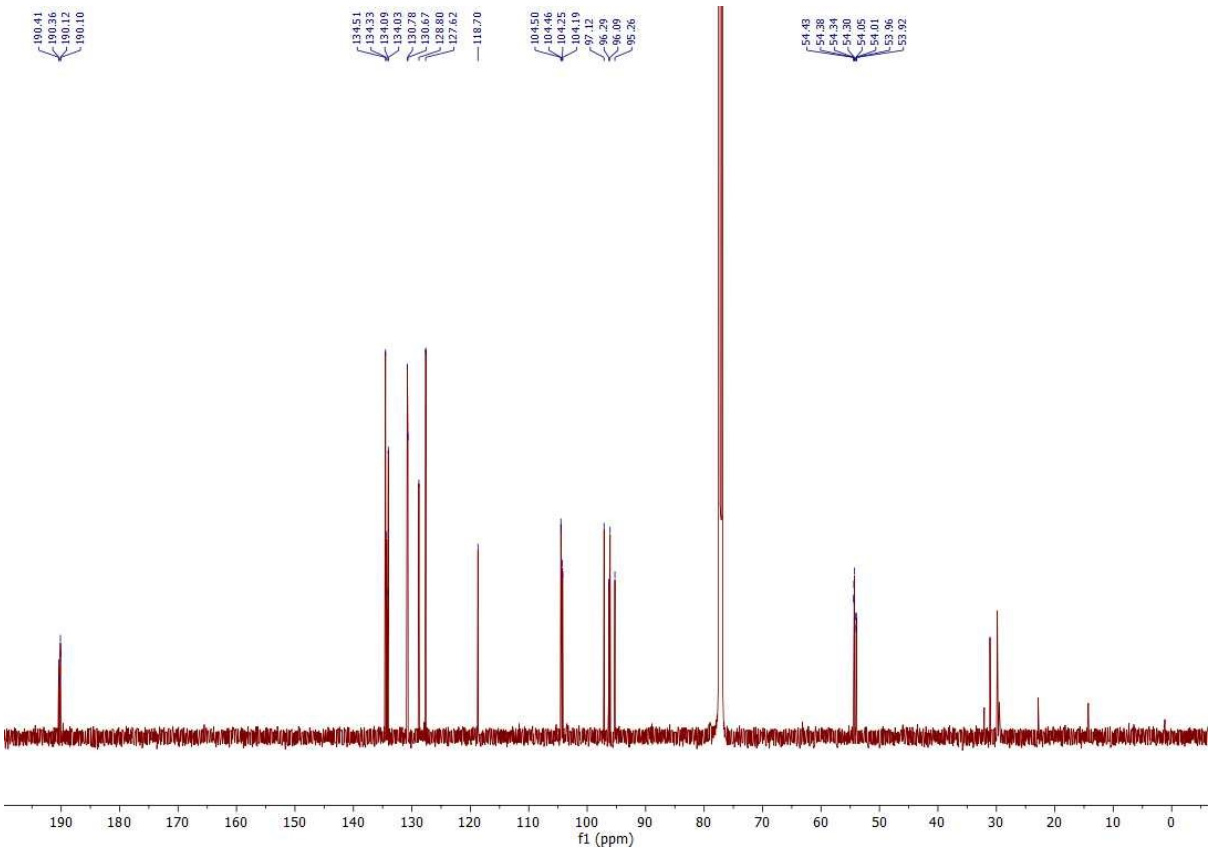
^{1}H NMR (300 MHz, $CDCl_3$)-**4l**:



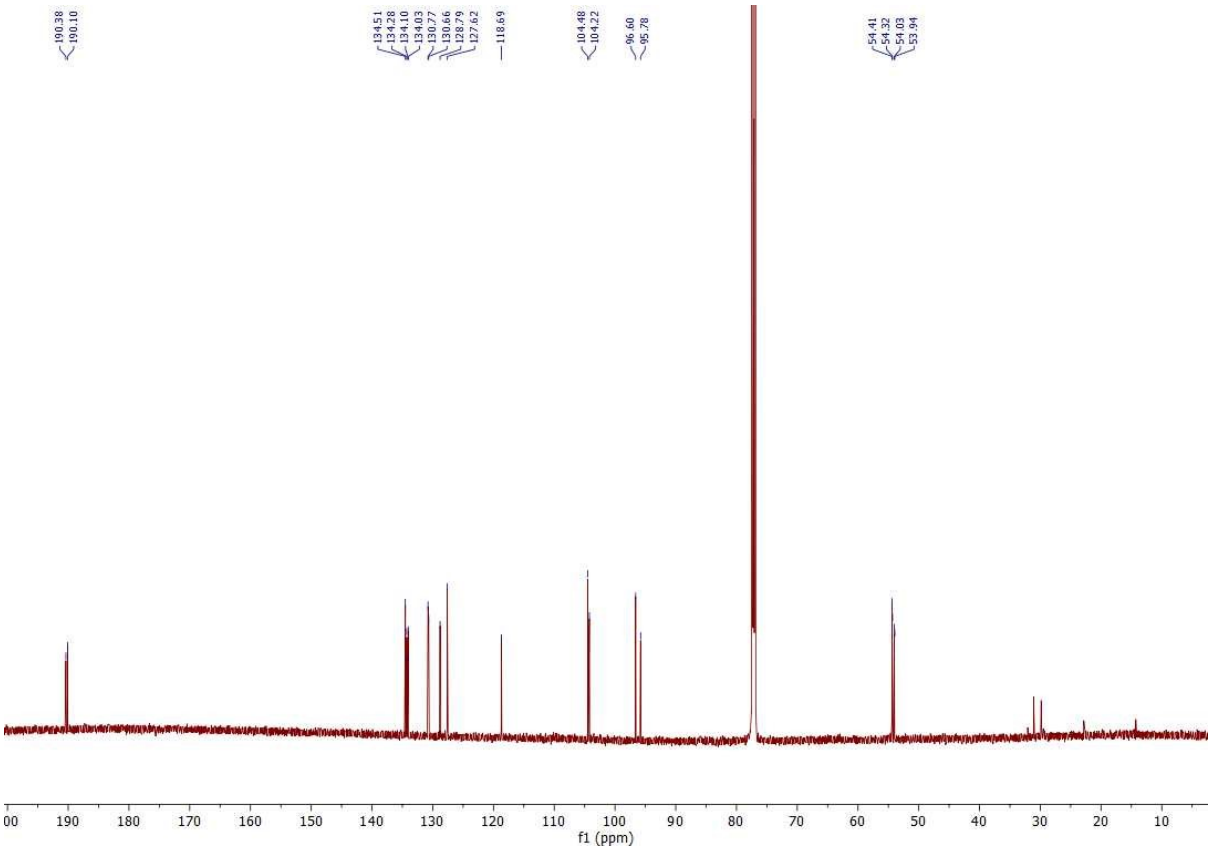
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**4l**:



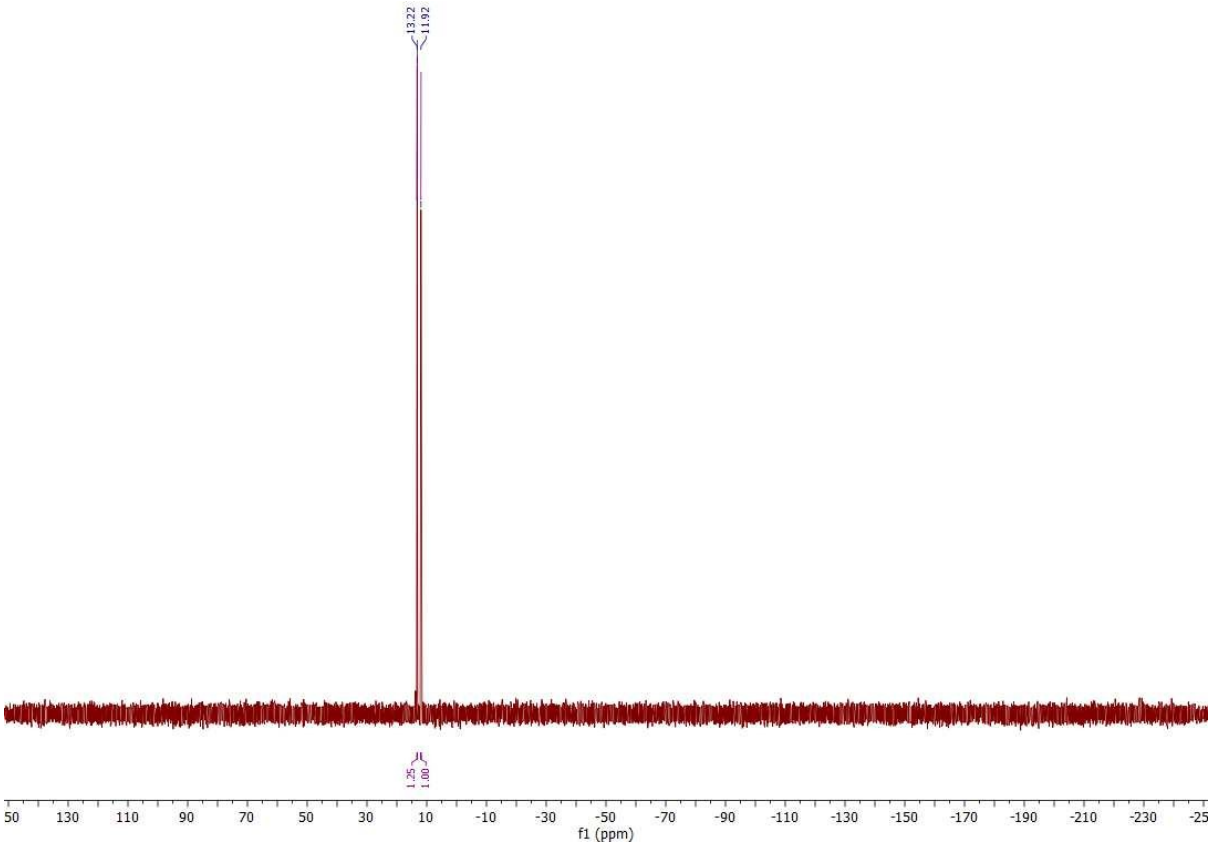
^{13}C NMR (151 MHz, $CDCl_3$)-**4l**:



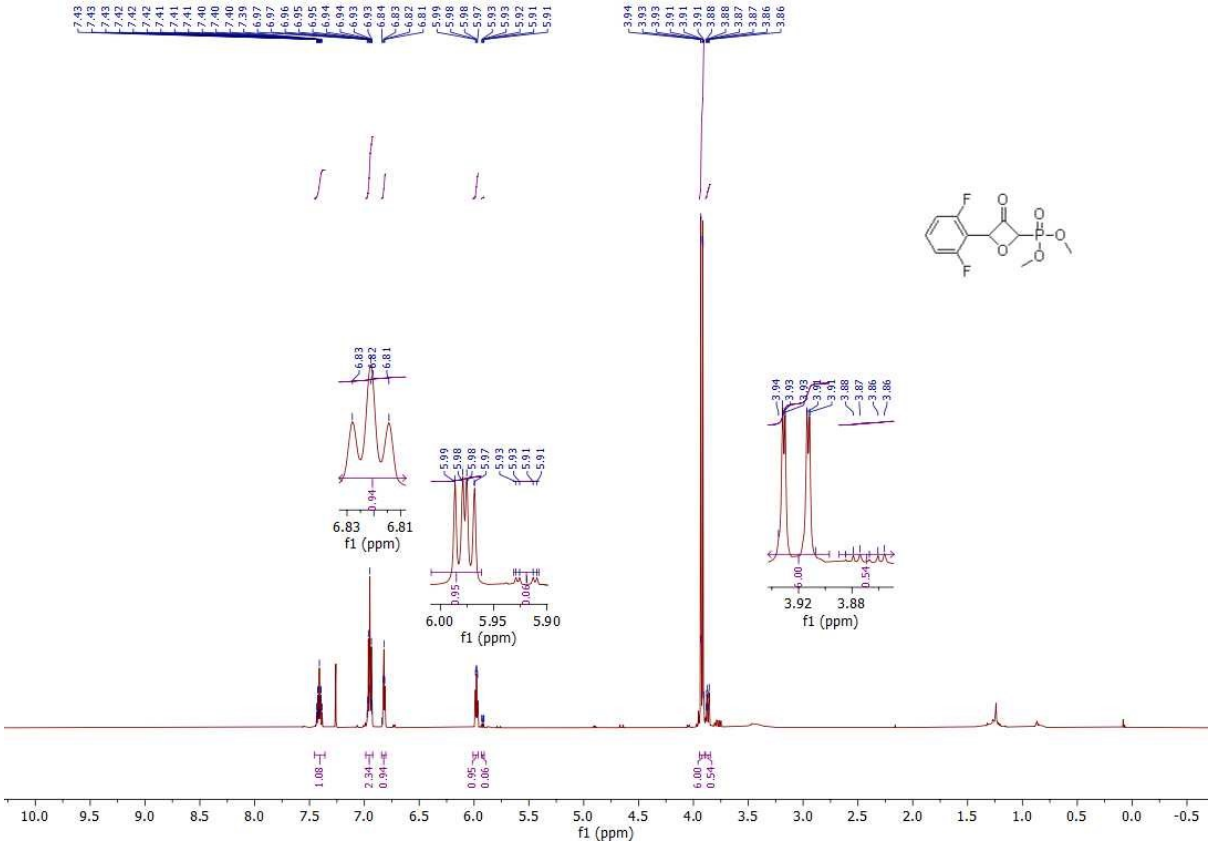
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4l**:



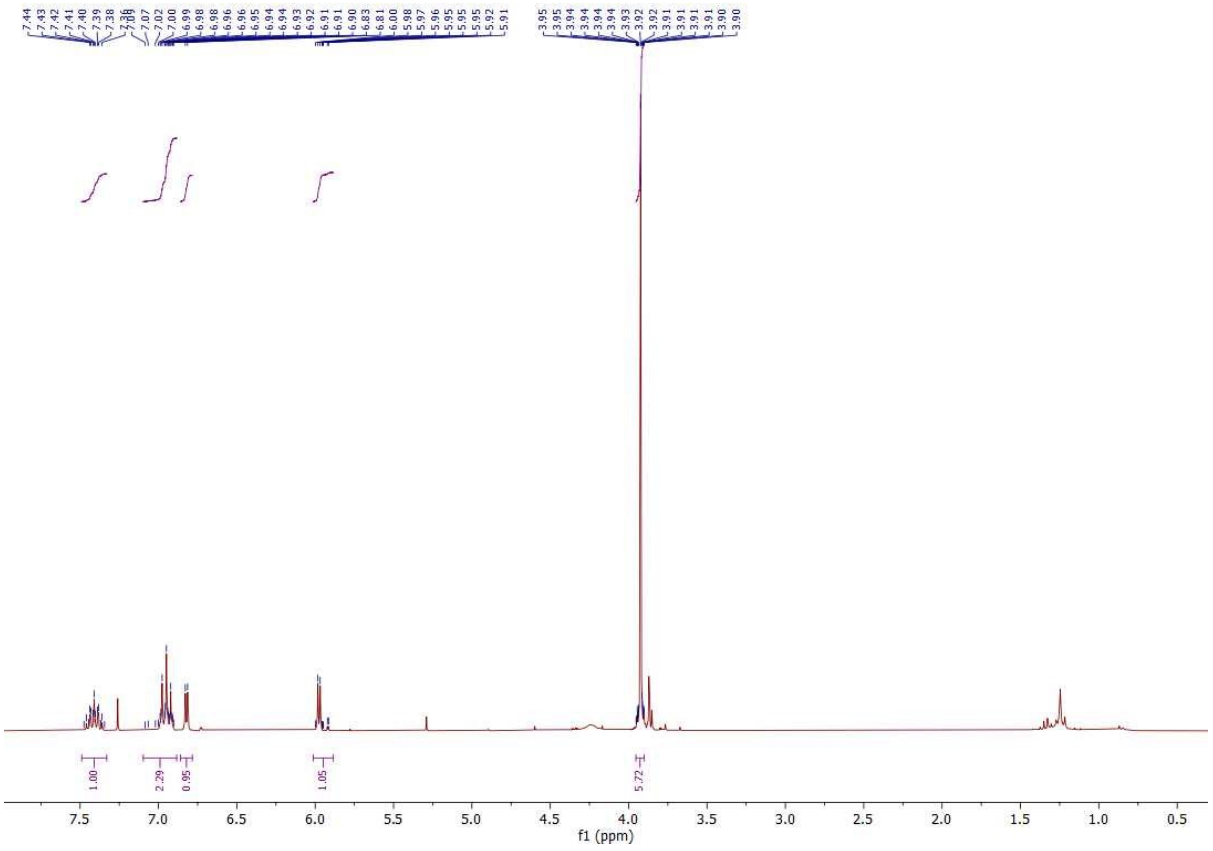
^{31}P NMR (121 MHz, $CDCl_3$)-**4l**:



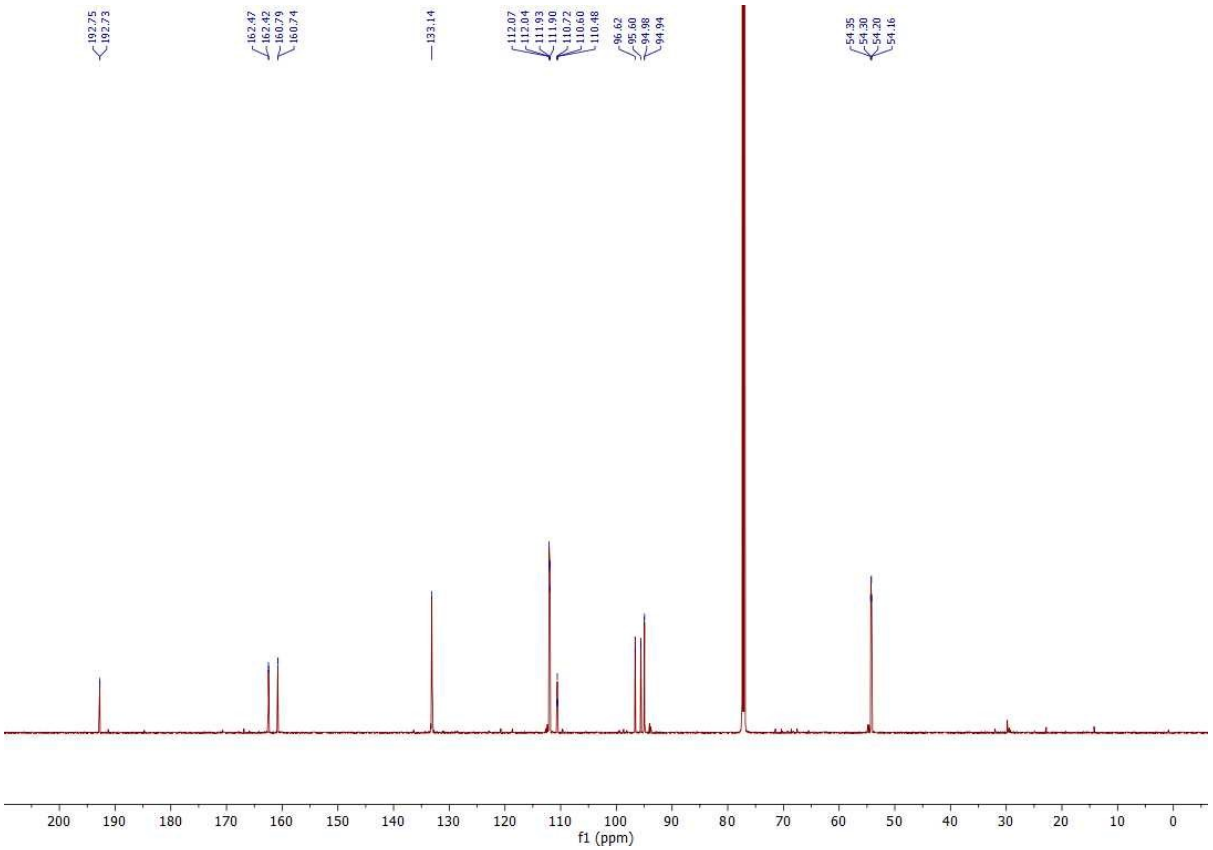
^{1}H NMR (600 MHz, $CDCl_3$)-**4m**:



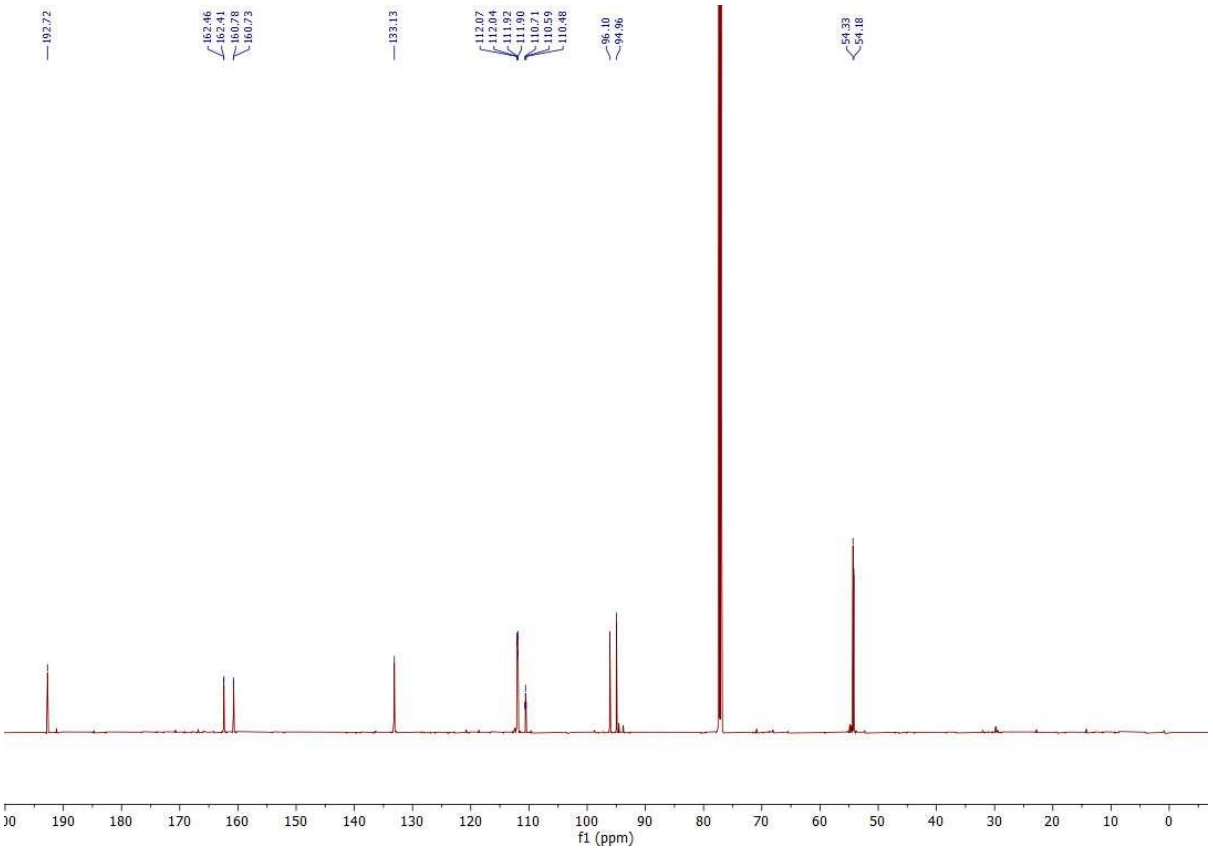
^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$)-**4m**:



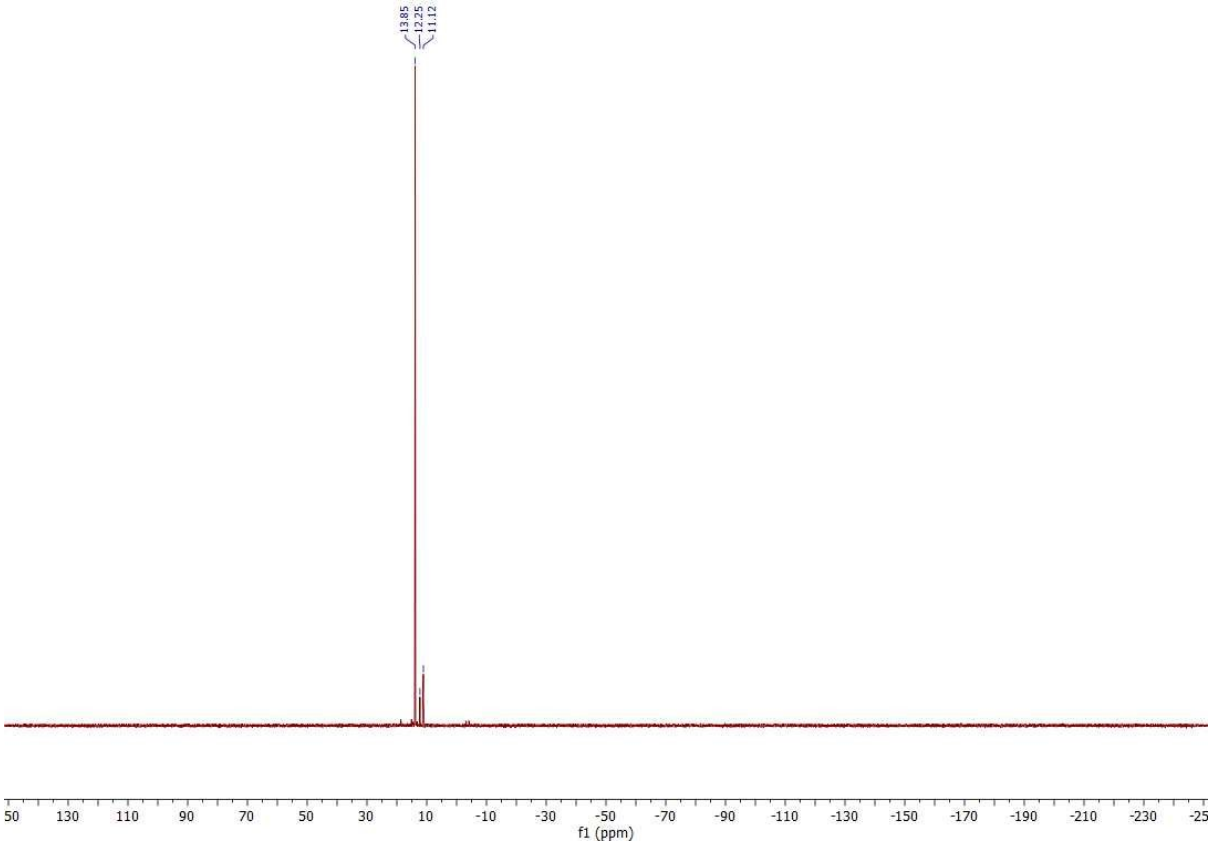
^{13}C NMR (151 MHz, $CDCl_3$)-**4m**:



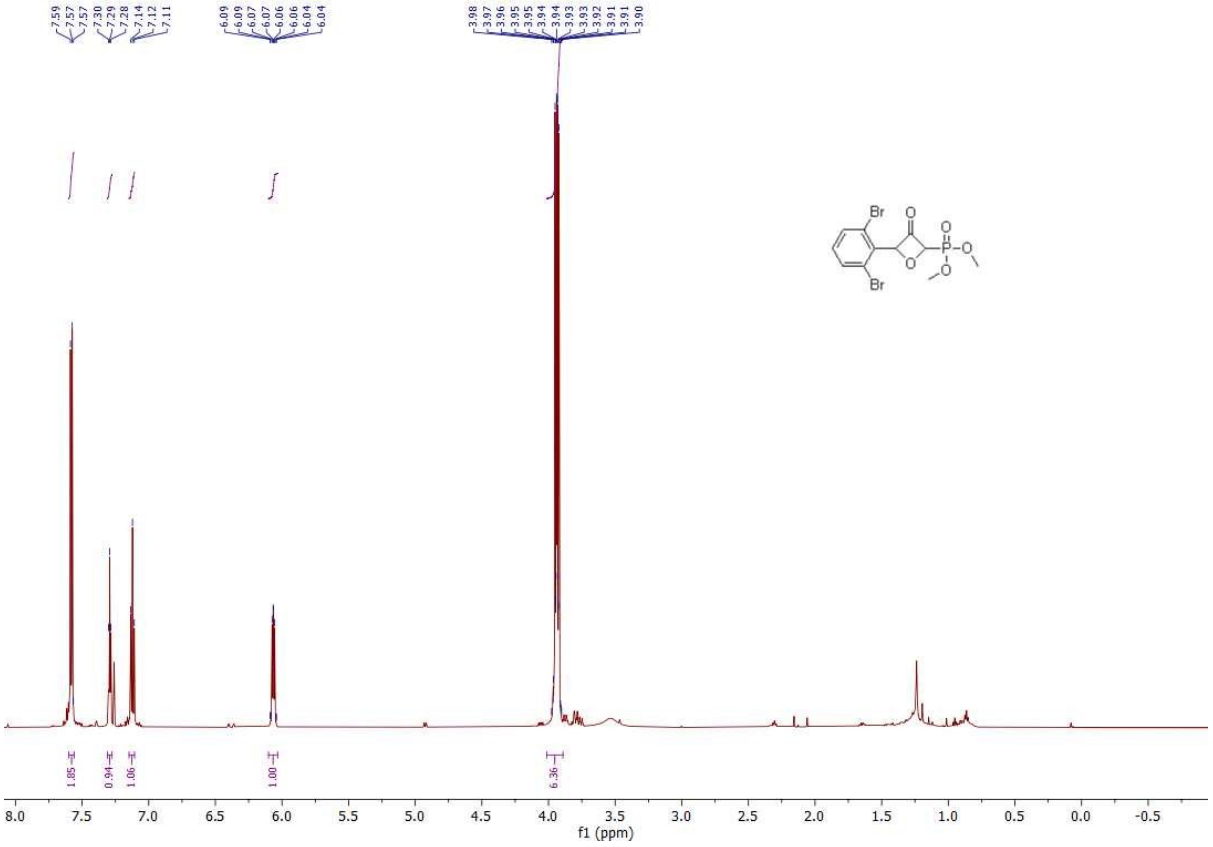
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4m**:



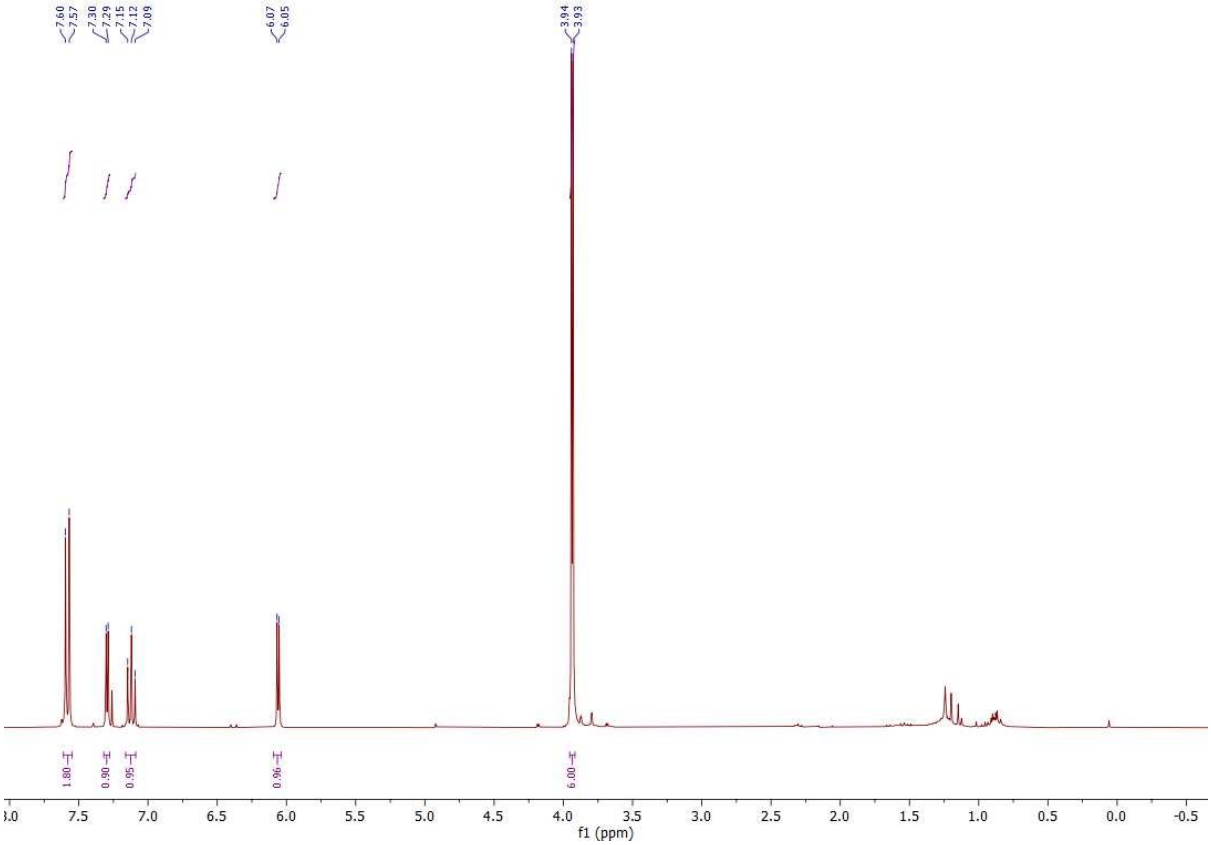
^{31}P NMR (121 MHz, $CDCl_3$)-**4m**:



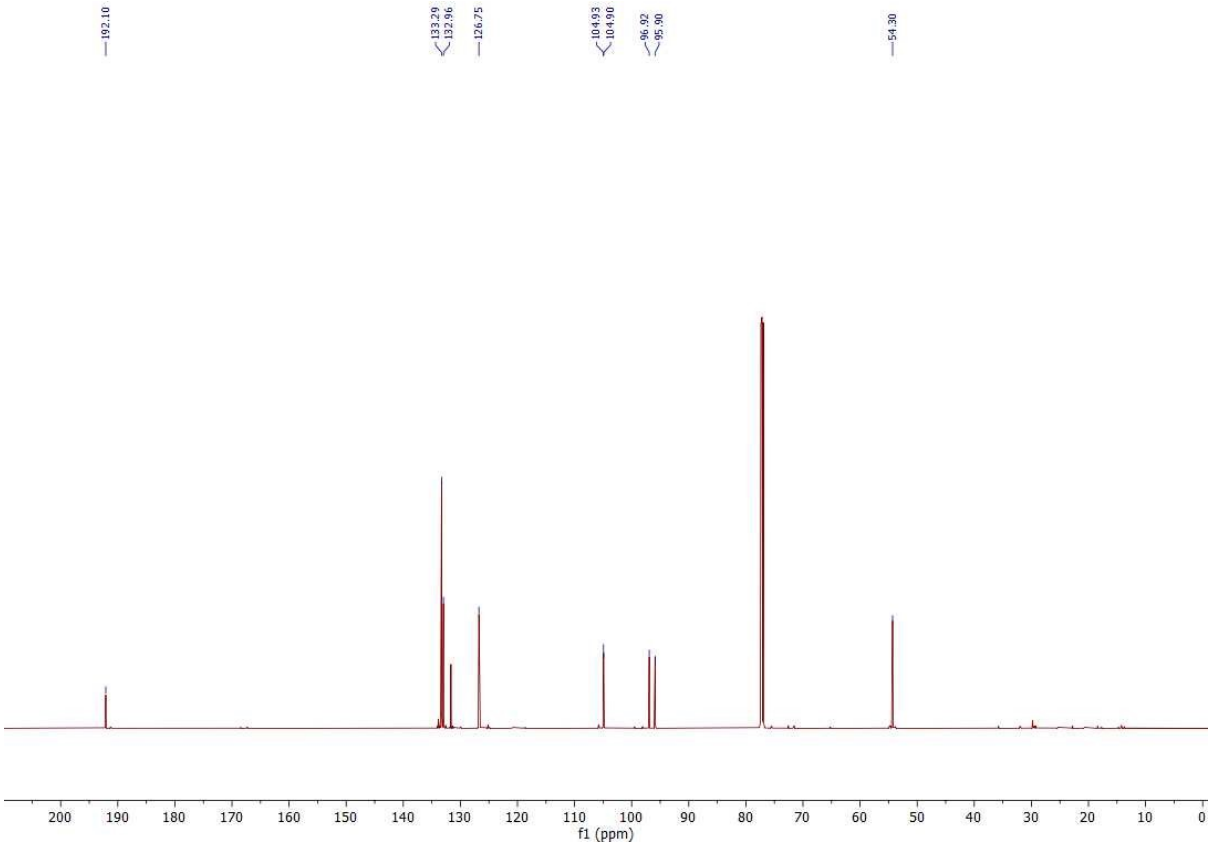
^{1}H NMR (600 MHz, $CDCl_3$)-**4n**:



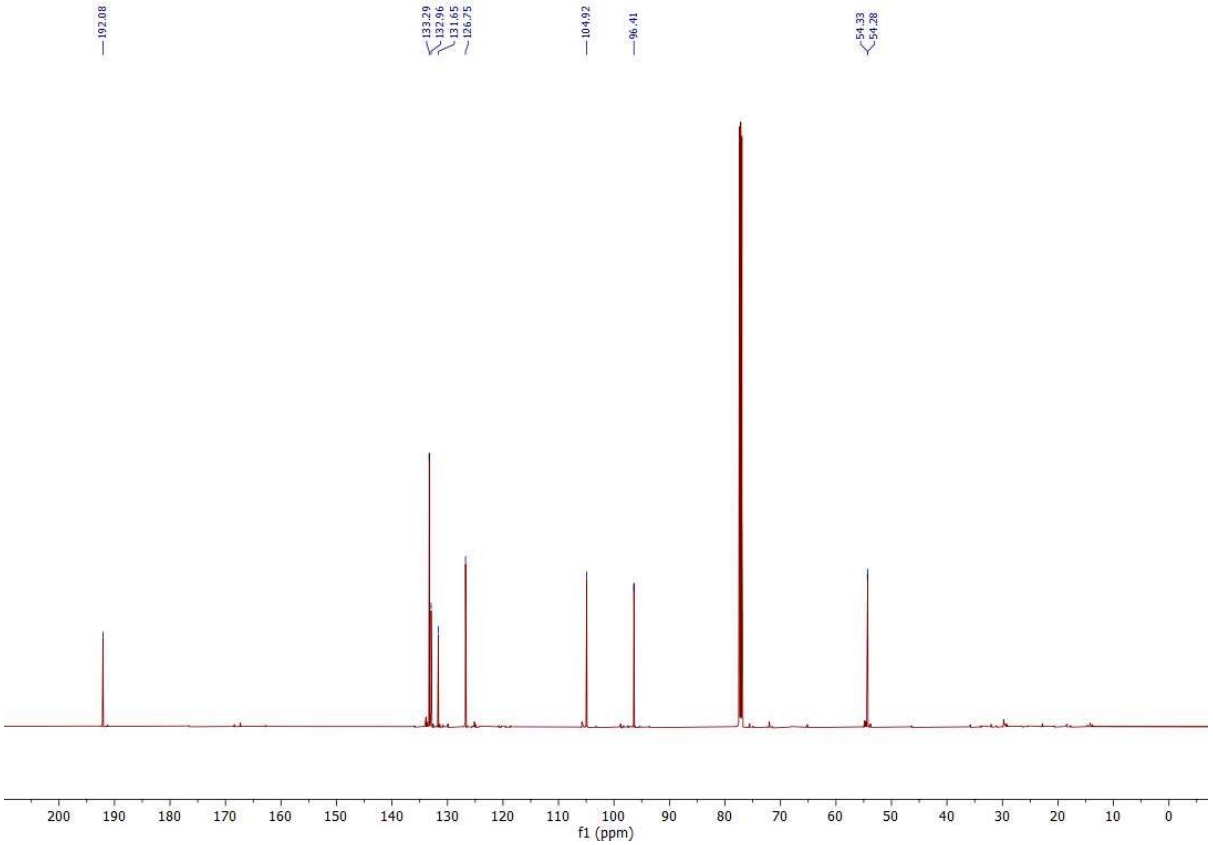
$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$)-**4n**:



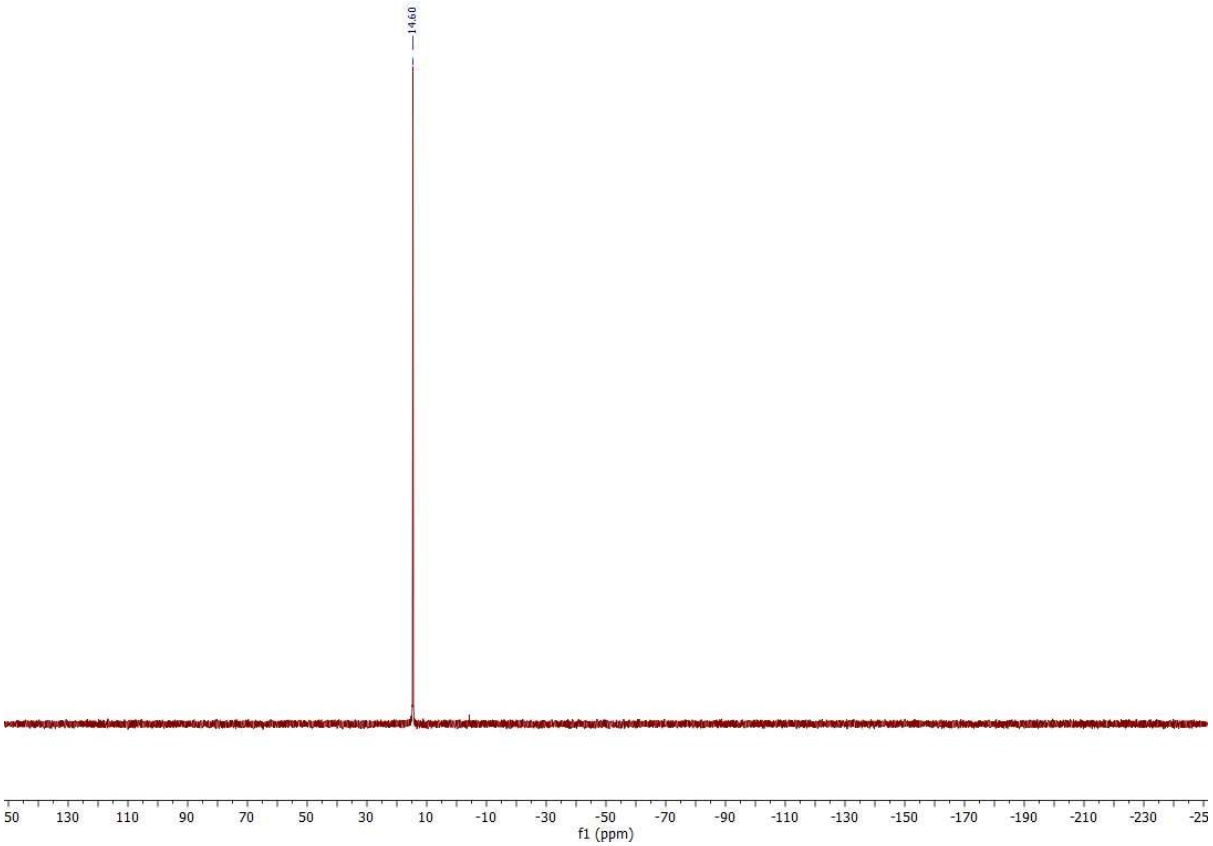
^{13}C NMR (151 MHz, $CDCl_3$)-**4n**:



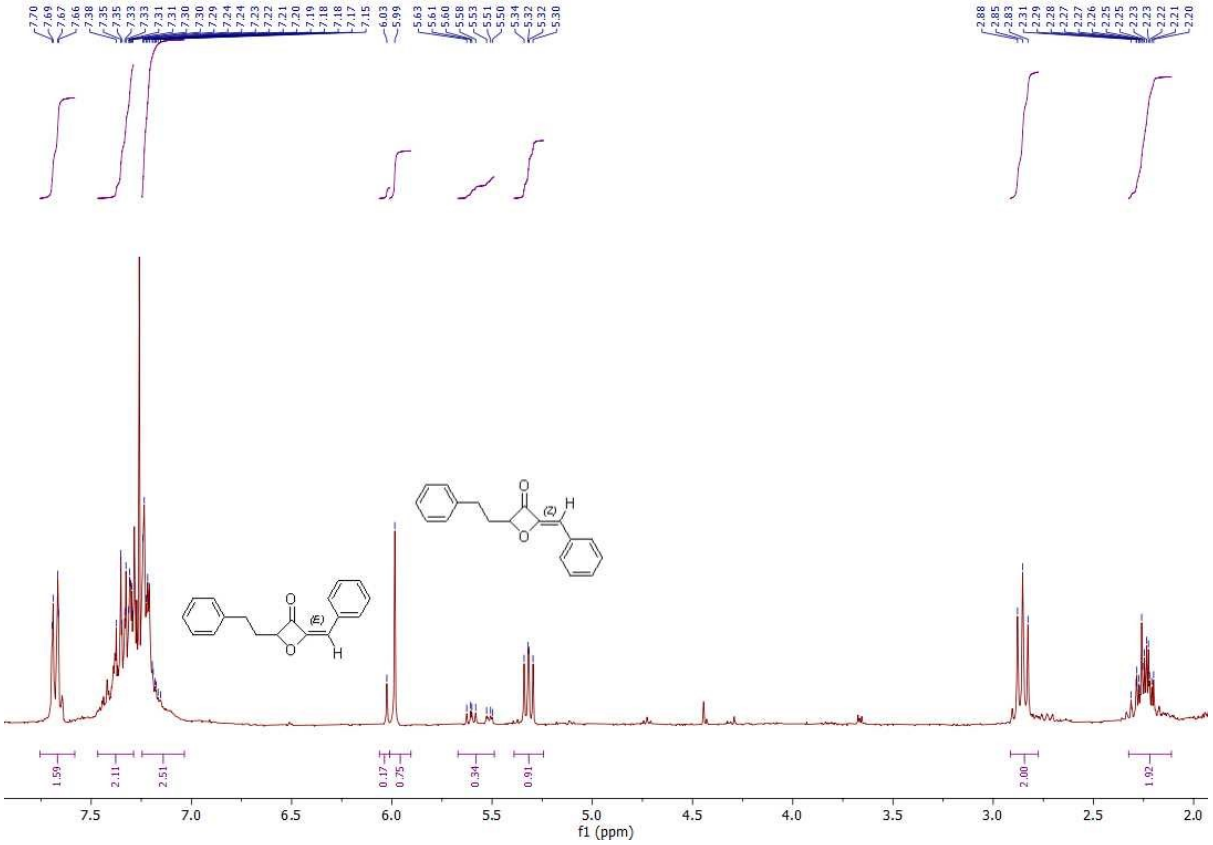
$^{13}C\{^{31}P\}$ NMR (151 MHz, $CDCl_3$)-**4n**:



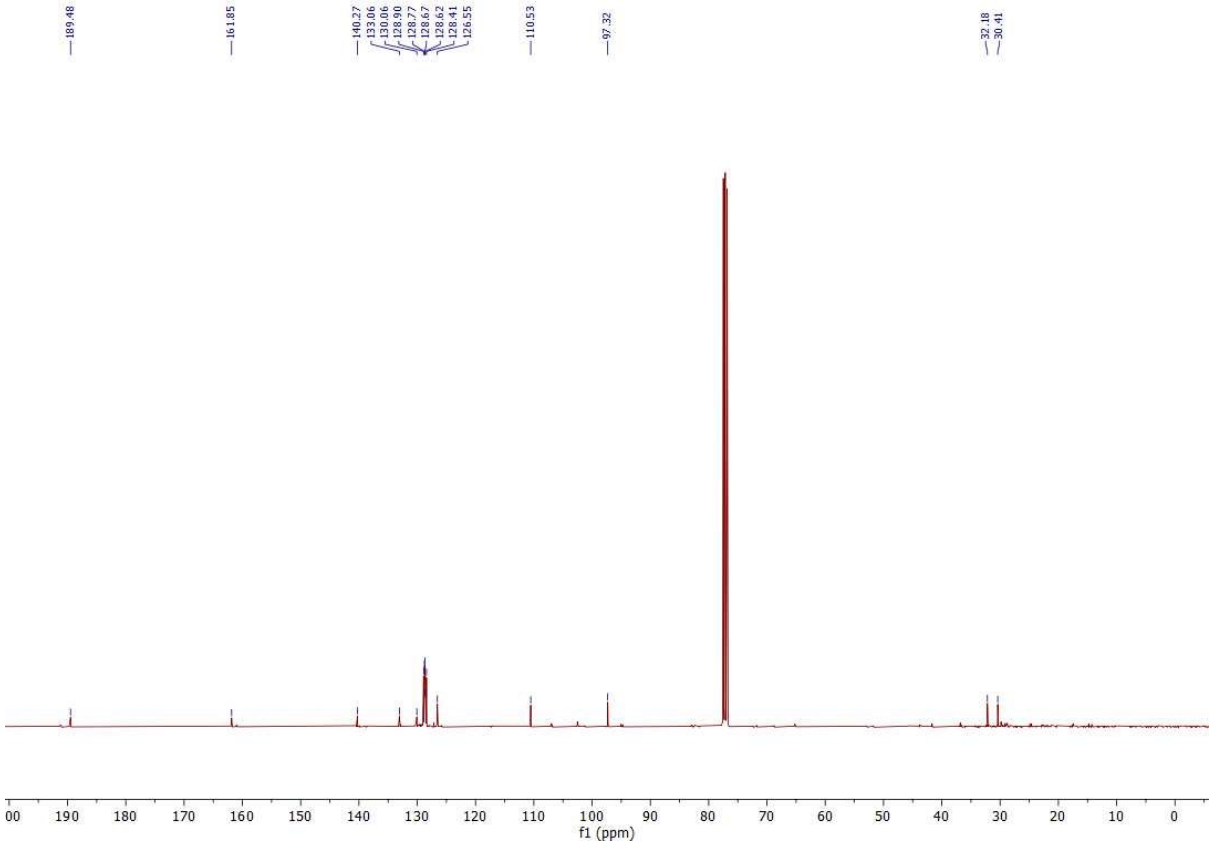
^{31}P NMR (121 MHz, $CDCl_3$)-**4n**:



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



^{13}C NMR (101 MHz, $CDCl_3$)-**5a**:



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