Supporting Information

Palladium-Catalyzed C-P Cross-Coupling of Allenic Alcohols with *H*-phosphonates Leading to 2-Phosphinoyl-1,3-butadienes

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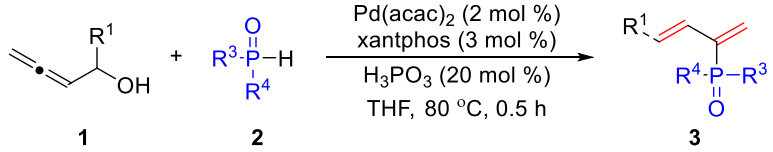
Contents

1. General information and experimental section

1.1. General information

Substrates **1a**−**1t**,[1] **1u**,[2] **1v-1aa**,[3] **1ab-1ag**,[4] **1ai**,[4] **1ah**,[5] **1ai**,[6] were prepared according to the known references. Other reagents were obtained from commercial suppliers and used without further purification. All the heating experiments were performed in an oil bath. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker Av500 spectrometer using tetramethylsilane (TMS) in $CDCl_3$ as the internal standard. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm) and 85% H_3PO_4 as external standard for ^{31}P NMR. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. HRMS spectra of new compounds were carried out with Waters Micromass LCT Premier TOF-MS apparatus. Infrared spectra were recorded on a Nicollet Avatar 330 spectrometer. Melting points were conducted with WRS-1B Digital Melting-Point apparatus. Silica gel column chromatography was performed using 300-400 mesh.

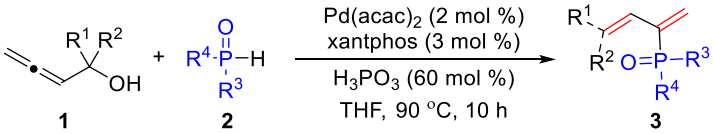
1.2. General procedure for the synthesis of 3a-3u, 3ak-3am



1 2 3

In an oven dried pressure tube equipped with stir bar, $Pd(acac)_2$ (1.8 mg, 2 mol %), xantphos (5.2 mg, 3 mol %), **1** (0.33 mmol, 1.1 equiv) were evacuated and purged with argon three times. **2** (0.3 mmol), H_3PO_3 (0.15 mL, 20 mol %, 0.4 M in THF) and THF (4.5 mL) were sequentially added to the system at room temperature. The mixture was stirred at 80 ℃ in an oil bath for 0.5 h. Then the resulting mixture was cooled down to room temperature and purified by flash chromatography (petroleum ether/ethyl acetate = 10:1-2:1) to afford the corresponding product **3**.

1.3. General procedure for the synthesis of 3v-3aa, 3aj, 3an and 3ao

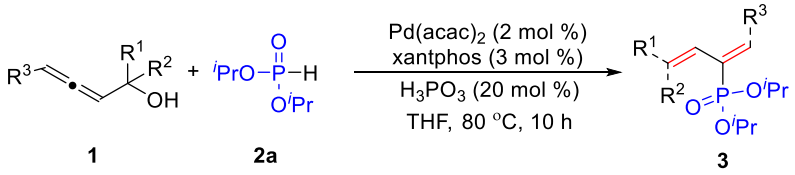


1 2 3

In an oven dried pressure tube equipped with stir bar, $Pd(acac)_2$ (1.8 mg, 2 mol %), xantphos (5.2 mg, 3 mol %), **1** (0.33 mmol, 1.1 equiv) were evacuated and purged with argon three times. **2**

(0.3 mmol), H_3PO_3 (0.45 mL, 60 mol %, 0.4 M in THF) and THF (4.5 mL) were sequentially added to the system at room temperature. The mixture was stirred at 90 ℃ in an oil bath for 10 h. Then the resulting mixture was cooled down to room temperature and purified by flash chromatography (petroleum ether/ethyl acetate = 10:1-2:1) to afford the corresponding product **3**.

1.4. General procedure for the synthesis of 3ab-3ai

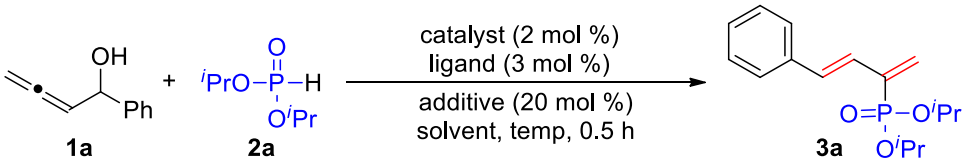


In an oven dried pressure tube equipped with stir bar, $Pd(acac)_2$ (1.8 mg, 2 mol %), xantphos (5.2 mg, 3 mol %), **1** (0.33 mmol, 1.1 equiv) were evacuated and purged with argon three times. **2a** (0.3 mmol), H_3PO_3 (0.15 mL, 20 mol %, 0.4 M in THF) and THF (4.5 mL) were sequentially added to the system at room temperature. The mixture was stirred at 80 ℃ in an oil bath for 10 h. Then the resulting mixture was cooled down to room temperature and purified by flash chromatography (petroleum ether/ethyl acetate = 10:1-2:1) to afford the corresponding product **3**.

2. Optimization of the reaction conditions

Initially, the model reaction of 1-phenylbuta-2,3-dien-1-ol (**1a**) and diisopropyl phosphonate (**2a**) was conducted to find the optimal reaction conditions (Table S1). Unfortunately, reacting **1a** with **2a** in the presence of $Pd(acac)_2$ (2 mol %) and xantphos (3 mol %) as ligand did not give any desired product (Table S1, entry 1), probably due to the lack of the suitable acid for activating hydroxyl group of **1a** in the reaction system. Thus, a subsequent survey on the role of various acids as additives including AcOH, HCOOH, H_3PO_3 and HOTf, disclosed that reducing acids, especially H_3PO_3, was found to be the most effective additive to generate the desired product **3a** in 60% yield (Table S1, entry 5), while other acids examined were poorly effective (Table S1, entries 2-4). To advance the process further, the effect of other metal salts such as $Pd(OAc)_2$, $Pd(PPh_3)_4$, $PdCl_2$, $Pd_2(dba)_3$, $Ni(cod)_2$ and $Cu(OAc)_2$ was investigated, with the finding that $Pd(OAc)_2$, $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ were less effective and other salts completely suppressed this reaction (Table S1, entries 6-11). Apart from xantphos, other phosphine ligands failed to give the expected product **3a** (Table S1, entries 12-14), revealing that xantphos plays a crucial role in the reaction due to its large bite angle.[16] Among the variety of solvent screened, tetrahydrofuran (THF) turned to be the best choice, while others like toluene, 1,4-dioxane and 1,2-dichloroethane (DCE) led to the yield reduction (Table S1, entries 15-17). To our delight, increasing the temperature to 80 ℃ could improve the product yield up to 92% (Table S1, entry 18), but further enhancing or lowering the temperature resulted in a decrease of yield (Table S1, entries 19-20). We observed a slightly decrease in yield when the reaction was carried out under air (Table S1, entry 21).

Table S1 Optimization of the reaction conditions[a]

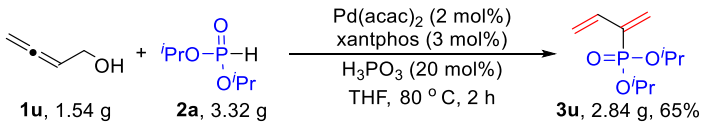


entry	catalyst (%)	ligand (%)	additive (%)	solvent	yield (%)[b]
1	$Pd(acac)_2$	xantphos	-	THF	0
2	$Pd(acac)_2$	xantphos	AcOH	THF	trace
3	$Pd(acac)_2$	xantphos	HCOOH	THF	20
4	$Pd(acac)_2$	xantphos	HOTf	THF	trace
5	$Pd(acac)_2$	xantphos	H_3PO_3	THF	60
6	$Pd(OAc)_2$	xantphos	H_3PO_3	THF	40
7	$Pd(PPh_3)_4$	xantphos	H_3PO_3	THF	15
8	$PdCl_2$	xantphos	H_3PO_3	THF	0
9	$Pd_2(dba)_3$	xantphos	H_3PO_3	THF	55
10	$Ni(cod)_2$	xantphos	H_3PO_3	THF	0
11	$Cu(OAc)_2$	xantphos	H_3PO_3	THF	0
12	$Pd(acac)_2$	PPh_3	H_3PO_3	THF	0
13	$Pd(acac)_2$	dppf	H_3PO_3	THF	0
14	$Pd(acac)_2$	dppb	H_3PO_3	THF	0
15	$Pd(acac)_2$	xantphos	H_3PO_3	toluene	40
16	$Pd(acac)_2$	xantphos	H_3PO_3	1,4-dioxane	35
17	$Pd(acac)_2$	xantphos	H_3PO_3	DCE	50
18[c]	$Pd(acac)_2$	xantphos	H_3PO_3	THF	80
19[d]	**$Pd(acac)_2$**	**xantphos**	**H_3PO_3**	**THF**	**92**
20[e]	$Pd(acac)_2$	xantphos	H_3PO_3	THF	88
21[d, f]	$Pd(acac)_2$	xantphos	H_3PO_3	THF	85

[a]Reaction conditions: **1a** (0.33 mmol), **2a** (0.30 mmol), catalyst (2 mol %), ligand (3 mol %), additive (20 mol %), solvent (4.5 mL), 40 ℃, 0.5 h, under argon. [b]Isolated yields. [c]60 ℃. [d]80 ℃. [e]90 ℃. [f]Under air.

3. Application studies

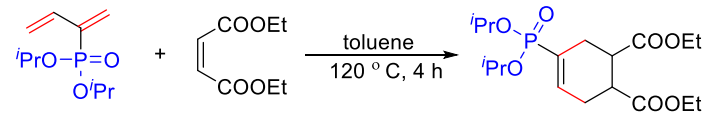
3.1. Gram-scale preparation of 3u



In a 100 mL two-necked flask equipped with a reflux condenser and a magnetic stir bar,

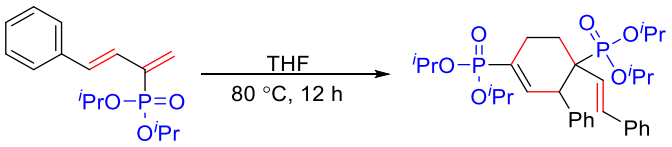
$Pd(acac)_2$ (121.8 mg, 2 mol %), xantphos (347.2 mg, 3 mol %), H_3PO_3 (328 mg, 20 mol %), **1u** (1.54 g, 1.1 equiv) were evacuated and purged with argon three times. Then **2a** (3.32 g, 20 mmol) and THF (50 mL) were added by syringe. The mixture was stirred at 80 ℃ in an oil bath for 10 h. Then the resulting mixture was cooled down to room temperature and purified by flash chromatography (petroleum ether/ethyl acetate = 10:1-2:1) to afford the corresponding product **3u**.

3.2. [4+2] Cycloadditions of dienes 3u and 3a



3u, 0.3 mmol **2h**, 0.6 mmol **4a**, 72%

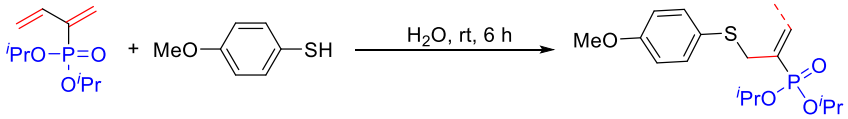
Diisopropyl buta-1,3-dien-2-ylphosphonate **3u** (65.4 mg, 0.3 mmol), diethyl maleate **2h** (103.3 mg, 0.6 mmol) and toluene 1 mL were added to an oven dried pressure tube (10 mL) equipped with stir bar. Then the mixture was stirred at 120 ℃ in an oil bath for 4 h. The crude reaction mixture was purified by flash chromatography (petroleum ether/ethyl acetate = 2:1) to afford the corresponding product **4a**.



3a, 0.4 mmol **4b**, 65%

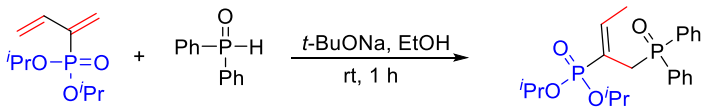
(*E*)-diisopropyl (4-phenylbuta-1,3-dien-2-yl)phosphonate **3a** (117.64 mg, 0.4 mmol) and THF (1 mL) were added to an oven dried pressure tube (10 mL) equipped with stir bar. Then the mixture was stirred at 80 ℃ in an oil bath for 12 h. The crude reaction mixture was purified by flash chromatography (CH_2Cl_2/CH_3OH = 100:1-50:1) to afford the corresponding product **4b** in 65% yield.

3.3. The Michael addition of 3u and nucleophiles



3u, 0.6 mmol **2i**, 1.2 mmol **5a**, 51% (*E*/*Z* = 71: 29)

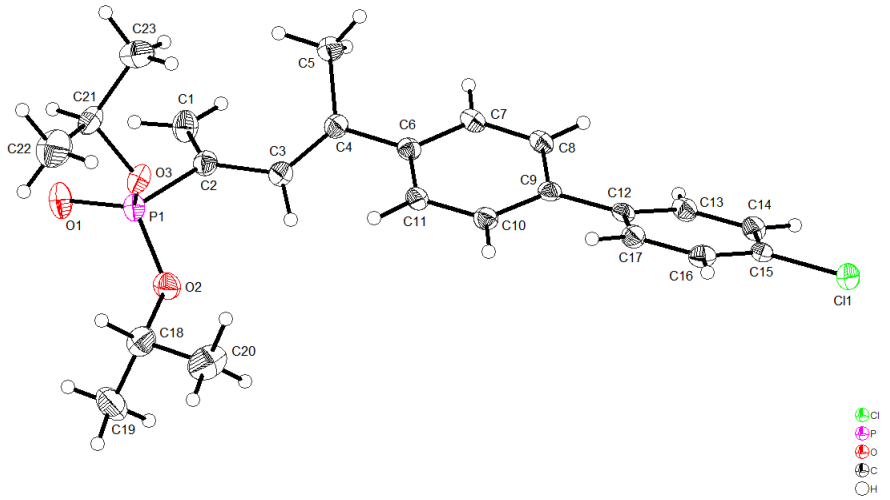
To an oven dried Schlenk tube equipped with stir bar was added **3u** (0.6 mmol), **2i** (1.2 mmol) under argon and then H_2O (5 mL) was added. The mixture was stirred at room temperature for 6 h. Then the resulting mixture was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1) to afford the corresponding product **5a** in 51% yield.



3u, 0.6 mmol **2g**, 1.2 mmol **5b**, 77%

To an oven dried Schlenk tube equipped with stir bar was added **3u** (0.6 mmol), **2g** (1.2 mmol) and *t*-BuONa (63.4 mg, 0.66 mmol) under argon and then EtOH (5 mL) was added. The mixture was stirred at room temperature for 1 h. Then the resulting mixture was purified by flash chromatography (CH_2Cl_2/CH_3OH = 50:1-30:1) to afford the corresponding product **5b** in 77% yield.

4. Crystallographic detail of 3aa



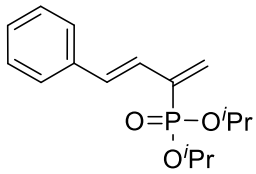
Crystals were obtained by slow volatilization of mixture solution of **3aa** in *n*-hexane and ethyl acetate (5:1, v/v, concentration 2 mol/L) at room temperature.

Single crystal X-ray structure of compound **3aa**, showing 50% probability displacement ellipsoids (arbitrary spheres for H atoms). Compound **3aa** crystallizes in the triclinic P -1 space group with two **3aa** per unit cell. There are two independent molecules and one H_2O molecule in the asymmetric unit of **3aa**. Detector with graphite-monochromated CuKa radiation (λ = 1.54184 Å) at 100 K. All of the data were corrected for absorption effects using the multi-scan technique. The structures were solved by direct methods using OLEX2 (Version 1.2.7) program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. Some

crystal data for **3aa**: C23 H28 Cl O3 P ; triclinic, space group P -1, colorless plate, a = 9.6365(3) Å, b = 11.8750(5) Å, c = 21.5769(6) Å, α = 99.134(3)°, β = 92.375(2)°, γ = 111.125(3)°, V = 2260.90(14) Å3, Z = 1, D_x = 1.270 g ·cm-3, F(000) = 918.0, T = 100 K. Final R *7281 with I > 2σ(I)+ = 0.0472, wR2 (8402) = 0.1344. Further details on the crystal structure investigation have been deposited at the Cambridge Crystallographic Data Centre as the deposition number CCDC 2034498.

5. Spectral data and characterization of 3a-3ao

(*E*)-diisopropyl (4-phenylbuta-1,3-dien-2-yl)phosphonate (3a, new compound)



Following general procedure 1.2, **3a** was obtained as clear oil (81.2 mg, 92% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45-7.43 (m, 2H), 7.36-7.32 (m, 2H), 7.28-7.26 (m, 1H), 7.09 (d, *J* = 16.4 Hz, 1H), 6.79 (dd, J_1 = 26.3 Hz, J_2 = 16.5 Hz, 1H), 6.21 (d, *J* = 20.5 Hz, 1H), 6,05 (d, *J* = 44.8Hz, 1H), 4.76-4,68 (m, 2H), 1.39 (d, *J* = 6.0 Hz, 6H), 1.29(d, *J* = 6.0 Hz, 6H);

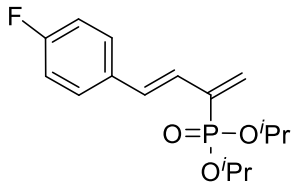
^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.9 (d, *J* = 172.9 Hz), 136.9, 133.6 (d, *J* = 4.8 Hz), 131.4 (d, *J* = 8.3 Hz), 128.7, 128.2, 126.8, 125.8 (d, *J* = 11.9 Hz), 70.0 (d, *J* = 5.5 Hz), 24.2 (d, *J* = 3.7 Hz), 23.8 (d, *J* = 5.0 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.79;

IR (film) υ_{max}: 3501, 3058, 2959, 1645, 1540, 1240, 1107, 982, 616 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{23}O_3PH^+$ 295.1458; found 295.1453.

(*E*)-diisopropyl (4-(4-fluorophenyl)buta-1,3-dien-2-yl)phosphonate (3b, new compound)



Following general procedure 1.2, **3b** was obtained as clear oil (80.5 mg, 86% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36-7.33 (m, 2H), 7.0 (d, *J* = 16.4 Hz, 1H), 6.96-6.95 (m, 2H), 6.65 (dd, J_1 = 25.6 Hz, J_2 = 16.4 Hz, 1H), 6.13 (dd, J_1 = 20.6 Hz, J_2 = 1.5 Hz, 1H), 5.97 (d, *J* = 44.65 Hz, 1H), 4.69-4.62 (m, 2H), 1.33 (d, *J* = 6.2 Hz, 6H), 1.24 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.6 (d, *J* = 247.7 Hz), 137.8 (d, *J* = 173.1 Hz), 133.1 (d, *J* = 3.2 Hz), 132.3 (d, *J* = 4.9 Hz), 131.3 (d, *J* = 8.3 Hz), 128.2 (d, *J* = 8.3 Hz), 125.6 (dd, J_1 = 11.6 Hz, J_2 = 2.3 Hz), 115.6 (d, *J* = 21.8 Hz), 70.9 (d, *J* = 5.5 Hz), 24.1 (d, *J* = 3.6 Hz), 23.7 (d, *J* = 4.9 Hz);

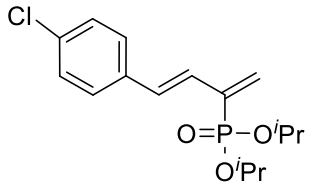
^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.53;

^{19}F NMR (471 MHz, CDCl3): δ -133.46.

IR (film) υ_{max}: 3454, 3054, 2950, 2910, 1618, 1386, 1182, 1105, 983, 615 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{22}FO_3PNa^+$ 335.1183; found 335.1177.

(*E*)-diisopropyl (4-(4-chlorophenyl)buta-1,3-dien-2-yl)phosphonate (3c, new compound)



Following general procedure 1.2, **3c** was obtained as clear oil (80.7 mg, 82% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 4.0 Hz, 2H), 7.02 (d, *J* = 16.4 Hz, 1H), 6.74 (dd, J_1 = 25.6 Hz, J_2 = 16.4 Hz, 1H), 6.19 (d, *J* = 20.5 Hz, 1H), 6.02 (d, *J* = 44.4 Hz, 1H), 4.72-4.66 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.27 (d, *J* = 6.2 Hz, 6H);

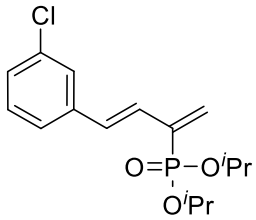
^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.8 (d, *J* = 173.2 Hz), 135.4, 133.7, 132.2 (d, *J* = 5.1 Hz), 131.7 (d, *J* = 8.3 Hz), 128.8, 127.8, 126.4 (d, *J* = 12.0 Hz), 70.9 (d, *J* = 5.5 Hz), 24.1 (d, *J* = 3.5 Hz), 23.8 (d, *J* = 4.6 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.36;

IR (film) υ_{max}: 3452, 3055, 2987, 2924, 2848, 1607, 1557, 1196, 1142, 1075, 980, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{22}ClNaO_3P\ Na^+$ 351.0887; found 351.0879.

(*E*)-diisopropyl (4-(3-chlorophenyl)buta-1,3-dien-2-yl)phosphonate (3d, new compound)



Following general procedure 1.2, **3d** was obtained as clear oil (78.7 mg, 80% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 (s, 1H), 7.29-7.18 (m, 3H), 7.00 (d, *J* = 16.4 Hz, 1H), 6.76 (dd, J_1 = 25.6 Hz, J_2 =16.4 Hz, 1H), 6.21 (d, *J* = 20.5 Hz, 1H), 6.03 (d, *J* = 44.2 Hz, 1H), 4.73-4.65 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.27 (d, *J* = 6.2 Hz, 6H);

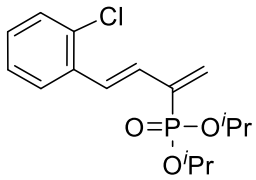
^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.8, 137.7 (d, *J* = 173.6 Hz), 134.6, 132.2 (d, *J* = 8.6 Hz), 132.1 (d, *J* = 4.8 Hz), 129.9 , 127.9, 127.2 (d, *J* = 11.9 Hz), 126.4, 124.9, 71.0 (d, *J* = 5.6 Hz), 24.1 (d, *J* = 3.7 Hz), 23.7 (d, *J* = 5.1 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.20;

IR (film) υ_{max}: 3462, 3053, 2978, 2931, 1607, 1469, 1196, 1142, 1175, 1105, 982, 752, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{22}ClO_3PH^+$ 329.1068; found 329.1069.

(*E*)-diisopropyl (4-(2-chlorophenyl)buta-1,3-dien-2-yl)phosphonate (3e, new compound)



Following general procedure 1.2, **3e** was obtained as clear oil (59.1 mg, 60% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 16.3 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.20 (dd, J_1 =7.4 Hz, J_2 = 7.3 Hz, 1H), 7.15 (dd, J_1 = 7.5 Hz, J_2 = 7.3 Hz, 1H), 6.73 (dd, J_1 =25.9 Hz, J_2 = 16.4 Hz, 1H), 6.25 (d, *J* = 20.6 Hz, 1H), 6.05 (d, *J* = 44.7 Hz, 1H), 4.73-4.68 (m,

2H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H);

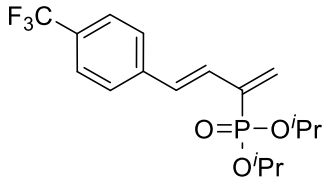
^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.9 (d, *J* = 173.9 Hz), 135.2, 133.8, 132.7 (d, *J* = 8.7 Hz), 129.9 (d, *J* = 4.4 Hz), 129.8 , 129.0, 128.3 (d, *J* = 11.3 Hz), 126.9, 126.4, 71.0 (d, *J* = 5.7 Hz), 24.2 (d, *J* = 4.1 Hz), 23.9 (d, *J* = 5.0 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.36;

IR (film) υ_{max}: 3466, 3056, 2978, 2930, 2871, 1521, 1471, 1385, 1235, 1105, 983, 778 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{22}ClO_3PH^+$ 329.1068; found 329.1069.

(*E*)-diisopropyl (4-(4-(trifluoromethyl)phenyl)buta-1,3-dien-2-yl)phosphonate (3f, new compound)



Following general procedure 1.2, **3f** was obtained as clear oil (72.8 mg, 67% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 16.4 Hz, 1H), 6.83 (dd, J_1 = 25.6 Hz, *J* = 16.4 Hz, 1H), 6.22 (dd, J_2 =20.2 Hz, *J* = 1.5 Hz, 1H), 6.05 (d, *J* = 44.0 Hz, 1H), 4.71-4.66 (m, 2H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.26 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.4, 137.7 (d, *J* = 173.9 Hz), 132.7 (d, *J* = 8.6 Hz), 132.1 (d, *J* = 4.5 Hz), 129.8 (q, *J* = 32.6 Hz), 128.3 (d, *J* = 12.1 Hz), 126.8, 125.6 (q, *J* = 4.3 Hz), 124.2 (q, *J* = 271.8 Hz), 70.1 (d, *J* = 5.9 Hz), 24.1 (d, *J* = 3.3 Hz), 23.8 (d, *J* = 4.9 Hz);

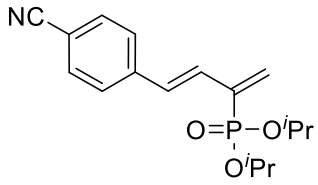
^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.06;

^{19}F NMR (471 MHz, CDCl3): δ -62.62.

IR (film) υ_{max}: 3450, 3055, 2980, 2932, 2857, 1613, 1533, 1325, 1180, 1164, 1075, 985, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}F_3O_3PH^+$ 363.1331; found 363.1329.

(*E*)-diisopropyl (4-(4-cyanophenyl)buta-1,3-dien-2-yl)phosphonate (3g, new compound)



Following general procedure 1.2, **3g** was obtained as clear oil (53.6 mg, 56% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 16.4 Hz, 1H), 6.85 (dd, J_1 = 25.7 Hz, J_2 = 16.4 Hz, 1H), 6.23 (dd, J_1 = 20.5 Hz, J_2 = 1.3 Hz 1H), 6.07 (d, *J* = 43.9 Hz, 1H), 4.71-4.65 (m, 2H), 1.34 (d, *J* = 6.2 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H);

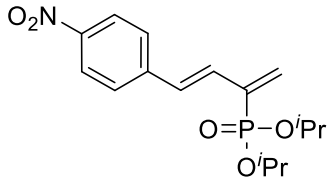
^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.4, 137.6 (d, *J* = 174.7 Hz), 133.3 (d, *J* = 8.1 Hz), 132.5, 131.7 (d, *J* = 4.8 Hz), 129.4 (d, *J* = 12.1 Hz), 127.1, 118.9, 111.1, 71.2 (d, *J* = 5.4 Hz), 24.1 (d, *J* = 3.3 Hz), 23.8 (d, *J* = 5.3 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 13.72;

IR (film) υ_{max}: 3462, 3054, 2978, 2925, 2225, 1605, 1385, 1238, 1179, 1141, 1075, 983, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{23}F_3NO_3PNa^+$ 342.1230; found 342.1227.

(*E*)-diisopropyl (4-(4-nitrophenyl)buta-1,3-dien-2-yl)phosphonate (3h, new compound)



Following general procedure 1.2, **3h** was obtained as yellow oil (68.1 mg, 67% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 16.4 Hz, 1H), 6.92 (dd, J_1 = 25.4 Hz, J_2 =16.5 Hz, 1H), 6.29 (d, *J* = 20.4 Hz, 1H), 6.12 (d, *J* = 43.5 Hz, 1H), 4.74-4.69 (m, 2H), 1.38 (d, *J* = 6.1 Hz, 6H), 1.28 (d, *J* = 6.0 Hz, 6H);

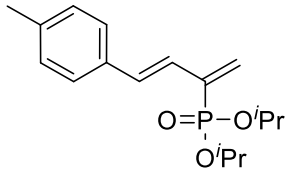
^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.1, 143.3, 137.6 (d, *J* = 174.6 Hz), 133.7 (d, *J* = 7.9 Hz), 131.2 (d, *J* = 4.3 Hz), 130.3 (d, *J* = 12.1 Hz), 127.1, 124.0, 71.2 (d, *J* = 5.6 Hz), 24.1 (d, *J* = 4.3 Hz), 23.8 (d, *J* = 4.9 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 13.55;

IR (film) υ_{max}: 3463, 3053, 2978, 2926, 1605, 1518, 1385, 1195, 1179, 1141, 1075, 983, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{22}NO_5PNa^+$ 362.1128; found 362.1129.

(*E*)-diisopropyl (4-(p-tolyl)buta-1,3-dien-2-yl)phosphonate (3i, new compound)



Following general procedure 1.2, **3i** was obtained as clear oil (74.8 mg, 81% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 16.3 Hz, 1H), 6.75 (dd, J_1 = 26.7 Hz, J_2 = 16.3 Hz, 1H), 6.17 (d, *J* = 20.6 Hz, 1H), 6.01 (d, *J* = 44.6 Hz, 1H), 4.73-4.68 (m, 2H), 2.33 (s, 3H), 1.38 (d, *J* = 6.6 Hz, 6H), 1.28(d, *J* = 6.5 Hz, 6H);

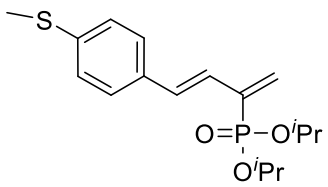
^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.1, 137.9 (d, *J* = 172.3 Hz), 134.2, 133.5 (d, *J* = 4.9 Hz), 130.8 (d, *J* = 8.6 Hz), 129.4, 126.6, 124.8 (d, *J* = 12.0 Hz), 70.9 (d, *J* = 5.4 Hz), 24.2 (d, *J* = 3.6 Hz), 23.8 (d, *J* = 4.9 Hz), 21.2;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.35;

IR (film) υ_{max}: 3465, 3056, 2977, 2935, 2856, 1645, 1513, 1375, 1196, 1175, 1107, 983, 617 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{25}O_3PNa^+$ 331.1434; found 331.1425.

(*E*)-diisopropyl (4-(4-(methylthio)phenyl)buta-1,3-dien-2-yl)phosphonate (3j, new compound)



Following general procedure 1.2, **3j** was obtained as clear oil (82.6 mg, 81% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 16.5 Hz, 1H), 6.71 (dd, J_1 = 25.6 Hz, J_2 = 16.5 Hz, 1H), 6.13 (d, *J* = 20.6 Hz 1H), 5.97 (d, *J* = 44.4 Hz, 1H), 4.68-4.65 (m, 2H), 1.33 (d, *J* = 6.0 Hz, 6H), 1.24 (d, *J* = 6.0 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.6, 137.8 (d, *J* = 172.4 Hz), 133.7, 132.9 (d, *J* = 5.1 Hz), 130.9

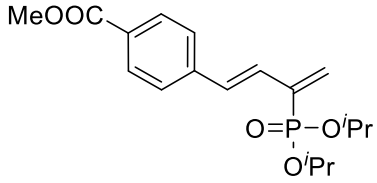
(d, *J* = 8.1 Hz), 127.0, 126.5, 125.1 (d, *J* = 12.5 Hz), 70.9 (d, *J* = 5.9 Hz), 24.1 (d, *J* = 3.7 Hz), 23.7 (d, *J* = 5.1 Hz), 15.6;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.66;

IR (film) υ_{max}: 3463, 3055, 2981, 2926, 2853, 1654, 1606, 1492, 1195, 1141, 1105, 983, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{25}O_3SPH^+$ 341.1335; found 325.1333.

(*E*)-methyl 4-(3-(diisopropoxyphosphoryl)buta-1,3-dien-1-yl)benzoate (3k, new compound)



Following general procedure 1.2, **3k** was obtained as clear oil (86.6 mg, 82% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93 (d, *J* = 9.5 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.83 (dd, J_1 = 25.4 Hz, J_2 = 16.5 Hz, 1H), 6.19 (d, *J* = 20.4 Hz, 1H), 6.03 (d, *J* = 44.5 Hz, 1H), 4.69-4,64 (m, 2H), 3.84 (s, 3H), 1.33 (d, *J* = 6.0 Hz, 6H), 1.23 (d, *J* = 6.0 Hz, 6H);

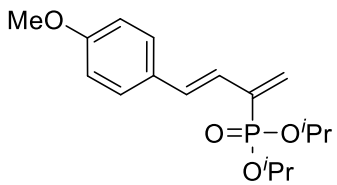
^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7, 141.3, 137.8 (d, *J* = 173.8 Hz), 132.5 (d, *J* = 9.2 Hz), 132.5 (d, *J* = 4.8 Hz), 129.9, 129.4, 128.3 (d, *J* = 12.0 Hz), 126.5, 71.0 (d, *J* = 5.5 Hz), 52.0, 24.1 (d, *J* = 3.7 Hz), 23.7 (d, *J* = 4.7 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.08;

IR (film) υ_{max}: 3473, 3055, 2983, 2924, 2854, 1721, 1661, 1622, 1279, 1142, 1105, 983, 617 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{25}O_5PH^+$ 353.1512; found 353.1510.

(*E*)-diisopropyl (4-(4-methoxyphenyl)buta-1,3-dien-2-yl)phosphonate (3l, new compound)



Following general procedure 1.2, **3l** was obtained as clear oil (72.9 mg, 75% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 16.4 Hz, 1H), 6.84 (d, *J* = 8.8

Hz, 2H), 6.64 (dd, J = 25.7 Hz, J = 16.4 Hz, 1H), 6.11 (dd, J_1 = 20.6 Hz, J_2 = 1.6 Hz 1H), 5.97 (d, J = 44.7 Hz, 1H), 4.70-4.65 (m, 2H), 1.36 (d, J = 6.2 Hz, 6H), 1.26 (d, J = 6.2 Hz, 6H);

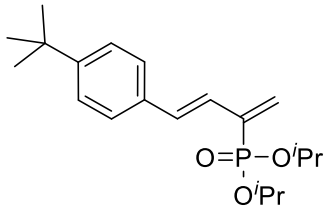
^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.7, 137.9 (d, J = 172.0 Hz), 133.1 (d, J = 5.2 Hz), 130.3 (d, J = 8.6 Hz), 129.7, 123.7 (d, J = 12.0 Hz), 114.2, 70.9 (d, J = 5.5 Hz), 24.2 (d, J = 4.1 Hz), 23.8 (d, J = 4.9 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.01;

IR (film) υ_{max}: 3465, 3056, 2981, 2930, 2834, 1607, 1621, 1245, 1174, 1142, 1106, 981, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{25}O_4PH^+$ 325.1563; found 325.1564

(*E*)-diisopropyl (4-(4-(tert-butyl)phenyl)buta-1,3-dien-2-yl)phosphonate (3m, new compound)



Following general procedure 1.2, **3m** was obtained as clear oil (87.2 mg, 83% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37-7.33 (m, 4H), 7.05 (d, J = 16.1 Hz, 1H), 6.75 (dd, J_1 = 26.0 Hz, J_2 = 16.1 Hz, 1H), 6.17 (d, J = 20.8 Hz, 1H), 6.01 (d, J = 44.0 Hz, 1H), 4.72-4.66 (m, 2H), 1.37 (d, J = 6.2 Hz, 6H), 1.30 (s, 9H), 1.27 (d, J = 6.2 Hz, 6H);

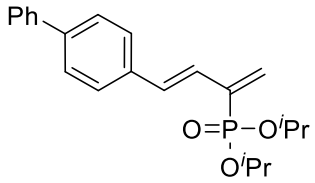
^{13}C NMR ($CDCl_3$, 125 MHz): δ 151.3, 137.9 (d, J = 172.2 Hz), 134.2, 133.4 (d, J = 5.4 Hz), 130.9 (d, J = 8.5 Hz), 126.4, 125.6, 125.0 (d, J = 11.7 Hz), 70.8 (d, J = 5.3 Hz), 34.6, 31.3, 24.2 (d, J = 3.6 Hz), 23.7 (d, J = 5.5 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.85;

IR (film) υ_{max}: 3465, 3054, 2975, 2925, 2853, 1734, 1660, 1626, 1174, 1142, 1105, 982, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{31}NO_3PNa^+$ 373.1903; found 373.1905.

(*E*)-diisopropyl (4-([1,1'-biphenyl]-4-yl)buta-1,3-dien-2-yl)phosphonate (3n, new compound)



Following general procedure 1.2, **3n** was obtained as clear oil (85.5 mg, 77% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61-7.57 (m, 4H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.43 (dd, *J* = 7.5 Hz, *J* = 7.3 Hz 2H), 7.33 (dd, J_1 = 7.0 Hz, J_2 = 6.7 Hz, 1H), 7.14 (d, *J* = 16.4 Hz, 1H), 6.85 (dd, J_1 = 25.5 Hz, J_2 = 16.4 Hz, 1H), 6.22 (d, *J* = 20.1 Hz, 1H), 6.05 (d, *J* = 44.2 Hz, 1H), 4.78-4.69 (m, 2H), 1.40 (d, *J* = 6.3 Hz, 6H), 1.31 (d, *J* = 6.0 Hz, 6H);

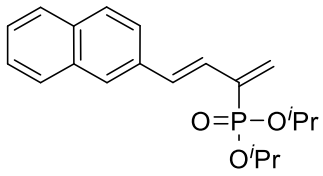
^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.9, 140.5, 137.9 (d, *J* = 173.1 Hz), 135.9, 133.1 (d, *J* = 4.9 Hz), 131.3 (d, *J* = 7.3 Hz), 128.8, 127.4, 127.3, 127.1, 126.9, 125.8 (d, *J* = 12.0 Hz), 70.9 (d, *J* = 5.4 Hz), 24.2 (d, *J* = 3.6 Hz), 23.8 (d, *J* = 4.8 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.69;

IR (film) υ_{max}: 3451, 3057, 2977, 2926, 1619, 1508, 1233, 1175, 1143, 1106, 983, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{27}O_3PH^+$ 371.1771; found 371.1774.

(*E*)-diisopropyl (4-(naphthalen-2-yl)buta-1,3-dien-2-yl)phosphonate (3o, new compound)



Following general procedure 1.2, **3o** was obtained as yellow oil (86.7 mg, 84% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 16.1 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.54-7.45 (m, 3H), 6.84 (dd, J_1 = 26.9 Hz, J_2 = 16.1 Hz, 1H), 6.28 (d, *J* = 20.8 Hz 1H), 6.09 (d, *J* = 44.5 Hz, 1H), 4.81-4.76 (m, 2H), 1.43 (d, *J* = 6.2 Hz, 6H), 1.34 (d, *J* = 6.2 Hz, 6H);

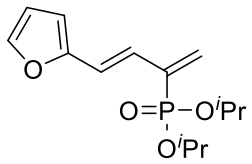
^{13}C NMR ($CDCl_3$, 125 MHz): δ138.2 (d, *J* = 172.5 Hz), 134.6, 133.7, 131.9 (d, *J* = 8.5 Hz), 131.5, 131.1 (d, *J* = 4.6 Hz), 128.7 (d, *J* = 11.4 Hz), 128.6, 128.5, 126.3, 125.9, 125.6, 123.4, 71.0 (d, *J* = 5.5 Hz), 24.3 (d, *J* = 3.5 Hz), 23.9 (d, *J* = 4.7 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.89;

IR (film) υ_{max}: 3477, 3055, 2973, 2922, 2681, 1381, 1277, 1178, 1106, 982, 616 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{25}NO_3PNa^+$ 367.1434; found 367.1433.

(*E*)-diisopropyl (4-(furan-2-yl)buta-1,3-dien-2-yl)phosphonate (3p, new compound)



Following general procedure 1.2, **3p** was obtained as yellow oil (57.1 mg, 67% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34 (s, 1H), 6.84 (d, J = 16.3 Hz, 1H), 6.69 (dd, J_1 = 27.3 Hz, J_2 = 16.3 Hz, 1H), 6.36 (d, J_1 = 3.3 Hz, J_2 = 1.8 Hz, 1H), 6.30 (d, J = 3.3 Hz, 1H), 6.12 (d, J = 20.6 Hz, 1H), 5.96 (d, J = 44.4 Hz, 1H), 4.68-4.63 (m, 2H), 1.33 (d, J = 6.2 Hz, 6H), 1.24 (d, J = 6.2 Hz, 6H);

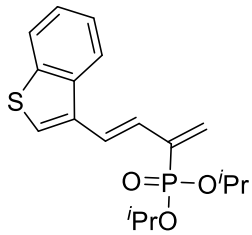
^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.7, 142.6, 137.6 (d, J = 172.2 Hz), 131.4 (d, J = 8.4 Hz), 124.2 (d, J = 11.8 Hz), 121.3 (d, J = 4.4 Hz), 111.8, 109.9, 71.0 (d, J = 5.6 Hz), 24.2 (d, J = 3.3 Hz), 23.8 (d, J = 4.4 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.49;

IR (film) υ_{max}: 3463, 3055, 2977, 2930, 2857, 1734, 1606, 1195, 1179, 1142, 1075, 983, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}O_4PH^+$ 285.1250; found 285.1249.

(*E*)-diisopropyl (4-(benzo[b]thiophen-3-yl)buta-1,3-dien-2-yl)phosphonate (3q, new compound)



Following general procedure 1.2, **3q** was obtained as yellow oil (79.8 mg, 76% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.91 (d, 7.8 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 7.9 Hz,

1H), 7.23 (dd, J_1 = 7.8 Hz, J_2 = 4.8 Hz, 1H), 7.03 (d, J = 16.5 Hz, 1H),6.80 (dd, J_1 = 25.5 Hz, J_2 = 16.5 Hz, 1H), 6.21 (d, J = 20.6 Hz, 1H), 6.04 (d, J = 44.0 Hz, 1H), 4.71-4.65 (m, 2H), 1.35 (d, J = 6.2 Hz, 6H), 1.25 (d, J = 6.2 Hz, 6H);

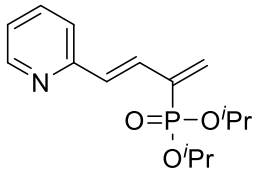
^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.9, 148.6, 137.7 (d, J = 174.3 Hz), 132.9, 132.5 (d, J = 8.4 Hz), 129.9 (d, J = 5.0 Hz), 128.0 (d, J = 12.1 Hz), 132.6, 71.1 (d, J = 5.5 Hz), 24.2 (d, J = 4.4 Hz), 23.8 (d, J = 5.2 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.66;

IR (film) υ_{max}: 3463, 3055, 2977, 2930, 2857, 1734, 1606, 1195, 1179, 1142, 1075, 983, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{23}O_3SPH^+$ 351.1178; found 351.1183.

(*E*)-diisopropyl (4-(pyridin-2-yl)buta-1,3-dien-2-yl)phosphonate (3r, new compound)



Following general procedure 1.2, 3r was obtained as yellow oil (66.4 mg, 75% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

1H NMR (CDCl3, 500 MHz): δ 8.60 (d, 1.3 Hz, 1H), 8.44 (dd, J_1 = 4.7 Hz, J_2 = 1.0 Hz, 1H), 7.51 (s, 1H), 7.41-7.37 (m, 3H), 6.87 (dd, J_1 = 26.1 Hz, J_2 = 16.0 Hz, 1H), 6.23 (d, J = 21.1 Hz, 1H), 6.06 (d, J = 44.4 Hz, 1H), 4.78-4.71 (m, 2H), 1.41 (d, J = 6.0 Hz, 6H), 1.32 (d, J = 5.9 Hz, 6H);

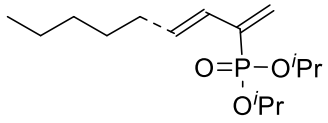
^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.5, 138.1 (d, J = 172.6 Hz), 137.9, 133.9, 131.5 (d, J = 8.3 Hz), 127.4 (d, J = 12.6 Hz), 125.7 (d, J = 4.8 Hz), 124.7, 124.5, 123.0, 122.3, 121.9, 71.1 (d, J = 5.5 Hz), 24.3 (d, J = 3.6 Hz), 23.9 (d, J = 4.8 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.01;

IR (film) υ_{max}: 3462, 3054, 2977, 2928, 2855, 1734, 1610, 1384, 1180, 1142, 1075, 982, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{22}NO_3PNa^+$ 318.1230; found 318.1228.

Diisopropyl nona-1,3-dien-2-ylphosphonate (3s, new compound)



Following general procedure 1.2, **3s** (*E*/*Z* = 41:59) was obtained as yellow oil (73.4 mg, 85% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

(*E*)-diisopropyl nona-1,3-dien-2-ylphosphonate with

(*Z*)-diisopropyl nona-1,3-dien-2-ylphosphonate ((*E*)-3s:(*Z*)-3s = 2.80:1)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.23 (d, J = 20.5 Hz, 1H), 6.19 (dt, J_1 = 16.1 Hz, J_2 = 6.6 Hz, 2.8H), 6.06 (dd, J_1 = 25.0 Hz, J_2 = 16.1 Hz, 2.8H), 6.02 (d, J = 20.5 Hz, 2.8H), 5.96 (d, J_1 = 11.3 Hz, J_2 = 5.5 Hz, 1H), 5.82 (d, J = 45.1 Hz, 2.8H), 5.78 (d, J = 48.4 Hz, 1H), 5.71 (dt, J_1 = 11.3 Hz, J_2 = 7.7 Hz, 1H), 4.69-4.64 (m, 7.6H), 2.02 (dt, J_1 = 7.7 Hz, J_2 = 7.4 Hz, 2H), 2.12 (dt, J_1 = 7.0 Hz, J_2 = 7.0 Hz, 5.6H), 1.43-1.27 (m, 68.4H), 0.89 (t, J = 7.0 Hz, 11.4H);

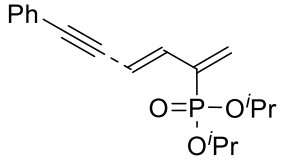
^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.9 (d, J = 171.6 Hz), 137.0 (d, J = 174.4 Hz), 136.5 (d, J = 4.4 Hz), 135.8 (d, J = 12.8 Hz), 130.4 (d, J = 7.7 Hz), 129.2 (d, J = 8.5 Hz), 126.9 (d, J = 11.8 Hz), 124.1 (d, J = 9.3 Hz), 70.6 (d, J = 5.8 Hz), 70.5 (d, J = 6.1 Hz), 33.2, 31.6, 31.3, 29.5, 28.7, 28.4, 24.1 (d, J = 4.2 Hz), 24.0 (d, J = 4.2 Hz), 23.8 (d, J = 4.4 Hz) , 23.7 (d, J = 4.7 Hz), 22.5, 14.0;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.47, 15.30;

IR (film) υ_{max}: 3460, 3054, 2976, 2924, 2028, 2853, 1958, 1642, 1195, 1180, 1075, 910 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{29}O_3PNa^+$ 311.1747; found 311.1749.

Diisopropyl (6-phenylhexa-1,3-dien-5-yn-2-yl)phosphonate (3t, new compound)



Following general procedure 1.2, **3t** (*E*/*Z* = 41:59) was obtained as yellow oil (76.3 mg, 80% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

(*E*)-diisopropyl (6-phenylhexa-1,3-dien-5-yn-2-yl)phosphonate with

(*Z*)-diisopropyl (6-phenylhexa-1,3-dien-5-yn-2-yl)phosphonate ((*E*)-3t:(*Z*)-3t = 1:2.24)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44-7.34 (m, 2H), 7.41-7.39 (m, 3H), 7.33-7.30 (m, 11.24H), 6.93 (d, J = 47.7 Hz, 2.24H), 6.71 (dd, J_1 = 26.8 Hz, J_2 = 16.2 Hz, 1H), 6.47 (d, J = 23.8 Hz, 2.24H), 6.37 (dd, J_1 = 11.4 Hz, J_2 = 7.7 Hz, 2.24H), 6.36 (d, J = 16.5 Hz, 1H), 6.21 (d, J = 20.2 Hz, 1H),

5.99 (d, *J* = 44.0 Hz, 1H), 5.93 (d, *J* = 11.7 Hz, 2.24H), 4.71-4.64 (m, 6.48H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.35 (d, *J* = 6.2, 13.44H), 1.29 (d, *J* = 6.2 Hz, 19.44H);

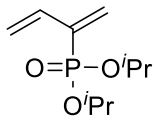
^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.4, 138.3, 137.7 (d, *J* = 173. 9 Hz), 136.0 (d, *J* = 177.2 Hz), 133.3 (d, *J* = 11.0 Hz), 133.1 (d, *J* = 8.8 Hz), 131.9 (d, *J* = 5.5 Hz), 131.7, 131.6, 128.7, 128.6, 128.5 (d, *J* = 7.3 Hz), 123.2, 123.1, 113.7 (d, *J* = 4.4 Hz), 110.9 (d, *J* = 14.3 Hz), 97.0, 93.1, 88.7, 87.3 (d, *J* = 3.3 Hz), 71.2 (d, *J* = 5.6 Hz), 71.0 (d, *J* = 5.5 Hz), 24.2 (d, *J* = 3.5 Hz), 24.2 (d, *J* = 4.2 Hz), 24.0 (d, *J* = 4.0 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.07, 15.65;

IR (film) υ_{max}: 3456, 3055, 2975, 2928, 2855, 1958, 1635, 1385, 1180, 1142, 1075, 981, 621 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{23}O_3PNa^+$ 341.1277; found 341.1280.

Diisopropyl buta-1,3-dien-2-ylphosphonate (3u, new compound)



Following general procedure 1.2, **3u** was obtained as clear oil (47.1 mg, 72% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.36 (ddd, J_1 = 24.7 Hz, J_2 = 17.6 Hz, J_3 = 11.2 Hz, 1H), 6.14 (d, *J* = 21.7 Hz, 1H), 5.92 (d, *J* = 44.9 Hz, 1H), 5.68 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 4.68-4.63 (m, 2H), 1.34 (d, *J* = 6.2 Hz, 6H), 1.26 (d, *J* = 6.2 Hz, 6H);

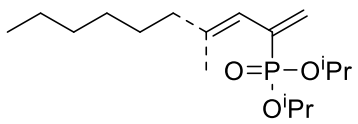
^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.5 (d, *J* = 173.6 Hz), 133.9 (d, *J* = 11.4 Hz), 131.8 (d, *J* = 8.4 Hz), 119.3 (d, *J* = 5.6 Hz), 70.9 (d, *J* = 5.5 Hz), 24.2 (d, *J* = 3.5 Hz), 23.8 (d, *J* = 5.5 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.62;

IR (film) υ_{max}: 3456, 3058, 2953, 2928, 2028, 2853, 1619, 1547, 1141, 1075, 930 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{19}O_3PH^+$ 219.1145; found 219.1142.

Diisopropyl (4-methyldeca-1,3-dien-2-yl)phosphonate (3v, new compound)



Following general procedure 1.3, **3v** (*E*/*Z* = 50:50) was obtained as clear oil (81.5 mg, 86% yield). For full characterization, see (*E*)-**3v** and (*Z*)-**3v**. Purification: flash chromatography was used with

10% EtOAc in petroleum ether.

(*E*)-diisopropyl (4-methyldeca-1,3-dien-2-yl)phosphonate ((*E*)-3v).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.13 (dd, J_1 = 23.4 Hz, J_2 = 2.3 Hz, 1H), 5.72 (d, *J* = 5.3 Hz, 1H), 5.64 (dm, *J* = 48.7 Hz, 1H), 4.64-4.57 (m, 2H), 2.10 (t, *J* = 7.5 Hz, 1H), 1.77-1.76 (m, 3H), 1.41-1.35 (m, 2H), 1.30 (d, *J* = 6.2 Hz, 6H), 1.27-1.23 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.6 (d, *J* = 13.6 Hz), 137.8 (d, *J* = 172.6 Hz), 130.2 (d, *J* = 8.1 Hz), 120.0 (d, *J* = 9.6 Hz), 70.5 (d, *J* = 5.6 Hz), 40.4, 31.8, 29.0, 27.8, 24.2 (d, *J* = 3.7 Hz), 23.9 (d, *J* = 5.1 Hz), 22.7, 17.7 (d, *J* = 1.9 Hz), 14.2;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.27;

IR (film) υ_{max}: 3444, 3058, 2973, 2928, 2028, 1958, 1180, 1142, 1075, 984 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{33}O_3PNa^+$ 339.2060; found 339.2061.

(*Z*)-diisopropyl (4-methyldeca-1,3-dien-2-yl)phosphonate ((*Z*)-3v)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.13 (dd, J_1 = 23.4 Hz, J_2 = 2.3 Hz, 1H), 5.72 (d, *J* = 5.6 Hz, 1H), 5.65 (dm, *J* = 48.7 Hz, 1H), 4.65-4.58 (m, 2H), 2.10 (t, *J* = 8.5 Hz, 1H), 1.78-1.77 (m, 3H), 1.40-1.35 (m, 2H), 1.30 (d, *J* = 6.2 Hz, 6H), 1.28-1.24 (m, 10H), 0.86 (t, *J* = 7.1 Hz, 3H);

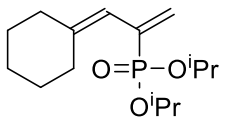
^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.3 (d, *J* = 13.4 Hz), 137.7 (d, *J* = 173.3 Hz), 129.6 (d, *J* = 8.2 Hz), 120.5 (d, *J* = 9.5 Hz), 70.6 (d, *J* = 6.1 Hz), 32.9 (d, *J* = 1.8 Hz), 31.8, 29.6, 28.6 (d, *J* = 1.8 Hz), 24.2 (d, *J* = 3.7 Hz), 23.9, 23.88 (d, *J* = 5.1 Hz), 22.7, 14.2;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.14;

IR (film) υ_{max}: 3455, 3054, 2974, 2929, 2028, 1958, 1254, 1179, 1141, 1107, 982 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{33}O_3PNa^+$ 339.2060; found 339.2062.

Diisopropyl (3-cyclohexylideneprop-1-en-2-yl)phosphonate (3w, new compound)



Following general procedure 1.3, **3w** was obtained as clear oil (67.8 mg, 79% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.14 (dd, J_1 = 22.6 Hz, J_2 = 2.4 Hz, 1H), 5.68 (d, *J* = 4.7 Hz, 1H), 5.63 (dm, *J* = 43.3 Hz, 1H), 4.64-4.58 (m, 2H), 2.25 (t, *J* = 6.2 Hz, 2H), 2.15 (t, *J* = 6.8 Hz, 2H), 1.56-1.54 (m, 4H), 1.51-1.47 (m, 2H), 1.31 (d, *J* = 6.2 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H);

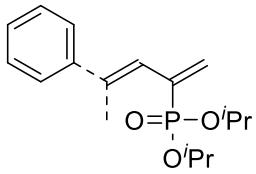
^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.2 (d, *J* = 12.3 Hz), 137.4 (d, *J* = 173.2 Hz), 130.3 (d, *J* = 8.8 Hz), 117.6 (d, *J* = 9.5 Hz), 70.6 (d, *J* = 5.5 Hz), 37.6, 29.5 (d, *J* = 2.2 Hz), 28.5 (d, *J* = 2.2 Hz), 28.0, 26.7, 24.2 (d, *J* = 3.5 Hz), 23.9 (d, *J* = 5.4 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.98;

IR (film) υ_{max}: 3467, 3057, 2975, 2928, 2853, 2028, 1958, 1438, 1227, 1120, 1034, 951, 745 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{29}O_3PNa^+$ 309.1590; found 309.1596.

Diisopropyl (4-phenylpenta-1,3-dien-2-yl)phosphonate (3x, new compound)



Following general procedure 1.3, **3x** (*E/Z* = 83:17) was obtained as clear oil (75.8 mg, 82% yield). Purification: flash chromatography was used with 10% EtOAc in petroleum ether. For full characterization, see (*E*)-**3x** and (*Z*)-**3x**.

(*E*)-diisopropyl (4-phenylpenta-1,3-dien-2-yl)phosphonate ((*E*)-3x)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45-7.43 (m, 2 H), 7.36-7.33 (m, 2H), 7.29-7.26 (m, 1H), 6.36 (dd, J_1 = 23.3 Hz, J_2 = 6.39 Hz, 1H), 6.34 (dm, *J* = 6.75 Hz, 1H), 5.88 (dm, *J* = 48.3 Hz, 1H), 4.72-4,65 (m, 2H), 2.20-2.19 (m, 3H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.29 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.1, 140.1 (d, *J* = 12.9 Hz), 138.1 (d, *J* = 174.5 Hz), 131.0 (d, *J* = 7.5 Hz), 128.4, 127.6, 126.0, 122.8 (d, *J* = 9.6 Hz), 70.8 (d, *J* = 5.4 Hz), 24.2 (d, *J* = 3.8 Hz), 23.9 (d, *J* = 4.7 Hz), 17.4 (d, *J* = 2.7 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.48;

IR (film) υ_{max}: 3454, 3056, 2973, 2028, 1958, 1650, 1180, 1141, 1075, 981, 623 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{25}O_3PNa^+$ 331.1434; found 331.1439.

(*Z*)-diisopropyl (4-phenylpenta-1,3-dien-2-yl)phosphonate ((*Z*)-3x)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.29-7.20 (m, 5H), 6.01 (d, *J* = 5.9 Hz, 1H), 5.82 (dd, J_1 = 23.8 Hz, J_2 = 1.4 Hz, 1H), 5.27 (d, *J* = 49.2Hz, 1H), 4.73-4,67 (m, 2H), 2.14 (s, 3H) 1.37 (d, *J* = 6.2 Hz, 6H), 1.33 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.3 (d, *J* = 14.0 Hz), 141.5, 136.8 (d, *J* = 177.2 Hz), 131.3 (d, *J* =

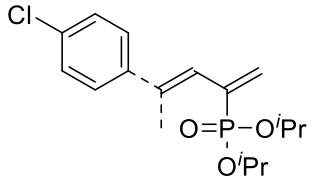
6.9 Hz), 128.5, 127.9, 127.1, 121.4 (d, *J* = 10.7 Hz), 70.8 (d, *J* = 5.7 Hz), 26.9, 24.3 (d, *J* = 3.4 Hz), 24.0 (d, *J* = 5.5 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.33;

IR (film) υ_{max}: 3454, 3057, 2975, 2927, 2028, 1958, 1647, 1385, 1252, 1075, 962, 699 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{25}O_3PNa^+$ 331.1434; found 331.1438.

Diisopropyl (4-(4-chlorophenyl)penta-1,3-dien-2-yl)phosphonate (3y, new compound)



Following general procedure 1.3, **3y** (*E/Z* = 85:15) was obtained as clear oil (72.9 mg, 71% yield). Purification: flash chromatography was used with 10% EtOAc in petroleum ether. For full characterization, see (*E*)-**3y** and (*Z*)-**3y**.

(*E*)-diisopropyl (4-(4-chlorophenyl)penta-1,3-dien-2-yl)phosphonate ((*E*)-3y)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.34 (dd, J_1 = 23.4 Hz, J_2 = 1.7 Hz, 1H), 6.31 (d, *J* = 7.3 Hz, 1H), 5.85 (d, *J* = 48.1 Hz, 1H), 4.70-4.65 (m, 2H), 2.15 (s, 3H), 1.33 (d, *J* = 6.2 Hz, 6H), 1.27 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.5, 138.9 (d, *J* = 13.2 Hz), 138.0 (d, *J* = 175.2 Hz), 133.4, 131.2 (d, *J* = 7.5 Hz), 128.6, 127.3, 123.3 (d, *J* = 9.9 Hz), 70.9 (d, *J* = 5.6 Hz), 24.2 (d, *J* = 4.4 Hz), 23.9 (d, *J* = 5.3 Hz), 17.3 (d, *J* = 2.0 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.18;

IR (film) υ_{max}: 3459, 3055, 2978, 2028, 1958, 1647, 1488, 1246, 1142, 1075, 982, 588 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{24}ClO_3PH^+$ 343.1224; found 343.1221.

(*Z*)-diisopropyl (4-(4-chlorophenyl)penta-1,3-dien-2-yl)phosphonate ((*Z*)-3y).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.04 (d, *J* = 5.6 Hz, 1H), 5.85 (dd, J_1 = 23.5 Hz, J_2 = 1.2Hz, 1H), 5.29 (d, *J* = 48.7 Hz, 1H), 4.75-4.69 (m, 2 H), 2.11 (s, 3 H), 1.38 (d, *J* = 6.2 Hz, 6 H), 1.34 (d, *J* = 6.2 Hz, 6 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.9 (d, *J* = 13.4 Hz), 139.7, 136.9 (d, *J* = 178.5 Hz), 132.9, 131.5 (d, *J* = 7.6 Hz), 129.4, 128.7, 122.3 (d, *J* = 10.2 Hz), 70.9 (d, *J* = 5.6 Hz), 26.6, 24.2 (d, *J* = 3.9 Hz),

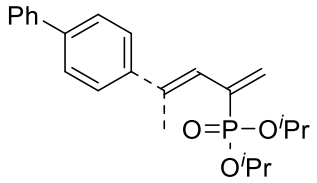
24.1 (d, *J* = 5.5 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.76;

IR (film) υ_{max}: 3432, 3055, 2977, 2922, 2861, 2036, 1958, 1490, 1385, 1180, 1105, 982, 614 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{24}ClO_3PH^+$ 343.1224; found 343.1228.

Diisopropyl (4-([1,1'-biphenyl]-4-yl)penta-1,3-dien-2-yl)phosphonate (3z, new compound)



Following general procedure 1.3, **3z** (*E*/*Z* = 90:10) was obtained as clear oil (102.6 mg, 89% yield). Purification: flash chromatography was used with 10% EtOAc in petroleum ether. For full characterization, see (*E*)-**3z** and (*Z*)-**3z**.

(*E*)-diisopropyl (4-([1,1'-biphenyl]-4-yl)penta-1,3-dien-2-yl)phosphonate ((*E*)-3z)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62-7.59 (m, 4H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.43-7.46 (m, 2H), 7.36-7.34 (m, 1H), 6.43 (d, *J* = 6.1 Hz, 1H), 6.38 (dd, J_1 = 23.4 Hz, J_2 = 1.9 Hz, 1H), 5.90 (d, *J* = 48.2 Hz, 1H), 4.73-4.68 (m, 2H), 2.24-2.23 (m, 3H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.31 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.0, 140.7, 140.5, 139.6 (d, *J* = 13.4 Hz), 138.2 (d, *J* = 174.3 Hz), 131.2 (d, *J* = 7.7 Hz), 128.9, 127.5, 127.2, 127.1, 126.5, 122.8 (d, *J* = 9.2 Hz), 70.9 (d, *J* = 6.4 Hz), 24.3 (d, *J* = 3.4 Hz), 24.0 (d, *J* = 4.9 Hz), 17.4 (d, *J* = 1.9 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.46;

IR (film) υ_{max}: 3432, 3057, 2979, 2897, 1958, 1719, 1648, 1382, 1156, 1105, 1012, 982, 614 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{29}O_3PNa^+$ 407.1747; found 407.1743.

(*Z*)-diisopropyl (4-([1,1'-biphenyl]-4-yl)penta-1,3-dien-2-yl)phosphonate ((*Z*)-3z)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60-7.32 (m, 9H), 6.05 (d, *J* = 6.0 Hz, 1H), 5.87 (dd, J_1 = 23.7 Hz, J_2 = 1.9 Hz, 1H), 5.38 (d, *J* = 49.0 Hz, 1H), 4.76-4.70 (m, 2H), 2.17-2.167 (m, 3H), 1.39 (d, *J* = 6.2 Hz, 6H), 1.35 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.7 (d, *J* = 13.3 Hz), 140.8, 140.3, 139.9, 136.9 (d, *J* = 178.0 Hz), 131.5 (d, *J* = 6.9 Hz), 128.9, 128.4, 127.4, 127.1, 127.0, 121.7 (d, *J* = 10.6 Hz), 70.8 (d, *J* =

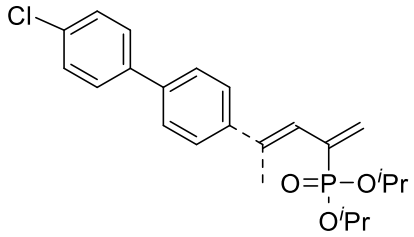
5.7Hz), 26.8, 24.3 (d, J = 3.5 Hz), 24.1 (d, J = 5.2 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.23;

IR (film) υ_{max}: 3433, 3054, 2979, 2897, 1958, 1719, 1680, 1605, 1181, 1116, 974, 613 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{29}O_3PNa^+$ 407.1747; found 407.1744.

Diisopropyl (4-(4'-chloro-[1,1'-biphenyl]-4-yl)penta-1,3-dien-2-yl)phosphonate (3aa, new compound)



Following general procedure 1.3, **3aa** (*E/Z* = 87:13) was obtained (97.8 mg, 78% yield). Purification: flash chromatography was used with 10% EtOAc in petroleum ether. For full characterization, see (*E*)-**3aa** and (*Z*)-**3aa**.

(*E*)-diisopropyl (4-(4'-chloro-[1,1'-biphenyl]-4-yl)penta-1,3-dien-2-yl)phosphonate ((*E*)-3aa)

White solid, mp 62-64 ℃;

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53-7.48 (m, 6H), 7.38 (d, J = 8.5 Hz, 2H), 6.42 (d, J = 6.1 Hz, 1H), 6.37 (dd, J_1 = 23.3 Hz, J_2 = 1.7 Hz, 1H), 5.88 (d, J = 48.2 Hz, 1H), 4.73-4.66 (m, 2H), 2.21 (s, 3H), 1.35 (d, J = 6.2 Hz, 6H), 1.29 (d, J = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.3, 139.4 (d, J = 13.2 Hz), 139.1, 139.0, 138.0 (d, J = 174.8 Hz), 133.5, 131.1 (d, J = 7.6 Hz), 129.0, 128.2, 126.9, 126.5, 122.9 (d, J = 9.6 Hz), 70.8 (d, J = 6.6 Hz), 24.2 (d, J = 3.7 Hz), 23.9 (d, J = 4.5 Hz), 17.3 (d, J = 2.0 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.76;

IR (film) υ_{max}: 3314, 3057, 2976, 2908, 1655, 1605, 1528, 1247, 1106, 985, 613 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{28}ClO_3PH^+$ 419.1537; found 419.1536.

(*Z*)-diisopropyl (4-(4'-chloro-[1,1'-biphenyl]-4-yl)penta-1,3-dien-2-yl)phosphonate ((*Z*)-3aa)

Clear oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.05 (d, J = 6.1 Hz, 1H), 5.86 (d, J = 23.2 Hz, 1H), 5.36 (d, J = 49.0 Hz, 1H), 4.75-4.70 (m, 2H), 2.16 (s, 3H), 1.38 (d, J = 6.1 Hz, 6H), 1.34 (d, J = 6.1 Hz, 6H);

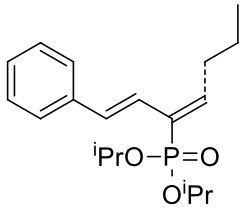
^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.6 (d, *J* = 13.2 Hz), 140.7, 139.3, 138.6, 136.9 (d, *J* = 179.4 Hz), 133.5, 131.5 (d, *J* = 6.6 Hz), 129.0, 128.6, 128.3, 127.0, 121.9 (d, *J* = 9.9 Hz), 70.9 (d, *J* = 5.5 Hz), 26.7, 24.3 (d, *J* = 3.3 Hz), 24.1 (d, *J* = 4.4 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.09;

IR (film) υ_{max}: 3236, 3058, 2976, 2908, 1665, 1605, 1528, 1247, 1106, 985, 613 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{28}ClO_3PH^+$ 419.1537; found 419.1536.

Diisopropyl((1*E*)-1-phenylhepta-1,3-dien-3-yl)phosphonate (3ab, new compound)



Following general procedure 1.4, **3ab** (1*E*,3*E*/1*E*,3*Z* = 90:10) was obtained as clear oil (94.8 mg, 94% yield). Purification: flash chromatography was used with 10% EtOAc in petroleum ether. For full characterization, see (*E*)-**3ab** and (*Z*)-**3ab**.

Diisopropyl((1*E*,3*E*)-1-phenylhepta-1,3-dien-3-yl)phosphonate ((*E*)-3ab)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.32-7.30 (m, 2H), 7.23-7.21 (m, 1H), 6.90 (d, *J* = 16.3 Hz, 1H), 6.76 (d, *J* = 16.7 Hz, 1H), 6.55 (dt, J_1 = 47.7 Hz, J_2 = 7.7 Hz, 1H), 4.72-4.67 (m, 2H), 2.70-2.66 (m, 2H), 1.55-1.49 (m, 2H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H), 0.99 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.4 (d, *J* = 11.9 Hz), 137.7, 130.1 (d, *J* = 6.6 Hz), 129.2 (d, *J* = 174.7 Hz), 128.9 (d, *J* = 13.2 Hz), 128.7, 127.6, 126.5, 70.5 (d, *J* = 5.5 Hz), 32.4 (d, *J* = 5.4 Hz), 24.3 (d, *J* = 4.0 Hz), 24.0 (d, *J* = 4.6 Hz), 22.8 (d, *J* = 1.6 Hz), 14.0;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.70;

IR (film) υ_{max}: 3421, 3055, 2983, 2930, 2630, 1953, 1605, 1437, 1232, 1180, 1142, 979, 636 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{33}O_3PNa^+$ 359.1747; found 359.1750.

Diisopropyl ((1*E*,3*Z*)-1-phenylhepta-1,3-dien-3-yl)phosphonate ((*Z*)-3ab)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.32-7.30 (m, 2H), 7.23-7.21 (m, 1H), 7.05 (d, *J* = 16.6 Hz, 1H), 6.92 (dd, *J* = 28.8 Hz, *J* = 16.7 Hz, 1H), 6.75 (dt, *J* = 22.8 Hz, *J* = 7.4 Hz, 1H), 4.68-4.62 (m, 2H), 2.39-2.35 (m, 2H), 1.56-1.50 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H), 0.95 (t, *J* = 7.3 Hz, 3H);

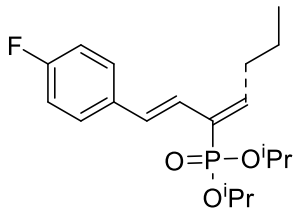
^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.2 (d, *J* = 8.8 Hz), 137.6, 133.6 (d, *J* = 4.6 Hz), 128.7, 128.3 (d, *J* = 175.8 Hz), 127.9, 126.5, 121.1 (d, *J* = 11.0 Hz), 70.5 (d, *J* = 5.4 Hz), 30.9 (d, *J* = 16.8 Hz), 24.2 (d, *J* = 4.4 Hz), 23.8 (d, *J* = 4.4 Hz), 22.1 (d, *J* = 2.2 Hz), 13.9;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.97;

IR (film) υ_{max}: 3423, 3056, 2985, 2931, 2635, 1952, 1608, 1429, 1234, 1179, 1142, 978, 621 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{33}O_3PNa^+$ 359.1747; found 359.1746.

Diisopropyl ((1*E*)-1-(4-fluorophenyl)hepta-1,3-dien-3-yl)phosphonate (3ac, new compound)



Following general procedure 1.4, **3ac** (1*E*,3*E*/1*E*,3*Z* = 86:14) was obtained as clear oil (95.6 mg, 90% yield). Purification: flash chromatography was used with 10% EtOAc in petroleum ether. For full characterization, see (*E*)-**3ac** and (*Z*)-**3ac**.

Diisopropyl ((1*E*,3*E*)-1-(4-fluorophenyl)hepta-1,3-dien-3-yl)phosphonate ((*E*)-3ac)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39-7.37 (m, 2H), 7.03-6.99 (m, 3H), 6.87 (dd, J_1 = 28.9 Hz, J_2 = 16.5 Hz, 1H), 6.74 (dt, J_1 = 22.7 Hz, J_2 = 7.4 Hz, 1H), 4.69-4.63 (m, 2H), 2.39-2.35 (m, 2H), 1.57-1.51 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H), 0.96 (t, *J* = 6.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.6 (d, *J* = 247.4 Hz), 149.2 (d, *J* = 8.8 Hz), 133.8 (d, *J* = 3.9 Hz), 132.4 (d, *J* = 4.1 Hz), 128.3 (d, *J* = 176.1 Hz), 128.1 (d, *J* = 8.0 Hz), 121.0 (dd, J_1 = 11.2 Hz, J_2 = 2.0 Hz), 115.7 (d, *J* = 21.4 Hz), 70.7 (d, *J* = 5.4 Hz), 31.0 (d, *J* = 17.1 Hz), 24.2 (d, *J* = 3.6 Hz), 23.9 (d, *J* = 5.4 Hz), 22.2, 14.0;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.89;

^{19}F NMR (471 MHz, CDCl3): δ -113.93;

IR (film) υ_{max}: 3453, 3054, 2973, 2930, 2861, 1952, 1614, 1507, 1234, 1180, 1142, 982, 621 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{32}FO_3PNa^+$ 377.1652; found 377.1656.

Diisopropyl((1*E*,3*Z*)-1-(4-fluorophenyl)hepta-1,3-dien-3-yl)phosphonate ((*E*)-3ac)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37-7.35 (m, 2H), 7.01-6.98 (m, 2H), 6.87 (d, *J* = 16.2 Hz, 1H), 7.00 (dd, J_1 = J_2 = 17.1 Hz, 1H), 6.52 (dt, J_1 = 47.5 Hz, J_2 = 7.7 Hz, 1H), 4.73-4.65 (m, 2H),

2.68-2.64 (m, 2H), 1.54-1.48 (m, 2H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H), 0.98 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.4 (d, *J* = 247.2 Hz), 150.3 (d, *J* = 11.3 Hz), 133.9 (d, *J* = 3.4 Hz), 129.1 (d, *J* = 174.8 Hz), 128.9 (d, *J* = 6.4 Hz), 128.8 (dd, *J* = 13.2 Hz, *J* = 2.2 Hz), 115.6 (d, *J* = 21.0 Hz), 70.6 (d, *J* = 5.4 Hz), 32.4 (d, *J* = 5.2 Hz), 24.3 (d, *J* = 3.3 Hz), 24.0 (d, *J* = 5.2 Hz), 22.8, 14.0;

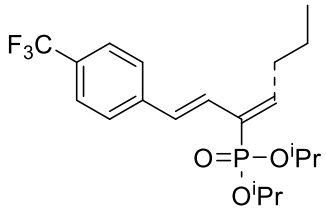
^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.67;

^{19}F NMR (471 MHz, CDCl3): δ -114.56;

IR (film) υ_{max}: 3453, 3056, 2973, 2930, 1952, 1601, 1507, 1230, 1179, 1142, 981, 632 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{32}FO_3PNa^+$ 377.1652; found 377.1658.

Diisopropyl((1*E*)-1-(4-(trifluoromethyl)phenyl)hepta-1,3-dien-3-yl)phosphonate (3ad, new compound)



Following general procedure 1.4, **3ad** (1*E*,3*E*/1*E*,3*Z* = 85:15) was obtained as clear oil (107.9 mg, 89% yield). Purification: flash chromatography was used with 10% EtOAc in petroleum ether. For full characterization, see (*E*)-**3ad** and (*Z*)-**3ad**.

Diisopropyl((1*E*,3*E*)-1-(4-(trifluoromethyl)phenyl)hepta-1,3-dien-3-yl)phosphonate ((*E*)-3ad)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 16.5 Hz, 1H), 7.00 (dd, J_1 = 28.0 Hz, J_2 = 16.5 Hz, 1H), 6.80 (dt, J_1 = 22.7 Hz, J_2 = 7.4 Hz, 1H), 4.70-4.63 (m, 2H), 2.40-2.36 (m, 2H), 1.57-1.51 (m, 2H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H), 0.96 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.5 (d, *J* = 8.1 Hz), 141.1, 132.1 (d, *J* = 4.4 Hz), 129.5 (q, *J* = 32.9 Hz), 128.2 (d, *J* = 176.9 Hz), 126.7, 125.6 (q, *J* = 3.5 Hz), 124.2 (q, *J* = 271.8 Hz), 123.6 (d, *J* = 11.2 Hz), 70.8 (d, *J* = 5.4 Hz), 31.0 (d, *J* = 16.6 Hz), 24.2 (d, *J* = 3.4 Hz), 23.8 (d, *J* = 4.4 Hz), 22.1 (d, *J* = 2.2 Hz), 13.9;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.37;

^{19}F NMR (471 MHz, CDCl3): δ -62.57;

IR (film) υ_{max}: 3357, 3057, 2974, 2921, 2860, 1633, 1469, 1325, 1241, 1165, 1125, 983, 623 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{32}F_3O_3PNa^+$ 427.1620; found 427.1620.

Diisopropyl ((1*E*,3*Z*)-1-(4-(trifluoromethyl)phenyl)hepta-1,3-dien-3-yl)phosphonate ((*Z*)-3ad)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 16.5 Hz, 1H), 6.83 (dd, J_1 = 18.7 Hz, J_2 = 16.5 Hz, 1H), 6.59 (dt, J_1 = 47.1 Hz, J_2 = 8.0 Hz, 1H), 4.74-4.67 (m, 2H), 2.70-2.66 (m, 2H), 1.55-1.49 (m, 2H), 1.38 (d, *J* = 6.2 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H), 0.99 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.0 (d, *J* = 11.1 Hz), 141.2, 131.6 (d, *J* = 13.6 Hz), 129.2 (q, *J* = 32.2 Hz), 129.0 (d, *J* = 175.6 Hz), 128.7 (d, *J* = 6.2 Hz), 126.6, 125.6 (q, *J* = 4.1 Hz), 124.4 (q, *J* = 271.8 Hz), 70.7 (d, *J* = 5.5 Hz), 32.6 (d, *J* = 5.4 Hz), 24.3 (d, *J* = 3.3 Hz), 24.0 (d, *J* = 5.5 Hz), 22.8 (d, *J* = 2.2 Hz), 14.0;

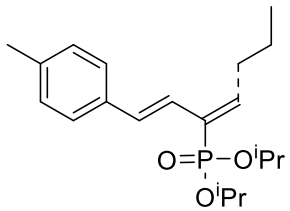
^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.14;

^{19}F NMR (471 MHz, CDCl3): δ -62.44;

IR (film) υ_{max}: 3432, 3058, 2971, 2930, 2867, 1634, 1469, 1324, 1241, 1165, 1127, 983, 623 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{32}F_3O_3PNa^+$ 427.1620; found 427.1623.

Diisopropyl ((1*E*)-1-(p-tolyl)hepta-1,3-dien-3-yl)phosphonate (3ae, new compound)



Following general procedure 1.4, **3ae** (1*E*,3*E*/1*E*,3*Z* = 90:10) was obtained as clear oil (95.6 mg, 91% yield). Purification: flash chromatography was used with 10% EtOAc in petroleum ether. For full characterization, see (*E*)-**3ae** and (*Z*)-**3ae**.

Diisopropyl ((1E,3E)-1-(p-tolyl)hepta-1,3-dien-3-yl)phosphonate ((*E*)-3ae)

^{1}H NMR (CDCl3, 500 MHz): δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 16.5 Hz, 1H), 6.89 (dd, J_1 = 28.9 Hz, J_2 = 16.9 Hz, 1H), 6.74 (dt, J_1 = 22.8 Hz, J_2 = 7.5 Hz, 1H), 4.69-4.63 (m, 2H), 2.41-2.36 (m, 2H), 2.34 (s, 3H), 1.55 (q, *J* = 7.4 Hz, 2H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.26 (d, *J* = 6.2 Hz, 6H), 0.97 (t, *J* = 6.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.8 (d, *J* = 9.1 Hz), 137.9, 134.9, 133.6 (d, *J* = 4.5 Hz), 129.5, 128.5 (d, *J* = 175.2 Hz), 126.5, 120.3 (d, *J* = 11.1 Hz), 70.6 (d, *J* = 5.3 Hz), 31.0 (d, *J* = 16.9 Hz), 24.3 (d, *J* = 3.6 Hz), 23.9 (d, *J* = 5.1 Hz), 22.2 (d, *J* = 1.8 Hz), 21.3, 14.0;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.87;

IR (film) υ_{max}: 3445, 3057, 2976, 2923, 2030, 1958, 1179, 1247, 1141, 1075, 980, 587 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{31}O_3PNa^+$ 373.1903; found 373.1902.

Diisopropyl ((1*E*,3*Z*)-1-(p-tolyl)hepta-1,3-dien-3-yl)phosphonate ((*Z*)-3ae)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 16.3 Hz, 1H), 6.71 (dd, $J_1 = J_2$ = 16.7 Hz, 1H), 6.53 (dt, J_1 = 47.9 Hz, J_2 = 7.8 Hz, 1H), 4.72-4.65 (m, 2H), 2.70-2.65 (m, 2H), 2.33 (s, 3H), 1.51 (q, *J* = 7.4 Hz, 2H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H), 0.98 (t, *J* = 6.2 Hz, 3H);

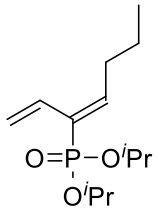
^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.9 (d, *J* = 11.0 Hz), 137.5, 134.9, 130.0 (d, *J* = 6.6 Hz), 129.4, 129.2 (d, *J* = 174.0 Hz), 128.0 (d, *J* = 13.1 Hz), 126.5, 70.5 (d, *J* = 5.4 Hz), 32.4 (d, *J* = 5.3 Hz), 24.3 (d, *J* = 3.7 Hz), 24.0 (d, *J* = 4.9 Hz), 22.9, 21.3, 14.0;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.87;

IR (film) υ_{max}: 3445, 3058, 2979, 2926, 2861, 1956, 1385, 1179, 1142, 1075, 980, 587 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{31}O_3PNa^+$ 373.1903; found 373.1903.

(*E*)-diisopropyl hepta-1,3-dien-3-ylphosphonate (3af, new compound).



Following general procedure 1.4, **3af** was obtained as clear oil (63.2mg, 81% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.66 (dt, J_1 = 23.2 Hz, J_2 = 7.7 Hz, 1H), 6.46 (ddd, J_1 = 27.7 Hz, J_2 = 17.8 Hz, J_3 = 11.5 Hz, 1H), 5.60 (d, *J* = 17.8 Hz, 1H), 5.27 (dd, J_1 = 11.5 Hz, J_2 = 1.1 Hz, 1H), 4.61-4.56 (m, 2H), 2.24 (ddt, J_1 = 7.4 Hz, J_2 = 7.3 Hz, J_3 = 3.4 Hz, 2H), 1.47-1.43 (m, 2H), 1.29 (d, *J* = 6.2 Hz, 6H), 1.21 (d, *J* = 6.2 Hz, 6H), 0.89 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.1 (d, *J* = 8.7 Hz), 129.0 (d, *J* = 10.9 Hz), 128.9 (d, *J* = 176.5

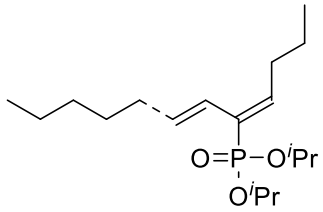
Hz), 119.4 (d, *J* = 4.7 Hz), 70.4 (d, *J* = 4.9 Hz), 30.7 (d, *J* = 17.4 Hz), 24.1 (d, *J* = 4.4 Hz), 23.8 (d, *J* = 4.7 Hz), 22.0 (d, *J* = 2.2 Hz), 13.9;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.96;

IR (film) υ_{max}: 3459, 3055, 2977, 2928, 2869, 1622, 1385, 1248, 1179, 1141, 979, 774 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{29}O_3PH^+$ 261.1614; found 261.1613.

Diisopropyl (4*E*)-dodeca-4,6-dien-5-ylphosphonate (3ag, new compound).



Following general procedure 1.4, **3ag** (4E,6*E*/4*E*,6*Z* = 50:50) was obtained as clear oil (88.2 mg, 89% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

Diisopropyl(4*E*,6*E*)-dodeca-4,6-dien-5-ylphosphonate with

Diisopropyl(4*E*,6*Z*)-dodeca-4,6-dien-5-ylphosphonate ((*E*)-3ag:(*Z*)-3ag = 1:1.24)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.54 (dt, J_1 = 24.1 Hz, J_2 = 7.4 Hz, 1H), 6.52 (dt, J_1 = 23.2 Hz, J_2 = 7.6 Hz, 1.24H), 6.11 (dd, J_1 = 27.2 Hz, J_2 = 16.1 Hz, 1H), 6.08 (dt, J_1 = 15.8 Hz, J_2 = 6.7 Hz, 1H), 5.71 (dt, J_1 = 11.3 Hz, J_2 = 3.0 Hz, 1.24H), 5.60 (ddt, J_1 = 11.4Hz, J_2 = 7.1 Hz, J_3 = 1.0 Hz, 1.24H), 4.61-4.54 (m, 4.48H), 2.23-2.19 (m, 2H), 2.09-2.06 (m, 2H), 2.02-1.98 (m, 2.48H), 1.88-1.84 (m, 2.48H), 1.46-1.19 (m, 44.8H), 0.90-0.81 (m, 13.44H);

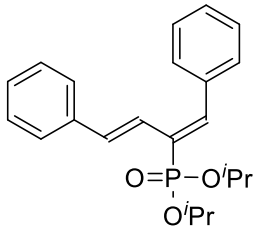
^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.9 (d, *J* = 8.8 Hz), 146.8 (d, *J* = 8.7 Hz), 136.7 (d, *J* = 4.7 Hz), 135.7 (d, *J* = 11.0 Hz), 128.7 (d, *J* = 180.2 Hz), 128.4 (d, *J* = 174.9 Hz), 122.1 (d, *J* = 11.0 Hz), 121.8 (d, *J* = 8.0 Hz), 70.2 (d, *J* = 5.0 Hz), 70.1 (d, *J* = 5.6 Hz), 33.8, 32.1 (d, *J* = 18.7 Hz), 31.8, 31.4, 30.7 (d, *J* = 17.3 Hz), 29.3 (d, *J* = 2.0 Hz), 29.0, 28.8, 24.2 (d, *J* = 4.3 Hz), 24.1 (d, *J* = 4.3 Hz), 24.0 (d, *J* = 5.1 Hz), 23.8 (d, *J* = 4.4 Hz), 22.6, 22.55, 22.1 (d, *J* = 2.0 Hz), 21.7;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 17.69, 16.88;

IR (film) υ_{max}: 3514, 3057, 2965, 2928, 2869, 1958, 1384, 1249, 1180, 1141,1075, 980 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{35}O_3PNa^+$ 353.2216; found 353.2216.

Diisopropyl ((1*E*,3*E*)-1,4-diphenylbuta-1,3-dien-2-yl)phosphonate (3ah, new compound)



Following general procedure 1.4, **3ah** was obtained as clear oil (45.5mg, 41% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67 (d, *J* = 22.7 Hz, 1H), 7.46-7.24 (m, 11H), 7.17 (dd, J_1 = 29.7 Hz, J_2 = 16.7 Hz, 1H), 4.80-4.47 (m, 2H), 1.43 (d, *J* = 6.0 Hz, 6H), 1.32 (d, *J* = 6.3 Hz, 6H);

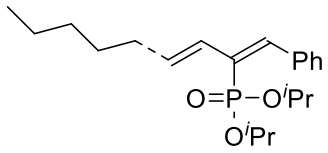
^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.1 (d, *J* = 10.3 Hz), 137.6, 136.0 (d, *J* = 21.1 Hz), 134.9 (d, *J* = 5.4 Hz), 130.1, 128.97 (d, *J* = 175.1 Hz), 128.85, 128.82, 128.6, 128.1, 126.8, 122.6 (d, *J* = 8.8 Hz), 71.0 (d, *J* = 5.4 Hz), 24.3 (d, *J* = 3.8 Hz), 23.9 (d, *J* = 5.0 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.01;

IR (film) υ_{max}: 3421,3057, 2928, 2028, 1958, 1449, 1246, 1141, 1104, 1075, 981 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{33}O_3PNa^+$ 393.1590; found 393.1591.

Diisopropyl ((1*Z*)-1-phenylnona-1,3-dien-2-yl)phosphonate (2ai, new compound)



Following general procedure 1.4, **3ai** (1*Z*,3*E*/1*Z*,3*Z* = 50:50) was obtained as clear oil (55.7 mg, 51% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

Diisopropyl ((1*Z*,3*E*)-1-phenylnona-1,3-dien-2-yl)phosphonate with

Diisopropyl ((1*Z*,3*Z*)-1-phenylnona-1,3-dien-2-yl)phosphonate ((*E*)-3ai:(*Z*)-3ai = 1:1.38).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57-7.26 (m, 14.28H), 6.398 (dd, J_1 = 24.5 Hz, J_2 = 16.1 Hz, 1H), 6.37 (dt, J_1 = 16.1 Hz, J_2 = 6.6 Hz, 1H), 6.04 (ddd, J_1 = 11.3 Hz, J_2 = 5.8 Hz, J_3 = 1.5 Hz, 1.38H), 5.61 (ddt, J_1 = 11.3 Hz, J_2 = 7.3 Hz, J_3 = 2.2 Hz, 1.38H), 4.75-4.68 (m, 4.76H), 2.16-2.13 (m, 2H), 1.75-1.74 (m, 2.76H), 1.46-1.42 (m, 2H), 1.39 (d, *J* = 6.2 Hz, 6H), 1.37 (d, *J* = 6.2 Hz, 8.28H), 1.33-1.30 (m, 17.04H), 1.16-1.05 (m, 9.52H), 0.90 (t, *J* = 6.9 Hz, 3H), 0.78 (t, *J* = 7.0 Hz, 4.14H);

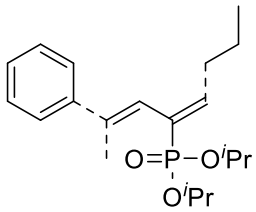
^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.3 (d, *J* = 10.7 Hz), 141.9 (d, *J* = 10.1 Hz), 138.2 (d, *J* = 4.4 Hz), 136.2 (d, *J* = 11.4 Hz), 136.1 (d, *J* = 6.5 Hz), 135.9 (d, *J* = 4.4 Hz), 129.9, 129.7, 129.1 (d, *J* = 174.0 Hz), 128.8, 128.7 (d, *J* = 179.3 Hz), 128.4, 128.34, 128.31, 123.4 (d, *J* = 9.1 Hz), 122.0 (d, *J* = 5.0 Hz), 70.7 (d, *J* = 5.5 Hz), 70.6 (d, *J* = 6.2 Hz), 33.8, 31.7, 31.5, 29.3 (d, *J* = 1.9 Hz), 28.8, 28.2 (d, *J* = 1.9 Hz), 24.3 (d, *J* = 3.6 Hz), 24.2 (d, *J* = 4.1 Hz), 24.0 (d, *J* = 5.2 Hz), 23.9 (d, *J* = 5.2 Hz), 22.58, 22.55, 14.1, 14.0;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 17.49, 17.13;

IR (film) υ_{max}: 3443, 3059, 2975, 2927, 2030, 1958,1247, 1141, 1075, 980, 607 cm^{-1};

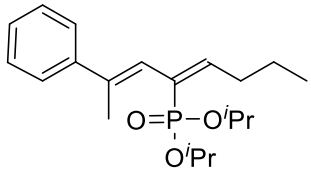
HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{33}O_3PNa^+$ 387.2060; found 387.2063.

Diisopropyl (2-phenylocta-2,4-dien-4-yl)phosphonate (3aj, new compound)



Following general procedure 1.3, **3aj** (2*E*,4*Z*/2*E*,4*E*/2*Z*,4*E* = 23:70:7) was obtained as clear oil (77.7 mg, 74% yield). Purification: flash chromatography was used with 10% EtOAc in petroleum ether. For full characterization, see (2*E*,4*Z*)-**3aj**, (2*E*,4*E*)-**3aj** and (2*Z*,4*E*)-**3aj**.

Diisopropyl ((2*E*,4*Z*)-2-phenylocta-2,4-dien-4-yl)phosphonate ((2*E*,4*Z*)-3aj)



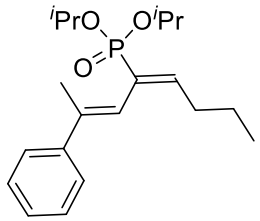
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.34-7.32 (m, 2H), 7.26-7.24 (m, 1H), 6.37-6.36 (m, 1H), 6.25 (ddt, J_1 = 50.4 Hz, J_2 = 7.7 Hz, J_3 = 1.4 Hz, 1H), 4.70-4.64 (m, 2H), 2.68-2.67 (m, 2H), 2.134-2.128 (m, 3H), 1.55-1.52 (m, 2H), 1.34 (d, *J* = 6.2 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H), 1.00 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.5 (d, *J* = 10.6 Hz), 143.4, 137.4 (d, *J* = 11.8 Hz), 128.7 (d, *J* = 176.0 Hz), 128.4, 127.3, 126.4 (d, *J* = 10.4 Hz), 126.0, 70.3 (d, *J* = 5.9 Hz), 32.3 (d, *J* = 6.4 Hz), 24.3 (d, *J* = 3.5 Hz), 24.0 (d, *J* = 4.5 Hz), 22.8 (d, *J* = 2.2 Hz), 17.1(d, *J* = 2.2 Hz), 14.1;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.88;

IR (film) υ_{max}: 3448, 3058, 2965, 2912, 1685, 1637, 1545, 1141, 1014, 980, 613 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{31}O_3PH^+$ 351.2084; found 351.2085.



Diisopropyl ((2*E*,4*E*)-2-phenylocta-2,4-dien-4-yl)phosphonate ((2*E*,4*Z*)-3aj)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47-7.46 (m, 2H), 7.36-7.34 (m, 2H), 7.29-7.26 (m, 1H), 6.67 (dt, J_1 = 23.5 Hz, J_2 = 7.3 Hz, 1H), 6.21 (dm, *J* = 4.6 Hz, 1H), 4.68-4.63 (m, 2H), 2.11-2.07 (m, 2H), 1.97-1.96 (m, 3H), 1.51-1.45 (m, 2H), 1.32 (d, *J* = 6.2 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H), 0.91 (t, *J* = 7.4 Hz, 3H);

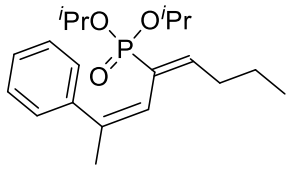
^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.4 (d, *J* = 8.9 Hz), 142.5 (d, *J* = 1.9 Hz), 139.9 (d, *J* = 11.2 Hz), 129.6 (d, *J* = 179.9 Hz), 128.4, 127.5, 126.0, 120.9 (d, *J* = 7.7 Hz), 70.4 (d, *J* = 5.5 Hz), 32.4 (d, *J* = 18.3 Hz), 24.3 (d, *J* = 3.6 Hz), 24.0 (d, *J* = 5.2 Hz), 21.7, 17.5 (d, *J* = 2.1 Hz), 14.1;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 16.74;

IR (film) υ_{max}: 3297, 3057, 2957, 2855, 1719, 1685, 1637, 1545, 1141, 1014, 978, 613 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{31}O_3PNa^+$ 373.1903; found 373.1904.

Diisopropyl ((2*Z*,4*E*)-2-phenylocta-2,4-dien-4-yl)phosphonate ((2*Z*,4*E*)-3aj)



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35-7.34 (m, 2H), 7.25-7.22 (m, 2H), 7.19-7.16 (m, 1H), 6.21 (dt, J_1 = 24.4 Hz, J_2 = 7.1 Hz, 1H), 5.87 (d, *J* = 4.0 Hz, 1H), 4.76-4.70 (m, 2H), 2.18-2.17 (m, 3H), 1.55-1.51 (m, 2H), 1.37 (d, *J* = 6.1 Hz, 6H), 1.33 (d, *J* = 6.1 Hz, 6H), 0.95-0.89 (m, 2H), 0.66 (t, *J* = 7.2 Hz, 3H);

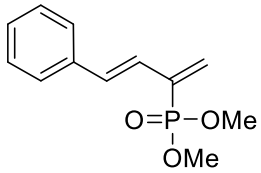
^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.4 (d, *J* = 8.6 Hz), 141.7 (d, *J* = 12.9 Hz), 141.6 (d, *J* = 2.0 Hz), 128.5 (d, *J* = 182.7 Hz), 128.1, 127.8, 127.1, 119.9 (d, *J* = 9.0 Hz), 70.6 (d, *J* = 6.6 Hz), 32.1 (d, *J* = 18.7 Hz), 25.5, 24.3 (d, *J* = 3.5 Hz), 24.1 (d, *J* = 4.5 Hz), 21.1, 14.1;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 17.49;

IR (film) υ_{max}: 3483, 3057, 2957, 2912, 1679, 1637, 1547, 1141, 1019, 978, 613 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{31}O_3PH^+$ 351.2084; found 351.2084.

(*E*)-dimethyl (4-phenylbuta-1,3-dien-2-yl)phosphonate (3ak, new compound)



Following general procedure 1.2, **3ak** was obtained as clear oil (50.0 mg, 70% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46-7.44 (m, 2H), 7.32-7.35 (m, 2H), 7.27-7.23 (m, 1H), 7.05 (d, *J* = 16.4 Hz, 1H), 6.80 (dd, J_1 = 25.9 Hz, J_2 = 16.4 Hz, 1H), 6.18 (d, *J* = 20.8 Hz, 1H), 6.11 (d, *J* = 45.0 Hz, 1H), 3.78 (d, *J* = 11.2 Hz, 6H);

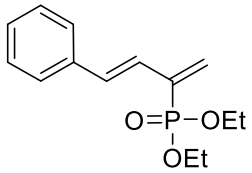
^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.7, 135.5 (d, *J* = 172.6 Hz), 133.7 (d, *J* = 5.4 Hz), 132.2 (d, *J* = 7.9Hz), 128.7, 128.4, 126.9, 125.3 (d, *J* = 12.1 Hz), 52.7 (d, *J* = 5.4 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 20.07;

IR (film) υ_{max}: 3465, 3055, 2963, 2849, 2031, 1957, 1682, 1241, 1026, 1075, 967, 828 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{15}O_3PNa^+$ 261.0651; found 261.0652.

(*E*)-diethyl (4-phenylbuta-1,3-dien-2-yl)phosphonate (3al, new compound)



Following general procedure 1.2, **3al** was obtained as clear oil (67.9, 85% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44-7.43 (m, 2H), 7.34-7.31 (m, 2H), 7.27-7.24 (m, 1H), 7.08 (d, *J* = 16.5 Hz, 1H), 6.79 (dd, J_1 = 25.6 Hz, J_2 = 16.4 Hz, 1H), 6.17 (dd, J_1 = 20.5 Hz, J_2 = 1.0 Hz, 1H), 6.06 (d, *J* = 44.7 Hz, 1H), 4.17-4.08 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H);

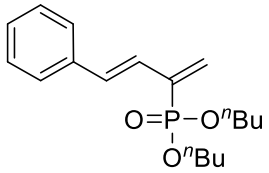
^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.8, 136.7 (d, *J* = 171.7 Hz), 133.6 (d, *J* = 5.2 Hz), 131.8 (d, *J* = 8.4Hz), 128.7, 128.3, 126.8, 125.6 (d, *J* = 12.1 Hz), 62.2 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 6.0 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 17.05;

IR (film) υ_{max}: 3472, 3062, 2982, 2930, 1642, 1236, 1051, 1023, 968, 756 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{19}O_3PNa^+$ 289.0964; found 289.0965.

(*E*)-dibutyl (4-phenylbuta-1,3-dien-2-yl)phosphonate (3am, new compound)



Following general procedure 1.2, **3am** was obtained as clear oil (87.0mg, 90% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.33-7.31 (m, 2H), 7.26-7.24 (m, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.78 (dd, J_1 = 26.1 Hz, J_2 = 16.4 Hz, 1H), 6.18 (dd, J_1 = 20.6 Hz, J_2 = 0.9 Hz, 1H), 6.06 (d, *J* = 44.8 Hz, 1H), 4.12-4.00 (m, 4H), 1.68-1.64 (m, 4H), 1.42-1.37 (m, 4H), 0.9 (t, *J* = 7.6 Hz, 6H);

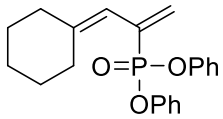
^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.8, 136.4 (d, *J* = 172.7 Hz), 133.6 (d, *J* = 4.5 Hz), 132.0 (d, *J* = 8.2 Hz), 128.7, 128.2, 126.7, 125.5 (d, *J* = 12.1 Hz), 66.0 (d, *J* = 5.5 Hz), 32.4 (d, *J* = 6.6 Hz), 18.8, 13.6;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 17.23;

IR (film) υ_{max}: 3469, 3067, 2959, 2873, 1643, 1464, 1240, 1064, 1022, 977, 755, 694 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{27}O_3P^+Na$ 345.1590; found 345.1584.

Diphenyl (3-cyclohexylideneprop-1-en-2-yl)phosphonate (3an, new compound)



Following general procedure 1.3, **3an** was obtained as clear oil (45.7 mg, 43% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32-7.30 (m, 4H), 7.23-7.21 (m, 4H), 7.16-7.14 (m, 2H), 6.40 (dd, J_1 = 24.5 Hz, J_2 = 1.6 Hz, 1H), 5.86 (d, *J* = 52.8 Hz, 1H), 5.855 (d, *J* = 4.5 Hz, 1H), 2.20-2.16 (m, 4H), 1.61-1.54 (m, 4H), 1.46-1.42 (m, 2H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.5 (d, *J* = 7.5 Hz), 148.0 (d, *J* = 13.2 Hz), 134.9 (d, *J* = 173.7

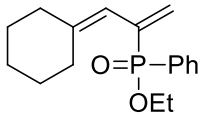
Hz), 133.9 (d, *J* = 9.5 Hz), 129.7, 125.1, 120.6 (d, *J* = 4.4 Hz), 116.3 (d, *J* = 9.9 Hz), 37.6, 29.5 (d, *J* = 2.2 Hz), 28.5, 27.8 (d, *J* = 2.2 Hz), 26.5;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 10.05;

IR (film) υ_{max}: 3487, 3055, 2928, 2848, 1590, 1489, 1274, 1189, 1025, 1022, 926, 771 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{23}O_3P^+Na$ 377.1277; found 377.1273.

Ethyl (3-cyclohexylideneprop-1-en-2-yl)(phenyl)phosphinate (3ao, new compound)



Following general procedure 1.3, **3ao** was obtained as clear oil (62.7 mg, 72% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69-7.66 (m, 2 H), 7.41-7.39 (m, 1H), 7.34-7.31 (m, 2H), 6.14 (dd, J_1 = 20.6 Hz, J_2 = 2.0 Hz, 1H), 5.62 (d, *J* = 42.3 Hz, 1H), 5.56 (s, 1H), 4.01-3.94 (m, 2H), 2.01-1.95 (m, 4H), 1.43-1.37 (m, 4H), 1.27-1.22 (m, 3H), 1.21-1.06 (m, 2H);

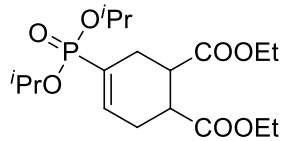
^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.7 (d, *J* = 11.0 Hz), 139.3 (d, *J* = 123.0 Hz), 131.9 (d, *J* = 2.1 Hz), 131.7 (d, *J* = 9.6 Hz), 130.5 (d, *J* = 134.0 Hz), 130.4 (d, *J* = 8.0 Hz), 128.1 (d, *J* = 12.6 Hz), 116.9 (d, *J* = 10.1 Hz), 60.7 (d, *J* = 6.1 Hz), 37.2, 29.2 (d, *J* = 2.2 Hz), 28.3, 27.6, 26.4, 16.4 (d, *J* = 6.5 Hz) ;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 30.58;

IR (film) υ_{max}: 3467, 3057, 2928, 2853, 1646, 1438, 1227, 1120, 1034, 951, 745 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{23}O_2P^+Na$ 313.1328; found 313.1319.

Diethyl 4-(diisopropoxyphosphoryl)cyclohex-4-ene-1,2-dicarboxylate (4a, new compound).



Following general procedure 2.2, **4a** was obtained as yellow oil (84.3 mg, 72% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.60-4.55 (m, 2H), 4.12-4.06 (m, 4H), 2.79-2.78 (m, 2H), 2.56 (d, *J* = 17.7 Hz, 2H), 2.29-2.21 (m, 2H), 1.27-1.26 (m, 6H), 1.23-1.18 (m, 12H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.1, 174.0, 139.4 (d, *J* = 10.1 Hz), 127.8 (d, *J* = 185.7 Hz), 70.45 (d, *J* = 5.4 Hz), 60.9 (d, *J* = 3.2 Hz), 40.1 (d, *J* = 10.1 Hz), 40.5, 28.6 (d, *J* = 18.7 Hz), 27.1 (d, *J* = 10.8 Hz), 24.1 (d, *J* = 3.8 Hz), 23.9 (d, *J* = 5.2 Hz), 23.87 (d, *J* = 4.6 Hz), 14.1 ;

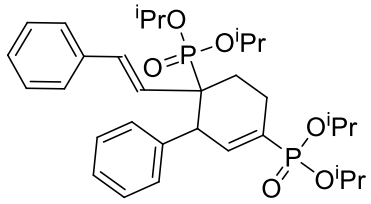
^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.85;

IR (film) υ_{max}: 3054, 2919, 1703, 1680, 1648, 1437, 1232, 1175, 1106, 974 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{31}O_3P^+H$ 391.1880; found 391.1881.

(*E*)-tetraisopropyl (2-styryl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,5-diyl)bis(phosphonate) (4b , new compound)

Following general procedure 2.2, **4b** was obtained as yellow oil (152.9 mg, 65% yield). Purification: flash chromatography was used with a gradient of 1 → 2% methanol in dichloromethane.



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30-7.11 (m, 10 H), 6.67 (d, *J* = 23.2 Hz, 1H), 6.46 (dd, *J* = 16.5 Hz, *J* = 5.5 Hz, 1H), 6.12 (dd, J_1 = 16.5 Hz, J_2 = 7.0 Hz, 1 H), 4.68-4.50 (m, 4H), 4.20 (dm, *J* = 12.5 Hz, 1H), 2.46-2.44 (m, 1H), 2.38-2.34 (m, 2H), 2.26-2.20 (m, 1H), 1.31-1.26 (m, 12H), 1.22-1.20 (m, 6H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.02 (d, *J* = 6.2 Hz, 3H);

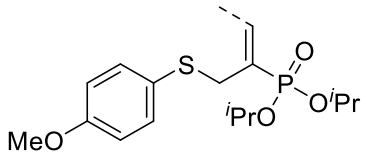
^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.4 (dd, J_1 = J_2 = 9.5 Hz), 134.0 (d, *J* = 5.5 Hz), 137.4 (d, *J* = 4.4 Hz), 131.7 (d, *J* = 11.0 Hz), 130.8, 128.8 (d, *J* = 183.8 Hz), 128.5, 127.9, 127.5, 127.2, 126.4 (d, *J* = 8.8 Hz), 126.2 (d, *J* = 2.2 Hz), 71.3 (d, *J* = 8.8 Hz), 71.0 (d, *J* = 7.7 Hz), 70.3 (d, *J* = 5.5 Hz), 71.29 (d, *J* = 6.6Hz), 47.8 (dd, J_1 = 17.6 Hz, J_2 = 3.3 Hz), 43.8 (d, *J* = 140.9 Hz), 25.5 (dd, J_1 = 11.0 Hz, J_2 = 3.3 Hz), 24.4 (d, *J* = 3.3 Hz), 24.3 (d, *J* = 3.3 Hz), 24.2 (d, *J* = 4.4 Hz), 24.1 (d, *J* = 4.4 Hz), 23.9 (d, *J* = 5.5 Hz), 23.86 (d, *J* = 4.4 Hz), 23.5 (d, *J* = 5.5 Hz), 21.2 (dd, J_1 = J_2 = 7.7 Hz) ;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 26.06, 16.79;

IR (film) υ_{max}: 3053, 2977, 2924, 2865, 2287, 1654, 1638, 1240, 1105, 978, 797 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{46}O_6P_2^+H$ 589.2842; found 589.2841.

Diisopropyl (1-((4-methoxyphenyl)thio)but-2-en-2-yl)phosphonate (5a, new compound)



Following general procedure 2.3, **5a** (*E*/*Z* = 71:29) was obtained as yellow oil (109.6 mg, 51% yield). Purification: flash chromatography was used with a gradient of 10→50% EtOAc in petroleum ether. For full characterization, see (*E*)-**5a** and (*Z*)-**5a**.

(*E*)-diisopropyl(1-((4-methoxyphenyl)thio)but-2-en-2-yl)phosphonate ((*E*)-5a)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 (d, *J* = 17.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.71 (dq, J_1 = 22.4 Hz, J_2 = 7.0 Hz, 1H), 4.69-4.63 (m, 2H), 3.78 (s, 3H), 3.63 (d, *J* = 18.1 Hz, 2H), 1.59 (dd, J_1 = 7.0 Hz, J_2 = 3.3 Hz, 3H), 1.34 (d, *J* = 6.1 Hz, 6H), 1.30 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.5, 144.8 (d, *J* = 10.9 Hz), 134.8, 127.8 (d, *J* = 185.8 Hz), 126.7, 114.6, 70.6 (d, *J* = 5.7 Hz), 55.4, 33.1 (d, *J* = 12.1 Hz), 24.2 (d, *J* = 3.4 Hz), 24.1 (d, *J* = 4.8 Hz), 14.7 (d, *J* = 19.7 Hz) ;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 17.50;

IR (film) υ_{max}: 3054, 2967, 2857, 2373, 1655, 1157, 1100, 1023, 907 cm^{-1};

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{27}O_4P^+H$ 359.1440; found 359.1443.

(*Z*)-diisopropyl (1-((4-methoxyphenyl)thio)but-2-en-2-yl)phosphonate ((*Z*)-5a)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 (d, *J* = 9.2 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.02 (dq, J_1 = 47.3 Hz, J_2 = 7.0 Hz, 1H), 4.74-4.69 (m, 2H), 3.78 (s, 3H), 3.58 (d, *J* = 14.3 Hz, 2H), 1.92 (dd, J_1 = 7.3 Hz, J_2 = 3.7 Hz, 3H), 1.34 (d, *J* = 6.2 Hz, 6H), 1.29 (d, *J* = 6.2 Hz, 6H);

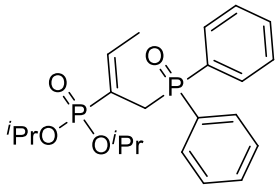
^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.4, 144.0 (d, *J* = 10.1 Hz), 134.7, 127.2 (d, *J* = 177.5 Hz), 126.0, 114.4, 70.4 (d, *J* = 5.6 Hz), 55.4, 41.2 (d, *J* = 14.4 Hz), 24.3 (d, *J* = 3.4 Hz), 24.0 (d, *J* = 4.7 Hz), 16.7 (d, *J* = 7.3 Hz) ;

^{31}P NMR ($CDCl_3$, 202 MHz): δ 15.46;

IR (film) υ_{max}: 3055, 2977, 2932, 2355, 1660, 1245, 1105, 1068, 977 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{27}O_4P^+Na$ 381.1260, found 381.1262.

(E)-diisopropyl (1-(diphenylphosphoryl)but-2-en-2-yl)phosphonate (5b, new compound)



Following general procedure 2.3, **5b** was obtained as yellow oil (194.0 mg, 77% yield). Purification: flash chromatography was used with a gradient of 2 → 4% methanol in dichloromethane.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.85-7.82 (m, 4H), 7.50-7.43 (m, 6H), 6.76 (dm, J = 22.3 Hz, 1H), 4.43-4.38 (m, 2H), 4.46 (dd, J_1 = J_2 = 22.3 Hz, 2H), 1.84-1.82 (m, 3H), 1.16 (d, J = 6.2 Hz, 6H), 1.08 (d, J = 6.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.2 (dd, J_1 = J_2 = 8.9 Hz), 133.3 (d, J = 98.9 Hz), 131.8 (d, J = 2.5 Hz), 131.4 (d, J = 9.6 Hz), 128.5 (d, J = 11.5 Hz), 122.7 (dd, J_1 = 188.3 Hz, J_2 = 9.1 Hz), 70.5 (d, J = 5.7 Hz), 30.3 (dd, J_1 = 67.1 Hz, J_2 = 12.7 Hz), 24.0 (d, J = 3.4 Hz), 23.8 (d, J = 4.8 Hz), 16.4 (dd, J_1 = 19.9 Hz, J_2 = 3.1 Hz);

^{31}P NMR ($CDCl_3$, 202 MHz): δ 29.09 (d, J = 8.7 Hz), 17.76 (d, J = 8.7 Hz);

IR (film) υ_{max}: 3055, 2978, 2928, 2354, 1630, 1438, 1105, 1065, 981 cm^{-1};

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{30}O_4P^+Na$ 443.1512; found 443.1512.

6. References

(1) (a) Luo, H.; Ma, S. CuI-Catalyzed Synthesis of Functionalized Terminal Allenes from 1-Alkynes. *Eur. J. Org. Chem.* **2013**, 3041-3048. (b) Petrone, D. A.; Isomura, M.; Franzoni, I.; Rössler, S. L.;Carreira, E. M. Allenylic Carbonates in Enantioselective Iridium-Alkylations. *J. Am. Chem. Soc.* **2018**, *140*, 4697–4704.

(2) Grugel, C. P.; Breit, B. Rhodium-Catalyzed Enantioselective Cyclization of 3-Allenyl-indoles: Access to Functionalized Tetrahydrocarbazoles. *Org. Lett.* **2019**, *21*, 5798–5802.

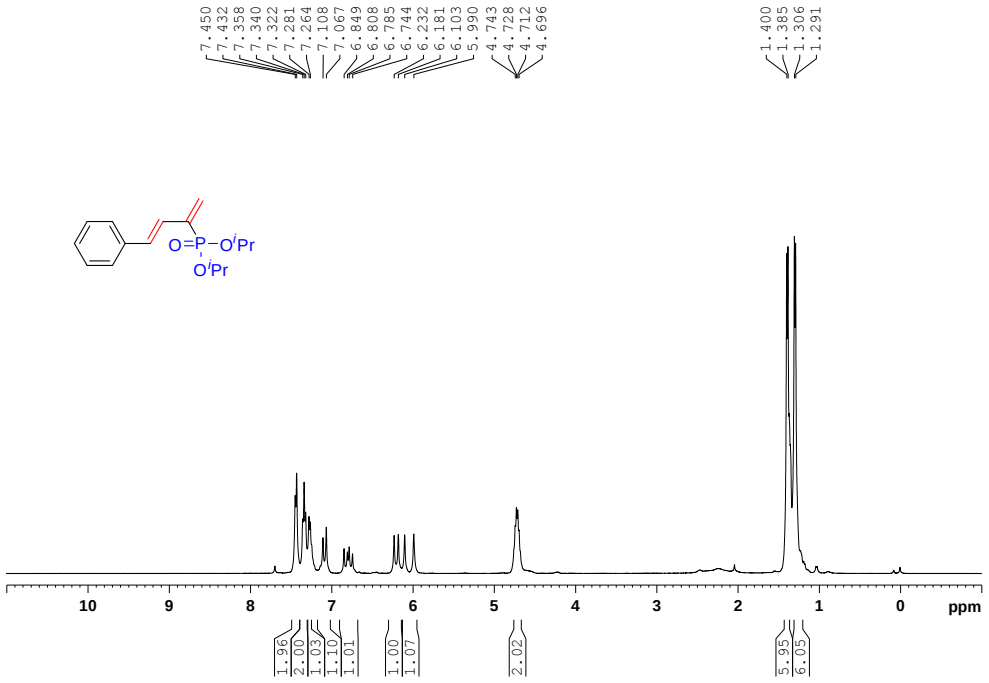
(3) Isomura, M.; Petrone, D. A.; Carreira, E. M. Coordination-Induced Stereocontrol over Carbocations: Asymmetric Reductive Deoxygenation of Racemic Tertiary Alcohols. *J. Am. Chem. Soc.* **2019**, *141*, 4738−4748.

(4) Kuang, J.; Luo, H.; Ma, S. Copper(I) Iodide-Catalyzed One-Step Preparation of Functionalized Allenes from Terminal Alkynes:Amine Effect. *Adv. Synth. Catal.* **2012**, *354*, 933-944.

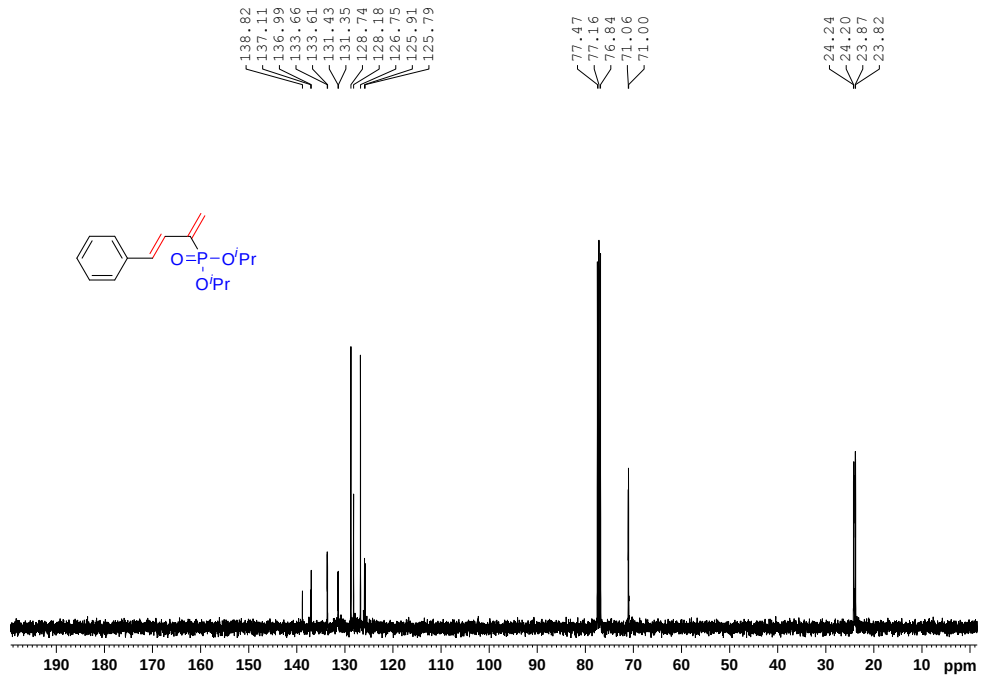
(5) Zhang, J.; Ye, J.; Ma, S. Harmony of CdI 2 with CuBr for the One-pot Synthesis of Optically Active *α*-Allenols. *Org. Biomol. Chem.* **2015**, *13*, 4080.

(6) Kuang J.; Ma, S. One-Pot Synthesis of 1,3-Disubstituted Allenes from 1-Alkynes, Aldehydes, and Morpholine..*J. Am. Chem. Soc.* **2010**, *132*, 1786–1787.

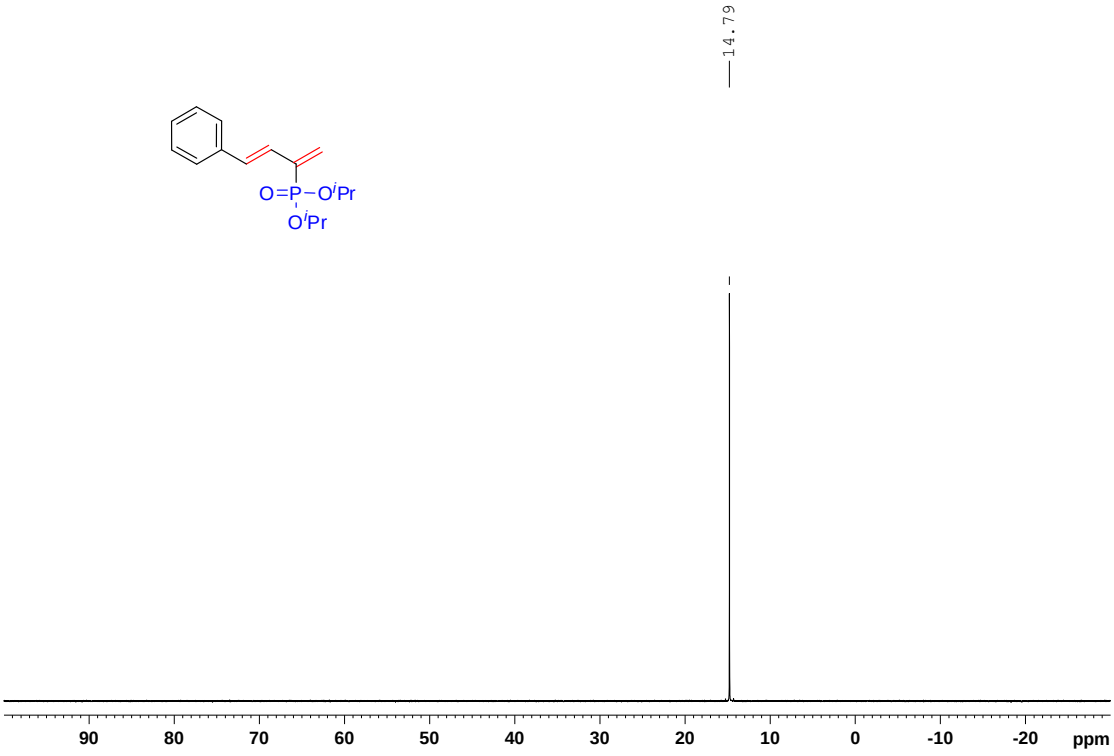
7. NMR spectra of the compounds 3a-3ab



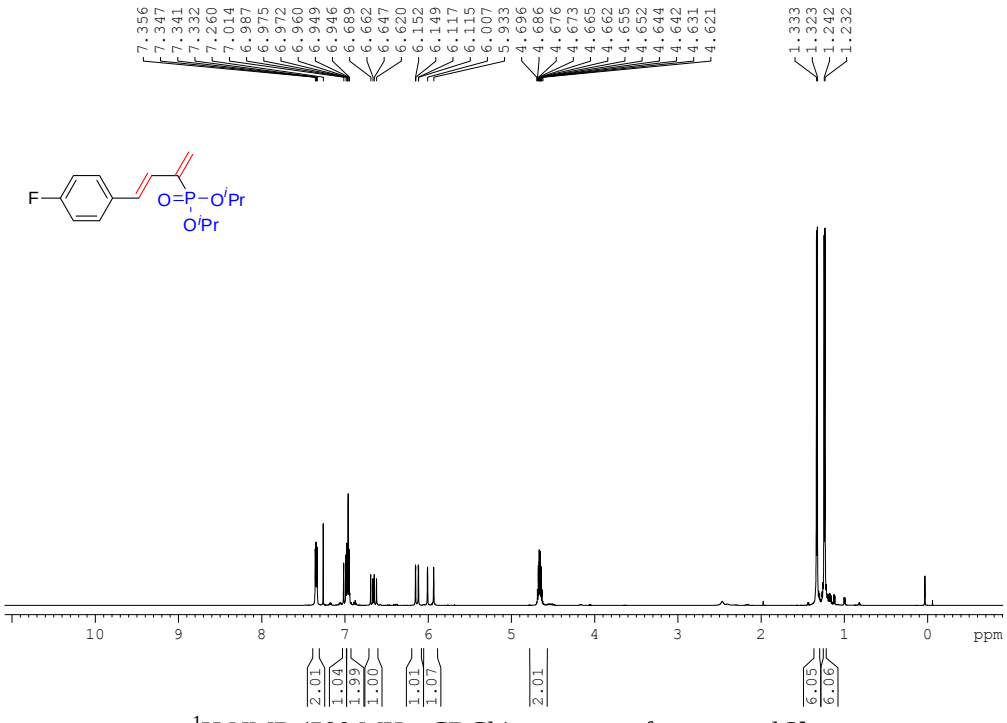
^{1}H NMR (500 MHz, CDCl3) spectrum of compound **3a**



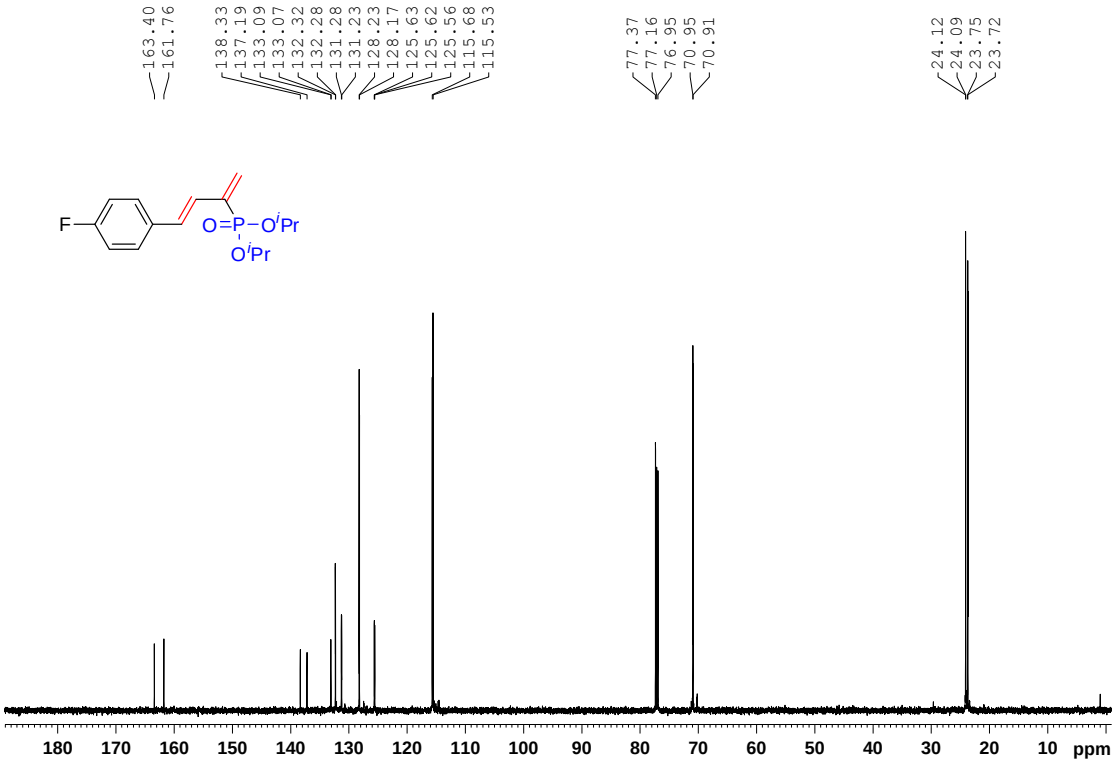
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3a**



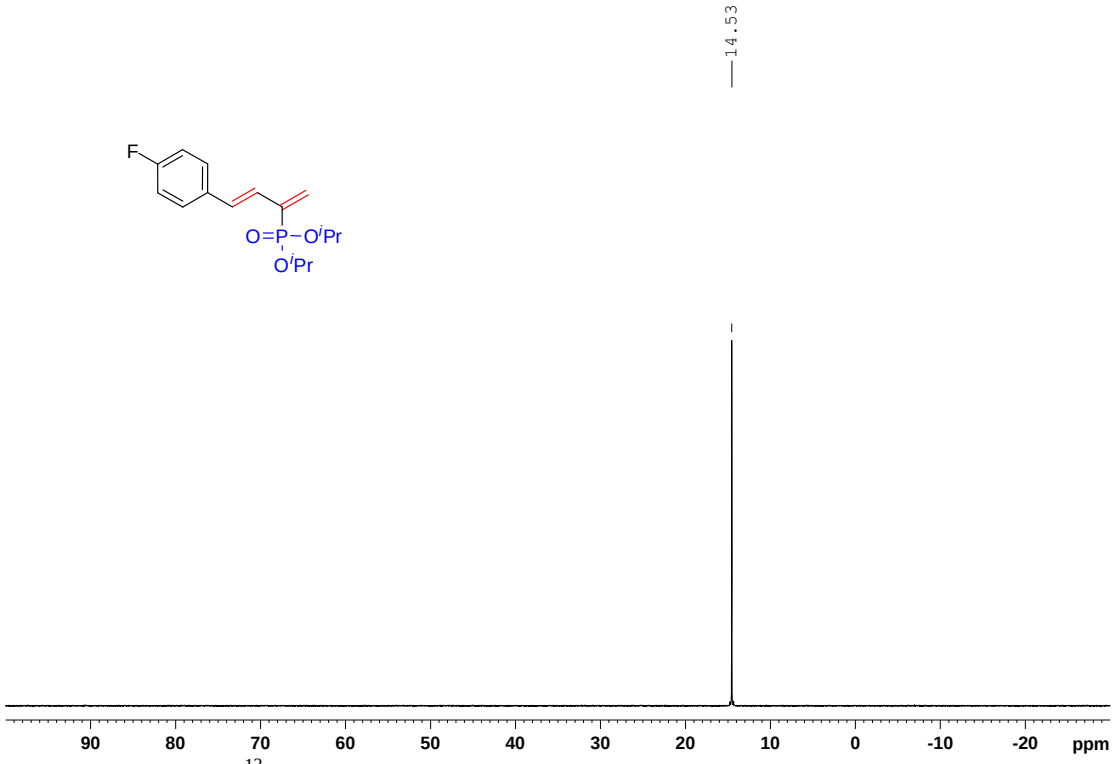
^{13}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3a**



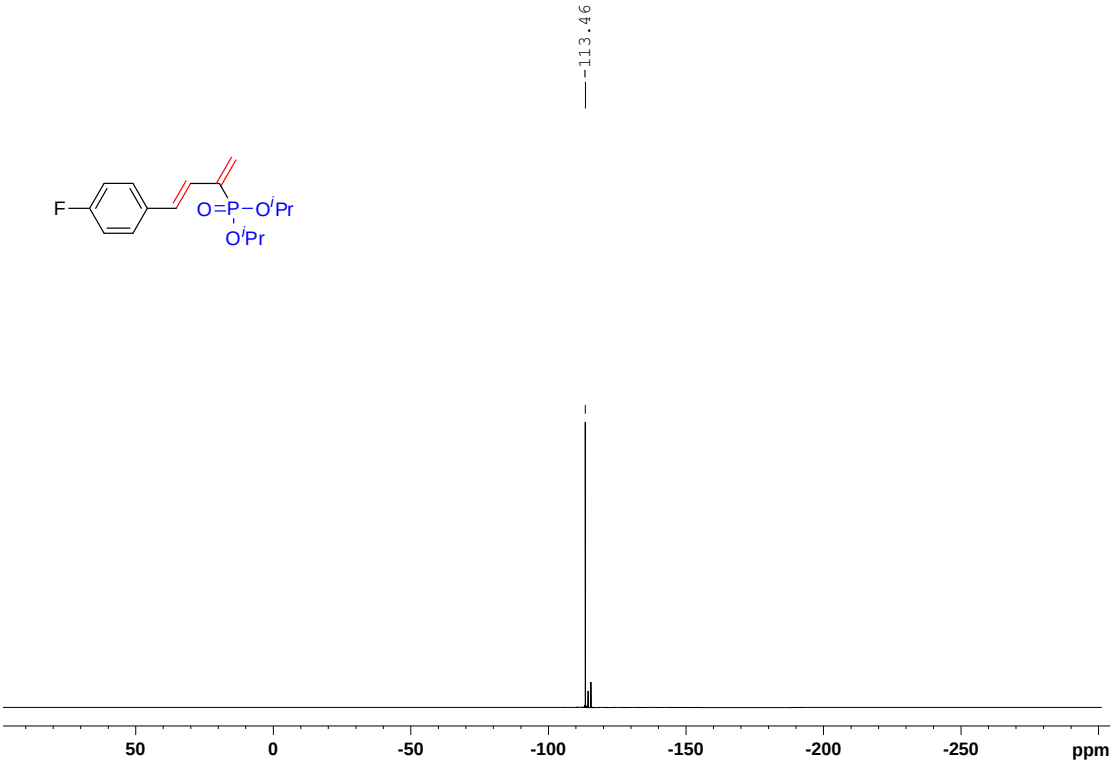
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3b**



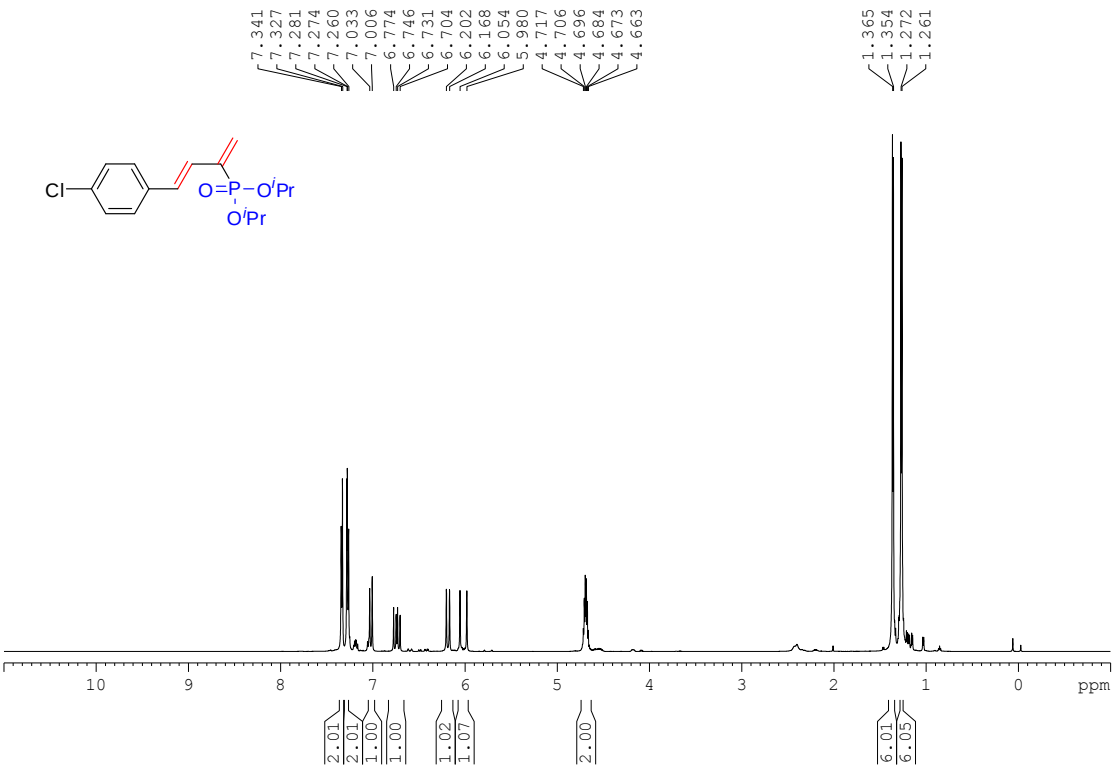
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3b**



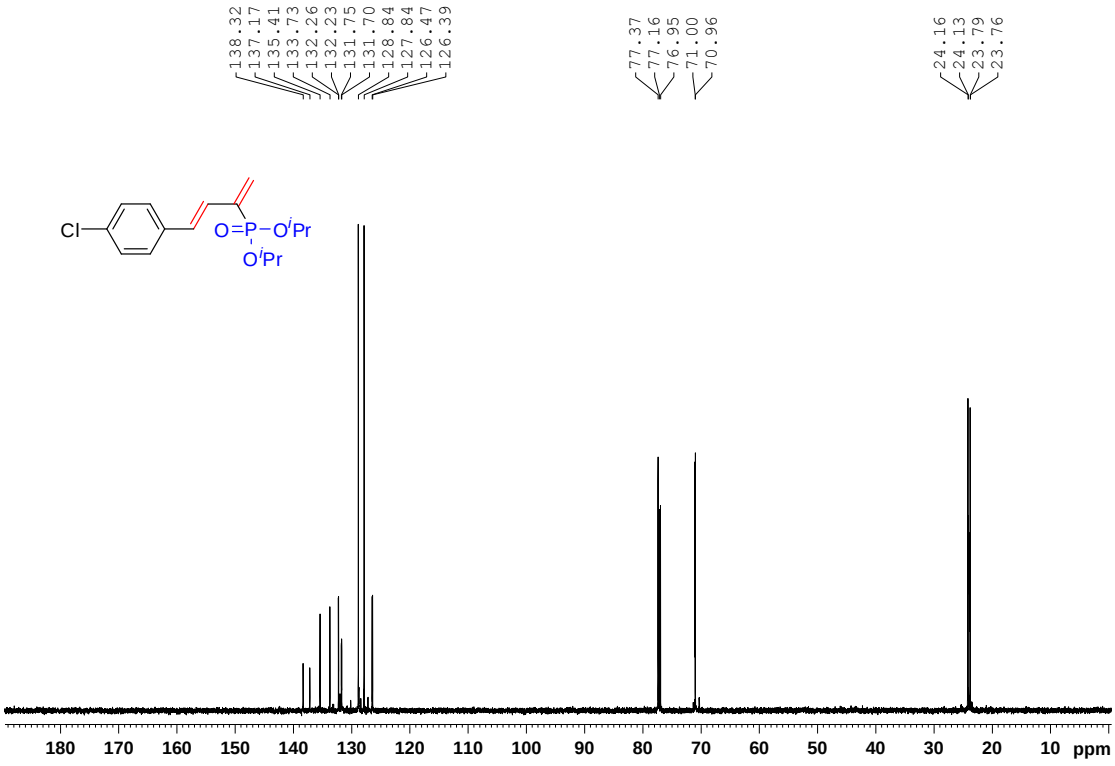
^{13}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3b**



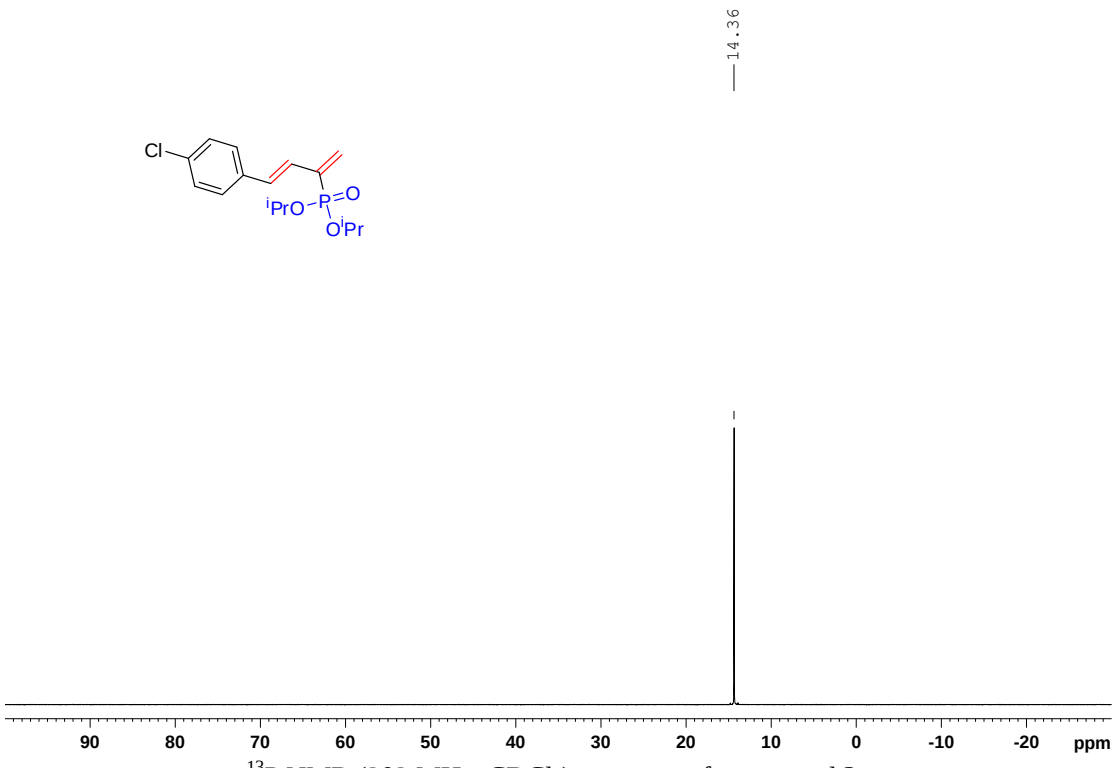
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound **3b**



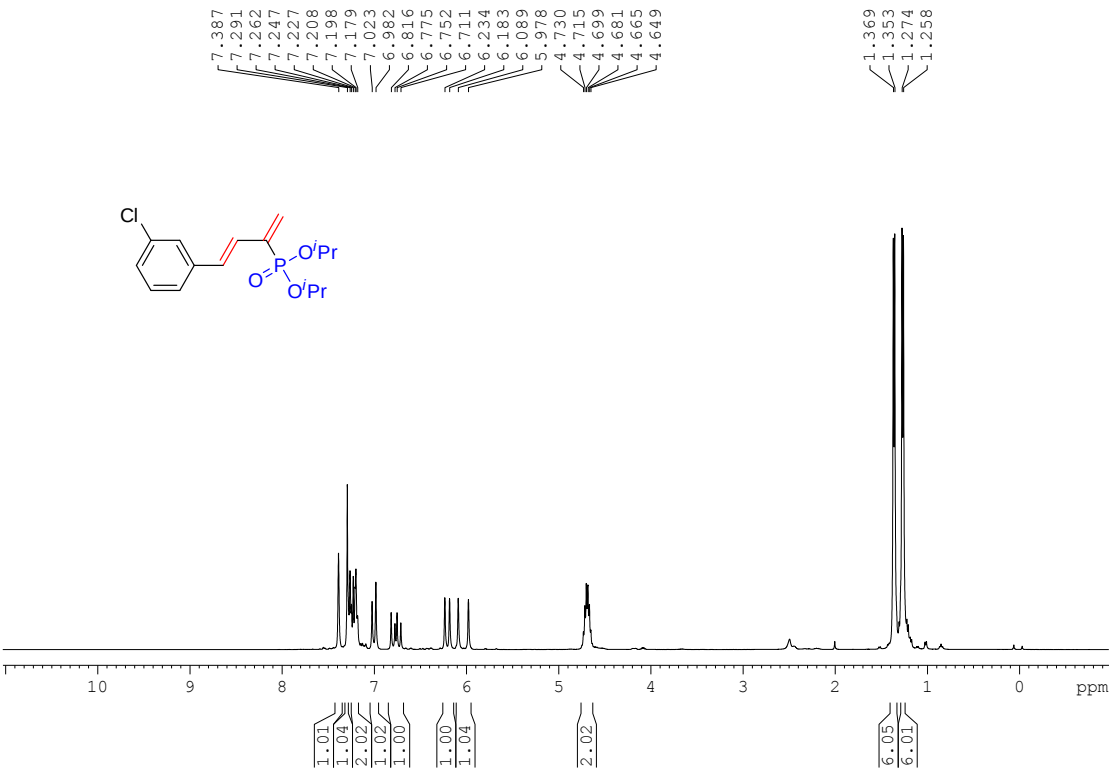
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3c**



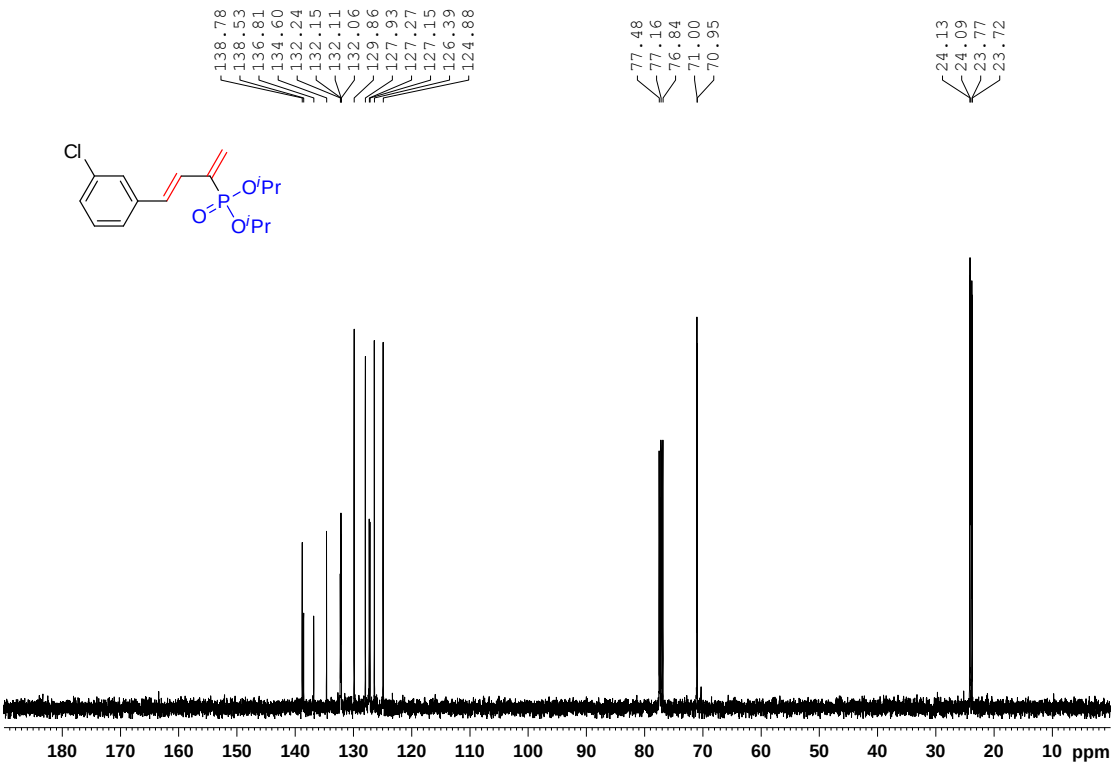
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3c**



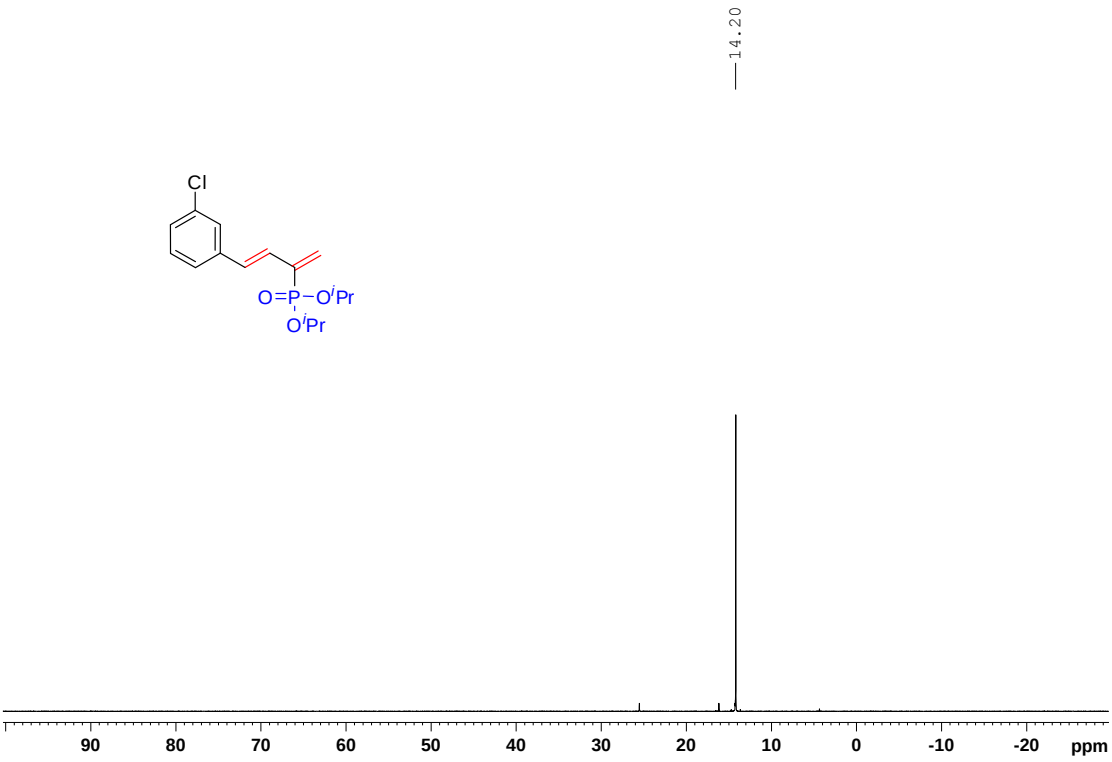
^{13}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3c**



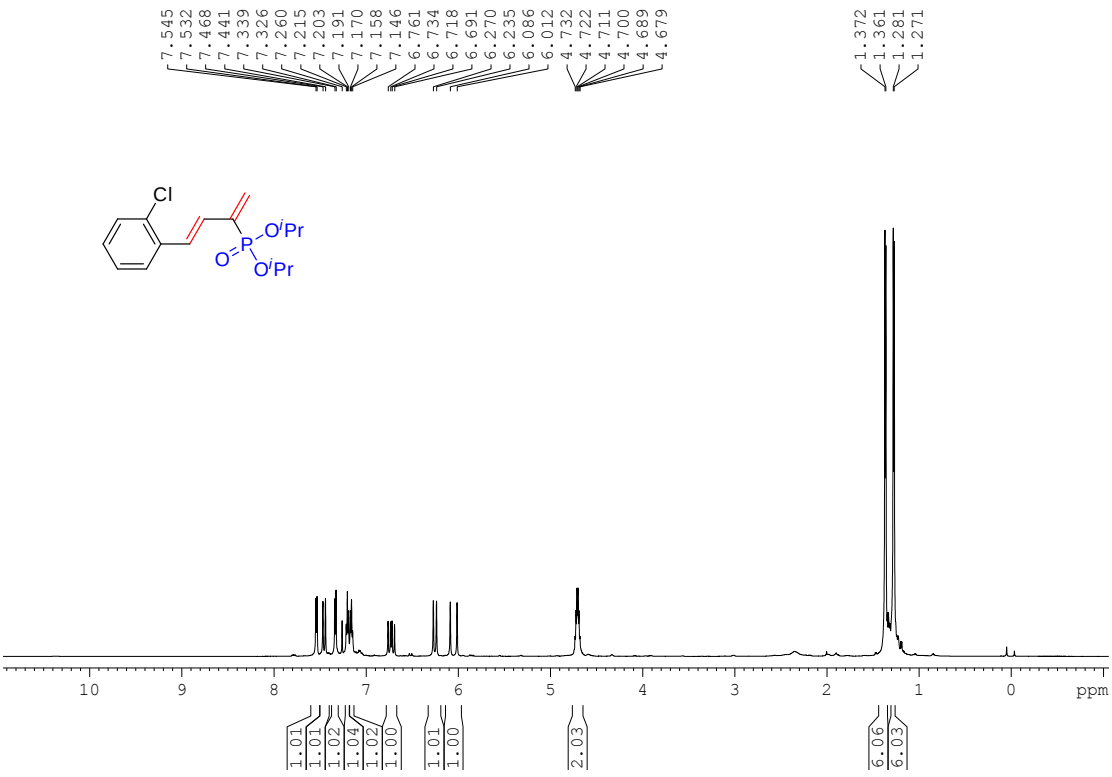
^{1}H NMR (500 MHz, CDCl3) spectrum of compound **3d**



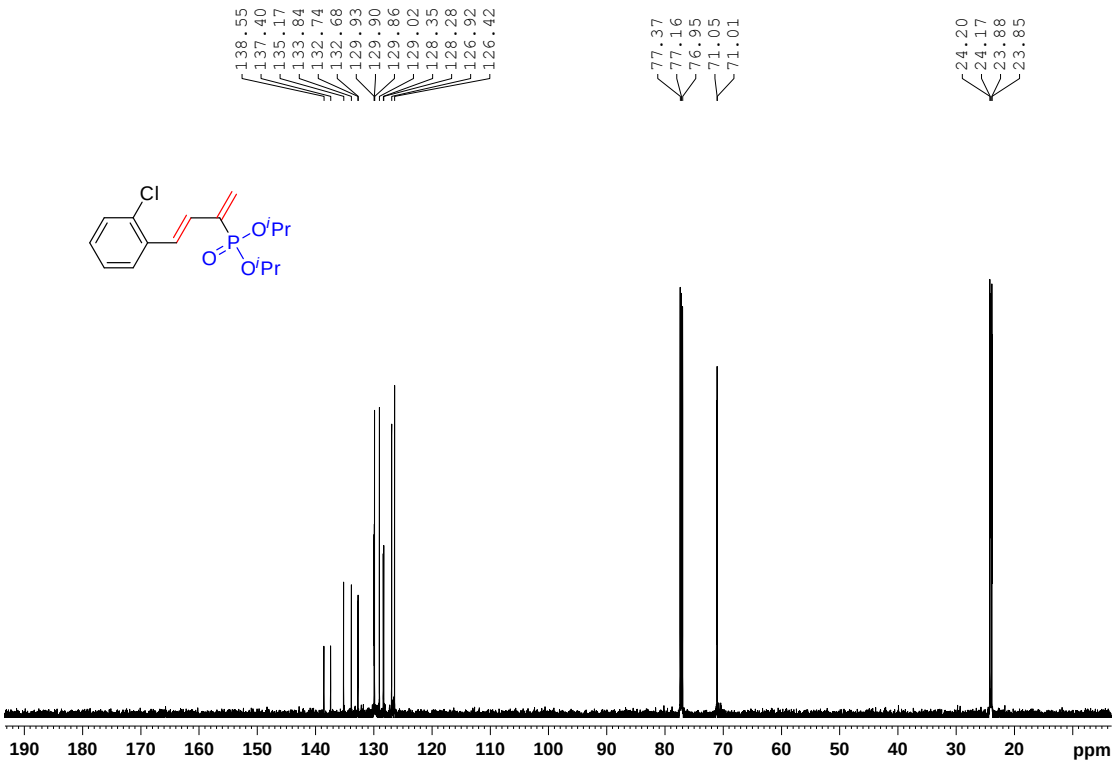
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3d**



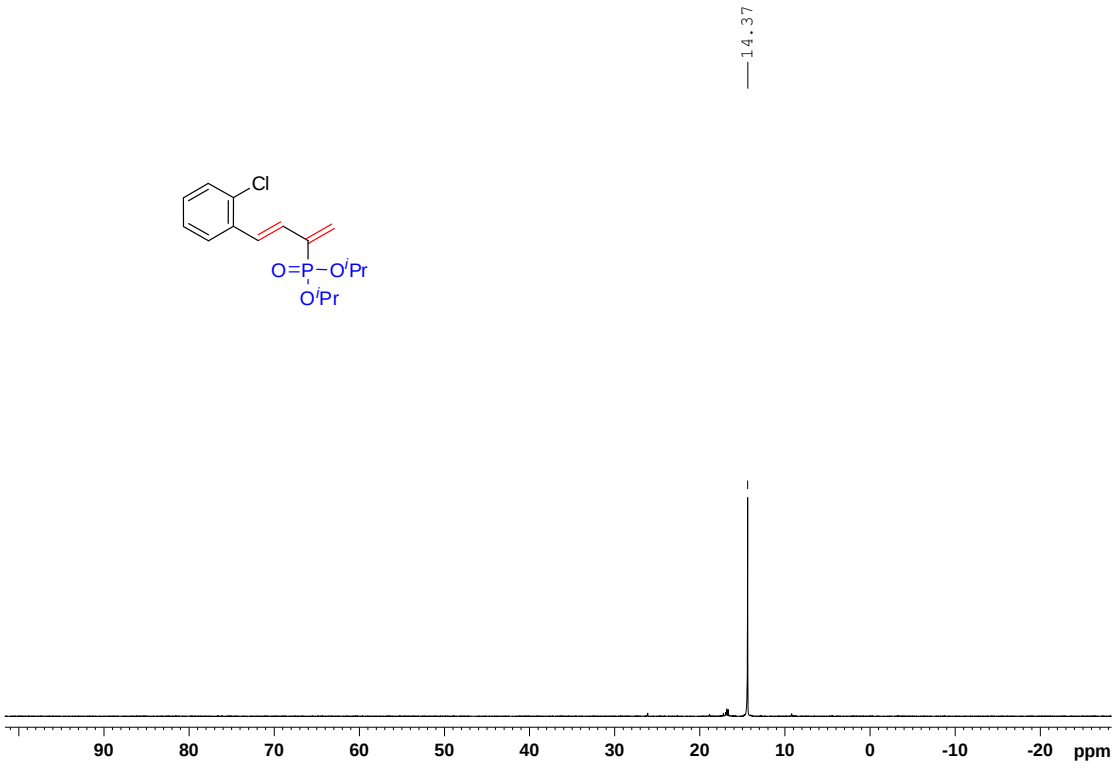
^{13}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3d**



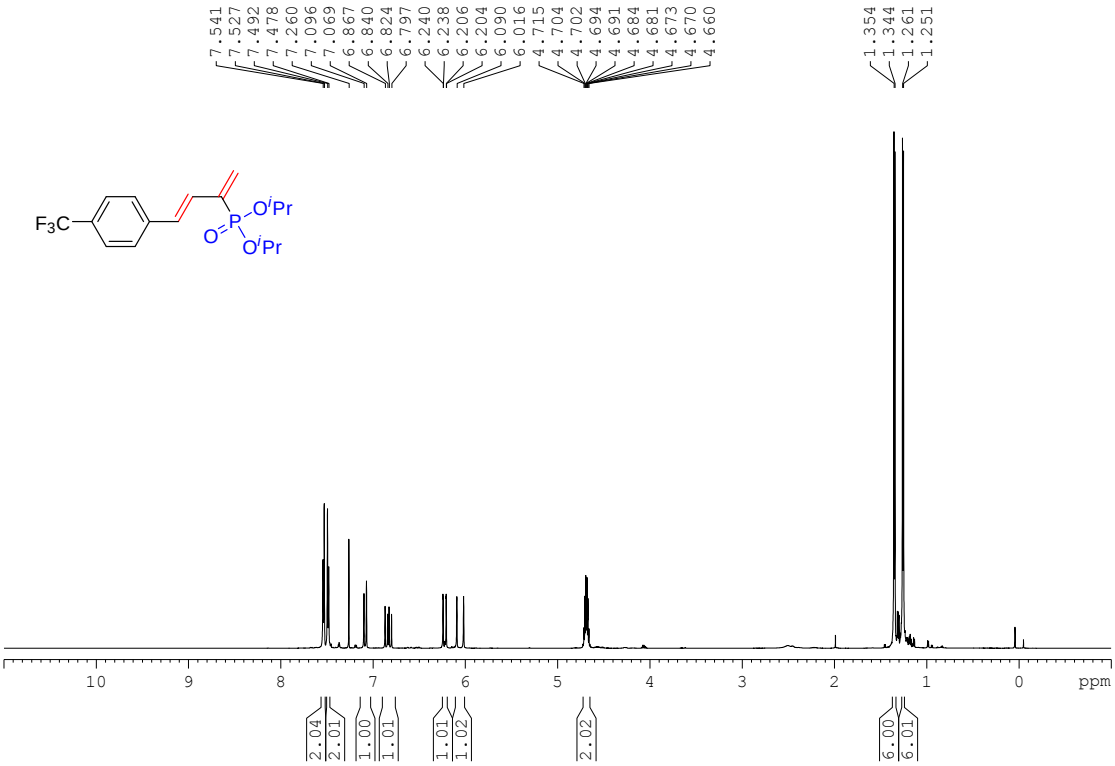
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3e**



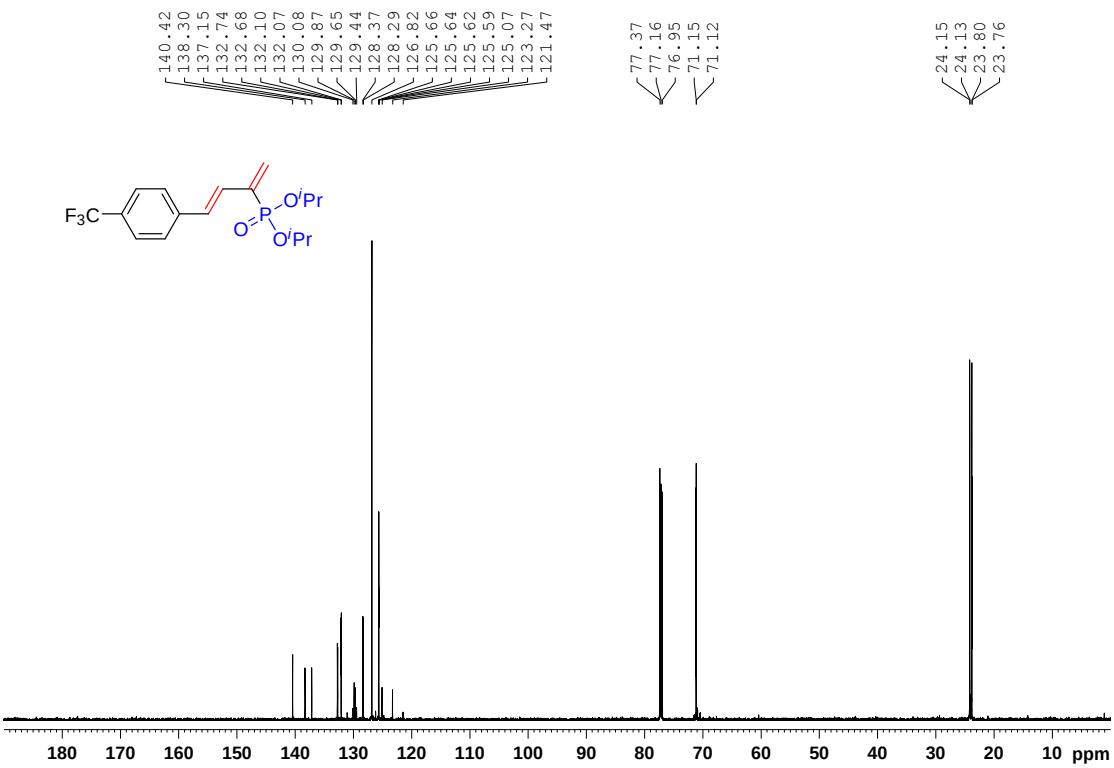
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3e**



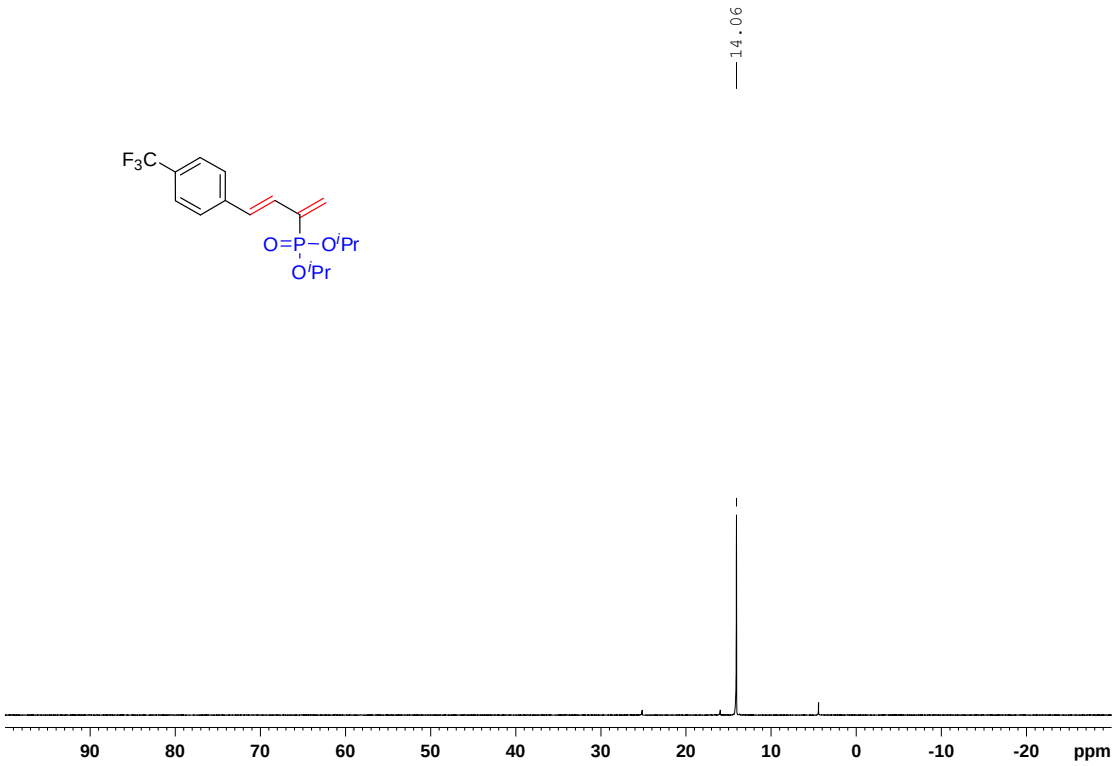
^{13}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3e**



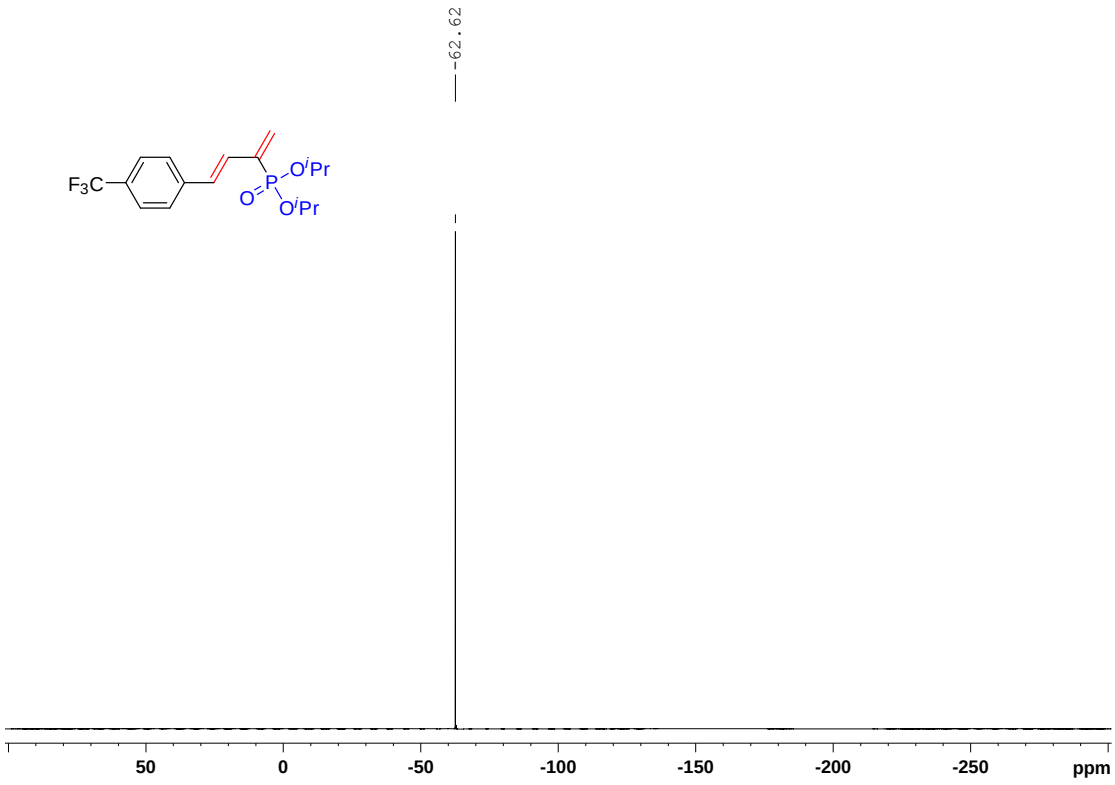
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3f**



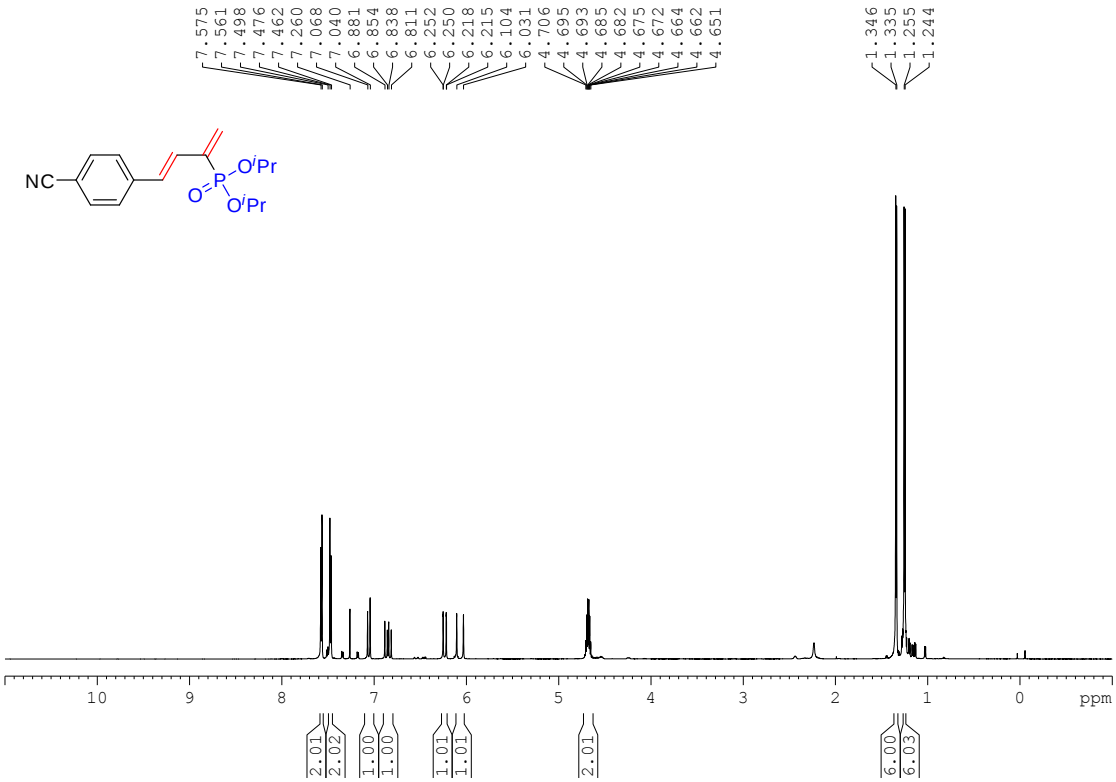
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3f**



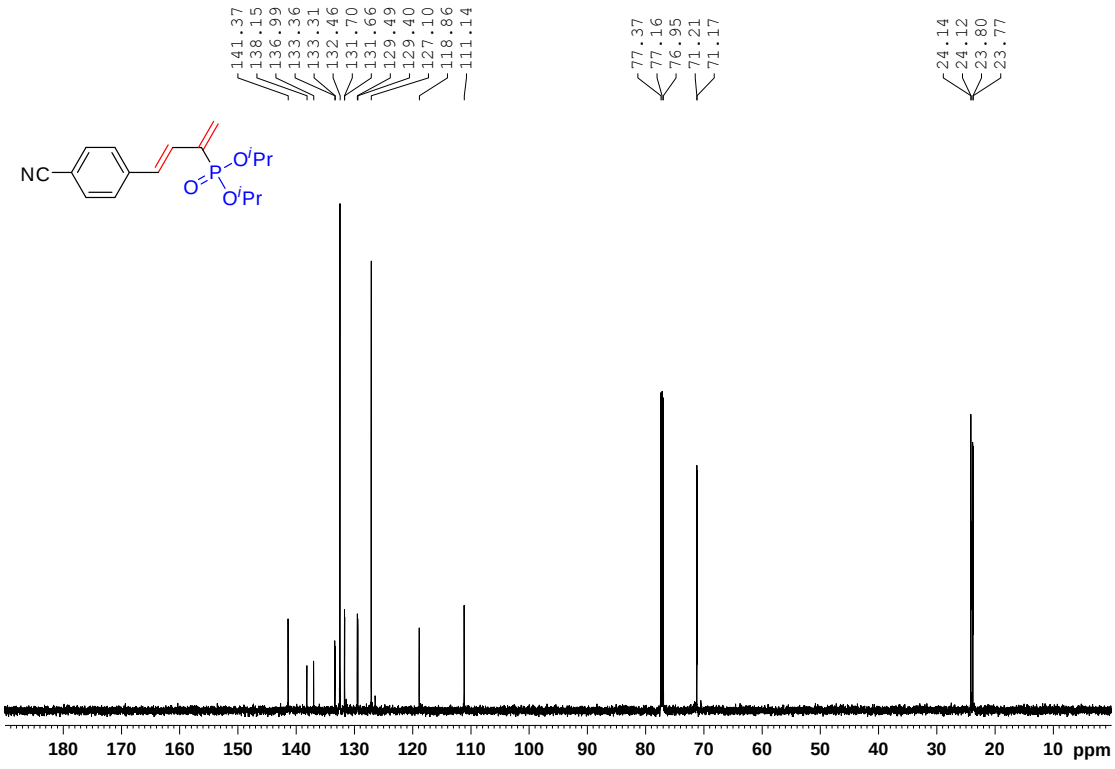
^{13}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3f**



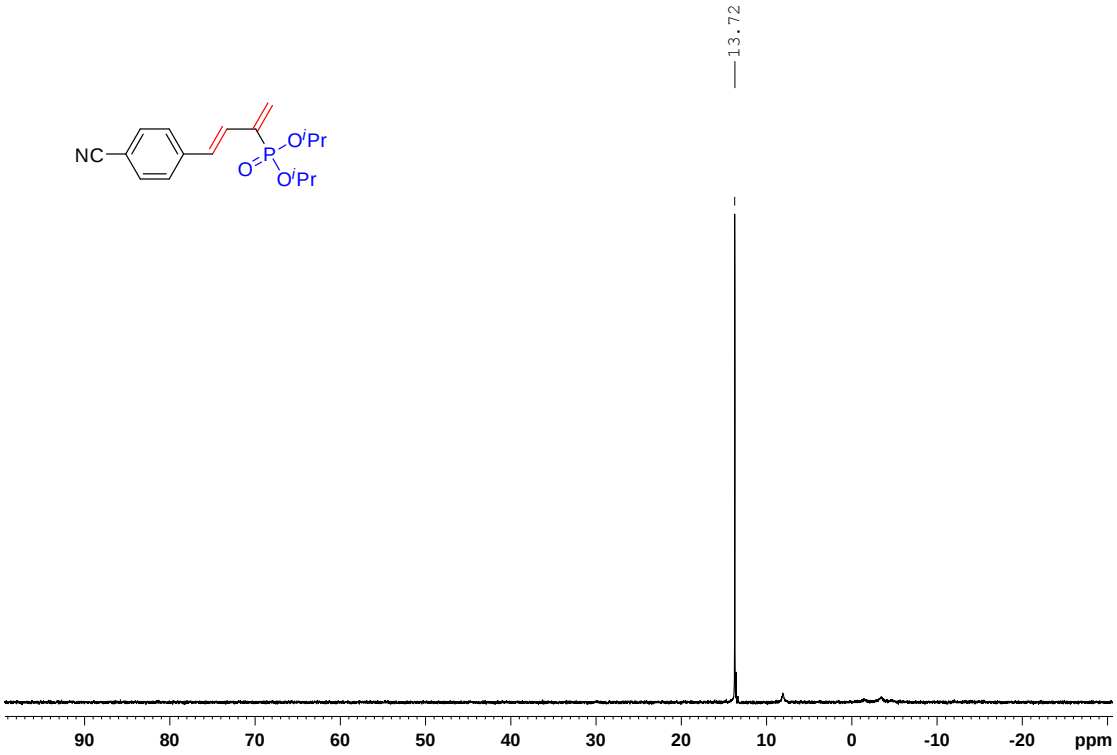
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound **3f**



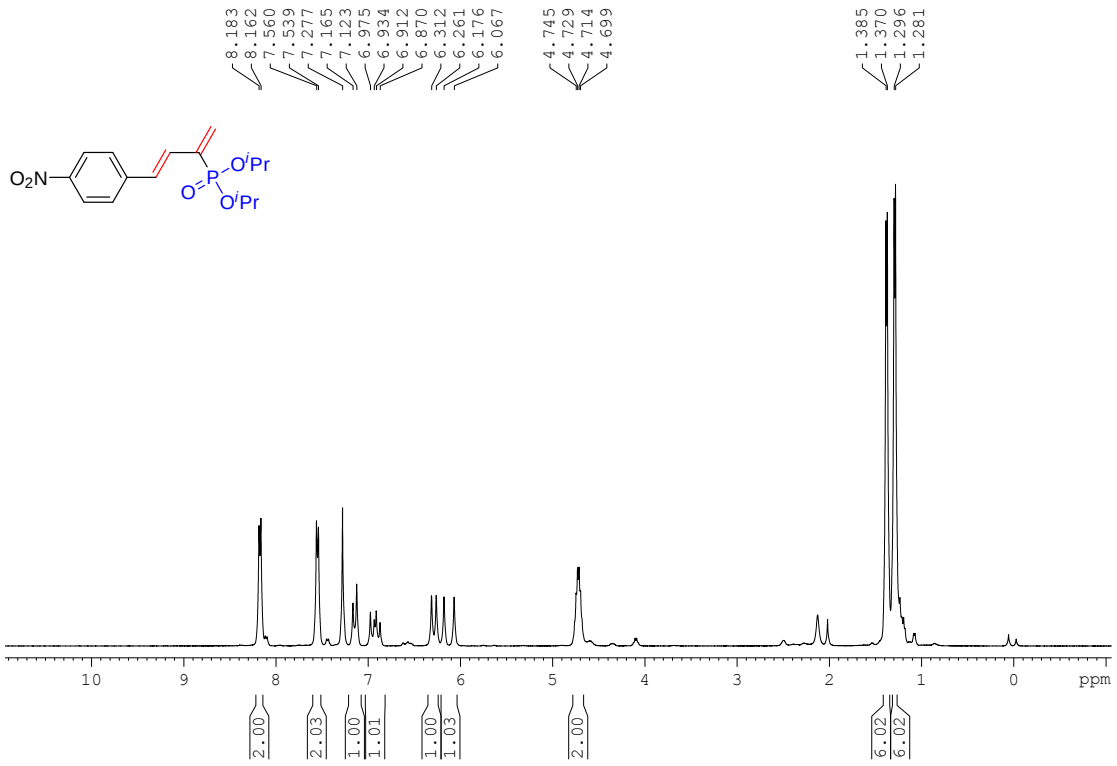
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3g**



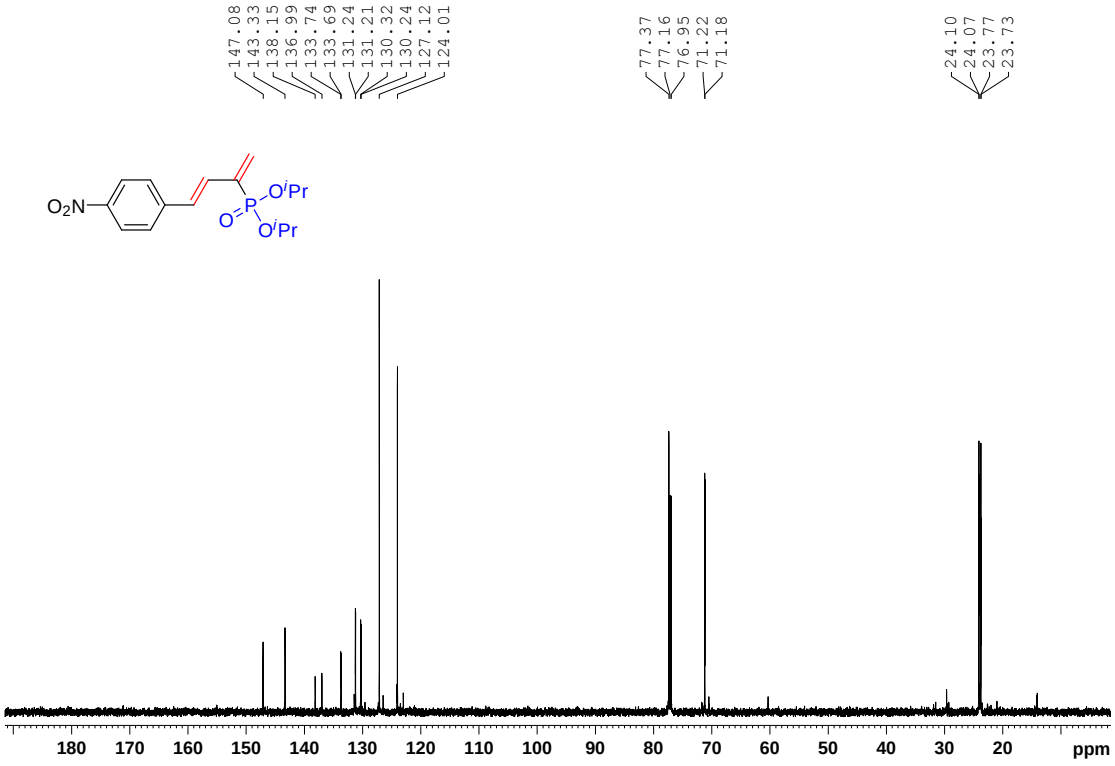
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3g**



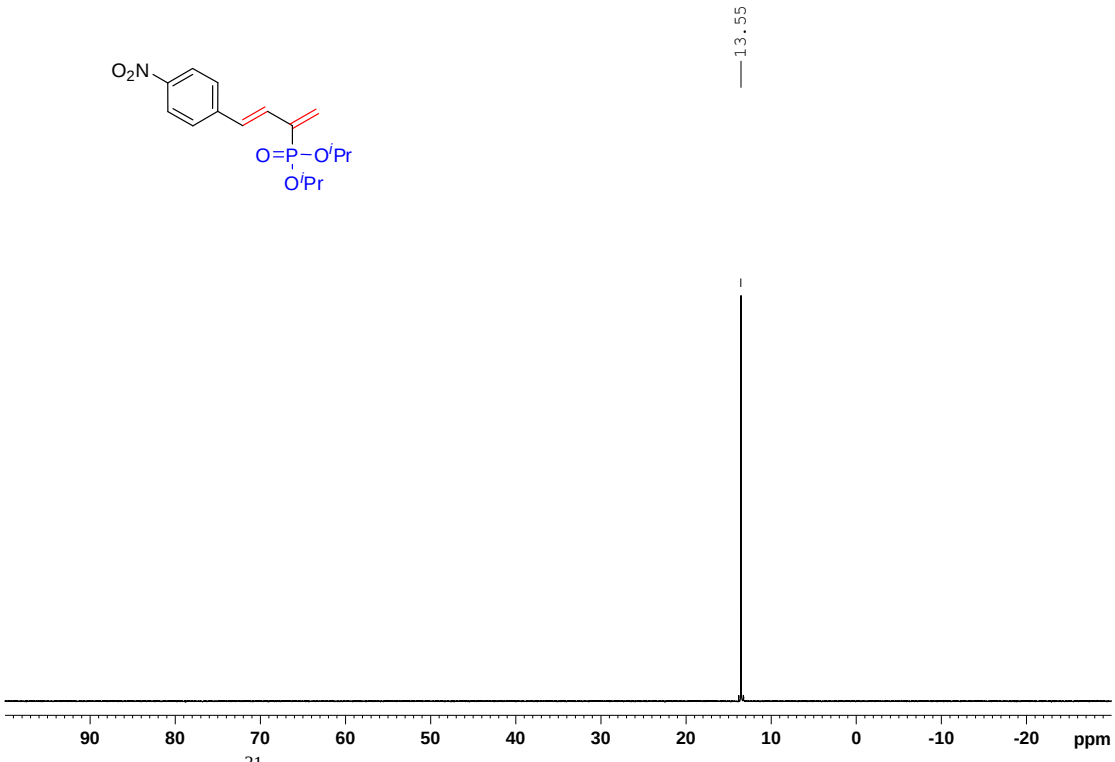
^{13}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3g**



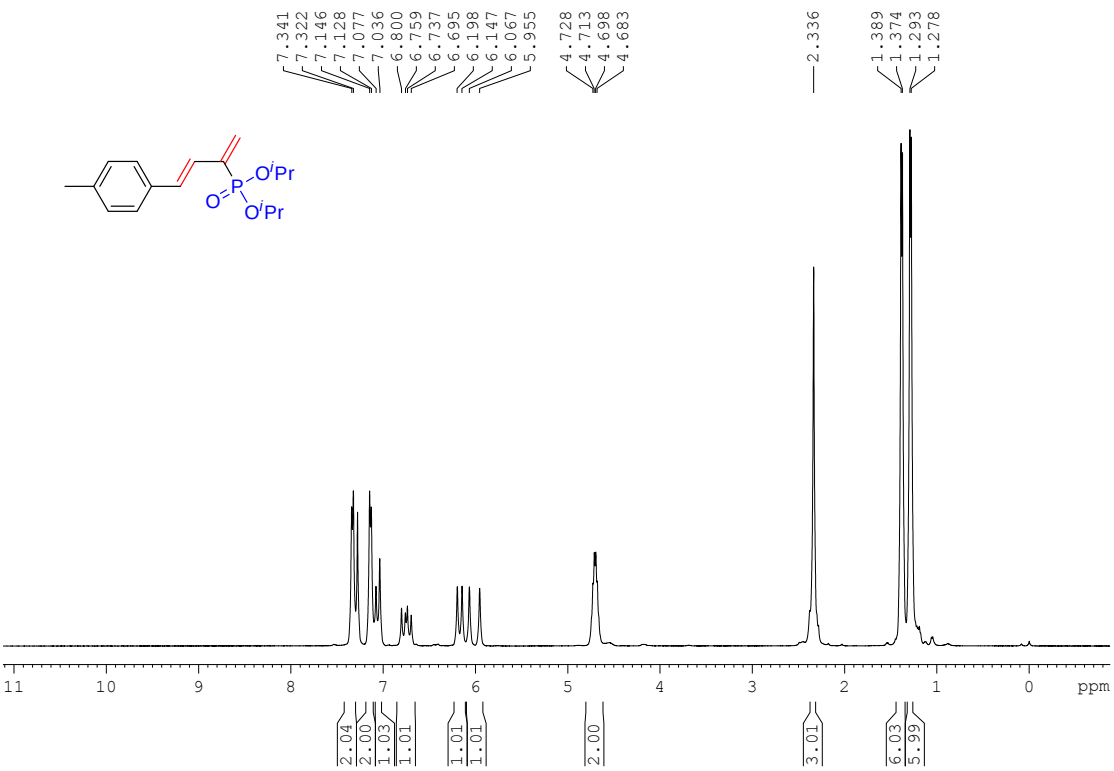
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3h**



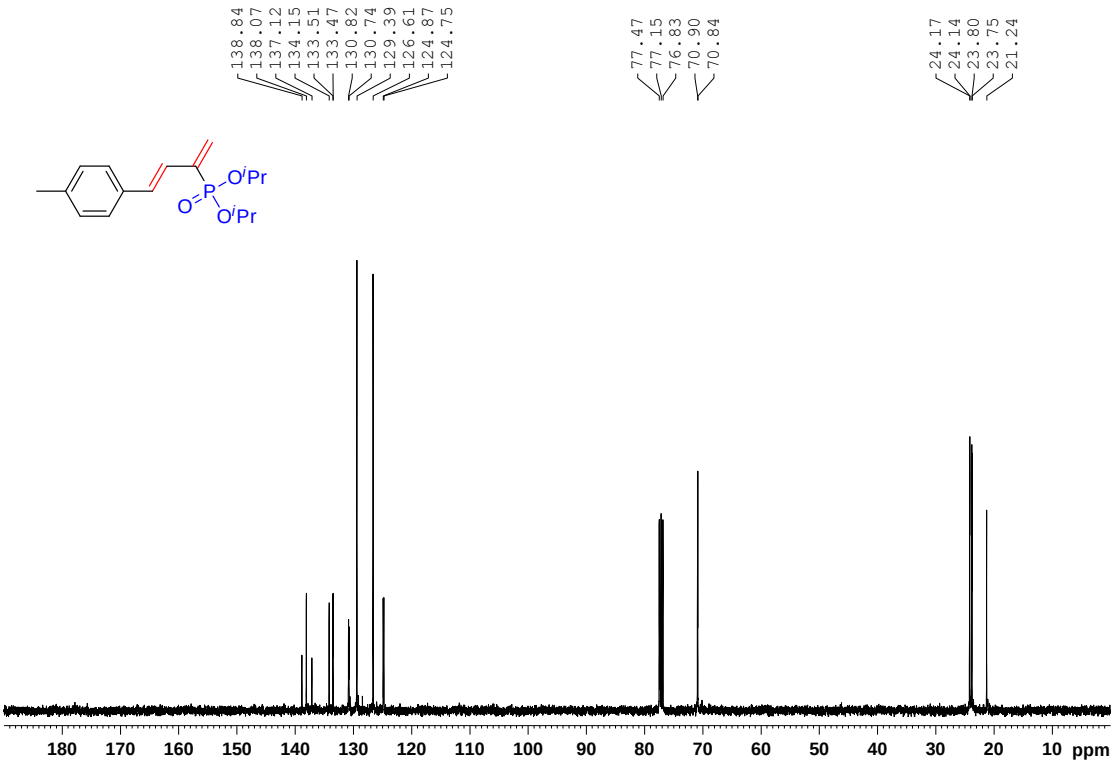
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3h**



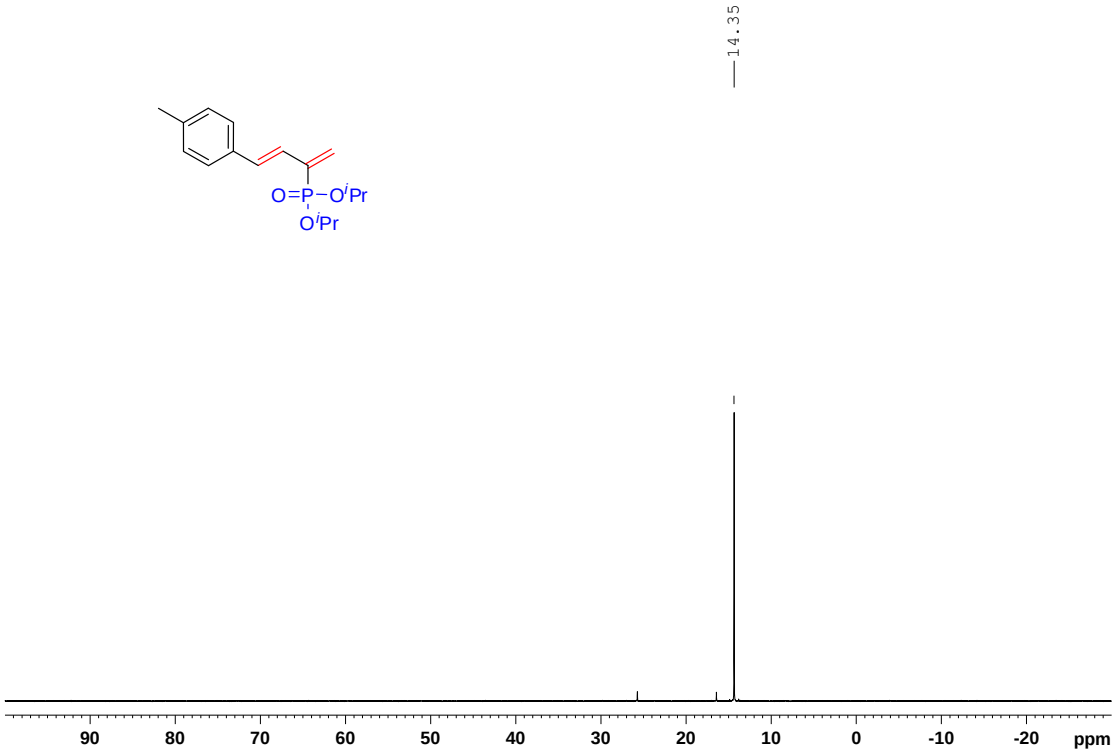
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3h**



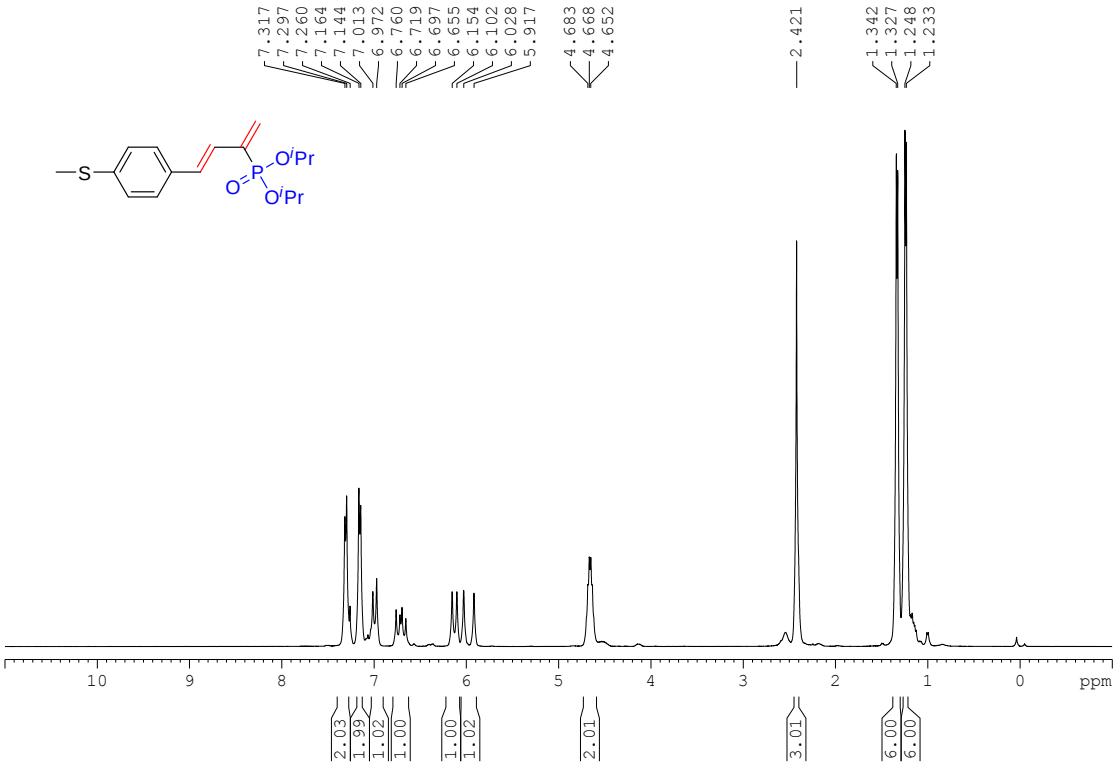
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3i**



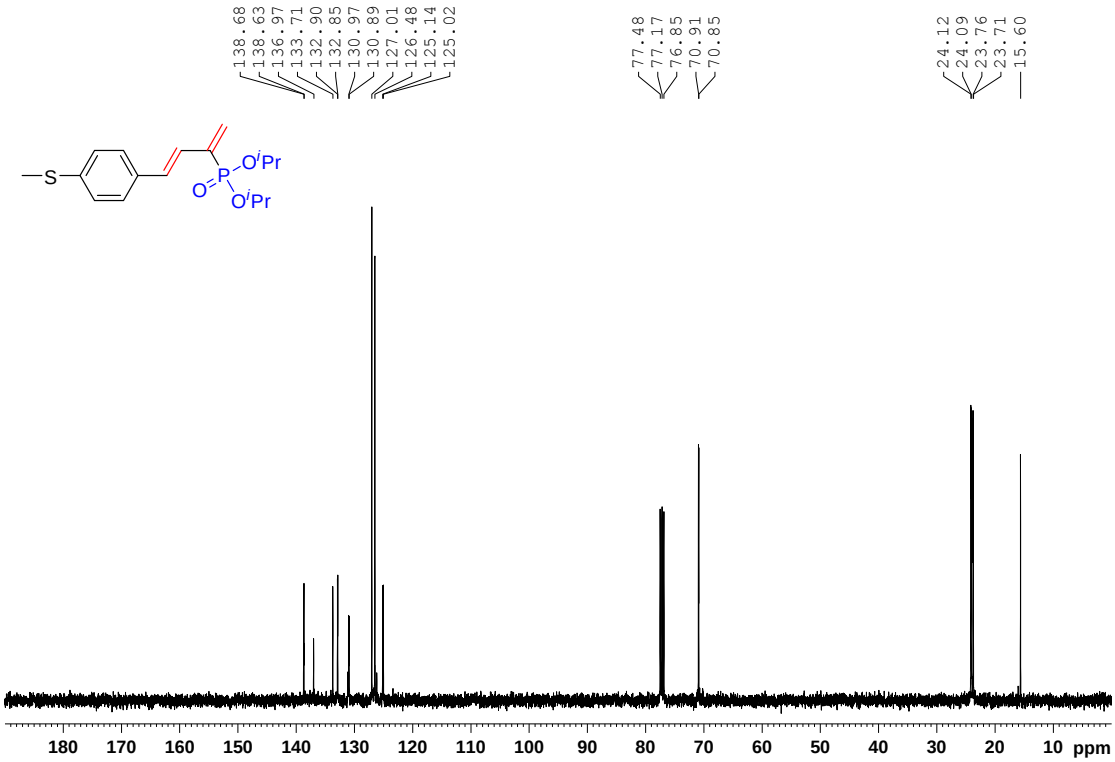
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3i**



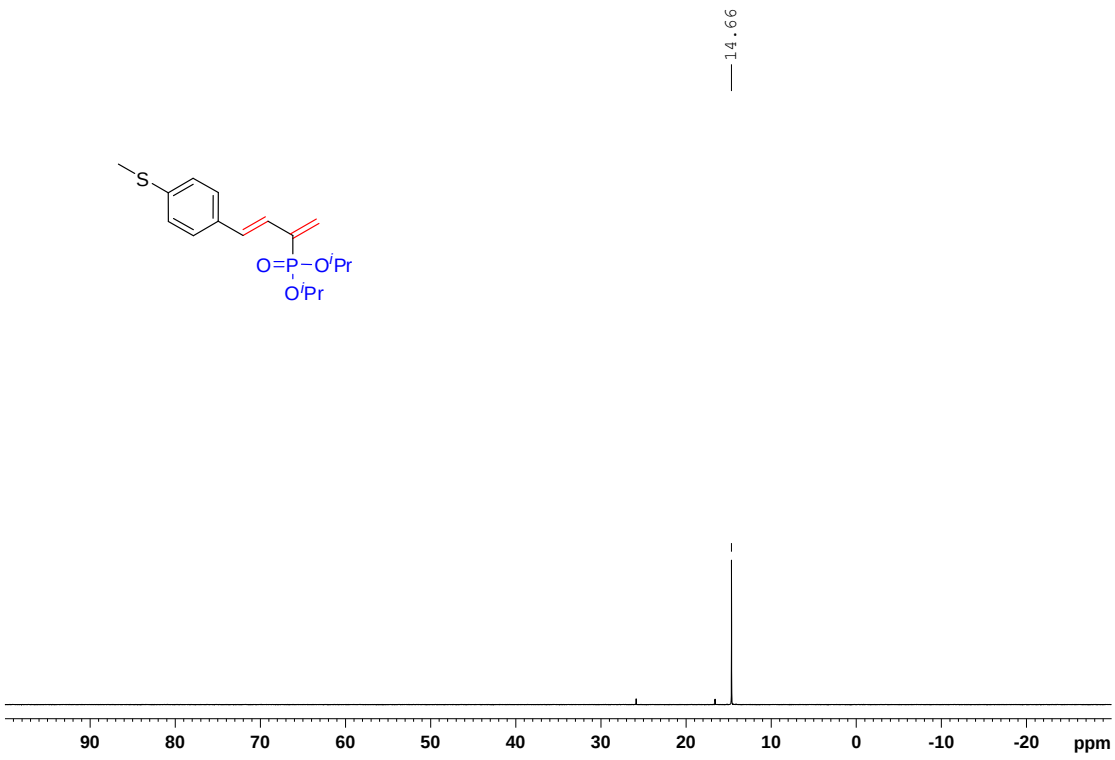
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3i**



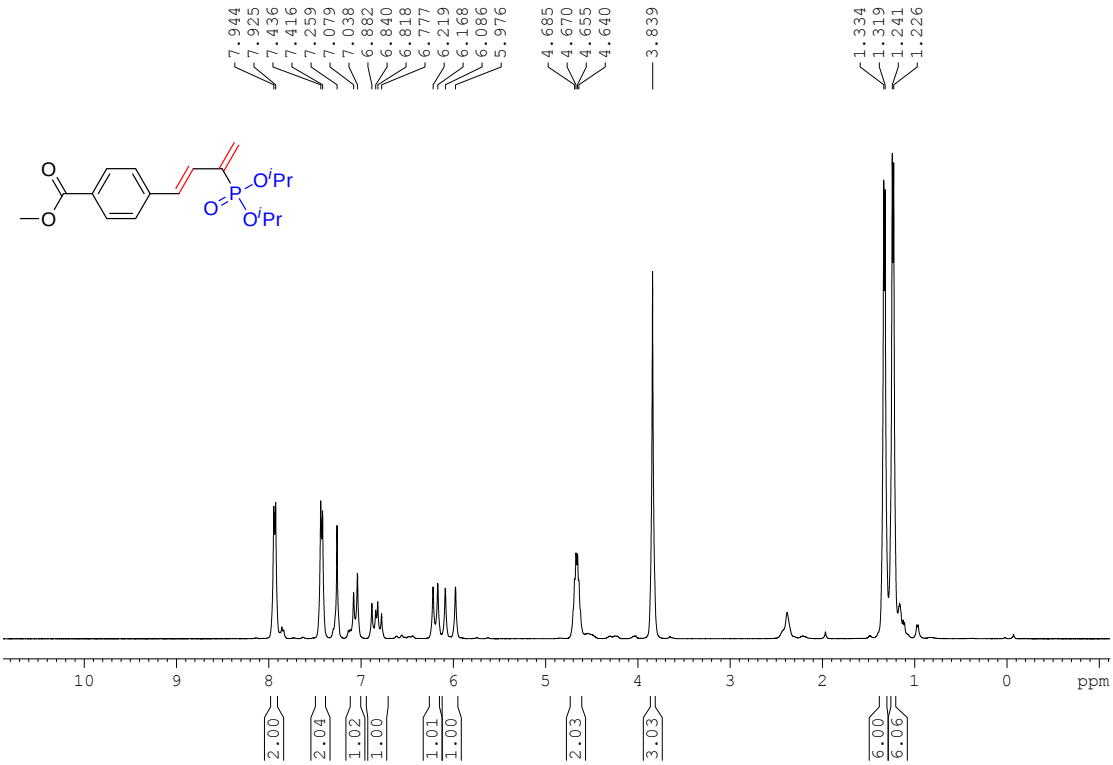
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3j**



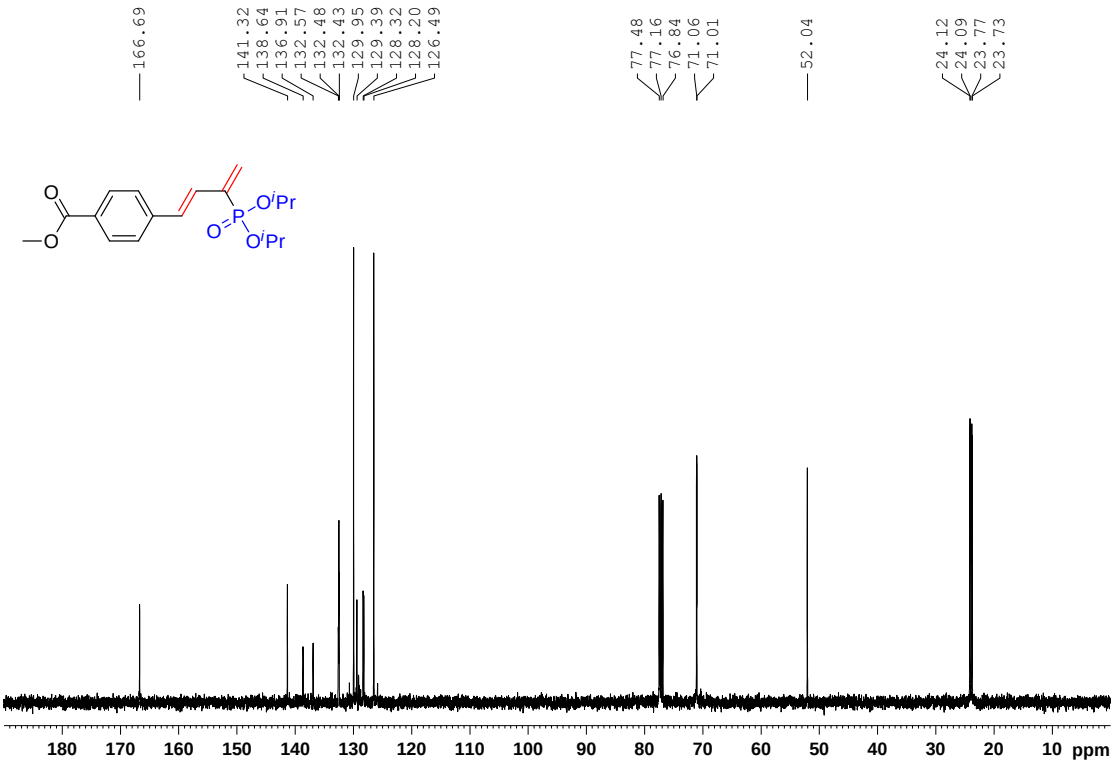
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3j**



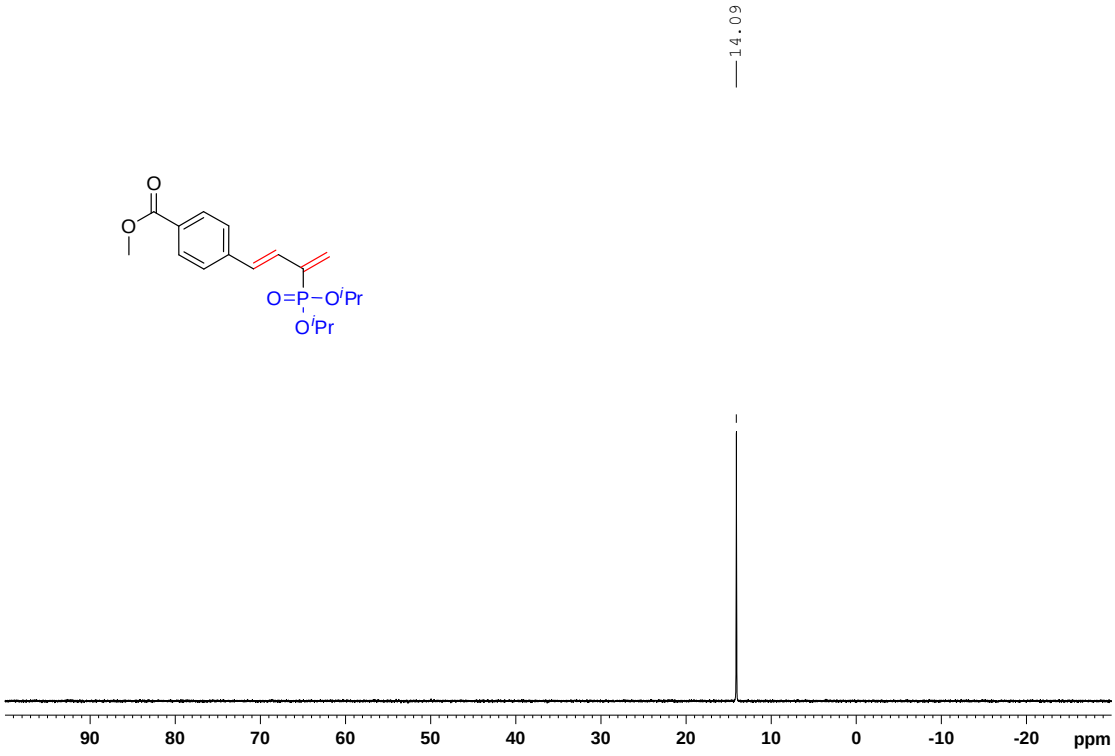
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3j**



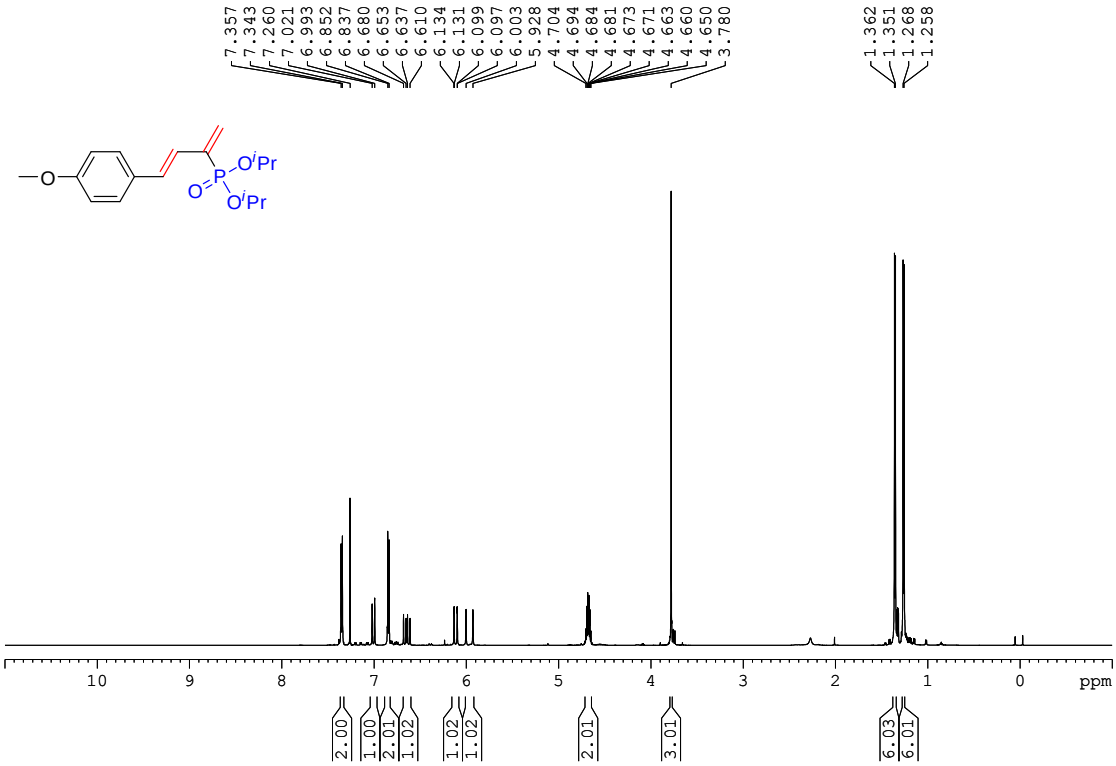
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3k**



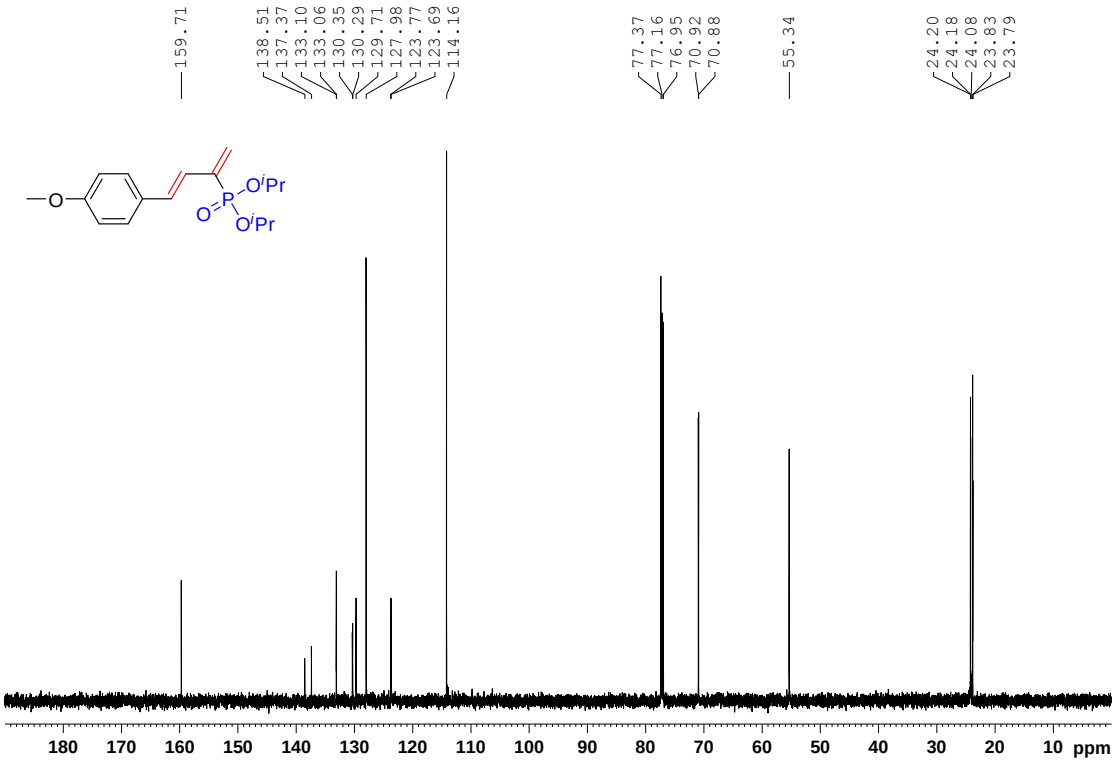
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3k**



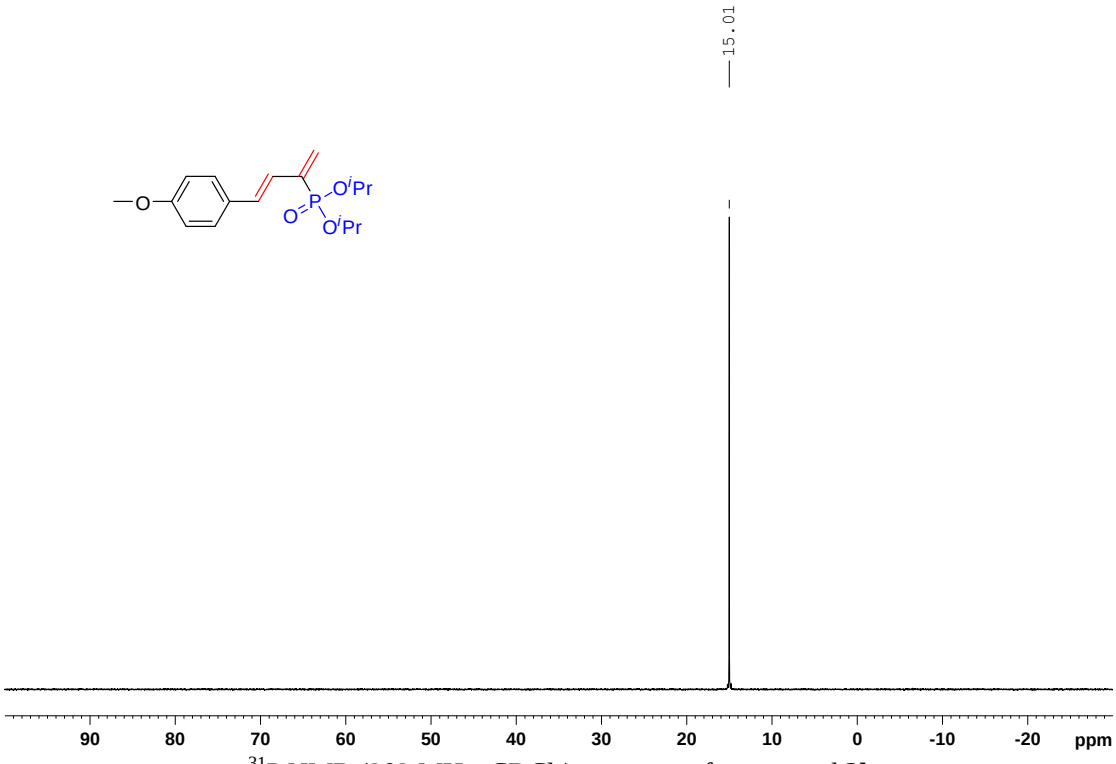
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3k**



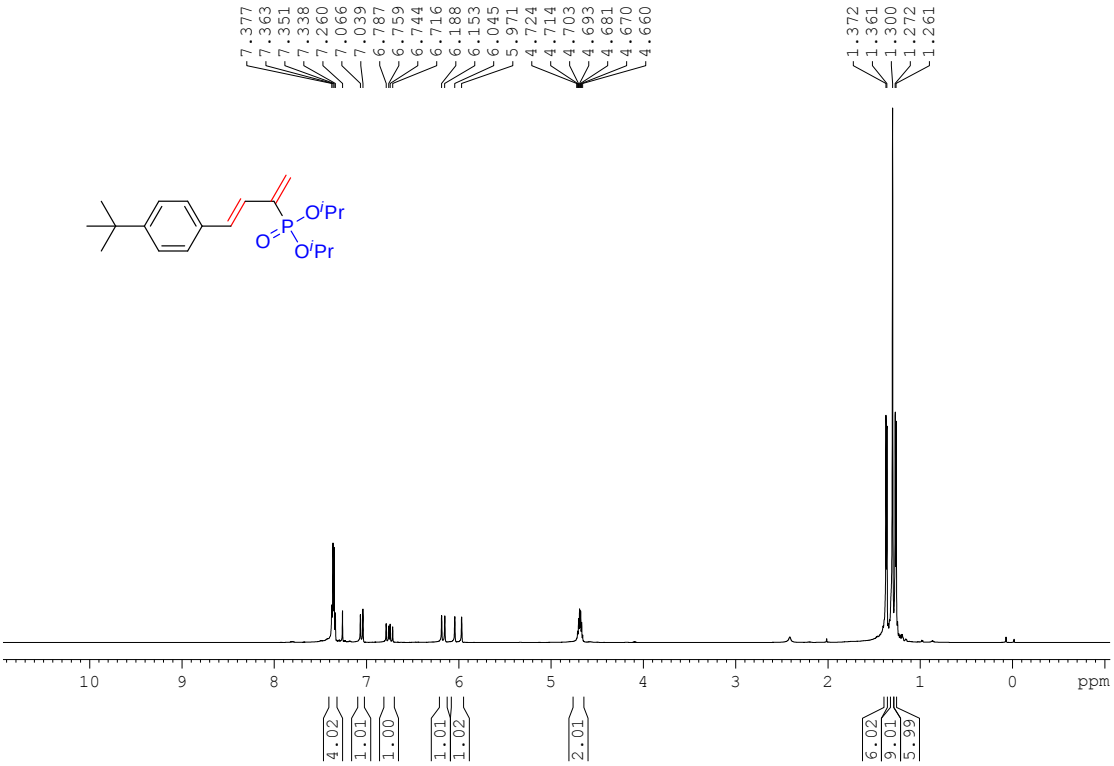
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3l**



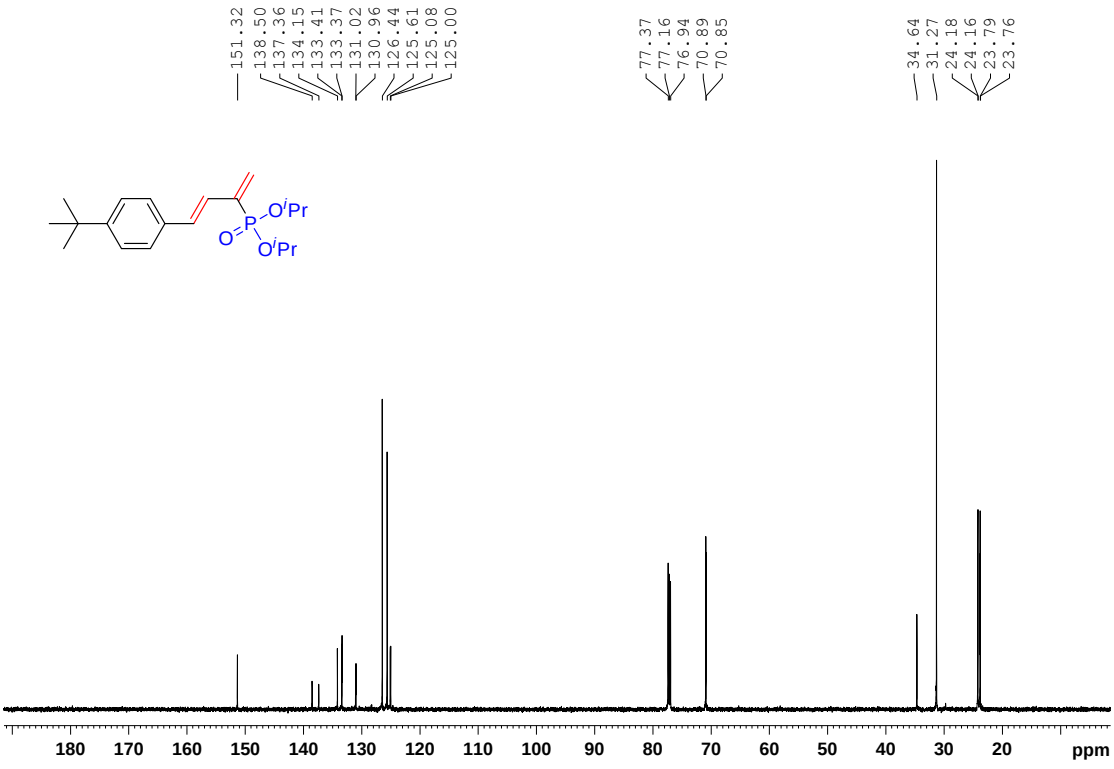
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3l**



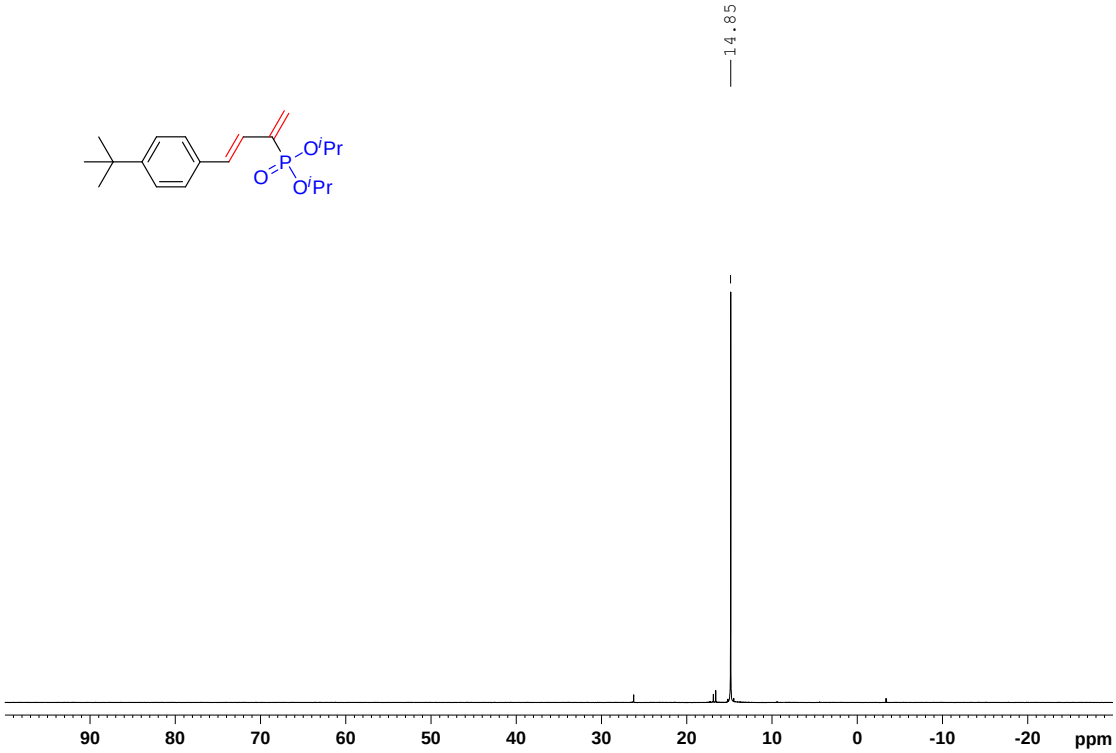
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3l**



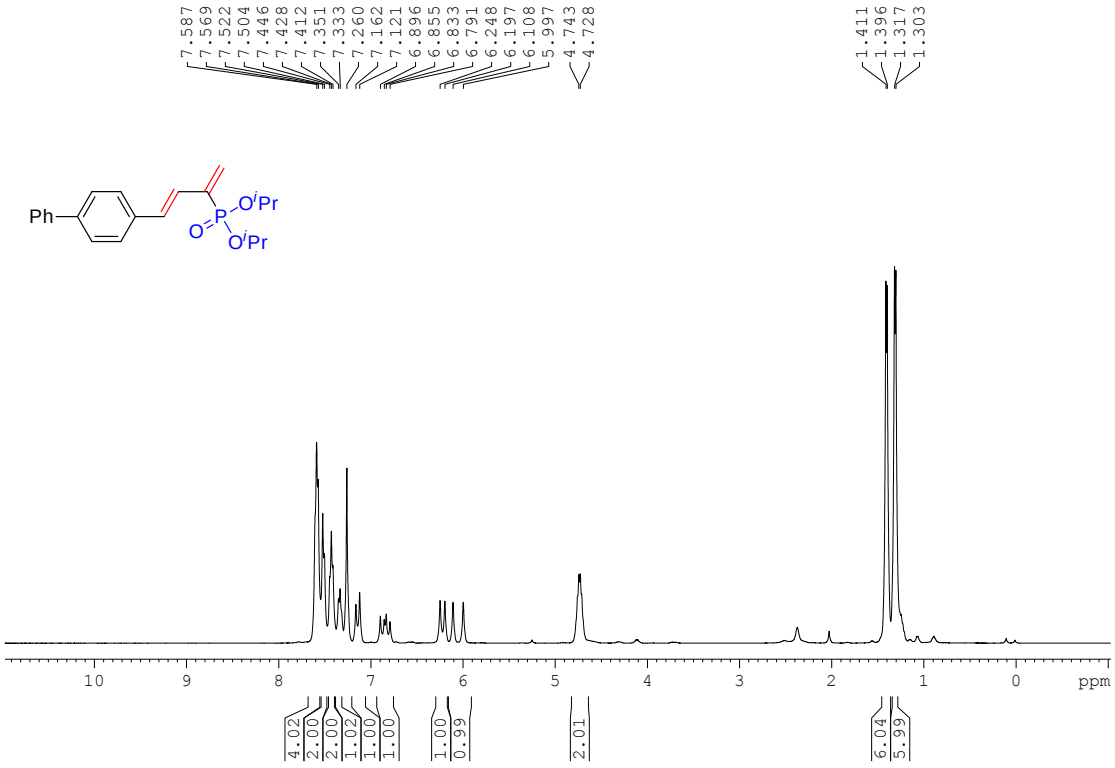
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3m**



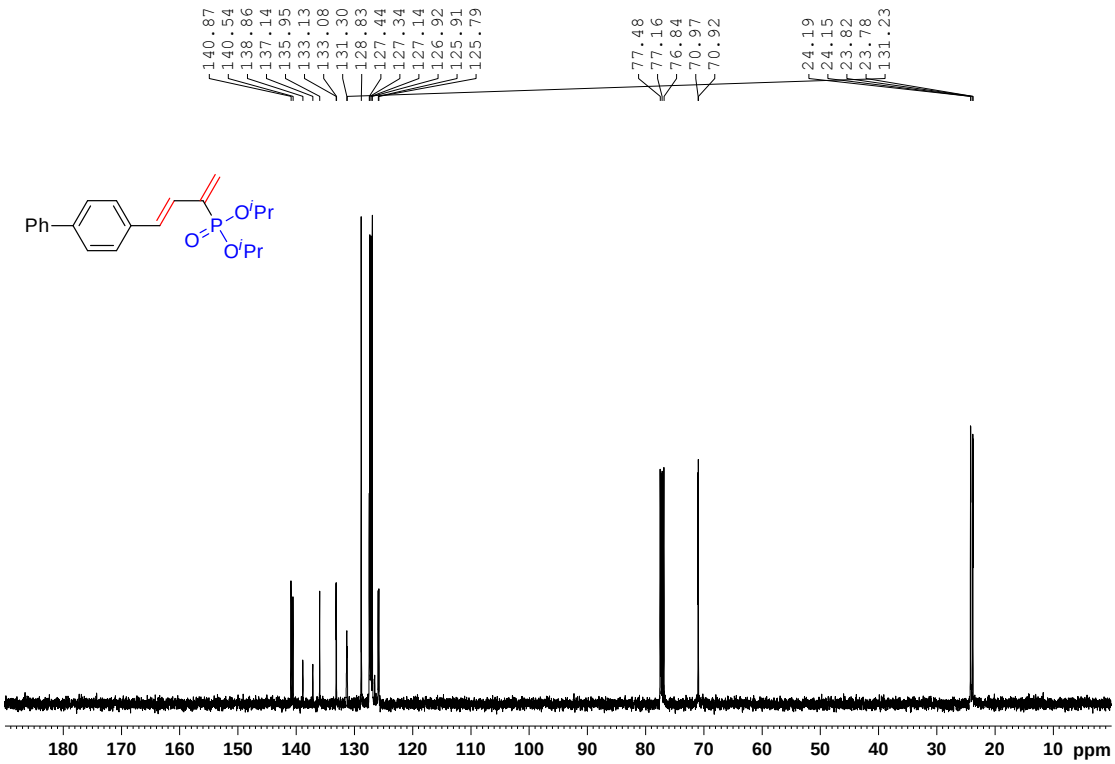
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3m**



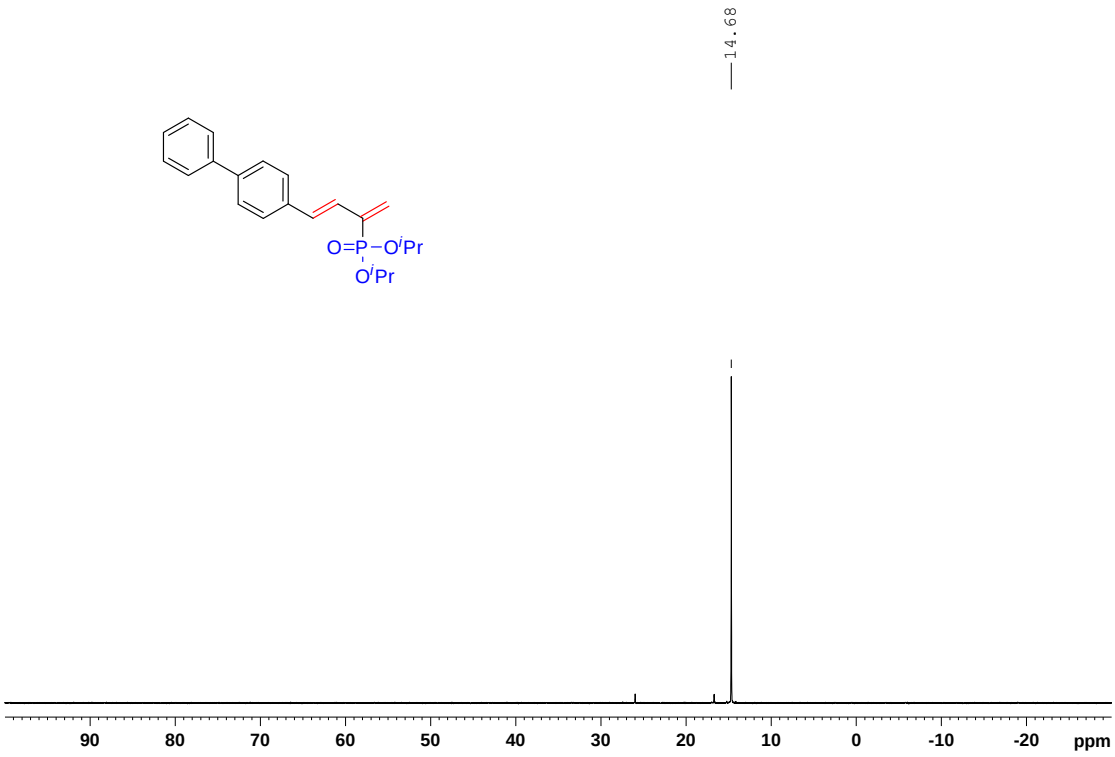
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3m**



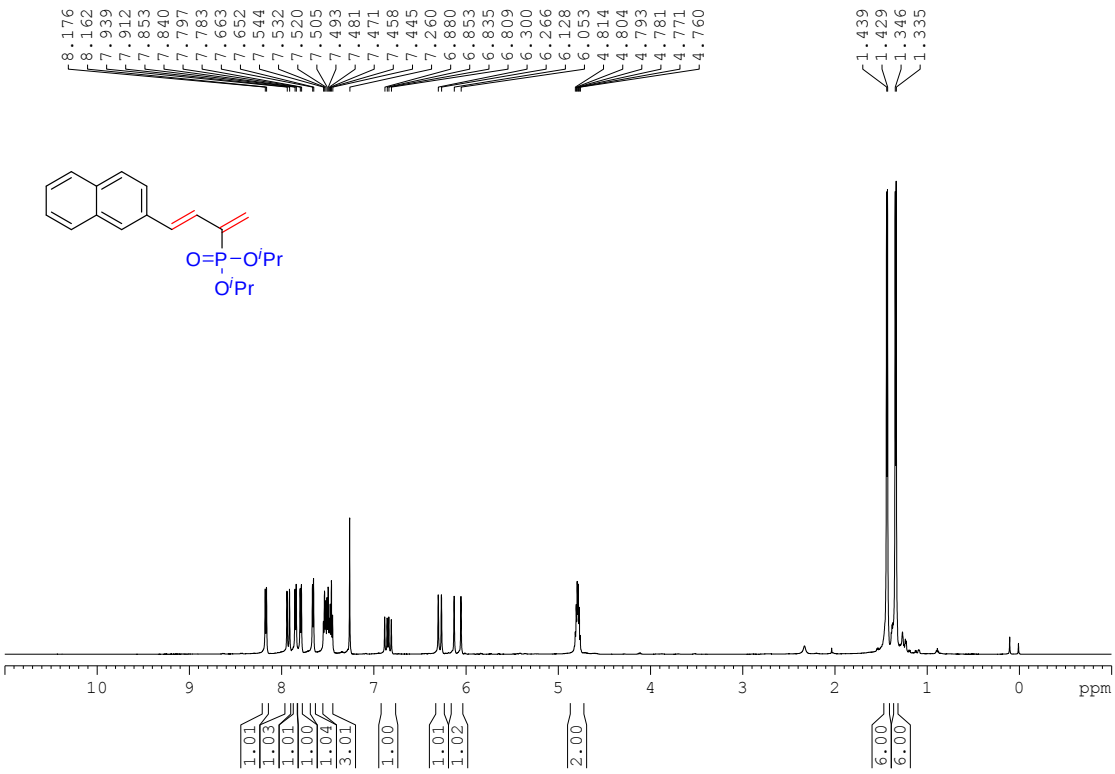
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3n**



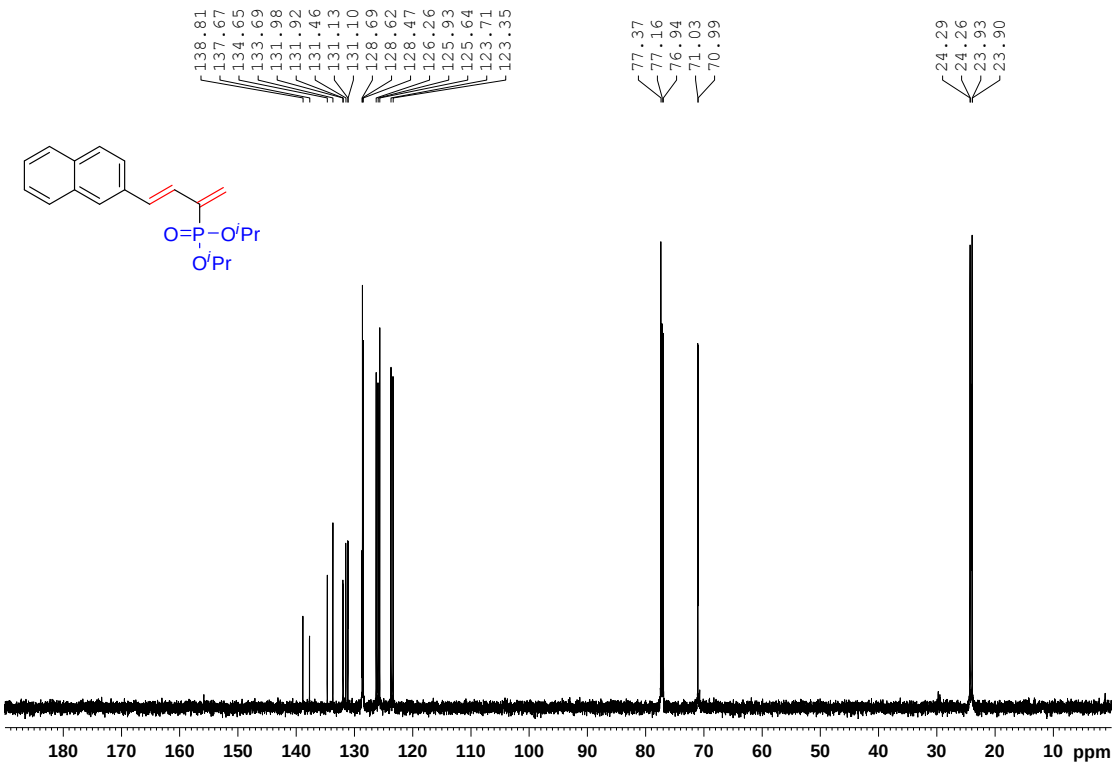
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3n**



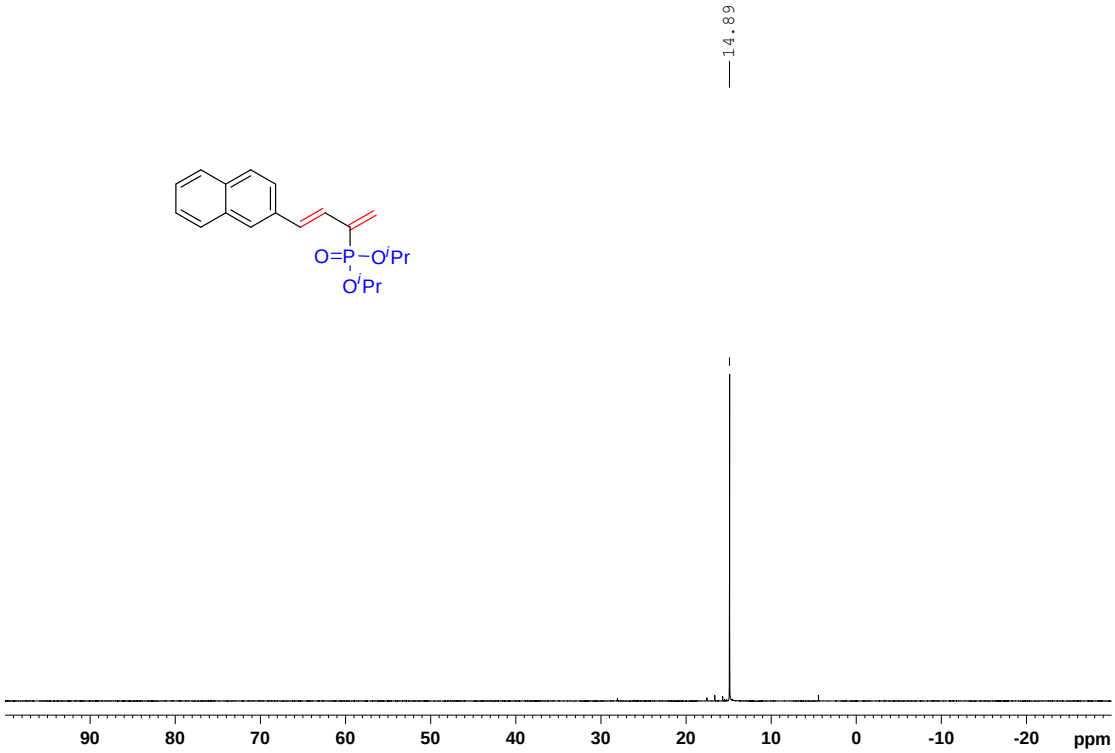
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3n**



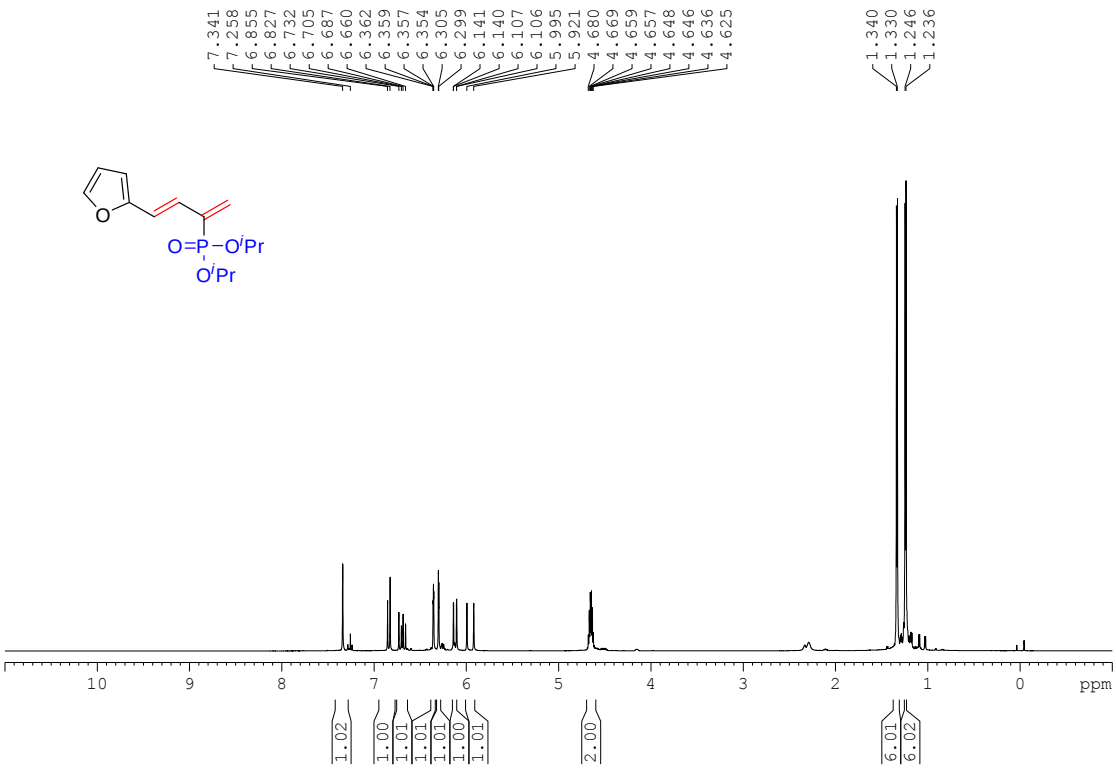
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3o**



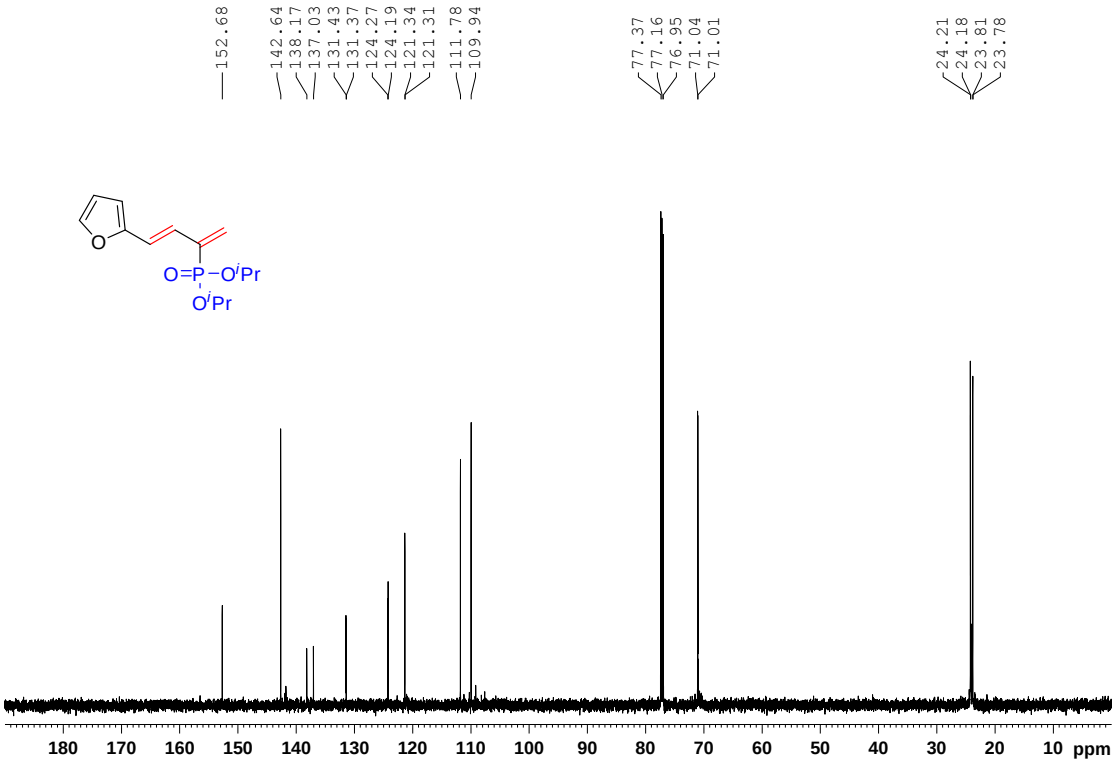
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3o**



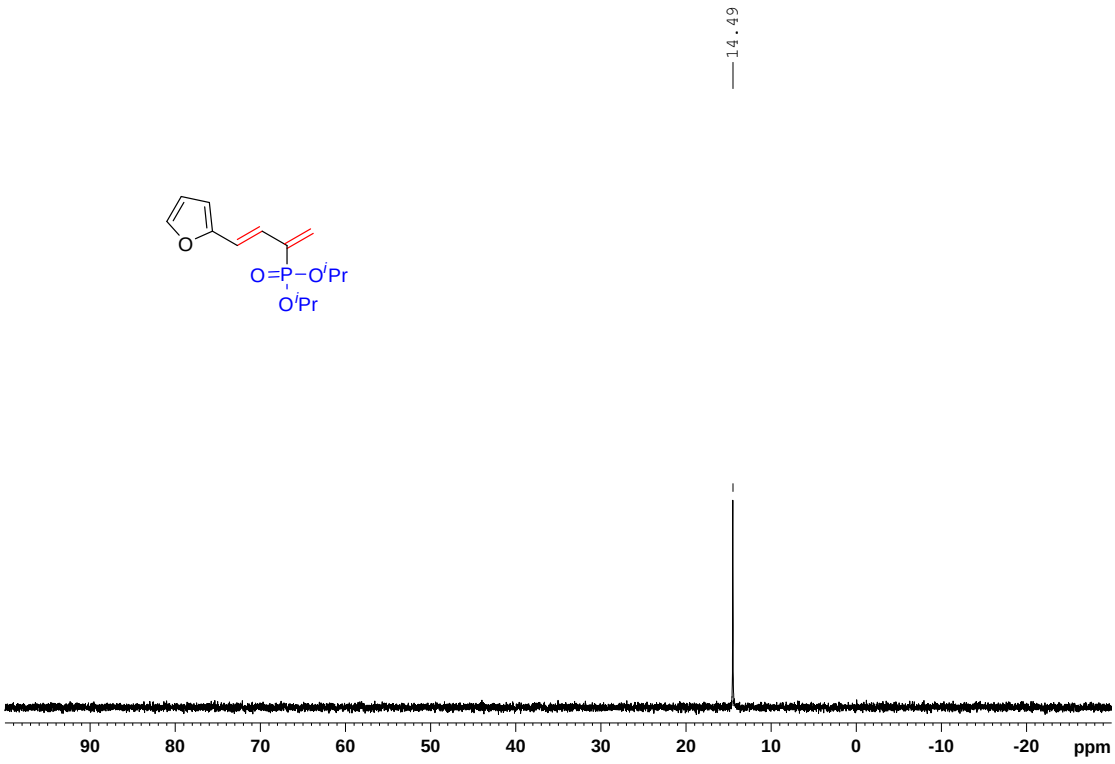
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3o**



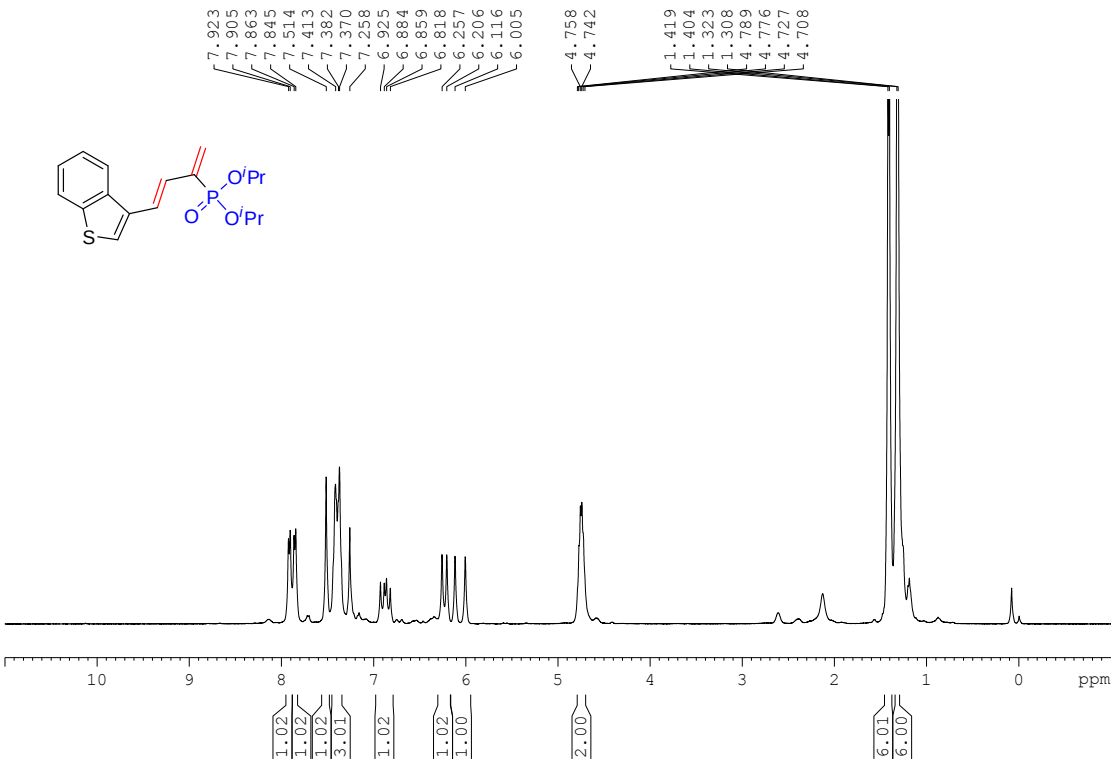
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3p**



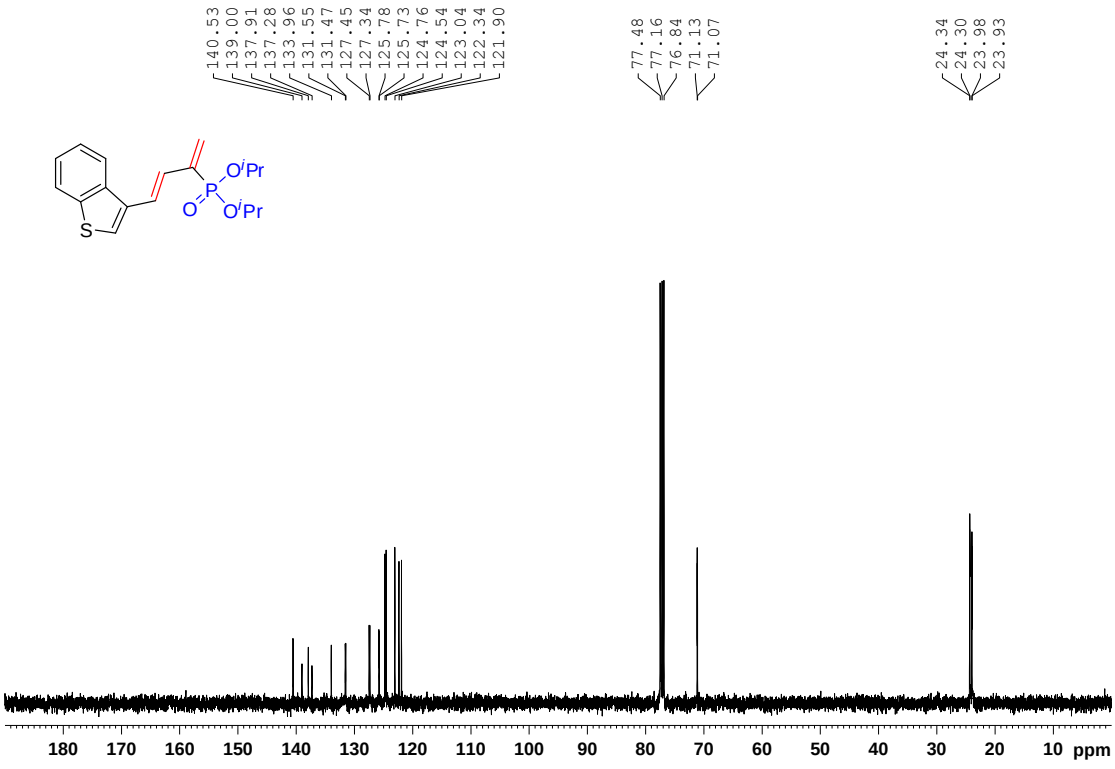
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3p**



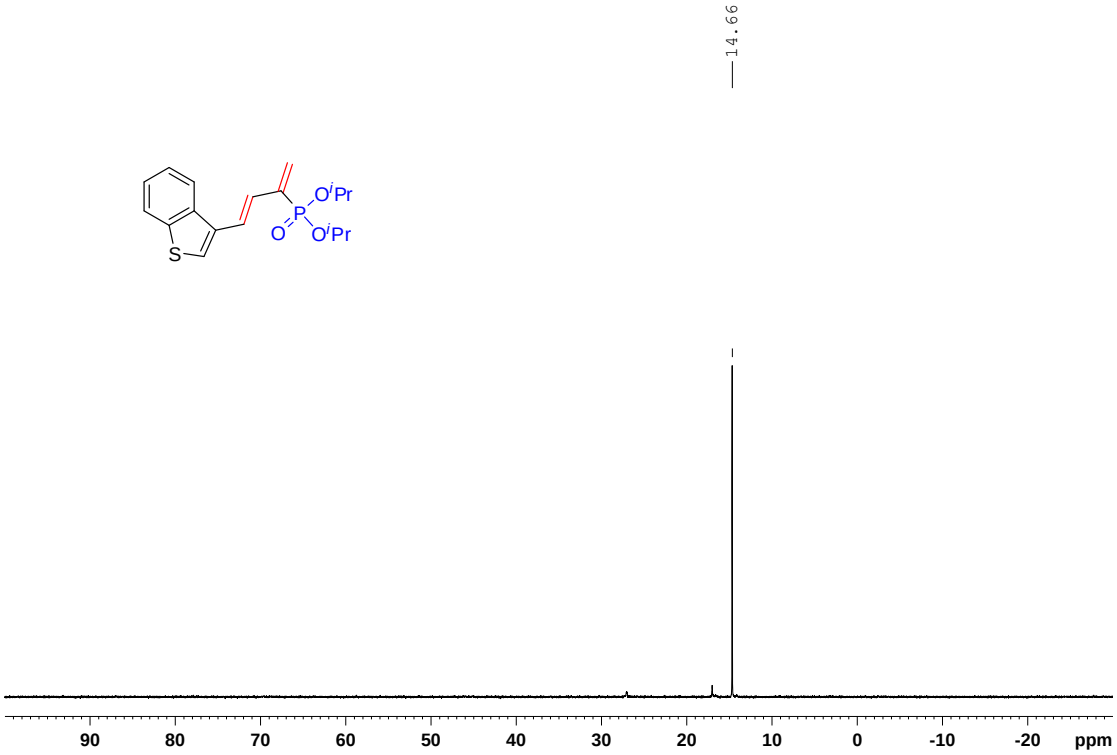
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3p**



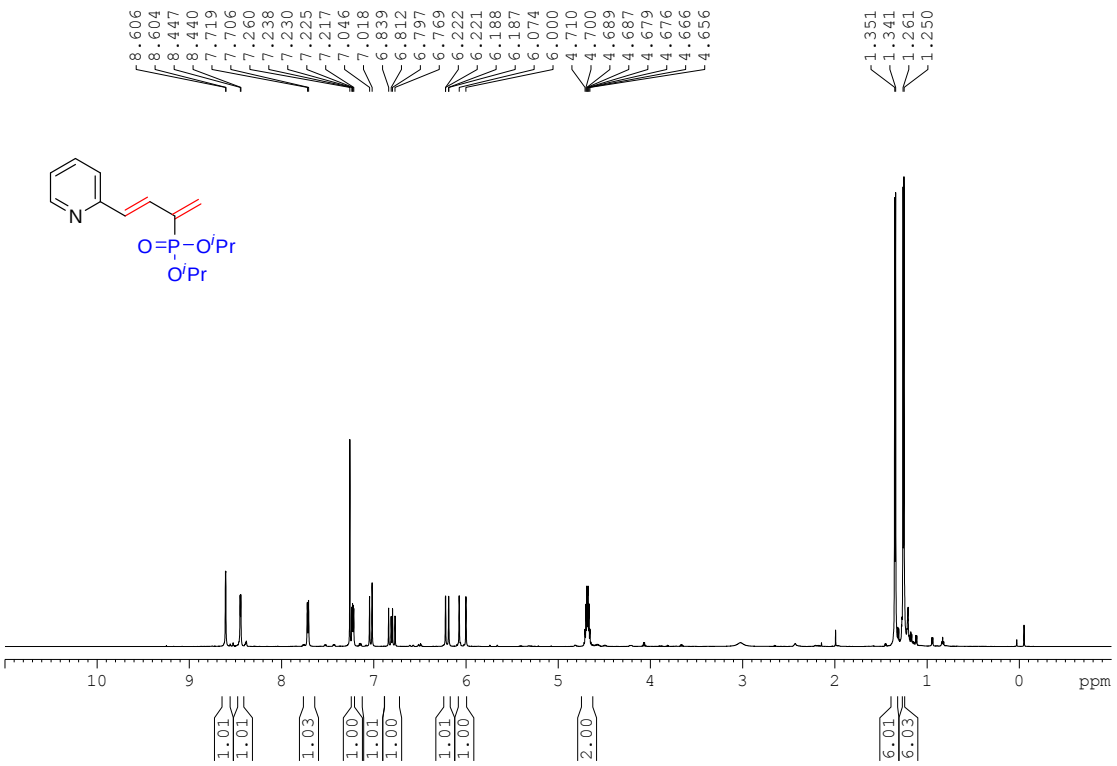
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3q**



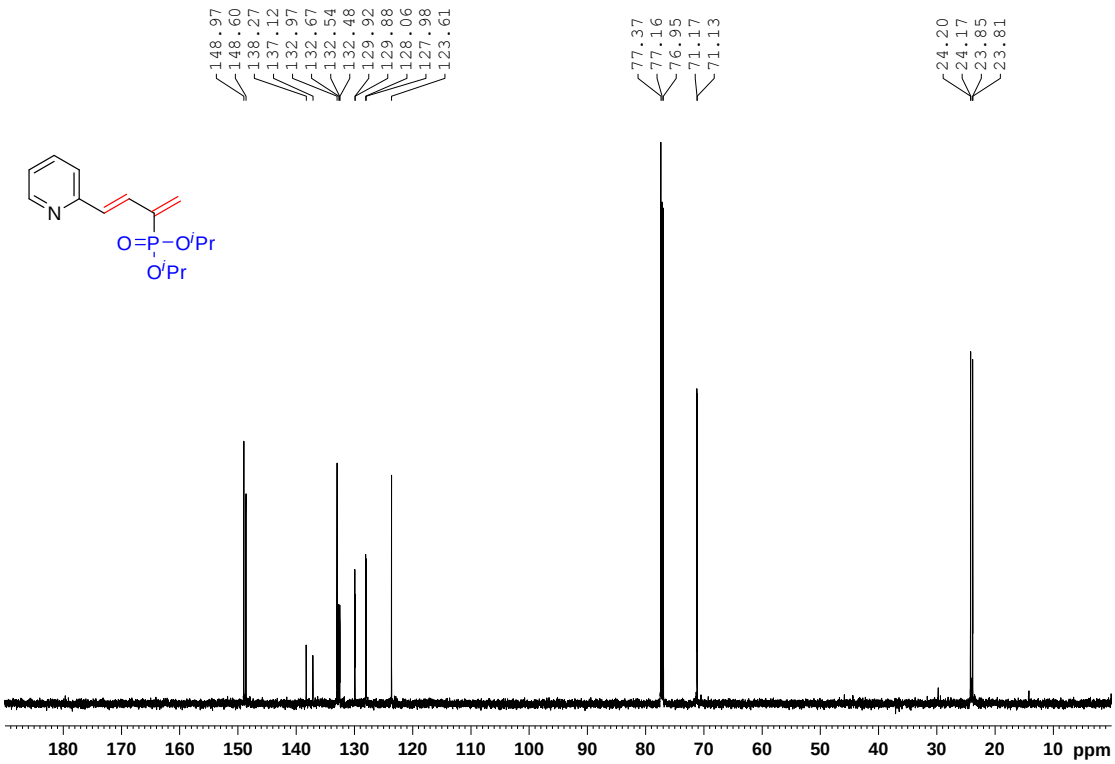
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3q**



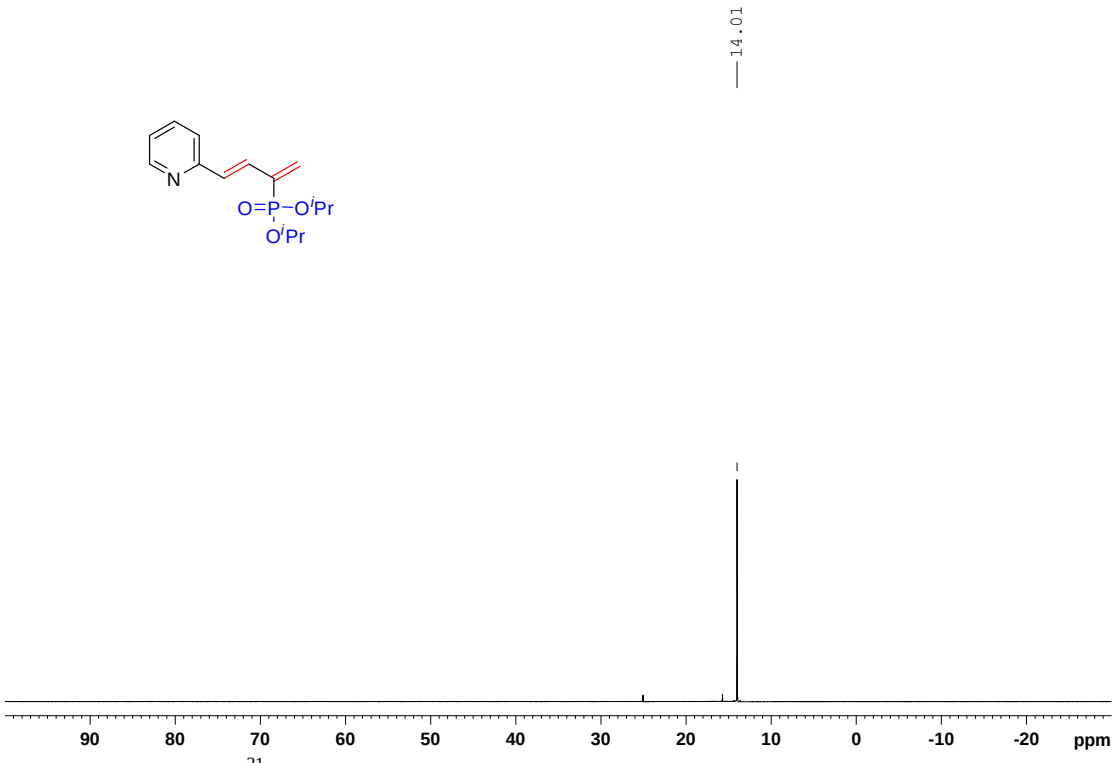
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3q**



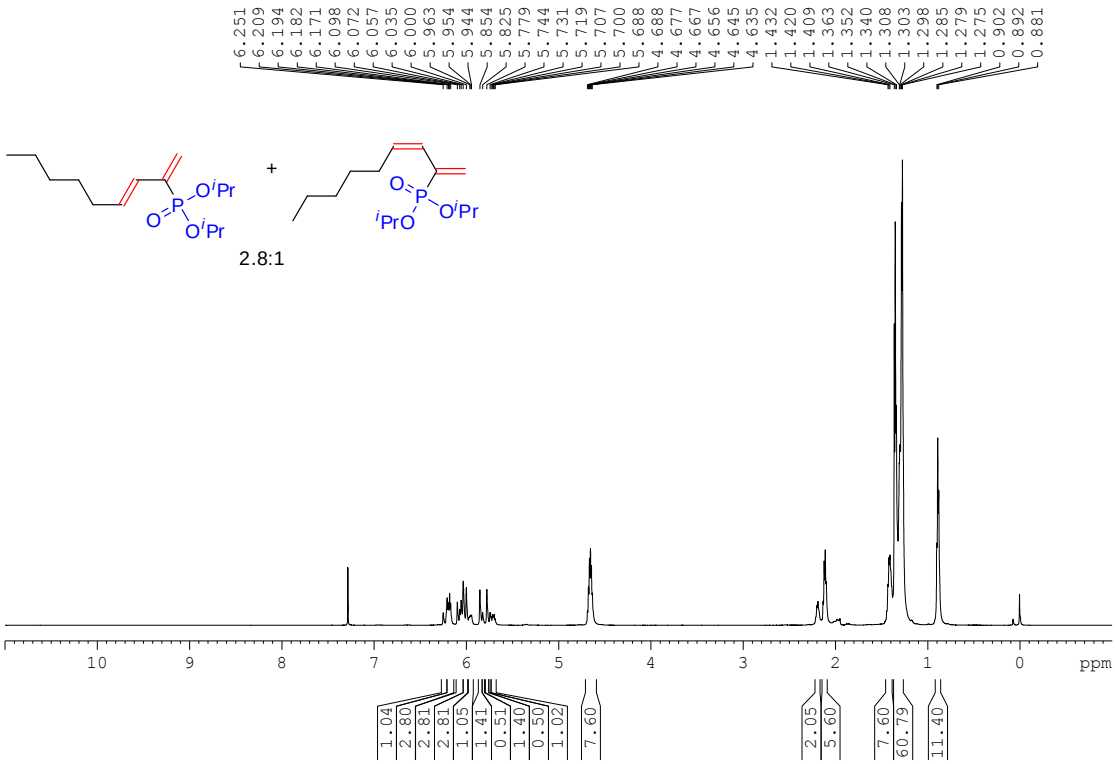
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3r**



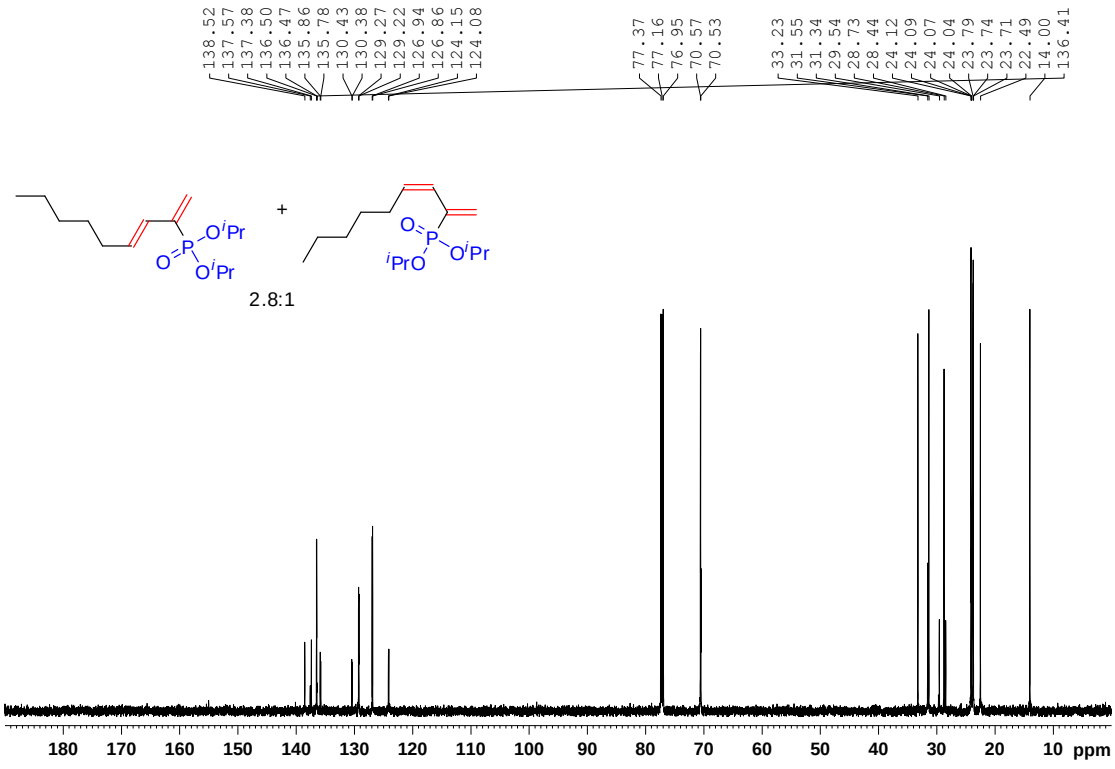
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3r**



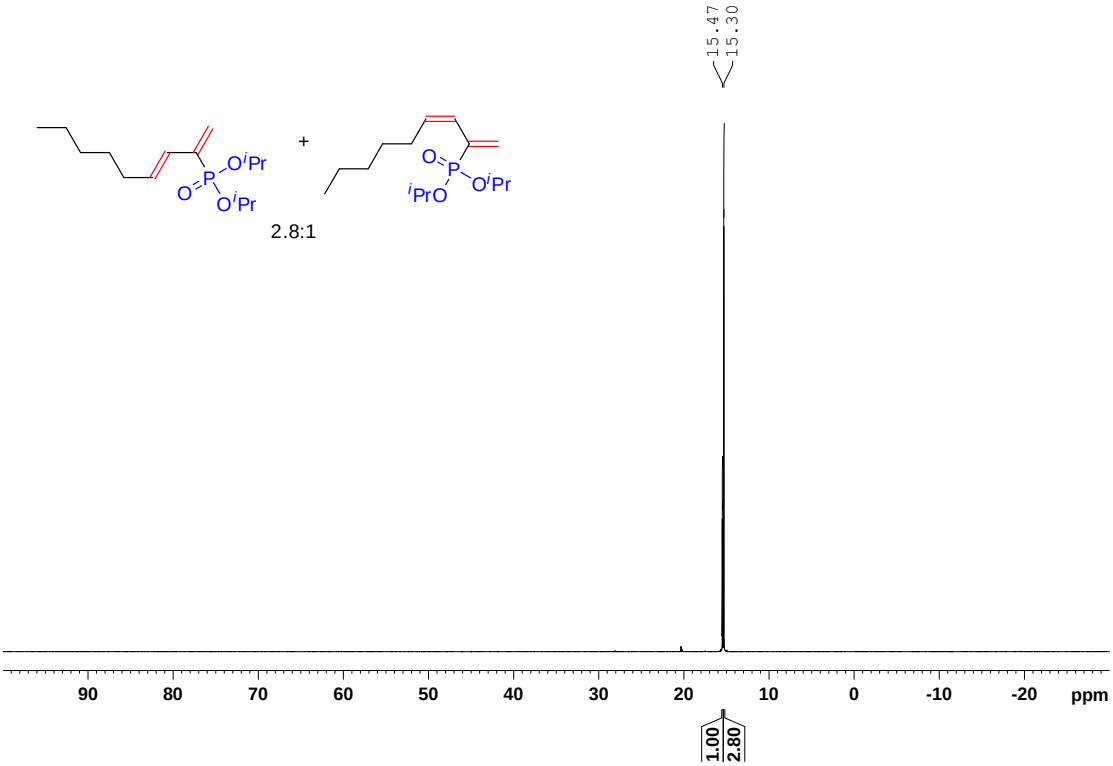
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3r**



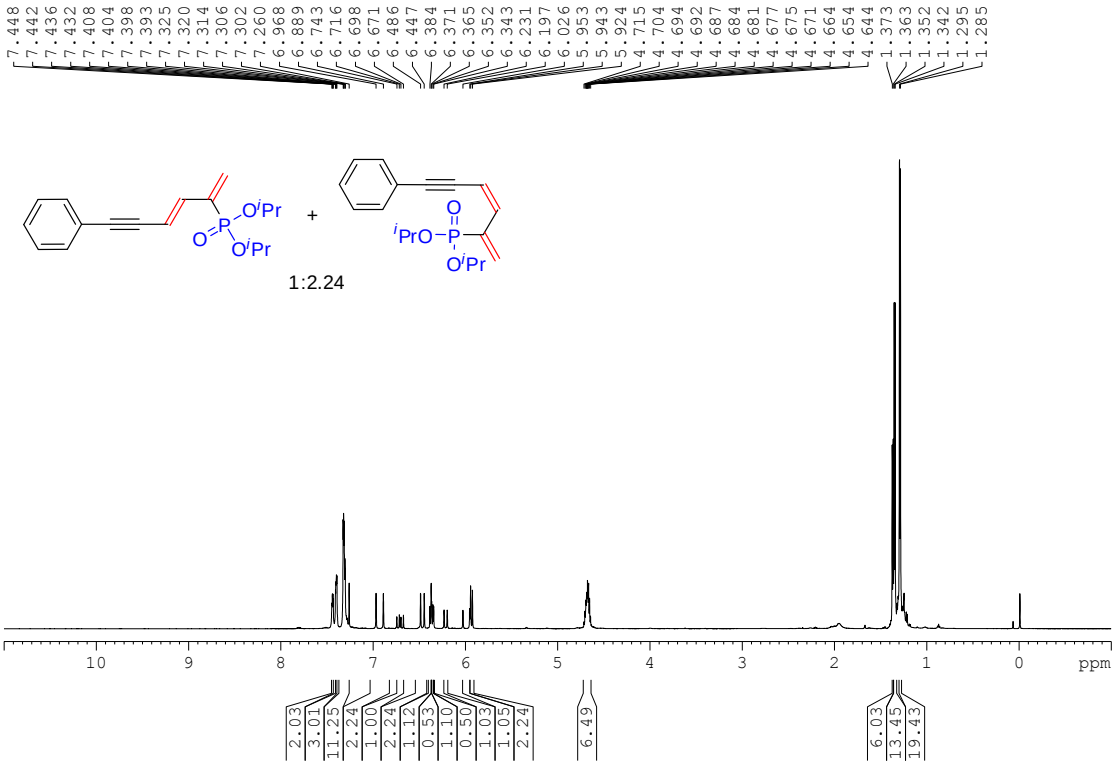
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3s** and (*Z*)-**3s** (2.80:1)



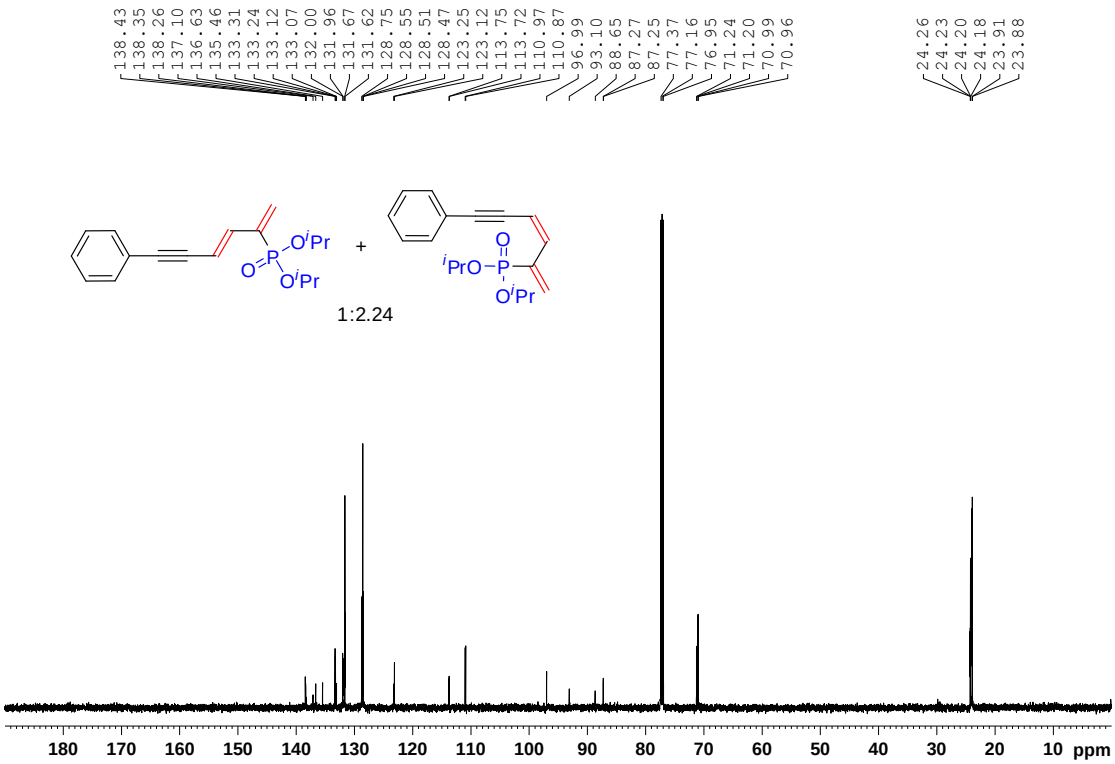
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3s** and (*Z*)-**3s** (2.80:1)



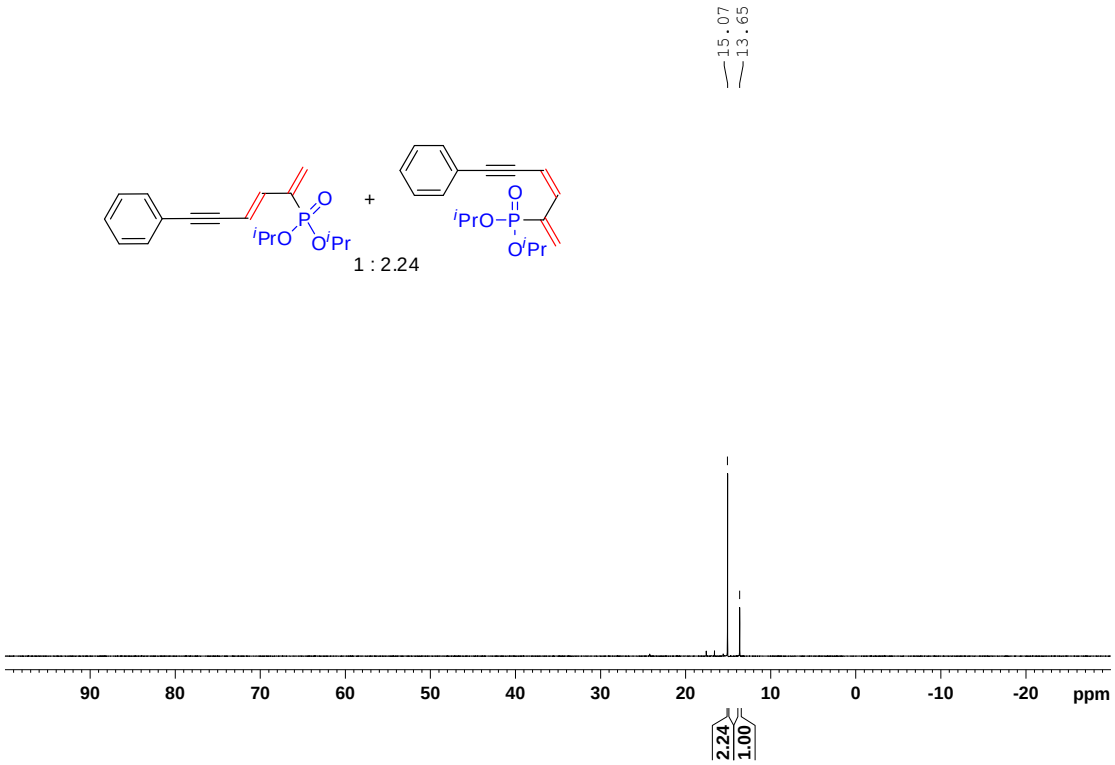
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3s** and (*Z*)-**3s** (2.80:1)



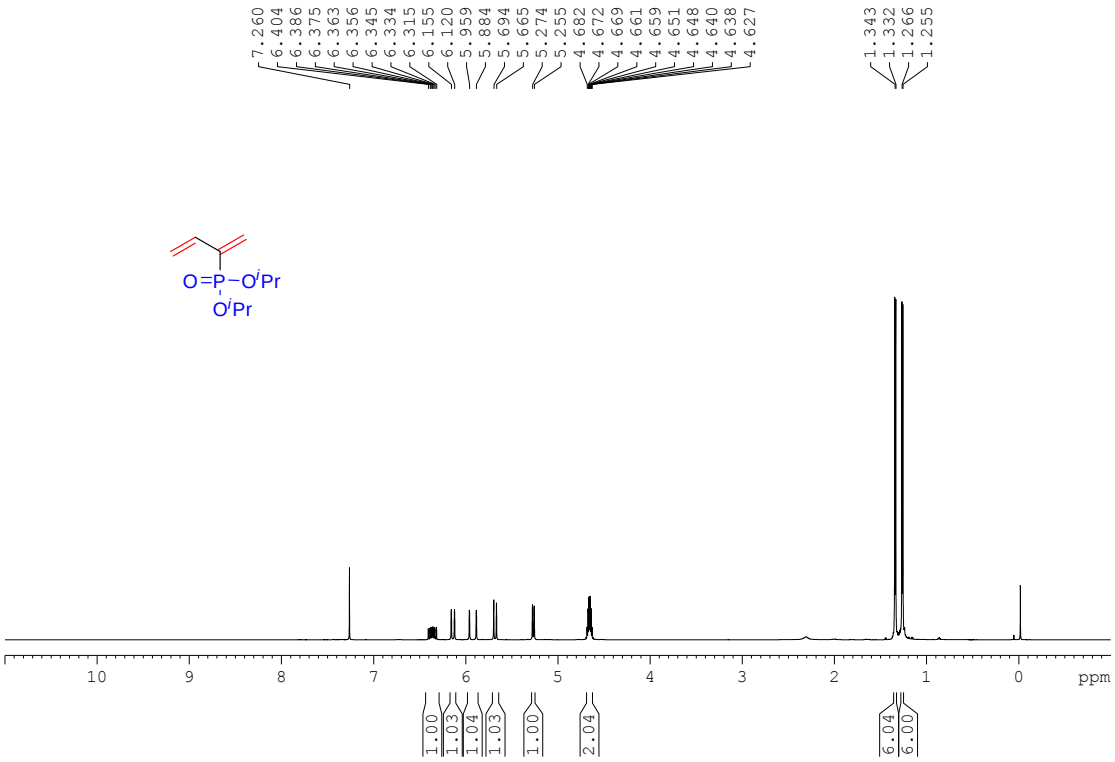
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3t** and (*Z*)-**3t** (1:2.24)



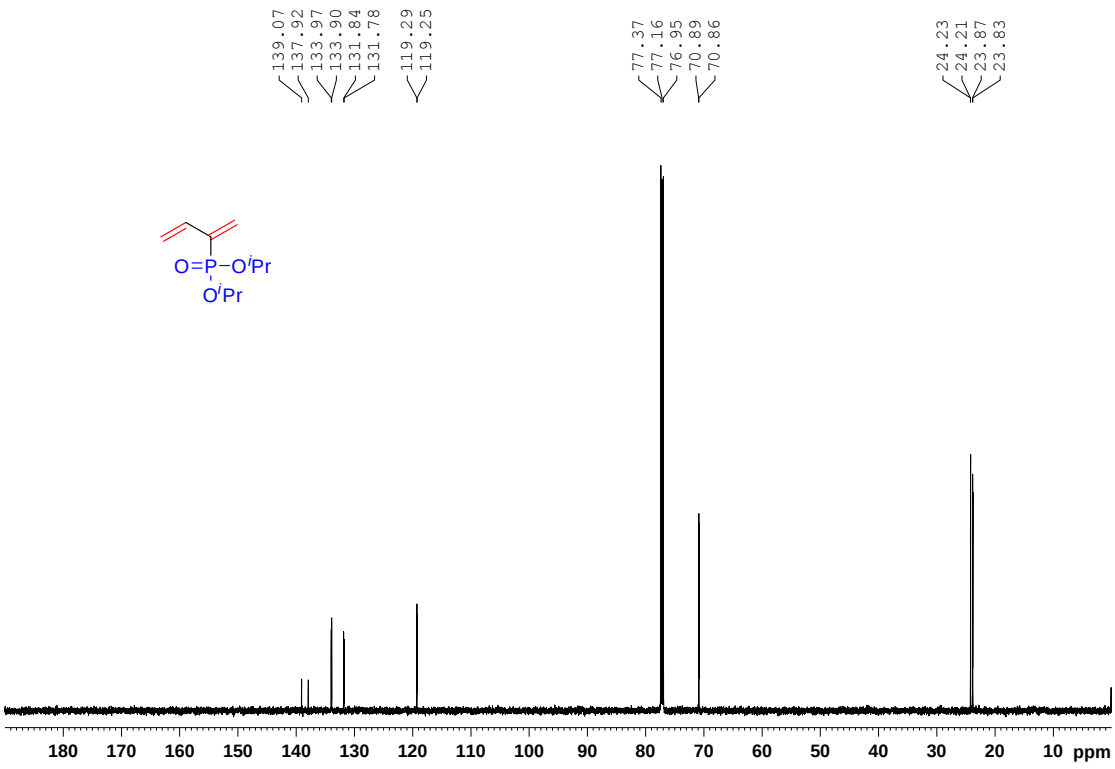
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3t** and (*Z*)-**3t** (1:2.24)



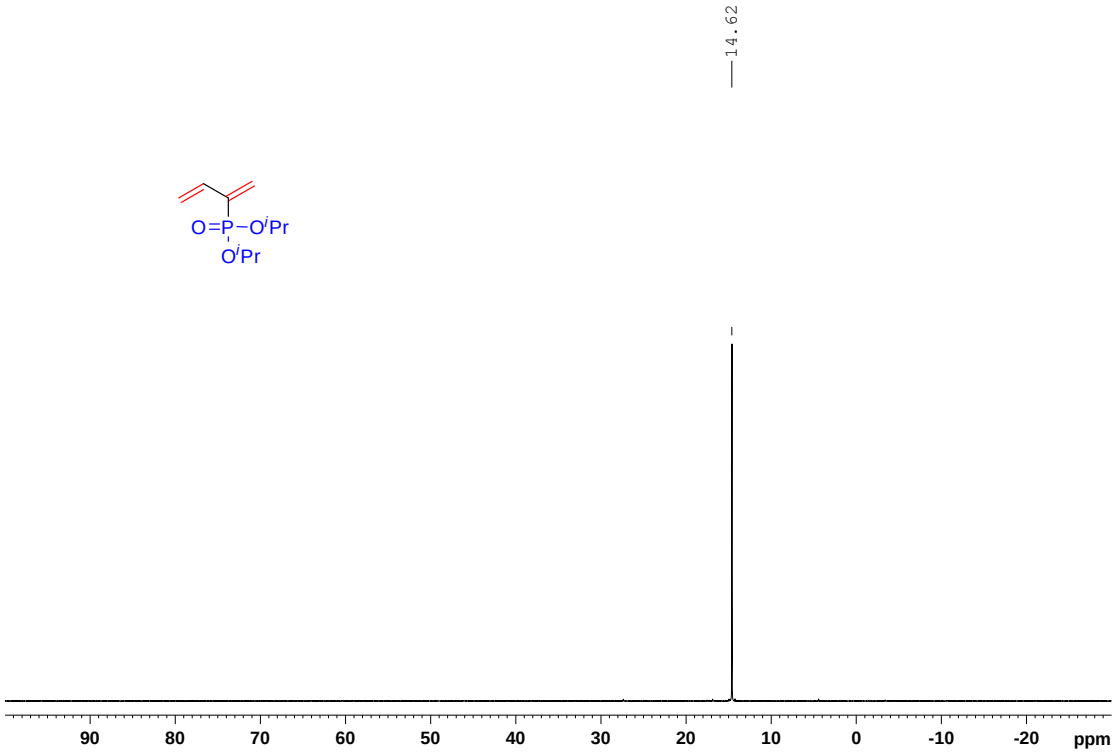
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3t** and (*Z*)-**3t** (1:2.24)



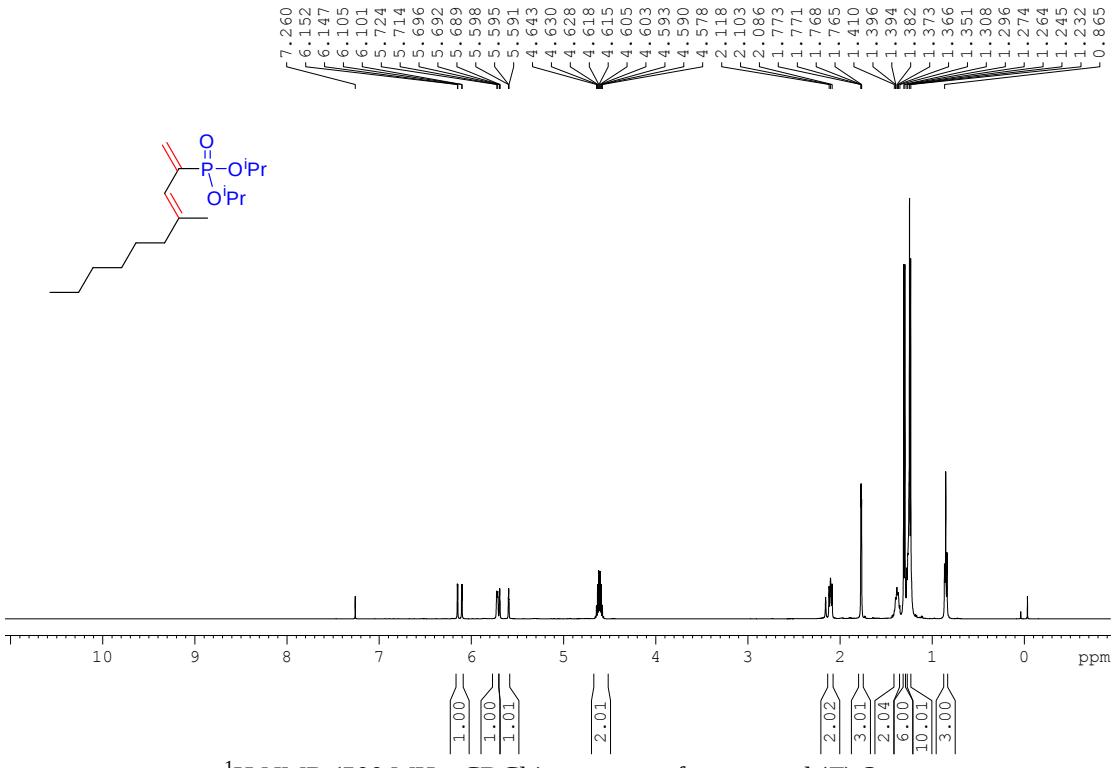
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3u**



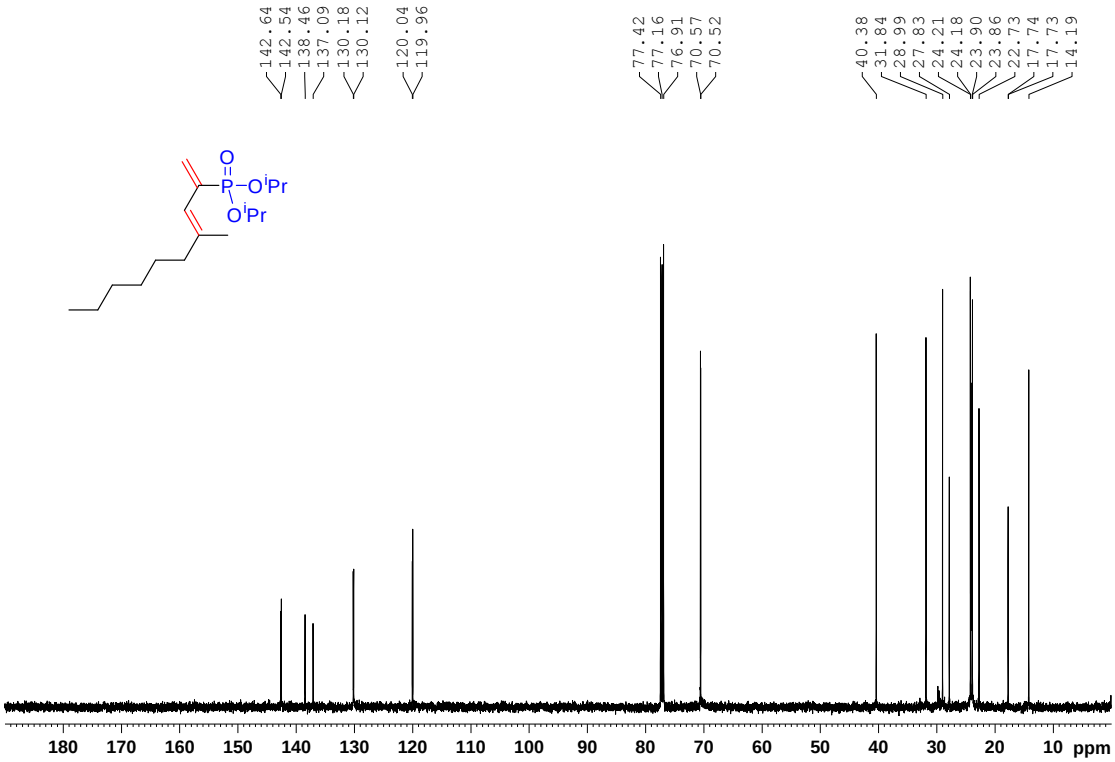
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3u**



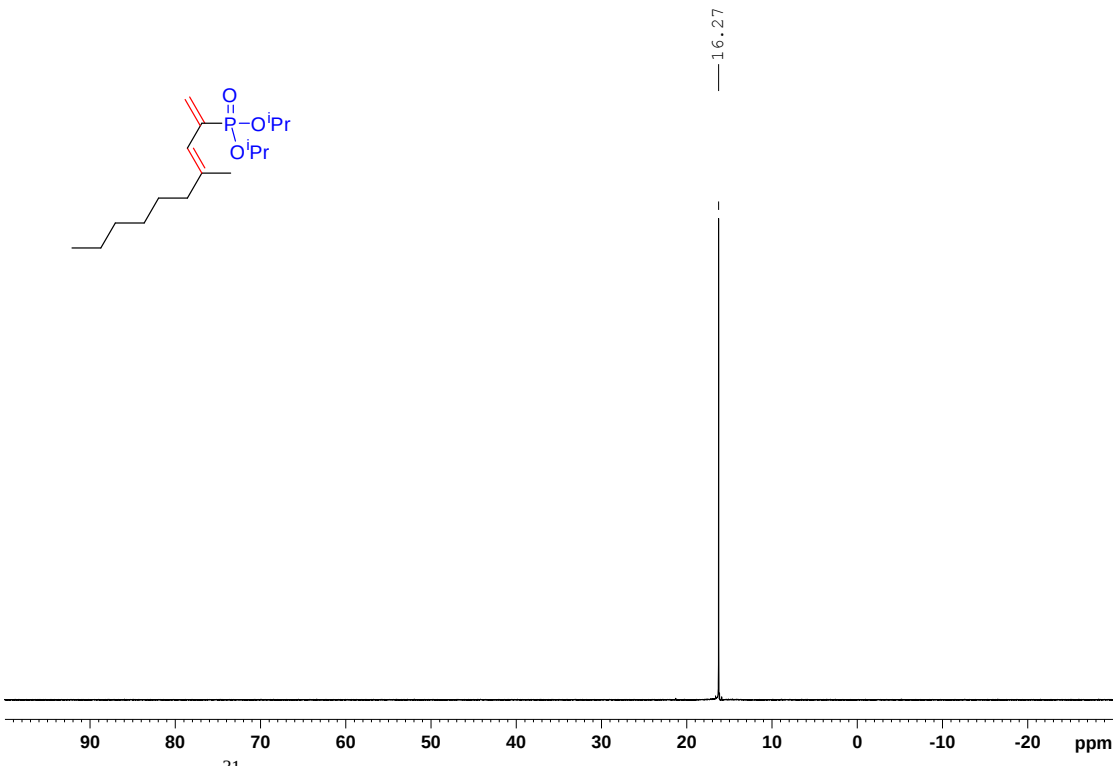
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3u**



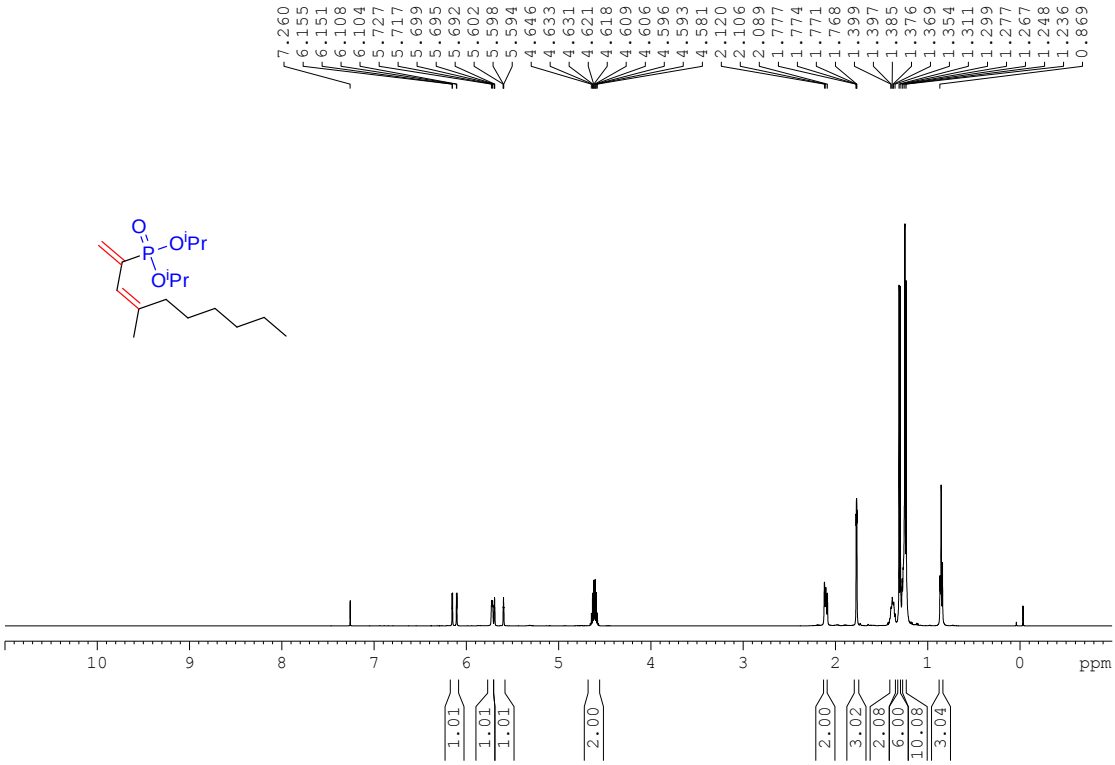
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3v**



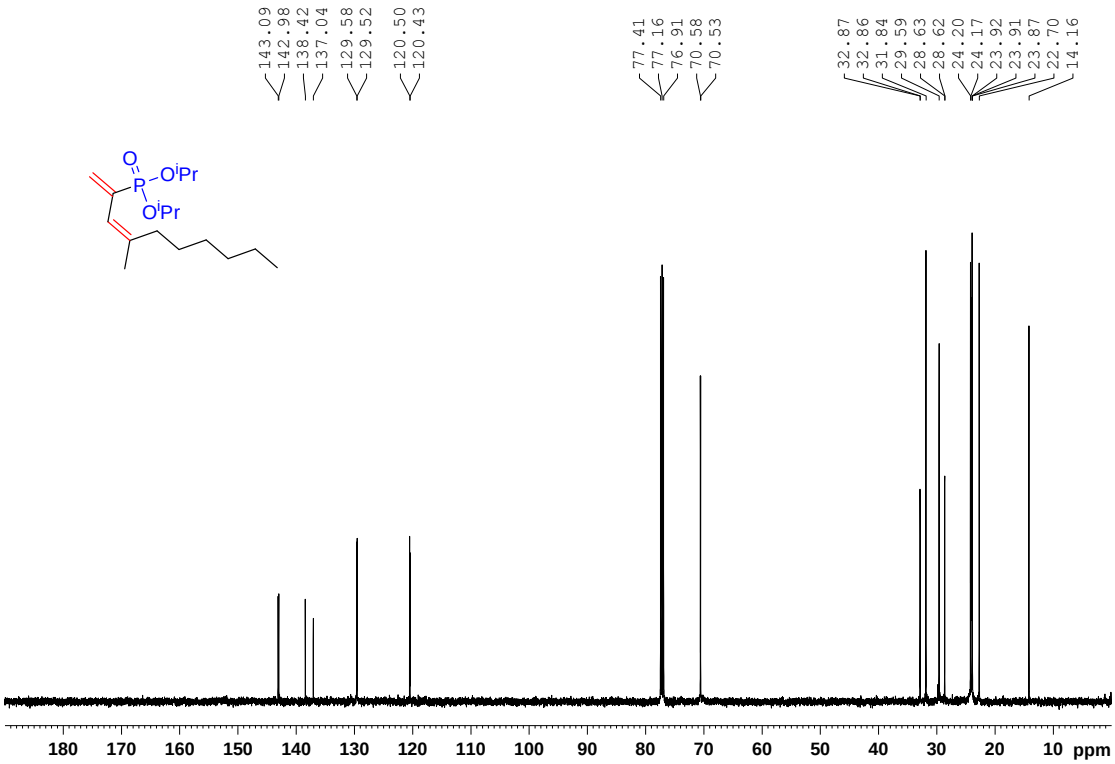
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3v**



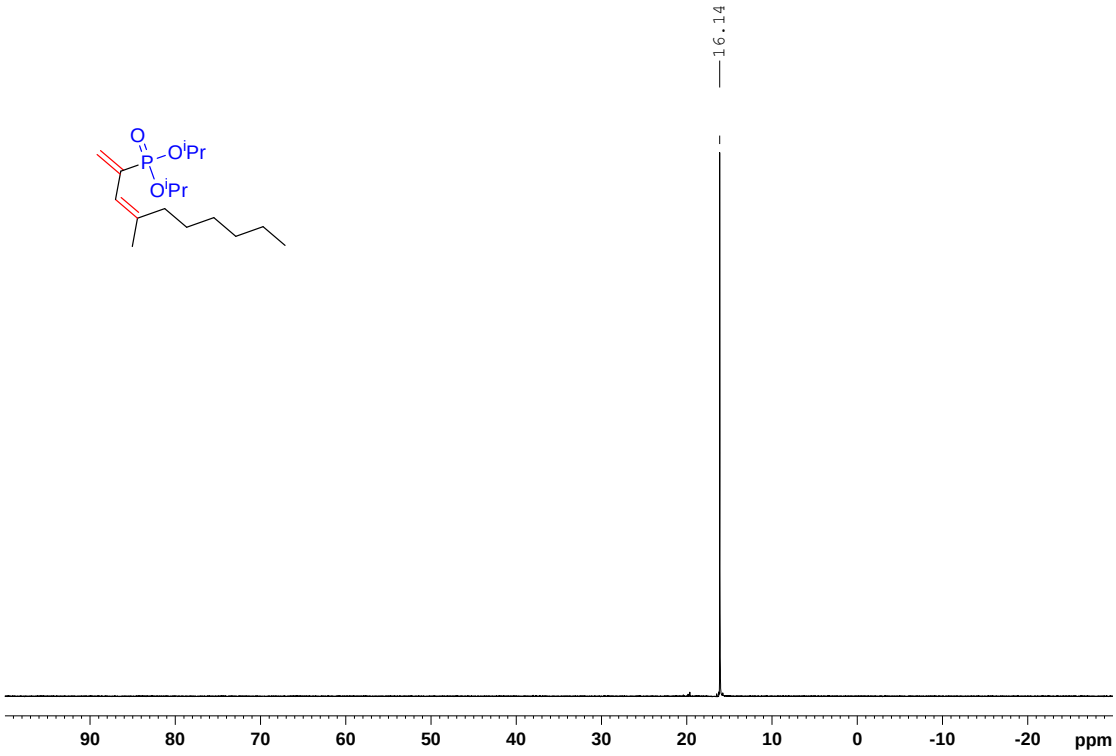
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3v**



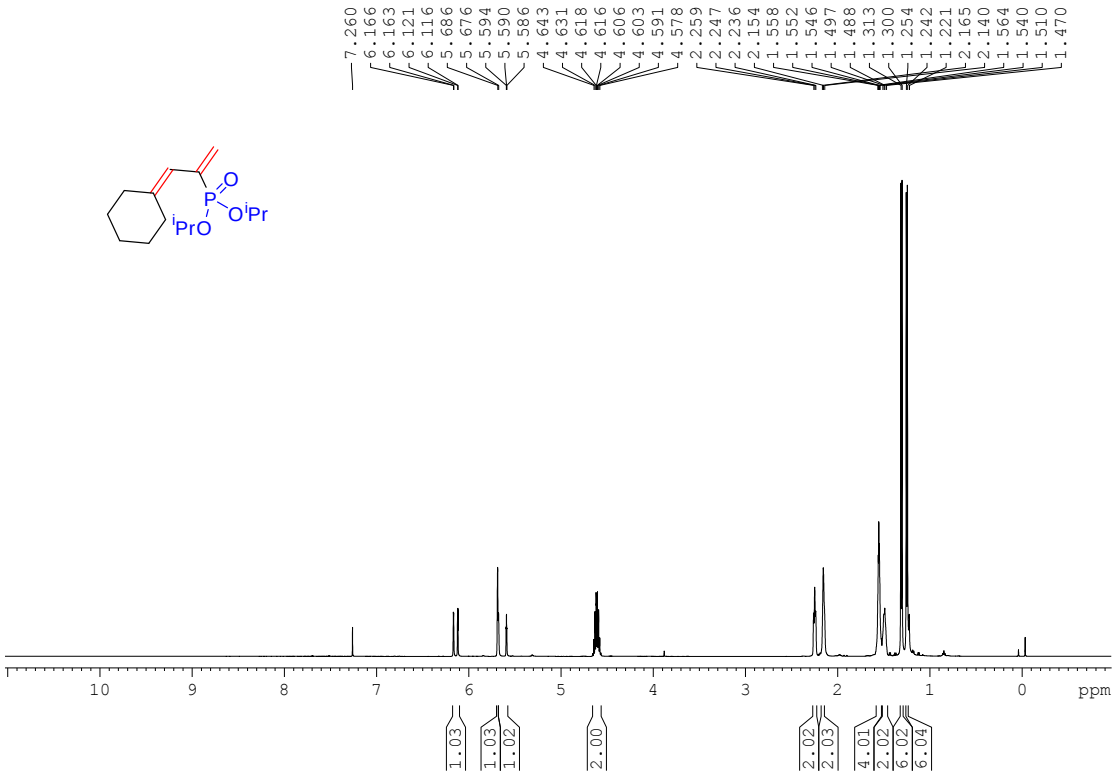
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3v**



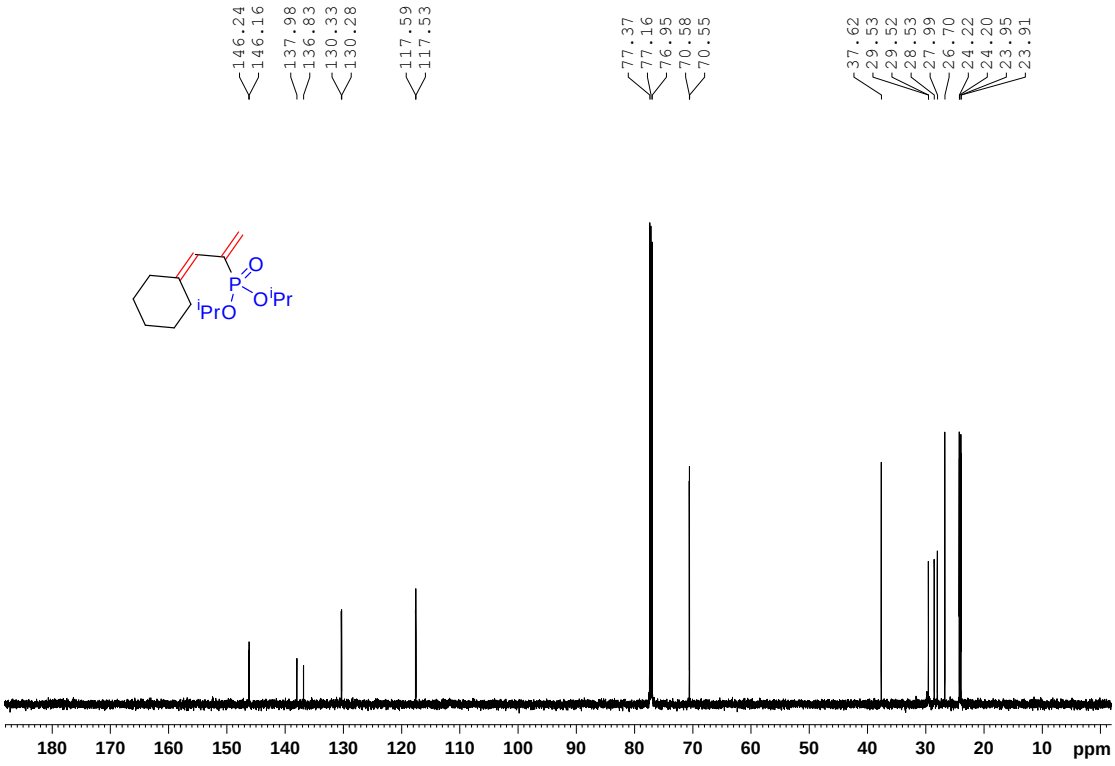
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3v**



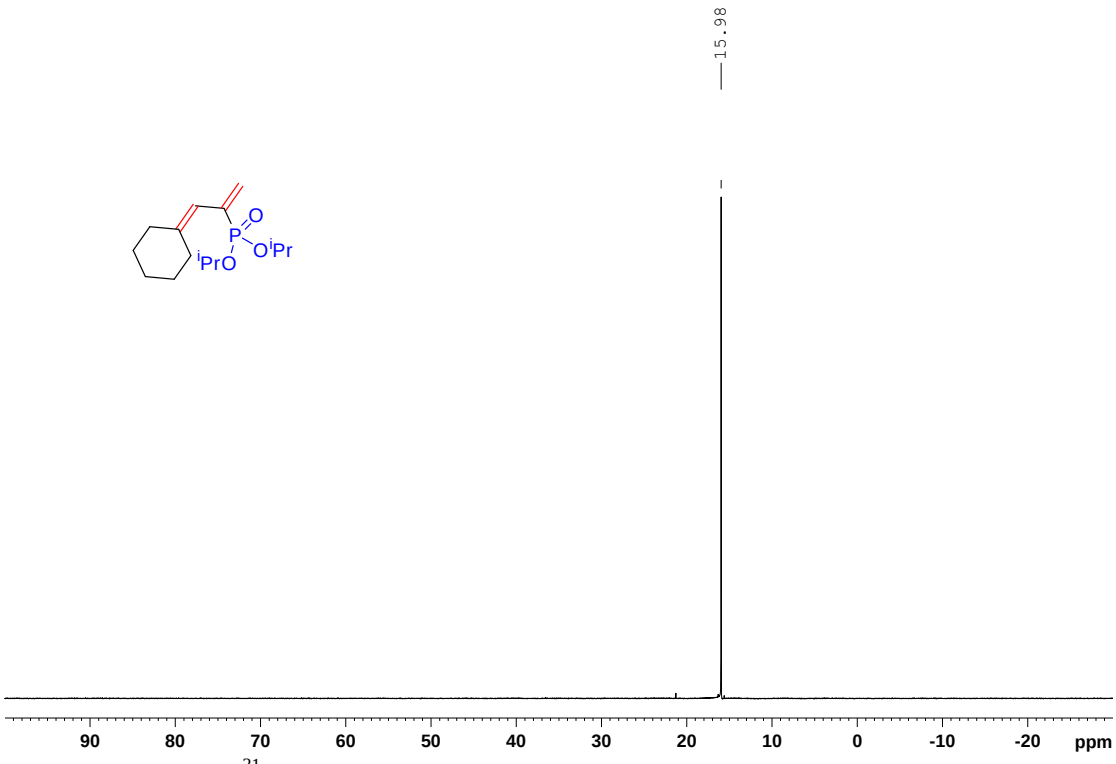
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3v**



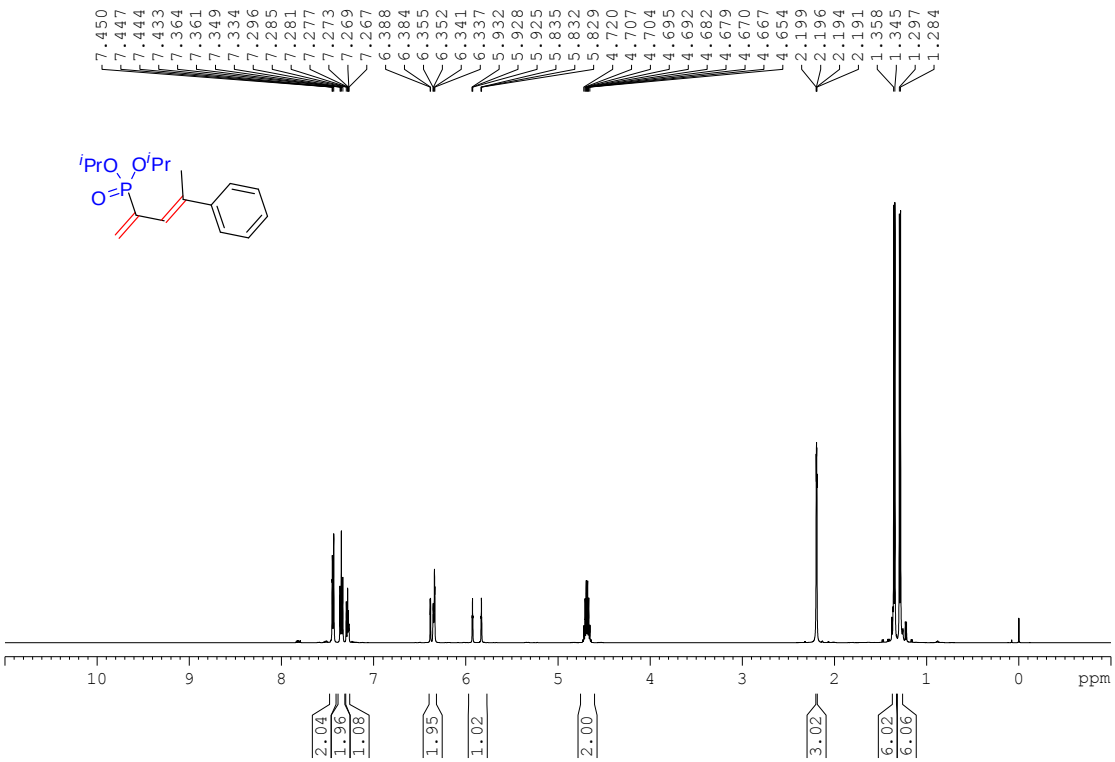
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3w**



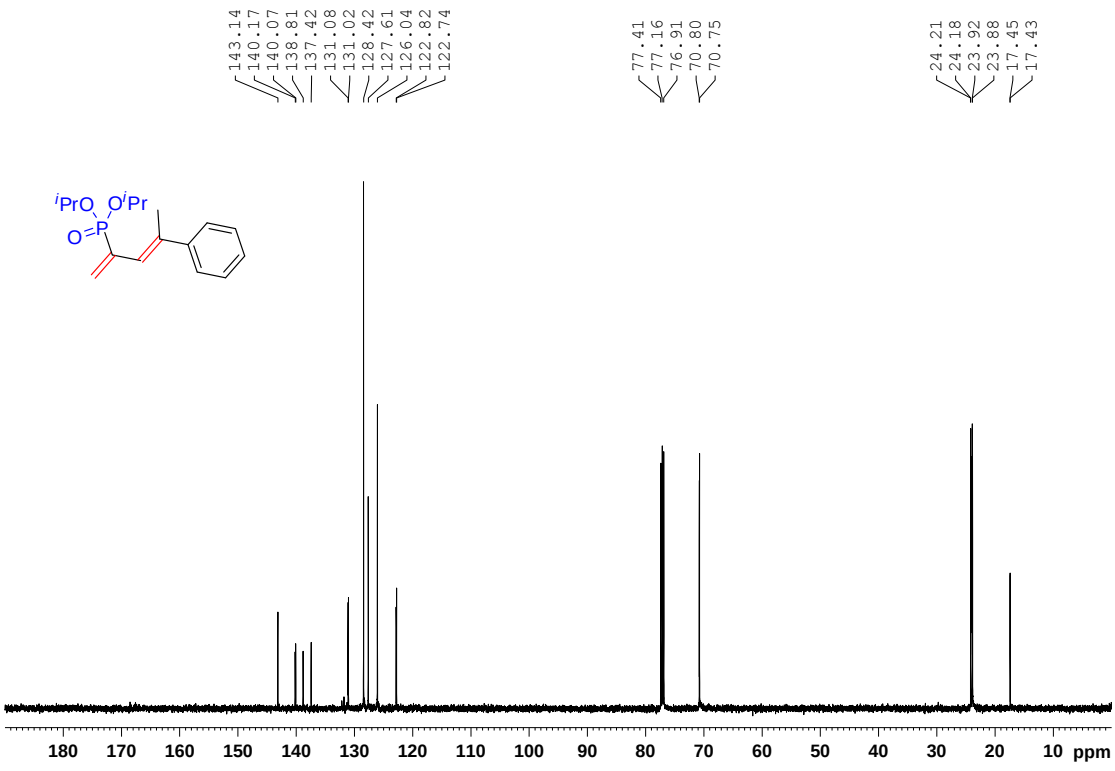
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3w**



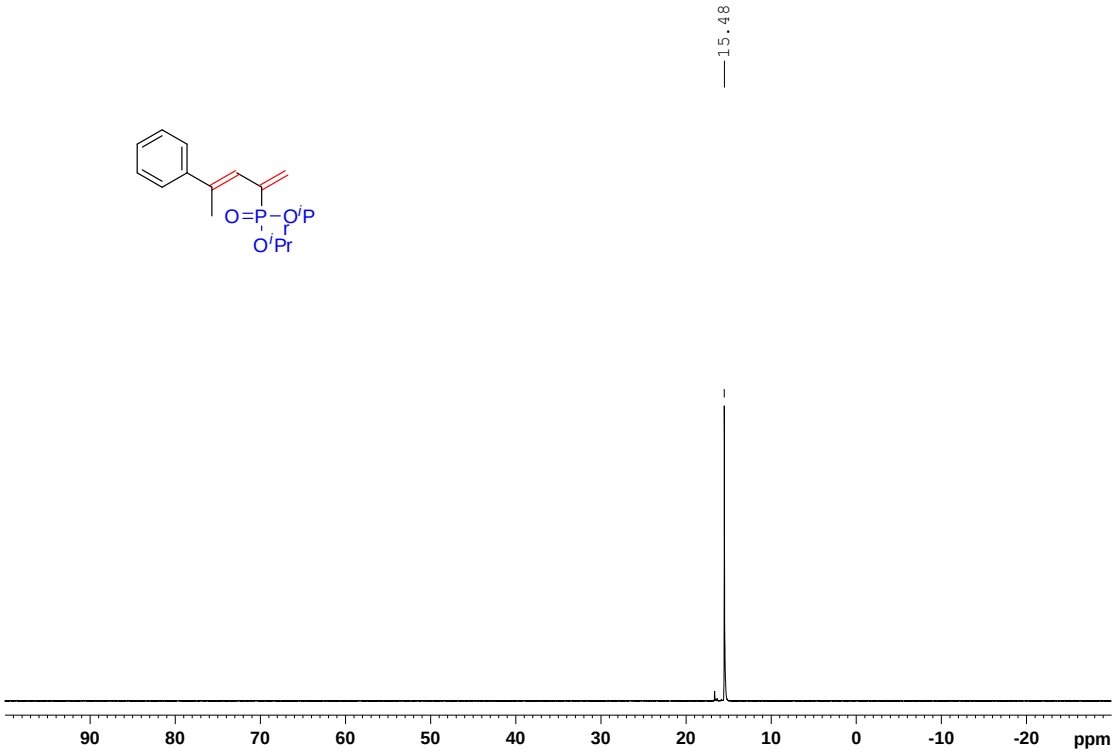
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3w**



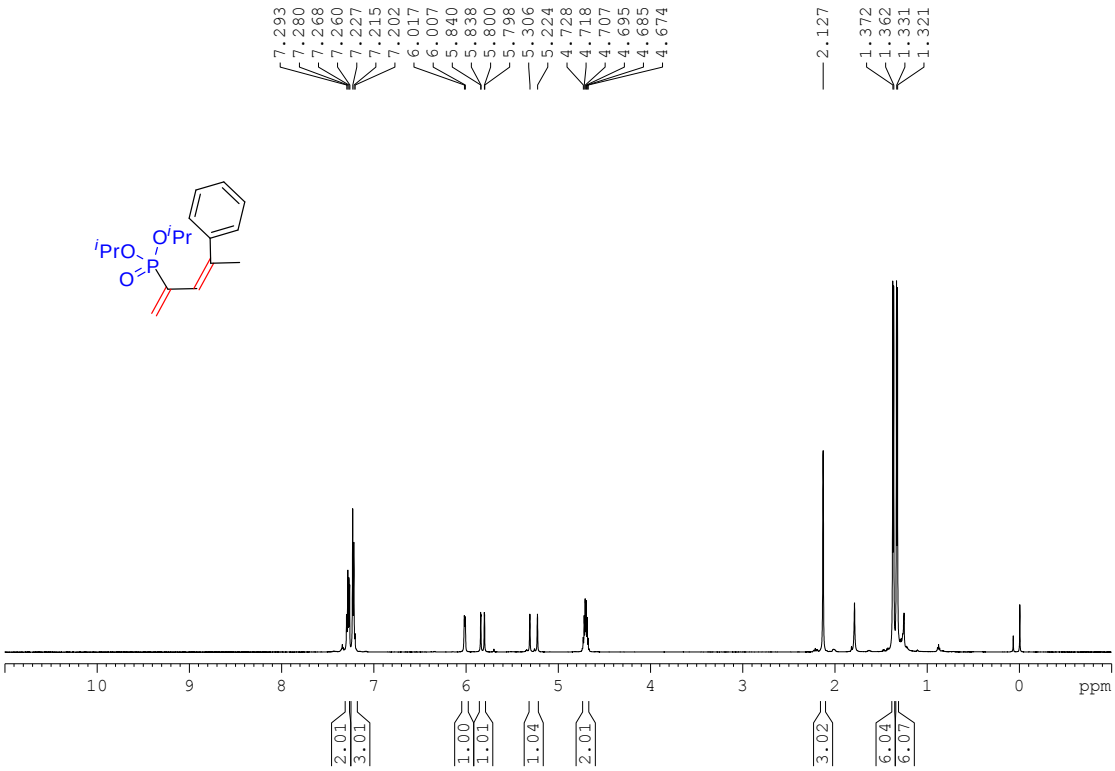
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3x**



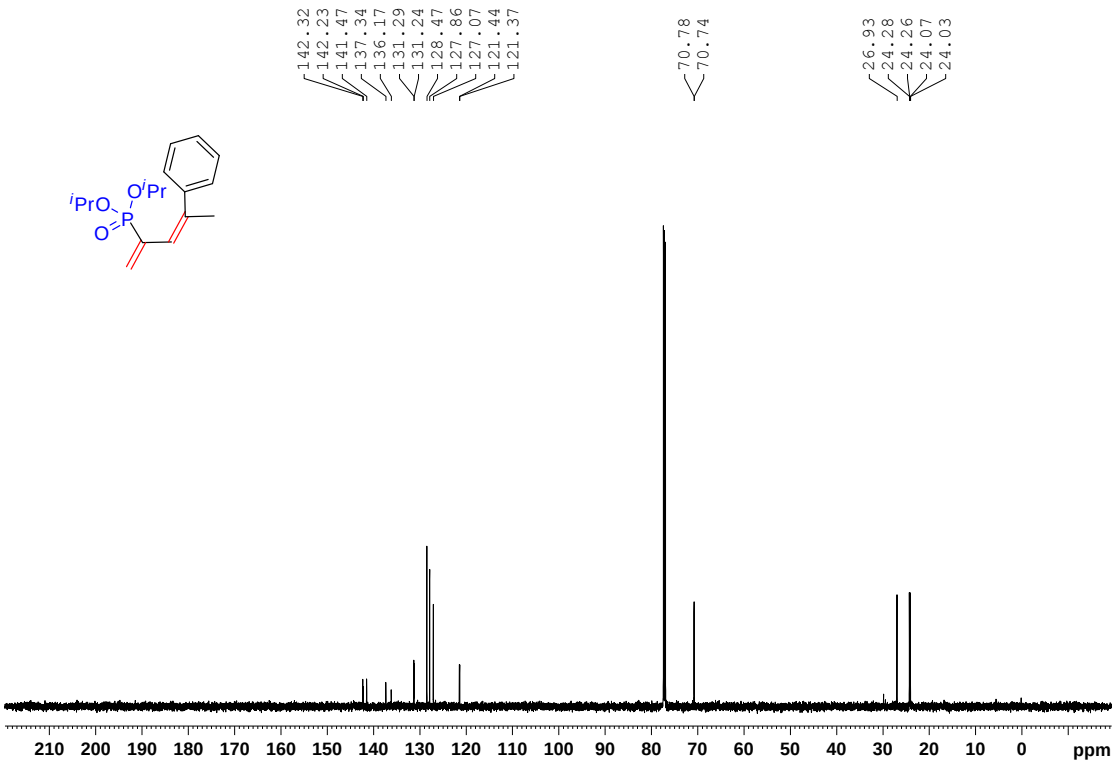
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3x**



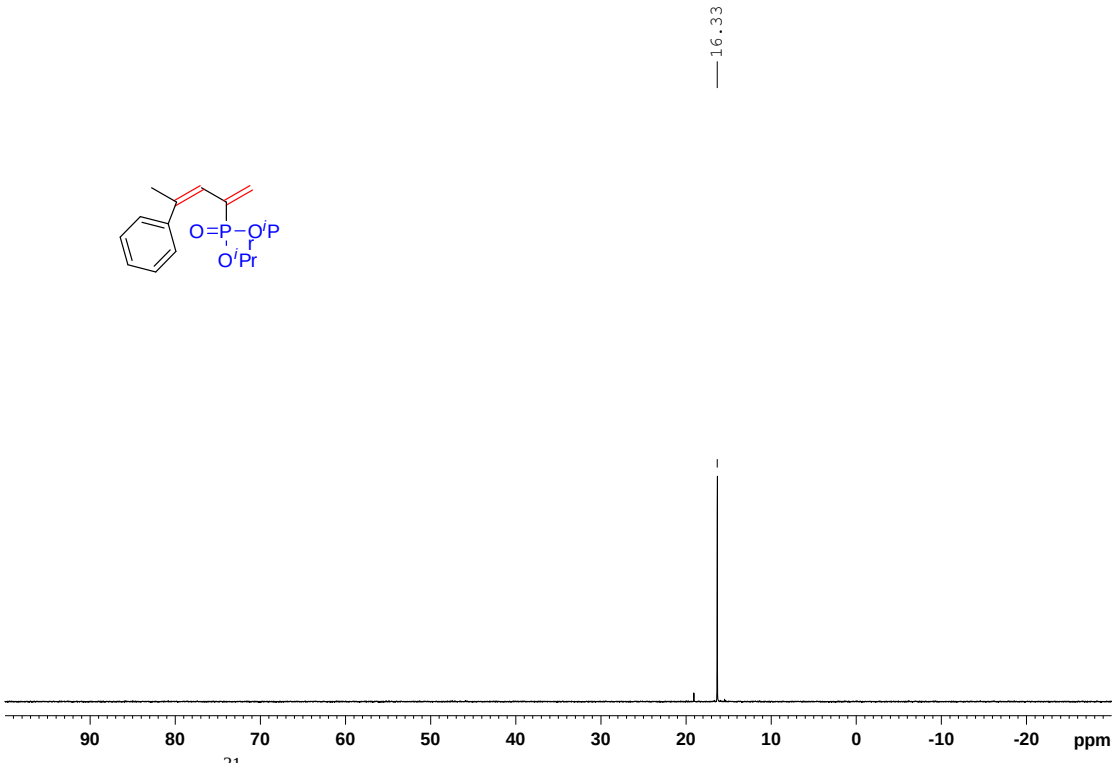
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3x**



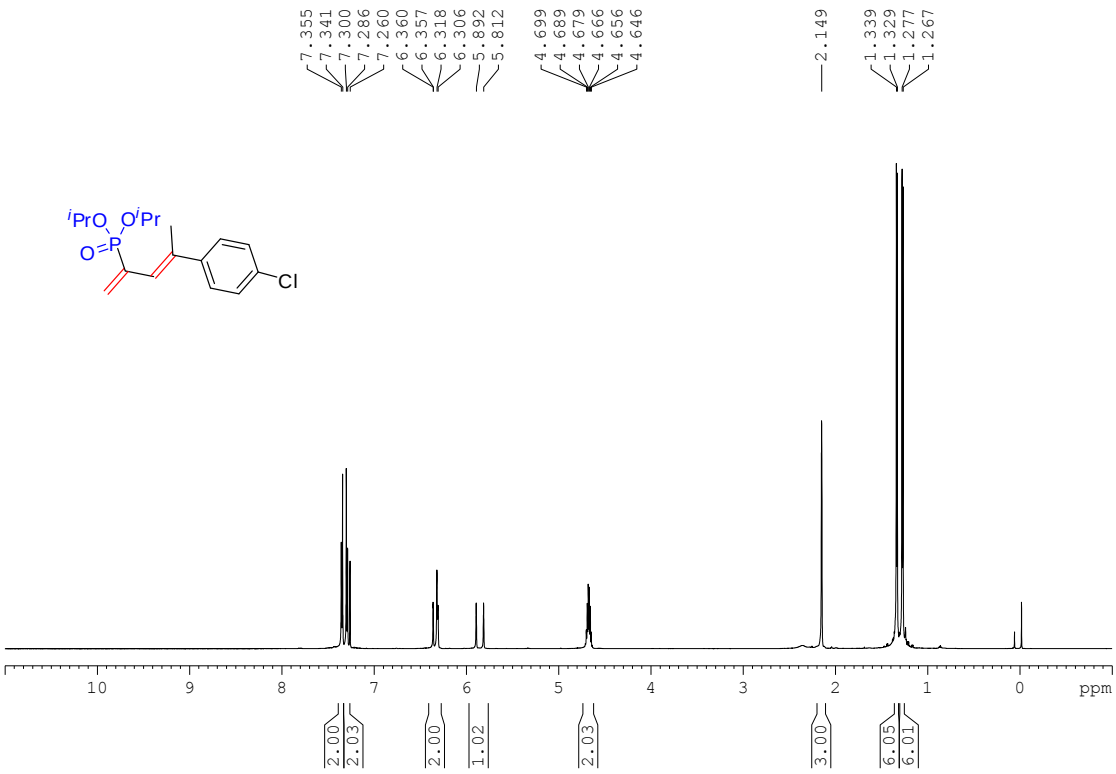
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3x**



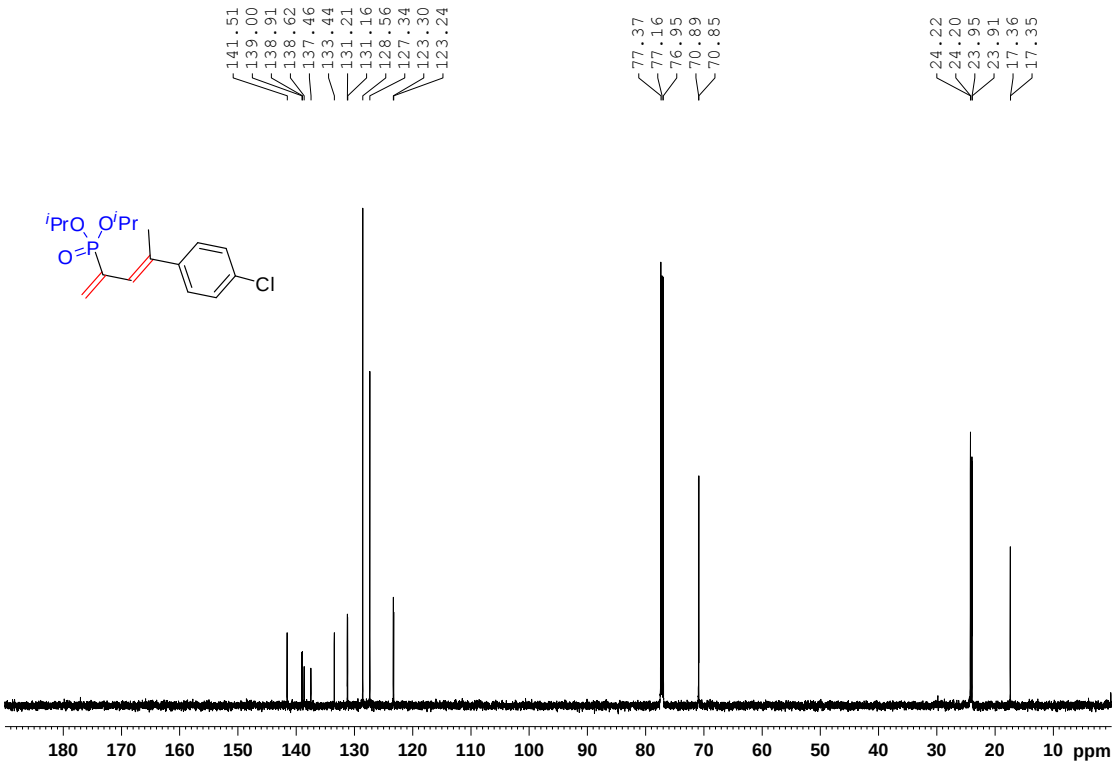
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3x**



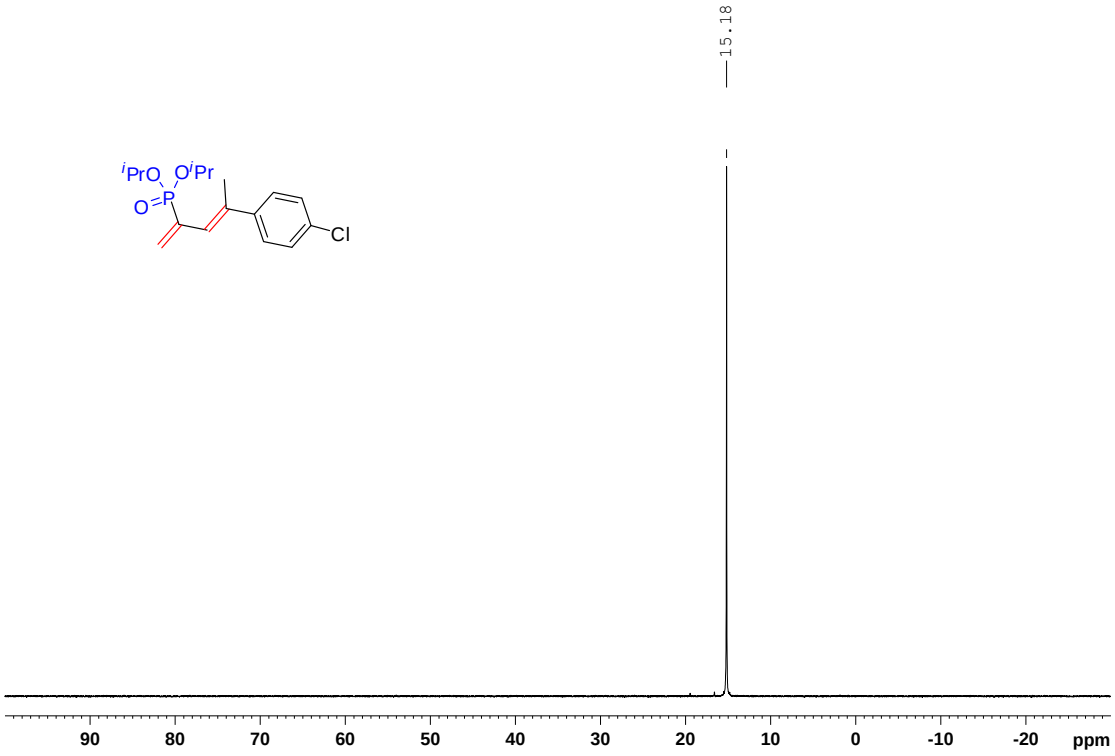
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3x**



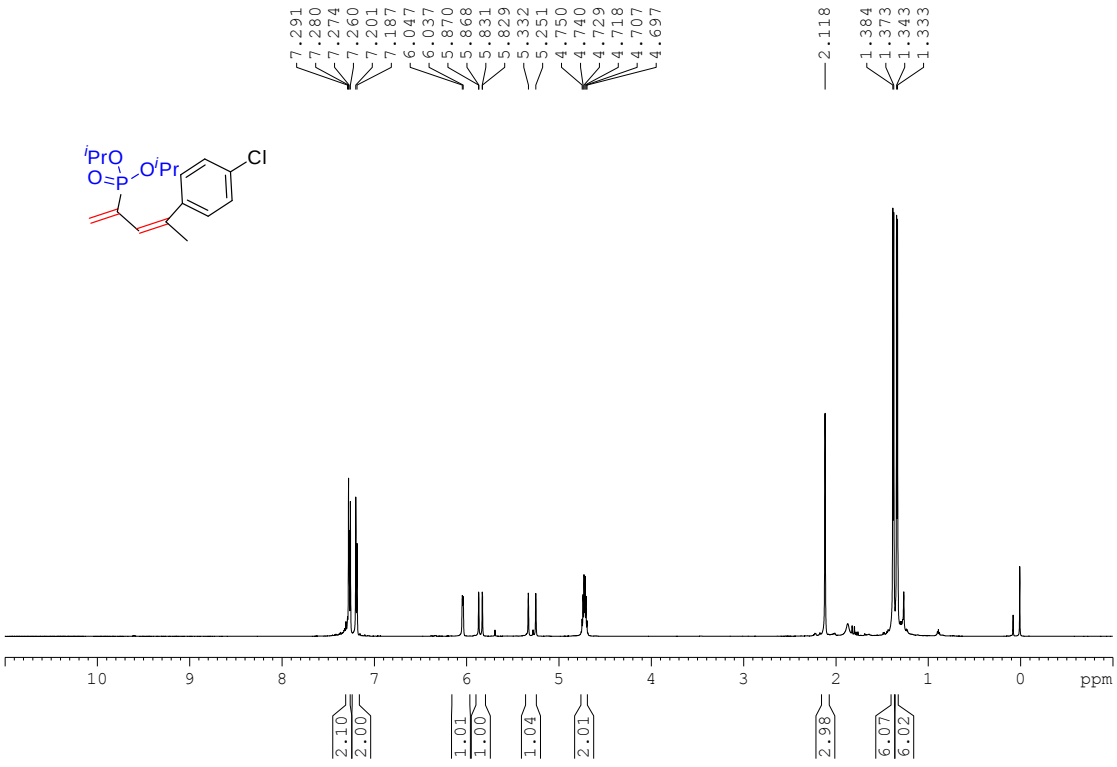
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3y**



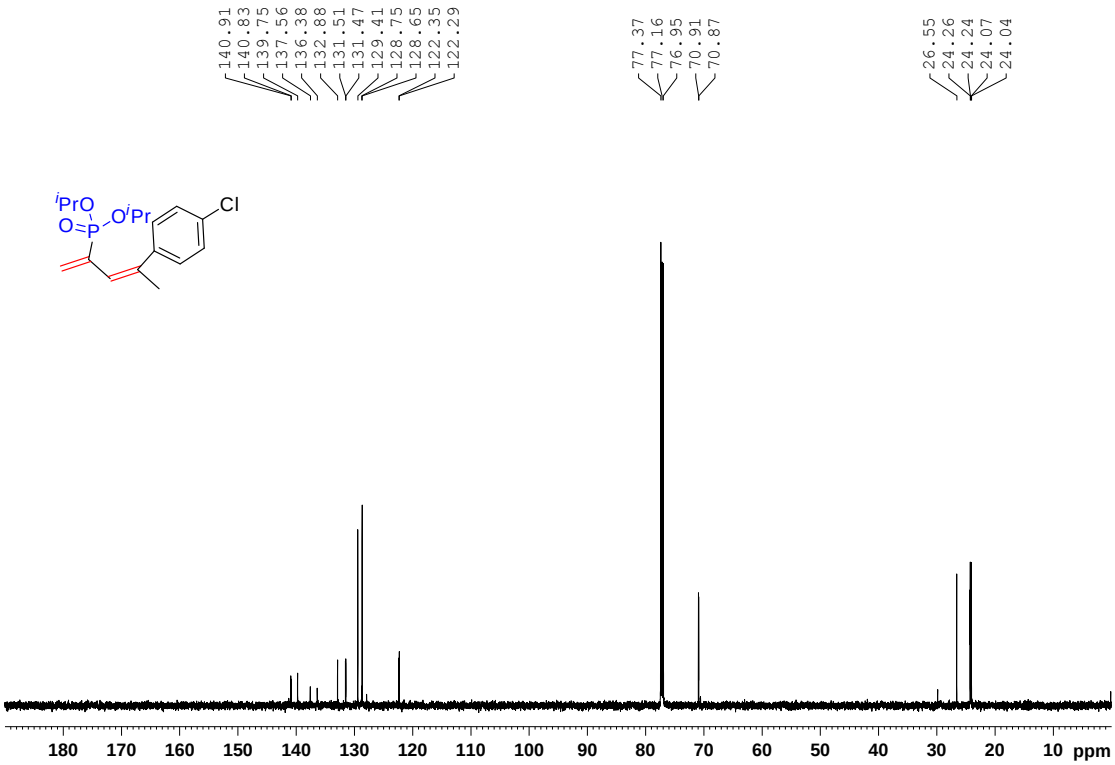
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3y**



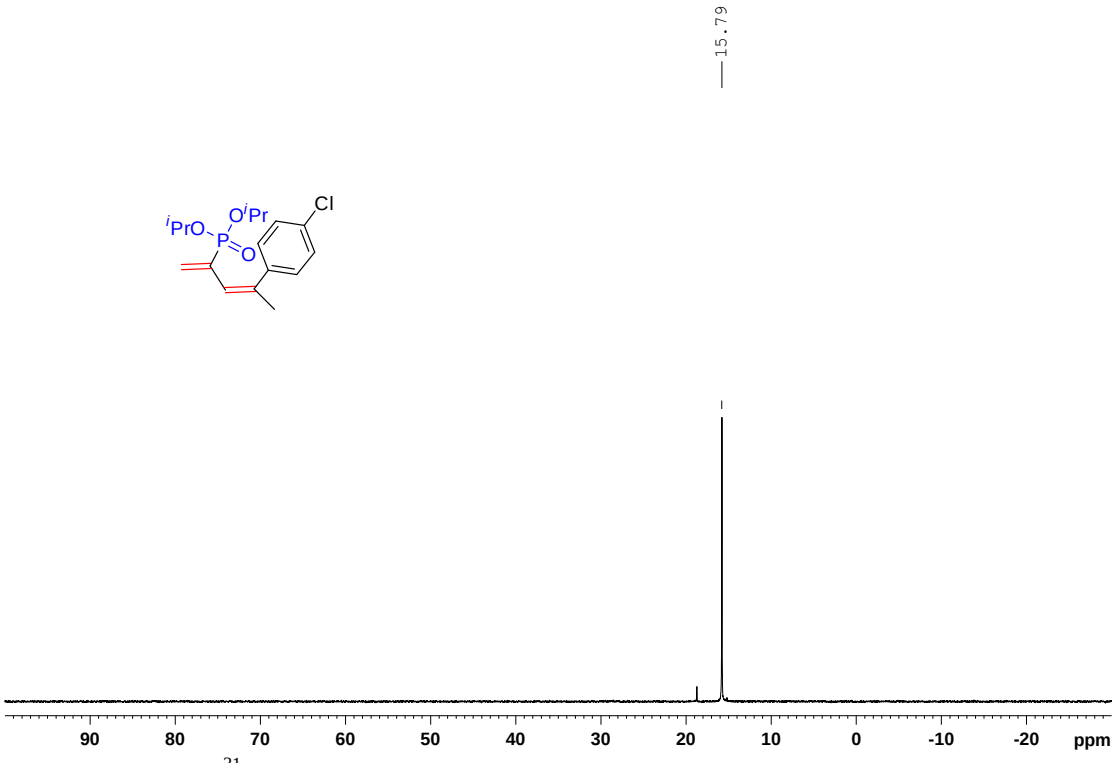
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3y**



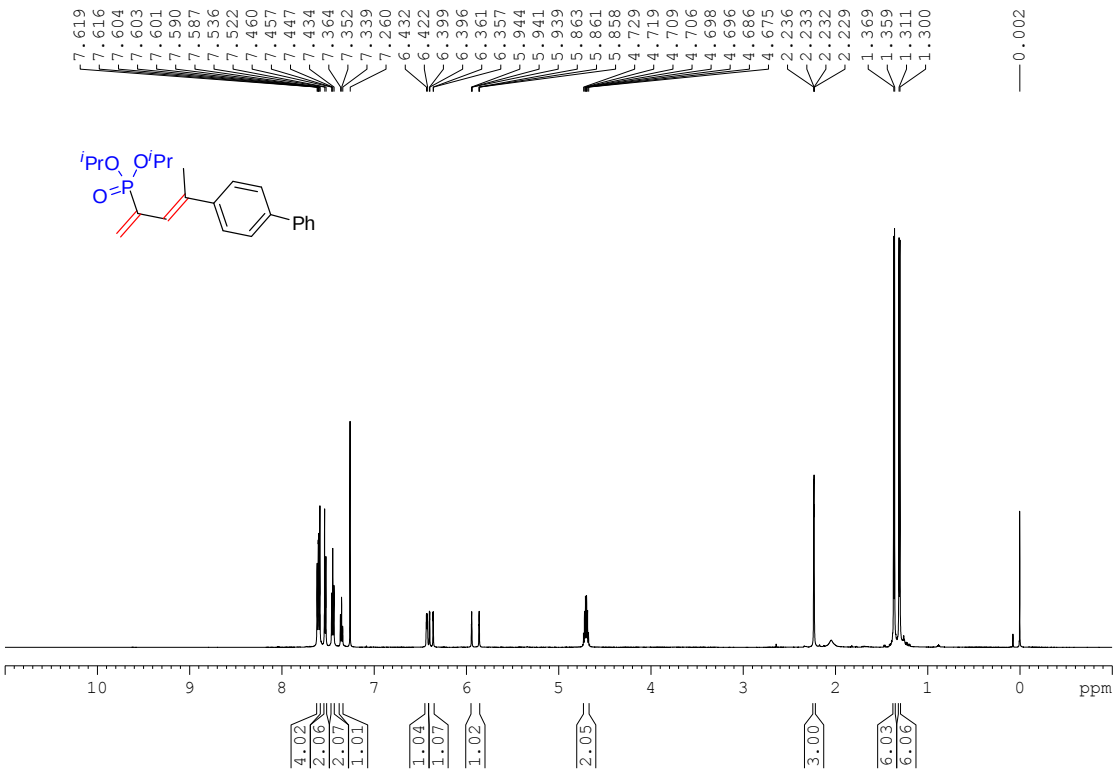
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3y**



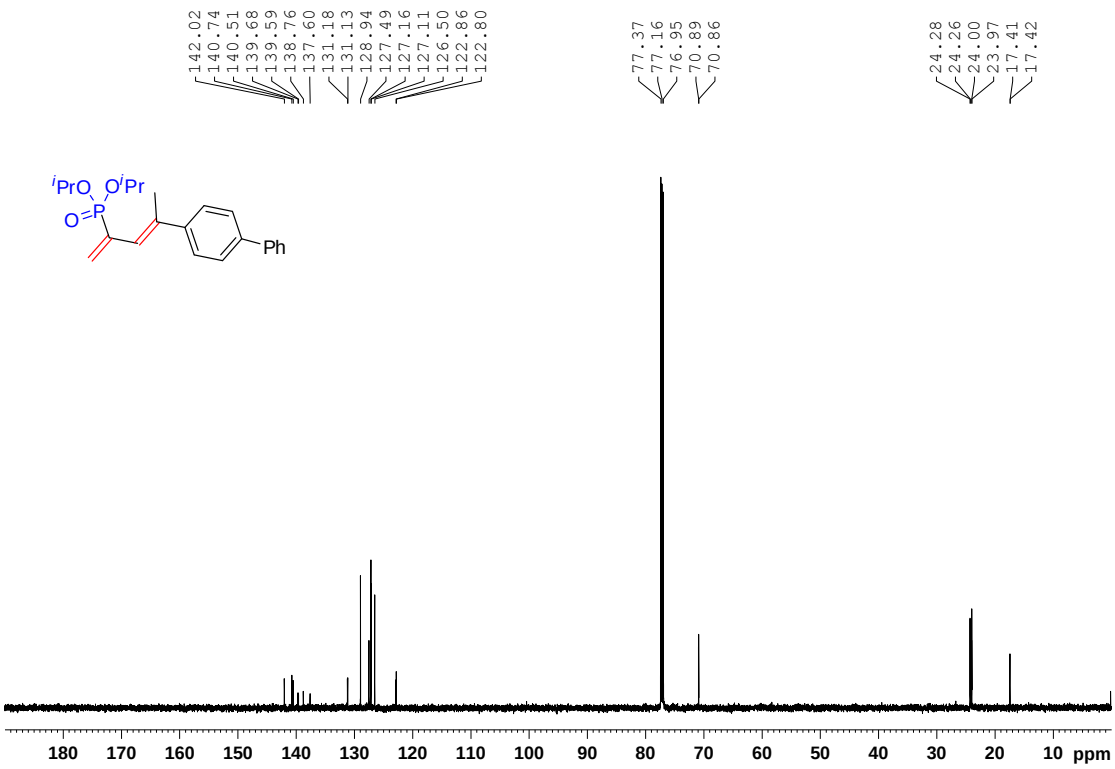
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3y**



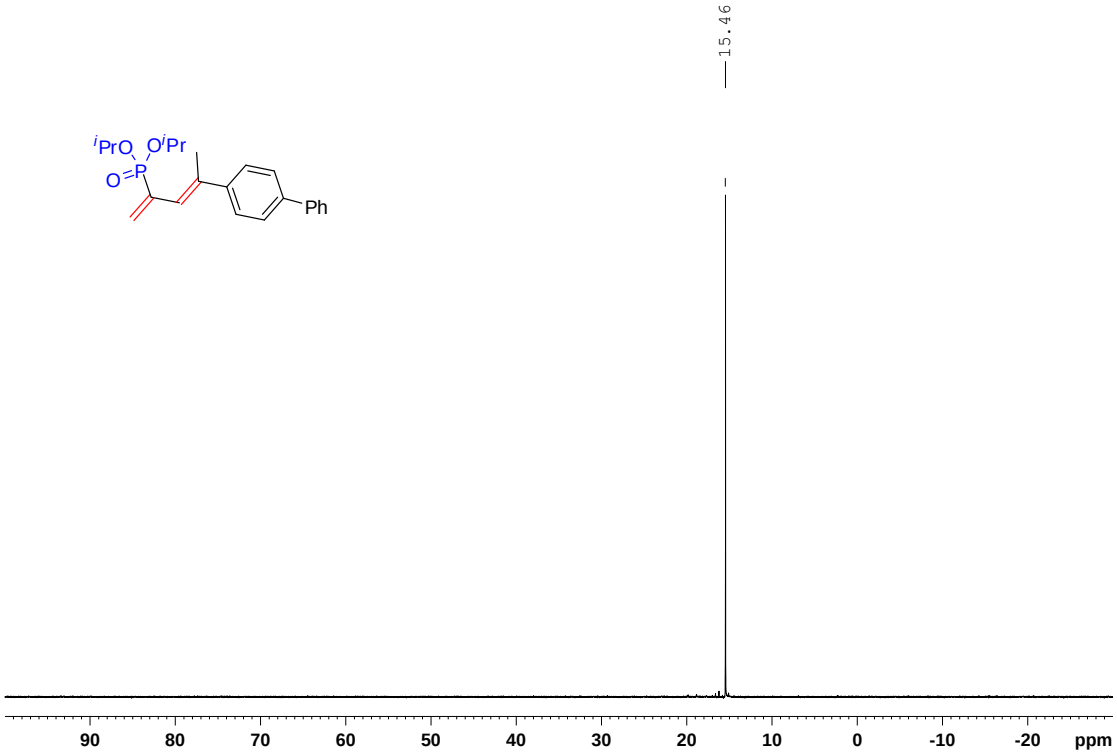
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3y**



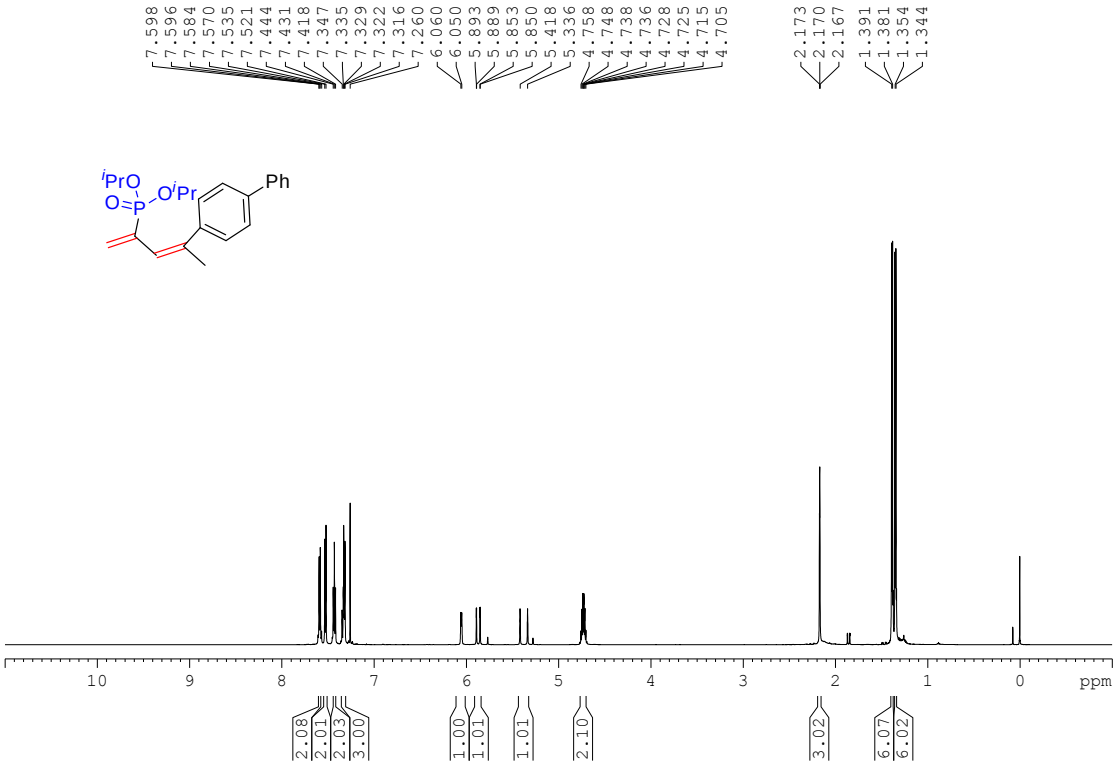
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3z**



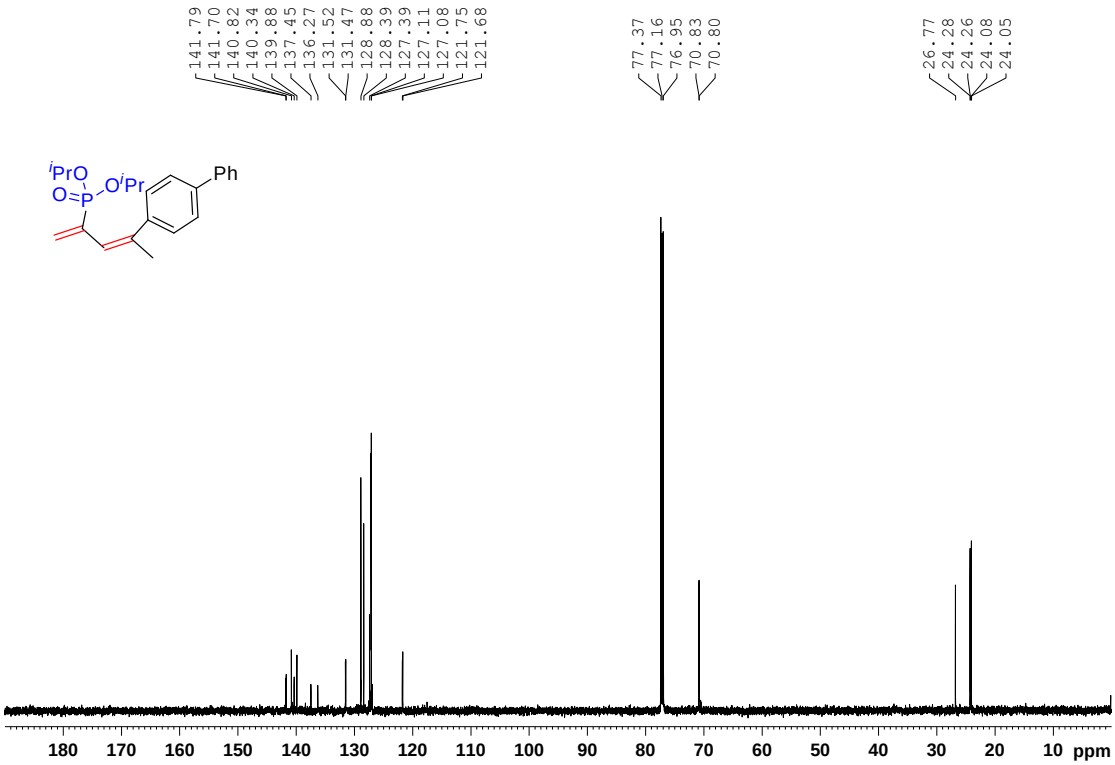
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3z**



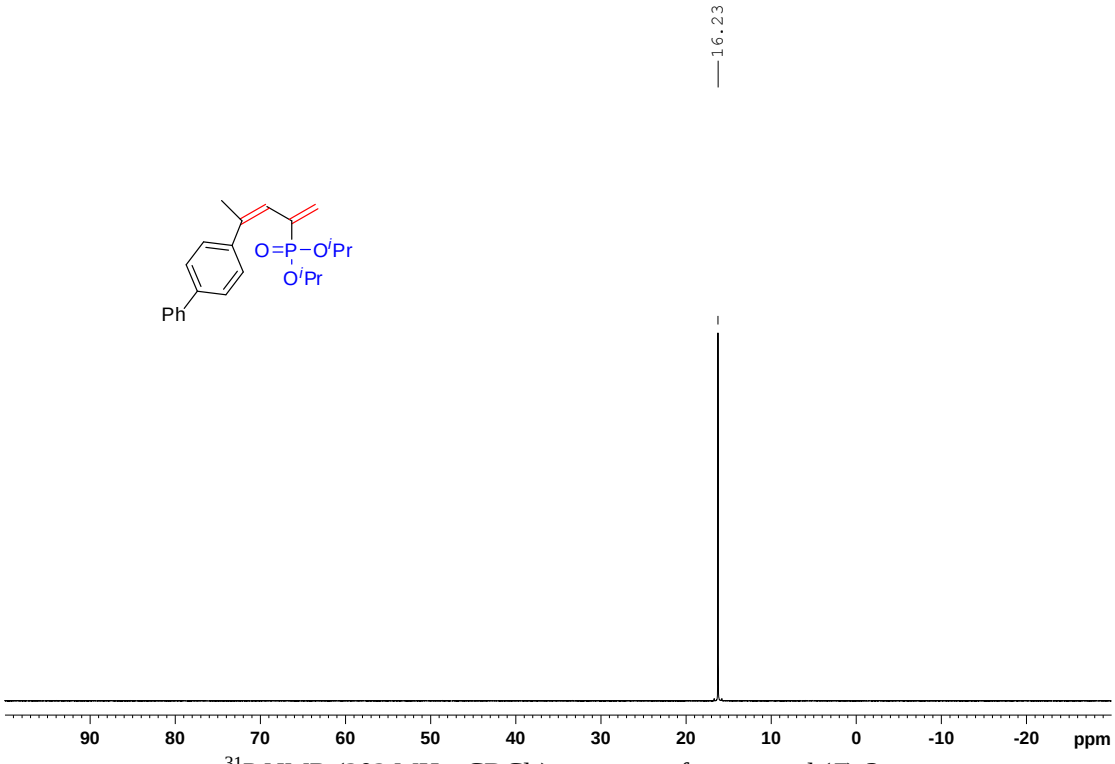
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3z**



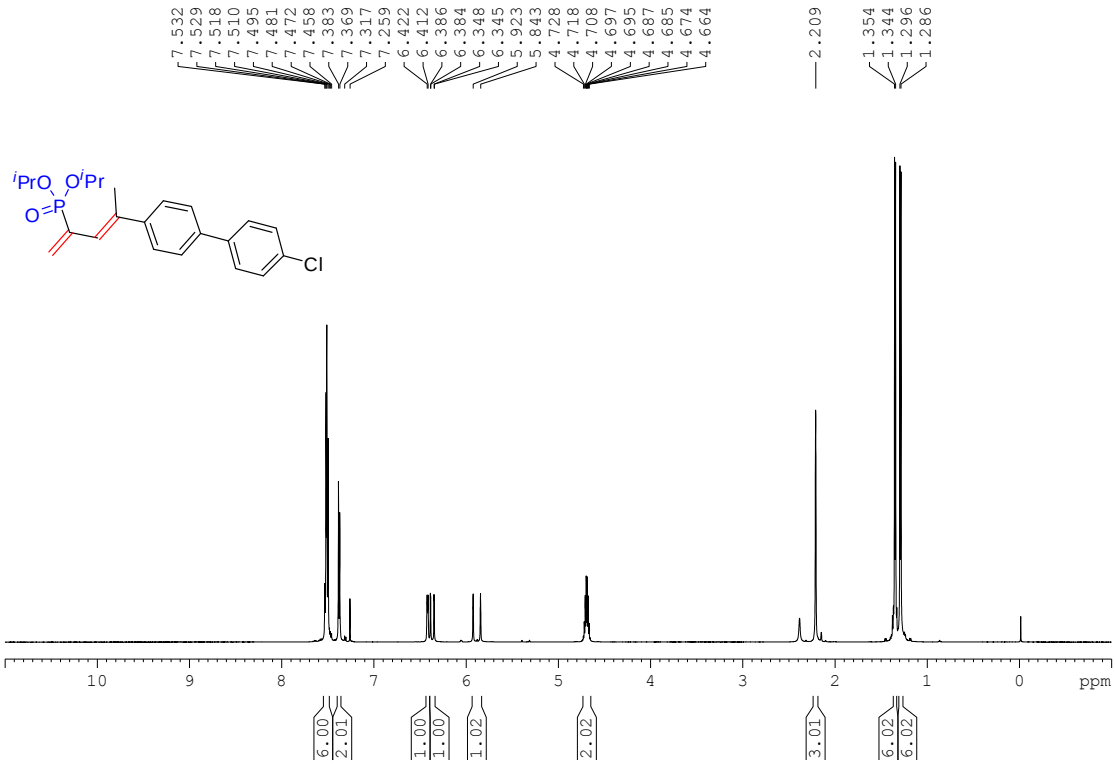
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3z**



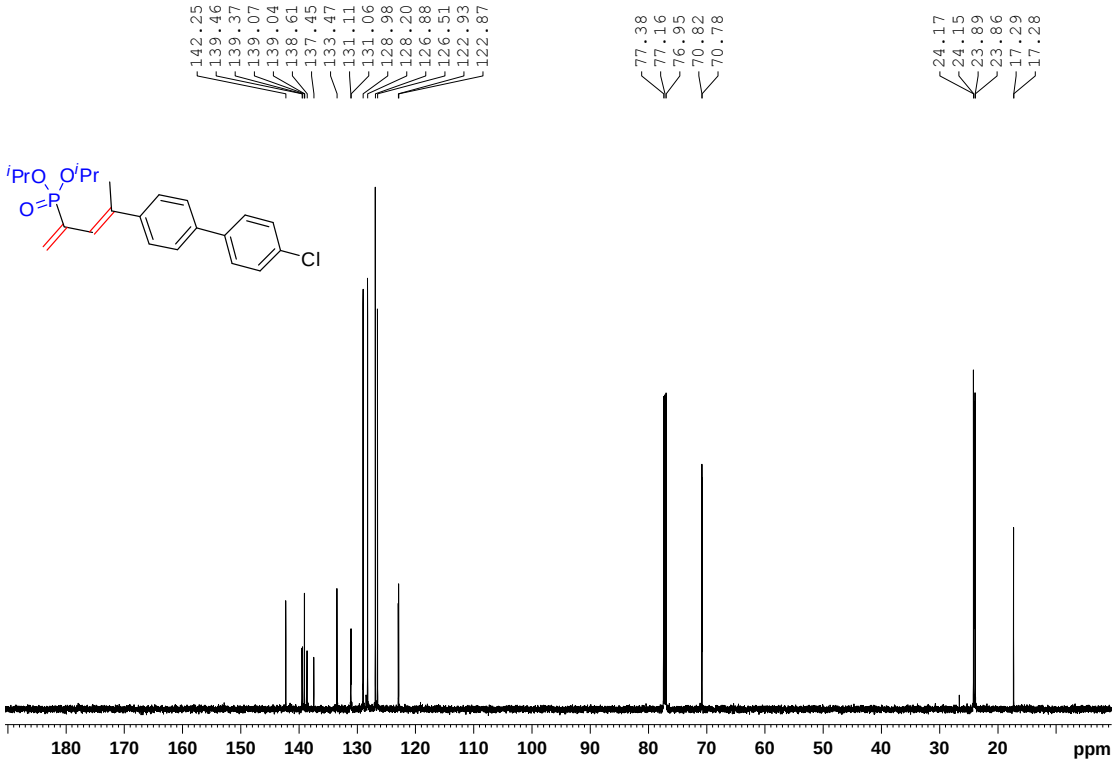
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3z**



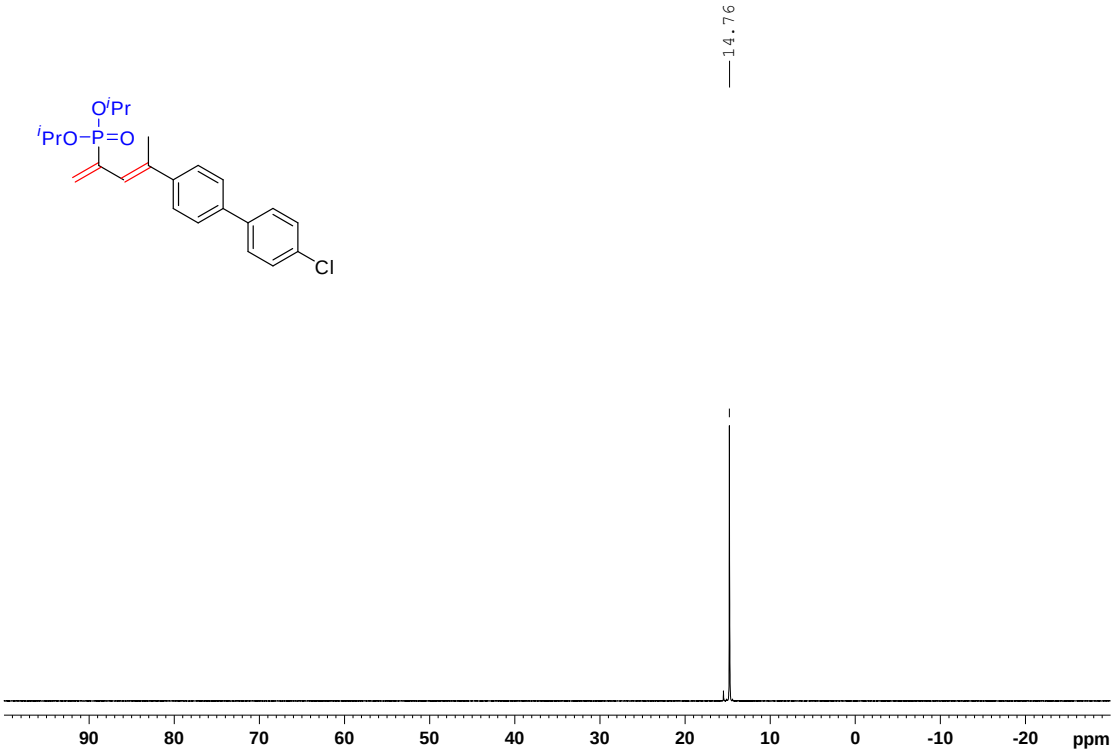
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3z**



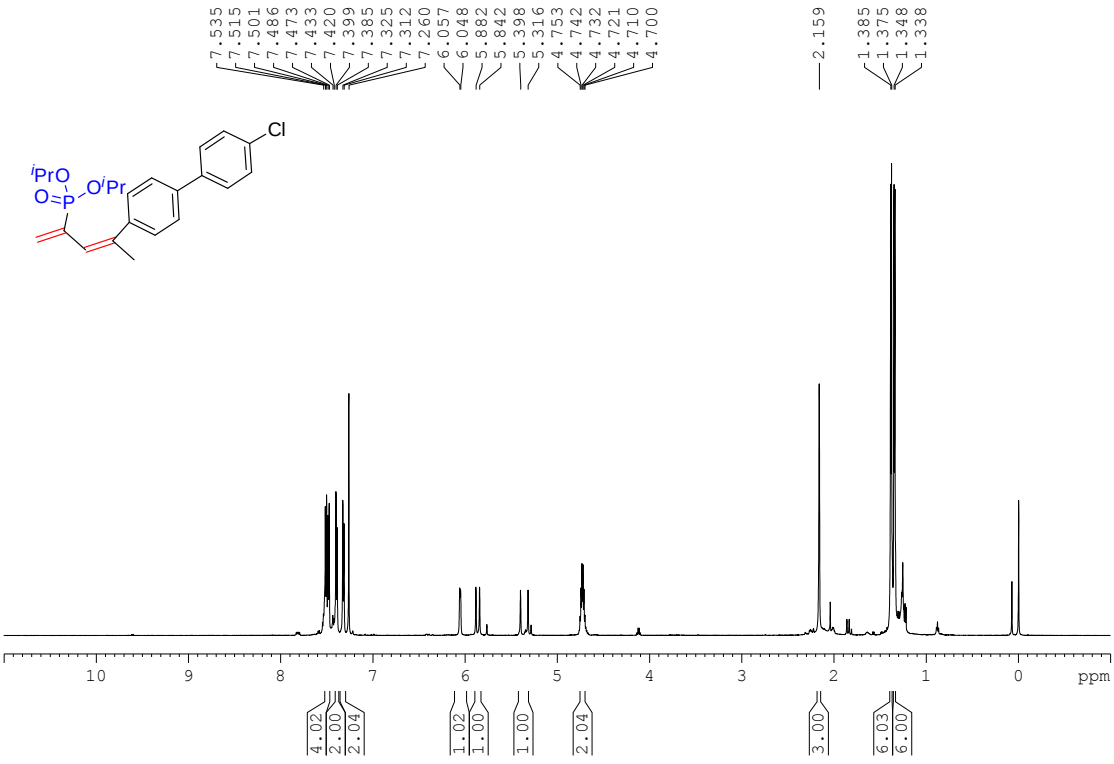
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3aa**



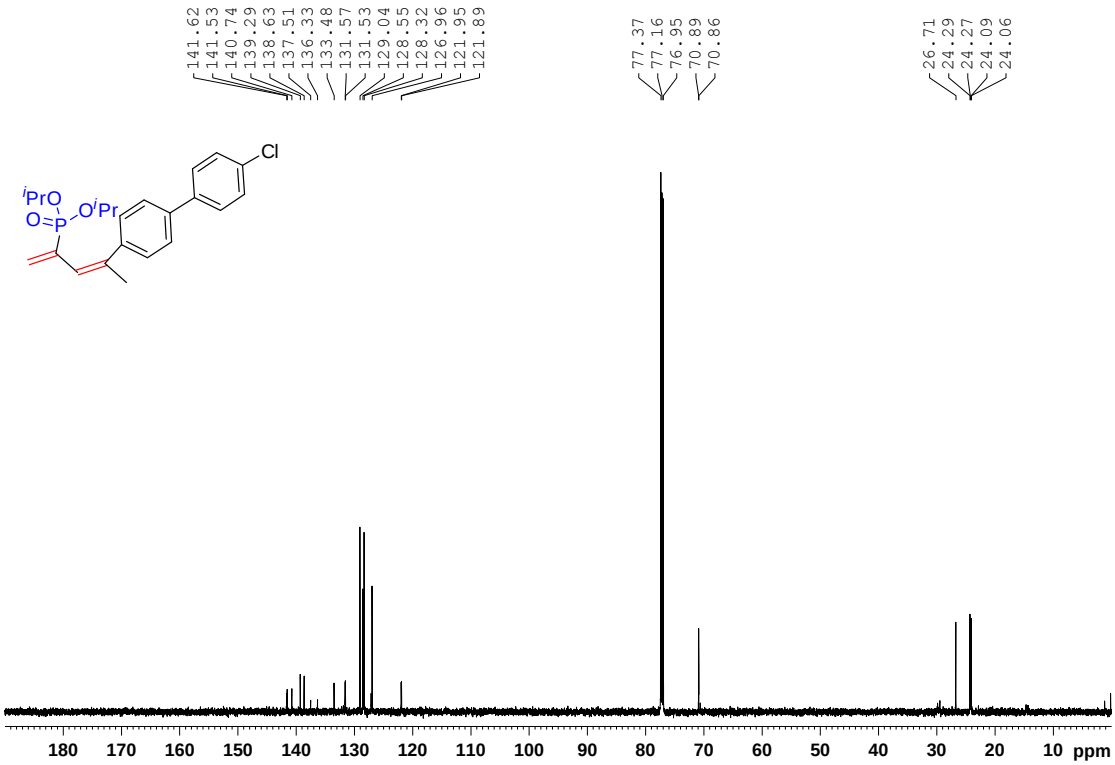
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3aa**



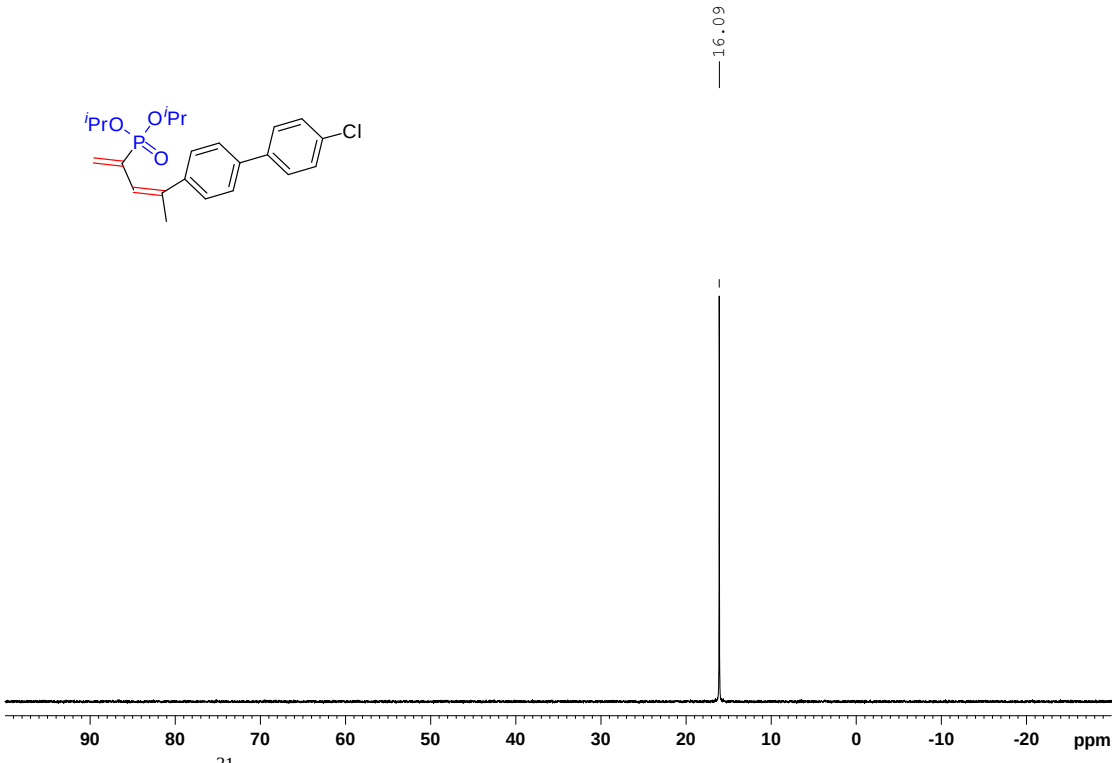
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3aa**



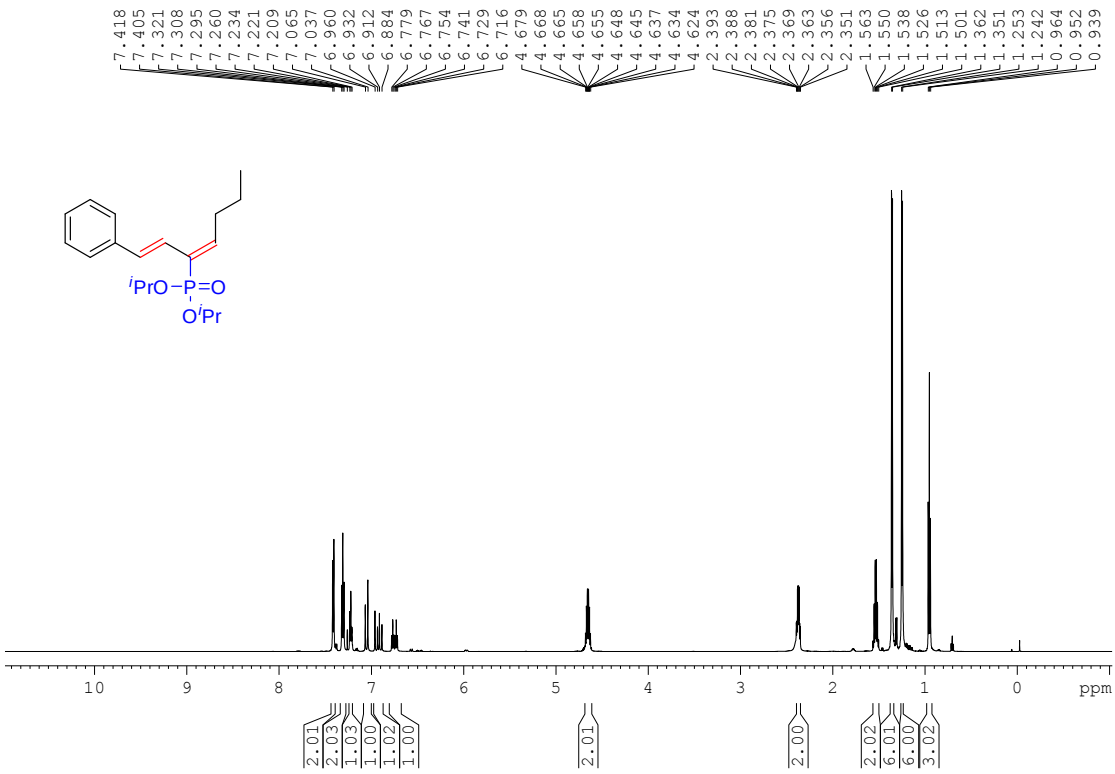
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3aa**



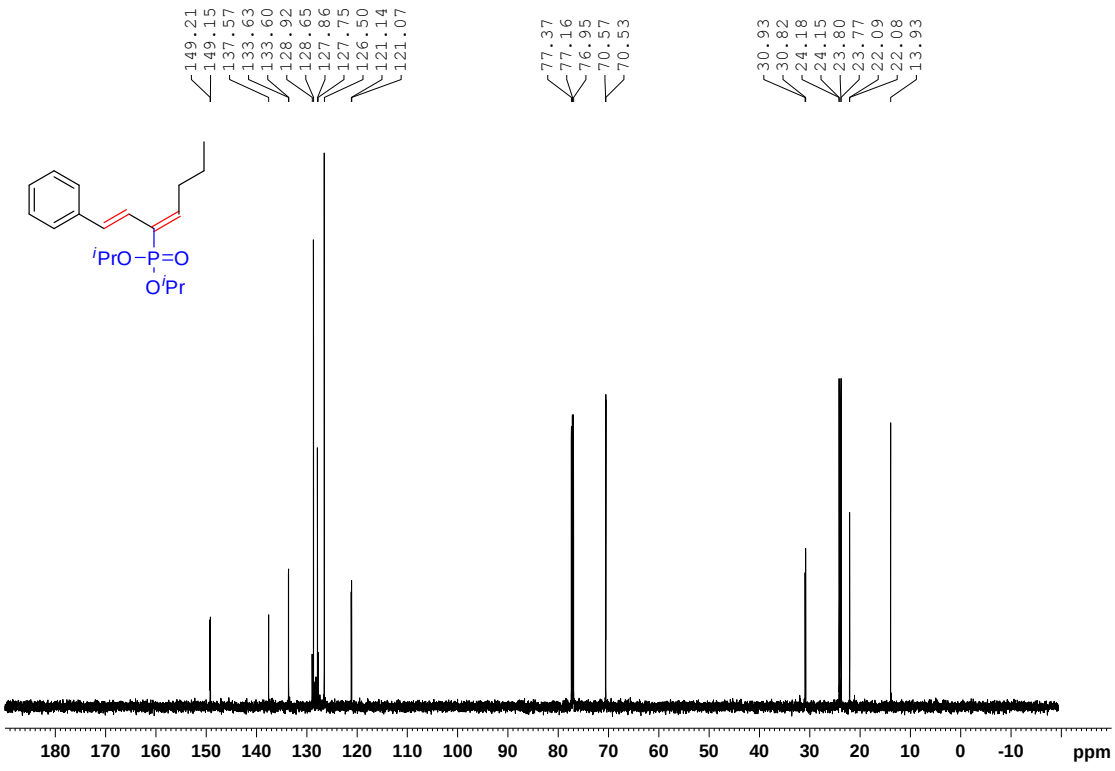
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3aa**



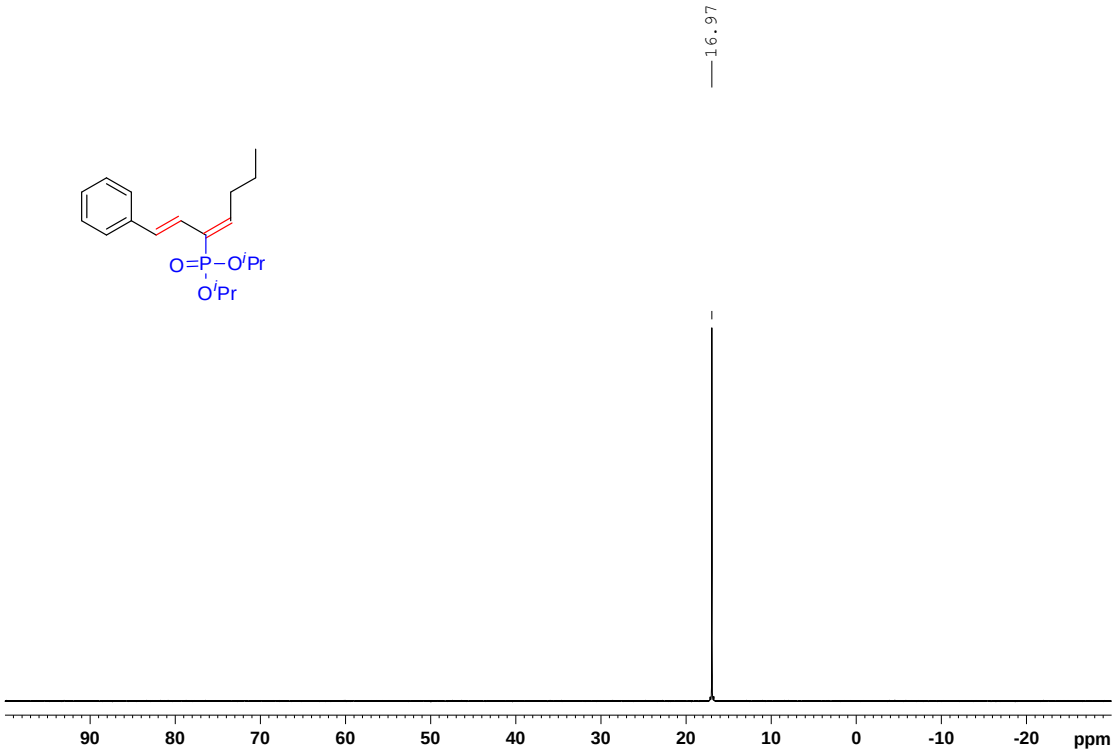
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3aa**



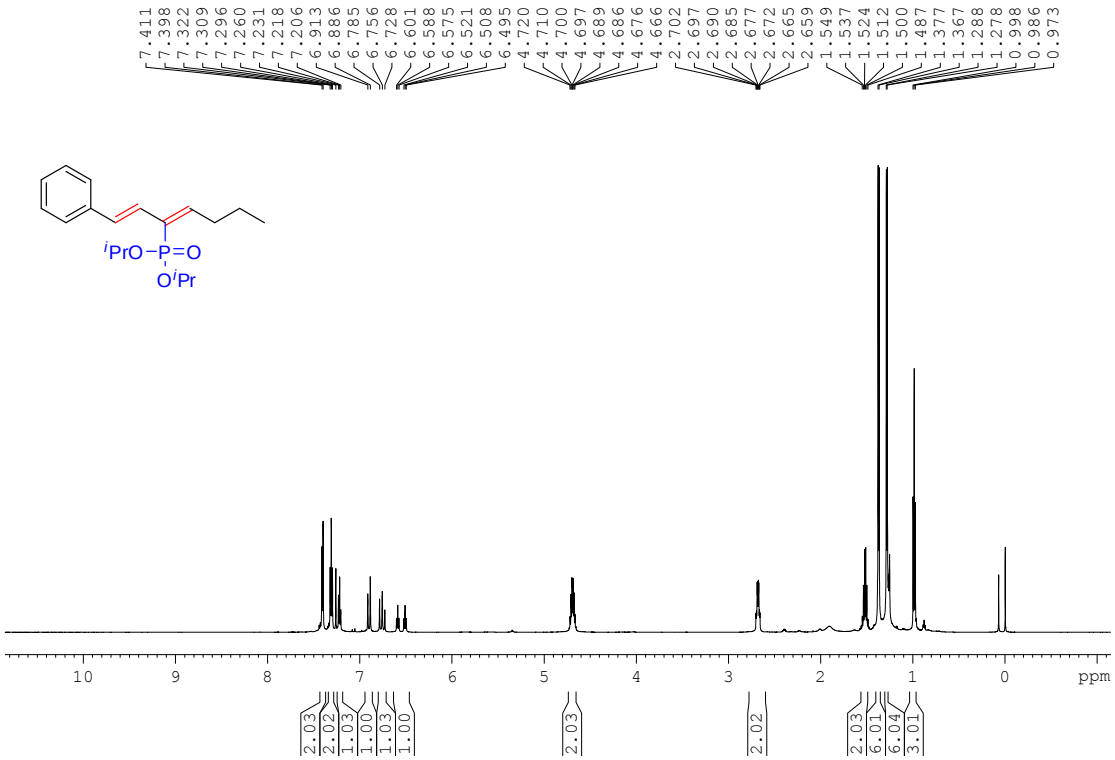
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ab**



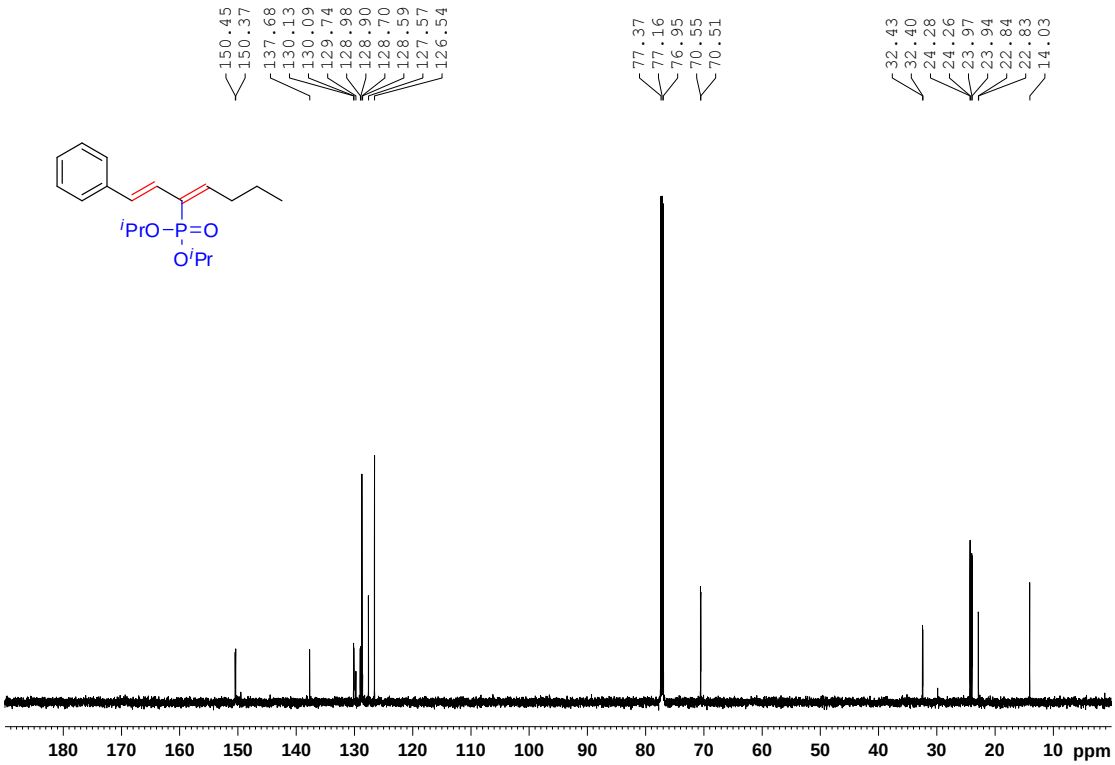
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ab**



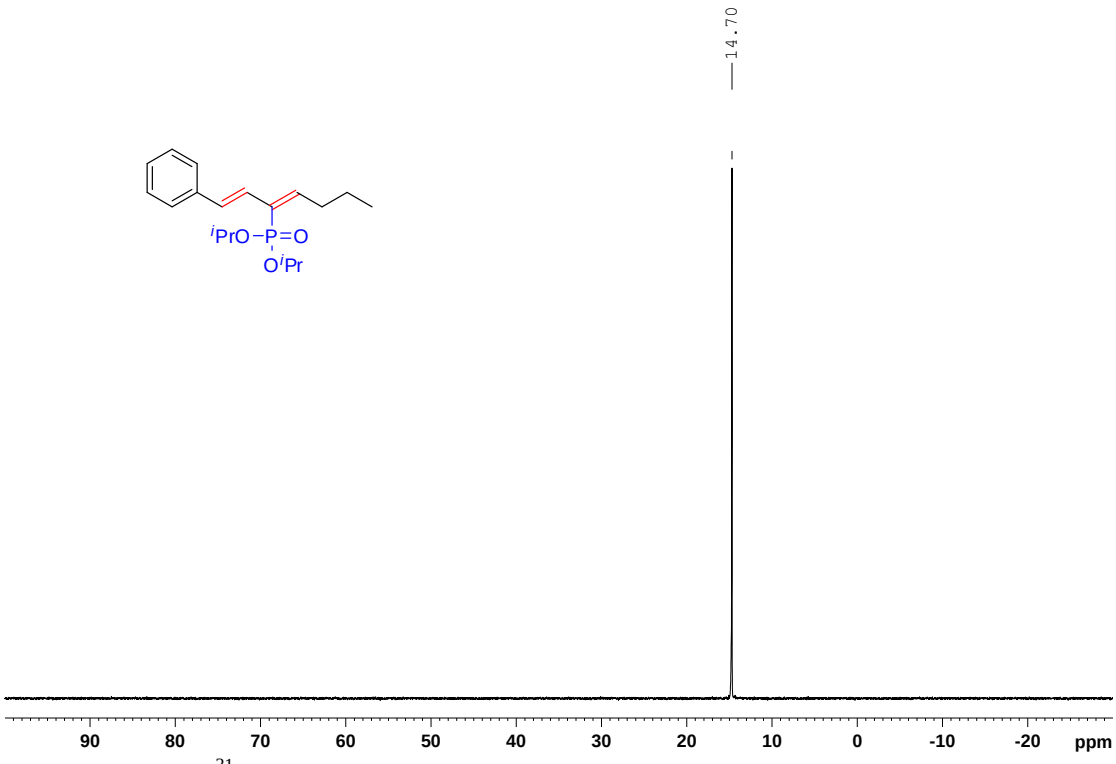
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ab**



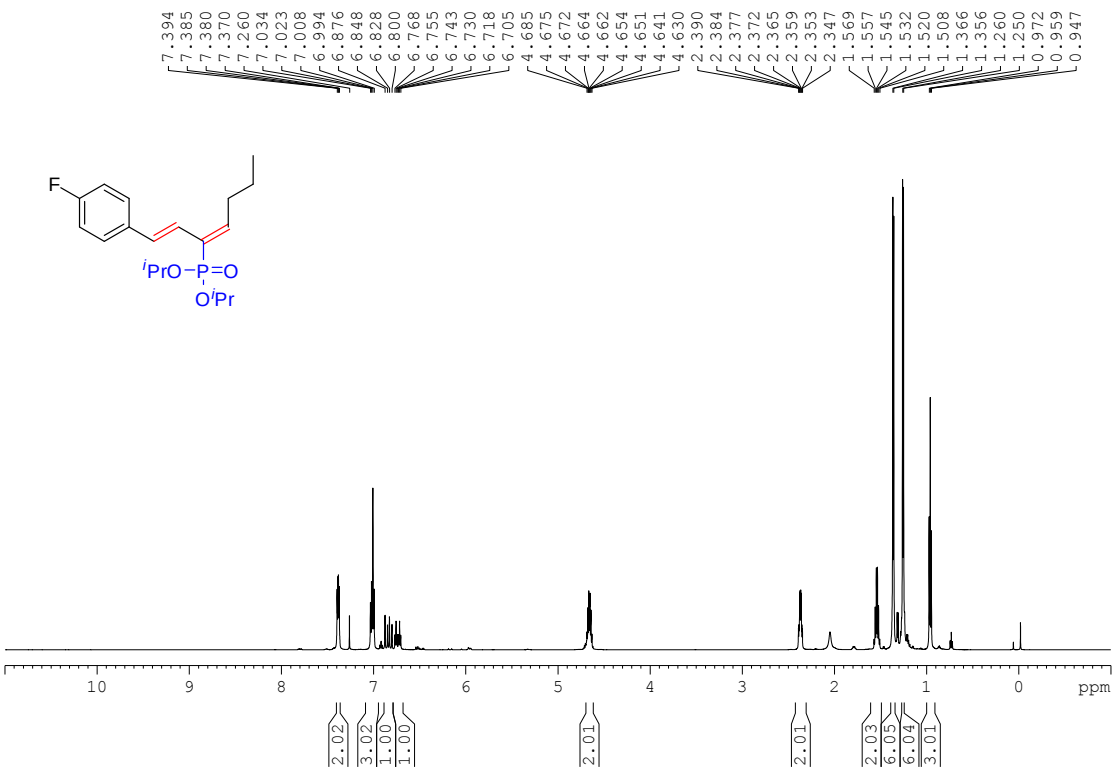
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ab**



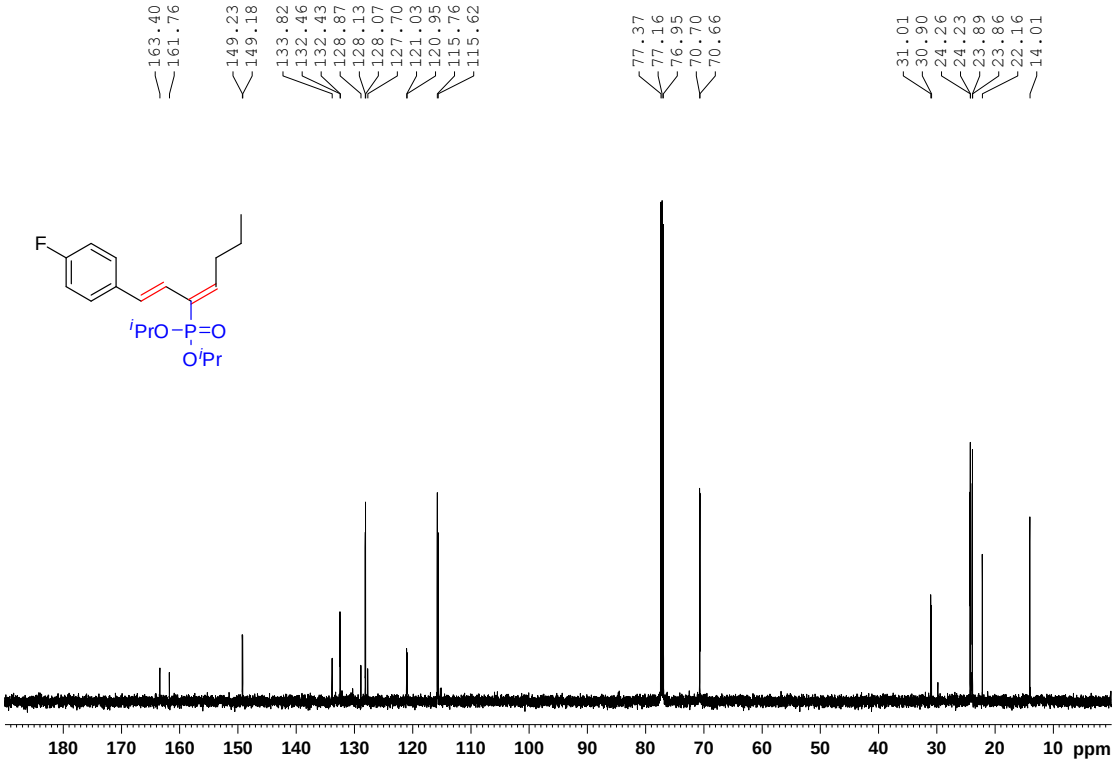
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ab**



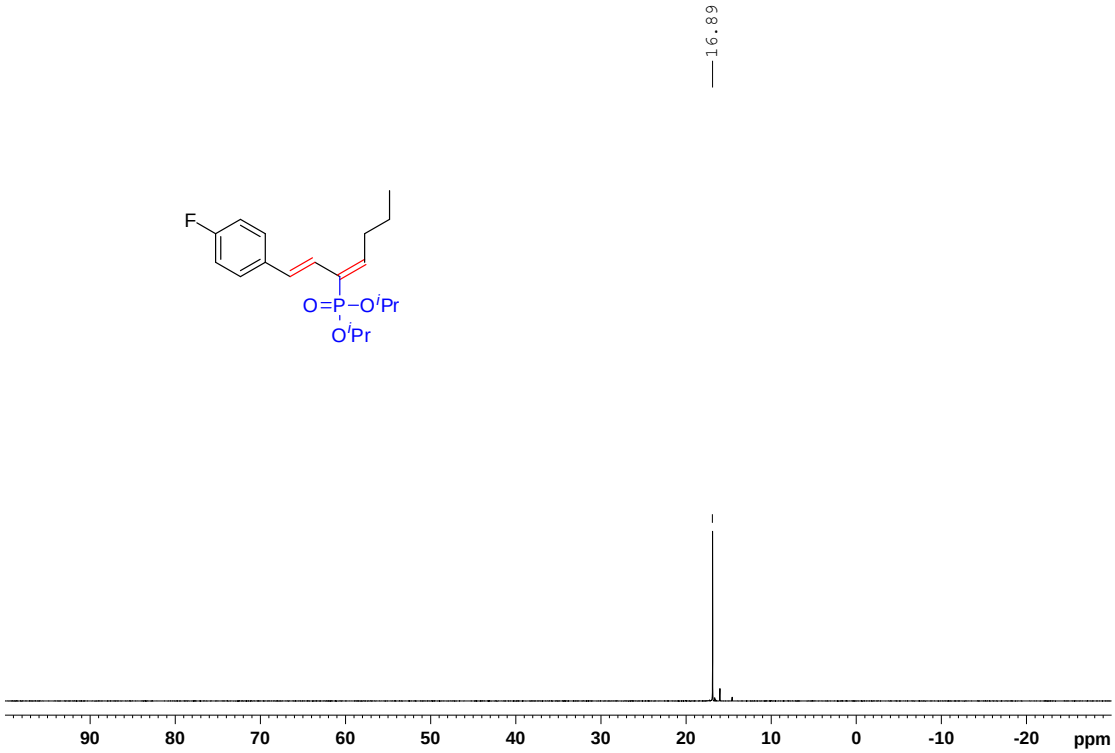
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ab**



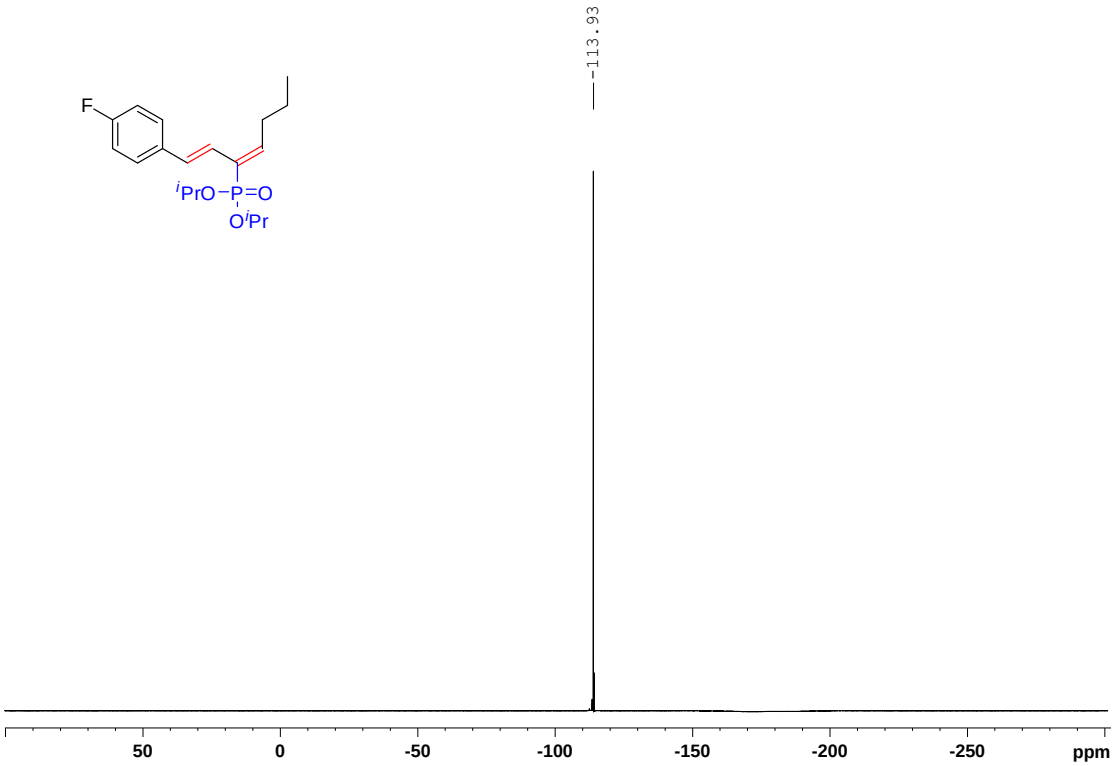
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ac**



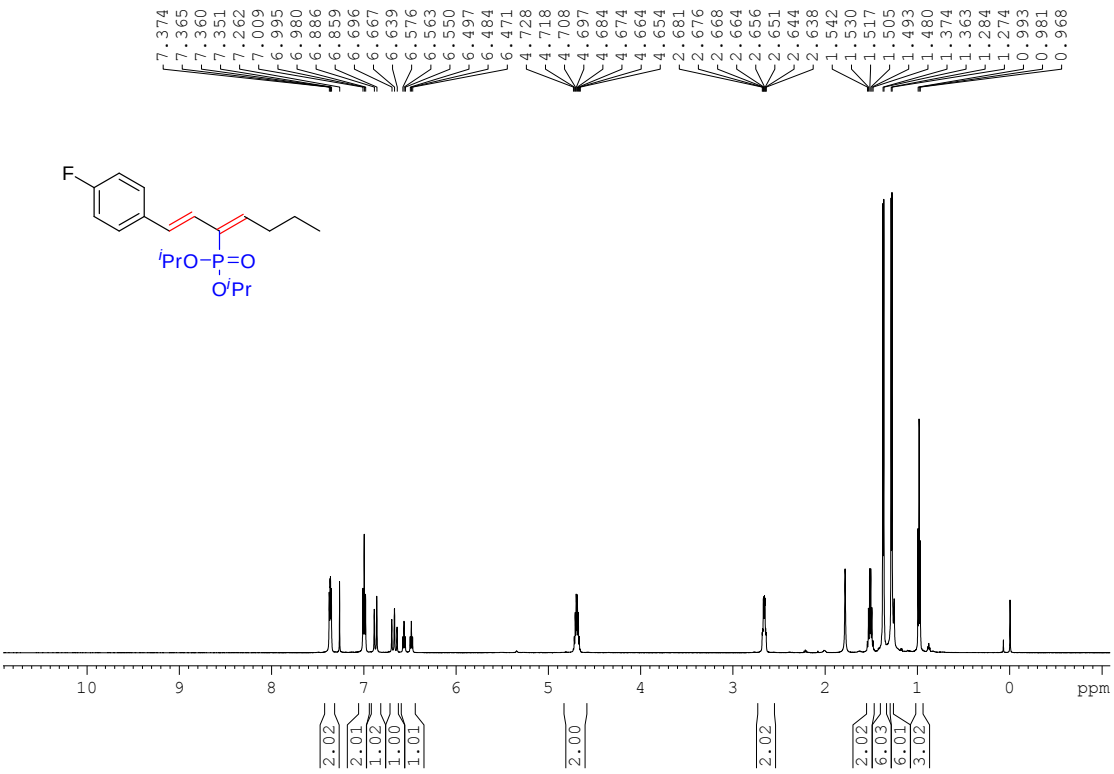
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ac**



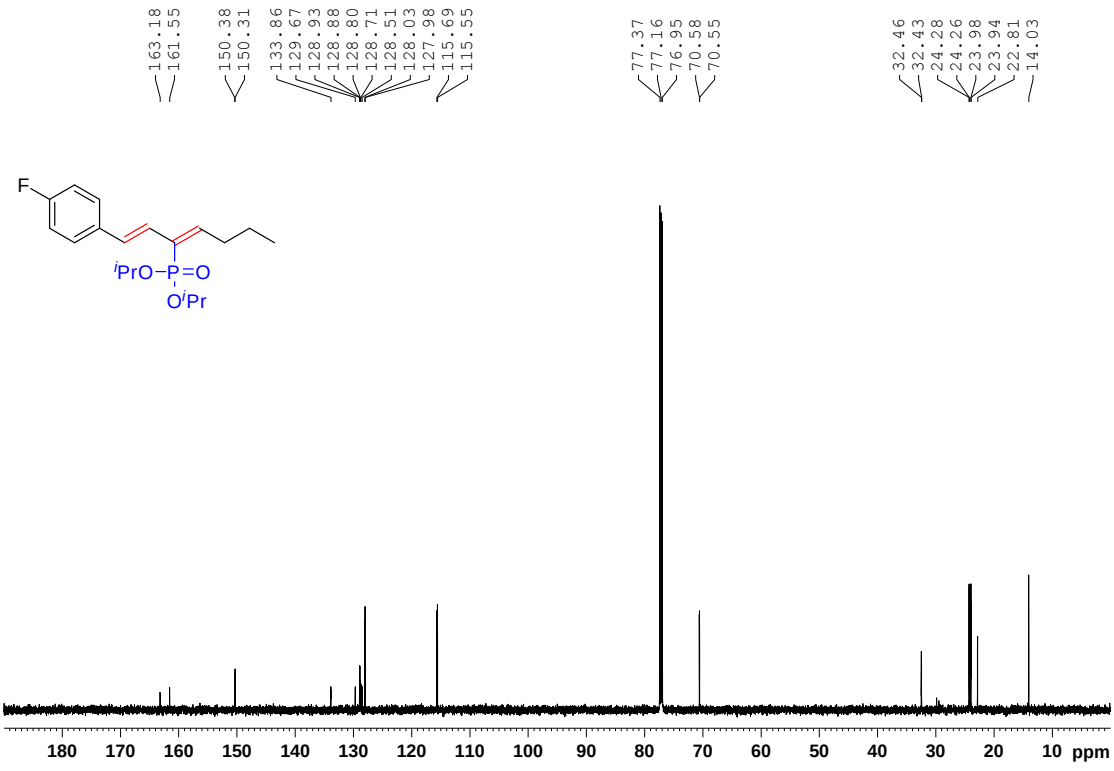
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ac**



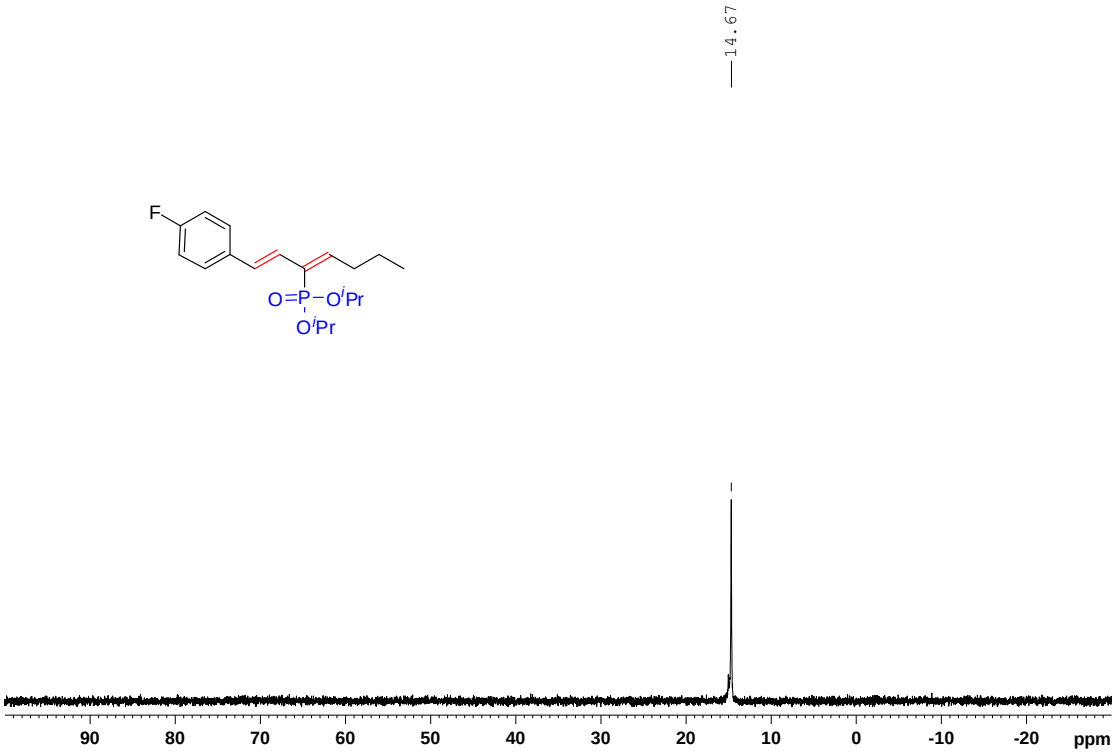
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ac**



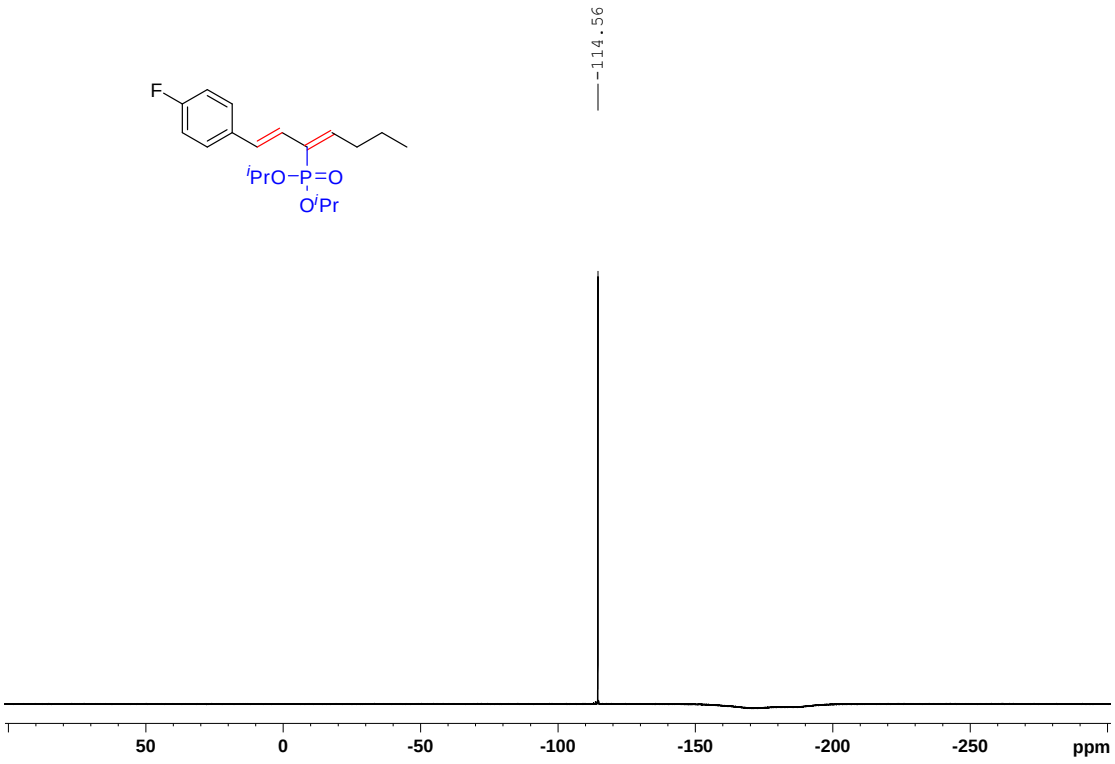
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ac**



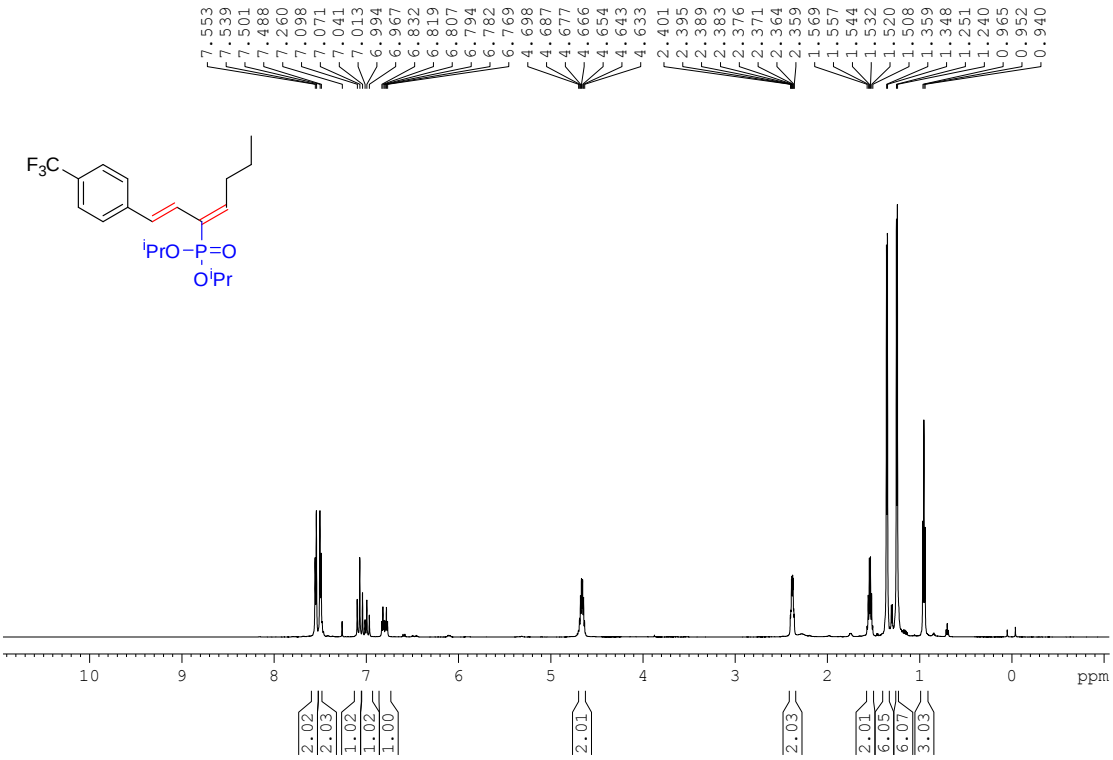
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ac**



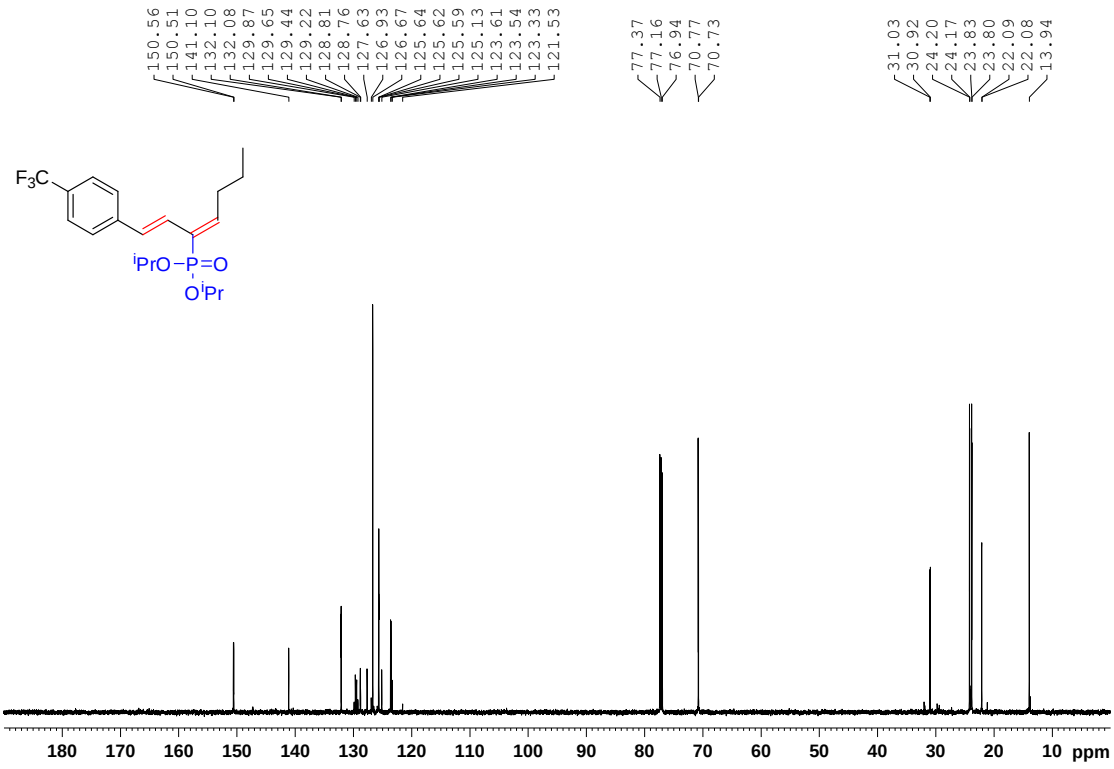
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ac**



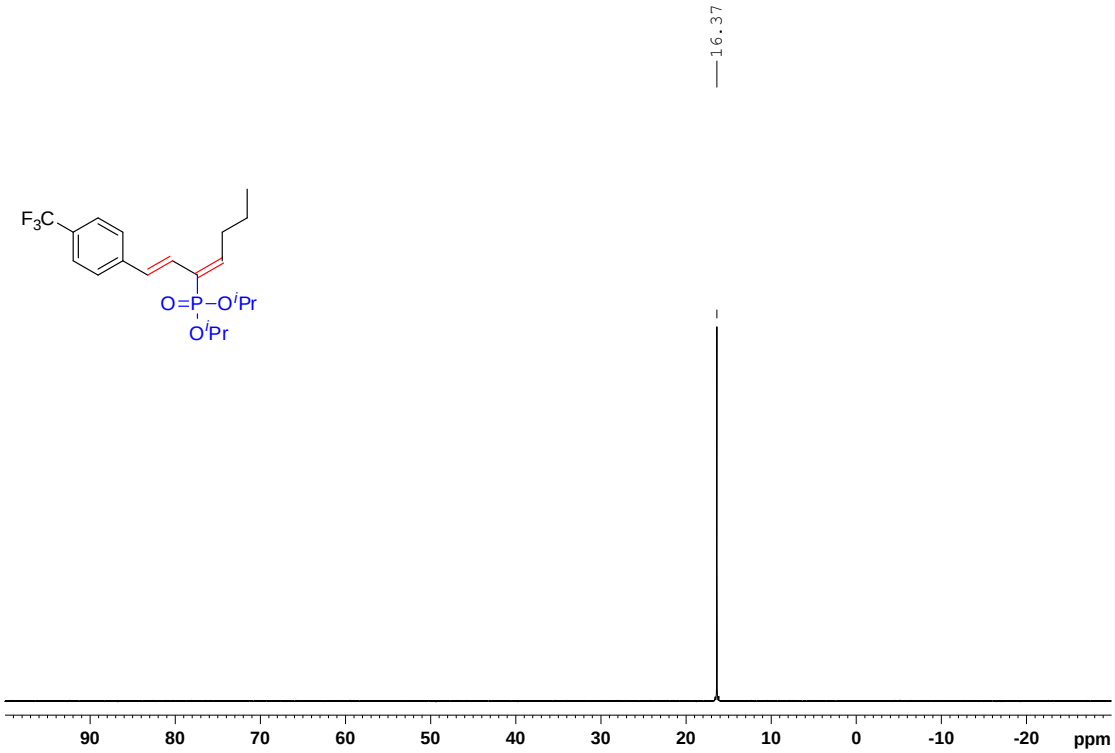
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ac**



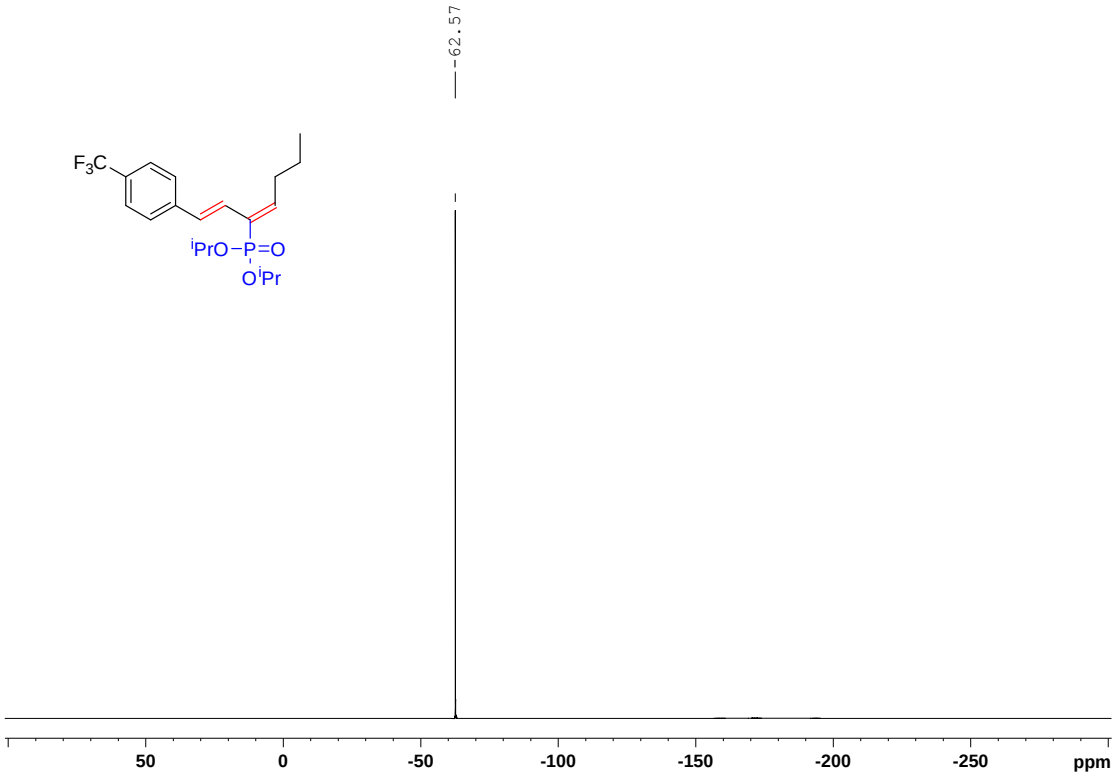
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ad**



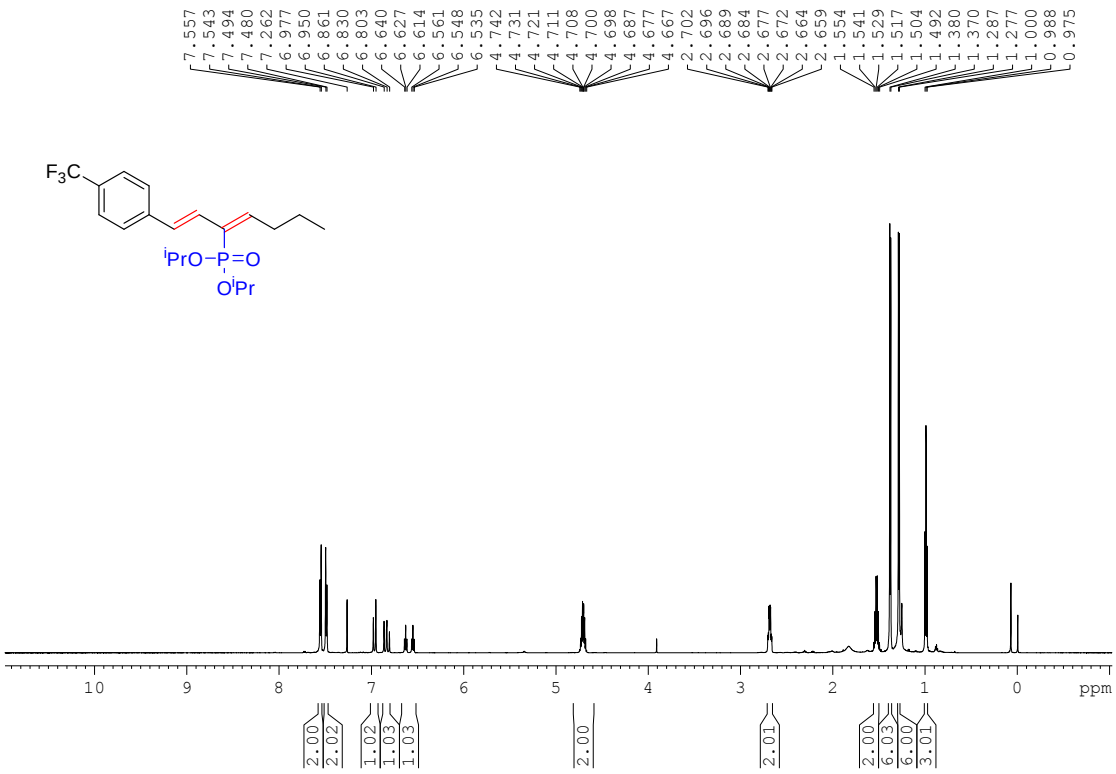
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ad**



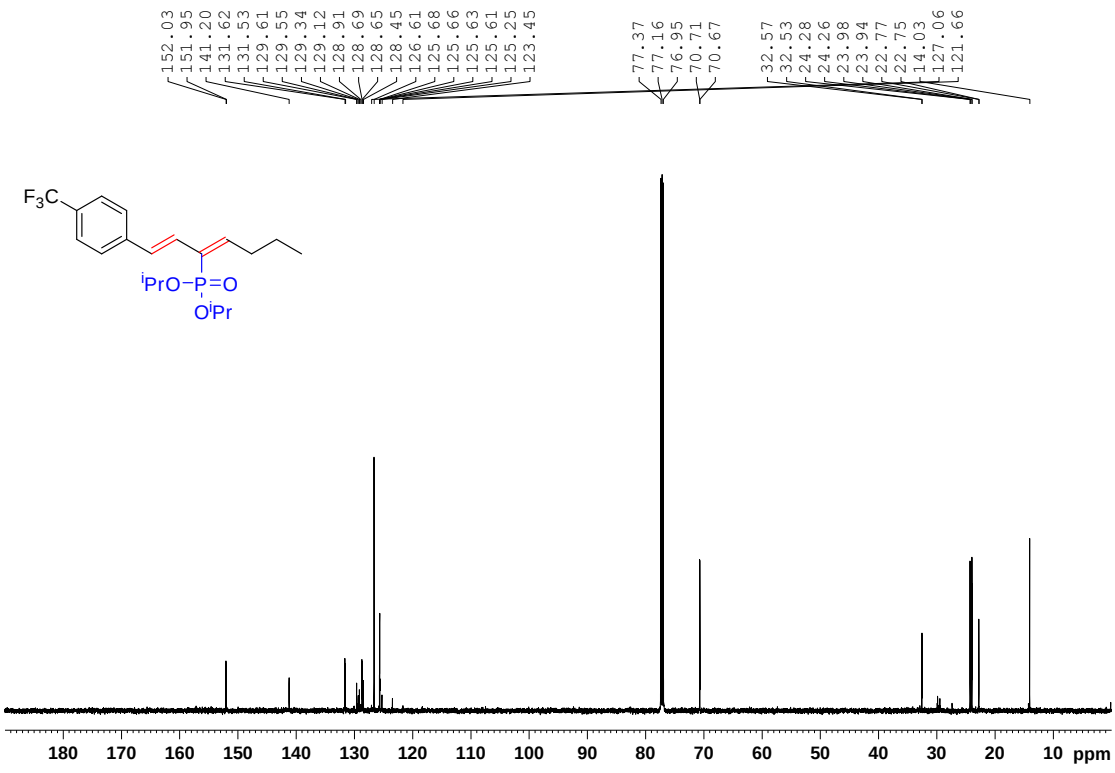
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ad**



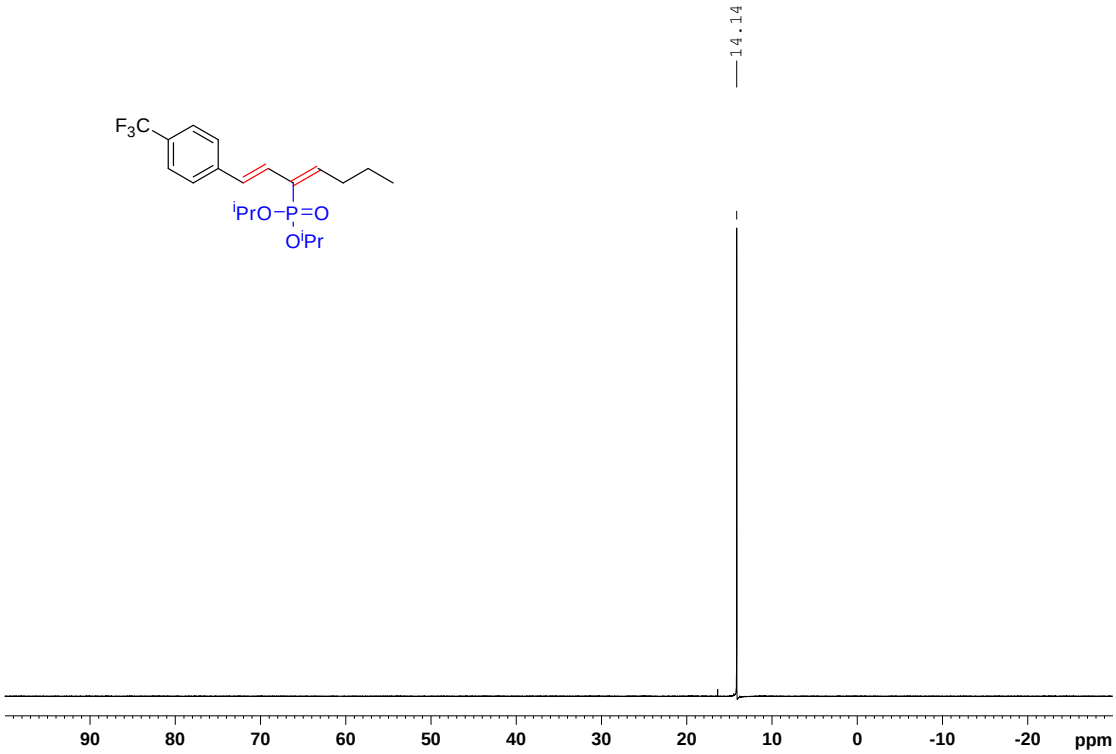
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ad**



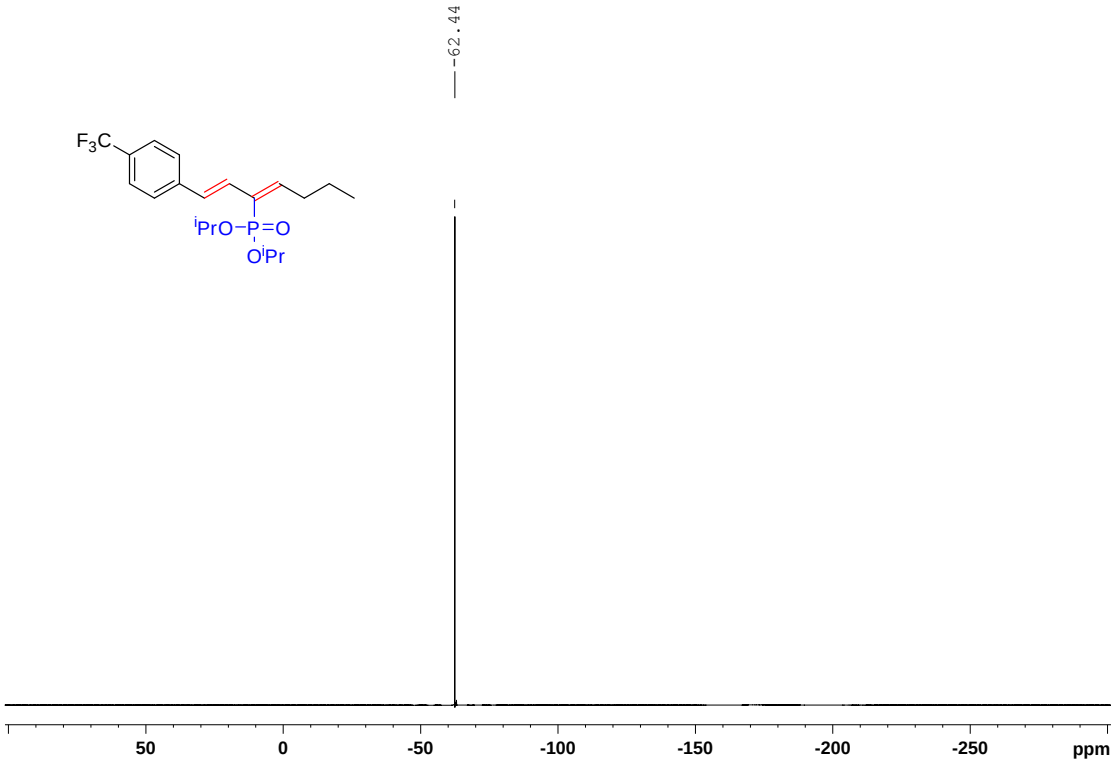
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ad**



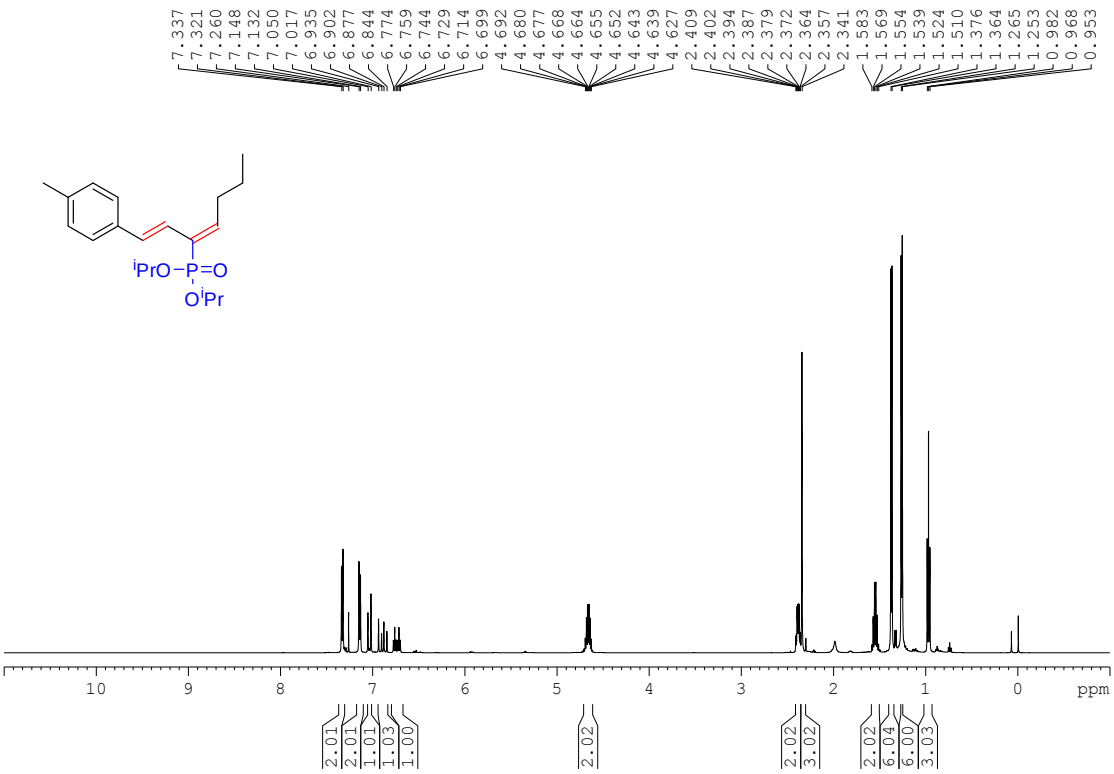
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ad**



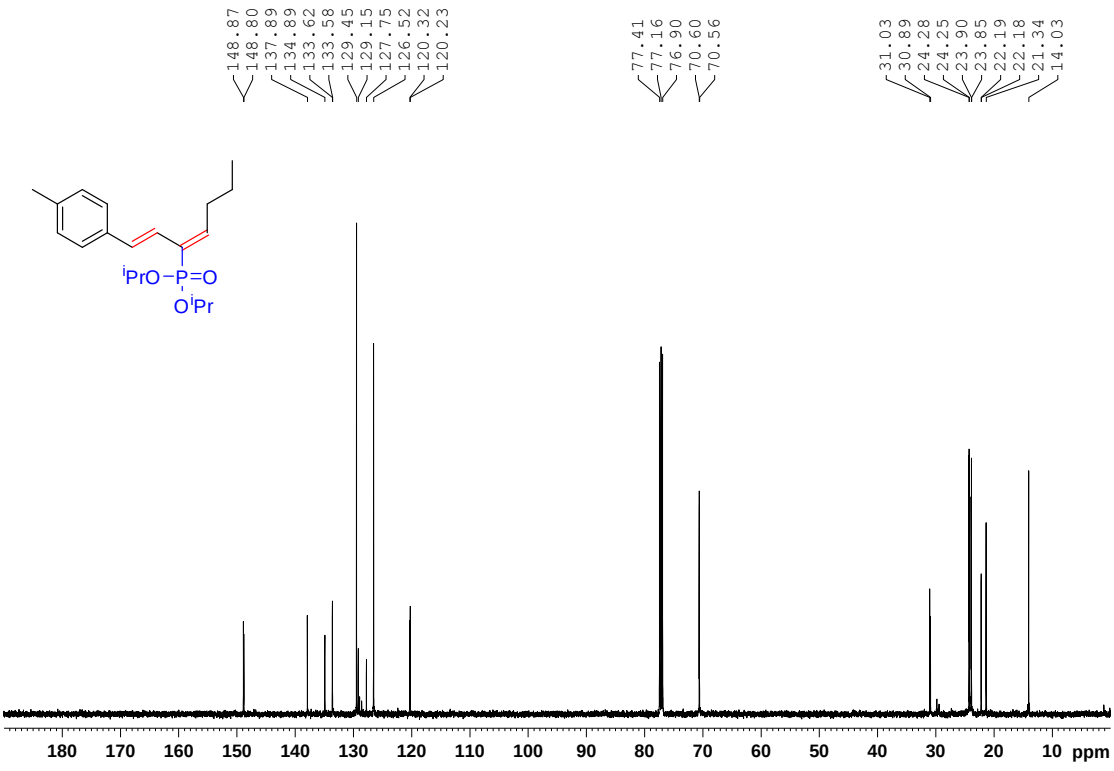
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ad**



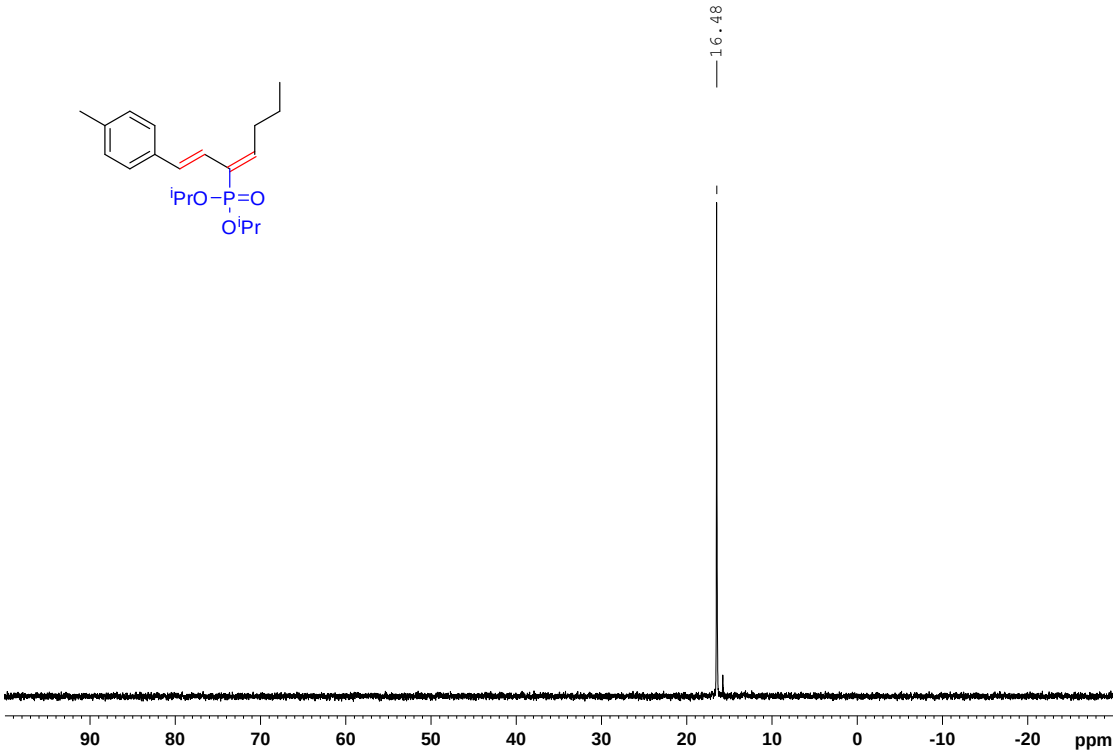
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ad**



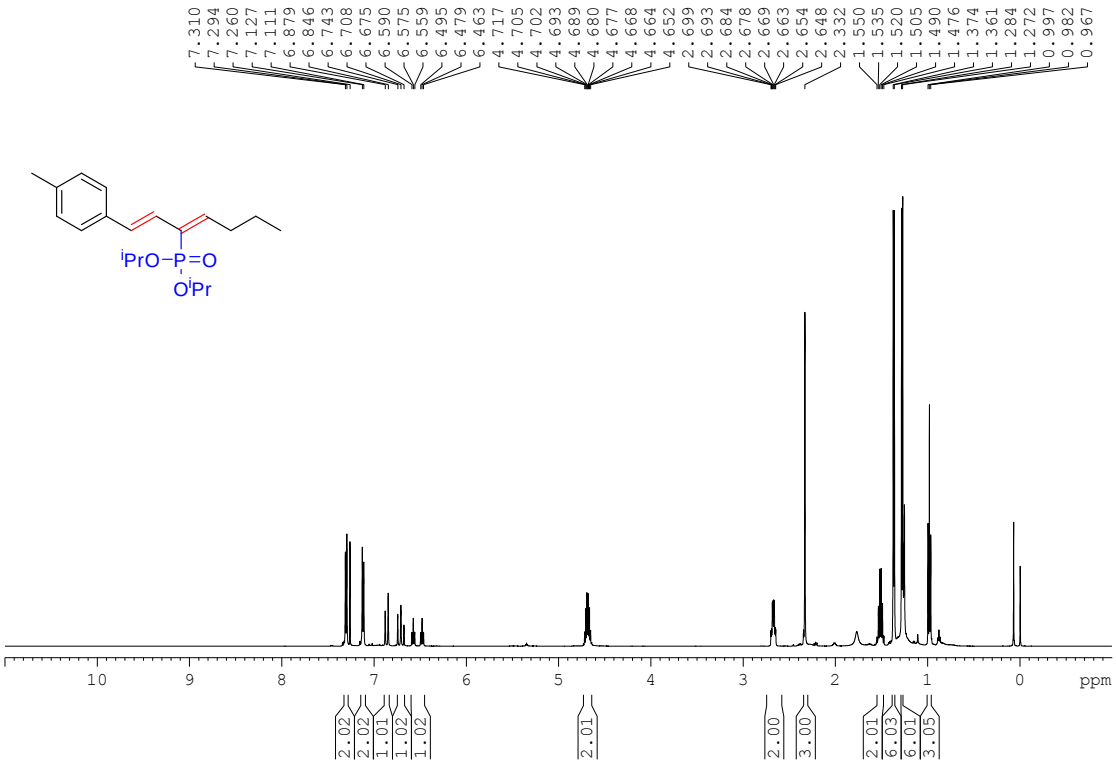
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ae**



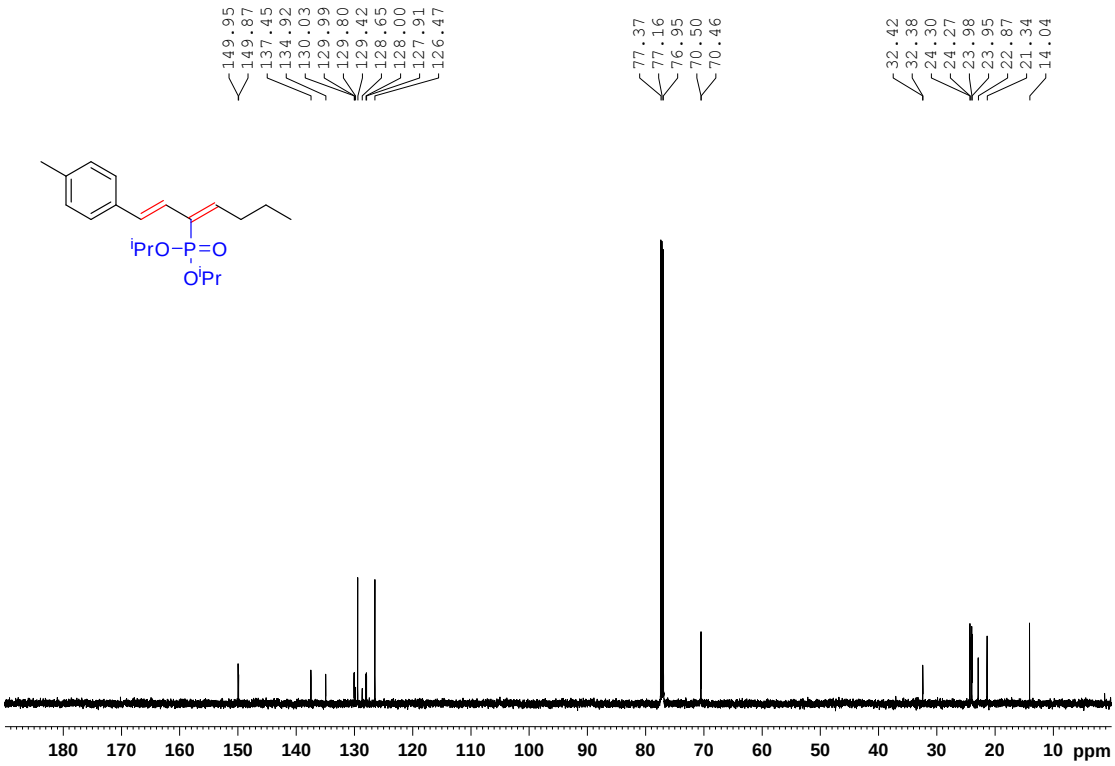
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ae**



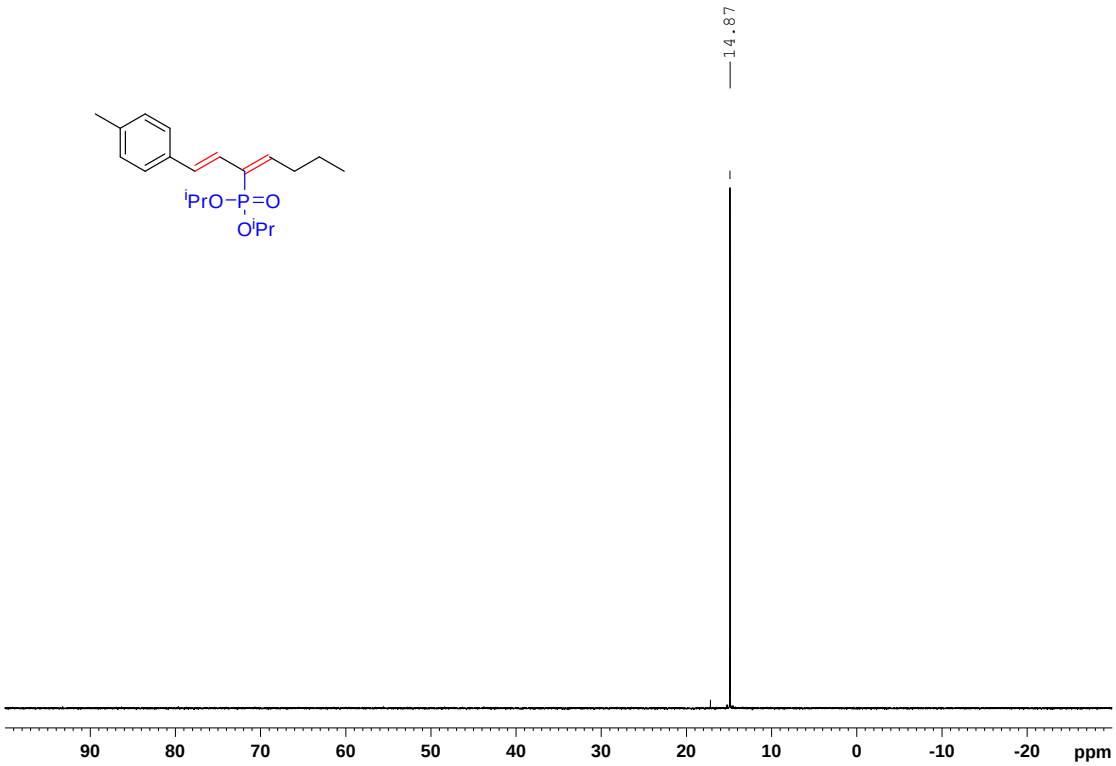
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ae**



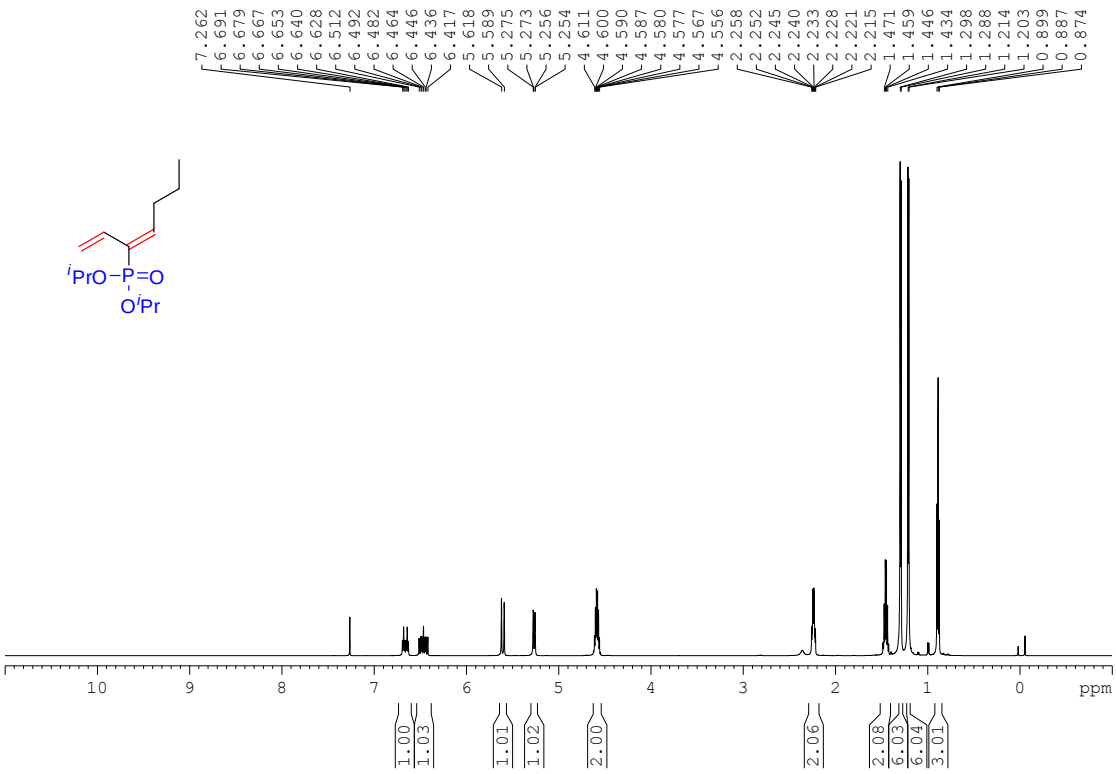
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ae**



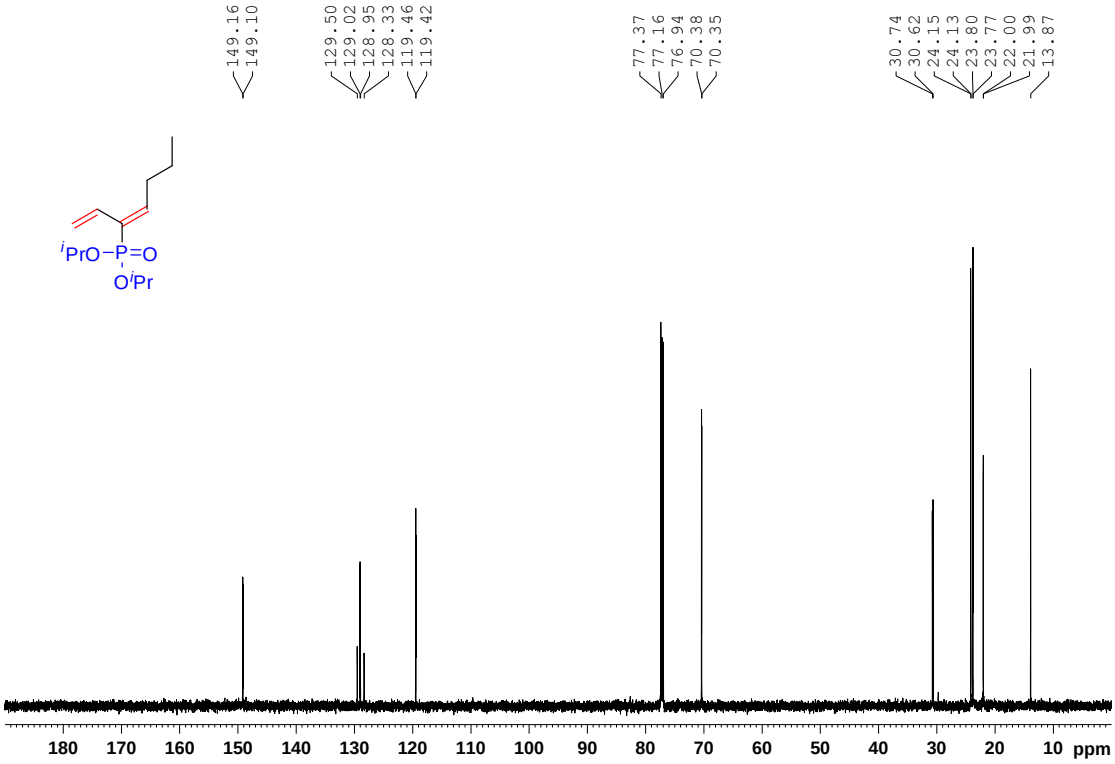
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ae**



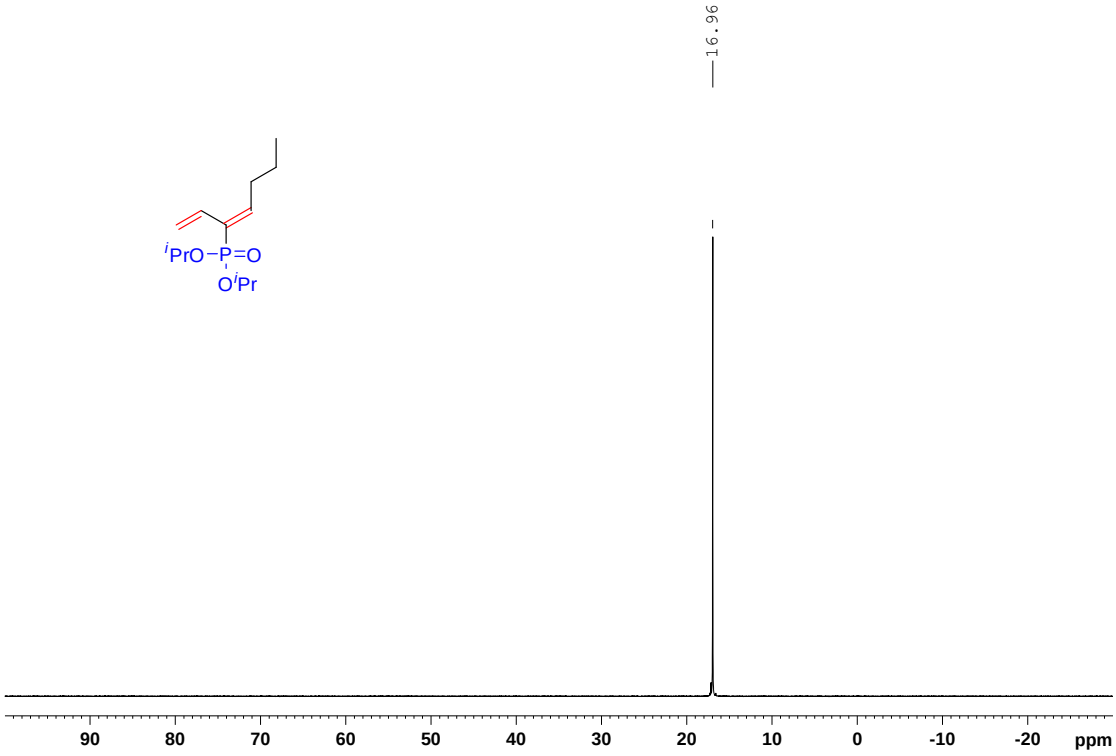
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**3ae**



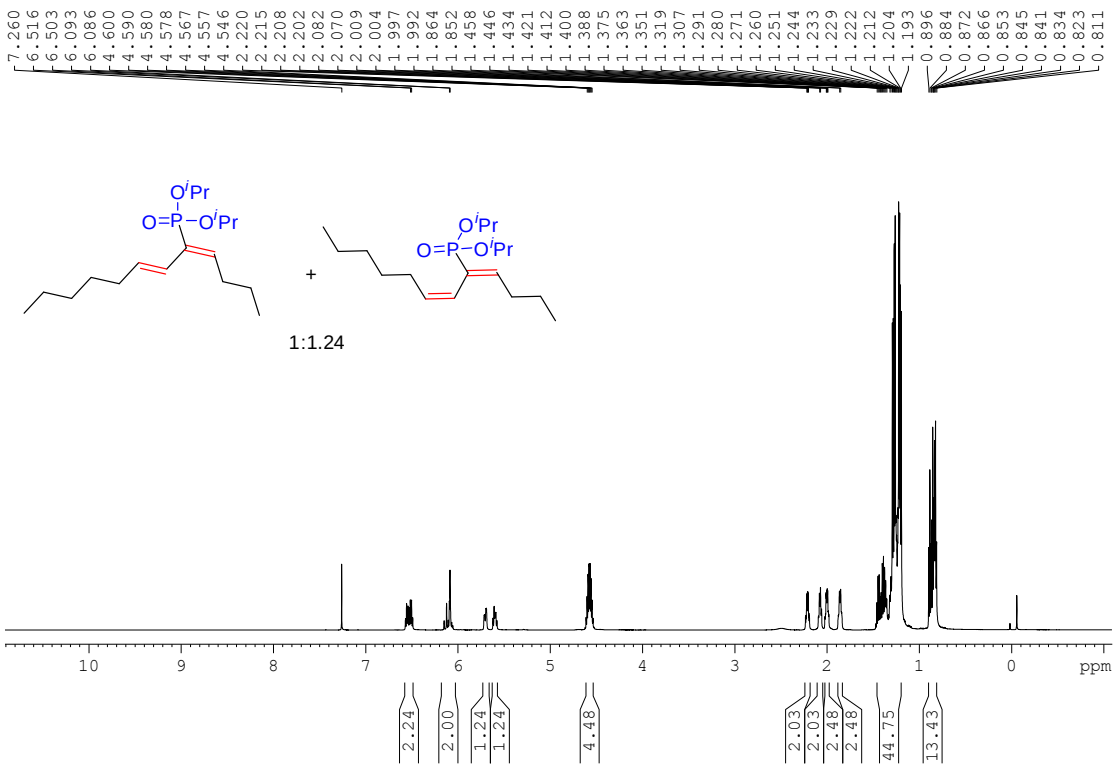
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3af**



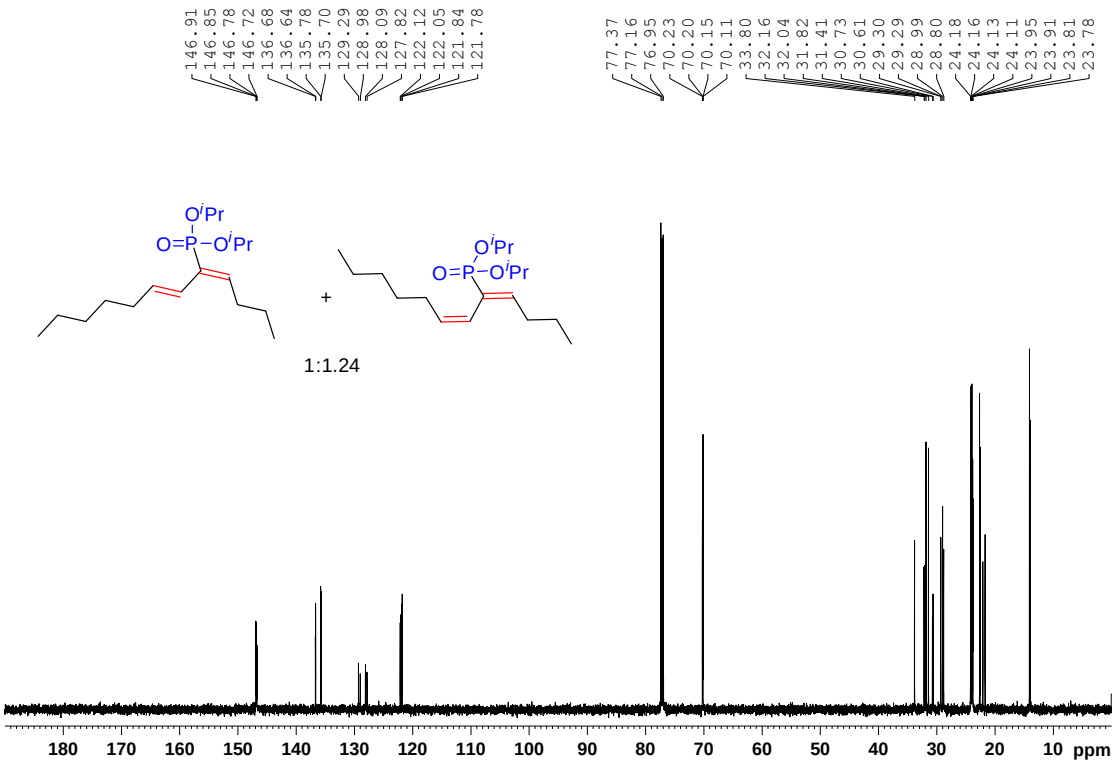
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3af**



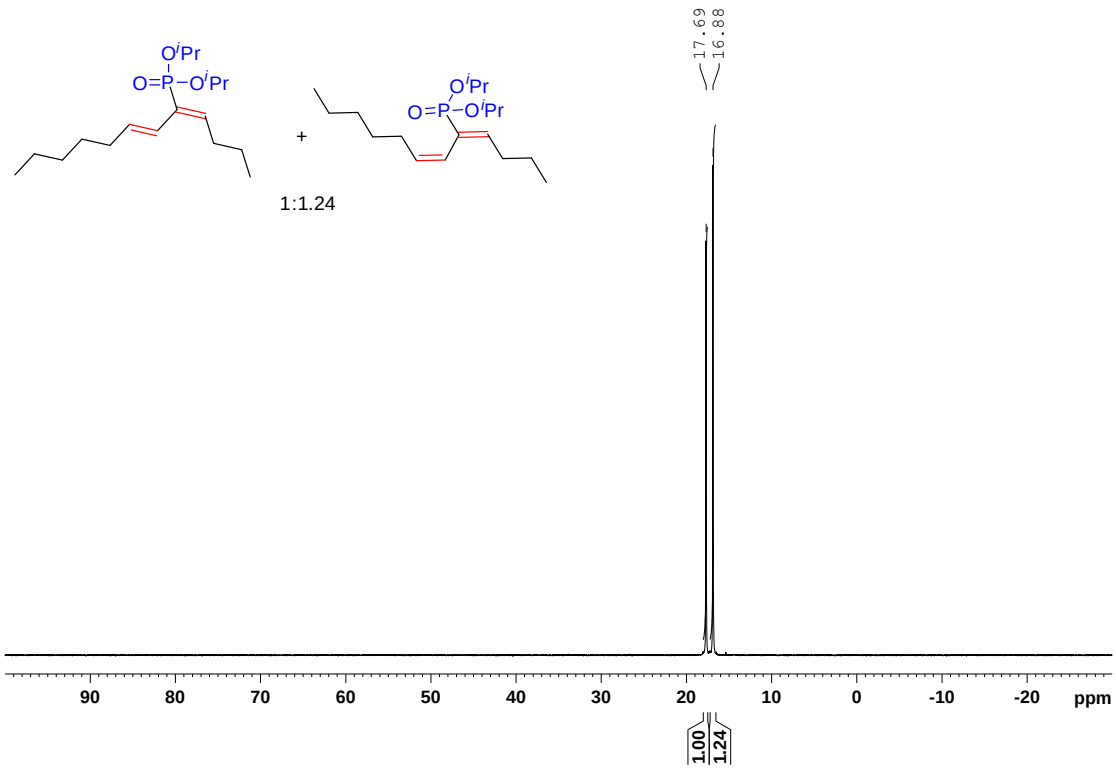
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3af**



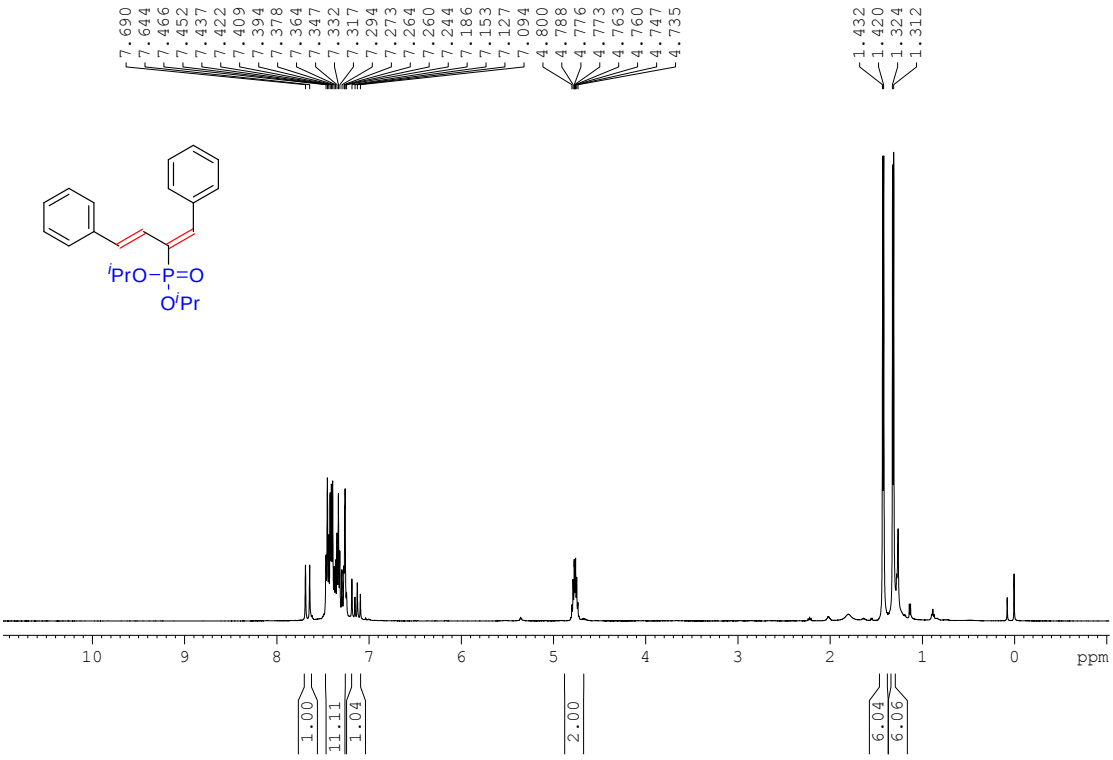
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ag** and (*Z*)-**3ag** (1:1.24)



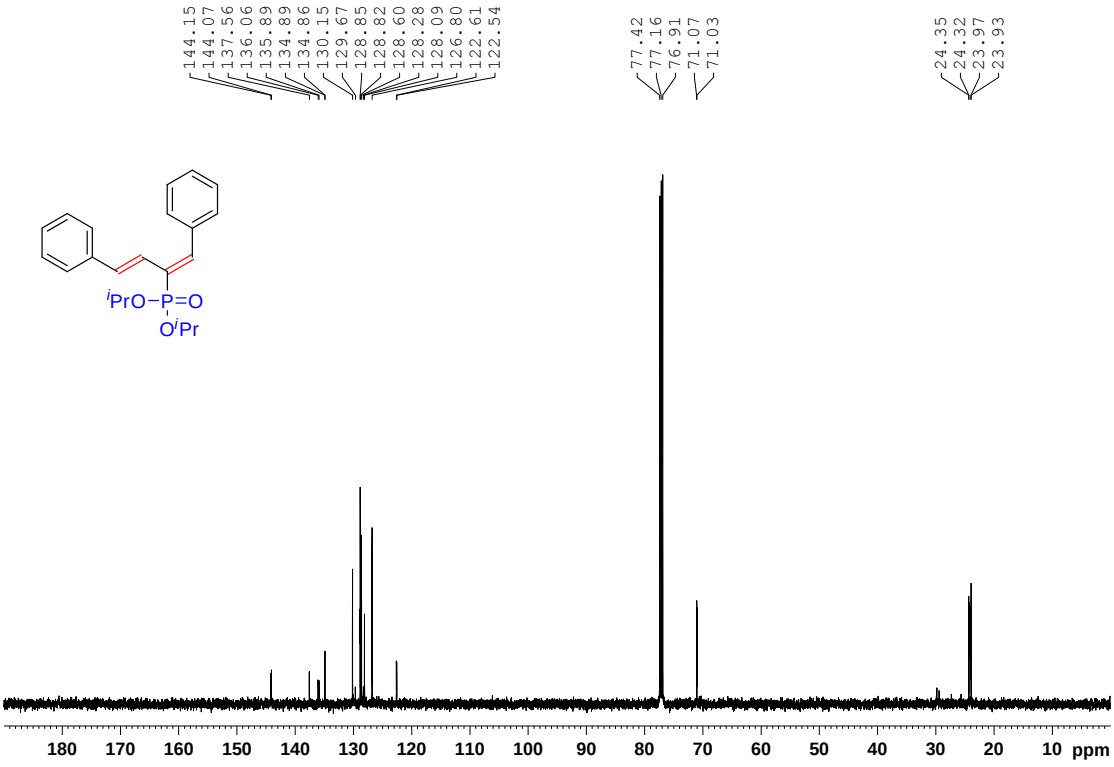
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ag** and (*Z*)-**3ag** (1:1.24)



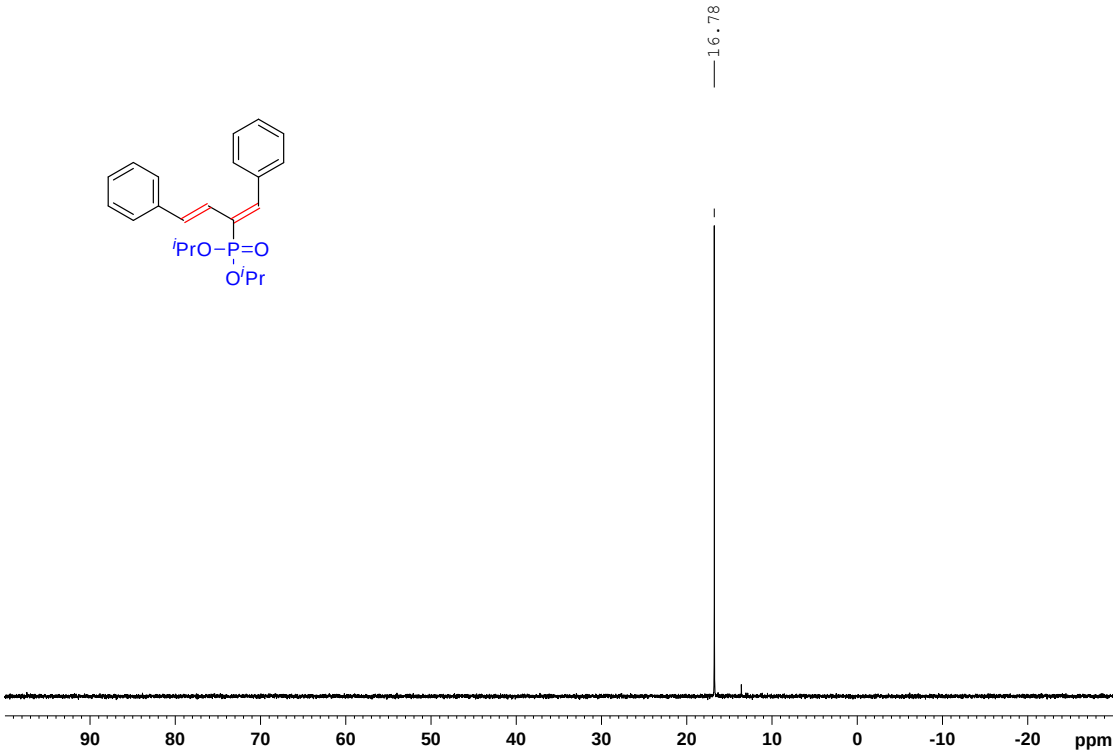
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ag** and (*Z*)-**3ag** (1:1.24)



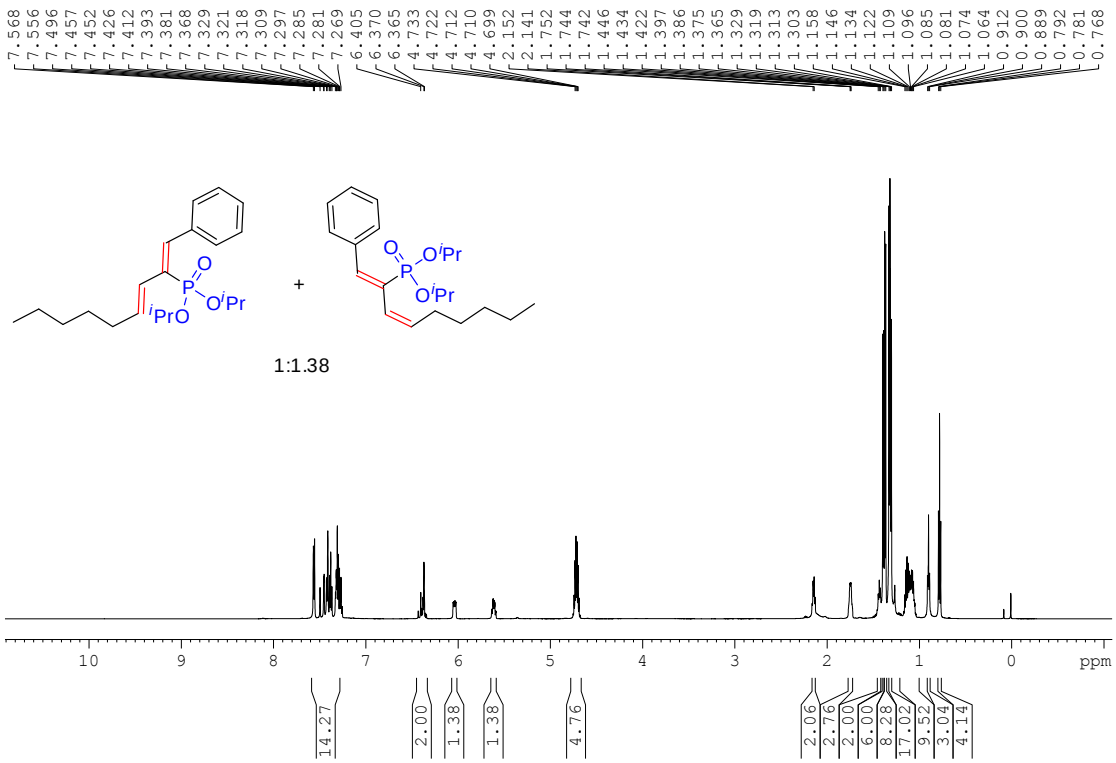
^{1}H NMR (500 MHz, CDCl3) spectrum of compound **3ah**



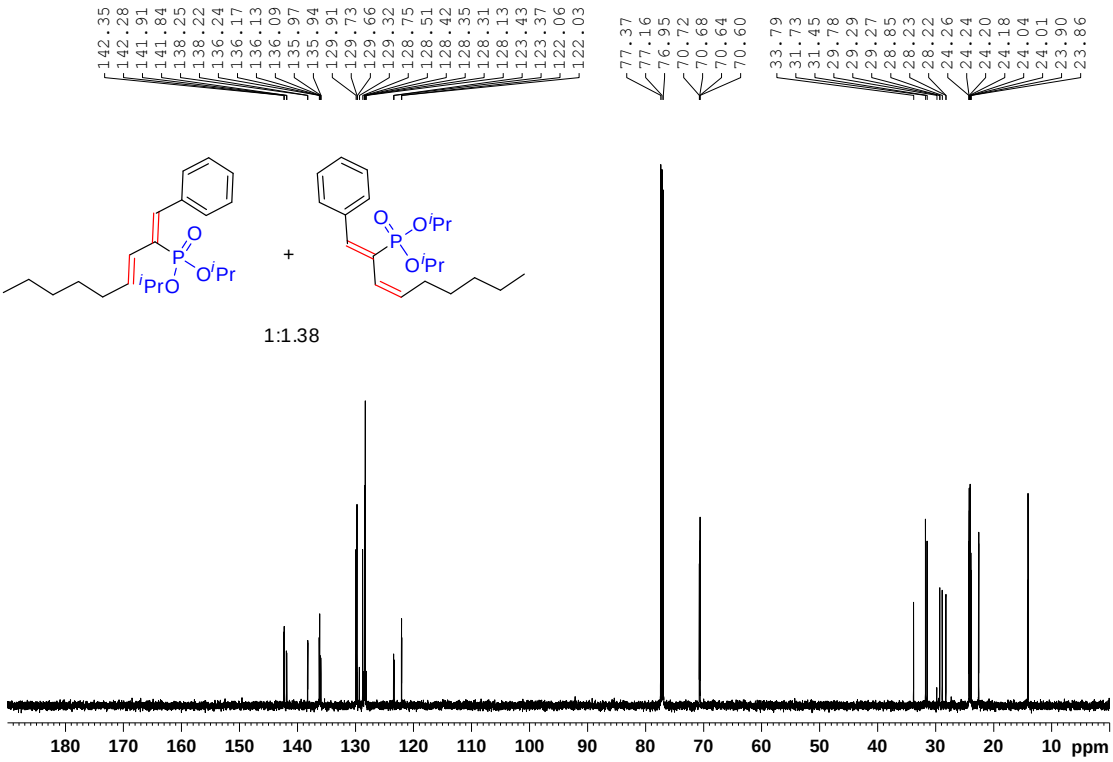
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3ah**



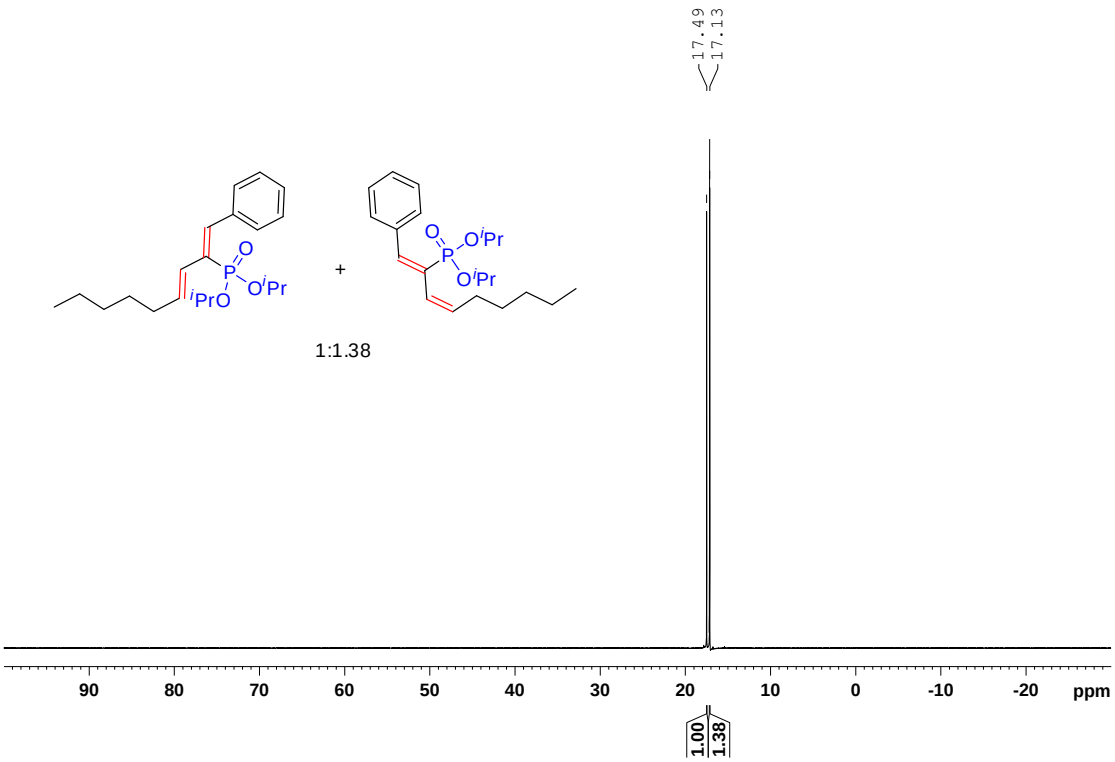
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ah**



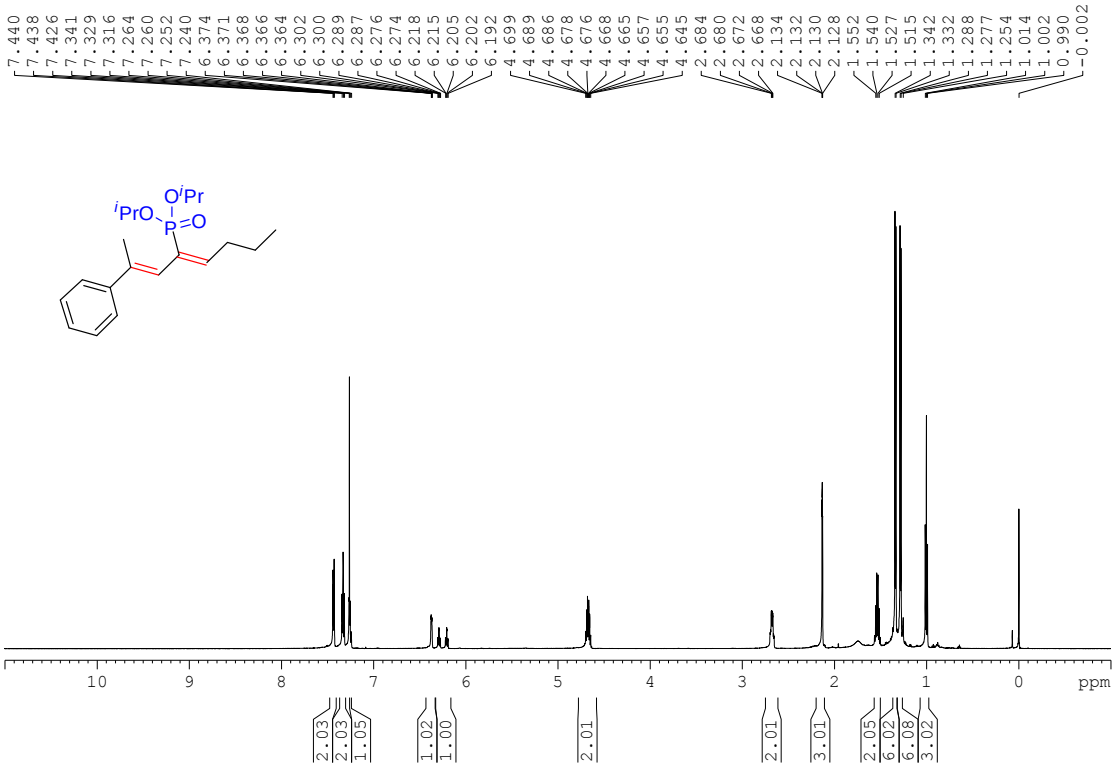
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ai** and (*Z*)-**3ai** (1:1.38)



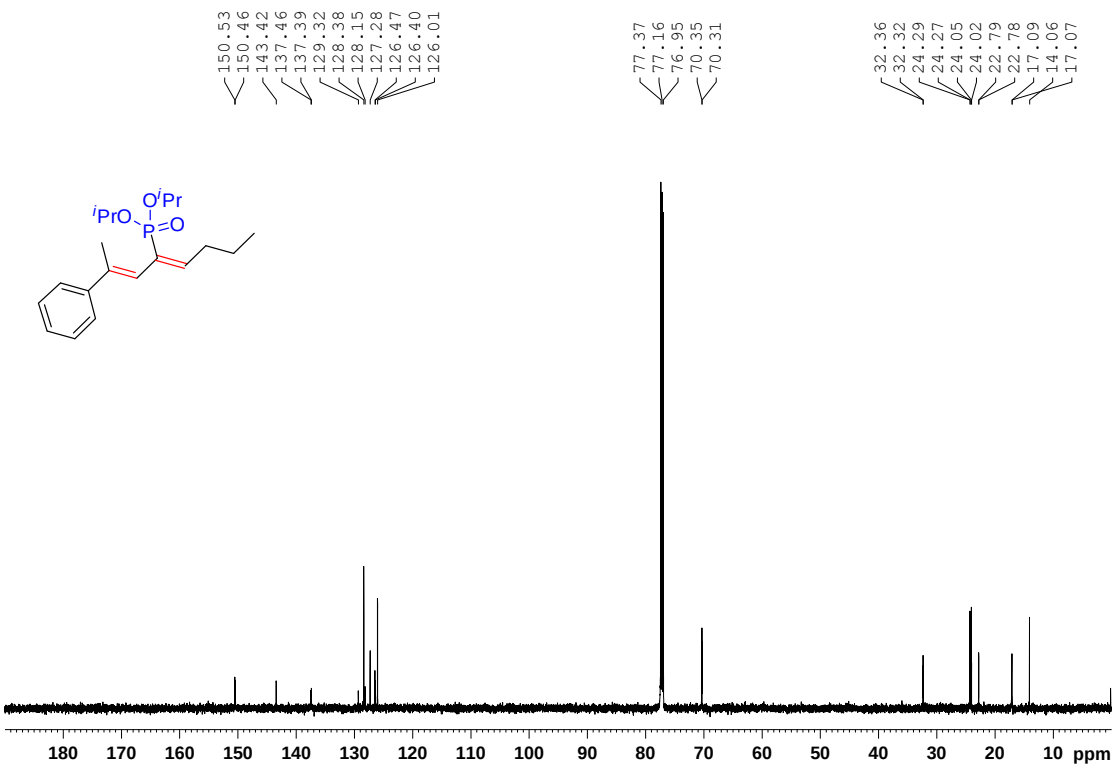
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ai** and (*Z*)-**3ai** (1:1.38)



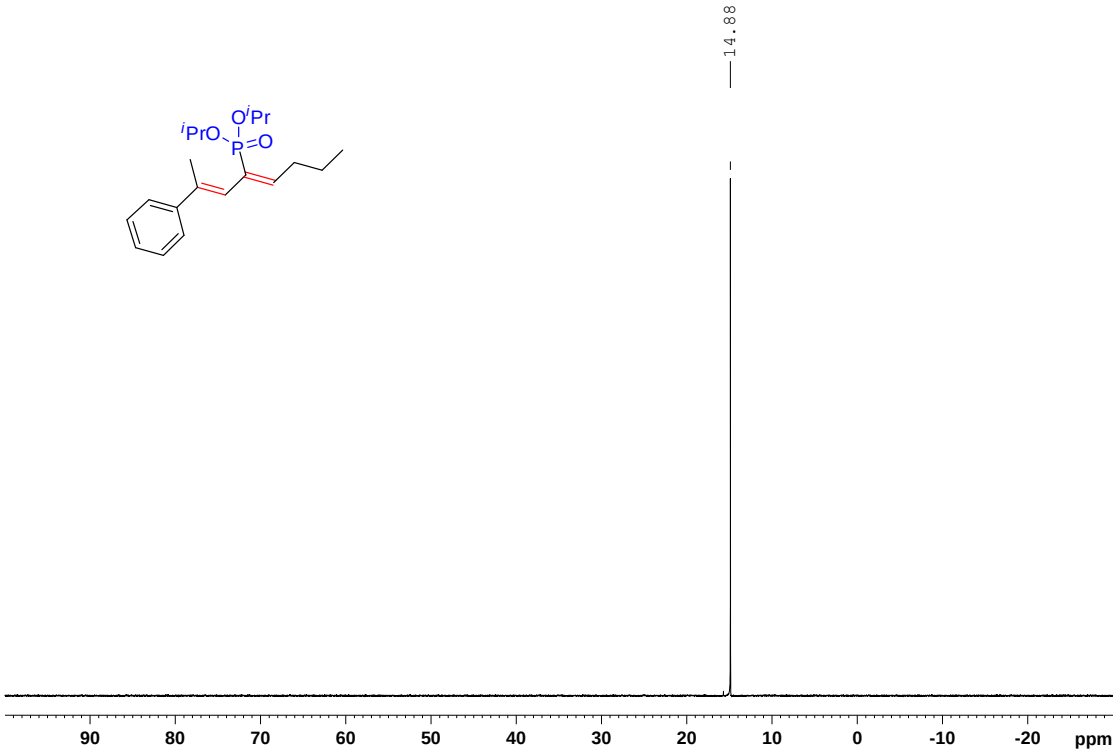
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**3ai** and (*Z*)-**3ai** (1:1.38)



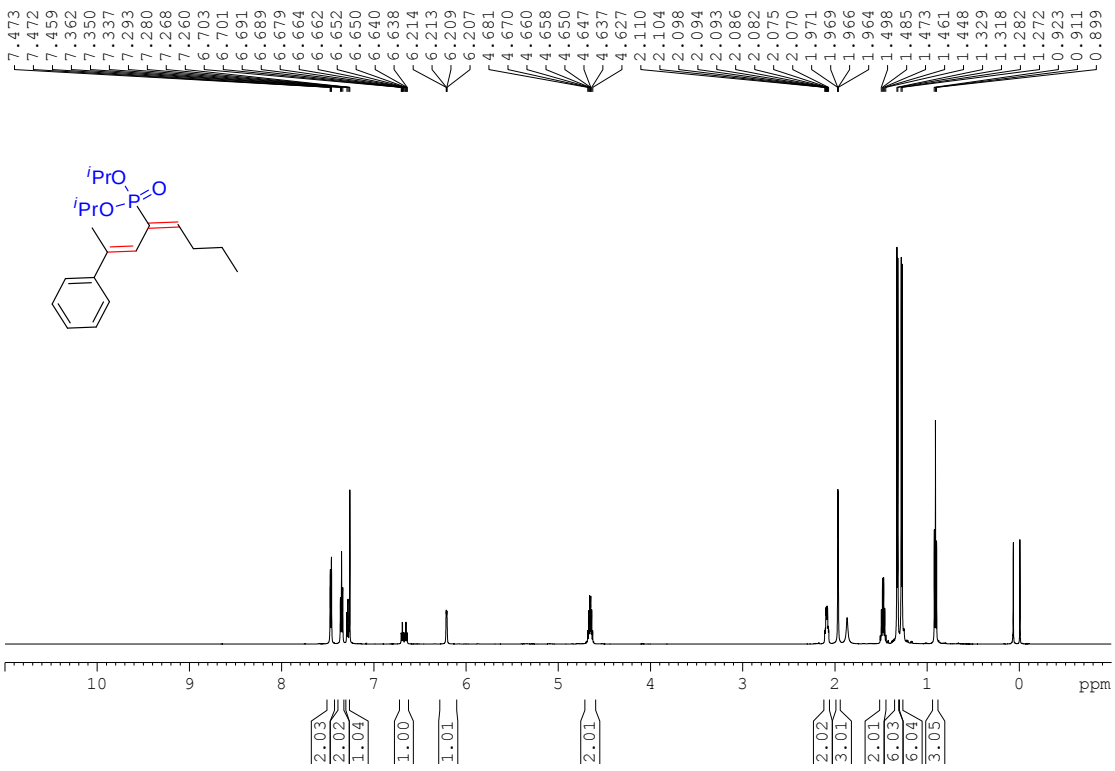
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (2*E*,4Z)-**3aj**



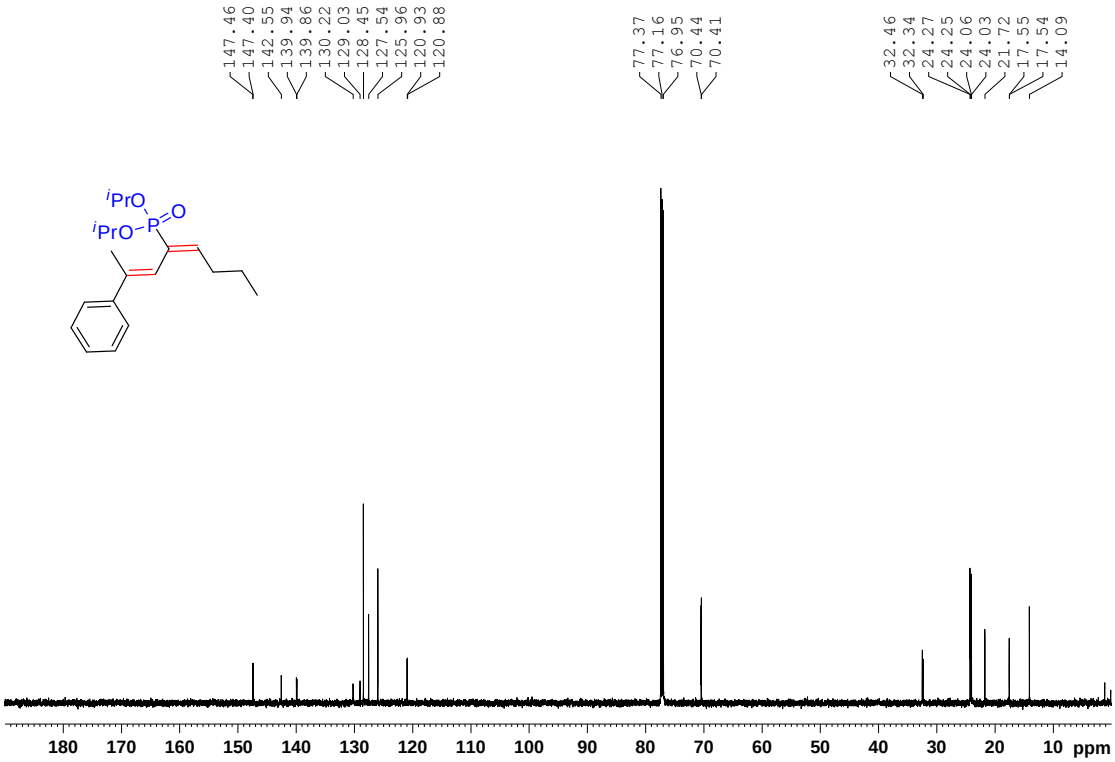
^{13}C (125 MHz, $CDCl_3$) NMR spectrum of compound (2*E*,4Z)-**3aj**



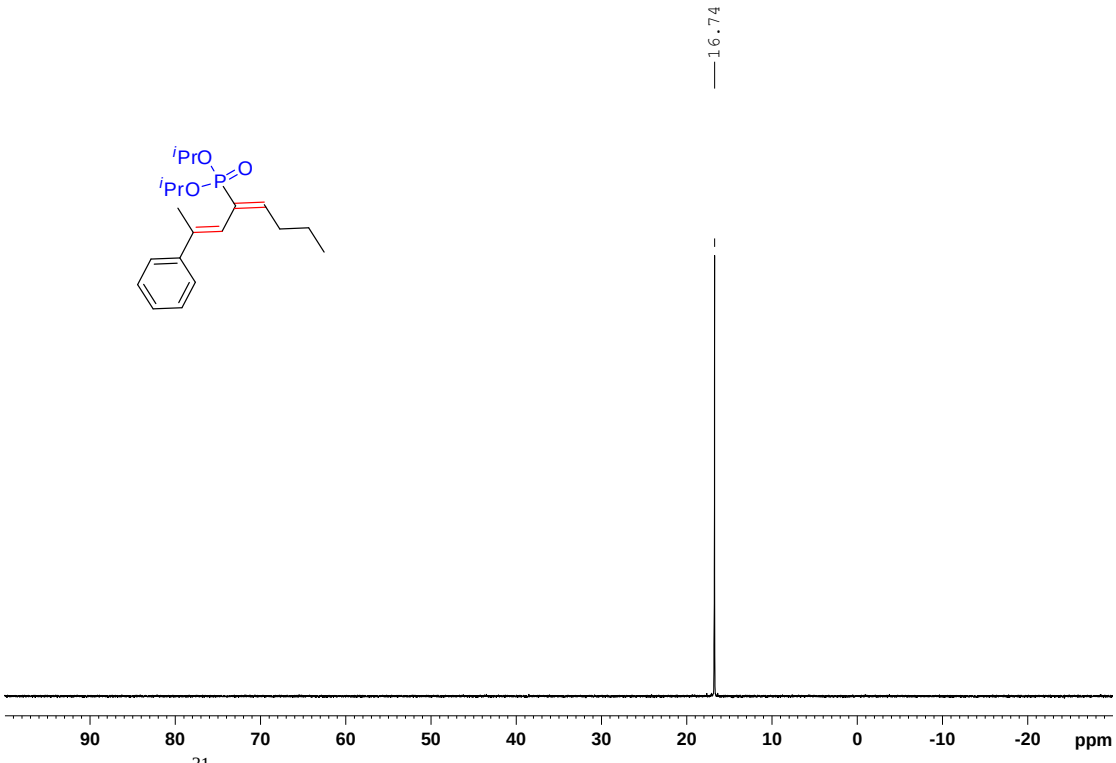
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (2*E*,4Z)-**3aj**



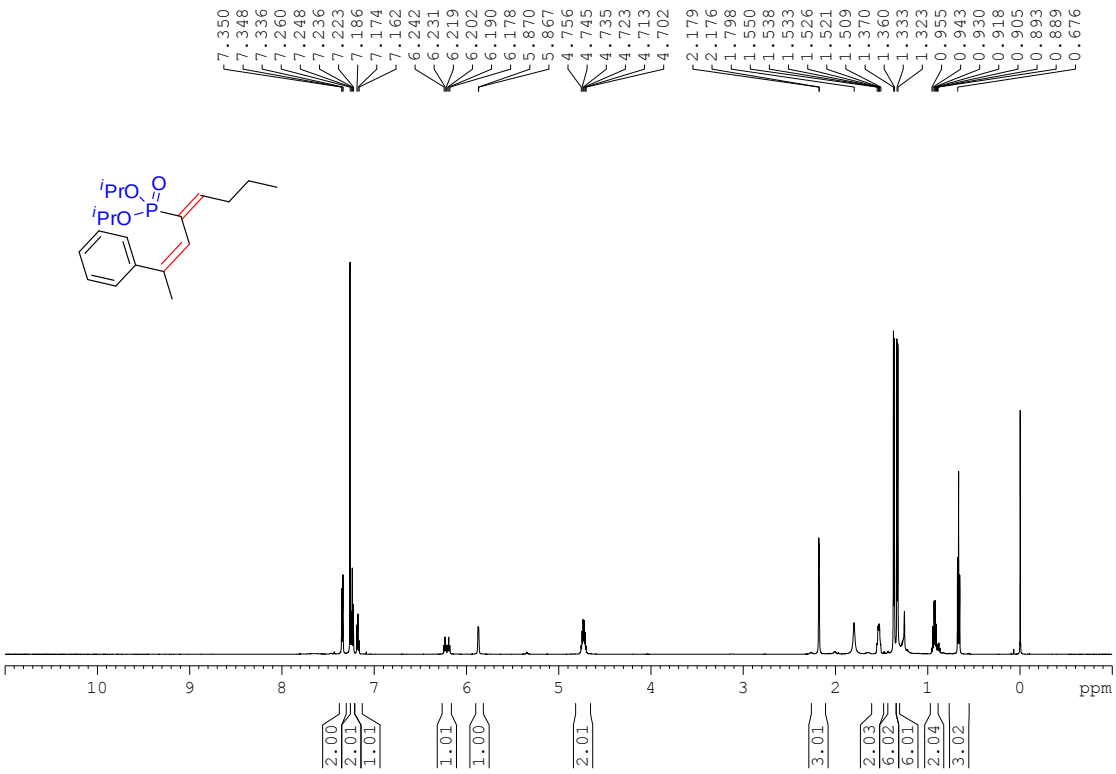
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (2*E*,4*E*)-**3aj**



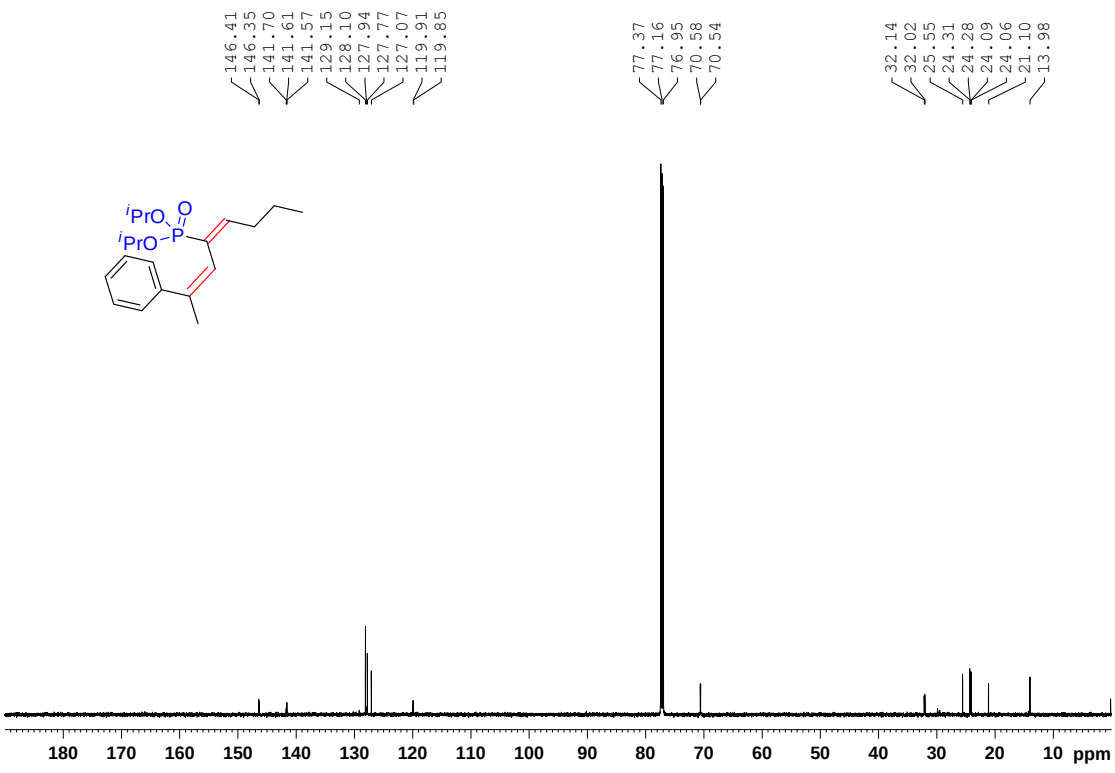
^{13}C (125 MHz, $CDCl_3$) NMR spectrum of compound (2*E*,4*E*)-**3aj**



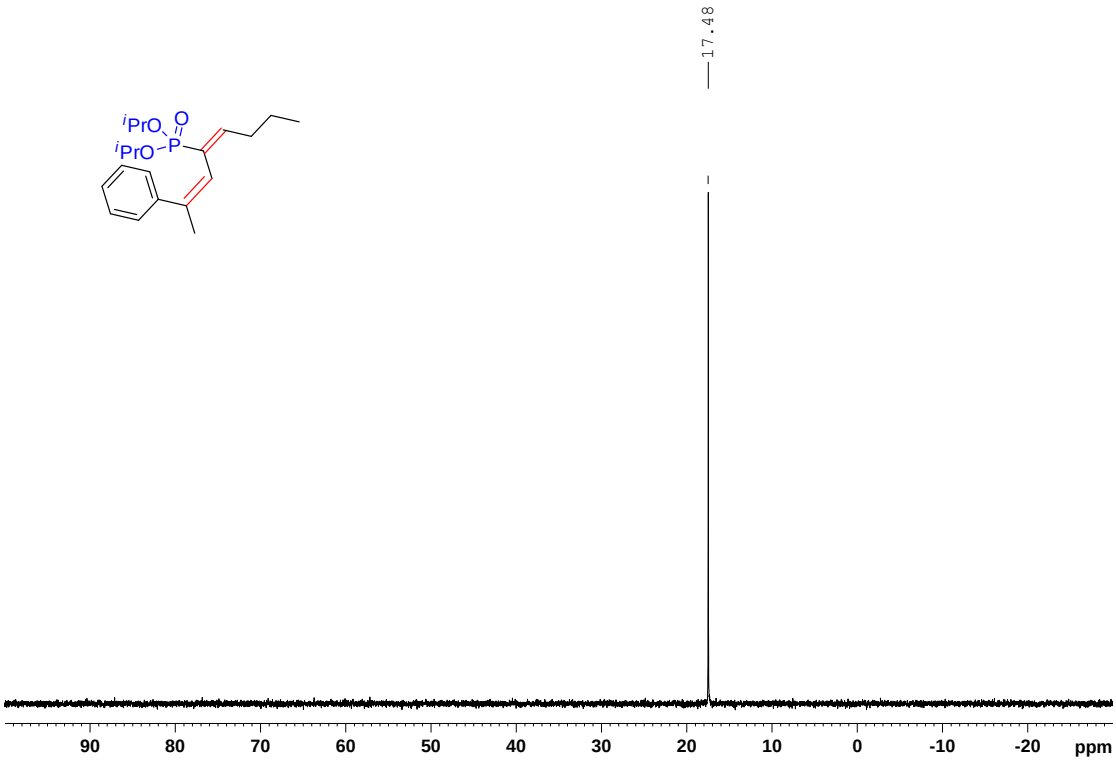
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (2*E*,4*E*)-**3aj**



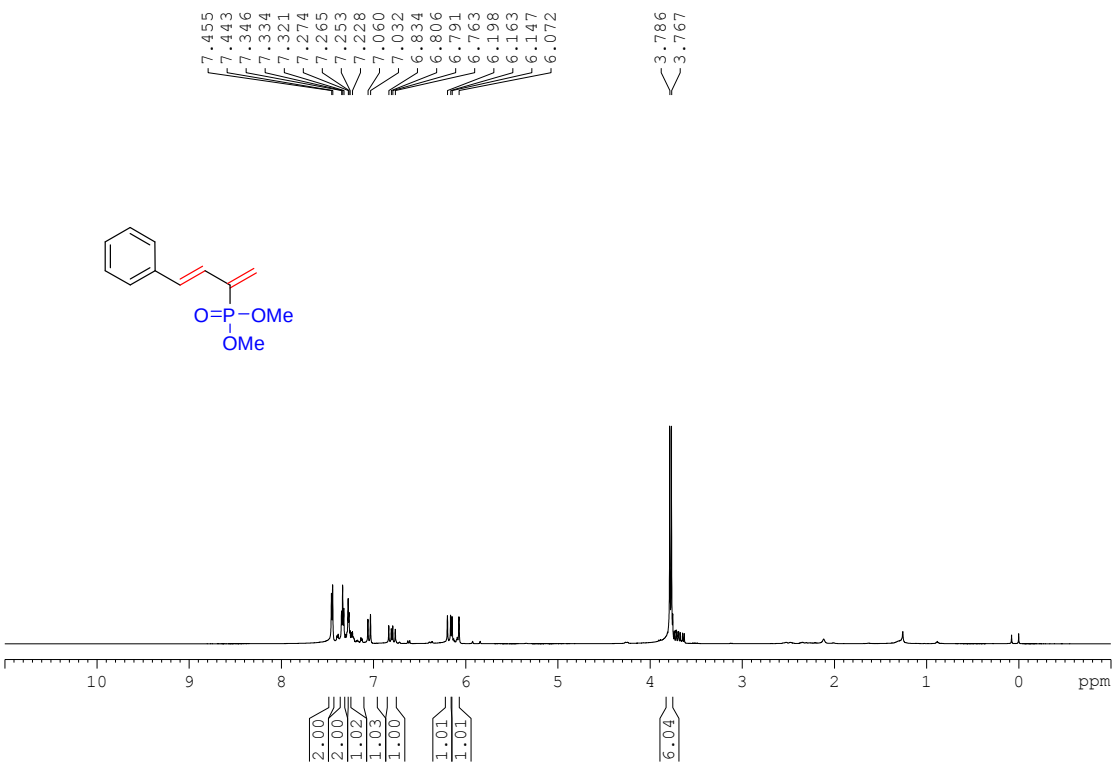
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (2*Z*,4*E*)-**3aj**



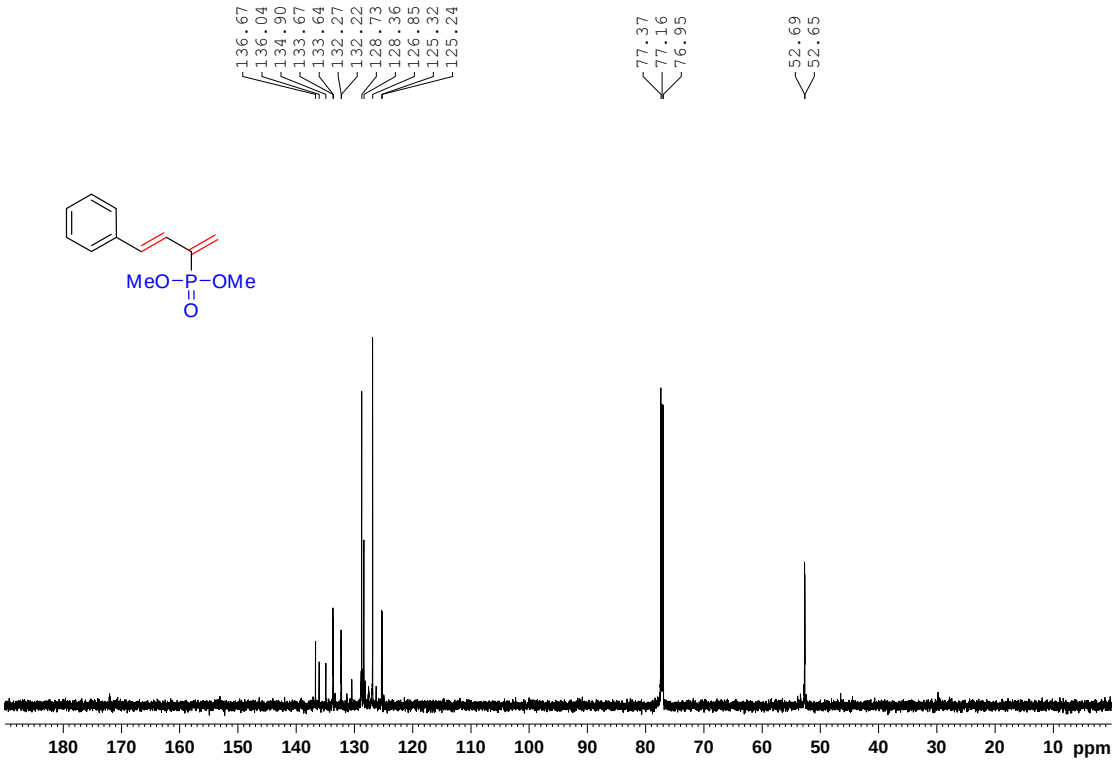
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (2*Z*,4*E*)-**3aj**



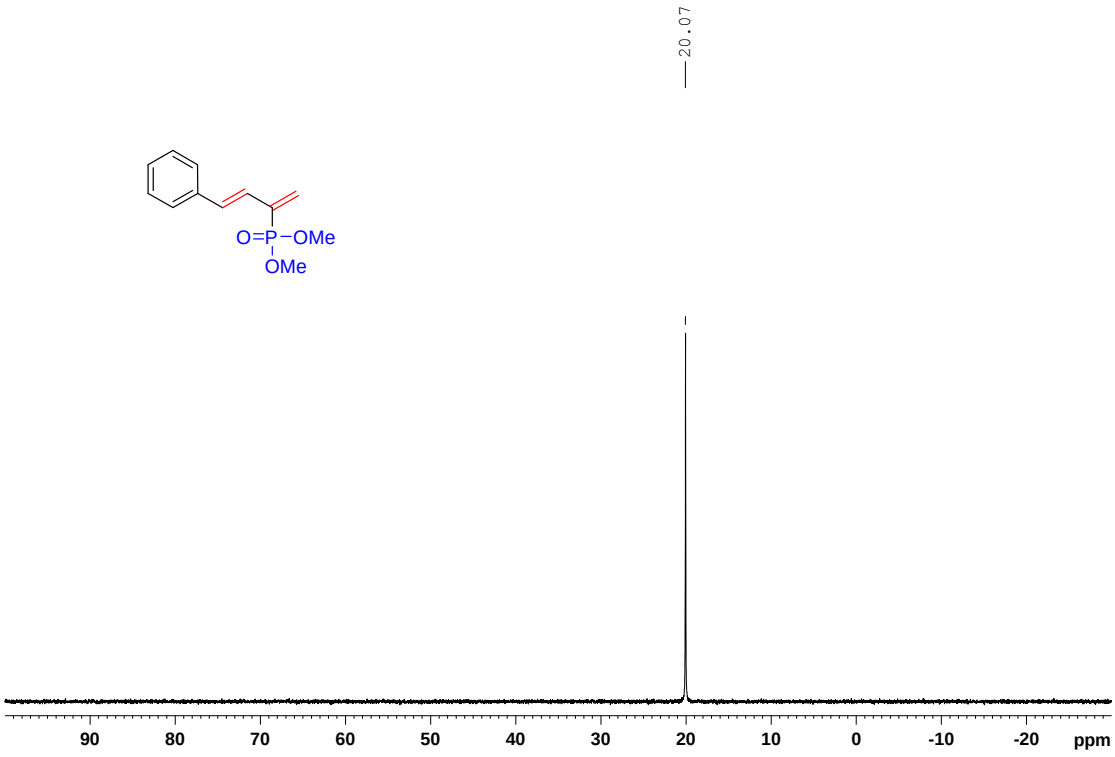
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (2*Z*,4*E*)-**3aj**



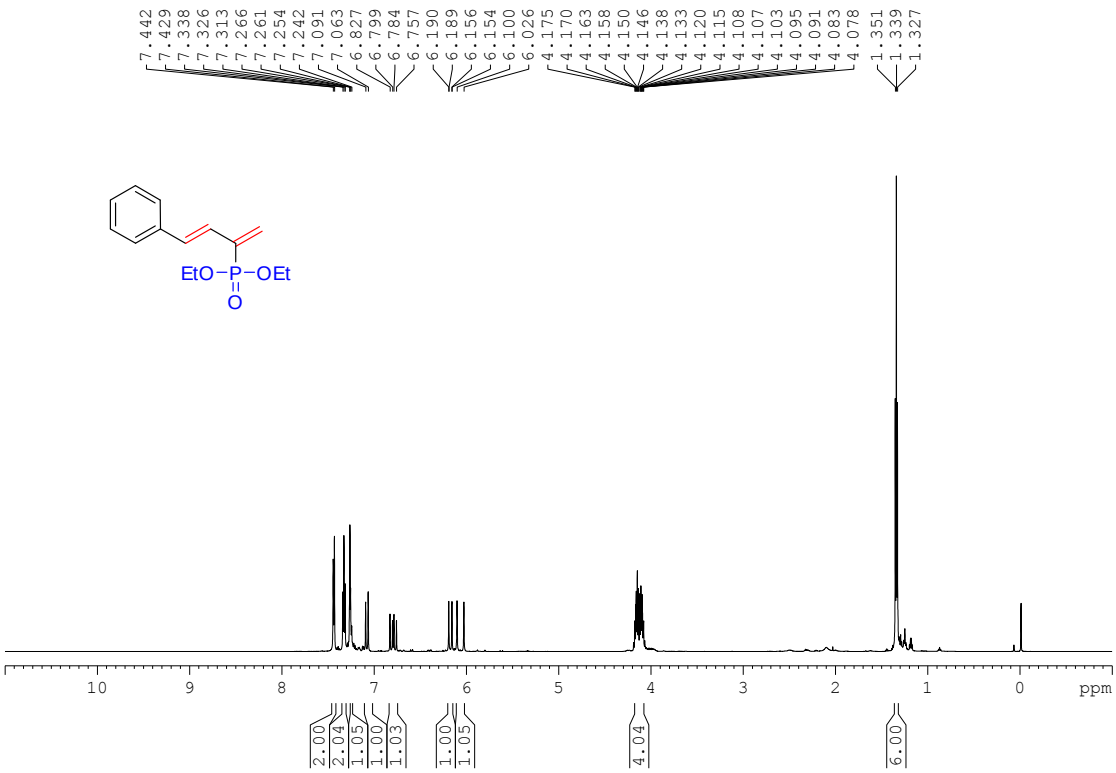
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ak**



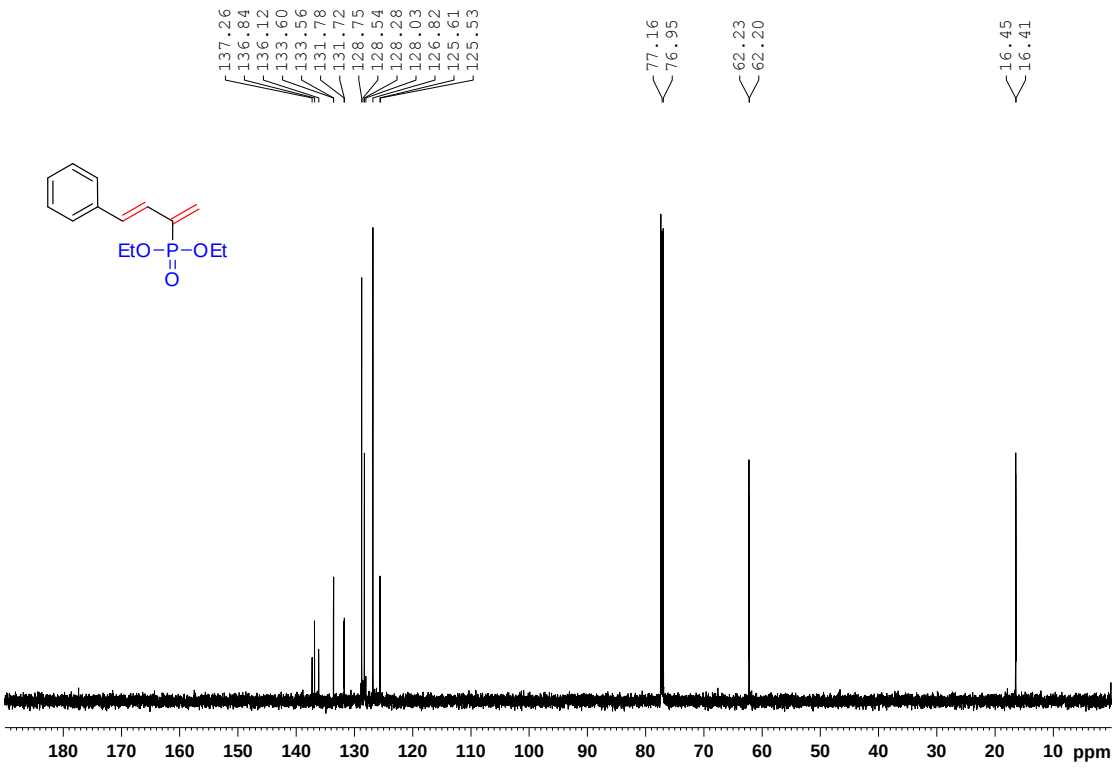
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3ak**



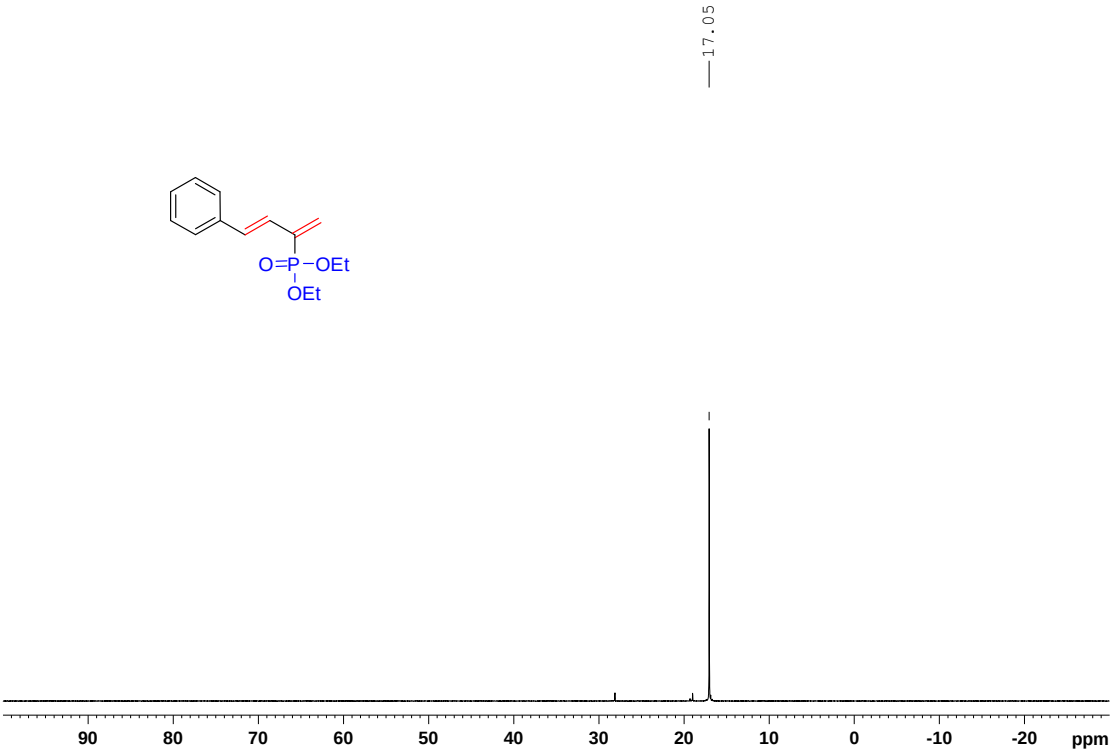
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ak**



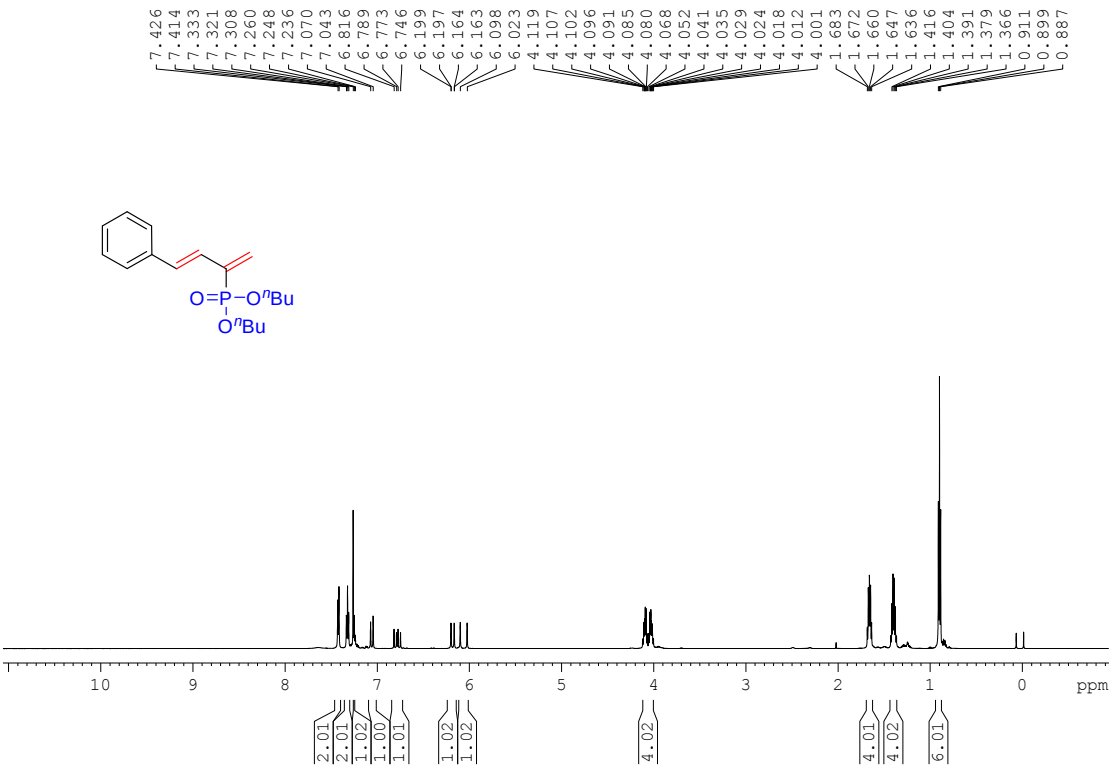
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3al**



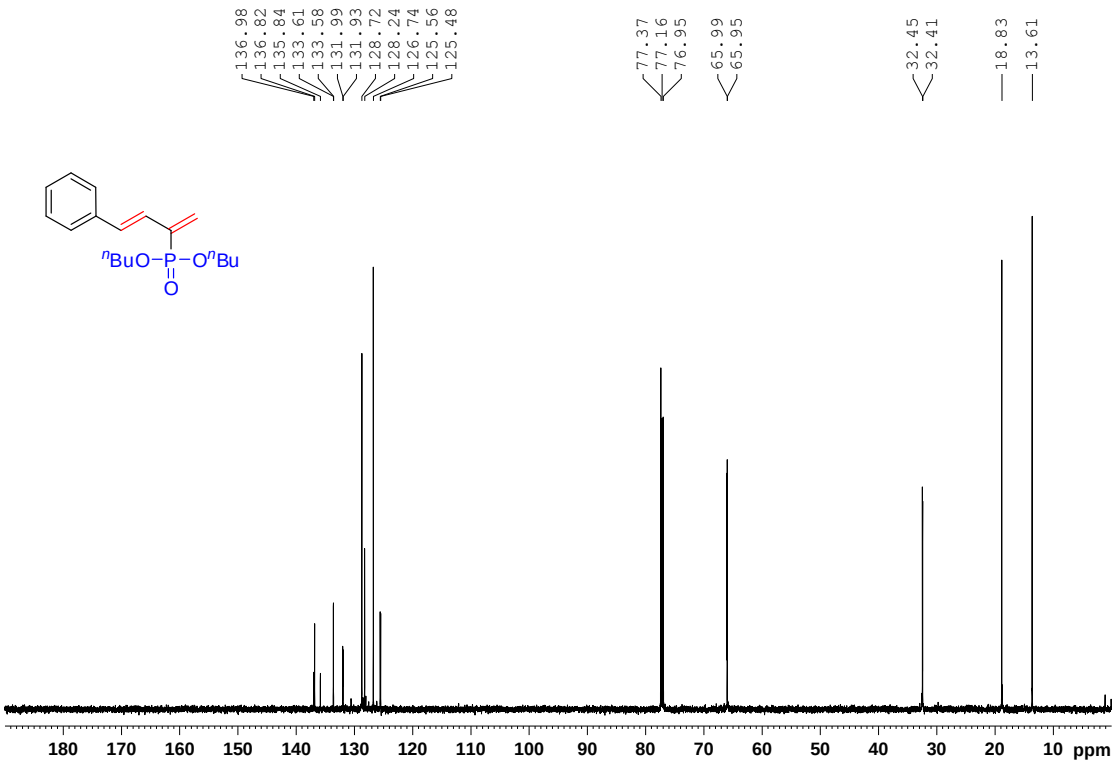
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3al**



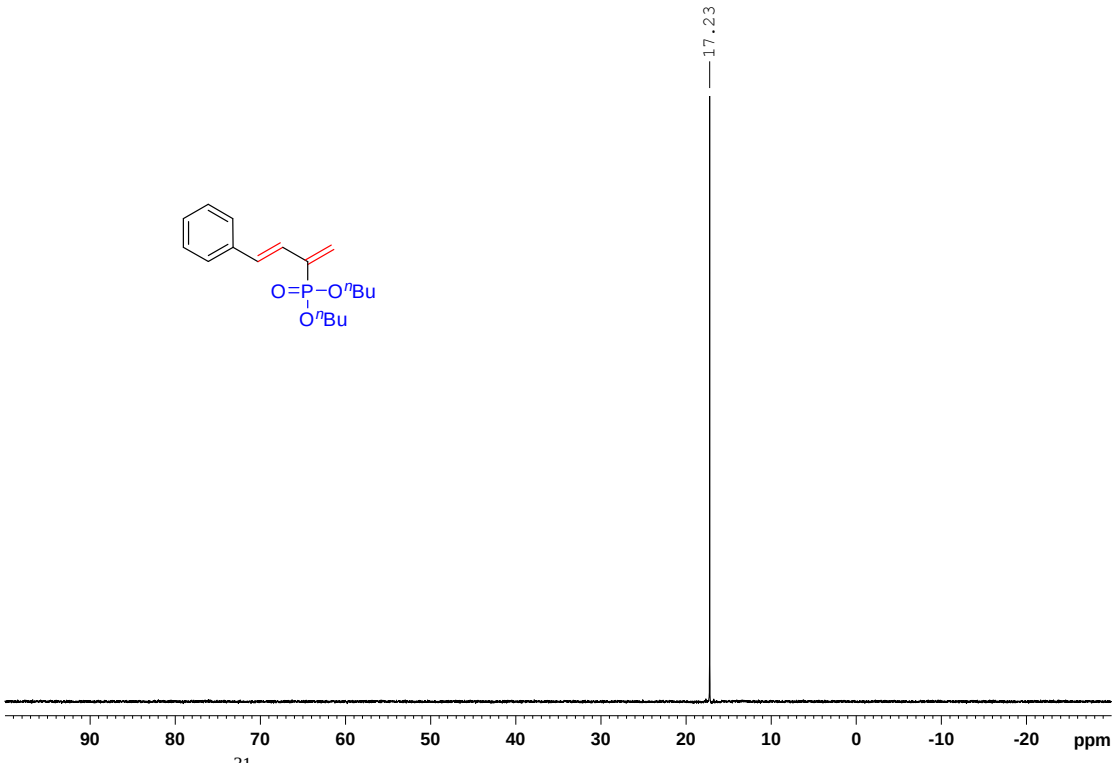
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3al**



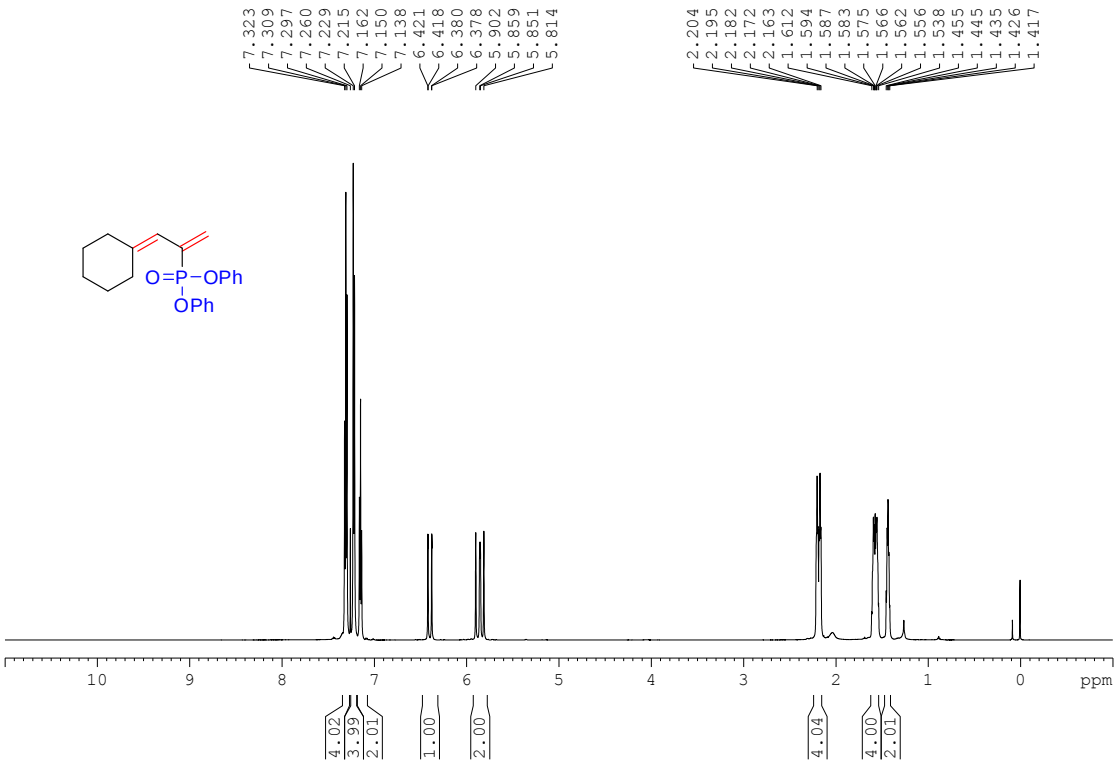
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3am**



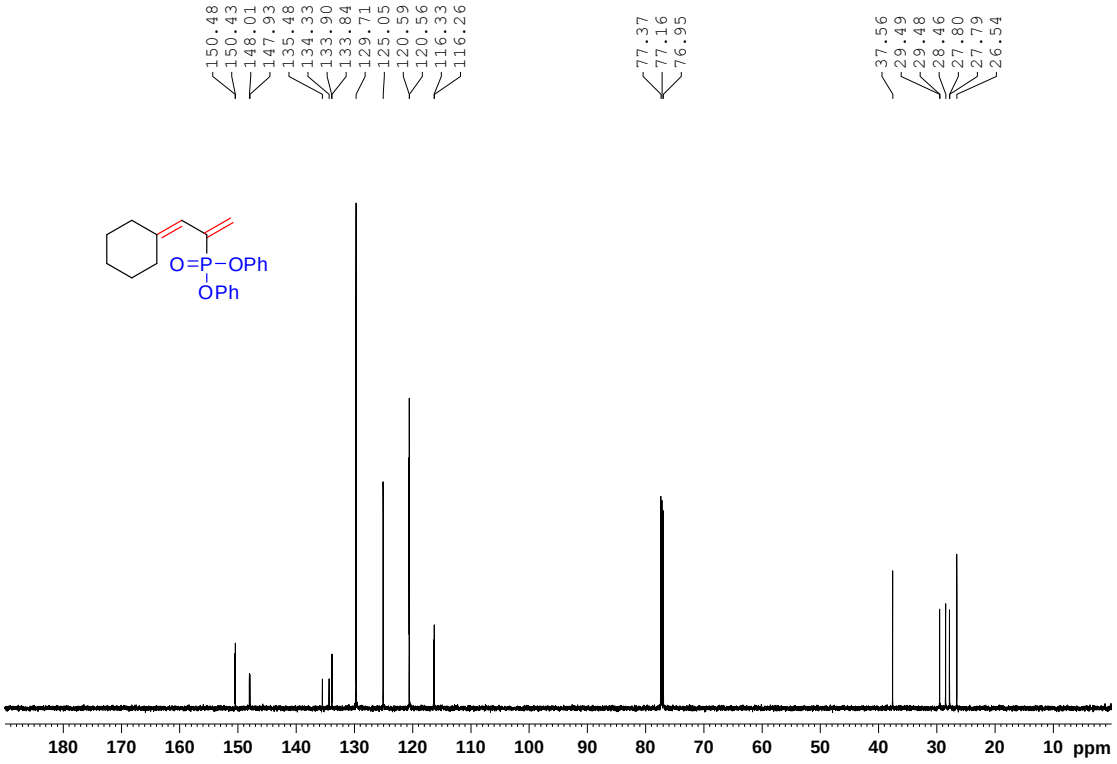
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3am**



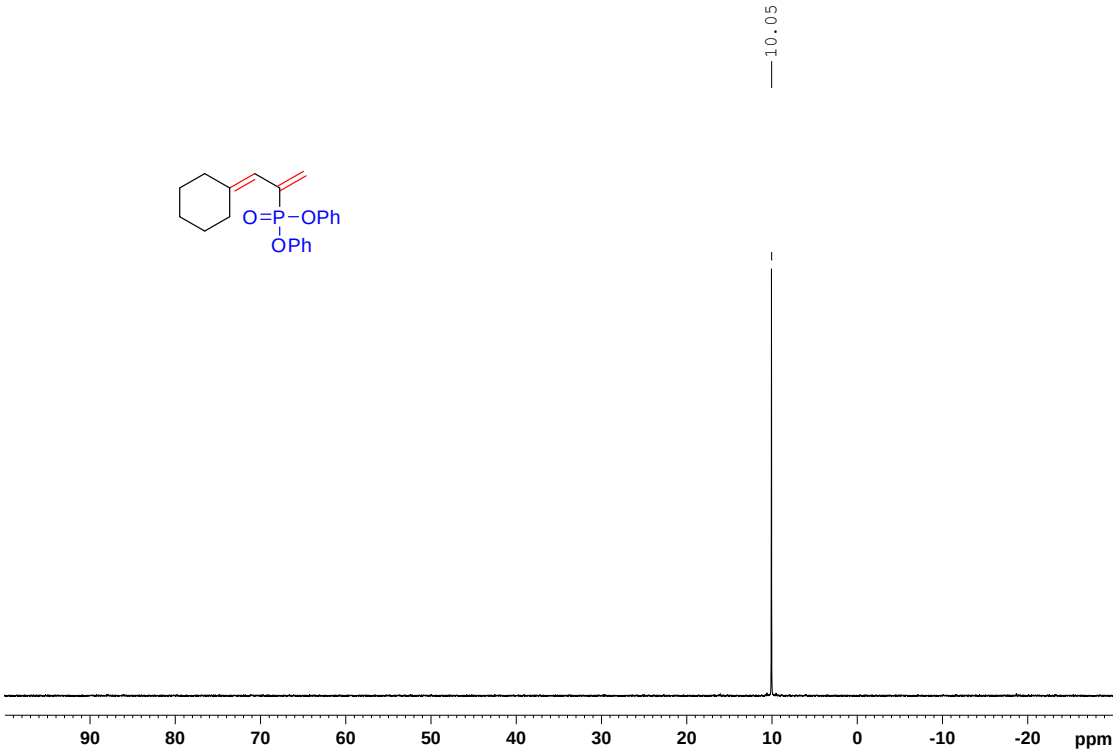
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3am**



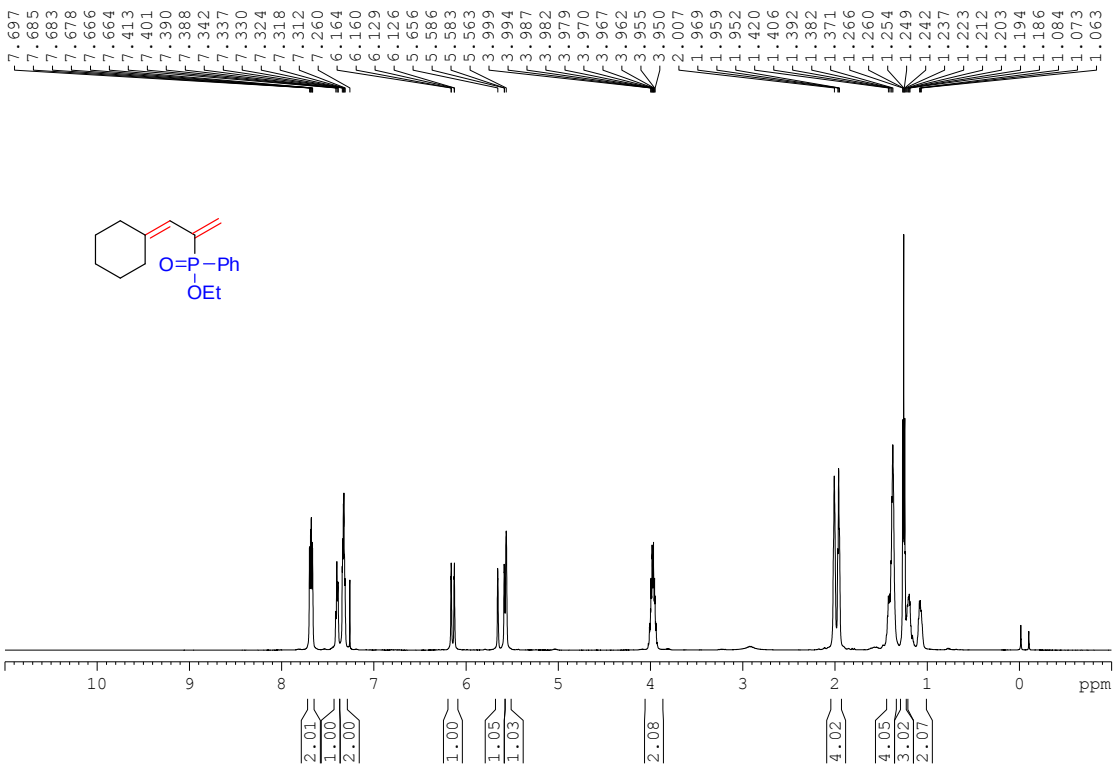
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3an**



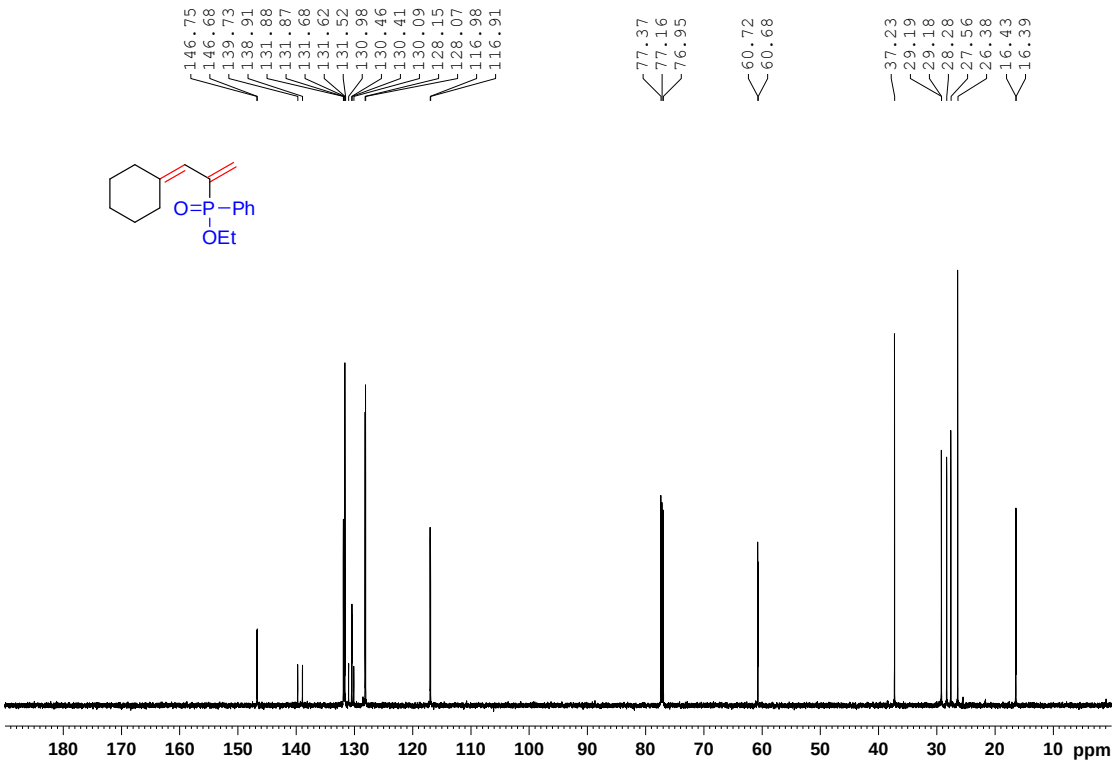
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3an**



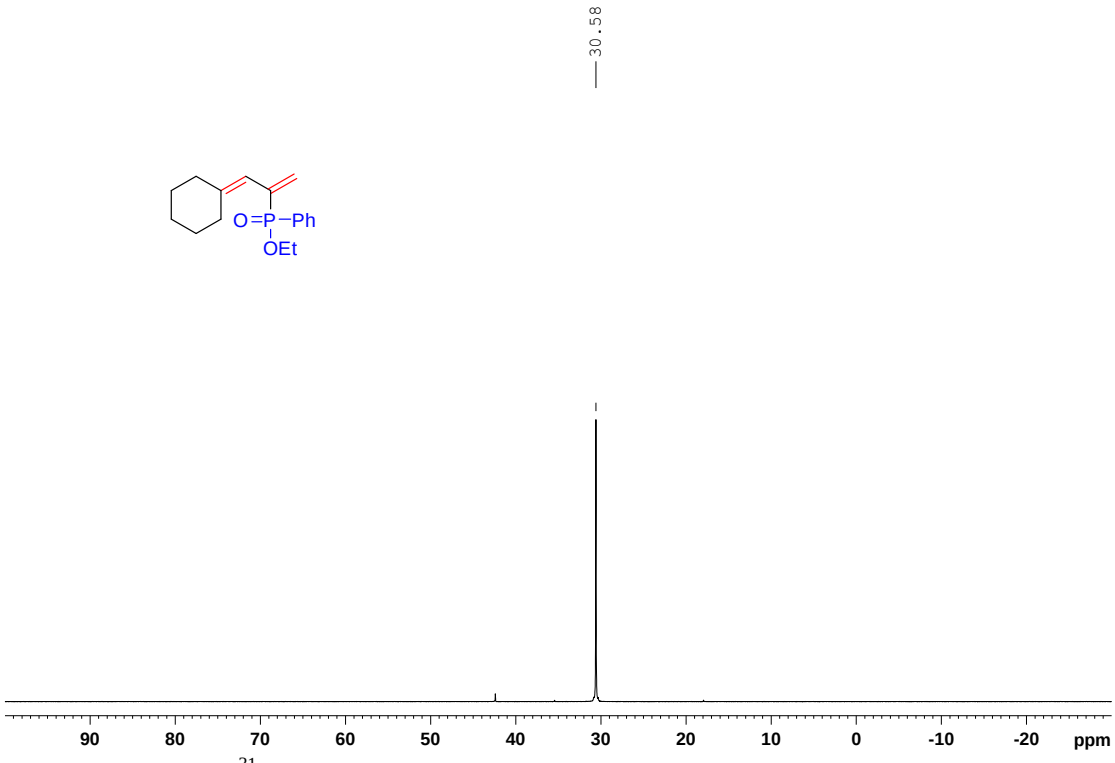
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3am**



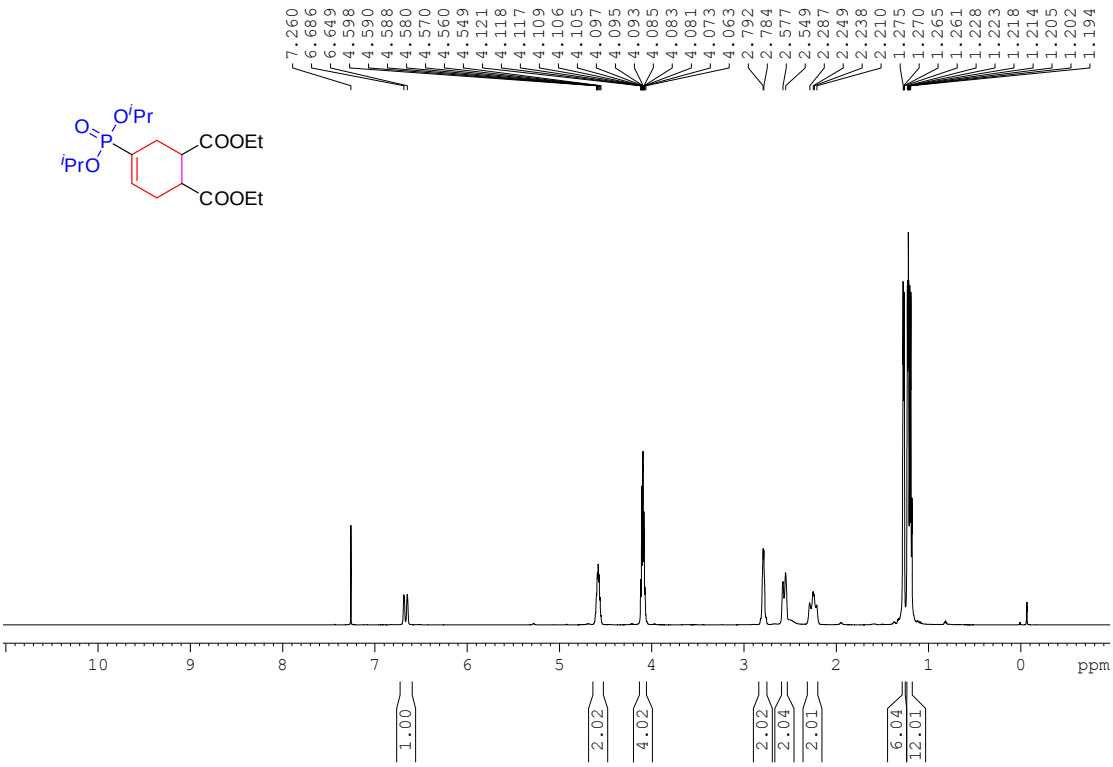
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3ao**



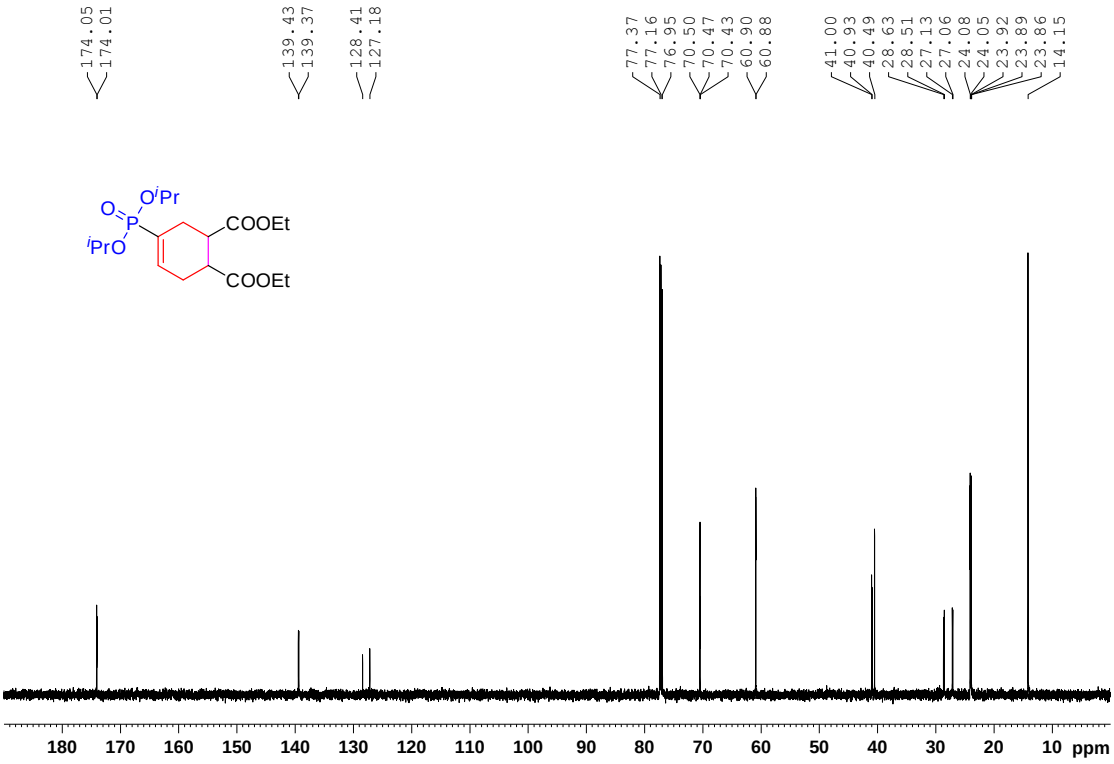
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3ao**



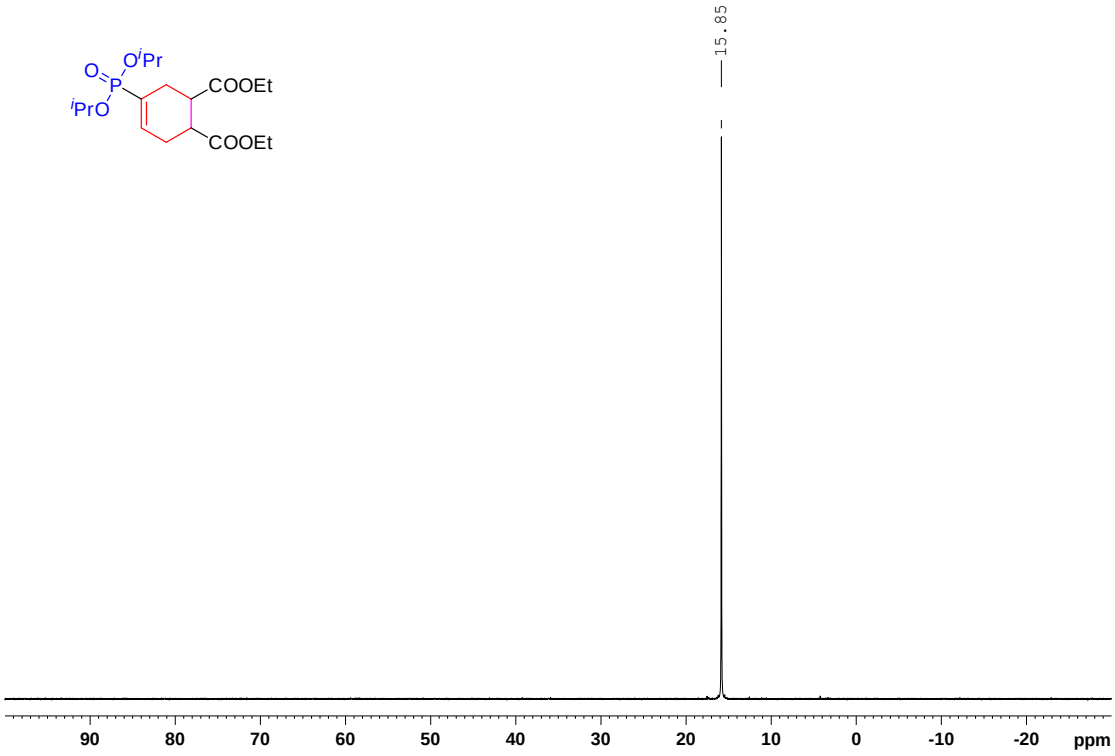
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **3ao**



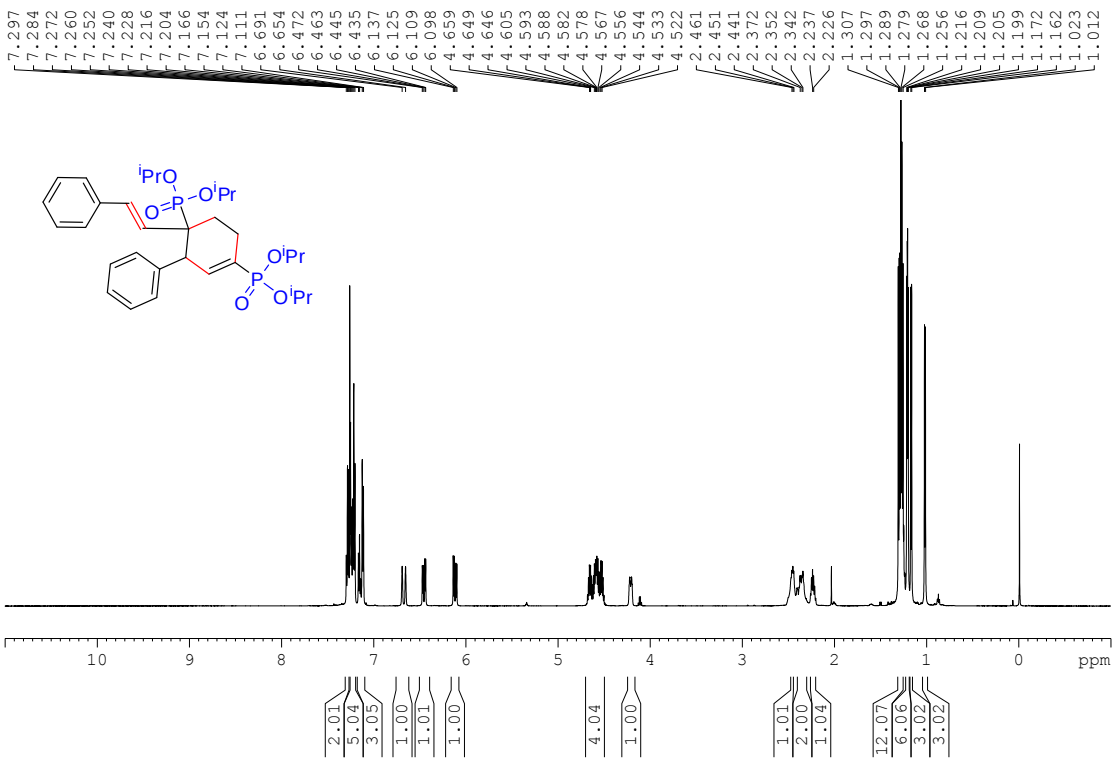
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4a**



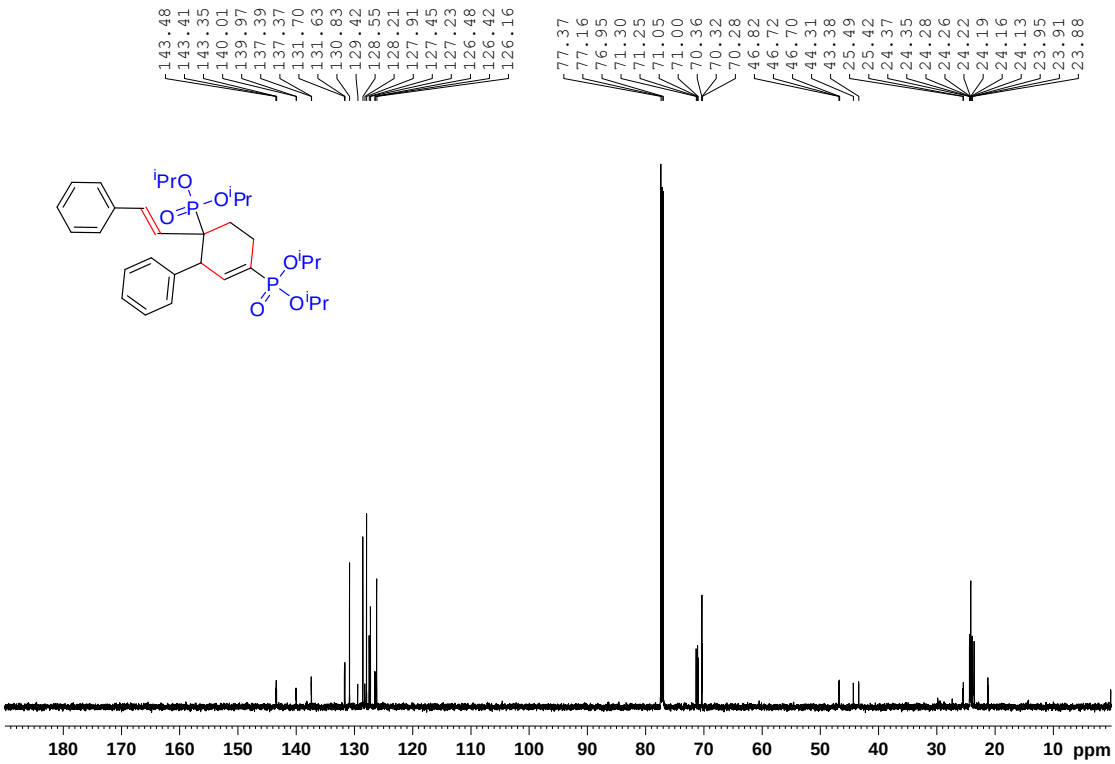
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4a**



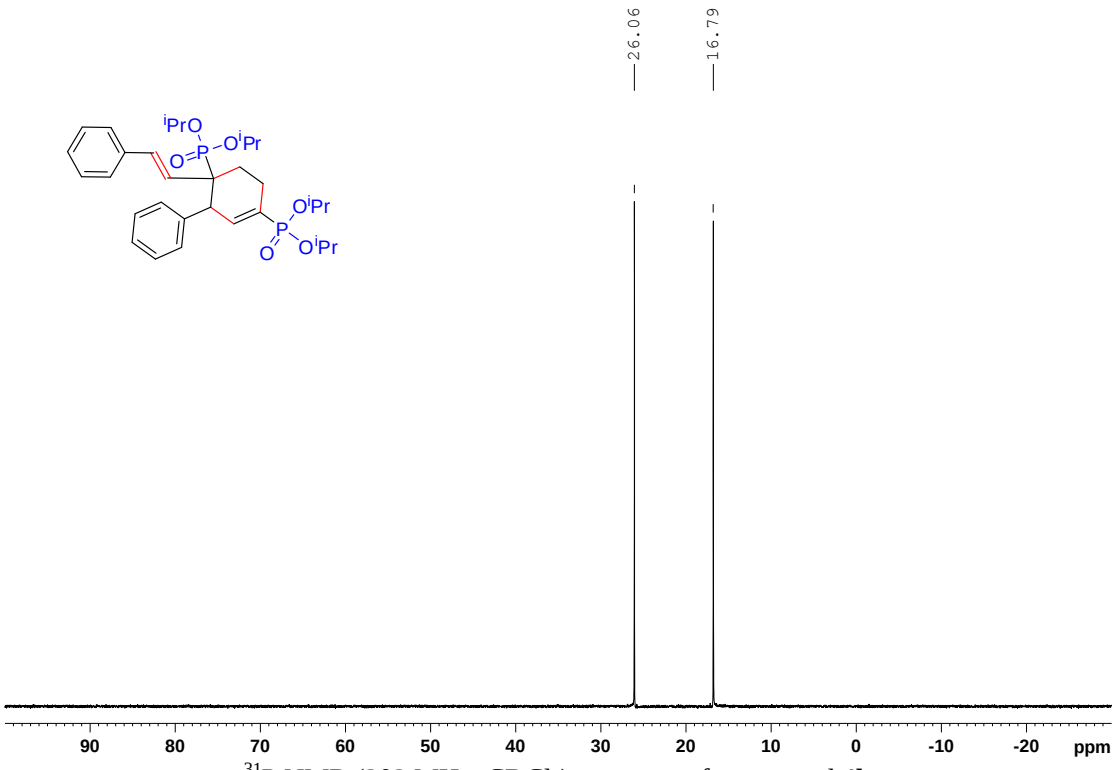
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **4a**



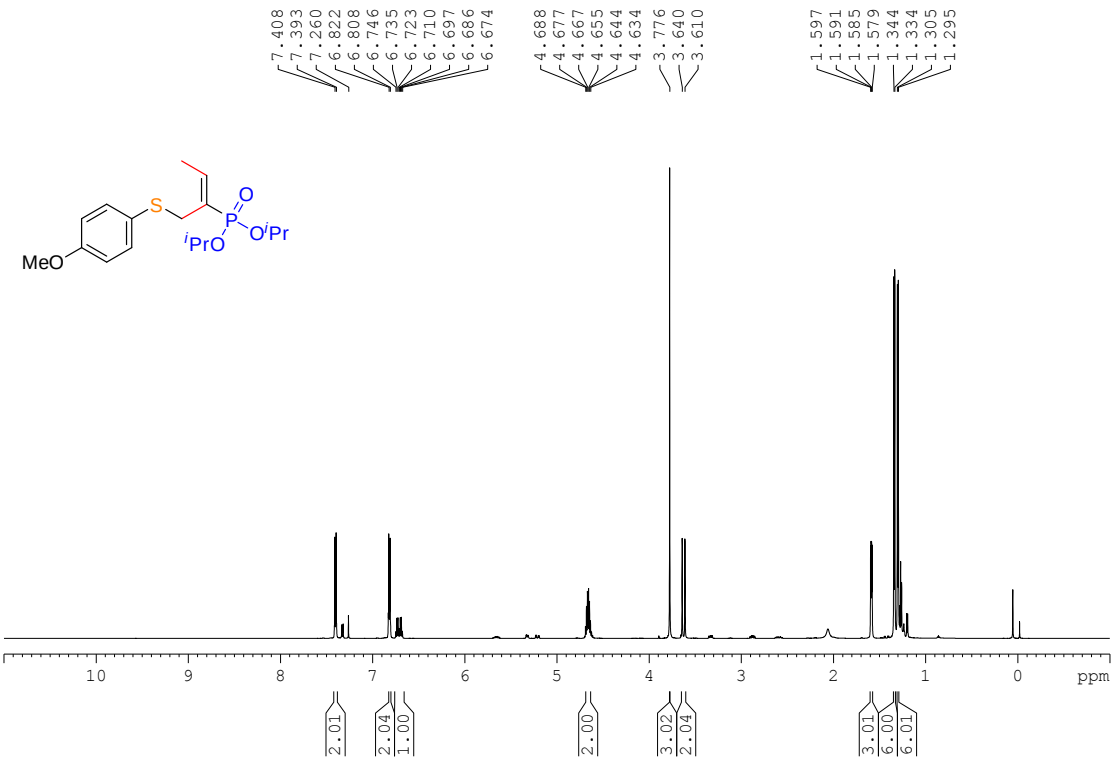
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4b**



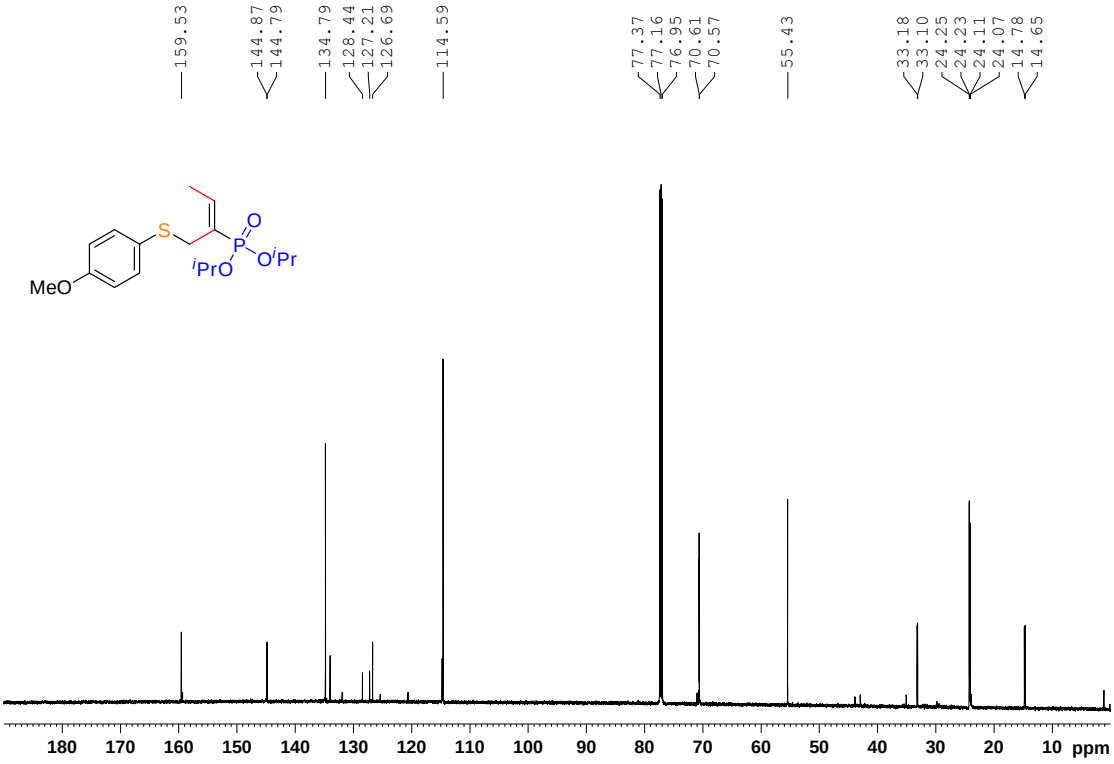
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4b**



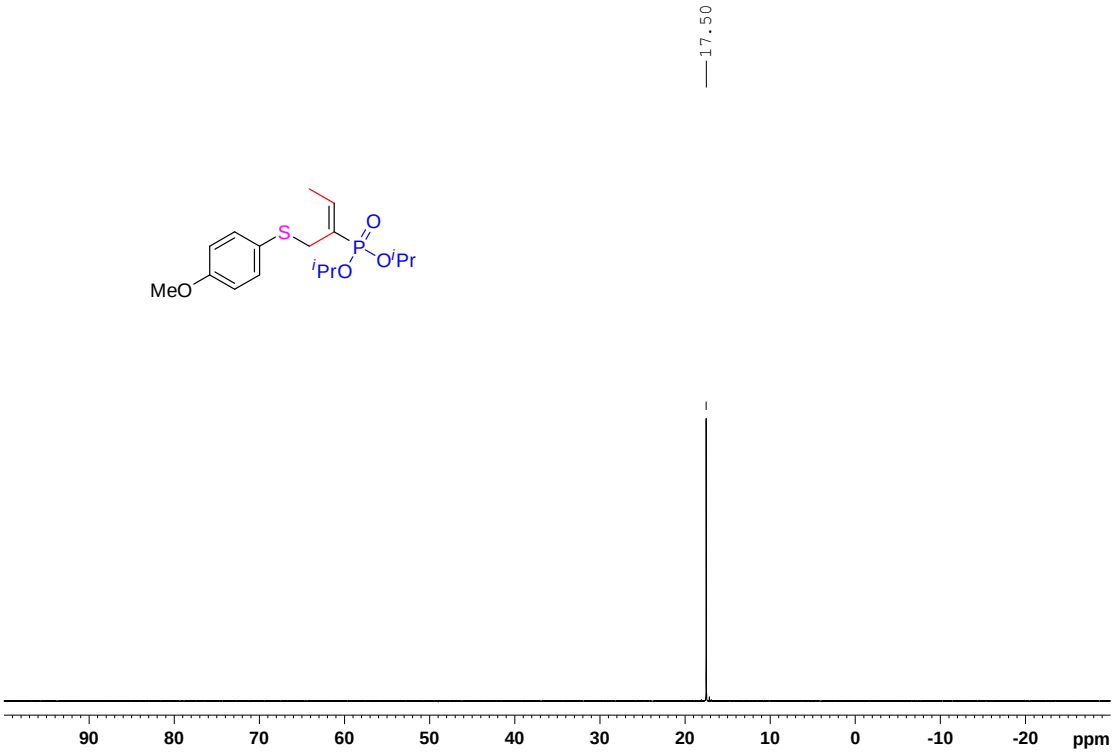
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **4b**



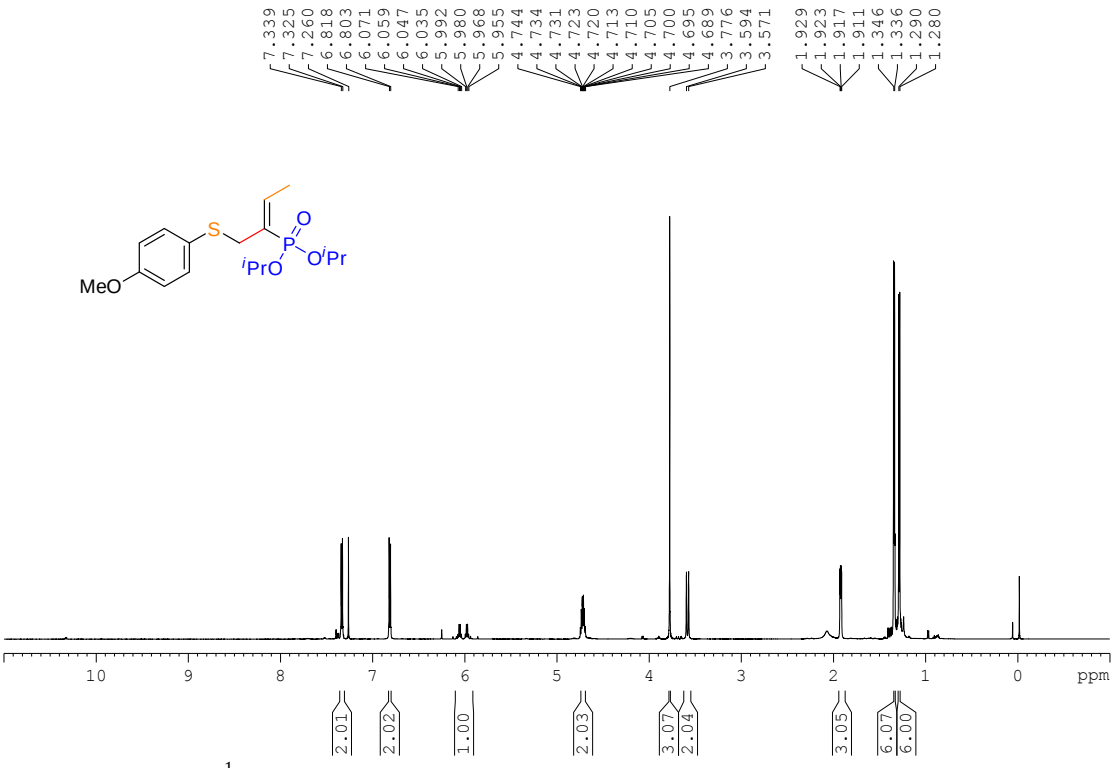
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*E*)-**5a**



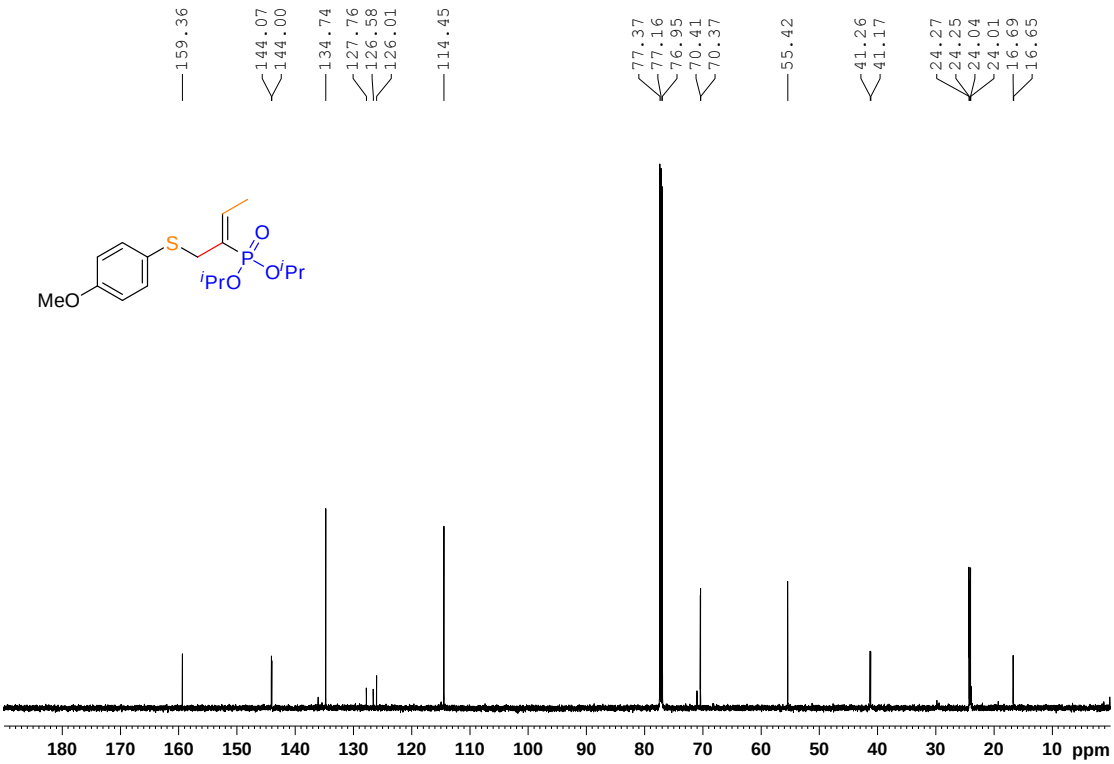
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*E*)-**5a**



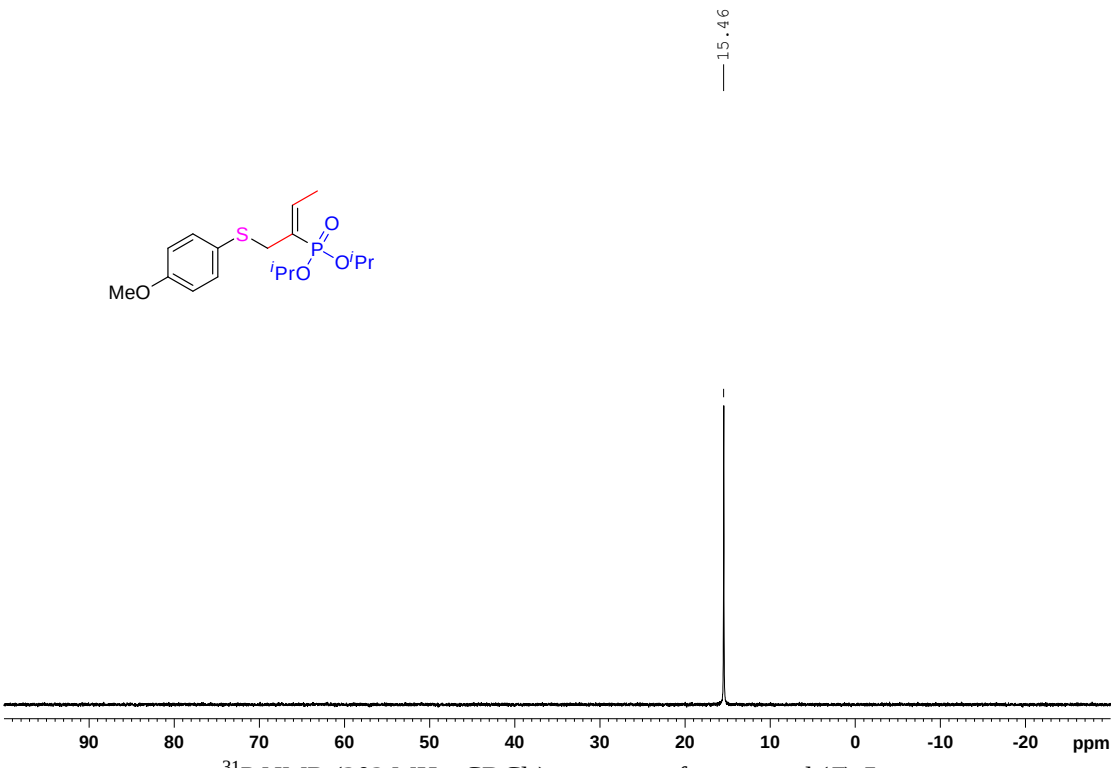
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*E*)-**5a**



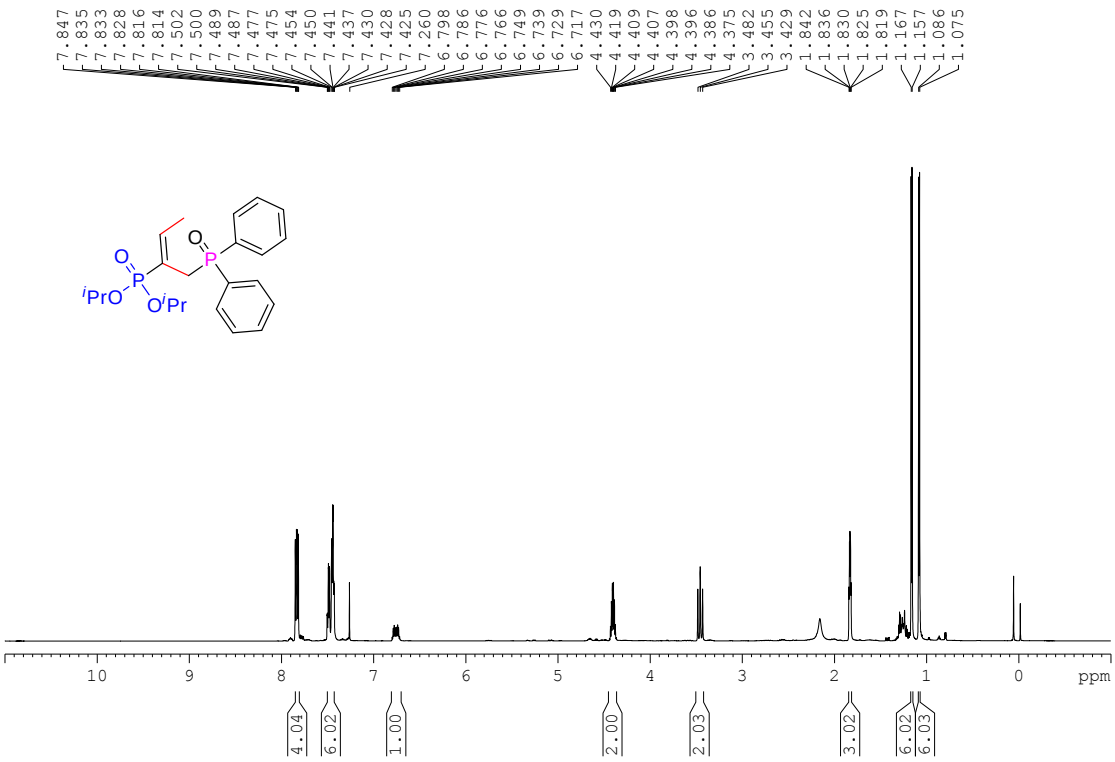
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*Z*)-**5a**



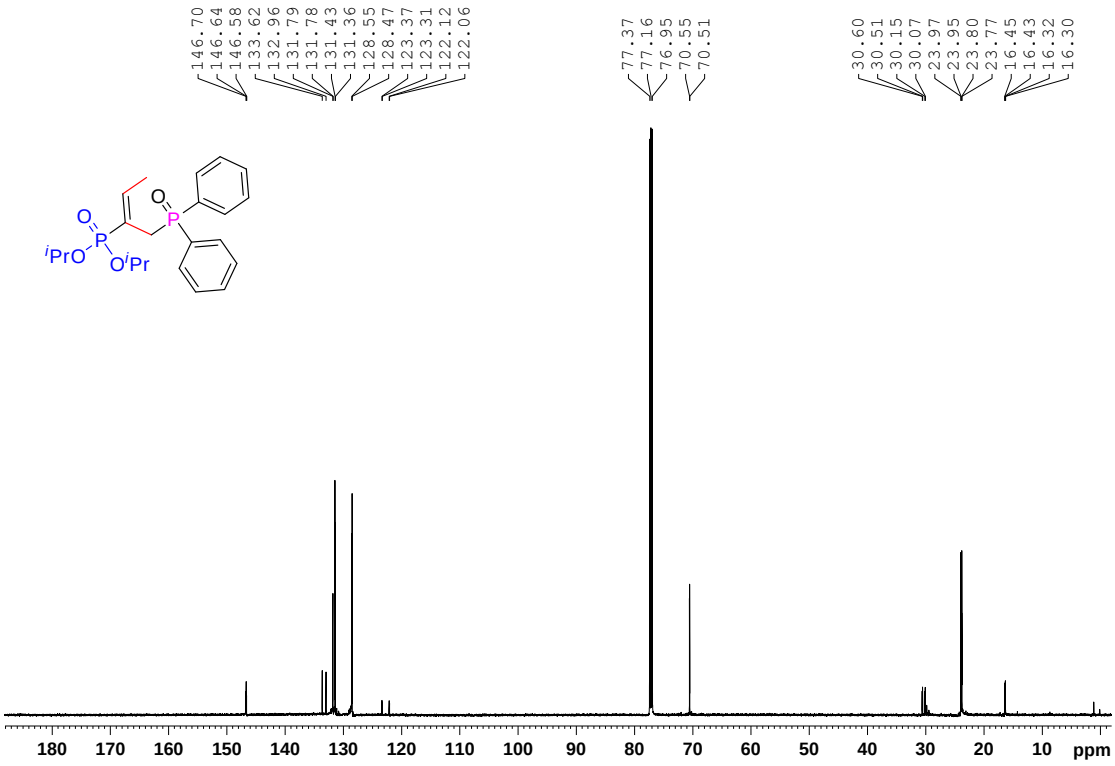
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound (*Z*)-**5a**



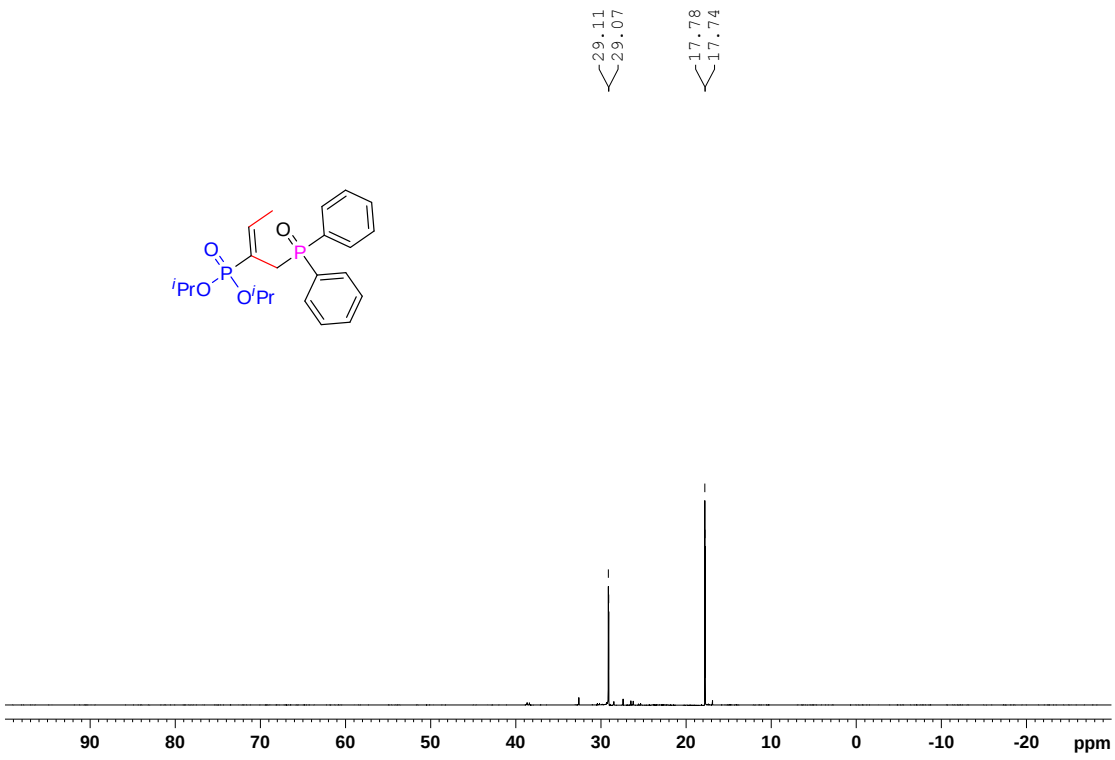
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound (*Z*)-**5a**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5b**



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **5b**



^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **5b**