Bisphosphorylation of Anhydrides - Convenient Access to Bisphosphonates with a P-O-C-P Motif

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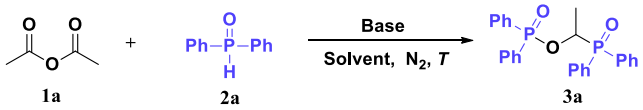
Contents

1. General information

^{1}H, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded on a 500M Bruker AVANCE NEO spectrometer in $CDCl_3$ with TMS as internal standard. High resolution mass spectroscopic (HRMS) and mass spectra were measured using Thermo Scientific DS II mass spectrometer, Thermo Q Exactive Focus and Bruker micro TOF-Q mass spectrometer. Thermo gravimetric analysis (TGA) of samples was carried out with Mettler TGA/DSC 3+ thermal analyzer from 25 ^{o}C to 800 ^{o}C at a heating rate of 10 ^{o}C /min. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM). Substrates of **2a-2c, 2e, 2f, 2h, 2j** were prepared according to literature procedure. [1-3]

2. Reaction Condition Optimization

2.1 Table S1. Condition Optimization of Using $Ph_2P(O)$-H as Substrate [a]

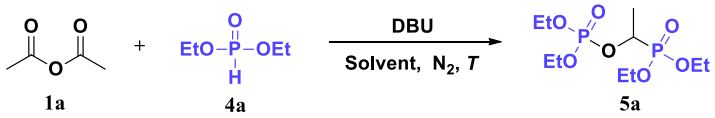


1a + **2a** → **3a**

Entry	Base (equiv.)	**1a** / **2a**	*T* (°C)	Solvent	Yield (%)
1	NaF(2.0)	1.0 : 3.0	100	MeCN	54
2	NaF(2.0)	1.0 : 3.0	100	DCE	45
3	NaF(2.0)	1.0 : 3.0	100	Toluene	63
4	NaF(2.0)	1.0 : 3.0	100	THF	55
5	NaF(2.0)	1.0 : 3.0	100	1,4-dioxane	34
6	NaF(2.0)	1.0 : 3.0	100	DMSO	trace
7	NaF(2.0)	1.0 : 3.0	100	DMF	trace
8	NaF(2.0)	1.0 : 3.0	100	DMAC	trace
9	NaF(2.0)	1.0 : 3.0	100	NMP	trace
10	NaF(0.2)	1.0 : 3.0	100	toluene	48
11	pyridine(0.2)	1.0 : 3.0	100	toluene	46
12	2-chloropyridine (0.2)	1.0 : 3.0	100	toluene	66
13	2-fluoropyridine (0.2)	1.0 : 3.0	100	toluene	72
14	2,6-lutidine (0.2)	1.0 : 3.0	100	toluene	65
15	2,6-dichloropyridine(0.2)	1.0 : 3.0	100	toluene	73
16	DBU(0.2)	1.0 : 3.0	100	toluene	57
17	DABCO(0.2)	1.0 : 3.0	100	toluene	55
18	DMAP(0.2)	1.0 : 3.0	100	toluene	74
19	Na_2CO_3(0.2)	1.0 : 3.0	100	toluene	54
20	$NaHCO_3$(0.2)	1.0 : 3.0	100	toluene	71
21	K_3PO_4(0.2)	1.0 : 3.0	100	toluene	51
22	K_2HPO_4(0.2)	1.0 : 3.0	100	toluene	40
23[b]	DMAP(0.2)	1.0 : 3.0	100	toluene	66
24[c]	DMAP(0.2)	1.0 : 3.0	100	toluene	61
25	DMAP(0.2)	1.0 : 2.5	100	toluene	70
26	DMAP(0.2)	1.0 : 3.5	100	toluene	75
27	DMAP(0.2)	1.0 : 3.0	110	toluene	74
28	DMAP(0.2)	**1.0 : 3.0**	**90**	**toluene**	**83**
29	DMAP(0.2)	1.0 : 3.0	80	toluene	58
30	DMAP(0.15)	1.0 : 3.0	90	toluene	67
31	DMAP(0.25)	1.0 : 3.0	90	toluene	69
32[d]	DMAP(0.2)	1.0 : 3.0	90	toluene	47
33	—	1.0 : 3.0	90	toluene	10

[a] Reaction conditions: **1a** (0.2 mmol), $Ph_2P(O)H$ (121.2mg, 3.0 equiv.), Base (0.2 equiv.), Solvent (2.0 mL), N_2, 100 ^{o}C overnight, isolated yield; [b] toluene (1.5 mL); [c] toluene (2.5 mL); [d] Under air.

2.1 Table S2. Condition Optimization of Using $(EtO)_2P(O)$-H as Substrate [a]



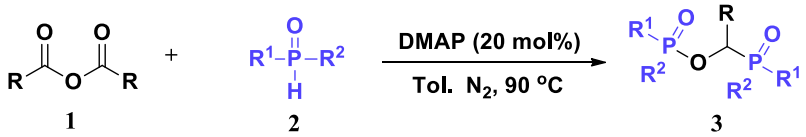
1a 4a 5a

Entry	DBU (equiv.)	1a / 2a	*T* (°C)	Solvent	Yield (%)
1	1.5	1.0 : 3.0	90	toluene	42
2	1.5	1.0 : 3.0	90	DCE	trace
3	1.5	1.0 : 3.0	90	THF	26
4	1.5	1.0 : 3.0	90	1,4-dioxane	20
5	1.5	1.0 : 3.0	90	DMSO	trace
6	1.5	1.0 : 3.0	90	DMF	trace
7	1.5	1.0 : 3.0	90	MeCN	17
8	1.5	1.0 : 3.0	60	toluene	32
9	**1.5**	**1.0 : 3.0**	**70**	**toluene**	**60**
10	1.5	1.0 : 3.0	80	toluene	49
11	1.5	1.0 : 3.0	100	toluene	34
12	1.5	1.0 : 2.5	70	toluene	33
13	1.5	1.0 : 3.5	70	toluene	36
14	0.5	1.0 : 3.0	70	toluene	22
15	1.0	1.0 : 3.0	70	toluene	43
16	2.0	1.0 : 3.0	70	toluene	32
17	2.5	1.0 : 3.0	70	toluene	33
18[b]	1.5	1.0 : 3.0	70	toluene	33
19[c]	1.5	1.0 : 3.0	70	toluene	35
20	DMAP (1.5)	1.0 : 3.0	70	toluene	trace
21	pyridine(1.5)	1.0 : 3.0	70	toluene	N.R
22	DABCO(1.5)	1.0 : 3.0	70	toluene	N.R
23	Na_2CO_3(1.5)	1.0 : 3.0	70	toluene	N.R
24	$NaHCO_3$(1.5)	1.0 : 3.0	70	toluene	N.R
25	K_3PO_4(1.5)	1.0 : 3.0	70	toluene	N.R
26	—	1.0 : 3.0	70	toluene	N.R

[a] Reaction conditions: **1a** (0.2 mmol), $(EtO)_2P(O)H$ (82.8 mg, 3.0 equiv.), DBU (1.5 equiv.), Solvent (2.0 mL), N_2, stirred at 70 °C overnight, isolated yield; [b] toluene (1.5 mL); [c] toluene (2.5 mL).

2.3 Reaction Conditions:

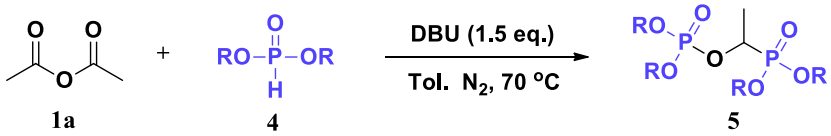
➢ **Condition A for $R^1R^2P(O)$-H**



1 2 3

Condition A: **1** (0.2 mmol, 1.0 eq.), **2** (0.6 mmol, 3.0 eq.), DMAP (4.9 mg, 0.2 eq.), toluene (2.0 mL), N_2, stirred at 90 °C overnight.

➢ **Condition B for $(RO)_2P(O)$-H**

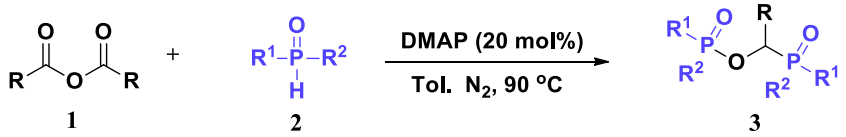


1a 4 5

Condition B: **1a** (20.4 mg, 0.2 mmol, 1.0 eq.), 4 (0.6 mmol, 3.0 eq.), DBU (45.7 mg, 1.5 eq.), toluene (2.0 mL), N_2, stirred at 70 °C overnight.

3. General Procedure for Bisphosphorylation

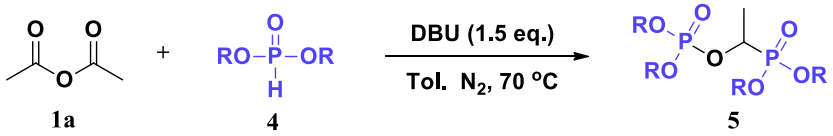
3.1 General procedure for bis-phosphorylation with $R^1R^2P(O)$-H as substrate



1 2 3

A mixture of **1** (0.2 mmol, 1.0 eq.), **2** (0.6 mmol, 3.0 eq.) and DMAP (4.9 mg, 20 mol%) was dissolved in toluene (2.0 mL) under N_2 atmosphere, stirred at 90 ^oC overnight. At the completion of the reaction, H_2O (20 mL) was added. The aqueous phase was extracted with ethyl acetate (3 x 50 mL). The combined organic fractions washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (dichloromethane / methanol = 100: 1) to afford the products **3**.

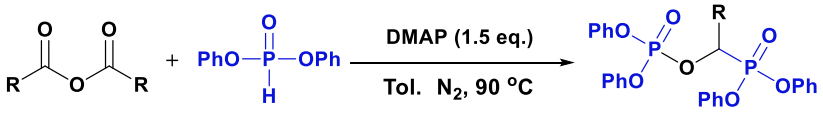
3.2 General procedure for bis-phosphorylation with $(RO)_2P(O)$-H as substrate



1a 4 5

A mixture of **1a** (20.4 mg, 0.2 mmol, 1.0 eq.), **4** (0.6 mmol, 3.0 eq.) and DBU (45.7 mg, 1.5 eq.) was dissolved in toluene (2.0 mL) under N_2 atmosphere, stirred at 70 ^oC overnight. At the completion of the reaction, the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2: 1, 300 mL, then dichloromethane / methanol = 30: 1) to afford the products **5**.

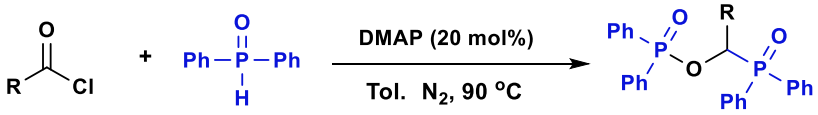
3.3 General procedure for bis-phosphorylation with $(PhO)_2P(O)$-H as substrate



1 4e 5e-5i

A mixture of **1** (0.2 mmol, 1.0 eq.), **4e** (140.4 mg, 0.6 mmol, 3.0 eq.), DMAP (36.7 mg, 0.3 mmol, 1.5 eq.) was dissolved in toluene (2.0 mL) under N_2 atmosphere, stirred at 90 ^oC overnight. At the completion of the reaction, the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6: 1) to afford products **5e-5i**.

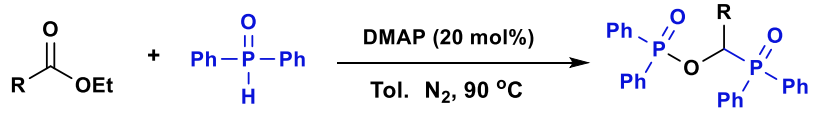
3.4 General procedure for bis-phosphorylation with RCO-Cl (**6a, 6b**) as substrate



6a, 6b 2a 3k, 3a

A mixture of **6a** (0.2 mmol, 28.1 mg, 1.0 eq.), or **6b** (0.2 mmol, 15.7 mg, 1.0 eq.), **2a** (0.6 mmol, 121.2 mg, 3.0 eq.) and DMAP (4.9 mg, 20 mol%) was dissolved in toluene (2.0 mL) under N_2 atmosphere, stirred at 90 ^oC overnight. At the completion of the reaction, H_2O (20 mL) was added. The aqueous phase was extracted with ethyl acetate (3 x 50 mL). The combined organic fractions washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (dichloromethane / methanol = 100: 1) to afford 72.2 mg of **3k** (0.142 mmol, 71%) or 29.4 mg of **3a** (0.066 mmol, 33%).

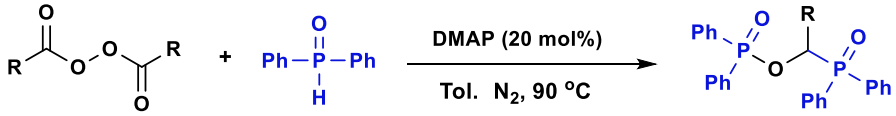
3.5 General procedure for bis-phosphorylation with RCOOEt (**6c, 6d**) as substrate



6c, 6d 2a 3a, 3f

A mixture of **6c** (0.2 mmol, 17.6 mg, 1.0 eq.), or **6d** (0.2 mmol, 28.4 mg, 1.0 eq.), **2a** (0.6 mmol, 121.2 mg, 3.0 eq.) and DMAP (4.9 mg, 20 mol%) was dissolved in toluene (2.0 mL) under N_2 atmosphere, stirred at 90 ^oC overnight. At the completion of the reaction, H_2O (20 mL) was added. The aqueous phase was extracted with ethyl acetate (3 x 50 mL). The combined organic fractions washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (dichloromethane / methanol = 100: 1) to afford 0 mg of **3a** (0%) or 29.0 mg of **3f** (0.058 mmol, 29%).

3.6 General procedure for bis-phosphorylation with peroxides (**6e, 6f**) as substrate



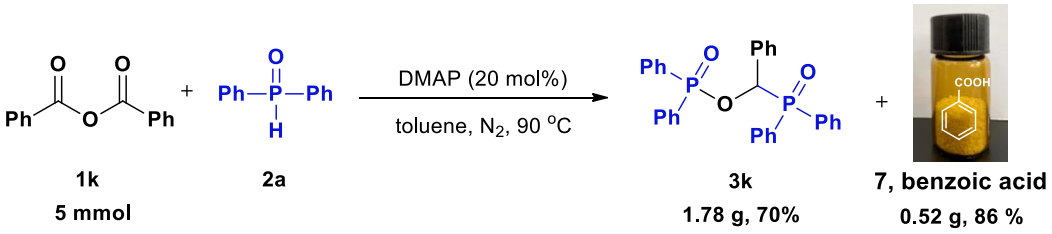
6e, 6f 2a 3r, 3k

A mixture of **6e** (0.2 mmol, 79.7 mg, 1.0 eq.), or **6f** (0.2 mmol, 48.4 mg, 1.0 eq.), **2a** (0.6 mmol, 121.2 mg, 3.0 eq.) and DMAP (4.9 mg, 20 mol%) was dissolved in

toluene (2.0 mL) under N_2 atmosphere, stirred at 90 ^oC overnight. At the completion of the reaction, H_2O (20 mL) was added. The aqueous phase was extracted with ethyl acetate (3 x 50 mL). The combined organic fractions washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (dichloromethane / methanol = 100: 1) to afford 73.9 mg of **3r** (0.126 mmol, 63%) or 45.7 mg of **3k** (0.09 mmol, 45%).

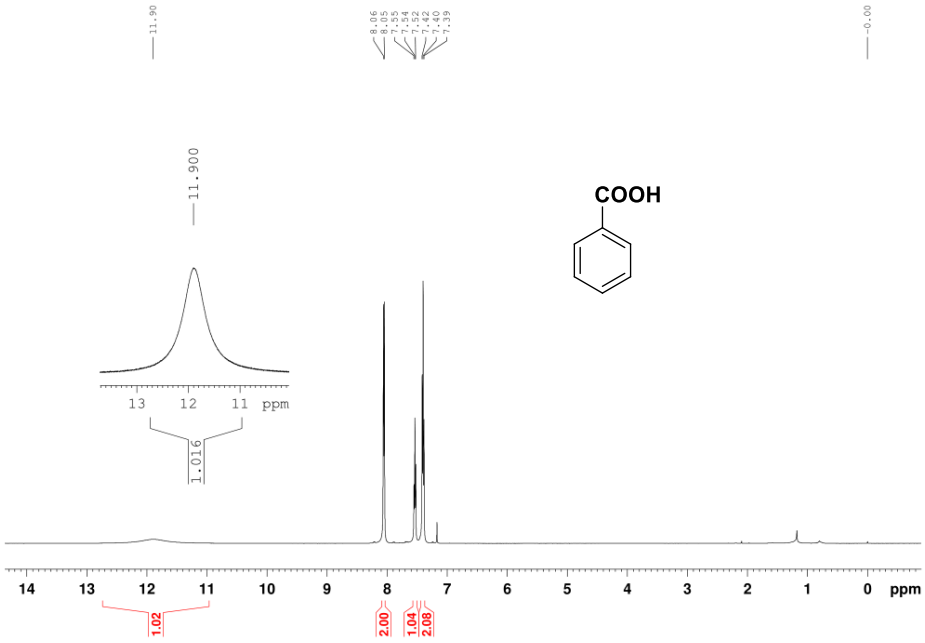
4. Applications

4.1 Large-Scale Preparation and Byproduct Recovery



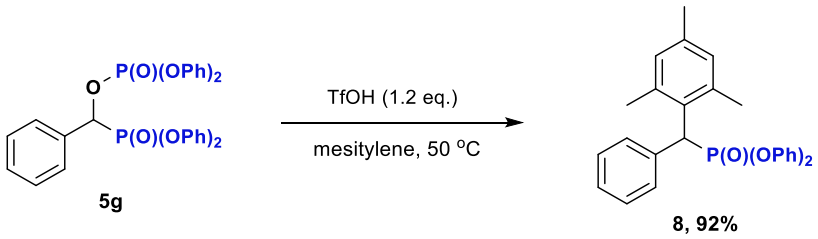
1k **5 mmol** + **2a** → **3k** **1.78 g, 70%** + **7, benzoic acid** **0.52 g, 86 %**

A mixture of **1k** (5 mmol, 1.13 g, 1.0 eq.), **2a** (15 mmol, 3.03 g, 3.0 eq.) and DMAP (122.2 mg, 20 mol%) was dissolved in toluene (45 mL) under N_2 atmosphere, stirred at 90 ^oC overnight. At the completion of the reaction, 50 mL of sat. aq. $NaHCO_3$ was added. The aqueous phase was extracted with ethyl acetate (3 x 100 mL). The combined organic fractions washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (dichloromethane / methanol = 100: 1) to afford 1.78g (3.5 mmol) of **3k** in 70% yield. Next, the conc. HCl was added to the aqueous phase until the pH = 1. After that, the white solid was dissolved by ethyl acetate (100 mL) and the aqueous phase was extracted with ethyl acetate (3 x 50 mL). The combined organic fractions dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1: 2 with 1% AcOH) to afford 0.52g (4.3 mmol) of benzoic acid (**7**) in 86% yield.

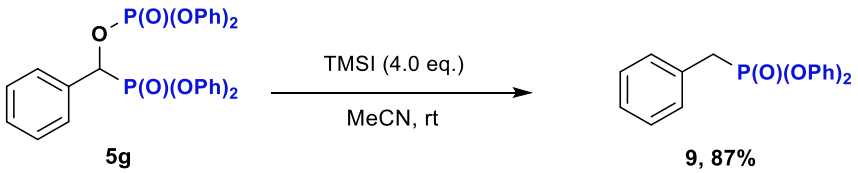


^{1}H NMR of benzoic acid **7**

4.2 Further transformations of **5h**



A mixture of **5g** (0.2 mmol, 114.4 mg, 1.0 eq.), TfOH (0.24 mmol, 36.0 mg, 1.2 eq.) was dissolved in mesitylene (0.3 mL), stirred at 50 °C overnight. At the completion of the reaction, the reaction was quenched with water, and the required compounds were extracted with EtOAc (3 × 25 mL). The combined organic layer was washed with brine, dried with Na_2SO_4, and then evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8 : 1) to afford the compound **8** in 92% yield (81.3 mg, 0.18 mmol).



A mixture of **5h** (0.2 mmol, 114.4 mg, 1.0 eq.), TMSI (iodotrimethylsilane) (0.8 mmol, 160.1 mg, 4.0 eq.) was dissolved in MeCN (2.0 mL), stirred at room

temperature for 20 min. At the completion of the reaction, the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5 : 1) to afford the compound **9** in 87% yield (56.4 mg, 0.17 mmol).

4.3 Thermal analysis of DOPO and selected bisphosphorylation samples.

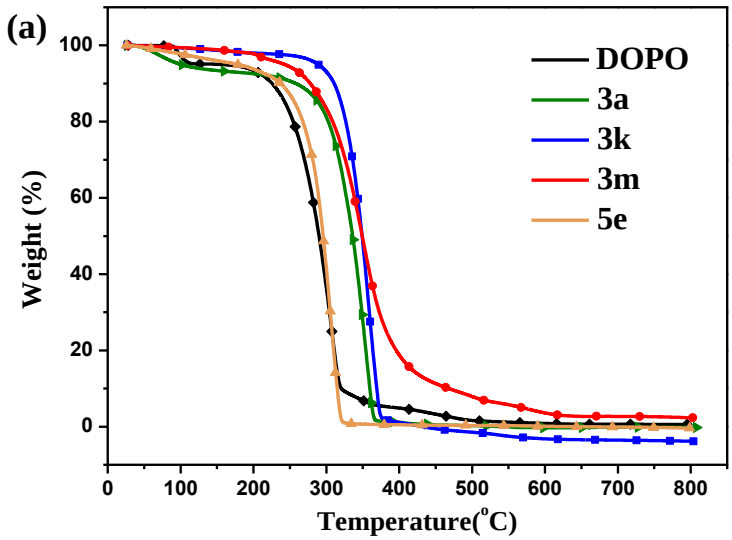


Figure. S1. TGA Curves of DOPO and **3a**, **3k**, **3m** and **5e**

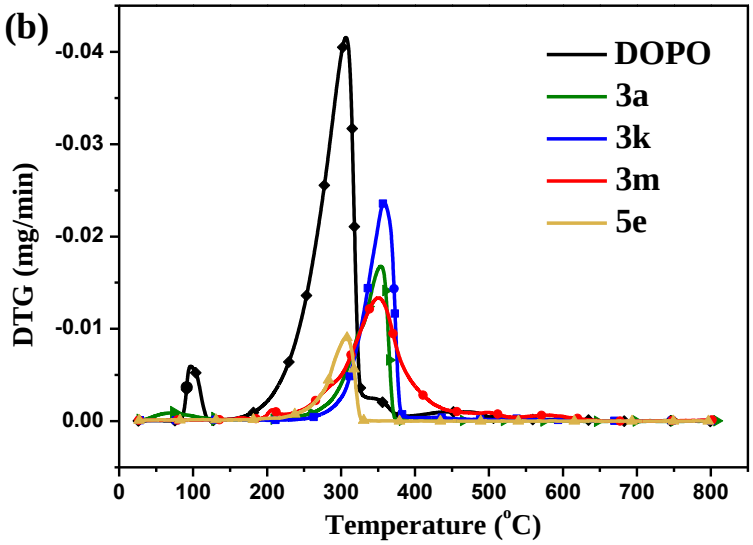
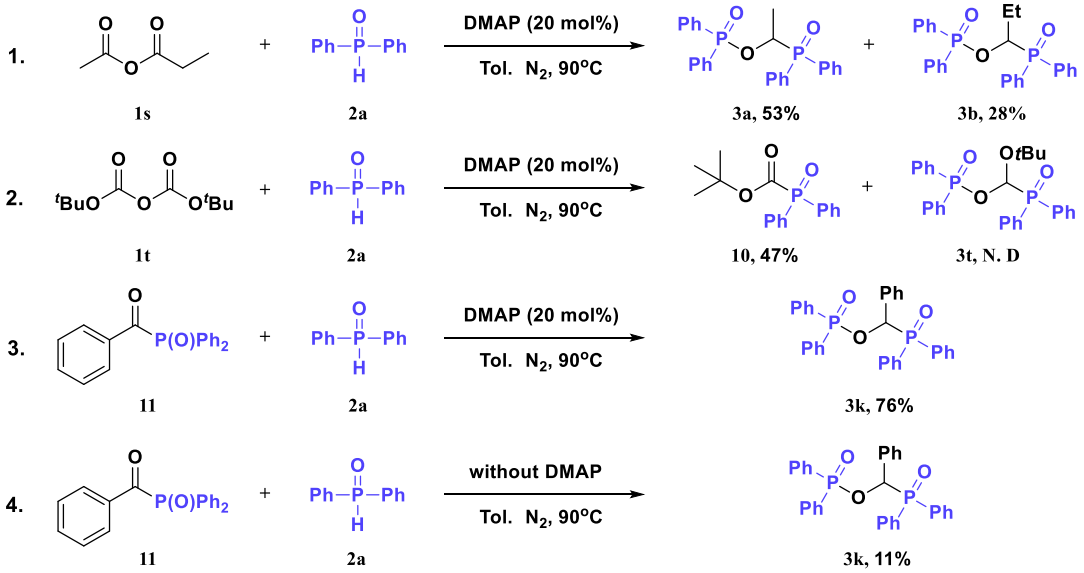


Figure. S2. DTG Curves of DOPO and **3a**, **3k**, **3m** and **5e**

Table S3. TGA and DTG data of DOPO, **3a**, **3k**, **3m** and **5e**

Sample	$T_{-5wt\%}$ (℃)	$T_{-50wt\%}$ (℃)	T_{max} (℃)
DOPO	155.2	289.9	306.6
3a	100.3	336.0	353.8
3k	289.0	349.0	358.1
3m	242.7	349.1	350.2
5e	178.5	295.5	307.0

5. Mechanism studies



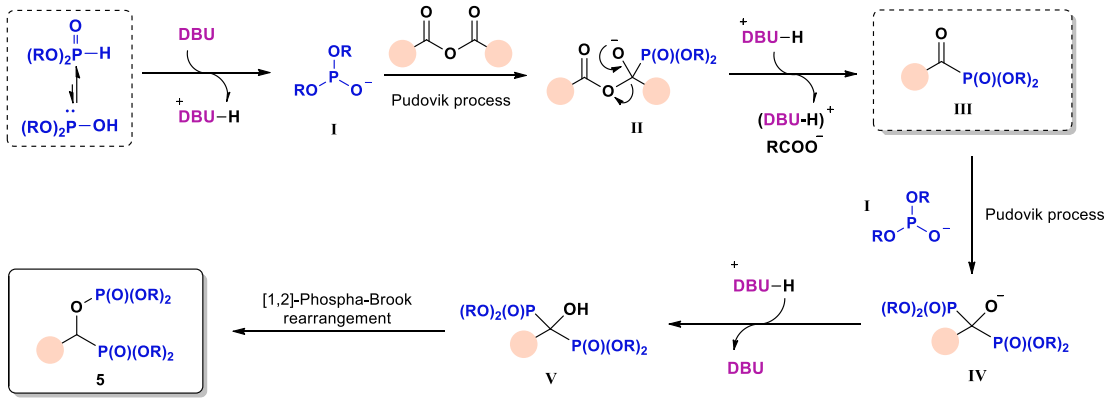
Scheme S1. Control experiments.[a]

Several control experiments were carried out to deduce key information about the reaction pathway (Scheme S1). When a mixed acid anhydride, acetic propionic anhydride (**1s**) was used as a substrate, we obtained the bisphosphorylation products **3a** and **3b** in a 53% and a 28% yield, respectively (Scheme S1-1). Moreover, by using di-*tert*-butyl dicarbonate (**1t**) as substrate, we only obtained acylphosphine oxide (**10**) instead of the bisphosphorylation product (**3t**) (Scheme S1-2). These results indicate that steric hindrance has an obvious effect and the reaction of anhydride with large steric hindrance may terminate in the first step to give acylphosphine oxide as the intermediate. To verify the above hypothesis, we employed compound **11** as the substrate (Scheme S1-3), and it could be smoothly converted into the desired bisphosphorylation product (**3k)** under the standard conditions. Without adding DMAP, the yield of **3k** dropped sharply (Scheme S1-4),

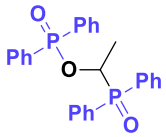
which indicate that DMAP also play an important role to promote the addition of **2a** to **11**.

[a] Compound **11** was prepared according to the literature: *Org. Lett.* **2020**, 22, 4633−4637.

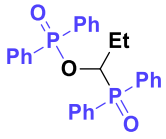
Scheme S2. Possible Mechanism for the DBU-promoted bisphosphorylation of anhydride with phosphite.



6. Characterization of the Products

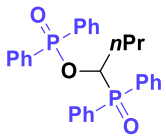


1-(diphenylphosphoryl)ethyl diphenylphosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 74.0 mg (0.166 mmol, 83%) of **3a** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97-7.93 (m, 2H), 7.80-7.76 (m, 2H), 7.71-7.66 (m, 2H), 7.56-7.39 (m, 10H), 7.30-7.22 (m, 4H), 5.48-5.41 (m, 1H), 1.53 (dd, J = 7.0 Hz, 14.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.4 (d, J_{C-P} = 2.6 Hz), 132.3, 132.2 (d, J_{C-P} = 8.9 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 131.6 (d, J_{C-P} = 4.4 Hz), 131.5 (d, J_{C-P} = 3.3Hz), 131.2 (d, J_{C-P} = 10.5 Hz), 130.7 (d, J_{C-P} = 132.2 Hz), 130.5 (d, J_{C-P} = 105.0 Hz), 128.7 (d, J_{C-P} = 11.6 Hz), 128.5 (d, J_{C-P} = 5.9 Hz), 128.4 (d, J_{C-P} = 7.4 Hz), 128.3 (d, J_{C-P} = 13.3Hz), 127.9, 70.0 (dd, J_1 = 7.7 Hz, J_2 = 89.1 Hz), 15.9. ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.91 (d, J = 26.8 Hz), 31.19 (d, J = 25.2 Hz). MS (ESI): 446.7 $(M+H)^+$.
The analytical data matched those reported in the literature.[4]

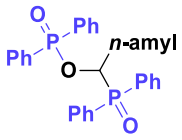


1-(diphenylphosphoryl)propyl diphenylphosphinate. Performed according to the general procedure (conditions A, 26.0 mg of **1b,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 67.2 mg (0.146 mmol, 73%) of **3b** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.79-7.75 (m, 2H), 7.72-7.68 (m, 2H), 7.51-7.48 (m, 2H), 7.46-7.35 (m, 8H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 2H), 5.43-5.38 (m, 1H),

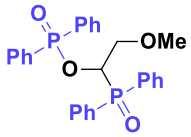
2.03-1.93 (m, 2H), 0.85 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.8, 132.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.3 Hz), 132.0 (d, $J_{C\text{-}P}$ = 8.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 1.7 Hz), 131.3, 131.1 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.9, 130.0 (d, $J_{C\text{-}P}$ = 142.7 Hz), 128.7, 128.6, 128.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 1.4 Hz), 128.51 (d, $J_{C\text{-}P}$ = 13.1 Hz), 75.1 (dd, J_1 = 8.3 Hz, J_2 = 87.2 Hz), 24.1, 10.7 (d, $J_{C\text{-}P}$ = 7.8 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.73 (d, J = 22.1 Hz), 30.38 (d, J = 21.9 Hz). HRMS calc. for $C_{27}H_{27}O_3P_2$ (M+H) $^+$: 461.1430, found 461.1426.



1-(diphenylphosphoryl)butyl diphenylphosphinate Performed according to the general procedure (conditions A, 31.6 mg of **1c,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 68.3 mg (0.144 mmol, 72%) of **3c** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95-7.91 (m, 2H), 7.78-7.74 (m, 2H), 7.71-7.67 (m, 2H), 7.51-7.48 (m, 2H), 7.46-7.35 (m, 8H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 2H), 5.49-5.44 (m, 1H), 1.92-1.85 (m, 2H), 1.36-1.21 (m, 2H), 0.66 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.8, 132.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.1 (d, $J_{C\text{-}P}$ = 5.3 Hz), 132.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.4, 131.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 96.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.7 Hz), 130.0 (d, $J_{C\text{-}P}$ = 155.4 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.4 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.2 (d, $J_{C\text{-}P}$ = 13.5 Hz), 73.7 (dd, J_1 = 8.3 Hz, J_2 = 87.5 Hz), 32.7, 19.3 (d, $J_{C\text{-}P}$ = 8.1 Hz), 13.6. ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.62 (d, J = 20.2 Hz), 30.6 (d, J = 21.0 Hz). HRMS calc. for $C_{28}H_{29}O_3P_2$ (M+H) $^+$: 475.1586, found 475.1583.

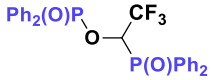


1-(diphenylphosphoryl)hexyl diphenylphosphinate Performed according to the general procedure (conditions A, 42.9 mg of **1d,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 61.2 mg (0.122 mmol, 61%) of **3d** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96-7.92 (m, 2H), 7.79-7.68 (m, 4H), 7.50-7.47 (m, 2H), 7.45-7.34 (m, 8H), 7.30-7.26 (m, 2H), 7.21-7.17 (m, 2H), 5.50-5.45 (m, 1H), 1.92-1.85 (m, 2H), 1.27-1.18 (m, 2H), 1.05-0.94 (m, 4H), 0.67 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.9, 132.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 131.8, 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.4 (d, $J_{C\text{-}P}$ = 5.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 4.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 96.7 Hz), 130.1 (d, $J_{C\text{-}P}$ = 161.7 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.5, 128.4 (d, $J_{C\text{-}P}$ = 12.6 Hz), 128.1 (d, $J_{C\text{-}P}$ = 13.5 Hz), 73.8 (dd, J_1 = 8.4 Hz, J_2 = 87.5 Hz), 31.2, 30.5, 25.5 (d, $J_{C\text{-}P}$ = 8.0 Hz), 22.0, 13.7. ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.55 (d, J = 20.1 Hz), 30.5 (d, J = 20.1 Hz). HRMS calc. for $C_{30}H_{33}O_3P_2$ (M+H) $^+$: 503.1899, found 503.1895.



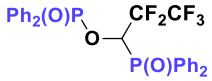
(diphenylphosphoryl)(methoxy)methyl diphenylphosphinate. Performed according to the general procedure (conditions A, 32.4 mg of **1e,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 71.4 mg (0.15 mmol, 75%) of **3e** as

colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95-7.91 (m, 2H), 7.84-7.80 (m, 2H), 7.74-7.69 (m, 2H), 7.54-7.36 (m, 10H), 7.29-7.24 (m, 2H), 7.22-7.18 (m, 2H), 5.68-5.63 (m, 1H), 3.82-3.78 (m, 1H), 3.73-3.68 (m, 1H), 2.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.6, 132.3 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.1, 132.0 (d, $J_{C\text{-}P}$ = 9.3 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.5, 131.4 (d, $J_{C\text{-}P}$ = 10.2 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.2 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.3 Hz), 129.7 (d, $J_{C\text{-}P}$ = 97.1 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.6, 128.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.1 (d, $J_{C\text{-}P}$ = 9.9 Hz), 128.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 72.6 (dd, J_1 = 8.4 Hz, J_2 = 86.2 Hz), 70.6 (d, $J_{C\text{-}P}$ = 6.7 Hz), 58.0. ^{31}P NMR (203 MHz, $CDCl_3$): δ 34.93 (d, J = 20.3 Hz), 28.74 (d, J = 20.3 Hz). HRMS calc. for $C_{27}H_{27}O_4P_2$ $(M+H)^+$: 477.1379, found 477.1375.



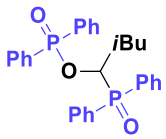
1-(diphenylphosphoryl)-2,2,2-trifluoroethyl diphenylphosphinate. Performed according to the general procedure (conditions A at 120°C instead, 42.0 mg of **1f,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 52.0 mg (0.104 mmol, 52%) of **3f** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92-7.83 (m, 4H), 7.74-7.70 (m, 2H), 7.55-7.50 (m, 2H), 7.46-7.32 (m, 8H), 7.30-7.26 (m, 2H), 7.22-7.19 (m, 2H), 6.01-5.93 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.7 (dd, $J_{C\text{-}F}$ = 2.7 Hz, $J_{C\text{-}P}$ = 11.1 Hz), 132.1, 132.0 (d, $J_{C\text{-}P}$ = 9.3 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.7 Hz), 131.3 (d, $J_{C\text{-}P}$ = 10.6 Hz), 131.1, 130.8 (d, $J_{C\text{-}P}$ = 10.9 Hz), 130.0 (d, $J_{C\text{-}P}$ = 3.6 Hz), 129.2 (d, $J_{C\text{-}P}$ = 103.1 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 7.7 Hz), 128.4 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.2 (d, $J_{C\text{-}P}$ = 13.7 Hz), 127.5 (d, $J_{C\text{-}P}$ = 104.7 Hz), 69.9 (qd, J_1 = 7.7 Hz, J_2 = 32.1 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 38.32 (d, J = 10.7 Hz), 24.93 (d, J = 12.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -66.72 (d, $J_{P\text{-}F}$ = 3.1 Hz). MS (ESI): 500.9 $(M+H)^+$.

The analytical data matched those reported in the literature.[5]



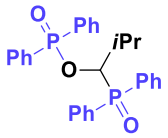
1-(diphenylphosphoryl)-2,2,3,3,3-pentafluoropropyl diphenylphosphinate. Performed according to the general procedure (conditions A at 120°C instead, 121.2 mg of **1g,** 60.6 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 50.6 mg (0.092 mmol, 46%) of **3g** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91-7.81 (m, 4H), 7.73-7.69 (m, 2H), 7.50-7.47 (m, 2H), 7.41-7.33 (m, 8H), 7.30-7.27 (m, 2H), 7.22-7.19 (m, 2H), 6.18-6.10 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.6 (dd, $J_{C\text{-}F}$ = 2.9 Hz, $J_{C\text{-}P}$ = 5.9 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.8, 131.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.3, 131.0 (d, $J_{C\text{-}P}$ = 10.7 Hz), 130.7 (d, $J_{C\text{-}P}$ = 10.3 Hz), 130.4 (d, $J_{C\text{-}P}$ = 47.0 Hz), 129.5 (d, $J_{C\text{-}P}$ = 103.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.6 Hz), 128.4 (d, $J_{C\text{-}P}$ = 7.2Hz), 128.3 (d, $J_{C\text{-}P}$ = 8.4 Hz), 128.2 (d, $J_{C\text{-}P}$ = 13.6 Hz), 127.6 (d, $J_{C\text{-}P}$ = 104.1 Hz), 70.3-69.2 (m). ^{31}P NMR (203 MHz, $CDCl_3$): δ 37.48 (d, J = 7.5 Hz), 24.80. ^{19}F NMR (470 MHz, $CDCl_3$): δ -81.13, -113.82 (ddd, J_1 = 7.1 Hz, J_2 = 282.7 Hz, J_3 = 1036.7 Hz). MS (ESI): 550.9 $(M+H)^+$.

The analytical data matched those reported in the literature.[6]

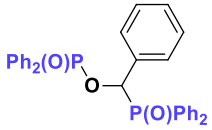


1-(diphenylphosphoryl)-3-methylbutyl diphenylphosphinate. Performed according to the general procedure (conditions A, 37.3 mg of **1h,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 69.3 mg (0.142 mmol, 71%)

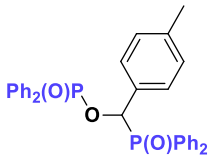
of **3h** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95-7.91 (m, 2H), 7. 80-7.76 (m, 2H), 7.72-7.67 (m, 2H), 7.50-7.46 (m, 2H), 7.42-7.28 (m, 10H), 7.21-7.17 (m, 2H), 5.56-5.52 (m, 1H), 1.93-1.85 (m, 1H), 1.67-1.60 (m, 1H), 1.53-1.46 (m, 1H), 0.73 (d, J = 6.5 Hz, 3H), 0.63 (d, J = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.0, 132.1, 132.0 (d, J_{C-P} = 2.8 Hz), 132.0 (d, J_{C-P} = 8.6 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 131.4 (d, J_{C-P} = 5.7 Hz), 131.3 (d, J_{C-P} = 6.8 Hz), 131.2 (d, J_{C-P} = 130.3 Hz), 131.0 (d, J_{C-P} = 10.4 Hz), 129.9 (d, J_{C-P} = 169.7Hz), 128.6 (d, J_{C-P} = 11.4 Hz), 128.4, 128.3 (d, J_{C-P} = 12.4 Hz), 128.1(d, J_{C-P} = 13.2 Hz), 72.3 (dd, J_1 = 8.6 Hz, J_2 = 87.5 Hz), 39.3, 24.6 (d, J_{C-P} = 9.2 Hz), 22.8, 21.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.42 (d, J = 17.8 Hz), 31.11 (d, J = 20.1 Hz). MS (ESI): 488.9 $(M+H)^+$.
The analytical data matched those reported in the literature.[7]



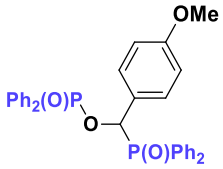
1-(diphenylphosphoryl)-2-methylpropyl diphenylphosphinate Performed according to the general procedure (conditions A, 31.6 mg of **1i,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 37.9 mg (0.08 mmol, 40%) of **3i** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91-7.87 (m, 2H), 7. 83-7.73 (m, 4H), 7.49-7.47 (m, 2H), 7.43-7.39 (m, 4H), 7.35-7.23 (m, 6H), 7.17-7.14 (m, 2H), 5.54 (dd, J_1 = 2.7 Hz, J_2 = 11.6 Hz, 1H), 2.34-2.26 (m, 1H), 1.00 (d, J = 6.9 Hz, 3H), 0.85 (d, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.3, 132.3 (d, J_{C-P} = 7.3 Hz), 132.2, 132.1 (d, J_{C-P} = 2.7 Hz), 132.0, 131.9 (d, J_{C-P} = 8.9 Hz), 131.8 (d, J_{C-P} = 2.7 Hz), 131.4 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 49.9 Hz), 131.2 (d, J_{C-P} = 10.1 Hz), 131.1 (d, J_{C-P} = 9.0 Hz), 130.9 (d, J_{C-P} = 10.6 Hz), 130.0 (d, J_{C-P} = 97.7 Hz), 128.7 (d, J_{C-P} = 11.5 Hz), 128.4 (d, J_{C-P} = 13.4 Hz), 128.2 (d, J_{C-P} = 11.6 Hz), 128.0 (d, J_{C-P} = 13.4 Hz), 77.9 (dd, J_1 = 8.6 Hz, J_2 = 85.3 Hz), 30.0, 21.2 (d, J_{C-P} = 10.7 Hz), 17.5 (d, J_{C-P} = 1.4 Hz).. ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.50 (d, J = 16.8 Hz), 28.63 (d, J = 17.0 Hz). HRMS calc. for $C_{28}H_{29}O_3P_2$ $(M+H)^+$: 475.1586, found 475.1587.



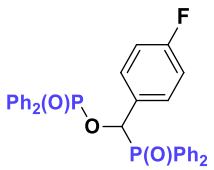
(diphenylphosphoryl)(phenyl)methyl diphenylphosphinate. Performed according to the general procedure (conditions A, 45.2 mg of **1k,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 75.2 mg (0.148 mmol, 74%) of **3k** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-7.99 (m, 2H), 7. 62-7.59 (m, 2H), 7. 54-7.51 (m, 1H), 7.47-7.39 (m, 6H), 7.36-7.22 (m, 7H), 7.17-7.07 (m, 5H), 7.01 (t, J = 7.7 Hz, 2H), 6.32 (dd, J_1 = 2.6 Hz, J_2 = 10.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.5 (d, J_{C-P} = 8.5 Hz), 132.4, 132.3 (d, J_{C-P} = 2.5 Hz), 132.1 (d, J_{C-P} = 6.9 Hz), 131.9 (d, J_{C-P} = 2.9 Hz), 131.7 (d, J_{C-P} = 10.8 Hz), 131.6 (d, J_{C-P} = 9.1 Hz), 131.2 (d, J_{C-P} = 10.7 Hz), 131.0 (d, J_{C-P} = 81.6 Hz), 130.2 (d, J_{C-P} = 7.9 Hz), 129.5 (d, J_{C-P} = 107.1 Hz), 129.2 (d, J_{C-P} = 4.7 Hz), 128.6, 128.5, 128.4 (d, J_{C-P} = 3.0 Hz), 128.3 (d, J_{C-P} = 6.5 Hz), 128.0 (d, J_{C-P} = 31.1 Hz), 127.8 (d, J_{C-P} = 6.9 Hz), 74.7 (dd, J_1 = 7.6 Hz, J_2 = 85.6 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.43 (d, J = 25.0 Hz), 28.93 (d, J = 23.5 Hz). MS (ESI): 508.9 $(M+H)^+$.
The analytical data matched those reported in the literature.[8]



(diphenylphosphoryl)(p-tolyl)methyl diphenylphosphinate. Performed according to the general procedure (conditions A, 50.9 mg of **1l,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 83.5 mg (0.160 mmol, 80%) of **3l** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02-7.98 (m, 2H), 7.64-7.60 (m, 2H), 7.54-7.51 (m, 1H), 7.47-7.38 (m, 6H), 7.35-7.29 (m, 5H), 7.27-7.22 (m, 2H), 7.16-7.12 (m, 2H), 7.06 (d, J = 7.1 Hz, 2H), 6.82 (d, J = 7.9 Hz, 2H), 6.27 (dd, J_1 = 2.3 Hz, J_2 = 10.2 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4 (d, $J_{C\text{-}P}$ = 1.7 Hz), 132.4 (d, $J_{C\text{-}P}$ = 8.6 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 6.4 Hz), 131.7 (d, $J_{C\text{-}P}$ = 3.3 Hz), 131.6 (d, $J_{C\text{-}P}$ = 4.6 Hz), 131.5, 131.4 (d, $J_{C\text{-}P}$ = 8.7 Hz), 131.2 (d, $J_{C\text{-}P}$ = 10.7 Hz), 130.4 (d, $J_{C\text{-}P}$ = 98.9 Hz), 130.3 (d, $J_{C\text{-}P}$ = 2.2 Hz), 129.3, 129.1 (d, $J_{C\text{-}P}$ = 4.9 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.2 (d, $J_{C\text{-}P}$ = 8.6 Hz), 128.1, 127.8 (d, $J_{C\text{-}P}$ = 13.4 Hz), 74.7 (dd, J_1 = 7.6 Hz, J_2 = 86.6 Hz), 21.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 35.24 (d, J = 25.2 Hz), 28.84 (d, J = 25.2 Hz). HRMS calc. for $C_{32}H_{29}O_3P_2$ $(M+H)^+$: 523.1586, found 523.1585.

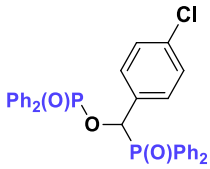


(diphenylphosphoryl)(4-methoxyphenyl)methyl diphenylphosphinate. Performed according to the general procedure (conditions A, 57.3 mg of **1m,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 82.9 mg (0.154 mmol, 77%) of **3m** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-7.99 (m, 2H), 7.62-7.52 (m, 3H), 7.49-7.37 (m, 6H), 7.34-7.29 (m, 5H), 7.27-7.22 (m, 2H), 7.17-7.12 (m, 4H), 6.56 (d, J = 8.7 Hz, 2H), 6.26 (dd, J_1 = 1.9 Hz, J_2 = 10.1 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8 (d, $J_{C\text{-}P}$ = 1.6 Hz), 132.4 (d, $J_{C\text{-}P}$ = 8.9 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.0 (d, $J_{C\text{-}P}$ = 6.1 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.6 Hz), 131.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.5, 131.2 (d, $J_{C\text{-}P}$ = 10.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 67.5 Hz), 130.8 (d, $J_{C\text{-}P}$ = 5.2 Hz), 130.4 (d, $J_{C\text{-}P}$ = 3.7 Hz), 129.7 (d, $J_{C\text{-}P}$ = 102.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.2 (d, $J_{C\text{-}P}$ = 13.5 Hz),127.8 (d, $J_{C\text{-}P}$ = 13.4 Hz), 124.4, 113.3, 74.4 (dd, J_1 = 7.6 Hz, J_2 = 87.7 Hz), 55.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 35.21 (d, J = 25.5 Hz), 28.89 (d, J = 25.3 Hz). HRMS calc. for $C_{32}H_{29}O_4P_2$ $(M+H)^+$: 539.1536, found 539.1531.

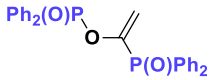


(diphenylphosphoryl)(4-fluorophenyl)methyl diphenylphosphinate. Performed according to the general procedure (conditions A, 52.4 mg of **1n,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 80.0 mg (0.152 mmol, 76%) of **3n** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-7.99 (m, 2H), 7.62-7.54 (m, 3H), 7.50-7.38 (m, 6H), 7.35-7.30 (m, 5H), 7.28-7.24 (m, 2H), 7.18-7.15 (m, 4H), 6.70 (t, J = 8.7 Hz, 2H), 6.30 (dd, J_1 = 2.2 Hz, J_2 = 10.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7 (dd, $J_{C\text{-}P}$ = 1.8 Hz, $J_{C\text{-}F}$ = 246.7 Hz),

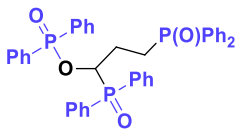
132.4, 132.3 (d, J_{C-P} = 3.6 Hz), 132.2 (d, J_{C-P} = 2.6 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 131.6 (d, J_{C-P} = 10.6 Hz), 131.5 (d, J_{C-P} = 9.0 Hz), 131.2 (d, J_{C-P} = 10.7 Hz), 131.1 (d, J_{C-P} = 8.1 Hz), 130.8 (d, J_{C-P} = 69.0 Hz), 130.1 (d, J_{C-P} = 9.3 Hz), 129.3 (d, J_{C-P} = 102.5 Hz), 128.6, 128.5 (d, J_{C-P} = 2.6 Hz), 128.4, 128.2 (d, J_{C-P} = 13.6 Hz), 128.1, 127.9 (d, J_{C-P} = 13.1 Hz), 114.7 (d, J_{C-F} = 21.0 Hz), 73.8 (dd, J_1 = 7.7 Hz, J_2 = 86.2 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 35.51 (d, J = 25.0 Hz), 28.85 (d, J = 25.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.54 (d, J_{P-F} = 2.8 Hz). HRMS calc. for $C_{31}H_{26}FO_3P_2$ $(M+H)^+$: 527.1336, found 527.1335.



(4-chlorophenyl)(diphenylphosphoryl)methyl diphenylphosphinate. Performed according to the general procedure (conditions A, 59.0 mg of **1o,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 87.8 mg (0.162 mmol, 81%) of **3o** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01-7.98 (m, 2H), 7.63-7.54 (m, 3H), 7.49-7.31 (m, 11H), 7.28-7.24 (m, 2H), 7.20-7.16 (m, 2H), 7.10-7.08 (m, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.28 (dd, J_1 = 2.7 Hz, J_2 = 10.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.6 (d, J_{C-P} = 2.3 Hz), 132.4 (d, J_{C-P} = 2.8 Hz), 132.3, 132.2 (d, J_{C-P} = 3.3 Hz), 132.2 (d, J_{C-P} = 2.7 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 131.6 (d, J_{C-P} = 10.8 Hz), 131.5 (d, J_{C-P} = 9.1 Hz), 131.1 (d, J_{C-P} = 10.8 Hz), 131.0, 130.6 (d, J_{C-P} = 80.9 Hz), 130.4 (d, J_{C-P} = 4.9 Hz), 129.9 (d, J_{C-P} = 16.4 Hz), 129.1 (d, J_{C-P} = 104.8 Hz), 128.5 (d, J_{C-P} = 8.7 Hz), 128.4 (d, J_{C-P} = 8.7 Hz), 128.2 (d, J_{C-P} = 13.5 Hz), 128.0, 127.9, 73.9 (dd, J_1 = 7.6 Hz, J_2 = 85.1 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 35.68 (d, J = 23.8 Hz), 28.82 (d, J = 24.8 Hz). HRMS calc. for $C_{31}H_{26}ClO_3P_2$ $(M+H)^+$: 543.1040, found 543.1040.

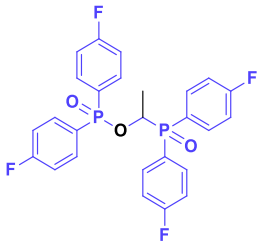


1-(diphenylphosphoryl)vinyl diphenylphosphinate. Performed according to the general procedure (conditions A, 34.2 mg of **1p,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 51.5 mg (0.116 mmol, 58%) of **3p** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.74 (m, 4H), 7.61-7.58 (m, 2H), 7.54-7.45 (m, 10H), 7.37-7.33 (m, 4H), 6.05 (ddd, J_1 = 1.0 Hz, J_2 = 3.3 Hz, J_3 = 28.3 Hz), 5.70 (ddd, J_1 = 1.5 Hz, J_2 = 3.2 Hz, J_3 = 9.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1 (dd, J_1 = 12.1 Hz, J_2 = 127.4 Hz), 132.5 (dd, J_1 = 2.7 Hz, J_2 = 10.9 Hz), 132.1 (d, J_{C-P} = 10.2 Hz), 131.5 (d, J_{C-P} = 10.8 Hz), 130.4 (d, J_{C-P} = 26.2 Hz), 129.4 (d, J_{C-P} = 3.6 Hz), 128.6 (d, J_{C-P} = 7.2 Hz), 128.5 (d, J_{C-P} = 8.3 Hz), 113.7 (dd, J_1 = 6.2 Hz, J_2 = 18.1 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 32.22 (d, J = 16.8 Hz), 22.34 (d, J = 17.3 Hz). HRMS calc. for $C_{26}H_{23}O_3P_2$ $(M+H)^+$: 445.1117, found 445.1114.

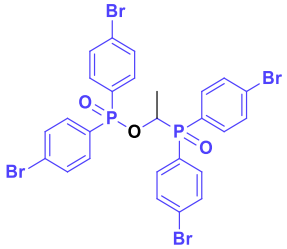


1,3-bis(diphenylphosphoryl)propyl diphenylphosphinate. Performed according to the general procedure (conditions A, 25.2 mg of **1q,** 121.2 mg of **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 21.1 mg (0.032 mmol, 16%) of **3q** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.86-7.82 (m, 2H), 7.73-7.68 (m, 4H), 7.52-7.44

(m, 8H), 7.41-7.27 (m, 14H), 7.21-7.17 (m, 2H), 5.57-5.53 (m, 1H), 2.53-2.46 (m, 1H), 2.42-2.33 (m, 1H), 2.25-2.18 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.9, 132.5 (d, J_{C-P} = 4.2 Hz), 132.3 (td, J_1 = 2.6 Hz, J_2 = 10.4 Hz), 132.1, 131.9 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 9.0 Hz), 131.6 (d, J_{C-P} = 31.9 Hz), 131.6 (t, J_{C-P} = 2.5 Hz), 131.4, 131.3, 131.2, 131.0 (d, J_{C-P} = 10.3 Hz), 130.7, 130.6, 130.5, 130.4 (d, J_{C-P} = 62.9 Hz), 129.4 (d, J_{C-P} = 106.2 Hz), 128.8, 128.7 (d, J_{C-P} = 3.9 Hz), 128.6, 128.5 (d, J_{C-P} = 11.8 Hz), 128.3 (d, J_{C-P} = 13.5 Hz), 128.2, 73.6 (ddd, J_1 = 8.3 Hz, J_2 = 15.4 Hz, J_3 = 86.0 Hz), 26.0 (dd, J_1 = 7.2 Hz, J_2 = 71.0 Hz), 23.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 34.43 (d, J = 19.4 Hz), 31.9, 30.5 (d, J = 18.0 Hz). HRMS calc. for $C_{39}H_{36}O_4P_3$ $(M+H)^+$: 661.1821, found 661.1816.

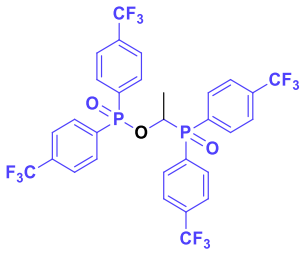


1-(bis(4-fluorophenyl)phosphoryl)ethyl bis(4-fluorophenyl)phosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 142.8 mg of bis(4-fluorophenyl)phosphine oxide **2b** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 90.1 mg (0.174 mmol, 87%) of **3aa** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93-7.88 (m, 2H), 7.81-7.69 (m, 4H), 7.35-7.30 (m, 2H), 7.19-7.12 (m, 6H), 7.01-6.97 (m, 2H), 5.52-5.46 (m, 1H), 1.49 (dd, J_1 = 7.0 Hz, J_2 = 14.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4 (dd, J_1 = 1.9 Hz, J_2 = 252.9 Hz), 165.2 (ddd, J_1 = 3.2 Hz, J_2 = 25.0 Hz, J_3 = 253.4 Hz), 134.5, 134.4, 134.3, 134.1 (d, J_{C-P} = 8.8 Hz), 134.0 (d, J_{C-P} = 8.9 Hz), 133.9 (d, J_{C-P} = 4.7 Hz), 133.8, 133.6 (d, J_{C-P} = 9.0 Hz), 133.5 (d, J_{C-P} = 9.0 Hz), 127.6 (dd, J_1 = 3.2 Hz, J_2 = 112.4 Hz), 126.7 (dd, J_1 = 3.4 Hz, J_2 = 74.1 Hz), 125.8 (dd, J_1 = 3.4 Hz, J_2 = 58.7 Hz), 124.1 (dd, J_1 = 3.5 Hz, J_2 = 102.4 Hz), 116.4 (d, J_{C-P} = 12.7 Hz), 116.3, 116.2, 116.1 (d, J_{C-P} = 12.7 Hz), 116.0 (d, J_{C-P} = 3.3 Hz), 115.9 (d, J_{C-P} = 4.0 Hz), 115.8 (d, J_{C-P} = 6.5 Hz), 115.6, 69.7 (dd, J_1 = 7.8 Hz, J_2 = 90.1 Hz), 15.7. ^{31}P NMR (203 MHz, $CDCl_3$): δ 32.42 (d, J = 23.3 Hz), 29.69 (d, J = 23.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -105.0 (d, J = 118.7 Hz), -105.3 (d, J = 123.1 Hz). HRMS calc. for $C_{26}H_{21}F_4O_3P_2$ $(M+H)^+$: 519.0897, found 519.0892.

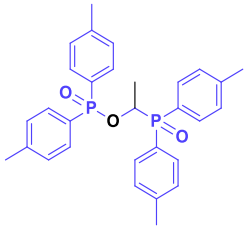


1-(bis(4-bromophenyl)phosphoryl)ethyl bis(4-bromophenyl)phosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 214.7 mg of bis(4-bromophenyl)phosphine oxide **2c** and 4.9 mg of DMAP),, and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 144.8 mg (0.19 mmol, 95%) of **3ab** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.69 (m, 2H), 7.63-7.52 (m, 10H), 7.45-7.43 (m, 2H), 7.16-7.12 (m, 2H), 5.52-5.46 (m, 1H), 1.50 (dd, J_1 = 7.0 Hz, J_2 = 14.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.3 (d, J_{C-P} = 9.3 Hz), 132.7 (t, J_{C-P} = 9.3 Hz), 132.4, 132.2 (d, J_{C-P} = 2.4 Hz), 132.1 (d, J_{C-P} = 4.8 Hz), 132.0, 131.9 (d, J_{C-P} = 13.7 Hz), 131.7, 130.3 (d, J_{C-P} = 131.5 Hz), 129.5 (d, J_{C-P} = 81.3 Hz), 128.5 (d, J_{C-P} = 45.5 Hz), 128.2 (d, J_{C-P} = 3.5 Hz), 128.1 (dd, J_1 = 3.7 Hz, J_2 = 34.9 Hz), 128.0, 127.1 (d, J_{C-P} = 100.2 Hz), 69.6 (dd, J_1 = 7.7 Hz,

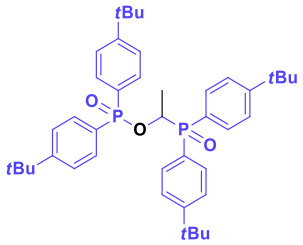
J_2 = 89.4 Hz), 15.8. ^{31}P NMR (203 MHz, $CDCl_3$): δ 32.86 (d, J = 22.6 Hz), 29.79 (d, J = 22.6 Hz). HRMS calc. for $C_{26}H_{21}Br_4O_3P_2$ $(M+H)^+$: 762.7653, found 762.7652.



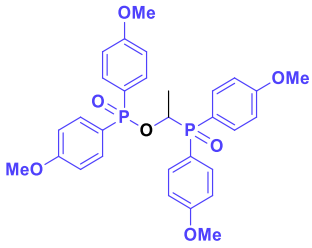
1-(bis(4-(trifluoromethyl)phenyl)phosphoryl)ethyl bis(4-(trifluoromethyl)phenyl)phosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 202.8 mg of bis(4-(trifluoromethyl)phenyl)phosphine oxide **2d** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 140.7 mg (0.196 mmol, 98%) of **3ac** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09-7.89 (m, 6H), 7.77-7.74 (m, 4H), 7.68-7.66 (m, 2H), 7.55-7.47 (m, 4H), 5.81-5.75 (m, 1H), 1.59 (dd, J_1 = 7.0 Hz, J_2 = 14.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.9, 134.8 (d, $J_{C\text{-}P}$ = 3.8 Hz), 134.7, 134.6 (dd, J_1 = 2.7 Hz, J_2 = 32.9 Hz), 134.5 (d, $J_{C\text{-}F}$ = 133.9 Hz), 134.4 (d, $J_{C\text{-}P}$ = 3.1 Hz), 134.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 134.1, 133.5 (d, $J_{C\text{-}P}$ = 42.4 Hz), 132.6 (d, $J_{C\text{-}P}$ = 97.0 Hz), 132.3 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.8 (d, $J_{C\text{-}P}$ = 6.1 Hz), 131.7 (d, $J_{C\text{-}P}$ = 4.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 10.8 Hz), 126.4, 125.9-125.7 (m), 125.6-125.2 (m), 123.1 (ddd, J_1 = 3.1 Hz, J_2 = 9.8 Hz, J_3 = 271.4 Hz), 119.8 (dd, J_1 = 5.5 Hz, J_2 = 14.8 Hz,), 69.8 (dd, J_1 = 7.4 Hz, J_2 = 88.7 Hz), 15.7. ^{31}P NMR (203 MHz, $CDCl_3$): δ 30.85 (d, J = 20.8 Hz), 27.93 (d, J = 20.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -63.5, -63.67 (d, J = 80.7 Hz). HRMS calc. for $C_{30}H_{21}F_{12}O_3P_2$ $(M+H)^+$: 719.0769, found 719.0765.



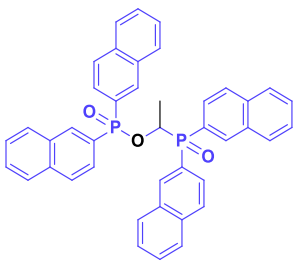
1-(di-p-tolylphosphoryl)ethyl di-p-tolylphosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 138.1 mg of di-p-tolylphosphine oxide **2e** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 64.3 mg (0.128 mmol, 64%) of **3ad** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (dd, J_1 = 8.1 Hz, J_2 = 10.9 Hz, 2H), 7.63 (dd, J_1 = 8.1 Hz, J_2 = 11.2 Hz, 2H), 7.54 (dd, J_1 = 8.0 Hz, J_2 = 12.2 Hz, 2H), 7.278-7.12 (m, 8H), 7.04-7.02 (m, 2H), 5.37-5.31 (m, 1H), 2.39 (s, 6H), 2.37 (s, 3H), 2.34 (s, 3H), 1.50 (dd, J_1 = 7.0 Hz, J_2 = 14.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.7 (dd, J_1 = 2.7 Hz, J_2 = 14.6 Hz), 142.6, 132.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.2 (d, $J_{C\text{-}P}$ = 8.9 Hz), 131.5 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.3 (d, $J_{C\text{-}P}$ = 11.0 Hz), 129.3, 129.2 (d, $J_{C\text{-}P}$ = 5.0 Hz), 129.1 (d, $J_{C\text{-}P}$ = 4.1 Hz), 129.0, 128.9 (d, $J_{C\text{-}P}$ = 13.7 Hz), 128.1 (d, $J_{C\text{-}P}$ = 35.2 Hz), 127.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 125.1(d, $J_{C\text{-}P}$ = 101.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 13.3Hz), 69.8 (dd, J_1 = 8.0 Hz, J_2 = 89.6 Hz), 21.5 (d, $J_{C\text{-}P}$ = 4.0 Hz), 16.0. ^{31}P NMR (203 MHz, $CDCl_3$): δ 34.72 (d, J = 25.1 Hz), 31.84 (d, J = 26.8 Hz). HRMS calc. for $C_{30}H_{33}O_3P_2$ $(M+H)^+$: 503.1899, found 503.1897.



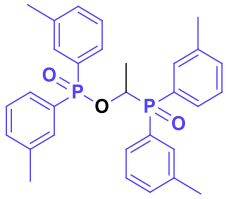
1-(bis(4-(tert-butyl)phenyl)phosphoryl)ethyl bis(4-(tert-butyl)phenyl)phosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 188.5 mg of bis(4-(tert-butyl)phenyl)phosphine oxide **2f** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 101.8 mg (0.152 mmol, 76%) of **3ae** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (dd, J_1 = 8.4 Hz, J_2 = 10.7 Hz, 2H), 7.73 (dd, J_1 = 8.4 Hz, J_2 = 11.0 Hz, 2H), 7.58 (dd, J_1 = 8.4 Hz, J_2 = 12.0 Hz, 2H), 7.53-7.48 (m, 4H), 7.41-7.39 (m, 2H), 7.28-7.25 (m, 2H), 7.17-7.13 (m, 2H), 5.35-5.28 (m, 1H), 1.51 (dd, J_1 = 7.0 Hz, J_2 = 14.6 Hz, 3H), 1.34 (d, J = 2.1 Hz, 18H), 1.31 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6 (dd, J_1 = 2.8 Hz, J_2 = 4.6 Hz), 155.5 (dd, J_1 = 2.6 Hz, J_2 = 25.8 Hz), 132.1 (d, $J_{C\text{-}P}$ = 8.9 Hz), 131.6, 131.5, 131.4, 131.3 (d, $J_{C\text{-}P}$ = 11.0 Hz), 129.2, 128.1, 127.2 (d, $J_{C\text{-}P}$ = 36.2 Hz), 125.6, 125.5 (d, $J_{C\text{-}P}$ = 2.1 Hz), 125.4 (d, $J_{C\text{-}P}$ = 6.9 Hz), 125.2, 125.1, 124.7, 70.1 (dd, J_1 = 8.1 Hz, J_2 = 89.9 Hz), 35.0, 34.9 (d, $J_{C\text{-}P}$ = 9.1 Hz), 31.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 31.0 (d, $J_{C\text{-}P}$ = 3.7 Hz), 15.9. ^{31}P NMR (203 MHz, $CDCl_3$): δ 34.26 (d, J = 26.1 Hz), 31.54 (d, J = 27.4 Hz). HRMS calc. for $C_{42}H_{57}O_3P_2$ $(M+H)^+$: 671.3778, found 671.3773.



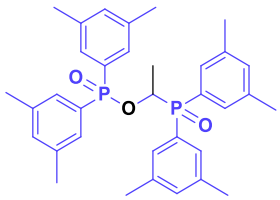
1-(bis(4-methoxyphenyl)phosphoryl)ethyl bis(4-methoxyphenyl)phosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 157.2 mg of bis(4-methoxyphenyl)phosphine oxide **2g** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 83.8 mg (0.148 mmol, 74%) of **3af** as white solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J_1 = 8.8 Hz, J_2 = 10.6 Hz, 2H), 7.68-7.56 (m, 4H), 7.20 (dd, J_1 = 8.8 Hz, J_2 = 12.1 Hz, 2H), 6.97-6.89 (m, 6H), 6.74 (dd, J_1 = 2.7 Hz, J_2 = 8.8 Hz, 2H), 5.33-5.29 (m, 1H), 3.84 (d, J = 3.5 Hz, 6H), 3.81 (d, J = 7.2 Hz, 6H), 1.50 (dd, J_1 = 7.0 Hz, J_2 = 14.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6 (t, J = 2.2 Hz), 162.4 (dd, J_1 = 2.7 Hz, J_2 = 31.3 Hz), 134.0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 133.4 (d, $J_{C\text{-}P}$ = 11.2 Hz), 133.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 123.4 (d, $J_{C\text{-}P}$ = 126.3 Hz), 122.7 (d, $J_{C\text{-}P}$ = 38.8 Hz), 121.7 (d, $J_{C\text{-}P}$ = 17.2 Hz), 119.4 (d, $J_{C\text{-}P}$ = 105.0 Hz), 114.2, 114.1, 114.0 (d, $J_{C\text{-}P}$ = 3.6 Hz), 113.8 (d, $J_{C\text{-}P}$ = 11.2 Hz), 113.6, 69.8 (dd, J_1 = 8.0 Hz, J_2 = 90.6 Hz), 55.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 55.1 (d, $J_{C\text{-}P}$ = 4.1 Hz), 16.0. ^{31}P NMR (203 MHz, $CDCl_3$): δ 34.65 (d, J = 25.6 Hz), 31.73 (d, J = 25.3 Hz). HRMS calc. for $C_{30}H_{33}O_7P_2$ $(M+H)^+$: 567.1696, found 567.1694.



1-(di(naphthalen-2-yl)phosphoryl)ethyl di(naphthalen-2-yl)phosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 181.3 mg of di(naphthalen-2-yl)phosphine oxide **2h** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 86.6 mg (0.134 mmol, 67%) of **3ag** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.69 (d, J = 13.2 Hz, 1H), 8.43 (d, J = 13.3 Hz, 1H), 8.34 (d, J = 14.4 Hz, 1H), 7.98-7.75 (m, 12H), 7.68-7.47 (m, 9H), 7.39-7.34 (m, 2H), 7.28-7.25 (m, 1H), 7.10-7.06 (m, 1H), 5.81-5.78 (m, 1H), 1.68 (dd, J_1 = 7.0 Hz, J_2 = 14.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 134.6 (dd, J_1 = 1.9 Hz, J_2 = 38.5 Hz), 133.6 (dd, J_1 = 8.5 Hz, J_2 = 12.0 Hz), 133.2 (d, $J_{C\text{-}P}$ = 10.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 12.8 Hz), 132.3 (d, $J_{C\text{-}P}$ = 14.6 Hz), 131.9 (d, $J_{C\text{-}P}$ = 14.6 Hz), 129.5, 128.9 (d, $J_{C\text{-}P}$ = 4.4 Hz), 128.8 (d, $J_{C\text{-}P}$ = 17.7 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.3 Hz), 128.5, 128.4 (d, $J_{C\text{-}P}$ = 2.2 Hz), 128.3 (d, $J_{C\text{-}P}$ = 4.1 Hz), 128.2 (d, $J_{C\text{-}P}$ = 7.3 Hz), 128.1, 127.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 127.8, 127.7 (d, $J_{C\text{-}P}$ = 17.7 Hz), 127.2 (d, $J_{C\text{-}P}$ = 30.5 Hz), 127.0 (d, $J_{C\text{-}P}$ = 8.5 Hz), 126.8 (d, $J_{C\text{-}P}$ = 31.6 Hz), 126.5 (d, $J_{C\text{-}P}$ = 10.0 Hz), 126.2 (d, $J_{C\text{-}P}$ = 11.2 Hz), 126.0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 125.7 (d, $J_{C\text{-}P}$ = 98.9 Hz), 125.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 70.1 (dd, J_1 = 7.7 Hz, J_2 = 89.3 Hz), 16.3. ^{31}P NMR (203 MHz, $CDCl_3$): δ 34.54 (d, J = 25.1 Hz), 31.53 (d, J = 25.1 Hz). HRMS calc. for $C_{42}H_{33}O_3P_2$ $(M+H)^+$: 647.1899, found 647.1897.

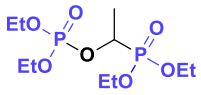


1-(di-m-tolylphosphoryl)ethyl di-m-tolylphosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 138.1 mg of di-*o*-tolylphosphine oxide **2i** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 79.3 mg (0.158 mmol, 79%) of **3ah** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, J = 11.6 Hz, 1H), 7.75-7.71 (m, 1H), 7.62 (d, J = 11.7 Hz, 1H), 7.55-7.53 (m, 2H), 7.48-7.44 (m, 1H), 7.34-7.27 (m, 6H), 7.23-7.10 (m, 3H), 7.03-6.99 (m, 1H), 5.44-5.38 (m, 1H), 2.34 (s, 6H), 2.33 (s, 3H), 2.23 (s, 3H), 1.52 (dd, J_1 = 7.0 Hz, J_2 = 14.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6 (d, $J_{C\text{-}P}$ = 11.3 Hz), 138.3 (d, $J_{C\text{-}P}$ = 10.3 Hz), 138.2, 138.0 (d, $J_{C\text{-}P}$ = 13.3 Hz), 133.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.9 (dd, J_1 = 2.7 Hz, J_2 = 5.6 Hz), 132.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.7 (d, $J_{C\text{-}P}$ = 8.3 Hz), 131.9 (t, $J_{C\text{-}P}$ = 11.0 Hz), 131.8 (t, $J_{C\text{-}P}$ = 134.3 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 131.0 (d, $J_{C\text{-}P}$ = 30.8 Hz), 130.1 (d, $J_{C\text{-}P}$ = 7.3 Hz), 129.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.8, 128.6 (d, $J_{C\text{-}P}$ = 7.7 Hz), 128.5, 128.4 (d, $J_{C\text{-}P}$ = 5.1 Hz), 128.3, 128.2, 128.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.0, 69.9 (dd, J_1 = 7.9 Hz, J_2 = 88.9 Hz), 21.3, 21.2 (d, $J_{C\text{-}P}$ = 6.9 Hz), 15.9. ^{31}P NMR (203 MHz, $CDCl_3$): δ 34.46 (d, J = 27.2 Hz), 31.29 (d, J = 25.9 Hz). HRMS calc. for $C_{30}H_{33}O_3P_2$ $(M+H)^+$: 503.1899, found 503.1896.

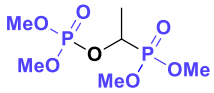


1-(bis(3,5-dimethylphenyl)phosphoryl)ethyl bis(3,5-dimethylphenyl)phosphinate. Performed according to the general procedure (conditions A, 20.4 mg of **1a,** 154.9 mg of bis(3,5-dimethylphenyl)phosphine oxide **2j** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 34.6 mg (0.062 mmol, 31%) of **3ai** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 11.4 Hz, 2H), 7.40 (d, J = 11.5 Hz, 2H), 7.33

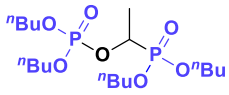
(d, J = 12.7 Hz, 2H), 7.11 (s, 3H), 7.02 (s, 1H), 6.92 (d, J = 12.9 Hz, 2H), 5.46-5.40 (m, 1H), 2.30 (s, 6H), 2.27 (s, 12H), 2.17 (s, 6H), 1.50 (dd, J_1 = 7.0 Hz, J_2 = 14.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3 (d, J_{C-P} = 12.0 Hz), 138.1 (d, J_{C-P} = 1.6 Hz), 138.0 (d, J_{C-P} = 3.6 Hz), 137.7 (d, J_{C-P} = 14.0 Hz), 133.8 (ddd, J_1 = 2.7 Hz, J_2 = 11.8 Hz, J_3 = 23.0 Hz), 132.2 (d, J_{C-P} = 132.9 Hz), 130.8 (d, J_{C-P} = 135.0 Hz), 130.6 (t, J_{C-P} = 96.5 Hz), 129.5 (t, J_{C-P} = 8.7 Hz), 129.0 (d, J_{C-P} = 10.2 Hz), 128.9 (d, J_{C-P} = 8.9 Hz), 128.8 (d, J_{C-P} = 87.9 Hz), 128.7 (d, J_{C-P} = 10.4 Hz), 69.7 (dd, J_1 = 7.8 Hz, J_2 = 88.6 Hz), 21.2 (d, J_{C-P} = 3.8 Hz), 21.1, 15.9. ^{31}P NMR (203 MHz, $CDCl_3$): δ 35.03 (d, J = 26.0 Hz), 30.97 (d, J = 25.3 Hz). HRMS calc. for $C_{34}H_{41}O_3P_2$ $(M+H)^+$: 559.2525, found 559.2525.



1-(diethoxyphosphoryl)ethyl diethyl phosphate. Performed according to the general procedure (conditions B, 20.4 mg of **1a,** 82.8 mg of diethyl phosphonate **4a** and 45.7 mg of DBU), and purified by column chromatography (petroleum ether/ethyl acetate = 2: 1, 300 mL, then dichloromethane / methanol = 30: 1) to afford 38.2 mg (0.12 mmol, 60%) of **5a** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.74-4.66 (m, 1H), 4.24-4.10 (m, 8H), 1.59 (dd, J_1 = 7.1 Hz, J_2 = 16.7 Hz, 3H), 1.37-1.34 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 69.1 (dd, J_1 = 7.0 Hz, J_2 = 173.1 Hz), 64.0 (dd, J_1 = 6.1 Hz, J_2 = 16.0 Hz), 62.9 (dd, J_1 = 6.7 Hz, J_2 = 18.3 Hz), 16.6, 16.4 (t, J_{C-P} = 5.7 Hz), 16.0 (d, J_{C-P} = 6.8 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 20.30 (d, J = 32.6 Hz), -1.17 (d, J = 32.6 Hz). MS (ESI): 318.6 $(M+H)^+$.
The analytical data matched those reported in the literature.[9]

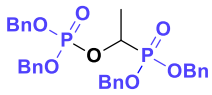


1-(dimethoxyphosphoryl)ethyl dimethyl phosphate Performed according to the general procedure (conditions B, 20.4 mg of **1a,** 66.0 mg of dimethyl phosphonate **4b** and 45.7 mg of DBU),, and purified by column chromatography (petroleum ether/ethyl acetate = 2: 1, 300 mL, then dichloromethane / methanol = 30: 1) to afford 21.5 mg (0.164 mmol, 41%) of **5b** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.78-4.71 (m, 1H), 3.86-3.78 (m, 12H), 1.59 (dd, J_1 = 7.1 Hz, J_2 = 16.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 69.1 (dd, J_1 = 6.6 Hz, J_2 = 172.9 Hz), 54.5 (dd, J_1 = 6.1 Hz, J_2 = 19.0 Hz), 53.5 (dd, J_1 = 6.7 Hz, J_2 = 22.8 Hz), 16.6. ^{31}P NMR (203 MHz, $CDCl_3$): δ 22.54 (d, J = 30.1 Hz), 1.08 (d, J = 30.9 Hz). MS (ESI): 262.6 $(M+H)^+$.
The analytical data matched those reported in the literature.[9]

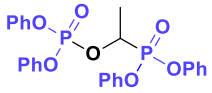


dibutyl (1-(dibutoxyphosphoryl)ethyl) phosphate. Performed according to the general procedure (conditions B, 20.4 mg of **1a,** 116.4 mg of dibutyl phosphonate **4c** and 45.7 mg of DBU), and purified by column chromatography (petroleum ether/ethyl acetate = 2: 1, 300 mL, then dichloromethane / methanol = 30: 1) to afford 35.7 mg (0.076 mmol, 38%) of **5c** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.74-4.66 (m, 1H), 4.16-4.03 (m, 8H), 1.70-1.64 (m, 8H), 1.58 (dd, J_1 = 7.1 Hz, J_2 = 16.7 Hz, 3H), 1.45-1.34 (m, 8H), 0.94 (td, J_1 = 1.1 Hz, J_2 = 7.4 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 69.2 (dd, J_1 = 7.0 Hz, J_2 = 173.1 Hz), 67.7 (dd, J_1 = 6.3 Hz, J_2 = 14.1 Hz), 66.6 (dd, J_1 = 7.1 Hz, J_2 = 19.8 Hz), 32.5 (dd, J_1 = 4.2 Hz, J_2 = 5.6 Hz), 32.2 (dd, J_1 = 2.5 Hz, J_2 = 7.2 Hz), 18.6 (d, J_{C-P} = 1.8 Hz), 16.7, 13.5 (d, J_{C-P} = 2.7 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 20.26 (d, J = 32.7 Hz), -0.93 (d, J = 32.7 Hz).

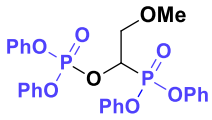
HRMS calc. for $C_{18}H_{41}O_7P_2$ $(M+H)^+$: 431.2322, found 431.2320.



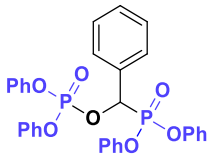
dibenzyl (1-(bis(benzyloxy)phosphoryl)ethyl) phosphate. Performed according to the general procedure (conditions B, 20.4 mg of **1a,** 157.3 mg of dibenzyl phosphonate **4d** and 45.7 mg of DBU), and purified by column chromatography (petroleum ether/ethyl acetate = 2: 1, 300 mL, then dichloromethane / methanol = 30: 1) to afford 54.3 mg (0.096 mmol, 48%) of **5d** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.25 (m, 20H), 5.06-4.97 (m, 8H), 4.86-4.76 (m, 1H), 1.52 (dd, J_1 = 7.1 Hz, J_2 = 17.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.8 (dd, J_1 = 5.7 Hz, J_2 = 7.2 Hz), 135.5 (t, $J_{C\text{-}P}$ = 7.3 Hz), 128.5, 128.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.3, 128.0 (d, $J_{C\text{-}P}$ = 9.5 Hz), 127.8 (d, $J_{C\text{-}P}$ = 3.4 Hz), 69.7 (dd, J_1 = 7.1 Hz, J_2 = 173.2 Hz), 69.4 (d, $J_{C\text{-}P}$ = 5.6 Hz), 68.2 (dd, J_1 = 7.0 Hz, J_2 = 18.3 Hz), 16.5. ^{31}P NMR (203 MHz, $CDCl_3$): δ 20.95 (d, J = 32.6 Hz), -1.22 (d, J = 32.6 Hz). HRMS calc. for $C_{30}H_{33}O_7P_2$ $(M+H)^+$: 567.1696, found 567.1693.



1-(diphenoxyphosphoryl)ethyl diphenyl phosphate. Performed according to the general procedure (conditions B, 20.4 mg of **1a,** 140.4 mg of diphenyl phosphonate **4e** and 36.7 mg of DMAP, stirred at 90 °C instead), and purified by column chromatography (petroleum ether/ethyl acetate = 6: 1) to afford 78.6 mg (0.154 mmol, 77%) of **5e** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.09 (m, 20H), 5.29-5.21 (m, 1H), 1.72 (dd, J_1 = 7.1 Hz, J_2 = 17.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2 (dd, J_1 =7.4 Hz, J_2 = 12.9 Hz), 149.9 (dd, J_1 = 9.3 Hz, J_2 = 17.3 Hz), 129.8, 129.7 (d, $J_{C\text{-}P}$ = 3.1 Hz), 125.5 (d, $J_{C\text{-}P}$ = 15.5 Hz), 125.4, 120.5 (dd, J_1 = 2.1 Hz, J_2 = 3.9 Hz), 120.1 (dd, J_1 = 4.7 Hz, J_2 = 8.3 Hz), 70.5 (dd, J_1 = 7.1 Hz, J_2 = 175.5 Hz), 16.6. ^{31}P NMR (203 MHz, $CDCl_3$): δ 12.2 (d, J = 35.6 Hz), -12.01 (d, J = 36.7 Hz). HRMS calc. for $C_{26}H_{25}O_7P_2$ $(M+H)^+$: 511.1070, found 511.1065.

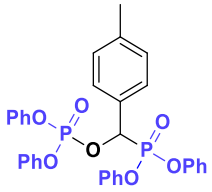


1-(diphenoxyphosphoryl)-2-methoxyethyl diphenyl phosphate. Performed according to the general procedure (conditions B, 32.4 mg of **1e,** 140.4 mg of diphenyl phosphonate **4e** and 36.7 mg of DMAP, stirred at 90 °C instead), and purified by column chromatography (petroleum ether/ethyl acetate = 6: 1) to afford 70.2 mg (0.13 mmol, 65%) of **5f** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.23 (m, 12H), 7.22-7.09 (m, 8H), 5.39-5.33 (m, 1H), 3.91-3.89 (m, 2H), 3.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5 (dd, J_1 =7.4 Hz, J_2 = 15.3 Hz), 149.8 (dd, J_1 = 9.2 Hz, J_2 = 25.7 Hz), 129.8, 129.7 (d, $J_{C\text{-}P}$ = 5.3 Hz), 125.5 (d, $J_{C\text{-}P}$ = 10.6 Hz), 120.7 (dd, J_1 = 4.0 Hz, J_2 = 9.4 Hz), 120.3, 120.2 (d, $J_{C\text{-}P}$ = 4.1Hz), 73.6 (dd, J_1 = 7.3 Hz, J_2 = 169.7 Hz), 70.8 (dd, J_1 = 1.5 Hz, J_2 = 4.6 Hz), 58.9. ^{31}P NMR (203 MHz, $CDCl_3$): δ 9.61 (d, J = 27.6 Hz), -11.92 (d, J = 27.7 Hz). HRMS calc. for $C_{27}H_{27}O_8P_2$ $(M+H)^+$: 541.1176, found 541.1173.

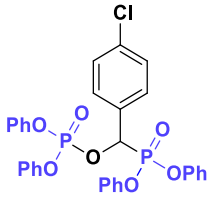


(diphenoxyphosphoryl)(phenyl)methyl diphenyl phosphate. Performed according to the general

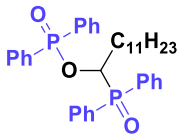
procedure (conditions B, 45.2 mg of **1k,** 140.4 mg of diphenyl phosphonate **4e** and 36.7 mg of DMAP, stirred at 90 °C instead), and purified by column chromatography (petroleum ether/ethyl acetate = 6: 1) to afford 77.8 mg (0.136 mmol, 68%) of **5g** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.37-7.30 (m, 3H), 7.27-7.06 (m, 14H), 7.03-7.01(m, 2H), 6.93-6.88 (m, 4H), 6.12 (dd, J_1 = 10.4 Hz, J_2 = 13.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1 (dd, J_1 = 7.4 Hz, J_2 = 29.1 Hz), 150.0 (dd, J_1 = 5.7 Hz, J_2 = 8.1 Hz), 131.6, 129.6 (d, $J_{C\text{-}P}$ = 7.4 Hz), 129.6 (d, $J_{C\text{-}P}$ = 4.4 Hz), 128.6 (d, $J_{C\text{-}P}$ = 1.7 Hz), 128.5 (d, $J_{C\text{-}P}$ = 6.4 Hz), 125.4, 125.3 (d, $J_{C\text{-}P}$ = 2.3 Hz), 120.3 (dd, J_1 = 4.4 Hz, J_2 = 9.9 Hz), 120.1 (d, $J_{C\text{-}P}$ = 5.1 Hz), 119.9 (d, $J_{C\text{-}P}$ = 5.1 Hz), 75.9 (dd, J_1 = 6.7 Hz, J_2 = 176.5 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 8.33 (d, J = 40.1 Hz), -11.69 (d, J = 40.2 Hz). HRMS calc. for $C_{31}H_{27}O_7P_2$ $(M+H)^+$: 573.1226, found 573.1222.



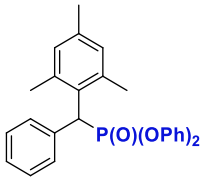
(diphenoxyphosphoryl)(p-tolyl)methyl diphenyl phosphate. Performed according to the general procedure (conditions B, 50.9 mg of **1l,** 140.4 mg of diphenyl phosphonate **4e** and 36.7 mg of DMAP, stirred at 90 °C instead), and purified by column chromatography (petroleum ether/ethyl acetate = 6: 1) to afford 73.8 mg (0.126 mmol, 63%) of **5h** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (dd, J_1 = 1.8 Hz, J_2 = 8.1 Hz, 2H), 7.27-7.07 (m, 16H), 7.03 (d, J = 7.0 Hz, 2H), 6.94-6.89 (m, 4H), 6.08 (dd, J_1 = 10.3 Hz, J_2 = 12.8 Hz, 1H), 2.34 (d, J = 0.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2 (dd, J_1 =7.3 Hz, J_2 = 25.1 Hz), 150.0 (dd, J_1 = 10.0 Hz, J_2 = 13.6 Hz), 139.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 129.6 (d, $J_{C\text{-}P}$ = 6.1 Hz), 129.5 (d, $J_{C\text{-}P}$ = 7.6 Hz), 129.3 (d, $J_{C\text{-}P}$ = 1.6 Hz), 128.5 (d, $J_{C\text{-}P}$ = 6.9 Hz), 125.4 (d, $J_{C\text{-}P}$ = 25.5 Hz), 125.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 120.4 (dd, J_1 = 4.3 Hz, J_2 = 9.6 Hz), 120.1 (d, $J_{C\text{-}P}$ = 4.9 Hz), 119.9 (d, $J_{C\text{-}P}$ = 4.8 Hz), 75.9 (dd, J_1 = 7.1 Hz, J_2 = 178.0 Hz), 21.3. ^{31}P NMR (203 MHz, $CDCl_3$): δ 8.55 (d, J = 40.5 Hz), -11.74 (d, J = 40.1 Hz). HRMS calc. for $C_{32}H_{29}O_7P_2$ $(M+H)^+$: 587.1383, found 587.1379.



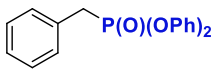
(diphenoxyphosphoryl)(p-tolyl)methyl diphenyl phosphate. Performed according to the general procedure (conditions B, 59.0 mg of **1o,** 140.4 mg of diphenyl phosphonate **4e** and 36.7 mg of DMAP, stirred at 90 °C instead), and purified by column chromatography (petroleum ether/ethyl acetate = 6: 1) to afford 72.7 mg (0.12 mmol, 60%) of **5i** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (dd, J_1 = 2.0 Hz, J_2 = 8.5 Hz, 2H), 7.29-7.10 (m, 16H), 7.03 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.07 (dd, J_1 = 10.5 Hz, J_2 = 13.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2 (d, $J_{C\text{-}P}$ = 7.3 Hz), 150.0, 149.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 149.8 (d, $J_{C\text{-}P}$ = 9.2 Hz), 135.7 (d, $J_{C\text{-}P}$ = 3.5 Hz), 130.3, 129.8, 129.7, 129.6 (d, $J_{C\text{-}P}$ = 3.3 Hz), 129.5, 128.8 (d, $J_{C\text{-}P}$ = 1.6 Hz), 125.6, 125.4 (d, $J_{C\text{-}P}$ = 5.8 Hz), 120.3 (dd, J_1 = 4.2 Hz, J_2 = 8.8 Hz), 120.1 (d, $J_{C\text{-}P}$ = 5.2 Hz), 119.8 (d, $J_{C\text{-}P}$ = 4.9 Hz), 75.1 (dd, J_1 = 7.0 Hz, J_2 = 177.1 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 7.77 (d, J = 38.1 Hz), -11.68 (d, J = 40.1 Hz). HRMS calc. for $C_{31}H_{26}ClO_7P_2$ $(M+H)^+$: 607.0837, found 607.0835.



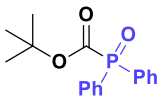
1-(diphenylphosphoryl)dodecyl diphenylphosphinate Performed according to the general procedure (conditions A, 79.7 mg of **6e,** 121.2 mg of diphenylphosphine oxide **2a** and 4.9 mg of DMAP), and purified by column chromatography (dichloromethane / methanol = 100: 1) to afford 73.9 mg (0.126 mg, 63%) of **3r** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.80-7.69 (m, 4H), 7.50-7.47 (m, 2H), 7.43-7.34 (m, 8H), 7.30-7.26 (m, 2H), 7.20-7.19 (m, 2H), 5.52-5.47 (m, 1H), 1.92-1.85 (m, 2H), 1.29-1.10 (m, 14H), 1.03-1.01 (m, 2H), 0.97-0.95 (m, 2H), 0.90-0.87 (td, J_1 = 1.3 Hz, J_2 = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.8, 132.1 (d, J_{C-P} = 2.6 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 8.9 Hz), 131.7 (d, J_{C-P} = 2.1 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.4, 131.3 (d, J_{C-P} = 7.2 Hz), 131.2 (d, J_{C-P} = 6.0 Hz), 131.0 (d, J_{C-P} = 10.3Hz), 130.6, 129.3, 128.6 (d, J_{C-P} = 11.8 Hz), 128.3 (d, J_{C-P} = 12.6 Hz), 128.1 (d, J_{C-P} = 13.2 Hz), 73.8 (dd, J_1 = 8.3 Hz, J_2 = 87.4 Hz), 31.8, 30.4, 29.5 (d, J_{C-P} = 1.6 Hz), 29.2, 29.1, 29.0, 28.9, 25.9, 25.8, 22.6, 14.0. ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.65 (d, J = 20.1 Hz), 30.7 (d, J = 20.1 Hz). HRMS calc. for $C_{36}H_{45}O_3P_2$ (M+H) $^{+}$: 587.2838, found 587.2840.



diphenyl (mesityl(phenyl)methyl)phosphonate. Performed according to the literature [10] with 1.0 eq. compound **5h** (0.2 mmol, 114.4 mg) and 1.2 eq. TfOH (36.0 mg) in mesitylene (0.3 ml) at 50 ^{o}C, and purified by column chromatography (petroleum ether/ethyl acetate = 5: 1) to afford 81.3 mg (0.184 mmol, 92%) of **8** as yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 4H), 7.23 (d, J = 7.4 Hz, 1H), 7.20-7.15 (m, 3H), 7.11-7.08 (m, 2H), 7.02-6.98 (m, 1H), 6.89 (s, 1H), 6.77 (s, 1H), 6.58-6.57 (m, 2H), 5.48 (d, J = 31.3 Hz, 1H), 2.45 (s, 1H), 2.24 (d, J = 1.8 Hz, 1H), 2.09 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4 (dd, J_1 = 3.5 Hz, J_2 = 9.6 Hz), 139.5 (d, J_{C-P} = 4.5 Hz), 137.9 (d, J_{C-P} = 8.3 Hz), 137.2 (d, J_{C-P} = 3.5 Hz), 136.3, 131.2 (d, J_{C-P} = 3.1 Hz), 129.9 (d, J_{C-P} = 6.3 Hz), 129.7, 129.3, 129.2, 128.9 (d, J_{C-P} = 11.0 Hz), 128.4, 126.6, 125.2, 124.6, 120.9 (d, J_{C-P} = 4.3 Hz), 120.1 (d, J_{C-P} = 4.4 Hz), 44.87 (d, J_{C-P} = 141.8 Hz), 21.5, 21.4, 20.7. ^{31}P NMR (203 MHz, $CDCl_3$): δ 19.15. HRMS calc. for $C_{28}H_{28}O_3P$ (M+Na) $^{+}$: 443.1771, found 443.1766.



diphenyl benzylphosphonate. Performed according to the literature [11] with 1.0 eq. compound **5h** (0.2 mmol, 114.4 mg) and TMSI (0.8 mmol, 160.1 mg, 4.0 eq.) in MeCN (2.0 ml) at r.t, and purified by column chromatography (petroleum ether/ethyl acetate = 5: 1) to afford 56.4 mg (0.174 mmol, 87%) of **9** as brown oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.28 (m, 5H), 7.26 (t, J = 7.8 Hz, 4H), 7.14-7.11 (m, 2H), 7.04-7.02 (m, 4H), 3.50 (d, J = 21.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.3 (d, J_{C-P} = 9.2 Hz), 130.2 (d, J_{C-P} = 9.4 Hz), 130.0 (d, J_{C-P} = 7.1 Hz), 129.6, 128.7 (d, J_{C-P} = 3.4 Hz), 127.3 (d, J_{C-P} = 3.7 Hz), 125.1, 120.5 (d, J_{C-P} = 4.3 Hz), 33.8 (d, J_{C-P} = 138.5 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 19.55. HRMS calc. for $C_{19}H_{18}O_3P$ (M+Na) $^{+}$: 325.0988, found 325.0984.



tert-butyl (diphenylphosphoryl)formate. Performed according to the general procedure (conditions A, 43.7 mg of **1t,** 121.2 mg of diphenylphosphine oxide **2a** and 4.9 mg of DMAP),, and purified by column chromatography (petroleum ether/ethyl acetate = 6: 1) to afford 28.4 mg (0.094 mmol, 47%) of **10** as colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88-7.84 (m, 4H), 7.60-7.57 (m, 2H), 7.52-7.48 (m, 4H), 1.53 (d, *J* = 0.5 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9 (d, J_{C-P} = 143.9 Hz), 132.6 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 9.9 Hz), 129.3 (d, J_{C-P} = 100.6 Hz), 128.6 (d, J_{C-P} = 12.6 Hz), 86.2 (d, J_{C-P} = 4.0 Hz), 28.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 15.40. HRMS calc. for $C_{17}H_{19}O_3PNa$ $(M+Na)^+$: 325.0964, found 325.0959.

7. Reference

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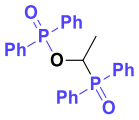
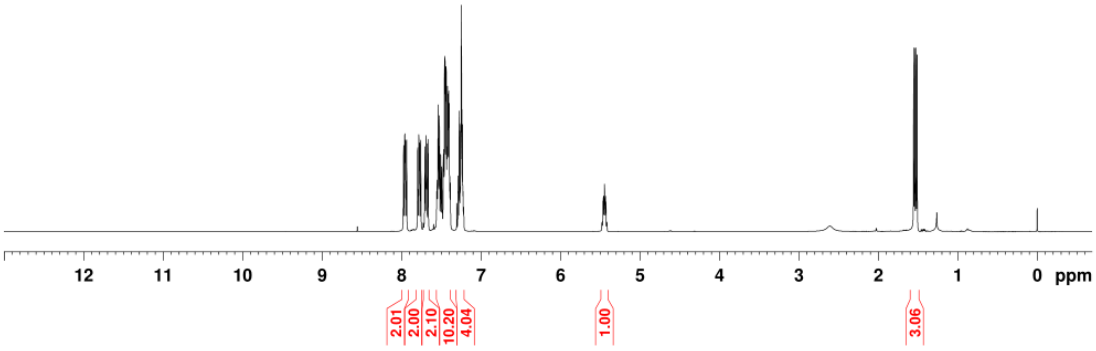
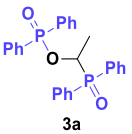
8. Charts of compounds



3a

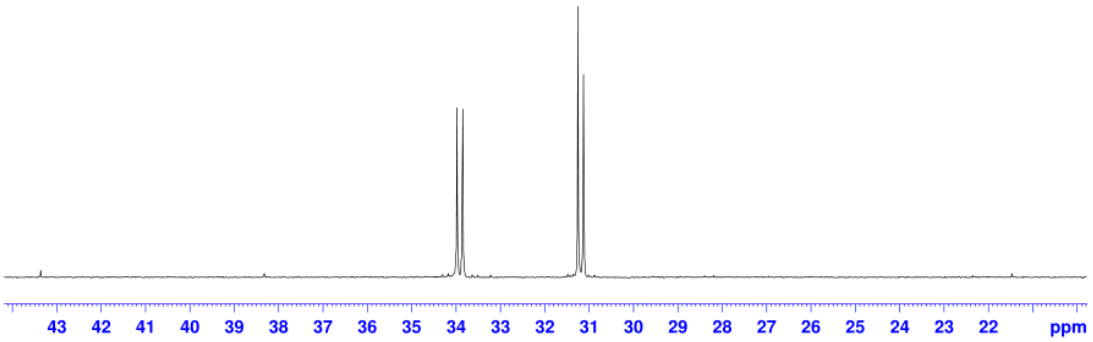
^{1}H NMR (500 MHz, $CDCl_3$)

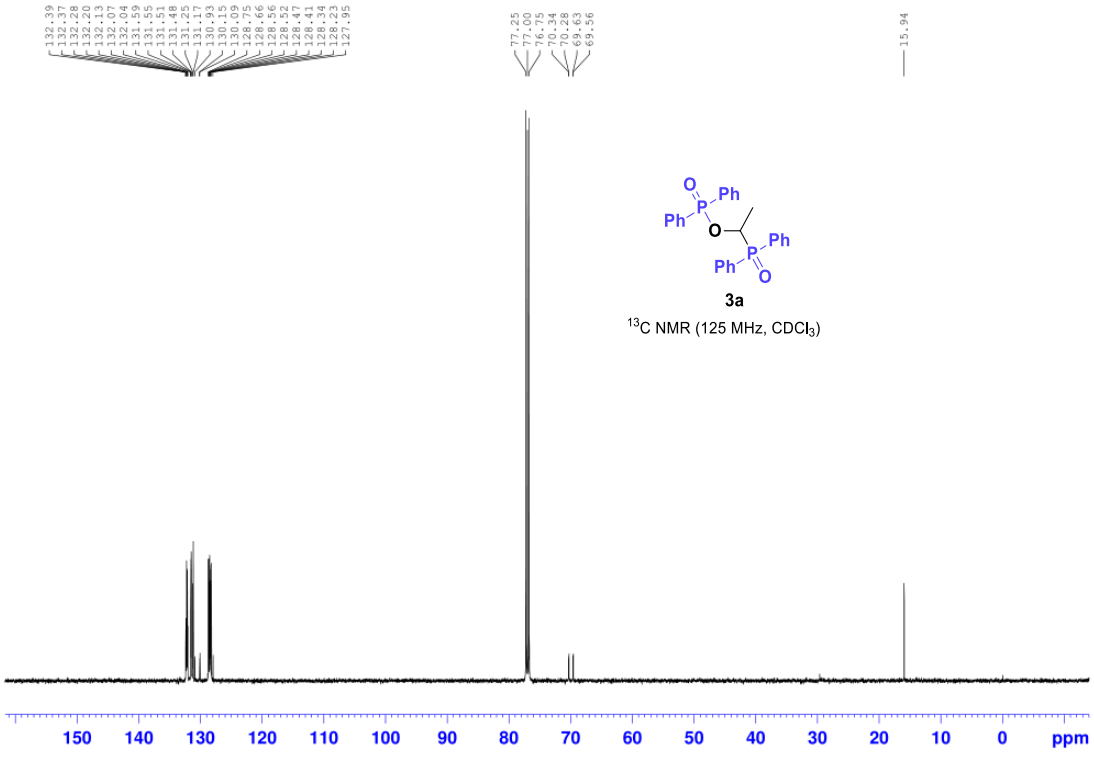




3a

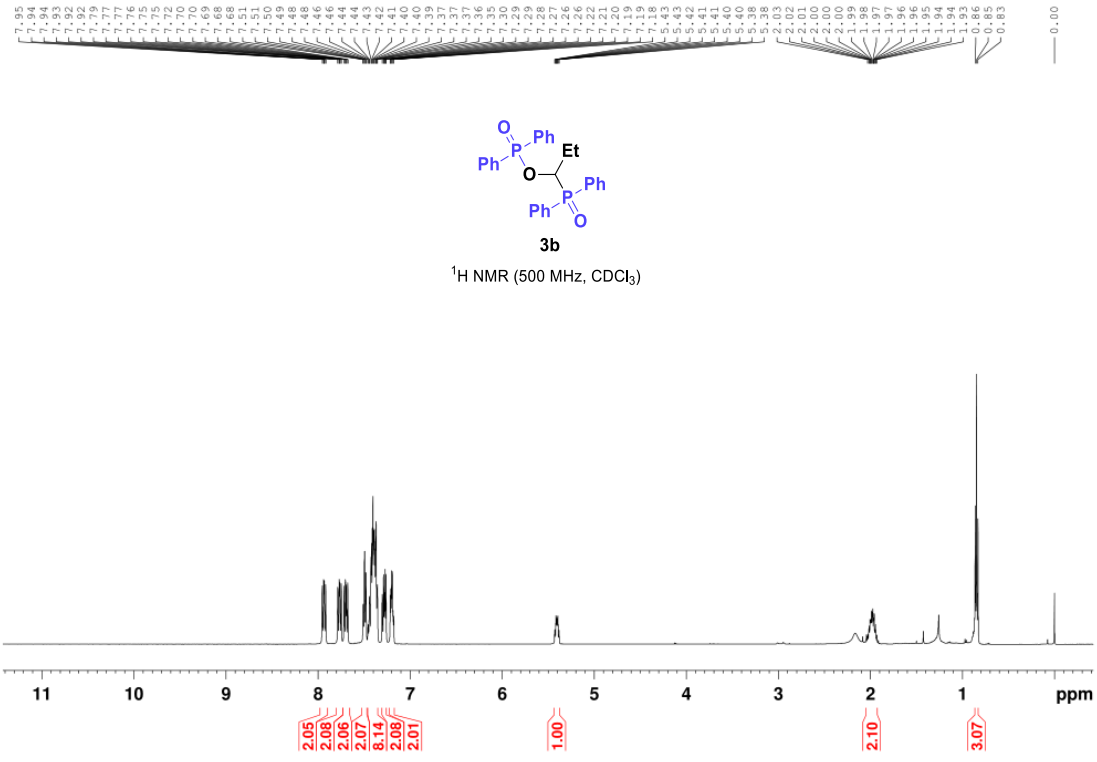
^{31}P NMR (203 MHz, $CDCl_3$)





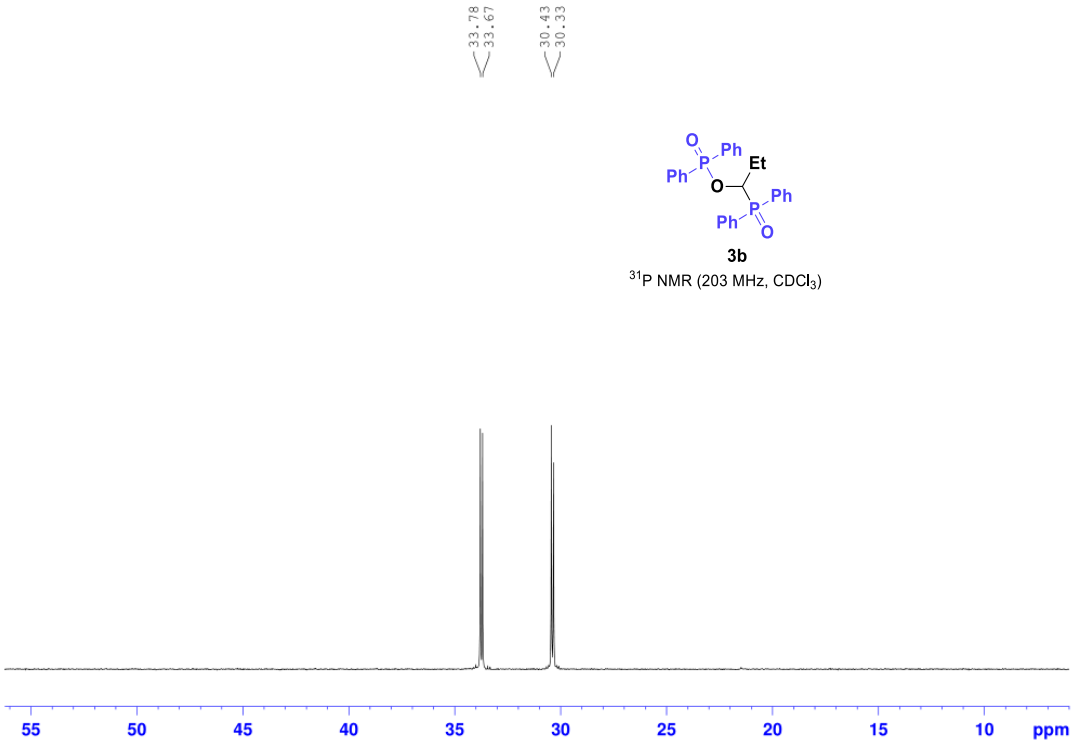
3a

^{13}C NMR (125 MHz, $CDCl_3$)



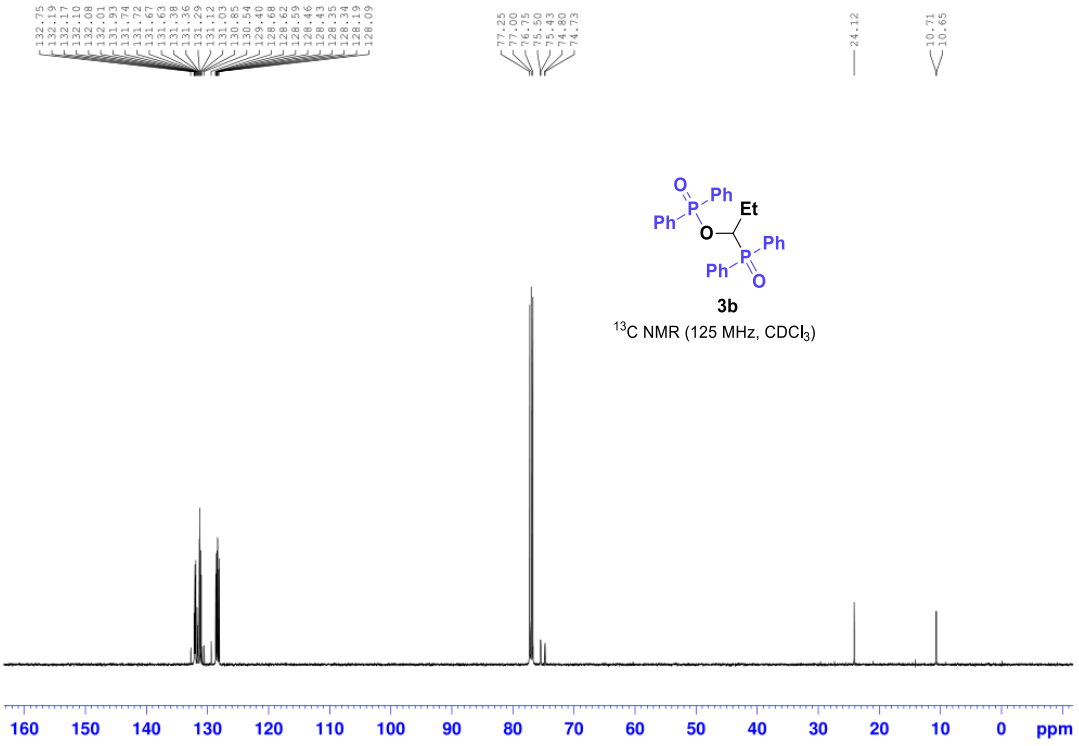
3b

^{1}H NMR (500 MHz, $CDCl_3$)



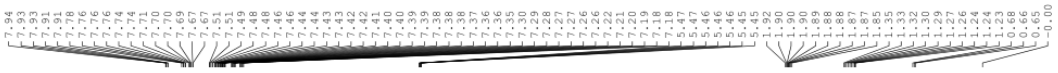
3b

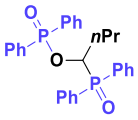
^{31}P NMR (203 MHz, $CDCl_3$)



3b

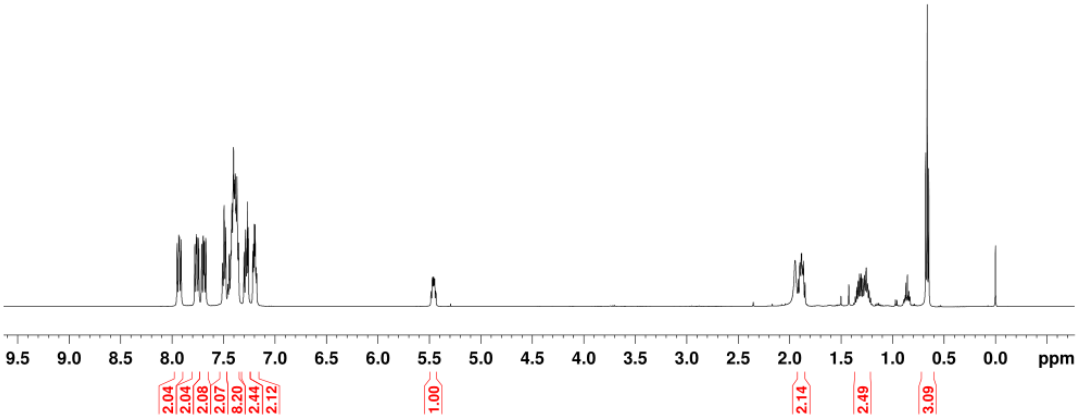
^{13}C NMR (125 MHz, $CDCl_3$)

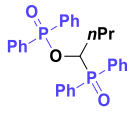




3c

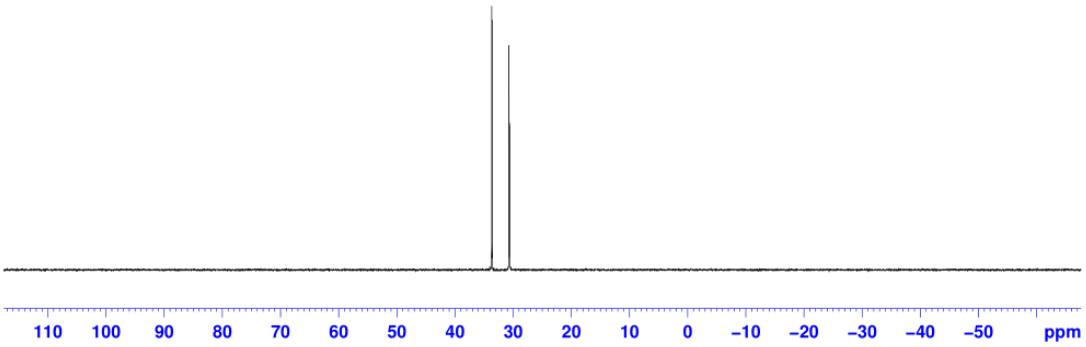
^{1}H NMR (500 MHz, $CDCl_3$)

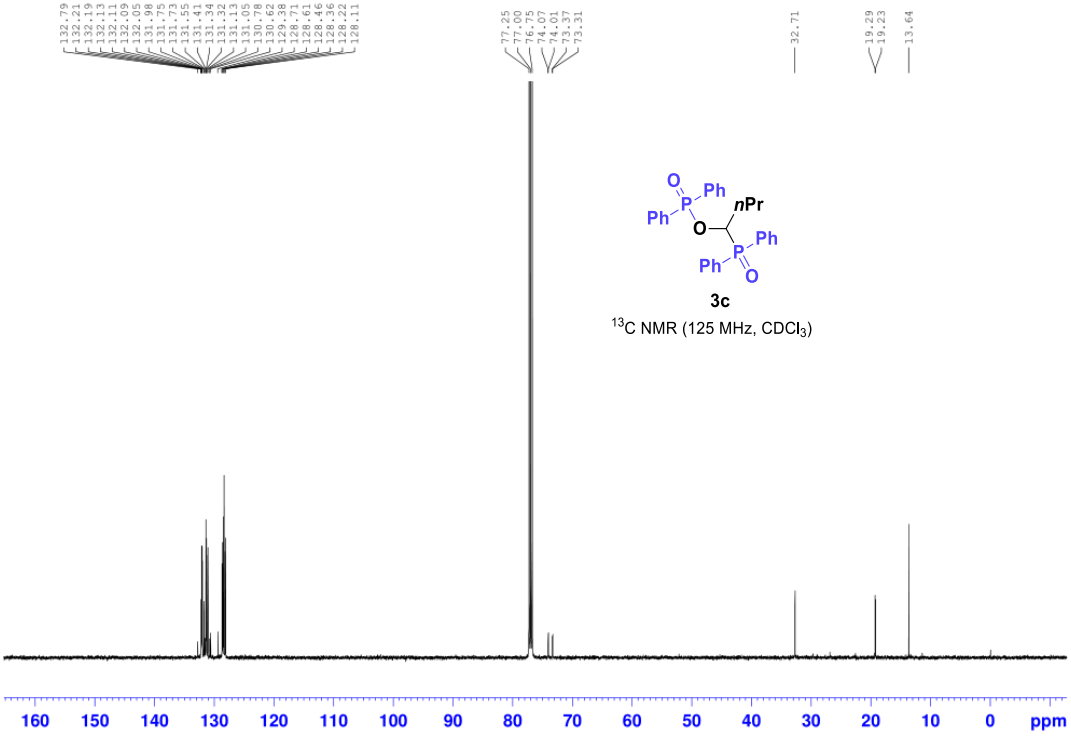


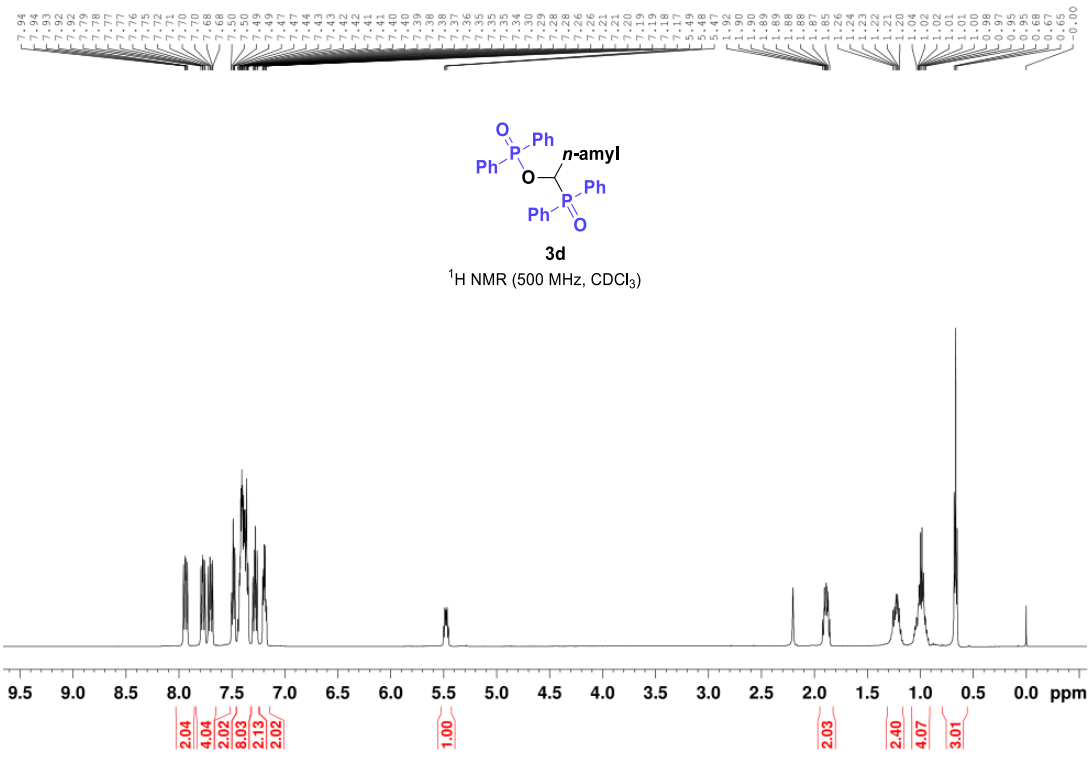


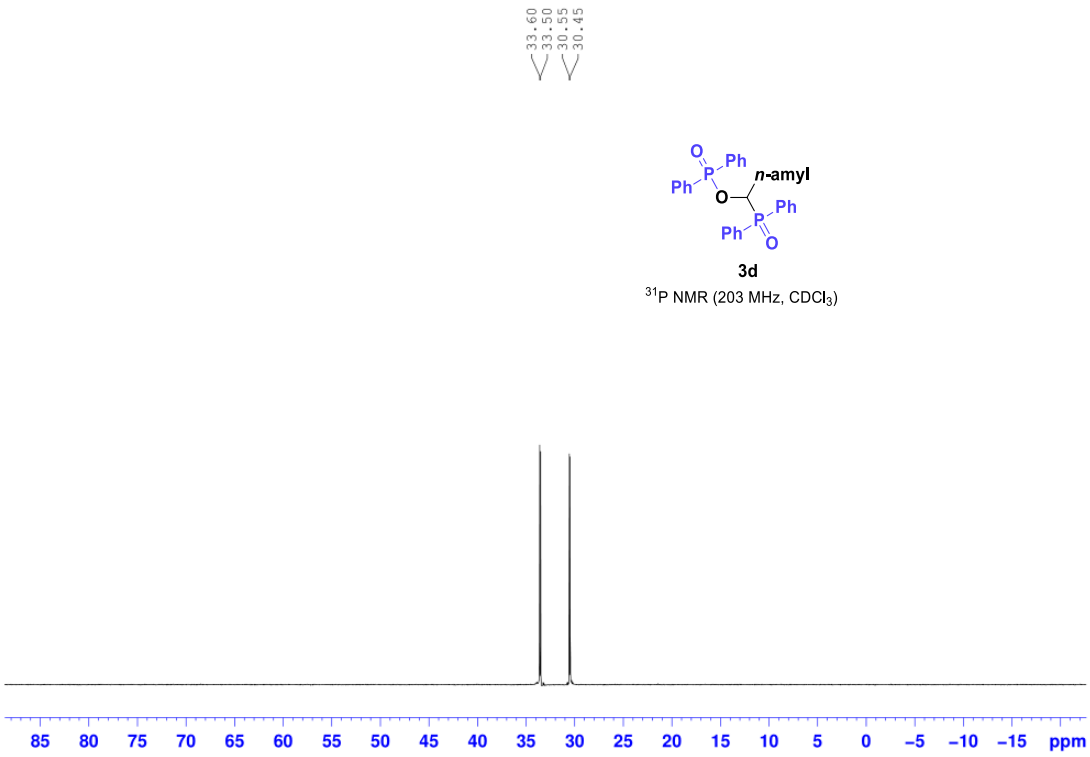
3c

^{31}P NMR (203 MHz, $CDCl_3$)



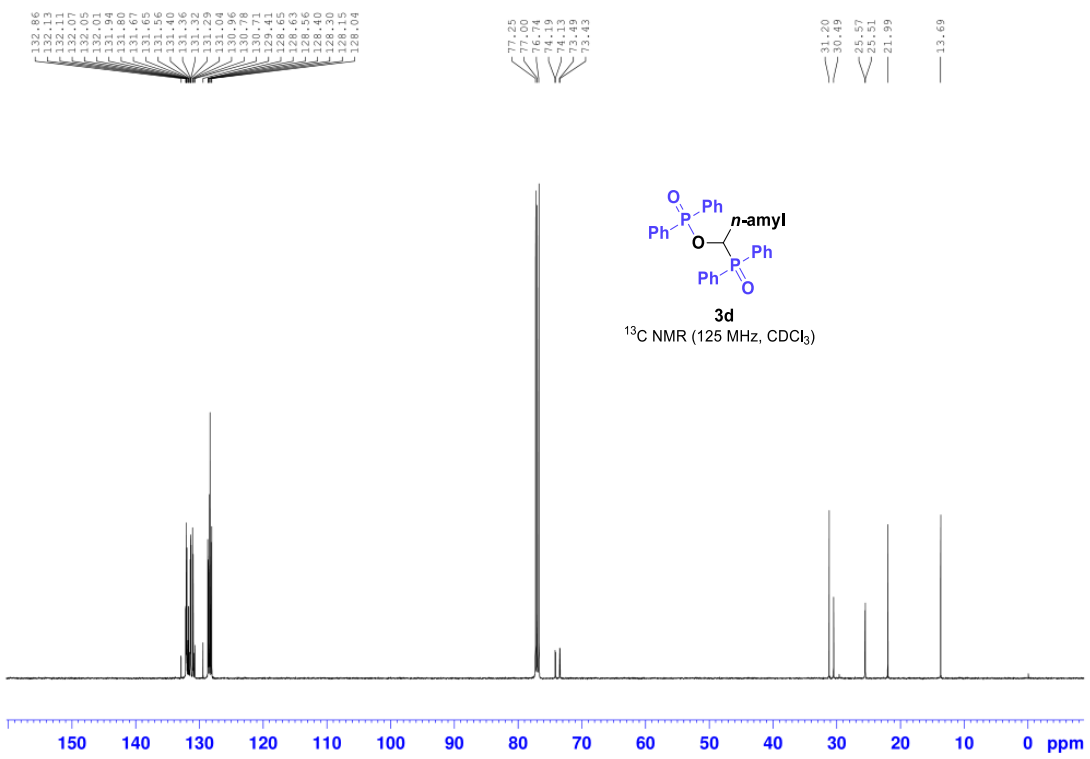

nPr
3c
13C NMR (125 MHz, CDCl3)
ppm


n-amyl
3d
1H NMR (500 MHz, CDCl3)
ppm



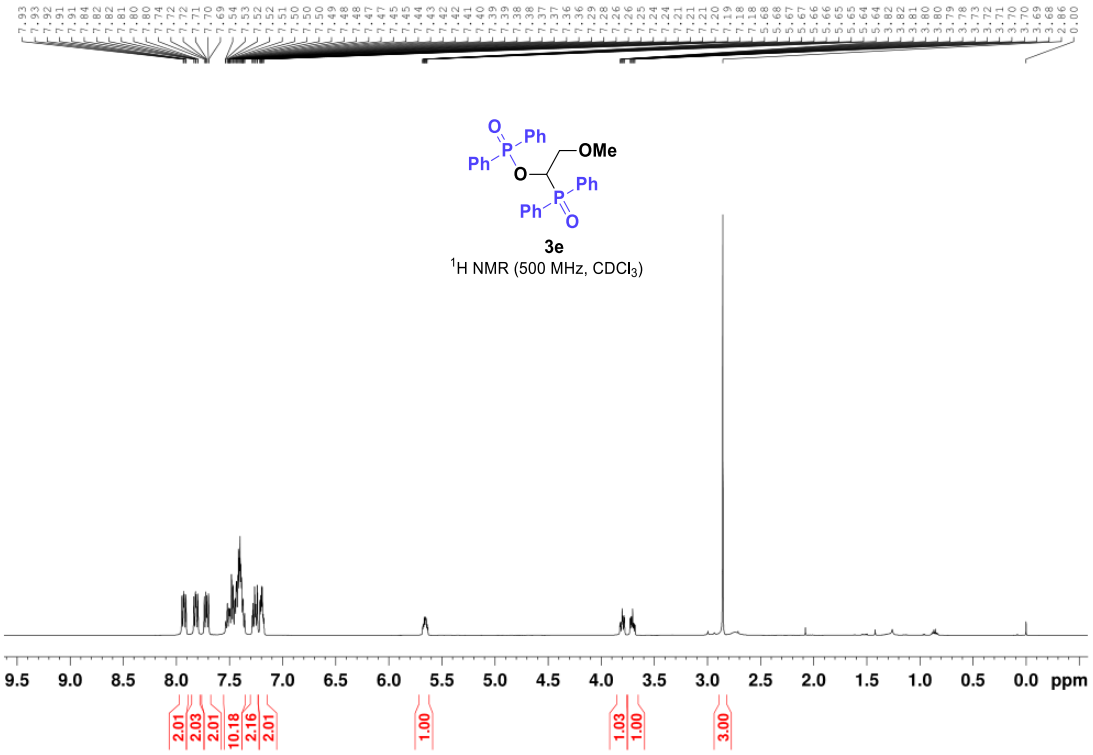
3d

^{31}P NMR (203 MHz, $CDCl_3$)



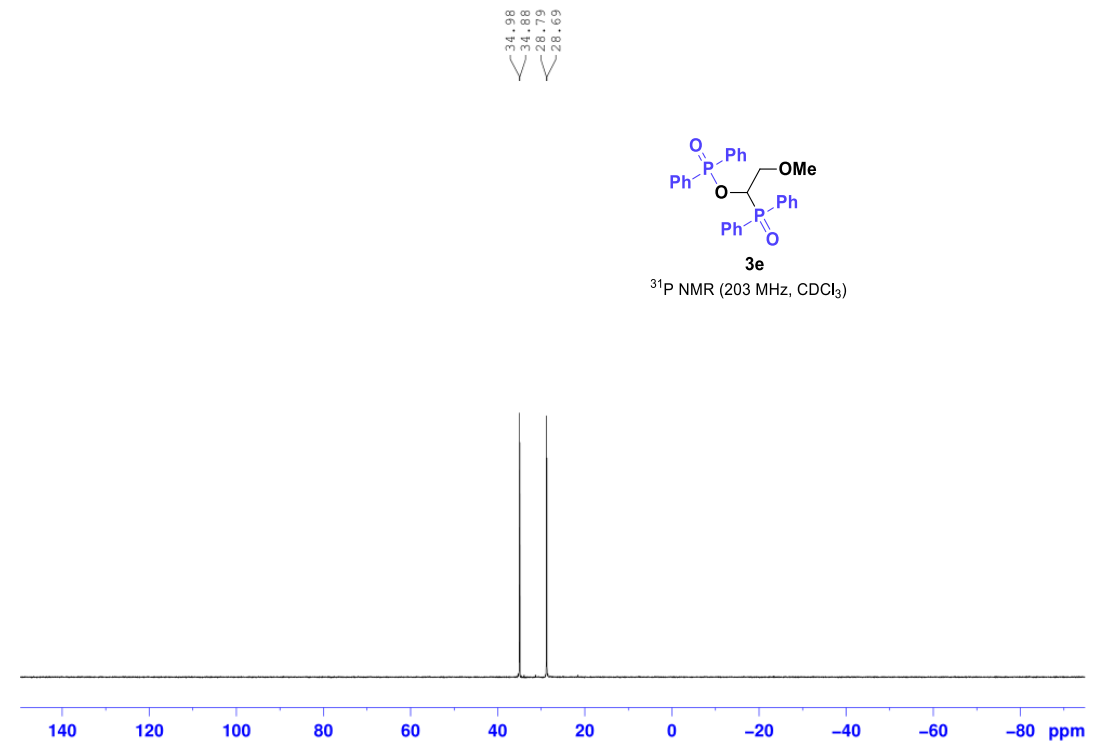
3d

^{13}C NMR (125 MHz, $CDCl_3$)



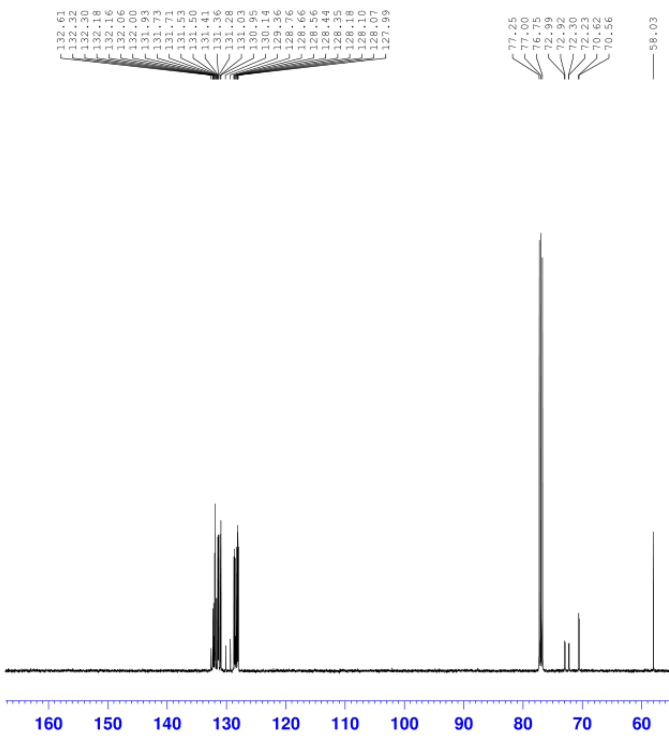
3e

^{1}H NMR (500 MHz, $CDCl_3$)



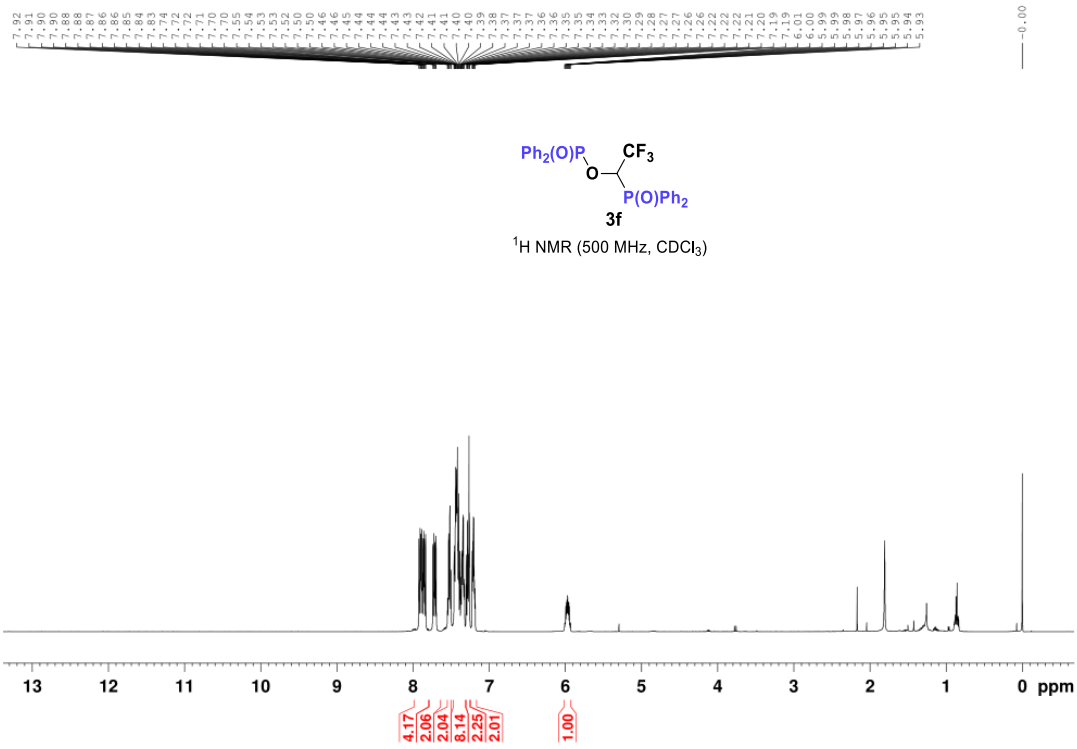
3e

^{31}P NMR (203 MHz, $CDCl_3$)



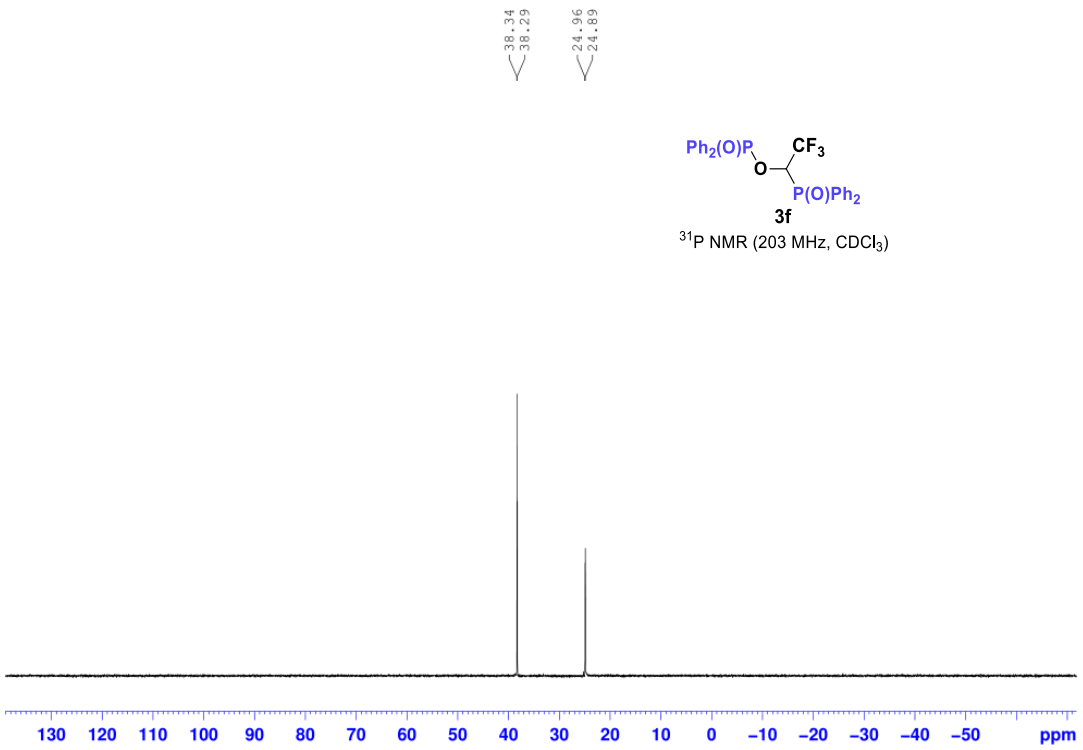
3e

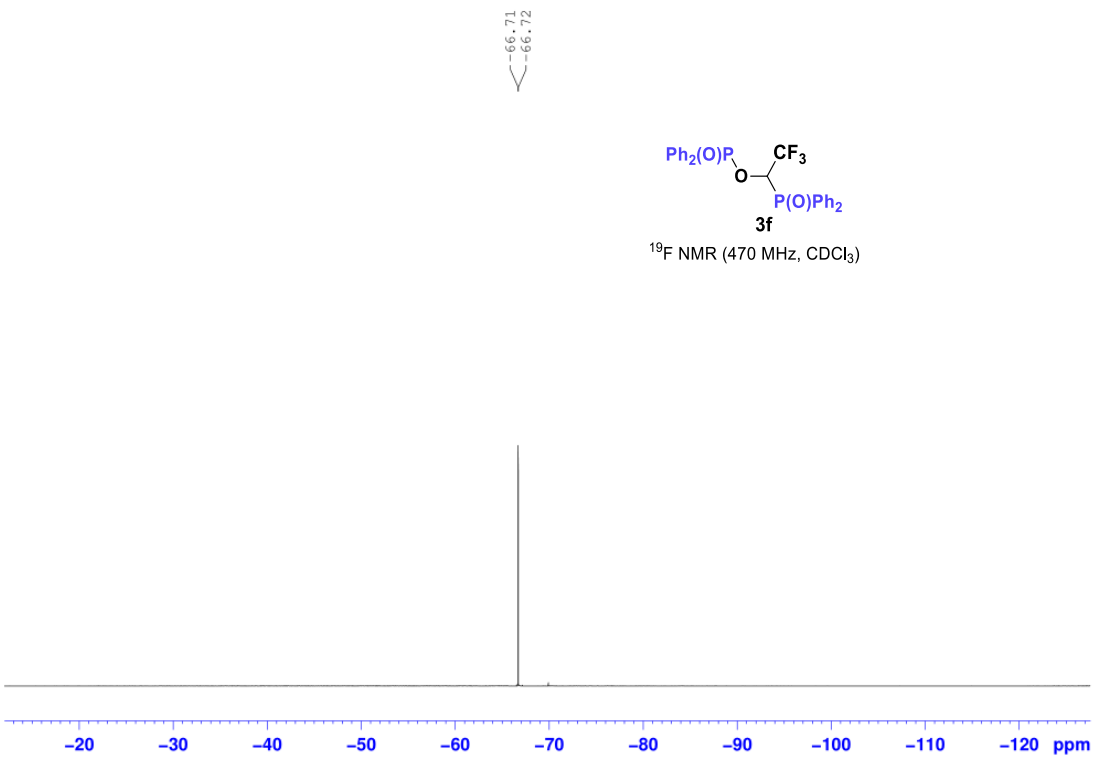
^{13}C NMR (125 MHz, $CDCl_3$)

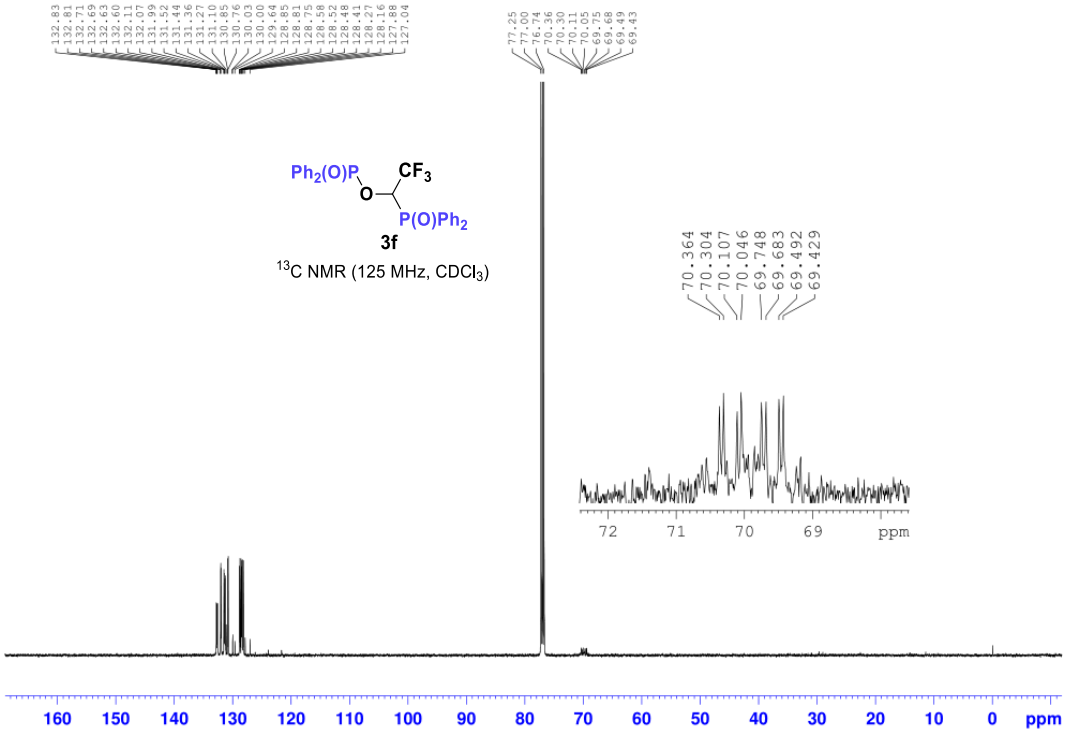


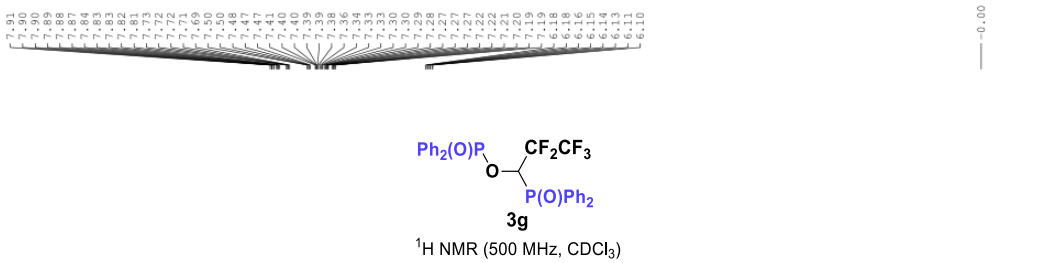
3f

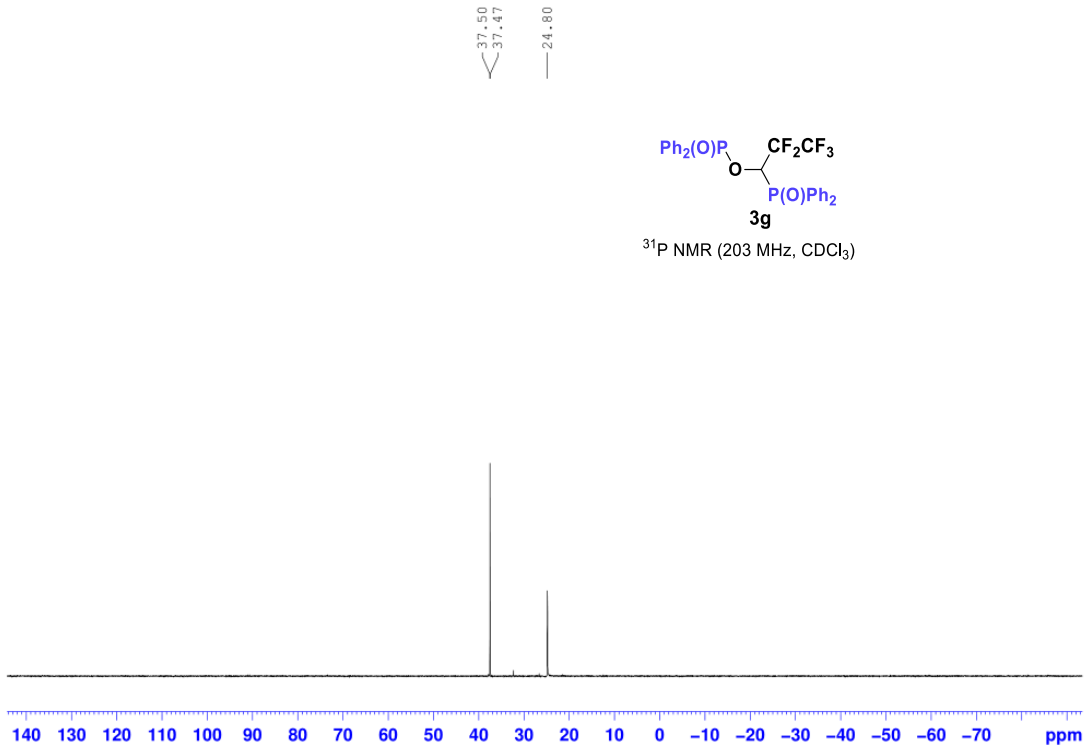
^{1}H NMR (500 MHz, $CDCl_3$)

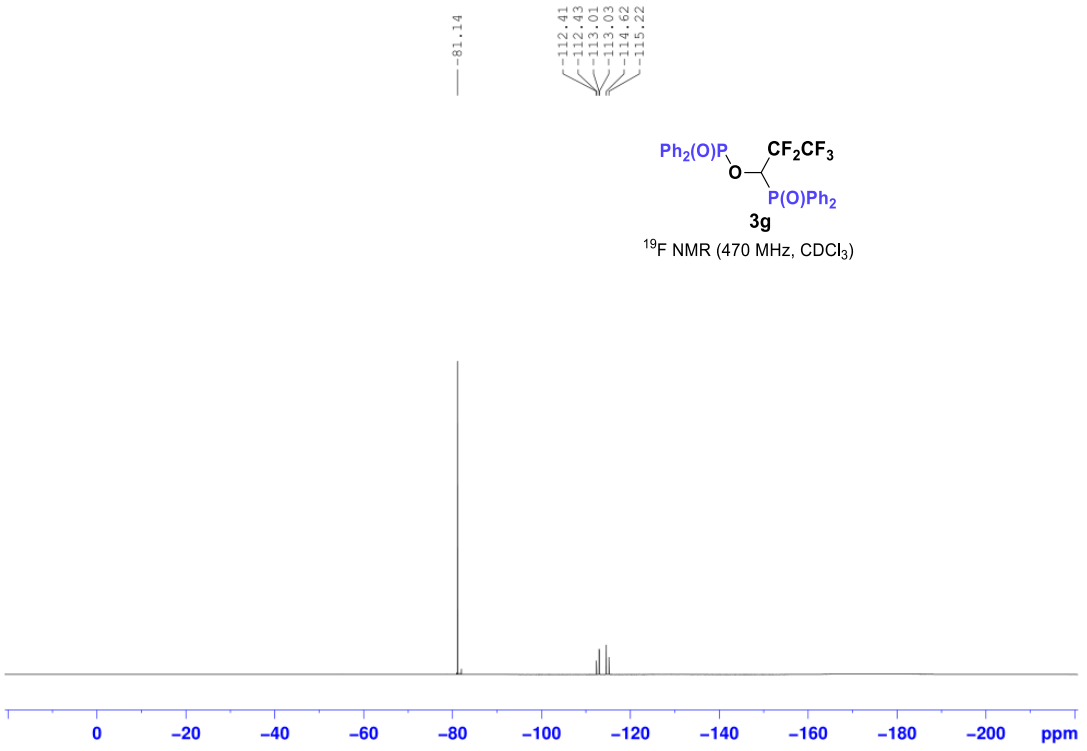

38.34
38.29
24.96
24.89
Ph2(O)P
CF3
O
P(O)Ph2
3f
31P NMR (203 MHz, CDCl3)
130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 ppm

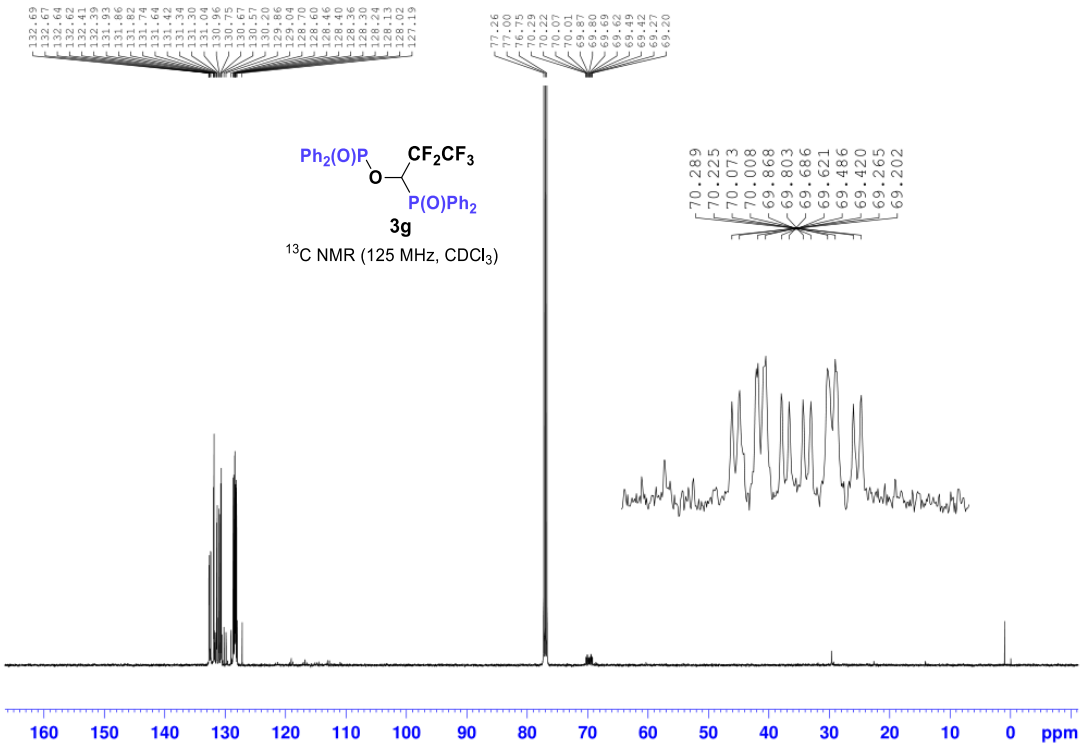

66.71
66.72
Ph2(O)P
CF3
O
P(O)Ph2
3f
19F NMR (470 MHz, CDCl3)
−20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 ppm

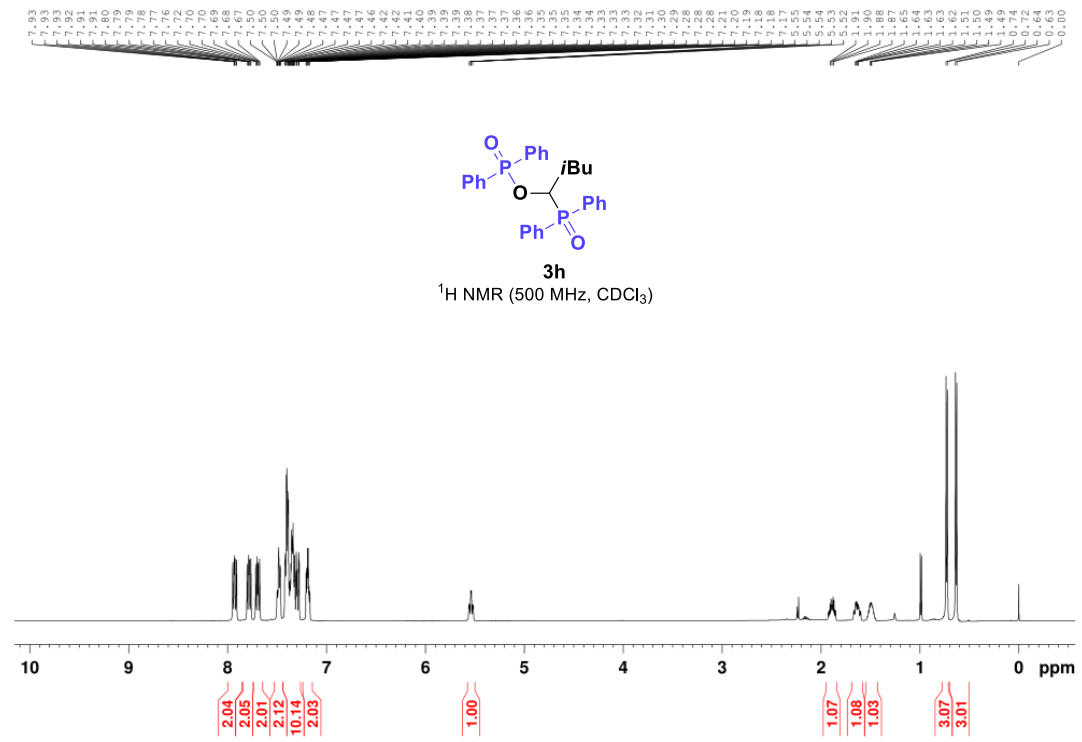

Ph2(O)P
CF3
O
P(O)Ph2
3f
13C NMR (125 MHz, CDCl3)
72
71
70
69
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

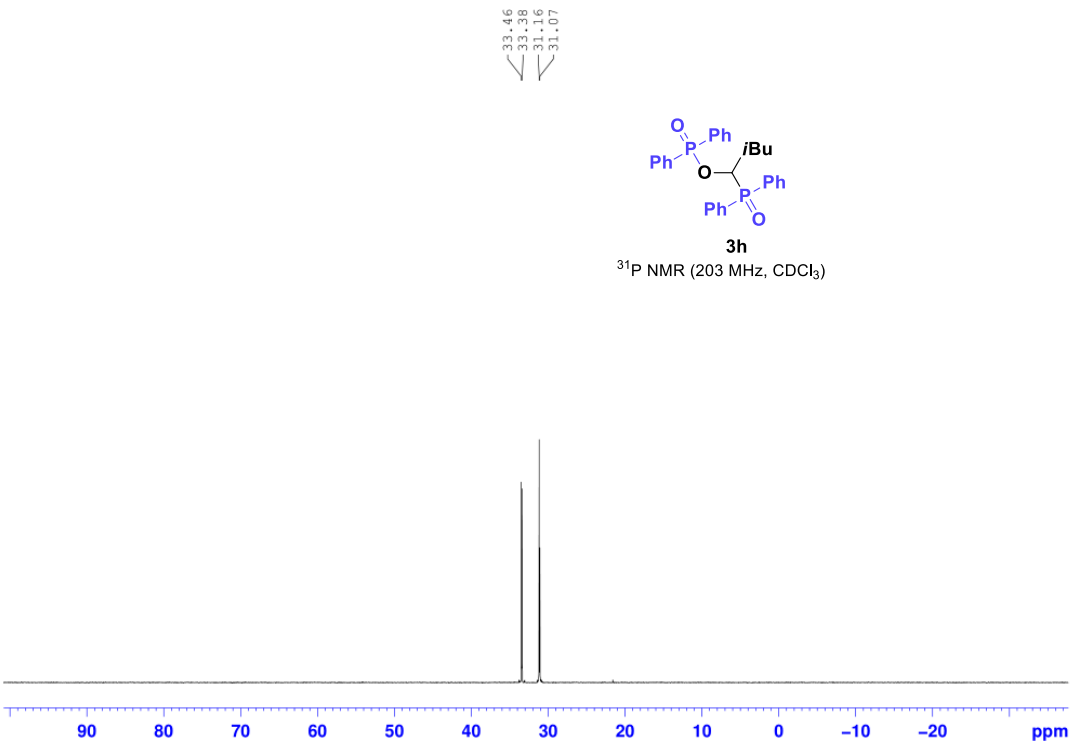

Ph2(O)P
CF2CF3
O
P(O)Ph2
3g
1H NMR (500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.10
2.04
2.06
8.13
2.24
2.02
1.00


37.50
37.47
24.80
Ph2(O)P
CF2CF3
O
P(O)Ph2
3g
31P NMR (203 MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 ppm


−81.14
−112.41
−112.43
−113.01
−113.03
−114.62
−115.22
Ph2(O)P
CF2CF3
O
P(O)Ph2
3g
19F NMR (470 MHz, CDCl3)
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm

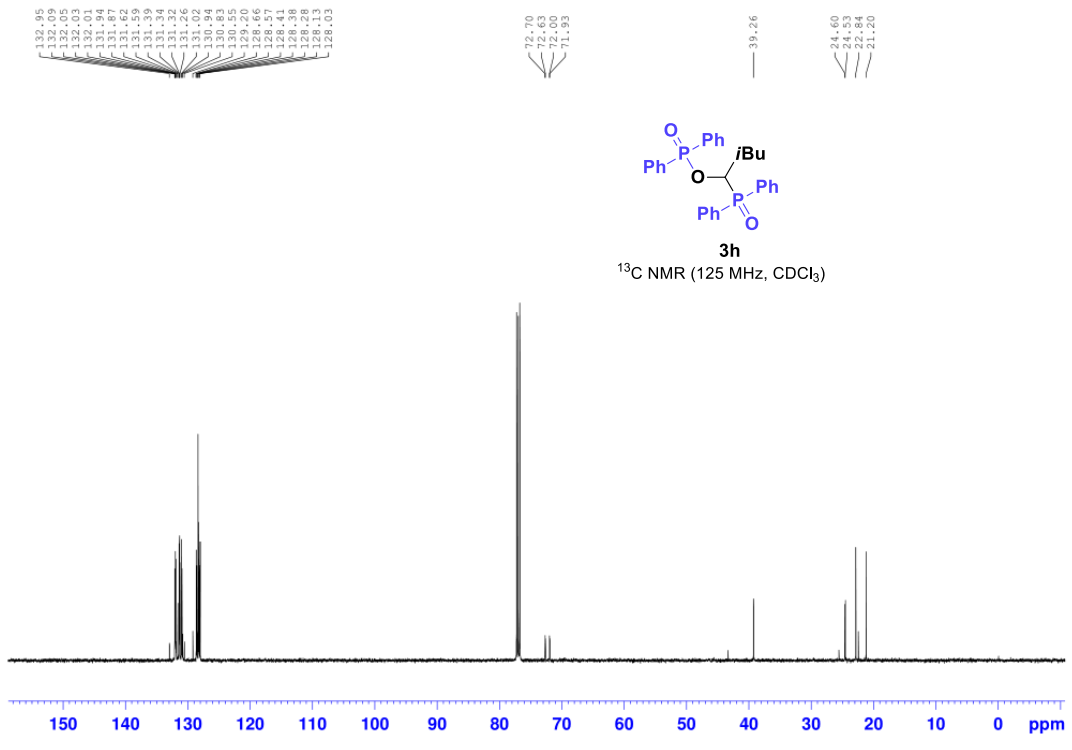

Ph2(O)P
CF2CF3
O
P(O)Ph2
3g
13C NMR (125 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
Ph
Ph
P
iBu
O
Ph
Ph
P
O
3h
1H NMR (500 MHz, CDCl3)
10 9 8 7 6 5 4 3 2 1 0 ppm
2.04 2.05 2.01 2.12 10.14 2.03
1.00
1.07 1.08 1.03
3.07 3.01



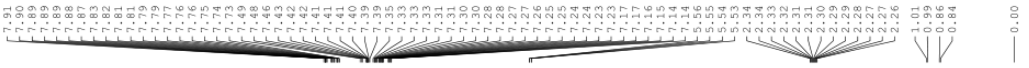
3h

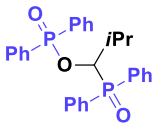
^{31}P NMR (203 MHz, $CDCl_3$)



3h

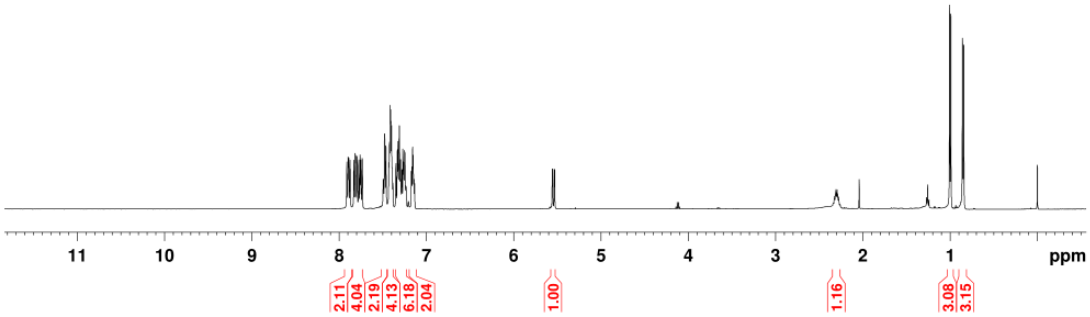
^{13}C NMR (125 MHz, $CDCl_3$)

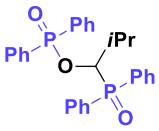




3i

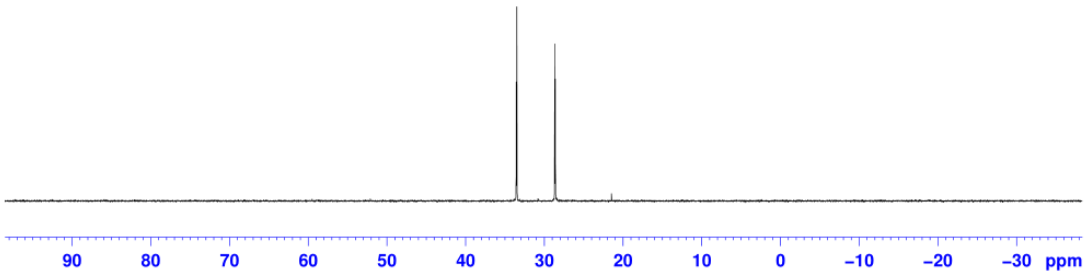
^{1}H NMR (500 MHz, $CDCl_3$)

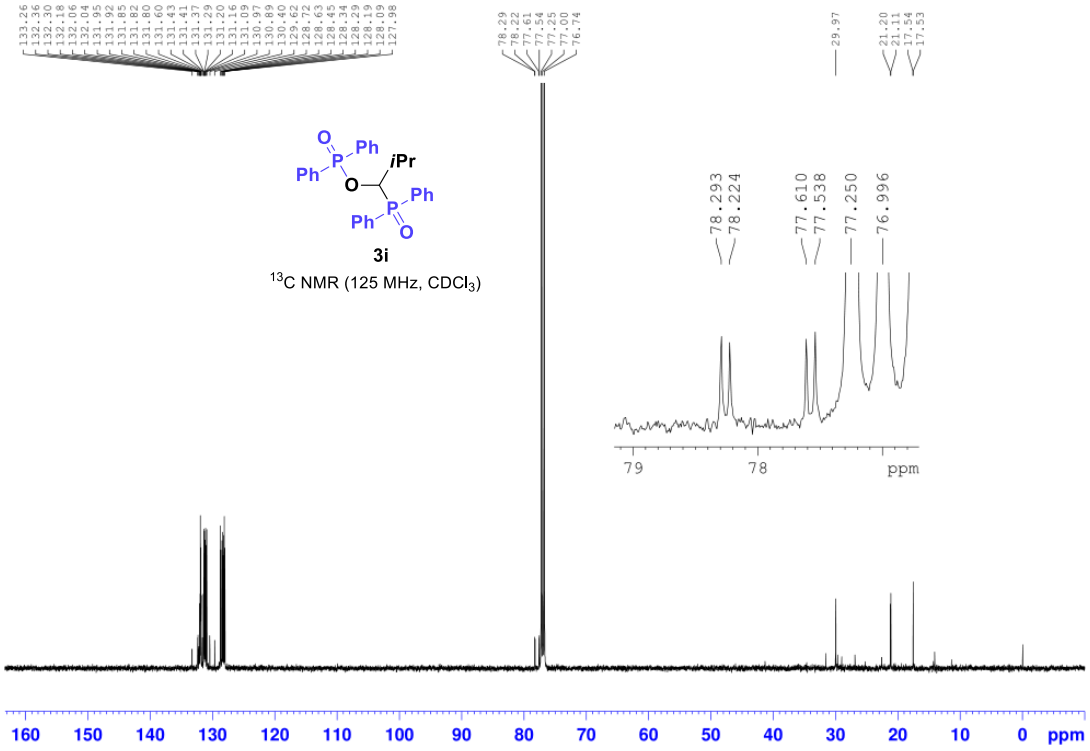


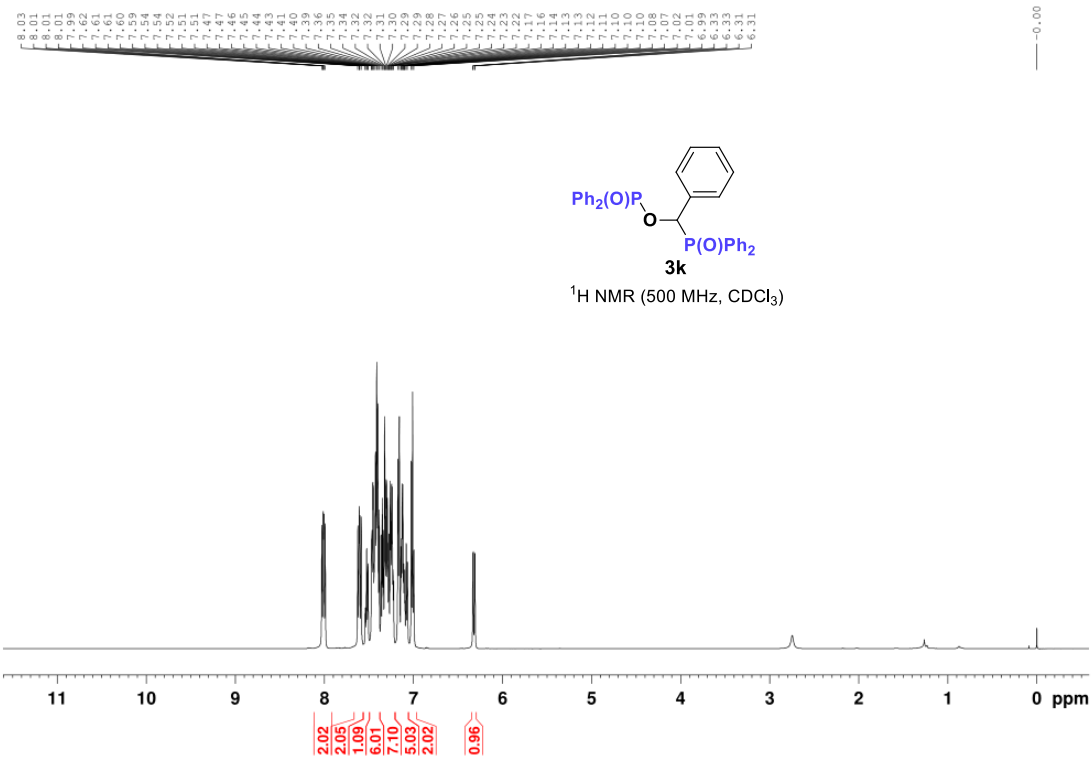


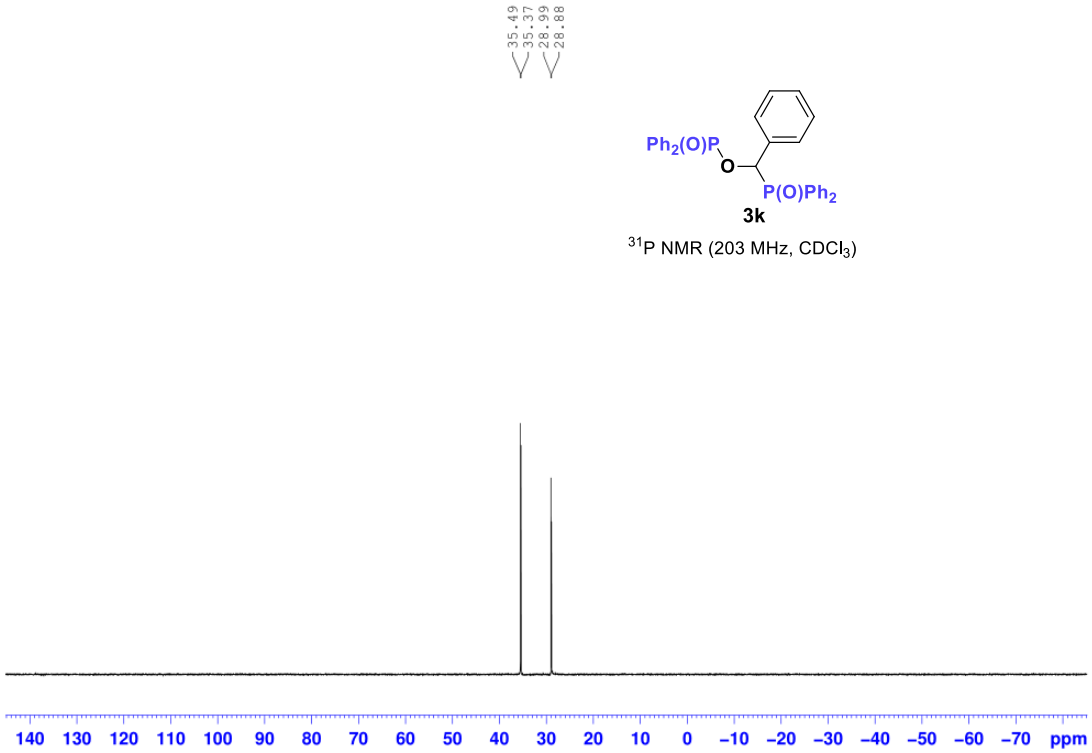
3i

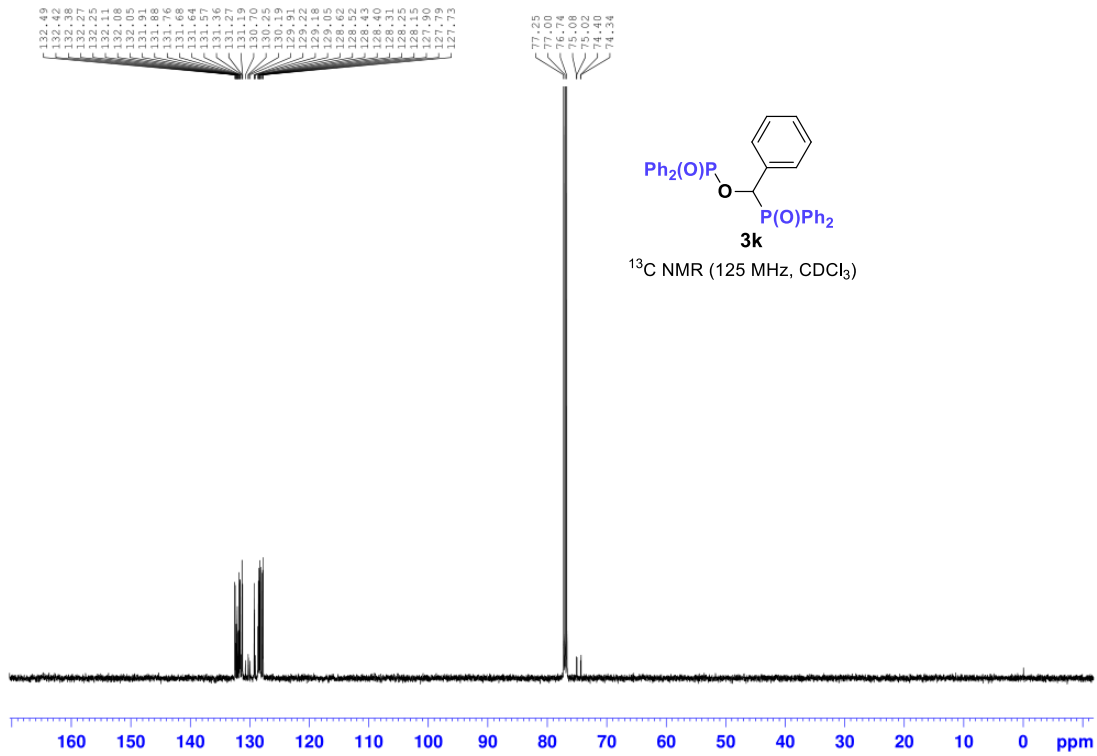
^{31}P NMR (203 MHz, $CDCl_3$)

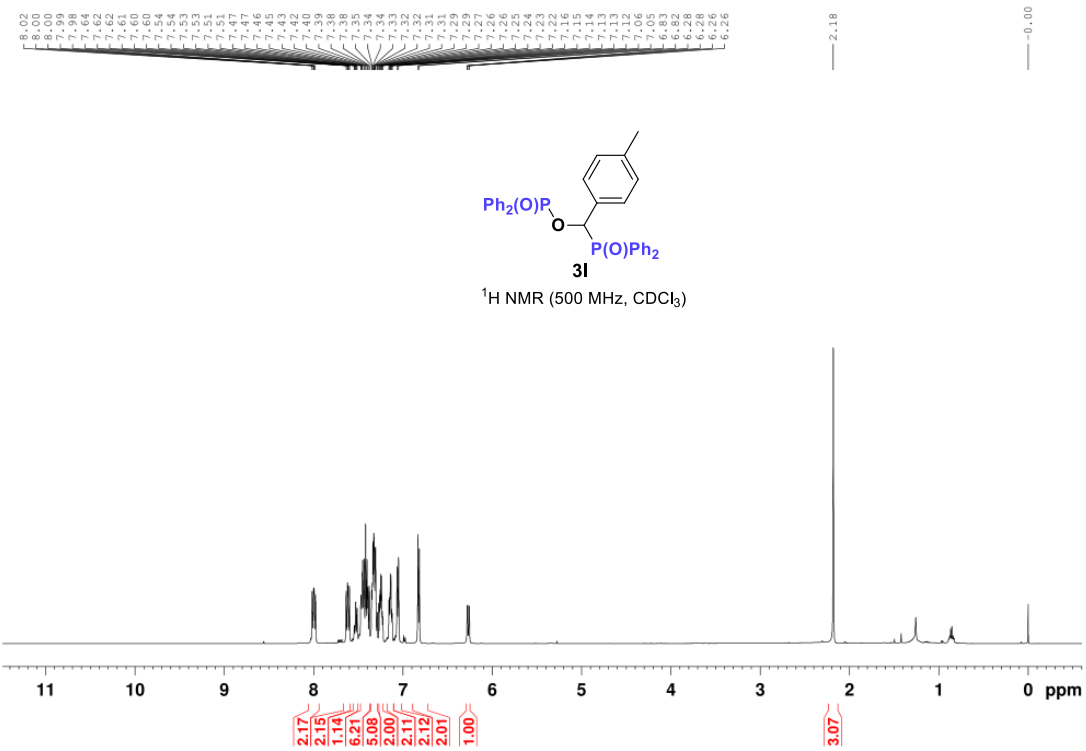



3i
13C NMR (125 MHz, CDCl3)
78.293
78.224
77.610
77.538
77.250
76.996
79
78
ppm
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

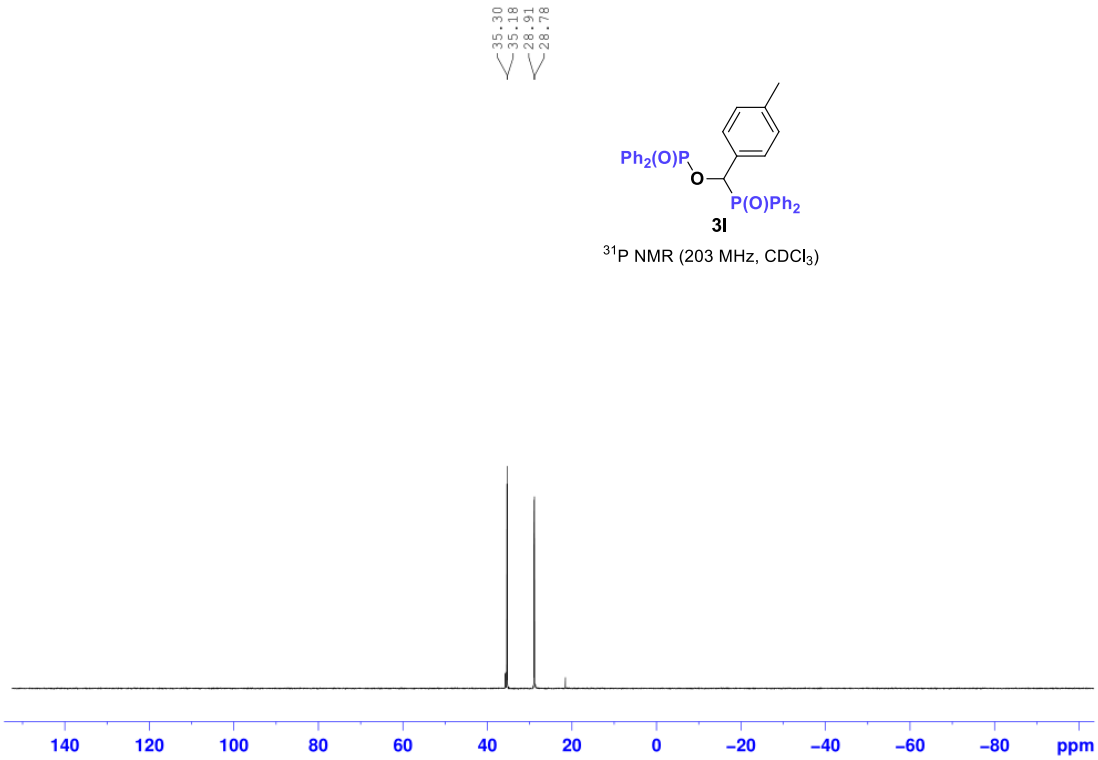

Ph2(O)P
P(O)Ph2
3k
1H NMR (500 MHz, CDCl3)
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.02
2.05
1.09
6.01
7.10
5.03
2.02
0.96


35.49
35.37
28.99
28.88
Ph2(O)P
O
P(O)Ph2
3k
31P NMR (203 MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 ppm

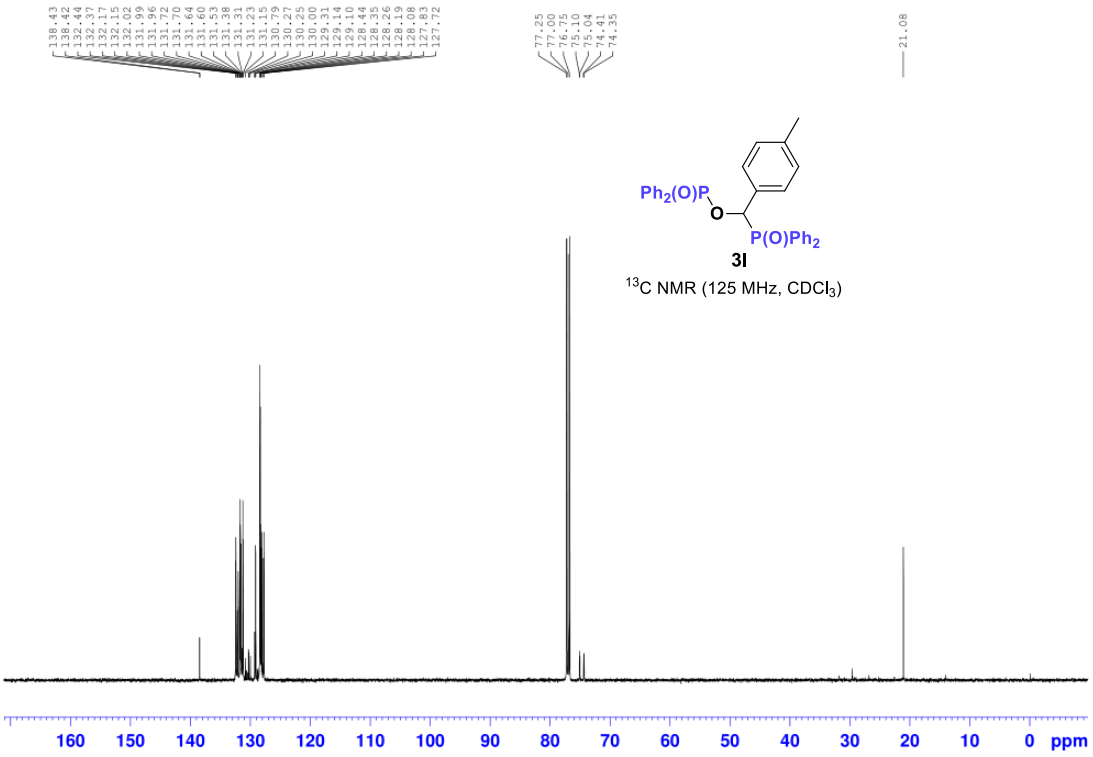

132.49
132.42
132.38
132.27
132.25
132.11
132.08
132.05
131.91
131.88
131.76
131.68
131.64
131.57
131.36
131.27
131.19
131.00
130.25
130.19
129.91
129.22
129.18
129.05
128.62
128.52
128.43
128.40
128.31
128.25
128.15
127.90
127.79
127.73
77.25
77.00
76.74
75.08
75.02
74.40
74.34
Ph2(O)P
O
P(O)Ph2
3k
13C NMR (125 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

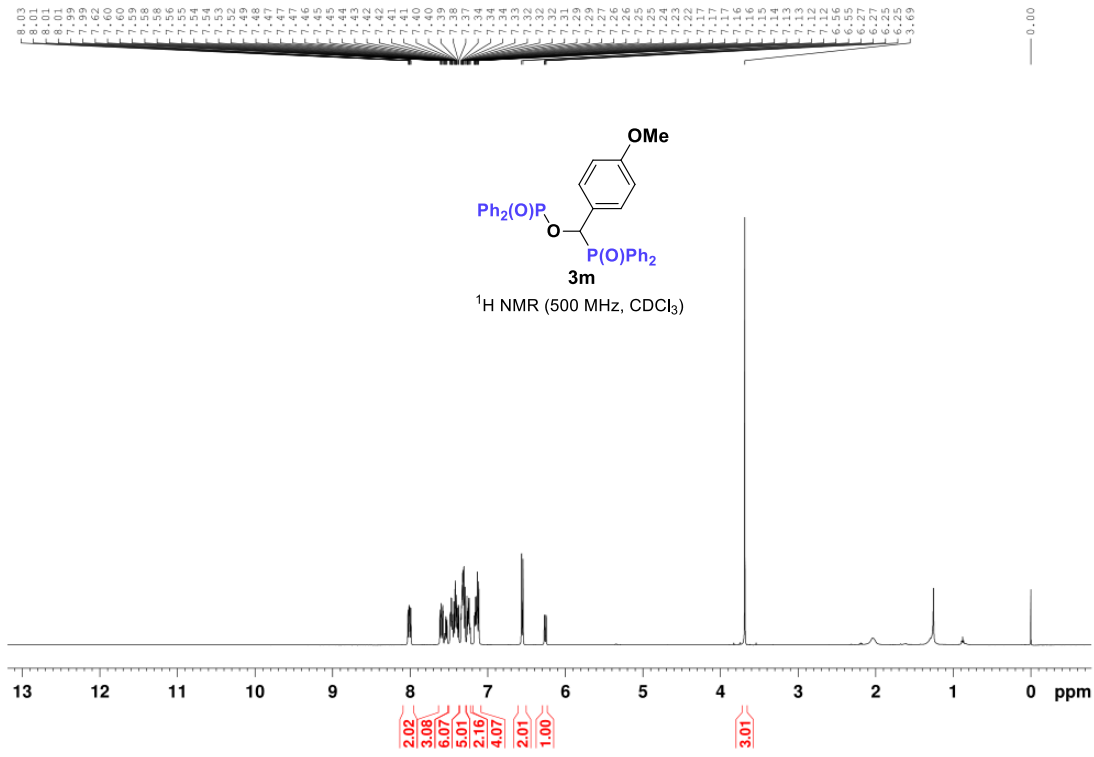


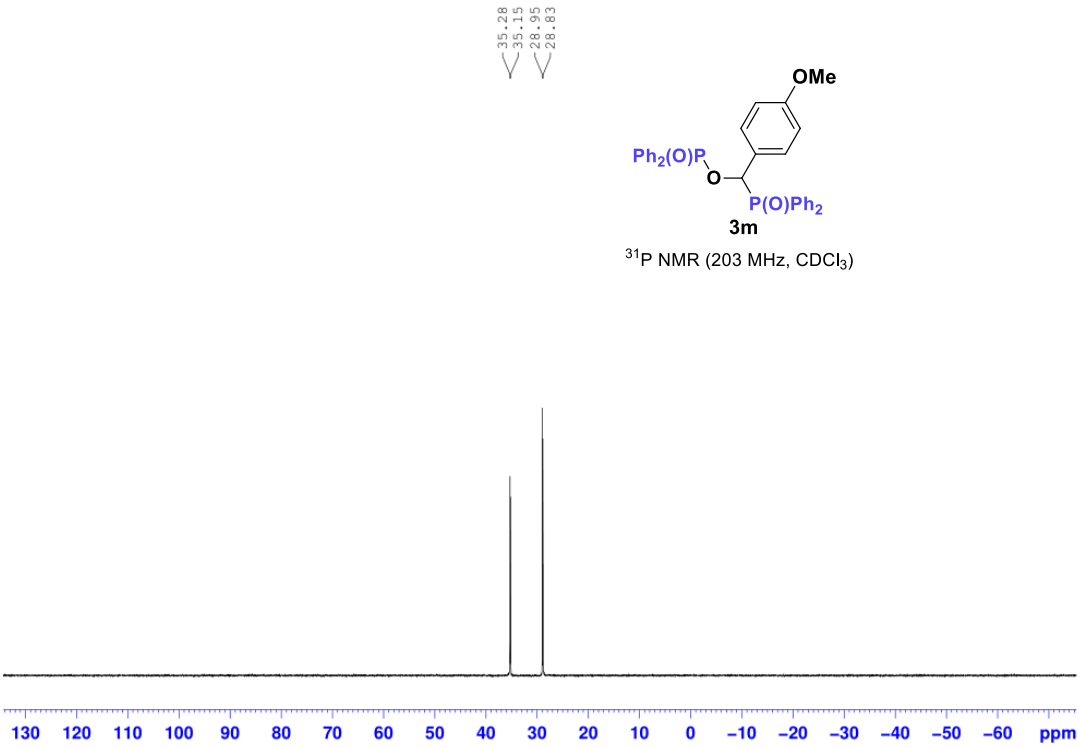
^{1}H NMR (500 MHz, $CDCl_3$)

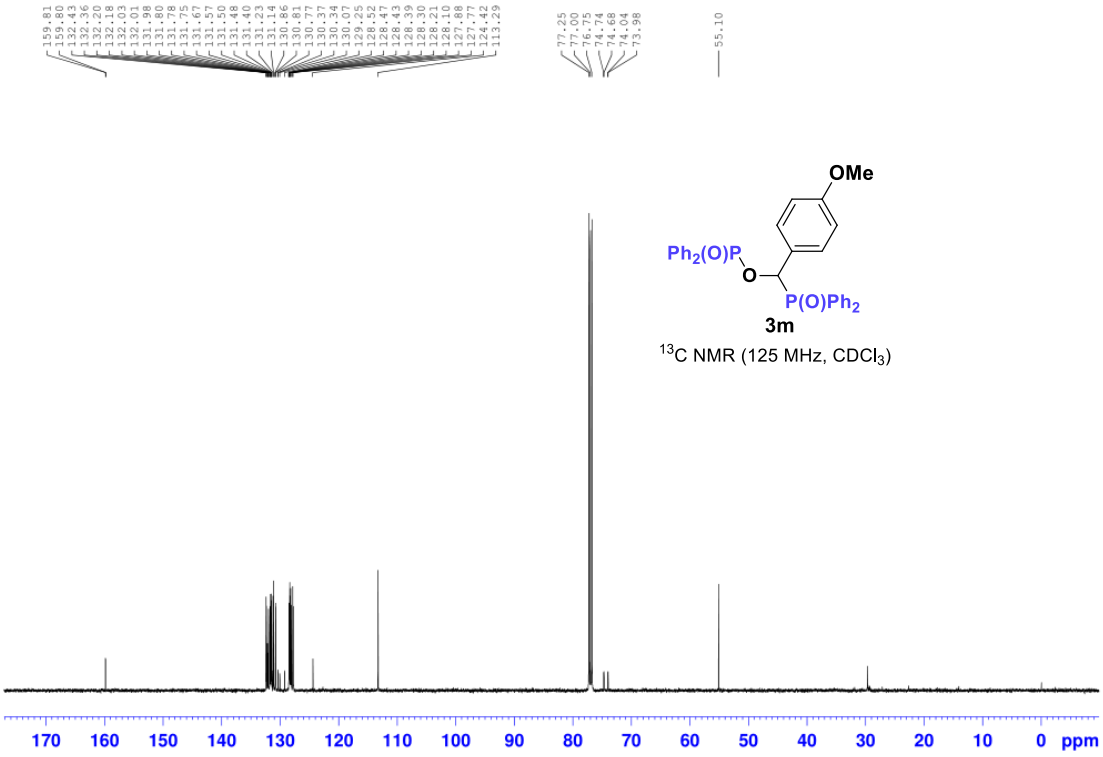


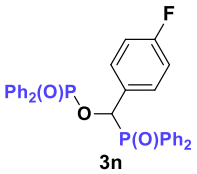
^{31}P NMR (203 MHz, $CDCl_3$)


Ph2(O)P
O
P(O)Ph2
3l
13C NMR (125 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
Ph2(O)P
O
P(O)Ph2
3m
1H NMR (500 MHz, CDCl3)
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.02 3.08 6.07 5.01 2.16 4.07 2.01 1.00 3.01

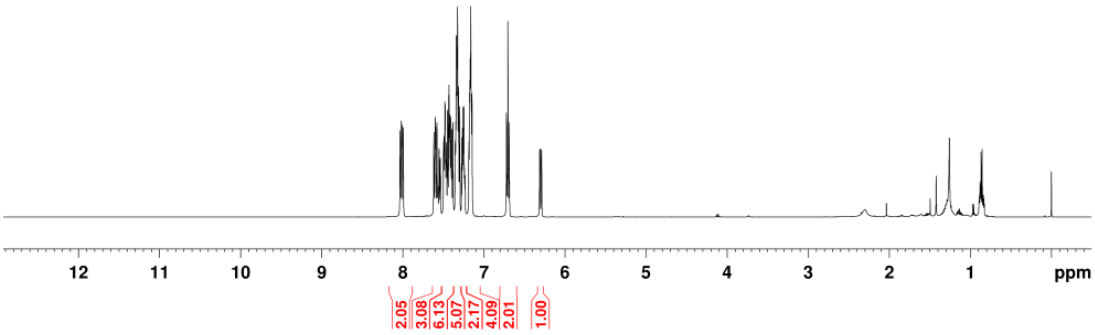

35.28
35.15
28.95
28.83
OMe
Ph2(O)P
O
P(O)Ph2
3m
31P NMR (203 MHz, CDCl3)
130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

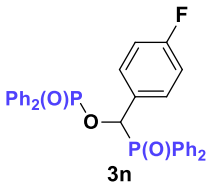

159.81
159.80
132.43
132.36
132.20
132.18
132.03
132.01
131.98
131.80
131.78
131.75
131.67
131.57
131.50
131.48
131.40
131.23
131.14
130.86
130.81
130.77
130.37
130.34
130.07
129.25
128.52
128.47
128.43
128.39
128.30
128.21
128.10
127.88
127.77
124.42
113.29
77.25
77.00
76.75
74.74
74.68
74.04
73.98
55.10
OMe
Ph2(O)P
O
P(O)Ph2
3m
13C NMR (125 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



3n

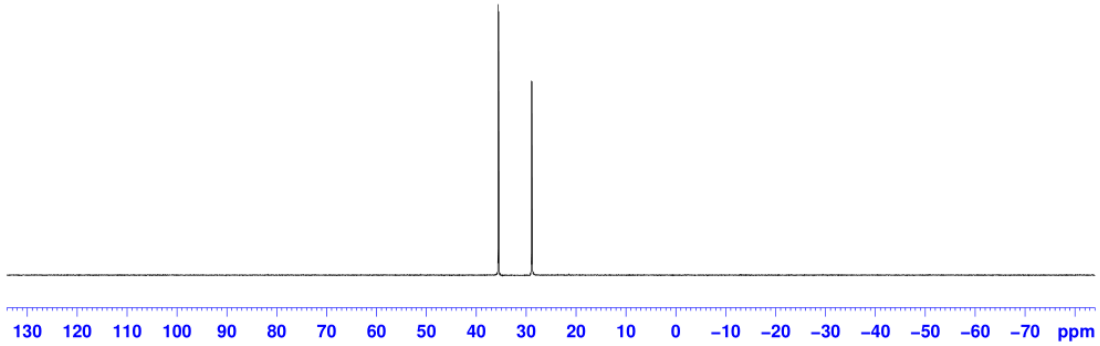
^{1}H NMR (500 MHz, $CDCl_3$)

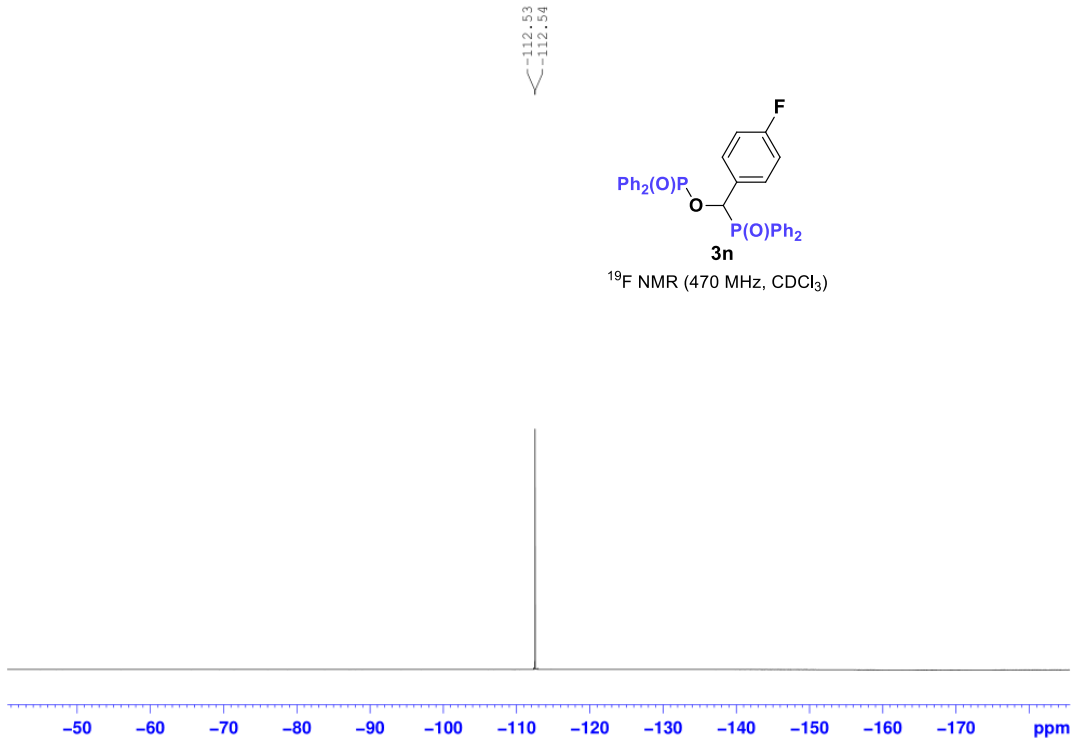




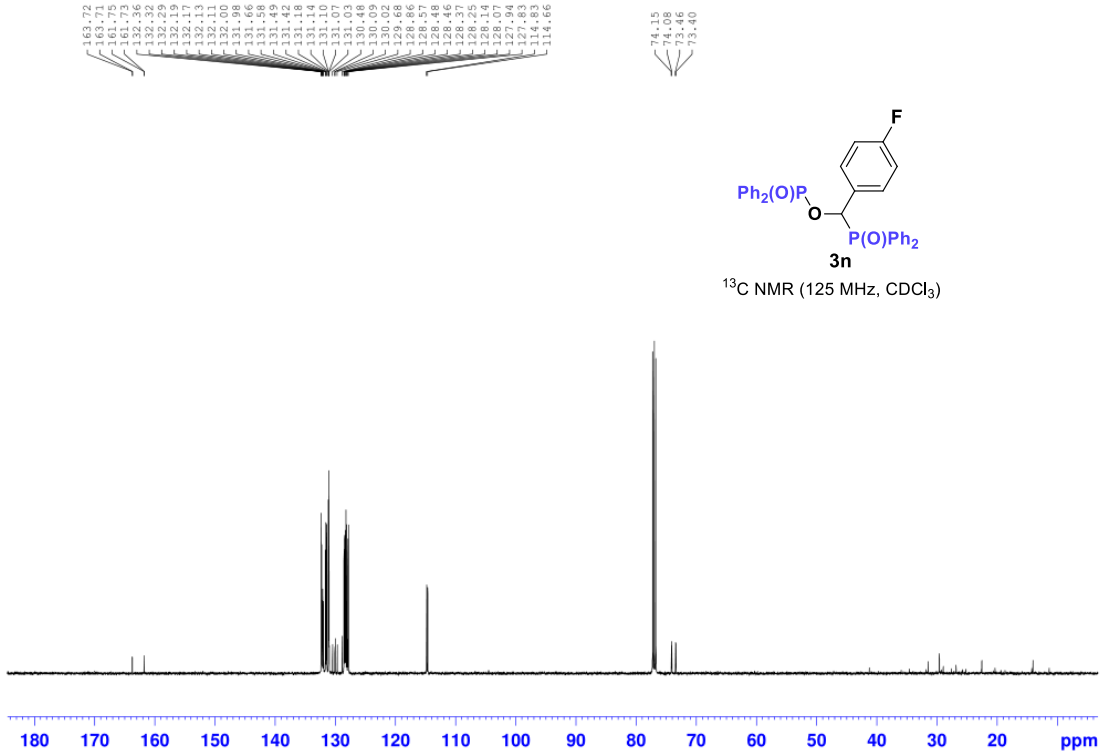
3n

^{31}P NMR (203 MHz, $CDCl_3$)

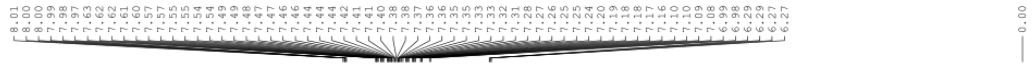


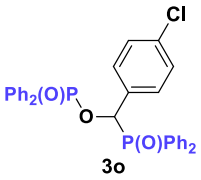


^{19}F NMR (470 MHz, $CDCl_3$)



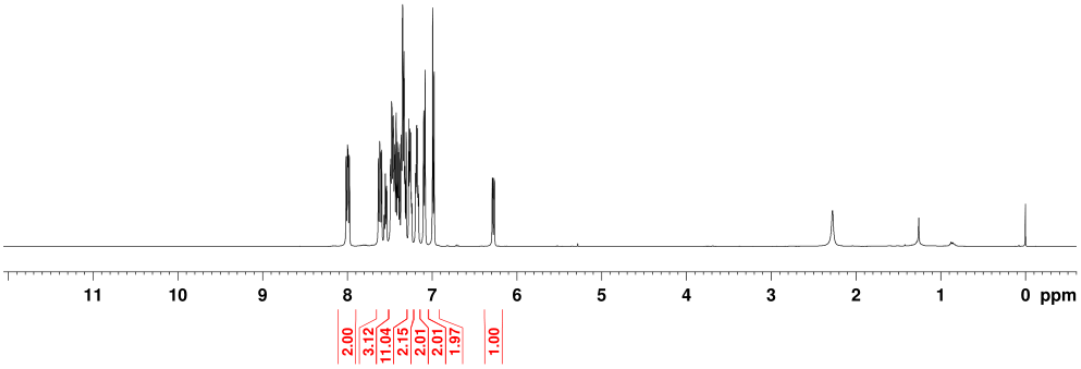
^{13}C NMR (125 MHz, $CDCl_3$)

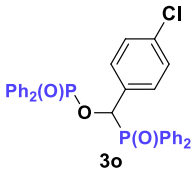




3o

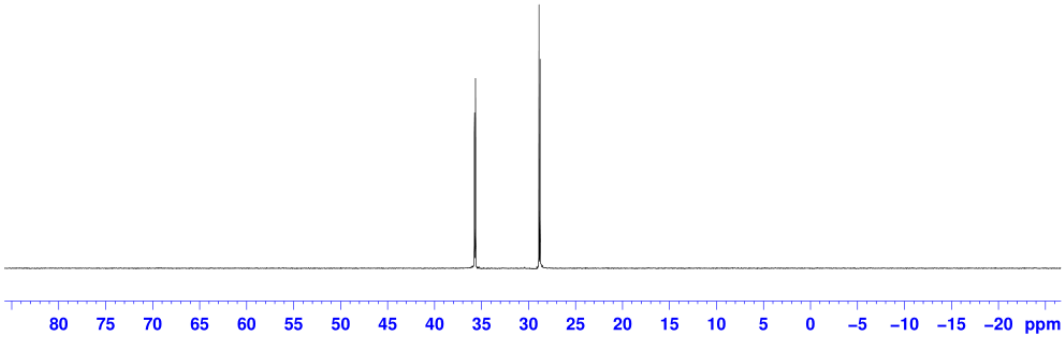
^{1}H NMR (500 MHz, $CDCl_3$)

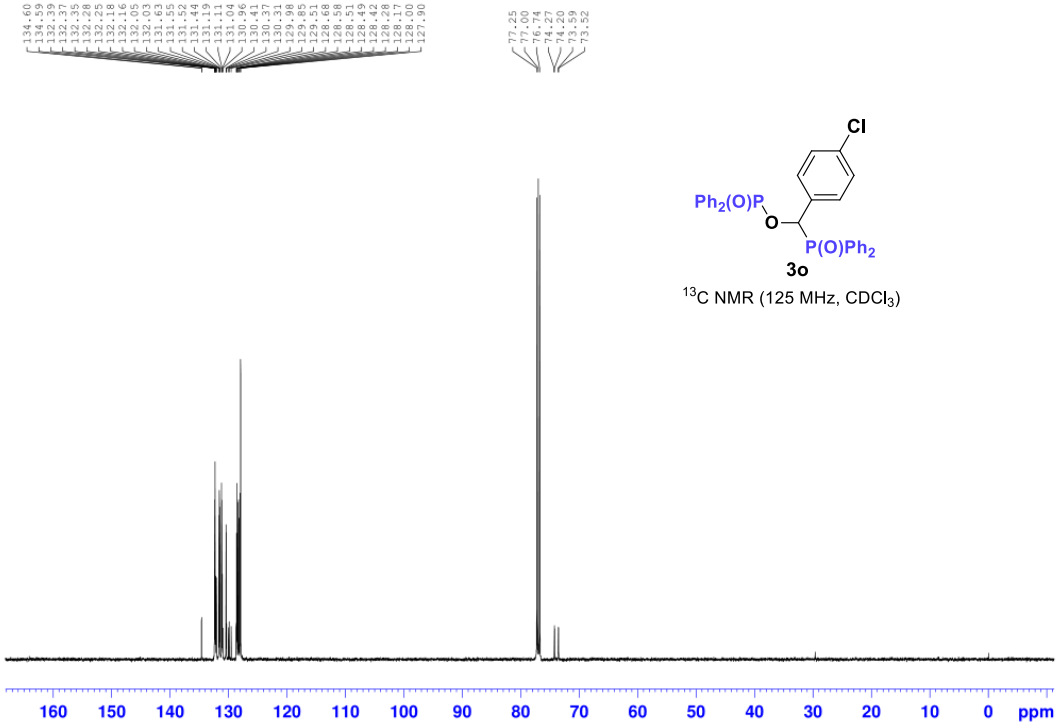




3o

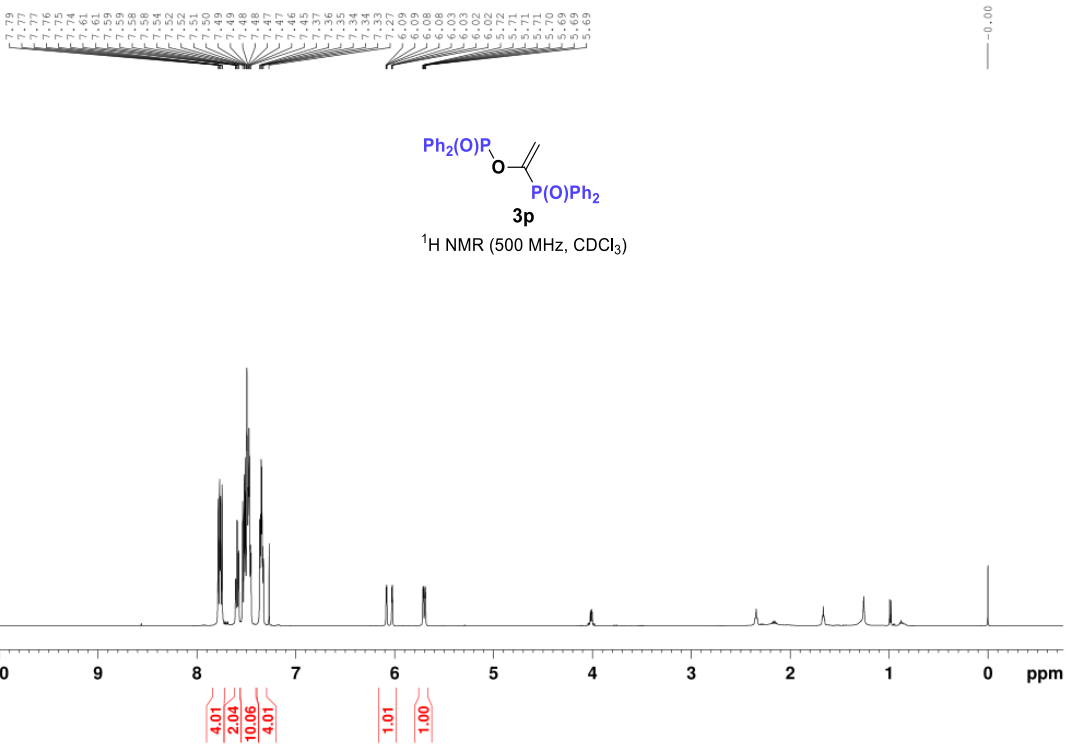
^{31}P NMR (203 MHz, $CDCl_3$)





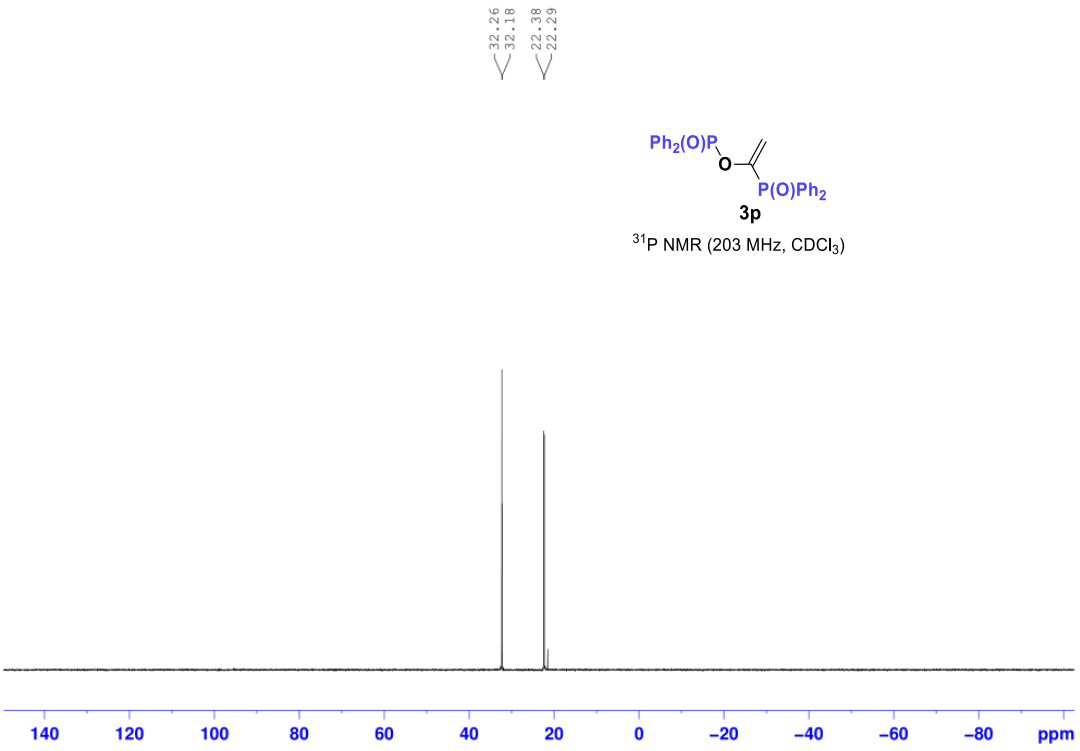
3o

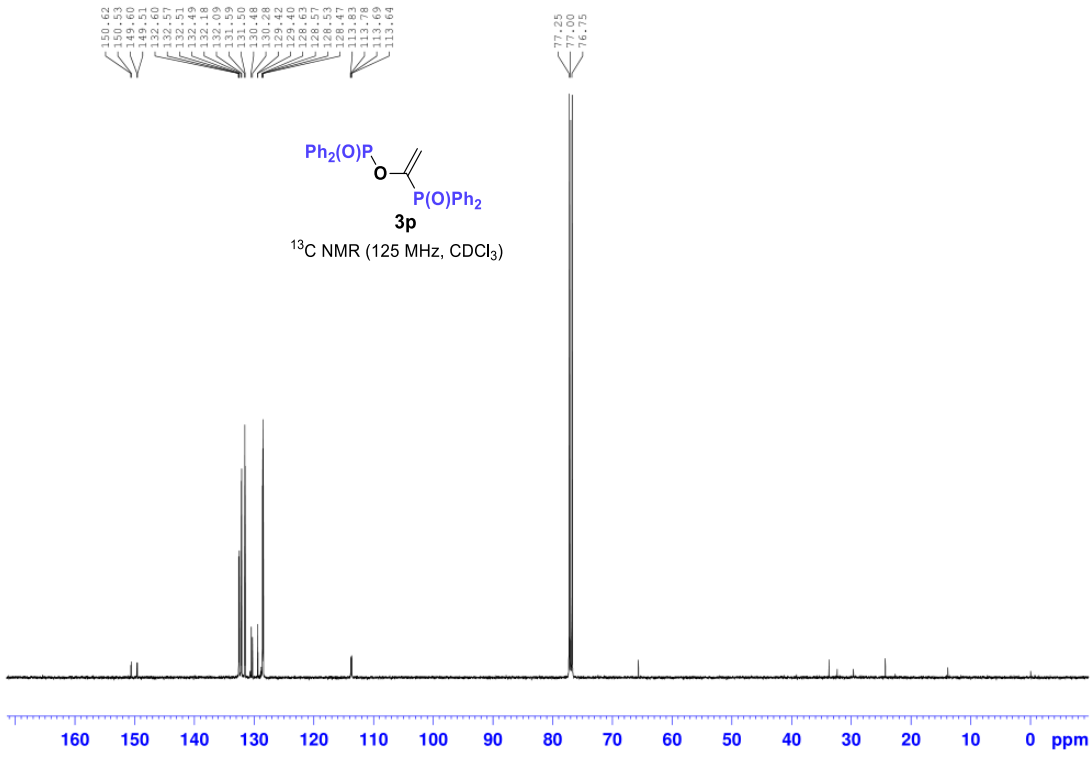
^{13}C NMR (125 MHz, $CDCl_3$)

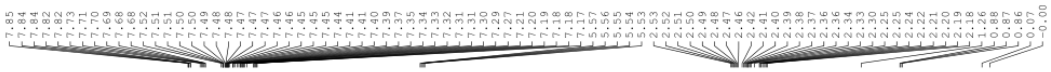


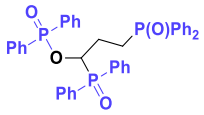
3p

^{1}H NMR (500 MHz, $CDCl_3$)


32.26
32.18
22.38
22.29
Ph2(O)P
O
P(O)Ph2
3p
31P NMR (203 MHz, CDCl3)
140
120
100
80
60
40
20
0
−20
−40
−60
−80
ppm

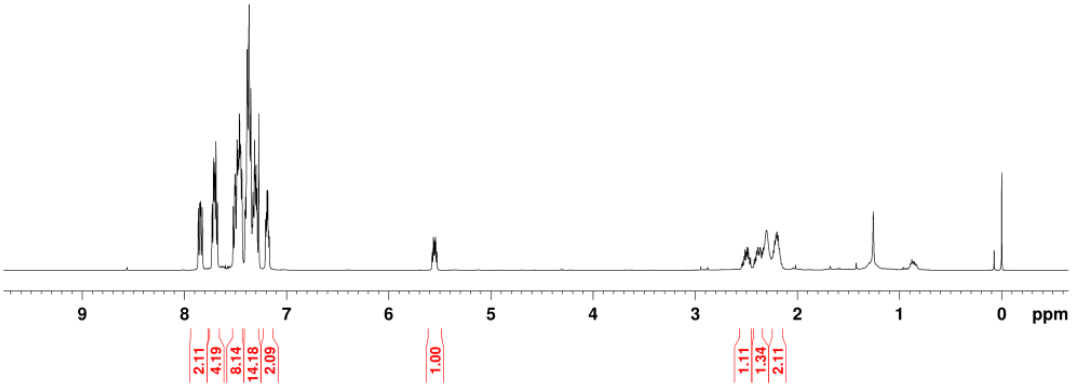

150.62
150.53
149.60
149.51
132.60
132.57
132.51
132.49
132.18
132.09
131.59
131.50
130.48
130.28
129.42
129.40
128.63
128.57
128.53
128.47
113.83
113.78
113.69
113.64
77.25
77.00
76.75
Ph2(O)P
O
P(O)Ph2
3p
13C NMR (125 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

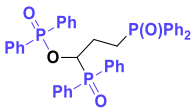




3q

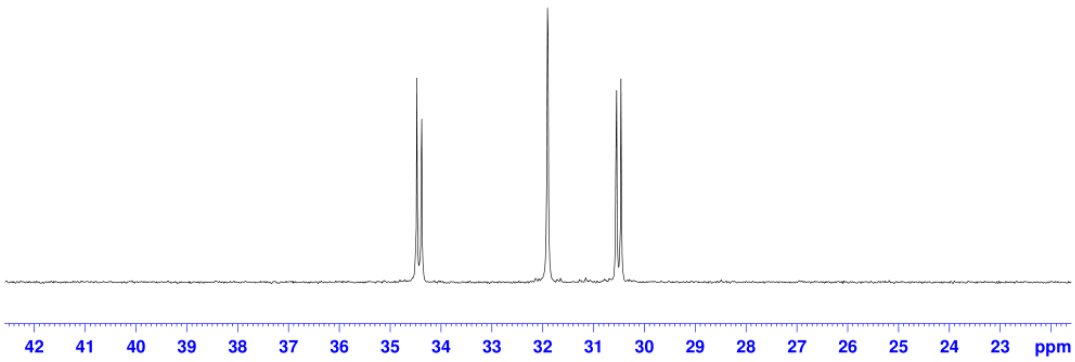
^{1}H NMR (500 MHz, $CDCl_3$)

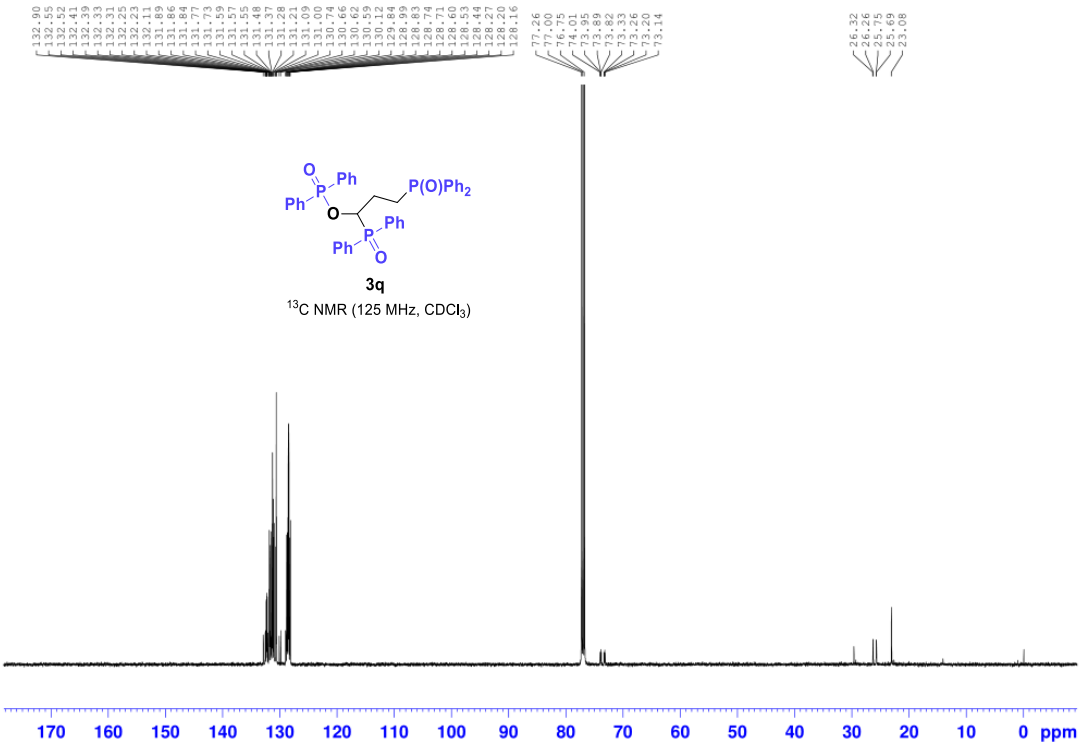




3q

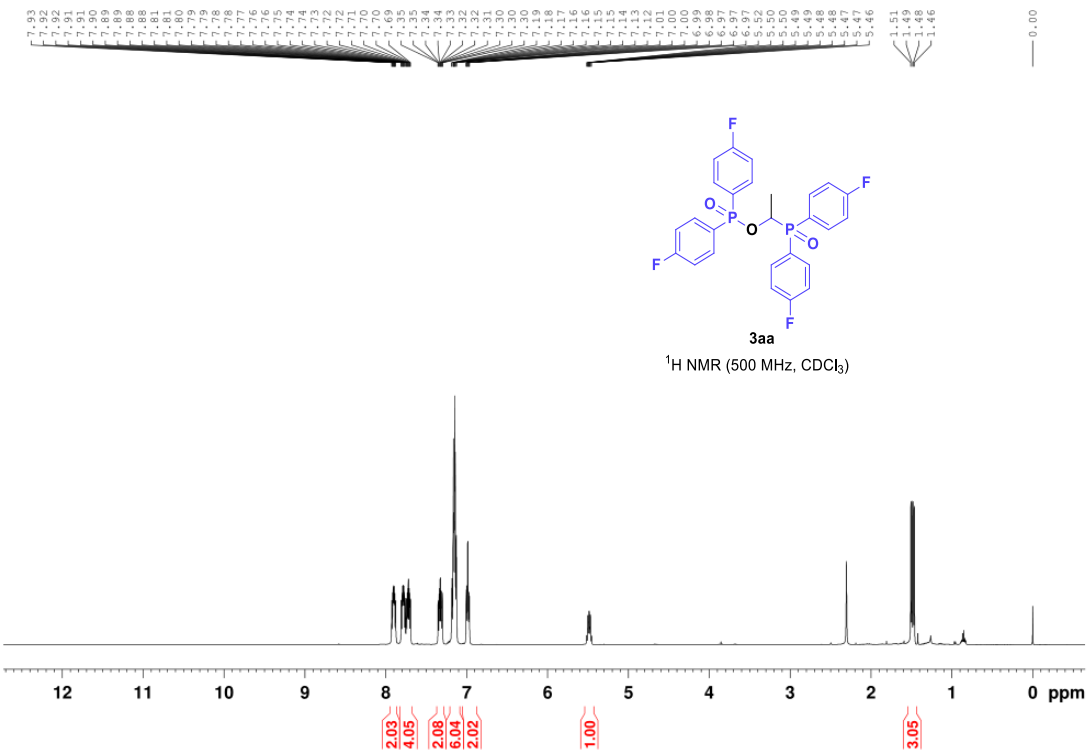
^{31}P NMR (203 MHz, $CDCl_3$)





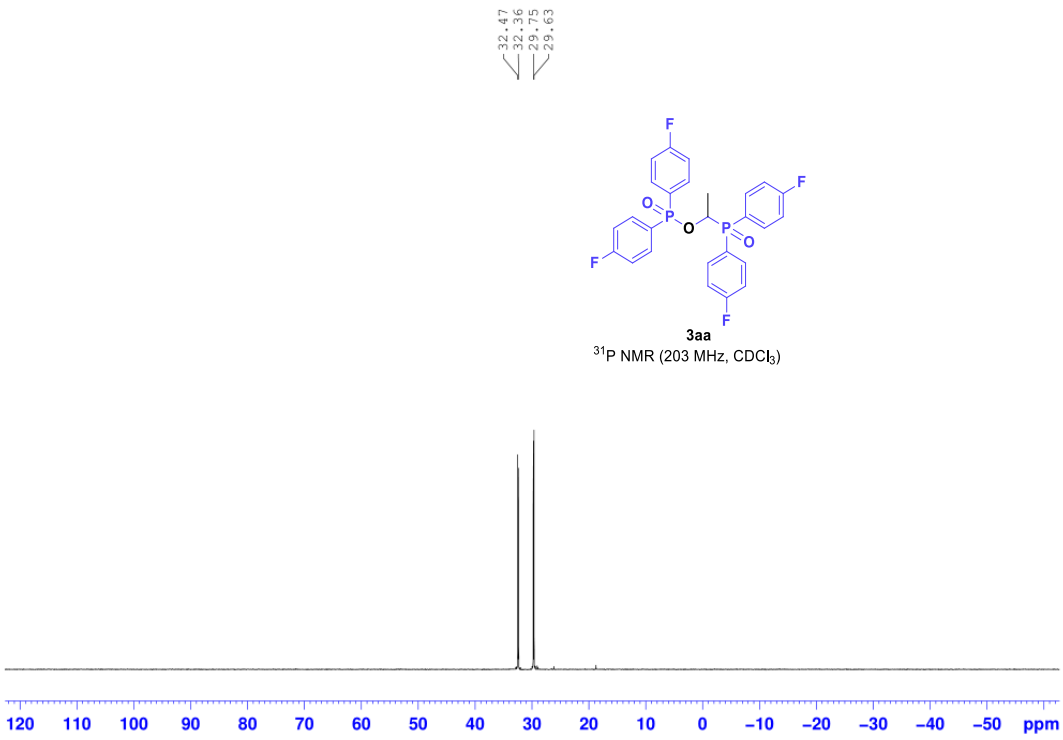
3q

^{13}C NMR (125 MHz, $CDCl_3$)



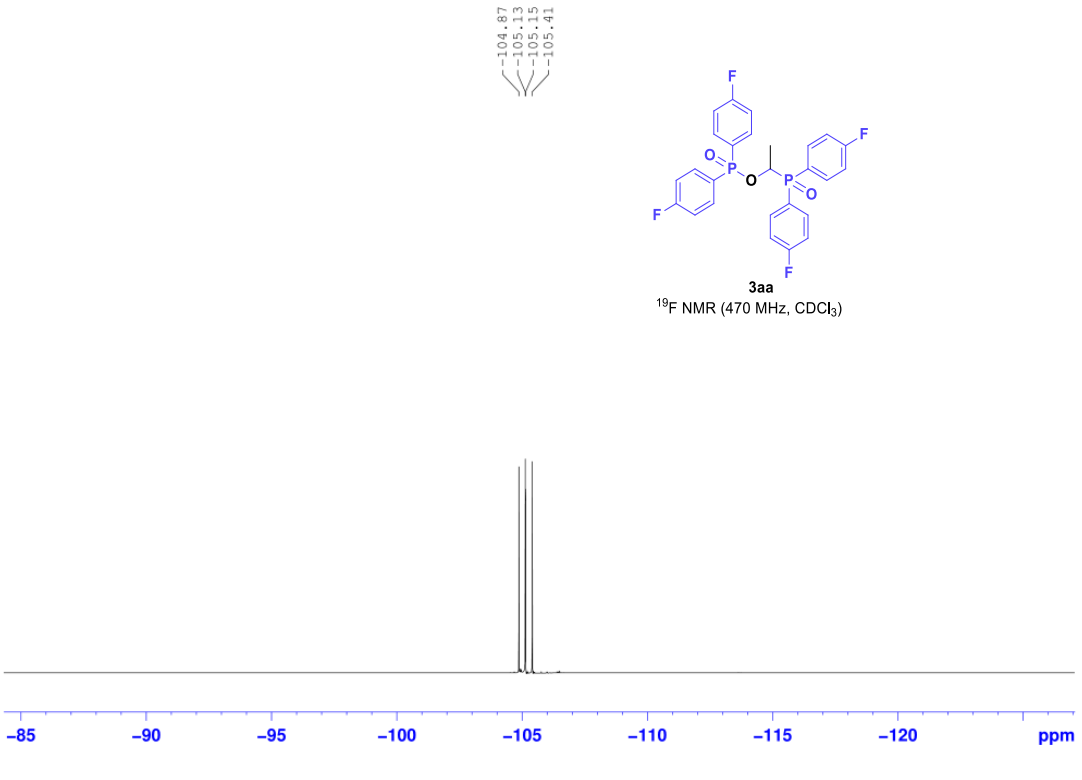
3aa

^{1}H NMR (500 MHz, $CDCl_3$)



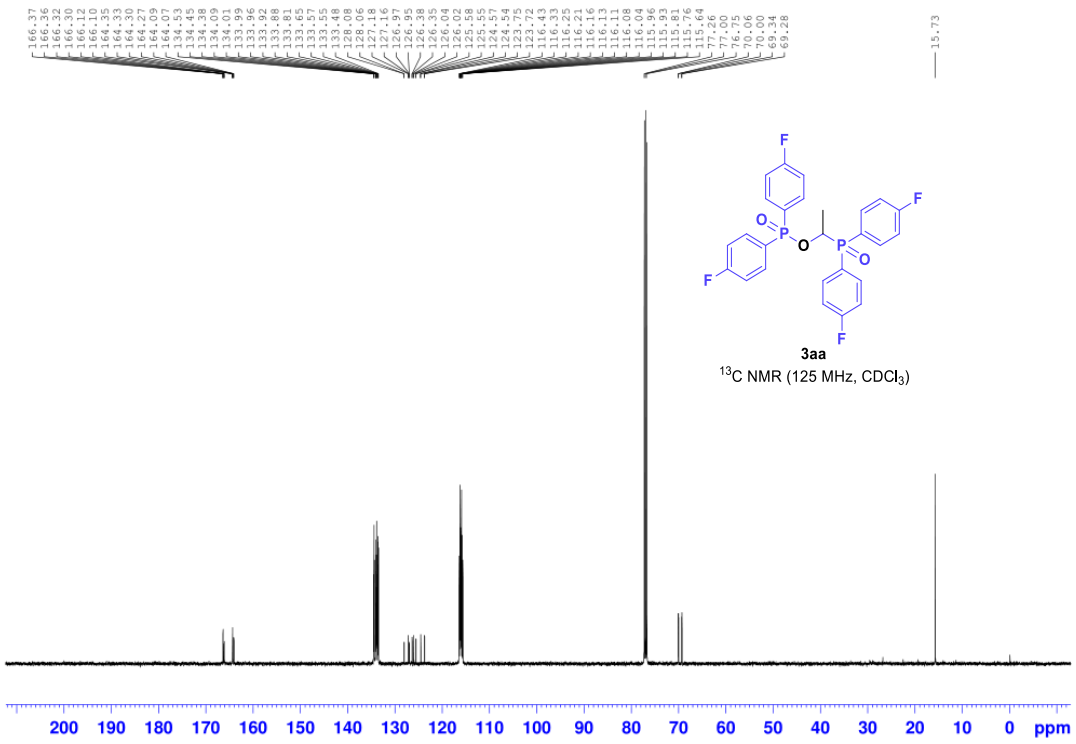
3aa

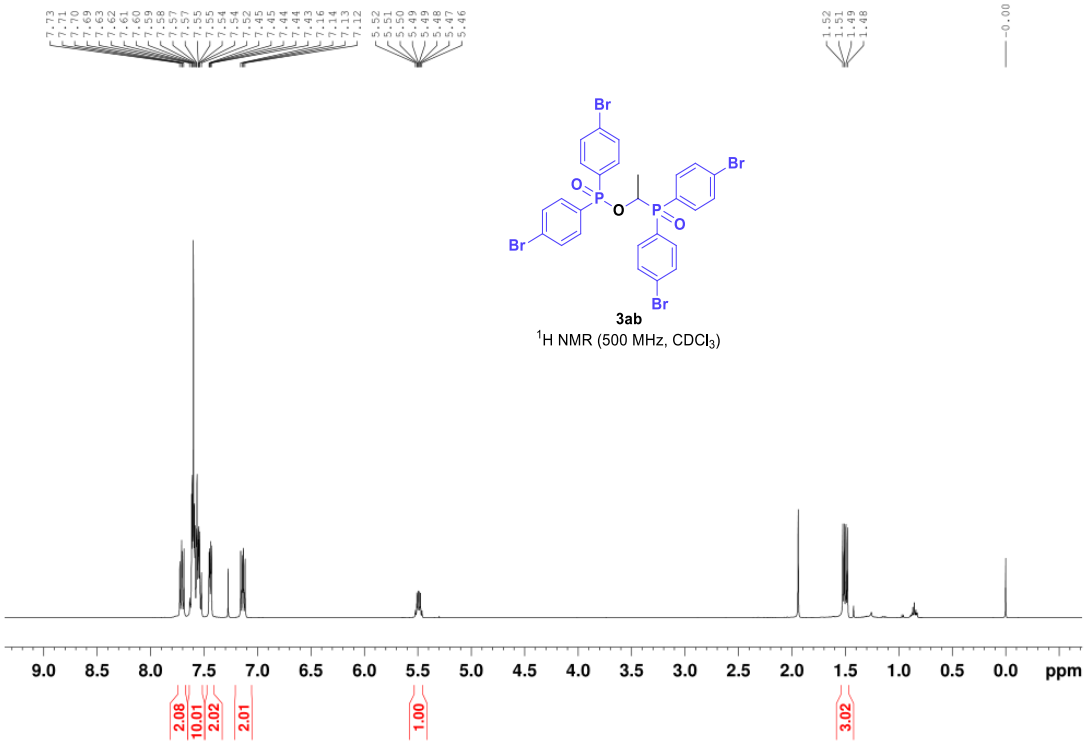
^{31}P NMR (203 MHz, $CDCl_3$)

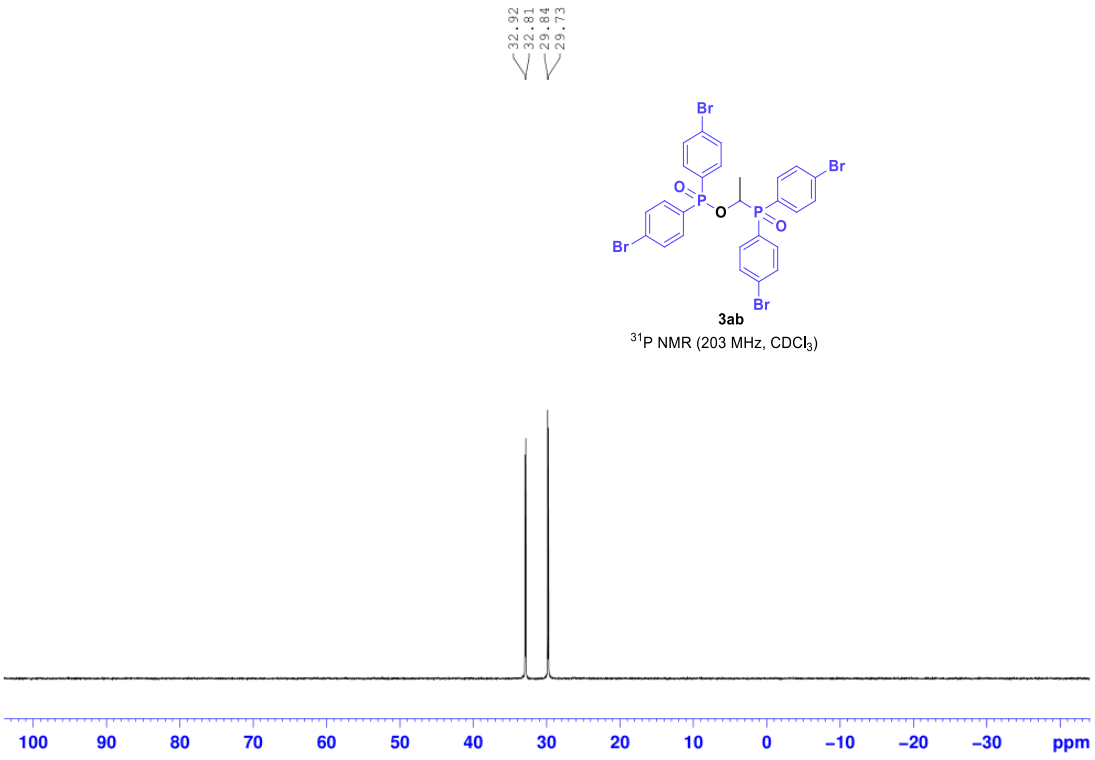


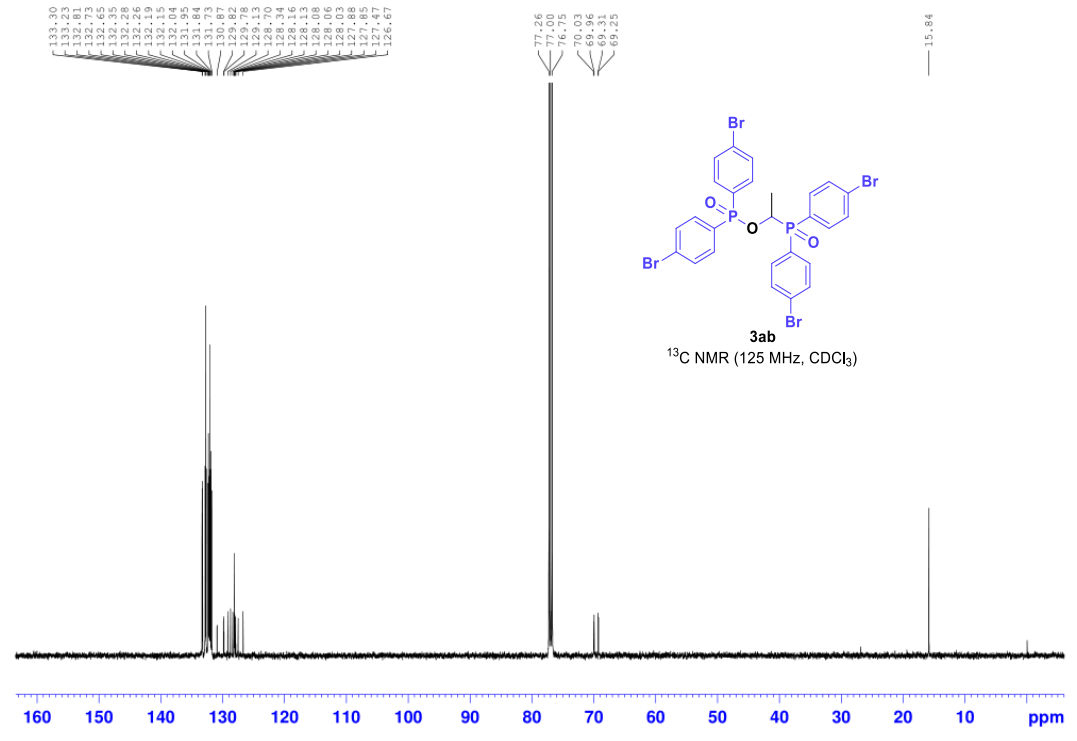
3aa

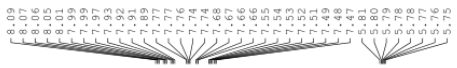
^{19}F NMR (470 MHz, $CDCl_3$)

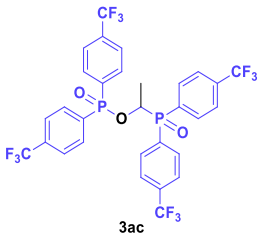

166.37
166.36
166.32
166.30
166.12
166.10
164.35
164.33
164.30
164.27
164.09
164.07
134.53
134.45
134.38
134.09
134.01
133.99
133.96
133.92
133.88
133.61
133.55
133.57
133.55
133.48
128.08
128.06
127.18
127.16
126.97
126.95
126.38
126.35
126.04
126.02
125.58
125.55
124.57
124.54
123.72
123.75
116.43
116.33
116.25
116.21
116.16
116.13
116.11
116.08
116.04
115.96
115.93
115.81
115.76
115.64
77.26
77.00
76.75
70.06
70.00
69.34
69.28
15.73
F
F
F
F
O
P
O
P
O
3aa
^{13}C NMR (125 MHz, CDCl$_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.73
7.71
7.70
7.69
7.63
7.62
7.61
7.60
7.59
7.58
7.57
7.57
7.55
7.55
7.54
7.54
7.52
7.52
7.45
7.45
7.44
7.44
7.43
7.16
7.14
7.13
7.12
5.52
5.51
5.50
5.49
5.49
5.48
5.47
5.46
1.52
1.51
1.49
1.48
0.00
Br
Br
Br
Br
O
P
O
P
O
3ab
^{1}H NMR (500 MHz, CDCl$_3$)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.08
10.01
2.02
2.01
1.00
3.02


32.92
32.81
29.84
29.73
Br
Br
Br
Br
O
P
O
P
O
3ab
31P NMR (203 MHz, CDCl3)
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
ppm

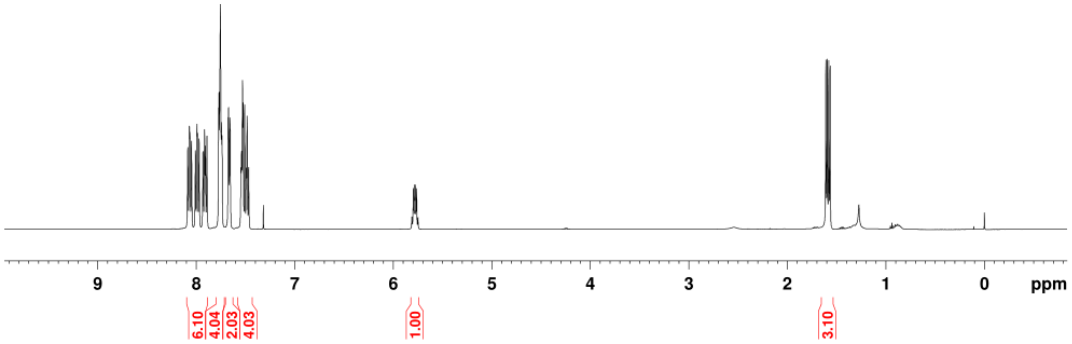

133.30
133.23
132.81
132.73
132.65
132.35
132.28
132.26
132.19
132.15
132.04
131.95
131.84
131.73
130.87
129.82
129.78
129.13
128.70
128.34
128.16
128.13
128.08
128.06
128.03
127.88
127.85
127.47
126.67
77.26
77.00
76.75
70.03
69.96
69.31
69.25
15.84
Br
Br
Br
Br
O
P
O
P
O
3ab
13C NMR (125 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

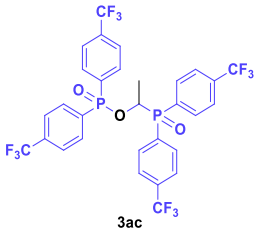




3ac

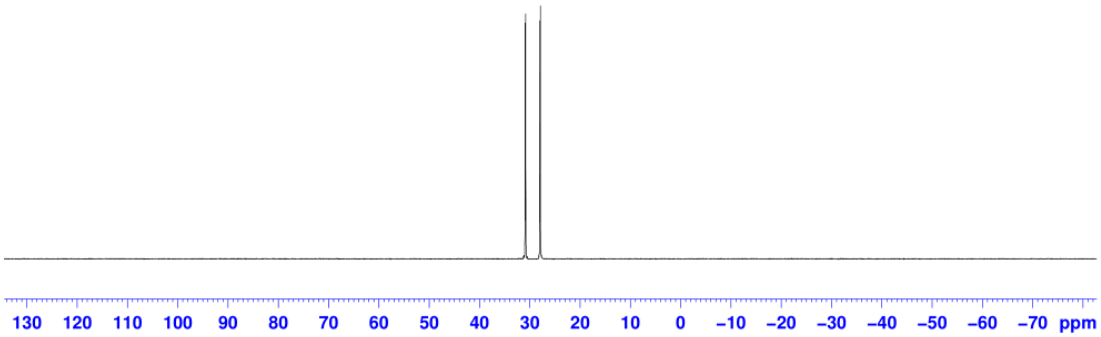
^{1}H NMR (500 MHz, $CDCl_3$)

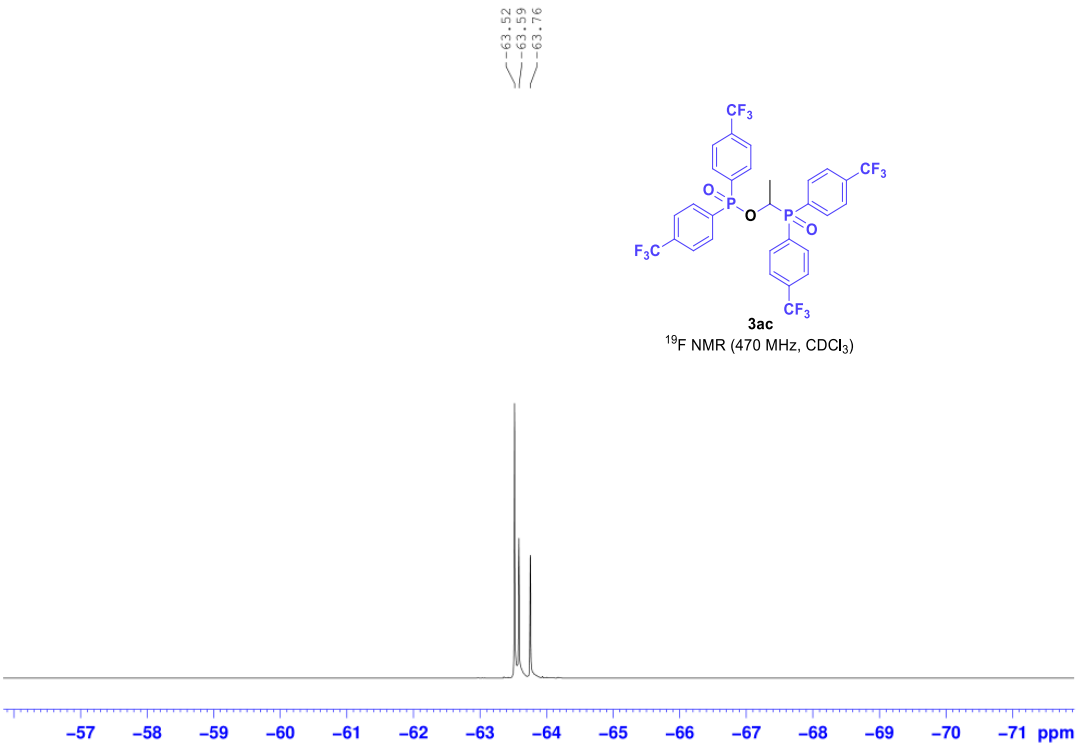


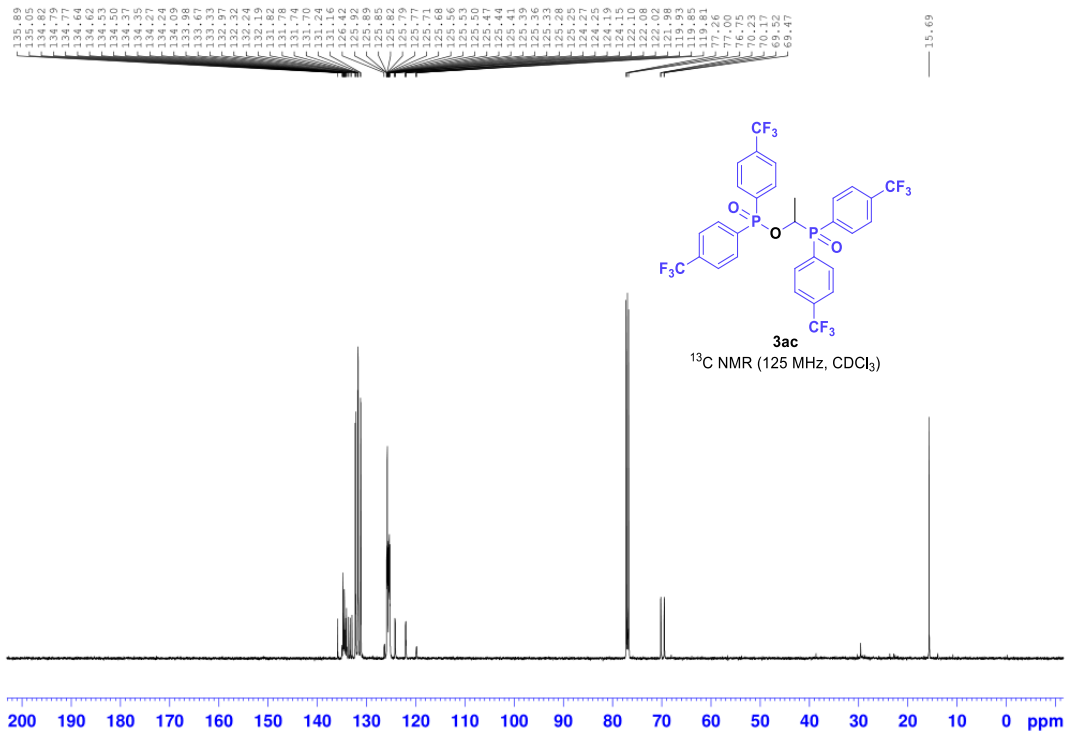


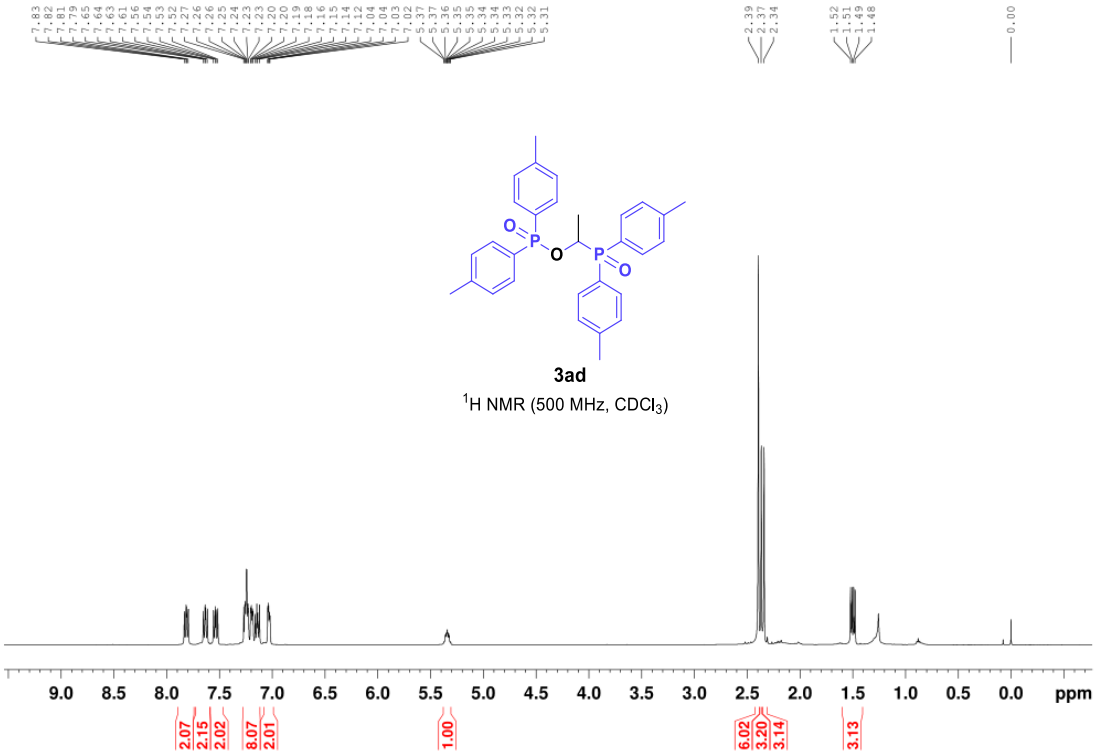
3ac

^{31}P NMR (203 MHz, $CDCl_3$)



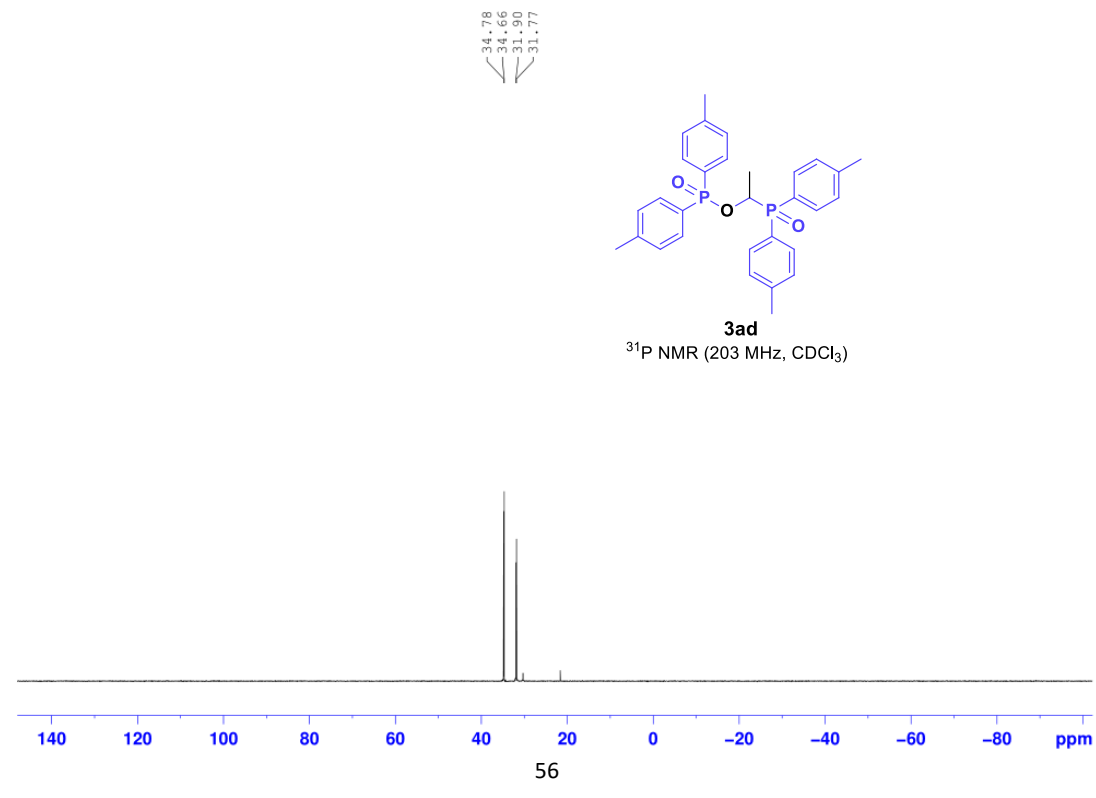

-63.52
-63.59
-63.76
CF3
CF3
O
P
O
P
O
F3C
CF3
3ac
19F NMR (470 MHz, CDCl3)
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
ppm


15.69
CF3
CF3
O
P
O
P
O
F3C
CF3
3ac
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



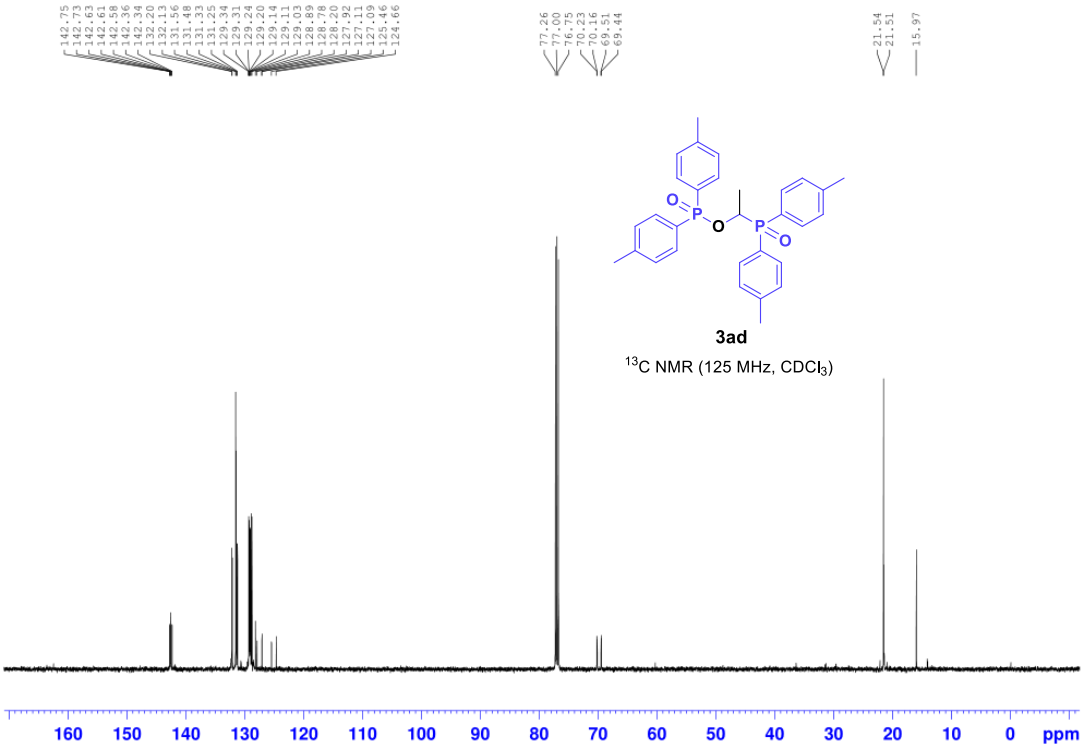
3ad

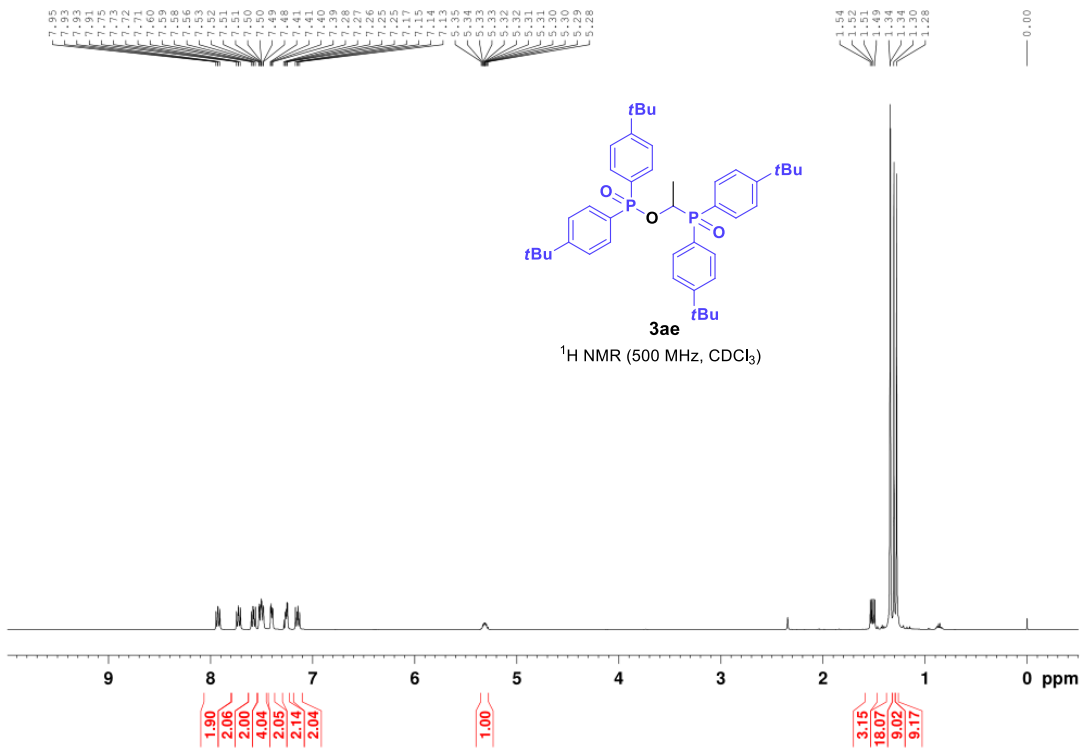
^{1}H NMR (500 MHz, $CDCl_3$)

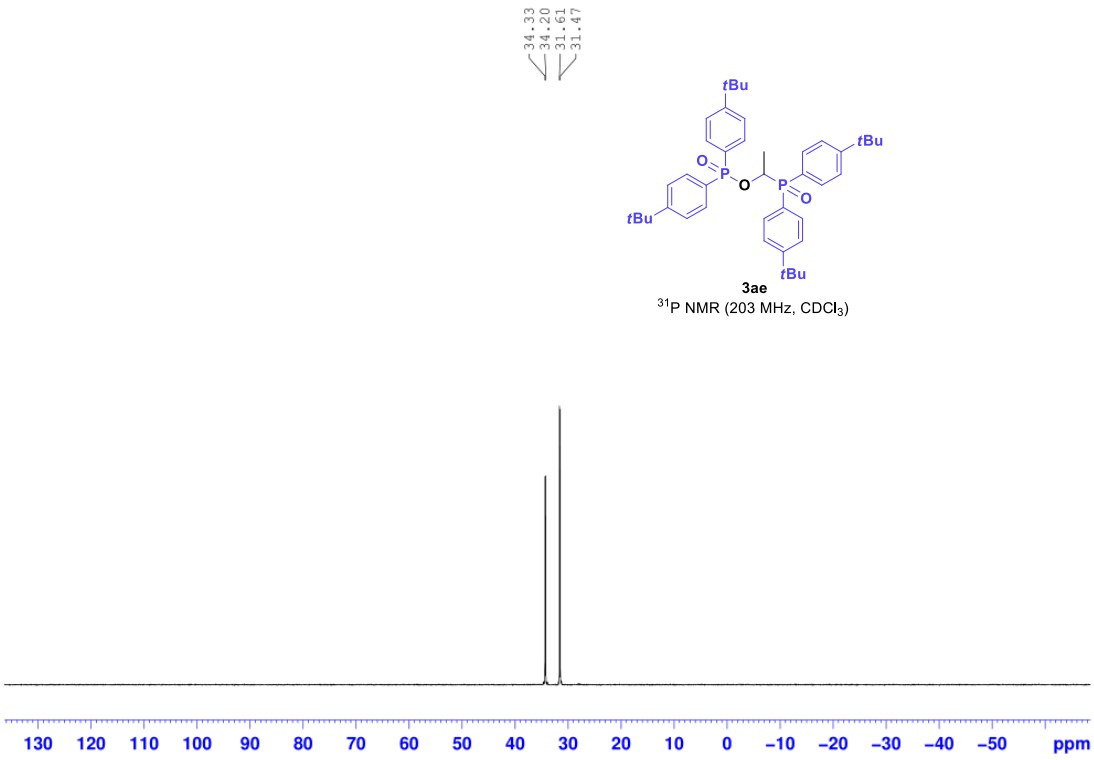


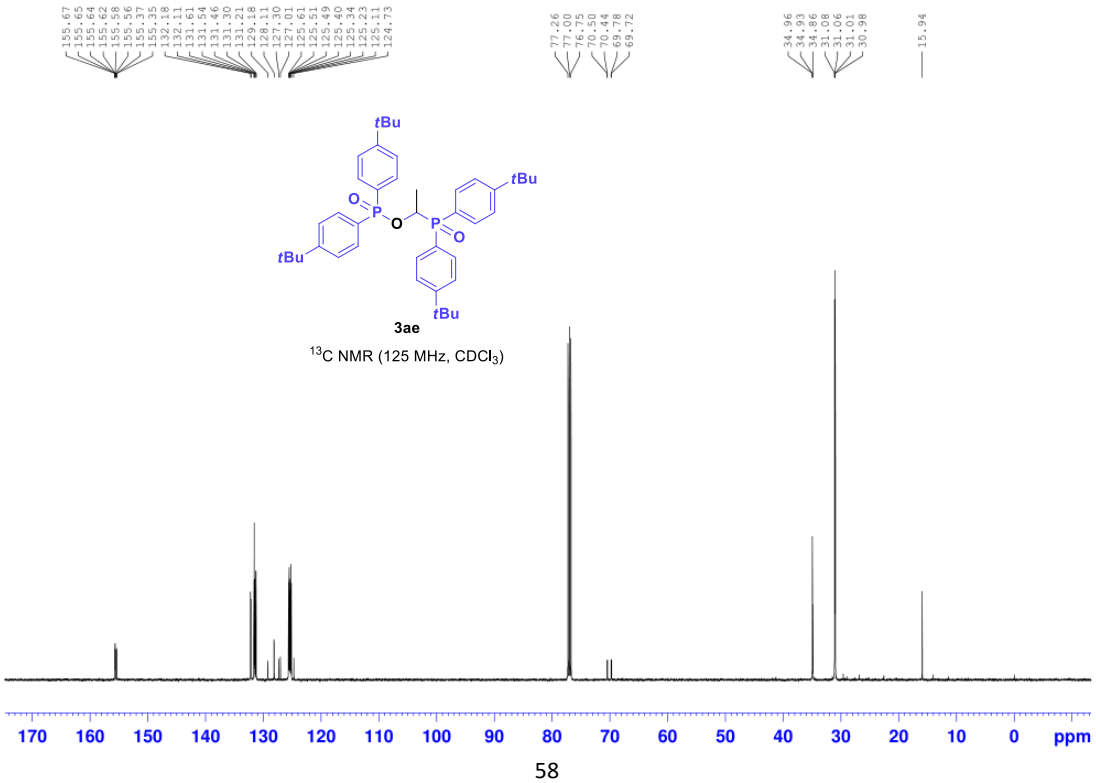
3ad

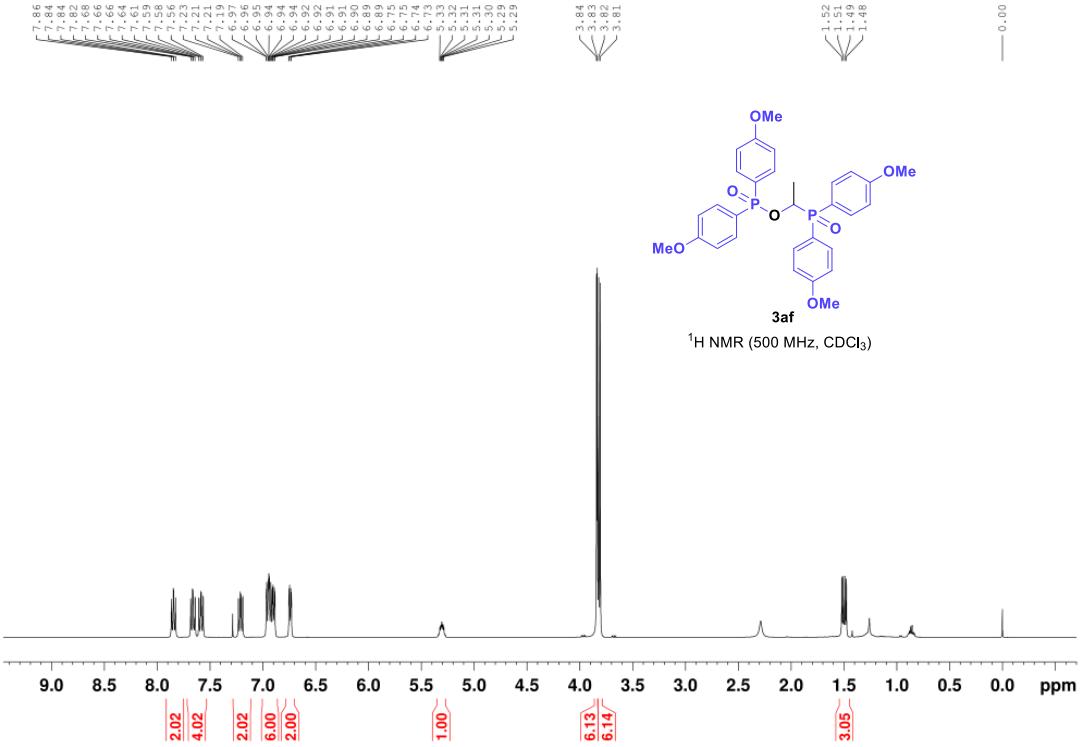
^{31}P NMR (203 MHz, $CDCl_3$)


142.75
142.73
142.63
142.61
142.58
142.56
142.38
132.20
132.13
131.56
131.48
131.33
131.25
131.04
129.31
129.24
129.20
129.14
129.11
129.03
128.89
128.78
128.20
128.00
127.92
127.11
127.09
125.46
124.66
77.26
77.00
76.75
70.23
70.16
69.51
69.44
21.54
21.51
15.97
O
P
O
P
O
O
3ad
13C NMR (125 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.95
7.93
7.93
7.91
7.75
7.73
7.72
7.71
7.60
7.59
7.58
7.56
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.41
7.41
7.40
7.39
7.28
7.27
7.26
7.25
7.17
7.15
7.14
7.13
5.35
5.34
5.33
5.33
5.32
5.32
5.31
5.31
5.30
5.30
5.29
5.28
1.54
1.52
1.51
1.49
1.34
1.34
1.30
1.28
0.00
tBu
tBu
tBu
tBu
O
P
O
P
O
3ae
1H NMR (500 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
1.90
2.06
2.00
4.04
2.05
2.14
2.04
1.00
3.15
18.07
9.02
9.17

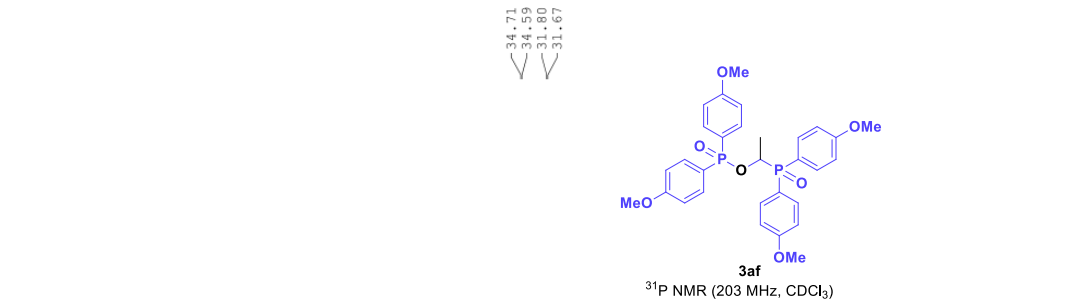

34.33
34.20
31.61
31.47
tBu
tBu
tBu
tBu
O
P
O
P
O
3ae
31P NMR (203 MHz, CDCl3)
130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 ppm


155.67
155.65
155.64
155.62
155.58
155.56
155.37
155.35
132.18
132.11
131.61
131.54
131.46
131.36
131.21
129.18
128.11
127.30
127.01
125.61
125.51
125.40
125.34
125.23
125.11
124.73
77.26
77.00
76.75
70.50
70.44
69.78
69.72
34.96
34.93
34.86
31.08
31.06
31.01
30.98
15.94
tBu
tBu
tBu
tBu
O
P
O
P
O
3ae
13C NMR (125 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



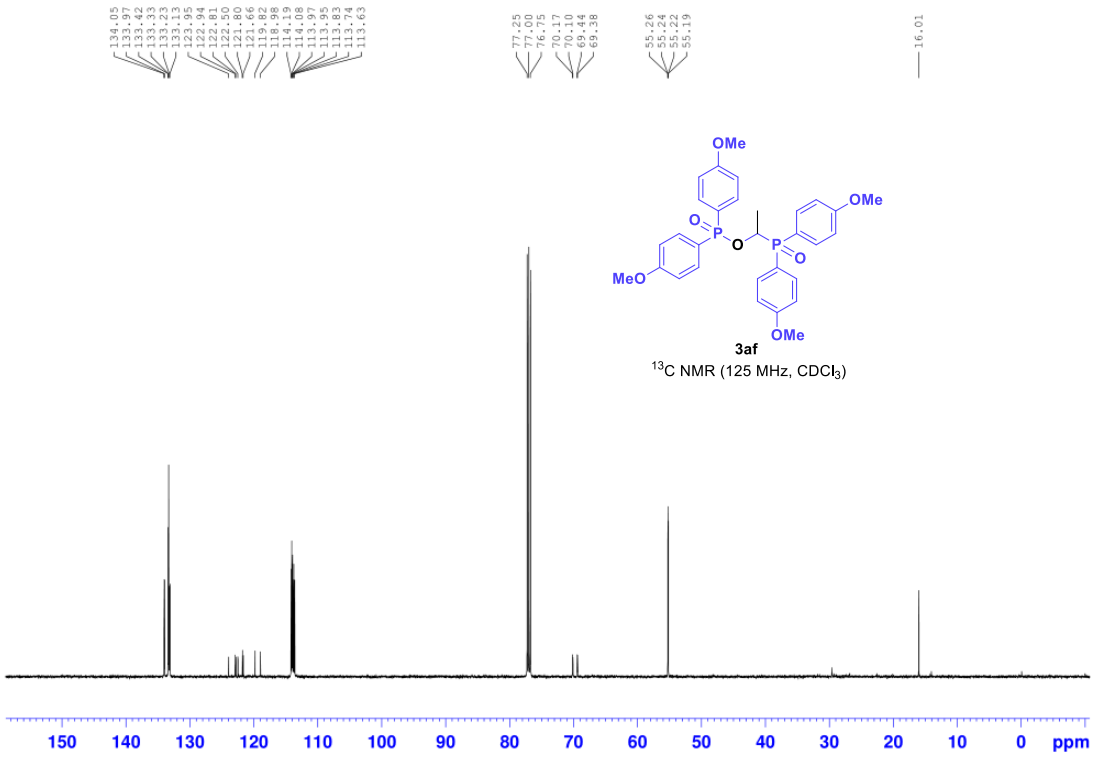
3af

^{1}H NMR (500 MHz, $CDCl_3$)



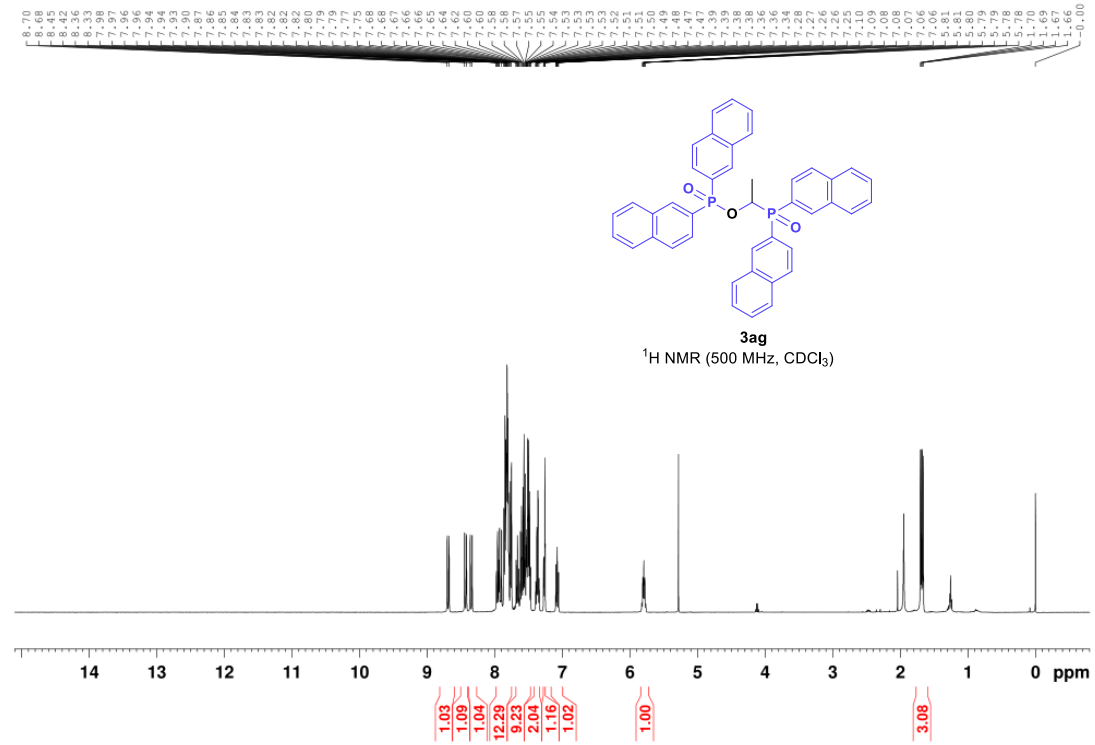
3af

^{31}P NMR (203 MHz, $CDCl_3$)



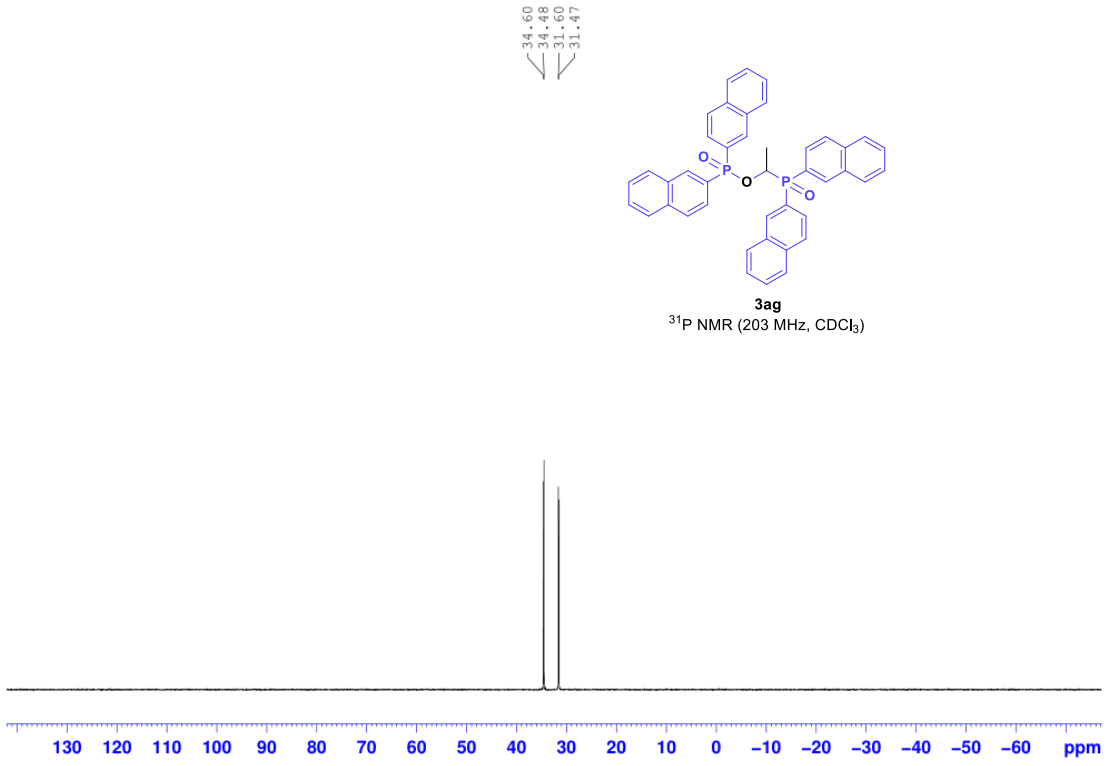
3af

^{13}C NMR (125 MHz, $CDCl_3$)



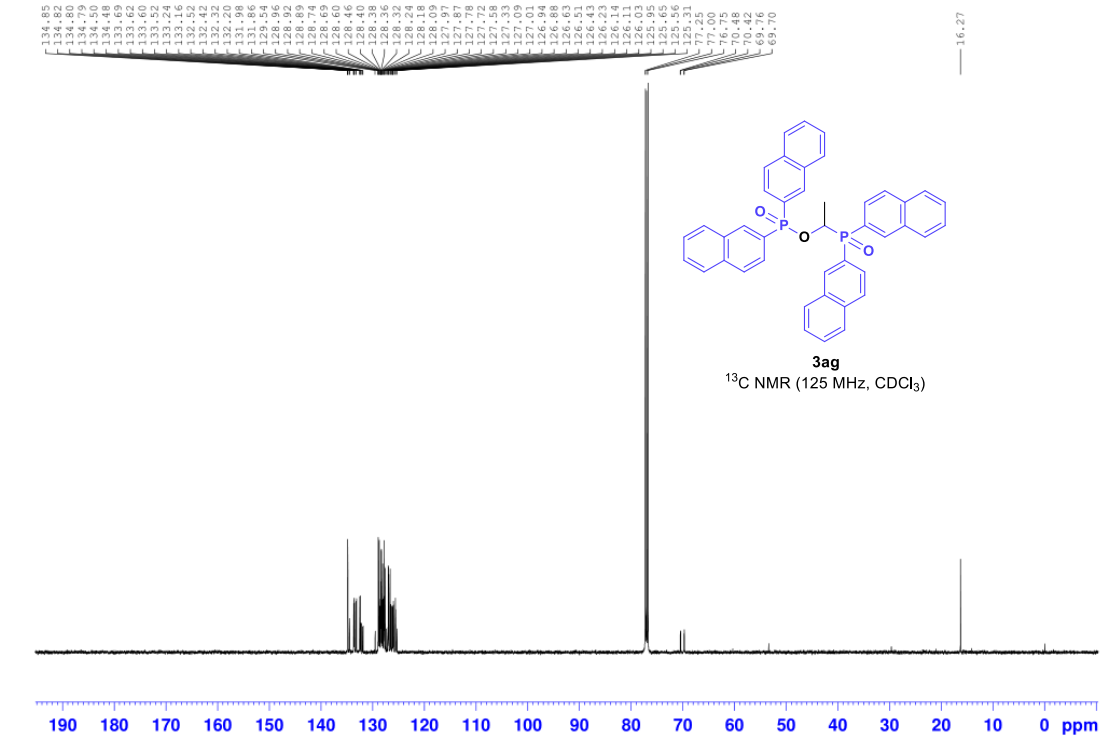
3ag

^{1}H NMR (500 MHz, $CDCl_3$)



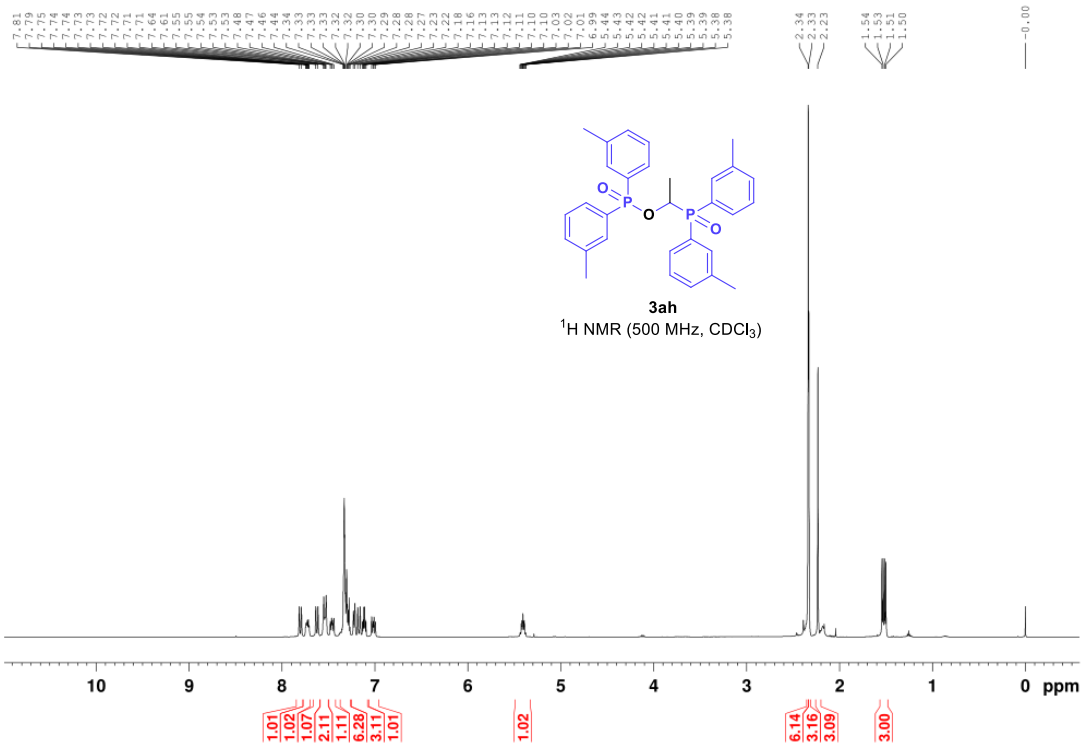
3ag

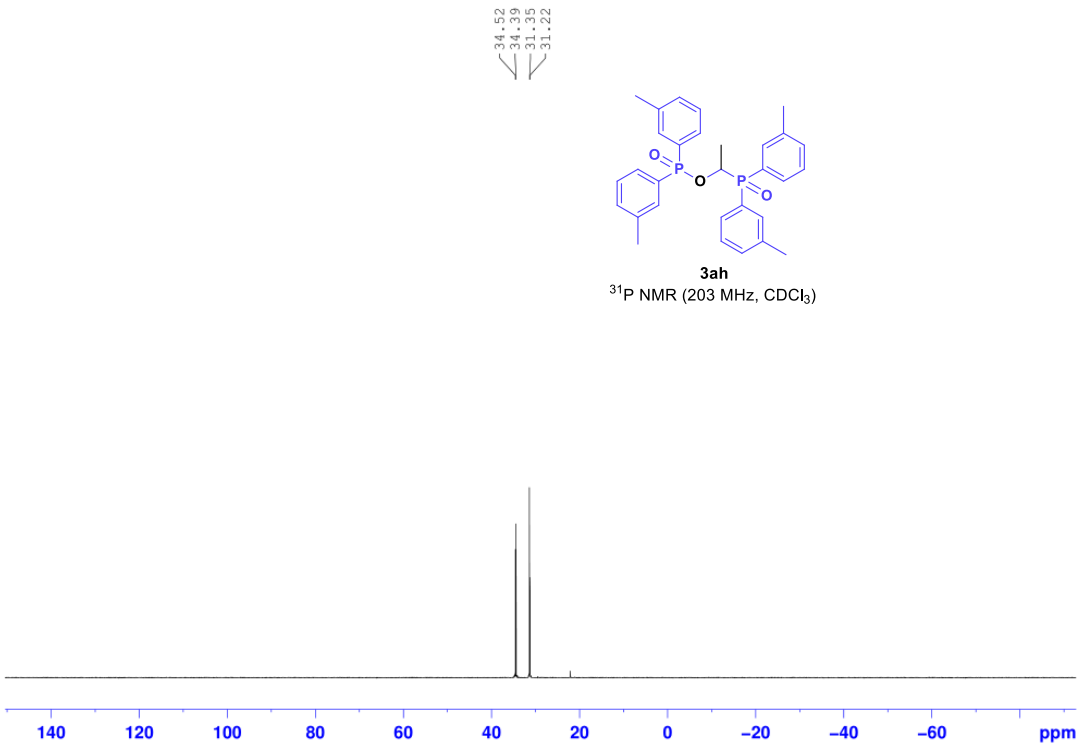
^{31}P NMR (203 MHz, $CDCl_3$)

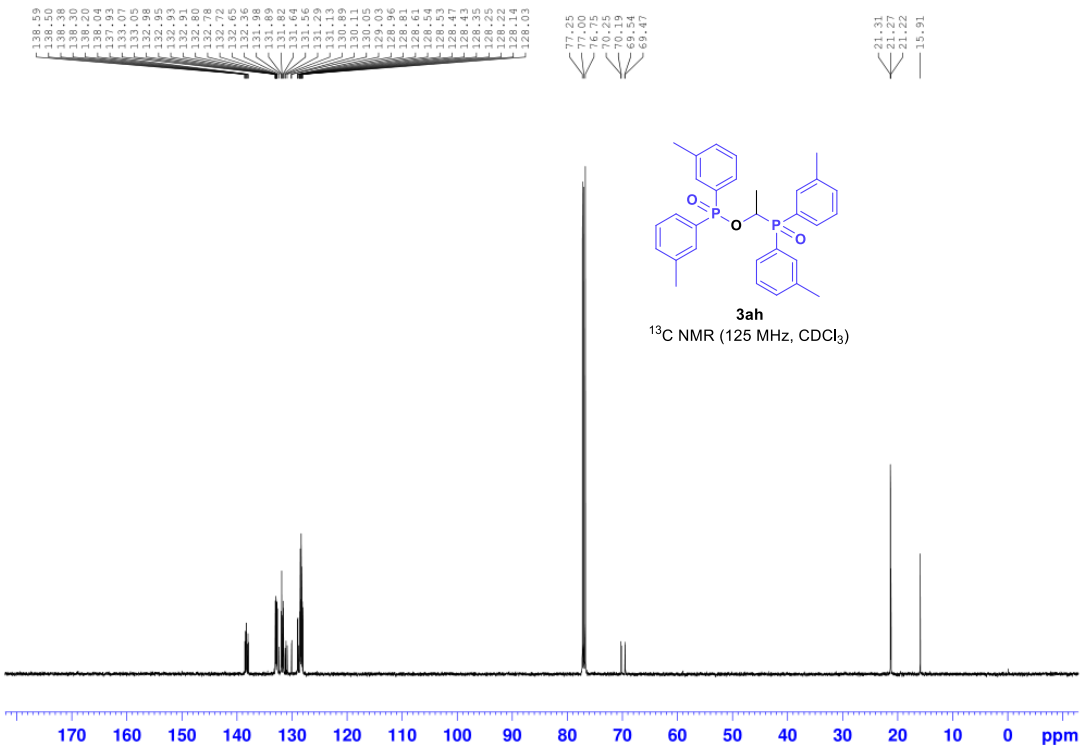


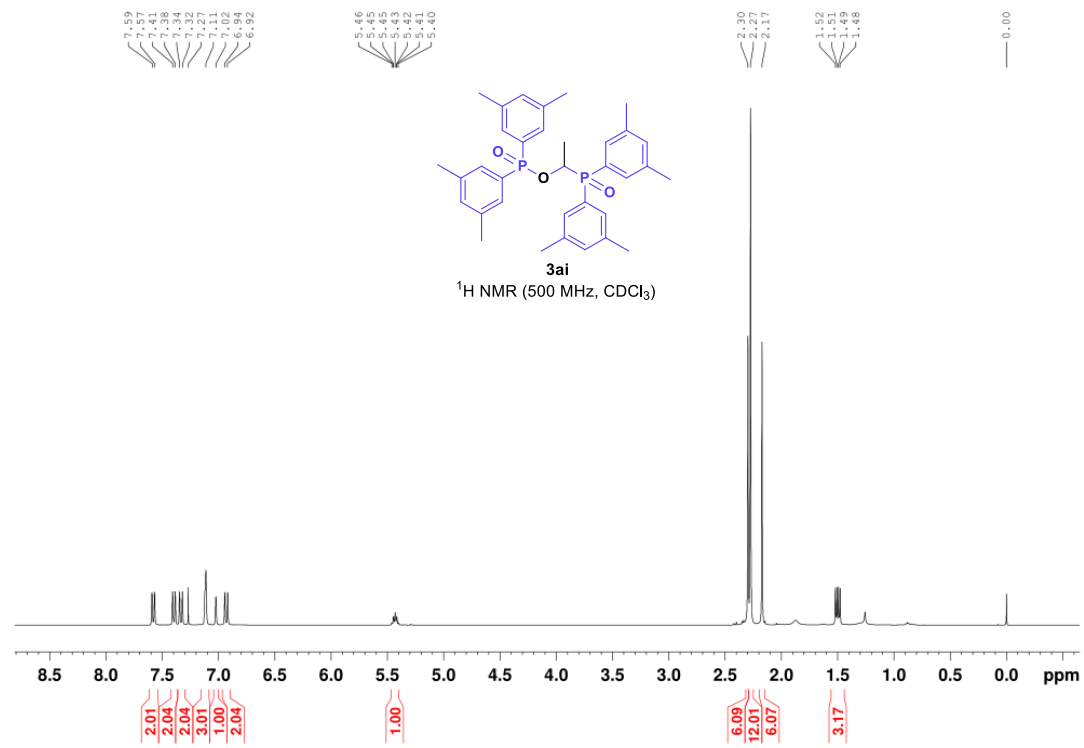
3ag

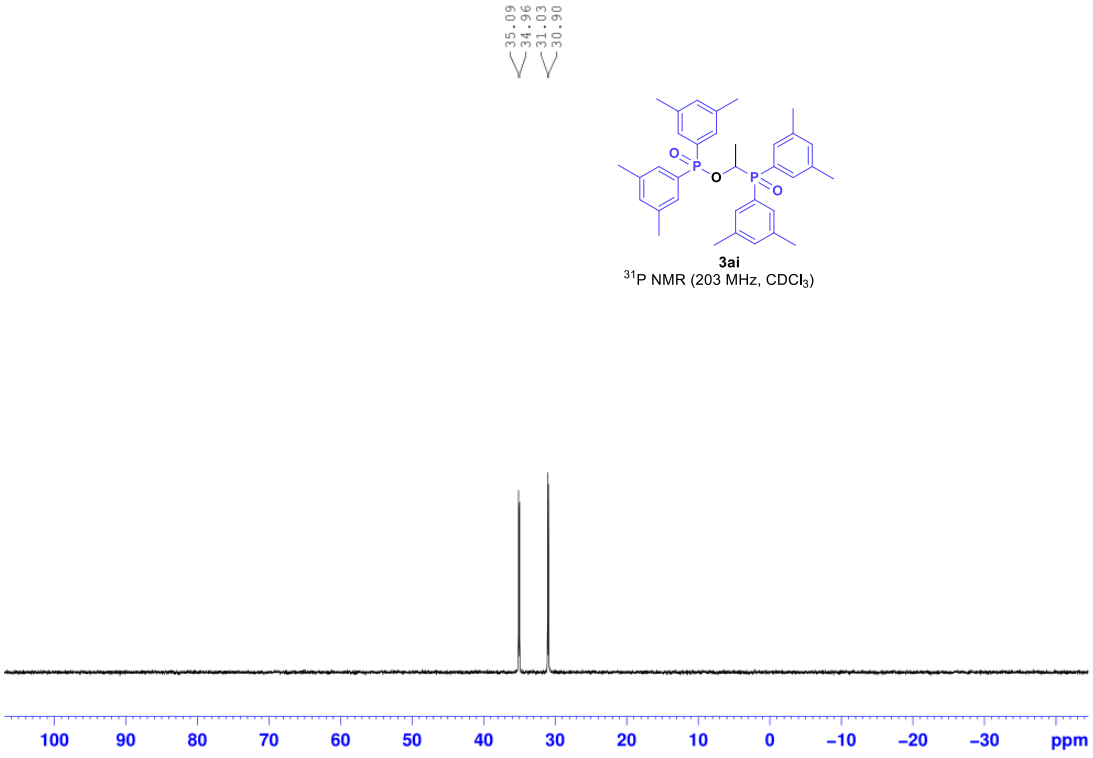
^{13}C NMR (125 MHz, $CDCl_3$)

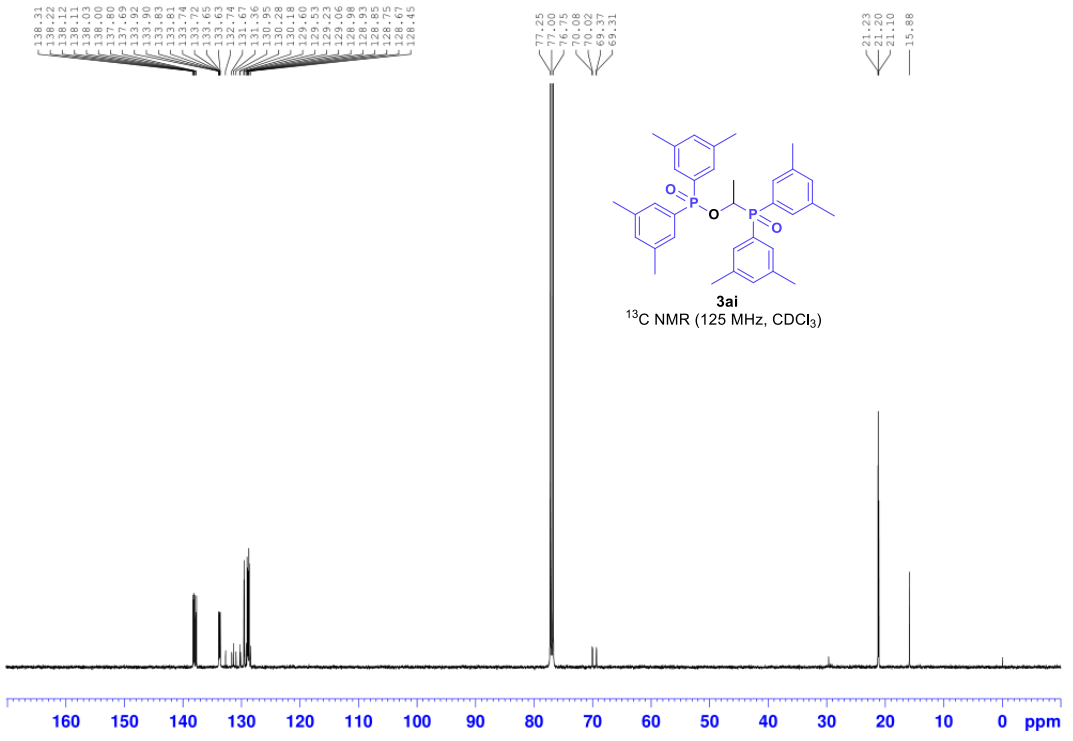

7.81 7.79 7.75 7.74 7.74 7.73 7.73 7.72 7.72 7.71 7.71 7.64 7.61 7.55 7.55 7.54 7.53 7.53 7.48 7.47 7.46 7.44 7.44 7.34 7.33 7.33 7.32 7.32 7.30 7.29 7.28 7.28 7.27 7.23 7.22 7.18 7.16 7.13 7.12 7.11 7.10 7.10 7.03 7.02 7.01 6.99 6.44 5.43 5.42 5.41 5.41 5.40 5.39 5.39 5.38 5.38
2.34 2.33 2.23
1.54 1.53 1.51 1.50
-0.00
O P O O P O
3ah
^{1}H NMR (500 MHz, $CDCl_3$)
10 9 8 7 6 5 4 3 2 1 0 ppm
1.01 1.02 1.07 2.11 1.11 6.28 3.11 1.01
1.02
6.14 3.16 3.09
3.00

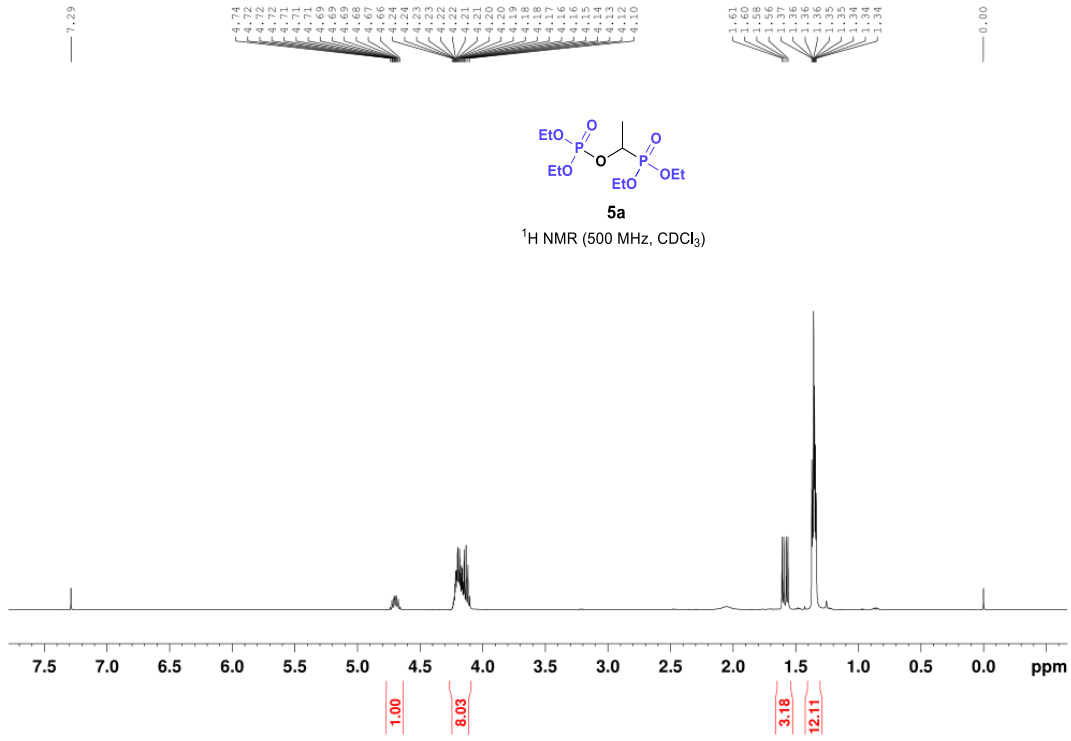

34.52 34.39 31.35 31.22
O P O O P O
3ah
^{31}P NMR (203 MHz, $CDCl_3$)
140 120 100 80 60 40 20 0 −20 −40 −60 ppm


138.59
138.50
138.38
138.30
138.20
138.04
137.93
133.07
133.05
132.98
132.95
132.93
132.91
132.80
132.78
132.72
132.65
132.36
131.98
131.89
131.82
131.64
131.56
131.29
131.13
130.89
130.11
130.05
129.03
128.96
128.81
128.61
128.54
128.53
128.47
128.43
128.35
128.25
128.22
128.14
128.03
77.25
77.00
76.75
70.25
70.19
69.54
69.47
21.31
21.27
21.22
15.91
3ah
13C NMR (125 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.59
7.57
7.41
7.38
7.34
7.32
7.27
7.11
7.10
6.94
6.92
5.46
5.45
5.45
5.43
5.42
5.41
5.40
2.30
2.27
2.17
1.52
1.51
1.49
1.48
0.00
3ai
1H NMR (500 MHz, CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
2.04
2.04
3.01
1.00
2.04
1.00
6.09
12.01
6.07
3.17

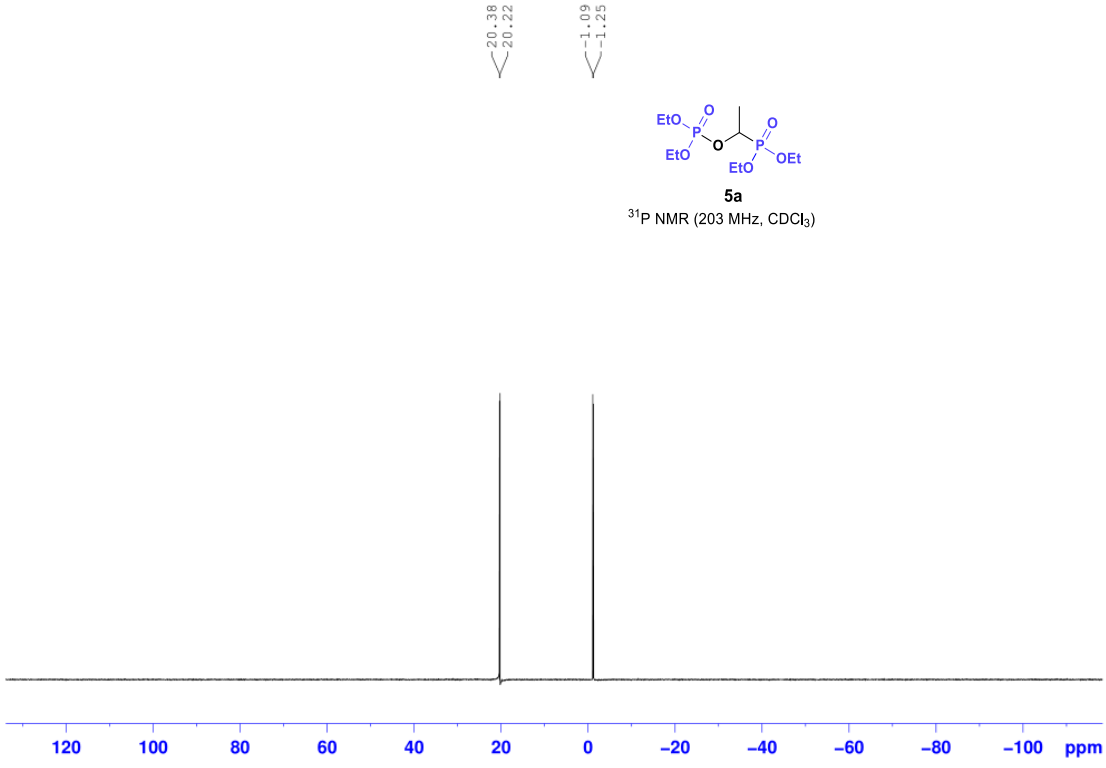

35.09
34.96
31.03
30.90
3ai
31P NMR (203 MHz, CDCl3)
100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 ppm


138.31
138.22
138.12
138.11
138.03
138.00
137.80
137.69
133.92
133.90
133.83
133.81
133.74
133.72
133.65
133.63
132.74
131.67
131.36
130.95
130.28
130.18
129.60
129.53
129.23
129.06
128.98
128.93
128.85
128.75
128.67
128.45
77.25
77.00
76.75
70.08
70.02
69.37
69.31
21.23
21.20
21.10
15.88
3ai
13C NMR (125 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



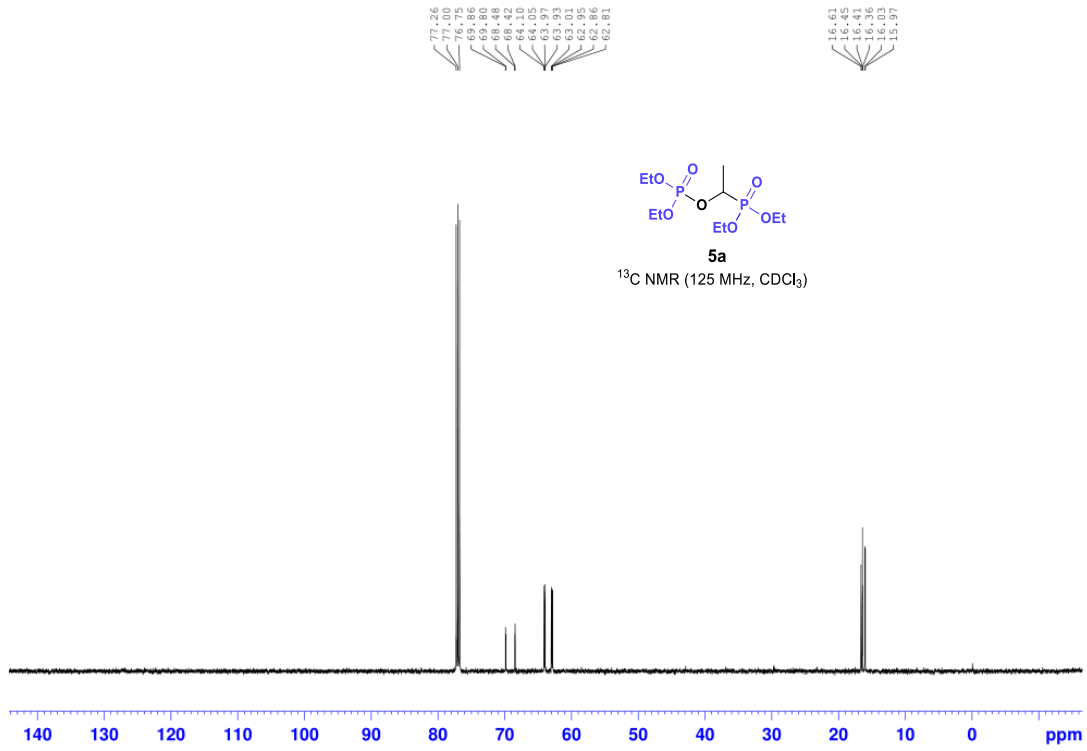
5a

^{1}H NMR (500 MHz, $CDCl_3$)



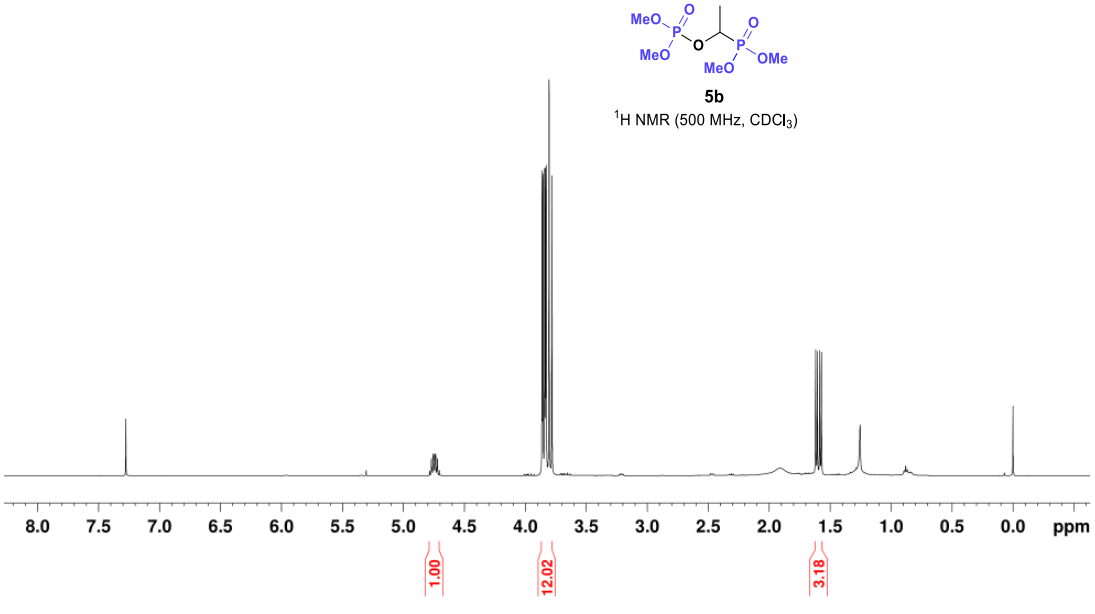
5a

^{31}P NMR (203 MHz, $CDCl_3$)



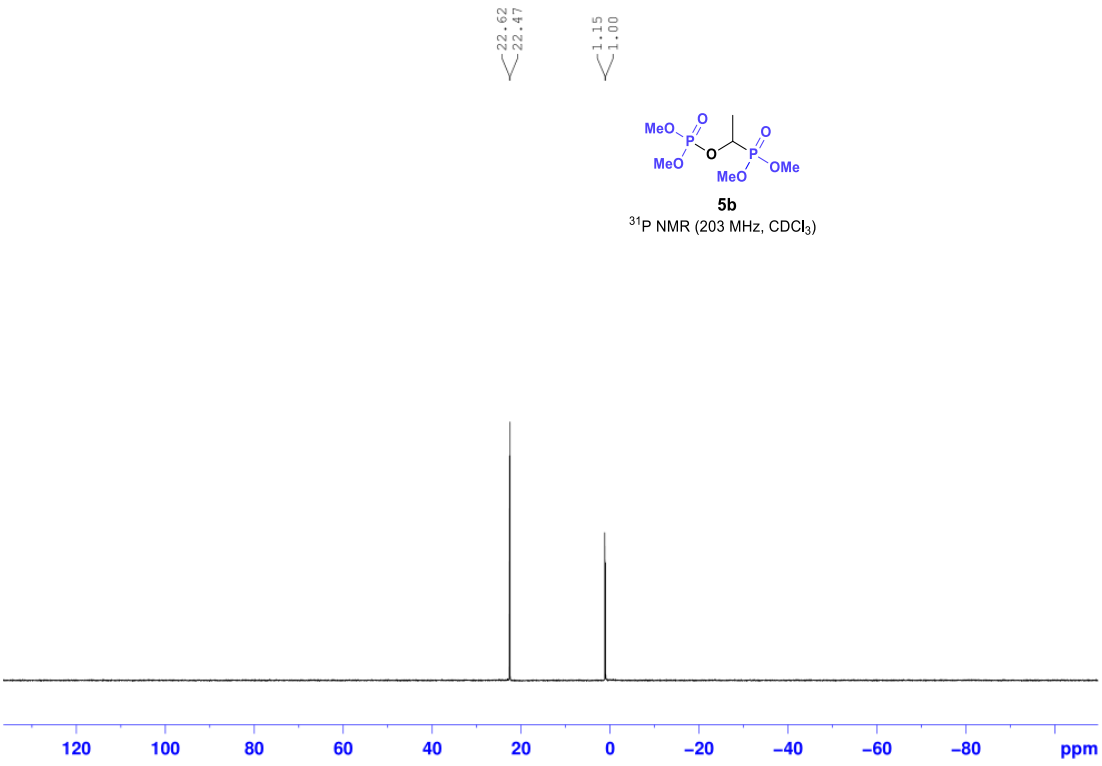
5a

^{13}C NMR (125 MHz, $CDCl_3$)



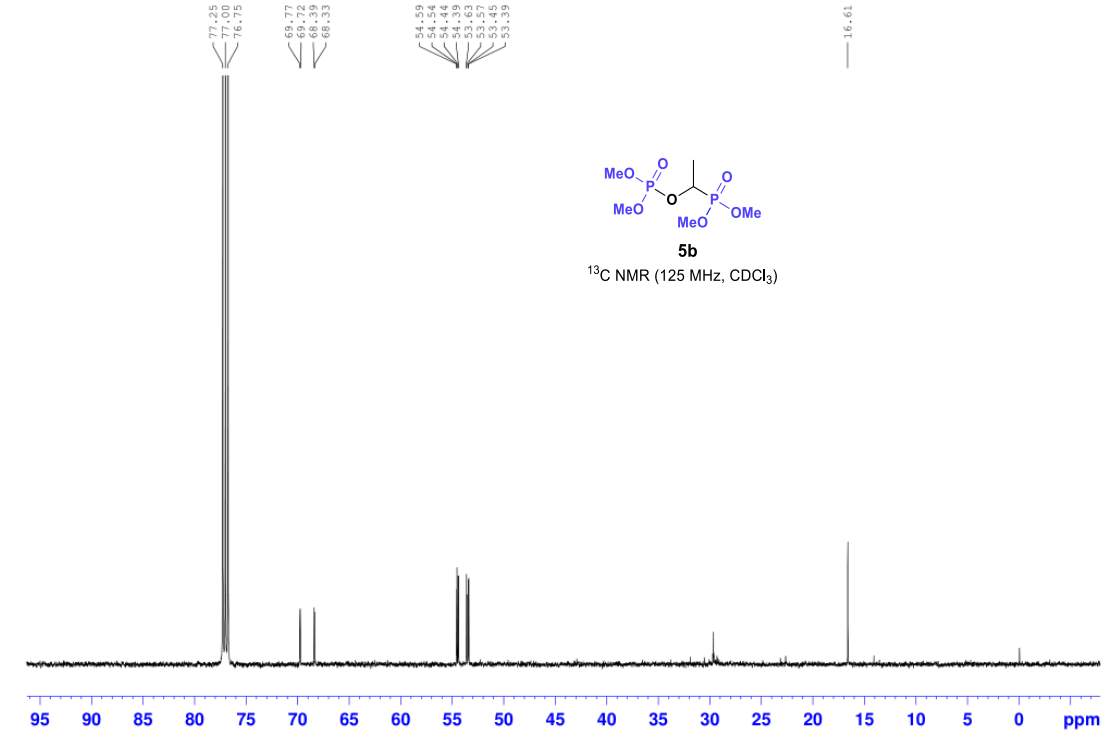
5b

^{1}H NMR (500 MHz, $CDCl_3$)



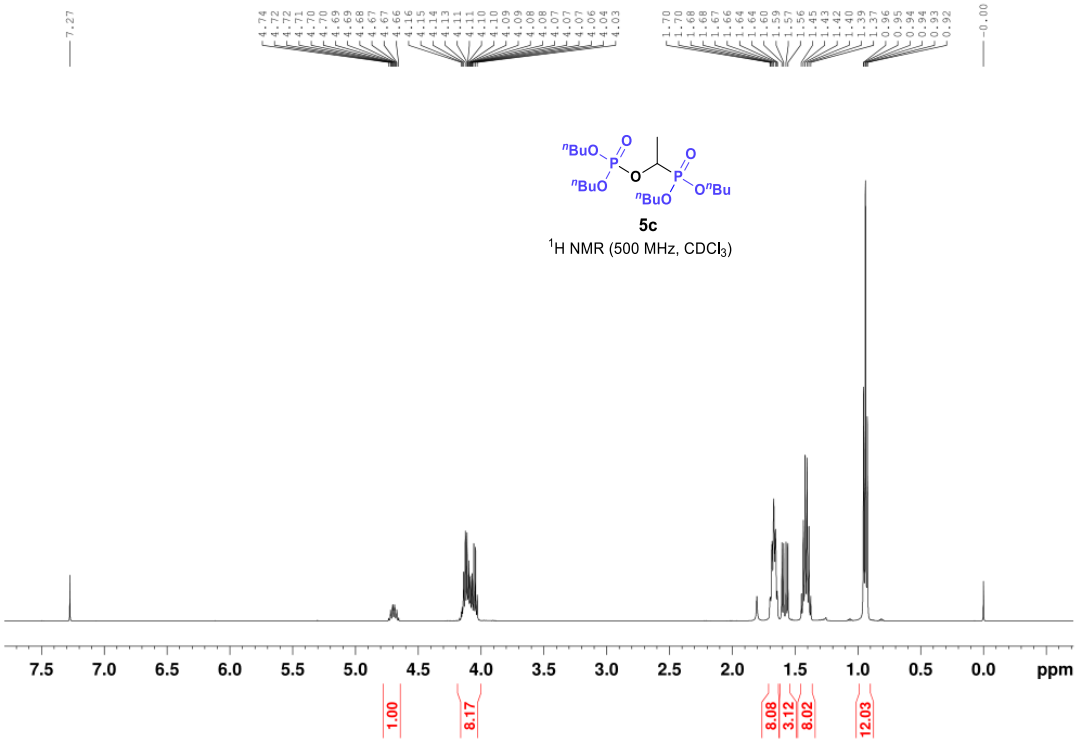
5b

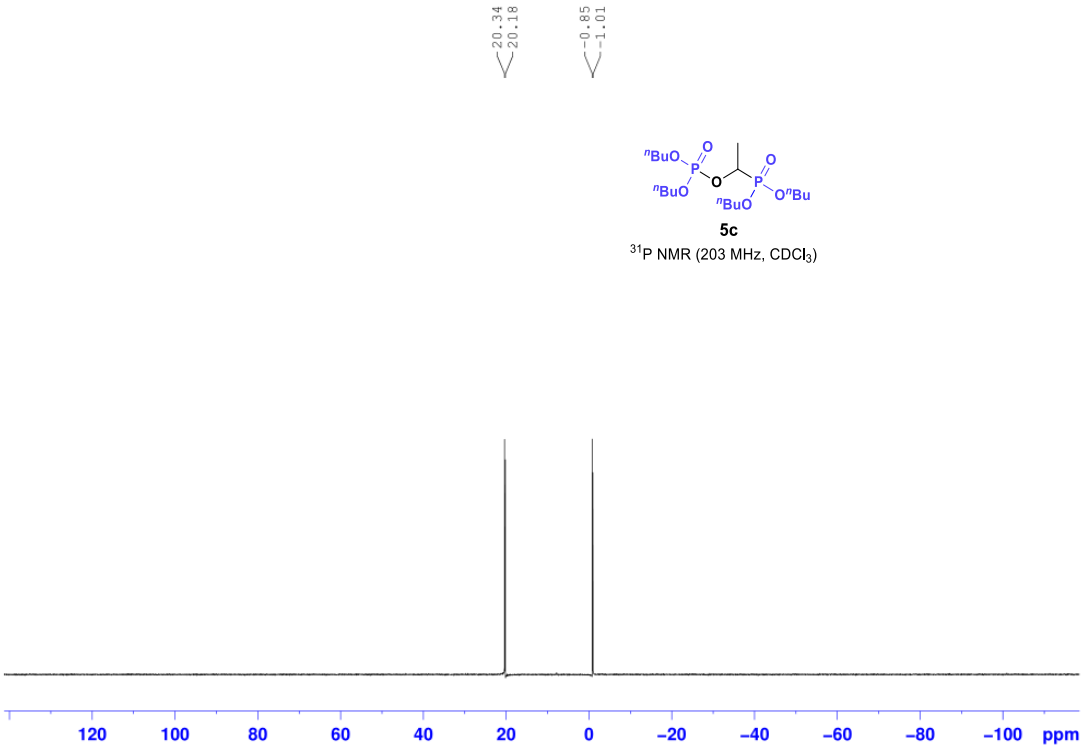
^{31}P NMR (203 MHz, $CDCl_3$)

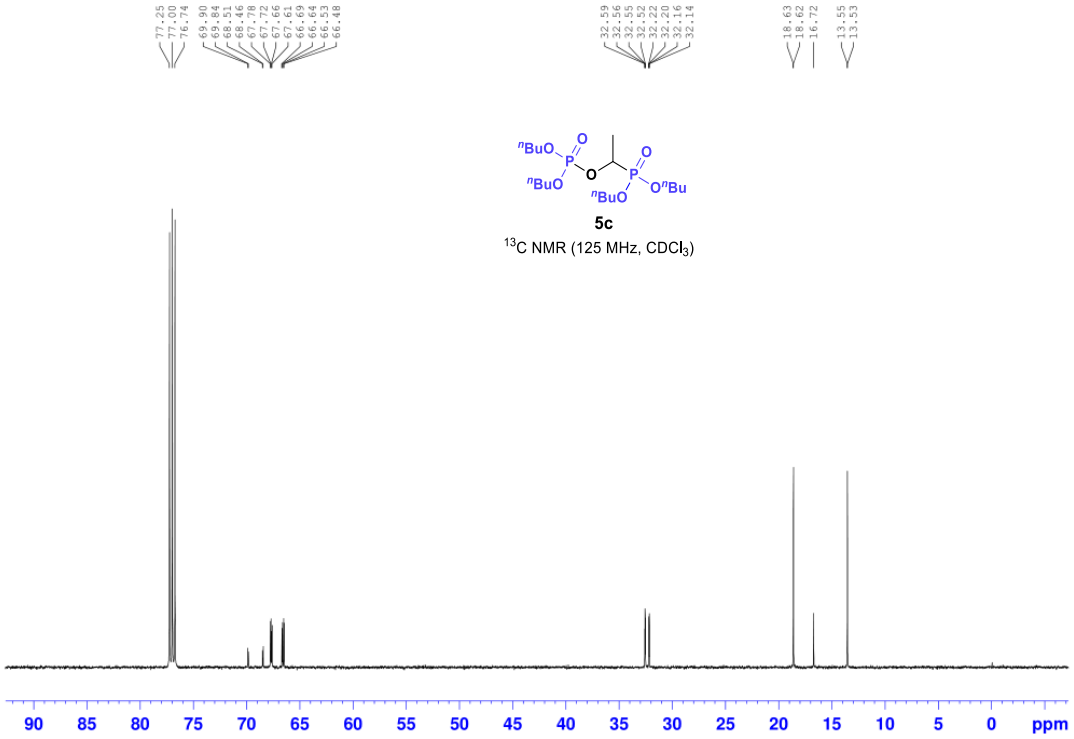


5b

^{13}C NMR (125 MHz, $CDCl_3$)

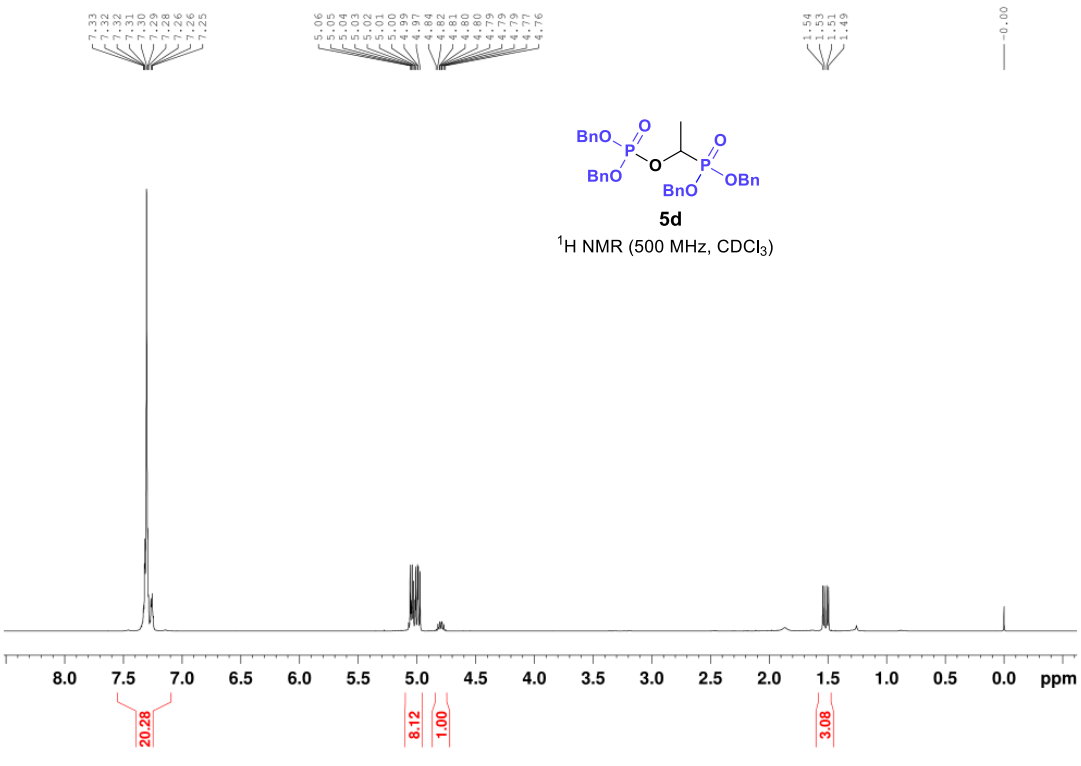

7.27
4.74
4.72
4.72
4.71
4.70
4.70
4.69
4.69
4.68
4.67
4.67
4.66
4.16
4.15
4.14
4.13
4.11
4.10
4.09
4.09
4.08
4.08
4.07
4.07
4.07
4.06
4.04
4.03
1.70
1.70
1.68
1.68
1.67
1.66
1.64
1.64
1.60
1.59
1.57
1.56
1.45
1.43
1.42
1.40
1.39
1.37
0.96
0.95
0.94
0.94
0.93
0.92
0.00
nBuO
O
P
O
nBuO
O
P
O
nBuO
OnBu
5c
1H NMR (500 MHz, CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
8.17
8.08
3.12
8.02
12.03


20.34
20.18
-0.85
-1.01
nBuO
O
P
O
nBuO
O
P
O
nBuO
OnBu
5c
31P NMR (203 MHz, CDCl3)
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm



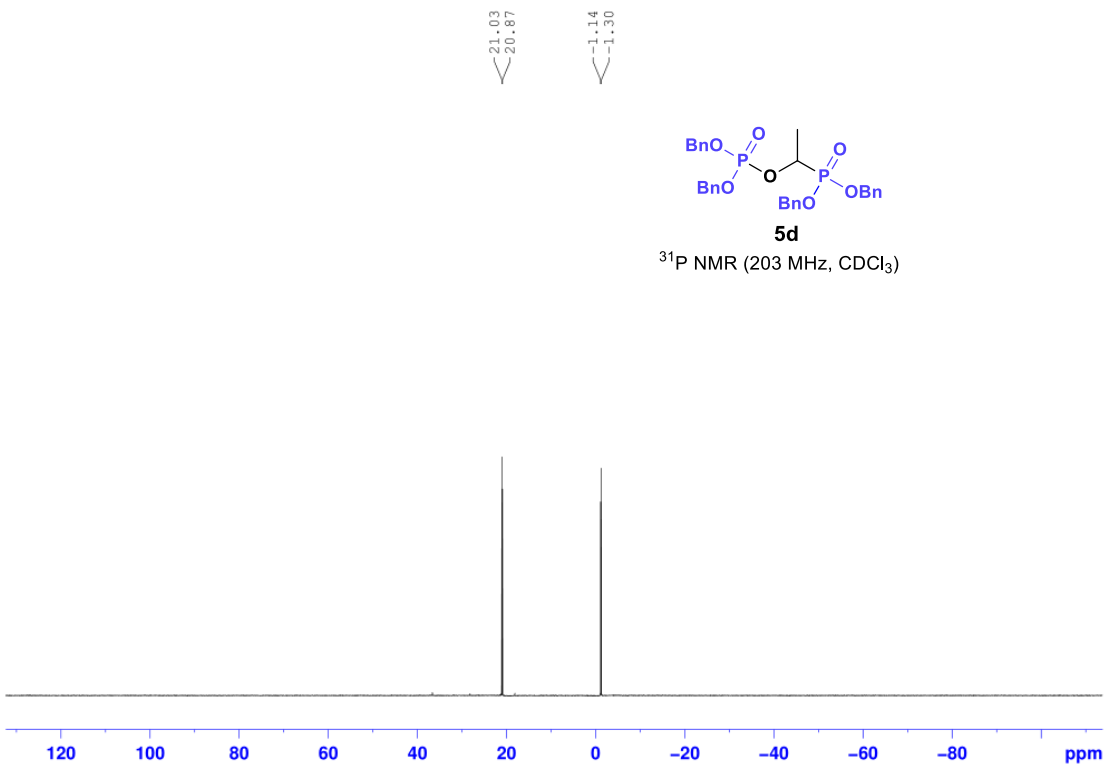
5c

^{13}C NMR (125 MHz, $CDCl_3$)



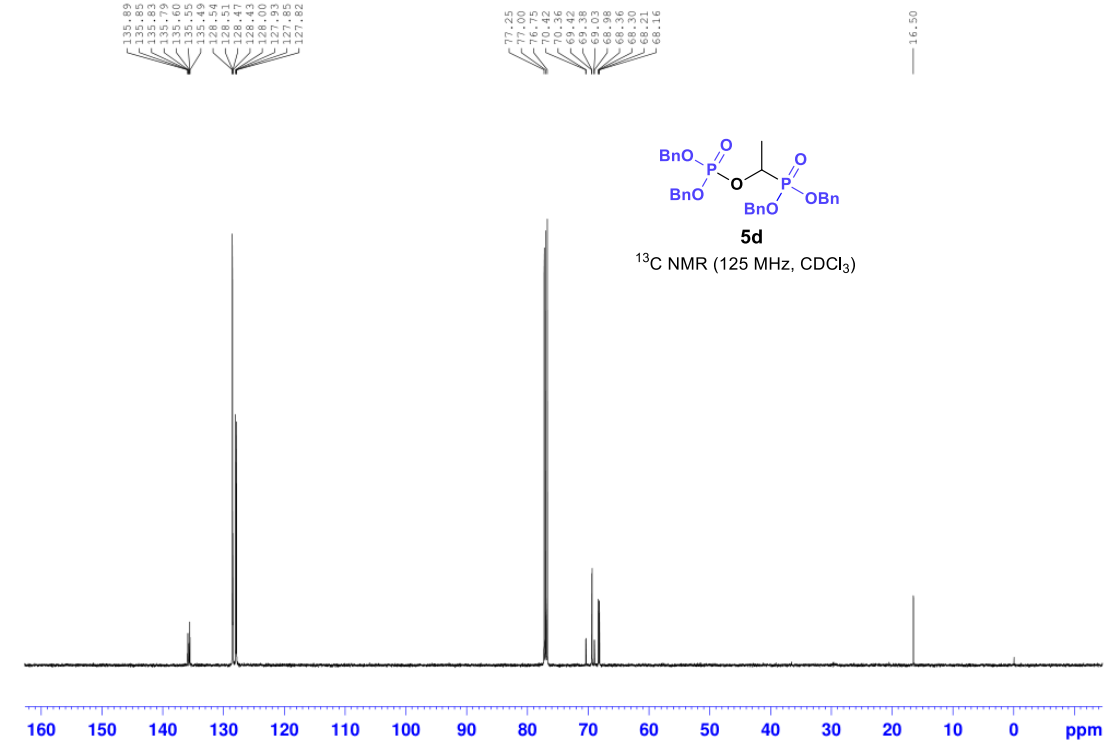
5d

^{1}H NMR (500 MHz, $CDCl_3$)



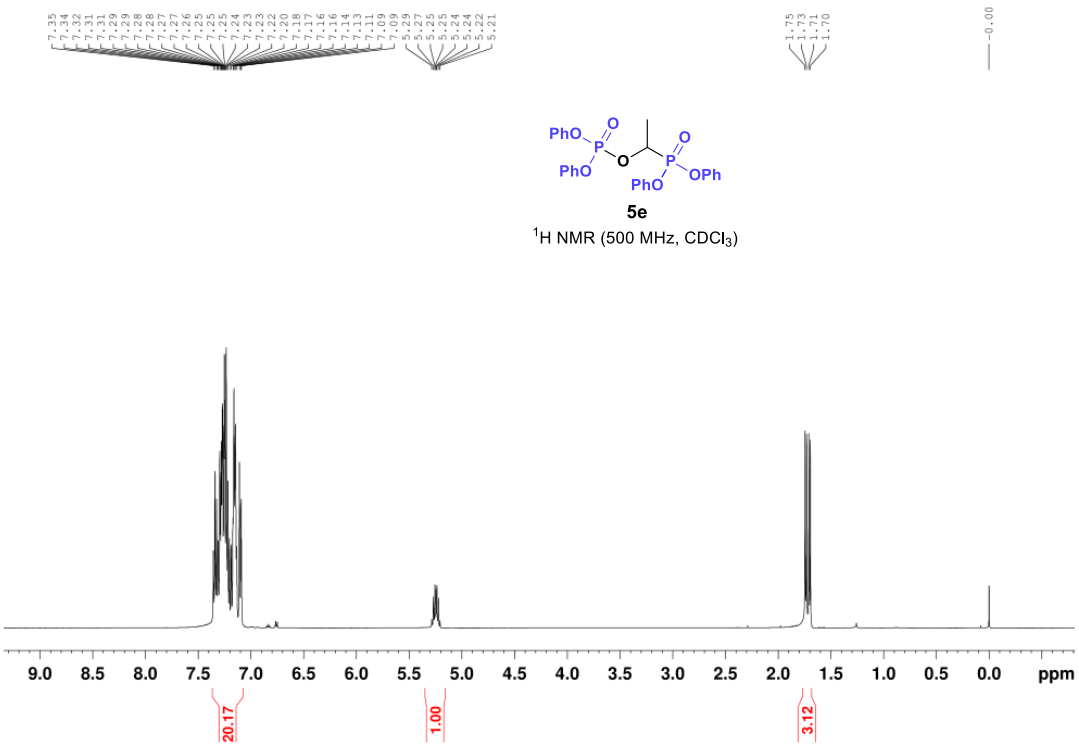
5d

^{31}P NMR (203 MHz, $CDCl_3$)



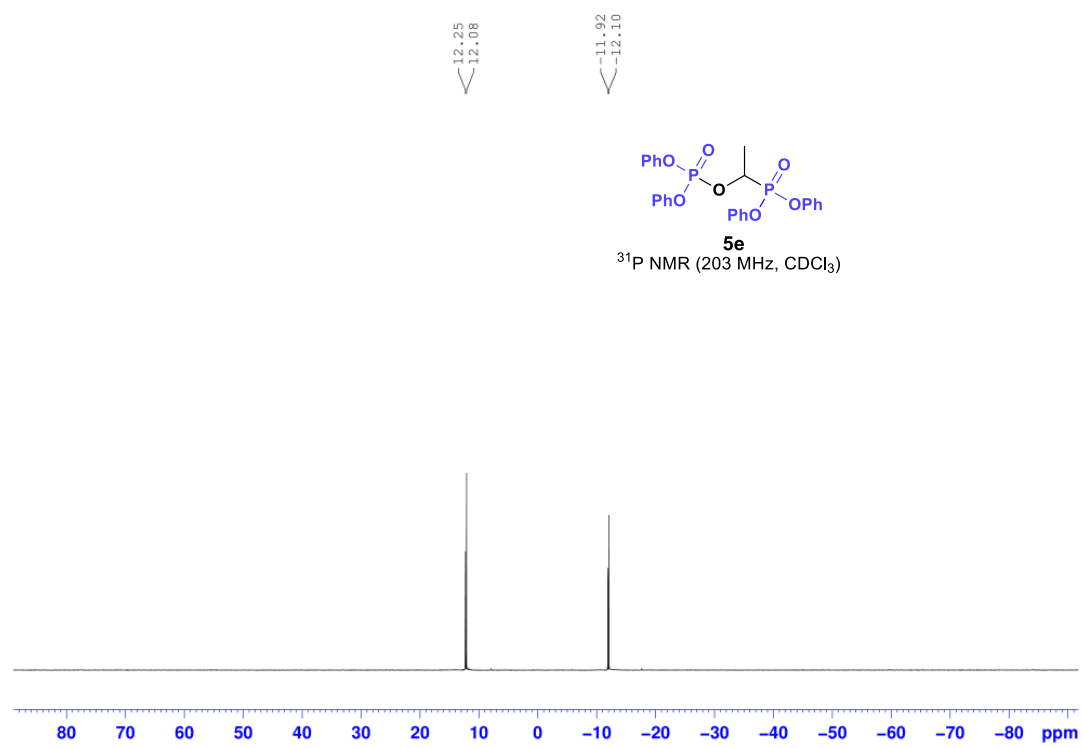
5d

^{13}C NMR (125 MHz, $CDCl_3$)



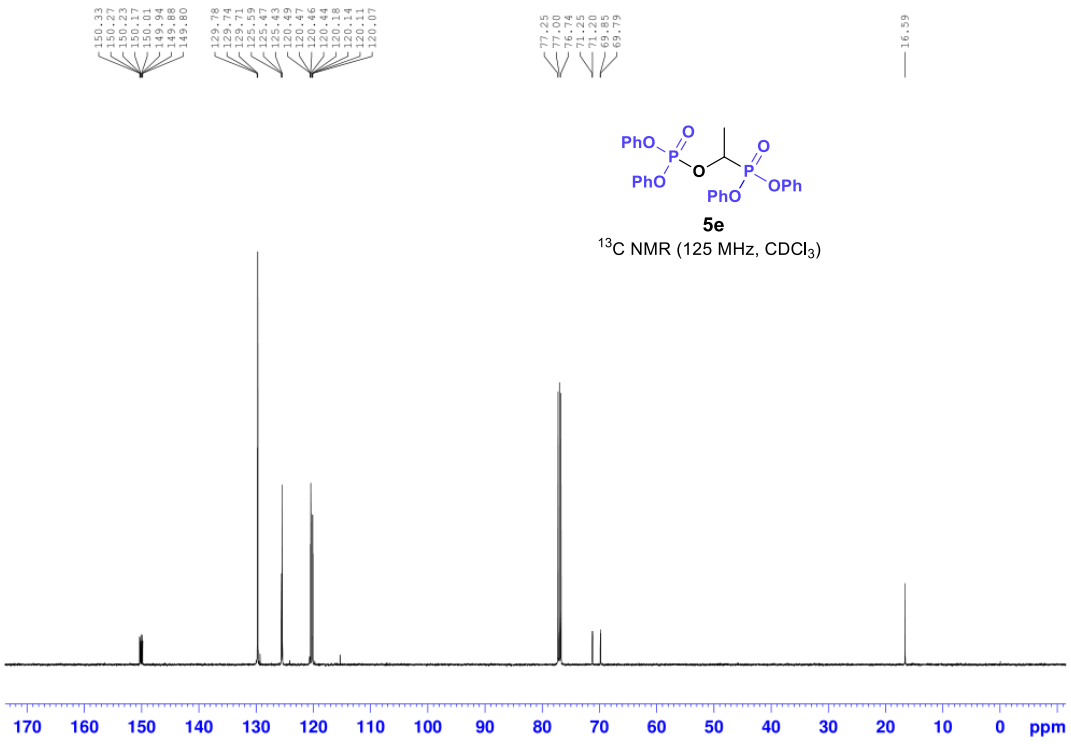
5e

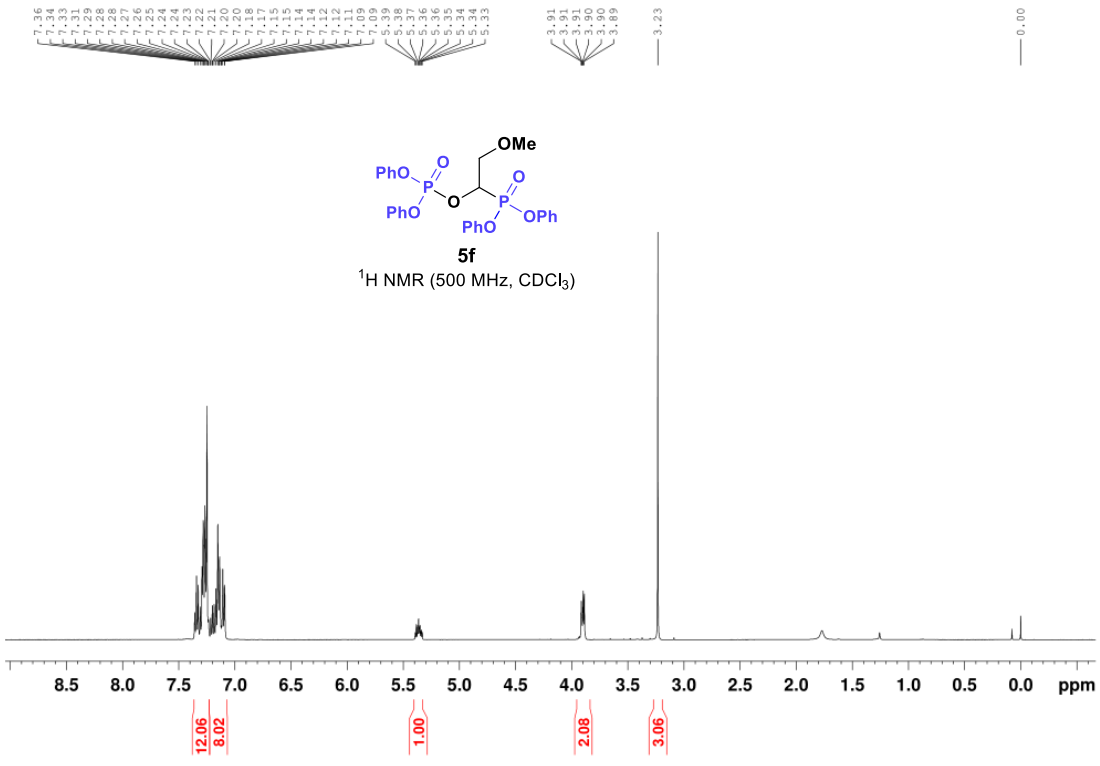
^{1}H NMR (500 MHz, $CDCl_3$)

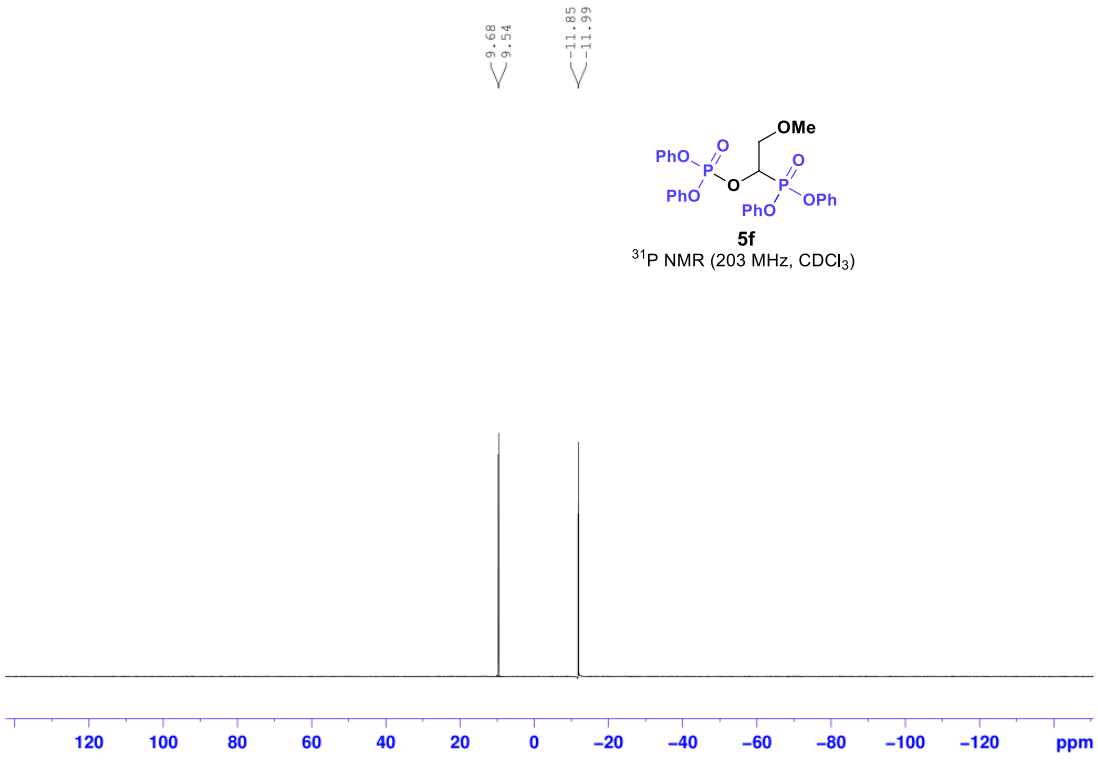


5e

^{31}P NMR (203 MHz, $CDCl_3$)

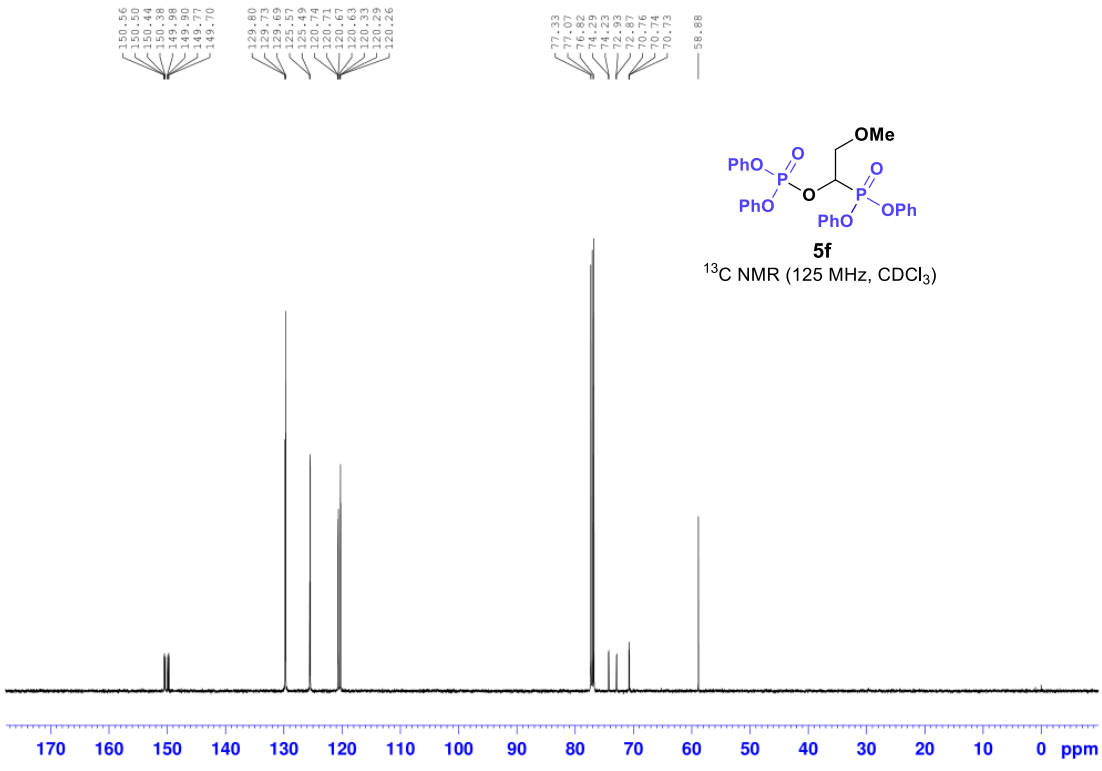

PhO
PhO
O
P
O
P
O
PhO
OPh
5e
13C NMR (125 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
PhO
PhO
O
P
O
P
O
PhO
OPh
5f
1H NMR (500 MHz, CDCl3)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
12.06
8.02
1.00
2.08
3.06



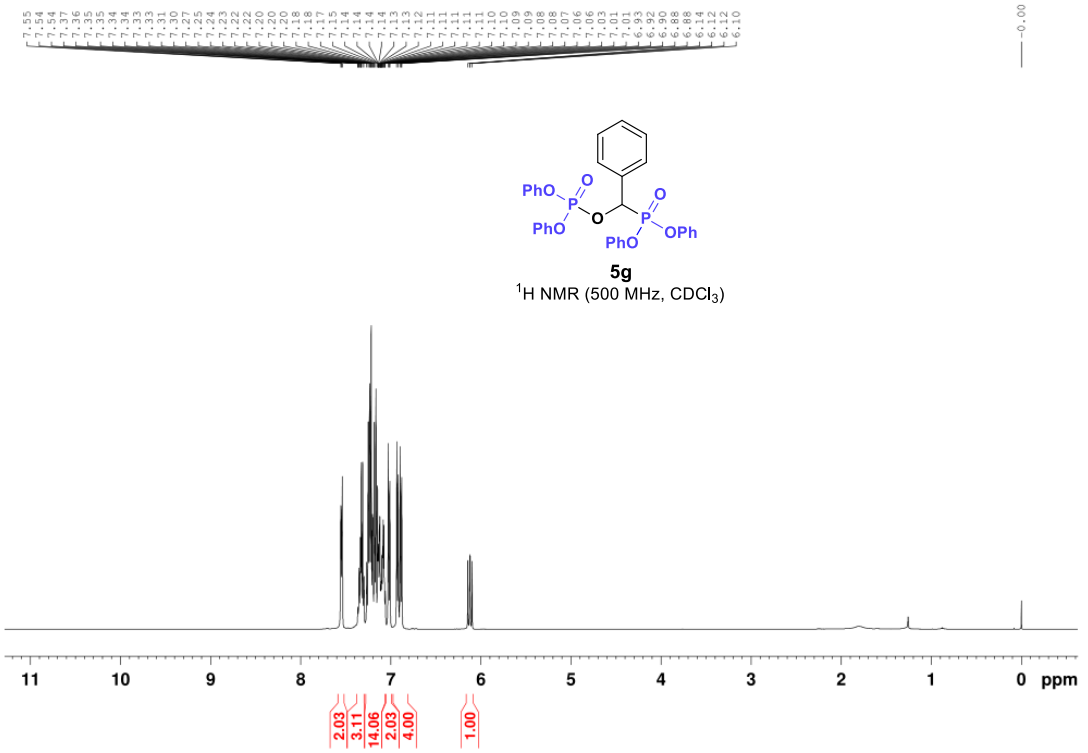
5f

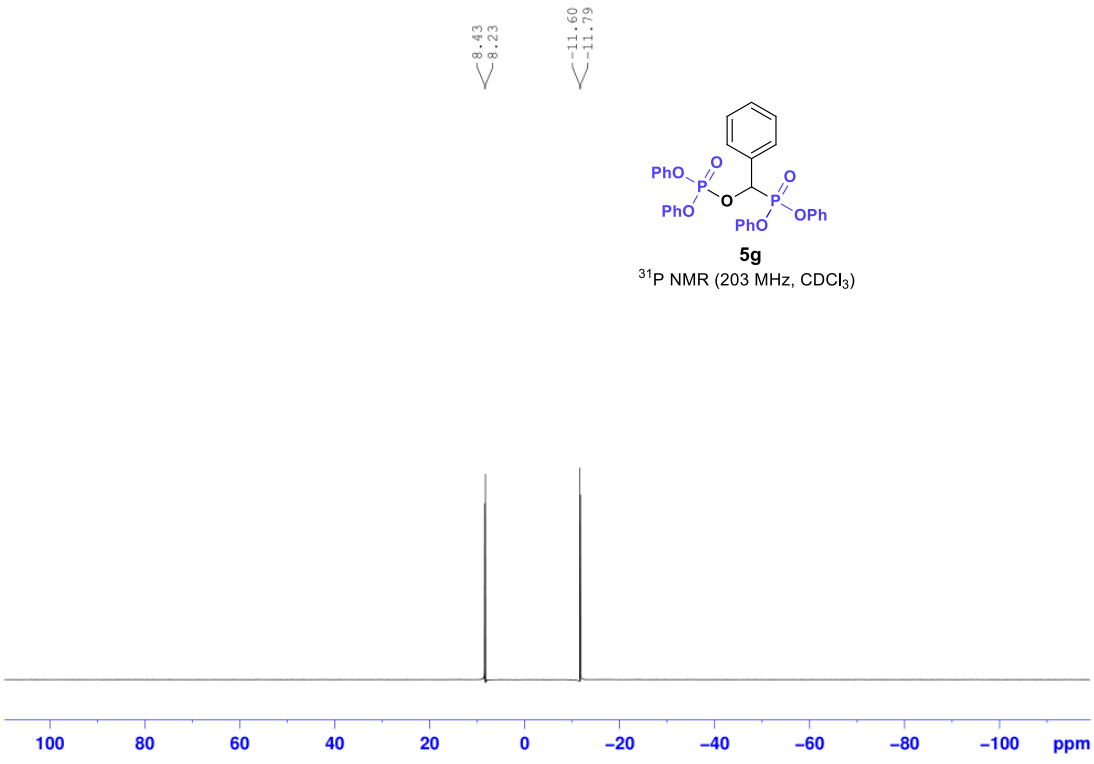
^{31}P NMR (203 MHz, $CDCl_3$)

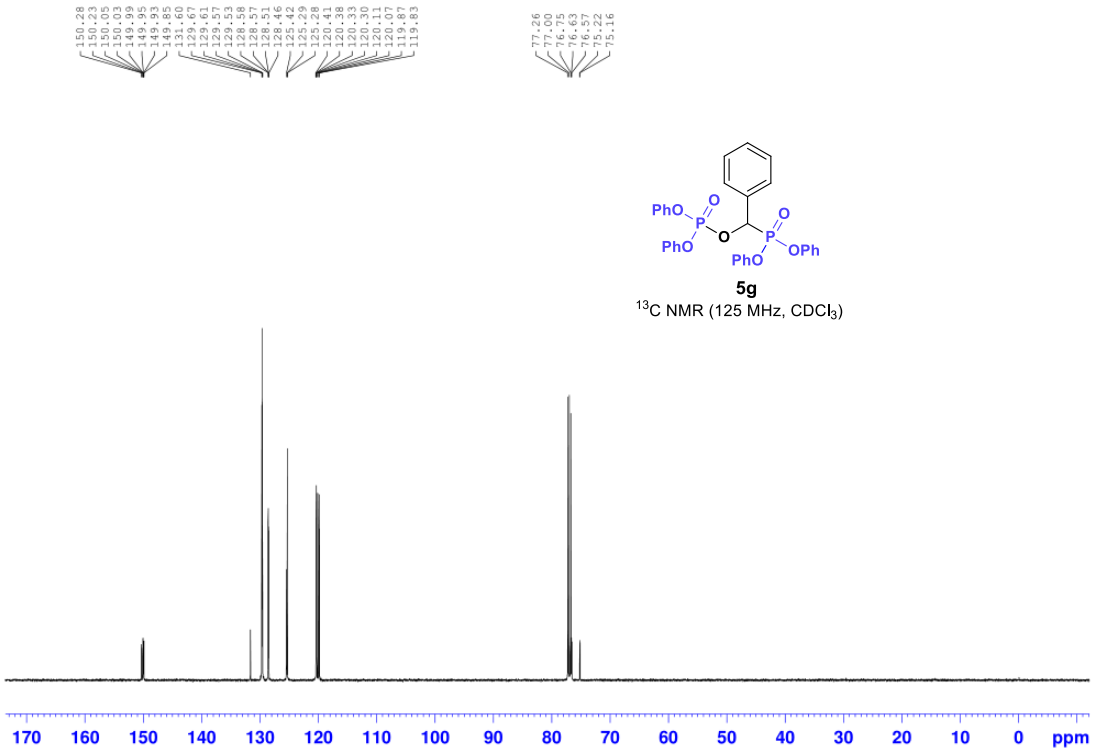


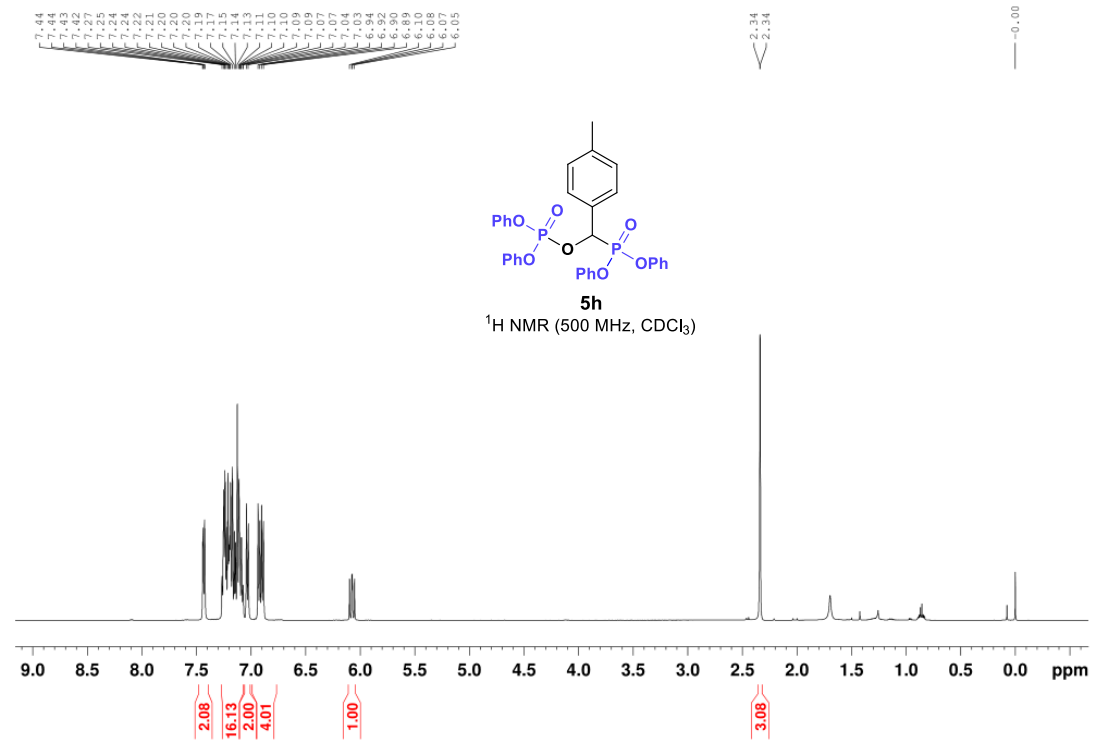
5f

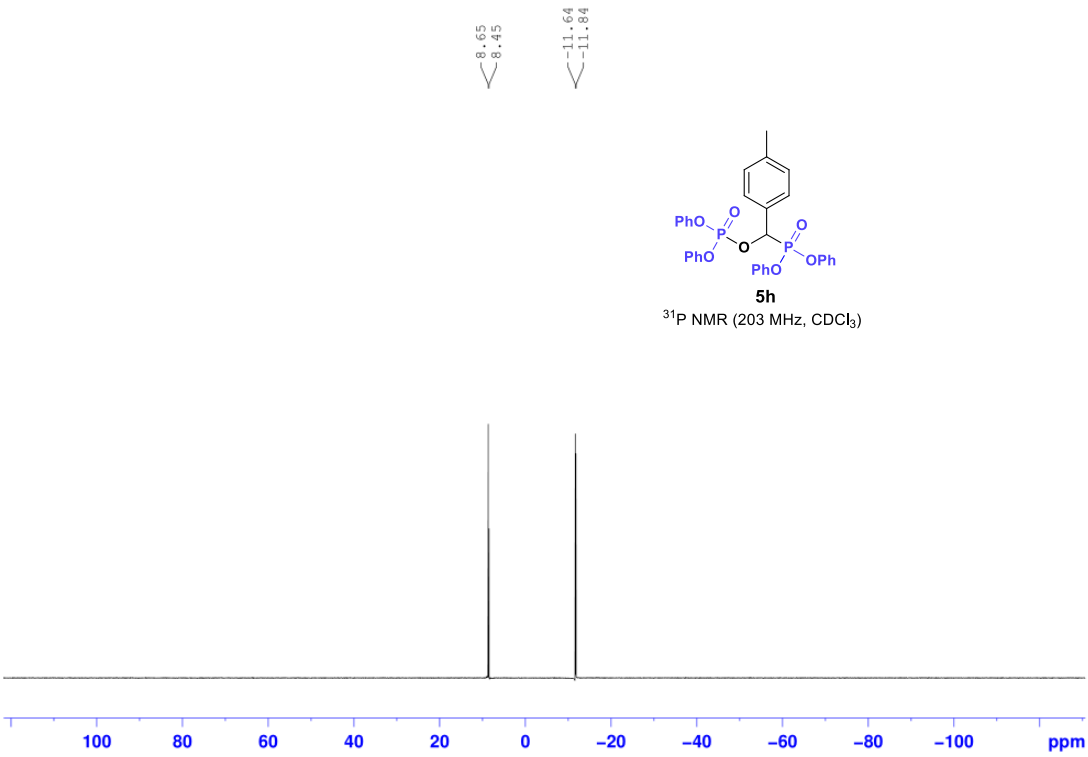
^{13}C NMR (125 MHz, $CDCl_3$)


PhO
PhO
PhO
OPh
5g
1H NMR (500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
3.11
14.06
2.03
4.00
1.00


8.43
8.23
-11.60
-11.79
PhO
PhO
PhO
OPh
5g
31P NMR (203 MHz, CDCl3)
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

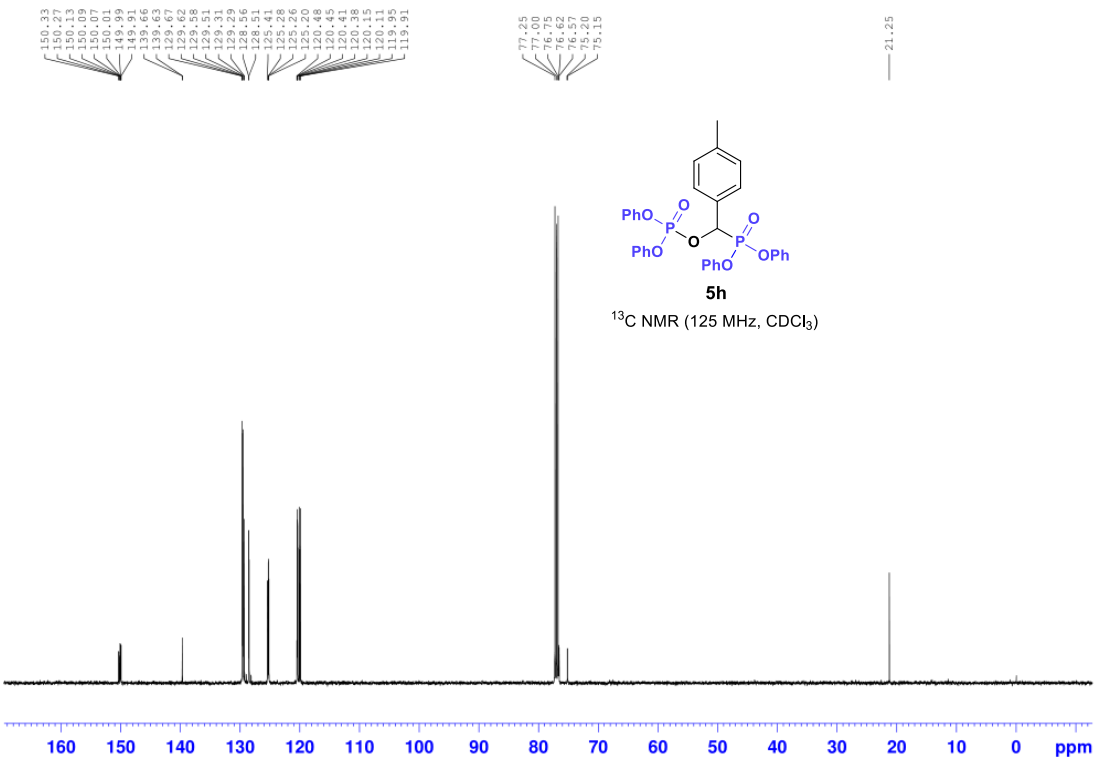

150.28
150.23
150.05
150.03
149.99
149.95
149.83
149.85
131.60
129.67
129.61
129.57
129.53
128.58
128.57
128.51
128.46
125.42
125.29
125.28
120.41
120.38
120.33
120.30
120.11
120.07
119.87
119.83
77.26
77.00
76.75
76.63
76.57
75.22
75.16
PhO
PhO
PhO
OPh
5g
13C NMR (125 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.44
7.44
7.43
7.42
7.27
7.25
7.24
7.24
7.22
7.21
7.20
7.20
7.20
7.19
7.17
7.15
7.14
7.13
7.11
7.10
7.09
7.09
7.09
7.07
7.04
7.03
6.94
6.92
6.90
6.89
6.10
6.08
6.07
6.05
2.34
2.34
-0.00
PhO
PhO
PhO
OPh
5h
1H NMR (500 MHz, CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.08
16.13
2.00
4.01
1.00
3.08



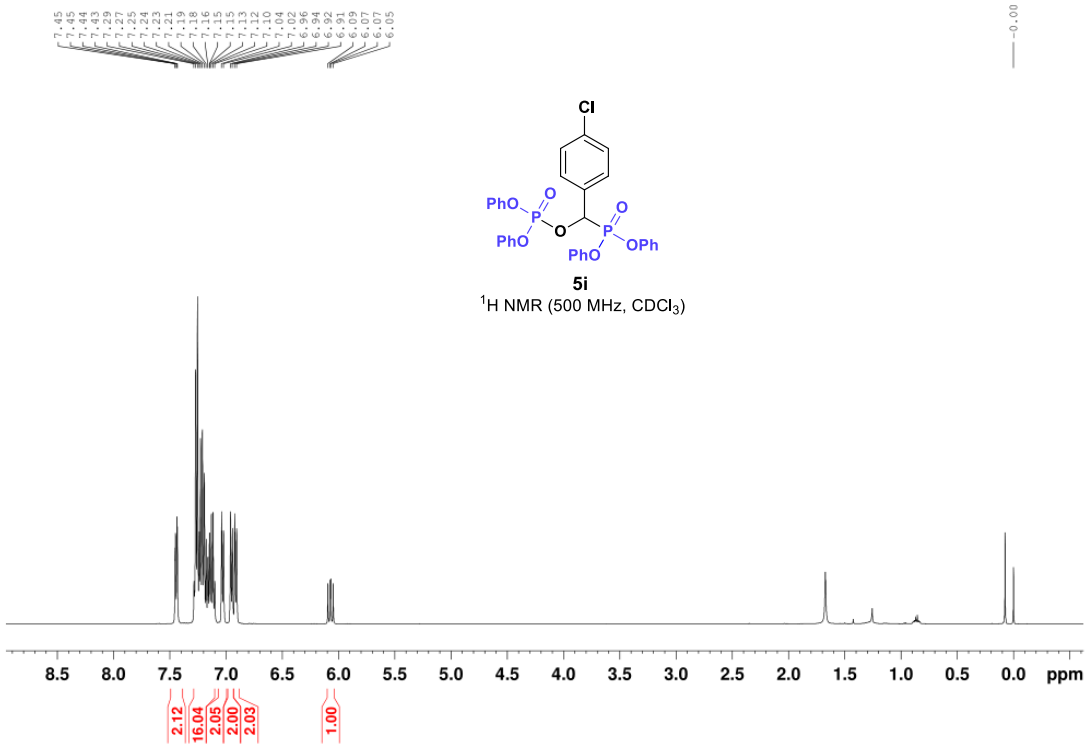
5h

^{31}P NMR (203 MHz, $CDCl_3$)



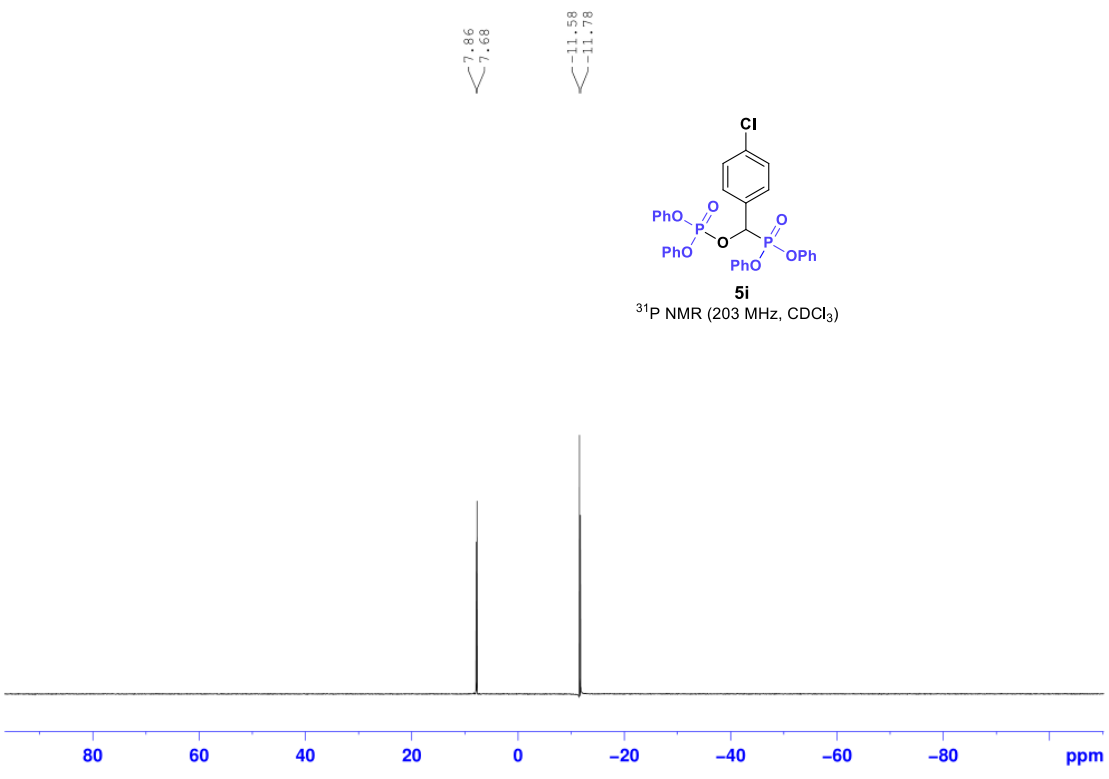
5h

^{13}C NMR (125 MHz, $CDCl_3$)



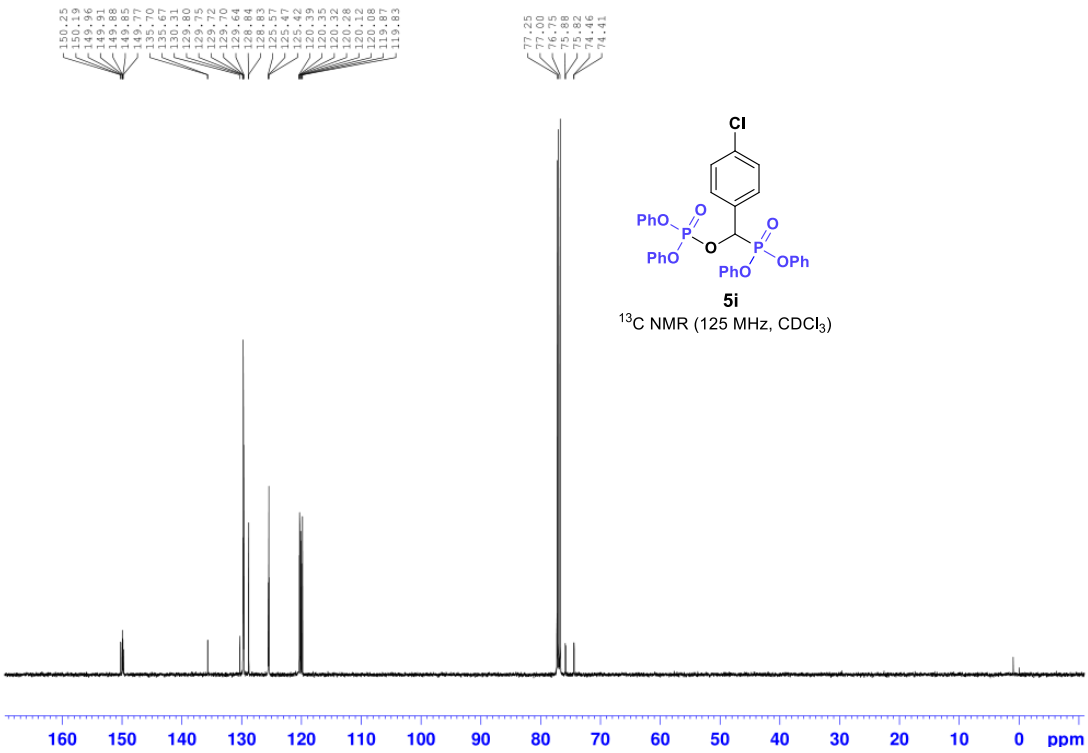
5i

^{1}H NMR (500 MHz, $CDCl_3$)



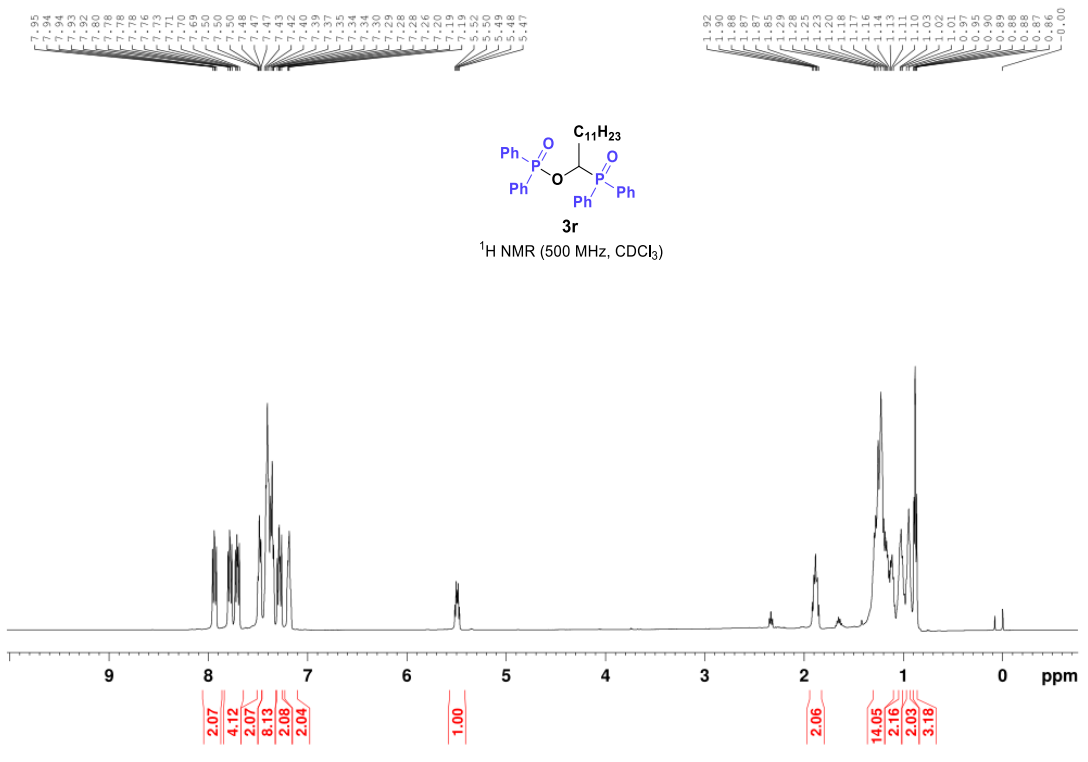
5i

^{31}P NMR (203 MHz, $CDCl_3$)



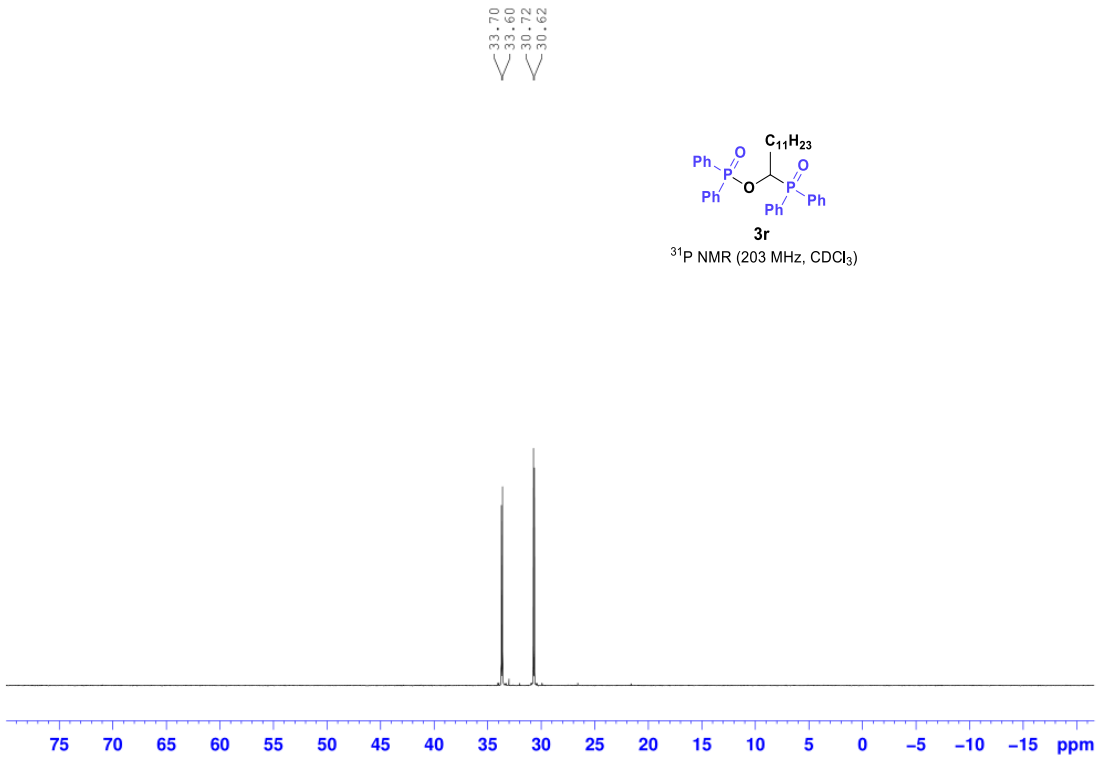
5i

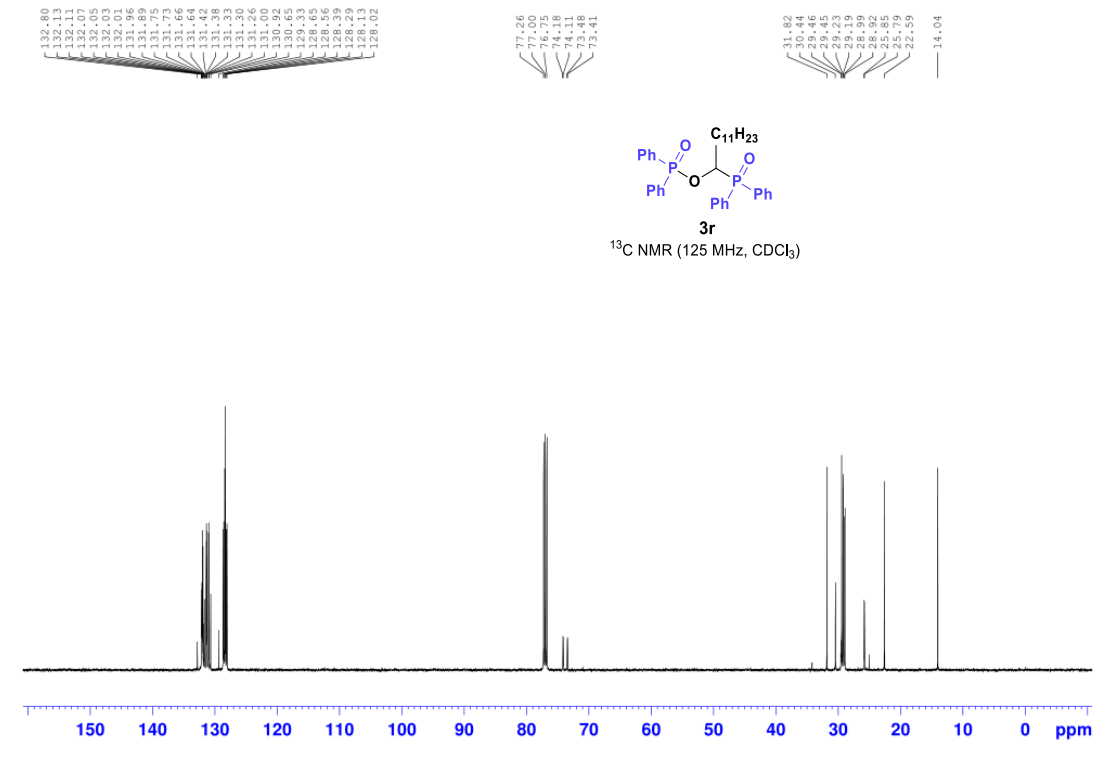
^{13}C NMR (125 MHz, $CDCl_3$)

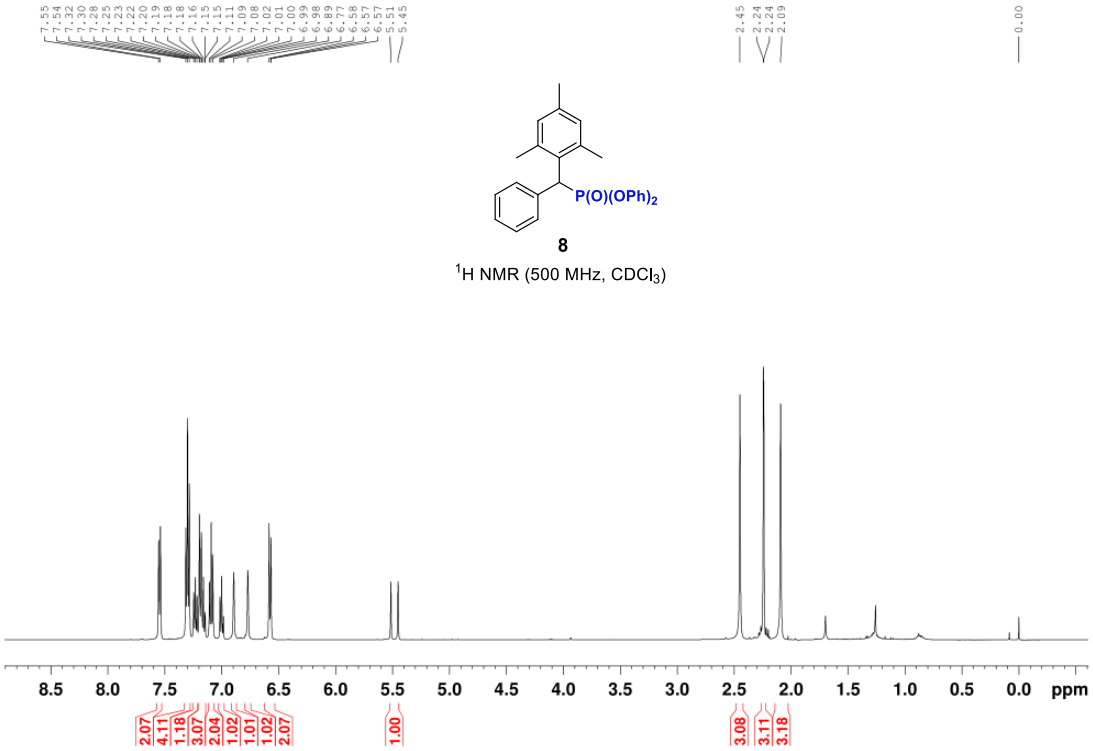


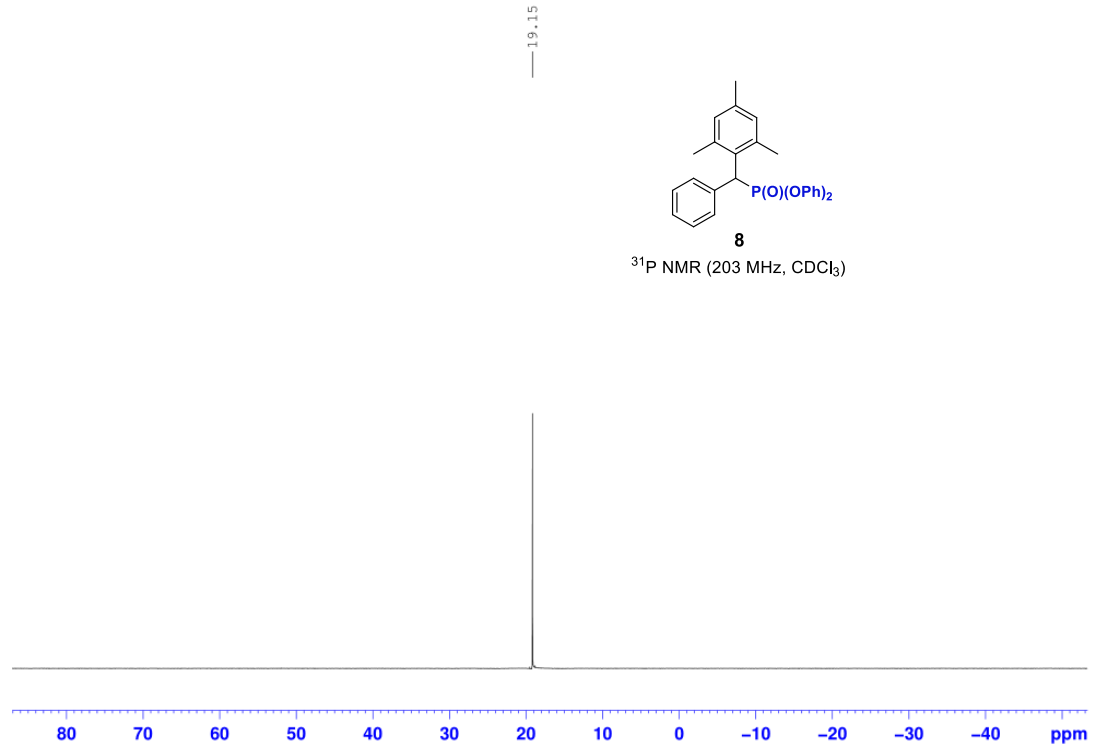
3r

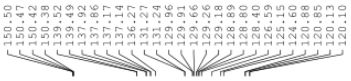
^{1}H NMR (500 MHz, $CDCl_3$)

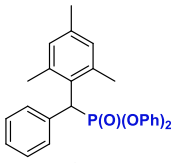

33.70
33.60
30.72
30.62
C11H23
Ph
O
P
O
Ph
Ph
P
Ph
Ph
3r
31P NMR (203 MHz, CDCl3)
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 ppm


132.80
132.13
132.11
132.07
132.05
132.03
132.01
131.96
131.89
131.75
131.73
131.66
131.64
131.42
131.38
131.33
131.30
131.26
131.00
130.92
130.65
130.33
128.65
128.56
128.39
128.29
128.13
128.02
77.26
77.00
76.75
74.18
74.11
73.48
73.41
31.82
30.44
29.46
29.45
29.23
29.19
28.99
28.92
25.85
25.79
22.59
14.04
C11H23
Ph
O
P
O
Ph
Ph
P
Ph
Ph
3r
13C NMR (125 MHz, CDCl3)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.55
7.54
7.32
7.30
7.28
7.25
7.23
7.22
7.20
7.19
7.18
7.16
7.15
7.11
7.09
7.08
7.02
7.01
7.00
6.99
6.98
6.89
6.77
6.58
6.57
5.57
5.51
5.45
2.45
2.24
2.24
2.09
0.00
P(O)(OPh)2
8
1H NMR (500 MHz, CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.07
4.11
1.18
3.07
2.04
1.02
1.01
1.02
2.07
1.00
3.08
3.11
3.18

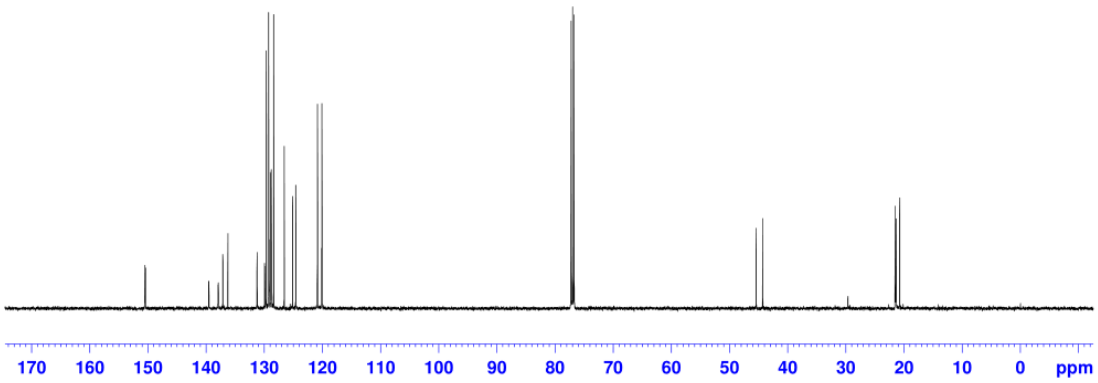

19.15
P(O)(OPh)2
8
31P NMR (203 MHz, CDCl3)
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
ppm

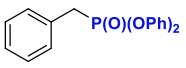




8

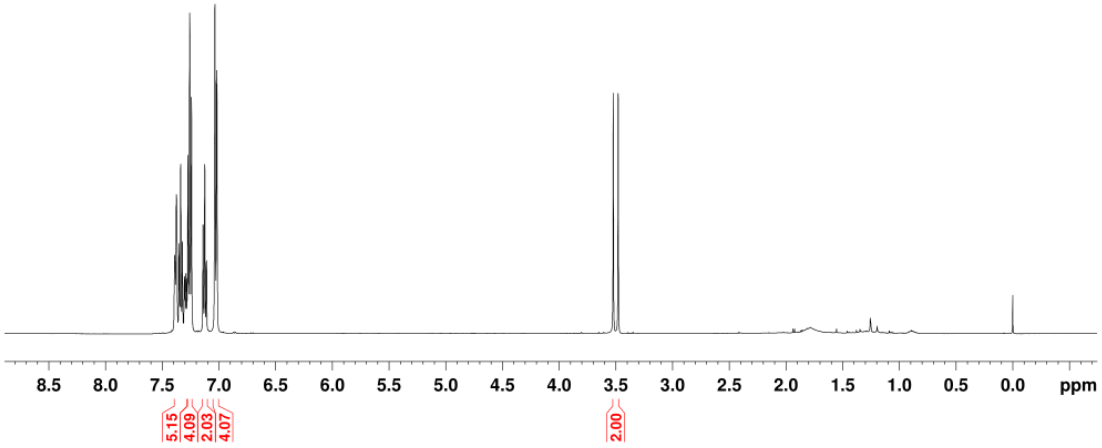
^{13}C NMR (125 MHz, $CDCl_3$)

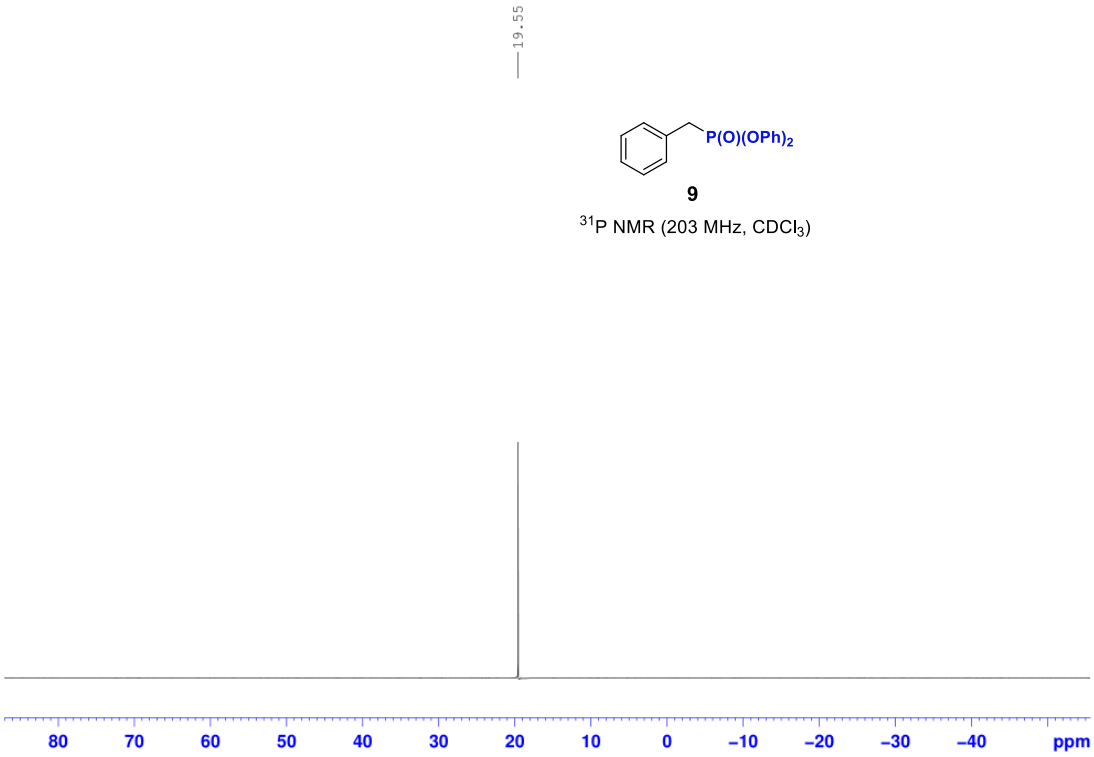




9

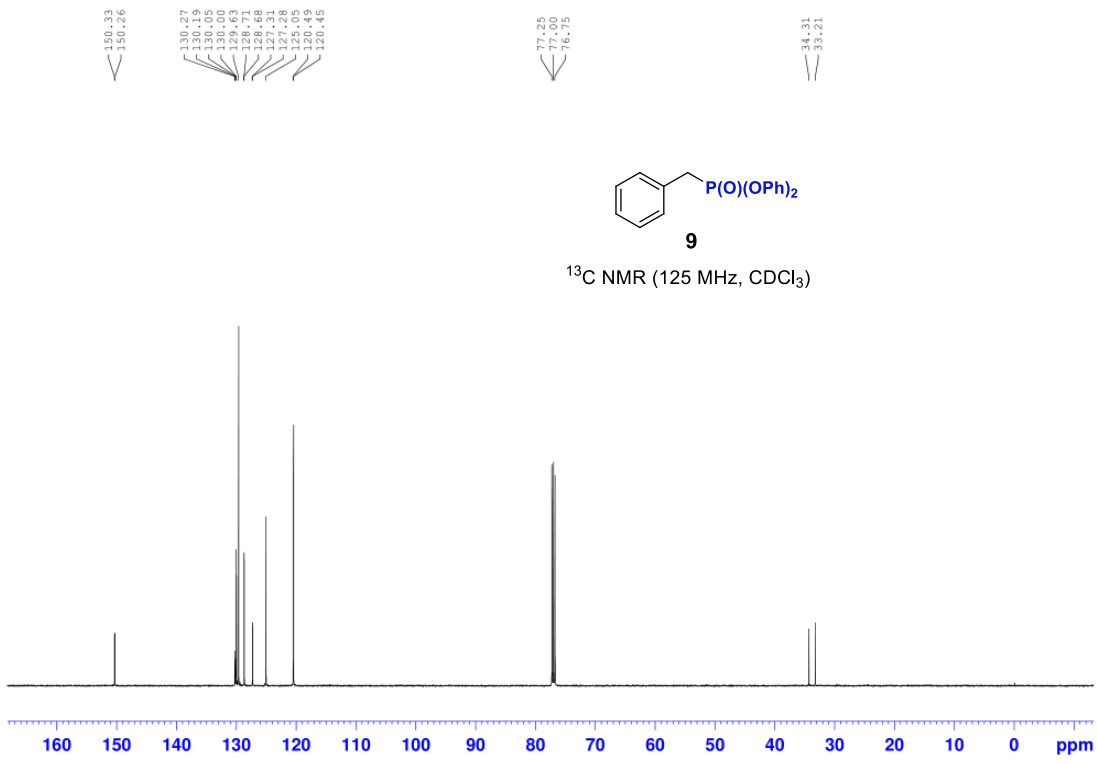
^{1}H NMR (500 MHz, $CDCl_3$)





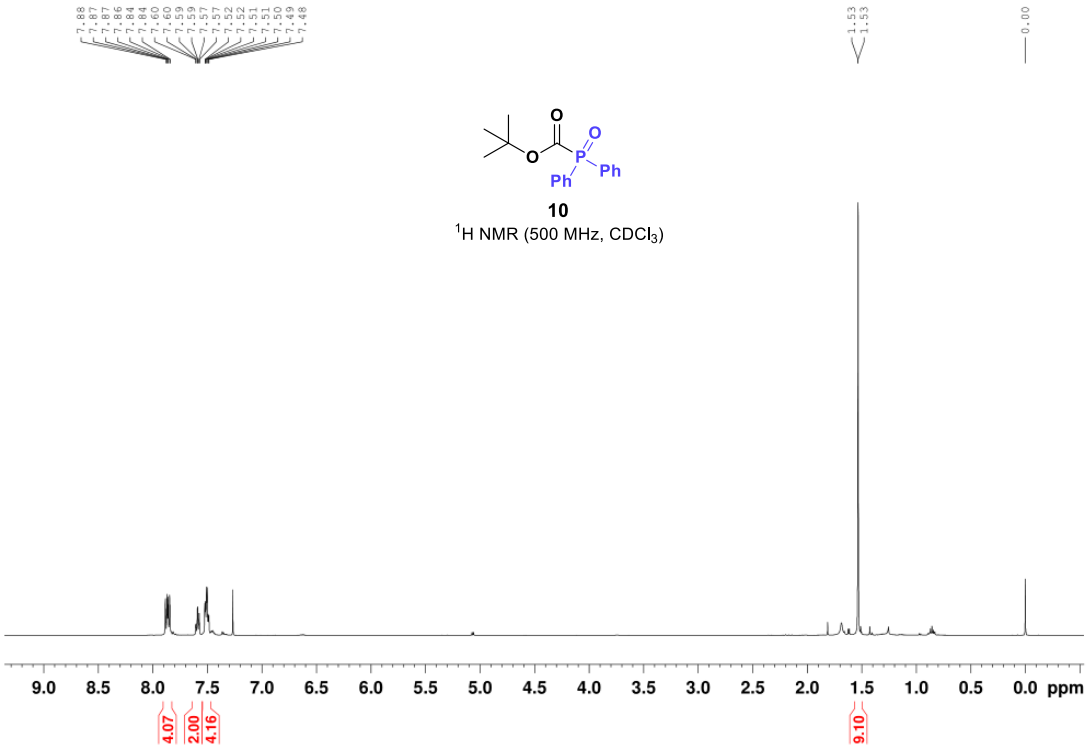
9

^{31}P NMR (203 MHz, $CDCl_3$)



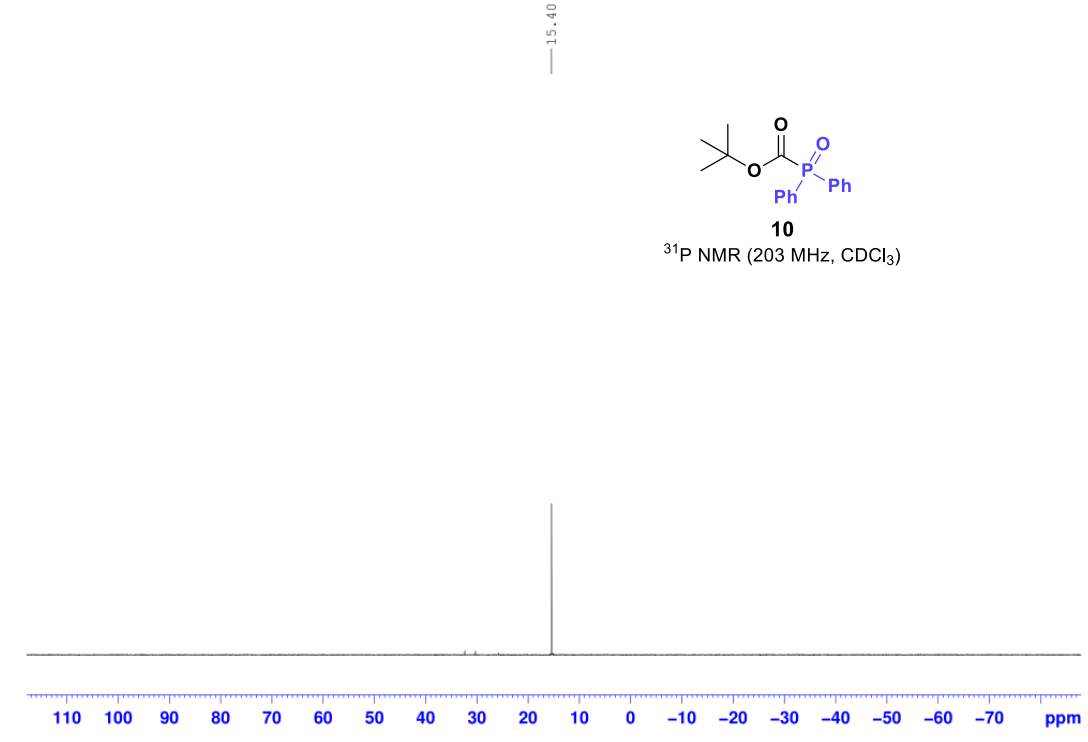
9

^{13}C NMR (125 MHz, $CDCl_3$)



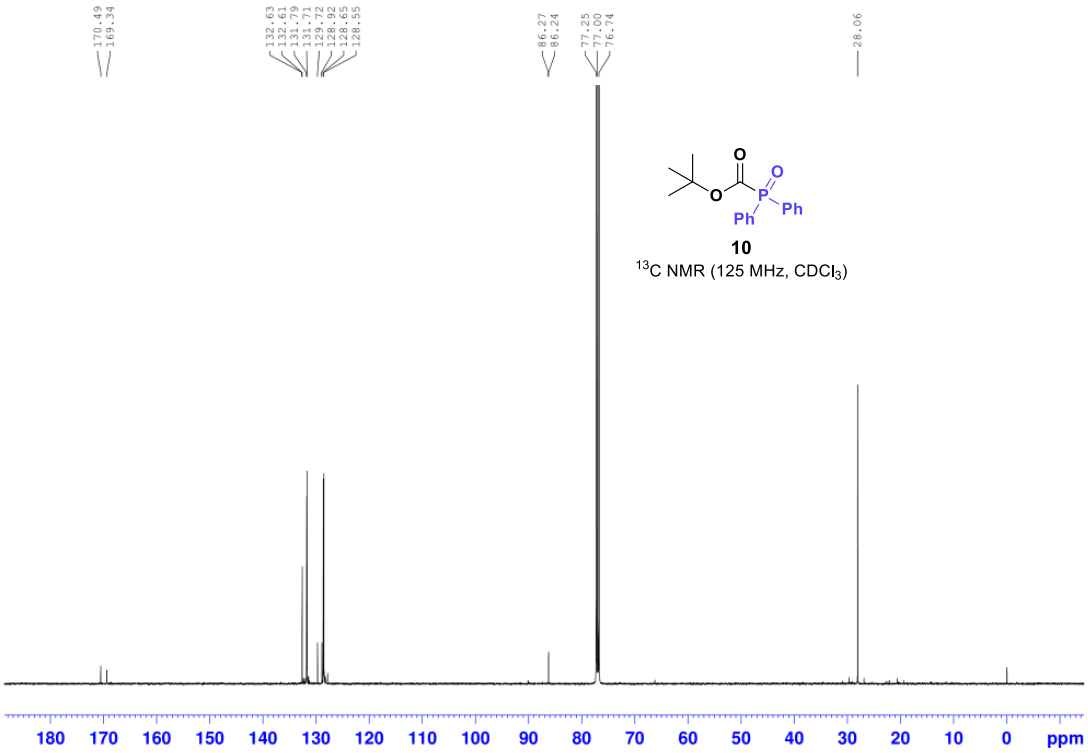
10

^{1}H NMR (500 MHz, $CDCl_3$)



10

^{31}P NMR (203 MHz, $CDCl_3$)



10

^{13}C NMR (125 MHz, $CDCl_3$)