Mn(II)-Catalyzed Switchable Synthesis of P(O)–C and P(O)–O Bonds from Alcohols and Diarylphosphine Oxides via Phospha-Brook Rearrangement

Hirak Jyoti Phukan,[a] Arup Samanta,[a] Kailash Mohar,[a] Avijit Mondal,[a] Rinku Dihingia[a] and Dipankar Srimani*[a]

[a]Department of Chemistry, Indian Institute of Technology-Guwahati, Kamrup, Assam 781039, India.
E-mail: dsrimani@iitg.ac.in

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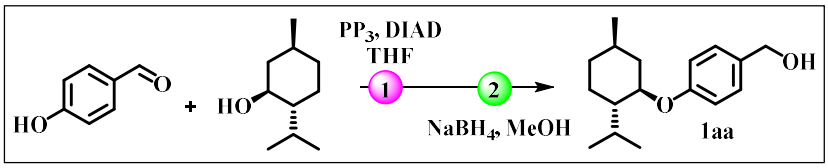
1. General considerations:

Unless otherwise mentioned, all chemicals were purchased from common commercially available sources and used as received. All solvents were dried by using standard procedure. The catalyst Mn (1- 4) was prepared according to the previous reported procedure.[1] All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques. DRX-400 Varian spectrometer and Bruker Advance III 400 MHz, 500 MHz and 600 MHz spectrometers were used to record ^{1}H and ^{13}C NMR spectra using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (*J*) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dt = doublet of triplet, td = triplet of doublet, dd = triplet of doublet and ddd = doublet of doublet of doublet. Q-TOF ESI-MS instrument (Agilent: 6546 LC/Q-TOF) was used for recording mass spectra. PerkinElmer clarus-590 GC instrument using Elite Plot-Q is used for GC analysis. Single crystal X-RAY diffractometer (BRUKER D8QUEST) is used for single crystal data collection. SRL silica gel (100-200 mesh) was used for column chromatography.

2. Preparation of starting materials:

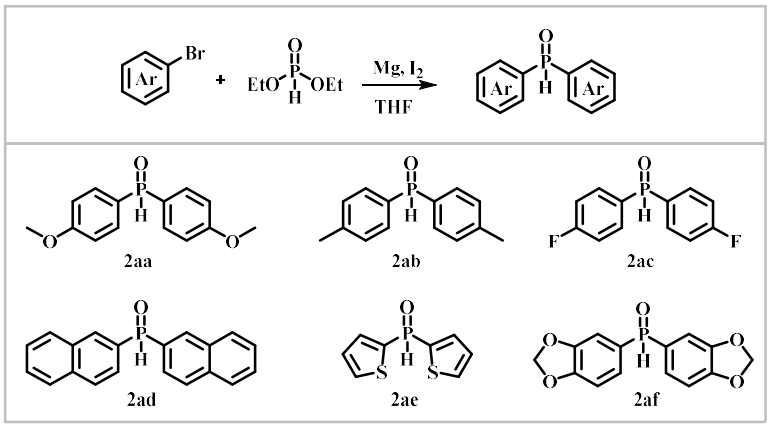
2.1. Preparation of (4-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl) methanol:



Substrate 1aa was prepared according to the reported procedure.[1] PPh_3 (1 equiv.) and DIAD (1 equiv.) were added sequentially to a solution of the 4'-hydroxy acetophenone (1.0 equiv.) and corresponding alcohol (1 equiv.) in THF (0.1 M). The resulting suspension was stirred vigorously at room temperature for 48 h. Then, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel (n-hexane/EtOAc) afforded the desired ethers.

To an oven dried 25 mL round bottomed flask, aldehyde (685.0 mg, 2.5 mmol, 1.0 equiv.) was dissolved in 15 mL of methanol and $NaBH_4$ (190 mg, 5.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired alcohol 1aa in 80% (2.0 mmol) yield.

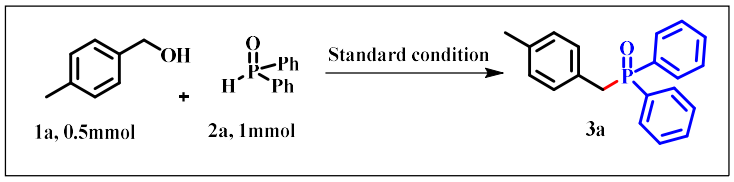
2.4. Preparation of diarylphosphine oxide compounds:[2]



Substrates 2aa – 2af were prepared according to the reported procedure.[2] Diethylphosphite (1.29 mL, 10.0 mmol) was added dropwise at 0 °C to a solution of phenylmagnesium bromide in tetrahydrofuran which was prepared from aryl bromides (32.6 mmol) and magnesium (0.95 g, 39.6 mmol). The mixture was aged for 30 min at 0 °C, then stirred at ambient temperature for 16 h. After that it was cooled again to 0 °C, and 75 mL NH4Cl aqueous was then added slowly. The mixture was extracted with diethyl ether and the organic phase was washed with $NaHCO_3$ aqueous and brine, then it was dried over Na_2SO_4. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel to give the product.

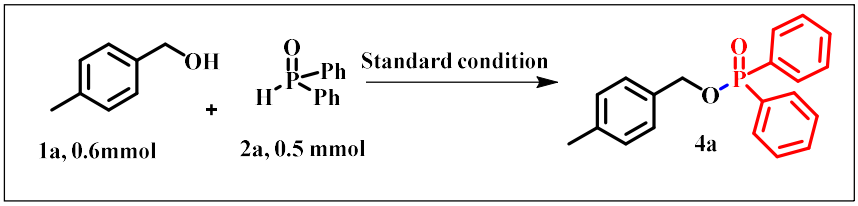
3. General Procedure

3.1: General Procedure for synthesising of P(O)-C compounds:



To an oven dried 100 mL seal tube 4-methylbezyl alcohol, **1a** (0.5 mmol), $HPOPh_2$, **2b** (**1** mmol), Cs_2CO_3 (50 mol%) and **Mn 1** (5 mol%) were taken and connected with high vacuum for 10 minutes. Then 2 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100-200 mesh) with petroleum ether/ethyl acetate mixture (1:1) as eluent.

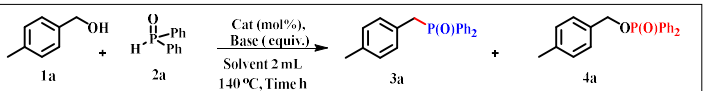
3.2. General Procedure for synthesising of P(O)-O compounds:



In an oven dried well-capped 100 mL ace pressure tube 4-methylbezyl alcohol **1a** (0.6 mmol), diphenylphosphine oxide **2a** (0.5 mmol), Cs_2CO_3 (50 mol%), Mn 1 catalyst (5 mol%) and Hexane (2 mL) were added in a gentle stream of argon. The tube was then closed and stirred in a preheated oil bath at 140 °C for 24 h. After that, reaction mixture was cooled to room temperature and it was filtered through celite and concentrated in vacuum, subsequently purified by column chromatography over silica gel (100–200 mesh) with petroleum-ether/ethyl acetate mixture as eluent.

4. Optimization table:

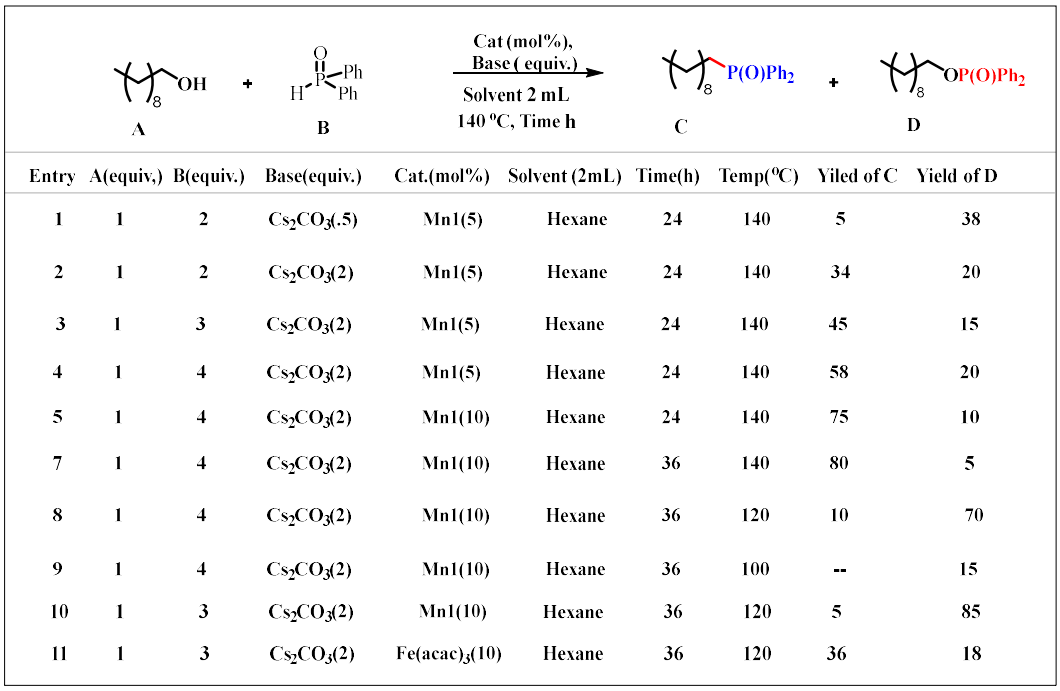
4.1. Optimization table for benzylic alcohol:



Entry	1a(equiv.)	2a(equiv.)	Base(equiv.)	Cat.(mol%)	Solvent (2mL)	Time (h)	Temp(°C)	% Yiled of 3a	% Yield of 4a
1	1	2	KO'Bu(1)	Mn1(5)	Hexane	24	140	-	-
2	1	2	KOH(1)	Mn1(5)	Hexane	24	140	13	<5
3	1	2	K_2CO_3(1)	Mn1(5)	Hexane	24	140	26	10
4	1	2	Na_2CO_3(1)	Mn1(5)	Hexane	24	140	-	-
5	1	2	Cs_2CO_3(1)	Mn1(5)	Hexane	24	140	91	<5
6	1	2	Cs_2CO_3(.75)	Mn1(5)	Hexane	24	140	88	<5
7	1	2	Cs_2CO_3(.5)	Mn1(5)	Hexane	24	140	90	<5
8	1	2	Cs_2CO_3(.4)	Mn1(5)	Hexane	24	140	65	<5
9	1	2	Cs_2CO_3(.5)	Mn1(5)	Hexane	36	140	90	<5
10	1	2	Cs_2CO_3(.5)	Mn1(5)	Hexane	12	140	54	5
11	1	2	Cs_2CO_3(.5)	---------	Hexane	24	140	6	15
12	1	1	Cs_2CO_3(.5)	Mn1(5)	Hexane	24	140	31	28
13	1.2	1	Cs_2CO_3(.5)	Mn1(5)	Hexane	24	140	30	65
14	1.2	1	Cs_2CO_3(.5)	$Fe(acac)_3$(5)	Hexane	24	140	50	<5
15	1.2	1	Cs_2CO_3(.5)	$Fe(acac)_3$(5)	Cyclohexane	24	140	40	<5
16	1.2	1	Cs_2CO_3(.5)	$Fe(acac)_3$(5)	Cyclohexane	24	80	00	00
17	1	2	Cs_2CO_3(.5)	Mn1(5)	Cyclohexane	24	140	71	5
18	1	2	Cs_2CO_3(.5)	Mn1(5)	Decaline	24	140	-	6
19	1	2	Cs_2CO_3(.5)	Mn1(5)	Xylene	24	140	6	24
20	1	2	Cs_2CO_3(.5)	Mn1(5)	Toluene	24	140	60	20
21	1	2	Cs_2CO_3(.5)	Mn1(5)	THF	24	140	60	<5
22	1	2	Cs_2CO_3(.5)	Mn1(5)	Hexane	24	120	46	12
23	1	2	CsF(.5)	Mn1(5)	Hexane	24	140	0	10
24	1	2	$CsOH.H_2O$(.5)	Mn1(5)	Hexane	24	140	0	0
25	1	2	Cs_2CO_3(.5)	Mn2(5)	Hexane	24	140	75	<5
26	1	2	Cs_2CO_3(.5)	Mn3(5)	Hexane	24	140	80	<5
27	1	2	Cs_2CO_3(.5)	Mn4(5)	Hexane	24	140	60	<5

[a]**Conditions:** 1a (0.5 – 0.6 mmol), 2a (0.5 - 1.0 mmol), Base (0.4-1.0 equiv.), Mn-catalyst (5 mol%), Hexane (2.0 mL), Under argon, Temperature: 120 - 140 °C, Time: 12 - 36 h, isolated yield.

4.2. Optimization table for long chain aliphatic alcohol:

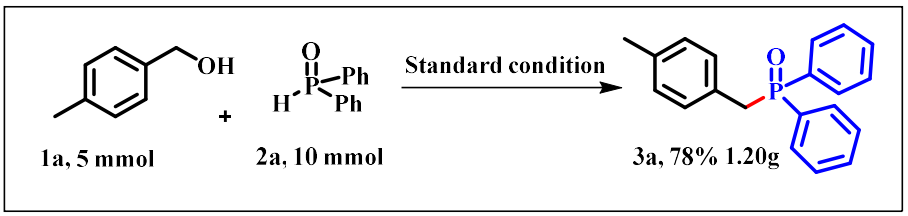


Entry	A(equiv.)	B(equiv.)	Base(equiv.)	Cat.(mol%)	Solvent (2mL)	Time(h)	Temp(°C)	Yiled of C	Yield of D
1	1	2	Cs_2CO_3(.5)	Mn1(5)	Hexane	24	140	5	38
2	1	2	Cs_2CO_3(2)	Mn1(5)	Hexane	24	140	34	20
3	1	3	Cs_2CO_3(2)	Mn1(5)	Hexane	24	140	45	15
4	1	4	Cs_2CO_3(2)	Mn1(5)	Hexane	24	140	58	20
5	1	4	Cs_2CO_3(2)	Mn1(10)	Hexane	24	140	75	10
7	1	4	Cs_2CO_3(2)	Mn1(10)	Hexane	36	140	80	5
8	1	4	Cs_2CO_3(2)	Mn1(10)	Hexane	36	120	10	70
9	1	4	Cs_2CO_3(2)	Mn1(10)	Hexane	36	100	--	15
10	1	3	Cs_2CO_3(2)	Mn1(10)	Hexane	36	120	5	85
11	1	3	Cs_2CO_3(2)	$Fe(acac)_3$(10)	Hexane	36	120	36	18

[a]**Conditions:** 1a (0.5 mmol), 2a (1 - 2.0 mmol), Base (0.5 – 2 equiv.), Mn-catalyst (5.0-10 mol%), Hexane (2.0 mL), Under argon, Temperature: 100 - 140 °C, Time: 24 - 36 h; isolated yield.

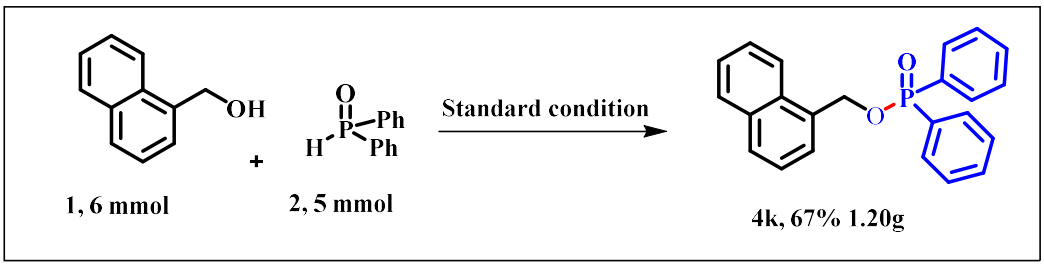
This study revealed that an appropriate dehydrogenation rate appears to be crucial in comparison to the 1,2-phospha-Brook rearrangement step and the subsequent interconversion between P(O)–O and P(O)–C bonds. If the dehydrogenation process is significantly slower than these competing steps, achieving selectivity toward the P(O)–O product may become difficult. This scenario could explain the observed limitations in selectivity with the Fe(acac)3

5. Gram Scale synthesis:



To an oven dried 100 mL seal tube 4-methylbezyl alcohol, **1a** (5 mmol), $HPOPh_2$, **2b** (**10** mmol), Cs_2CO_3 (50 mol%) and **Mn 1** (5 mol%) were taken and connected with high vacuum for 10 minutes. Then 10 mL Hexane were added to the mixture under argon. The resulting

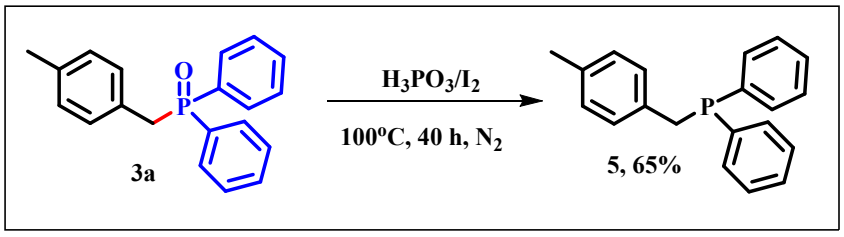
mixture was then placed into the preheated oil bath at 140 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100-200 mesh) with petroleum ether/ethyl acetate mixture (1:1) as eluent, and 1.20 g of **4a** was obtained. Yield 78%, white solid.



To an oven dried 100 mL seal tube naphthalen-1-ylmethanol, **1** (6 mmol), $HPOPh_2$, **2** (**5** mmol), Cs_2CO_3 (50 mol%) and **Mn 1** (5 mol%) were taken and connected with high vacuum for 10 minutes. Then 10 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100-200 mesh) with petroleum ether/ethyl acetate mixture (1:1) as eluent, and 1.20 g of **4k** was obtained. Yield 67%, colourless oil.

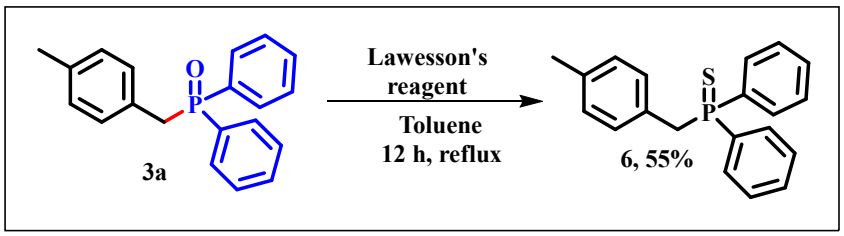
6. Procedure for post synthetic applications

6.1. General procedure for synthesis of (4-methylbenzyl)diphenylphosphane:[3]



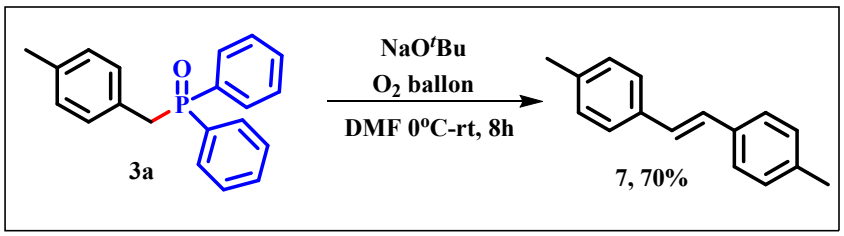
Under argon, a mixture of phosphine oxide **3a** (0.3mmol), H_3PO_3 (0.9mmol), and I_2 (0.3mmol) was stirred in a 10 mL closed sealed tube in a heating mantle at 100 °C for 40 h. After the mixture was cooled to room temperature, the reaction was quenched with water and the mixture was extracted with $CHCl_3$. The combined organic layer was dried over Na_2SO_4 and filtered. After the evaporation of the solvent under reduced pressure, the residue was further purified by column chromatography on silica gel to give product **5**.

6.2. General procedure for synthesis of (4-methylbenzyl)diphenylphosphine sulphide:[4]



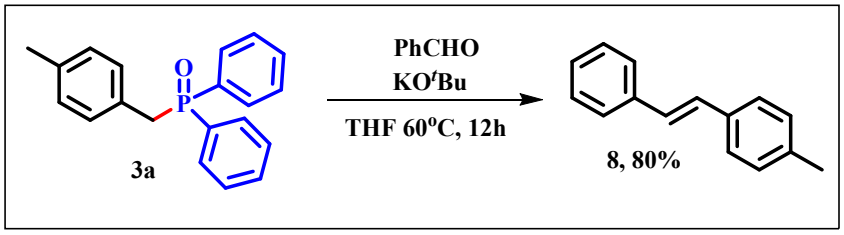
A dry reaction tube was charged with **3a** (0.2 mmol, 1.0 equiv.) and Lawesson's Reagent (0.1 mmol, 0.5 equiv.) under an argon atmosphere, then dry toluene (2 mL) was added. The reaction mixture was refluxed and stirred for 6 h. Upon completion, the reaction mixture was cooled to room temperature. Then the solution was concentrated in vacuum. And then the residue was purified by flash chromatography on silica gel (PE:EA=30:1-10:1) to give the product **6** in 55% yield.

6.3. General procedure for synthesis of symmetrical (E)-1,2-di-p-tolylethene:[5]



Under O_2, a mixture of **3a** (0.3 mmol), *t*-BuONa (0.45mmol, 1.5equiv), and DMF (1.5 mL) was stirred in a 25 mL sealed tube in a heating mantle at 0 °C for 30 min. Then the mixture was further stirred at room temperature for 12 h. After the reaction had reached completion, the mixture was concentrated and the residue was further purified by column chromatography on silica gel to give product **7**.

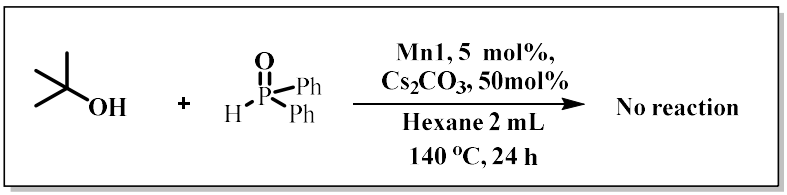
6.4. General procedure for synthesis of asymmetrical (E)-1-methyl-4-styrylbenzene:[5]



Under argon, a mixture of aldehydes 1(0.3 mmol), 4 (0.3 mmol, 1.0 equiv), t-BuOK (0.6mmol, 2.0 equiv,6 7.2 mg), and THF (1.5mL) was stirred in a 10 mL sealed tube in a heating mantle at 60 °C for 12 h. After the mixture was cooled to room temperature, 3 mL of THF was added to dilute the reaction mixture. The organic layer was concentrated, and the residue was further purified by column chromatography on silica gel to give product 8.

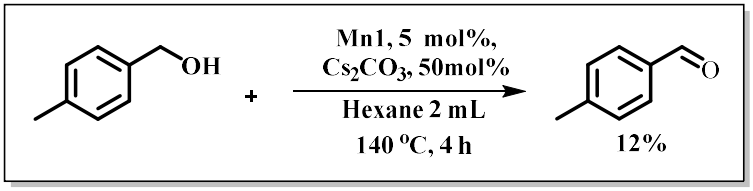
7. Mechanistic studies:

7.1. Test for carbocation;



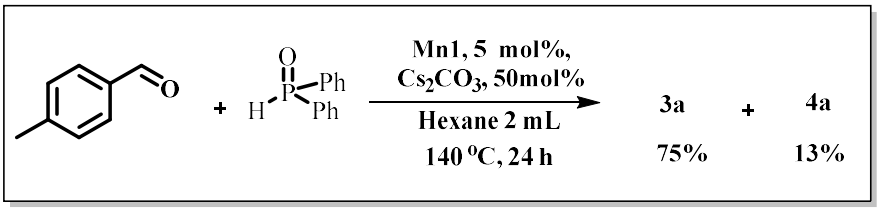
To an oven dried 100 mL seal tube , tert-butyl alcohol (0.5 mmol), $HPOPh_2$ (**1** mmol), Cs_2CO_3 (50 mol%) and **Mn 1** (5 mol%) were taken and connected with high vacuum for 10 minutes. Then 2 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, and the residue was analyzed by NMR spectroscopy which indicates that no P(O)-C and P(O)-O were formed which clearly reveals that the product formation does not occur via carbocation formation.

7.2. Test for alcohol dehydrogenation:



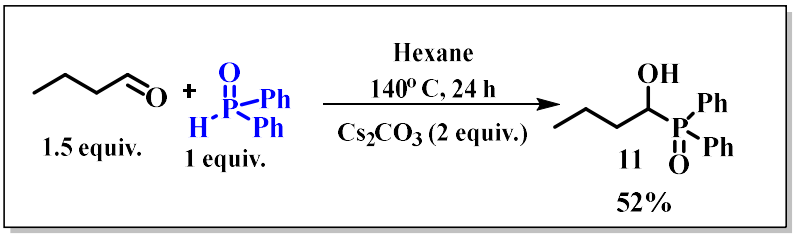
To an oven dried 100 mL seal tube , 4-methyl benzyl alcohol (0.5 mmol), Cs_2CO_3 (50 mol%) and **Mn 1** (5 mol%) were taken and connected with high vacuum for 10 minutes. Then 2 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, and the residue was analyzed by NMR spectroscopy which indicates that 12% of 4-methylbenzaldehyde was formed which clearly reveals that aldehyde is forming during the reaction.

7.3. Detection of intermediate:



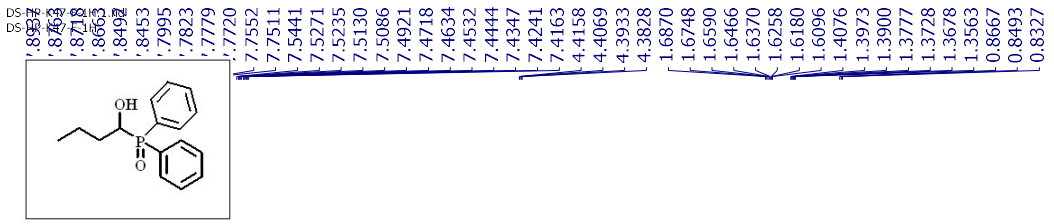
To an oven dried 100 mL seal tube, 4-methylbenzaldehyde (0.5 mmol), $HPOPh_2$ (**1** mmol), Cs_2CO_3 (50 mol%) and Mn 1 (5 mol%) were taken and connected with high vacuum for 10

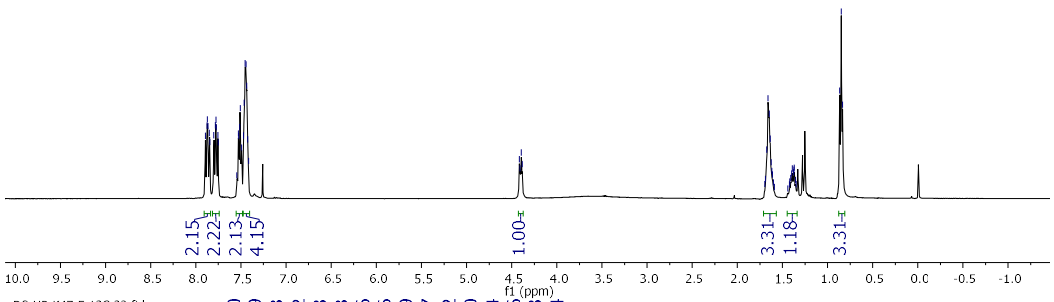
minutes. Then 2 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100-200 mesh) with petroleum ether/ethyl acetate mixture (1:1) as eluent. 75% of **3a** and 13% of **4a** was formed which indicates that the reaction proceeds via involvement of aldehyde.



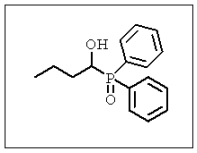
To an oven dried 100 mL seal tube, butyraldehyde (1.5 mmol), $HPOPh_2$ (**1** mmol), Cs_2CO_3 (2 equiv.) were taken and connected with high vacuum for 10 minutes. Then 2 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100-200 mesh) with petroleum ether/ethyl acetate mixture (1:1) as eluent. 52% of **11** was formed.

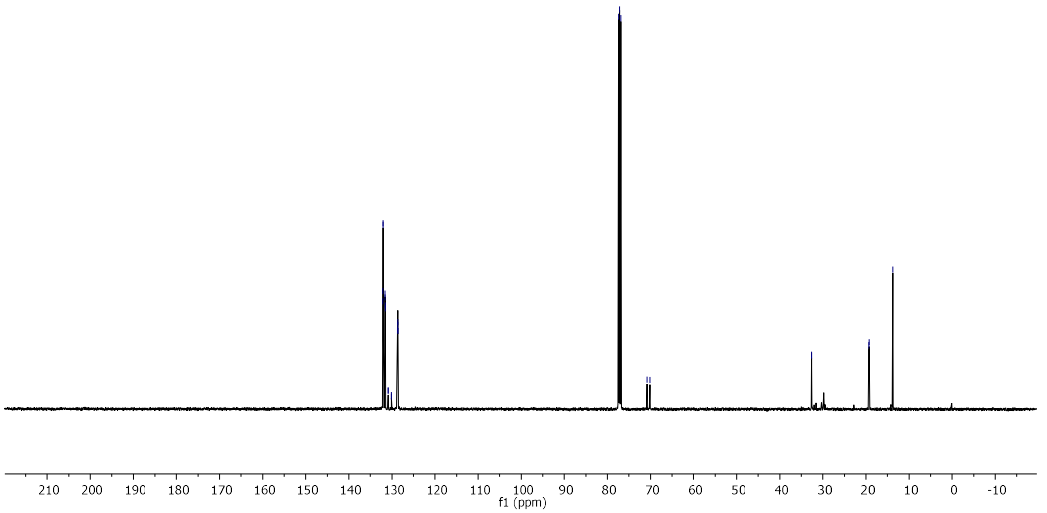
(1-hydroxybutyl)diphenylphosphine oxide (11): White solid, yield: 71 mg 52 %, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.79 – 7.75 (m, 2H), 7.54 – 7.49 (m, 2H), 7.47 – 7.41 (m, 4H), 4.41 – 4.38 (m, 1H), 1.69 – 1.59 (m, 3H), 1.44 – 1.34 (m, 1H), 0.85 (t, J = 6.9 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 132.1 (d, J_{C-P} = 8.7 Hz), 132.0 (d, J_{C-P} = 8.7 Hz), 131.6 (d, J_{C-P} = 8.5 Hz), 131.5 (d, J_{C-P} = 8.5 Hz), 130.5 (d, J_{C-P} = 95.9 Hz), 130.4 (d, J_{C-P} = 95.9 Hz), 128.7 (d, J_{C-P} = 10.8 Hz), 128.6 (d, J_{C-P} = 10.5 Hz), 70.5 (d, J_{C-P} = 83.3 Hz), 32.6 (d, J_{C-P} = 3.0 Hz), 19.3 (d, J_{C-P} = 12.0 Hz), 13.7. **^{31}P NMR (200 MHz, $CDCl_3$) δ** 32.1. **HRMS (ESI+):** m/z calcd. $C_{16}H_{19}O_2P$ For $[M+H]^+$: 275.1196; Found: 275.1190.





DS-HP-K47-F-13C.32.fid
DS-HP-K47-F-13C





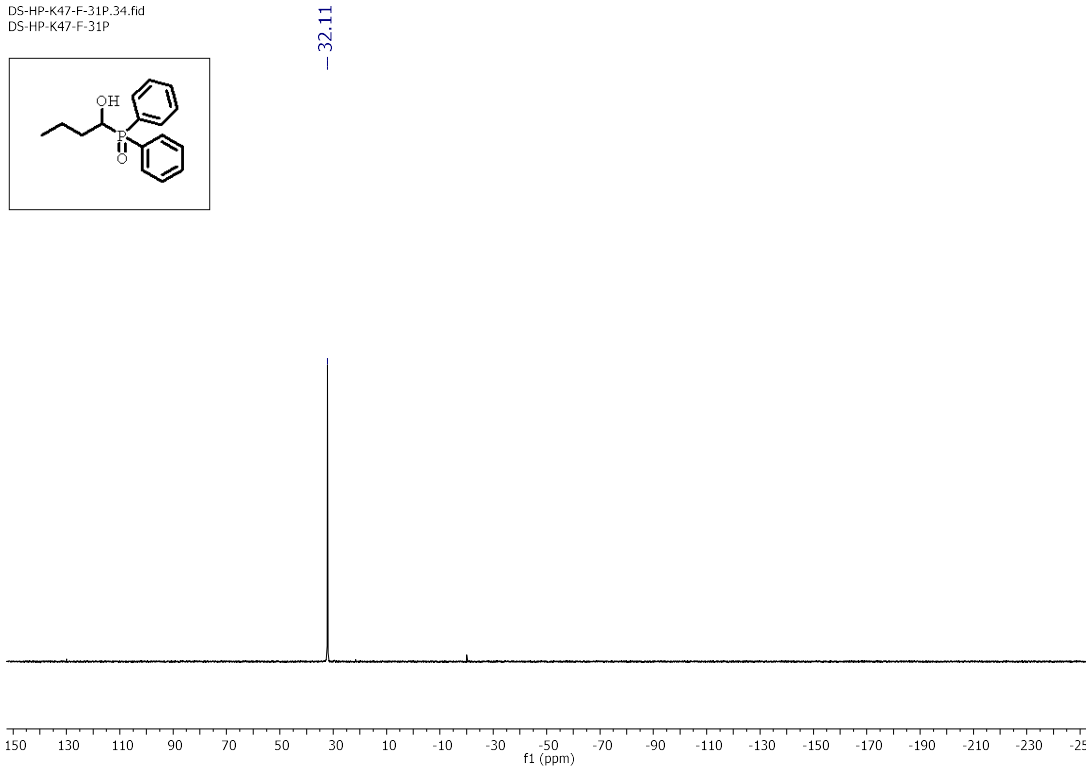
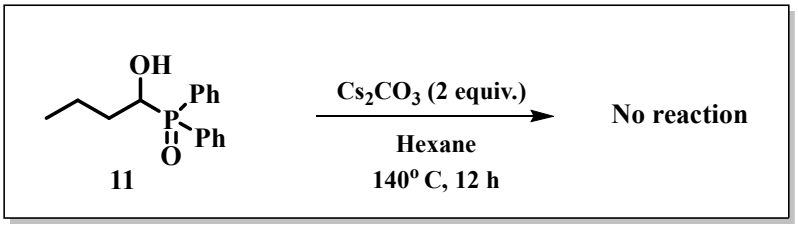
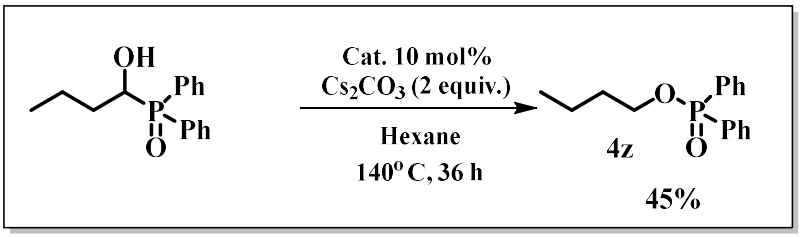


Figure S1. ^{1}H NMR (400 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 11 in $CDCl_3$



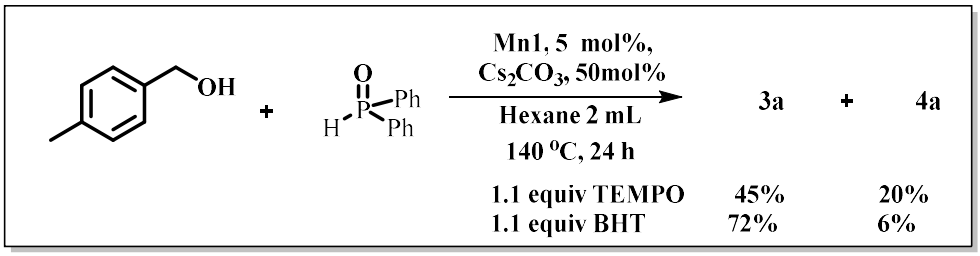
To an oven dried 100 mL seal tube, α-hydroxy phosphine oxide 11 (1 equiv.) and Cs_2CO_3 (2 equiv.) were taken and connected with high vacuum for 10 minutes. Then 2 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 12 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum and resulted no product formation.



To an oven dried 100 mL seal tube, α-hydroxy phosphine oxide 11 (1 equiv.), Cs_2CO_3 (2 equiv.) and Mn 1 (10 mol%) were taken and connected with high vacuum for 10 minutes. Then

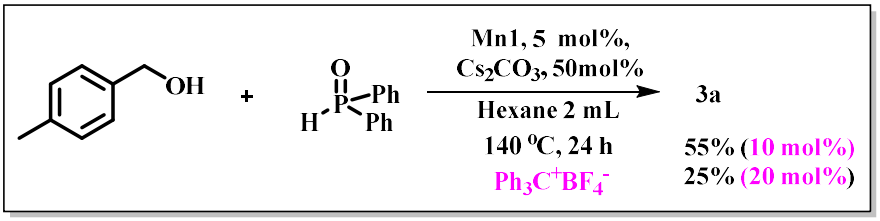
2 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 12 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100-200 mesh) with petroleum ether/ethyl acetate mixture (1:1) as eluent. 45% of **4z** was formed. The results suggest that the conversion of α-hydroxy phosphine oxides derived from aliphatic aldehydes into the corresponding Brook-type rearrangement products cannot be accomplished by cesium carbonate alone. We have clearly observed that our catalyst plays a crucial role in promoting this transformation and enabling the rearrangement step. Moreover, *insitu* slow generation of aldehyde from alcohol is essential for the formation of high yield of the desired compounds.

7.4. Radical quencing Test:



To an oven dried 100 mL seal tube , 4-methylbenzyl alcohol (0.5 mmol), $HPOPh_2$ (**1** mmol), Cs_2CO_3 (50 mol%), **Mn 1** (5 mol%) and radical inhibitor (TEMPO or BHT) were taken and connected with high vacuum for 10 minutes. Then 2 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100-200 mesh) with petroleum ether/ethyl acetate mixture (1:1) as eluent. Addition of TEMPO and BHT did not hamper the reaction indicating non-radical pathway.

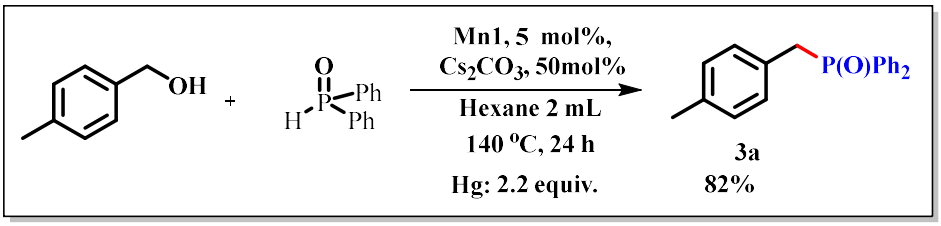
7.5. Hydride trapping experiment:



In an oven dried 100 mL seal tube , 4-methylbenzyl alcohol (0.5 mmol), $HPOPh_2$ (**1** mmol), Cs_2CO_3 (50 mol%), **Mn 1** (5 mol%) were added sequentially inside the argon filled glove box. Then reaction mixture was stirred at room temperature. After stirring for 20 mins, tritylium

tetrafluoroborate is added to the previous reaction mixture. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100-200 mesh) with petroleum ether/ethyl acetate mixture (1:1) as eluent. This result indicates the in-situ formation of Mn-H.

7.6. Homogeneity test:



To a 100 ml oven dried pressure tube containing magnetic stir bar 4-methylbenzyl alcohol (0.5 mmol), $HPOPh_2$ (**1** mmol), Cs_2CO_3 (50 mol%), **Mn 1** (5 mol%) were added followed by addition of Hg (1.1 mmol), and Hexane (2 mL). Tube was sealed under argon and placed in preheated oil bath at 120 ºC for 12 h. After completion of the reaction tube was cooled to room temperature and crude reaction mixture was filtered through small plug of celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100-200 mesh) with petroleum ether/ethyl acetate mixture (1:1) as eluent which resulted 82% of 3a formation and this indicates that our reaction protocol is homogeneous in nature.

7.7. Detection of evolved hydrogen gas by GC-Thermal Detector (GC-TCD):

To an oven dried 100 mL seal tube 4-methylbezyl alcohol, **1a** (5 mmol), $HPOPh_2$, **2b** (10 mmol), Cs_2CO_3 (50 mol%) and **Mn 1** (5 mol%) were taken and connected with high vacuum for 10 minutes. Then 10 mL Hexane were added to the mixture under argon. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h. After completion of the reaction, the Ace pressure tube was cooled at 0 °C, the evolved gas was syringed out and detected from PerkinElmer clarus-590 GC instrument using Elite-Q PLOT Capillary Column (30 m length x 530 µm x 20 µm ID) employing the following method:

TCD starting temperature: 40 °C

Oven temperature: 60 °C

Time at starting temperature: 0 min

Hold time: 5 min

Ramp: 28 °C/ min up to 200 °C

Flow rate: 5 mL/ min (N2)

Split ration: 20

Inlet temperature: 40 °C

Detector temperature TCD: 200 °C

The detected gas chromatogram was shown in figure S2 (right).

Oven temperature: 60 °C

Time at starting temperature: 0 min

Hold time: 5 min

Ramp: 28 °C/ min up to 200 °C

Flow rate: 5 mL/ min (N2)

Split ration: 20

Inlet temperature: 40 °C

Detector temperature TCD: 200 °C

The detected gas chromatogram was shown in figure S2 (right).

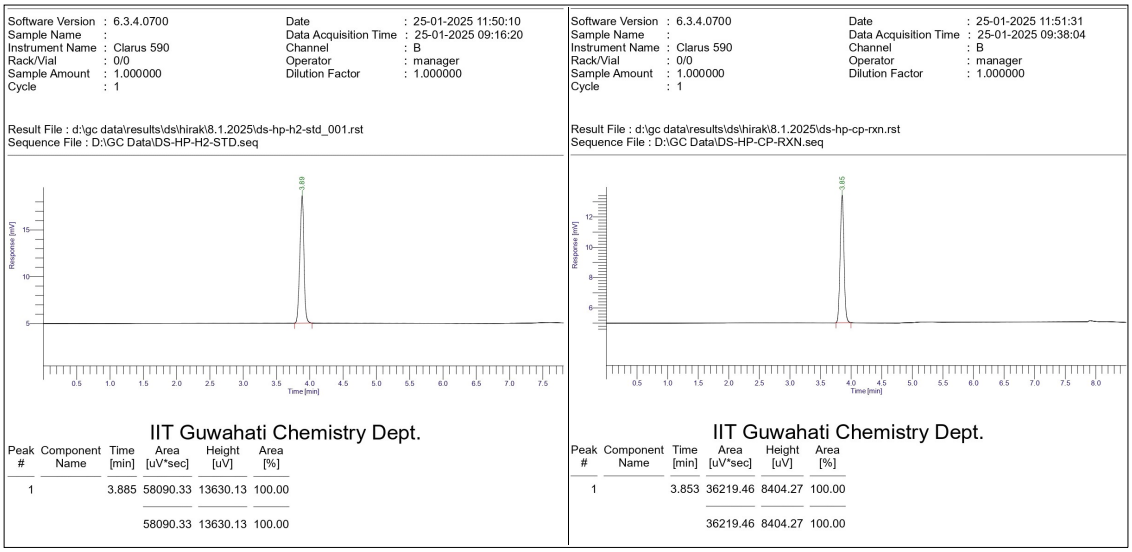
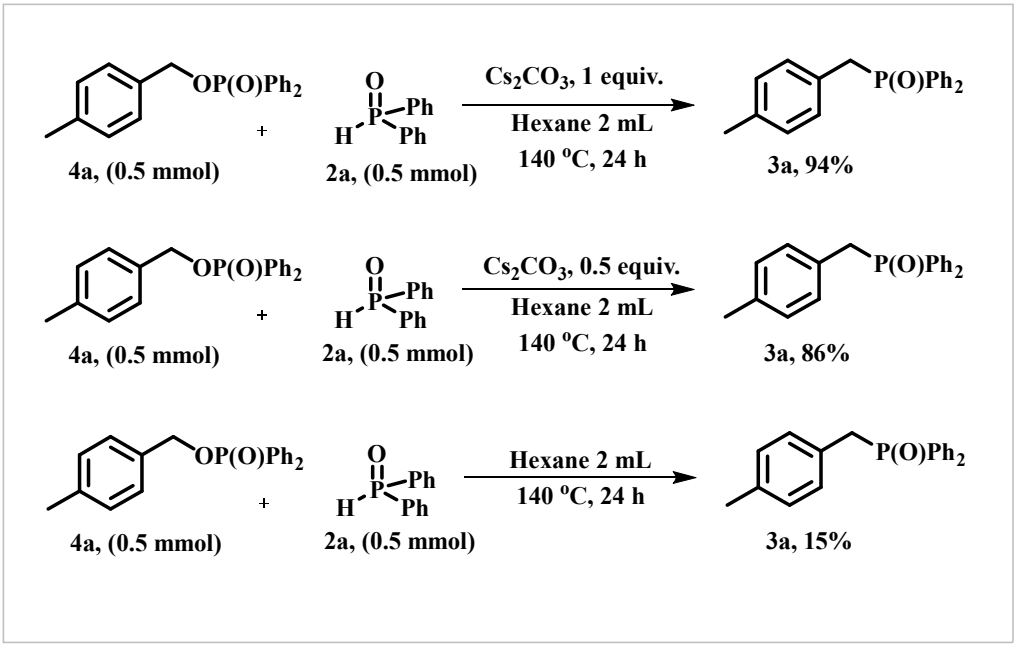
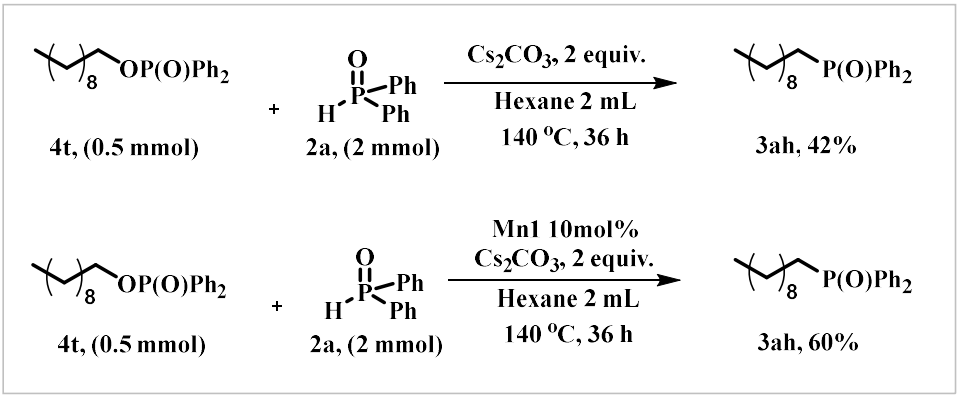


Figure S2. Chromatogram of standard hydrogen gas (left) and evolved hydrogen gas during catalysis (right).

7.8 Influence of base and catalyst in the substitution steps





8. Kinetic studies

8.1 Experimental procedure:

Nine different reactions were set up under the standard reaction condition and the reaction mixtures were analyzed by ^{1}H NMR after 1h, 2h, 4h, 6h, 10h, 14h, 18h, 22h and 24h respectively using CH_3NO_2 as external standard. The data was accomplished to draw the percentage (%) vs time (h) plot.

Time (h)	1a (%)	2a (%)	3a (%)	4a (%)
0	100	100	-	-

1	80	68	5	7
2	75	56	8	10
4	57	47.5	28	15
6	40	42.5	45	15
10	35	33.5	52	10
14	30	22.5	65	5
18	20	13.5	72	5
22	15	7.5	80	5
24	5	1.5	88	3.5

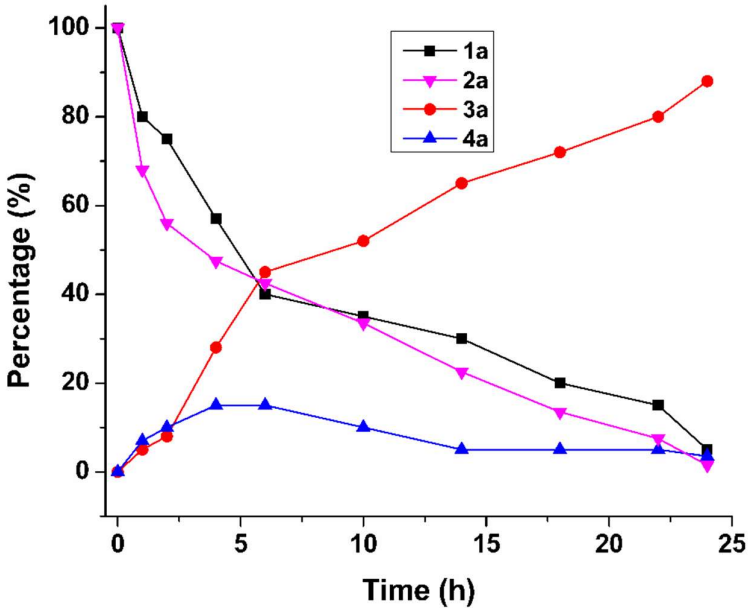
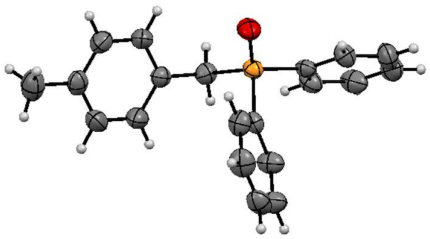


Fig. S3: Overall reaction kinetics.

9. SC-XRD data of substrate 3a and xx:

9.1. Crystal data of substrate 3a:



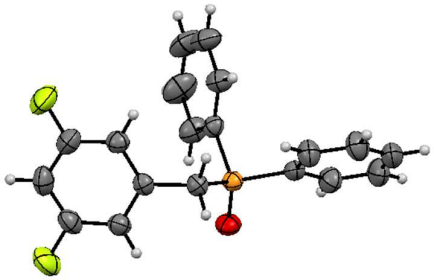
CCDC	2525491	
Empirical formula	C20 H19 O P	
Formula weight	306.34	
Temperature, T	295(2)	
Crystal system	monoclinic	
Space group	'P 1 21/c 1'	

Unit cell dimensions	a=5.7473(7)Å α=90° b=17.567(2) Å β=97.413(3)° c=16.107(2) Å γ=90°	
Volume, V ($Å^3$)	1612.6(4)	
Z	4	
Density (calculated), g cm^{-3}	1.262	
Absorption coefficient, μ (mm^{-1})	0.170	
F (000)	648.740	
Crystal size, mm^3	0.46 × 0.38 × 0.33	
Theta range for data collection	2.32 to 25.00	
Index ranges	-6 ≤ h ≤ 6 -20 ≤ k ≤ 20 -19 ≤ l ≤ 19	
Reflections collected	2797	
Independent reflections	2464	
Completeness to theta	0.9869	
Absorption correction	none	
Refinement method	'\f and \w scans'	
Data / restraints / parameters	2797 /0/ 200	
Goodness-of-fit on F^2	1.0837	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1075	
R indices (all data)	R1 = 0.0548, wR2 = 0.1125	
Largest diff. peak and hole	0.2960 and -0.3475 e·$Å^{-3}$	
Bond Distances [Å]	Bond angles [°]	
P001 O002 1.4841(17) P001 C003 1.808(2) P001 C004 1.804(2) P001 C008 1.809(2) C003 C009 1.381(3) C003 C00D 1.385(3) C004 C005 1.384(3) C004 C00B 1.389(3) C005 H005 0.9300 C005 C00J 1.394(4) C006 H006 0.9300 C006 C007 1.384(3) C006 C00A 1.378(4) C007 C008 1.513(3) C007 C00H 1.381(3) C008 H00a 0.9700 C008 H00b 0.9700 C009 H009 0.9300 C009 C00K 1.377(4) C00A H00c 0.9300 C00A C00C 1.379(4) C00B H00d 0.9300	C003 P001 O002 111.40(11) C004 P001 O002 112.39(10) C004 P001 C003 104.17(10) C008 P001 O002 113.79(11) C008 P001 C003 106.32(11) C008 P001 C004 108.15(11) C009 C003 P001 119.02(19) C00D C003 P001 122.42(18) C00D C003 C009 118.5(2) C005 C004 P001 124.83(19) C00B C004 P001 115.89(18) C00B C004 C005 119.2(2) H005 C005 C004 120.18(15) C00J C005 C004 119.6(2) C00J C005 H005 120.18(17) C007 C006 H006 119.53(15) C00A C006 H006 119.53(16) C00A C006 C007 120.9(2) C008 C007 C006 120.7(2) C00H C007 C006 117.6(2) C00H C007 C008 121.7(2) C007 C008 P001 110.24(16)	

C00B C00E 1.382(4) C00C C00I 1.379(4) C00C C00M 1.511(4) C00D H00e 0.9300 C00D C00L 1.382(4) C00E H00f 0.9300 C00E C00G 1.371(4) C00F H00g 0.9300 C00F C00K 1.366(4) C00F C00L 1.370(4) C00G H00h 0.9300 C00G C00J 1.367(4) C00H H00i 0.9300 C00H C00I 1.384(4) C00I H00j 0.9300 C00J H00k 0.9300 C00K H00l 0.9300 C00L H00m 0.9300 C00M H00n 0.9600 C00M H00o 0.9600 C00M H00p 0.9600	H00a C008 P001 109.61(8) H00a C008 C007 109.61(13) H00b C008 P001 109.61(8) H00b C008 C007 109.61(13) H00b C008 H00a 108.1 H009 C009 C003 119.62(15) C00K C009 C003 120.8(3) C00K C009 H009 119.62(17) H00c C00A C006 119.15(16) C00C C00A C006 121.7(3) C00C C00A H00c 119.15(16) H00d C00B C004 119.75(14) C00E C00B C004 120.5(2) C00E C00B H00d 119.75(17) C00I C00C C00A 117.3(2) C00M C00C C00A 120.7(3) C00M C00C C00I 122.0(3) H00e C00D C003 119.84(14) C00L C00D C003 120.3(2) C00L C00D H00e 119.84(17) H00f C00E C00B 120.10(17) C00G C00E C00B 119.8(3) C00G C00E H00f 120.10(17) C00K C00F H00g 120.05(16) C00L C00F H00g 120.05(17) C00L C00F C00K 119.9(3) H00h C00G C00E 119.76(17) C00J C00G C00E 120.5(3) C00J C00G H00h 119.76(16) H00i C00H C007 119.47(16) C00I C00H C007 121.1(3) C00I C00H H00i 119.47(16) C00H C00I C00C 121.4(3) H00j C00I C00C 119.31(16) H00j C00I C00H 119.31(16) C00G C00J C005 120.3(3) H00k C00J C005 119.85(17) H00k C00J C00G 119.85(16) C00F C00K C009 120.2(3) H00l C00K C009 119.90(17) H00l C00K C00F 119.90(16) C00F C00L C00D 120.3(3) H00m C00L C00D 119.87(17) H00m C00L C00F 119.87(17) H00n C00M C00C 109.5 H00o C00M C00C 109.5 H00o C00M H00n 109.5 H00p C00M C00C 109.5 H00p C00M H00n 109.5	

	H00p C00M H00o 109.5	

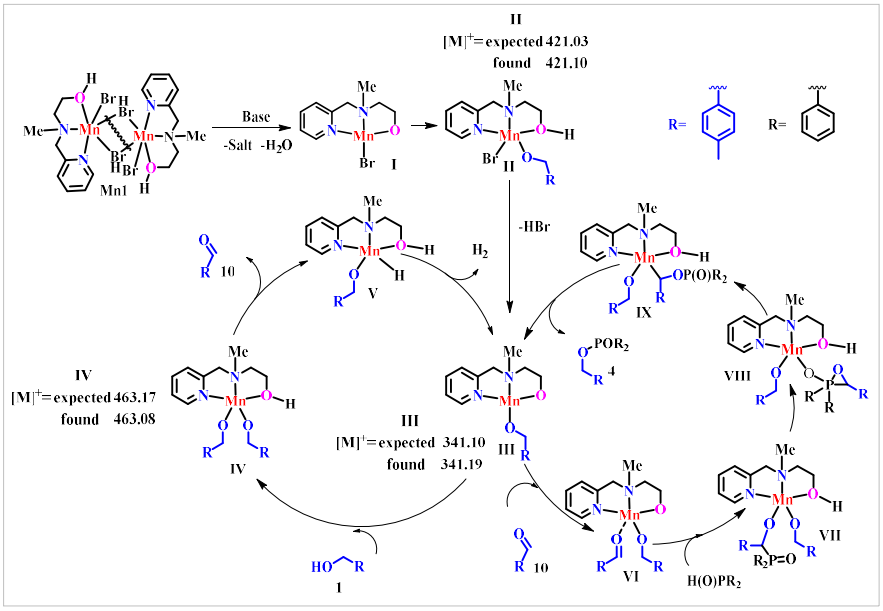
9.1. Crystal data of substrate 3r

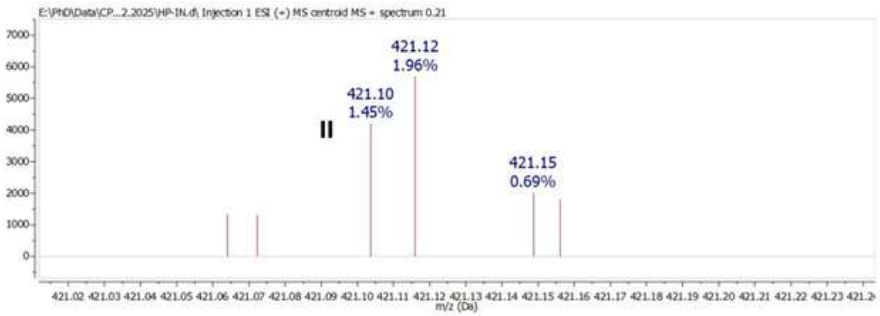


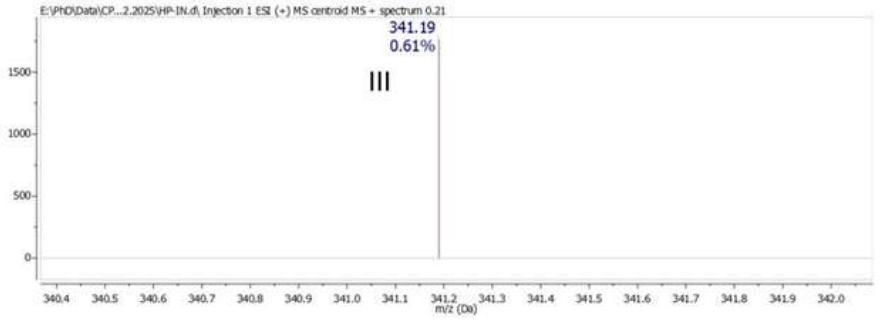
CCDC	2525490
Empirical formula	C19 H15 F2 O P
Formula weight	328.28
Temperature, T	295(2)
Crystal system	triclinic
Space group	'P -1'
Unit cell dimensions	a=5.8317(4)Å α=67.662(2) b=11.0586(8)Å β=81.084(2)° c=13.6838(10)Å γ=81.329(2)
Volume, V ($Å^3$)	802.30(10)
Z	2
Density (calculated), g cm^{-3}	1.359
Absorption coefficient, μ (mm^{-1})	0.193
F (000)	340
Crystal size, mm^3	0.46 × 0.38 × 0.33
Theta range for data collection	2.999 to 24.999
Index ranges	-6 ≤ h ≤ 6 -13 ≤ k ≤ 13 -16 ≤ l ≤ 16
Reflections collected	2783
Independent reflections	2552
Completeness to theta	0.988
Absorption correction	none
Refinement method	'\f and \w scans'
Data / restraints / parameters	2783 /0/ 208
Goodness-of-fit on F^2	0.695
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0983
R indices (all data)	R1 = 0.0359, wR2 = 0.1080
Largest diff. peak and hole	0.283 and -0.264 e·$Å^{-3}$
Bond Distances [Å]	Bond angles [°]
P001 O1 1.4843(11) P001 C007 1.8031(15) P001 C00A 1.8051(15) P001 C006 1.8098(15)	O1 P001 C007 111.85(7) O1 P001 C00A 111.81(7) C007 P001 C00A 105.70(7) O1 P001 C006 113.97(7)

F1 C00G 1.355(2) F2 C00F 1.359(2) C005 C009 1.390(2) C005 C008 1.390(2) C005 C006 1.508(2) C007 C00I 1.378(2) C007 C00B 1.388(2) C008 C00G 1.373(2) C009 C00F 1.371(2) C00A C00C 1.382(2) C00A C00D 1.388(2) C00B C00K 1.384(3) C00C C00E 1.387(2) C00D C00L 1.379(3) C00E C00J 1.372(3) C00F C00H 1.370(3) C00G C00H 1.370(3) C00I C00N 1.390(3) C00J C00L 1.373(3) C00K C00M 1.370(3) C00M C00N 1.365(3)	C007 P001 C006 106.48(7) C00A P001 C006 106.49(7) C009 C005 C008 119.68(14) C009 C005 C006 119.15(14) C008 C005 C006 121.17(14) C005 C006 P001 112.58(10) C00I C007 C00B 119.29(15) C00I C007 P001 118.66(13) C00B C007 P001 122.02(12) C00G C008 C005 118.36(15) C00F C009 C005 118.61(16) C00C C00A C00D 118.70(15) C00C C00A P001 124.67(12) C00D C00A P001 116.63(12) C00K C00B C007 119.96(18) C00A C00C C00E 120.45(16) C00L C00D C00A 120.62(17) C00J C00E C00C 120.06(18) F2 C00F C00H 117.92(16) F2 C00F C009 118.45(17) C00H C00F C009 123.63(16) F1 C00G C00H 117.87(16) F1 C00G C008 118.42(17) C00H C00G C008 123.71(16) C00F C00H C00G 116.00(16) C007 C00I C00N 120.07(19) C00E C00J C00L 120.03(17) C00M C00K C00B 120.2(2) C00J C00L C00D 120.14(17) C00N C00M C00K 120.27(18) C00M C00N C00I 120.2(2)

10. Mass spectrometric data of catalytic intermediate:







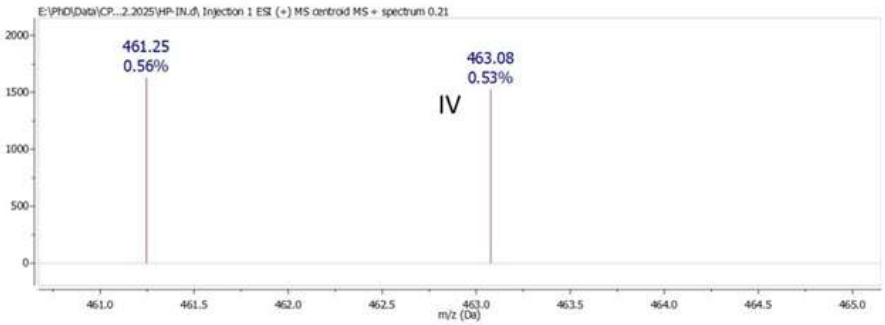
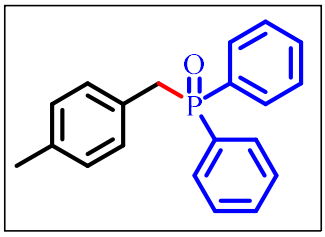


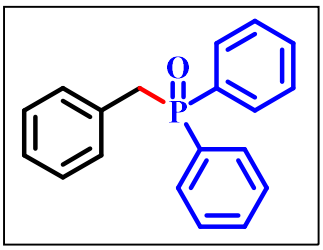
Figure S4: Mass spectrometric data of catalytic intermediate

10. NMR data of substrate scope:

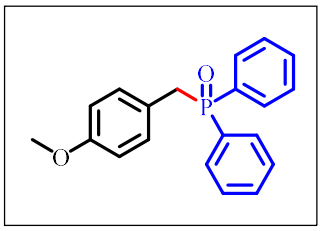
(4-Methylbenzyl)diphenylphosphine oxide (3a):[7] Isolated as white solid; Yield: 138 mg (90%); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.72– 7.67 (m, 4H), 7.52 – 7.48 (m, 2H), 7.45 – 7.42 (m, 4H), 6.99 (s, 4H), 3.61 (d, J = 13.6 Hz, 2H), 2.25 (d, J = 1.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.5 (d, J_{C-P} = 3.0 Hz), 132.6 (d, J_{C-P} = 98.6 Hz), 131.9(d, J_{C-P} = 2.5 Hz), 131.3 (d, J_{C-P} = 8.9 Hz), 130.1 (d, J_{C-P} = 5.2 Hz), 129.2 (d, J_{C-P} = 2.3 Hz), 128.6 (d, J_{C-P} = 11.6 Hz), 128.0 (d, J_{C-P} = 8.0 Hz), 37.8 (d, J_{C-P} = 66.6 Hz), 21.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.4.



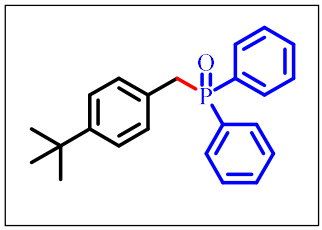
Benzyldiphenylphosphine oxide (3b):[7] Isolated as white solid; Yield: 105 mg (72%); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.70 – 7.66 (m, 4H), 7.51 – 7.47 (m, 2H), 7.43 – 7.40 (m, 4H), 7.17 – 7.16 (m, 3H), 7.10 – 7.09 (s, 2H), 3.65 (d, J = 13.1 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 132.3 (d, J_{C-P} = 99.1 Hz), 131.9, 131.2 (d, J_{C-P} = 8.4 Hz), 131.2, 130.2 (d, J_{C-P} = 4.4 Hz), 128.6 (d, J_{C-P} = 11.3 Hz), 128.5, 126.9, 38.2 (d, J_{C-P} = 66.0 Hz).**^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.6.



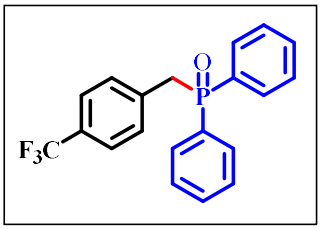
(4-Methoxybenzyl)diphenylphosphine oxide (3c):[8] Isolated as white solid; Yield: 126 mg (78%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.69 – 7.66 (m, 4H), 7.51 – 7.49 (m, 2H), 7.44 – 7.41 (m, 4H), 7.0 (d, J = 7.5 Hz, 2H), 6.72 (d, J = 7.0 Hz, 2H), 3.73 (s, 3H), 3.59 (d, J = 13.1 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.6 (d, J_{C-P} = 2.6 Hz), 132.5 (d, J_{C-P} = 97.3 Hz), 131.9 (d, J_{C-P} = 2.4 Hz) 131.3 (d, J_{C-P} = 8.9 Hz), 131.2 (d, J_{C-P} = 5.0 Hz), 128.6 (d, J_{C-P} = 11.5 Hz), 123.0 (d, J_{C-P} = 7.9 Hz), 114.0 (d, J_{C-P} = 2.1 Hz), 55.3, 37.2 (d, J_{C-P} = 67.3 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.6.



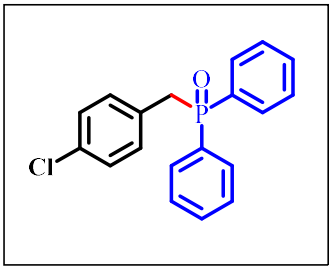
(4-(Tert-butyl)benzyl)diphenylphosphine oxide (3f):[8] Isolated as white solid; Yield: 146 mg (84%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.71 – 7.67 (m, 4H), 7.52 – 7.49 (m, 2H), 7.45 – 7.42 (m, 4H), 7.20 (d, J = 7.7 Hz, 2H), 7.02 (d, J = 7.5 Hz, 2H), 3.63 (d, J = 13.4 Hz, 2H), 1.2 (s, 9H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 149.8 (d, J_{C-P} = 3.1 Hz), 132.6 (d, J_{C-P} = 98.1 Hz), 131.9 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 129.9 (d, J_{C-P} = 5.1 Hz), 128.6 (d, J_{C-P} = 11.5 Hz), 128.0 (d, J_{C-P} = 7.9 Hz), 125.5 (d, J_{C-P} = 2.5 Hz), 37.6 (d, J_{C-P} = 66.5 Hz), 34.5, 31.4. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.7.



Diphenyl(4-(trifluoromethyl)benzyl)phosphine oxide (3g):[8] Isolated as white solid; Yield: 94 mg (61%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.71 – 7.68 (m, 4H), 7.54 – 7.51 (m, 2H), 7.47 – 7.42 (m, 6H), 7.23 – 7.21 (m, 2H), 3.70 (d, J = 13.2 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 135.7 (d, J_{C-P} = 7.3 Hz), 132.2 (d, J_{C-P} = 2.1 Hz), 132.0 (d, J_{C-P} = 100.0 Hz), 131.2 (d, J_{C-P} = 8.9 Hz), 130.5 (d, J_{C-P} = 4.6 Hz), 129.2 (qd, J_{C-F} = 33.2 Hz, J_{C-P}=2.5 Hz), 128.8 (d, J_{C-P} = 11.6 Hz), 125.4 (q, J_{C-F} = 4.7 Hz), 124.2 (q, J_{C-F} = 270.3 Hz), 38.2 (d, J_{C-P} = 65.9 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.0. **^{19}F NMR (470 MHz, CDCl$_3$)** δ -62.5.

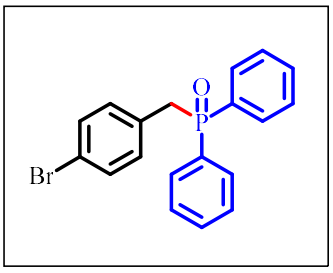


(4-Fluorobenzyl)diphenylphosphine oxide (3h):[8] Isolated as white solid; Yield: 96 mg (62%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.70 – 7.66 (m, 4H), 7.53 – 7.50 (m, 2H), 7.45 – 7.42 (m, 4H), 7.07 – 7.05 (m, 2H), 6.87 (t, J = 8.4 Hz, 2H), 3.61 (d, J = 13.2 Hz, 2H).**^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.0 (dd, J_{C-F} = 243.9 Hz, J_{C-P} = 3.2 Hz), 132.2 (d, J_{C-P} = 98.3 Hz), 132.0 (d, J_{C-P} = 2.6 Hz), 131.7 (dd, J_{C-F} = 7.9 Hz, J_{C-P} = 5.1 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 128.7 (d, J_{C-P} = 11.6 Hz), 126.9 (dd, J_{C-F} = 7.9 Hz, J_{C-P} = 3.1 Hz), 115.4 (dd, J_{C-F} = 21.5 Hz, J_{C-P} = 2.4 Hz), 37.3 (d, J_{C-P} = 66.3 Hz), **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.32. **^{19}F NMR (470 MHz, CDCl$_3$)** δ -115.9 (d, J_{P-F} = 4.4 Hz).

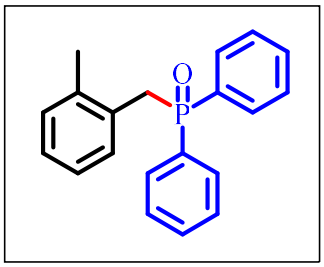


(4-Chlorobenzyl)diphenylphosphine oxide (3i):[7] Isolated as white solid; Yield: 106 mg (65%); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.70 – 7.66 (m, 4H), 7.53 – 7.50 (m, 2H), 7.46 – 7.42 (m, 4H), 7.15 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 3.61 (d, J = 13.5 Hz, 2H).**^{13}C NMR (125 MHz, CDCl$_3$)** δ 133.0 (d, J_{C-P} = 3.4 Hz), 132.2 (d, J_{C-P} = 98.6 Hz), 132.1(d, J_{C-P} = 2.4 Hz), 131.5(d, J_{C-P} = 5.0 Hz), 131.2(d, J_{C-P} = 9.0 Hz), 129.8(d, J_{C-P} = 7.8 Hz), 128.8, 128.7(d, J_{C-P} = 4.0 Hz), 37.6(d, J_{C-P} = 65.7 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.1.

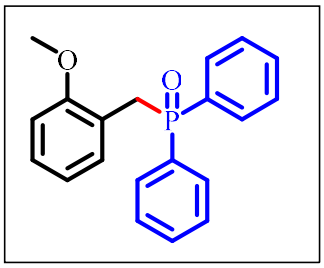
(4-Bromobenzyl)diphenylphosphine oxide (3j):[8] Isolated as white solid; Yield: 111 mg (60%); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.70 – 7.65 (m, 4H), 7.55 – 7.50 (m, 2H), 7.47 – 7.42 (m, 4H), 7.30 (d, J = 8.0 Hz, 2H), 6.99 – 6.96 (m, 2H), 3.59 (d, J = 13.5 Hz, 2H).**^{13}C NMR (125 MHz, CDCl$_3$)** δ 132.1 (d, J_{C-P} = 99.1 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 5.1 Hz), 131.6 (d, J_{C-P} = 2.4 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 130.9 (d, J_{C-P} = 7.8 Hz), 128.7 (d, J_{C-P} = 11.7 Hz), 121.1(d, J_{C-P} = 3.8 Hz), 37.7(d, J_{C-P} = 65.5 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.0.



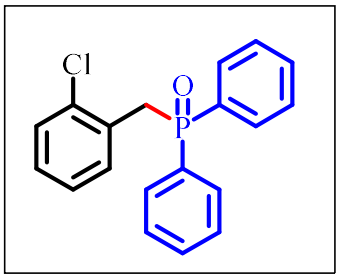
(2-Methylbenzyl)diphenylphosphine oxide (3k):[7] Isolated as white solid; Yield: 107 mg (70%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.69 – 7.65 (m, 4H), 7.53 – 7.50 (m, 2H), 7.45 – 7.42 (m, 4H), 7.09 – 7.07 (m, 2H), 7.00 – 6.94 (m, 2H), 3.67 (d, J = 13.9 Hz, 2H), 2.14 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 137.5 (d, J_{C-P} = 5.4 Hz), 132.6 (d, J_{C-P} = 97.2 Hz), 131.9 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 131.3 (d, J_{C-P} = 4.4 Hz), 130.6 (d, J_{C-P} = 2.6 Hz), 129.8 (d, J_{C-P} = 8.1 Hz), 128.6 (d, J_{C-P} = 11.4 Hz), 127.1 (d, J_{C-P} = 3.2 Hz), 125.9 (d, J_{C-P} = 2.8 Hz), 35.4 (d, J_{C-P} = 66.1 Hz), 20.2. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.6.



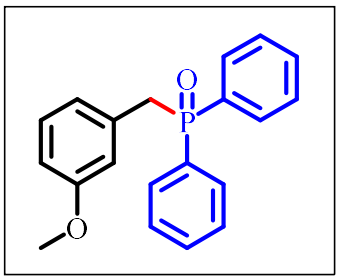
(2-Methoxybenzyl)diphenylphosphine oxide(3l):[12] Isolated as white solid; Yield: 105 mg (65 %); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.72 – 7.68 (m, 4H), 7.48 – 7.45 (m, 2H), 7.41 – 7.34 (m, 5H), 7.16 – 7.12 (m, 1H), 6.88 – 6.84 (m, 1H), 6.66 – 6.64 (m, 1H), 3.75 (d, J = 14.0 Hz, 2H), 3.45 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 157.0 (d, J_{C-P} = 5.1 Hz), 133.0 (d, J_{C-P} = 98.0 Hz), 131.8 (d, J_{C-P} = 4.9 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 9.1 Hz), 128.3 (d, J_{C-P} = 11.5 Hz), 128.2 (d, J_{C-P} = 3.9 Hz), 120.7 (d, J_{C-P} = 2.8 Hz), 120.0 (d, J_{C-P} = 7.9 Hz), 110.3 (d, J_{C-P} = 2.4 Hz), 55.0, 31.2 (d, J_{C-P} = 67.5 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 30.07.



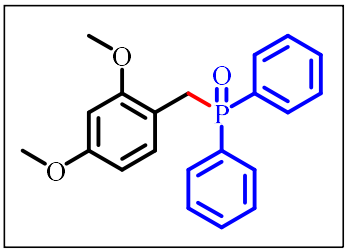
(2-Chlorobenzyl)diphenylphosphine oxide(3m):[10] Isolated as white solid; Yield: 98 mg (60%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.72 – 7.68 (m, 4H), 7.54 – 7.49 (m, 3H), 7.44 – 7.41 (m, 4H), 7.23 – 7.22 (m, 1H), 7.18 – 7.10 (m, 2H), 3.87 (d, J = 13.8 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 133.4 (d, J_{C-P} = 6.8 Hz), 131.2 (d, J_{C-P} = 99.0 Hz), 131.1 (d, J_{C-P} = 4.1 Hz), 131.1 (d, J_{C-P} = 2.7 Hz), 130.3 (d, J_{C-P} = 9.3 Hz), 128.8 (d, J_{C-P} = 6.9 Hz), 128.53 (d, J_{C-P} = 2.0 Hz), 127.6 (d, J_{C-P} = 11.6 Hz), 127.4 (d, J_{C-P} = 2.6 Hz), 126.0 (d, J_{C-P} = 2.3 Hz), 33.7 (d, J_{C-P} = 66.8 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.7.



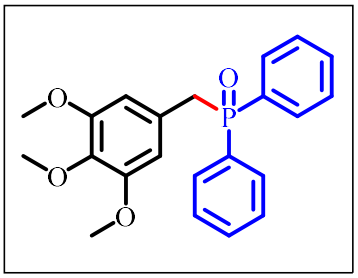
(3-Methoxybenzyl)diphenylphosphine oxide(3n):[11] Isolated as white solid; Yield: 110 mg (68 %); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.71 – 7.67 (m, 4H), 7.52 – 7.49 (m, 2H), 7.45 – 7.42 (m, 4H), 7.07 (t, J = 8.2 Hz, 1H), 6.72-6.67 (m, 2H), 6.62 (s, 1H), 3.64 (s, 3H), 3.64 – 3.61 (m, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 159.5 (d, J_{C-P} = 2.1 Hz), 132.7 (d, J_{C-P} = 7.6 Hz), 132.4 (d, J_{C-P} = 97.3 Hz), 131.9 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 8.9 Hz),129.4 (d, J_{C-P} = 2.3 Hz), 128.6 (d, J_{C-P} = 11.6 Hz), 122.7 (d, J_{C-P} = 5.3 Hz), 115.3 (d, J_{C-P} = 4.9 Hz), 113.2 (d, J_{C-P} = 2.8 Hz), 55.2, 38.3 (d, J_{C-P} = 66.2 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.5.



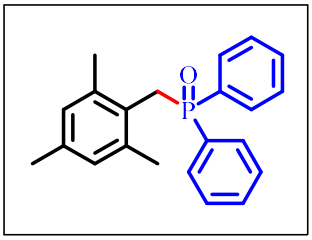
(2,4-Dimethoxybenzyl)diphenylphosphine oxide (3o): Isolated as white solid; Yield: 110 mg (62 %); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.71 – 7.67 (m, 4H), 7.48 - 7.45 (m, 2H), 7.41 – 7.38 (m, 4H), 7.28 – 7.26 (m, 1H), 6.4 (d, *J*=8.2 Hz, 1H), 6.24 (s, 1H)3.75 (s, 3H), 3.67 (d, *J* = 13.6 Hz, 2H), 3.42 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 160.0 (d, J_{C-P} = 2.7 Hz), 157.8 (d, J_{C-P} = 5.3 Hz), 133.0 (d, J_{C-P} = 97.7 Hz), 132.1 (d, J_{C-P} = 4.5 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 9.1 Hz), 128.3 (d, J_{C-P} = 11.4 Hz), 112.2 (d, J_{C-P} = 7.8 Hz), 104.4 (d, J_{C-P} = 2.6 Hz), 98.4 (d, J_{C-P} = 2.2 Hz), 55.4, 55.0 30.4 (d, J_{C-P} = 68.4 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 30.2. **HRMS (ESI+):** m/z calcd. $C_{21}H_{21}O_3P$ For $[M+H]^+$: 353.1302; Found: 353.1278.



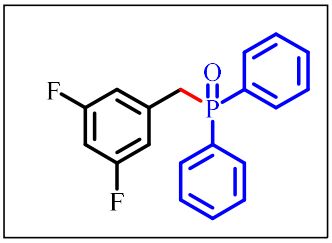
Diphenyl(3,4,5-trimethoxybenzyl)phosphine oxide (3p):[7] Isolated as white solid; Yield: 130 mg (68 %); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.73 – 7.69 (m, 4H), 7.52 – 7.50 (m, 2H), 7.47 – 7.44 (m, 4H), 6.24 – 6.23 (m, 2H), 3.77 (s, 3H), 3.60 (s, 6H), 3.59 (d, *J* = 13.1 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 152.9 (d, J_{C-P} = 2.7 Hz), 136.9 (d, J_{C-P} = 3.5 Hz), 132.2 (d, J_{C-P} = 98.5 Hz), 131.9 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 128.6 (d, J_{C-P} = 11.5 Hz), 126.6 (d, J_{C-P} = 7.9 Hz), 107.3 (d, J_{C-P} = 5.3 Hz), 60.9, 56.0, 38.4 (d, J_{C-P} = 66.3 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.5.



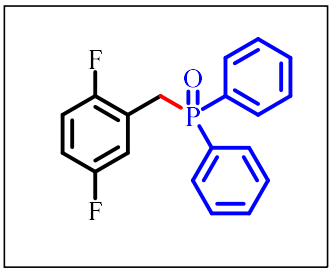
Diphenyl(2,4,6-trimethylbenzyl)phosphine oxide (3q):[14] Isolated as white solid; Yield: 134 mg (80 %); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.67 – 7.64 (m, 4H), 7.53- 7.50 (m, 2H), 7.44 – 7.41 (m, 4H), 6.77 (s, 2H), 3.71 (d, *J* = 13.8 Hz, 2H), 2.24 (s, 3H), 1.99 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 137.8 (d, J_{C-P} = 4.6 Hz), 136.2 (d, J_{C-P} = 3.4 Hz), 133.2 (d, J_{C-P} = 96.3 Hz) 131.9 (d, J_{C-P} = 2.5 Hz), 131.3 (d, J_{C-P} = 8.9 Hz), 129.2 (d, J_{C-P} = 2.9 Hz), 128.5 (d, J_{C-P} = 11.4 Hz), 125.6 (d, J_{C-P} = 8.7 Hz), 33.0 (d, J_{C-P} = 66.5 Hz), 21.0, 20.8. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 28.7.



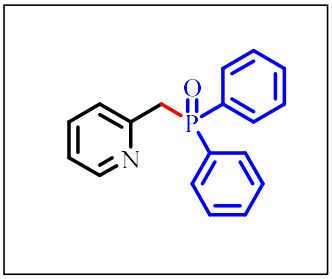
(3,5-Difluorobenzyl)diphenylphosphine oxide(3r): Isolated as white solid; Yield: 99 mg (60 %); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.65 – 7.60 (m, 4H), 7.47 – 7.44 (m, 2H), 7.40 -7.36 (m, 4H), 6.58 – 6.57 (m, 2H), 6.55 – 6.51 (m, 1H), 3.54 (d, *J* = 13.5 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.8 (ddd, J_{C-F} = 246.8 Hz, J_{C-F} = 12.8 Hz, J_{C-P} = 2.7 Hz), 135.2 (m), 132.2 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 99.6 Hz), 131.1 (d, J_{C-P} = 9.2 Hz), 128.8 (d, J_{C-P} = 11.8 Hz), 113.2 (dt, J_{C-F} = 20.0 Hz, J_{C-F} = 5.5 Hz), 102.6 (td, J_{C-F} = 24.9 Hz, J_{C-P} = 2.9 Hz), 38.3 (d, J_{C-P} = 65.8 Hz, J_{C-F} = 1.8 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 28.7. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -109.9. **HRMS (ESI+):** m/z calcd. $C_{19}H_{15}F_2OP$ For $[M+H]^+$: 329.0902; Found: 329.0880.



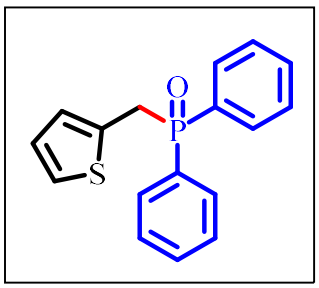
(2,5-Difluorobenzyl)diphenylphosphine oxide(3s): Isolated as white solid; Yield: 102 mg (62 %); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.75 – 7.70 (m, 4H), 7.54 – 7.49 (m, 2H), 7.47 – 7.42 (m, 4H), 7.18 – 7.13 (m, 1H), 6.85 – 6.81 (m, 2H), 3.66 (d, J = 13.6 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 158.4 (dt, $J_{C–F}$ = 241.2 Hz, $J_{C–F}$ = 2.6 Hz), 156.8 (ddd, $J_{C–F}$ = 240.2 Hz, $J_{C–F}$ = 6.0 Hz, $J_{C–F}$ = 2.2 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 132.0(d, J_{C-P} = 99.7 Hz), 131.1 (d, J_{C-P} = 9.3 Hz) 128.7 (d, J_{C-P} = 11.8 Hz), 120.6 (dt, J_{C-F} = 17.9 Hz, J_{C-F} = 7.9 Hz), 118.56 (dt, J_{C-F} = 24.7 Hz, J_{C-F} = 4.0 Hz), 116.1(ddd, $J_{C–F}$ = 25.2 Hz, $J_{C–F}$ = 8.6 Hz, $J_{C–P}$ = 2.3 Hz), 115.3 (ddd, $J_{C–F}$ = 24.0 Hz, $J_{C–F}$ = 8.5 Hz, $J_{C–P}$ = 2.8 Hz), 30.5 (d, J_{C-P} = 66.4 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.05. **^{19}F NMR (470 MHz, CDCl$_3$)** δ -118.3 (dd, $J_{C–P}$ = 17.4 Hz, $J_{C–P}$ = 1.4 Hz), -123.1 (dd, $J_{C–P}$ = 17.3 Hz, $J_{C–P}$ = 2.6 Hz). **HRMS (ESI+):** m/z calcd. $C_{19}H_{15}F_2OP$ For $[M+H]^+$: 329.0902; Found: 329.0880.



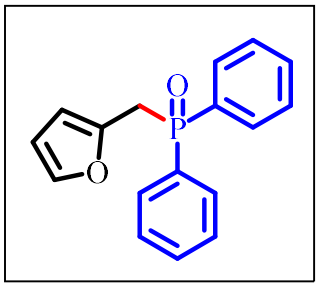
Diphenyl(pyridin-2-ylmethyl)phosphine oxide(3t)[9] Isolated as white solid; Yield: 81 mg (55 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.38 – 8.37 (m, 1H), 7.77 – 7.3 (m, 4H), 7.56 – 7.53 (m, 1H), 7.50 – 7.47 (m, 3H), 7.44 – 7.41 (m, 4H), 7.08 – 7.06 (m, 1H), 3.94 (d, J = 14.1 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 152.6 (d, $J_{C–P}$ = 7.2 Hz), 149.3, 136.4 (d, $J_{C–P}$ = 2.1 Hz), 132.4 (d, $J_{C–P}$ = 100 Hz), 131.9 (d, $J_{C–P}$ = 2.7 Hz), 131.2 (d, $J_{C–P}$ = 9.4 Hz), 128.5 (d, $J_{C–P}$ = 11.8 Hz), 125.1 (d, $J_{C–P}$ = 3.4 Hz), 121.9 (d, $J_{C–P}$ = 2.4 Hz), 41.0 (d, $J_{C–P}$ = 64.0 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.8.



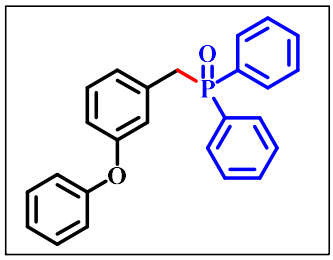
Diphenyl(thiophen-2-ylmethyl)phosphine oxide(3u):[9] Isolated as white solid; Yield: 102 mg (68 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.74 – 7.70 (m, 4H), 7.53 – 7.50 (m, 2H), 7.46 – 7.43 (m, 4H), 7.08 – 7.07 (m, 1H), 6.86 – 6.83 (m, 2H), 3.79 (d, J = 13.1 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 132.0 (d, $J_{C–P}$ = 2.8 Hz), 131.9 (d, $J_{C–P}$ = 8.6 Hz), 131.8 (d, $J_{C–P}$ = 99.1 Hz), 131.2 (d, $J_{C–P}$ = 9.1 Hz), 128.6 (d, $J_{C–P}$ = 11.8 Hz), 127.9 (d, $J_{C–P}$ = 6.4 Hz), 127.1 (d, $J_{C–P}$ = 2.8 Hz), 124.9 (d, $J_{C–P}$ = 3.1 Hz), 32.6 (d, $J_{C–P}$ = 68.3 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 28.5.



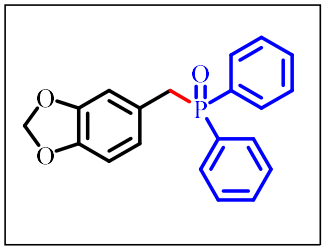
(Furan-2-ylmethyl)diphenylphosphine oxide(3v):[9] Isolated as white solid; Yield: 99 mg (70 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.72 – 7.68 (m, 4H), 7.55 – 7.52 (m, 2H), 7.47 – 7.44 (m, 4H), 7.24 (s, 1H), 6.24 (s, 1H), 6.09 (s, 1H), 3.76 (d, J = 14.0 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 145.4 (d, J_{C-P} = 7.9 Hz), 142.1 (d, J_{C-P} = 2.9 Hz), 132.1 (d, J_{C-P} = 2.9 Hz), 132.1 (d, J_{C-P} = 100 Hz), 131.2 (d, J_{C-P} = 9.3 Hz), 128.7 (d, J_{C-P} = 11.7 Hz), 111.0 (d, J_{C-P} = 2.7 Hz), 109.2 (d, J_{C-P} = 5.9 Hz), 31.5 (d, J_{C-P} = 68.9 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 28.3.



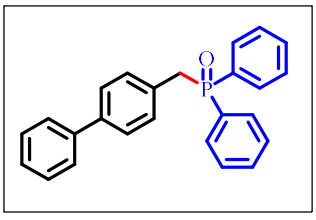
(3-Phenoxybenzyl)diphenylphosphine oxide(3x): Isolated as white solid; Yield: 150 mg (78 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.70 – 7.66 (m, 4H), 7.52 – 7.49 (m, 2H), 7.44 – 7.41 (m, 4H), 7.28 – 7.24 (m, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 6.83 – 6.80 (m, 3H), 6.65 (s, 1H), 3.62 (d, J = 13.7 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.14, 157.1 (d, J_{C-P} = 2.7 Hz), 133.1 (d, J_{C-P} = 7.8 Hz), 132.3 (d, J_{C-P} = 98.7 Hz), 131.9 (d, J_{C-P} = 2.8 Hz), 131.2 (d, J_{C-P} = 9.0 Hz), 129.8 (d, J_{C-P} = 2.6 Hz), 129.7, 128.6 (d, J_{C-P} = 11.7 Hz), 125.3 (d, J_{C-P} = 5.0 Hz), 123.2, 120.6 (d, J_{C-P} = 5.4 Hz), 118.9, 117.6 (d, J_{C-P} = 2.9 Hz), 38.2 (d, J_{C-P} = 65.8 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.36. **HRMS (ESI+):** m/z calcd. $C_{25}H_{21}O_2P$ For $[M+H]^+$: 385.1352; Found: 385.1344.



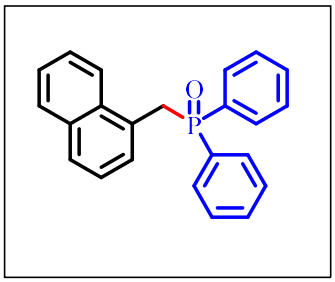
(Benzo[d][1,3]dioxol-5-ylmethyl)diphenylphosphino oxide(3y):[9] Isolated as white solid; Yield: 118 mg (70 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.71 – 7.68 (m, 4H), 7.53 – 7.50 (m, 2H), 7.46 – 7.43 (m, 4H), 6.64 – 6.61 (m, 2H), 6.52 (d, J = 7.9 Hz, 1H), 5.88 (s, 2H), 3.57 (d, J = 13.3 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 147.6 (d, J_{C-P} = 2.4 Hz), 146.6 (d, J_{C-P} = 2.9 Hz), 132.8, 131.9 (d, J_{C-P} = 3.0 Hz), 131.2 (d, J_{C-P} = 9.0 Hz), 128.6 (d, J_{C-P} = 11.5 Hz), 124.5 (d, J_{C-P} = 8.1 Hz), 123.4 (d, J_{C-P} = 6.0 Hz), 110.6 (d, J_{C-P} = 4.7 Hz), 108.3 (d, J_{C-P} = 2.7 Hz), 101.0, 37.8 (d, J_{C-P} = 67.1 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.4.



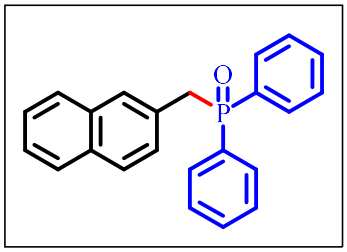
([1,1'-Biphenyl]-4-ylmethyl)diphenylphosphine oxide(3z):[7] Isolated as white solid; Yield: 174 mg (95 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.74 – 7.70 (m, 4H), 7.54 – 7.50 (m, 4H), 7.46 – 7.39 (m, 8H), 7.31 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 7.7 Hz, 2H), 3.70 (d, J = 13.6 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.8 (d, J_{C-P} = 1.2 Hz), 139.7 (d, J_{C-P} = 3.0 Hz), 132.4 (d, J_{C-P} = 98.5 Hz), 132.0 (d, J_{C-P} = 2.8 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 130.6 (d, J_{C-P} = 5.2 Hz), 130.3 (d, J_{C-P} = 8 Hz), 128.9, 128.7 (d, J_{C-P} = 11.6 Hz), 127.4, 127.2 (d, J_{C-P} = 2.6 Hz), 127.1, 37.9 (d, J_{C-P} = 65.8 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.5.



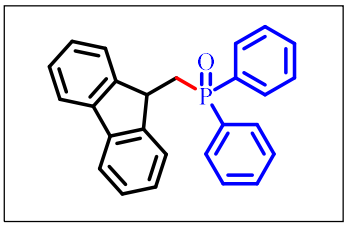
(Naphthalen-1-ylmethyl)diphenylphosphine oxide(3aa):[8] Isolated as white solid; Yield: 141 mg (82 %)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.66 (m, 5H), 7.47 – 7.44 (m, 2H), 7.40 – 7.34 (m, 6H), 7.25 – 7.22 (m, 2H), 4.11 (d, *J* = 13.9 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 133.8 (d, J_{C-P} = 1.9 Hz), 132.5 (d, J_{C-P} = 4.3 Hz), 132.4 (d, J_{C-P} = 98.3 Hz), 131.8 (d, J_{C-P} = 2.6 Hz), 131.2 (d, J_{C-P} = 9 Hz), 128.7 (d, J_{C-P} = 6.1 Hz), 128.6, 128.5, 127.8 (d, J_{C-P} = 8.2 Hz), 127.7 (d, J_{C-P} = 3.1 Hz), 126.0, 125.6, 125.1 (d, J_{C-P} = 3.0 Hz), 124.4, 35.0 (d, J_{C-P} = 66.5 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.5.



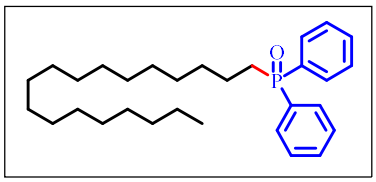
(Naphthalen-2-ylmethyl)diphenylphosphine oxide(3ab)[7] Isolated as white solid; Yield: 137 mg (80 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.75 – 7.71 (m, 5H), 7.66 – 7.65 (m, 2H), 7.56 (s, 1H), 7.51 – 7.48 (m, 2H), 7.43 – 7.40 (m, 6H), 7.25 – 7.22 (m, 1H), 3.81 (d, *J* = 13.8 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 133.4 (d, J_{C-P} = 2.4 Hz), 133.4 (d, J_{C-P} = 99.0 Hz), 132.3 (d, J_{C-P} = 2.0 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 129.1 (d, J_{C-P} = 6.7 Hz), 128.8 (d, J_{C-P} = 7.9 Hz), 128.6 (d, J_{C-P} = 11.7 Hz), 128.3 (d, J_{C-P} = 4.2 Hz), 128.0 (d, J_{C-P} = 1.8 Hz), 127.75, 127.7, 126.1, 125.8, 38.8 (d, J_{C-P} = 66.2 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.4.



((9H-Fluoren-9-yl)methyl)diphenylphosphine oxide(3ac):[7] Isolated as white solid; Yield: 152 mg (80 %) **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 – 7.80 (m, 4H), 7.62 (d, *J* = 7.5 Hz, 4H), 7.45 – 7.39 (m, 6H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.20 – 7.17 (m, 2H), 4.27-4.20 (m, 1H), 2.80 – 2.74 (m, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 147.0 (d, J_{C-P} = 6.8 Hz), 140.3, 133.5, 132.7, 131.7 (d, J_{C-P} = 2.7 Hz), 130.8 (d, J_{C-P} = 9.0 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 127.2 (d, J_{C-P} = 10.8 Hz), 125.3, 119.6, 40.8 (d, J_{C-P} = 3.8 Hz), 34.5 (d, J_{C-P} = 69.8 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 30.8.



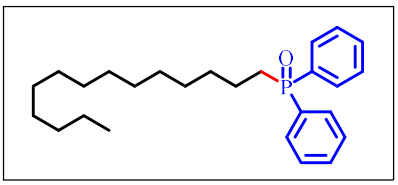
Octadecyldiphenylphosphine oxide(3ad) Isolated as white solid; Yield: 205 mg (90 %) **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.74 – 7.70 (m, 4H), 7.51 – 7.42 (m, 6H), 2.27 – 2.20 (m, 2H), 1.65 – 1.55 (m, 2H), 1.40 – 1.33 (m, 2H), 1.27 – 1.20 (m, 28H), 0.86 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 133.3 (d, J_{C-P} = 97.3 Hz), 131.7 (d, J_{C-P} = 2.3 Hz), 130.9 (d, J_{C-P} = 9.2 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 32.0, 31.5, 31.1(d, J_{C-P} = 14.5 Hz), 30.3, 29.84 (d, J_{C-P} = 71.6 Hz), 29.8, 29.78, 29.76, 29.71, 29.7, 29.5, 29.2, 22.8, 21.5 (d, J_{C-P} = 3.8 Hz), 14.2. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 32.7. **HRMS (ESI+):** m/z calcd. $C_{30}H_{47}OP$ For $[M+H]^+$: 455.3438; Found: 455.3411.



Hexadecyldiphenylphosphine oxide(3ae): Isolated as white solid; Yield: 192 mg (90 %) **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.75 – 7.71 (m, 4H), 7.52 – 7.44 (m, 6H), 2.28 – 2.21 (m, 2H), 1.66 – 1.56 (m, 2H), 1.41 – 1.34 (m, 2H), 1.28 – 1.21 (m, 24H), 0.87 (t, *J* = 6.4 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 133.3 (d, J_{C-P} = 97.4 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 130.8 (d, J_{C-P} = 9.1 Hz), 128.7 (d,

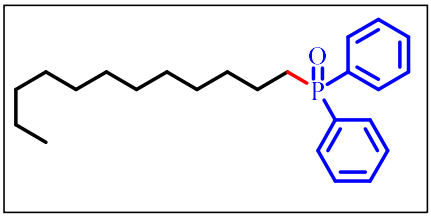
J_{C-P} = 11.4 Hz), 32.0, 31.1 (d, J_{C-P} = 14.5 Hz), 29.86 (d, J_{C-P} = 71.6 Hz) 29.81, 29.80, 29.78, 29.77, 29.72, 29.67, 29.5, 29.2, 22.8, 21.5 (d, J_{C-P} = 3.7 Hz), 14.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.7. **HRMS (ESI+):** m/z calcd. $C_{28}H_{43}OP$ For $[M+H]^+$: 427.3125; Found: 427.3096.

Diphenyl(tetradecyl)phosphine oxide(3af): Isolated as white solid; Yield: 176 mg (88 %)



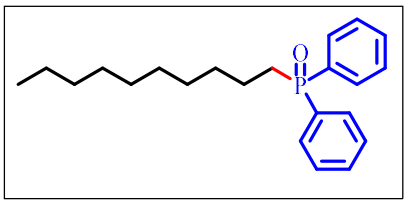
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 4H), 7.54 – 7.43 (m, 6H), 2.28 – 2.21 (m, 2H), 1.66 – 1.56 (m, 2H), 1.41 – 1.36 (m, 2H), 1.28 – 1.21 (m, 20H), 0.87 (t, J = 6.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 133.3 (d, J_{C-P} = 96.9 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 130.9 (d, J_{C-P} = 9.0 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 32.0, 31.1 (d, J_{C-P} = 14.4 Hz), 29.8. (d, J_{C-P} = 71.6 Hz), 29.8, 29.77, 29.73, 29.68, 29.49, 29.48, 29.2, 22.8, 21.5 (d, J_{C-P} = 3.8 Hz), 14.2. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.6. **HRMS (ESI+):** m/z calcd. $C_{26}H_{39}OP$ For $[M+H]^+$: 399.2812; Found: 399.2785.

Dodecyldiphenylphosphine oxide(3ag): Isolated as white solid; Yield: 160 mg (86 %)



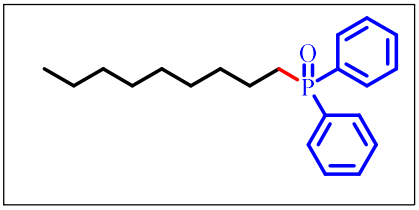
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 4H), 7.52 – 7.49 (m, 2H), 7.47 – 7.44 (m, 4H), 2.27 – 2.22 (m, 2H), 1.65 – 1.57 (m, 2H), 1.40 – 1.35 (m, 2H), 1.27 – 1.21 (m, 16H), 0.87 (t, J = 6.6 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 133.3 (d, J_{C-P} = 97.2 Hz), 131.7 (d, J_{C-P} = 2.3 Hz), 130.8 (d, J_{C-P} = 9.1 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 32.0, 31.1 (d, J_{C-P} = 14.5 Hz), 29.8 (d, J_{C-P} = 71.2 Hz), 29.7, 29.6, 29.5, 29.4, 29.2, 22.80, 21.5 (d, J_{C-P} = 3.6 Hz), 14.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.8. **HRMS (ESI+):** m/z calcd. $C_{24}H_{35}OP$ For $[M+H]^+$: 371.2499; Found: 371.2480.

Decyldiphenylphosphine oxide(3ah):[16] Isolated as white solid; Yield: 144 mg (84 %)



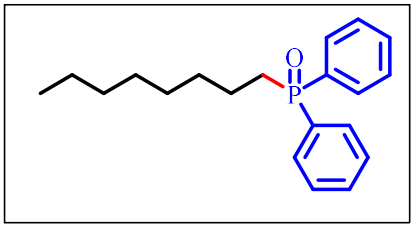
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 4H), 7.51 – 7.41 (m, 6H), 2.27 – 2.20 (m, 2H), 1.65 - 1.53 (m, 2H), 1.40 – 1.33 (m, 2H), 1.26 – 1.20 (m, 12H), 0.85 (t, J = 6.7 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 133.3 (d, J_{C-P} = 97.1 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 130.8 (d, J_{C-P} = 9.1 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 31.9, 31.1 (d, J_{C-P} = 14.5 Hz), 29.8 (d, J_{C-P} = 71.5 Hz), 29.6, 29.4, 29.3, 29.1, 22.7, 21.5 (d, J_{C-P} = 3.8 Hz), 14.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.7.

Nonyldiphenylphosphine oxide(3ai):[15] Isolated as white solid; Yield: 135 mg (82 %)

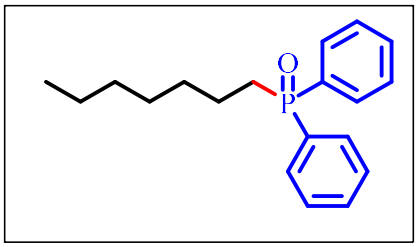


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 – 7.70 (m, 4H), 7.51 – 7.48 (m, 2H), 7.46 – 7.43 (m, 4H), 2.27 – 2.21 (m, 2H), 1.64 – 1.54 (m, 2H), 1.40 – 1.34 (m, 2H), 1.27 – 1.20 (m, 10H), 0.85 (t, J = 7.2 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 133.2 (d, J_{C-P} = 97.2 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 130.8 (d, J_{C-P} = 9.1 Hz), 128.7 (d, J_{C-P} = 11.5 Hz), 31.9, 31.1 (d, J_{C-P} = 14.7 Hz), 29.8 (d, J_{C-P} = 71.6 Hz), 29.4, 29.3, 29.2, 22.7, 21.5 (d, J_{C-P} = 4.0 Hz), 14.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.9.

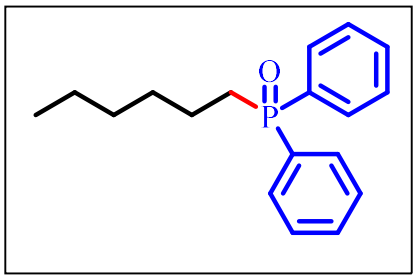
Octyldiphenylphosphine oxide(3aj):[15] Isolated as white solid; Yield: 123 mg (78 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.72 – 7.69 (m, 4H), 7.50 – 7.47 (m, 2H), 7.45 – 7.42 (m, 4H), 2.26 – 2.20 (m, 2H), 1.62 – 1.54 (m, 2H), 1.39 – 1.33 (m, 2H), 1.23 – 1.19 (m, 8H), 0.83 (t, J = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 133.15 (d, J_{C-P} = 97.3 Hz), 131.7 (d, J_{C-P} = 2.3 Hz), 130.8 (d, J_{C-P} = 9.0 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 31.8, 31.0 (d, J_{C-P} = 14.5 Hz), 29.8(d, J_{C-P} = 71.2 Hz), 29.76 29.0, 22.7, 21.4 (d, J_{C-P} = 3.6 Hz), 14.1. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.8.



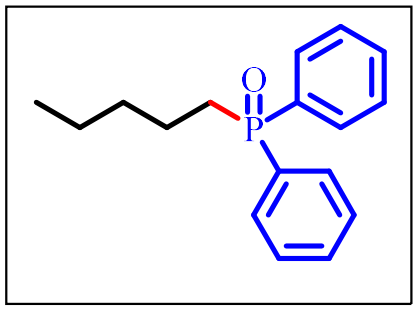
Heptyldiphenylphosphine oxide(3ak):[15] Isolated as white solid; Yield: 108 mg (72 %) **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.76 – 7.70 (m, 4H), 7.53 – 7.49 (m, 2H), 7.48 – 7.43 (m, 4H), 2.28 – 2.21 (m, 2H), 1.66 – 1.56 (m, 2H), 1.42 – 1.34 (m, 2H), 1.28 – 1.21 (m, 6H), 0.84 (t, J = 6.6 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 133.3 (d, J_{C-P} = 97.0 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 130.9 (d, J_{C-P} = 9.1 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 31.7, 31.1 (d, J_{C-P} = 14.5 Hz), 30.4 (d, J_{C-P} = 71.5 Hz), 28.9, 22.7, 21.5 (d, J_{C-P} = 3.8 Hz), 14.1. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.7.



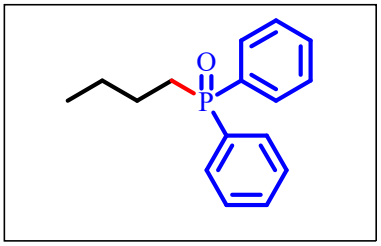
Hexyldiphenylphosphine oxide(3al)[10] Isolated as white solid; Yield: 93 mg (65 %) **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.76 – 7.70 (m, 4H), 7.53 – 7.49 (m, 2H), 7.48 7.43 (m, 4H), 2.29 – 2.22 (m, 2H), 1.64 – 1.57 (m, 2H), 1.42 – 1.35 (m, 2H), 1.26 – 1.23 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 133.2 (d, J_{C-P} = 97.1 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 130.9 (d, J_{C-P} = 9.1 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 31.4, 30.8 (d, J_{C-P} = 14.5 Hz), 29.8 (d, J_{C-P} = 71.5 Hz), 22.5, 21.5 (d, J_{C-P} = 3.9 Hz), 14.1. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.7.



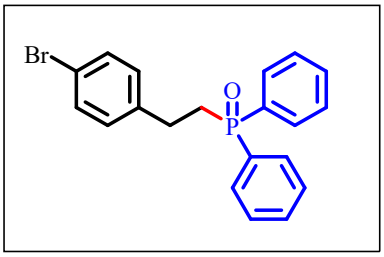
Pentyldiphenylphosphine oxide(3am):[15] Isolated as white solid; Yield: 85 mg (62 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.74 – 7.70 (m, 4H), 7.51 – 7.48 (m, 2H), 7.46 – 7.43 (m, 4H), 2.26 – 2.21 (m, 2H), 1.64 – 1.58 (m, 2H), 1.39 – 1.35 (m, 2H), 1.27 – 1.24 (m, 3H), 0.83 (t, J = 7.2 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 133.2 (d, J_{C-P} = 97.3 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 130.8 (d, J_{C-P} = 9.1 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 33.2 (d, J_{C-P} = 14.5 Hz), 29.8 (d, J_{C-P} = 71.2 Hz), 22.2, 21.2 (d, J_{C-P} = 3.8 Hz), 13.9. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.8.



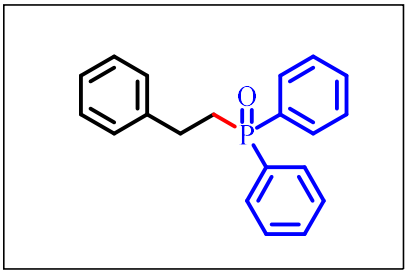
Butyldiphenylphosphine oxide(3an):[17] Isolated as white solid; Yield: 71 mg (55 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.74 – 7.71 (m, 4H), 7.53 – 7.49 (m, 2H), 7.47 – 7.44 (m, 4H), 2.28 – 2.23 (m, 2H), 1.63 – 1.53 (m, 2H), 1.44 – 1.39 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 133.1 (d, $J_{C–P}$ = 97.3 Hz), 131.7 (d, $J_{C–P}$ = 2.6 Hz), 130.9 (d, $J_{C–P}$ = 9.2 Hz), 128.7 (d, $J_{C–P}$ = 11.4 Hz), 29.5 (d, $J_{C–P}$ = 68.9 Hz), 24.2 (d, $J_{C–P}$ = 14.8 Hz), 23.5 (d, $J_{C–P}$ = 3.8 Hz), 13.7. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 33.0.



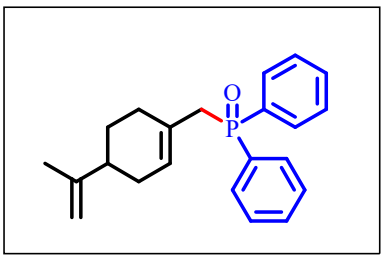
(4-Bromophenethyl)diphenylphosphino oxide (3ao):[13] Isolated as white solid; Yield: 135 mg (70 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.76 – 7.72 (m, 4H), 7.53 – 7.51 (m, 2H), 7.48 – 7.47 (m, 4H), 7.35 – 7.34 (m, 2H), 7.03 – 7.01 (m, 2H), 2.89 – 2.87 (m, 2H), 2.56 – 2.53 (m, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 140.2 (d, $J_{C–P}$ = 14.2 Hz), 132.7, 132.0, 131.7, 130.9 (d, $J_{C–P}$ = 7.8 Hz), 130.0, 128.9 (d, $J_{C–P}$ = 10.7 Hz), 120.2, 31.8 (d, $J_{C–P}$ = 68.9 Hz), 27.2. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 31.6.

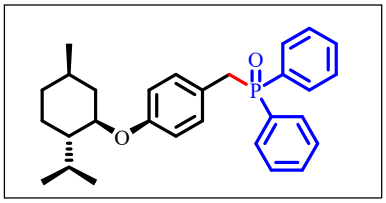


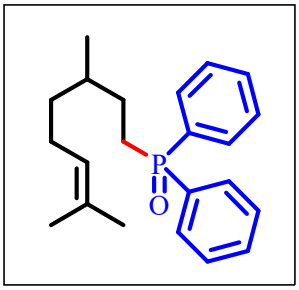
Phenethyldiphenylphosphine oxide(3ap):[7] Isolated as white solid; Yield: 138 mg (90 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.78 – 7.75 (m, 4H), 7.54 – 7.51 (m, 2H), 7.49 – 7.46 (m, 4H), 7.26 – 7.24 (m, 2H), 7.19 – 7.15 (m, 3H), 2.95 – 2.90 (m, 2H), 2.61 – 2.55 (m, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 141.2 (d, $J_{C–P}$ = 15.2 Hz), 132.8 (d, $J_{C–P}$ = 97.7 Hz), 131.95 (d, $J_{C–P}$ = 2.6 Hz), 130.9 (d, $J_{C–P}$ = 9.2 Hz), 128.8 (d, $J_{C–P}$ = 11.6 Hz), 128.7, 128.2, 126.4, 32.0 (d, $J_{C–P}$ = 69.3 Hz), 27.6 (d, $J_{C–P}$ = 2.9 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 31.8.

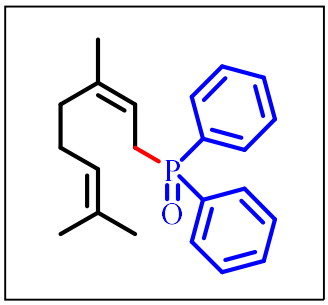


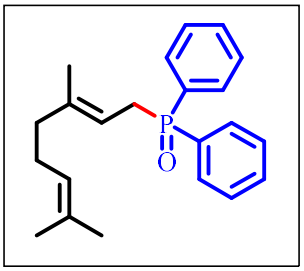
Diphenyl((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)phosphine oxide(3aq):[10] Isolated as white solid; Yield: 110 mg (65 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.77 – 7.72 (m, 4H), 7.52 – 7.49 (m, 2H), 7.47 – 7.43 (m, 4H), 5.44 – 5.42 (m, 1H), 4.60 (d, J = 25.1 Hz, 2H), 3.03 (d, J = 13.6 Hz, 2H), 2.07 – 1.98 (m, 4H), 1.85 – 1.83 (m, 1H), 1.72 – 1.68 (m, 1H), 1.67 (s, 3H), 1.39 – 1.31 (m, 1H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 149.8, 133.6 (d, $J_{C–P}$ = 17.8 Hz), 132.8 (d, $J_{C–P}$ = 17.3 Hz), 131.7, 131.16, 131.15 (d, $J_{C–P}$ = 18.8 Hz), 128.5 (d, $J_{C–P}$ = 11.5 Hz), 128.1 (d, $J_{C–P}$ = 9.2 Hz), 127.1 (d, $J_{C–P}$ = 10.0 Hz), 108.7, 40.4, 39.4 (d, $J_{C–P}$ = 67.6 Hz), 31.0 (d, $J_{C–P}$ = 2.2 Hz), 30.8 (d, $J_{C–P}$ = 2.3 Hz), 27.8, 20.9. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.7.



(4-(((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)benzyl)diphenylphosphine oxide(3ar) Isolated as white solid; Yield: 125 mg (70 %)  **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.70 – 7.66 (m, 4H), 7.51 – 7.48 (m, 2H), 7.44 – 7.41 (m, 4H), 6.98 – 6.97 (m, 2H), 6.72 – 6.70 (m, 2H), 4.52 – 4.48 (m, 1H), 3.58 (d, J = 13.2 Hz, 2H), 2.02 (d, J = 14.2 Hz, 1H), 1.76 – 1.61 (m, 4H), 1.53 (q, J = 12.8 Hz, 1H), 1.02 – 0.97 (m, 1H), 0.94 – 0.86 (m, 5H), 0.83 – 0.79 (m, 6H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 157.4 (d, J_{C-P} = 2.8 Hz), 132.6 (d, J_{C-P} = 97.7 Hz), 131.8 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 131.2 (d, J_{C-P} = 5.1 Hz), 128.5 (d, J_{C-P} = 11.4 Hz), 122.3 (d, J_{C-P} = 8.1 Hz), 115.9 (d, J_{C-P} = 2.3 Hz), 47.9, 37.8, 37.2 (d, J_{C-P} = 67.2 Hz), 35.1, 29.3, 26.2, 24.9, 22.4, 21.1, 20.9. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.7. **HRMS (ESI+):** m/z calcd. $C_{29}H_{35}O_2P$ For $[M+H]^+$: 447.2448; Found: 447.2418.

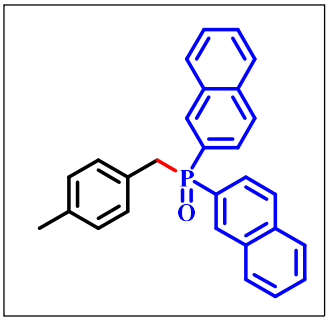
(3,7-Dimethyloct-6-en-1-yl)diphenylphosphine oxide(3as) Isolated as white solid; Yield: 102 mg (60 %)  **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.73 – 7.69 (m, 4H), 7.50 – 7.47 (m, 2H), 7.46 – 7.42 (m, 4H), 5.04 (t, J = 7.3 Hz, 1H), 2.27 – 2.17 (m, 2H), 1.95 – 1.83 (m, 2H), 1.63 (s, 3H), 1.53 (s, 3H), 1.48 – 1.41 (m, 2H), 1.32 – 1.26 (m, 2H), 1.15 – 1.07 (m, 1H), 0.89 (d, J = 6.3 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 133.6 (d, J_{C-P} = 6.9 Hz), 132.8 (d, J_{C-P} = 6.8 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 130.8 (d, J_{C-P} = 9.1 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 124.6, 36.4, 33.4 (d, J_{C-P} = 14.1 Hz), 29.8, 28.0 (d, J_{C-P} = 3.7 Hz), 27.3 (d, J_{C-P} = 71.8 Hz), 25.6 (d, J_{C-P} = 40.1 Hz), 19.1, 17.7. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 33.2.

(Z)-(3,7-Dimethylocta-2,6-dien-1-yl)diphenylphosphine oxide(3au) Isolated as white solid; Yield: 115 mg (68 %)  **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.72 – 7.69 (m, 4H), 7.49 – 7.46 (m, 2H), 7.43 – 7.40 (m, 4H), 5.23 – 5.19 (m, 1H), 4.96 – 4.94 (m, 1H), 3.08-3.04 (m, 2H), 1.94 – 1.93 (m, 4H), 1.59 (s, 3H), 1.51 (s, 3H), 1.41 – 1.40 (m, 3H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 141.1 (d, J_{C-P} = 11.8 Hz), 132.9 (d, J_{C-P} = 97.2 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 131.6, 131.1 (d, J_{C-P} = 9.0 Hz), 128.4 (d, J_{C-P} = 11.3 Hz), 123.9, 112.3 (d, J_{C-P} = 8.5 Hz), 39.7 (d, J_{C-P} = 2.3 Hz), 30.9 (d, J_{C-P} = 69.8 Hz) 26.4 (d, J_{C-P} = 2.7 Hz), 25.7, 17.7, 16.3 (d, J_{C-P} = 2.2 Hz). **^{31}P NMR (243 MHz, CDCl$_3$)** δ 31.0. **HRMS (ESI+):** m/z calcd. $C_{22}H_{27}OP$ For $[M+H]^+$: 339.1873; Found: 339.1853.

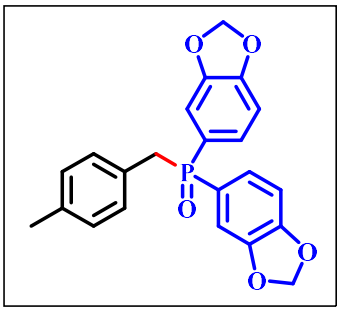
(E)-(3,7-Dimethylocta-2,6-dien-1-yl)diphenylphosphine oxide(3at):[10] Isolated as white solid; Yield: 110 mg (65 %)  **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.72 – 7.69 (m, 4H), 7.50 – 7.47 (m, 2H), 7.45 – 7.41 (m, 4H), 5.23 – 5.19 (m, 1H), 5.01 – 4.99 (m, 1H), 3.09-3.05 (m, 2H), 1.89 – 1.88 (m, 4H), 1.65 – 1.63 (m, 6H), 1.53 (s, 3H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 141.2 (d, J_{C-P} = 12.8 Hz), 133.9 (d, J_{C-P} = 97.3 Hz), 131.9, 131.7 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 8.9 Hz), 128.6 (d, J_{C-P} = 11.5 Hz), 123.9, 112.7 (d, J_{C-P} = 7.9 Hz), 32.1 (d, J_{C-P} = 2.0 Hz), 30.5 (d, J_{C-P} = 70.3 Hz), 26.1 (d, J_{C-P} = 2.1 Hz), 25.7, 23.5 (d, J_{C-P} = 2.2 Hz), 17.7.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.8.

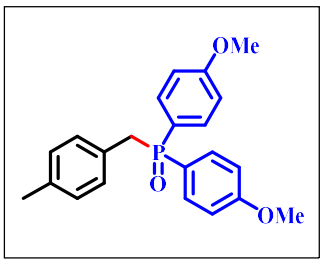
(4-Methylbenzyl)di(naphthalen-2-yl)phosphine oxide(3av): Isolated as white solid; Yield: 138 mg (68 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.37 – 8.34 (m, 2H), 7.90 – 7.85 (m, 6H), 7.70 (t, J = 9.0 Hz, 2H), 7.58 (t, J = 7.1 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.06 – 7.04 (m, 2H), 6.97 – 6.96 (m, 2H), 3.81 (d, J = 13.5 Hz, 2H), 2.23 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.6 (d, J_{C-P} = 3.1 Hz), 134.7 (d, J_{C-P} = 2.3 Hz), 133.4 (d, J_{C-P} = 8.1 Hz), 132.6 (d, J_{C-P} = 12.6 Hz), 130.1 (d, J_{C-P} = 5.1 Hz), 129.7 (d, J_{C-P} = 98.4 Hz), 129.3 (d, J_{C-P} = 2.4 Hz), 129.0, 128.4 (d, J_{C-P} = 11.5 Hz), 128.3, 128.0, 127.9, 127.0, 126.1 (d, J_{C-P} = 10.2 Hz), 37.6 (d, J_{C-P} = 66.9 Hz), 21.1. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.8. **HRMS (ESI+):** m/z calcd. $C_{28}H_{23}OP$ For $[M+H]^+$: 407.1560; Found: 407.1557.



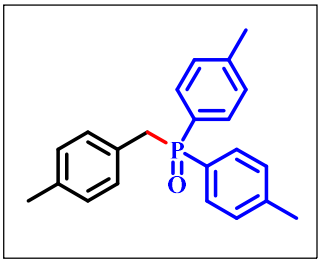
Bis(benzo[d][1,3]dioxol-5-yl)(4-methylbenzyl)phosphine oxide(3aw): Isolated as white solid; Yield: 142 mg (72 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.22 – 7.18 (m, 2H), 7.07 – 7.05 (m, 2H), 7.02 – 6.99 (m, 4H), 6.87 – 6.84 (m, 2H), 6.01 (s, 4H), 3.53 (d, J = 13.5 Hz, 2H), 2.27 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 150.7 (d, J_{C-P} = 2.2 Hz), 148.0 (d, J_{C-P} = 16.4 Hz), 136.5 (d, J_{C-P} = 2.5 Hz), 130.0 (d, J_{C-P} = 4.9 Hz), 129.2 (d, J_{C-P} = 2.9 Hz), 128.0 (d, J_{C-P} = 7.8 Hz), 126.5 (d, J_{C-P} = 10.0 Hz), 125.7 (d, J_{C-P} = 102.3 Hz), 110.7 (d, J_{C-P} = 11.8 Hz), 108.7 (d, J_{C-P} = 14.2 Hz), 101.7, 38.9 (d, J_{C-P} = 68.2 Hz), 21.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.9. **HRMS (ESI+):** m/z calcd. $C_{22}H_{19}O_5P$ For $[M+H]^+$: 396.1077 ; Found: 396.1097.



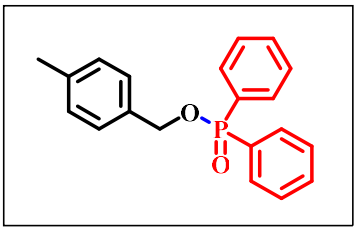
Bis(4-methoxyphenyl)(4-methylbenzyl)phosphine oxide(3ax): Isolated as white solid; Yield: 150 mg (82 %) **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.59 – 7.56 (m, 4H), 7.00 – 6.96 (m, 4H), 6.93 – 6.92 (m, 4H), 3.82 (s, 6H), 3.55 (d, J = 13.6 Hz, 2H), 2.26 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.3 (d, J_{C-P} = 2.2 Hz), 136.3 (d, J_{C-P} = 2.8 Hz), 133.1 (d, J_{C-P} = 10.0 Hz), 130.1 (d, J_{C-P} = 4.7 Hz), 129.1 (d, J_{C-P} = 1.75 Hz), 128.4 (d, J_{C-P} = 7.6 Hz), 123.9 (d, J_{C-P} = 104.9 Hz), 114.0 (d, J_{C-P} = 14.9 Hz), 55.4, 38.2 (d, J_{C-P} = 67.7 Hz), 21.1.**^{31}P NMR (200 MHz, $CDCl_3$)** δ 29.7. **HRMS (ESI+):** m/z calcd. $C_{22}H_{23}O_3P$ For $[M+H]^+$: 367.1458; Found: 367.1456.



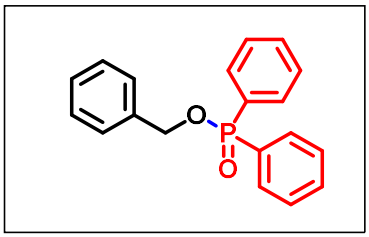
(4-Methylbenzyl)di-p-tolylphosphine oxide(3ay): Isolated as white solid; Yield: 154 mg (92 %) **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.58 – 7.53 (m, 4H), 7.23 – 7.20 (m, 4H), 6.98 (s, 4H), 3.57 (d, J = 13.6 Hz, 2H), 2.36 (s, 6H), 2.25 (d, J=1.8 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 142.1 (d, J_{C-P} = 2.7 Hz), 136.3 (d, J_{C-P} = 3.2 Hz), 131.2 (d, J_{C-P} = 9.4 Hz), 130.0 (d, J_{C-P} = 5.1 Hz), 129.4 (d, J_{C-P} = 100.5 Hz), 129.2 (d, J_{C-P} = 12.0 Hz), 129.1 (d, J_{C-P} = 2.5 Hz), 128.3 (d, J_{C-P} = 8.0 Hz), 37.0, 21.6, 21.1.**^{31}P NMR (200 MHz, CDCl$_3$)** δ 29.8. **HRMS (ESI+):** m/z calcd. $C_{22}H_{23}O_3P$ For $[M+H]^+$: 335.1560; Found: 335.1548.



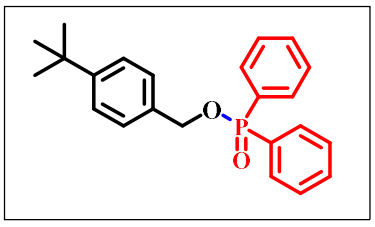
4-Methylbenzyl diphenylphosphinate (4a):[18] Isolated as colourless oil Yield. 100 mg 62 % **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.85 – 7.80 (m, 4H), 7.53 – 7.50 (m, 2H), 7.45 – 7.42 (m, 4H), 7.25 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 5.02 (d, J = 6.6 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 138.3, 133.4 (d, J_{C-P} = 7.6 Hz), 132.3 (d, J_{C-P} = 2.7 Hz), 132.8 (d, J_{C-P} = 10.2 Hz), 131.5 (d, J_{C-P} = 135.9 Hz), 129.4, 128.6 (d, J_{C-P} = 13.1 Hz), 128.2, 66.4 (d, J_{C-P} = 5.5 Hz), 21.3. **^{31}P NMR (200 MHz, CDCl$_3$) δ** 32.1.

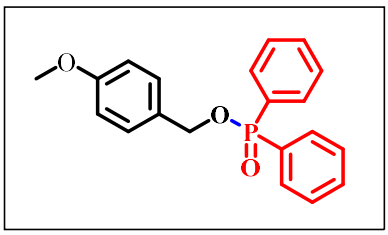


Benzyl diphenylphosphinate (4b):[18] Isolated as colourless oil yield: 93 mg 60 % ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 4H), 7.41 – 7.38 (m, 2H), 7.34 – 7.31 (m, 4H), 7.26 – 7.16 (m, 5H), 4.97 (d, J = 6.8 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 135.3 (d, J_{C-P} = 7.5 Hz), 135.2 (d, J_{C-P} = 2.8 Hz), 130.7 (d, J_{C-P} = 10.2 Hz), 130.3 (d, J_{C-P} = 135.8 Hz), 127.6, 127.5 (d, J_{C-P} = 3.6 Hz), 127.3, 126.9, 65.3 (d, J_{C-P} = 5.4 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 32.4.

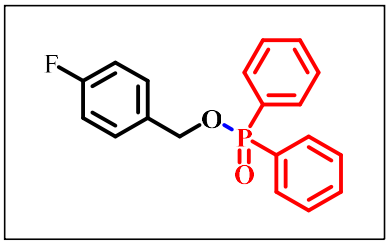


4-(Tert-butyl)benzyl diphenylphosphinate (4c):[18] Isolated as colourless oil yield: 117 mg 65 % ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 – 7.81 (m, 4H), 7.52 – 7.49 (m, 2H), 7.44 – 7.41 (m, 4H), 7.37 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 5.04 (d, J = 6.7 Hz, 2H), 1.31 (s, 9H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 151.4, 133.4 (d, J_{C-P} = 7.6 Hz) 132.2 (d, J_{C-P} = 2.7 Hz), 132.8 (d, J_{C-P} = 10.1 Hz), 131.5 (d, J_{C-P} = 136.0 Hz), 128.6 (d, J_{C-P} = 12.9 Hz), 127.9, 125.6, 66.3 (d, J_{C-P} = 5.5 Hz), 34.7, 31.4. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 32.2**.**

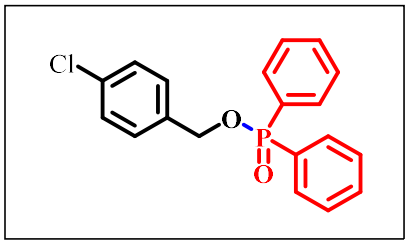


4-Methoxybenzyl diphenylphosphinate(4d):[18] Isolated as colourless oil yield: 102 mg 60 % 

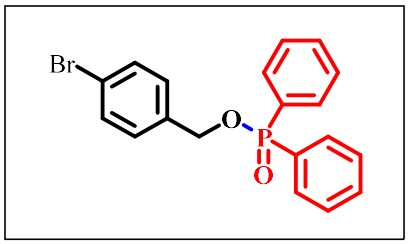
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 4H), 7.52 – 7.49 (m,2H), 7.45 – 7.41 (m, 4H), 7.29 – 7.26 (m, 2H), 6.87 – 6.85 (m, 2H), 5.00 (d, J = 6.9 Hz, 2H), 3.80 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 159.8, 132.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.6 (d, $J_{C\text{-}P}$ = 135.9 Hz), 129.9, 128.6 (d, $J_{C\text{-}P}$ = 12.9 Hz), 128.5, 114.0, 66.3 (d, $J_{C\text{-}P}$ = 5.5 Hz), 55.4. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 32.1.

4-Fluorobenzyl diphenylphosphinate (4e): [18] Isolated as colourless oil yield: 85 mg 52 % 

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.79 (m, 4H), 7.53 – 7.50 (m, 2H), 7.45 – 7.41 (m, 4H), 7.34 – 7.31 (m, 2H), 7.01 (t, J = 8.6 Hz, 2H), 5.02 (d, J = 7.3 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.7 6 (d, $J_{C\text{-}F}$ = 245.6 Hz), 132.4 6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.2 6 (dd, $J_{C\text{-}F}$ = 7 Hz, $J_{C\text{-}P}$ = 3.1 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.3 (d, $J_{C\text{-}P}$ = 136.0 Hz), 130.0 (d, $J_{C\text{-}P}$ = 8.3 Hz), 128.7 (d, $J_{C\text{-}P}$ = 13.2 Hz), 115.6 (d, $J_{C\text{-}P}$ = 21.5 Hz), 65.8 (d, $J_{C\text{-}P}$ = 5.4 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 32.6. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -113.5(d, $J_{P\text{-}F}$=2.6 Hz)

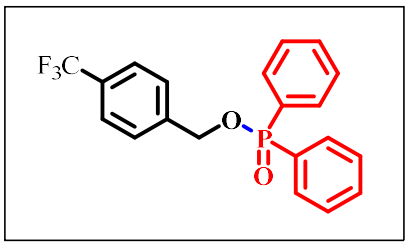
4-Chlorobenzyl diphenylphosphinate (4f):[18] Isolated as colourless oil yield: 95 mg 55 % 

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.78 (m, 4H), 7.54 – 7.51 (m, 2H), 7.46 – 7.42 (m, 4H), 7.31 – 7.27 (m, 4H), 5.02 (d, J = 7.2 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 135.0 (d, $J_{C\text{-}P}$ = 27.2 Hz), 134.3, 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.2 (d, $J_{C\text{-}P}$ = 135.5 Hz), 129.4, 128.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 128.7, 65.7 (d, $J_{C\text{-}P}$ = 5.4 Hz)**. ^{31}P NMR (200 MHz, CDCl$_3$)** δ 32.7.

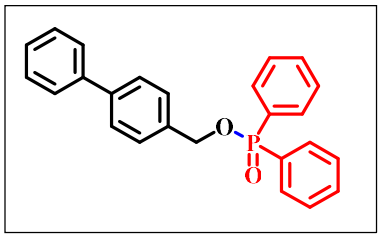
4-Bromobenzyl diphenylphosphinate (4g):[18] Isolated as colourless oil yield: 116 mg 60 % 

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.78 (m, 4H), 7.54 – 7.50 (m, 2H), 7.46 – 7.42 (m, 6H), 7.23 (d, J = 8.3 Hz, 2H), 5.00 (d, J = 7.2 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 135.5 (d, $J_{C\text{-}P}$ = 7.0 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 138.1, 131.7 (d, $J_{C\text{-}P}$ = 7.4 Hz), 131.2 (d, $J_{C\text{-}P}$ = 136.0 Hz), 129.7, 128.7 (d, $J_{C\text{-}P}$ = 13.2 Hz), 122.5, 65.7 (d, $J_{C\text{-}P}$ = 5.4 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 32.7.

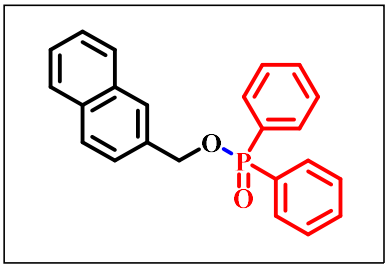
4-(Trifluoromethyl)benzyl diphenylphosphinat(4h):[20] ^{1}H NMR (500 MHz, Chloroform-*d*) Isolated as colourless oil yield: 98 mg 52 % δ 7.85 – 7.80 (m, 4H), 7.61 – 7.59 (m, 2H), 7.56 – 7.52 (m, 2H), 7.48 – 7.43 (m, 6H), 5.11 (d, J = 7.2 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.5 (d, J_{C-P} = 7.2 Hz), 132.5 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 10.1 Hz), 131.1 (d, J_{C-P} = 136.0 Hz), 130.70-130.19 (m), 128.8, 128.8 (d, J_{C-P} = 13.0 Hz), 126.5 (q, J_{C-F} = 270.7 Hz), 125.6 (q, J_{C-F} = 3.8 Hz), 65.5 (d, J_{C-P} = 5.2 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 33.1. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.6.



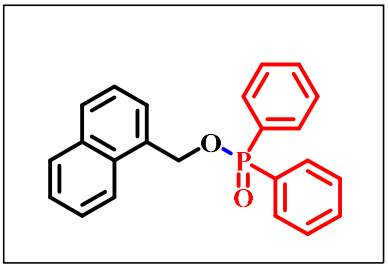
[1,1'-Biphenyl]-4-ylmethyl diphenylphosphinate(4i):[25] Isolated as colourless oil yield: 131 mg 68 % ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.83 (m, 4H), 7.59 – 7.56 (m, 4H), 7.55 – 7.51 (m, 2H), 7.47 – 7.43 (m, 8H), 7.37 – 7.34 (m, 1H), 5.11 (d, J = 7 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 141.4, 140.8, 135.4 (d, J_{C-P} = 7.4 Hz), 132.3 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 10.1 Hz), 131.4 (d, J_{C-P} = 136.0 Hz), 129.0, 128.8 (d, J_{C-P} = 13.21 Hz),128.5, 127.5, 127.4, 127.2, 66.3 (d, J_{C-P} = 5.4 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.5.



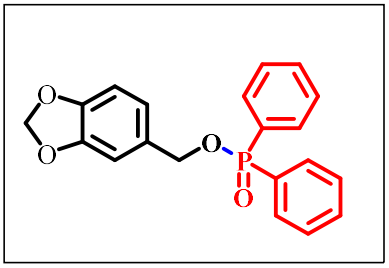
Naphthalen-2-ylmethyl diphenylphosphinate(4j):[18] Isolated as colourless oil yield: 133 mg 74 % ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.78 (m, 8H), 7.53 – 7.42 (m, 9H), 5.23 (d, J = 6.9 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 132.8 (d, J_{C-P} = 7.4 Hz), 132.2 (d, J_{C-P} = 3.1 Hz), 131.3 (d, J_{C-P} = 2.8 Hz), 130.9, 130.8, 130.3 (d, J_{C-P} = 136.5 Hz), 127.7, 127.6, 127.5, 127.1, 126.8, 126.1, 125.4 (d, J_{C-P} = 2.7 Hz), 124.7, 65.6 (d, J_{C-P} = 5.4 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.6.



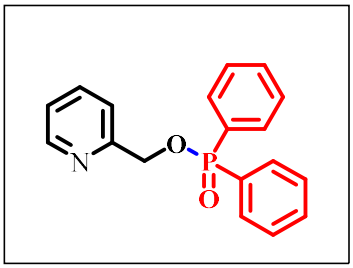
Naphthalen-1-ylmethyl diphenylphosphinate(4k):[18] Isolated as colourless oil yield: 129 mg 72 % ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.87 – 7.79 (m, 5H), 7.55 – 7.45 (m, 5H), 7.45 – 7.39 (m, 5H), 5.54 (d, J = 6.7 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 133.8, 132.3 (d, J_{C-P} = 2.8 Hz), 131.9 (d, J_{C-P} = 7.3 Hz), 131.8 (d, J_{C-P} = 10.2 Hz), 131.5, 131.4 (d, J_{C-P} = 135.8 Hz), 129.5, 128.7, 128.6 (d, J_{C-P} = 13.0 Hz), 127.0, 126.7, 126.1, 125.3, 123.7, 64.8 (d, J_{C-P} = 5.4 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.5.



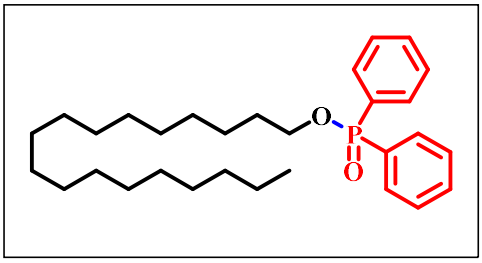
Benzo[d][1,3]dioxol-5-ylmethyl diphenylphosphinate(4n):[23] Isolated as colourless oil yield: 92 mg 56 % ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.79 (m, 4H), 7.53 – 7.50 (m, 2H), 7.45 – 7.42 (m, 4H), 6.86 (s, 1H), 6.80 – 6.78 (m, 1H), 6.78 – 6.73 (m, 1H), 5.95 (s, 2H), 4.96 (d, J = 6.9 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 147.8 (d, J_{C-P} = 14.1 Hz), 132.3 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 10.2 Hz), 131.4 (d, J_{C-P} = 136.0 Hz), 130.2 (d, J_{C-P} = 7.3 Hz), 128.7, 128.6, 122.1, 108.9, 108.3, 101.3, 66.5 (d, J_{C-P} = 5.4 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.3.

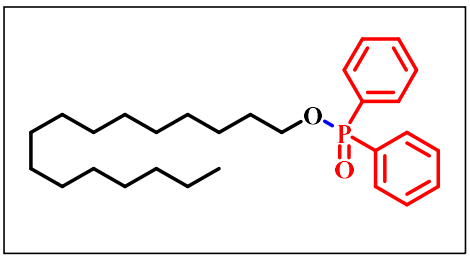


Pyridin-2-ylmethyl diphenylphosphinate(4o):[24] Isolated as colourless oil yield: 82 mg 53 % ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.54 (d, J = 4.0 Hz, 1H), 7.88 – 7.84 (m, 4H), 7.71 – 7.68 (m, 1H), 7.55 – 7.50 (m, 3H), 7.47 – 7.44 (m, 4H), 7.22 – 7.19 (m, 1H), 5.16 (d, J = 7.4 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 156.5 (d, J_{C-P} = 8.0 Hz), 149.3, 137.0, 132.5 (d, J_{C-P} = 2.9 Hz), 131.8 (d, J_{C-P} = 10.1 Hz), 131.1 (d, J_{C-P} = 136.2 Hz), 128.8 (d, J_{C-P} = 13.2 Hz), 123.0, 121.8, 67.1 (d, J_{C-P} = 5.3 Hz). **^{31}P NMR (200 MHz, $CDCl_3$)** δ 33.1.

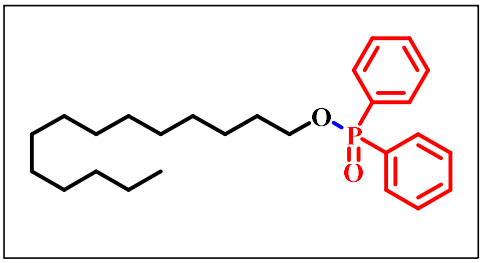


Octadecyl diphenylphosphinate Isolated(4p)[20] as colourless oil yield: 212 mg 90 % ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.78 (m, 4H), 7.53 – 7.49 (m, 2H), 7.46 – 7.42 (m, 4H), 4.02 (q, J = 6.6 Hz, 2H), 1.75 – 1.68 (m, 2H), 1.41 – 1.36 (m, 2H), 1.25 – 1.24 (m, 28H), 0.88 (t, J = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 132.2 (d, J_{C-P} = 2.6 Hz), 131.8 (d, J_{C-P} = 9.8 Hz), 131.7 (d, J_{C-P} = 136.9 Hz), 128.6 (d, J_{C-P} = 13.0 Hz), 65.2 (d, J_{C-P} = 5.9 Hz), 32.1, 30.6 (d, J_{C-P} = 6.5 Hz), 29.83, 29.80, 29.79, 29.77, 29.7, 29.62, 29.5, 29.3, 25.7, 22.8, 14.2. **^{31}P NMR (200 MHz, $CDCl_3$) δ 31.2.**

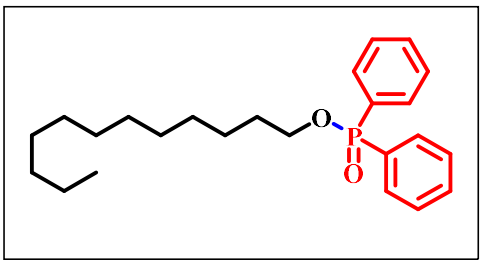


Hexadecyl diphenylphosphinate Isolated as colourless oil yield (4q): 191 mg 86 % 

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.77 (m, 4H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 4H), 4.03-3.98 (m, 2H), 1.74 – 1.67 (m, 2H), 1.41 – 1.35 (m, 2H), 1.27 – 1.23 (m, 24H), 0.87 (t, J = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 131.2 (d, J_{C-P} = 2.7 Hz), 130.8 (d, J_{C-P} = 136.2 Hz), 130.7 (d, J_{C-P} = 10.0 Hz), 127.6 (d, J_{C-P} = 13.0 Hz), 64.2 (d, J_{C-P} = 6.2 Hz), 31.0, 30.0, 29.6 (d, J_{C-P} = 6.5 Hz), 28.8, 28.79, 28.77, 28.75, 28.7 28.6, 28.5, 28.3, 24.7, 21.8, 13.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 31.2. **HRMS (ESI+):** m/z calcd. $C_{28}H_{43}O_2P$ For $[M+H]^+$: 443.3074; Found: 443.3041.

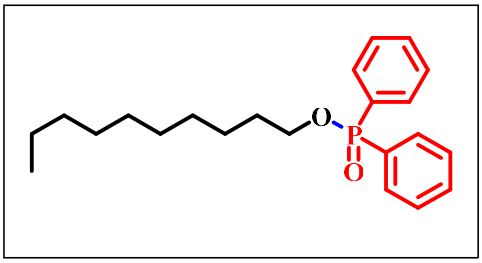
Tetradecyl diphenylphosphinate Isolated as colourless oil yield (4r) 183 mg 88 % 

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.78 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 – 7.42 (m, 4H), 4.03 – 3.99 (m, 2H),1.74-1.68 (m, 2H) 1.39 – 1.34 (m, 2H), 1.28 – 1.22 (m, 20H), 0.87 (t, J = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 132.2 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 136.6 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 128.6 (d, J_{C-P} = 13.0 Hz), 65.2 (d, J_{C-P} = 6.0 Hz), 32.0, 30.7 (d, J_{C-P} = 6.6 Hz), 29.81, 29.79, 29.77, 29.76, 29.68, 29.62, 29.5, 29.3, 25.7, 22.8, 14.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 31.1. **HRMS (ESI+):** m/z calcd. $C_{26}H_{39}O_2P$ For $[M+H]^+$: 399.2812; Found: 399.2785.

Dodecyl diphenylphosphinate Isolated as Colourless Colourless oil yield(4s): 166 mg 86 % 

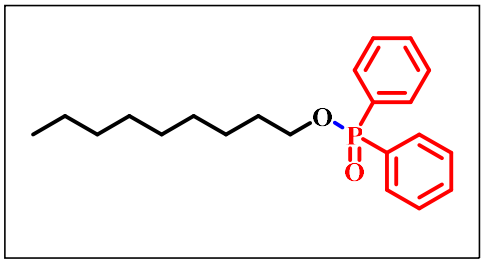
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.77 (m, 4H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 4H), 4.03 – 3.98 (m, 2H), 1.74 – 1.67 (m, 2H), 1.39 – 1.33 (m, 2H), 1.26 – 1.24 (m, 16H), 0.87 (t, J = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 132.2, 131.8 (d, J_{C-P} = 137.8 Hz), 131.7 (d, J_{C-P} = 9.6 Hz), 128.6 (d, J_{C-P} = 12.8 Hz), 65.2 (d, J_{C-P} = 5.3 Hz), 32.0, 30.6 (d, J_{C-P} = 5.9 Hz), 29.74, 29.67, 29.6, 29.5, 29.3, 25.7, 22.8, 14.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 31.2. **HRMS (ESI+):** m/z calcd. $C_{24}H_{35}O_2P$ For $[M+H]^+$: 387.2448; Found: 387.2430.

Decyl diphenylphosphinate(4t):[22] ^{1}H NMR (500 MHz, Chloroform-*d*) Isolated as Colourless Colourless oil yield: 152 mg 85 % δ 7.77 – 7.70 (m, 4H), 7.45 – 7.42 (m, 2H), 7.39 – 7.35 (m, 4H), 3.96 – 3.92 (m, 2H), 1.68 – 1.54 (m, 3H), 1.21 – 1.15 (m, 13H), 0.81 (t, J = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 132.1 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 136.1 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 128.7 (d, J_{C-P} = 13.1 Hz), 65.1 (d, J_{C-P} = 6.0 Hz), 32.0 , 30.6 (d, J_{C-P} = 6.5 Hz), 29.60, 29.58, 29.4, 29.23 25.7, 22.8, 14.2.

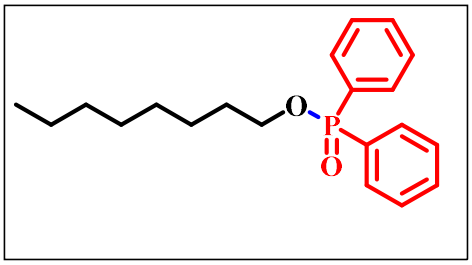


^{31}P NMR (200 MHz, $CDCl_3$) δ 31.1.

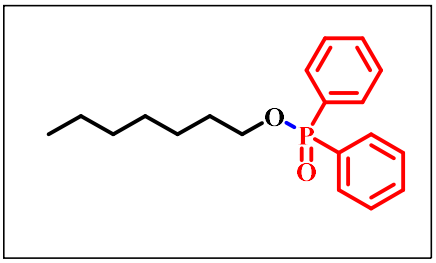
Nonyl diphenylphosphinate(4u):[20] ^{1}H NMR (500 MHz, Chloroform-*d*) Isolated as Colourless Colourless oil yield: 138 mg 80 % δ 7.81 – 7.77 (m, 4H), 7.51 – 7.48 (m, 2H), 7.44 – 7.41 (m, 4H), 4.02-3.98 (m, 2H), 1.73 – 1.68 (m, 2H), 1.39 – 1.35 (m, 2H), 1.27 – 1.22 (m, 10H), 0.86 (t, J = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 131.1 (d, J_{C-P} = 2.6 Hz), 130.7 (d, J_{C-P} = 136.2 Hz), 130.7 (d, J_{C-P} = 9.8 Hz), 127.6 (d, J_{C-P} = 12.9 Hz), 64.2 (d, J_{C-P} = 5.9 Hz), 30.9, 29.6 (d, J_{C-P} = 6.4 Hz), 28.5, 28.3, 28.2, 24.7, 21.7, 13.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 31.2.



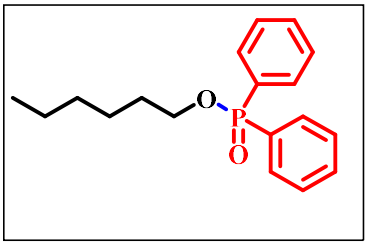
Octyl diphenylphosphinate (4v):[19] ^{1}H NMR (500 MHz, Chloroform-*d*) Isolated as Colourless Colourless oil yield: 129 mg 78 % δ 7.82 – 7.78 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 – 7.41 (m, 4H), 4.03 – 3.98 (m, 2H), 1.72 – 1.69 (m, 2H), 1.38 – 1.35 (m, 2H), 1.27 – 1.20 (m, 8H), 0.87 – 0.83 (m, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 132.2 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 136.2 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 128.7 (d, J_{C-P} = 13.0 Hz), 65.1 (d, J_{C-P} = 6.0 Hz), 31.9, 30.6 (d, J_{C-P} = 6.6 Hz), 29.24, 29.20, 25.7, 22.7, 14.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 31.2.



Heptyl diphenylphosphinate (4w):[20] ^{1}H NMR (400 MHz, DMSO-*d*$_6$) Isolated as colourless oil yield: 119 mg 75 % δ 7.83 – 7.78 (m, 4H), 7.53 – 7.49 (m, 2H), 7.46 – 7.41 (m, 4H), 4.04-3.99 (m, 2H), 1.75 – 1.68 (m, 3H), 1.40 – 1.35 (m, 2H), 1.28 – 1.22 (m, 5H), 0.88 – 0.84 (m, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 132.2 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 136.5 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 128.7 (d, J_{C-P} = 12.9 Hz), 65.2 (d, J_{C-P} = 6.0 Hz), 31.8, 30.7 (d, J_{C-P} = 6.7 Hz), 29.0, 25.7, 22.7, 14.2. **^{31}P NMR (200 MHz, CDCl$_3$) δ** 31.1.



Hexyl diphenylphosphinate (4x):[20] ^{1}H NMR (500 MHz, Chloroform-*d*) Isolated as colourless oil yield: 105 mg 70 % δ 7.82 – 7.78 (m, 4H), 7.52 – 7.49 (m, 2H), 7.45 – 7.42 (m, 4H), 4.04 – 4.00 (m, 2H), 1.74 – 1.68 (m, 2H), 1.41 – 1.36 (m, 2H), 1.31 – 1.23 (m, 4H), 0.88 – 0.84 (m, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 132.2 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 136.4 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 128.7 (d, J_{C-P} = 13.0 Hz), 65.2 (d, J_{C-P} = 6.0 Hz), 31.4, 30.6 (d, J_{C-P} = 6.5 Hz), 25.4, 22.6, 14.1. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 31.1.



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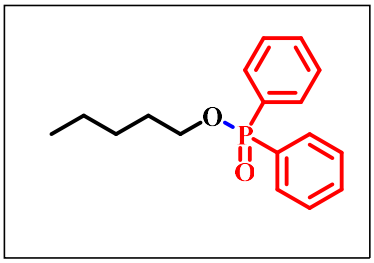
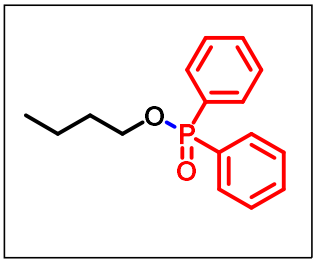
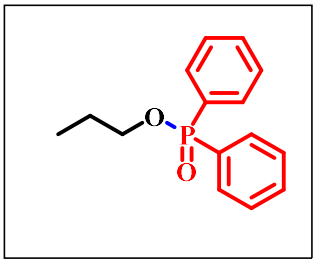
Pentyl diphenylphosphinate (4y):[20] ^{1}H NMR (400 MHz, Chloroform-*d*) Isolated as colourless oil yield: 94 mg 65 % δ 7.82 – 7.77 (m, 4H), 7.51 – 7.47 (m, 2H), 7.44 – 7.40 (m, 4H), 4.03 – 4.01 (m, 2H), 1.74 – 1.67 (m, 2H), 1.39 – 1.26 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 131.1 (d, J_{C-P} = 2.8 Hz), 130.8 (d, J_{C-P} = 136.2 Hz), 130.7 (d, J_{C-P} = 10.0 Hz),127.6 (d, J_{C-P} = 13.1 Hz), 64.1 (d, J_{C-P} = 6.1 Hz), 29.3 (d, J_{C-P} = 6.6 Hz), 26.8, 21.3, 13.0. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 31.1.



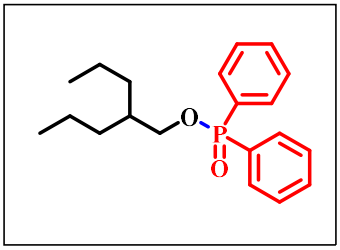
Butyl diphenylphosphinate (4z):[19] ^{1}H NMR (500 MHz, Chloroform-*d*) Isolated as colourless oil yield: 69 mg 50 % δ 7.84 – 7.77 (m, 4H), 7.51 – 7.48 (m, 2H), 7.46 – 7.41 (m, 4H), 4.05 – 3.99 (m, 2H), 1.73 – 1.65 (m, 2H), 1.45 – 1.39 (m, 2H), 0.91 (t, J = 7.1 Hz, 3H**). ^{13}C NMR (126 MHz, CDCl$_3$)** δ 132.2 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 136.2 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 128.6 (d, J_{C-P} = 12.9 Hz), 64.8 (d, J_{C-P} = 6.0 Hz), 32.7 (d, J_{C-P} = 6.7 Hz), 19.0, 13.8. **^{31}P NMR (200 MHz, CDCl$_3$) δ** 31.2.



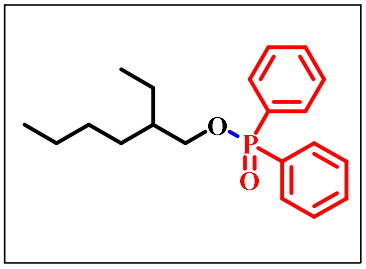
Propyl diphenylphosphinate (4aa):[20] **^{1}H NMR (500 MHz, Chloroform-*d*) Isolated as colourless oil yield: 46 mg 35 %** δ 7.82 – 7.78 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 – 7.41 (m, 4H), 4.00 –3.96 (m, 2H), 1.77 –1.74 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 132.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 136.3 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 13.1 Hz), 66.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 24.0 (d, $J_{C\text{-}P}$ = 6.7 Hz), 10.3. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 31.1.



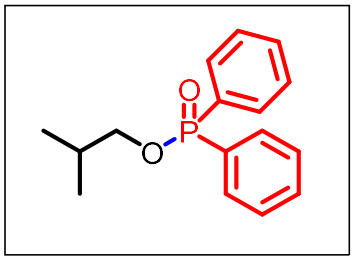
2-Propylpentyl diphenylphosphinate Isolated as colourless oil yield (4ab): 109 mg 65 % **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.82 – 7.76 (m, 4H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 4H), 3.98 – 3.86 (m, 2H), 1.64 – 1.55 (m, 1H), 1.50 – 1.30 (m, 4H), 1.28 – 1.18 (m, 4H), 0.85 (t, J = 7.3 Hz, 6H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 132.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 136.4 Hz, $J_{C\text{-}P}$ = 3.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.0 Hz, $J_{C\text{-}P}$ = 1.8 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.0 Hz), 66.8 (d, $J_{C\text{-}P}$ = 6.2 Hz), 40.3 (d, $J_{C\text{-}P}$ = 6.8 Hz), 30.1, 29.0, 23.6, 23.0, 14.1, 11.1. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 30.8. **HRMS (ESI+):** m/z calcd. $C_{20}H_{27}O_2P$ For $[M+H]^+$: 331.1822; Found: 331.1810.



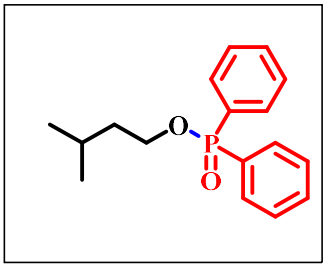
2-Ethylhexyl diphenylphosphinate Isolated as colourless oil yield (4ac): 104 mg 62 % **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.81 – 7.77 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 – 7.42 (m, 4H), 3.95 – 3.87 (m, 2H), 1.63 – 1.56 (m, 1H), 1.47 – 1.30 (m, 4H), 1.28 – 1.19 (m, 4H), 0.85 (t, J = 7.3 Hz, 6H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 132.16, 132.14 131.82 (d, $J_{C\text{-}P}$ = 136.4 Hz), 131.80 (d, $J_{C\text{-}P}$ = 136.1 Hz), 131.75 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.74 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.7, 128.6, 66.8 (d, $J_{C\text{-}P}$ = 6.2 Hz), 40.3 (d, $J_{C\text{-}P}$ = 7.0 Hz), 30.1, 29.0, 23.6, 23.0, 14.1, 11.1.**^{31}P NMR (200 MHz, CDCl$_3$)** δ 30.9. **HRMS (ESI+):** m/z calcd. $C_{20}H_{27}O_2P$ For $[M+H]^+$: 331.1822; Found: 331.1808.



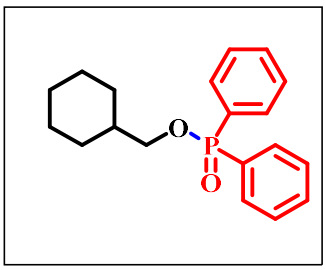
Isobutyl diphenylphosphinate (4ad): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 - 7.68 (m, 4H), 7.40 – 7.29 (m, 16H), 3.71 – 3.65 (m, 2H), 1.96 – 1.85 (m, 1H), 0.88 – 0.82 (m, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 131.9, 131.5 (d, J_{C-P} = 136.3 Hz), 131.4 (d, J_{C-P} = 9.9 Hz), 128.3 (d, J_{C-P} = 13.0 Hz), 70.5 (d, J_{C-P} = 6.1 Hz), 29.0 (d, J_{C-P} = 6.8 Hz), 18.7. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 30.7.



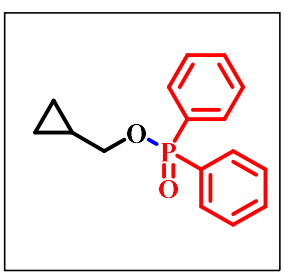
Isopentyl diphenylphosphinate (4ae):[19] Isolated as colourless oil yield: 87 mg 60 % ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 4H), 7.50 – 7.45 (m, 2H), 7.43 – 7.39 (m, 4H), 4.05 – 4.01 (m, 2H), 1.78 – 1.71 (m, 1H), 1.61 – 1.57 (m, 2H), 0.87 – 0.84 (m, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 132.1 (d, J_{C-P} = 2.8 Hz), 131.7 (d, J_{C-P} = 136.1 Hz), 131.6 (d, J_{C-P} = 10.0 Hz), 128.6 (d, J_{C-P} = 12.9 Hz), 63.5 (d, J_{C-P} = 6.2 Hz), 39.3 (d, J_{C-P} = 6.4 Hz), 24.7, 22.4. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 31.1.

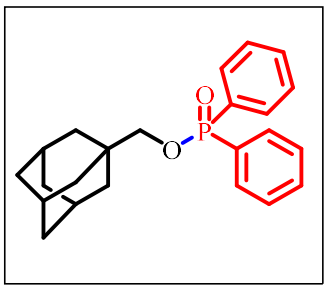


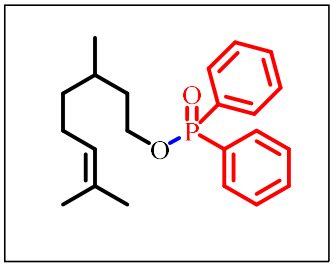
Cyclohexylmethyl diphenylphosphinate (4af): Isolated as colourless oil yield: 142 mg 95 % ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 4H), 7.46 – 7.42 (m, 2H), 7.40 – 7.34 (m, 4H), 3.77 (t, *J* = 6.3 Hz, 2H), 1.76 – 1.59 (m, 6H), 1.24 – 1.06 (m, 3H), 0.98 – 0.88 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 132.0 (d, J_{C-P} = 2.8 Hz), 131.7 (d, J_{C-P} = 136.2 Hz), 131.6 (d, J_{C-P} = 10.0 Hz), 128.5 (d, J_{C-P} = 12.9 Hz), 69.7 (d, J_{C-P} = 6.2 Hz), 38.5 (d, J_{C-P} = 6.6 Hz), 29.4, 26.3, 25.6. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 30.9. **HRMS (ESI+):** m/z calcd. $C_{19}H_{23}O_2P$ For $[M+H]^+$: 315.1509; Found: 315.1535.

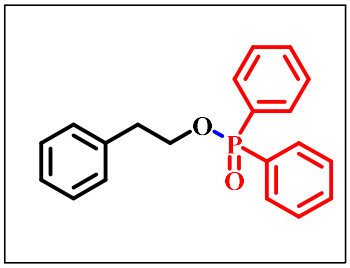


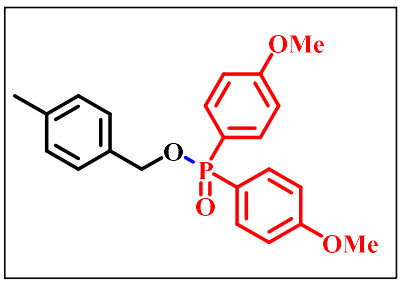
Cyclopropylmethyl diphenylphosphinate (4ag):[24] ^{1}H NMR (500 MHz, Chloroform-*d*) Isolated as colourless oil yield: 82 mg 60 % δ 7.83 – 7.79 (m, 4H), 7.49 – 7.46 (m, 2H), 7.43 – 7.41 (m, 4H), 3.87 (t, *J* = 7.4 Hz, 2H), 1.19 – 1.14 (m, 1H), 0.54 – 0.49 (m, 2H), 0.27 – 0.22 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 131.1 (d, J_{C-P} = 2.8 Hz), 130.9 (d, J_{C-P} = 136.1 Hz), 130.7 (d, J_{C-P} = 10.0 Hz), 127.6 (d, J_{C-P} = 12.9 Hz), 69.0 (d, J_{C-P} = 5.8 Hz), 10.5 (d, J_{C-P} = 7.0 Hz), 2.6. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 31.1.

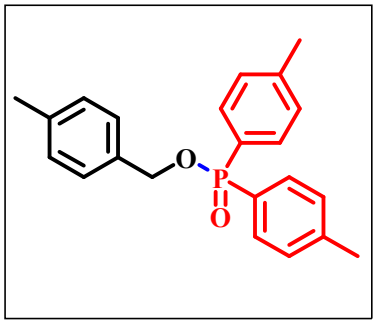


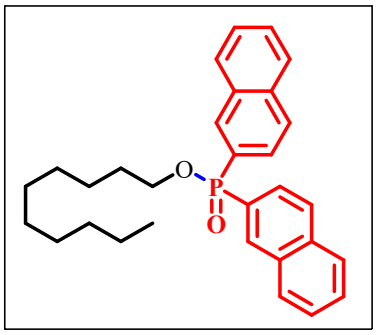
((1s,3s)-Adamantan-1-yl)methyl diphenylphosphinate (4ah):[21] Isolated as colourless oil yield: 132 mg 72 %  **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.83 – 7.77 (m, 4H), 7.51 – 7.47 (m, 2H), 7.45 – 7.40 (m, 4H), 3.57 – 3.53 (m, 2H), 2.00 – 1 .96 (m, 3H), 1.71 (d, *J* = 12.0 Hz, 3H), 1.64 (d, *J* = 12.1 Hz, 3H), 1.58 (s, 6H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 132.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 136.3 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.9 Hz), 74.2 (d, $J_{C\text{-}P}$ = 6.5 Hz), 39.2, 34.1 (d, $J_{C\text{-}P}$ = 7.2 Hz)37.0, 28.1. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 30.7.

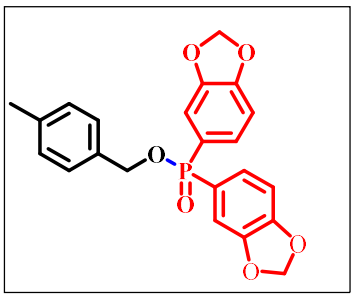
3,7-Dimethyloct-6-en-1-yl diphenylphosphinate (4ai):[20] Isolated as colourless oil yield: 104 mg 58 %  **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.82 – 7.76 (m, 4H), 7.51 – 7.48 (m, 2H), 7.44 – 7.40 (m, 4H), 5.06 (t, *J* = 6.7 Hz, 1H), 4.10 – 4.01 (m, 2H), 2.01 – 1.88 (m, 2H), 1.80 – 1.73 (m, 1H), 1.66 (s, 3H), 1.57 (s, 3H), 1.54 – 1.47 (m, 1H), 1.34 – 1.27 (m, 2H), 1.18 – 1.11 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 132.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.7 (d, $J_{C\text{-}P}$ = 136.1 Hz, *J* = 1.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.4, 128.7 (d, $J_{C\text{-}P}$ = 12.9 Hz), 124.6, 63.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 37.5 (d, $J_{C\text{-}P}$ = 6.6 Hz), 37.0, 29.1, 25.8, 25.4, 19.4, 17.7. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 31.2.

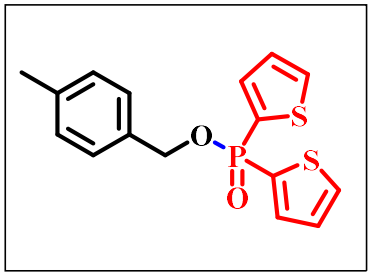
Phenethyl diphenylphosphinate (4aj):[10] Isolated as olourless oil yield: 145 mg 90 %  **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.72 – 7.68 (m, 4H), 7.40 – 7.47 (m, 2H), 7.41 – 7.38 (m, 4H), 7.31 – 7.28 (m, 2H), 7.26 – 7.24 (m, 1H), 7.21 – 7.19 (m, 2H), 4.24 – 4.20 (m, 2H), 3.05 – 3.02 (m, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 137.6, 132.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 136.2 Hz), 129.2, 128.6, 128.5 (d, $J_{C\text{-}P}$ = 4.5 Hz), 126.7, 65.4 (d, $J_{C\text{-}P}$ = 5.9 Hz), 37.2 (d, $J_{C\text{-}P}$ = 6.9 Hz). **^{31}P NMR (200 MHz, CDCl$_3$)** δ 31.6.

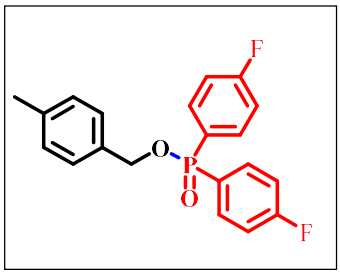
4-Methylbenzyl bis(4-methoxyphenyl)phosphinate (4ak): Isolated as Colourless Colourless oil yield: 134 mg 70 %  **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.75 – 7.70 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 2.6 Hz, 2H),6.91(d, *J* = 2.6 Hz, 2H), 4.97 (d, *J* = 6.6 Hz, 2H), 3.82 (s, 6H), 2.34 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 138.1, 133.8, 133.7 (d, $J_{C\text{-}P}$ = 11.3 Hz), 129.3, 128.1, 123.2 (d, $J_{C\text{-}P}$ = 143.4 Hz), 114.1 (d, $J_{C\text{-}P}$ = 14.0 Hz), 66.0 (d, $J_{C\text{-}P}$ = 5.4 Hz), 55.4, 21.3. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 33.03. **HRMS (ESI+):** m/z calcd. $C_{22}H_{23}O_4P$ For $[M+H]^+$: 383.1407; Found: 383.1377.

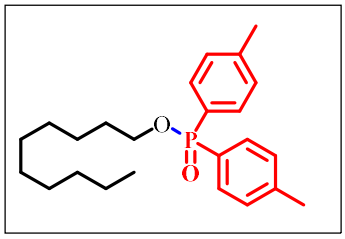
4-Methylbenzyl di-p-tolylphosphinate (4al): Isolated as Colourless Colourless oil yield: 126 mg 72 %  **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.73 – 7.68 (m, 4H), 7.26 – 7.22 (m, 6H), 7.16 – 7.14 (m, 2H), 4.99 (d, *J* = 6.5 Hz, 2H), 2.37 (s, 6H), 2.34 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 141.7 (d, J_{C-P} = 2.8 Hz), 138.1, 133.7 (d, J_{C-P} = 7.7 Hz), 131.8 (d, J_{C-P} = 10.5 Hz), 129.4, 129.3 (d, J_{C-P} = 2.7 Hz), 128.4 (d, J_{C-P} = 138.4 Hz), 120.1, 66.2 (d, J_{C-P} = 5.5 Hz), 21.7, 21.3. **^{31}P NMR (200 MHz, CDCl$_3$) δ 33.2. HRMS (ESI+):** m/z calcd. $C_{22}H_{23}O_2P$ For $[M+H]^+$: 351.1509; Found: 351.1483.

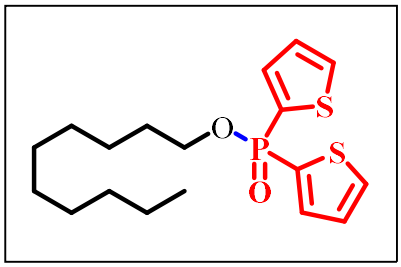
Decyl di(naphthalen-2-yl)phosphinate (4am): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50  (d, *J* = 2.3 Hz, 2H), 7.96 – 7.88 (m, 4H), 7.86 – 7.78 (m, 4H), 7.59 – 7.52 (m, 4H), 4.11 (q, *J* = 6.7 Hz, 2H), 1.80 – 1.75 (m, 2H), 1.45 – 1.39 (m, 14H), 0.89 – 0.85 (m, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 135.0 (d, J_{C-P} = 2.4 Hz), 134.0 (d, J_{C-P} = 9.8 Hz), 132.6 (d, J_{C-P} = 14.3 Hz), 129.1, 128.9 (d, J_{C-P} = 137 Hz), 128.5 (d, J_{C-P} = 12.6 Hz), 128.3, 127.9, 127.0, 126.5 (d, J_{C-P} = 10.7 Hz), 65.4 (d, J_{C-P} = 6.1 Hz), 32.0, 30.7 (d, J_{C-P} = 6.5 Hz), 29.8, 29.6, 29.4, 29.3, 25.8, 22.8, 14.2. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 31.44. **HRMS (ESI+):** m/z calcd. $C_{30}H_{35}O_2P$ For $[M+H]^+$: 459.2448; Found: 459.2437.

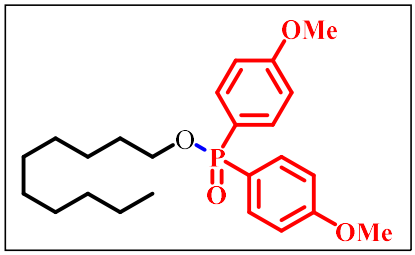
4-Methylbenzyl bis(benzo[d][1,3]dioxol-5-yl)phosphinate (4an): Isolated as Colourless Colourless oil yield: 140 mg 68 %  **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.38 – 7.33 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.20 (s, 1H), 7.17 – 7.14 (m, 3H), 6.86 – 6.84 (m, 2H), 5.99 (s, 4H), 4.98 (d, *J* = 6.7 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 151.1 (d, J_{C-P} = 3.1 Hz), 148.1 (d, J_{C-P} = 19.8 Hz), 138.3, 133.4 (d, J_{C-P} = 7.4 Hz), 129.4, 128.2, 127.3 (d, J_{C-P} = 11.0 Hz), 125.8 (d, J_{C-P} = 142.0 Hz), 111.2 (d, J_{C-P} = 12.7 Hz), 108.8 (d, J_{C-P} = 16.4 Hz), 101.7, 66.4 (d, J_{C-P} = 5.5 Hz), 21.3. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 32.0. **HRMS (ESI+):** m/z calcd. $C_{22}H_{23}O_3P$ For $[M+H]^+$: 411.0993; Found: 411.0974.

4-Methylbenzyl di(thiophen-2-yl)phosphinate (4ao): Isolated as Colourless Colourless oil yield: 107 mg 64 % 
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.64 (m, 4H), 7.27 – 7.25 (m, 2H), 7.16 – 7.13 (m, 4H), 5.09 (d, J = 7.4 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.3, 136.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 134.0 (d, $J_{C\text{-}P}$ = 6.4 Hz), 133.0 (d, $J_{C\text{-}P}$ = 7.8 Hz), 132.1 (d, $J_{C\text{-}P}$ = 162.1 Hz), 129.3, 128.4 (d, $J_{C\text{-}P}$ = 16.4 Hz), 128.1, 67.1 (d, $J_{C\text{-}P}$ = 5.4 Hz), 21.3. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 19.1. **HRMS (ESI+):** m/z calcd. $C_{22}H_{23}O_3P$ For $[M+H]^+$: 367.1458; Found: 367.1456.

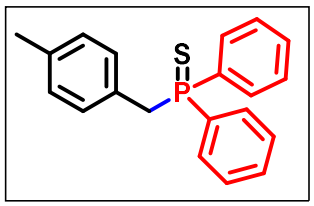
4-Methylbenzyl bis(4-fluorophenyl)phosphinate (4ap): Isolated as Colourless Colourless oil yield: 111 mg 62 % 
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.76 (m, 4H), 7.23 – 7.21 (m, 2H), 7.16 – 7.10 (m, 6H), 5.01 (d, J = 7.1 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 165.4 (dd, $J_{C\text{-}F}$ = 252.4 Hz, $J_{C\text{-}P}$ = 3.3 Hz), 138.5, 134.4 (dd, $J_{C\text{-}F}$ = 11.7 Hz, $J_{C\text{-}P}$ = 8.9 Hz), 133.1 (d, $J_{C\text{-}P}$ = 7.1 Hz), 129.4, 128.3, 127.4 (dd, $J_{C\text{-}F}$ = 140.6 Hz, $J_{C\text{-}P}$ = 3.4 Hz), 116.1 (dd, $J_{C\text{-}F}$ = 21.3 Hz, $J_{C\text{-}P}$ = 14.3 Hz), 66.7 (d, $J_{C\text{-}P}$ = 5.4 Hz), 21.3. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 30.3. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -105.9. **HRMS (ESI+):** m/z calcd. $C_{20}H_{18}O_2F_2P$ For $[M+H]^+$: 359.1007; Found: 359.1020.

Decyl di-p-tolylphosphinate (4aq): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 4H), 7.24 – 7.21 (m, 4H), 4.00 – 3.95 (m, 2H), 2.36 (m, 6H), 1.72 – 1.65 (m, 2H), 1.39 – 1.32 (m, 2H), 1.27 – 1.23 (m, 12H), 0.86 (t, J = 6.5 Hz, 3H). 
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.45 Hz), 129.3 (d, $J_{C\text{-}P}$ = 13.3 Hz), 128.7 (d, $J_{C\text{-}P}$ = 138.8 Hz), 64.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 32.0, 30.6 (d, $J_{C\text{-}P}$ = 6.5 Hz), 29.6 (d, $J_{C\text{-}P}$ = 2.1 Hz), 29.4, 29.3, 25.7, 22.8, 21.7, 14.2. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 32.1.

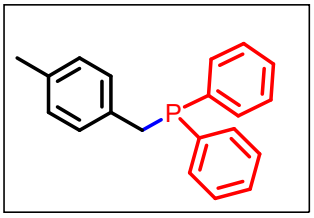
Decyl di(thiophen-2-yl)phosphinate (4ar): Isolated as Colourless Colourless oil yield: 145 mg 78 %  **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.69 (t, *J* = 4.6 Hz, 2H), 7.65 – 7.63 (m, 2H), 7.17 – 7.13 (m, 2H), 4.08 (q, *J* = 6.8 Hz, 2H), 1.74 – 1.69 (m, 2H), 1.39 – 1.35 (m, 2H), 1.27 – 1.21 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 135.5 (d, $J_{C\text{-}P}$ = 12.1 Hz), 132.8 (d, $J_{C\text{-}P}$ = 6.4 Hz), 131.4 (d, $J_{C\text{-}P}$ = 162.1 Hz), 127.3 (d, $J_{C\text{-}P}$ = 16.4 Hz), 65.1 (d, $J_{C\text{-}P}$ = 6.0 Hz), 31.0, 29.5 (d, $J_{C\text{-}P}$ = 7.1 Hz), 28.8, 28.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 28.4, 28.2, 24.6, 21.8, 13.2. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 18.3**. HRMS (ESI+):** m/z calcd. $C_{22}H_{23}O_3P$ For $[M+Na]^+$: 393.1083; Found: 393.1047

Decyl bis(4-methoxyphenyl)phosphinate (4as): Isolated as Colourless Colourless oil yield: 168 mg 80 %  **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.72 – 7.68 (m, 4H), 6.94 – 6.91 (m, 4H), 3.96 (q, *J* = 6.7 Hz, 2H), 3.82 (s, 6H), 1.71 – 1.65 (m, 2H), 1.37 – 1.34 (m, 2H), 1.27 – 1.20 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H**). ^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 133.6 (d, $J_{C\text{-}P}$ = 11.4 Hz), 123.5 (d, $J_{C\text{-}P}$ = 143.6 Hz), 114.1 (d, $J_{C\text{-}P}$ = 13.8 Hz), 64.8 (d, $J_{C\text{-}P}$ = 5.8 Hz), 55.4, 32.0, 30.7 (d, $J_{C\text{-}P}$ = 6.8 Hz), 29.6 (d, $J_{C\text{-}P}$ = 1.8 Hz), 29.4, 29.3, 25.8, 22.7, 14.2. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 31.9 **HRMS (ESI+):** m/z calcd. $C_{24}H_{35}O_4P$ For $[M+H]^+$: 419.1822; Found: 419.1810.

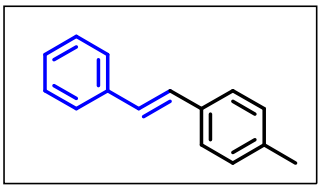
(4-Methylbenzyl)diphenylphosphine sulphide ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 – 7.77 (m, 4H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 4H), 6.97 – 6.96 (m, 2H), 6.88 – 6.86 (m, 2H), 3.81 (d, *J* = 13.3 Hz, 2H), 2.27 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 135.9 (d, $J_{C\text{-}P}$ = 4.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 79.4 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.4 (d, $J_{C\text{-}P}$ = 5.3 Hz), 127.8 (d, $J_{C\text{-}P}$ = 3.2 Hz), 127.6 (d, $J_{C\text{-}P}$ = 11.9 Hz), 126.6 (d, $J_{C\text{-}P}$ = 7.7 Hz), 39.6 (d, $J_{C\text{-}P}$ = 50.6 Hz), 20.2. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 42.0.



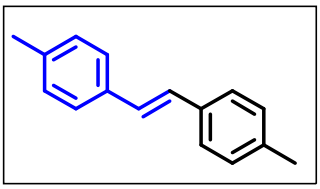
(4-Methylbenzyl)diphenylphosphane ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.40 (m, 4H), 7.34 – 7.31 (m, 6H), 7.02 -7.00 (m, 2H), 6.98 – 6.96 (m, 2H), 3.40 (s, 2H), 2.30 (m, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 138.4 (d, $J_{C\text{-}P}$ = 14.9 Hz), 135.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 134.4 (d, $J_{C\text{-}P}$ = 8.2 Hz), 133.0 (d, $J_{C\text{-}P}$ = 18.2 Hz), 129. (d, $J_{C\text{-}P}$ = 6.6 Hz), 129.1 (d, $J_{C\text{-}P}$ = 1.6 Hz), 128.8, 128.4 (d, $J_{C\text{-}P}$ = 6.4 Hz), 35.6 (d, $J_{C\text{-}P}$ = 15.0 Hz), 21.1. **^{31}P NMR (200 MHz, CDCl$_3$)** δ -10.2. **HRMS (ESI+):** m/z calcd. $C_{20}H_{19}P$ For $[M+H]^+$: 291.1298; Found: 291.1288.

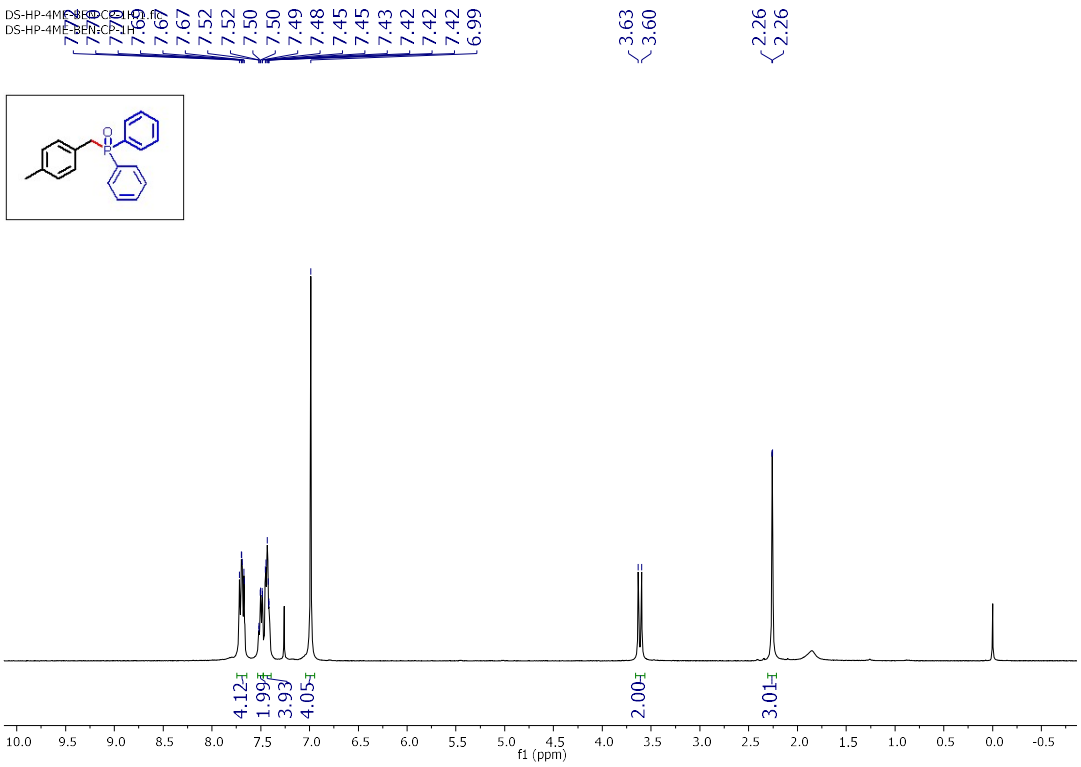


(E)-1-Methyl-4-styrylbenzene ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.41 (m, 2H), 7.35 – 7.33 (m, 2H), 7.29 – 7.25 (m, 2H), 7.19 – 7.14 (m, 2H), 7.10 – 7.07 (m, 2H), 7.00 – 6.99 (m, 2H), 2.28 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 137.7, 137.6, 134.7, 129.5, 128.8, 128.7, 127.8, 127.5, 126.6, 126.5, 21.4.



(E)-1,2-Di-p-tolylethene ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.39 (m, 4H), 7.17 – 7.15 (m, 4H), 7.04 (s, 2H), 2.36 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.42, 134.88, 129.51, 127.78, 126.45, 21.4.

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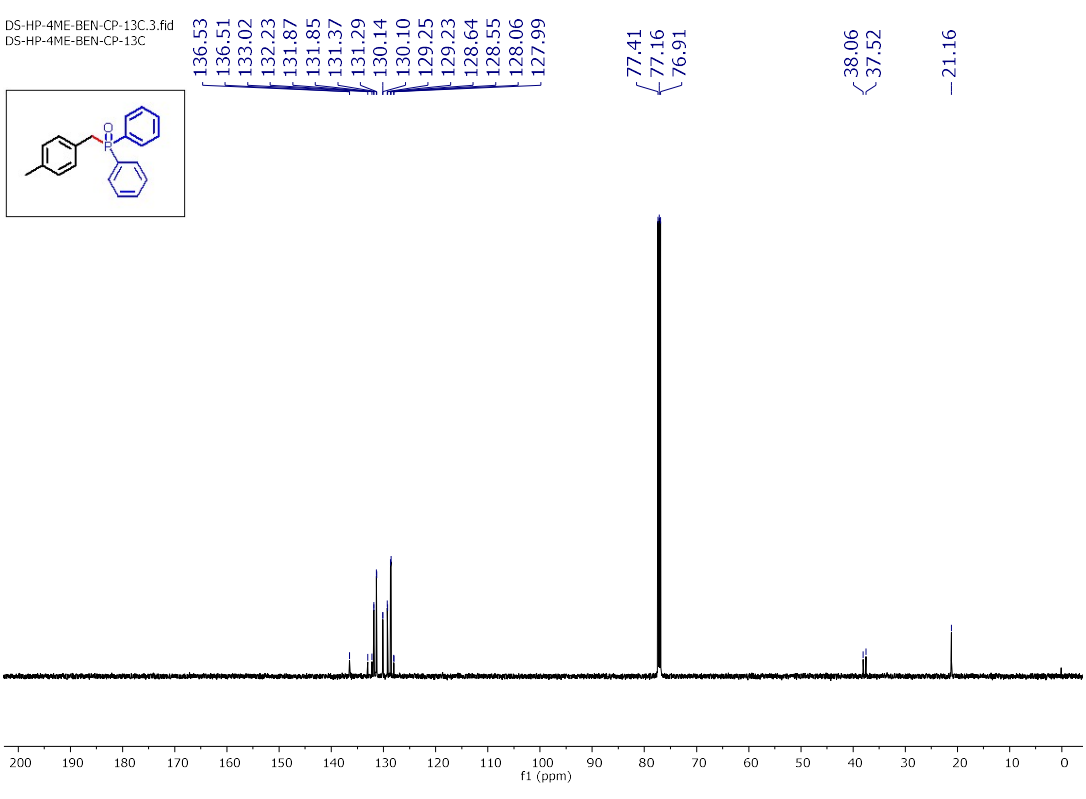
3.01
f1 (ppm)


DS-HP-4ME-BEN-CP-13C.3.fid
DS-HP-4ME-BEN-CP-13C
136.53
136.51
133.02
132.23
131.87
131.85
131.37
131.29
130.14
130.10
129.25
129.23
128.64
128.55
128.06
127.99
77.41
77.16
76.91
38.06
37.52
21.16
f1 (ppm)

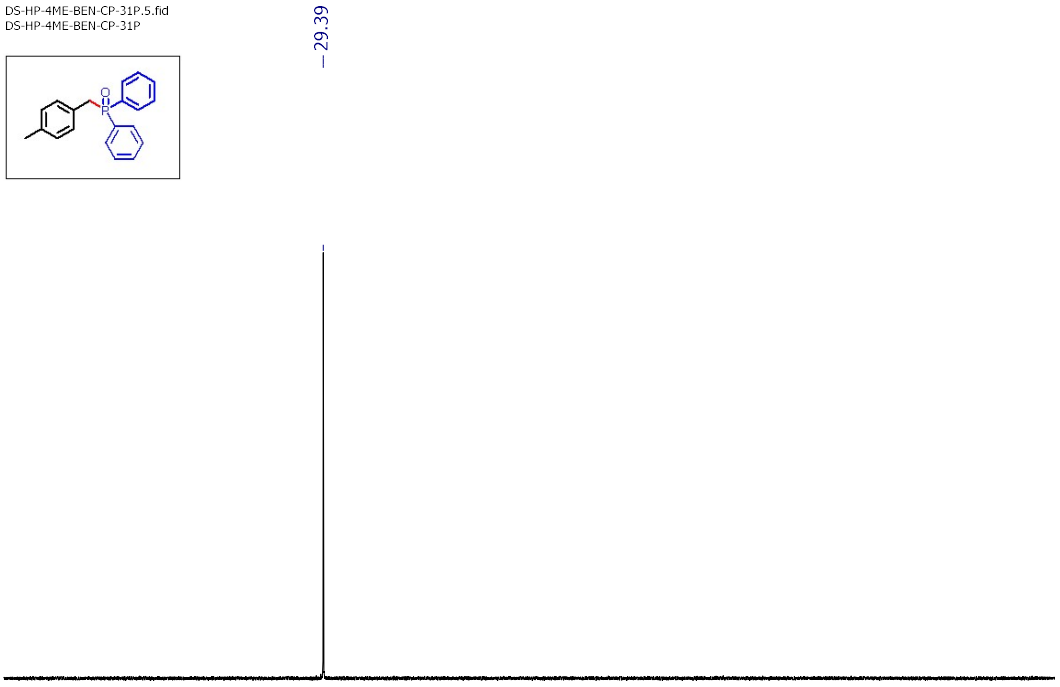
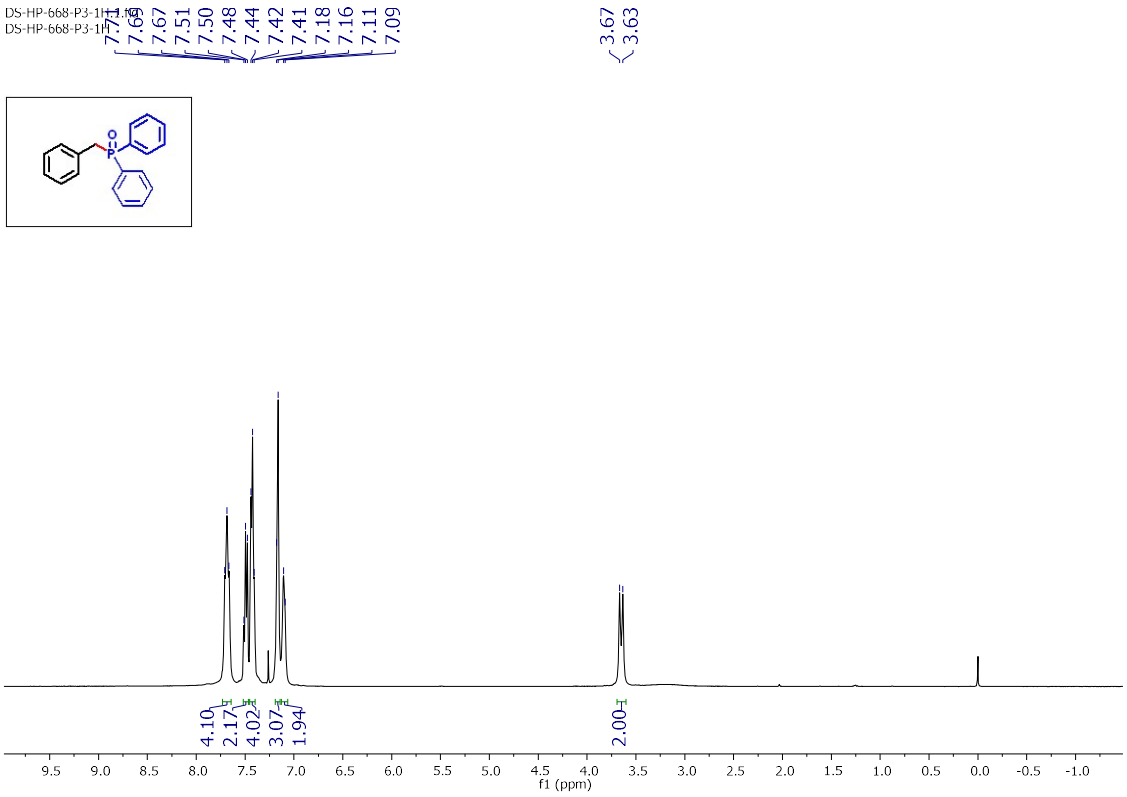


Figure S4: ^{1}H NMR (400 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz) and ^{31}P $\{1H\}$ NMR (200 MHz) spectrum of Compound 3a in $CDCl_3$



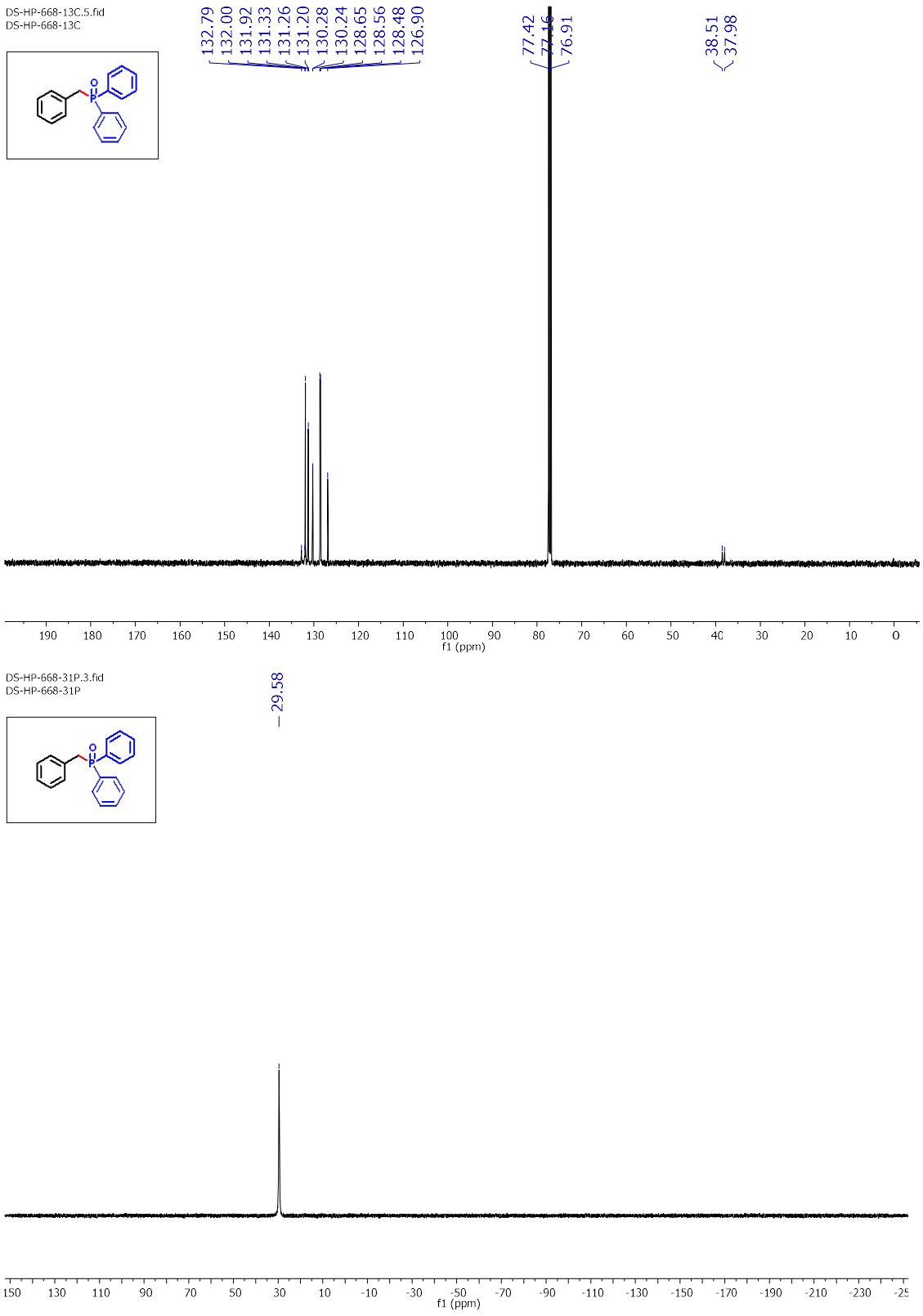
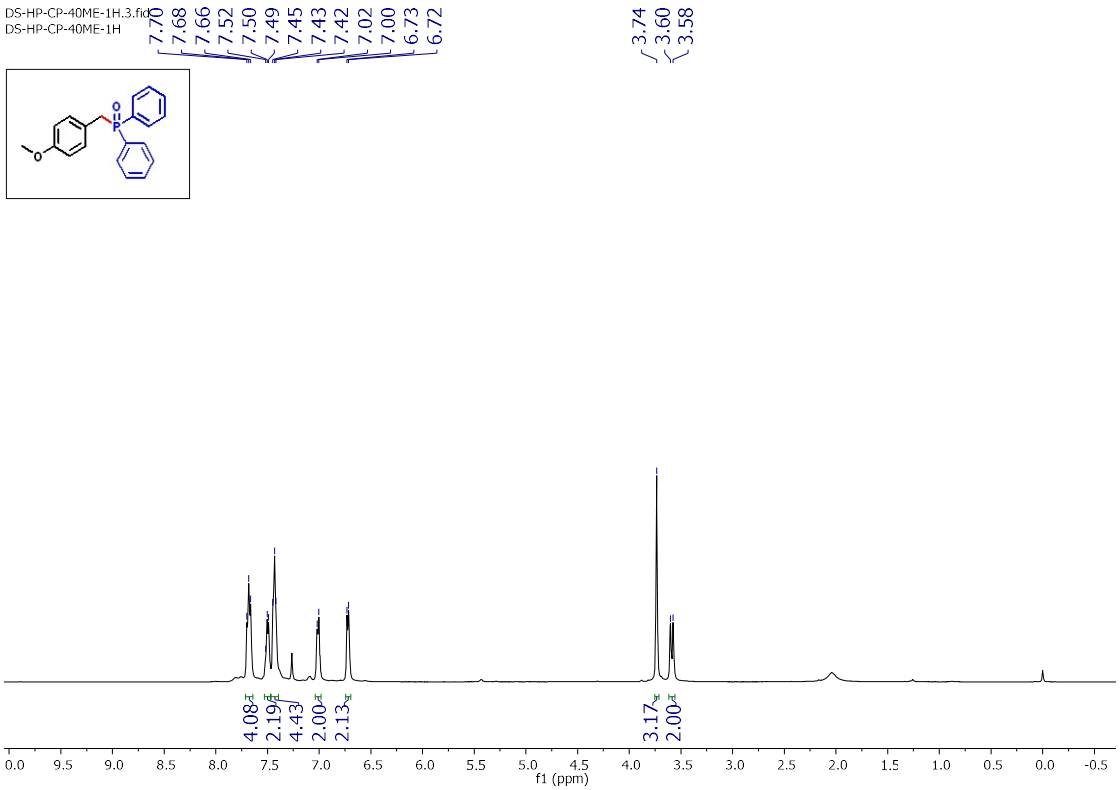
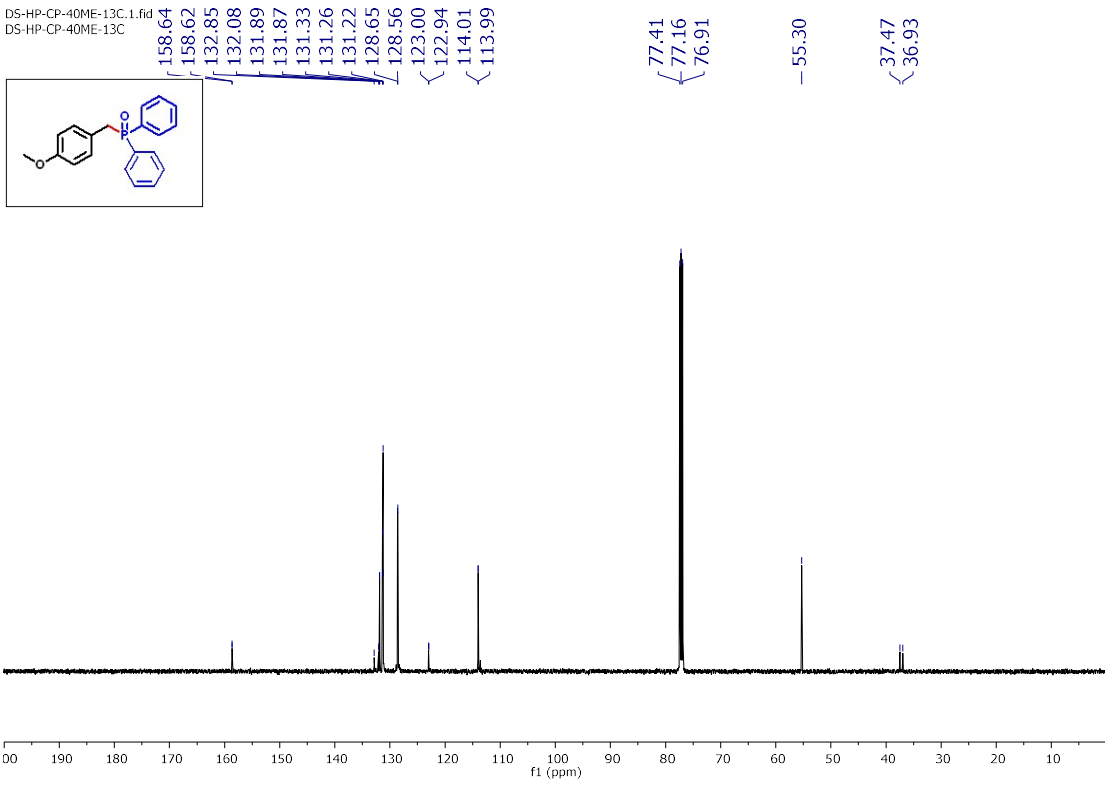


Figure S5: ^{1}H NMR (400 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz) and ^{31}P {1H} NMR (200 MHz) spectrum of Compound 3b in $CDCl_3$


DS-HP-CP-40ME-1H.3.fid
DS-HP-CP-40ME-1H
7.70
7.68
7.66
7.52
7.50
7.49
7.45
7.43
7.42
7.02
7.00
6.73
6.72
3.74
3.60
3.58
4.08
2.19
4.43
2.00
2.13
3.17
2.00
f1 (ppm)


DS-HP-CP-40ME-13C.1.fid
DS-HP-CP-40ME-13C
158.64
158.62
132.85
132.08
131.89
131.87
131.33
131.26
131.22
128.65
128.56
123.00
122.94
114.01
113.99
77.41
77.16
76.91
55.30
37.47
36.93
f1 (ppm)

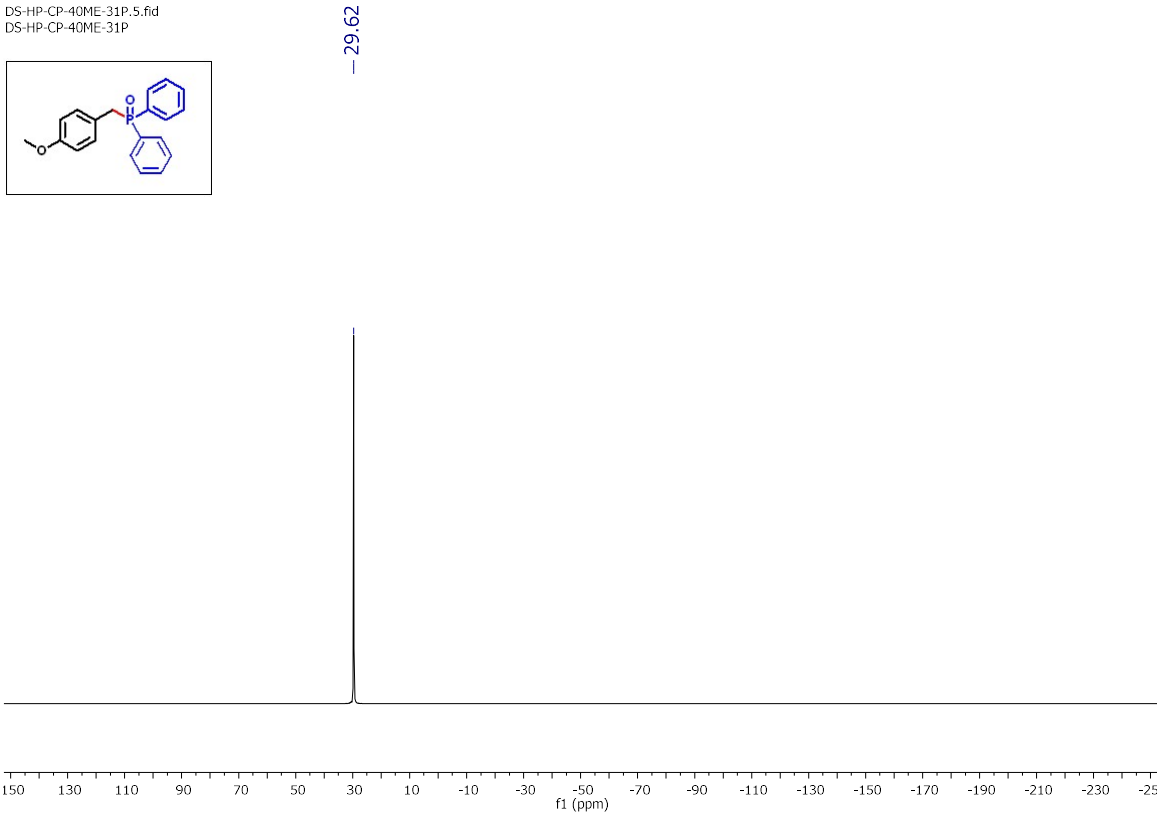
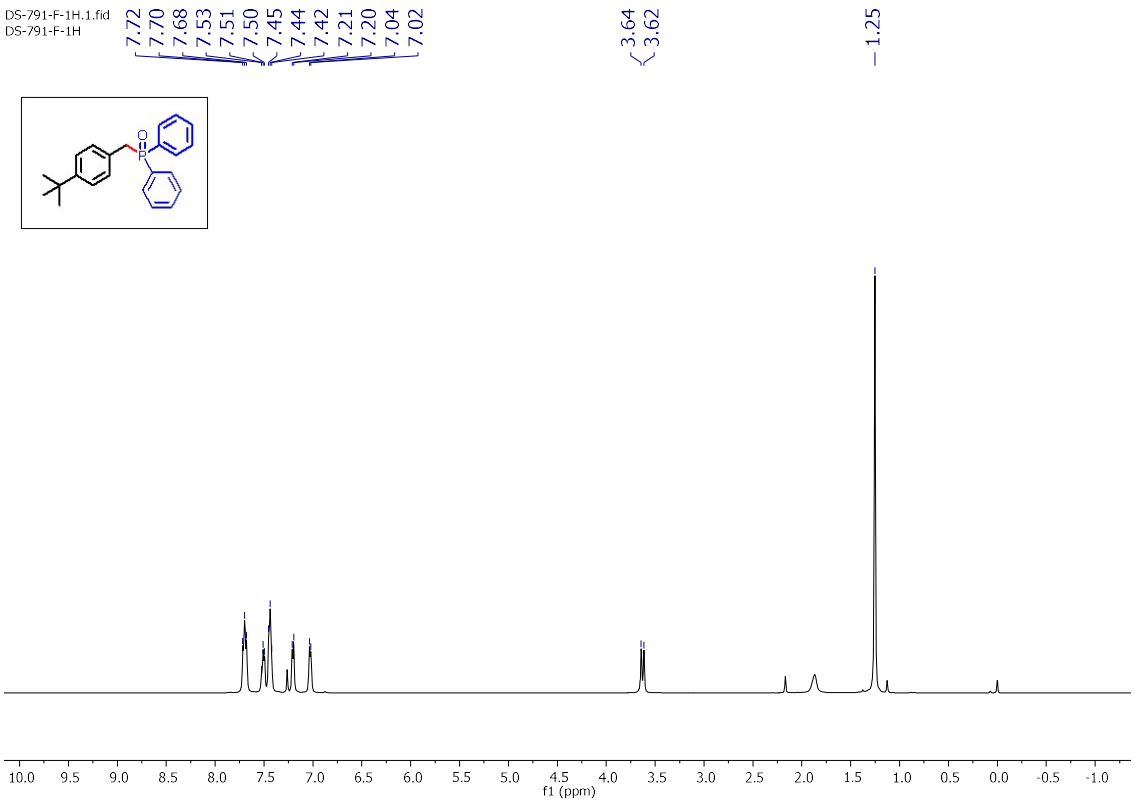
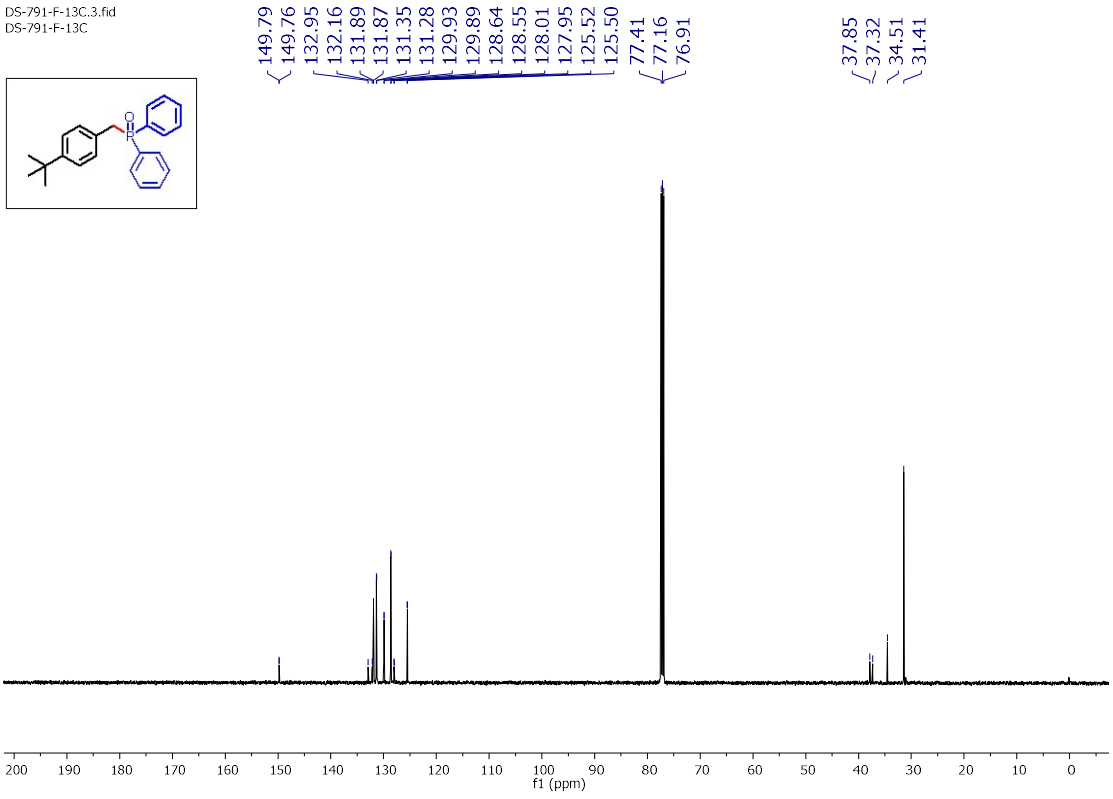


Figure S6. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz) and ^{31}P {1H} NMR (200 MHz) spectrum of Compound 3c in $CDCl_3$


DS-791-F-1H.1.fid
DS-791-F-1H
7.72
7.70
7.68
7.53
7.51
7.50
7.45
7.44
7.42
7.21
7.20
7.04
7.02
3.64
3.62
1.25
f1 (ppm)


DS-791-F-13C.3.fid
DS-791-F-13C
149.79
149.76
132.95
132.16
131.89
131.87
131.35
131.28
129.93
129.89
128.64
128.55
128.01
127.95
125.52
125.50
77.41
77.16
76.91
37.85
37.32
34.51
31.41
f1 (ppm)

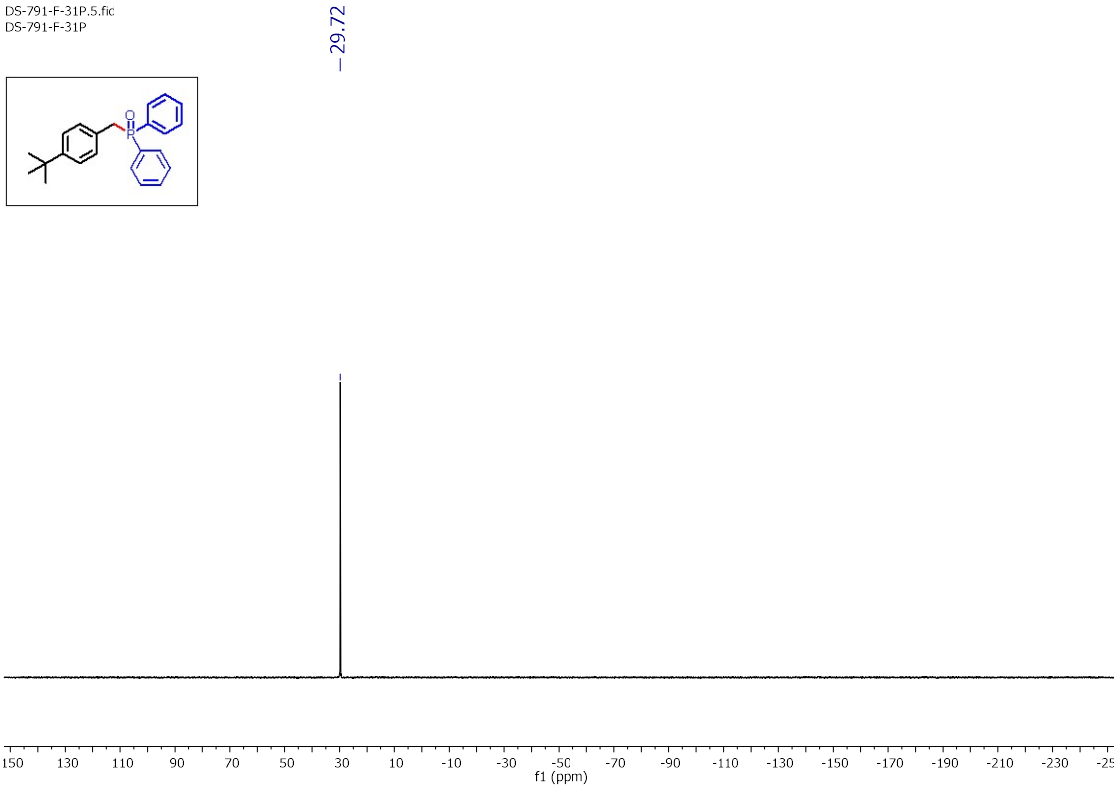
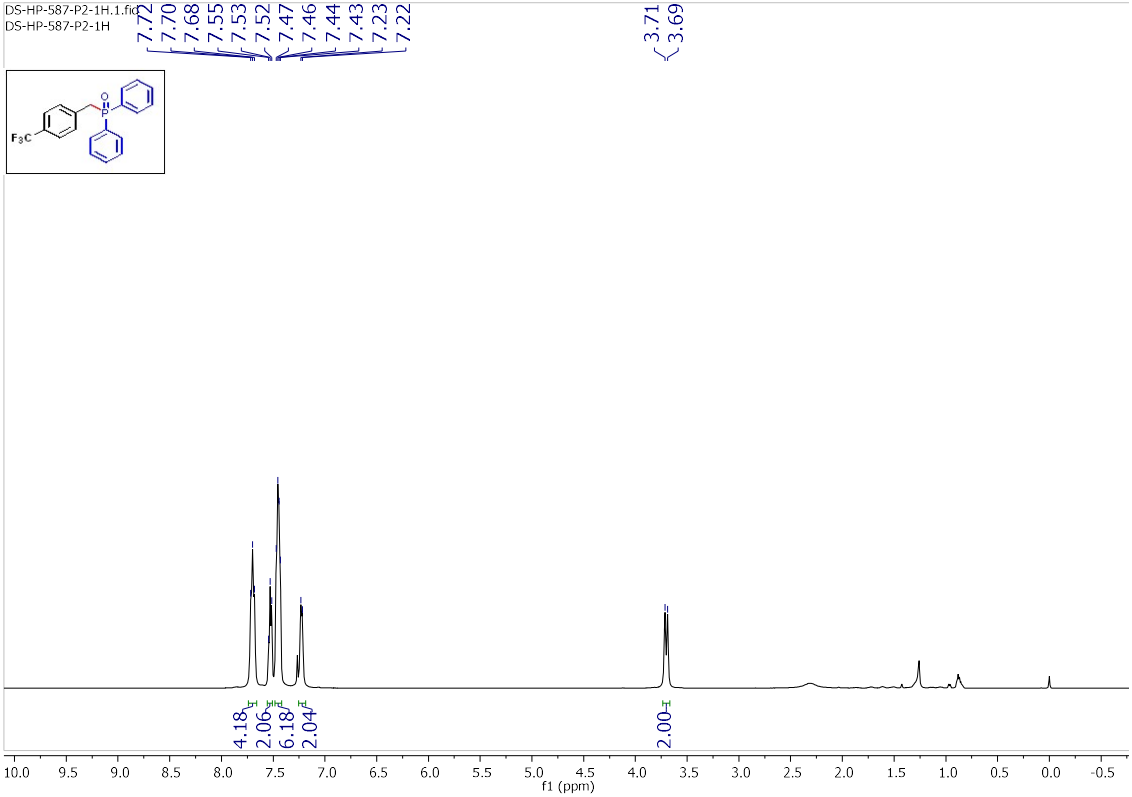
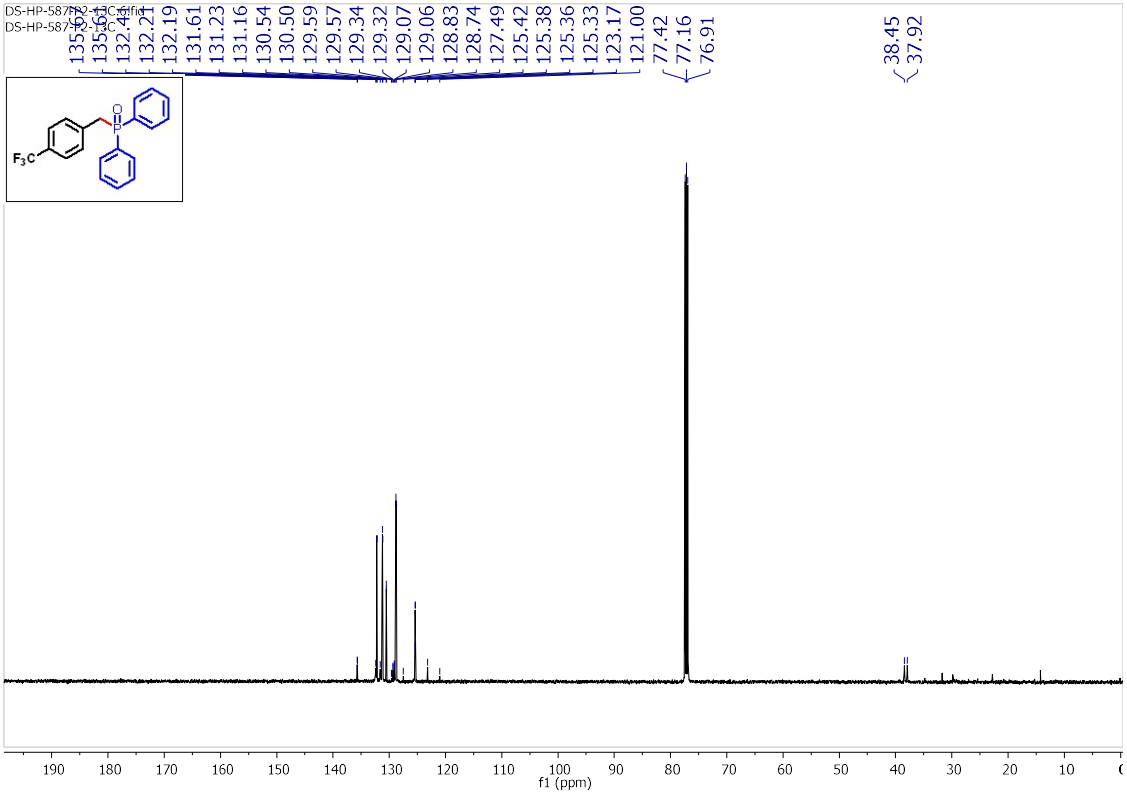
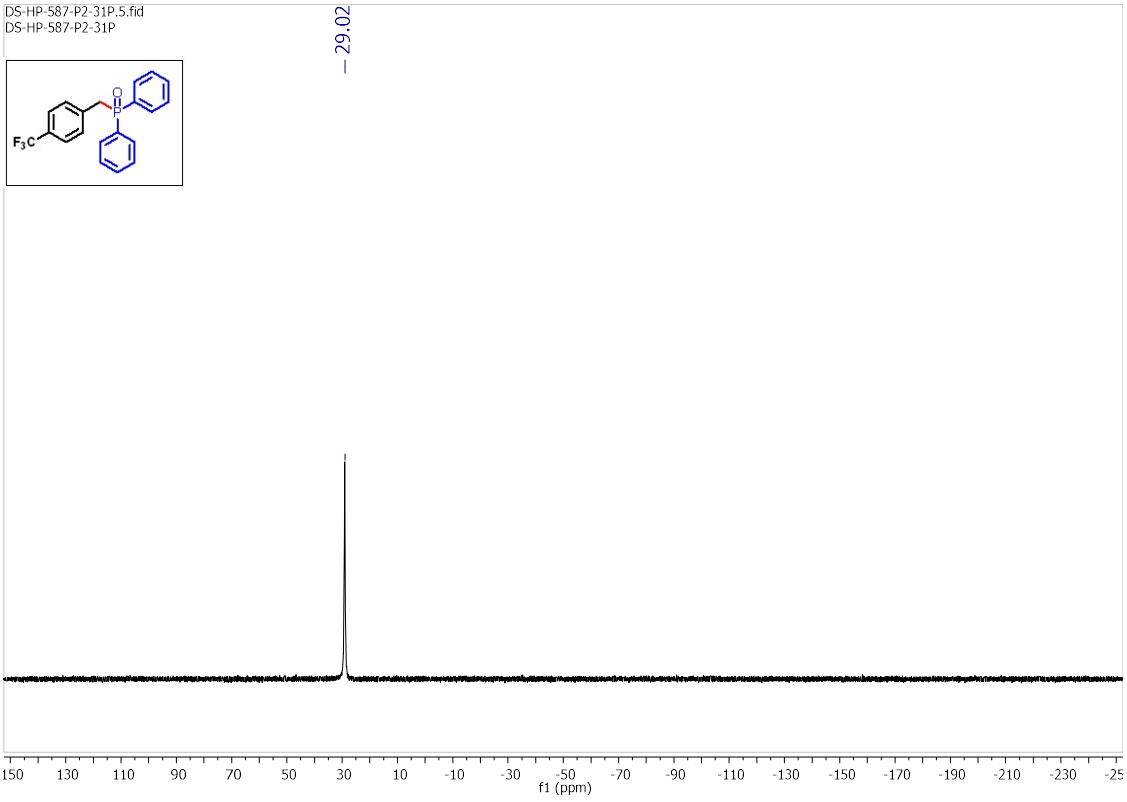


Figure S7. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz) and ^{31}P {1H} NMR (200 MHz) spectrum of Compound 3f in $CDCl_3$




DS-HP-587-P2-13C.fid
DS-HP-587-P2-13C
135.56
135.50
132.45
132.21
132.19
131.61
131.23
131.16
130.54
130.50
129.59
129.57
129.34
129.32
129.07
129.06
128.83
128.74
127.49
125.42
125.38
125.36
125.33
123.17
121.00
77.42
77.16
76.91
38.45
37.92
F3C
O
P
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


DS-HP-587-P2-31P.5.fid
DS-HP-587-P2-31P
29.02
F3C
O
P
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)

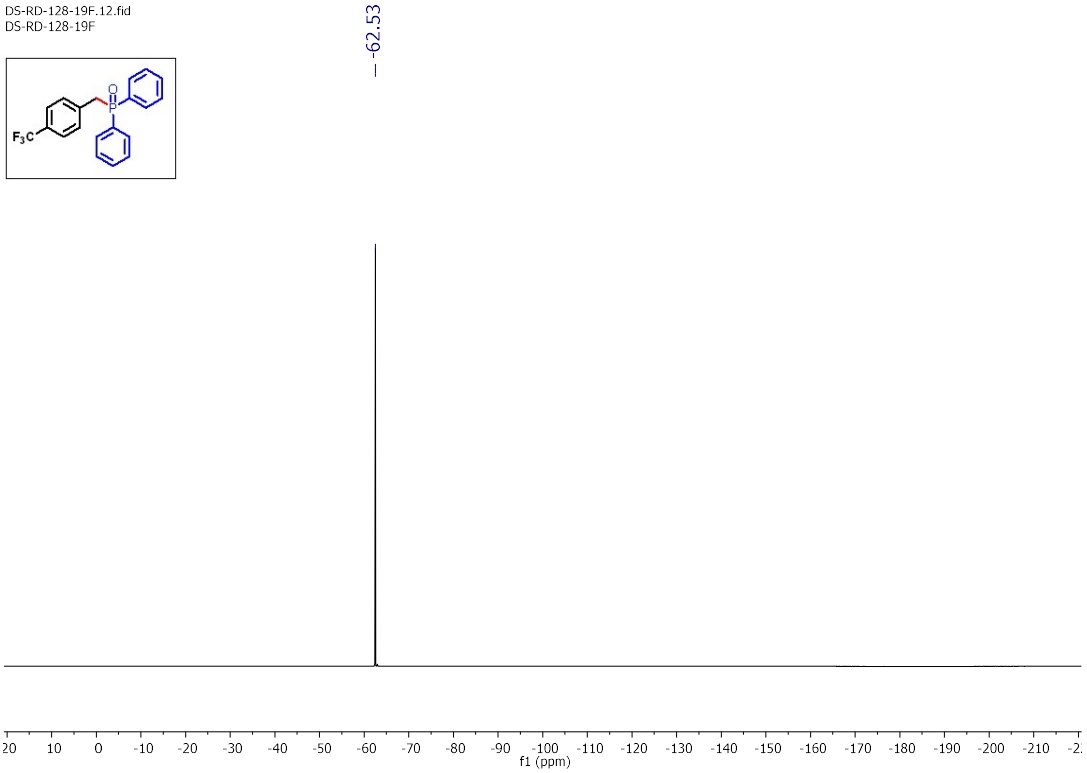
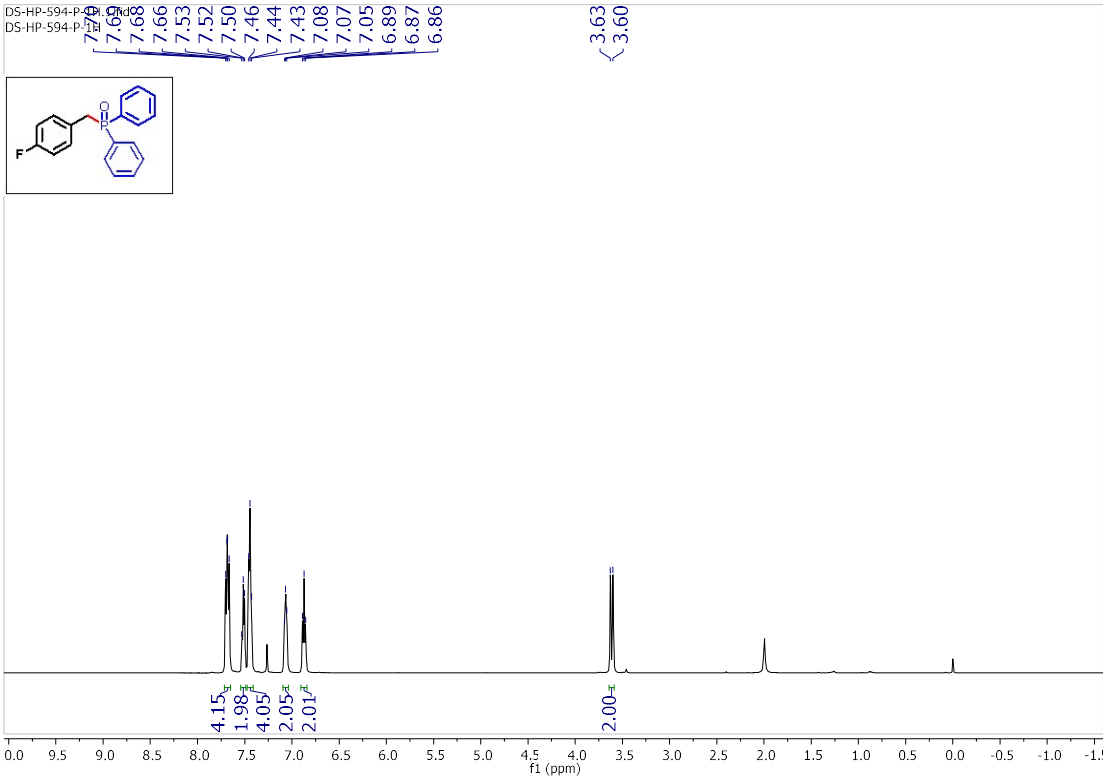
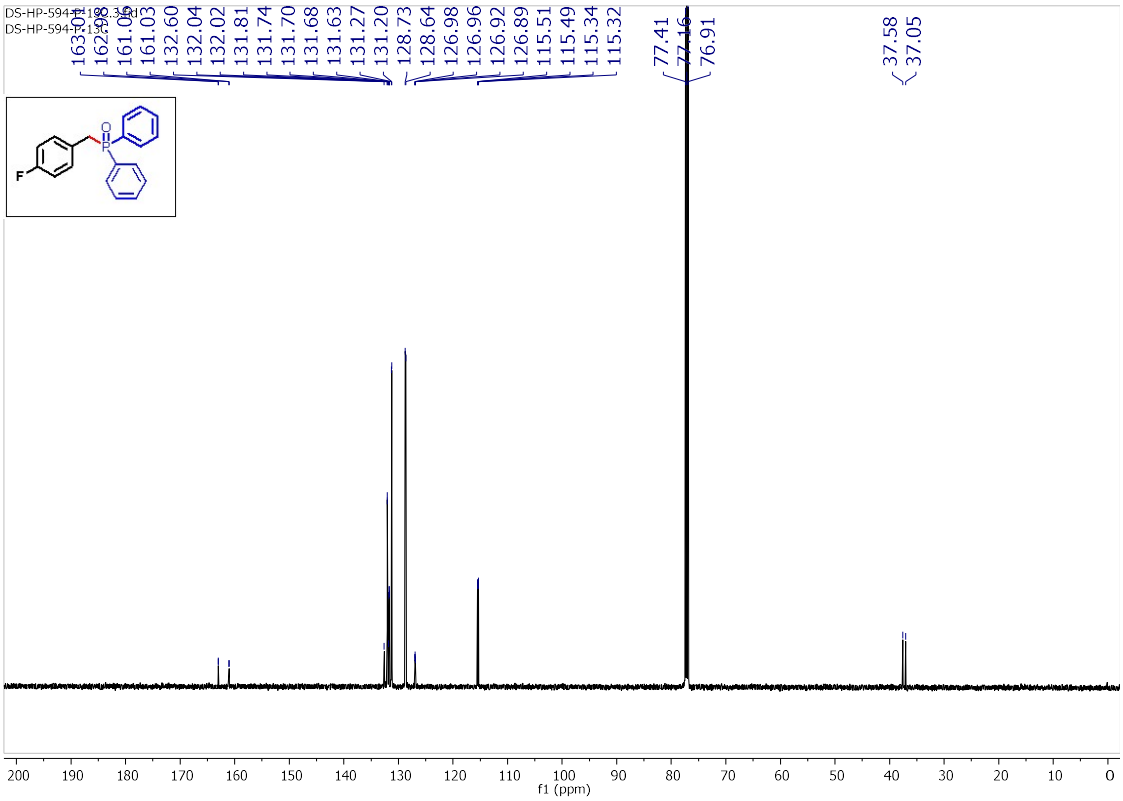
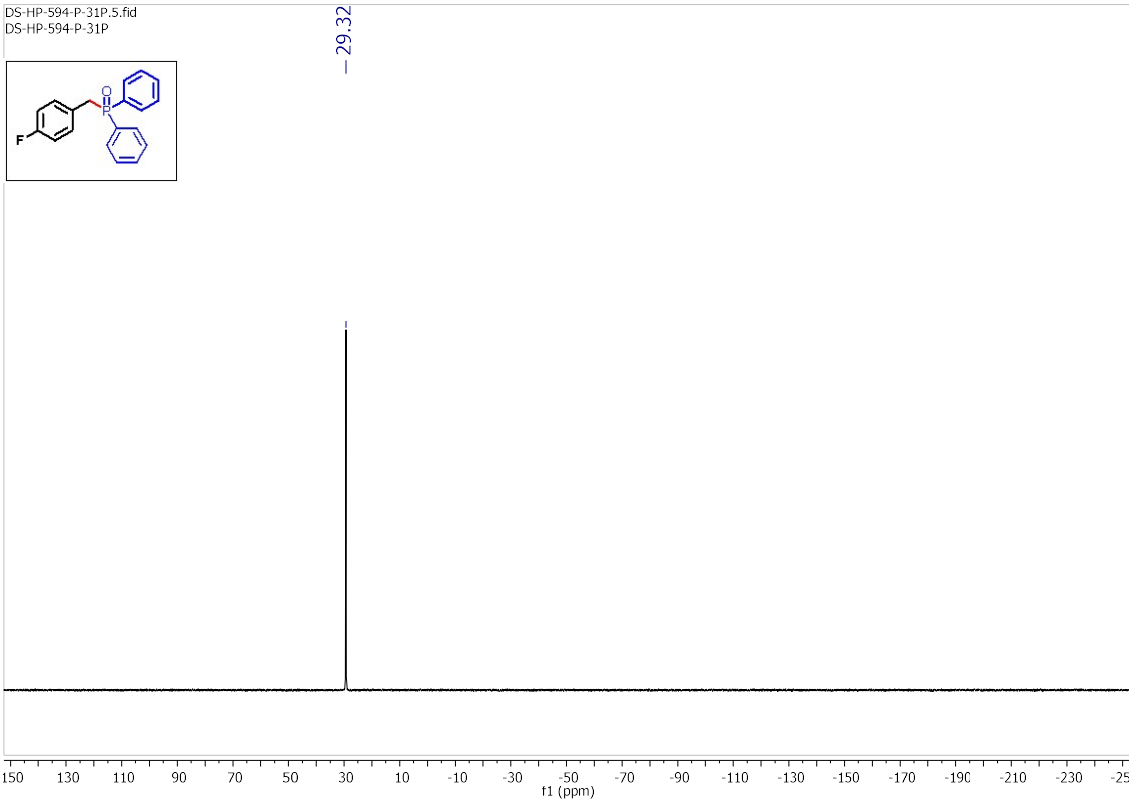


Figure S8. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), ^{31}P and ^{19}F {1H} NMR (200 MHz) spectrum of Compound 3g in $CDCl_3$




DS-HP-594-P-13C.fid
163.04
162.80
161.06
161.03
132.60
132.04
132.02
131.81
131.74
131.70
131.68
131.63
131.27
131.20
128.73
128.64
126.98
126.96
126.92
126.89
115.51
115.49
115.34
115.32
77.41
77.16
76.91
37.58
37.05
F
O
P
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


DS-HP-594-P-31P.5.fid
DS-HP-594-P-31P
29.32
F
O
P
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)

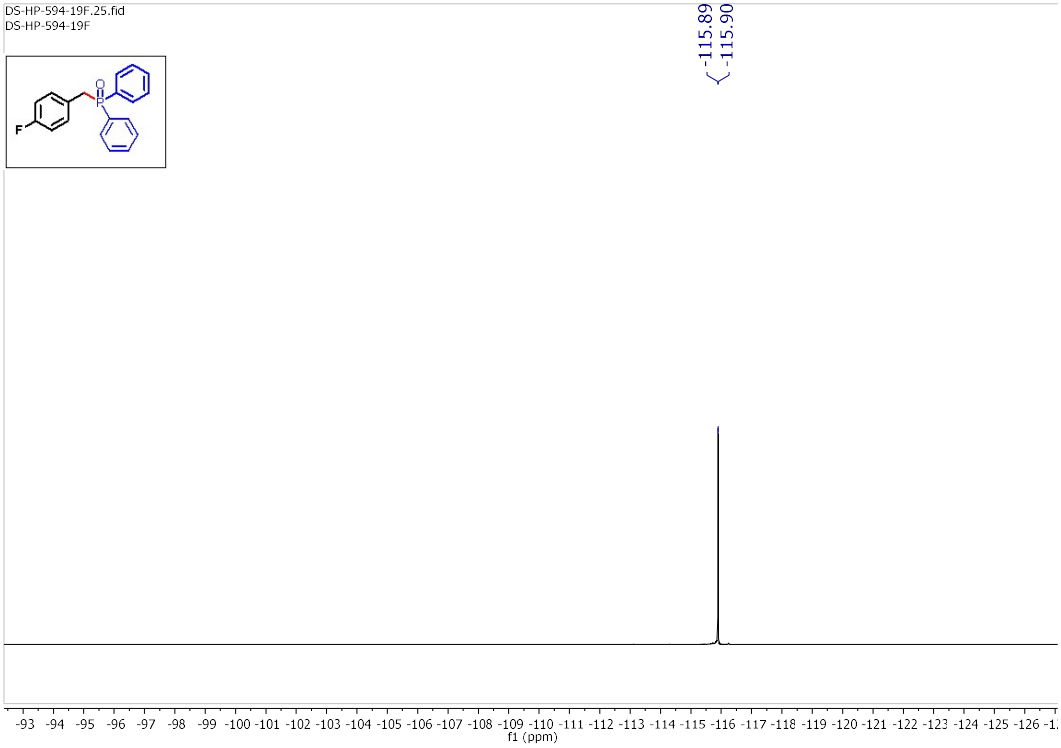
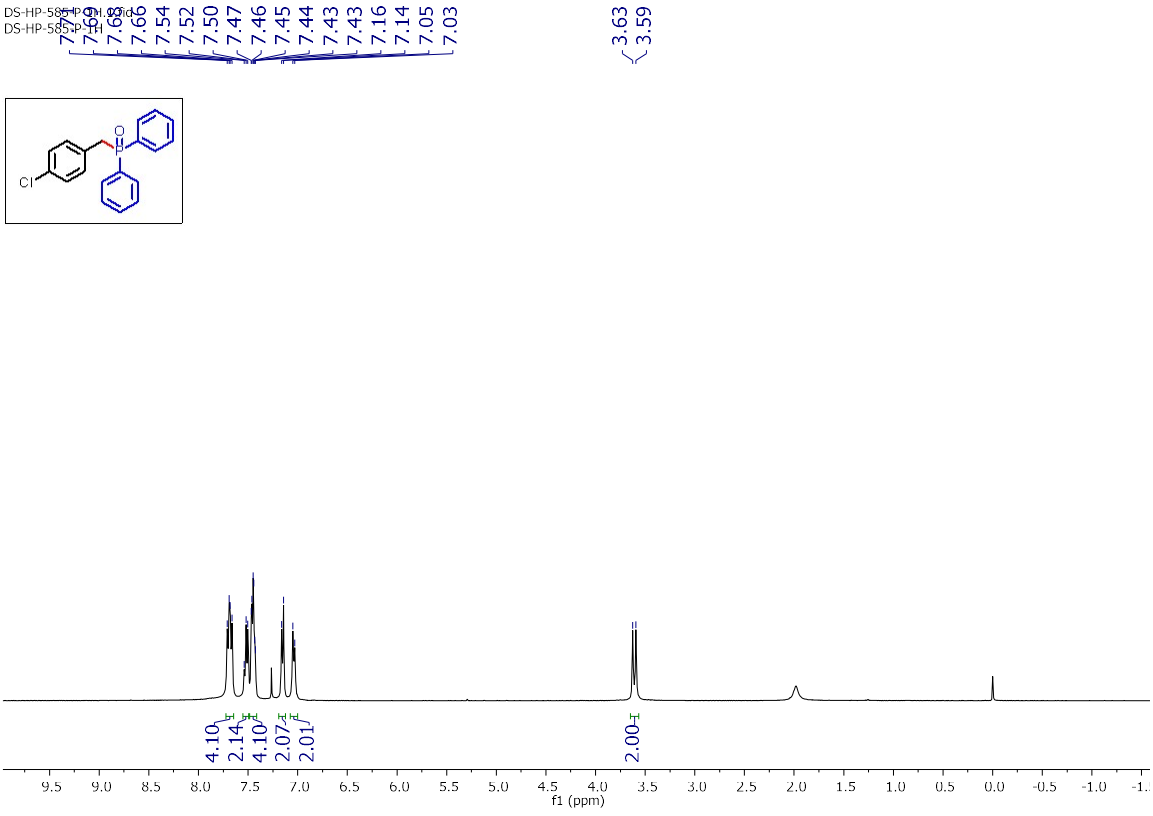


Figure S9. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), ^{31}P and ^{19}F {1H} NMR (200 MHz) spectrum of Compound 3h in $CDCl_3$



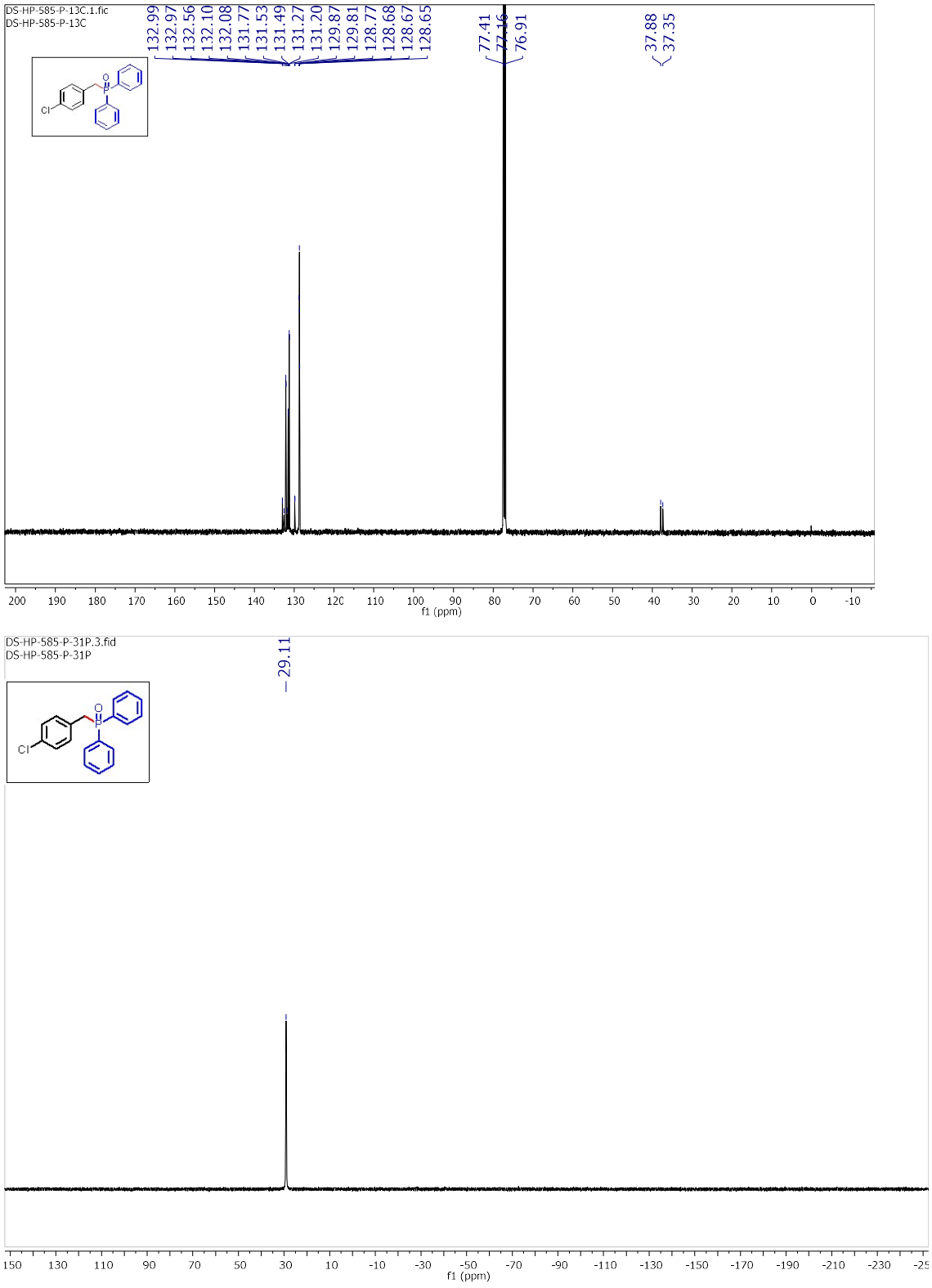
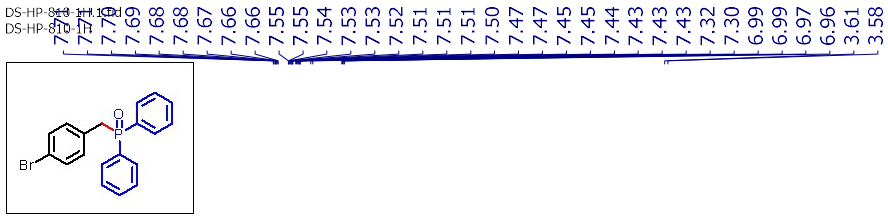
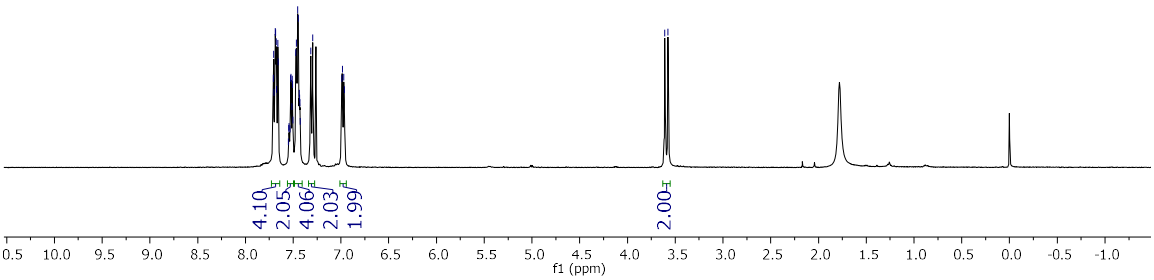
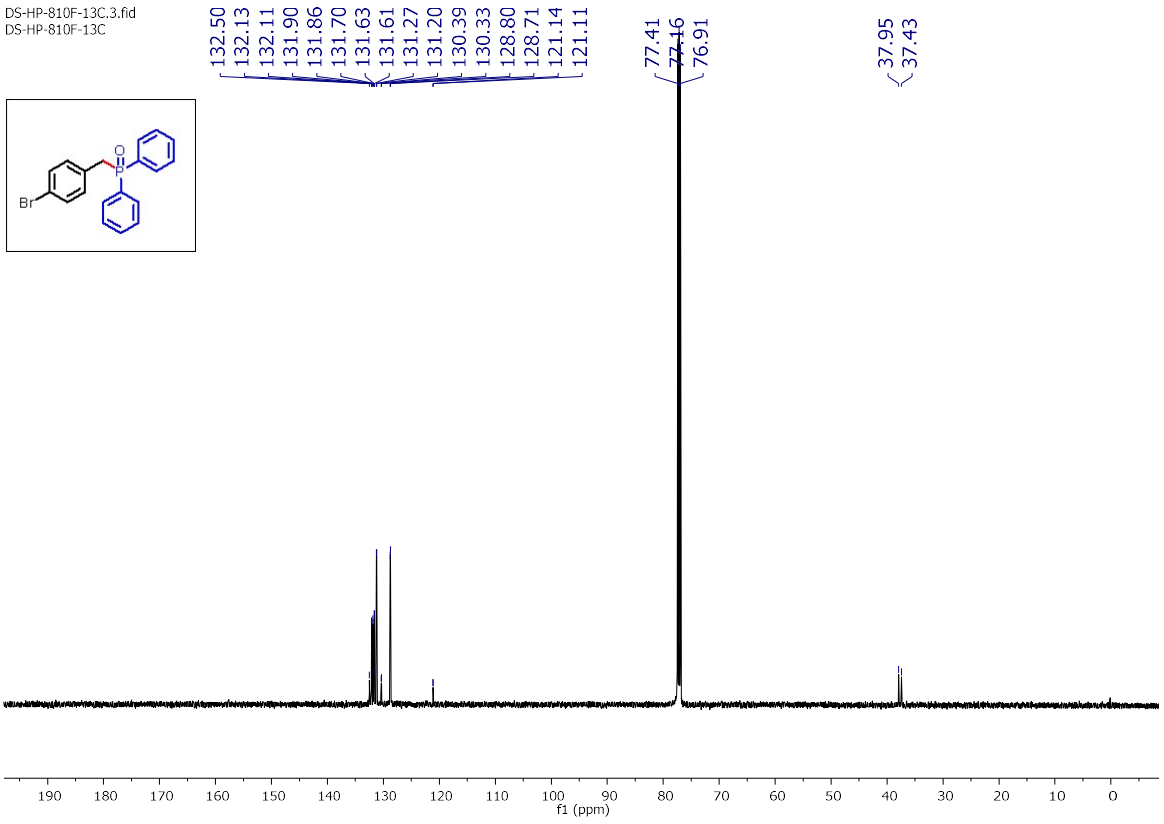


Figure S10. ^{1}H NMR (400 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3i in $CDCl_3$


7.78
7.77
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.51
7.50
7.47
7.47
7.45
7.45
7.44
7.43
7.43
7.43
7.32
7.30
6.99
6.99
6.97
6.96
3.61
3.58


4.10
2.05
4.06
2.03
1.99
2.00
f1 (ppm)


DS-HP-810F-13C.3.fid
DS-HP-810F-13C
132.50
132.13
132.11
131.90
131.86
131.70
131.63
131.61
131.27
131.20
130.39
130.33
128.80
128.71
121.14
121.11
77.41
77.16
76.91
37.95
37.43
f1 (ppm)

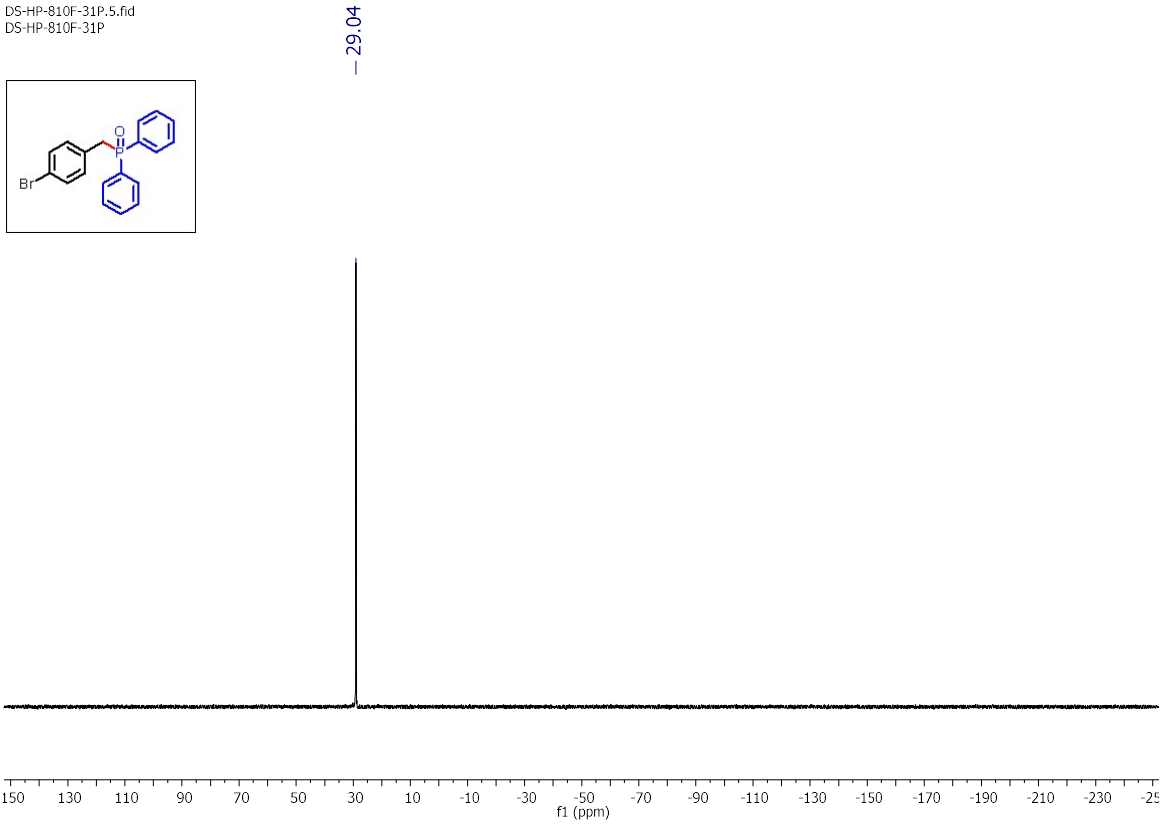
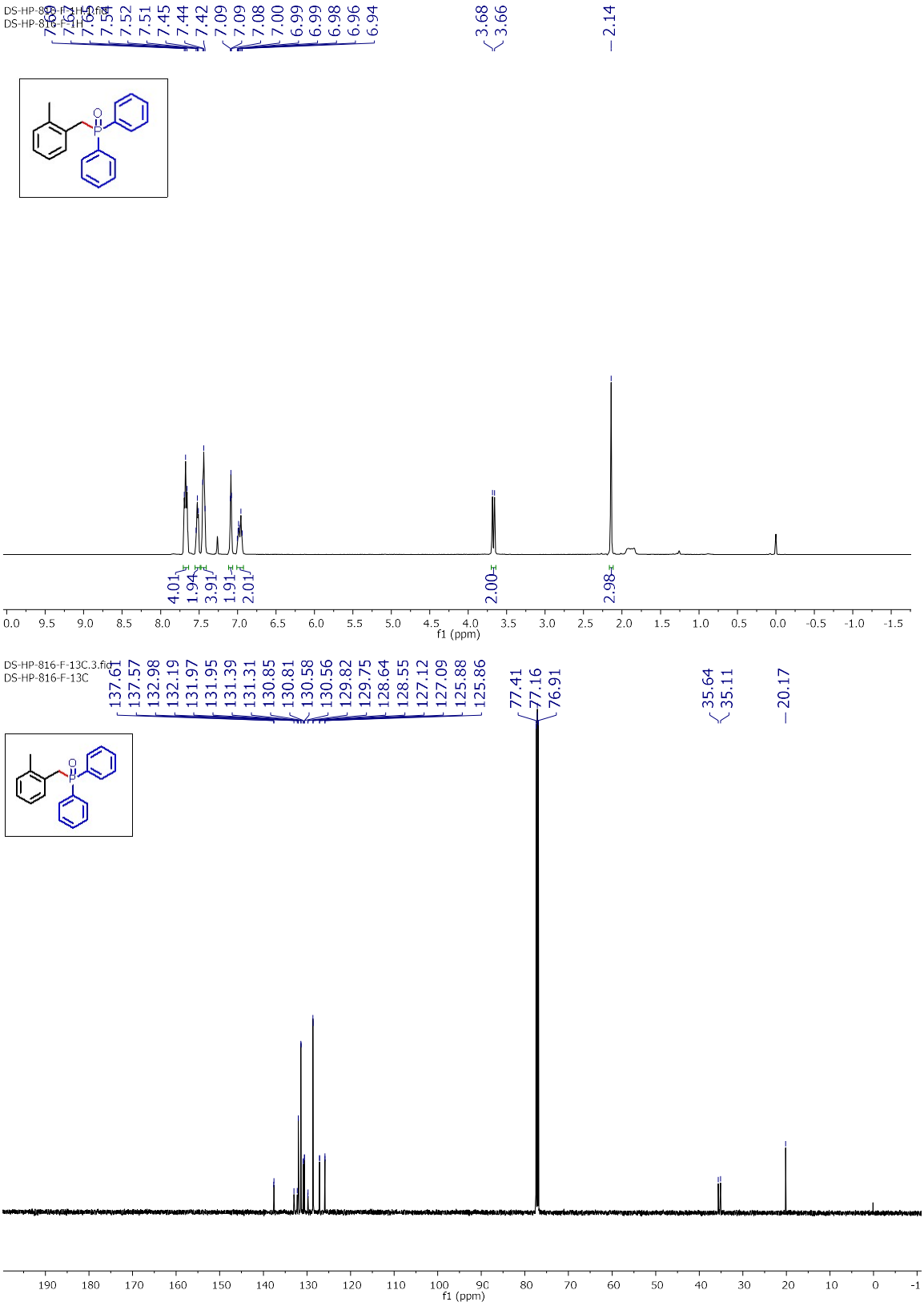


Figure S11. ^{1}H NMR (400 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3j in $CDCl_3$


DS-HP-816-F-1H.fid
DS-HP-816-F-1H
7.69
7.67
7.64
7.54
7.52
7.51
7.45
7.44
7.42
7.09
7.09
7.08
7.00
6.99
6.99
6.98
6.96
6.94
3.68
3.66
2.14
4.01
1.94
3.91
1.91
2.01
2.00
2.98
f1 (ppm)
DS-HP-816-F-13C.3.fid
DS-HP-816-F-13C
137.61
137.57
132.98
132.19
131.97
131.95
131.39
131.31
130.85
130.81
130.58
130.56
129.82
129.75
128.64
128.55
127.12
127.09
125.88
125.86
77.41
77.16
76.91
35.64
35.11
20.17
f1 (ppm)

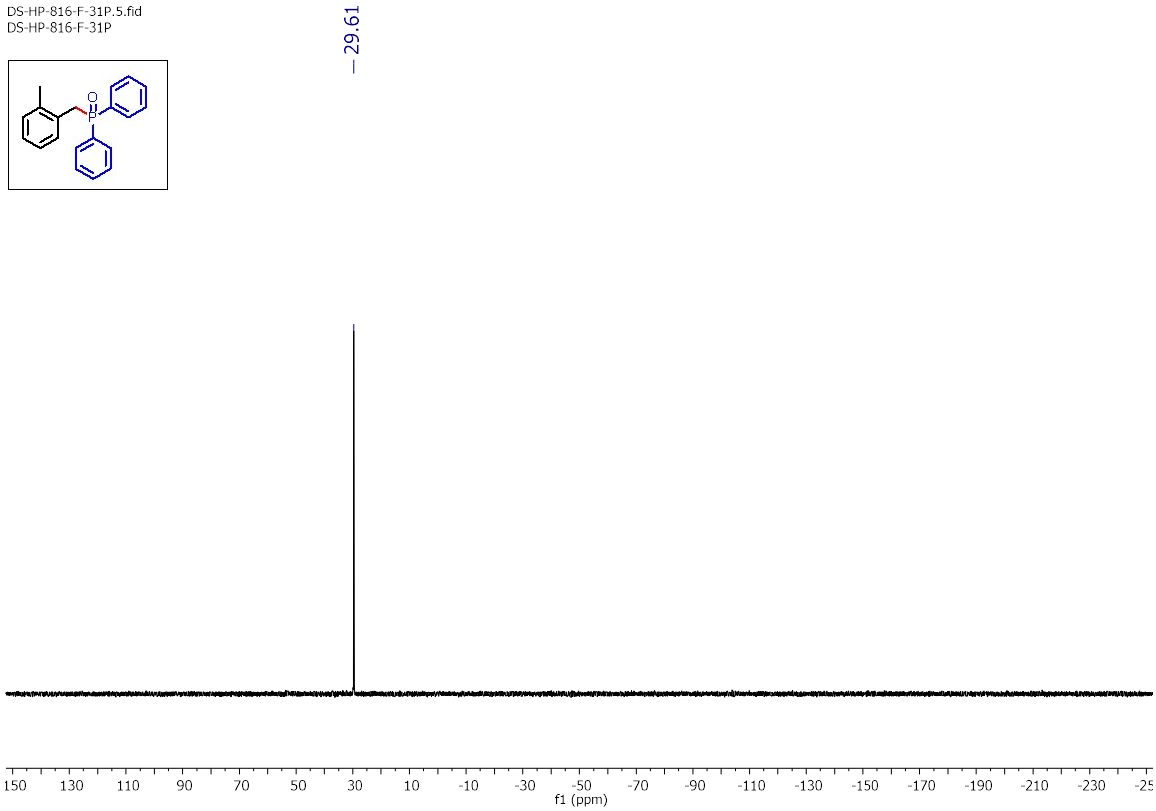
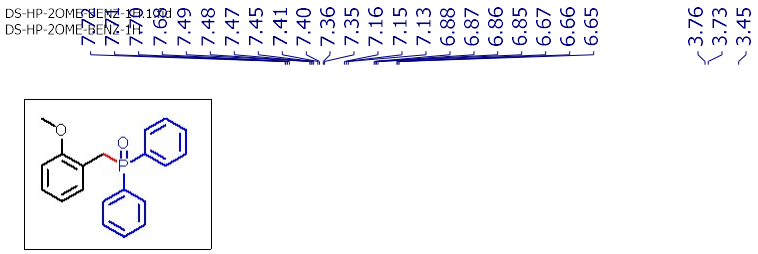
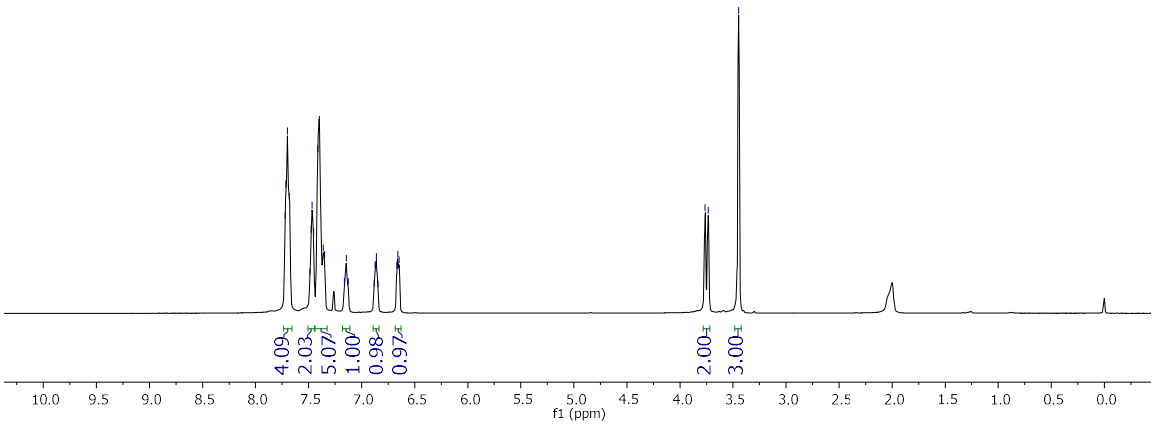
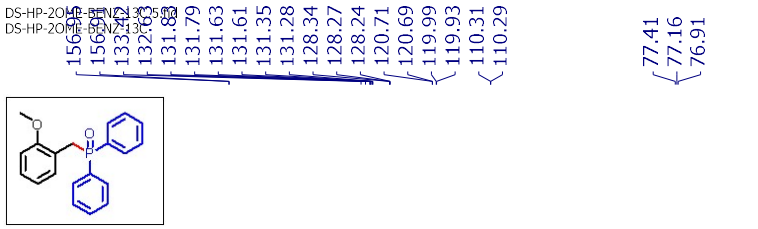
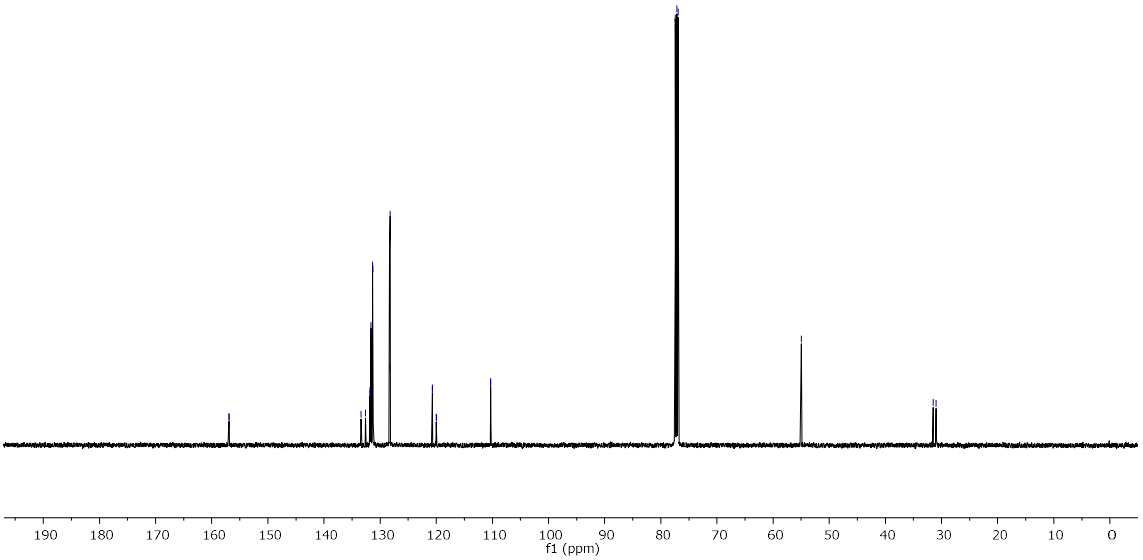


Figure S12. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3k in $CDCl_3$


DS-HP-2OME-BENZ-1H-100d
DS-HP-2OME-BENZ-1H
7.71
7.70
7.69
7.68
7.49
7.48
7.47
7.45
7.41
7.40
7.36
7.35
7.16
7.15
7.13
6.88
6.87
6.86
6.85
6.67
6.66
6.65
3.76
3.73
3.45


4.09
2.03
5.07
1.00
0.98
0.97
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


DS-HP-2OME-BENZ-13C-50d
DS-HP-2OME-BENZ-13C
156.90
156.89
133.42
132.63
131.83
131.79
131.63
131.61
131.35
131.28
128.34
128.27
128.24
120.71
120.69
119.99
119.93
110.31
110.29
77.41
77.16
76.91
54.97
31.51
30.97


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

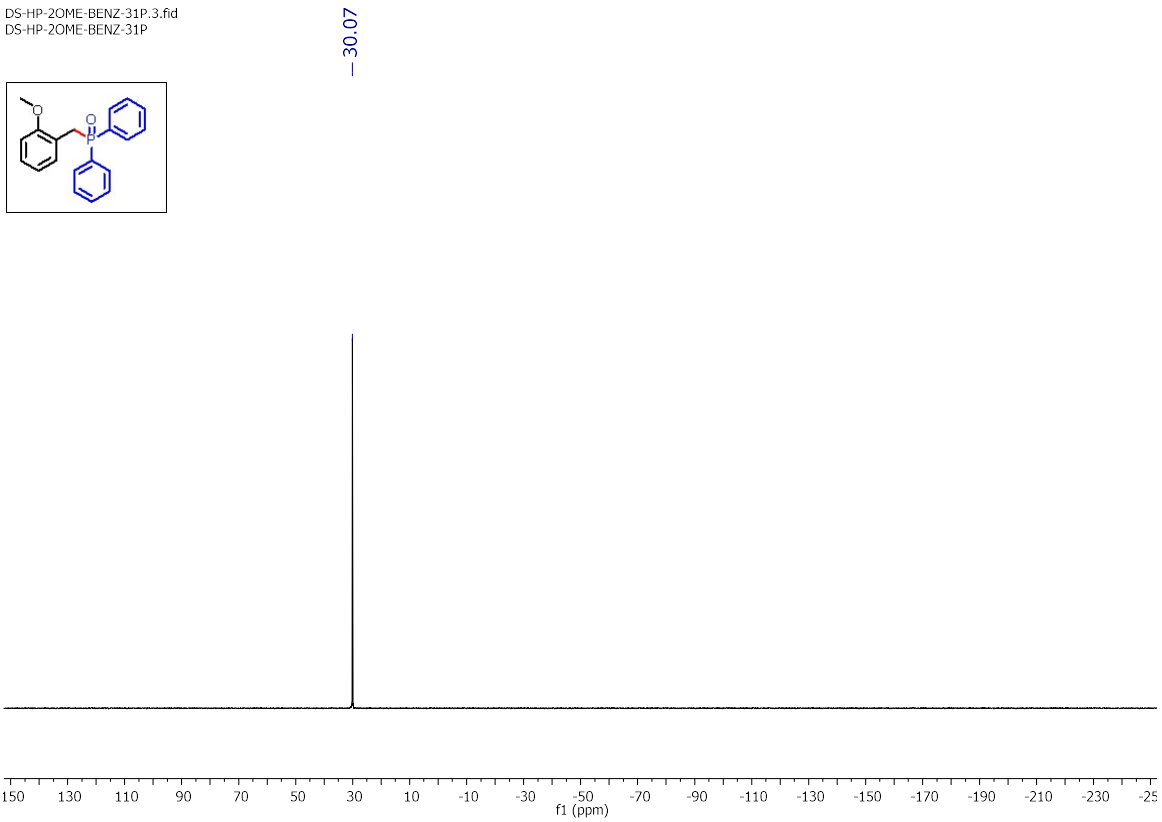
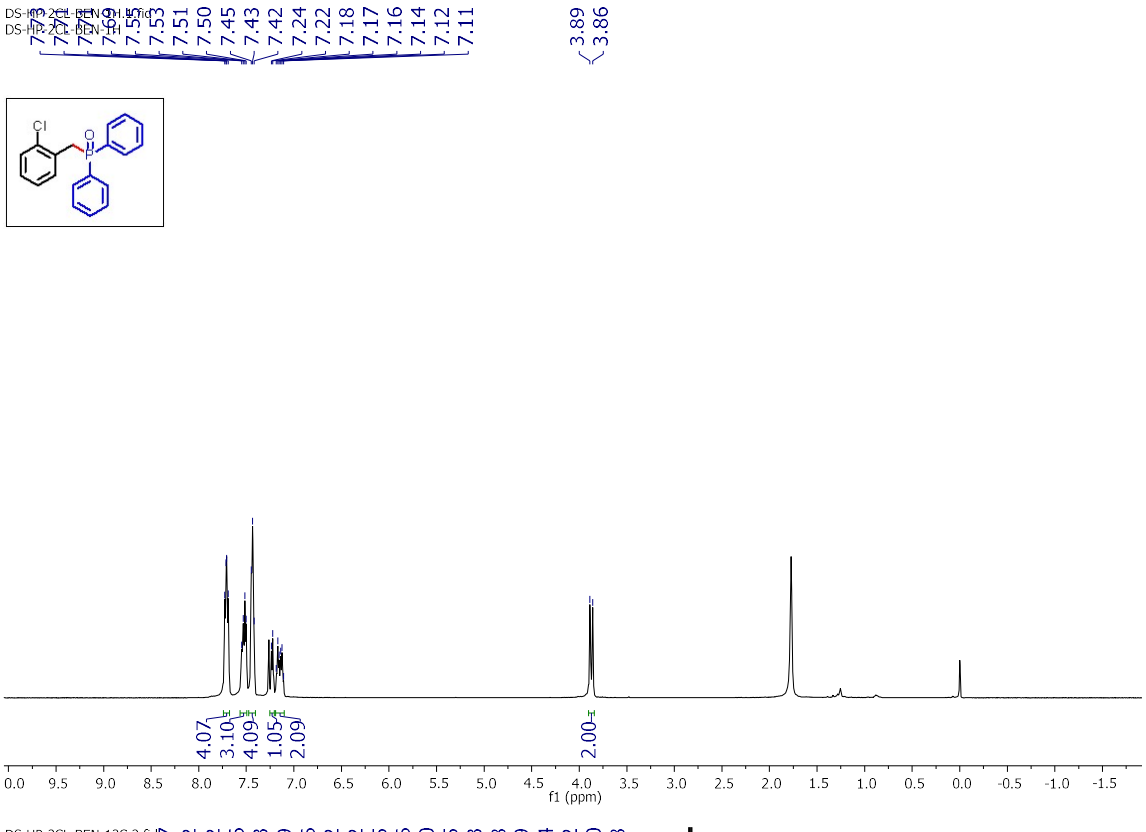
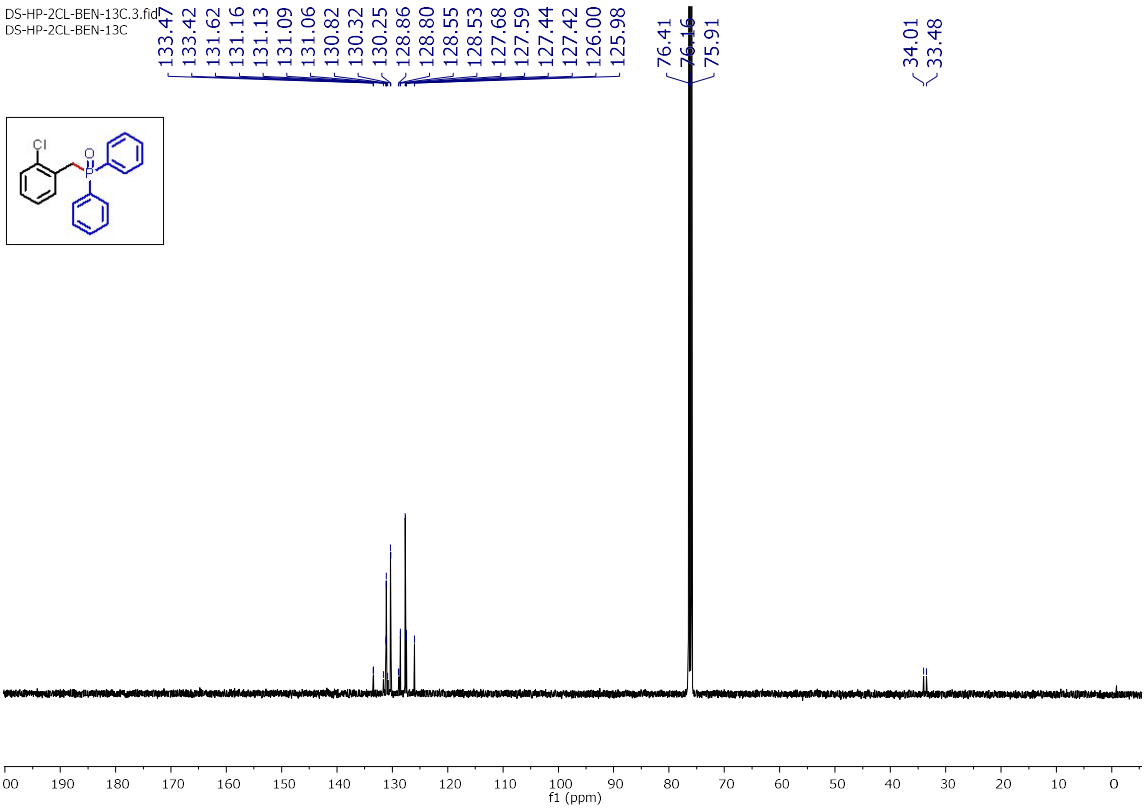


Figure S13. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3l in $CDCl_3$


DS-HP-2CL-BEN-1H.fid
DS-HP-2CL-BEN-1H
7.53
7.51
7.50
7.45
7.43
7.42
7.24
7.22
7.18
7.17
7.16
7.14
7.12
7.11
3.89
3.86
Cl
O
P
4.07
3.10
4.09
1.05
2.09
2.00
f1 (ppm)


DS-HP-2CL-BEN-13C.3.fid
DS-HP-2CL-BEN-13C
133.47
133.42
131.62
131.16
131.13
131.09
131.06
130.82
130.32
130.25
128.86
128.80
128.55
128.53
127.68
127.59
127.44
127.42
126.00
125.98
76.41
76.16
75.91
34.01
33.48
Cl
O
P
f1 (ppm)

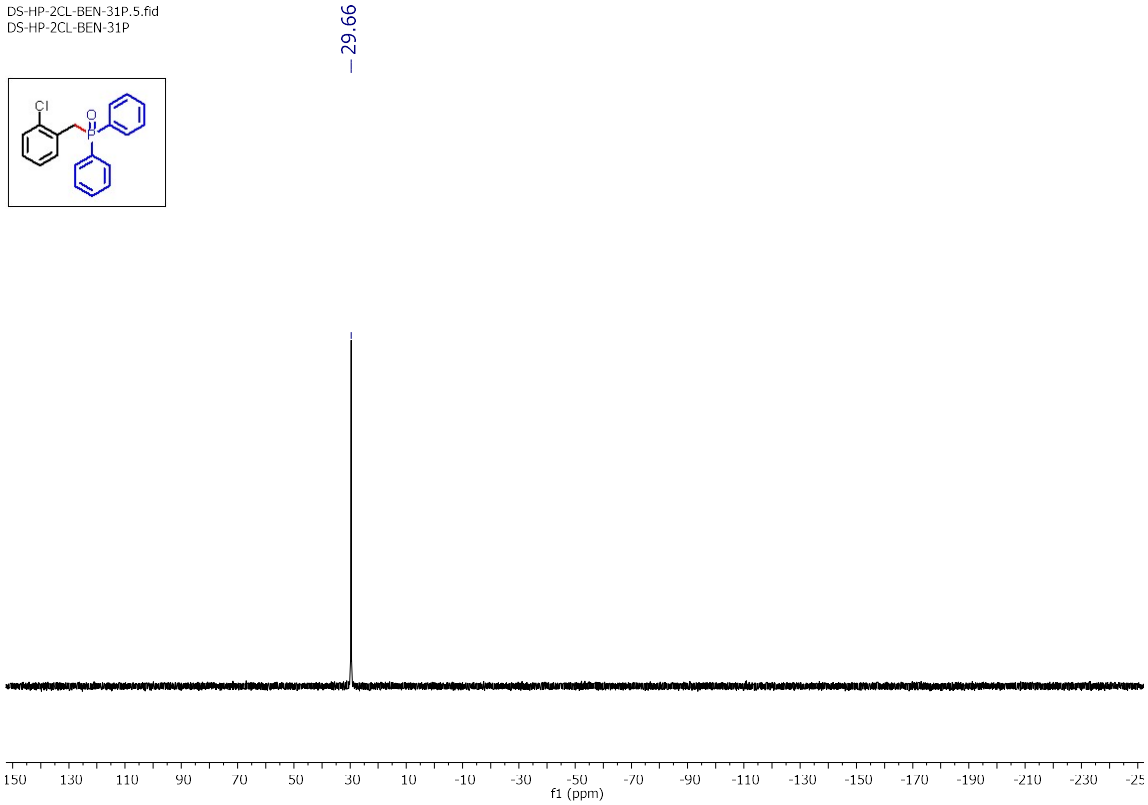
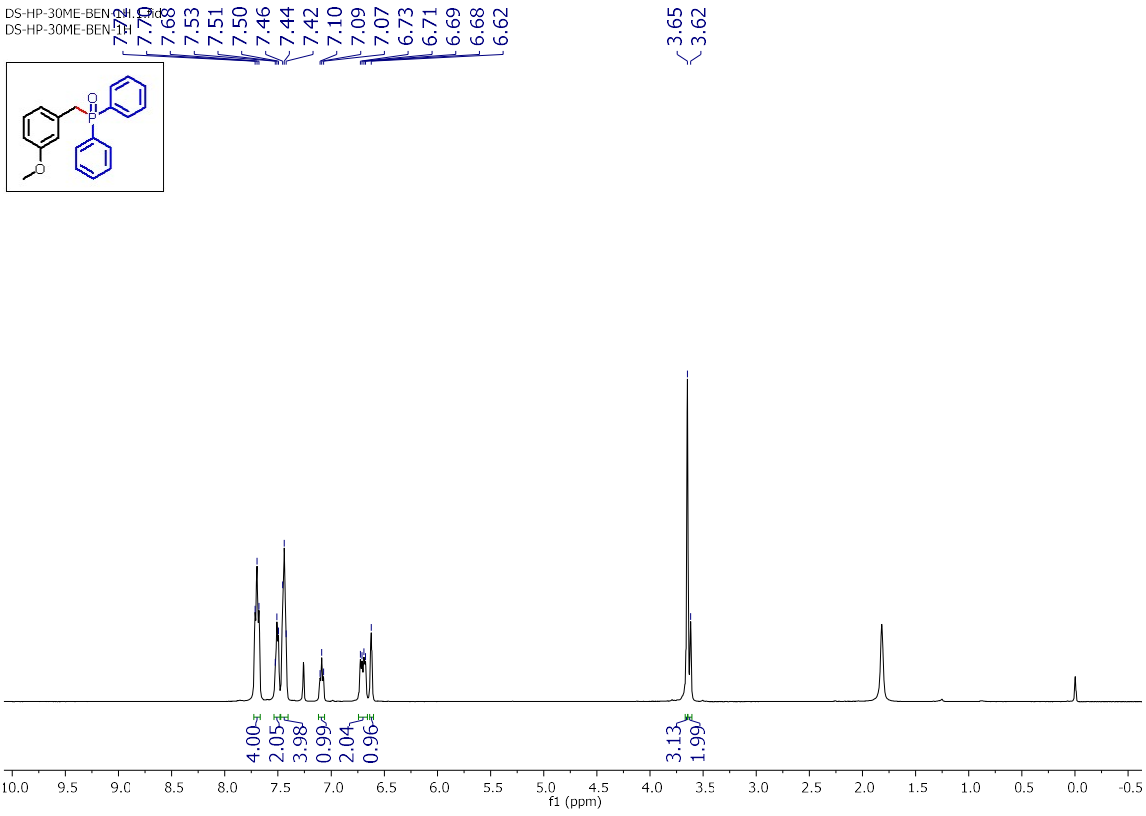
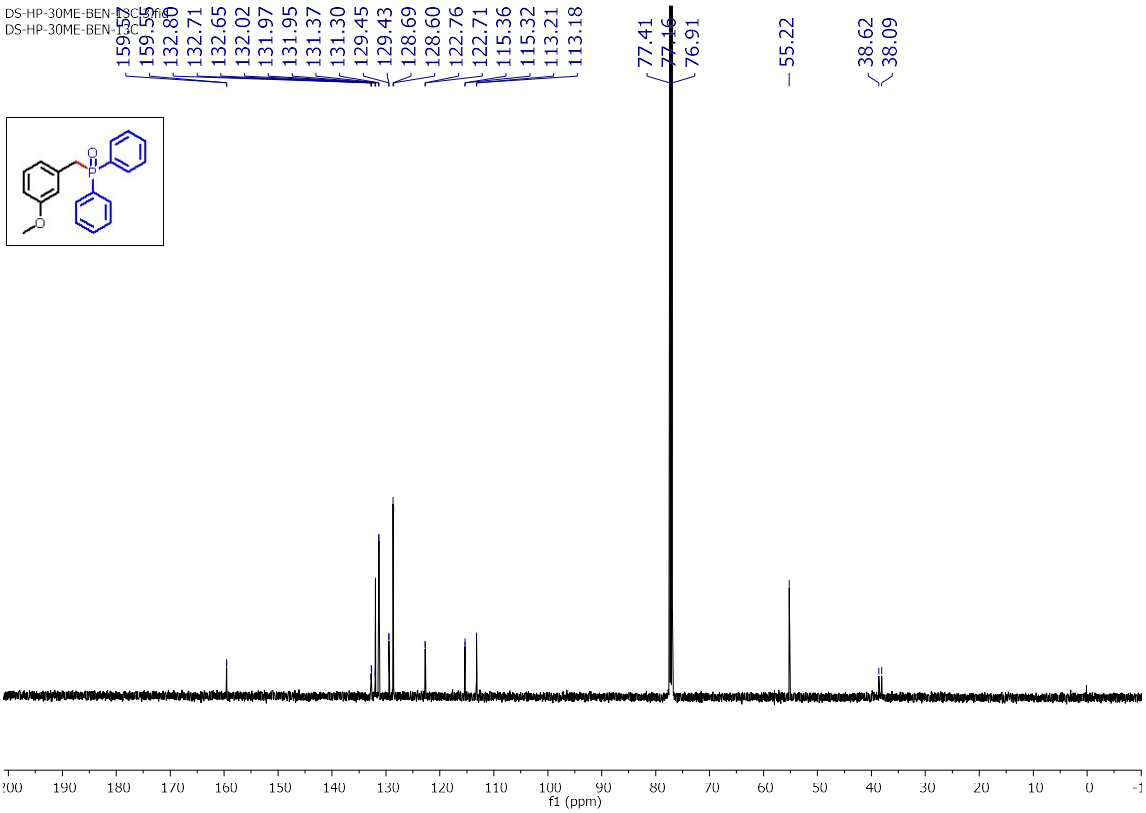


Figure S14. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3m in $CDCl_3$


DS-HP-30ME-BEN-1H.1.fid
DS-HP-30ME-BEN-1H
7.77
7.76
7.68
7.53
7.51
7.50
7.46
7.44
7.42
7.10
7.09
7.07
6.73
6.71
6.69
6.68
6.62
3.65
3.62
4.00
2.05
3.98
0.99
2.04
0.96
3.13
1.99
f1 (ppm)


DS-HP-30ME-BEN-13C.10.fid
DS-HP-30ME-BEN-13C
159.50
159.45
132.80
132.71
132.65
132.02
131.97
131.95
131.37
131.30
129.45
129.43
128.69
128.60
122.76
122.71
115.36
115.32
113.21
113.18
77.41
77.16
76.91
55.22
38.62
38.09
f1 (ppm)

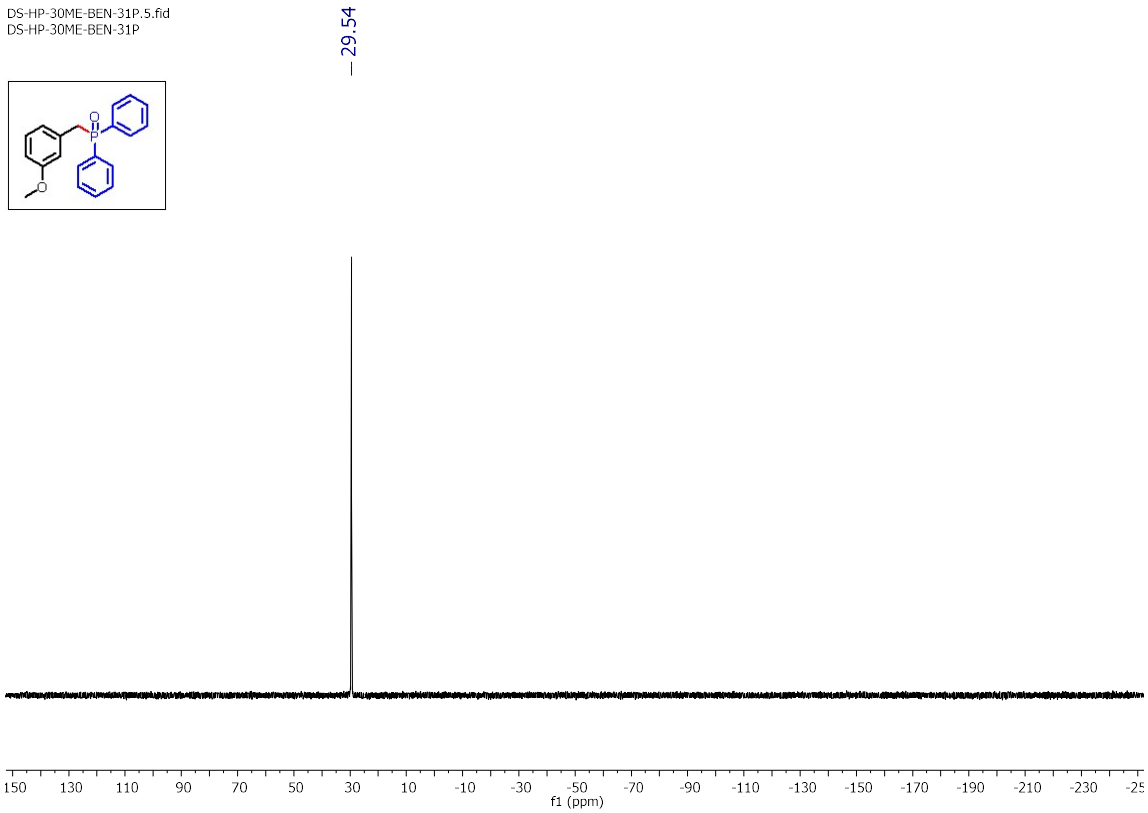
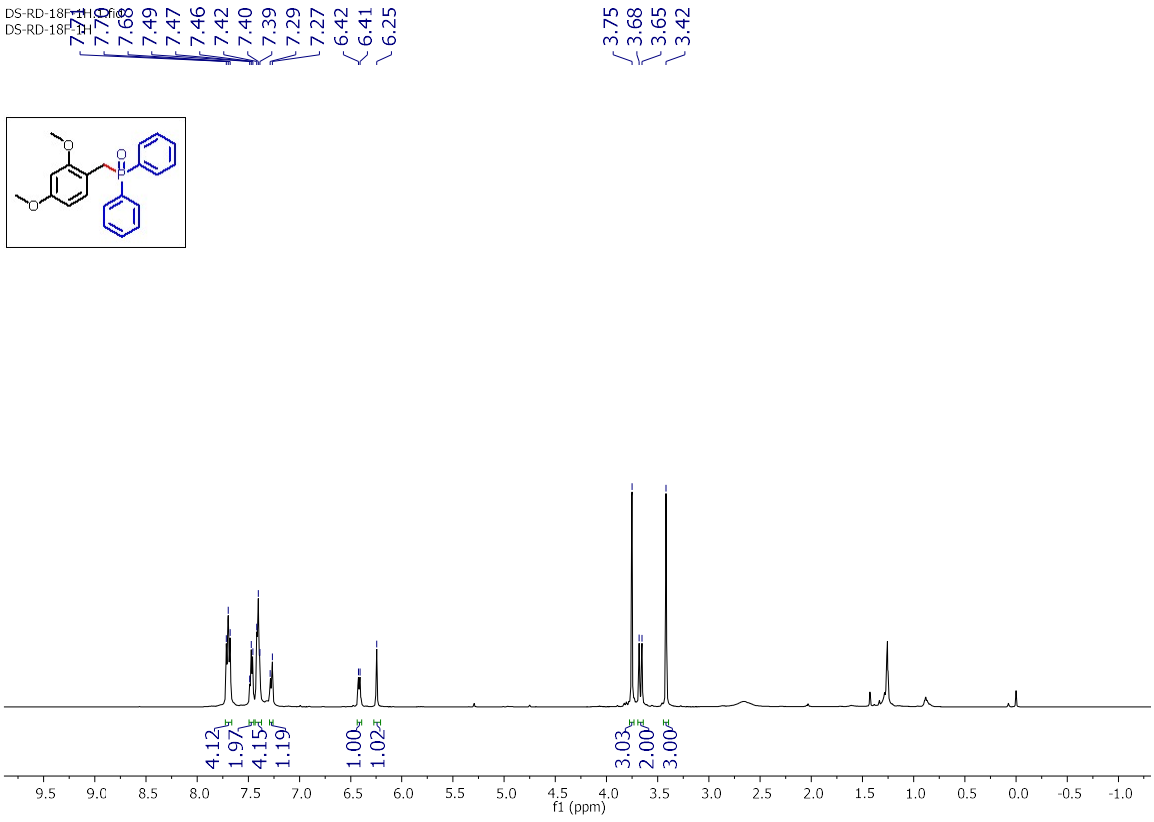
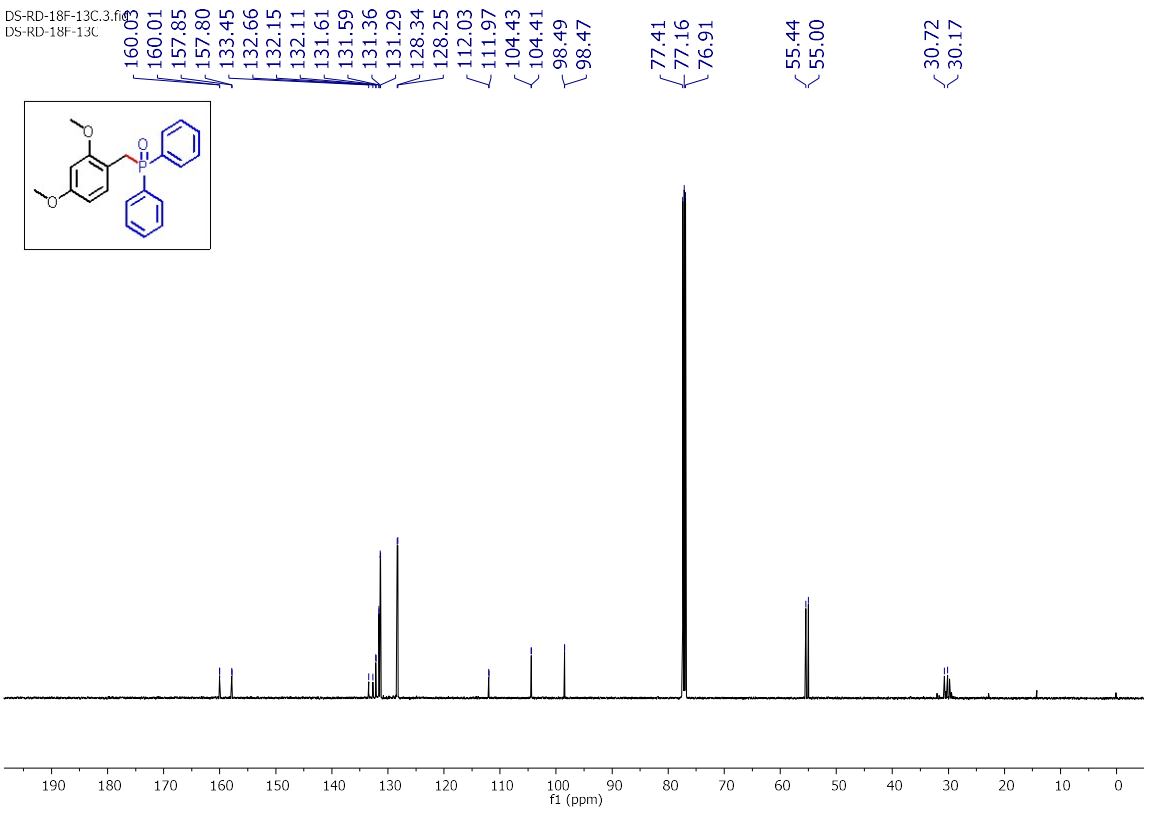


Figure S15. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3n in $CDCl_3$


DS-RD-18F-1H.3.fid
DS-RD-18F-1H
7.71
7.70
7.68
7.49
7.47
7.46
7.42
7.40
7.39
7.29
7.27
6.42
6.41
6.25
3.75
3.68
3.65
3.42
4.12
1.97
4.15
1.19
1.00
1.02
3.03
2.00
3.00
f1 (ppm)


DS-RD-18F-13C.3.fid
DS-RD-18F-13C
160.03
160.01
157.85
157.80
133.45
132.66
132.15
132.11
131.61
131.59
131.36
131.29
128.34
128.25
112.03
111.97
104.43
104.41
98.49
98.47
77.41
77.16
76.91
55.44
55.00
30.72
30.17
f1 (ppm)

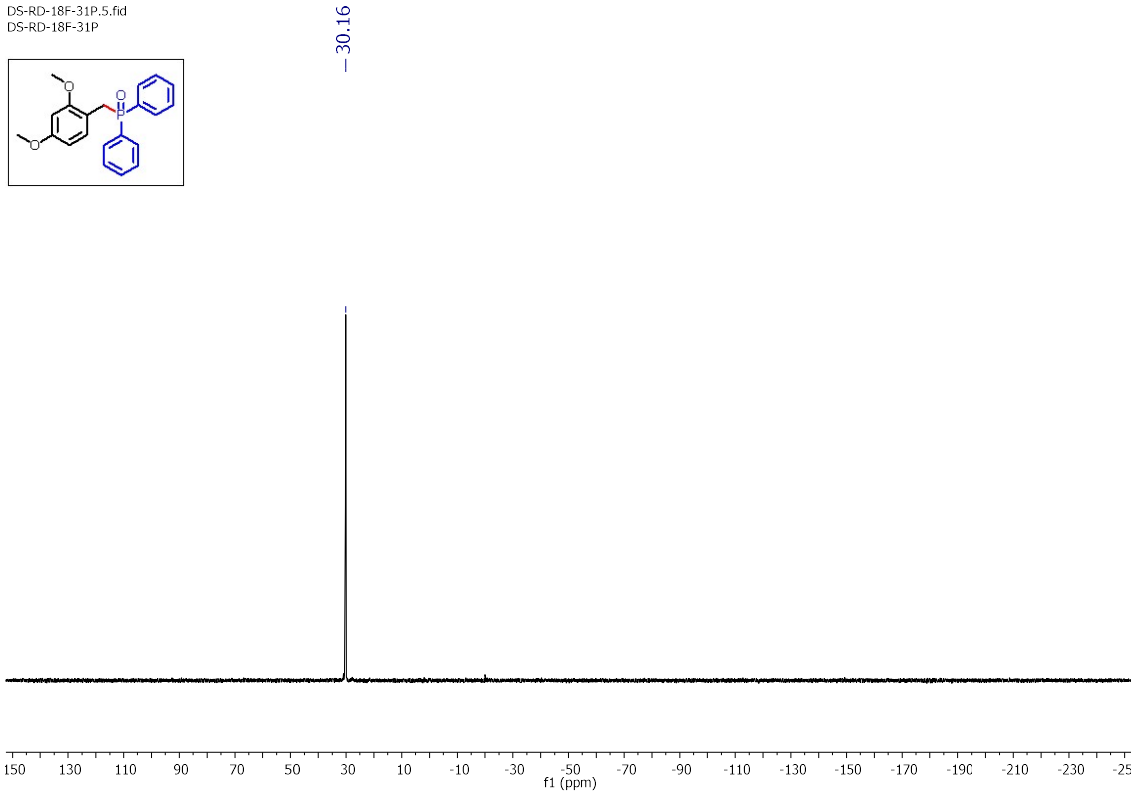
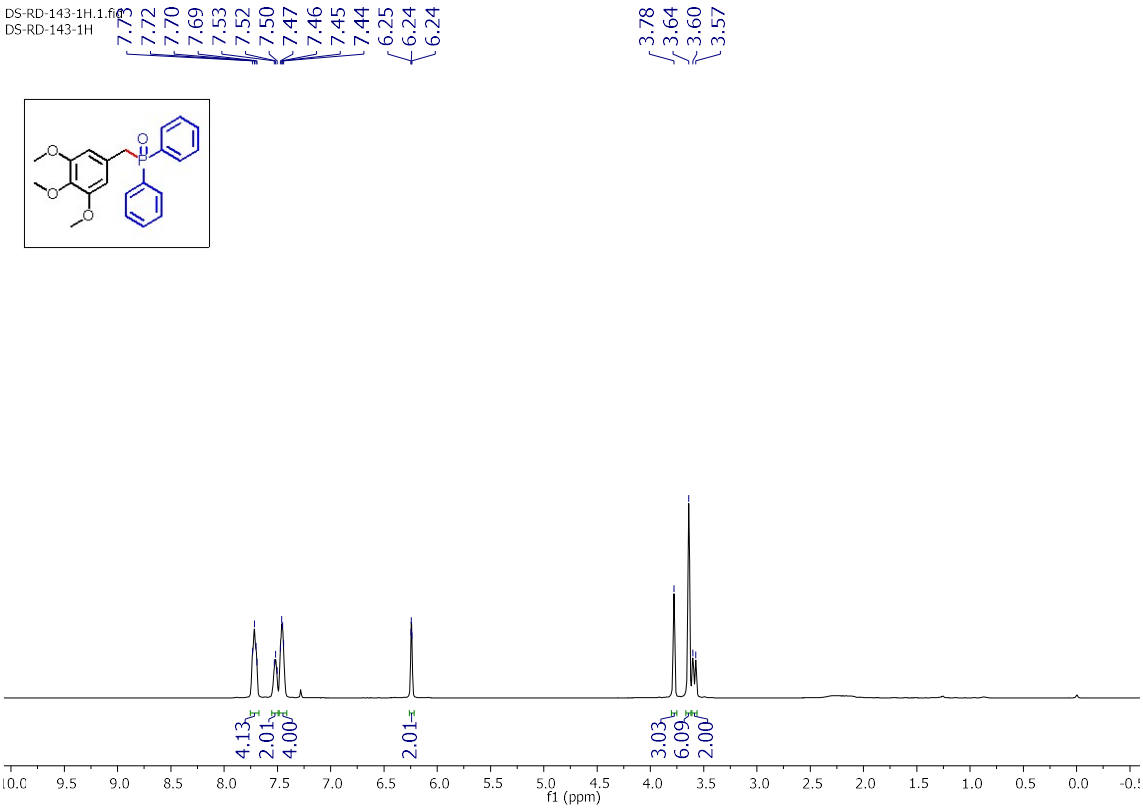
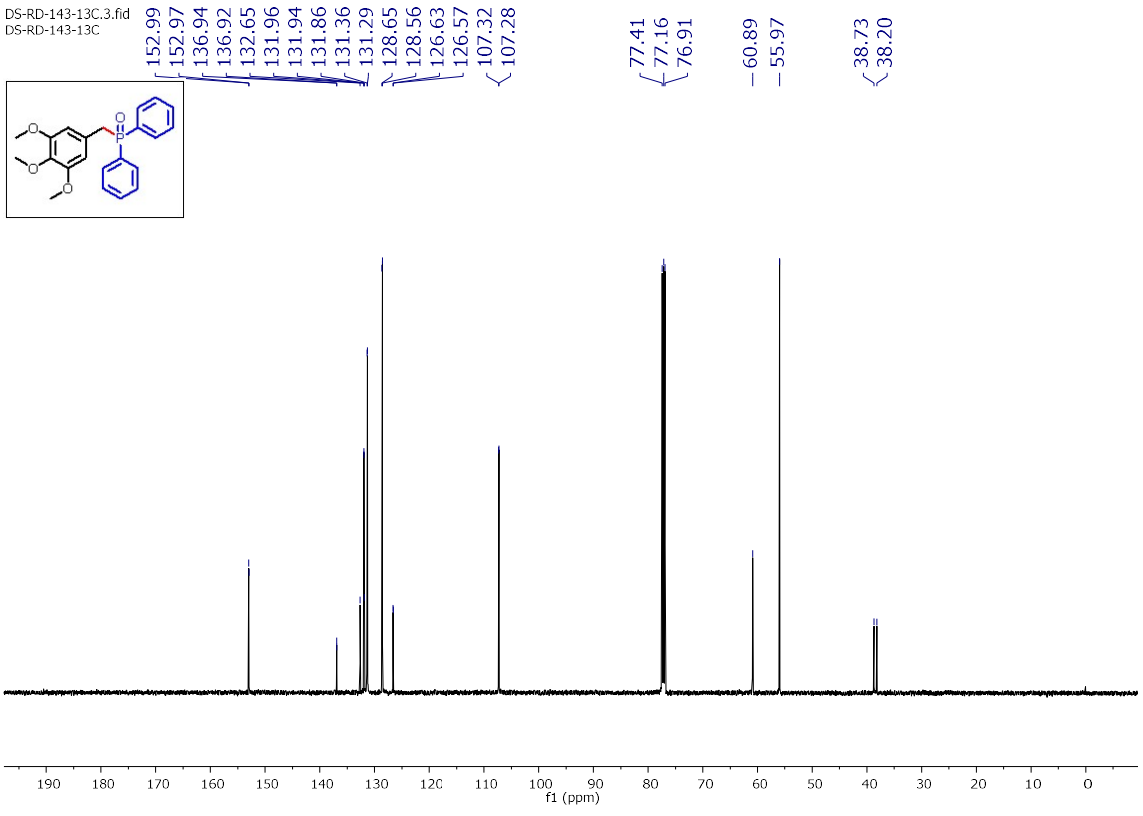


Figure S16. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3o in $CDCl_3$


DS-RD-143-1H.1.fid
DS-RD-143-1H
7.73
7.72
7.70
7.69
7.53
7.52
7.50
7.47
7.46
7.45
7.44
6.25
6.24
6.24
3.78
3.64
3.60
3.57
4.13
2.01
4.00
2.01
3.03
6.09
2.00
f1 (ppm)


DS-RD-143-13C.3.fid
DS-RD-143-13C
152.99
152.97
136.94
136.92
132.65
131.96
131.94
131.86
131.36
131.29
128.65
128.56
126.63
126.57
107.32
107.28
77.41
77.16
76.91
60.89
55.97
38.73
38.20
f1 (ppm)

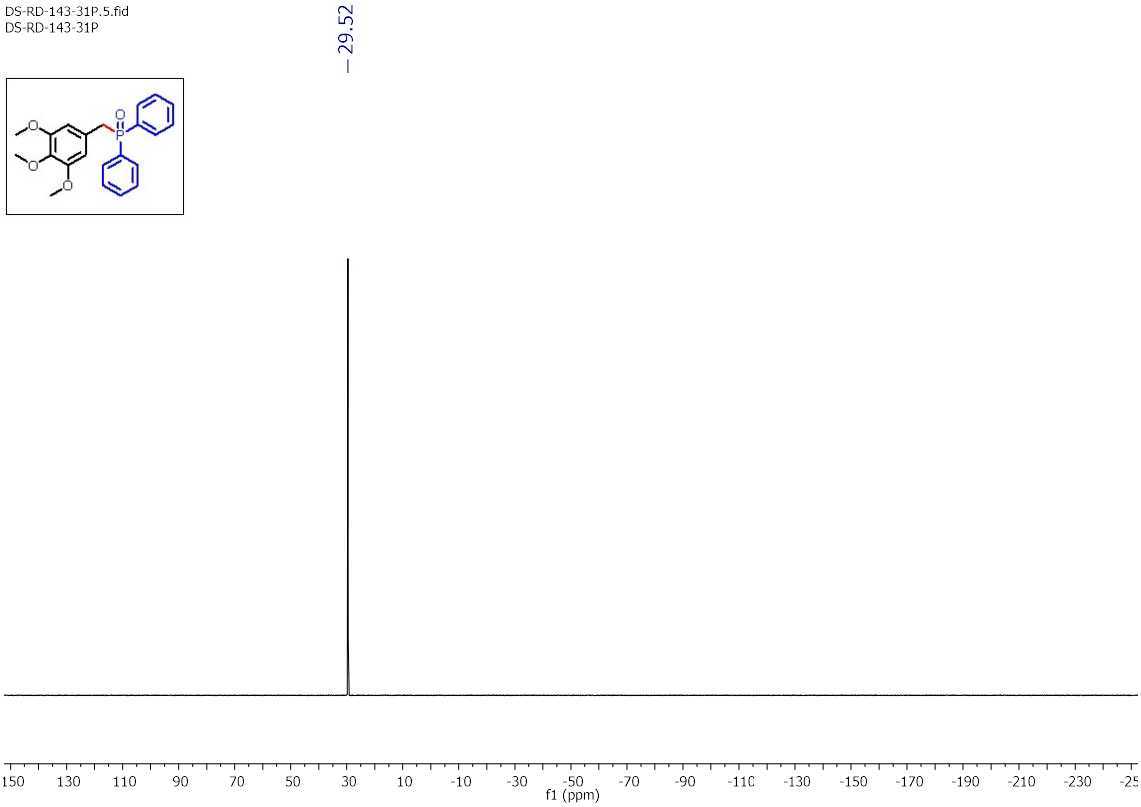
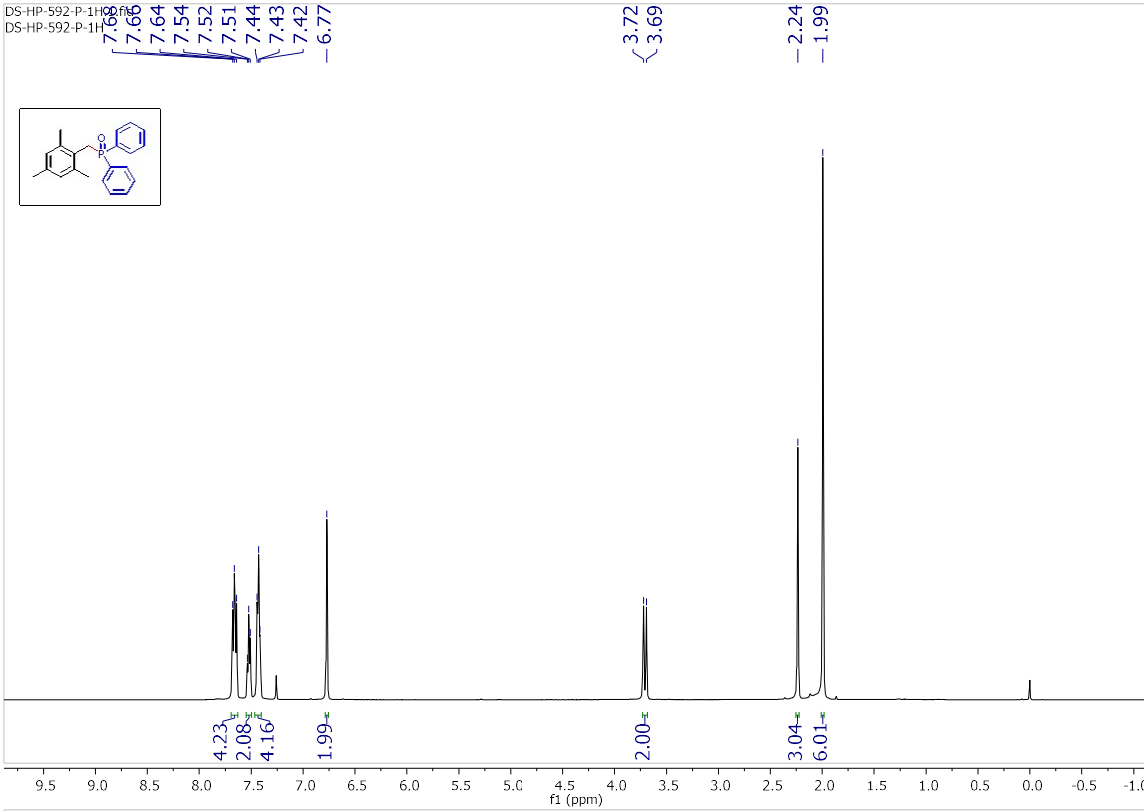
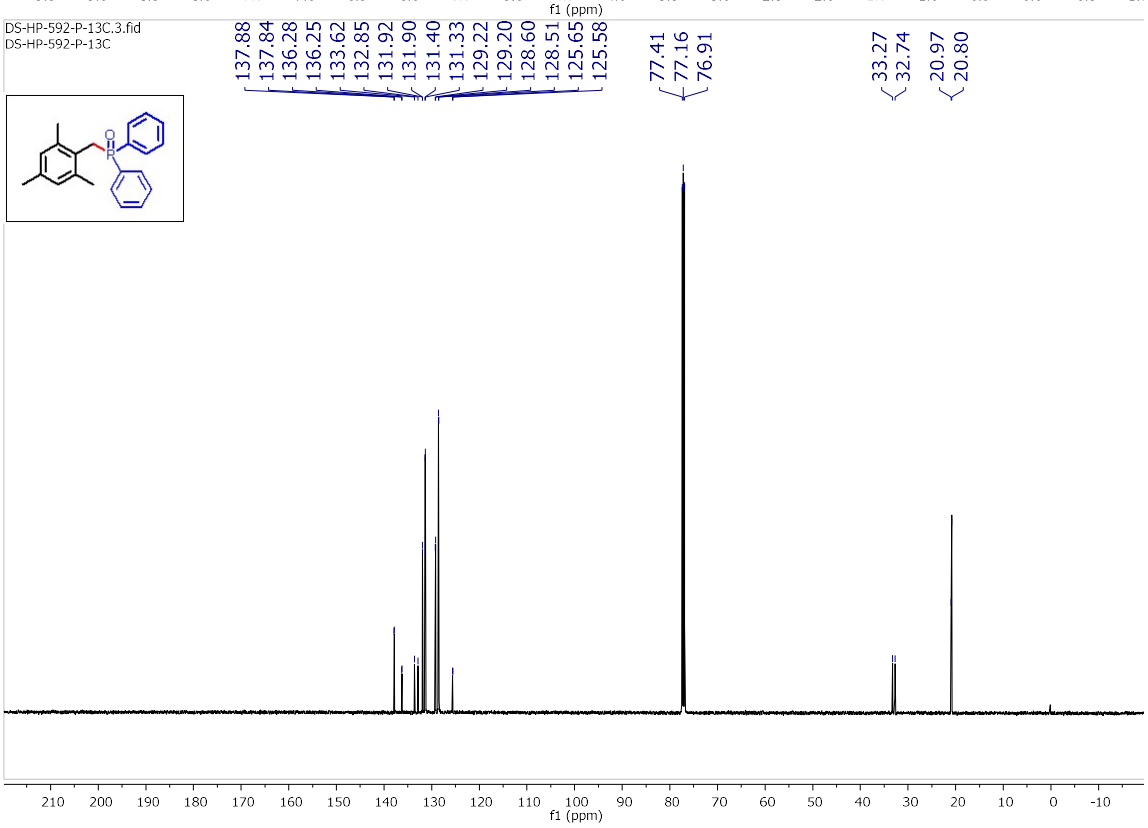


Figure S17. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3p in $CDCl_3$


DS-HP-592-P-1H.3.fid
DS-HP-592-P-1H
7.68
7.66
7.64
7.54
7.52
7.51
7.44
7.43
7.42
6.77
3.72
3.69
2.24
1.99
4.23
2.08
4.16
1.99
2.00
3.04
6.01
f1 (ppm)


DS-HP-592-P-13C.3.fid
DS-HP-592-P-13C
137.88
137.84
136.28
136.25
133.62
132.85
131.92
131.90
131.40
131.33
129.22
129.20
128.60
128.51
125.65
125.58
77.41
77.16
76.91
33.27
32.74
20.97
20.80
f1 (ppm)

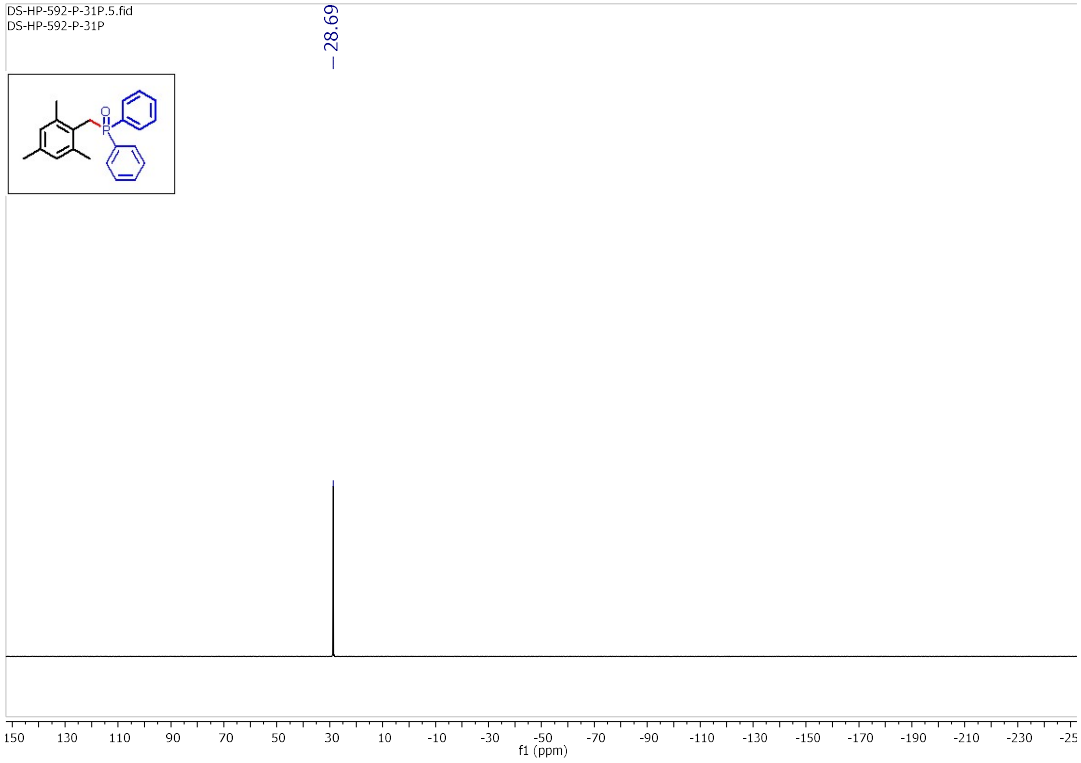
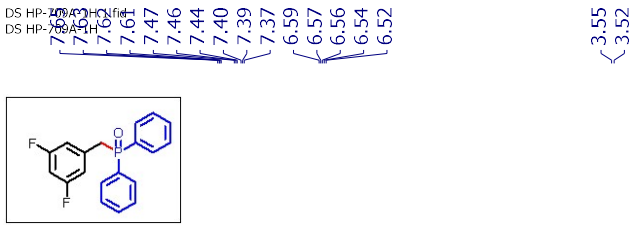
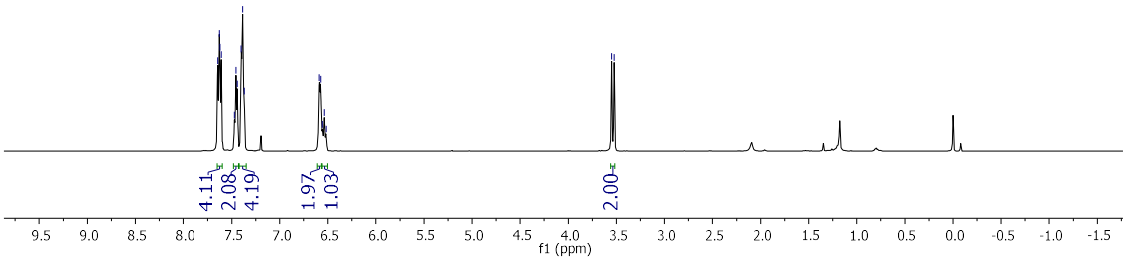
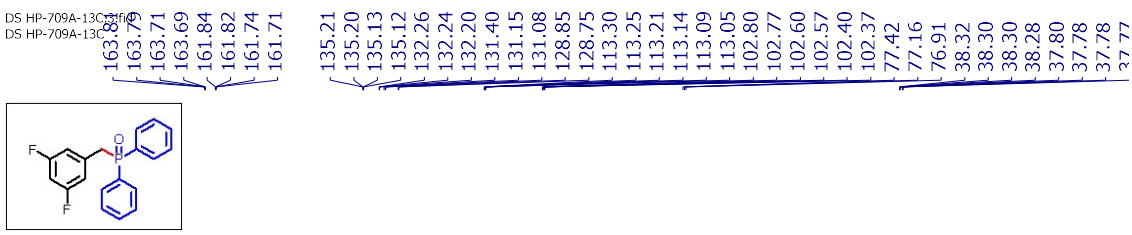
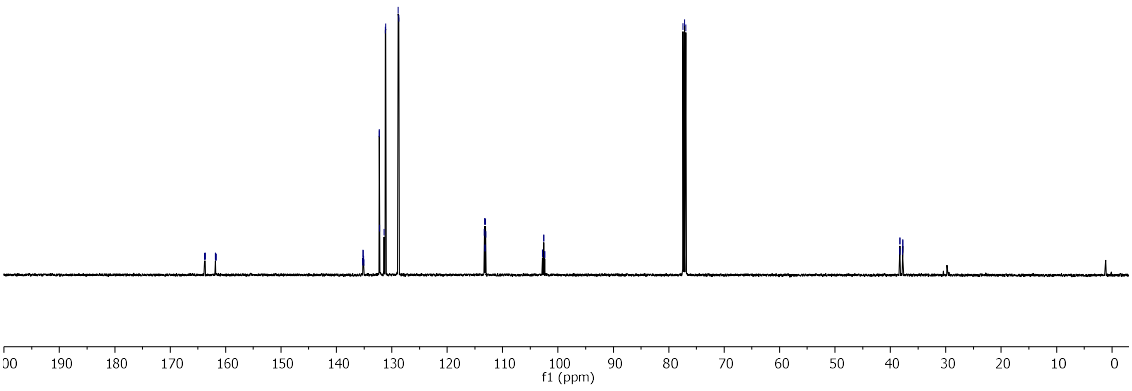


Figure S18. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3q in $CDCl_3$


DS HP-709A-1H.fid
7.63
7.61
7.47
7.46
7.44
7.40
7.39
7.37
6.59
6.57
6.56
6.54
6.52
3.55
3.52
F
O
P
F


4.11
2.08
4.19
1.97
1.03
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


DS HP-709A-13C.fid
163.79
163.71
163.69
161.84
161.82
161.74
161.71
135.21
135.20
135.13
135.12
132.26
132.24
132.20
131.40
131.15
131.08
128.85
128.75
113.30
113.25
113.21
113.14
113.09
113.05
102.80
102.77
102.60
102.57
102.40
102.37
77.42
77.16
76.91
38.32
38.30
38.30
38.28
37.80
37.78
37.78
F
O
P
F


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

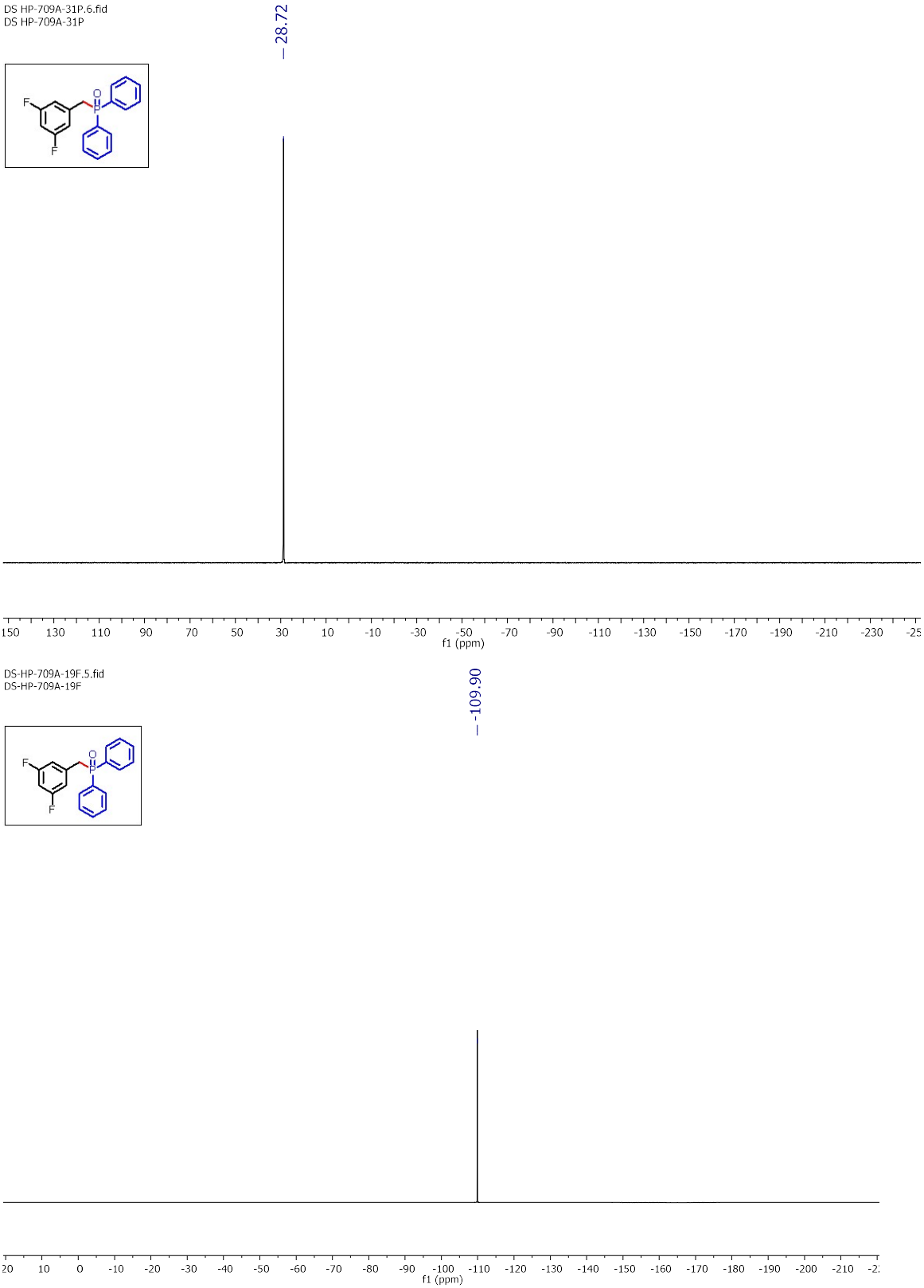
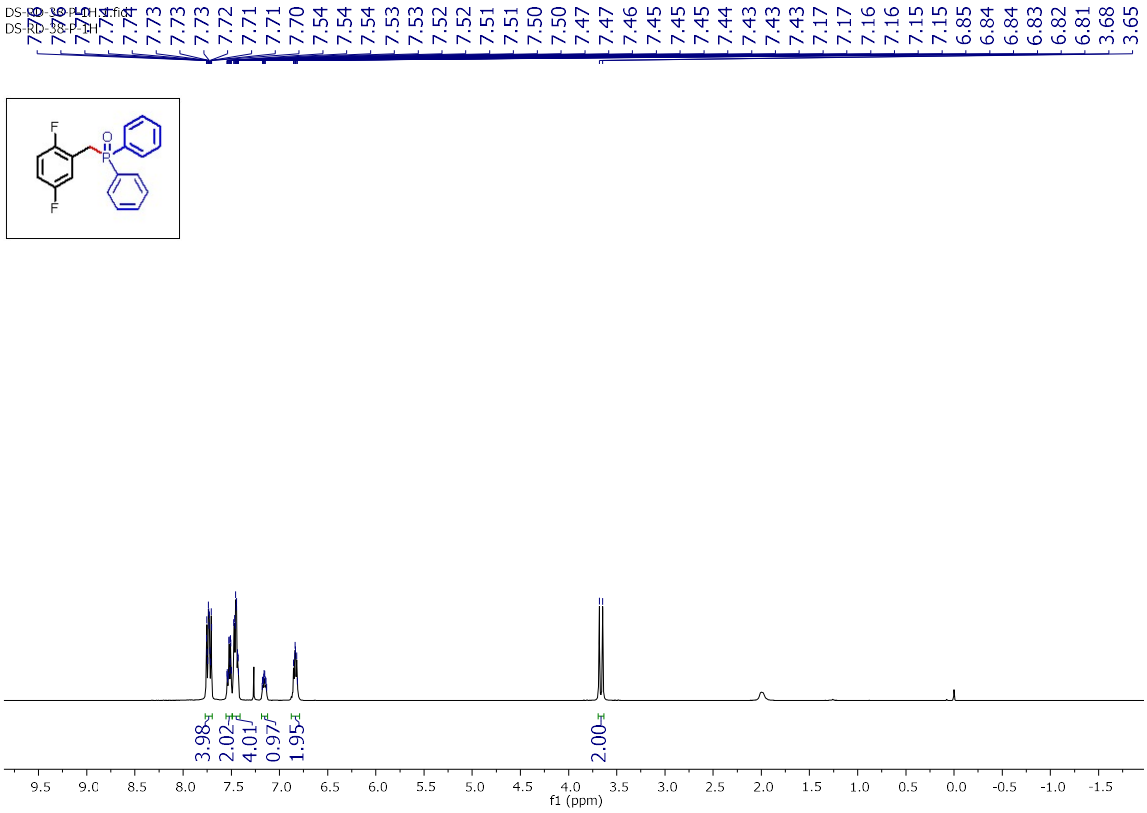
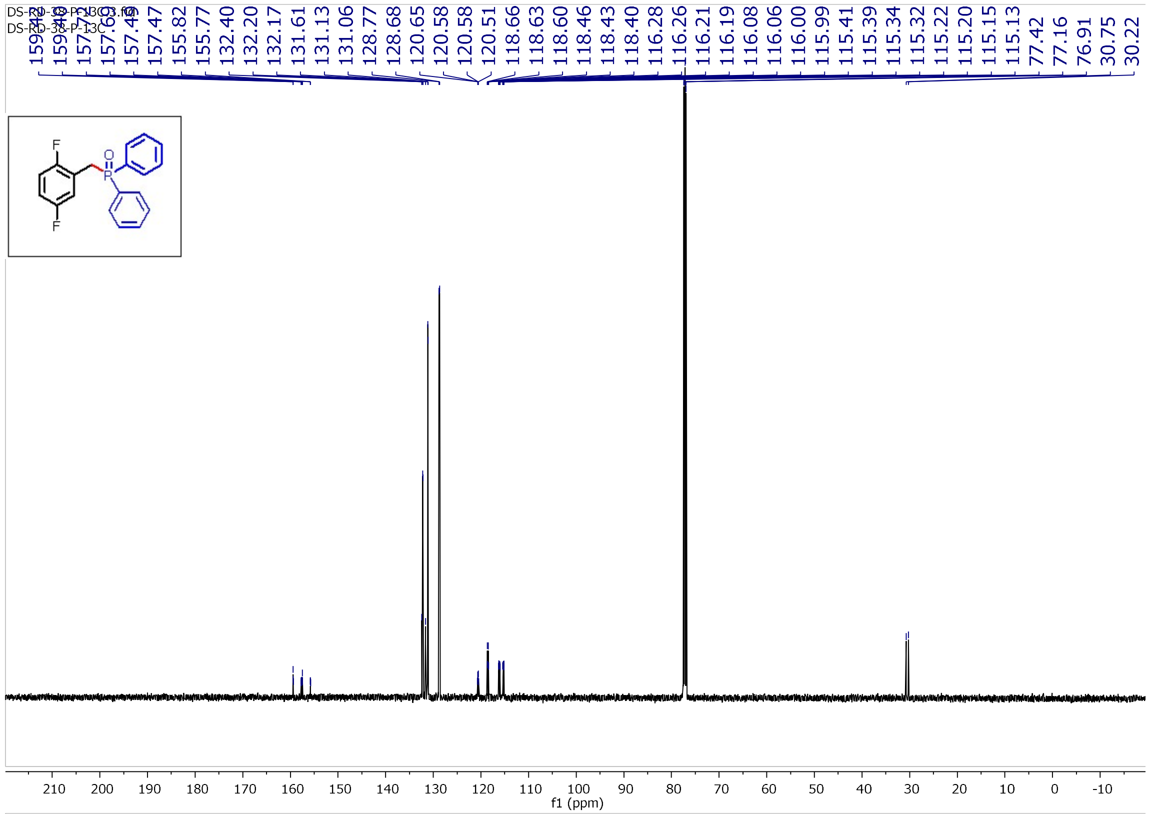
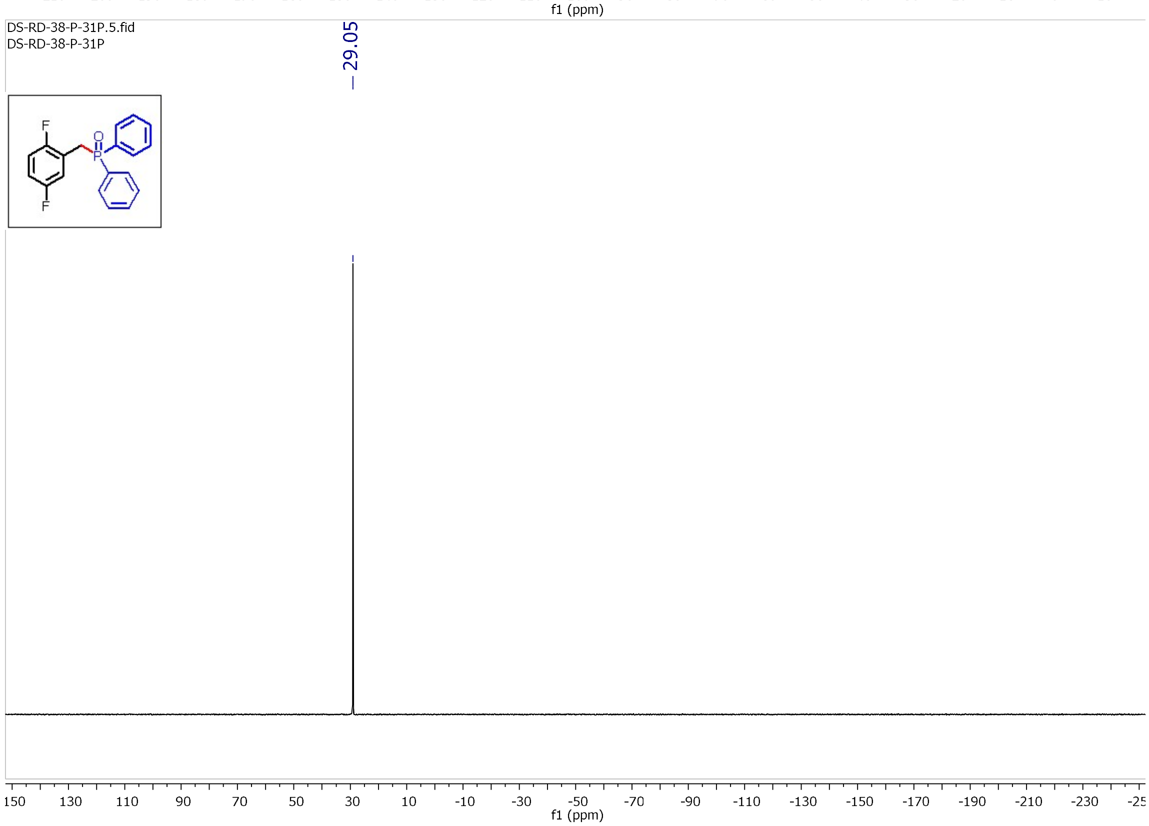


Figure S19. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3r in $CDCl_3$


DS-SD-26-PH-1H-f2
DS-SD-26-PH-1H
7.78
7.76
7.75
7.74
7.74
7.73
7.73
7.73
7.72
7.71
7.71
7.70
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.47
7.47
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.43
7.17
7.17
7.16
7.16
7.15
7.15
6.85
6.84
6.84
6.83
6.82
6.81
3.68
3.65
F
O
P
F
3.98
2.02
4.01
0.97
1.95
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


DS-RD-38-P-13C
157.69
157.49
157.47
155.82
155.77
132.40
132.20
132.17
131.61
131.13
131.06
128.77
128.68
120.65
120.58
120.58
120.51
118.66
118.63
118.60
118.46
118.43
118.40
116.28
116.26
116.21
116.19
116.08
116.06
116.00
115.99
115.41
115.39
115.34
115.32
115.22
115.20
115.15
115.13
77.42
77.16
76.91
30.75
30.22
F
O
P
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


DS-RD-38-P-31P.5.fid
DS-RD-38-P-31P
29.05
F
O
P
F
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

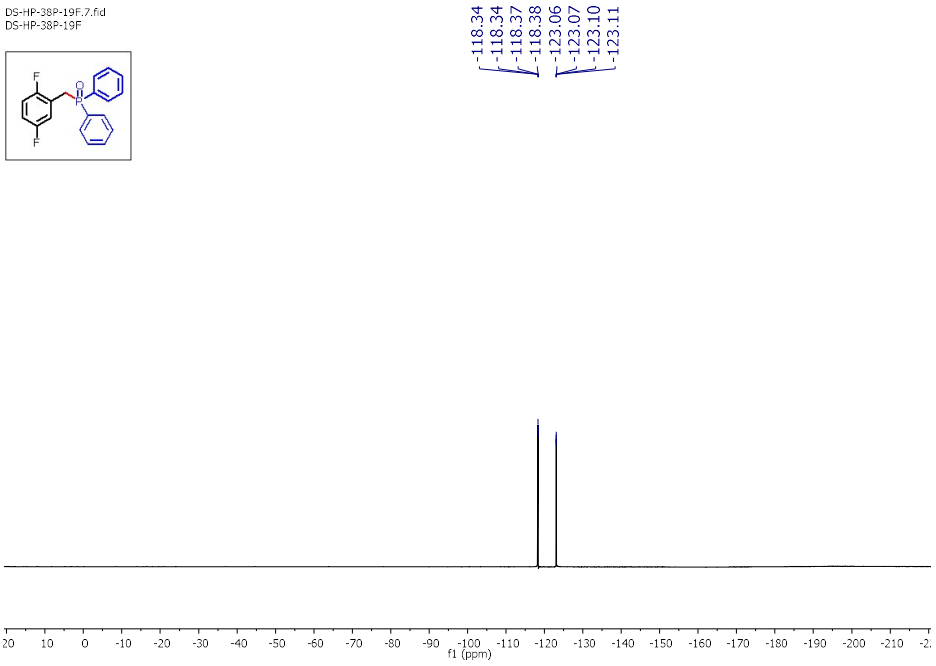
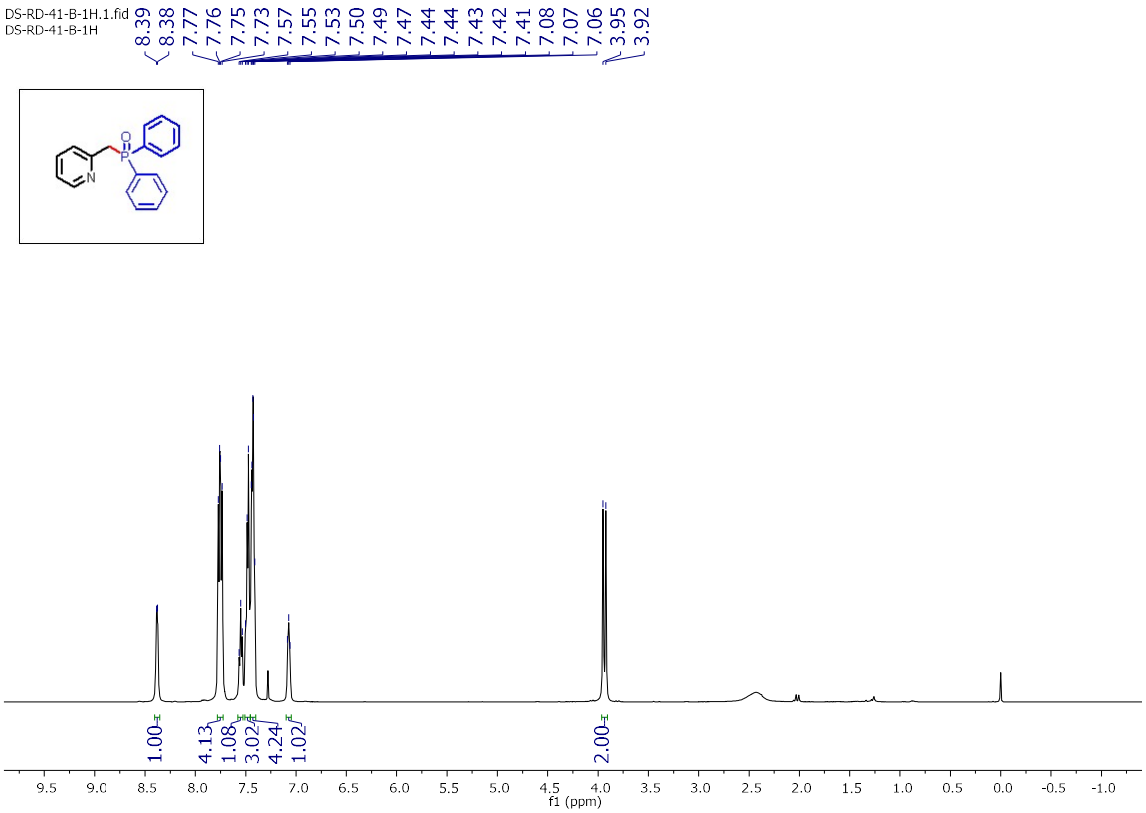


Figure S20. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3s in $CDCl_3$



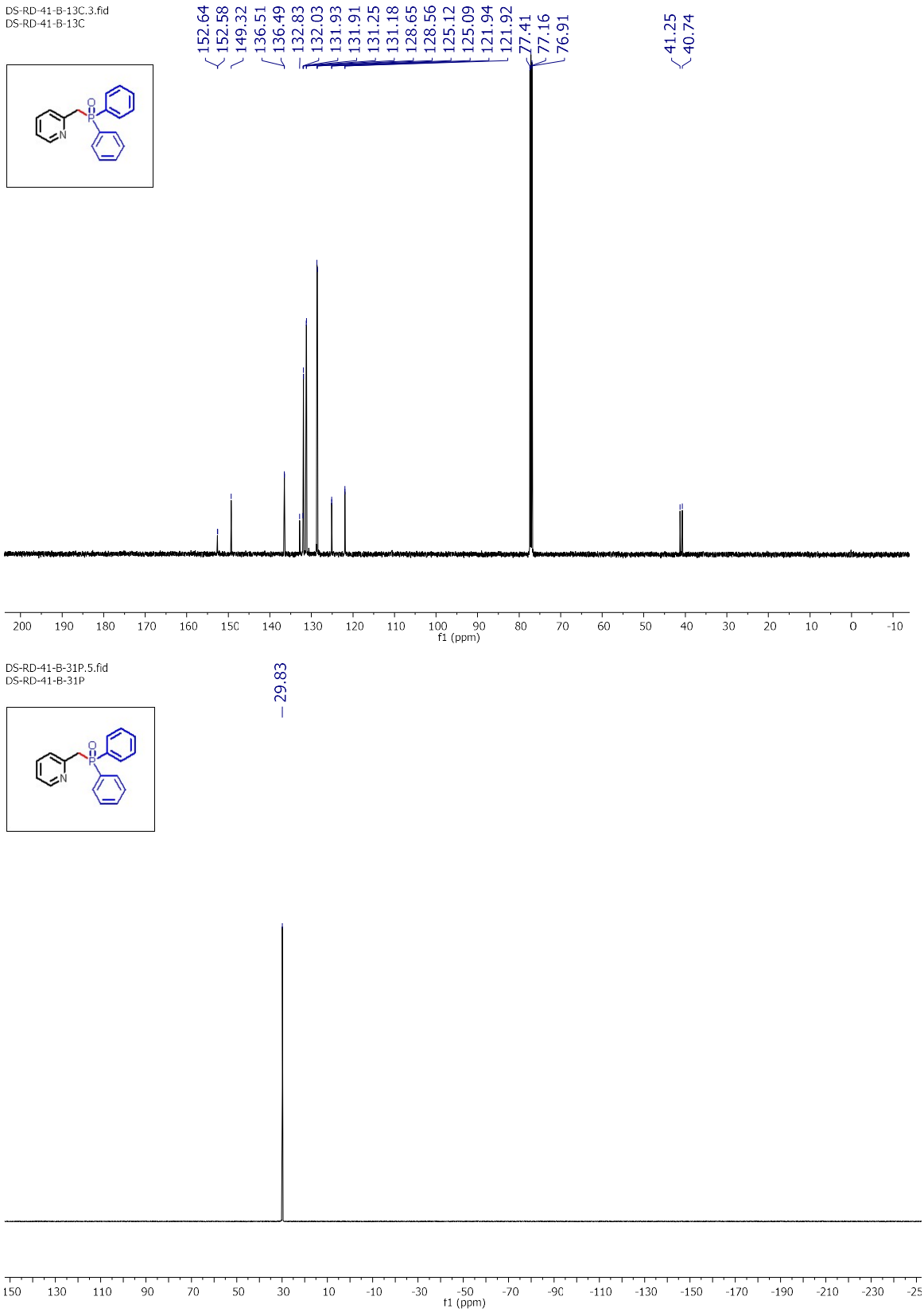
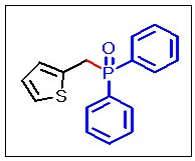
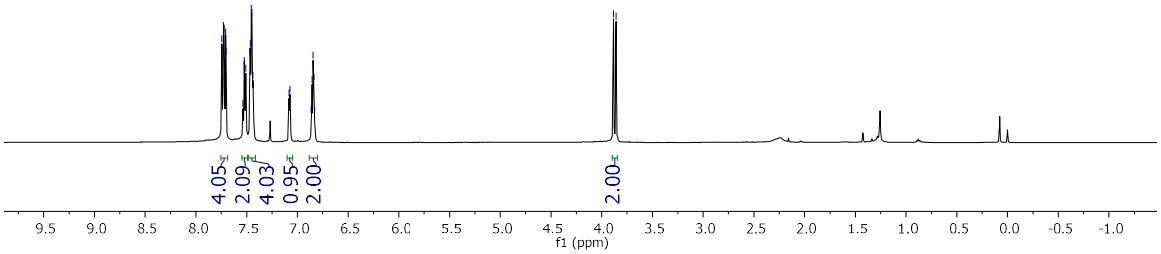
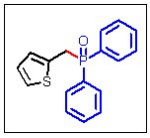


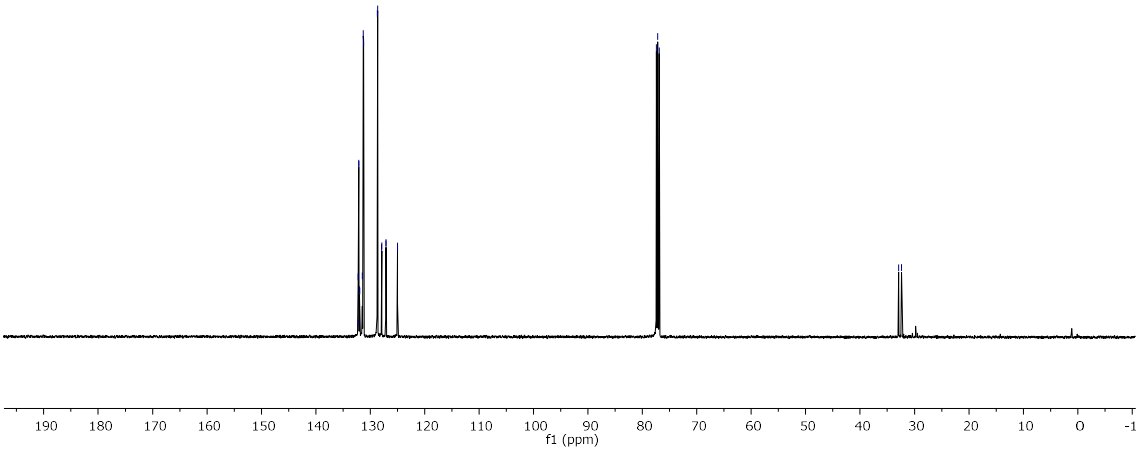
Figure S21. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3t in $CDCl_3$





DS-RD-33-A-13C.3.fid
DS-RD-33-A-13C





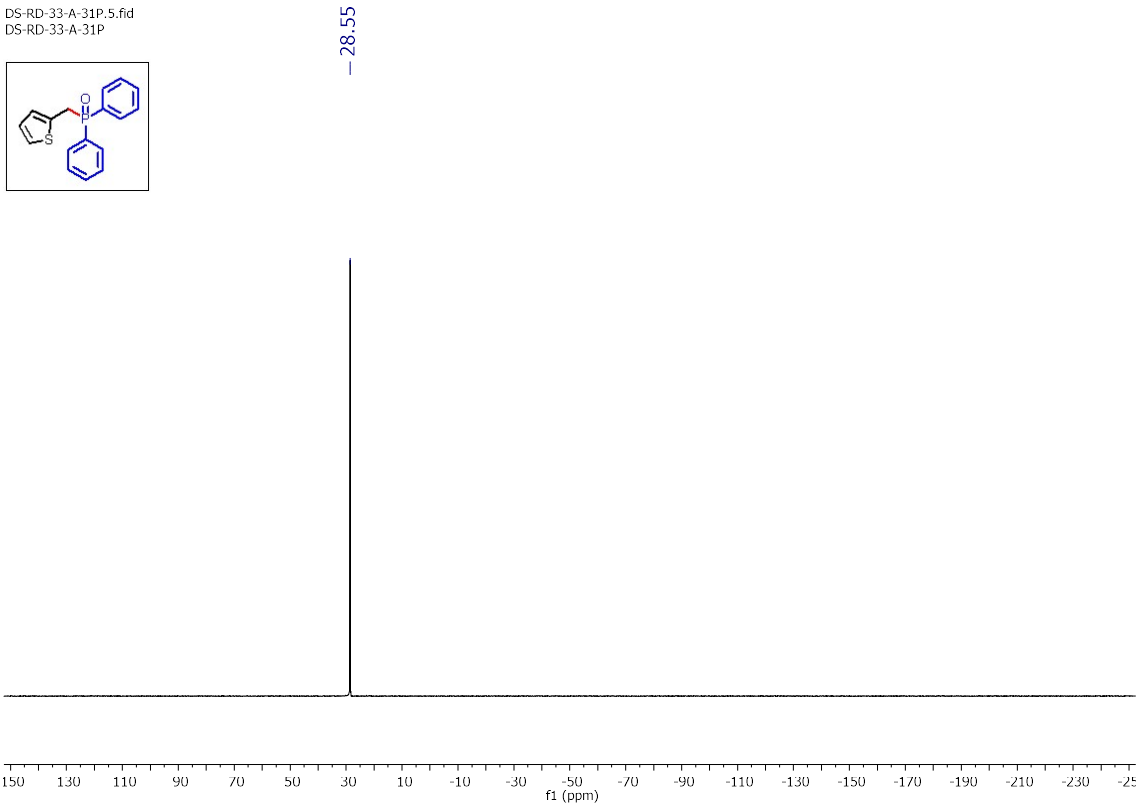
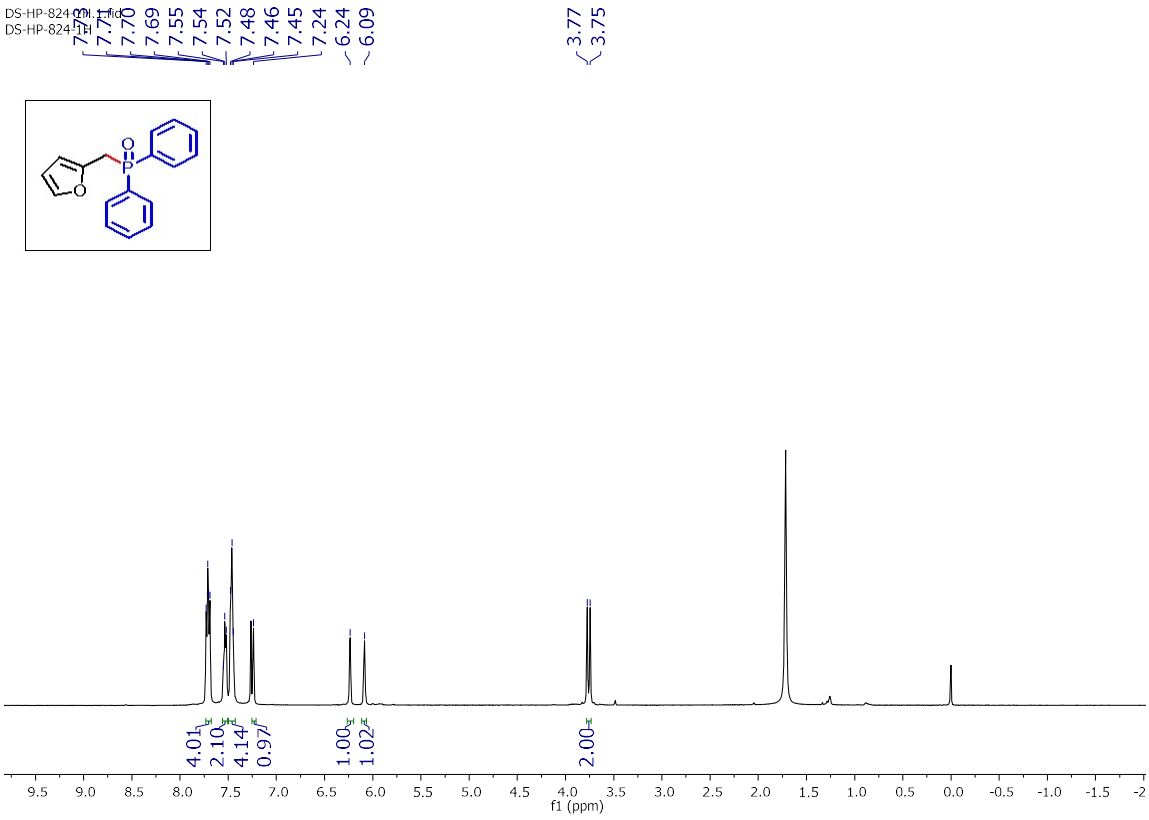
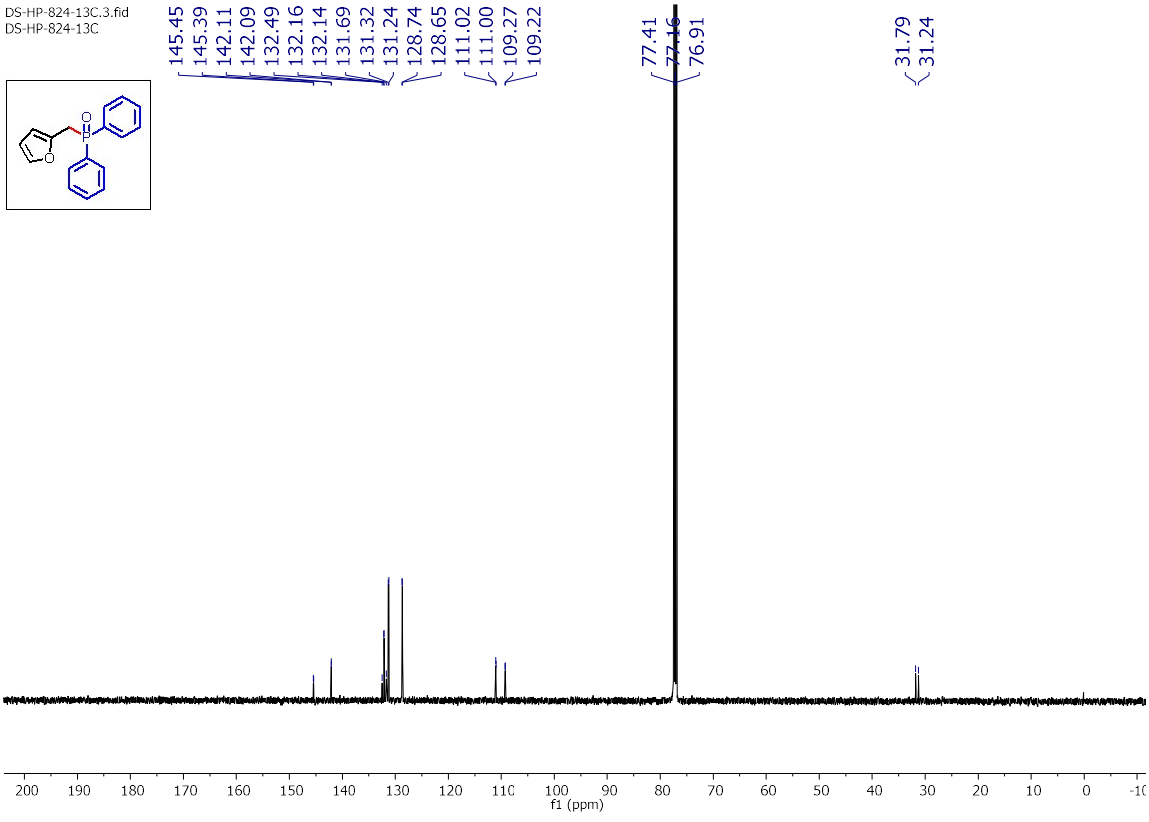


Figure S22. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3u in $CDCl_3$


DS-HP-824-01H.1.fid
DS-HP-824-1H
7.71
7.70
7.69
7.55
7.54
7.52
7.48
7.46
7.45
7.24
6.24
6.09
3.77
3.75
O
P
O
4.01
2.10
4.14
0.97
1.00
1.02
2.00
f1 (ppm)


DS-HP-824-13C.3.fid
DS-HP-824-13C
145.45
145.39
142.11
142.09
132.49
132.16
132.14
131.69
131.32
131.24
128.74
128.65
111.02
111.00
109.27
109.22
77.41
77.16
76.91
31.79
31.24
O
P
O
f1 (ppm)

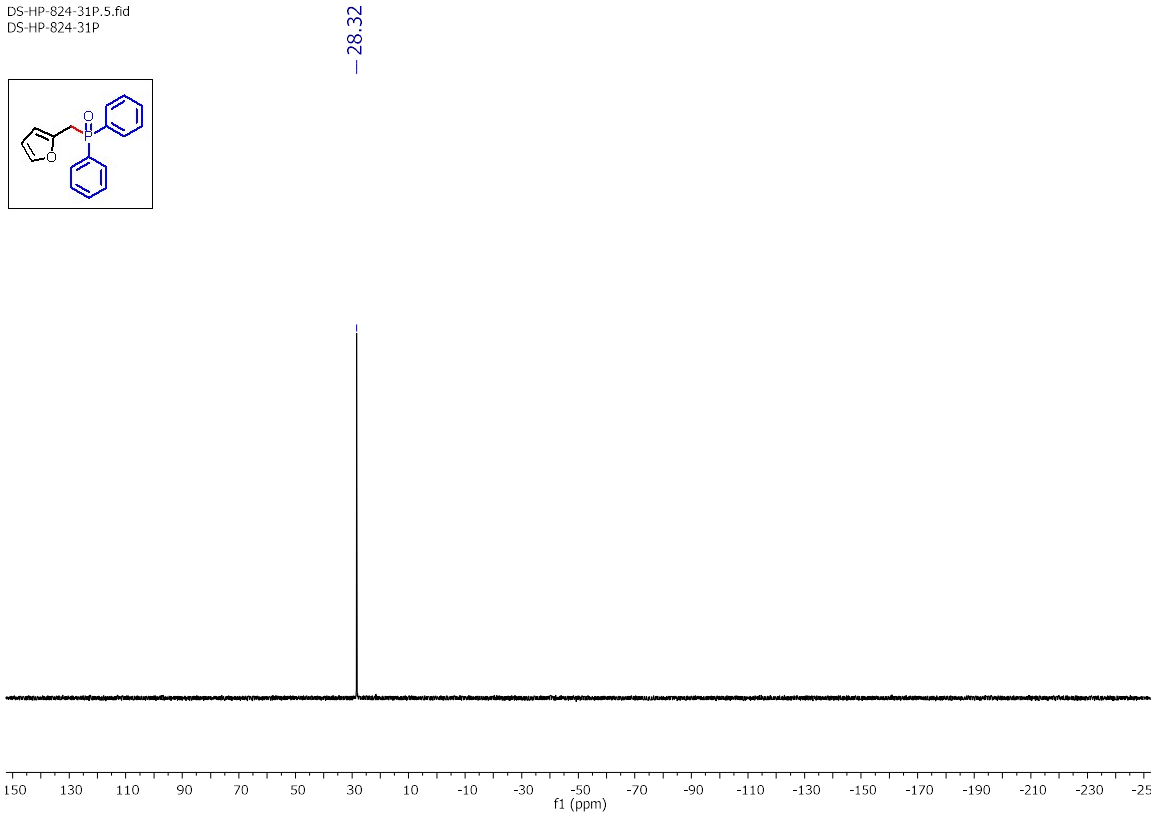
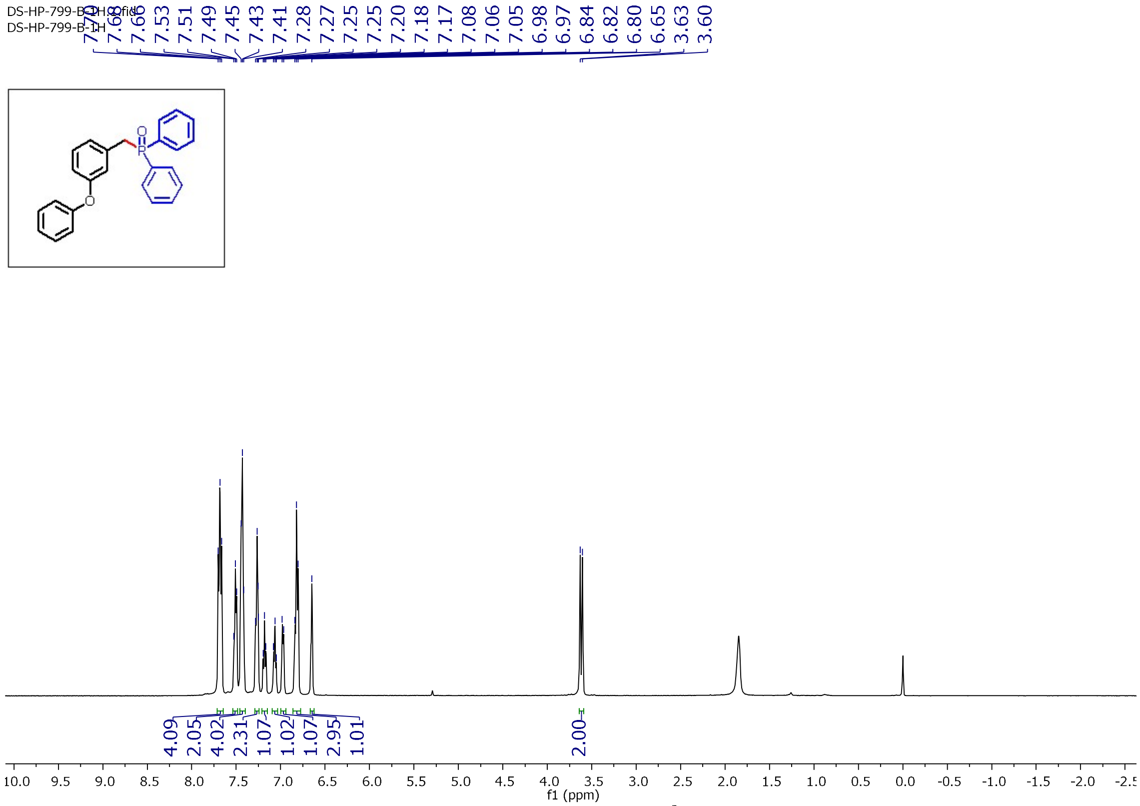
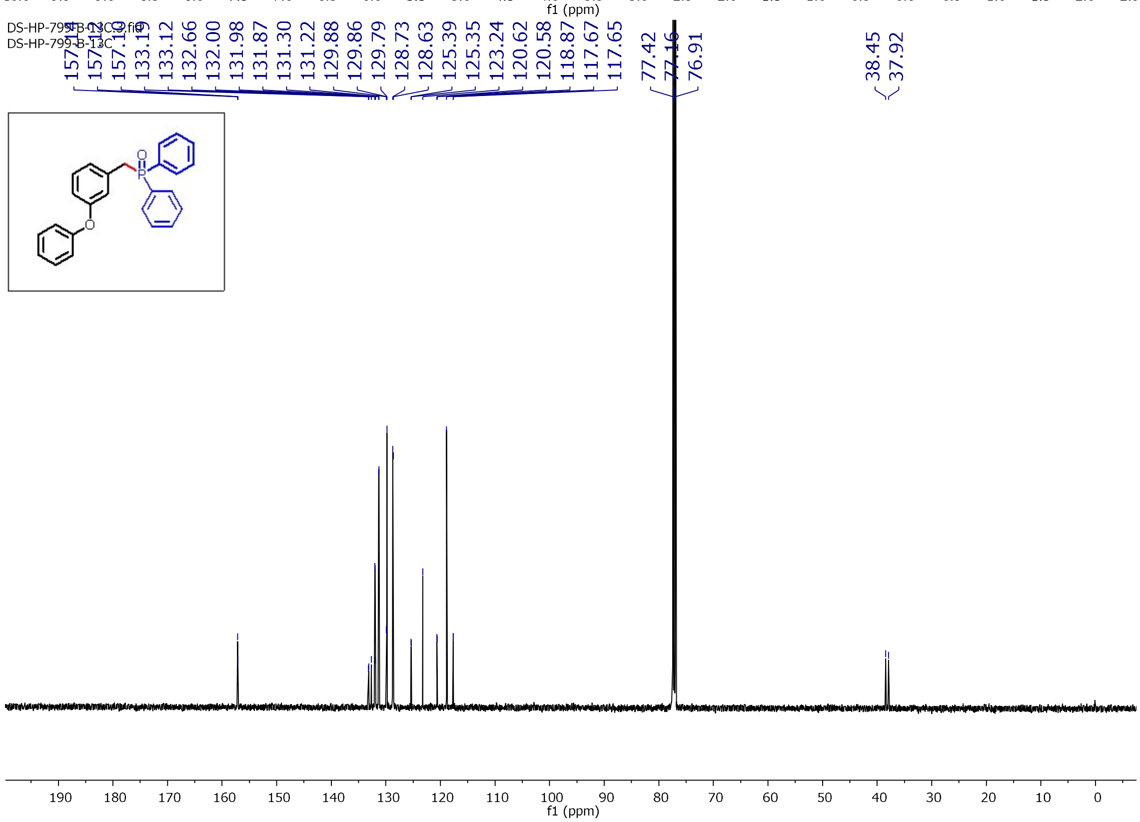


Figure S23. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3v in $CDCl_3$


DS-HP-799-B-1H
7.53 7.51 7.49 7.45 7.43 7.41 7.28 7.27 7.25 7.25 7.20 7.18 7.17 7.08 7.06 7.05 6.98 6.97 6.84 6.82 6.80 6.65 3.63 3.60
4.09 2.05 4.02 2.31 1.07 1.02 1.07 2.95 1.01 2.00
f1 (ppm)


DS-HP-799-B-13C
133.12 132.66 132.00 131.98 131.87 131.30 131.22 129.88 129.86 129.79 128.73 128.63 125.39 125.35 123.24 120.62 120.58 118.87 117.67 117.65 77.42 76.91 38.45 37.92
f1 (ppm)

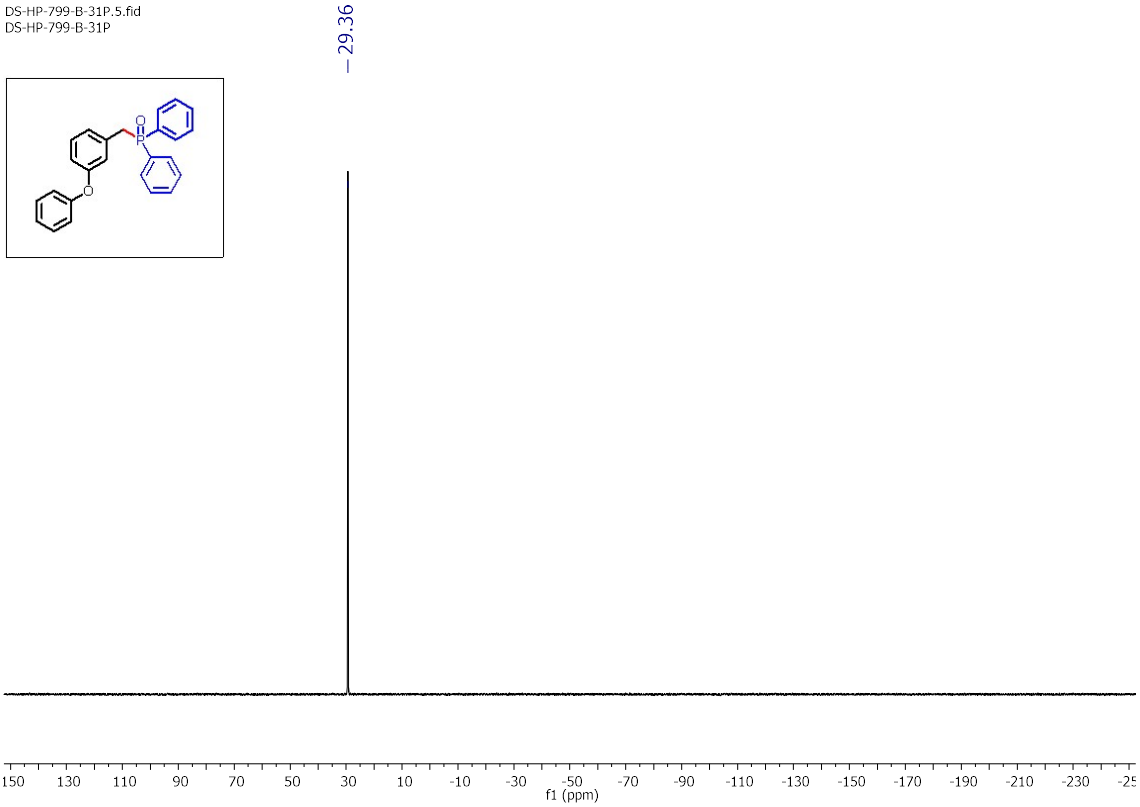
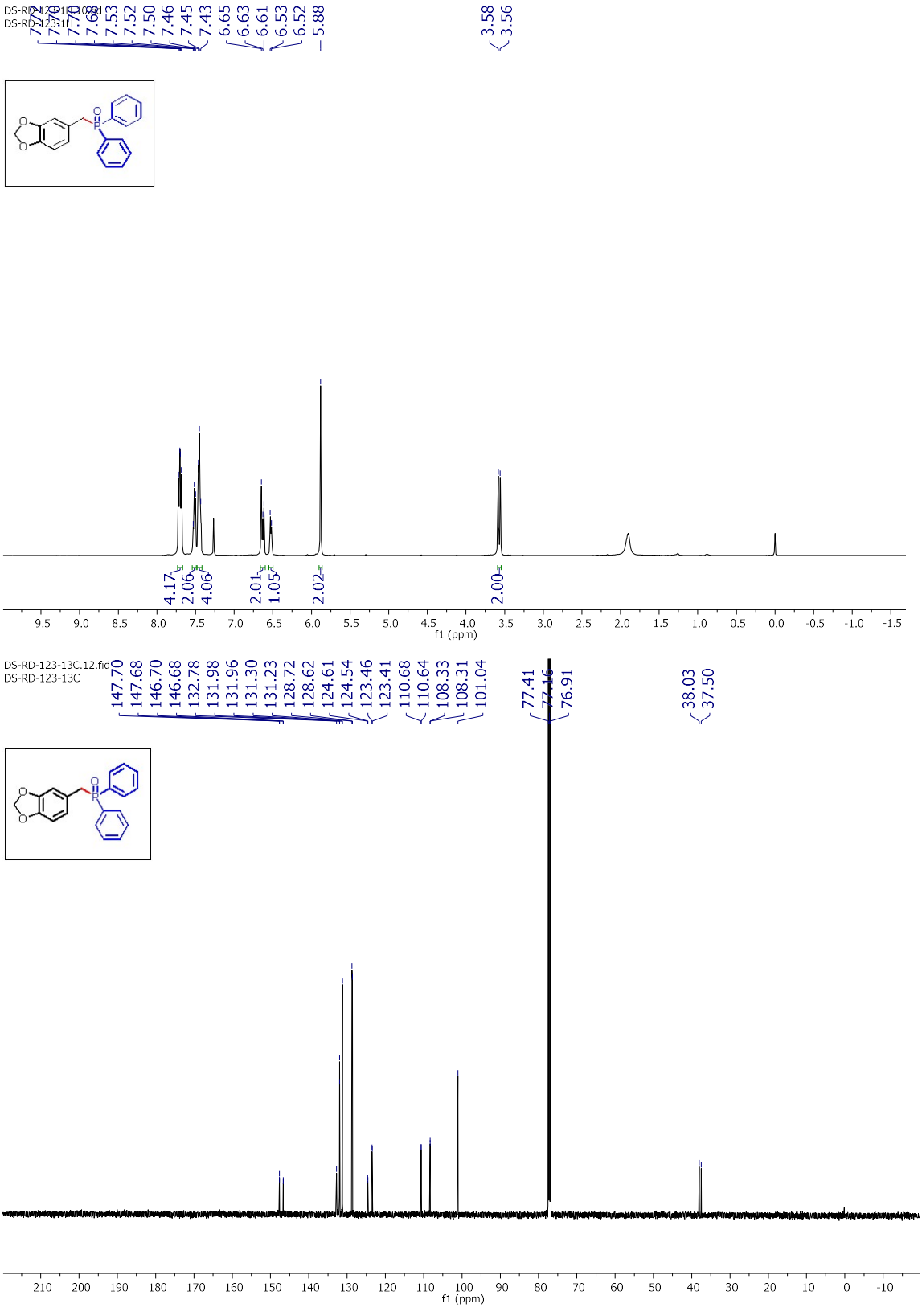


Figure S24. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3x in $CDCl_3$


DS-RD-123-1H
7.72
7.70
7.70
7.68
7.53
7.52
7.50
7.46
7.45
7.43
6.65
6.63
6.61
6.53
6.52
5.88
3.58
3.56
4.17
2.06
4.06
2.01
1.05
2.02
2.00
f1 (ppm)
DS-RD-123-13C.12.fid
DS-RD-123-13C
147.70
147.68
146.70
146.68
132.78
131.98
131.96
131.30
131.23
128.72
128.62
124.61
124.54
123.46
123.41
110.68
110.64
108.33
108.31
101.04
77.41
77.16
76.91
38.03
37.50
f1 (ppm)

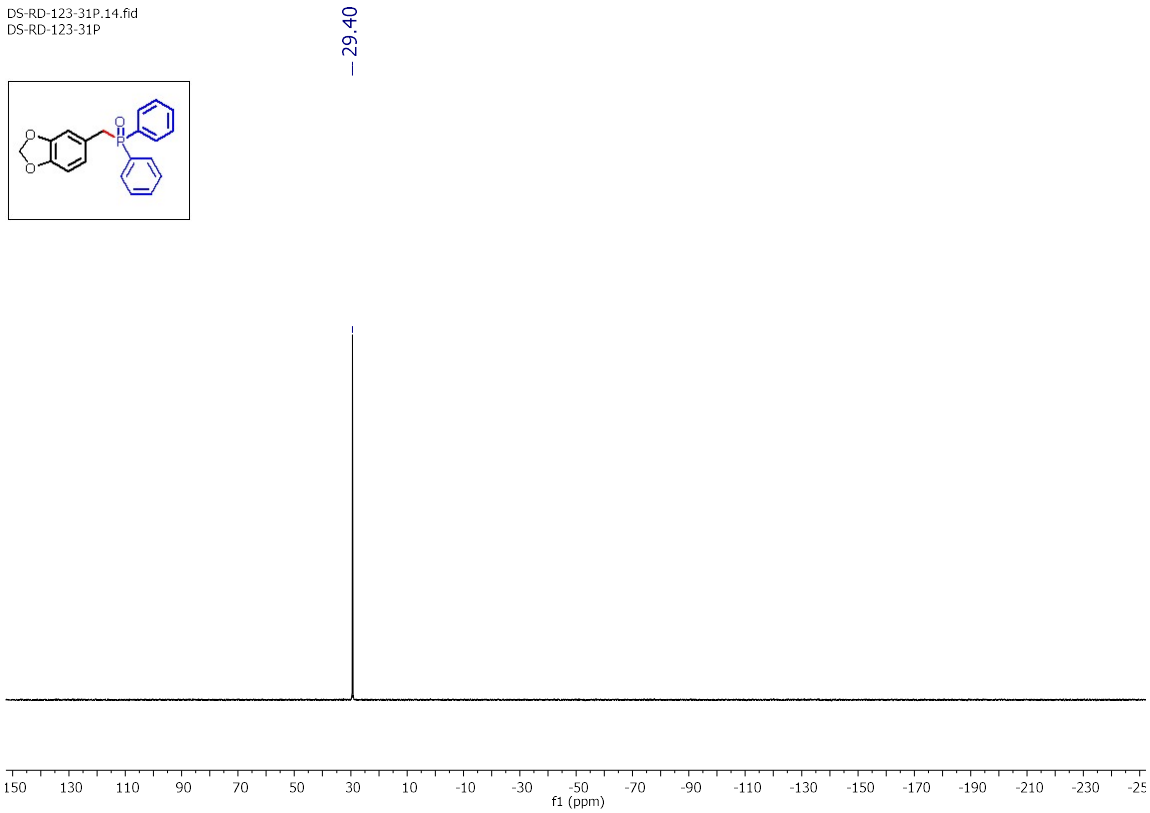
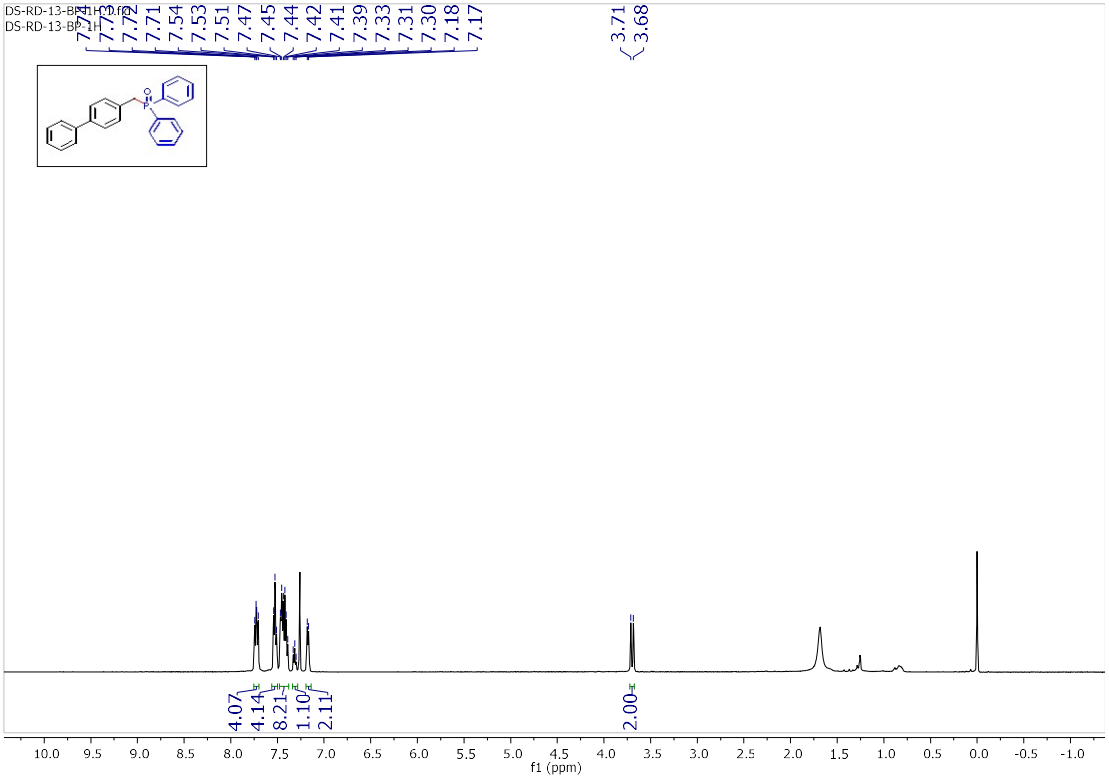
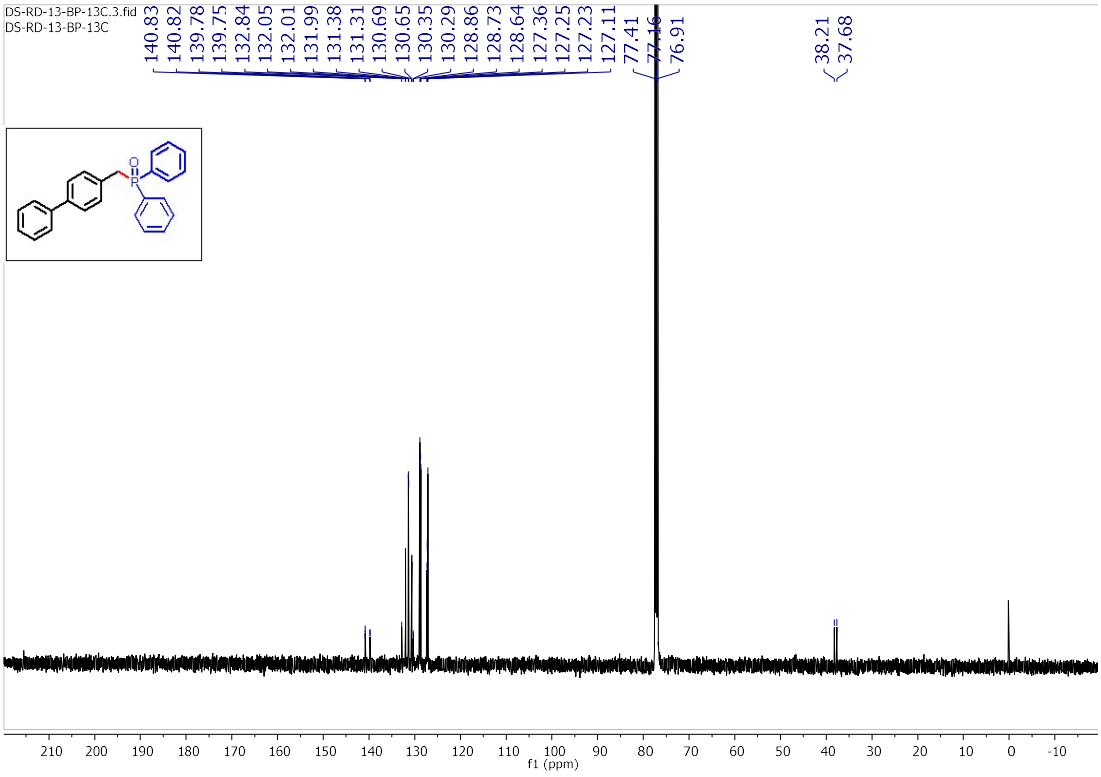


Figure S25. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3y in $CDCl_3$


DS-RD-13-BP-1H.3.fid
DS-RD-13-BP-1H
7.74
7.73
7.72
7.71
7.54
7.53
7.51
7.47
7.45
7.44
7.42
7.41
7.39
7.33
7.31
7.30
7.18
7.17
3.71
3.68
4.07
4.14
8.21
1.10
2.11
2.00
f1 (ppm)


DS-RD-13-BP-13C.3.fid
DS-RD-13-BP-13C
140.83
140.82
139.78
139.75
132.84
132.05
132.01
131.99
131.38
131.31
130.69
130.65
130.35
130.29
128.86
128.73
128.64
127.36
127.25
127.23
127.11
77.41
77.16
76.91
38.21
37.68
f1 (ppm)

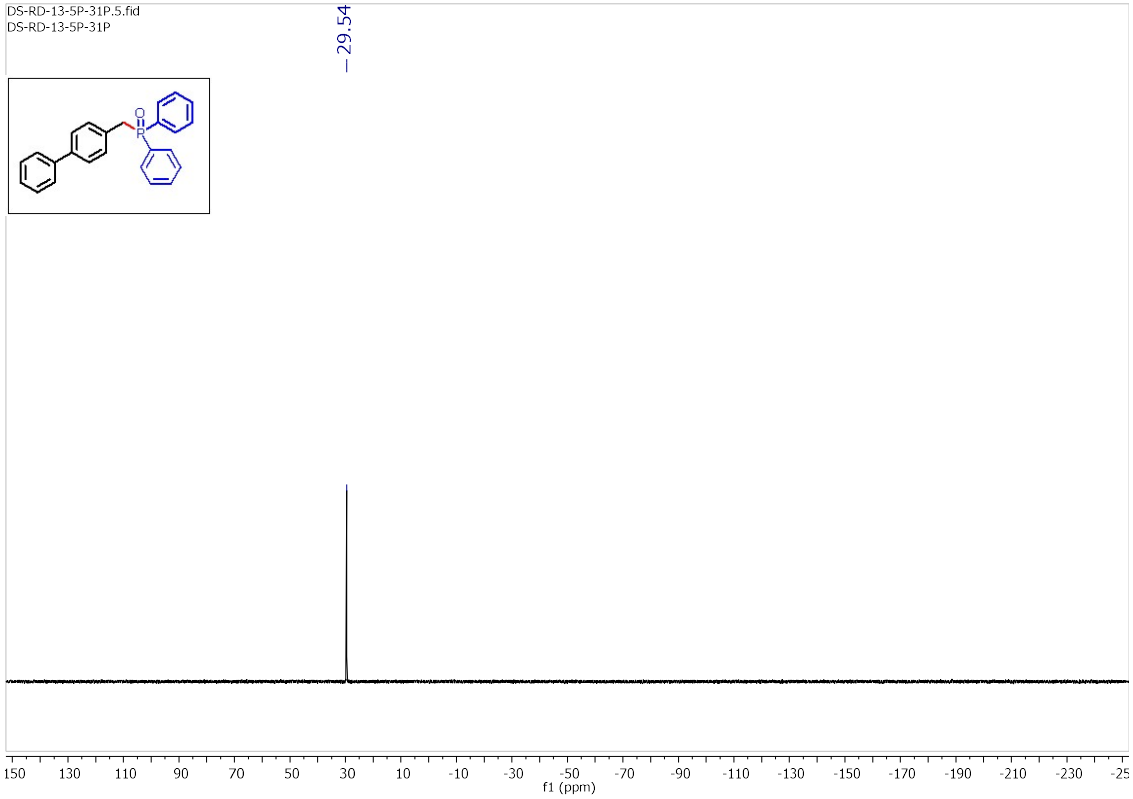
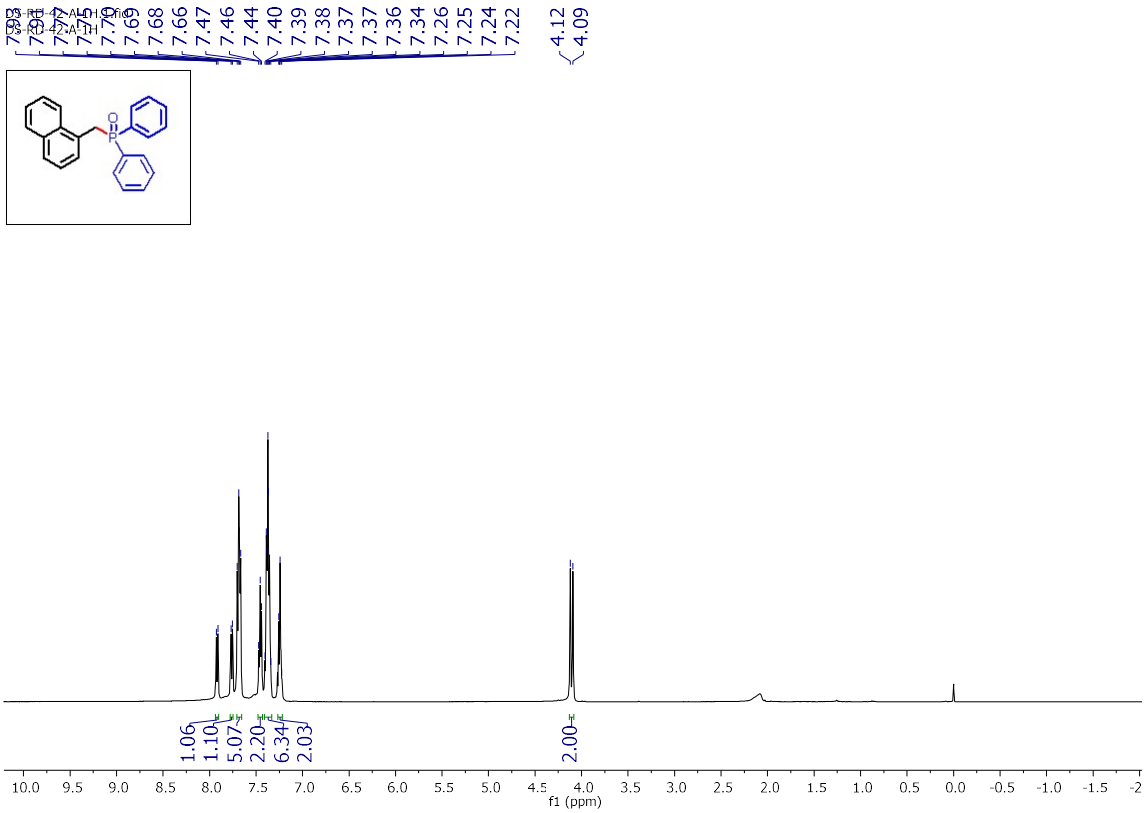
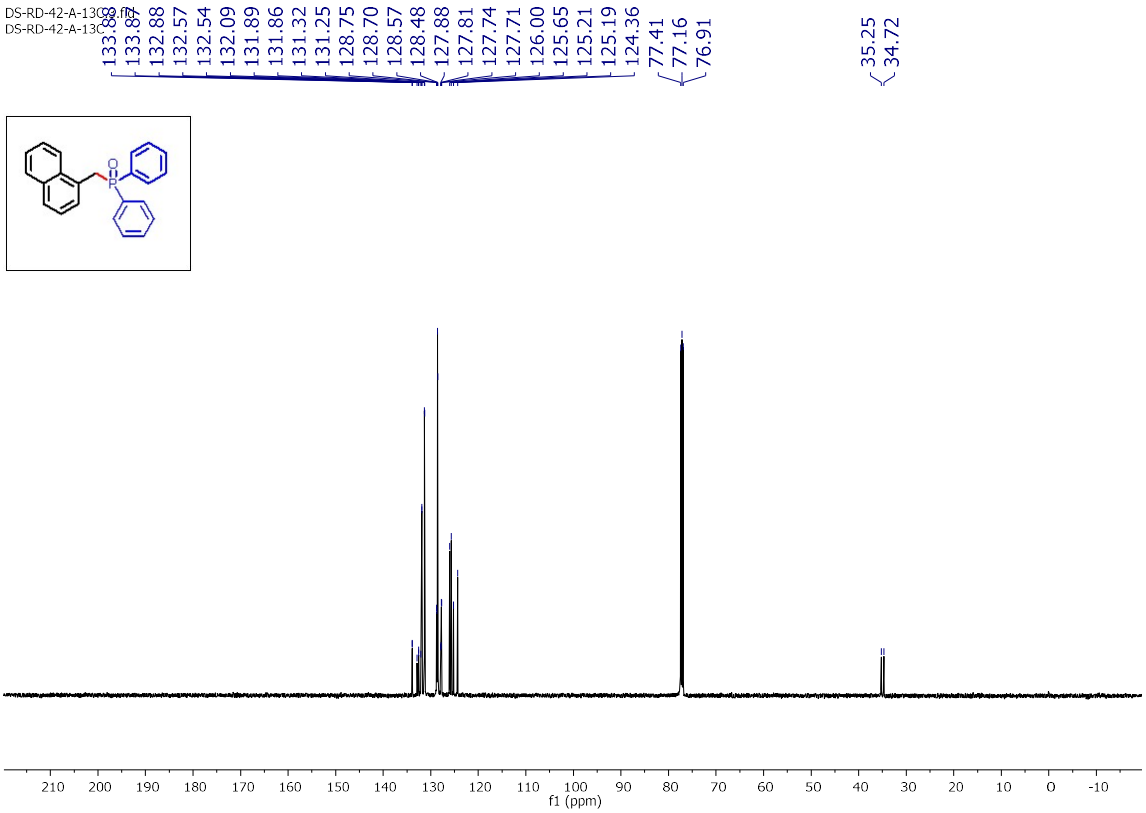


Figure S26. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3z in $CDCl_3$


7.75
7.74
7.73
7.71
7.70
7.69
7.68
7.66
7.47
7.46
7.44
7.40
7.39
7.38
7.37
7.37
7.36
7.34
7.26
7.25
7.24
7.22
4.12
4.09
1.06
1.10
5.07
2.20
6.34
2.03
2.00
f1 (ppm)


133.87
133.87
132.88
132.57
132.54
132.09
131.89
131.86
131.32
131.25
128.75
128.70
128.57
128.48
127.88
127.81
127.74
127.71
126.00
125.65
125.21
125.19
124.36
77.41
77.16
76.91
35.25
34.72
f1 (ppm)

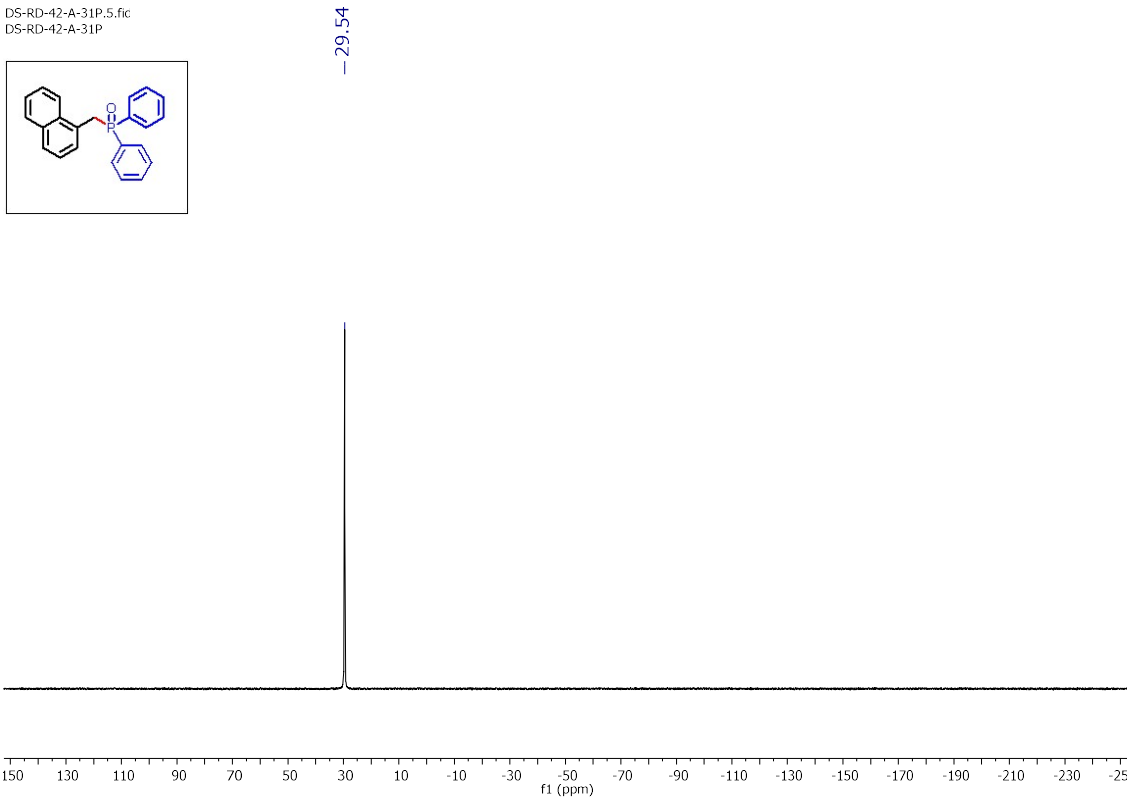
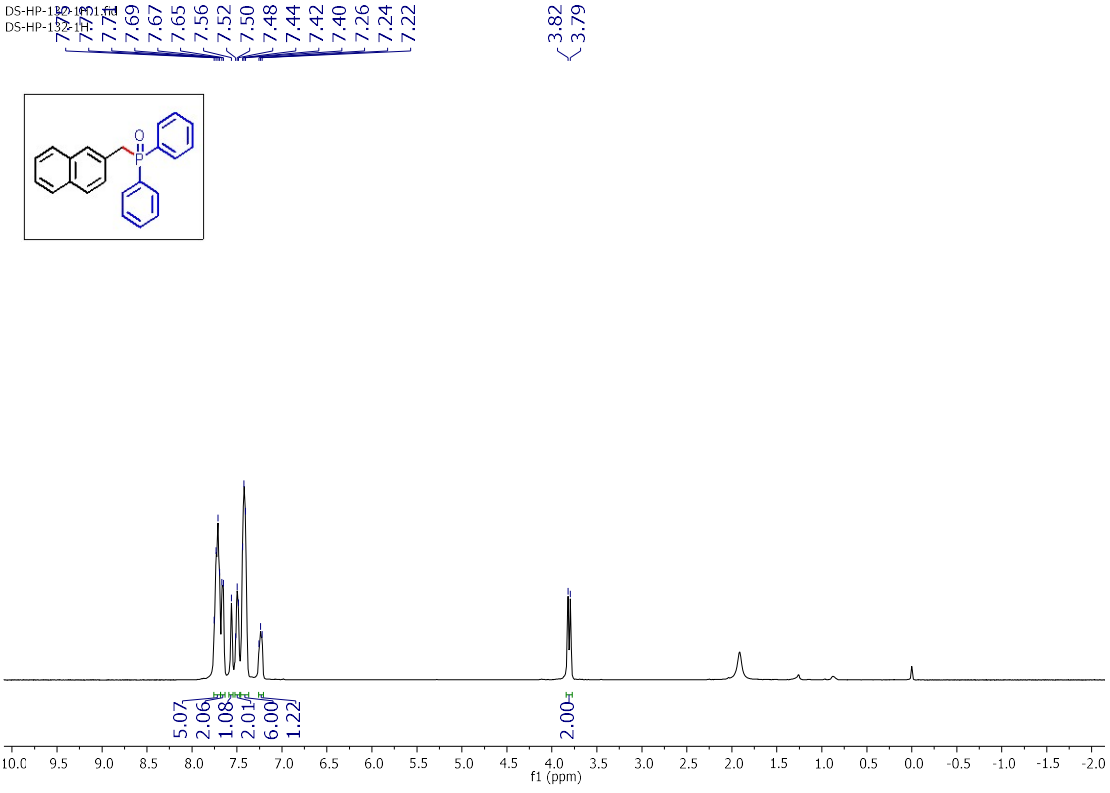


Figure S27. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3aa in $CDCl_3$



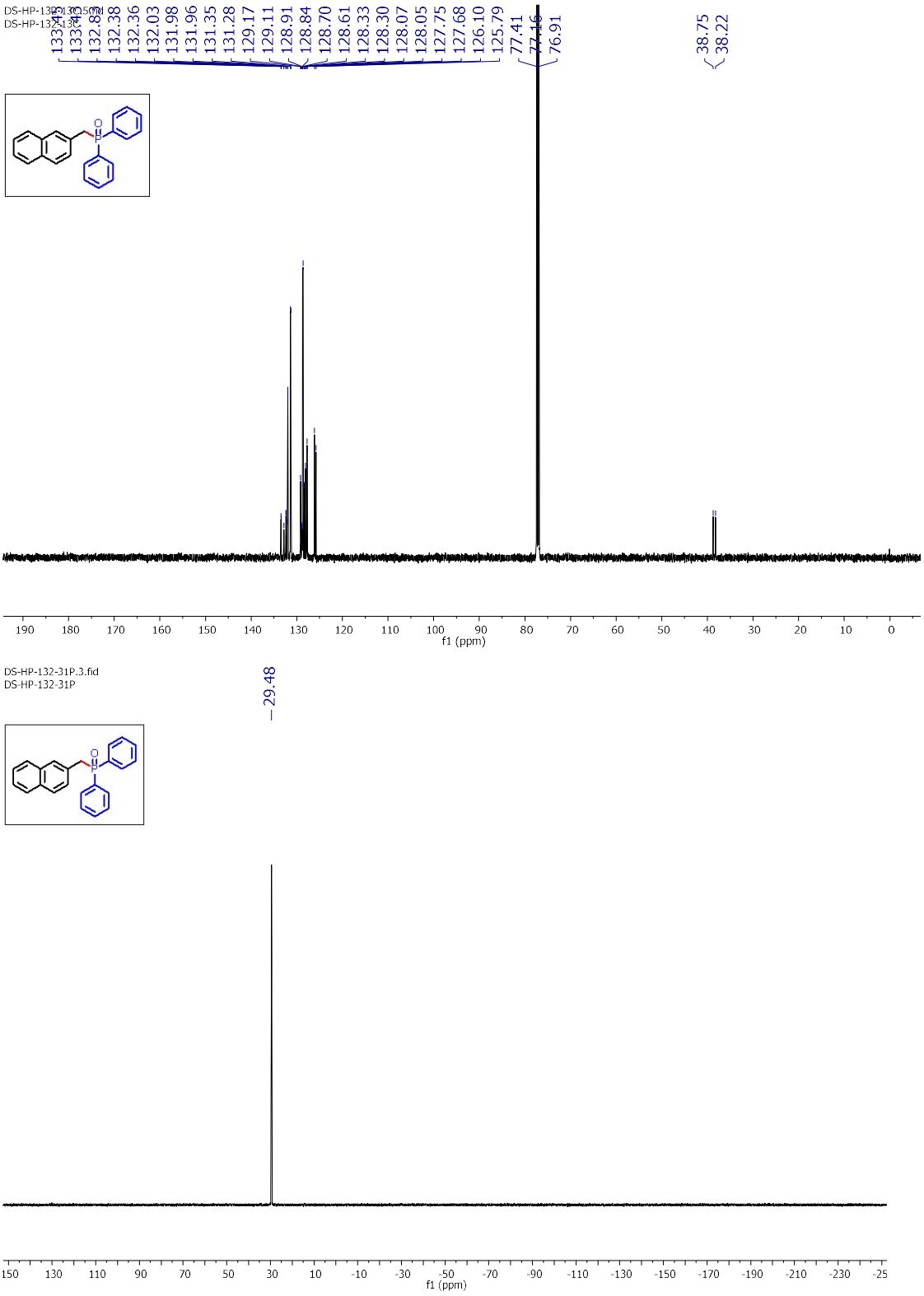
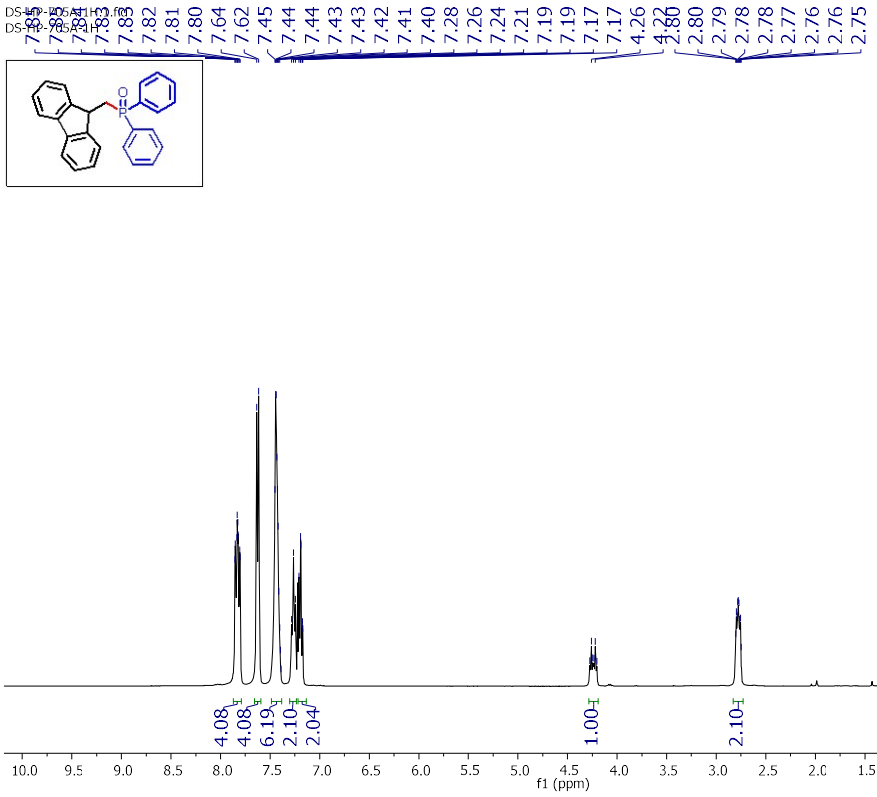
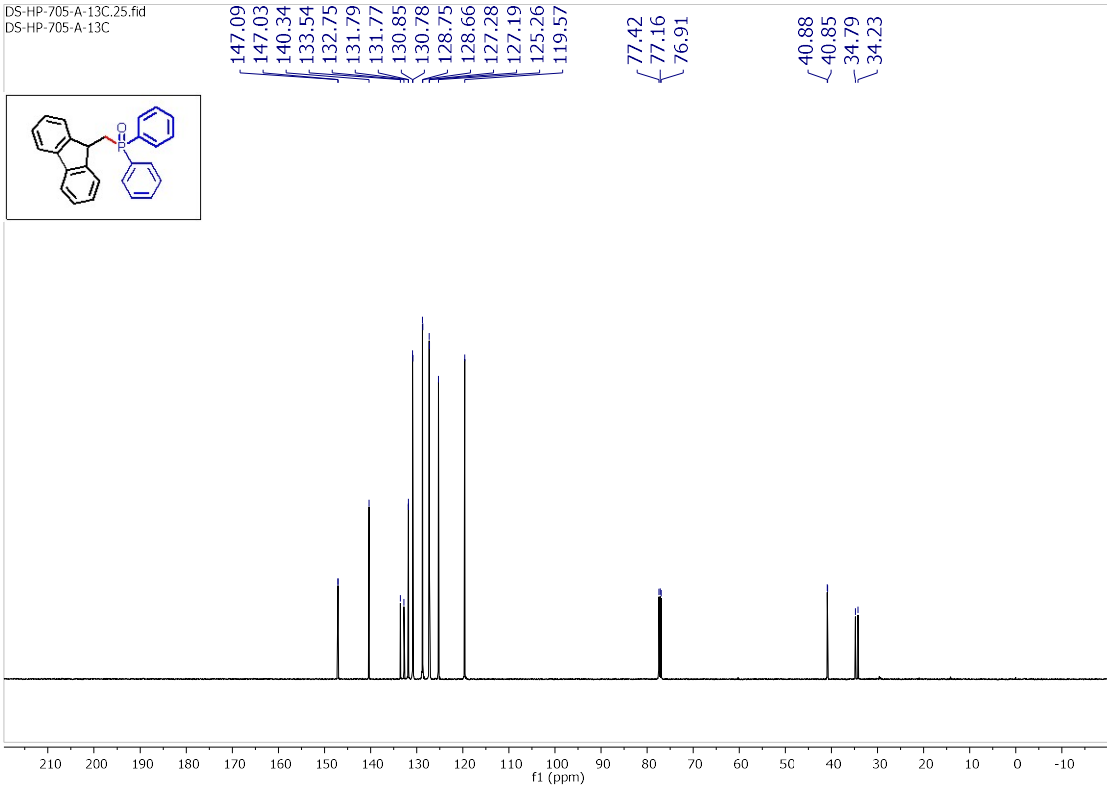


Figure S28. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ab in $CDCl_3$


DS-HP-705-A-1H
7.85
7.83
7.82
7.81
7.80
7.64
7.62
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.28
7.26
7.24
7.21
7.19
7.19
7.17
7.17
4.26
2.80
2.80
2.79
2.78
2.78
2.77
2.76
2.76
2.75
4.08
4.08
6.19
2.10
2.04
1.00
2.10
f1 (ppm)


DS-HP-705-A-13C.25.fid
DS-HP-705-A-13C
147.09
147.03
140.34
133.54
132.75
131.79
131.77
130.85
130.78
128.75
128.66
127.28
127.19
125.26
119.57
77.42
77.16
76.91
40.88
40.85
34.79
34.23
f1 (ppm)

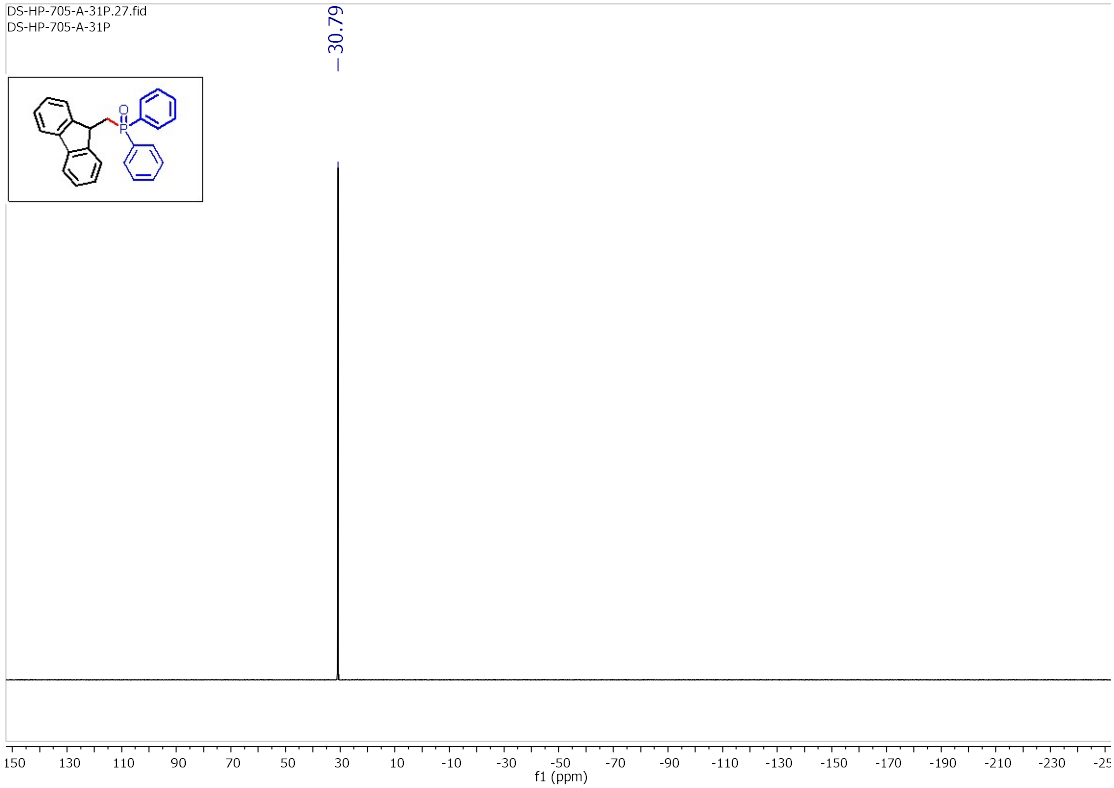
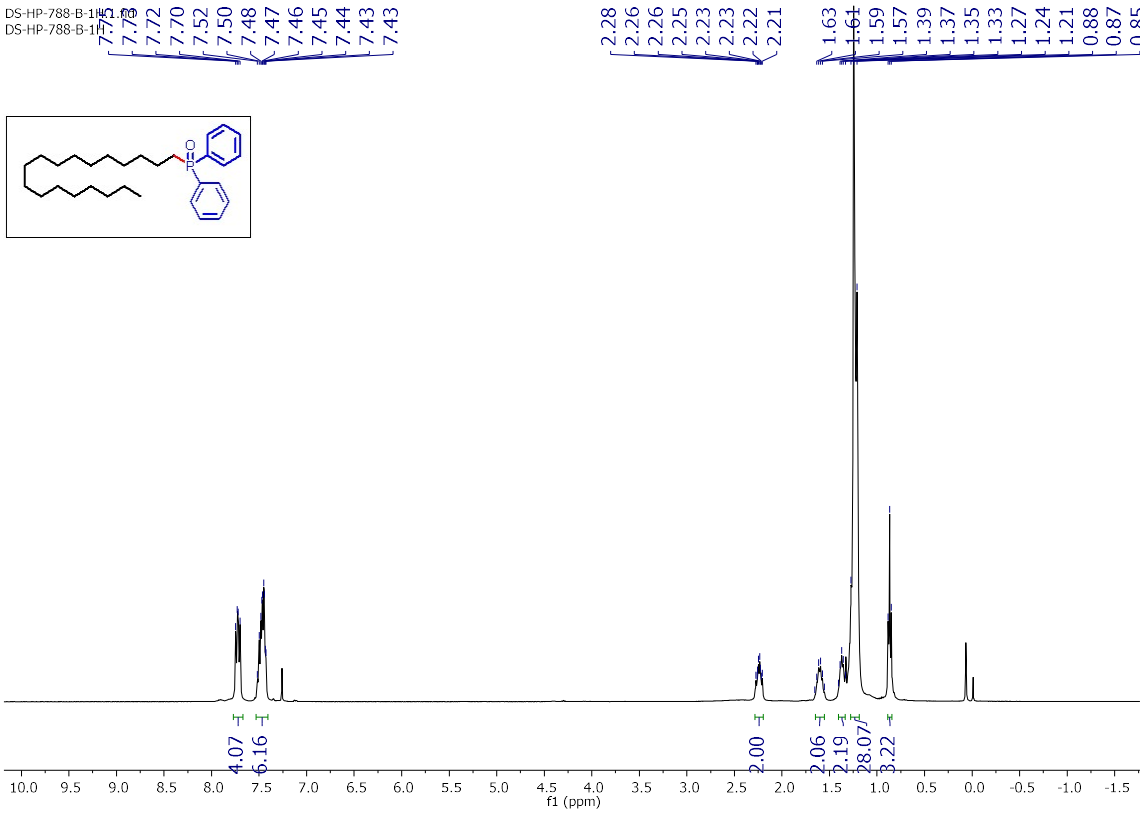
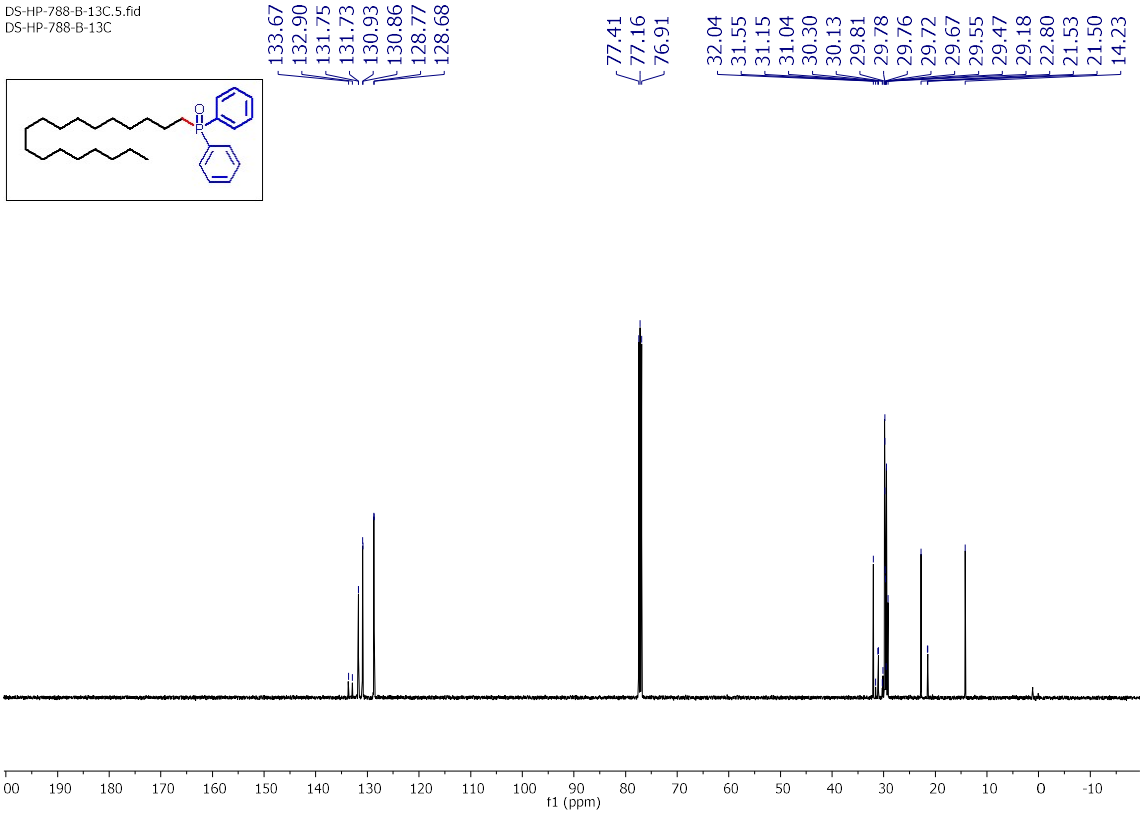


Figure S29. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ac in $CDCl_3$


DS-HP-788-B-1H.fid
DS-HP-788-B-1H
7.75
7.73
7.72
7.70
7.52
7.50
7.48
7.47
7.46
7.45
7.44
7.43
7.43
2.28
2.26
2.26
2.25
2.23
2.23
2.22
2.21
1.63
1.61
1.59
1.57
1.39
1.37
1.35
1.33
1.27
1.24
1.21
0.88
0.87
4.07
6.16
2.00
2.06
2.19
28.07
3.22
f1 (ppm)


DS-HP-788-B-13C.5.fid
DS-HP-788-B-13C
133.67
132.90
131.75
131.73
130.93
130.86
128.77
128.68
77.41
77.16
76.91
32.04
31.55
31.15
31.04
30.30
30.13
29.81
29.78
29.76
29.72
29.67
29.55
29.47
29.18
22.80
21.53
21.50
14.23
f1 (ppm)

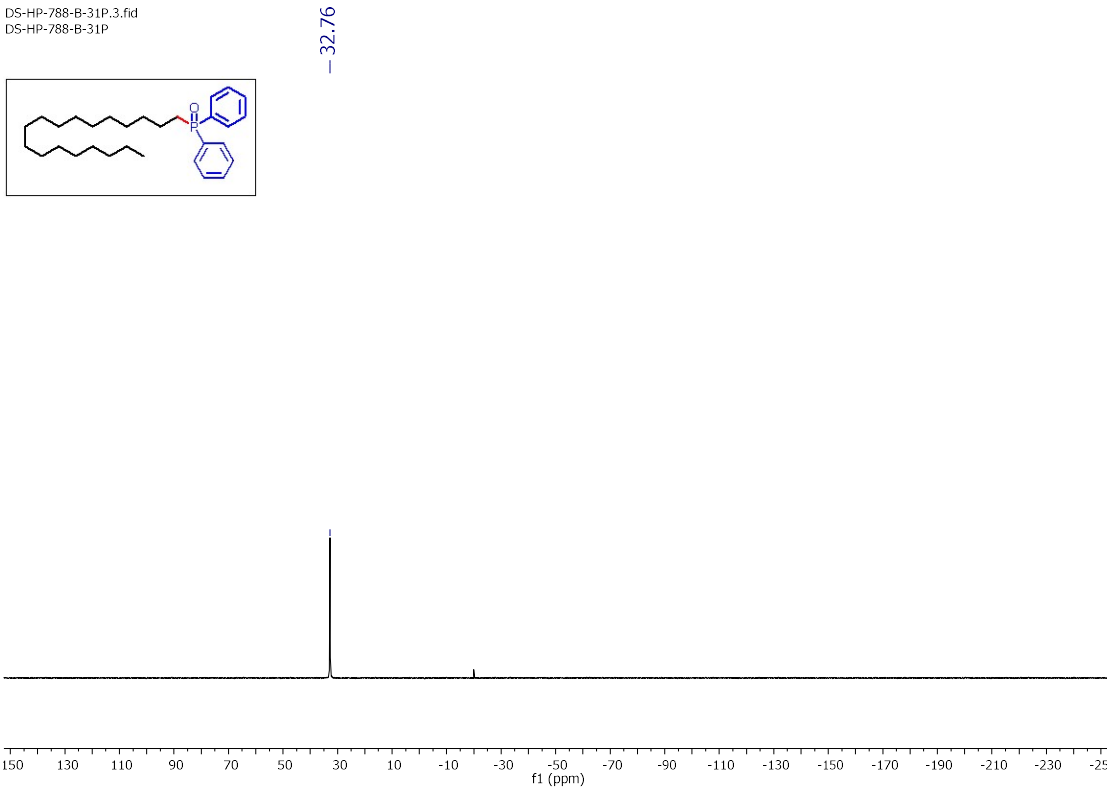
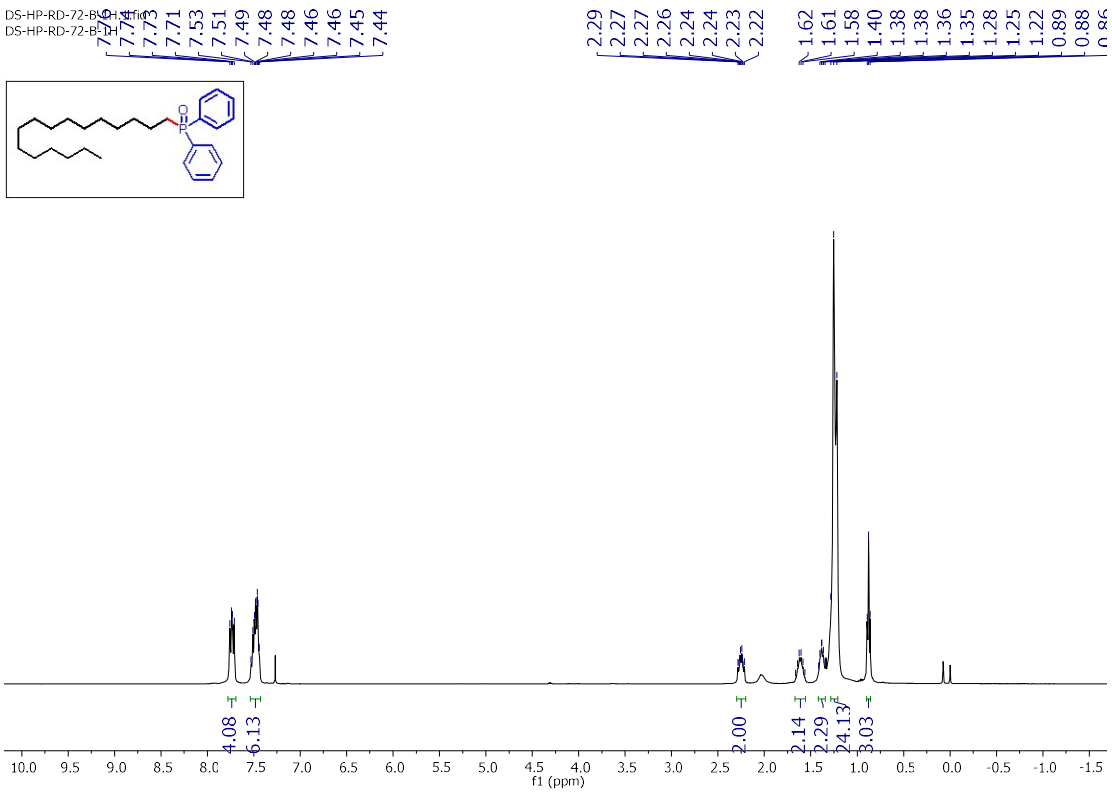


Figure S30. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ad in $CDCl_3$



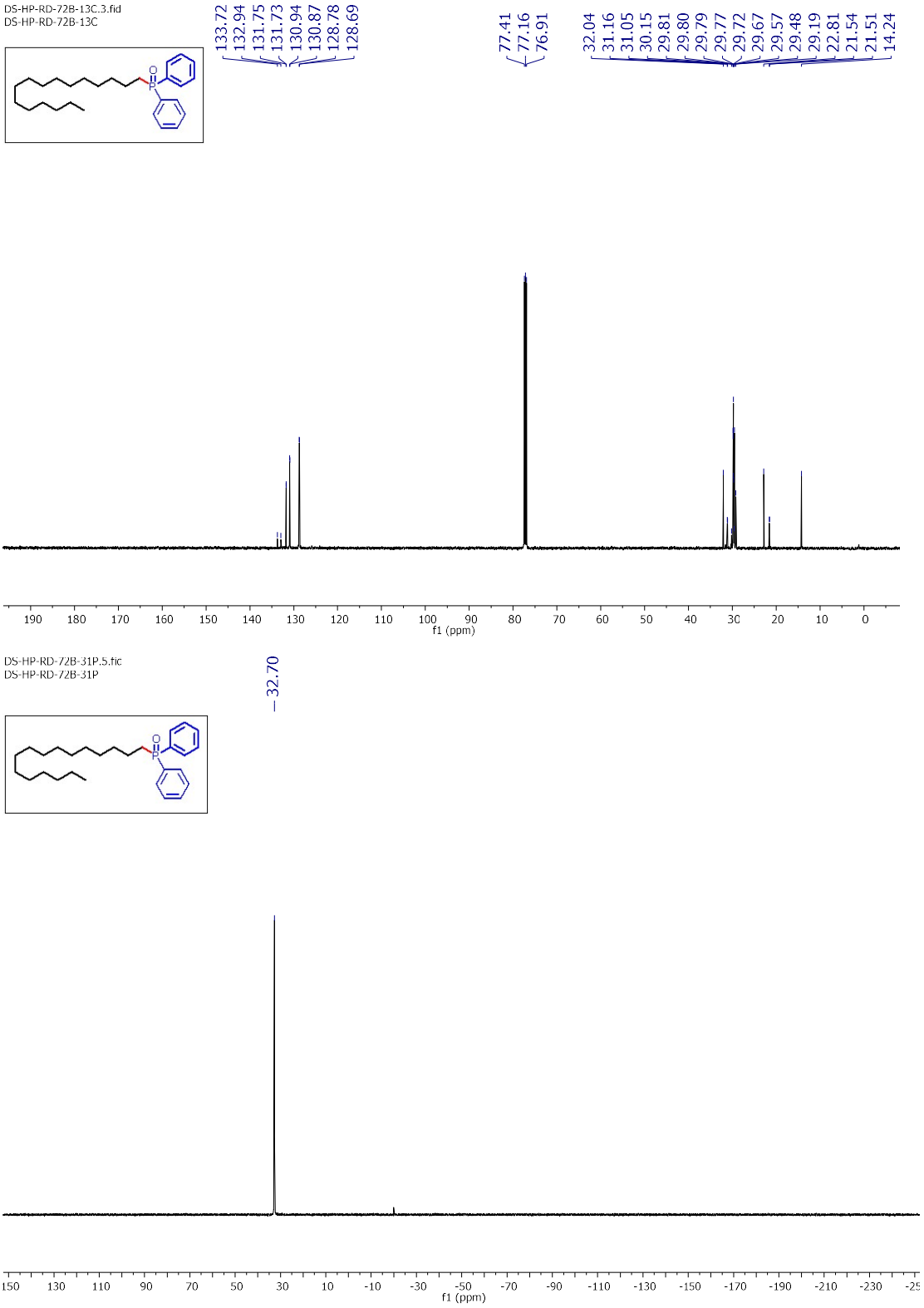
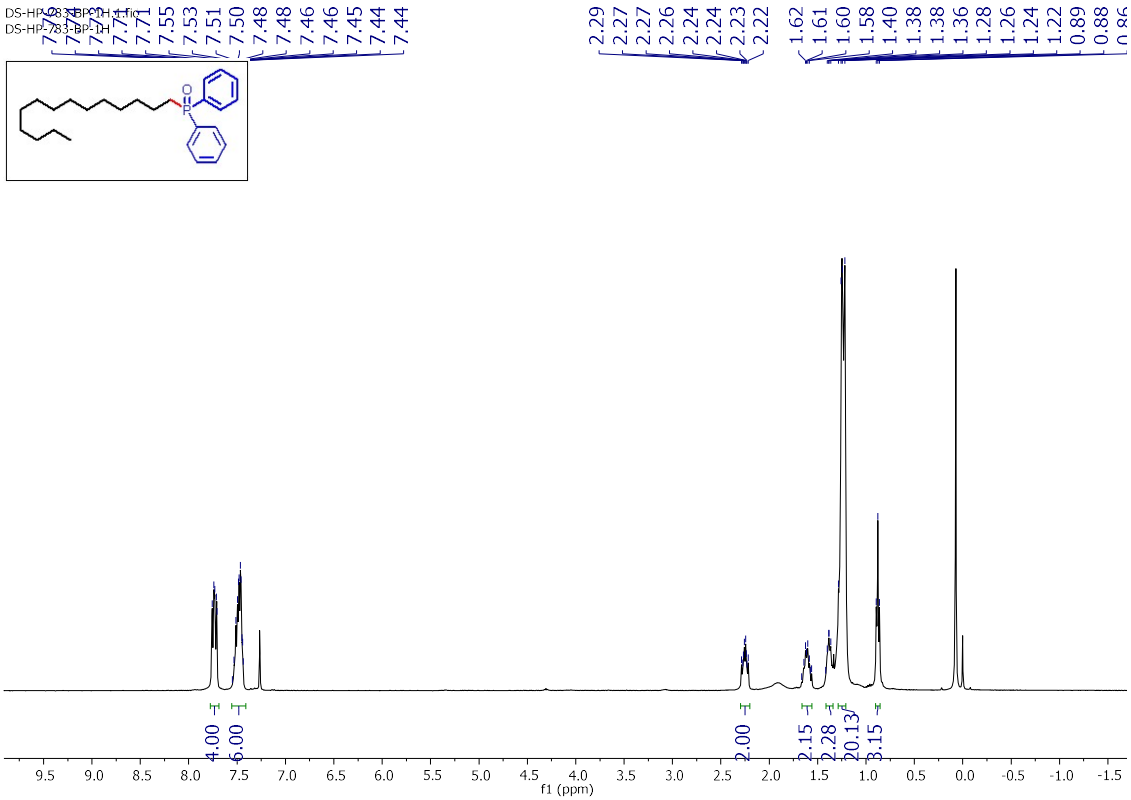
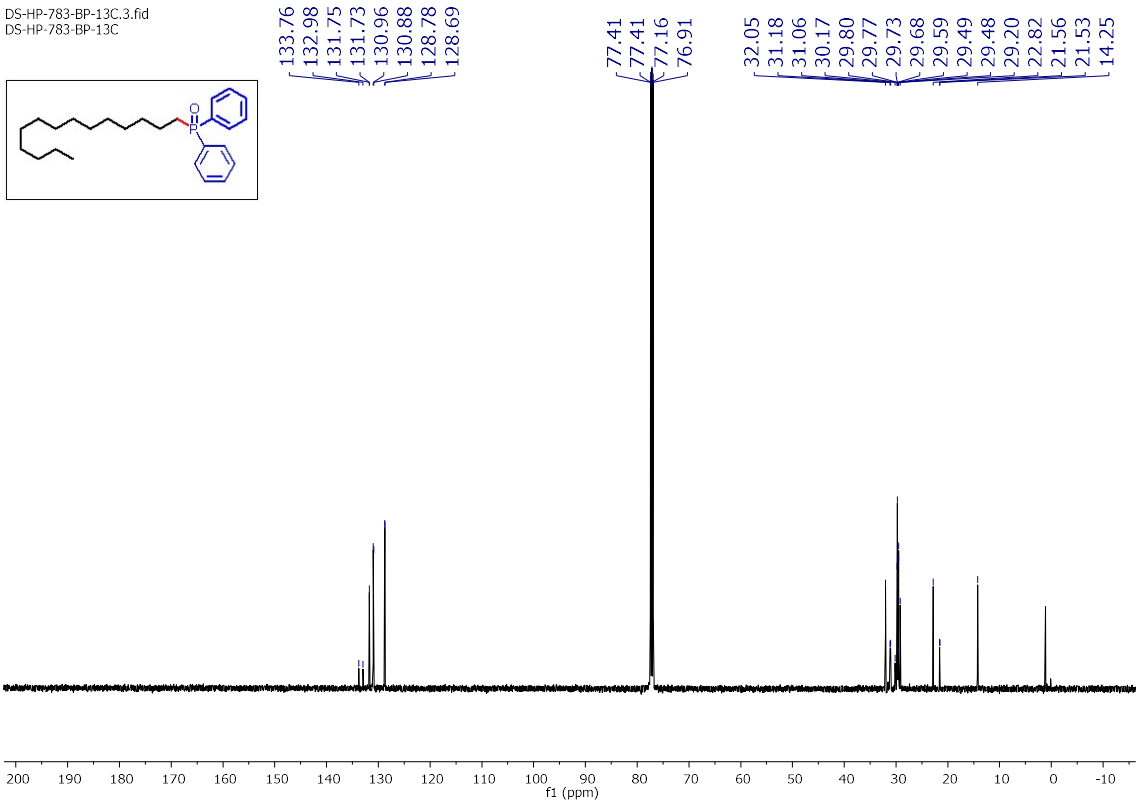


Figure S31. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ae in $CDCl_3$


DS-HP-783-BP-1H.4.fid
DS-HP-783-BP-1H
7.77
7.77
7.76
7.76
7.71
7.71
7.55
7.53
7.51
7.50
7.48
7.48
7.46
7.46
7.45
7.44
7.44
2.29
2.27
2.27
2.26
2.24
2.24
2.23
2.22
1.62
1.61
1.60
1.58
1.40
1.38
1.36
1.28
1.26
1.24
1.22
0.89
0.88
4.00
6.00
2.00
2.15
2.28
20.13
3.15
f1 (ppm)


DS-HP-783-BP-13C.3.fid
DS-HP-783-BP-13C
133.76
132.98
131.75
131.73
130.96
130.88
128.78
128.69
77.41
77.41
77.16
76.91
32.05
31.18
31.06
30.17
29.80
29.77
29.73
29.68
29.59
29.49
29.48
29.20
22.82
21.56
21.53
14.25
f1 (ppm)

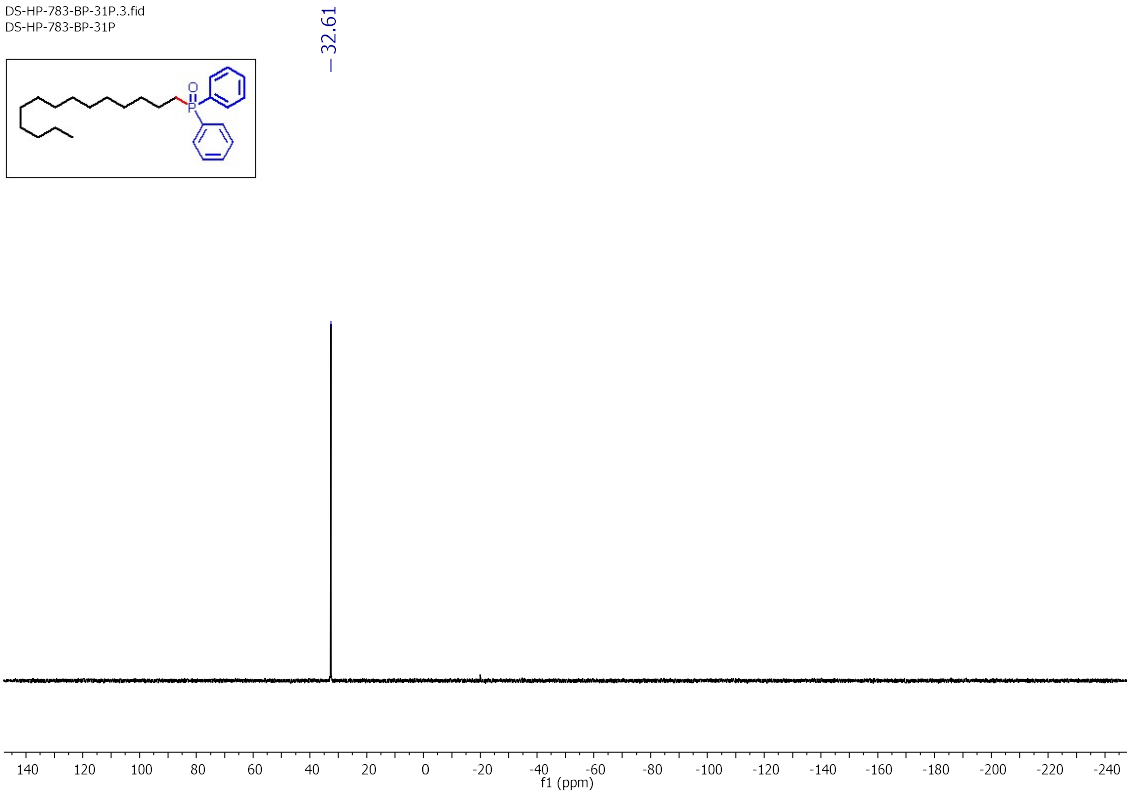
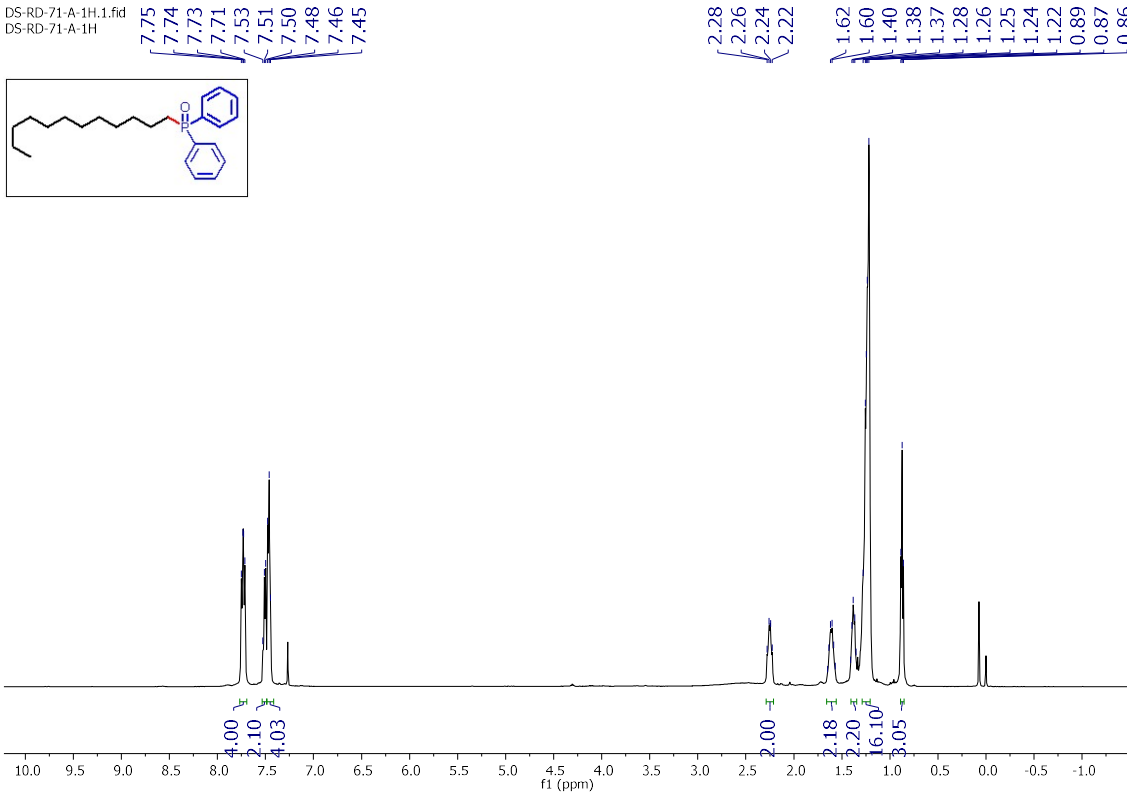


Figure S32. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3af in $CDCl_3$



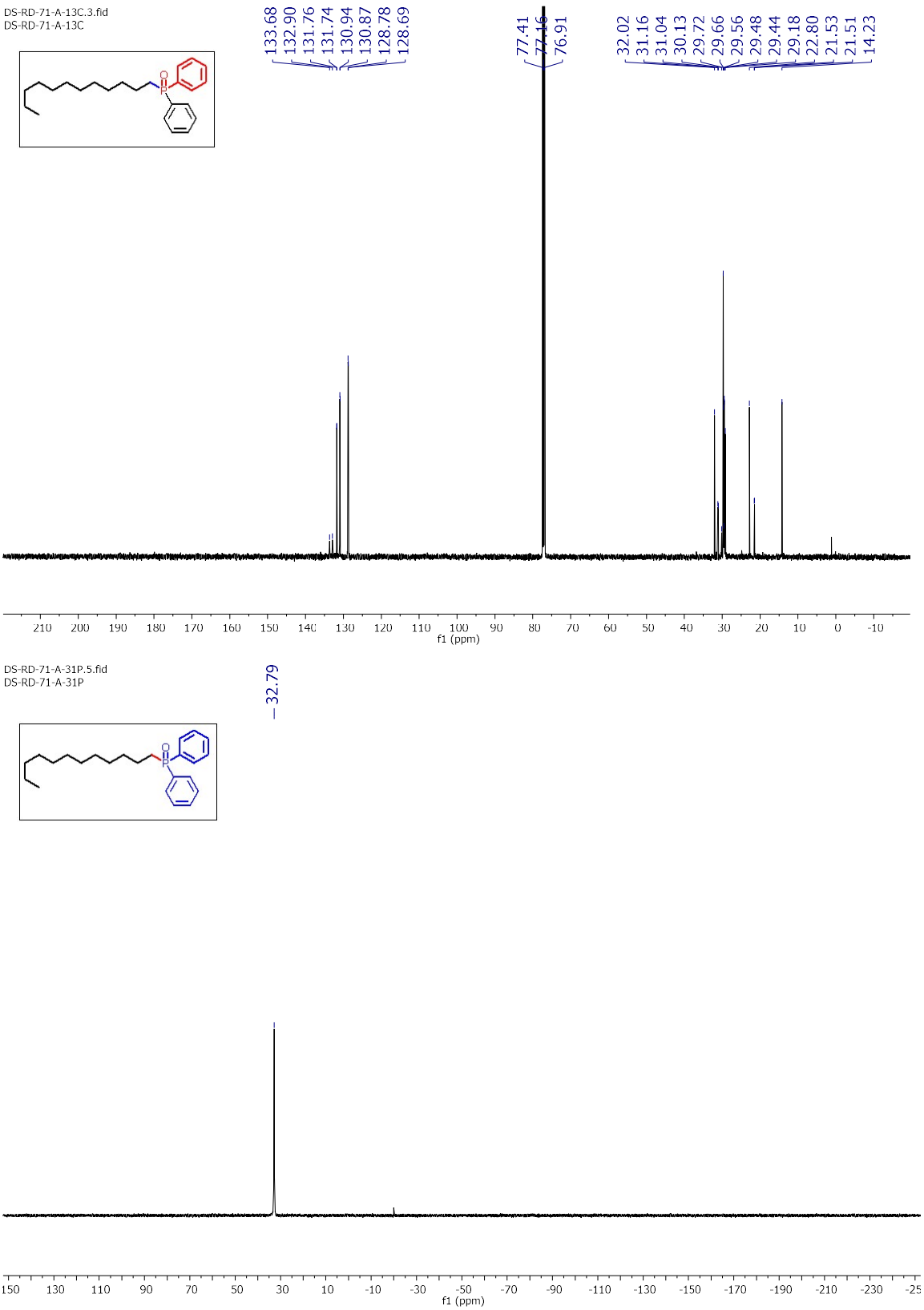
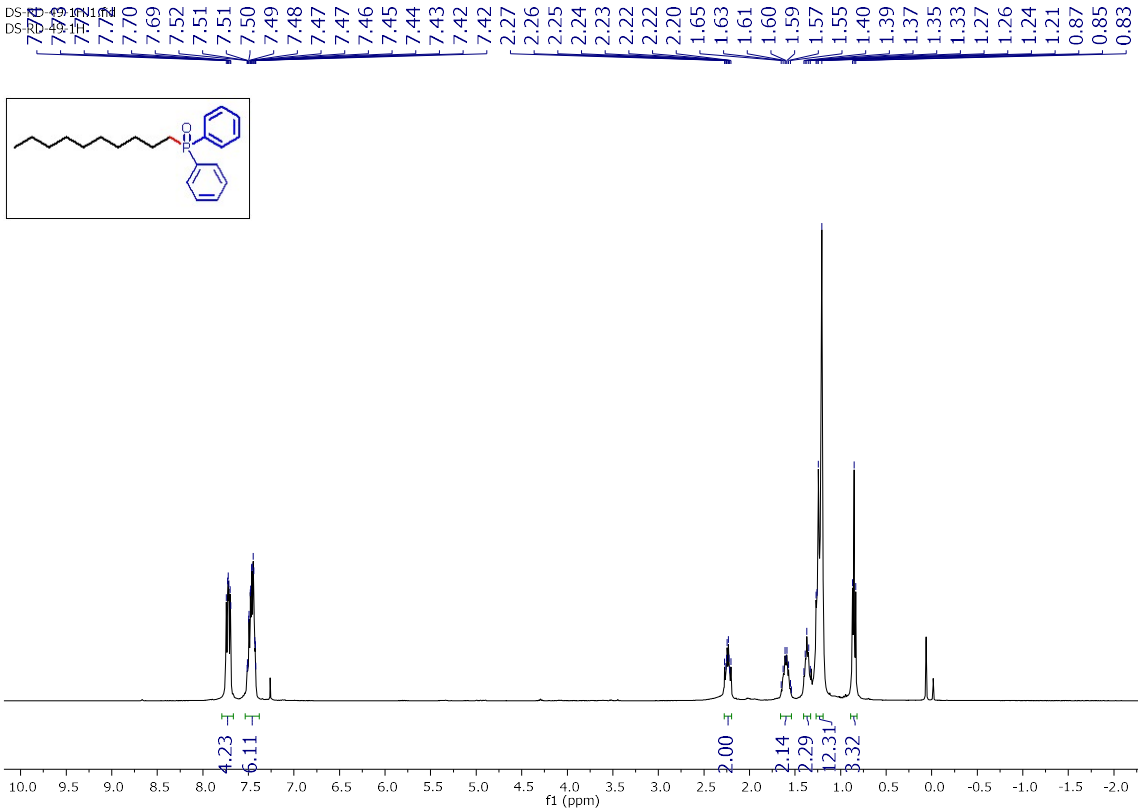
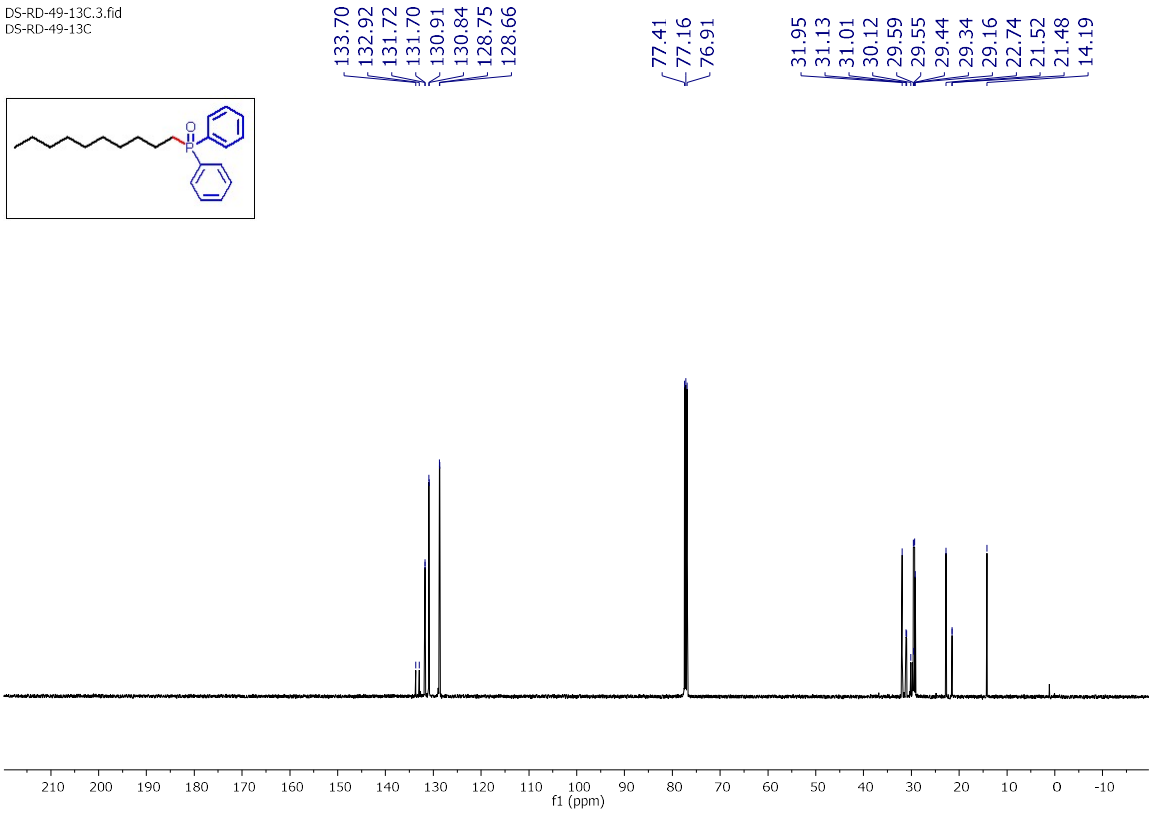


Figure S33. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ag in $CDCl_3$


7.77
7.76
7.72
7.71
7.70
7.69
7.52
7.51
7.51
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.42
7.42
2.27
2.26
2.25
2.24
2.23
2.22
2.22
2.20
1.65
1.63
1.61
1.60
1.59
1.57
1.55
1.40
1.39
1.37
1.35
1.33
1.27
1.26
1.24
1.21
0.87
0.85
0.83
4.23
6.11
2.00
2.14
2.29
12.31
3.32
f1 (ppm)


DS-RD-49-13C.3.fid
DS-RD-49-13C
133.70
132.92
131.72
131.70
130.91
130.84
128.75
128.66
77.41
77.16
76.91
31.95
31.13
31.01
30.12
29.59
29.55
29.44
29.34
29.16
22.74
21.52
21.48
14.19
f1 (ppm)

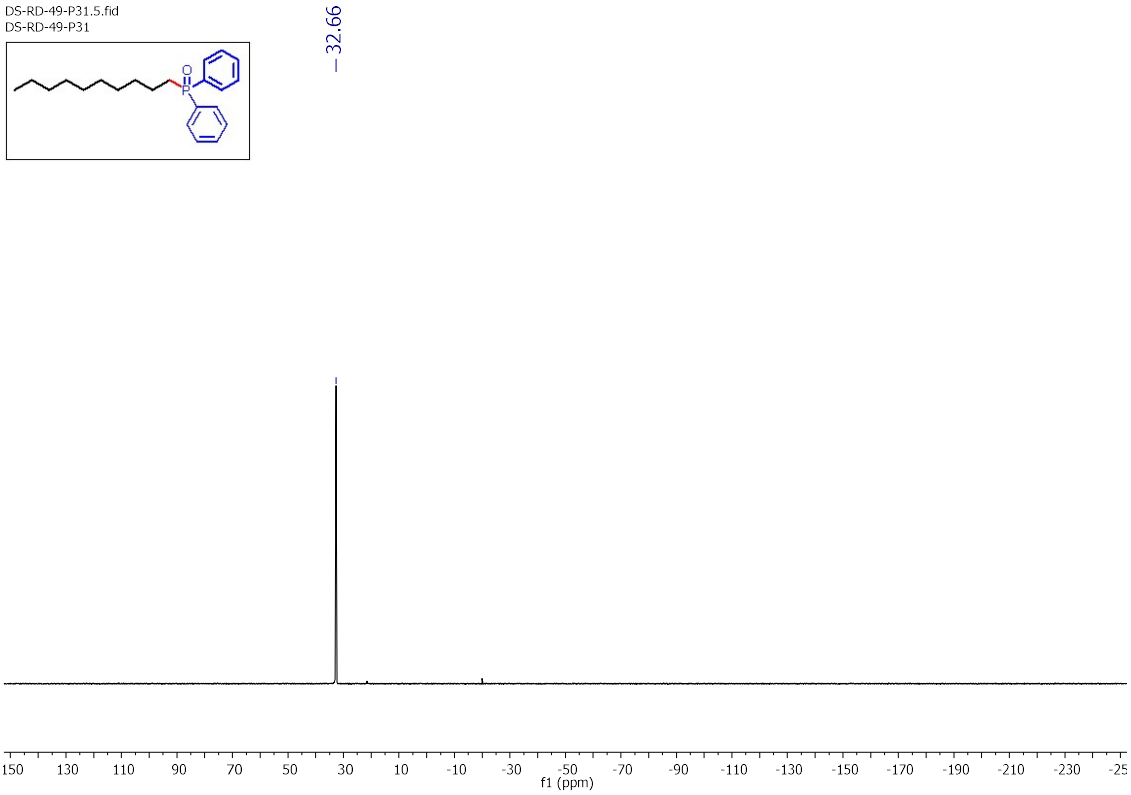
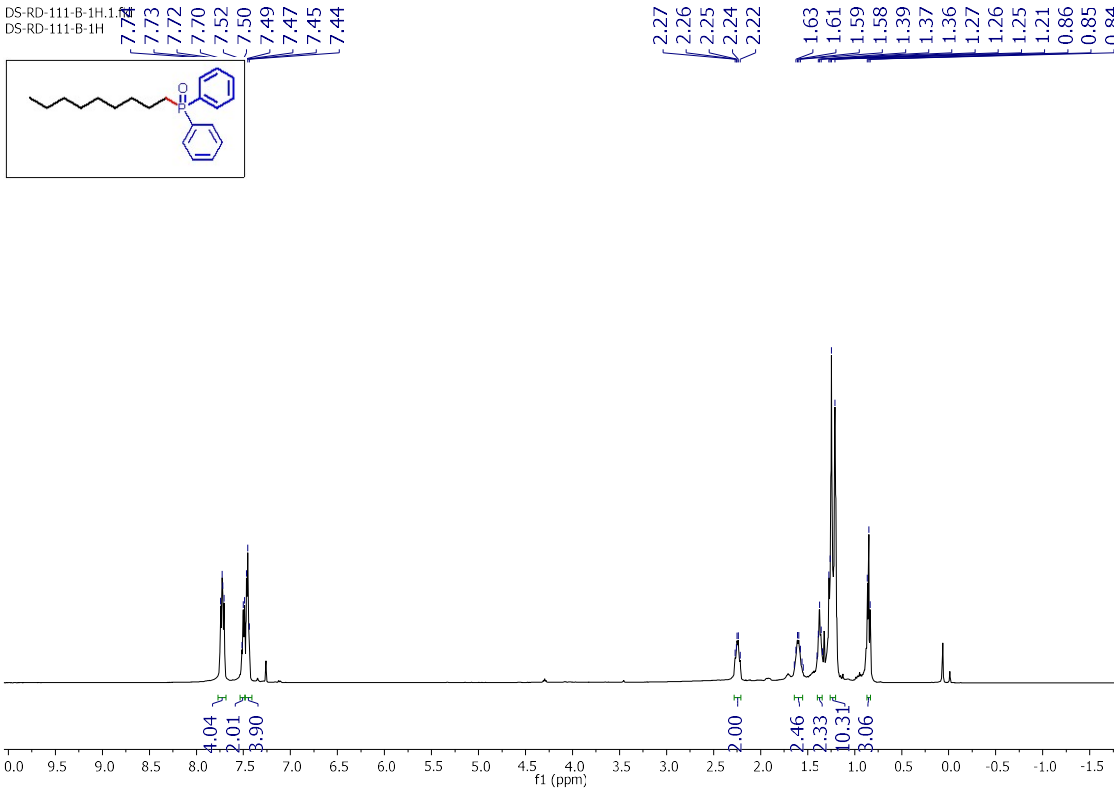


Figure S34. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ah in $CDCl_3$



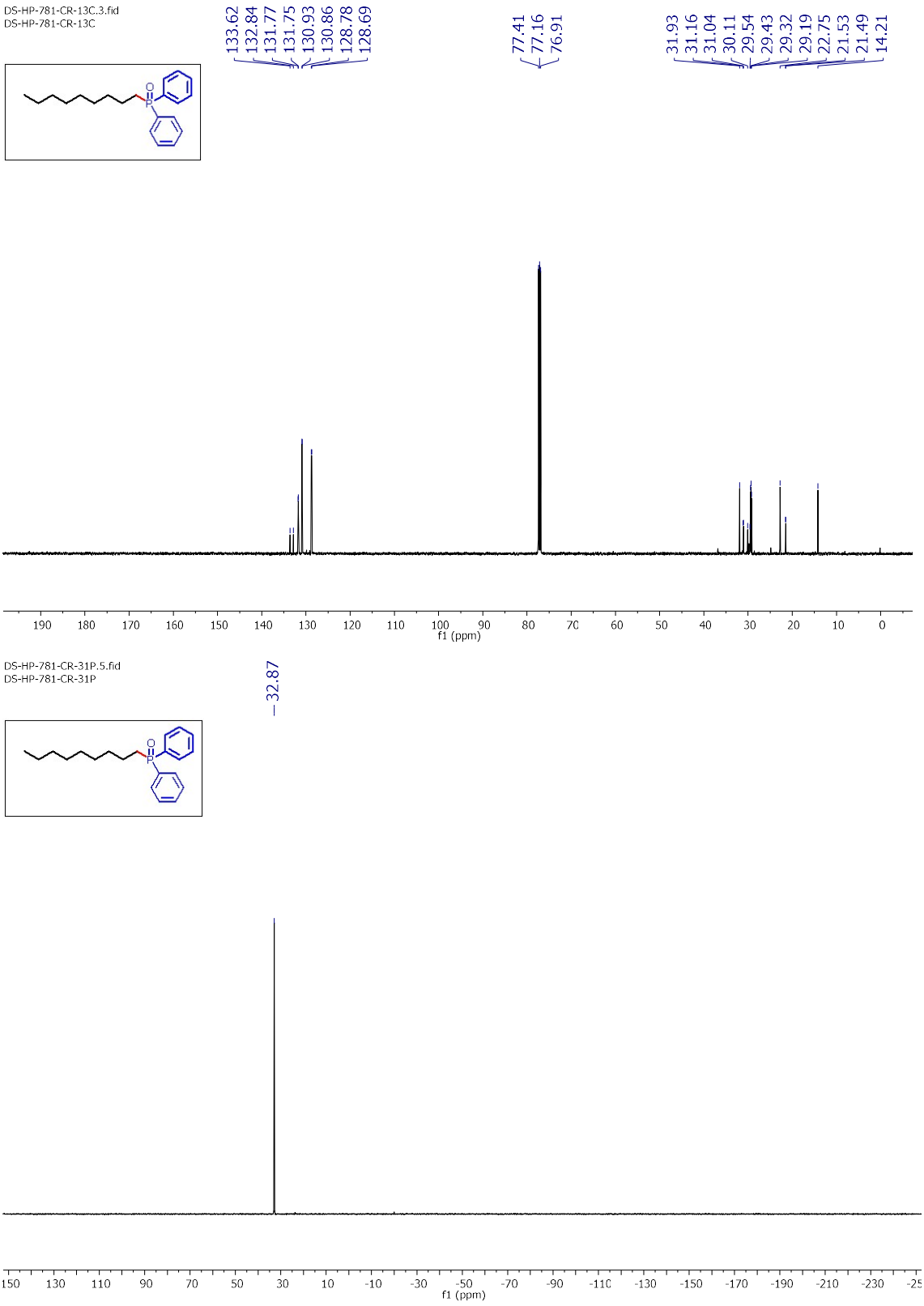
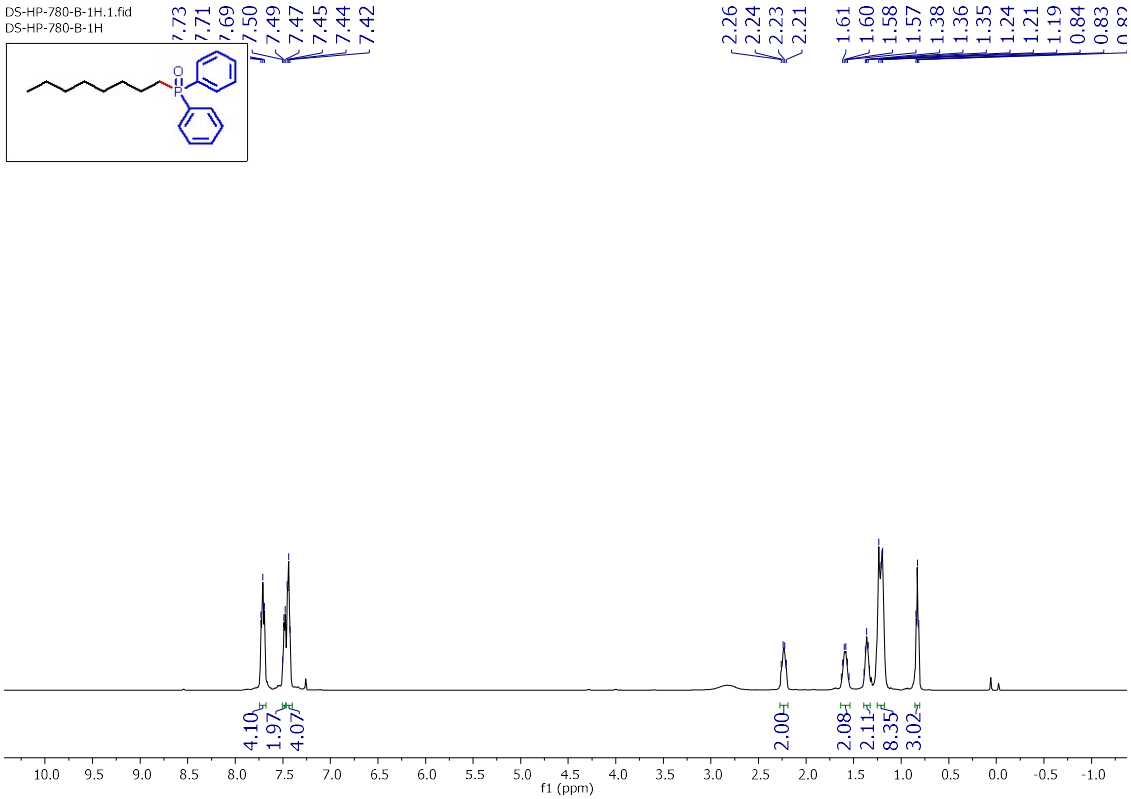
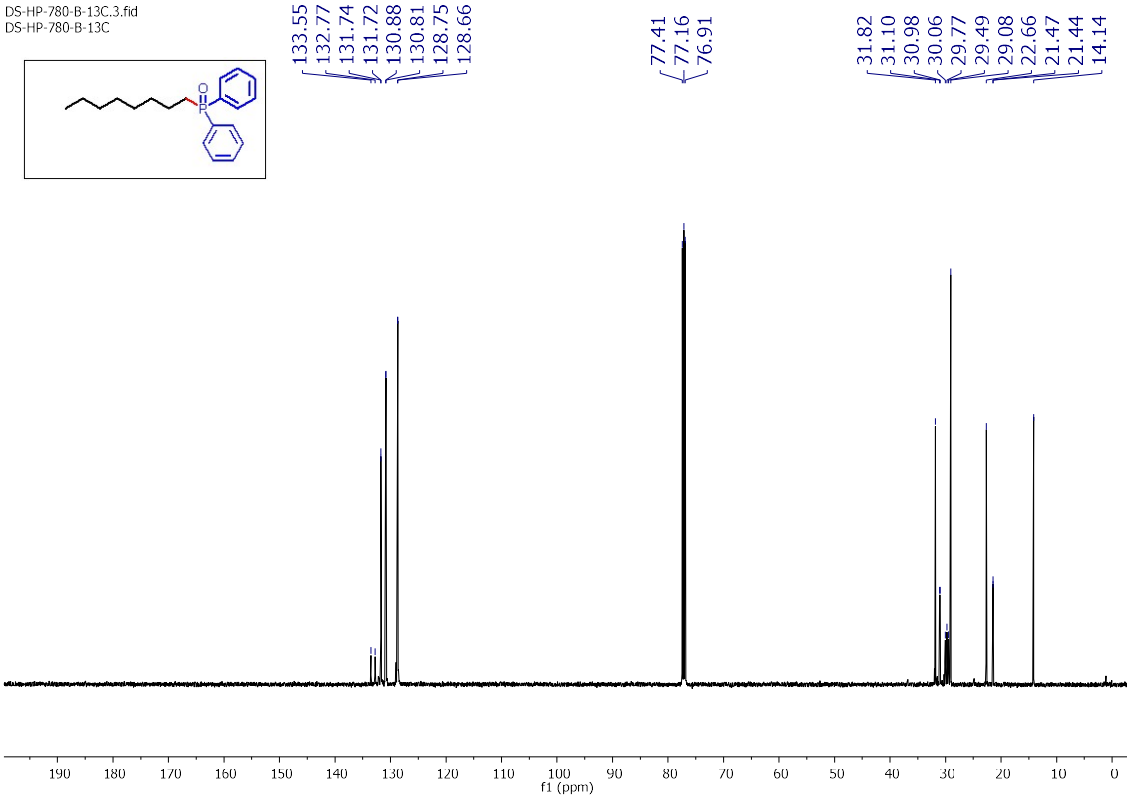


Figure S35. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ai in $CDCl_3$


DS-HP-780-B-1H.1.fid
DS-HP-780-B-1H
7.73
7.71
7.69
7.50
7.49
7.47
7.45
7.44
7.42
2.26
2.24
2.23
2.21
1.61
1.60
1.58
1.57
1.38
1.36
1.35
1.24
1.21
1.19
0.84
0.83
4.10
1.97
4.07
2.00
2.08
2.11
8.35
3.02
f1 (ppm)


DS-HP-780-B-13C.3.fid
DS-HP-780-B-13C
133.55
132.77
131.74
131.72
130.88
130.81
128.75
128.66
77.41
77.16
76.91
31.82
31.10
30.98
30.06
29.77
29.49
29.08
22.66
21.47
21.44
14.14
f1 (ppm)

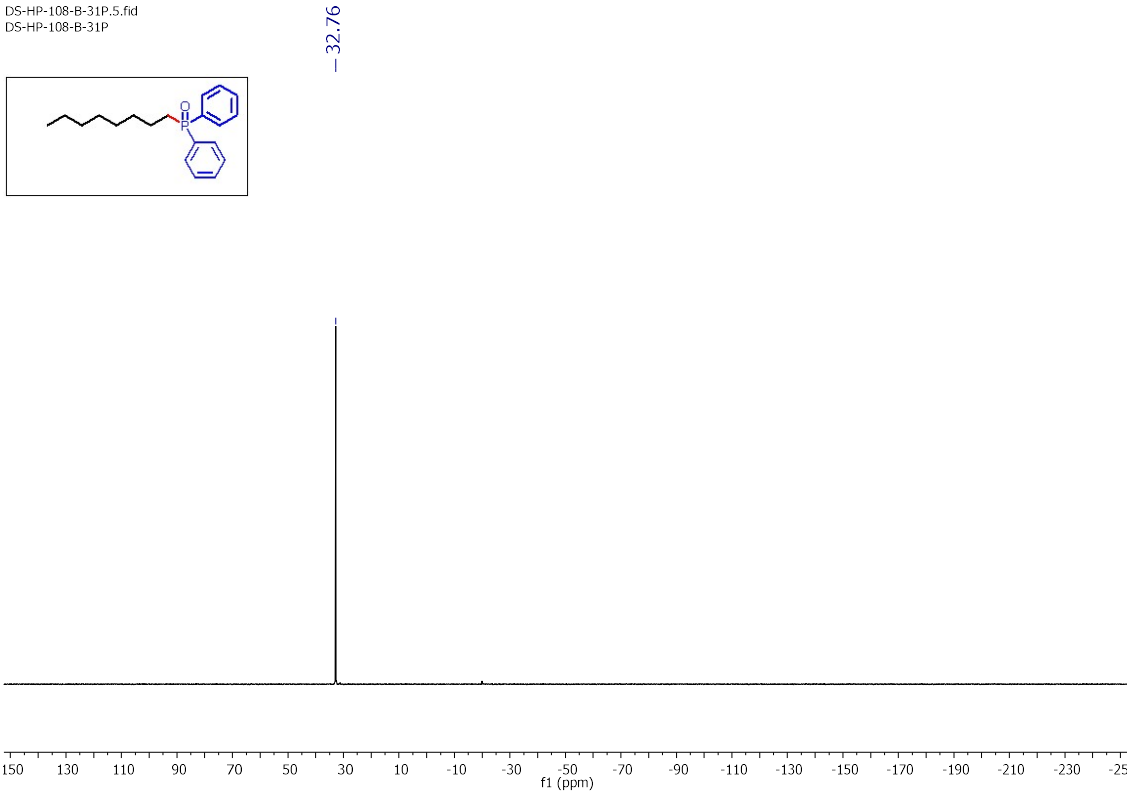
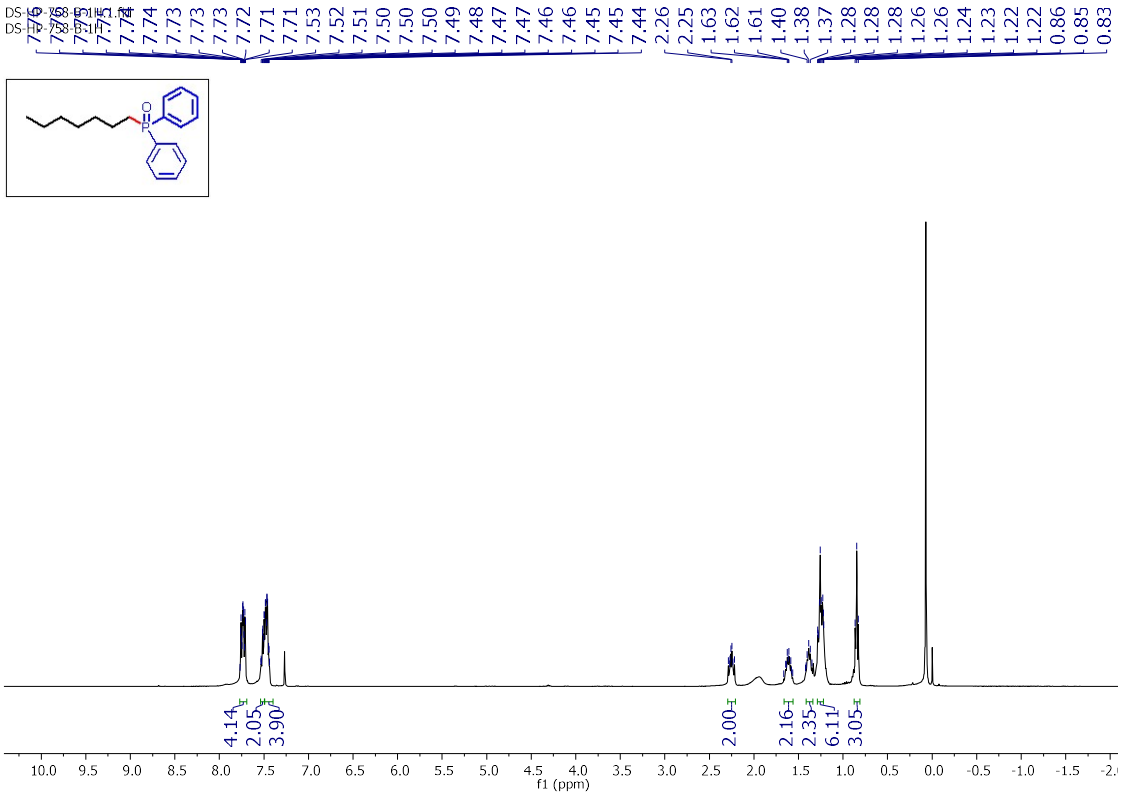


Figure S36. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3aj in $CDCl_3$



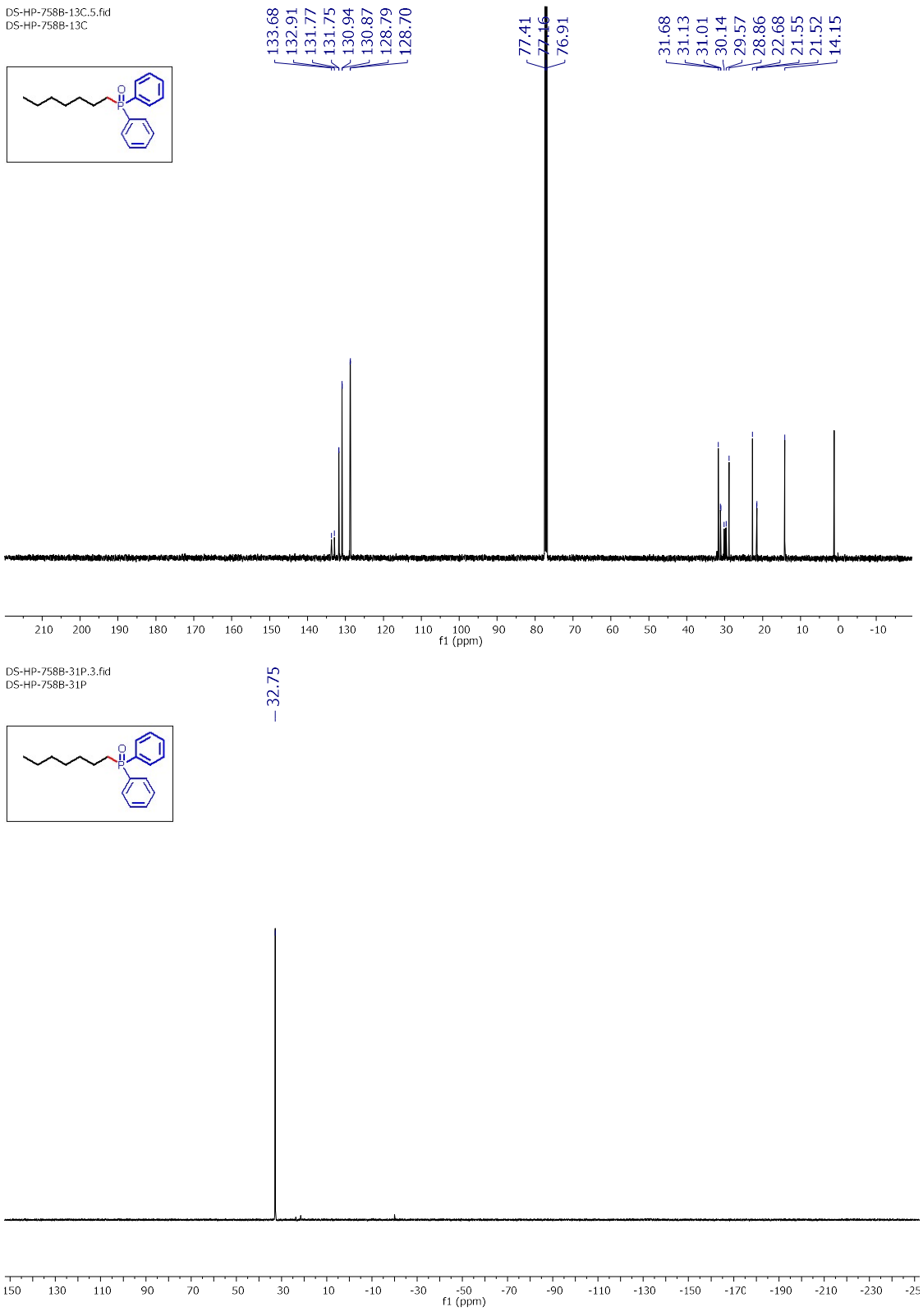
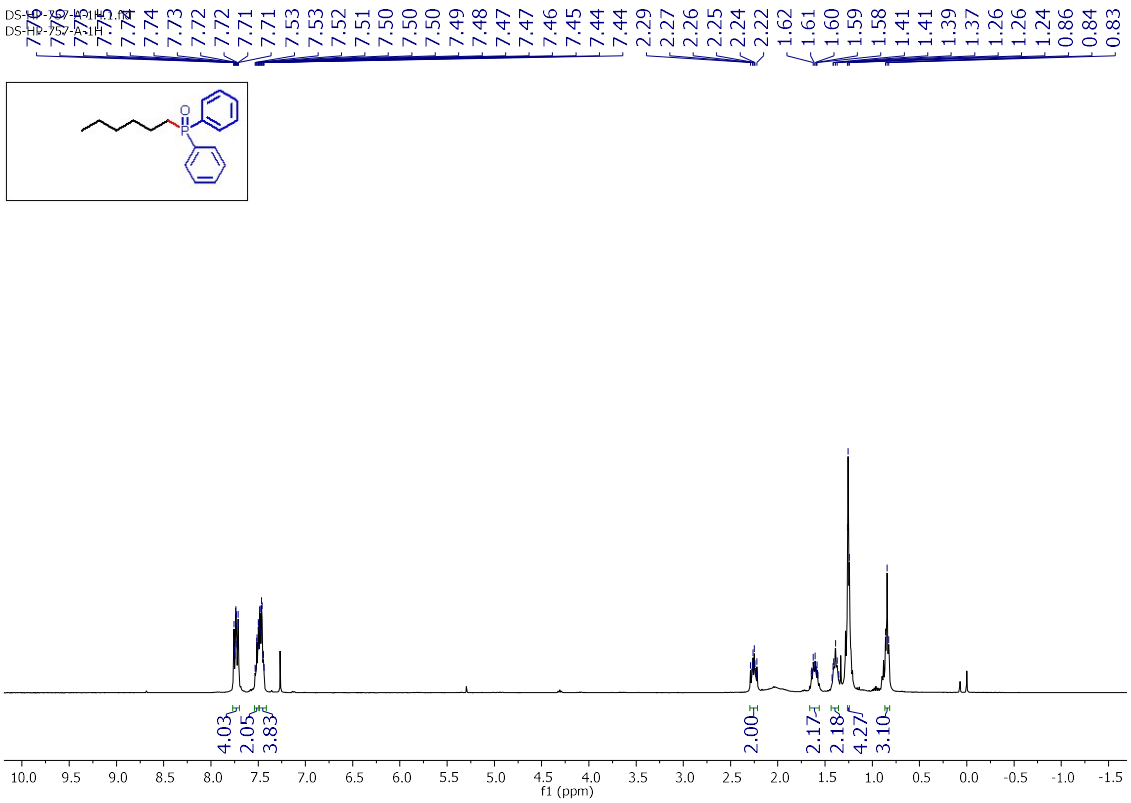
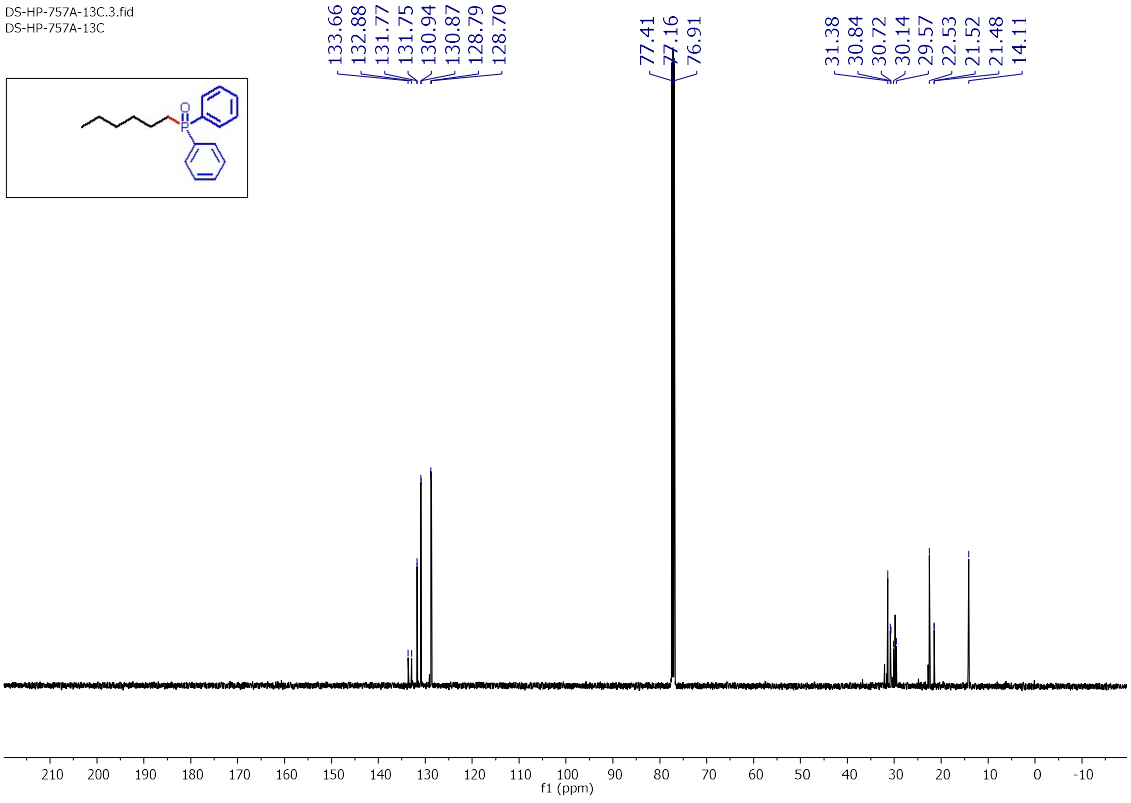


Figure S37. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ak in $CDCl_3$


7.76
7.75
7.74
7.73
7.72
7.71
7.53
7.52
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.44
2.29
2.27
2.26
2.25
2.24
2.22
1.62
1.61
1.60
1.59
1.58
1.41
1.39
1.37
1.26
1.24
0.86
0.84
0.83
4.03
2.05
3.83
2.00
2.17
2.18
4.27
3.10
f1 (ppm)


DS-HP-757A-13C.3.fid
DS-HP-757A-13C
133.66
132.88
131.77
131.75
130.94
130.87
128.79
128.70
77.41
77.16
76.91
31.38
30.84
30.72
30.14
29.57
22.53
21.52
21.48
14.11
f1 (ppm)

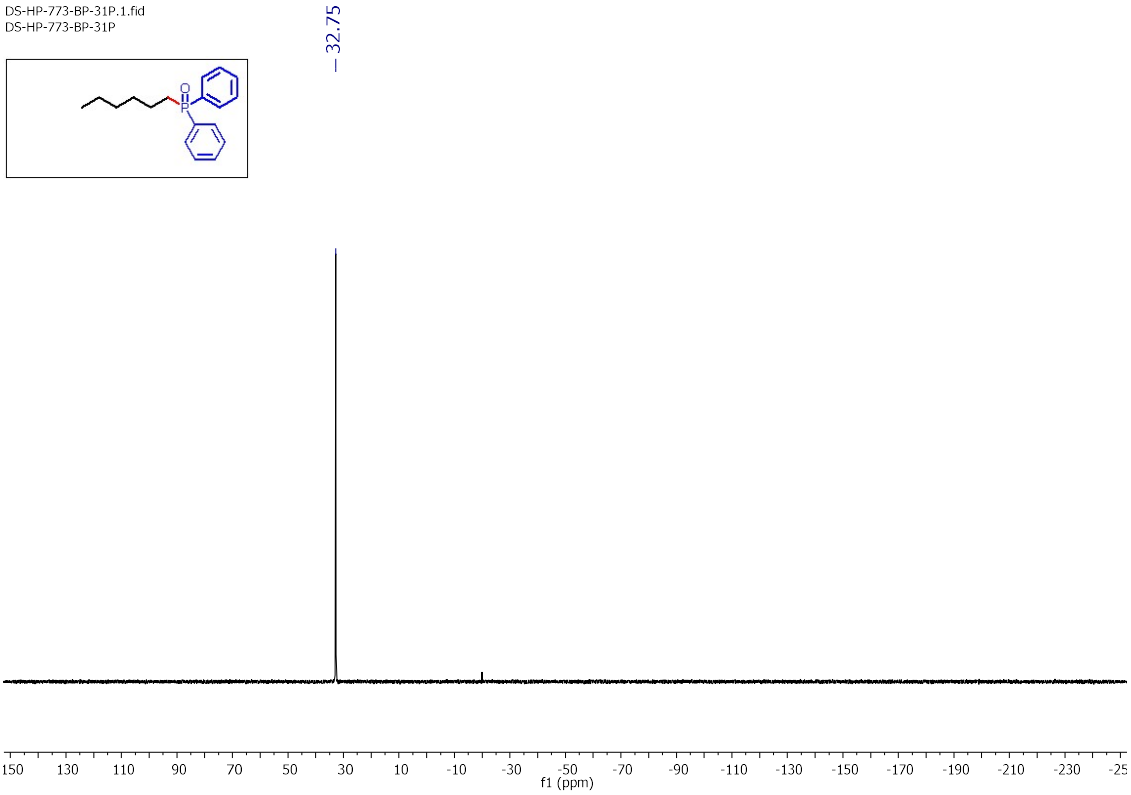
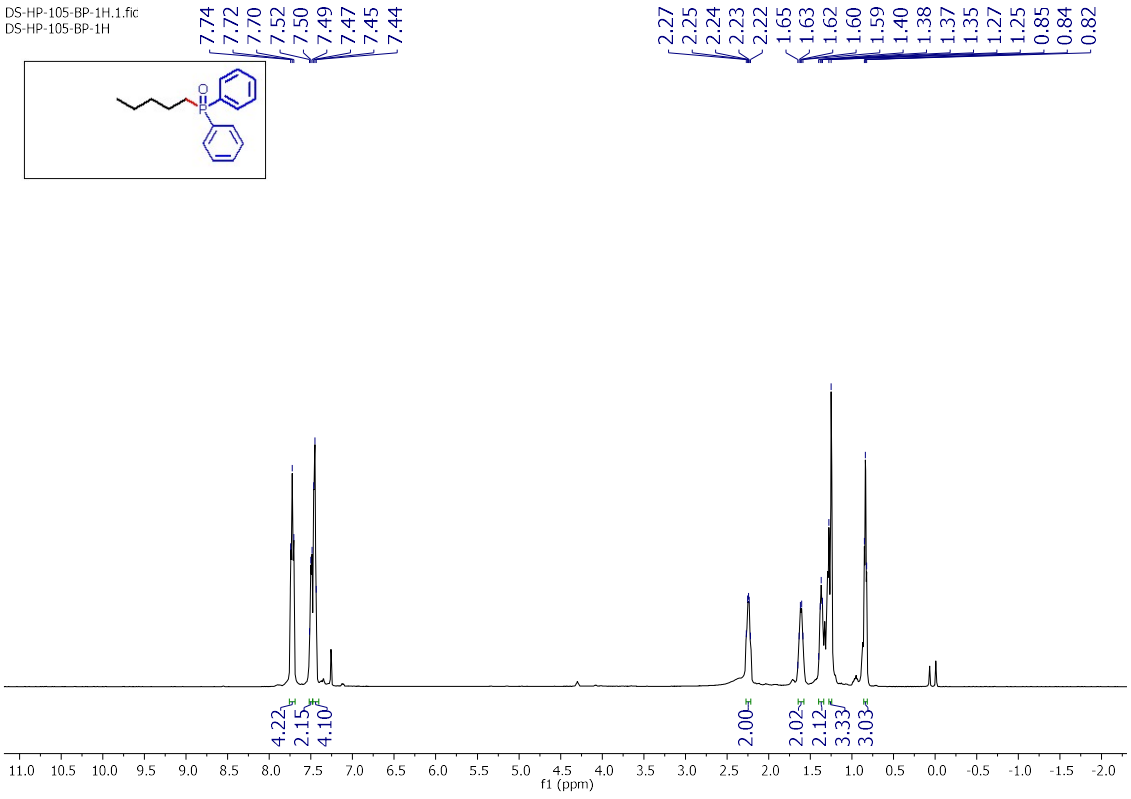


Figure S38. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3al in $CDCl_3$



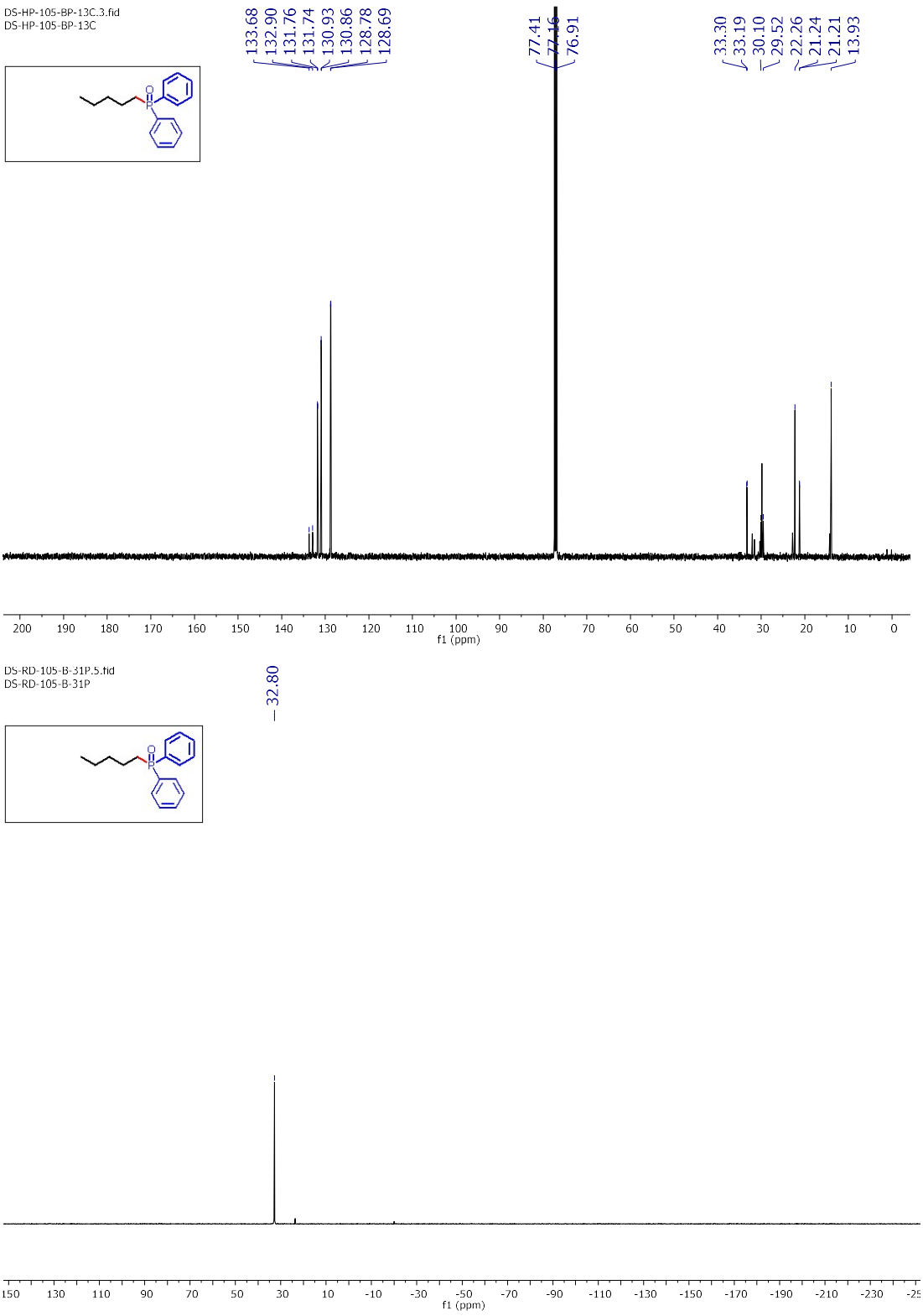
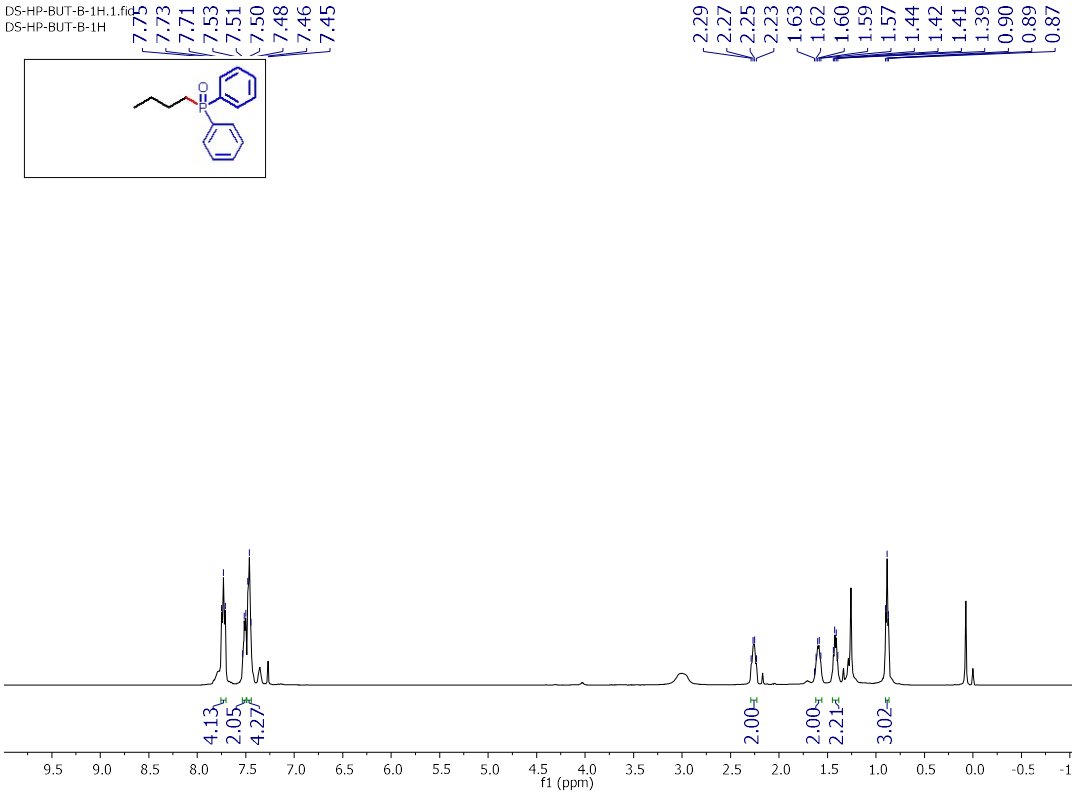


Figure S39. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3am in $CDCl_3$


DS-HP-BUT-B-1H.1.fid
DS-HP-BUT-B-1H
7.75
7.73
7.71
7.53
7.51
7.50
7.48
7.46
7.45
2.29
2.27
2.25
2.23
1.63
1.62
1.60
1.59
1.57
1.44
1.42
1.41
1.39
0.90
0.89
0.87
O
P
4.13
2.05
4.27
2.00
2.00
2.21
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

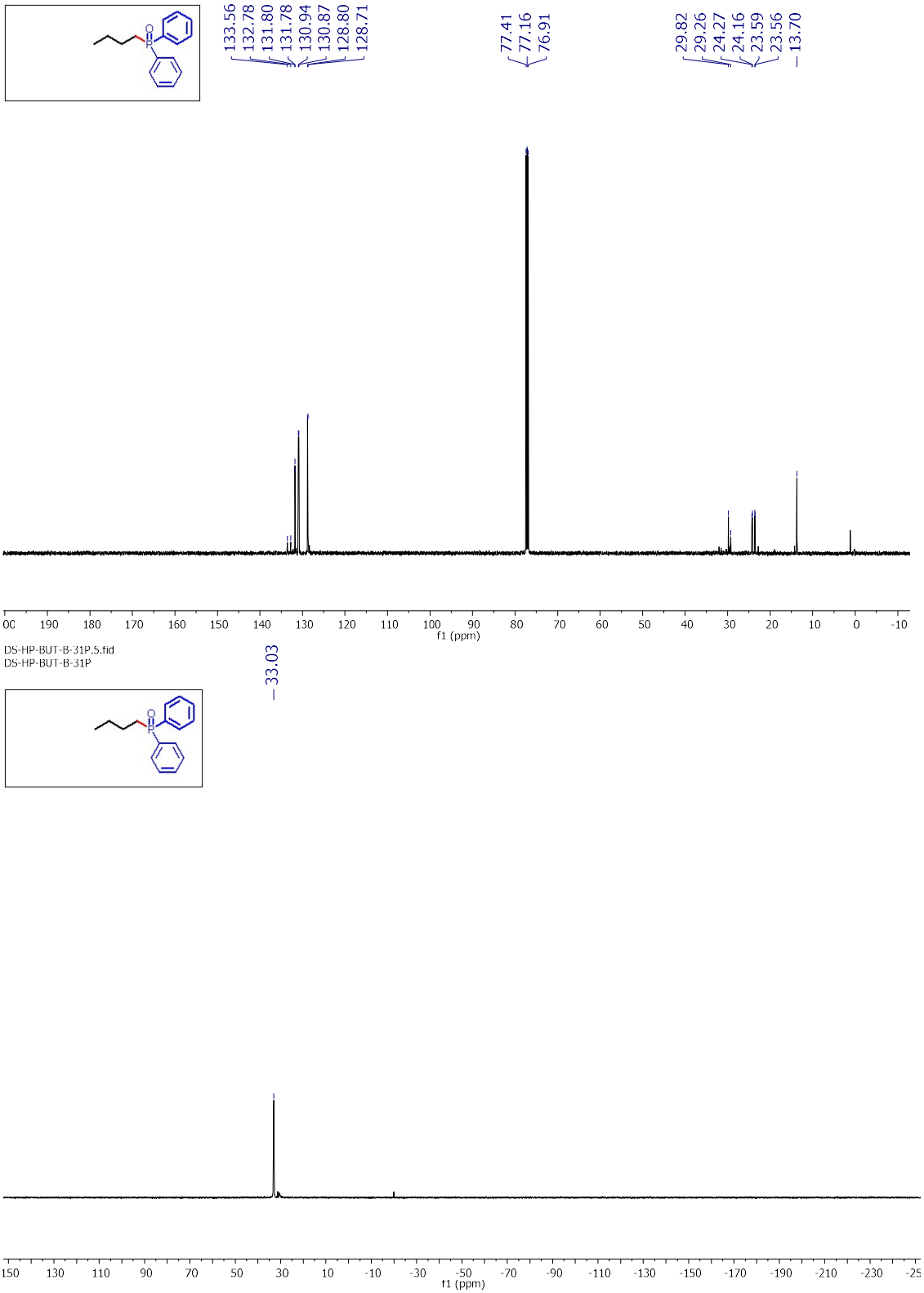
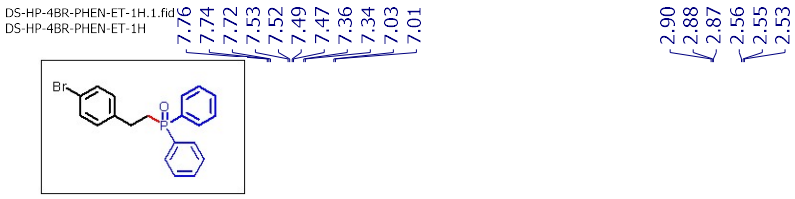
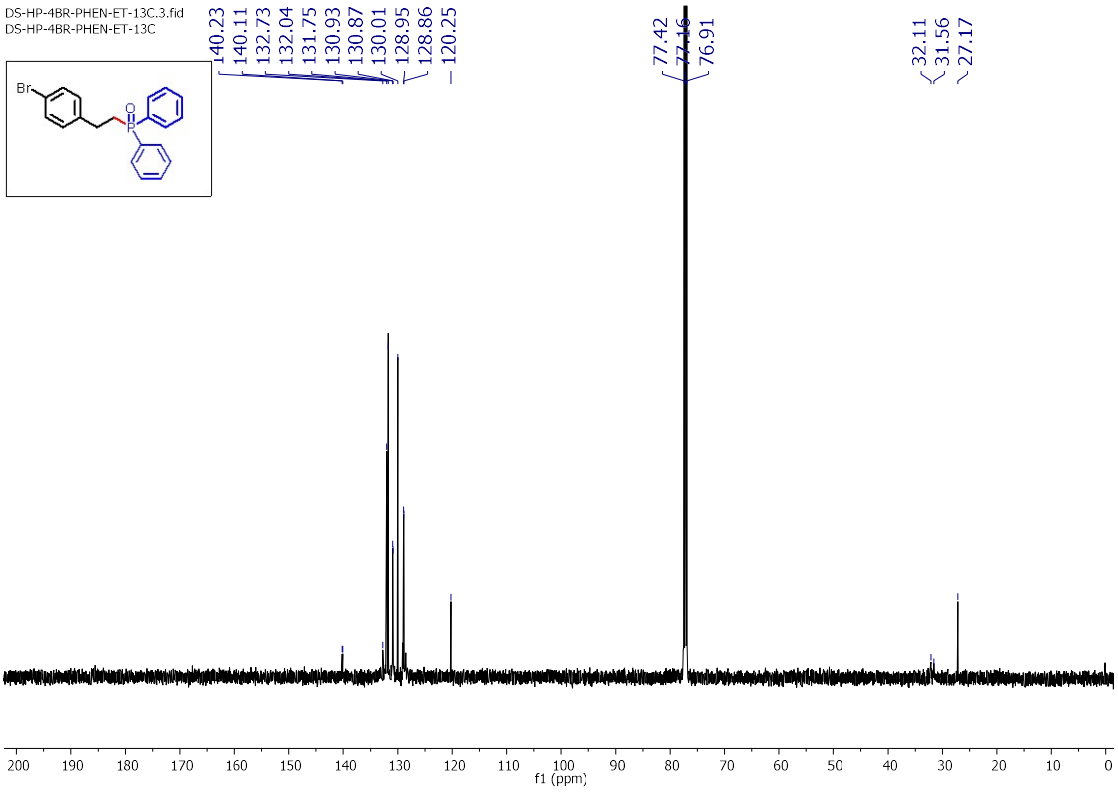


Figure S40. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3an in $CDCl_3$


DS-HP-4BR-PHEN-ET-1H.1.fid
DS-HP-4BR-PHEN-ET-1H
7.76
7.74
7.72
7.53
7.52
7.49
7.47
7.36
7.34
7.03
7.01
2.90
2.88
2.87
2.56
2.55
2.53
Br
O
P
4.12
2.15
4.13
2.20
2.07
2.00
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


DS-HP-4BR-PHEN-ET-13C.3.fid
DS-HP-4BR-PHEN-ET-13C
140.23
140.11
132.73
132.04
131.75
130.93
130.87
130.01
128.95
128.86
120.25
77.42
77.16
76.91
32.11
31.56
27.17
Br
O
P
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

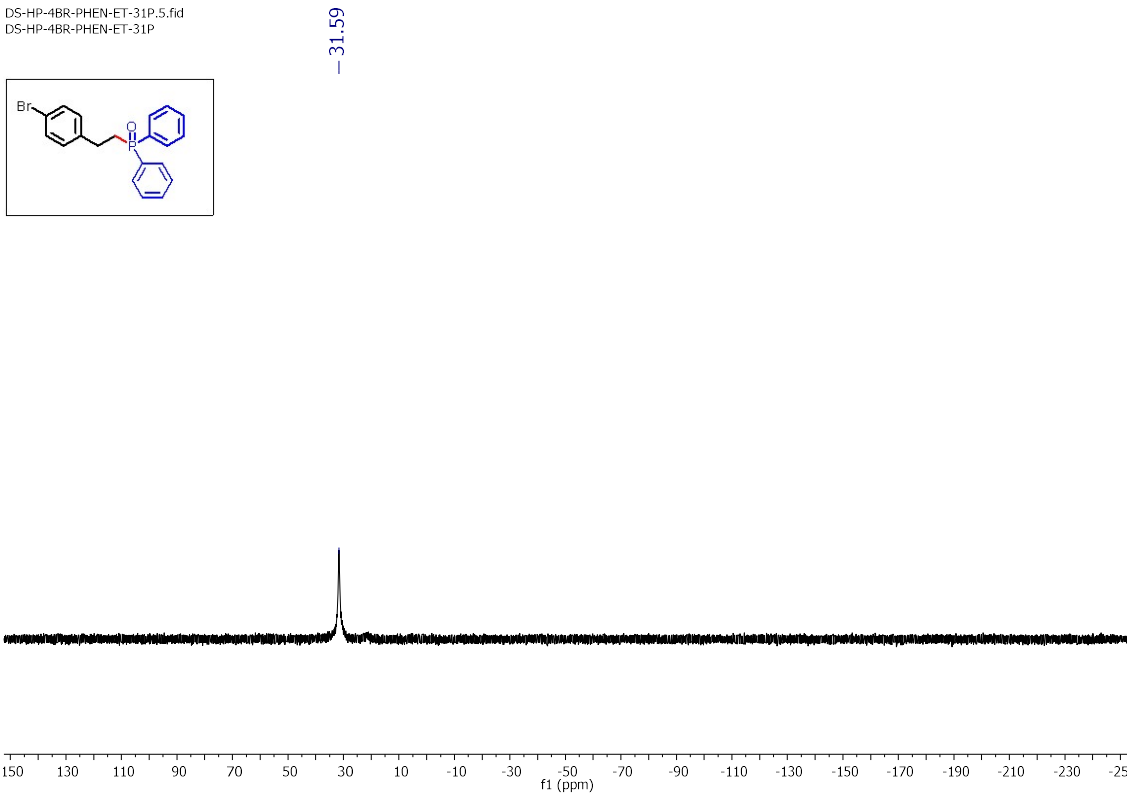
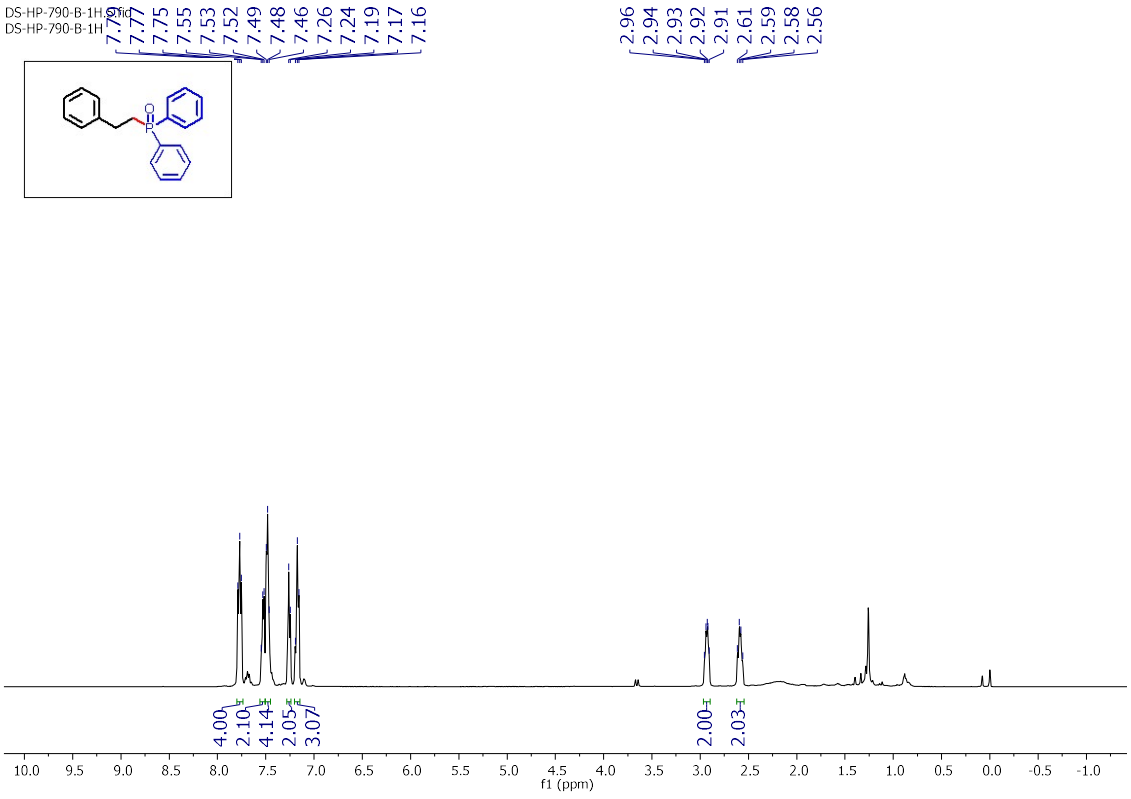


Figure S41. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ao in $CDCl_3$



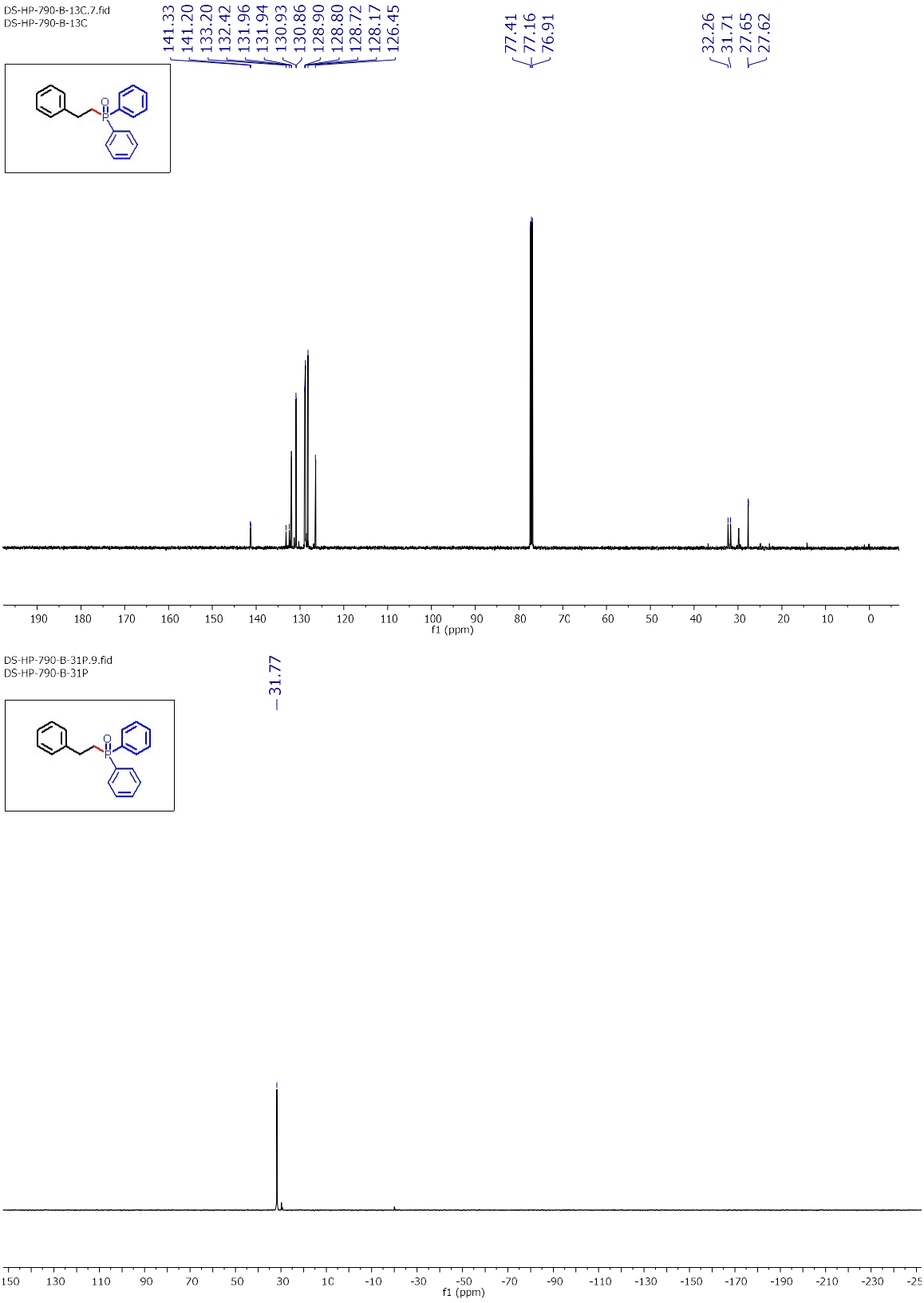
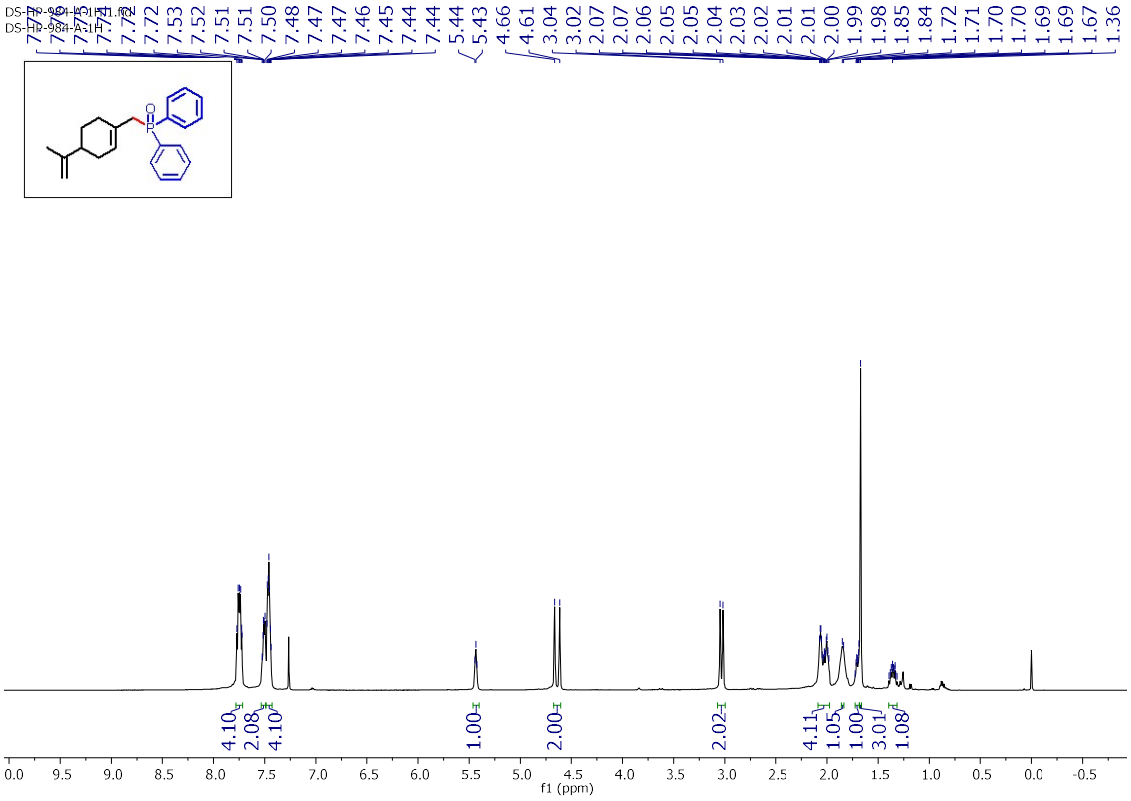
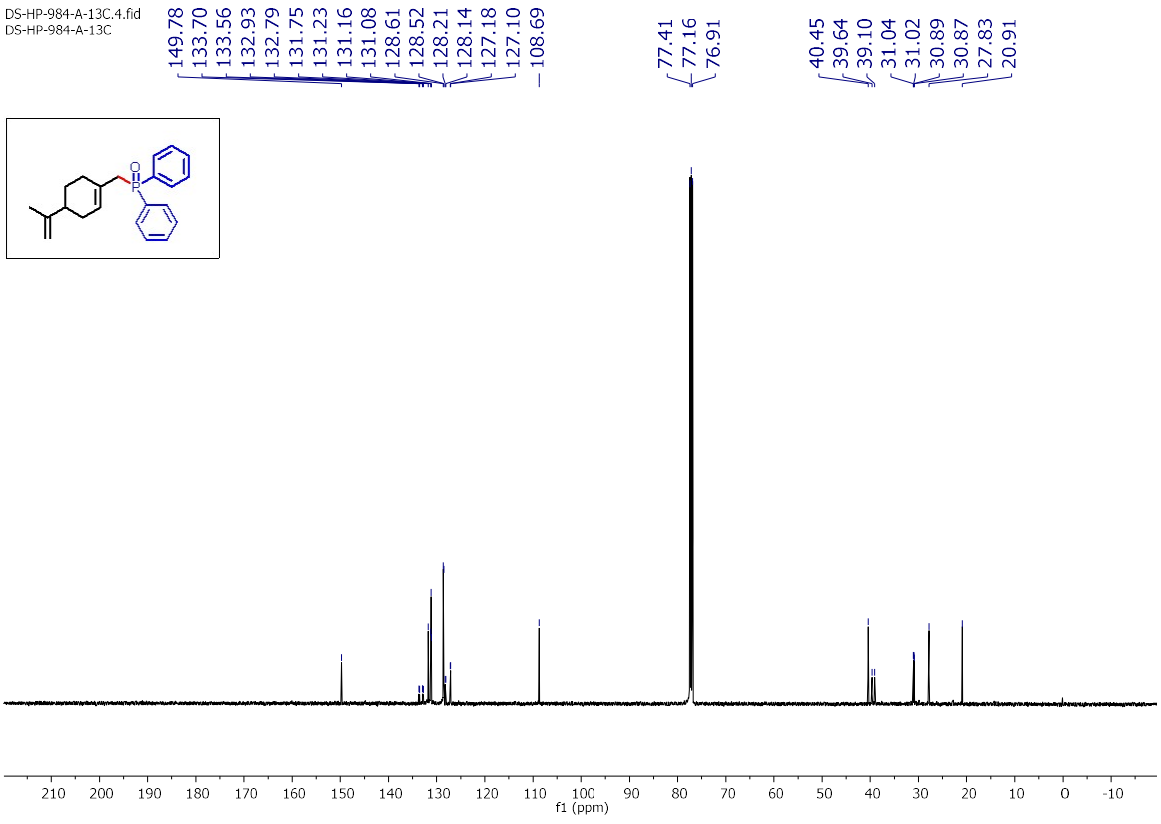


Figure S42. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ap in $CDCl_3$


7.77 7.75 7.74 7.72 7.72 7.53 7.52 7.51 7.51 7.50 7.48 7.47 7.47 7.46 7.45 7.44 7.44 5.44 5.43 4.66 4.61 3.04 3.02 2.07 2.07 2.06 2.05 2.05 2.04 2.03 2.02 2.01 2.01 2.00 1.99 1.98 1.85 1.84 1.72 1.71 1.70 1.70 1.69 1.69 1.67 1.36
4.10 2.08 4.10 1.00 2.00 2.02 4.11 1.05 1.00 3.01 1.08
f1 (ppm)


DS-HP-984-A-13C.4.fid
DS-HP-984-A-13C
149.78 133.70 133.56 132.93 132.79 131.75 131.23 131.16 131.08 128.61 128.52 128.21 128.14 127.18 127.10 108.69 77.41 77.16 76.91 40.45 39.64 39.10 31.04 31.02 30.89 30.87 27.83 20.91
f1 (ppm)

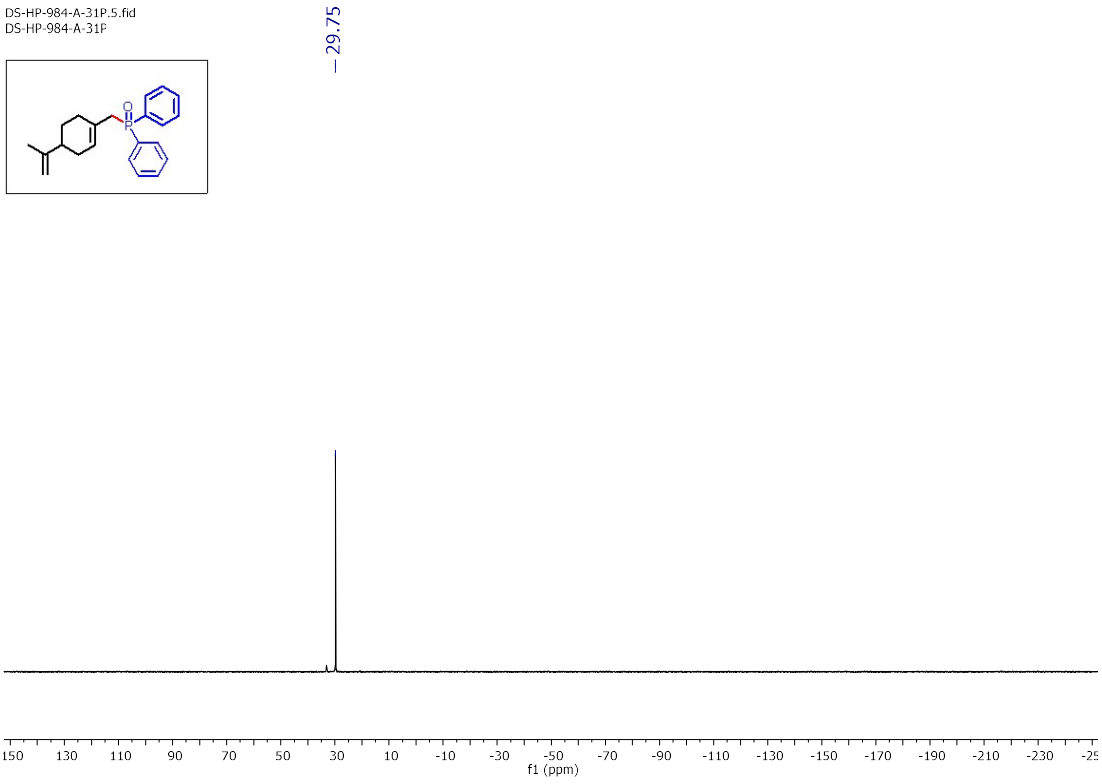
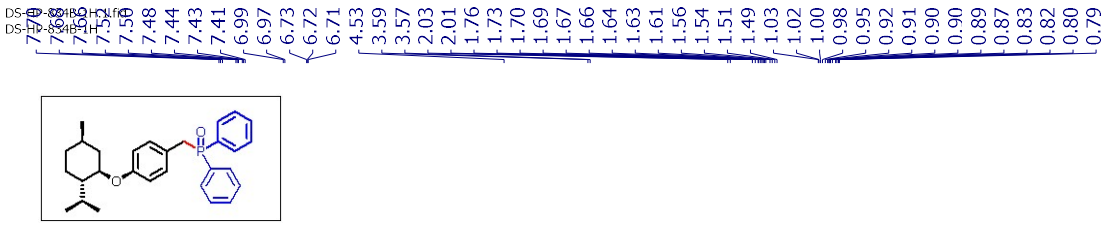
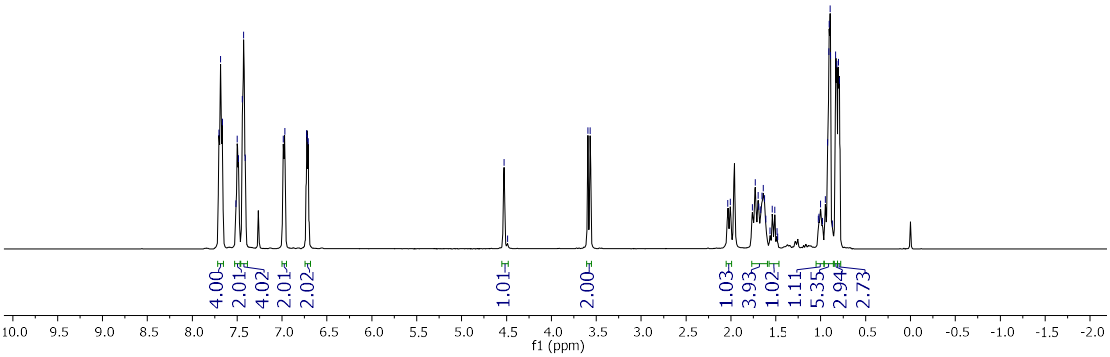
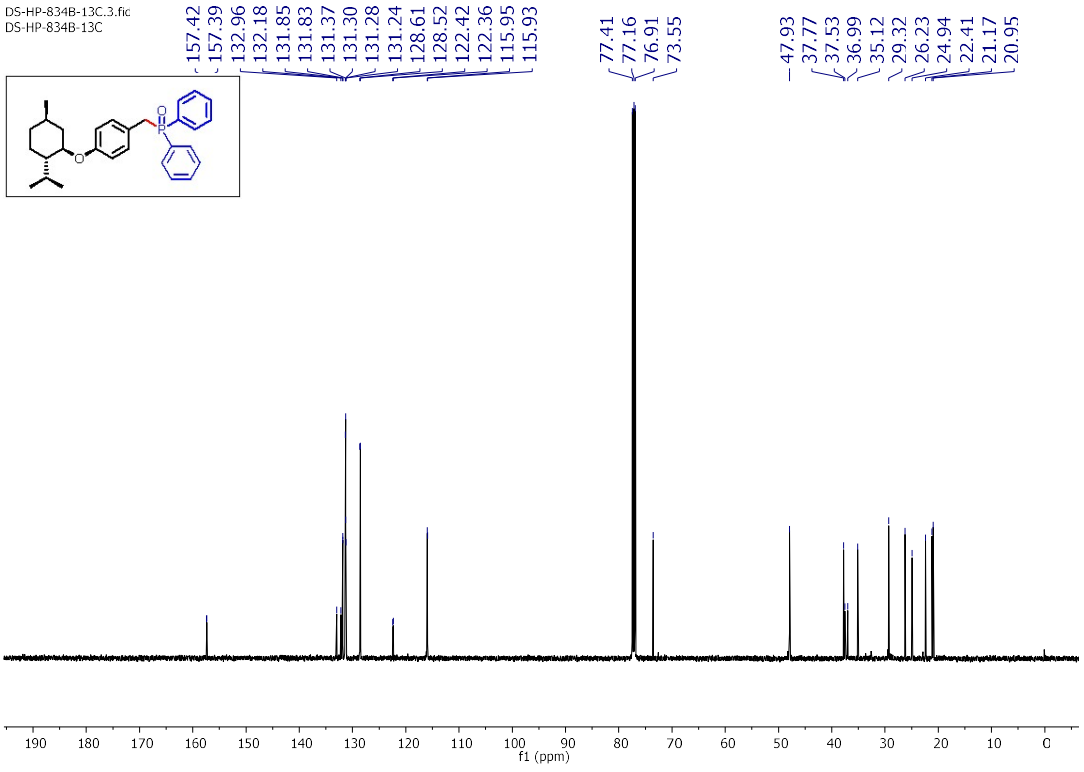


Figure S43. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3aq in $CDCl_3$


7.59
7.48
7.44
7.43
7.41
6.99
6.97
6.73
6.72
6.71
4.53
3.59
3.57
2.03
2.01
1.76
1.73
1.70
1.69
1.67
1.66
1.64
1.63
1.61
1.56
1.54
1.51
1.49
1.03
1.02
1.00
0.98
0.95
0.92
0.91
0.90
0.90
0.89
0.87
0.83
0.82
0.80
0.79


4.00
2.01
4.02
2.01
2.02
1.01
2.00
1.03
3.93
1.02
1.11
5.35
2.94
2.73
f1 (ppm)


DS-HP-834B-13C.3.fic
DS-HP-834B-13C
157.42
157.39
132.96
132.18
131.85
131.83
131.37
131.30
131.28
131.24
128.61
128.52
122.42
122.36
115.95
115.93
77.41
77.16
76.91
73.55
47.93
37.77
37.53
36.99
35.12
29.32
26.23
24.94
22.41
21.17
20.95
f1 (ppm)

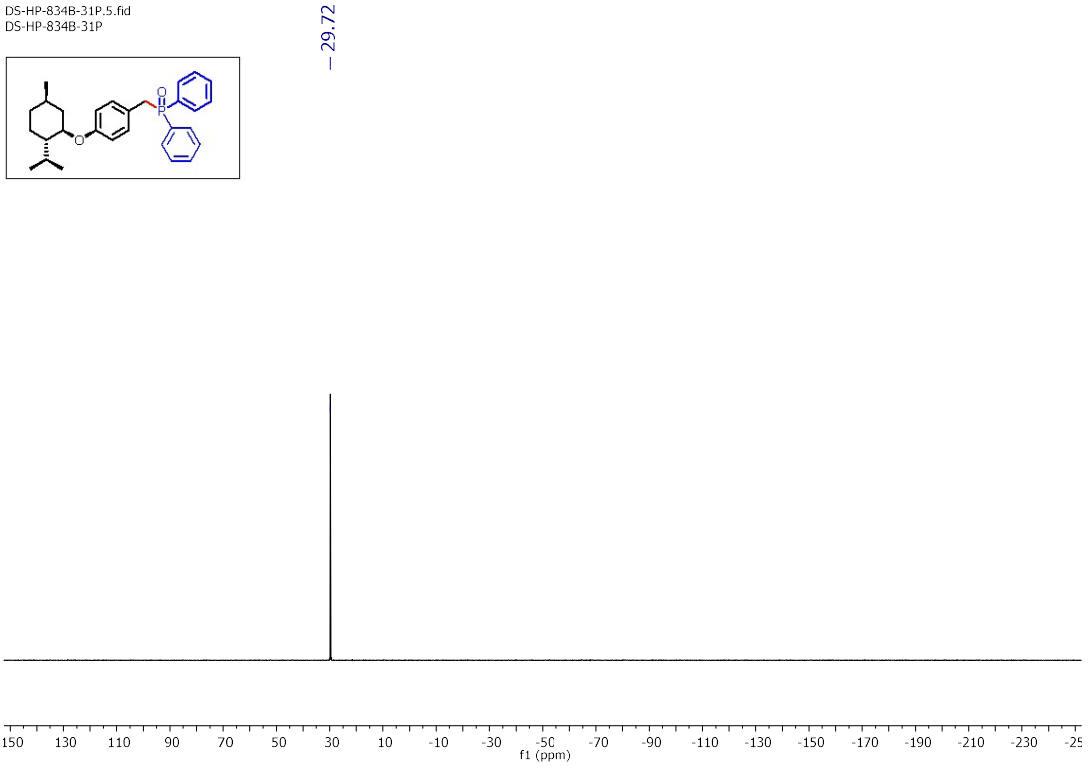
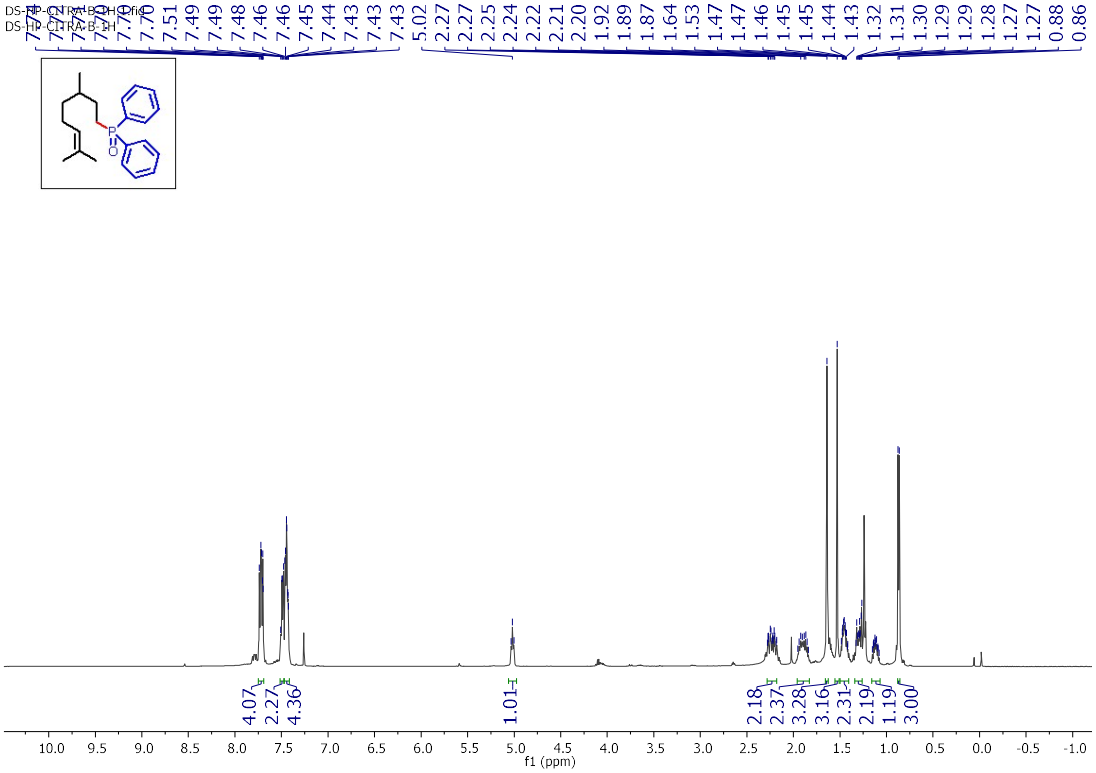


Figure S44. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ar in $CDCl_3$



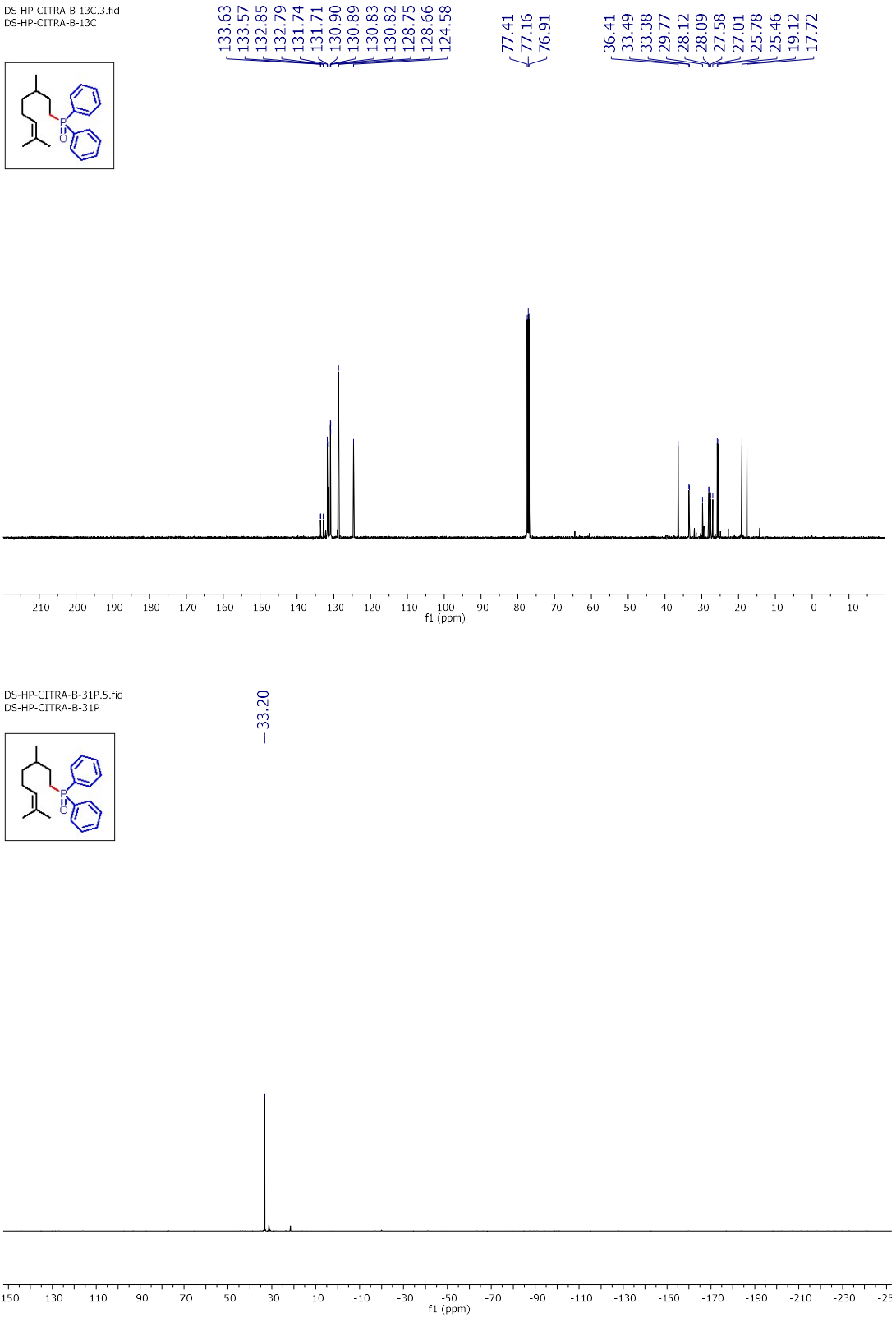
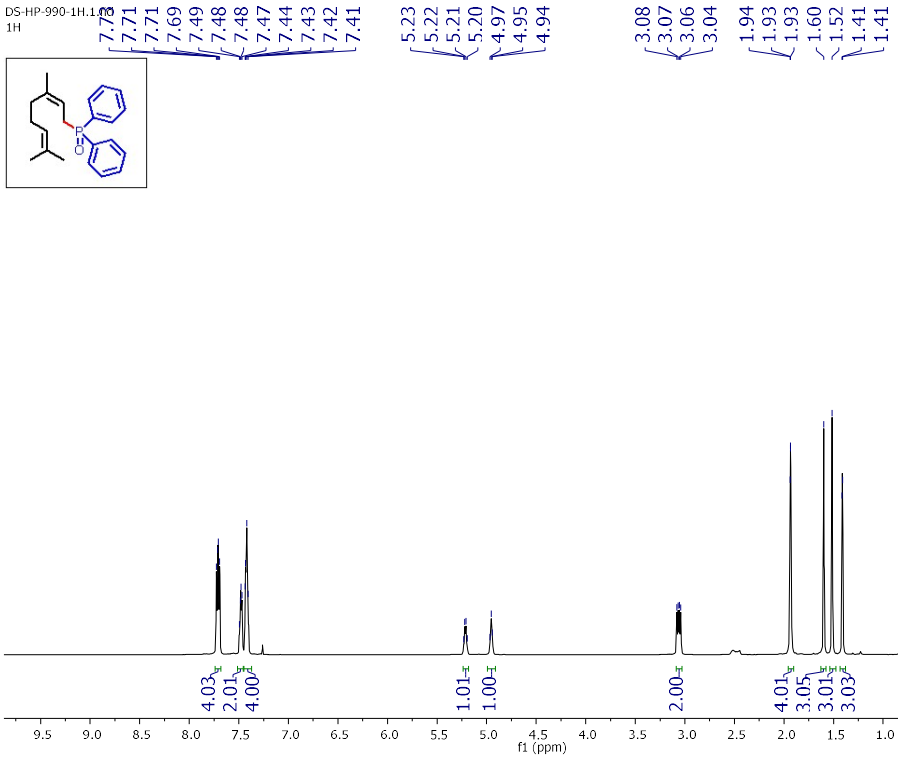
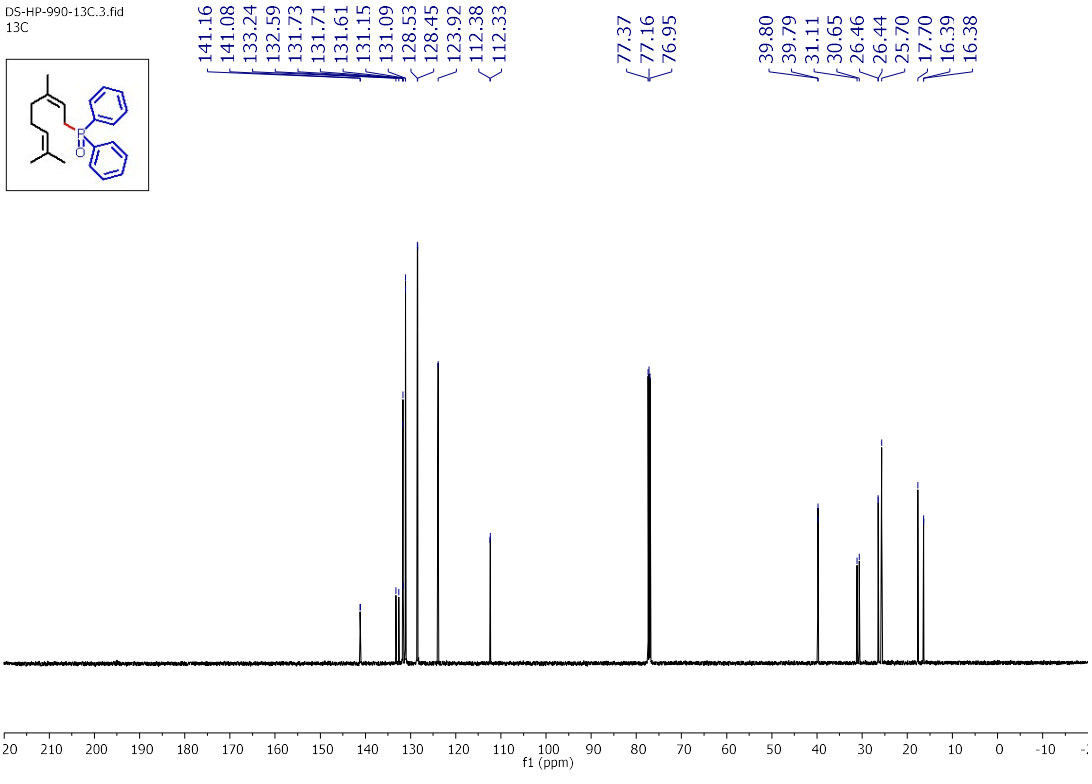


Figure S45. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3as in $CDCl_3$


DS-HP-990-1H.1.fid
1H
7.73
7.71
7.71
7.69
7.49
7.48
7.48
7.47
7.44
7.43
7.42
7.41
5.23
5.22
5.21
5.20
4.97
4.95
4.94
3.08
3.07
3.06
3.04
1.94
1.93
1.93
1.60
1.52
1.41
1.41
4.03
2.01
4.00
1.01
1.00
2.00
4.01
3.05
3.01
3.03
f1 (ppm)


DS-HP-990-13C.3.fid
13C
141.16
141.08
133.24
132.59
131.73
131.71
131.61
131.15
131.09
128.53
128.45
123.92
112.38
112.33
77.37
77.16
76.95
39.80
39.79
31.11
30.65
26.46
26.44
25.70
17.70
16.39
16.38
f1 (ppm)

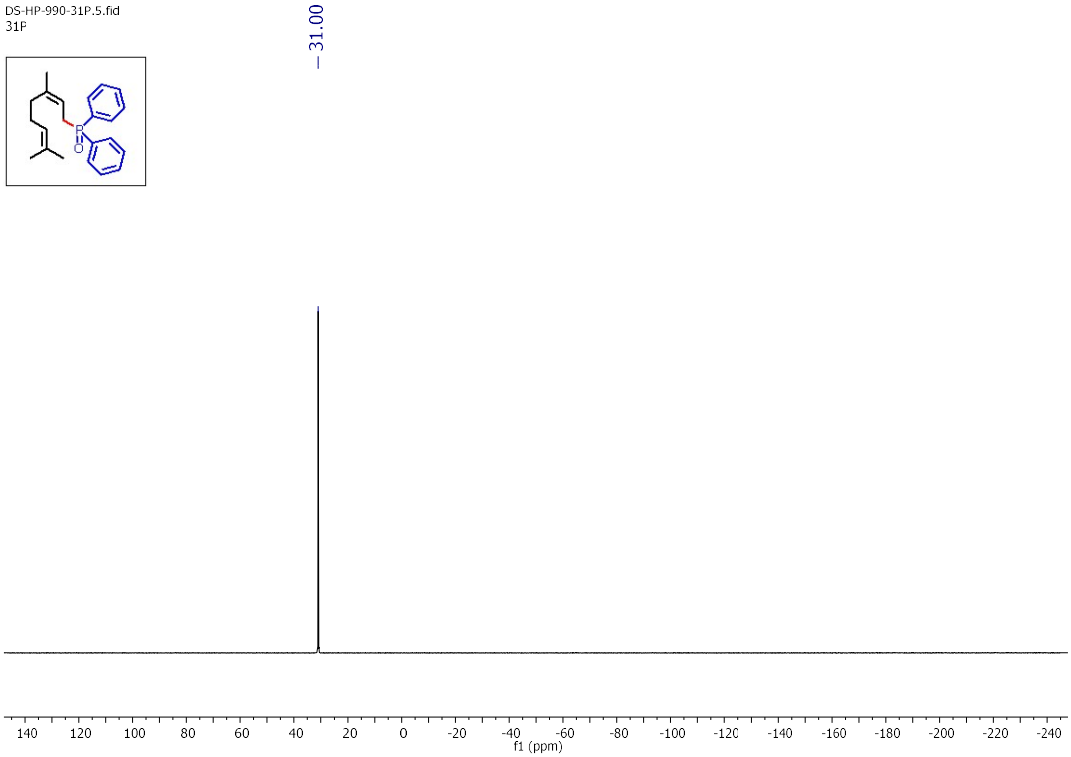
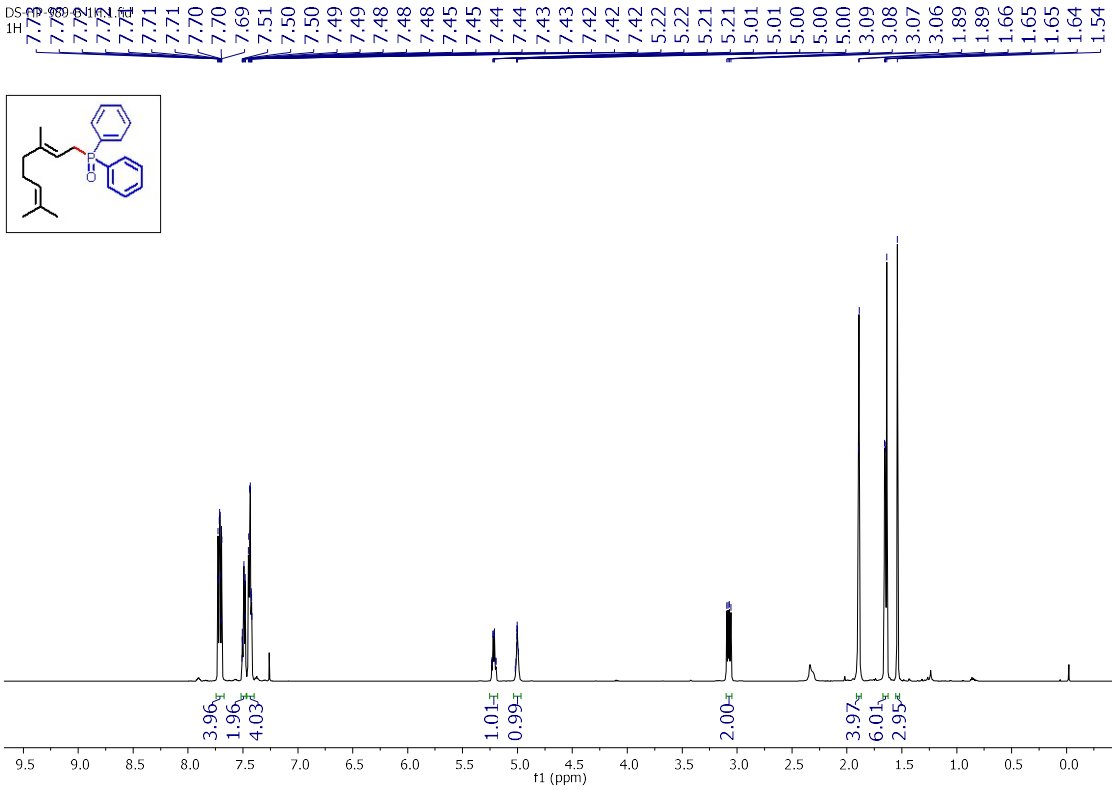


Figure S46. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3at in $CDCl_3$



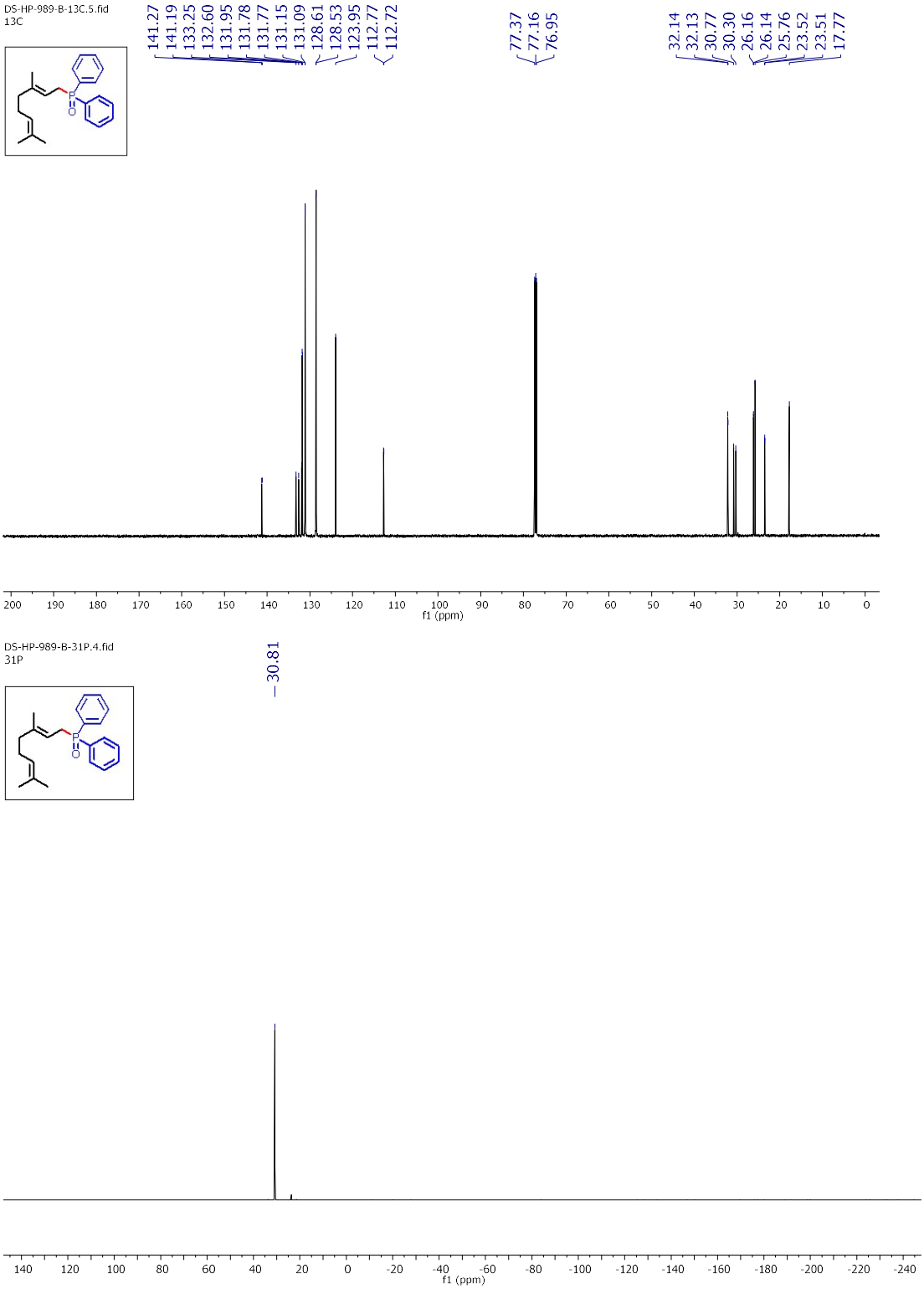
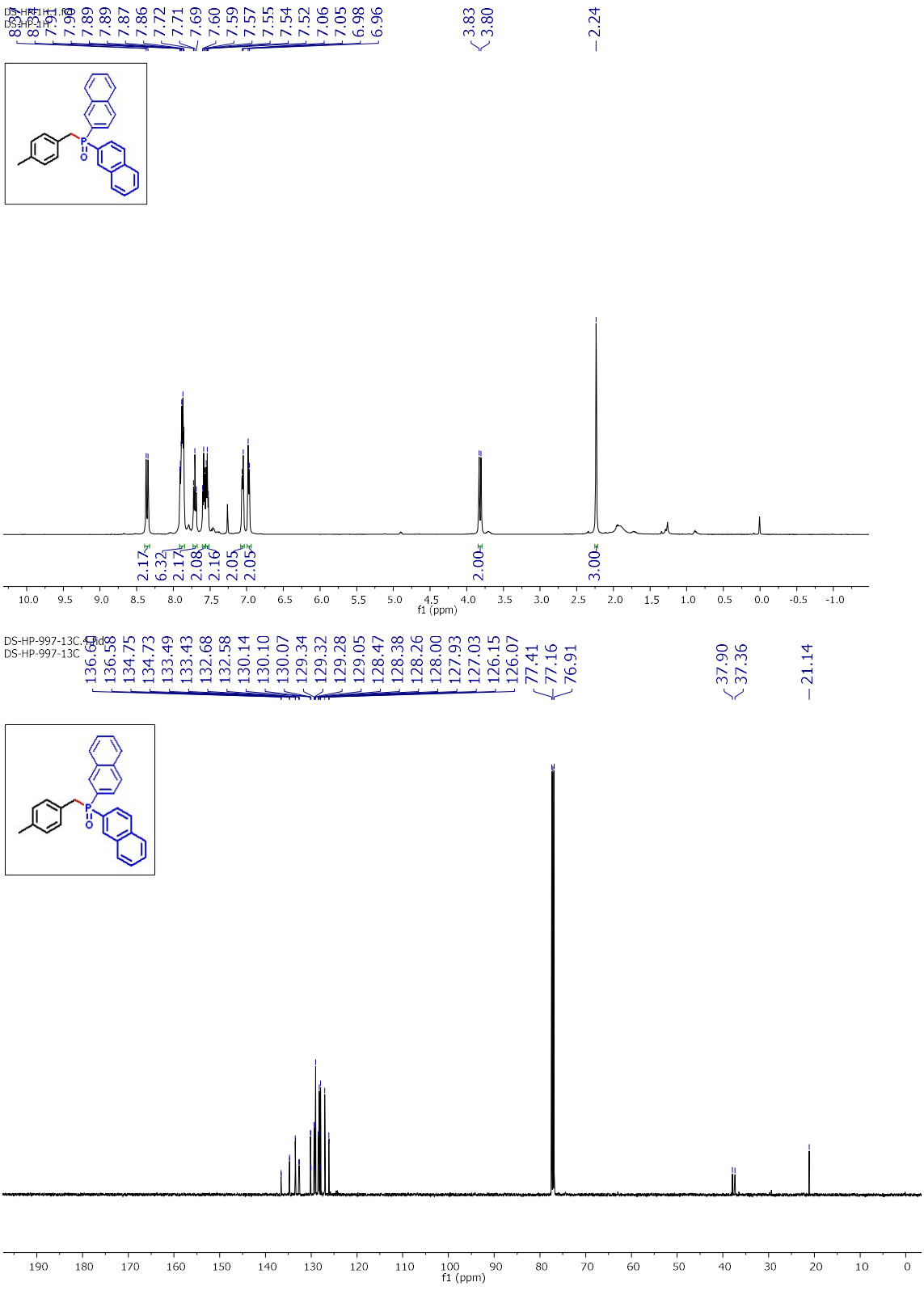


Figure S47. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3au in $CDCl_3$


8.21
8.21
7.91
7.90
7.89
7.89
7.87
7.86
7.72
7.71
7.69
7.60
7.59
7.57
7.55
7.54
7.52
7.06
7.05
6.98
6.96
3.83
3.80
2.24
2.17
6.32
2.17
2.08
2.16
2.05
2.05
2.00
3.00
f1 (ppm)
DS-HP-997-13C.10.fid
DS-HP-997-13C
136.67
136.58
134.75
134.73
133.49
133.43
132.68
132.58
130.14
130.10
130.07
129.34
129.32
129.28
129.05
128.47
128.38
128.26
128.00
127.93
127.03
126.15
126.07
77.41
77.16
76.91
37.90
37.36
21.14
f1 (ppm)

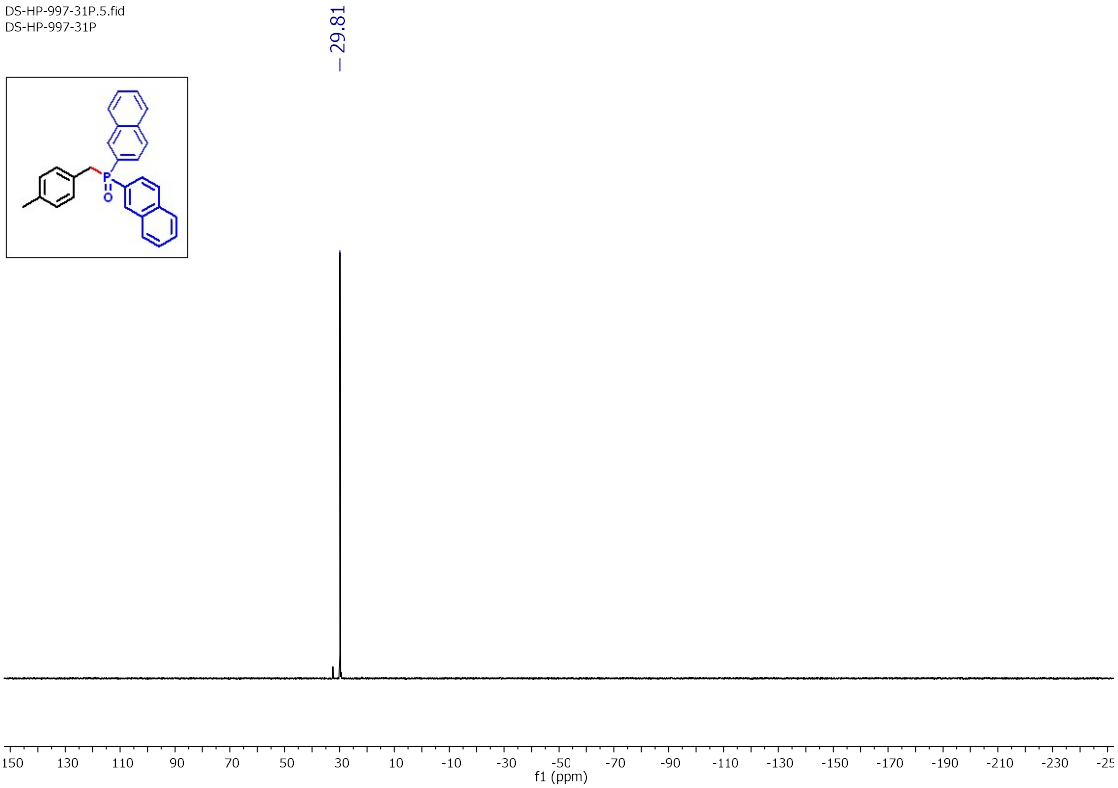
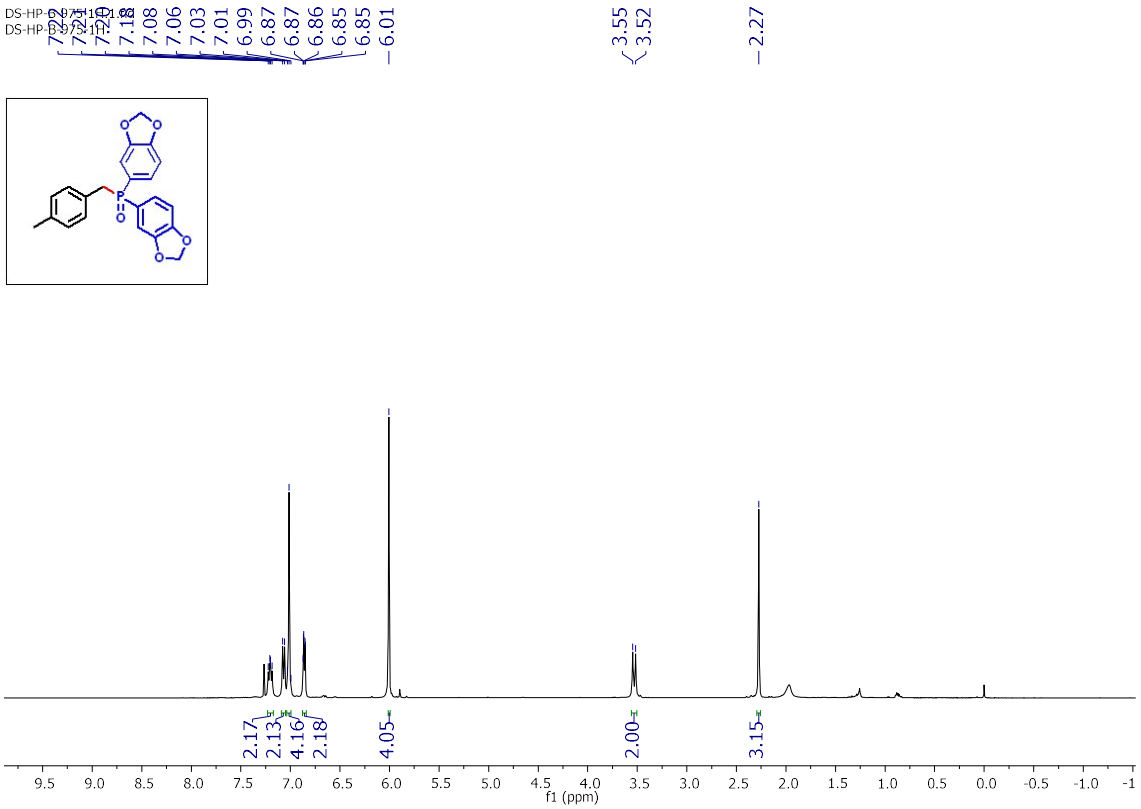
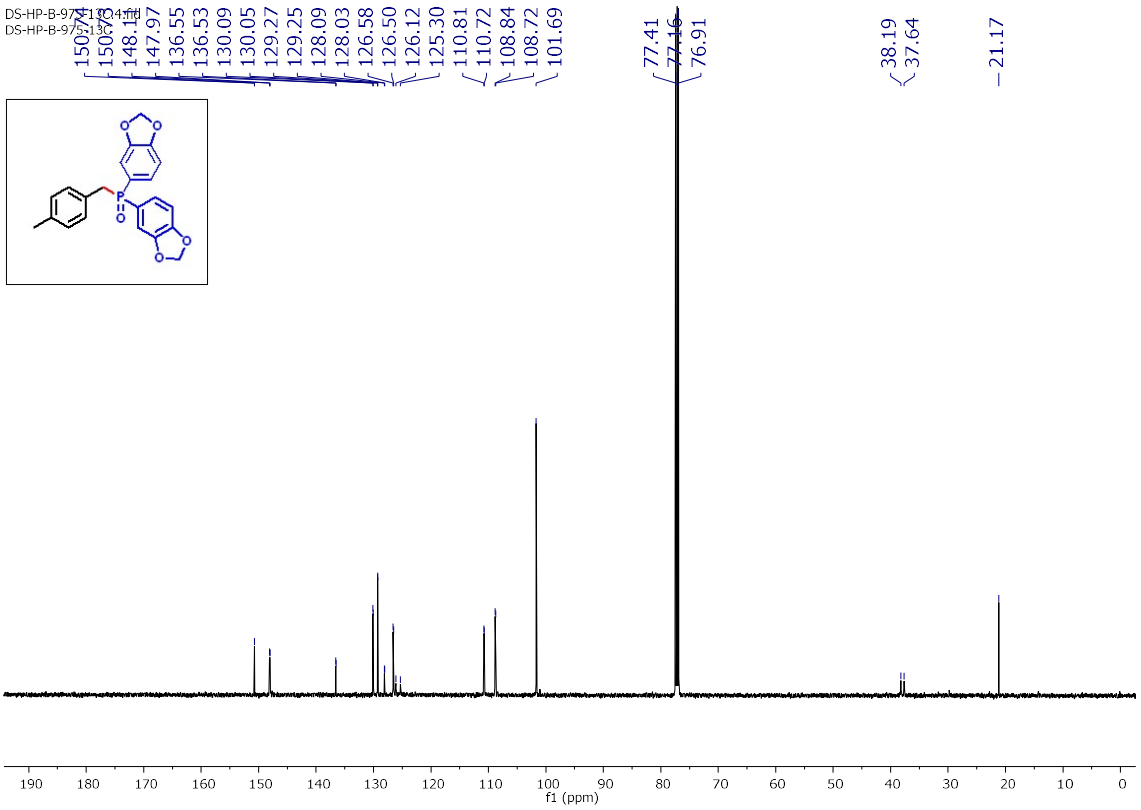


Figure S48. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3av in $CDCl_3$


7.22
7.21
7.18
7.08
7.06
7.03
7.01
6.99
6.87
6.87
6.86
6.85
6.85
6.01
3.55
3.52
2.27
2.17
2.13
4.16
2.18
4.05
2.00
3.15
f1 (ppm)


150.74
150.27
148.11
147.97
136.55
136.53
130.09
130.05
129.27
129.25
128.09
128.03
126.58
126.50
126.12
125.30
110.81
110.72
108.84
108.72
101.69
77.41
77.16
76.91
38.19
37.64
21.17
f1 (ppm)

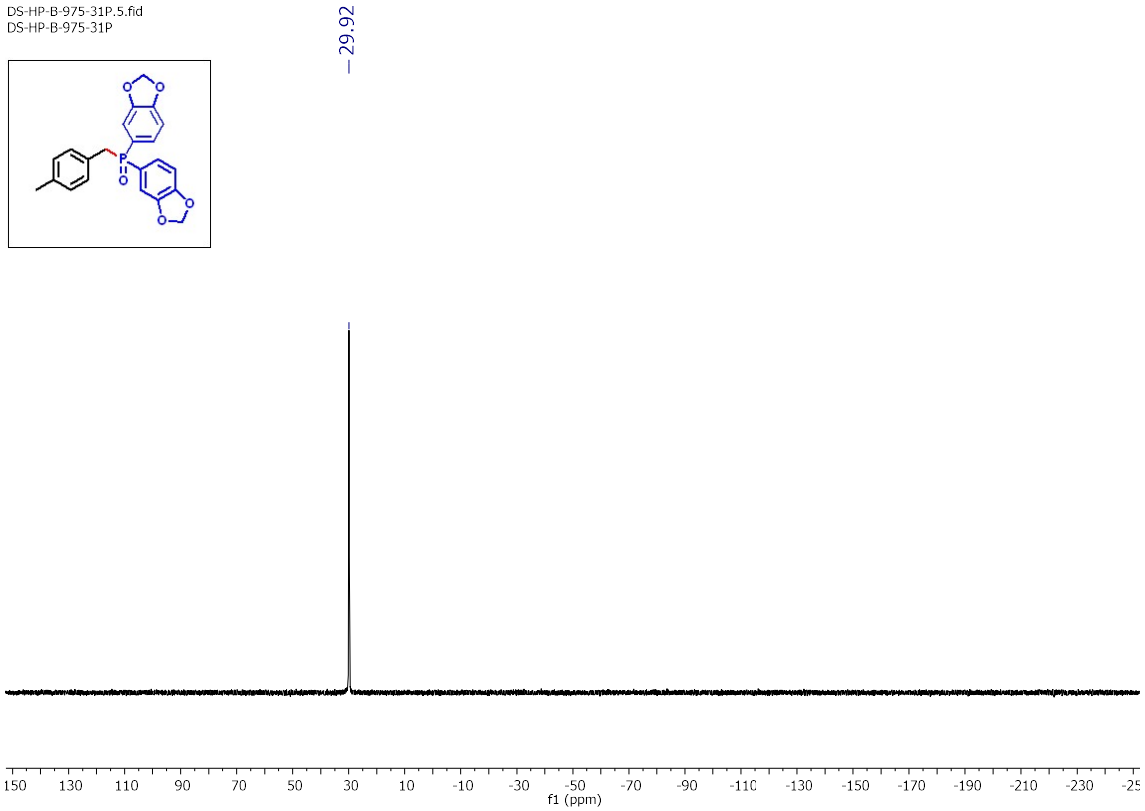
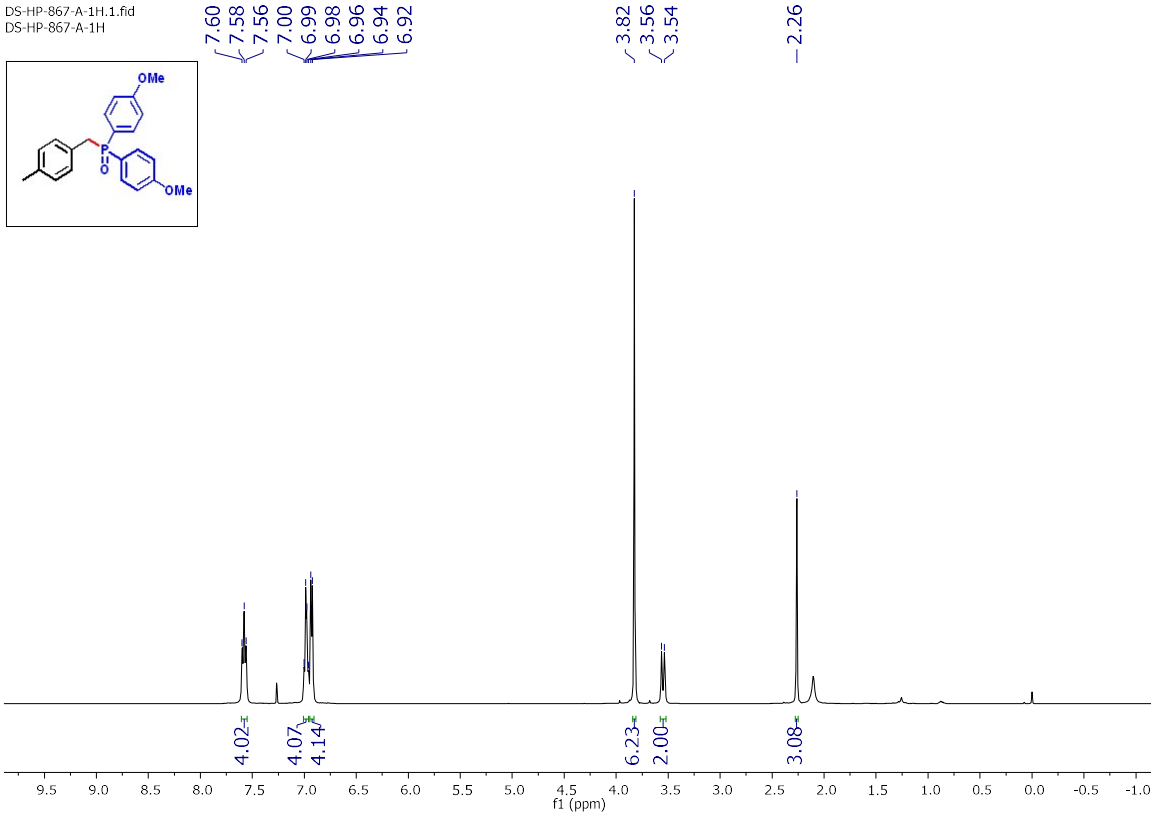
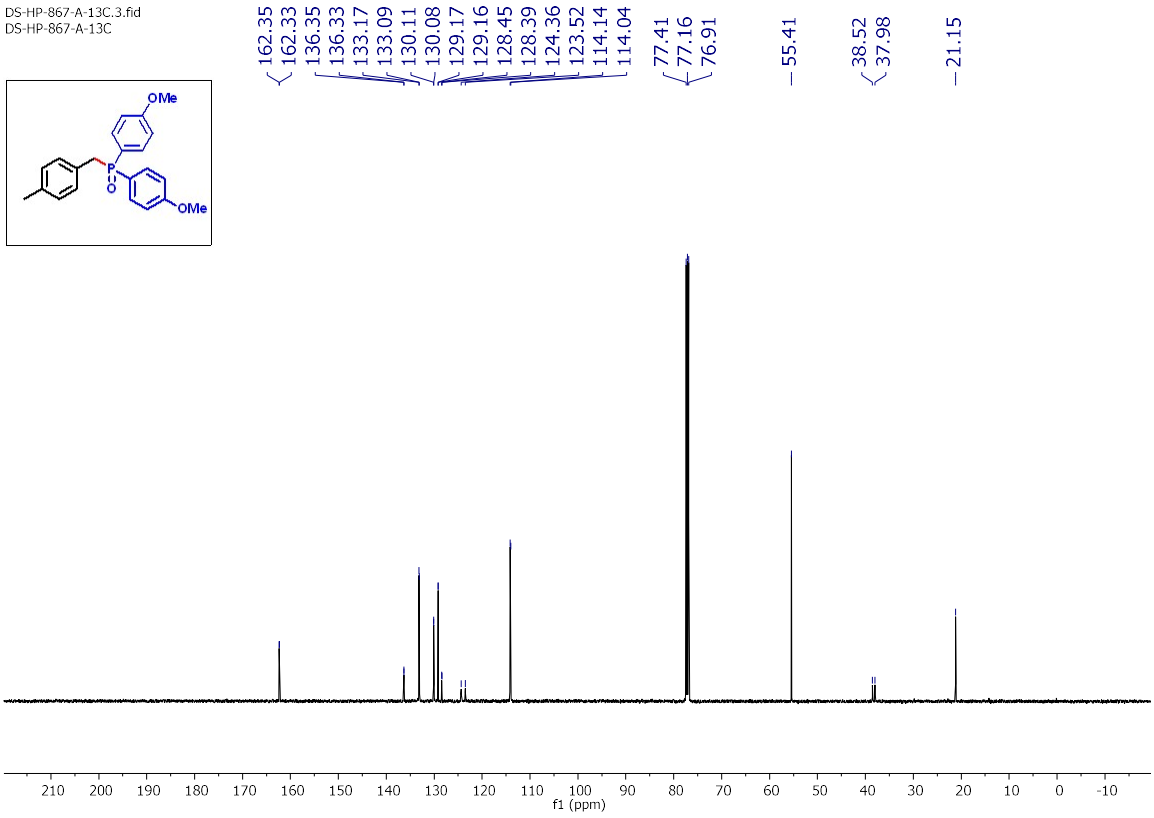


Figure S49. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3aw in $CDCl_3$


DS-HP-867-A-1H.1.fid
DS-HP-867-A-1H
7.60
7.58
7.56
7.00
6.99
6.98
6.96
6.94
6.92
3.82
3.56
3.54
2.26
OMe
OMe
4.02
4.07
4.14
6.23
2.00
3.08
f1 (ppm)


DS-HP-867-A-13C.3.fid
DS-HP-867-A-13C
162.35
162.33
136.35
136.33
133.17
133.09
130.11
130.08
129.17
129.16
128.45
128.39
124.36
123.52
114.14
114.04
77.41
77.16
76.91
55.41
38.52
37.98
21.15
OMe
OMe
f1 (ppm)

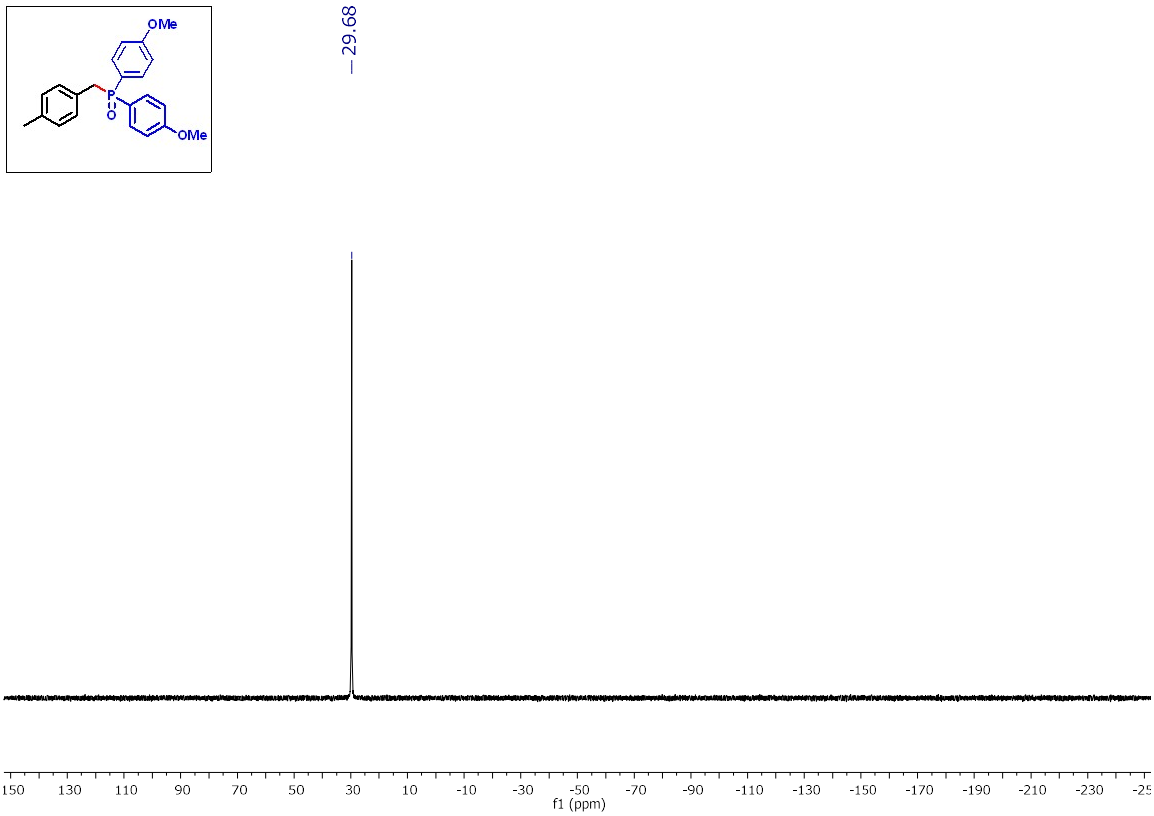
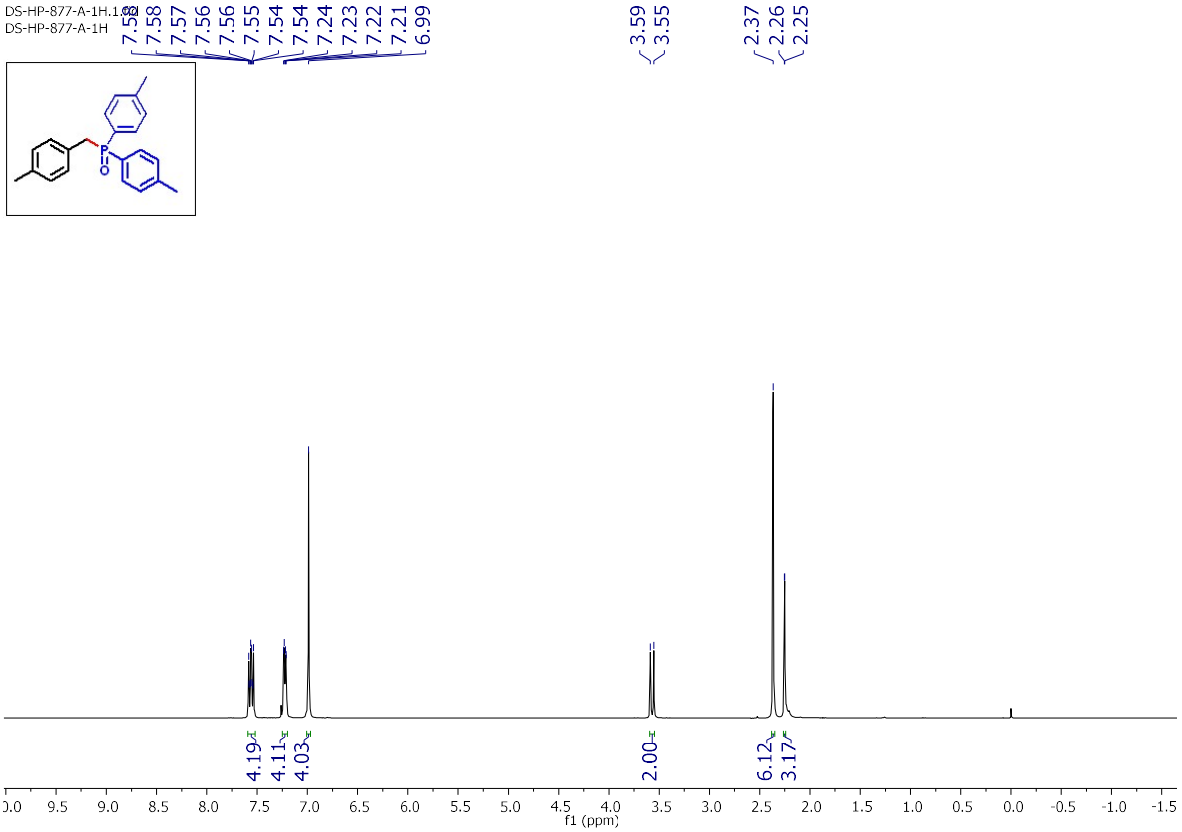
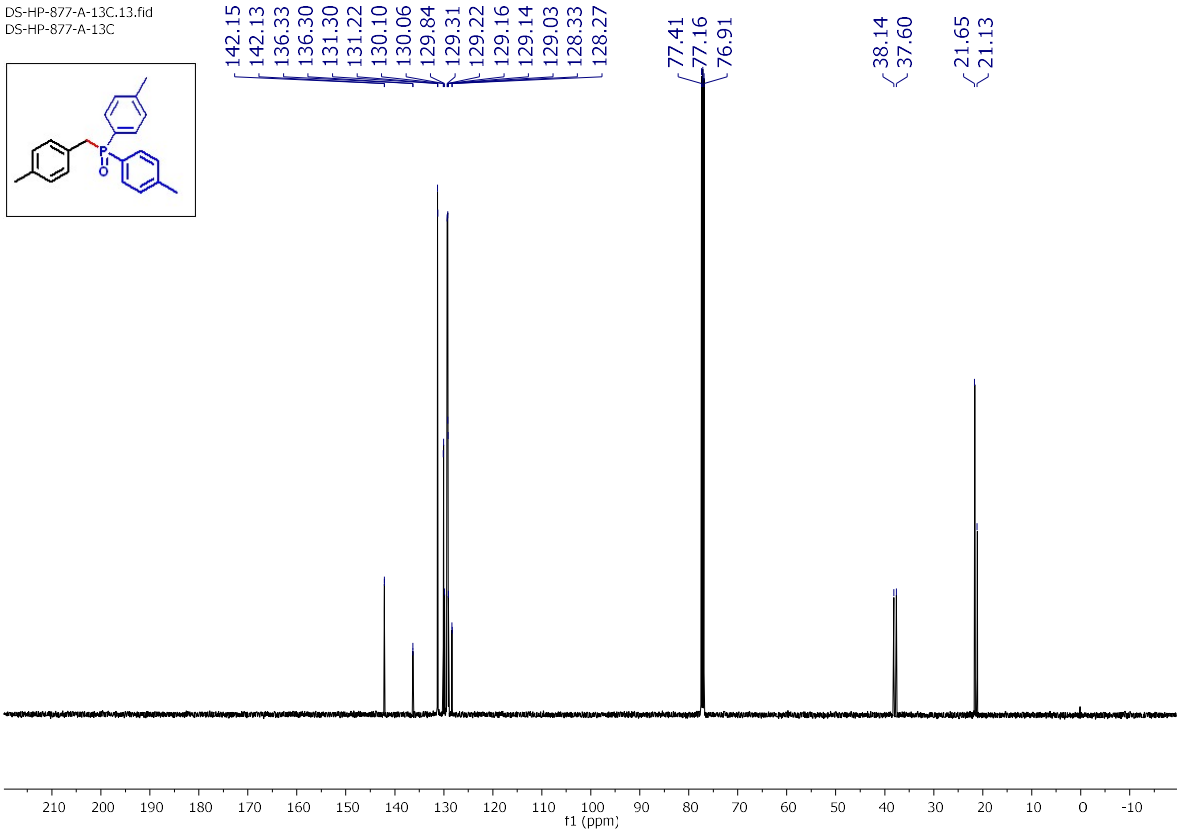


Figure S50. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ax in $CDCl_3$


DS-HP-877-A-1H
7.58
7.57
7.56
7.56
7.55
7.54
7.54
7.24
7.23
7.22
7.21
6.99
3.59
3.55
2.37
2.26
2.25
4.19
4.11
4.03
2.00
6.12
3.17
f1 (ppm)


DS-HP-877-A-13C
142.15
142.13
136.33
136.30
131.30
131.22
130.10
130.06
129.84
129.31
129.22
129.16
129.14
129.03
128.33
128.27
77.41
77.16
76.91
38.14
37.60
21.65
21.13
f1 (ppm)

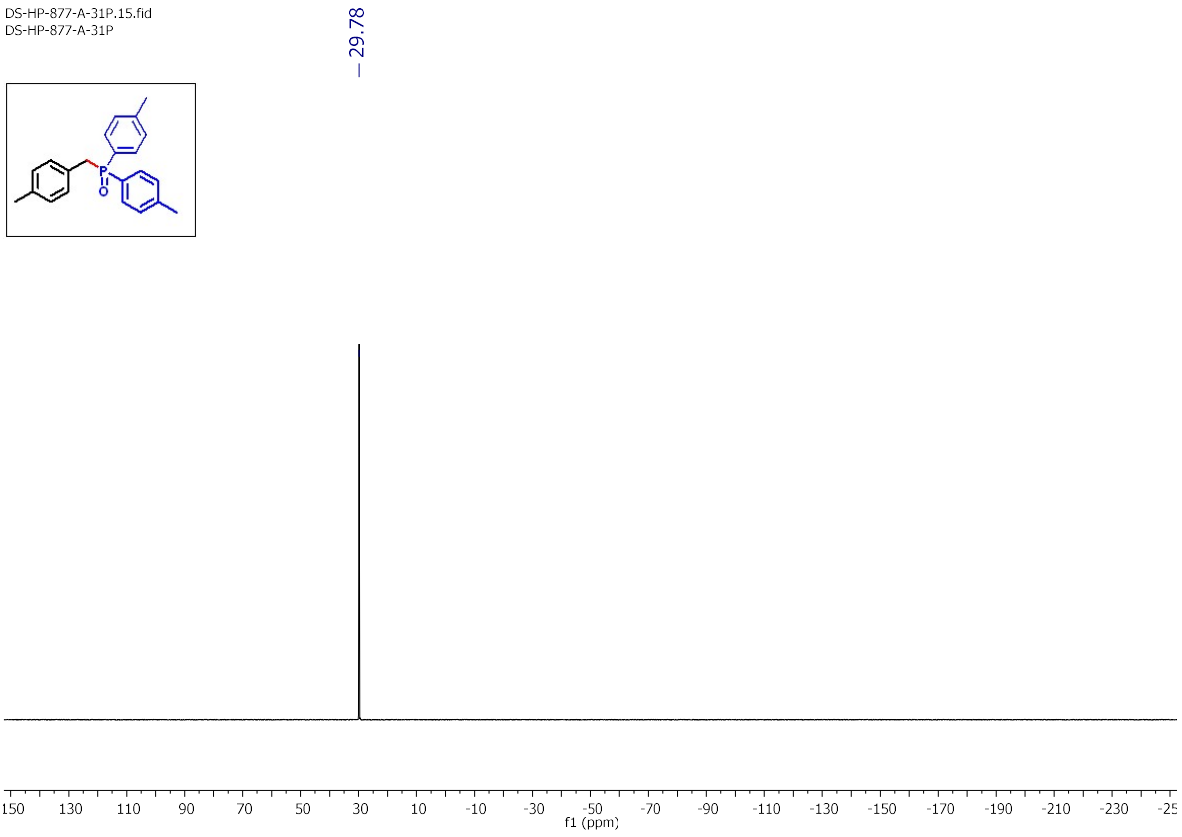
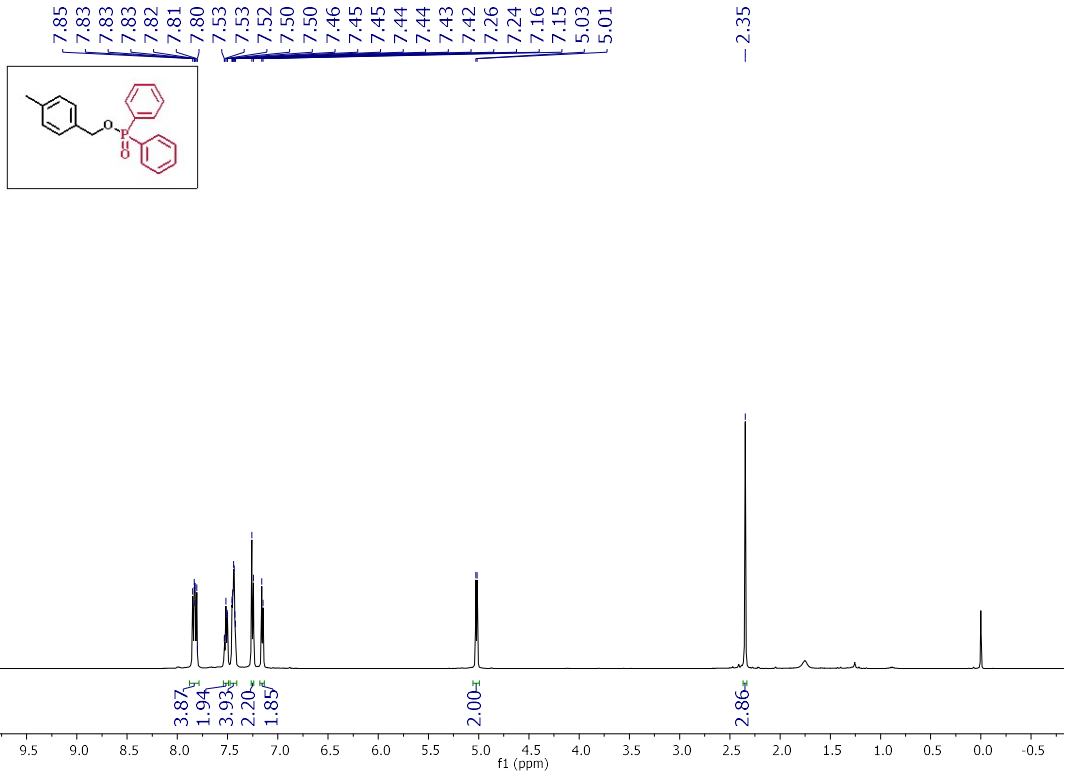
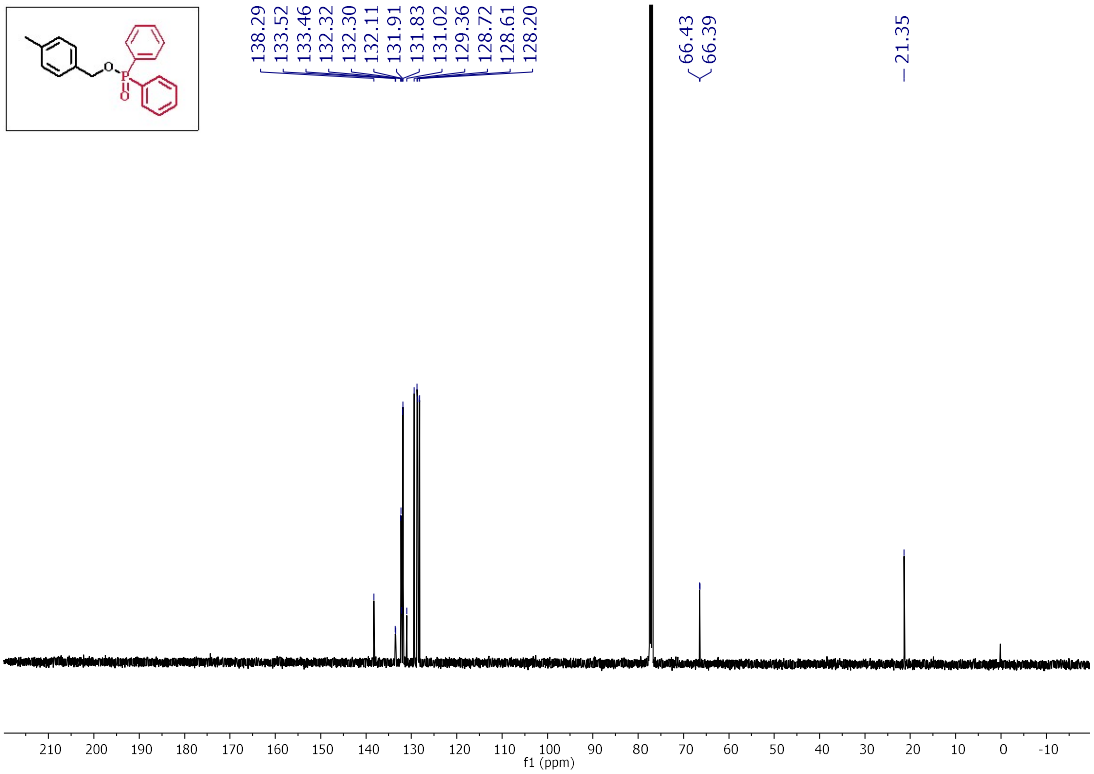


Figure S51. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 3ay in $CDCl_3$


7.85
7.83
7.83
7.83
7.82
7.81
7.80
7.53
7.53
7.52
7.50
7.50
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.26
7.24
7.16
7.15
5.03
5.01
2.35
3.87
1.94
3.93
2.20
1.85
2.00
2.86
f1 (ppm)


138.29
133.52
133.46
132.32
132.30
132.11
131.91
131.83
131.02
129.36
128.72
128.61
128.20
66.43
66.39
21.35
f1 (ppm)

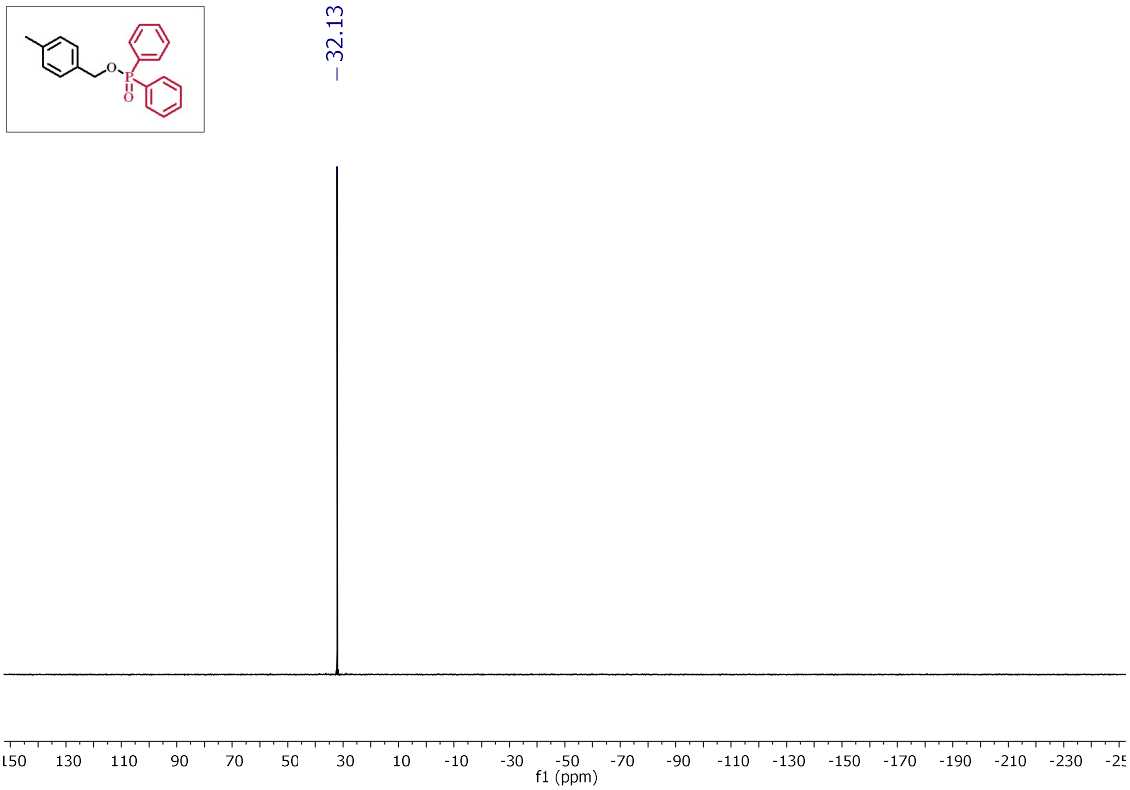
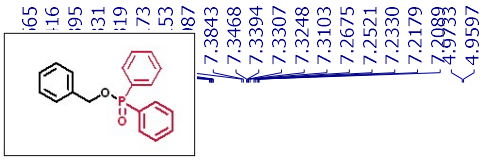
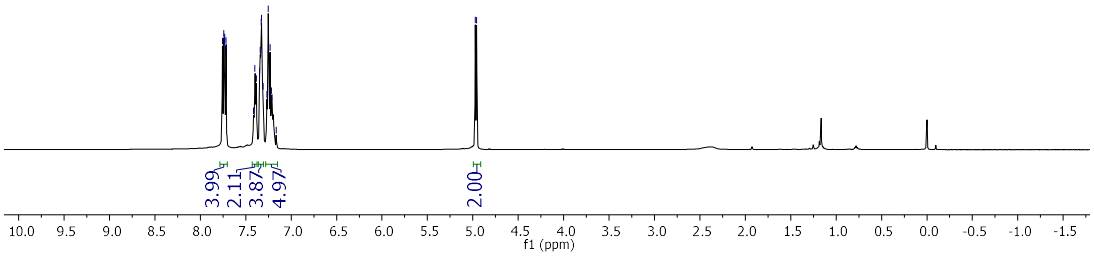
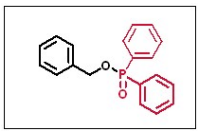


Figure S52. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4a in $CDCl_3$

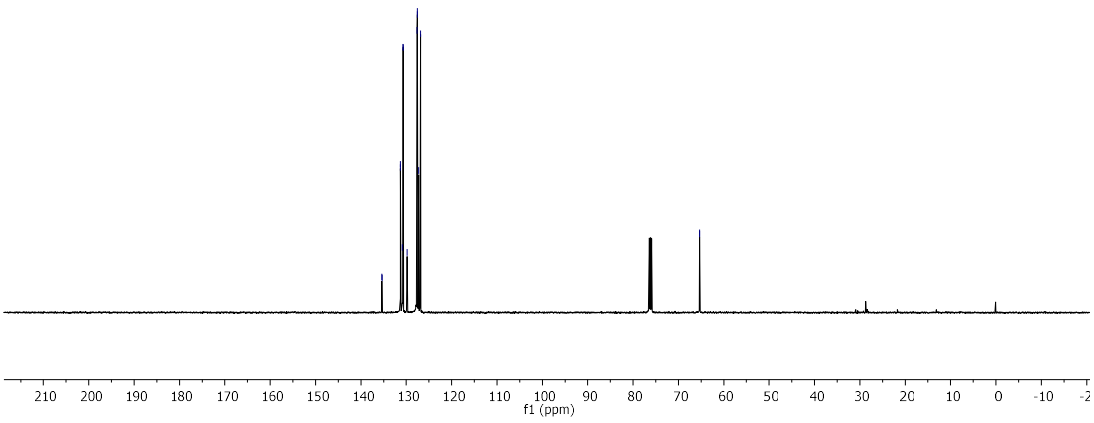


7.3843
7.3468
7.3394
7.3307
7.3248
7.3103
7.2675
7.2521
7.2330
7.2179
4.9597


3.99
2.11
3.87
4.97
2.00
f1 (ppm)




135.39
135.33
131.29
131.27
130.88
130.76
130.68
129.79
127.65
127.57
127.54
127.31
126.88
65.35
65.31


f1 (ppm)

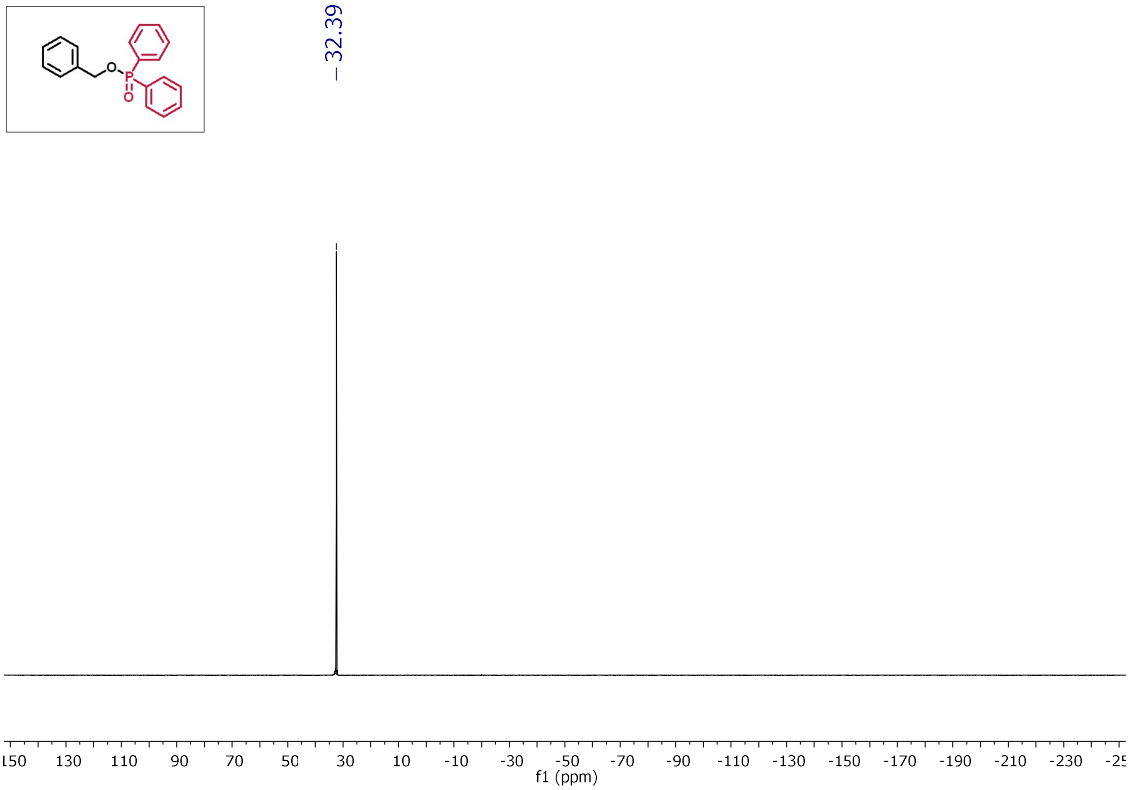
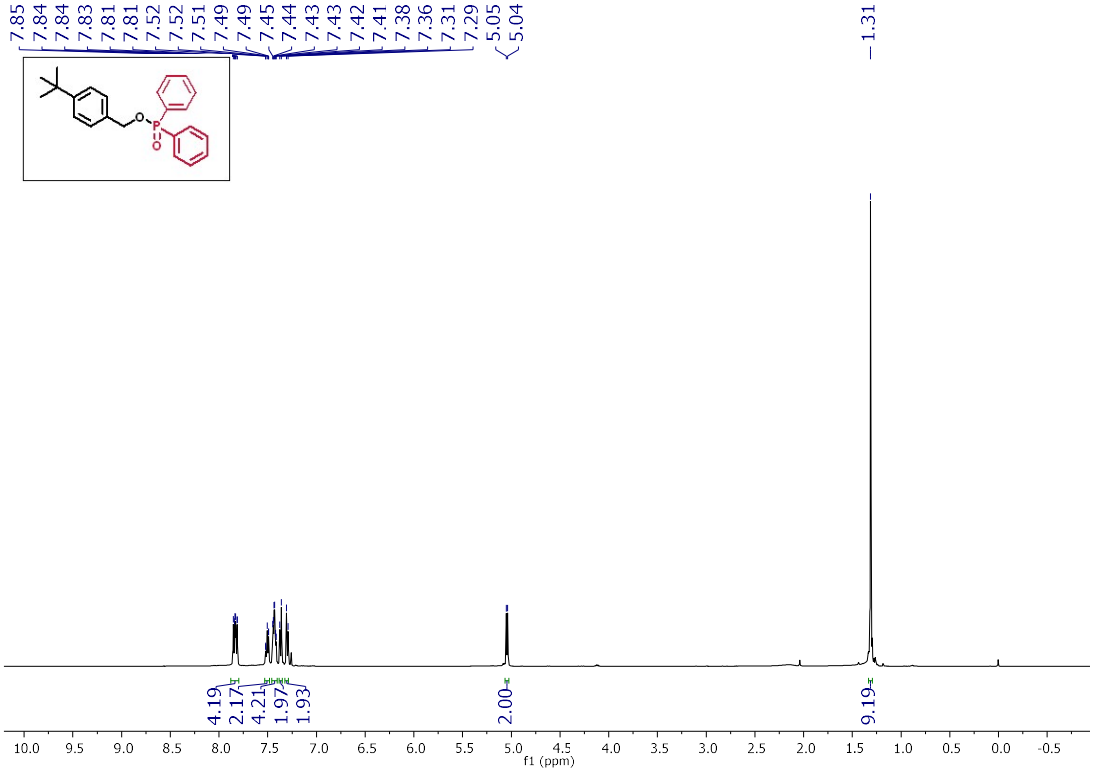


Figure S53. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4b in $CDCl_3$



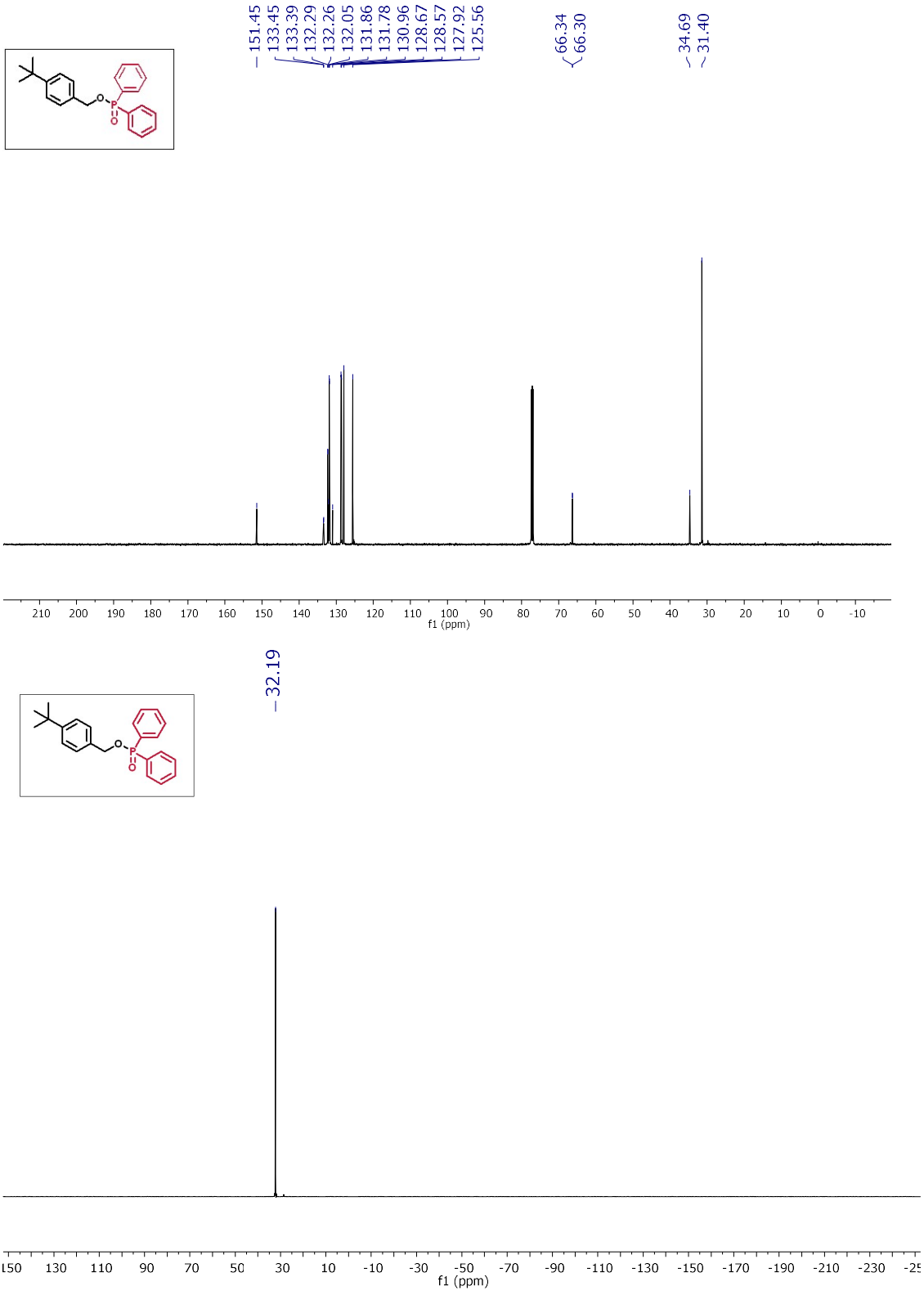
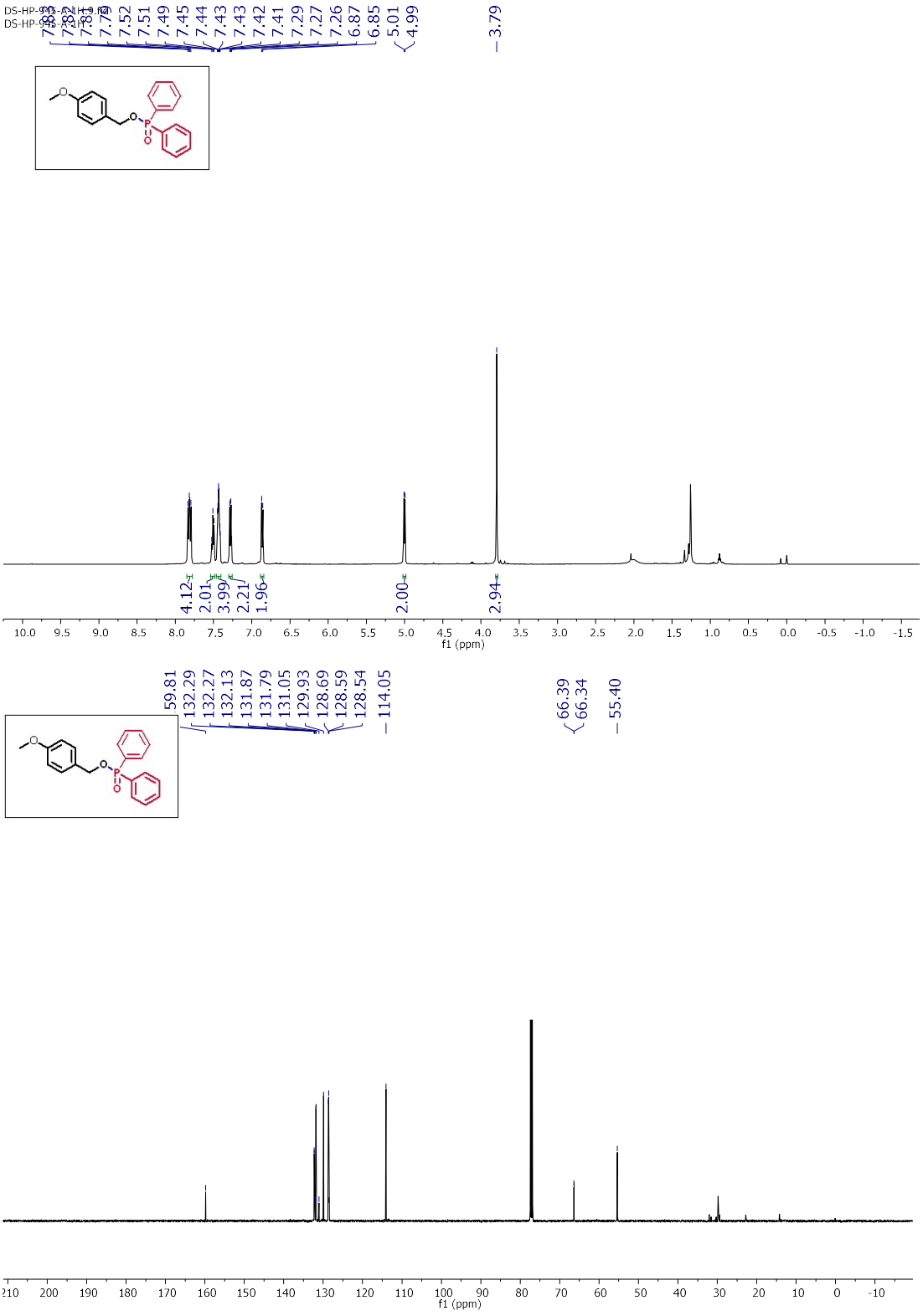


Figure S54. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4c in $CDCl_3$


7.80
7.79
7.78
7.77
7.52
7.51
7.49
7.45
7.44
7.43
7.43
7.42
7.41
7.29
7.27
7.26
6.87
6.85
5.01
4.99
3.79
4.12
2.01
3.99
2.21
1.96
2.00
2.94
f1 (ppm)
59.81
132.29
132.27
132.13
131.87
131.79
131.05
129.93
128.69
128.59
128.54
114.05
66.39
66.34
55.40
f1 (ppm)

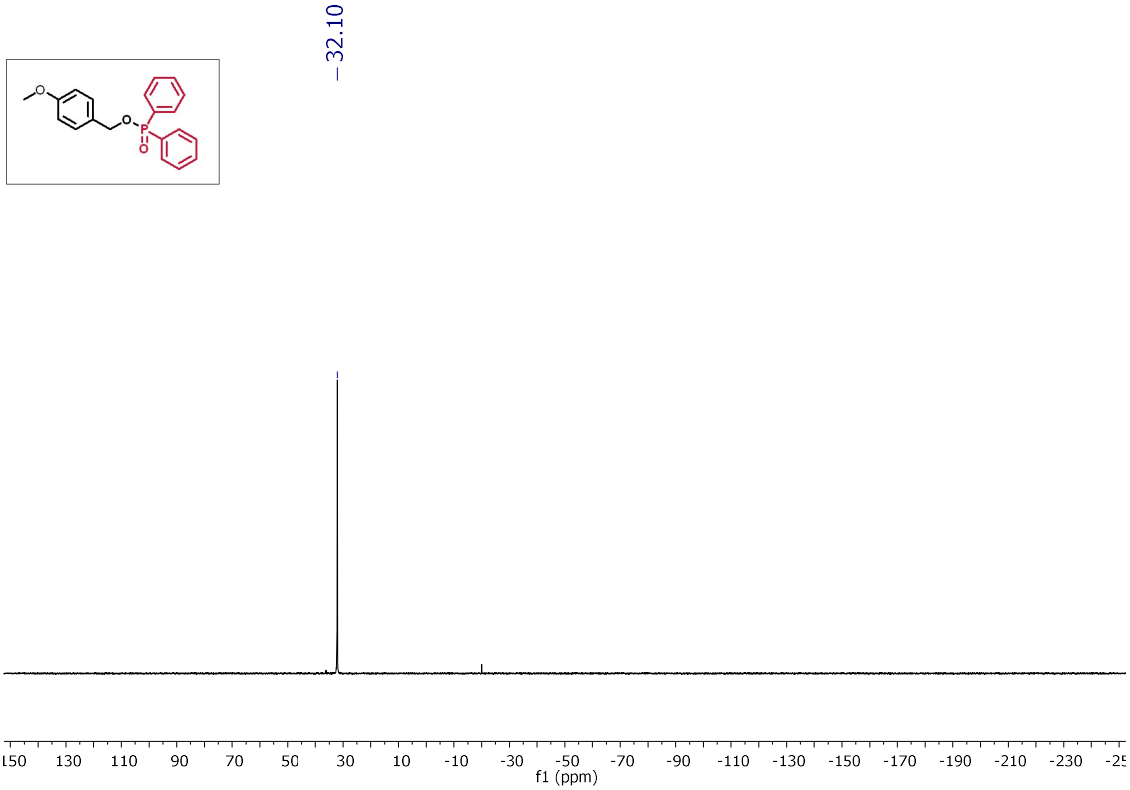
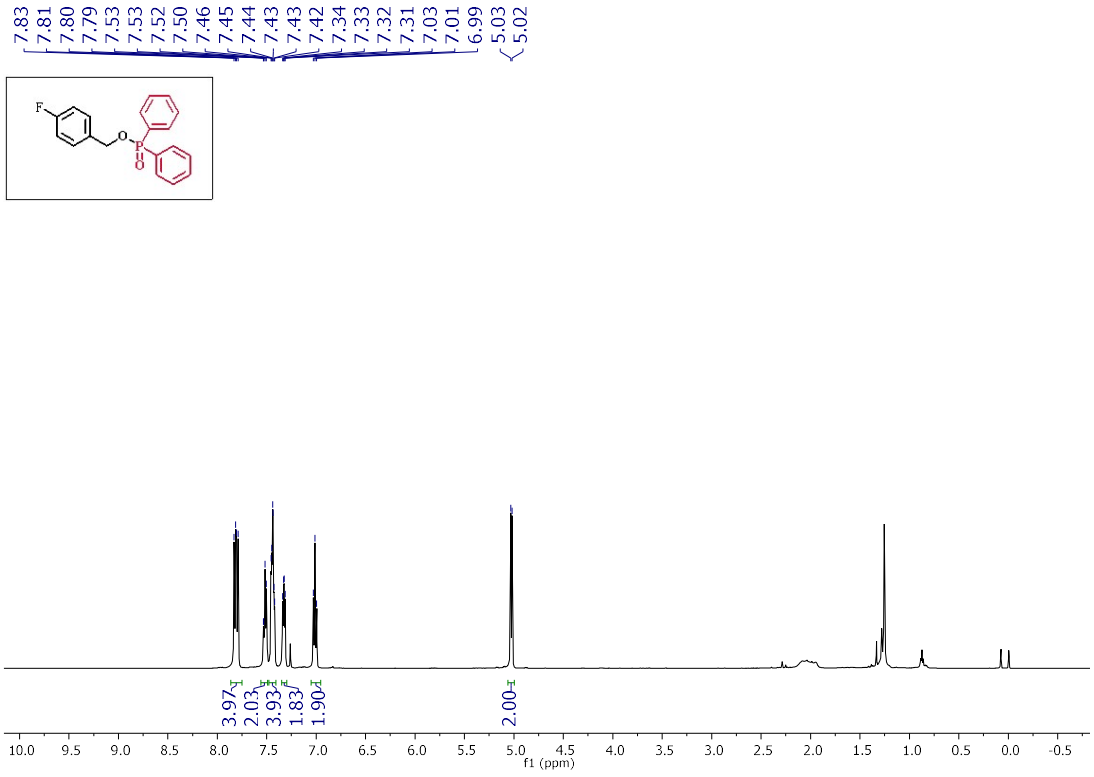
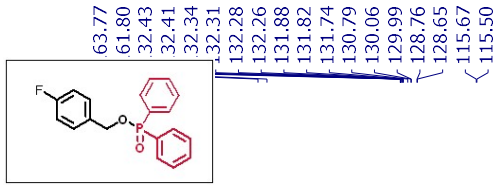
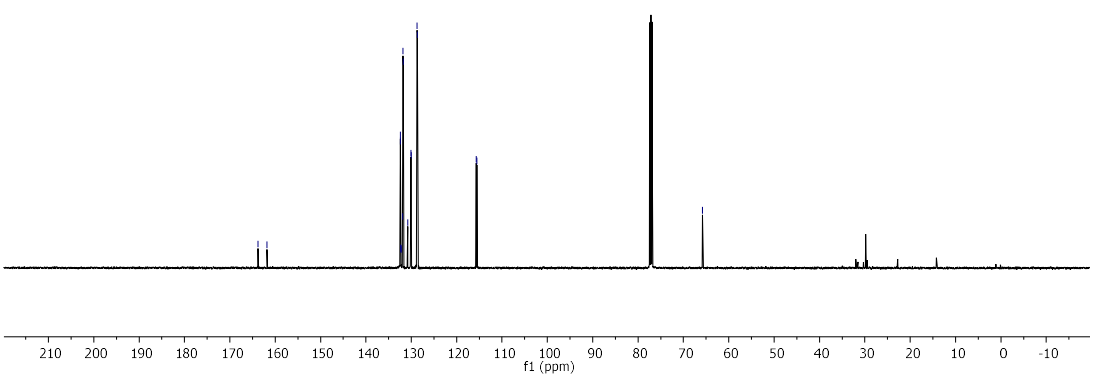
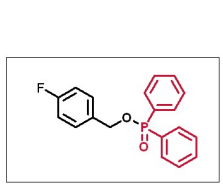


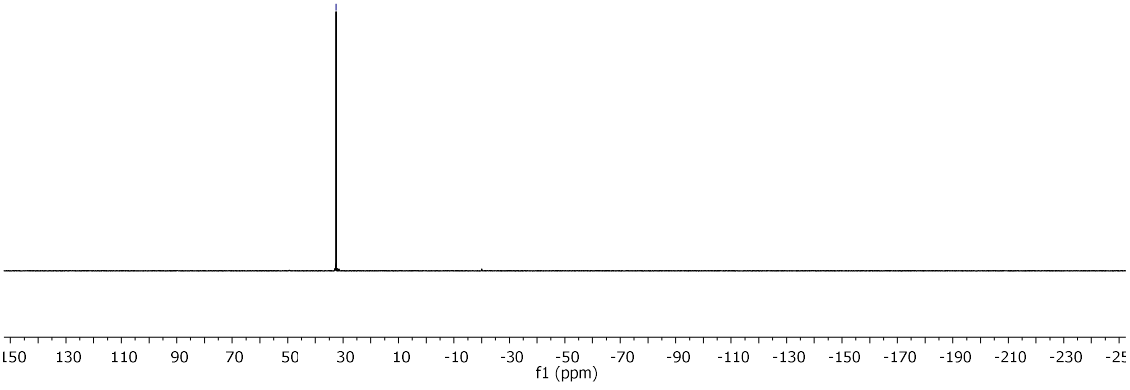
Figure S55. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4d in $CDCl_3$




63.77
61.80
32.43
32.41
32.34
32.31
132.28
132.26
131.88
131.82
131.74
130.79
130.06
129.99
128.76
128.65
115.67
115.50
65.82
65.78
F
O
P
O


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


32.57
F
O
P
O


150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)

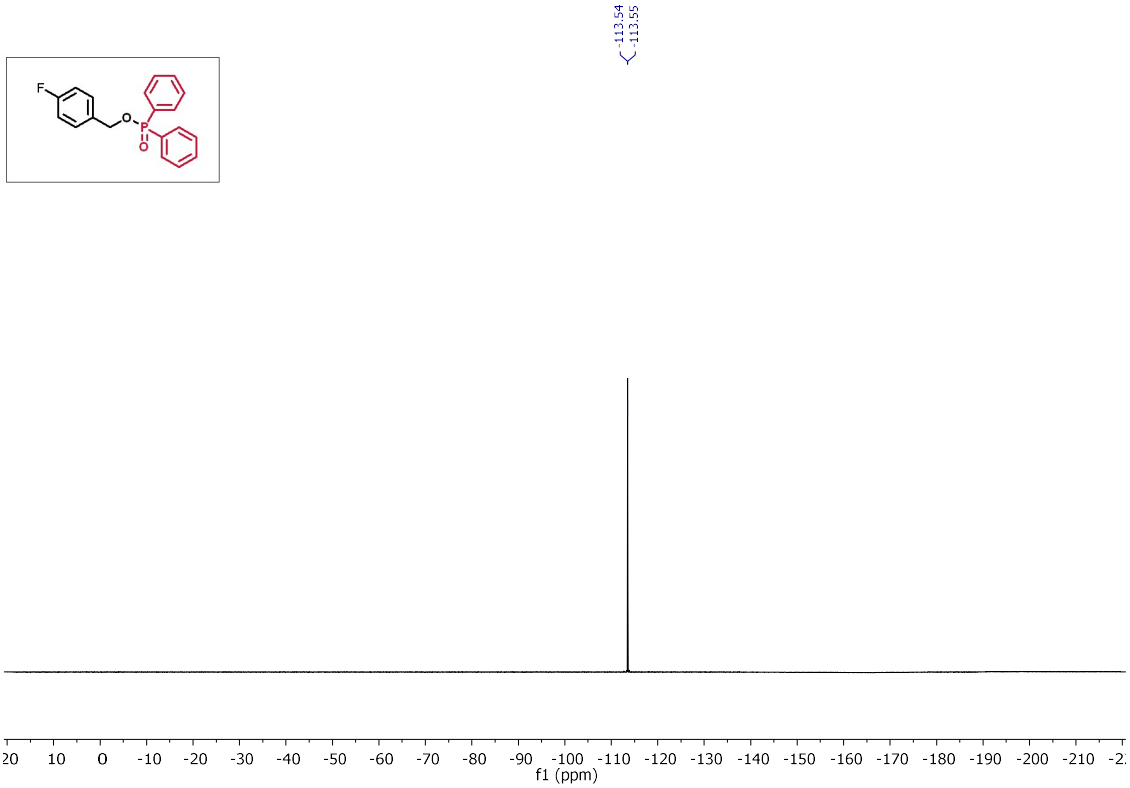
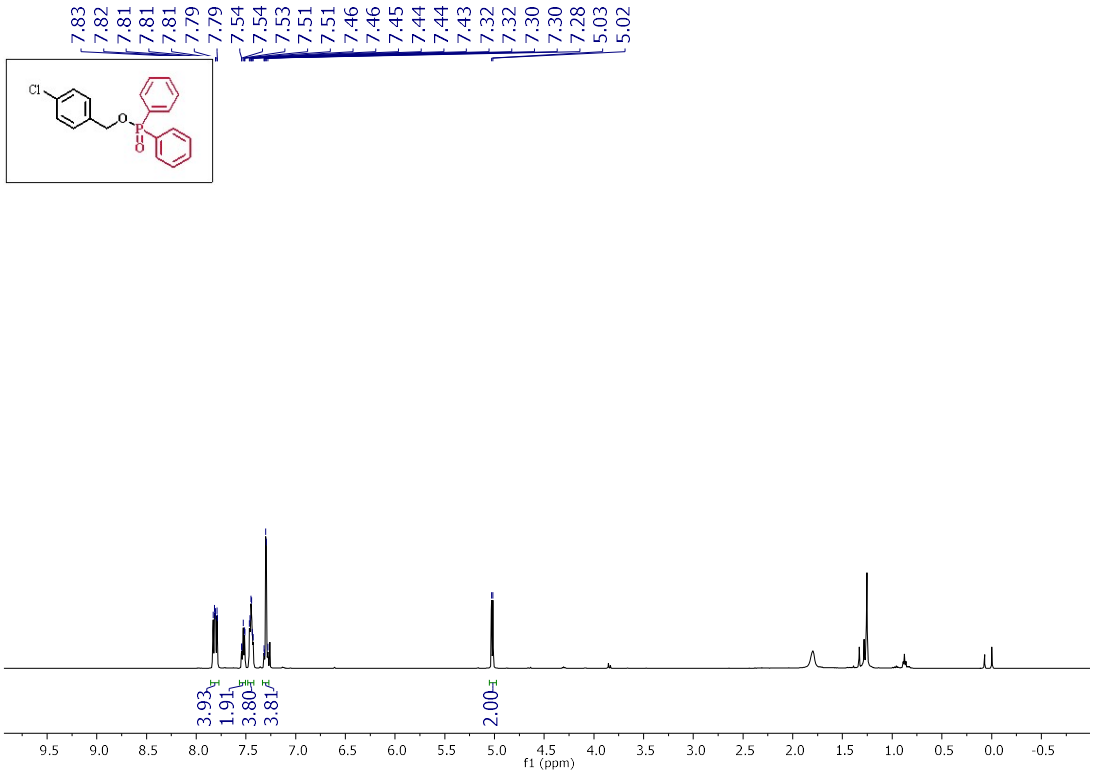


Figure S56. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) ^{19}F $\{^{1}H\}$ NMR (402 MHz) spectrum of Compound 4e in $CDCl_3$



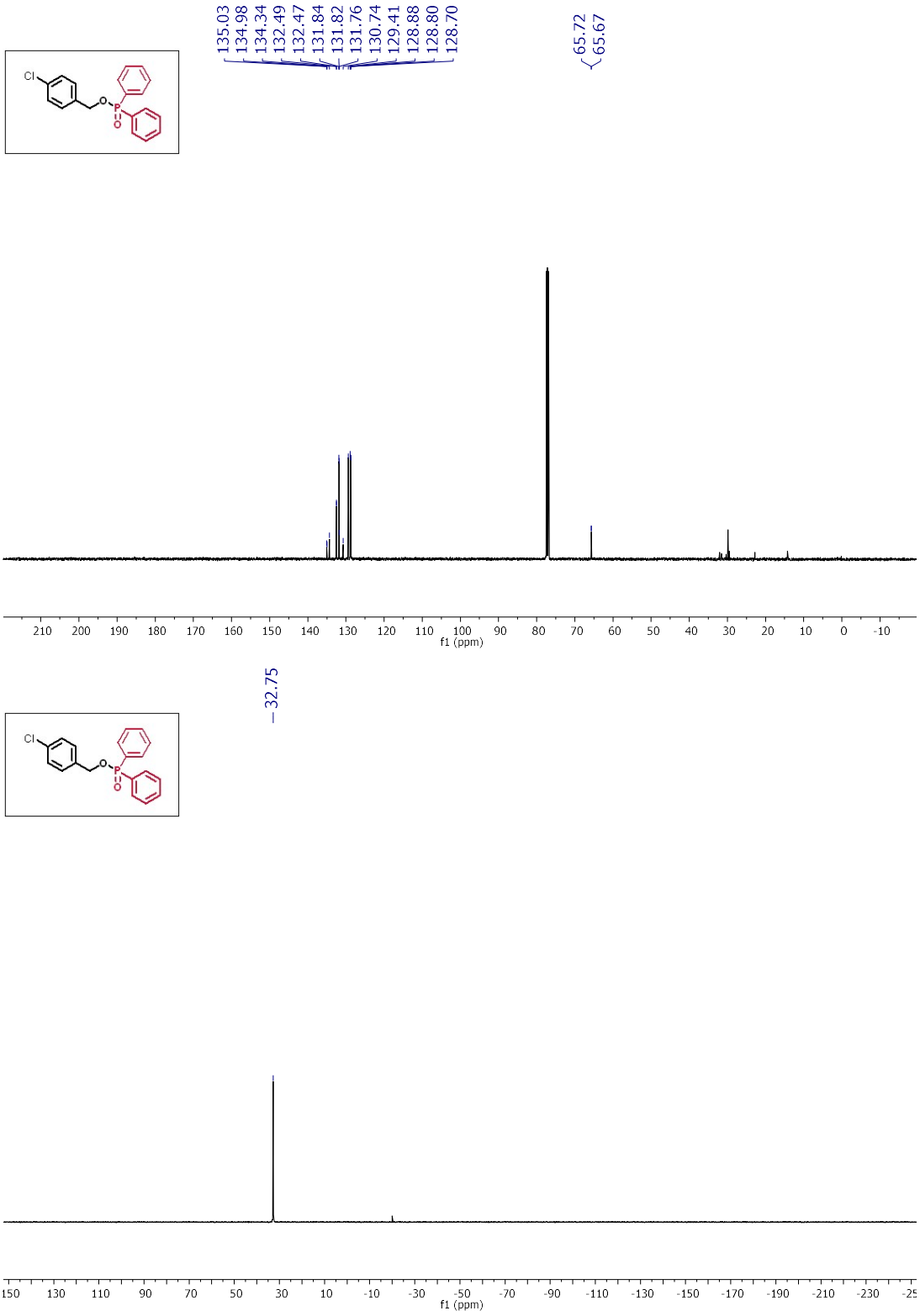
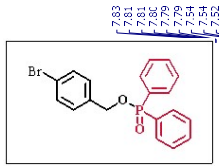
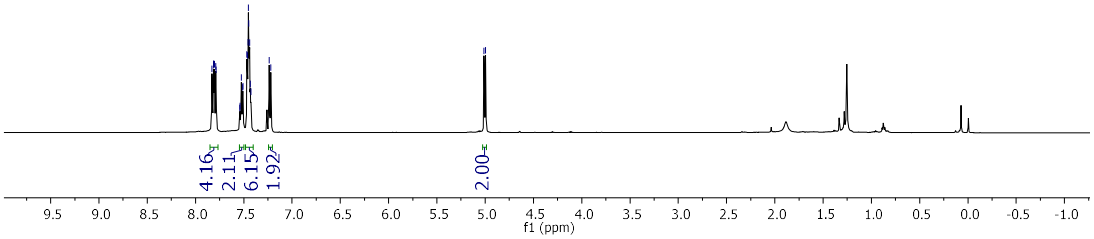
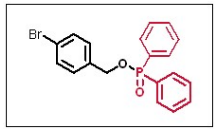


Figure S57. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4f in $CDCl_3$


Br
O
P
O

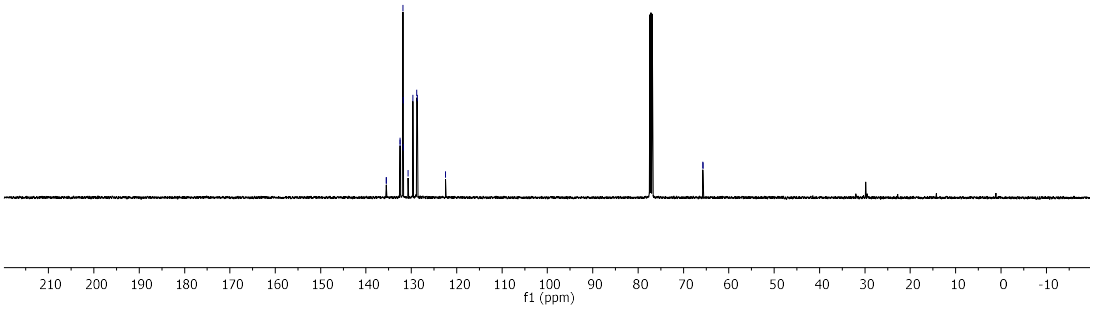

7.83
7.81
7.81
7.80
7.79
7.79
7.54
7.54
7.52
7.51
7.51
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.24
7.22
5.01
5.00


4.16
2.11
6.15
1.92
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


Br
O
P
O


135.55
135.49
132.48
132.46
131.83
131.81
131.75
130.72
129.68
128.80
128.69
122.46

65.72
65.68


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

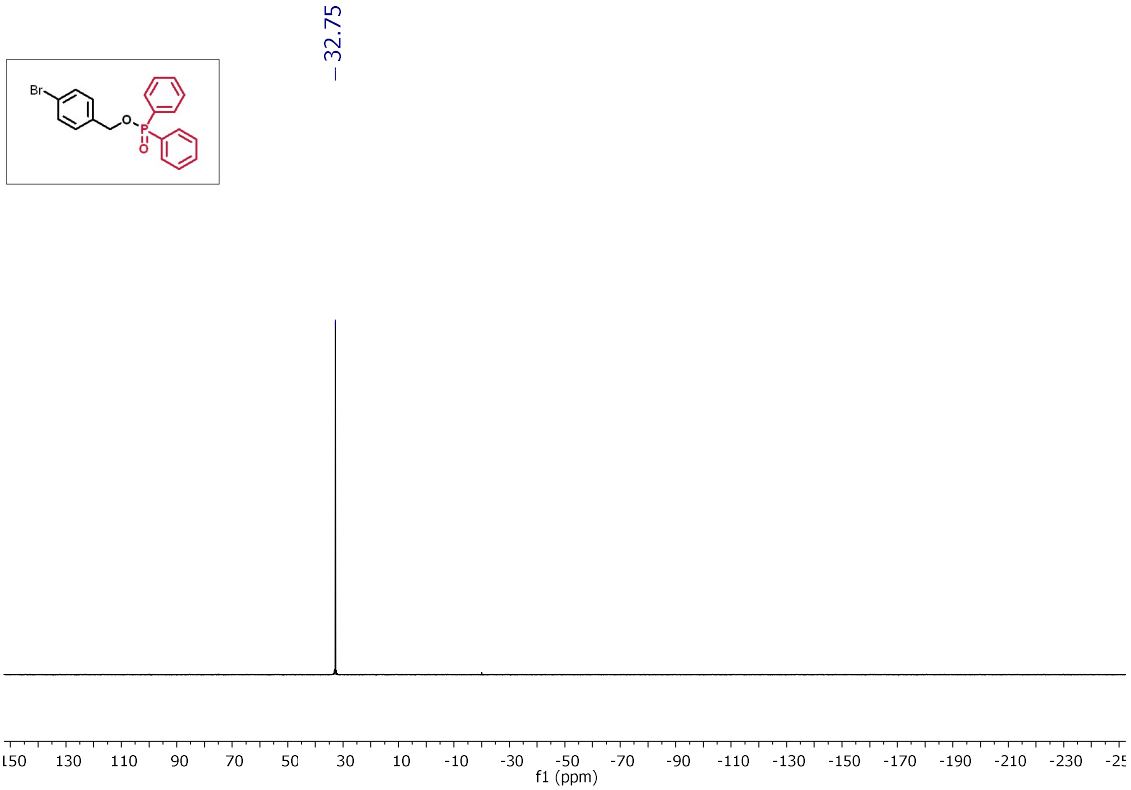
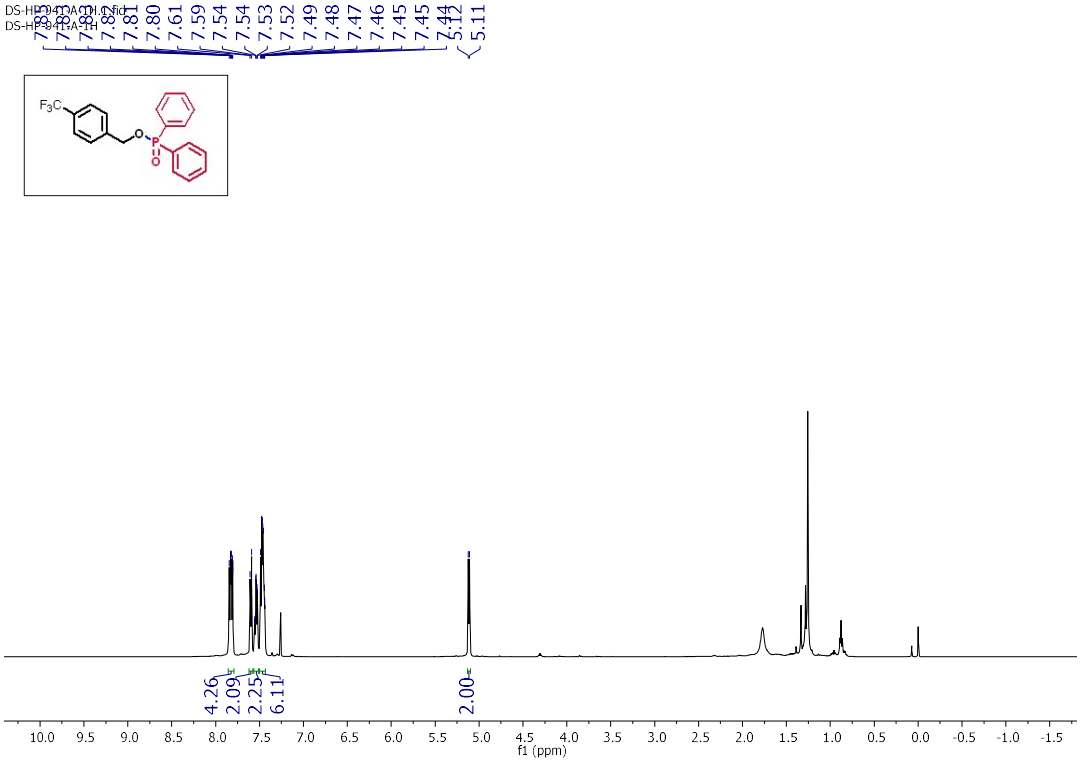
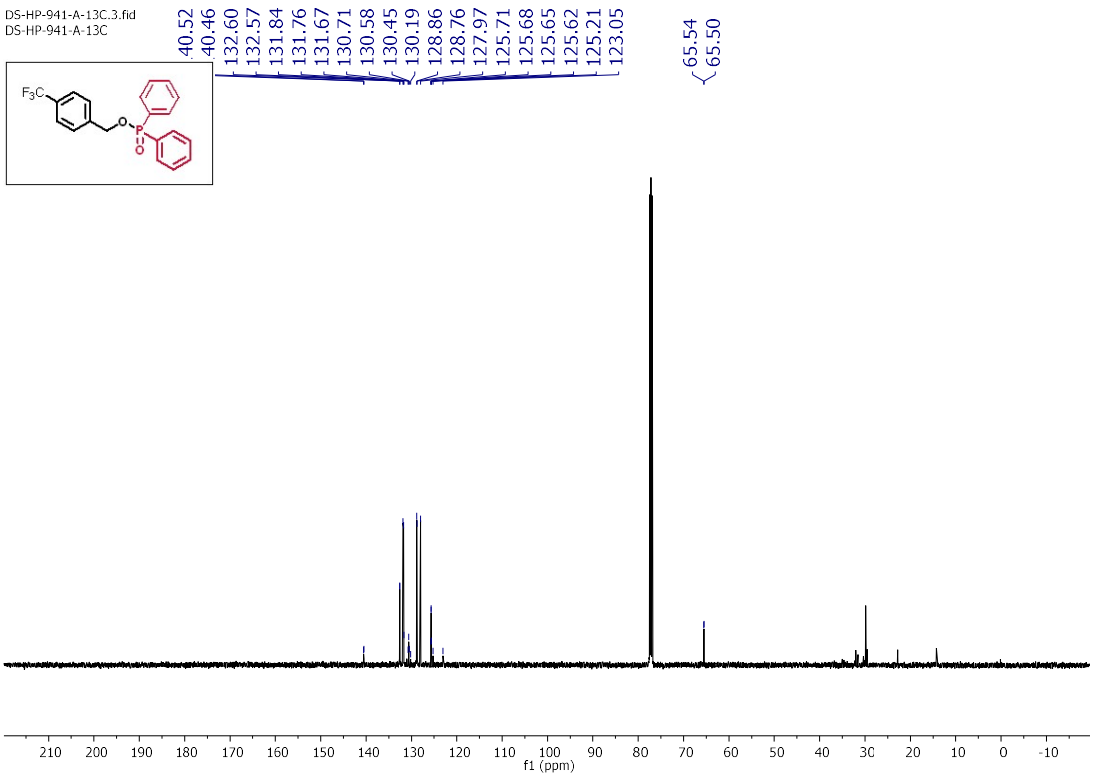
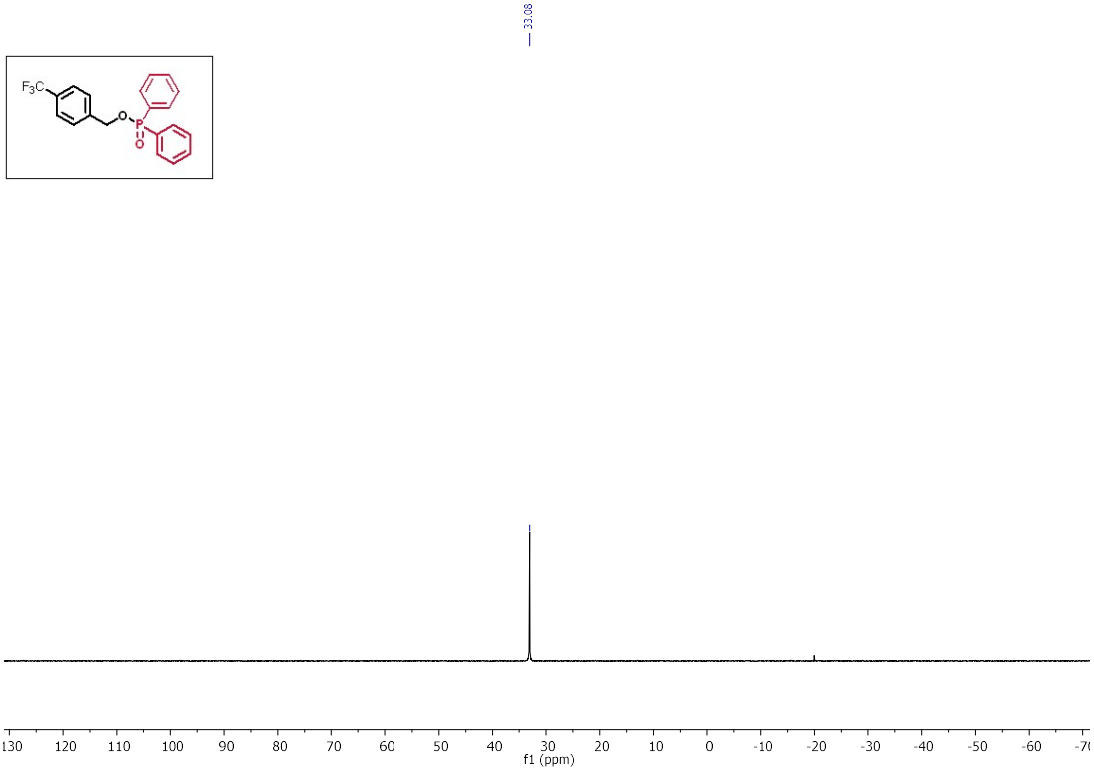


Figure S58. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4g in $CDCl_3$




DS-HP-941-A-13C.3.fid
DS-HP-941-A-13C
40.52
40.46
132.60
132.57
131.84
131.76
131.67
130.71
130.58
130.45
130.19
128.86
128.76
127.97
125.71
125.68
125.65
125.62
125.21
123.05
65.54
65.50
F3C
O
P
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


33.08
F3C
O
P
O
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

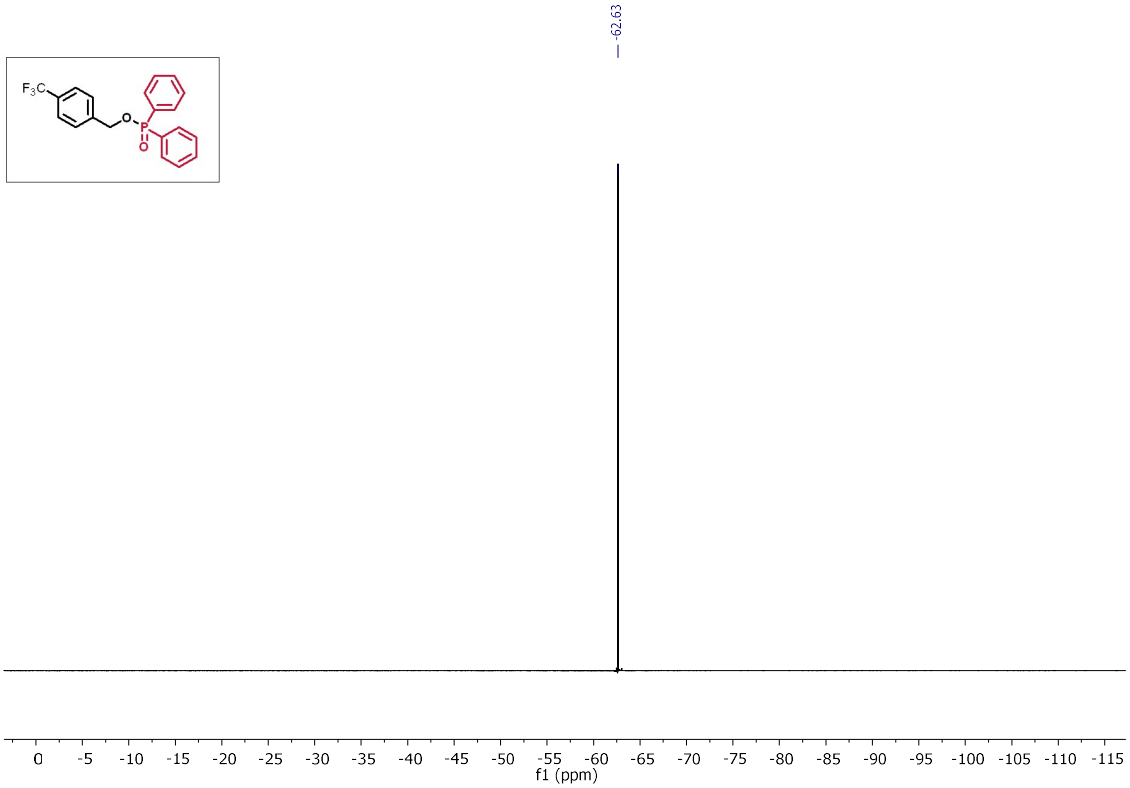
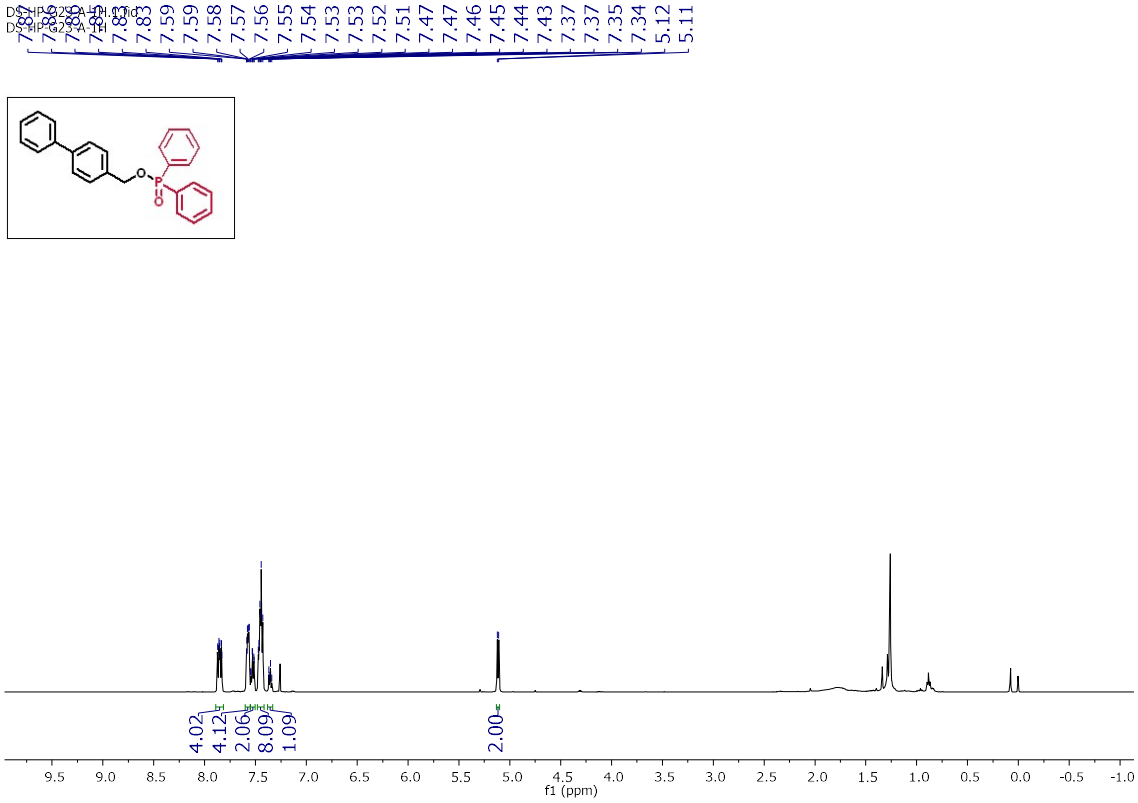


Figure S59. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) ^{19}F $\{^{1}H\}$ NMR (402 MHz) spectrum of Compound 4h in $CDCl_3$



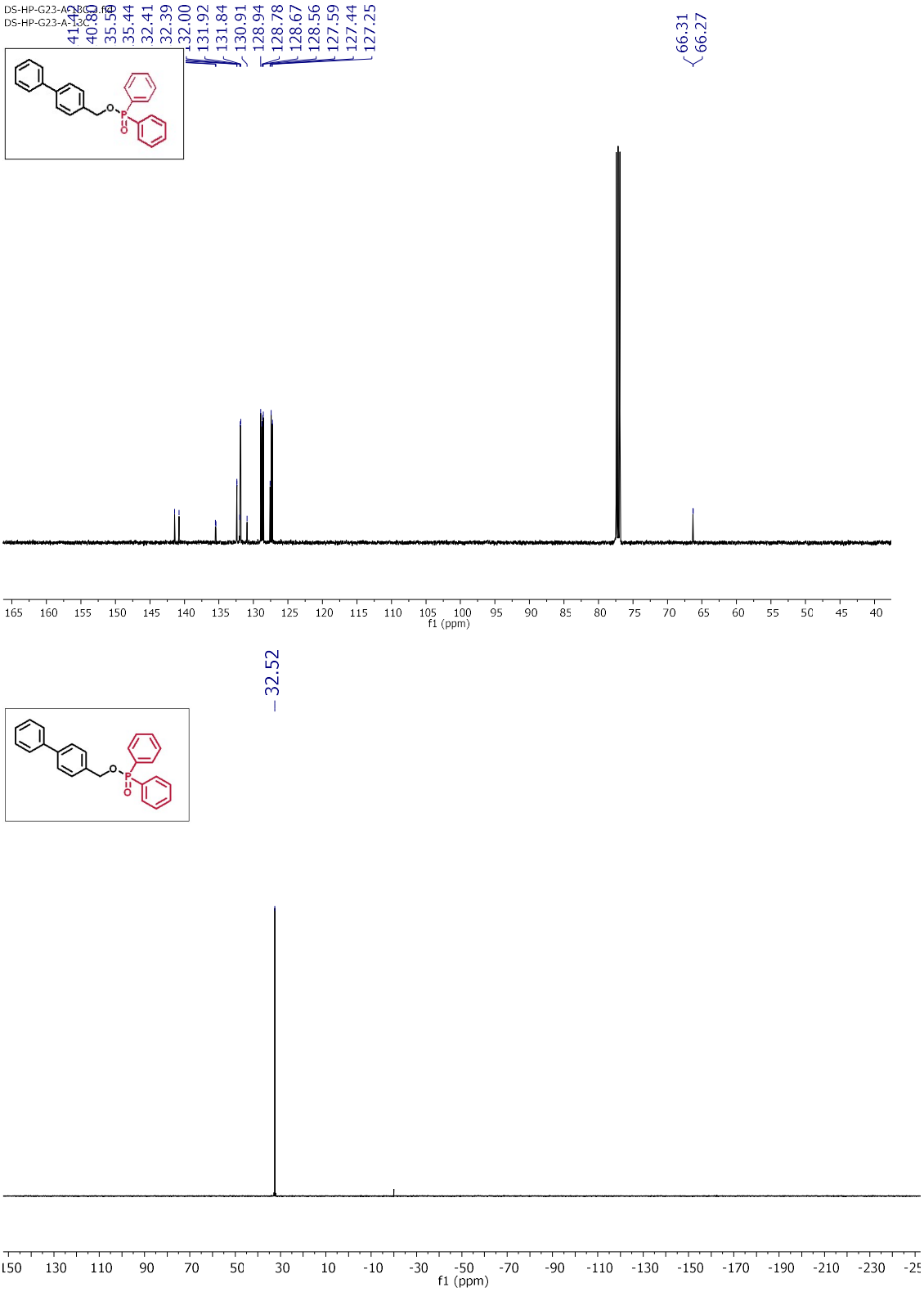
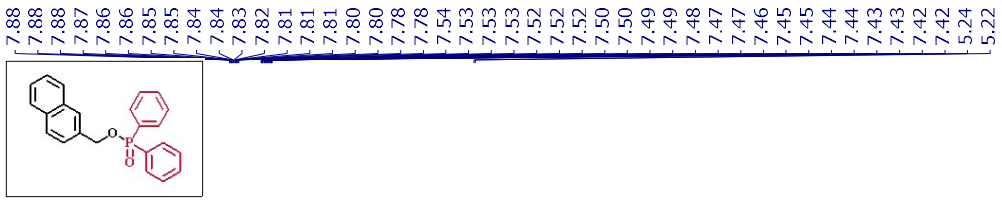
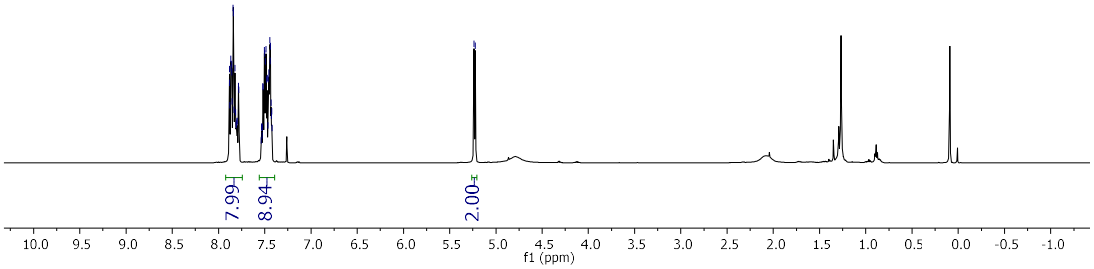
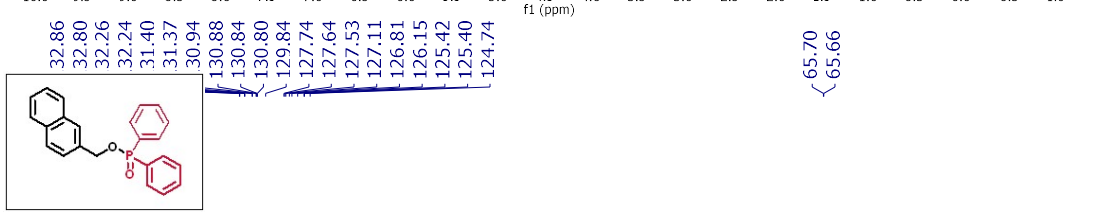
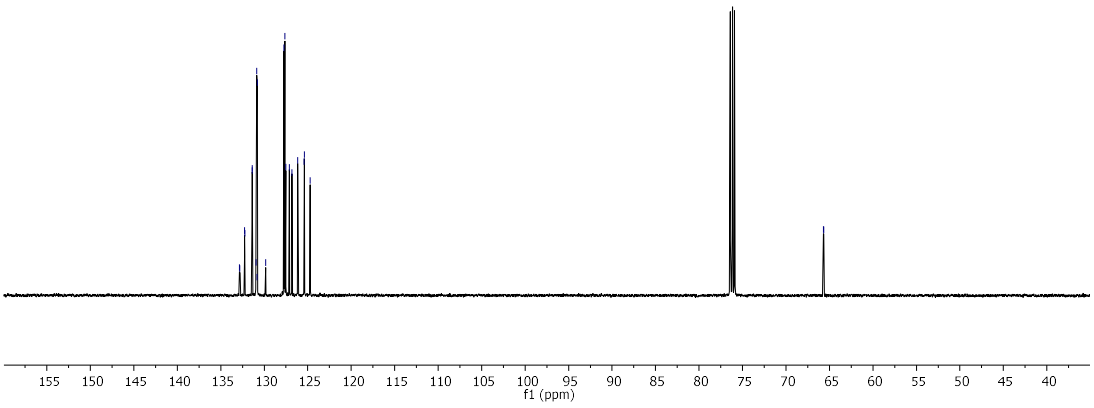


Figure S60. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4i in $CDCl_3$


7.88
7.88
7.88
7.87
7.86
7.86
7.85
7.85
7.84
7.84
7.83
7.82
7.81
7.81
7.81
7.80
7.80
7.78
7.78
7.54
7.53
7.53
7.52
7.52
7.52
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
5.24
5.22


7.99
8.94
2.00
f1 (ppm)


32.86
32.80
32.26
32.24
31.40
31.37
30.94
130.88
130.84
130.80
129.84
127.74
127.64
127.53
127.11
126.81
126.15
125.42
125.40
124.74
65.70
65.66


f1 (ppm)

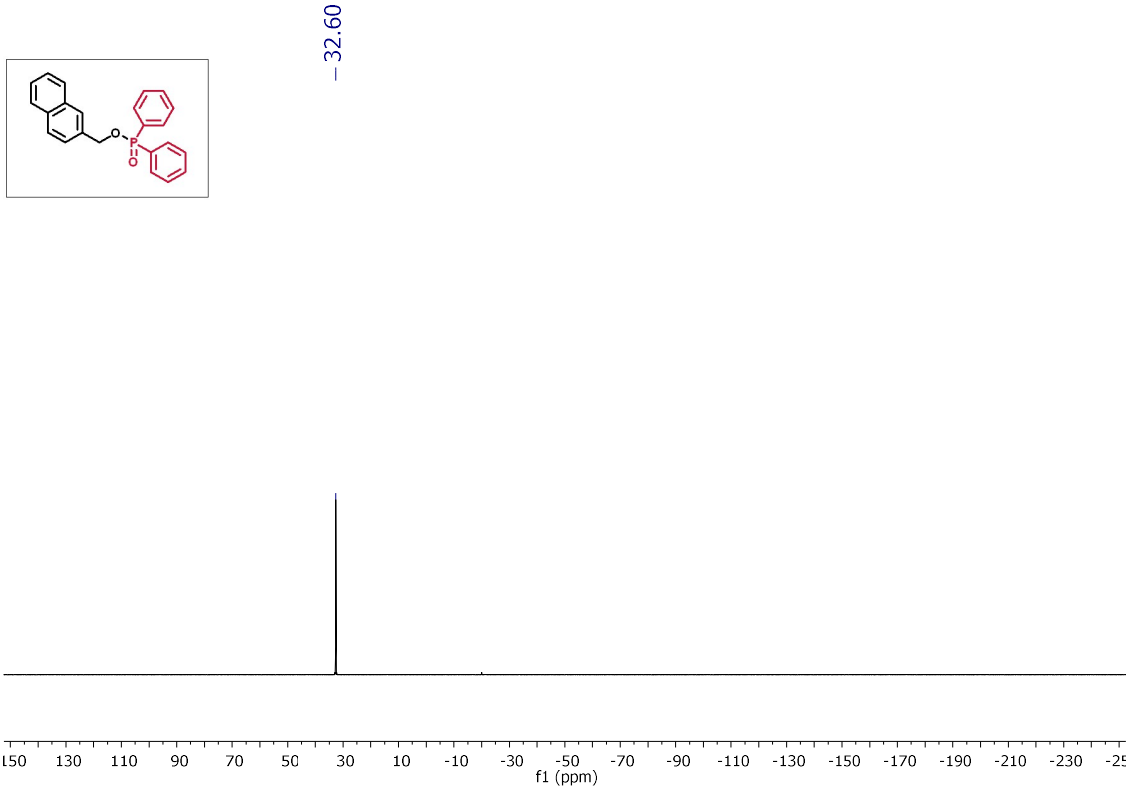
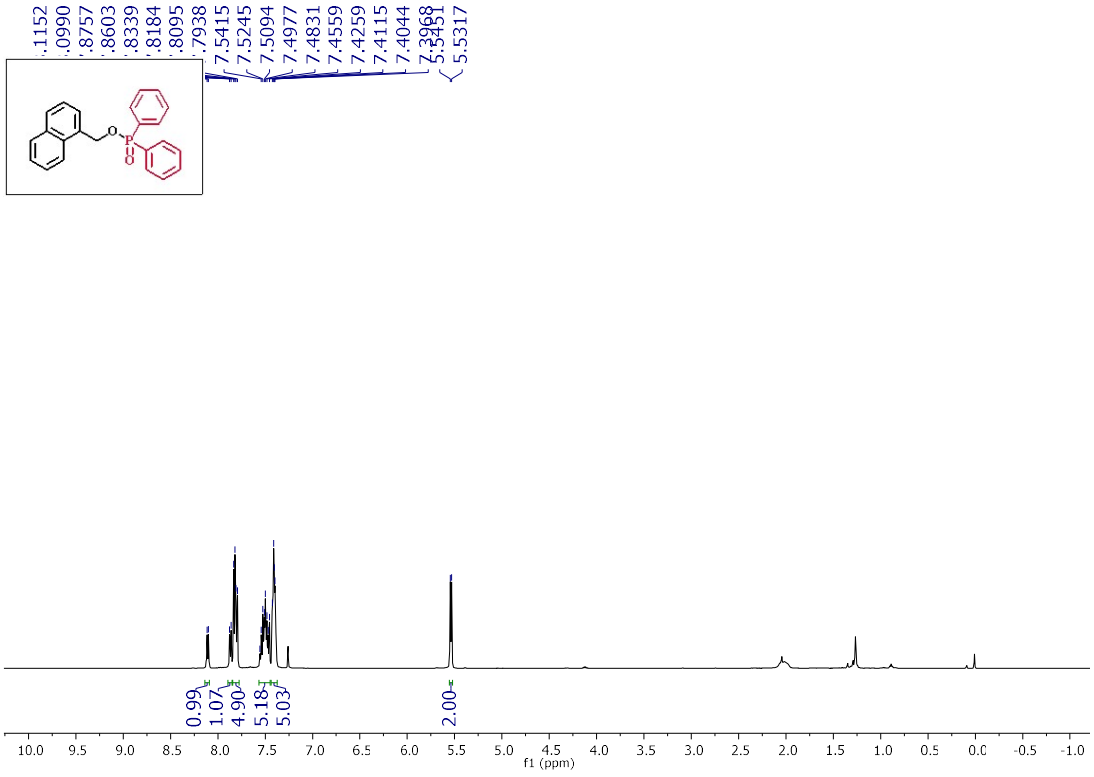


Figure S61. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4j in $CDCl_3$



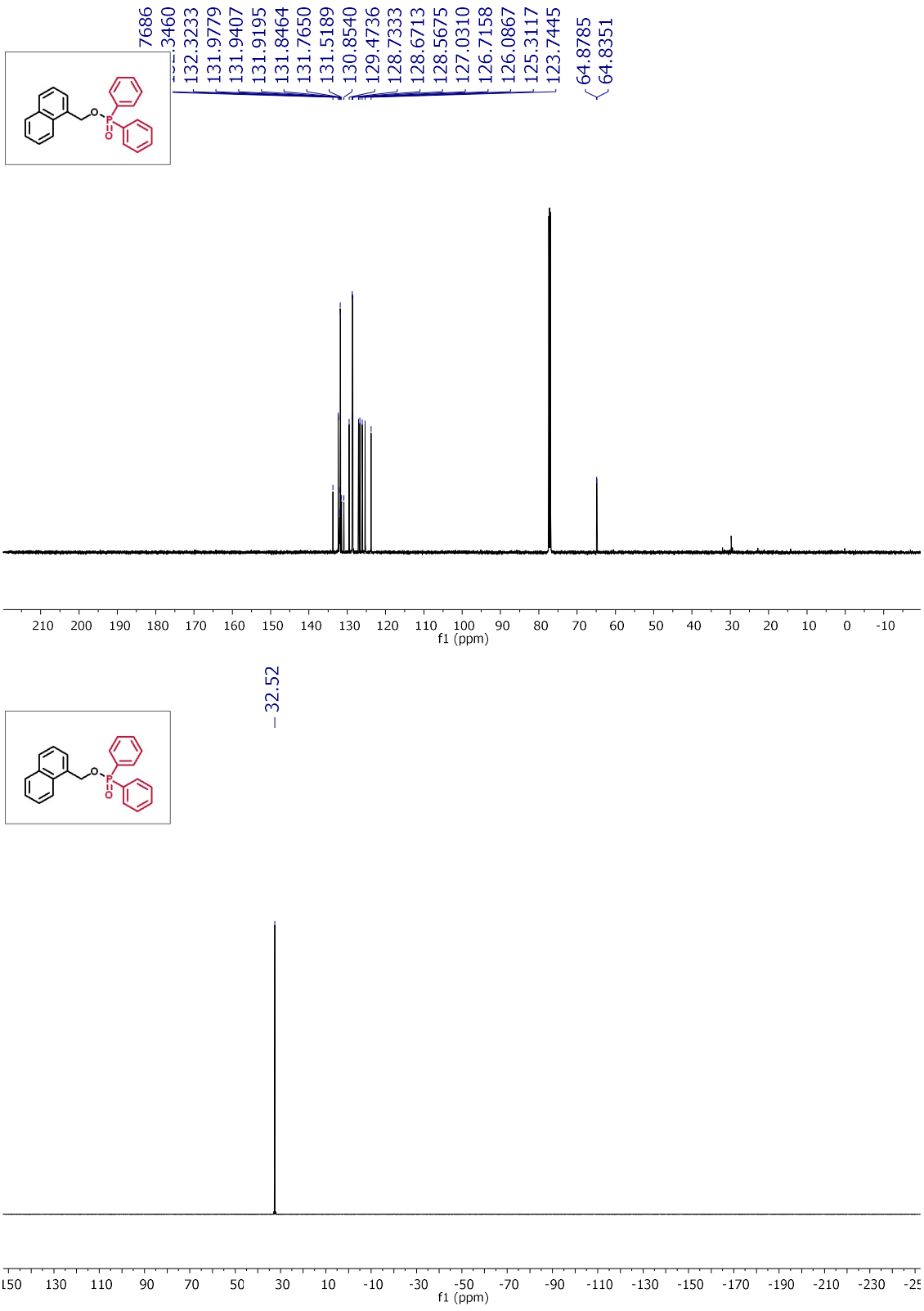
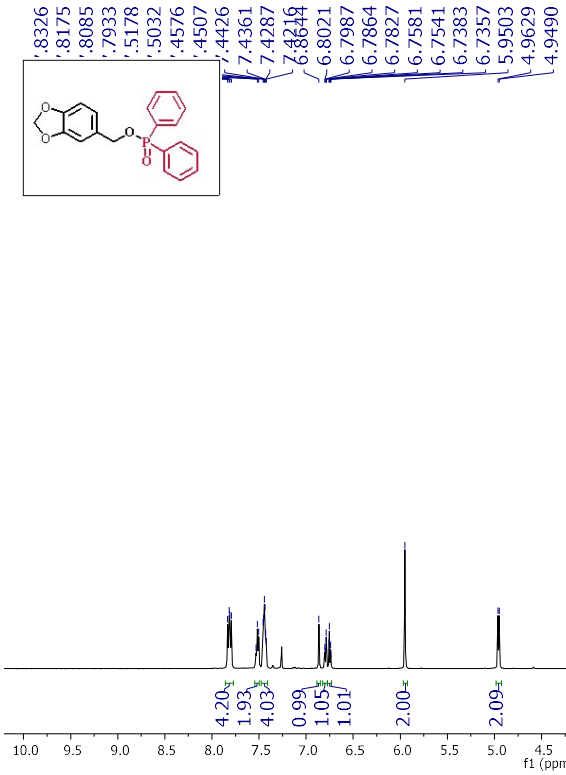
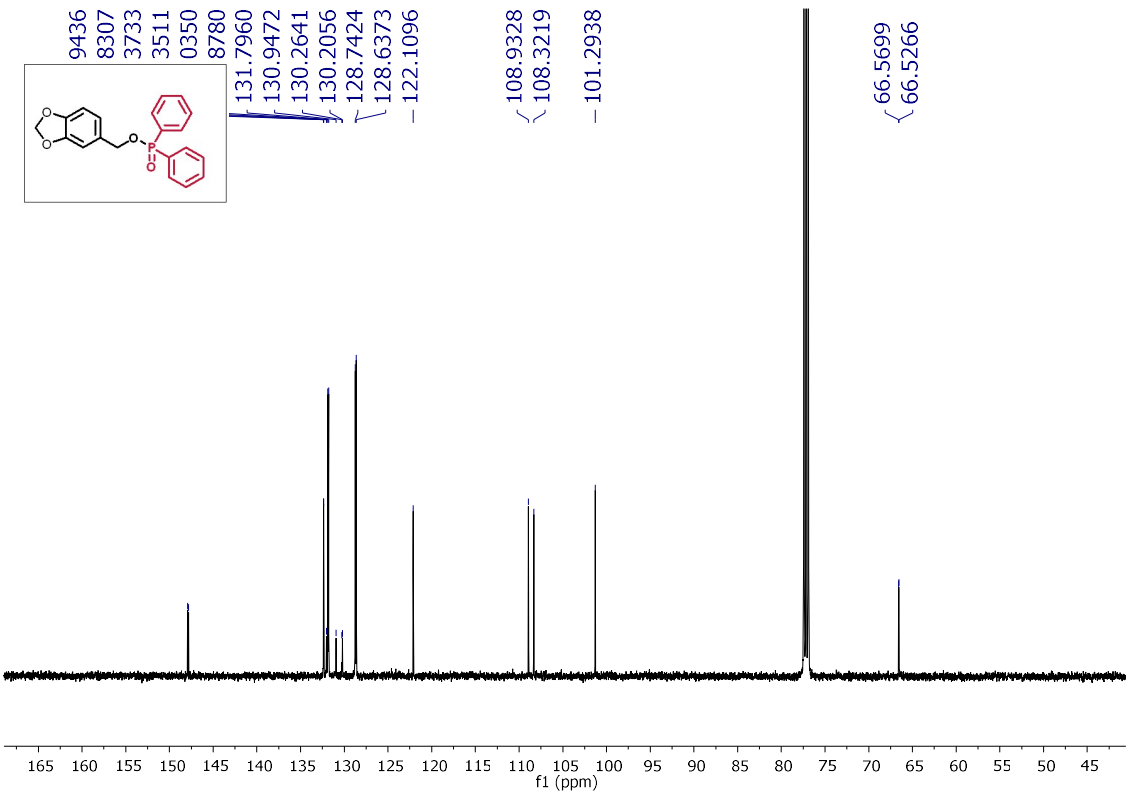


Figure S62. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4k in $CDCl_3$


8326
8175
8085
7933
5178
5032
4576
4507
4426
7.4361
7.4287
6.8644
6.8021
6.7987
6.7864
6.7827
6.7581
6.7541
6.7383
6.7357
5.9503
4.9629
4.9490
4.20
1.93
4.03
0.99
1.05
1.01
2.00
2.09
f1 (ppm)


9436
8307
3733
3511
0350
8780
131.7960
130.9472
130.2641
130.2056
128.7424
128.6373
122.1096
108.9328
108.3219
101.2938
66.5699
66.5266
f1 (ppm)

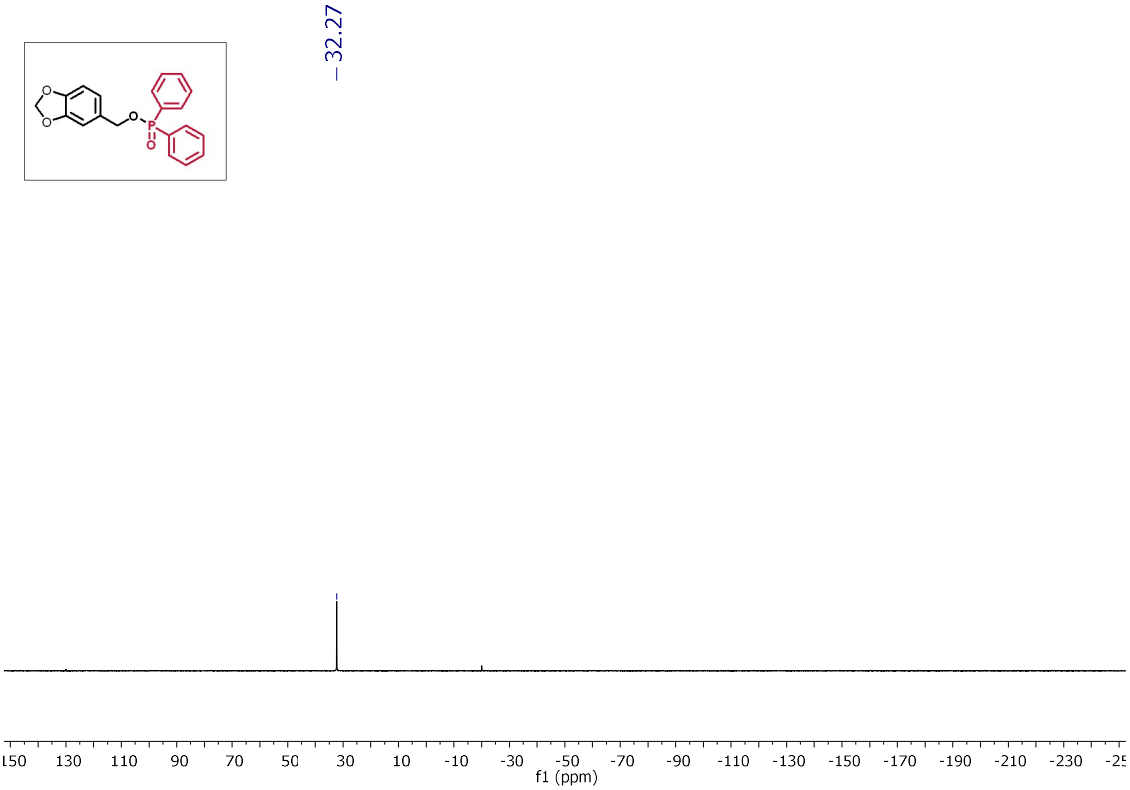
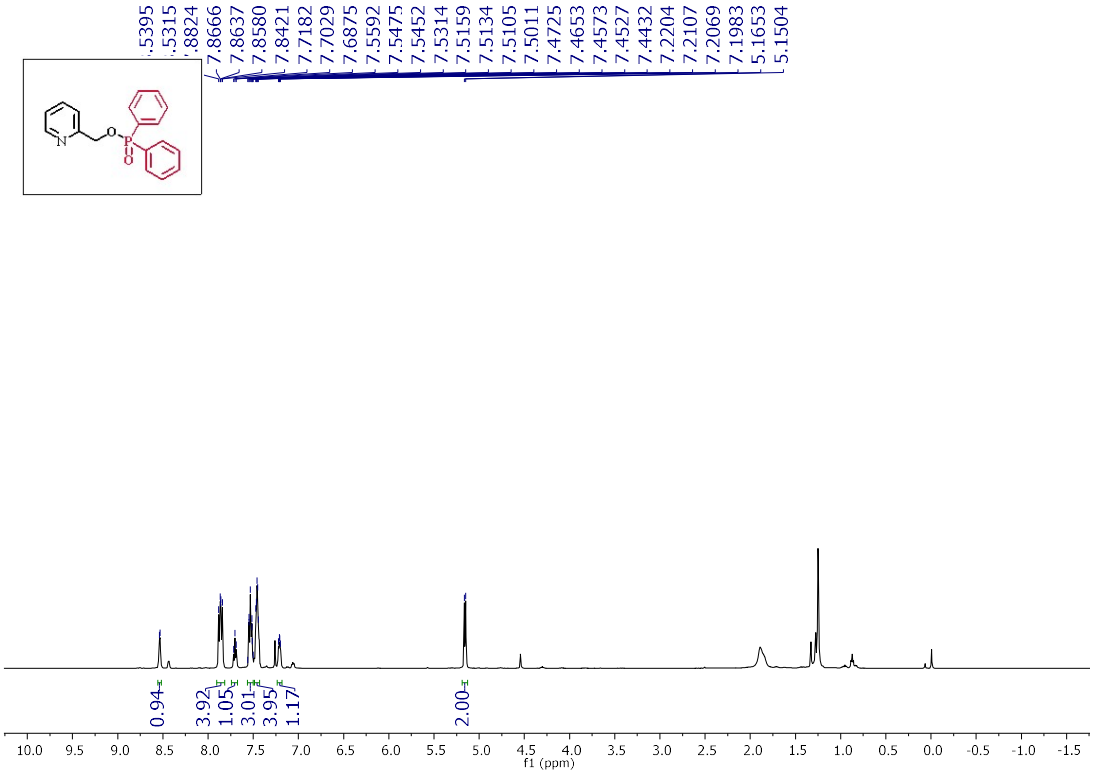


Figure S63. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4n in $CDCl_3$



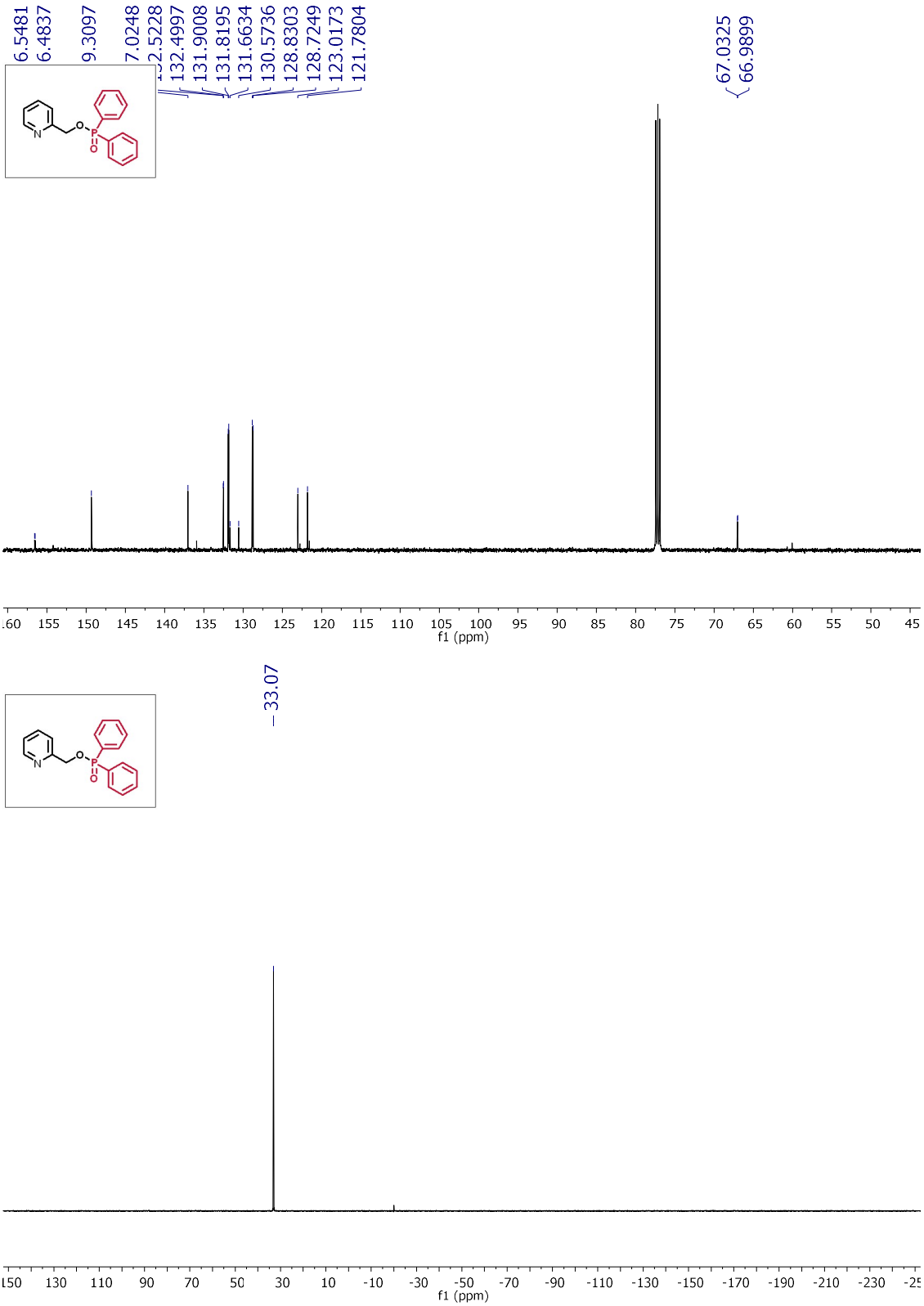
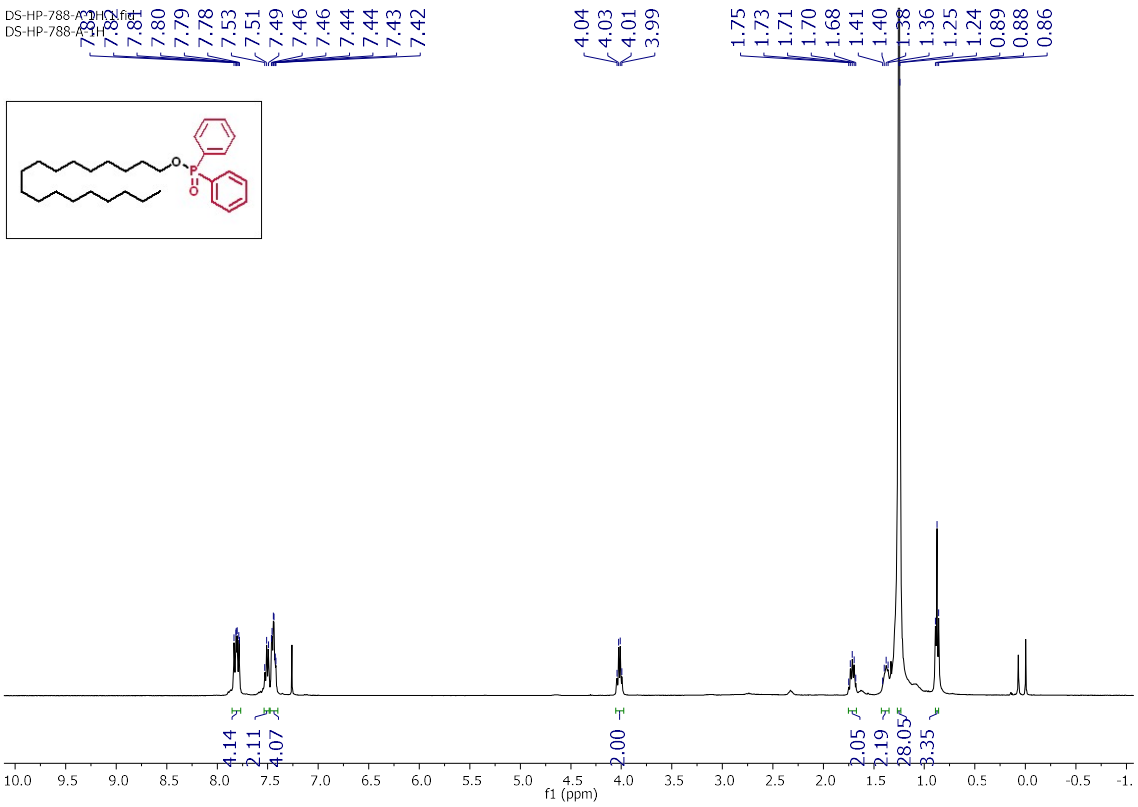
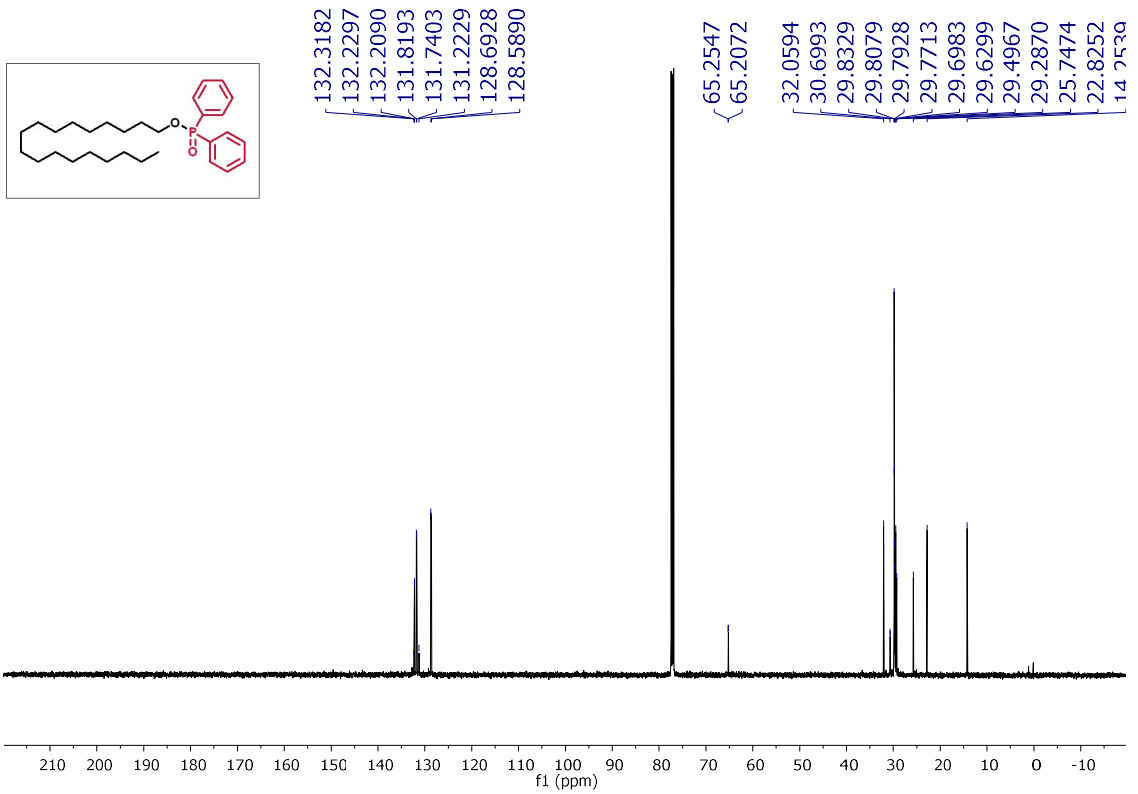


Figure S64. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4o in $CDCl_3$


DS-HP-788-A31H.fid
7.81
7.80
7.79
7.78
7.53
7.51
7.49
7.46
7.46
7.44
7.44
7.43
7.42
4.04
4.03
4.01
3.99
1.75
1.73
1.71
1.70
1.68
1.41
1.40
1.38
1.36
1.25
1.24
0.89
0.88
0.86
4.14
2.11
4.07
2.00
2.05
2.19
28.05
3.35
f1 (ppm)


132.3182
132.2297
132.2090
131.8193
131.7403
131.2229
128.6928
128.5890
65.2547
65.2072
32.0594
30.6993
29.8329
29.8079
29.7928
29.7713
29.6983
29.6299
29.4967
29.2870
25.7474
22.8252
f1 (ppm)

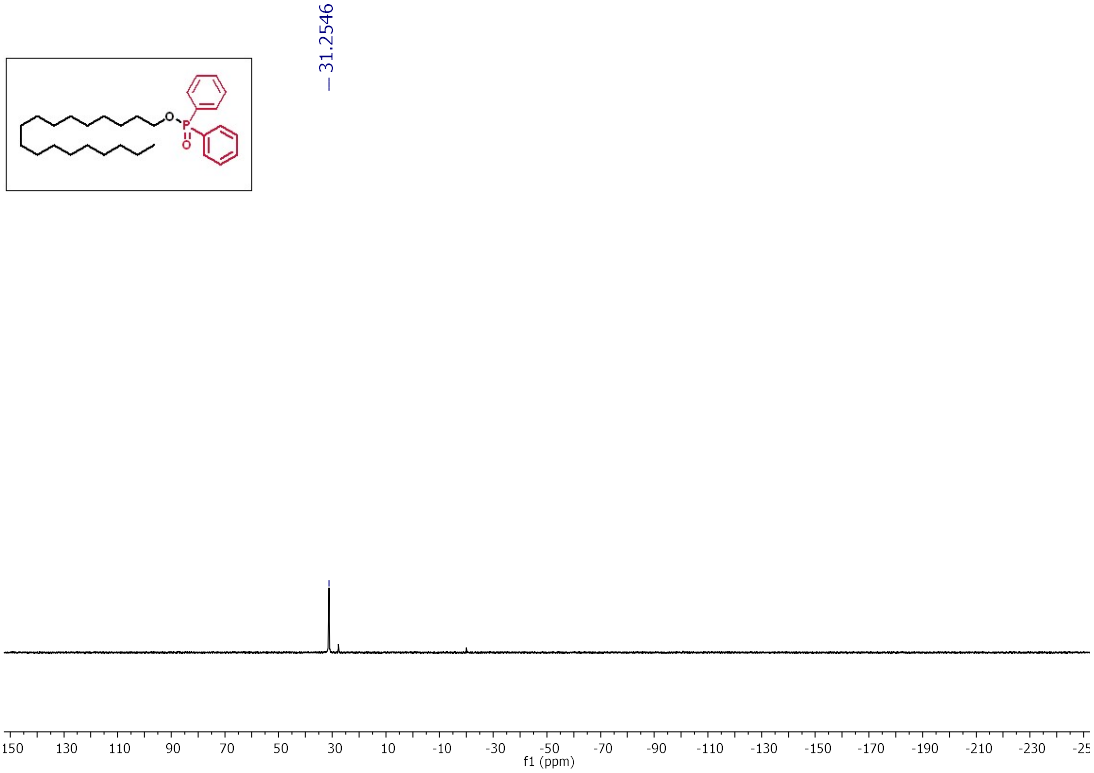
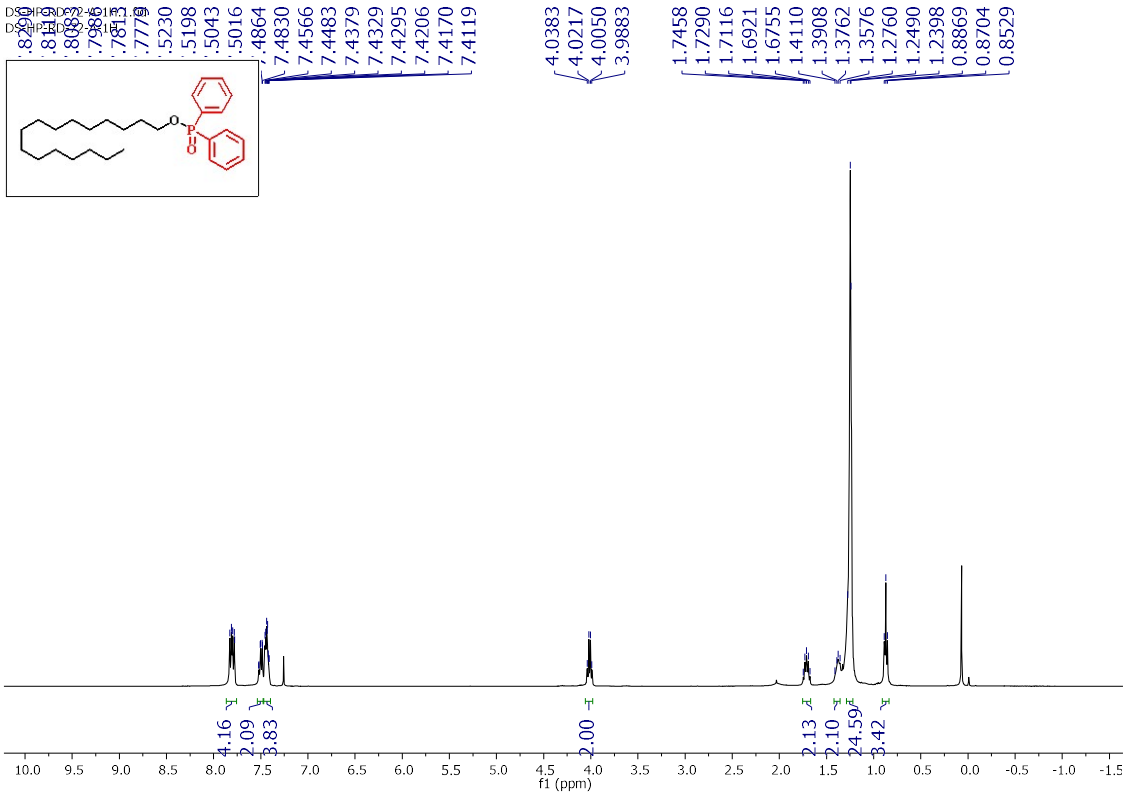
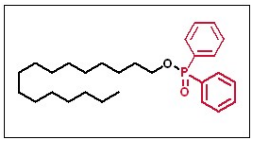


Figure S65. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4p in $CDCl_3$

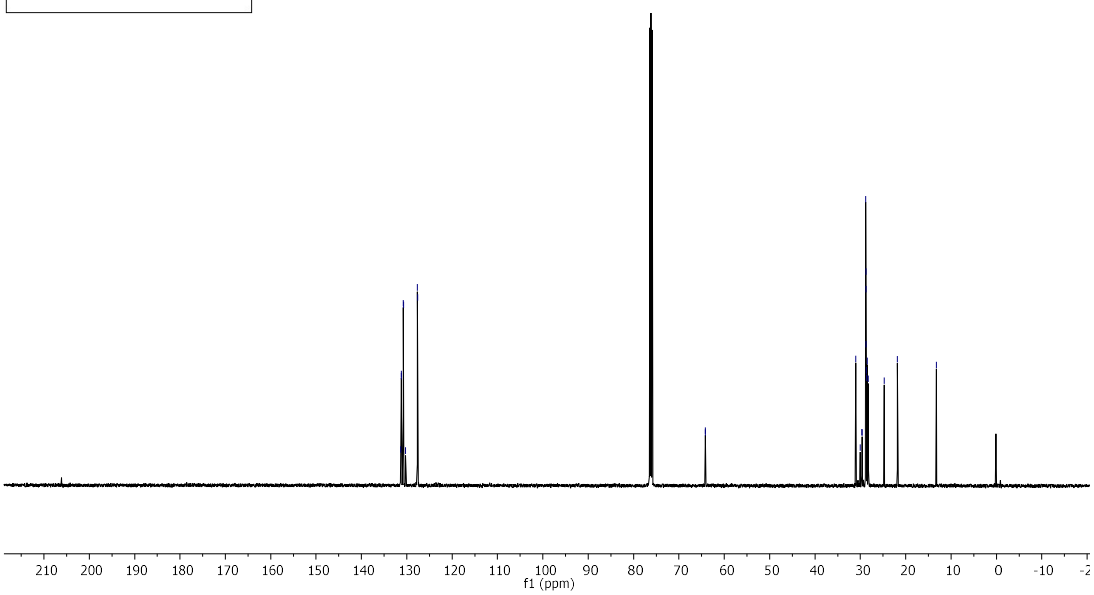


DS-HP-RD-72-A-13C.3.fid
DS-HP-RD-72-A-13C

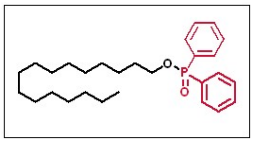


131.3351
131.2013
131.1794
130.7968
130.7165
130.2451
127.6724
127.5685

64.1911
64.1409
31.0453
30.0525
29.6864
29.6342
28.8146
28.7943
28.7798
28.7577
28.6845
28.6167
28.4846
28.2717
24.7327
21.8141
13.2487



31.16



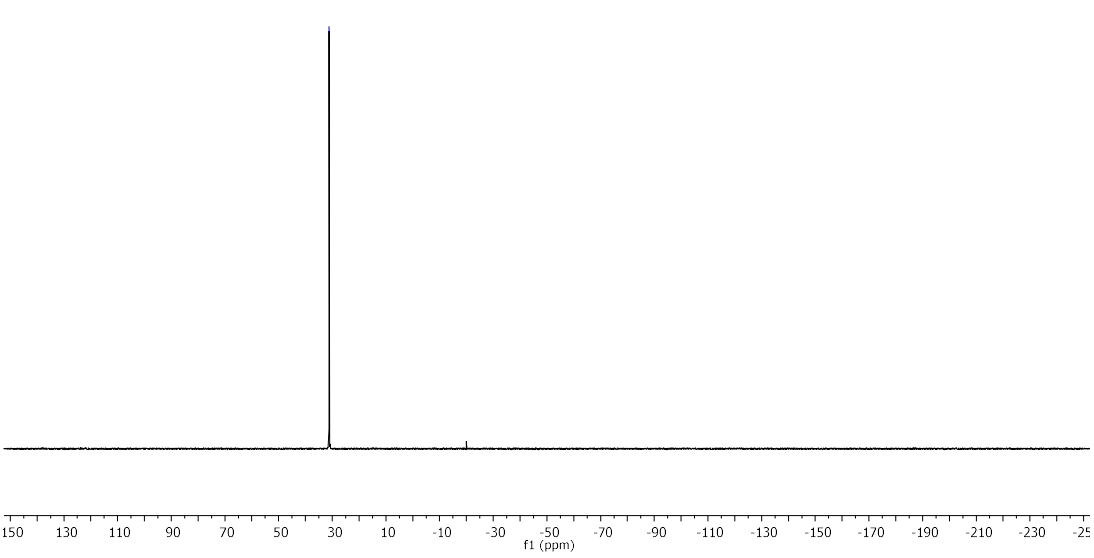
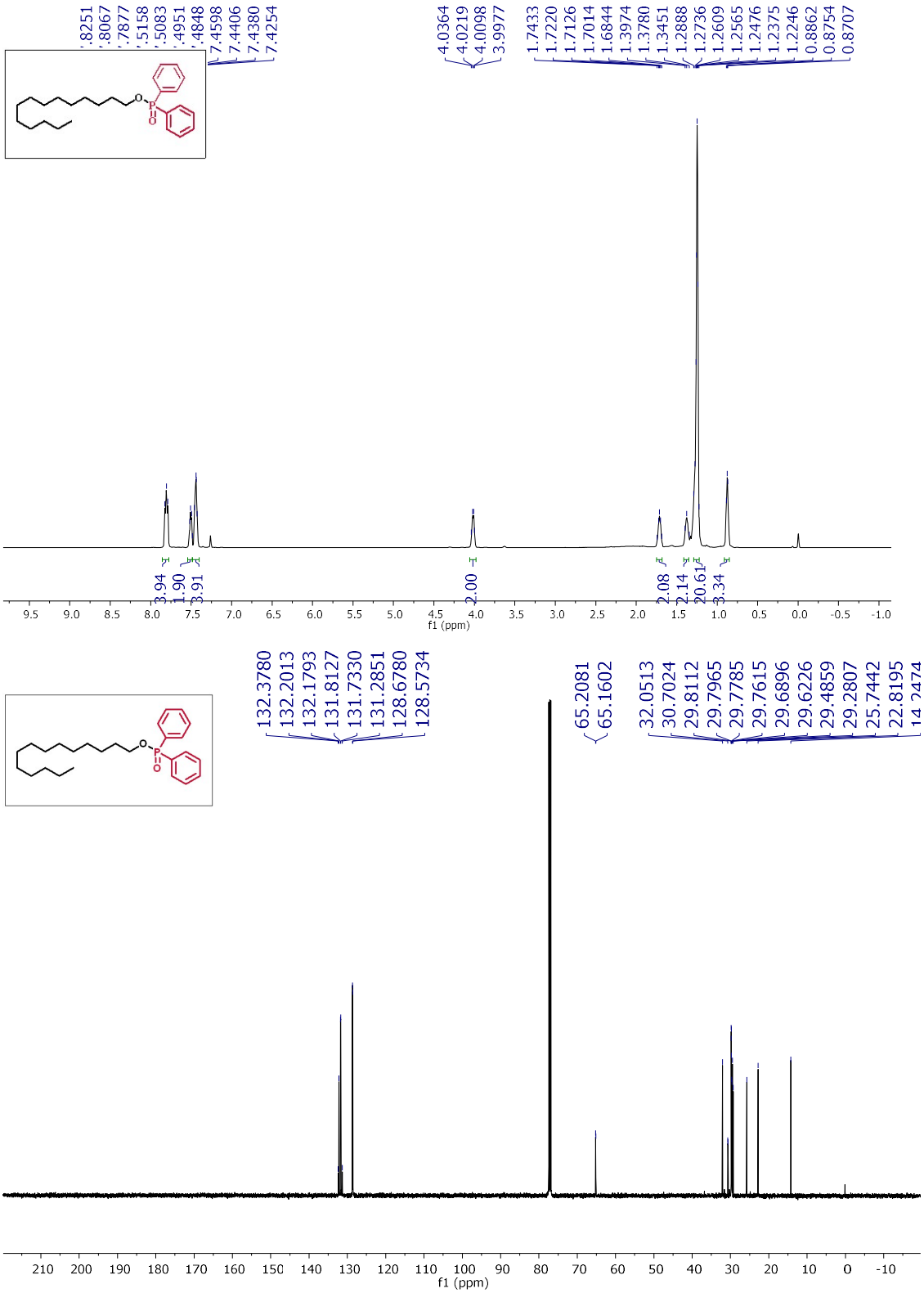


Figure S66. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4q in $CDCl_3$



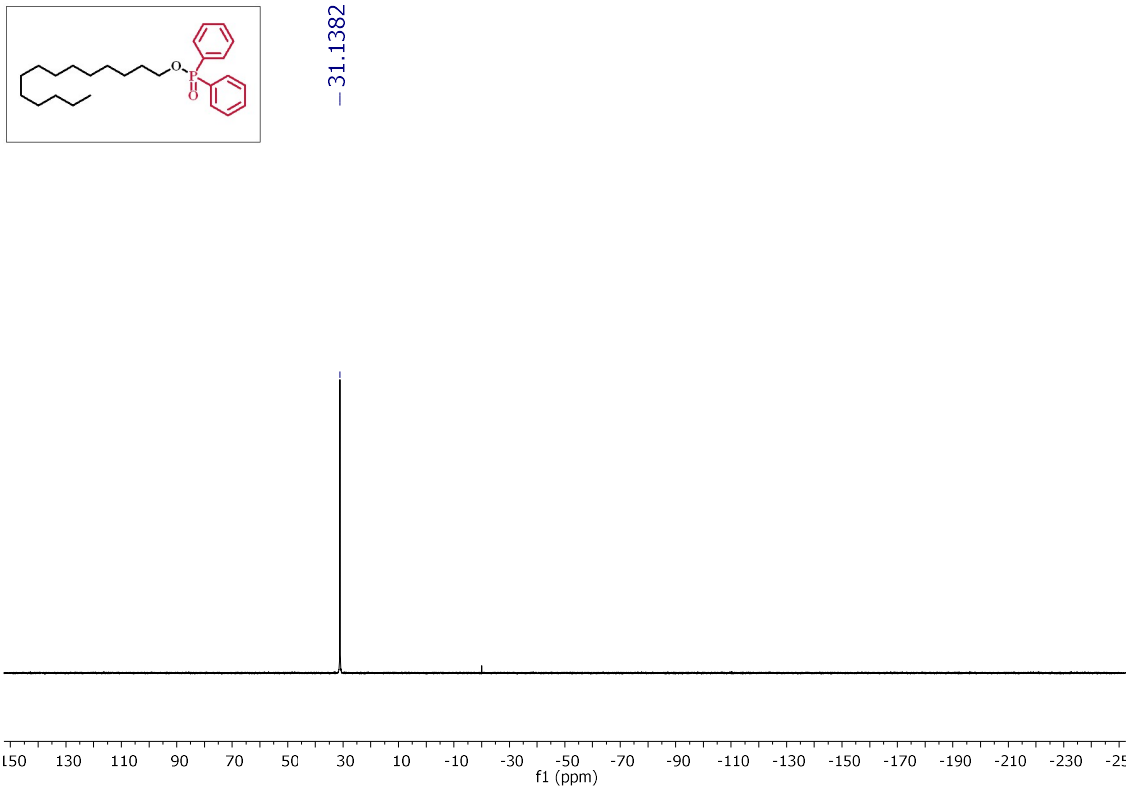
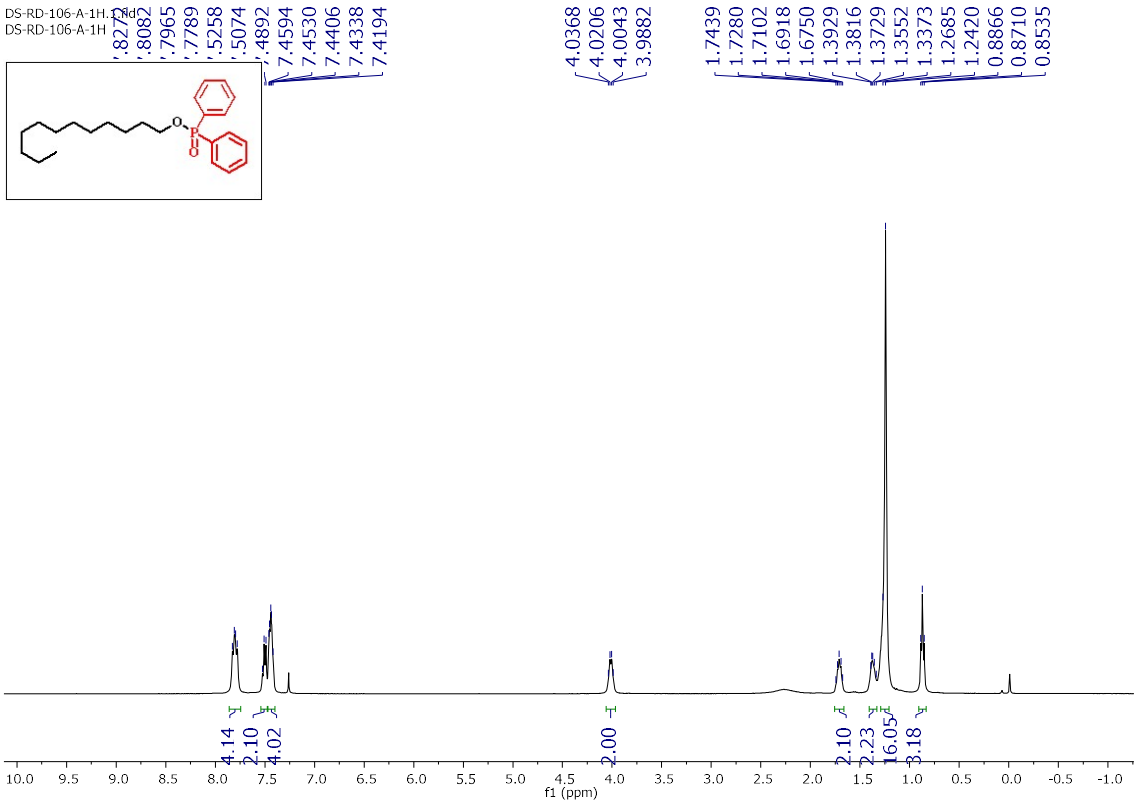
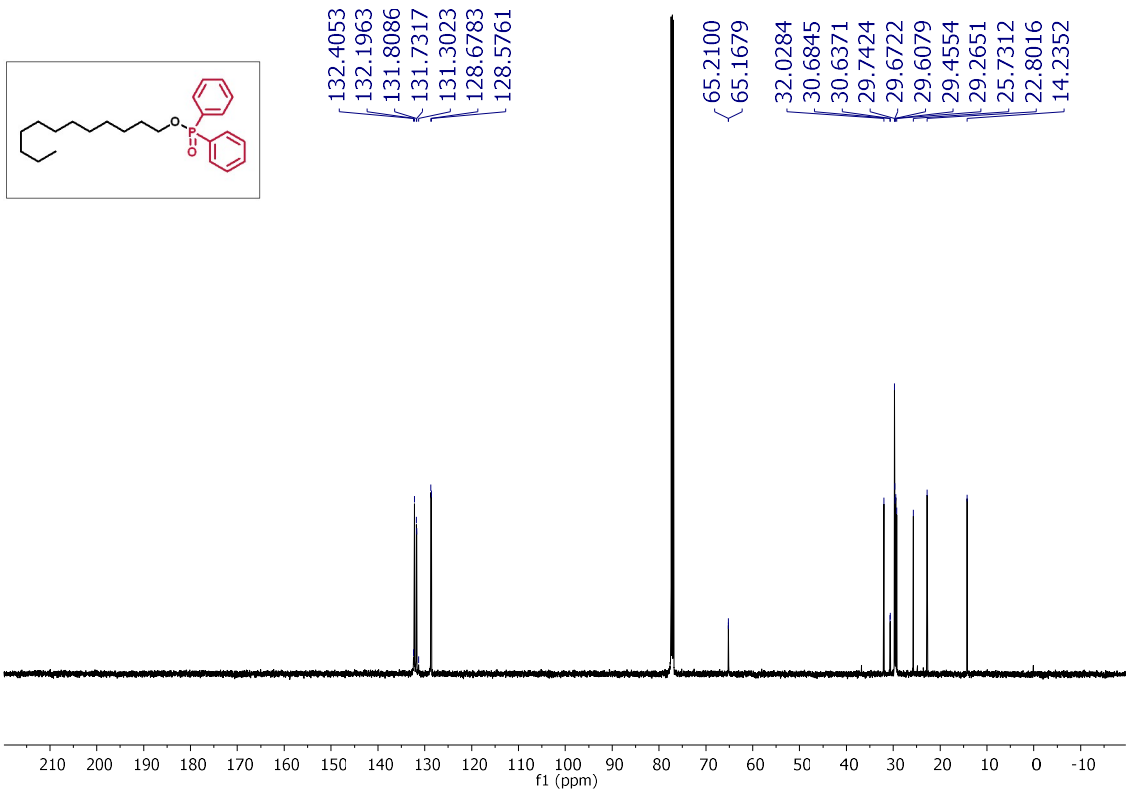


Figure S67. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4r in $CDCl_3$


DS-RD-106-A-1H.1.fid
DS-RD-106-A-1H
7.8274
7.8082
7.7965
7.7789
7.5258
7.5074
7.4892
7.4594
7.4530
7.4406
7.4338
7.4194
4.0368
4.0206
4.0043
3.9882
1.7439
1.7280
1.7102
1.6918
1.6750
1.3929
1.3816
1.3729
1.3552
1.3373
1.2685
1.2420
0.8866
0.8710
0.8535
4.14
2.10
4.02
2.00
2.10
2.23
16.05
3.18
f1 (ppm)


132.4053
132.1963
131.8086
131.7317
131.3023
128.6783
128.5761
65.2100
65.1679
32.0284
30.6845
30.6371
29.7424
29.6722
29.6079
29.4554
29.2651
25.7312
22.8016
14.2352
f1 (ppm)

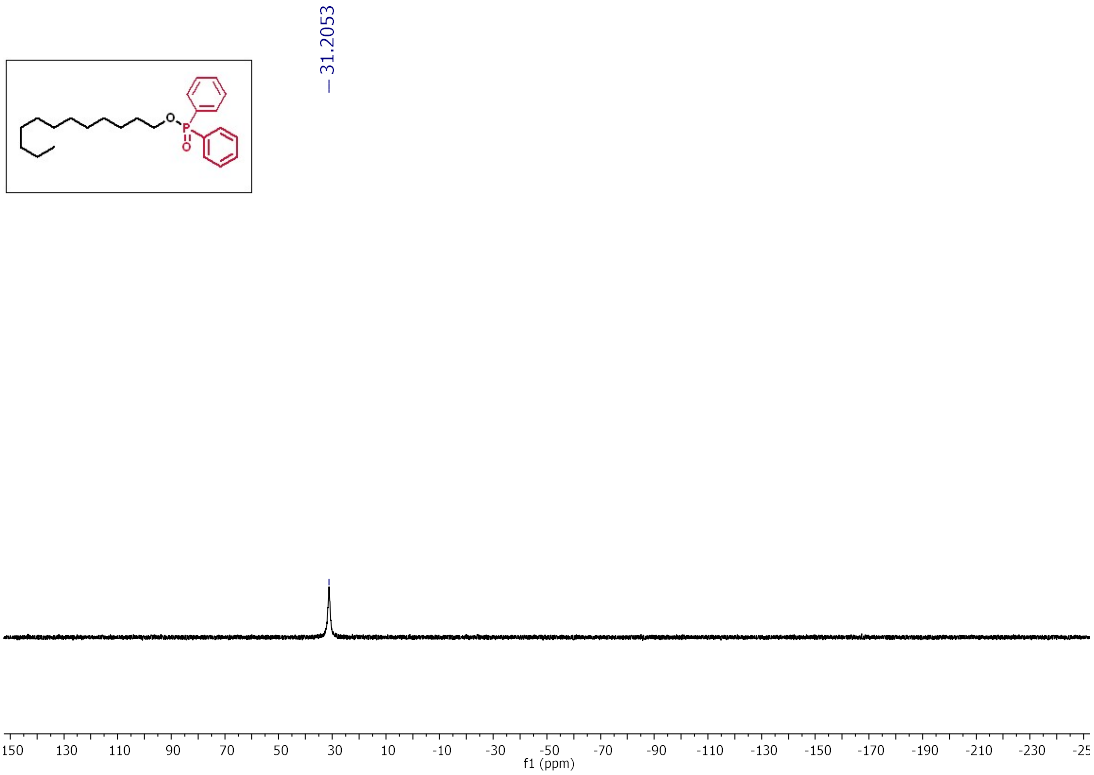
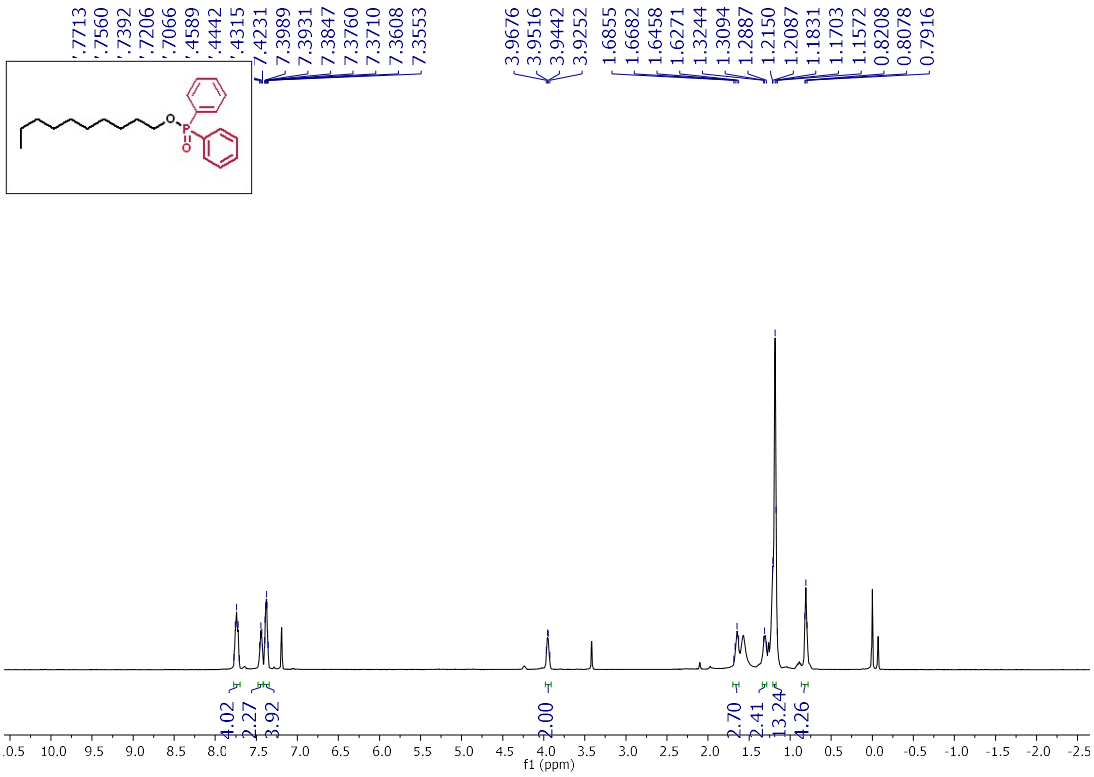


Figure S68. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4s in $CDCl_3$



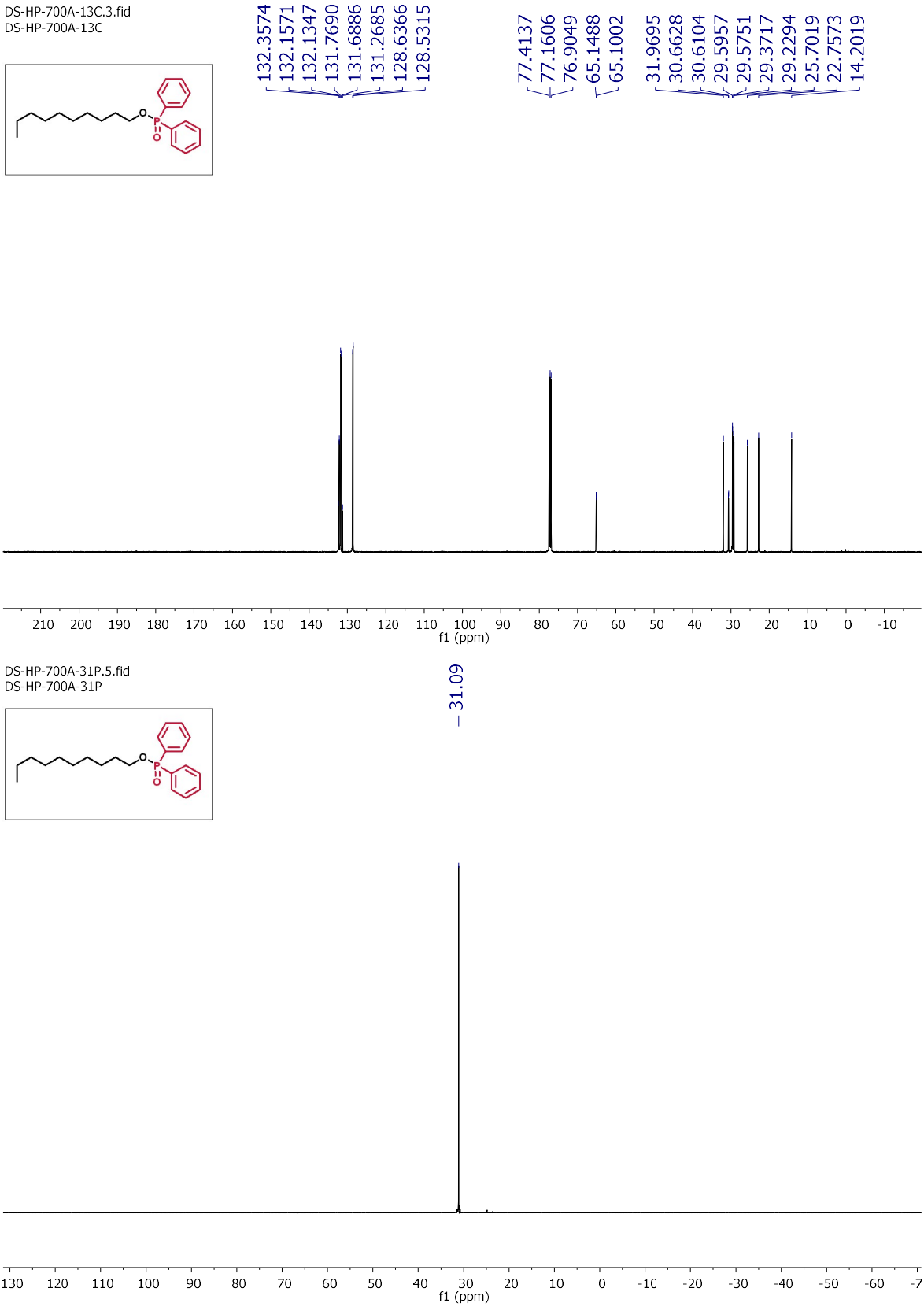
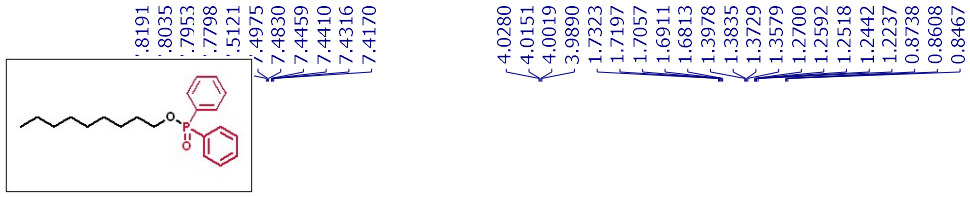
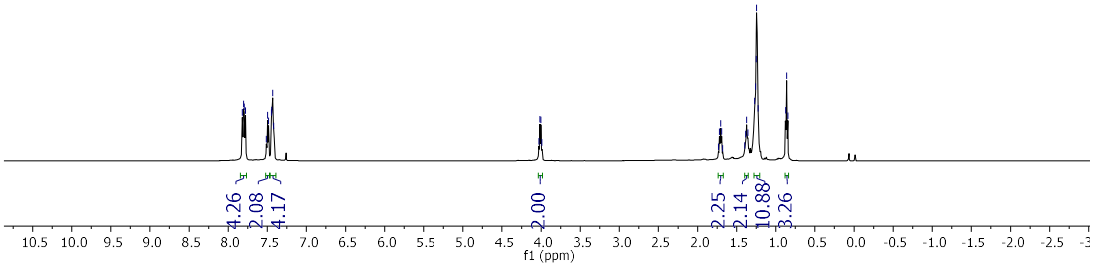
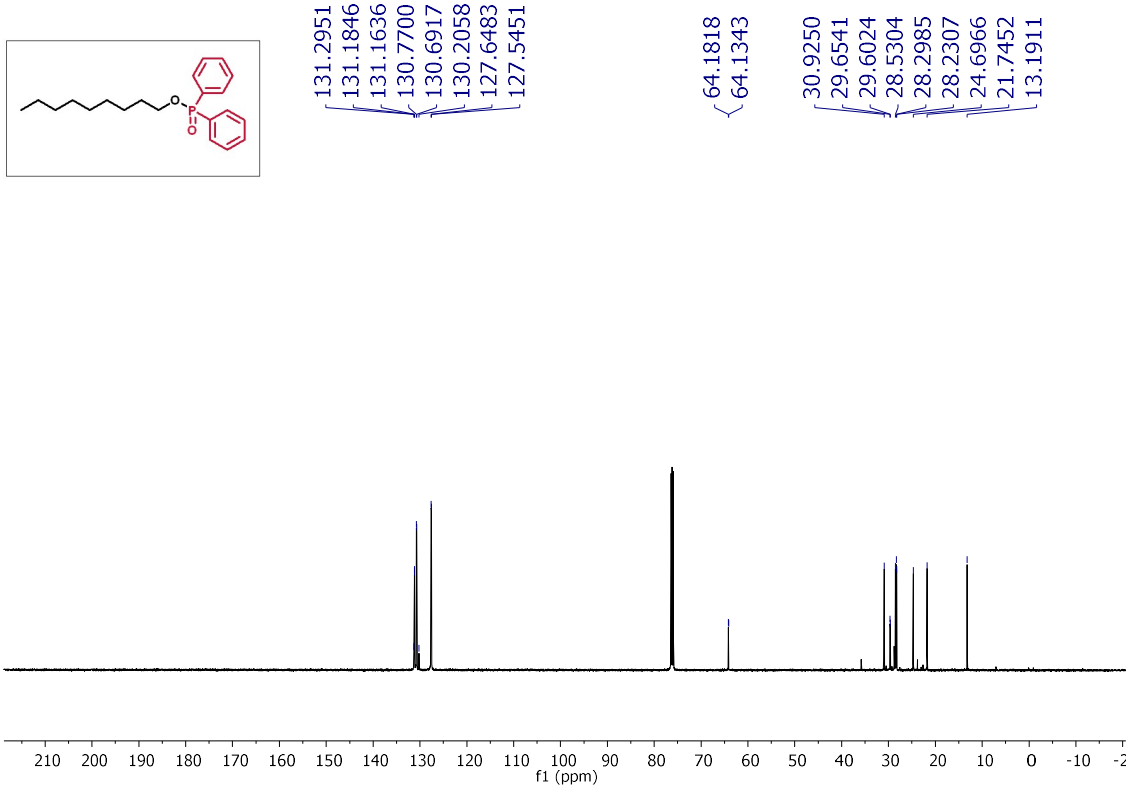


Figure S69. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4t in $CDCl_3$


8191
8035
7953
7798
5121
4975
4830
4459
4410
4316
4170
4.0280
4.0151
4.0019
3.9890
1.7323
1.7197
1.7057
1.6911
1.6813
1.3978
1.3835
1.3729
1.3579
1.2700
1.2592
1.2518
1.2442
1.2237
0.8738
0.8608
0.8467


4.26
2.08
4.17
2.00
2.25
2.14
10.88
3.26
f1 (ppm)


131.2951
131.1846
131.1636
130.7700
130.6917
130.2058
127.6483
127.5451
64.1818
64.1343
30.9250
29.6541
29.6024
28.5304
28.2985
28.2307
24.6966
21.7452
13.1911
f1 (ppm)

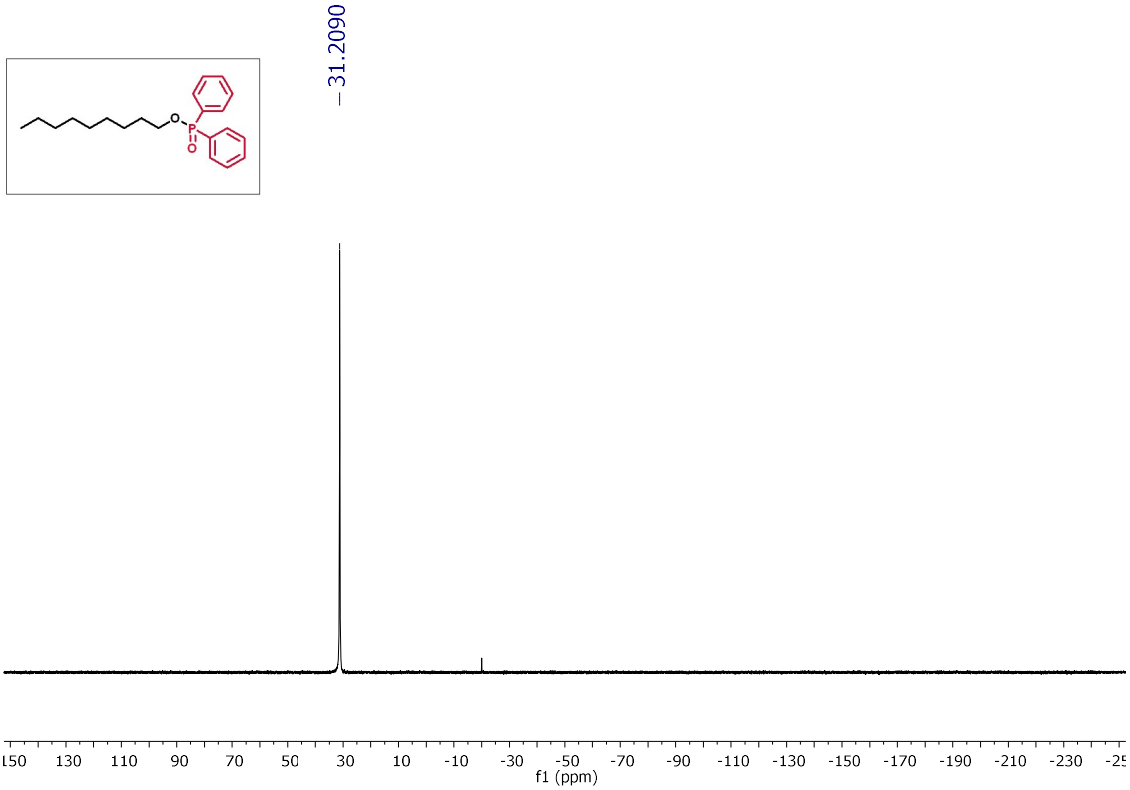
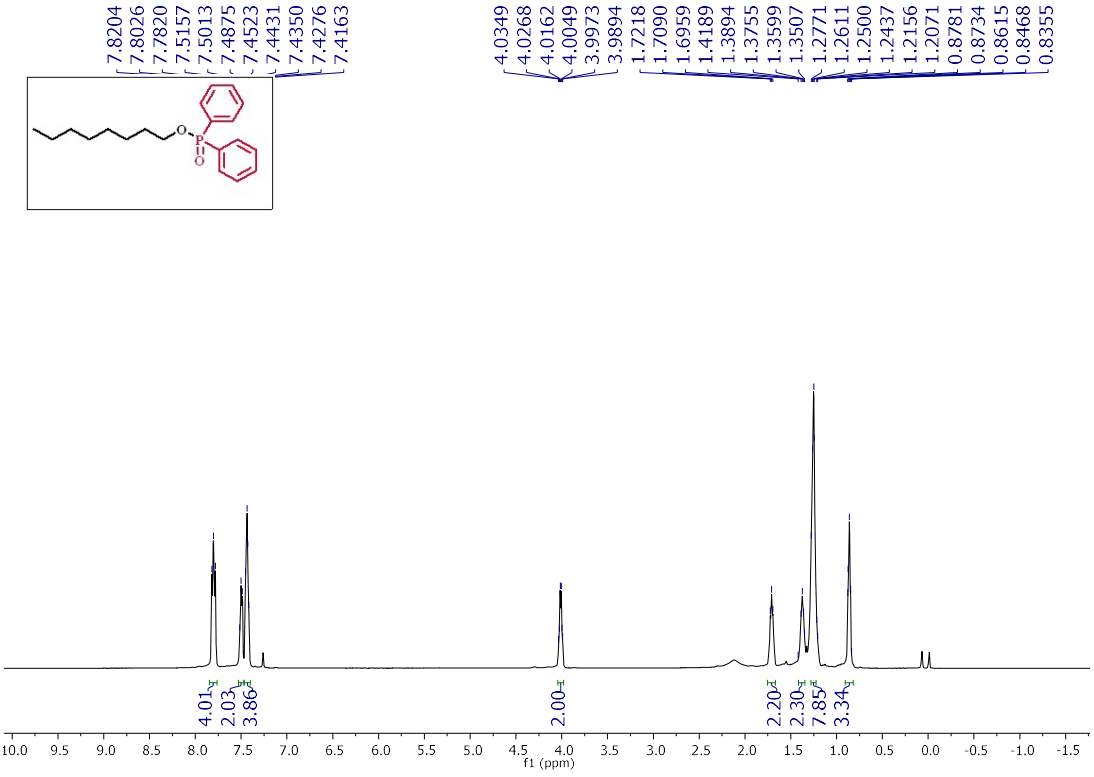


Figure S70. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4u in $CDCl_3$



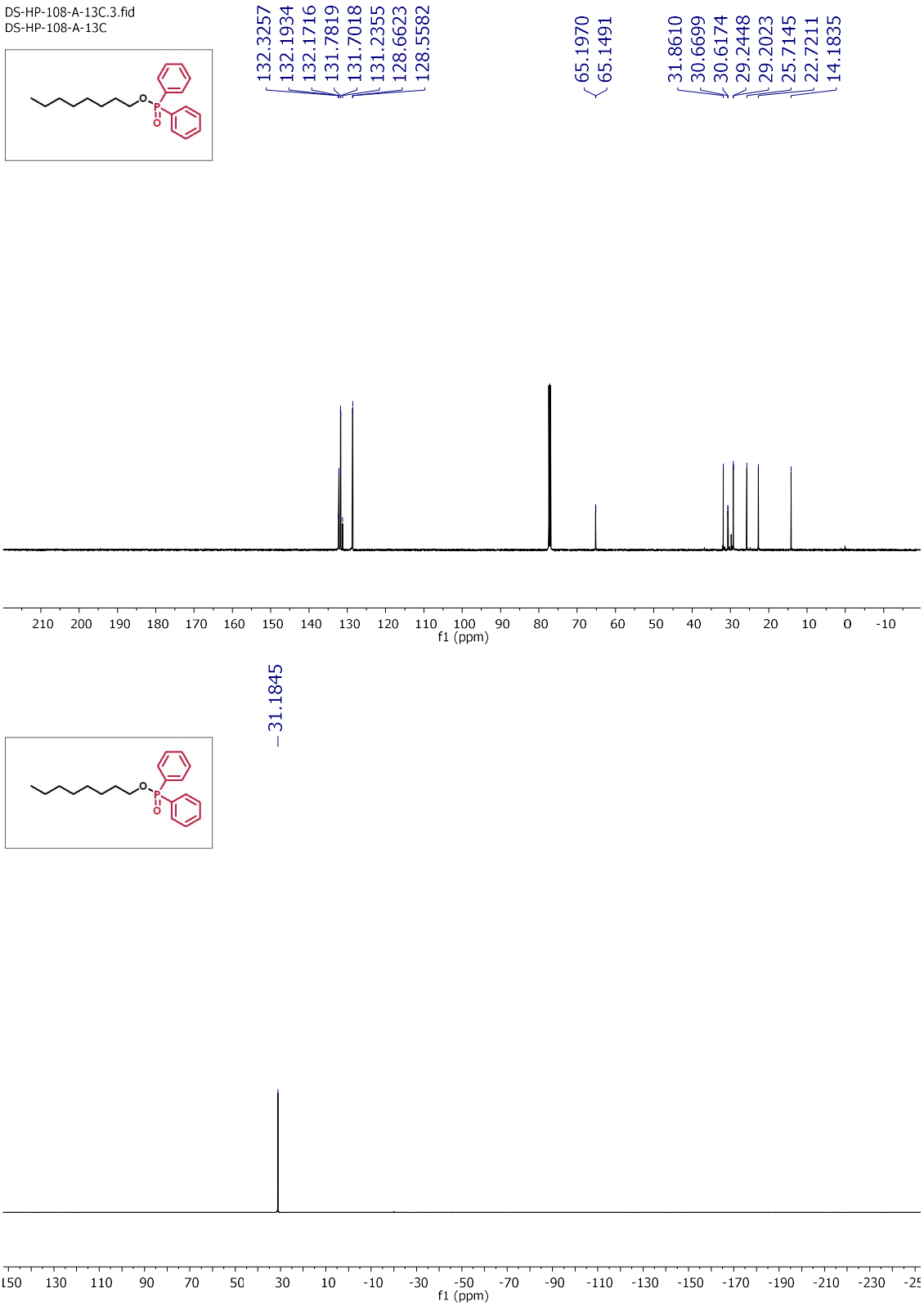
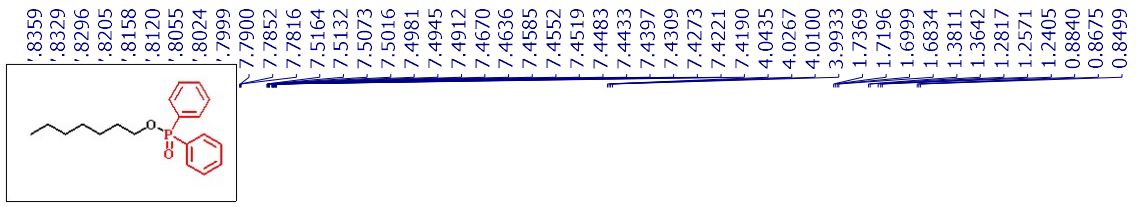
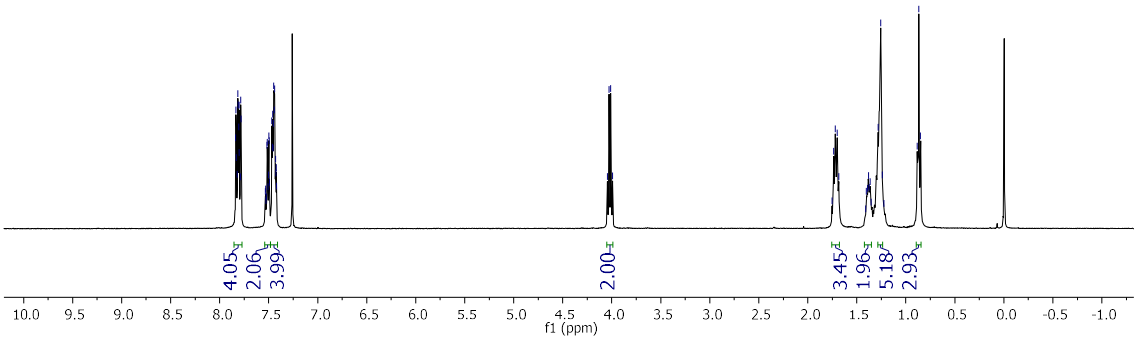
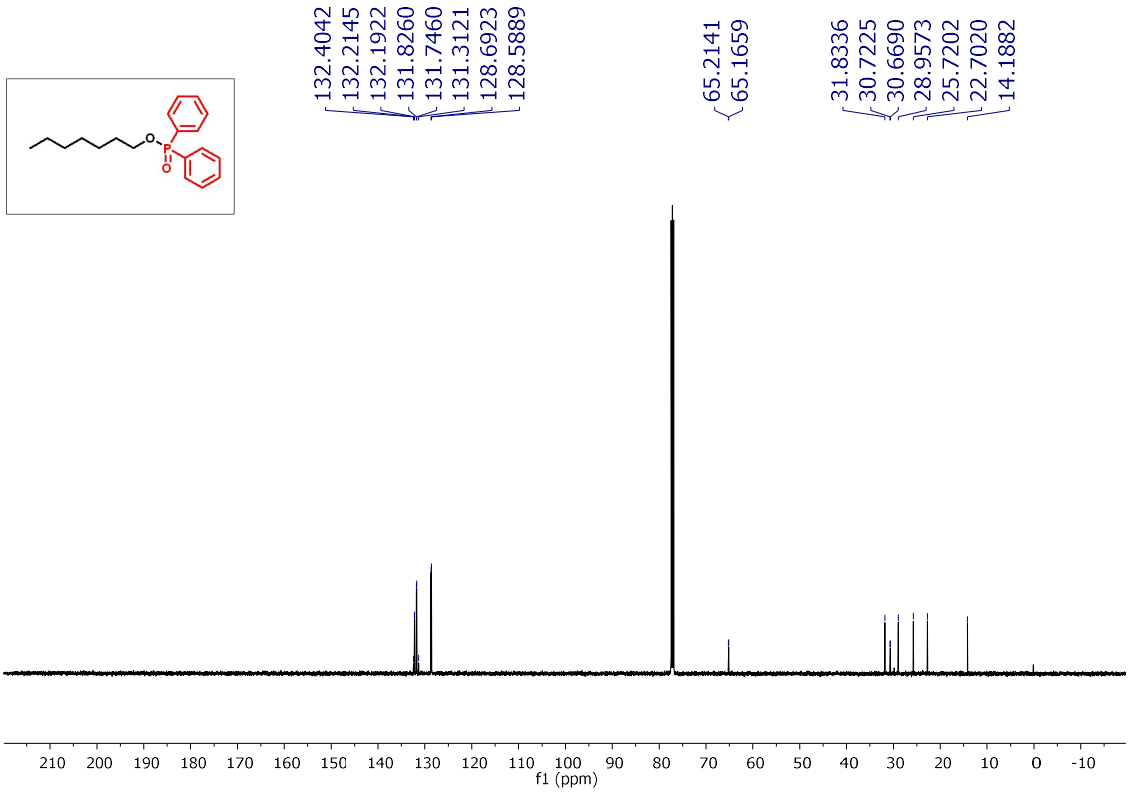


Figure S71. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4v in $CDCl_3$


8359
8329
8296
8205
8158
8120
8055
8024
7999
7900
7852
7816
7164
7132
7073
7016
4981
4945
4912
4670
4636
4585
4552
4519
4483
4433
4397
4309
4273
4221
4190
4035
4267
4100
3933
1369
1196
1999
1834
1811
1642
1817
1571
1405
0840
0675
0499


4.05
2.06
3.99
2.00
3.45
1.96
5.18
2.93
f1 (ppm)


132.4042
132.2145
132.1922
131.8260
131.7460
131.3121
128.6923
128.5889
65.2141
65.1659
31.8336
30.7225
30.6690
28.9573
25.7202
22.7020
14.1882
f1 (ppm)

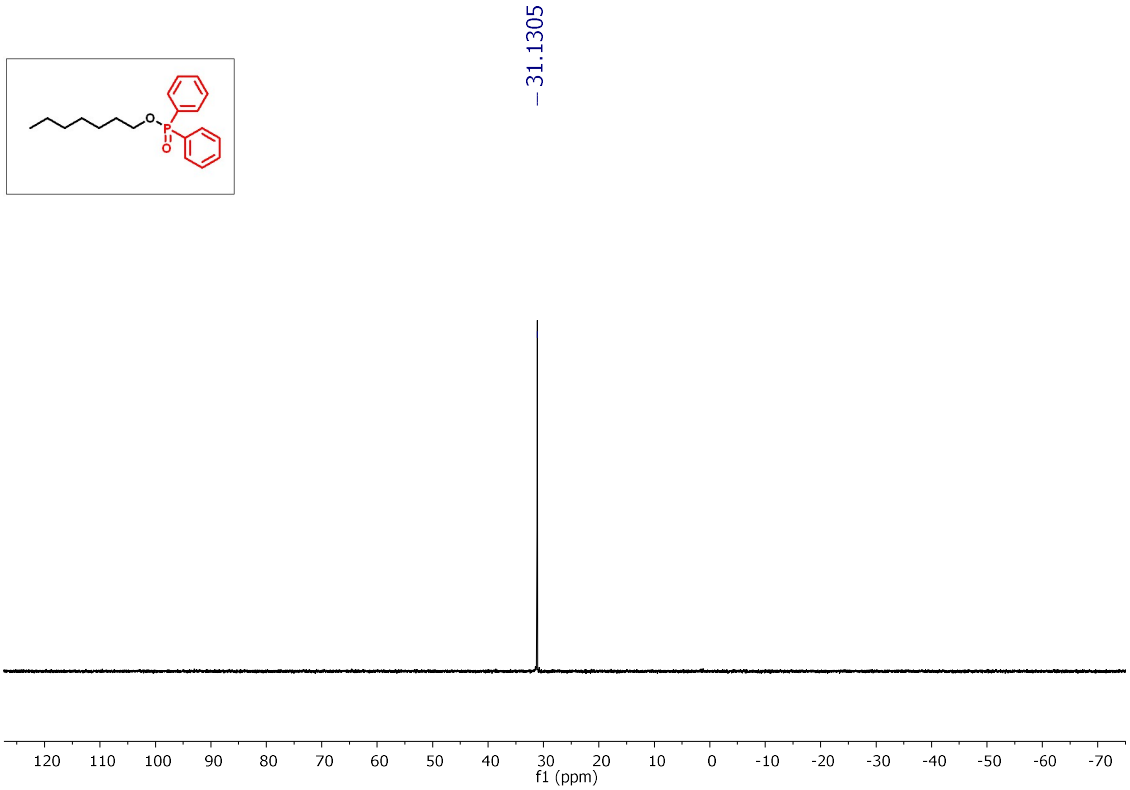
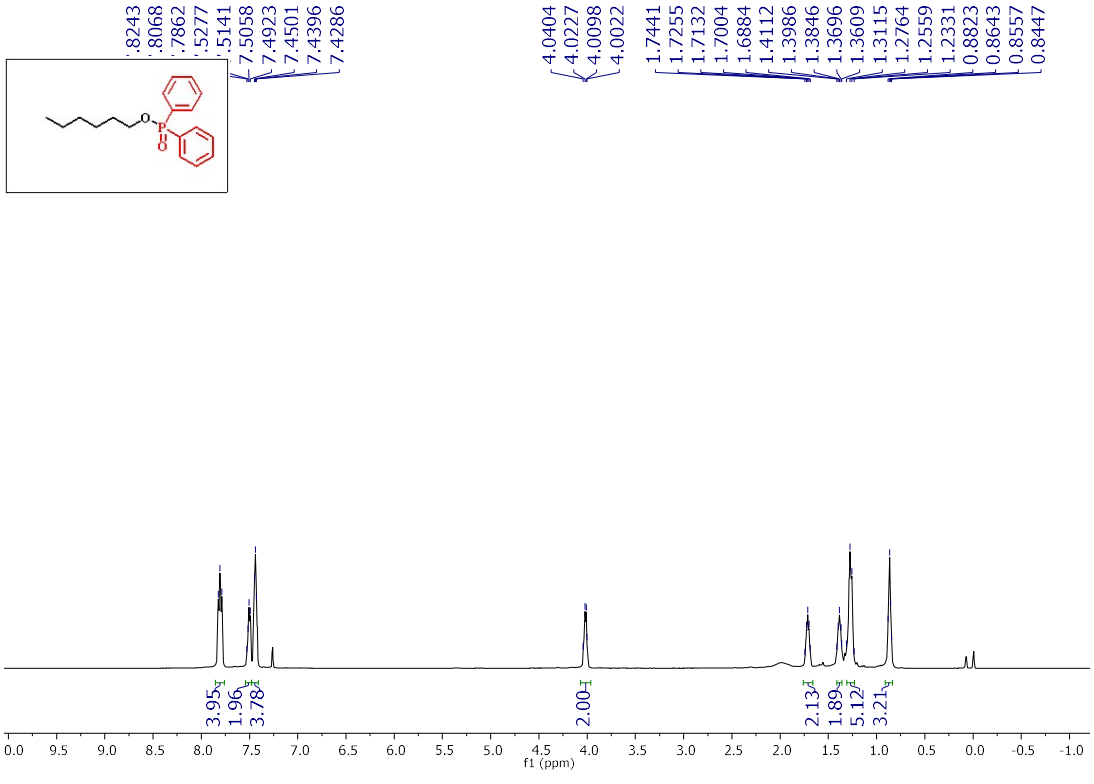


Figure S72. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4w in $CDCl_3$



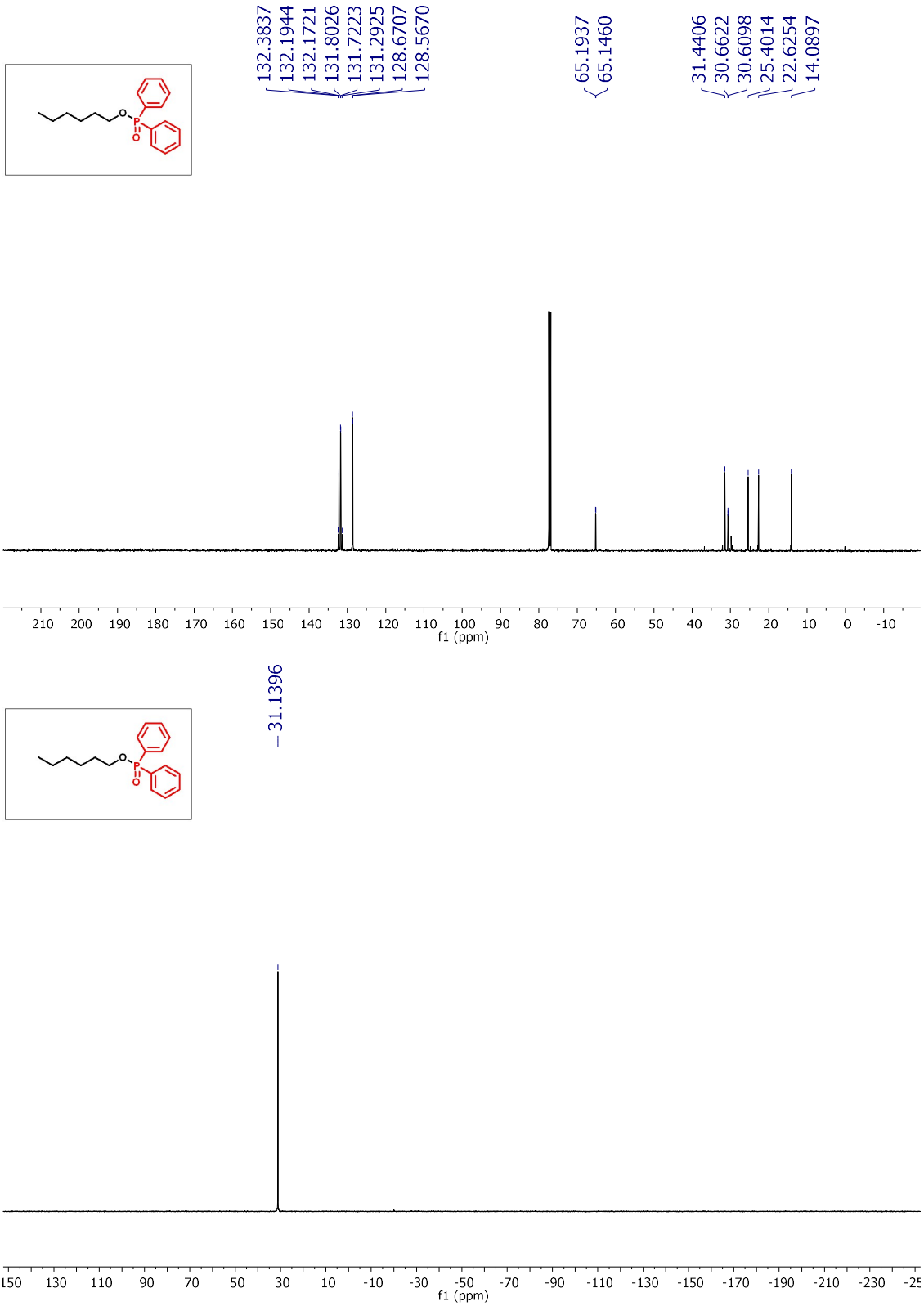
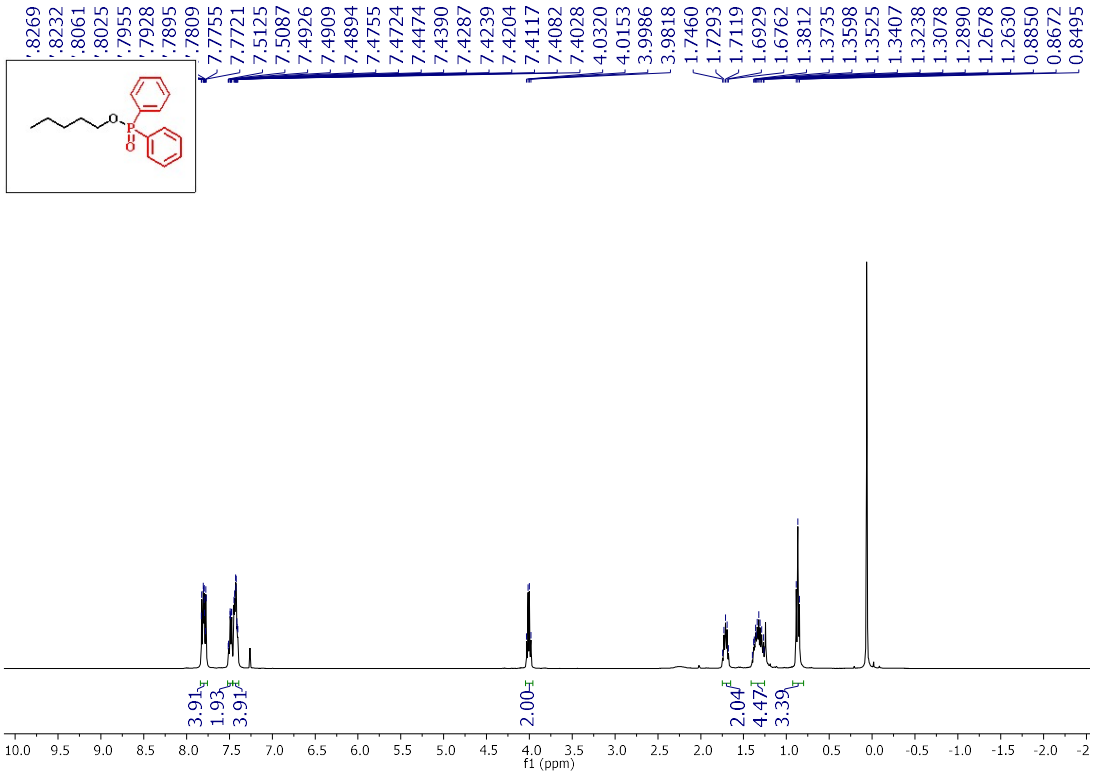
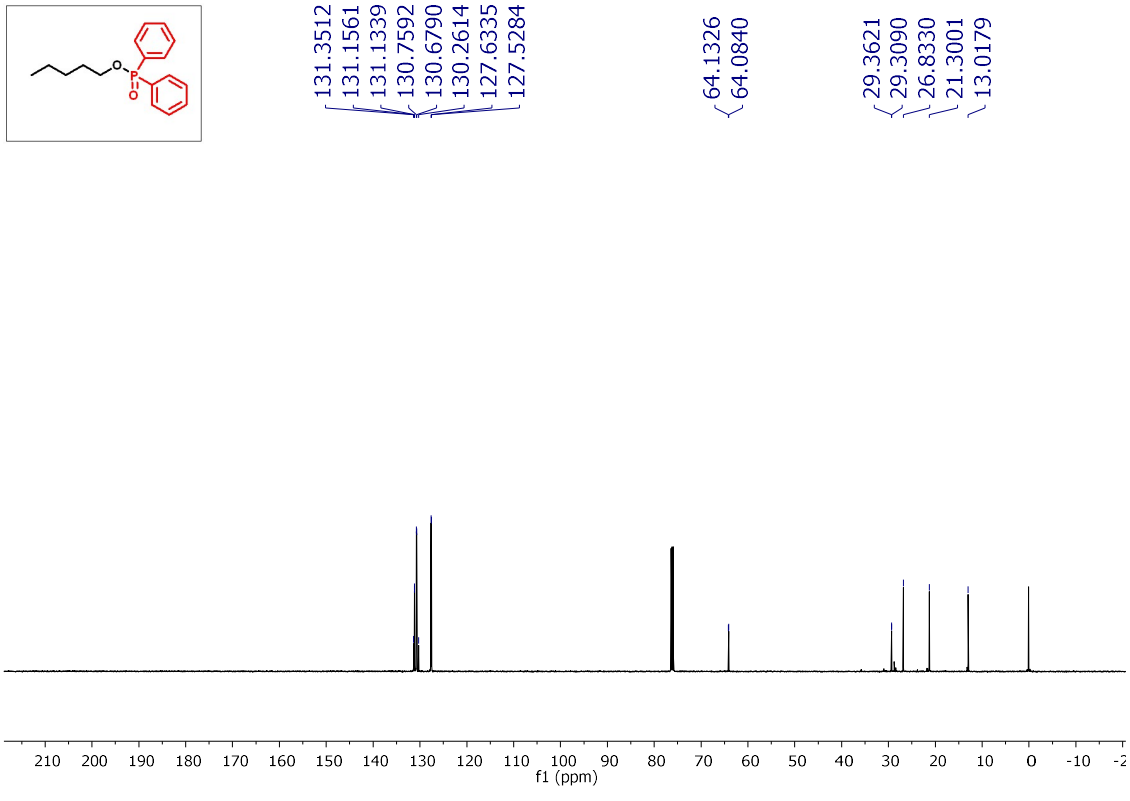


Figure S73. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4x in $CDCl_3$


8.269
8.232
8.061
8.025
7.955
7.928
7.895
7.809
7.755
7.721
7.512
7.508
7.492
7.490
7.489
7.475
7.472
7.447
7.439
7.428
7.420
7.411
7.408
7.402
4.032
4.015
3.998
3.981
1.746
1.729
1.711
1.692
1.676
1.381
1.373
1.359
1.352
1.340
1.323
1.307
1.289
1.267
1.263
0.885
0.867
0.849
3.91
1.93
3.91
2.00
2.04
4.47
3.39
f1 (ppm)


131.3512
131.1561
131.1339
130.7592
130.6790
130.2614
127.6335
127.5284
64.1326
64.0840
29.3621
29.3090
26.8330
21.3001
13.0179
f1 (ppm)

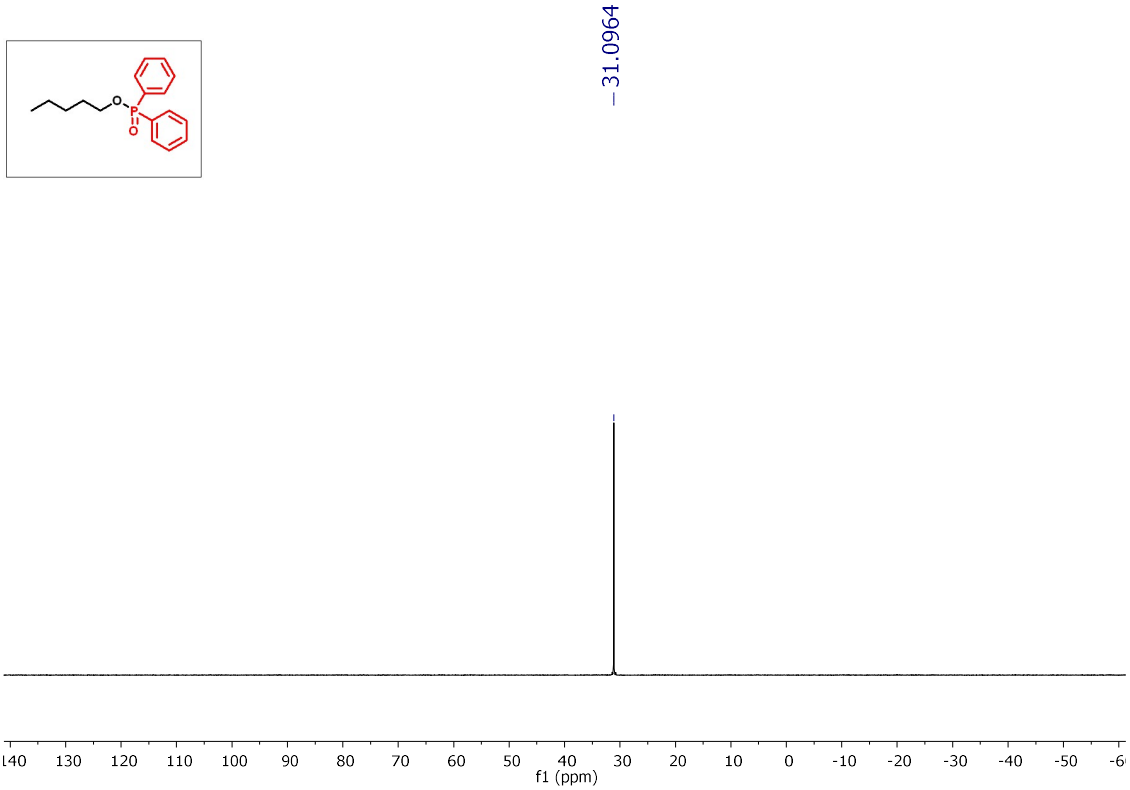
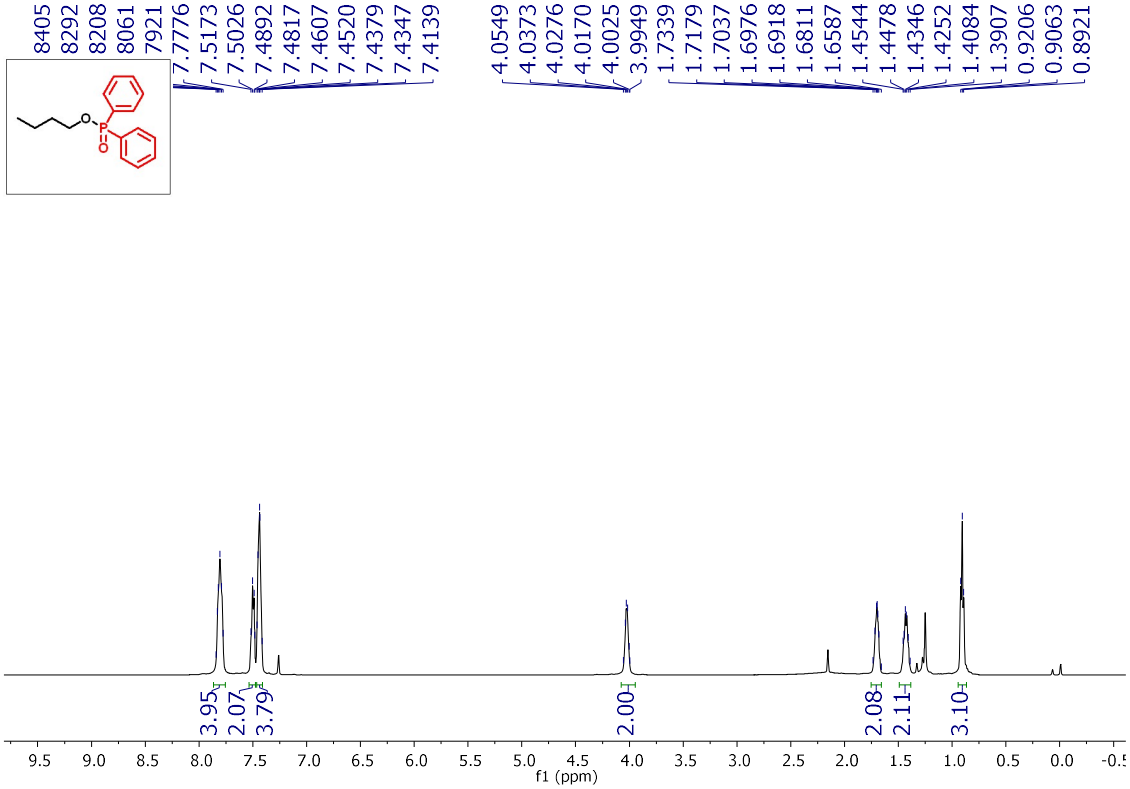


Figure S74. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4y in $CDCl_3$



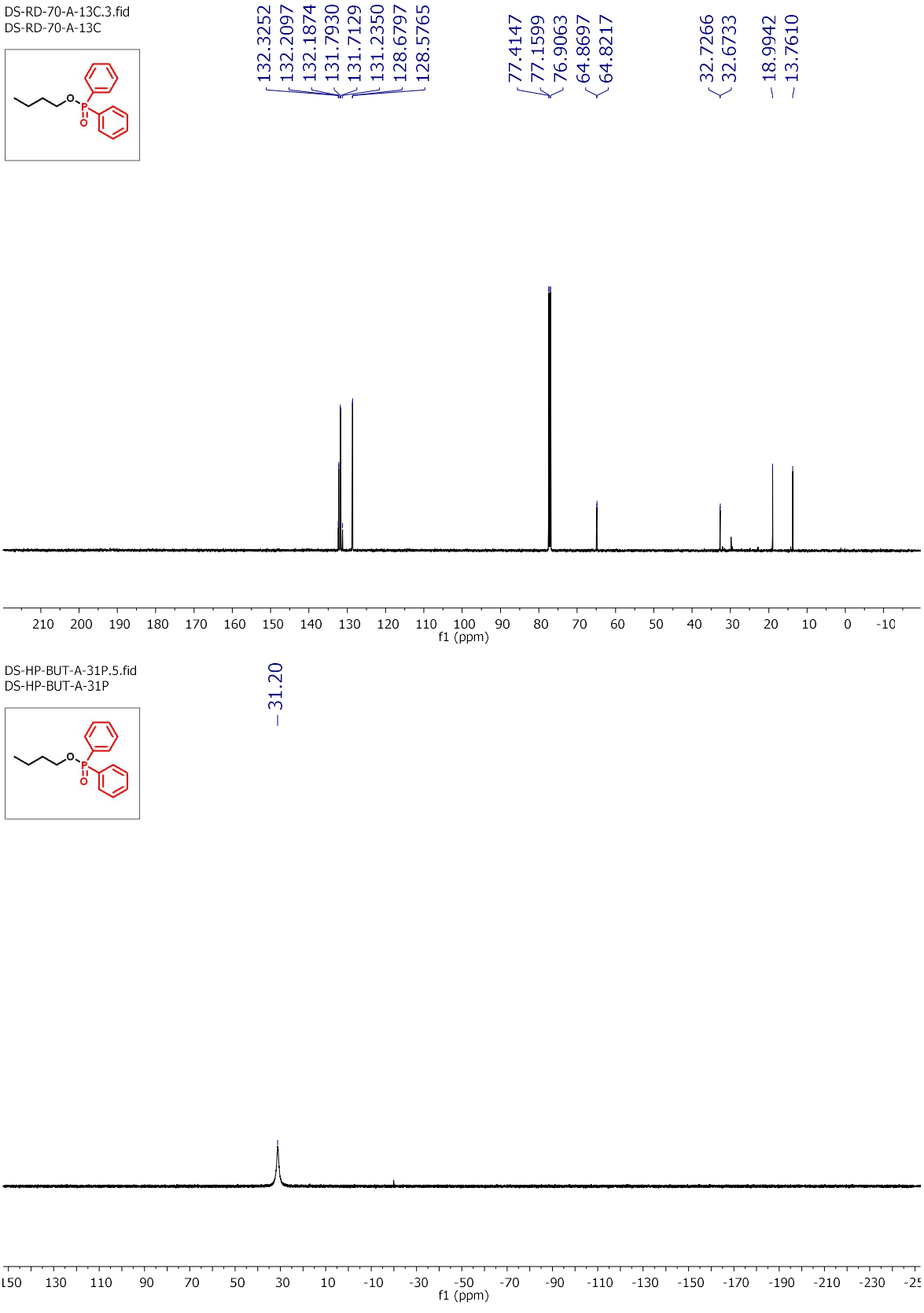
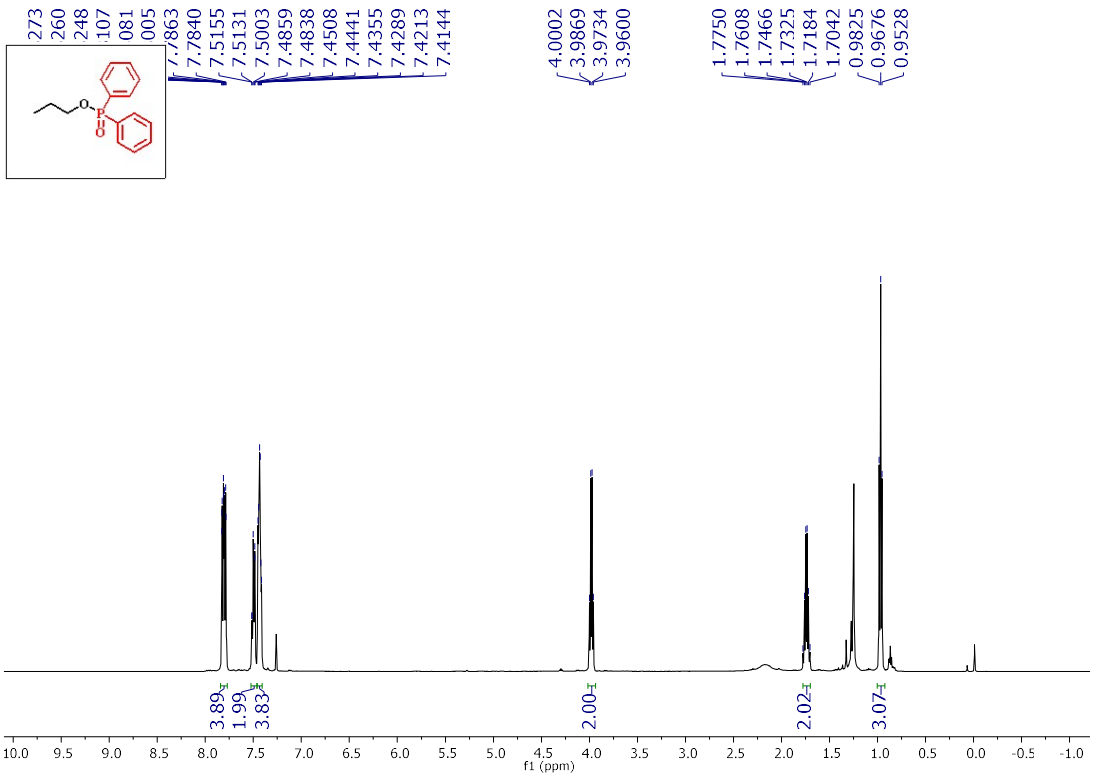
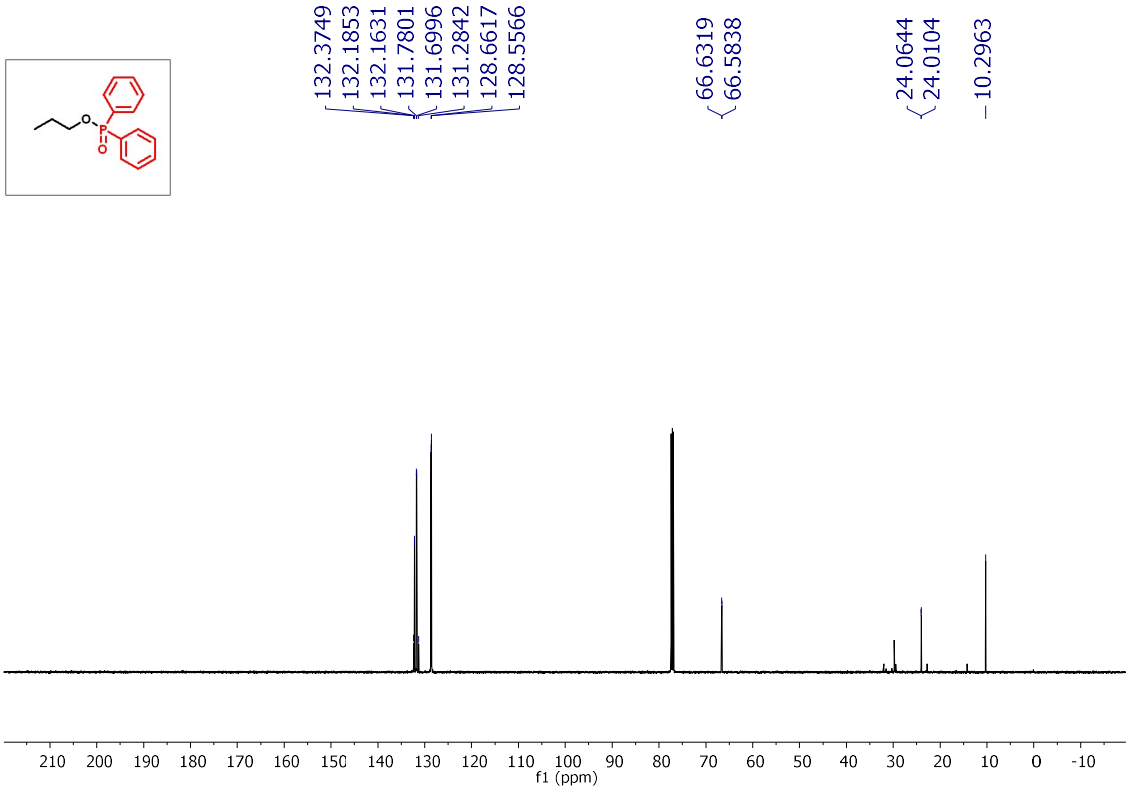


Figure S75. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4z in $CDCl_3$


8.273
8.260
8.248
8.107
8.081
8.005
7.863
7.840
7.515
7.513
7.500
7.485
7.483
7.450
7.444
7.435
7.428
7.421
7.414
4.000
3.986
3.973
3.960
1.775
1.760
1.746
1.732
1.718
1.704
0.982
0.967
0.952
3.89
1.99
3.83
2.00
2.02
3.07
f1 (ppm)


132.374
132.185
132.163
131.780
131.699
131.284
128.661
128.556
66.631
66.583
24.064
24.010
10.296
f1 (ppm)

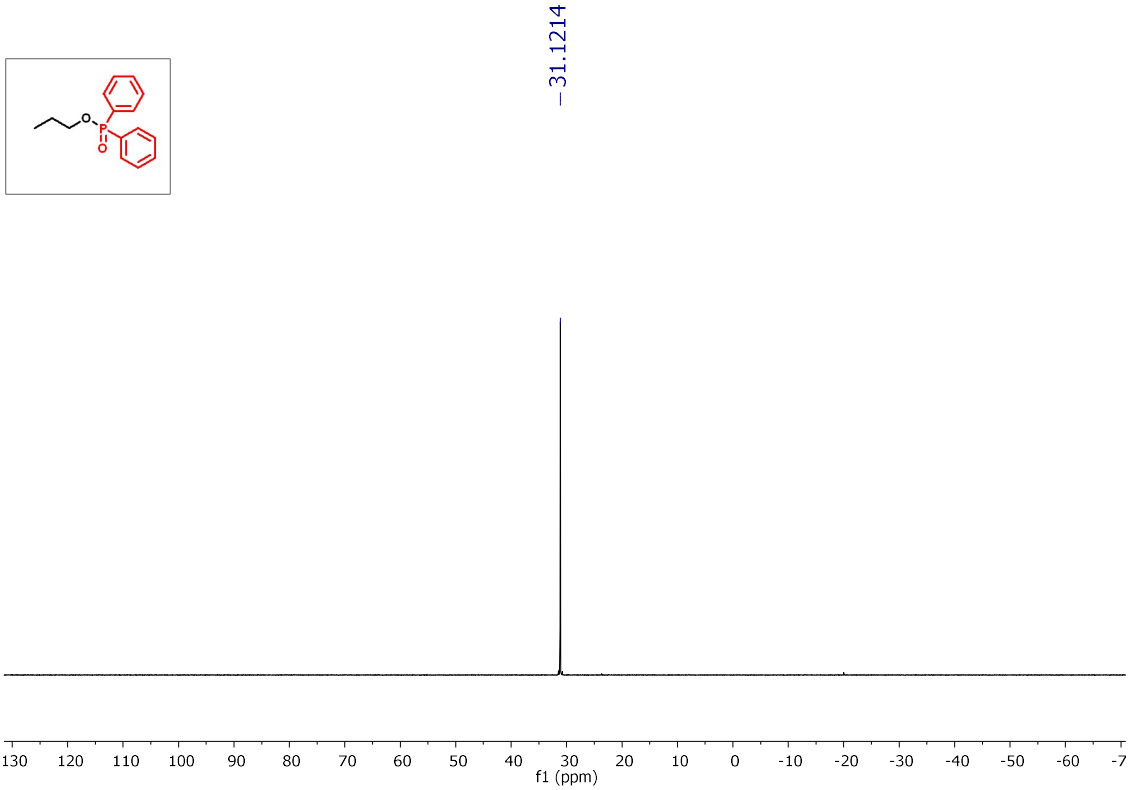
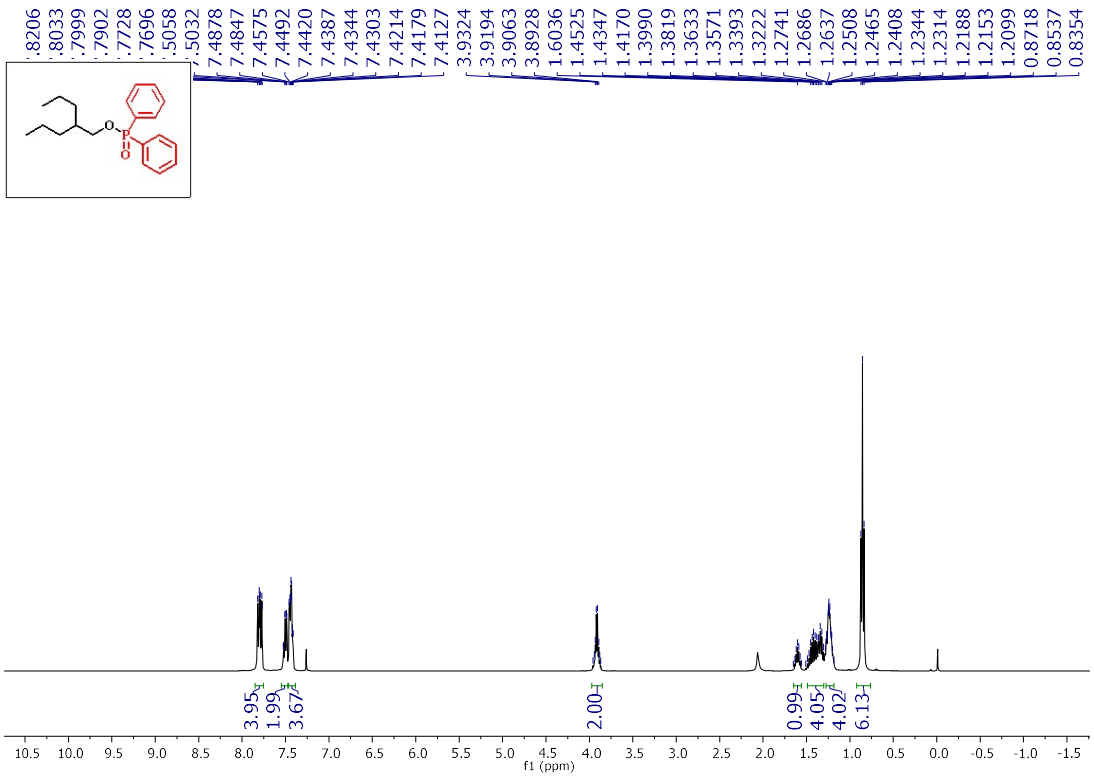


Figure S76. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4aa in $CDCl_3$



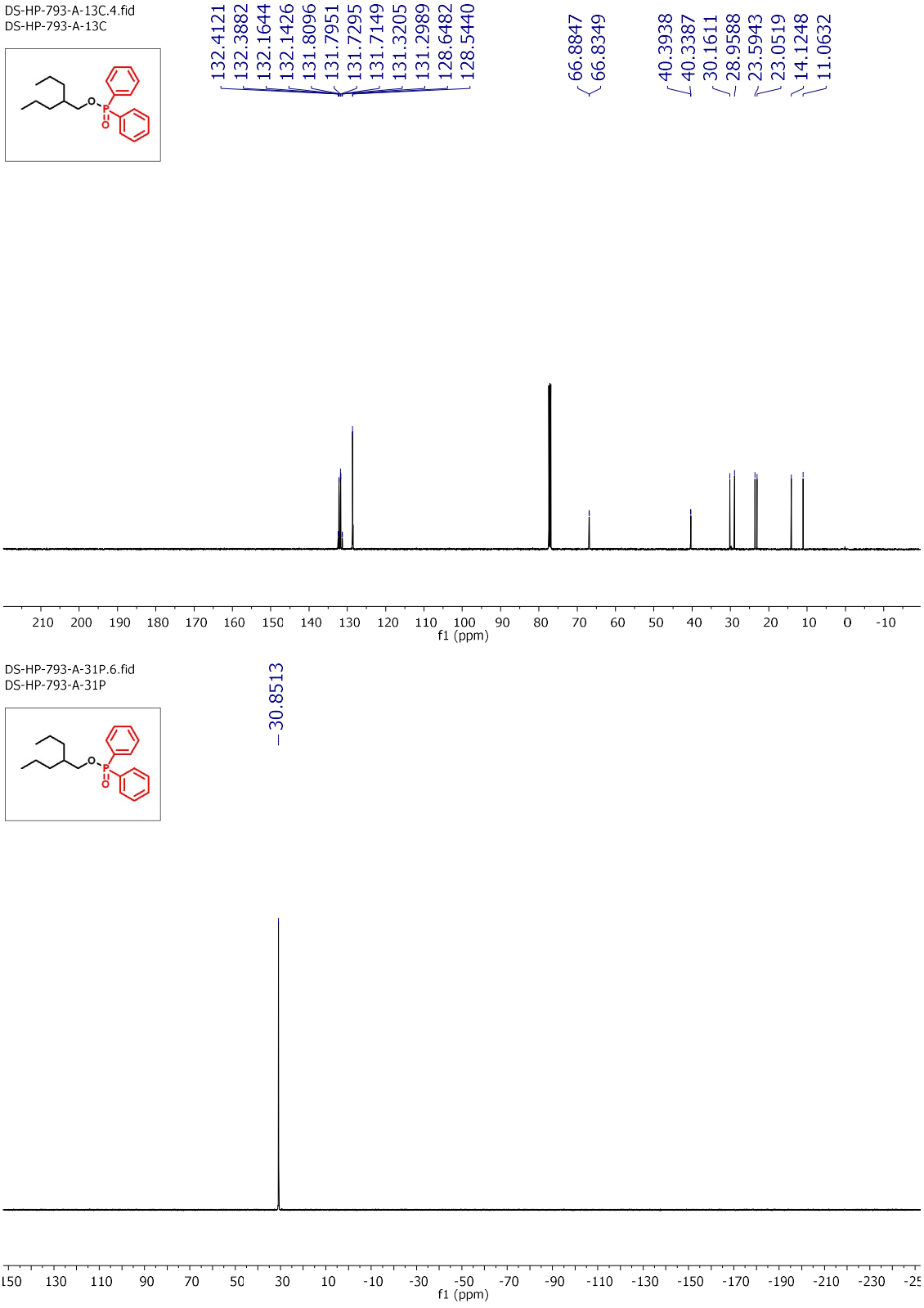
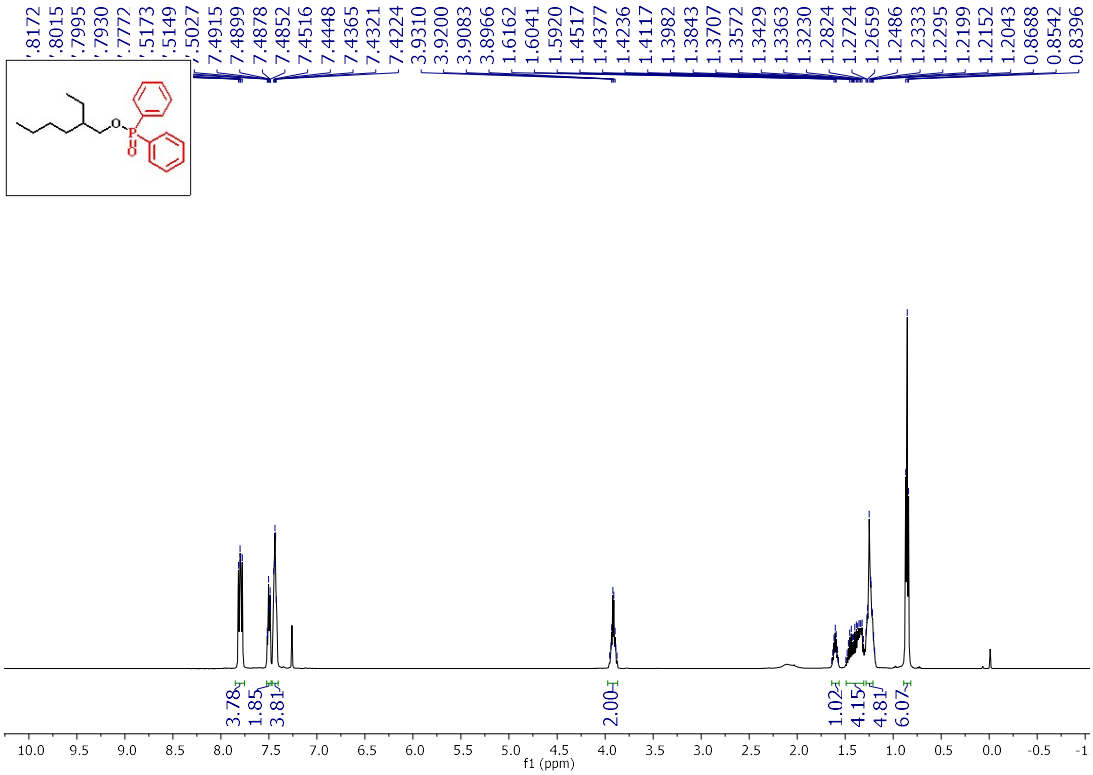
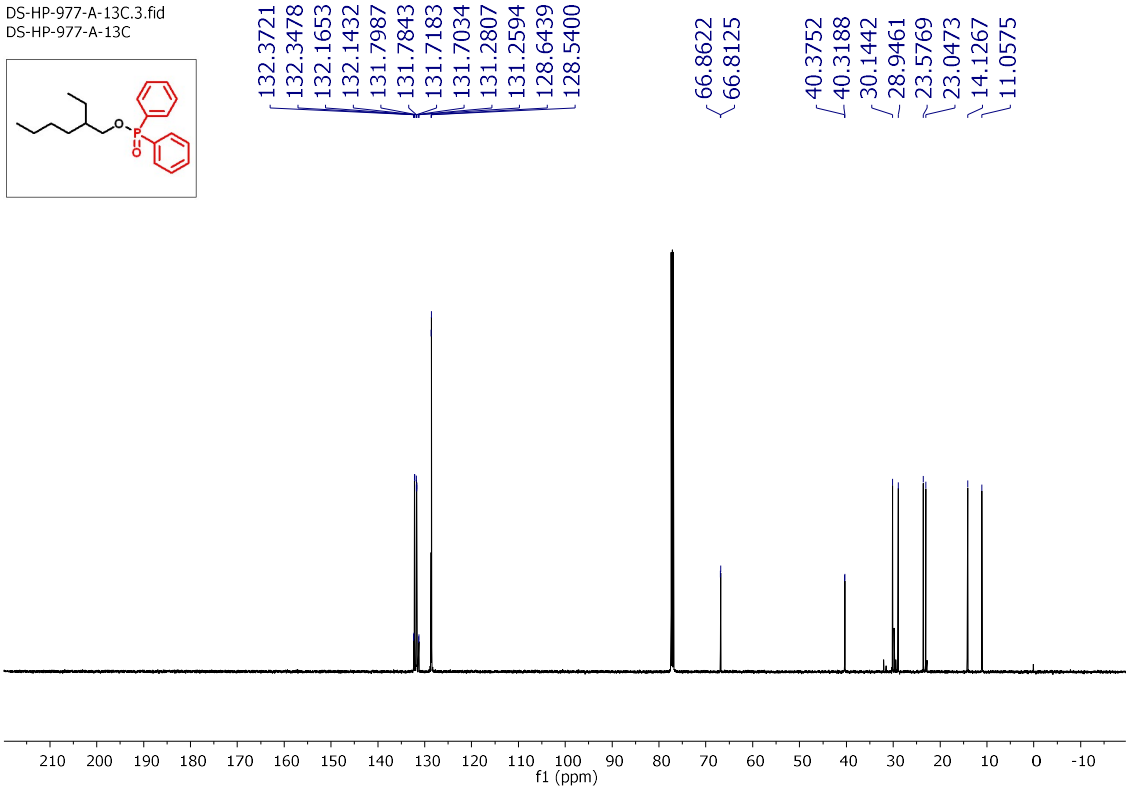


Figure S77. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ab in $CDCl_3$


8172
8015
7995
7930
7772
5173
5149
5027
7.4915
7.4899
7.4878
7.4852
7.4516
7.4448
7.4365
7.4321
7.4224
3.9310
3.9200
3.9083
3.8966
1.6162
1.6041
1.5920
1.4517
1.4377
1.4236
1.4117
1.3982
1.3843
1.3707
1.3572
1.3429
1.3363
1.3230
1.2824
1.2724
1.2659
1.2486
1.2333
1.2295
1.2199
1.2152
1.2043
0.8688
0.8542
0.8396
3.78
1.85
3.81
2.00
1.02
4.15
4.81
6.07
f1 (ppm)


DS-HP-977-A-13C.3.fid
DS-HP-977-A-13C
132.3721
132.3478
132.1653
132.1432
131.7987
131.7843
131.7183
131.7034
131.2807
131.2594
128.6439
128.5400
66.8622
66.8125
40.3752
40.3188
30.1442
28.9461
23.5769
23.0473
14.1267
11.0575
f1 (ppm)

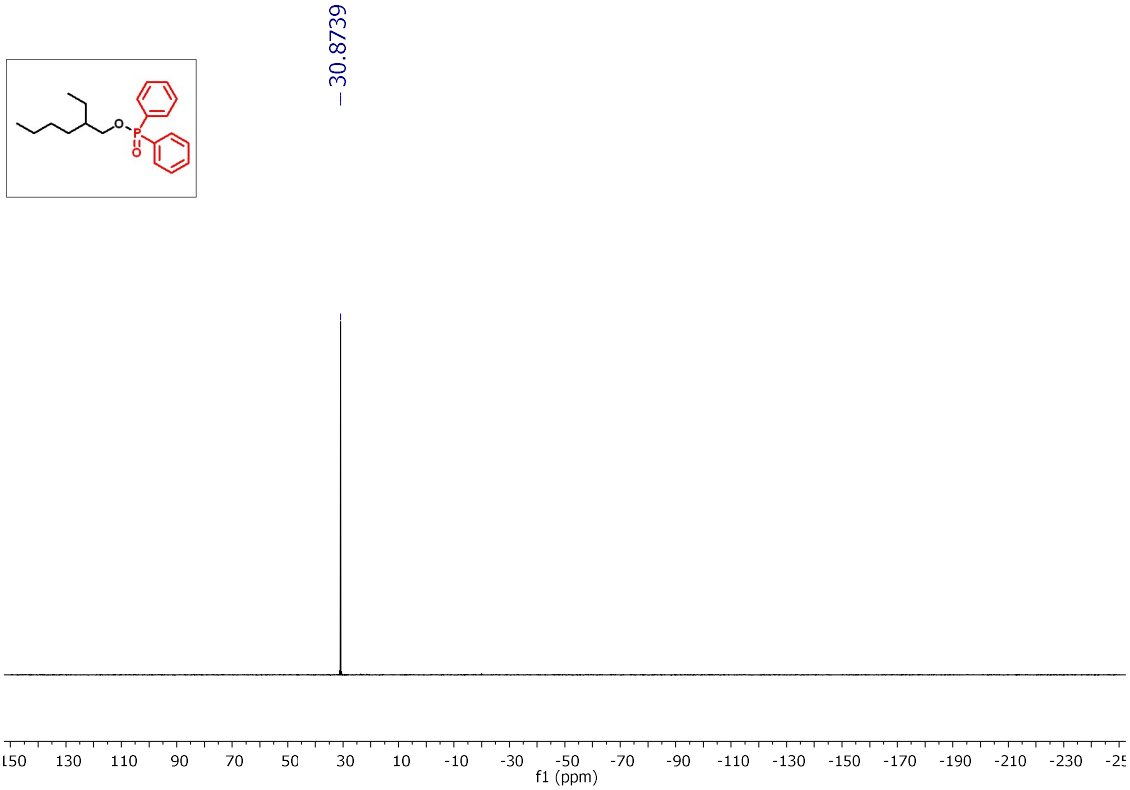
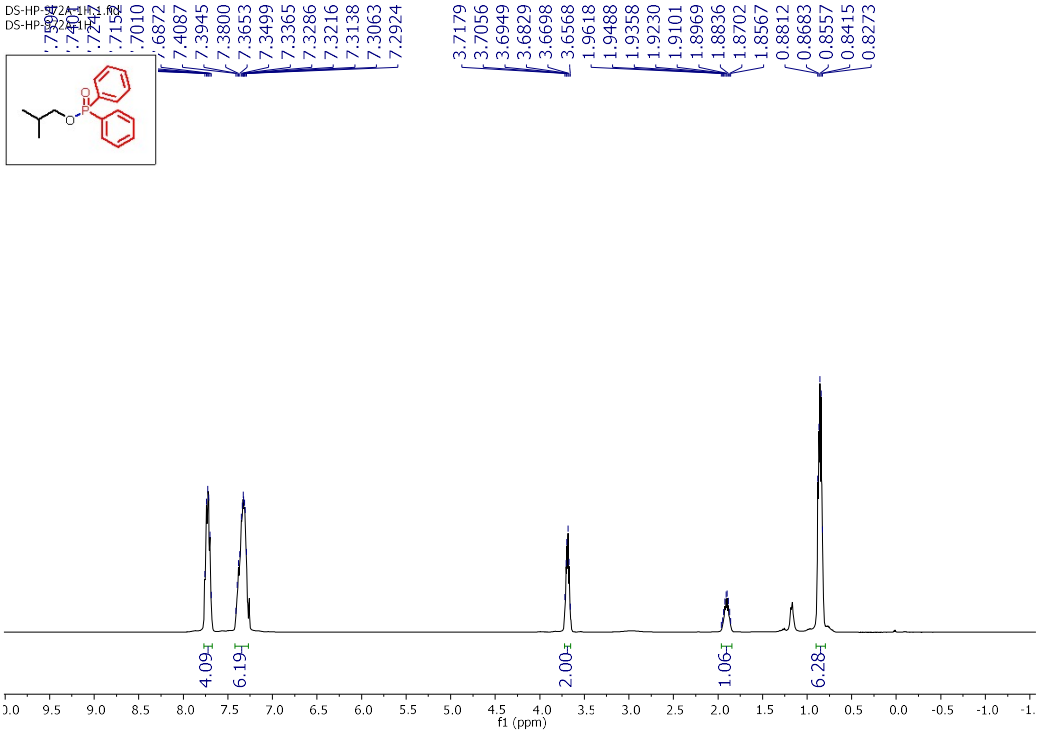


Figure S78. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ac in $CDCl_3$



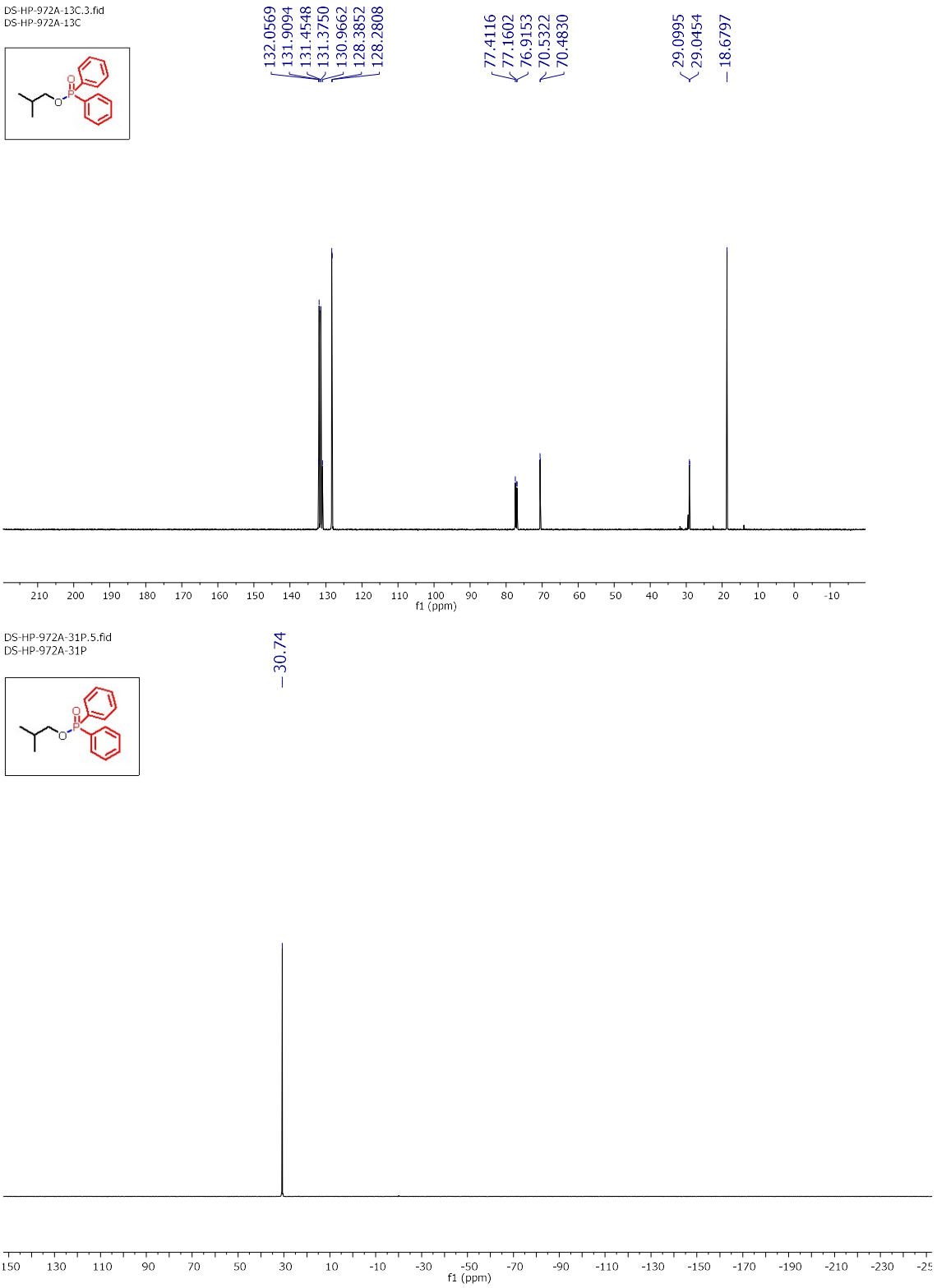
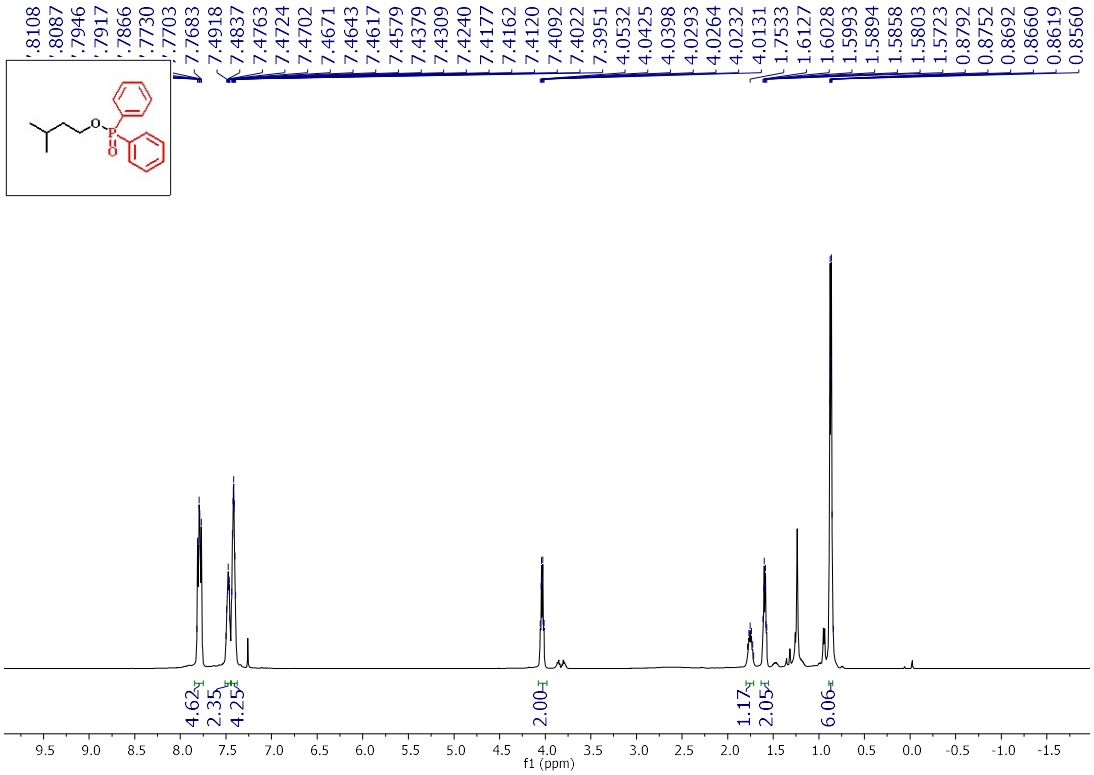
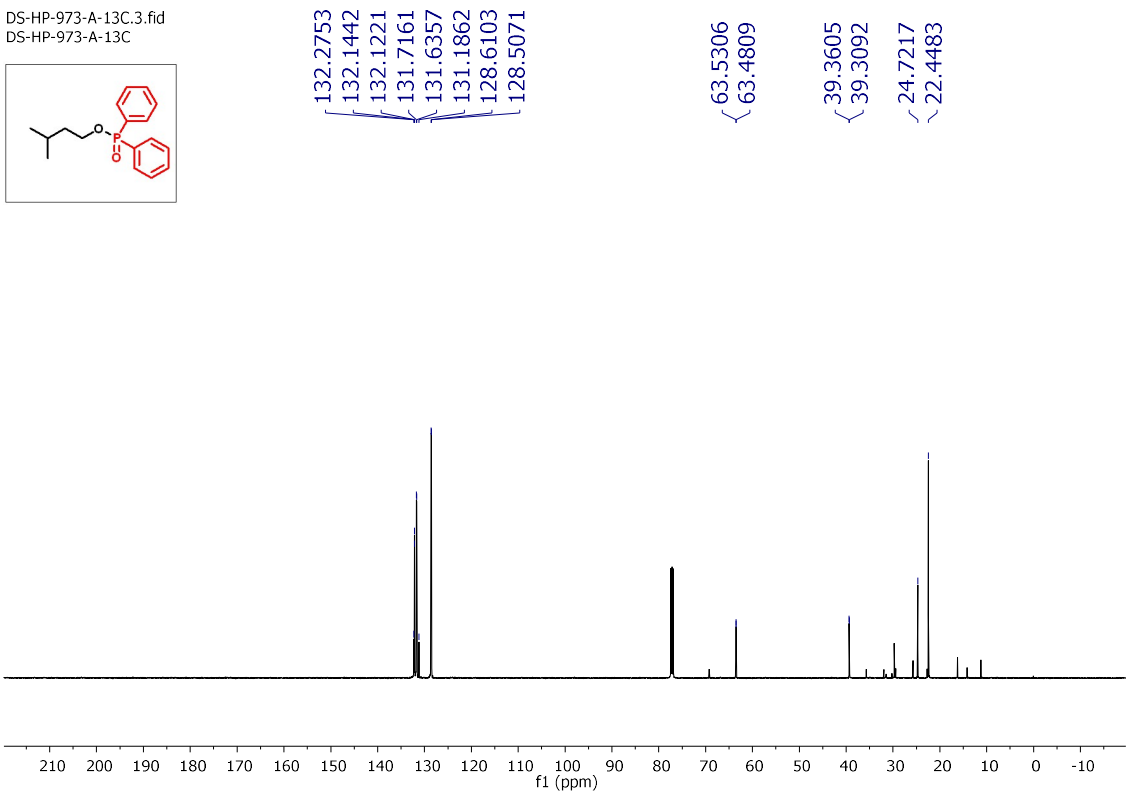


Figure S79. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ad in $CDCl_3$


8108
8087
7946
7917
7866
7730
7703
7683
7.4918
7.4837
7.4763
7.4724
7.4702
7.4671
7.4643
7.4617
7.4579
7.4379
7.4309
7.4240
7.4177
7.4162
7.4120
7.4092
7.4022
7.3951
4.0532
4.0425
4.0398
4.0293
4.0264
4.0232
4.0131
1.7533
1.6127
1.6028
1.5993
1.5894
1.5858
1.5803
1.5723
0.8792
0.8752
0.8692
0.8660
0.8619
0.8560
4.62
2.35
4.25
2.00
1.17
2.05
6.06
f1 (ppm)


DS-HP-973-A-13C.3.fid
DS-HP-973-A-13C
132.2753
132.1442
132.1221
131.7161
131.6357
131.1862
128.6103
128.5071
63.5306
63.4809
39.3605
39.3092
24.7217
22.4483
f1 (ppm)

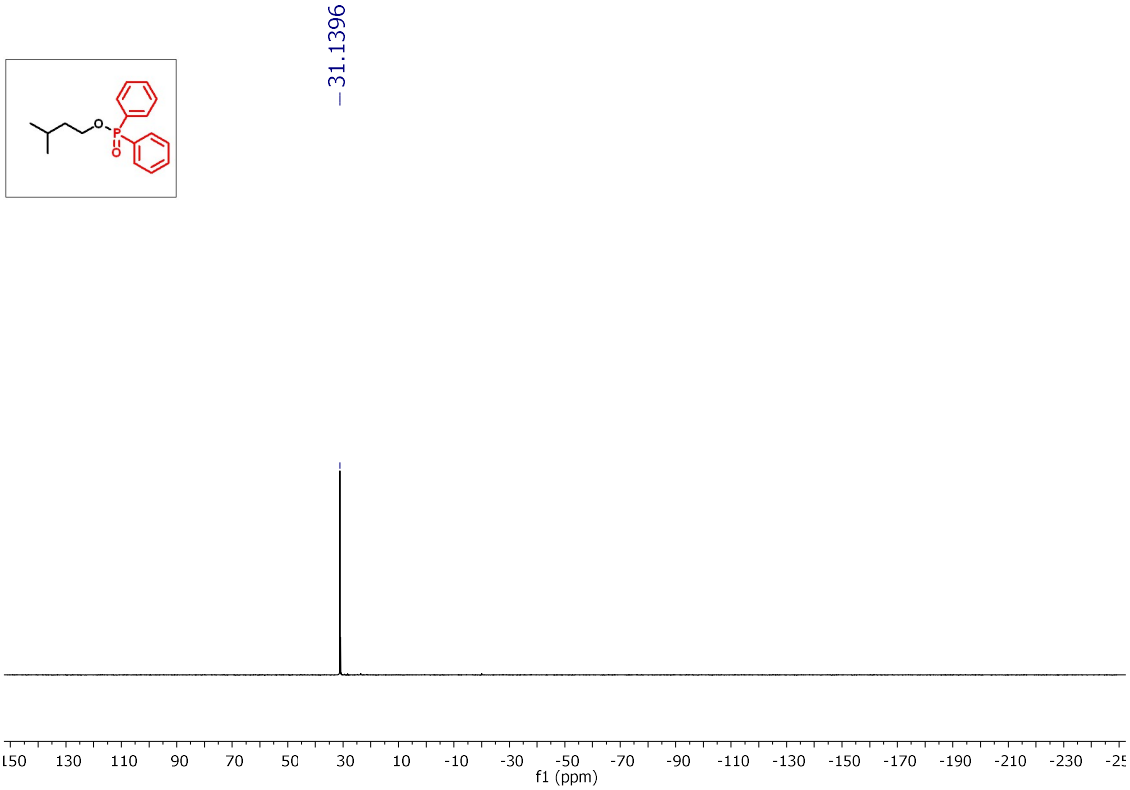
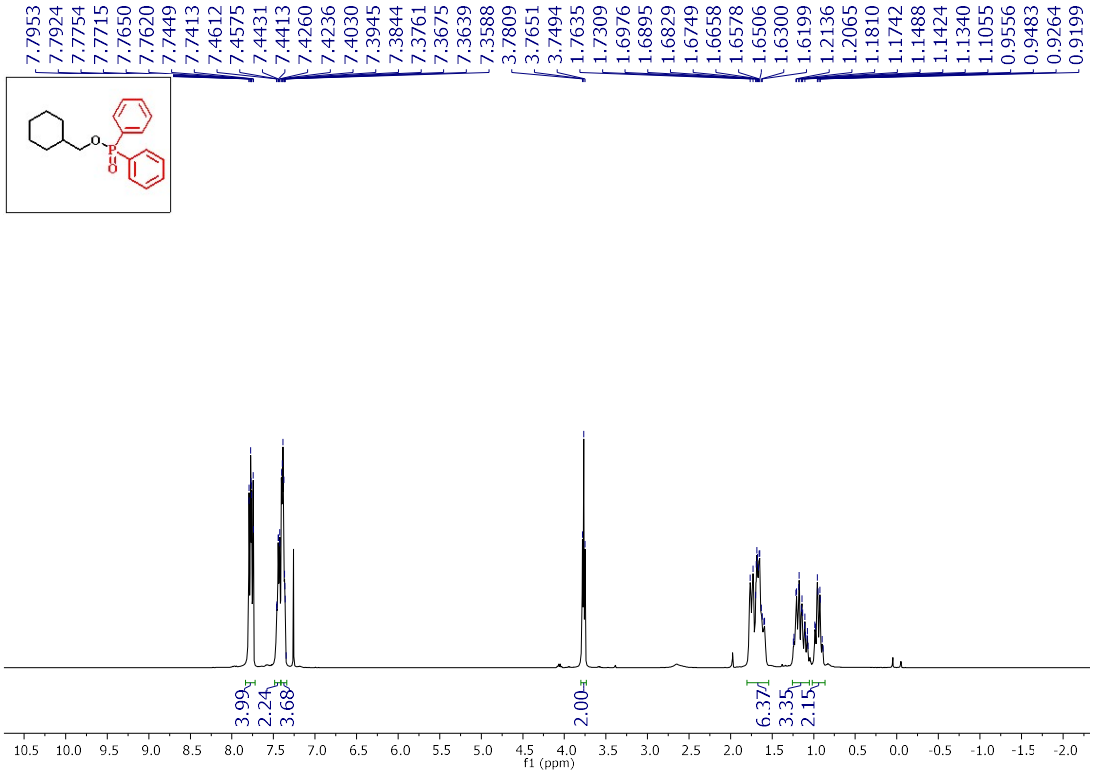


Figure S80. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ae in $CDCl_3$



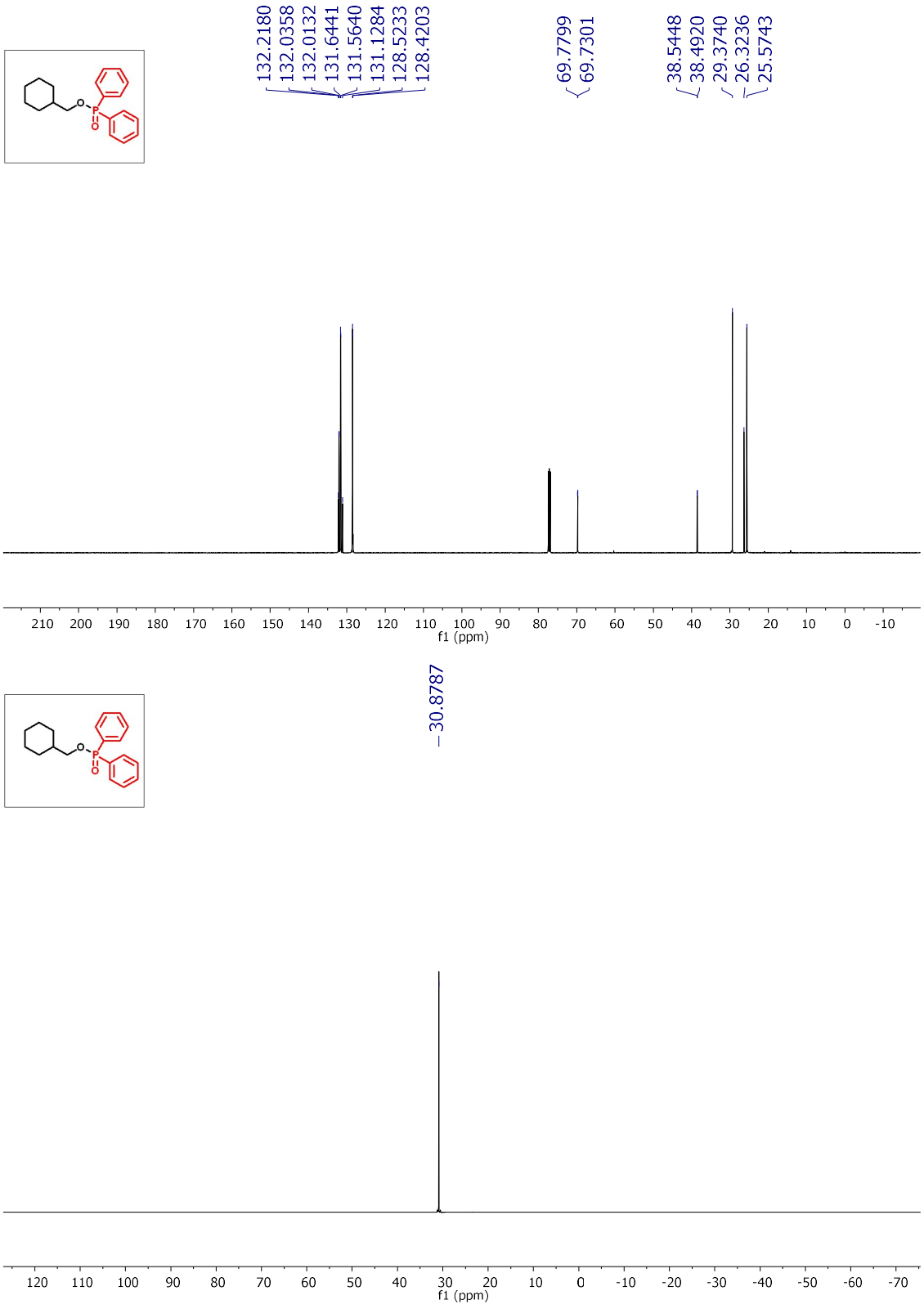
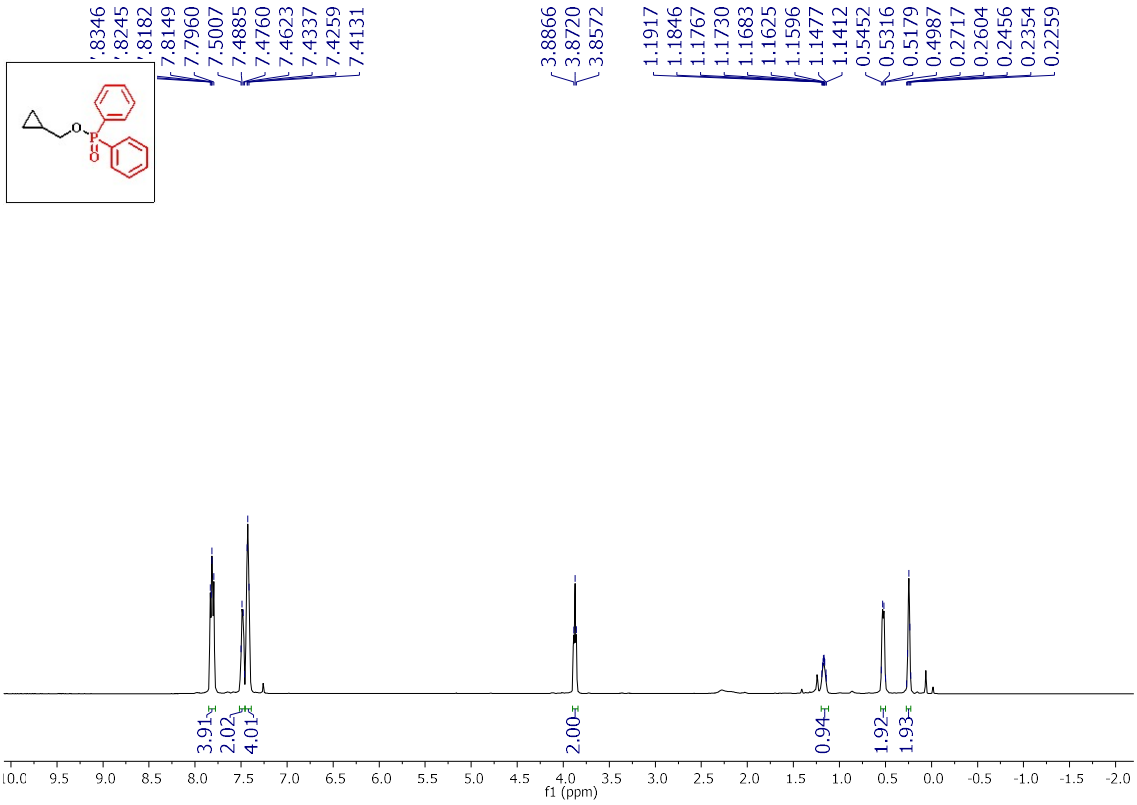
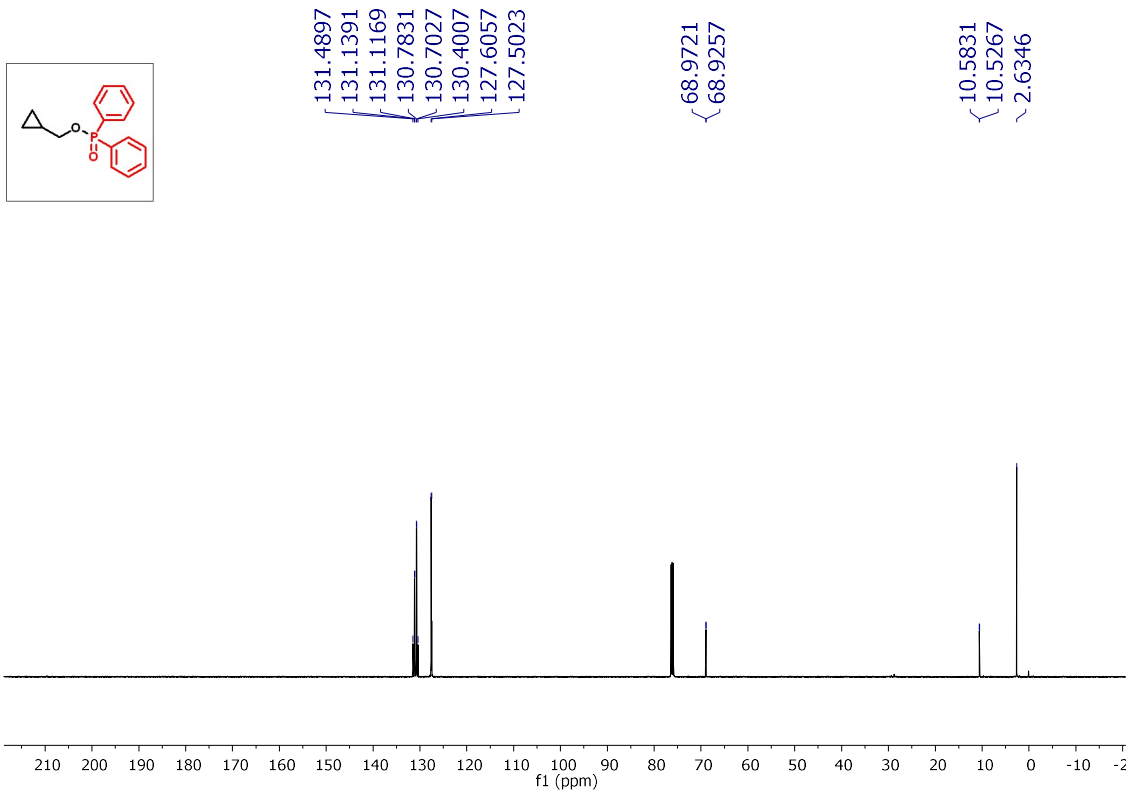


Figure S81. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4af in $CDCl_3$


7.8346
7.8245
7.8182
7.8149
7.7960
7.5007
7.4885
7.4760
7.4623
7.4337
7.4259
7.4131
3.8866
3.8720
3.8572
1.1917
1.1846
1.1767
1.1730
1.1683
1.1625
1.1596
1.1477
1.1412
0.5452
0.5316
0.5179
0.4987
0.2717
0.2604
0.2456
0.2354
0.2259
3.91
2.02
4.01
2.00
0.94
1.92
1.93
f1 (ppm)


131.4897
131.1391
131.1169
130.7831
130.7027
130.4007
127.6057
127.5023
68.9721
68.9257
10.5831
10.5267
2.6346
f1 (ppm)

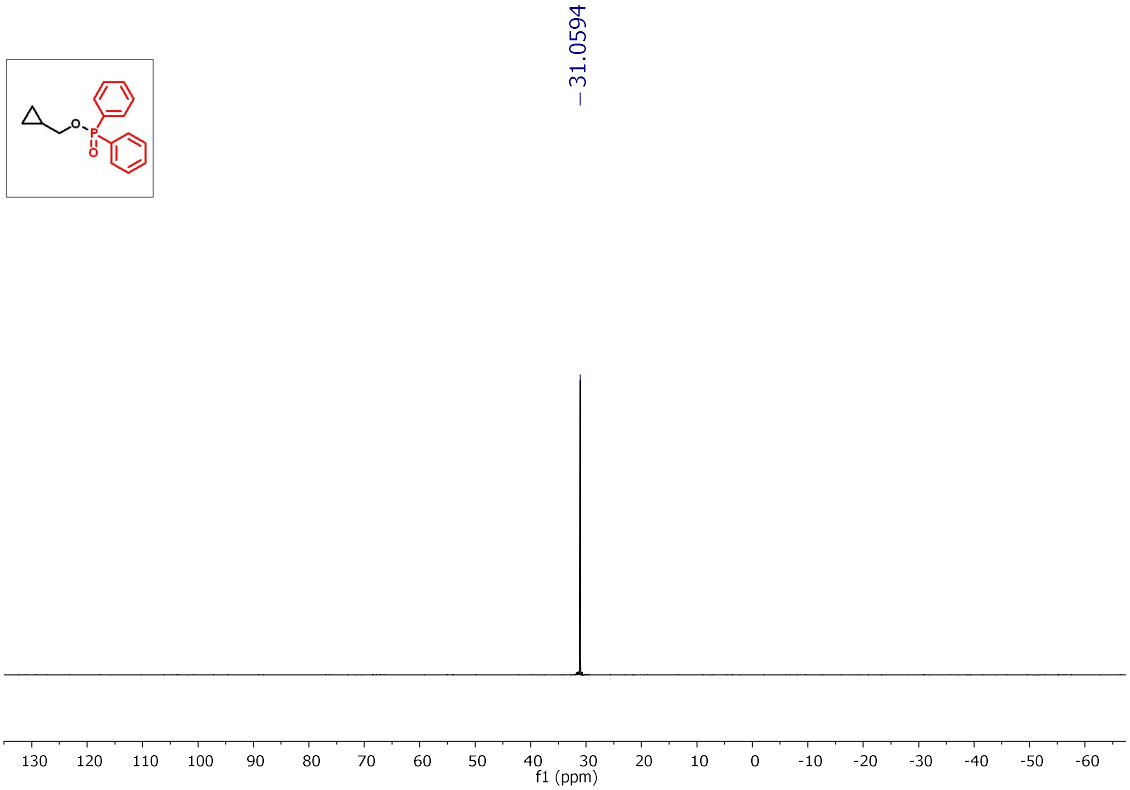
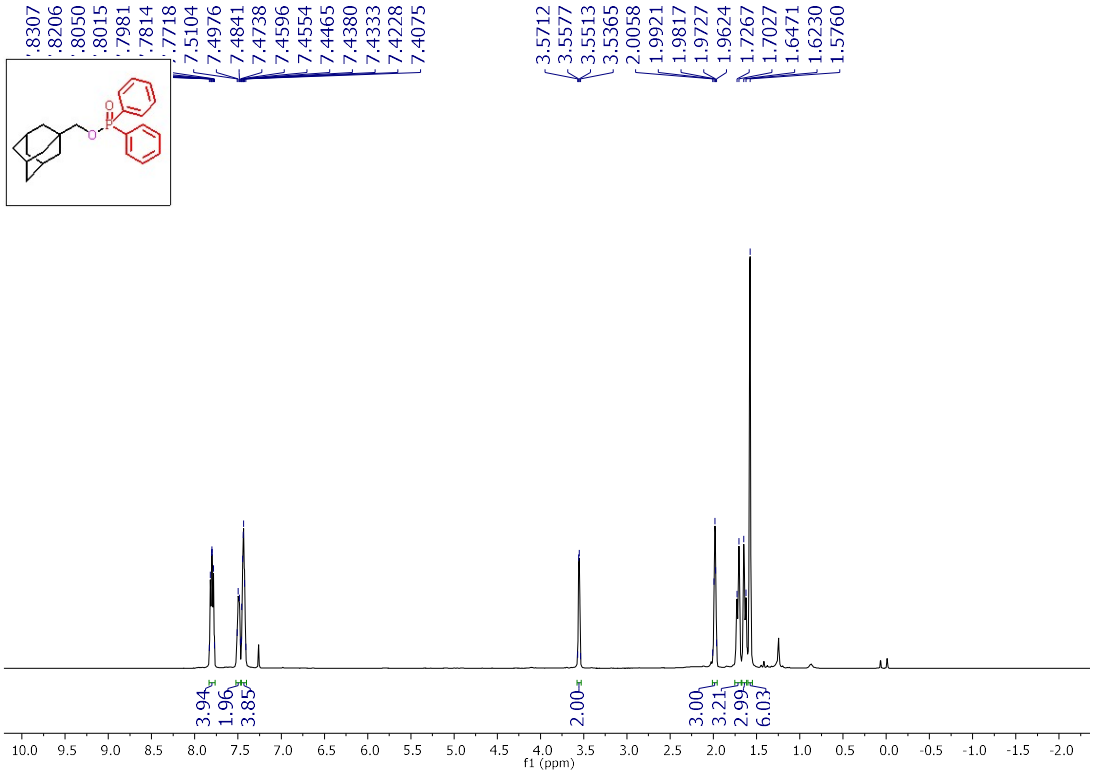


Figure S82. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ag in $CDCl_3$



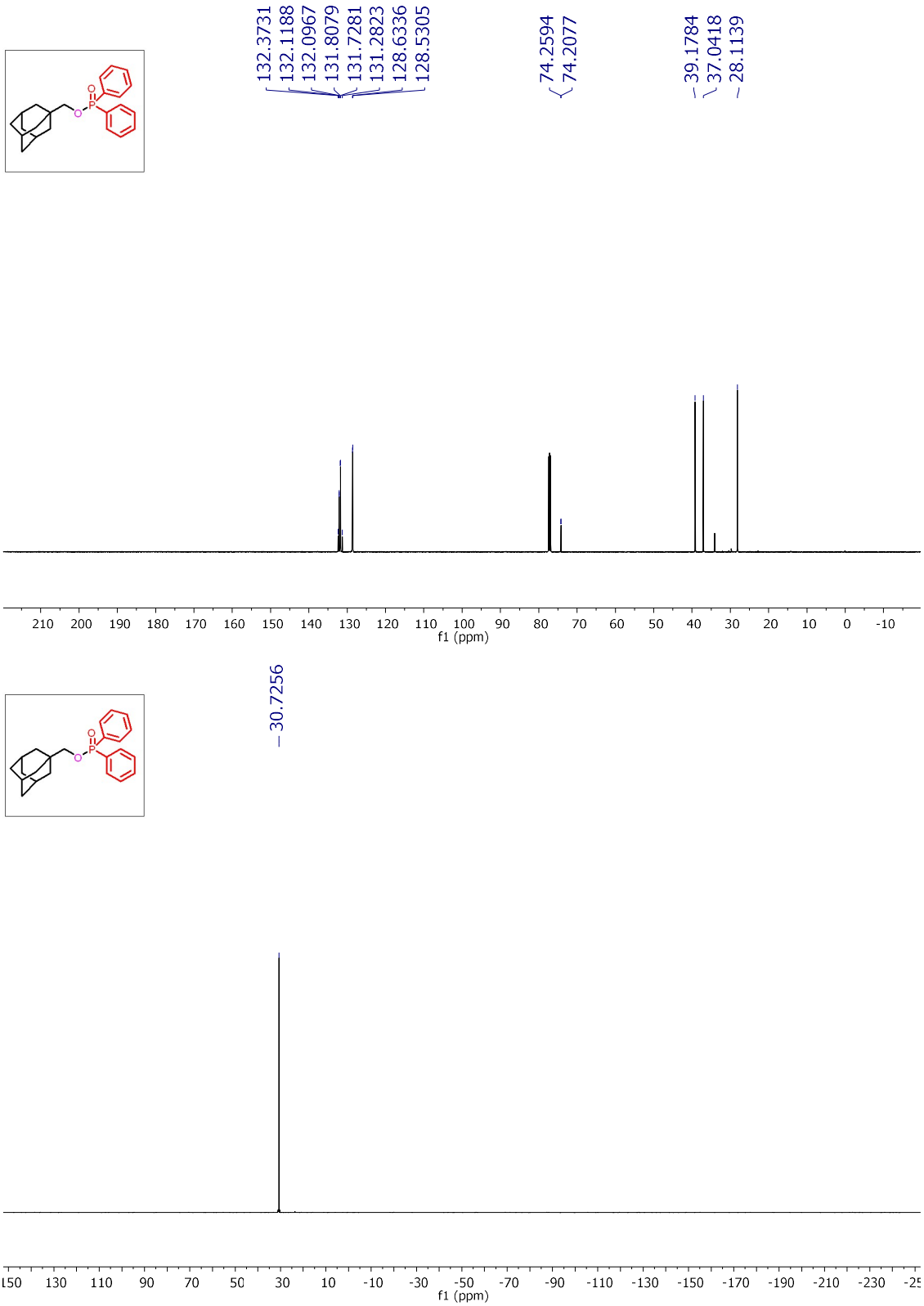
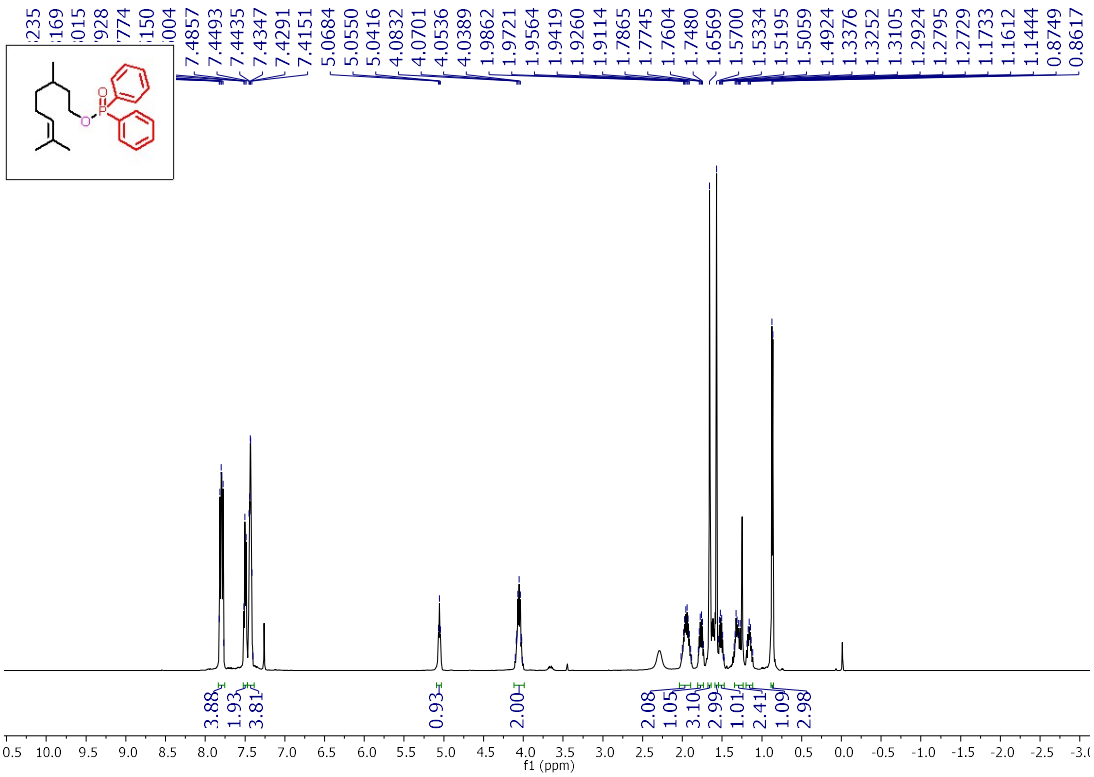
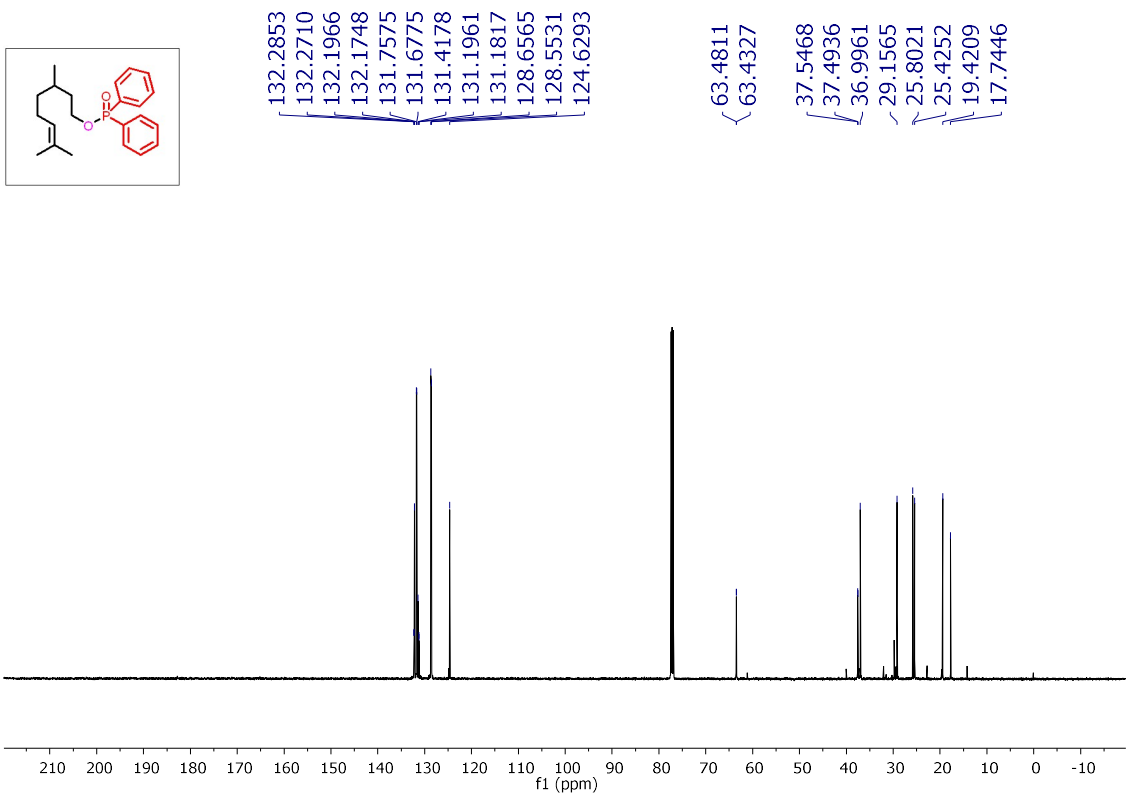


Figure S83. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ah in $CDCl_3$


7.4857
7.4493
7.4435
7.4347
7.4291
7.4151
5.0684
5.0550
5.0416
4.0832
4.0701
4.0536
4.0389
1.9862
1.9721
1.9564
1.9419
1.9260
1.9114
1.7865
1.7745
1.7604
1.7480
1.6569
1.5700
1.5334
1.5195
1.5059
1.4924
1.3376
1.3252
1.3105
1.2924
1.2795
1.2729
1.1733
1.1612
1.1444
0.8749
0.8617
3.88
1.93
3.81
0.93
2.00
2.08
1.05
3.10
2.99
1.01
2.41
1.09
2.98
f1 (ppm)


132.2853
132.2710
132.1966
132.1748
131.7575
131.6775
131.4178
131.1961
131.1817
128.6565
128.5531
124.6293
63.4811
63.4327
37.5468
37.4936
36.9961
29.1565
25.8021
25.4252
19.4209
17.7446
f1 (ppm)

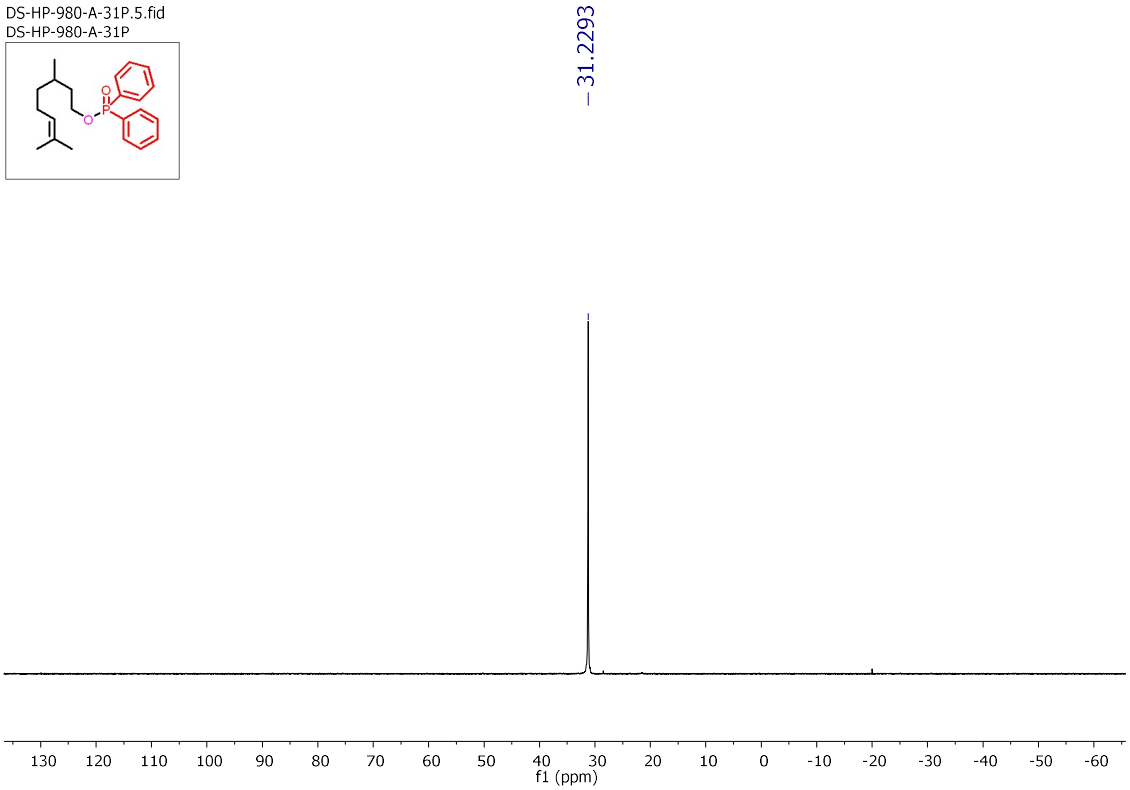
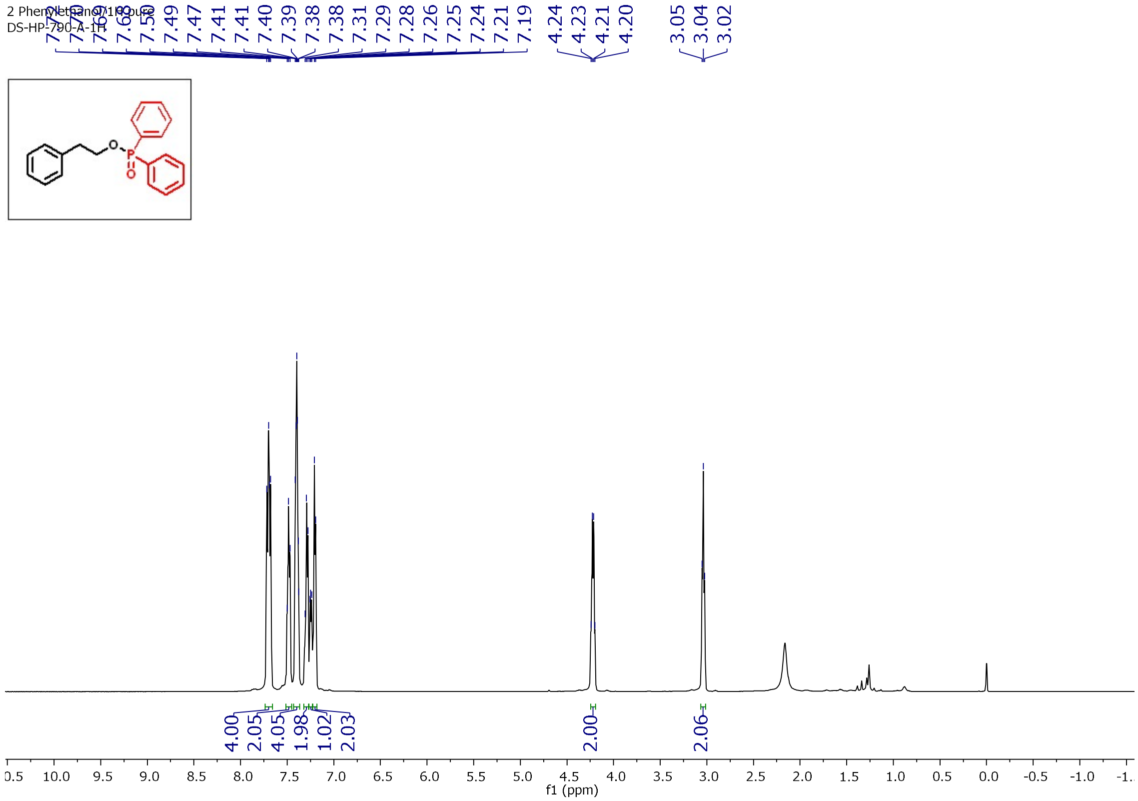
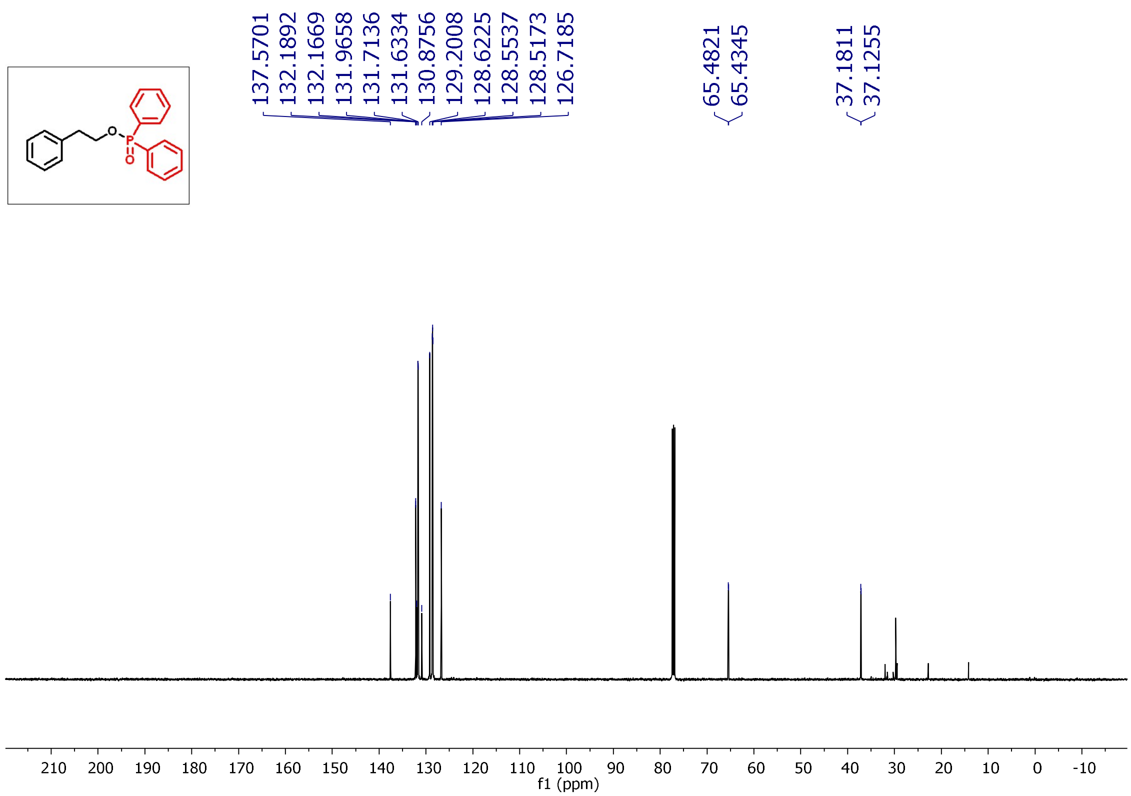


Figure S84. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ai in $CDCl_3$


2 Phenylethanol/1H pure
DS-HP-790-A-1H
7.50 7.49 7.47 7.41 7.41 7.40 7.39 7.38 7.38 7.31 7.29 7.28 7.26 7.25 7.24 7.21 7.19
4.24 4.23 4.21 4.20
3.05 3.04 3.02
4.00 2.05 4.05 1.98 1.02 2.03
2.00
2.06
f1 (ppm)


137.5701 132.1892 132.1669 131.9658 131.7136 131.6334 130.8756 129.2008 128.6225 128.5537 128.5173 126.7185
65.4821 65.4345
37.1811 37.1255
f1 (ppm)

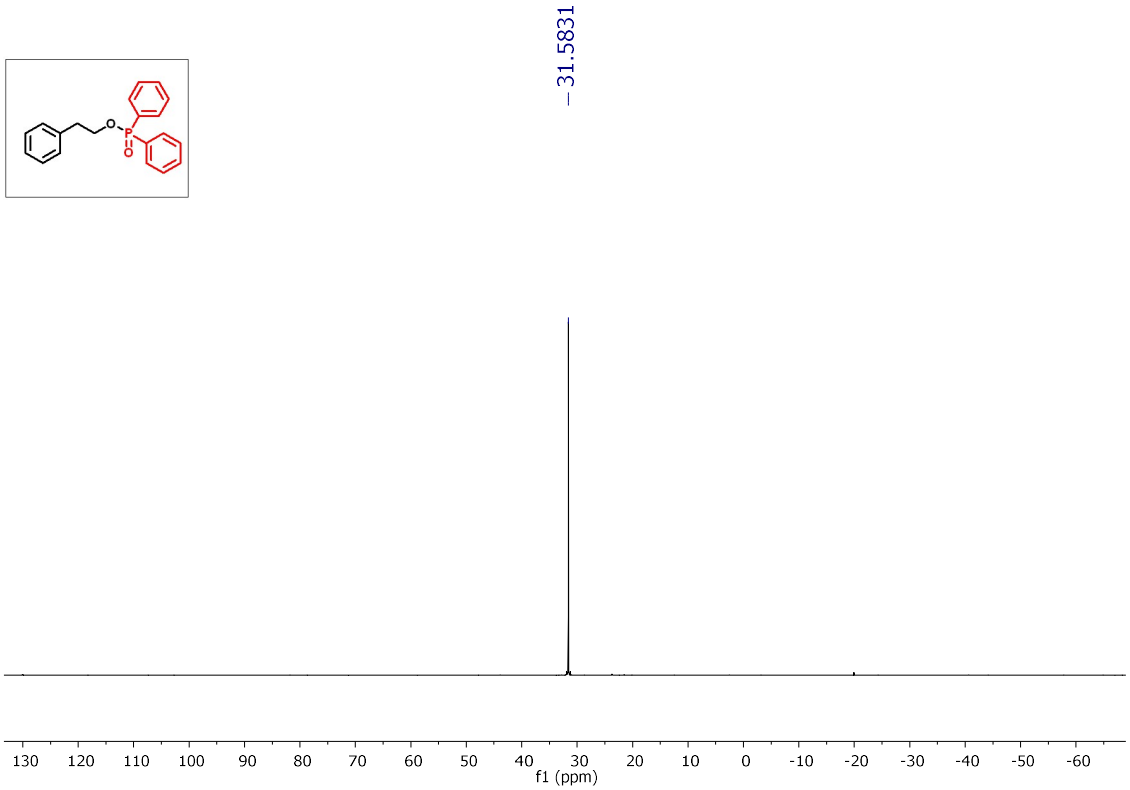
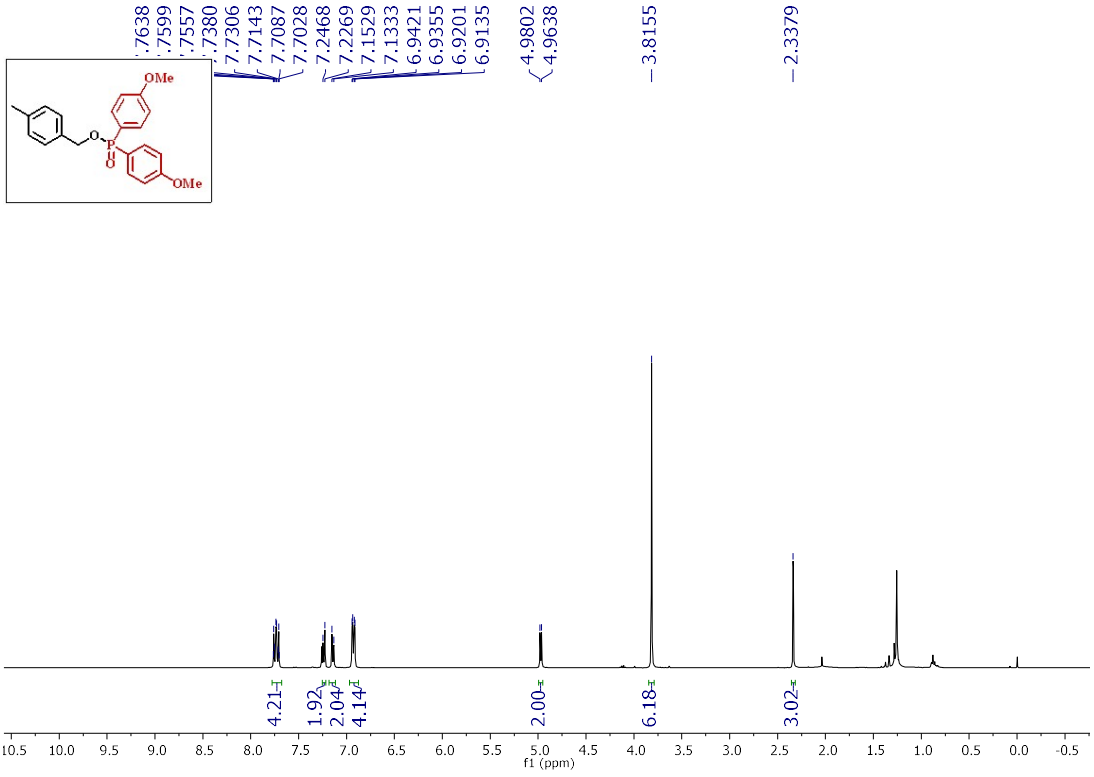


Figure S85. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4aj in $CDCl_3$



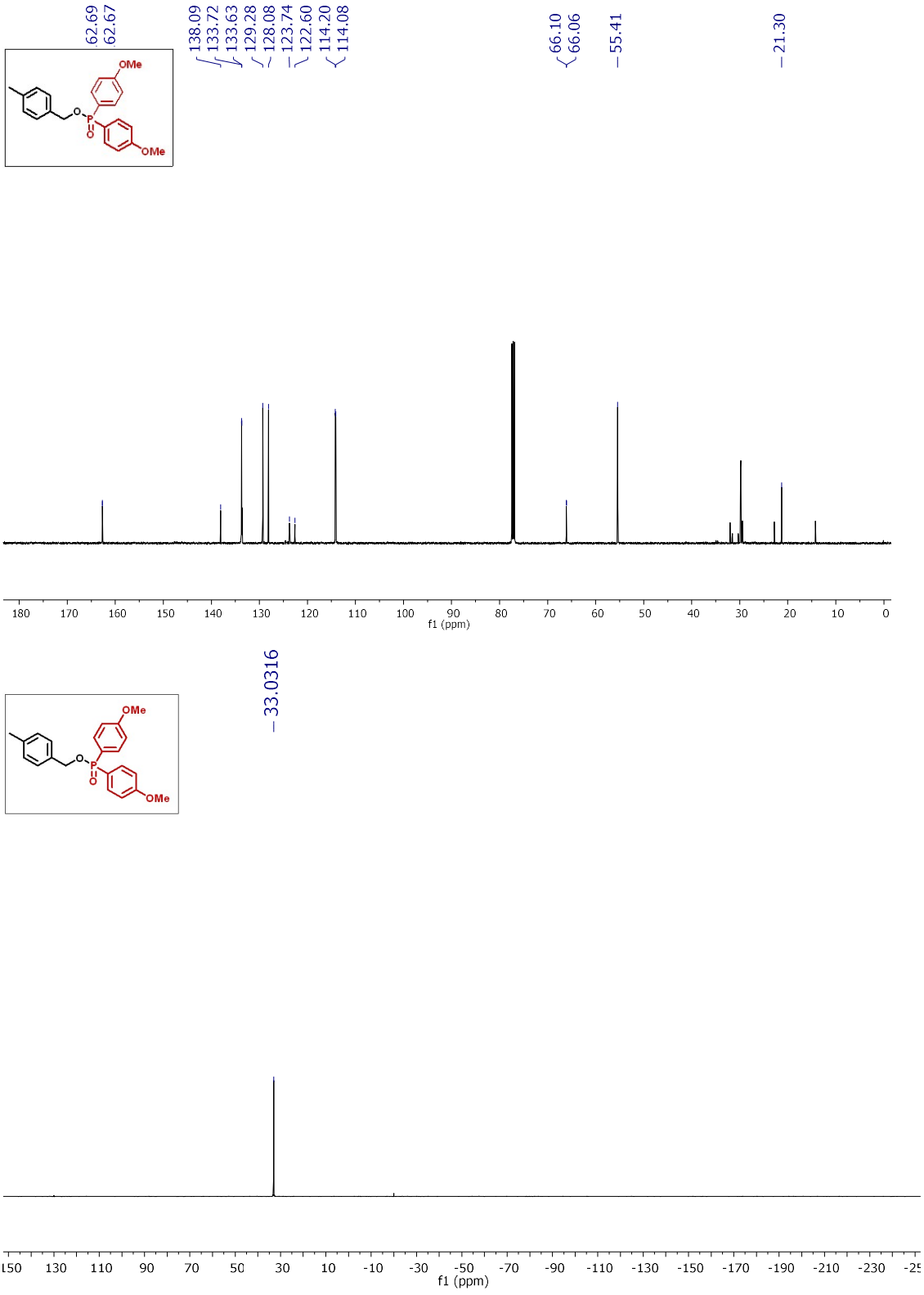
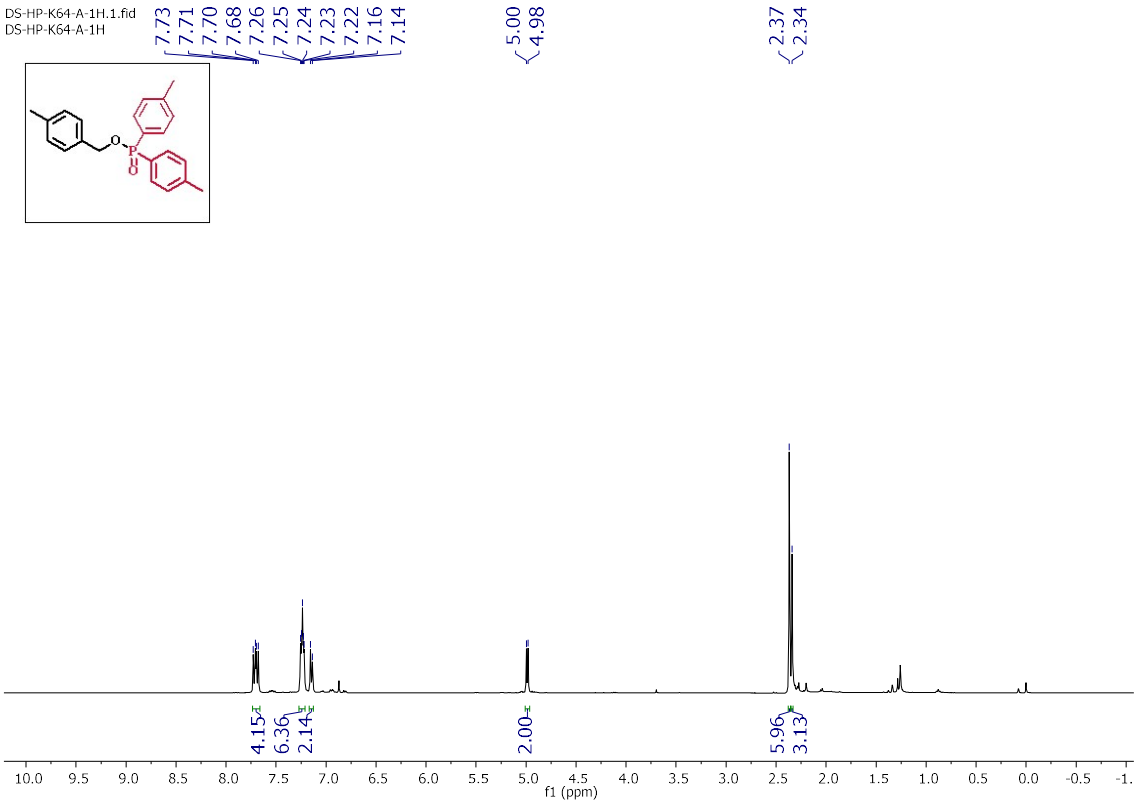
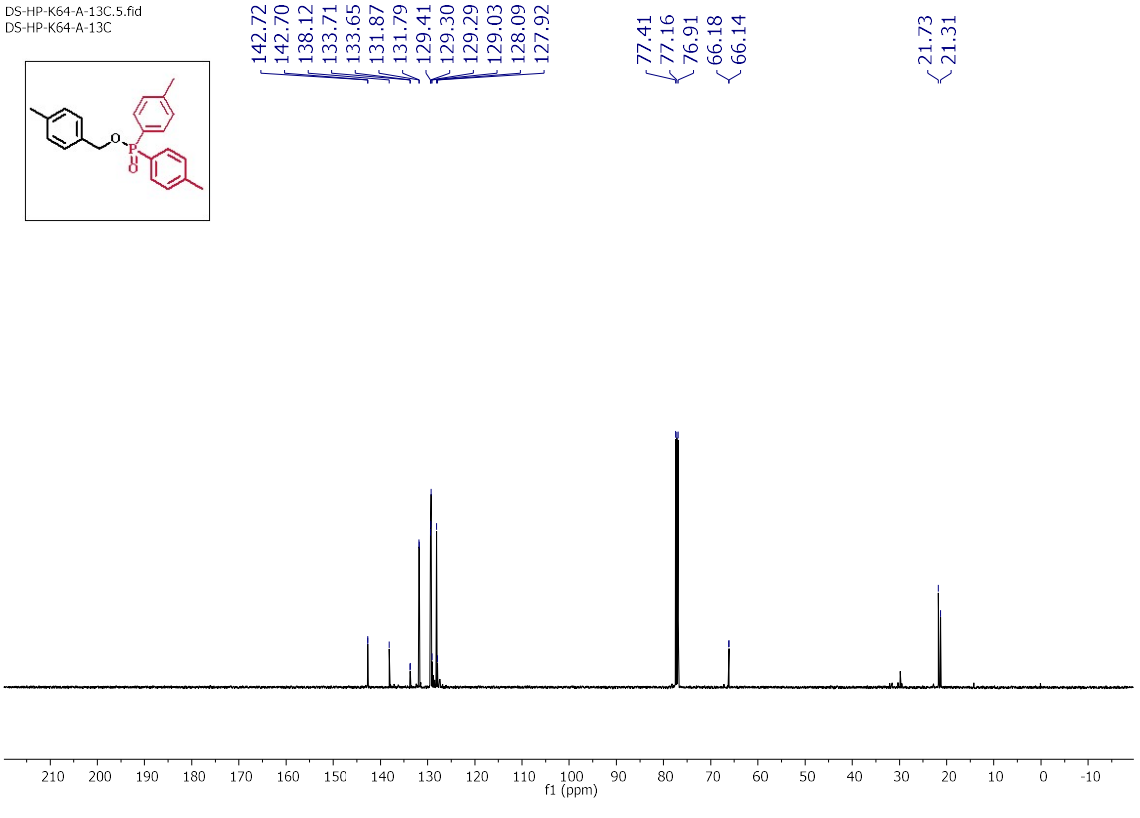


Figure S86. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ak in $CDCl_3$


DS-HP-K64-A-1H.1.fid
DS-HP-K64-A-1H
7.73
7.71
7.70
7.68
7.26
7.25
7.24
7.23
7.22
7.16
7.14
5.00
4.98
2.37
2.34
4.15
6.36
2.14
2.00
5.96
3.13
f1 (ppm)


DS-HP-K64-A-13C.5.fid
DS-HP-K64-A-13C
142.72
142.70
138.12
133.71
133.65
131.87
131.79
129.41
129.30
129.29
129.03
128.09
127.92
77.41
77.16
76.91
66.18
66.14
21.73
21.31
f1 (ppm)

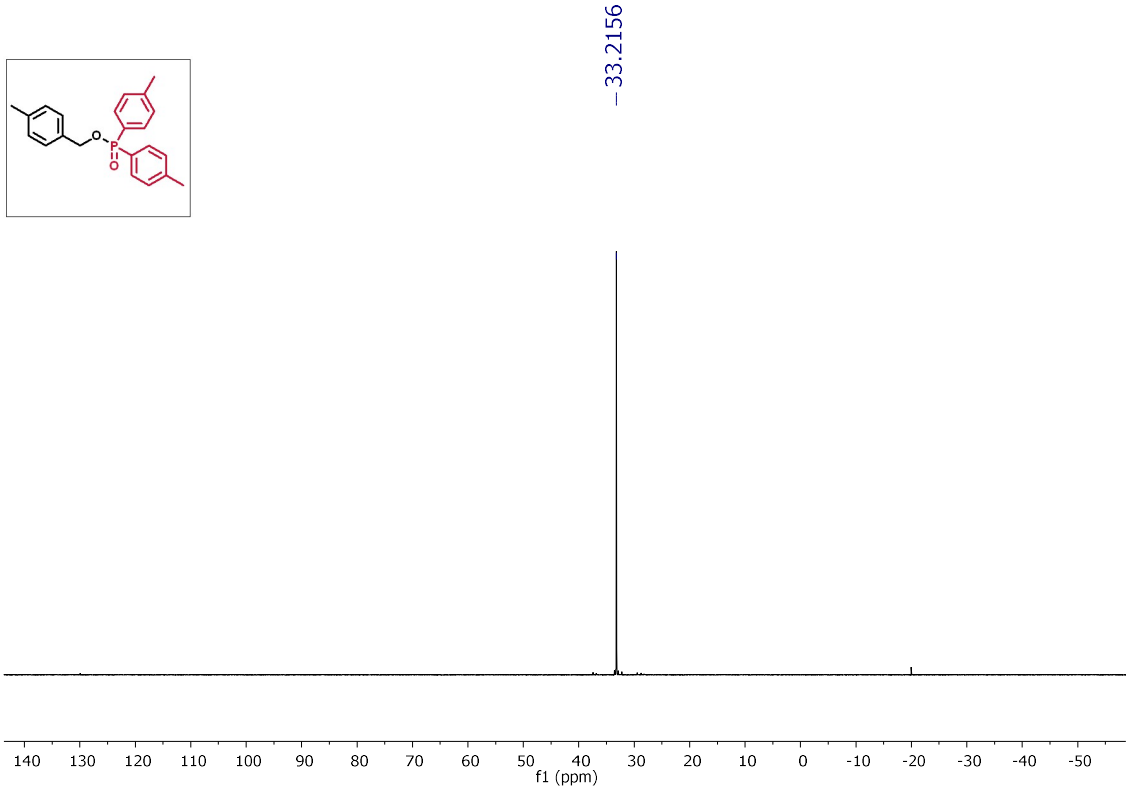
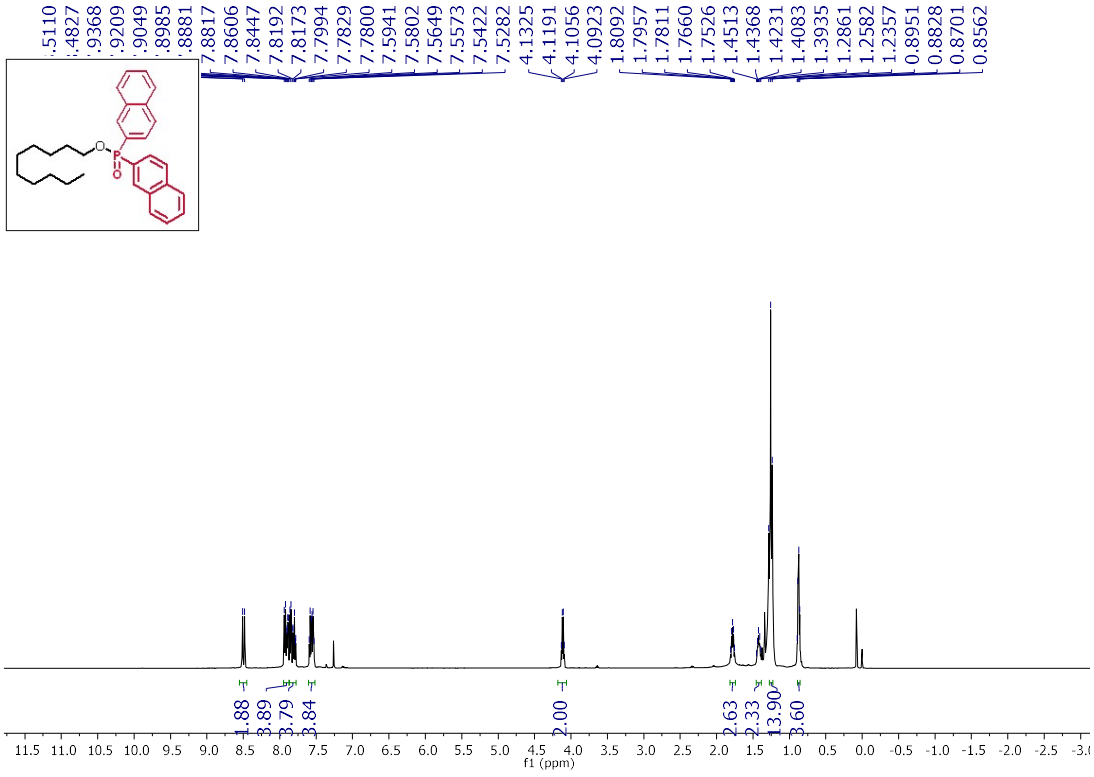


Figure S87. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4al in $CDCl_3$



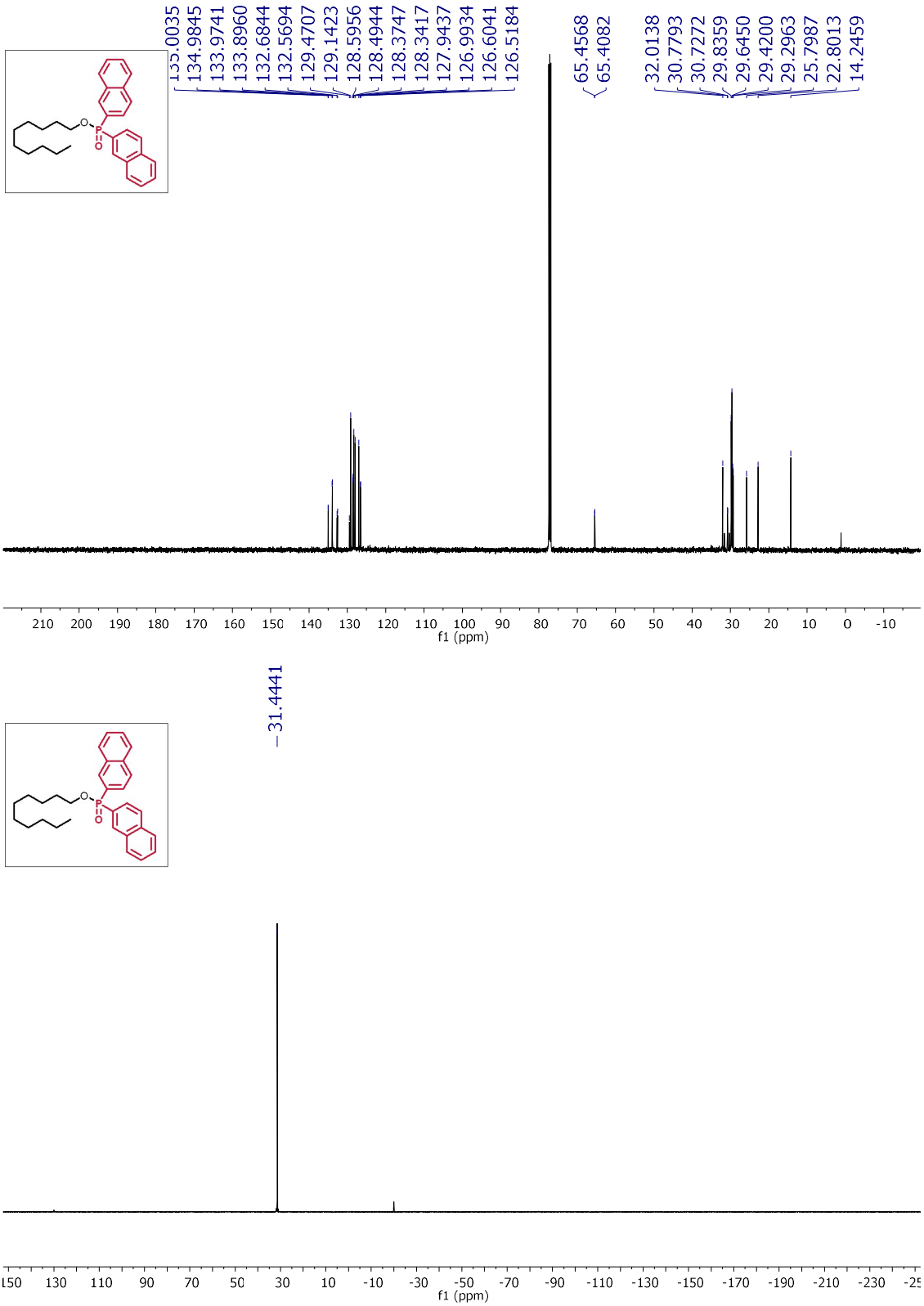
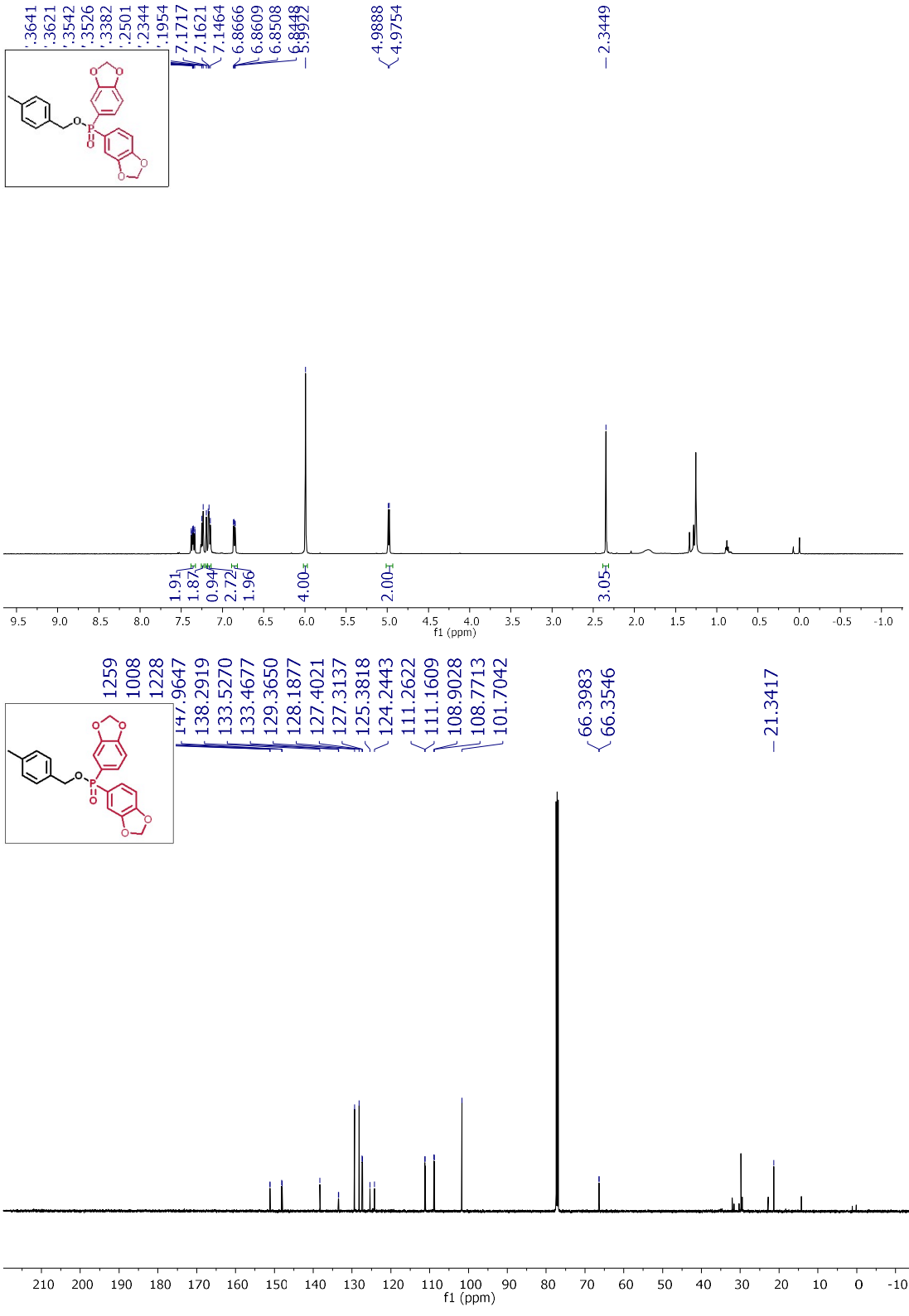


Figure S88. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4am in $CDCl_3$


7.1717
7.1621
7.1464
6.8666
6.8609
6.8508
4.9888
4.9754
2.3449
1.91
1.87
0.94
2.72
1.96
4.00
2.00
3.05
f1 (ppm)
147.9647
138.2919
133.5270
133.4677
129.3650
128.1877
127.4021
127.3137
125.3818
124.2443
111.2622
111.1609
108.9028
108.7713
101.7042
66.3983
66.3546
21.3417
f1 (ppm)

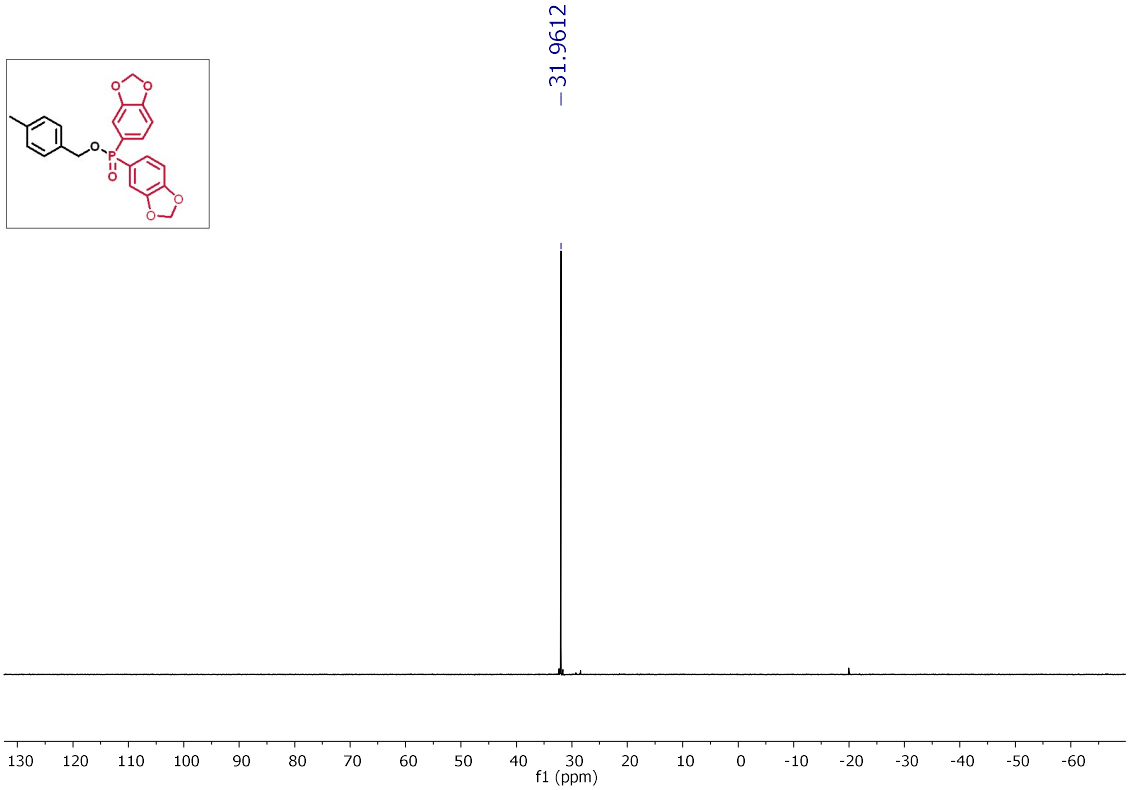
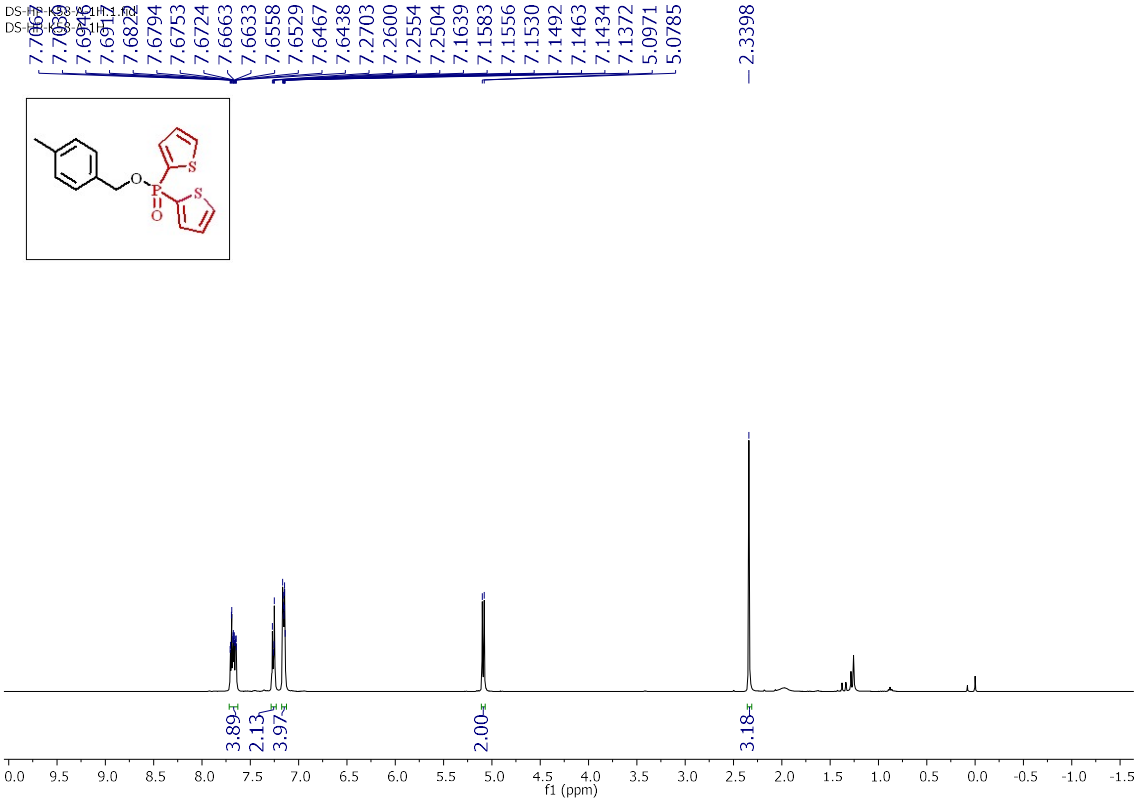
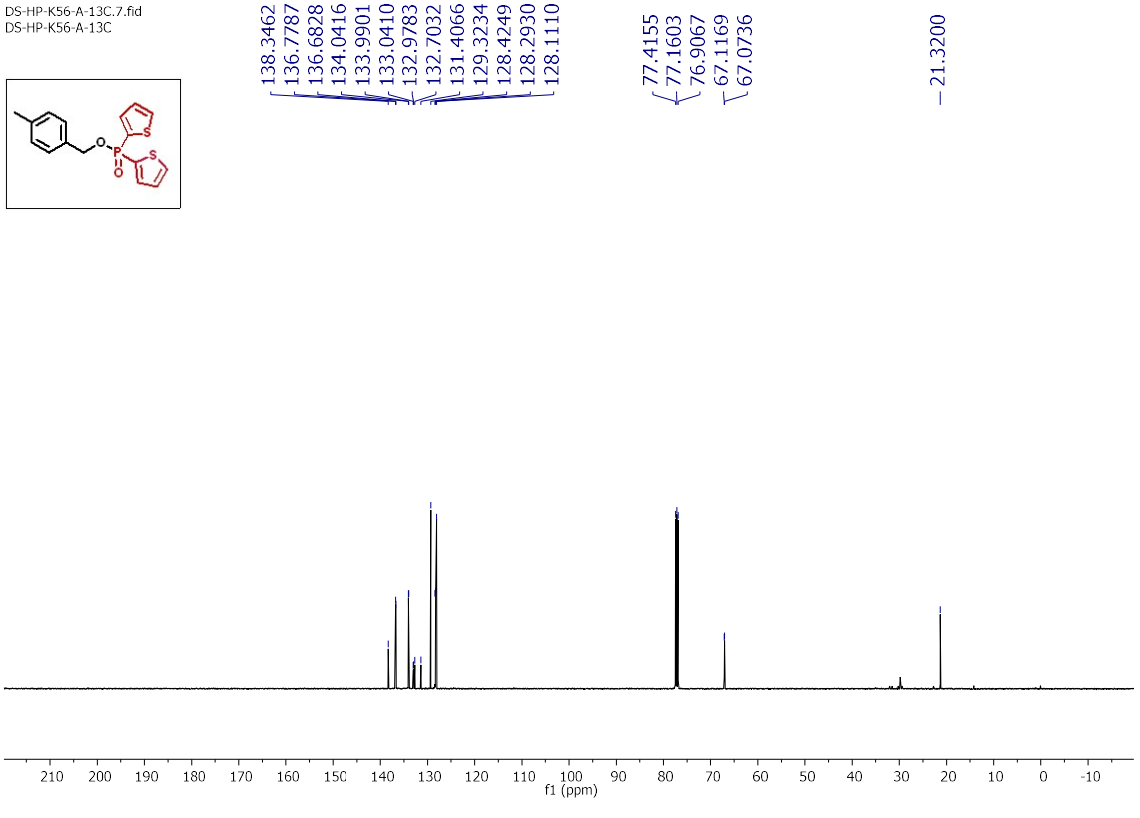


Figure S89. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4an in $CDCl_3$


7.7660
7.7638
7.6941
7.6911
7.6822
7.6794
7.6753
7.6724
7.6663
7.6633
7.6558
7.6529
7.6467
7.6438
7.2703
7.2600
7.2554
7.2504
7.1639
7.1583
7.1556
7.1530
7.1492
7.1463
7.1434
7.1372
5.0971
5.0785
2.3398
3.89
2.13
3.97
2.00
3.18
f1 (ppm)


DS-HP-K56-A-13C.7.fid
DS-HP-K56-A-13C
138.3462
136.7787
136.6828
134.0416
133.9901
133.0410
132.9783
132.7032
131.4066
129.3234
128.4249
128.2930
128.1110
77.4155
77.1603
76.9067
67.1169
67.0736
21.3200
f1 (ppm)

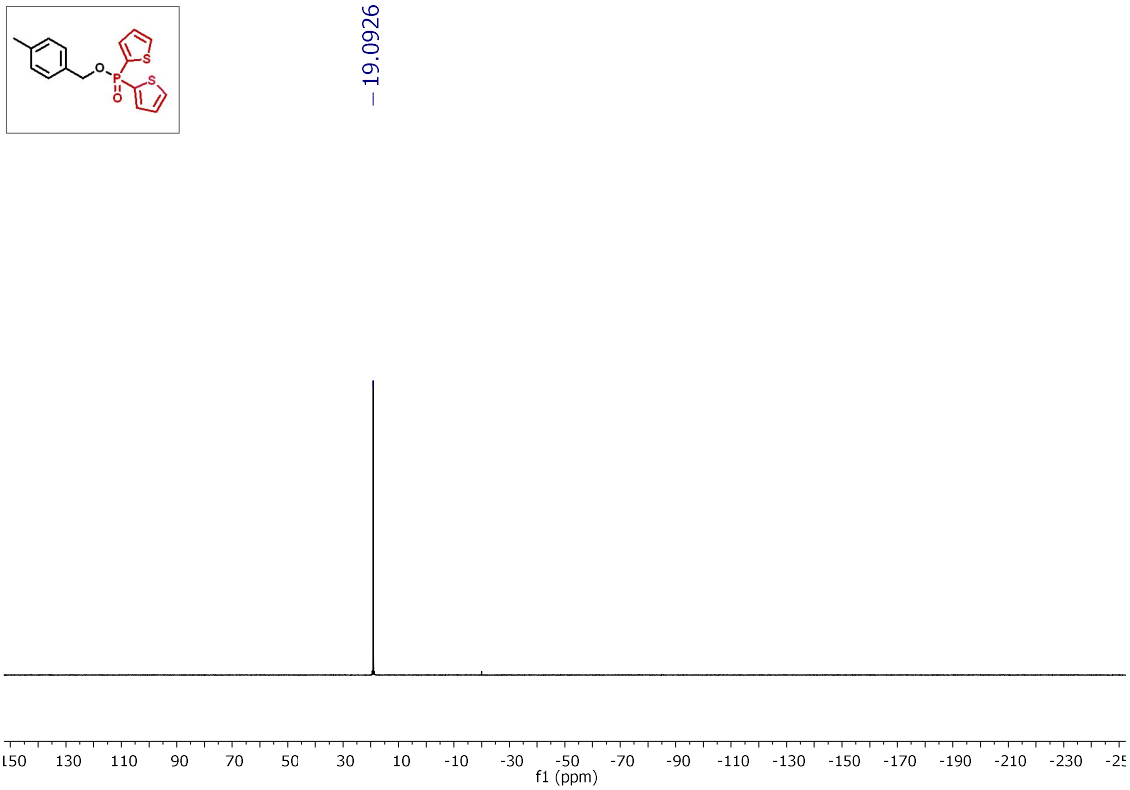
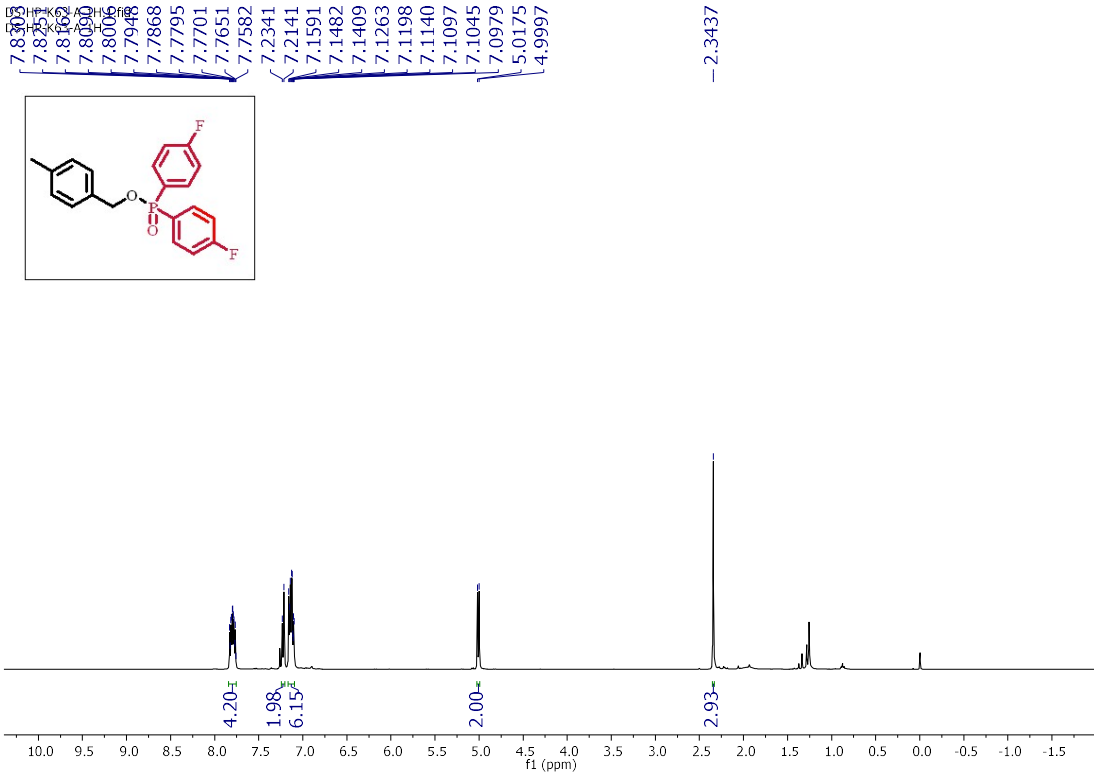
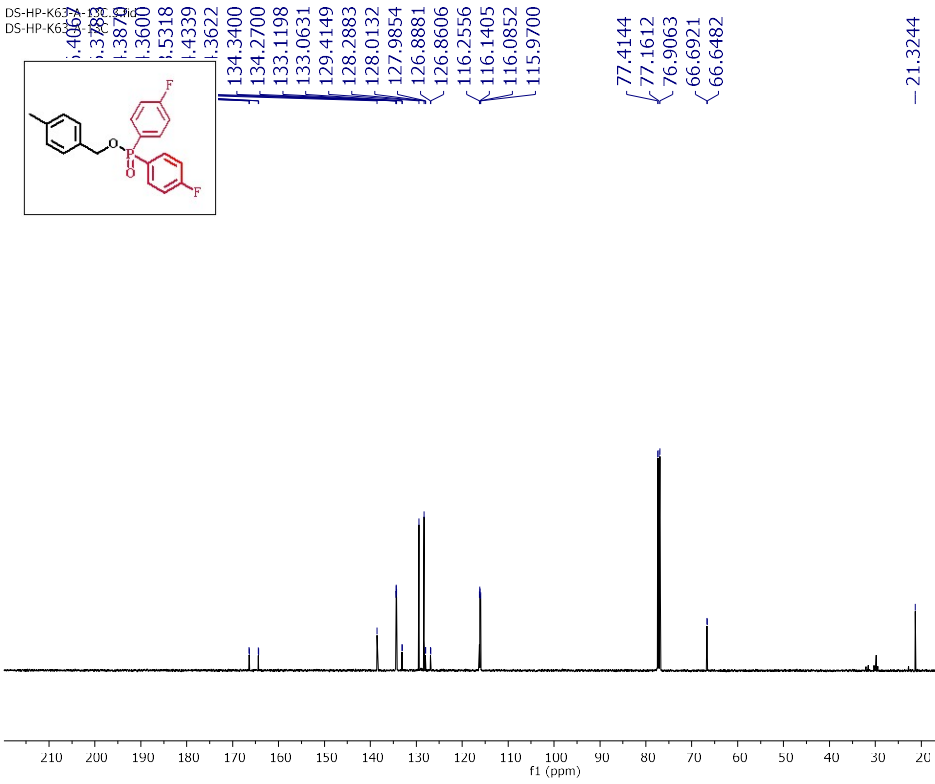
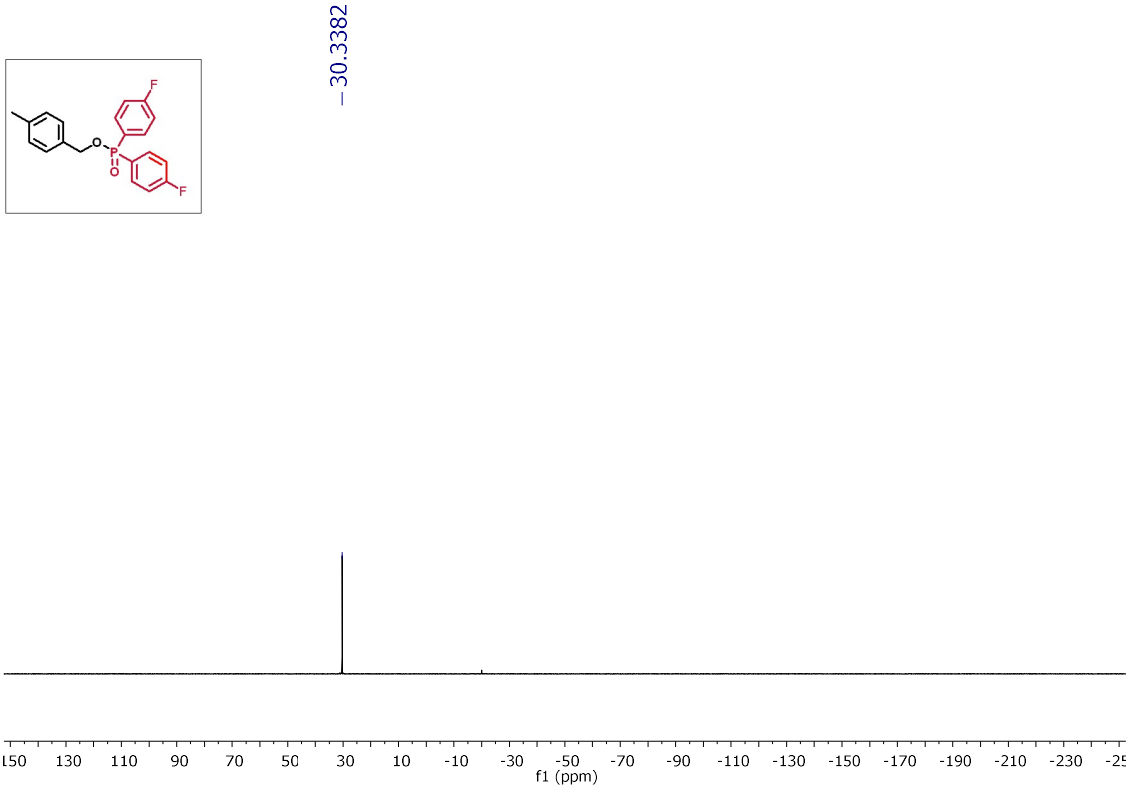


Figure S90. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ao in $CDCl_3$




DS-HP-K637
DS-HP-K637A-1
134.3400
134.2700
133.1198
133.0631
129.4149
128.2883
128.0132
127.9854
126.8881
126.8606
116.2556
116.1405
116.0852
115.9700
77.4144
77.1612
76.9063
66.6921
66.6482
21.3244
f1 (ppm)


30.3382
f1 (ppm)

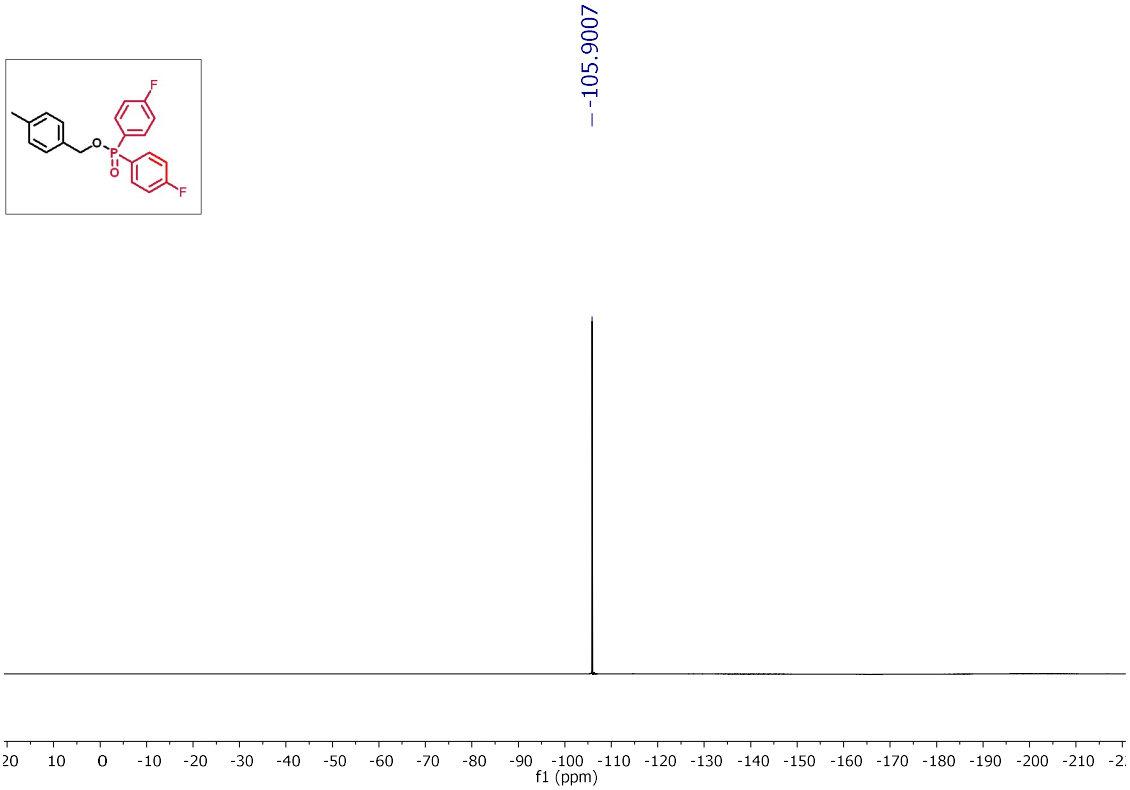
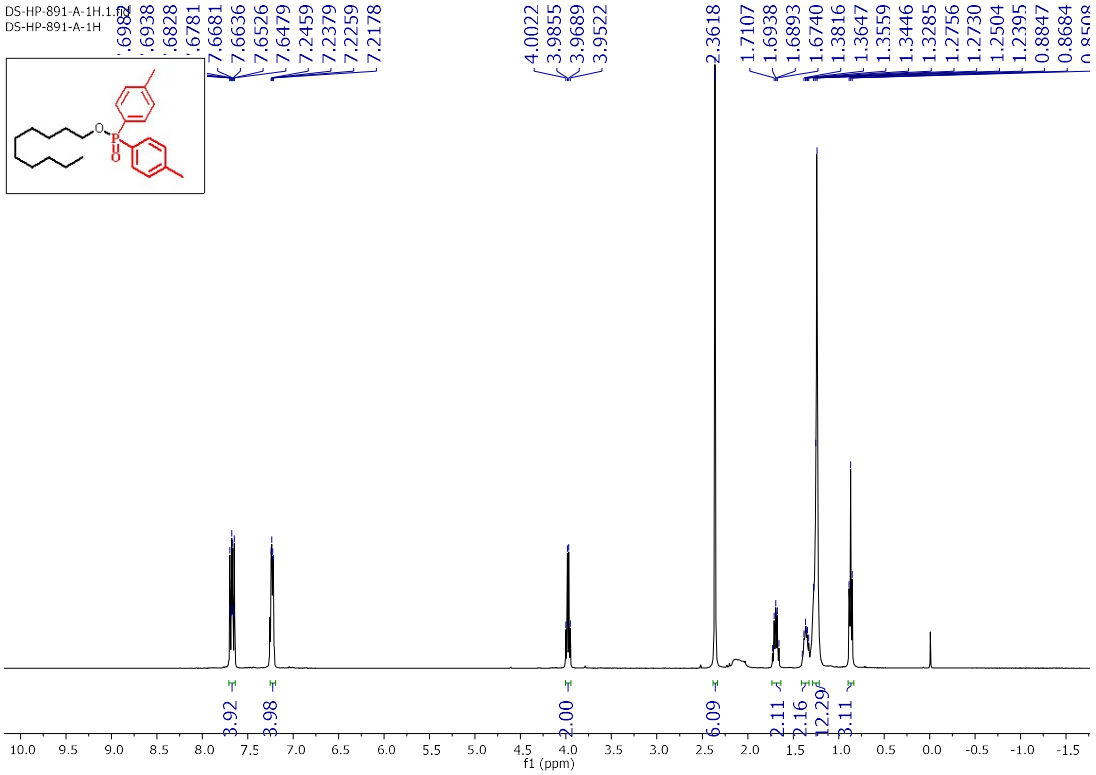
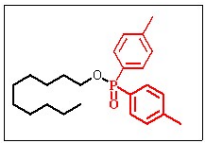


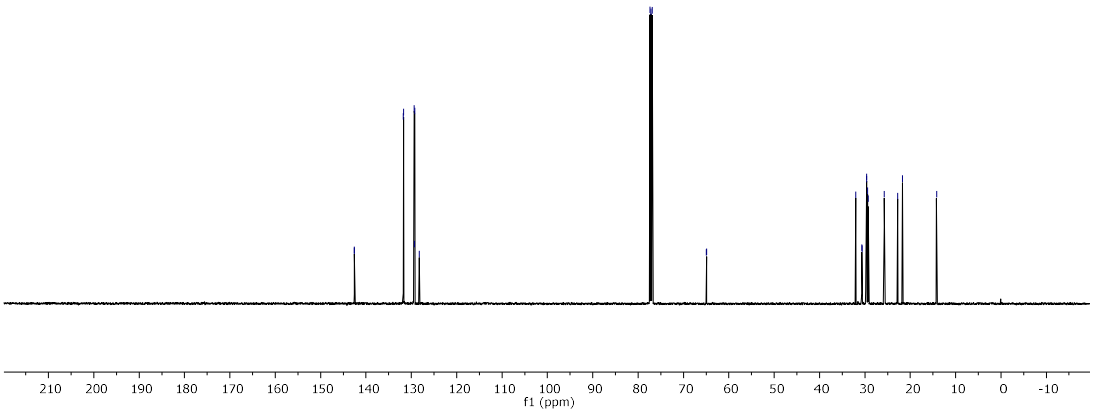
Figure S91. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) ^{19}F $\{^{1}H\}$ NMR (402 MHz) spectrum of Compound 4ap in $CDCl_3$.



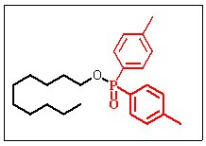
DS-HP-891-A-13C.3.fid
DS-HP-891-A-13C



142.5675
142.5445
131.7816
131.6980
129.3704
129.3340
129.2639
128.2236
77.4149
77.1609
76.9069
64.9722
64.9242
31.9950
30.6930
30.6408
29.6212
29.6046
29.3951
29.2596
25.7331
22.7751
21.7029
14.2068

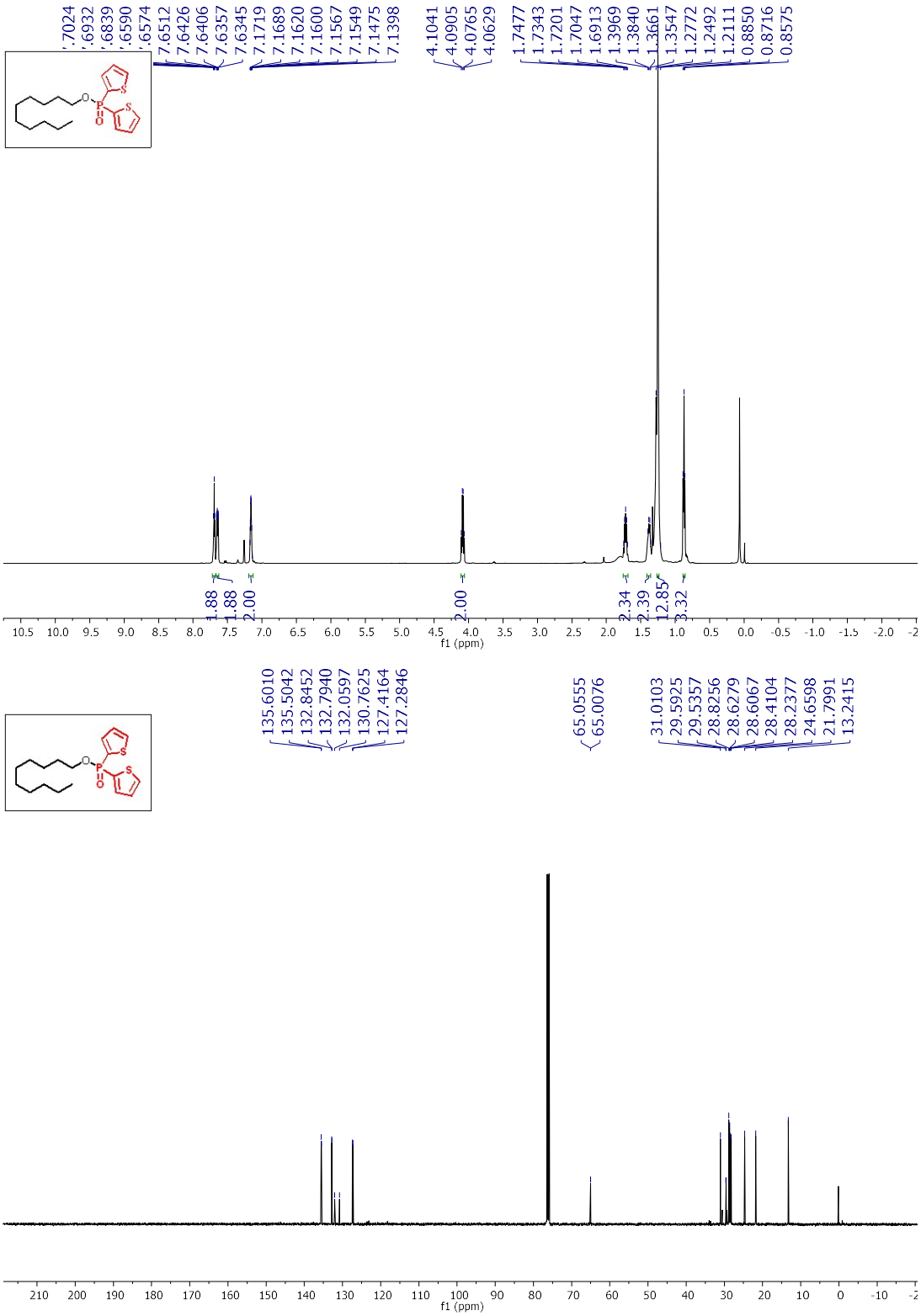


DS-HP-891-A-31P.5.fid
DS-HP-891-A-31P



32.11

Figure S92. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4aq in $CDCl_3$



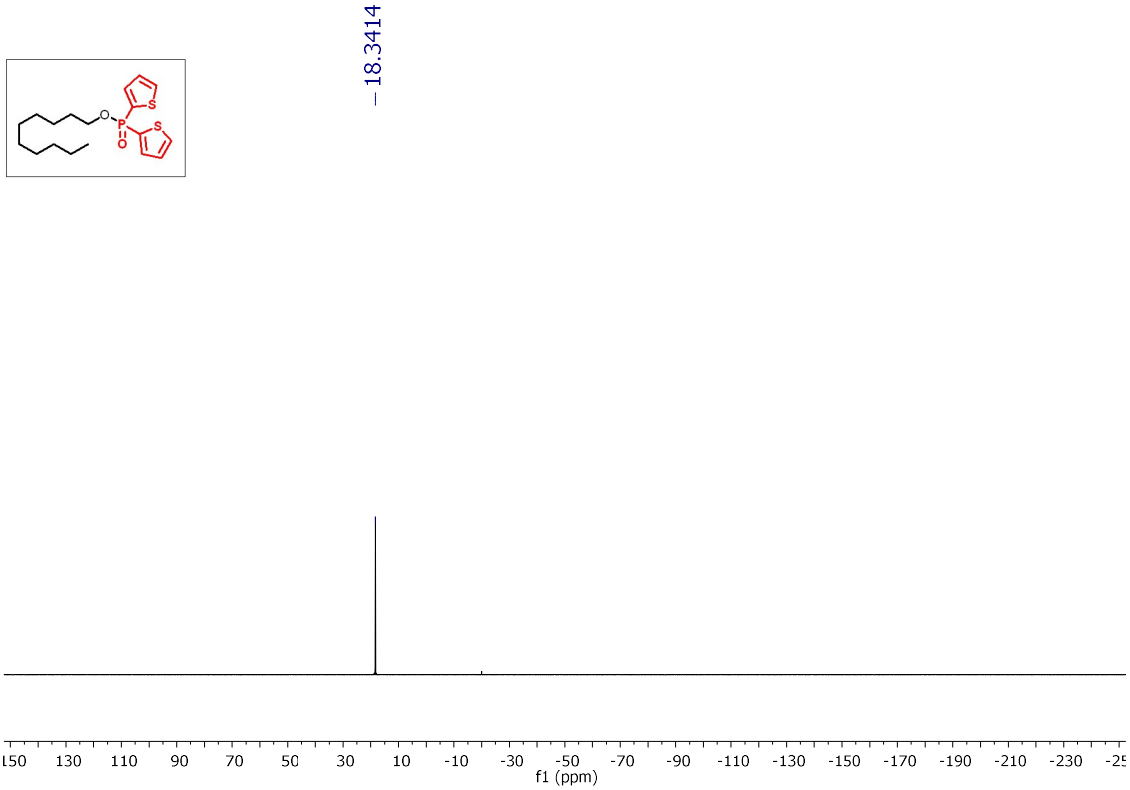
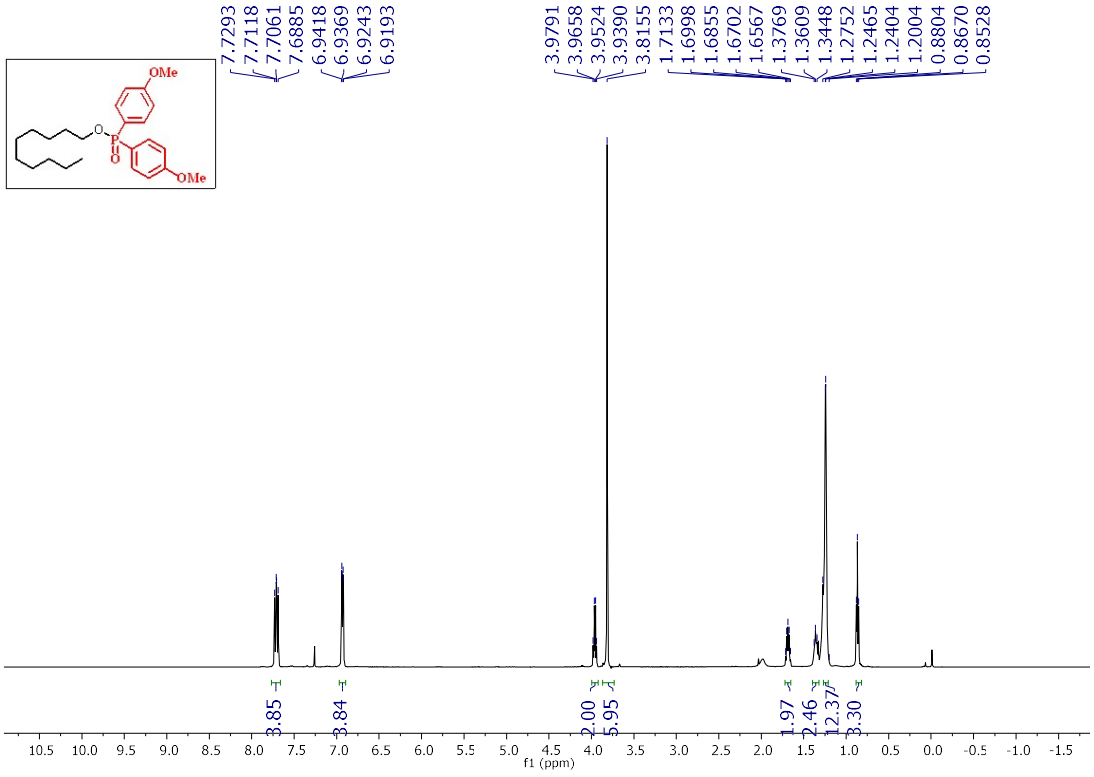


Figure S93. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4ar in $CDCl_3$



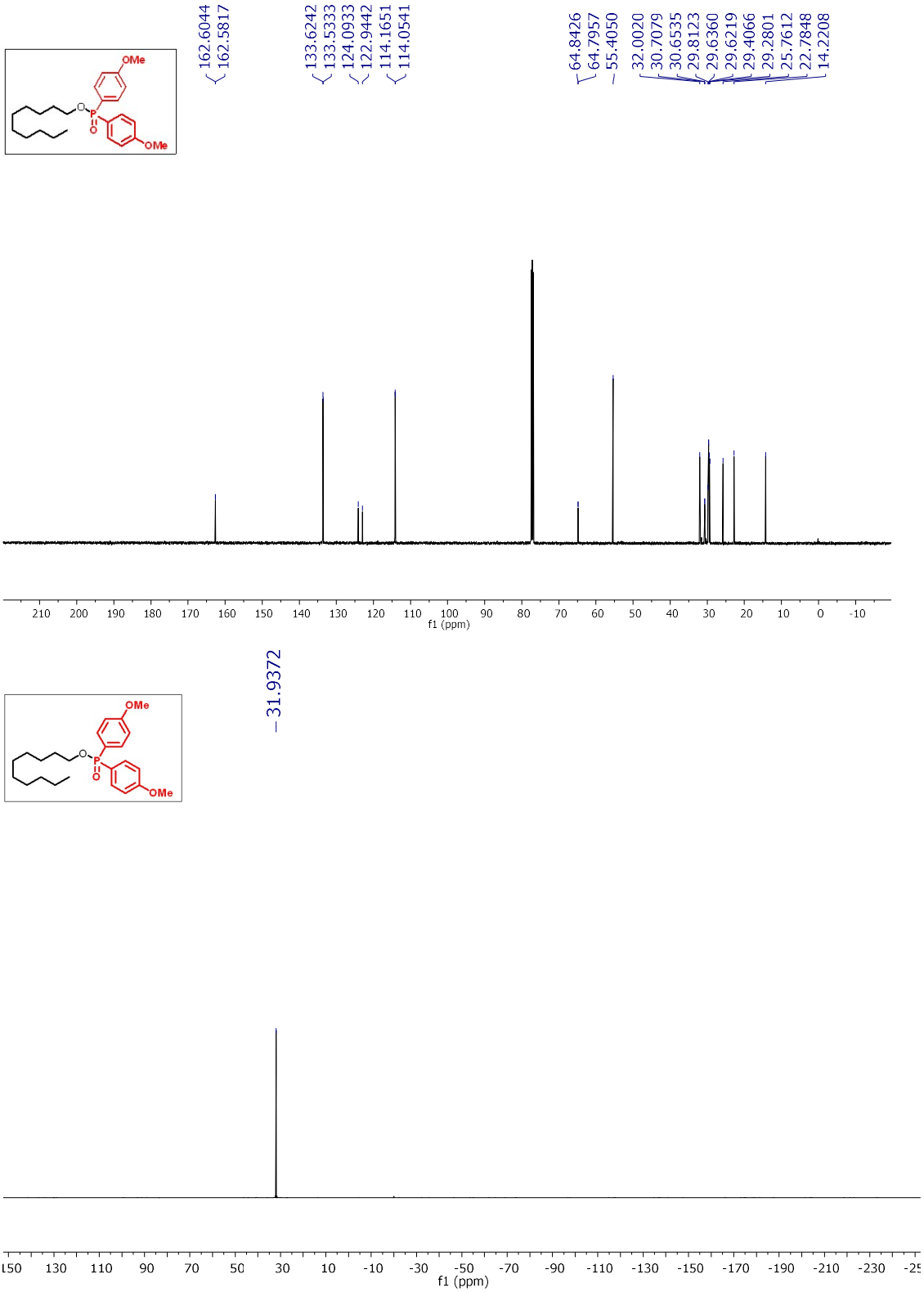
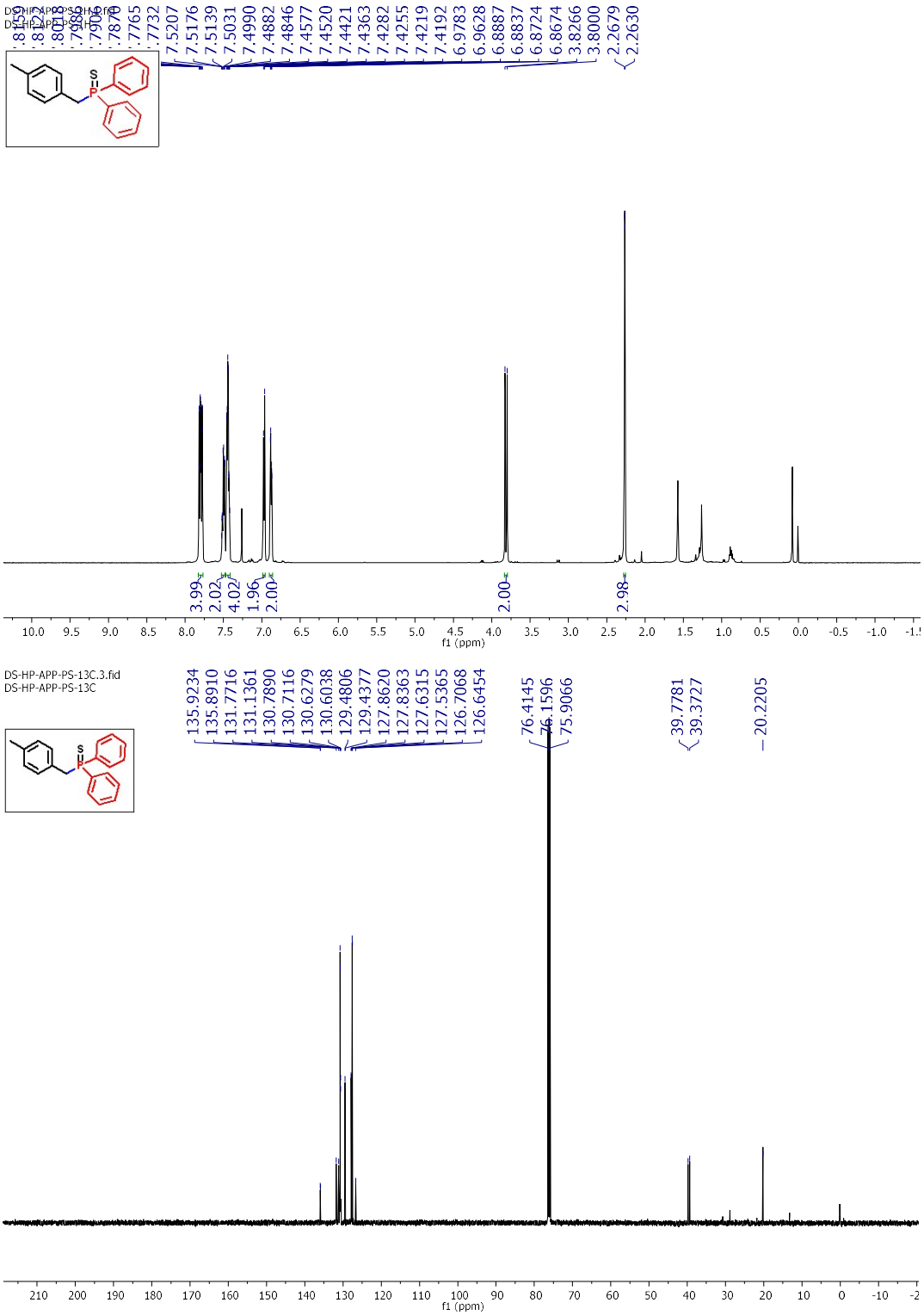


Figure S94. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 4as in $CDCl_3$


8.159
8.122
8.018
7.989
7.900
7.870
7.765
7.732
7.5207
7.5176
7.5139
7.5031
7.4990
7.4882
7.4846
7.4577
7.4520
7.4421
7.4363
7.4282
7.4255
7.4219
7.4192
6.9783
6.9628
6.8887
6.8837
6.8724
6.8674
3.8266
3.8000
2.2679
2.2630
3.99
2.02
4.02
1.96
2.00
2.00
2.98
f1 (ppm)
DS-HP-APP-PS-13C.3.fid
DS-HP-APP-PS-13C
135.9234
135.8910
131.7716
131.1361
130.7890
130.7116
130.6279
130.6038
129.4806
129.4377
127.8620
127.8363
127.6315
127.5365
126.7068
126.6454
76.4145
76.1596
75.9066
39.7781
39.3727
20.2205
f1 (ppm)

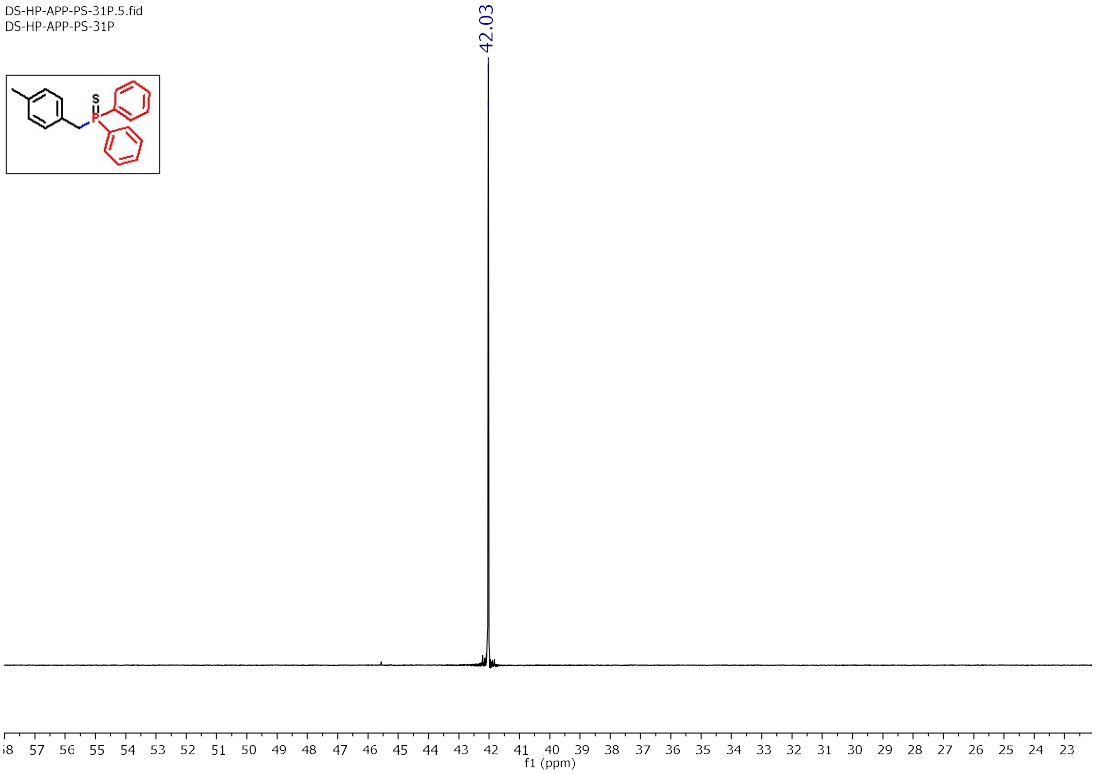
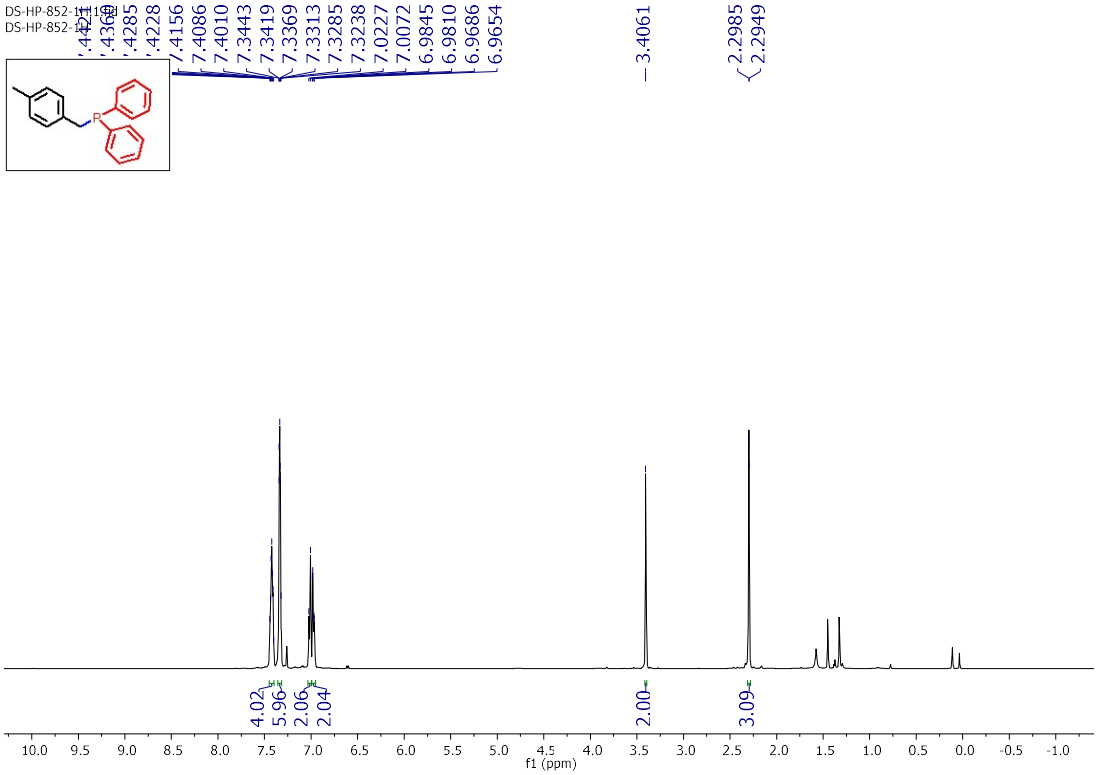


Figure S95. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and ^{31}P $\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 6 in $CDCl_3$



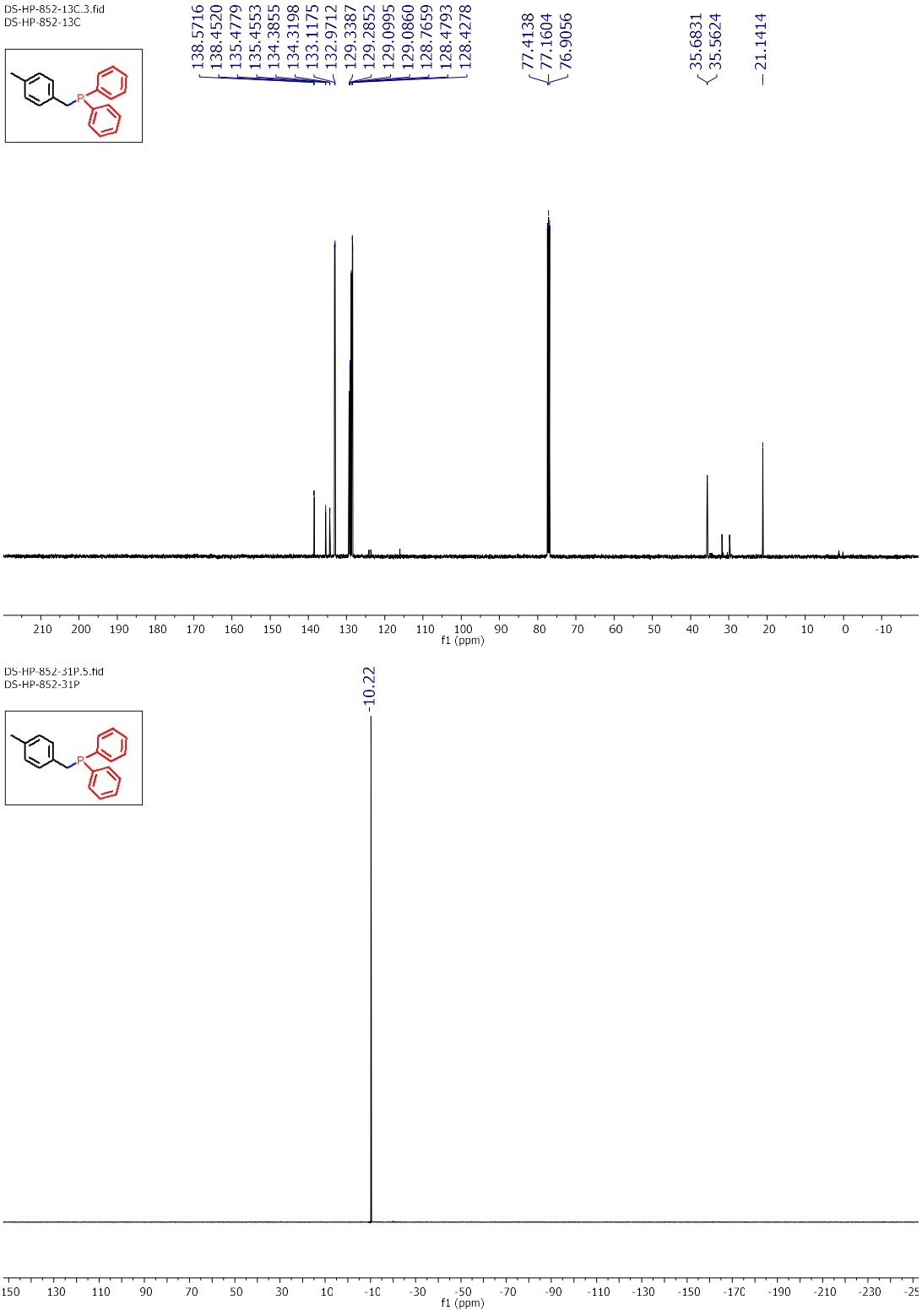


Figure S96. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 5 in $CDCl_3$

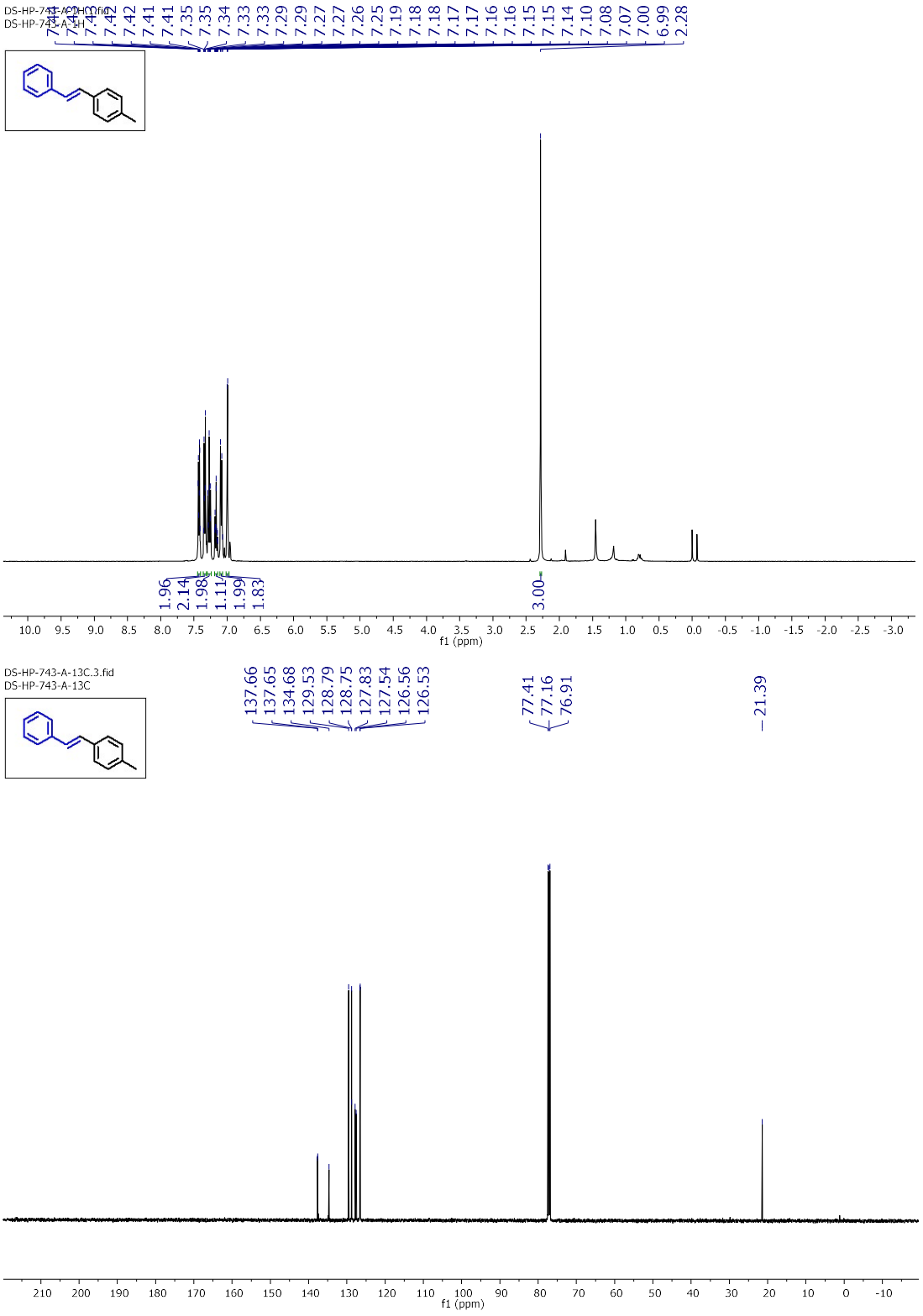


Figure S97. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\ \{^{1}H\}$ NMR (200 MHz) spectrum of Compound 8 in $CDCl_3$

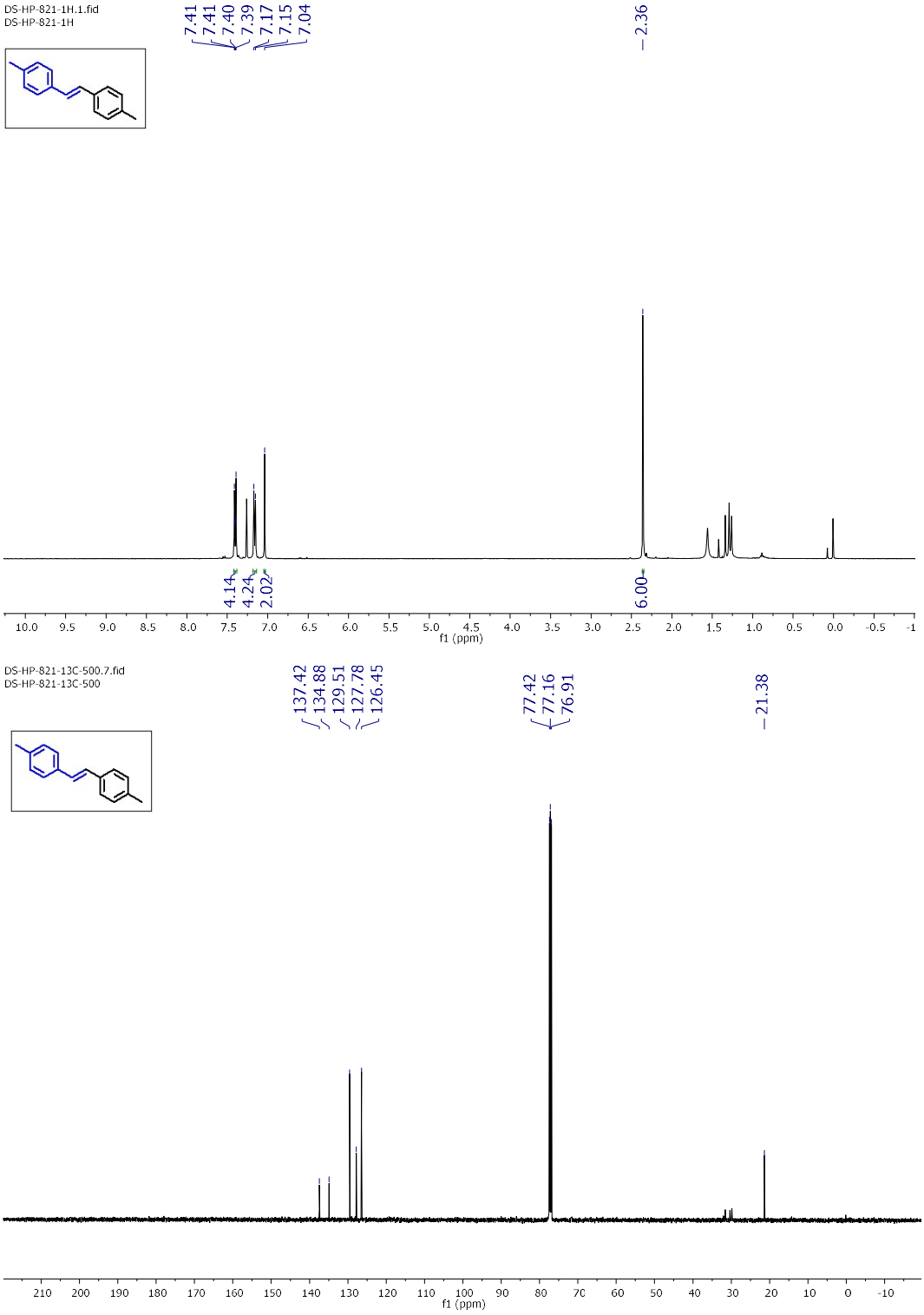


Figure S98. ^{1}H NMR (500 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz), and $^{31}P\{^{1}H\}$ NMR (200 MHz) spectrum of Compound 7 in $CDCl_3$

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