Supporting Information

Transition-Metal-Free Photoredox Phosphonation of Aryl C–N and C–X Bonds in Aqueous Solvent Mixtures

Lei Pan,[a] Alexandra S. Kelley,[a] Maria Victoria Cooke,[a] Macy M. Deckert,[a] and Sébastien Laulhé*[a]

[a]Department of Chemistry and Chemical Biology, Indiana University-Purdue University Indianapolis, Indianapolis, IN 46202, USA.

Number of pages: 93

Number of figures: 125

Number of schemes: 6

Number of tables: 2

Table of Contents

General Information

All the solvents and commercially available reagents were purchased from commercial sources (Acros Organics,TCI, Alfa Aesar, Sigma-Aldrich, Oakwood) and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light or stains for TLC Plates. Column chromatography was performed on EMD Silica Gel 60 (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE III-400 or 500 spectrometer. ^{1}H NMR data was reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data was reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). High Resolution Mass Spectrometry (HRMS) analysis was obtained using Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS system. UV-Vis was obtained using GENESYS™ 10S UV-Vis Spectrophotometer and fisherbrand macro quartz cuvettes (cat. No. 14-958-112). A Kessil (456, 427 or 390 nm) Blue LED lamp 40W was used for this light-promoted reaction. The vial was placed approximately 4 cm away from the Blue LED, with the LED shining directly at the side of the vial. 10ml microwave reaction vial secured by 20mm aluminum seals with 0.125-inch thick, blue PTFE / white silicone septa was used for the reaction.

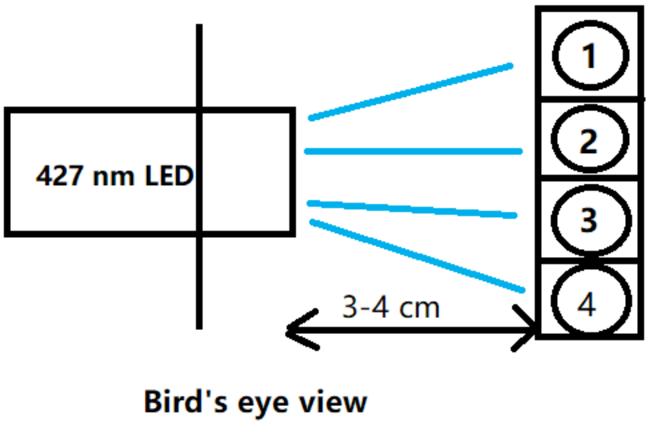
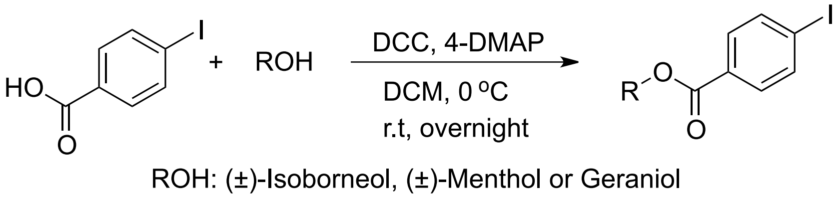


Figure S1. Representation of the Kessil LED lamp and its location and distance to the reaction flasks. No more than 4 reactions were irradiated simultaneously.

Procedure for preparation of starting materials

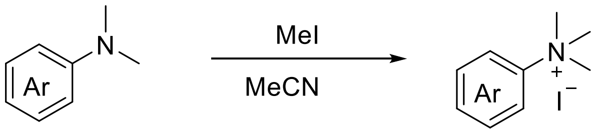
1. The general procedure for the preparation of starting materials aryl iodides for the synthesis of 31, 32, and 33:[1-3]



Scheme S1. Esterification or 4-iodobenzoic acid.

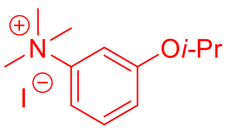
A 25 mL round bottom flask equipped with a stir bar was charged with 4-iodobenzoic acid (3 mmol), natural product alcohol (isoborneol, methol, or geraniol) ((2 mmol), DCC (0.6 g, 3 mmol) and 12 mL of CH_2Cl_2. Then 4-DMAP (0.4 mmol) was added in one portion. The reaction was stirred for 4 h at room temperature. After filtration, the solution was concentrated under reduced pressure. The residue was purified by flash column chromatography to give the desired aryl iodides.

2. The general procedure for the preparation of ammonium salts:[4]



Scheme S2. Methylation reaction for the synthesis of aryl ammonium salts.

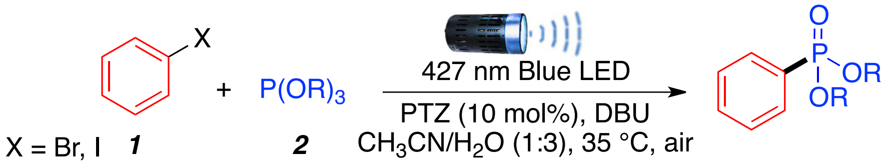
To a solution of *N,N*-dimethylaniline (3 mmol) in CH_3CN (5 mL) was added CH_3I (1.28 g, 9 mmol). The solution was stirred for 8 h at 90° C in a screw-capped vial. At the conclusion of the reaction, diethyl ether was added (40 mL), the precipitate was isolated by filtration, washed with ethyl ether to afford the desired products.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (t, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.29 (s, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 4.80 (dt, *J* = 11.6, 5.7 Hz, 1H), 4.01 (s, 9H), 1.37 (d, *J* = 5.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.48 (s), 148.50 (s), 131.65 (s), 117.15 (s), 111.10 (s), 107.79 (s), 71.21 (s), 57.80 (s), 21.86 (s).

General procedure for the synthesis of Aromatic Phosphonates.



Scheme S3. General procedure for the phosphonation reaction.

A 10 mL microwave vial was charged with aryl halides (0.2 mmol), trialkyl phosphites (0.6 mmol), DBU (0.4 mmol), PTZ (0.02 mmol), H_2O/CH_3CN (0.75/0.25 mL) and capped with 20 mm microwave crimp caps with septa. And then put the vial approximately 4 cm away from the Blue LED (427 nm) and stirred (Room temperature was 35 °C near the reaction flask, due to lamp induced heating). After 24h, the product was determined by GC-MS. The reaction mixture was quenched with DI water and diluted and extracted with EtOAc. The organic layer was filtered through a Pasteur monster pipette of dry reagent grade Na_2SO_4, and the filtrate was concentrated in vacuo. Then the residue was purified by flash chromatography on silica gel to yield the desired products.

Same procedure was followed for aryl ammonium salts but using 390 nm lamp and with a H_2O/CH_3CN (0.25/0.75 mL).

Procedure for the gram scale reaction.

Scheme S4. Procedure for large-scale phosphonation reaction.

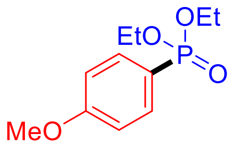
A 20 mL scintillation vials was charged with 1-iodo-4-methoxybenzene (1.170 g, 5 mmol), triethyl phosphite (1.662 g, 10 mmol), DBU (1.522 g, 10 mmol), PTZ (100 mg, 0.5 mmol), H_2O/CH_3CN (12/4 mL) and capped with white polyethylene caps. And then put the vial approximately 4 cm away from the Blue LED and stirred. After 48h, the transformation was determined by GC-MS (99% transformation). The reaction mixture was quenched with DI water and diluted and extracted with EtOAc. The organic layer was filtered through a Pasteur monster pipette of dry reagent grade Na_2SO_4, and the filtrate was concentrated in vacuo. Then the residue was purified by flash chromatography (ethyl acetate/hexane= 2/1) on silica gel to yield the desired products (1.003 g, 82%).

Full optimization of reaction conditions[a]

Entry	Base (eq.)	**2a** (eq.)	Solvent (mL)	Yield (%)[b] **3**	**1a**
1	DBU (3.0)	3.0	CH_3CN (1.0)	89(**A**)	-
2	Et_3N (3.0)	3.0	CH_3CN (1.0)	10(**A**)	90
3	DIPEA (3.0)	3.0	CH_3CN (1.0)	12(**A**)	87
4	Cs_2CO_3 (3.0)	3.0	CH_3CN (1.0)	27(**B**)	72
5	K_2CO_3 (3.0)	3.0	CH_3CN (1.0)	34(**B**)	60
6	LiO*t*Bu (3.0)	3.0	CH_3CN (1.0)	58(**B**)	39
7	NaO*t*Bu (3.0)	3.0	CH_3CN (1.0)	46(**B**)	35
8	-	3.0	CH_3CN (1.0)	9(**B**)	90
9[c]	DBU (3.0)	3.0	CH_3CN (1.0)	6(**B**)	83
10[d]	DBU (3.0)	3.0	CH_3CN (1.0)	-(**B**)	97
11[e]	DBU (3.0)	3.0	CH_3CN (1.0)	85(**B**)	trace
12	DBU (2.0)	3.0	CH_3CN (1.0)	92(**B**)	trace
13	DBU (3.0)	2.0	CH_3CN (1.0)	66(**B**)	23
14[e]	DBU (2.0)	3.0	CH_3CN (1.0)+H_2O (0.1)	95(91)[f](**B**)	trace
15[e]	DBU (2.0)	3.0	CH_3CN/H_2O (1:1)	92(**B**)	trace
16[e]	DBU (2.0)	3.0	CH_3CN/H_2O (1:3)	90(**B**)	4
17[e]	DBU (2.0)	3.0	CH_3CN/H_2O (1:9)	87(**B**)	6
18[e]	DBU (2.0)	3.0	H_2O (1.0)	72(**B**)	15
19[e]	DBU (2.0)	3.0	THF (1.0)	26(**B**)	22
20[e]	DBU (2.0)	3.0	EtOH (1.0)	67(**B**)	20
21[e]	DBU (2.0)	3.0	CH_3CN (1.0)	85	-
22[c][e]	DBU (2.0)	3.0	CH_3CN (1.0)	trace	95

Table S1. Reaction Optimization. [a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), DBU (0.6 mmol), Solvent (1 mL), 35°C (Heating caused by the 456 nm (**A**) or 427 nm (**B**) LED lamp), under argon, 24h. [b] Yields are based on **1a**, determined by ^{1}H-NMR using dibromomethane as an internal standard. [c] The reaction was performed in the absence of PTH. [d] The reaction was performed in the dark, covered by aluminium foil. [e] The reaction was performed in air. [f] Isolated yield.

Analytical Data of compounds



3

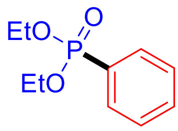
diethyl (4-methoxyphenyl)phosphonate[5]

Conditions: 1-iodo-4-methoxybenzene (47 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (44.4 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 12.7, 8.7 Hz, 2H), 6.90 (dd, J = 8.7, 3.3 Hz, 2H), 4.13 – 3.90 (m, 4H), 3.78 (s, 3H), 1.25 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, J = 3.4 Hz), 133.7 (d, J = 11.3 Hz), 119.5 (d, J = 194.9 Hz), 114.0 (d, J = 16.0 Hz), 61.9 (d, J = 5.3 Hz), 55.3 (s), 16.3 (d, J = 6.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 20.36 – 18.98 (m).



4

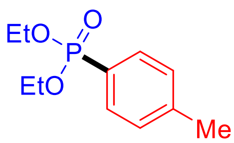
diethyl phenylphosphonate[5]

Conditions: iodobenzene (41 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (38.9 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.72 (m, 2H), 7.55 (td, J = 7.6, 1.3 Hz, 1H), 7.46 (td, J = 7.4, 4.2 Hz, 2H), 4.16 – 4.03 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4 (d, J = 3.0 Hz), 131.8 (d, J = 9.8 Hz), 128.5 (d, J = 186 Hz), 128.5 (d, J = 14.9 Hz), 62.1 (d, J = 5.4 Hz), 16.3 (d, J = 6.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.47 – 18.03 (m).



5

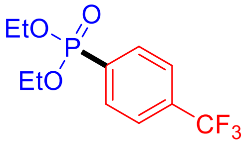
diethyl p-tolylphosphonate[6]

Conditions: 1-iodo-4-methylbenzene (44 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (42.4 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 13.1, 8.0 Hz, 2H), 7.25 (dd, J = 7.8, 4.0 Hz, 2H), 4.15 – 3.97 (m, 4H), 2.37 (s, 3H), 1.29 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9 (d, J = 3.2 Hz), 131.8 (d, J = 10.3 Hz), 129.2 (d, J = 15.4 Hz), 125.0 (d, J = 189 Hz), 61.9 (d, J = 5.3 Hz), 21.6 (d, J = 1.2 Hz), 16.3 (d, J = 6.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.51 (d, J = 4.0 Hz).



6

diethyl (4-(trifluoromethyl)phenyl)phosphonate[5]

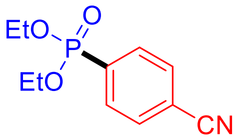
Conditions: 1-iodo-4-(trifluoromethyl)benzene (54 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (46.8 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 13.0, 8.0 Hz, 2H), 7.70 (dd, *J* = 8.1, 3.5 Hz, 2H), 4.22 – 4.02 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0 (qd, *J* =33, 3.3 Hz), 132.9 (d, *J* = 187 Hz), 132.2 (d, *J* = 10.1 Hz), 125.3 (dq, *J* = 15.1, 3.7 Hz), 123.6 (q, *J* = 272 Hz), 62.5 (d, *J* = 5.6 Hz), 16.3 (d, *J* = 6.3 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -63.35 (s).

^{31}P NMR (162 MHz, $CDCl_3$) δ 16.22 (s).



7

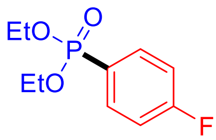
diethyl (4-cyanophenyl)phosphonate[16]

Conditions: 4-bromobenzonitrile (36 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (23.9 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 13.1, 8.3 Hz, 2H), 7.78 – 7.71 (m, 2H), 4.25 – 4.03 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1 (d, *J* = 187.7 Hz), 132.3 (d, *J* = 9.8 Hz), 132.0 (d, *J* = 15.0 Hz), 117.8 (d, *J* = 1.4 Hz), 116.0 (d, *J* = 3.5 Hz), 62.7 (d, *J* = 5.7 Hz), 16.3 (d, *J* = 6.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 15.31 (dtd, *J* = 12.5, 8.3, 4.1 Hz).



8

diethyl (4-fluorophenyl)phosphonate[5]

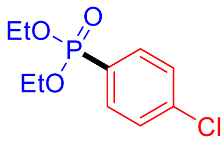
Conditions: 1-fluoro-4-iodobenzene (44 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (40.8 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.71 (m, 2H), 7.18 – 7.09 (m, 2H), 4.18 – 4.00 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (dd, *J* = 253, 3.9 Hz), 134.4 (dd, *J* = 11.3, 8.9 Hz), 124.6 (dd, *J* = 192, 4 Hz), 115.8 (dd, *J* = 21.4, 16.3 Hz), 62.2 (d, *J* = 5.4 Hz), 16.3 (d, *J* = 6.5 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -106.08 (d, *J* = 1.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.46 – 17.09 (m).



9

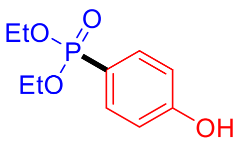
diethyl (4-chlorophenyl)phosphonate[5]

Conditions: 1-chloro-4-iodobenzene (48 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (34.8 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.66 (m, 2H), 7.51 – 7.39 (m, 2H), 4.22 – 3.97 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0 (d, J = 4.1 Hz), 133.2 (d, J = 10.7 Hz), 128.8 (d, J = 15.7 Hz), 127.1 (d, J = 190.9 Hz), 62.3 (d, J = 5.5 Hz), 16.3 (d, J = 6.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.59 (ddd, J = 12.3, 8.2, 4.0 Hz).



10

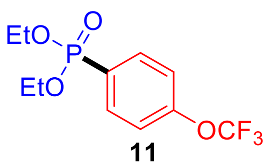
diethyl (4-hydroxyphenyl)phosphonate[7]

Conditions: 4-iodophenol (44 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (29.1 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.63 (dd, J = 13.0, 8.6 Hz, 2H), 7.04 – 6.91 (m, 2H), 4.26 – 3.94 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, J = 3.3 Hz), 133.8 (d, J = 11.7 Hz), 116.5 (d, J = 196 Hz), 116.0 (d, J = 16.4 Hz), 62.3 (d, J = 5.4 Hz), 16.3 (d, J = 6.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 20.91 (ddd, J = 16.0, 8.2, 4.1 Hz).



11

diethyl (4-(trifluoromethoxy)phenyl)phosphonate[12]

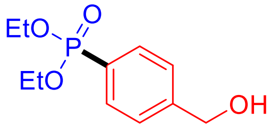
Conditions: 1-iodo-4-(trifluoromethoxy)benzene (58 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 1/1 with 0.5% Et_3N) as a light yellow oil (45.8 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 12.8, 8.6 Hz, 2H), 7.33 – 7.27 (m, 2H), 4.25 – 4.02 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2 (dd, J = 3.8, 1.8 Hz), 133.8 (d, J = 11.0 Hz), 127.2 (d, J = 191.5 Hz), δ 120.5 (d, J = 15.9 Hz), 120.3 (d, J = 258.7 Hz), 62.3 (d, J = 5.5 Hz), 16.3 (d, J = 6.4 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -57.63 (s).

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.71 – 16.34 (m).



12

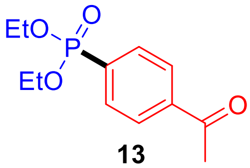
diethyl (4-(hydroxymethyl)phenyl)phosphonate[8]

Conditions: (4-iodophenyl)methanol (47 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (36.6 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 13.1, 8.1 Hz, 2H), 7.44 (dd, J = 7.9, 4.0 Hz, 2H), 4.74 (s, 2H), 4.20 – 3.96 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2 (d, J = 3.2 Hz), 131.9 (d, J = 10.3 Hz), 126.8 (d, J = 188 Hz), 126.6 (d, J = 15.4 Hz), 64.3 (d, J = 1.0 Hz), 62.2 (d, J = 5.5 Hz), 16.3 (d, J = 6.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.03 (dd, J = 7.9, 3.9 Hz).



13

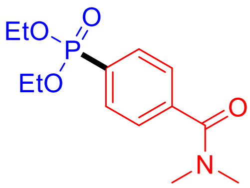
diethyl (4-acetylphenyl)phosphonate[5]

Conditions: 1-(4-iodophenyl)ethan-1-one (49 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (27.1 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.91 (dd, J = 12.8, 8.4 Hz, 2H), 4.24 – 4.03 (m, 4H), 2.63 (s, 3H), 1.33 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5 (s), 139.9 (d, J = 3.1 Hz), 133.5 (d, J = 186.6 Hz), 132.1 (d, J = 10.0 Hz), 128.1 (d, J = 15.1 Hz), 62.4 (d, J = 5.5 Hz), 26.8 (s), 16.3 (d, J = 6.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 16.85 (ddd, J = 12.3, 8.3, 4.1 Hz).



14

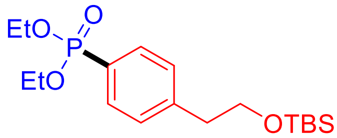
diethyl (4-(dimethylcarbamoyl)phenyl)phosphonate

Conditions: 4-bromo-*N,N*-dimethylbenzamide (46 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 3/1) as a orange oil (22.8 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 13.1, 8.3 Hz, 2H), 7.50 – 7.43 (m, 2H), 4.18 – 3.99 (m, 4H), 3.09 (s, 3H), 2.92 (s, 3H), 1.29 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5 (s), 140.2 (d, J = 3.2 Hz), 131.9 (d, J = 10.1 Hz), 129.8 (d, J = 188.4 Hz), 126.9 (d, J = 15.1 Hz), 62.3 (d, J = 5.5 Hz), 39.4 (s), 35.3 (s), 16.3 (d, J = 6.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.45 (dddd, *J* = 16.5, 12.5, 8.2, 4.0 Hz).
HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{21}NO_4P^+$, 286.1203 m/z; found, 286.1205m/z.



15

diethyl (4-(2-((tert-butyldimethylsilyl)oxy)ethyl)phenyl)phosphonate

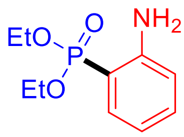
Conditions: (4-bromophenethoxy)(tert-butyl)dimethylsilane (63 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (38.7 mg, 52%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 13.1, 8.0 Hz, 2H), 7.30 (dd, *J* = 7.9, 4.0 Hz, 2H), 4.19 – 3.97 (m, 4H), 3.81 (t, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 6.7 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 6H), 0.83 (s, 9H), -0.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4 (d, *J* = 3.1 Hz), 131.8 (d, *J* = 10.2 Hz), 129.4 (d, *J* = 15.3 Hz), 125.8 (d, *J* = 189.2 Hz), 63.8 (s), 62.0 (d, *J* = 5.3 Hz), 39.5 (s), 25.9 (s), 18.3 (s), 16.3 (d, *J* = 6.5 Hz), -5.5 (s).

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.38 (ddd, *J* = 12.4, 8.3, 4.4 Hz).

HRMS (ESI): $[M+Na]^+$ calcd for $C_{18}H_{33}NaO_4PSi^+$, 395.1778 m/z; found, 395.1745 m/z .



16

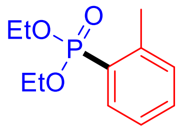
diethyl (2-aminophenyl)phosphonate[9]

Conditions: 2-iodoaniline (44 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a orange oil (31.1 mg, 68%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (ddd, *J* = 14.3, 7.7, 1.3 Hz, 1H), 7.31 – 7.21 (m, 1H), 6.73 – 6.61 (m, 2H), 5.14 (s, 2H), 4.19 – 3.96 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2 (d, *J* = 8.5 Hz), 133.8 (d, *J* = 2.4 Hz), 133.2 (d, *J* = 7.2 Hz), 116.9 (d, *J* = 13.9 Hz), 116.3 (d, *J* = 12.7 Hz), 108.1 (d, *J* = 183.5 Hz), 62.0 (d, *J* = 4.9 Hz), 16.3 (d, *J* = 6.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 21.20 (dd, *J* = 11.9, 7.1 Hz).

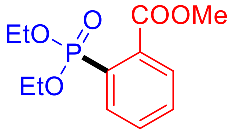


17

diethyl o-tolylphosphonate[10]

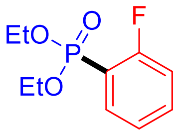
Conditions: 1-iodo-2-methylbenzene (44 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (39.7 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.31 – 7.23 (m, 2H), 4.20 – 4.03 (m, 4H), 2.59 (s, 3H), 1.34 (t, J = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8 (d, J = 10.2 Hz), 133.9 (d, J = 10.3 Hz), 132.4 (d, J = 3.0 Hz), 131.2 (d, J = 14.9 Hz), 126.9 (d, J = 183.9 Hz), 125.4 (d, J = 14.9 Hz), 61.9 (d, J = 5.5 Hz), 21.2 (d, J = 3.6 Hz), 16.3 (d, J = 6.5 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 19.44 (s).



18

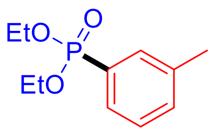
methyl 2-(diethoxyphosphoryl)benzoate[11]
Conditions: methyl 2-iodobenzoate (52 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (16.9 mg, 31%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 1H), 7.75 – 7.68 (m, 1H), 7.62 – 7.52 (m, 2H), 4.25 – 4.05 (m, 4H), 3.93 (s, 3H), 1.34 (t, J = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5 (d, J = 4.8 Hz), 136.2 (d, J = 8.8 Hz), 133.9 (d, J = 8.2 Hz), 132.1 (d, J = 2.8 Hz), 130.6 (d, J = 13.9 Hz), 129.2 (d, J = 12.5 Hz), 127.6 (d, J = 187.3 Hz), 62.5 (d, J = 5.7 Hz), 52.7 (s), 16.3 (d, J = 6.5 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 16.12 (d, J = 6.6 Hz).



19

diethyl (2-fluorophenyl)phosphonate[12]
Conditions: 1-bromo-2-fluorobenzene (35 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.1/0.9 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (38.0 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (ddd, J = 14.3, 7.9, 1.7 Hz, 1H), 7.55 (ddd, J = 9.2, 7.4, 1.0 Hz, 1H), 7.27 – 7.19 (m, 1H), 7.12 (td, J = 8.9, 6.5 Hz, 1H), 4.31 – 4.05 (m, 4H), 1.34 (t, J = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (d, J = 253.0 Hz), 135.0 (dd, J = 6.1, 3.7 Hz), 134.8 (dd, J = 8.6, 2.2 Hz), 124.1 (dd, J = 13.8, 3.6 Hz), δ 116.4 (dd, J = 188.0, 18.3 Hz), 116.1 (dd, J = 22.6, 8.0 Hz), 62.5 (d, J = 5.6 Hz), 16.3 (d, J = 6.5 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 13.65 (dd, J = 14.3, 8.1 Hz).
^{19}F NMR (377 MHz, $CDCl_3$) δ -103.72 (dt, J = 9.6, 5.9 Hz).



20

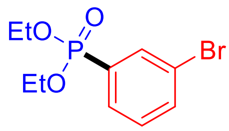
diethyl m-tolylphosphonate[6]

Conditions: 1-iodo-3-methylbenzene (44 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (37.8 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.54 (m, 2H), 7.34 (dd, J = 4.8, 3.9 Hz, 2H), 4.22 – 3.97 (m, 4H), 2.38 (s, 3H), 1.31 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (d, J = 15.0 Hz), 133.2 (d, J = 3.2 Hz), 132.3 (d, J = 10.0 Hz), 128.8 (d, J = 9.7 Hz), 128.4 (d, J = 15.8 Hz), 128.2 (d, J = 186 Hz), 62.0 (d, J = 5.4 Hz), 21.3 (s), 16.33 (d, J = 6.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.27 (s).



21

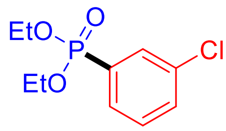
diethyl (3-bromophenyl)phosphonate[13]

Conditions: 1-bromo-3-iodobenzene (57 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (45.1 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 13.6 Hz, 1H), 7.72 (dd, J = 12.9, 7.6 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.33 (td, J = 7.8, 4.8 Hz, 1H), 4.21 – 4.00 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4 (d, J = 3.0 Hz), 134.5 (d, J = 10.6 Hz), 131.1 (d, J = 186 Hz), 130.2 (d, J = 4.9 Hz), 130.1 (d, J = 11.7 Hz), 122.9 (d, J = 19.8 Hz), 62.4 (d, J = 5.5 Hz), 16.3 (d, J = 6.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 16.34 – 16.05 (m).



22

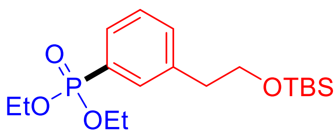
diethyl (3-chlorophenyl)phosphonate[14]

Conditions: 1-chloro-3-iodobenzene (48 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (40.3 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 1H), 7.71 – 7.63 (m, 1H), 7.53 – 7.47 (m, 1H), 7.39 (td, J = 7.8, 4.8 Hz, 1H), 4.21 – 4.01 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8 (d, J = 20.3 Hz), 132.5 (d, J = 3.1 Hz), 131.7 (d, J = 10.7 Hz), 130.8 (d, J = 187 Hz), δ 129.9 (d, J = 16.4 Hz), δ 129.8 (d, J = 9.2 Hz), 62.4 (d, J = 5.5 Hz), 16.3 (d, J = 6.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 16.51 (dt, J = 13.1, 5.1 Hz).



24

diethyl (3-(2-((tert-butyldimethylsilyl)oxy)ethyl)phenyl)phosphonate

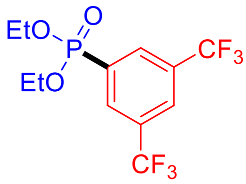
Conditions: (3-bromophenethoxy)(tert-butyl)dimethylsilane (63 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.1/0.9 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (46.1 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.58 (m, 2H), 7.44 – 7.33 (m, 2H), 4.21 – 3.99 (m, 4H), 3.82 (t, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 6.7 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 6H), 0.84 (s, 9H), -0.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9 (d, *J* = 14.7 Hz), 133.4 (d, *J* = 3.1 Hz), 132.4 (d, *J* = 10.1 Hz), 129.5 (d, *J* = 9.8 Hz), 128.3 (d, *J* = 15.7 Hz), 128.2 (d, *J* = 187.0 Hz), 64.0 (s), 62.0 (d, *J* = 5.4 Hz), 39.3 (s), 25.9 (s), 18.3 (s), 16.3 (d, *J* = 6.5 Hz), -5.5 (s).

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.18 (dd, *J* = 12.8, 7.6 Hz).

HRMS (ESI): $[M+K]^+$ calcd for $C_{18}H_{33}KO_4PSi^+$, 411.1517 m/z; found, 411.1515 m/z .



25

diethyl (3,5-bis(trifluoromethyl)phenyl)phosphonate[10]

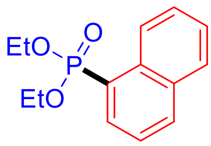
Conditions: 1-bromo-3,5-bis(trifluoromethyl)benzene (59 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (46.9 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 13.3 Hz, 2H), 8.03 (s, 1H), 4.29 – 4.07 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.3 (d, *J* = 192.2 Hz), δ 132.1 (dd, *J* = 101.8, 15.3 Hz), δ 132.1 (dd, *J* = 34.0, 15.4 Hz), δ 131.9 – 131.7 (m), δ 125.9 (dq, *J* = 7.2, 3.6 Hz), δ 122.9 (qd, *J* = 273.2, 2.2 Hz), 63.0 (d, *J* = 5.7 Hz), 16.3 (d, *J* = 6.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 14.46 – 13.10 (m).

^{19}F NMR (377 MHz, $CDCl_3$) δ -63.03 (s).



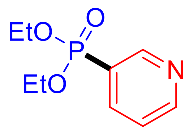
26

diethyl naphthalen-1-ylphosphonate[6]

Conditions: 1-iodonaphthalene (51 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (48.6 mg, 92%).

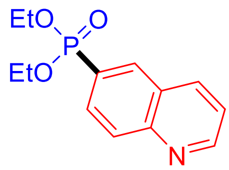
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.5 Hz, 1H), 8.24 (ddd, *J* = 16.3, 7.0, 1.1 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.57 – 7.48 (m, 2H), 4.27 – 4.01 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6 (d, J = 9.1 Hz), 133.6 (d, J = 12 Hz), 133.6 (d, J = 3 Hz), 132.7 (d, J = 10.9 Hz), 128.8 (d, J = 1.8 Hz), 127.4 (s), 126.7 (d, J = 4.2 Hz), 126.4 (s), 124.7 (d, J = 181 Hz), 124.5 (d, J = 16.6 Hz), 62.2 (d, J = 5.2 Hz), 16.4 (d, J = 6.5 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 19.63 – 18.68 (m).



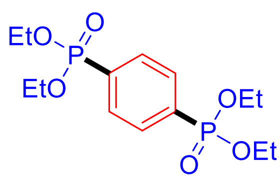
27

diethyl pyridin-3-ylphosphonate[5]
Conditions: 3-iodopyridine (41 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/MeOH= 50/1) as a light yellow oil (19.8 mg, 46%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 6.2 Hz, 1H), 8.80 – 8.70 (m, 1H), 8.09 (ddt, J = 13.3, 7.8, 1.8 Hz, 1H), 7.42 – 7.35 (m, 1H), 4.25 – 4.05 (m, 4H), 1.33 (t, J = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9 (d, J = 1.7 Hz), 152.2 (d, J = 12.2 Hz), 139.5 (d, J = 8.3 Hz), 125.1 (d, J = 188.9 Hz), 123.4 (d, J = 11.5 Hz), 62.6 (d, J = 5.6 Hz), 16.3 (d, J = 6.4 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 15.69 (s).



28

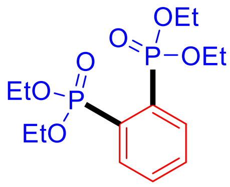
diethyl quinolin-6-ylphosphonate[15]
Conditions: 6-iodoquinoline (51 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 3/1) as a light yellow oil (30.21 mg, 57%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (dd, J = 4.2, 1.6 Hz, 1H), 8.42 (dd, J = 15.1, 1.2 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H), 8.17 (dd, J = 8.6, 3.8 Hz, 1H), 7.98 (ddd, J = 10.5, 8.7, 1.6 Hz, 1H), 7.47 (dd, J = 8.3, 4.2 Hz, 1H), 4.24 – 4.04 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5 (s), 149.5 (d, J = 3.1 Hz), 137.0 (s), 134.1 (d, J = 10.7 Hz), 130.2 (d, J = 9.7 Hz), 130.0 (d, J = 14.0 Hz), 127.4 (d, J = 17.4 Hz), 126.8 (d, J = 187 Hz), 122.1 (s), 62.4 (d, J = 5.4 Hz), 16.4 (d, J = 6.4 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 18.37 – 16.97 (m).



29

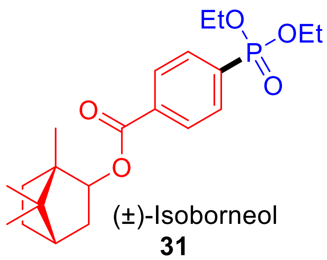
tetraethyl 1,4-phenylenebis(phosphonate)[16]
Conditions: 1,4-diiodobenzene (66 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (122 mg, 0.8 mmol), triethyl phosphite (200 mg, 1.2 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by

flash chromatography (acetate/MeOH= 50/1) as a yellow oil (43.4 mg, 62%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 10.4, 6.7 Hz, 4H), 4.22 – 4.02 (m, 8H), 1.32 (t, *J* = 7.1 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9 (dd, *J* = 186.8, 3.1 Hz), 131.8 – 131.4 (m), 63.2 – 61.5 (m), 17.4 – 15.1 (m).
^{31}P NMR (162 MHz, $CDCl_3$) δ 16.78 (dd, *J* = 15.5, 8.3 Hz).



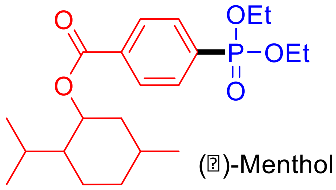
30

tetraethyl 1,2-phenylenebis(phosphonate)
Conditions: 1-bromo-2-iodobenzene (57 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a yellow oil (51.1 mg, 73%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.04 (m, 2H), 7.67 – 7.58 (m, 2H), 4.28 – 4.07 (m, 8H), 1.35 (t, *J* = 7.1 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1 (t, *J* = 11.4 Hz), 131.7 (p, *J* = 11.6 Hz), 131.6 (dd, *J* = 11.6, 188 Hz), 62.7 (t, *J* = 2.9 Hz), 16.3 (t, *J* = 3.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 15.69 (d, *J* = 7.6 Hz).
HRMS (ESI): $[M+K]^+$ calcd for $C_{14}H_{24}KO_6P_2^+$, 389.0680 m/z; found, 389.0718 m/z.



31

(1S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(diethoxyphosphoryl)benzoate
Conditions: 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-iodobenzoate (77 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (42.6 mg, 54%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 3.9 Hz, 2H), 7.87 (dd, *J* = 12.9, 8.2 Hz, 2H), 4.92 (dd, *J* = 7.1, 4.3 Hz, 1H), 4.23 – 4.01 (m, 4H), 1.97 – 1.85 (m, 2H), 1.80 (t, *J* = 3.7 Hz, 1H), 1.78 – 1.68 (m, 1H), 1.60 (td, *J* = 12.1, 3.8 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 6H), 1.27 – 1.18 (m, 1H), 1.14 (dd, *J* = 11.9, 3.8 Hz, 1H), 1.10 (s, 3H), 0.90 (d, *J* = 13.9 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (s), 134.3 (d, *J* = 3.2 Hz), 133.1 (d, *J* = 186.4 Hz), 131.8 (d, *J* = 10.0 Hz), 129.3 (d, *J* = 15.0 Hz), 82.2 (s), 62.4 (d, *J* = 5.5 Hz), 49.1 (s), 47.1 (s), 45.1 (s), 38.9 (s), 33.7 (s), 27.0 (s), 20.1 (d, *J* = 3.9 Hz), 16.3 (d, *J* = 6.4 Hz), 11.6 (s).
^{31}P NMR (162 MHz, $CDCl_3$) δ 17.05 (dtd, *J* = 12.5, 8.3, 4.1 Hz).
HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{32}O_5P^+$, 395.1982 m/z; found, 395.1960 m/z.



32

2-isopropyl-5-methylcyclohexyl 4-(diethoxyphosphoryl)benzoate

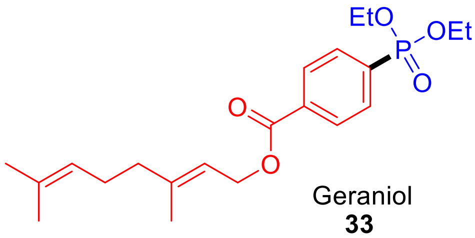
Conditions: 2-isopropyl-5-methylcyclohexyl 4-iodobenzoate (77 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (57.8 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.0, 3.9 Hz, 2H), 7.86 (dd, J = 12.9, 8.0 Hz, 2H), 4.93 (td, J = 10.9, 4.4 Hz, 1H), 4.24 – 3.98 (m, 4H), 2.10 (d, J = 12.0 Hz, 1H), 1.91 (dtd, J = 13.8, 6.9, 2.4 Hz, 1H), 1.71 (d, J = 12.0 Hz, 2H), 1.62 – 1.45 (m, 2H), 1.30 (t, J = 7.0 Hz, 6H), 1.20 – 1.02 (m, 2H), 0.96 – 0.84 (m, 7H), 0.77 (d, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (s), 134.3 (d, J = 3.2 Hz), 133.1 (d, J = 186.3 Hz), 131.8 (d, J = 10.1 Hz), 129.4 (d, J = 15.0 Hz), 75.5 (s), 62.3 (d, J = 5.5 Hz), 47.2 (s), 40.9 (s), 34.3 (s), 31.4 (s), 26.5 (s), 23.6 (s), 22.0 (s), 20.7 (s), 16.5 (s), 16.3 (d, J = 6.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.09 (ddd, J = 16.4, 8.2, 4.1 Hz).

HRMS (ESI): $[M+Na]^+$ calcd for $C_{21}H_{33}NaO_5P^+$, 419.1958 m/z; found, m/z 419.1944.



33

(E)-3,7-dimethylocta-2,6-dien-1-yl 4-(diethoxyphosphoryl)benzoate

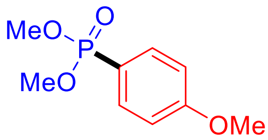
Conditions: (E)-3,7-dimethylocta-2,6-dien-1-yl 4-iodobenzoate (77 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (33.9 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.1, 3.9 Hz, 2H), 7.87 (dd, J = 12.9, 8.0 Hz, 2H), 5.45 (t, J = 7.1 Hz, 1H), 5.08 (t, J = 6.4 Hz, 1H), 4.85 (d, J = 7.1 Hz, 2H), 4.29 – 3.93 (m, 4H), 2.17 – 2.02 (m, 4H), 1.76 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H), 1.31 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (s), 142.9 (s), 134.0 (d, J = 3.2 Hz), 133.2 (d, J = 185 Hz), 131.9 (s), 131.7 (d, J = 10.0 Hz), 129.4 (d, J = 15.0 Hz), 123.7 (s), 118.0 (s), 62.4 (s), 62.3 (d, J = 4.3 Hz), 39.5 (s), 26.3 (s), 25.7 (s), 17.7 (s), 16.6 (s), 16.3 (d, J = 6.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.09 (ddd, J = 12.4, 8.3, 4.2 Hz).

HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{32}O_5P^+$, 395.1982 m/z; found, 395.2019 m/z.



34

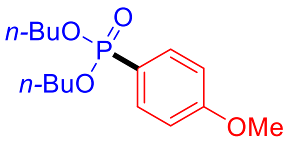
dimethyl (4-methoxyphenyl)phosphonate[17]

Conditions: 1-iodo-4-methoxybenzene (47 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), trimethyl phosphite (74 mg, 0.6 mmol), H_2O/CH_3CN (0.1/0.9 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (37.2 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 12.7, 8.8 Hz, 2H), 7.00 – 6.92 (m, 2H), 3.84 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, J = 3.4 Hz), 133.9 (d, J = 11.3 Hz), 118.1 (d, J = 196.0 Hz), 114.1 (d, J = 16.1 Hz), 55.3 (s), 52.5 (d, J = 5.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 23.59 – 22.30 (m).



35

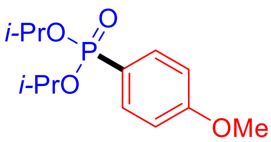
dibutyl (4-methoxyphenyl)phosphonate[18]

Conditions: 1-iodo-4-methoxybenzene (47 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), tributyl phosphite (150 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (55.2 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 12.7, 8.7 Hz, 2H), 6.95 (dd, J = 8.7, 3.3 Hz, 2H), 3.99 (ddq, J = 32.1, 10.0, 6.7 Hz, 4H), 3.84 (s, 3H), 1.67 – 1.58 (m, 4H), 1.37 (dq, J = 14.7, 7.3 Hz, 4H), 0.89 (t, J = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, J = 3.4 Hz), 133.8 (d, J = 11.2 Hz), 119.6 (d, J = 195.1 Hz), 114.0 (d, J = 16.0 Hz), 65.6 (d, J = 5.6 Hz), 55.3 (s), 32.5 (d, J = 6.6 Hz), 18.8 (s), 13.6 (s).

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.70 (ddd, J = 13.4, 6.6, 3.6 Hz).



36

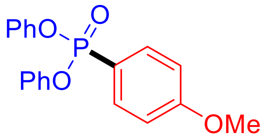
diisopropyl (4-methoxyphenyl)phosphonate[19]

Conditions: 1-iodo-4-methoxybenzene (47 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triisopropyl phosphite (125 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (47.9 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.64 (m, 2H), 7.02 – 6.85 (m, 2H), 4.63 (tt, J = 14.1, 6.2 Hz, 2H), 3.83 (s, 3H), 1.34 (d, J = 6.2 Hz, 6H), 1.20 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, J = 3.4 Hz), 133.7 (d, J = 11.3 Hz), 121.3 (d, J = 195.3 Hz), 113.8 (d, J = 16.0 Hz), 70.4 (d, J = 5.4 Hz), 55.3 (s), 24.1 (d, J = 3.9 Hz), 23.8 (d, J = 4.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.13 – 17.33 (m).



37

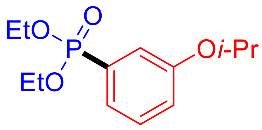
diphenyl (4-methoxyphenyl)phosphonate[20]

Conditions: 1-iodo-4-methoxybenzene (47 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triphenyl phosphite (187 mg, 0.6 mmol), H_2O/CH_3CN (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 1/5) as a light yellow oil (14.28 mg, 21%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 13.3, 8.8 Hz, 2H), 7.23 (dd, J = 13.0, 5.4 Hz, 4H), 7.17 – 7.12 (m, 4H), 7.09 (t, J = 7.3 Hz, 2H), 6.97 – 6.90 (m, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (d, J = 3.5 Hz), 150.5 (d, J = 7.4 Hz), 134.4 (d, J = 12.0 Hz), 129.7 (s), 125.0 (d, J = 1.0 Hz), 120.7 (d, J = 4.6 Hz), 118.0 (d, J = 200.5 Hz), 114.2 (d, J = 17.0 Hz), 55.4 (s).

^{31}P NMR (162 MHz, $CDCl_3$) δ 12.66 (t, J = 13.2 Hz).



38

diethyl (3-isopropoxyphenyl)phosphonate

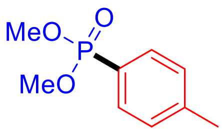
Conditions: 3-isopropoxy-*N,N,N*-trimethylbenzenaminiumiodide (64 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), triethyl phosphite (100 mg, 0.6 mmol), H_2O/CH_3CN (0.25/0.75 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 2/1) as a light yellow oil (34.3 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 3H), 7.04 (dt, J = 6.6, 2.4 Hz, 1H), 4.59 (hept, J = 6.1 Hz, 1H), 4.20 – 4.00 (m, 4H), 1.35 – 1.29 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (d, J = 18.9 Hz), 129.8 (d, J = 17.7 Hz), 129.6 (d, J = 186.5 Hz), 123.7 (d, J = 9.2 Hz), 120.4 (d, J = 3.2 Hz), 118.5 (d, J = 11.1 Hz), 70.2 (s), 62.1 (d, J = 5.4 Hz), 22.0 (s), 16.3 (d, J = 6.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.43 – 18.03 (m).

HRMS (ESI): $[M+K]^+$ calcd for $C_{13}H_{21}KO_4P^+$, 311.0809 m/z; found, 311.0821 m/z.

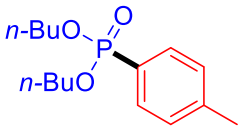


39

dimethyl p-tolylphosphonate[21]

Conditions: *N*,*N*,*N*,4-tetramethylbenzenaminium iodide (277 mg, 1 mmol), PTZ (4 mg, 0.02 mmol), DBU (304 mg, 2 mmol), trimethyl phosphite (372 mg, 3 mmol), PTZ (28 mg, 10 mol %), CH_3CN (3.00 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexane= 1/1 to 100% ethyl acetate) and then (dichloromethane/ethyl acetate= 1/1 to 100% ethyl acetate) as a light yellow oil (42.1 mg, 21%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 13.1, 7.9 Hz, 2H), 7.21 (dd, *J* = 7.6, 3.9 Hz, 2H), 3.67 (d, *J* = 11.1 Hz, 6H), 2.33 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3 (d, *J* = 3.1 Hz), 131.9 (d, *J* = 10.3 Hz), 129.3 (d, *J* = 15.5 Hz), 123.5 (d, *J* = 191.1 Hz), 52.6 (d, *J* = 5.5 Hz), 21.6 (d, *J* = 1.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 22.52 – 22.26 (m).



40

dibutyl p-tolylphosphonate[21]
Conditions: *N*,*N*,*N*,4-tetramethylbenzenaminium iodide (55 mg, 0.2 mmol), PTZ (4 mg, 0.02 mmol), DBU (61 mg, 0.4 mmol), tributyl phosphite (150 mg, 0.6 mmol), PTZ (5.5 mg, 10 mol %), CH_3CN/H_2O (0.75/0.25 ml), 24h. The product was isolated by flash chromatography (ethyl acetate/hexanes= 1/1) as alight yellow oil (23.2 mg, 41%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 13.0, 7.9 Hz, 2H), 7.23 – 7.15 (m, 2H), 4.09 – 3.76 (m, 4H), 2.33 (s, 3H), 1.63 – 1.52 (m, 4H), 1.38 – 1.25 (m, 4H), 0.83 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.81 (d, *J* = 3.1 Hz), 131.8 (d, *J* = 10.2 Hz), 129.2 (d, *J* = 15.4 Hz), 125.1 (d, *J* = 190.5 Hz), 65.7 (d, *J* = 5.7 Hz), 32.5 (d, *J* = 6.5 Hz), 21.6 (s), 18.74 (s), 13.6 (s).
^{31}P NMR (162 MHz, $CDCl_3$) δ 19.48 (s).

Fluorescence quenching measurements

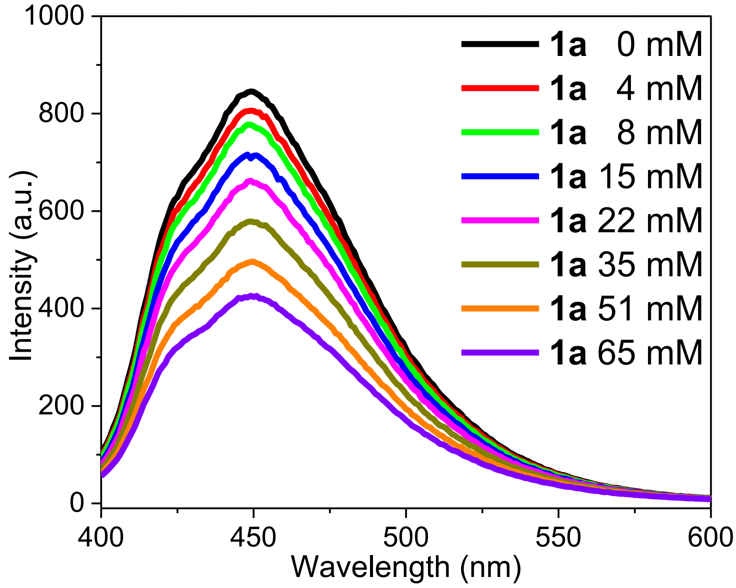


Figure S2. Fluorescence emission spectra of PTZ (0.4 mM) in different concentrations of 4-iodoanisole **1a** in MeCN:H_2O (3:1).

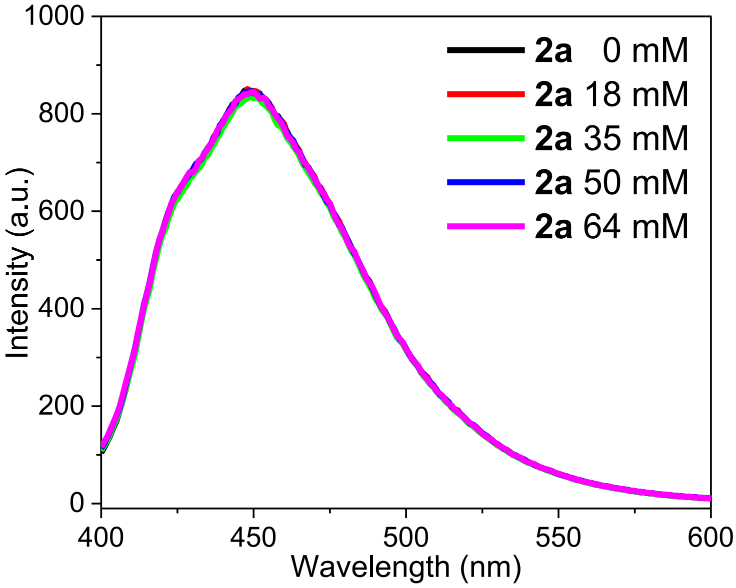


Figure S3. Fluorescence emission spectra of PTZ (0.4 mM) in different concentrations of triethylphosphite **2a** in MeCN:H_2O (3:1).

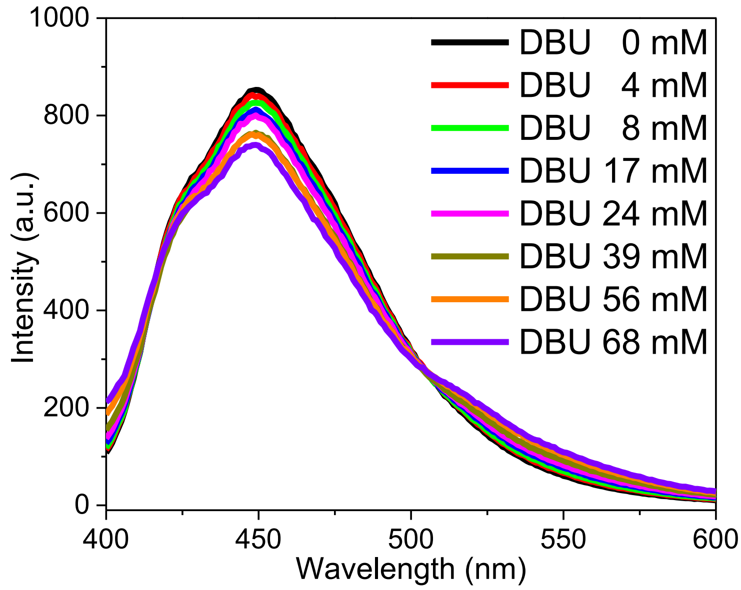


Figure S4. Fluorescence emission spectra of PTZ (0.4 mM) in different concentrations of DBU in MeCN:H_2O (3:1).

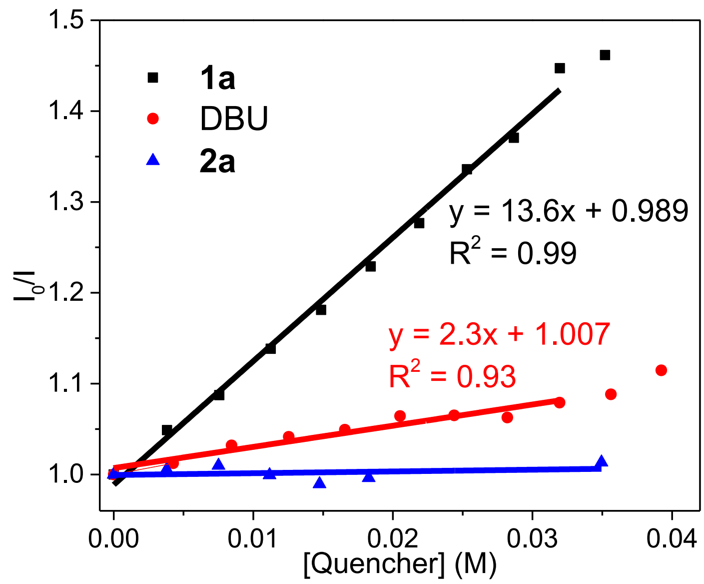


Figure S5. Stern-Volmer plots of PTZ (0.4 mM) for quenchers 4-iodoanisole **1a**, triethylphosphite **2a** and DBU in MeCN:H_2O (3:1).

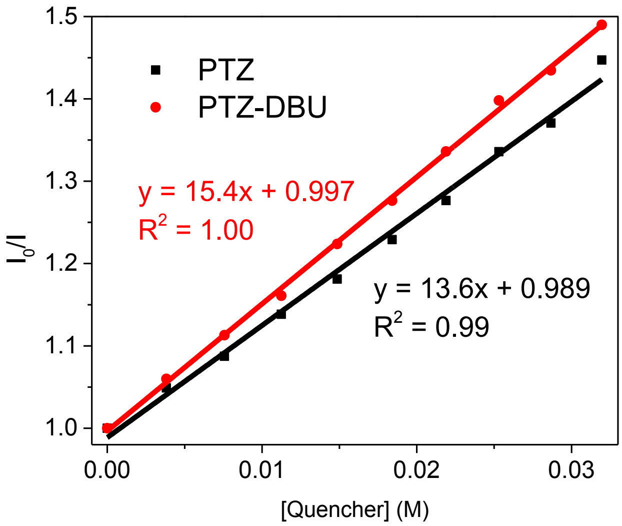
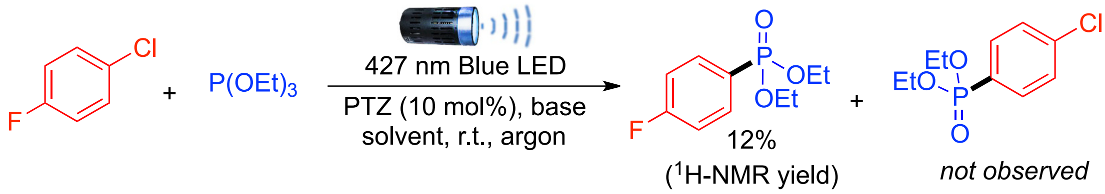


Figure S6. Stern-Volmer plots of PTZ (0.4 mM) and PTZ:DBU (0.4:8 mM) mixture for quencher 4-iodoanisole **1a** in MeCN:H_2O (3:1).

Aryl Halide Reactivity Trend & Experiments:

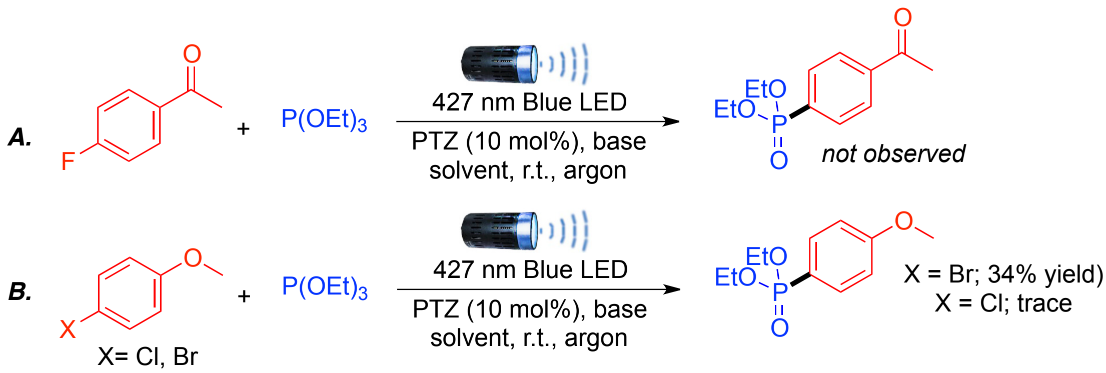
When using 1-chloro-4-fluorobenzene as starting materials:



Scheme S5. Competition reaction between chloro and fluoro substituents.

These results imply that while aryl chlorides react in low yields, aryl fluorides remain completely unreactive.

Similarly, when using 1-(4-fluorophenyl)ethan-1-one as starting materials, no desired product was detected.



Scheme S6. Reactivity comparison between fluoro, chloro, and bromo substituents.

The trend of reactivity for the aryl halides follows the order ArI>ArBr>ArCl>>ArF.

GC-MS Spectra from Radical Trapping Experiments

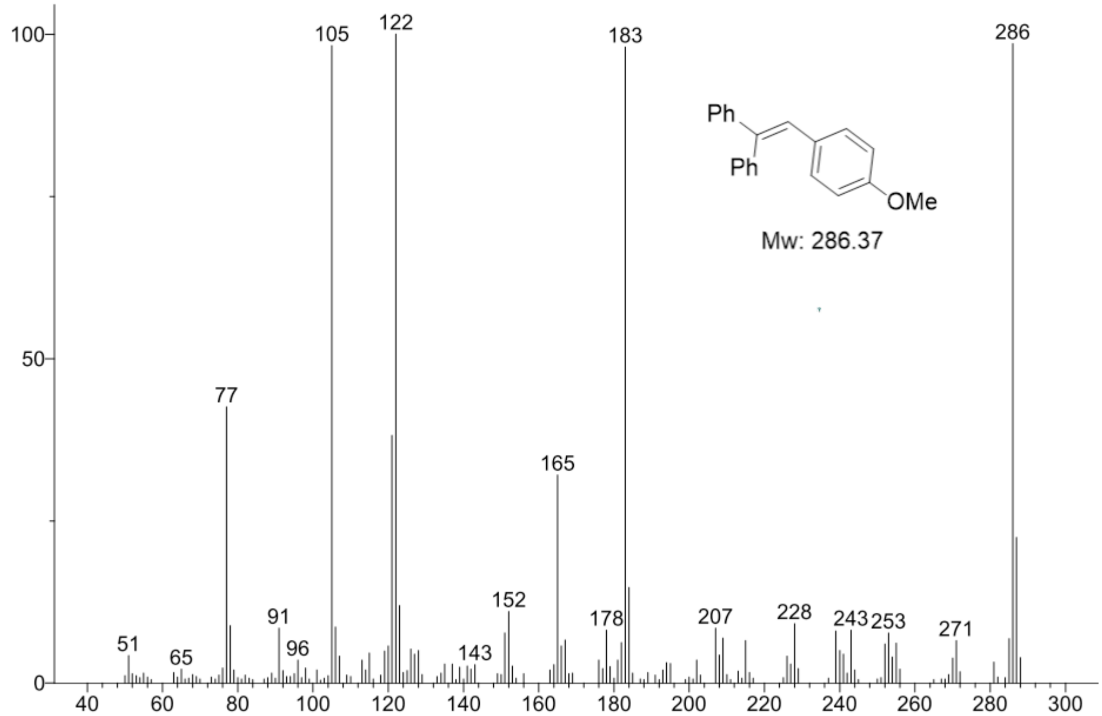


Figure S7. GC-MS fragmentation of trapped 4-methoxybenzene radical with 1,1-DPE.

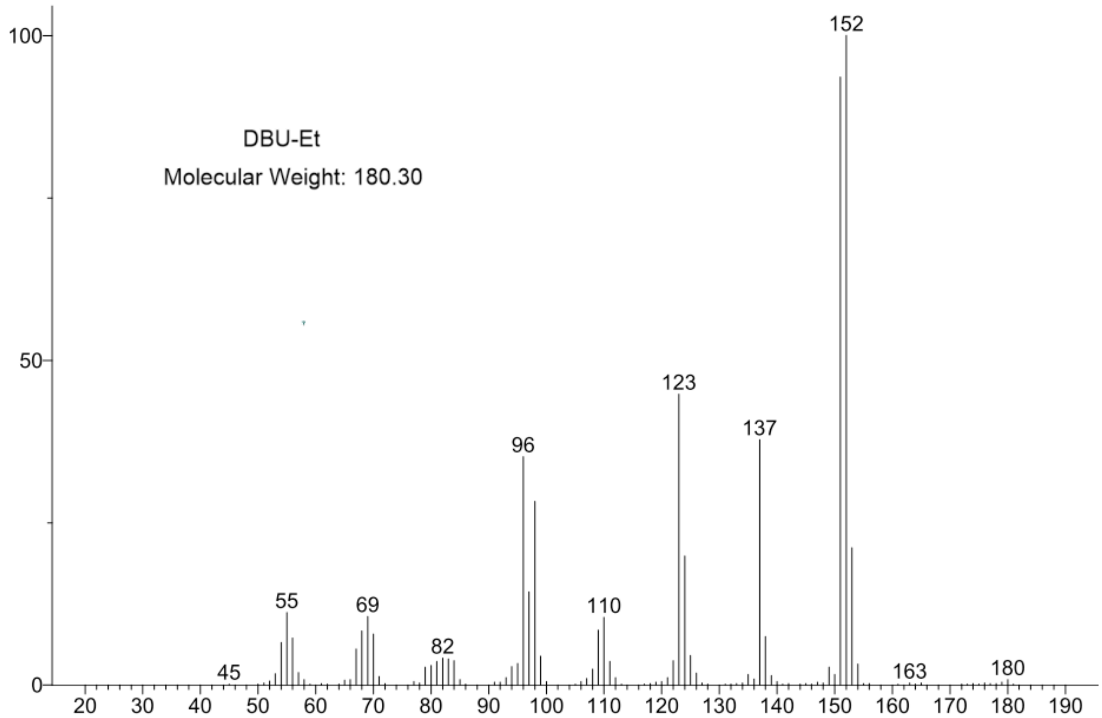


Figure S8. GC-MS fragmentation of DBU-Et by product.

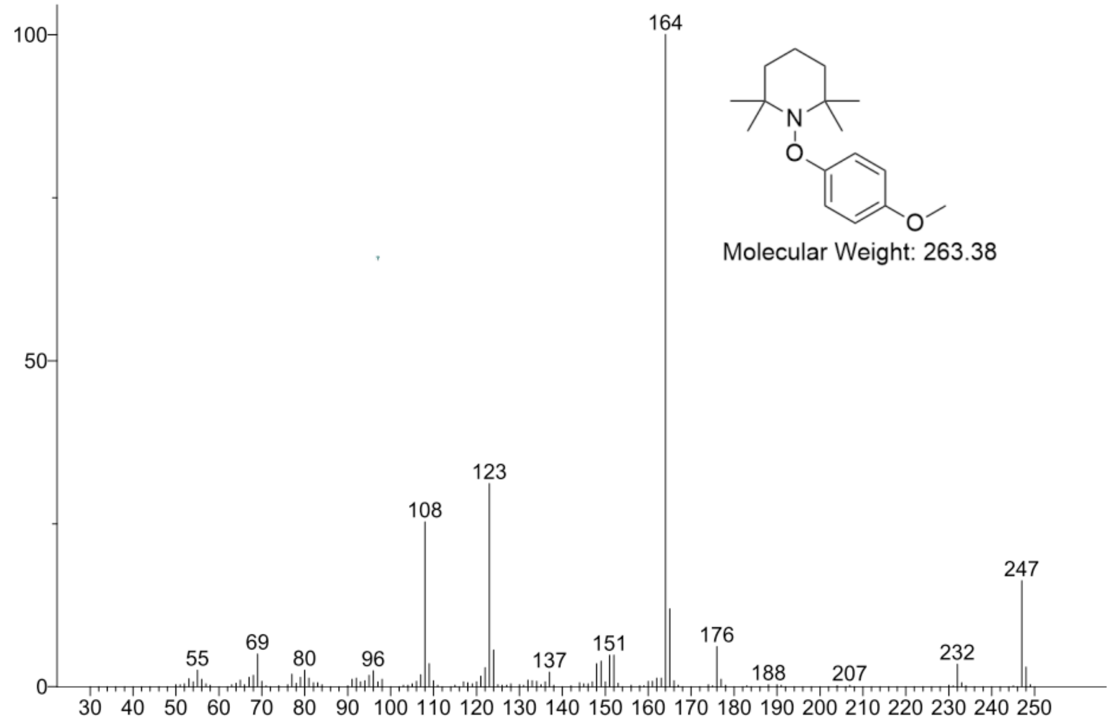
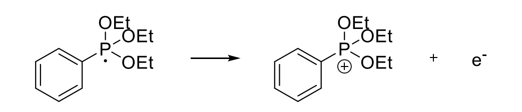
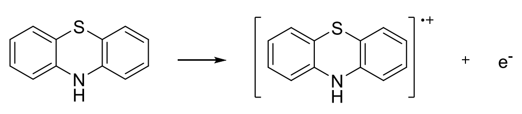
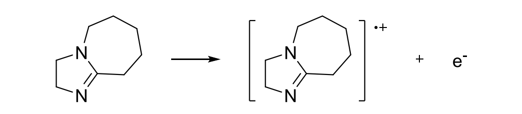


Figure S9. GC-MS fragmentation of trapped 4-methoxybenzene radical with TEMPO.

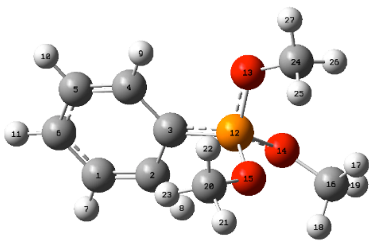
Computational Details

The structure optimization was performed at the density functional theory level using the program suite Gaussian 09.[22] The wB97XD method[23] was employed for all calculations along with the 6-311+G(d,p) basis set for all atoms The gradient threshold used for all geometry optimization was 4.5×10^{-4} Hartree/Bohr. Acetonitrile was used as an implicit solvent for all calculations and the method employed was the polarizable conductor calculation model (CPCM).[24-25] Frequency calculations were conducted to determine if each optimization was a minimum in the potential energy surface. Gibbs free energies were obtained from the thermochemistry section of the frequency calculation denoted as the "Sum of electronic and thermal Free Energies". The oxidation potentials were obtained following the methodology described by Nicewicz group.[26]

Table S2. Calculated oxidation potentials

	-1.87 V
	0.71 V
	1.21 V

Phosphoranyl radical



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.074844	-1.221629	-0.147813
2	6	0	1.704500	-1.246508	-0.091730
3	6	0	0.963280	-0.032746	0.202100
4	6	0	1.725181	1.183608	0.409486
5	6	0	3.093630	1.159083	0.344326
6	6	0	3.807409	-0.032082	0.066596
7	1	0	3.604828	-2.145868	-0.359086

8	1	0	1.173702	-2.178445	-0.256189
9	1	0	1.206067	2.110681	0.622956
10	1	0	3.639351	2.082998	0.512319
11	1	0	4.889425	-0.030744	0.015819
12	15	0	-0.718052	-0.046765	0.152230
13	8	0	-1.242802	1.288185	0.839455
14	8	0	-1.322054	-1.334864	0.853268
15	8	0	-1.492602	-0.141590	-1.263310
16	6	0	-2.514557	-2.038528	0.445671
17	1	0	-3.371992	-1.365452	0.428089
18	1	0	-2.366278	-2.482590	-0.537558
19	1	0	-2.665783	-2.813330	1.193431
20	6	0	-1.074556	0.694535	-2.354421
21	1	0	-1.636377	0.363972	-3.224759
22	1	0	-1.300679	1.742262	-2.144229
23	1	0	-0.003791	0.574635	-2.532257
24	6	0	-2.623093	1.690731	0.811763
25	1	0	-3.016370	1.661393	-0.205556
26	1	0	-3.212425	1.040491	1.460503
27	1	0	-2.649062	2.708834	1.191896

Zero-point correction= 0.219440 (Hartree/Particle)

Thermal correction to Energy= 0.234782

Thermal correction to Enthalpy= 0.235726

Thermal correction to Gibbs Free Energy= 0.175221

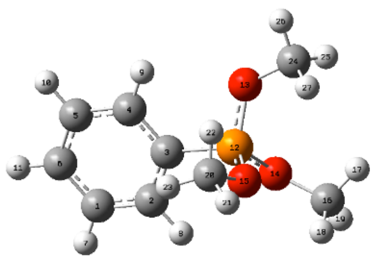
Sum of electronic and zero-point Energies= -918.122751

Sum of electronic and thermal Energies= -918.107409

Sum of electronic and thermal Enthalpies= -918.106464

Sum of electronic and thermal Free Energies= -918.166970

Phosphoranyl radical cation



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.065085	1.214205	0.143002

2	6	0	1.678853	1.231328	0.127390
3	6	0	0.985509	0.053240	-0.168919
4	6	0	1.668991	-1.134941	-0.441501
5	6	0	3.056284	-1.136310	-0.420970
6	6	0	3.749908	0.033676	-0.130157
7	1	0	3.610187	2.123129	0.365359
8	1	0	1.145089	2.151351	0.334609
9	1	0	1.124087	-2.042297	-0.670009
10	1	0	3.594118	-2.051807	-0.633911
11	1	0	4.833590	0.026372	-0.116643
12	15	0	-0.776929	0.071776	-0.102014
13	8	0	-1.241573	-1.188063	-0.898875
14	8	0	-1.286272	1.414632	-0.698842
15	8	0	-1.367999	0.040446	1.352916
16	6	0	-2.513679	2.113602	-0.351797
17	1	0	-3.370093	1.550354	-0.718259
18	1	0	-2.563821	2.245614	0.727027
19	1	0	-2.444691	3.072566	-0.855600
20	6	0	-1.001331	-0.960954	2.338475
21	1	0	-1.585526	-0.724279	3.222241
22	1	0	-1.251679	-1.955761	1.970567
23	1	0	0.064513	-0.883174	2.553090
24	6	0	-2.613981	-1.648889	-1.017527
25	1	0	-3.099661	-1.097501	-1.820365
26	1	0	-2.547570	-2.704165	-1.263773
27	1	0	-3.141693	-1.512898	-0.073688

Zero-point correction= 0.223246 (Hartree/Particle)

Thermal correction to Energy= 0.238479

Thermal correction to Enthalpy= 0.239423

Thermal correction to Gibbs Free Energy= 0.178328

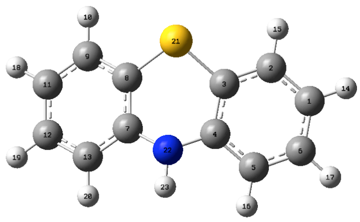
Sum of electronic and zero-point Energies= -918.028346

Sum of electronic and thermal Energies= -918.013114

Sum of electronic and thermal Enthalpies= -918.012169

Sum of electronic and thermal Free Energies= -918.073264

PTZ



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.352036	0.596053	3.637150
2	6	0	-1.181243	0.350164	2.548261
3	6	0	-0.646034	-0.109892	1.350292
4	6	0	0.734789	-0.287631	1.215673
5	6	0	1.562859	-0.018018	2.305463
6	6	0	1.019788	0.404935	3.511746
7	6	0	0.734789	-0.287631	-1.215673
8	6	0	-0.646034	-0.109892	-1.350292
9	6	0	-1.181243	0.350164	-2.548261
10	1	0	-2.251817	0.500200	-2.632267
11	6	0	-0.352036	0.596053	-3.637150
12	6	0	1.019788	0.404935	-3.511746
13	6	0	1.562859	-0.018018	-2.305463
14	1	0	-0.777058	0.938955	4.572731
15	1	0	-2.251817	0.500200	2.632267
16	1	0	2.635246	-0.147411	2.203107
17	1	0	1.676741	0.598946	4.351728
18	1	0	-0.777058	0.938955	-4.572731
19	1	0	1.676741	0.598946	-4.351728
20	1	0	2.635246	-0.147411	-2.203107
21	16	0	-1.711156	-0.563803	0.000000
22	7	0	1.268410	-0.740223	-0.000000
23	1	0	2.275934	-0.806297	-0.000000

Zero-point correction= 0.179886 (Hartree/Particle)

Thermal correction to Energy= 0.190017

Thermal correction to Enthalpy= 0.190961

Thermal correction to Gibbs Free Energy= 0.143875

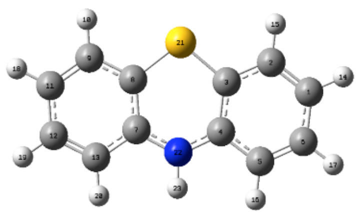
Sum of electronic and zero-point Energies= -915.424869

Sum of electronic and thermal Energies= -915.414738

Sum of electronic and thermal Enthalpies= -915.413794

Sum of electronic and thermal Free Energies= -915.460879

PTZ radical cation



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000099	0.406459	3.756986
2	6	0	0.000099	1.209134	2.639711
3	6	0	0.000035	0.632737	1.360955
4	6	0	-0.000007	-0.770243	1.227295
5	6	0	-0.000011	-1.575313	2.382511
6	6	0	0.000035	-0.992701	3.624660
7	6	0	-0.000007	-0.770243	-1.227295
8	6	0	0.000035	0.632737	-1.360955
9	6	0	0.000099	1.209134	-2.639711
10	1	0	0.000152	2.287984	-2.738697
11	6	0	0.000099	0.406459	-3.756986
12	6	0	0.000035	-0.992701	-3.624660
13	6	0	-0.000011	-1.575313	-2.382511
14	1	0	0.000167	0.857368	4.741042
15	1	0	0.000152	2.287984	2.738697
16	1	0	-0.000040	-2.653649	2.274934
17	1	0	0.000031	-1.617994	4.508508
18	1	0	0.000167	0.857368	-4.741042
19	1	0	0.000031	-1.617994	-4.508508
20	1	0	-0.000040	-2.653649	-2.274934
21	16	0	-0.000235	1.708467	0.000000
22	7	0	0.000039	-1.373852	-0.000000
23	1	0	-0.000126	-2.386802	-0.000000

Zero-point correction= 0.180256 (Hartree/Particle)

Thermal correction to Energy= 0.190469

Thermal correction to Enthalpy= 0.191413

Thermal correction to Gibbs Free Energy= 0.143467

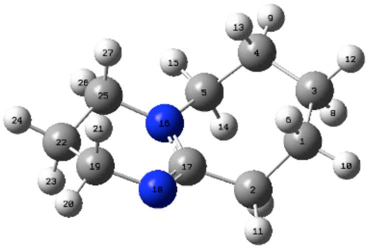
Sum of electronic and zero-point Energies= -915.235579

Sum of electronic and thermal Energies= -915.225366

Sum of electronic and thermal Enthalpies= -915.224422

Sum of electronic and thermal Free Energies= -915.272368

DBU



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.048971	1.283606	-0.339099
2	6	0	0.941446	1.405369	0.721320
3	6	0	2.801861	-0.046276	-0.320785
4	6	0	1.923355	-1.282640	-0.507425
5	6	0	0.848283	-1.439875	0.572623
6	1	0	1.608518	1.452038	-1.329051
7	1	0	1.301665	1.020124	1.681498
8	1	0	3.327487	-0.138064	0.638519
9	1	0	2.561290	-2.172043	-0.487125
10	1	0	2.769374	2.091048	-0.178245
11	1	0	0.689093	2.455345	0.865528
12	1	0	3.573297	-0.030563	-1.096878
13	1	0	1.436171	-1.263812	-1.489340
14	1	0	1.275053	-1.213591	1.556201
15	1	0	0.525604	-2.481141	0.613202
16	7	0	-0.359789	-0.649401	0.354328
17	6	0	-0.343048	0.720883	0.313697
18	7	0	-1.316622	1.479515	-0.062606
19	6	0	-2.546267	0.849885	-0.527098
20	1	0	-3.382265	1.514672	-0.290990
21	1	0	-2.515510	0.769579	-1.622450
22	6	0	-2.777471	-0.528797	0.075580
23	1	0	-2.974704	-0.434778	1.148432
24	1	0	-3.640775	-1.017740	-0.381636
25	6	0	-1.530795	-1.368361	-0.135403
26	1	0	-1.606343	-2.312293	0.409968
27	1	0	-1.411078	-1.612337	-1.200149

Zero-point correction= 0.247750 (Hartree/Particle)

Thermal correction to Energy= 0.257381

Thermal correction to Enthalpy= 0.258325

Thermal correction to Gibbs Free Energy= 0.212873

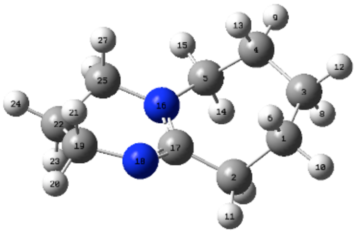
Sum of electronic and zero-point Energies= -461.835734

Sum of electronic and thermal Energies= -461.826103

Sum of electronic and thermal Enthalpies= -461.825159

Sum of electronic and thermal Free Energies= -461.870611

DBU radical cation



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.107634	-1.298675	0.245154
2	6	0	0.934408	-1.379602	-0.747427
3	6	0	2.830130	0.045618	0.230328
4	6	0	1.944439	1.250758	0.543353
5	6	0	0.822422	1.503722	-0.466343
6	1	0	1.742463	-1.527080	1.251808
7	1	0	1.230001	-0.974558	-1.719821
8	1	0	3.290730	0.192952	-0.753534
9	1	0	2.562018	2.151970	0.546780
10	1	0	2.815774	-2.086361	-0.019767
11	1	0	0.644337	-2.419162	-0.895526
12	1	0	3.647353	0.016221	0.955447
13	1	0	1.507255	1.165360	1.543568
14	1	0	1.166040	1.348422	-1.493413
15	1	0	0.473675	2.530816	-0.387048
16	7	0	-0.366308	0.658674	-0.252399
17	6	0	-0.292543	-0.668428	-0.265363
18	7	0	-1.260883	-1.415594	0.268473
19	6	0	-2.575698	-0.883551	0.479090
20	1	0	-3.288615	-1.647662	0.152126
21	1	0	-2.701068	-0.828068	1.570956
22	6	0	-2.802174	0.457001	-0.193194
23	1	0	-2.906978	0.323258	-1.272701
24	1	0	-3.711717	0.926620	0.179888
25	6	0	-1.615340	1.346226	0.100426
26	1	0	-1.645104	2.264041	-0.486197
27	1	0	-1.555493	1.623257	1.158774

Zero-point correction= 0.247058 (Hartree/Particle)

Thermal correction to Energy= 0.256798

Thermal correction to Enthalpy= 0.257742

Thermal correction to Gibbs Free Energy= 0.211644

Sum of electronic and zero-point Energies= -461.628258

```
Sum of electronic and thermal Energies=           -461.618518
Sum of electronic and thermal Enthalpies=          -461.617574
Sum of electronic and thermal Free Energies=       -461.663672
```

Supplementary References

(1) Y. Y. Che, Y. Yue, L. Z. Lin, B. Pei, X. Deng, C. Feng. *Angew.Chem. Int. Ed.* **2020**, *59*, 16414–16419.

(2) A. Matsumura, F. Yang, H. Goto. *Polymers.* **2015**, *7*, 147−155.

(3) F. Yuan, Z.-L. Hou, P. K. Pramanick, B. Yao. *Org. Lett.* **2019**, *21*, 9381−9385.

(4) S. Jin, H. T. Dang, G. C. Haug, R. He, V. D. Nguyen, V. T. Nguyen, H. D. Arman, K. S. Schanze, O. V. Larionov. *J. Am. Chem. Soc.* **2020**, *142*, 1603–1613.

(5) W. Lecroq, P. Bazille, F. Morlet-Savary, M. Breugst, J. Lalevee, A.-C. Gaumont, S. Lakhdar. *Org. Lett.* **2018**, *20*(14), 4164−4167.

(6) Y. Bai, N. Liu, S. Wang, S. Wang, S. Ning, L. Shi, L. Cui, Z. Zhang, J. Xiang. *Org. Lett.* **2019**, *21*, 6835−6838.

(7) J. Park, J.-M. Oh, S. E. Creager, D. W. Smith, Jr. *Chem. Commun.* **2012**, *48*, 8225−8227.

(8) G. S. Prasad, M. Manjunath, K. R. K. K. Reddy, O. V. S. Reddy, C. S. Reddy. *Arkivoc.* **2006**, *16*, 128–135.

(9) B. R. Aluri, B. Niaz, M. K. Kindermann, P. G. Jones, J. P. Heinicke. *Dalton Trans.* **2011**, *40*, 211−224.

(10) S. Wang, C. Yang, S. Sun, J. Wang. *Chem. Commun.* **2019**, *55*, 14035–14038.

(11) D. Villemin, A. Elbilali, F. Simeon, P.-A. Jaffre, G. Maheut, M. Mosaddak, A. Hakiki. *J. Chem. Res.* **2003**, *2003*, 436–437.

(12) G. Keglevich, A. Grün, A. Bölcskei, L. Drahos, M. Kraszni, G. T. Balogh. *Heteroat. Chem.* **2012**, *23*, 574−582.

(13) Y. He, H. Wu, F. D. Toste. *Chem. Sci.* **2015**, *6*, 1194−1198.

(14) G. Dargo, A. Bo´¨lcskei, A. Grün, S. Beni, Z. Sza´ nto´ , A. Lopata,´ G. Keglevich, G. T. Balogh. *J. Pharm. Biomed. Anal.* **2017**, *143*, 101−109.

(15) W.-C. Fu, C.-M. So, F.-Y. Kwong. *Org. Lett.* **2015**, *17*, 5906−5909.

(16) R. S. Shaikh, S. J. S. Düsel, B. König. *ACS Catal.* **2016**, *6*, 8410−8414.

(17) X.-Y. Jiao, W. G. Bentrude. *J. Org. Chem.* **2003**, *68*, 3303−3306.

(18) S. Sengmany, A. Ollivier, E. Le Gall, E. Leonel. *Org. Biomol. Chem.* **2018**, *16*, 4495−4500.

(19) K. Xu, H. Hu, F. Yang, Y. Wu. *Eur. J. Org. Chem.* **2013**, *2013*, 319−325.

(20) D. Qiu, C. Lian, J. Mao, Y. Ding, Z. Liu, L. Wei, M. Fagnoni, S. Protti. *Adv. Synth. Catal.* **2019**, *361*, 5239−5244.

(21) T. Miao, L. Wang. *Adv. Synth. Catal.* **2014**, *356*, 967–971.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G .A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski J.; Fox, D. J. Gaussian 09 Revision E.01. Gaussian Inc. Wallingford CT 2009.

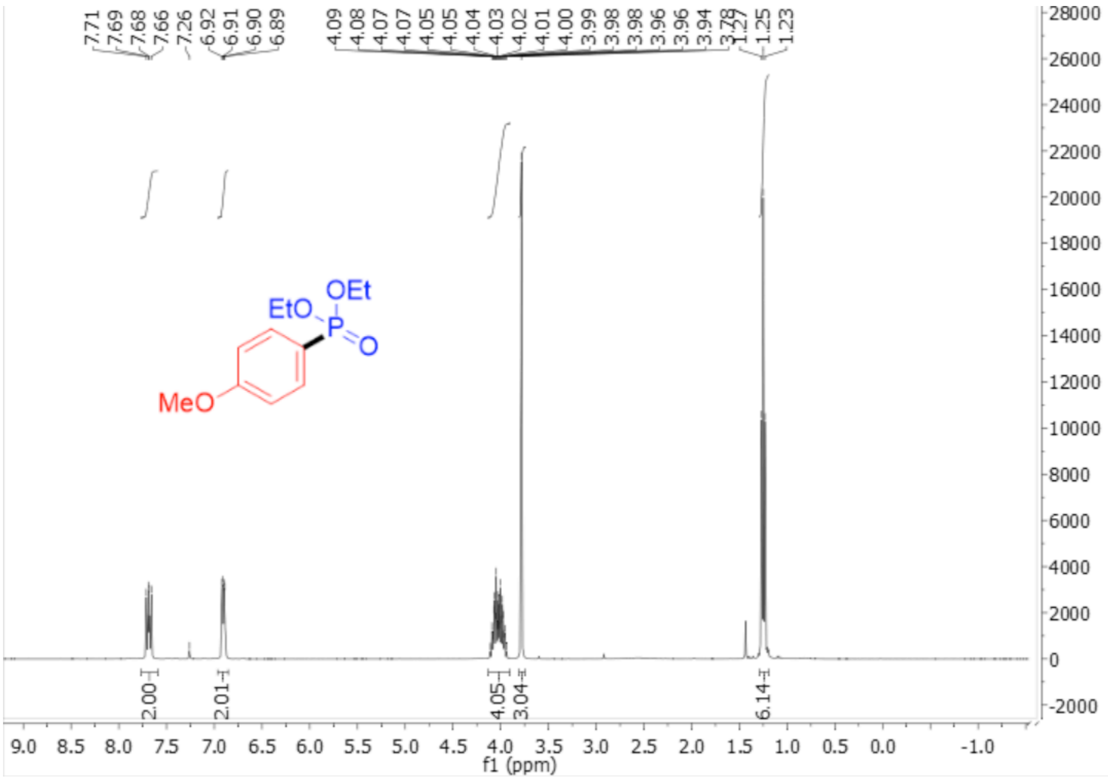
(23) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.*, **2008**, *10*, 6615-6620.

(24) Barone, V.; Cossi, M. *J. Phys. Chem. A*, **1998**, *102*, 1995-2001.

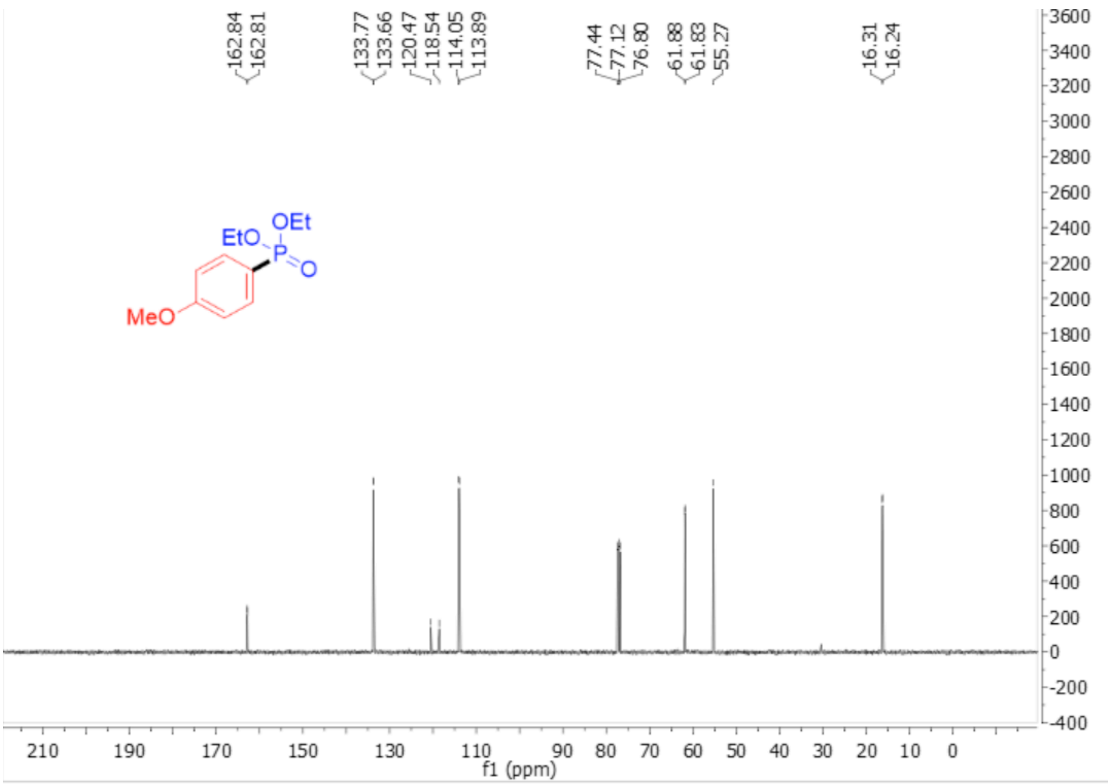
(25) Cossi, M.; Rega, N.; Scalmani G.; Barone, V. *J. Comput. Chem.*, **2003**, *24*, 669-681.

(26) H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett*, **2016**, *27*, 714-723.

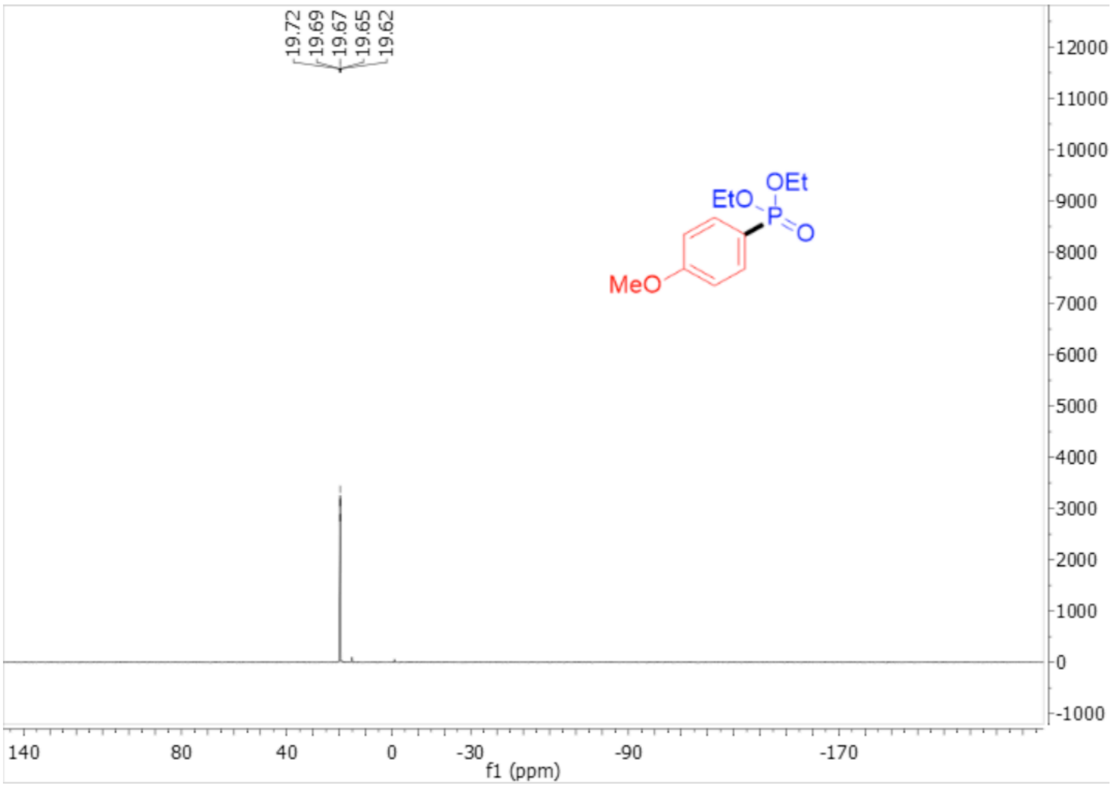
^1H and ^{13}C NMR Spectra



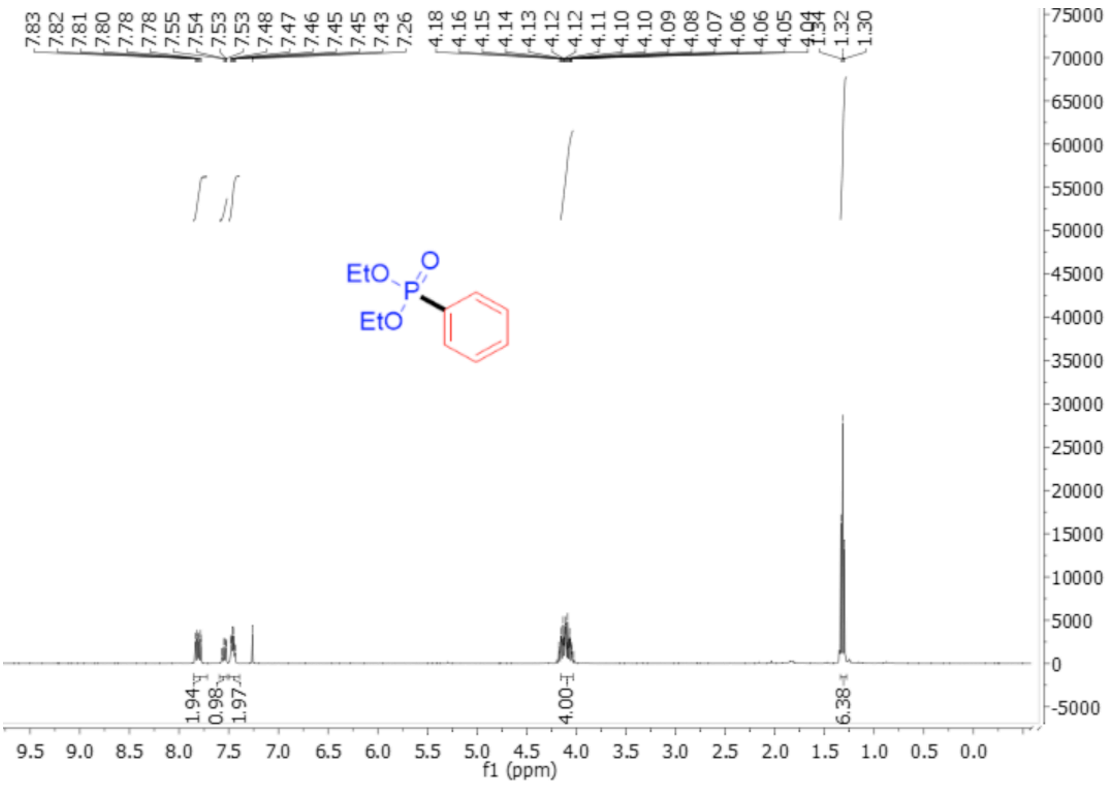
Supplementary Figure S10. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum for 3.**



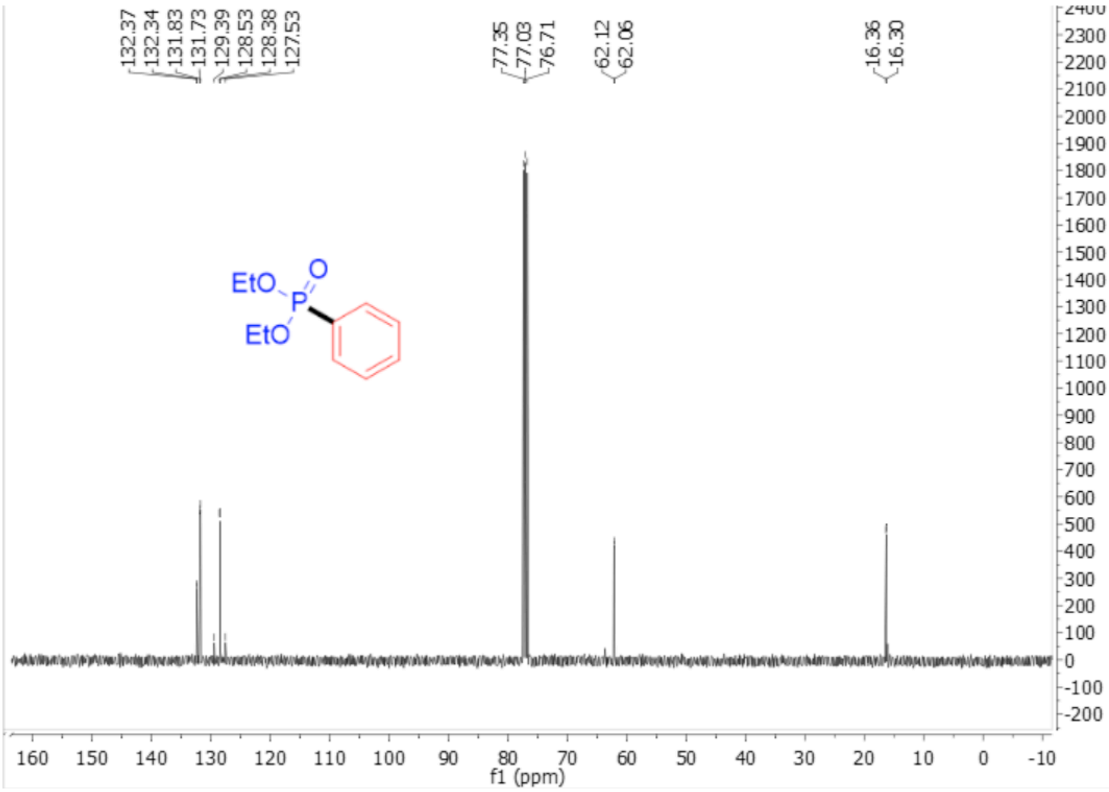
Supplementary Figure S11. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 3.**



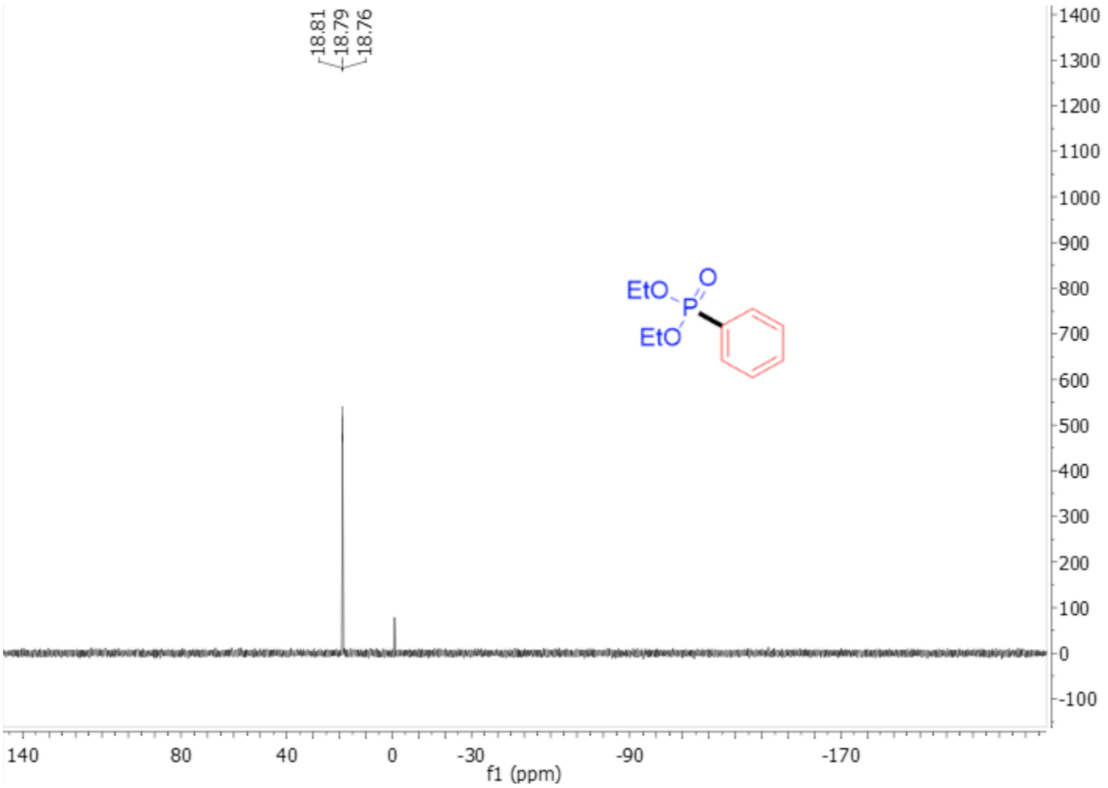
Supplementary Figure S12. ^{31}P NMR (162 MHz, CDCl3) spectrum for 3.



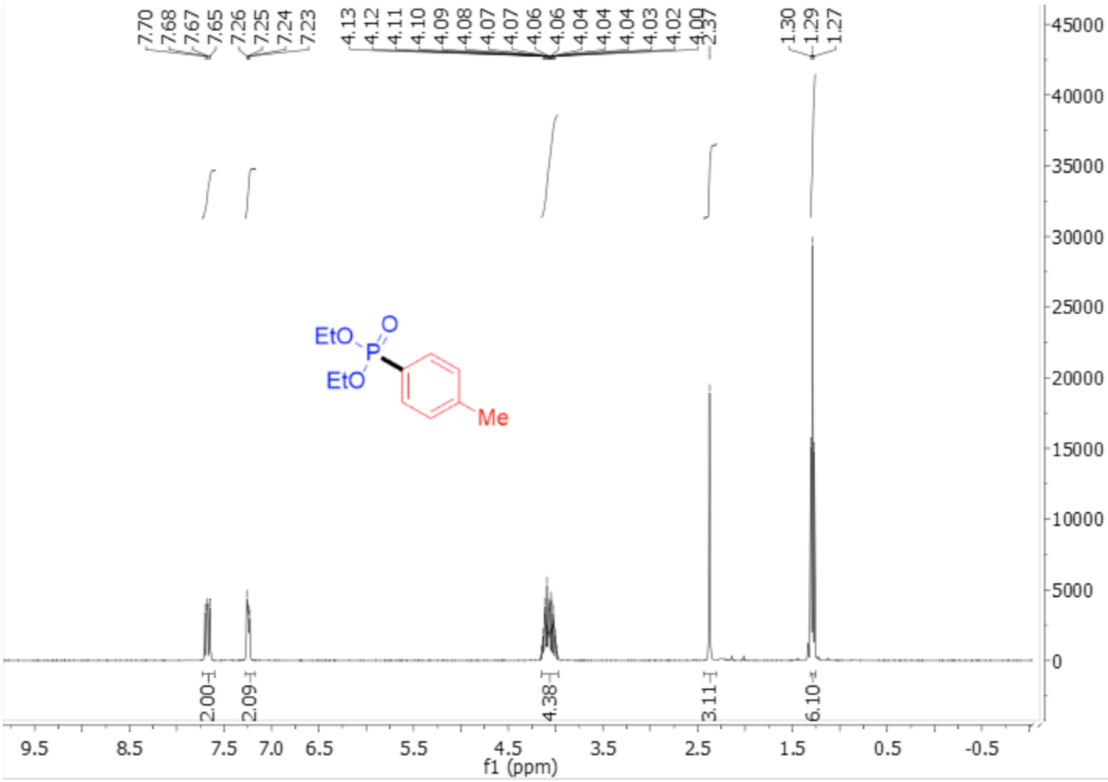
Supplementary Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4.



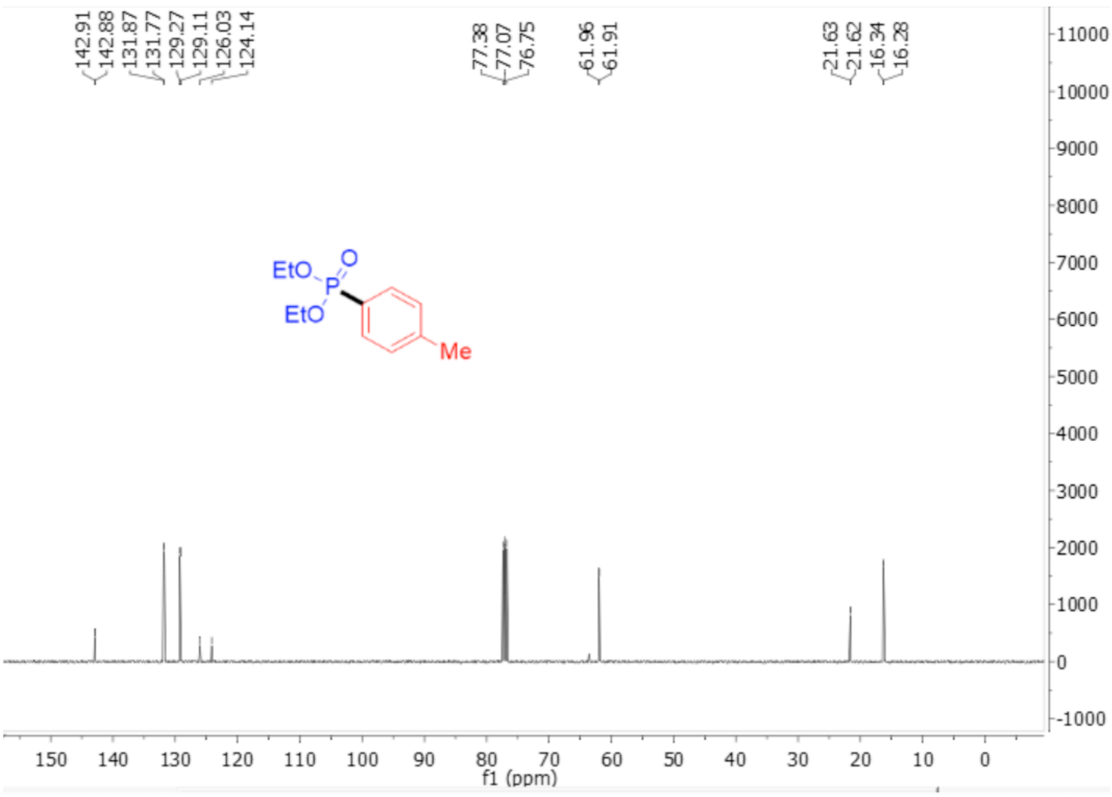
Supplementary Figure S14. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 4.**



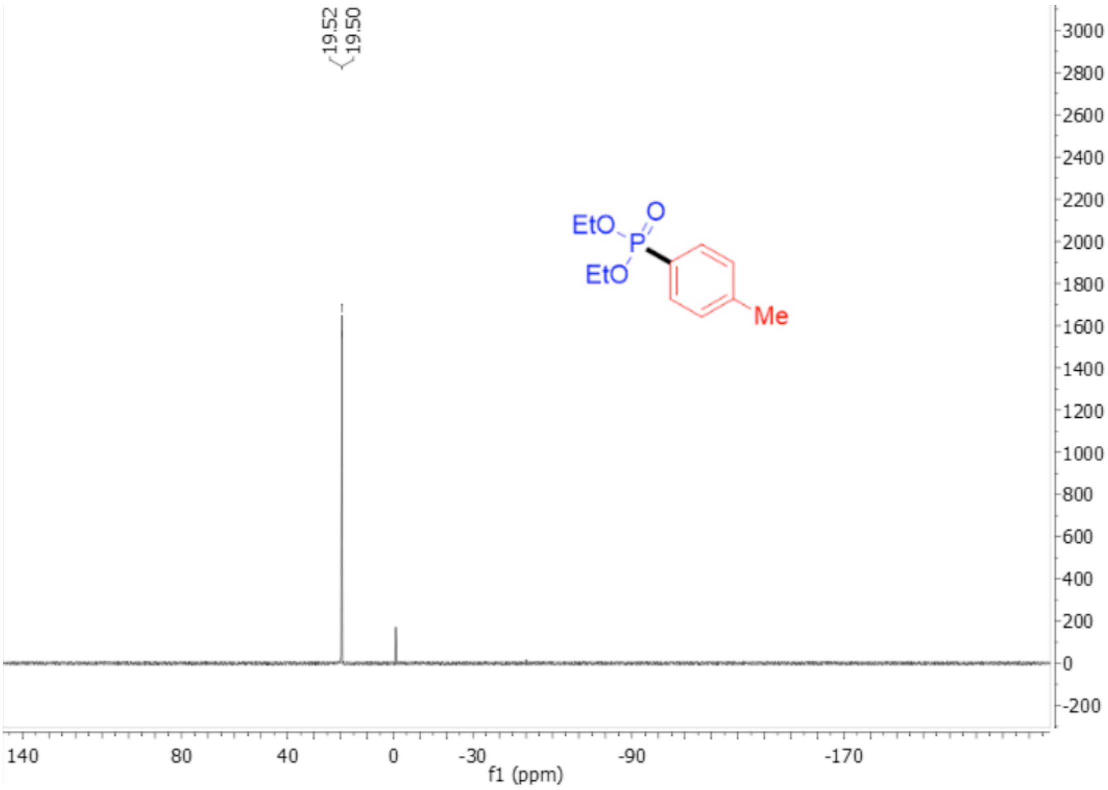
Supplementary Figure S15. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 4.**



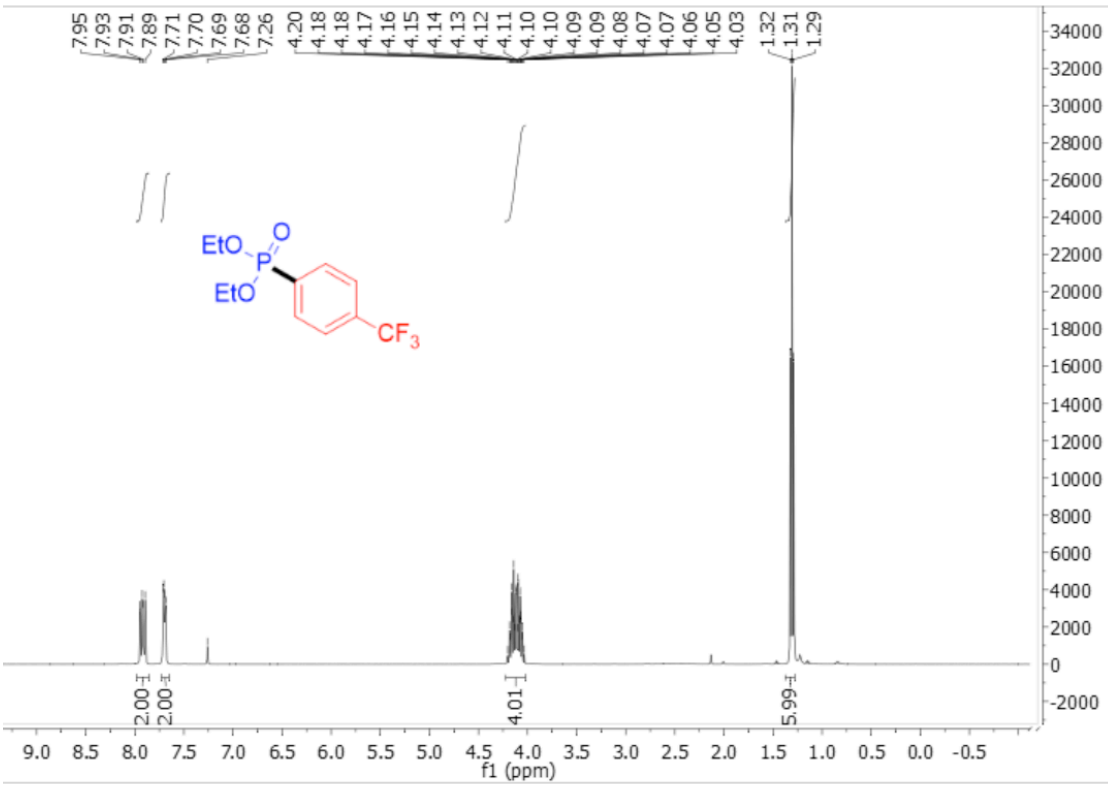
Supplementary Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5.



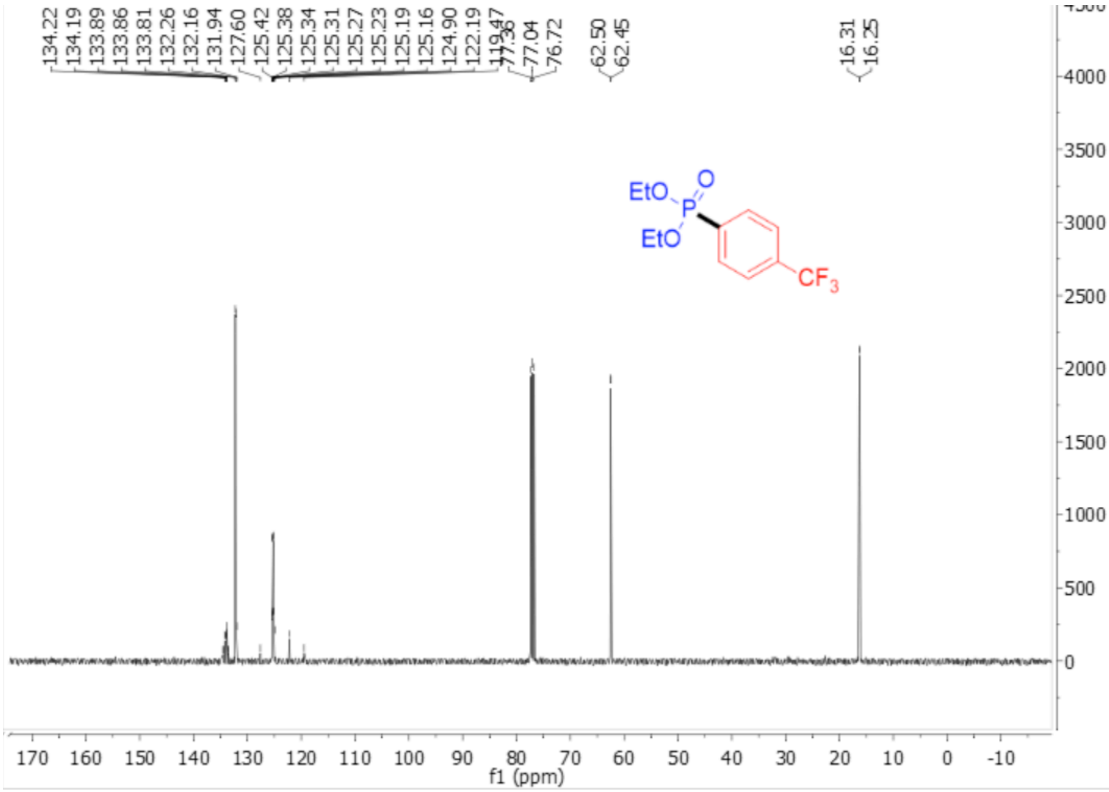
Supplementary Figure S17. ^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 5.



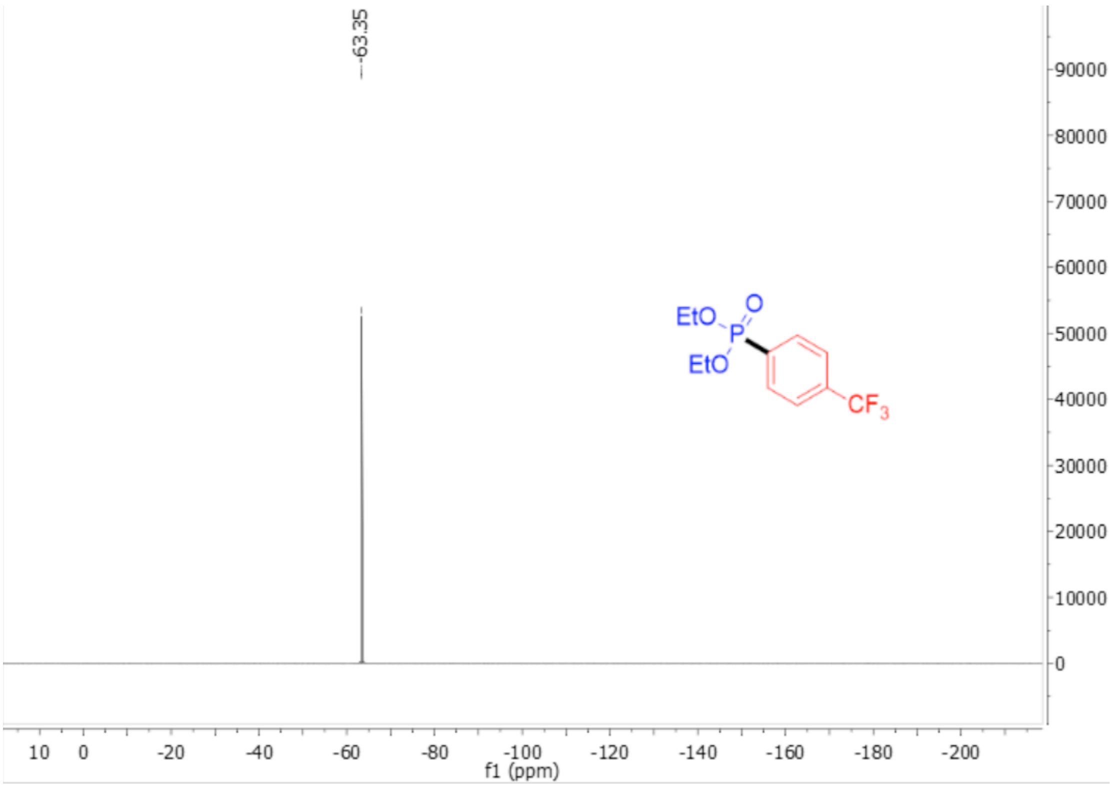
Supplementary Figure S18. ^{31}**PNMR (162 MHz, CDCl3) spectrum for 5.**



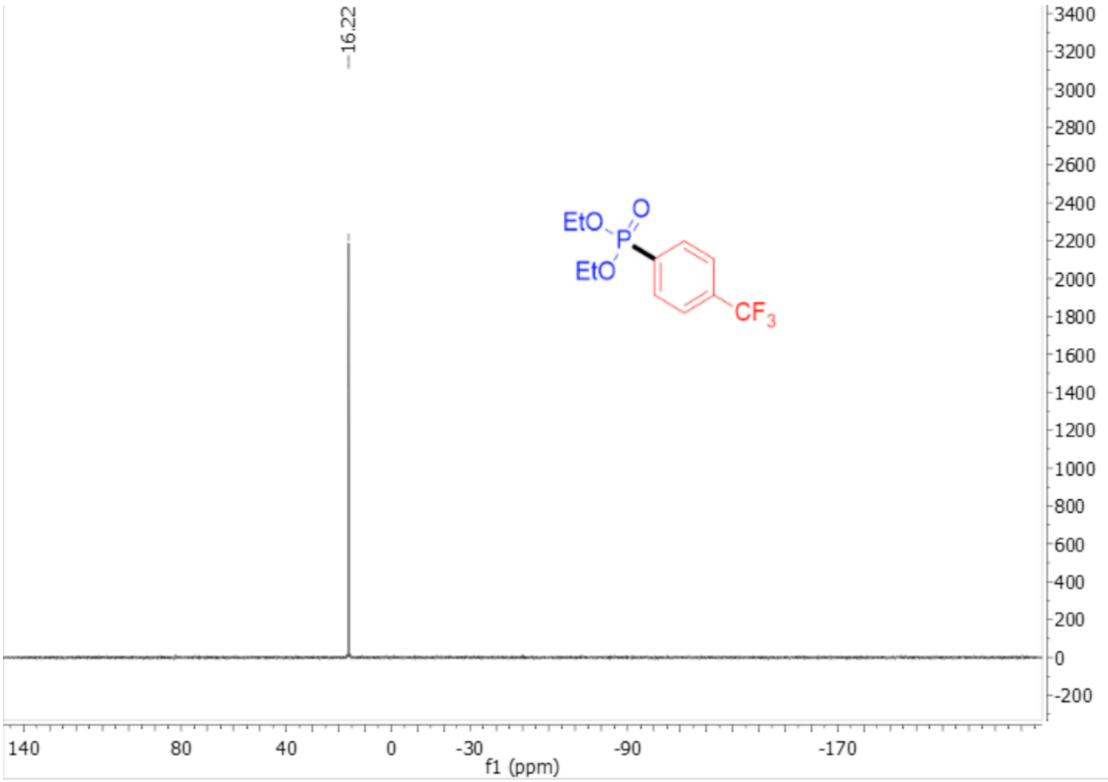
Supplementary Figure S19. ^{1}**HNMR (400 MHz, $CDCl_3$) spectrum for 6.**



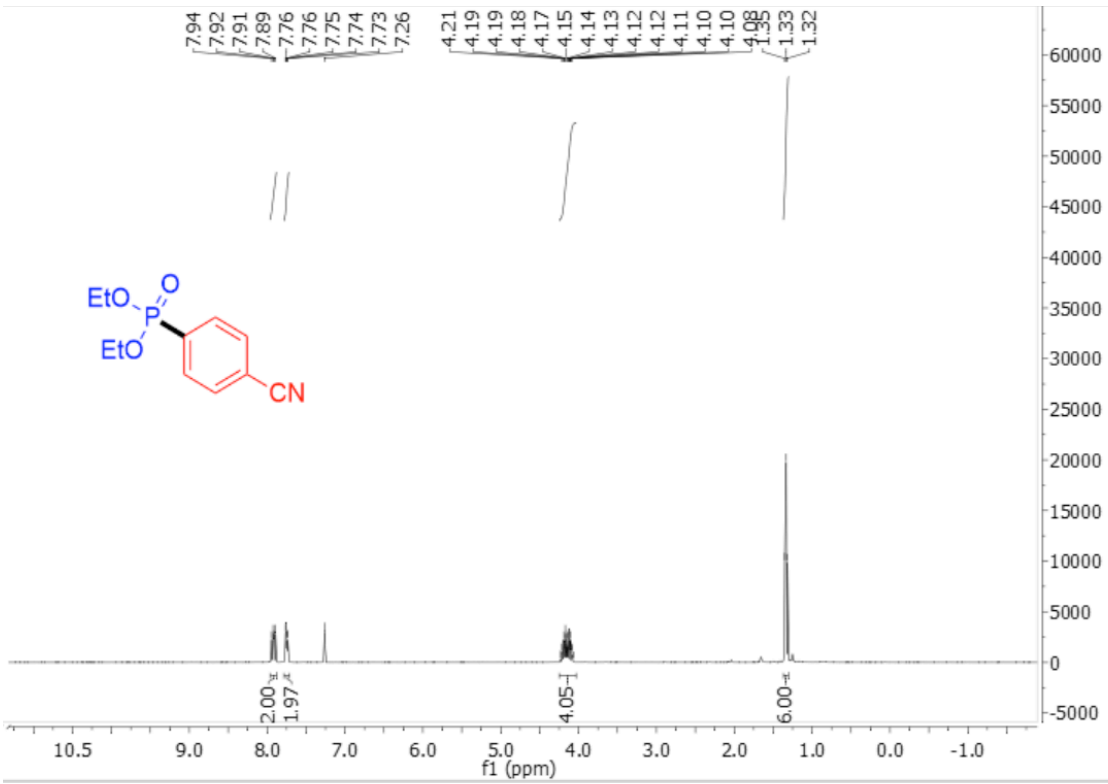
Supplementary Figure S20. **^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 6.**



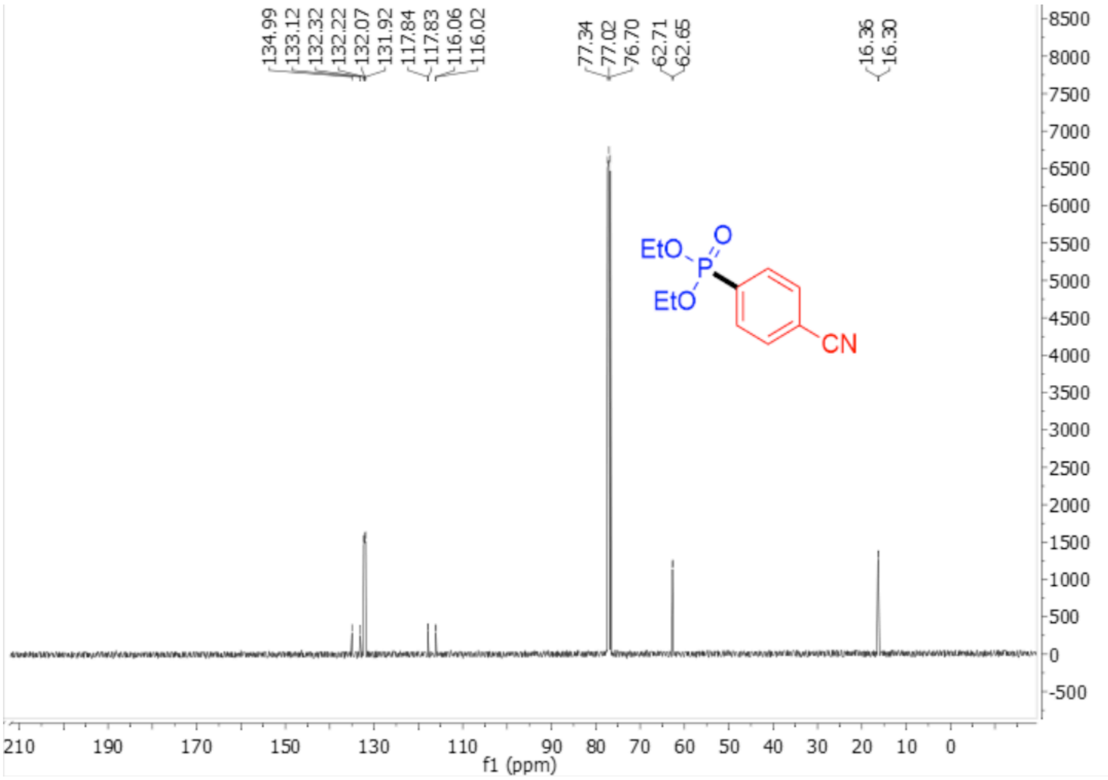
Supplementary Figure S21. **^{19}F NMR (377 MHz, CDCl3)spectrum for 6.**



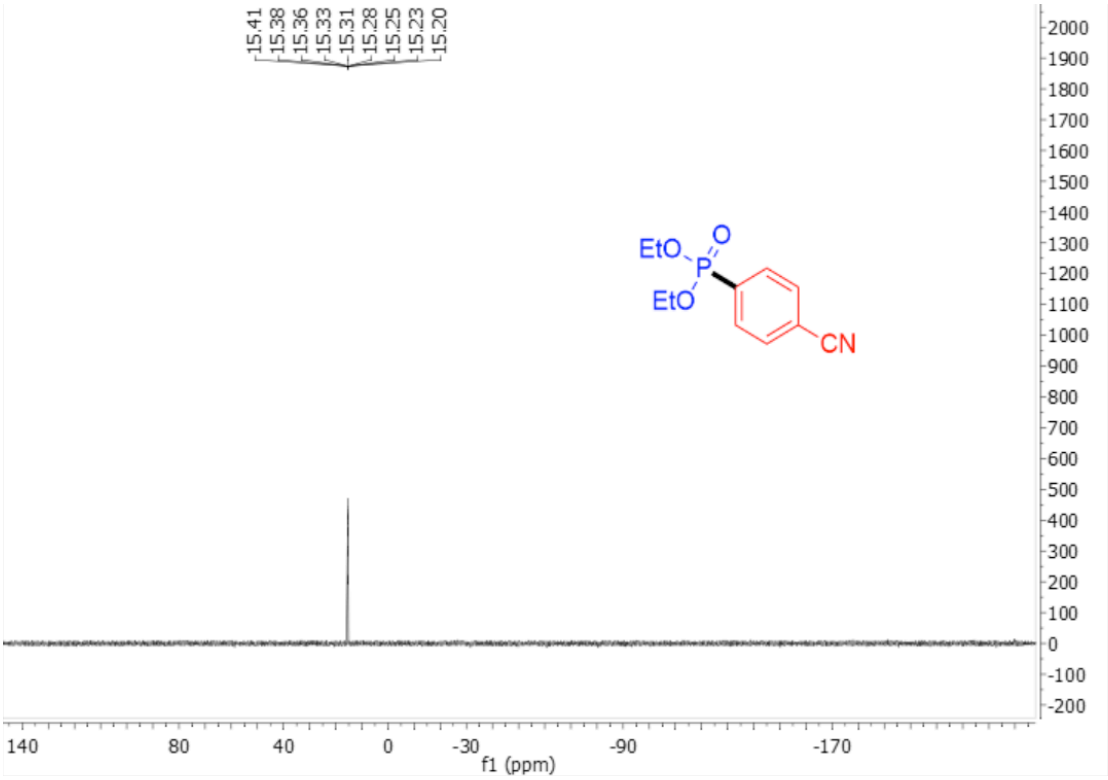
Supplementary Figure S22. ^{31}P NMR (162 MHz, CDCl3) spectrum for 6.



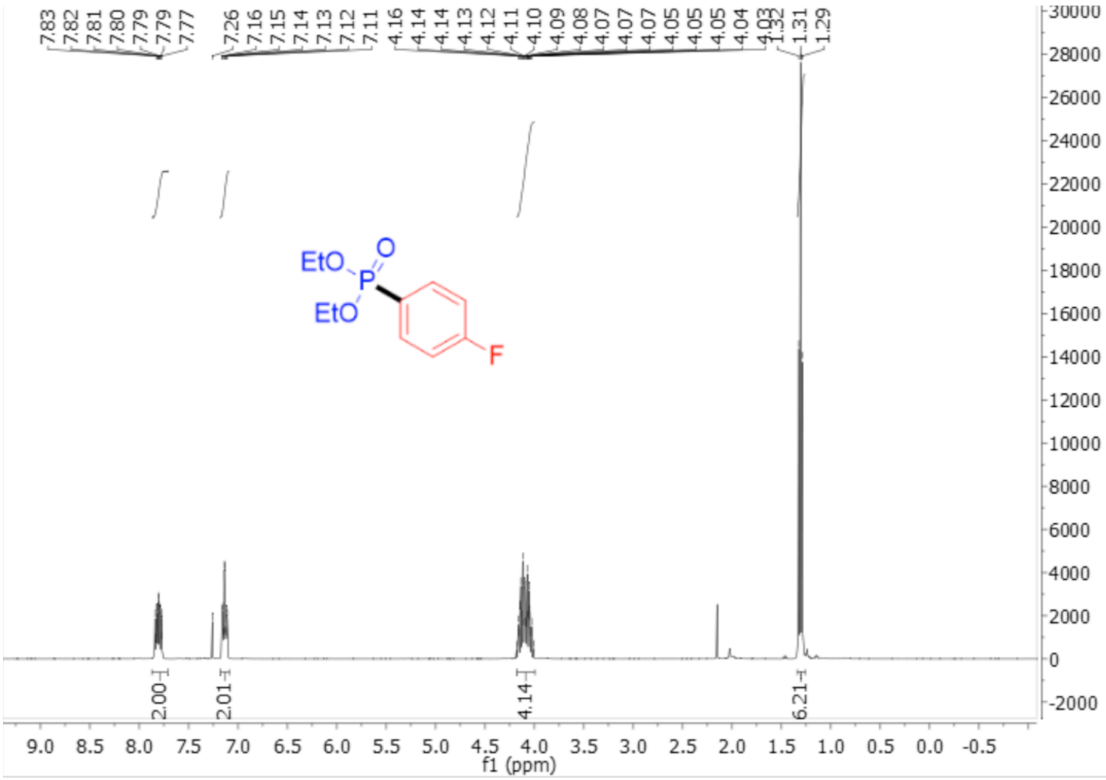
Supplementary Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 7.



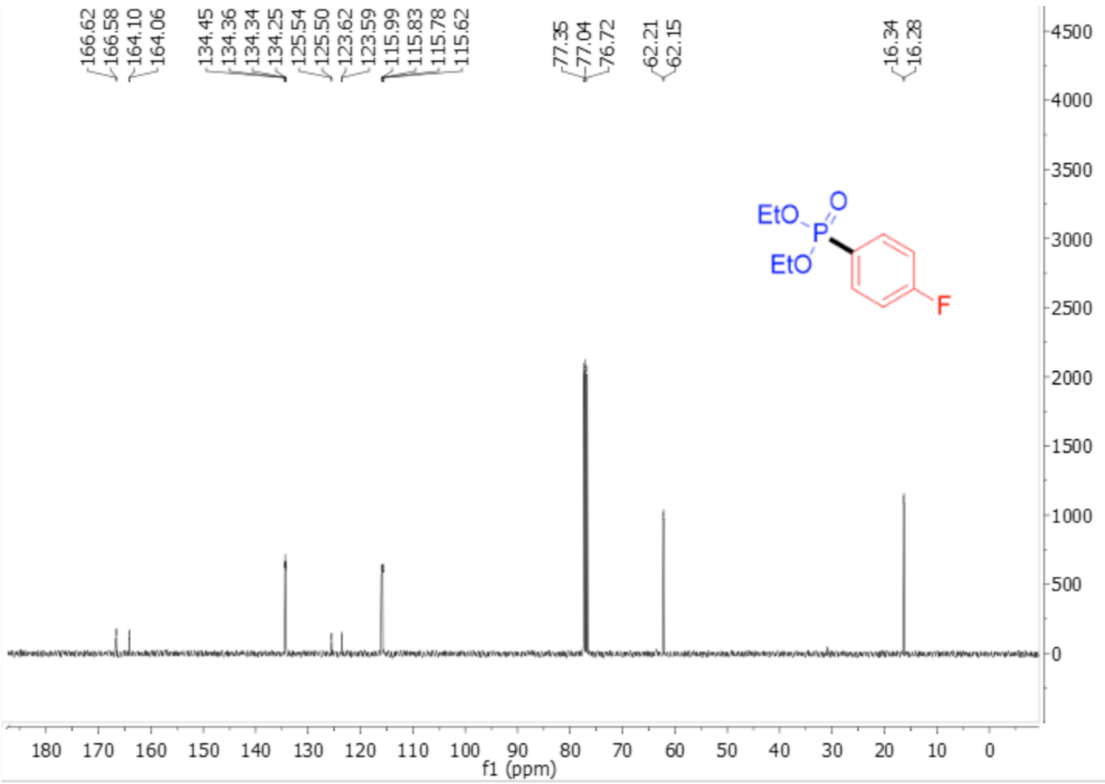
Supplementary Figure S24. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 7.**



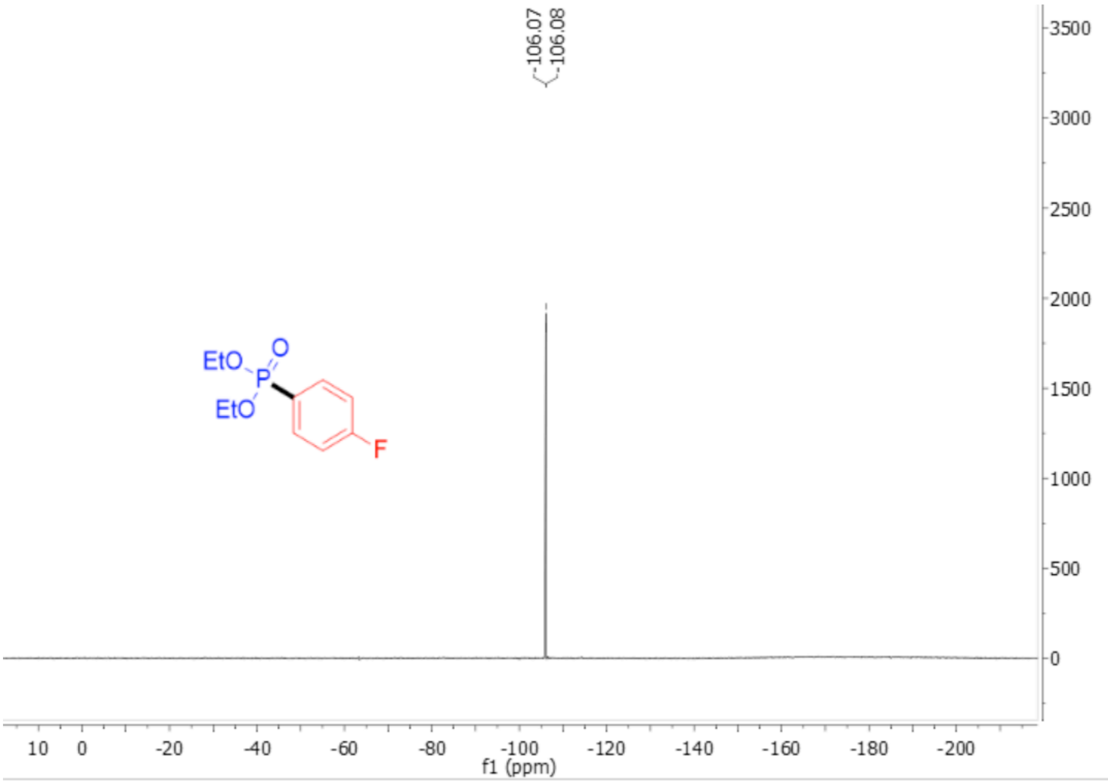
Supplementary Figure S25. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 7.**



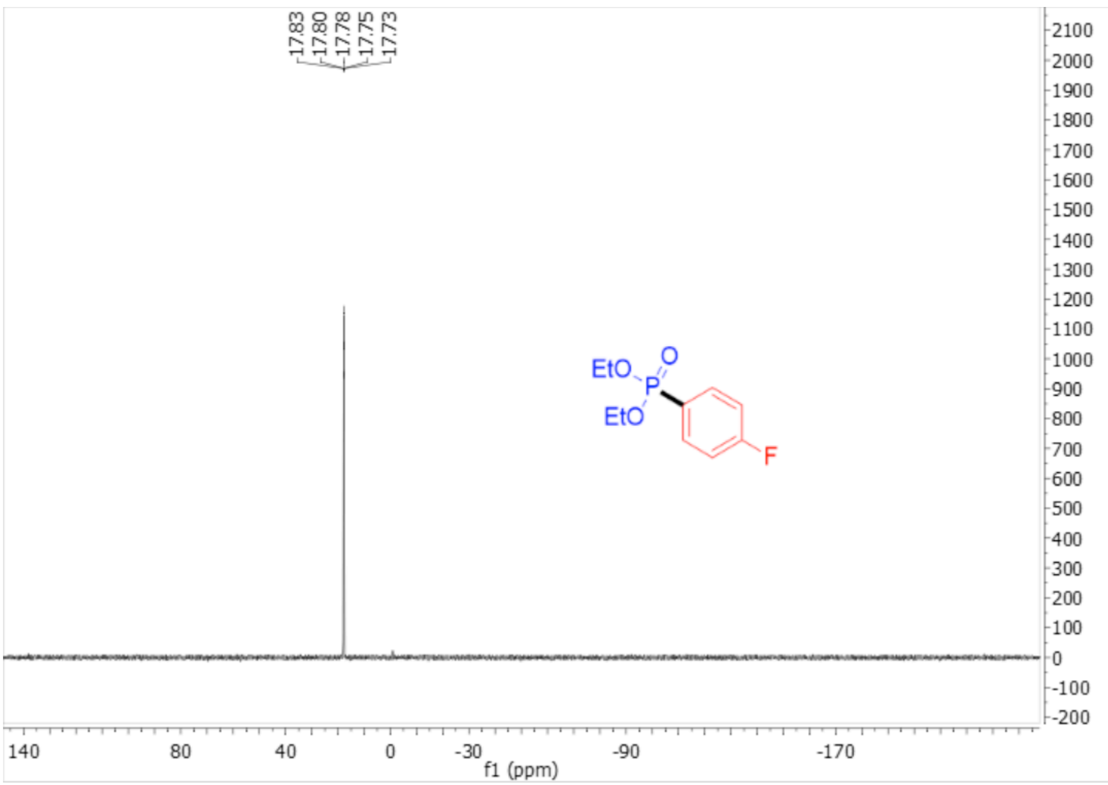
Supplementary Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 8.



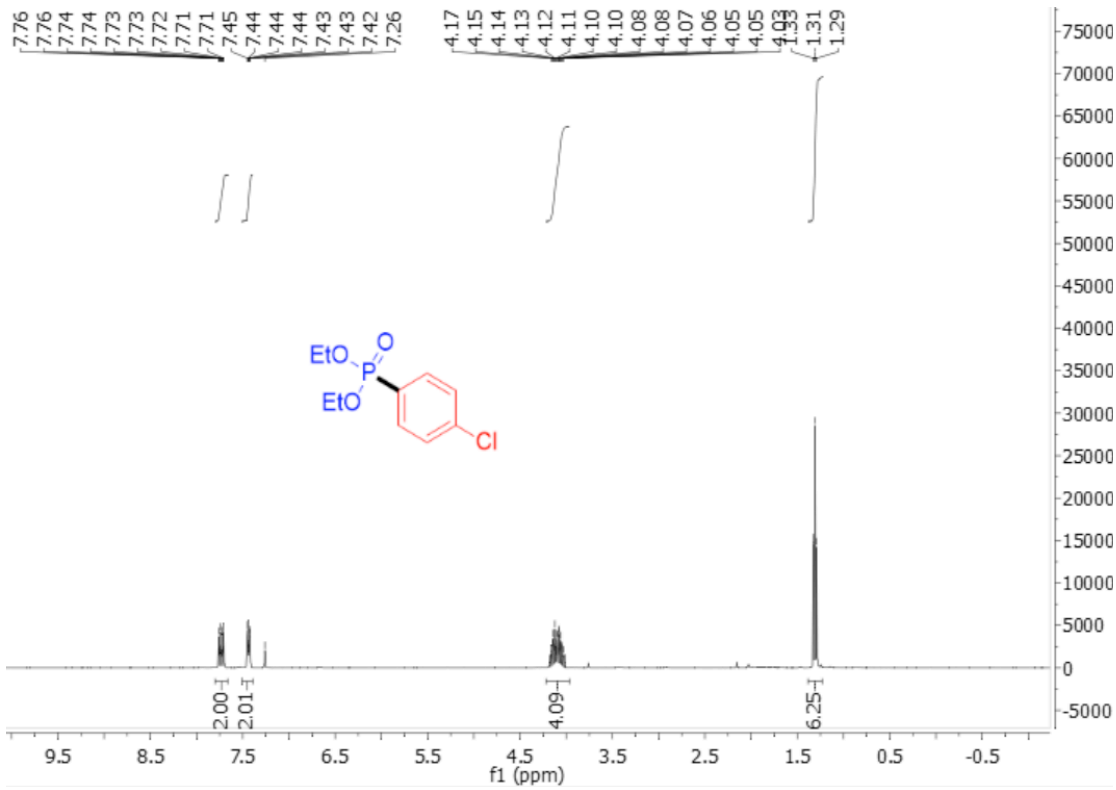
Supplementary Figure S27. ^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 8.



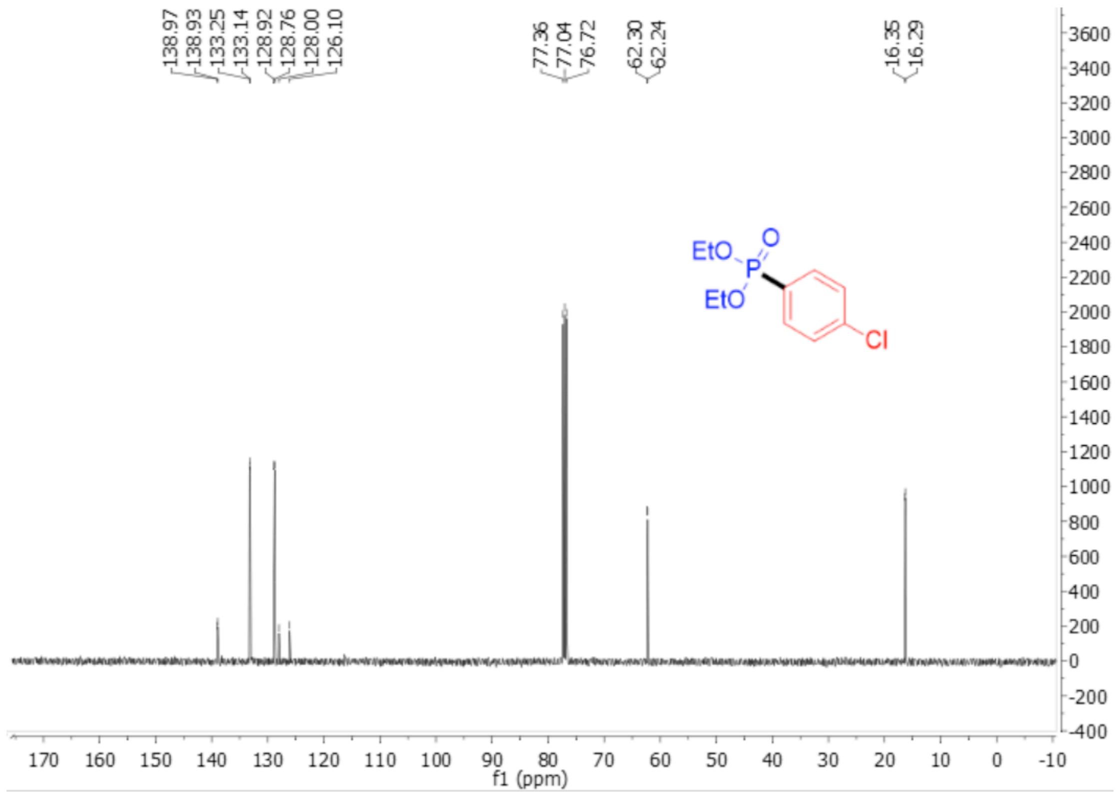
Supplementary Figure S28. ^{19}**F NMR (377 MHz, CDCl3) spectrum for 8.**



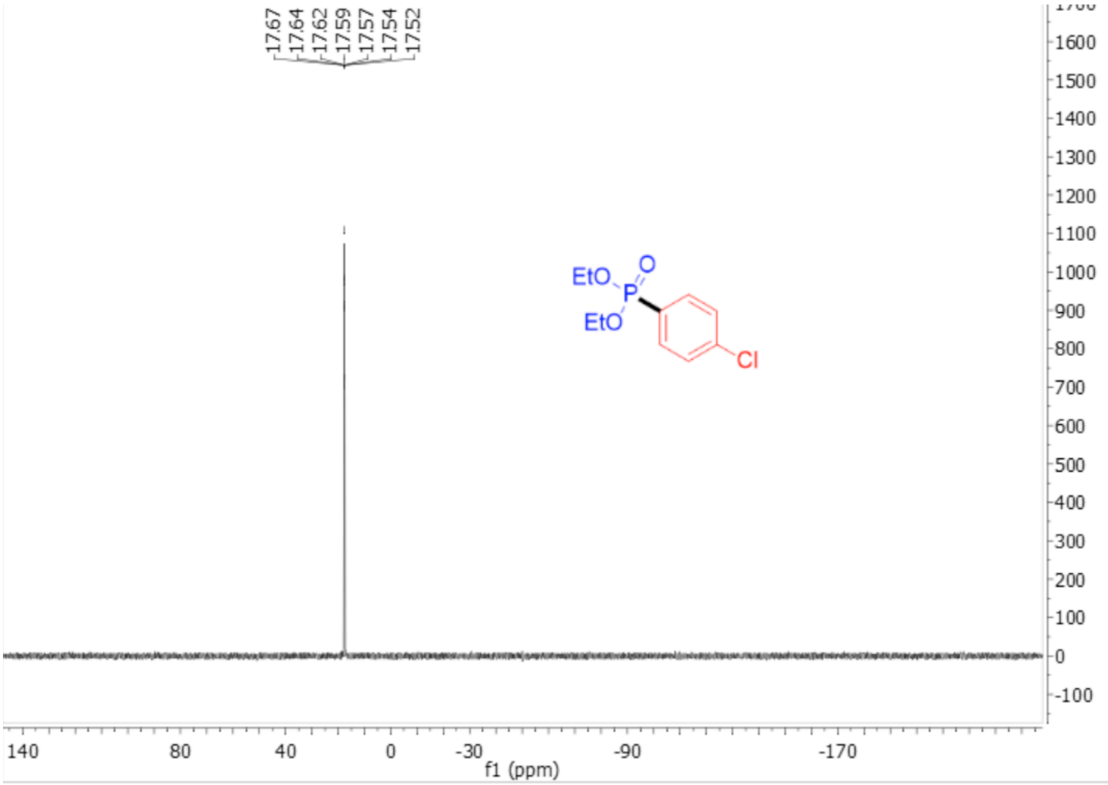
Supplementary Figure S29. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 8.**



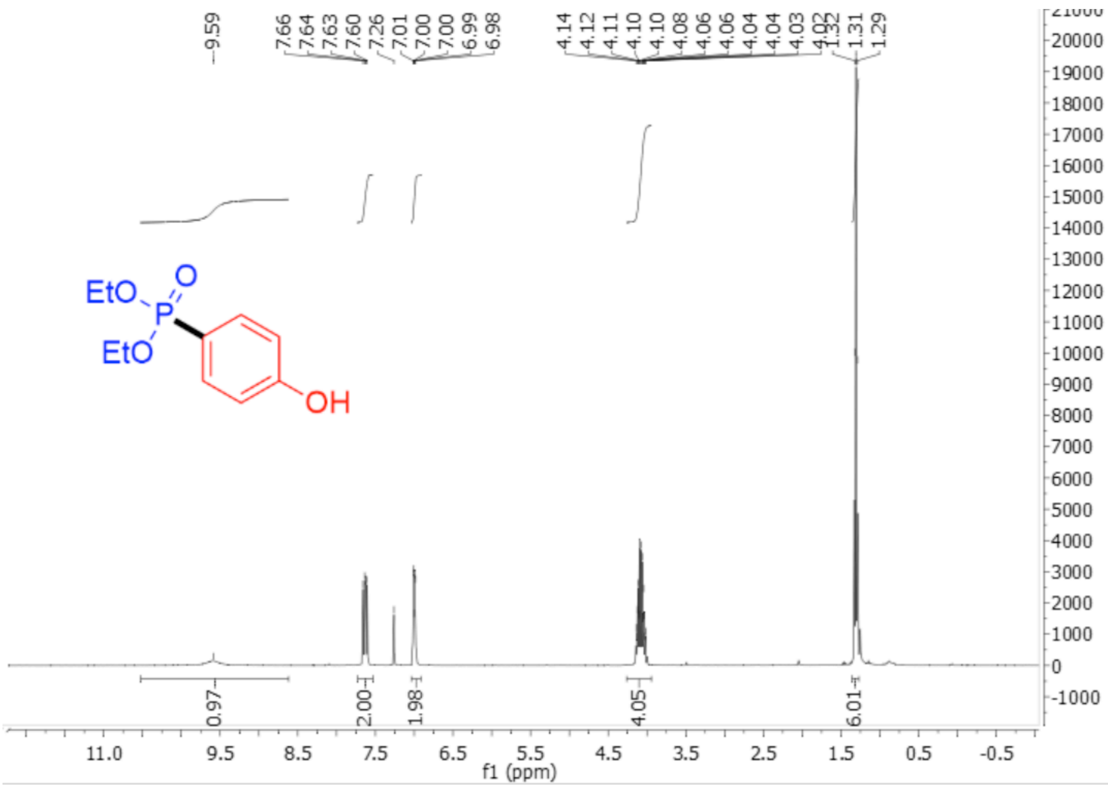
Supplementary Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 9.



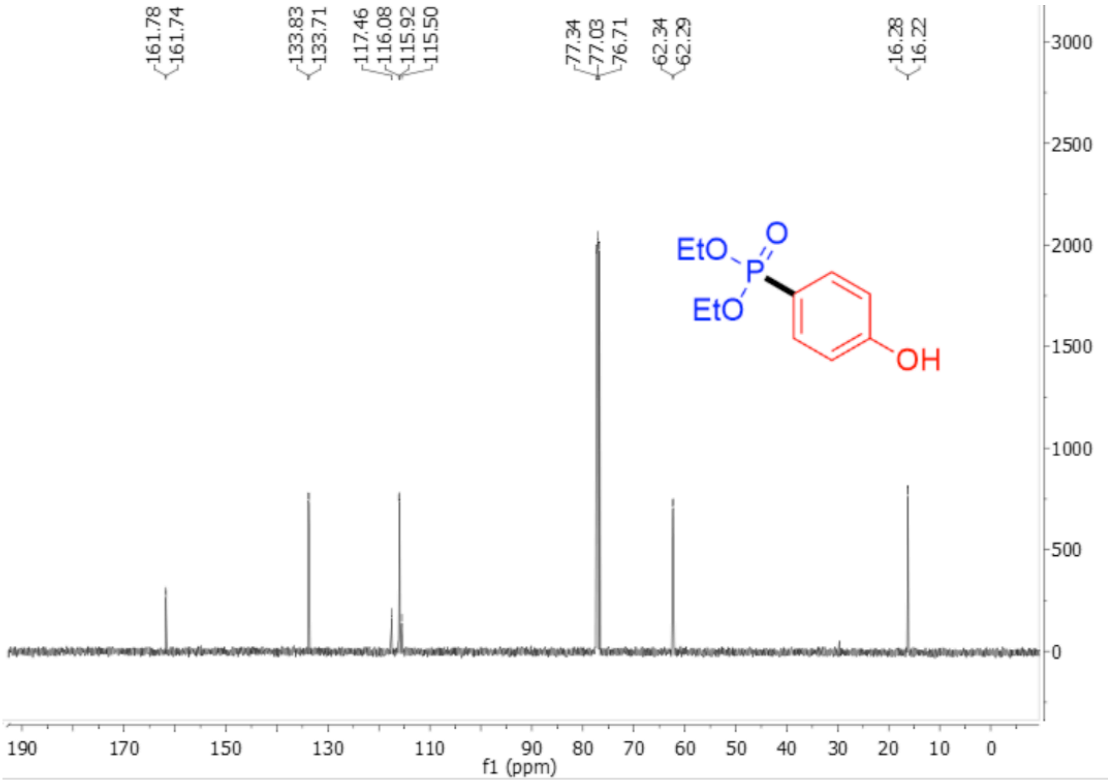
Supplementary Figure S31. ^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 9.



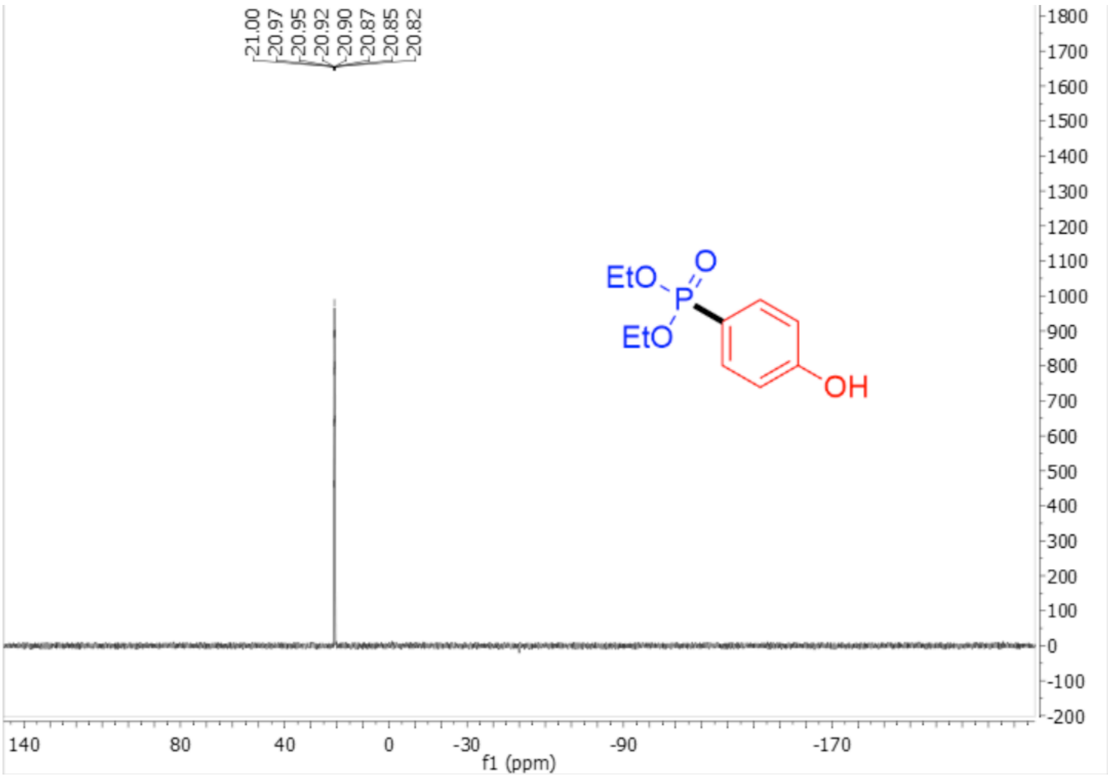
Supplementary Figure S32. ^{31}P NMR (162 MHz, CDCl3) spectrum for 9.



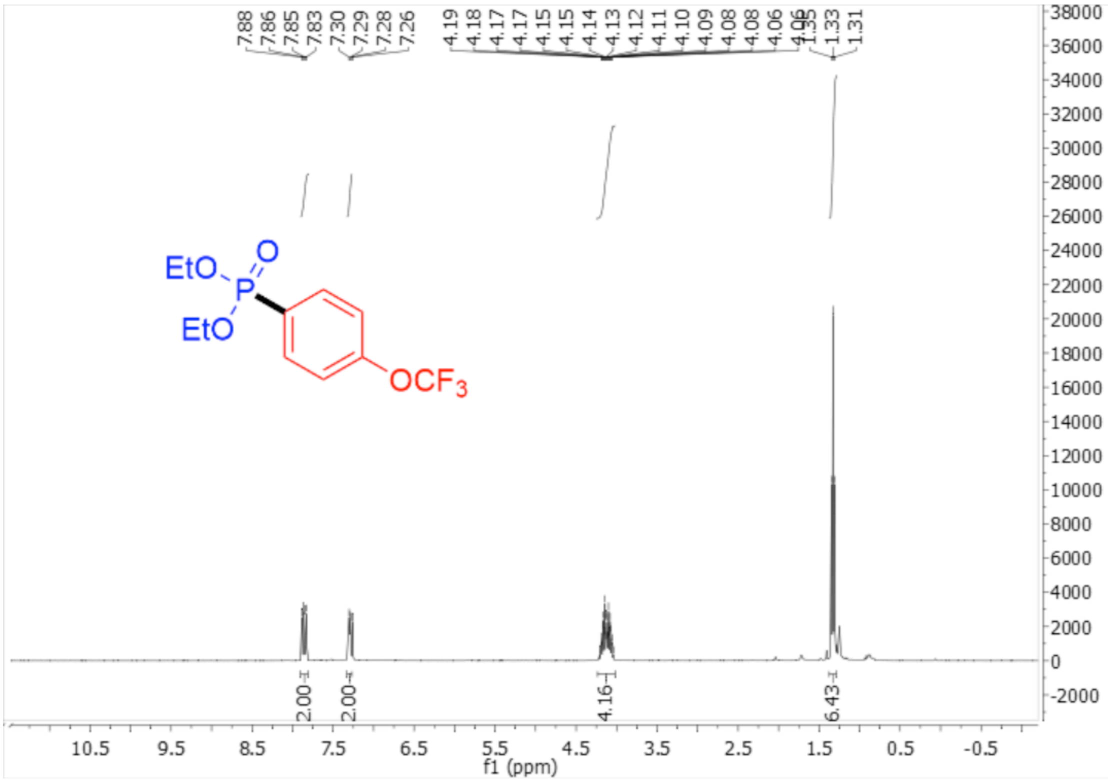
Supplementary Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 10.



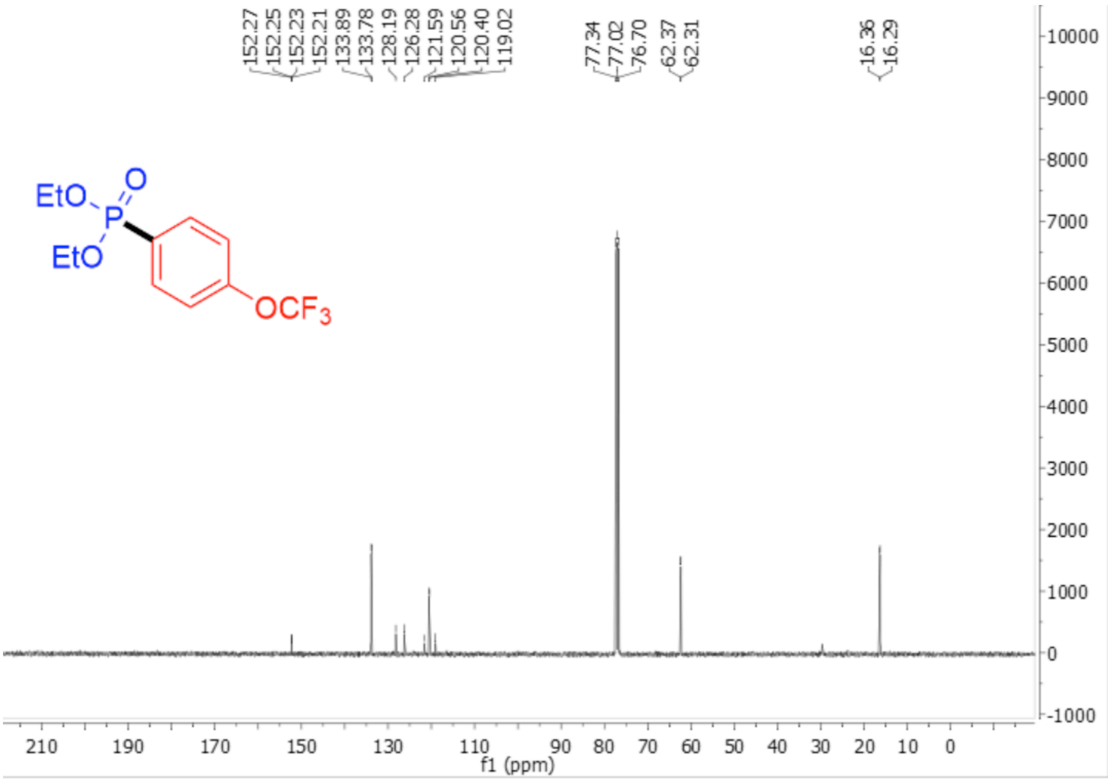
Supplementary Figure S34. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 10.**



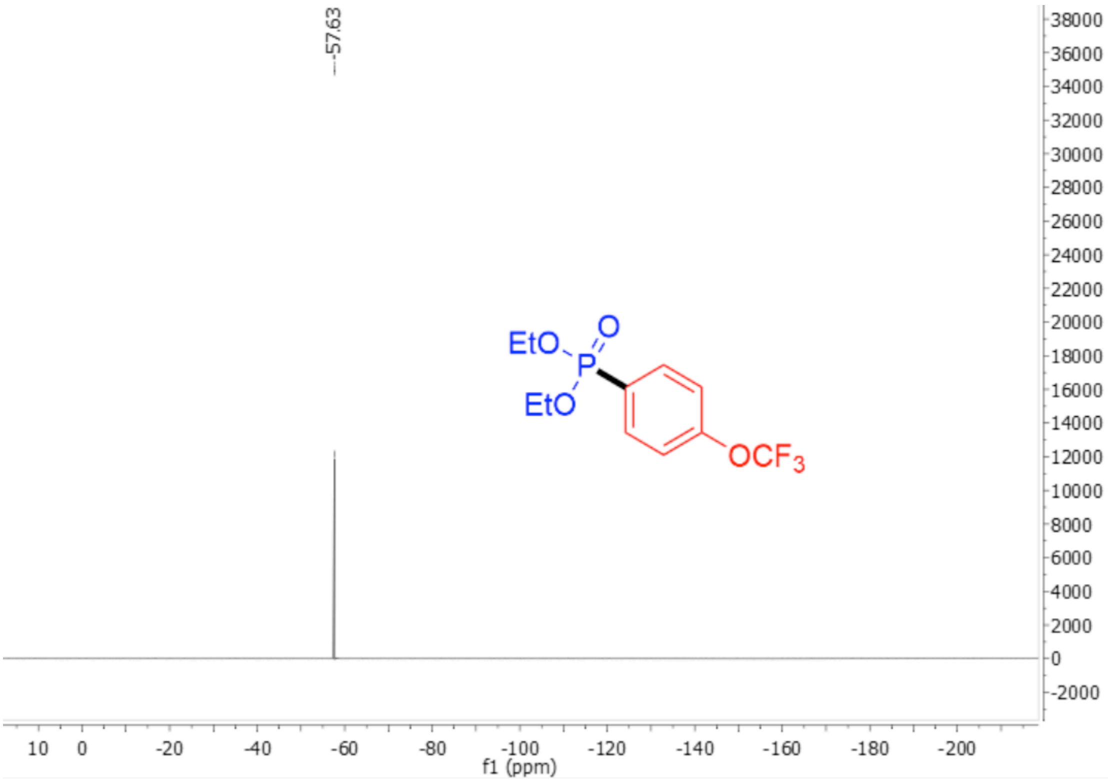
Supplementary Figure S35. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 10.**



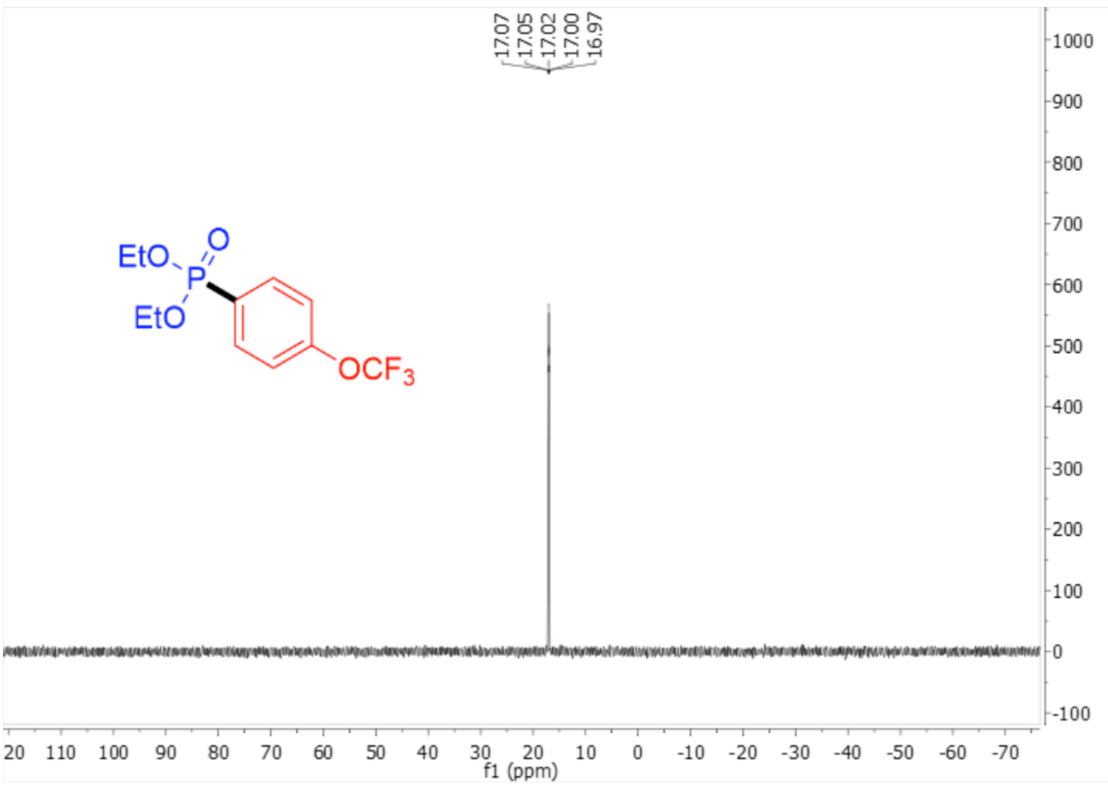
Supplementary Figure S36. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum for 11.



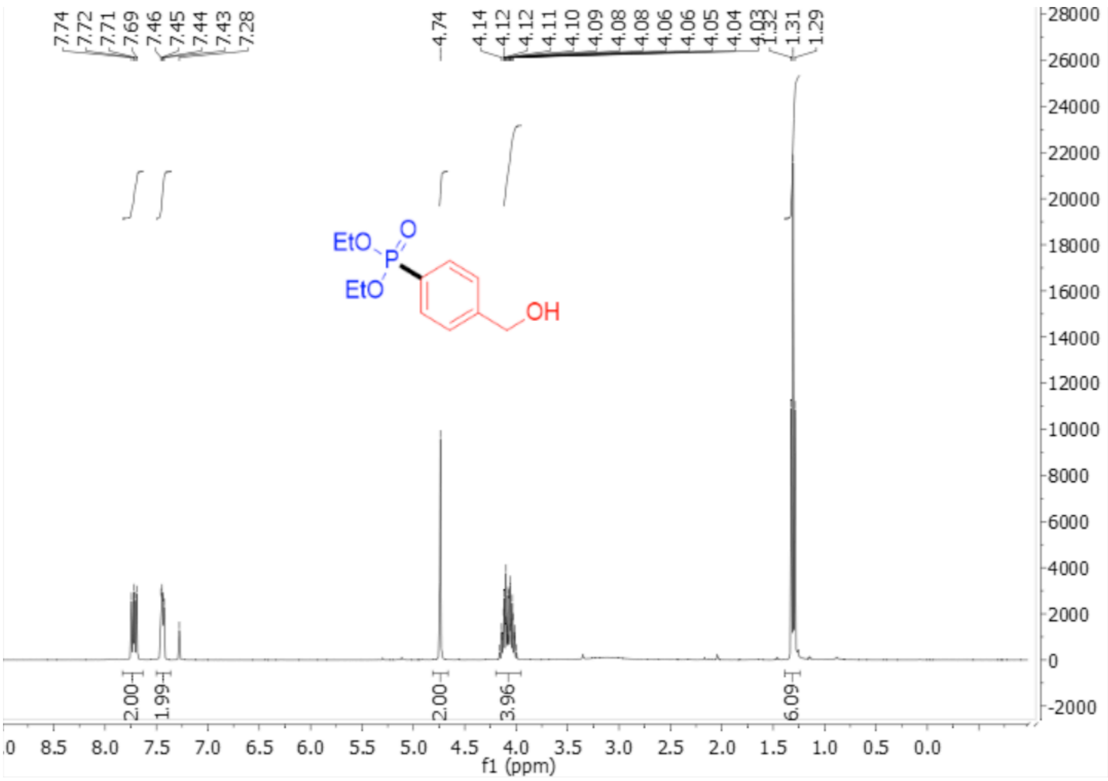
Supplementary Figure S37. ^{13}CNMR(101 MHz, CDCl$_3$) spectrum for 11.



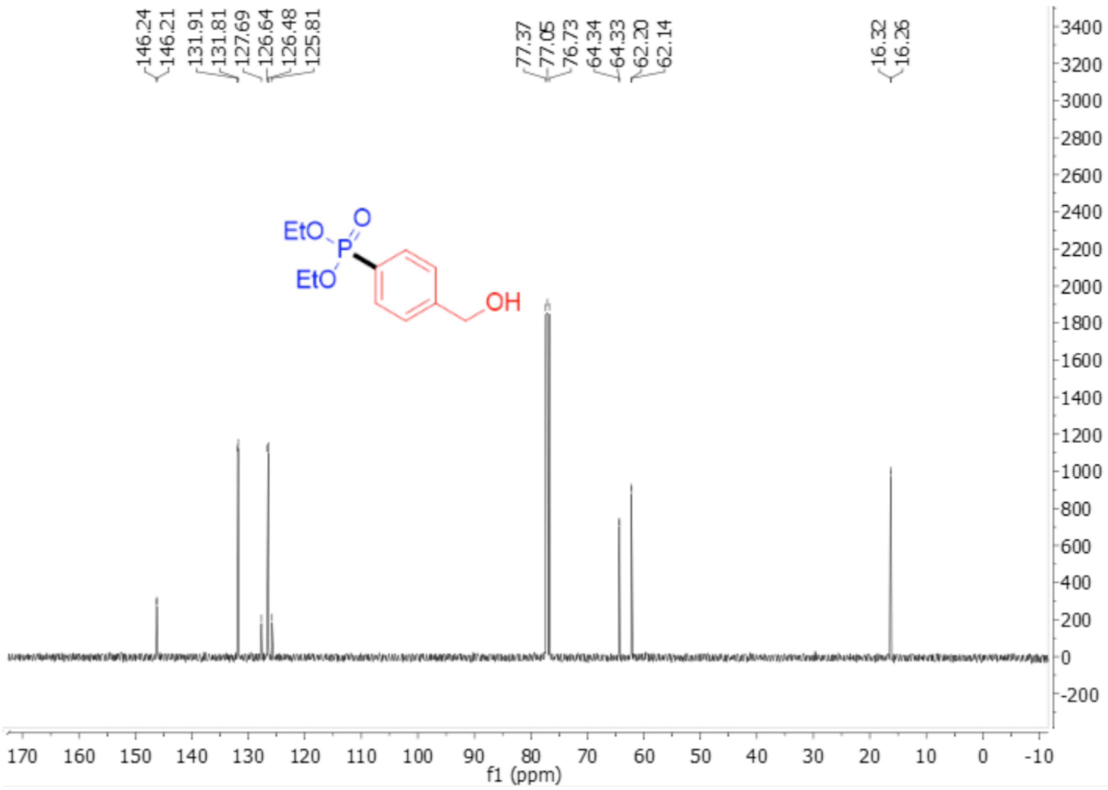
Supplementary Figure S38. [19]F NMR (377 MHz, CDCl3) spectrum for 11.



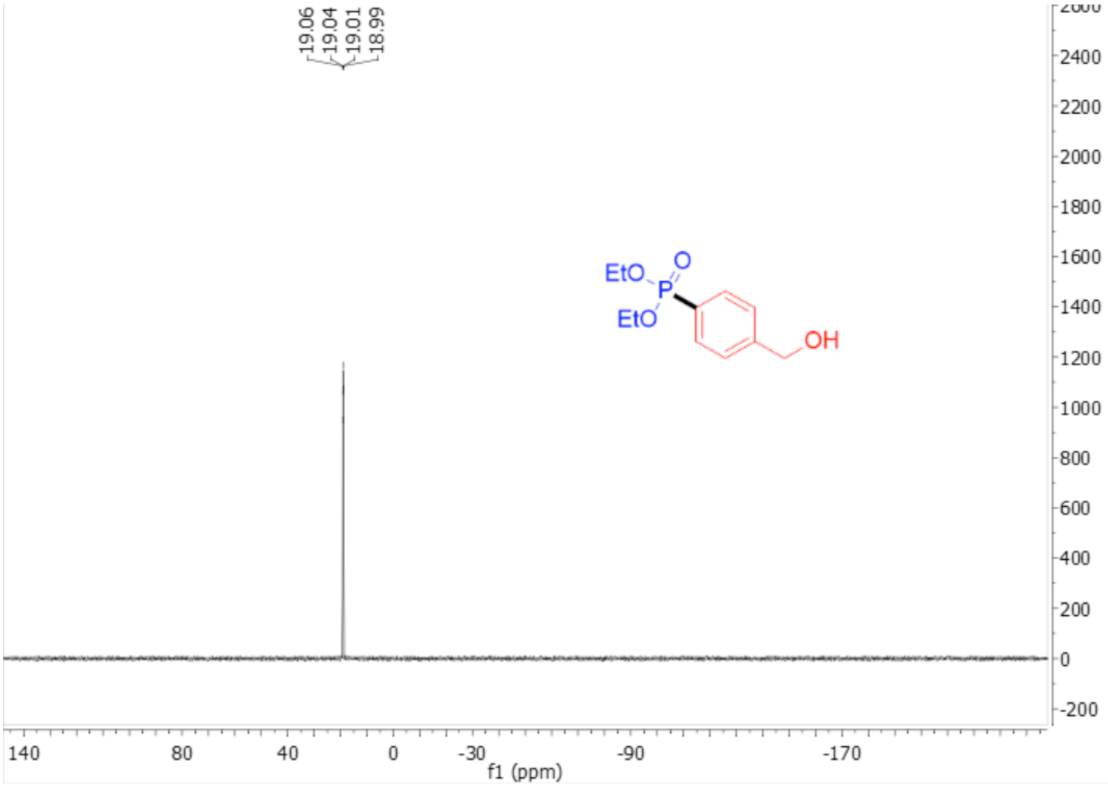
Supplementary Figure S39. [31]P NMR (162 MHz, CDCl3) spectrum for 11.



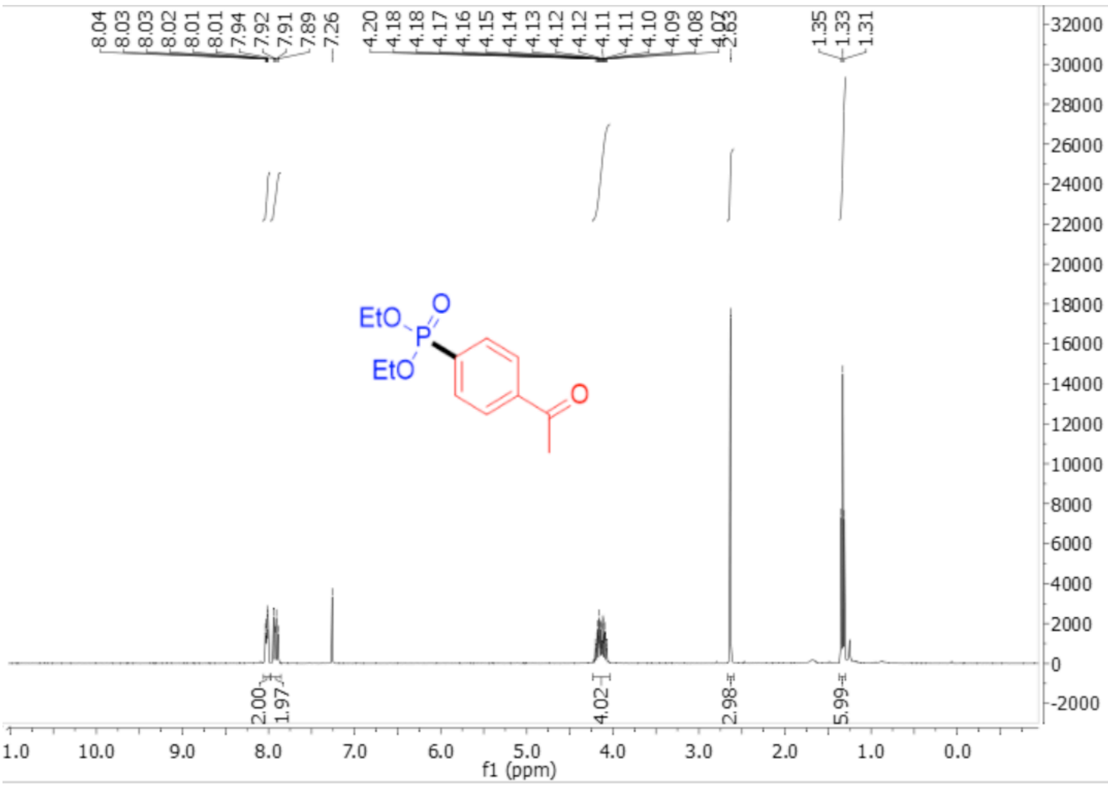
Supplementary Figure S40. [1]H NMR (400 MHz, $CDCl_3$) spectrum for 12.



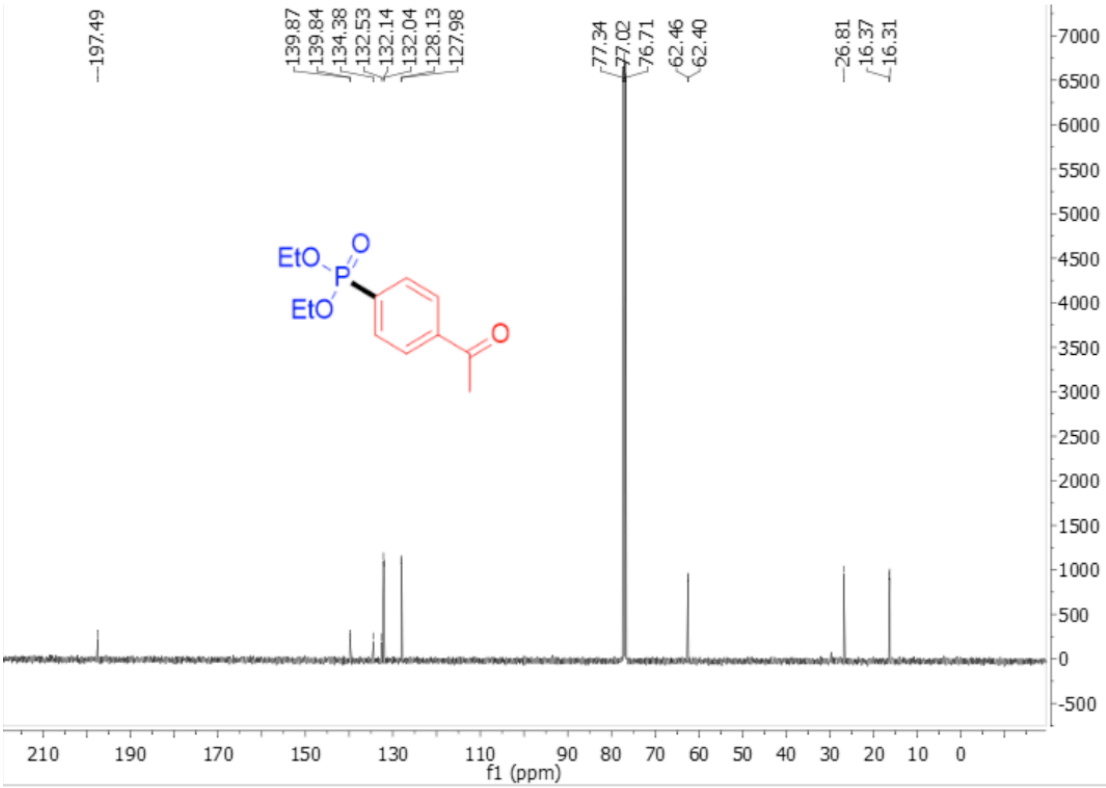
Supplementary Figure S41. [13]CNMR(101 MHz, $CDCl_3$) spectrum for 12.



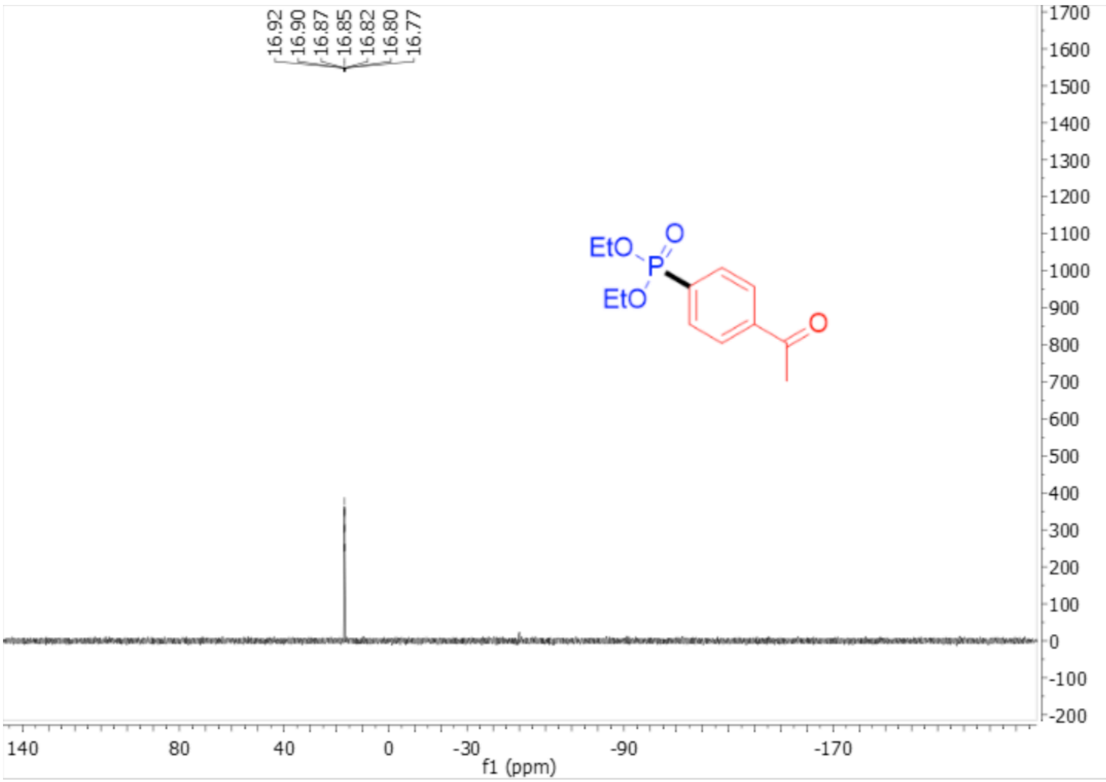
Supplementary Figure S42. ^{31}P NMR (162 MHz, CDCl3) spectrum for 12.



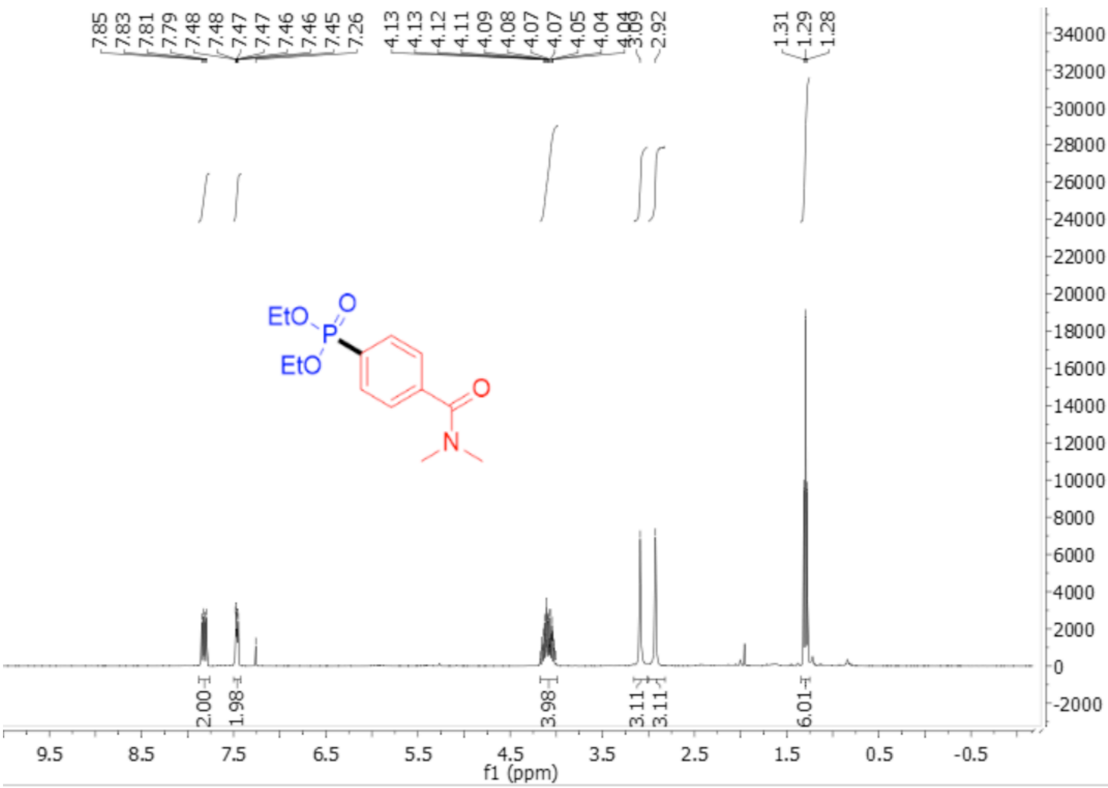
Supplementary Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 13.



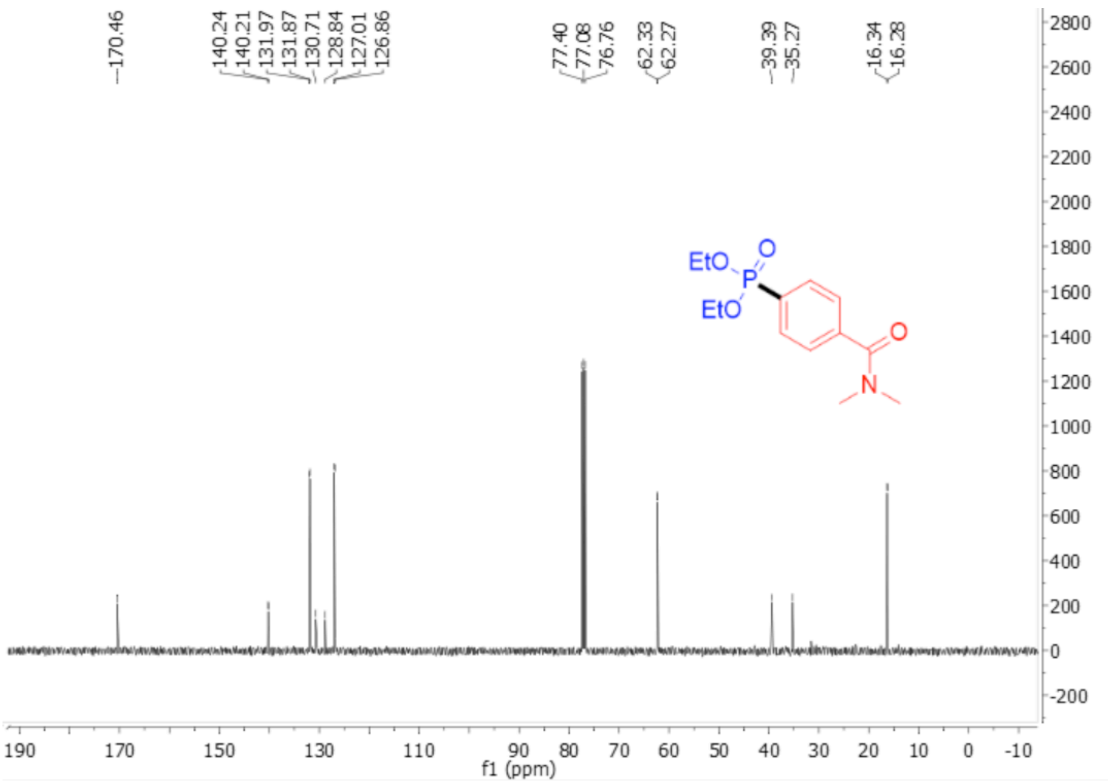
Supplementary Figure S44. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 13.**



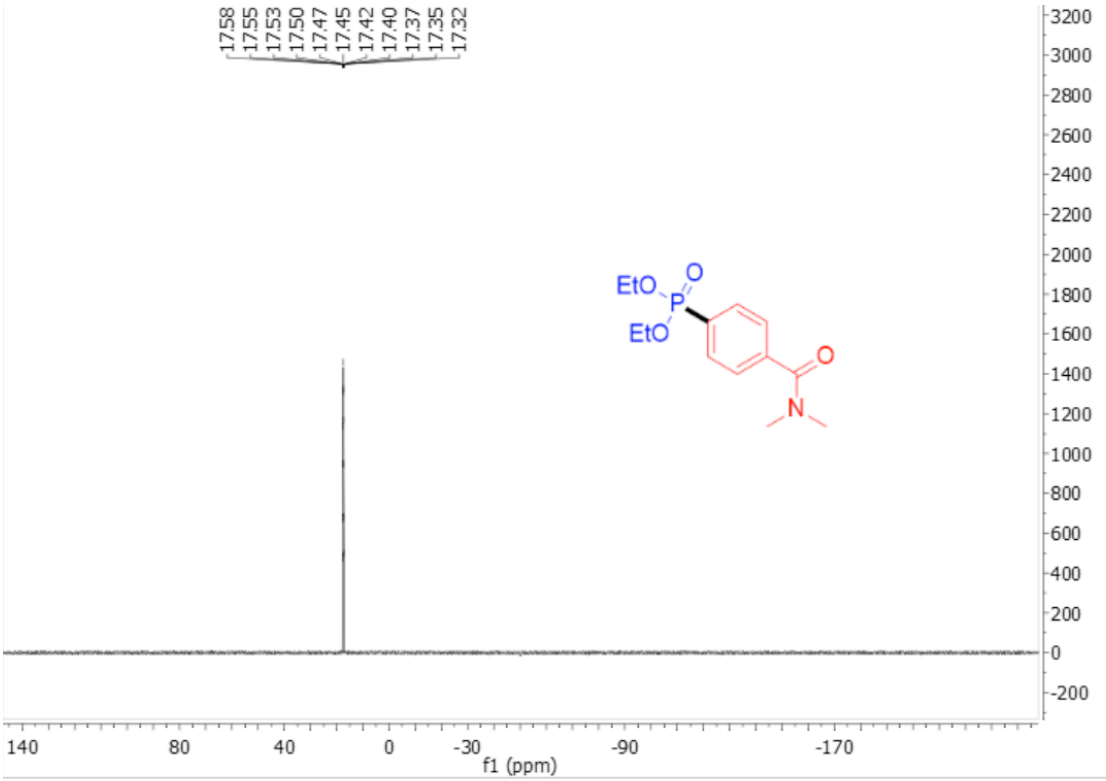
Supplementary Figure S45. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 13.**



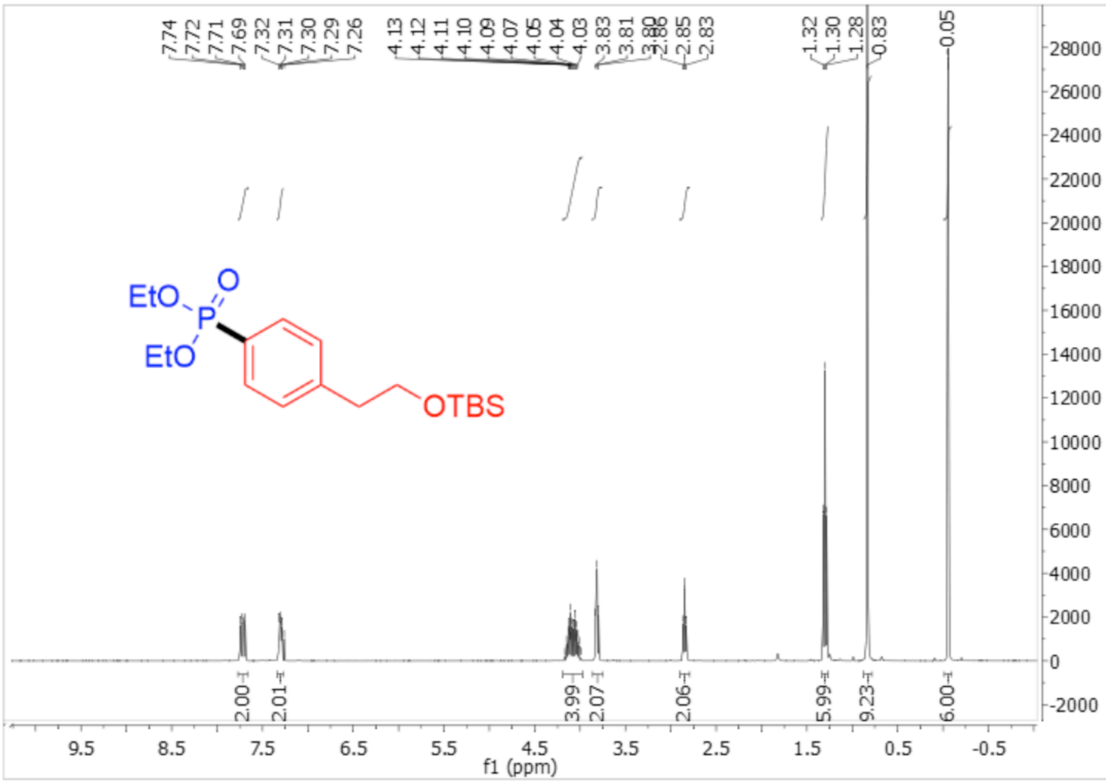
Supplementary Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 14.



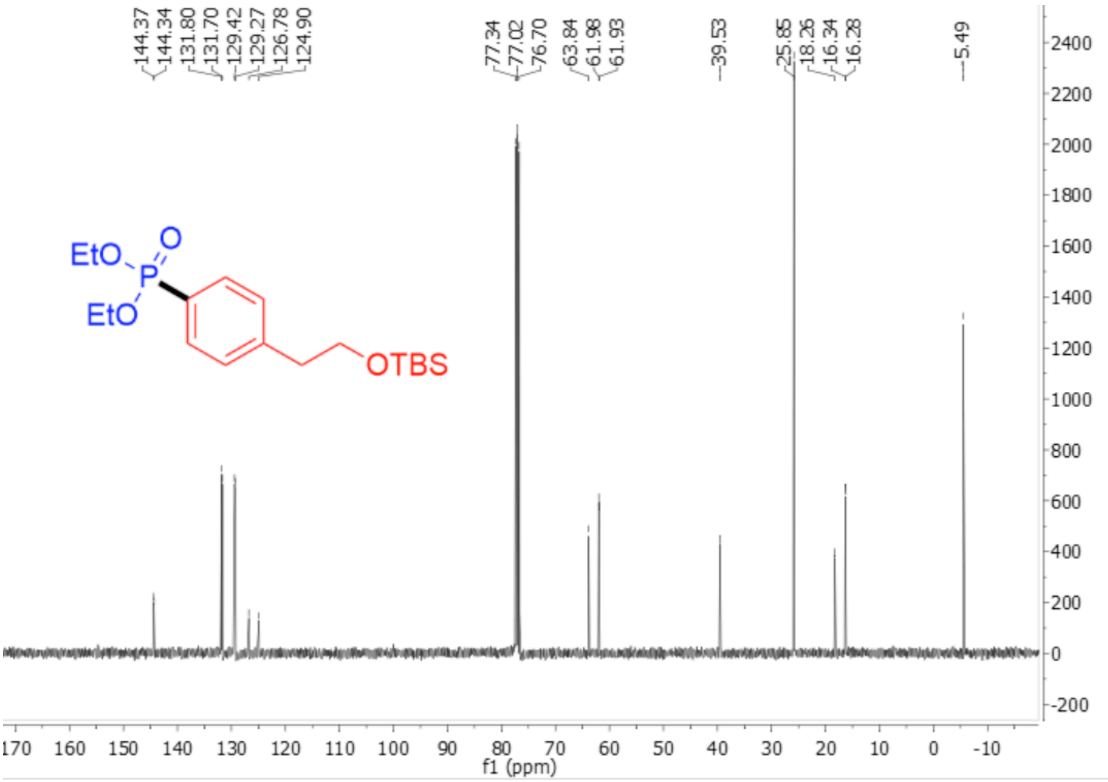
Supplementary Figure S47. ^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 14.



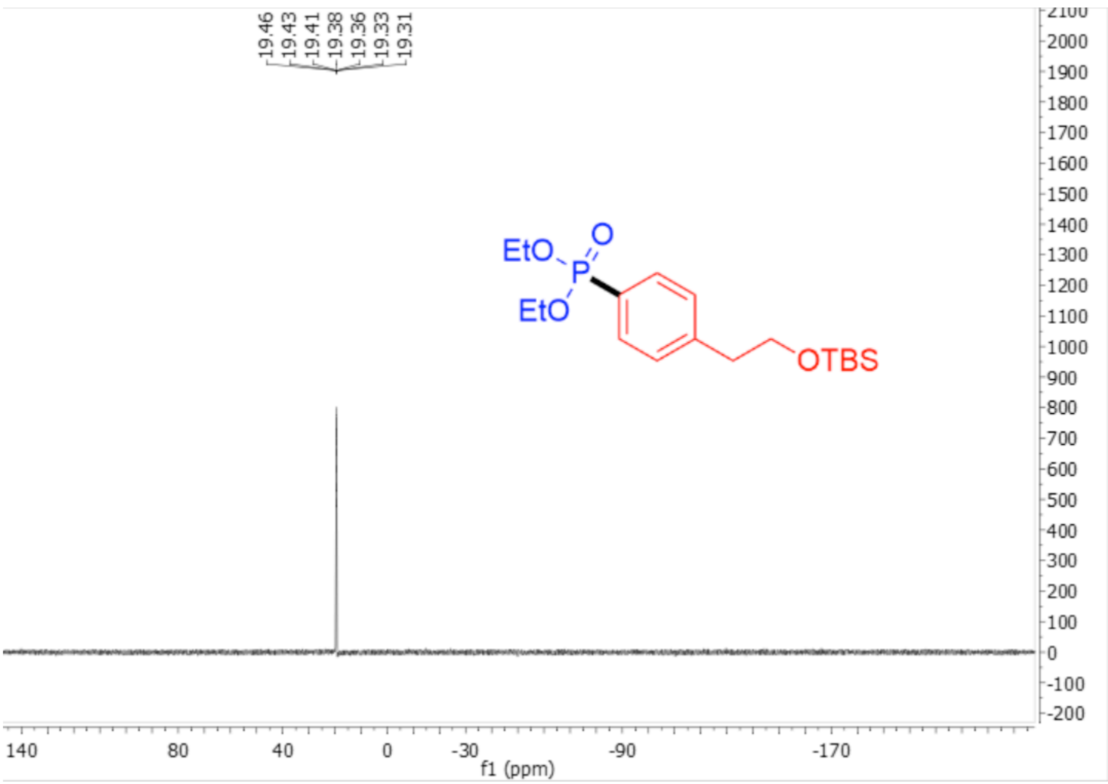
Supplementary Figure S48. ^{31}P NMR (162 MHz, CDCl3) spectrum for 14.



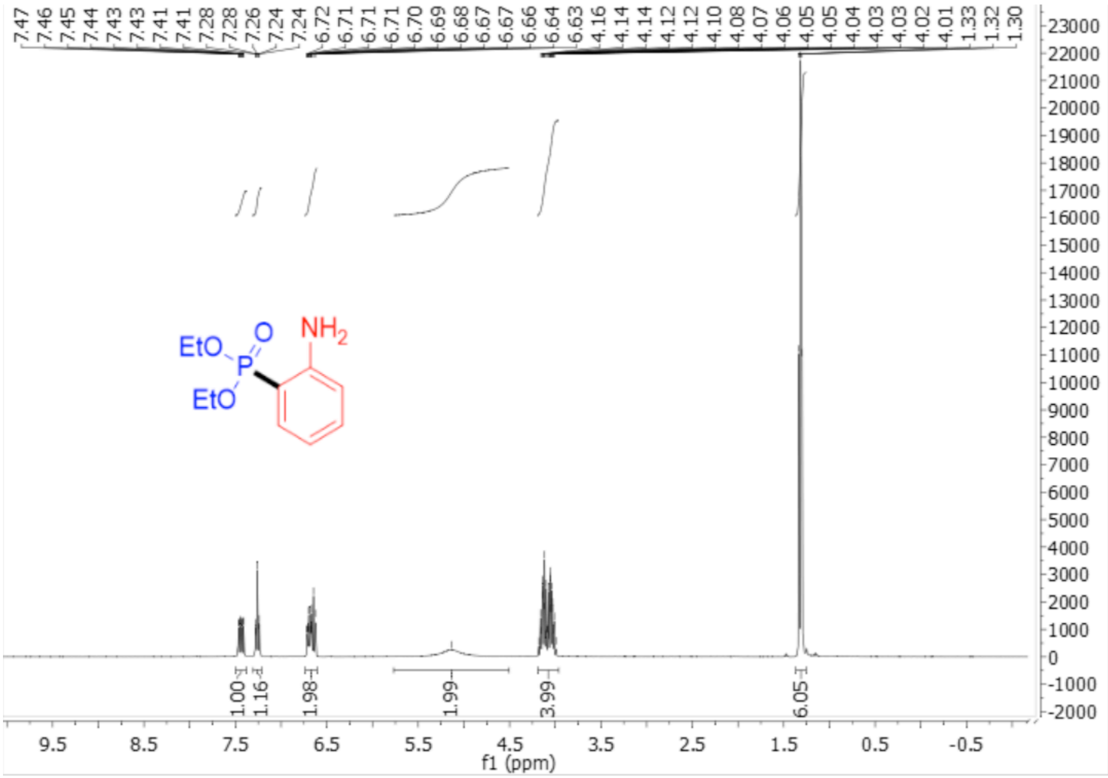
Supplementary Figure S49. ^{1}H NMR (400 MHz, CDCl3) spectrum for 15.



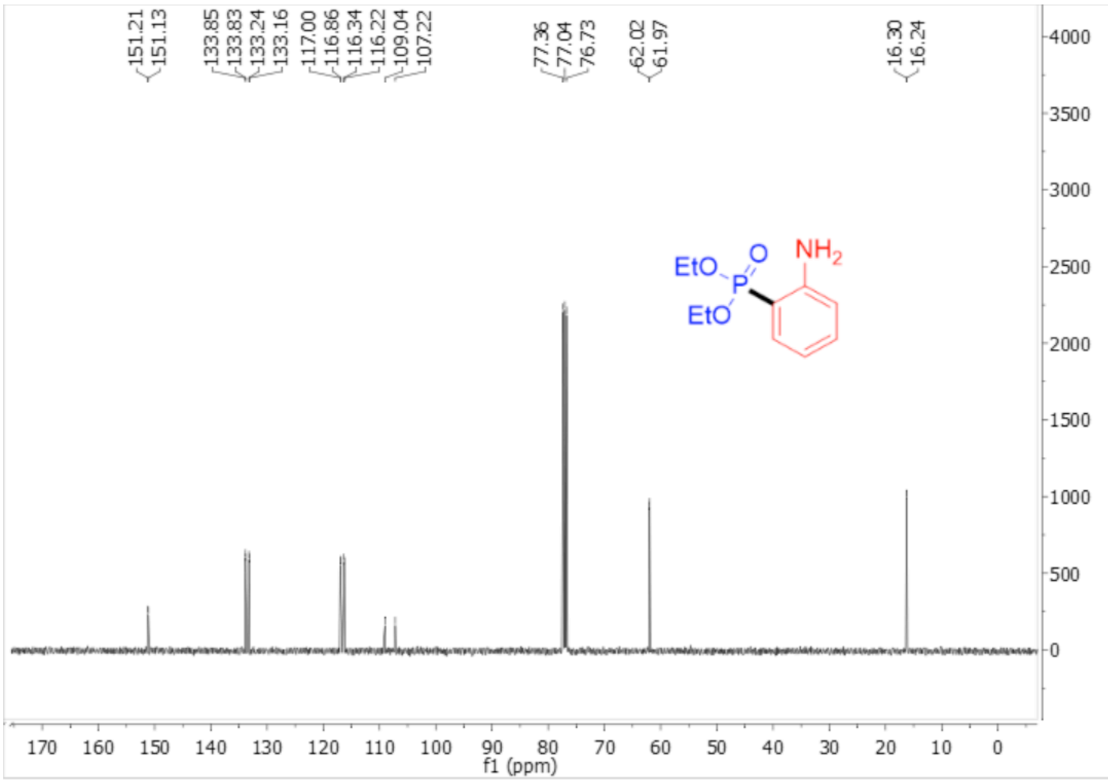
Supplementary Figure S50. ^{13}C NMR (101 MHz, CDCl3) spectrum for 15.



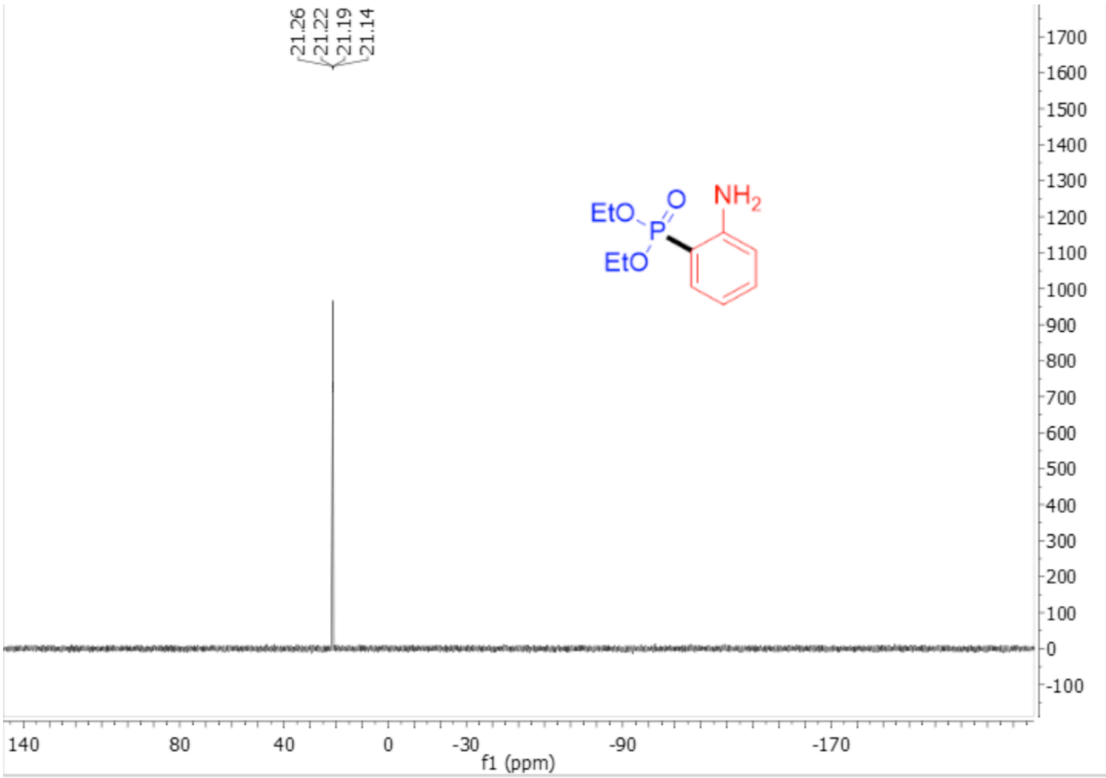
Supplementary Figure S51. ^{31}P NMR (162 MHz, CDCl3) spectrum for 15.



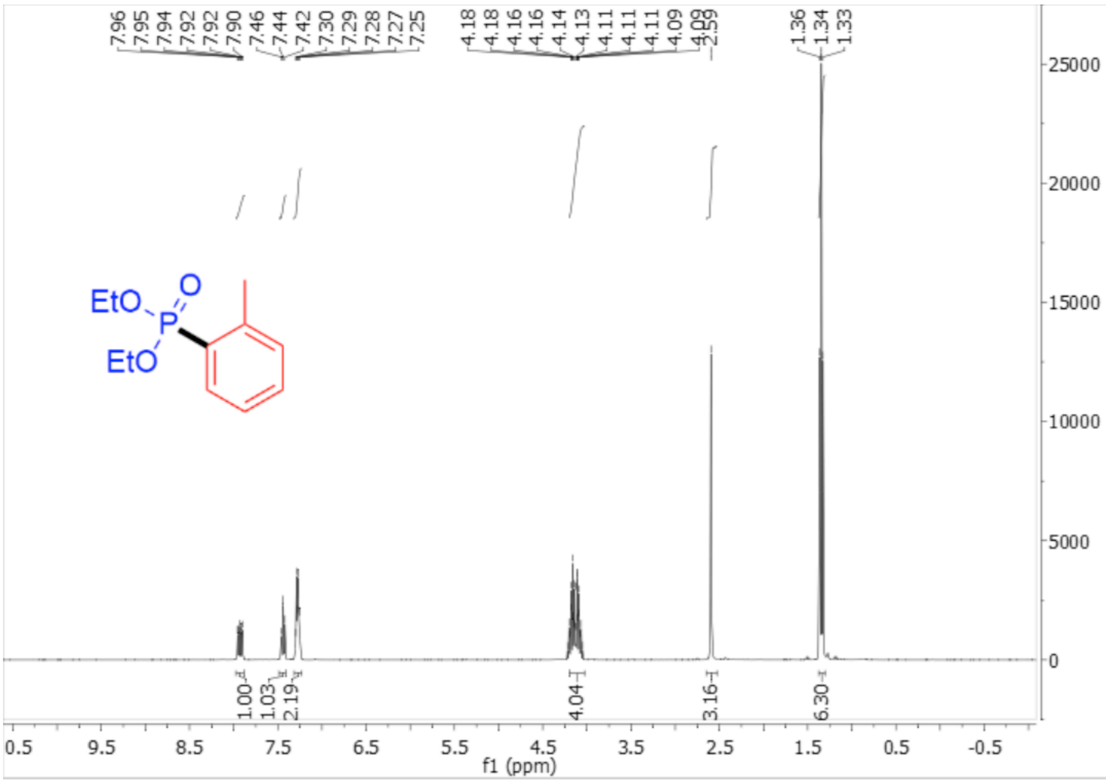
Supplementary Figure S52. **[1]H NMR (400 MHz, $CDCl_3$) spectrum for 16.**



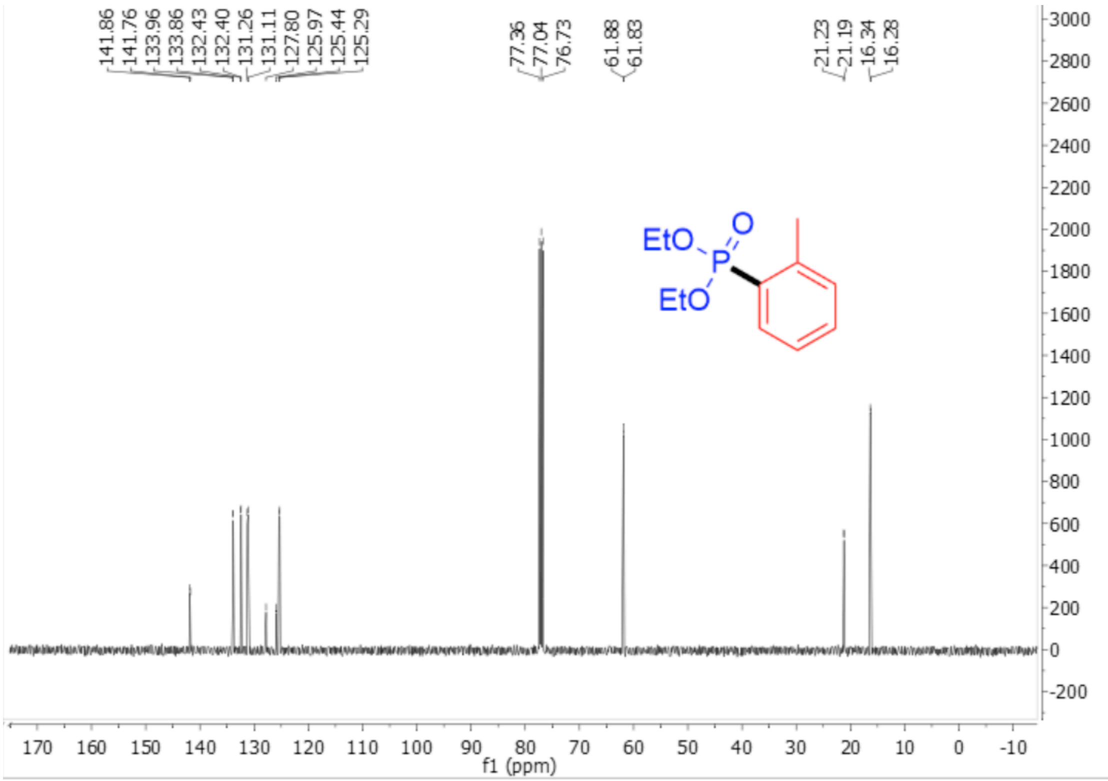
Supplementary Figure S53. **[13]CNMR(101 MHz, $CDCl_3$) spectrum for 16.**



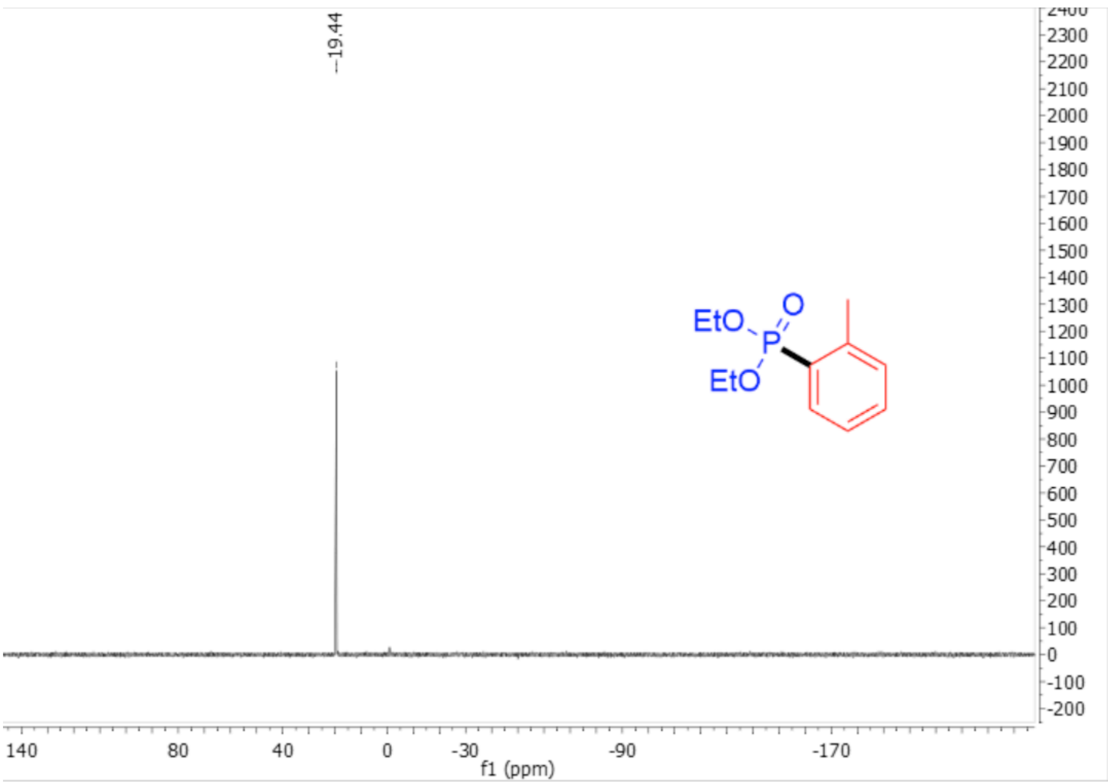
Supplementary Figure S54. [31]P NMR (162 MHz, CDCl3) spectrum for 16.



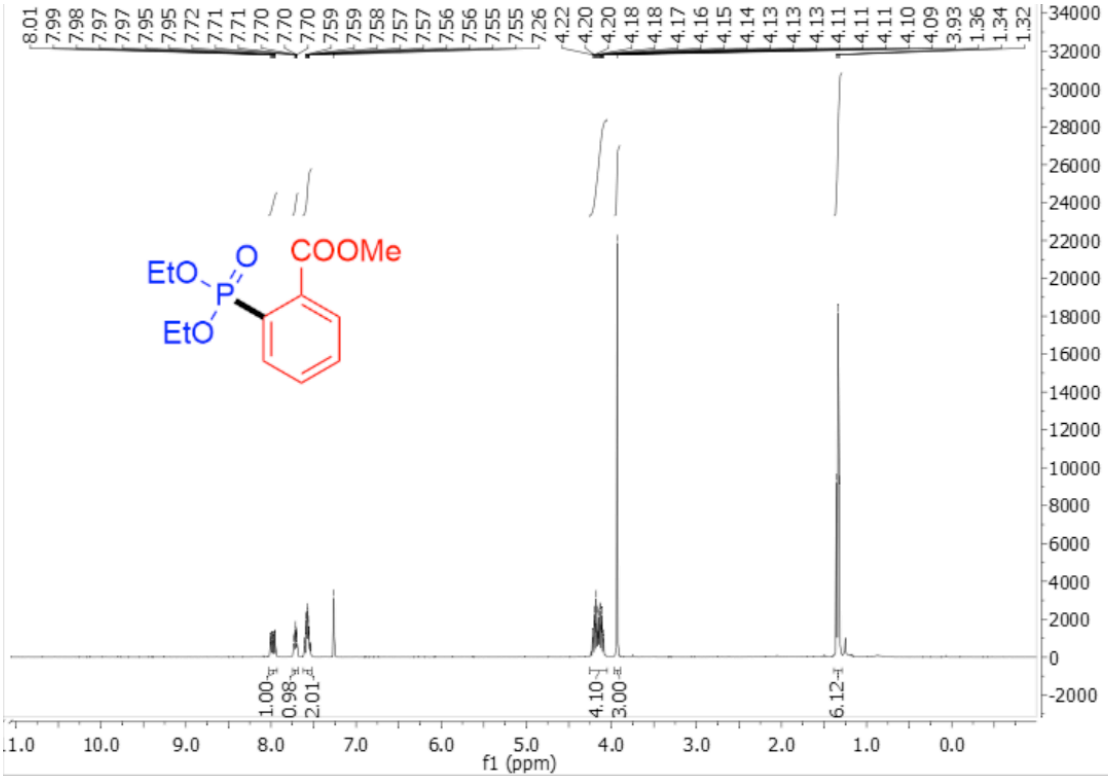
Supplementary Figure S55. [1]H NMR (400 MHz, $CDCl_3$) spectrum for 17.



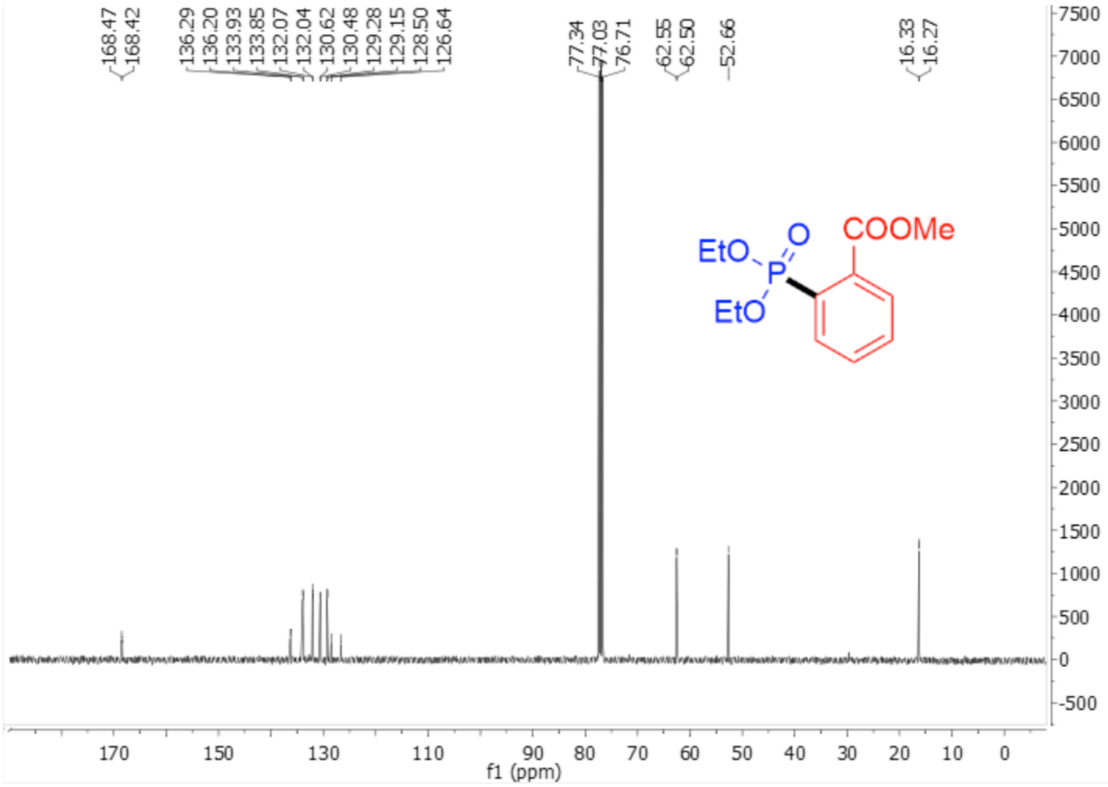
Supplementary Figure S56. ^{13}**CNMR(101 MHz,** $CDCl_3$**) spectrum for 17.**



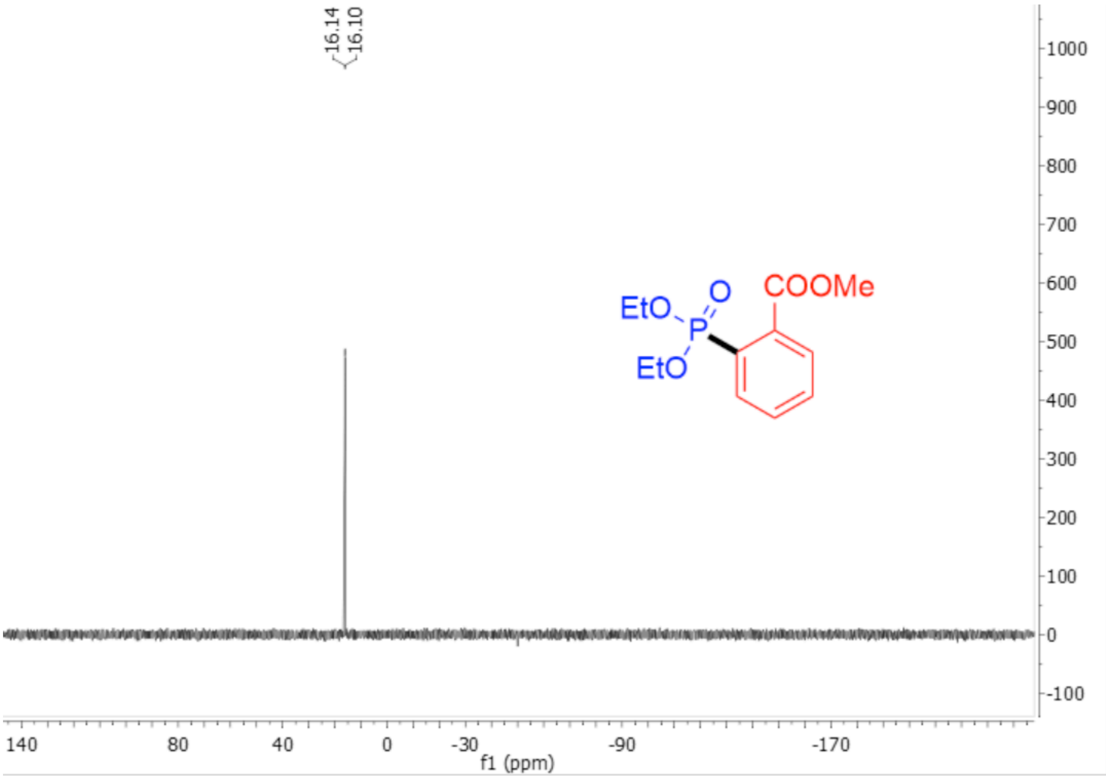
Supplementary Figure S57. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 17.**



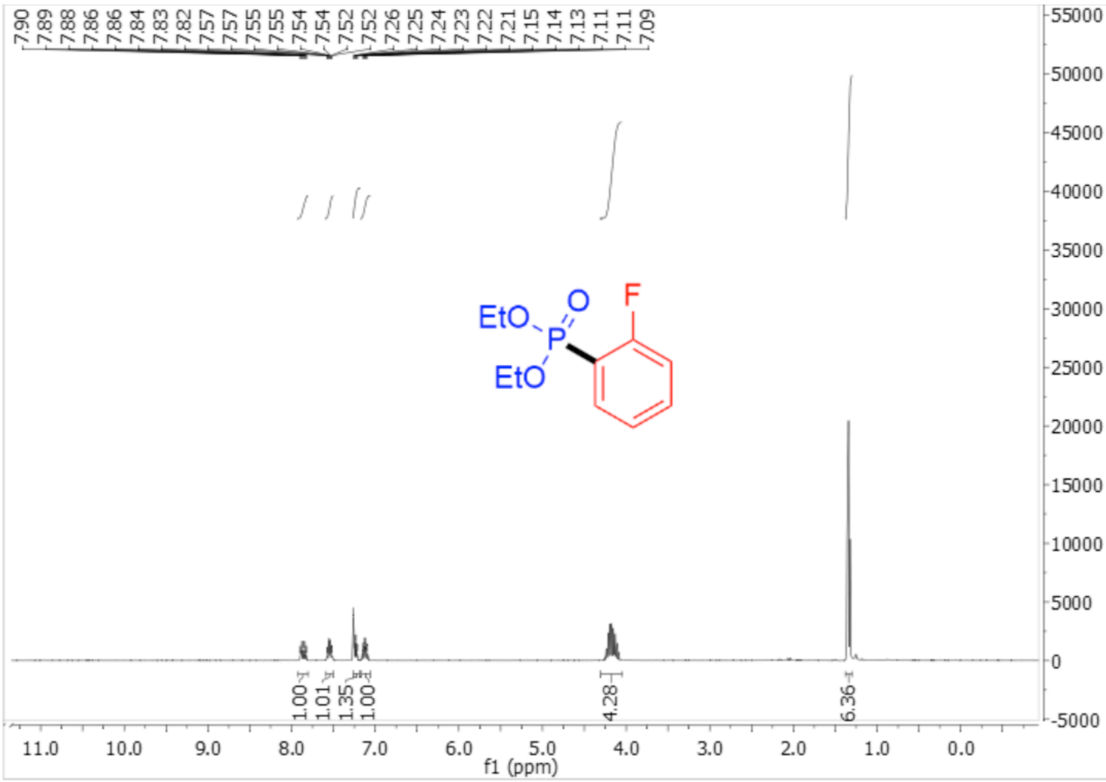
Supplementary Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 18.



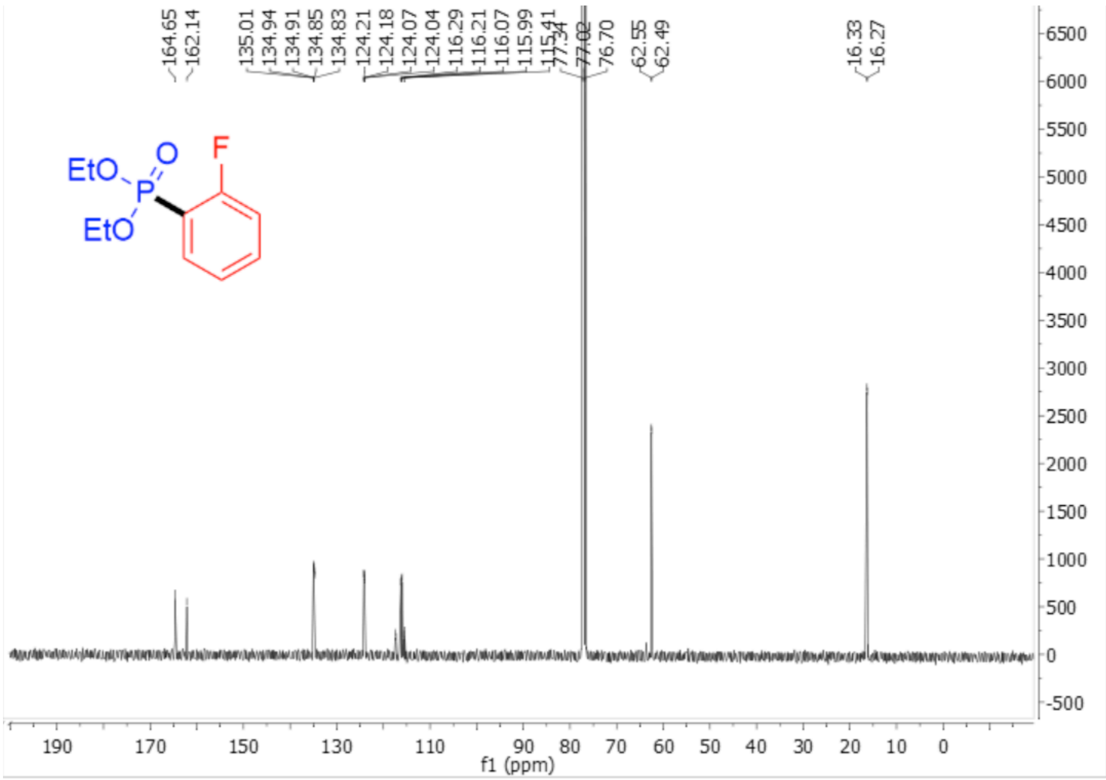
Supplementary Figure S59. ^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 18.



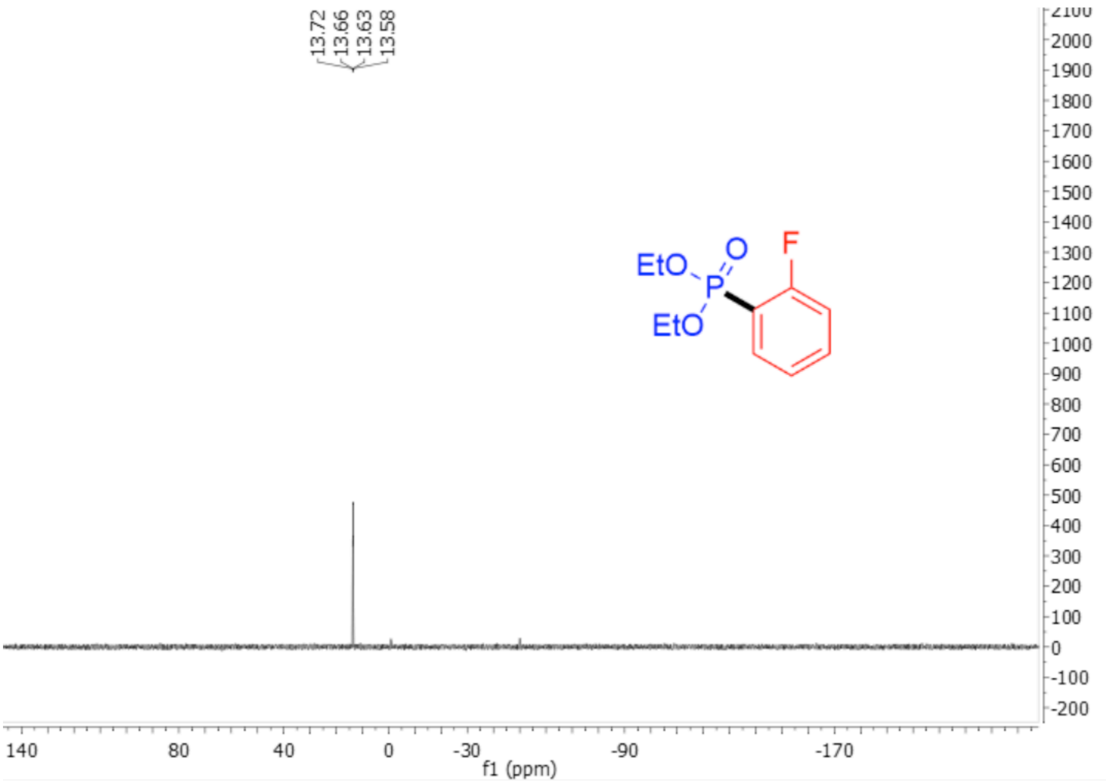
Supplementary Figure S60. ^{31}P NMR (162 MHz, CDCl3) spectrum for 18.



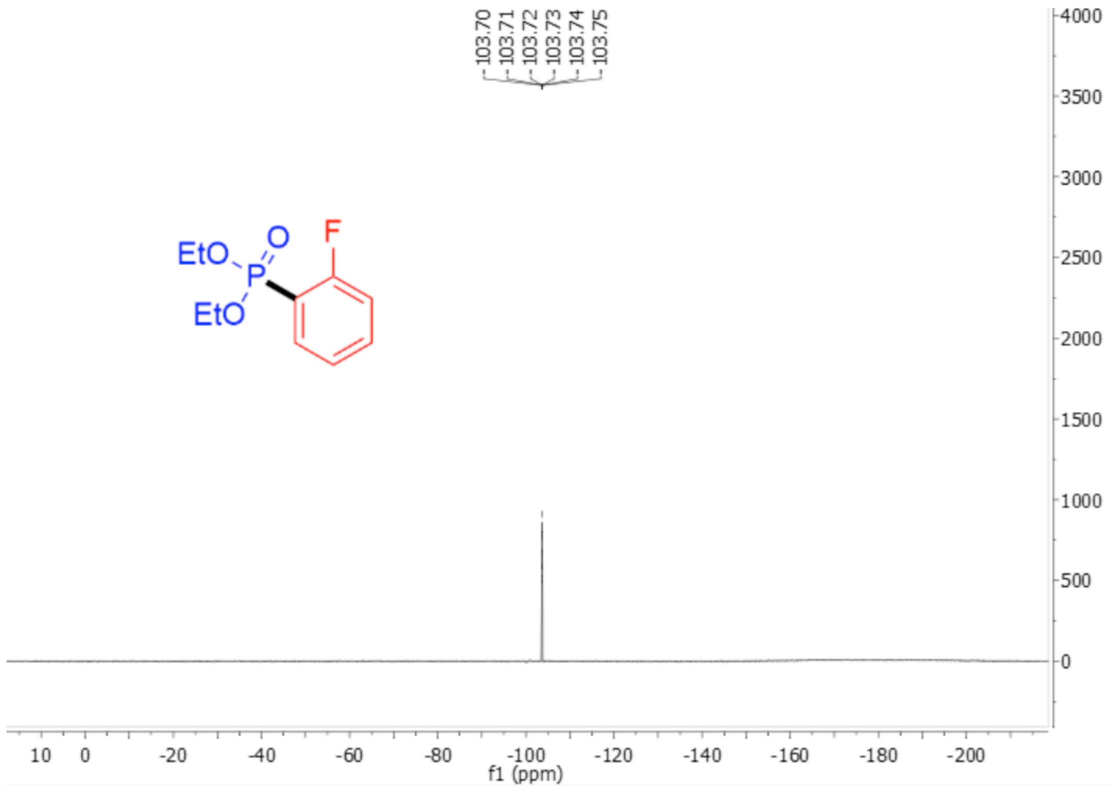
Supplementary Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 19.



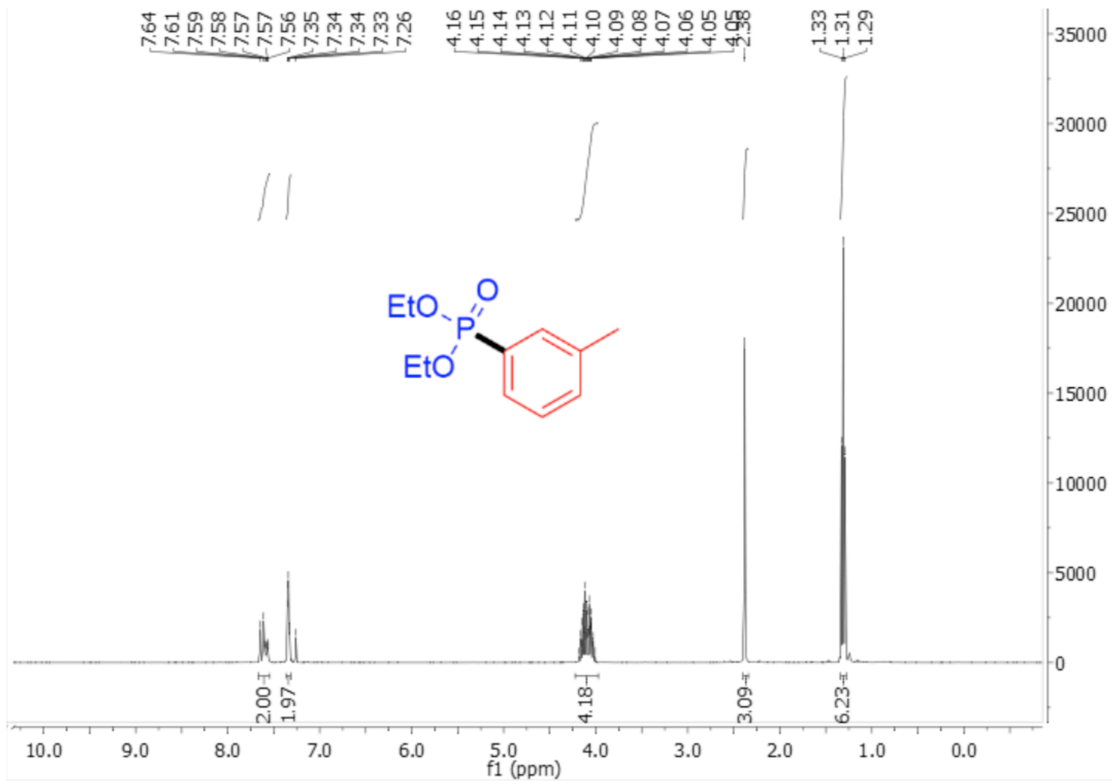
Supplementary Figure S62. **^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 19.**



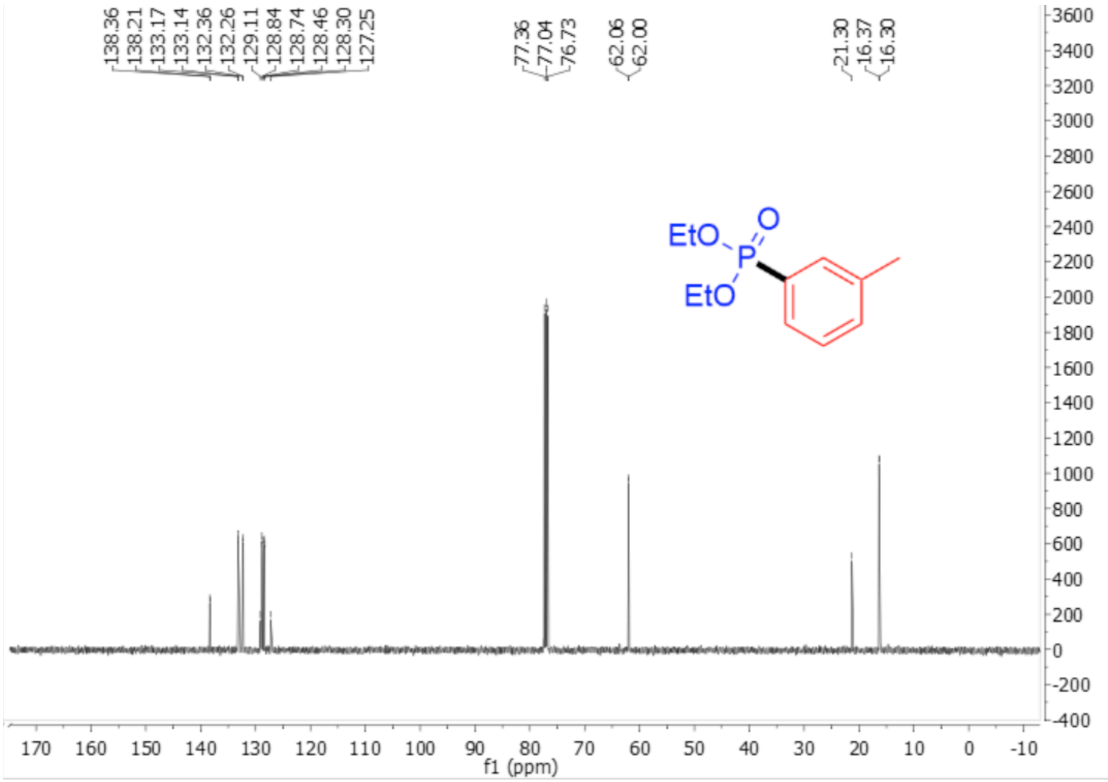
Supplementary Figure S63. **^{31}P NMR (162 MHz, CDCl3) spectrum for 19.**



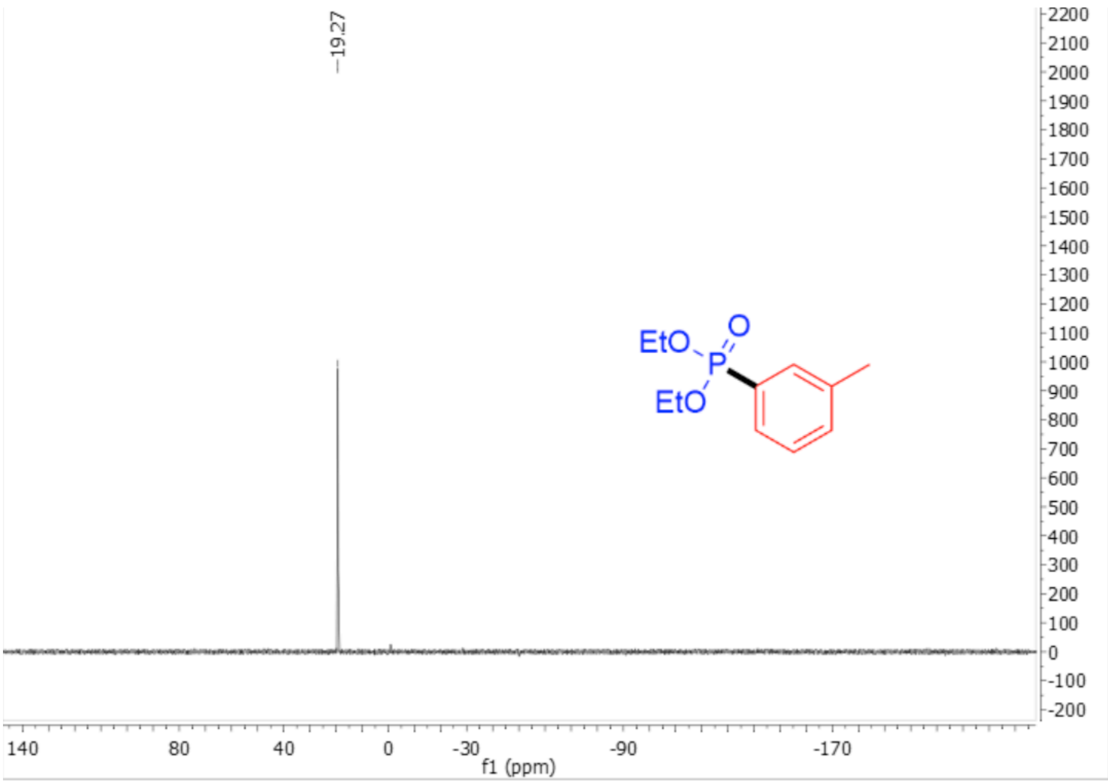
Supplementary Figure S64. [19]F NMR (377 MHz, CDCl3) spectrum for 19.



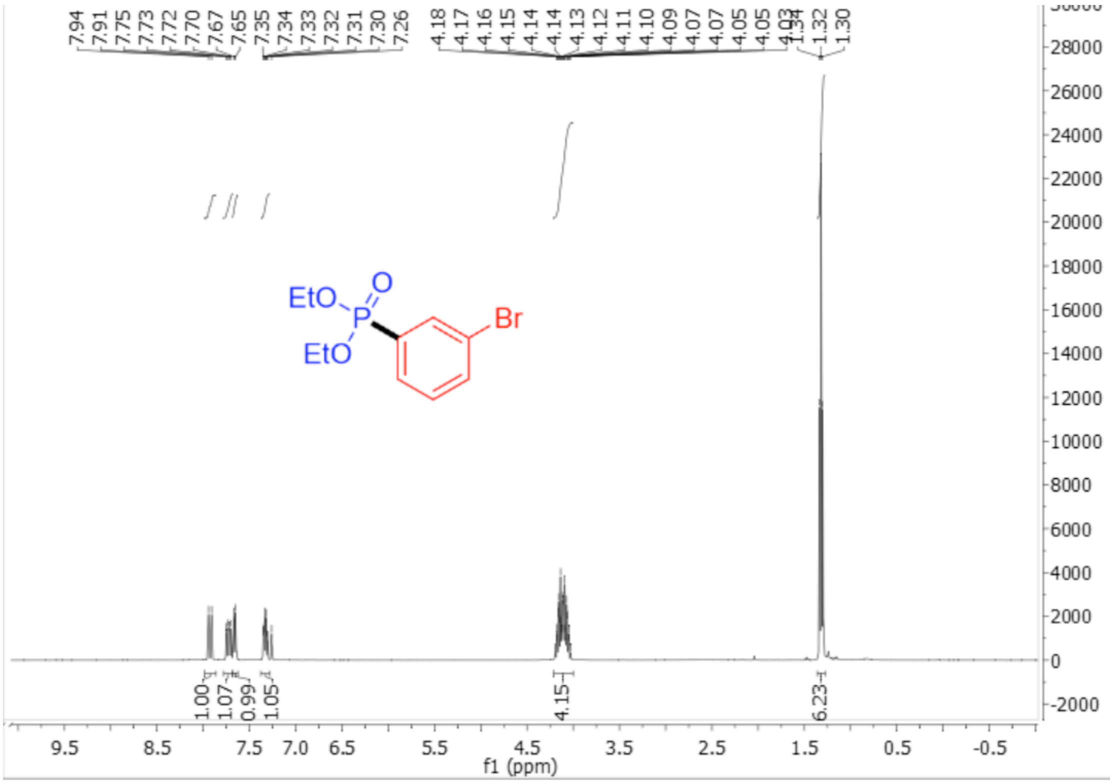
Supplementary Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 20.



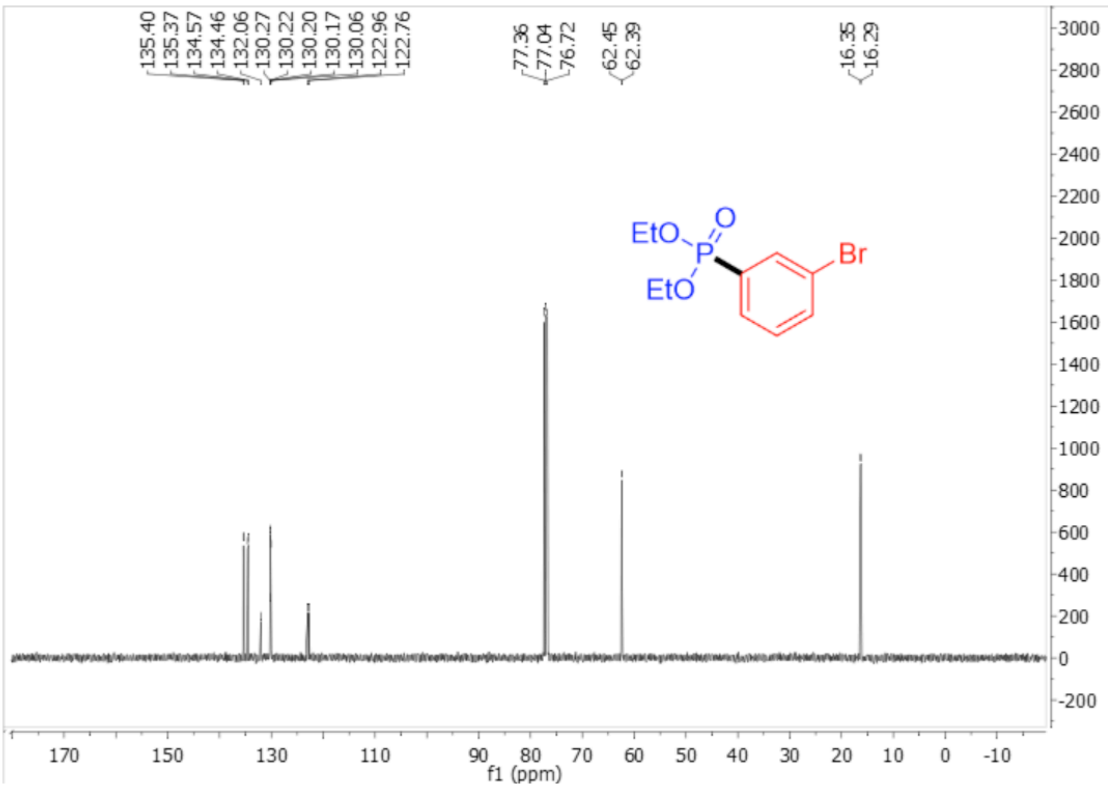
Supplementary Figure S66. **^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 20.**



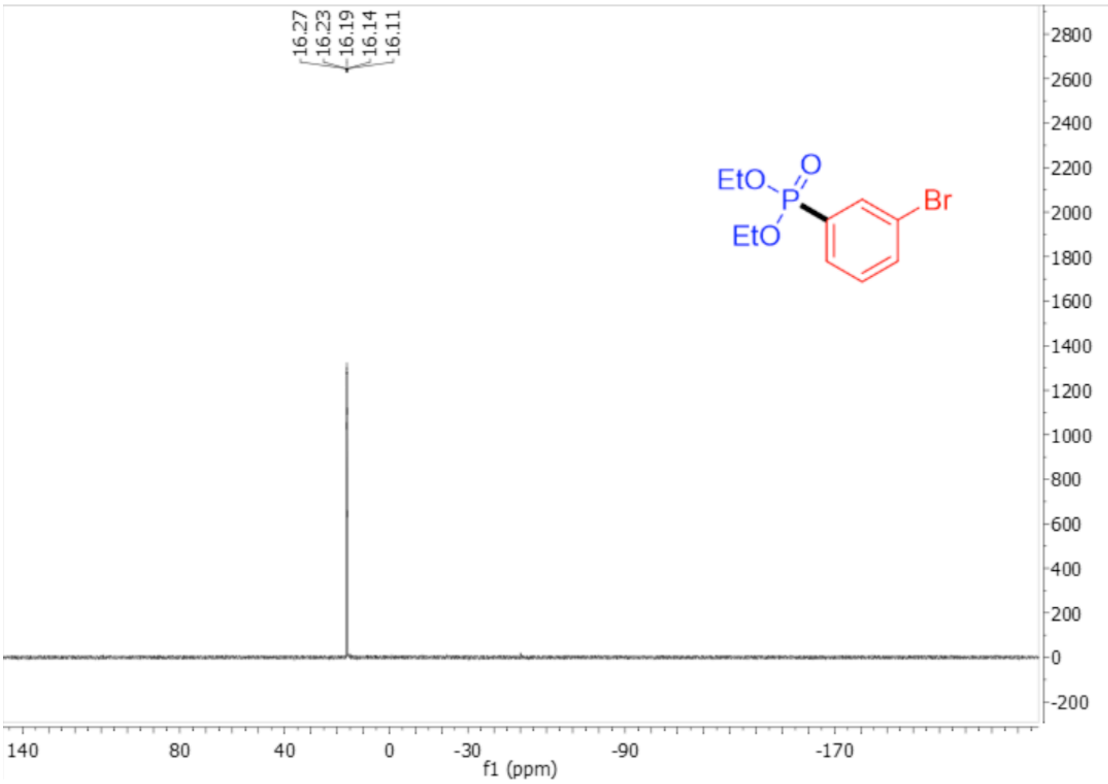
Supplementary Figure S67. **^{31}P NMR (162 MHz, CDCl3) spectrum for 20.**



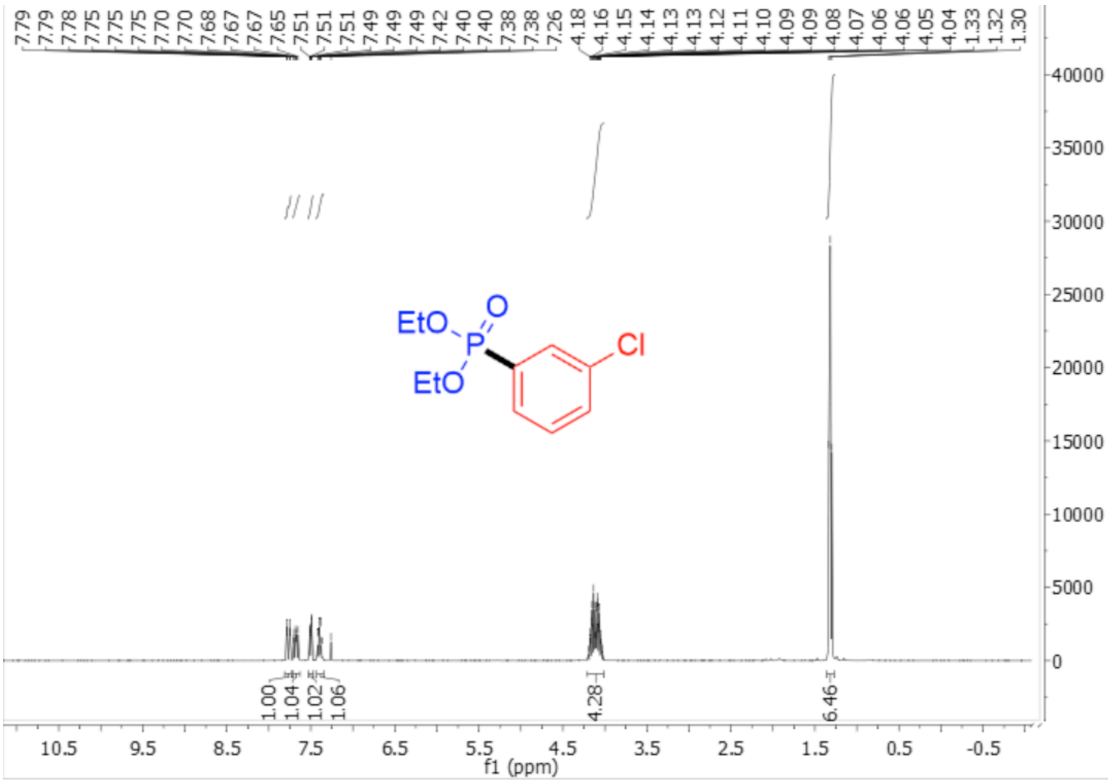
Supplementary Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 21.



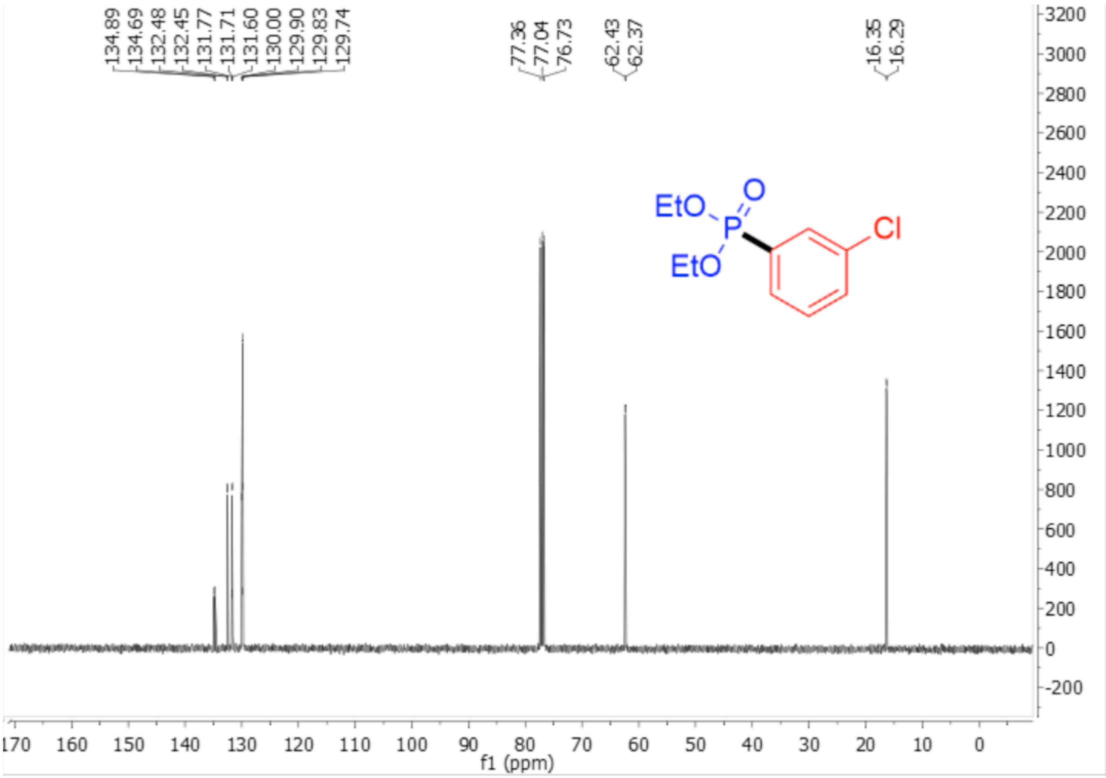
Supplementary Figure S69. ^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 21.



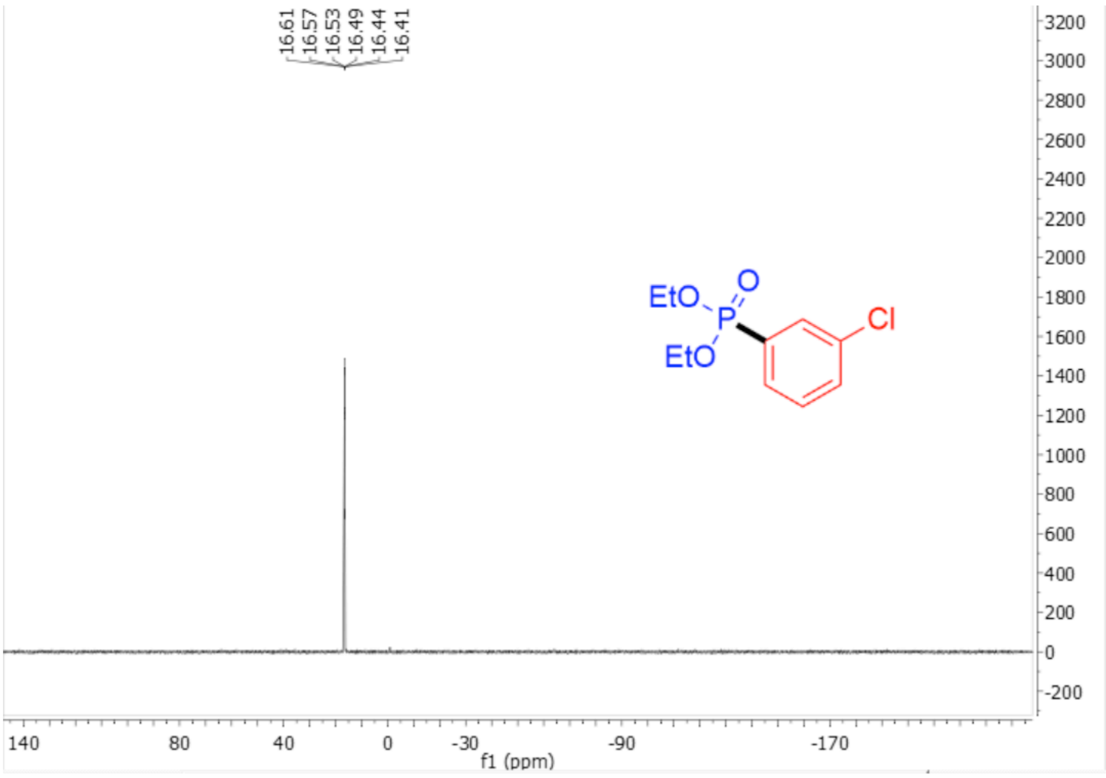
Supplementary Figure S70. [31]P NMR (162 MHz, CDCl3) spectrum for 21.



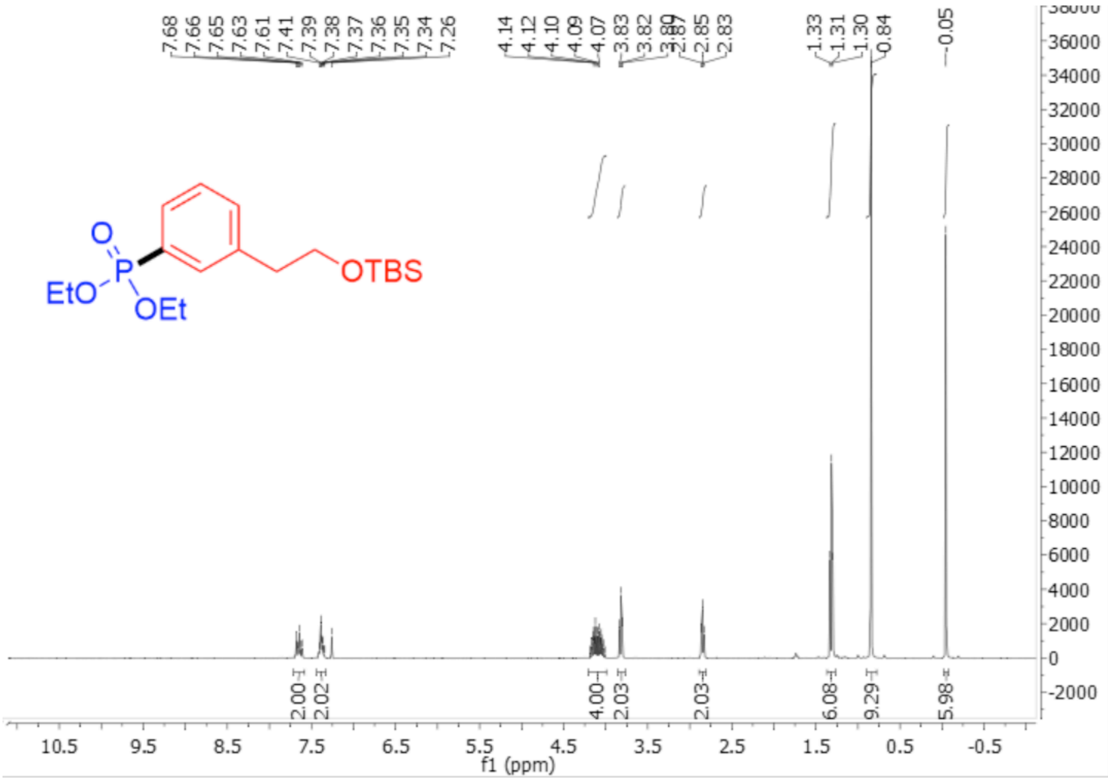
Supplementary Figure S71. [1]H NMR (400 MHz, $CDCl_3$) spectrum for 22.



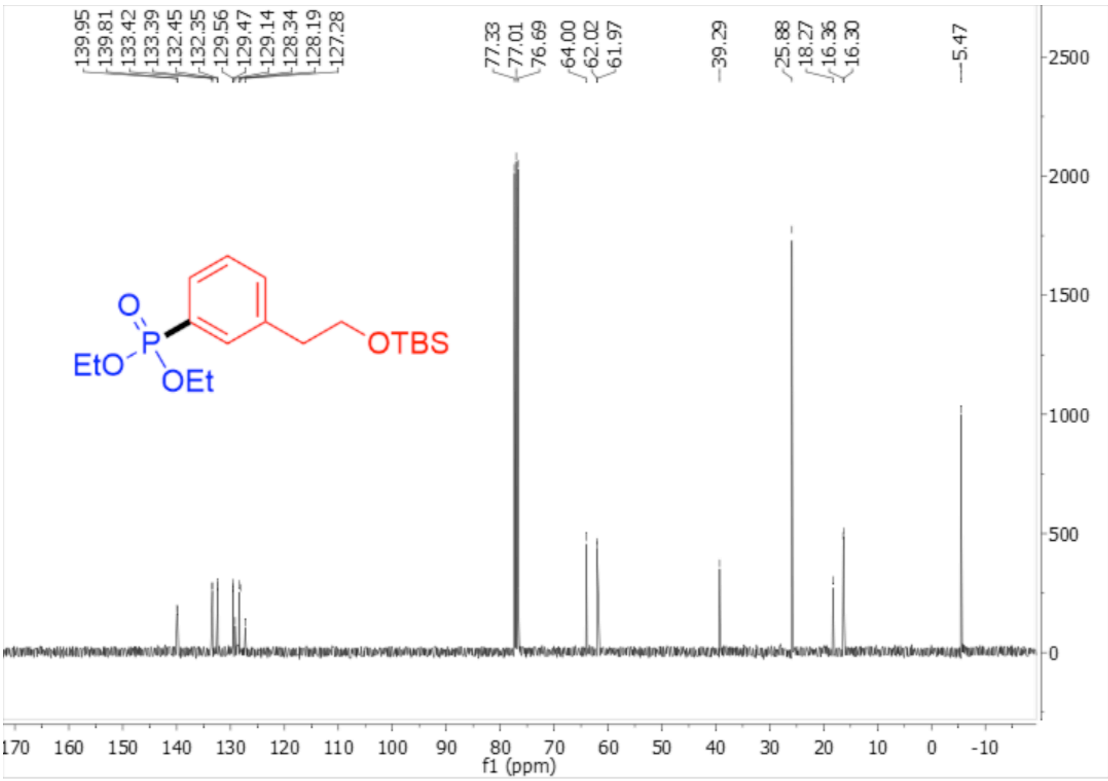
Supplementary Figure S72. ^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 22.



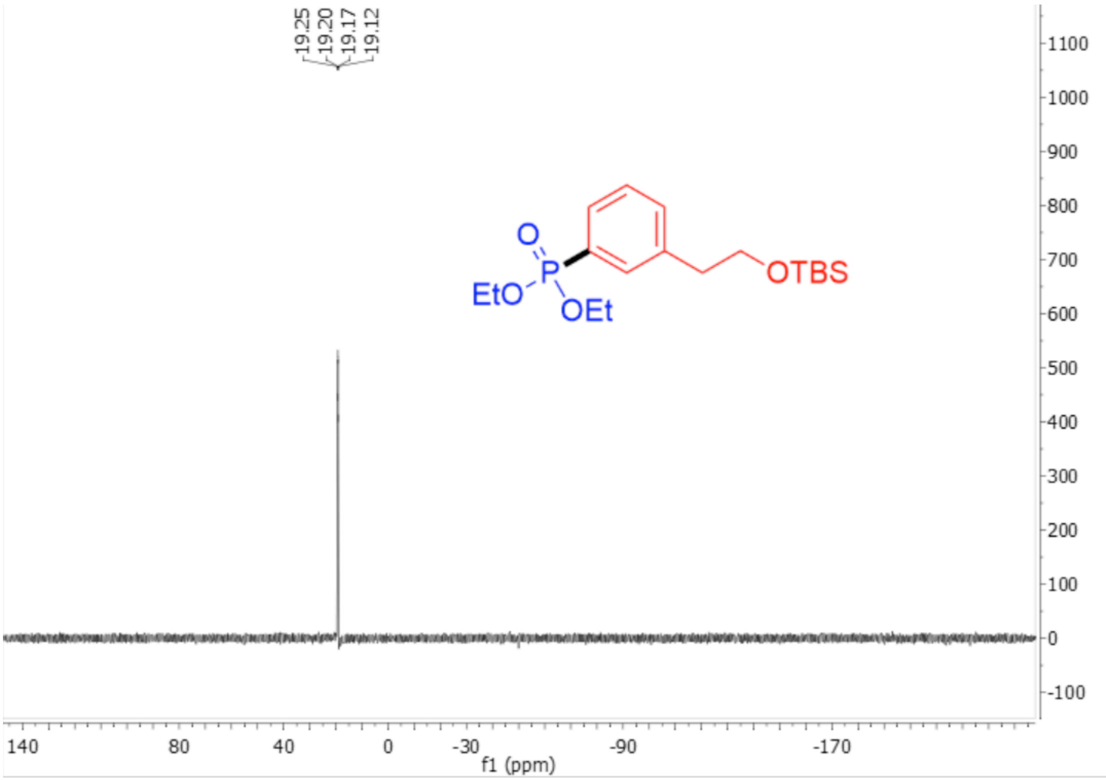
Supplementary Figure S73. ^{31}P NMR (162 MHz, CDCl3) spectrum for 22.



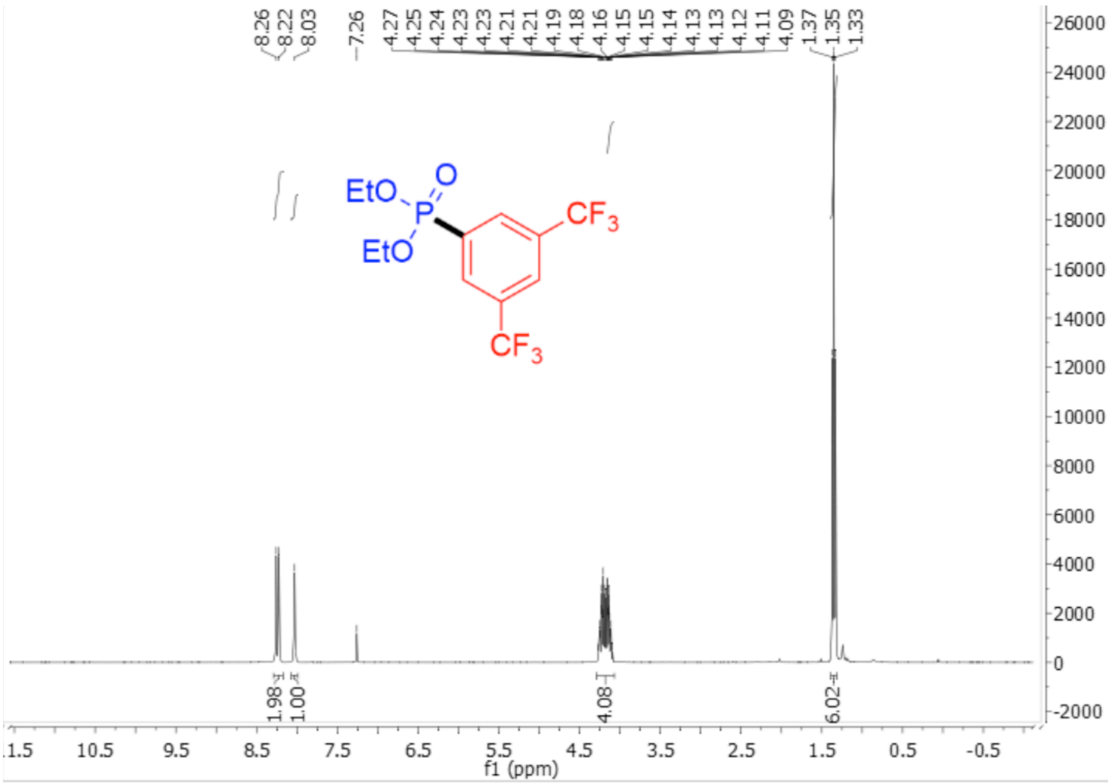
Supplementary Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 24.



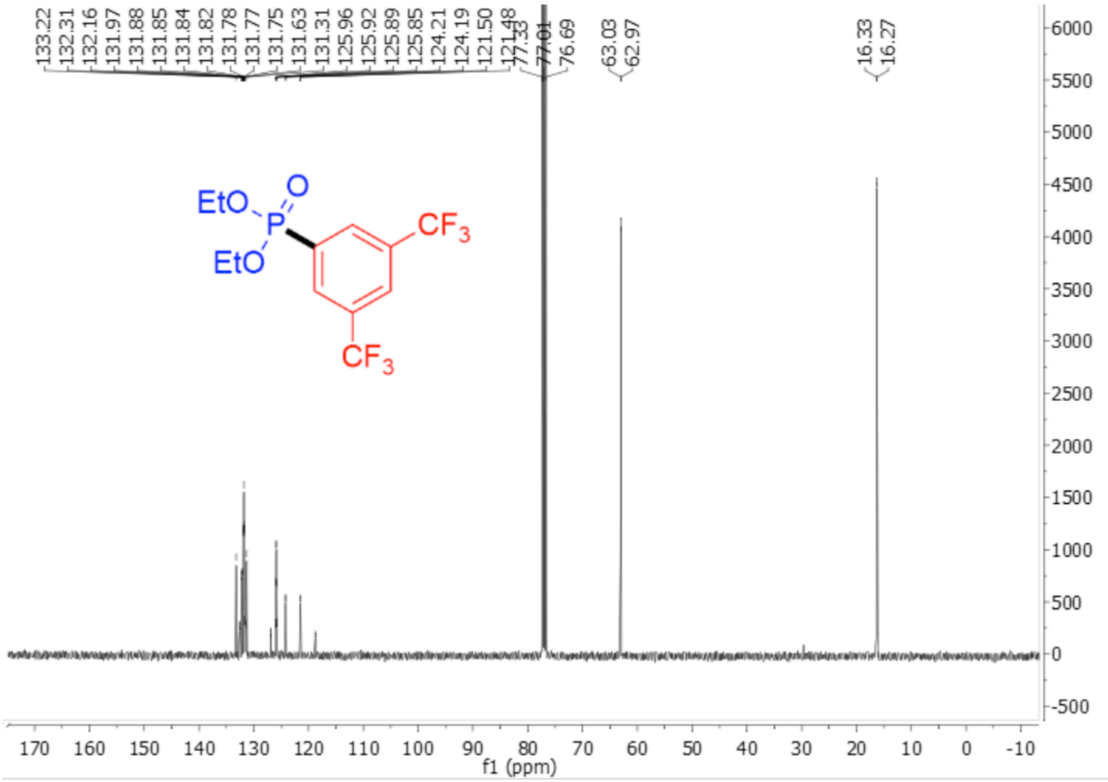
Supplementary Figure S75. ^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 24.



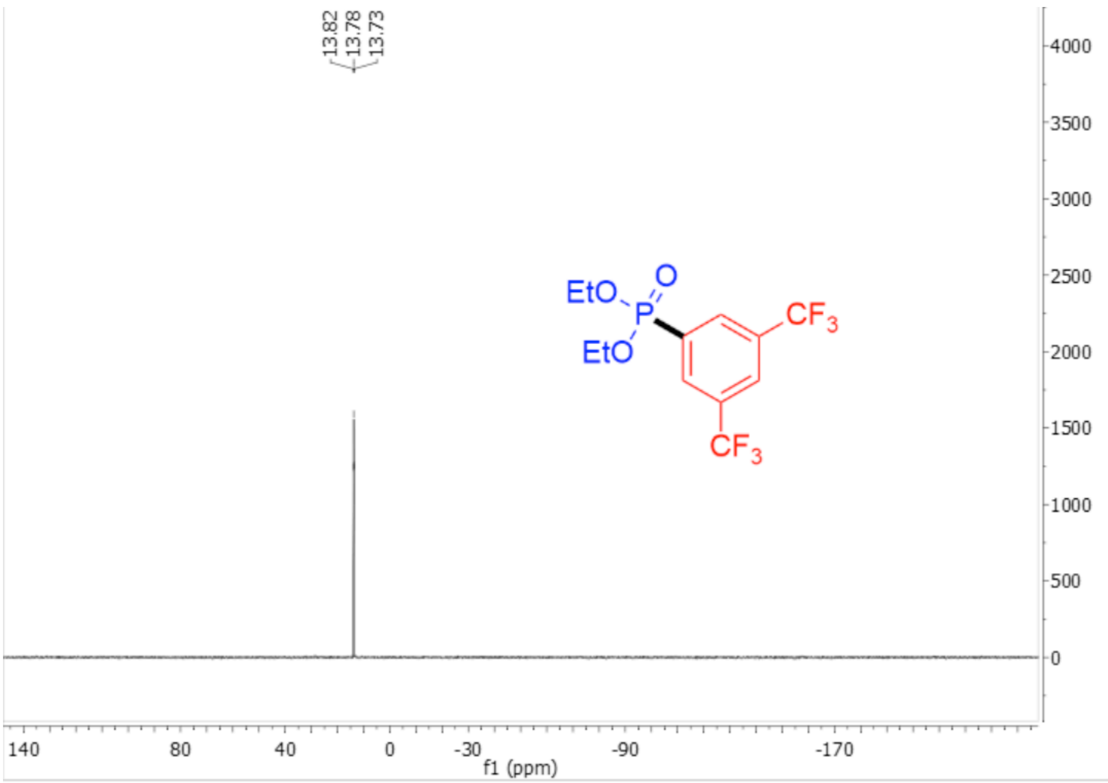
Supplementary Figure S76. ^{31}P NMR (162 MHz, CDCl3) spectrum for 24.



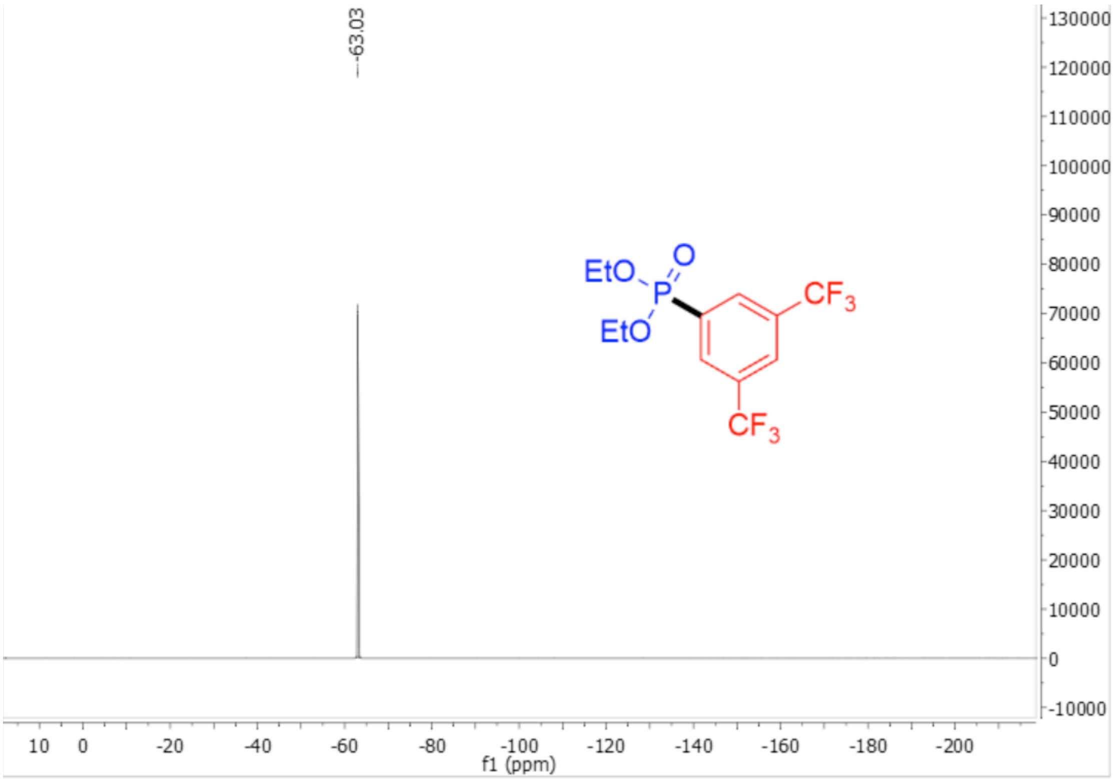
Supplementary Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 25.



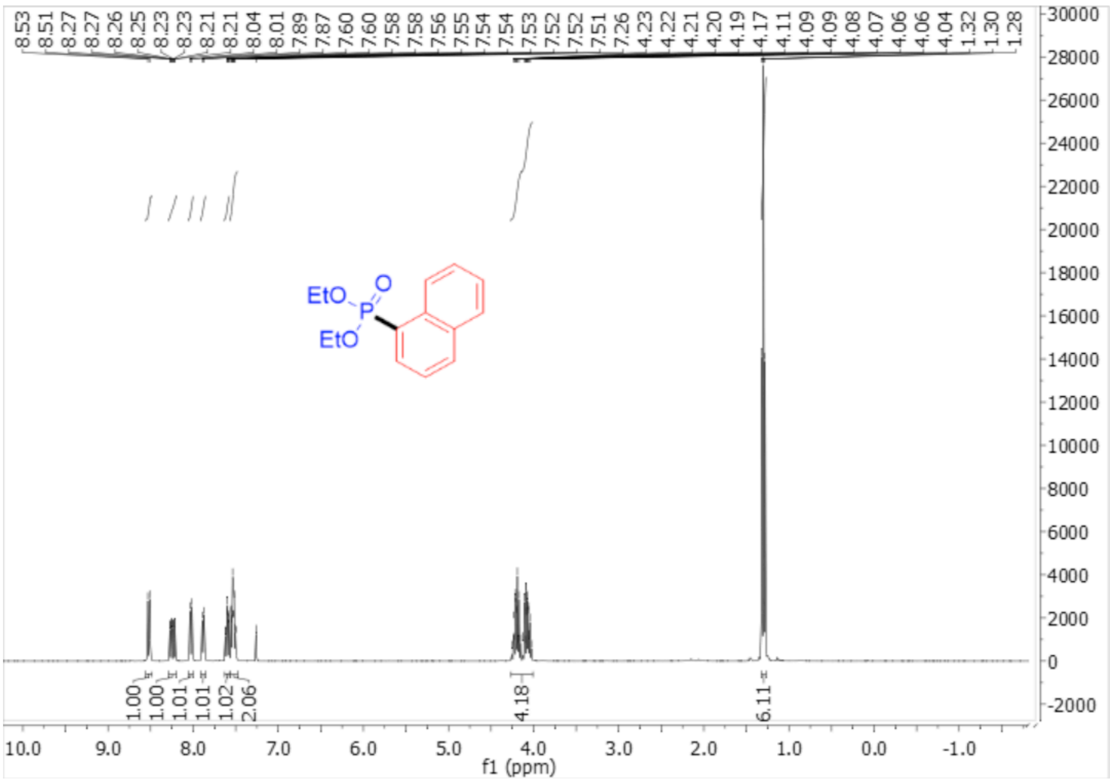
Supplementary Figure S78. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 25.**



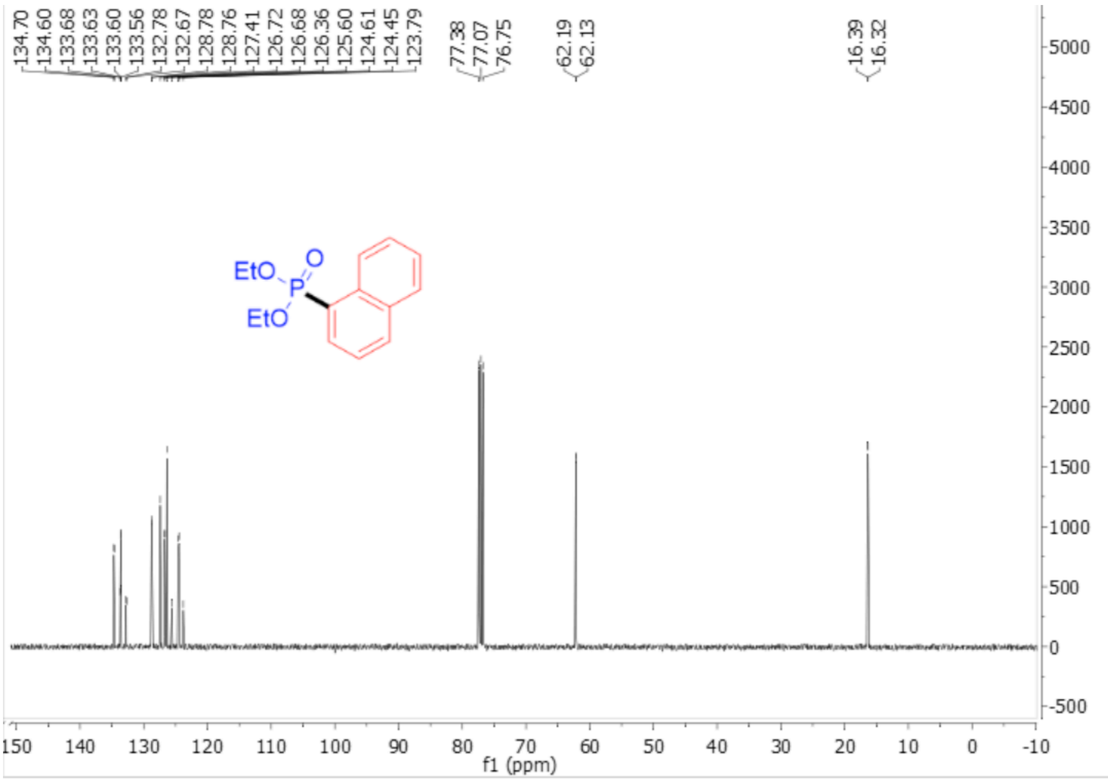
Supplementary Figure S79. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 25.**



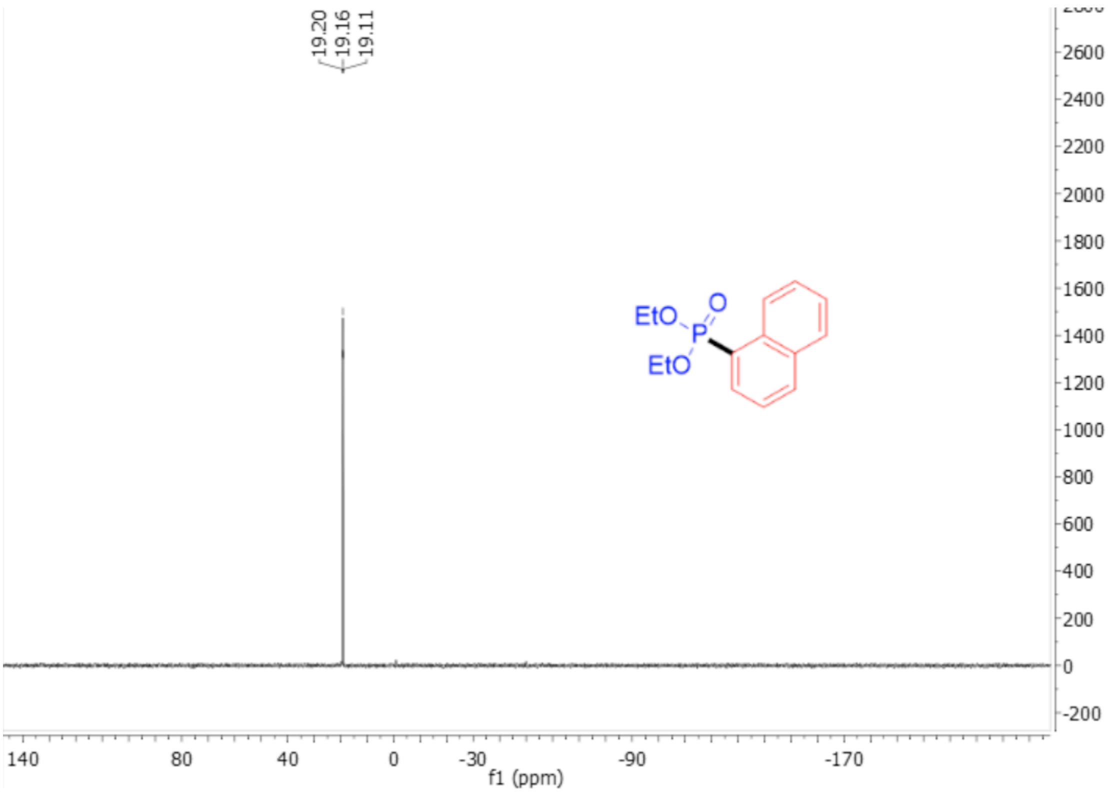
Supplementary Figure S80. ^{19}F NMR (377 MHz, CDCl3) spectrum for 25.



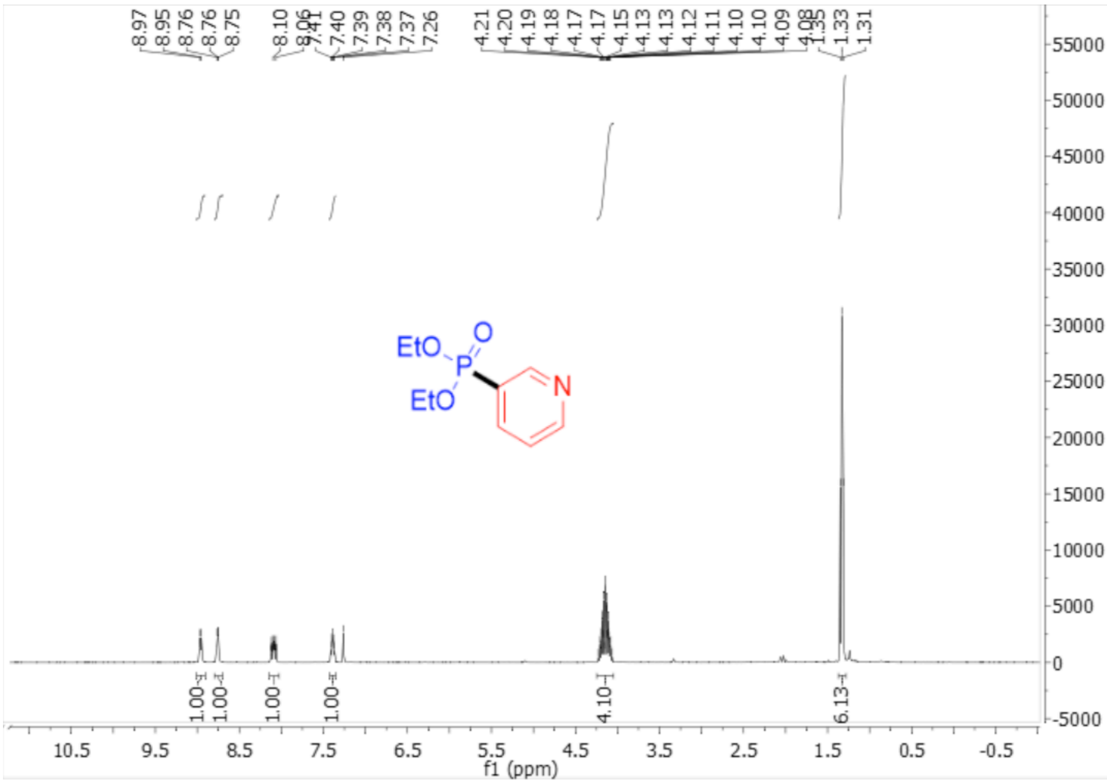
Supplementary Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 26.



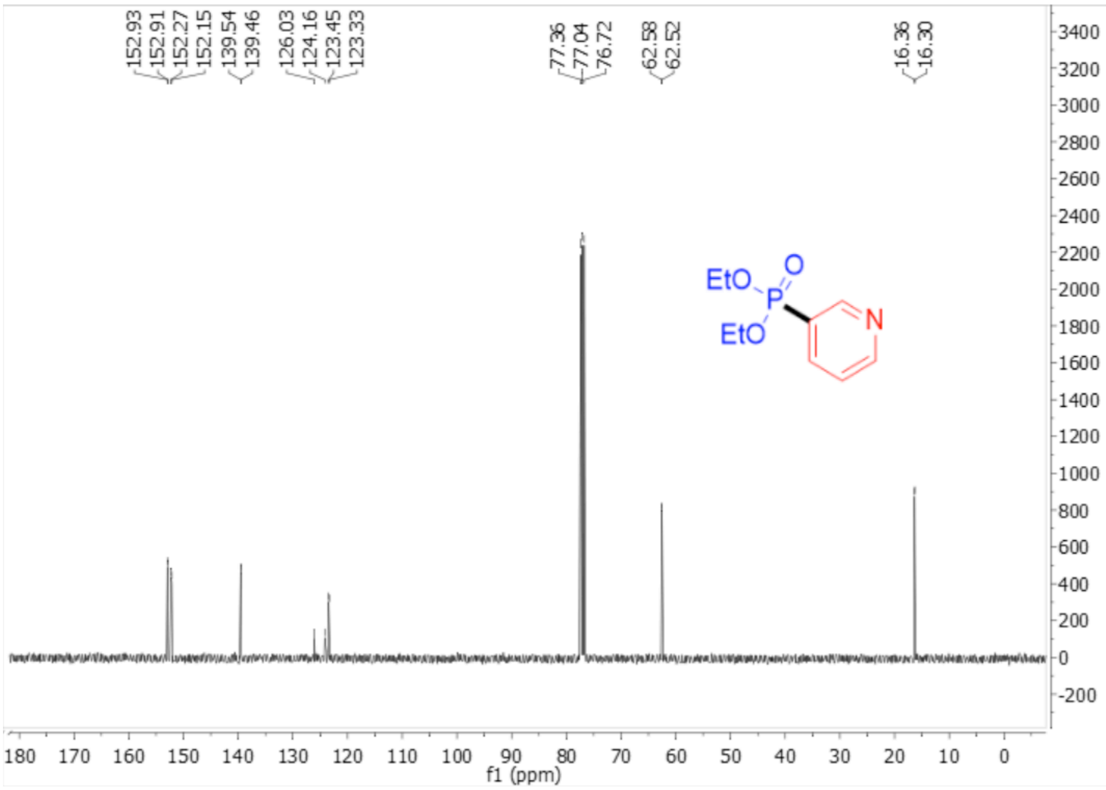
Supplementary Figure S82. **[13]CNMR(101 MHz, $CDCl_3$) spectrum for 26.**



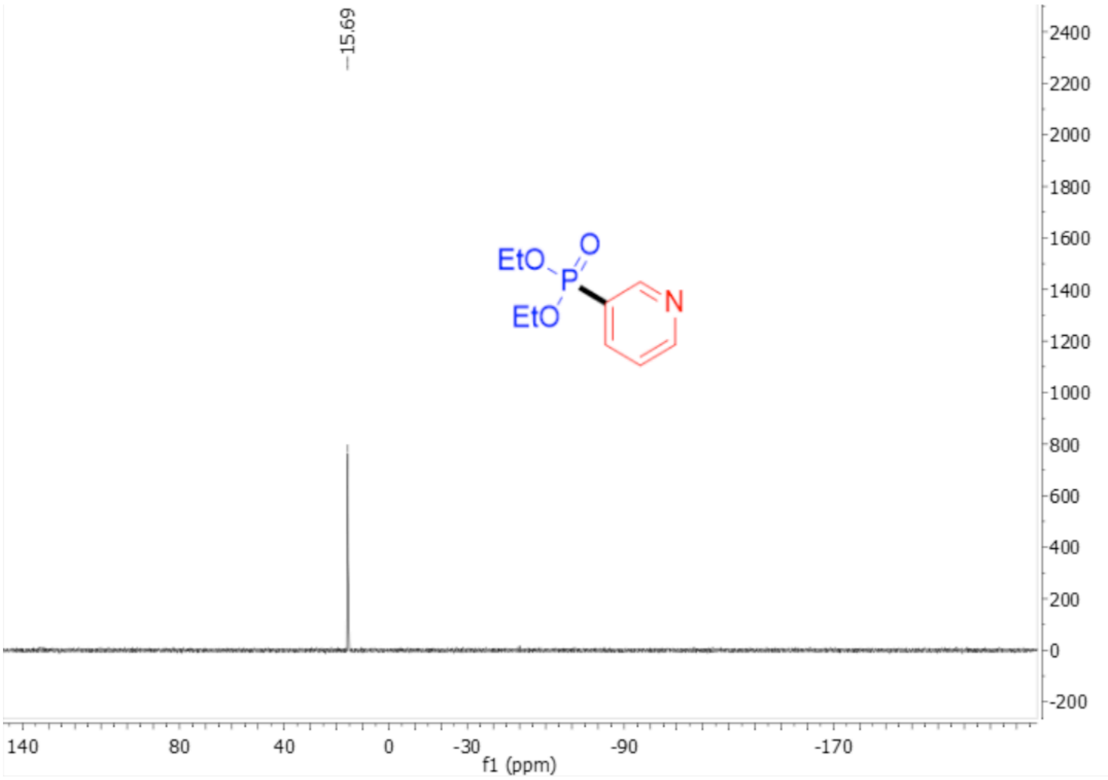
Supplementary Figure S83. **[31]P NMR (162 MHz, CDCl3) spectrum for 26.**



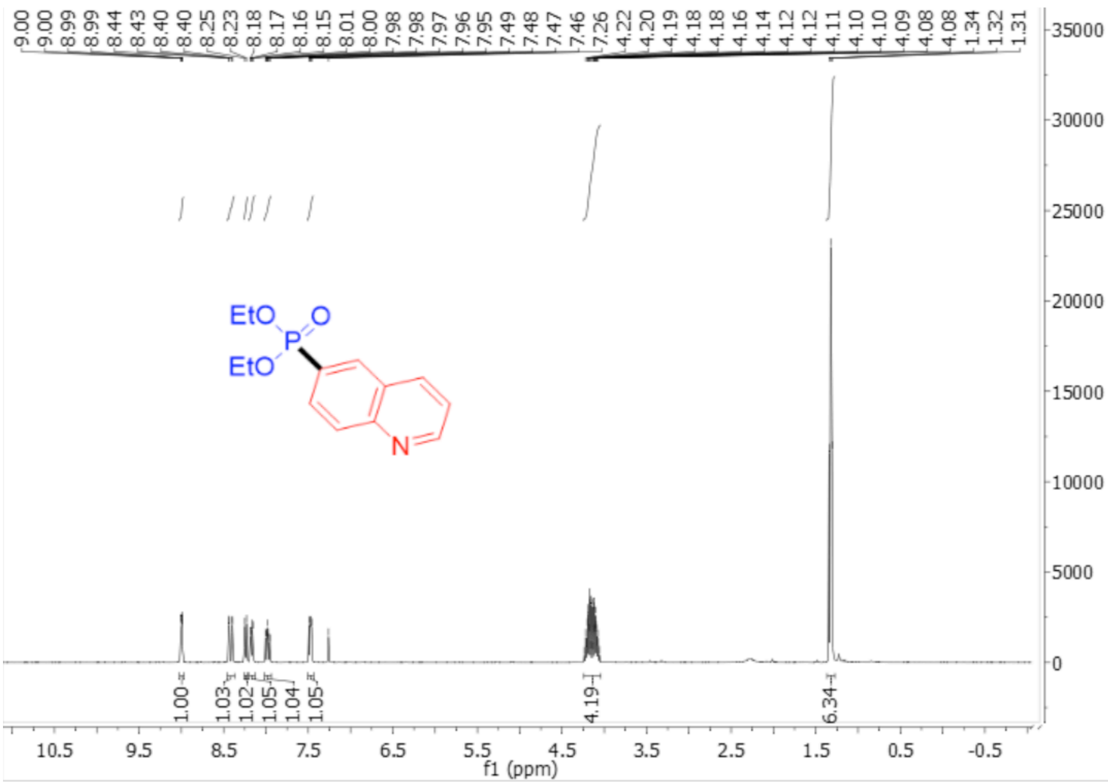
Supplementary Figure S84. **^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 27.**



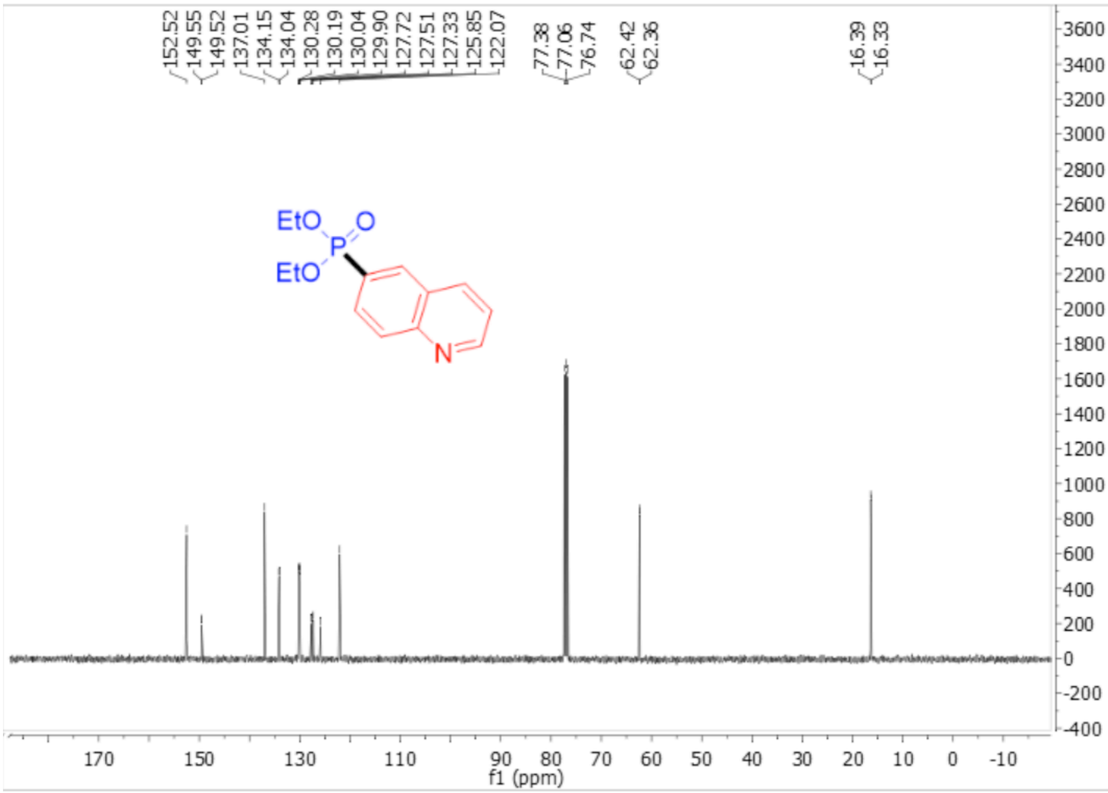
Supplementary Figure S85. **^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 27.**



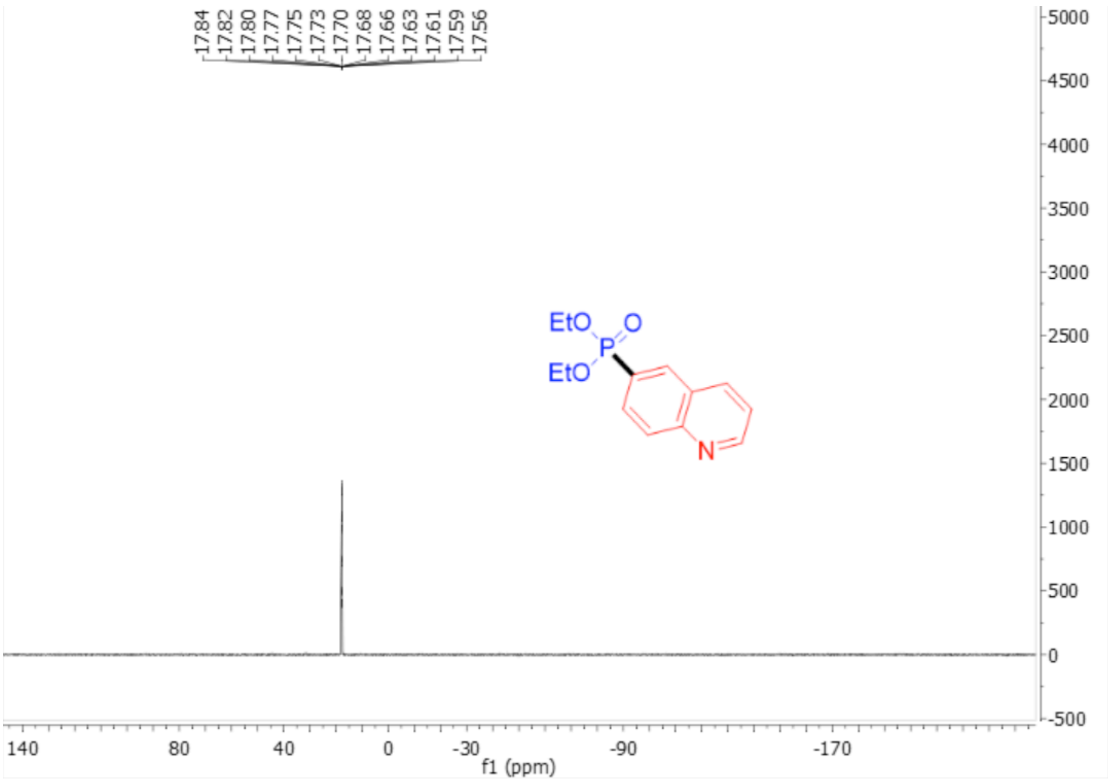
Supplementary Figure S86. ^{31}P NMR (162 MHz, CDCl3) spectrum for 27.



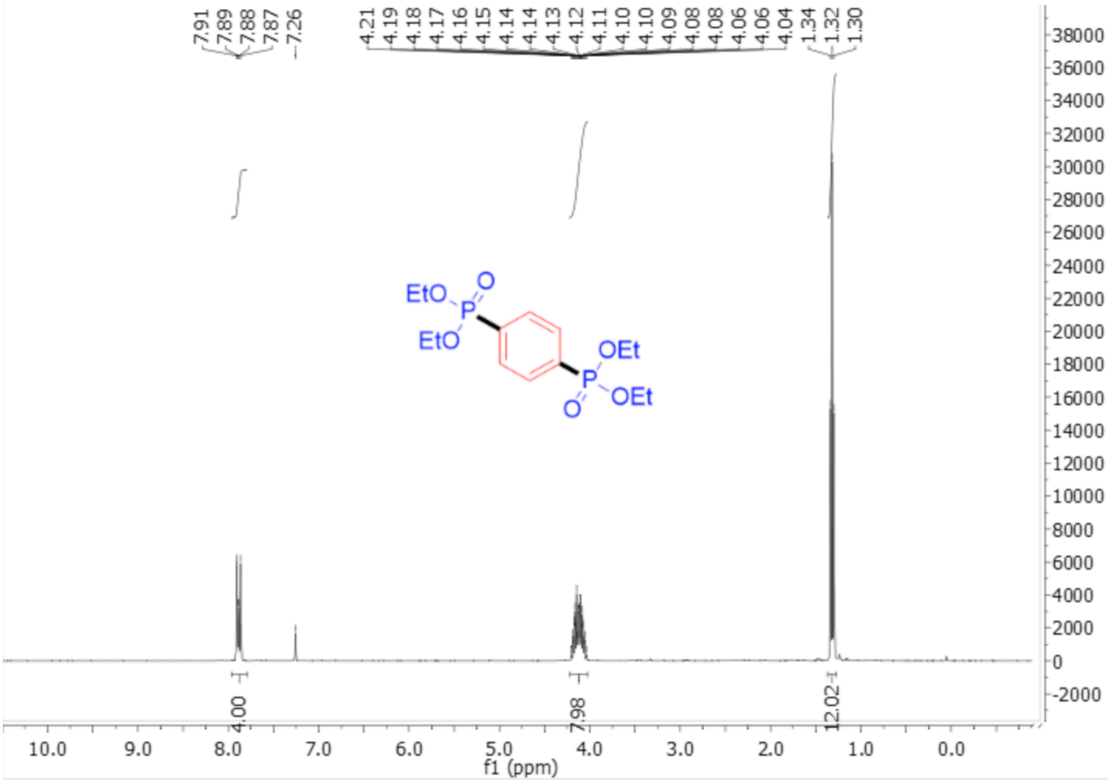
Supplementary Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 28.



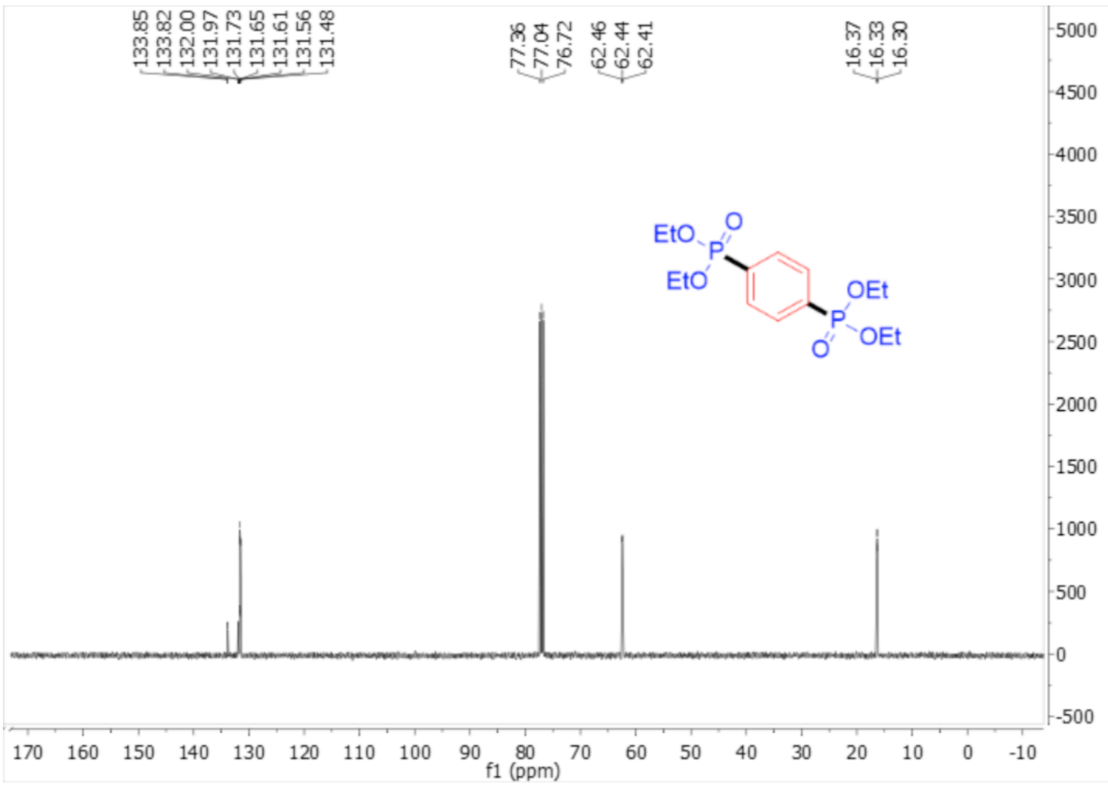
Supplementary Figure S88. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 28.**



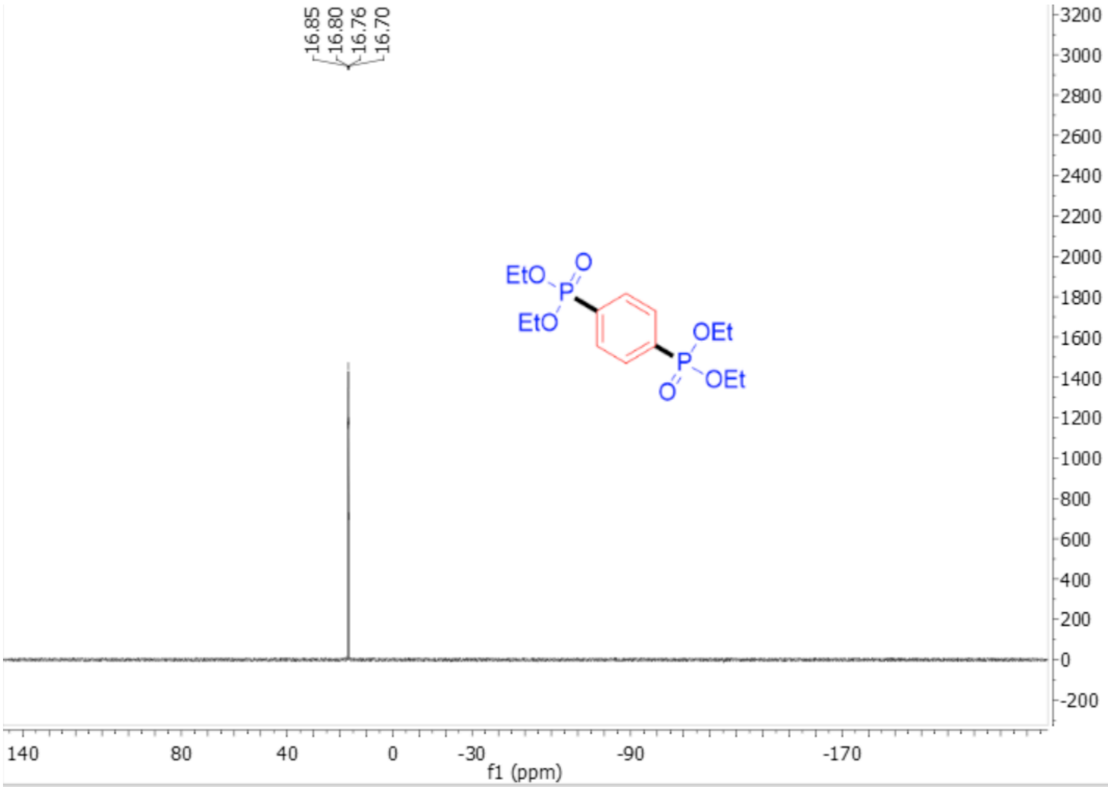
Supplementary Figure S89. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 28.**



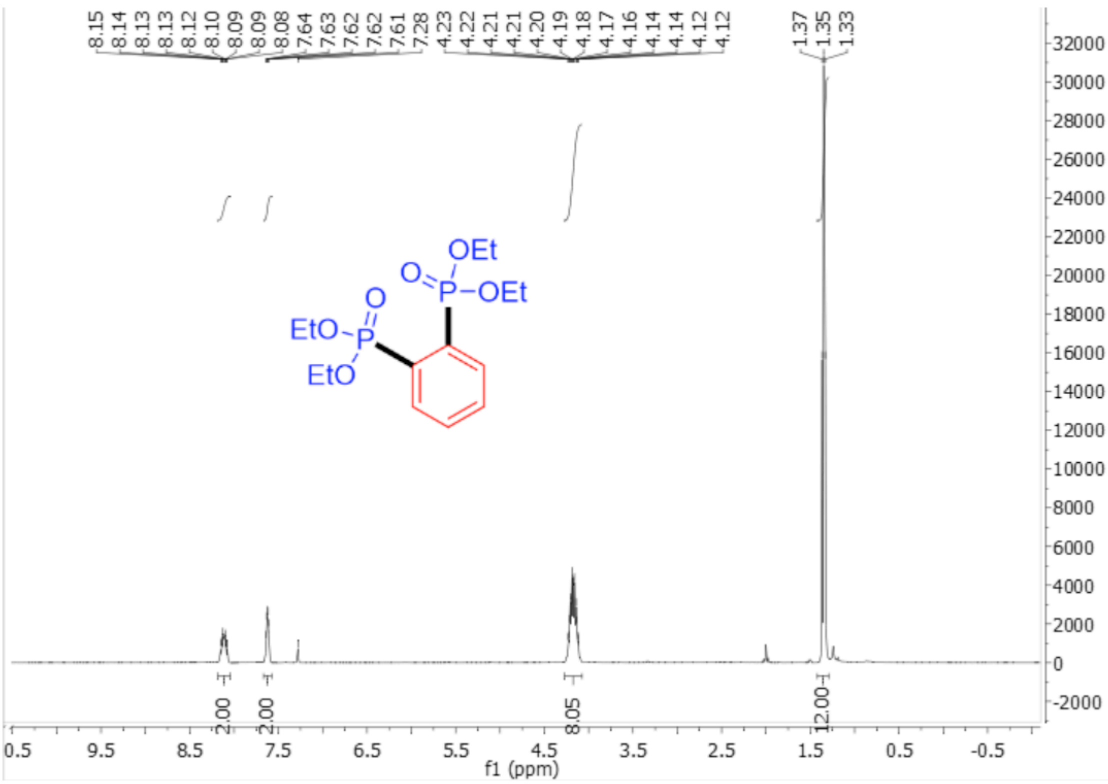
Supplementary Figure S90. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 29.



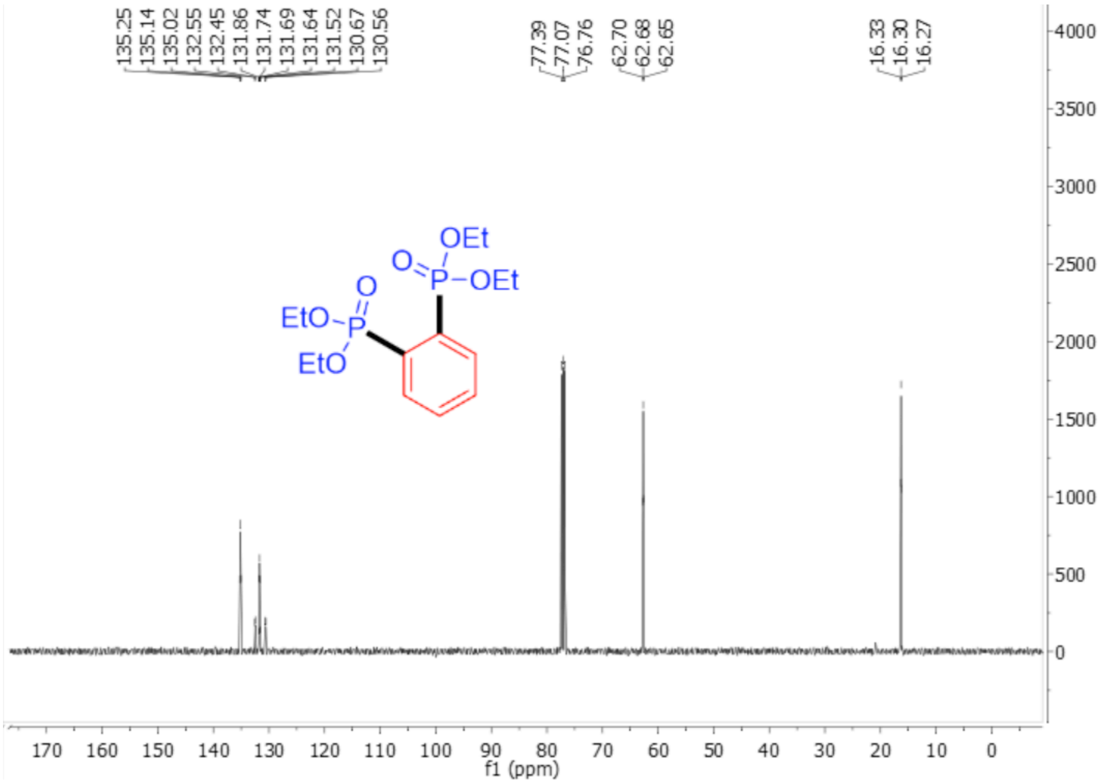
Supplementary Figure S91. ^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 29.



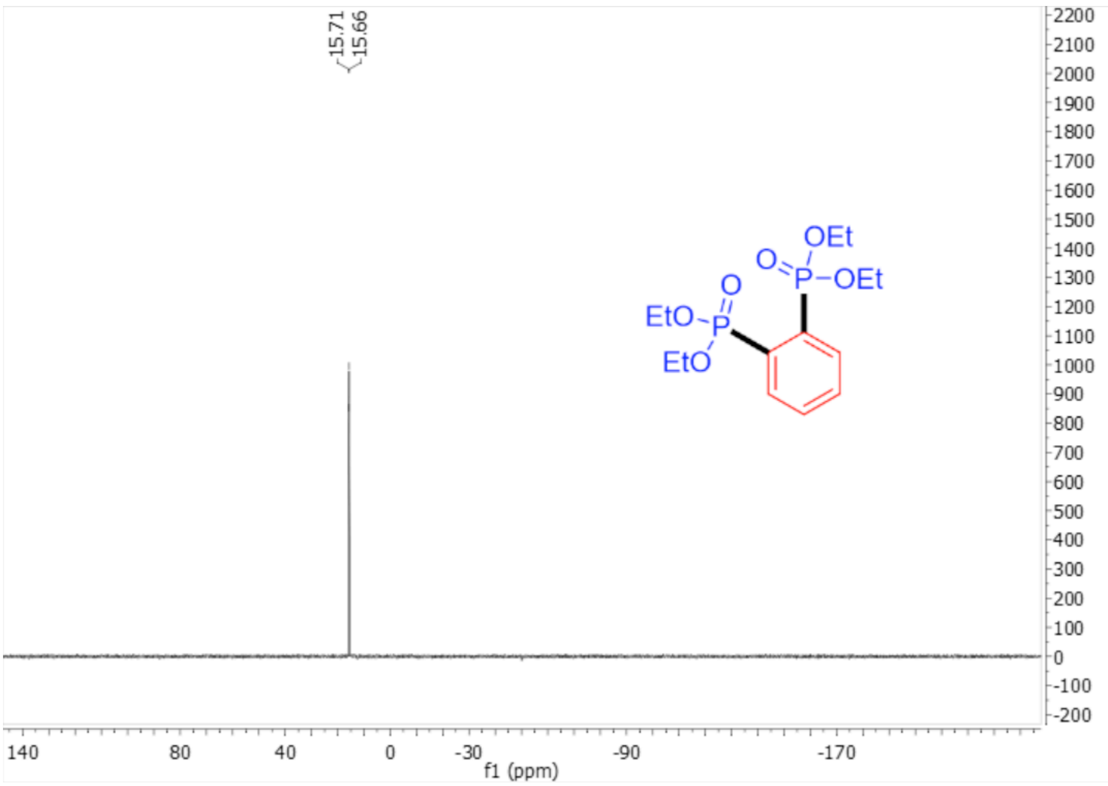
Supplementary Figure S92. [31]P NMR (162 MHz, CDCl3) spectrum for 29.



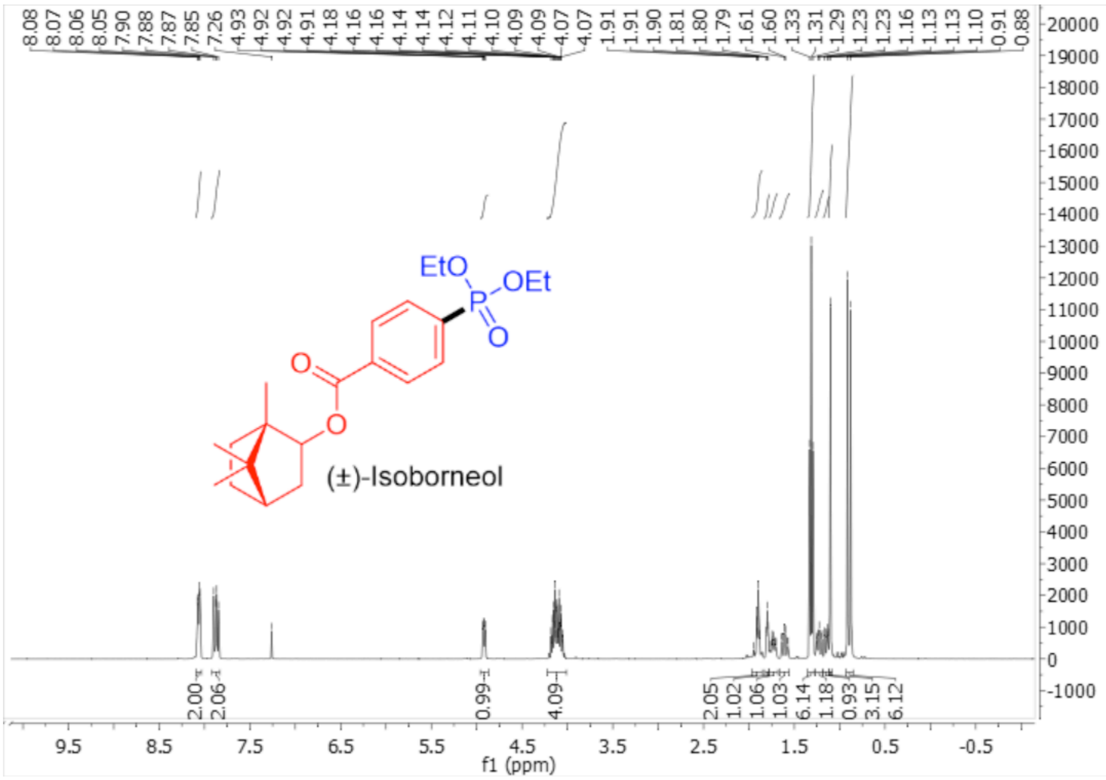
Supplementary Figure S93. [1]H NMR (400 MHz, $CDCl_3$) spectrum for 30.



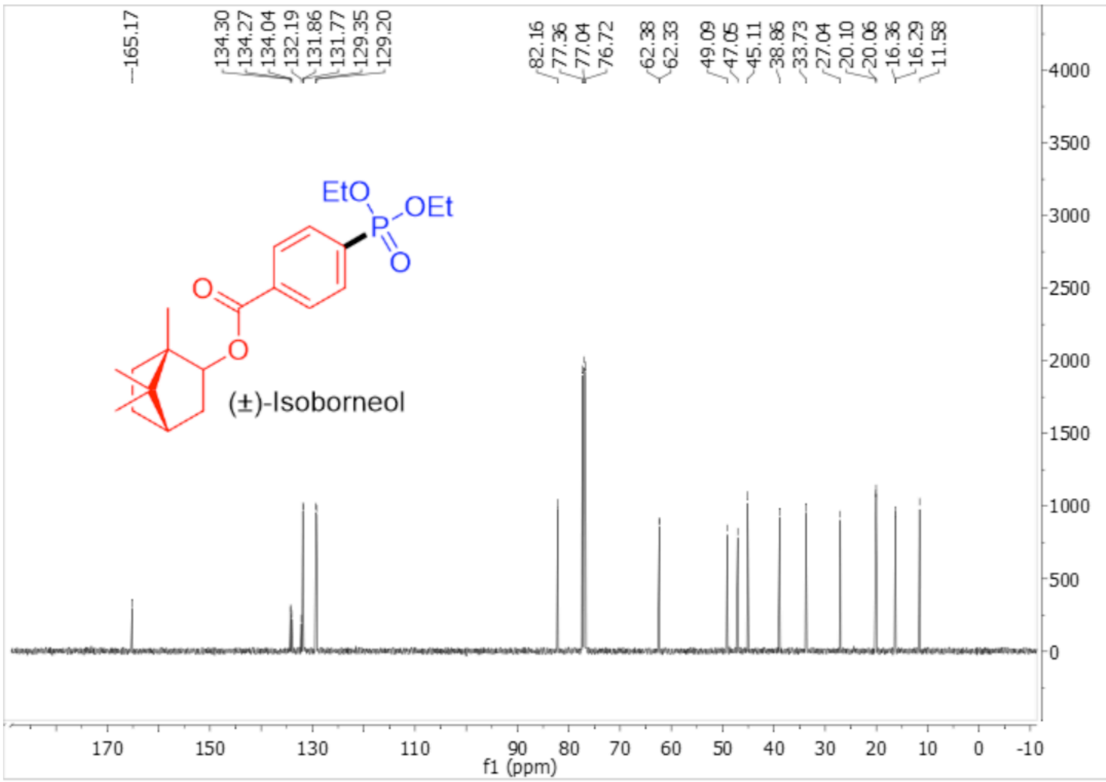
Supplementary Figure S94. **^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 30.**



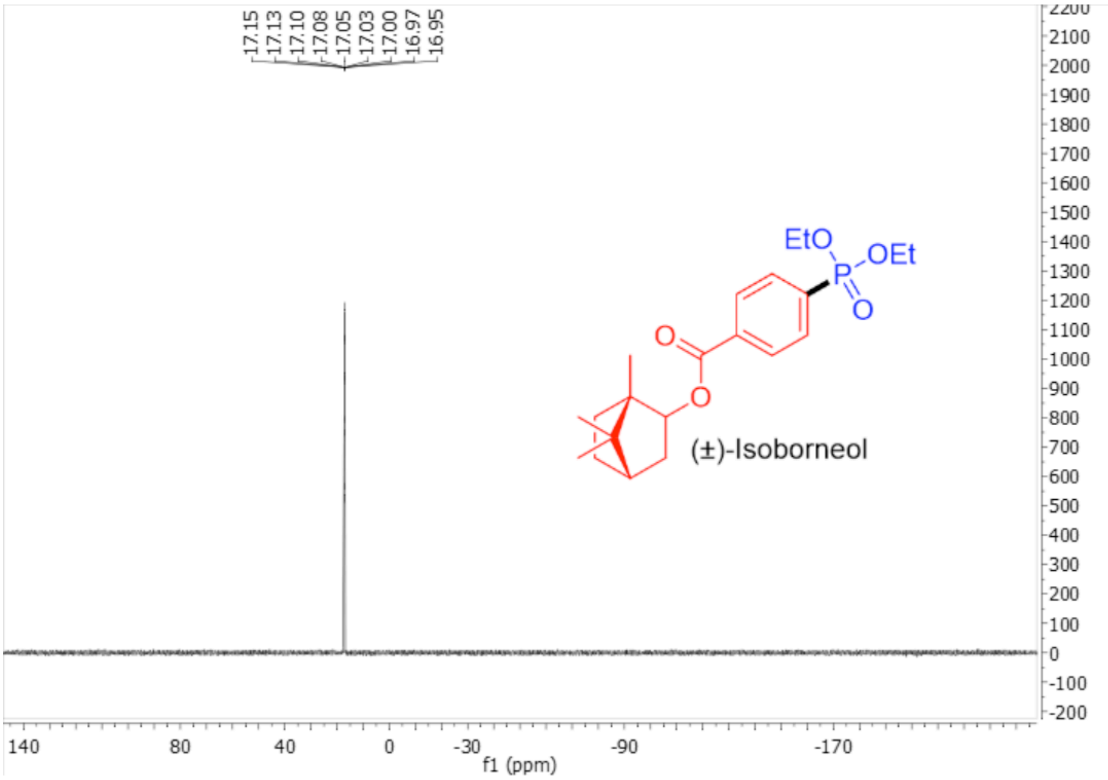
Supplementary Figure S95. **^{31}P NMR (162 MHz, CDCl3) spectrum for 30.**



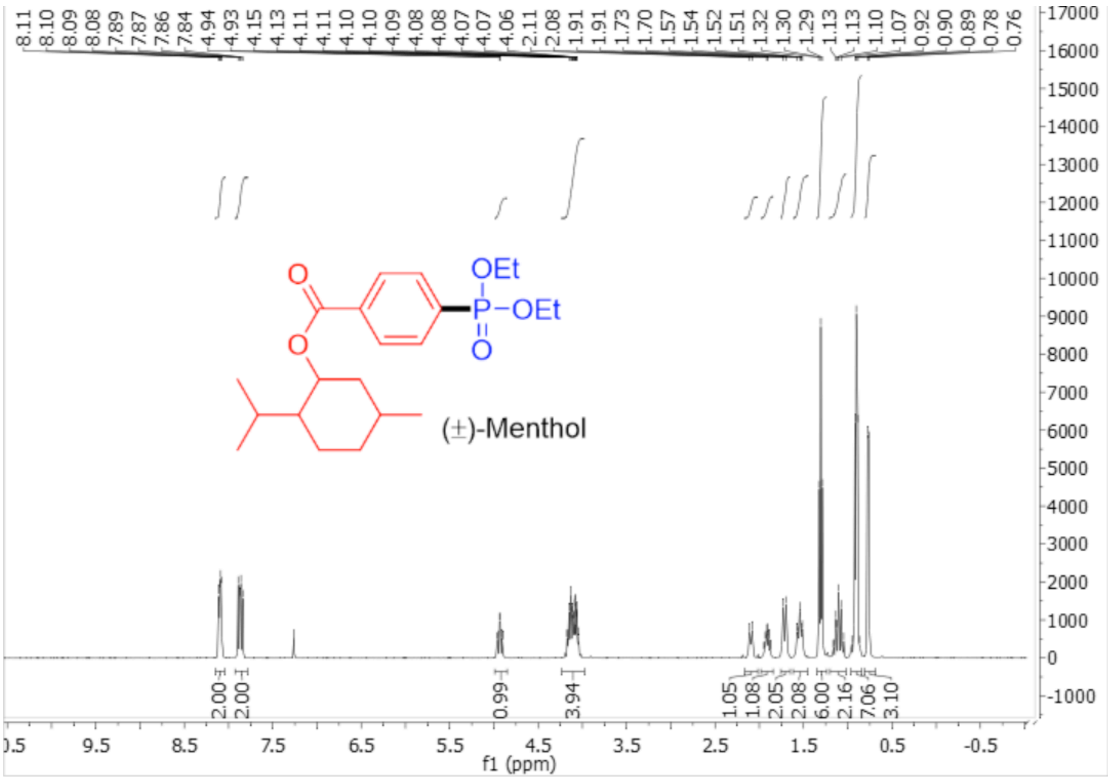
Supplementary Figure S96. **^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 31.**



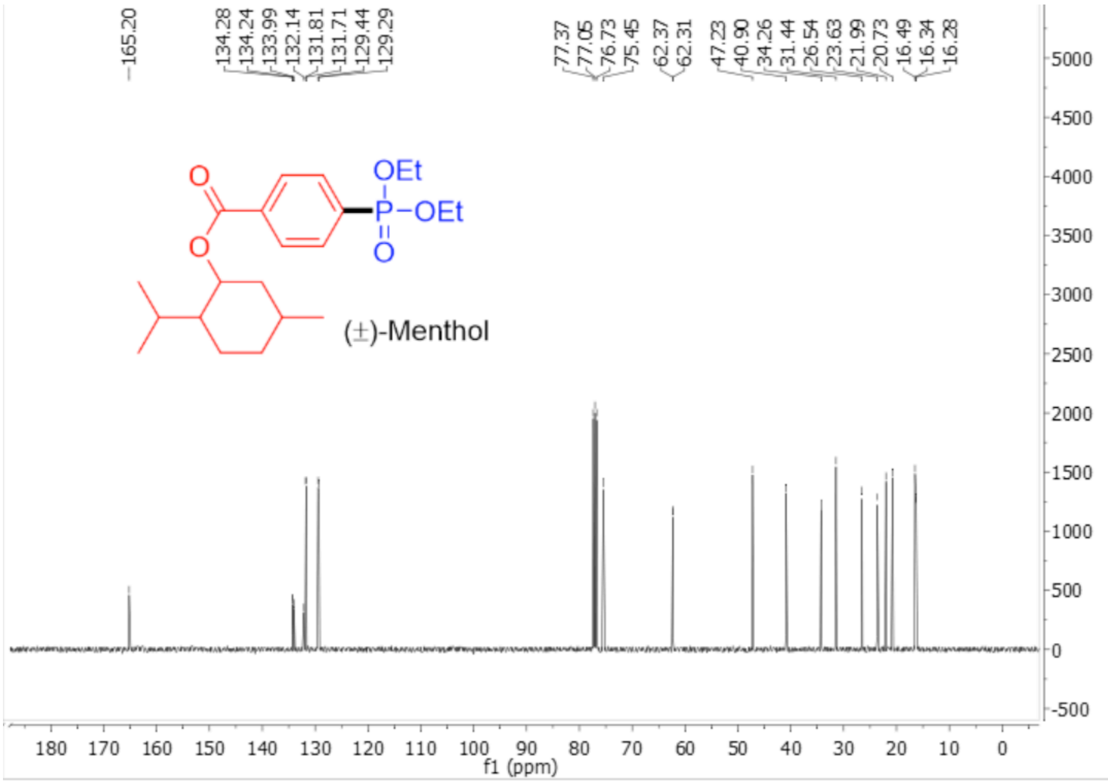
Supplementary Figure S97. **^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 31.**



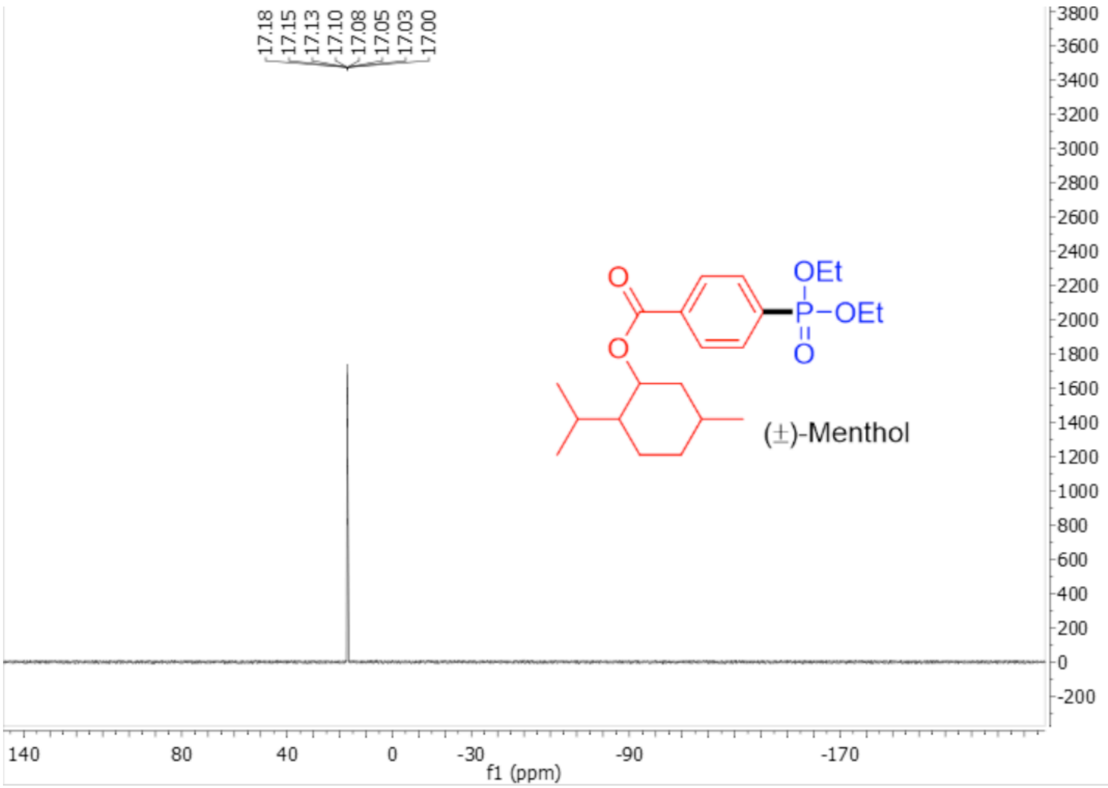
Supplementary Figure S98. ³¹P NMR (162 MHz, CDCl3) spectrum for 31.



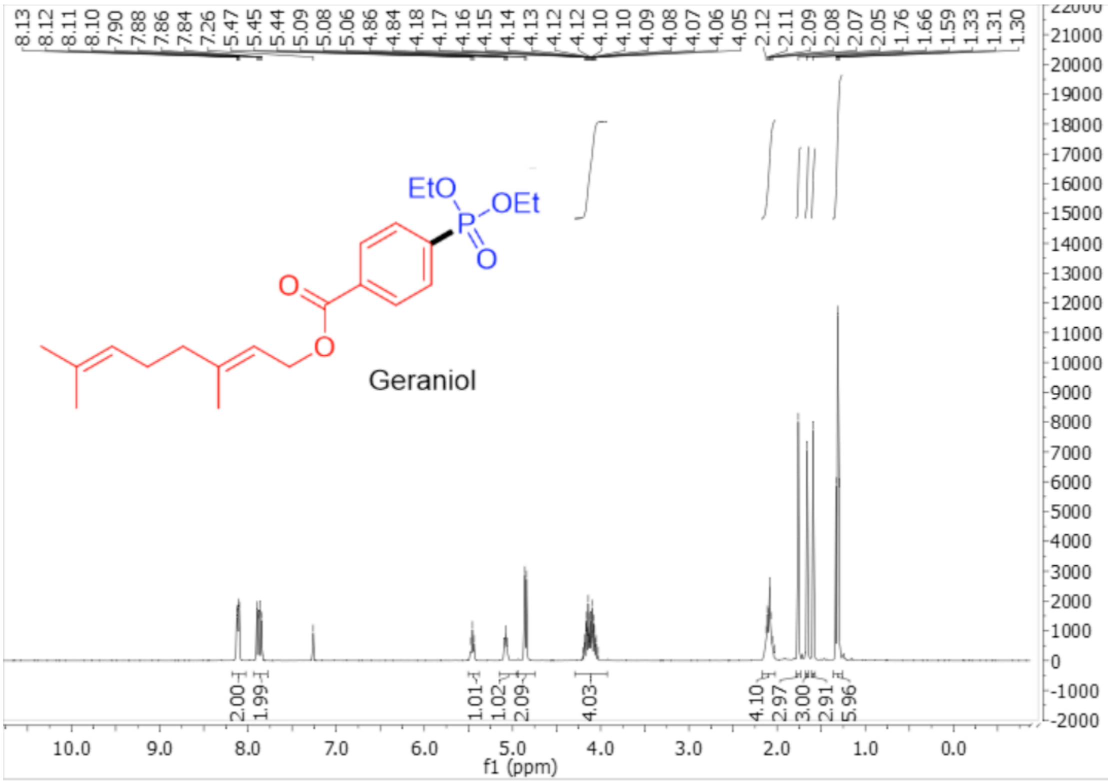
Supplementary Figure S99. ¹H NMR (400 MHz, $CDCl_3$) spectrum for 32.



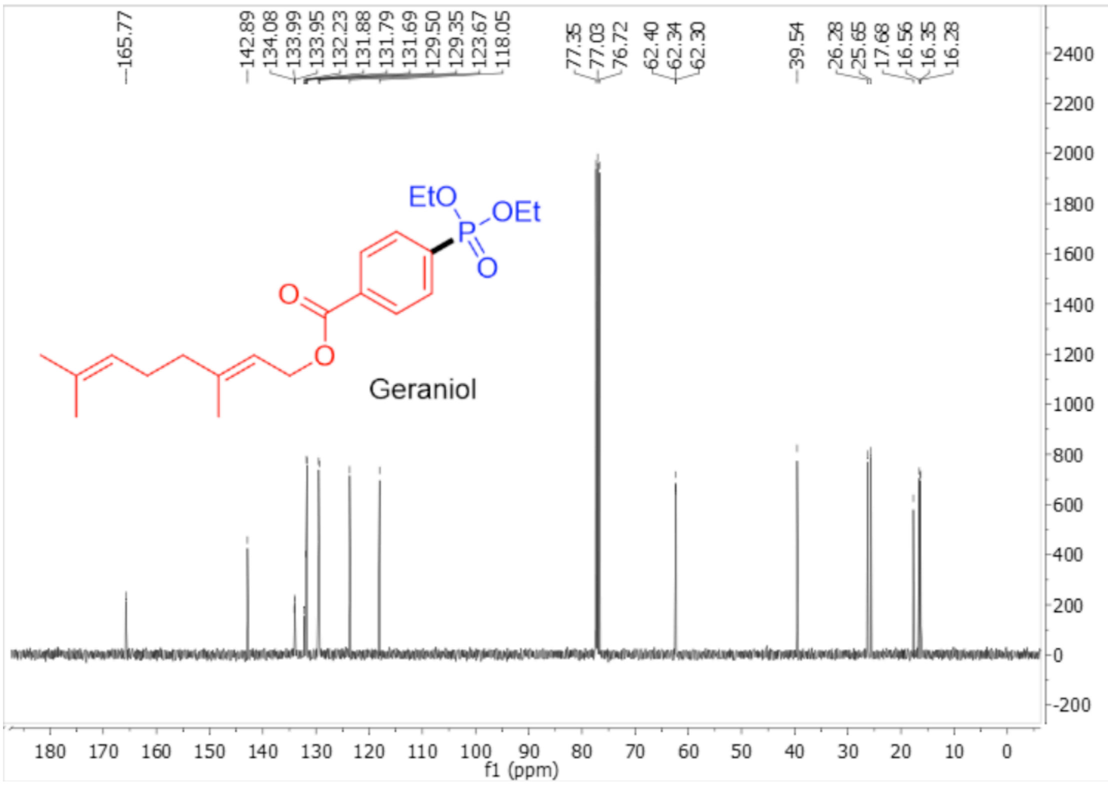
Supplementary Figure S100. [13]**CNMR(101 MHz, $CDCl_3$) spectrum for 32.**



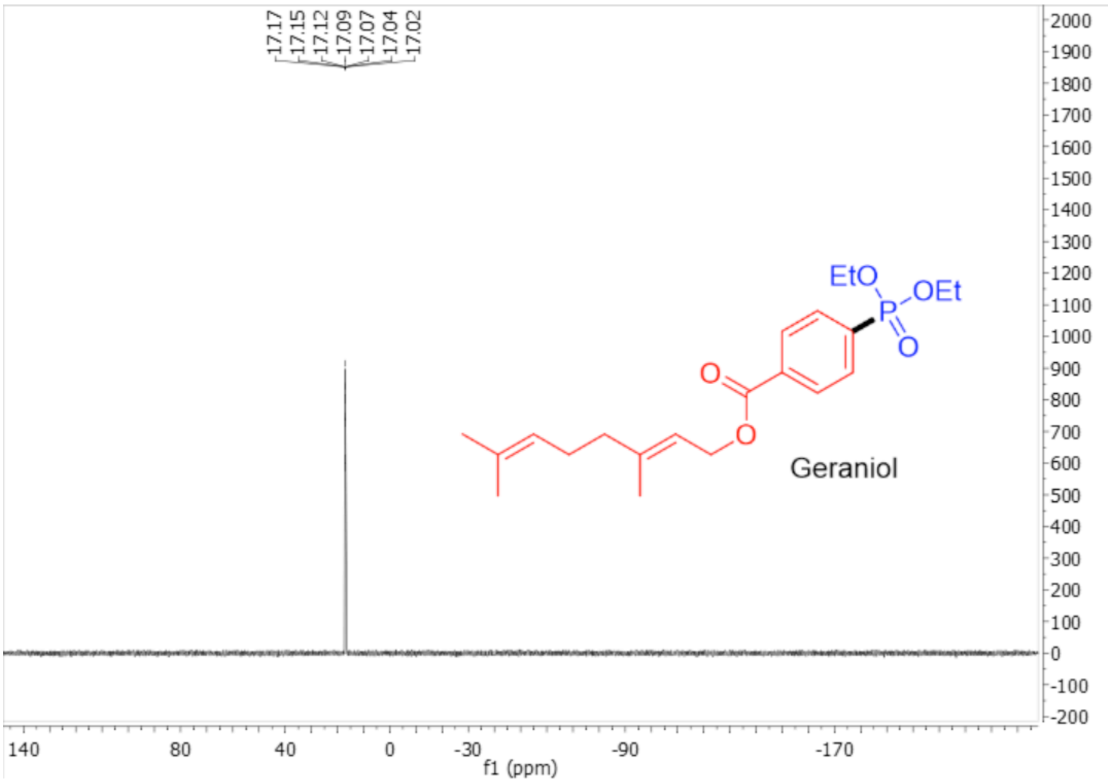
Supplementary Figure S101. [31]**P NMR (162 MHz, CDCl3) spectrum for 32.**



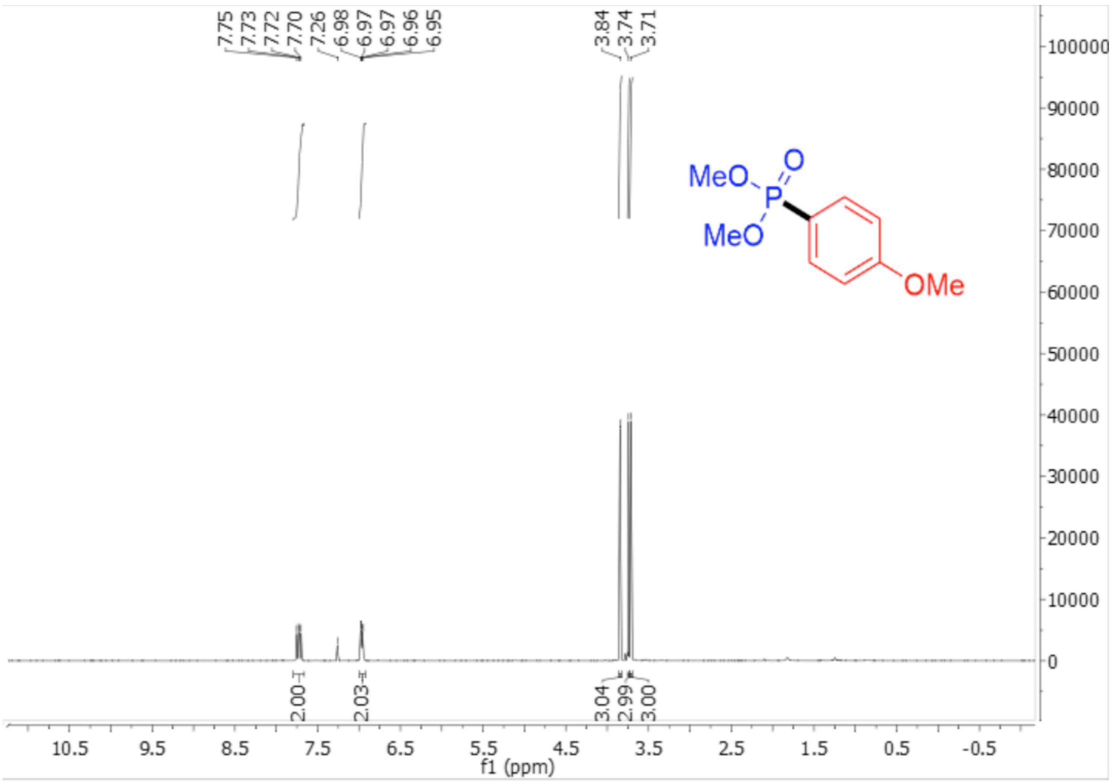
Supplementary Figure S102. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum for 33.**



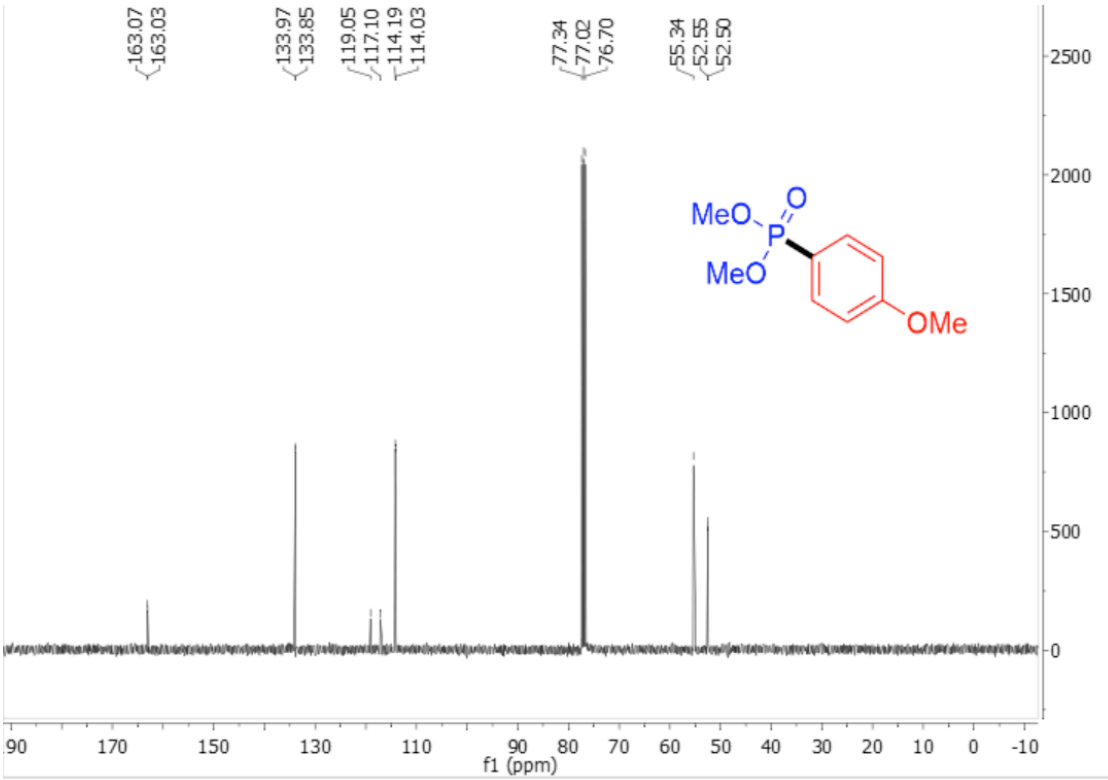
Supplementary Figure S103. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 33.**



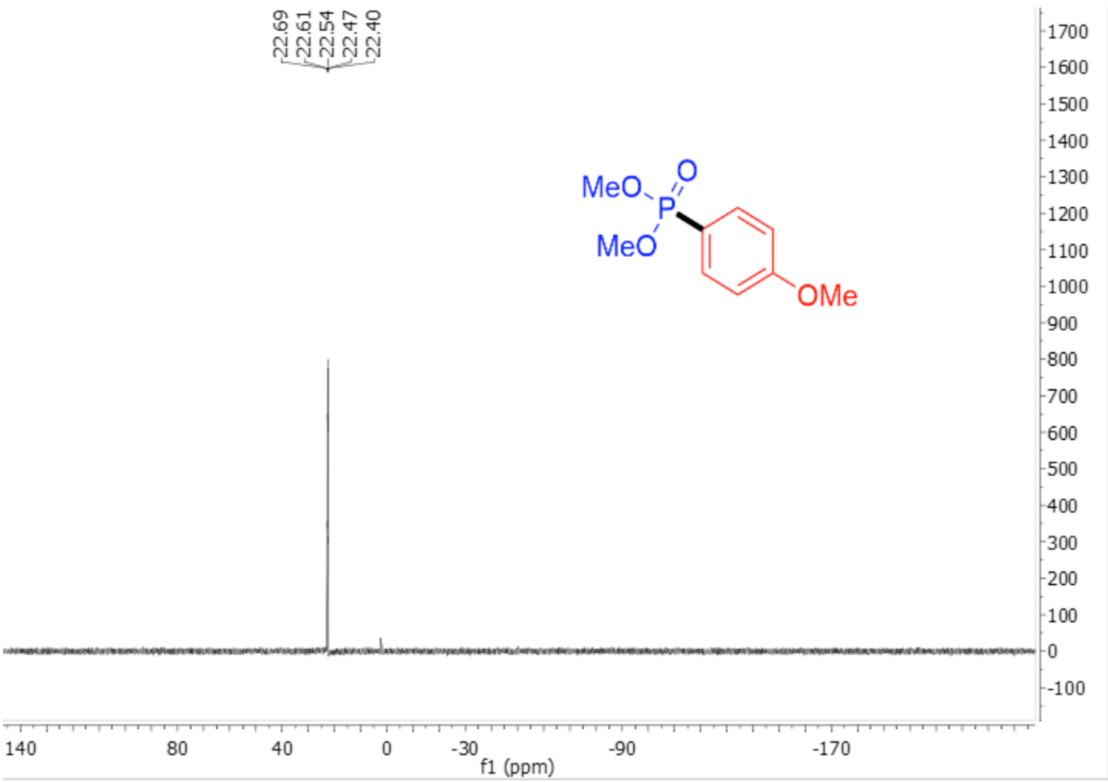
Supplementary Figure S104. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 33.**



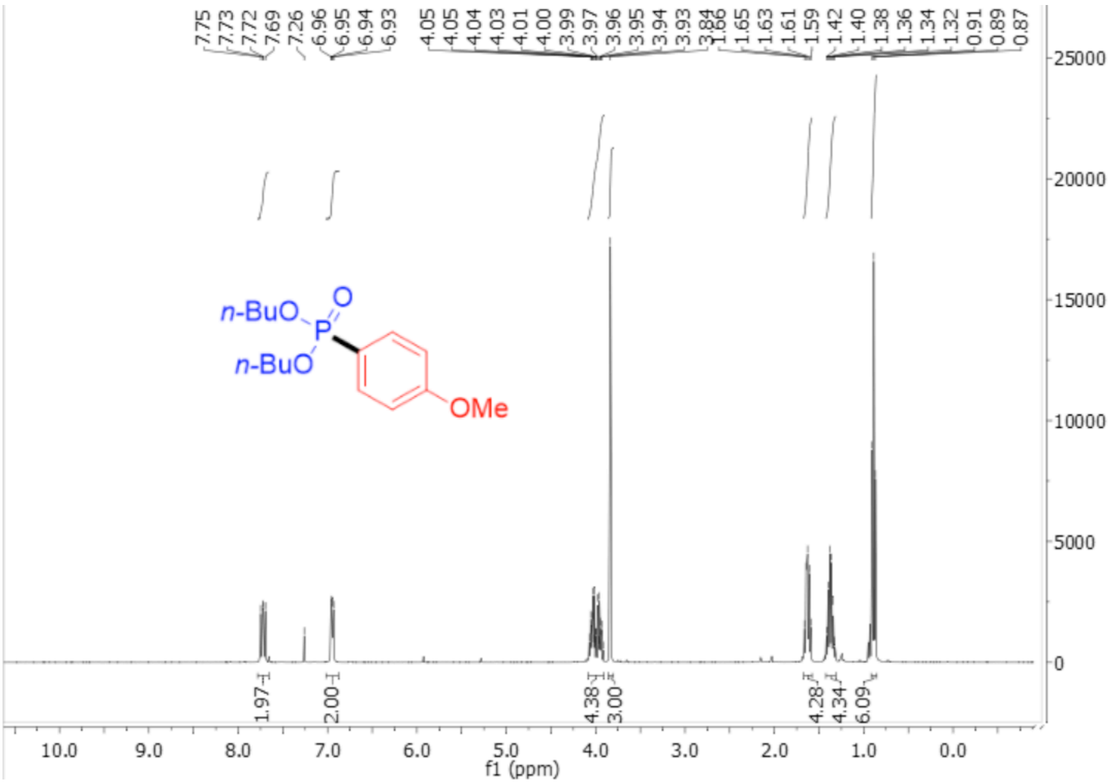
Supplementary Figure S105. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum for 34.**



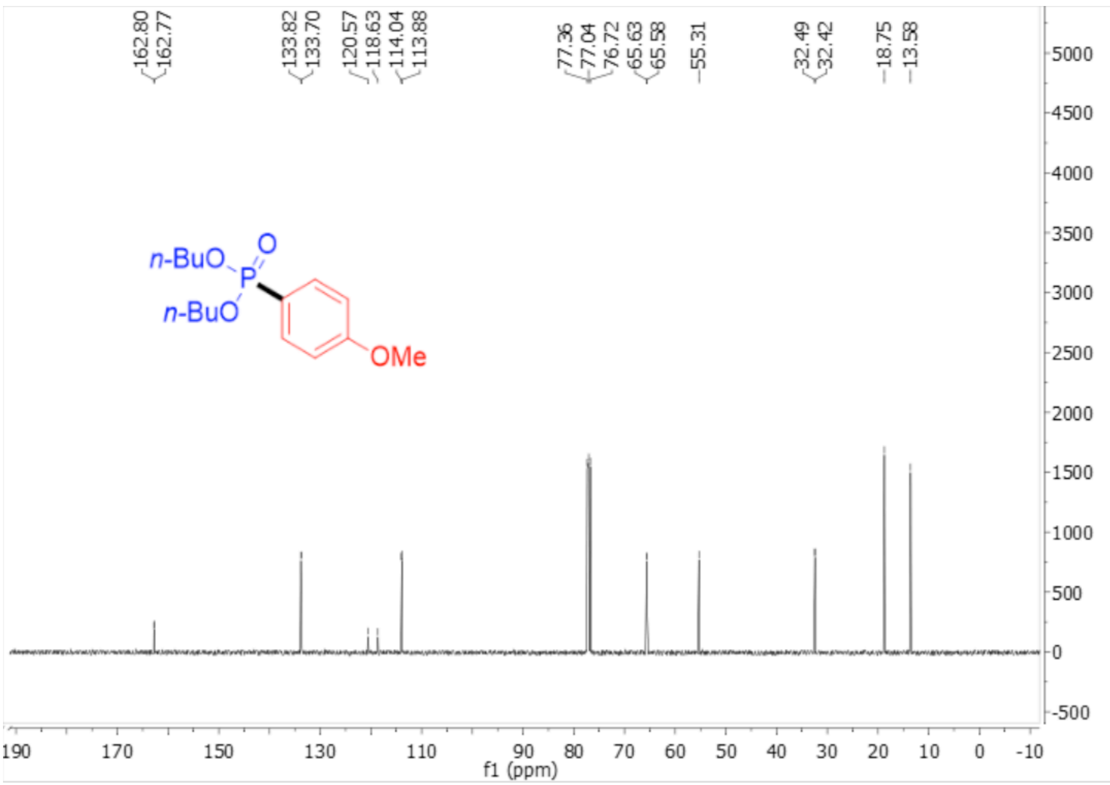
Supplementary Figure S106. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 34.**



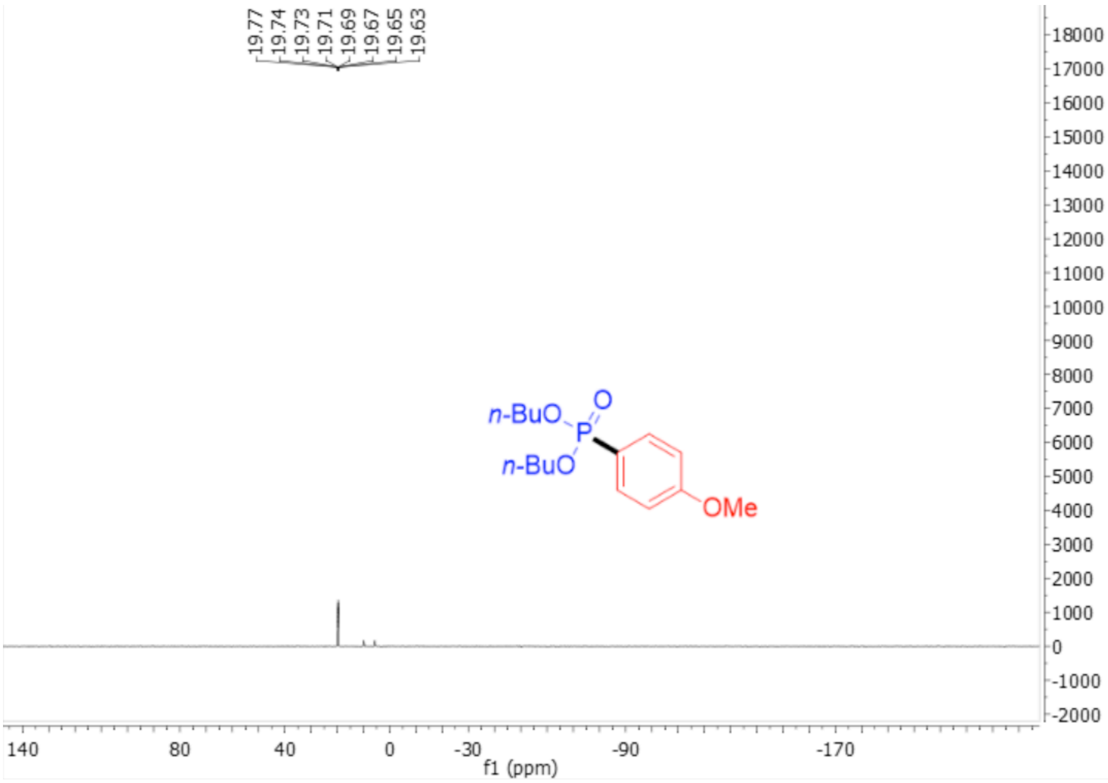
Supplementary Figure S107. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 34.**



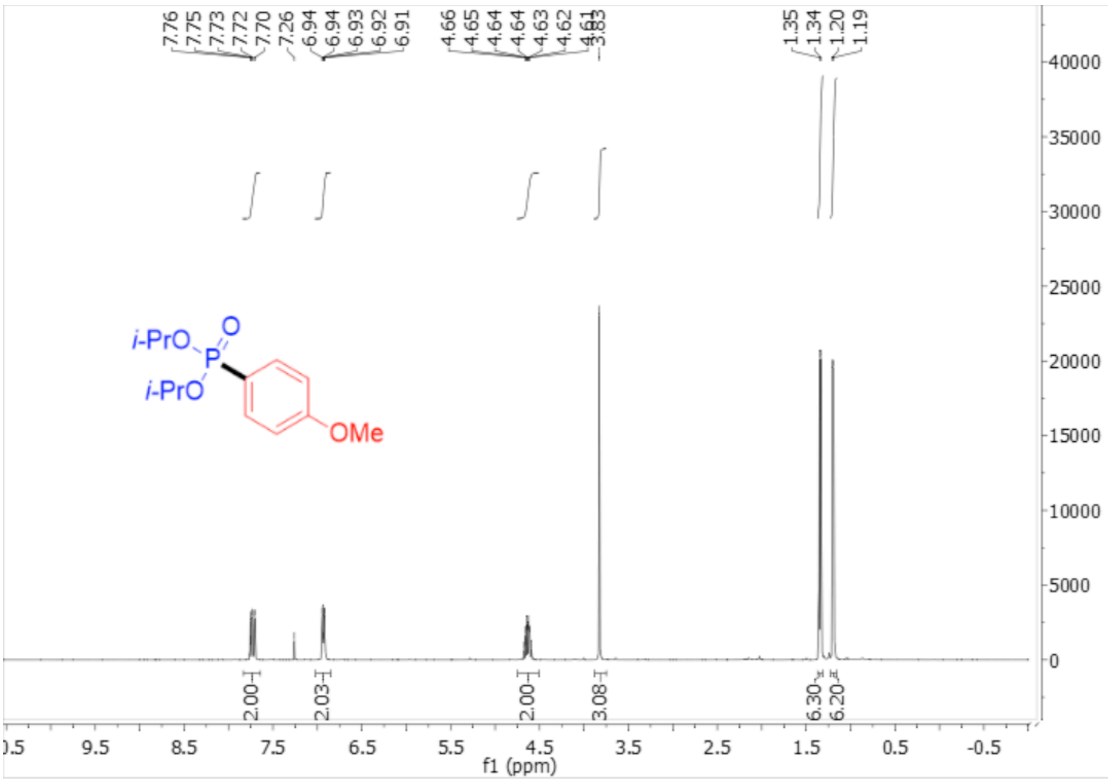
Supplementary Figure S108. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum for 35.**



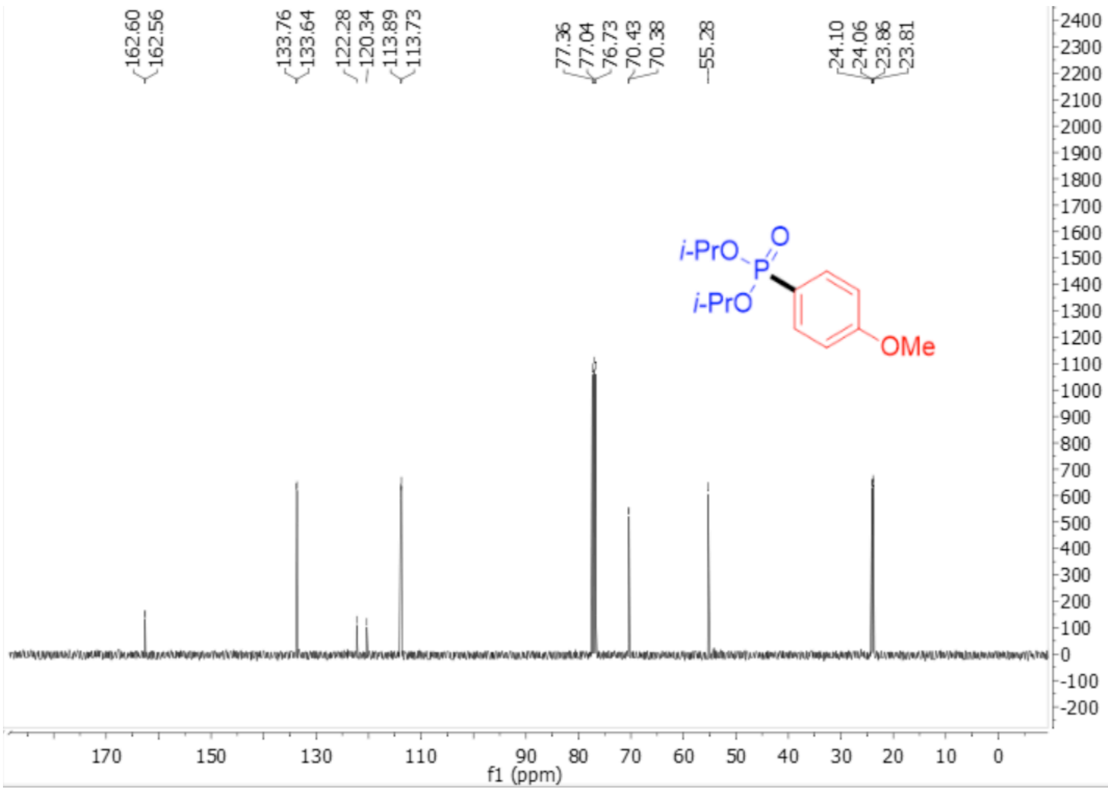
Supplementary Figure S109. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 35.**



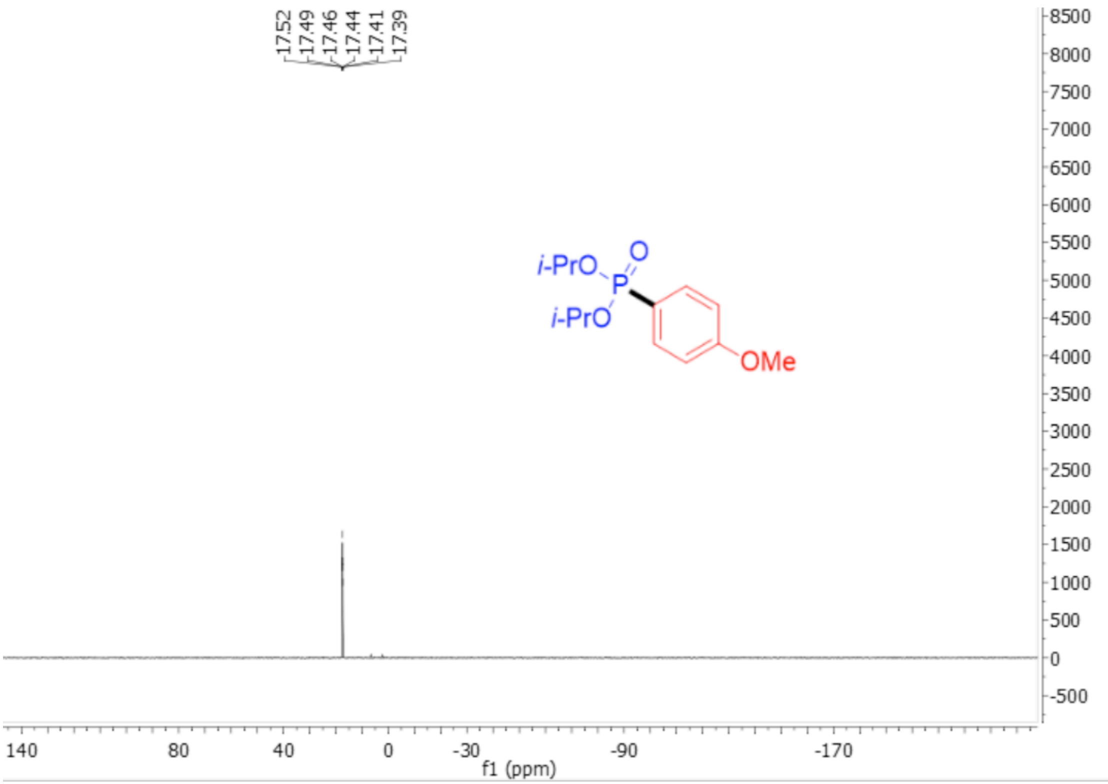
Supplementary Figure S110. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 35.**



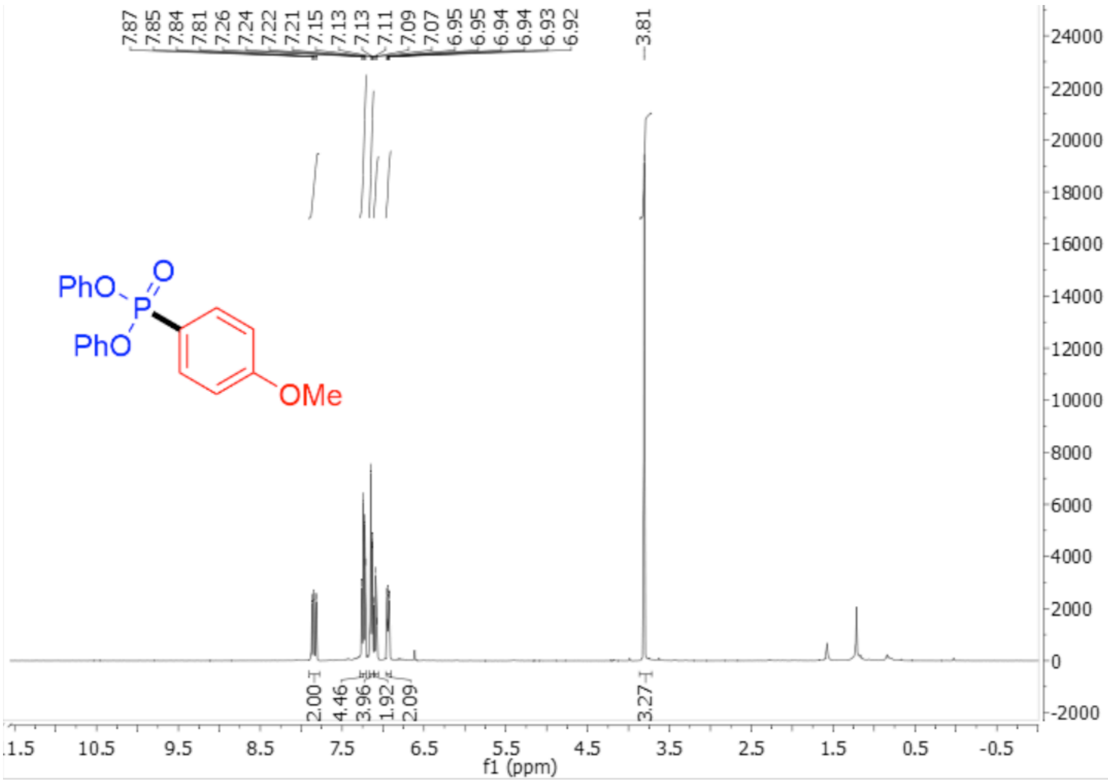
Supplementary Figure S111. ^{1}**H NMR (400 MHz, $CDCl_3$) spectrum for 36.**



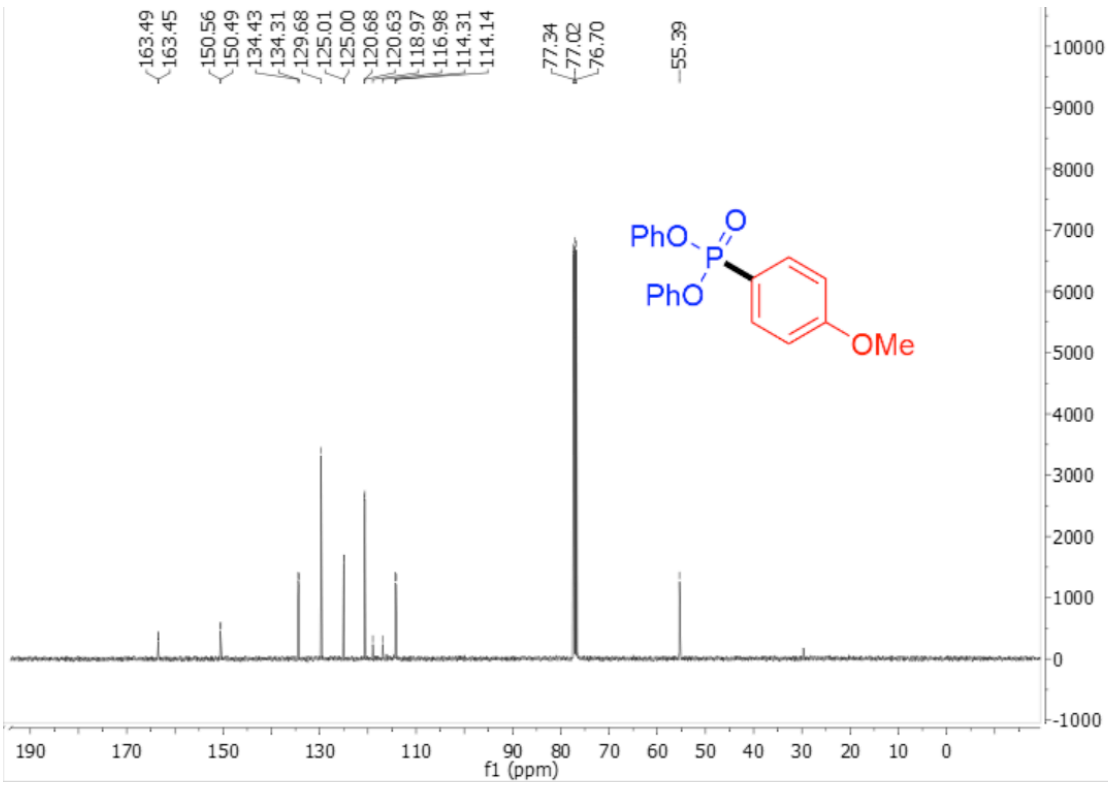
Supplementary Figure S112. ^{13}**CNMR(101 MHz, CDCl$_3$) spectrum for 36.**



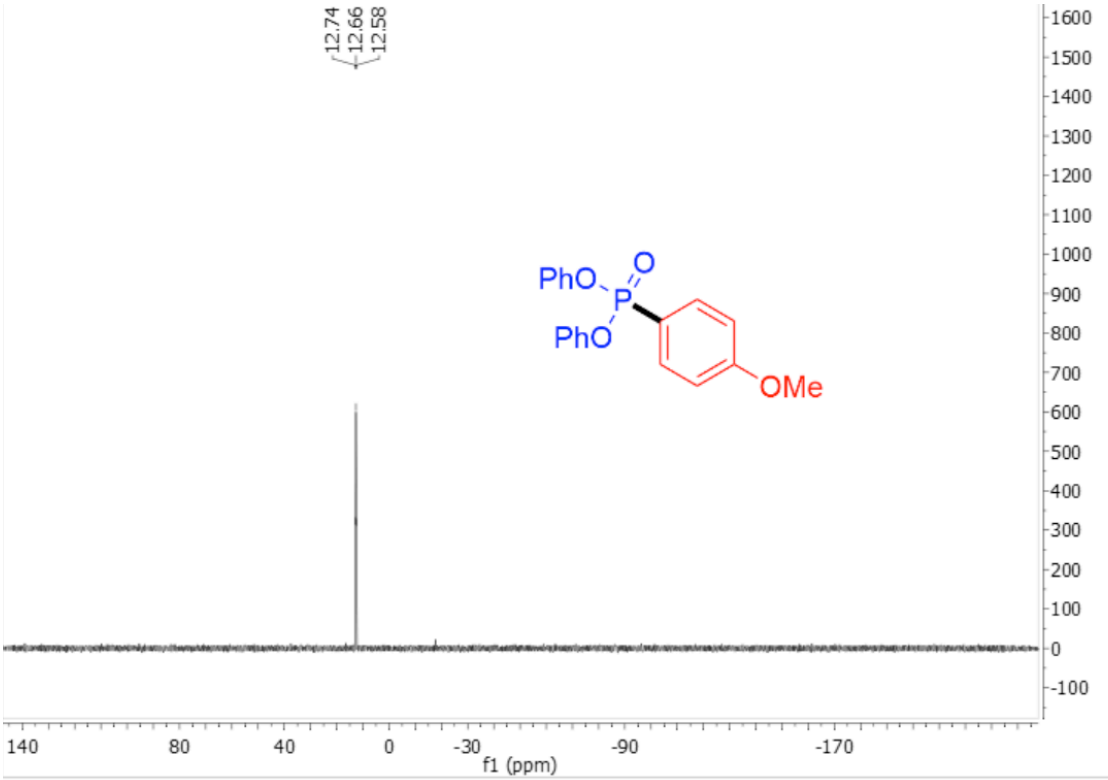
Supplementary Figure S113. ^{31}**P NMR (162 MHz, CDCl3) spectrum for 36.**



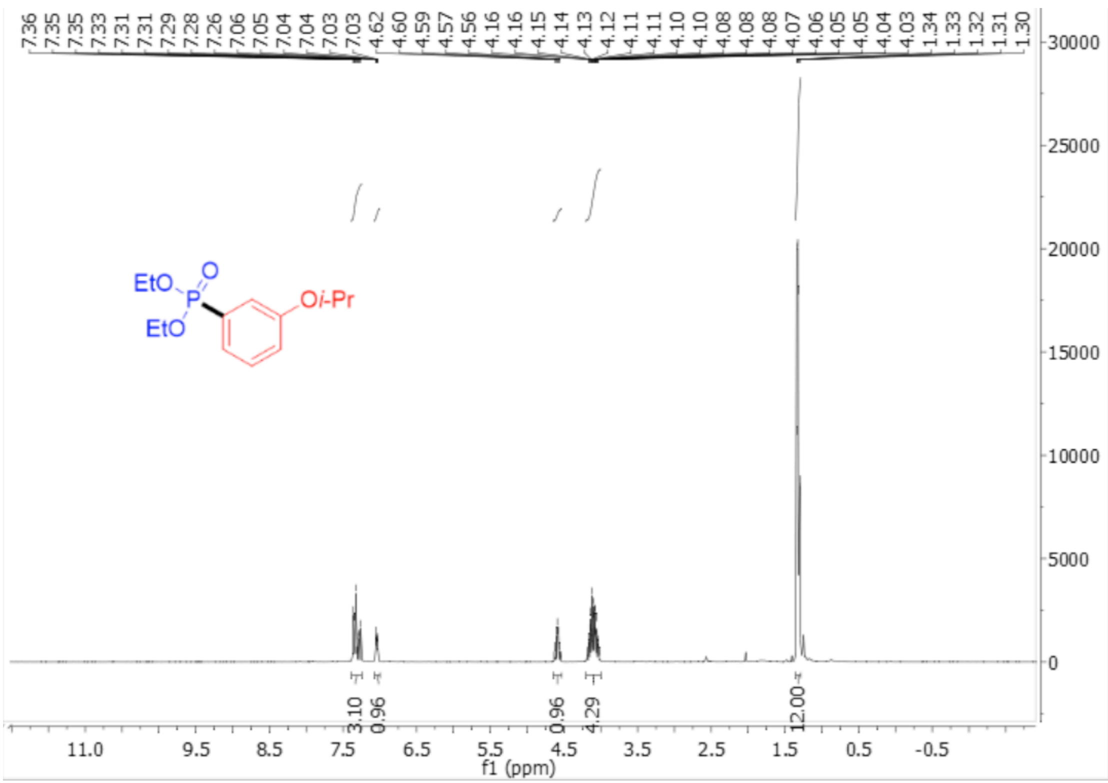
Supplementary Figure S114. ^{1}**H NMR (400 MHz, $CDCl_3$) spectrum for 37.**



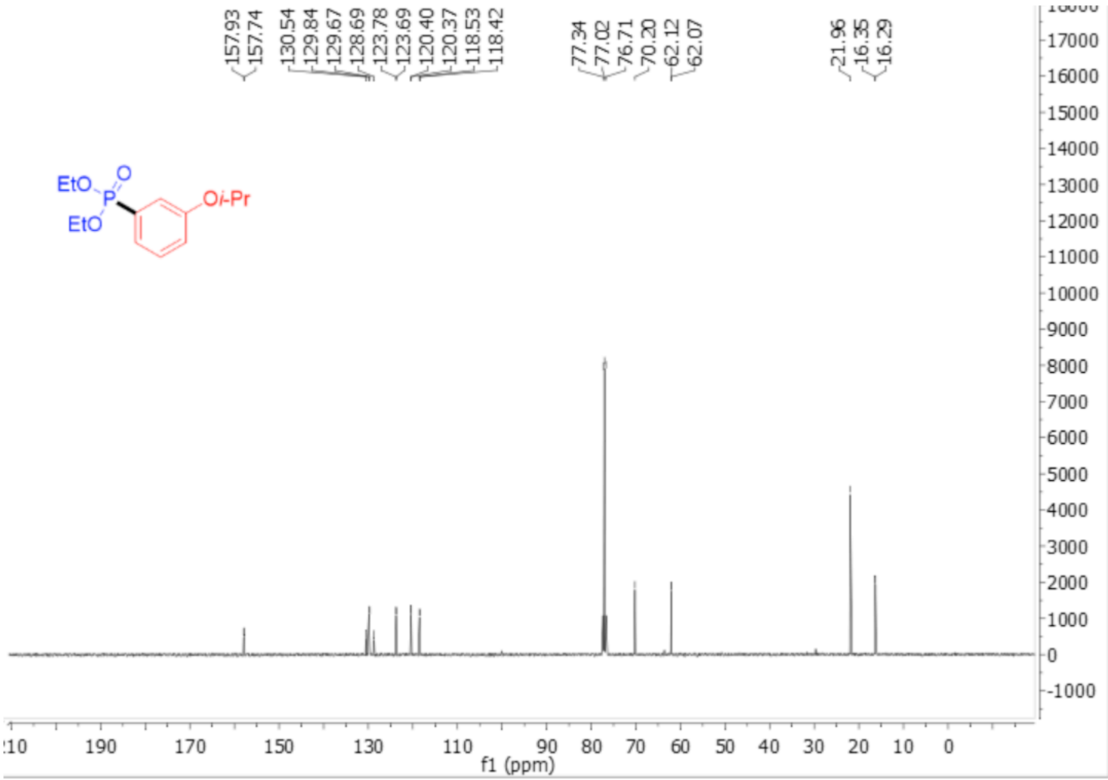
Supplementary Figure S115. ^{13}**CNMR(101 MHz, $CDCl_3$) spectrum for 37.**



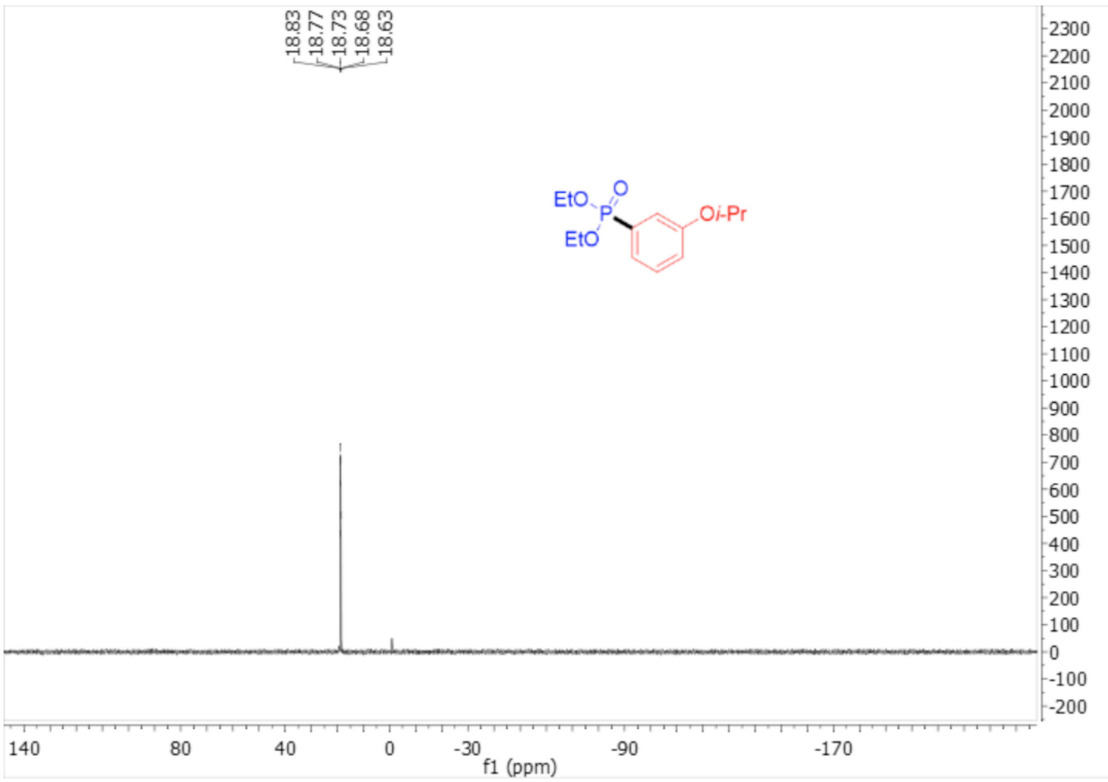
Supplementary Figure S116. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 37.



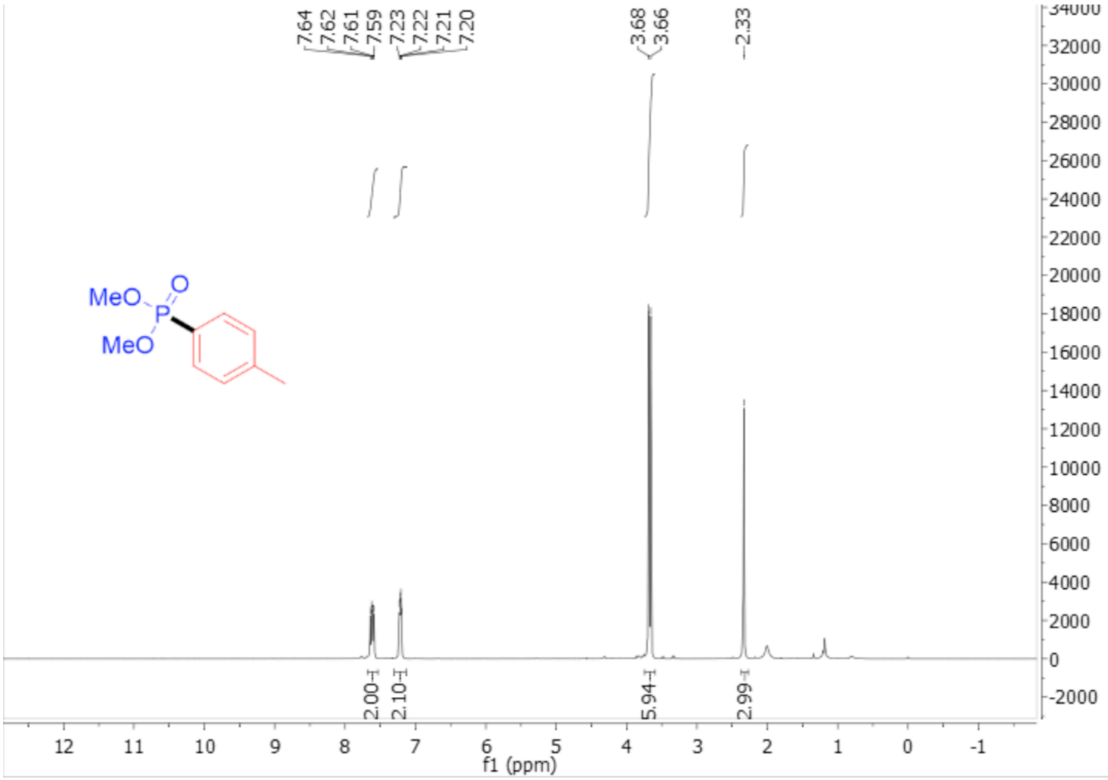
Supplementary Figure S117. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 38.



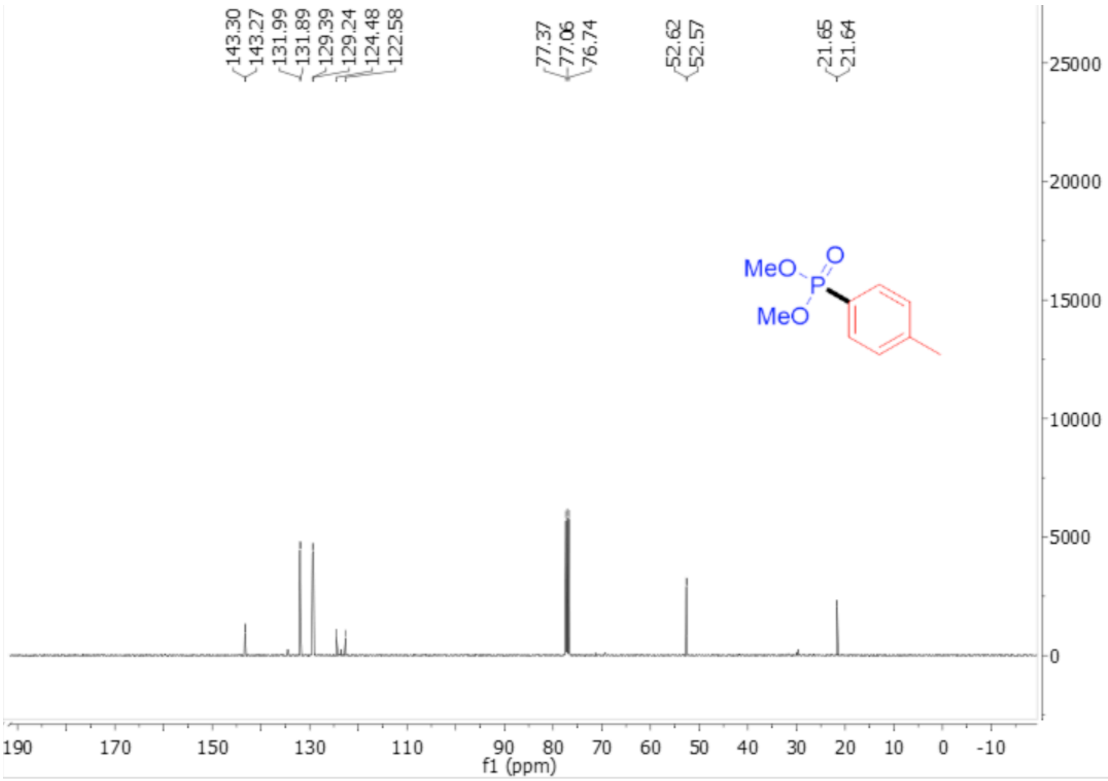
Supplementary Figure S118. [13]CNMR(101 MHz, $CDCl_3$) spectrum for 38.



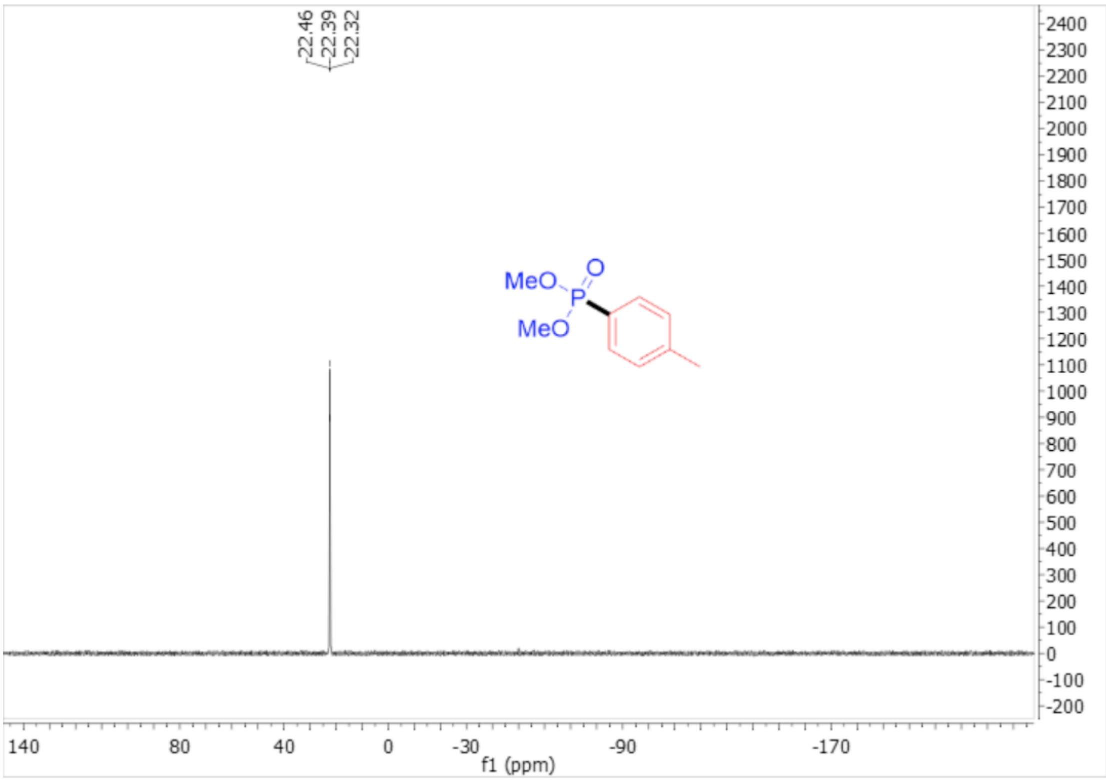
Supplementary Figure S119. [31]P NMR (162 MHz, $CDCl_3$) spectrum for 38.



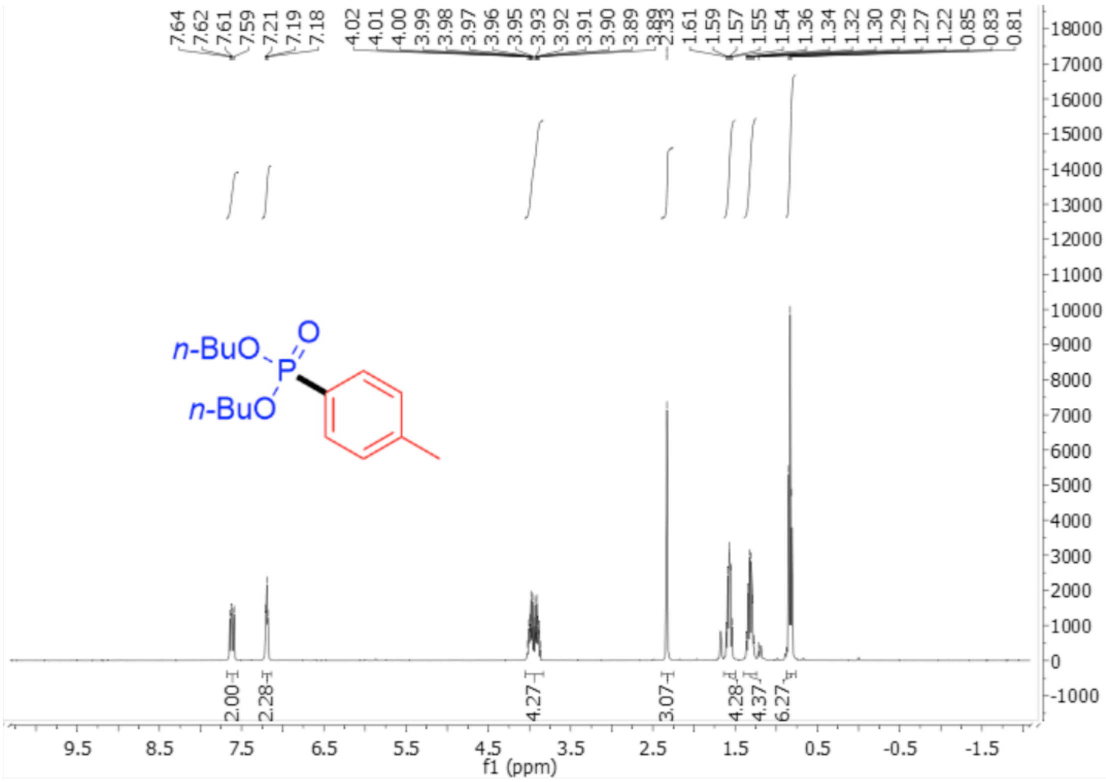
Supplementary Figure S120. ^{1}**H NMR (400 MHz,** $CDCl_3$**) spectrum for 39.**



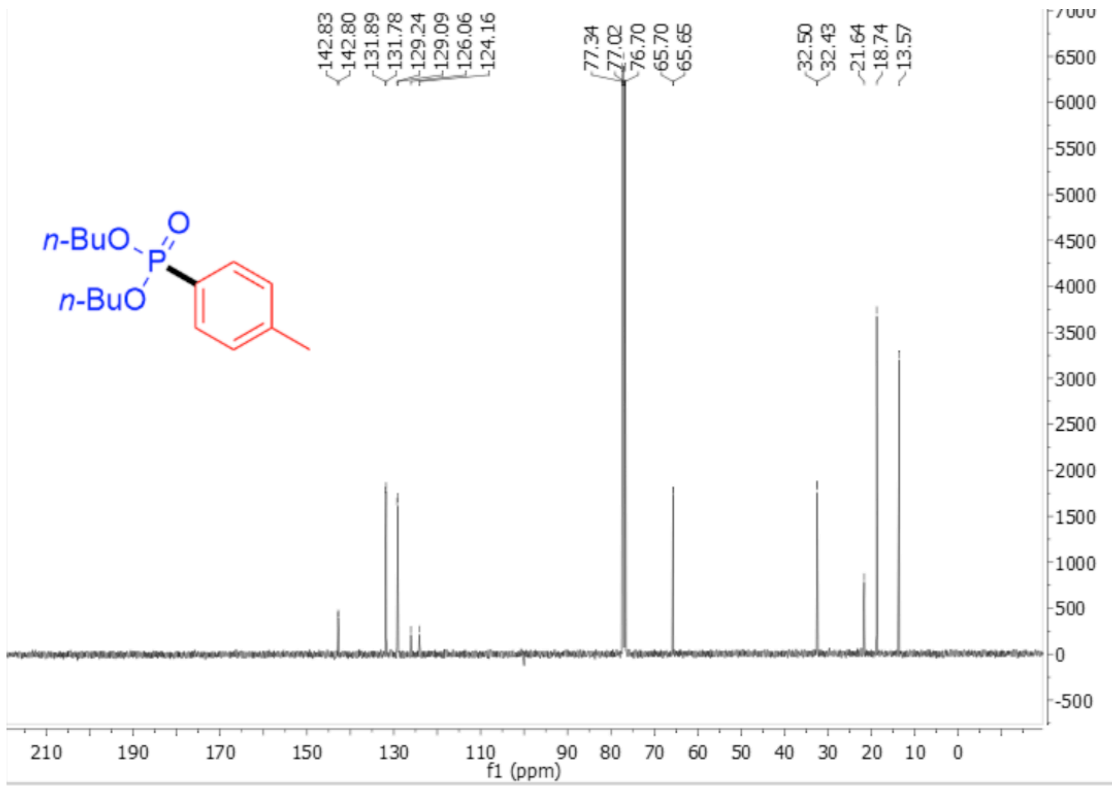
Supplementary Figure S121. ^{13}**CNMR(101 MHz,** $CDCl_3$**) spectrum for 39.**



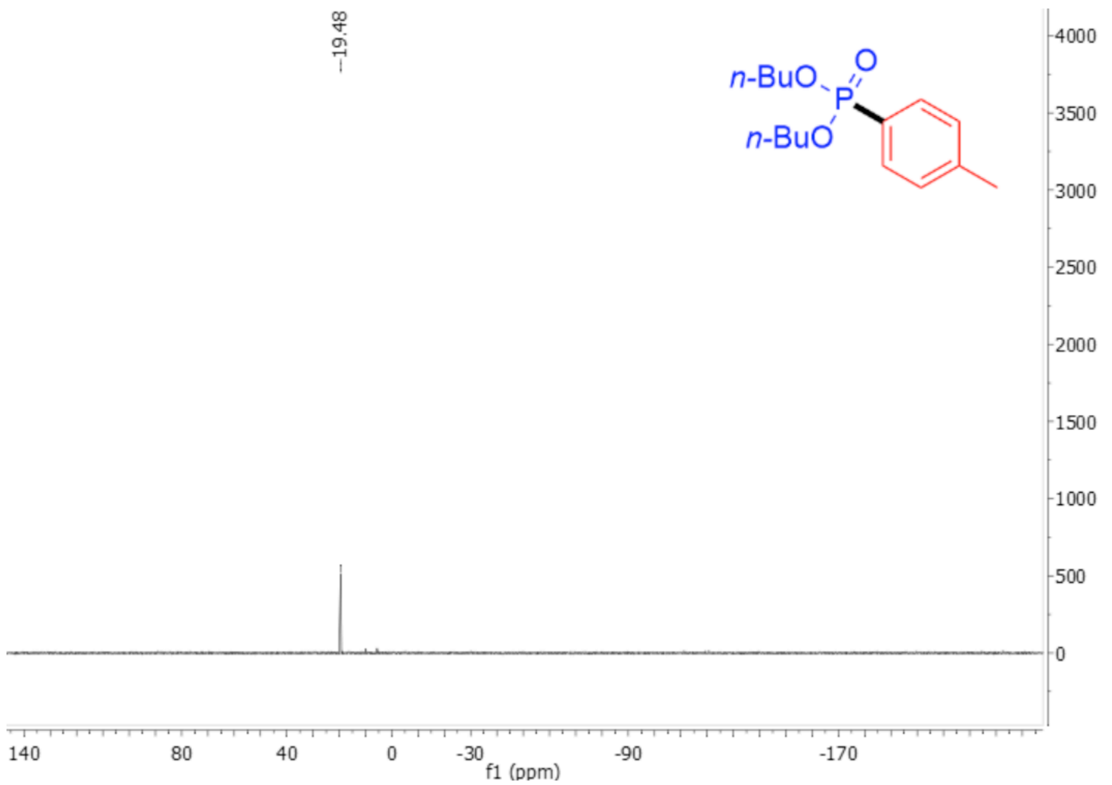
Supplementary Figure S122. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 39.



Supplementary Figure S123. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 40.



Supplementary Figure S124. **^{13}CNMR(101 MHz, $CDCl_3$) spectrum for 40.**



Supplementary Figure S125. **^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 40.**