Palladium-Catalyzed (Z)-Selective Allylation of Phosphine Oxides with Vinylethylene Carbonates to Construct Phosphorus Allyl Alcohols

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Supporting Information

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1. General Information

General Procedures. All reactions were performed in oven-dried or flame-dried reaction vessels, modified Schlenk flasks, or round-bottom flasks. The flasks were fitted with Teflon screw caps and reactions were conducted under an atmosphere of argon if needed. Gas-tight syringes with stainless steel needles were used to transfer air- and moisture-sensitive liquids. All moisture and/or air sensitive solid compounds were manipulated inside normal desiccators. Flash column chromatography was performed over silica gel (40 – 45 μm, 300 – 400 mesh).

Analytical thin layer chromatography (TLC) was performed on silica gel $HSGF_{254}$ glass plates (purchased from Jiangyou silica gel development Co., Ltd, Yantai, China) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) or I_2 and to a solution of $KMnO_4$ (1 g of $KMnO_4$, 6 g of K_2CO_3 and 0.1 g of KOH in 100 mL of H_2O) or vanillin (2 g of vanillin and 4 mL of concentrated H_2SO_4 in 100 mL of EtOH) followed by heating.

Organic solutions were concentrated at 30 – 40 °C on rotary evaporators at ~80 mbar followed by drying on vacuum pump below 1 mbar. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Materials. Commercial reagents and solvents were were obtained from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin, Energy Chemical and Leyan and used as received with the following exceptions: THF, 1,4-dioxane and toluene were purified by refluxing over Na-benzophenone under positive argon pressure followed by distillation.[1] The variety of substituted P(O)−H compounds (**1b, 1c, 1d, 1e, 1f**) were synthesized according to literature procedures.[2] The vinylethylene carbonates (VECs) **2** were synthesized according to the reported literature procedures.[3]

Instrumentation.

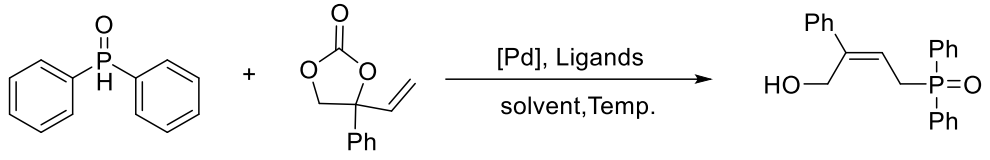
- Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured on a JEOL JNM-ECZ600R/S1 spectrometer at ambient temperature for ^{1}H at 600 MHz. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using tetramethylsilane (TMS) as an internal standard or residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$) or DMSO-d_6: δ 2.50 (CD_2HSOCD_3)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet

of doublets, td = triplet of doublets, brs = broad singlet), coupling constant(s) (Hz), integration].

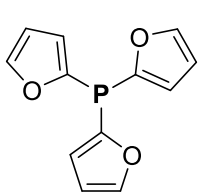
- Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra measured on a JEOL JNM-ECZ600R/S1 spectrometer at ambient temperature for ^{13}C at 151 MHz. Carbon chemical shifts are reported in parts per million (δ scale), and are referenced using the carbon resonances of the solvent (δ 77.00 ($CDCl_3$) or δ 39.52 (DMSO-d_6)). Data are reported as follows: chemical shift [multiplicity (if not singlet), assignment (C_q = fully substituted carbon)].
- Phosphorus-31 nuclear magnetic resonance (^{31}P NMR) spectra measured on a JEOL JNM-ECZ600R/S1 spectrometer at ambient temperature for ^{31}P at 243 MHz.
- High resolution mass spectra (HRMS) were performed on an Agilent 6230 time-of-flight (TOF) LC/MS instrument or a Waters SYNAPT G2 mass spectrometer by using an electrospray ionization (ESI) ionization source analyzed by quadrupole time-of-flight (Q-TOF). Melting points were determined on a SGW X-4 digital melting point apparatus and temperatures were not corrected.

2. Further Optimization Studies

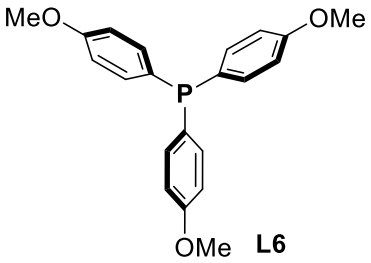
Table S1. Optimization of the diphenylphosphine oxide **1a** and VEC **2a** [a]



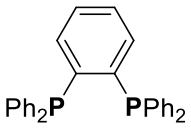
1a **2a** **3a**



L5



L6



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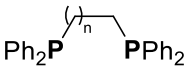
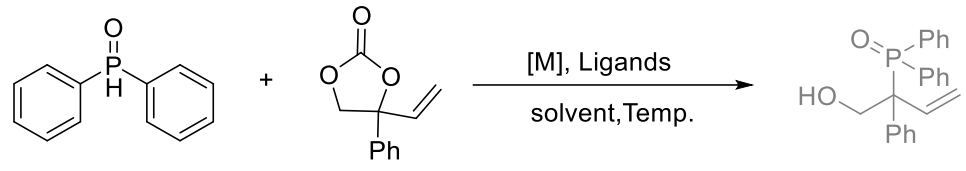


L8 n = 0
L9 n = 1
L10 n = 2

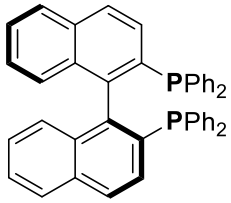
Entry	[Pd]	Ligands	Solvent	Temp.	Yield[%] [b]
1	$Pd_2(dba)_3$•$CHCl_3$	**L5**			<5
2	$Pd_2(dba)_3$•$CHCl_3$	**L6**	Toluene	R.T.	23
3	$Pd_2(dba)_3$•$CHCl_3$	**L7**			<5
4	$Pd_2(dba)_3$•$CHCl_3$	**L8**	Toluene	R.T.	<5
5	$Pd_2(dba)_3$•$CHCl_3$	**L9**	Toluene	R.T.	<5
6	$Pd_2(dba)_3$•$CHCl_3$	**L10**	Toluene	R.T.	<5
7	$Pd_2(dba)_3$•$CHCl_3$	**L3**	Mesitylene	60 °C	92
8	$Pd_2(dba)_3$•$CHCl_3$	**L3**	Chlorobenzene	60 °C	95

[a] Reactions condition: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), [Pd] (5% mmol), Ligands (12% mmol) in 1.0 mL of solvent for 2 hours. [b] Isolated yield. R.T.: Room Temperature.

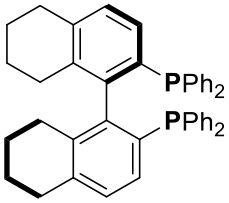
Table S2. Optimization of reaction conditions for **3'** [a]



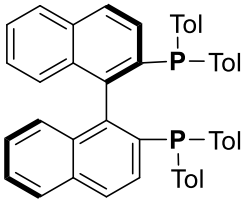
1a **2a** **3a'**



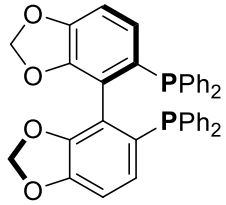
L11



L12



L13



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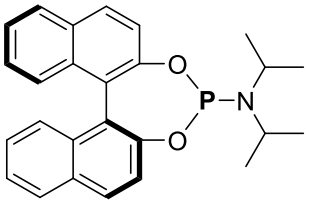
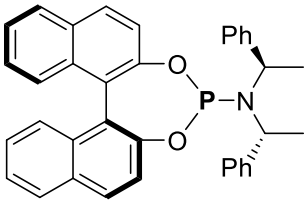


L15

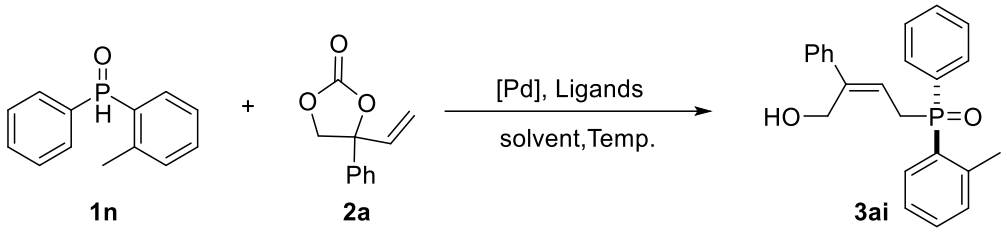


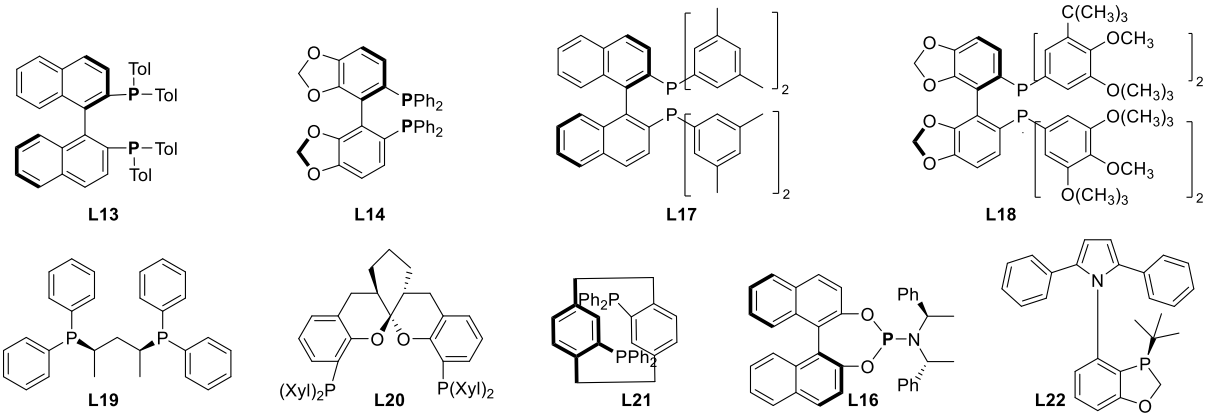
L16

Entry	[M]	Ligands	Solvent	Temp.	Yield[%][b]
1	$[(C_6H_5)_3P]_3RhCl$	**L5**	Toluene	60 °C	-
2	$RuCl_2(PPh_3)_3$	**L5**	Toluene	60 °C	-
3	$[Ir(cod)Cl]_2$	**L5**	Toluene	60 °C	-
4	$[Ir(cod)Cl]_2$	**L1**	Toluene	60 °C	-
5	$[Ir(cod)Cl]_2$	**L2**	Toluene	60 °C	-
6	$[Ir(cod)Cl]_2$	**L3**	Toluene	60 °C	-
7	$[Ir(cod)Cl]_2$	**L6**	Toluene	60 °C	-
8	$[Ir(cod)Cl]_2$	**L7**	Toluene	60 °C	-
9	$[Ir(cod)Cl]_2$	**L10**	Toluene	60 °C	-
10	$[Ir(cod)Cl]_2$	**L3**	DCM	60 °C	-
11	$[Ir(cod)Cl]_2$	**L3**	THF	60 °C	-
12	$[Ir(cod)Cl]_2$	**L3**	MeCN	60 °C	-
13	$[Ir(cod)Cl]_2$	**L3**	Mesitylene	60 °C	
14	$[Ir(cod)Cl]_2$	**L3**	Chlorobenzene	60 °C	
15	$[Ir(cod)Cl]_2$	**L9**	DCM	60 °C	-
16	$[Ir(cod)Cl]_2$	**L9**	THF	60 °C	-
17	$[Ir(cod)Cl]_2$	**L9**	MeCN	60 °C	-
18	$[Ir(cod)Cl]_2$	**L11**	Toluene	60 °C	-
19	$[Ir(cod)Cl]_2$	**L12**	Toluene	60 °C	-
20	$[Ir(cod)Cl]_2$	**L13**	Toluene	60 °C	-
21	$[Ir(cod)Cl]_2$	**L14**	Toluene	60 °C	-
22	$[Ir(cod)Cl]_2$	**L15**	Toluene	60 °C	-
23	$[Ir(cod)Cl]_2$	**L16**	Toluene	60 °C	-

[a] Reactions condition: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), [M] (5% mmol), Ligands (12% mmol) in 1.0 mL of solvent. [b] Isolated yield.

Table S3. Optimization of reaction conditions for stereogenic-at-phosphorus compounds **3ai**[a]

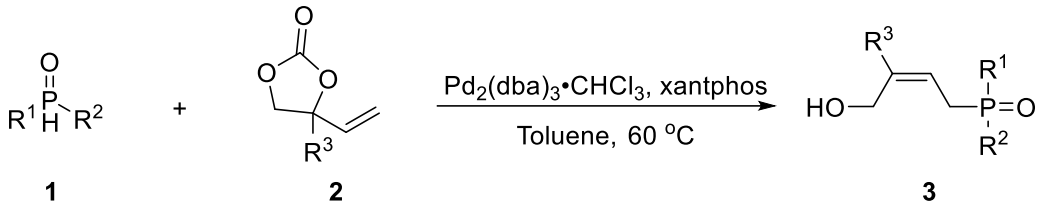




Entry	[Pd]	Ligands	Solvent	Base	Yield[%][b]	E.r.(%)[c]
1	$Pd_2(dba)_3$•$CHCl_3$	**L13**	Toluene	K_3PO_4	46	44:56
2	$Pd_2(dba)_3$•$CHCl_3$	**L14**	Toluene	K_3PO_4	31	38:62
3	$Pd_2(dba)_3$•$CHCl_3$	**L16**	Toluene	K_3PO_4	<5	N.D.[d]
4	$Pd_2(dba)_3$•$CHCl_3$	**L17**	Toluene	K_3PO_4	38	47:53
5	$Pd_2(dba)_3$•$CHCl_3$	**L18**	Toluene	K_3PO_4	37	51:49
6	$Pd_2(dba)_3$•$CHCl_3$	**L19**	Toluene	K_3PO_4	6	41:56
7	$Pd_2(dba)_3$•$CHCl_3$	**L20**	Toluene	K_3PO_4	<5	N.D.
8	$Pd_2(dba)_3$•$CHCl_3$	**L21**	Toluene	K_3PO_4	<5	N.D.
9	$Pd_2(dba)_3$•$CHCl_3$	**L22**	Toluene	K_3PO_4	<5	N.D.
10	$Pd(OAc)_2$	**L14**	Toluene	K_3PO_4	<5	N.D.
11	$PdCl_2$	**L14**	Toluene	K_3PO_4	13	37:63
12	$Pd_2(dba)_3$	**L14**	Toluene	K_3PO_4	20	36:64
13	$Pd_2(dba)_3$	**L14**	Toluene	KH_2PO_4	<5	N.D.
14	$Pd_2(dba)_3$	**L14**	Toluene	K_2HPO_4	<5	N.D.
15	$Pd_2(dba)_3$	**L14**	Toluene	Cs_2CO_3	29	40:60
16	$Pd_2(dba)_3$	**L14**	Toluene	DBU	20	34:66
17	$Pd_2(dba)_3$	**L14**	Toluene	TEA	<5	N.D.
18	$Pd_2(dba)_3$	**L14**	DCM	DBU	20	50:50
19	$Pd_2(dba)_3$	**L14**	THF	DBU	10	39:61
20	$Pd_2(dba)_3$	**L14**	MeCN	DBU	<5	N.D.
21	$Pd_2(dba)_3$	**L14**	PhCF3	DBU	8	39:61
22	$Pd_2(dba)_3$	**L14**	Mesitylene	DBU	15	32:68
23[e]	$Pd_2(dba)_3$	**L14**	Mesitylene	DBU	10	28:72
24[f]	**$Pd_2(dba)_3$**	**L14**	**Mesitylene**	**DBU**	**10**	**27:73**

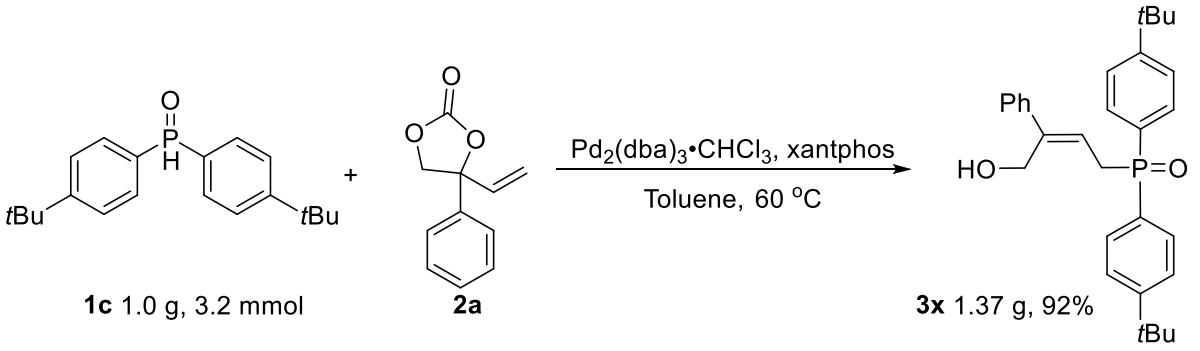
[a] Reactions condition: **1n** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), [Pd] (5% mmol), Ligands (12% mmol), base (0.1 mmol, 1.0 equiv) in 2.0 mL solvent, at 60 °C, 12 hours. [b] NMR yield with the use of CH_2Br_2 as the internal standard. [c] Determined by HPLC analysis on a chiral stationary phase. [d] N.D.: No Detect. [e] at 40 °C, 24 hours. [f] 3.0 mL solvent, at 40 °C, 24 hours.

3. General Procedure for the 3.



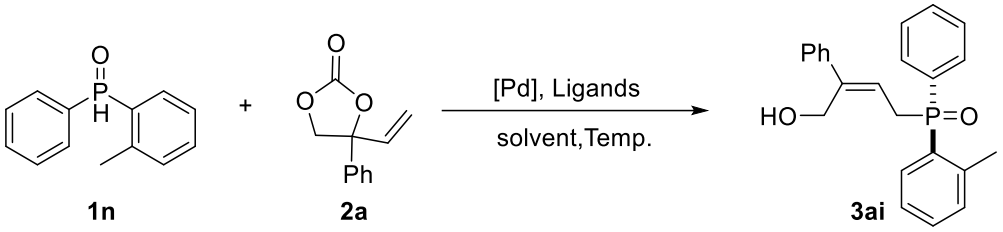
To an oven-dried Schlenk tube was added $Pd_2(dba)_3$•$CHCl_3$ (1 mol%) and Xantphos (3 mol%), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (1.0 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, P(O)H compounds **1** (0.10 mmol) and vinylethylene carbonates **2** (0.15 mmol) were added and the reaction mixture was stirred at 60 °C for 2 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 3/1, 2:1 to 1/1) to afford the corresponding **3** in 52–99% yields, which were dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc.*

Gram-scale synthesis of the nine-membered product **3x**



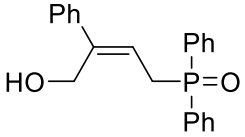
To an oven-dried Schlenk tube was added $Pd_2(dba)_3$•$CHCl_3$ (0.032 mmol, 32.74 mg) and Xantphos (0.096 mmol, 55.55 mg), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (32 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, P(O)H compounds **1c** (3.2 mmol, 1.01 g) and vinylethylene carbonate **2a** (4.8 mmol, 0.91 g) were added and the reaction mixture was stirred at 60 °C for 2 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 3/1, 2:1 to 1/1) to afford the corresponding **3x** (1.37 g) as white solid in 92% yields.

Procedure for the asymmetric synthesis of product **3ai.**



To a flame-dried Schlenk tube were added [Pd] (5% mmol) and **Ligands** (12% mmol), after which the tube was evacuated and back-filled with argon three times. Then, under the protection of Ar, solvent (1.0 mL) was added and stirred at room temperature for 30 min.. Subsequently, under the protection of Ar, P(O)H compounds **1n** (0.10 mmol), VEC **2a** (0.15 mmol) and base (0.1 mmol) were added and the reaction mixture was stirred at 60 °C for 12 hours. After which the reaction mixture was concentrated under reduced pressure and the resulting crude material was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (3:1, 2:1 to 1:1) as eluents to afford the chiral corresponding products **3ai**, which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, chiral HPLC analysis, *etc*.

***(Z)-(4-hydroxy-3-phenylbut-2-en-1-yl)diphenylphosphine oxide* 3a**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3a** (34.1 mg, 98% yield) as a white solid, m.p. = 151 – 155 ^{o}C.

NMR and HRMS data for the product **3a**:

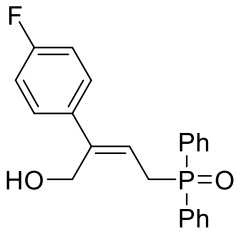
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.74 (m, 4H), 7.59 – 7.53 (m, 2H), 7.52 – 7.46 (m, 4H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.25 – 7.21 (m, 1H), 5.64 – 5.59 (m, 1H), 4.48 (s, 2H), 3.40 (dd, *J* = 13.8, 8.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 147.0 (d, $J_{C\text{-}P}$ = 10.1 Hz), 141.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.2, 131.8 (d, $J_{C\text{-}P}$ = 99.8 Hz), 130.9 (d, $J_{C\text{-}P}$ = 8.8 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.2, 127.3, 126.2, 117.2 (d, $J_{C\text{-}P}$ = 11.5 Hz), 59.9, 31.0 (d, $J_{C\text{-}P}$ = 65.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.02.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{21}O_2PNa^+$ 371.1172; Found: 371.1171.

***(Z)-(3-(4-fluorophenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide* 3b**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3b** (35.5 mg, 97% yield) as a white solid, m.p. = 142 – 145 ^{o}C.

NMR and HRMS data for the product **3b**:

^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.80 – 7.73 (m, 4H), 7.59 – 7.54 (m, 2H), 7.53 – 7.47 (m, 4H), 7.42 – 7.36 (m, 2H), 6.95 (t, J = 9.0 Hz, 2H), 5.58 – 5.53 (m, 1H), 5.39 (br., 1H), 4.44 (s, 2H), 3.38 (dd, J = 14.4, 8.4 Hz, 2H).

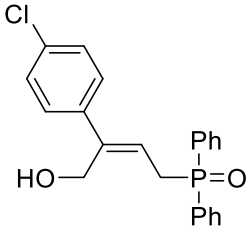
^{13}C NMR (151 MHz, CDCl$_3$) δ (ppm): 162.2 (d, $^{1}J_{C\text{-}F}$ = 245.8 Hz), 146.0 (d, $J_{C\text{-}P}$ = 10.1 Hz), 137.6, 132.3, 131.6 (d, $J_{C\text{-}P}$ = 101.2 Hz), 130.8 (d, $J_{C\text{-}P}$ = 8.8 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 127.8 (d, $^{3}J_{C\text{-}F}$ = 7.2 Hz), 117.1 (d, $J_{C\text{-}P}$ = 11.6 Hz), 115.0 (d, $^{2}J_{C\text{-}F}$ = 21.7 Hz), 59.8, 30.9 (d, $J_{C\text{-}P}$ = 65.1 Hz).

^{31}P NMR (243 MHz, CDCl$_3$) δ (ppm): 29.10.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}FO_2PNa^+$ 389.1078; Found: 389.1073.

^{19}F NMR (564 MHz, CDCl$_3$) δ (ppm): -115.15 (s, 1F).

***(Z)-(3-(4-chlorophenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide* 3c**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3c** (35.6 mg, 93% yield) as a white solid, m.p. = 108 – 111 ^{o}C.

NMR and HRMS data for the product **3c**:

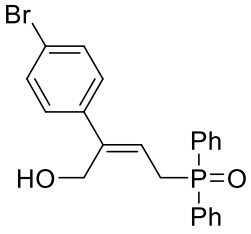
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.73 (m, 4H), 7.59 – 7.54 (m, 2H), 7.53 – 7.47 (m, 4H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.62 – 5.56 (m, 1H), 4.43 (s, 2H), 3.38 (dd, *J* = 13.8, 7.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.0 (d, $J_{C\text{-}P}$ = 11.6 Hz), 140.0 (d, $J_{C\text{-}P}$ = 4.4 Hz), 133.2, 132.3, 131.6 (d, $J_{C\text{-}P}$ = 101.2 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.4, 127.5, 117.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.7, 31.0 (d, $J_{C\text{-}P}$ = 66.6 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.96.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}ClO_2PNa^+$ 405.0782 (^{35}Cl), 407.0753 (^{37}Cl); Found: 405.0783, 407.0753.

(Z)-(3-(4-bromophenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide **3d**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3d** (40.6 mg, 95% yield) as a white solid, m.p. = 141 – 145 °C.

NMR and HRMS data for the product **3d**:

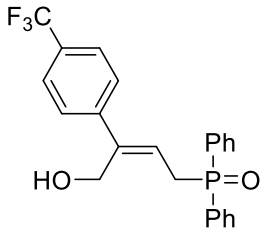
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.78 – 7.73 (m, 4H), 7.59 – 7.54 (m, 2H), 7.53 – 7.47 (m, 4H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 9.0 Hz, 2H), 5.62 – 5.57 (m, 1H), 5.38 (br., 1H), 4.43 (s, 2H), 3.38 (dd, *J* = 14.4, 9.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 145.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 140.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.3, 131.5 (d, $J_{C\text{-}P}$ = 101.3 Hz), 131.3, 130.8 (d, $J_{C\text{-}P}$ = 8.6 Hz), 128.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 127.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 121.4, 117.9 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.6, 31.0 (d, $J_{C\text{-}P}$ = 66.4 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.99.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}BrO_2PNa^+$ 449.0277 (^{79}Br), 451.0257 (^{81}Br); Found: 449.0281, 451.0265.

***(Z)-(4-hydroxy-3-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)diphenylphosphine oxide* 3e**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3e** (38.3 mg, 92% yield) as a white solid, m.p. = 136 – 139 °C.

NMR and HRMS data for the product **3e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.81 – 7.74 (m, 4H), 7.60 – 7.55 (m, 2H), 7.55 – 7.48 (m, 8H), 5.70 – 5.65 (m, 1H), 4.47 (s, 2H), 3.42 (dd, J = 14.4, 8.4 Hz, 2H).

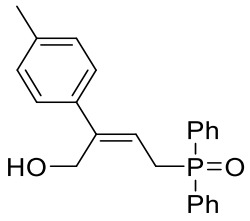
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.0 (d, $J_{C\text{-}P}$ = 11.5 Hz), 145.1, 132.4, 131.6 (d, $J_{C\text{-}P}$ = 99.8 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 129.3 (d, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 128.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 126.5, 125.2 (d, $^{3}J_{C\text{-}F}$ = 4.4 Hz), 124.2 (t, $^{1}J_{C\text{-}F}$ = 271.8 Hz), 119.4 (d, $J_{C\text{-}P}$ = 13.0 Hz), 59.6, 31.1 (d, $J_{C\text{-}P}$ = 65.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.88.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{20}F_3O_2PNa^+$ 439.1046; Found: 439.1053.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -62.35 (s, 3F).

***(Z)-(4-hydroxy-3-(p-tolyl)but-2-en-1-yl)diphenylphosphine oxide* 3f**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3f** (33.0 mg, 91% yield) as a white solid, m.p. = 116 – 121 °C.

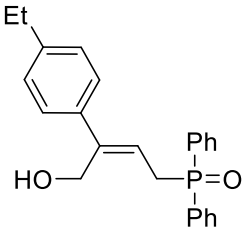
NMR and HRMS data for the product **3f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.74 (m, 4H), 7.58 – 7.53 (m, 2H), 7.52 – 7.47 (m, 4H), 7.33 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 5.62 – 5.57 (m, 1H), 5.30 (br., 1H), 4.46 (s, 2H), 3.38 (dd, J = 13.8, 8.4 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.7 (d, $J_{C\text{-}P}$ = 11.6 Hz), 138.6 (d, $J_{C\text{-}P}$ = 4.4 Hz), 137.1, 132.2, 131.8 (d, $J_{C\text{-}P}$ = 99.8 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.9, 128.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 126.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 116.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 59.8, 30.9 (d, $J_{C\text{-}P}$ = 64.9 Hz), 21.0.
^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.16.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{23}O_2PNa^+$ 385.1328; Found: 385.1333.

***(Z)-(3-(4-ethylphenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide* 3g**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3g** (35.8 mg, 95% yield) as a white solid, m.p. = 120 – 123 °C.

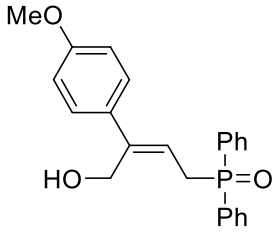
NMR and HRMS data for the product **3g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.75 (m, 4H), 7.57 – 7.53 (m, 2H), 7.52 – 7.47 (m, 4H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.63 – 5.58 (m, 1H), 5.29 (br., 1H), 4.47 (s, 2H), 3.39 (dd, *J* = 13.8, 8.4 Hz, 2H), 2.61 (q, *J* = 7.8 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.7 (d, $J_{C\text{-}P}$ = 10.1 Hz), 143.5, 138.8 (d, $J_{C\text{-}P}$ = 4.4 Hz), 132.1, 131.5, 130.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 127.7, 126.1, 116.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 59.8, 30.9 (d, $J_{C\text{-}P}$ = 64.9 Hz), 28.4, 15.5.
^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.10.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{25}O_2PNa^+$ 399.1485; Found: 399.1490.

***(Z)-(4-hydroxy-3-(4-methoxyphenyl)but-2-en-1-yl)diphenylphosphine oxide* 3h**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3h** (33.3 mg, 88% yield) as a white solid, m.p. = 164 – 167 °C.

NMR and HRMS data for the product **3h**:

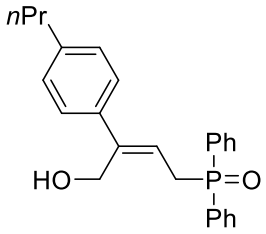
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.79 – 7.74 (m, 4H), 7.58 – 7.54 (m, 2H), 7.52 – 7.47 (m, 4H), 7.36 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.56 – 5.52 (m, 1H), 5.26 (br., 1H), 4.45 (s, 2H), 3.78 (s, 3H), 3.37 (dd, *J* = 13.2, 7.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.1, 146.3 (d, $J_{C\text{-}P}$ = 11.6 Hz), 134.0 (d, $J_{C\text{-}P}$ = 4.4 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.5, 130.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 127.3, 115.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 113.6, 59.9, 55.3, 30.9 (d, $J_{C\text{-}P}$ = 64.9 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.10.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{23}O_3PNa^+$ 401.1278; Found: 401.1281.

***(Z)-(4-hydroxy-3-(4-propylphenyl)but-2-en-1-yl)diphenylphosphine oxide* 3i**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3i** (27.3 mg, 70% yield) as a white solid, m.p. = 122 – 127 ºC.

NMR and HRMS data for the product **3i**:

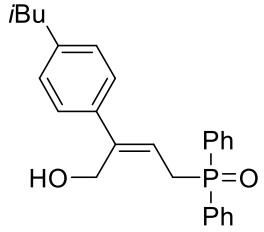
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.75 (m, 4H), 7.58 – 7.53 (m, 2H), 7.52 – 7.47 (m, 4H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.63 – 5.58 (m, 1H), 5.29 (br., 1H), 4.47 (s, 2H), 3.39 (dd, *J* = 14.4, 7.8 Hz, 2H), 2.54 (t, *J* = 7.8 Hz, 2H), 1.64 – 1.57 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.7 (d, $J_{C\text{-}P}$ = 10.1 Hz), 142.0, 138.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.1, 131.8 (d, $J_{C\text{-}P}$ = 101.2 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.8 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.3, 126.0, 116.3 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.8, 37.6, 30.9 (d, $J_{C\text{-}P}$ = 66.4 Hz), 24.5, 13.8.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.47.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{25}H_{27}O_2PNa^+$ 413.1641; Found: 413.1646.

***(Z)-(4-hydroxy-3-(4-isobutylphenyl)but-2-en-1-yl)diphenylphosphine oxide* 3j**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3j** (29.9 mg, 74% yield) as a white solid, m.p. = 130 – 134 °C.

NMR and HRMS data for the product **3j**:

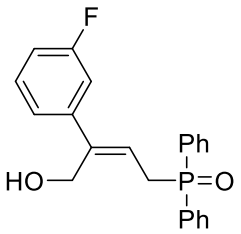
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.78 – 7.75 (m, 4H), 7.58 – 7.53 (m, 2H), 7.52 – 7.47 (m, 4H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 5.63 – 5.59 (m, 1H), 4.47 (s, 2H), 3.39 (dd, *J* = 14.4, 8.4 Hz, 2H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.87 – 1.79 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.8 (d, $J_{C\text{-}P}$ = 10.1 Hz), 141.0, 138.8 (d, $J_{C\text{-}P}$ = 4.4 Hz), 132.2, 131.9 (d, $J_{C\text{-}P}$ = 99.8 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 129.0, 128.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 125.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 116.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 59.8, 45.0, 31.0 (d, $J_{C\text{-}P}$ = 65.1 Hz), 30.2, 22.4.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.08.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{29}O_2PNa^+$ 427.1798; Found: 427.1803.

***(Z)-(3-(3-fluorophenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide* 3k**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3k** (28.2 mg, 77% yield) as a white solid, m.p. = 139 – 141 °C.

NMR and HRMS data for the product **3k**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.71 (m, 4H), 7.61 – 7.54 (m, 2H), 7.54 – 7.46 (m, 4H), 7.25 – 7.18 (m, 2H), 7.12 (d, *J* = 10.2 Hz, 1H), 6.96 – 6.89 (m, 1H), 5.66 – 5.59 (m, 1H), 4.45 (s, 2H), 3.39 (dd, *J* = 14.4, 9.0 Hz, 2H).

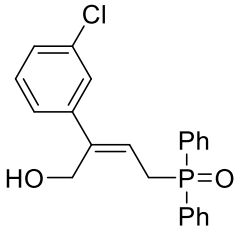
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 162.8 (C-F, $^1J_{C\text{-}F}$ = 245.8 Hz), 146.0 (d, $J_{C\text{-}P}$ = 8.8 Hz), 143.8, 132.3, 131.6 (d, $J_{C\text{-}P}$ = 101.2 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 129.7 (C-F, $^3J_{C\text{-}F}$ = 8.6 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.6 Hz), 121.9, 118.3 (d, $J_{C\text{-}P}$ = 11.6 Hz), 114.1 (C-F, $^2J_{C\text{-}F}$ = 20.2 Hz), 113.2 (C-F, $^2J_{C\text{-}F}$ = 21.6 Hz), 59.7, 31.0 (d, $J_{C\text{-}P}$ = 64.9 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.96.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}FO_2PNa^+$ 389.1078; Found: 389.1070.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -113.43 (s, 1F).

***(Z)-(3-(3-chlorophenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide* 3l**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3l** (32.2 mg, 84% yield) as a white solid, m.p. = 116 – 120 °C.

NMR and HRMS data for the product **3l**:

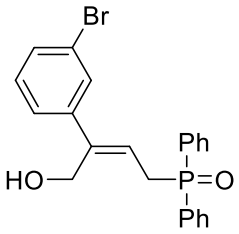
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.81 – 7.73 (m, 4H), 7.60 – 7.54 (m, 2H), 7.53 – 7.47 (m, 4H), 7.39 (s, 1H), 7.36 – 7.31 (m, 1H), 7.20 (d, *J* = 4.8 Hz, 2H), 5.64 – 5.58 (m, 1H), 4.43 (s, 2H), 3.39 (dd, *J* = 14.4, 8.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 145.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 143.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 134.1, 132.3, 131.5 (d, $J_{C\text{-}P}$ = 99.7 Hz), 130.8 (d, $J_{C\text{-}P}$ = 10.1 Hz), 129.5, 128.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 127.3, 126.4, 124.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 118.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 59.6, 31.0 (d, $J_{C\text{-}P}$ = 65.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.02.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}ClO_2PH^+$ 383.0963 (^{35}Cl), 385.0933 (^{37}Cl); Found: 383.0966, 385.0941.

***(Z)-(3-(3-bromophenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide* 3m**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3m** (35.5 mg, 83% yield) as a white solid, m.p. = 122 – 123 °C.

NMR and HRMS data for the product **3m**:

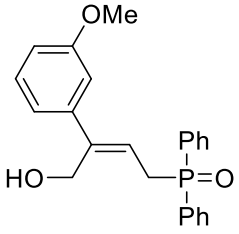
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.73 (m, 4H), 7.60 – 7.55 (m, 2H), 7.54 (s, 1H), 7.53 – 7.48 (m, 4H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 5.63 – 5.56 (m, 1H), 5.40 (br., 1H), 4.43 (s, 2H), 3.39 (dd, *J* = 14.4, 8.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 145.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 143.7 (d, $J_{C\text{-}P}$ = 4.4 Hz), 132.3, 131.6 (d, $J_{C\text{-}P}$ = 101.2 Hz), 130.9 (d, $J_{C\text{-}P}$ = 8.8 Hz), 130.3, 129.8, 129.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 128.9 (d, $J_{C\text{-}P}$ = 13.1 Hz), 124.9, 122.4, 118.6 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.7, 31.0 (d, $J_{C\text{-}P}$ = 65.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.96.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}BrO_2PNa^+$ 449.0277 (^{79}Br), 451.0257 (^{81}Br); Found: 449.0277, 451.0261.

***(Z)-(4-hydroxy-3-(3-methoxyphenyl)but-2-en-1-yl)diphenylphosphine oxide* 3n**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3n** (28.8 mg, 76% yield) as a white solid, m.p. = 118 – 123 °C.

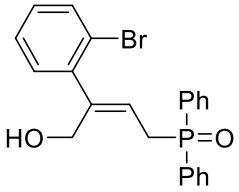
NMR and HRMS data for the product **3n**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.75 (m, 4H), 7.59 – 7.54 (m, 2H), 7.53 – 7.47 (m, 4H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.96 (s, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.63 – 5.59 (m, 1H), 4.46 (s, 2H), 3.77 (s, 3H), 3.39 (dd, *J* = 14.4, 9.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.5, 147.0 (d, J_{C-P} = 10.1 Hz), 143.1 (d, J_{C-P} = 2.9 Hz), 132.2, 131.8 (d, J_{C-P} = 99.8 Hz), 130.9 (d, J_{C-P} = 8.6 Hz), 129.2, 128.8 (d, J_{C-P} = 11.6 Hz), 118.8, 117.5 (d, J_{C-P} = 11.6 Hz), 113.1, 111.8, 60.0, 55.2, 31.0 (d, J_{C-P} = 66.6 Hz).
^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.05.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{23}O_3PNa^+$ 401.1278; Found: 401.1280.

***(Z)-(3-(2-bromophenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide* 3o**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3o** (41.0 mg, 96% yield) as a white solid, m.p. = 141 – 144 °C.

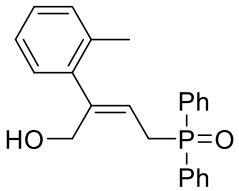
NMR and HRMS data for the product **3o**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.77 (m, 4H), 7.59 – 7.54 (m, 2H), 7.54 – 7.47 (m, 5H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 5.33 – 5.28 (m, 1H), 4.39 (s, 2H), 3.43 (dd, *J* = 13.8, 8.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 148.1 (d, J_{C-P} = 10.1 Hz), 143.0 (d, J_{C-P} = 2.9 Hz), 132.4, 132.2, 131.8 (d, J_{C-P} = 99.7 Hz), 131.1 (d, J_{C-P} = 2.9 Hz), 130.9 (d, J_{C-P} = 10.3 Hz), 128.8 (d, J_{C-P} = 11.6 Hz), 128.7, 127.2, 122.0 (d, J_{C-P} = 2.9 Hz), 120.3 (d, J_{C-P} = 11.6 Hz), 60.7, 30.4 (d, J_{C-P} = 65.1 Hz).
^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.33.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}BrO_2PNa^+$ 449.0277 (^{79}Br), 451.0257 (^{81}Br); Found: 449.0267, 451.0251.

***(Z)-(4-hydroxy-3-(o-tolyl)but-2-en-1-yl)diphenylphosphine oxide* 3p**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3p** (32.6 mg, 90% yield) as a white solid, m.p. = 117 – 120 °C.

NMR and HRMS data for the product **3p**:

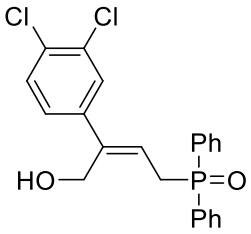
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.77 (m, 4H), 7.58 -7.53 (m, 2H), 7.53 – 7.48 (m, 4H), 7.14 – 7.06 (m, 3H), 7.03 (d, *J* = 6.0 Hz, 1H), 5.25 – 5.20 (m, 1H), 4.34 (s, 2H), 3.44 (dd, *J* = 13.8, 8.4 Hz, 2H), 2.12 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 148.1 (d, J_{C-P} = 10.1 Hz), 142.2 (d, J_{C-P} = 2.9 Hz), 135.2, 132.1, 132.0 (d, J_{C-P} = 99.7 Hz), 130.9 (d, J_{C-P} = 10.1 Hz), 129.9, 128.8 (d, J_{C-P} = 11.5 Hz), 127.1, 125.4, 118.4 (d, J_{C-P} = 10.1 Hz), 62.2, 30.4 (d, J_{C-P} = 65.1 Hz), 19.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.69.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{23}O_2PNa^+$ 385.1328; Found: 385.1334.

***(Z)-(3-(3,4-dichlorophenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide* 3q**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3q** (41.3 mg, 99% yield) as a white solid, m.p. = 156 – 159 °C.

NMR and HRMS data for the product **3q**:

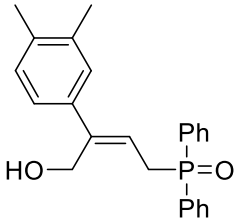
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.79 – 7.73 (m, 4H), 7.60 – 7.55 (m, 2H), 7.54 – 7.48 (m, 5H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 5.62 – 5.57 (m, 1H), 4.41 (s, 2H), 3.38 (dd, *J* = 13.8, 8.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 145.0 (d, J_{C-P} = 10.1 Hz), 141.6 (d, J_{C-P} = 4.4 Hz), 132.4, 132.3, 131.5 (d, J_{C-P} = 101.3 Hz), 131.3, 130.8 (d, J_{C-P} = 10.1 Hz), 130.1, 128.9 (d, J_{C-P} = 11.5 Hz), 128.2, 125.6 (d, J_{C-P} = 3.0 Hz), 118.9 (d, J_{C-P} = 11.5 Hz), 59.5, 31.0 (d, J_{C-P} = 65.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.88.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{19}Cl_2O_2PNa^+$ 439.0392 (^{35}Cl), 441.0363 (^{37}Cl); Found: 439.0383, 441.0356.

***(Z)-(3-(3,4-dimethylphenyl)-4-hydroxybut-2-en-1-yl)diphenylphosphine oxide* 3r**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3r** (34.3 mg, 91% yield) as a white solid, m.p. = 148 – 152 °C.

NMR and HRMS data for the product **3r**:

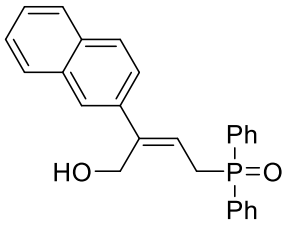
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.75 (m, 4H), 7.57 – 7.53 (m, 2H), 7.52 – 7.47 (m, 4H), 7.22 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 5.61 – 5.57 (m, 1H), 5.29 (br., 1H), 4.46 (s, 2H), 3.38 (dd, *J* = 14.4, 9.0 Hz, 2H), 2.22 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.8 (d, $J_{C\text{-}P}$ = 10.1 Hz), 139.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 136.3, 135.8, 132.1, 131.5, 130.9 (d, $J_{C\text{-}P}$ = 8.8 Hz), 129.5, 128.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 127.5, 123.5, 116.2 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.9, 30.9 (d, $J_{C\text{-}P}$ = 66.6 Hz), 19.8, 19.4.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.13.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{25}O_2PNa^+$ 399.1485; Found: 399.1490.

***(Z)-(4-hydroxy-3-(naphthalen-2-yl)but-2-en-1-yl)diphenylphosphine oxide* 3s**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3s** (31.9 mg, 80% yield) as a white solid, m.p. = 185 – 188 °C.

NMR and HRMS data for the product **3s**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.94 (s, 1H), 7.83 – 7.76 (m, 6H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.53 – 7.47 (m, 4H), 7.47 – 7.41 (m, 2H), 5.79 – 5.73 (m, 1H), 4.59 (s, 2H), 3.45 (dd, *J* = 13.8, 8.4 Hz, 2H).

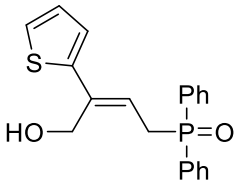
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 138.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.3, 132.6, 132.2, 131.7 (d, $J_{C\text{-}P}$ = 99.8 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.6

Hz), 128.2, 127.7, 127.4, 126.1, 125.8, 125.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 124.4, 117.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.9, 31.2 (d, $J_{C\text{-}P}$ = 65.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.13.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{23}O_2PNa^+$ 421.1328; Found: 421.1335.

***(E)-(4-hydroxy-3-(thiophen-2-yl)but-2-en-1-yl)diphenylphosphine oxide* 3t**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3t** (31.9 mg, 90% yield) as a white solid, m.p. = 119 – 123 °C.

NMR and HRMS data for the product **3t**:

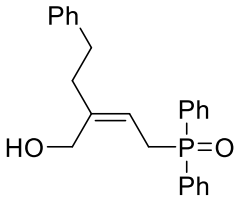
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.79 – 7.73 (m, 4H), 7.59 – 7.53 (m, 2H), 7.53 – 7.47 (m, 4H), 7.15 (d, *J* = 4.2 Hz, 1H), 7.10 (d, *J* = 4.8 Hz, 1H), 6.96 (dd, *J* = 4.2, 3.0 Hz, 1H), 5.73 – 5.68 (m, 1H), 5.35 (br., 1H), 4.49 (s, 2H), 3.35 (dd, *J* = 13.8, 8.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 144.7 (d, $J_{C\text{-}P}$ = 5.9 Hz), 140.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 132.2, 131.5 (d, $J_{C\text{-}P}$ = 101.3 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.3 Hz), 128.8 (d, $J_{C\text{-}P}$ = 13.0 Hz), 127.6, 124.13, 124.07 (d, $J_{C\text{-}P}$ = 2.9 Hz), 115.3 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.4, 30.7 (d, $J_{C\text{-}P}$ = 65.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.38.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{19}O_2PNa^+$ 377.0736; Found: 377.0742.

***(Z)-(3-(hydroxymethyl)-5-phenylpent-2-en-1-yl)diphenylphosphine oxide* 3u**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3u** (25.2 mg, 67% yield) as a white solid, m.p. = 109 – 112 °C.

NMR and HRMS data for the product **3u**:

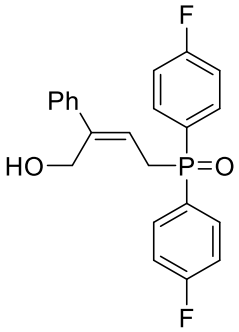
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.73 – 7.68 (m, 4H), 7.56 – 7.53 (m, 2H), 7.50 – 7.46 (m, 4H), 7.25 – 7.21 (m, 2H), 7.17 – 7.12 (m, 3H), 5.08 – 5.02 (m, 1H), 4.10 (s, 2H), 3.19 (dd, *J* = 13.2, 7.8 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.47 – 2.41 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 147.3 (d, J_{C-P} = 10.1 Hz), 141.8, 132.0, 131.9 (d, J_{C-P} = 99.8 Hz), 130.9 (d, J_{C-P} = 8.8 Hz), 128.7 (d, J_{C-P} = 11.5 Hz), 128.4, 128.2, 125.7, 114.5 (d, J_{C-P} = 11.6 Hz), 60.1, 38.5, 34.6, 29.9 (d, J_{C-P} = 65.1 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.52.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}O_2PH^+$ 377.1665; Found: 377.1669.

***(Z)-bis(4-fluorophenyl)(4-hydroxy-3-phenylbut-2-en-1-yl)phosphine oxide* 3v**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3v** (33.4 mg, 87% yield) as a white solid, m.p. = 97 – 102 °C.

NMR and HRMS data for the product **3v**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.81 – 7.73 (m, 4H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.27 – 7.23 (m, 1H), 7.23 – 7.18 (m, 4H), 5.61 – 5.56 (m, 1H), 5.16 (br., 1H), 4.47 (s, 2H), 3.38 (dd, *J* = 14.4, 7.8 Hz, 2H).

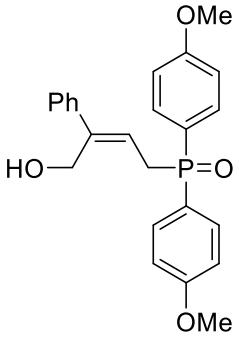
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 165.2 (C-F, $^{1}J_{C-F}$ = 258.8 Hz), 147.4 (d, J_{C-P} = 11.6 Hz), 141.3 (d, J_{C-P} = 4.4 Hz), 133.4 (t, J_{C-P} = 11.6 Hz), 128.3, 127.53, 127.47 (d, J_{C-P} = 105.5 Hz), 126.1, 116.6 (d, J_{C-P} = 11.6 Hz), 116.5 (dd, *J* = 21.6, 13.0 Hz), 59.9, 31.2 (d, J_{C-P} = 68.0 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.09.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{19}F_2O_2PNa^+$ 407.0983; Found: 407.0978.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -105.47 (s, 2F).

***(Z)-(4-hydroxy-3-phenylbut-2-en-1-yl)bis(4-methoxyphenyl)phosphine oxide* 3w**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3w** (38.8 mg, 95% yield) as a white solid, m.p. = 163 – 168 °C.

NMR and HRMS data for the product **3w**:

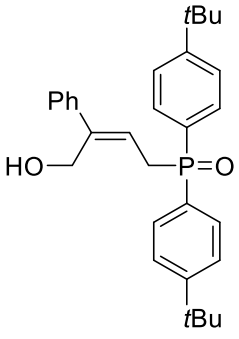
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.69 – 7.64 (m, 4H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 4H), 5.64 – 5.60 (m, 1H), 4.47 (s, 2H), 3.84 (s, 6H), 3.32 (dd, *J* = 15.0, 9.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 162.5, 146.6 (d, $J_{C\text{-}P}$ = 11.6 Hz), 141.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.7 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.2, 127.2, 126.2, 123.2 (d, $J_{C\text{-}P}$ = 107.1 Hz), 117.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 114.3 (d, $J_{C\text{-}P}$ = 13.0 Hz), 59.8, 55.4, 31.5 (d, $J_{C\text{-}P}$ = 66.6 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.94.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{25}O_4PNa^+$ 431.1383; Found: 431.1386.

***(Z)-bis(4-(tert-butyl)phenyl)(4-hydroxy-3-phenylbut-2-en-1-yl)phosphine oxide* 3x**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3x** (45.6 mg, 99% yield) as a white solid, m.p. = 213 – 217 °C.

NMR and HRMS data for the product **3x**:

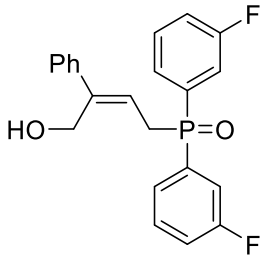
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.72 – 7.68 (m, 4H), 7.50 (d, *J* = 9.0 Hz, 4H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.68 – 5.63 (m, 1H), 4.46 (s, 2H), 3.36 (dd, *J* = 14.4, 9.0 Hz, 2H), 1.33 (s, 18H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 155.6, 146.7 (d, J_{C-P} = 11.6 Hz), 141.8 (d, J_{C-P} = 2.9 Hz), 130.8 (d, J_{C-P} =10.1 Hz), 128.7 (d, J_{C-P} =102.7 Hz), 128.2, 127.2, 126.3, 125.8 (d, J_{C-P} =11.6 Hz), 117.8 (d, J_{C-P} = 11.6 Hz), 59.9, 35.0, 31.5, 31.1.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.82.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{30}H_{37}O_2PNa^+$ 483.2424; Found: 483.2432.

***(Z)-bis(3-fluorophenyl)(4-hydroxy-3-phenylbut-2-en-1-yl)phosphine oxide* 3y**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3y** (21.9 mg, 57% yield) as a white solid, m.p. = 139 – 143 °C.

NMR and HRMS data for the product **3y**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 – 7.54 (m, 2H), 7.54 – 7.49 (m, 2H), 7.49 – 7.41 (m, 4H), 7.33 – 7.23 (m, 5H), 5.62 – 5.57 (m, 1H), 4.47 (s, 2H), 3.41 (dd, *J* = 13.8, 8.4 Hz, 2H).

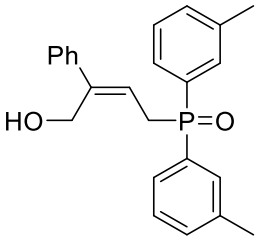
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 162.7 (dd, *J* = 251.6, 15.9 Hz), 147.7 (d, J_{C-P} = 10.1 Hz), 141.3 (d, J_{C-P} = 4.2 Hz), 133.9 (dd, *J* = 101.2, 5.7 Hz), 131.1 (dd, *J* = 13.0, 7.2 Hz), 128.3, 127.6, 126.5 (dd, *J* = 8.6, 2.9 Hz), 126.2, 119.7 (d, J_{C-F} = 21.6 Hz), 117.8 (dd, *J* = 23.1, 10.1 Hz), 116.1 (d, J_{C-P} = 11.5 Hz), 60.1, 30.7 (d, J_{C-P} = 66.6 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 27.42.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{19}F_2O_2PNa^+$ 407.0983; Found: 407.0981.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -109.83 (s, 2F).

***(Z)-(4-hydroxy-3-phenylbut-2-en-1-yl)di-m-tolylphosphine oxide* 3z**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3z** (23.3 mg, 62% yield) as a white solid, m.p. = 96 – 100 °C.

NMR and HRMS data for the product **3z**:

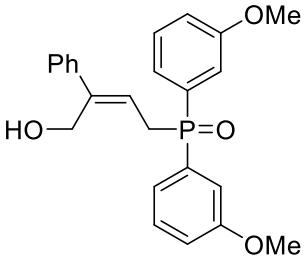
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.62 (d, *J* = 12.0 Hz, 2H), 7.52 (dd, *J* = 11.4, 7.2 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.29 – 7.25 (m, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.65 – 5.60 (m, 1H), 5.40 (br., 1H), 4.47 (s, 2H), 3.38 (dd, *J* = 14.4, 9.0 Hz, 2H), 2.38 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.7 (d, $J_{C\text{-}P}$ = 11.6 Hz), 141.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 138.7 (d, $J_{C\text{-}P}$ = 11.6 Hz), 132.9, 131.6 (d, $J_{C\text{-}P}$ = 99.8 Hz), 131.4 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.2, 127.7 (d, $J_{C\text{-}P}$ = 10.1 Hz), 127.3, 126.2, 117.5 (d, $J_{C\text{-}P}$ = 13.0 Hz), 59.8, 31.0 (d, $J_{C\text{-}P}$ = 65.1 Hz), 21.4.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.22.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{25}O_2PNa^+$ 399.1485; Found: 399.1488.

***(Z)-(4-hydroxy-3-phenylbut-2-en-1-yl)bis(3-methoxyphenyl)phosphine oxide* 3aa**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3aa** (21.2 mg, 52% yield) as a white solid, m.p. = 95 – 98 °C.

NMR and HRMS data for the product **3aa**:

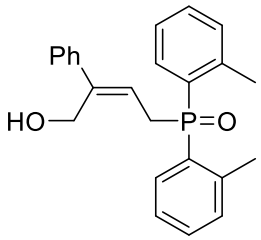
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.45 (d, *J* = 7.8 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.25 (m, 6H), 7.24 – 7.21 (m, 1H), 7.06 (d, *J* = 6.6 Hz, 2H), 5.66 – 5.62 (m, 1H), 5.34 (br., 1H), 4.47 (s, 2H), 3.78 (s, 6H), 3.37 (dd, *J* = 14.4, 9.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.7 (d, $J_{C\text{-}P}$ = 14.5 Hz), 146.8 (d, $J_{C\text{-}P}$ = 10.1 Hz), 141.5 (d, $J_{C\text{-}P}$ = 4.4 Hz), 132.9 (d, $J_{C\text{-}P}$ = 98.3 Hz), 130.0 (d, $J_{C\text{-}P}$ = 14.5 Hz), 128.2, 127.3, 126.1, 122.6 (d, $J_{C\text{-}P}$ = 10.1 Hz), 118.2, 117.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 115.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 59.8, 55.4, 30.9 (d, $J_{C\text{-}P}$ = 66.6 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.36.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{25}O_4PNa^+$ 431.1383; Found: 431.1383.

(Z)-(4-hydroxy-3-phenylbut-2-en-1-yl)di-o-tolylphosphine oxide **3ab**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3ab** (30.1 mg, 80% yield) as a white solid, m.p. = 124 – 127 °C.

NMR and HRMS data for the product **3ab**:

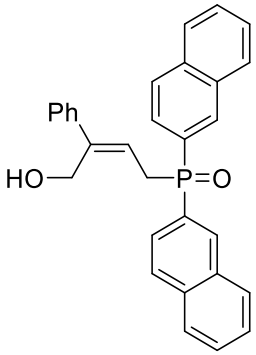
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.68 (dd, *J* = 13.2, 7.8 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.25 (m, 4H), 7.25 – 7.21 (m, 3H), 5.57 – 5.53 (m, 1H), 4.49 (s, 2H), 3.53 (dd, *J* = 14.4, 7.8 Hz, 2H), 2.36 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 147.1 (d, $J_{C\text{-}P}$ = 11.6 Hz), 141.9 (d, $J_{C\text{-}P}$ = 8.6 Hz), 141.8 (d, $J_{C\text{-}P}$ = 4.2 Hz), 132.1, 132.0 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.7 (d, $J_{C\text{-}P}$ = 11.6 Hz), 130.6 (d, $J_{C\text{-}P}$ = 96.8 Hz), 128.2, 127.3, 126.2, 125.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 117.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 60.0, 30.4 (d, $J_{C\text{-}P}$ = 65.1 Hz), 21.3 (d, $J_{C\text{-}P}$ = 2.9 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 31.46.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{25}O_2PNa^+$ 399.1485; Found: 399.1491.

***(Z)-(4-hydroxy-3-phenylbut-2-en-1-yl)di(naphthalen-2-yl)phosphine oxide* 3ac**



Prepared according to ***General Procedure*.** The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3ac** (42.2 mg, 94% yield) as a white solid, m.p. = 172 – 176 °C.

NMR and HRMS data for the product **3ac**:

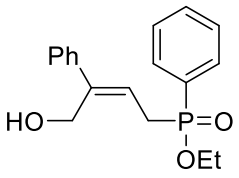
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.45 (s, 1H), 8.43 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.77 (t, *J* = 9.0 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.27 – 7.18 (m, 3H), 5.72 – 5.67 (m, 1H), 5.47 (br., 1H), 4.55 (s, 2H), 3.60 (dd, *J* = 14.4, 8.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 147.1 (d, $J_{C\text{-}P}$ = 11.6 Hz), 141.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 134.7, 133.1 (d, $J_{C\text{-}P}$ = 8.6 Hz), 132.5 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.9, 128.79 (d, $J_{C\text{-}P}$ = 99.8 Hz), 128.76 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.4, 128.2, 127.8, 127.3, 127.2, 126.2, 125.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 117.3 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.9, 31.0 (d, $J_{C\text{-}P}$ = 66.6 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.36.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{30}H_{25}O_2PNa^+$ 471.1485; Found: 471.1492.

***ethyl (Z)-(4-hydroxy-3-phenylbut-2-en-1-yl)(phenyl)phosphinate* 3ad**



Prepared according to ***General Procedure*.** The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3ad** (17.1 mg, 54% yield) as a colorless oil.

NMR and HRMS data for the product **3ad**:

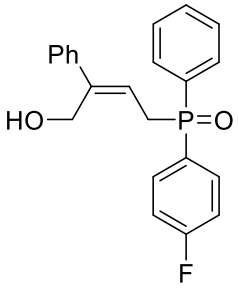
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 (dd, *J* = 11.4, 7.2 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 5.71 – 5.65 (m, 1H), 4.66 (br., 1H), 4.48 (d, *J* = 12.6 Hz, 1H), 4.40 (d, *J* = 12.6 Hz, 1H), 4.15 – 4.08 (m, 1H), 3.96 – 3.89 (m, 1H), 3.16 – 3.07 (m, 1H), 2.98 – 2.90 (m, 1H), 1.31 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 145.8 (d, $J_{C\text{-}P}$ = 13.0 Hz), 141.4 (d, $J_{C\text{-}P}$ = 4.4 Hz), 132.7, 133.7 (d, $J_{C\text{-}P}$ = 10.1 Hz), 130.1 (d, $J_{C\text{-}P}$ = 127.3 Hz), 128.8 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.3, 127.4, 126.1, 117.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 61.5 (d, $J_{C\text{-}P}$ = 7.2 Hz), 59.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 31.9 (d, $J_{C\text{-}P}$ = 95.4 Hz), 16.4 (d, $J_{C\text{-}P}$ = 5.7 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 40.35.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{21}O_3PNa^+$ 339.1121; Found: 339.1121.

***(Z)-(4-fluorophenyl)(4-hydroxy-3-phenylbut-2-en-1-yl)(phenyl)phosphine oxide* 3ae**



Prepared according to ***General Procedure*.** The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3ae** (26.7 mg, 73% yield) as a white solid, m.p. = 143 – 146 °C.

NMR and HRMS data for the product **3ae**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.78 – 7.73 (m, 4H), 7.60 – 7.55 (m, 1H), 7.53 – 7.48 (m, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 7.21 – 7.16 (m, 2H), 5.63 – 5.58 (m, 1H), 5.26 (br., 1H), 4.47 (s, 2H), 3.44 – 3.34 (m, 2H).

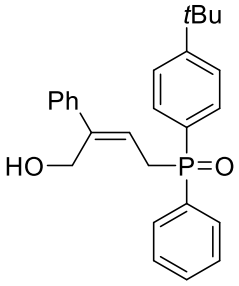
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 163.1 (dd, *J* = 254.4, 2.9 Hz), 147.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 141.4 (d, $J_{C\text{-}P}$ = 4.4 Hz), 133.4 (dd, *J* = 11.6, 8.6 Hz), 132.4, 131.5 (d, $J_{C\text{-}P}$ = 101.3 Hz), 130.8 (d, $J_{C\text{-}P}$ = 8.8 Hz), 128.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.3, 127.7 (d, $J_{C\text{-}P}$ = 102.7 Hz), 127.4, 126.2, 116.9 (d, $J_{C\text{-}P}$ = 11.5 Hz), 116.3 (dd, *J* = 21.8, 13.0 Hz), 59.9, 31.1 (d, $J_{C\text{-}P}$ = 66.4 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.60.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}FO_2PNa^+$ 389.1078; Found: 389.1074.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -105.89 (s, 1F).

***(Z)-(4-(tert-butyl)phenyl)(4-hydroxy-3-phenylbut-2-en-1-yl)(phenyl)phosphine oxide* 3af**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3af** (30.3 mg, 75% yield) as a white solid, m.p. = 178 – 180 °C.

NMR and HRMS data for the product **3af**:

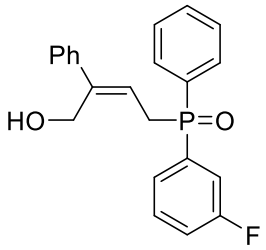
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.77 (dd, *J* = 12.0, 7.2 Hz, 2H), 7.70 (dd, *J* = 10.8, 8.4 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.52 – 7.46 (m, 4H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.24 – 7.21 (m, 1H), 5.66 – 5.61 (m, 1H), 5.39 (br., 1H), 4.47 (s, 2H), 3.41 – 3.35 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 155.7, 146.7 (d, J_{C-P} = 11.5 Hz), 141.7 (d, J_{C-P} = 4.4 Hz), 132.1 (d, J_{C-P} = 99.7 Hz), 132.0, 130.9 (d, J_{C-P} =8.8 Hz), 130.7 (d, J_{C-P} =10.1 Hz), 128.7 (d, J_{C-P} =11.5 Hz), 128.2, 128.0, 127.3, 126.2 (d, J_{C-P} = 2.9 Hz), 125.9 (d, J_{C-P} =11.5 Hz), 117.5 (d, J_{C-P} = 13.0 Hz), 59.9, 35.0, 31.1 (d, J_{C-P} = 65.1 Hz), 31.0.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.96.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{29}O_2PNa^+$ 427.1798; Found: 427.1801.

***(Z)-(3-fluorophenyl)(4-hydroxy-3-phenylbut-2-en-1-yl)(phenyl)phosphine oxide* 3ag**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3ag** (30.0 mg, 82% yield) as a white solid, m.p. = 132 – 134 °C.

NMR and HRMS data for the product **3ag**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.75 (m, 2H), 7.61 – 7.41 (m, 8H), 7.31 – 7.26 (m, 2H), 7.26 – 7.22 (m, 2H), 5.64 – 5.59 (m, 1H), 4.47 (s, 2H), 3.41 (dd, *J* = 14.4, 8.4 Hz, 2H).

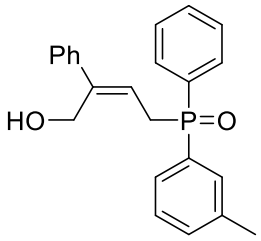
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 162.6 (dd, *J* = 251.6, 17.4 Hz), 147.3 (d, *J* = 11.6 Hz), 141.4 (d, *J* = 4.2 Hz), 134.6 (dd, *J* = 98.3, 4.4 Hz), 132.5 (d, *J* = 2.9 Hz), 131.1 (d, *J* = 101.2 Hz), 130.9 (d, *J* = 8.8 Hz), 130.8 (d, *J* = 8.6 Hz), 129.0 (d, *J* = 11.5 Hz), 128.3, 127.4, 126.5 (dd, *J* = 8.8, 2.9 Hz), 126.2, 116.4 (d, *J* = 20.4 Hz), 117.8 (dd, *J* = 23.1, 10.1 Hz), 116.7 (d, *J* = 13.0 Hz), 59.9, 30.8 (d, *J* = 66.4 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 28.35.

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{22}H_{20}FO_2PNa^+$ 389.1078; Found: 389.1077.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -110.22 (s, 1F).

***(Z)-(4-hydroxy-3-phenylbut-2-en-1-yl)(phenyl)(m-tolyl)phosphine oxide* 3ah**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3ah** (29.4 mg, 81% yield) as a white solid, m.p. = 129 – 132 °C.

NMR and HRMS data for the product **3ah**:

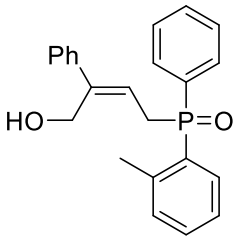
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.78 – 7.73 (m, 2H), 7.61 (d, *J* = 12.6 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.29 – 7.25 (m, 2H), 7.24 – 7.20 (m, 1H), 5.63 – 5.59 (m, 1H), 4.47 (s, 2H), 3.38 (dd, *J* = 14.4, 9.0 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.9 (d, $J_{C\text{-}P}$ = 11.6 Hz), 141.6 (d, $J_{C\text{-}P}$ = 4.4 Hz), 138.9 (d, $J_{C\text{-}P}$ = 11.5 Hz), 133.0, 132.1, 131.9 (d, $J_{C\text{-}P}$ =99.8 Hz), 131.8, 131.5 (d, $J_{C\text{-}P}$ = 8.8 Hz), 131.2, 130.9 (d, $J_{C\text{-}P}$ =8.6 Hz), 128.8 (d, $J_{C\text{-}P}$ =11.6 Hz), 128.7 (d, $J_{C\text{-}P}$ =11.5 Hz), 128.2, 127.7 (d, $J_{C\text{-}P}$ =10.1 Hz), 126.2 (d, $J_{C\text{-}P}$ =2.9 Hz), 117.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.9 (d, $J_{C\text{-}P}$ =2.9 Hz), 31.0 (d, $J_{C\text{-}P}$ =66.4 Hz), 21.4.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 29.16.

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{23}H_{23}O_2PNa^+$ 385.1328; Found: 385.1333.

***(Z)-(4-hydroxy-3-phenylbut-2-en-1-yl)(phenyl)(o-tolyl)phosphine oxide* 3ai**



Prepared according to ***General Procedure***. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 3:1, 2:1 to 1:1) to afford **3ai** (26.7 mg, 73% yield) as a white solid, m.p. = 127 – 130 ^{o}C.

Prepared according to the procedure for the asymmetric synthesis to afford **3ai** (3.4 mg) in 10 % yield. The enantiomeric ratio was measured to be 27:73 by chiral HPLC analysis on Chiralpak OD-H column (*n*-hexane /i-PrOH = 60:40, flow rate: 1.0 mL/min), UV 254 nm, tR (minor) = 5.86 min, tR (major) = 6.62 min.

NMR and HRMS data for the product **3ai**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.71 (dd, *J* = 13.2, 7.8 Hz, 1H), 7.64 (dd, *J* = 11.4, 6.6 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.25 – 7.21 (m, 1H), 5.62 – 5.57 (m, 1H), 4.51 (d, *J* = 12.6 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 3.58 (td, *J* = 14.4, 7.8 Hz, 1H), 3.36 (td, *J* = 13.8, 8.4 Hz, 1H), 2.42 (s, 3H).

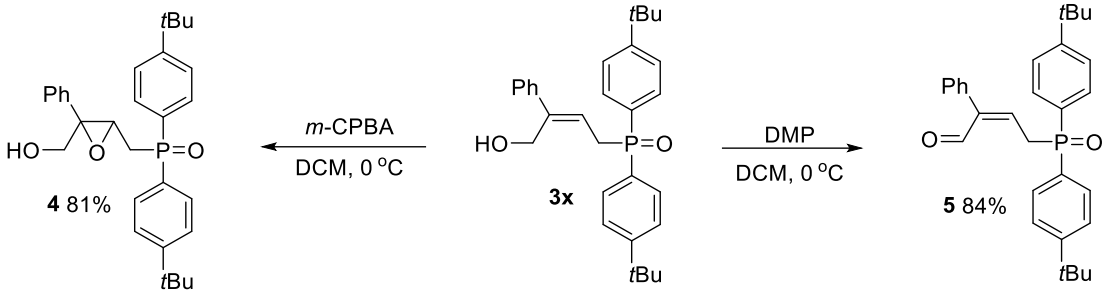
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 147.0 (d, $J_{C\text{-}P}$ = 10.1 Hz), 142.7 (d, $J_{C\text{-}P}$ = 8.8 Hz), 141.6 (d, $J_{C\text{-}P}$ = 4.2 Hz), 132.9, 132.4, 132.2 (d, $J_{C\text{-}P}$ =10.1 Hz), 132.0, 131.4 (d, $J_{C\text{-}P}$ =11.6 Hz), 130.8 (d, $J_{C\text{-}P}$ =10.1 Hz), 129.6 (d, $J_{C\text{-}P}$ =99.7 Hz), 128.7 (d, $J_{C\text{-}P}$ =11.5 Hz), 128.2, 127.3, 126.2, 125.7 (d, $J_{C\text{-}P}$ =11.5 Hz), 117.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 59.9, 30.8 (d, $J_{C\text{-}P}$ =65.1 Hz), 21.4 (d, $J_{C\text{-}P}$ =4.4 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 31.01.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{23}O_2PNa^+$ 385.1328; Found: 385.1327.

4. Synthetic Transformations of the Product 3x.

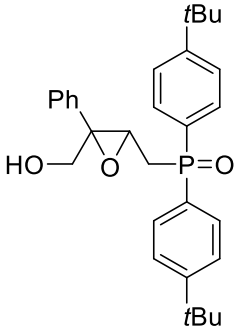
4.1 Synthetic transformations.



Synthesis of compound **4**.

To a solution of **3x** (46.1 mg, 0.10 mmol) in DCM (1.0 mL) was added *m*-CPBA (18.9 mg, 0.10 mmol) at 0 °C, and the mixture was stirred at same temperature for 2 h. After removing the solvent in vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether / ethyl acetate = 5:1 to 3:1) to gived compound **4**.

bis(4-(tert-butyl)phenyl)((3-(hydroxymethyl)-3-phenyloxiran-2-yl)methyl)phosphine oxide 4



White solid; 38.6 mg, 81 % yield; m.p. = 170 – 173 °C.

NMR and HRMS data for the product **4**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.74 (dd, *J* = 11.4, 9.0 Hz, 2H), 7.69 (dd, *J* = 12.0, 8.4 Hz, 2H), 7.55 – 7.48 (m, 4H), 7.47 – 7.44 (m, 2H), 7.30 – 7.23 (m, 2H), 5.97 (s, 1H), 4.12 (t, *J* = 12.0 Hz, 1H), 3.83 (d, *J* = 12.0, 1H), 3.14 (ddd, *J* = 15.0, 7.2, 4.8 Hz, 1H), 3.03 (dd, *J* = 10.2, 4.2 Hz, 1H), 2.59 – 2.51 (m, 1H), 1.33 (s, 9H), 1.31 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 156.1, 139.5, 130.8 (d, J_{C-P} = 10.1 Hz), 130.3 (d, J_{C-P} = 10.1 Hz), 129.0 (d, J_{C-P} = 105.5 Hz), 128.0, 127.8, 126.6, 63.9, 63.5, 58.9, 35.1, 31.03, 30.95 (d, J_{C-P} = 66.4 Hz).

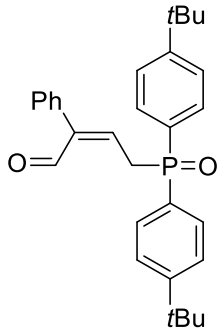
^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 30.23.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{30}H_{37}O_3PNa^+$ 499.2373; Found: 499.2378.

***Synthesis of compound* 5.**

The Dess-Martin periodinane (600 mg, 1.41 mmol) was added to a solution of **3x** (100 mg, 0.587 mmol) in CH_2Cl_2 (6 mL) at 0 °C. After 2 h, the reaction mixture was treated with 1:1 ratio of saturated $Na_2S_2O_3$ and saturated $NaHCO_3$ solution (1 mL: 1 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel chromatography (petroleum ether / ethyl acetate = 2:1 to 1:1) to gived compound **5**.

***(Z)-4-(bis(4-(tert-butyl)phenyl)phosphoryl)-2-phenylbut-2-enal* 5**



White solid; 38.5 mg, 84 % yield; m.p. = 162 – 165 °C.

NMR and HRMS data for the product **5**:

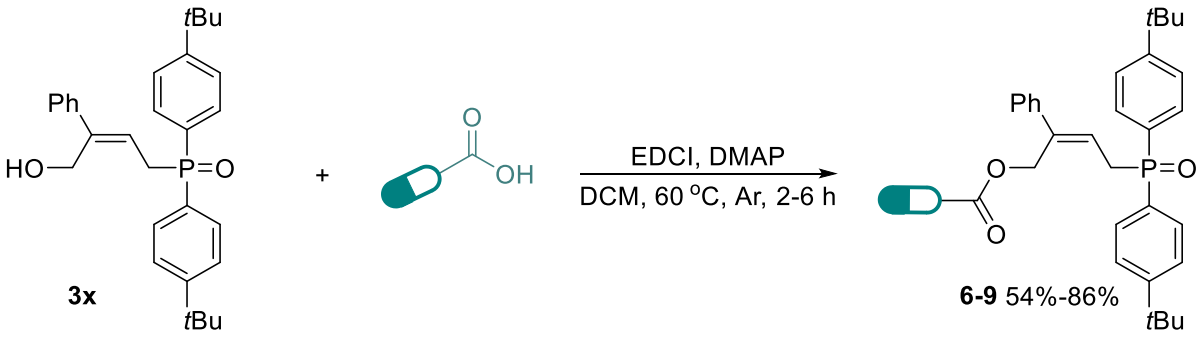
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.59 (s, 1H), 7.56 – 7.50 (m, 4H), 7.47 – 7.43 (m, 4H), 7.34 – 7.30 (m, 3H), 6.93 – 6.86 (m, 3H), 3.40 (dd, *J* = 15.0, 8.4 Hz, 2H), 1.32 (s, 18H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 192.8, 155.8, 147.2 (d, $J_{C\text{-}P}$ = 10.1 Hz), 144.1 (d, $J_{C\text{-}P}$ = 7.2 Hz), 131.5, 130.7 (d, $J_{C\text{-}P}$ = 8.6 Hz), 129.4, 128.5 (d, $J_{C\text{-}P}$ = 102.5 Hz), 128.3, 128.2, 125.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 35.0, 33.3 (d, $J_{C\text{-}P}$ = 65.1 Hz), 31.0.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 30.06.

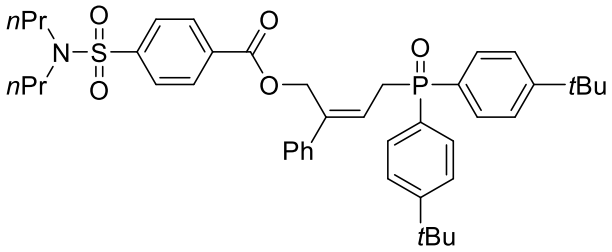
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{35}O_2PH^+$ 459.2448; Found: 459.2455.

4.2 Drug derivatization.



To a flame-dried Schlenk tube were added drugs containing carboxyl groups (0.20 mmol), after which the tube was evacuated and back filled with argon three times. Subsequently, under the protection of Ar, DCM (1.0 mL) was added. Then, DMAP (0.05 mmol) and EDCI (0.20 mmol) at room temperature were added at room temperature, and the mixture was stirred at same temperature for 10 min.. Under the protection of Ar, **3x** (0.1 mmol) was added. The resulting mixture was stirred for 2-6 h at 60 °C, after which the reaction mixture was concentrated under reduced pressure and the resulting crude material was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (3:1, 2:1 to 1:1) as eluents to afford the desired products **6-9**. All products were dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS analysis, etc.

***(Z)-4-(bis(4-(tert-butyl)phenyl)phosphoryl)-2-phenylbut-2-en-1-yl 4-(N,N-dipropylsulfamoyl)benzoate* 6**



Prepared according to the above procedure to afford **6** (40.0 mg, 55% yield) as a colorless oil.

NMR and HRMS data for the product **6**:

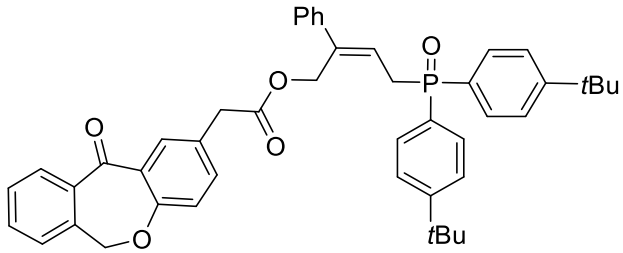
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.63 (m, 4H), 7.43 (d, *J* = 6.0 Hz, 4H), 7.28 – 7.19 (m, 5H), 6.07 – 6.02 (m, 1H), 5.03 (s, 2H), 3.43 (dd, *J* = 14.4, 8.4 Hz, 2H), 3.00 (t, *J* = 7.8 Hz, 4H), 1.50 – 1.43 (m, 4H), 1.26 (s, 18H), 0.79 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 165.0, 155.5, 144.2, 139.7 (d, J_{C-P} = 2.9 Hz), 138.6 (d, J_{C-P} = 10.1 Hz), 133.2, 130.9 (d, J_{C-P} = 10.3 Hz), 130.2, 129.1 (d, J_{C-P} = 102.7 Hz), 128.4, 127.7, 127.0, 126.3, 125.7 (d, J_{C-P} = 11.6 Hz), 123.2 (d, J_{C-P} = 8.8 Hz), 61.8, 49.9, 35.0, 32.0 (d, J_{C-P} = 68.0 Hz), 31.1, 21.9, 11.1.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 30.59.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{43}H_{54}NO_5PSNa^+$ 750.3353; Found: 750.3356.

***(Z)-4-(bis(4-(tert-butyl)phenyl)phosphoryl)-2-phenylbut-2-en-1-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate* 7**



Prepared according to the above procedure to afford **7** (61.1 mg, 86% yield) as a colorless oil.

NMR and HRMS data for the product **7**:

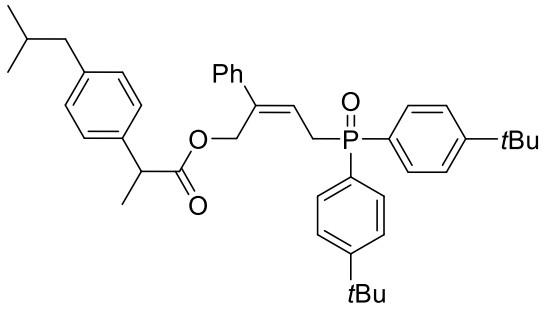
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.01 (s, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.67 (dd, *J* = 11.4, 8.4 Hz, 4H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.45 (m, 5H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.18 (m, 6H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.04 – 6.00 (m, 1H), 5.15 (s, 2H), 4.80 (s, 2H), 3.51 (s, 2H), 3.39 (dd, *J* = 14.4, 8.4 Hz, 2H), 1.31 (s, 18H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 190.7, 171.1, 160.4, 155.3, 140.4, 139.8, 138.9 (d, J_{C-P} = 11.6 Hz), 136.2, 135.5, 132.7, 132.3, 130.9 (d, J_{C-P} = 10.3 Hz), 129.5, 129.2, 128.2, 127.8, 127.5 (d, J_{C-P} = 7.1 Hz), 126.4, 125.6 (d, J_{C-P} = 11.5 Hz), 125.0, 122.7 (d, J_{C-P} = 8.6 Hz), 121.0, 73.6, 61.2, 40.1, 35.0, 31.9 (d, J_{C-P} = 68.0 Hz), 31.1.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 30.65.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{46}H_{47}O_5PNa^+$ 733.3054; Found: 733.3058.

***(Z)-4-(bis(4-(tert-butyl)phenyl)phosphoryl)-2-phenylbut-2-en-1-yl 2-(4-isobutylphenyl)propanoate* 8**



Prepared according to the above procedure to afford **7** (47.4 mg, 73% yield) as a colorless oil.

NMR and HRMS data for the product **7**:

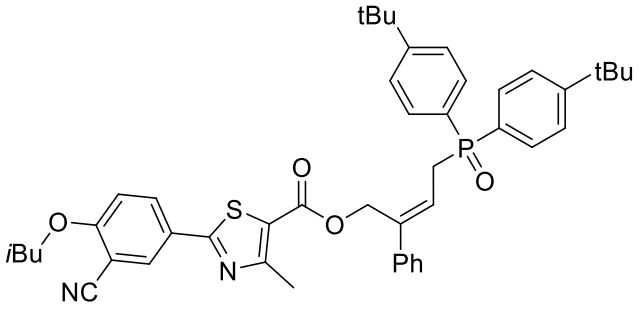
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.66 (dd, *J* = 11.4, 8.4 Hz, 4H), 7.48 (d, *J* = 8.4 Hz, 4H), 7.22 – 7.19 (m, 3H), 7.16 – 7.14 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.01 – 5.96 (m, 1H), 4.78 – 4.72 (m, 2H), 3.58 (q, *J* = 7.2 Hz, 1H), 3.34 (dd, *J* = 14.4, 8.4 Hz, 2H), 2.40 (d, *J* = 7.2 Hz, 2H), 1.84 – 1.77 (m, 1H), 1.36 (d, *J* = 7.8 Hz, 3H), 1.32 (s, 18H), 0.87 (d, *J* = 7.2 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 174.4, 155.3, 140.4, 139.9, 139.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 137.3, 130.9 (d, $J_{C\text{-}P}$ = 10.3 Hz), 129.20 (d, $J_{C\text{-}P}$ = 101.2 Hz), 129.19, 128.1, 127.4, 127.0, 126.4, 125. 6 (d, $J_{C\text{-}P}$ = 11.6 Hz), 122.5 (d, $J_{C\text{-}P}$ = 8.8 Hz), 61.2, 45.0, 44.9, 35.0, 31.8 (d, $J_{C\text{-}P}$ = 68.0 Hz), 31.1, 30.1, 22.4, 18.2.

^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 30.79.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{43}H_{53}O_3PNa^+$ 671.3625; Found: 671.3626.

***(Z)-4-(bis(4-(tert-butyl)phenyl)phosphoryl)-2-phenylbut-2-en-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate* 9**



Prepared according to the above procedure to afford **9** (47.4 mg, 73% yield) as a colorless oil.

NMR and HRMS data for the product **9**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.11 (s, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.71 (dd, *J* = 12.0, 9.0 Hz, 4H), 7.49 (d, *J* = 8.4 Hz, 4H), 7.32 – 7.30 (m, 4H), 7.27 – 7.25 (m, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.12 – 6.07 (m, 1H), 5.02 (s, 2H), 3.88 (d, *J* = 6.0 Hz, 2H), 3.49 (dd, *J* = 15.0, 7.8 Hz, 2H), 2.59 (s, 3H), 2.22 – 2.15 (m, 1H), 1.31 (s, 18H), 1.08 (d, *J* = 7.2 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 167.4, 162.4, 161.7, 161.2, 155.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 139.7, 138.6 (d, $J_{C\text{-}P}$ = 11.6 Hz), 132.5, 132.0, 130.9 (d, $J_{C\text{-}P}$ = 8.8 Hz), 129.0 (d, $J_{C\text{-}P}$ = 101.2 Hz), 128.3, 127.6, 126.4, 125.8, 125.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 122.9 (d, $J_{C\text{-}P}$ = 8.6 Hz), 121.6, 115.3, 112.5, 102.9, 75.6, 61.5, 34.9, 32.0 (d, $J_{C\text{-}P}$ = 68.0 Hz), 31.0, 28.1, 19.0, 17.3.

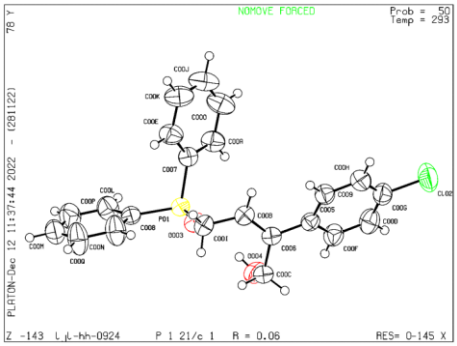
^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm): 30.84.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{46}H_{51}N_2O_4PSNa^+$ 781.3200; Found: 781.3202.

5. Crystal Data and Structure Refinement for Representative Product 3c

Crystal preparation and measurement

To a 5 mL penicillin bottle containing **3c** (30 mg) was added 0.5 mL DCM and 3.0 mL PE. The bottle was sealed up and kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the structure of **3c**. The data were collected by an Agilent Gemini equipped with a Cu radiation source (Kα = 1.54184 Å) at 293.0 K. CCDC 2313314 (**3c**) contains the supplementary crystallographic data for this paper.



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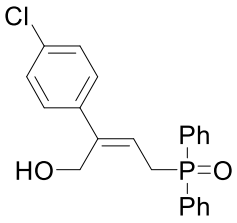


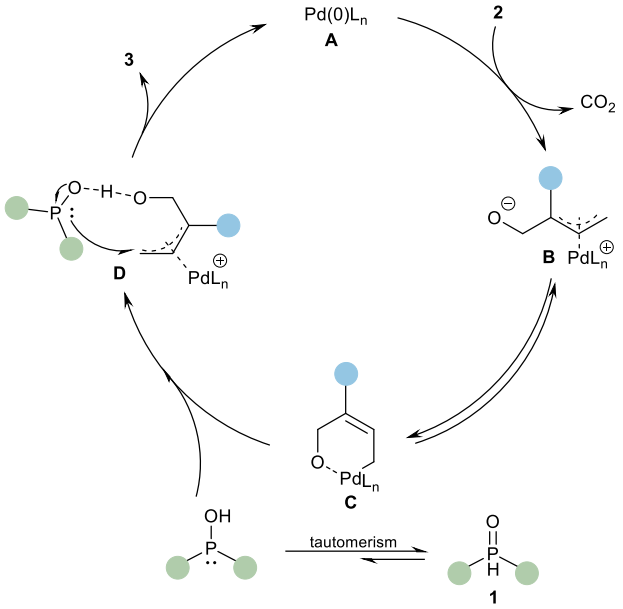
3c

Identification code	**3c**
Empirical formula	$C_{22}H_{20}ClO_2P$
Formula weight	382.80
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.74906(11)
b/Å	19.4433(5)
c/Å	17.5592(4)
α/°	90
β/°	93.9972(18)
γ/°	90
Volume/Å^3	1958.00(8)
Z	4
ρ_{calc}g/cm^3	1.299
μ/mm^{-1}	2.598
F(000)	800.0
Crystal size/mm^3	0.4 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.096 to 142.636
Index ranges	$-7 \le h \le 4$, $-20 \le k \le 23$, $-20 \le l \le 21$
Reflections collected	10742
Independent reflections	3732 [R_{int} = 0.0384, R_{sigma} = 0.0356]

Data/restraints/parameters	3732/0/236
Goodness-of-fit on F^2	1.019
Final R indexes [I>= 2σ (I)]	R_1 = 0.0618, wR_2 = 0.1706
Final R indexes [all data]	R_1 = 0.0718, wR_2 = 0.1865
Largest diff. peak/hole / e $Å^{-3}$	0.46/-0.33

6. Proposed mechanism.

According to our experimental results and previous research, a plausible mechanism has been proposed in **Scheme S1**. The reaction begins with the Pd-catalyzed decarboxylation of VECs **2**, leading to the formation of intermediate **B**. This intermediate then undergoes a tautomeric process to generate cyclopalladated complex **C** as a key intermediate. Due to the basic nature of complex **C**, a proton transfer from $HP(O)Ar_2$ **1** to complex **C** results in the formation of intermediate **D**. Finally, a nucleophilic attack gives rise to the product **3** and regenerates Pd(0) complex **A**.



Scheme S1 proposed mechanism.

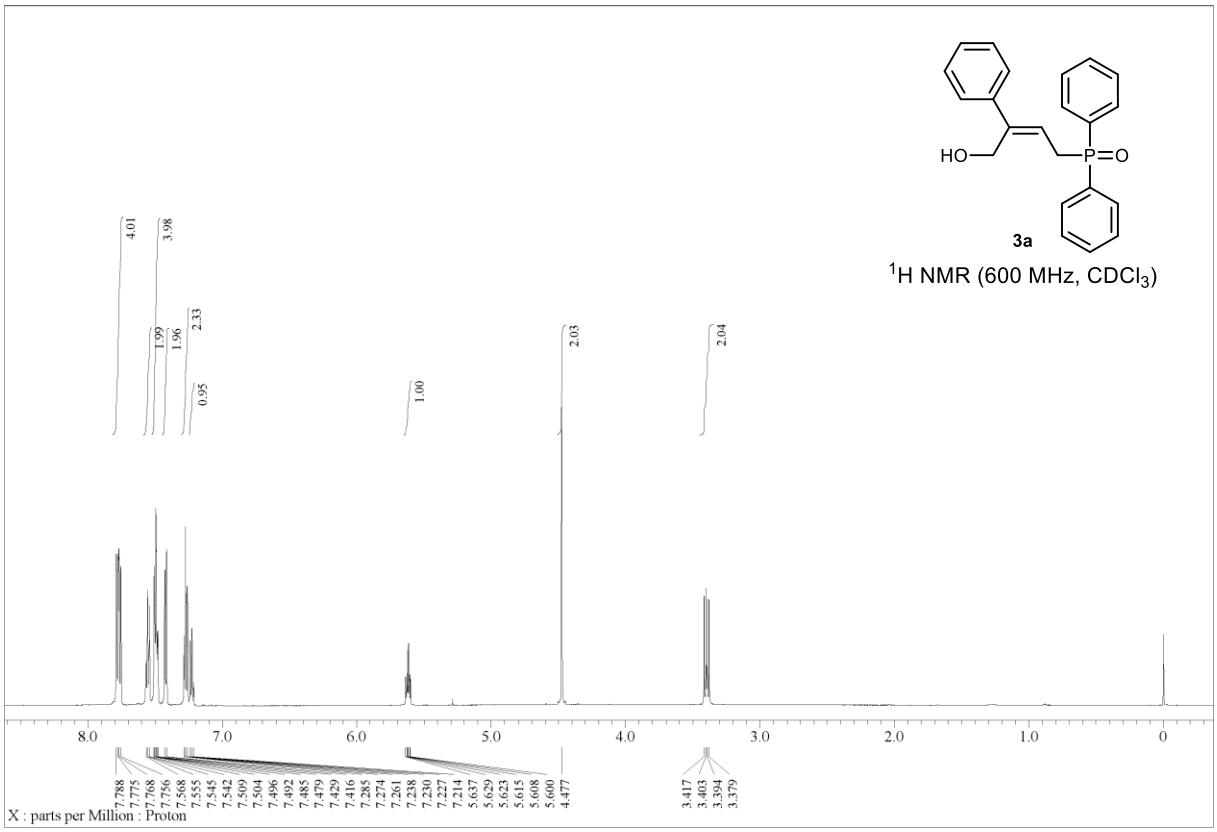
7. References and Notes.

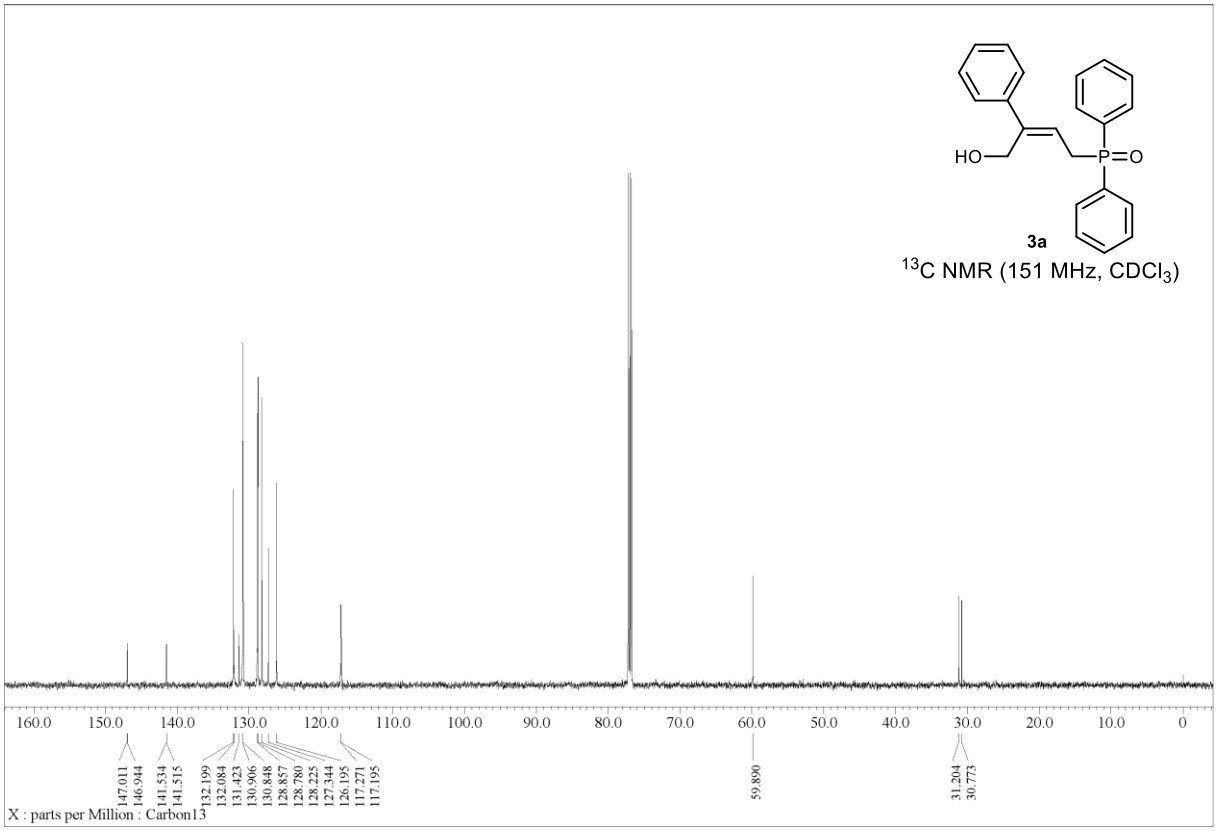
1. (a) E. Krell, *Handbook of Laboratory Distillation*, Elseriver Publishing Company, Amsterdam-London-New York, 1963. (b) M. Rosengart, *J. The Technique of Distillation and Rectification in the Laboratory*, VEB Verlag Technik, Berlin, 1954. (c) F. Stage, *The columns for laboratory distillation*, *Angew. Chem., Int. Ed.* 1947, **19**, 175–183.

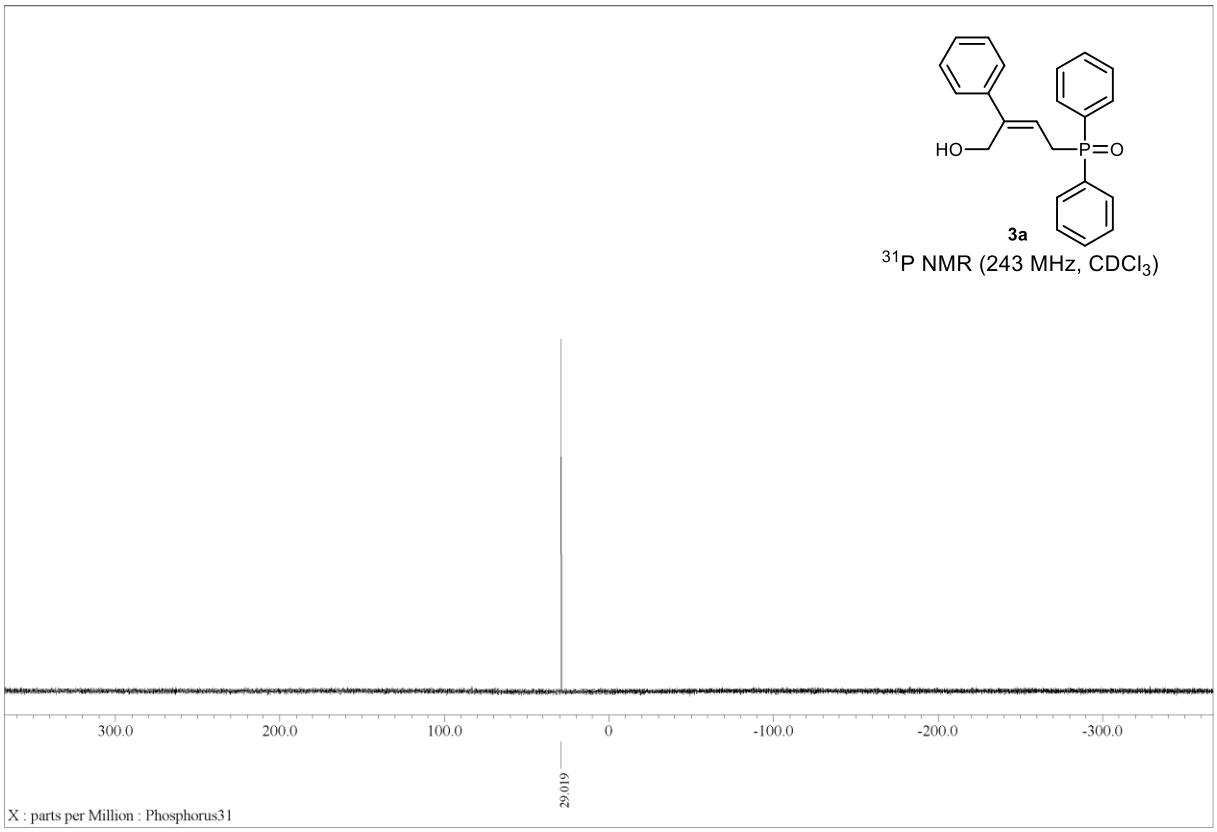
2. X. Dong, R. Wang, W. Jin and C. Liu, *Org. Lett.* 2020, **22**, 3062–3066.

3. (a) A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing and Y. J. Zhang, *Angew. Chem., Int. Ed.* 2014, **53**, 6439–6442; (b) Q.-W. Huang, T. Qi, Y. Liu, X. Zhang, Q.-Z. Li, C. Gou, Y.-M. Tao, H.-J. Leng and J.-L. Li, *ACS Catal.* 2021, **11**, 10148–10158.

8. Copies of ^{1}H, ^{13}C, ^{31}P NMR Spectra






HO
P=O
3a
31P NMR (243 MHz, CDCl3)
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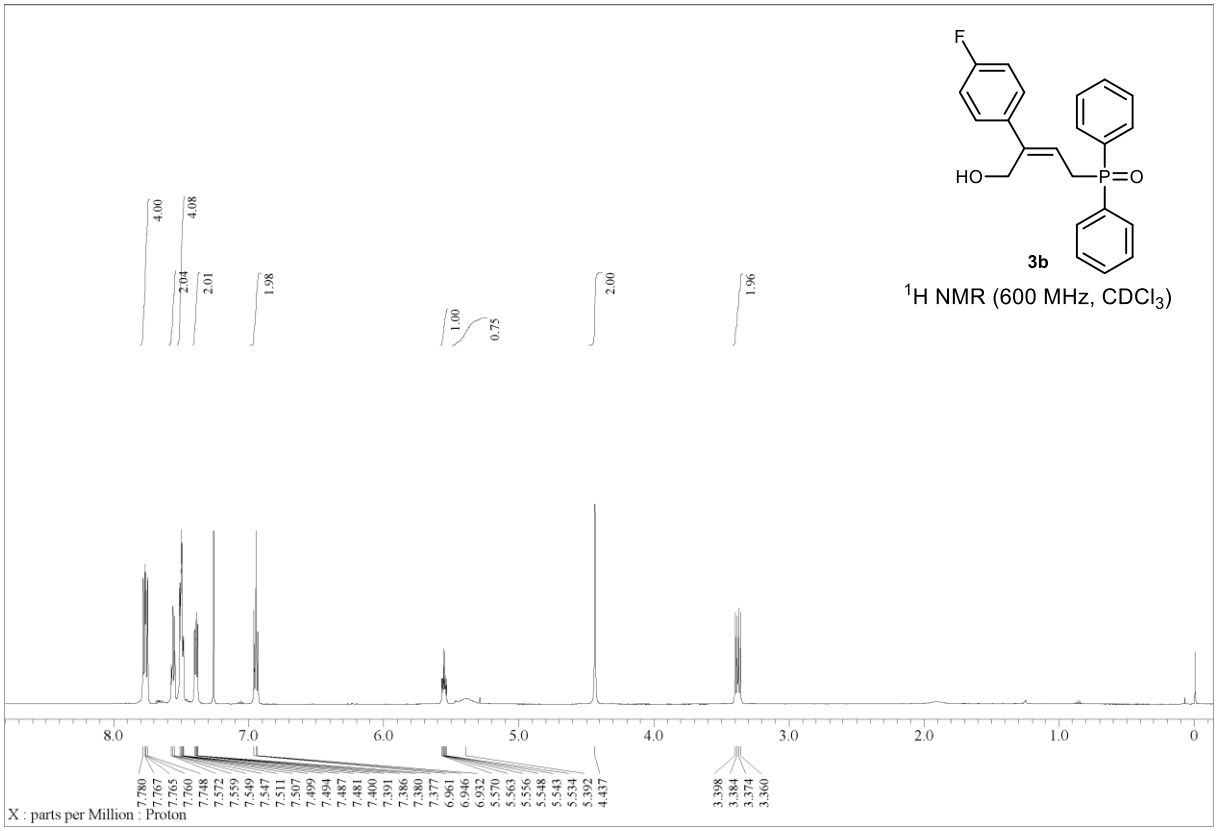
200.0
100.0
0
-100.0
-200.0
-300.0
29.019
X : parts per Million : Phosphorus31


F
HO
P=O
3b
1H NMR (600 MHz, CDCl3)
4.00
4.08
2.04
2.01
1.98
1.00
0.75
2.00
1.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.780
7.767
7.765
7.760
7.748
7.572
7.559
7.549
7.547
7.511
7.507
7.499
7.494
7.487
7.481
7.400
7.391
7.386
7.380
7.377
6.961
6.946
6.932
5.570
5.563
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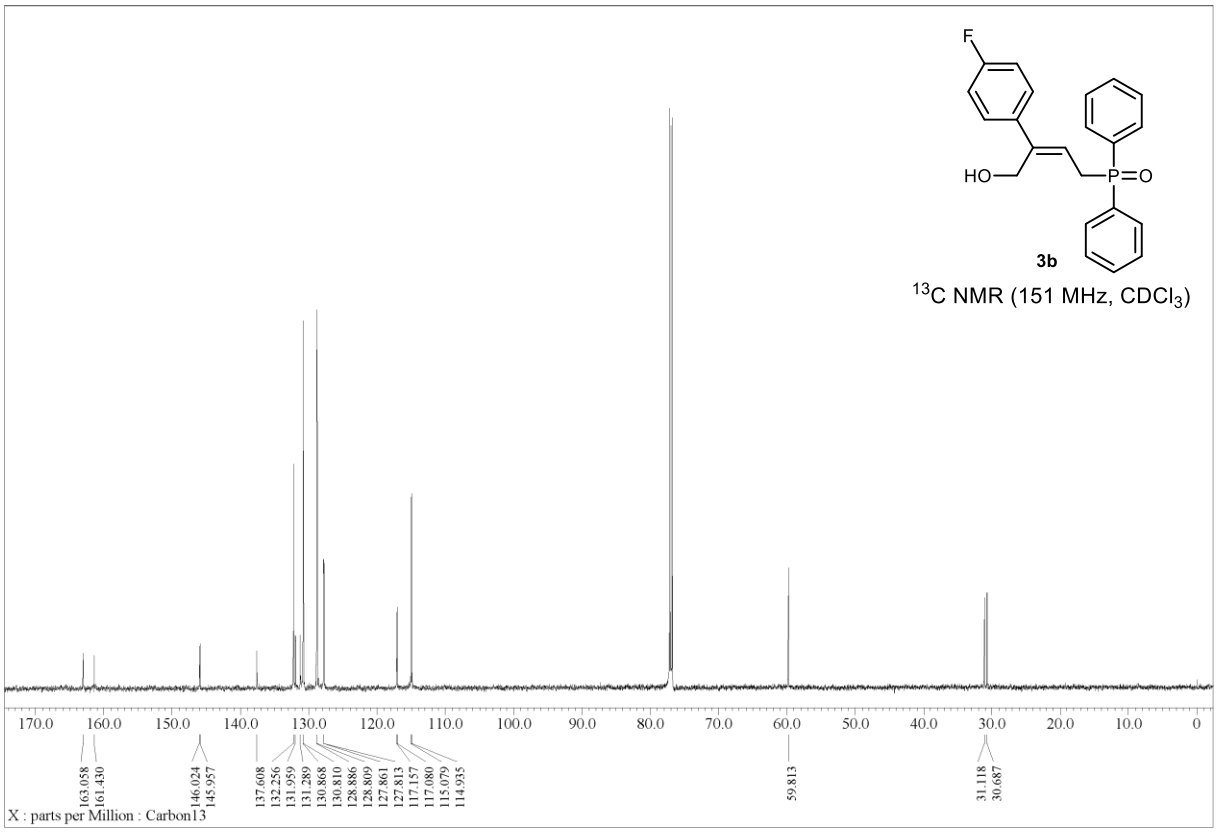
3.398
3.384
3.374
3.360
X : parts per Million : Proton


F
HO
P=O
3b
^{13}C NMR (151 MHz, CDCl$_3$)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
163.058
161.430
146.024
145.957
137.608
132.256
131.959
131.289
130.868
130.810
128.886
128.809
127.861
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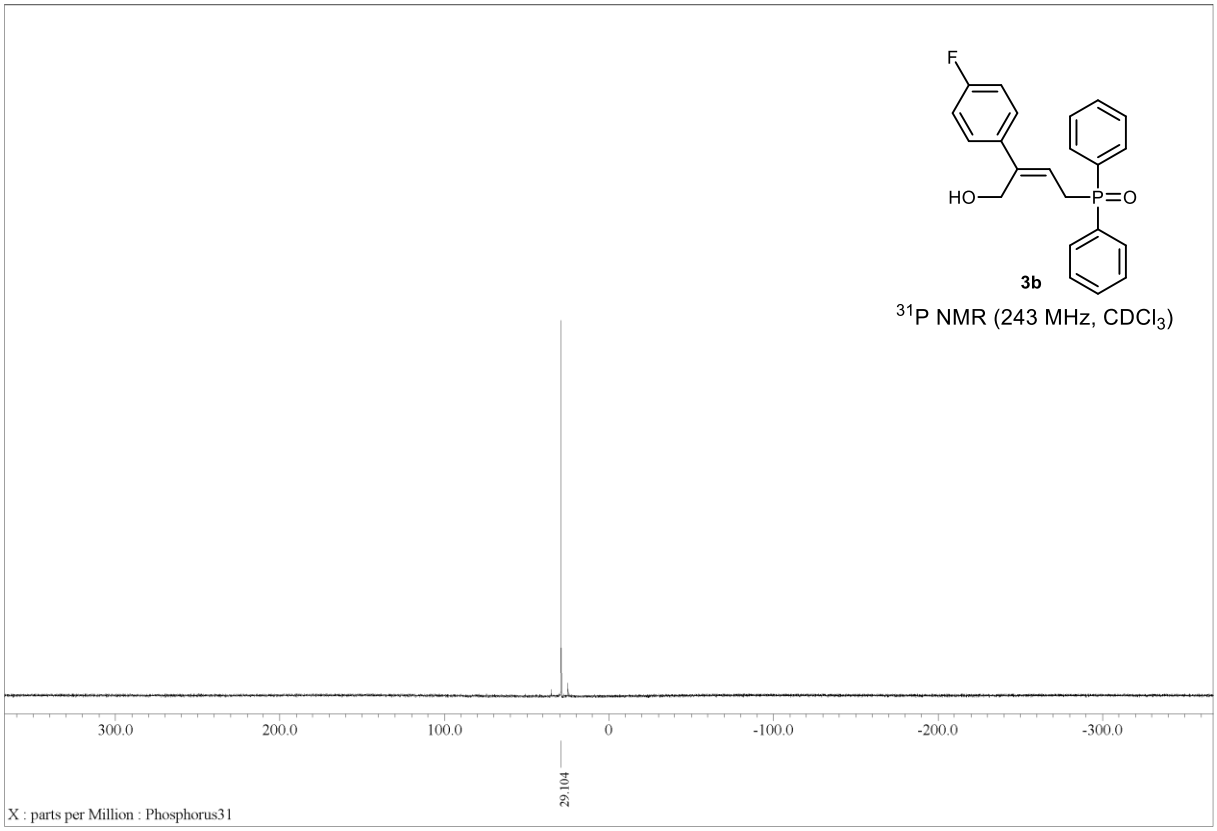
117.157
117.080
115.079
114.935
59.813
31.118
30.687
X : parts per Million : Carbon13


F
HO
P=O
3b
^{31}P NMR (243 MHz, CDCl$_3$)
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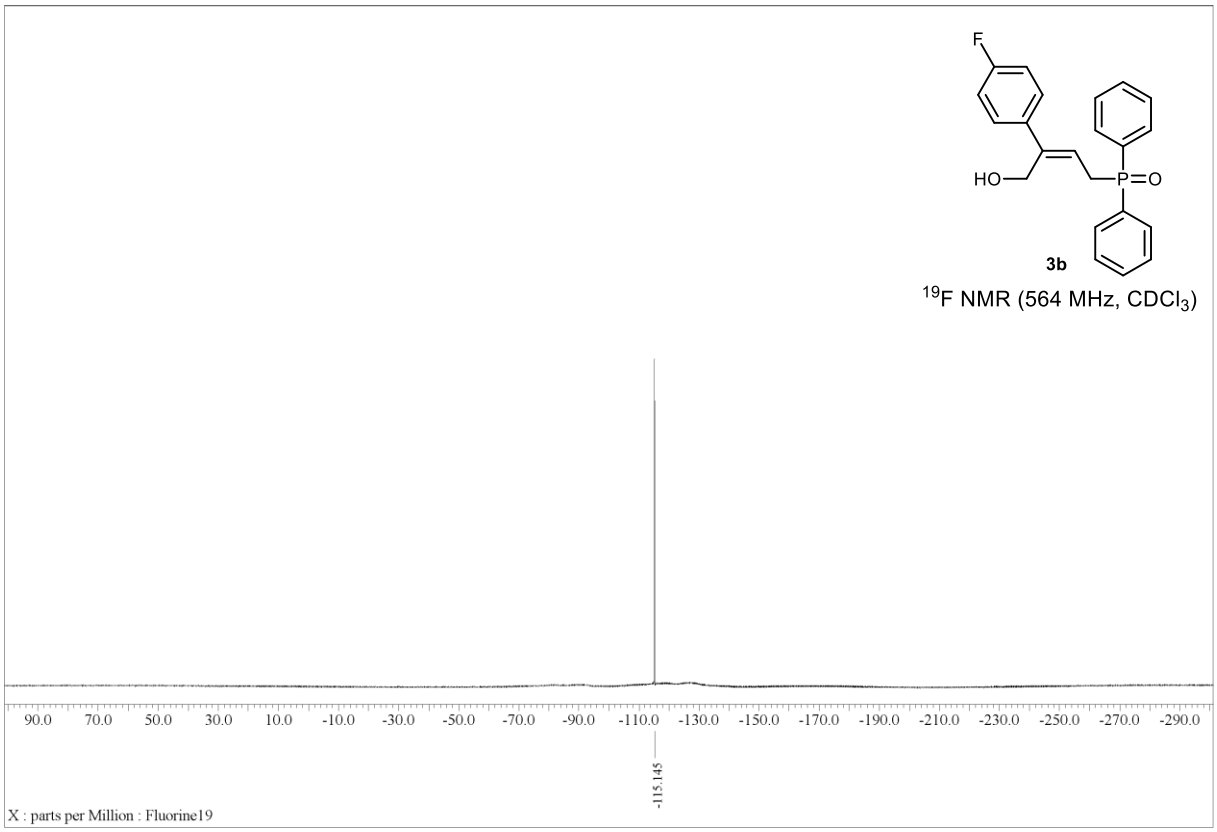
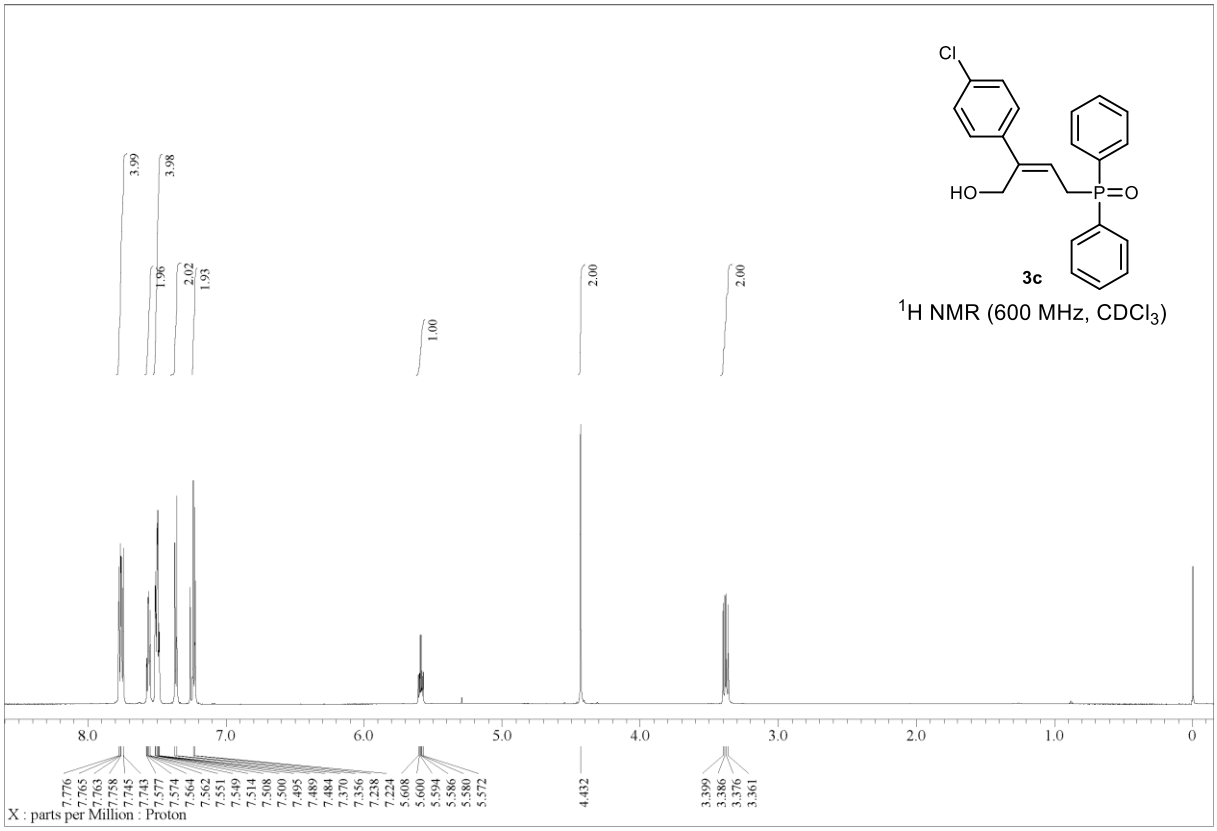
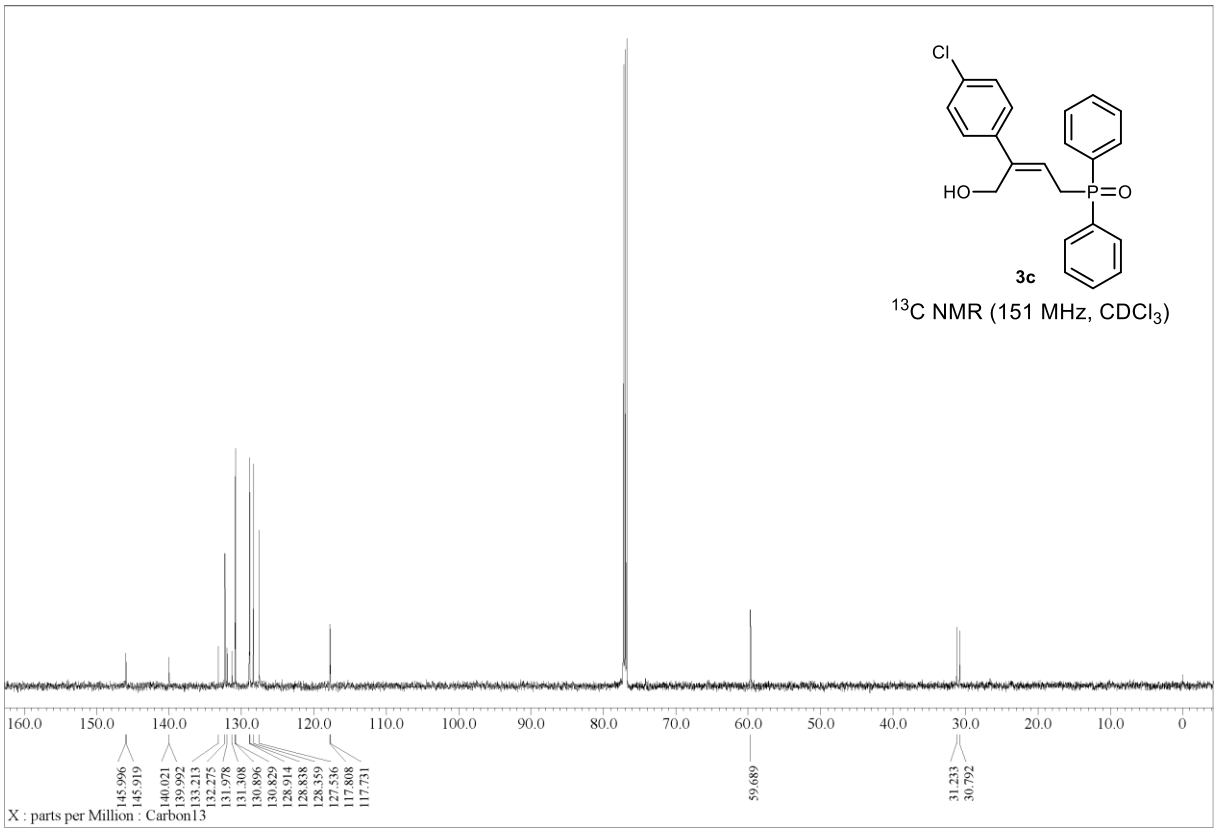
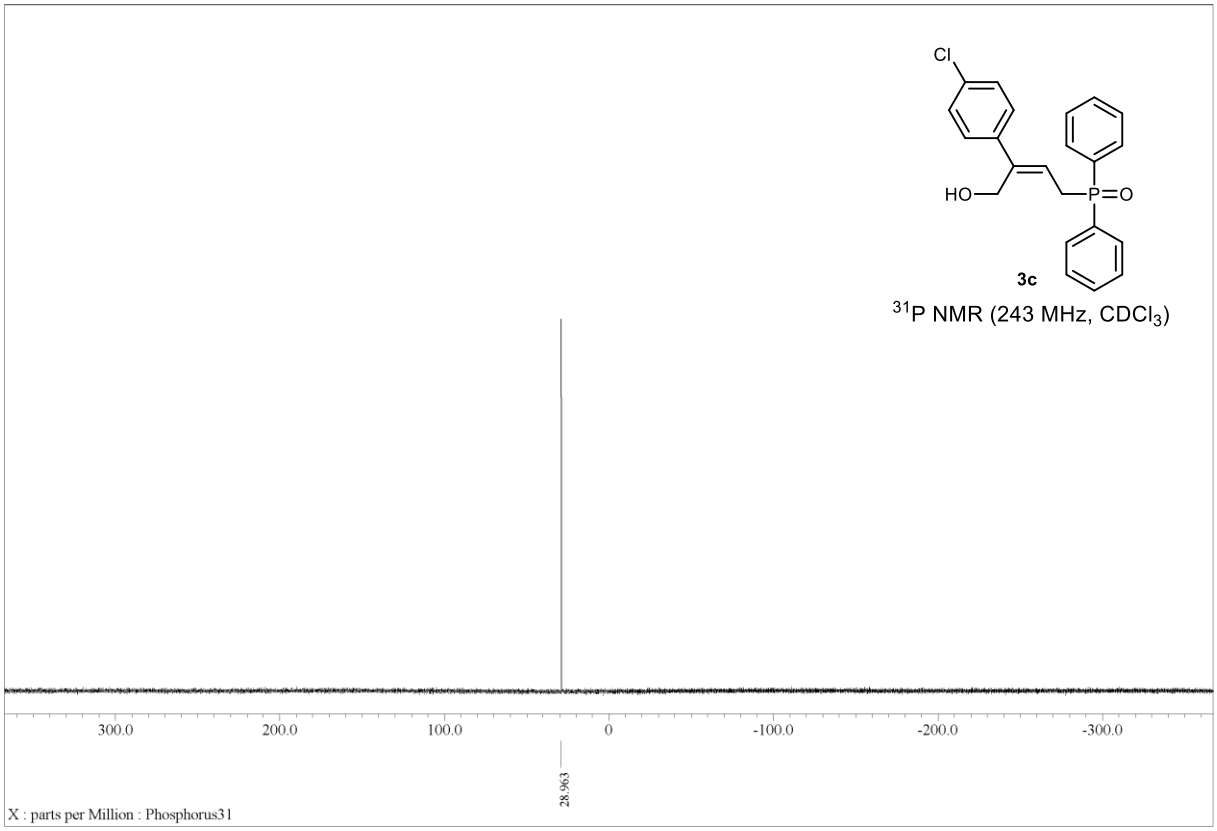
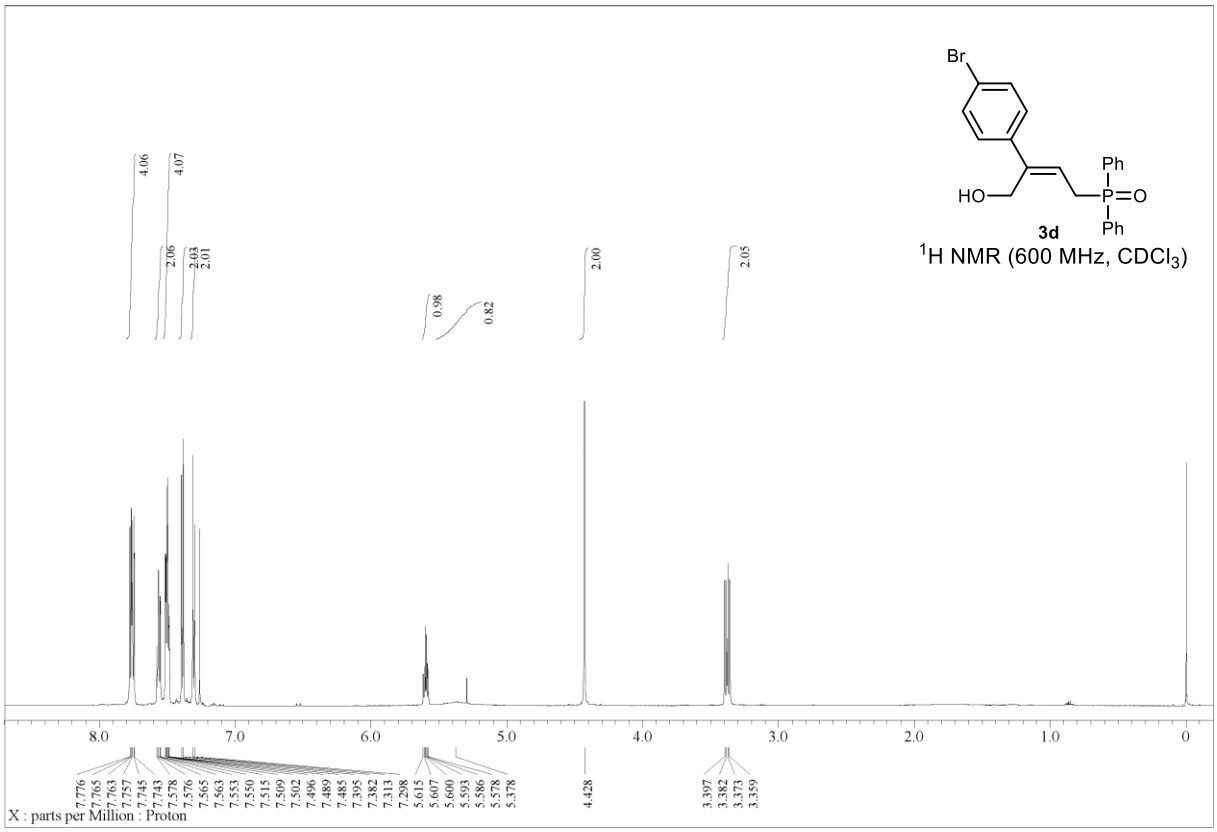
200.0
100.0
0
-100.0
-200.0
-300.0
29.104
X : parts per Million : Phosphorus31

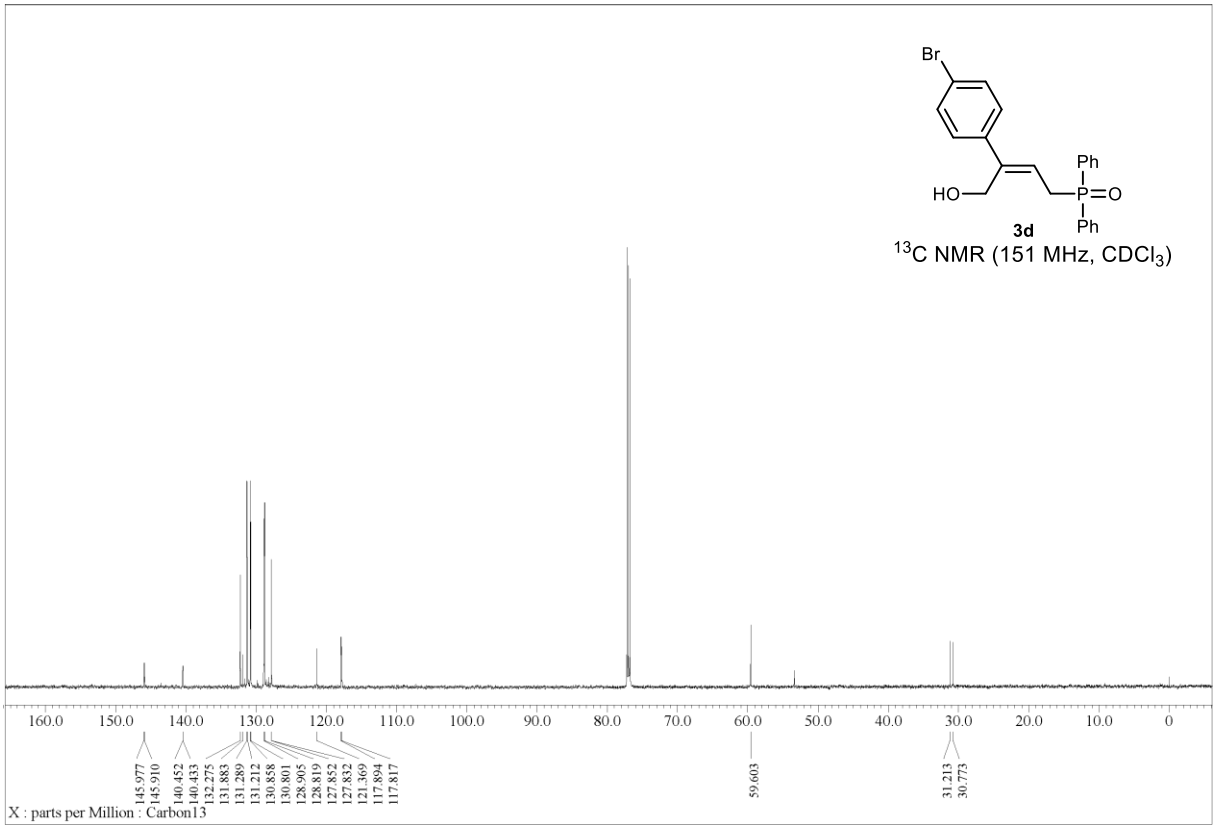

F
HO
P=O
3b
^{19}F NMR (564 MHz, CDCl$_3$)
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
-115.145
X : parts per Million : Fluorine19

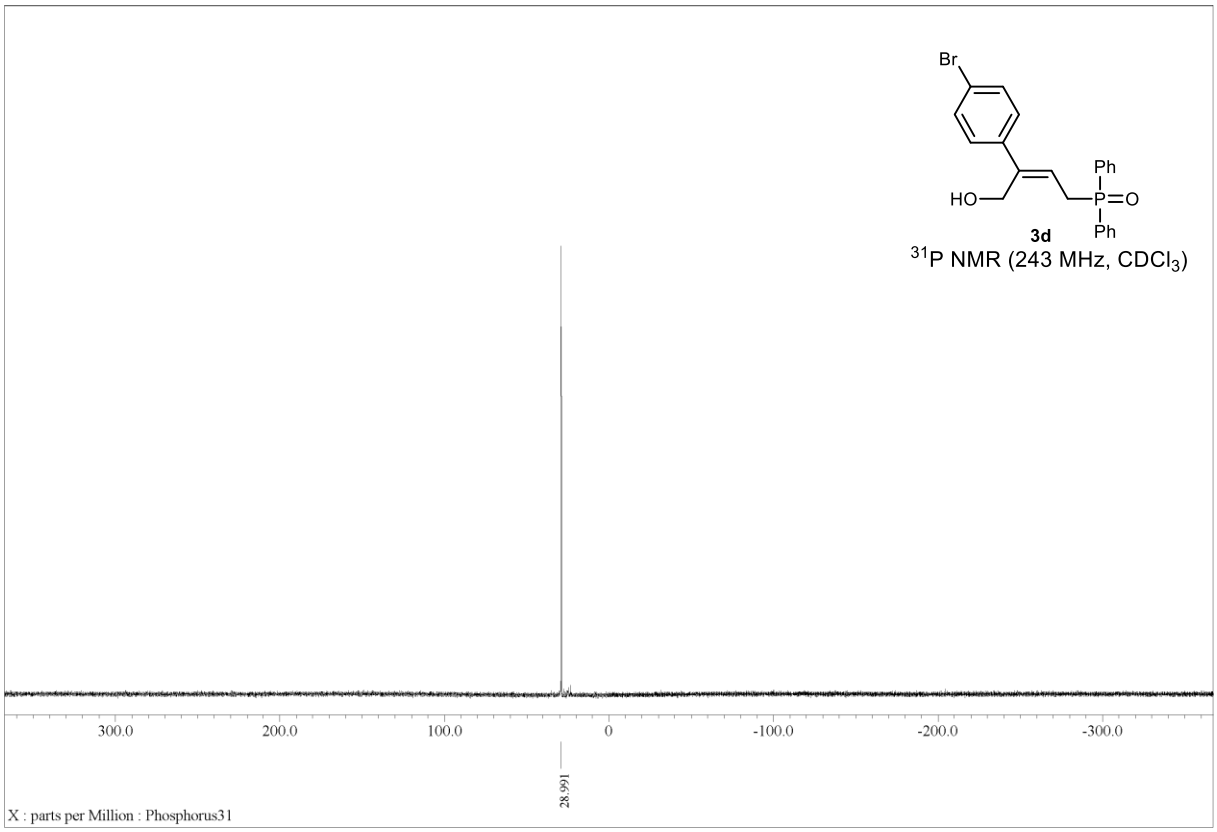

Cl
HO
P=O
3c
^{1}H NMR (600 MHz, CDCl$_3$)
3.99
3.98
1.96
2.02
1.93
1.00
2.00
2.00
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.776 7.765 7.763 7.758 7.745 7.743 7.577 7.574 7.564 7.562 7.551 7.549 7.514 7.508 7.500 7.495 7.489 7.484 7.370 7.356 7.238 7.224 5.608 5.600 5.594 5.586 5.580 5.572
4.432
3.399 3.386 3.376 3.361
X : parts per Million : Proton


Cl
HO
P=O
3c
^{13}C NMR (151 MHz, CDCl$_3$)
160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
145.996
145.919
140.021
139.992
133.213
132.275
131.978
131.308
130.896
130.829
128.914
128.838
128.359
127.536
117.808
117.731
59.689
31.233
30.792
X : parts per Million : Carbon13

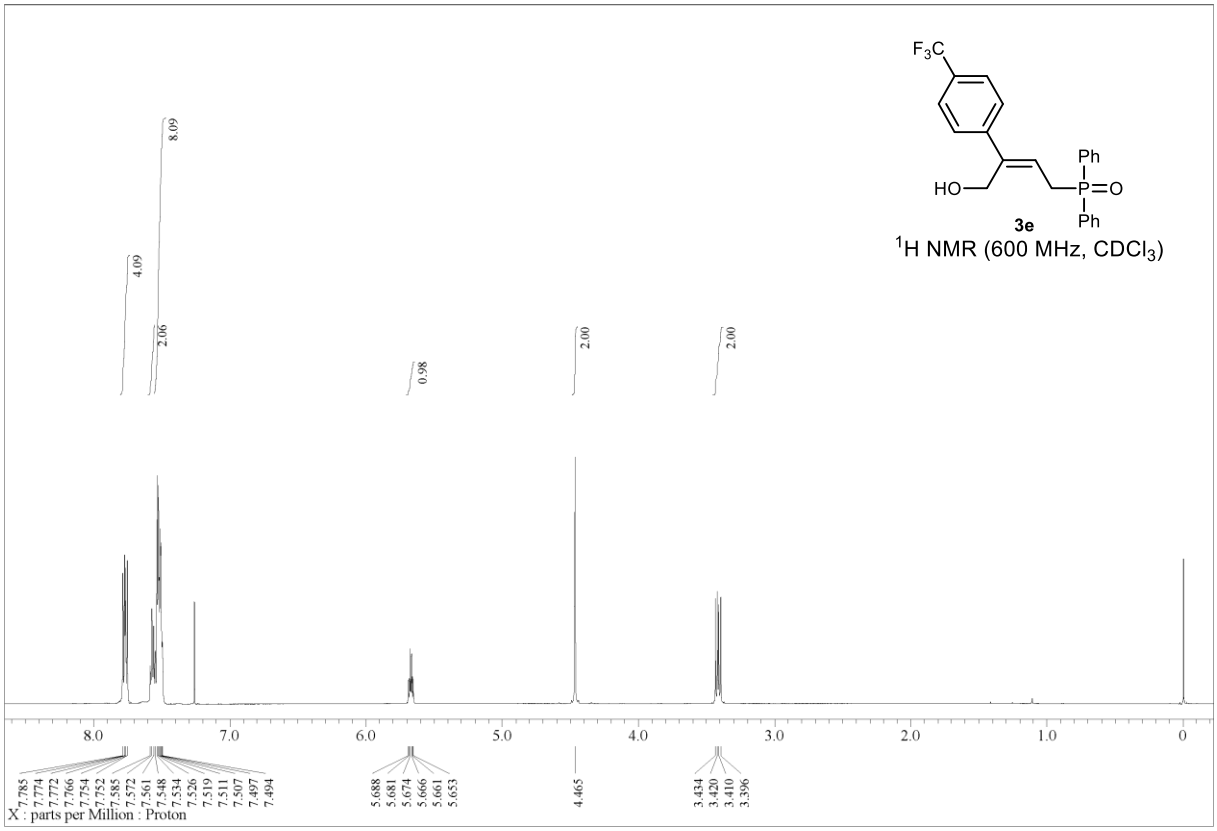

Cl
HO
P=O
3c
^{31}P NMR (243 MHz, CDCl$_3$)
300.0 200.0 100.0 0 -100.0 -200.0 -300.0
28.963
X : parts per Million : Phosphorus31


Br
Ph
HO
P=O
Ph
3d
1H NMR (600 MHz, CDCl3)
4.06
4.07
2.06
2.03
2.01
0.98
0.82
2.00
2.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.776
7.765
7.763
7.757
7.745
7.743
7.578
7.576
7.565
7.563
7.553
7.550
7.515
7.509
7.502
7.496
7.489
7.485
7.395
7.382
7.313
7.298
5.615
5.607
5.600
5.593
5.586
5.578
5.378
4.428
3.397
3.382
3.373
3.359
X : parts per Million : Proton

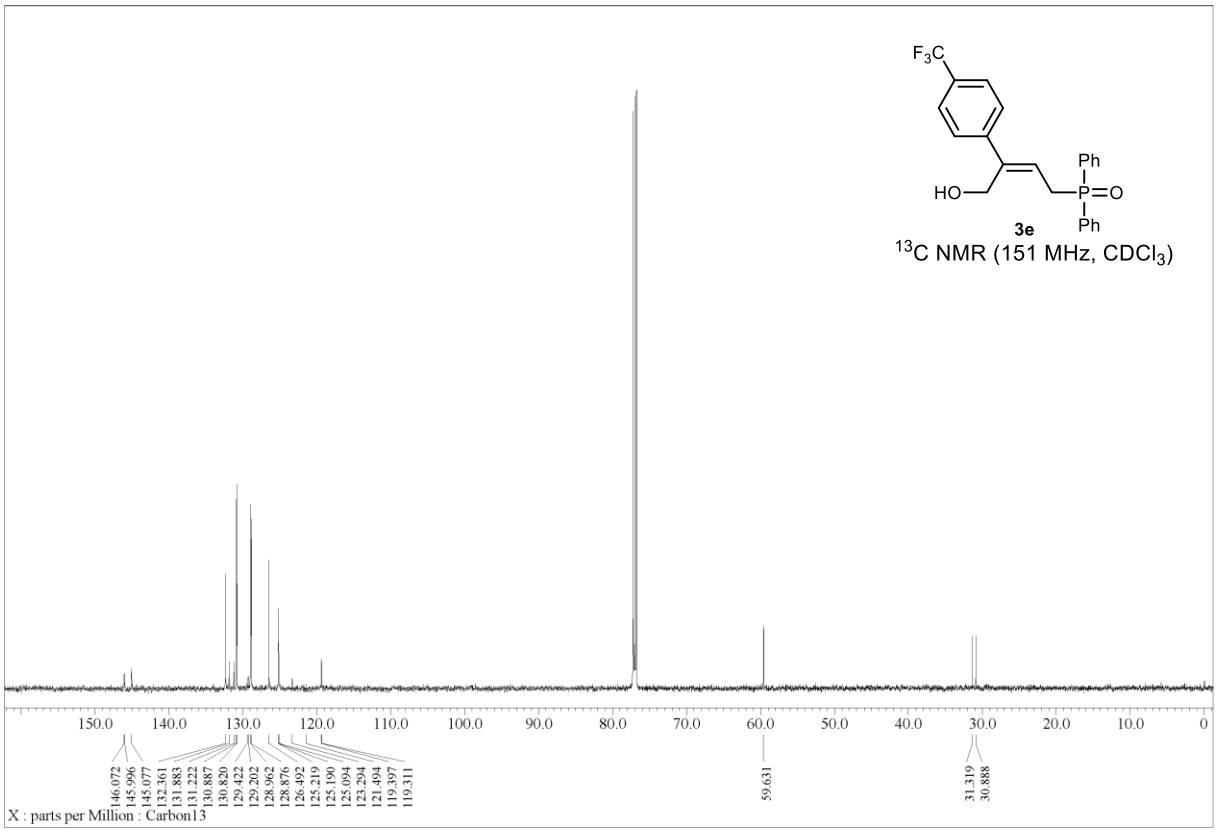

Br
Ph
HO
P=O
Ph
3d
13C NMR (151 MHz, CDCl3)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.977
145.910
140.452
140.433
132.275
131.883
131.289
131.212
130.858
130.801
128.905
128.819
127.852
127.832
121.369
117.894
117.817
59.603
31.213
30.773
X : parts per Million : Carbon13

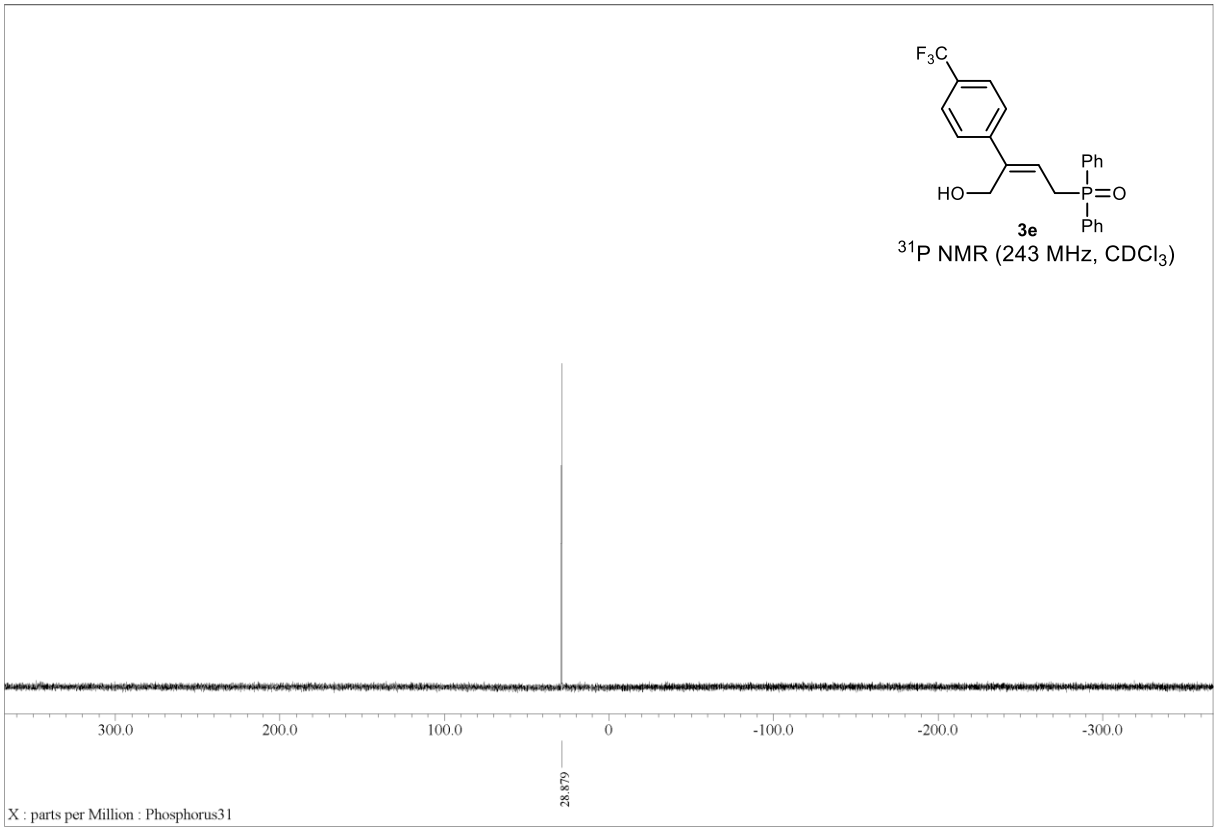


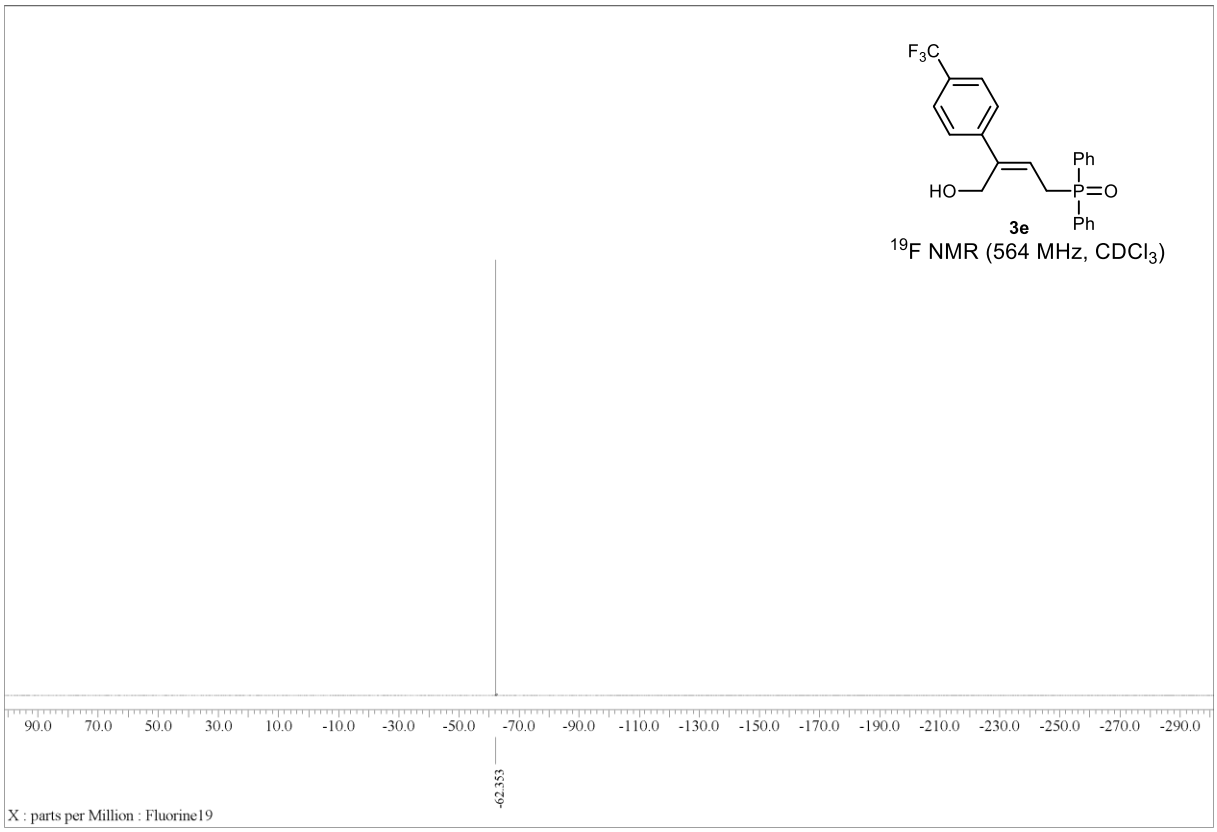
^{31}P NMR (243 MHz, $CDCl_3$)

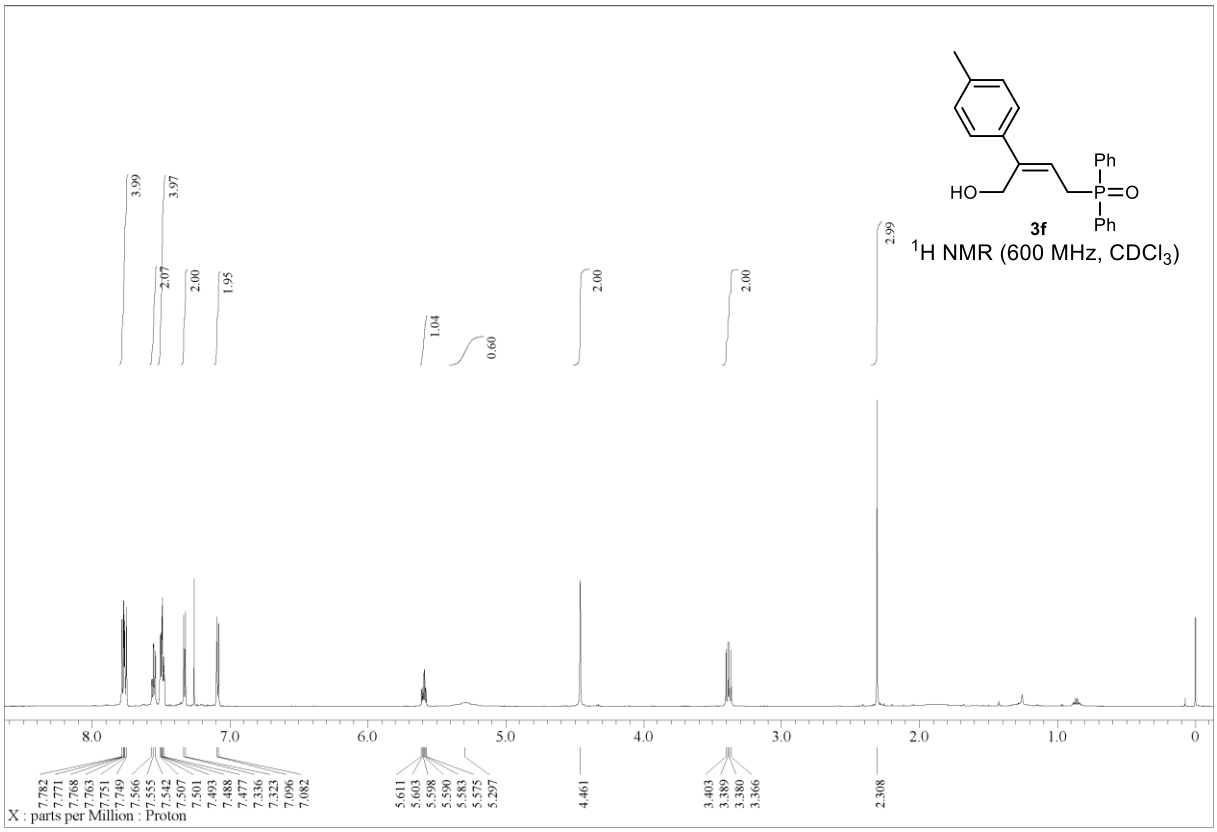


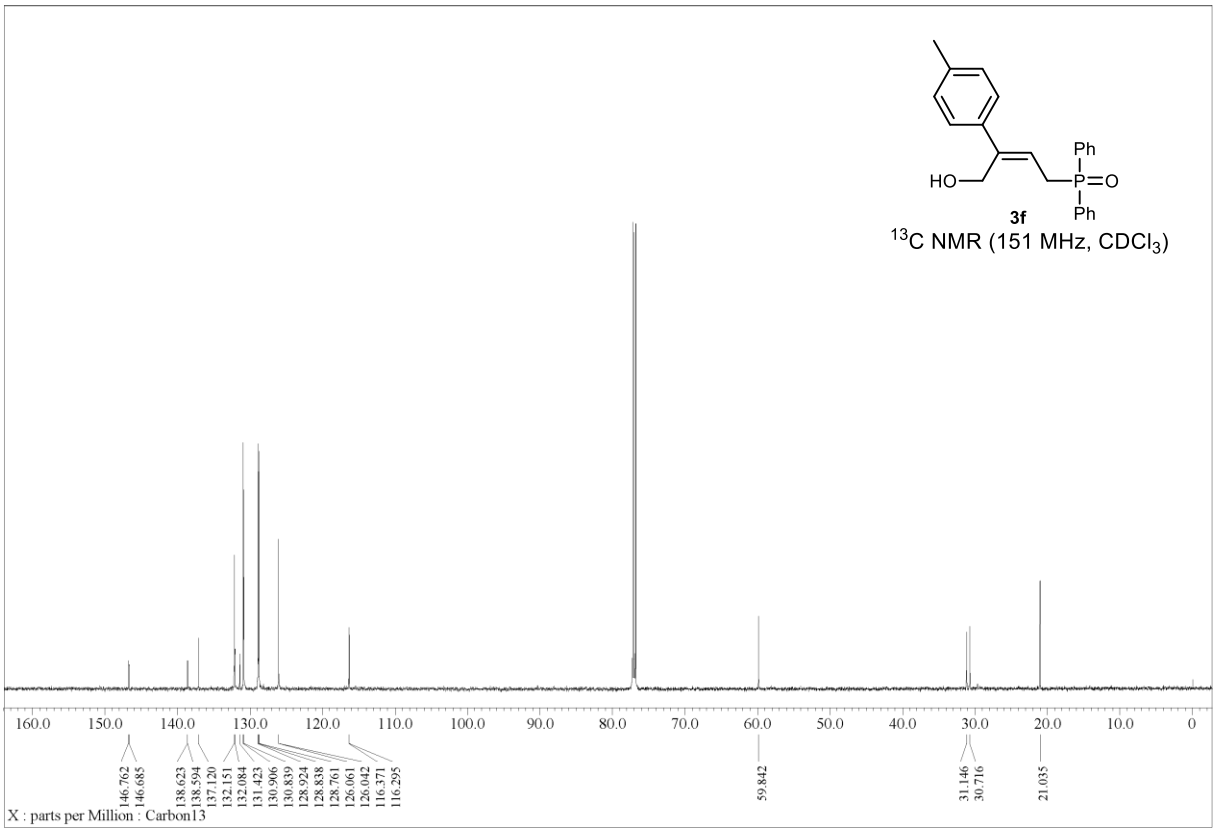
^{1}H NMR (600 MHz, $CDCl_3$)

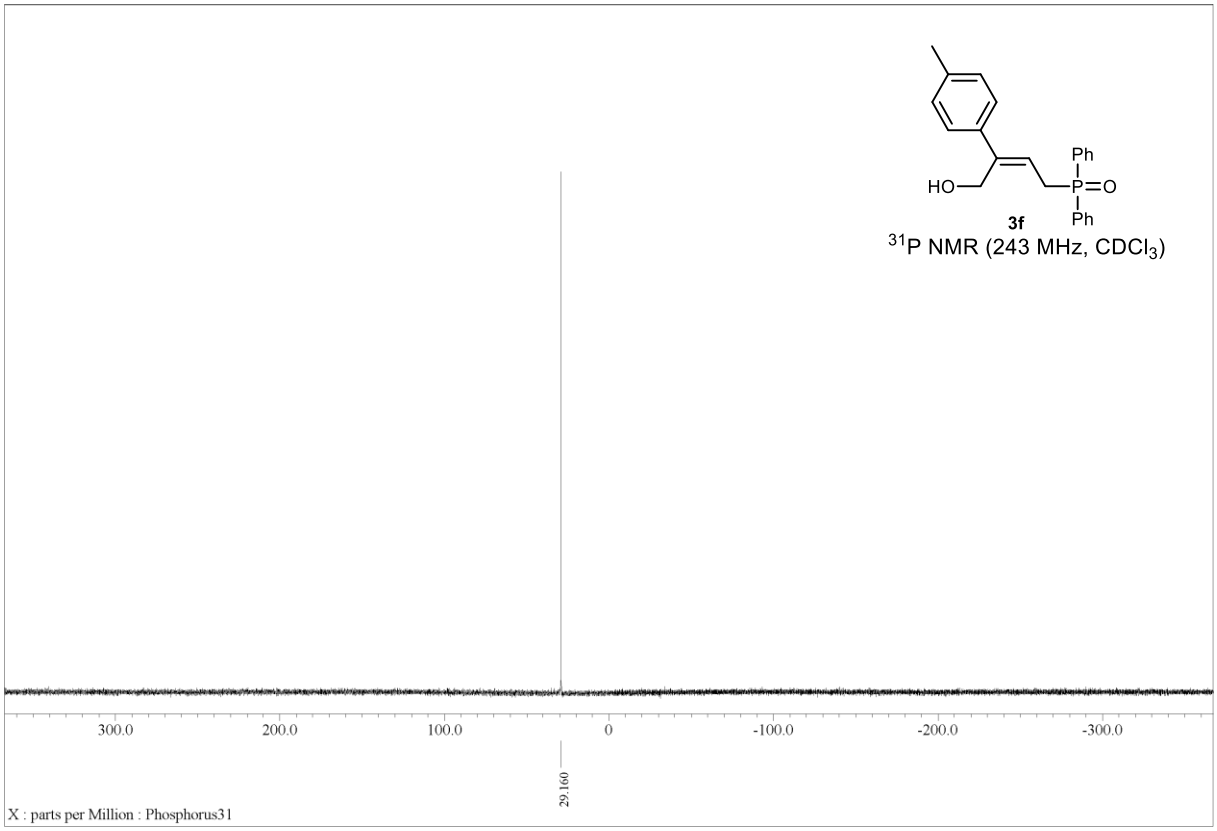

F3C
Ph
HO
P=O
Ph
3e
13C NMR (151 MHz, CDCl3)
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
146.072
145.996
145.077
132.361
131.883
131.222
130.887
130.820
129.422
129.202
128.962
128.876
126.492
125.219
125.190
125.094
123.294
121.494
119.397
119.311
59.631
31.319
30.888
X : parts per Million : Carbon13

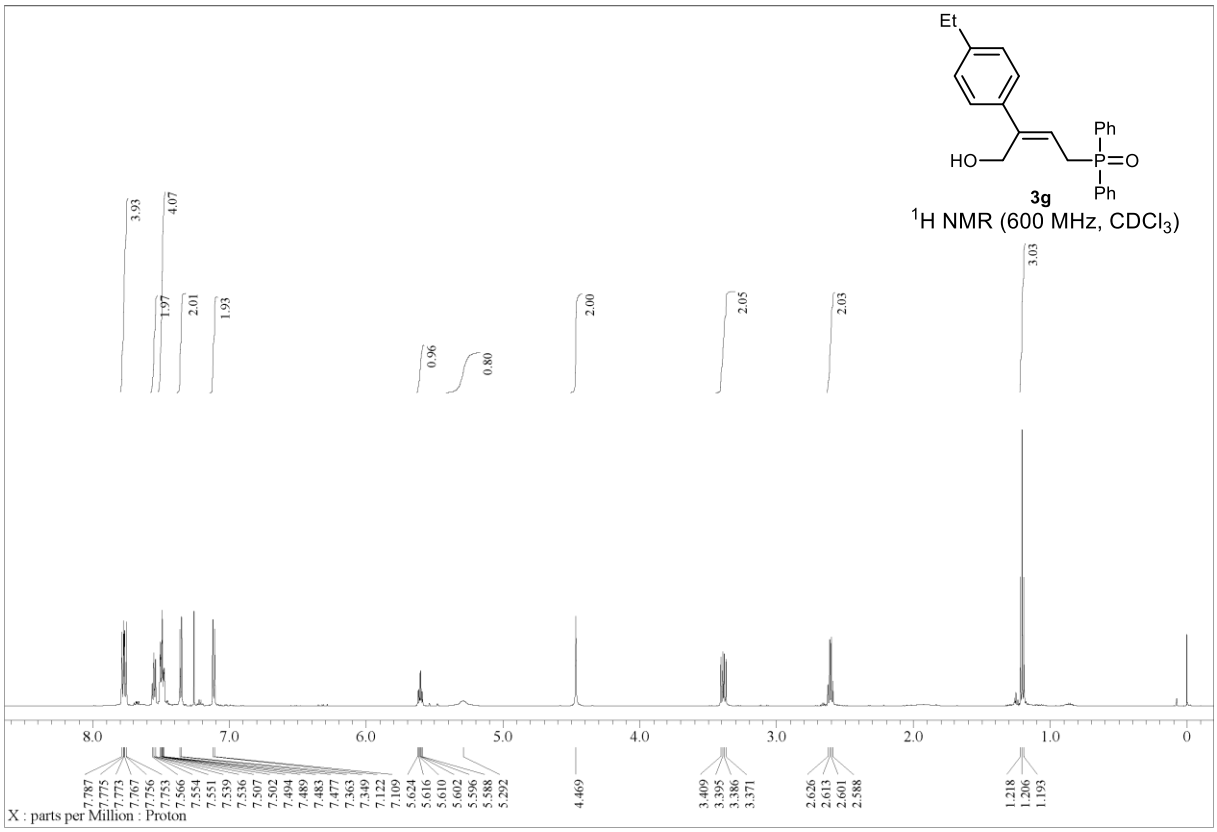

F3C
Ph
HO
P=O
Ph
3e
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
28.879
X : parts per Million : Phosphorus31

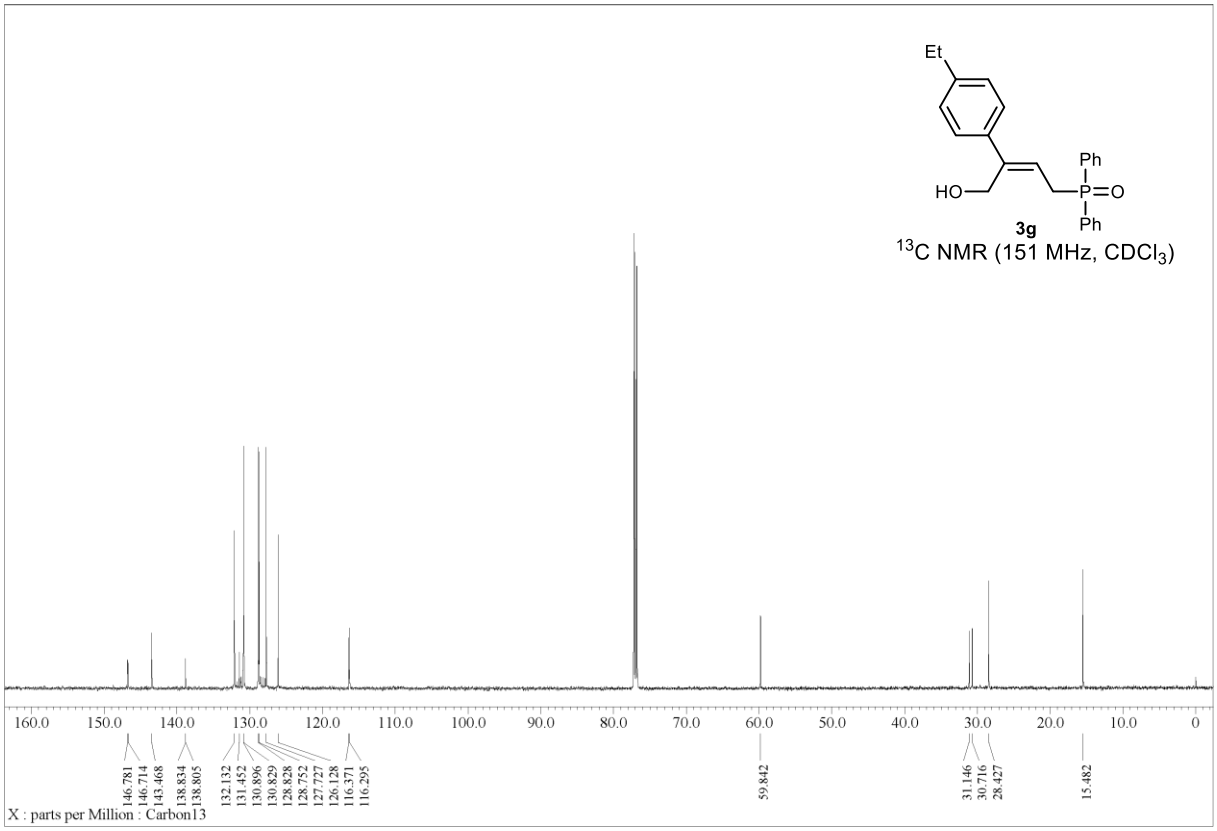

F3C
HO
Ph
P=O
Ph
3e
19F NMR (564 MHz, CDCl3)
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
-62.353
X : parts per Million : Fluorine19

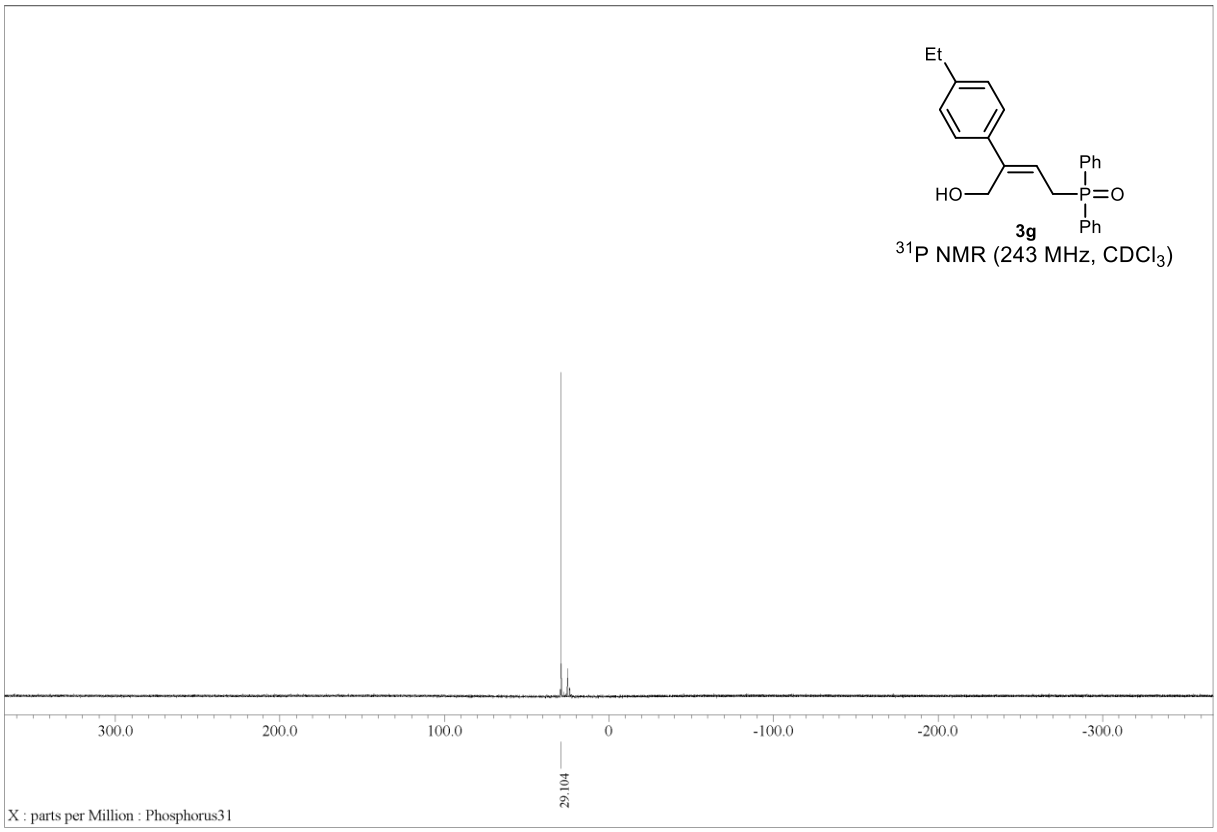

HO
Ph
P=O
Ph
3f
1H NMR (600 MHz, CDCl3)
3.99
3.97
2.07
2.00
1.95
1.04
0.60
2.00
2.00
2.99
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.782 7.771 7.768 7.763 7.751 7.749 7.566 7.555 7.542 7.507 7.501 7.493 7.488 7.477 7.336 7.323 7.096 7.082
5.611 5.603 5.598 5.590 5.583 5.575 5.297
4.461
3.403 3.389 3.380 3.366
2.308
X : parts per Million : Proton

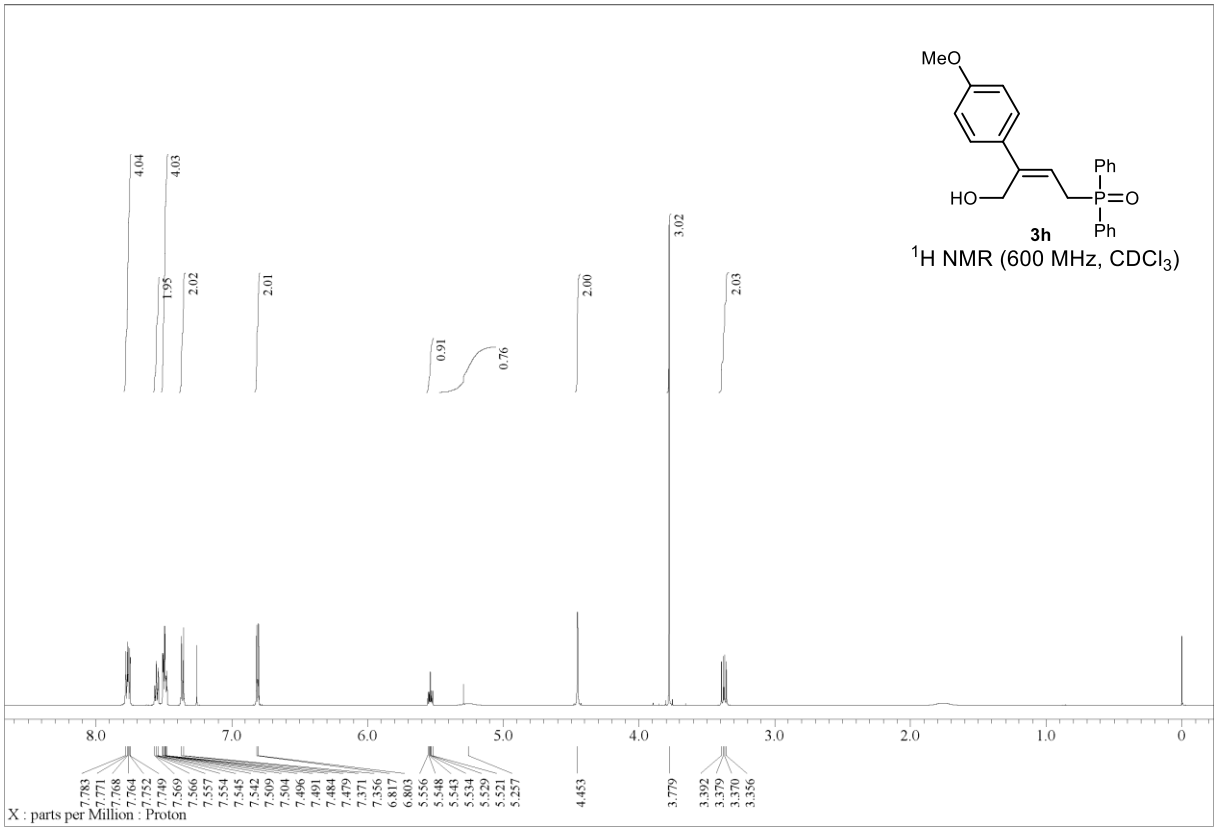

Ph
HO
P=O
Ph
3f
^{13}C NMR (151 MHz, CDCl$_3$)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
146.762
146.685
138.623
138.594
137.120
132.151
132.084
131.423
130.906
130.839
128.924
128.838
126.761
126.061
126.042
116.371
116.295
59.842
31.146
30.716
21.035
X : parts per Million : Carbon13

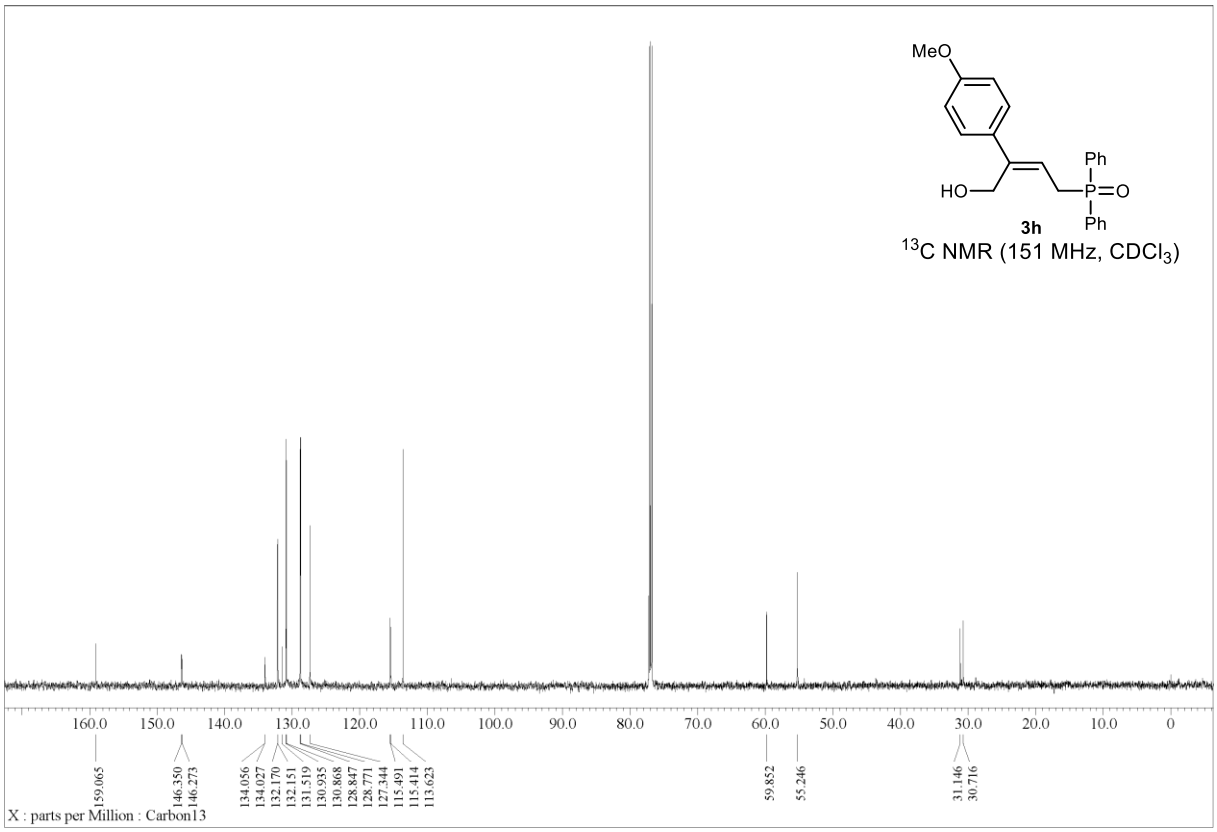

Ph
HO
P=O
Ph
3f
^{31}P NMR (243 MHz, CDCl$_3$)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
29.160
X : parts per Million : Phosphorus31

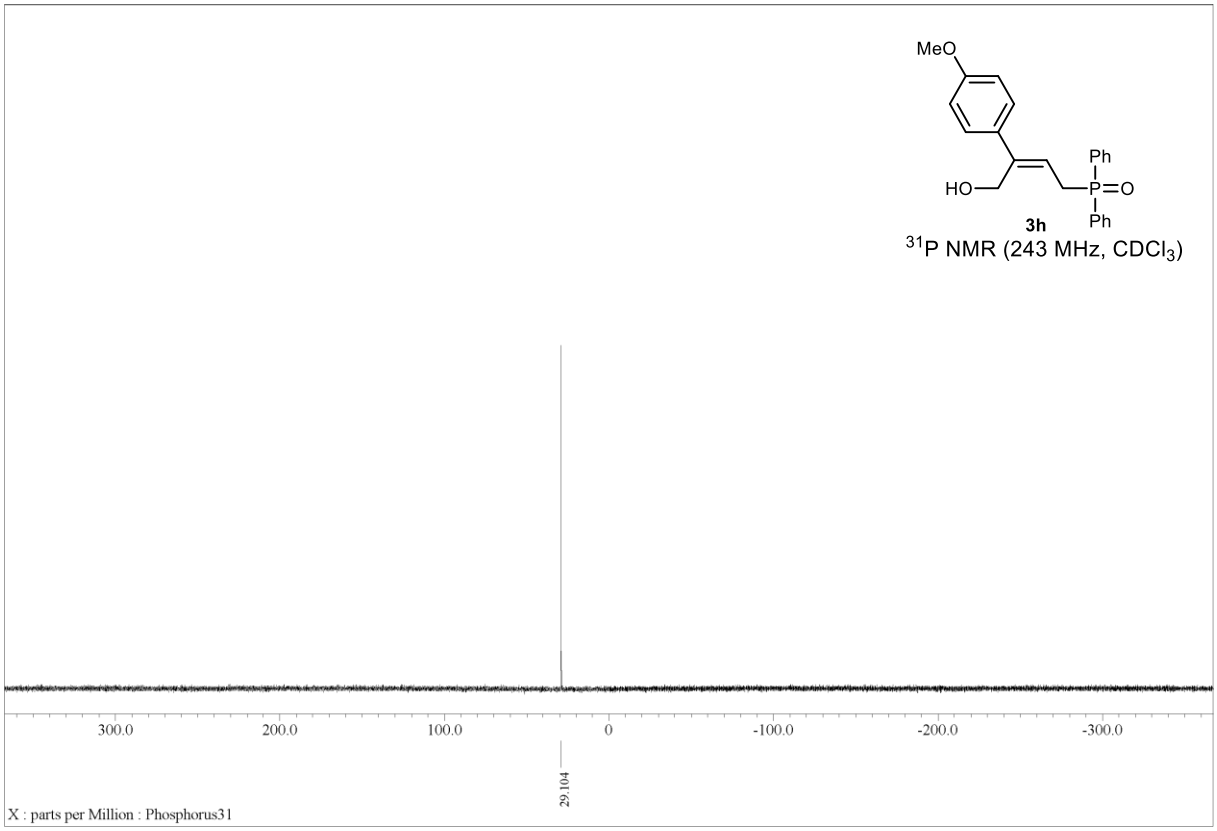

Et
Ph
HO
P=O
Ph
3g
^{1}H NMR (600 MHz, CDCl$_3$)
3.93
4.07
1.97
2.01
1.93
0.96
0.80
2.00
2.05
2.03
3.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.787
7.775
7.773
7.767
7.756
7.753
7.566
7.554
7.551
7.539
7.536
7.507
7.502
7.494
7.489
7.483
7.477
7.363
7.349
7.122
7.109
5.624
5.616
5.610
5.602
5.596
5.588
5.292
4.469
3.409
3.395
3.386
3.371
2.626
2.613
2.601
2.588
1.218
1.206
1.193
X : parts per Million : Proton

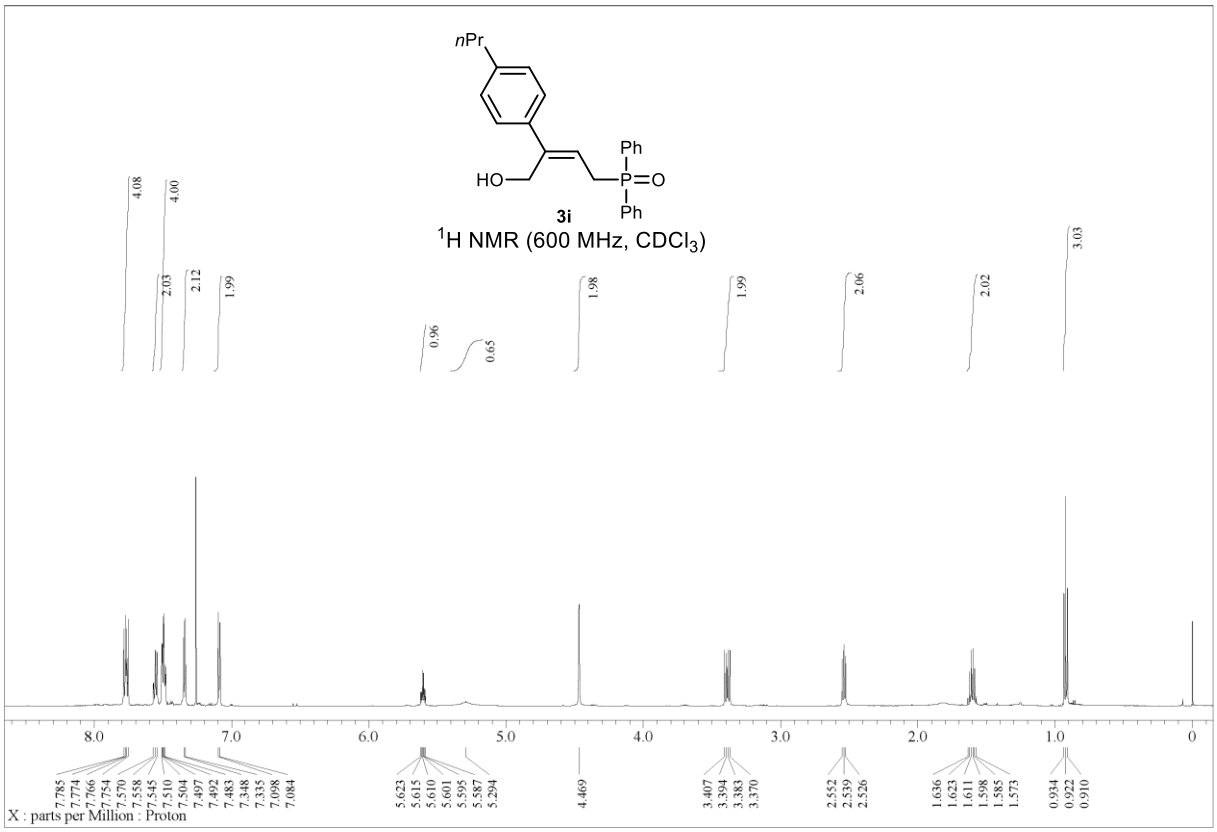

Et
Ph
HO
P=O
Ph
3g
^{13}C NMR (151 MHz, CDCl$_3$)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
146.781
146.714
143.468
138.834
138.805
132.132
131.452
130.896
130.829
128.828
128.752
127.727
126.128
116.371
116.295
59.842
31.146
30.716
28.427
15.482
X : parts per Million : Carbon13

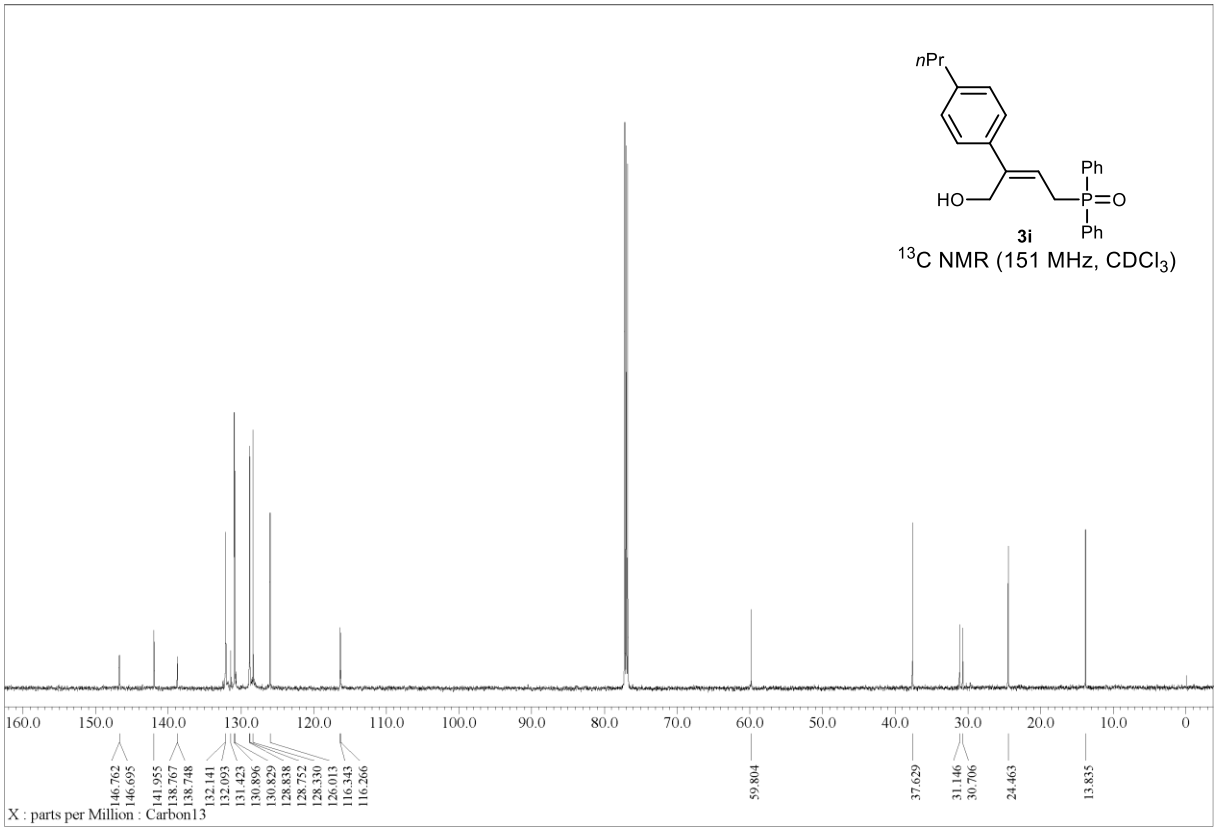

Et
HO
Ph
P=O
Ph
3g
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
29.104
X : parts per Million : Phosphorus31

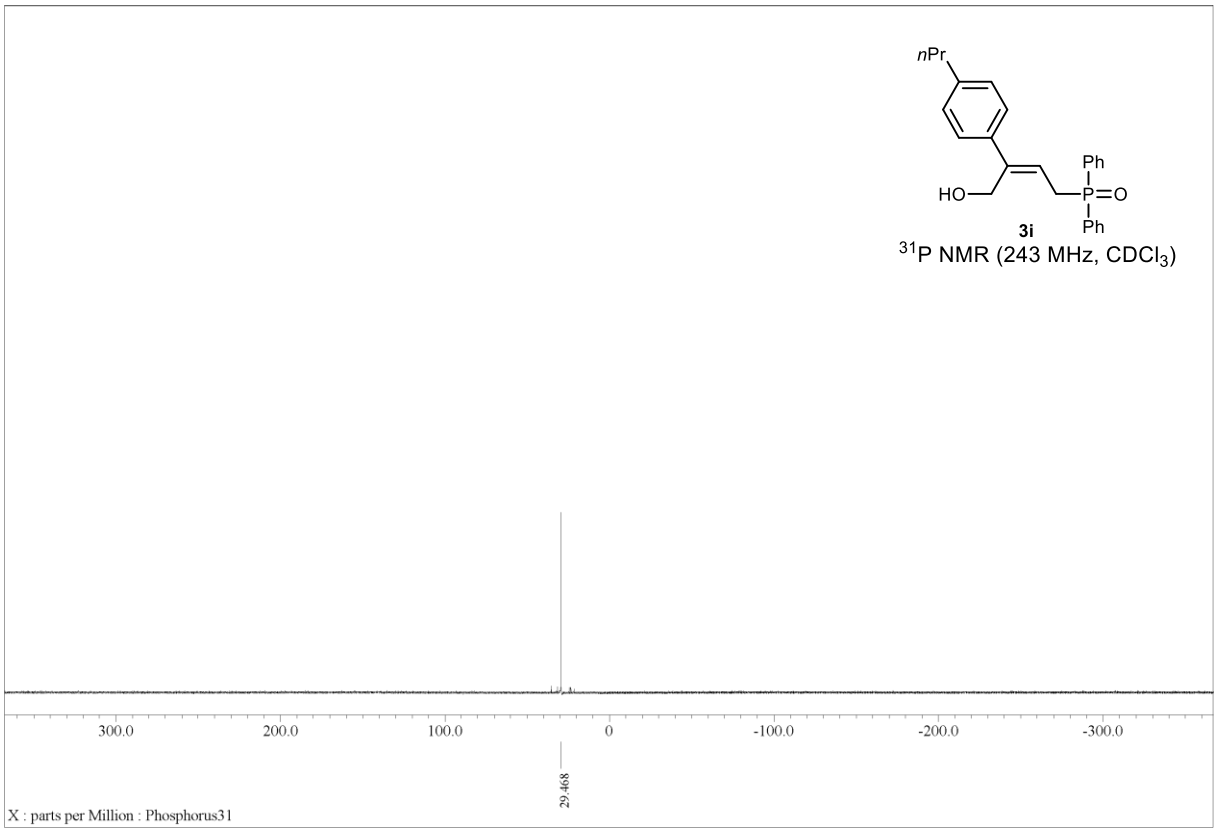

MeO
HO
Ph
P=O
Ph
3h
1H NMR (600 MHz, CDCl3)
4.04
4.03
1.95
2.02
2.01
0.91
0.76
2.00
3.02
2.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4.453
3.779
X : parts per Million : Proton

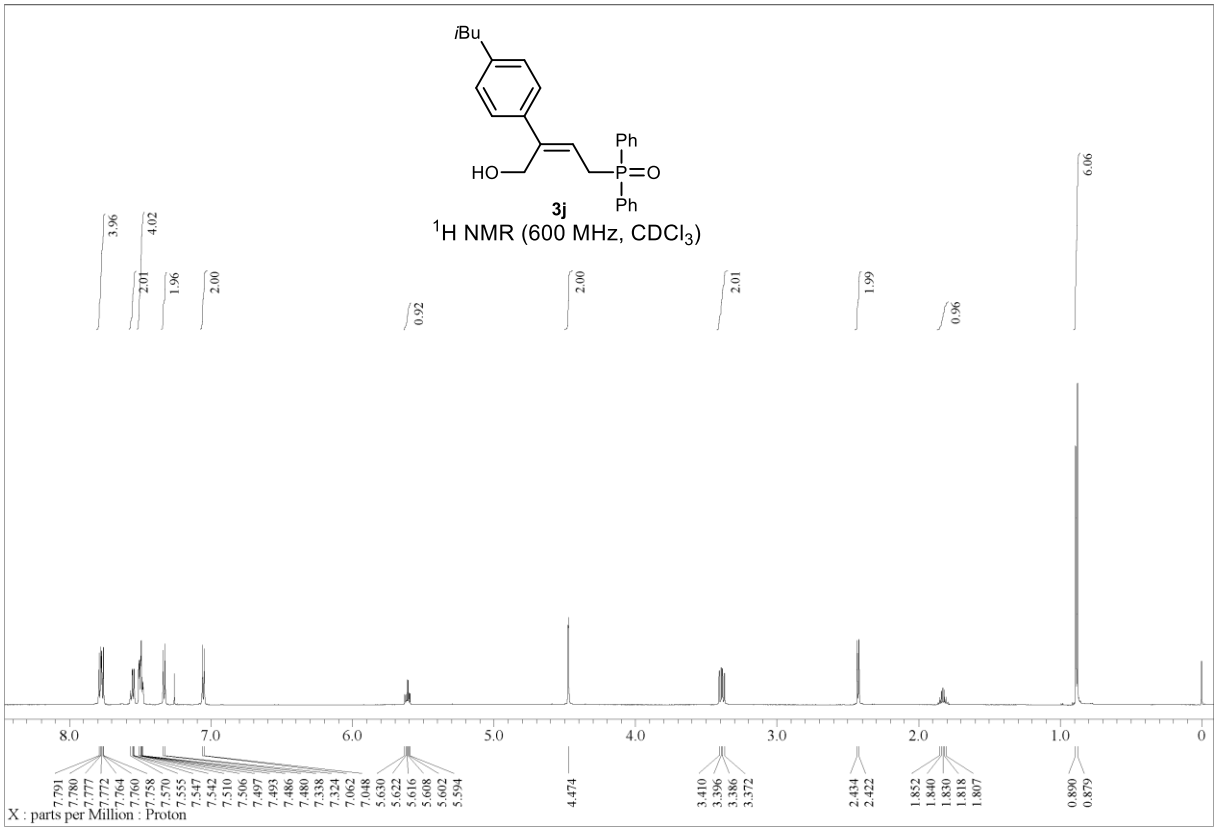

MeO
HO
Ph
P=O
Ph
3h
^{13}C NMR (151 MHz, CDCl$_3$)
160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
159.065
146.350
146.273
134.056
134.027
132.170
132.151
131.519
130.935
130.868
128.847
128.771
127.344
115.491
115.414
113.623
59.852
55.246
31.146
30.716
X : parts per Million : Carbon13

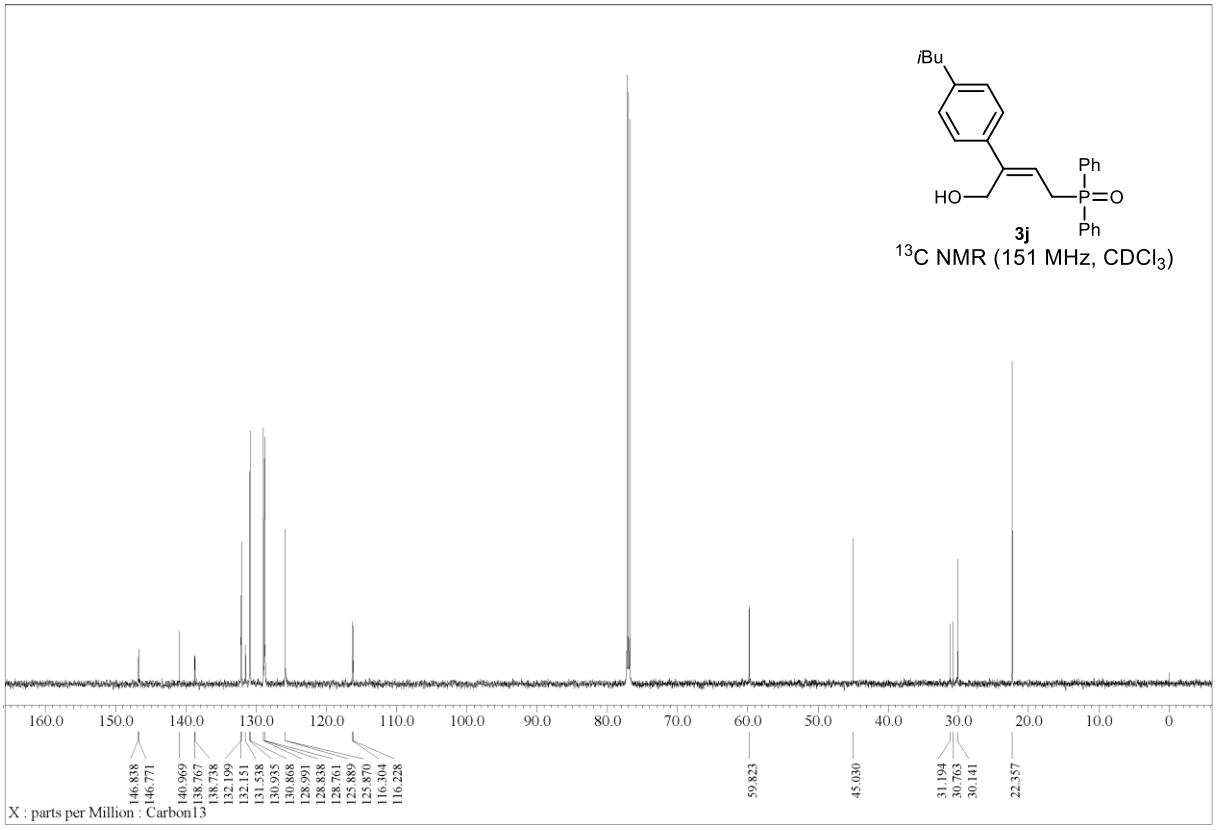

MeO
HO
Ph
P=O
Ph
3h
^{31}P NMR (243 MHz, CDCl$_3$)
300.0 200.0 100.0 0 -100.0 -200.0 -300.0
29.104
X : parts per Million : Phosphorus31

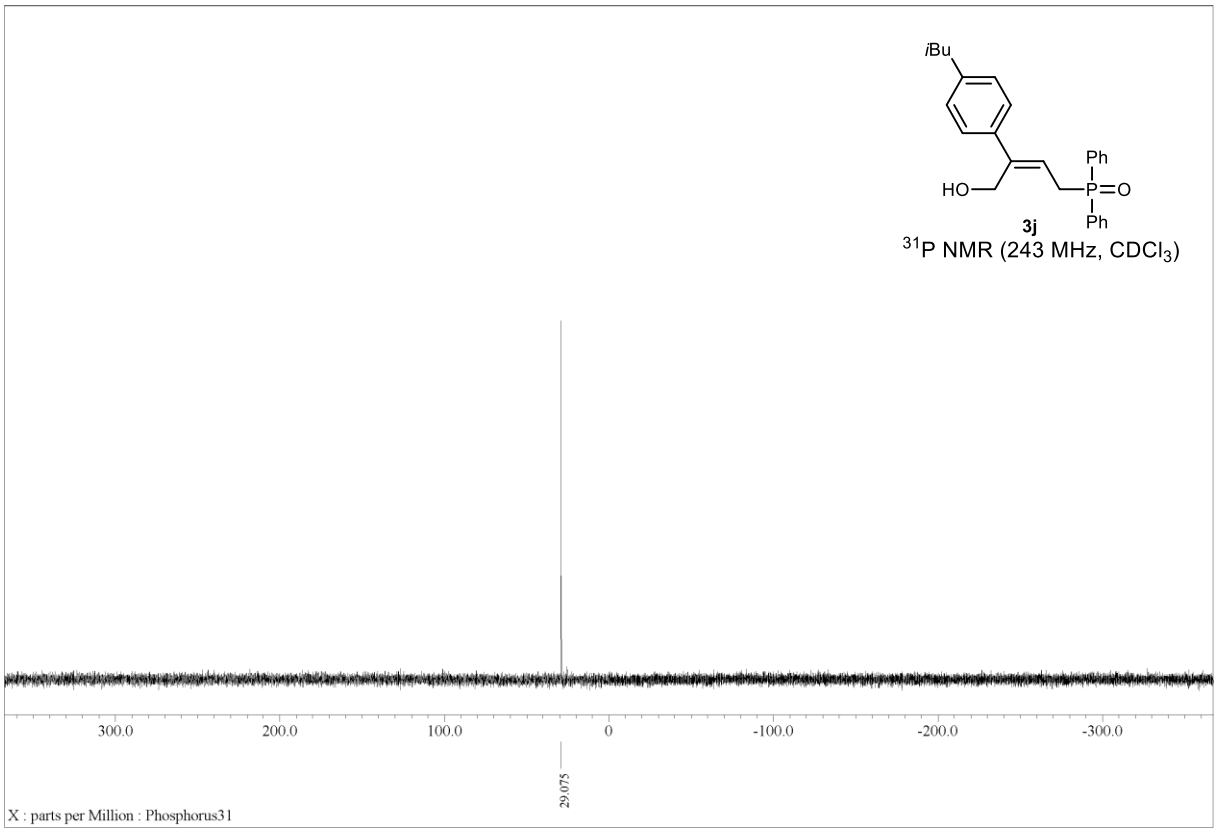

nPr
Ph
HO
P=O
Ph
3i
1H NMR (600 MHz, CDCl3)
4.08
4.00
2.03
2.12
1.99
0.96
0.65
1.98
1.99
2.06
2.02
3.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.785
7.774
7.766
7.754
7.570
7.558
7.545
7.510
7.504
7.497
7.492
7.483
7.348
7.335
7.098
7.084
5.623
5.615
5.610
5.601
5.595
5.587
5.294
4.469
3.407
3.394
3.383
3.370
2.552
2.539
2.526
1.636
1.623
1.611
1.598
1.585
1.573
0.934
0.922
0.910
X : parts per Million : Proton

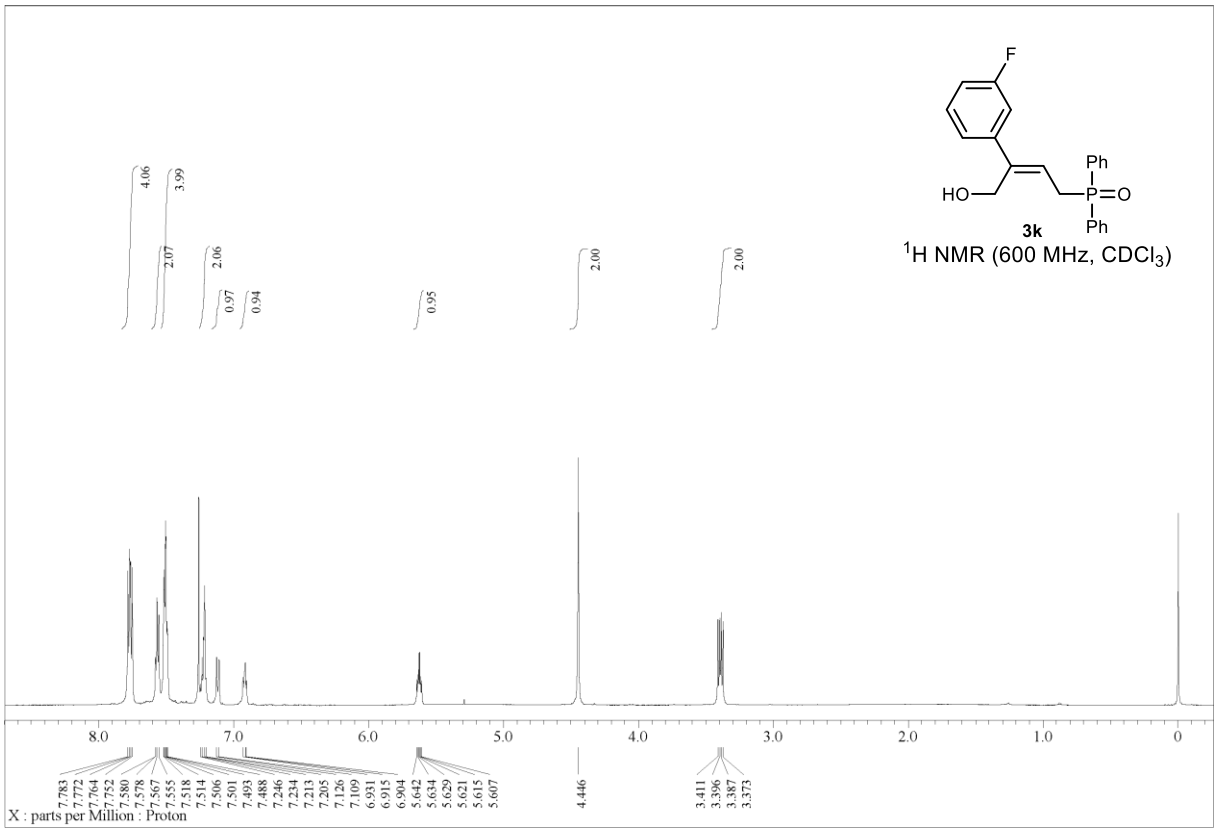

nPr
Ph
HO
P=O
Ph
3i
13C NMR (151 MHz, CDCl3)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
146.762
146.695
141.955
138.767
138.748
132.141
132.093
131.423
130.896
130.829
128.838
128.752
128.330
126.013
116.343
116.266
59.804
37.629
31.146
30.706
24.463
13.835
X : parts per Million : Carbon13

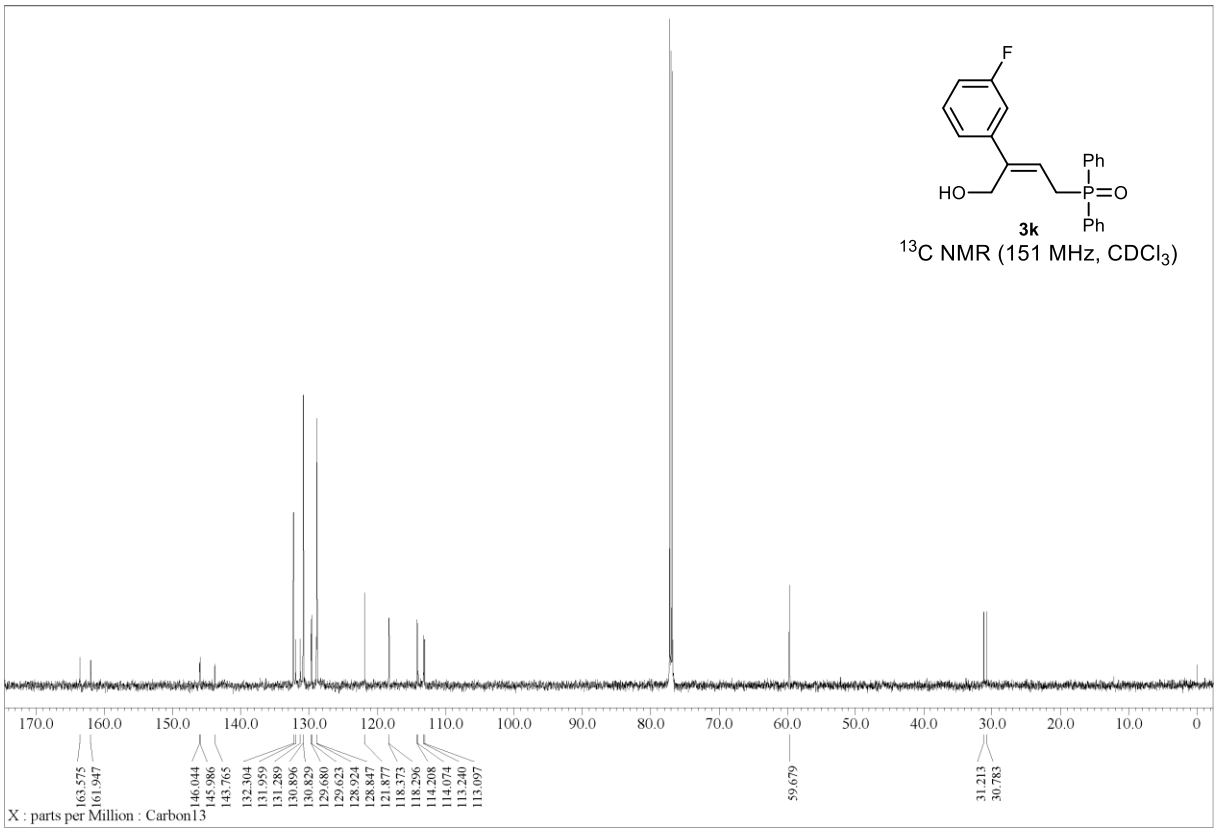

nPr
HO
Ph
P=O
Ph
3i
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
29.468
X : parts per Million : Phosphorus31

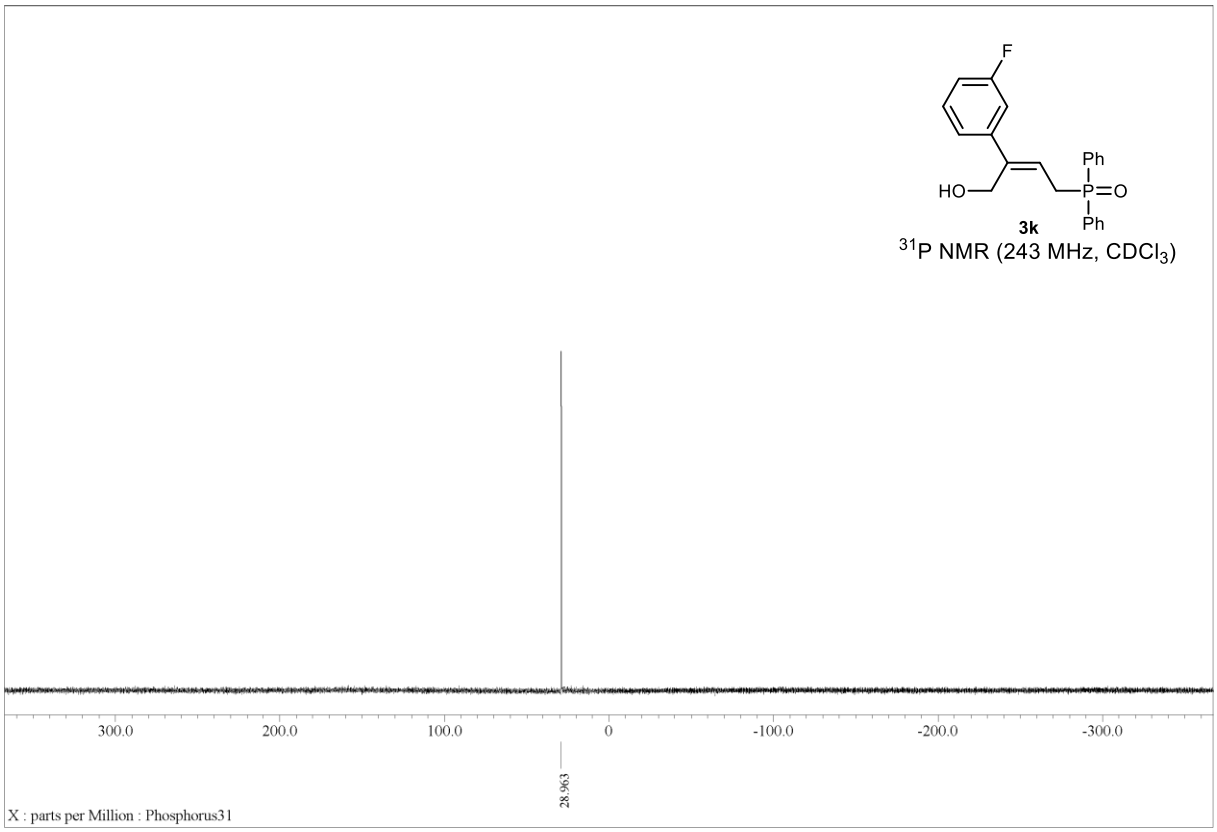

iBu
HO
Ph
P=O
Ph
3j
1H NMR (600 MHz, CDCl3)
3.96
4.02
2.01
1.96
2.00
0.92
2.00
2.01
1.99
0.96
6.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.791
7.780
7.777
7.772
7.764
7.760
7.758
7.570
7.555
7.547
7.542
7.510
7.506
7.497
7.493
7.486
7.480
7.338
7.324
7.062
7.048
5.630
5.622
5.616
5.608
5.602
5.594
4.474
3.410
3.396
3.386
3.372
2.434
2.422
1.852
1.840
1.830
1.818
1.807
0.890
0.879
X : parts per Million : Proton

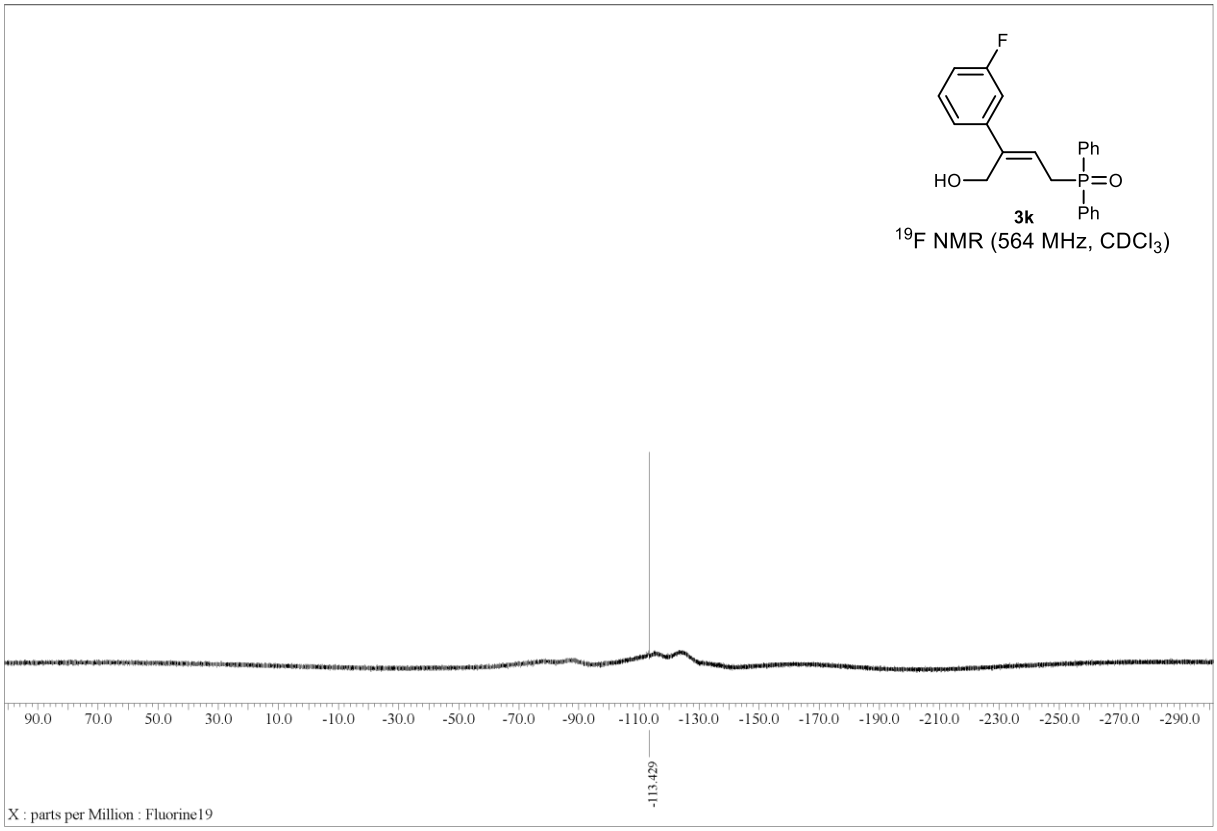

iBu
HO
Ph
P=O
Ph
3j
13C NMR (151 MHz, CDCl3)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
146.838
146.771
140.969
138.767
138.738
132.199
132.151
131.538
130.935
130.868
128.991
128.838
128.761
125.889
125.870
116.304
116.228
59.823
45.030
31.194
30.763
30.141
22.357
X : parts per Million : Carbon13

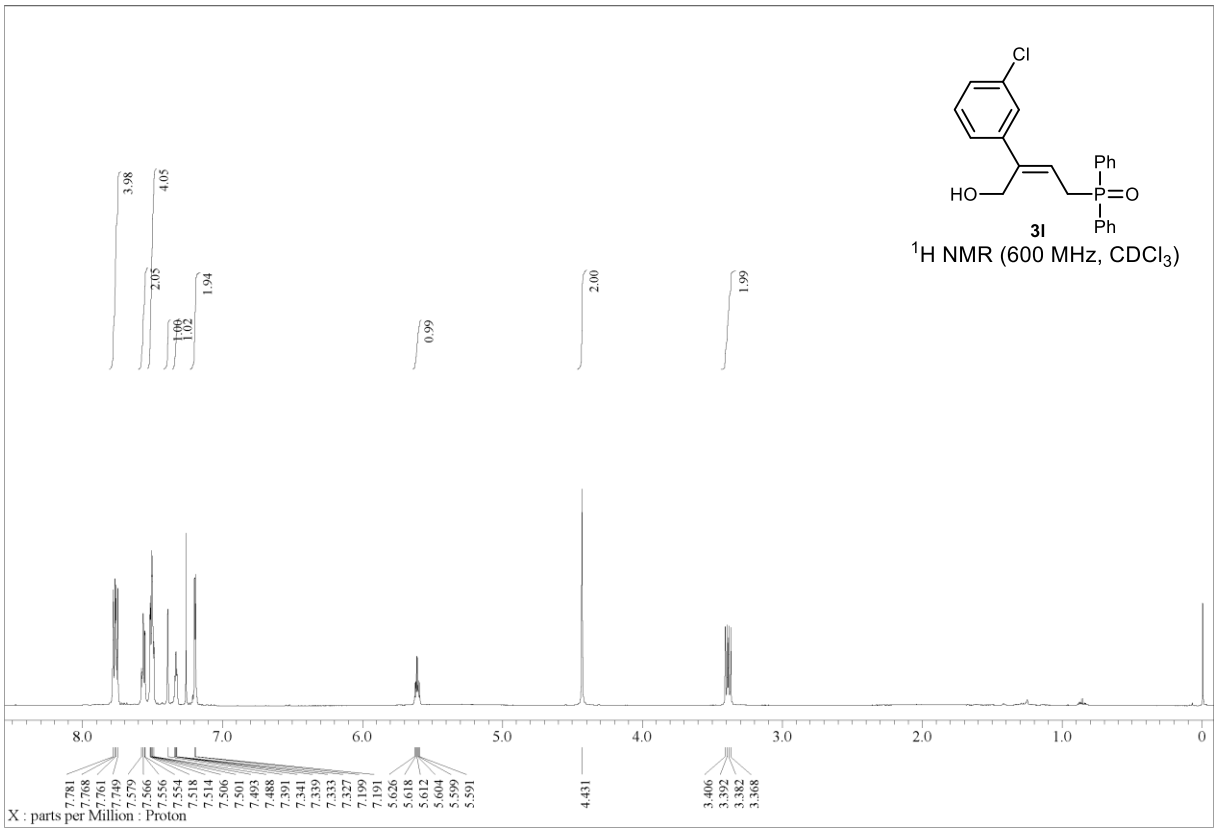

iBu
HO
Ph
P=O
Ph
3j
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
29.075
X : parts per Million : Phosphorus31

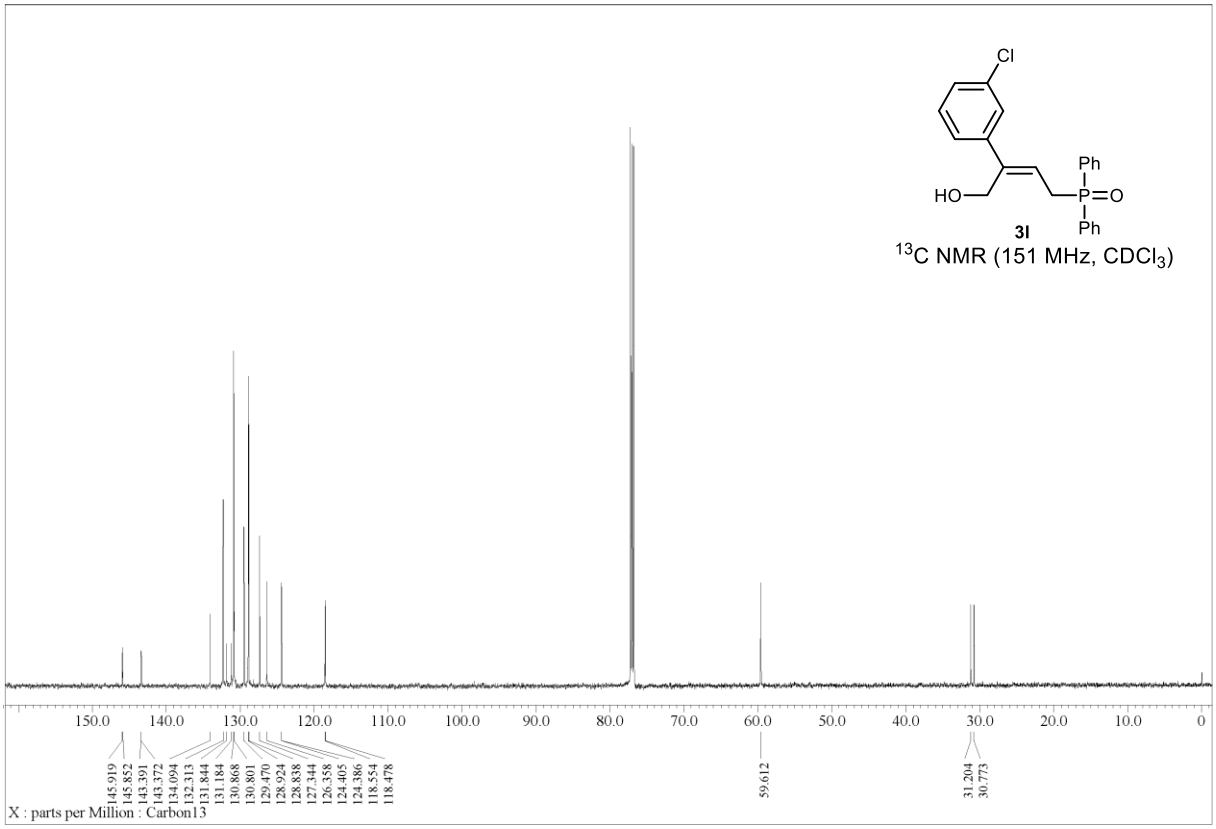

F
Ph
HO
P=O
Ph
3k
^{1}H NMR (600 MHz, $CDCl_3$)
4.06
3.99
2.07
2.06
0.97
0.94
0.95
2.00
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.783
7.772
7.764
7.752
7.580
7.578
7.567
7.555
7.518
7.514
7.506
7.501
7.493
7.488
7.246
7.234
7.213
7.205
7.126
7.109
6.931
6.915
6.904
5.642
5.634
5.629
5.621
5.615
5.607
4.446
3.411
3.396
3.387
3.373
X : parts per Million : Proton

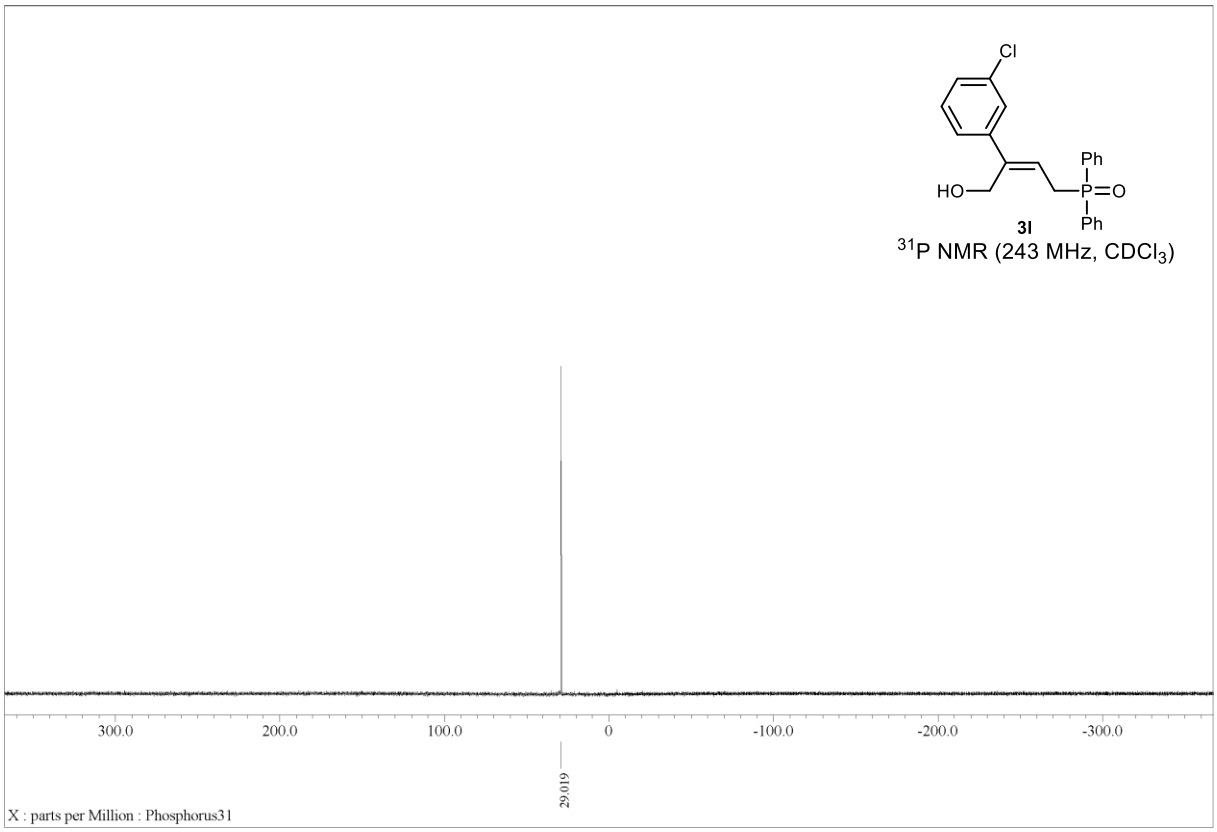

F
Ph
HO
P=O
Ph
3k
^{13}C NMR (151 MHz, $CDCl_3$)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
163.575
161.947
146.044
145.986
143.765
132.304
131.959
131.289
130.896
130.829
129.680
129.623
128.924
128.847
121.877
118.373
118.296
114.208
114.074
113.240
113.097
59.679
31.213
30.783
X : parts per Million : Carbon13

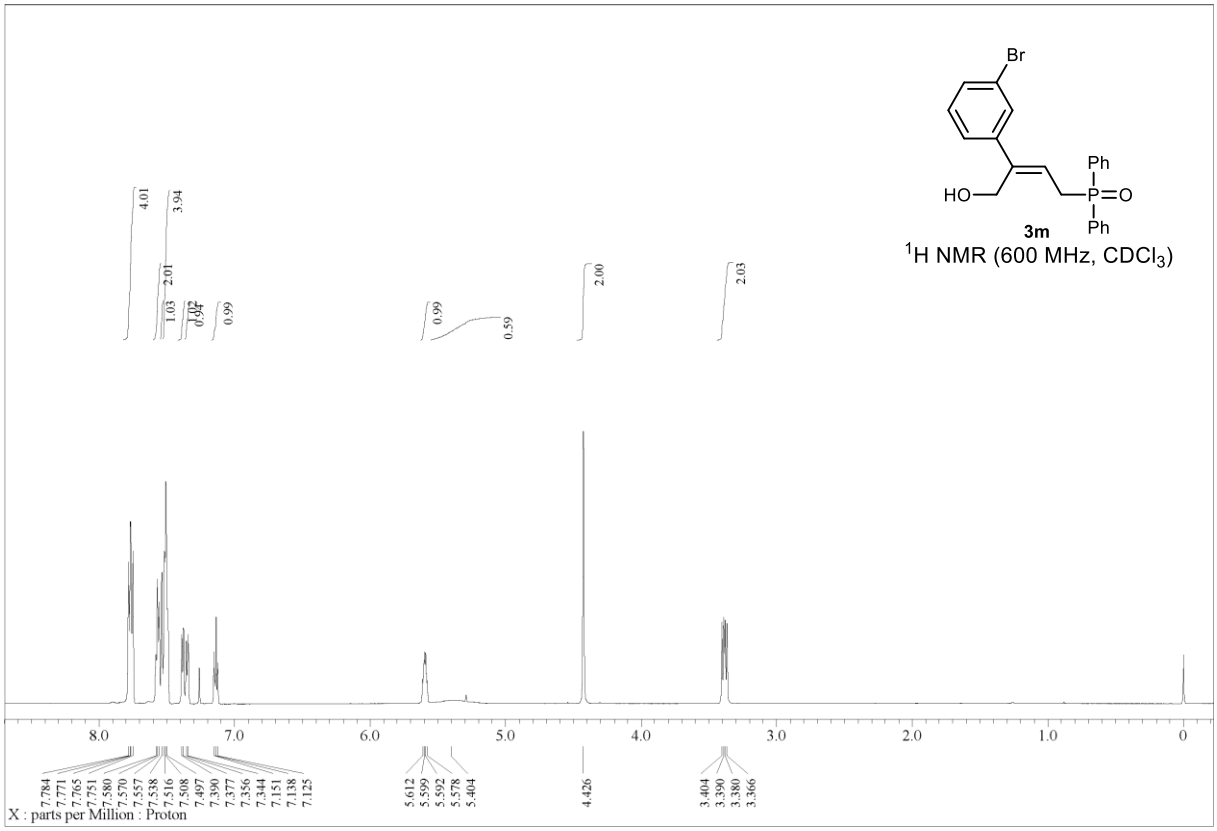

F
Ph
HO
P=O
Ph
3k
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
28.963
X : parts per Million : Phosphorus31

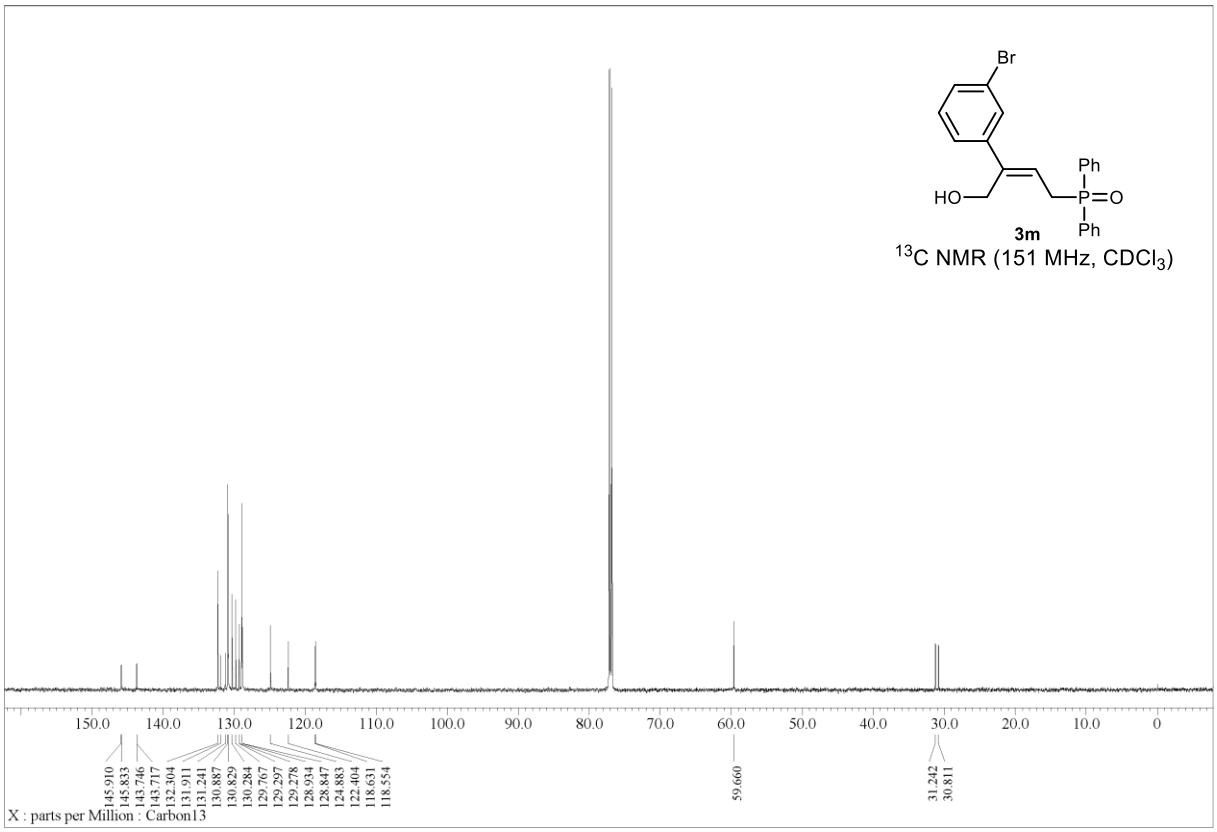

F
Ph
HO
P=O
Ph
3k
19F NMR (564 MHz, CDCl3)
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
-50.0
-70.0
-90.0
-110.0
-130.0
-150.0
-170.0
-190.0
-210.0
-230.0
-250.0
-270.0
-290.0
-113.429
X : parts per Million : Fluorine19

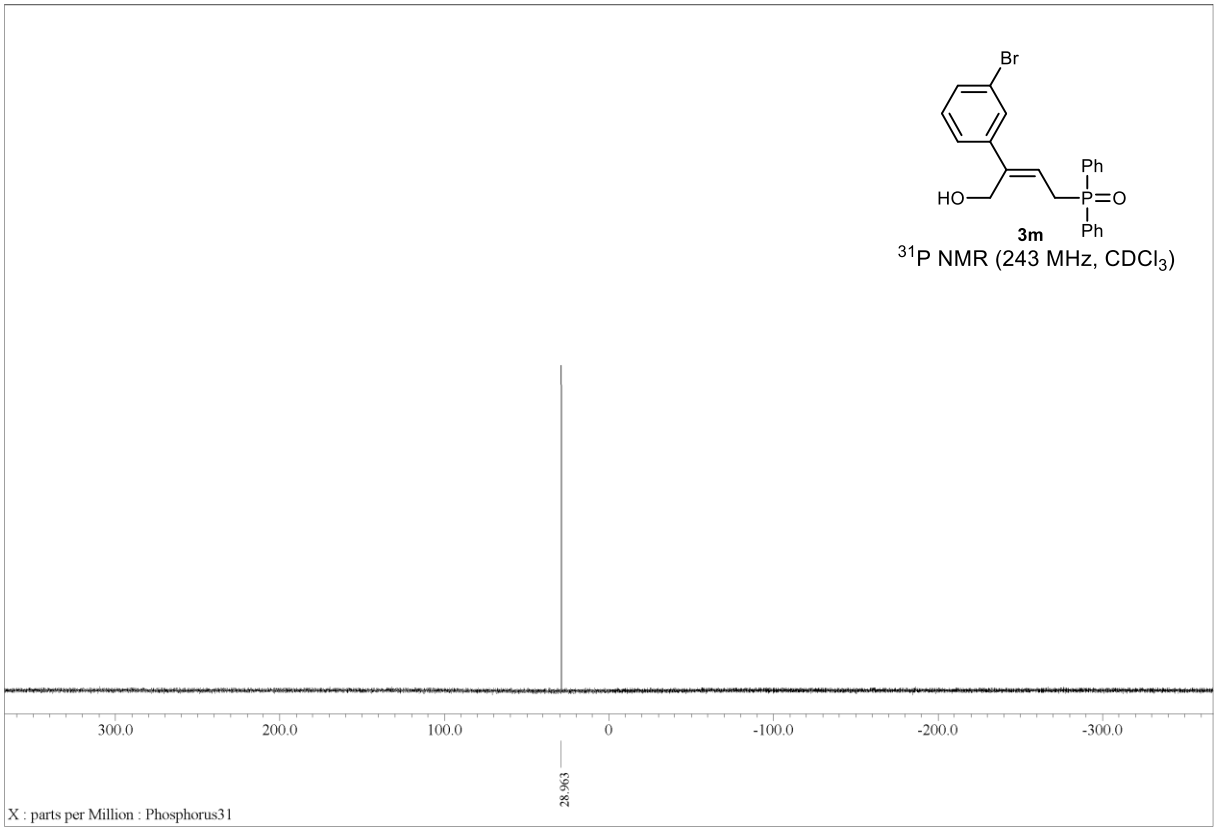

Cl
Ph
HO
P=O
Ph
3l
1H NMR (600 MHz, CDCl3)
3.98
4.05
2.05
1.94
1.09
1.02
0.99
2.00
1.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.781
7.768
7.761
7.749
7.579
7.566
7.556
7.554
7.518
7.514
7.506
7.501
7.493
7.488
7.391
7.341
7.339
7.333
7.327
7.199
7.191
5.626
5.618
5.612
5.604
5.599
5.591
4.431
3.406
3.392
3.382
3.368
X : parts per Million : Proton

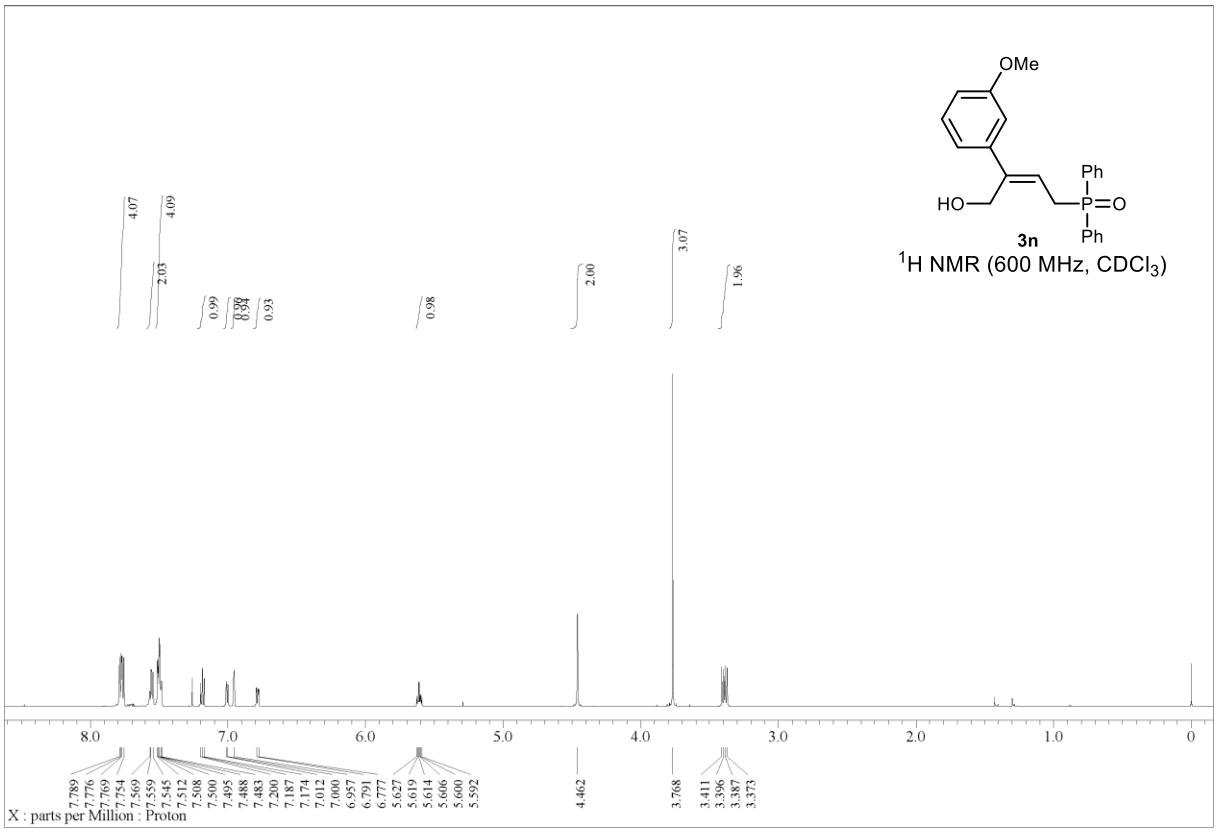

Cl
Ph
HO
P=O
Ph
3l
13C NMR (151 MHz, CDCl3)
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.919
145.852
143.391
143.372
134.094
132.313
131.844
131.184
130.868
130.801
129.470
128.924
128.838
127.344
126.358
124.405
124.386
118.554
118.478
59.612
31.204
30.773
X : parts per Million : Carbon13


Cl
Ph
HO
P=O
Ph
3l
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
29.019
X : parts per Million : Phosphorus31

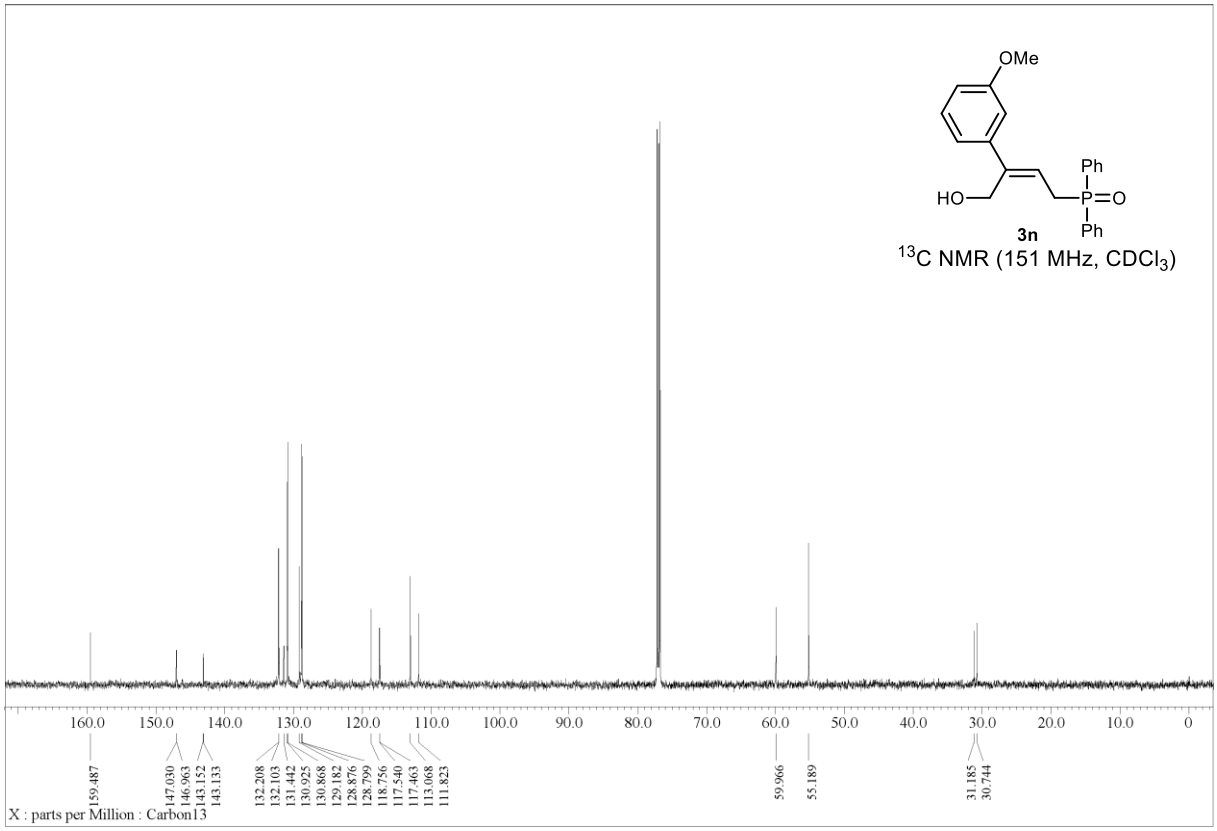

Br
Ph
HO
P=O
Ph
3m
1H NMR (600 MHz, CDCl3)
4.01
3.94
2.01
1.03
0.99
0.99
0.59
2.00
2.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.784
7.771
7.765
7.751
7.580
7.570
7.557
7.538
7.516
7.508
7.497
7.390
7.377
7.356
7.344
7.151
7.138
7.125
5.612
5.599
5.592
5.578
5.404
4.426
3.404
3.390
3.380
3.366
X : parts per Million : Proton


Br
Ph
HO
P=O
Ph
3m
^{13}C NMR (151 MHz, CDCl$_3$)
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.910
145.833
143.746
143.717
132.304
131.911
131.241
130.887
130.829
130.284
129.767
129.297
129.278
128.934
128.847
124.883
122.404
118.631
118.554
59.660
31.242
30.811
X : parts per Million : Carbon13

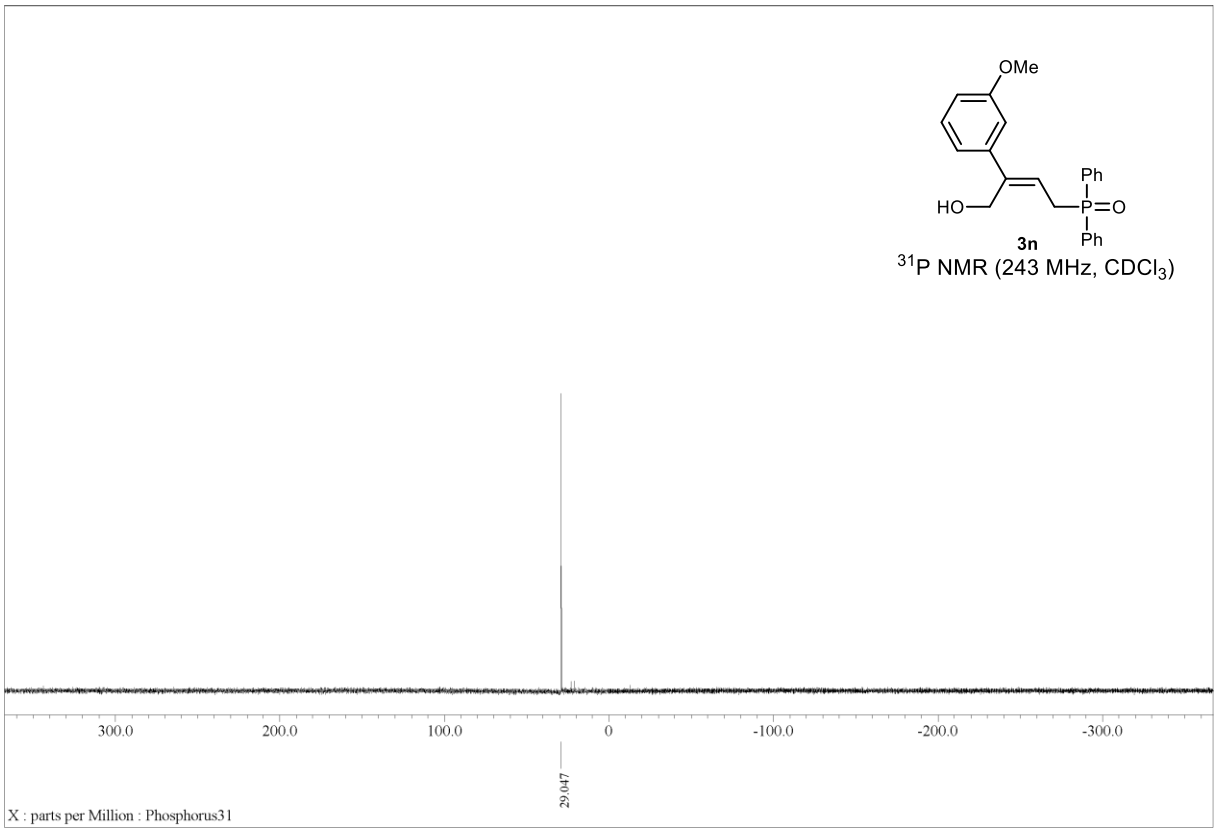

Br
Ph
HO
P=O
Ph
3m
^{31}P NMR (243 MHz, CDCl$_3$)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
28.963
X : parts per Million : Phosphorus31



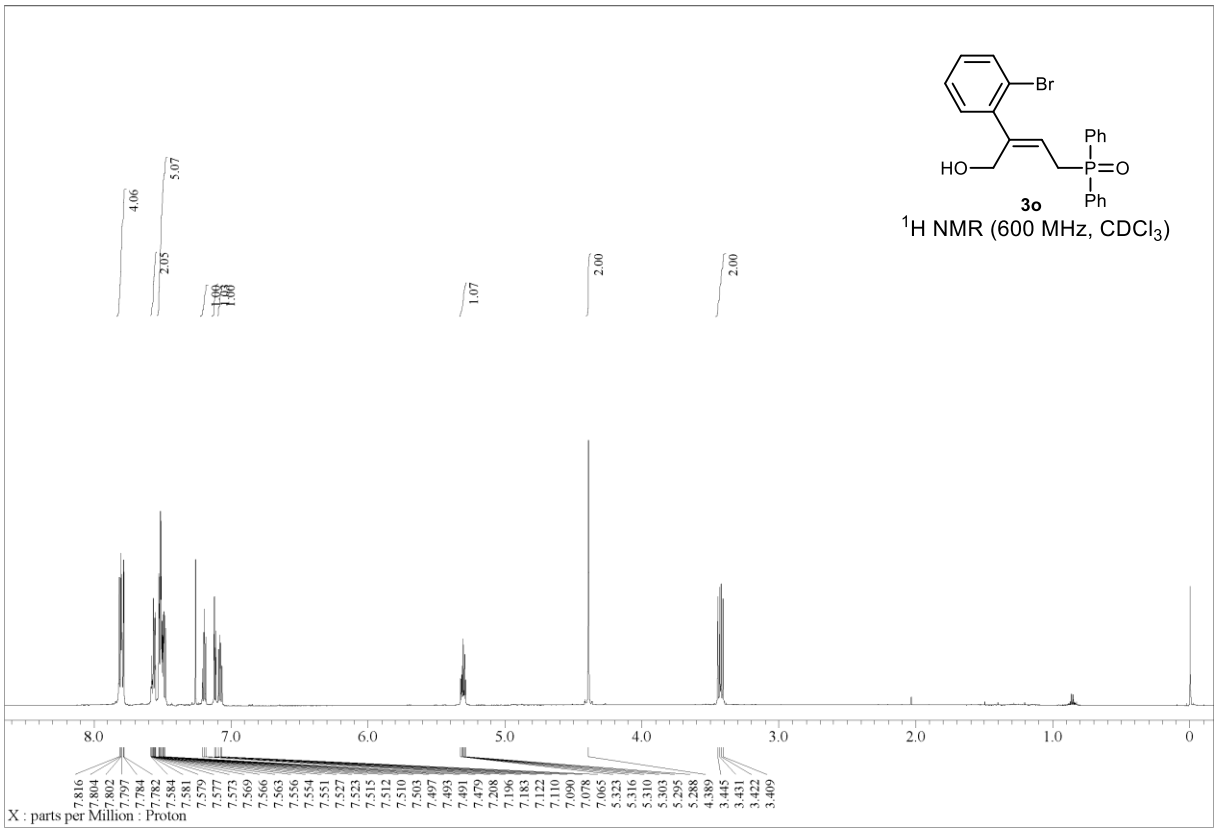
^{1}H NMR (600 MHz, $CDCl_3$)



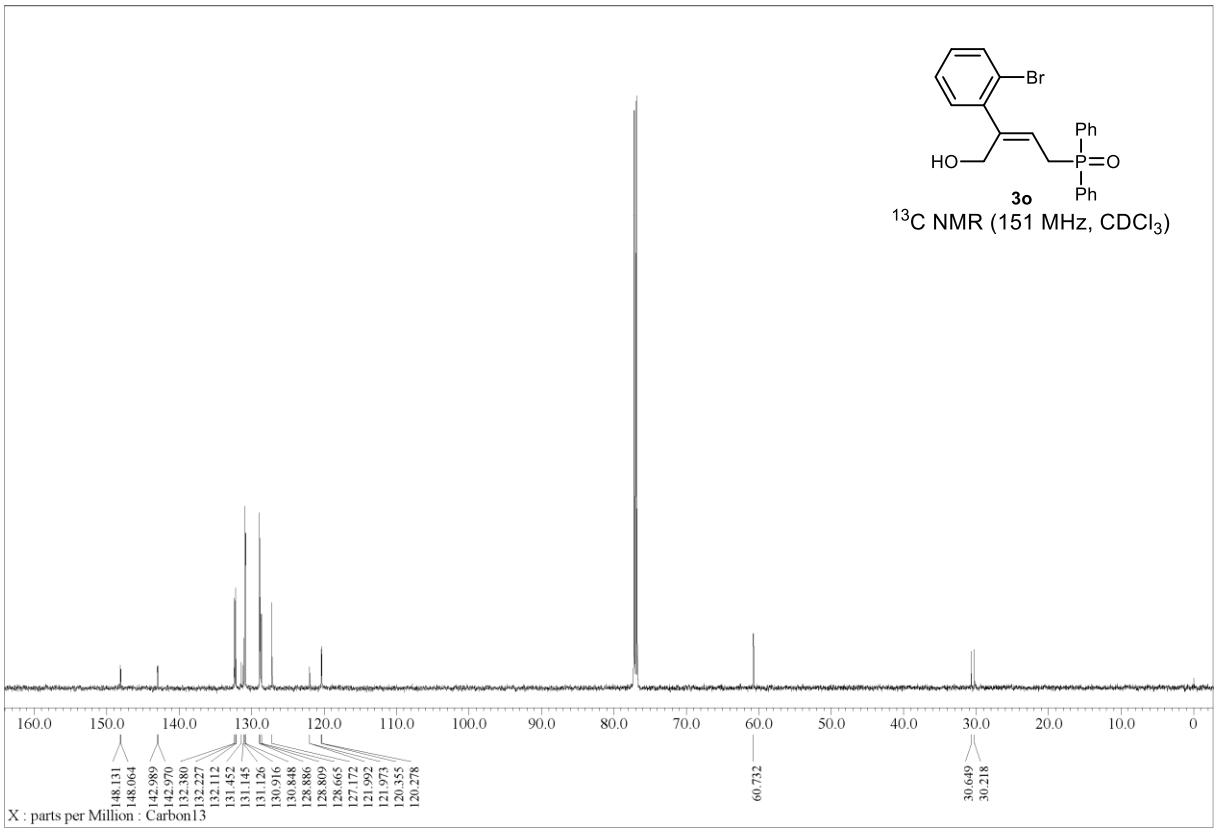
^{13}C NMR (151 MHz, $CDCl_3$)

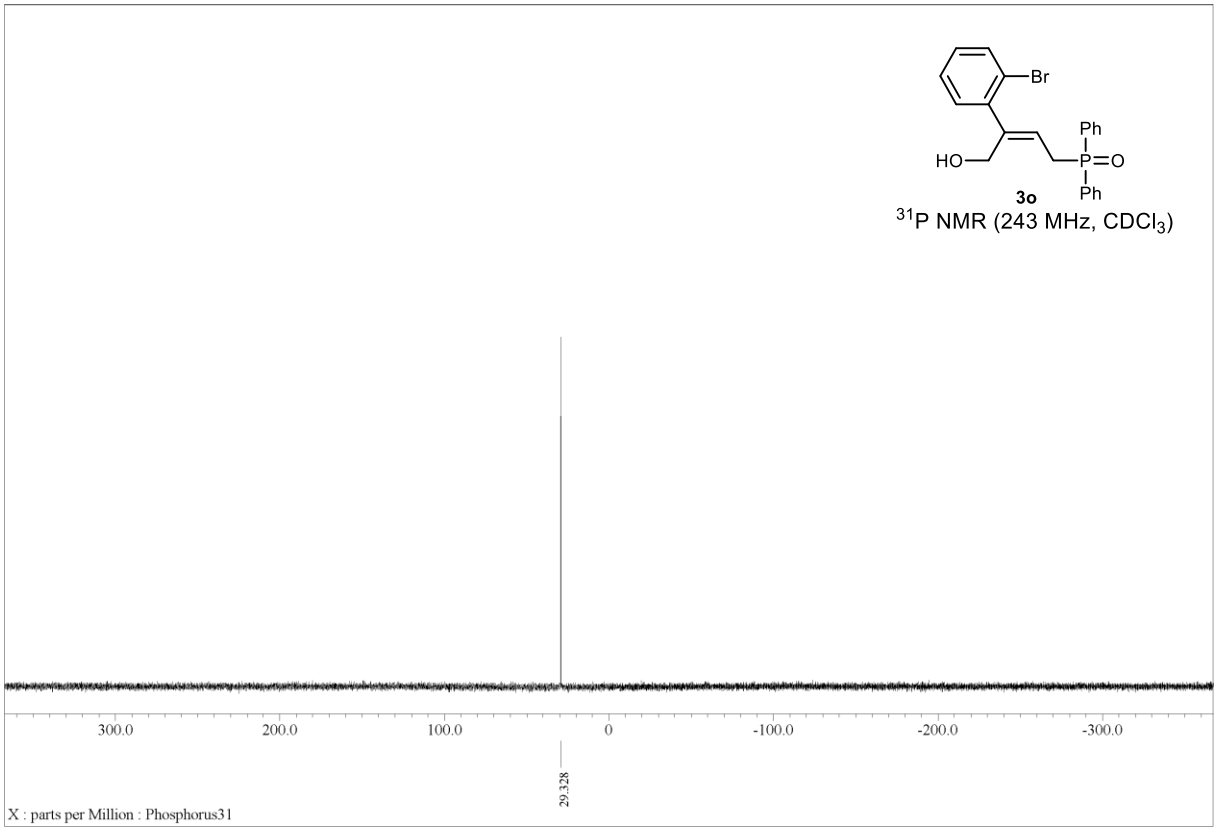


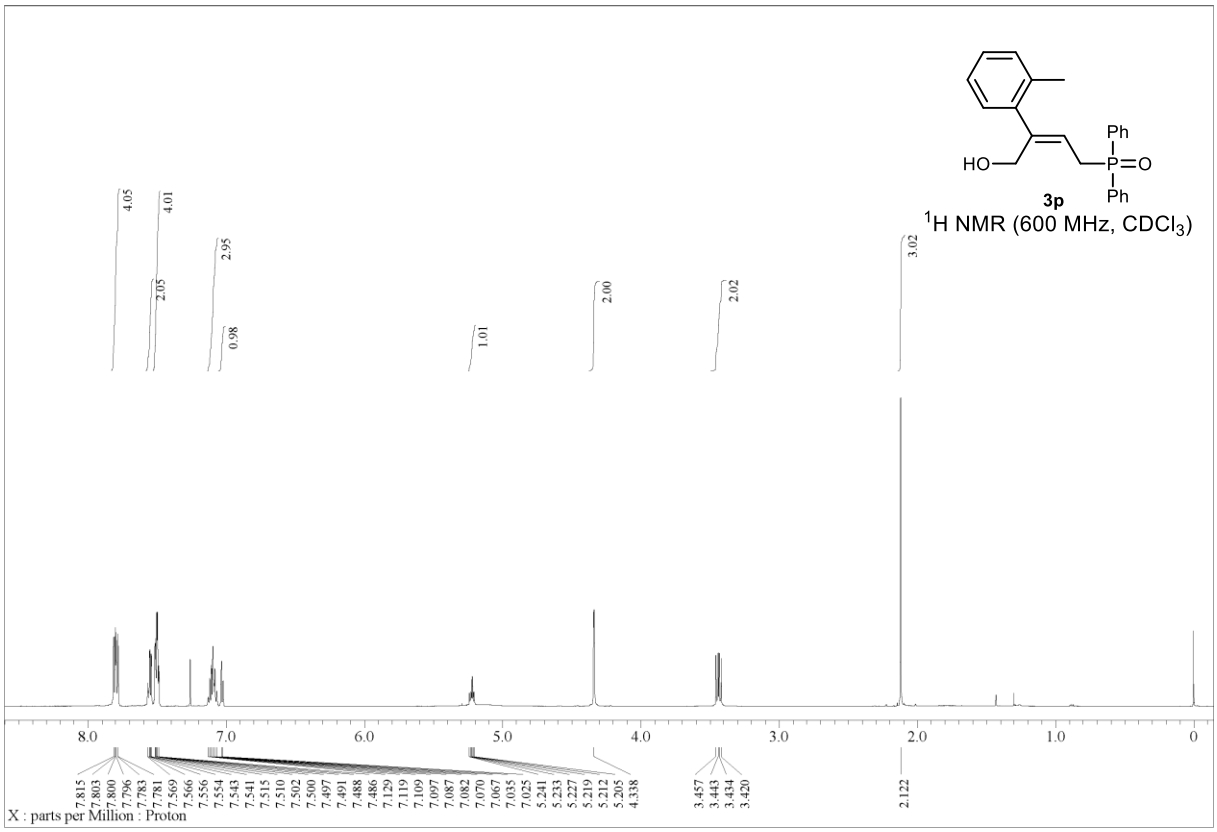
^{31}P NMR (243 MHz, $CDCl_3$)

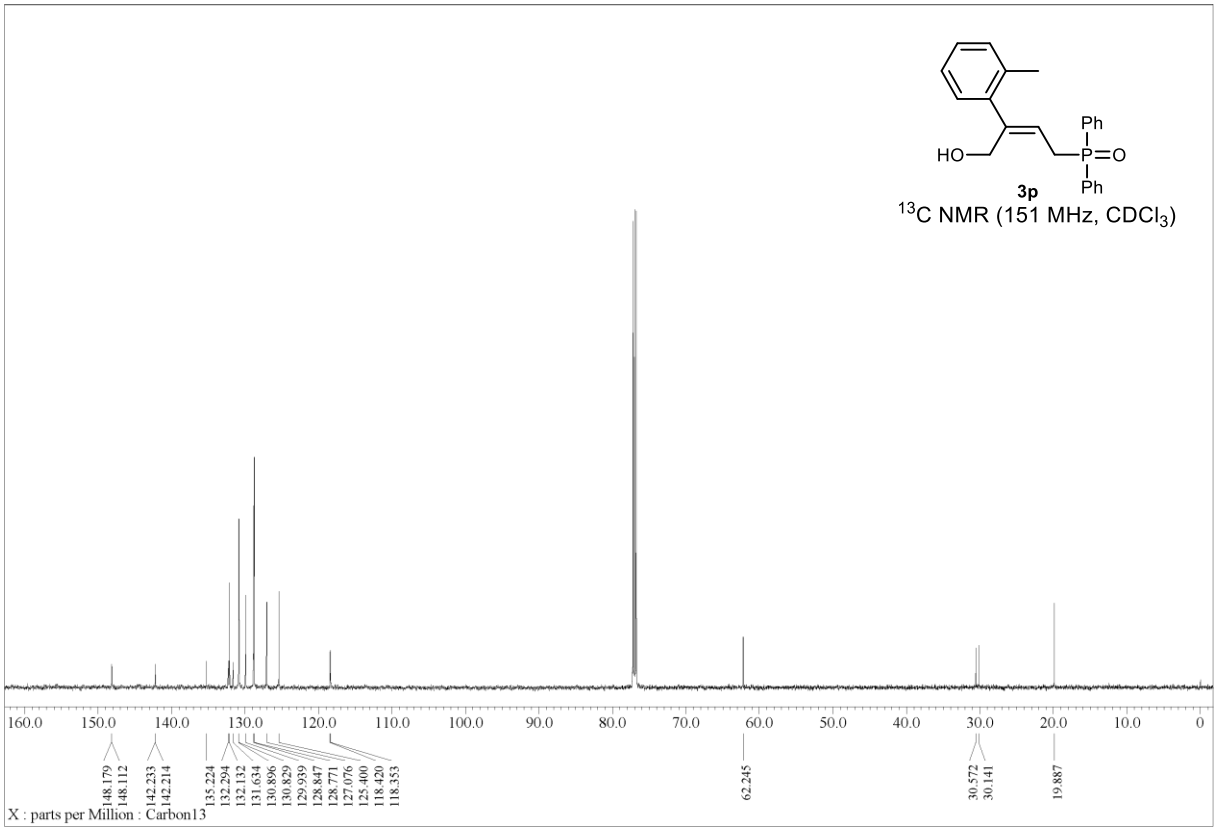


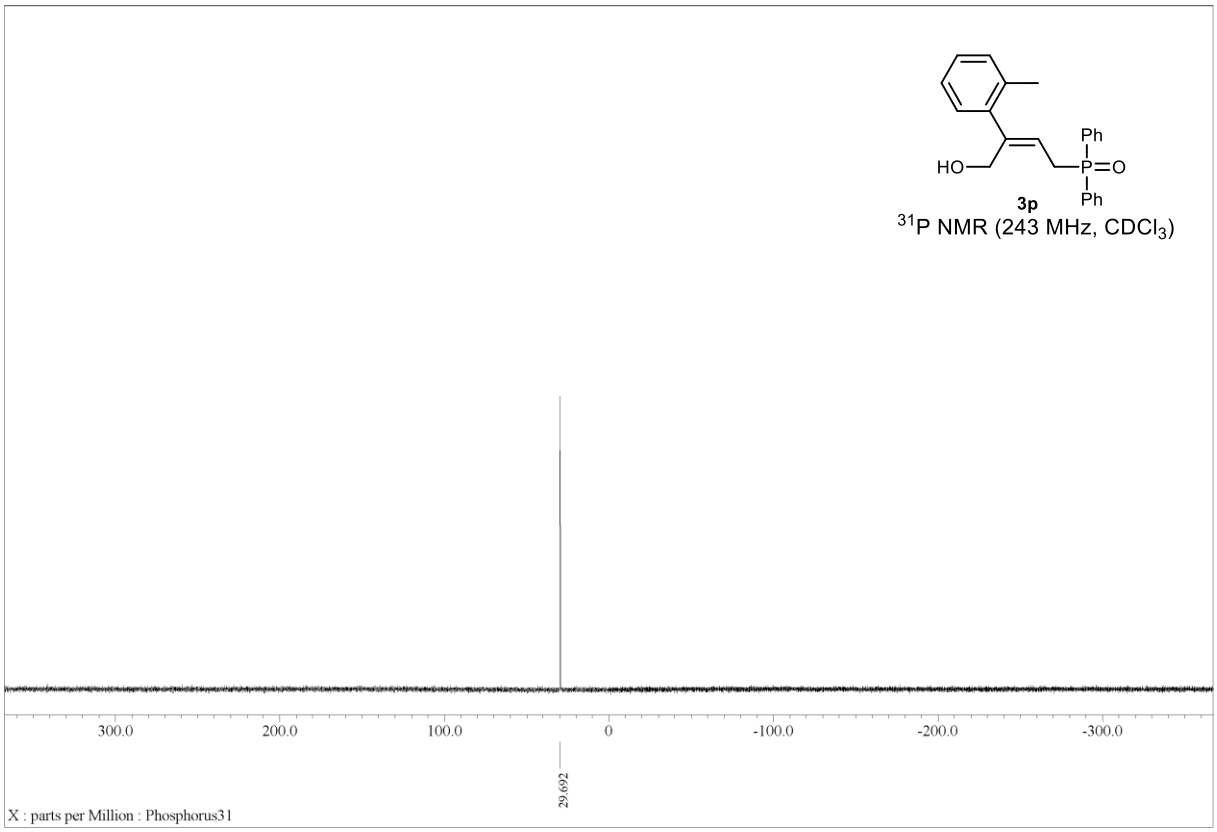
^{1}H NMR (600 MHz, $CDCl_3$)

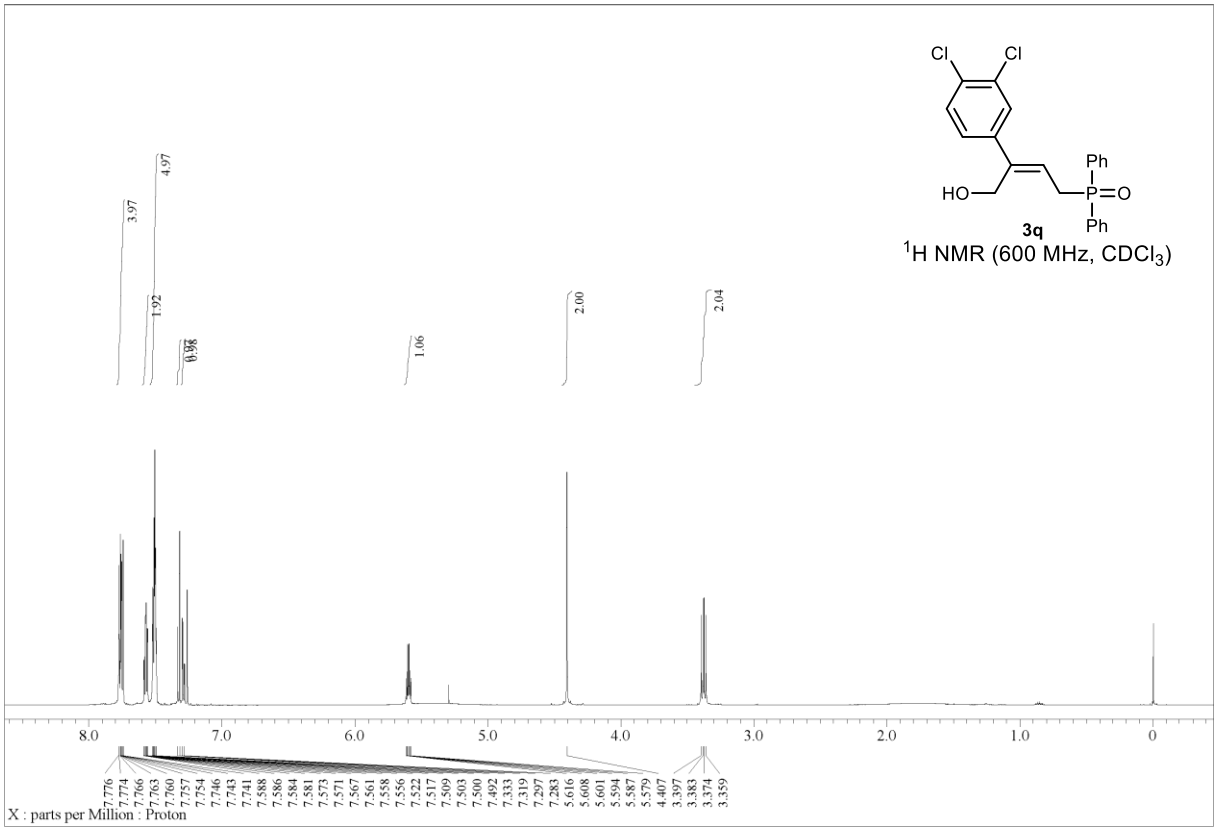

Br
Ph
HO
P=O
Ph
3o
^{13}C NMR (151 MHz, CDCl$_3$)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
148.131
148.064
142.989
142.970
132.380
132.227
132.112
131.452
131.145
131.126
130.916
130.848
128.886
128.809
128.665
127.172
121.992
121.973
120.355
120.278
60.732
30.649
30.218
X : parts per Million : Carbon13

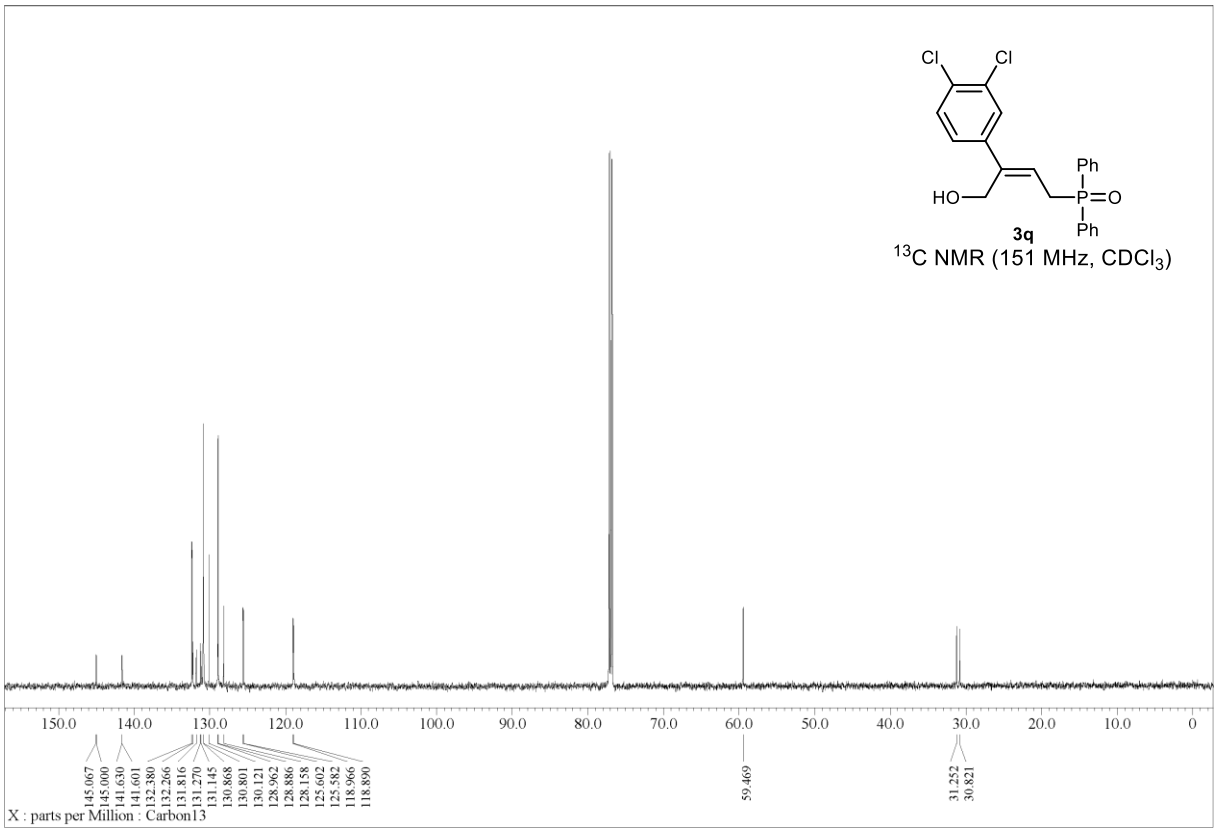

Br
Ph
HO
P=O
Ph
3o
^{31}P NMR (243 MHz, CDCl$_3$)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
29.328
X : parts per Million : Phosphorus31

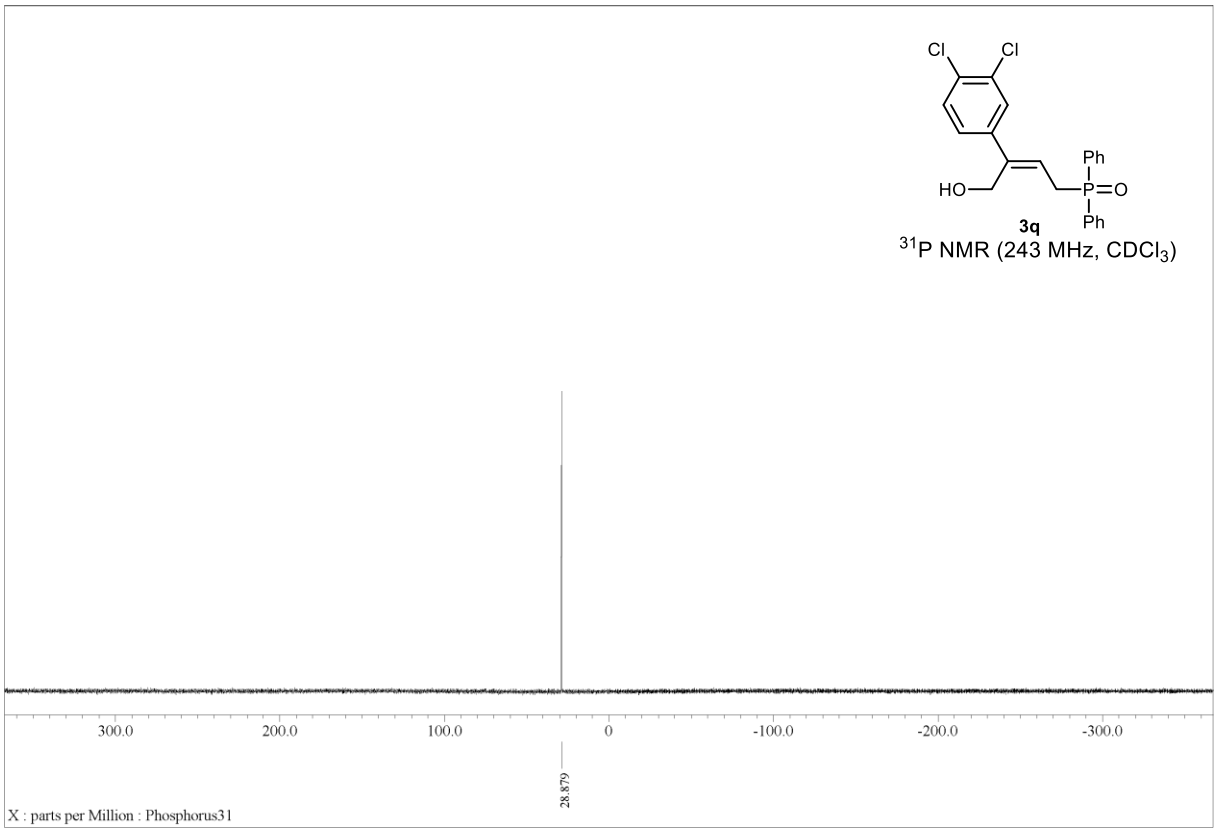

Ph
HO
P=O
Ph
3p
^{1}H NMR (600 MHz, CDCl$_3$)
4.05
4.01
2.05
2.95
0.98
1.01
2.00
2.02
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.815
7.803
7.800
7.796
7.783
7.781
7.569
7.566
7.556
7.554
7.543
7.541
7.515
7.510
7.502
7.500
7.497
7.491
7.488
7.486
7.129
7.119
7.109
7.097
7.087
7.082
7.070
7.067
7.035
7.025
5.241
5.233
5.227
5.219
5.212
5.205
4.338
3.457
3.443
3.434
3.420
2.122
X : parts per Million : Proton

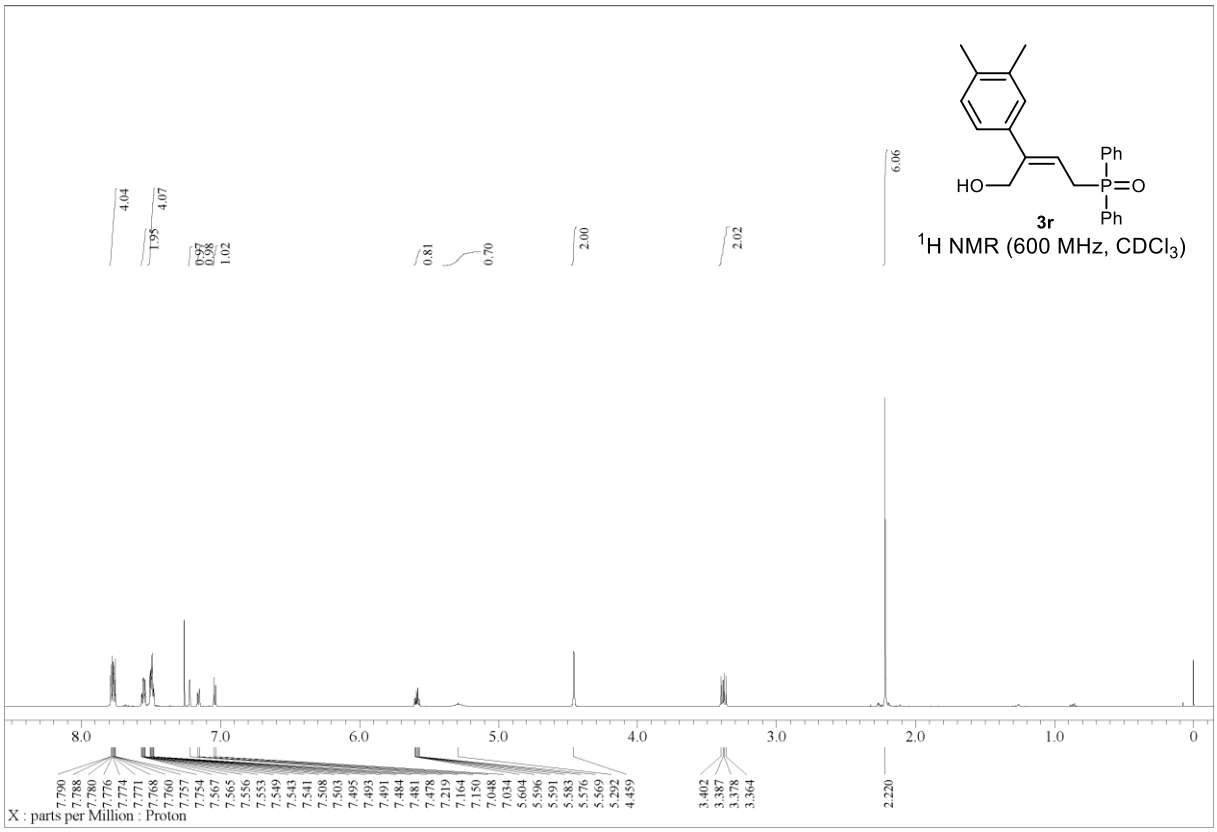

Ph
HO
P=O
Ph
3p
^{13}C NMR (151 MHz, CDCl$_3$)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
148.179
148.112
142.233
142.214
135.224
132.294
132.132
131.634
130.896
130.829
129.939
128.847
128.771
127.076
125.400
118.420
118.353
62.245
30.572
30.141
19.887
X : parts per Million : Carbon13

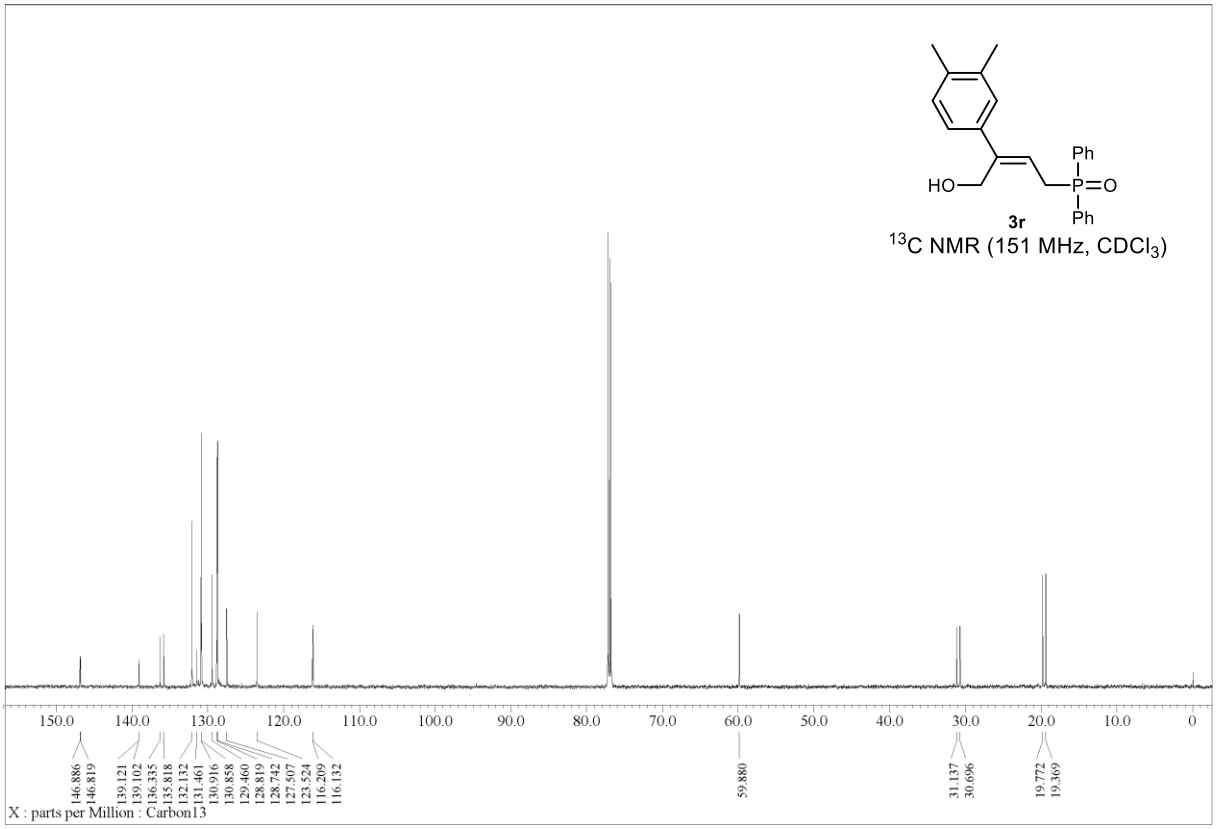

HO
Ph
P=O
Ph
3p
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
29.692
X : parts per Million : Phosphorus31

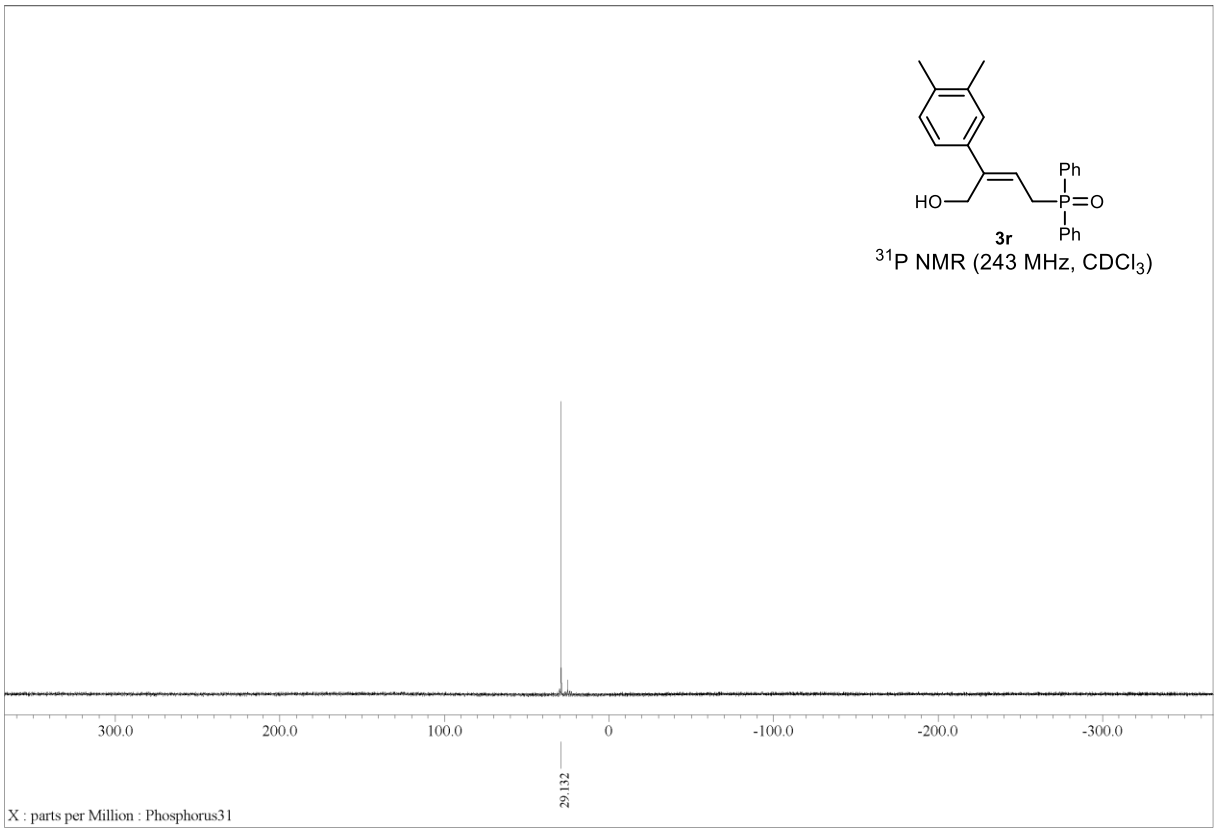

Cl
Cl
HO
Ph
P=O
Ph
3q
1H NMR (600 MHz, CDCl3)
3.97
4.97
1.92
1.06
2.00
2.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

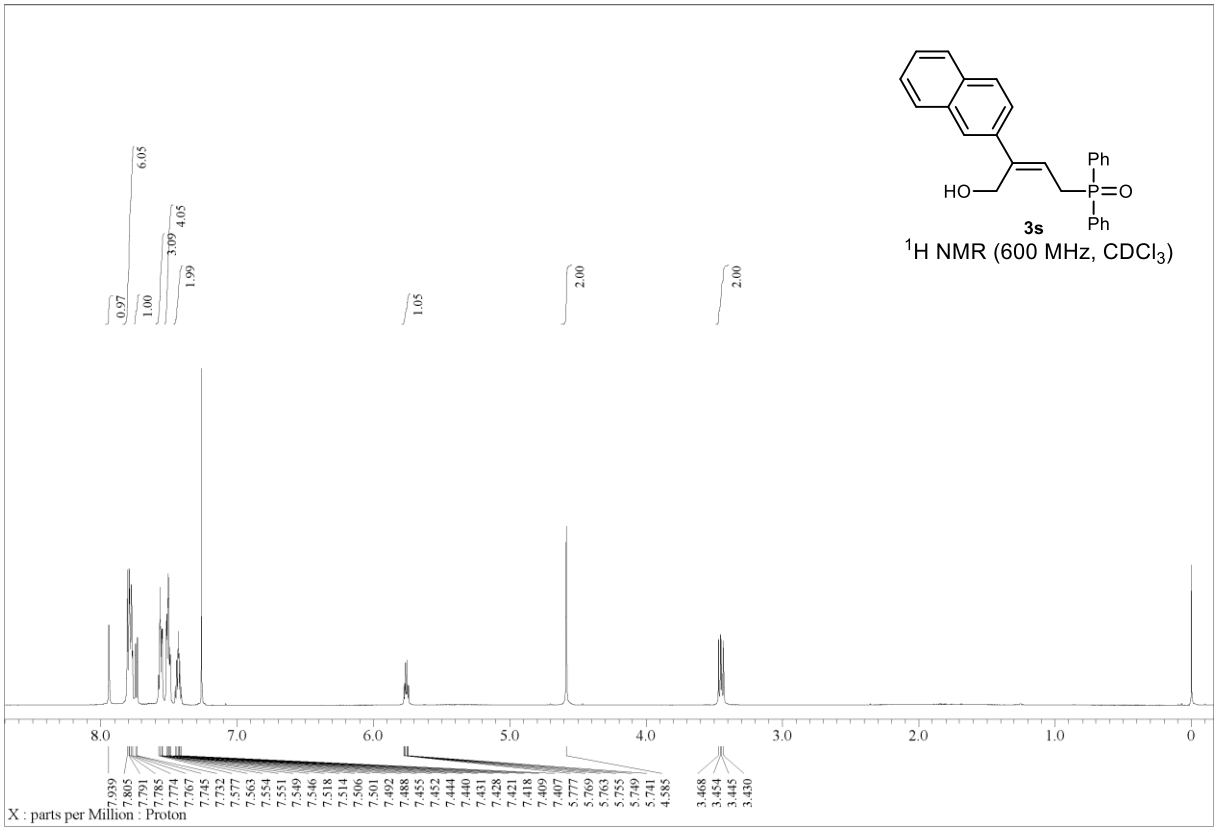

Cl
Cl
Ph
HO
P=O
Ph
3q
^{13}C NMR (151 MHz, CDCl$_3$)
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.067
145.000
141.630
141.601
132.380
132.266
131.816
131.270
131.145
130.868
130.801
130.121
128.962
128.886
128.158
125.602
125.582
118.966
118.890
59.469
31.252
30.821
X : parts per Million : Carbon13

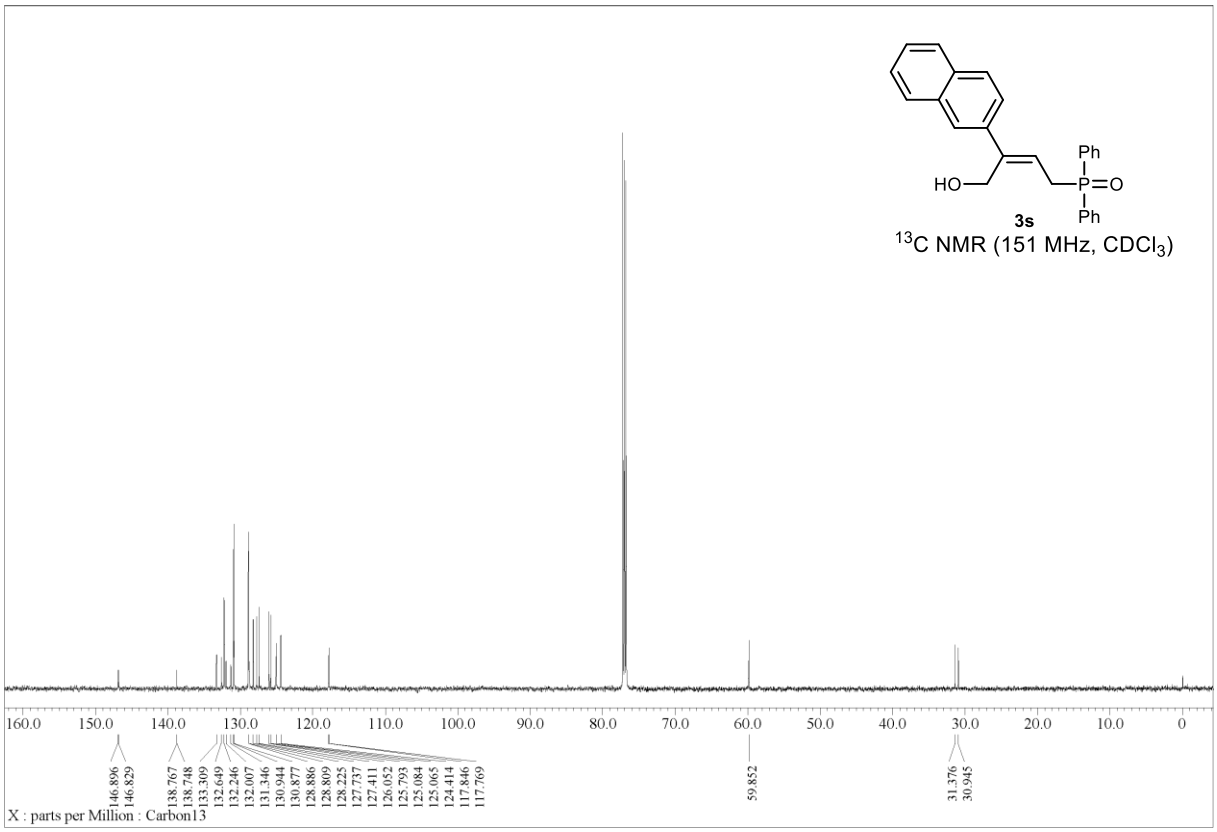

Cl
Cl
Ph
HO
P=O
Ph
3q
^{31}P NMR (243 MHz, CDCl$_3$)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
28.879
X : parts per Million : Phosphorus31


HO
Ph
P=O
Ph
3r
^{1}H NMR (600 MHz, CDCl$_3$)
X : parts per Million : Proton

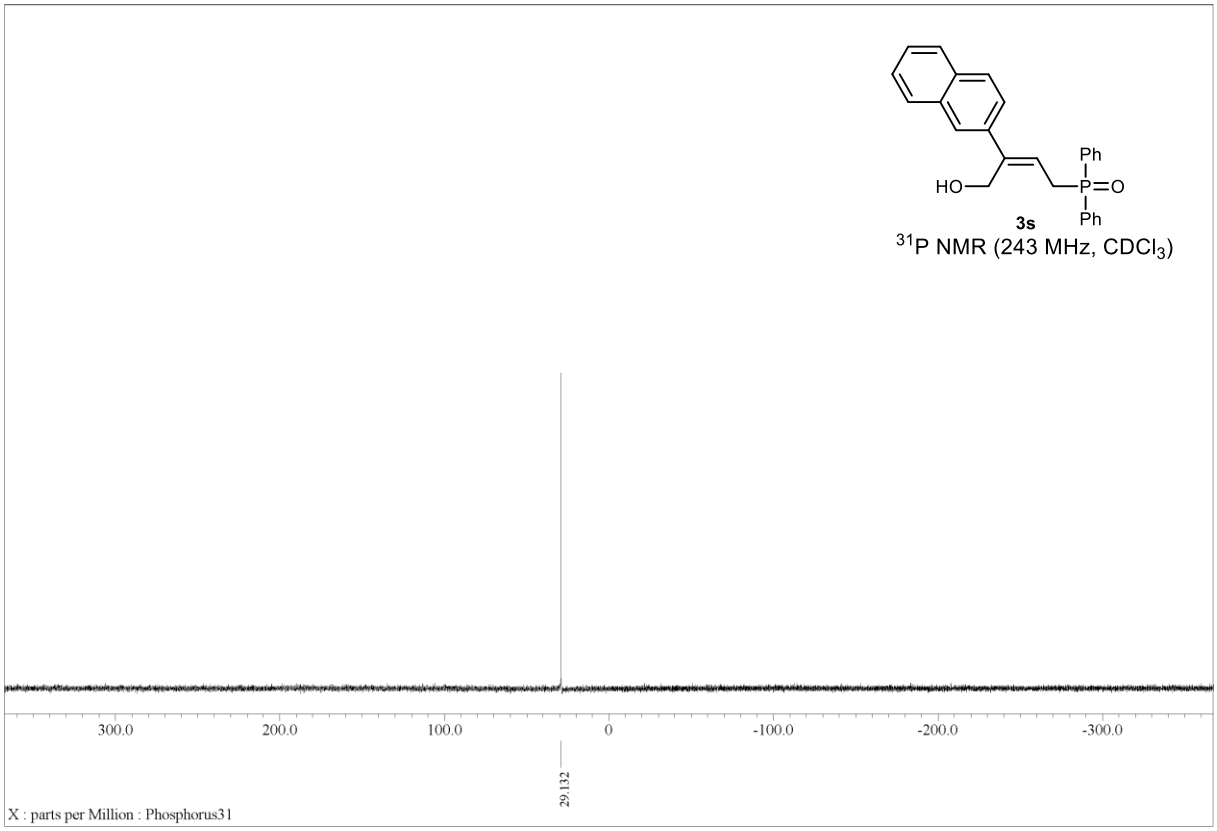

HO
Ph
P=O
Ph
3r
^{13}C NMR (151 MHz, CDCl$_3$)
X : parts per Million : Carbon13


HO
Ph
P=O
Ph
3r
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
29.132
X : parts per Million : Phosphorus31

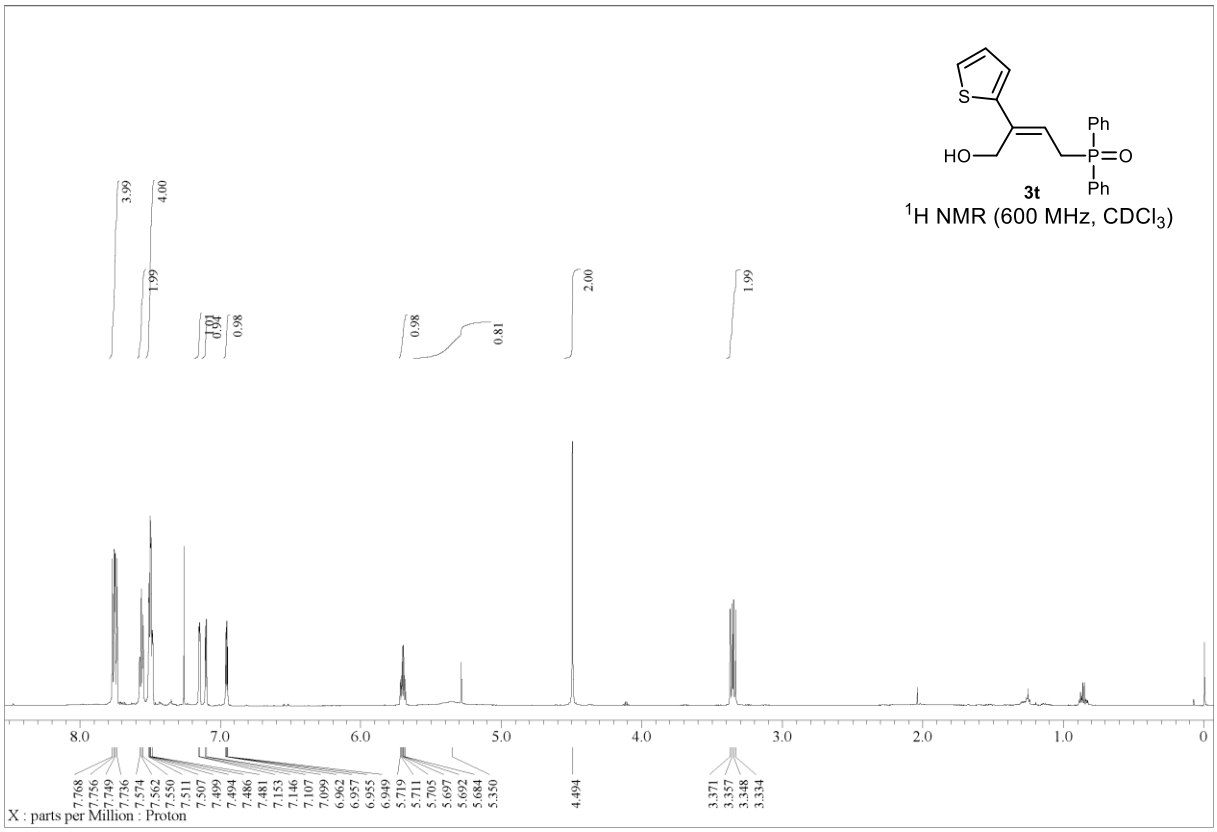

HO
Ph
P=O
Ph
3s
1H NMR (600 MHz, CDCl3)
6.05
4.05
3.09
1.99
0.97
1.00
1.05
2.00
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

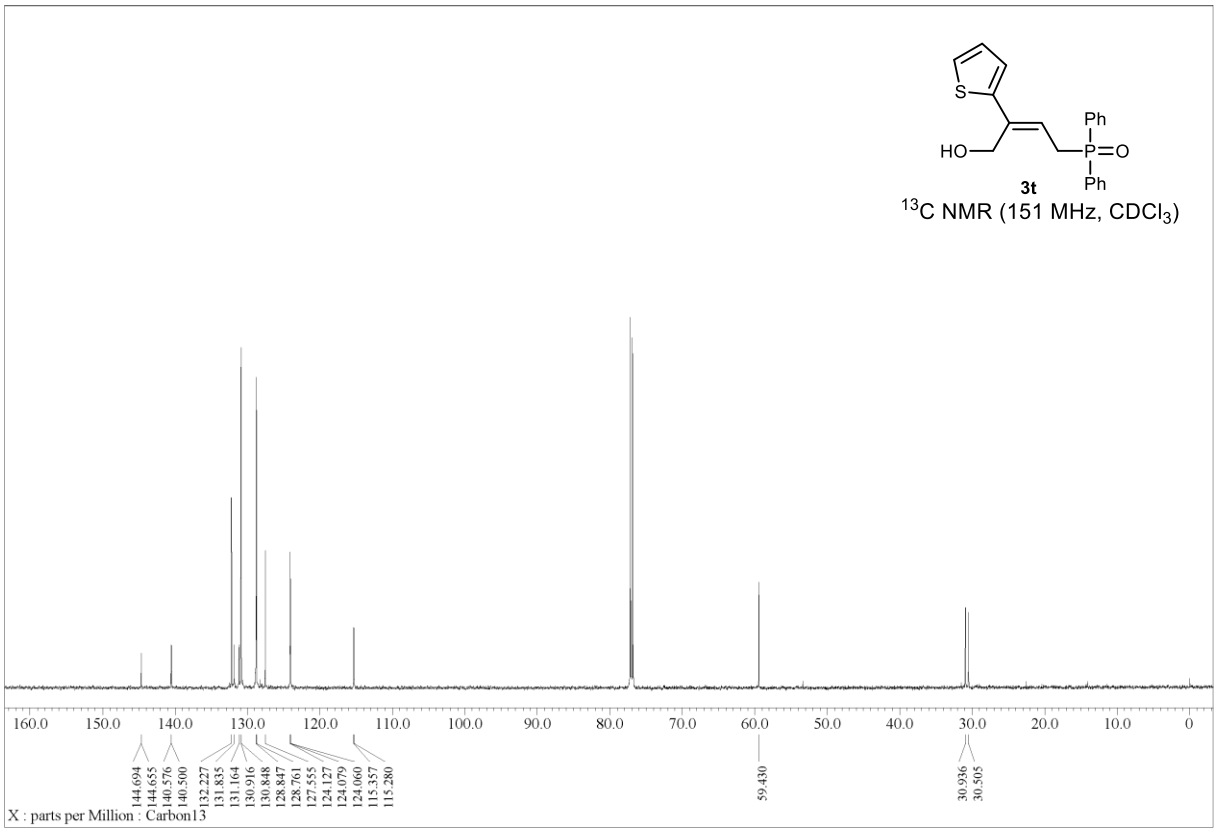


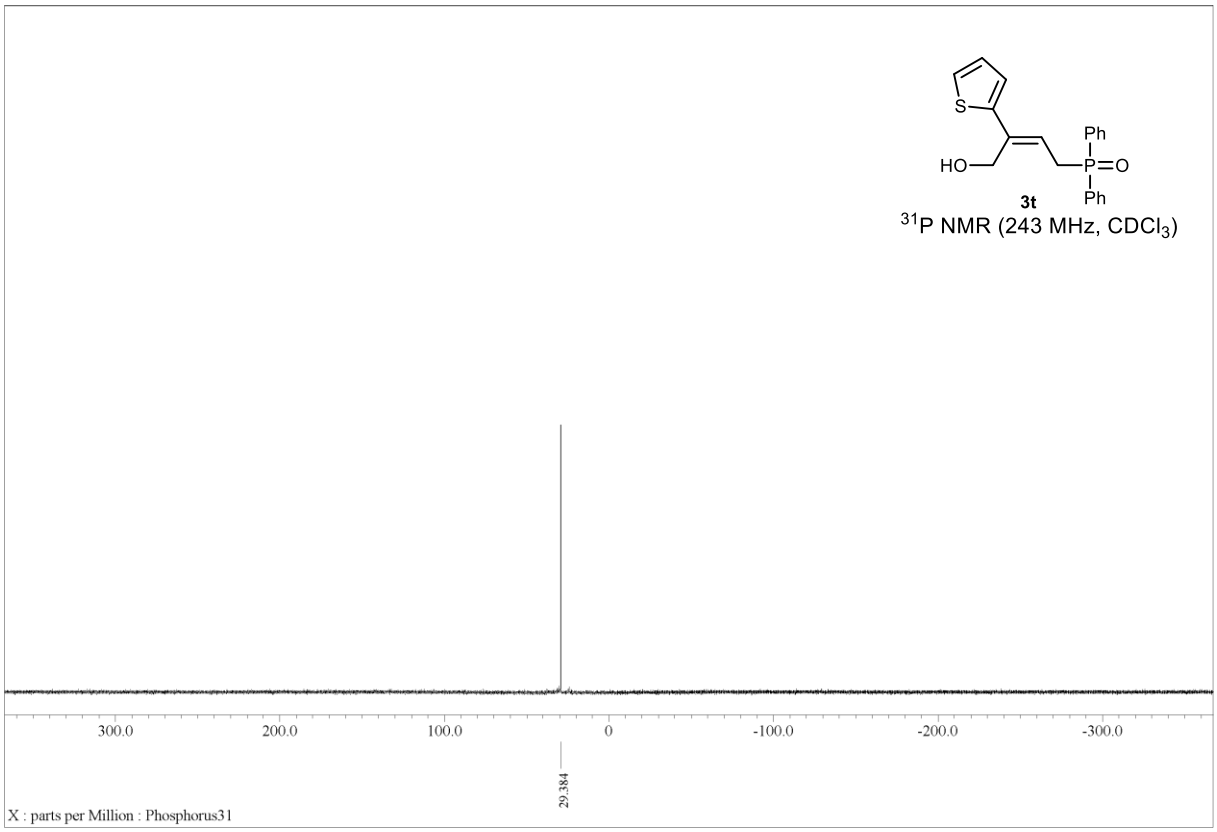
^{13}C NMR (151 MHz, $CDCl_3$)



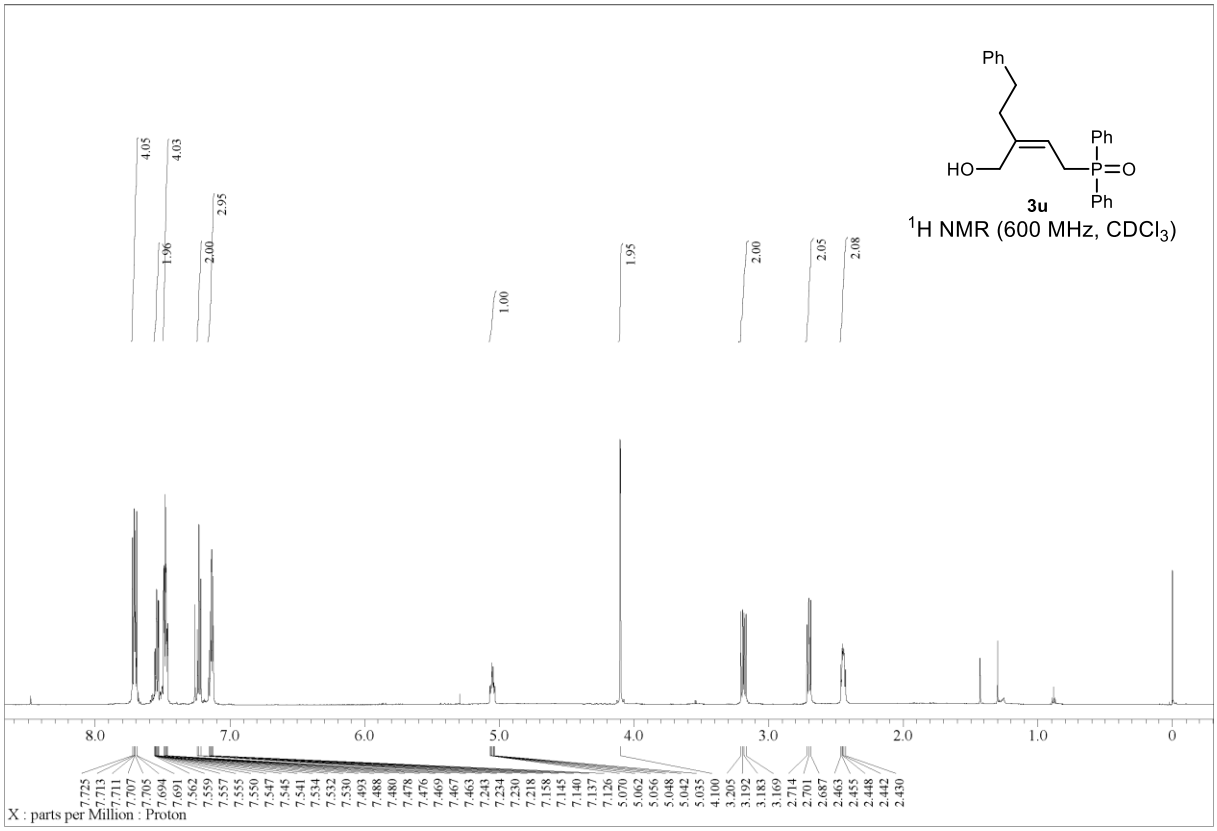
^{31}P NMR (243 MHz, $CDCl_3$)


S
HO
Ph
P=O
Ph
3t
^{1}H NMR (600 MHz, CDCl$_3$)
3.99
4.00
1.99
1.01
0.94
0.98
0.98
0.81
2.00
1.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.768
7.756
7.749
7.736
7.574
7.562
7.550
7.511
7.507
7.499
7.494
7.486
7.481
7.153
7.146
7.107
7.099
6.962
6.957
6.955
6.949
5.719
5.711
5.705
5.697
5.692
5.684
5.350
4.494
3.371
3.357
3.348
3.334
X : parts per Million : Proton

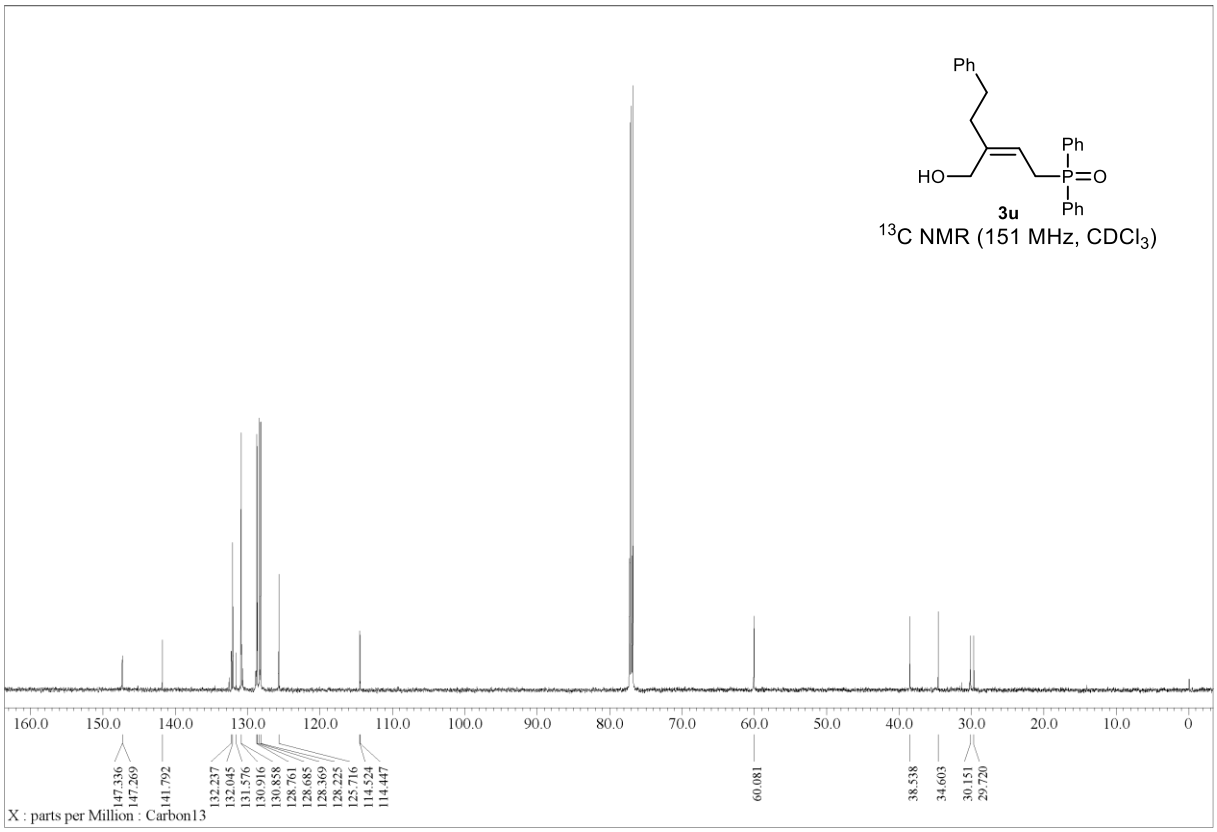

S
HO
Ph
P=O
Ph
3t
^{13}C NMR (151 MHz, CDCl$_3$)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
144.694
144.655
140.576
140.500
132.227
131.835
131.164
130.916
130.848
128.847
128.761
127.555
124.127
124.079
124.060
115.357
115.280
59.430
30.936
30.505
X : parts per Million : Carbon13

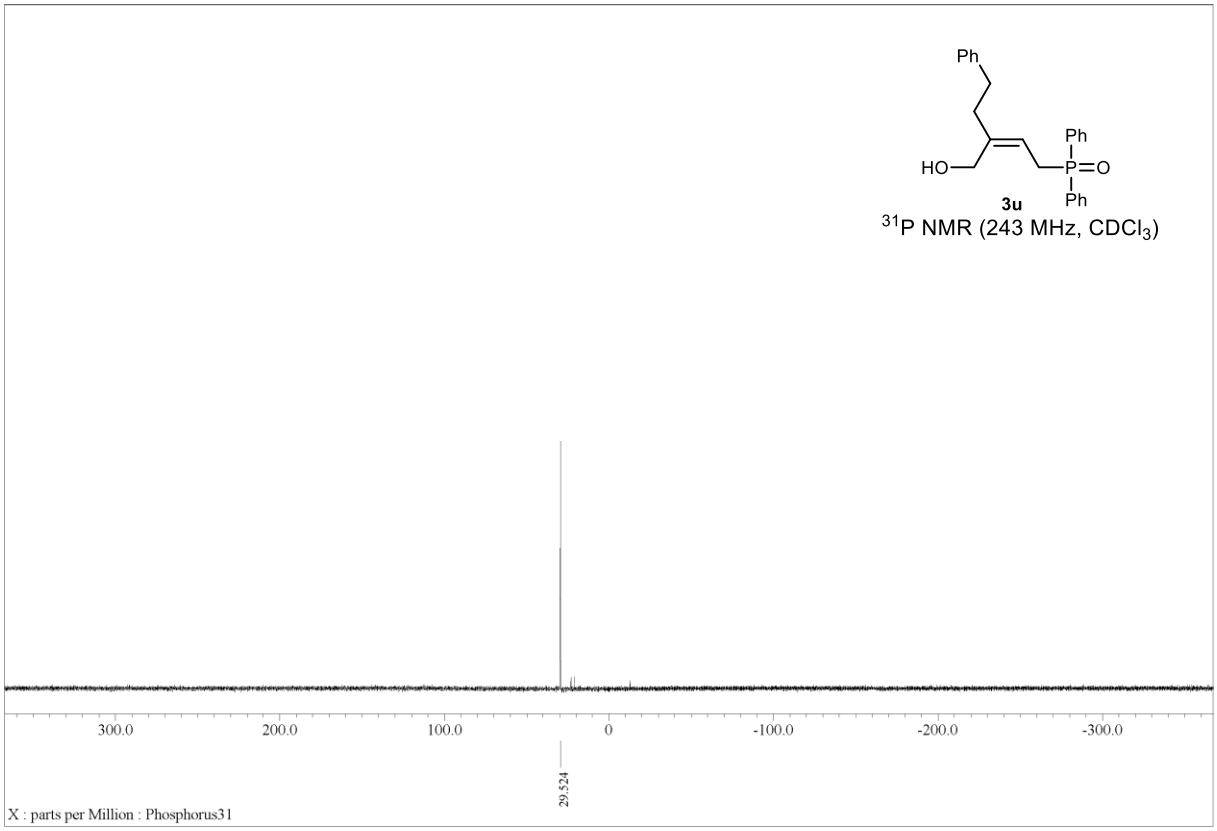


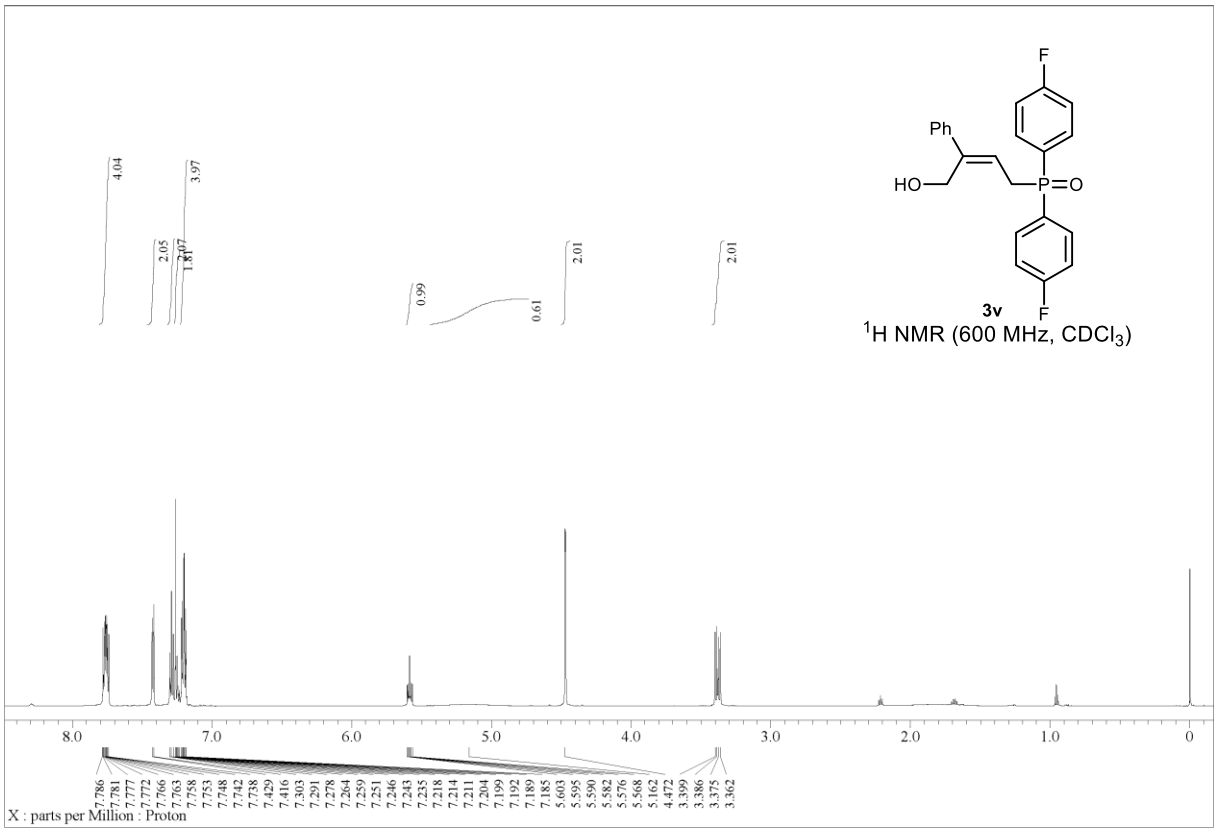
^{31}P NMR (243 MHz, $CDCl_3$)

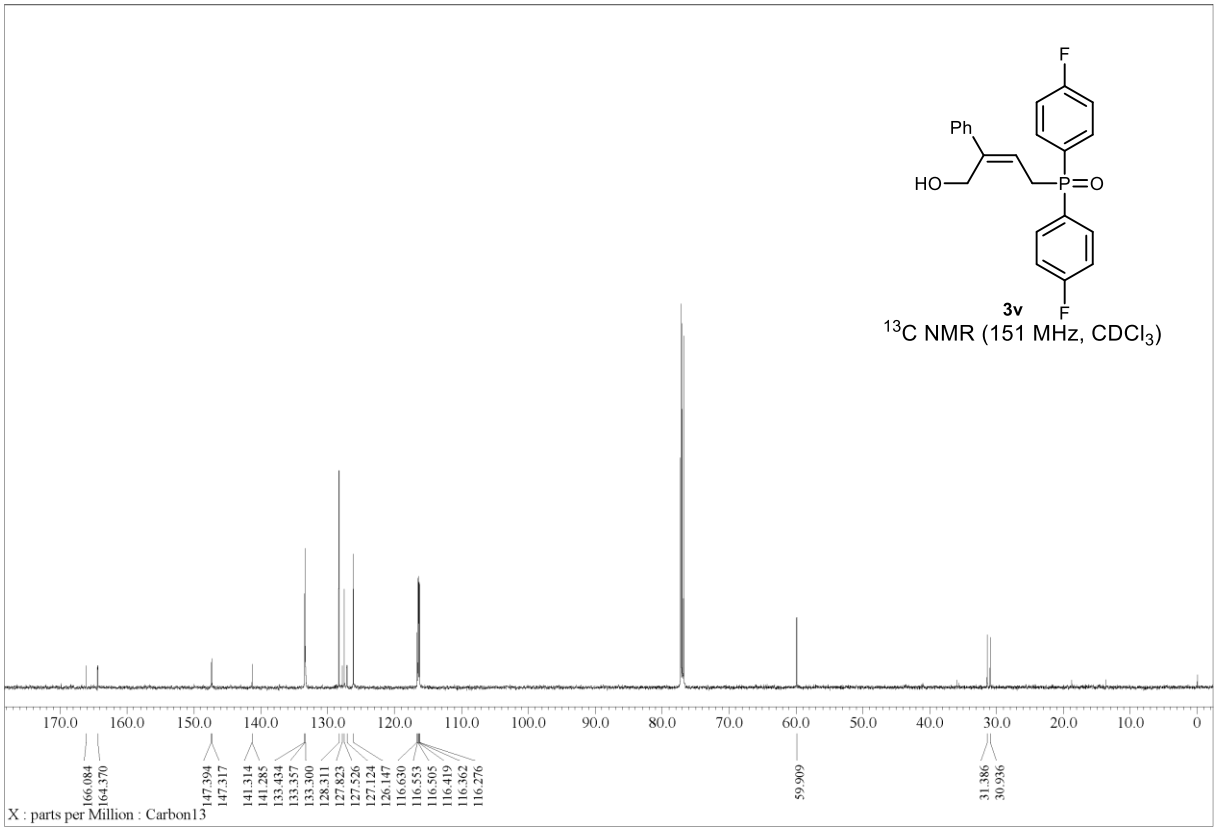


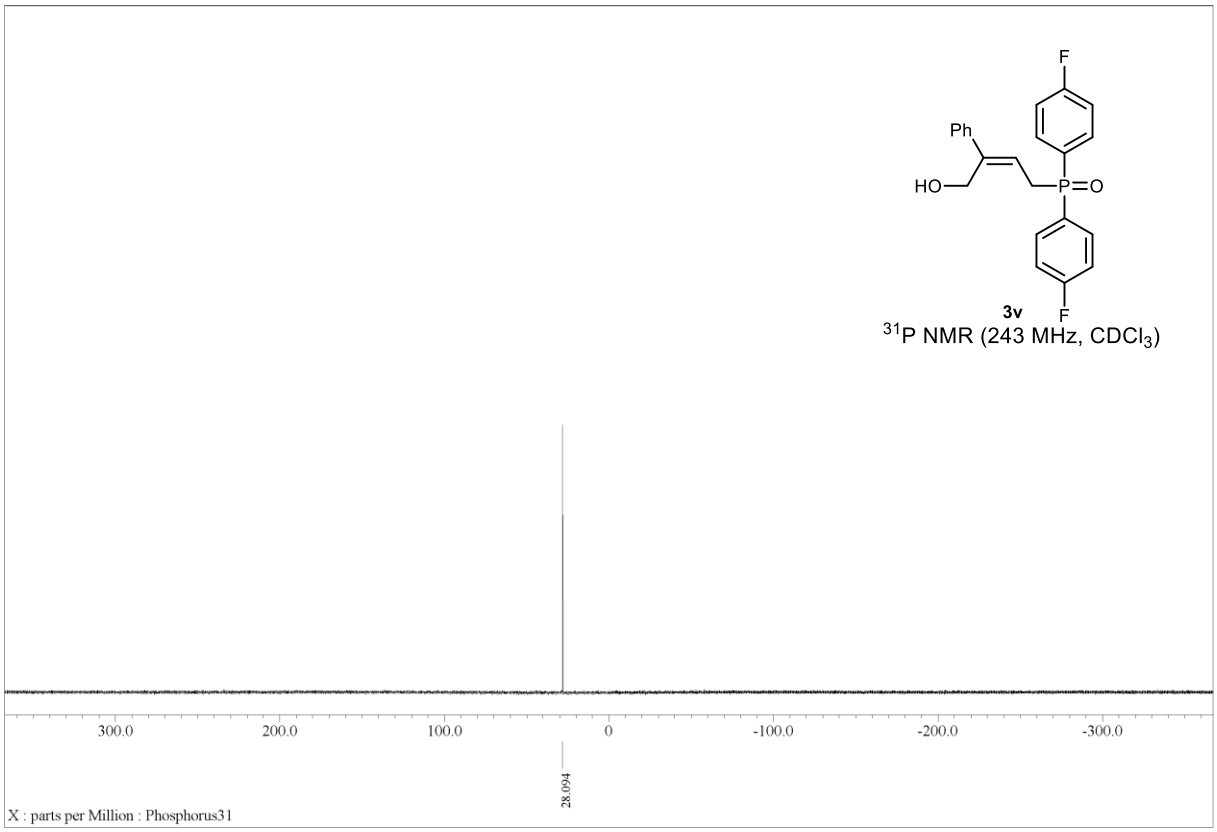
^{1}H NMR (600 MHz, $CDCl_3$)


Ph
HO
Ph
P=O
Ph
3u
^{13}C NMR (151 MHz, CDCl$_3$)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
147.336
147.269
141.792
132.237
132.045
131.576
130.916
130.858
128.761
128.685
128.369
128.225
125.716
114.524
114.447
60.081
38.538
34.603
30.151
29.720
X : parts per Million : Carbon13

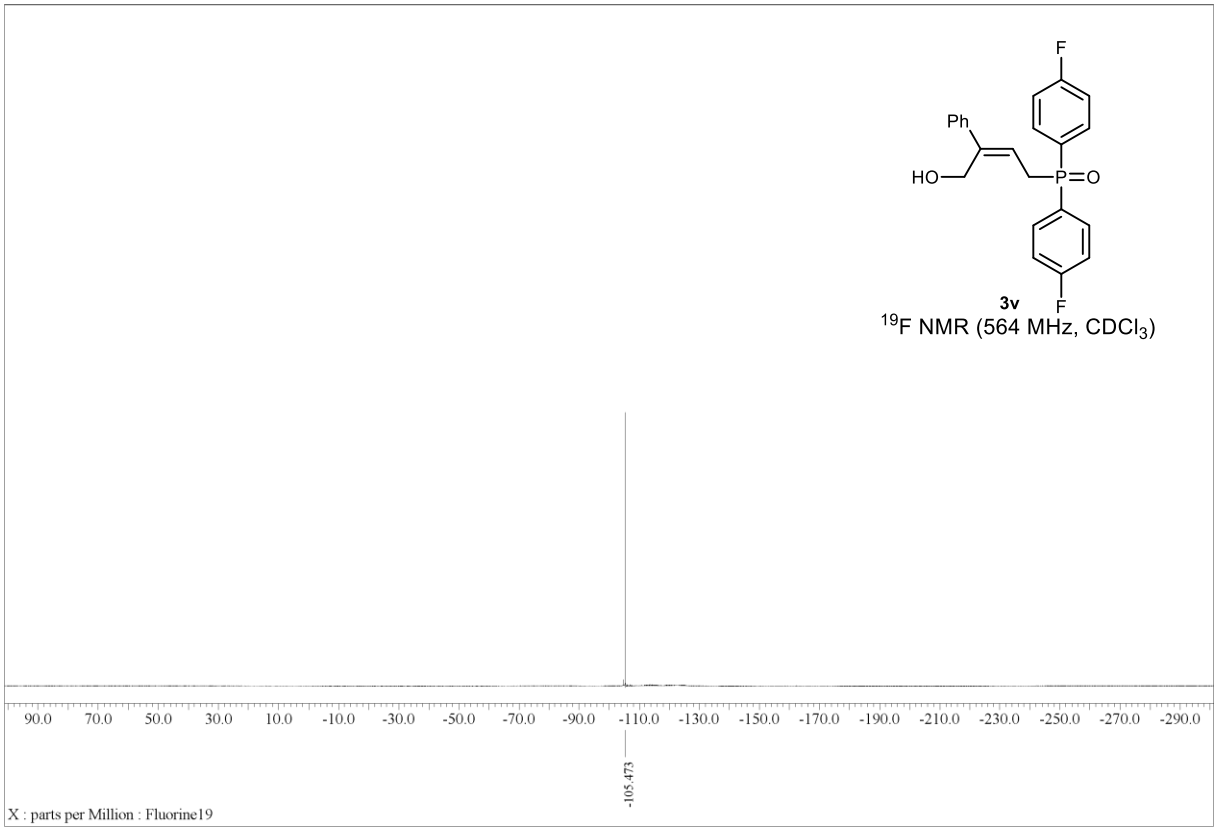

Ph
HO
Ph
P=O
Ph
3u
^{31}P NMR (243 MHz, CDCl$_3$)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
29.524
X : parts per Million : Phosphorus31


F
Ph
HO
P=O
F
3v
^{1}H NMR (600 MHz, CDCl$_3$)
4.04
3.97
2.05
2.07
1.80
0.99
0.61
2.01
2.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.786
7.781
7.777
7.772
7.766
7.763
7.758
7.753
7.748
7.742
7.738
7.429
7.416
7.303
7.291
7.278
7.264
7.259
7.251
7.246
7.243
7.235
7.218
7.214
7.211
7.204
7.199
7.192
7.189
7.185
5.603
5.595
5.590
5.582
5.576
5.568
5.162
4.472
3.399
3.386
3.375
3.362
X : parts per Million : Proton

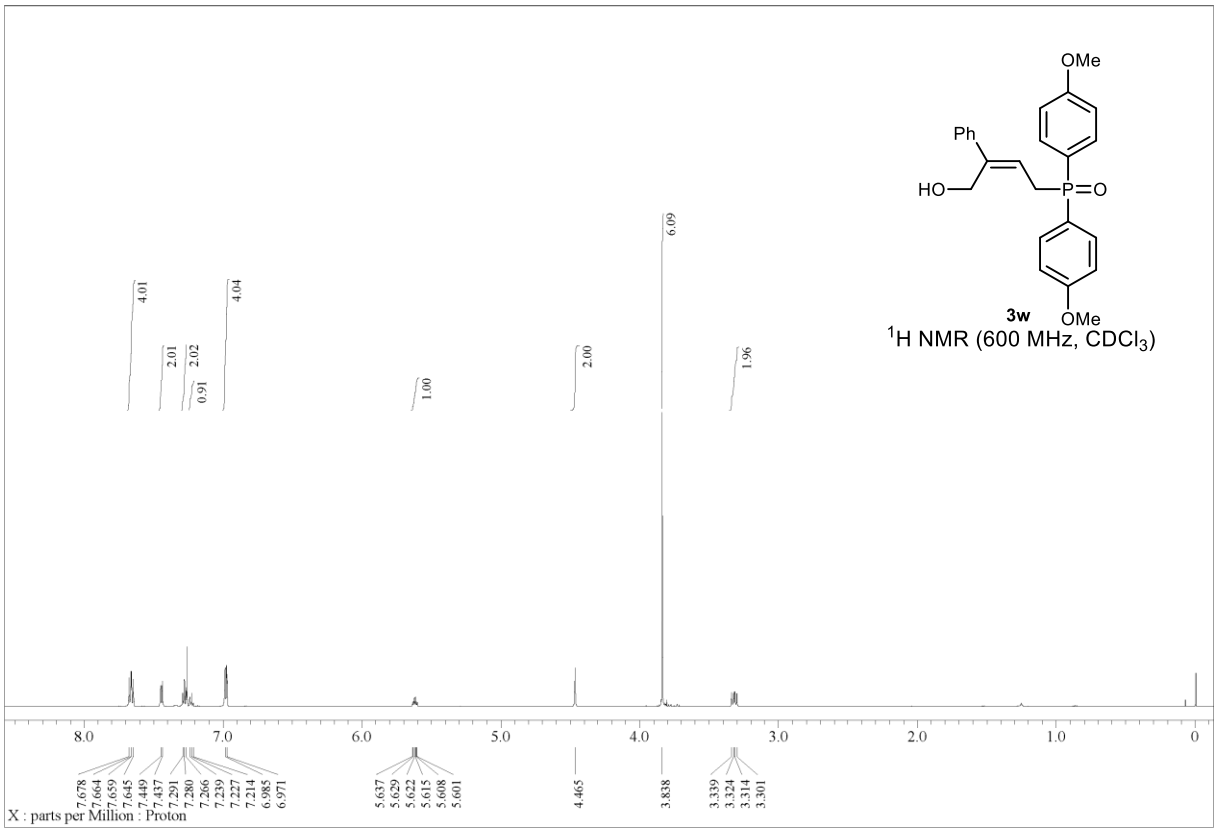

F
Ph
HO
P=O
F
3v
^{13}C NMR (151 MHz, CDCl$_3$)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
166.084
164.370
147.394
147.317
141.314
141.285
133.434
133.357
133.300
128.311
127.823
127.526
127.124
126.147
116.630
116.553
116.505
116.419
116.362
116.276
59.909
31.386
30.936
X : parts per Million : Carbon13

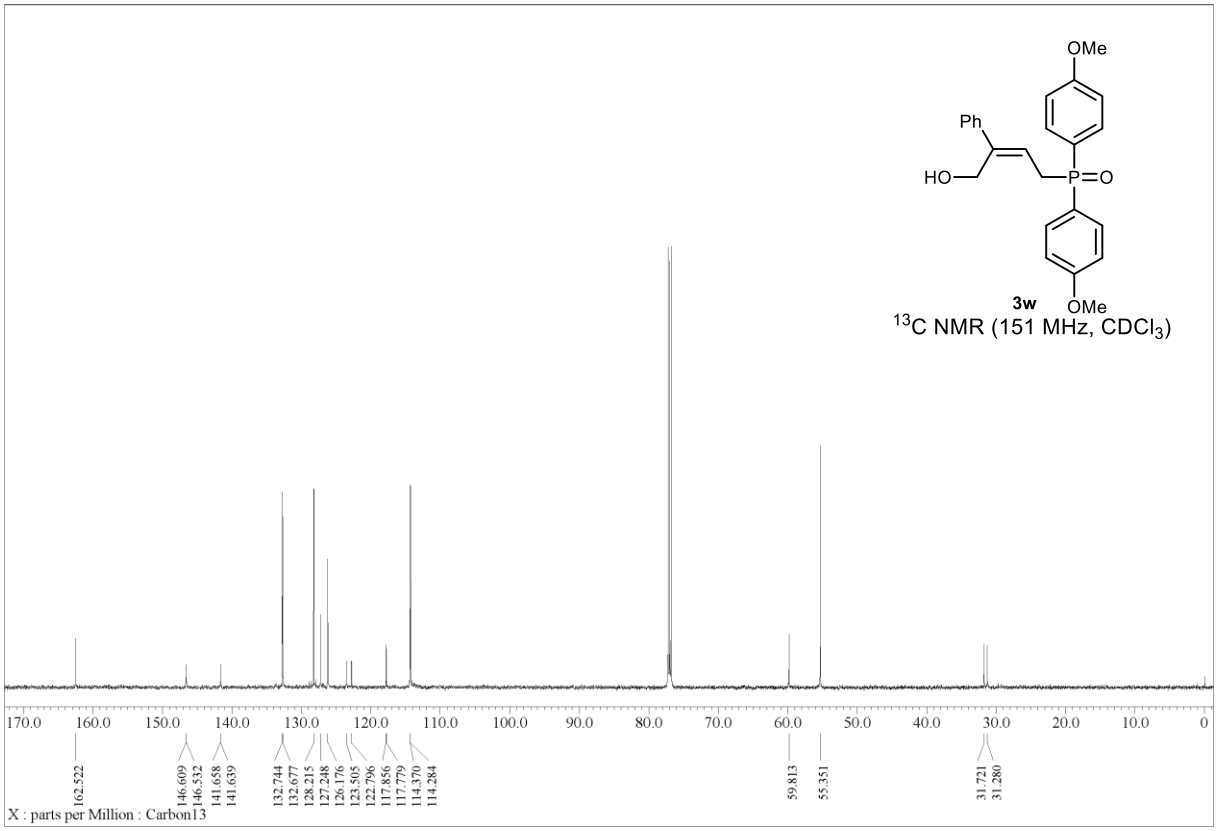


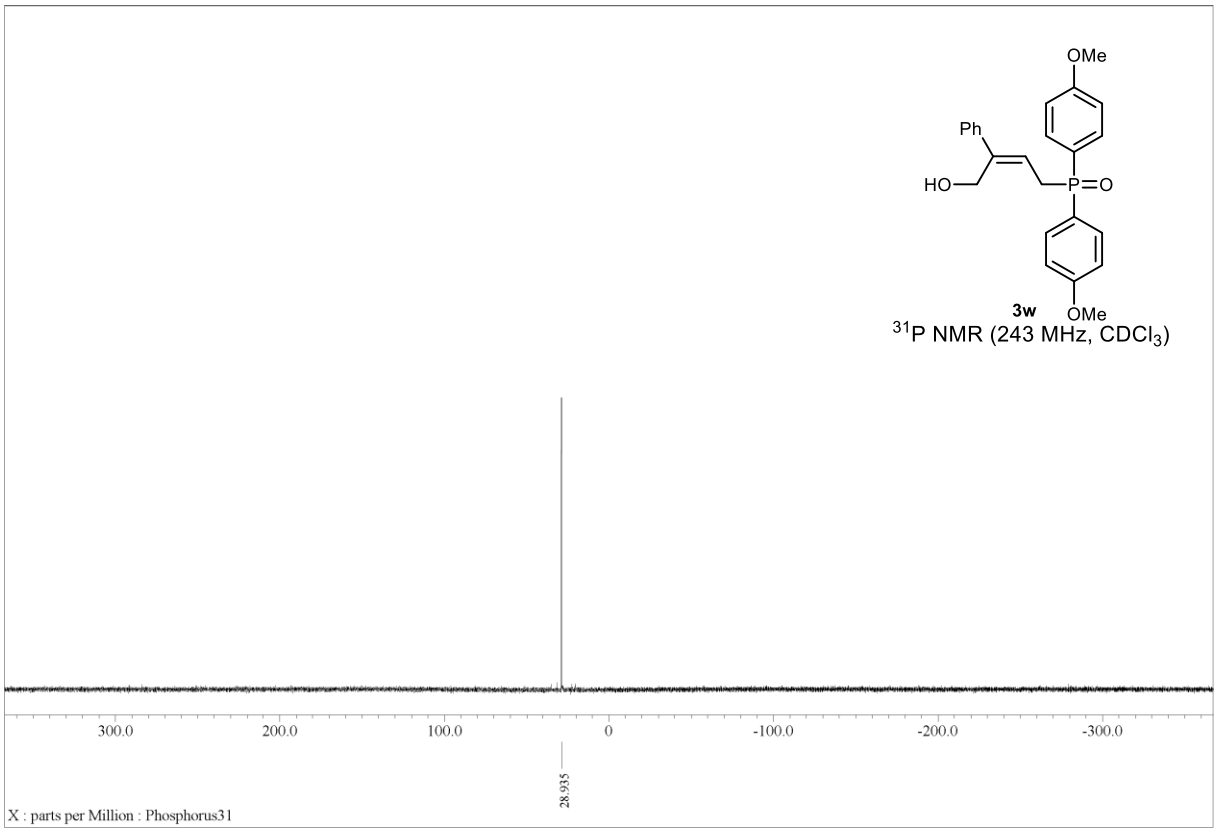
^{31}P NMR (243 MHz, $CDCl_3$)

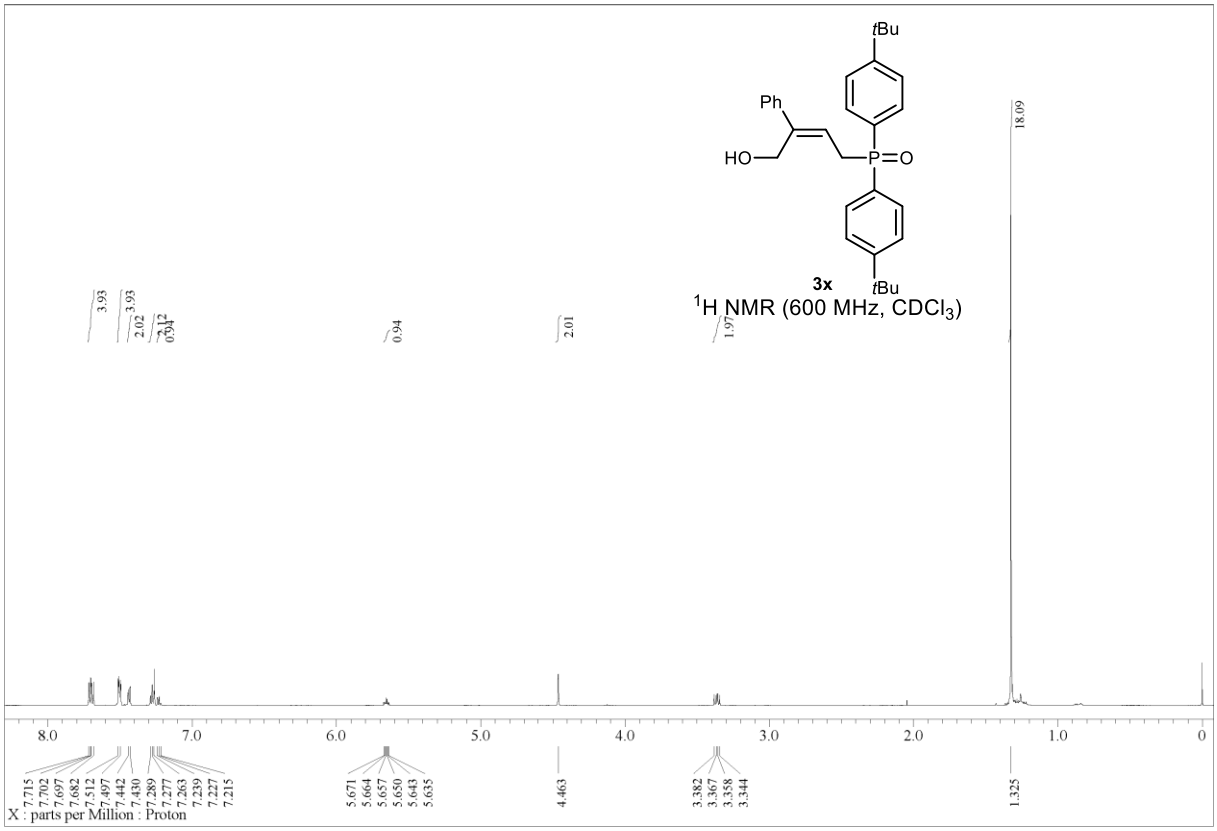


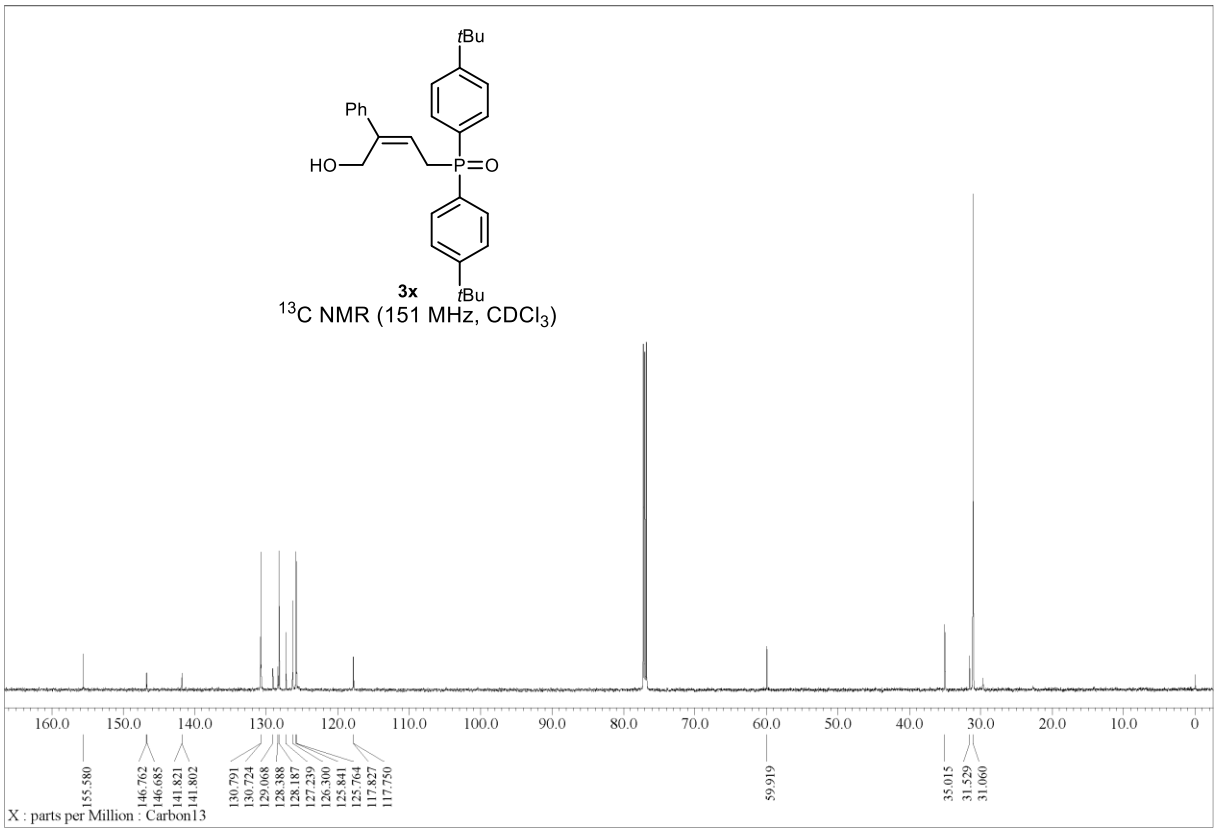
^{19}F NMR (564 MHz, $CDCl_3$)

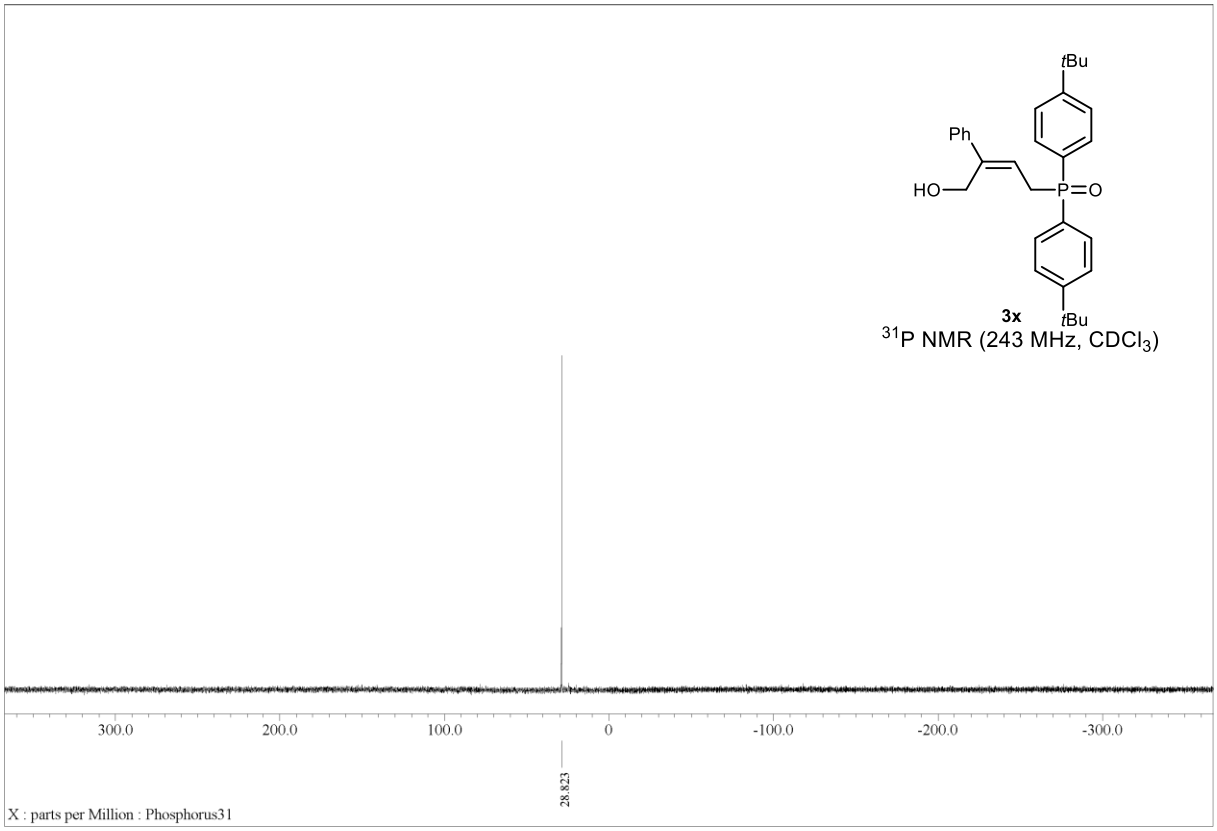

OMe
Ph
HO
P=O
OMe
3w
^{1}H NMR (600 MHz, CDCl$_3$)
4.01
2.01
2.02
0.91
4.04
1.00
2.00
6.09
1.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.678
7.664
7.659
7.645
7.449
7.437
7.291
7.280
7.266
7.239
7.227
7.214
6.985
6.971
5.637
5.629
5.622
5.615
5.608
5.601
4.465
3.838
3.339
3.324
3.314
3.301
X : parts per Million : Proton

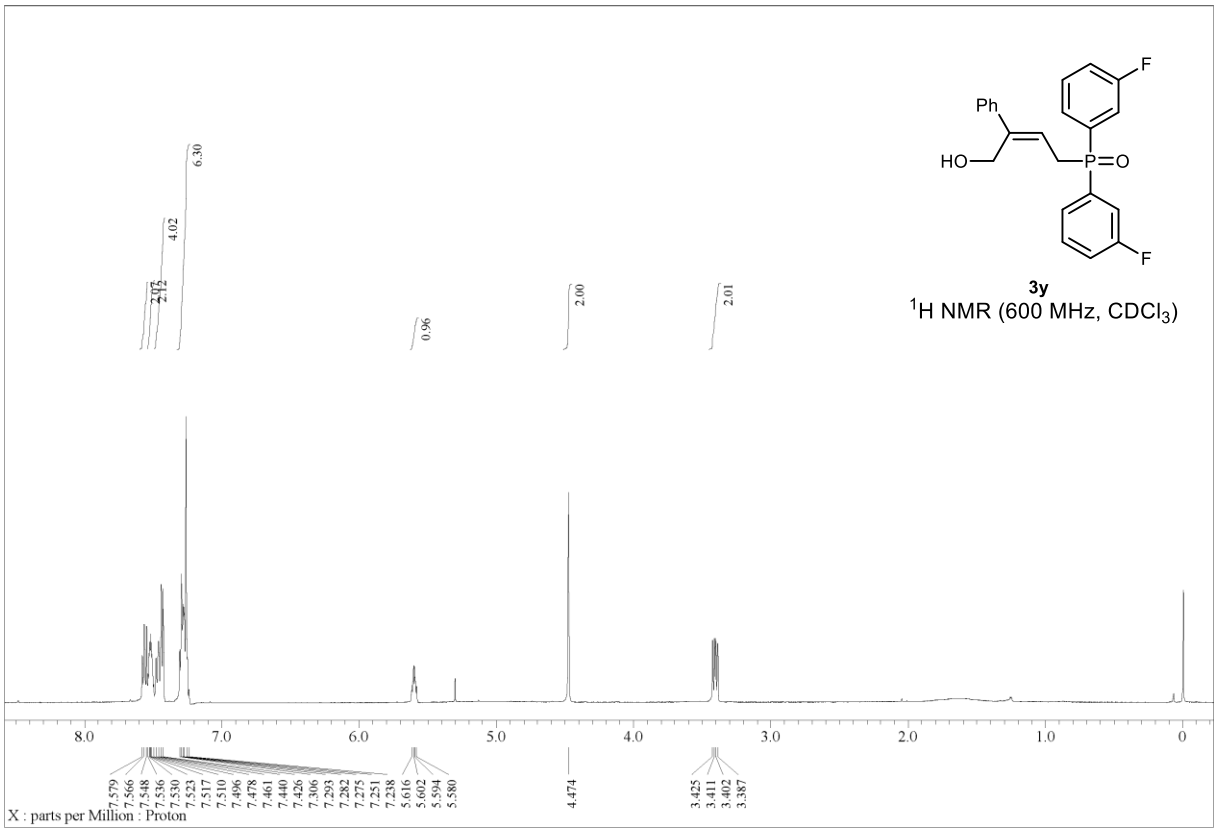

OMe
Ph
HO
P=O
OMe
3w
^{13}C NMR (151 MHz, CDCl$_3$)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.522
146.609
146.532
141.658
141.639
132.744
132.677
128.215
127.248
126.176
123.505
122.796
117.856
117.779
114.370
114.284
59.813
55.351
31.721
31.280
X : parts per Million : Carbon13

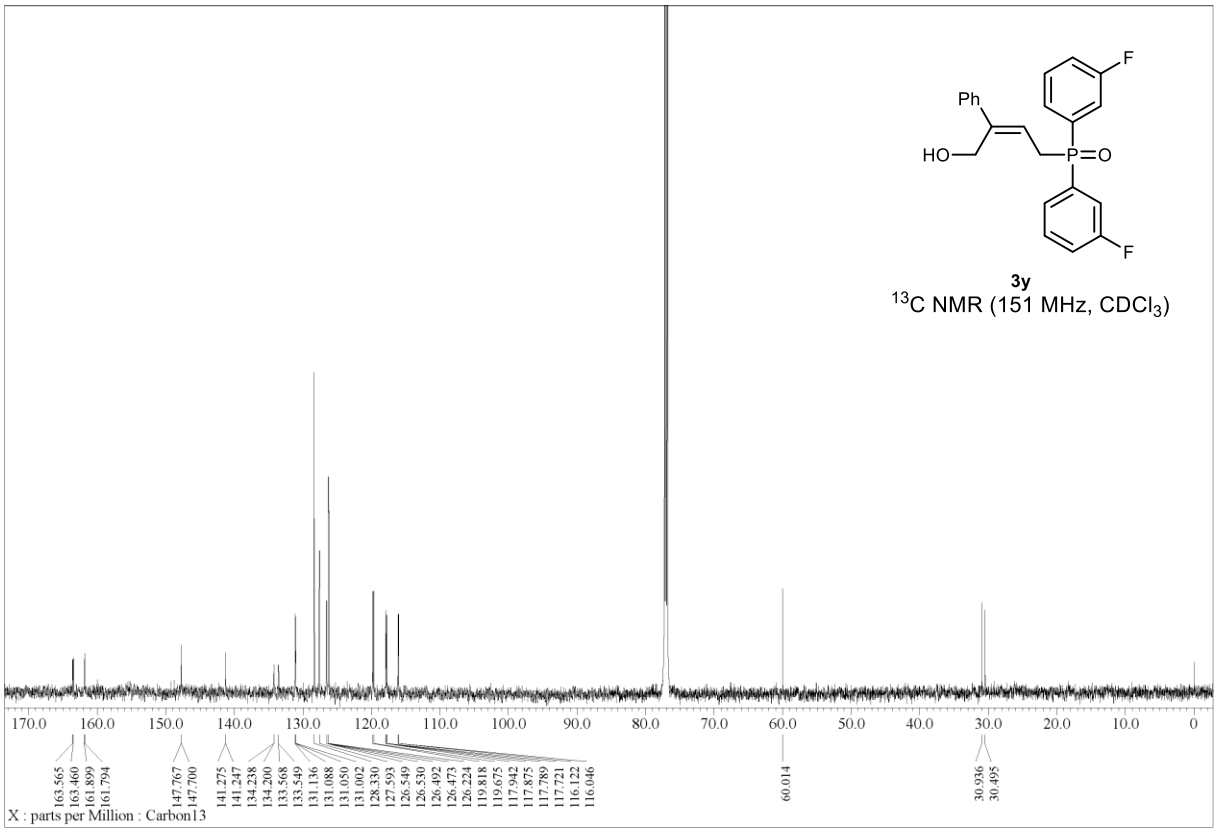

OMe
Ph
HO
P=O
OMe
3w
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
28.935
X : parts per Million : Phosphorus31

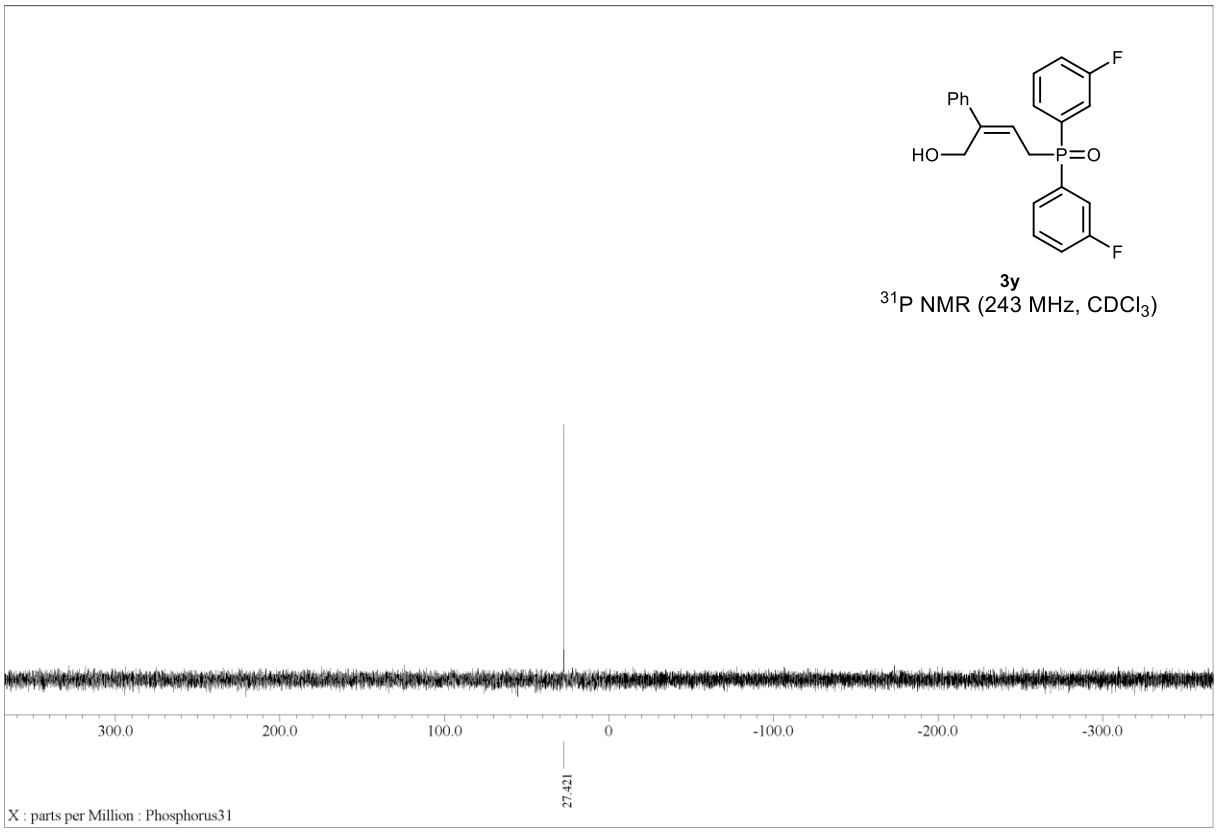

tBu
Ph
HO
P=O
tBu
3x
1H NMR (600 MHz, CDCl3)
3.93
3.93
2.02
2.12
0.94
0.94
2.01
1.97
18.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.715
7.702
7.697
7.682
7.512
7.497
7.442
7.430
7.289
7.277
7.263
7.239
7.227
7.215
5.671
5.664
5.657
5.650
5.643
5.635
4.463
3.382
3.367
3.358
3.344
1.325
X : parts per Million : Proton


tBu
Ph
HO
P=O
tBu
3x
^{13}C NMR (151 MHz, CDCl$_3$)
160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
155.580
146.762
146.685
141.821
141.802
130.791
130.724
129.068
128.388
128.187
127.239
126.300
125.841
125.764
117.827
117.750
59.919
35.015
31.529
31.060
X : parts per Million : Carbon13


tBu
Ph
HO
P=O
tBu
3x
^{31}P NMR (243 MHz, CDCl$_3$)
300.0 200.0 100.0 0 -100.0 -200.0 -300.0
28.823
X : parts per Million : Phosphorus31

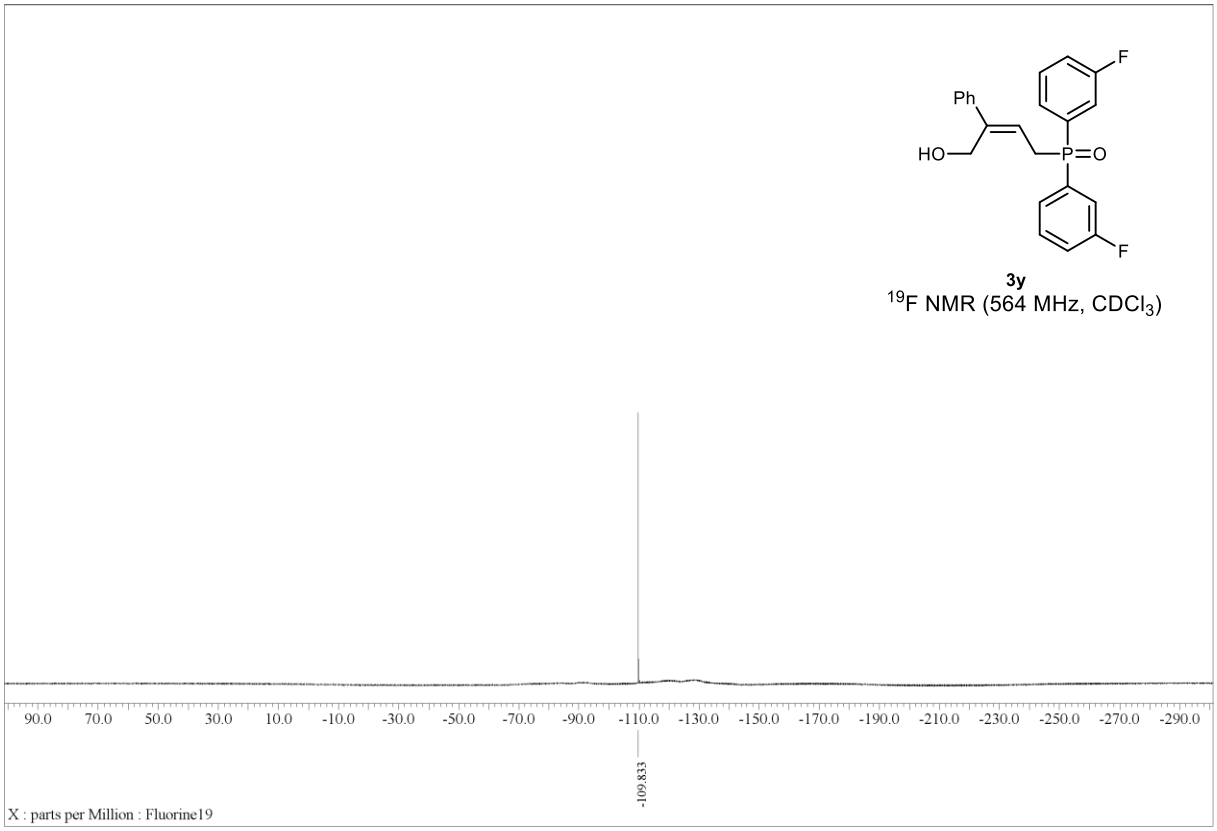

F
Ph
HO
P=O
F
3y
1H NMR (600 MHz, CDCl3)
6.30
4.02
2.02
2.00
0.96
2.00
2.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.579
7.566
7.548
7.536
7.530
7.523
7.517
7.510
7.496
7.478
7.461
7.440
7.426
7.306
7.293
7.282
7.275
7.251
7.238
5.616
5.602
5.594
5.580
4.474
3.425
3.411
3.402
3.387
X : parts per Million : Proton


F
Ph
HO
P=O
F
3y
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
163.565
163.460
161.899
161.794
147.767
147.700
141.275
141.247
134.238
134.200
133.568
133.549
131.136
131.088
131.050
131.002
128.330
127.593
126.549
126.530
126.492
126.473
126.224
119.818
119.675
117.942
117.875
117.789
117.721
116.122
116.046
60.014
30.936
30.495
X : parts per Million : Carbon13



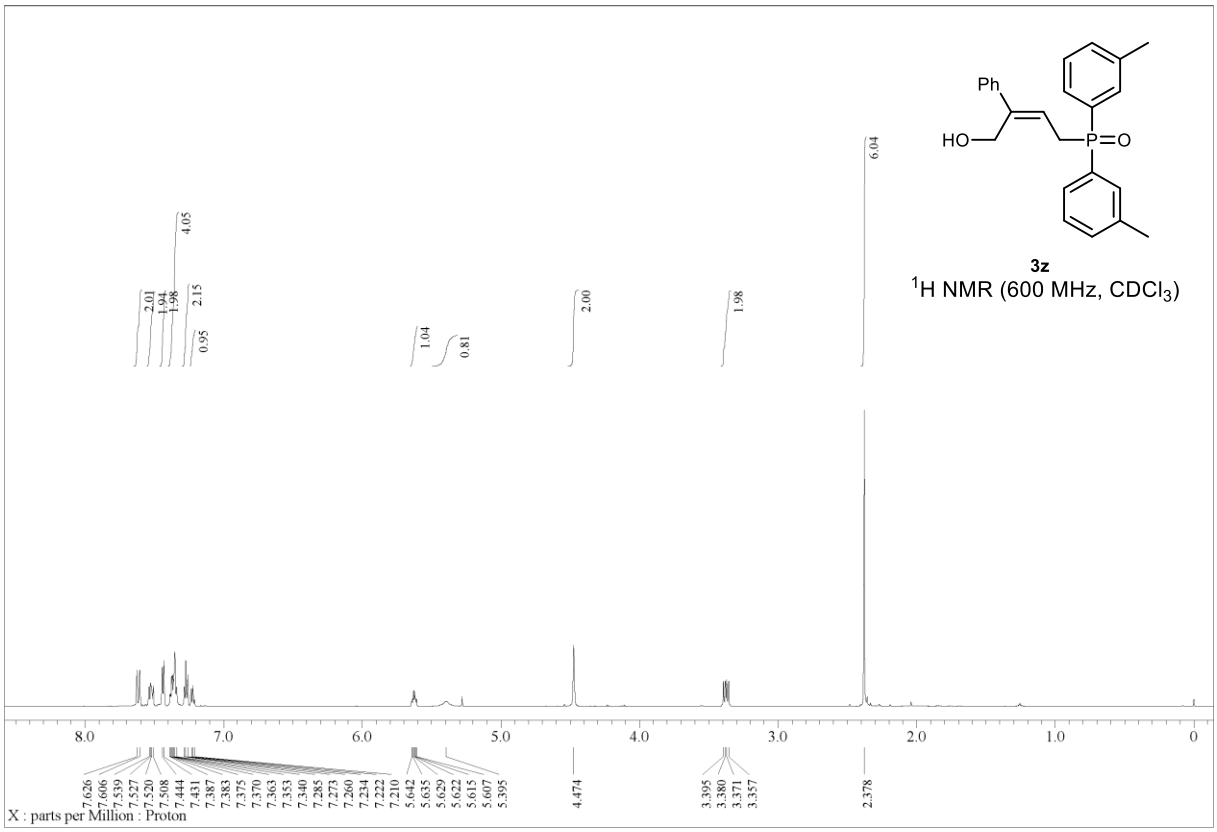
3y

^{31}P NMR (243 MHz, $CDCl_3$)



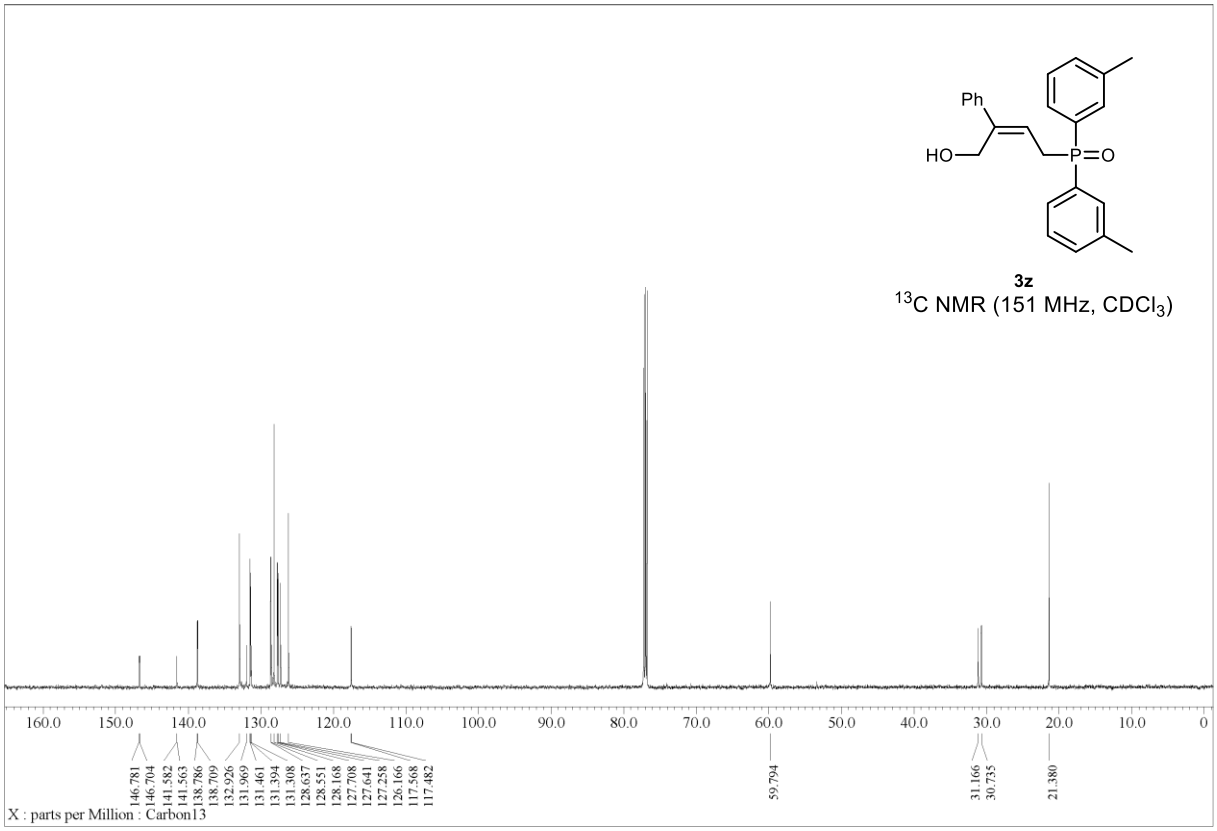
3y

^{19}F NMR (564 MHz, $CDCl_3$)



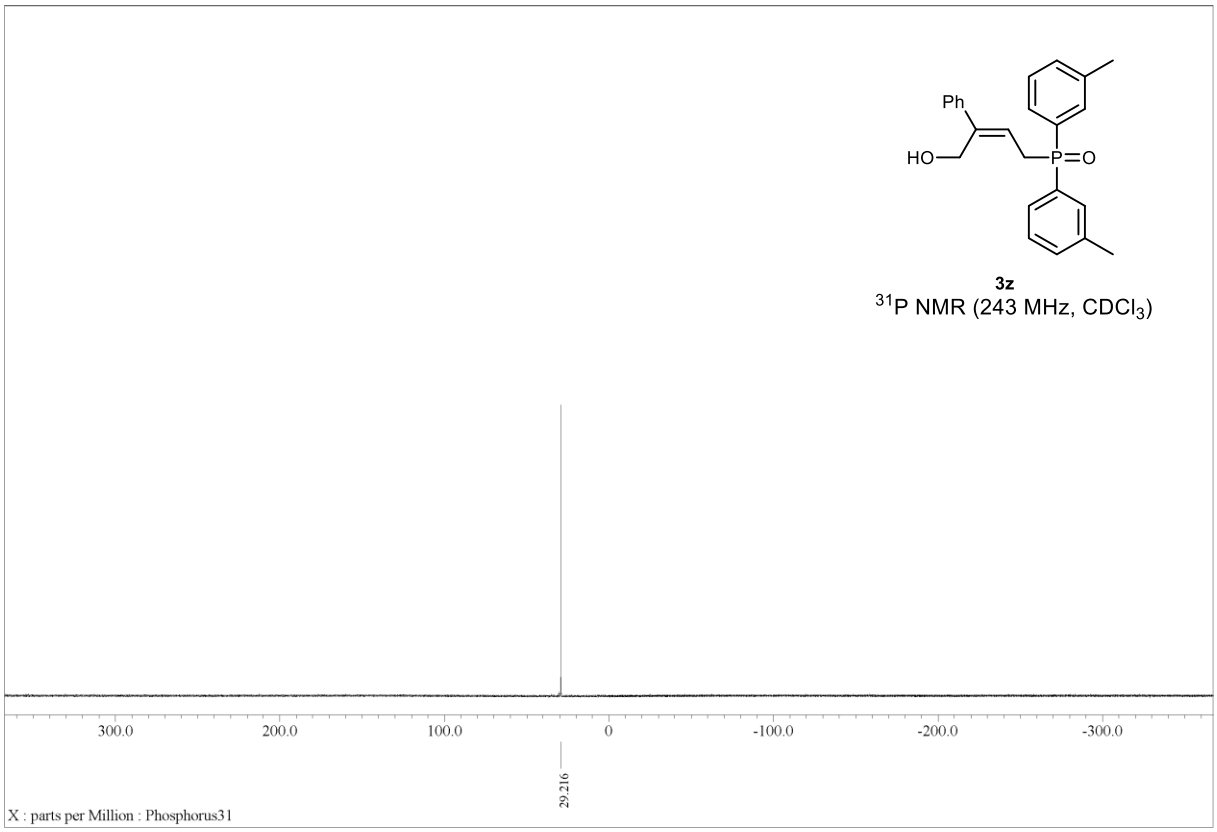
3z

^{1}H NMR (600 MHz, $CDCl_3$)



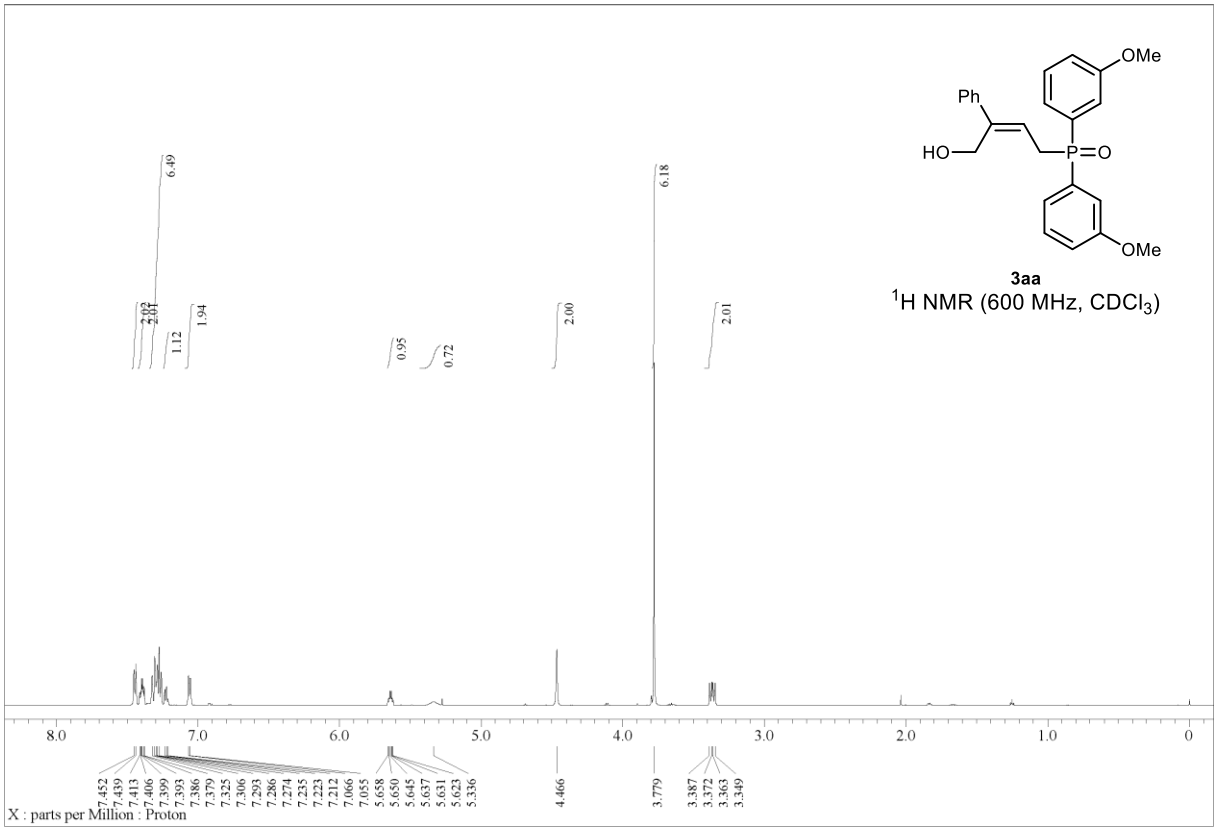
3z

^{13}C NMR (151 MHz, $CDCl_3$)



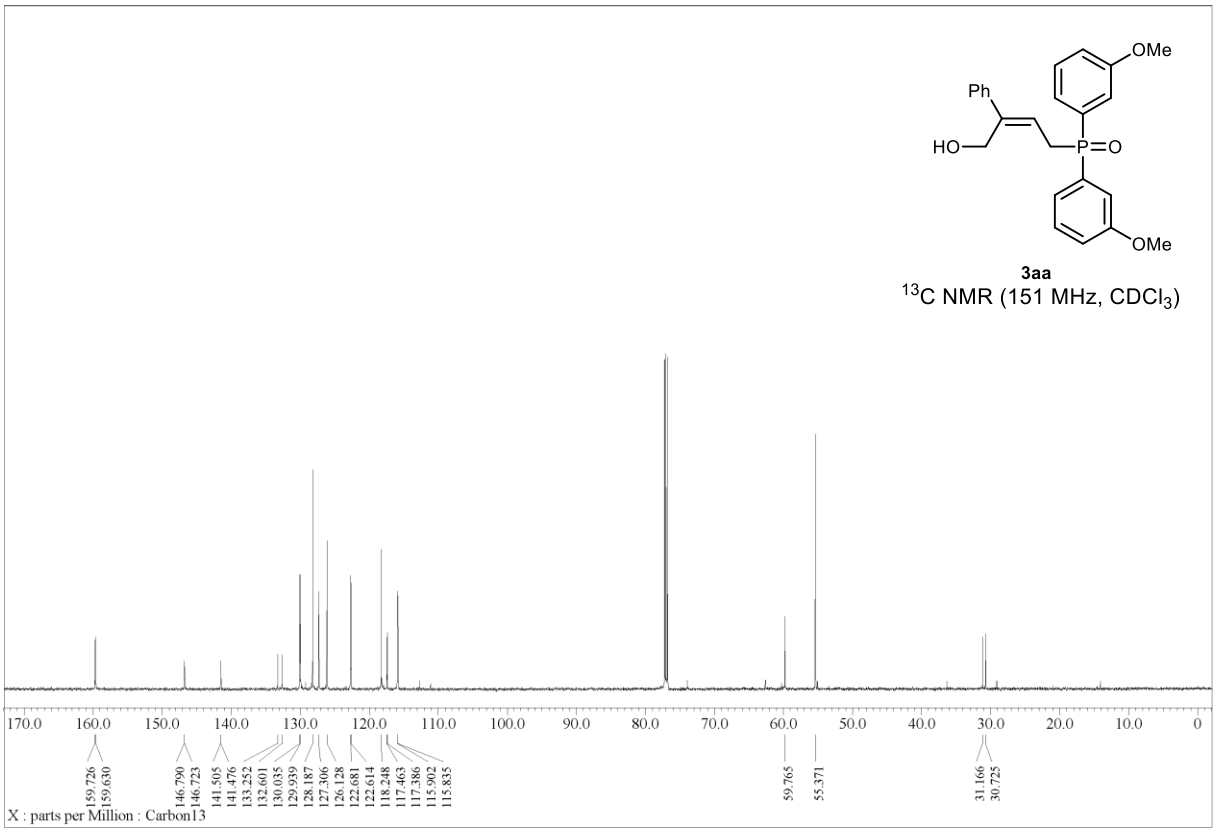
3z

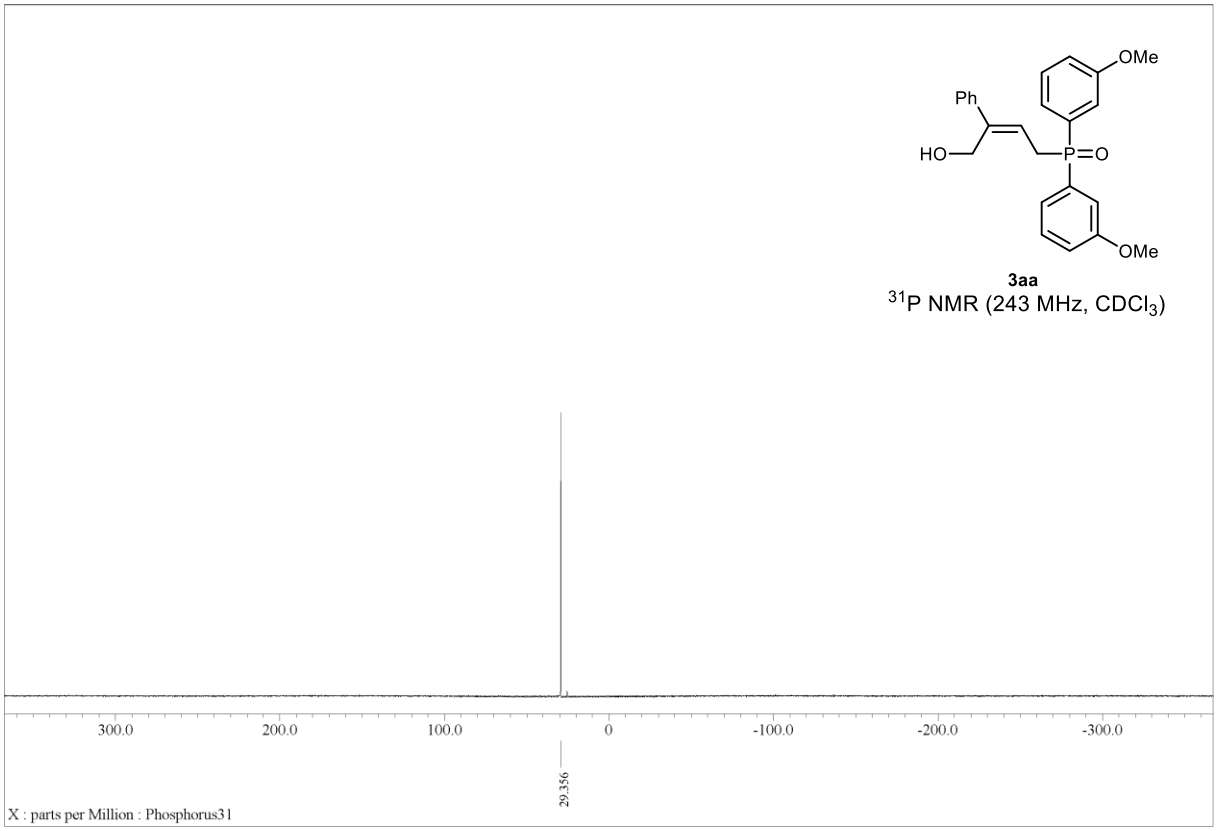
^{31}P NMR (243 MHz, $CDCl_3$)

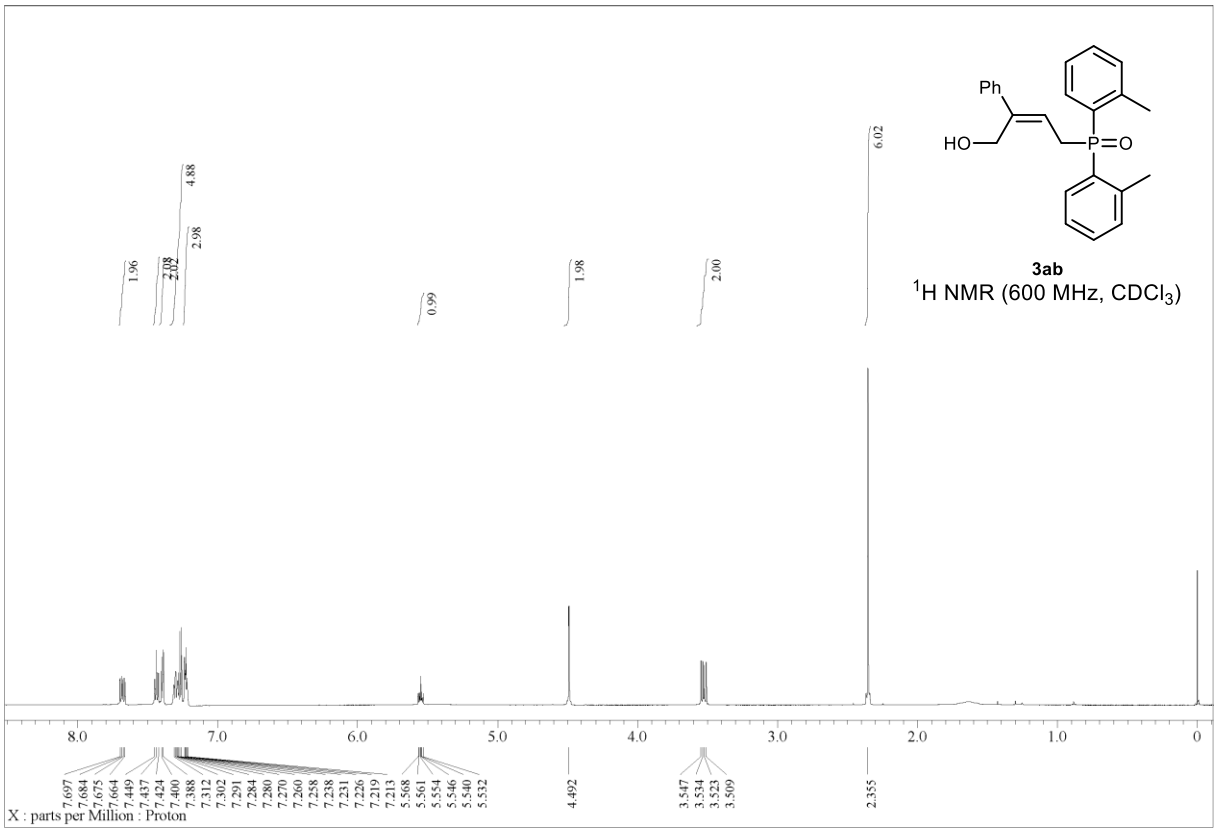


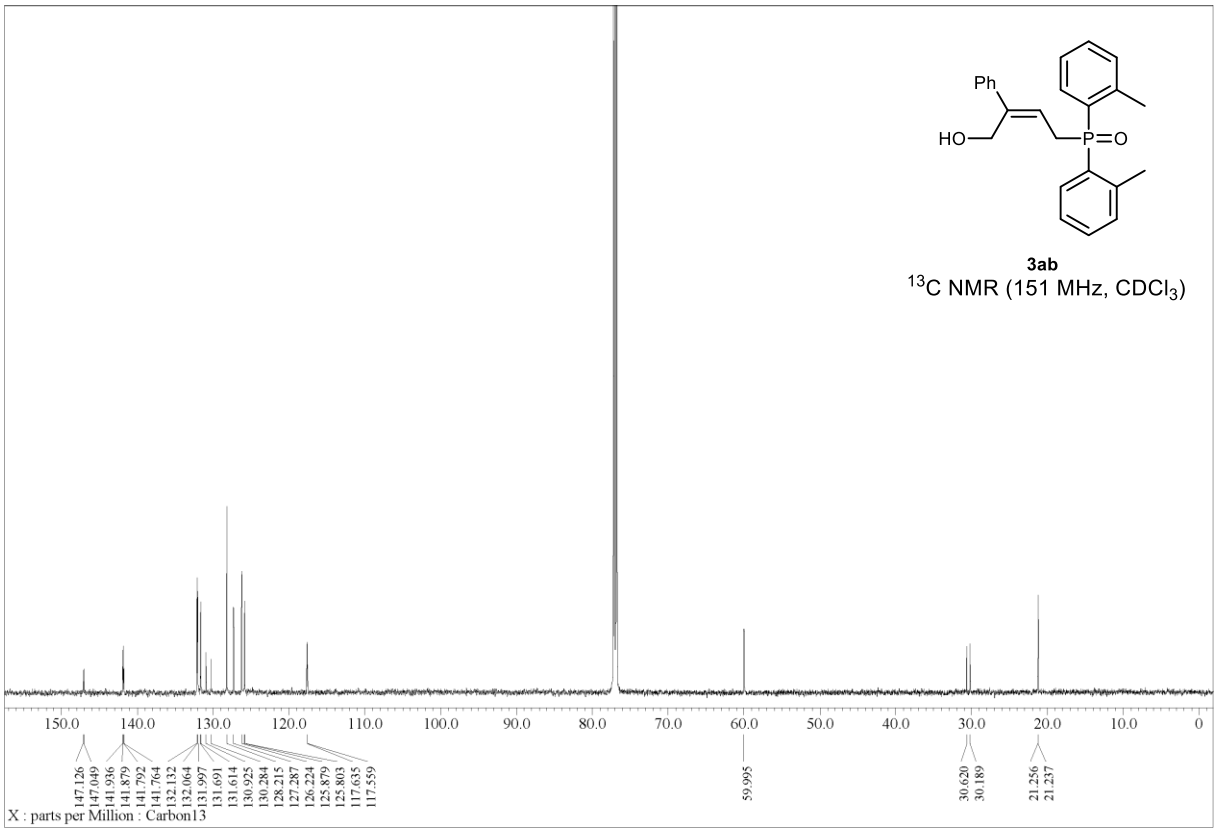
3aa

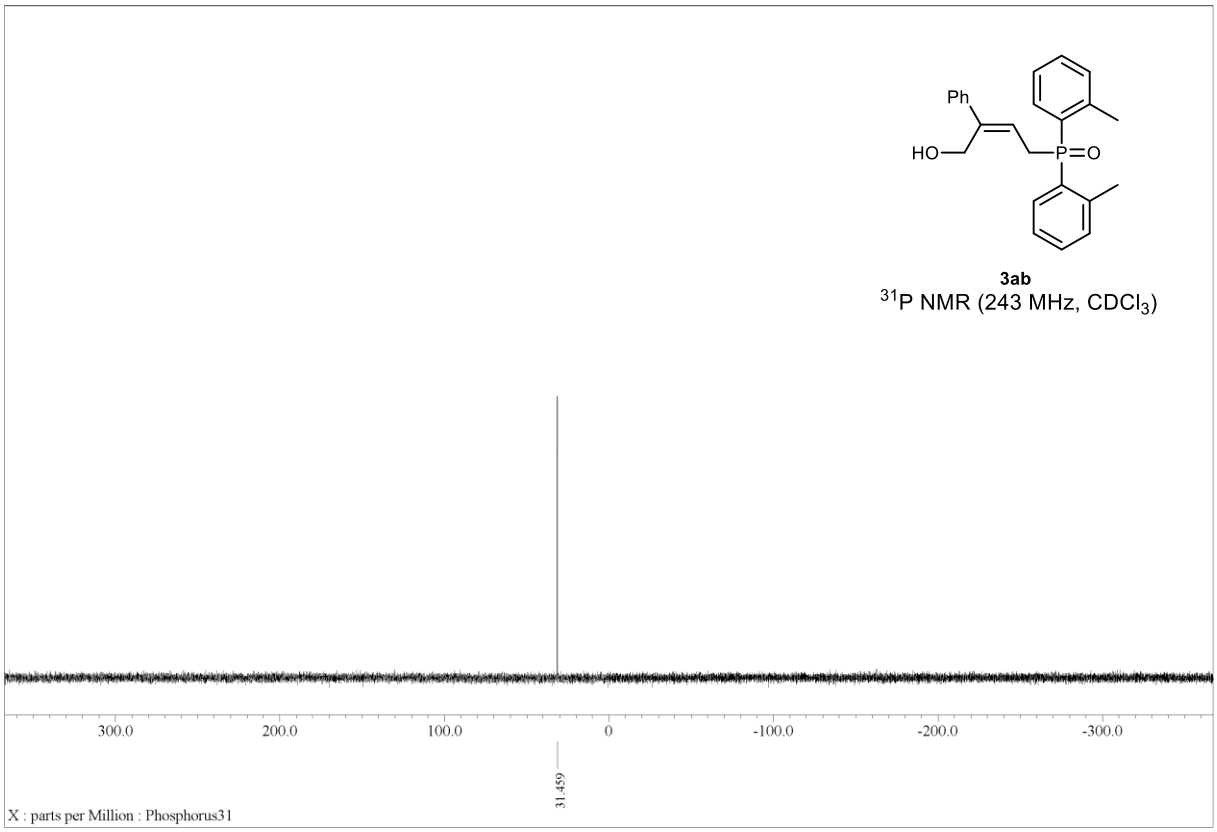
^{1}H NMR (600 MHz, $CDCl_3$)


OMe
Ph
HO
P=O
OMe
3aa
13C NMR (151 MHz, CDCl3)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
159.726
159.630
146.790
146.723
141.505
141.476
133.252
132.601
130.035
129.939
128.187
127.306
126.128
122.681
122.614
118.248
117.463
117.386
115.902
115.835
59.765
55.371
31.166
30.725
X : parts per Million : Carbon13


OMe
Ph
HO
P=O
OMe
3aa
31P NMR (243 MHz, CDCl3)
300.0 200.0 100.0 0 -100.0 -200.0 -300.0
29.356
X : parts per Million : Phosphorus31

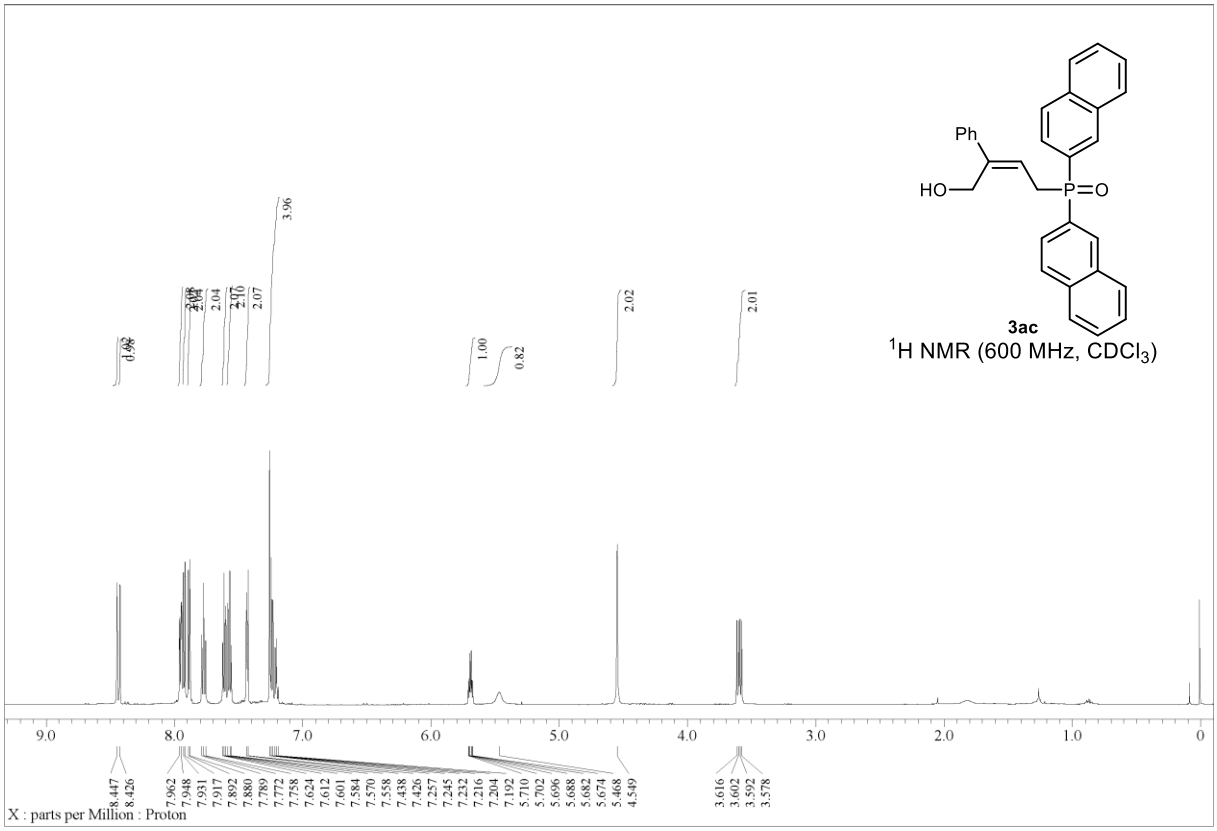

Ph
HO
P=O
3ab
1H NMR (600 MHz, CDCl3)
6.02
4.88
2.98
1.96
2.08
2.02
0.99
1.98
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.697
7.684
7.675
7.664
7.449
7.437
7.424
7.400
7.388
7.312
7.302
7.291
7.284
7.280
7.270
7.260
7.258
7.238
7.231
7.226
7.219
7.213
5.568
5.561
5.554
5.546
5.540
5.532
4.492
3.547
3.534
3.523
3.509
2.355
X : parts per Million : Proton


Ph
HO
P=O
3ab
13C NMR (151 MHz, CDCl3)
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
147.126
147.049
141.936
141.879
141.792
141.764
132.132
132.064
131.997
131.691
131.614
130.925
130.284
128.215
127.287
126.224
125.879
125.803
117.635
117.559
59.995
30.620
30.189
21.256
21.237
X : parts per Million : Carbon13



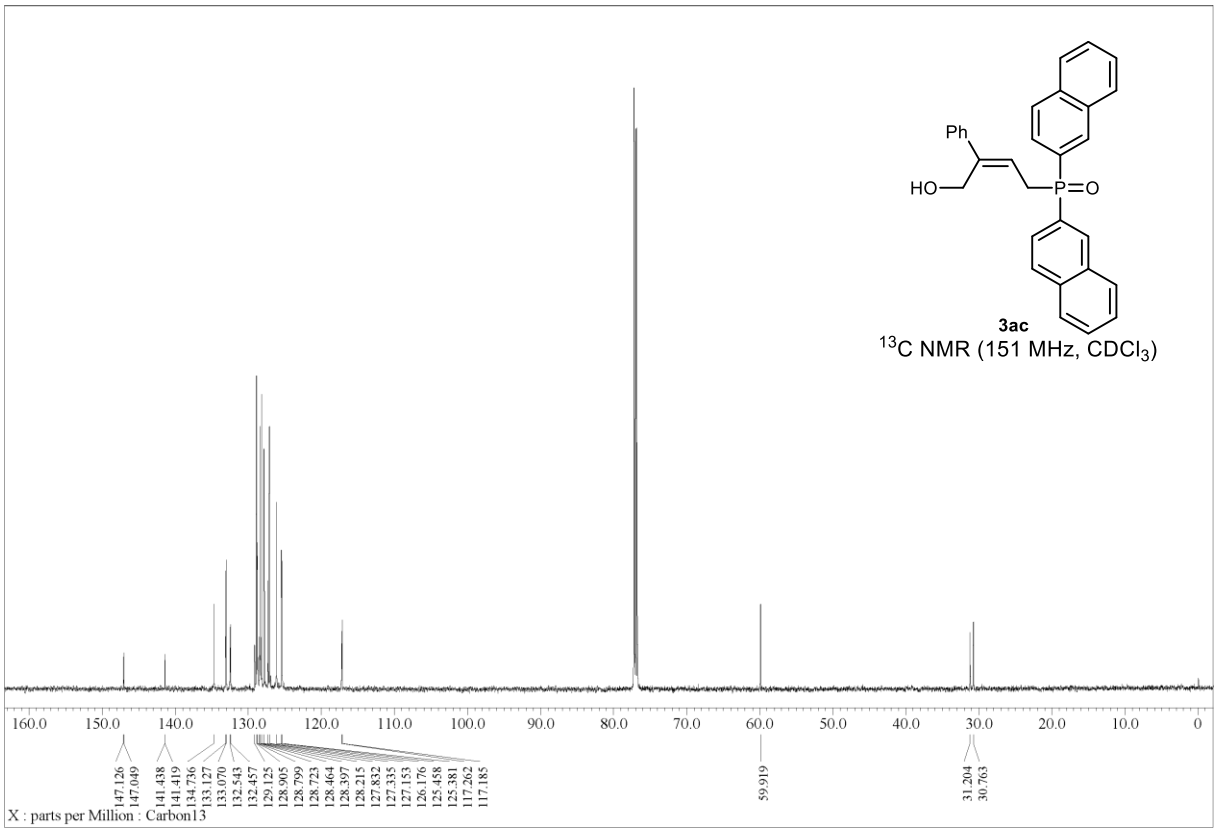
3ab

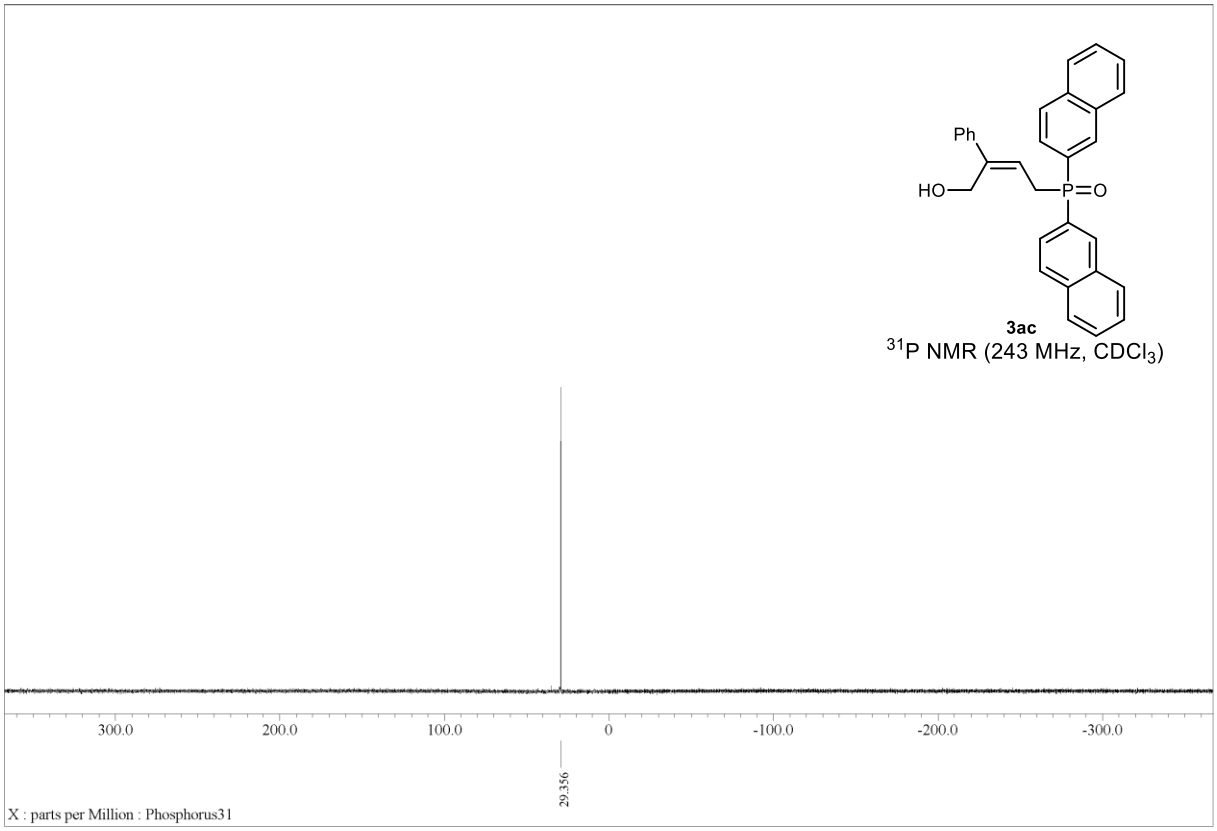
^{31}P NMR (243 MHz, $CDCl_3$)

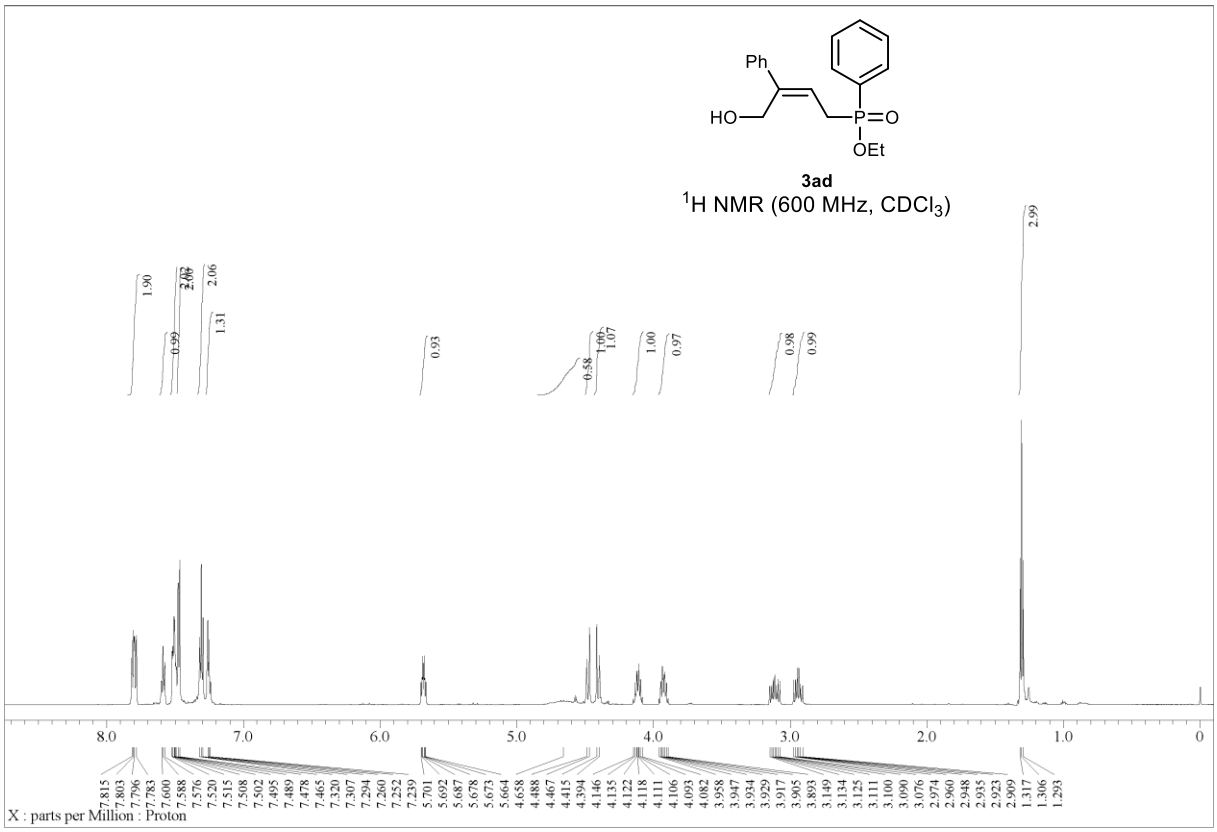


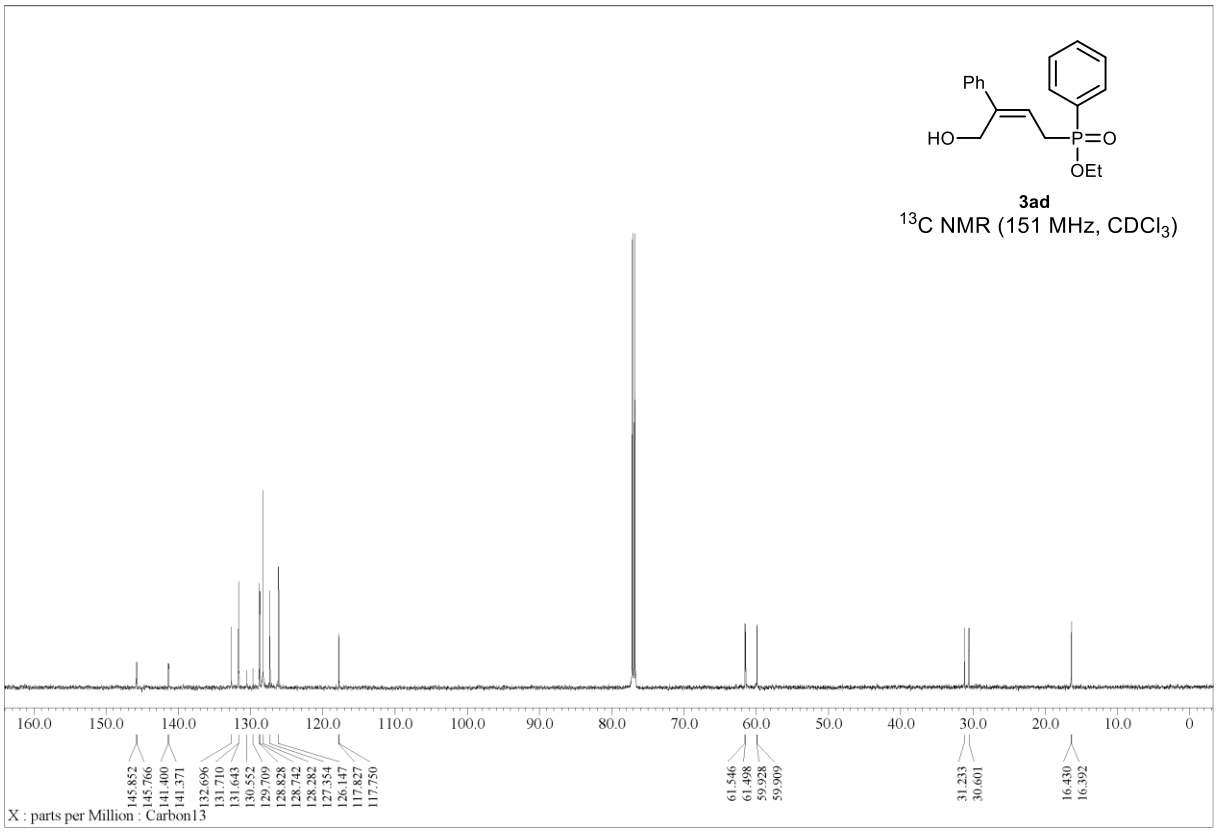
3ac

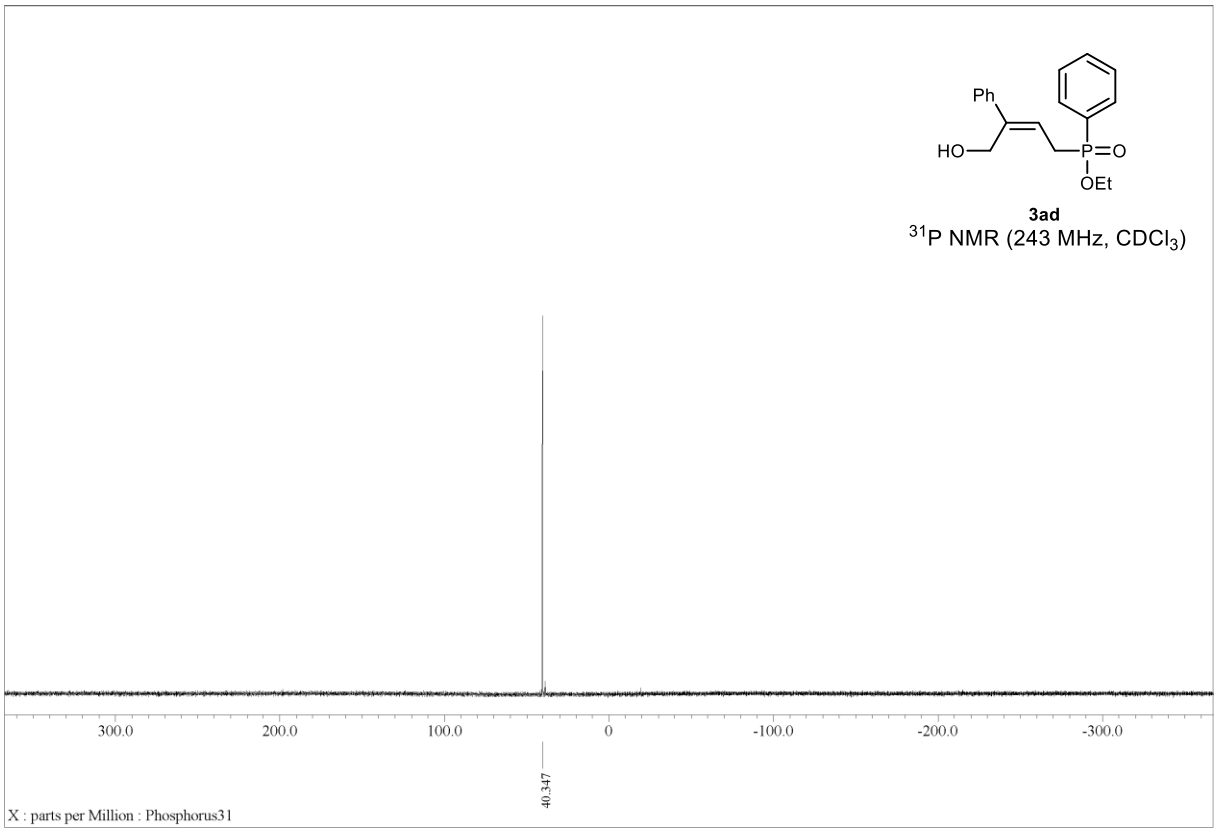
^{1}H NMR (600 MHz, $CDCl_3$)


Ph
HO
P=O
3ac
^{13}C NMR (151 MHz, CDCl$_3$)
160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
147.126
147.049
141.438
141.419
134.736
133.127
133.070
132.543
132.457
129.125
128.905
128.799
128.723
128.464
128.397
128.215
127.832
127.335
127.153
126.176
125.458
125.381
117.262
117.185
59.919
31.204
30.763
X : parts per Million : Carbon13


Ph
HO
P=O
3ac
^{31}P NMR (243 MHz, CDCl$_3$)
300.0 200.0 100.0 0 -100.0 -200.0 -300.0
29.356
X : parts per Million : Phosphorus31

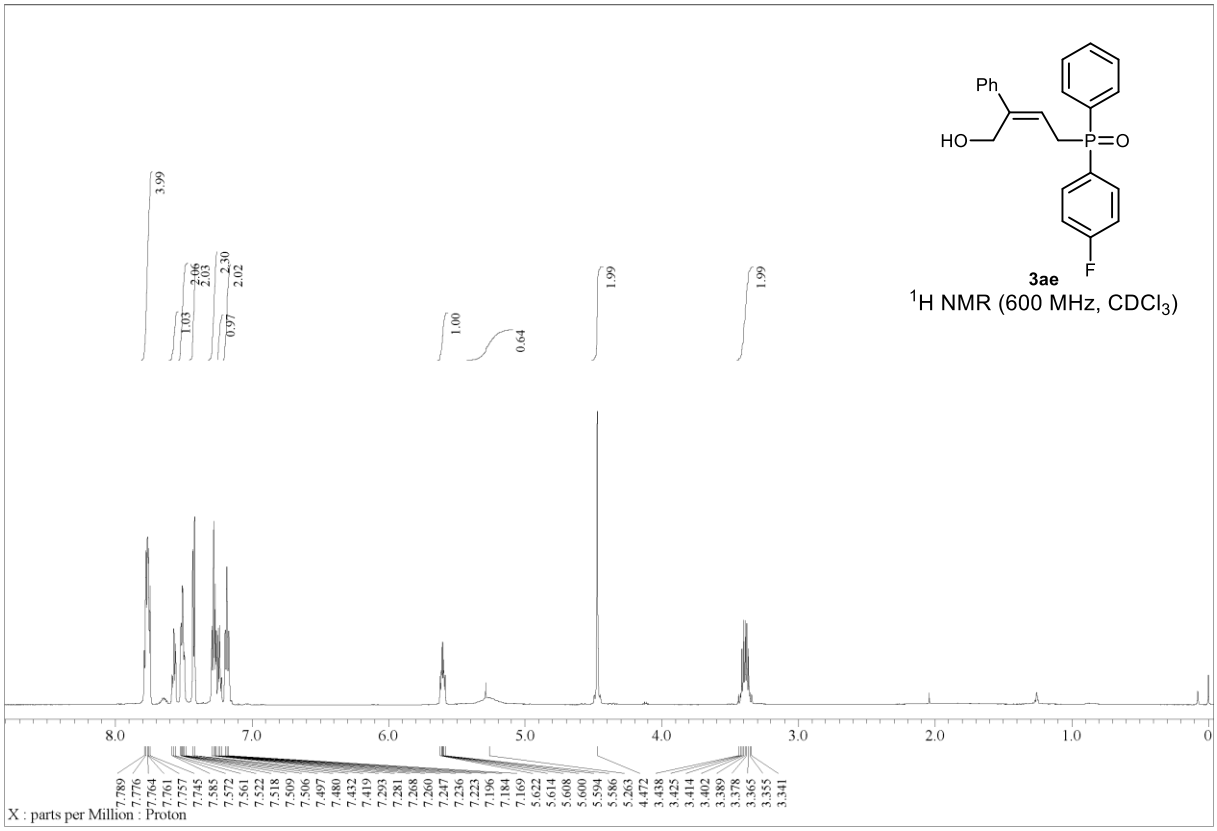

Ph
HO
P=O
OEt
3ad
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


Ph
HO
P=O
OEt
3ad
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



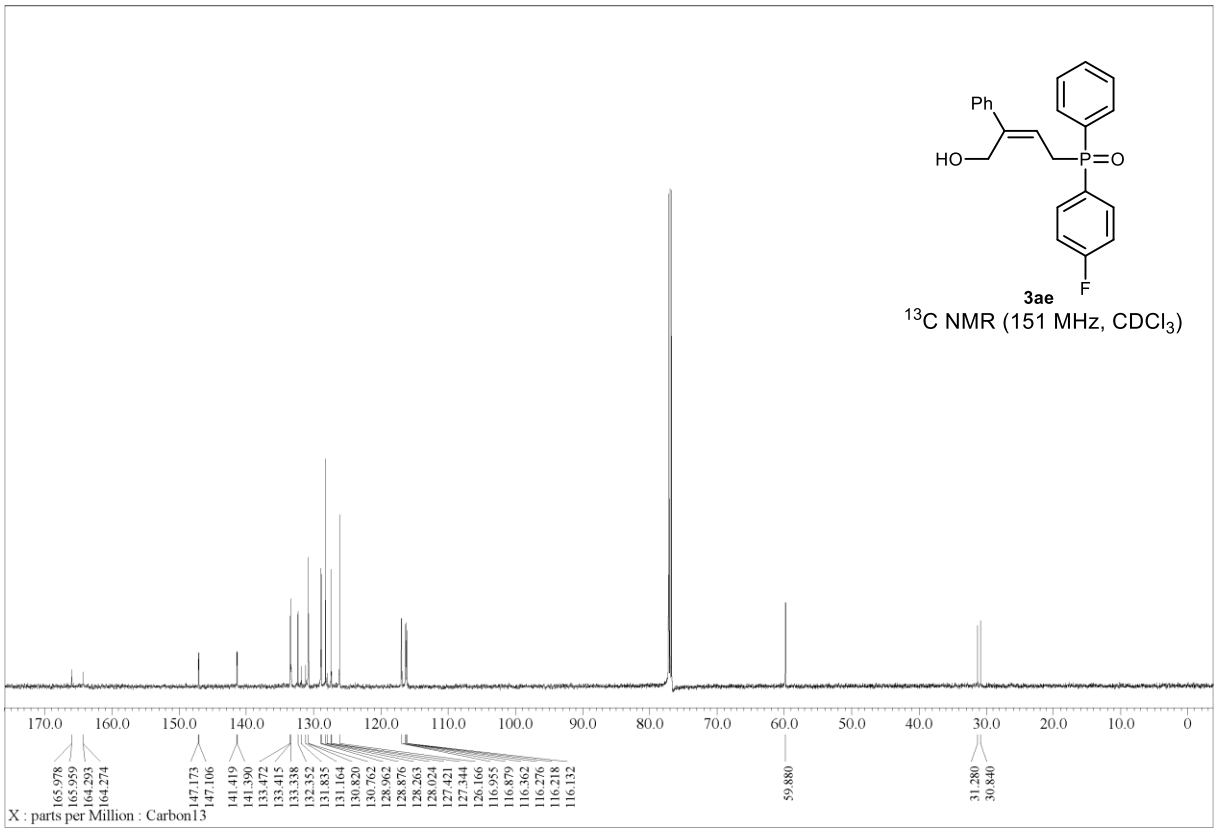
3ad

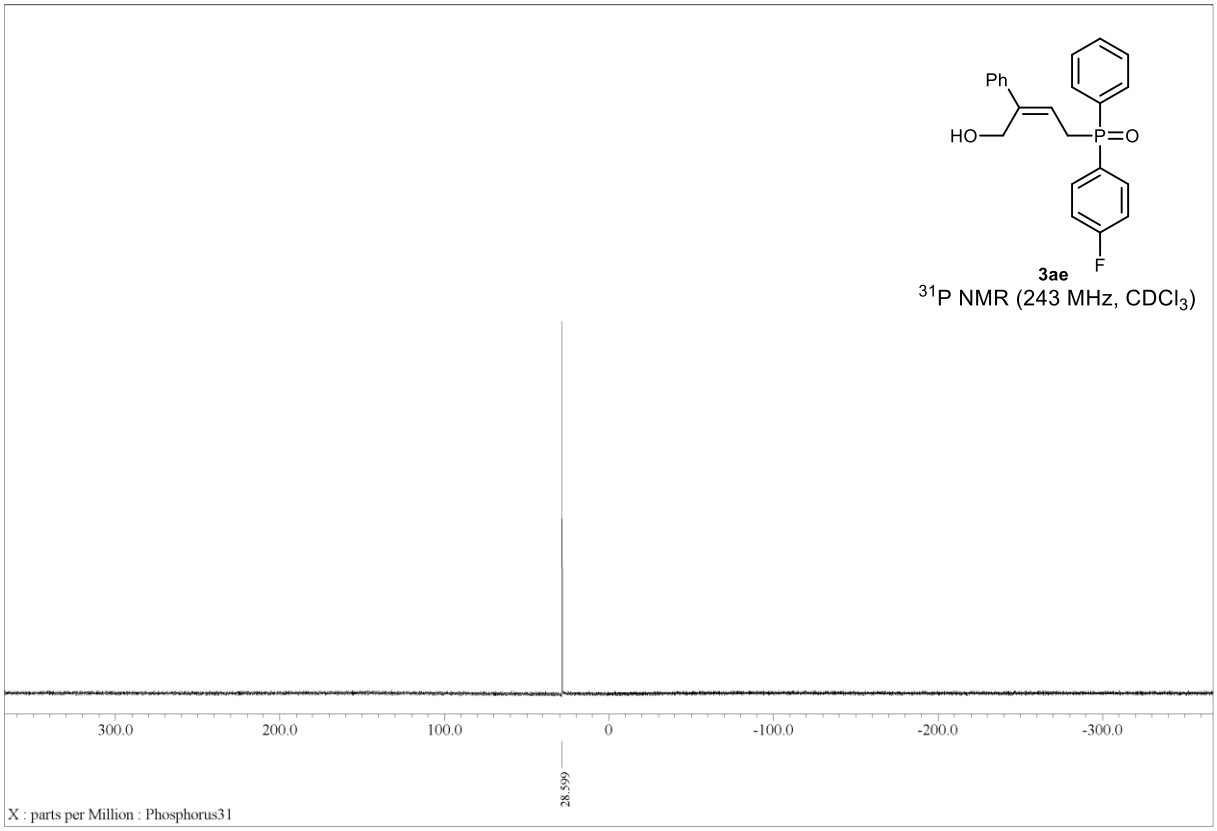
^{31}P NMR (243 MHz, $CDCl_3$)

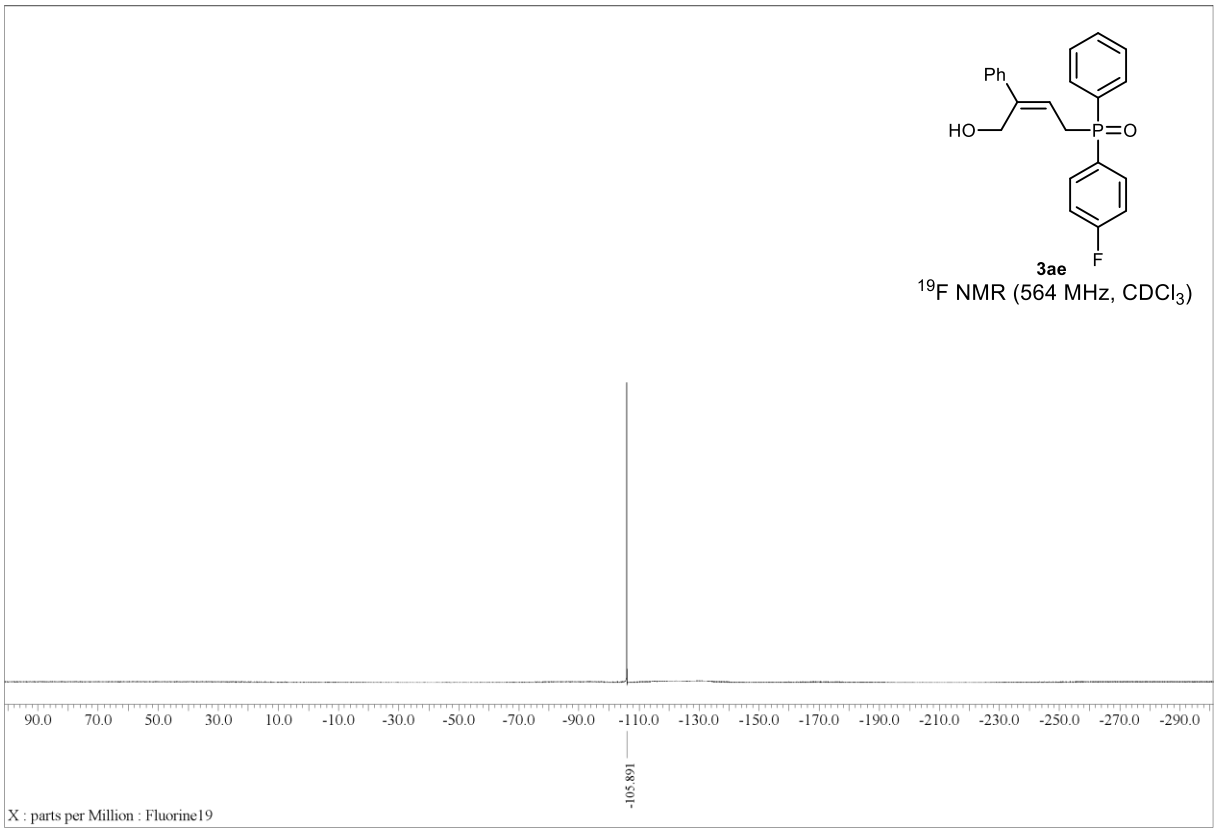


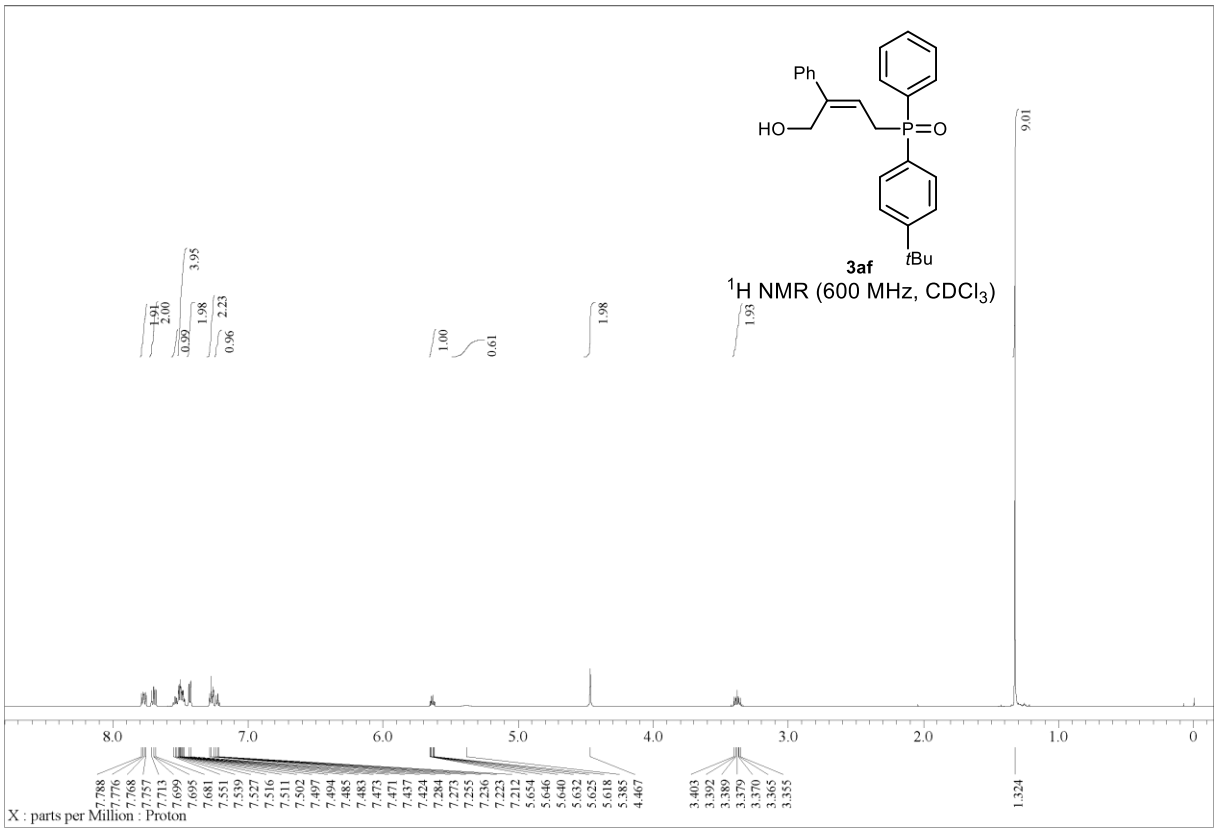
3ae

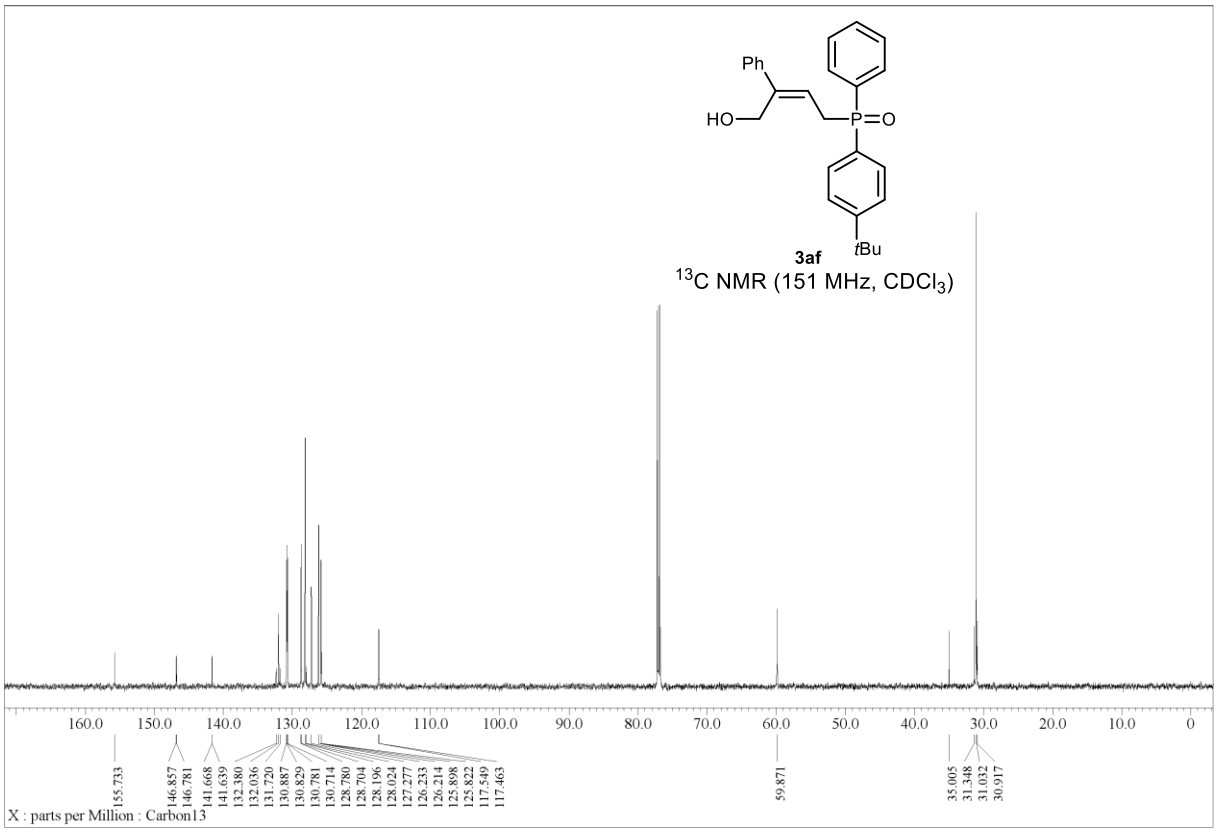
^{1}H NMR (600 MHz, $CDCl_3$)

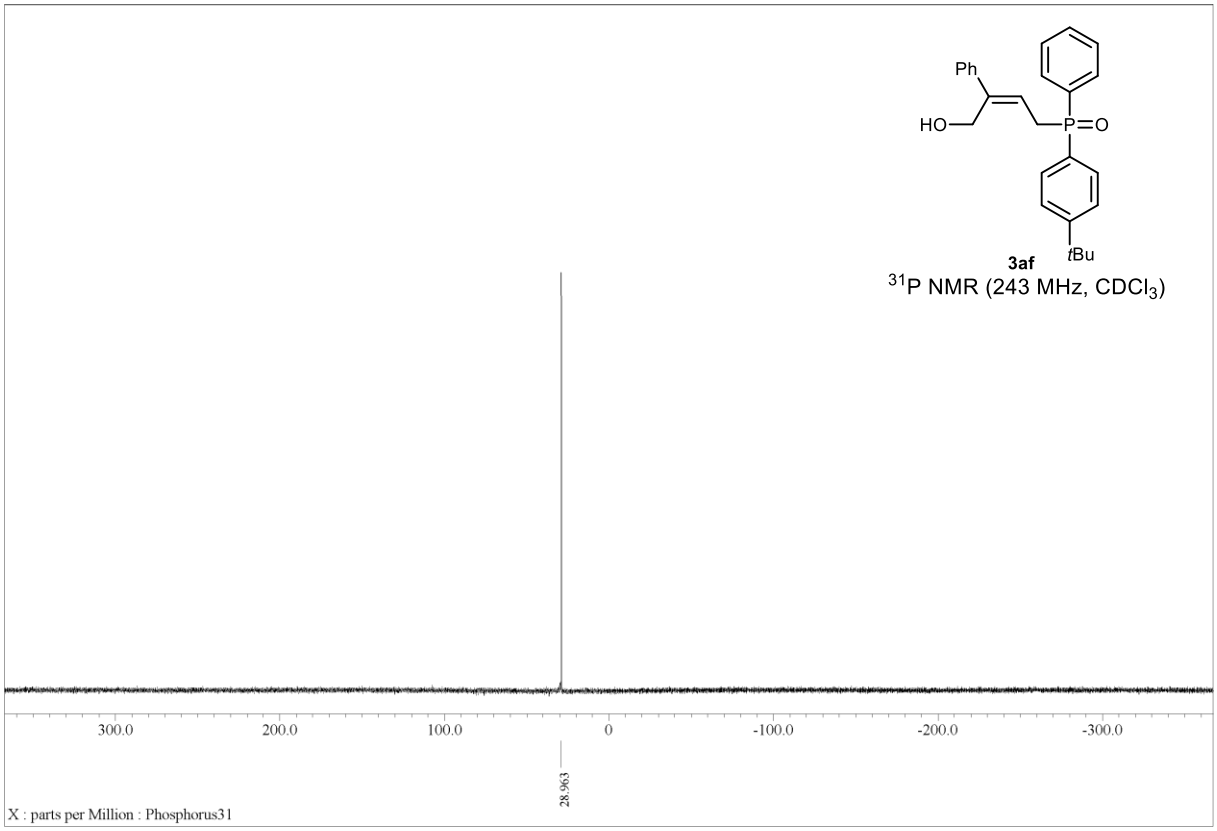

Ph
HO
P=O
F
3ae
^{13}C NMR (151 MHz, CDCl$_3$)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
165.978 165.959 164.293 164.274 147.173 147.106 141.419 141.390 133.472 133.415 133.338 132.352 131.835 131.164 130.820 130.762 128.962 128.876 128.263 128.024 127.421 127.344 126.166 116.955 116.879 116.362 116.276 116.218 116.132 59.880 31.280 30.840
X : parts per Million : Carbon13

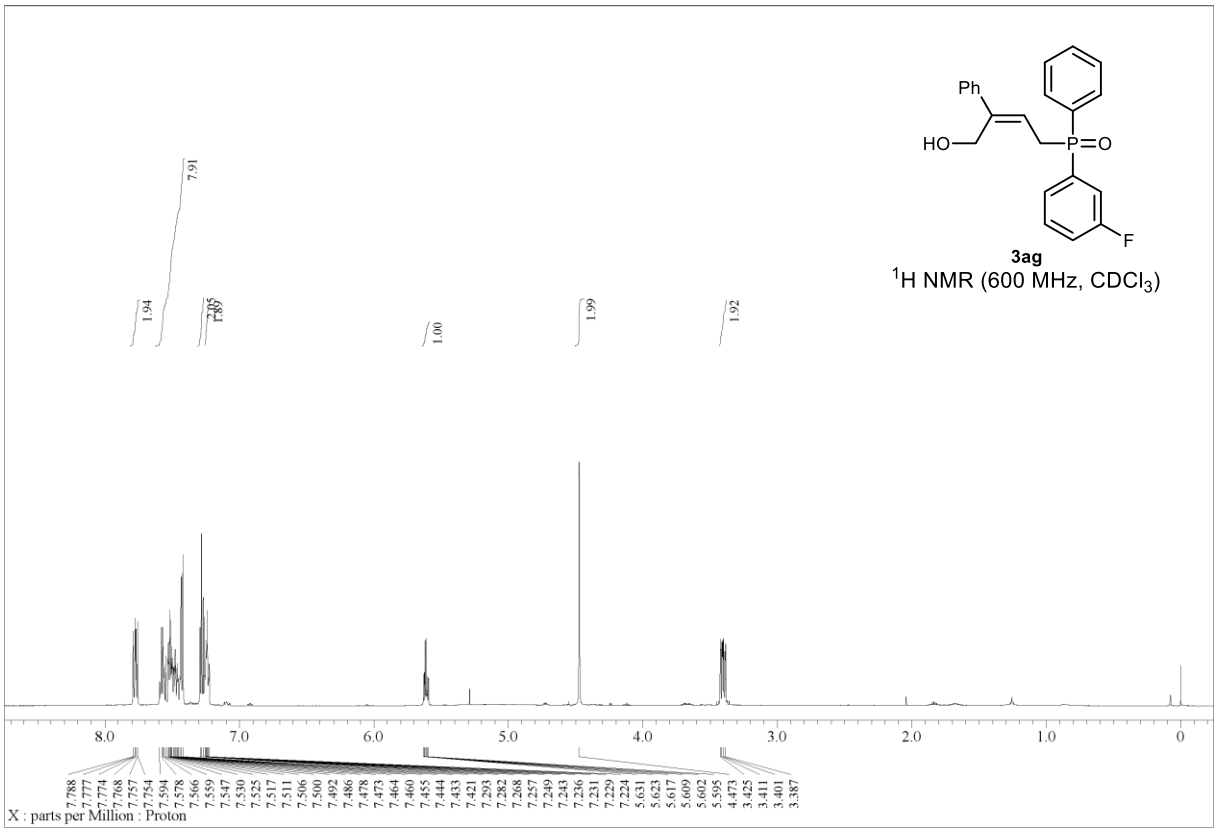

Ph
HO
P=O
F
3ae
^{31}P NMR (243 MHz, CDCl$_3$)
300.0 200.0 100.0 0 -100.0 -200.0 -300.0
28.599
X : parts per Million : Phosphorus31

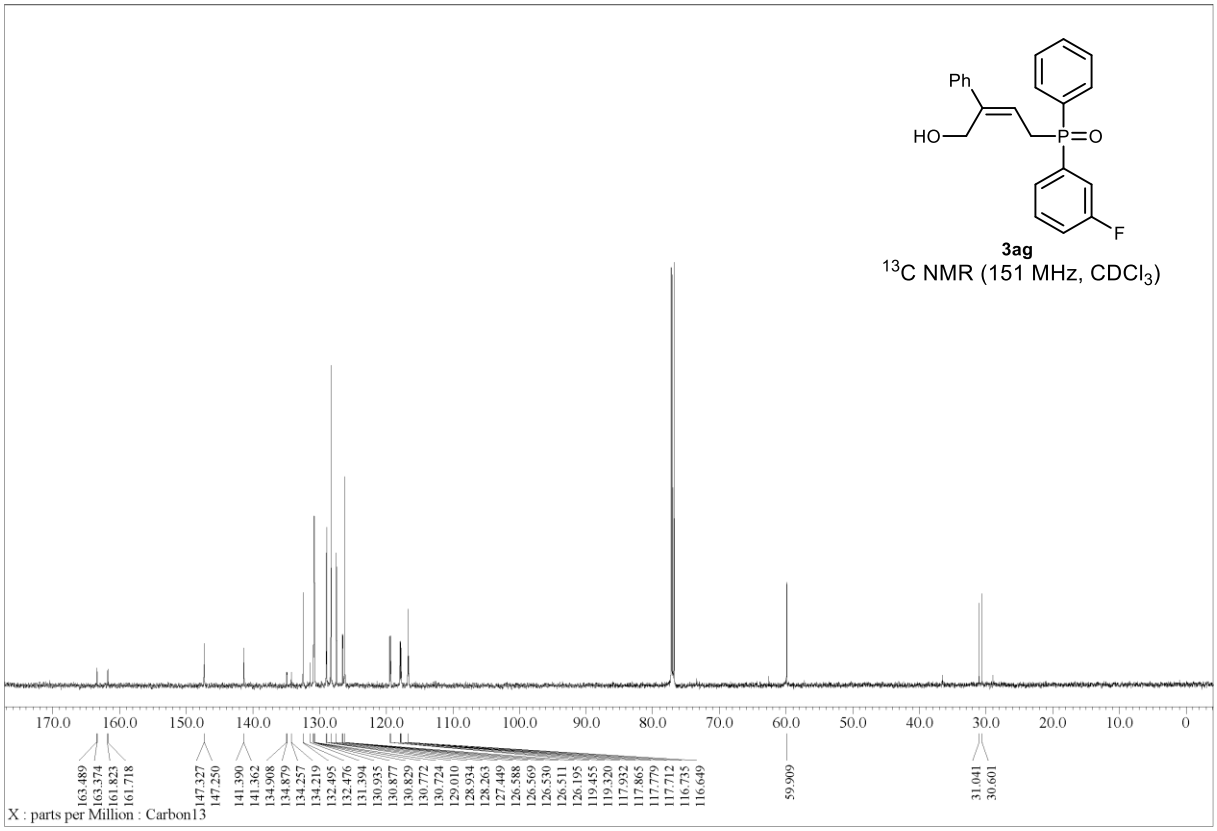

Ph
HO
P=O
F
3ae
19F NMR (564 MHz, CDCl3)
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
-105.891
X : parts per Million : Fluorine19

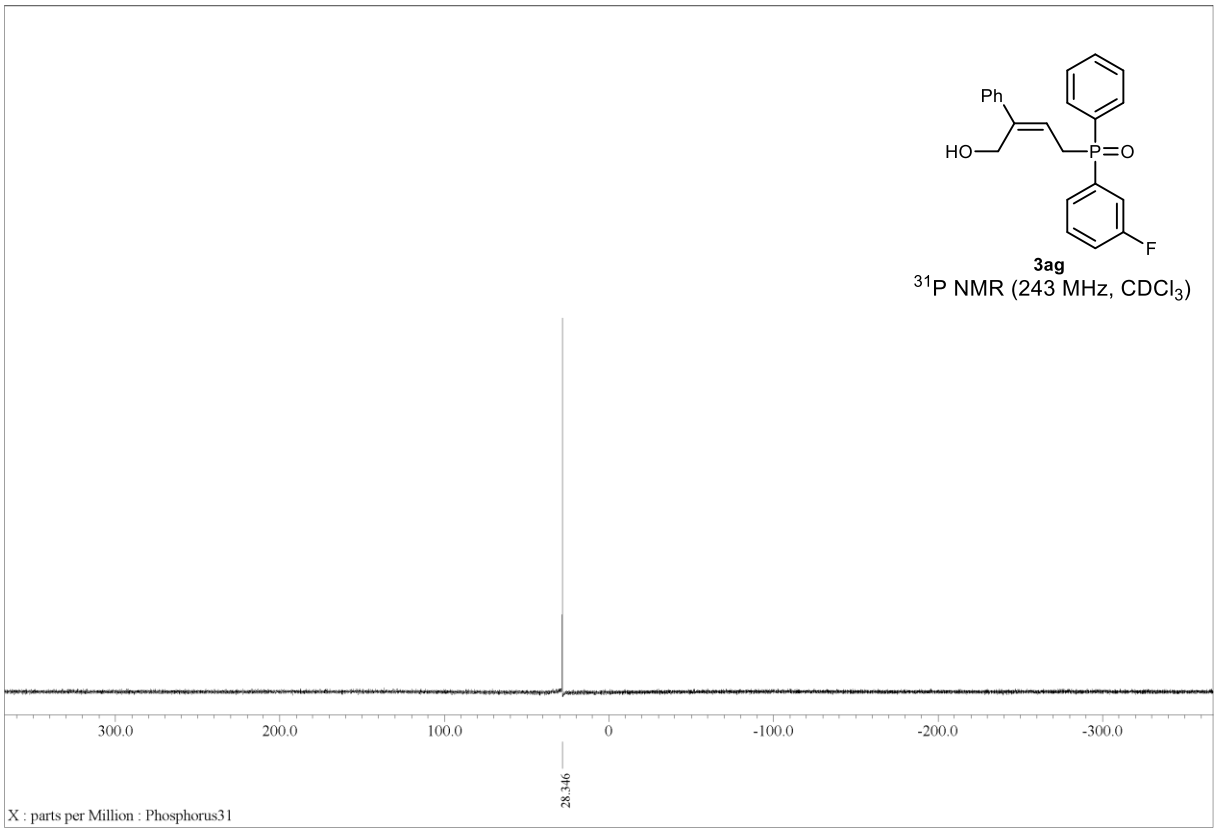

Ph
HO
P=O
tBu
3af
1H NMR (600 MHz, CDCl3)
3.95
1.91
2.00
0.99
1.98
2.23
0.96
1.00
0.61
1.98
1.93
9.01
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.788 7.776 7.768 7.757 7.713 7.699 7.695 7.681 7.551 7.539 7.527 7.516 7.511 7.502 7.497 7.494 7.485 7.483 7.473 7.471 7.437 7.424 7.284 7.273 7.255 7.236 7.223 7.212 5.654 5.646 5.640 5.632 5.625 5.618 5.385 4.467
3.403 3.392 3.389 3.379 3.370 3.365 3.355
1.324
X : parts per Million : Proton


Ph
HO
P=O
tBu
3af
^{13}C NMR (151 MHz, CDCl$_3$)
160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
155.733
146.857
146.781
141.668
141.639
132.380
132.036
131.720
130.887
130.829
130.781
130.714
128.780
128.704
128.196
128.024
127.277
126.233
126.214
125.898
125.822
117.549
117.463
59.871
35.005
31.348
31.032
30.917
X : parts per Million : Carbon13


Ph
HO
P=O
tBu
3af
^{31}P NMR (243 MHz, CDCl$_3$)
300.0 200.0 100.0 0 -100.0 -200.0 -300.0
28.963
X : parts per Million : Phosphorus31

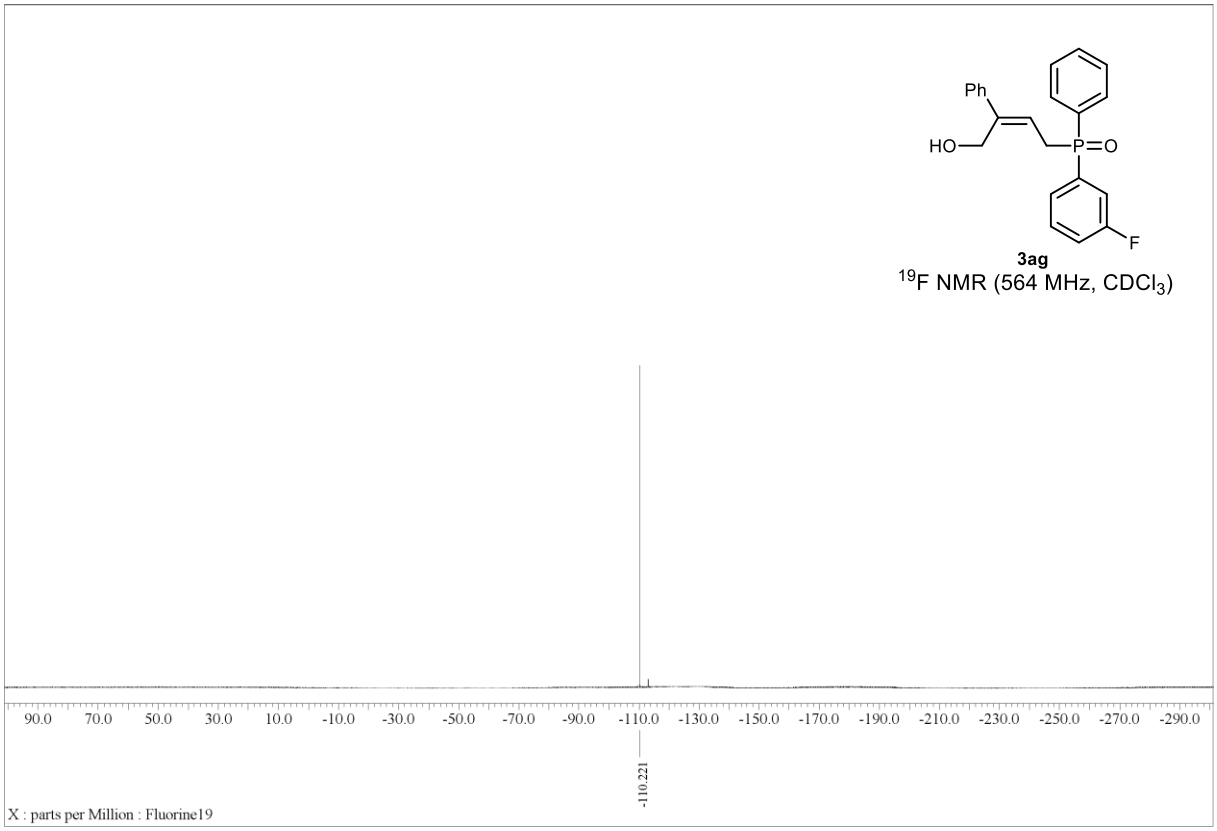

Ph
HO
P=O
F
3ag
1H NMR (600 MHz, CDCl3)
7.91
1.94
1.00
1.99
1.92
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


Ph
HO
P=O
F
3ag
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
59.909
31.041
30.601
X : parts per Million : Carbon13



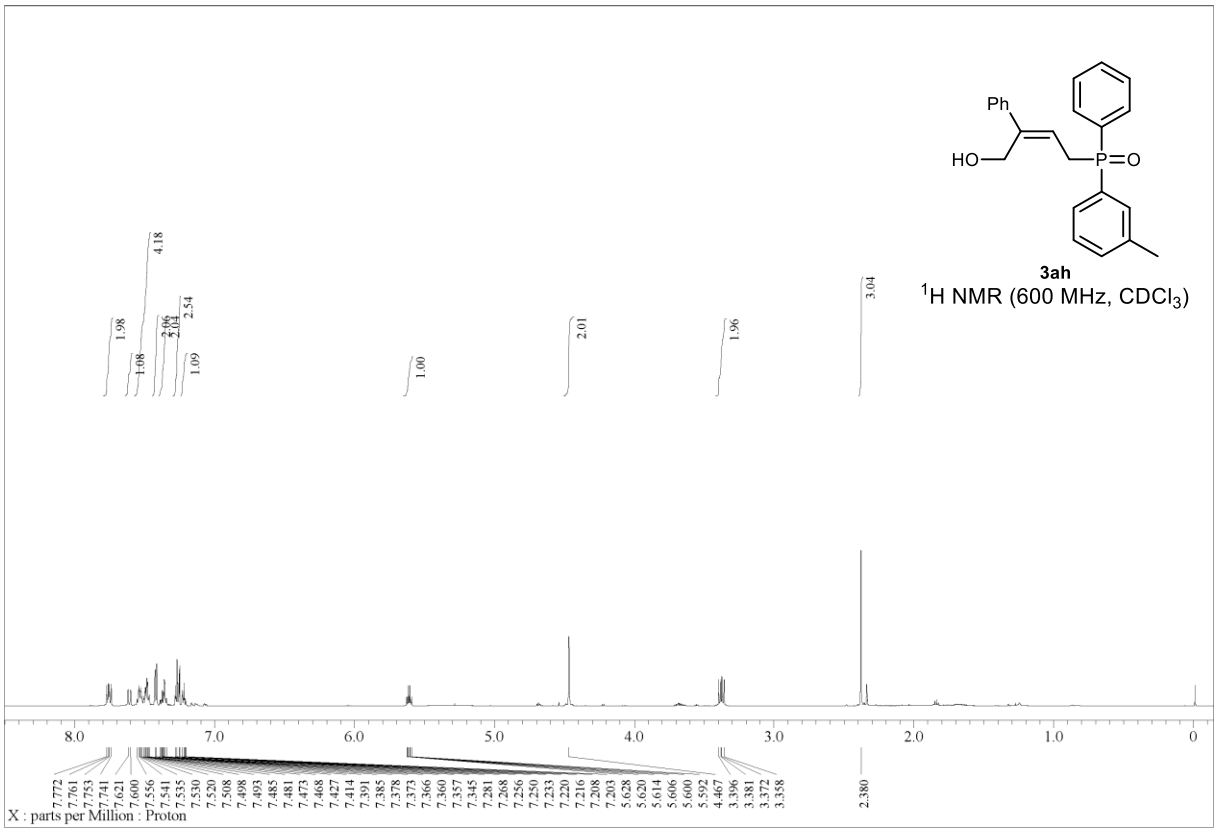
3ag

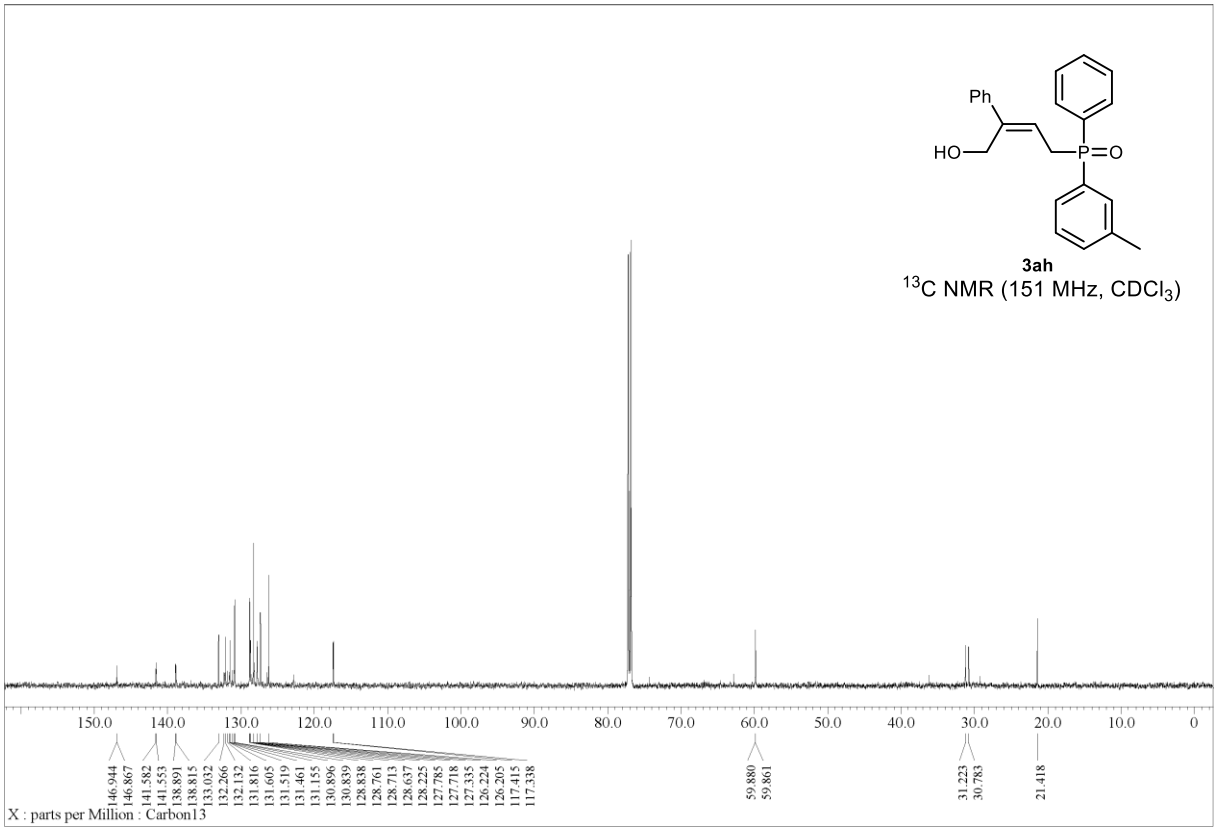
^{31}P NMR (243 MHz, $CDCl_3$)

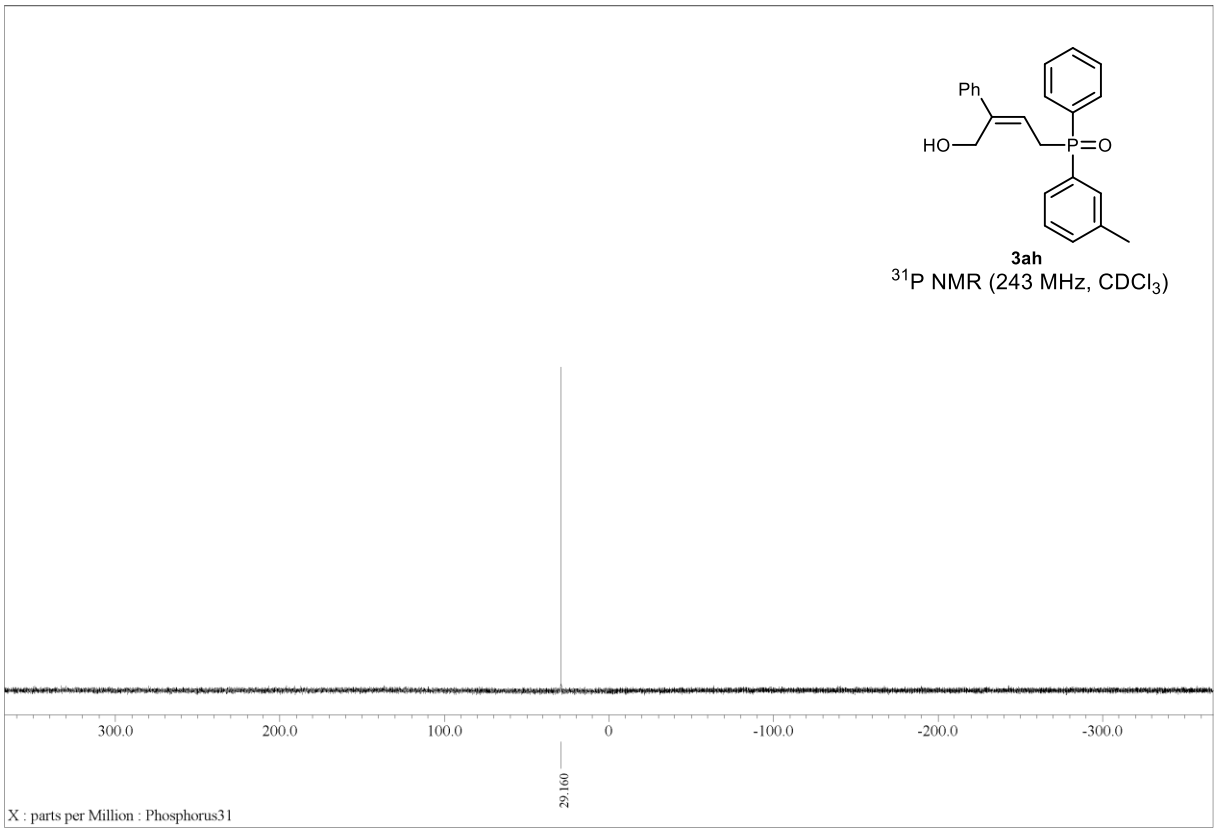


3ag

^{19}F NMR (564 MHz, $CDCl_3$)

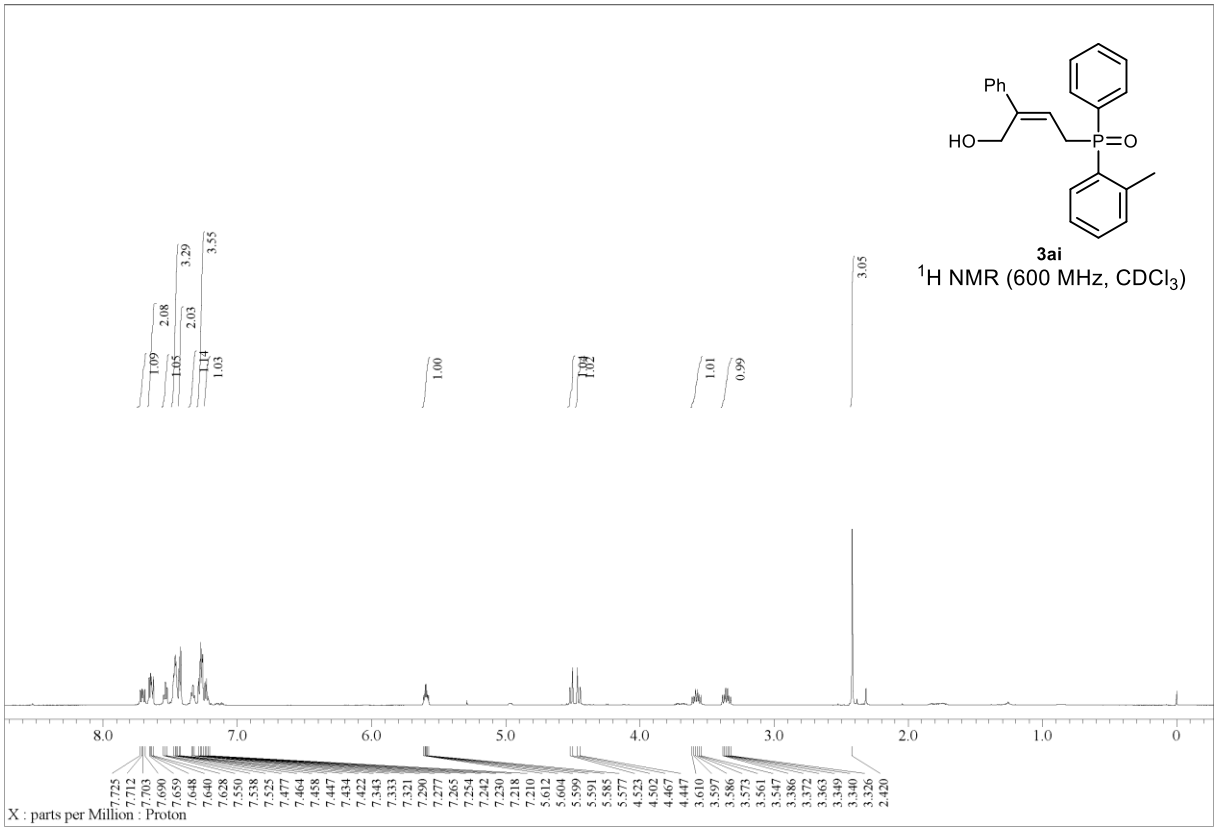

Ph
HO
P=O
3ah
1H NMR (600 MHz, CDCl3)
4.18
3.04
2.54
2.06
2.04
1.98
1.08
1.09
1.00
2.01
1.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.380
X : parts per Million : Proton


Ph
HO
P=O
3ah
13C NMR (151 MHz, CDCl3)
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
59.880
59.861
31.223
30.783
21.418
X : parts per Million : Carbon13



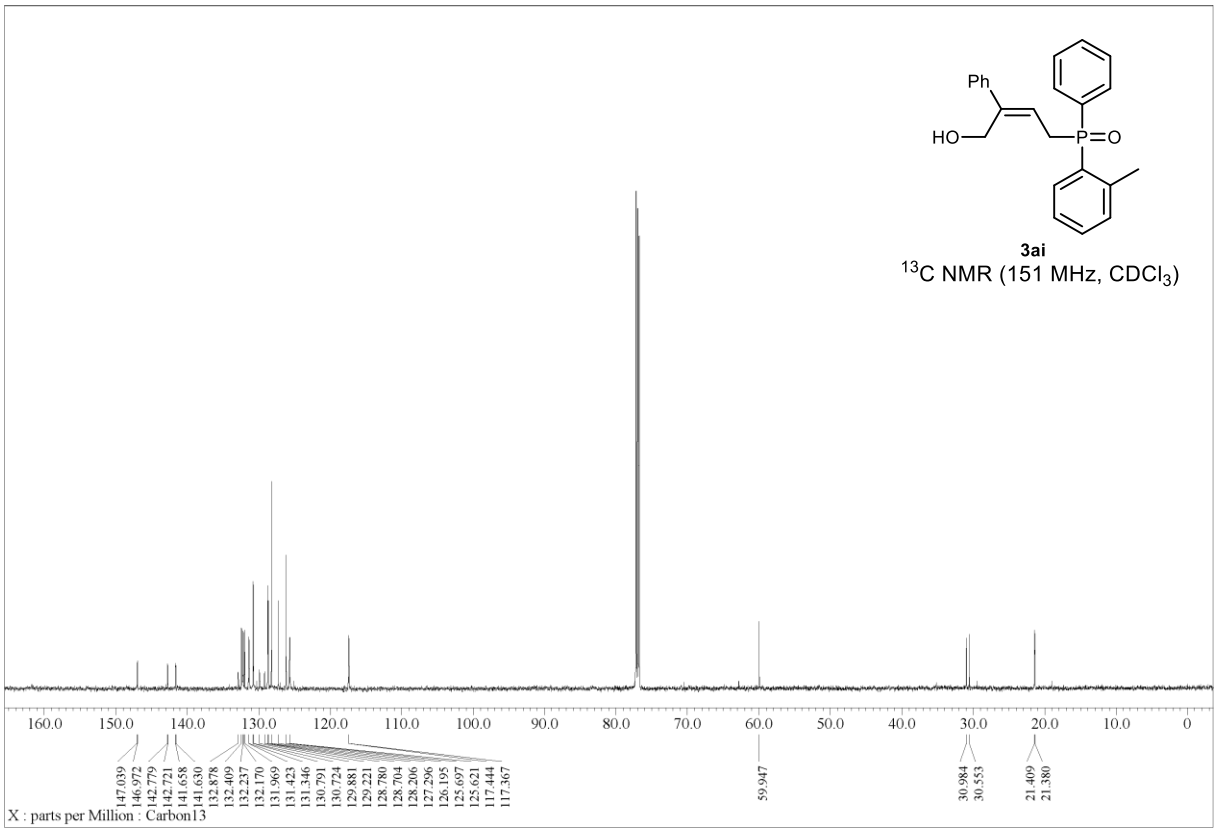
3ah

^{31}P NMR (243 MHz, $CDCl_3$)



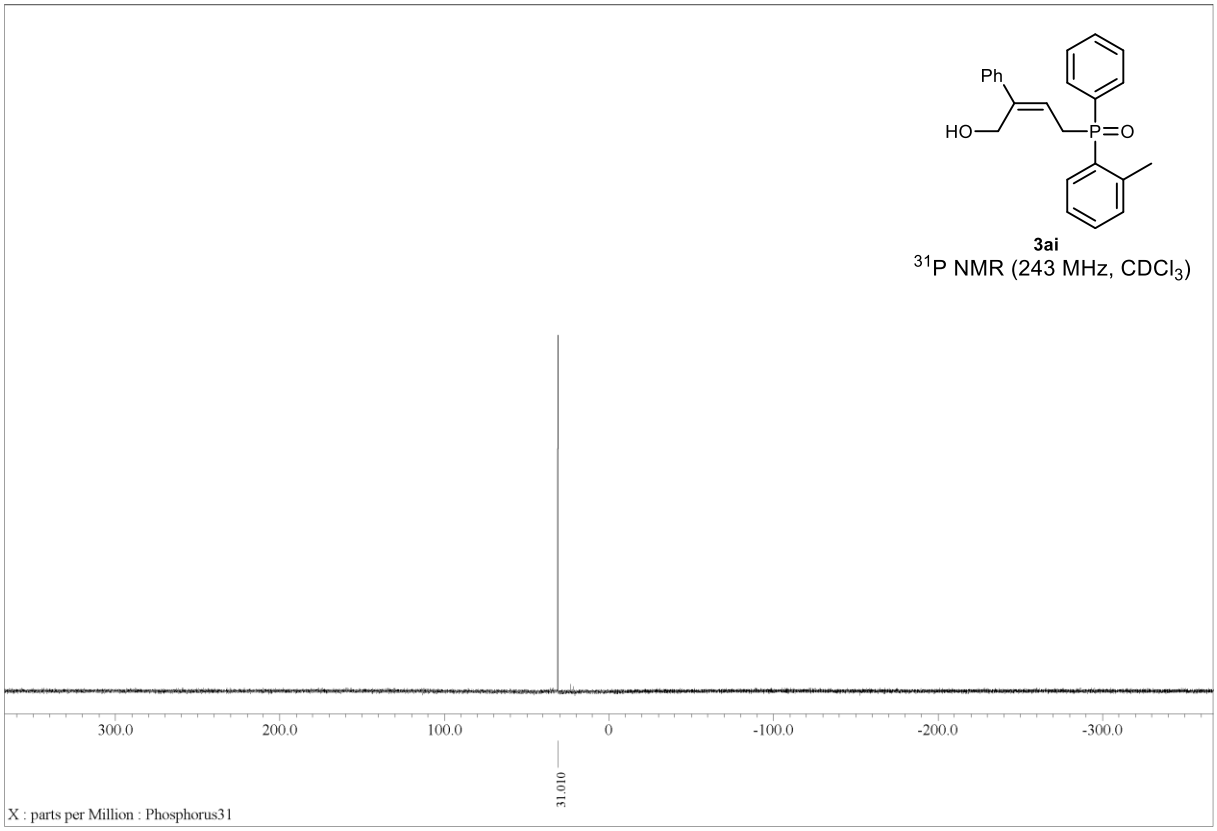
3ai

^{1}H NMR (600 MHz, $CDCl_3$)



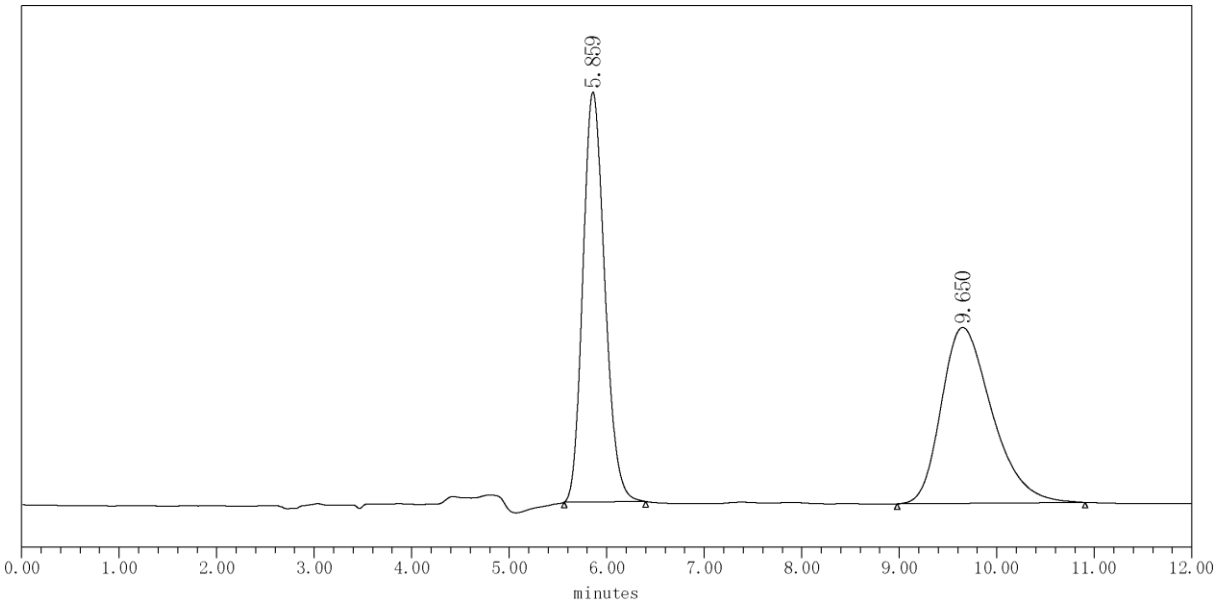
3ai

^{13}C NMR (151 MHz, $CDCl_3$)



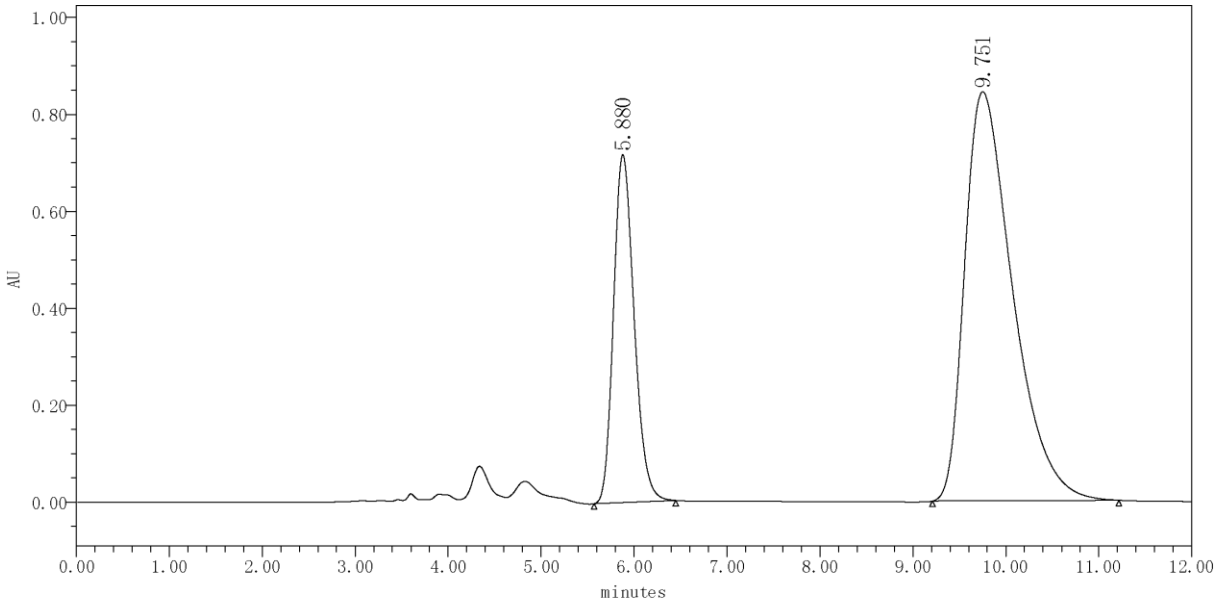
3ai

^{31}P NMR (243 MHz, $CDCl_3$)



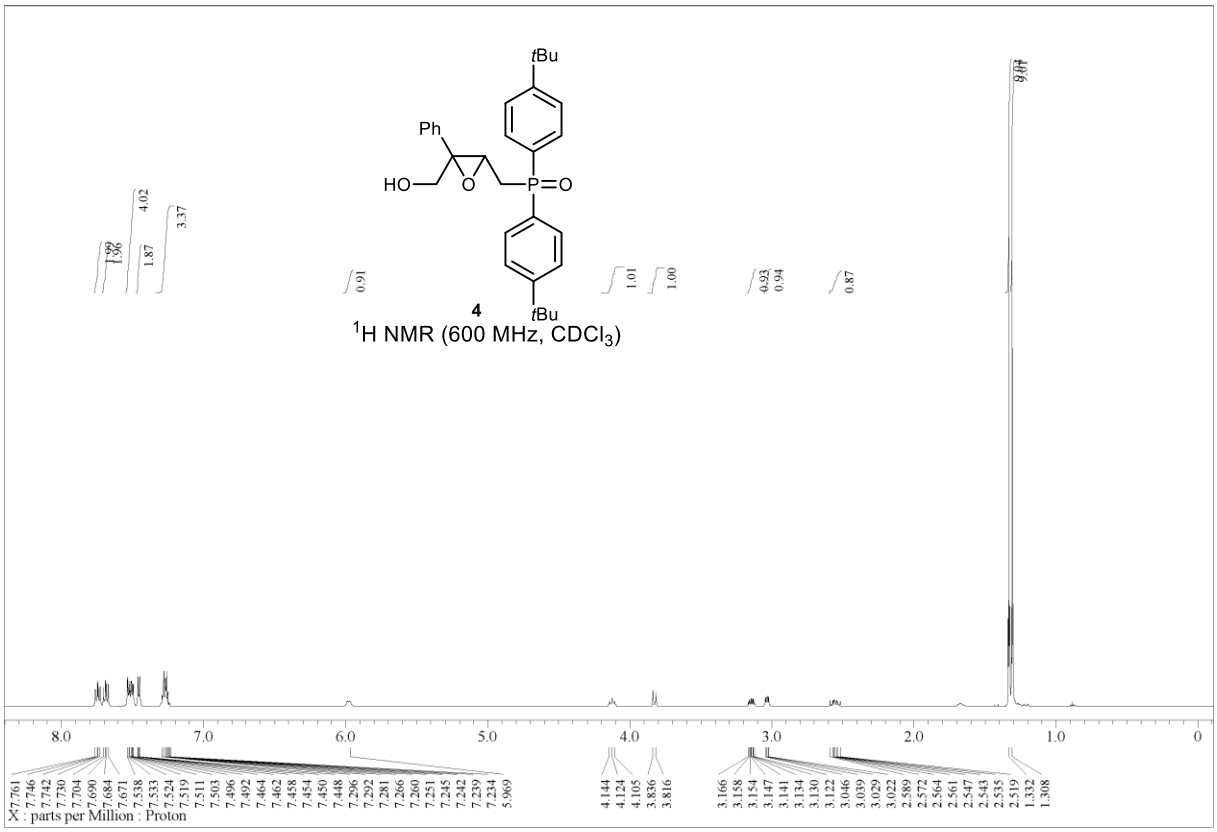
Peak Analysis Report

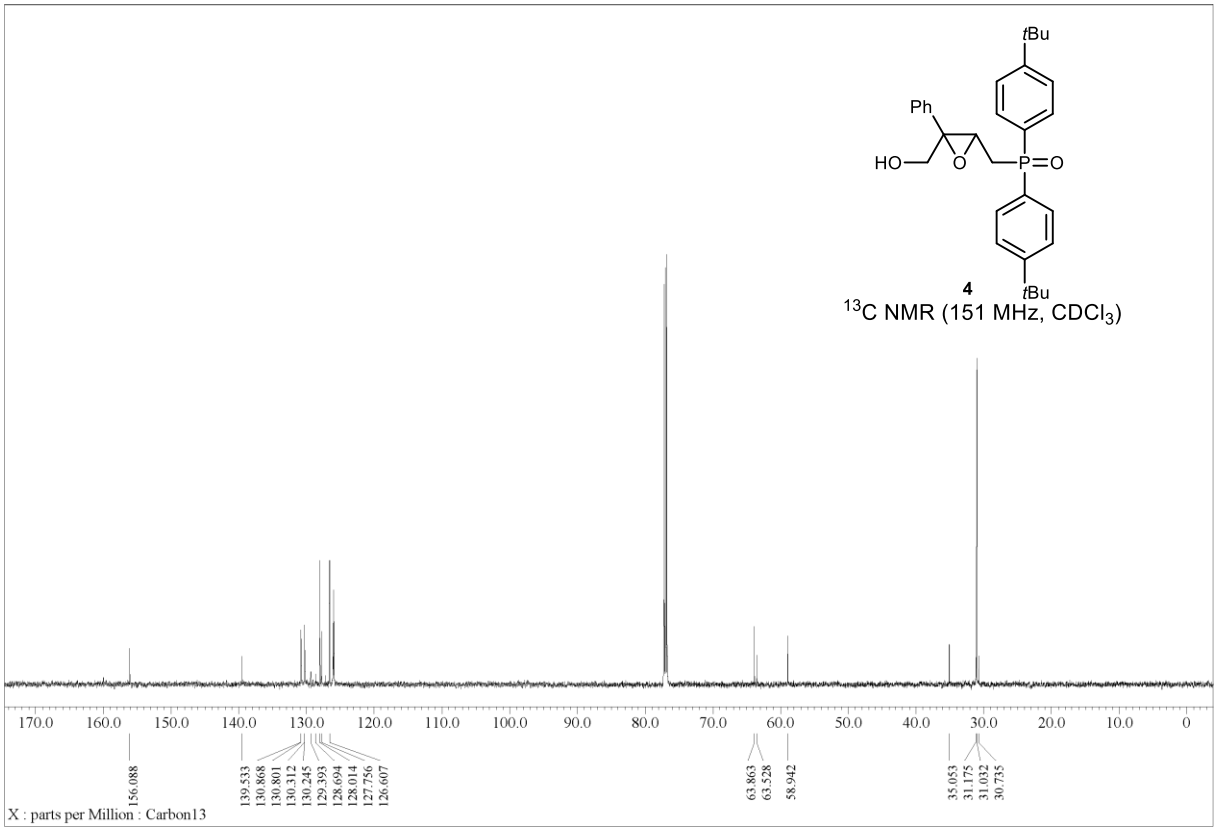
	Ret. Time (min)	Height (μV)	Area (μV*sec)	Rel. Area (%
1	5.859	379025	5913196	50.23
2	9.650	162653	5858841	49.77
Sum			11772037	100.00

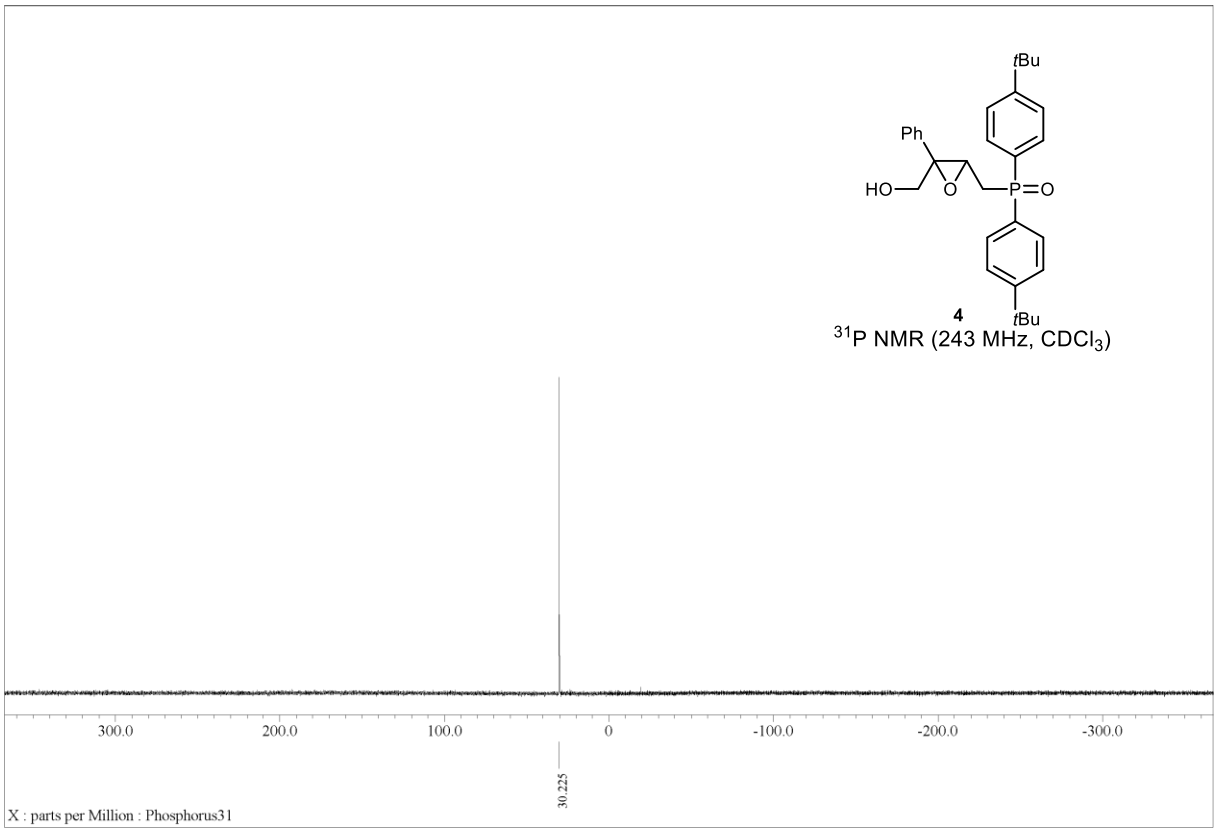


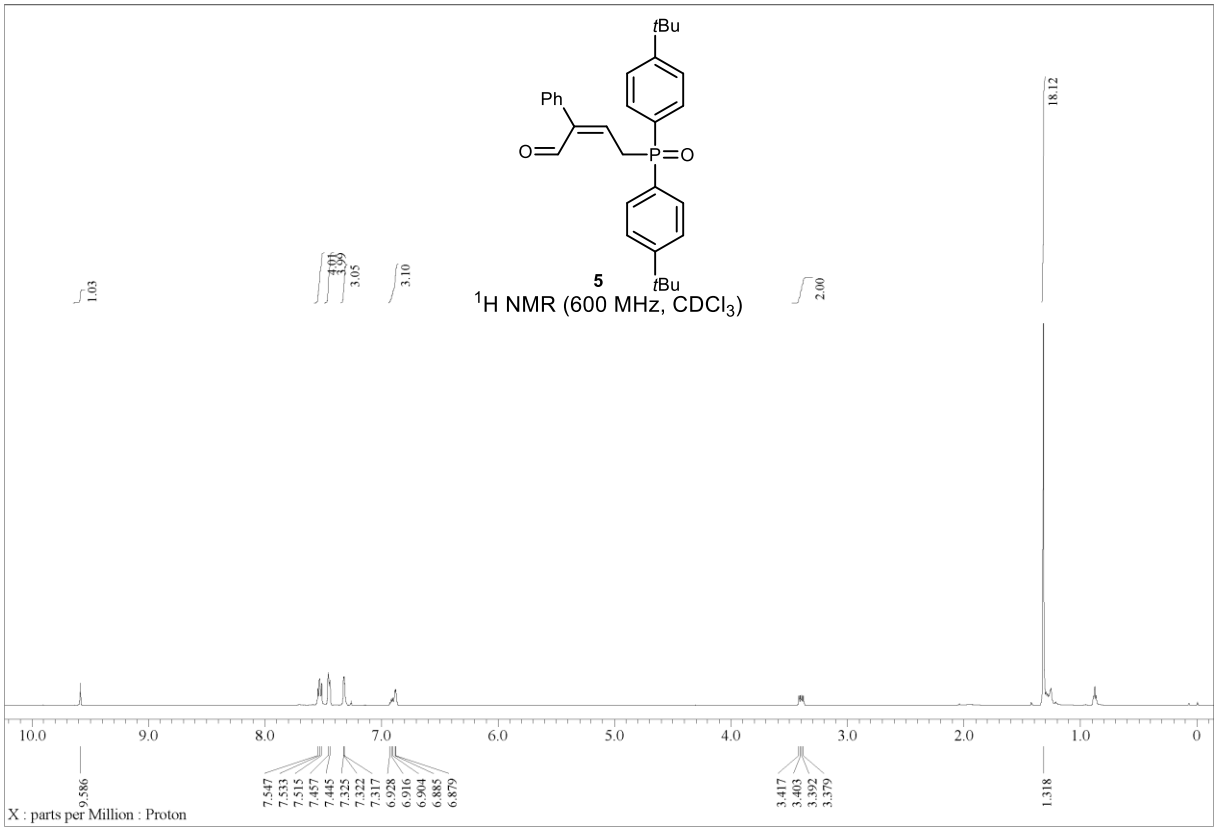
Peak Analysis Report

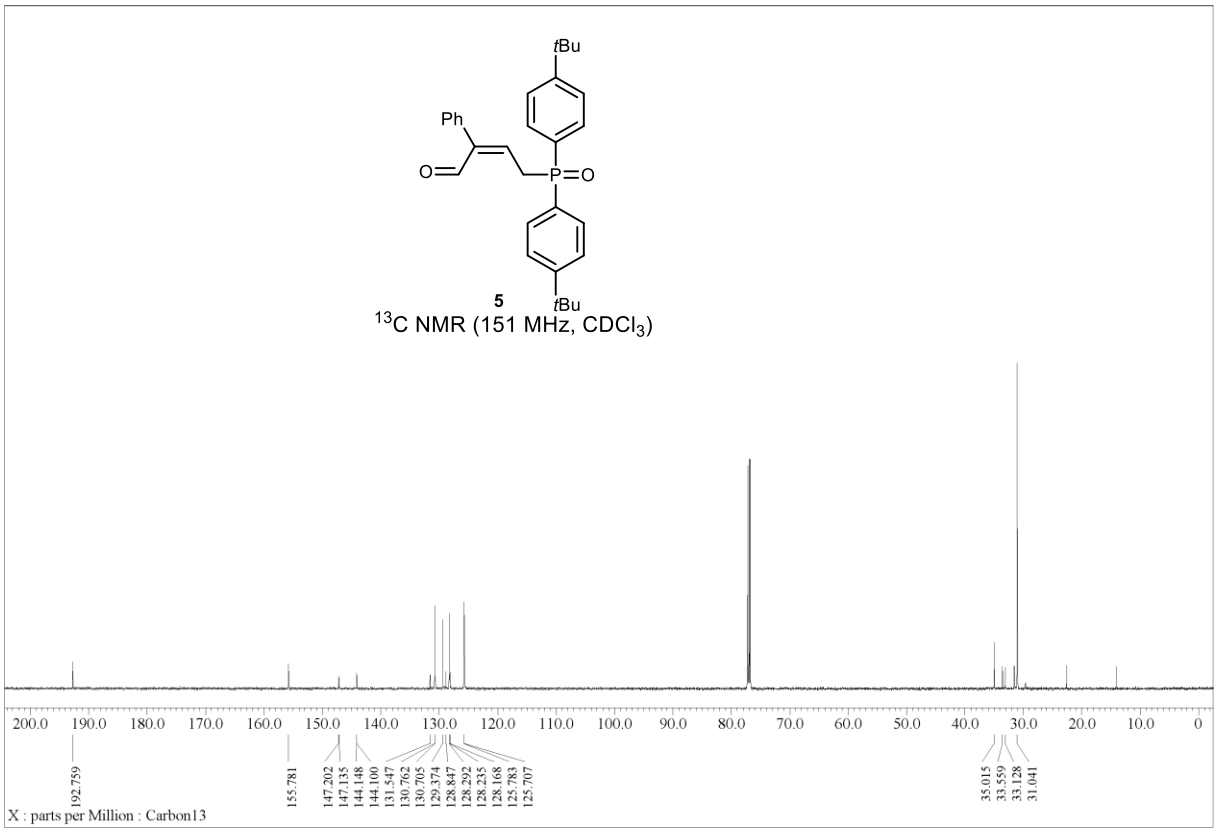
	Ret. Time (min)	Height (μV)	Area (μV*sec)	Rel. Area (%
1	5.880	718145	11048072	26.74
2	9.751	844144	30262655	73.26
Sum			41310727	100.00


tBu
Ph
HO
O
P=O
tBu
4
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


tBu
Ph
HO
O
P=O
tBu
4
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

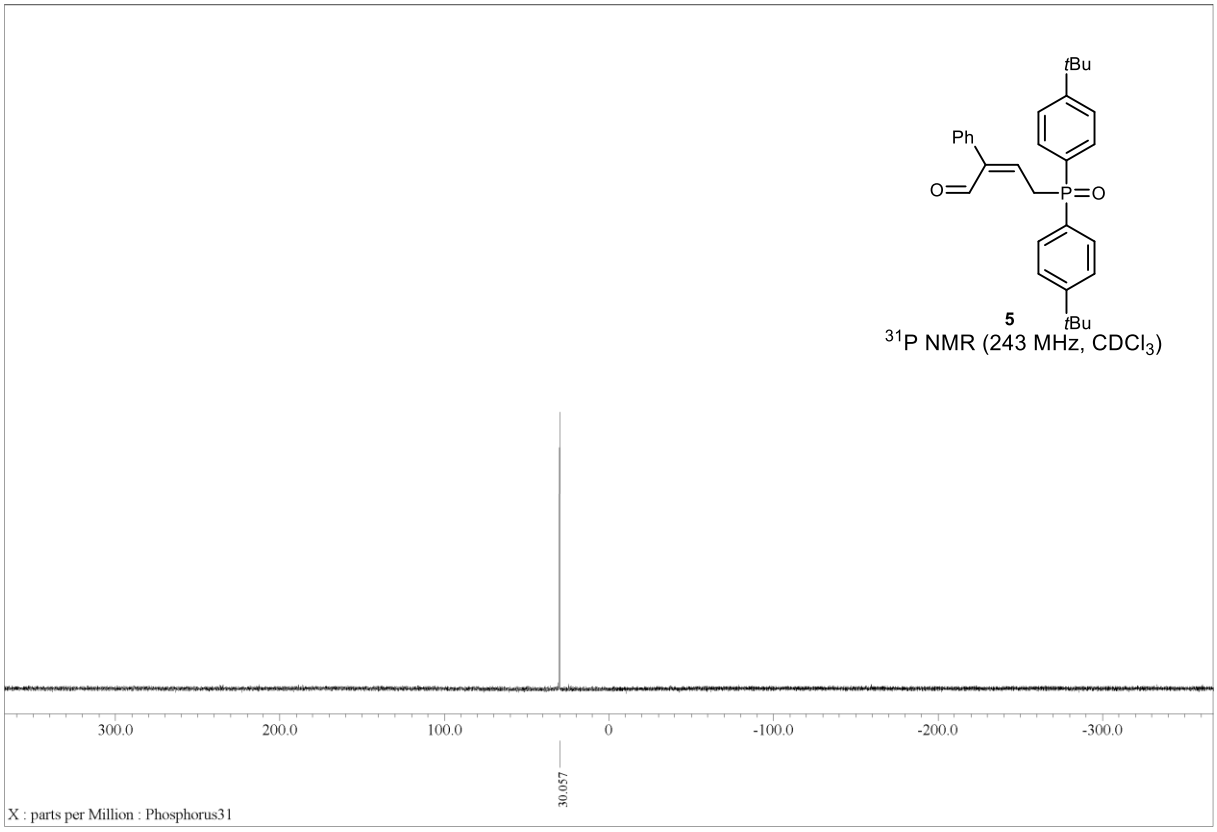

tBu
Ph
HO
O
P=O
tBu
4
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
30.225
X : parts per Million : Phosphorus31


tBu
Ph
O
P=O
tBu
5
1H NMR (600 MHz, CDCl3)
1.03
4.01
3.99
3.05
3.10
2.00
18.12
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.586
7.547
7.533
7.515
7.457
7.445
7.325
7.322
7.317
6.928
6.916
6.904
6.885
6.879
3.417
3.403
3.392
3.379
1.318
X : parts per Million : Proton



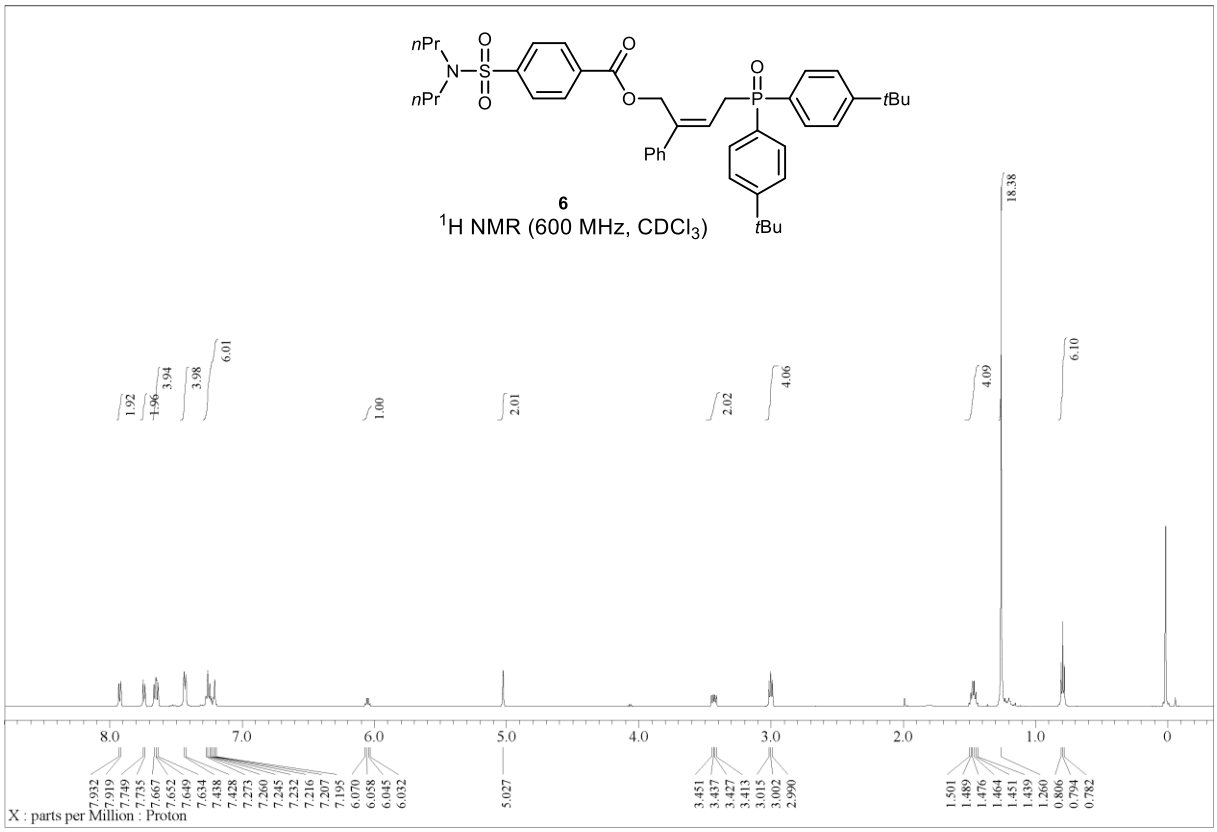
5

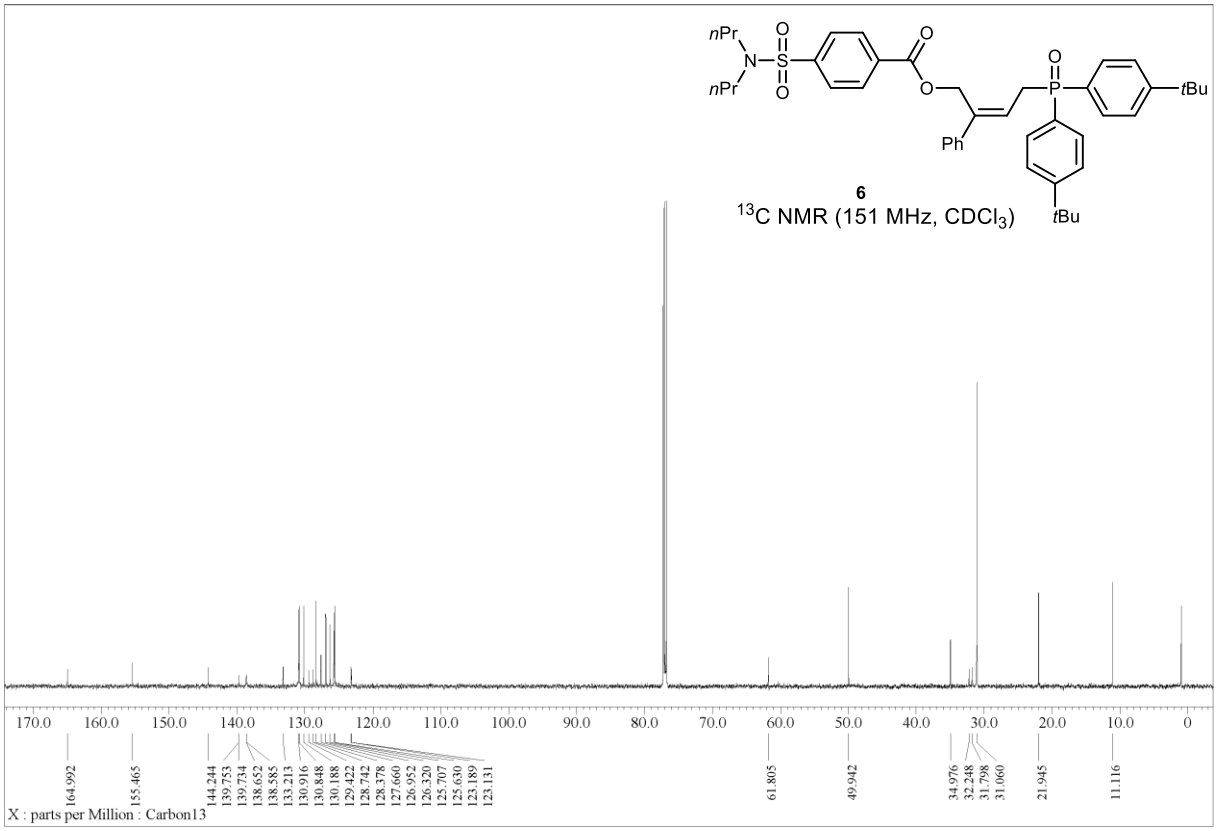
^{13}C NMR (151 MHz, $CDCl_3$)

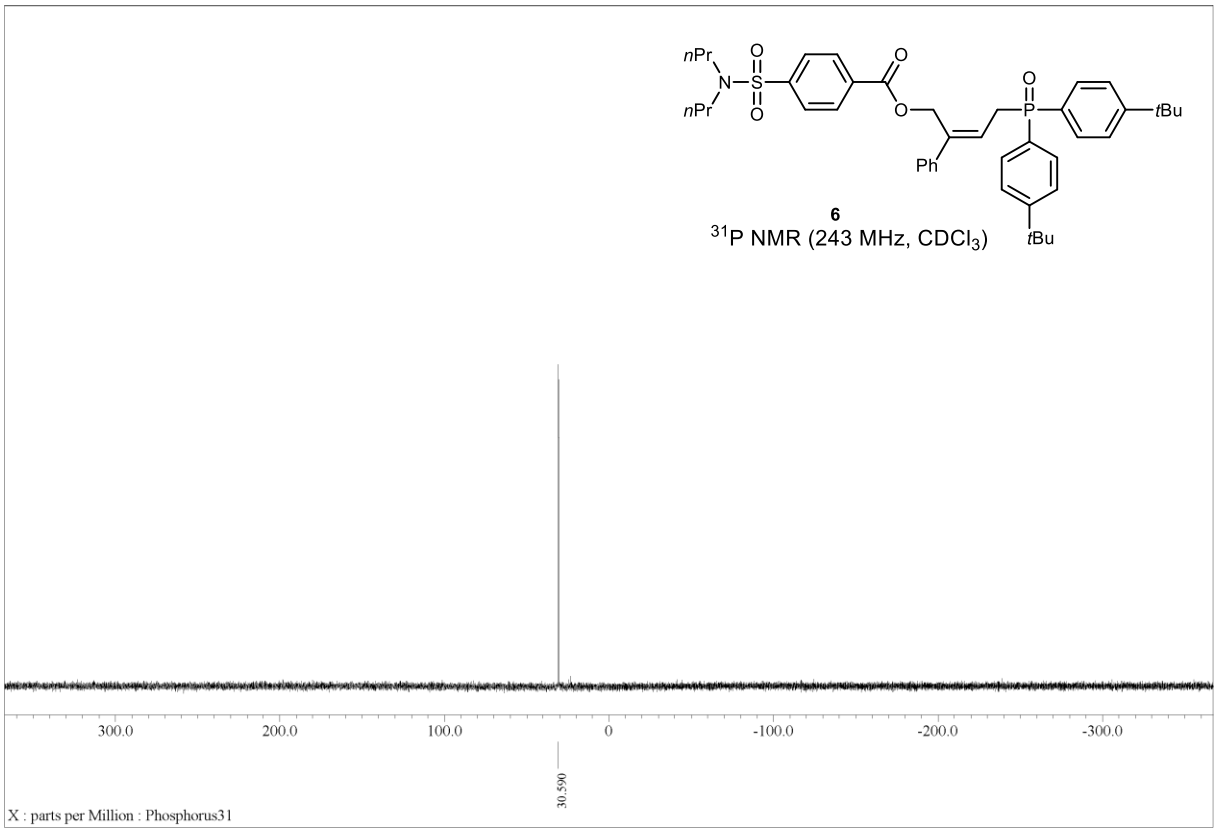


5

^{31}P NMR (243 MHz, $CDCl_3$)

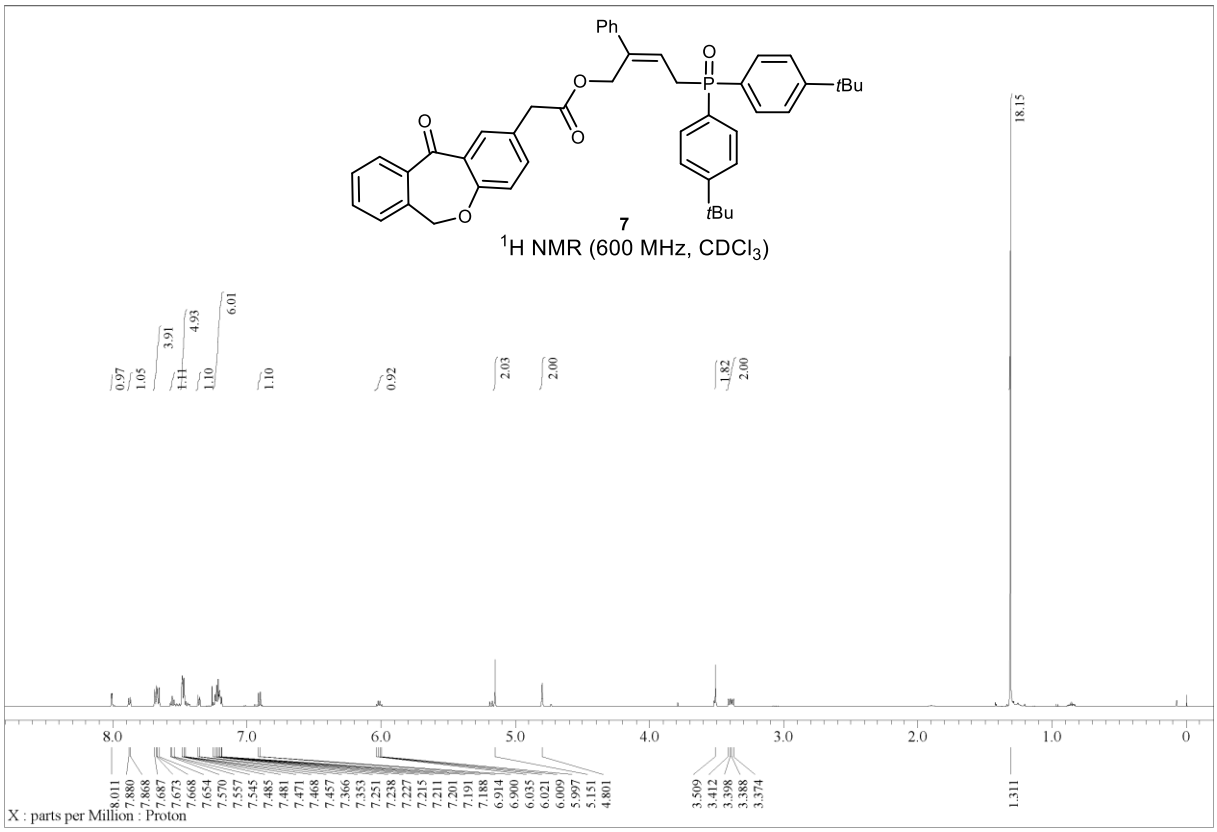

nPr
nPr
N
S
O
O
O
O
O
P
tBu
Ph
tBu
6
1H NMR (600 MHz, CDCl3)
1.92
1.96
3.94
3.98
6.01
1.00
2.01
2.02
4.06
4.09
18.38
6.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.932
7.919
7.749
7.735
7.667
7.652
7.649
7.634
7.438
7.428
7.273
7.260
7.245
7.232
7.216
7.207
7.195
6.070
6.058
6.045
6.032
5.027
3.451
3.437
3.427
3.413
3.015
3.002
2.990
1.501
1.489
1.476
1.464
1.451
1.439
1.260
0.806
0.794
0.782
X : parts per Million : Proton


nPr
nPr
N
S
O
O
O
O
O
P
tBu
Ph
tBu
6
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.992
155.465
144.244
139.753
139.734
138.652
138.585
133.213
130.916
130.848
130.188
129.422
128.742
128.378
127.660
126.952
126.320
125.707
125.630
123.189
123.131
61.805
49.942
34.976
32.248
31.798
31.060
21.945
11.116
X : parts per Million : Carbon13



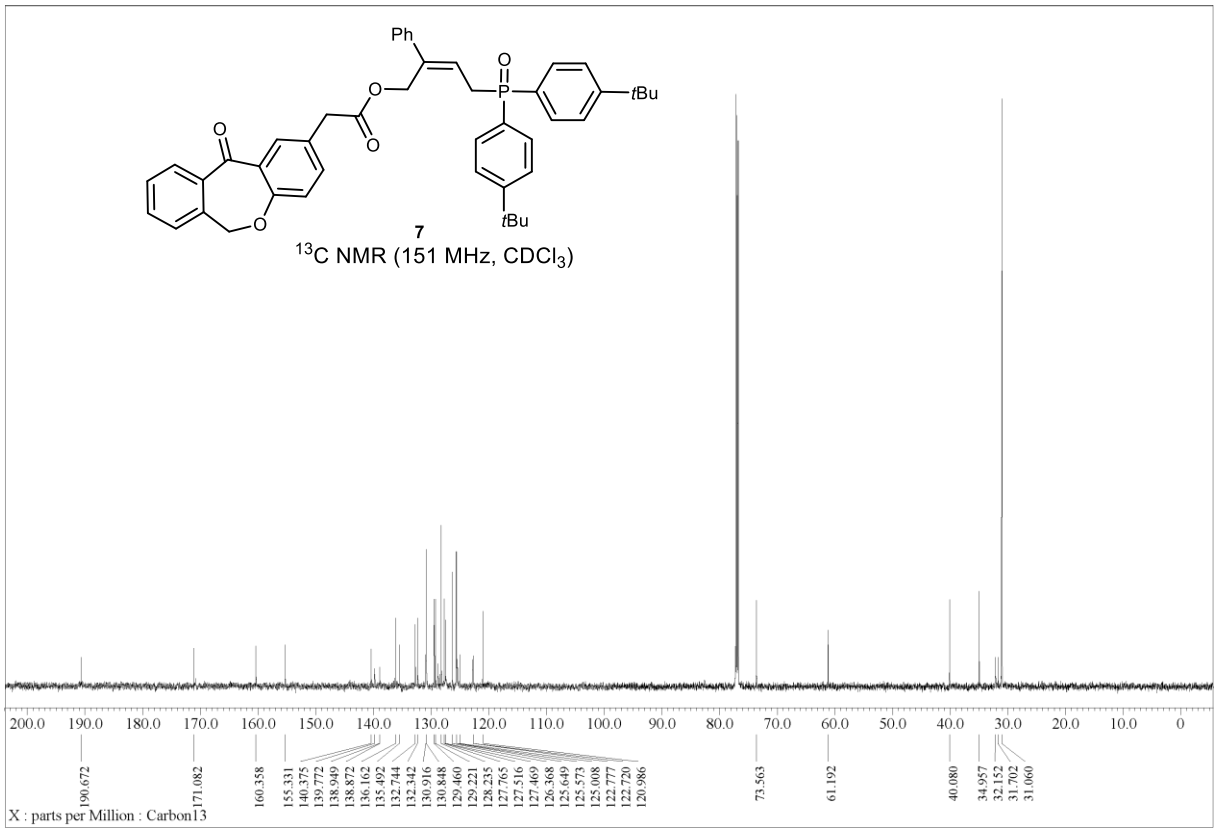
6

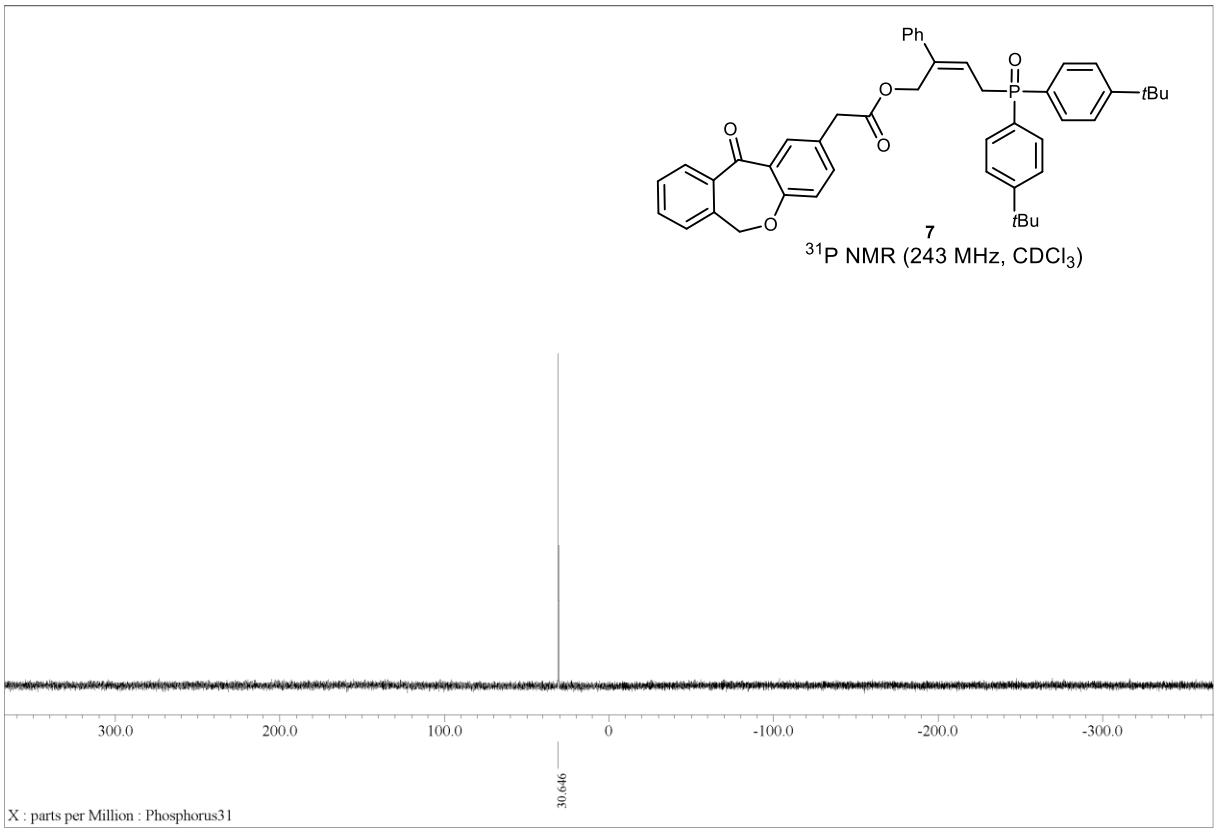
^{31}P NMR (243 MHz, $CDCl_3$)

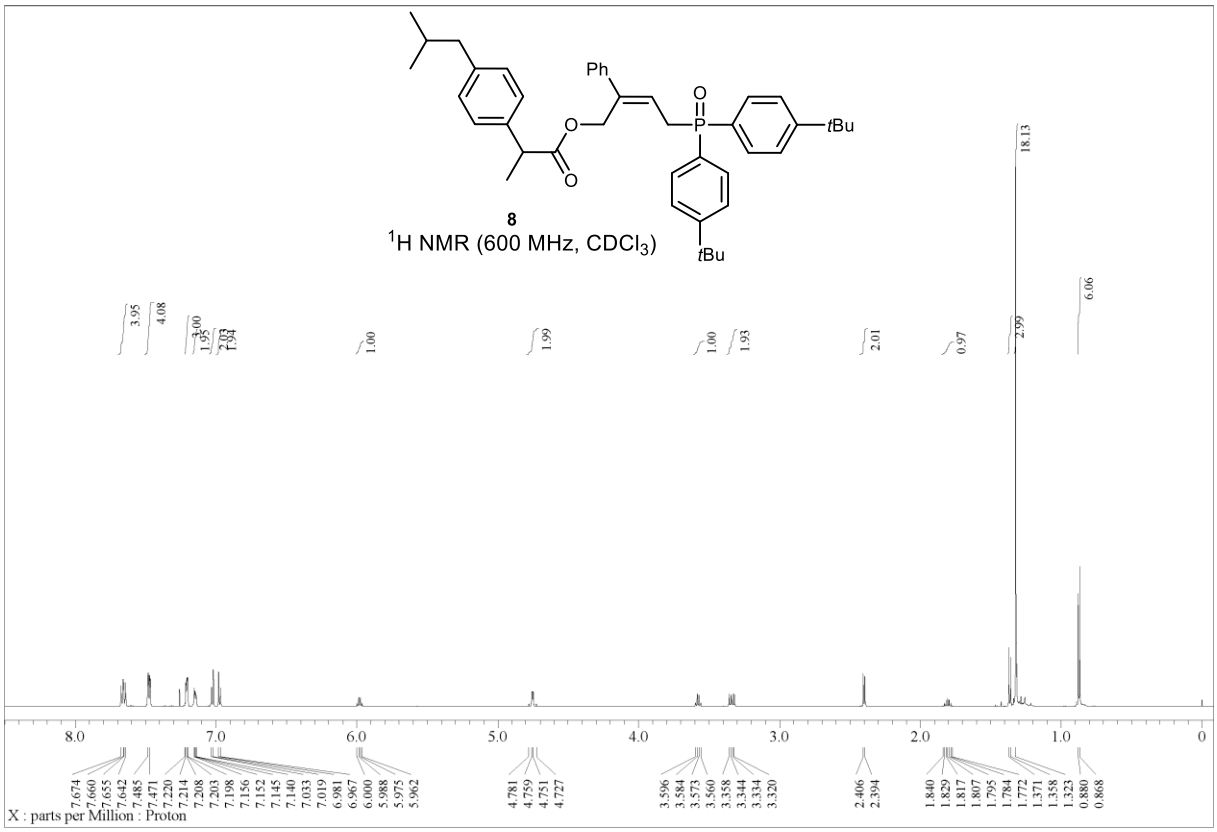


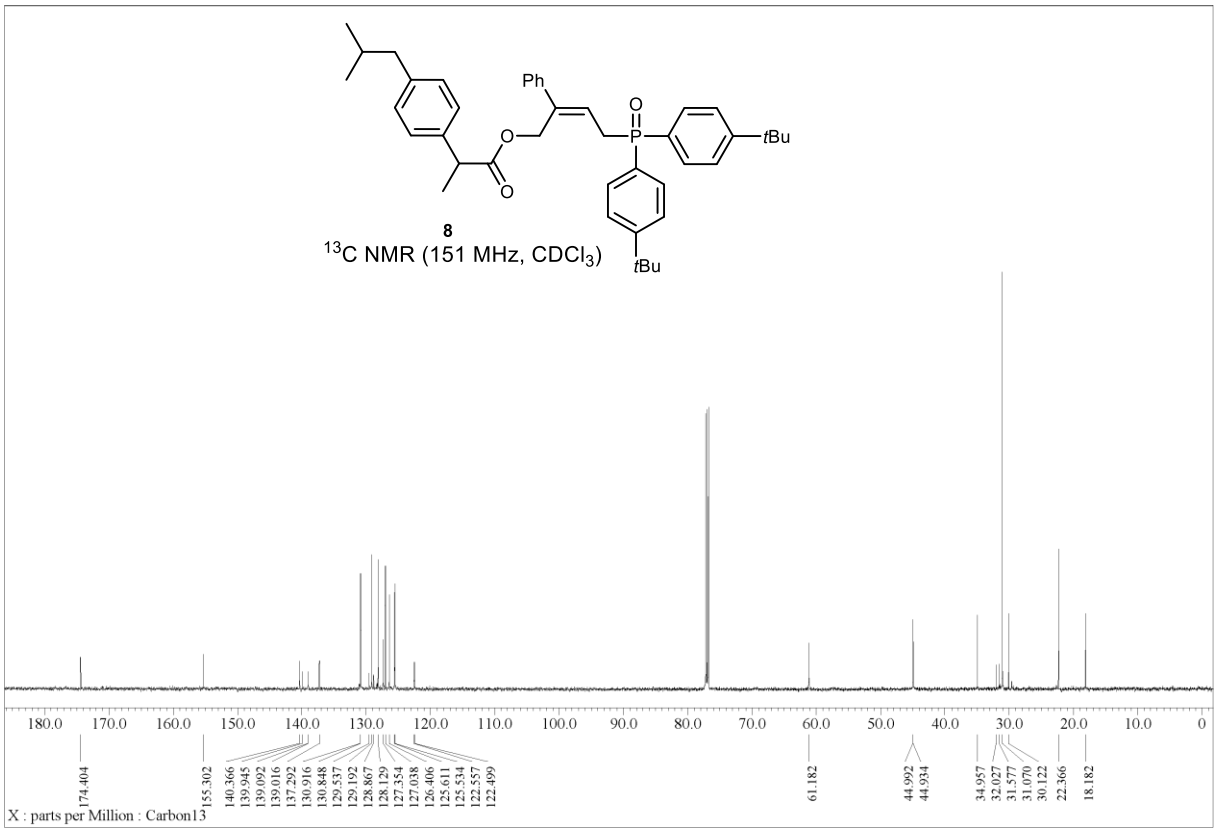
7

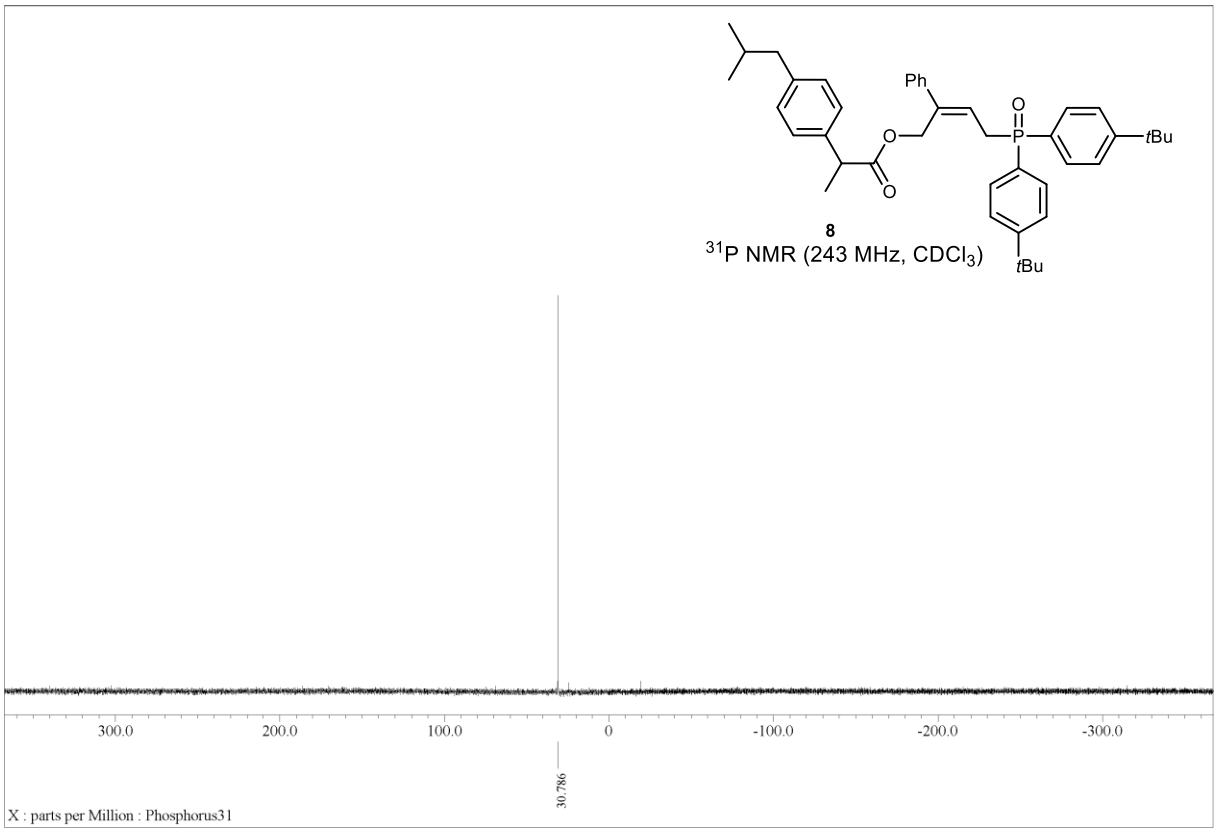
^{1}H NMR (600 MHz, $CDCl_3$)

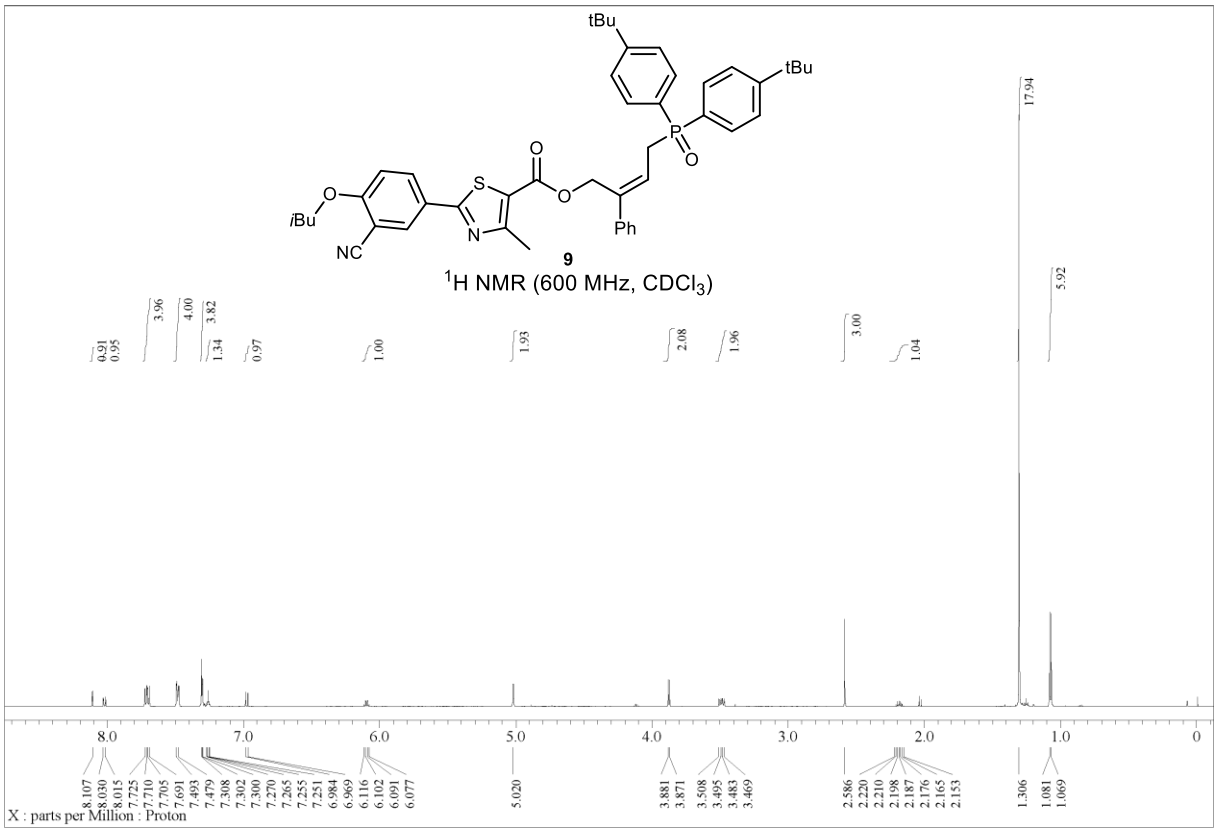

Ph
O
O
P
tBu
O
O
O
tBu
7
13C NMR (151 MHz, CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
190.672
171.082
160.358
155.331
140.375
139.772
138.949
138.872
136.162
135.492
132.744
132.342
130.916
130.848
129.460
129.221
128.235
127.765
127.516
127.469
126.368
125.649
125.573
125.008
122.777
122.720
120.986
73.563
61.192
40.080
34.957
32.152
31.702
31.060
X : parts per Million : Carbon13

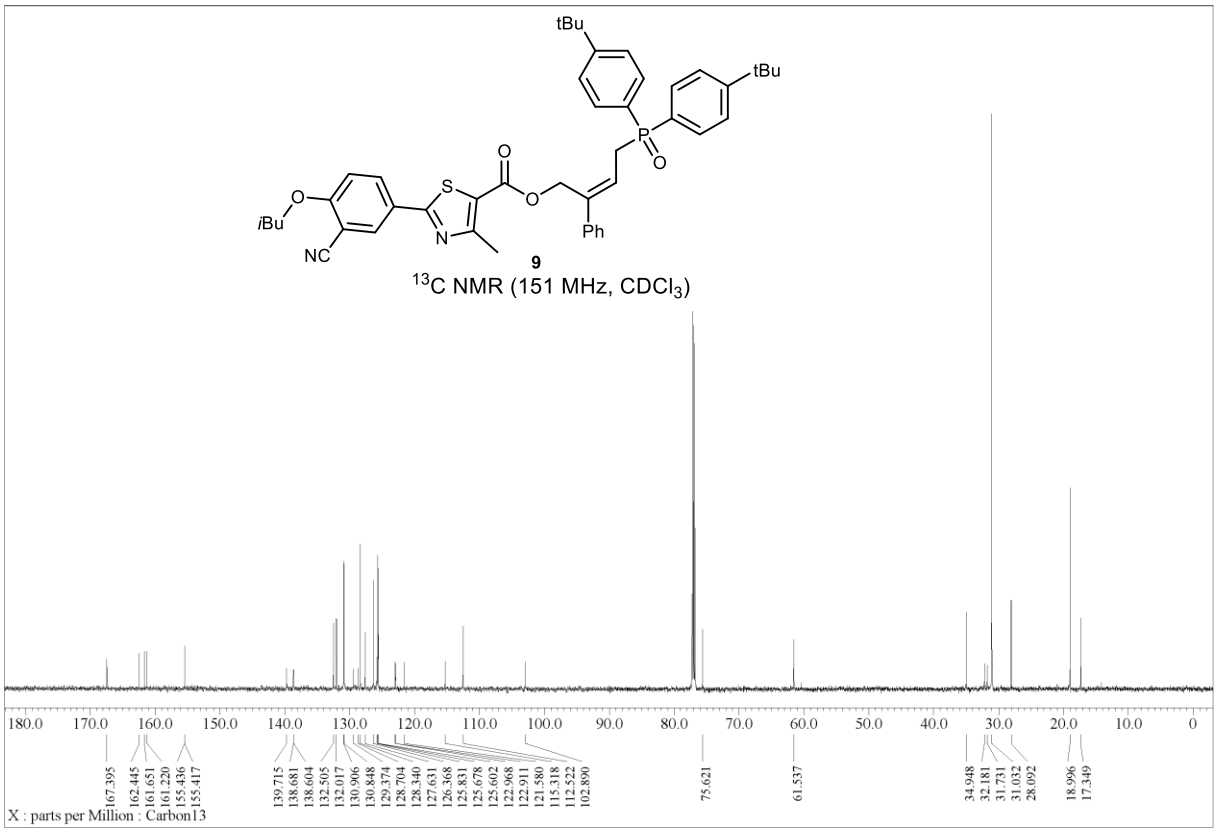

Ph
O
O
P
tBu
O
O
O
tBu
7
31P NMR (243 MHz, CDCl3)
300.0 200.0 100.0 0 -100.0 -200.0 -300.0
30.646
X : parts per Million : Phosphorus31

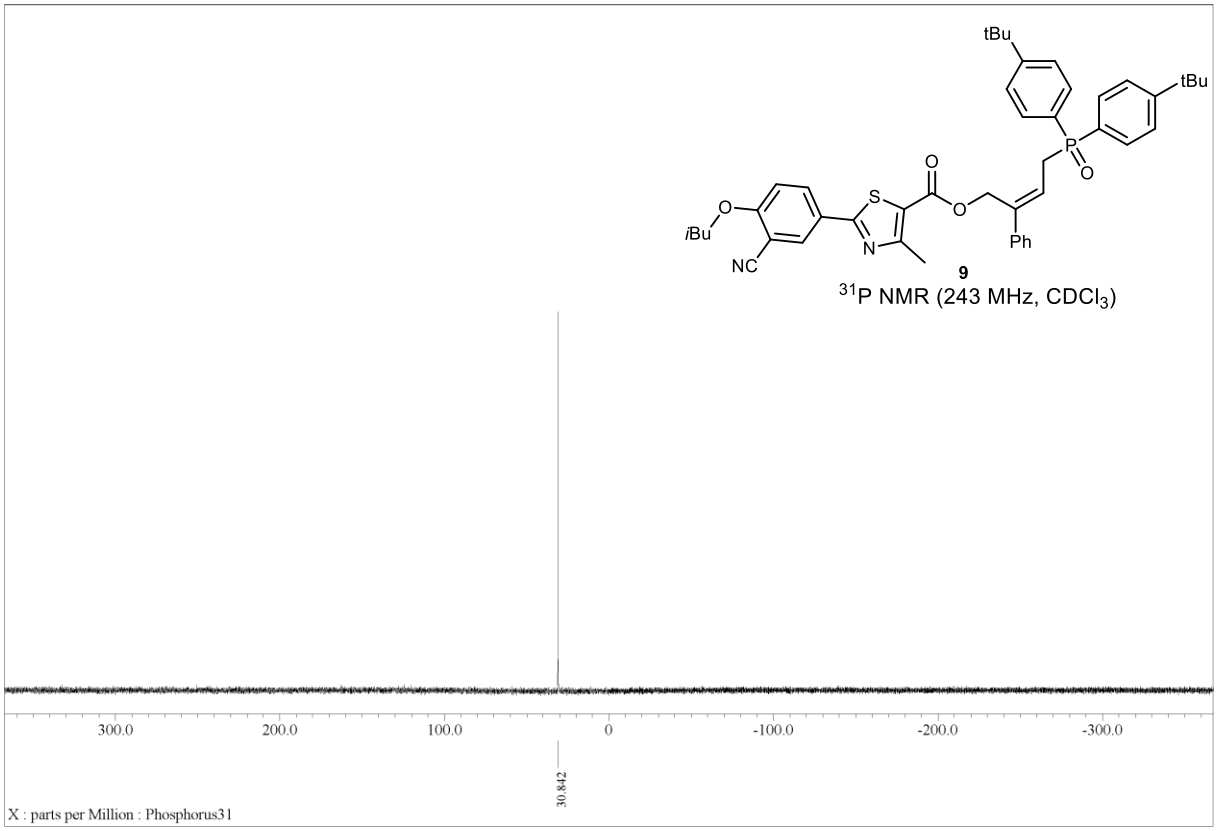

Ph
O
O
P
O
O
tBu
tBu
8
1H NMR (600 MHz, CDCl3)
3.95
4.08
3.00
1.00
1.99
1.00
1.93
2.01
0.97
2.99
18.13
6.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.674
7.660
7.655
7.642
7.485
7.471
7.220
7.214
7.208
7.203
7.198
7.156
7.152
7.145
7.140
7.033
7.019
6.981
6.967
6.000
5.988
5.975
5.962
4.781
4.759
4.751
4.727
3.596
3.584
3.573
3.560
3.358
3.344
3.334
3.320
2.406
2.394
1.840
1.829
1.817
1.807
1.795
1.784
1.772
1.371
1.358
1.323
0.880
0.868
X : parts per Million : Proton


Ph
O
O
P
O
O
tBu
tBu
8
13C NMR (151 MHz, CDCl3)
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.404
155.302
140.366
139.945
139.092
139.016
137.292
130.916
130.848
129.537
129.192
128.867
128.129
127.354
127.038
126.406
125.611
125.534
122.557
122.499
61.182
44.992
44.934
34.957
32.027
31.577
31.070
30.122
22.366
18.182
X : parts per Million : Carbon13


Ph
O
O
P
O
O
tBu
tBu
8
31P NMR (243 MHz, CDCl3)
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
30.786
X : parts per Million : Phosphorus31


tBu
tBu
P
O
O
S
N
O
O
iBu
NC
Ph
9
1H NMR (600 MHz, CDCl3)
17.94
5.92
3.96
4.00
3.82
3.00
2.08
1.96
1.93
1.04
1.00
1.34
0.97
0.91
0.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


tBu
tBu
P
O
O
O
S
O
iBu
N
Ph
NC
9
13C NMR (151 MHz, CDCl3)
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
167.395
162.445
161.651
161.220
155.436
155.417
139.715
138.681
138.604
132.505
132.017
130.906
130.848
129.374
128.704
128.340
127.631
126.368
125.831
125.678
125.602
122.968
122.911
121.580
115.318
112.522
102.890
75.621
61.537
34.948
32.181
31.731
31.032
28.092
18.996
17.349
X : parts per Million : Carbon13


tBu
tBu
P
O
O
O
S
O
iBu
N
Ph
NC
9
31P NMR (243 MHz, CDCl3)
300.0 200.0 100.0 0 -100.0 -200.0 -300.0
30.842
X : parts per Million : Phosphorus31