Substrate-Controlled Regioselective Hydrophosphorylation of Allenes to Enable Photocatalytic Synthesis of Alkenylphosphoryl Compounds

Tian-Ming Yang, Xin-Lu Fan, Wei Shi, Xuefei Zhao* and Xu-Hong Hu*

Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China.

ias_xfzhao@njtech.edu.cn (to X.Z.); ias_xhhu@njtech.edu.cn (to X.-H.H.)

Table of Contents

1. General information

Unless otherwise noted, all reagents and solvents were purchased from Energy Chemical, Bidepharm, Aladdin Bio-Chem and J&K Scientific, and were used without further purification. Reaction temperature refers to the temperature of a silicon oil bath, which is controlled by an electronic temperature modulator from IKA or Heidolph.

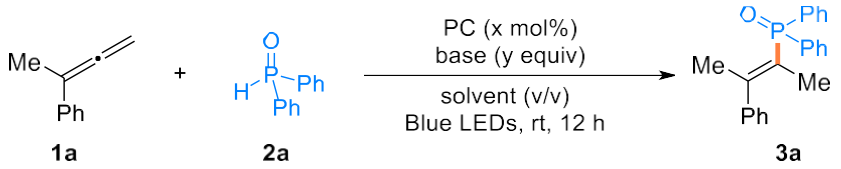
Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. Other visualization method was staining with a basic solution of potassium permanganate, followed by heating. Flash chromatography was performed using Nuotai silica gel (200–300 mesh) with the indicated solvent system. Column were typically packed as slurry and equilibrated with petroleum ether prior to use.

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C on JEOL 400M Hz spectrometers ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), and broad singlet (br s), etc. The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.16, triplet). To clarify the complete signal assignments, "× number" indicates the multiple carbons due to the superposition of chemical shifts.

Melting point was measured using a WRS-1C digital melting point apparatus (Shanghai Shenguang Instrument). High resolution mass spectral analysis (HRMS) was performed on Waters-XEVOG2Q-TOF (Thermo Electron Corporation).

2. Optimization of the reaction conditions

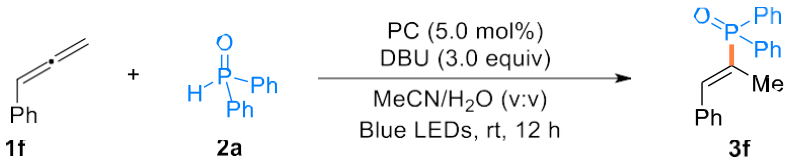
Table S1. Screening the reaction conditions for hydrophosphorylation of 1,1-disubstituted allene[a]



entry	PC (x mol%)	base (y equiv)	solvent (v/v)	yield	*E*/*Z*
1	$Ru(bpy)_3Cl_2$ (5.0)	DBU (1.0)	MeCN/H_2O (2.0 mL:0.2 mL)	21%	88:12
2	$Ru(bpy)_3Cl_2$ (5.0)	DBU (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	64%	88:12
3	$Ru(bpy)_3Cl_2$ (5.0)	DBU (4.0)	MeCN/H_2O (2.0 mL:0.2 mL)	52%	88:12
4	$Ru(bpy)_3Cl_2$ (5.0)	DABCO (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	22%	88:12
5	$Ru(bpy)_3Cl_2$ (5.0)	HTMP (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	trace	-
6	$Ru(bpy)_3Cl_2$ (5.0)	DMAP (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	trace	-
7	$Ru(bpy)_3Cl_2$ (5.0)	DBN (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	43%	89:11
8	$Ru(bpy)_3Cl_2$ (5.0)	DIPEA (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	trace	-
9	$Ru(bpy)_3Cl_2$ (5.0)	DBU (3.0)	DMF/H_2O (2.0 mL:0.2 mL)	37%	88:12
10	$Ru(bpy)_3Cl_2$ (5.0)	DBU (3.0)	THF/H_2O (2.0 mL:0.2 mL)	50%	86:14
11	$Ru(bpy)_3Cl_2$ (5.0)	DBU (3.0)	DMSO/H_2O (2.0 mL:0.2 mL)	trace	-
12	$Ru(bpy)_3Cl_2$ (5.0)	DBU (3.0)	1,2-DCE/H_2O (2.0 mL:0.2 mL)	n.d.	-
13	$Ru(bpy)_3Cl_2$ (5.0)	DBU (3.0)	MeCN/H_2O (1.0 mL:0.1 mL)	60%	88:12
14[b]	$Ru(bpy)_3Cl_2$ (5.0)	DBU (3.0)	MeCN/H_2O (1.5 mL:0.15 mL)	64%	88:12
15	$Ru(bpy)_3Cl_2$ (5.0)	DBU (3.0)	MeCN/HFIP (2.0 mL:0.2 mL)	n.d.	-
16	$Ru(bpy)_3Cl_2$ (5.0)	DBU (3.0)	MeCN/AcOH (2.0 mL:0.2 mL)	n.d.	-
17	$Ru(bpy)_3Cl_2$ (2.5)	DBU (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	39%	88:12
18[c]	$Ru(bpy)_3Cl_2$ (7.0)	DBU (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	59%	88:12
19	4CzIPN (5.0)	DBU (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	45%	86:14
20	Eosin Y (5.0)	DBU (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	52%	86:14
21	**$Ru(bpy)_3(PF_6)_2$ (5.0)**	**DBU (3.0)**	**MeCN/H_2O (2.0 mL:0.2 mL)**	**81%**	**88:12**
22[d]	$Ru(bpy)_3(PF_6)_2$ (5.0)	DBU (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	75%	88:12
23	-	DBU (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	trace	-
24	$Ru(bpy)_3(PF_6)_2$ (5.0)	-	MeCN/H_2O (2.0 mL:0.2 mL)	n.d.	-
25	$Ru(bpy)_3(PF_6)_2$ (5.0)	DBU (3.0)	MeCN/H_2O (2.0 mL:5.0 equiv)	trace	-
26	$Ru(bpy)_3(PF_6)_2$ (5.0)	DBU (3.0)	MeCN (2.0 mL)	trace	-
27[e]	$Ru(bpy)_3(PF_6)_2$ (5.0)	DBU (3.0)	MeCN/H_2O (2.0 mL:0.2 mL)	n.d.	-

[a]Reaction conditions: **1a** (0.15 mmol), **2a** (0.3 mmol), PC (x mol%), and base (y equiv) in solvent at room temperature for 12 h under N_2 atmosphere, 40 W Blue LEDs (λ = 455 nm); Yield of isolated product. The ratio of *E*/*Z* isomers was determined by ^{31}P NMR analysis. [b]16 h. [c]14 h. [d]8 h. [e]no light. n.d. = not detected. DBU = 1,8-diazabicyclo[5.4.0]undecane-7-ene, DABCO = 1,4-diazabicyclo[2.2.2]octane, HTMP = 2,2,6,6-tetramethylpiperidine, DMAP = 4-dimethylaminopyridine, DBN = 1,5-diazabicyclo[4.3.0]non-5-ene, DIPEA = *N*,*N*-diisopropylethylamine.

Table S2. Screening the reaction conditions for hydrophosphorylation of monosubstituted allene[a]

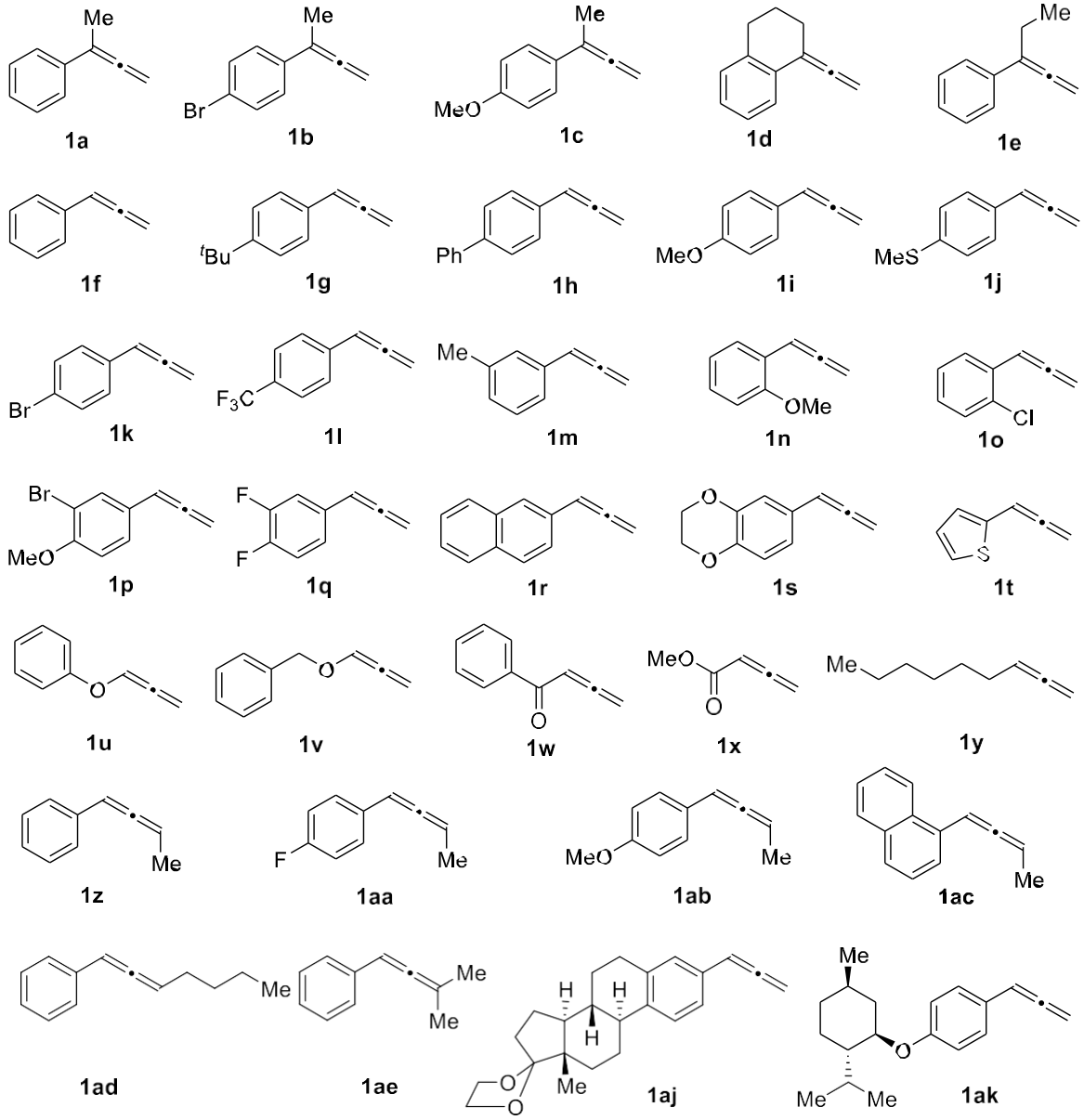


entry	PC	MeCN/H_2O (v/v)	yield	*E*/*Z*
1	$Ru(bpy)_3(PF_6)_2$	2.0 mL:0.2 mL	54%	98:2
2	$Ru(bpy)_3Cl_2$	2.0 mL:0.2 mL	25%	98:2
3	$Ru(bpy)_3(BF_4)_2$	2.0 mL:0.2 mL	28%	97:3
4[b]	$Ru(bpy)_3(PF_6)_2$	1.6 mL:0.4 mL	67%	98:2
5[b]	$Ru(bpy)_3(PF_6)_2$	1.6 mL:0.3 mL	60%	98:2
6[b,c]	**$Ru(bpy)_3(PF_6)_2$**	**1.6 mL:0.3mL**	**80%**	**>99:1**

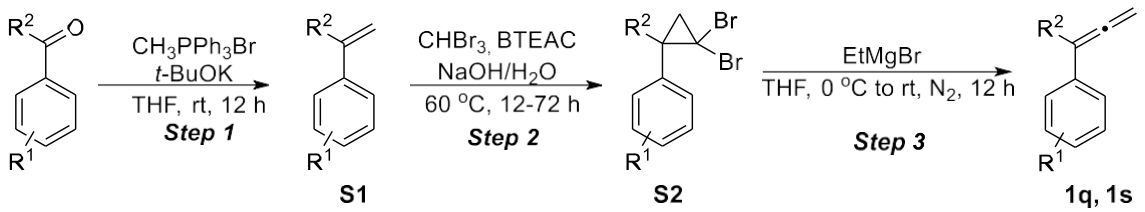
[a]Reaction conditions: **1f** (0.15 mmol), **2a** (0.3 mmol), PC (5.0 mol%), and DBU (3.0 equiv) in MeCN/H_2O at room temperature for 12 h under N_2 atmosphere, 40 W Blue LEDs (λ = 455 nm); Yield of isolated product.; The ratio of *E*/*Z* isomers was determined by ^{31}P NMR analysis. [b]16 h. [c]**2a** (0.45 mmol).

3. Preparation of the starting materials

3.1 Preparation of allenes



Allenes **1a**–**1d**, **1f**–**1t**, **1z**–**1ac** were prepared according to the known procedure in the literature.[1] Allenes **1e**,[2] **1u** and **1v**,[3] **1w**,[4] **1x**,[5] **1y**,[6] **1ad**,[7] **1ae**[8], **1aj**,[1,9] **1ak**[10] were prepared according to the known procedures in the literatures. The ^{1}H NMR spectra of all known compounds are in consistent with the reported data.

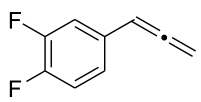


Step 1: To a 250 mL round-bottomed flask, methyl triphenylphosphonium bromide (12 mmol, 1.2 equiv) and THF (20 mL) was added. Then *t*-BuOK (12 mmol, 1.2 equiv) was added to the reaction mixture slowly and the resulting yellow suspension was stirred at room temperature for 30 min. To this suspension, a solution of ketone (10 mmol, 1.0 equiv) was added in one portion and the resulting mixture was further stirred at room temperature overnight. Water (50 mL) and CH_2Cl_2 (20 mL) were added to the reaction mixture, and the aqueous phase was extracted with CH_2Cl_2 (20 mL × 3). The combined organic phases were washed with saturated NaCl, dried over Na_2SO_4 and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography on silica gel using petroleum ether as eluent to afford the corresponding alkene **S1**.

Step 2: To a solution of alkene **S1** (1.0 equiv), bromoform (1.5 equiv) and $BnNEt_3Cl$ (BTEAC, 1.0 mol%) was added dropwise a solution of 50% NaOH (4.0 equiv), and the mixture was stirred at room temperature for 1 h, then heated to 60 °C and further stirred until conversion was complete as observed by TLC analysis. Water (20 mL) and CH_2Cl_2 (20 mL) were added and the aqueous phase was extracted with CH_2Cl_2 (20 mL × 3). The combined organic phases were washed with saturated NaCl, dried over Na_2SO_4 and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography on silica gel to afford **S2**.

Step 3: EtMgBr (1.0 M in THF, 1.5 equiv) was added dropwise to an ice-bath solution of **S2** (1.0 equiv) in dry THF (10 mL) under N_2. The mixture was then slowly warmed to room temperature, and stirred at room temperature for an additional 2 h. Then the reaction was quenched by HCl (0.5 M, 10 mL) solution, water was added, and the mixture was extracted with Et_2O (20 mL × 3). The combined organic layers were washed with saturated NaCl, dried over Na_2SO_4 and filtered. After removal the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the corresponding allene **1q** or **1s**.

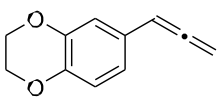
1,2-Difluoro-4-(propa-1,2-dien-1-yl)benzene (1q)



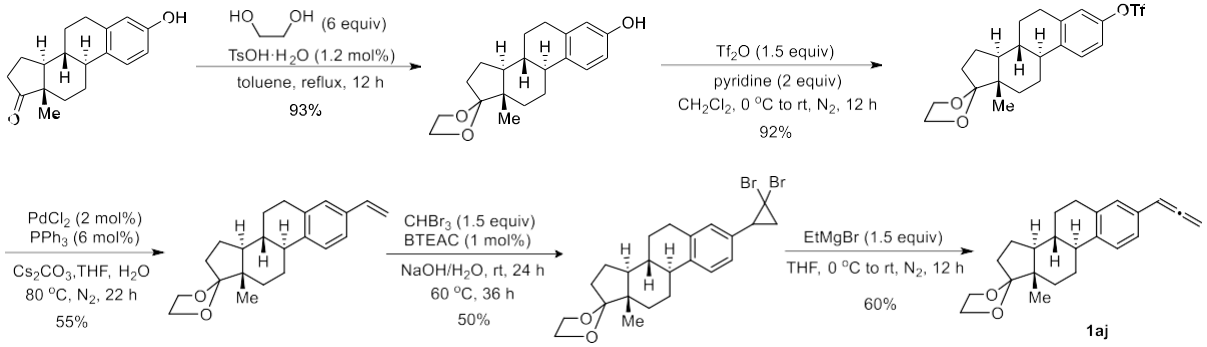
The title compound was prepared according to literature[1] and isolated as a pale yellow oil (509.2 mg, 3.35 mmol, 67%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.16 – 7.04 (m, 2H), 7.01 – 6.95 (m, 1H), 6.09 (t, *J* = 6.8 Hz, 1H), 5.19 (s, 1H), 5.18 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 209.9 (d, *J* = 2.5 Hz), 151.3 (dd, *J* = 124.4, 13.0 Hz), 148.8 (dd, *J* = 124.8, 13.0 Hz), 131.3 (dd, *J* = 5.9, 4.1 Hz), 122.7 (dd, *J* = 6.2, 3.4 Hz), 117.4 (d, *J* = 17.7 Hz), 115.2 (d, *J* = 18.1 Hz), 92.8, 79.7.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -137.74 – -137.93 (m), -139.89 – -140.08 (m). **HRMS** (ESI): m/z calculated for $C_9H_7F_2$ $[M + H]^+$: 153.0510, found: 153.0511.

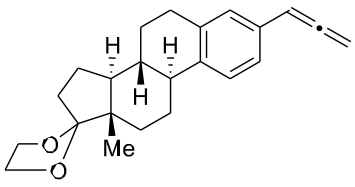
6-(Propa-1,2-dien-1-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine (1s)



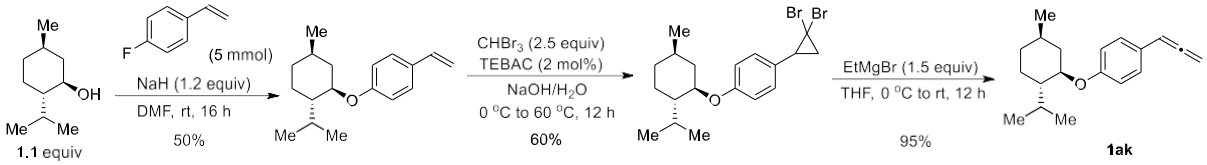
The title compound was prepared according to literature[1] and isolated as a pale yellow oil (609.1 mg, 3.50 mmol, 70%).**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.04 – 6.68 (m, 3H), 6.06 (t, *J* = 6.8 Hz, 1H), 5.12 (s, 1H), 5.11 (s, 1H), 4.25 (s, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 209.6, 143.8, 142.8, 127.4, 120.1, 117.5, 115.4, 93.5, 79.0, 64.5, 64.5. **HRMS** (ESI): m/z calculated for $C_{11}H_{11}O_2$ $[M + H]^+$: 175.0754, found: 175.0750.



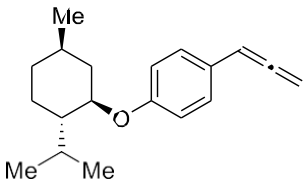
(8*R*,9*S*,13*S*,14*S*)-8,9,13,14-Tetramethyl-3-(propa-1,2-dien-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro spiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolane] (1aj)



The title compound was prepared according to literature[1,9] and isolated as a pale yellow oil (802.5 mg, 2.12 mmol, 60%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.2 Hz, 1H), 7.08 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.02 (s, 1H), 6.11 (t, *J* = 6.8 Hz, 1H), 5.12 (d, *J* = 6.7 Hz, 2H), 4.07 – 3.68 (m, 4H), 2.85 (dd, *J* = 8.4, 4.2 Hz, 2H), 2.40 – 2.21 (m, 2H), 2.08 – 2.01 (m, 1H), 1.95 – 1.73 (m, 4H), 1.70 – 1.61 (m, 1H), 1.58 – 1.28 (m, 5H), 0.89 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 209.8, 139.5, 137.2, 131.1, 127.3, 125.8, 124.1, 119.6, 93.7, 78.7, 65.4, 64.7, 49.6, 46.3, 44.2, 39.0, 34.4, 30.9, 29.6, 27.1, 26.1, 22.5, 14.5. **HRMS** (ESI): m/z calculated for $C_{23}H_{29}O_2^+$ $[M + H]^+$: 337.2162, found:337.2165.

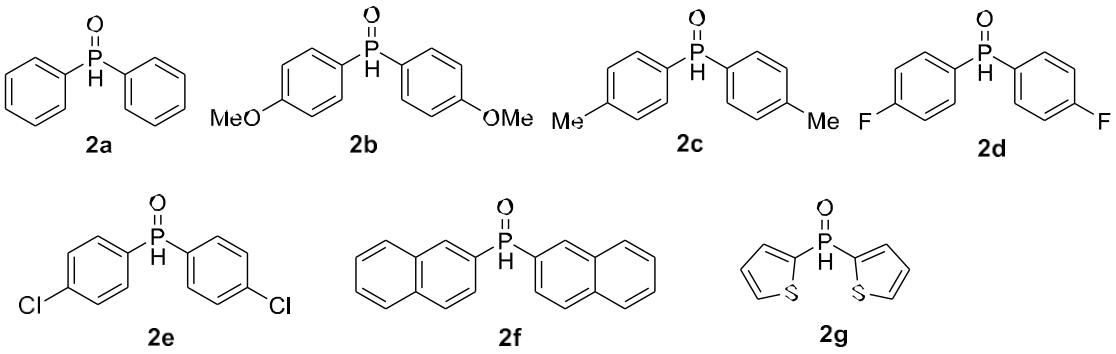


1-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)-4-(propa-1,2-dien-1-yl)benzene (1ak)



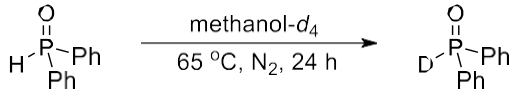
The title compound was prepared according to literature[10] and isolated as a pale yellow oil (386.7 mg, 1.43 mmol, 95%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 – 7.04 (m, 2H), 6.99 – 6.63 (m, 2H), 6.12 (t, *J* = 6.8 Hz, 1H), 5.12 (d, *J* = 6.8 Hz, 2H), 4.04 – 3.98 (m, 1H), 2.34 – 2.06 (m, 2H), 1.80 – 1.64 (m, 2H), 1.51 – 1.47 (m, 2H), 1.17 – 0.97 (m, 3H), 0.92 (dd, *J* = 6.8, 4.0 Hz, 6H), 0.77 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 209.5, 157.7, 127.9 × 2, 125.9, 116.2 × 2, 93.5, 78.8, 77.8, 48.1, 40.4, 34.6, 31.5, 26.1, 23.8, 22.2, 20.8, 16.6. **HRMS** (ESI): m/z calculated for $C_{19}H_{27}O^+$ $[M + H]^+$: 271.2056, found:271.2056.

3.2 Synthesis of diarylphosphine oxides

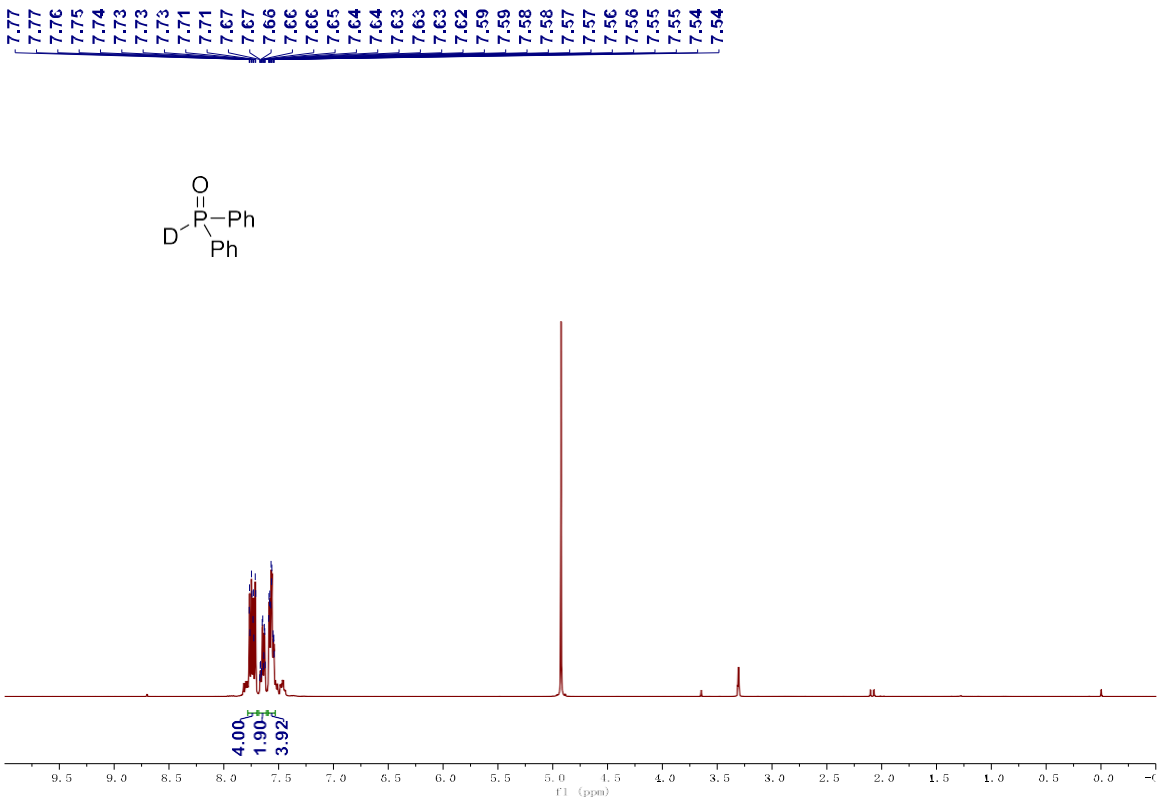


Phosphine oxides **2a**–**2g** were prepared according to the known procedure in the literature.[11] The ^{1}H NMR spectra of all known compounds are in consistent with the reported data.

3.3 Synthesis of 2a-D[12]

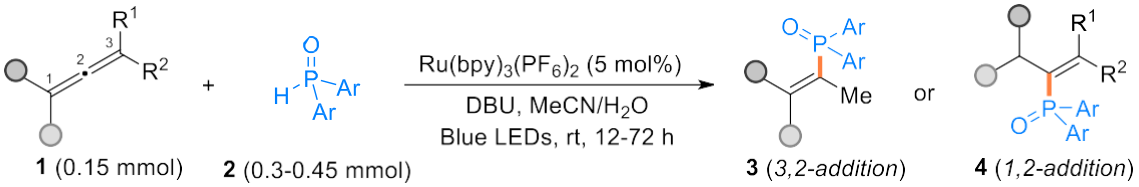


An oven-dried 8 mL round bottom flask equipped with a stir bar was charged with diphenylphosphine oxide **2a** (404.4 mg, 2 mmol). Next, methanol-d_4 (99.8% D, 2.0 mL) was added via syringe and the mixture was stirred and until all the solids dissolved. The resulting solution was stirred at 65 °C for 24 h. The resulting clear solution was concentrated in vacuo and resulted in quantitative yield (> 99%) of the title compound **2a-D**. ^{1}H NMR spectrum showed >99% D incorporation. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.77 – 7.71 (m, 4H), 7.67 – 7.62 (m, 2H), 7.60 – 7.54 (m, 4H).



^{1}H NMR spectrum of compound **2a-D** (CD_3OD)

3.4 General procedure (GP1) for the synthesis of 3 or 4



1 (0.15 mmol) **2** (0.3-0.45 mmol) **3** (*3,2-addition*) **4** (*1,2-addition*)

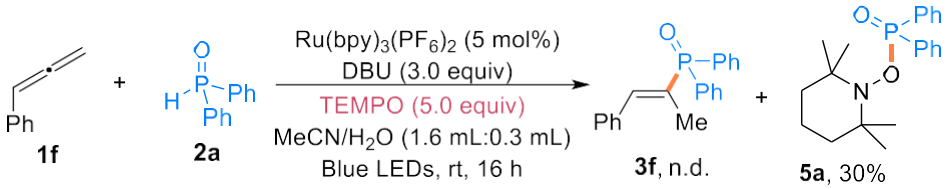
An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (6.4 mg, 0.0075 mmol, 5.0 mol%), **2** (0.3-0.45 mmol) and the tube was evacuated and backfilled with N_2 for 3 times. DBU (68.5 mg, 0.45 mmol, 3.0 equiv), **1** (0.15 mmol, 1.0 equiv) and $MeCN/H_2O$ were successively added via syringe. The sealed tube was placed into a 40 W Blue LEDs at room temperature with stirring for 12–72 h. After the completion of the reaction, the mixture was concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc = 1.2/1→1.5/1) on silica gel to afford the corresponding coupling product **3** or **4**.

3.6 Gram scale synthesis of 3h

An oven-dried 100 mL Schlenk tube equipped with a stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (171.9 mg, 0.2 mmol, 5.0 mol%), **2a** (2.43 g, 12 mmol, 3.0 equiv) and the tube was evacuated and backfilled with N_2 for 3 times. DBU (1.83 g, 12 mmol, 3.0 equiv), **1h** (769.0 mg, 4.0 mmol, 1.0 equiv) and MeCN/H_2O (42 mL:8 mL) were successively added via syringe. The sealed tube was placed into a 40 W Blue LEDs at room temperature with stirring for 44 h. After the completion of the reaction, the mixture was concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc = 1.2/1) on silica gel to afford the corresponding coupling product **3h** (1.36 g, 86%, *E*/*Z* > 99:1) as a white solid.

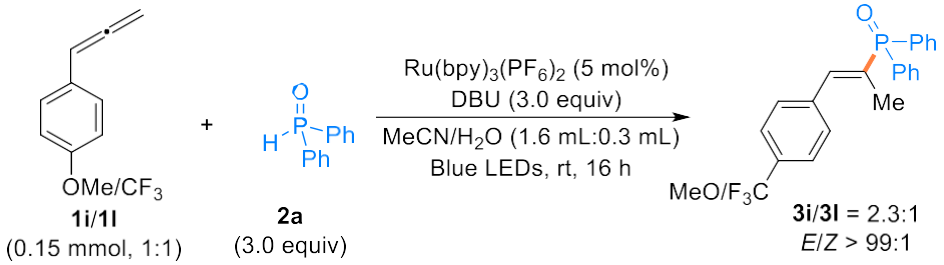
4. Mechanistic studies

4.1 Radical trapping experiment

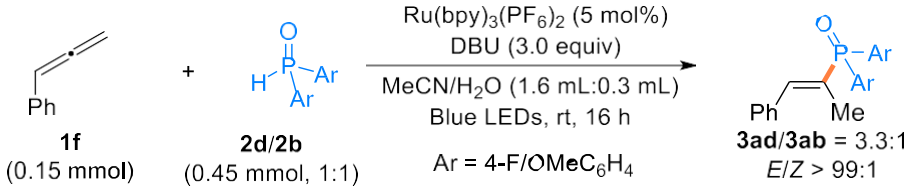


An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (6.4 mg, 0.0075 mmol, 5.0 mol%), **2a** (91.0 mg, 0.45 mmol, 3.0 equiv), TEMPO (117.2 mg, 0.75 mmol, 5.0 equiv) and the tube was evacuated and backfilled with N_2 for 3 times. DBU (68.5 mg, 0.45 mmol, 3.0 equiv), **1f** (17.4 mg, 0.15 mmol, 1.0 equiv) and MeCN/H_2O (1.6 mL:0.3 mL) were successively added via syringe. The sealed tube was placed into a 40 W Blue LEDs at room temperature with stirring for 16 h. After the completion of the reaction, the mixture was concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc = 1.5/1) on silica gel to afford the adduct **5a** (80.4 mg, 0.225 mmol, 30%). The adduct TEMPO–(O)$P(Ph)_2$ **5a** was observed, suggesting that the reaction might involve a phosphinoyl radical process.

4.2 Competitive experiments

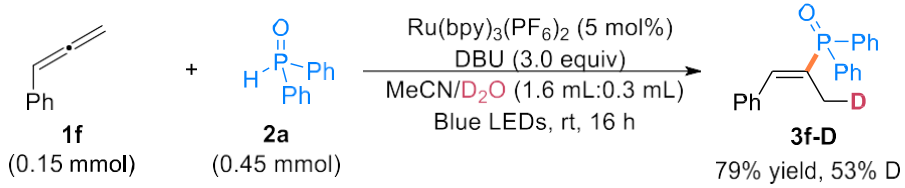


An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (6.4 mg, 0.0075 mmol, 5.0 mol%), **2a** (91.0 mg, 0.45 mmol, 3.0 equiv) and the tube was evacuated and backfilled with N_2 for 3 times. DBU (68.5 mg, 0.45 mmol, 3.0 equiv), **1i** (0.075 mmol, 11.0 mg) and **1l** (13.8 mg, 0.075 mmol) and MeCN/H_2O (1.6 mL:0.3 mL) were successively added via syringe. The sealed tube was placed into a 40 W Blue LEDs at room temperature with stirring for 16 h. After the completion of the reaction, the mixture was concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc = 1.2/1) on silica gel to afford the corresponding coupling product **3i** (14.4 mg, 0.041 mmol, 55%) and **3l** (7.0 mg, 0.018 mmol, 24%), **3i**/**3l** = 2.3/1.

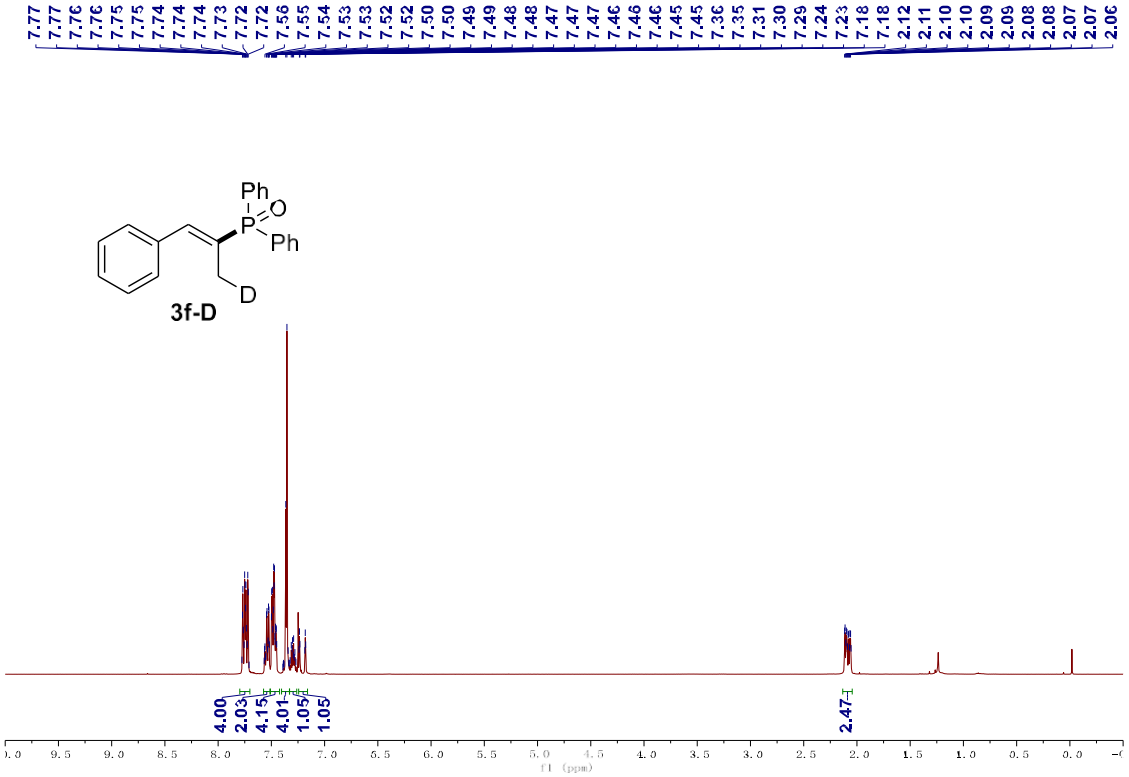


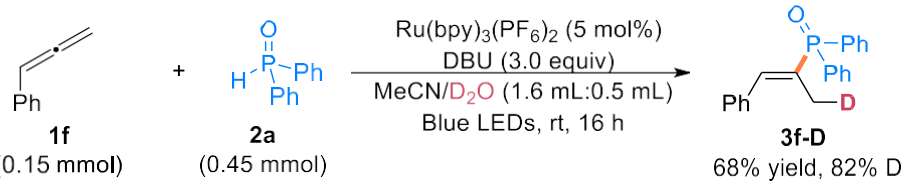
An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (6.4 mg, 0.0075 mmol, 5.0 mol%), **2d** (53.6 mg, 0.225 mmol) and **2b** (59.0 mg, 0.225 mmol) and the tube was evacuated and backfilled with N_2 for 3 times. DBU (68.5 mg, 0.45 mmol, 3.0 equiv), **1f** (17.4 mg, 0.15 mmol, 1.0 equiv) and MeCN/H_2O (1.6 mL:0.3 mL) were successively added via syringe. The sealed tube was placed into a 40 W Blue LEDs (λ = 455 nm) at room temperature with stirring for 16 h. After the completion of the reaction, the mixture was concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc = 1.2/1) on silica gel to afford the corresponding coupling product **3ad** (33.0 mg, 0.093 mmol, 62%) and **3ab** (10.8 mg, 0.029 mmol, 19%), **3ad**/**3ab** = 3.3/1.

4.3 Deuteration experiments



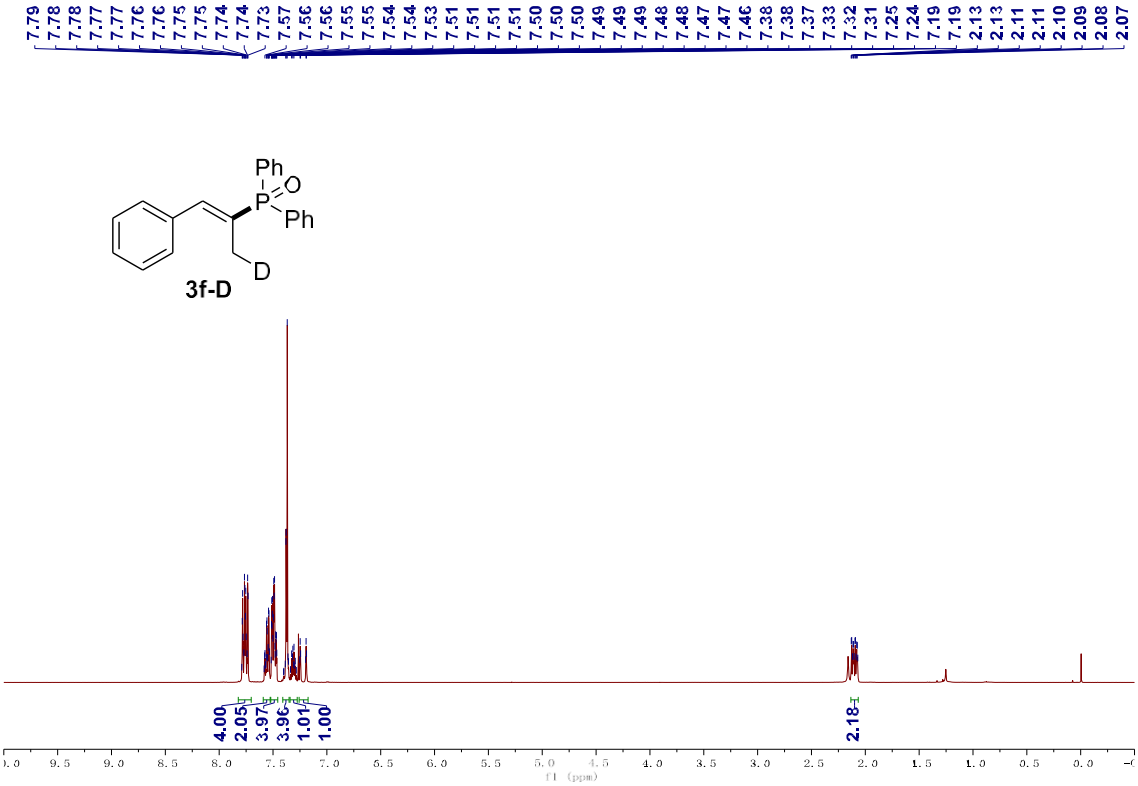
An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (6.4 mg, 0.0075 mmol, 5.0 mol%), **2a** (91.0 mg, 0.45 mmol, 3.0 equiv) and the tube was evacuated and backfilled with N_2 for 3 times. DBU (68.5 mg, 0.45 mmol, 3.0 equiv), **1f** (17.4 mg, 0.15 mmol, 1.0 equiv) and MeCN (1.6 mL), D_2O (0.3 mL) were successively added via syringe. The sealed tube was placed into a 40 W Blue LEDs at room temperature with stirring for 16 h. After the completion of the reaction, the mixture was concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc = 1.2/1) on silica gel to afford the corresponding coupling product **3f-D** (38.0 mg, 0.119 mmol, 79%, 53% D).

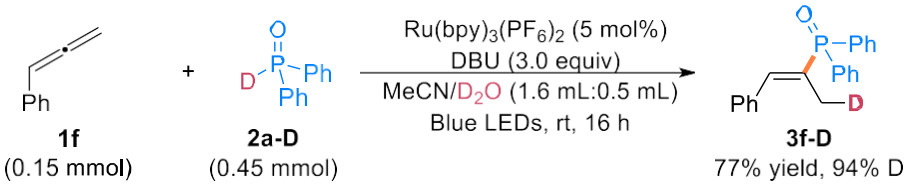




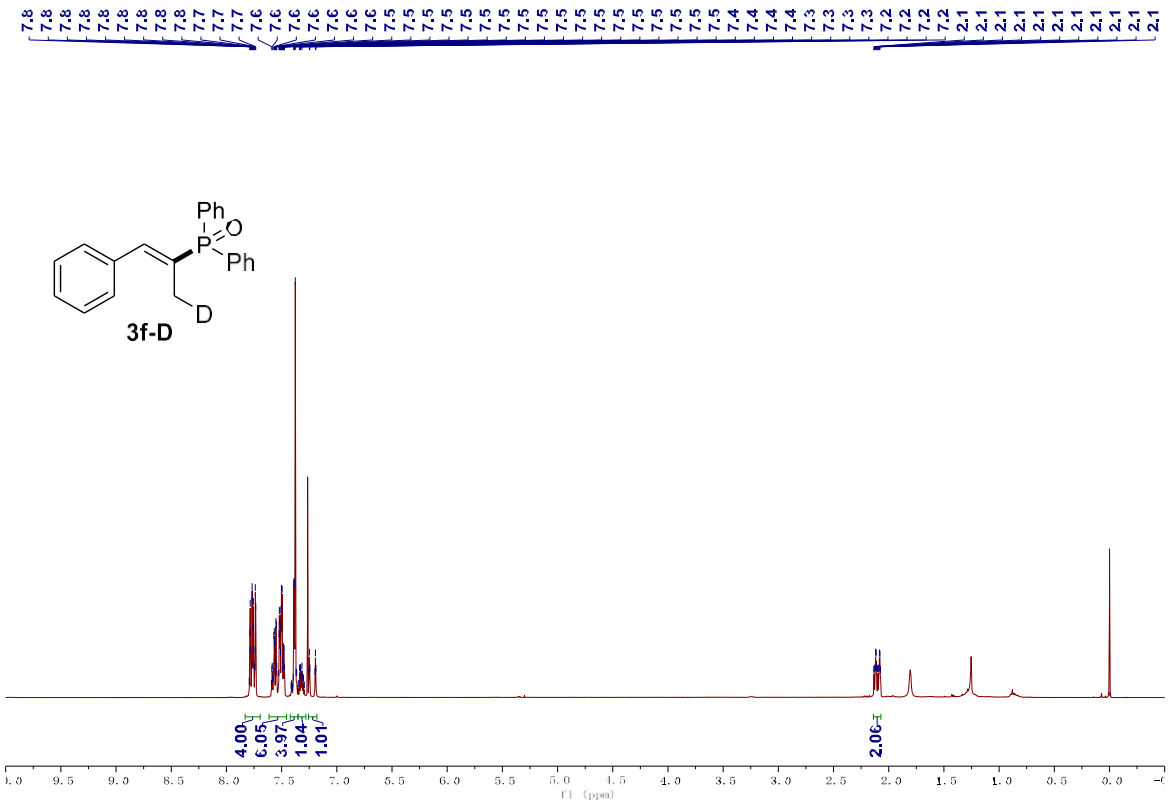
An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (6.4 mg, 0.0075 mmol, 5.0 mol%), **2a** (91.0 mg, 0.45 mmol, 3.0 equiv) and the tube was evacuated and backfilled with N_2 for 3 times. DBU (68.5 mg, 0.45 mmol, 3.0 equiv), **1f** (17.4 mg, 0.15 mmol, 1.0 equiv) and MeCN (1.6 mL), D_2O (0.5 mL) were successively added via syringe. The sealed tube was placed into a 40 W Blue LEDs at room temperature with stirring for 16 h. After the completion of the reaction, the mixture was

concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc = 1.2/1) on silica gel to afford the corresponding coupling product **3f-D** (32.6 mg, 0.102 mmol, 68%, 82% D).





An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (6.4 mg, 0.0075 mmol, 5.0 mol%), **2a-D** (91.4 mg, 0.45 mmol, 3.0 equiv) and the tube was evacuated and backfilled with N_2 for 3 times. DBU (68.5 mg, 0.45 mmol, 3.0 equiv), **1f** (17.4 mg, 0.15 mmol, 1.0 equiv) and MeCN/D_2O (1.6 mL:0.5 mL) were successively added via syringe. The sealed tube was placed into a 40 W Blue LEDs at room temperature with stirring for 16 h. After the completion of the reaction, the mixture was concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc = 1.2/1) on silica gel to afford the corresponding coupling product **3f-D** (37.0 mg, 0.116 mmol, 77%, 94% D).



4.4 Light on/off study

Procedures for light on/off experiments (Figure S1): To a mixture of $Ru(bpy)_3(PF_6)_2$ (6.4 mg, 0.0075 mmol, 5.0 mol%), **1f** (17.4 mg, 0.15 mmol, 1.0 equiv), **2a** (91.0 mg, 0.45 mmol, 3.0 equiv), DBU (68.5 mg, 0.45 mmol, 3.0 equiv) and MeCN/H_2O (1.6 mL:0.3 mL) were successively added into a 10 mL Schlenk tube with a stir bar. The reaction mixture was separately stirred and irradiated by 40 W blue LEDs (455 nm) at room temperature for 1 h, 2 h, and 3 h. After purification, the desired product **3f** was isolated in 41%, 54%, and 63% yields, respectively. Additionally, the reaction mixture was stirred and irradiated by 40 W blue LEDs at room temperature for 1 h, then the reaction mixture was continuously stirred in the dark for 1 h, the corresponding product was also obtained in 41% yield. Additionally, when the reaction mixture was stirred and irradiated by 40 W blue LEDs at room temperature for 2 h, then the reaction mixture was continuously stirred in the dark for 1 h, the corresponding product **3f** was obtained in 54% yield. Additionally, when the reaction mixture was stirred and irradiated by 40 W blue LEDs at room temperature for 3 h, then the reaction mixture was continuously stirred in the dark for 1 h, the corresponding product **3f** was still obtained in 63% yield.

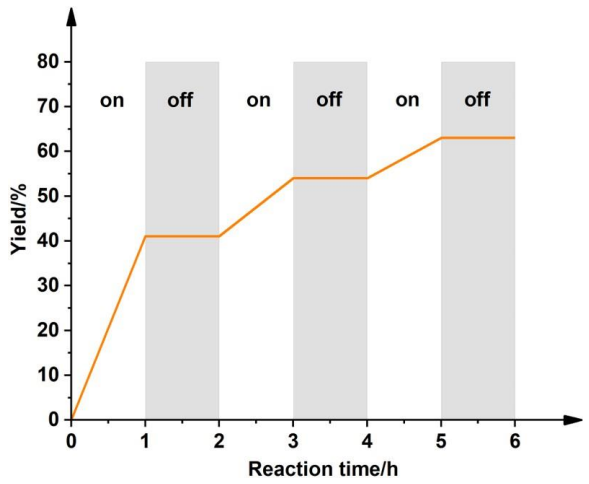


Figure S1. Light On/off experiments.

4.5 Fluorescence quenching experiments

Quenched by **2a**: For each quenching experiment, the emission intensity of photocatalyst $Ru(bpy)_3(PF_6)_2$ (1×10^{-5} M in MeCN) with different concentration of quencher **2a** (0, 0.01, 0.02, 0.03, 0.04 M) was collected. As shown in Figure S2, compound **2a** was capable of quenching the excited state of photocatalyst $Ru(bpy)_3(PF_6)_2$.

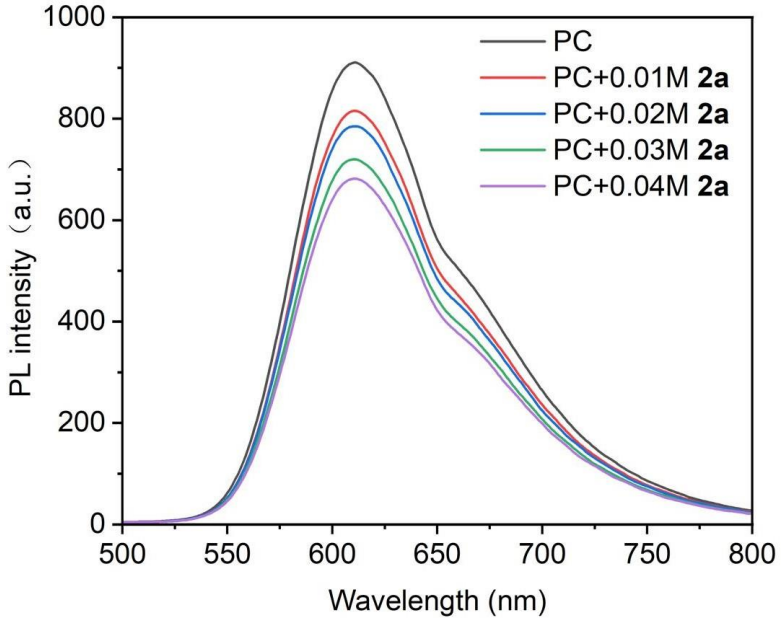


Figure S2. The fluorescence emission spectra of a solution of $Ru(bpy)_3(PF_6)_2$ in MeCN containing different concentration of **2a** and Stern-Volmer graph.

Quenched by DBU: For each quenching experiment, the emission intensity of photocatalyst $Ru(bpy)_3(PF_6)_2$ (1×10^{-5} M in MeCN) with different concentration of quencher DBU (0, 0.01, 0.02, 0.03,

0.04 M) was collected. As shown in Figure S3, compound DBU was capable of quenching the excited state of photocatalyst $Ru(bpy)_3(PF_6)_2$.

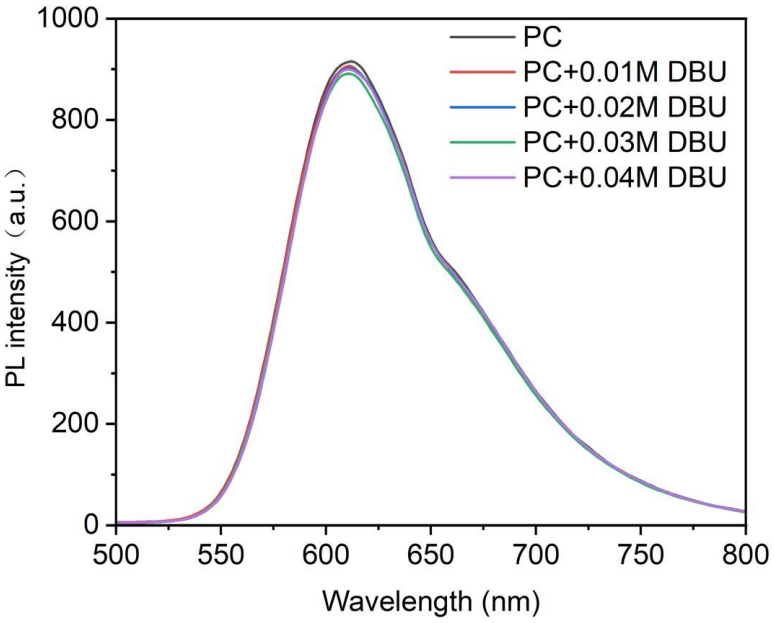


Figure S3. The fluorescence emission spectra of a solution of $Ru(bpy)_3(PF_6)_2$ in MeCN containing different concentration of DBU and Stern-Volmer graph.

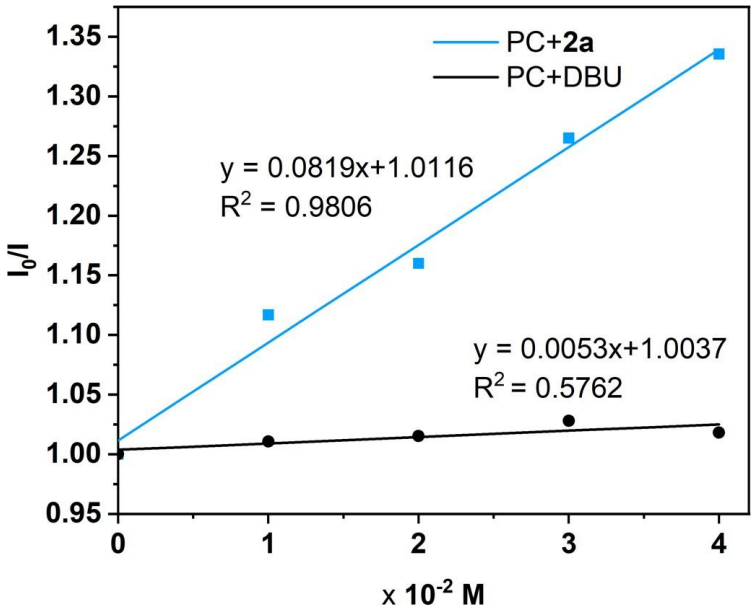


Figure S4. Stern-Volmer plot of PC (1 x 10^{-5} M) at different concentrations of **2a** and DBU.

Based on the luminescence quenching studies of each component, it was found that DBU did not have any impact on quenching efficiency, and the excited photocatalyst PC* was effectively quenched and linearly correlated with the concentration of **2a**, supporting the notion that **2a** was likely the initiation point of the photoredox catalytic cycle, and a reductive quenching of PC* could generate a P-centered radical cation.

5. DFT calculations for the reaction mechanism

DFT calculations were performed to gain insight into the mechanisms of phosphinoyl radical addition to allenes and elucidate the origin of substrate-controlled regioselectivity.

5.1 Computational details

All theoretical calculations were carried out using density functional theory with the Gaussian 16 program package,[13] and the structures were illustrated by CYLview (**Figures S5 and S6**).[14] The calculations were carried out for all molecules using the B3LYP functional[15-17] and 6-31G**[18] basis set with Grimme's D3 dispersion corrections and Becke-Johnson damping.[19] Intrinsic reaction coordinate (IRC)[20] calculations were conducted to verify the transition states indeed connect the corresponding minima (**Figures S7**–**S9**). The energetic results were then improved by the single-point calculations at the B3LYP+D3BJ/6-311+G**.[21,22]

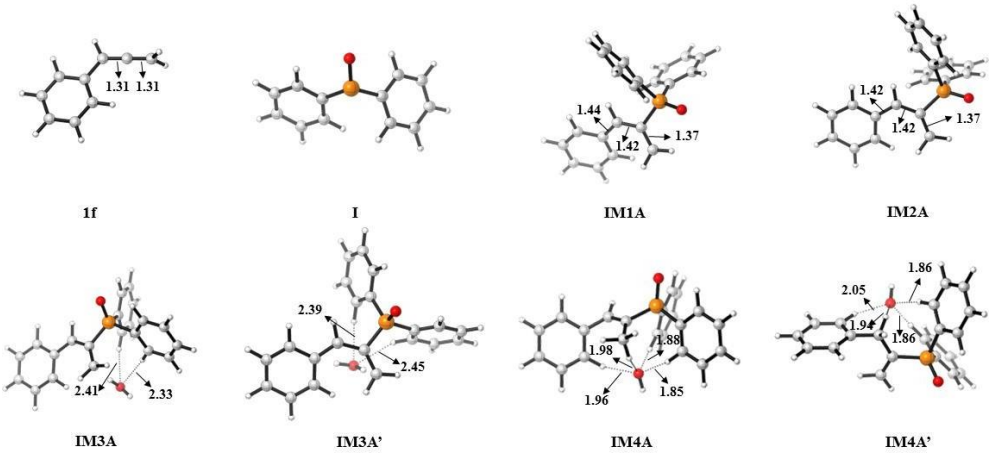


Figure S5. Computed structures of **1f**, **I**, **IM1A**, **IM2A**, **IM3A**, **IM3A'**, **IM4A**, **IM4A'**, selected bond distances are given in Å (color code, C: grey, P: orange, O: red, H: white, B: pink).

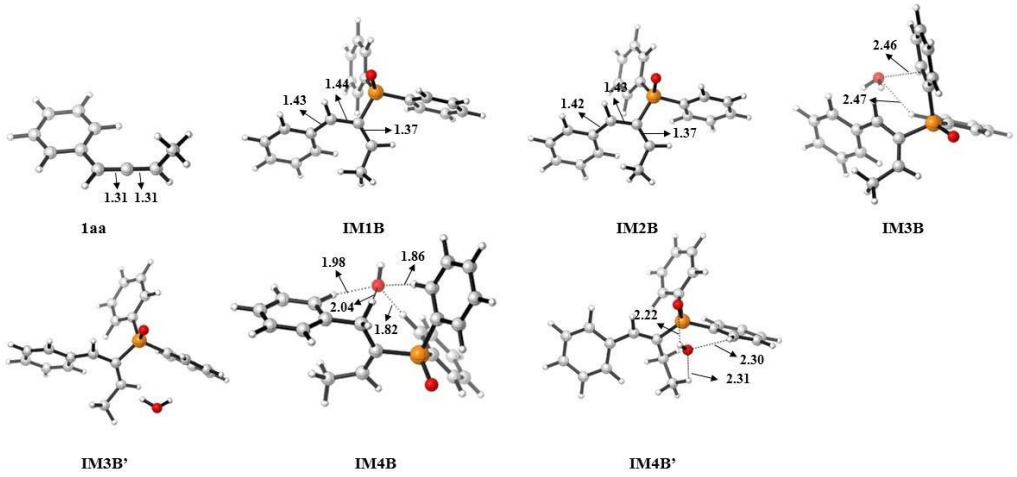


Figure S6. Computed structures of **1aa**, **IM1B**, **IM2B**, **IM3B**, **IM3B'**, **IM4B**, **IM4B'**, selected bond distances are given in Å (color code, C: grey, P: orange, O: red, H: white).

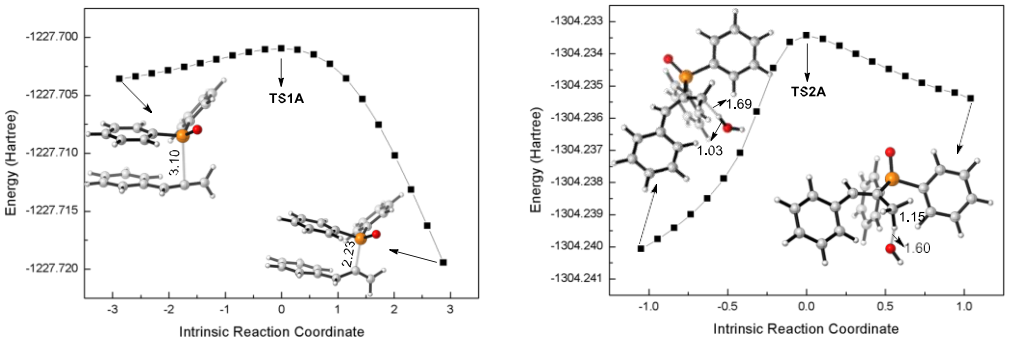


Figure S7. IRC analyses of MEP for **TS1A** and **TS2A**.

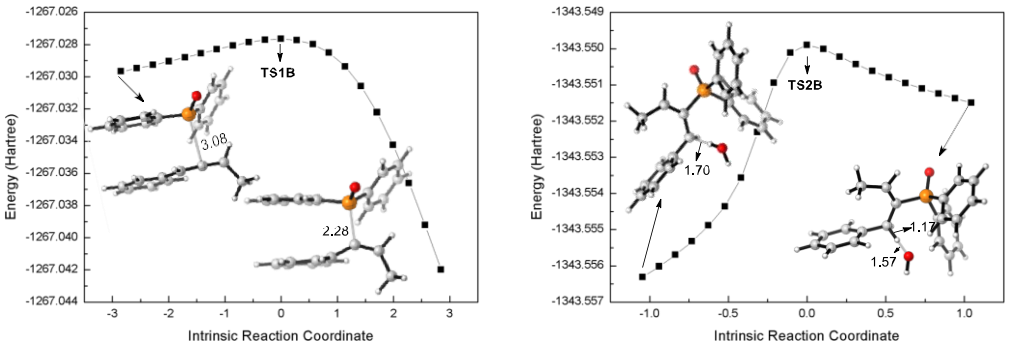


Figure S8. IRC analyses of MEP for **TS1B** and **TS2B**.

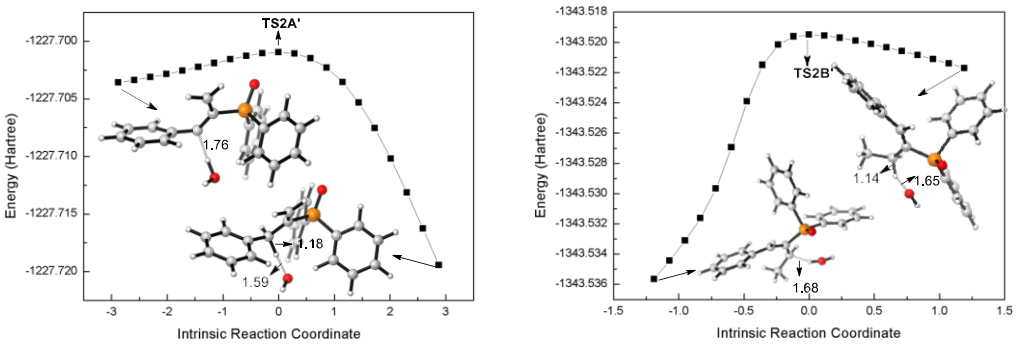


Figure S9. IRC analyses of MEP for **TS2A'** and **TS2B'**.

1f

Gibbs Free Energy = -347.7343183

C	-1.37468	1.436984	-0.07418
C	-0.35821	0.744875	0.362093
H	0.625749	0.826317	-0.09594
H	-0.45291	0.061798	1.204118
C	-2.40068	2.125615	-0.52108
H	-2.58233	3.111242	-0.0926
C	-3.34356	1.685108	-1.56317
C	-4.39701	2.530545	-1.94062
C	-3.22246	0.437135	-2.1968
C	-5.30584	2.142663	-2.9236
H	-4.50043	3.498247	-1.45723
C	-4.12961	0.051409	-3.17713
H	-2.40972	-0.22325	-1.9103
C	-5.17622	0.90172	-3.54604
H	-6.11506	2.810802	-3.20257
H	-4.02221	-0.91663	-3.65746
H	-5.88293	0.59763	-4.31187

I

Gibbs Free Energy = -879.9324278

P	-0.33308	0.85334	-0.3265
O	-0.86964	0.023714	0.824564
C	-1.09415	2.505303	-0.41921
C	-0.45397	3.62155	-0.97695
C	-2.41336	2.622494	0.0472
C	-1.12506	4.840109	-1.05744
H	0.571064	3.549005	-1.32202
C	-3.07623	3.844086	-0.03498
H	-2.89807	1.757431	0.48776
C	-2.43568	4.953798	-0.59052
H	-0.62074	5.704305	-1.47893
H	-4.09227	3.931947	0.3373
H	-2.95472	5.905026	-0.65592
C	1.473589	1.058774	-0.2883
C	2.187367	1.495063	-1.41445
C	2.164266	0.701572	0.879032
C	3.574103	1.619508	-1.35602
H	1.662937	1.726112	-2.33725
C	3.55139	0.822369	0.928357
H	1.604283	0.333145	1.731942
C	4.256279	1.286579	-0.18413
H	4.123068	1.96385	-2.22696
H	4.083889	0.554116	1.835674
H	5.337117	1.378843	-0.14189

TS1A

Gibbs Free Energy = -1227.655838

P	-0.41071	2.354294	-2.17233
O	-1.31497	1.422591	-1.39289
C	-1.11946	4.008356	-2.41697
C	-0.35661	5.180713	-2.50383
C	-2.50555	4.068331	-2.62932
C	-0.9739	6.394808	-2.7943
H	0.712939	5.151091	-2.33682
C	-3.11716	5.285758	-2.91855
H	-3.09378	3.159806	-2.5476
C	-2.35187	6.450086	-3.00607
H	-0.37536	7.297334	-2.86356
H	-4.19125	5.326949	-3.07286
H	-2.82806	7.397787	-3.23818
C	1.244914	2.524302	-1.44457
C	2.305234	3.129061	-2.13778
C	1.478981	1.937546	-0.19183
C	3.571721	3.188013	-1.56072
H	2.140252	3.546698	-3.12516
C	2.750478	1.993302	0.375643
H	0.65806	1.445676	0.319293
C	3.795889	2.622125	-0.30359
H	4.386967	3.665154	-2.09614
H	2.926381	1.546308	1.349422
H	4.78561	2.663011	0.14081
C	0.047162	1.655159	-4.74133
C	0.862768	0.646771	-4.54479
H	1.274293	0.109422	-5.39854
H	1.152926	0.301657	-3.5581
C	-0.6881	2.586667	-5.3605
H	-1.74749	2.384547	-5.51189
C	-0.22635	3.935464	-5.66818
C	-1.15586	4.927663	-6.02137
C	1.136735	4.284506	-5.6023
C	-0.74149	6.230987	-6.27702
H	-2.21039	4.673802	-6.0632
C	1.547061	5.587746	-5.85468
H	1.863783	3.51569	-5.36005
C	0.609476	6.570062	-6.18889
H	-1.4763	6.987346	-6.53505
H	2.601611	5.840922	-5.79749
H	0.931461	7.588129	-6.38414

IM1A

Gibbs Free Energy = -1227.704134

P	-0.51424	-1.32035	0.797601
O	-1.00899	-2.70327	1.113335
C	-1.68593	-0.01687	1.30168
C	-1.2905	1.266582	1.700111
C	-3.04836	-0.34436	1.27106
C	-2.25041	2.218791	2.042515
H	-0.23618	1.516851	1.757192
C	-4.00414	0.60897	1.616582
H	-3.34233	-1.35121	0.992642
C	-3.60645	1.892015	1.997453
H	-1.93942	3.211696	2.352773
H	-5.05835	0.350576	1.593745
H	-4.35205	2.633665	2.267607
C	1.062795	-0.92681	1.622826
C	1.965366	0.039904	1.159416
C	1.356551	-1.64682	2.788651
C	3.138681	0.296587	1.867952
H	1.761352	0.580384	0.240715
C	2.531694	-1.38874	3.492258
H	0.663825	-2.41358	3.119812
C	3.420754	-0.41437	3.035562
H	3.835824	1.04509	1.503905
H	2.756146	-1.95039	4.393849
H	4.336479	-0.21473	3.583824
C	-0.21407	-1.05028	-0.99912
C	-0.14325	-2.20624	-1.72956
H	-0.04922	-2.19655	-2.80943
H	-0.2621	-3.16309	-1.23346
C	-0.11666	0.282217	-1.47947
H	-0.55355	1.055961	-0.85363
C	0.473111	0.749393	-2.70523
C	0.168232	2.060684	-3.14709
C	1.38677	-0.00721	-3.47869
C	0.710665	2.570843	-4.31792
H	-0.51711	2.663614	-2.55785
C	1.932324	0.512451	-4.64567
H	1.694693	-0.98564	-3.13109
C	1.592541	1.797282	-5.07965
H	0.450219	3.574368	-4.64044
H	2.637668	-0.08307	-5.21745
H	2.02016	2.196443	-5.99387

IM2A

Gibbs Free Energy = -1227.76768

P	-0.58578	-1.34507	0.707218
O	-1.10513	-2.68128	1.184519
C	-1.73084	-0.01372	1.253341
C	-1.34409	1.31118	1.492867
C	-3.06522	-0.38268	1.464876
C	-2.28245	2.255509	1.909117
H	-0.308	1.601813	1.358976
C	-4.00311	0.560958	1.881939
H	-3.34282	-1.42056	1.310855
C	-3.61429	1.883996	2.100717
H	-1.97263	3.281817	2.087241
H	-5.03694	0.264713	2.039819
H	-4.34401	2.620931	2.426064
C	0.993441	-0.92115	1.539106
C	1.897882	0.021597	1.030265
C	1.294192	-1.59195	2.731511
C	3.078407	0.298251	1.720146
H	1.66704	0.509246	0.086014
C	2.473589	-1.30982	3.41993
H	0.597653	-2.34276	3.091602
C	3.365816	-0.35987	2.918054
H	3.778378	1.025629	1.317508
H	2.700672	-1.83384	4.34505
H	4.284947	-0.13856	3.454867
C	-0.27712	-1.14422	-1.07818
C	-0.02893	-2.35143	-1.68018
H	0.181541	-2.43035	-2.74008
H	-0.12443	-3.2718	-1.11634
C	-0.2079	0.2018	-1.53764
H	-0.7641	0.938693	-0.96781
C	0.446924	0.712697	-2.69456
C	0.285326	2.088965	-3.04913
C	1.324112	-0.03226	-3.54128
C	0.920475	2.656473	-4.14156
H	-0.3656	2.702926	-2.42872
C	1.965126	0.552797	-4.6263
H	1.528255	-1.06802	-3.30057
C	1.77302	1.898827	-4.95848
H	0.752147	3.709556	-4.36487
H	2.632866	-0.05962	-5.23163
H	2.264101	2.34136	-5.82083

IM3A

Gibbs Free Energy = -1304.22153

P	-0.5726	-1.06751	0.654112
O	-1.65515	-2.12262	0.66904

C	-1.22889	0.552956	1.209348
C	-0.52478	1.752528	1.033143
C	-2.47021	0.564791	1.853352
C	-1.06155	2.94616	1.514222
H	0.431657	1.759172	0.519266
C	-3.00657	1.763063	2.327173
H	-3.00535	-0.37407	1.958292
C	-2.30049	2.954787	2.160421
H	-0.51492	3.874477	1.37297
H	-3.97488	1.767408	2.821345
H	-2.71653	3.890115	2.526604
C	0.678692	-1.46464	1.942746
C	1.750334	-0.62607	2.279918
C	0.487266	-2.65528	2.651483
C	2.617113	-0.98569	3.311317
H	1.925235	0.287023	1.72052
C	1.357932	-3.01303	3.682211
H	-0.35595	-3.28159	2.377519
C	2.424182	-2.17734	4.01465
H	3.448326	-0.33345	3.567397
H	1.203435	-3.94187	4.225367
H	3.102841	-2.45152	4.818516
C	0.285919	-0.73176	-0.9216
C	1.623151	-1.14151	-1.00826
H	2.096307	-1.23925	-1.97952
H	2.031153	-1.77527	-0.22824
C	-0.55906	-0.08463	-1.8312
H	-1.58674	0.074036	-1.51223
C	-0.26954	0.399988	-3.14848
C	-1.34231	0.820055	-3.986
C	1.035934	0.547615	-3.6953
C	-1.13532	1.312554	-5.26493
H	-2.35571	0.739289	-3.59849
C	1.233811	1.051479	-4.97746
H	1.895942	0.323073	-3.07979
C	0.160198	1.428828	-5.78777
H	-1.99201	1.610652	-5.86715
H	2.251989	1.157304	-5.3485
H	0.324266	1.809069	-6.79245
O	2.733292	1.444486	-0.13006
H	3.55399	1.119969	0.262109
H	2.336699	0.606456	-0.50494

IM3A'

Gibbs Free Energy = -1304.224936

P	-0.28635	-1.00264	1.130351
O	-1.10971	-2.06391	1.824135
C	-1.0465	0.65436	1.336156
C	-0.6287	1.775575	0.604363
C	-2.05951	0.786636	2.290638
C	-1.21888	3.016021	0.843456
H	0.140111	1.674708	-0.15617
C	-2.6504	2.029806	2.523347
H	-2.37814	-0.10027	2.829782
C	-2.2283	3.146173	1.800975
H	-0.89673	3.882448	0.272229
H	-3.441	2.125891	3.263223
H	-2.68806	4.115288	1.978225
C	1.326723	-0.80724	1.990897
C	2.293469	0.138396	1.620881
C	1.55439	-1.62843	3.099314
C	3.471966	0.252467	2.35639
H	2.138353	0.77058	0.753204
C	2.736881	-1.51343	3.83281
H	0.788593	-2.3501	3.366216
C	3.696645	-0.57177	3.4624
H	4.219677	0.983713	2.061678
H	2.908459	-2.15851	4.690783
H	4.618491	-0.47952	4.031244
C	0.065892	-1.18958	-0.65162
C	1.296091	-1.76509	-0.95123
H	1.506795	-2.16297	-1.9364
H	1.951623	-2.09851	-0.15568
C	-0.97449	-0.70631	-1.46863
H	-1.86798	-0.36147	-0.95625
C	-1.00835	-0.5159	-2.88319
C	-2.20604	-0.01717	-3.4827
C	0.084313	-0.71426	-3.78036
C	-2.30747	0.24631	-4.83723
H	-3.06333	0.158129	-2.8363
C	-0.0266	-0.43143	-5.14021
H	1.033397	-1.06251	-3.39925
C	-1.21565	0.04226	-5.69614
H	-3.24845	0.620549	-5.23726
H	0.84089	-0.59108	-5.77854
H	-1.29522	0.246636	-6.76013
O	1.935361	1.160006	-1.65188
H	1.185929	1.191611	-2.2645
H	1.907726	0.213434	-1.37981

TS2A

Gibbs Free Energy = -1304.209843

P	-0.59866	-1.24343	0.52903	P	-0.79733	-1.31007	0.915354
O	-1.73101	-2.2443	0.590067	O	-1.4841	-2.42374	1.673799
C	-1.15159	0.416256	1.079637	C	-1.58486	0.301354	1.290022
C	-0.36733	1.568192	0.908845	C	-1.10842	1.544631	0.844951
C	-2.40217	0.502843	1.700259	C	-2.71879	0.239369	2.111165
C	-0.84846	2.791688	1.375672	C	-1.78241	2.706292	1.225636
H	0.608029	1.519311	0.418599	H	-0.24444	1.618861	0.184234
C	-2.87629	1.733271	2.157783	C	-3.38199	1.407386	2.486603
H	-2.99262	-0.40276	1.802257	H	-3.05652	-0.73588	2.447498
C	-2.09693	2.87934	1.997486	C	-2.91277	2.644499	2.042991
H	-0.24409	3.685243	1.243186	H	-1.41802	3.667186	0.872652
H	-3.85147	1.797493	2.634382	H	-4.26116	1.352061	3.123848
H	-2.46311	3.840214	2.351558	H	-3.42722	3.557881	2.332638
C	0.707729	-1.67849	1.742179	C	0.947315	-1.16176	1.456825
C	1.866107	-0.91304	1.951303	C	1.882984	-0.31119	0.849321
C	0.464963	-2.80741	2.532692	C	1.322922	-1.97283	2.5359
C	2.763552	-1.29326	2.949182	C	3.187105	-0.28143	1.348003
H	2.087995	-0.05441	1.312437	H	1.597489	0.331877	-0.00546
C	1.36909	-3.17906	3.52879	C	2.630648	-1.93455	3.019864
H	-0.4418	-3.37615	2.3509	H	0.576909	-2.62875	2.973848
C	2.519921	-2.4195	3.739482	C	3.565493	-1.08504	2.425854
H	3.664558	-0.70581	3.107793	H	3.915592	0.379559	0.883953
H	1.175122	-4.05813	4.1384	H	2.919116	-2.56601	3.856798
H	3.226572	-2.70447	4.515464	H	4.585941	-1.05159	2.801463
C	0.186805	-0.95103	-1.09472	C	-0.77978	-1.5557	-0.90448
C	1.611028	-1.21867	-1.23104	C	-0.51278	-2.82429	-1.26373
H	1.922067	-1.35324	-2.27128	H	-0.4754	-3.12057	-2.308
H	1.959986	-2.04598	-0.60926	H	-0.34277	-3.59535	-0.51904
C	-0.64953	-0.33806	-1.98578	C	-1.01145	-0.38513	-1.79762
H	-1.69871	-0.22589	-1.71638	H	-1.93185	0.12853	-1.49604
C	-0.28475	0.200466	-3.29382	C	-1.02589	-0.67261	-3.25843
C	-1.21186	0.172776	-4.35599	C	-2.16936	-0.48182	-4.05083
C	0.961951	0.825072	-3.5249	C	0.150601	-1.08436	-3.91465
C	-0.90131	0.701408	-5.60568	C	-2.14589	-0.69287	-5.42983
H	-2.18393	-0.28475	-4.18732	H	-3.08944	-0.16071	-3.56877
C	1.265131	1.352145	-4.77811	C	0.176677	-1.30699	-5.28845
H	1.652309	0.950624	-2.69414	H	1.051342	-1.21554	-3.32224
C	0.347169	1.286889	-5.83012	C	-0.97359	-1.11314	-6.05918
H	-1.63406	0.655357	-6.40843	H	-3.0496	-0.5343	-6.01431
H	2.226845	1.837004	-4.93054	H	1.101785	-1.6235	-5.76511
H	0.594132	1.699731	-6.80501	H	-0.95364	-1.28358	-7.13245
O	2.452786	1.124657	-0.42438	O	0.906121	1.431302	-1.36411
H	3.414635	1.145408	-0.3199	H	-0.10722	0.457858	-1.61505
H	2.162086	-0.08618	-0.8182	H	1.569215	1.237574	-2.04104

TS2A’

Gibbs Free Energy = -1304.207671

IM4A

Gibbs Free Energy = -1304.215828

P	-0.7394	-1.07771	0.785846	P	-0.49396	-0.79041	1.204662
O	-1.84576	-2.10069	0.928173	O	-1.30082	-1.84728	1.926898
C	-1.28909	0.591976	1.295719	C	-1.13274	0.878647	1.597663
C	-0.51625	1.739924	1.047375	C	-0.55849	2.065941	1.11584
C	-2.51391	0.685251	1.965821	C	-2.22472	0.922369	2.474682
C	-0.99763	2.972491	1.4928	C	-1.10216	3.285689	1.524108
H	0.456563	1.661455	0.511315	H	0.271025	2.026465	0.377296
C	-2.98104	1.926732	2.400065	C	-2.75323	2.14958	2.875128
H	-3.09033	-0.22129	2.125651	H	-2.63821	-0.01538	2.832941
C	-2.2196	3.072241	2.164063	C	-2.18941	3.334646	2.399481
H	-0.41155	3.869493	1.305263	H	-0.67105	4.21051	1.147248
H	-3.93539	1.999988	2.91604	H	-3.60085	2.180979	3.555426
H	-2.58067	4.042306	2.499271	H	-2.59902	4.293786	2.709316
C	0.661901	-1.4734	1.894184	C	1.255624	-0.81142	1.73743
C	1.84835	-0.7215	1.925436	C	2.258728	-0.07804	1.081411
C	0.481504	-2.55624	2.763503	C	1.56025	-1.60994	2.846734
C	2.839422	-1.07874	2.84193	C	3.564172	-0.15877	1.571784
H	2.009589	0.107	1.200829	H	2.018835	0.563535	0.200348
C	1.481084	-2.89674	3.675429	C	2.871293	-1.67979	3.319176
H	-0.44721	-3.11621	2.707893	H	0.760492	-2.17512	3.316052
C	2.662389	-2.15446	3.715765	C	3.875316	-0.95032	2.680425
H	3.766172	-0.50974	2.868712	H	4.35085	0.404026	1.073927
H	1.339405	-3.73778	4.349953	H	3.1082	-2.30228	4.178726
H	3.444745	-2.41694	4.424899	H	4.899302	-1.0023	3.044752
C	-0.04402	-0.83961	-0.88316	C	-0.4458	-0.99532	-0.61689
C	1.300388	-1.42888	-1.2096	C	0.138506	-2.1168	-1.05151
H	1.383687	-1.62252	-2.28328	H	0.204257	-2.34605	-2.11071
H	1.46963	-2.3631	-0.6653	H	0.582379	-2.82882	-0.3617
C	-0.7645	-0.06587	-1.71587	C	-1.03886	0.074892	-1.50852
H	-1.742	0.290079	-1.39163	H	-2.10125	0.205851	-1.26258
C	-0.29832	0.440192	-3.02206	C	-0.84526	-0.19589	-2.97882
C	-1.10113	0.345653	-4.16906	C	-1.79086	-0.87879	-3.75008
C	0.948272	1.093198	-3.09952	C	0.348708	0.239363	-3.5794
C	-0.66189	0.85717	-5.38952	C	-1.56256	-1.12404	-5.10648
H	-2.06994	-0.14386	-4.10091	H	-2.71185	-1.22151	-3.28317
C	1.373352	1.604467	-4.32643	C	0.572634	-0.01012	-4.93282
H	1.529812	1.22204	-2.1676	H	1.050533	0.779949	-2.92883
C	0.58237	1.48561	-5.47212	C	-0.37755	-0.69022	-5.70149
H	-1.28907	0.767276	-6.27335	H	-2.30796	-1.65305	-5.69597
H	2.333651	2.112193	-4.38649	H	1.495594	0.330742	-5.39739
H	0.926648	1.888789	-6.42187	H	-0.19637	-0.87967	-6.75718
O	2.087051	1.199779	-0.29401	O	1.337711	1.643613	-1.09578
H	2.72223	1.897898	-0.07563	H	-0.48942	1.005984	-1.28559
H	2.061179	-0.68282	-0.91888	H	1.8022	2.491998	-1.14713

IM4A’

Gibbs Free Energy = -1304.211098

1aa

Gibbs Free Energy = -387.0411026

C	-1.63927	1.607751	0.328084
C	-0.64653	0.976476	0.897064
H	-0.86552	0.298372	1.724276
C	-2.63436	2.234712	-0.2596
H	-2.93296	3.209899	0.12644
C	-3.40187	1.735544	-1.41385
C	-4.4392	2.51711	-1.94315
C	-3.12742	0.492545	-2.00822
C	-5.18265	2.07247	-3.03516
H	-4.66095	3.480335	-1.49153
C	-3.86942	0.049667	-3.09724
H	-2.3263	-0.11848	-1.6036
C	-4.90119	0.837031	-3.61712
H	-5.98194	2.692031	-3.43076
H	-3.64439	-0.91393	-3.54484
H	-5.47887	0.488679	-4.46765
C	0.804142	1.116204	0.50224
H	1.400954	1.490372	1.342387
H	1.2237	0.144622	0.216396
H	0.919628	1.804116	-0.33791
H	4.798492	2.64339	0.091068
C	0.049215	1.658994	-4.75683
C	0.881406	0.6619	-4.55894
H	1.141642	0.357361	-3.54769
C	-0.6957	2.586363	-5.36817
H	-1.75361	2.37847	-5.52573
C	-0.24578	3.941205	-5.67419
C	-1.18337	4.927538	-6.0209
C	1.1148	4.299913	-5.61513
C	-0.77948	6.234409	-6.27655
H	-2.23638	4.666405	-6.05769
C	1.515352	5.606227	-5.86733
H	1.84783	3.535233	-5.37757
C	0.569433	6.582733	-6.19517
H	-1.52091	6.986158	-6.5292
H	2.568488	5.866496	-5.8152
H	0.883441	7.603277	-6.39064
C	1.514962	-0.12058	-5.68389
H	2.608322	-0.0755	-5.61589
H	1.231924	-1.17795	-5.62321
H	1.209058	0.266716	-6.65789

TS1B

Gibbs Free Energy = -1266.963805

P	-0.42578	2.353395	-2.16282
O	-1.32732	1.433944	-1.36461
C	-1.12674	4.010773	-2.41047
C	-0.35776	5.17825	-2.50827
C	-2.51415	4.078439	-2.61144
C	-0.97028	6.395083	-2.79746
H	0.713045	5.14282	-2.35067
C	-3.12099	5.298537	-2.89934
H	-3.10713	3.17374	-2.52212
C	-2.34968	6.458051	-2.99714
H	-0.36684	7.293605	-2.87554
H	-4.19609	5.34553	-3.04479
H	-2.82219	7.407818	-3.22837
C	1.23817	2.519798	-1.4521
C	2.29508	3.111162	-2.16205
C	1.482642	1.941011	-0.19768
C	3.568686	3.164759	-1.60026
H	2.121366	3.522365	-3.15055
C	2.761094	1.991242	0.354572
H	0.664076	1.459207	0.32666
C	3.803378	2.606685	-0.34153
H	4.381119	3.631957	-2.14866
H	2.944905	1.550437	1.329739

IM1B

Gibbs Free Energy = -1267.011212

P	-0.60353	-1.01885	0.813395
O	-1.7457	-1.99612	0.862724
C	-1.11889	0.700213	1.121706
C	-0.42459	1.798647	0.598313
C	-2.25122	0.910508	1.91823
C	-0.84882	3.095458	0.884694
H	0.435025	1.639445	-0.04487
C	-2.67421	2.208168	2.201188
H	-2.79914	0.051328	2.291724
C	-1.97162	3.300304	1.688376
H	-0.31126	3.944022	0.472726
H	-3.55445	2.368365	2.816238
H	-2.30412	4.310543	1.907167
C	0.676072	-1.38087	2.059354
C	1.592671	-0.4232	2.512984
C	0.725462	-2.68541	2.566326
C	2.559534	-0.77351	3.453666
H	1.543334	0.594826	2.140054
C	1.692884	-3.03163	3.508962
H	-0.0081	-3.40794	2.223724
C	2.611619	-2.07803	3.949748
H	3.267207	-0.02888	3.805179

H	1.727222	-4.04291	3.902516
H	3.363721	-2.34796	4.684955
C	0.232458	-0.94735	-0.82027
C	1.552188	-1.2614	-0.92934
H	2.104566	-1.44381	-0.01131
C	-0.69352	-0.62635	-1.87696
H	-1.70914	-0.99203	-1.74109
C	-0.4677	0.21975	-3.00424
C	-1.45249	0.29547	-4.02467
C	0.673282	1.054678	-3.13431
C	-1.28738	1.125188	-5.12319
H	-2.3429	-0.32005	-3.93518
C	0.827082	1.887833	-4.2324
H	1.418037	1.054019	-2.34738
C	-0.14438	1.924952	-5.23934
H	-2.05134	1.155935	-5.8942
H	1.705342	2.522623	-4.30486
H	-0.01781	2.577064	-6.09758
C	2.317432	-1.49126	-2.19586
H	3.076754	-0.71499	-2.35747
H	2.856993	-2.44327	-2.12765
H	1.671132	-1.51532	-3.07365

IM2B

Gibbs Free Energy = -1267.070577

P	-0.62397	-1.20385	0.739974
O	-1.70019	-2.2296	1.016599
C	-1.22563	0.499647	1.045633
C	-0.70449	1.609781	0.367639
C	-2.21979	0.685092	2.012721
C	-1.16521	2.891241	0.671781
H	0.03431	1.469578	-0.41318
C	-2.68005	1.967599	2.314451
H	-2.63695	-0.18821	2.50515
C	-2.15041	3.072172	1.645462
H	-0.76624	3.746237	0.13327
H	-3.4545	2.10482	3.064916
H	-2.51125	4.071733	1.874913
C	0.714031	-1.36538	1.995745
C	1.723843	-0.40886	2.160079
C	0.690173	-2.487	2.829554
C	2.698678	-0.57605	3.141159
H	1.747387	0.460015	1.509654
C	1.669869	-2.65855	3.809918
H	-0.11196	-3.20619	2.695492
C	2.674529	-1.70399	3.967161
H	3.478685	0.170799	3.26322
H	1.648086	-3.53569	4.451714
H	3.437005	-1.83486	4.73074
C	0.138903	-1.15065	-0.90765
C	1.439304	-1.57805	-1.03382
H	2.008612	-1.83513	-0.14657
C	-0.73096	-0.63899	-1.92164
H	-1.79543	-0.83357	-1.80312
C	-0.37933	0.281805	-2.94445
C	-1.32852	0.648554	-3.95204
C	0.864908	0.989718	-3.00179
C	-1.05137	1.592484	-4.92544
H	-2.29985	0.157651	-3.93998
C	1.125516	1.941235	-3.98113
H	1.600002	0.8095	-2.22508
C	0.1868	2.255318	-4.96905
H	-1.81236	1.822945	-5.67055
H	2.085846	2.456313	-3.96767
H	0.404405	2.989009	-5.74026
C	2.086808	-1.82244	-2.35913
H	2.561036	-0.93282	-2.80596
H	2.854311	-2.60335	-2.28512
H	1.323138	-2.13182	-3.08517

IM3B

Gibbs Free Energy = -1343.526845

P	-0.58378	-1.15145	1.268439
O	-1.01131	-2.35538	2.077225
C	-1.72731	0.251903	1.553025
C	-1.37329	1.598024	1.400478
C	-3.03787	-0.07544	1.923706
C	-2.3275	2.599352	1.585096
H	-0.35749	1.876245	1.148745
C	-3.98846	0.926475	2.115284
H	-3.28793	-1.12198	2.066878
C	-3.63567	2.266208	1.938642
H	-2.04322	3.638476	1.447684
H	-5.00366	0.663697	2.401413
H	-4.37709	3.048237	2.081528
C	1.055279	-0.55247	1.829291
C	1.85873	0.328262	1.091196
C	1.523406	-1.05096	3.052556
C	3.103291	0.716612	1.587028
H	1.517809	0.717555	0.139739
C	2.769603	-0.66213	3.542362
H	0.898615	-1.75488	3.593301

C	3.561002	0.226187	2.811352
H	3.714202	1.404841	1.009924
H	3.125489	-1.05406	4.491966
H	4.532052	0.531979	3.192744
C	-0.45037	-1.37015	-0.53567
C	-0.16962	-2.65848	-0.89093
H	-0.03791	-3.3929	-0.10001
C	-0.57371	-0.20835	-1.38216
H	-1.43831	0.432229	-1.21621
C	0.221957	0.06478	-2.53295
C	-0.17597	1.049452	-3.49342
C	1.514348	-0.50879	-2.75313
C	0.631717	1.410522	-4.56293
H	-1.14543	1.526974	-3.36756
C	2.30918	-0.13872	-3.8287
H	1.894516	-1.21267	-2.02054
C	1.888276	0.820386	-4.75936
H	0.273171	2.16373	-5.26343
H	3.289953	-0.59976	-3.93775
H	2.514287	1.099863	-5.60172
C	-0.10861	-3.14228	-2.30492
H	0.882287	-3.01948	-2.77106
H	-0.37708	-4.20377	-2.36952
H	-0.79493	-2.55844	-2.92998
O	0.605494	2.718828	-0.95906
H	0.118168	1.875692	-0.89595
H	0.9896	2.625705	-1.8423

IM3B’

Gibbs Free Energy = -1343.52531

P	-0.7649	-0.80448	0.680518
O	-2.05607	-1.58443	0.743347
C	-0.9495	0.890205	1.351401
C	-0.32414	1.997264	0.765096
C	-1.73324	1.06783	2.498635
C	-0.46999	3.263829	1.333093
H	0.255051	1.868608	-0.14184
C	-1.8771	2.333941	3.065292
H	-2.24059	0.208929	2.927836
C	-1.24226	3.433468	2.483944
H	0.010004	4.119626	0.866812
H	-2.48727	2.465018	3.955226
H	-1.3565	4.42172	2.922056
C	0.457736	-1.55038	1.836928
C	1.554506	-0.84723	2.348916
C	0.268511	-2.88818	2.205011
C	2.45772	-1.47492	3.206042
H	1.699001	0.19251	2.071167
C	1.175642	-3.51903	3.059434
H	-0.59851	-3.41154	1.815301
C	2.27224	-2.81387	3.558686
H	3.306727	-0.92174	3.598419
H	1.025552	-4.55904	3.336303
H	2.978259	-3.30417	4.223521
C	0.012475	-0.59043	-0.94803
C	1.335434	-0.95627	-1.11868
H	1.933253	-1.22422	-0.25337
C	-0.88235	0.009698	-1.87471
H	-1.93937	-0.2139	-1.74878
C	-0.56688	1.009962	-2.84211
C	-1.54614	1.421525	-3.79749
C	0.65873	1.744135	-2.87403
C	-1.31325	2.440217	-4.70673
H	-2.50429	0.90605	-3.80064
C	0.878354	2.768618	-3.7876
H	1.419288	1.519894	-2.1352
C	-0.09162	3.130906	-4.72718
H	-2.09494	2.705292	-5.41748
H	1.828104	3.301475	-3.76013
H	0.091813	3.924067	-5.44661
C	2.005594	-1.03315	-2.45618
H	2.511244	-0.10728	-2.77696
H	2.750306	-1.83849	-2.46355
H	1.255888	-1.23599	-3.23068
O	1.225768	-4.02521	-0.66656
H	1.459022	-3.82953	0.249787
H	0.986968	-3.14015	-0.99979

TS2B

Gibbs Free Energy = -1343.50828

P	-0.52342	-1.16568	0.84702
O	-1.3303	-2.36863	1.284381
C	-1.47501	0.369802	1.173266
C	-0.97746	1.669152	0.990832
C	-2.76165	0.183272	1.69441
C	-1.77805	2.760982	1.32841
H	0.008933	1.825493	0.546751
C	-3.55415	1.28181	2.028571
H	-3.115	-0.83349	1.834664
C	-3.0615	2.574397	1.846896
H	-1.39552	3.767964	1.180522
H	-4.55253	1.128978	2.431011

H	-3.67538	3.433576	2.107215
C	0.981097	-1.01109	1.886935
C	2.012019	-0.09498	1.6289
C	1.070848	-1.87682	2.983863
C	3.113987	-0.0532	2.484501
H	1.963653	0.580644	0.771667
C	2.179409	-1.82911	3.829776
H	0.26398	-2.58449	3.147564
C	3.202659	-0.91332	3.581724
H	3.913068	0.656435	2.285477
H	2.245129	-2.50579	4.678422
H	4.068436	-0.8726	4.238779
C	0.037676	-1.19673	-0.89916
C	0.718107	-2.33505	-1.17541
H	0.887449	-3.02389	-0.34869
C	-0.25188	-0.00021	-1.71852
H	-1.28091	0.336445	-1.5495
C	0.071259	-0.0162	-3.17489
C	-0.9103	-0.18684	-4.16596
C	1.393574	0.221431	-3.6025
C	-0.58579	-0.16502	-5.52313
H	-1.93908	-0.35772	-3.85758
C	1.721047	0.232477	-4.9555
H	2.131959	0.44159	-2.83704
C	0.736015	0.031276	-5.92752
H	-1.36587	-0.31105	-6.26761
H	2.75023	0.413755	-5.25858
H	0.992689	0.041257	-6.984
C	1.27573	-2.79081	-2.49728
H	2.249143	-2.33189	-2.7218
H	1.420975	-3.87753	-2.4901
H	0.619914	-2.53818	-3.33252
O	1.561535	1.673145	-0.80044
H	0.595256	0.913721	-1.23881
H	1.395232	2.53622	-1.20394

TS2B’

Gibbs Free Energy = -1343.479473

P	-0.40359	-1.0769	0.726022
O	-1.77062	-1.71372	0.74349
C	-0.62353	0.58511	1.562757
C	0.23806	1.67342	1.371843
C	-1.69054	0.729037	2.457598
C	0.050994	2.867151	2.069387
H	1.049351	1.592319	0.654361
C	-1.88535	1.921756	3.154901
H	-2.37038	-0.10906	2.57604
C	-1.01167	2.994153	2.966097
H	0.726864	3.702935	1.904822
H	-2.72215	2.018453	3.842866
H	-1.16247	3.925565	3.506283
C	0.780943	-1.77687	1.936244
C	1.992069	-1.17104	2.285215
C	0.36666	-2.92126	2.634888
C	2.804218	-1.72863	3.275355
H	2.303754	-0.2568	1.791413
C	1.168543	-3.4657	3.633467
H	-0.58131	-3.36958	2.35799
C	2.397196	-2.87719	3.952748
H	3.750803	-1.2554	3.524653
H	0.839522	-4.35594	4.16401
H	3.025423	-3.30685	4.728784
C	0.352007	-0.47811	-0.85966
C	1.688681	-1.00014	-1.18683
H	2.436861	-0.77223	-0.41647
C	-0.55279	0.204356	-1.61303
H	-1.59484	0.171083	-1.29421
C	-0.31677	1.033956	-2.79458
C	-1.29152	1.121254	-3.80969
C	0.818668	1.859907	-2.91865
C	-1.12004	1.952765	-4.91223
H	-2.18637	0.510654	-3.72333
C	0.991895	2.691191	-4.02191
H	1.548583	1.858268	-2.11706
C	0.028493	2.740113	-5.03187
H	-1.8851	1.987242	-5.68427
H	1.878965	3.316739	-4.08722
H	0.163829	3.390402	-5.89183
C	2.249879	-0.8832	-2.59335
H	2.619142	0.110307	-2.88078
H	3.085803	-1.58543	-2.70566
H	1.488416	-1.15797	-3.33092
O	0.600142	-3.19363	-0.33417
H	1.136296	-3.64237	0.332634
H	1.39253	-2.17263	-0.91316

IM4B

Gibbs Free Energy = -1343.513275

P	-0.70759	-0.8744	1.083275
O	-1.57156	-2.0456	1.500655
C	-1.57739	0.699736	1.429188
C	-1.01526	1.9667	1.204694

C	-2.849	0.579678	2.005083
C	-1.75076	3.098838	1.561016
H	-0.03334	2.053052	0.691663
C	-3.56945	1.721002	2.358034
H	-3.24882	-0.41577	2.172049
C	-3.01814	2.984126	2.136974
H	-1.32794	4.084652	1.380185
H	-4.55639	1.624961	2.804228
H	-3.57701	3.876527	2.410989
C	0.839665	-0.81544	2.05914
C	1.906719	0.038752	1.732594
C	0.920036	-1.67279	3.163036
C	3.043545	0.017198	2.54374
H	1.837068	0.724954	0.855467
C	2.066079	-1.68247	3.959265
H	0.081371	-2.33021	3.372375
C	3.129648	-0.8335	3.649185
H	3.877385	0.673462	2.303525
H	2.129838	-2.35096	4.814584
H	4.025568	-0.83811	4.266714
C	-0.1787	-0.9106	-0.67453
C	0.679954	-1.90865	-0.9414
H	1.002796	-2.5042	-0.08716
C	-0.74815	0.156452	-1.5872
H	-1.84498	0.102265	-1.56647
C	-0.24069	0.177897	-3.0068
C	-0.96965	-0.36049	-4.07137
C	1.005631	0.778143	-3.25623
C	-0.45568	-0.33858	-5.37047
H	-1.93914	-0.81496	-3.87807
C	1.513276	0.795781	-4.55433
H	1.511518	1.225973	-2.38592
C	0.793471	0.23355	-5.61385
H	-1.02895	-0.76766	-6.18913
H	2.480487	1.255523	-4.74732
H	1.198488	0.249467	-6.62322
C	1.317563	-2.32847	-2.23937
H	2.229964	-1.74865	-2.42621
H	1.602767	-3.38534	-2.18752
H	0.670638	-2.18474	-3.10354
O	1.366321	1.843329	-0.50674
H	-0.42593	1.111606	-1.14497
H	1.771864	2.71468	-0.38501

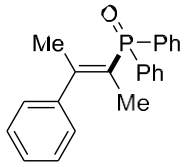
IM4B’

Gibbs Free Energy = -1343.506271

P	-0.65997	-1.06852	0.358812
O	-2.15823	-1.38911	0.328833
C	-0.91075	0.563159	1.432072
C	-0.44781	1.852077	1.133383
C	-1.65875	0.423833	2.615967
C	-0.7042	2.945639	1.970761
H	0.118339	2.021286	0.222187
C	-1.9189	1.500143	3.459604
H	-2.05202	-0.55864	2.861861
C	-1.4388	2.77553	3.141431
H	-0.32796	3.93152	1.702422
H	-2.50117	1.351733	4.367492
H	-1.64	3.620829	3.795894
C	0.569827	-1.70688	1.637988
C	1.445501	-0.87078	2.345253
C	0.574748	-3.07346	1.955815
C	2.316492	-1.3814	3.309876
H	1.435842	0.196516	2.156514
C	1.411624	-3.5827	2.948089
H	-0.07275	-3.72445	1.382593
C	2.296425	-2.7398	3.623653
H	2.998192	-0.71123	3.828335
H	1.384785	-4.64415	3.184643
H	2.961414	-3.13754	4.386799
C	0.146189	-0.14599	-1.03507
C	1.653537	-0.08099	-1.1051
H	1.955036	0.787608	-1.70299
C	-0.70509	0.453433	-1.8928
H	-1.76259	0.405152	-1.6321
C	-0.41504	1.236634	-3.09927
C	-1.30236	2.273354	-3.45548
C	0.68451	1.011148	-3.95109
C	-1.08685	3.065791	-4.5785
H	-2.16522	2.455116	-2.82048
C	0.902001	1.805858	-5.07523
H	1.35404	0.185667	-3.74547
C	0.023788	2.841887	-5.39598
H	-1.78745	3.861937	-4.81813
H	1.75898	1.603956	-5.71325
H	0.19477	3.45758	-6.27481
C	2.328257	-1.34984	-1.65093
H	2.022272	-1.54354	-2.68477
H	3.419625	-1.24186	-1.6278
H	2.023352	-2.21914	-1.06844
O	-0.20965	-2.5651	-0.60139
H	-1.06235	-2.78508	-0.99826
H	2.037205	0.09389	-0.09355

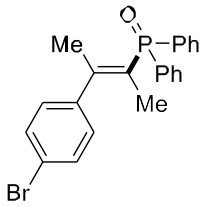
6. NMR data of the products

(*E*)-Diphenyl(3-phenylbut-2-en-2-yl)phosphine oxide (3a)



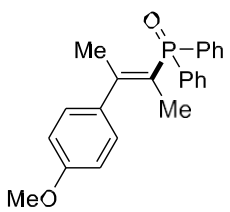
The title compound was prepared according to **GP1** and isolated as a colorless oil (40.6 mg, 0.122 mmol, 81%, *E*/*Z* = 88:12). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 – 7.70 (m, 4H), 7.54 – 7.44 (m, 6H), 7.42 – 7.34 (m, 2H), 7.33 – 7.27 (m, 1H), 7.22 – 7.14 (m, 2H), 2.31 (dd, *J* = 2.9, 1.6 Hz, 3H), 1.49 (dd, *J* = 14.2, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.5 (d, *J* = 8.1 Hz), 144.0 (d, *J* = 15.8 Hz), 134.4, 133.4, 131.7, 131.7, 131.7 × 2, 131.6 × 2, 128.8 × 2, 128.7 × 2, 128.6 × 2, 127.4, 127.1, 124.4, 123.4, 24.9 (d, *J* = 8.3 Hz), 21.0 (d, *J* = 14.1 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 31.98. **HRMS** (ESI): m/z calculated for $C_{22}H_{22}OP$ $[M + H]^+$: 333.1403, found: 333.1404.

(*E*)-(3-(4-Methoxyphenyl)but-2-en-2-yl)diphenylphosphine oxide (3b)



The title compound was prepared according to **GP1** and isolated as a white solid (50.2 mg, 0.122 mmol, 81%, *E*/*Z* = 80:20). M.p.: 122.4 – 122.7 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.67 (m, 4H), 7.53 – 7.46 (m, 6H), 7.31 – 7.27 (m, 1H), 7.09 – 7.04 (m, 2H), 7.04 – 6.86 (m, 1H), 2.28 (dd, *J* = 2.9, 1.6 Hz, 3H), 1.48 (dd, *J* = 14.1, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.0 (d, *J* = 8.3 Hz), 142.7 (d, *J* = 15.7 Hz), 134.0, 133.0, 131.8 × 2, 131.6 × 2, 131.5 × 2, 131.3 (d, *J* = 9.3 Hz), 130.7, 128.9 × 2, 128.8 × 2, 128.7 × 2, 128.3 (d, *J* = 11.9 Hz), 121.4, 24.7 (d, *J* = 8.3 Hz), 21.0 (d, *J* = 13.8 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 31.77. **HRMS** (ESI): m/z calculated for $C_{22}H_{21}{}^{79}BrOP$ $[M + H]^+$: 411.0508, found: 411.0514.

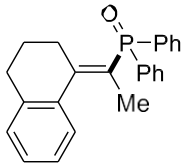
(*E*)-(3-(4-Methoxyphenyl)but-2-en-2-yl)diphenylphosphine oxide (3c)



The title compound was prepared according to **GP1** and isolated as a colorless oil (39.1 mg, 0.108 mmol, 72%, *E*/*Z* = 88:12). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.70 (m, 4H), 7.57 – 7.41 (m, 6H), 7.17 – 7.07 (m, 2H), 6.95 – 6.82 (m, 2H), 3.81 (s, 3H), 2.29 (dd, *J* = 2.9, 1.5 Hz, 3H), 1.52 (dd, *J* = 14.3, 1.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.8, 155.1 (d, *J* = 8.7 Hz), 136.1 (d, *J* = 15.6 Hz), 134.3, 133.3, 131.7, 131.7, 131.6 × 2, 131.5 × 2, 128.7 × 2, 128.6 × 2, 128.5 × 2, 123.8, 122.9, 113.8, 55.4, 25.0 (d, *J* = 8.5 Hz), 21.1 (d, *J* = 14.2 Hz). **^{31}P NMR** (162 MHz,

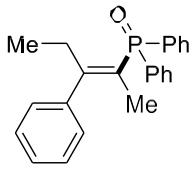
Chloroform-*d*) δ 32.13. **HRMS** (ESI): m/z calculated for $C_{23}H_{24}O_2P$ $[M + H]^+$: 363.1508, found: 363.1512.

(*E*)-(1-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)ethyl)diphenylphosphine oxide (3d)



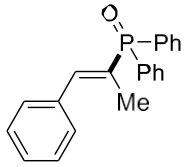
The title compound was prepared according to **GP1** and isolated as a colorless oil (35.0 mg, 0.098 mmol, 65%, *E*/*Z* = 88:12). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.70 (m, 4H), 7.54 – 7.42 (m, 6H), 7.38 – 7.33 (m, 1H), 7.24 – 7.20 (m, 1H), 7.19 – 7.10 (m, 2H), 2.88 – 2.81 (m, 2H), 2.73 (t, *J* = 6.8 Hz, 2H), 1.86 (d, *J* = 15.0 Hz, 3H), 1.77 – 1.68 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.6 (d, *J* = 8.9 Hz), 140.3, 134.7, 133.7, 131.7 × 2, 131.6, 131.6, 131.6 ×2 , 130.9 (d, *J* = 9.1 Hz), 129.0, 128.7 × 2, 128.6 × 2, 128.5, 128.2, 128.1, 124.9, 31.3 (d, *J* = 9.1 Hz), 28.8, 22.4, 22.0 (d, *J* = 13.8 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 32.86. **HRMS** (ESI): m/z calculated for $C_{24}H_{24}OP$ $[M + H]^+$: 359.1559, found: 359.1561.

(*E*)-Diphenyl(3-phenylpent-2-en-2-yl)phosphine oxide (3e)



The title compound was prepared according to **GP1** and isolated as a colorless oil (36.9 mg, 0.107 mmol, 71% *E*/*Z* = 86:14). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 – 7.69 (m, 4H), 7.55 – 7.44 (m, 6H), 7.41 – 7.34 (m, 2H), 7.31 – 7.27 (m, 1H), 7.17 – 7.11 (m, 2H), 2.94 – 2.72 (m, 2H), 1.45 (d, *J* = 14.0 Hz, 3H), 0.67 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.2 (d, *J* = 8.6 Hz), 141.9 (d, *J* = 15.4 Hz), 134.6, 133.6, 131.7 × 2, 131.7 × 2, 131.6 × 2, 128.7 × 2, 128.5 × 2, 128.4 × 2, 127.6, 127.2, 124.0, 123.1, 30.4 (d, *J* = 8.0 Hz), 20.8 (d, *J* = 14.1 Hz), 12.1. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 31.56. **HRMS** (ESI): m/z calculated for $C_{23}H_{24}OP$ $[M + H]^+$: 347.1559, found: 347.1559.

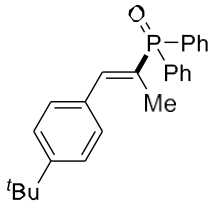
(*E*)-Diphenyl(1-phenylprop-1-en-2-yl)phosphine oxide (3f)



The title compound was prepared according to **GP1** and isolated as a colorless oil (38.2 mg, 0.120 mmol, 80%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.68 (m, 4H), 7.58 – 7.44 (m, 6H), 7.39 – 7.34 (m, 4H), 7.33 – 7.27 (m, 1H), 7.24 – 7.15 (m, 1H), 2.10 (dd, *J* = 13.8, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.8 (d, *J* = 10.8 Hz), 135.9 (d, *J* = 18.8 Hz), 132.2 × 2, 132.2 × 2, 132.1, 132.1, 131.8, 130.8,

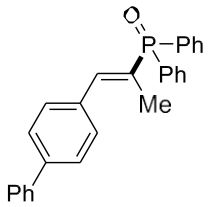
129.8, 129.6 × 2, 128.8 × 2, 128.7 × 2, 128.5 × 2, 128.5, 15.2 (d, *J* = 10.9 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.24. **HRMS** (ESI): m/z calculated for $C_{21}H_{20}OP$ $[M + H]^+$: 319.1246, found: 319.1249.

(*E*)-(1-(4-(*tert*-Butyl)phenyl)prop-1-en-2-yl)diphenylphosphine oxide (3g)



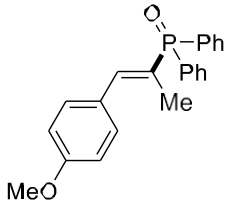
The title compound was prepared according to **GP1** and isolated as a colorless oil (45.0 mg, 0.120 mmol, 80%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 – 7.70 (m, 4H), 7.60 – 7.53 (m, 2H), 7.52 – 7.45 (m, 4H), 7.43 – 7.38 (m, 2H), 7.37 – 7.32 (m, 2H)., 7.19 (dd, *J* = 22.1, 1.7 Hz, 1H), 2.13 (dd, *J* = 13.8, 1.6 Hz, 3H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.8, 142.7 (d, *J* = 7.3 Hz), 133.2, 132.3 × 2, 132.2 × 2, 132.0 × 2, 130.9, 129.5 × 3, 128.8 × 2, 128.7 × 2, 125.5 × 3, 34.8, 31.3 × 3, 15.4 (d, *J* = 9.7 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.51. **HRMS** (ESI): m/z calculated for $C_{25}H_{28}OP$ $[M + H]^+$: 375.1872, found: 375.1870.

(*E*)-(1-([1,1'-Biphenyl]-4-yl)prop-1-en-2-yl)diphenylphosphine oxide (3h)



The title compound was prepared according to **GP1** and isolated as a white solid (50.3 mg, 0.128 mmol, 85%, *E*/*Z* > 99:1). M.p.: 156.1 – 157.9 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 – 7.73 (m, 4H), 7.65 – 7.55 (m, 6H), 7.55 – 7.43 (m, 8H), 7.42 – 7.33 (m, 1H), 7.26 (dd, *J* = 21.9, 1.7 Hz, 1H), 2.17 (dd, *J* = 13.9, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.3 (d, *J* = 10.8 Hz), 141.2, 140.4, 134.8 (d, *J* = 19.0 Hz), 132.2 × 2, 132.1 × 2, 132.1, 132.0, 131.8, 130.8, 130.2 (d, *J* = 97.2 Hz), 130.1 × 2, 129.0 × 2, 128.8 × 2, 128.7 × 2, 127.7, 127.1 × 2, 127.1 × 2, 15.4 (d, *J* = 10.9 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.24. **HRMS** (ESI): m/z calculated for $C_{27}H_{24}OP$ $[M + H]^+$: 395.1559, found: 395.1562.

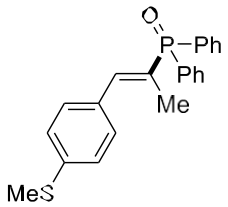
(*E*)-(1-(4-Methoxyphenyl)prop-1-en-2-yl)diphenylphosphine oxide (3i)



The title compound was prepared according to **GP1** and isolated as a colorless oil (43.4 mg, 0.125 mmol, 83%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.69 (m, 4H), 7.60 – 7.52 (m, 2H), 7.52 – 7.44 (m, 4H), 7.40 – 7.32 (m, 2H), 7.20 – 7.11 (m, 1H), 6.94 – 6.87 (m, 2H), 3.83 (s,

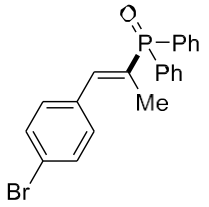
3H), 2.11 (dd, *J* = 13.9, 1.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.8, 142.4 (d, *J* = 11.3 Hz), 132.3 × 2, 132.2 × 2, 132.0, 132.0, 131.3 × 2, 131.0, 128.8 × 2, 128.6 × 2, 128.5, 127.9, 127.0, 113.9 × 2, 55.4, 15.3 (d, *J* = 11.1 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.69. **HRMS** (ESI): m/z calculated for $C_{22}H_{22}O_2P$ $[M + H]^+$: 349.1352, found: 349.1353.

(*E*)-(1-(4-(Methylthio)phenyl)prop-1-en-2-yl)diphenylphosphine oxide (3j)



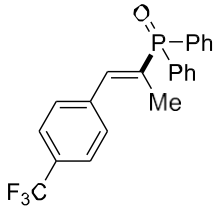
The title compound was prepared according to **GP1** and isolated as a white solid (45.4 mg, 0.125 mmol, 83%, *E*/*Z* > 99:1). M.p.: 144.2 – 146.4 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.69 (m, 4H), 7.60 – 7.53 (m, 2H), 7.52 – 7.45 (m, 4H), 7.35 – 7.29 (m, 2H), 7.26 – 7.21 (m, 2H), 7.17 (dd, *J* = 21.8, 1.7 Hz, 1H), 2.49 (s, 3H), 2.10 (dd, *J* = 13.9, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.2 (d, *J* = 10.8 Hz), 139.6, 132.4 (d, *J* = 19.2 Hz), 132.2 × 2, 132.1 × 2, 132.1, 132.1, 131.8, 130.8, 130.1 × 2, 129.9, 128.9, 128.8 × 2, 128.7 × 2, 125.9, 15.4, 15.4 (d, *J* = 12.2 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.27. **HRMS** (ESI): m/z calculated for $C_{22}H_{22}OPS$ $[M + H]^+$: 365.1123, found: 365.1127.

(*E*)-(1-(4-Bromophenyl)prop-1-en-2-yl)diphenylphosphine oxide (3k)



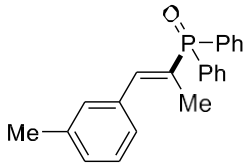
The title compound was prepared according to **GP1** and isolated as a white solid (43.5 mg, 0.110 mmol, 73%, *E*/*Z* > 99:1). M.p.: 138.4 – 140.1 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.69 (m, 4H), 7.60 – 7.54 (m, 2H), 7.53 – 7.44 (m, 6H), 7.25 – 7.22 (m, 2H), 7.17 (dd, *J* = 21.7, 1.8 Hz, 1H), 2.07 (dd, *J* = 13.8, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.5 (d, *J* = 10.9 Hz), 134.7 (d, *J* = 19.1 Hz), 132.2 × 2, 132.2 × 2, 132.1 × 2, 131.7 × 2, 131.6, 131.1 × 2, 130.5, 128.8 × 2, 128.7 × 2, 128.5, 122.6, 15.3 (d, *J* = 10.7 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 33.73. **HRMS** (ESI): m/z calculated for $C_{21}H_{19}{}^{79}BrOP$ $[M + H]^+$: 397.0351, found: 397.0353.

(*E*)-Diphenyl(1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)phosphine oxide (3l)



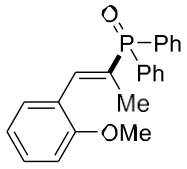
The title compound was prepared according to **GP1** and isolated as a colorless oil (23.6 mg, 0.061 mmol, 41%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.72 (m, 4H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.55 – 7.44 (m, 6H), 7.32 – 7.25 (m, 1H), 2.09 (dd, *J* = 13.7, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.2 (d, *J* = 10.7 Hz), 139.4 (d, *J* = 18.7 Hz), 133.7, 132.3, 132.3, 132.2 × 2, 132.1 × 2, 131.4 (d, *J* = 274.6 Hz), 131.4, 130.4, 129.7 × 2, 128.9 × 2, 128.8 × 2, 125.5, 125.5 (d, *J* = 4.0 Hz), 125.4, 15.3 (d, *J* = 10.4 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.57. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 33.35. **HRMS** (ESI): m/z calculated for $C_{22}H_{19}F_3OP$ $[M + H]^+$: 387.1120, found: 387.1126.

(*E*)-Diphenyl(1-(*m*-tolyl)prop-1-en-2-yl)phosphine oxide (3m)



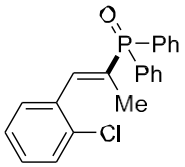
The title compound was prepared according to **GP1** and isolated as a colorless oil (34.9 mg, 0.105 mmol, 70%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 – 7.70 (m, 4H), 7.60 – 7.53 (m, 2H), 7.52 – 7.46 (m, 4H), 7.30 – 7.24 (m, 1H), 7.21 – 7.10 (m, 4H), 2.35 (s, 3H), 2.11 (dd, *J* = 13.8, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.0 (d, *J* = 11.0 Hz), 138.2, 135.8 (d, *J* = 19.0 Hz), 132.2 × 2, 132.1 × 2, 132.1, 132.0, 131.8, 130.8, 130.3, 130.1 (d, *J* = 97.0 Hz)., 129.3, 128.8 × 2, 128.7 × 2, 128.4, 126.6, 21.5, 15.2 (d, *J* = 10.7 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.52. **HRMS** (ESI): m/z calculated for $C_{22}H_{22}OP$ $[M + H]^+$: 333.1403, found: 333.1408.

(*E*)-(1-(2-Methoxyphenyl)prop-1-en-2-yl)diphenylphosphine oxide (3n)



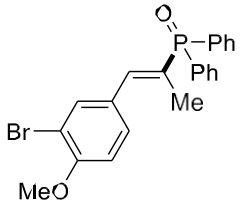
The title compound was prepared according to **GP1** and isolated as a colorless oil (45.5 mg, 0.131 mmol, 87%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 – 7.73 (m, 4H), 7.58 – 7.52 (m, 2H), 7.51 – 7.44 (m, 4H), 7.32 – 7.27 (m, 2H), 7.26 – 7.18 (m, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 3H), 2.02 (dd, *J* = 13.4, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.5, 139.2 (d, *J* = 12.8 Hz), 132.3 × 2, 132.2 × 2, 132.1, 131.9, 131.9, 131.0, 130.8, 129.9, 129.8, 128.7 × 2, 128.6 × 2, 124.9 (d, *J* = 18.8 Hz), 120.2, 110.8, 55.6, 14.9 (d, *J* = 11.0 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.74. **HRMS** (ESI): m/z calculated for $C_{22}H_{22}O_2P$ $[M + H]^+$: 349.1352, found: 349.1349.

(*E*)-(1-(2-Chlorophenyl)prop-1-en-2-yl)diphenylphosphine oxide (3o)



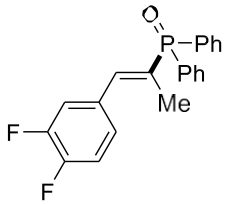
The title compound was prepared according to **GP1** and isolated as a white solid (32.3 mg, 0.092 mmol, 61%, *E*/*Z* > 99:1). M.p.: 140.6 – 142.3 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.67 (m, 4H), 7.62 – 7.41 (m, 6H), 7.23 – 7.04 (m, 5H), 2.06 (dd, *J* = 13.8, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.2 (d, *J* = 13.1 Hz), 134.4 (d, *J* = 19.1 Hz), 133.9 (d, *J* = 8.3 Hz), 133.0, 132.2 × 2, 132.2 × 2, 132.2 × 2, 131.4, 130.4, 130.3, 129.7, 129.5, 128.8 × 2, 128.7 × 2, 126.6, 14.5 (d, *J* = 10.4 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 33.45. **HRMS** (ESI): m/z calculated for $C_{21}H_{19}ClOP$ $[M + H]^+$: 353.0857, found: 353.0852.

(*E*)-(1-(3-Bromo-4-methoxyphenyl)prop-1-en-2-yl)diphenylphosphine oxide (3p)



The title compound was prepared according to **GP1** and isolated as a colorless oil (46.9 mg, 0.110 mmol, 73%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.65 (m, 4H), 7.58 – 7.51 (m, 3H), 7.50 – 7.43 (m, 4H), 7.30 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.07 (dd, *J* = 21.8, 1.8 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 3H), 2.08 (dd, *J* = 13.9, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.9, 140.9 (d, *J* = 11.1 Hz), 134.3, 132.2 × 2, 132.1 × 4, 131.7, 130.7, 130.2, 129.9, 129.7, 128.8 × 2, 128.7 × 2, 111.7, 111.6, 56.4, 15.2 (d, *J* = 10.8 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.17. **HRMS** (ESI): m/z calculated for $C_{22}H_{21}{}^{79}BrO_2P$ $[M + H]^+$: 427.0457, found: 427.0460.

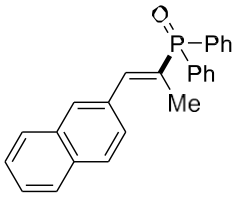
(*E*)-(1-(3,4-Difluorophenyl)prop-1-en-2-yl)diphenylphosphine oxide (3q)



The title compound was prepared according to **GP1** and isolated as a white solid (31.5 mg, 0.089 mmol, 59%, *E*/*Z* > 99:1). M.p.: 146.7 – 148.9 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 – 7.73 (m, 4H), 7.61 – 7.45 (m, 6H), 7.41 – 7.36 (m, 1H), 7.32 – 7.25 (m, 2H), 7.05 (dd, *J* = 21.6, 1.7 Hz, 1H), 1.98 (dd, *J* = 13.1, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.4 (d, *J* = 15.6 Hz), 148.9 (d, *J* = 14.4 Hz), 140.4 (d, *J* = 11.1 Hz), 132.9 (t, *J* = 5.9 Hz), 132.7 (t, *J* = 5.7 Hz), 132.2, 132.2, 132.2 × 2, 132.1 × 2, 131.3, 131.0 (d, *J* = 102.6 Hz), 128.9 × 2, 128.8 × 2, 126.1 (dd, *J* = 5.4, 4.0 Hz), 118.3 (d, *J* = 17.5 Hz), 117.5 (d, *J* = 17.3 Hz), 15.2 (d, *J* = 10.7 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -135.93 – -137.60 (m). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 33.47. **HRMS** (ESI):

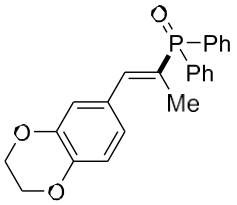
m/z calculated for $C_{21}H_{18}F_2OP$ [M + H]$^+$: 355.1058, found: 355.1055.

(*E*)-(1-(Naphthalen-2-yl)prop-1-en-2-yl)diphenylphosphine oxide (3r)



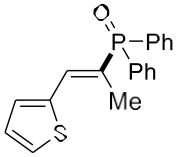
The title compound was prepared according to **GP1** and isolated as a colorless oil (36.9 mg, 0.100 mmol, 67%, *E*/*Z* = 96:4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.76 (m, 6H), 7.70 – 7.63 (m, 2H), 7.61 – 7.43 (m, 9H), 7.38 (dd, *J* = 21.9, 1.8 Hz, 1H), 2.20 (dd, *J* = 13.8, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.9 (d, *J* = 11.2 Hz), 133.4 (d, *J* = 19.2 Hz), 133.2, 133.0, 132.3 , 132.3, 132.2, 132.2, 132.1, 132.1, 132.1, 129.2, 128.8 × 2, 128.7 × 2, 128.7, 128.6, 128.4, 128.1 , 127.8, 127.0, 126.8, 126.6, 15.4 (d, *J* = 10.6 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.29. **HRMS** (ESI): m/z calculated for $C_{25}H_{22}OP$ [M + H]$^+$: 369.1403, found: 369.1403.

(*E*)-(1-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)prop-1-en-2-yl)diphenylphosphine oxide (3s)



The title compound was prepared according to **GP1** and isolated as a colorless oil (50.8 mg, 0.135 mmol, 90%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.66 (m, 4H), 7.58 – 7.52 (m, 2H), 7.51 – 7.44 (m, 4H), 7.12 – 7.02 (m, 1H), 6.94 (d, *J* = 1.9 Hz, 1H), 6.91 – 6.82 (m, 2H), 4.29 – 4.22 (m, 4H), 2.10 (dd, *J* = 14.0, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.7 (d, *J* = 69.2 Hz), 142.2 (d, *J* = 11.2 Hz), 132.2 × 2, 132.1 × 2, 132.0, 132.0, 131.9, 130.9, 129.5, 129.3, 128.8 × 2, 128.6 × 2, 127.7, 123.6, 118.5, 117.3, 64.6, 64.4, 15.3 (d, *J* = 10.9 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.67. **HRMS** (ESI): m/z calculated for $C_{23}H_{22}O_3P$ [M + H]$^+$: 377.1301, found: 377.1300.

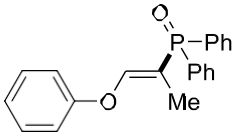
(*E*)-Diphenyl(1-(thiophen-2-yl)prop-1-en-2-yl)phosphine oxide (3t)



The title compound was prepared according to **GP1** and isolated as a yellowish solid (31.1 mg, 0.096 mmol, 64%, *E*/*Z* > 99:1). M.p.: 138.7 – 139.9 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.68 (m, 4H), 7.59 – 7.52 (m, 2H), 7.52 – 7.40 (m, 6H), 7.20 (d, *J* = 3.3 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H), 2.15 (dd, *J* = 13.8, 1.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 139.3 (d, *J* = 21.8 Hz), 135.3 (d, *J* = 12.5 Hz), 132.2 × 2, 132.1 × 2, 132.1, 132.1, 131.9, 131.5, 130.9, 128.8, 128.8 × 2, 128.7 × 2, 127.3, 126.5, 15.9 (d, *J* =

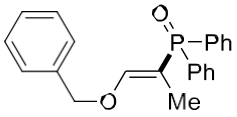
10.8 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.14. **HRMS** (ESI): m/z calculated for $C_{19}H_{18}OPS$ $[M + H]^+$: 325.0810, found: 325.0810.

(*E*)-(1-Phenoxyprop-1-en-2-yl)diphenylphosphine oxide (3u)



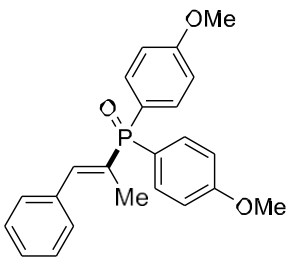
The title compound was prepared according to **GP1** and isolated as a colorless oil (19.8 mg, 0.059 mmol, 39%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.70 (m, 4H), 7.61 – 7.44 (m, 6H), 7.38 – 7.28 (m, 2H), 7.14 – 7.09 (m, 1H), 7.07 – 7.02 (m, 1H), 7.02 – 6.96 (m, 2H), 1.91 (dd, *J* = 12.9, 1.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.8, 152.9 (d, *J* = 25.0 Hz), 132.1 × 4, 132.0 × 2, 131.7 (d, *J* = 105.0 Hz), 129.9 × 2, 128.8 × 2, 128.7 × 2, 124.2 × 2, 117.1 × 2, 108.9 (d, *J* = 107.6 Hz), 10.6 (d, *J* = 6.8 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 31.55. **HRMS** (ESI): m/z calculated for $C_{21}H_{20}O_2P$ $[M + H]^+$: 335.1195, found: 335.1203.

(*E*)-(1-(Benzyloxy)prop-1-en-2-yl)diphenylphosphine oxide (3v)



The title compound was prepared according to **GP1** and isolated as a colorless oil (25.1 mg, 0.072 mmol, 48%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 4H), 7.54 – 7.47 (m, 2H), 7.46 – 7.40 (m, 4H), 7.39 – 7.31 (m, 3H), 7.30 – 7.25 (m, 2H), 6.76 (dd, *J* = 10.3, 1.4 Hz, 1H), 4.92 (s, 2H), 1.73 (dd, *J* = 13.0, 1.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.3 (d, *J* = 23.6 Hz), 136.4, 132.6, 132.1 × 2, 132.0 × 2, 131.9, 131.8, 131.5, 128.8 × 2, 128.6 × 2, 128.5 × 2, 127.8 × 2, 104.5, 103.4, 75.3, 10.4 (d, *J* = 7.3 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 32.12. **HRMS** (ESI): m/z calculated for $C_{22}H_{22}O_2P$ $[M + H]^+$: 349.1352, found: 349.1348.

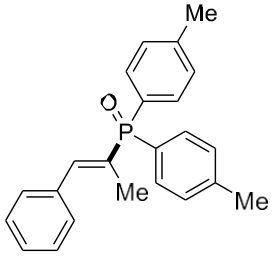
(*E*)-Bis(4-methoxyphenyl)(1-phenylprop-1-en-2-yl)phosphine oxide (3ab)



The title compound was prepared according to **GP1** and isolated as a colorless oil (28.9 mg, 0.076 mmol, 51%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 – 7.61 (m, 4H), 7.41 – 7.34 (m, 4H), 7.34 – 7.27 (m, 1H), 7.20 – 7.12 (m, 1H), 7.05 – 6.79 (m, 4H), 3.86 (s, 6H), 2.09 (dd, *J* = 13.7, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.5, 142.2 (d, *J* = 10.9 Hz), 136.1 (d, *J* = 18.7 Hz), 134.1 × 2, 134.0 × 2, 131.7, 130.7, 129.5 × 2,

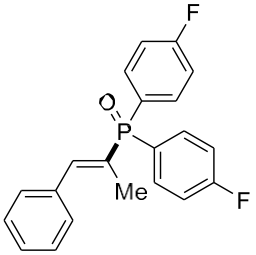
128.5 × 2, 128.4, 123.2, 122.2, 114.3 × 2, 114.2 × 2, 55.5 × 2, 15.2 (d, *J* = 11.0 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.00. **HRMS** (ESI): m/z calculated for $C_{23}H_{24}O_3P$ $[M + H]^+$: 379.1458, found: 379.1461.

(*E*)-(1-Phenylprop-1-en-2-yl)di-*p*-tolylphosphine oxide (3ac)



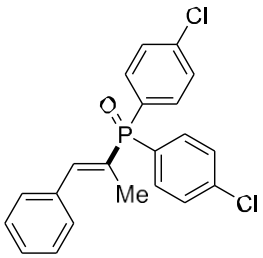
The title compound was prepared according to **GP1** and isolated as a colorless oil (35.6 mg, 0.103 mmol, 69%, *E*/*Z* = 95:5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 4H), 7.40 – 7.32 (m, 4H), 7.33 – 7.27 (m, 5H), 7.23 – 7.14 (m, 1H), 2.41 (s, 6H), 2.09 (dd, *J* = 13.7, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.5 (d, *J* = 2.7 Hz), 142.4 (d, *J* = 11.0 Hz), 136.0 (d, *J* = 19.0 Hz), 132.2 × 2, 132.1 × 2, 131.3, 130.3, 129.5 × 2, 129.5 × 2, 129.4 × 2, 128.6, 128.5 × 2, 128.4, 127.6, 21.7 × 2, 15.2 (d, *J* = 10.7 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.47. **HRMS** (ESI): m/z calculated for $C_{23}H_{24}OP$ $[M + H]^+$: 347.1559, found: 347.1553.

(*E*)-Bis(4-fluorophenyl)(1-phenylprop-1-en-2-yl)phosphine oxide (3ad)



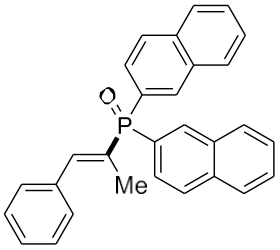
The title compound was prepared according to **GP1** and isolated as a white solid (47.8 mg, 0.135 mmol, 90%, *E*/*Z* > 99:1). M.p.: 137.5 – 139.1 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.68 (m, 4H), 7.45 – 7.28 (m, 5H), 7.24 – 7.14 (m, 5H), 2.10 (dd, *J* = 14.0, 1.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.5 (d, *J* = 2.8 Hz), 164.0 (d, *J* = 2.8 Hz), 143.2 (d, *J* = 11.0 Hz), 135.6 (d, *J* = 19.2 Hz), 134.7, 134.6, 134.6, 134.5, 129.8 (d, *J* = 98.6 Hz), 129.6 × 2, 128.7, 128.6 × 2, 127.6 (d, *J* = 3.3 Hz), 126.6 (d, *J* = 3.4 Hz), 116.4, 116.3, 116.2, 116.1, 15.1 (d, *J* = 11.0 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 32.66. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -106.2 (t, *J* = 7.5 Hz). **HRMS** (ESI): m/z calculated for $C_{21}H_{18}F_2OP$ $[M + H]^+$: 355.1058, found: 355.1058.

(*E*)-Bis(4-chlorophenyl)(1-phenylprop-1-en-2-yl)phosphine oxide (3ae)



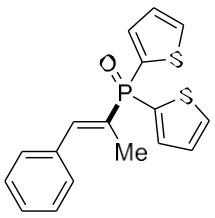
The title compound was prepared according to **GP1** and isolated as a white solid (46.1 mg, 0.119 mmol, 79%, *E*/*Z* > 99:1). M.p.: 119.9 – 120.3 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 – 7.62 (m, 4H), 7.51 – 7.45 (m, 4H), 7.43 – 7.29 (m, 5H), 7.24 – 7.15 (m, 1H), 2.10 (dd, *J* = 14.1, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.5 (d, *J* = 11.0 Hz), 139.0 (d, *J* = 3.1 Hz), 135.5 (d, *J* = 19.3 Hz), 133.6 × 2, 133.4 × 2, 132.7 (d, *J* = 10.4 Hz), 129.9 (d, *J* = 17.1 Hz), 129.6 × 2, 129.3 × 2, 129.2 × 2, 128.9 (d, *J* = 9.5 Hz), 128.8, 128.6 × 2, 127.8, 15.1 (d, *J* = 10.8 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 32.83. **HRMS** (ESI): m/z calculated for $C_{21}H_{18}Cl_2OP$ $[M + H]^+$: 387.0467, found: 387.0463.

(*E*)-Di(naphthalen-2-yl)(1-phenylprop-1-en-2-yl)phosphine oxide (3af)



The title compound was prepared according to **GP1** and isolated as a white solid (40.5 mg, 0.097 mmol, 65%, *E*/*Z* = 92:8). M.p.: 173.4 – 174.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (dd, *J* = 13.6, 1.4 Hz, 2H), 8.00 – 7.89 (m, 6H), 7.82 – 7.75 (m, 2H), 7.65 – 7.53 (m, 4H), 7.45 – 7.36 (m, 4H), 7.36 – 7.28 (m, 2H), 2.22 (dd, *J* = 13.8, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.0 (d, *J* = 11.1 Hz), 135.9 (d, *J* = 19.3 Hz), 134.9, 134.9, 134.3, 134.2, 132.8, 132.7, 131.0, 130.0, 129.6 × 2, 129.1 × 2, 128.6 × 2, 128.6 × 2, 128.5, 128.4 × 2, 128.1, 128.0 × 2, 127.1 × 2, 127.1, 127.0, 15.3 (d, *J* = 10.7 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.44. **HRMS** (ESI): m/z calculated for $C_{29}H_{24}OP$ $[M + H]^+$: 419.1559, found: 419.1559.

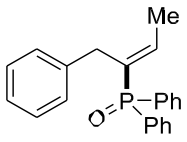
(*E*)-(1-Phenylprop-1-en-2-yl)di(thiophen-2-yl)phosphine oxide (3ag)



The title compound was prepared according to **GP1** and isolated as a white solid (26.3 mg, 0.080 mmol, 53%, *E*/*Z* = 93:7). M.p.: 161.3 – 163.4 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 2H), 7.67 – 7.62 (m, 2H), 7.54 – 7.45 (m, 1H), 7.44 – 7.37 (m, 4H), 7.36 – 7.30 (m, 1H), 7.25 – 7.21 (m, 2H), 2.16 (dd, *J* = 15.4, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7 (d, *J* = 10.9 Hz), 136.9, 136.8, 135.8 (d, *J* = 20.5 Hz), 134.0 (d, *J* = 5.1 Hz), 133.6, 132.4, 130.9, 129.9, 129.7 × 2,

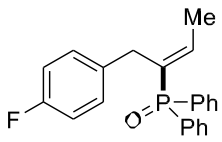
128.7, 128.6 ×2, 128.6, 128.4, 15.1 (d, *J* = 12.4 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 18.65. **HRMS** (ESI): m/z calculated for $C_{17}H_{16}OPS_2$ $[M + H]^+$: 331.0375, found: 331.0375.

(*E*)-Diphenyl(1-phenylbut-2-en-2-yl)phosphine oxide (4a)



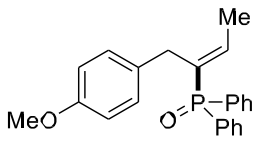
The title compound was prepared according to **GP1** and isolated as a white solid (39.9 mg, 0.120 mmol, 80%, *E*/*Z* = 96:4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 – 7.59 (m, 4H), 7.51 – 7.43 (m, 2H), 7.43 – 7.32 (m, 4H), 7.13 – 7.02 (m, 5H), 6.56 – 6.42 (m, 1H), 3.71 (d, *J* = 15.6 Hz, 2H), 1.85 (dd, *J* = 6.9, 2.8 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.8 (d, *J* = 10.9 Hz), 138.5 (d, *J* = 2.0 Hz), 133.4 (d, *J* = 99.1 Hz), 132.3, 132.2 × 2, 132.1 × 2, 131.8, 131.7, 131.3, 128.6 × 2, 128.5 × 2, 128.4 × 2, 128.2 × 2, 126.0, 33.1 (d, *J* = 11.7 Hz), 15.7 (d, *J* = 16.3 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 32.99. **HRMS** (ESI): m/z calculated for $C_{22}H_{22}OP$ $[M + H]^+$: 333.1403, found: 333.1406.

(*E*)-(1-(4-Fluorophenyl)but-2-en-2-yl)diphenylphosphine oxide (4b)



The title compound was prepared according to **GP1** and isolated as a colorless oil (45.1 mg, 0.129 mmol, 86%, *E*/*Z* = 96:4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 – 7.58 (m, 4H), 7.52 – 7.34 (m, 6H), 7.05 – 6.98 (m, 2H), 6.82 – 6.73 (m, 2H), 6.48 – 6.34 (m, 1H), 3.67 (d, *J* = 15.5 Hz, 2H), 1.83 (dd, *J* = 6.9, 3.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.3 (d, *J* = 243.7 Hz), 143.6 (d, *J* = 11.1 Hz), 134.2 (d, *J* = 3.0 Hz), 133.2, 132.2, 132.1 × 2, 132.0 × 2, 131.8, 131.8, 131.2, 130.1, 130.0, 128.5 × 2, 128.4 × 2, 115.0, 114.8, 32.2 (d, *J* = 11.6 Hz), 15.6 (d, *J* = 16.1 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -117.4 (td, *J* = 9.6, 5.1 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 33.01. **HRMS** (ESI): m/z calculated for $C_{22}H_{21}FOP$ $[M + H]^+$: 351.1309, found: 351.1304.

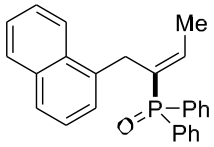
(*E*)-(1-(4-Methoxyphenyl)but-2-en-2-yl)diphenylphosphine oxide (4c)



The title compound was prepared according to **GP1** and isolated as a colorless oil (39.0 mg, 0.108 mmol, 72%, *E*/*Z* = 94:6). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.58 (m, 4H), 7.55 – 7.43 (m, 2H), 7.44 – 7.33 (m, 4H), 7.03 – 6.89 (m, 2H), 6.72 – 6.60 (m, 2H), 6.56 – 6.30 (m, 1H), 3.72 (s, 3H), 3.65 (d, *J* = 15.6 Hz, 2H), 1.84 (dd, *J* = 6.9, 3.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.8, 143.4 (d, *J* =

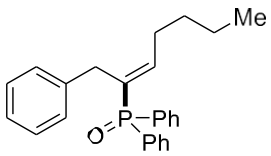
11.1 Hz), 133.9 (d, *J* = 98.9 Hz), 132.4, 132.2 × 2, 132.1 × 2, 131.7 × 2 (d, *J* = 2.7 Hz), 131.4, 130.6 (d, *J* = 2.1 Hz), 129.6 × 2, 128.5 × 2, 128.3 × 2, 113.7, 113.7, 55.3, 32.2 (d, *J* = 11.6 Hz), 15.6 (d, *J* = 16.3 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 33.02. **HRMS** (ESI): m/z calculated for $C_{23}H_{24}O_2P$ $[M + H]^+$: 363.1508, found: 363.1513.

(*E*)-(1-(Naphthalen-1-yl)but-2-en-2-yl)diphenylphosphine oxide (4d)



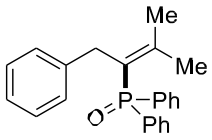
The title compound was prepared according to **GP1** and isolated as a colorless oil (32.1 mg, 0.084 mmol, 56%, *E*/*Z* = 94:6). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 – 7.89 (m, 1H), 7.80 – 7.73 (m, 1H), 7.70 – 7.62 (m, 4H), 7.60 – 7.54 (m, 1H), 7.49 – 7.37 (m, 4H), 7.35 – 7.28 (m, 4H), 7.24 – 7.13 (m, 2H), 6.95 – 6.60 (m, 1H), 4.12 (d, *J* = 14.9 Hz, 2H), 1.79 (dd, *J* = 6.9, 3.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.8 (d, *J* = 10.0 Hz), 133.6, 133.0 (d, *J* = 2.5 Hz), 132.8, 132.0 (d, *J* = 30.5 Hz), 132.0 × 2, 132.0 × 2, 131.8, 131.7, 131.7, 131.1, 128.8, 128.4 × 2, 128.3 × 2, 126.9, 125.8, 125.5, 125.4, 125.4, 123.2, 29.9 (d, *J* = 12.4 Hz), 15.7 (d, *J* = 16.0 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 32.28. **HRMS** (ESI): m/z calculated for $C_{26}H_{24}OP$ $[M + H]^+$: 383.1559 found: 383.1560.

(*E*)-Diphenyl(1-phenylhept-2-en-2-yl)phosphine oxide (4e)



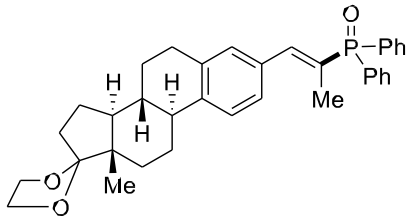
The title compound was prepared according to **GP1** and isolated as a colorless oil (44.8 mg, 0.120 mmol, 80%, *E*/*Z* = 91:9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 4H), 7.49 – 7.42 (m, 2H), 7.41 – 7.34 (m, 4H), 7.12 – 6.99 (m, 5H), 6.41 (dt, *J* = 21.0, 7.2 Hz, 1H), 3.69 (d, *J* = 15.7 Hz, 2H), 2.31 – 2.18 (m, 2H), 1.52 – 1.17 (m, 4H), 0.83 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.5 (d, *J* = 9.5 Hz), 138.7, 132.4 (d, *J* = 2.9 Hz), 132.1 × 2, 132.0 × 2, 131.7, 131.7, 131.4, 129.1, 128.5 × 2, 128.4 × 2, 128.3 × 2, 128.2 × 2, 125.9, 33.3 (d, *J* = 11.9 Hz), 30.7, 29.5 (d, *J* = 15.1 Hz), 22.5, 13.9. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 32.91. **HRMS** (ESI): m/z calculated for $C_{25}H_{28}OP$ $[M + H]^+$: 375.1872, found: 375.1877.

(3-Methyl-1-phenylbut-2-en-2-yl)diphenylphosphine oxide (4f)



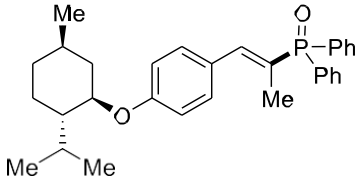
The title compound was prepared according to **GP1** and isolated as a colorless oil (40.6 mg, 0.117 mmol, 78%).**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 7.48 (m, 4H), 7.44 – 7.38 (m, 2H), 7.34 – 7.28 (m, 4H), 7.16 – 7.00 (m, 3H), 6.84 – 6.67 (m, 2H), 3.50 (d, *J* = 18.1 Hz, 2H), 2.12 (d, *J* = 2.7 Hz, 3H), 2.00 (d, *J* = 2.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.0 (d, *J* = 7.8 Hz), 138.4, 134.3, 133.3, 131.7 × 2, 131.6 × 2, 131.4, 131.3, 128.3 × 2, 128.2 × 3, 128.1 × 2, 126.0, 125.7, 124.7, 37.0 (d, *J* = 14.5 Hz), 25.0 (d, *J* = 9.1 Hz), 24.0 (d, *J* = 13.2 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 32.00. **HRMS** (ESI): m/z calculated for $C_{23}H_{24}OP$ $[M + H]^+$: 347.1559, found: 347.1554.

((*E*)-1-((8*R*,9*S*,13*S*,14*S*)-13-Methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a] phenanthrene-17,2'-[1,3]dioxolan]-3-yl)prop-1-en-2-yl)diphenylphosphine oxide (3aj)



The title compound was prepared according to **GP1** and isolated as a colorless oil (75.2 mg, 0.140 mmol, 93%, *E*/*Z* > 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.68 (m, 4H), 7.59 – 7.43 (m, 6H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.05 (m, 3H), 4.01 – 3.78 (m, 4H), 2.85 (dd, *J* = 8.3, 4.1 Hz, 2H), 2.37 –2.26 (m, 2H), 2.12 (dd, *J* = 13.9, 1.5 Hz, 3H), 2.07 – 1.98 (m, 1H), 1.95 – 1.71 (m, 4H), 1.70 – 1.21 (m, 6H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.8 (d, *J* = 10.9 Hz), 141.2, 137.0, 133.1 (d, *J* = 19.1 Hz), 132.2 × 2, 132.1 × 2, 132.0, 131.9, 130.9, 130.3, 129.6, 128.7 × 2, 128.6, 128.6 × 2, 126.8, 125.5, 119.4, 65.3, 64.7, 49.5, 46.1, 44.2, 38.8, 34.3, 30.7, 29.6, 26.9, 25.9, 22.4, 15.3 (d, *J* = 10.8 Hz), 14.4. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.59. **HRMS** (ESI): m/z calculated for $C_{35}H_{40}O_3P^+$ $[M + H]^+$: 539.2710, found: 539.2706.

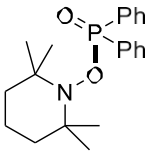
((*E*)-1-(4-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)phenyl)prop-1-en-2-yl)diphenyl phosphine oxide (3ak)



The title compound was prepared according to **GP1** and isolated as a colorless oil (42.5 mg, 0.090 mmol, 60%, *E*/*Z* = 98:2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.68 (m, 4H), 7.56 – 7.42 (m, 6H), 7.35 – 7.30 (m, 2H), 7.12 (dd, *J* = 22.2, 1.7 Hz, 1H), 6.91 – 6.85 (m, 2H), 4.08 – 4.01 (m, 1H), 2.16 (dt, *J* = 6.7, 3.4 Hz, 2H), 2.10 (dd, *J* = 13.9, 1.5 Hz,

3H), 1.75 – 1.65 (m, 2H), 1.53 – 1.41 (m, 2H), 1.12 – 0.93 (m, 3H), 0.90 (d, *J* = 6.8 Hz, 6H), 0.74 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.7, 142.4 (d, *J* = 11.2 Hz), 132.2 × 2, 132.1 × 2, 131.9, 131.9, 131.4 × 2, 131.0, 128.7 × 2, 128.6 × 2, 128.2, 128.1, 127.5, 115.4 × 2, 77.5, 48.0, 40.2, 34.5, 31.5, 26.2, 23.8, 22.2, 20.8, 16.6, 15.3 (d, *J* = 11.0 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 34.78. **HRMS** (ESI): m/z calculated for $C_{31}H_{38}O_2P^+$ $[M + H]^+$: 473.2604, found: 473.2602.

2,2,6,6-Tetramethylpiperidin-1-yl diphenylphosphinate (5a)



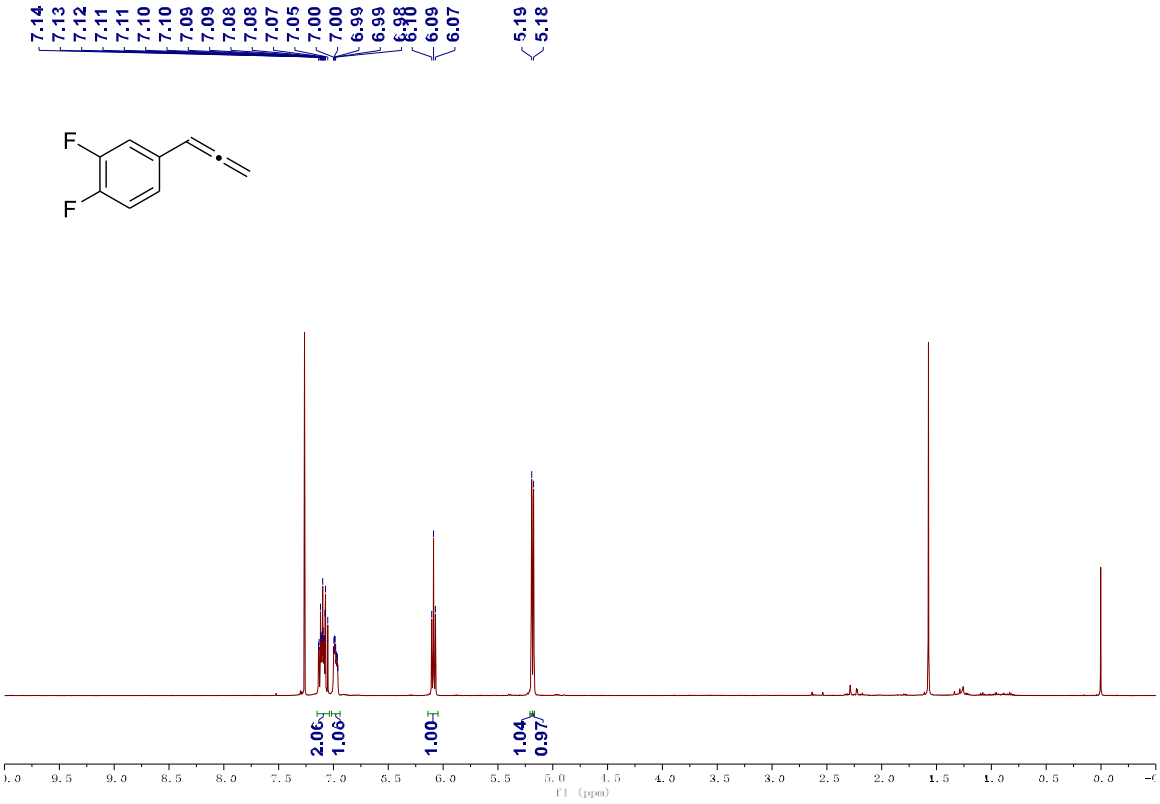
The title compound isolated as a colorless oil (80.4 mg, 0.225 mmol, 30%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 – 7.65 (m, 4H), 7.49 – 7.33 (m, 6H), 1.74 – 1.64 (m, 2H), 1.63 – 1.57 (m, 4H), 1.35 (s, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 139.5, 138.3, 133.1 × 2, 133.0 × 2, 130.9, 130.9, 127.8 × 2, 127.7 × 2, 56.6, 56.6, 43.8, 43.7, 32.5 × 4, 17.2. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 33.14. **HRMS** (ESI): m/z calculated for $C_{21}H_{29}NO_2P$ $[M + H]^+$: 358.1930, found: 358.1938.

7. Supplementary references

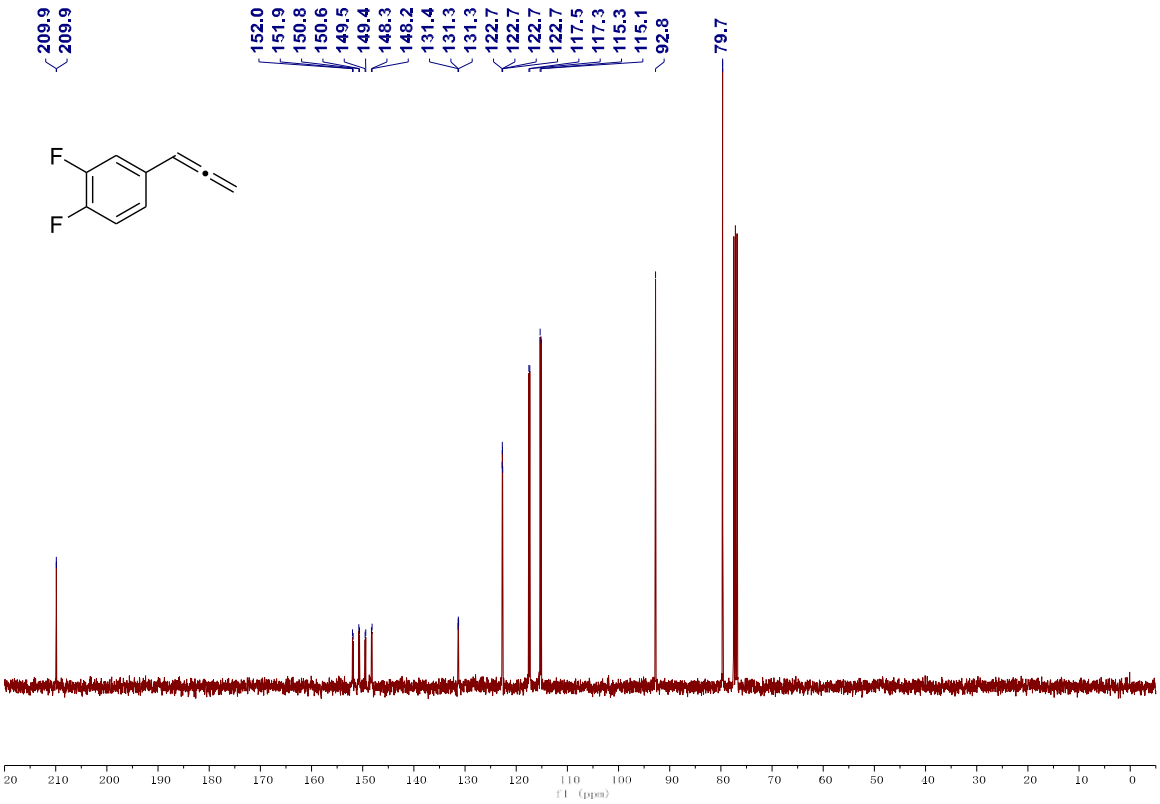
1. X. Xu, X. Zheng, X. Xu, Synthesis of Tetrahydroquinolines by Scandium-Catalyzed [3 + 3] Annulation of Anilines with Allenes and Dienes, *ACS Catal.*, 2021, **11**, 14995−15003.
2. Y. Yuan, X. Zhang, H. Qian, S. Ma, Catalytic Enantioselective Allene–Anhydride Approach to *β*,*γ*-Unsaturated Enones Bearing an *α*-All-Carbon-Quarternary Center, *Chem. Sci.*, 2020, **11**, 9115−9121.
3. Z. Yang, J. Wang, Enantioselective Palladium-Catalyzed Hydrophosphinylation of Allenes with Phosphine Oxides: Access to Chiral Allylic Phosphine Oxides, *Angew. Chem., Int. Ed.*, 2021, **60**, 27288−27292.
4. Z. Wang, X. Wang, P. Wang, J. Zhao, Allenone-Mediated Racemization/Epimerization-Free Peptide Bond Formation and Its Application in Peptide Synthesis, *J. Am. Chem. Soc*., 2021, **143**, 10374−10381.
5. W. Wu, S. Xu, Y. Zhang, X. Wang, R. Li, F. Sun, C. Yu, T. Li, D. Wei, C. Yao, NHC-Catalyzed *β*-Specific Addition of *N*-Based Nucleophiles to Allenoates, *Org. Chem. Front*., 2020, **7**, 1593−1599.
6. Y. Zhong, I. Douair, T. Wang, C. Wu, L. Maron, D. Cui, Access to Hydroxy-Functionalized Polypropylene through Coordination Polymerization, *Angew. Chem., Int. Ed.*, 2020, **59**, 4947−4952.
7. H. Xie, B. Breit, Organophotoredox/Ni-Cocatalyzed Allylation of Allenes: Regio- and Diastereoselective Access to Homoallylic Alcohols, *ACS Catal.*, 2022, **12**, 3249−3255.
8. (*a*) R. Shen, B. Luo, J. Yang, L. Zhang, L.-B. Han, Convenient Synthesis of Allenylphosphoryl Compounds via Cu-Catalysed Couplings of P(O)H Compounds with Propargyl Acetates, *Chem. Commun*., 2016, **52**, 6451−6454. (*b*) A. Boreux, K. Indukuri, F. Gagosz, O. Riant, Acyl Fluorides as Efficient Electrophiles for the Copper-Catalyzed Boroacylation of Allenes, *ACS Catal*., 2017, **7**, 8200−8204.
9. a) K. Chen, H. Zhu, Y. Li, Q. Peng, Y. Guo, X. Wang, Dinuclear Cobalt Complex-Catalyzed Stereodivergent Semireduction of Alkynes: Switchable Selectivities Controlled by H_2O. *ACS Catal*., 2021, **11**, 13696−13705. b) T. Zhang, J. Rabeah, S. Das, Red-Light-Mediated Copper-Catalyzed Photoredox Catalysis Promotes Regioselectivity Switch in the Difunctionalization of Alkenes. *Nat. Commun.*, 2024, **15**, 5208.
10. Y. Lei, Y. Kong, Z.-Q. Rong, W. Zhao, Asymmetric Dihydroboration of Allenes Enabled by Ligand Relay Catalysis. *Nat. Commun.*, 2024, **15**, 8186.
11. J.-X. Yu, Y.-Y. Cheng, B. Chen, C.-H. Tung, L.-Z. Wu, Cobaloxime Photocatalysis for the Synthesis of Phosphorylated Heteroaromatics, *Angew. Chem., Int. Ed.*, 2022, **61**, e202209293.
12. S. Duan, A. Pan, Y. Du, G. Zhu, X. Tian, H. Zhang, P. J. Walsh, X. Yang, Nickel-Catalyzed Enantioselective Hydrophosphinylation of 2-Azadienes to Access Enantioenriched *α*-Aminophosphine Oxides, *ACS Catal.*, 2023, **13**, 10887−10894.
13. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson et al. Gaussian 16, Revision A.03, *Gaussian, Inc., Wallingford, CT*, **2016**.
14. C. Y. Legault, CYLview, 1.0b; Université de Sherbrooke, Sherbrooke (Québec) Canada, **2009**, http://www.cylview.org.

15. A. D. Becke, Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.*, 1993, **98**, 5648−5652.
16. C. T. Lee, W. T. Yang, R. G. Parr, Development of the Colle-Salvetti Correlation-Energy Formula Into a Functional of the Electron Density, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785−789.
17. B. Miehlich, A. Savin, H. Stoll, H. Preuss, Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr, *Chem. Phys. Lett.*, 1989, **157**, 200−206.
18. G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Allaham, W. A. Shirley, J. Mantzaris, A Complete Basis Set Model Chemistry. I. The Total Energies of Closed-Shell Atoms and Hydrides of the First-Row Elements, *J. Chem. Phys.*, 1988, **89**, 2193−2218.
19. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A Consistent and Accurate AB Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu, *J. Chem. Phys.*, 2010, **132**, 154104.
20. K. Fukui, The Path of Chemical Reactions-the IRC Approach, *Acc. Chem. Res.*, 1981, **14**, 363−368.
21. M. J. Frisch, J. A. Pople, J. S. Binkley, Self-Consistent Molecular Orbital Methods 25. Supplementary Functions for Gaussian Basis Sets, *J. Chem. Phys.*, 1984, **80**, 3265−3269.
22. R. Ditchfield, W. J. Hehre, J. A. Pople, Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules, *J. Chem. Phys.*, 1971, **54**, 724−728.

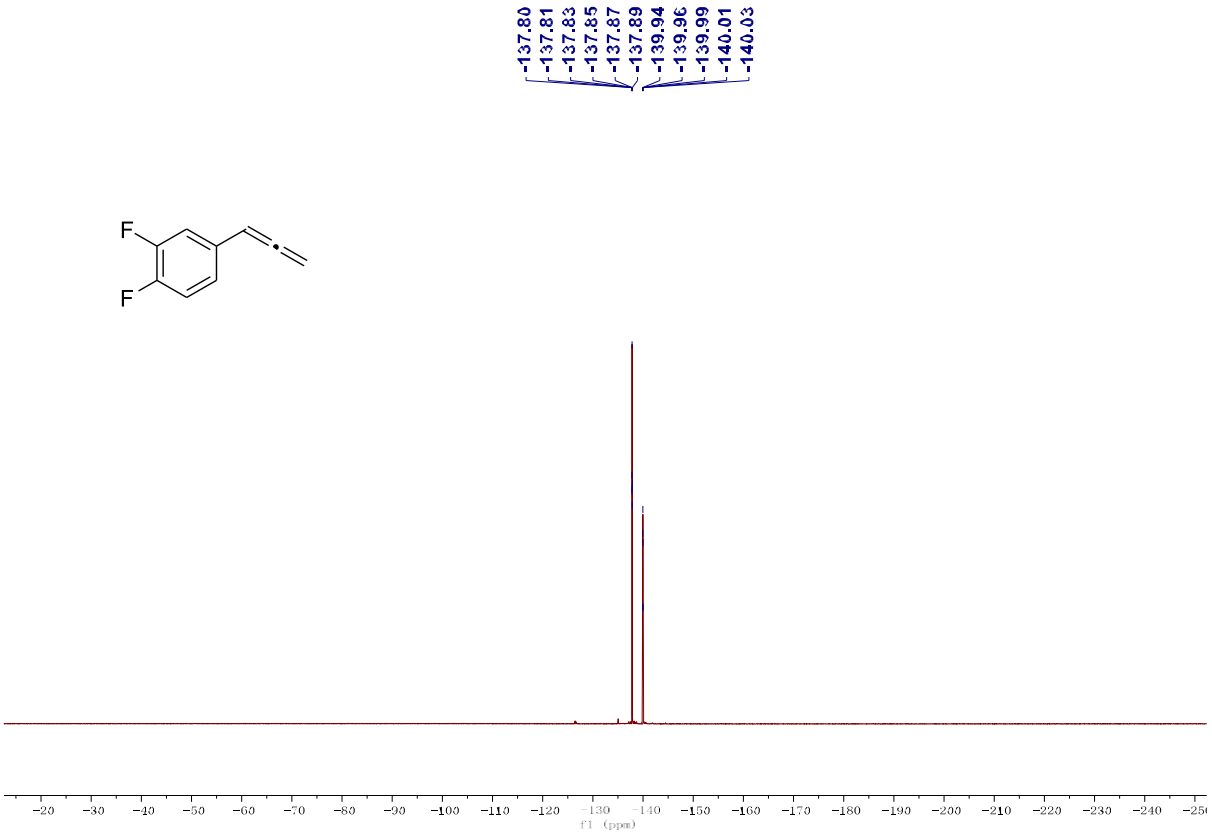
8. NMR spectra of the allenes



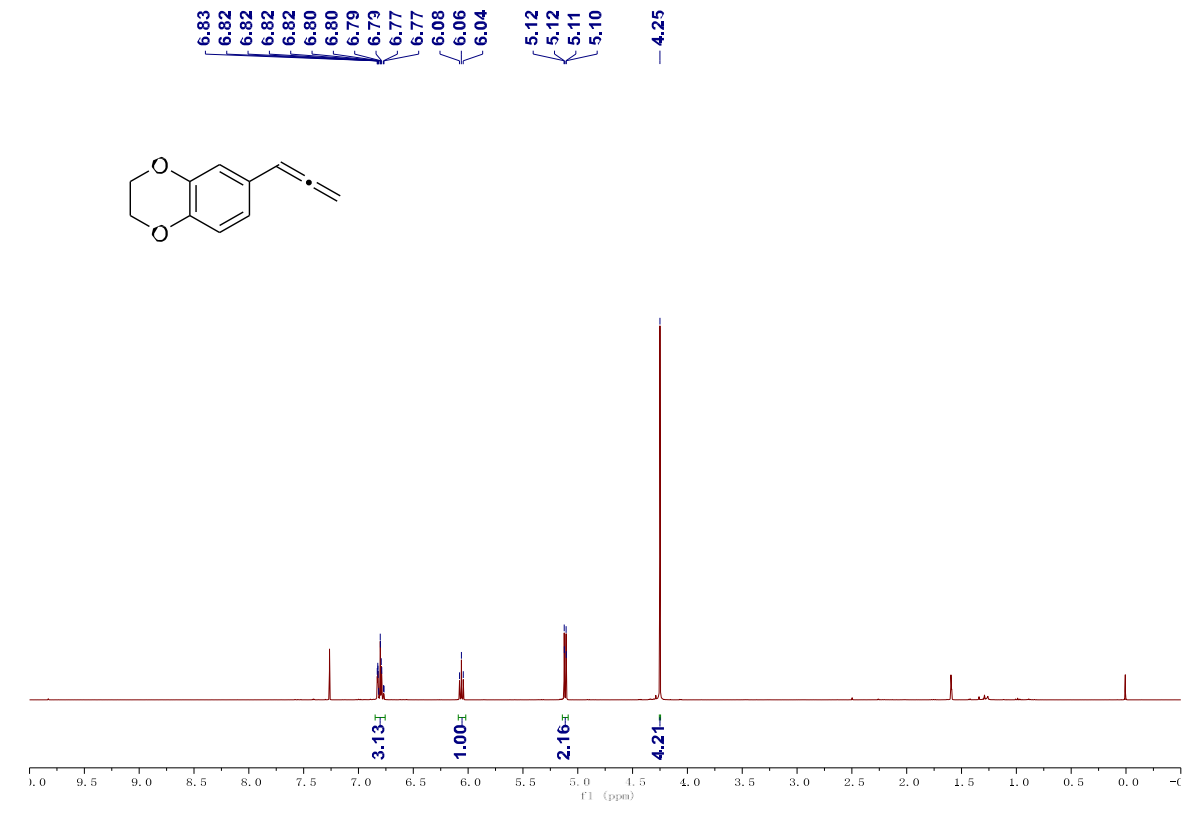
^{1}H NMR spectrum for compound **1q** ($CDCl_3$)



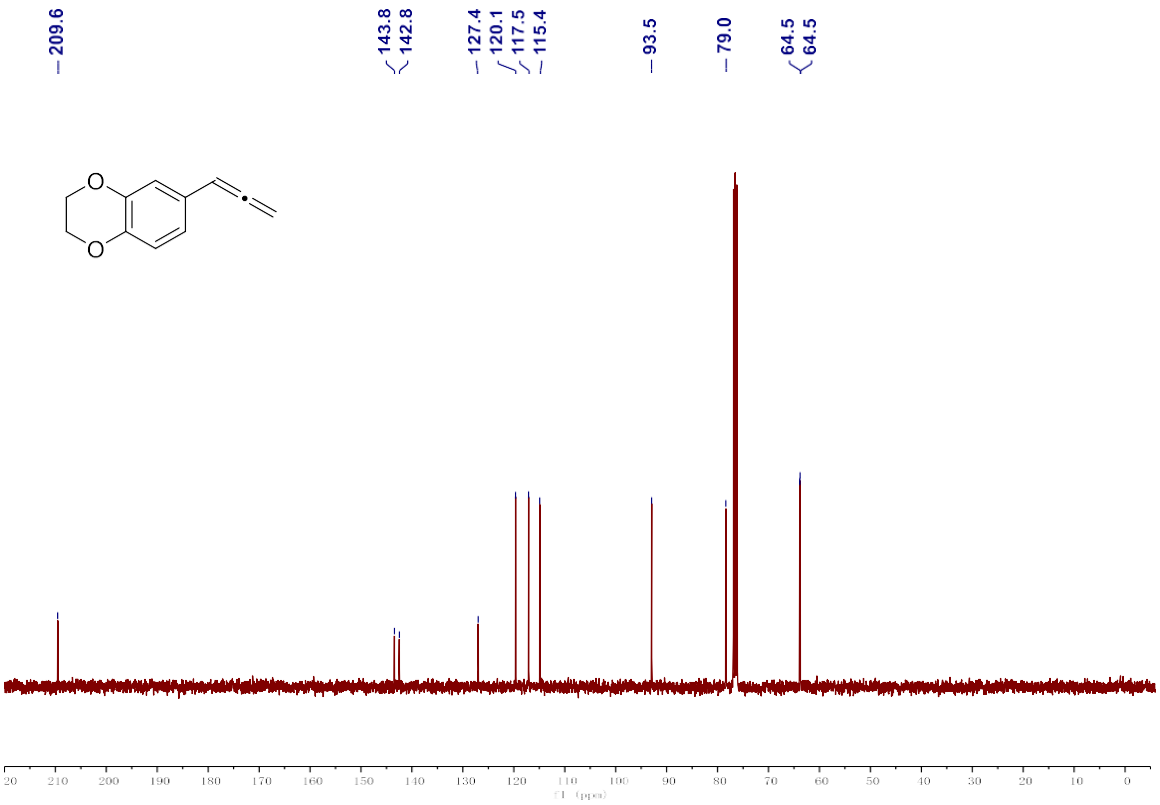
^{13}C NMR spectrum for compound **1q** ($CDCl_3$)



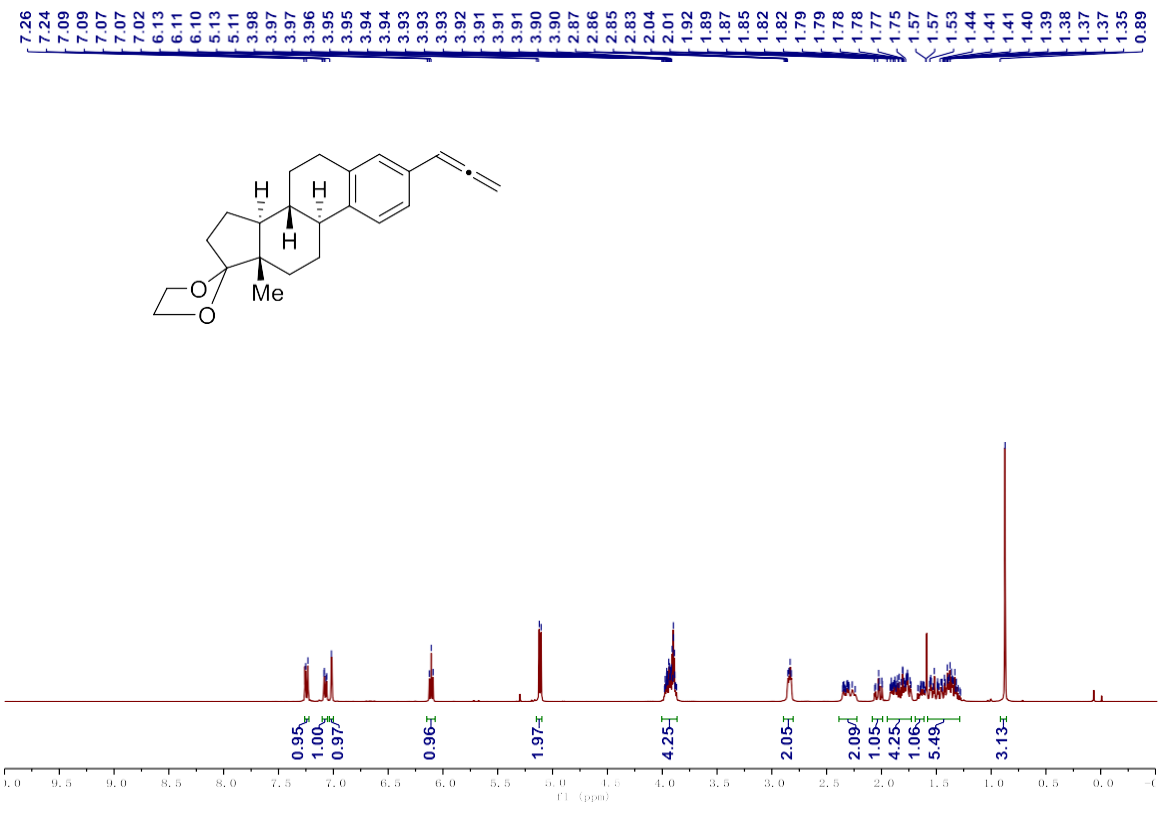
^{19}F NMR spectrum for compound **1q** ($CDCl_3$)



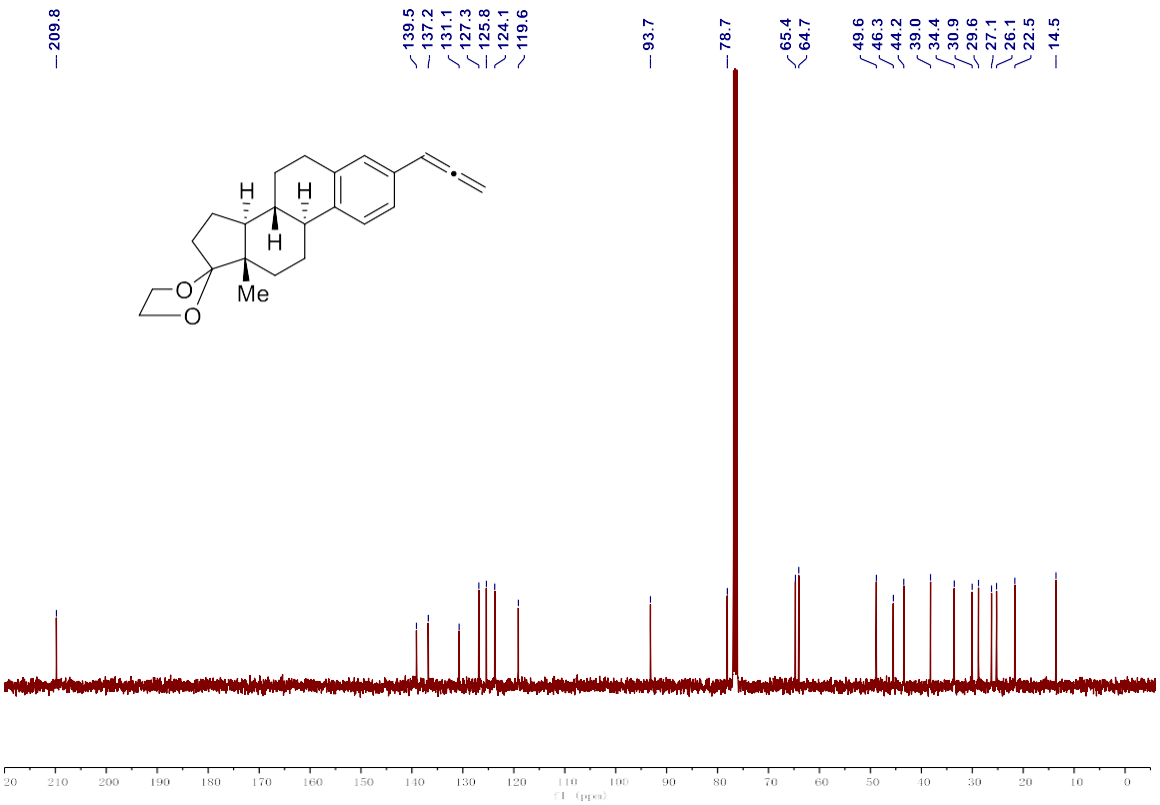
^{1}H NMR spectrum for compound **1s** ($CDCl_3$)



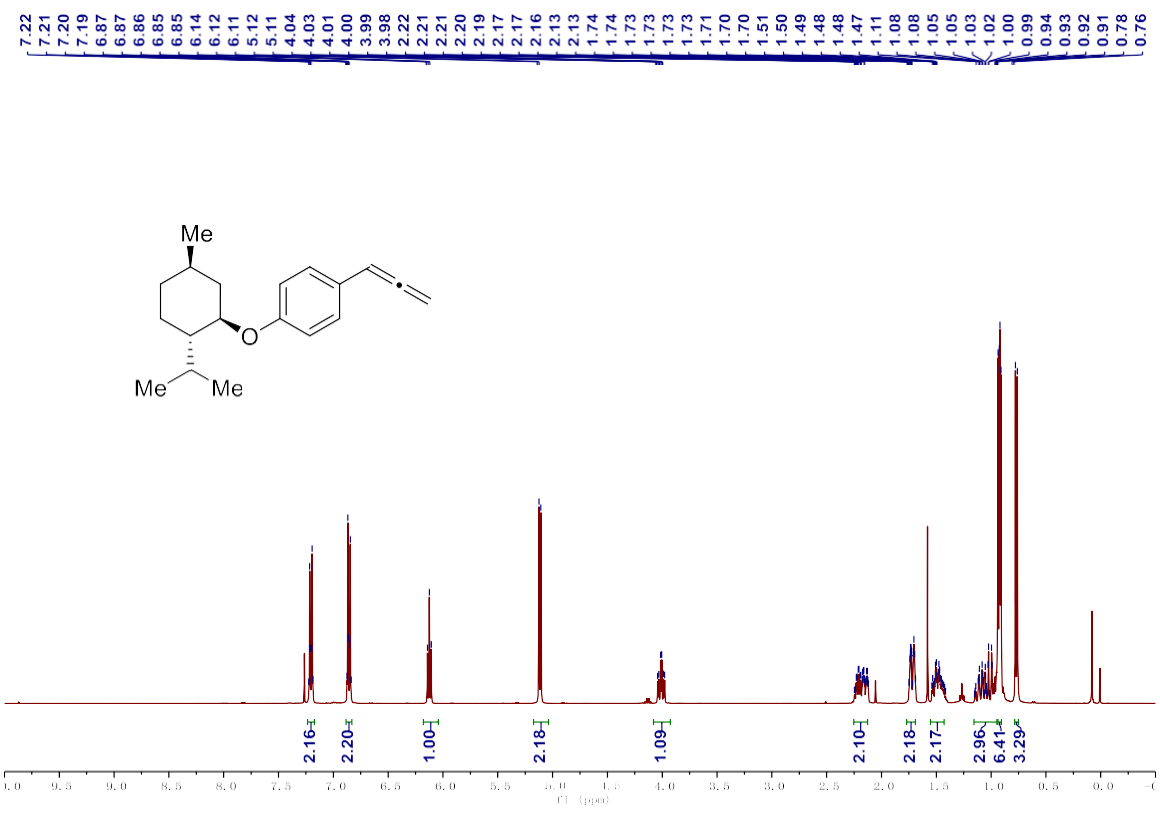
^{13}C NMR spectrum for compound **1s** ($CDCl_3$)



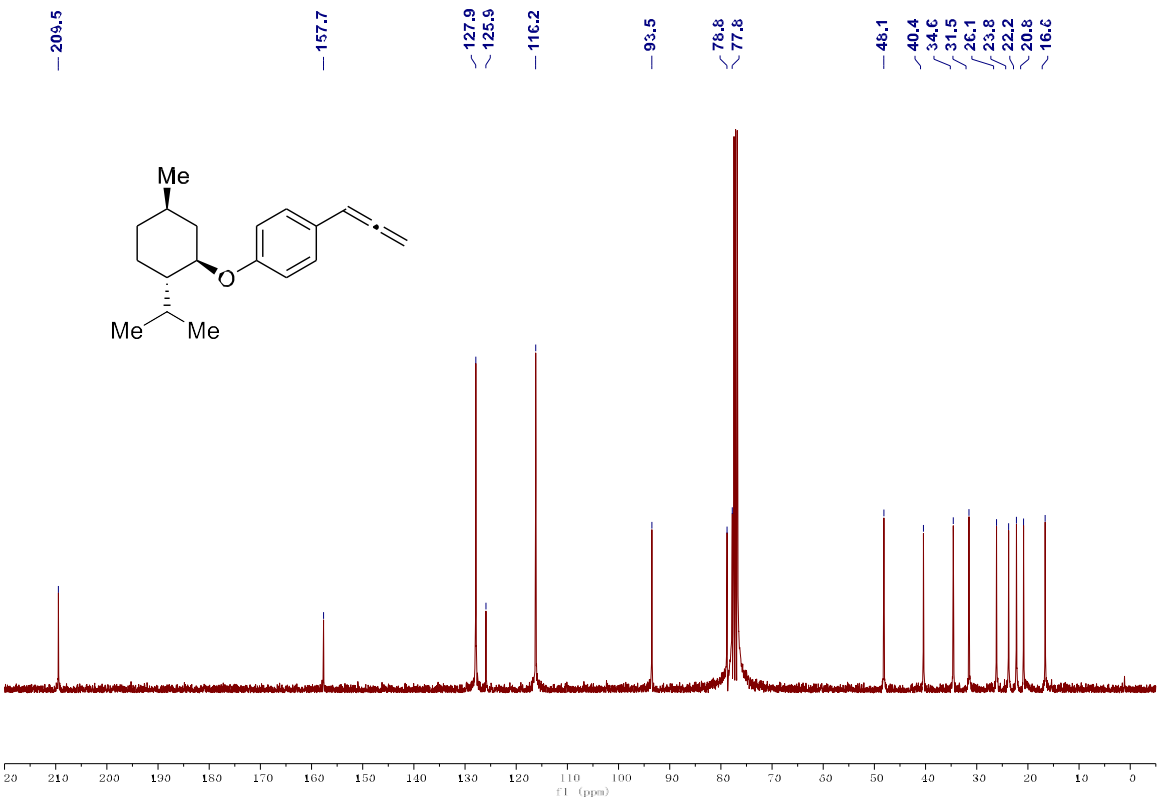
^{1}H NMR spectrum for compound **1aj** ($CDCl_3$)



^{13}C NMR spectrum for compound **1aj** ($CDCl_3$)

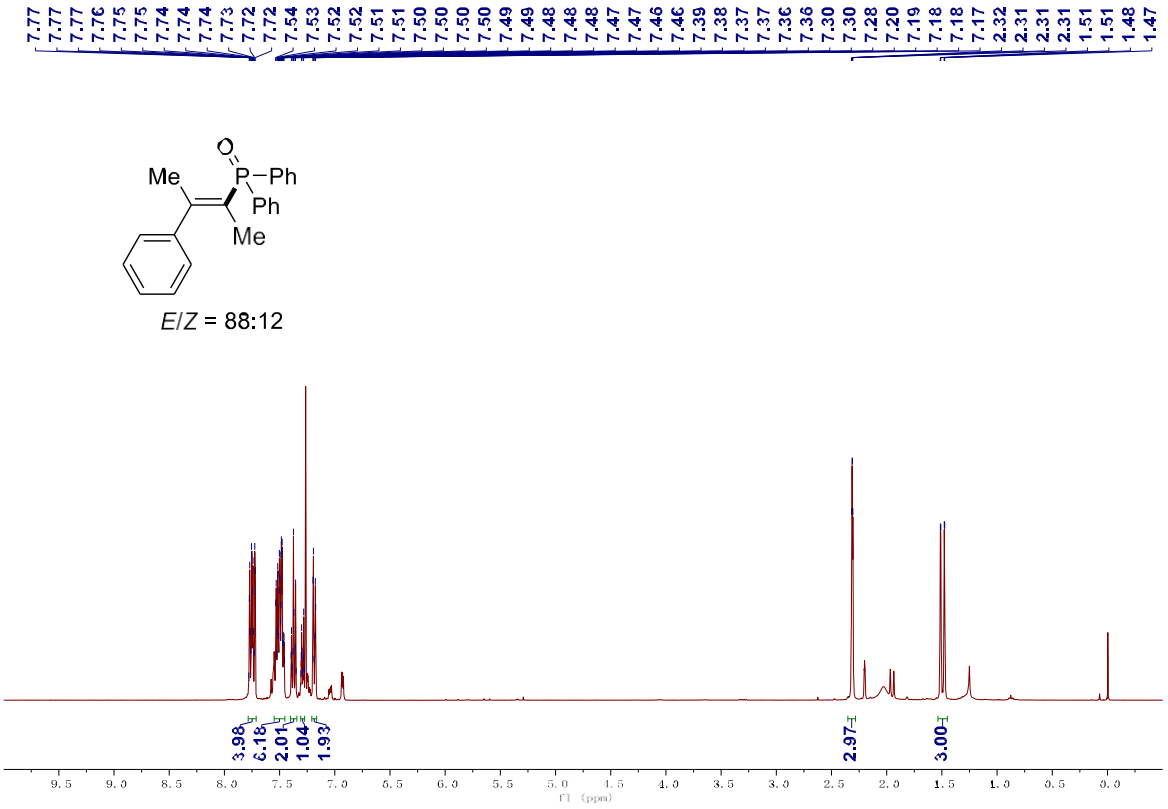


^{1}H NMR spectrum for compound **1ak** ($CDCl_3$)

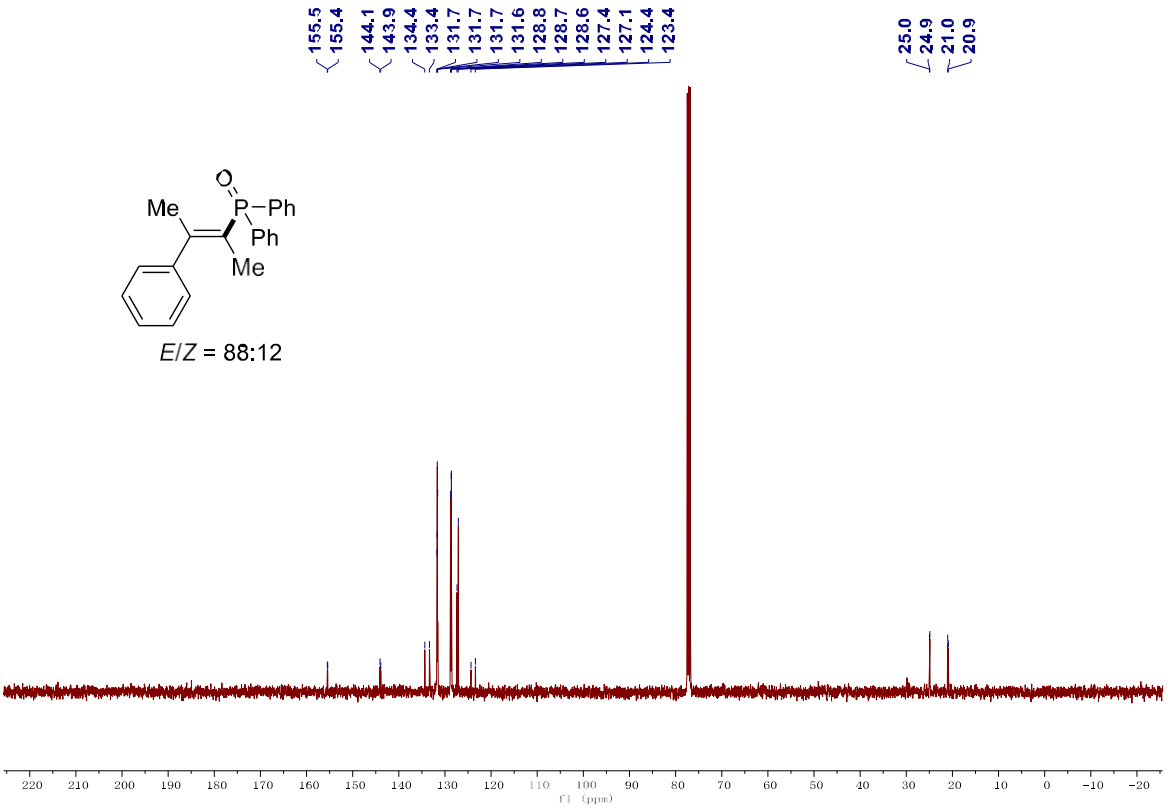


^{13}C NMR spectrum for compound **1ak** ($CDCl_3$)

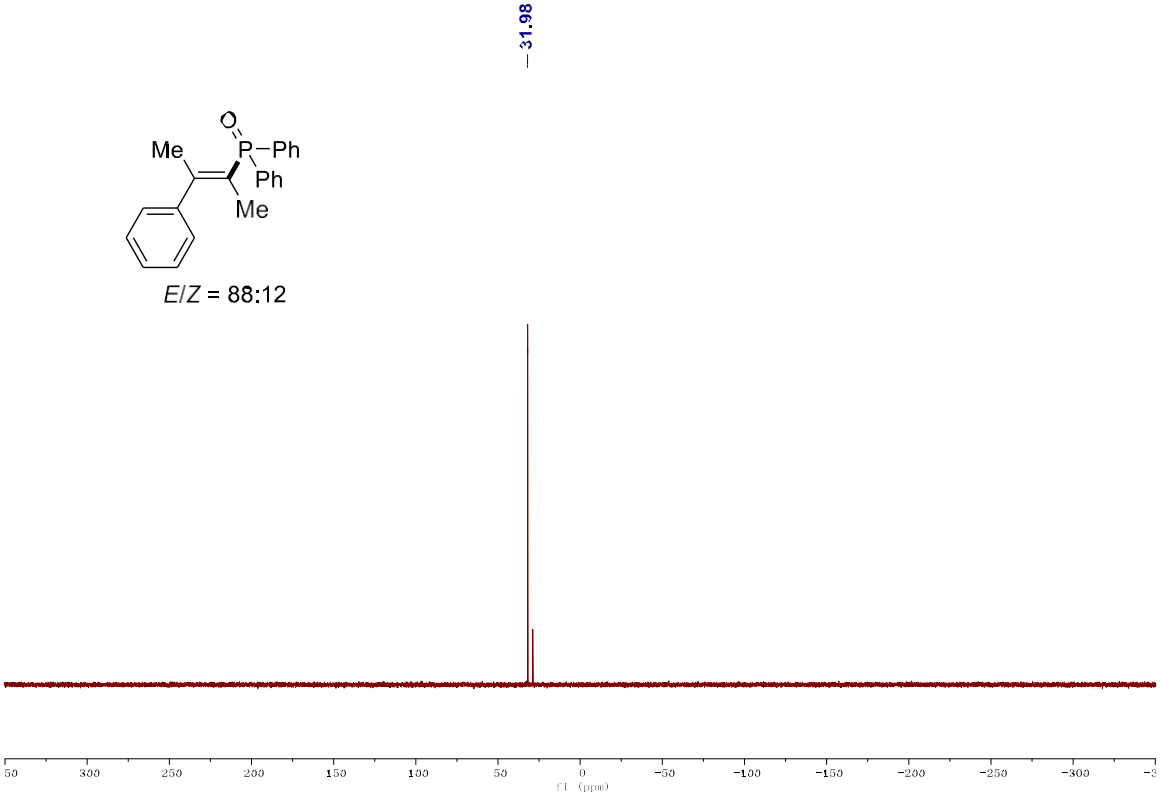
9. NMR spectra of the products



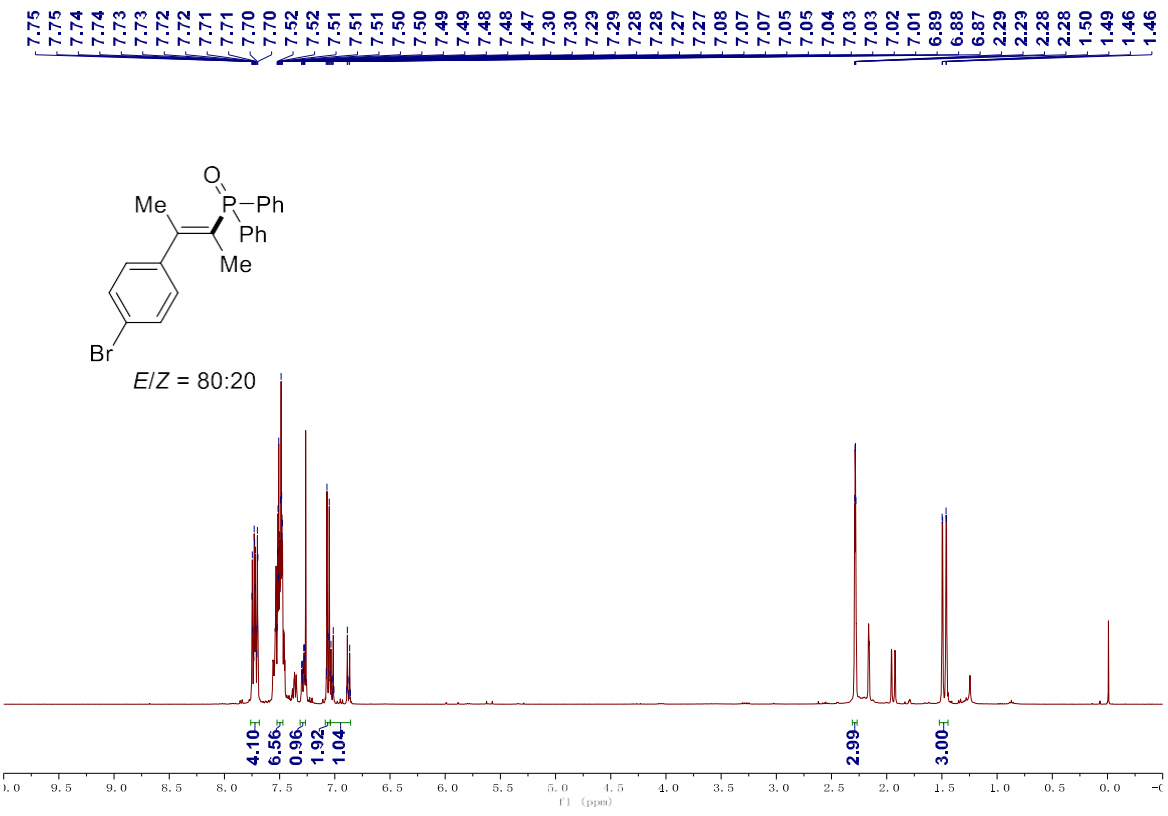
^{1}H NMR spectrum for compound **3a** ($CDCl_3$)



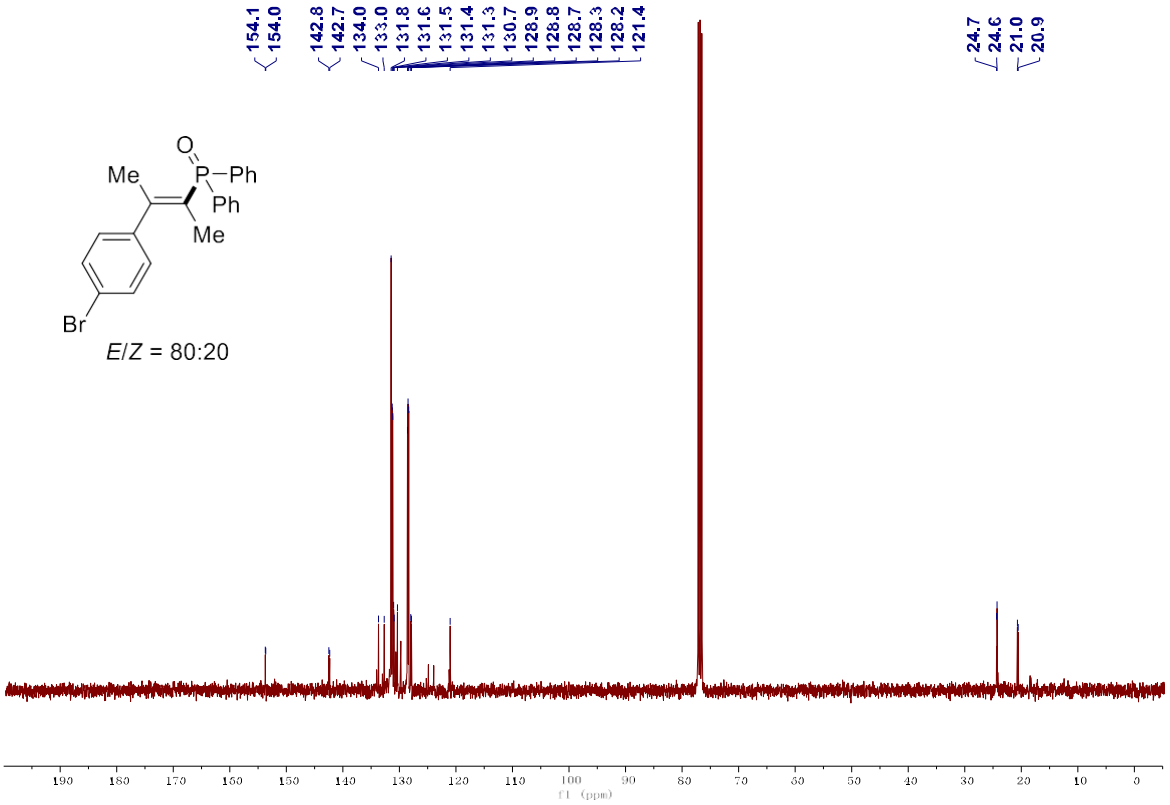
^{13}C NMR spectrum for compound **3a** ($CDCl_3$)



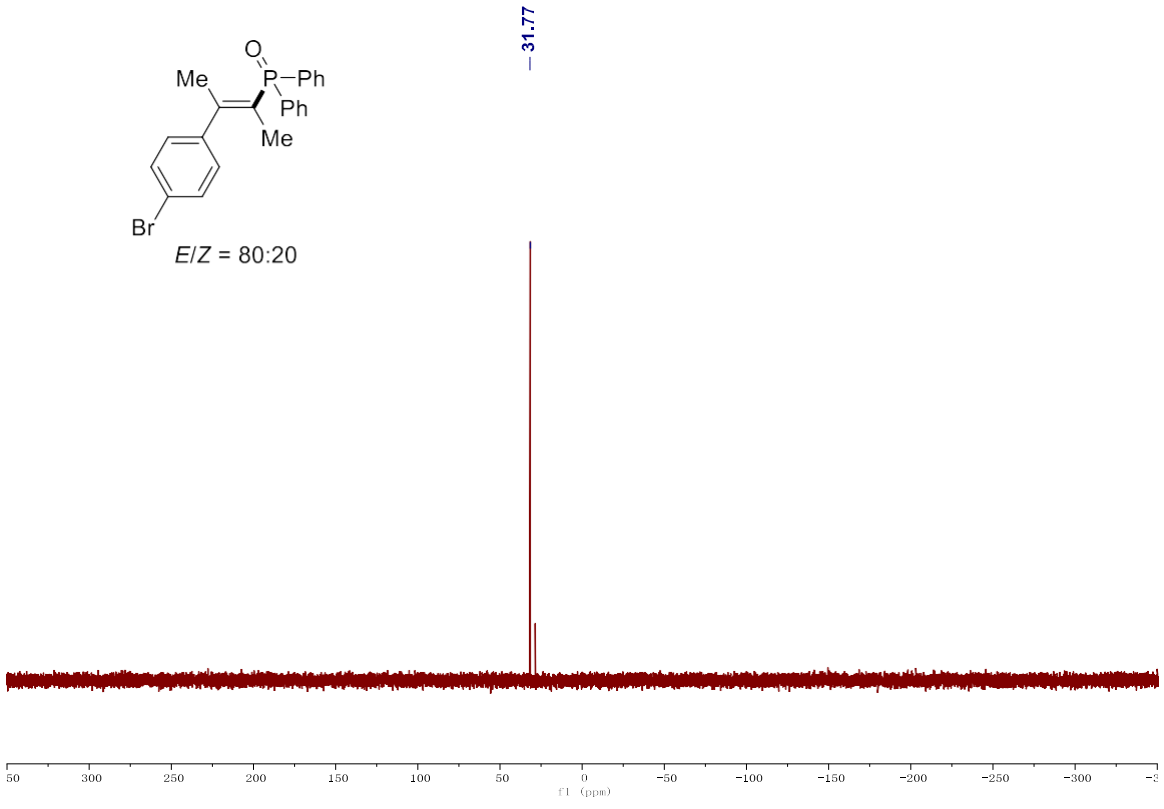
^{31}P NMR spectrum for compound **3a** ($CDCl_3$)



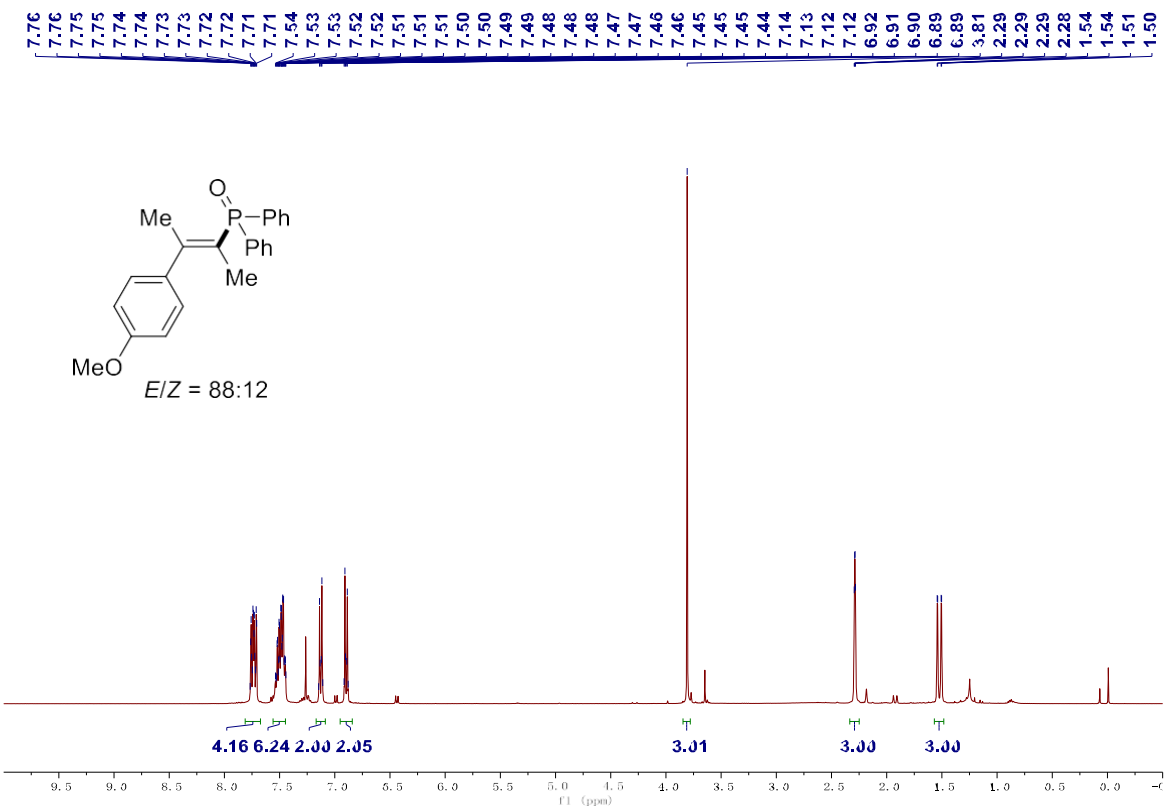
^{1}H NMR spectrum for compound **3b** ($CDCl_3$)



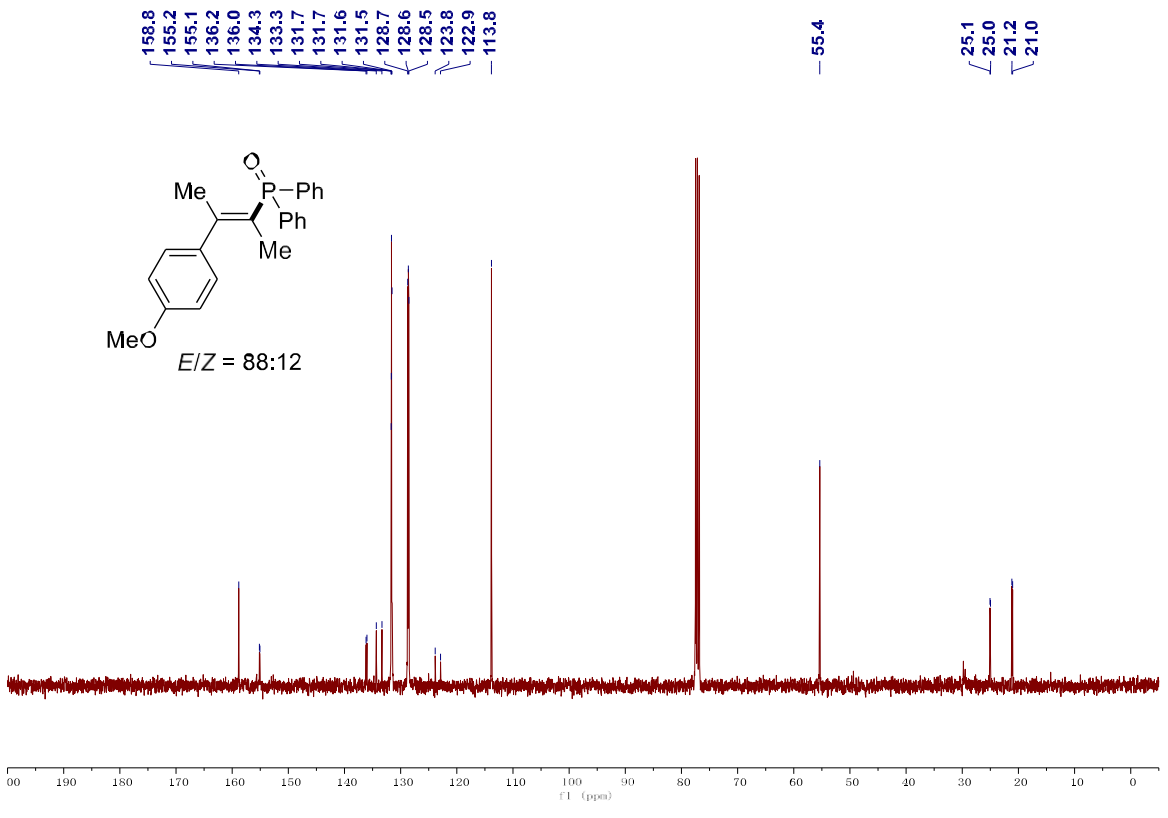
^{13}C NMR spectrum for compound **3b** ($CDCl_3$)



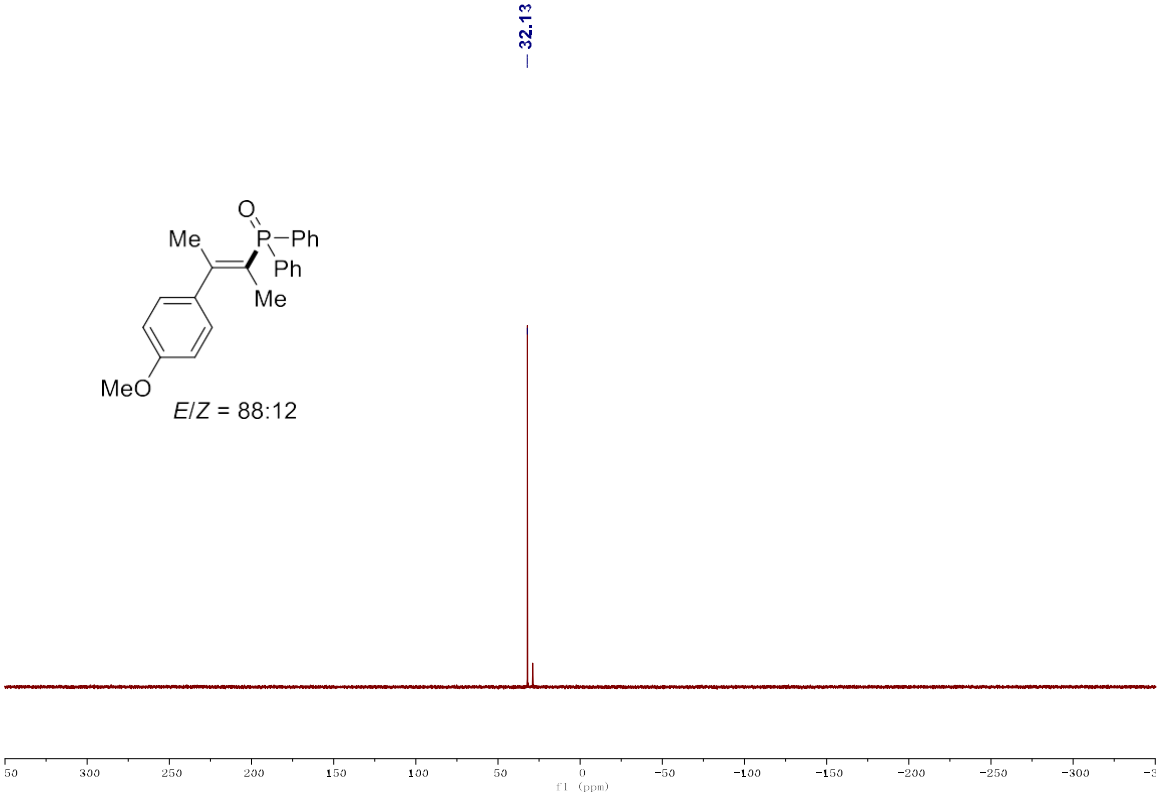
^{31}P NMR spectrum for compound **3b** ($CDCl_3$)



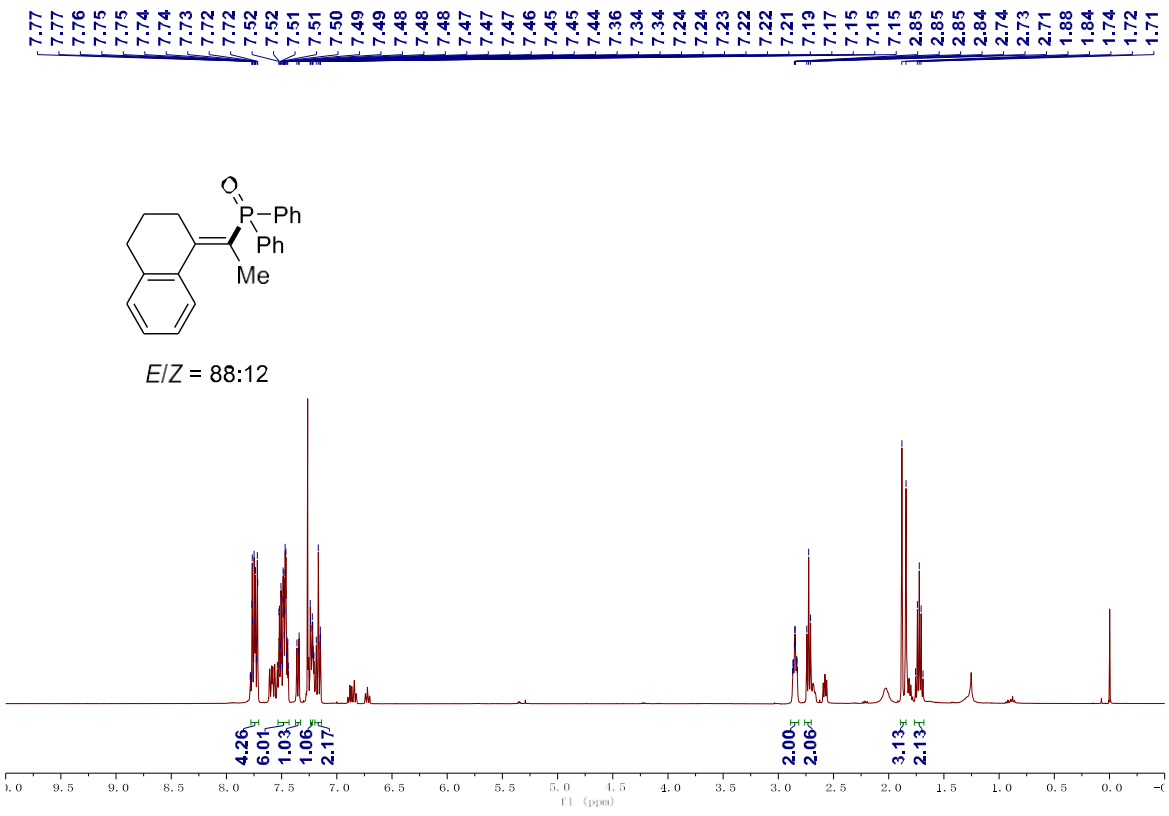
^{1}H NMR spectrum for compound **3c** ($CDCl_3$)



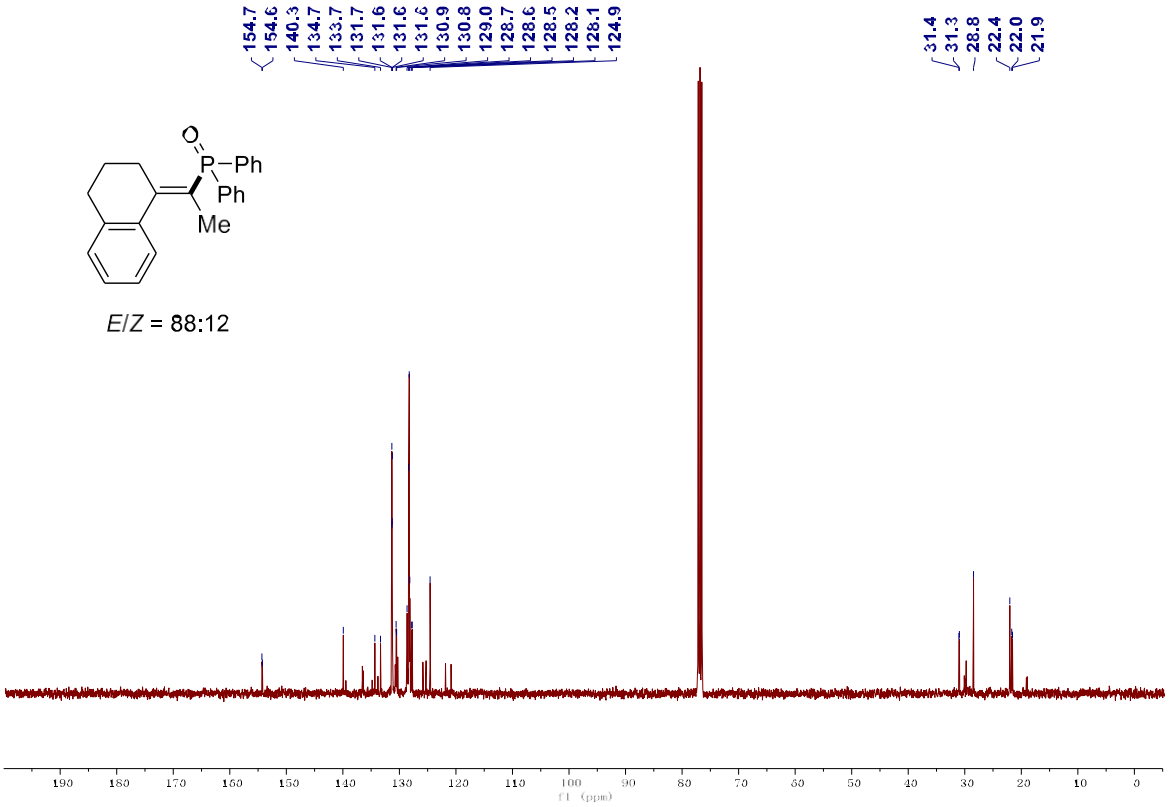
^{13}C NMR spectrum for compound **3c** ($CDCl_3$)



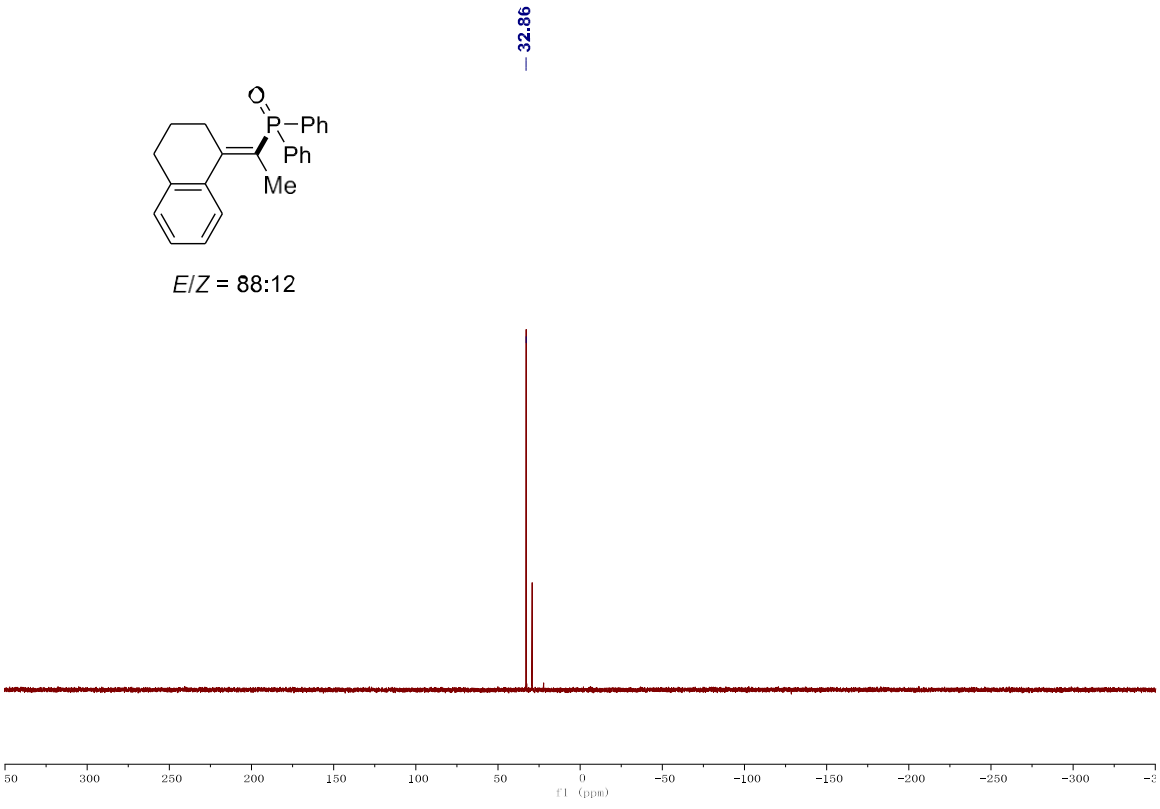
^{31}P NMR spectrum for compound **3c** ($CDCl_3$)



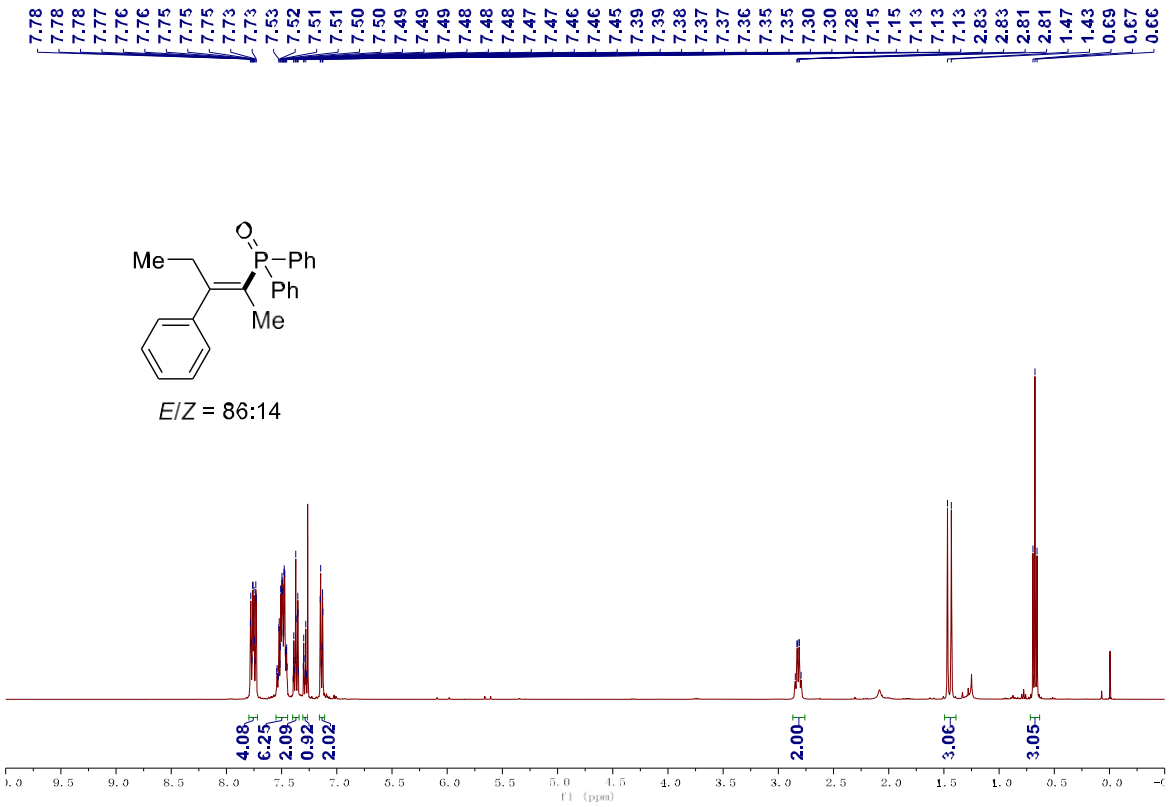
^{1}H NMR spectrum for compound **3d** ($CDCl_3$)



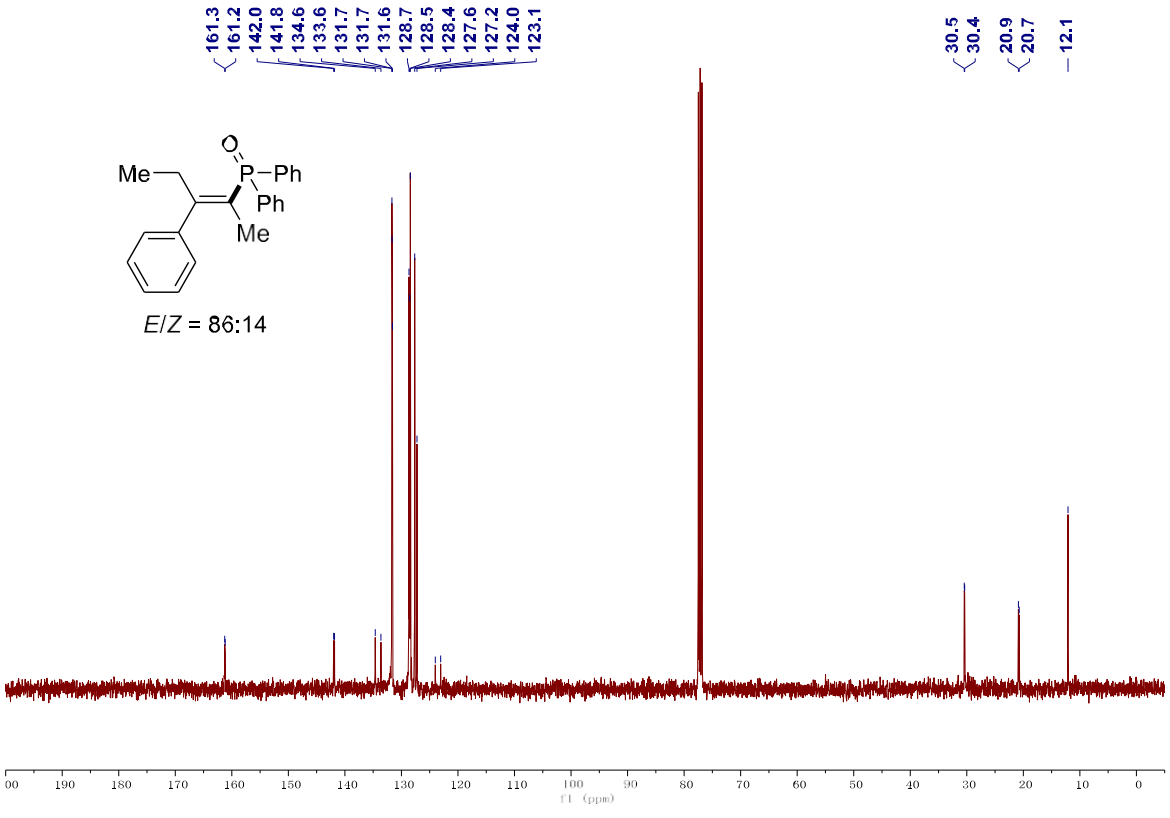
^{13}C NMR spectrum for compound **3d** ($CDCl_3$)



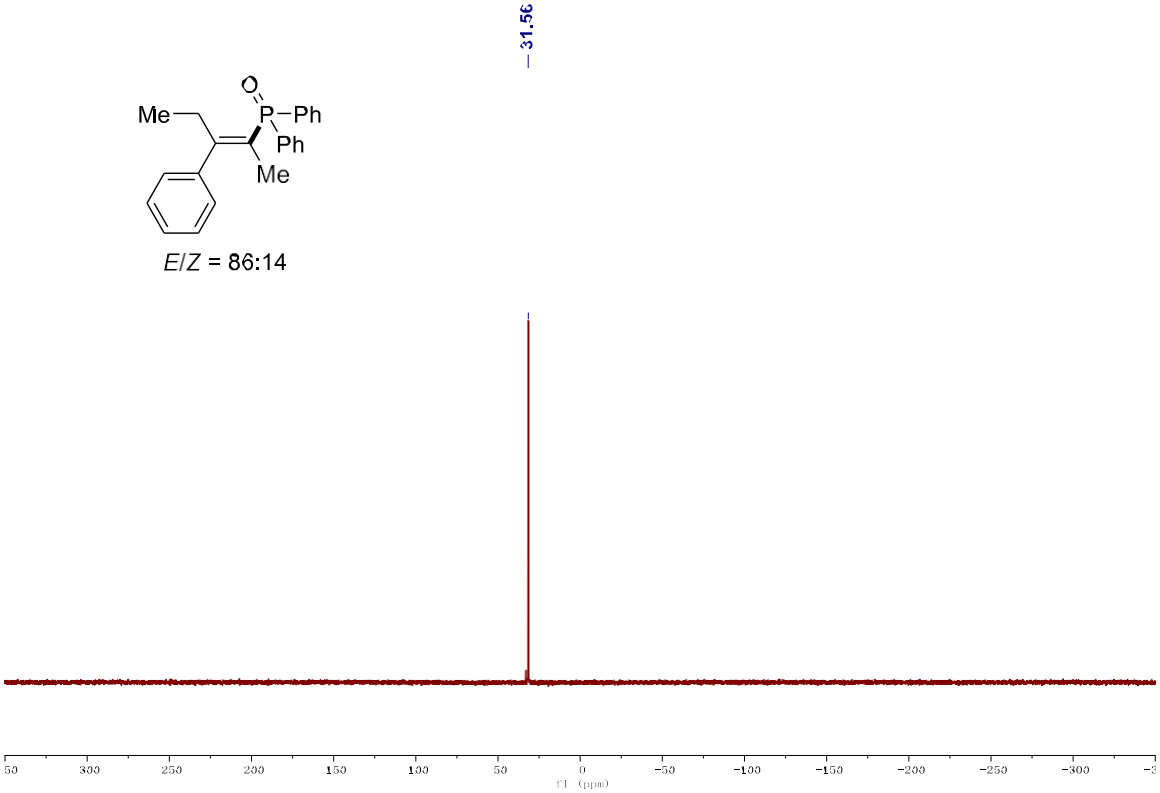
^{31}P NMR spectrum for compound **3d** ($CDCl_3$)



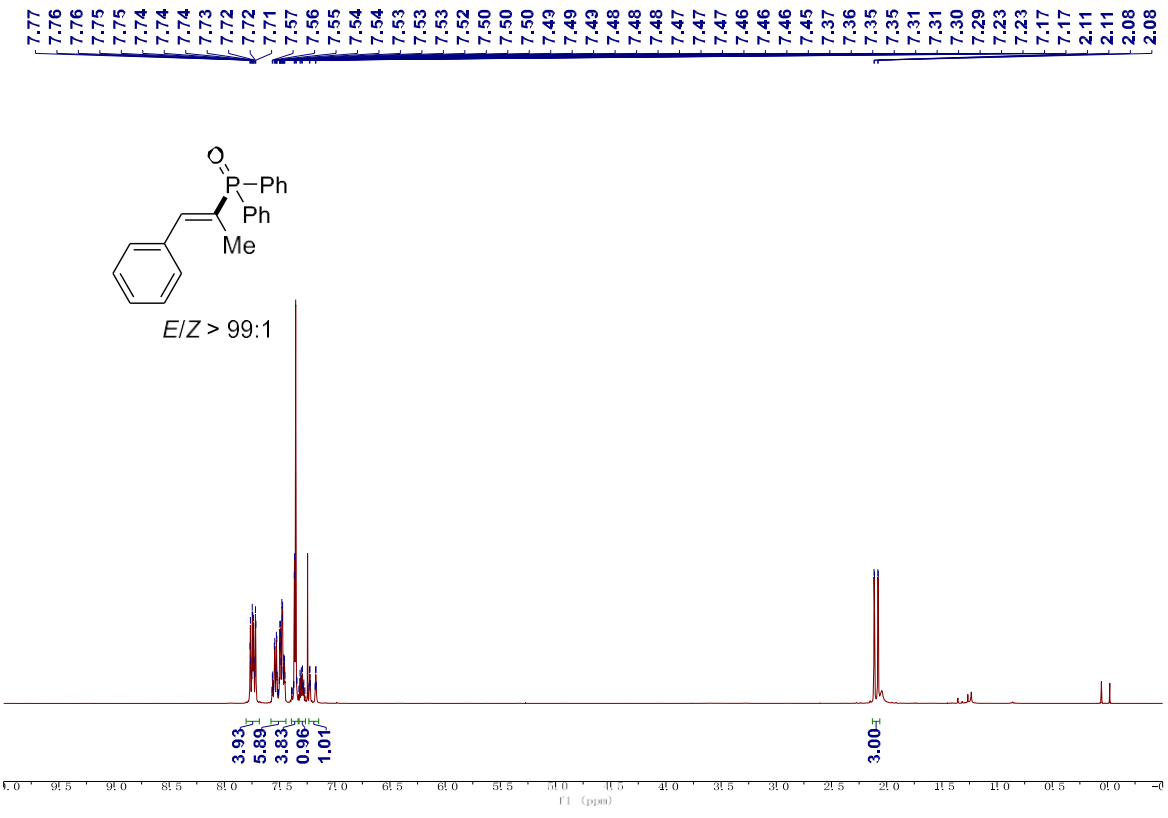
^{1}H NMR spectrum for compound **3e** ($CDCl_3$)



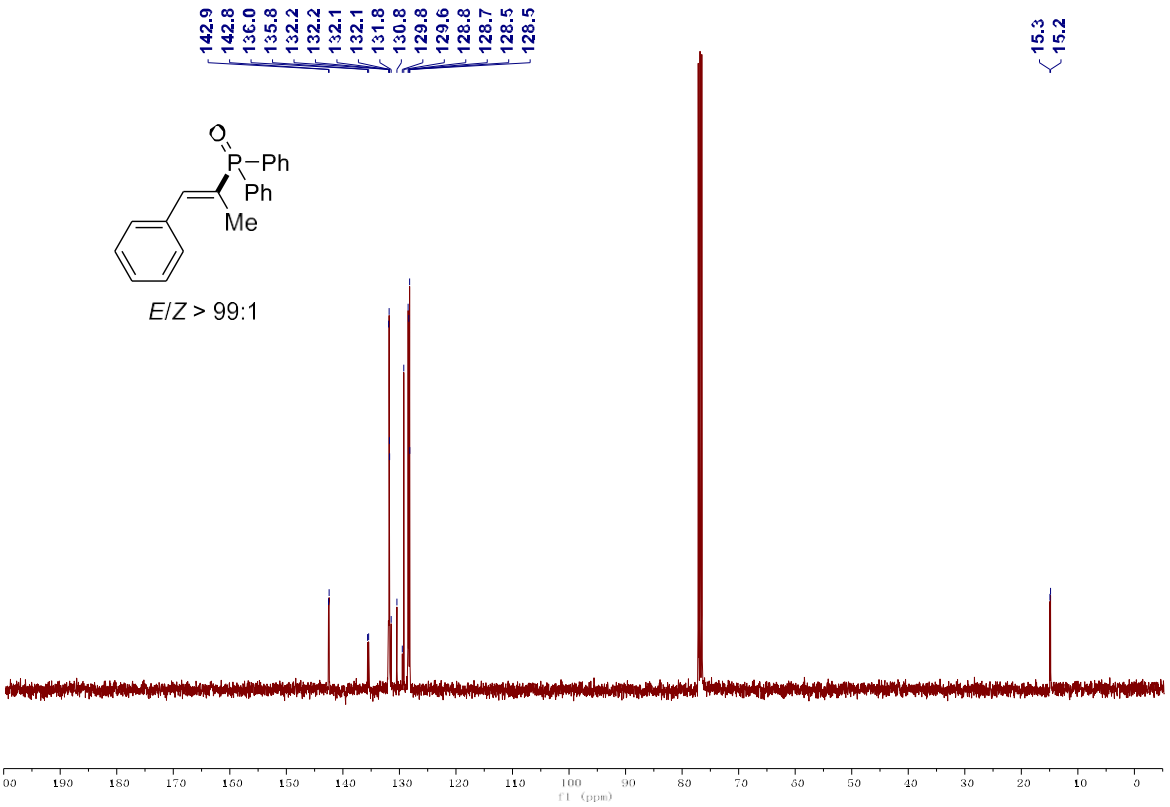
^{13}C NMR spectrum for compound **3e** ($CDCl_3$)



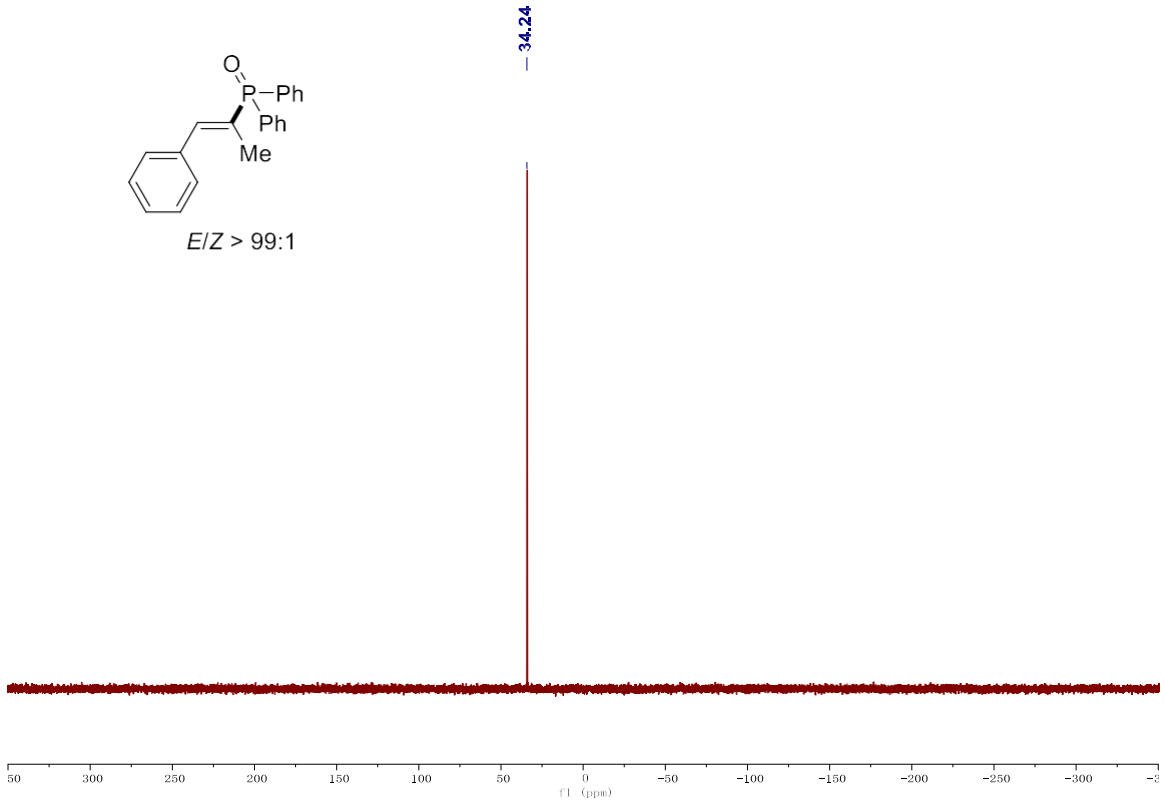
^{31}P NMR spectrum for compound **3e** ($CDCl_3$)



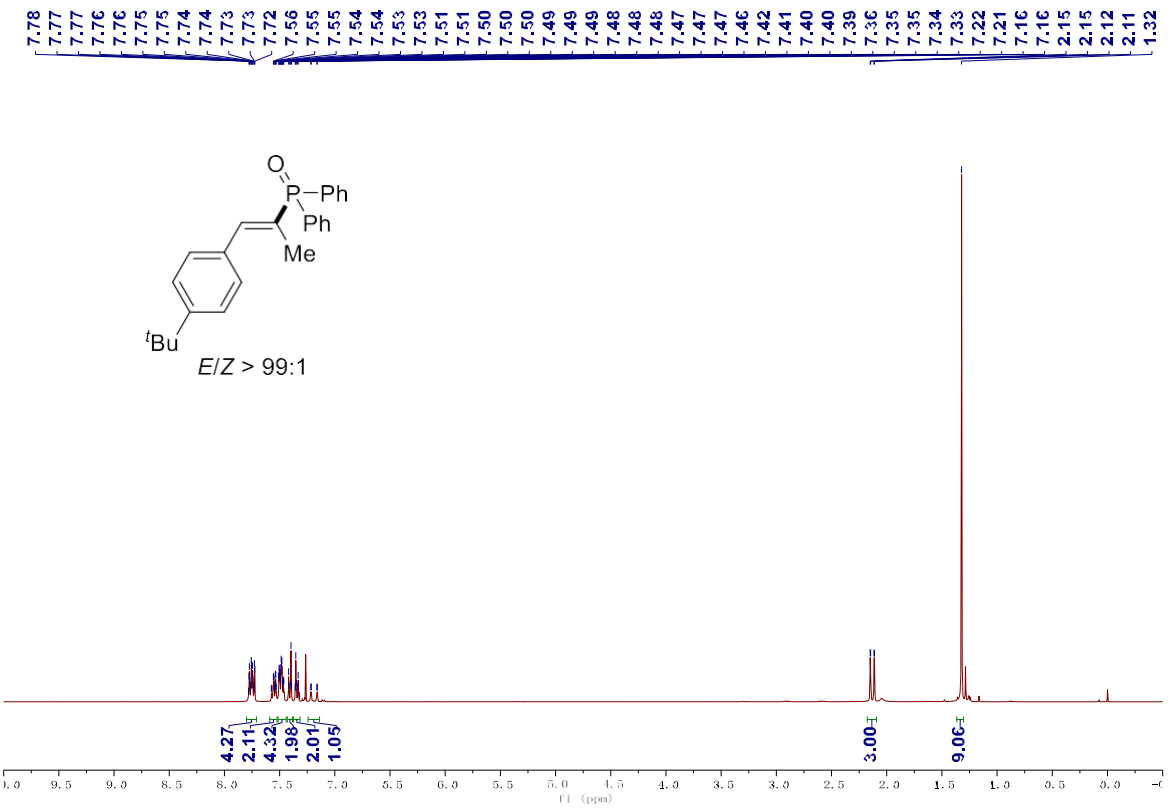
^{1}H NMR spectrum for compound **3f** ($CDCl_3$)



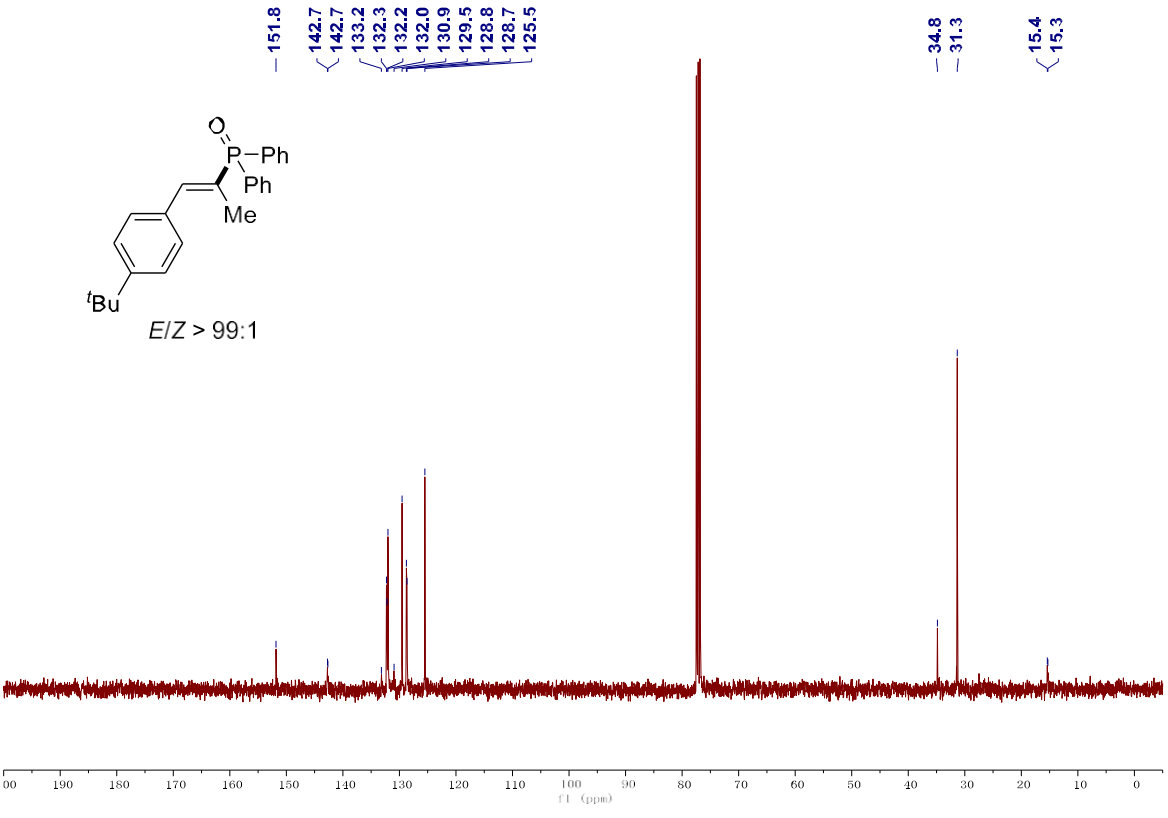
^{13}C NMR spectrum for compound **3f** ($CDCl_3$)



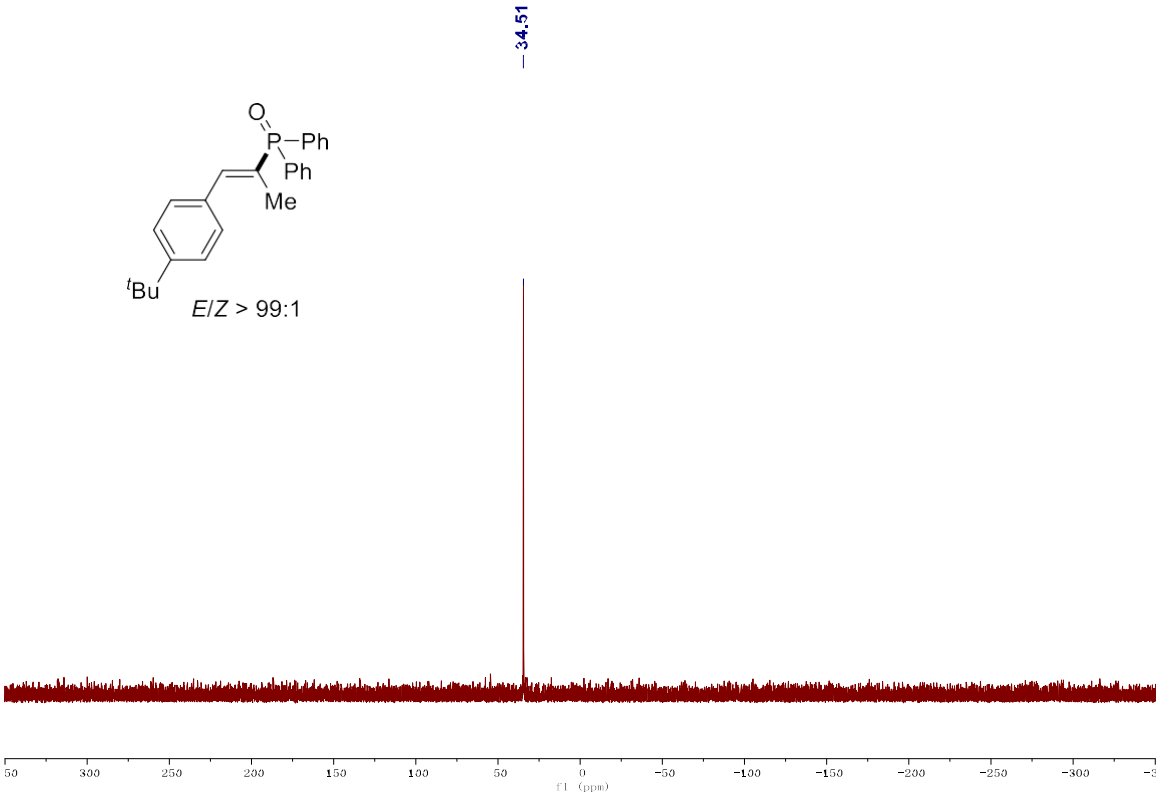
^{31}P NMR spectrum for compound **3f** ($CDCl_3$)



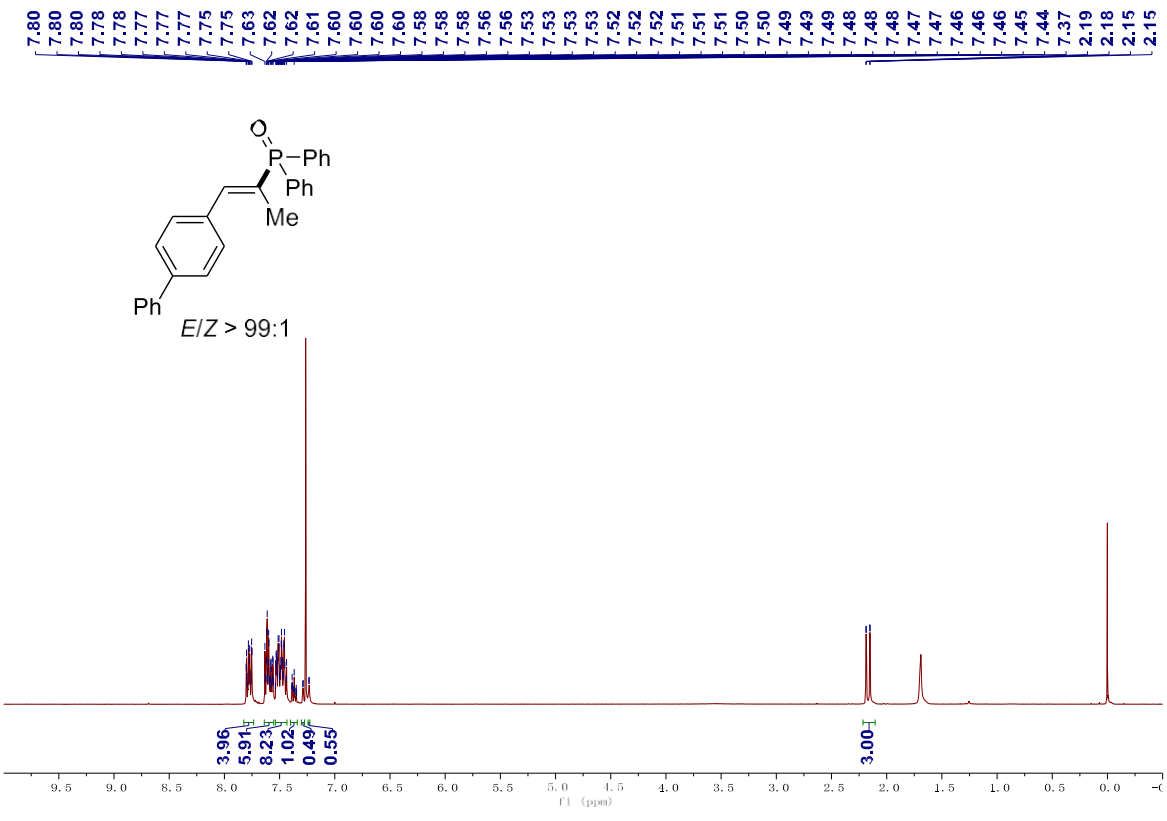
^{1}H NMR spectrum for compound **3g** ($CDCl_3$)



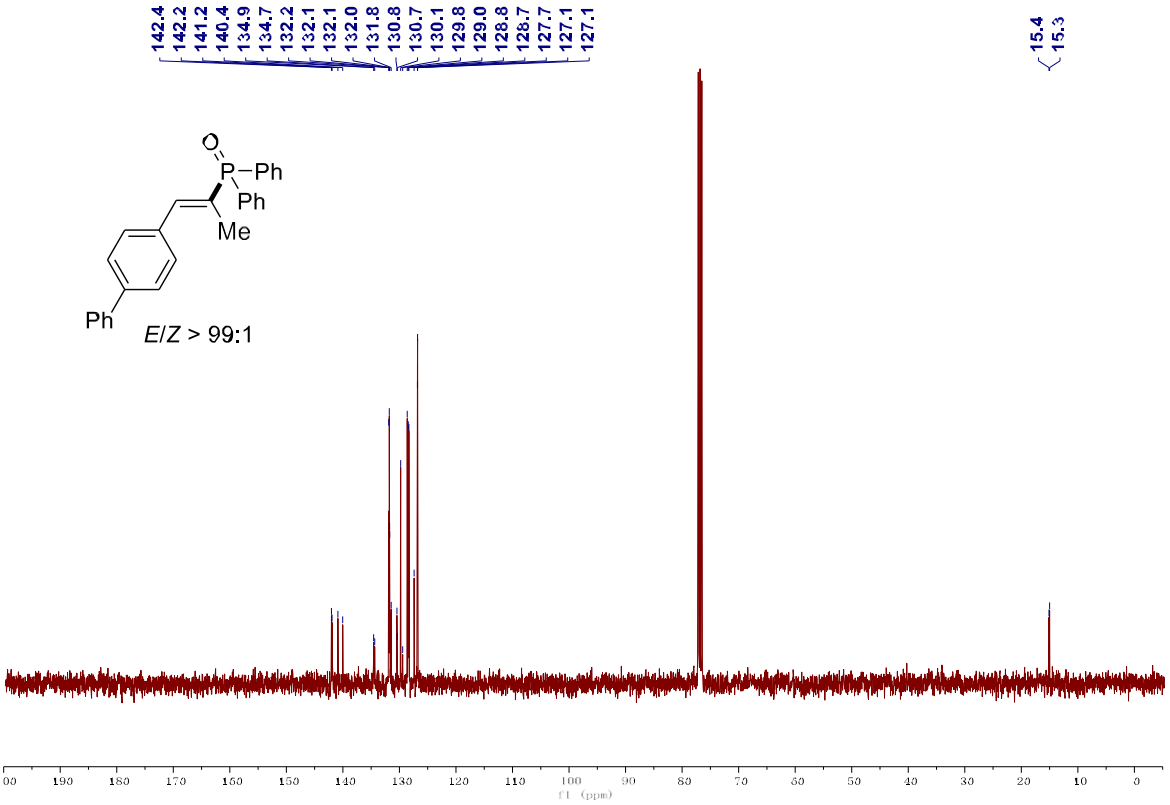
^{13}C NMR spectrum for compound **3g** ($CDCl_3$)



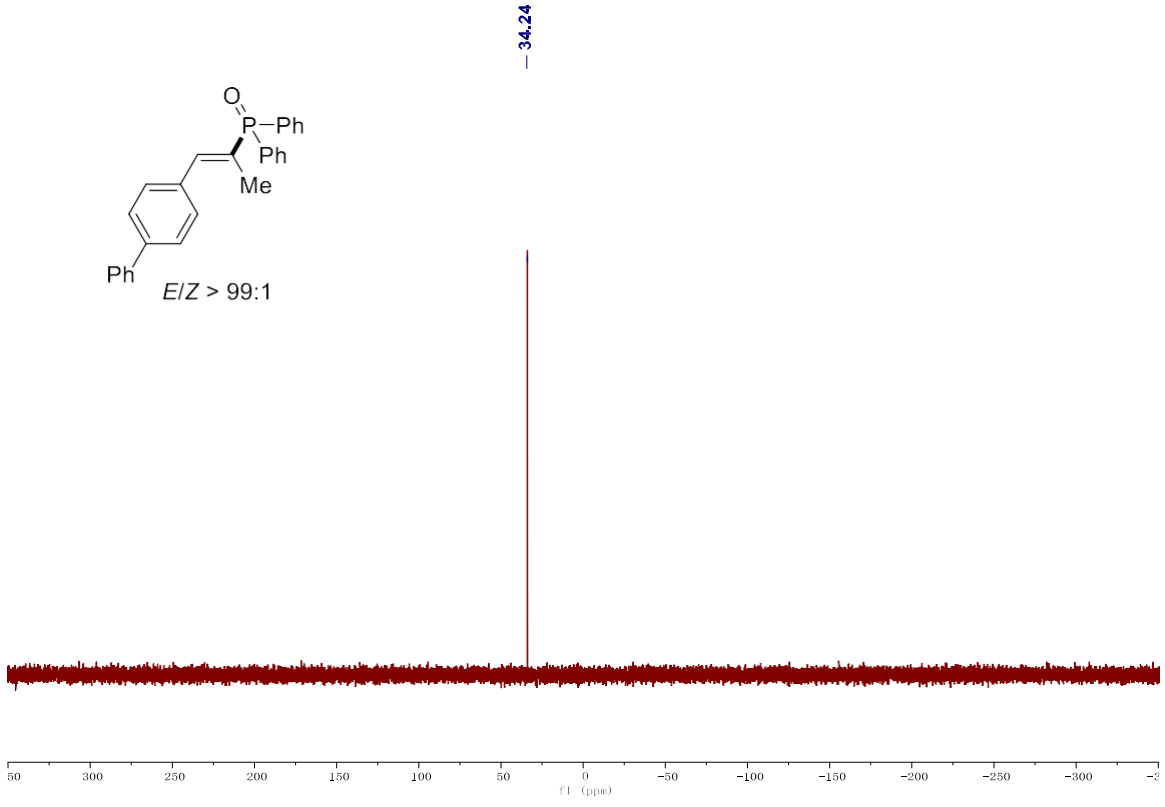
^{31}P NMR spectrum for compound **3g** ($CDCl_3$)



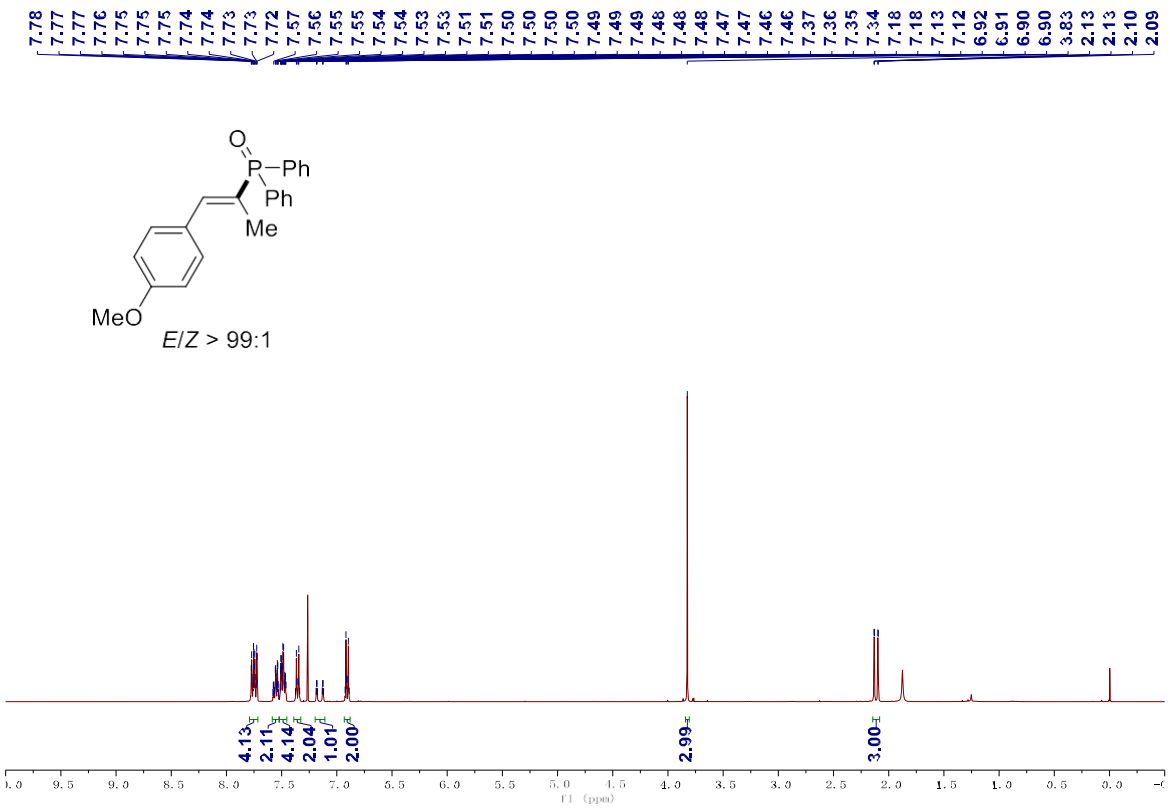
^{1}H NMR spectrum for compound **3h** ($CDCl_3$)



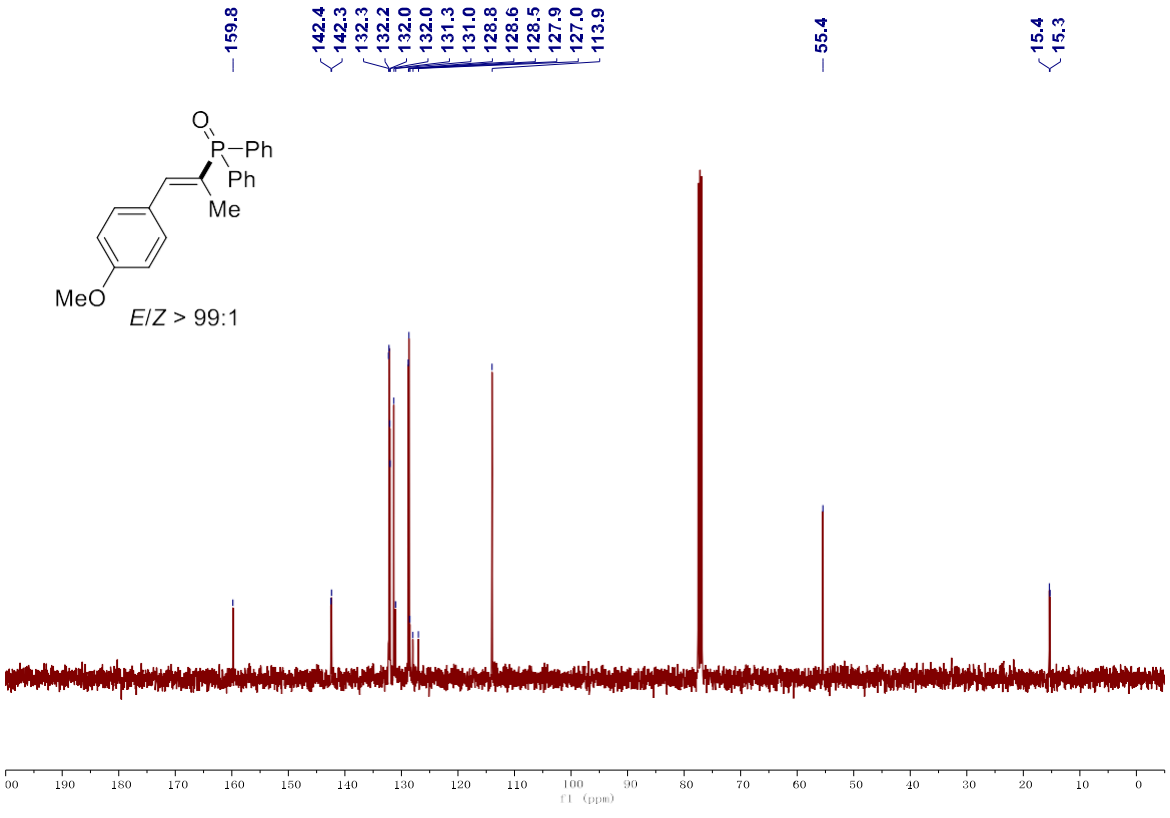
^{13}C NMR spectrum for compound **3h** ($CDCl_3$)



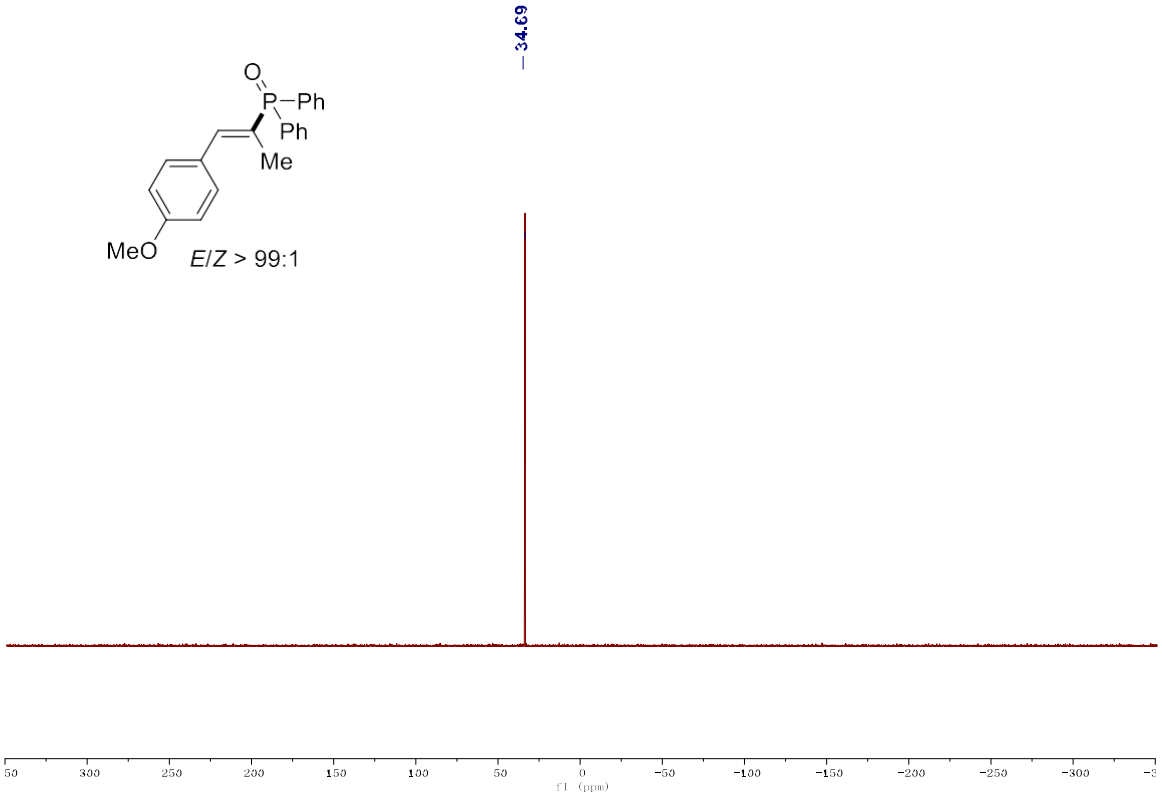
^{31}P NMR spectrum for compound **3h** ($CDCl_3$)



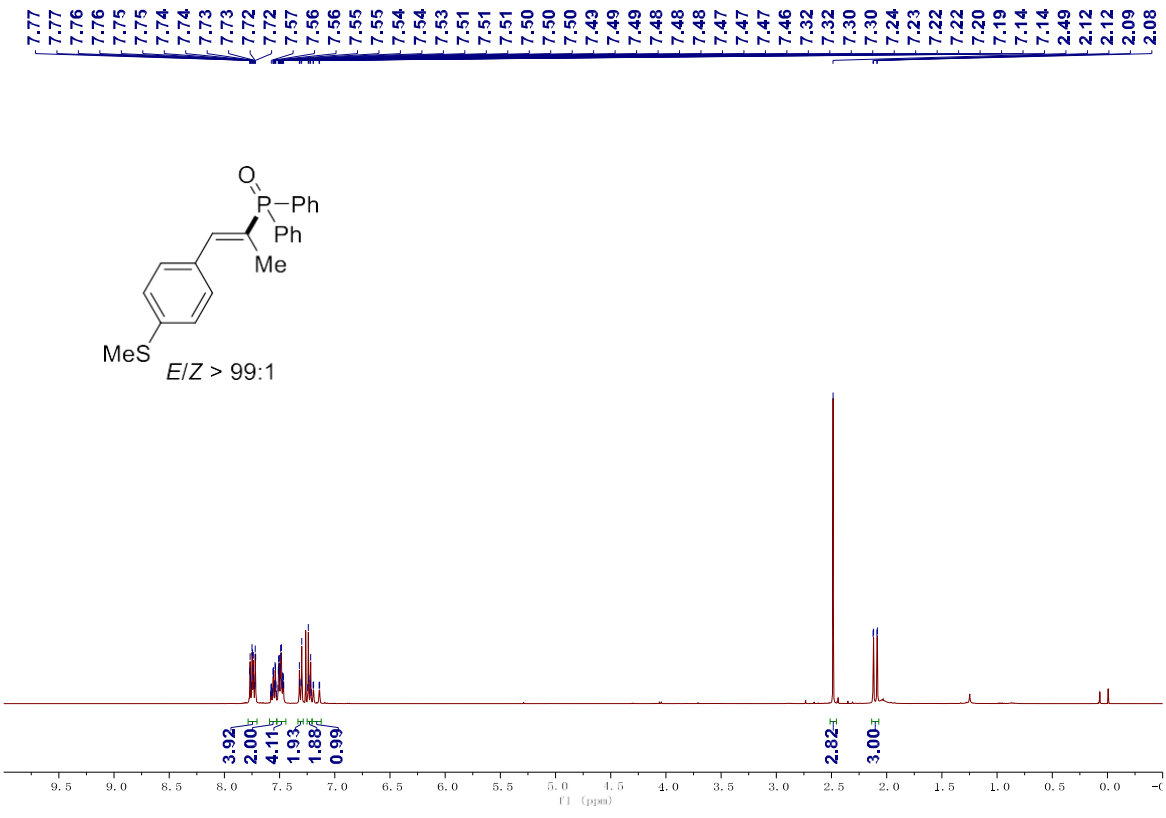
^{1}H NMR spectrum for compound **3i** ($CDCl_3$)



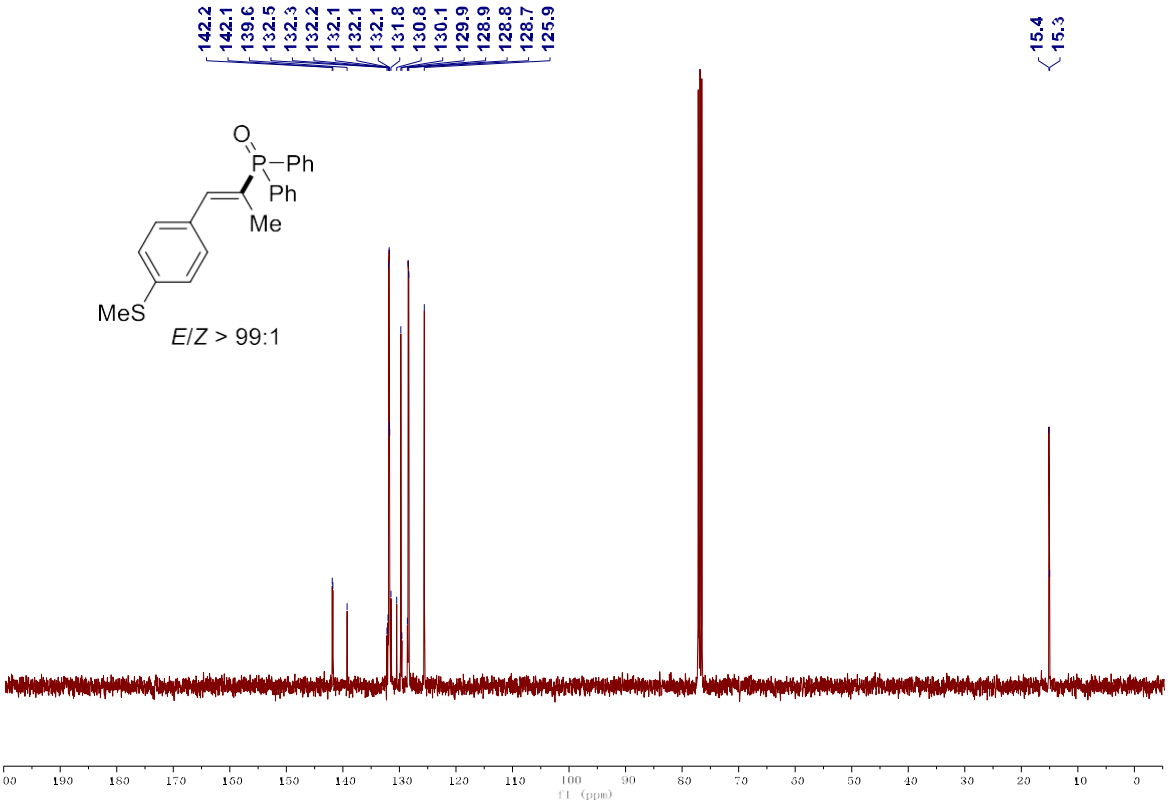
^{13}C NMR spectrum for compound **3i** ($CDCl_3$)



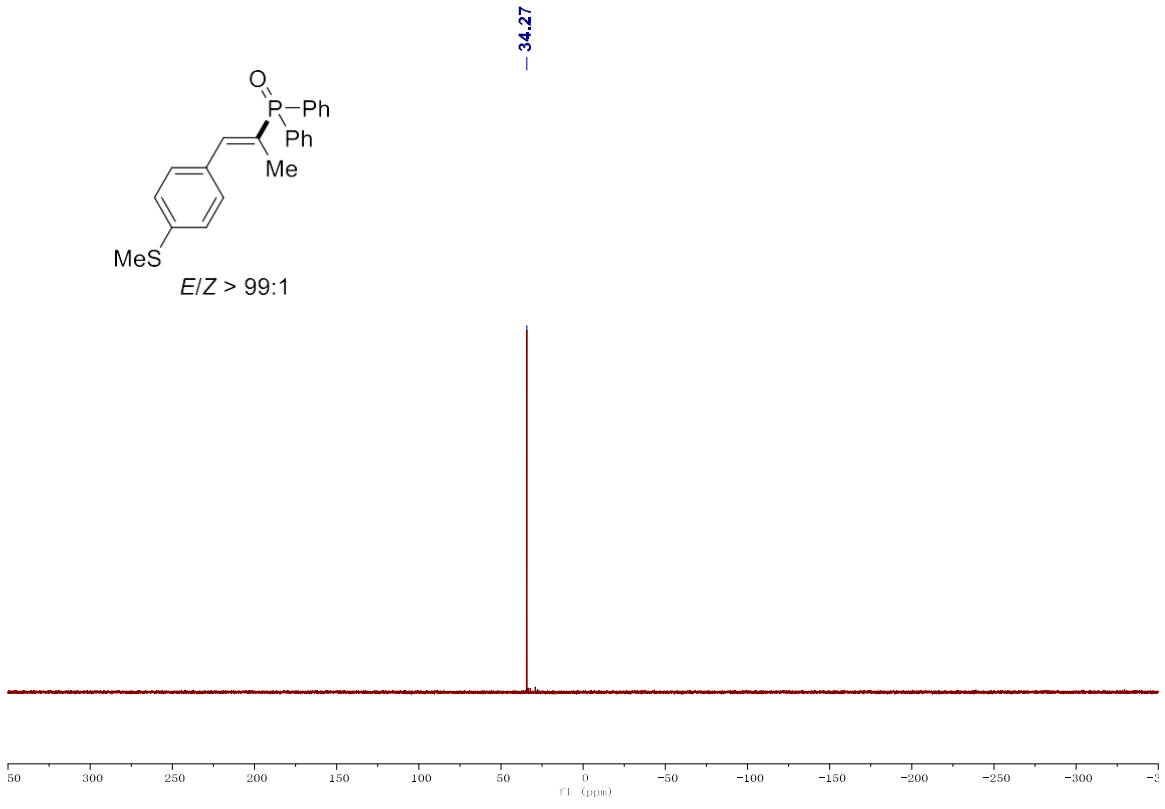
^{31}P NMR spectrum for compound **3i** ($CDCl_3$)



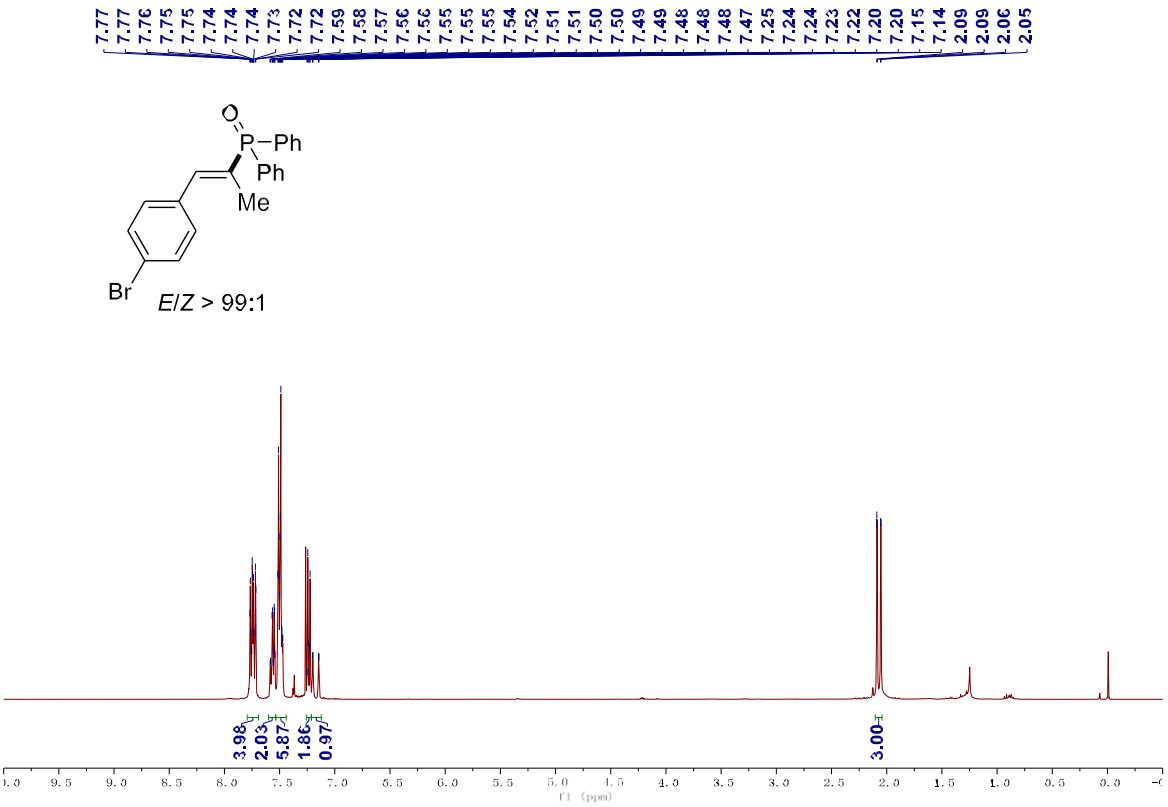
^{1}H NMR spectrum for compound **3j** ($CDCl_3$)



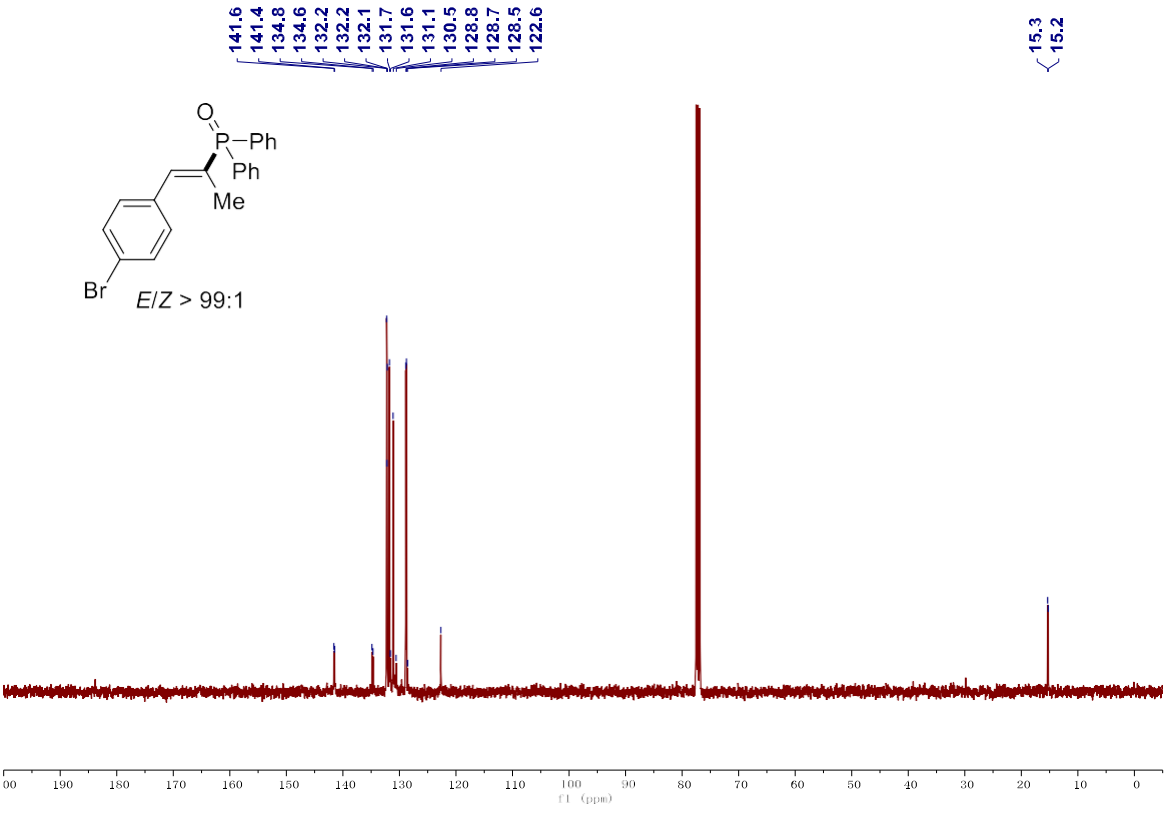
^{13}C NMR spectrum for compound **3j** ($CDCl_3$)



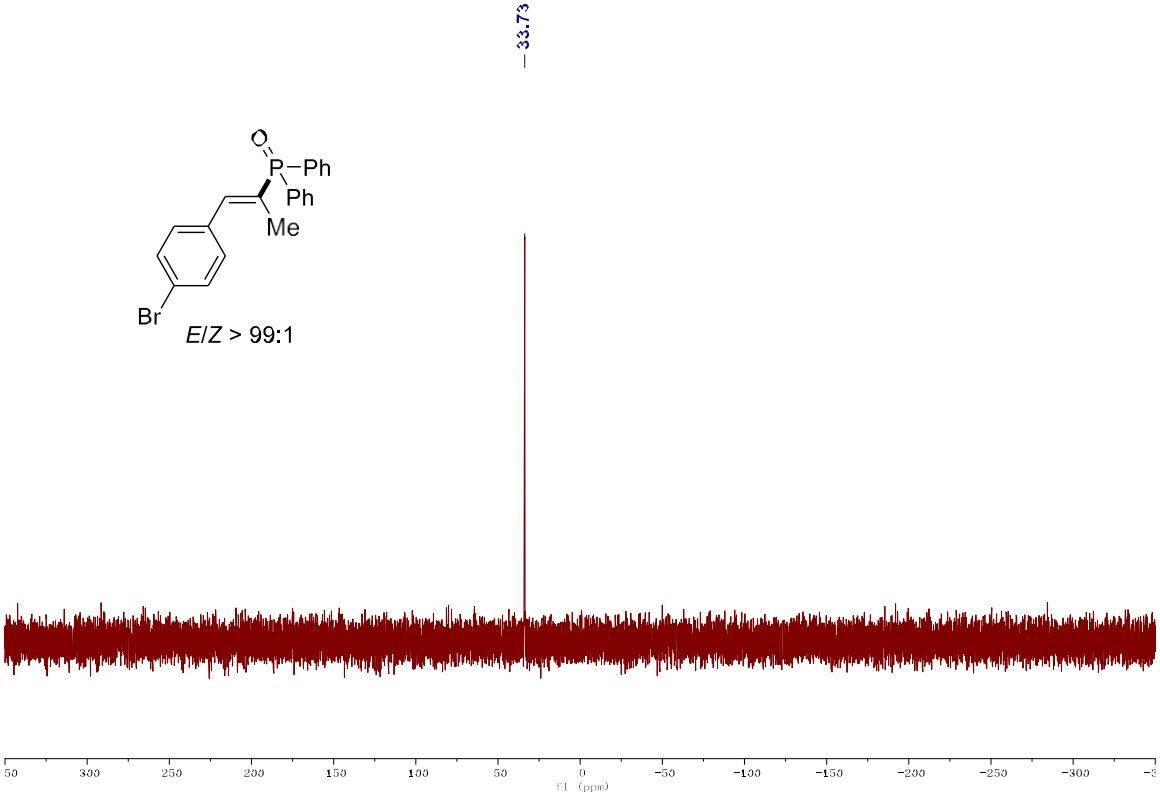
^{31}P NMR spectrum for compound **3j** ($CDCl_3$)



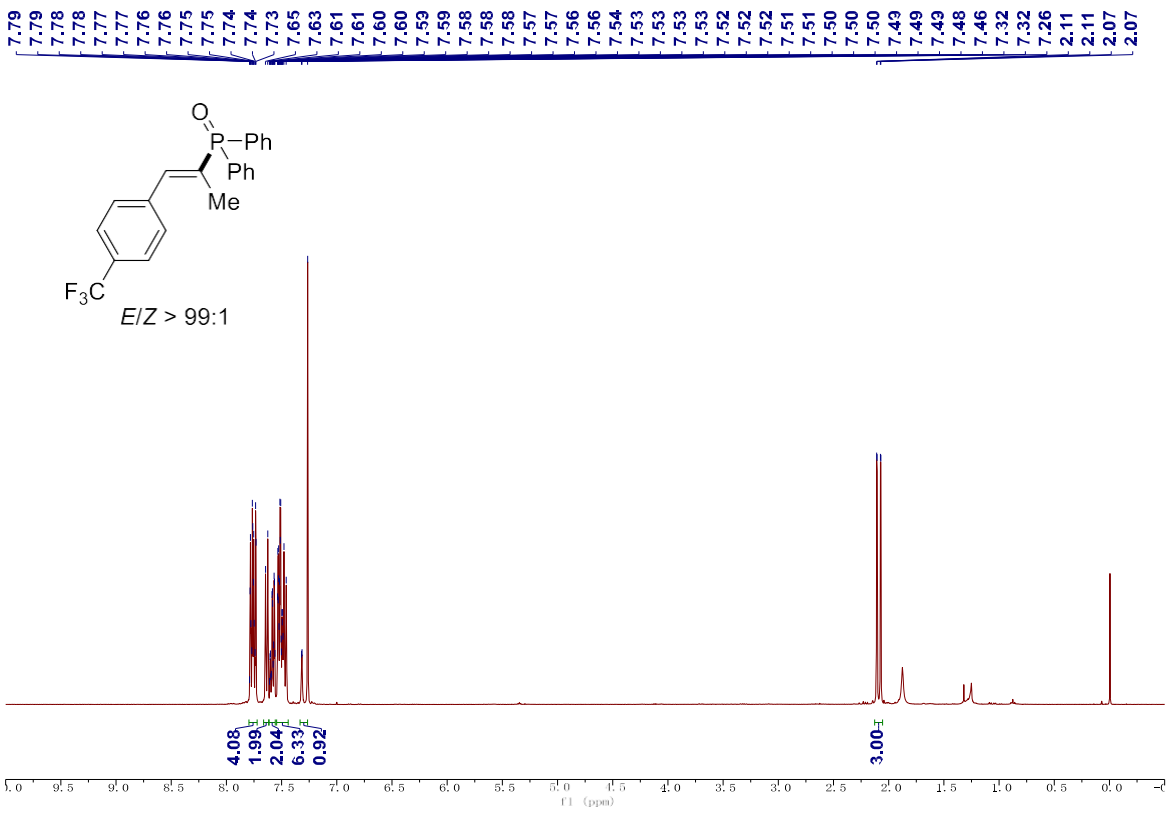
^{1}H NMR spectrum for compound **3k** ($CDCl_3$)



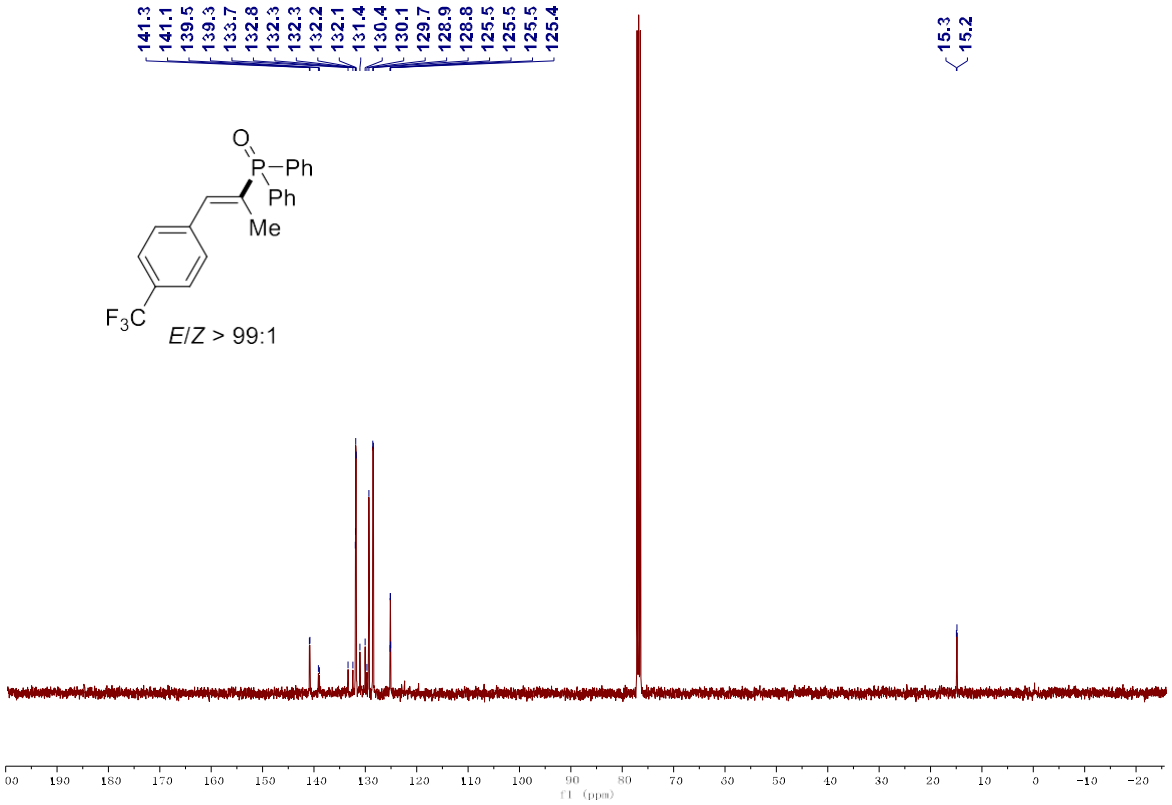
^{13}C NMR spectrum for compound **3k** ($CDCl_3$)



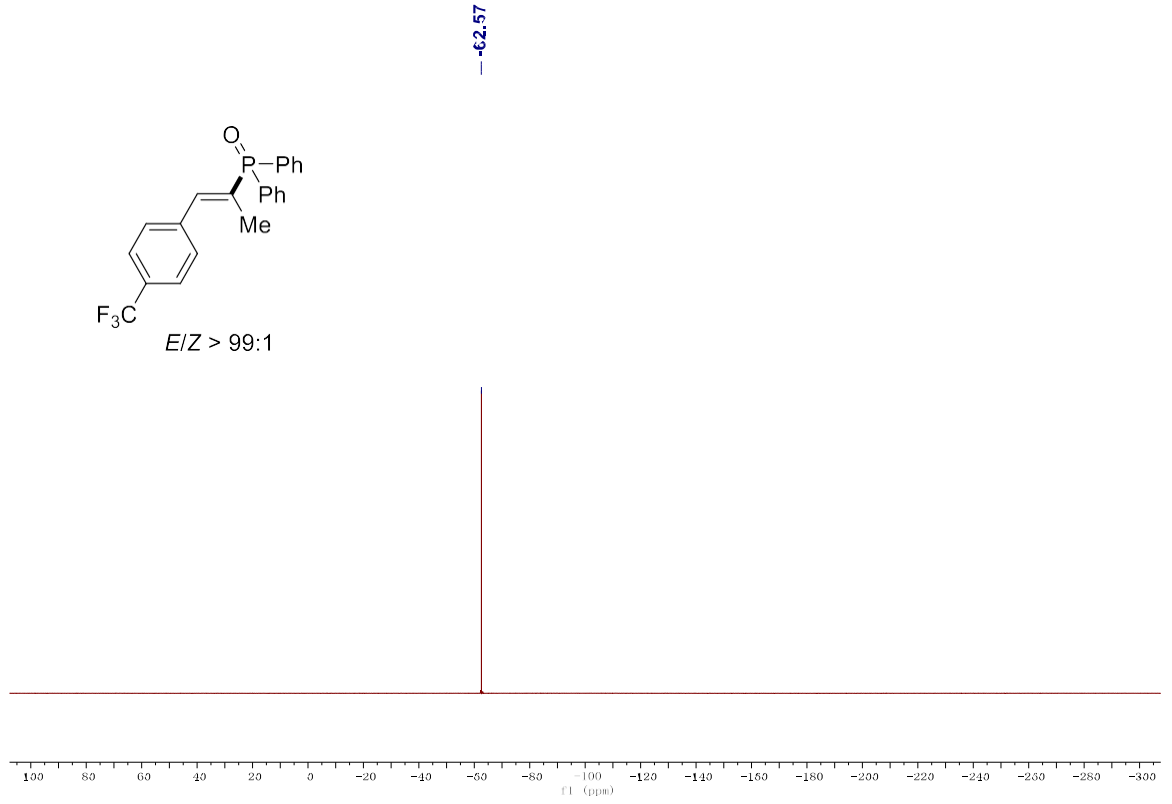
^{31}P NMR spectrum for compound **3k** ($CDCl_3$)



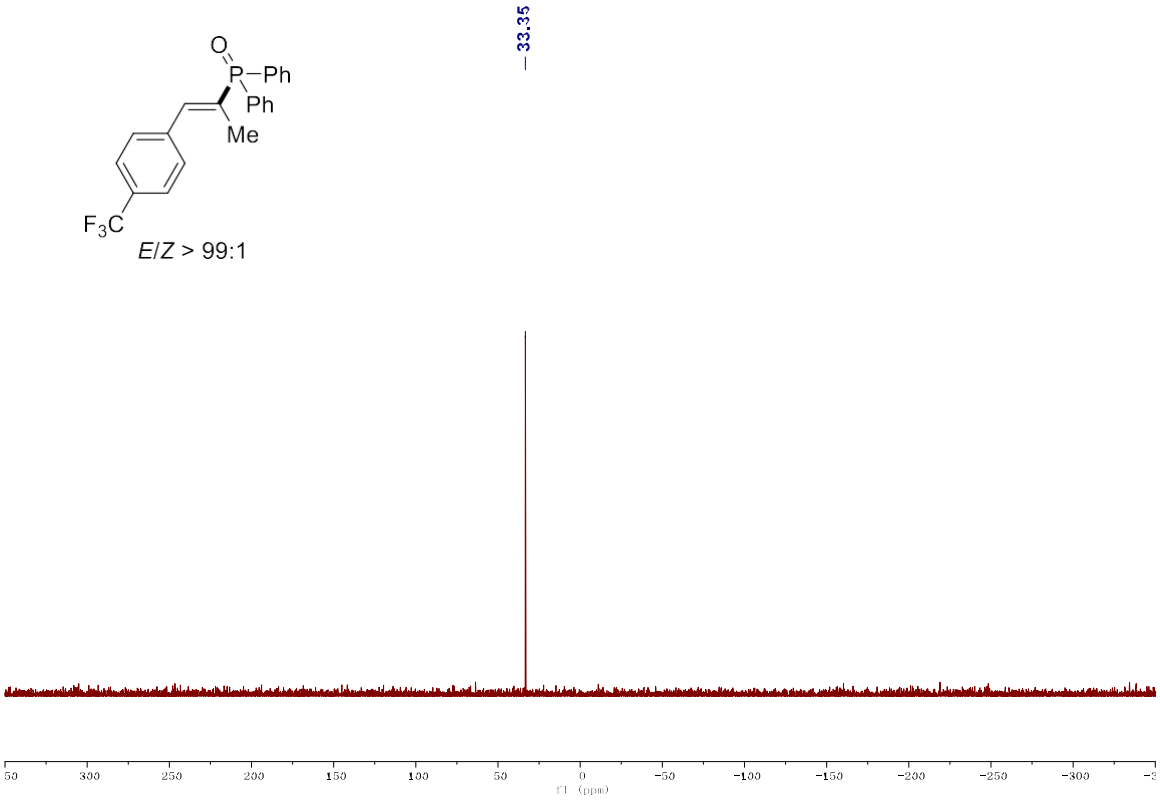
^{1}H NMR spectrum for compound **3l** ($CDCl_3$)



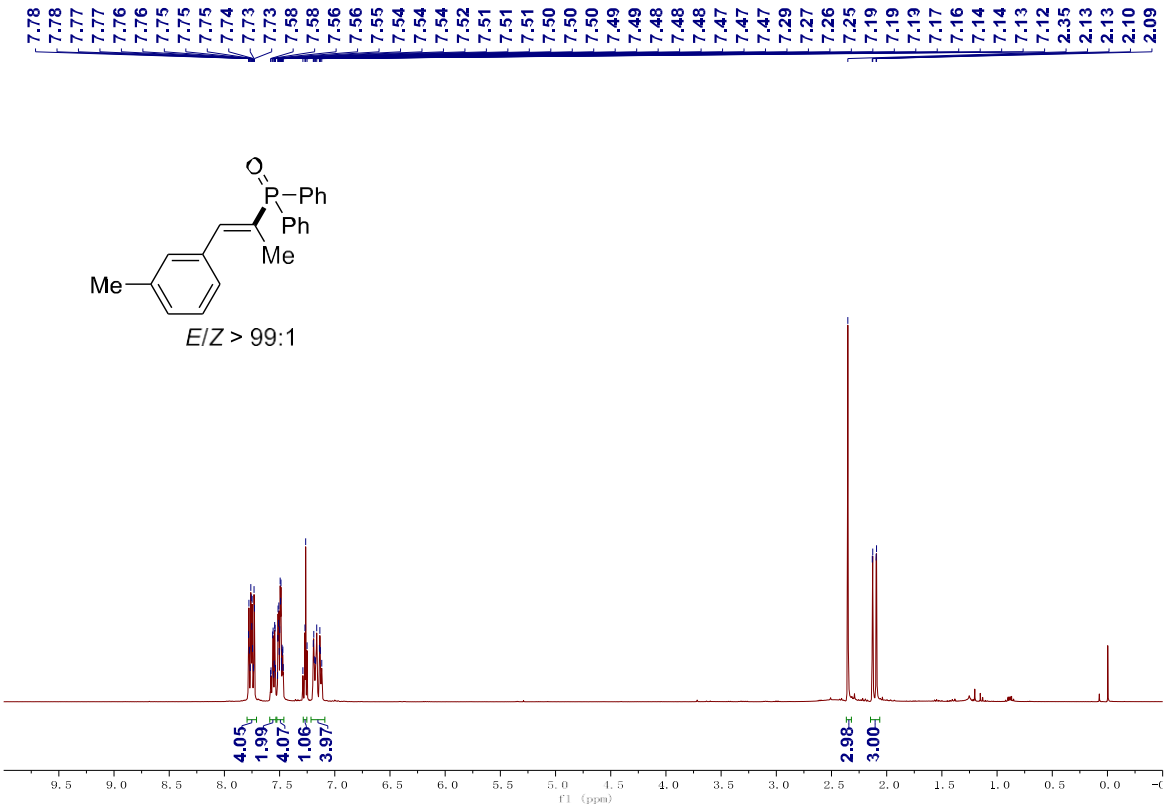
^{13}C NMR spectrum for compound **3l** ($CDCl_3$)



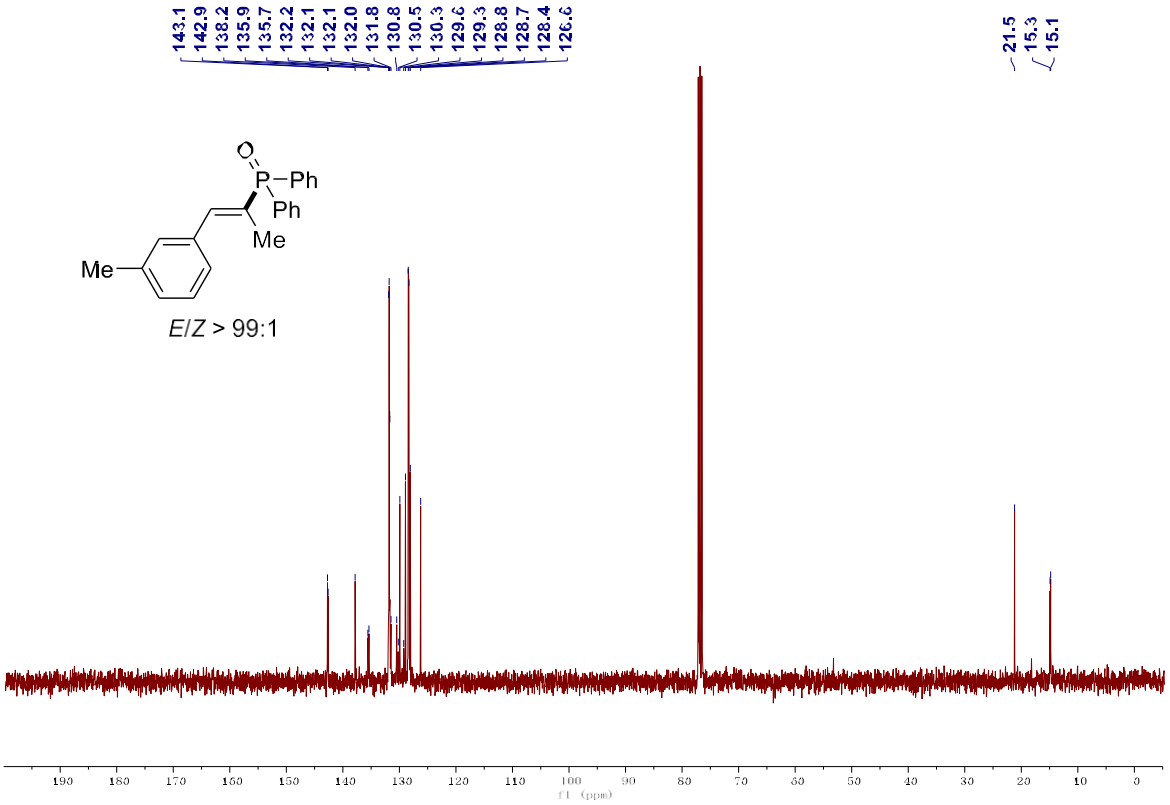
^{19}F NMR spectrum for compound **3l** ($CDCl_3$)



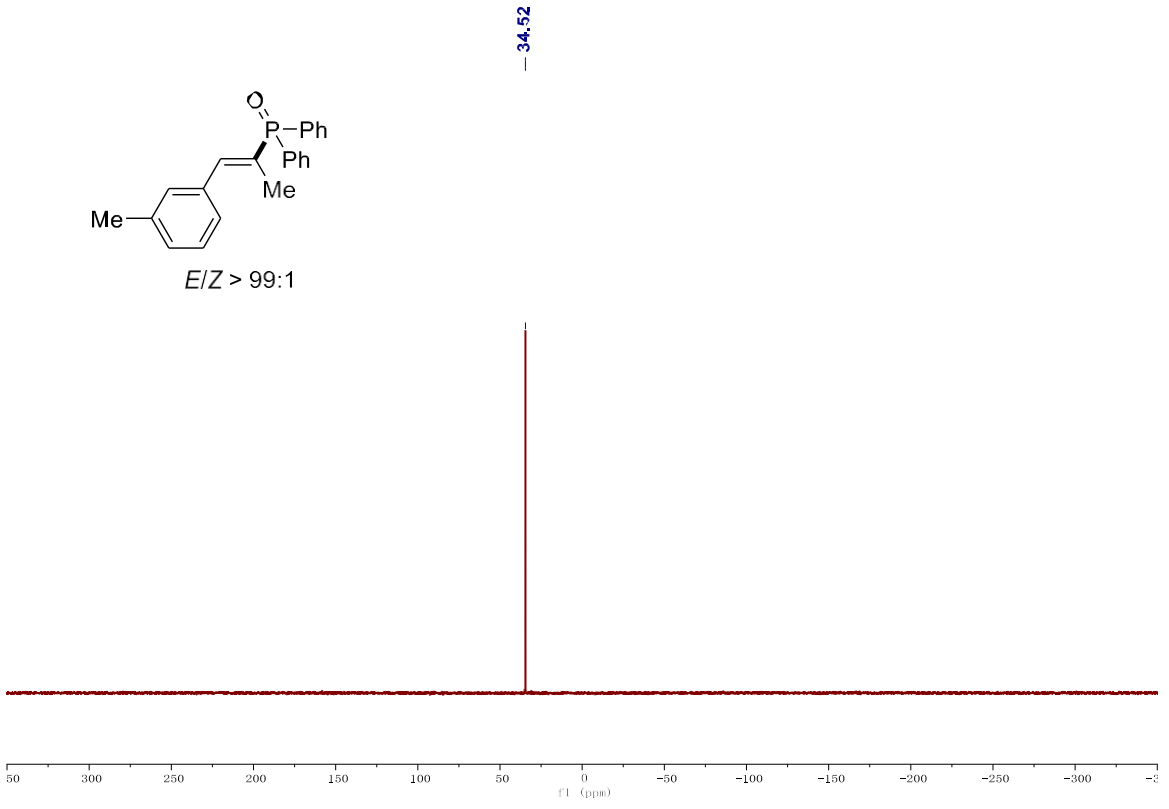
^{31}P NMR spectrum for compound **3l** ($CDCl_3$)



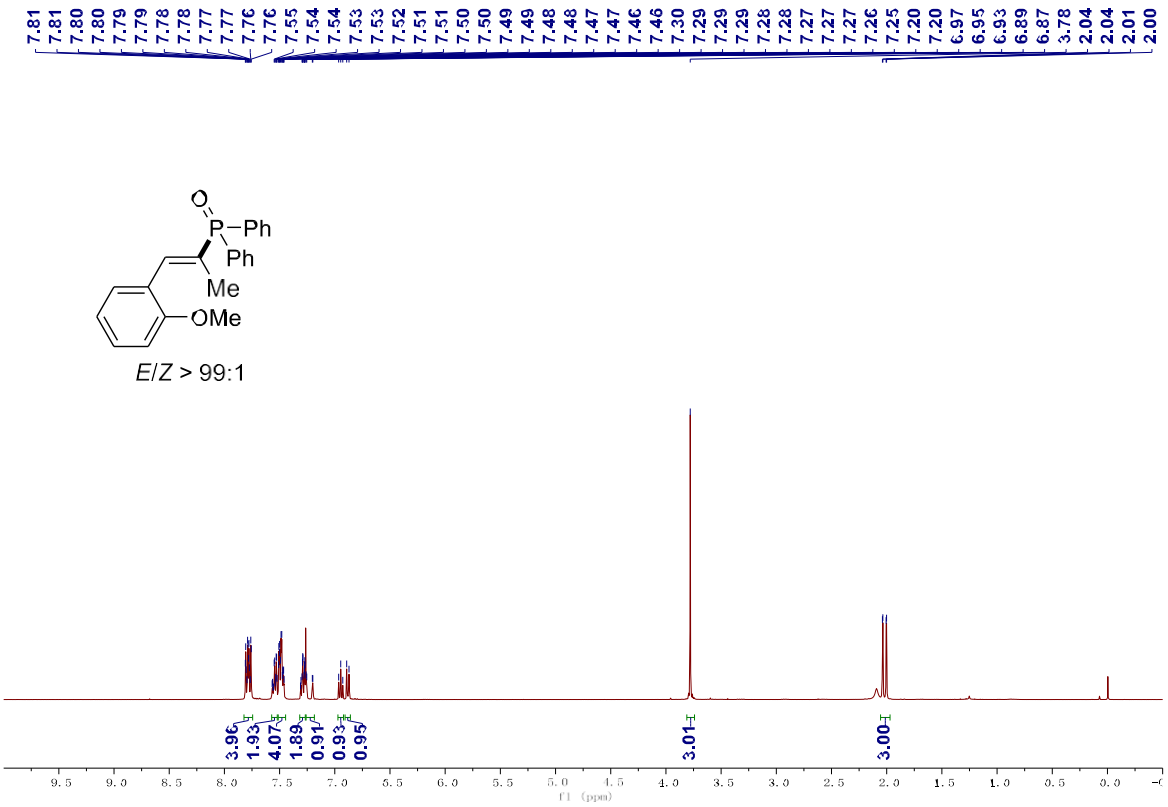
^{1}H NMR spectrum for compound **3m** ($CDCl_3$)



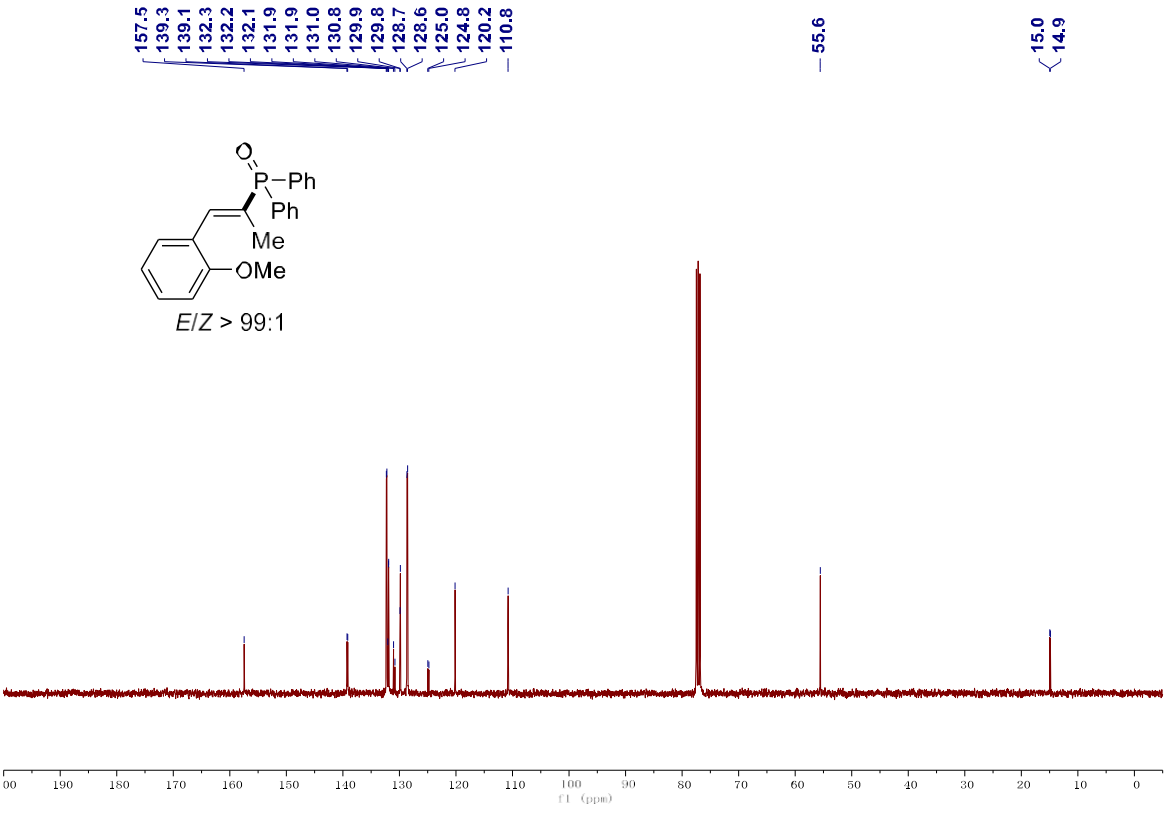
^{13}C NMR spectrum for compound **3m** ($CDCl_3$)



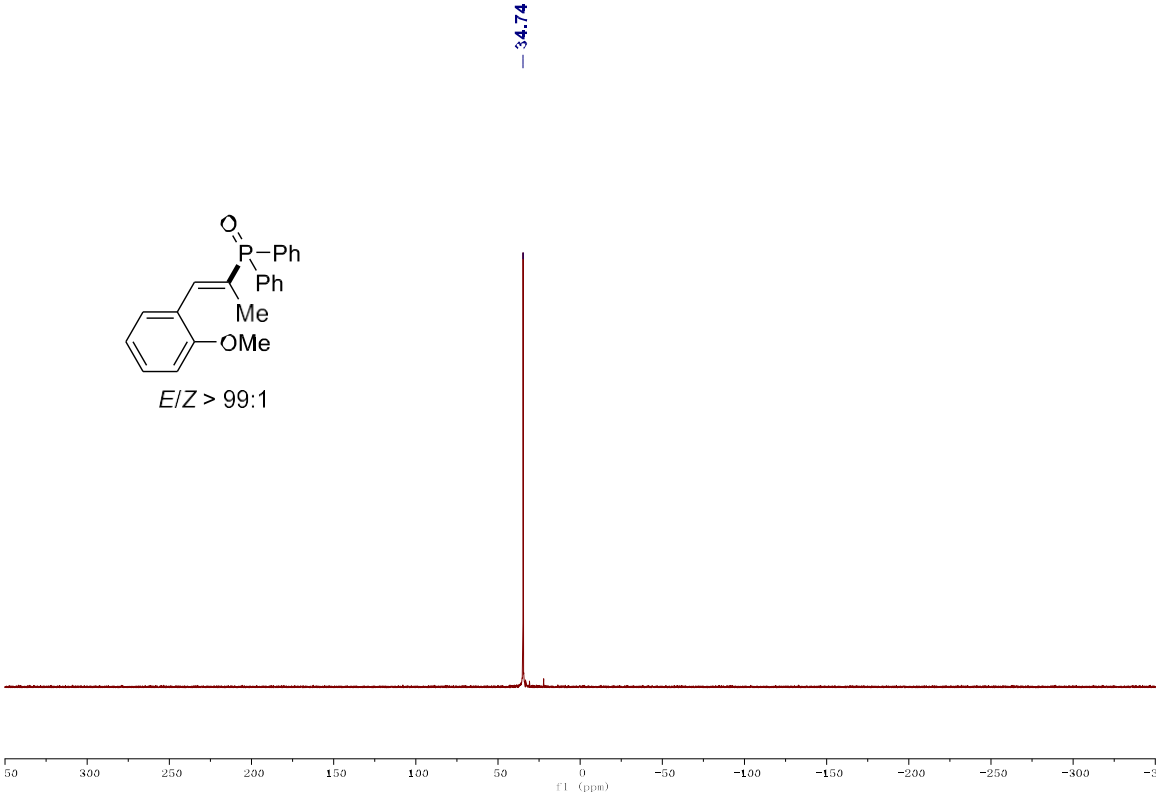
^{31}P NMR spectrum for compound **3m** ($CDCl_3$)



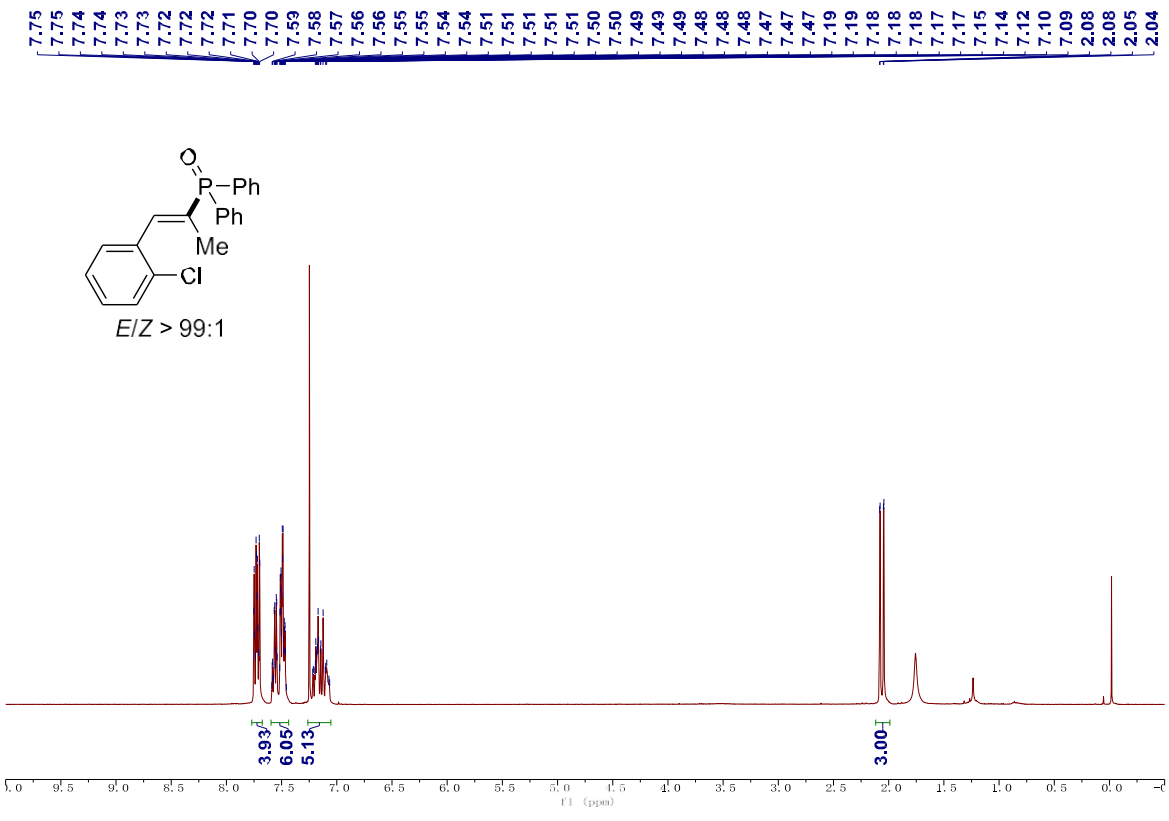
^{1}H NMR spectrum for compound **3n** ($CDCl_3$)



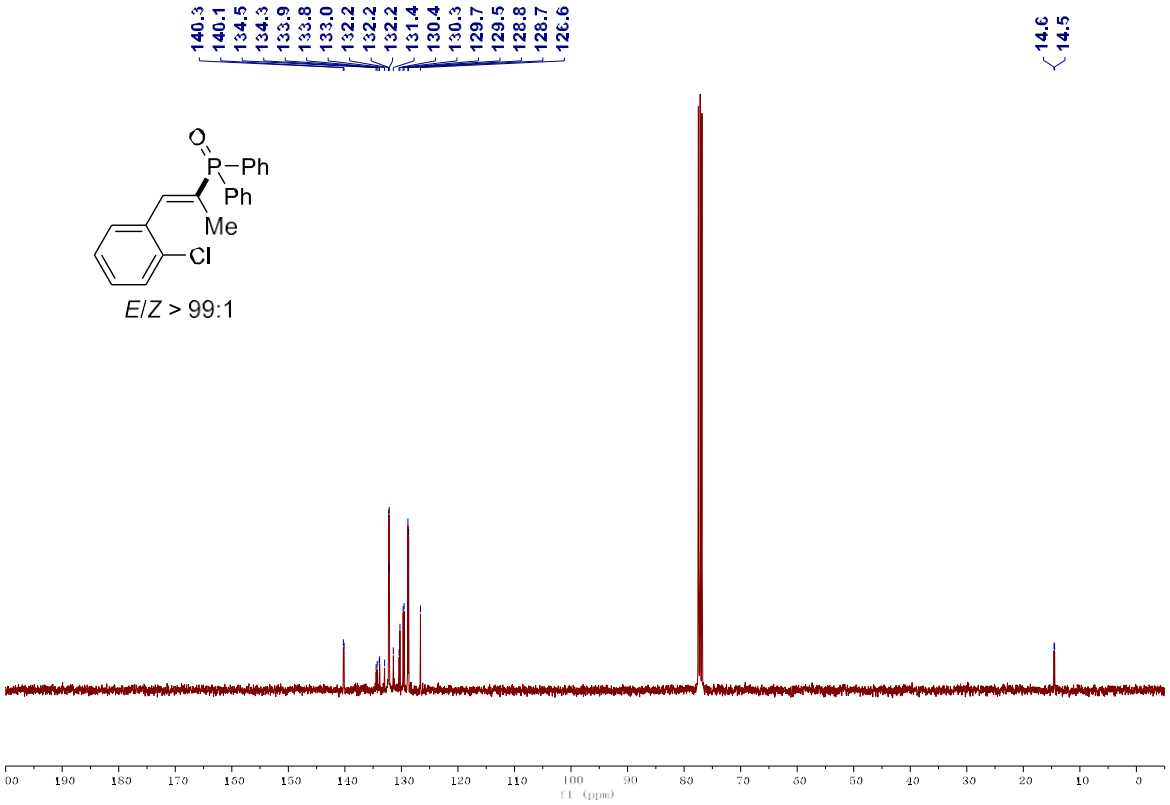
^{13}C NMR spectrum for compound **3n** ($CDCl_3$)



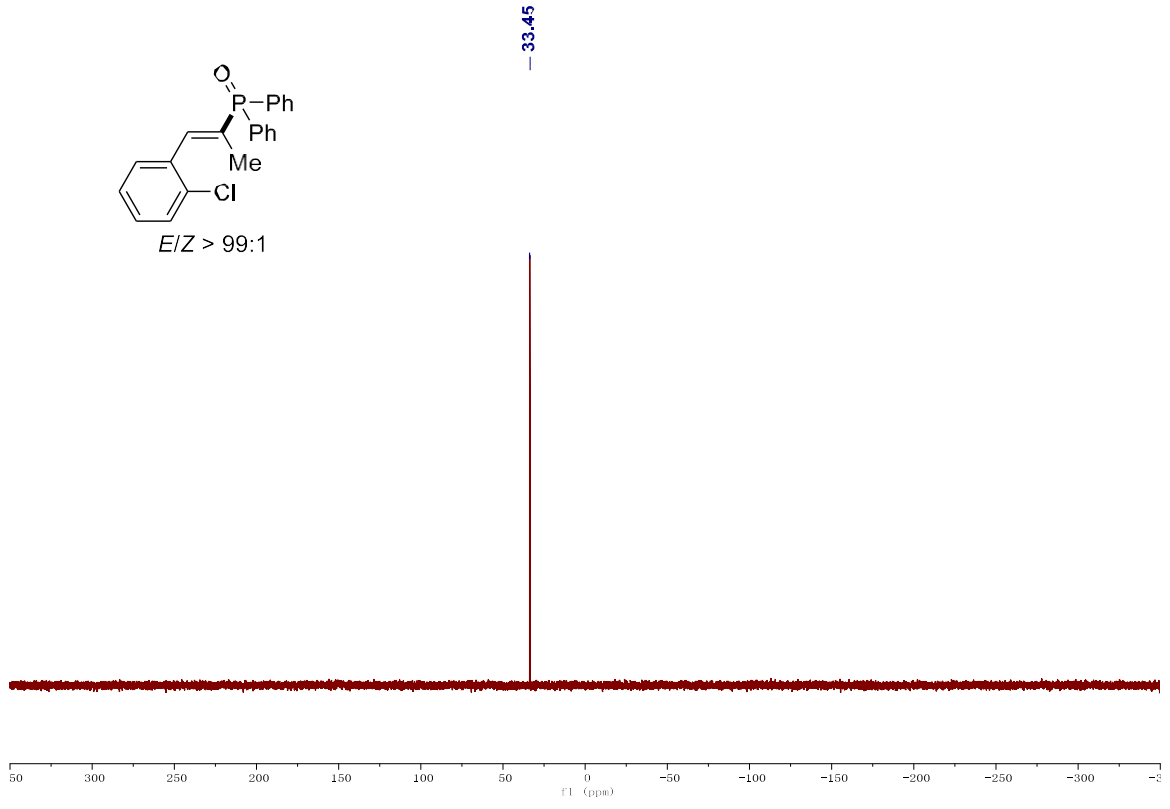
^{31}P NMR spectrum for compound **3n** ($CDCl_3$)



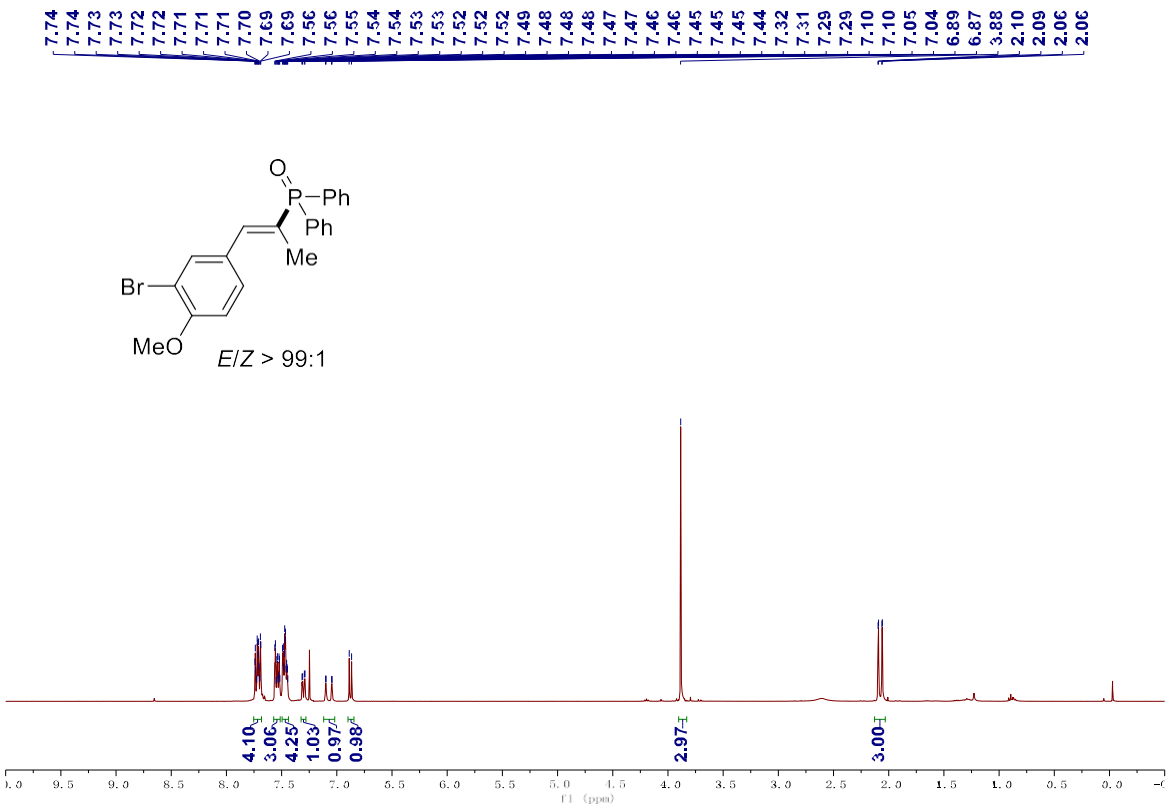
^{1}H NMR spectrum for compound **3o** ($CDCl_3$)



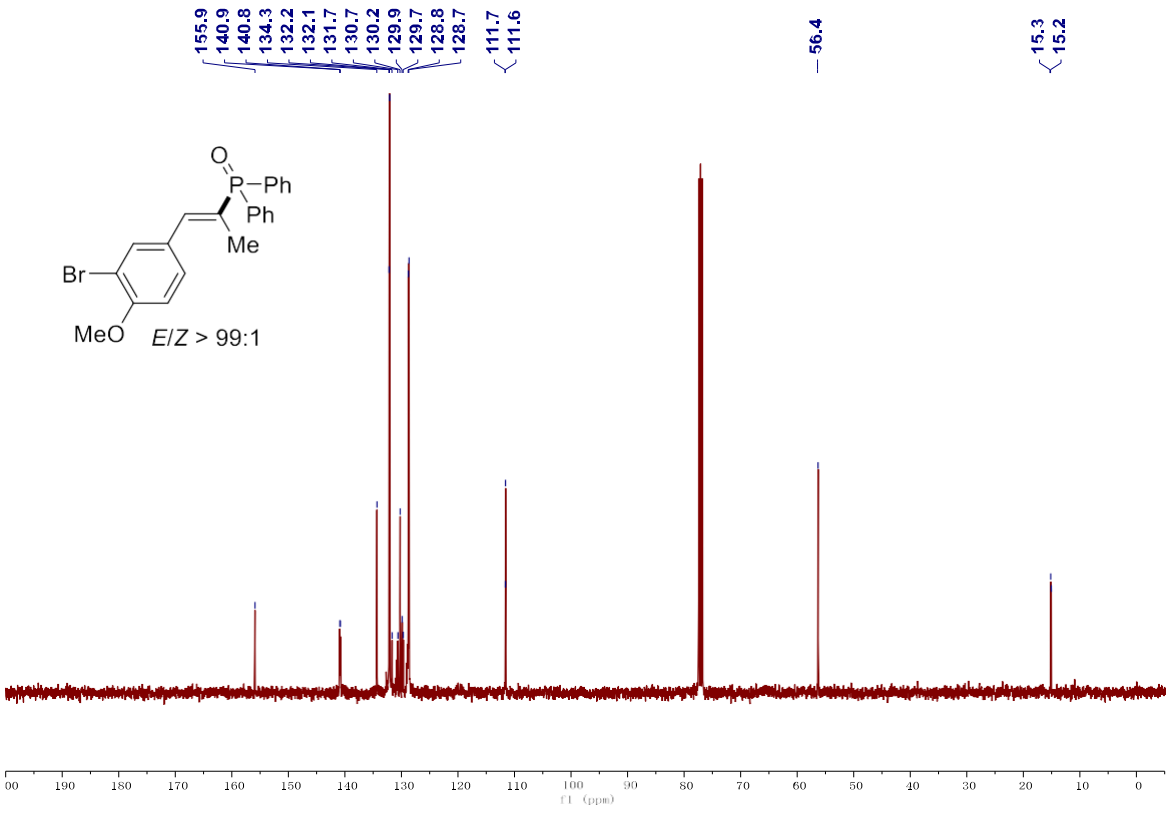
^{13}C NMR spectrum for compound **3o** ($CDCl_3$)



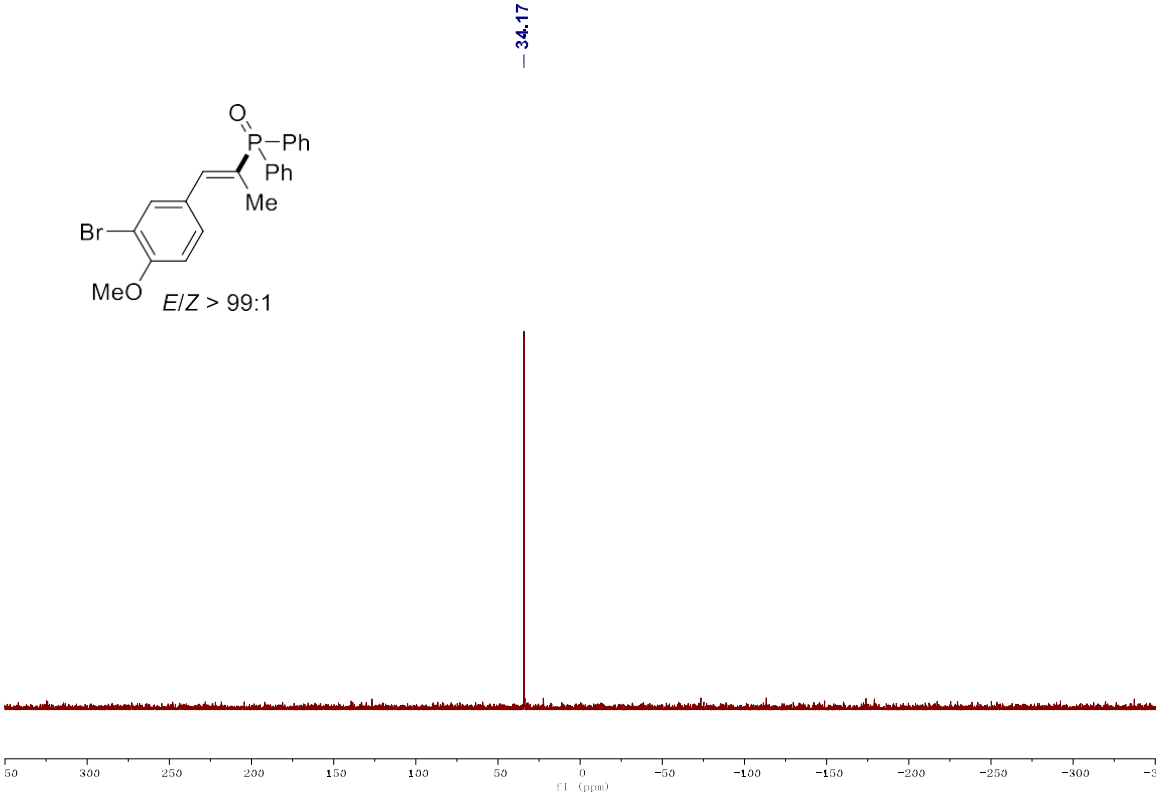
^{31}P NMR spectrum for compound **3o** ($CDCl_3$)



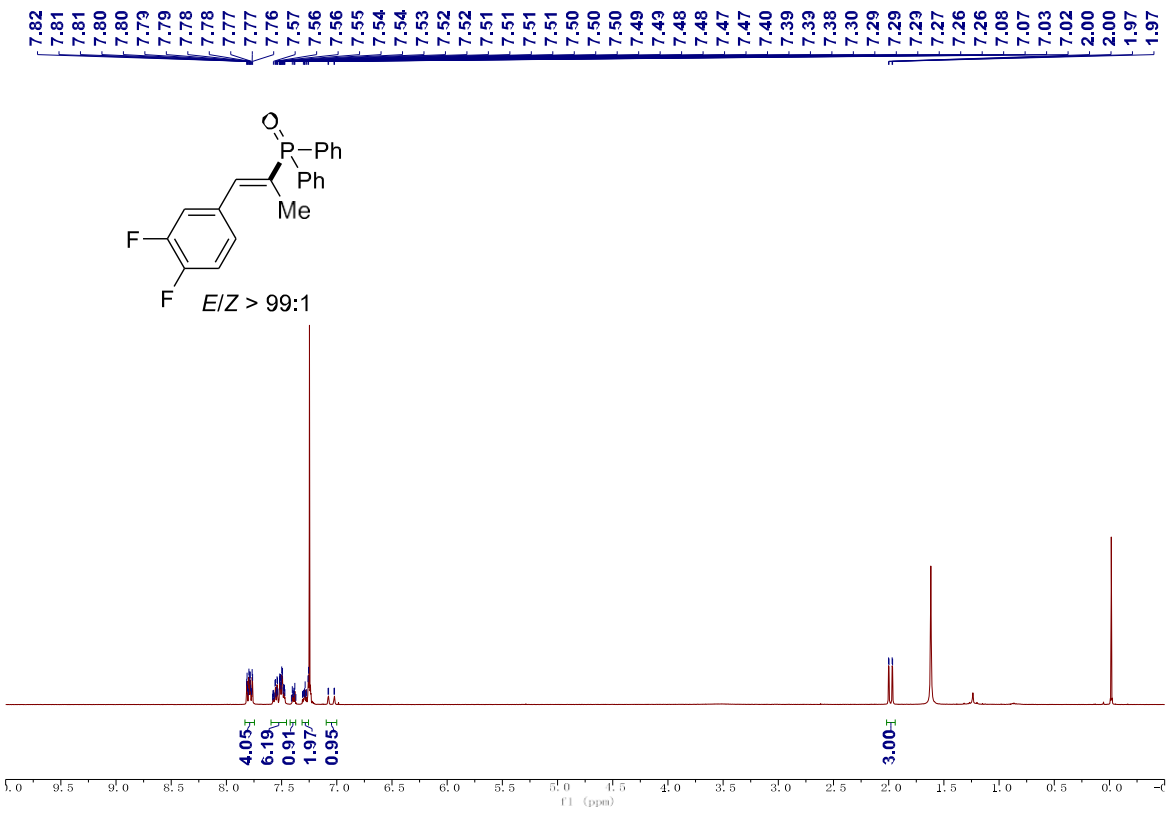
52. ^{1}H NMR spectrum for compound **3p** ($CDCl_3$)



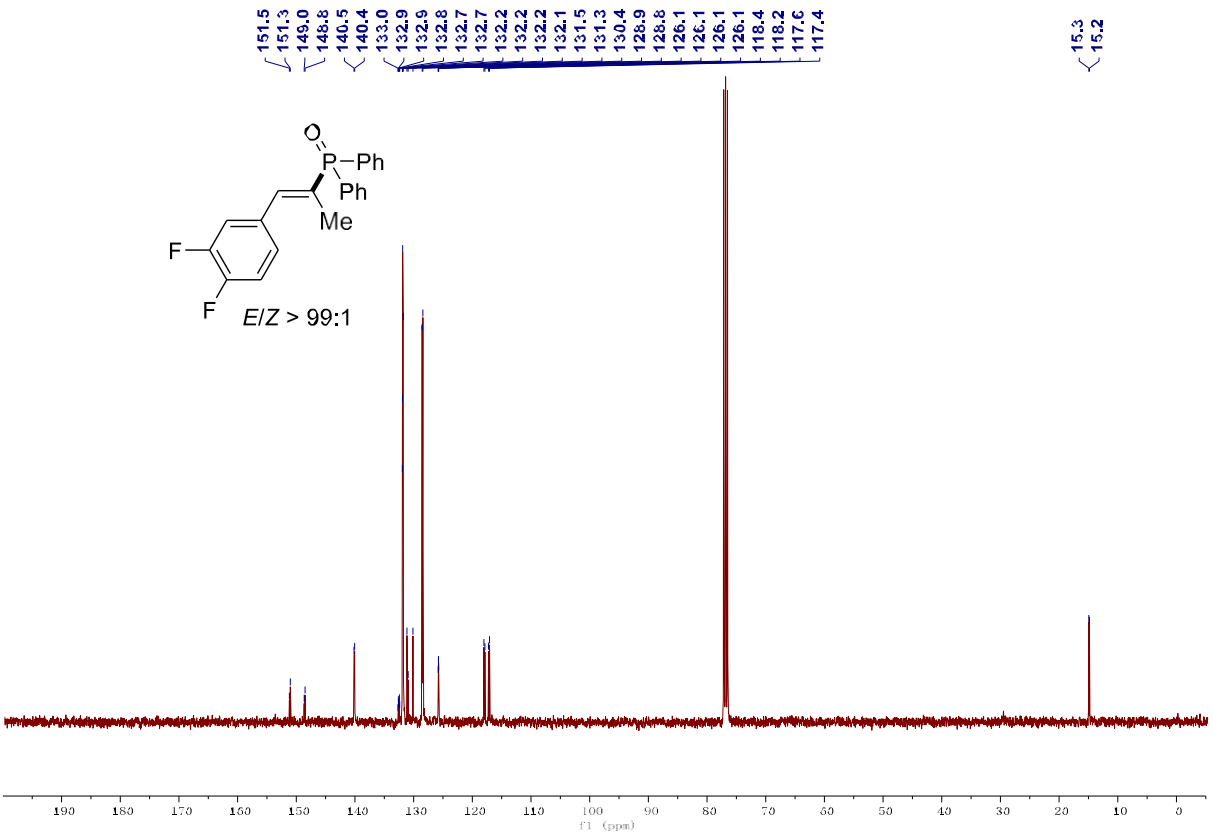
^{13}C NMR spectrum for compound **3p** ($CDCl_3$)



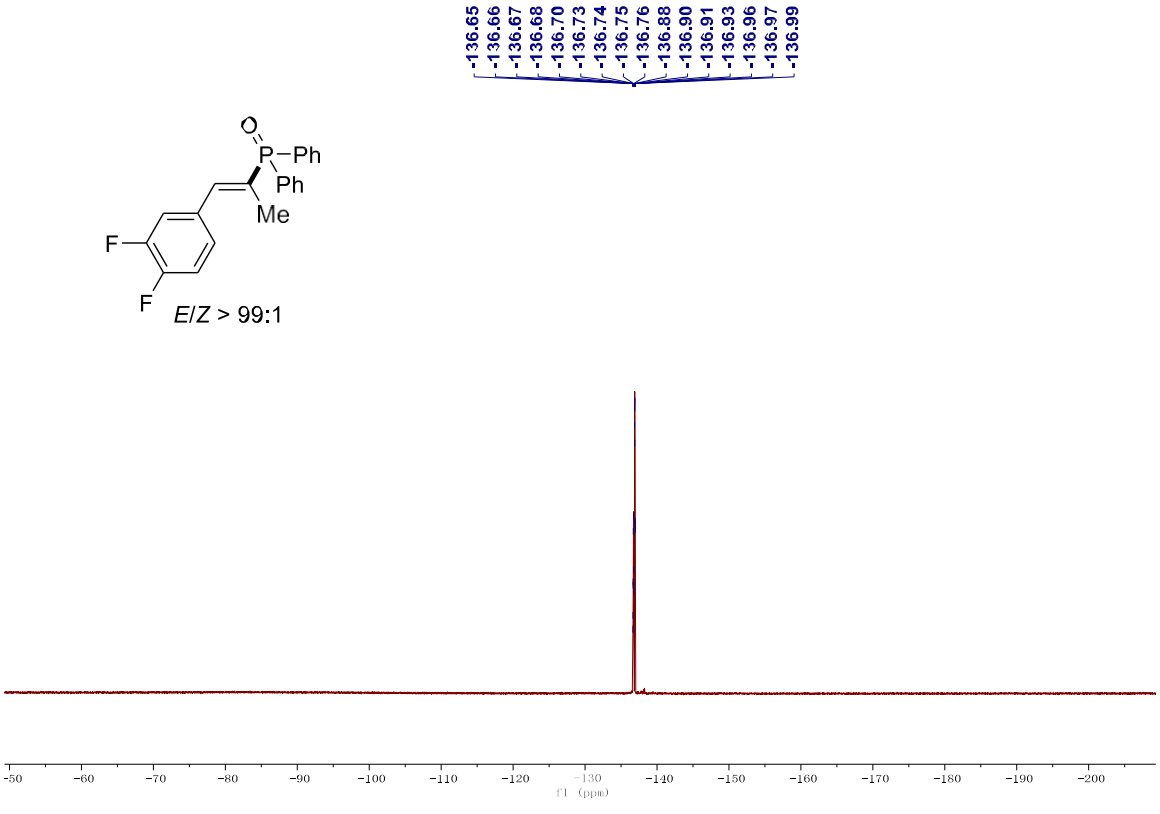
^{31}P NMR spectrum for compound **3p** ($CDCl_3$)



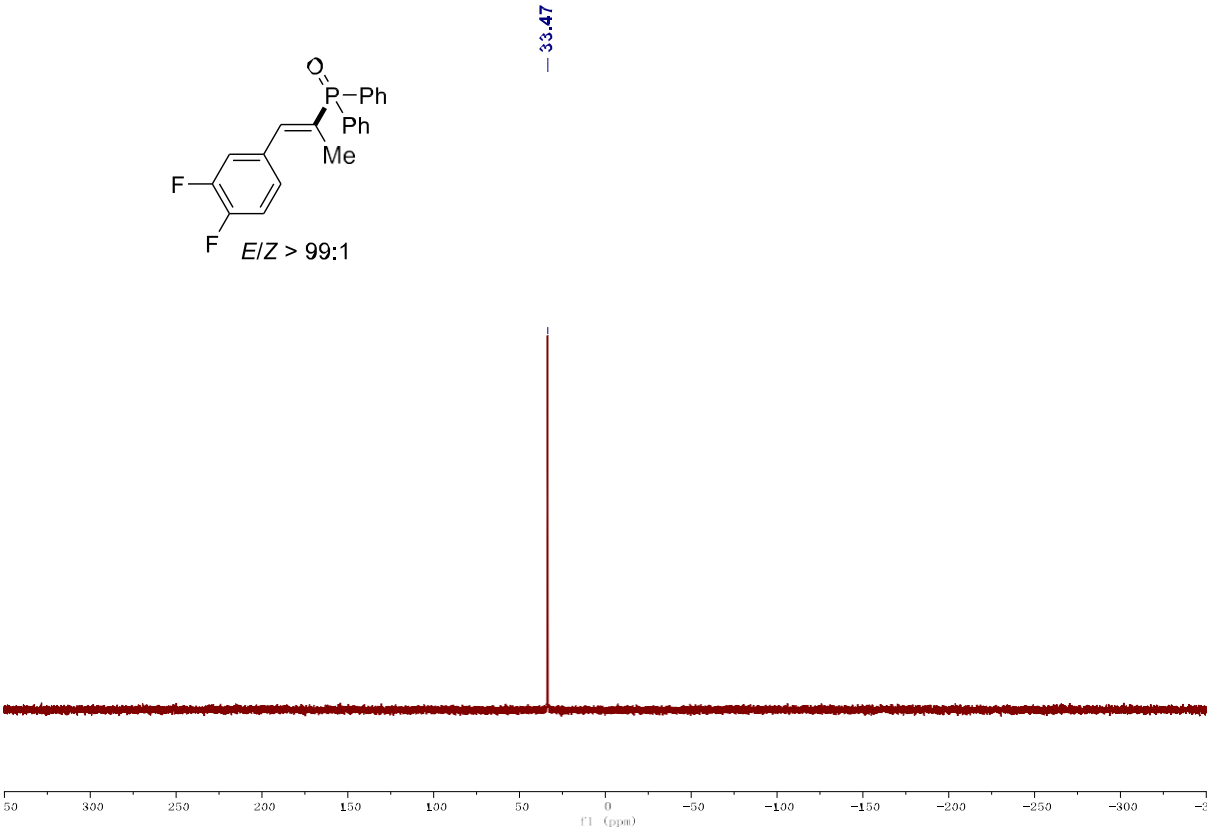
55. ^{1}H NMR spectrum for compound **3q** ($CDCl_3$)



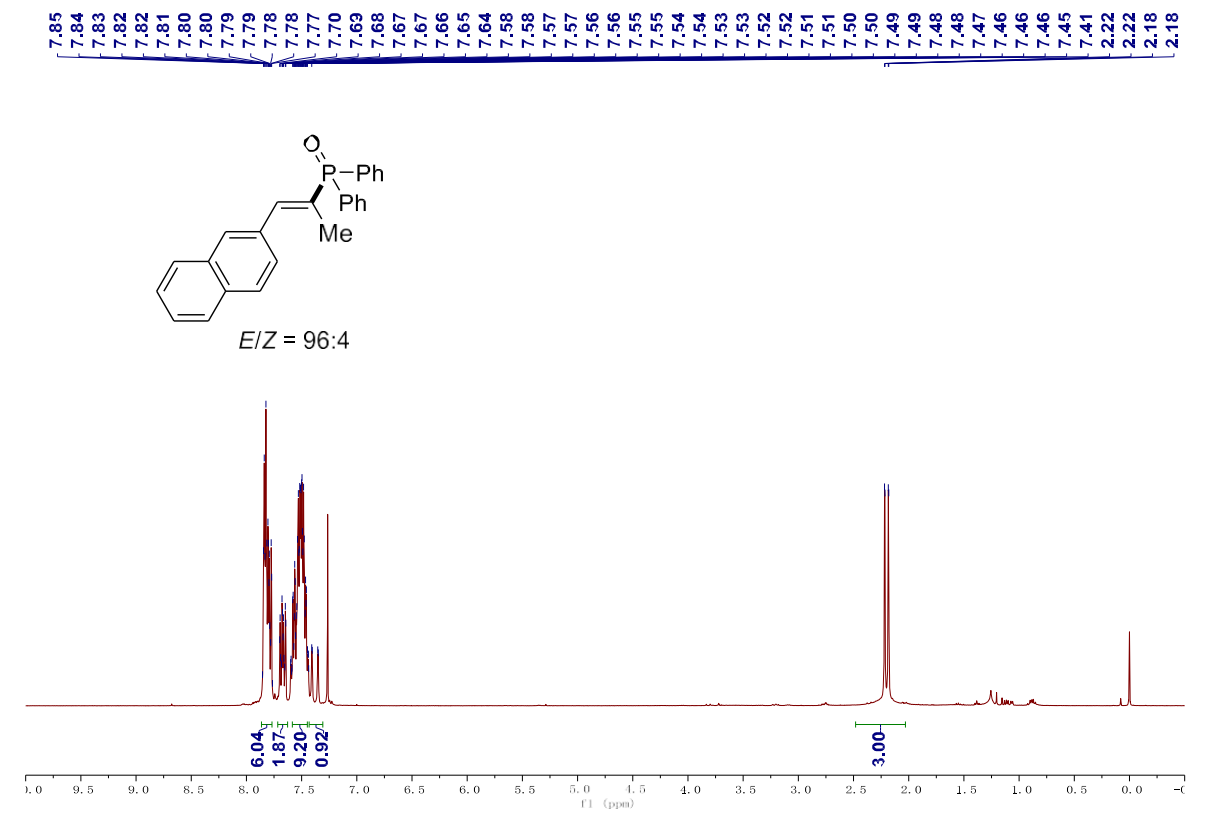
^{13}C NMR spectrum for compound **3q** ($CDCl_3$)



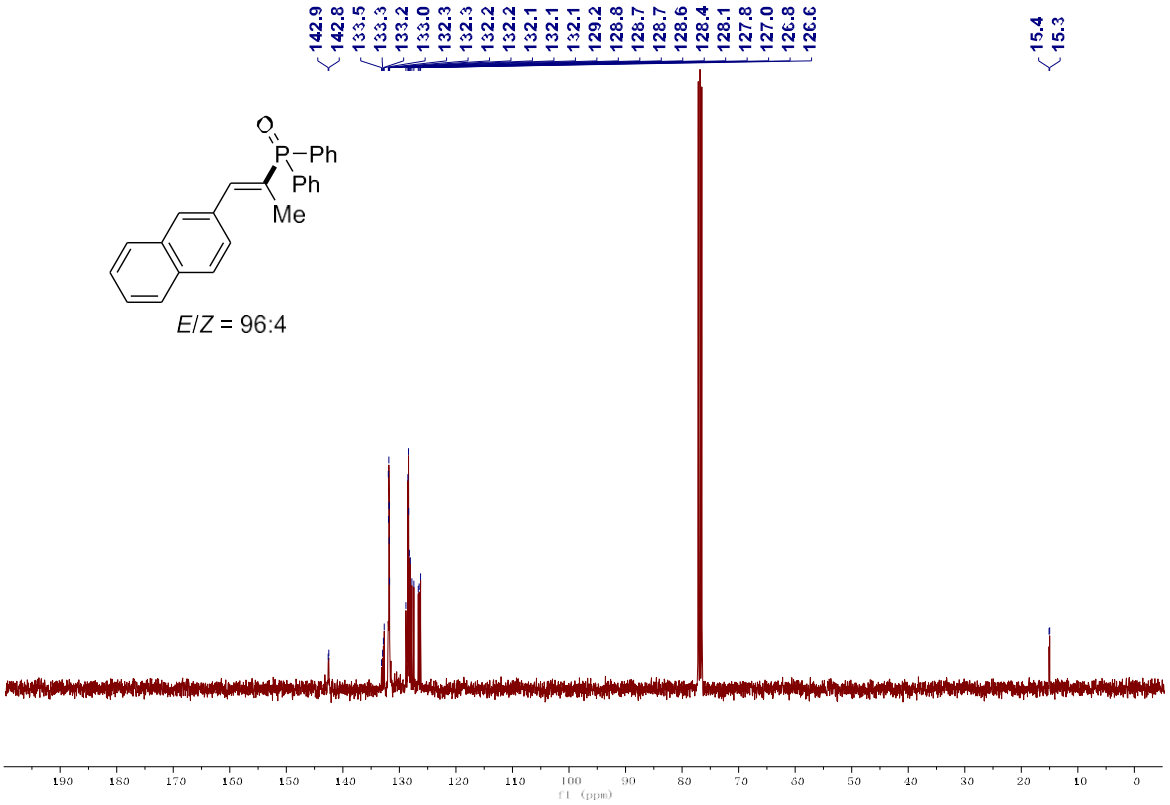
^{19}F NMR spectrum for compound **3q** ($CDCl_3$)



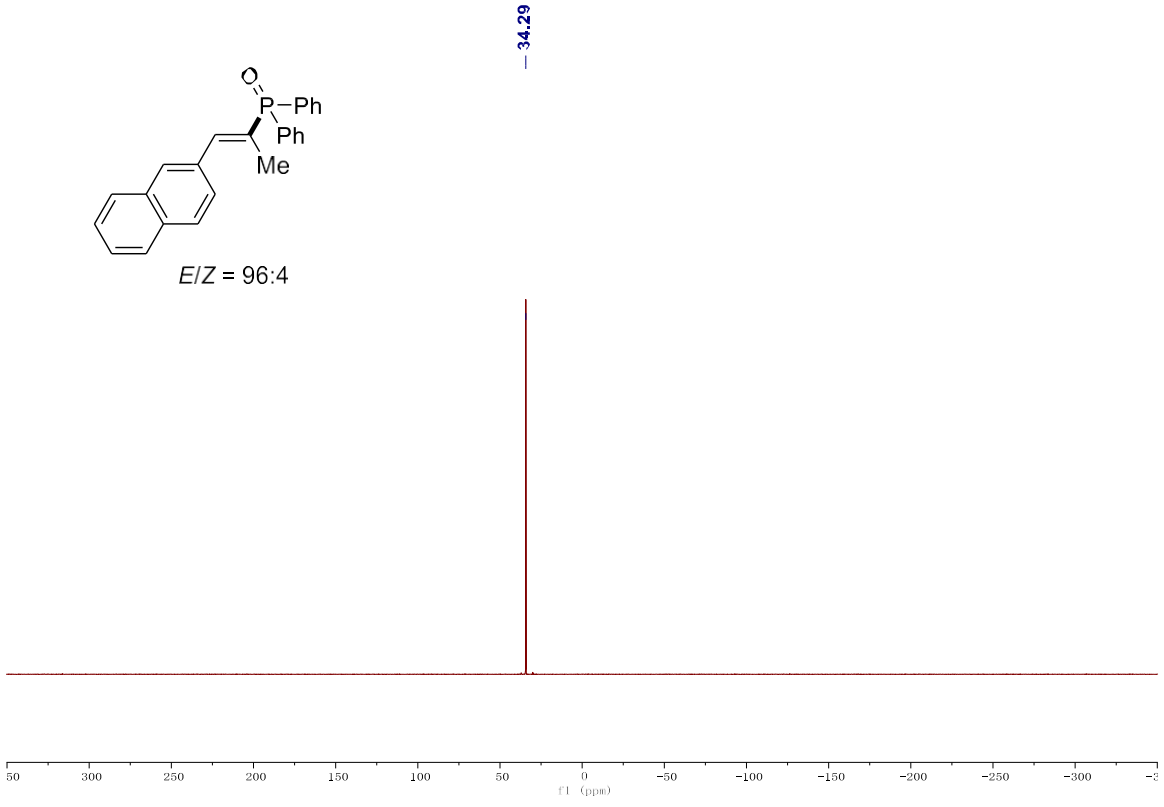
^{31}P NMR spectrum for compound **3q** ($CDCl_3$)



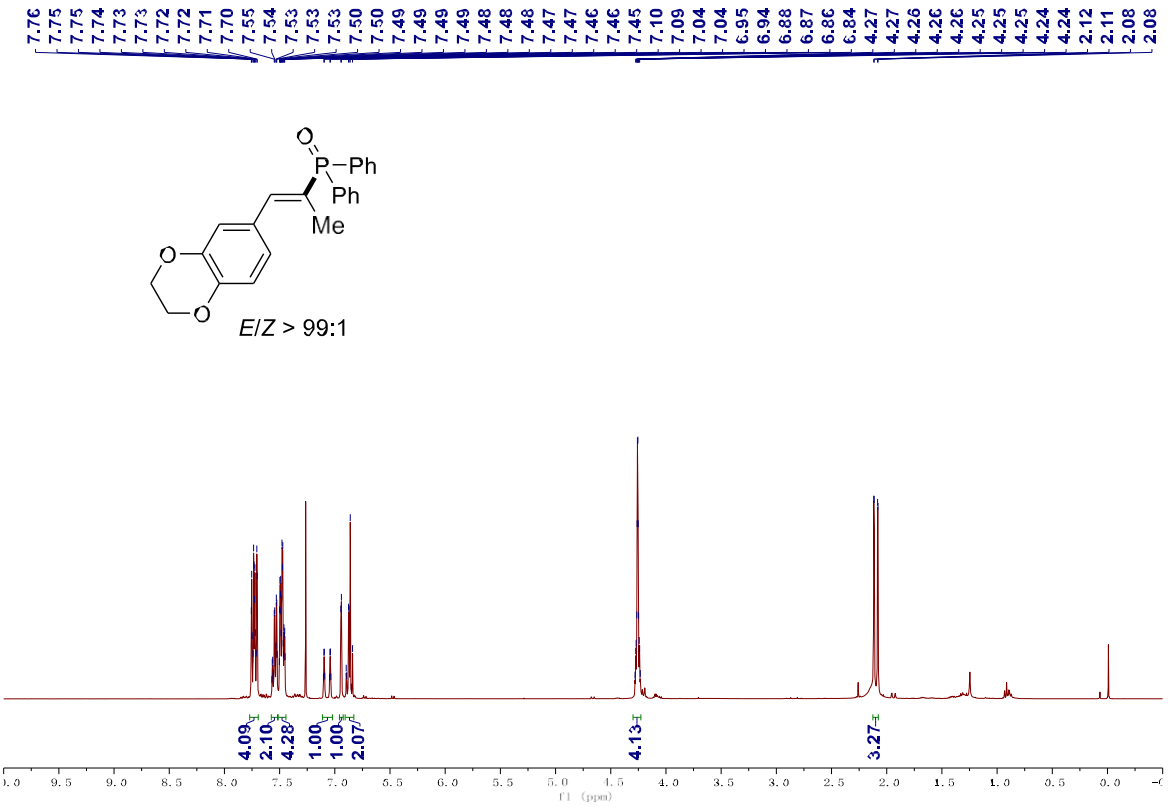
^{1}H NMR spectrum for compound **3r** ($CDCl_3$)



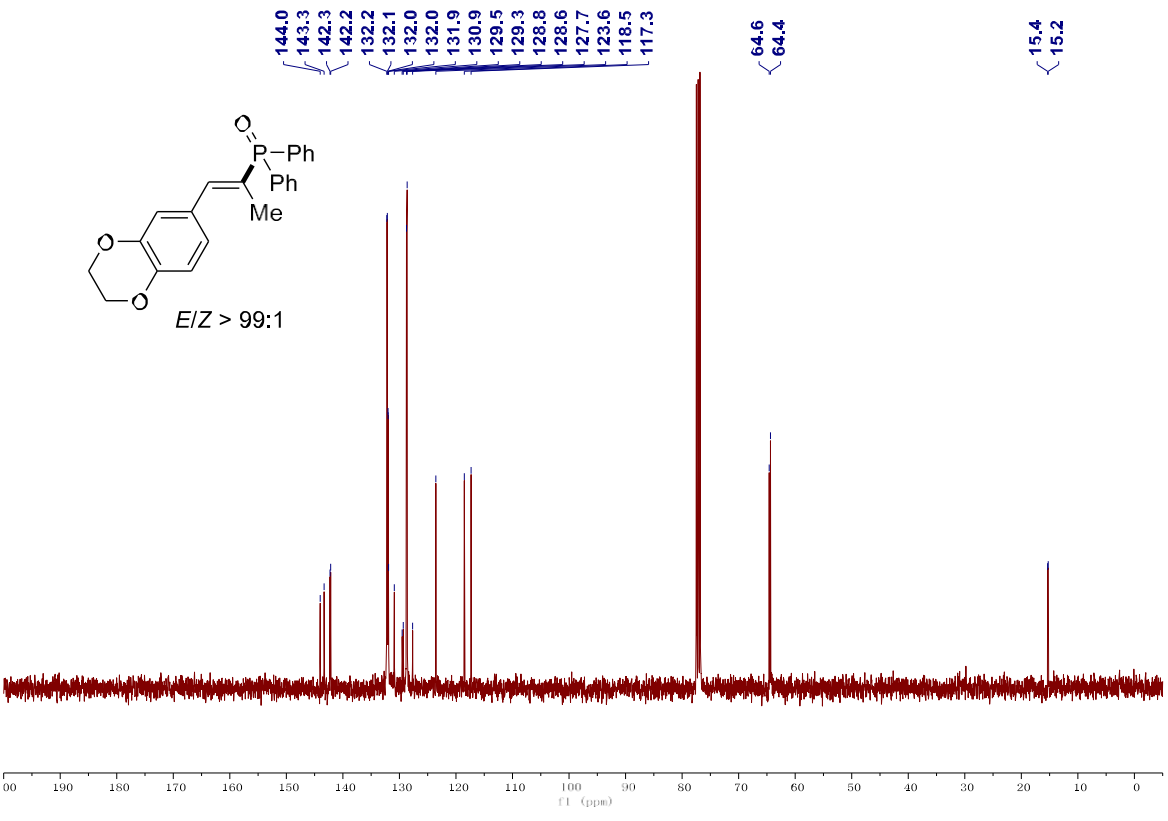
^{13}C NMR spectrum for compound **3r** ($CDCl_3$)



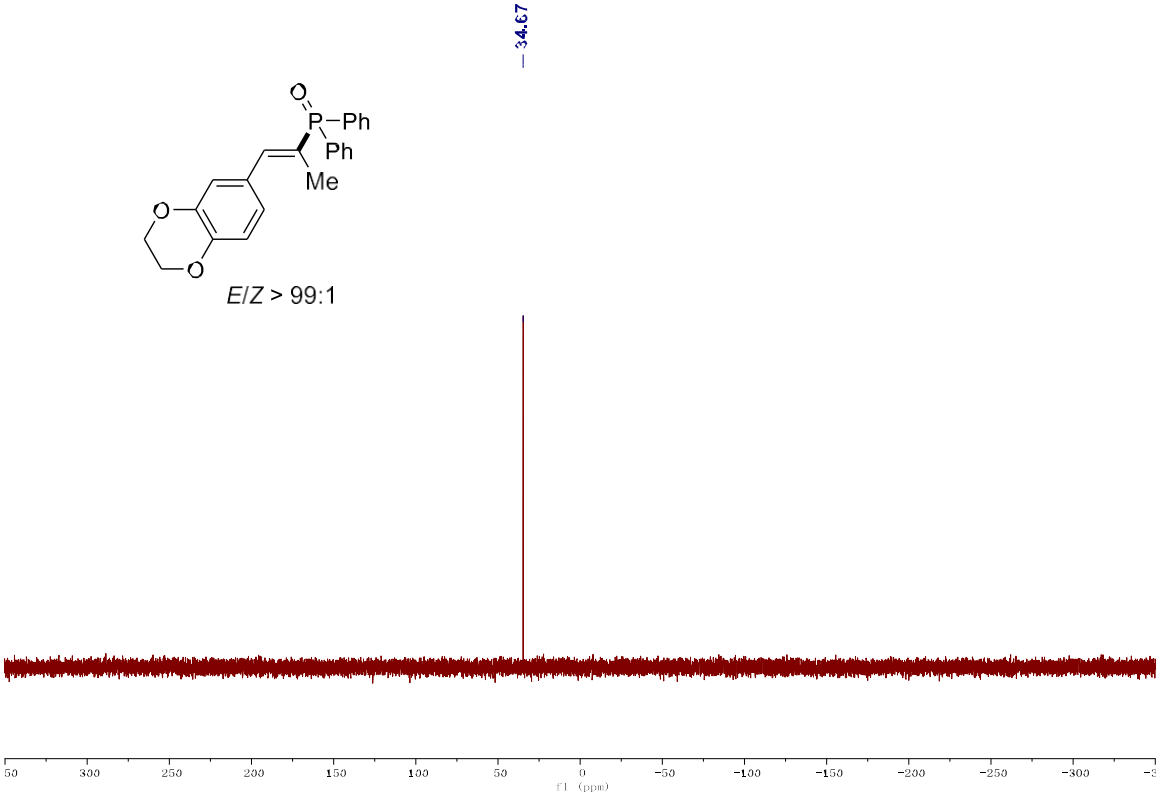
^{31}P NMR spectrum for compound **3r** ($CDCl_3$)



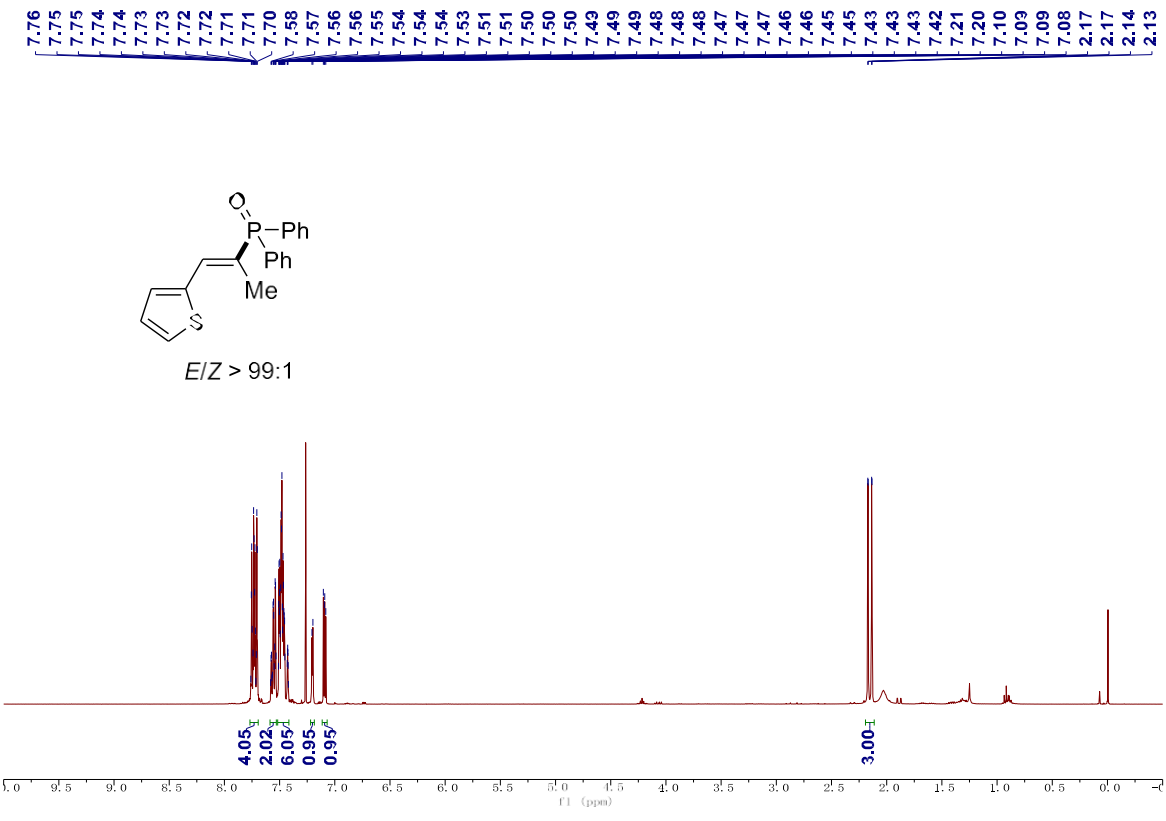
^{1}H NMR spectrum for compound **3s** ($CDCl_3$)



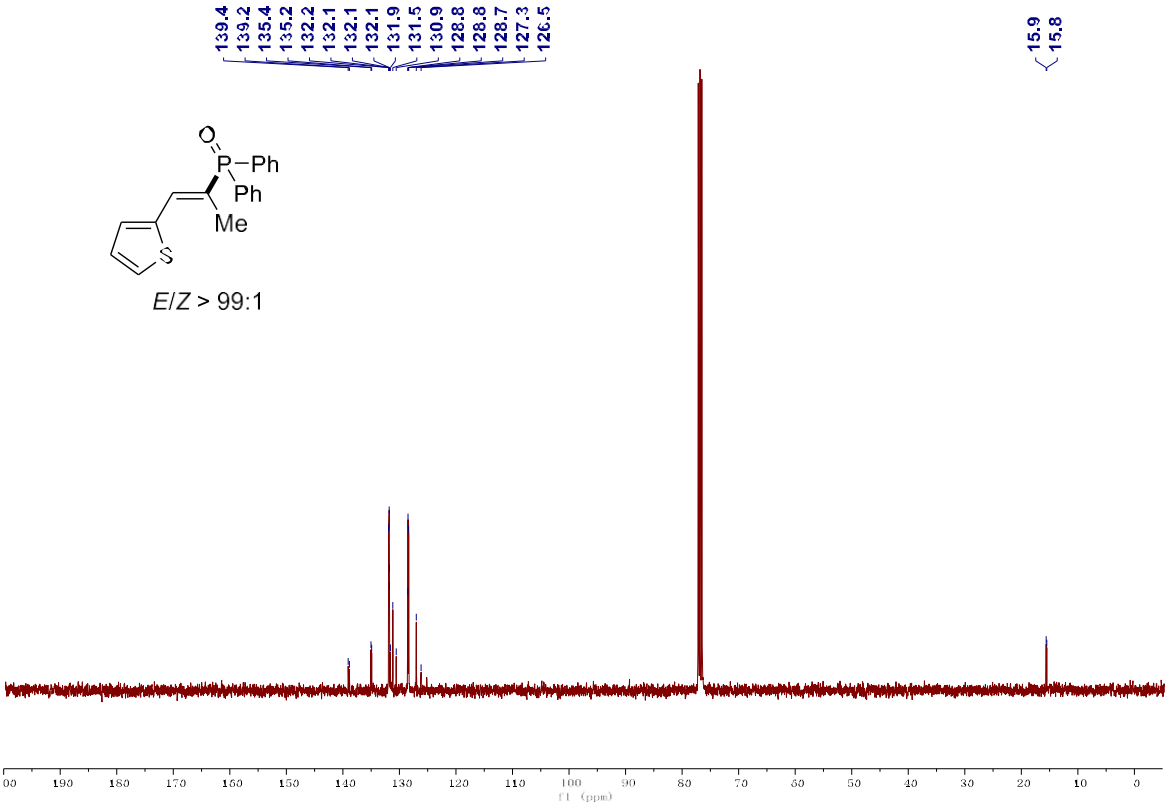
^{13}C NMR spectrum for compound **3s** ($CDCl_3$)



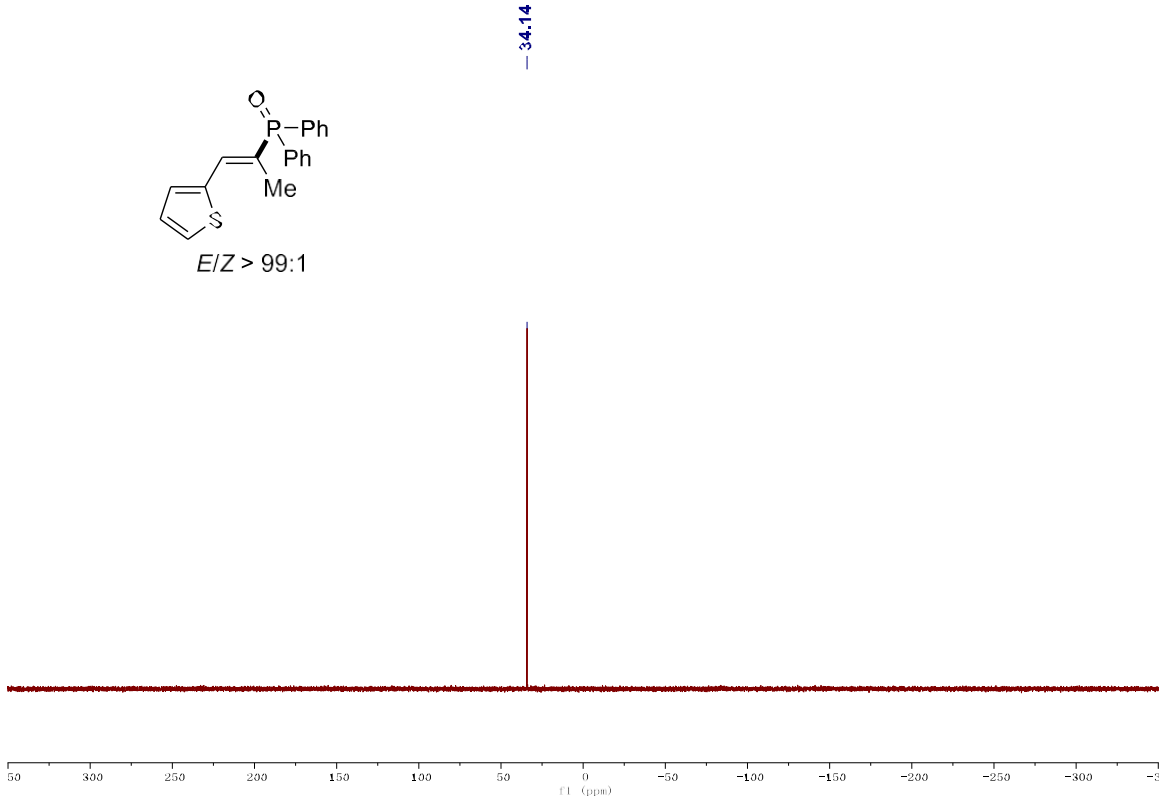
^{31}P NMR spectrum for compound **3s** ($CDCl_3$)



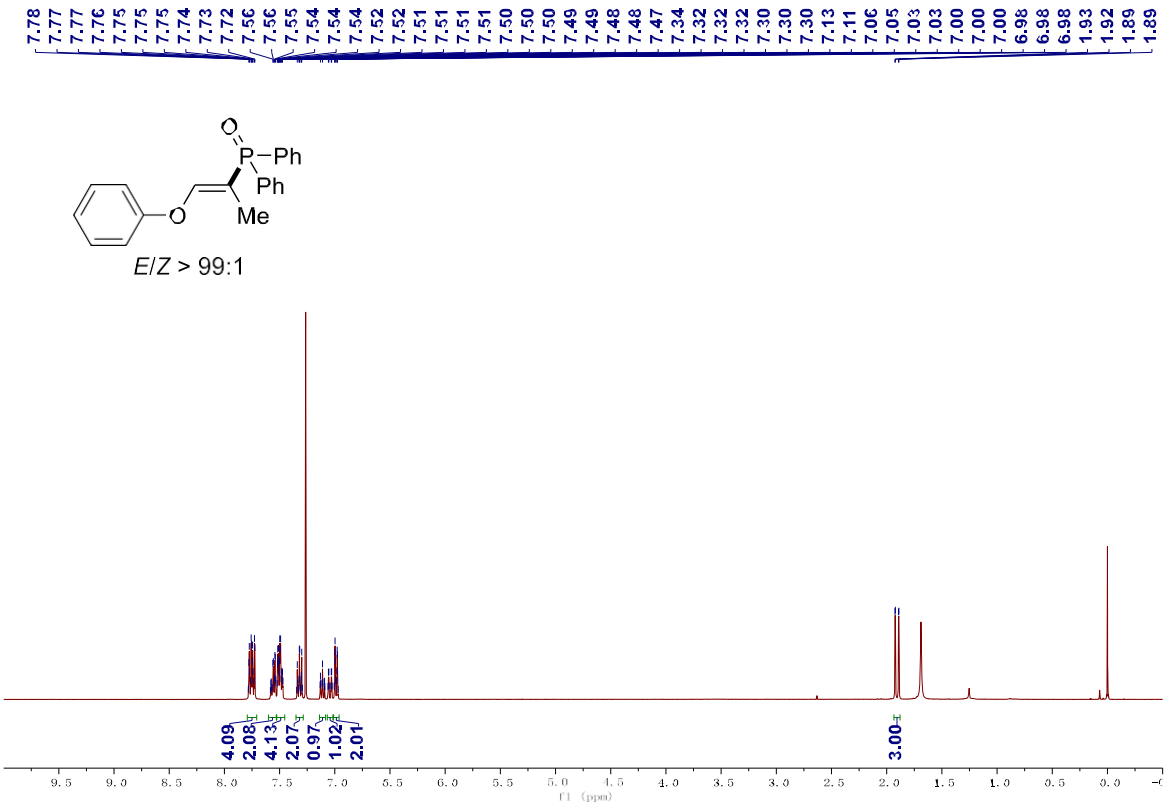
^{1}H NMR spectrum for compound **3t** ($CDCl_3$)



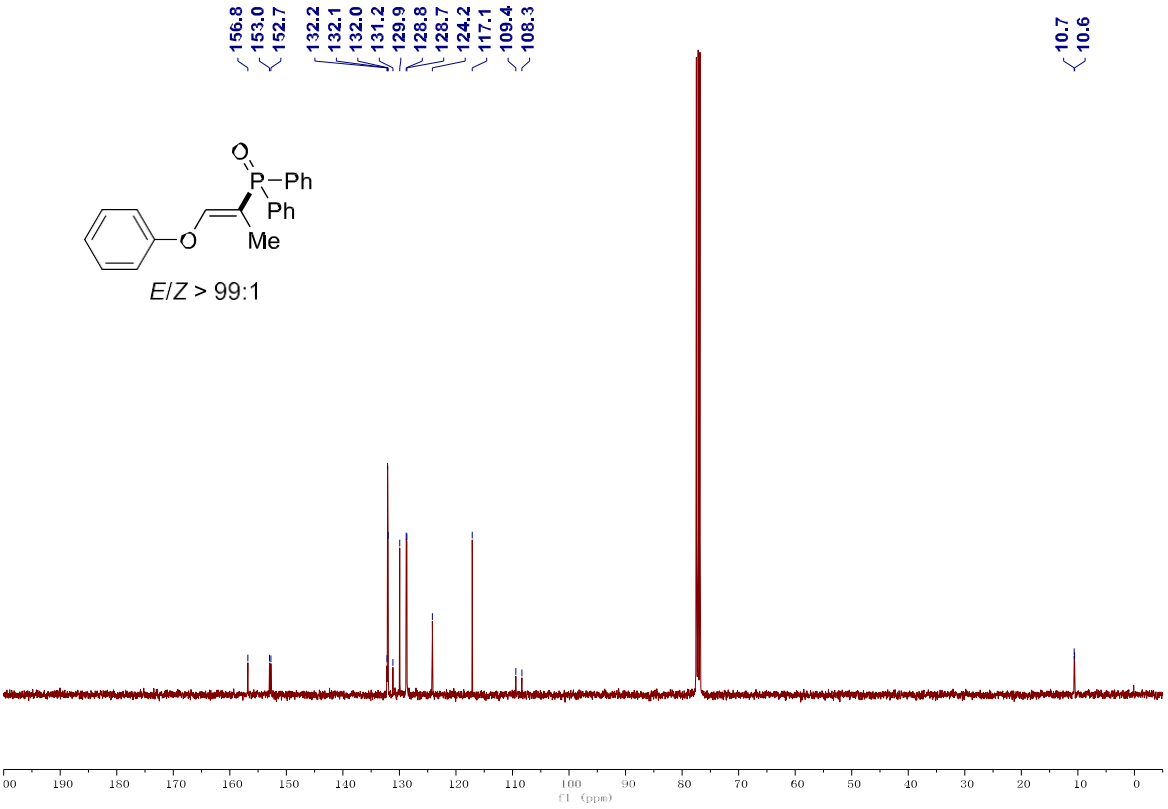
^{13}C NMR spectrum for compound **3t** ($CDCl_3$)



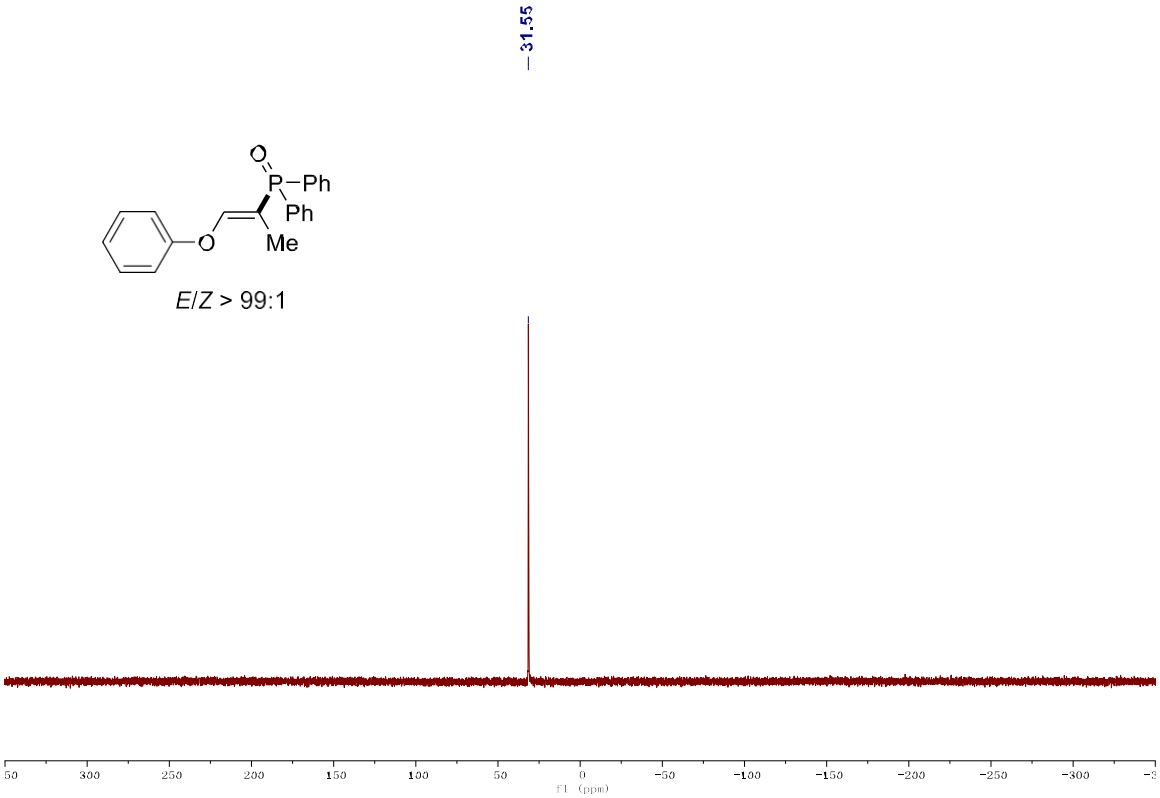
^{31}P NMR spectrum for compound **3t** ($CDCl_3$)



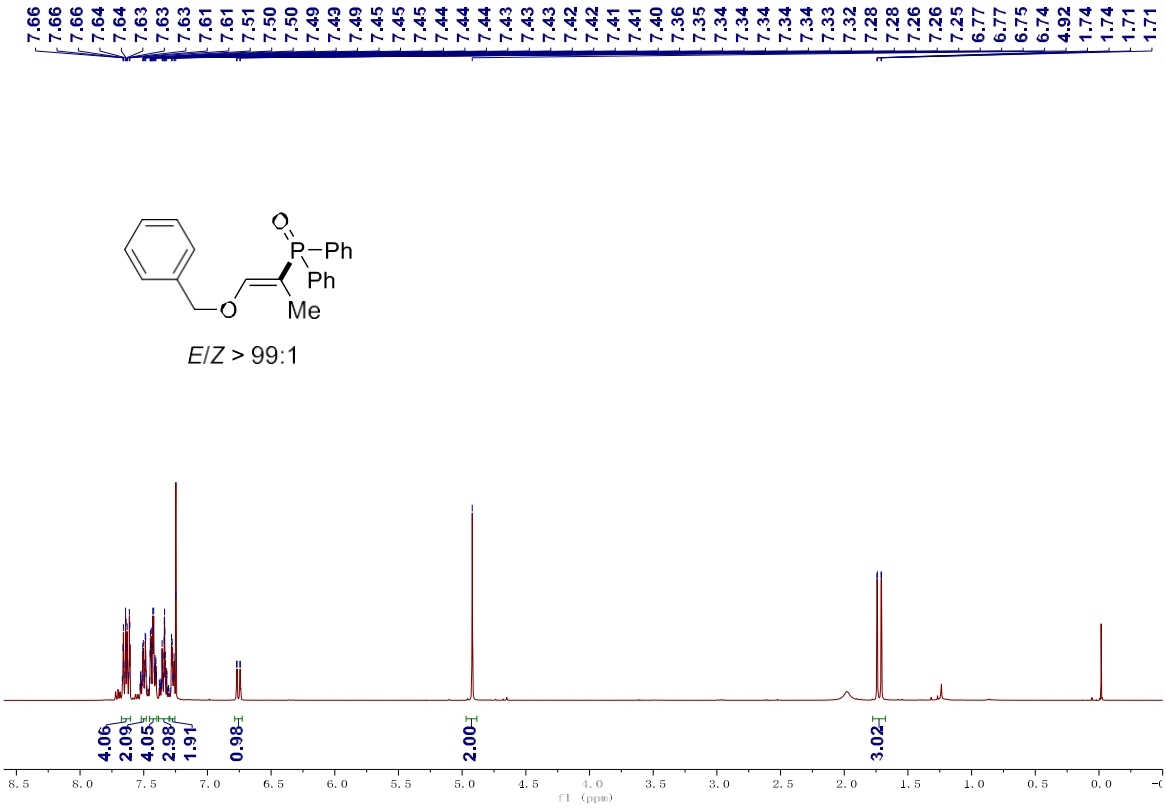
^{1}H NMR spectrum for compound **3u** ($CDCl_3$)



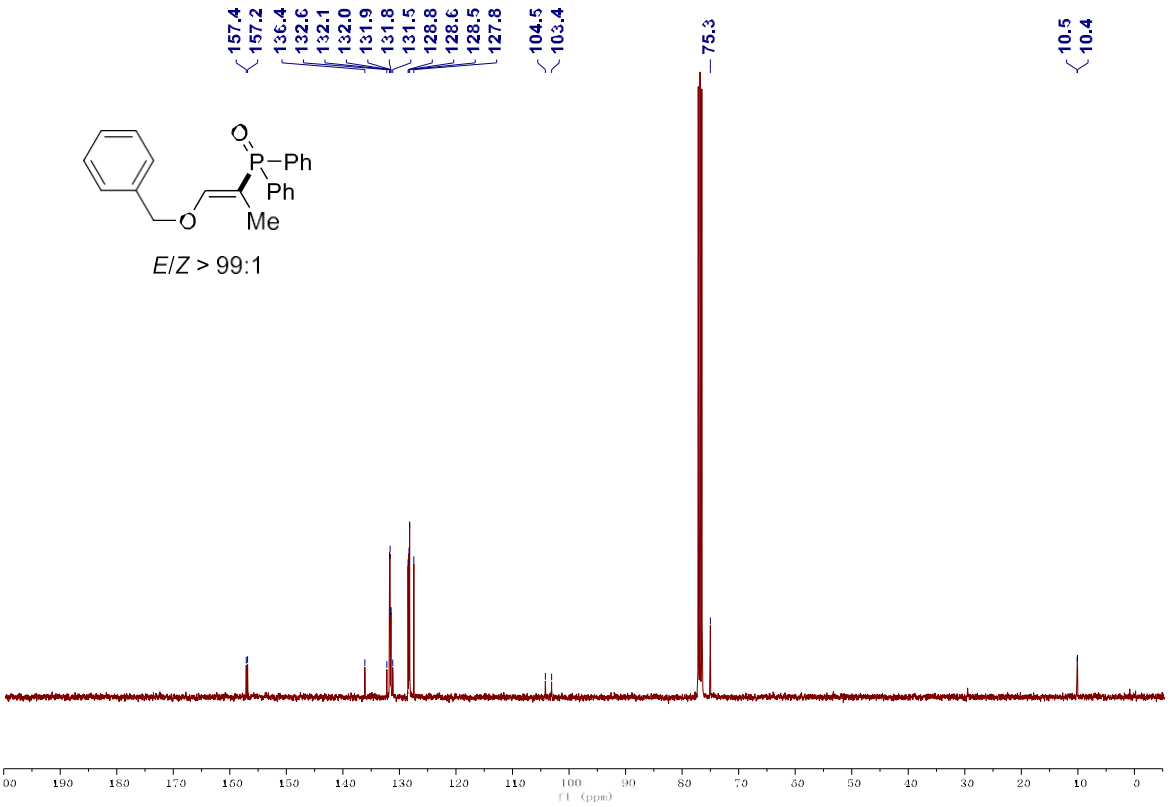
^{13}C NMR spectrum for compound **3u** ($CDCl_3$)



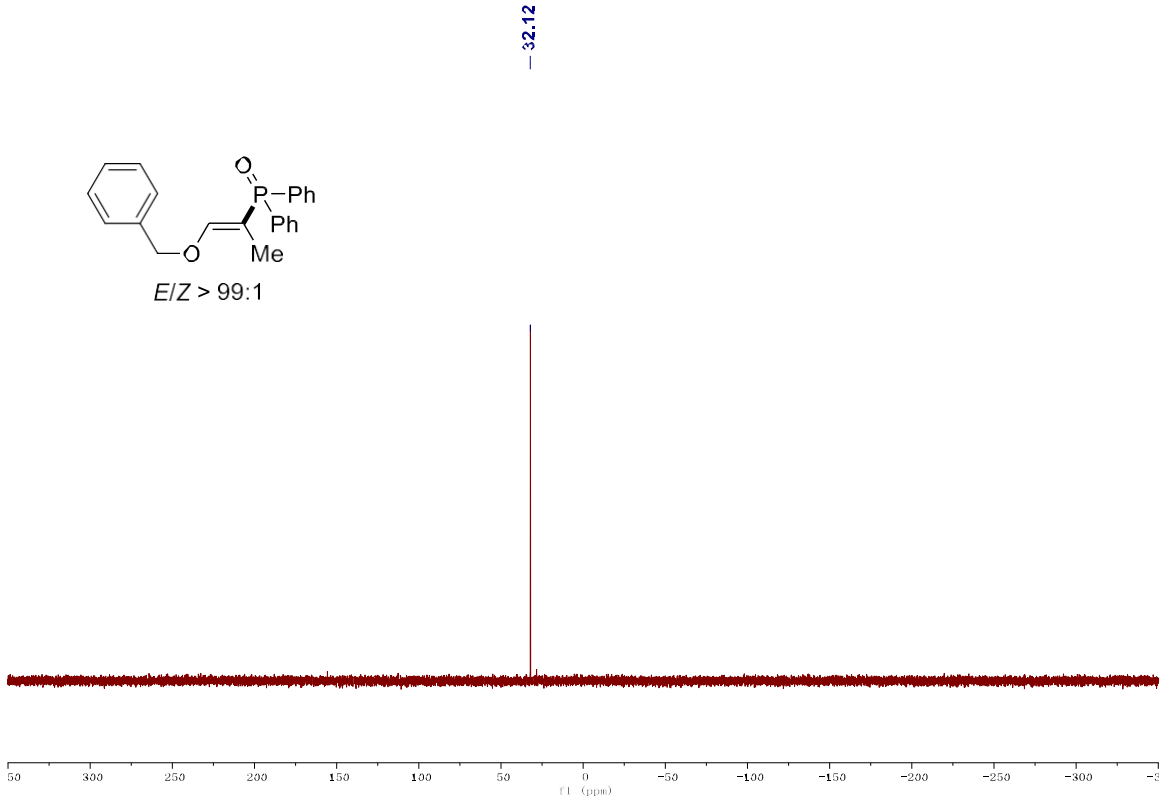
^{31}P NMR spectrum for compound **3u** ($CDCl_3$)



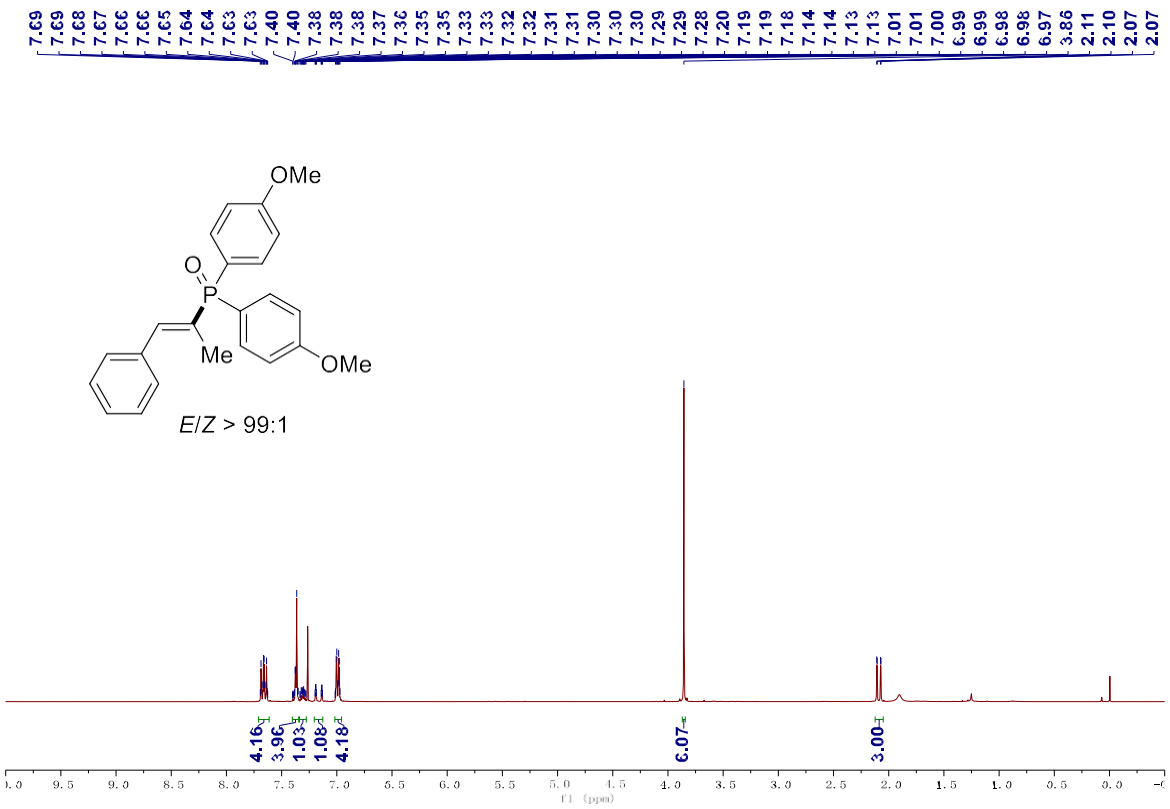
^{1}H NMR spectrum for compound **3v** ($CDCl_3$)



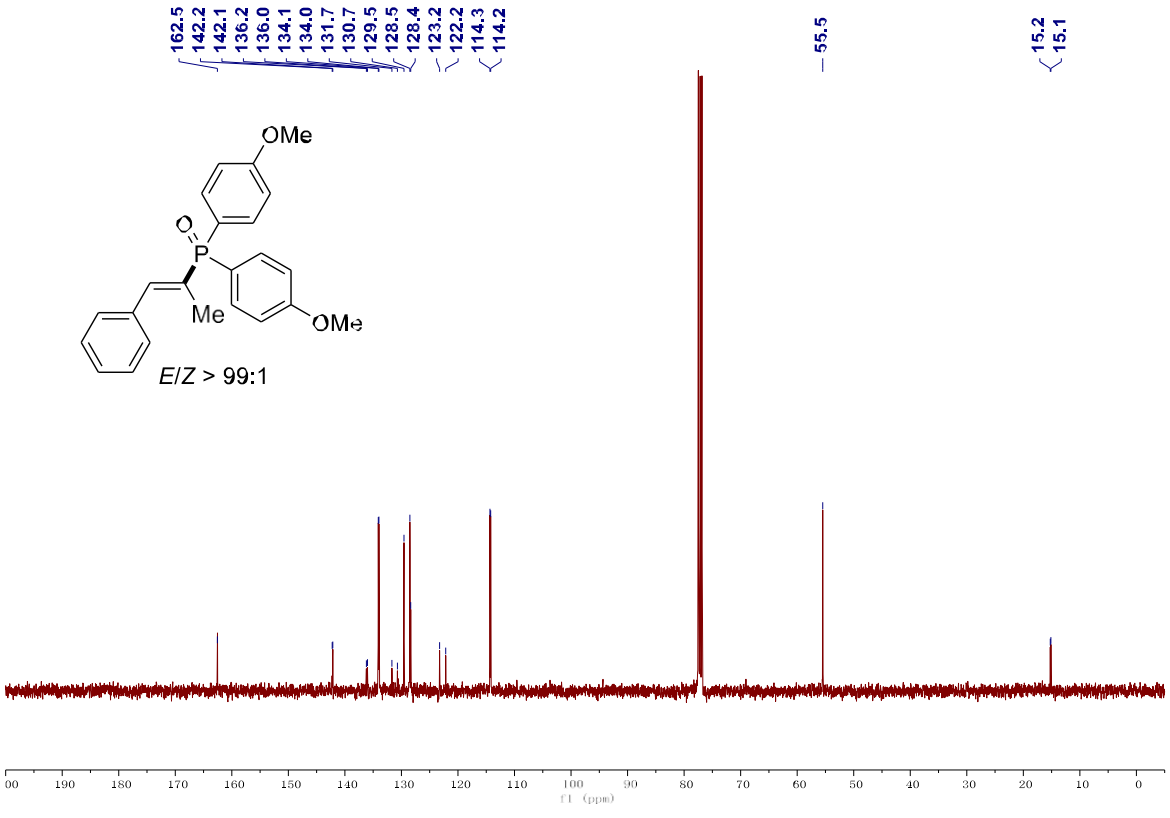
^{13}C NMR spectrum for compound **3v** ($CDCl_3$)



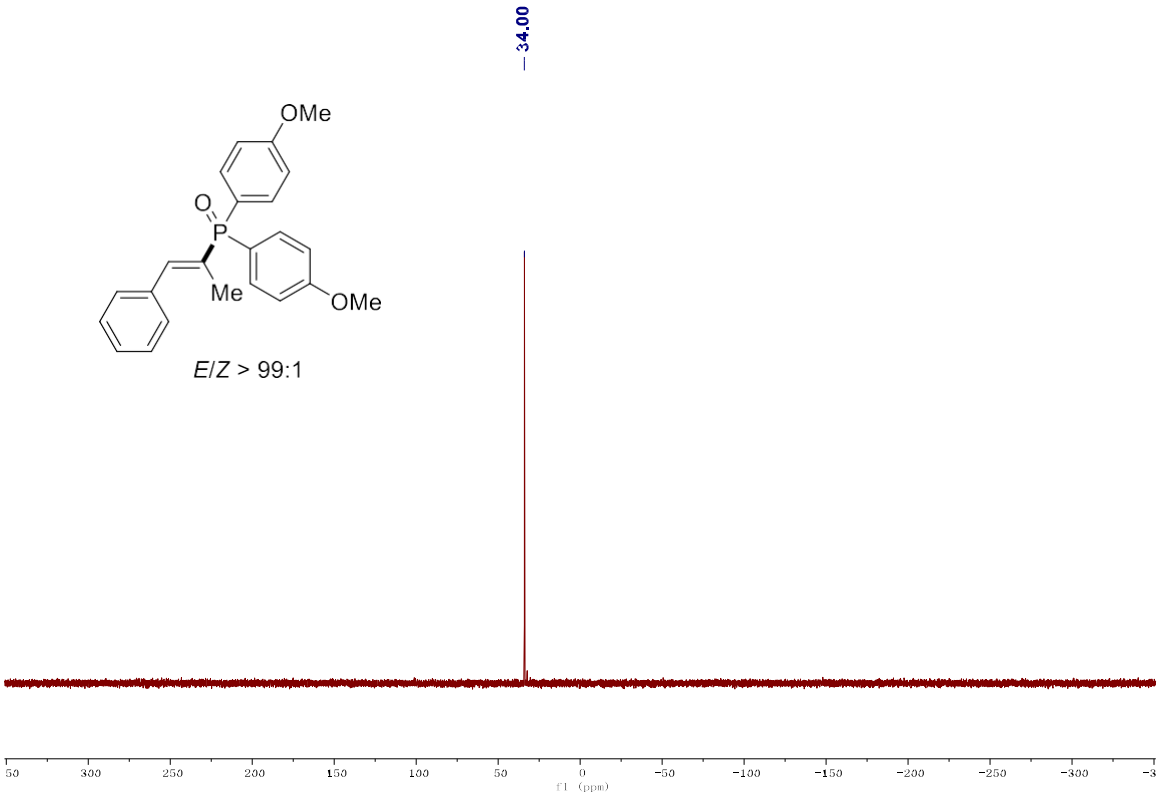
^{31}P NMR spectrum for compound **3v** ($CDCl_3$)



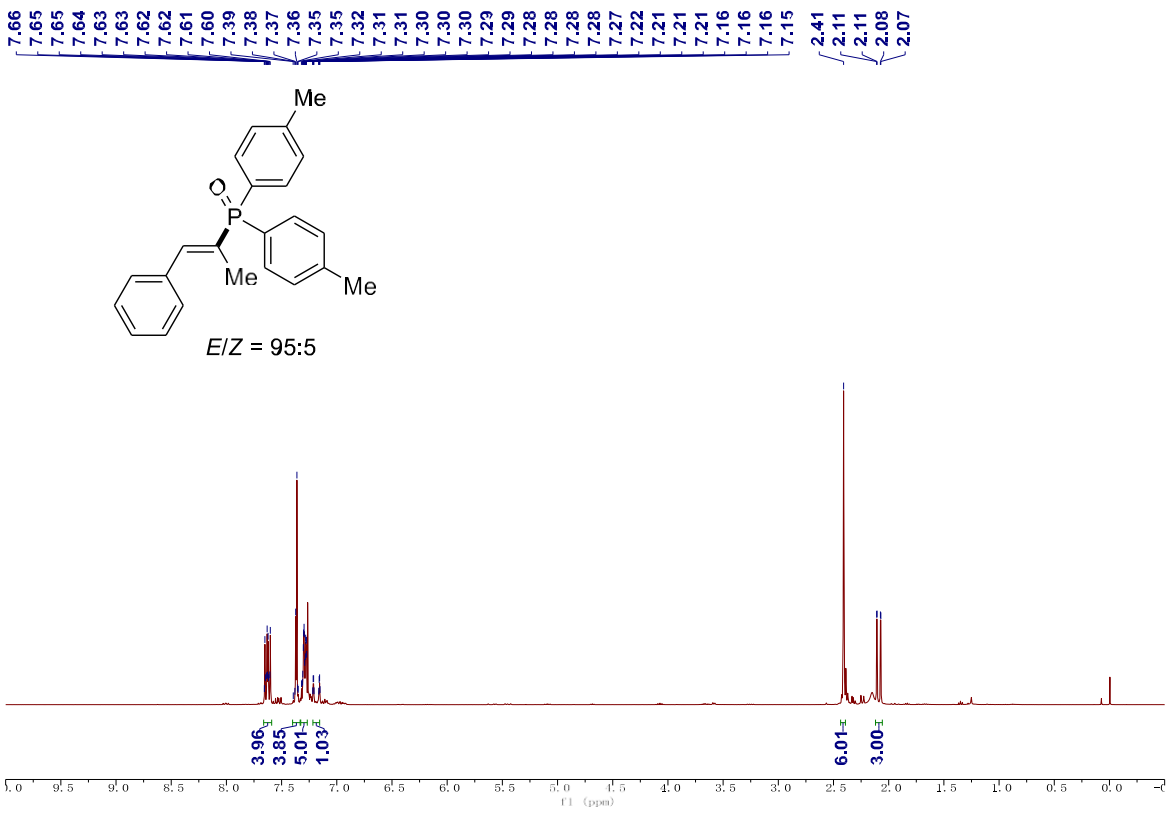
^{1}H NMR spectrum for compound **3ab** ($CDCl_3$)



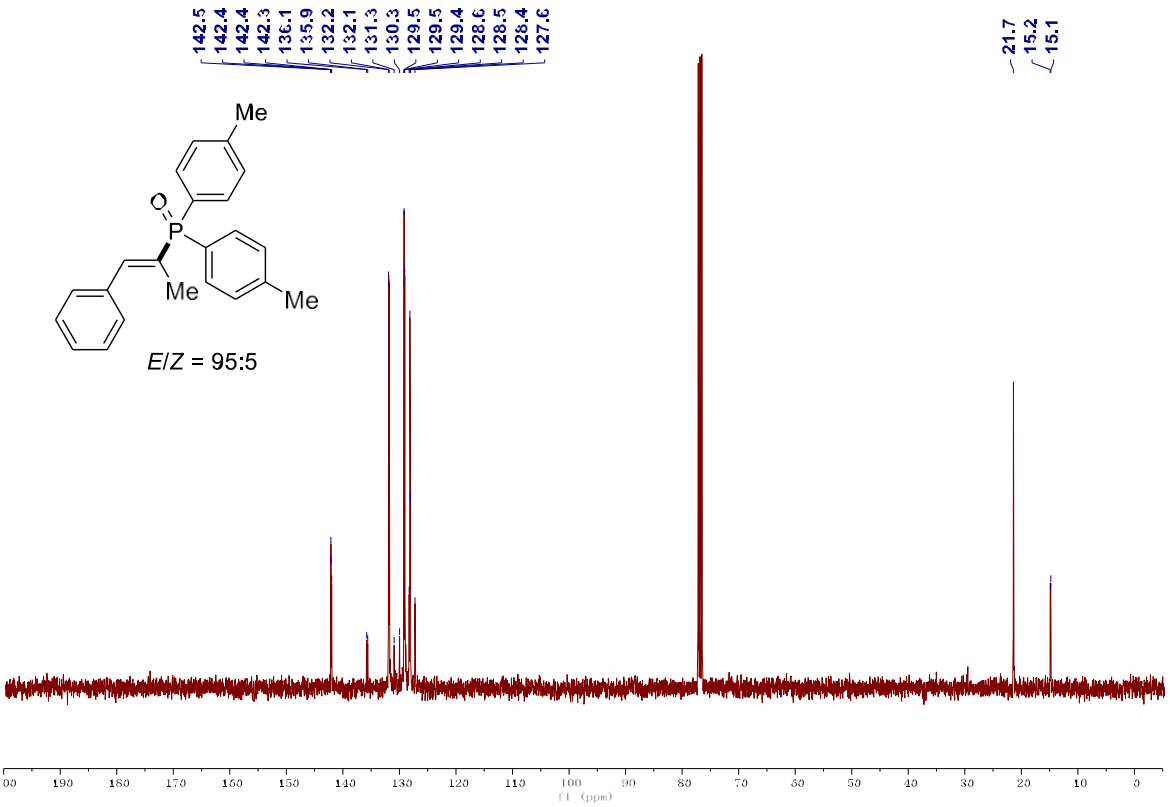
^{13}C NMR spectrum for compound **3ab** ($CDCl_3$)



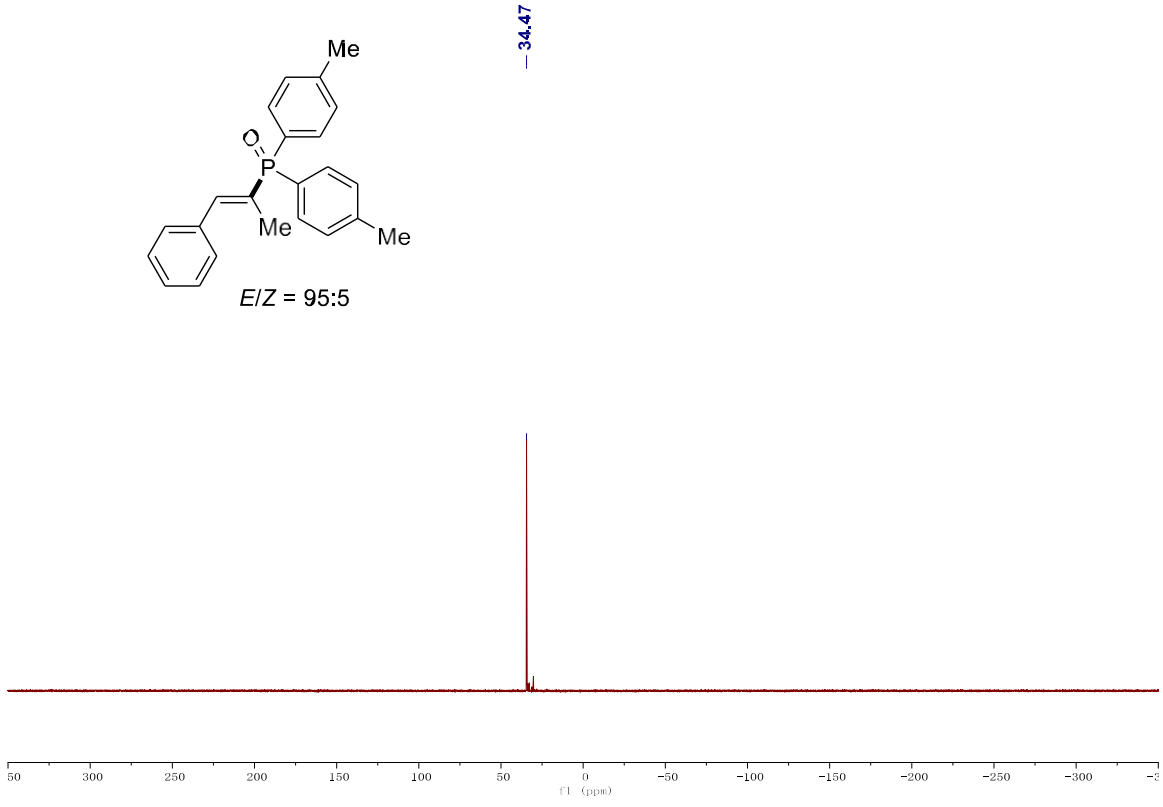
^{31}P NMR spectrum for compound **3ab** ($CDCl_3$)



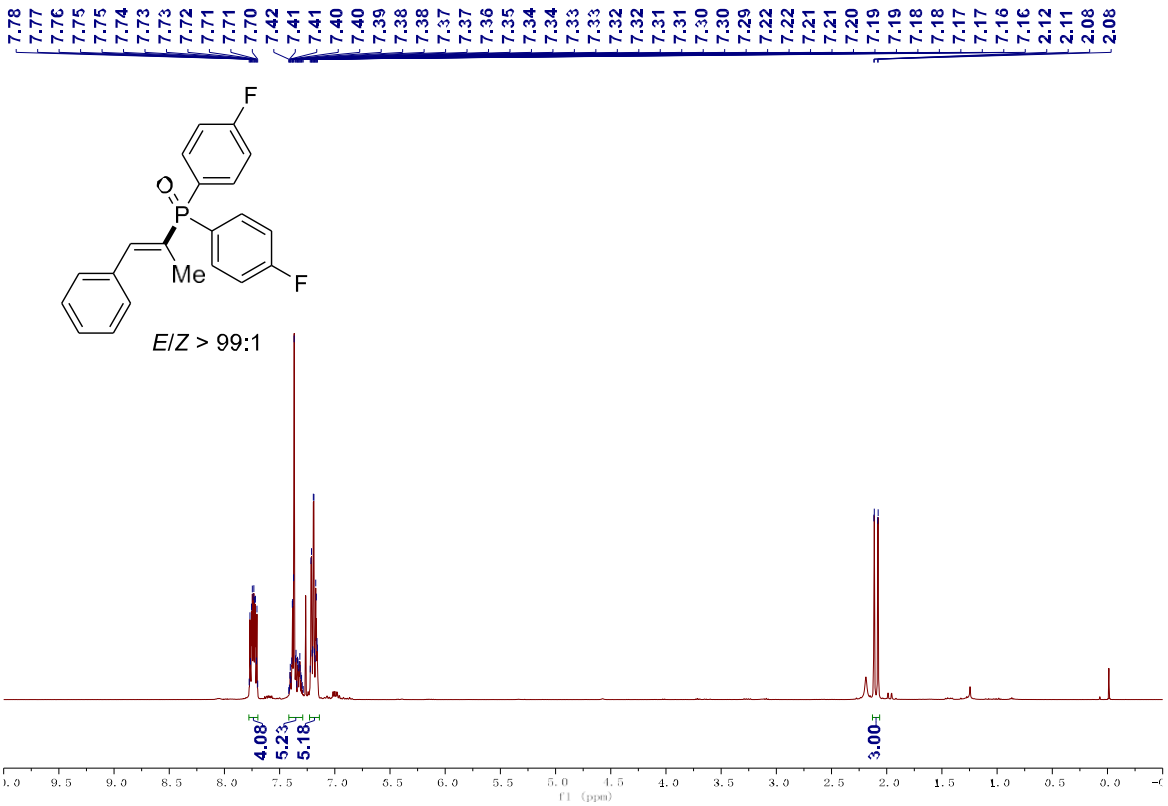
^{1}H NMR spectrum for compound **3ac** ($CDCl_3$)



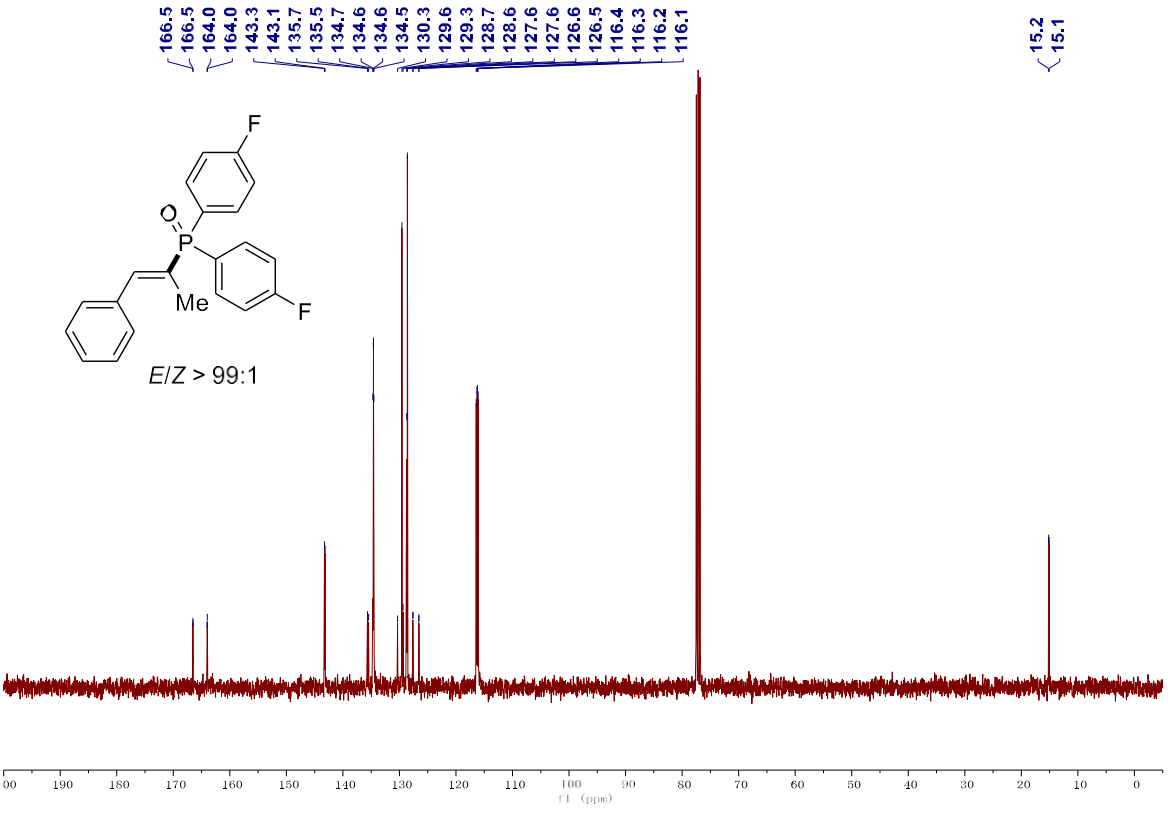
^{13}C NMR spectrum for compound 3ac ($CDCl_3$)



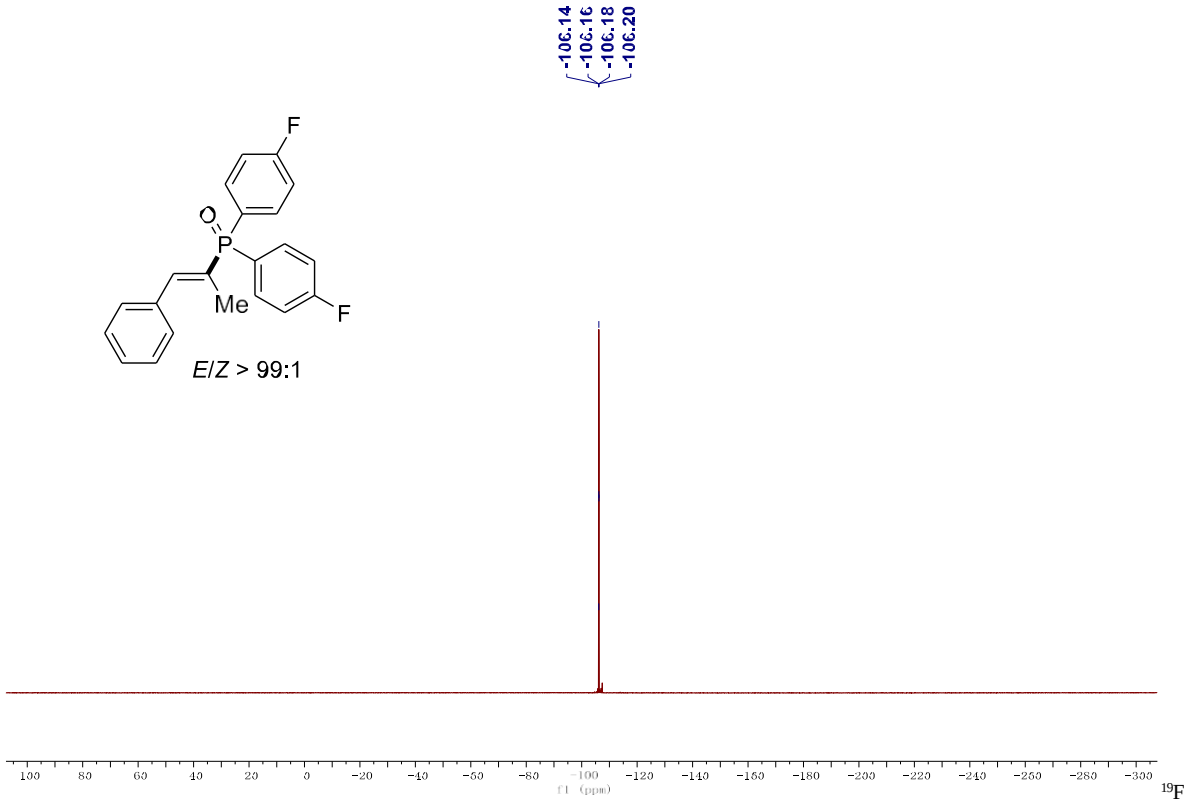
^{31}P NMR spectrum for compound **3ac** ($CDCl_3$)



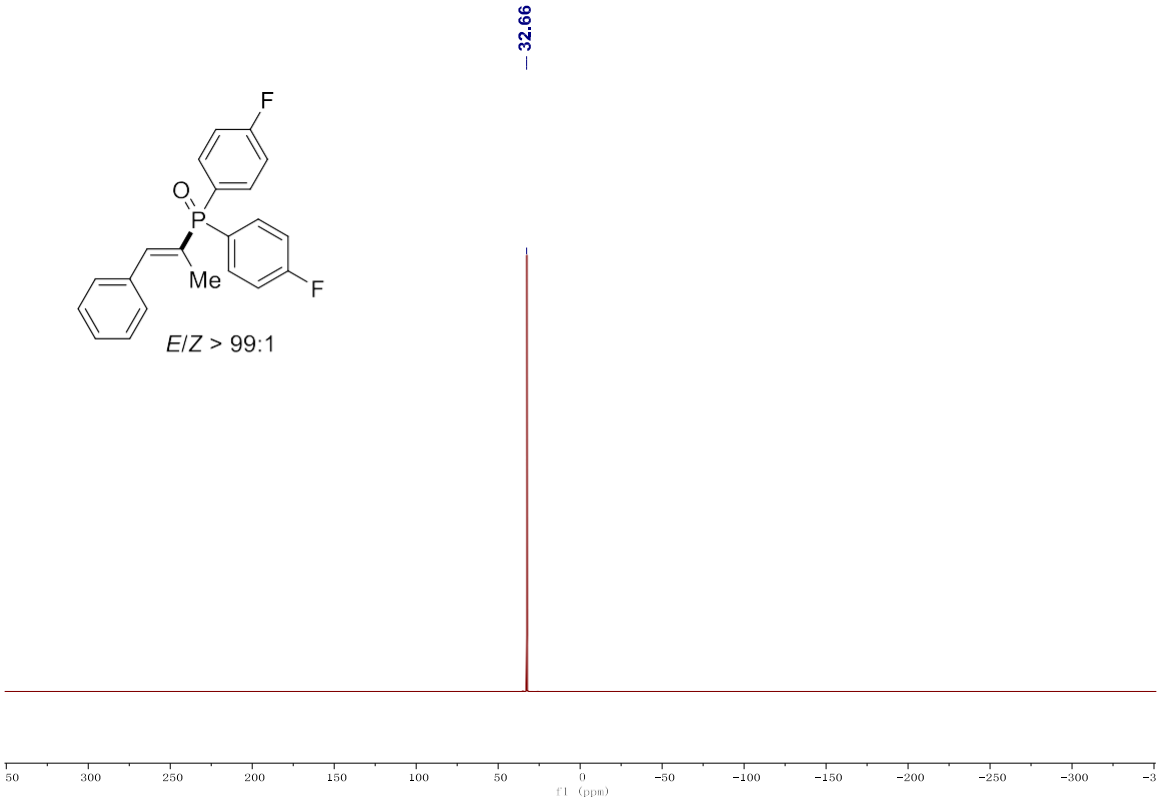
^{1}H NMR spectrum for compound **3ad** ($CDCl_3$)



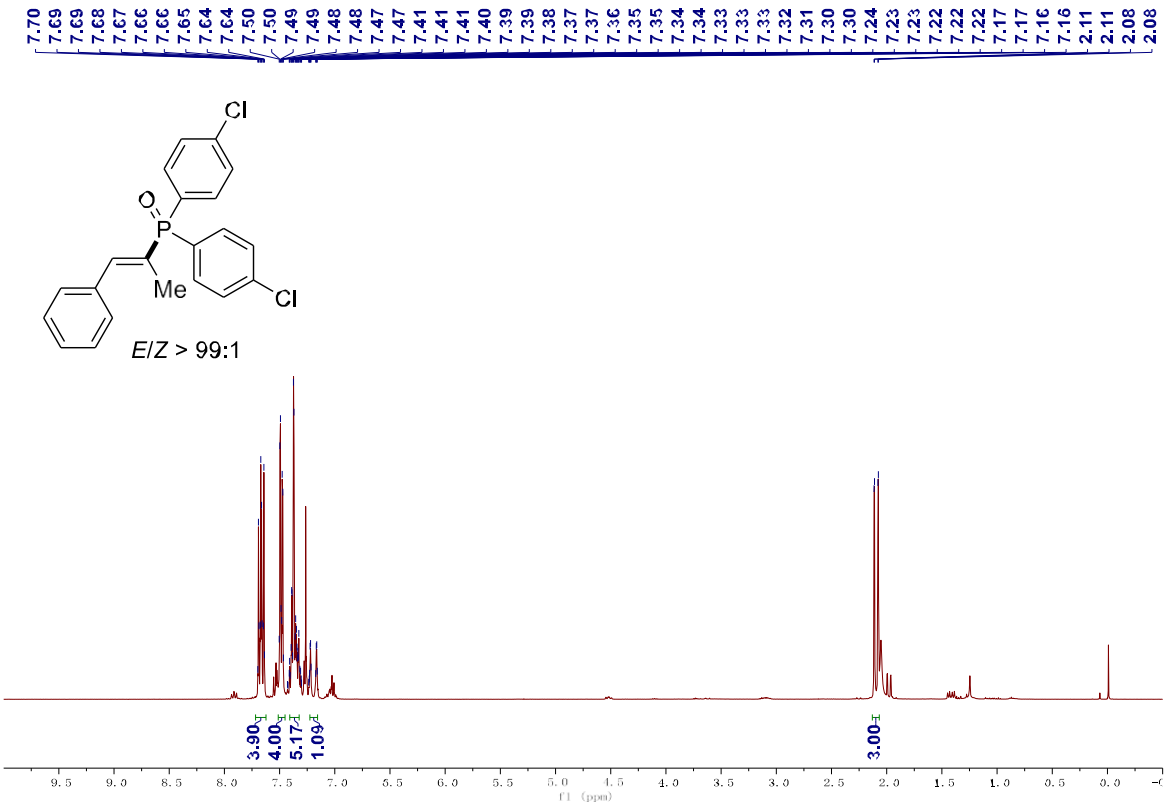
^{13}C NMR spectrum for compound **3ad** ($CDCl_3$)



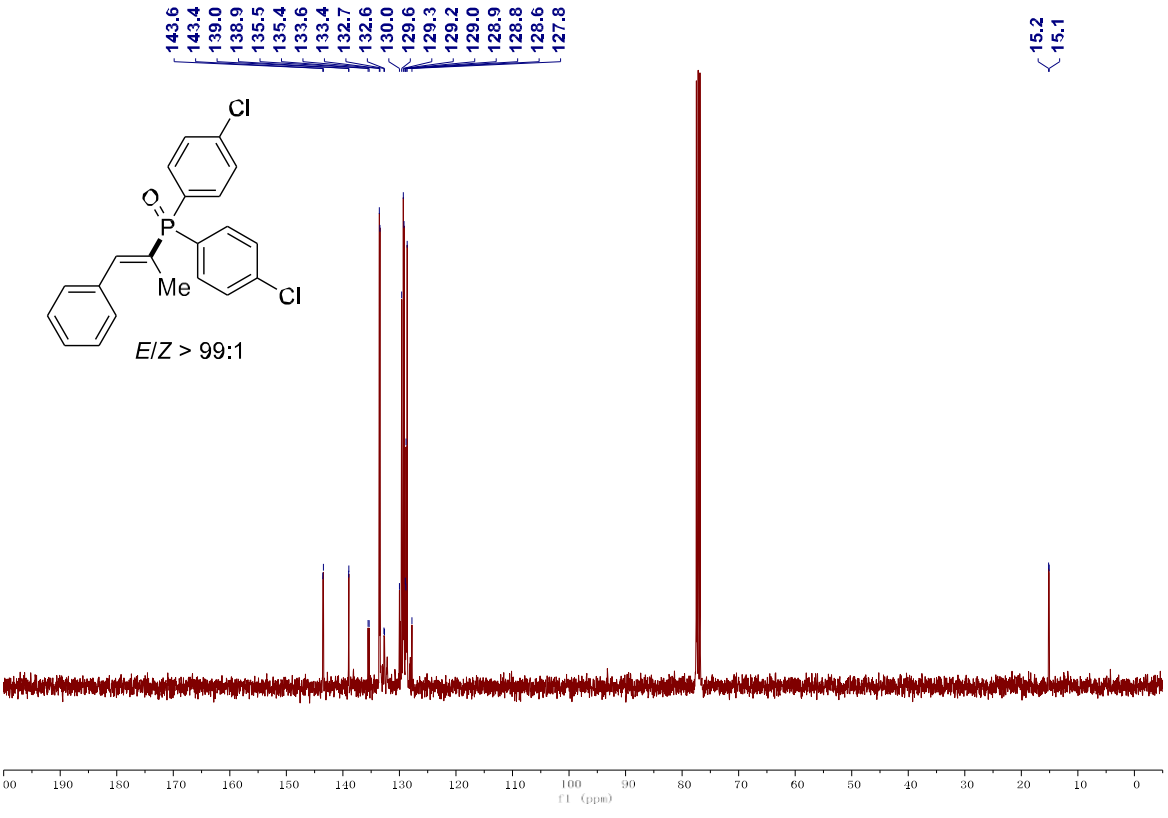
NMR spectrum for compound **3ad** ($CDCl_3$)



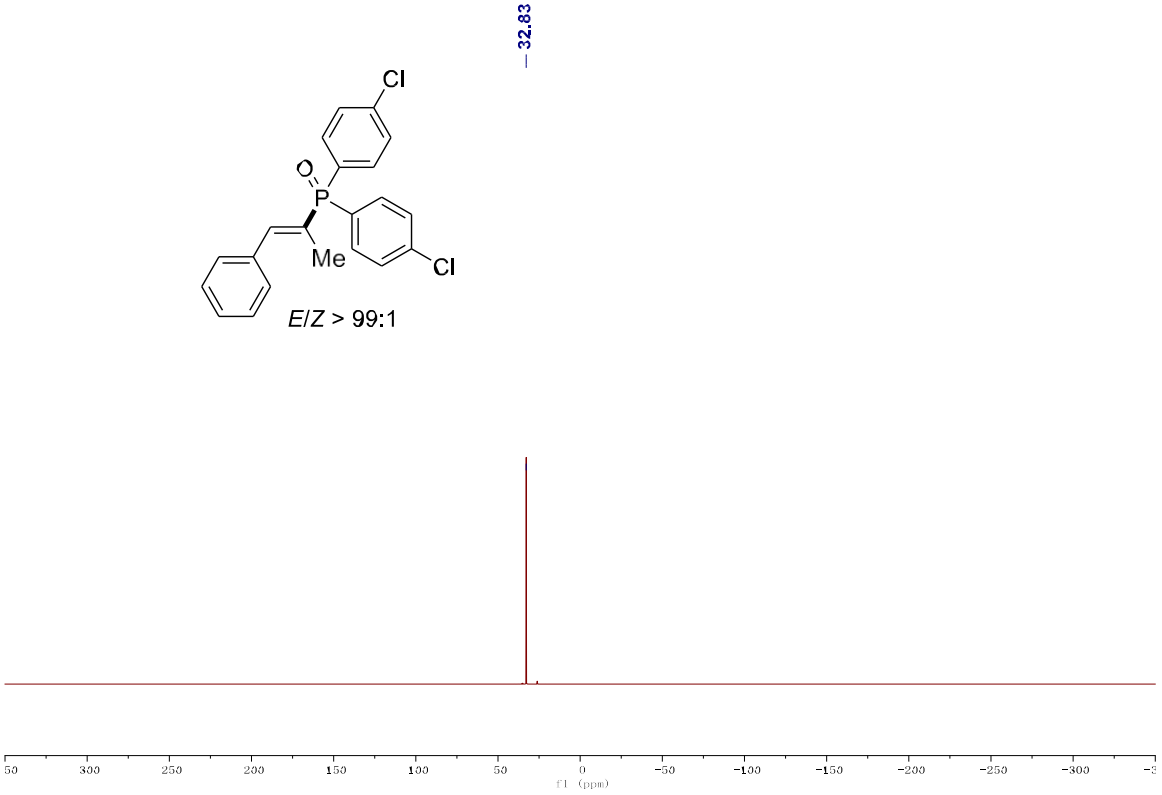
^{31}P NMR spectrum for compound **3ad** ($CDCl_3$)



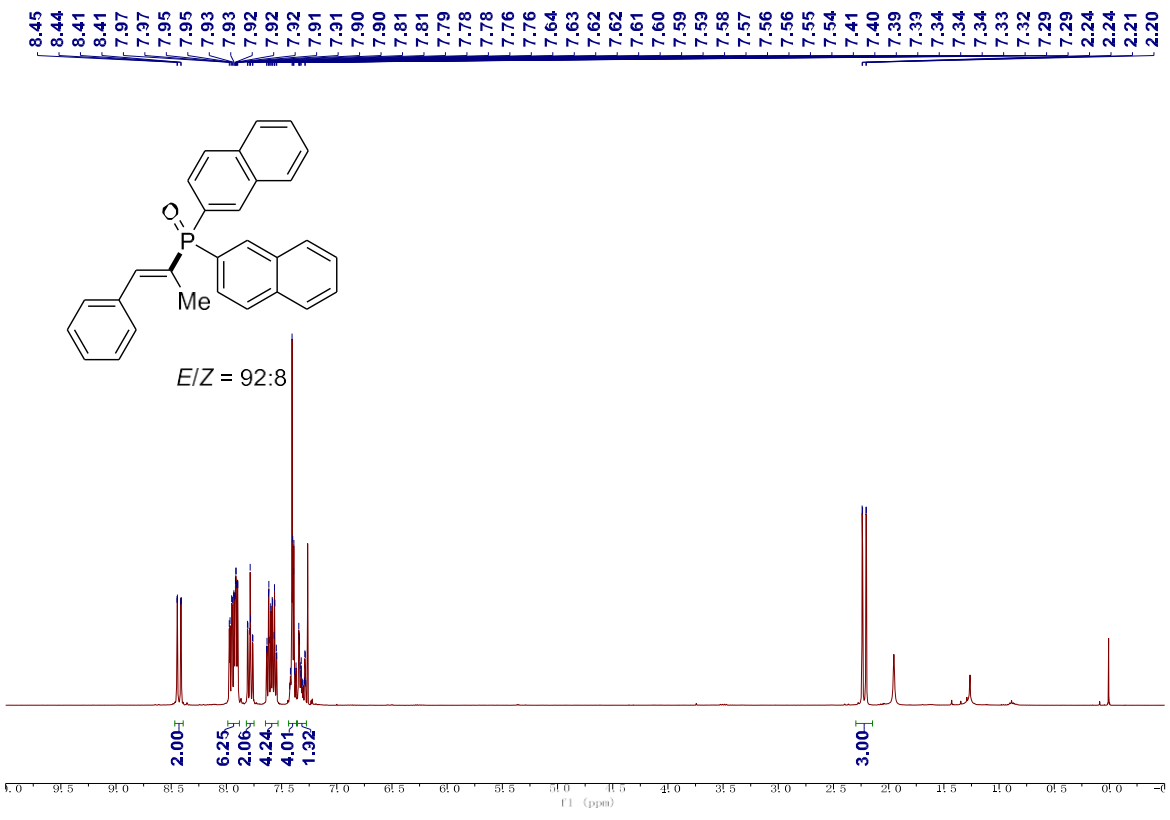
^{1}H NMR spectrum for compound **3ae** ($CDCl_3$)



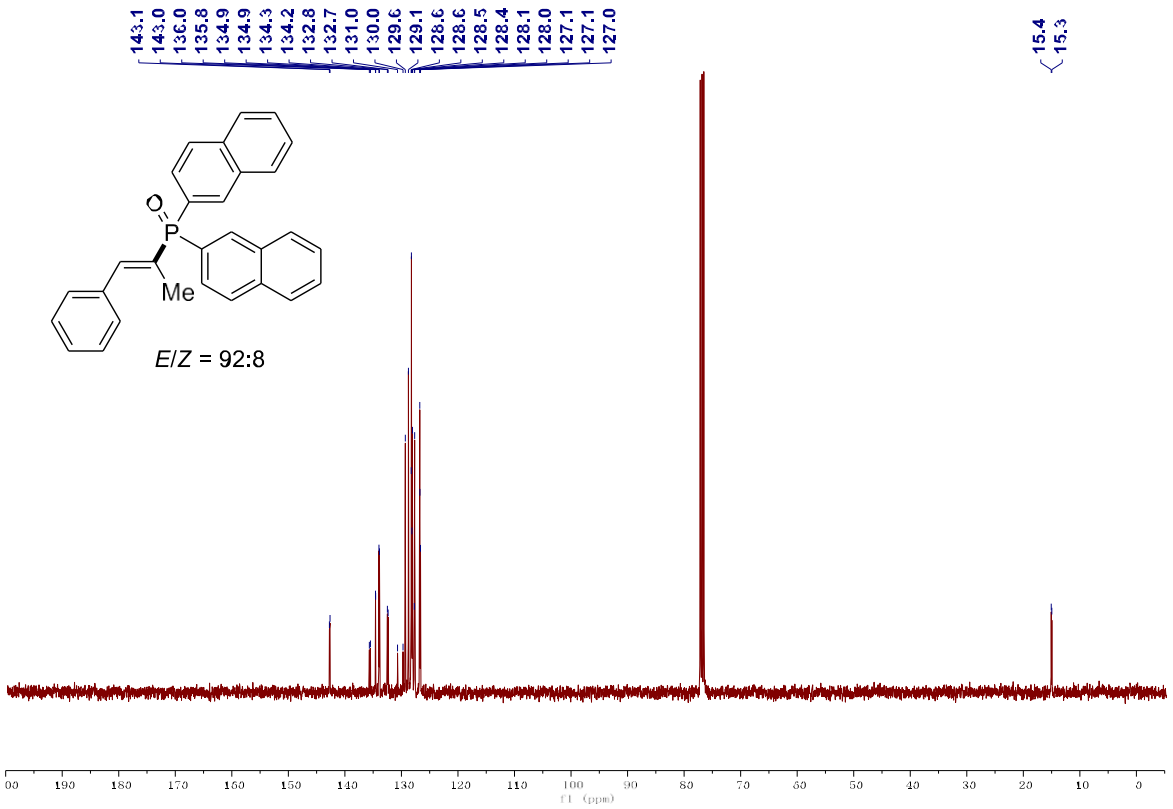
^{13}C NMR spectrum for compound **3ae** ($CDCl_3$)



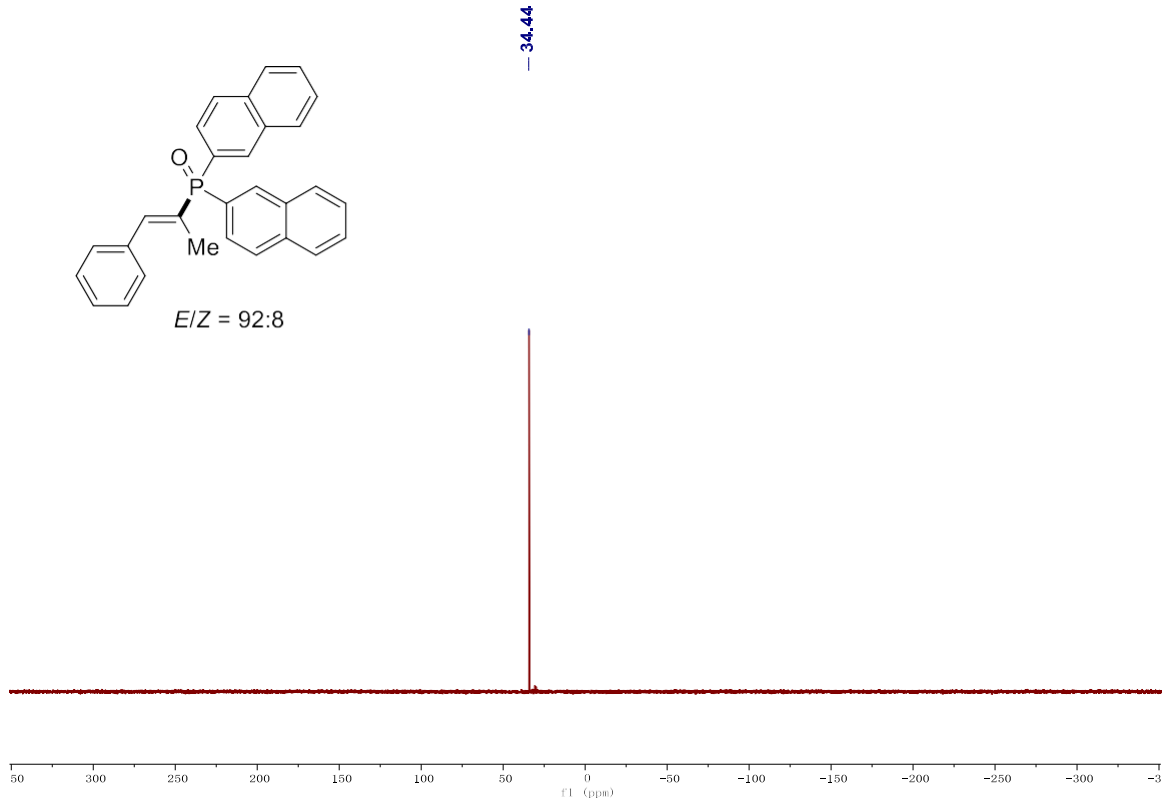
^{31}P NMR spectrum for compound **3ae** ($CDCl_3$)



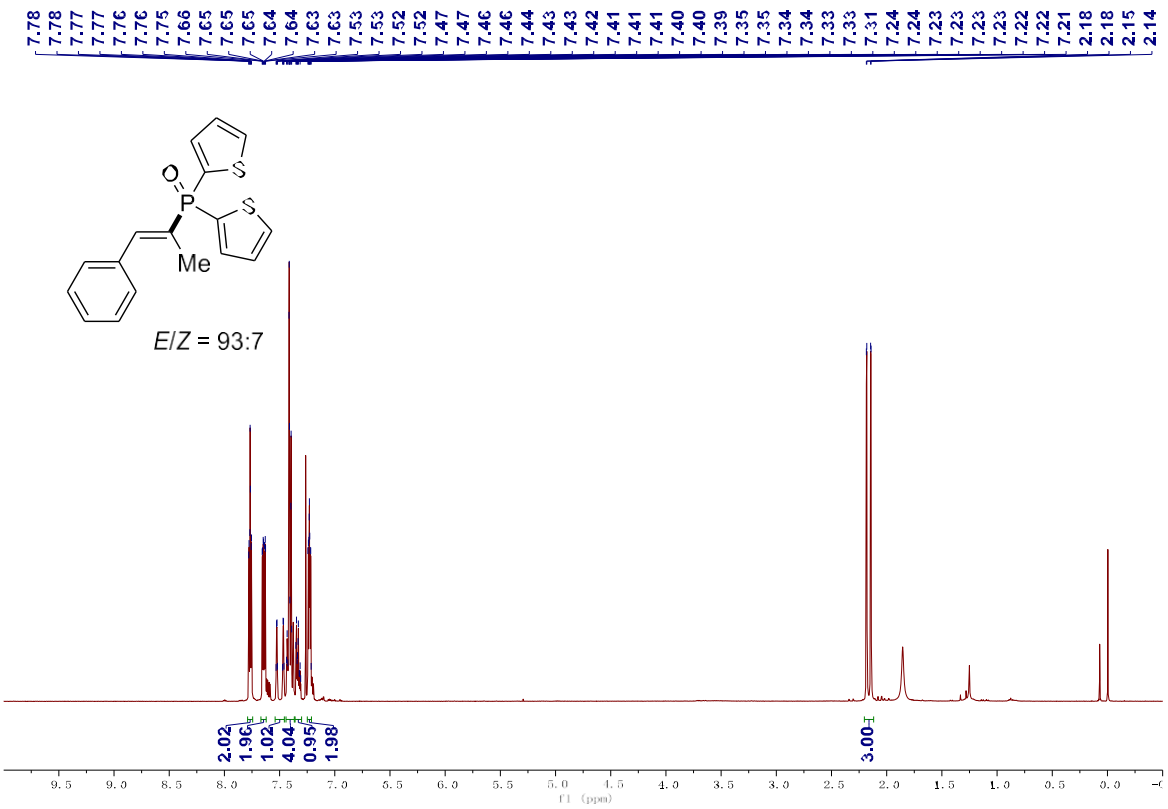
^{1}H NMR spectrum for compound **3af** ($CDCl_3$)



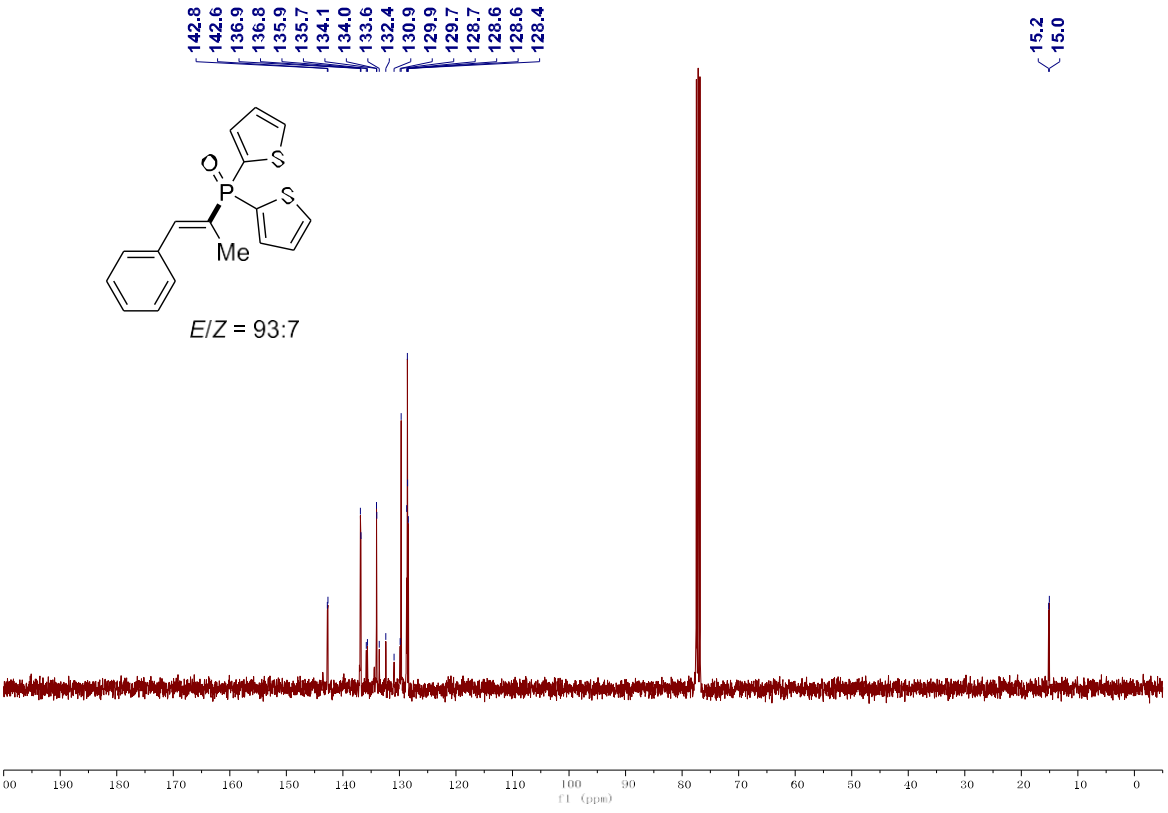
^{13}C NMR spectrum for compound **3af** ($CDCl_3$)



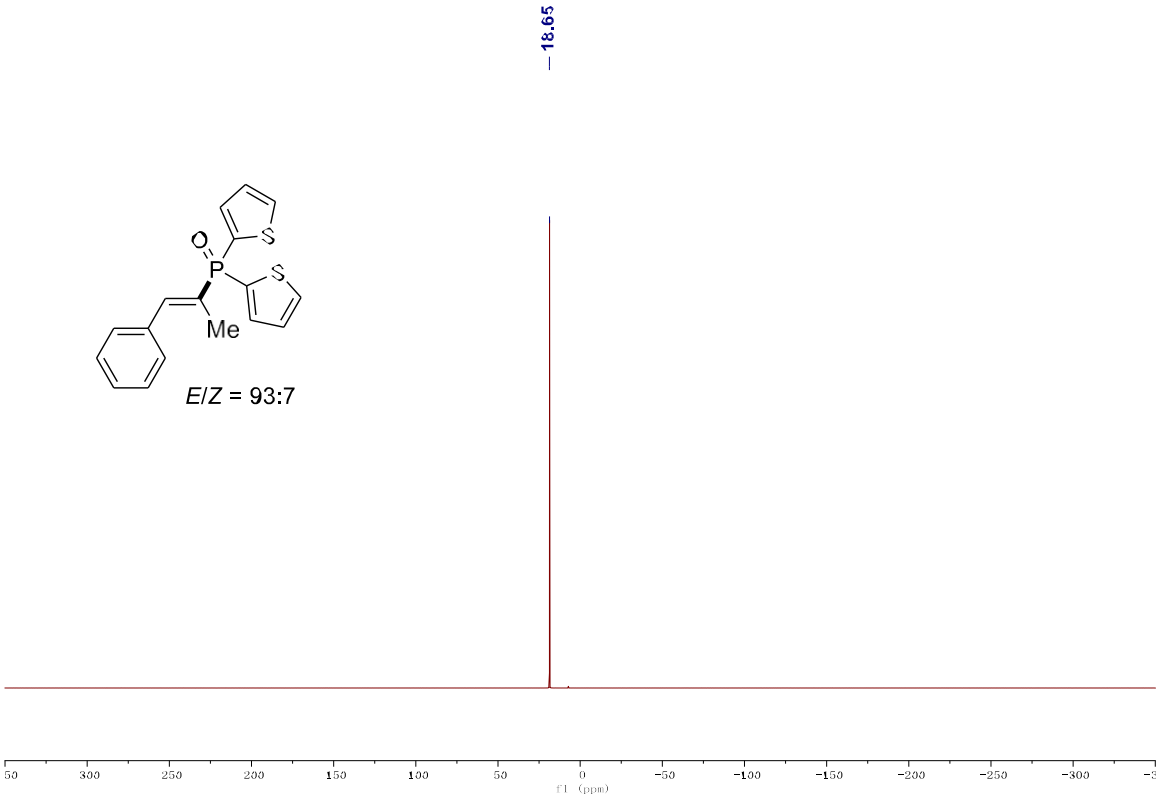
^{31}P NMR spectrum for compound **3af** ($CDCl_3$)



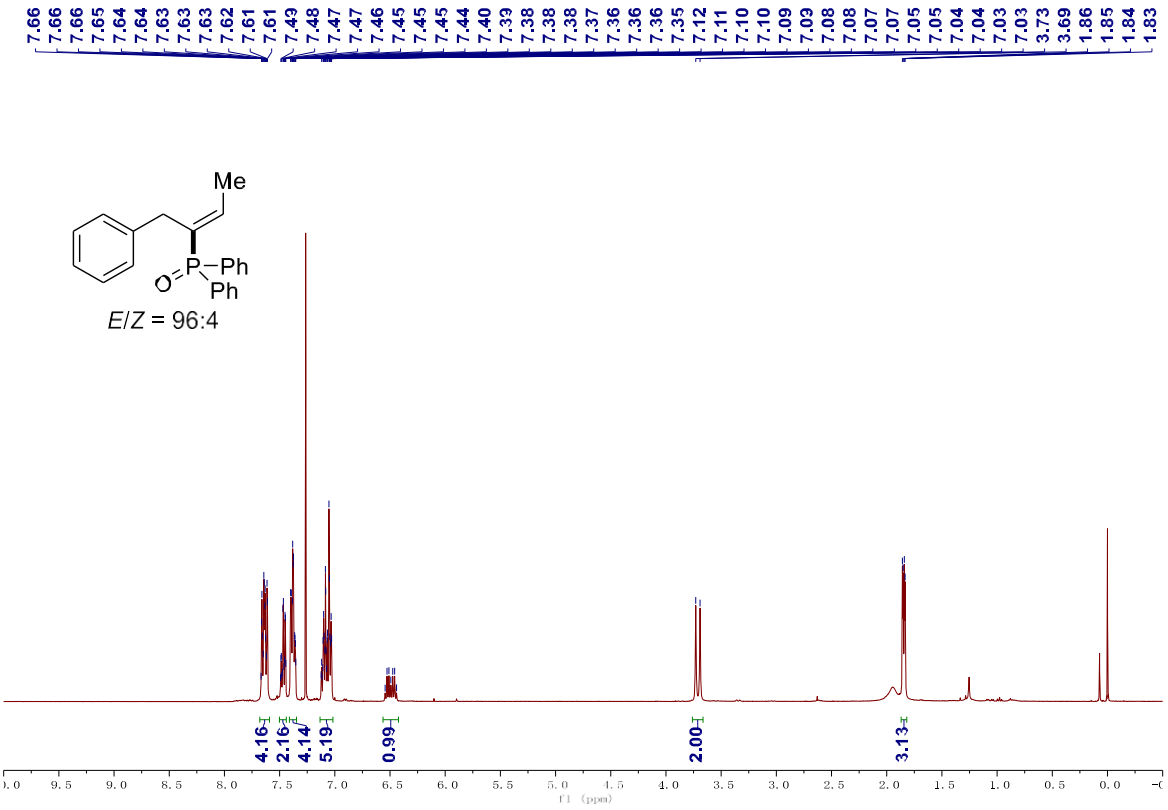
^{1}H NMR spectrum for compound **3ag** ($CDCl_3$)



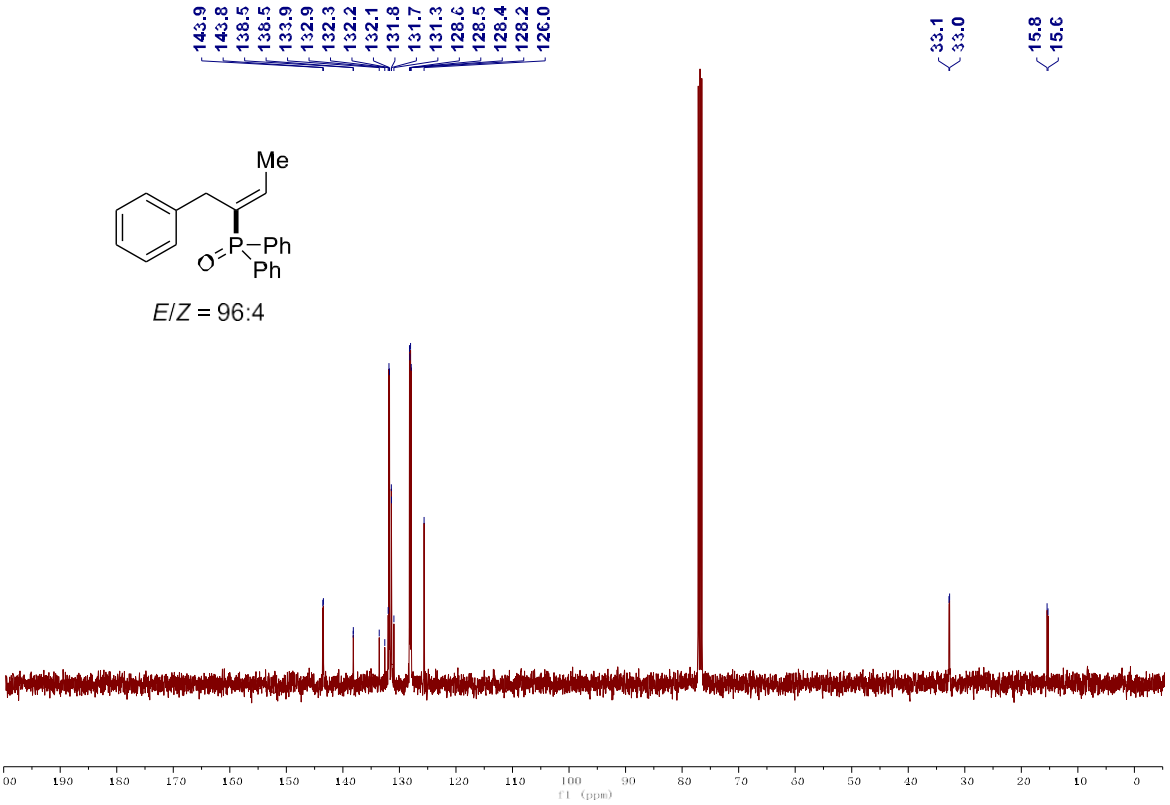
^{13}C NMR spectrum for compound **3ag** ($CDCl_3$)



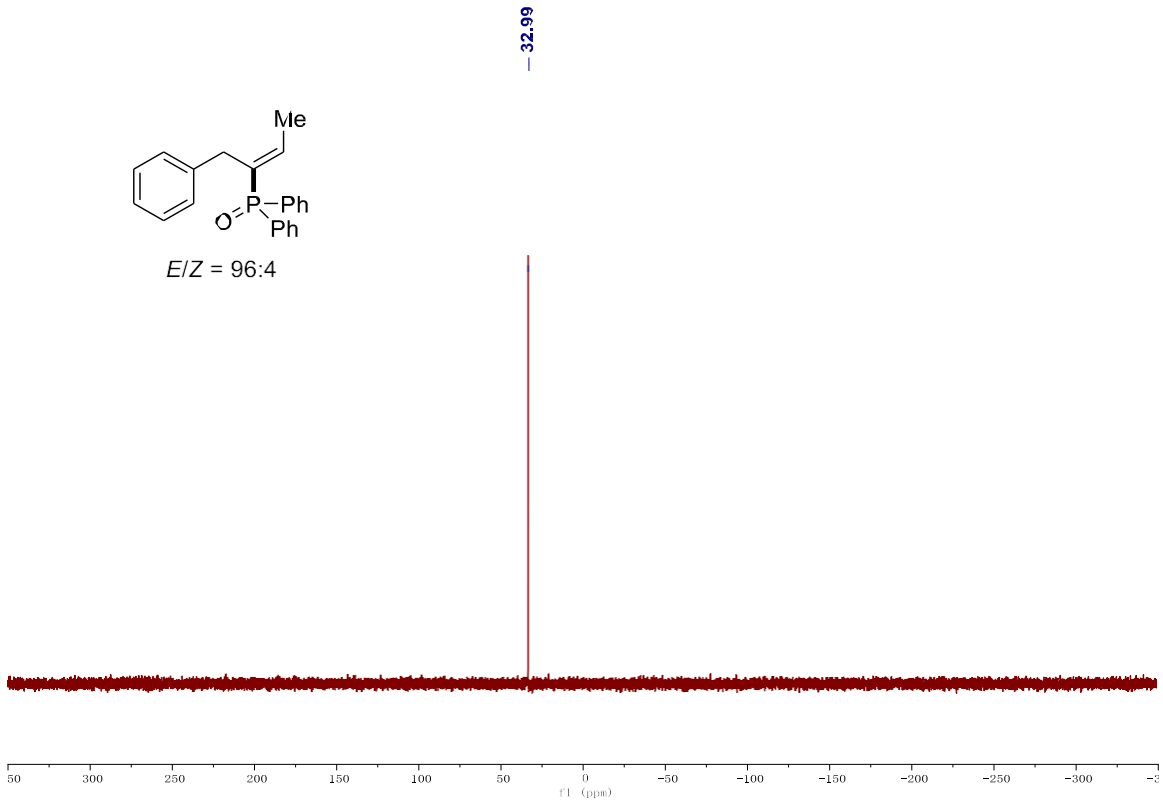
^{31}P NMR spectrum for compound **3ag** ($CDCl_3$)



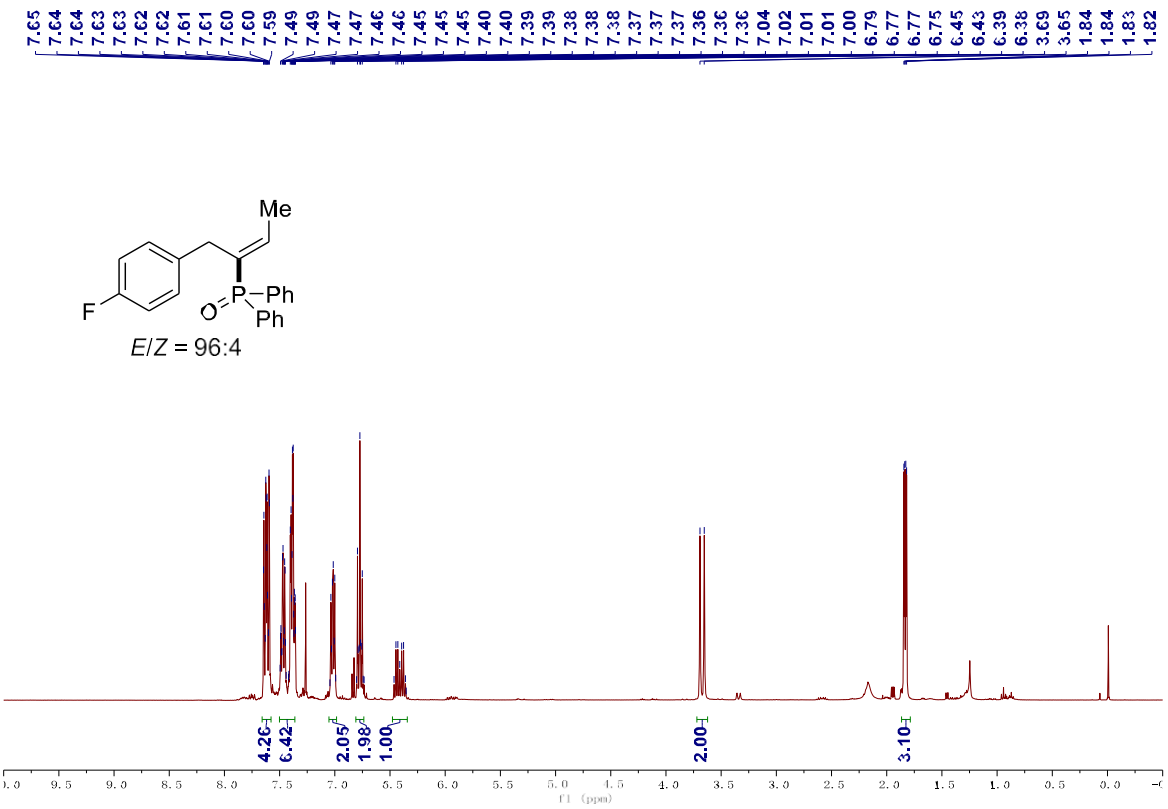
^{1}H NMR spectrum for compound **4a** ($CDCl_3$)



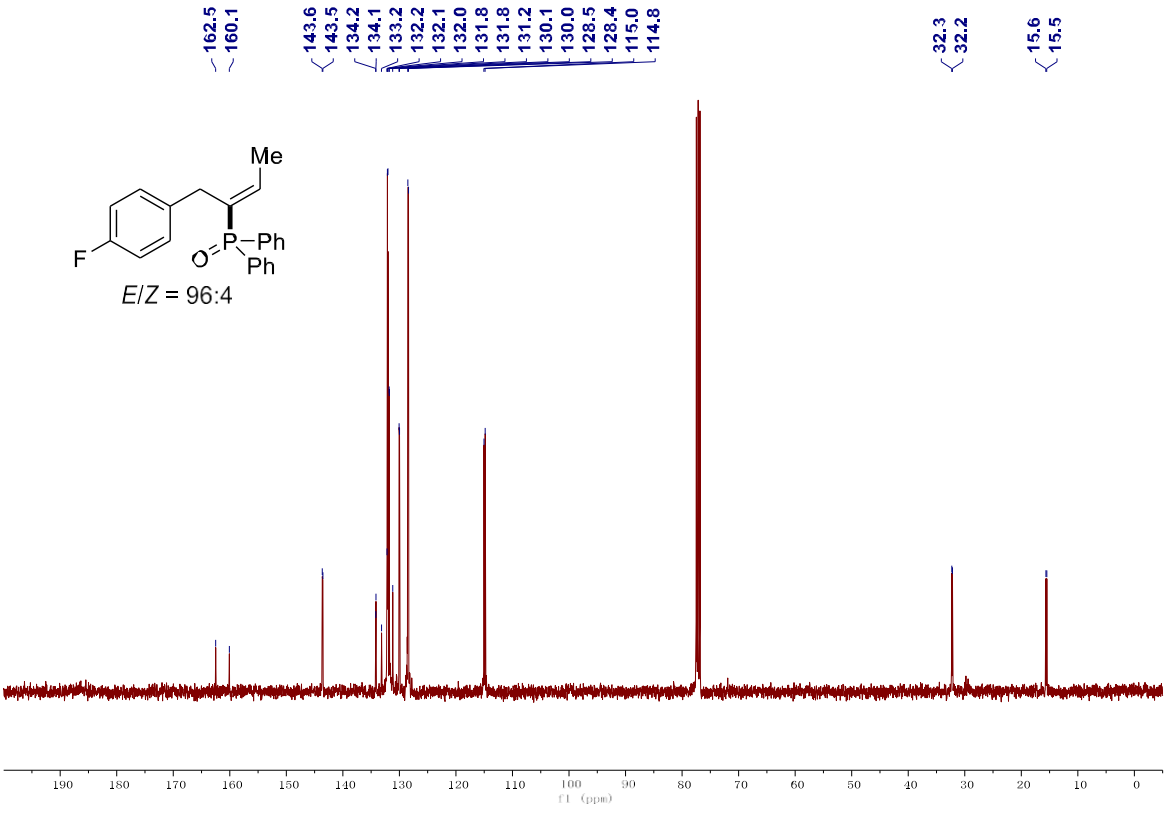
^{13}C NMR spectrum for compound **4a** ($CDCl_3$)



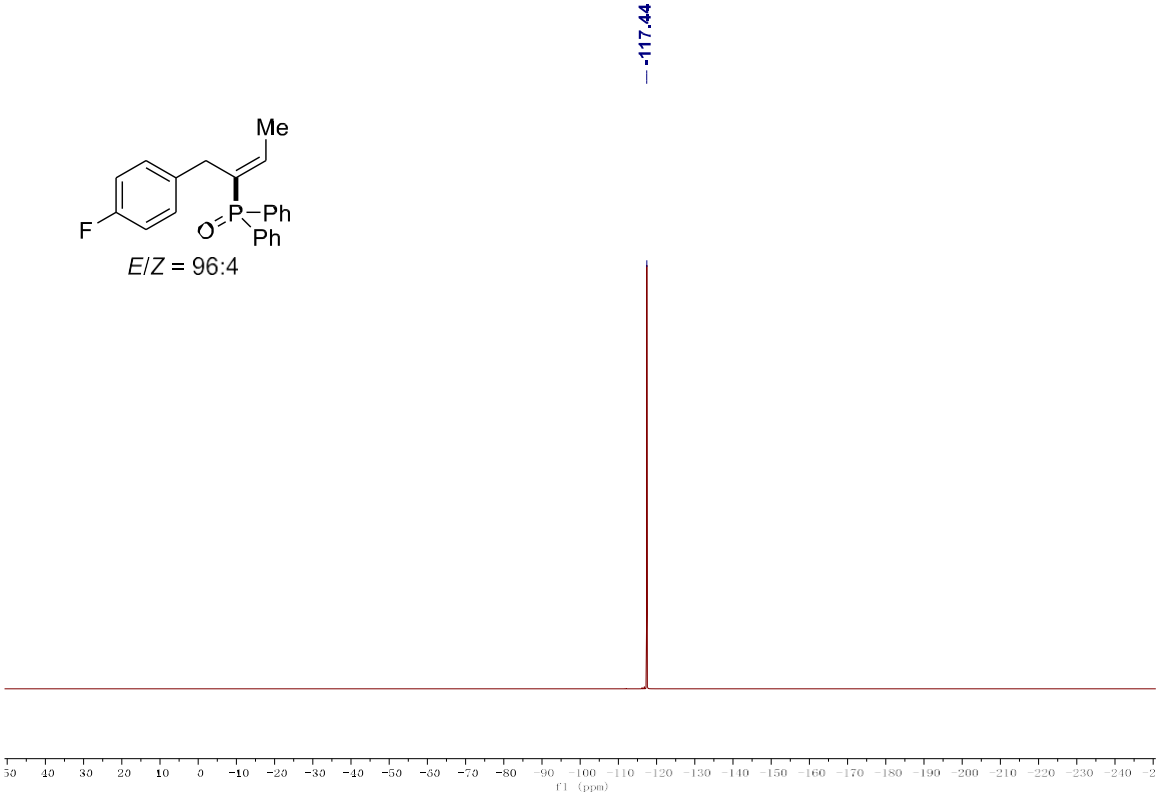
^{31}P NMR spectrum for compound **4a** ($CDCl_3$)



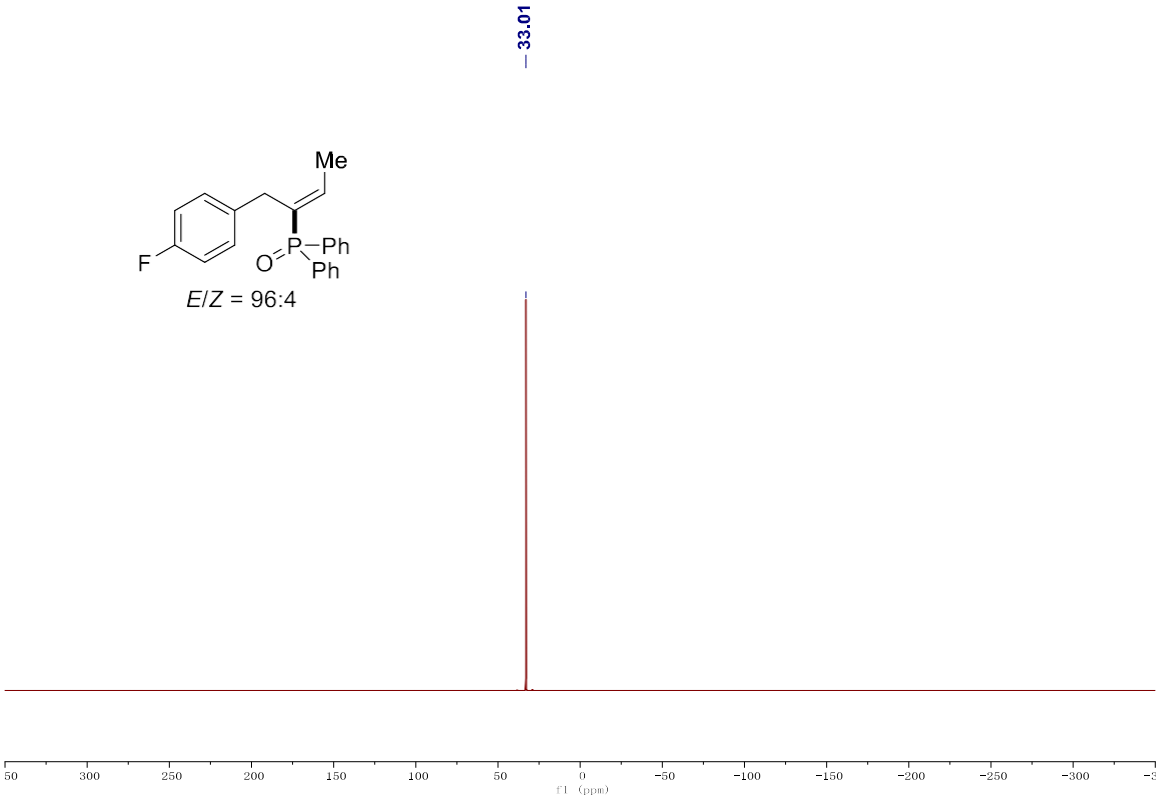
^{1}H NMR spectrum for compound **4b** ($CDCl_3$)



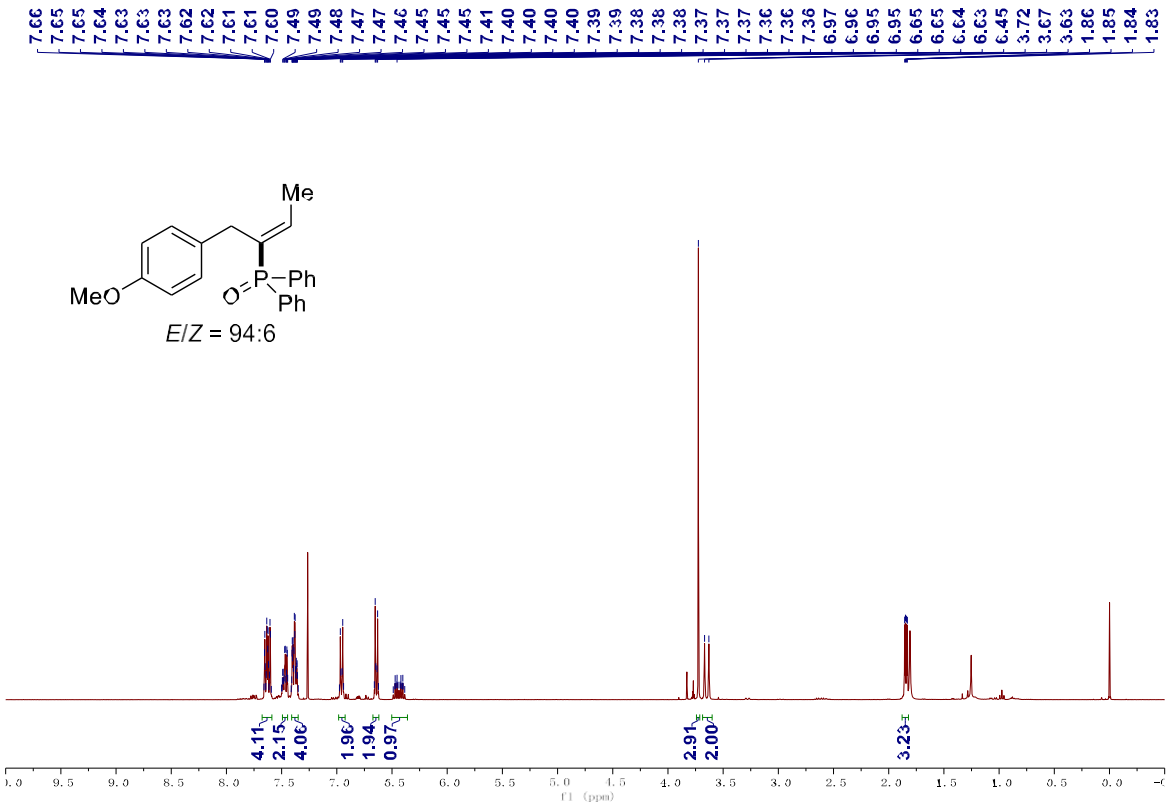
^{13}C NMR spectrum for compound **4b** ($CDCl_3$)



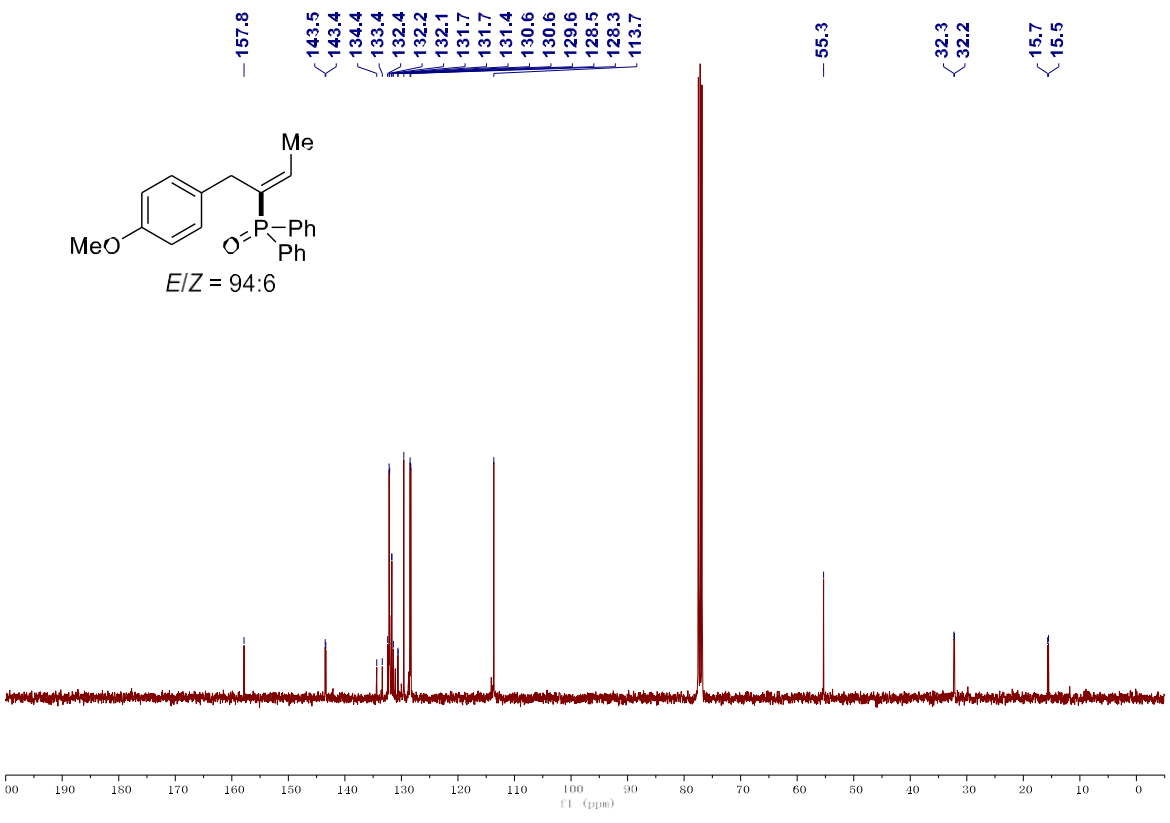
^{19}F NMR spectrum for compound **4b** ($CDCl_3$)



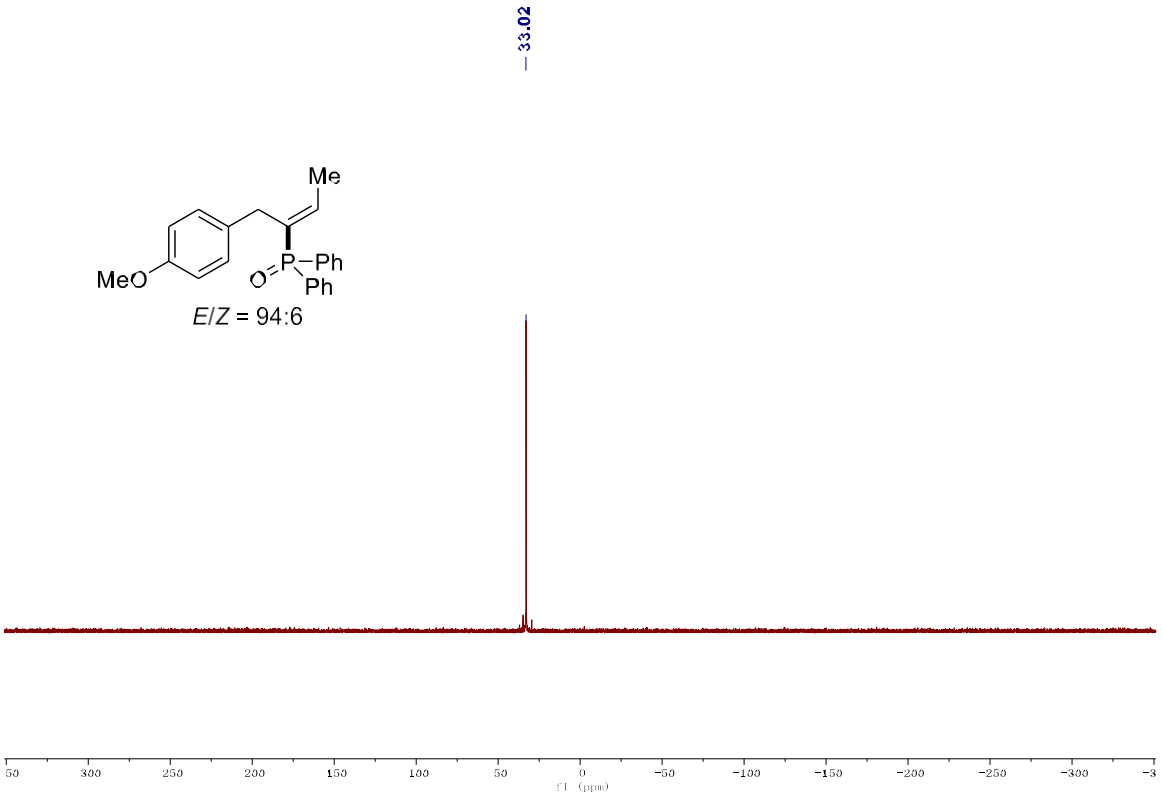
^{31}P NMR spectrum for compound **4b** ($CDCl_3$)



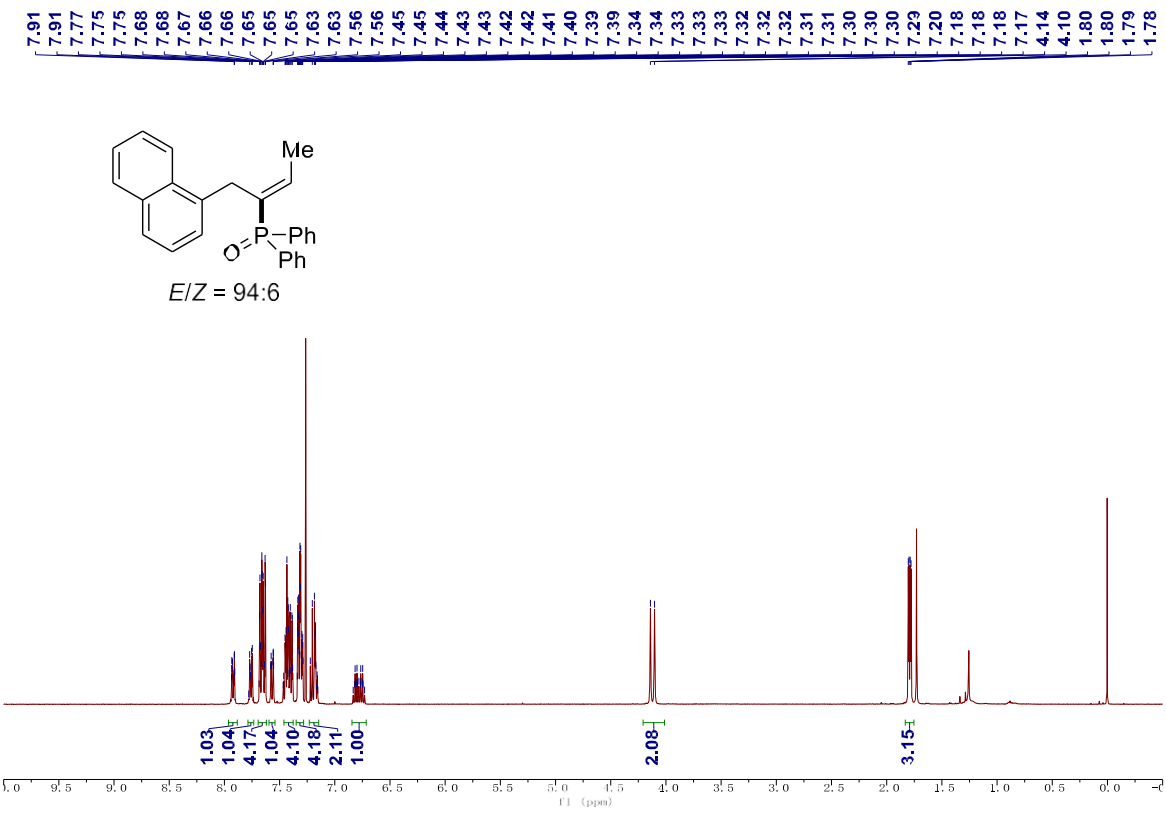
^{1}H NMR spectrum for compound **4c** ($CDCl_3$)



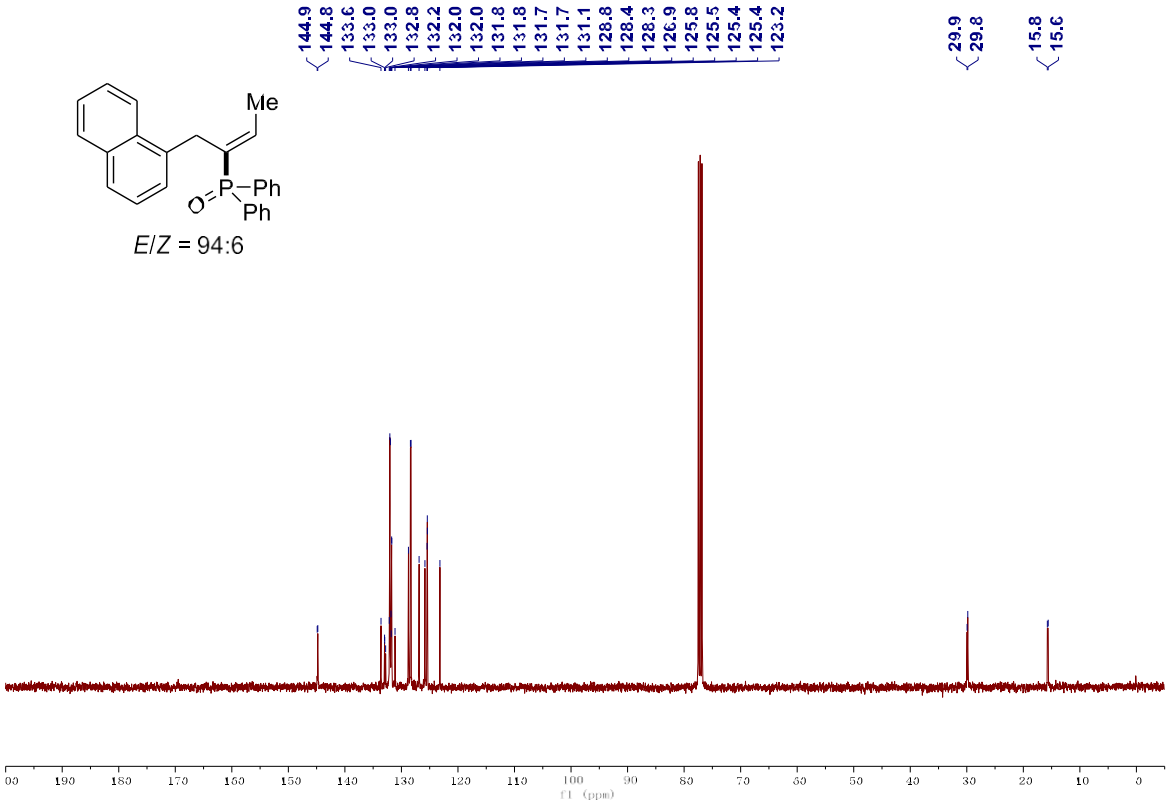
^{13}C NMR spectrum for compound **4c** ($CDCl_3$)



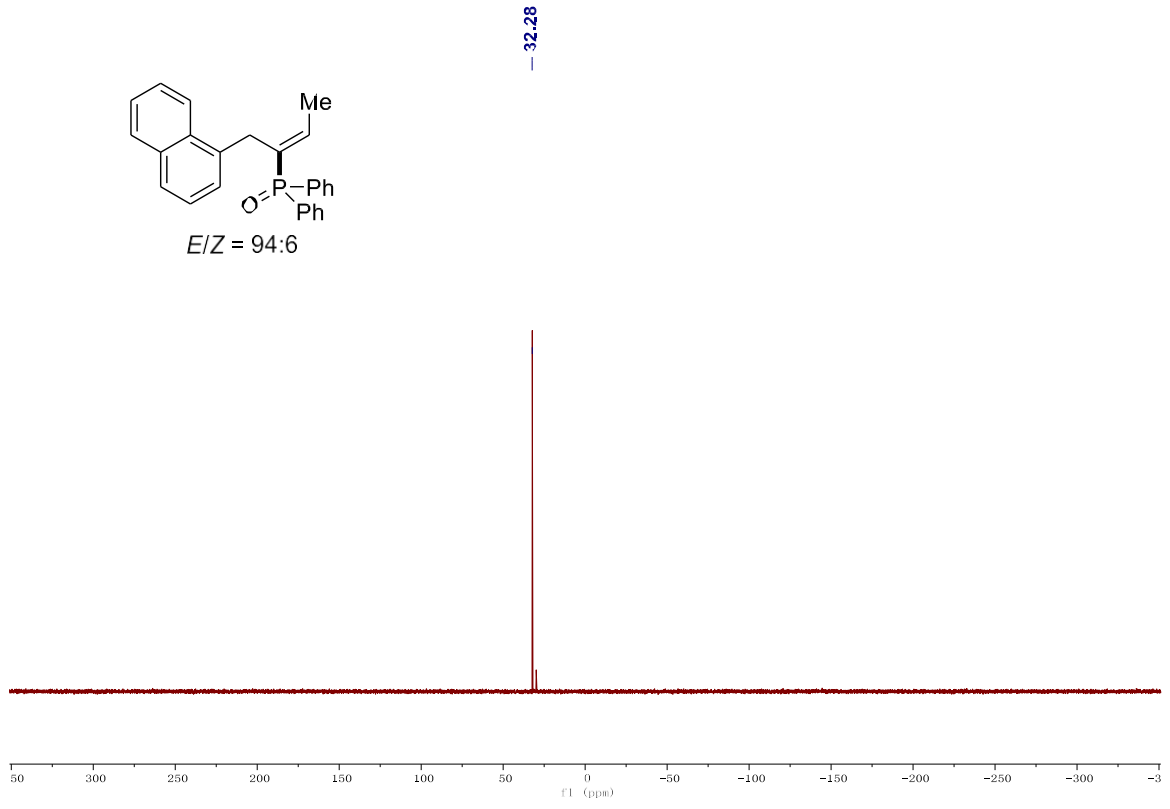
^{31}P NMR spectrum for compound **4c** ($CDCl_3$)



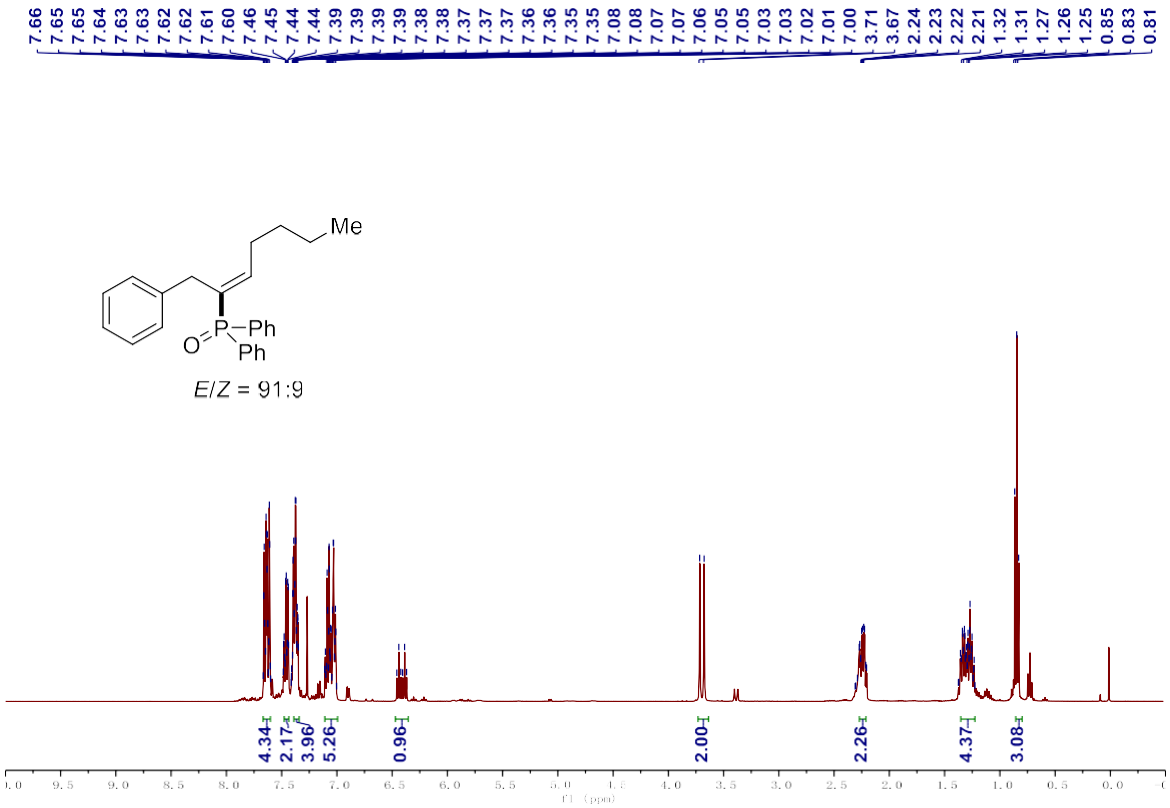
^{1}H NMR spectrum for compound **4d** ($CDCl_3$)



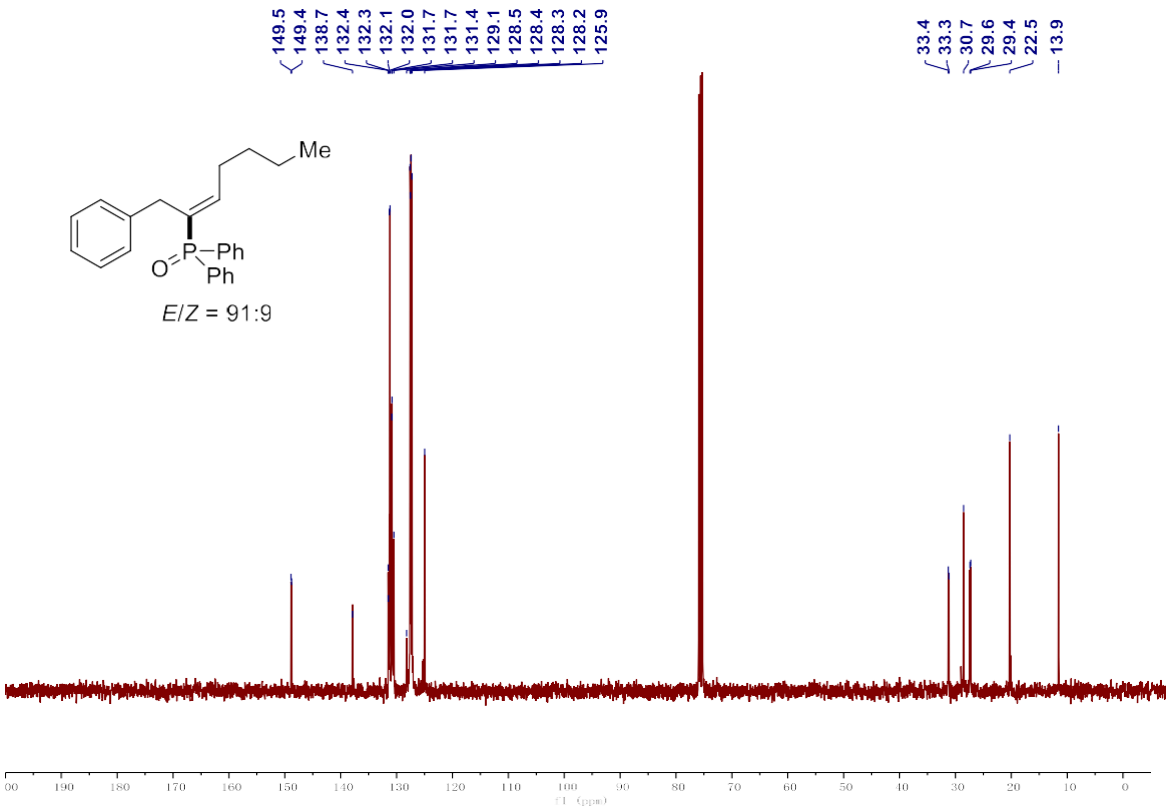
^{13}C NMR spectrum for compound **4d** ($CDCl_3$)



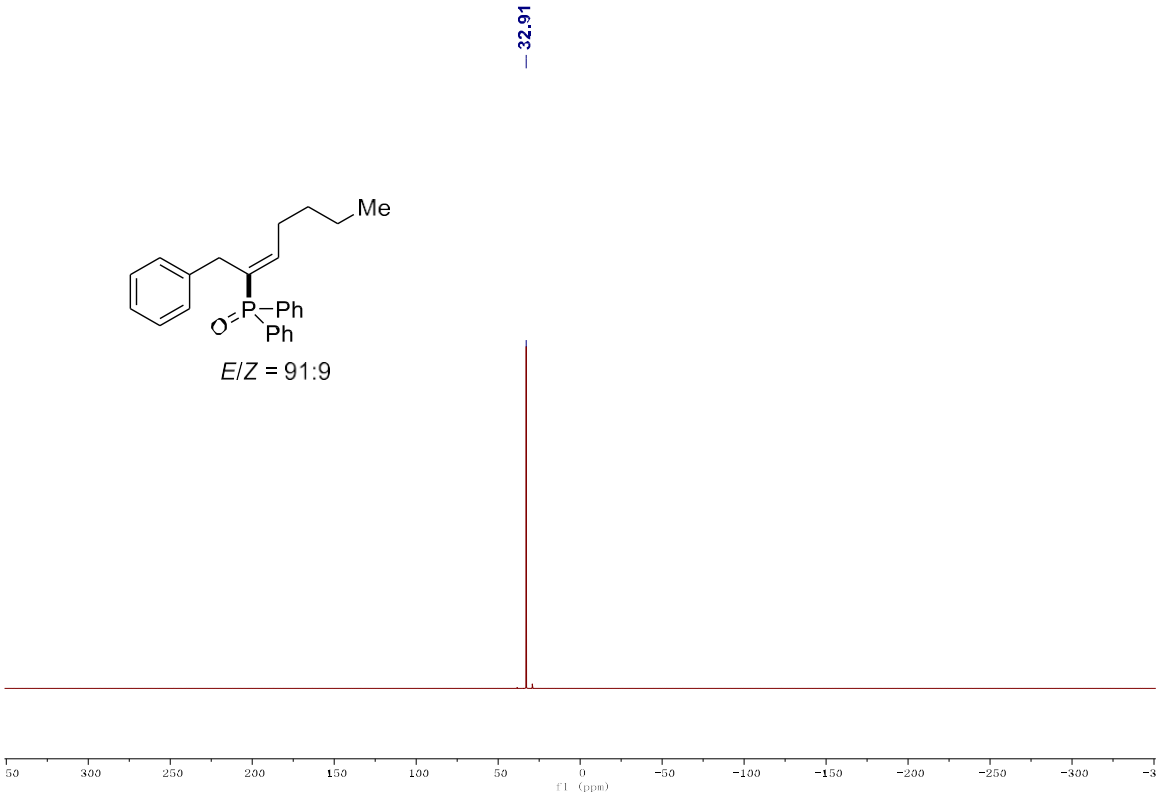
^{31}P NMR spectrum for compound **4d** ($CDCl_3$)



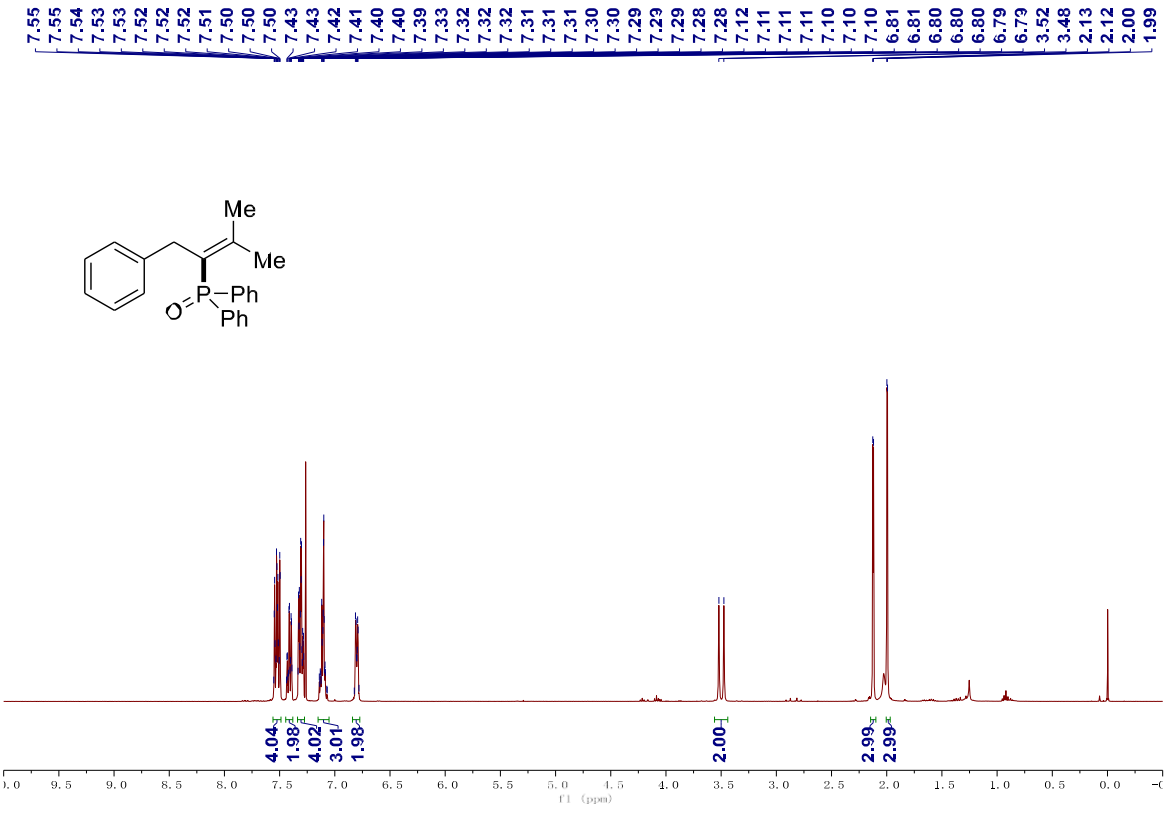
^{1}H NMR spectrum for compound **4e** ($CDCl_3$)



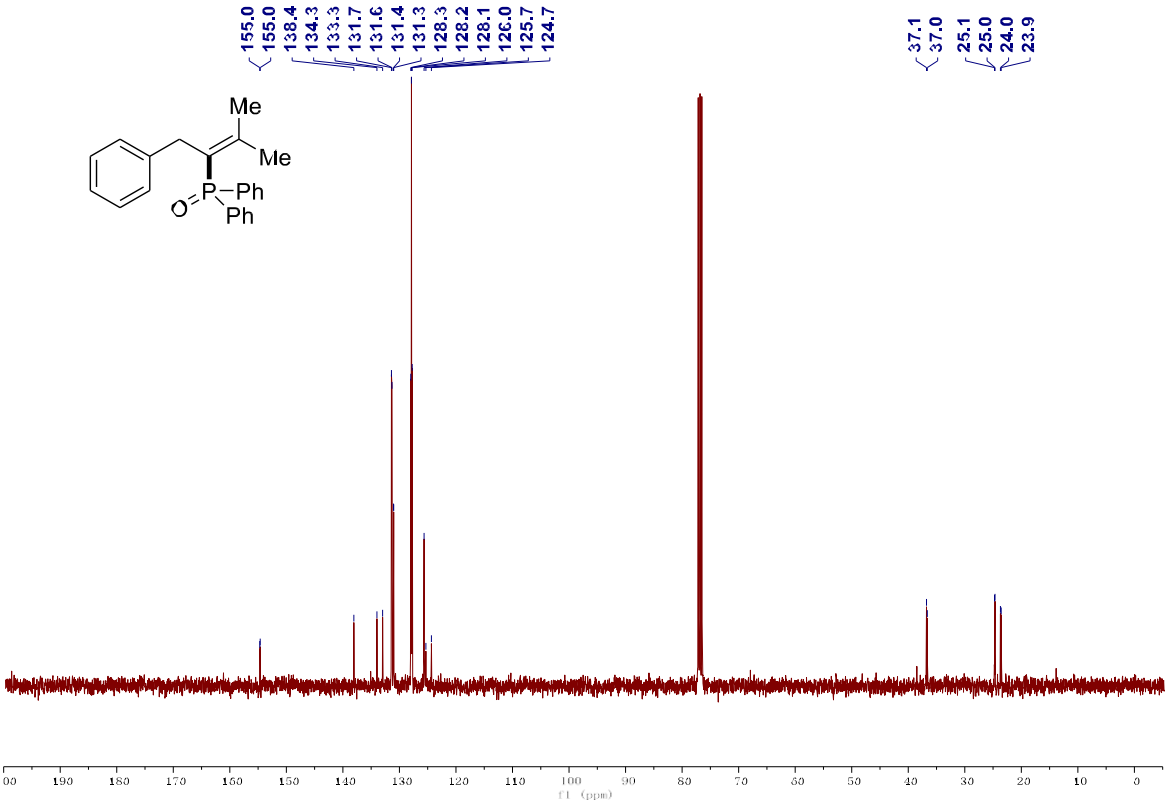
^{13}C NMR spectrum for compound **4e** ($CDCl_3$)



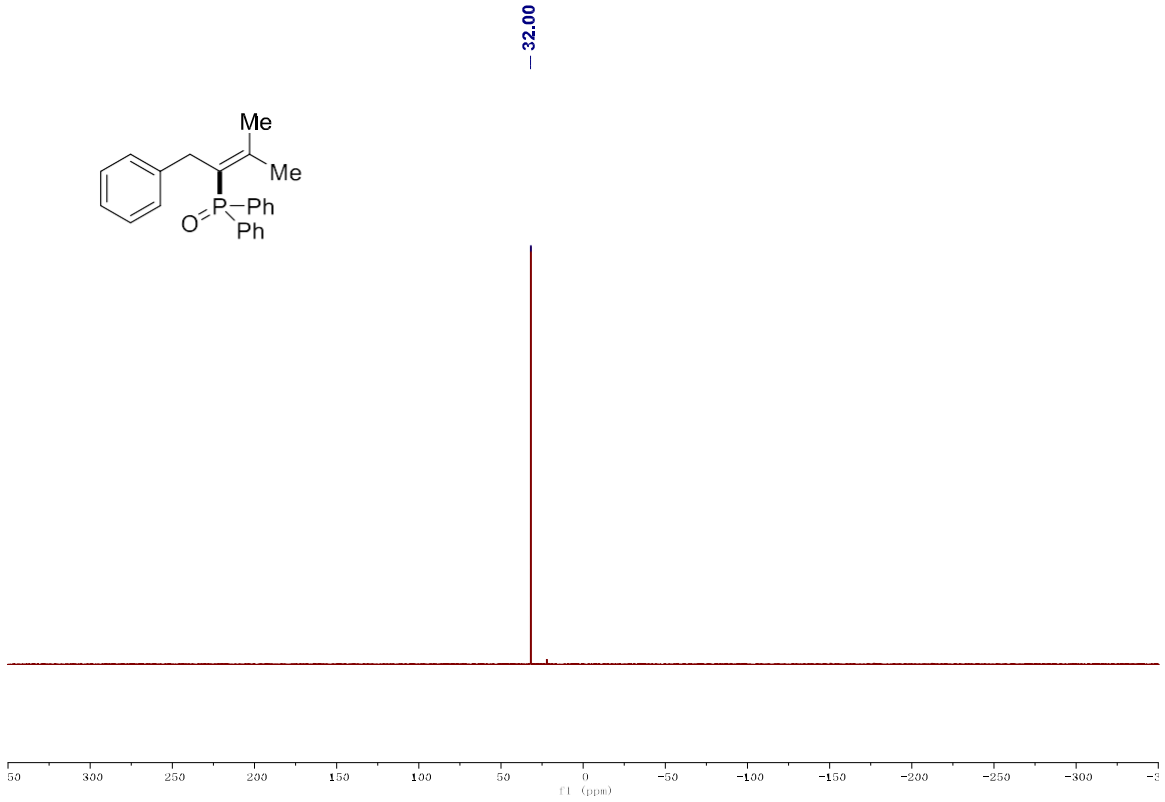
^{31}P NMR spectrum for compound **4e** ($CDCl_3$)



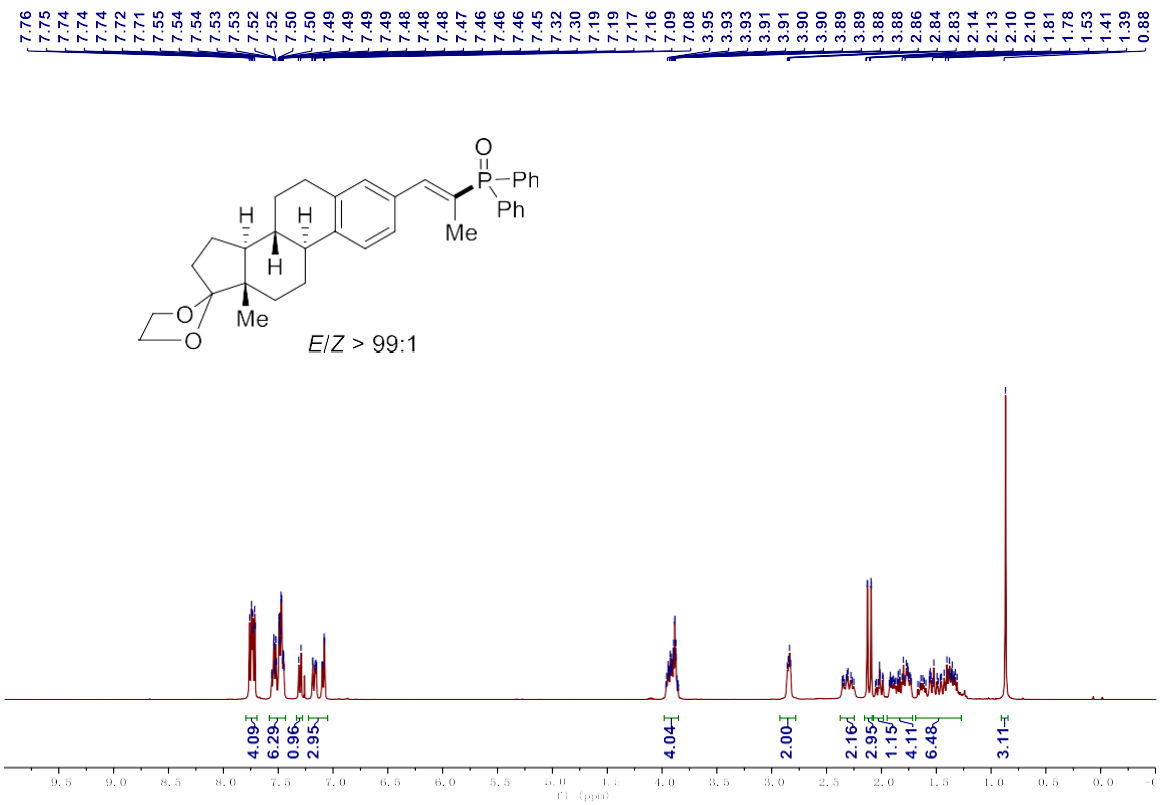
^{1}H NMR spectrum for compound **4f** ($CDCl_3$)



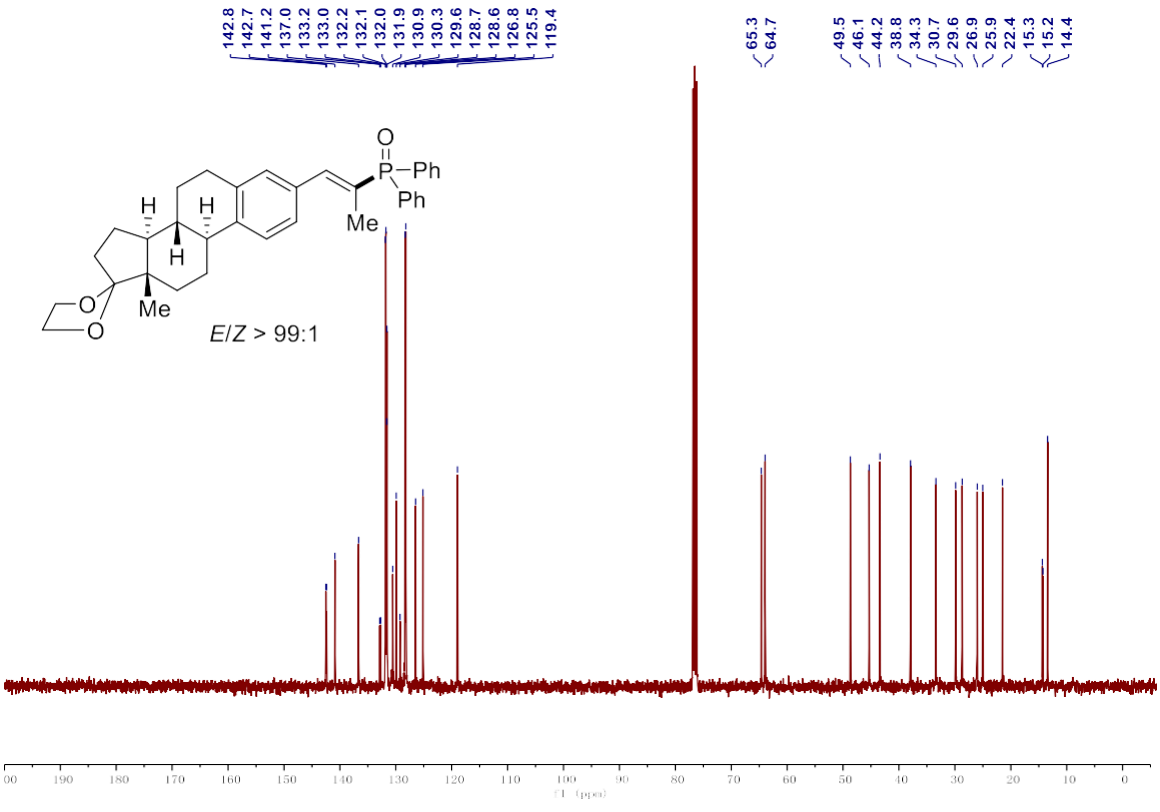
^{13}C NMR spectrum for compound **4f** ($CDCl_3$)



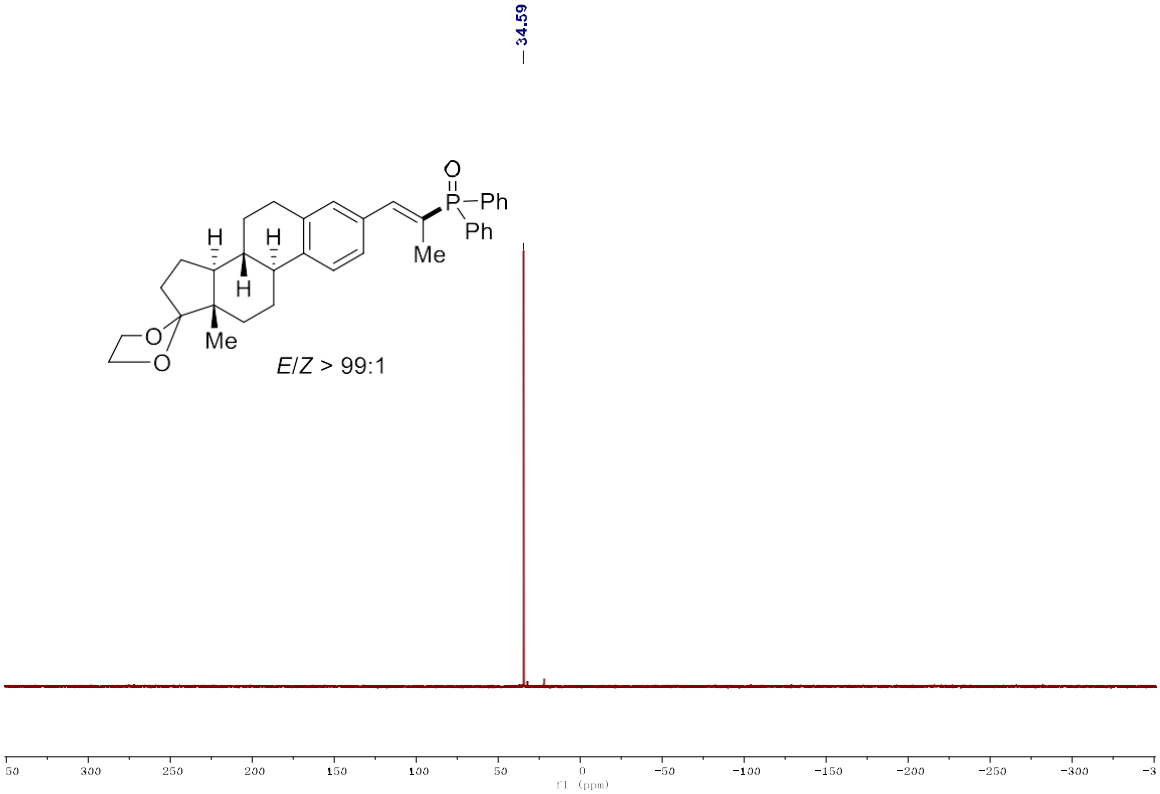
^{31}P NMR spectrum for compound **4f** ($CDCl_3$)



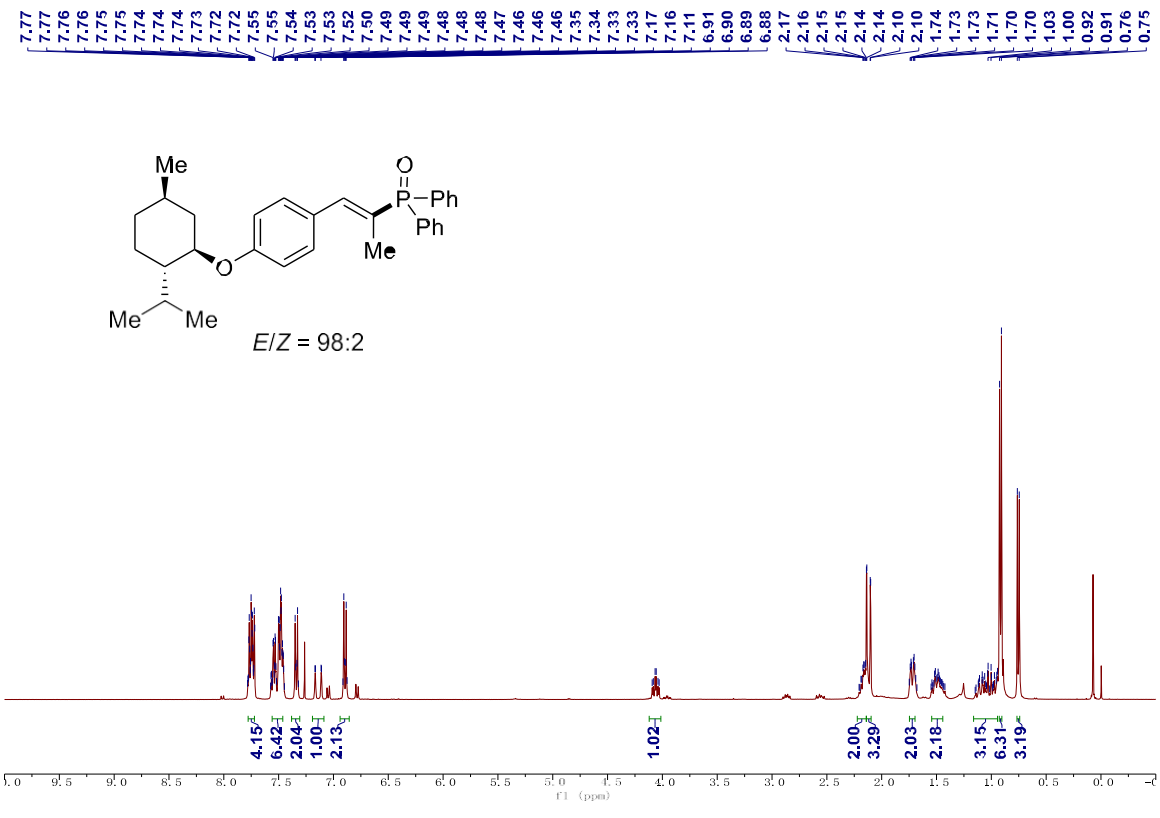
^{1}H NMR spectrum for compound **3aj** ($CDCl_3$)



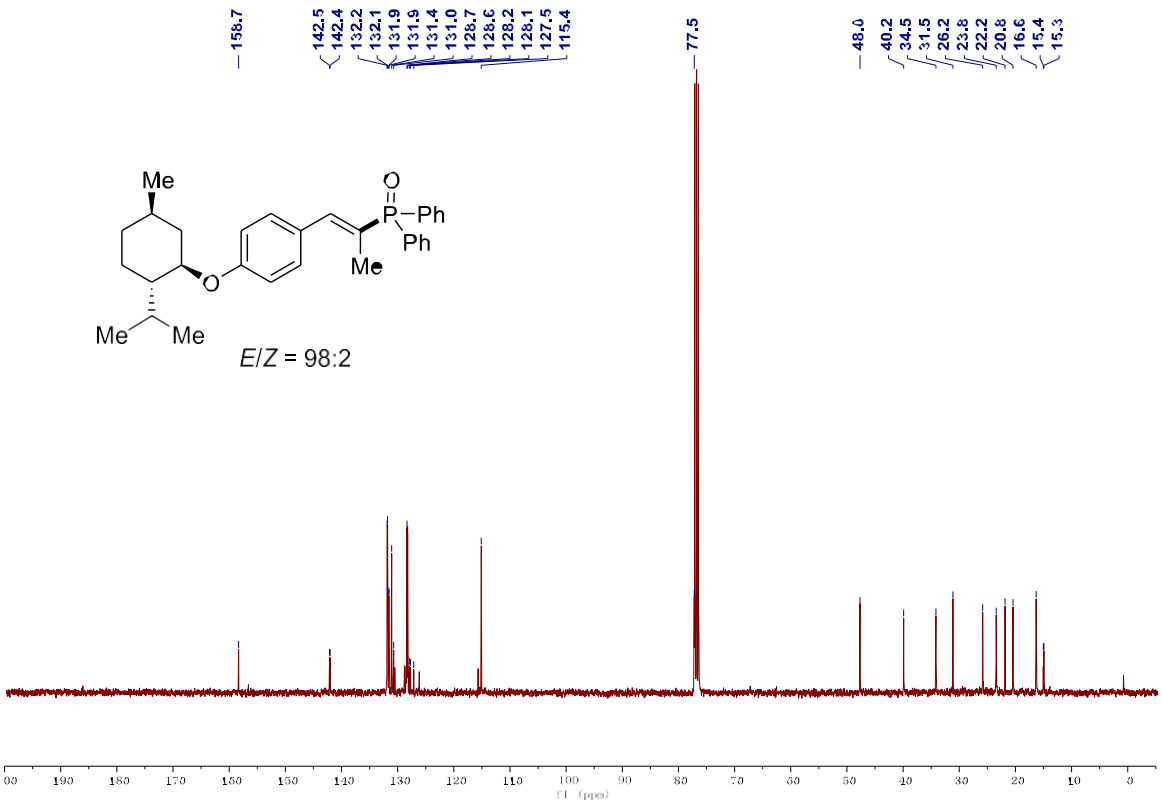
^{13}C NMR spectrum for compound **3aj** ($CDCl_3$)



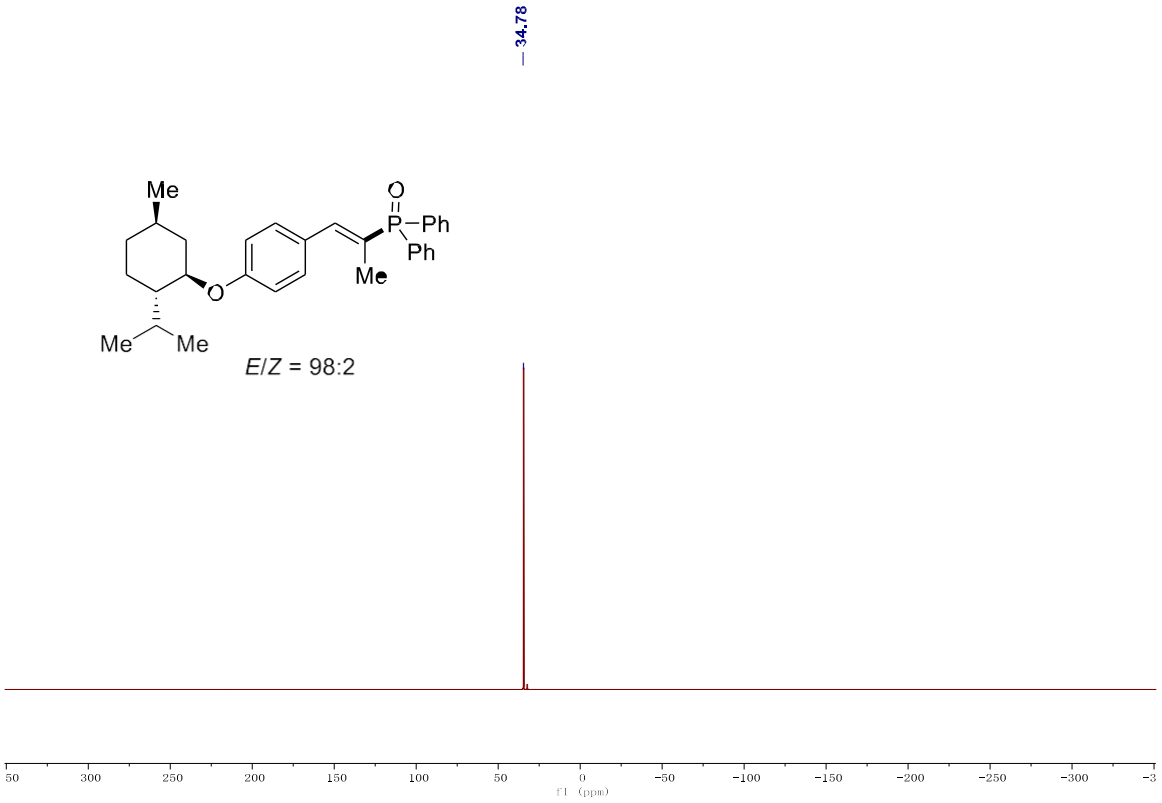
^{31}P NMR spectrum for compound **3aj** ($CDCl_3$)



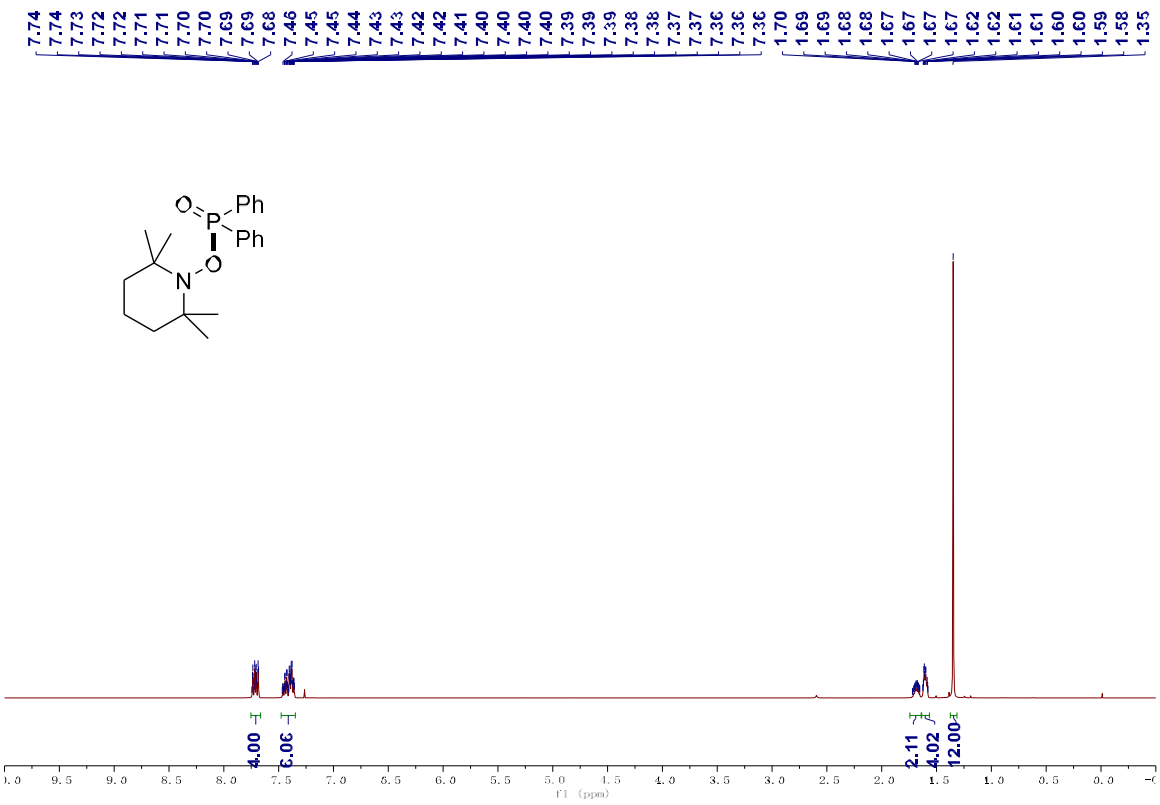
^{1}H NMR spectrum for compound **3ak** ($CDCl_3$)



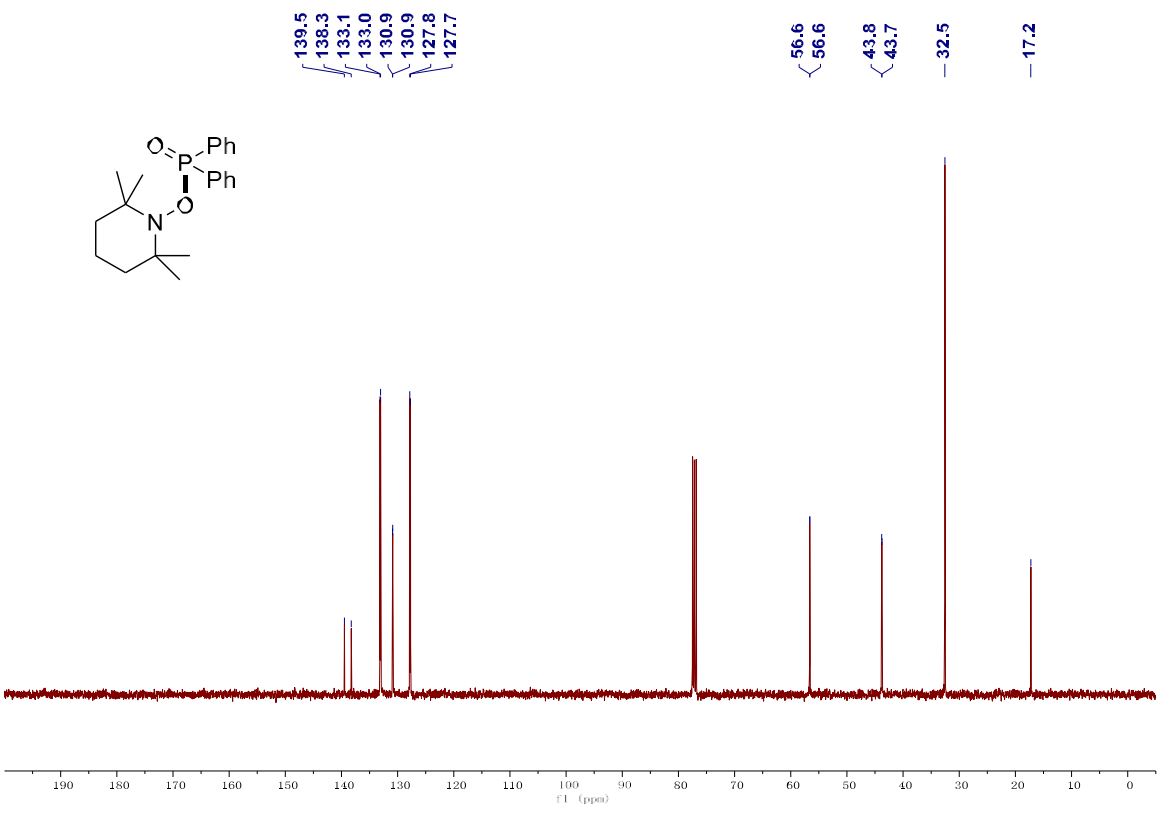
^{13}C NMR spectrum for compound **3ak** ($CDCl_3$)



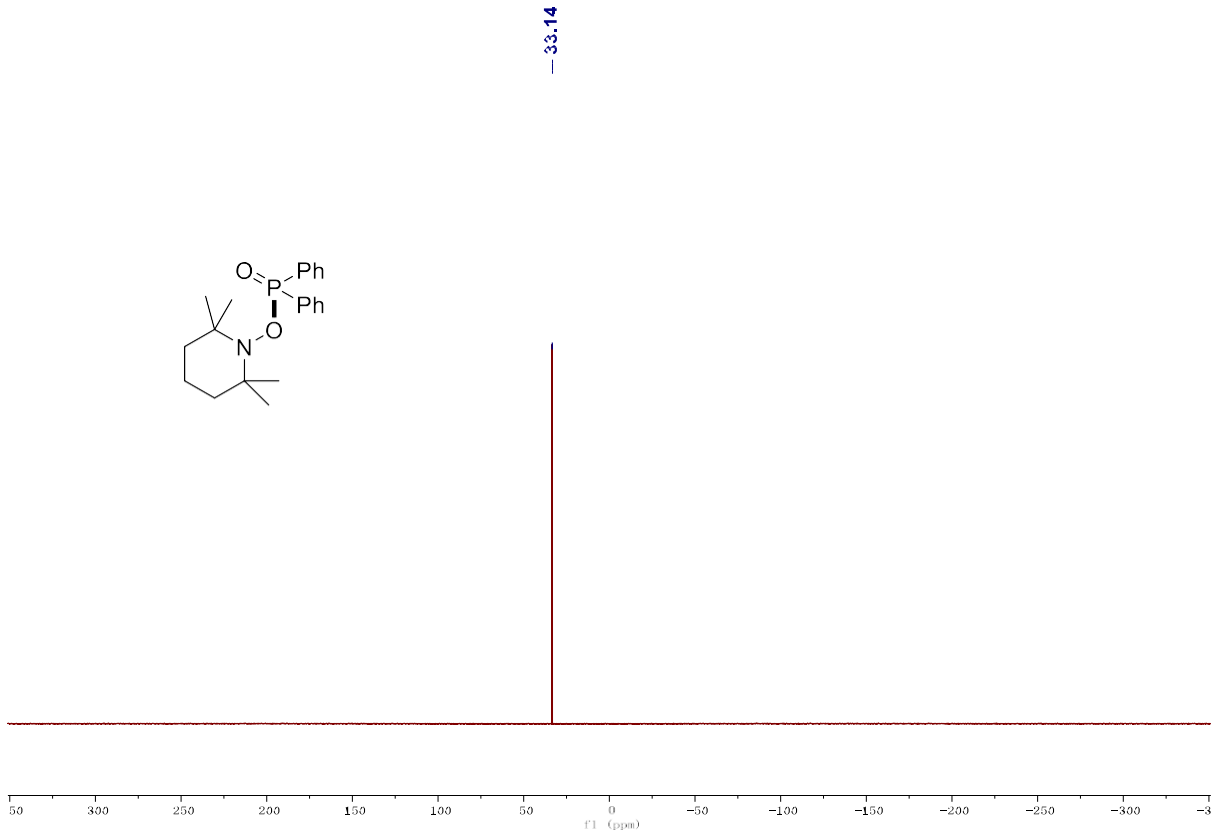
^{31}P NMR spectrum for compound **3ak** ($CDCl_3$)



^{1}H NMR spectrum for compound **5a** ($CDCl_3$)



^{13}C NMR spectrum for compound **5a** ($CDCl_3$)



^{31}P NMR spectrum for compound **5a** ($CDCl_3$)