One-pot Synthesis of α-Aminophosphonates via Cascade Sequence of Allylamine Isomerization/Hydrophosphonylation

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Contents:

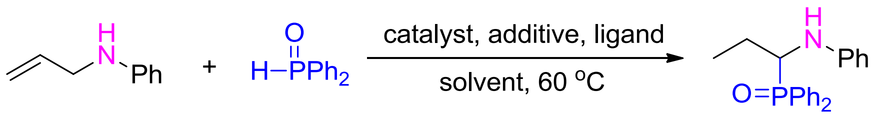
1. General information.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. ^{31}P NMR spectra and ^{19}F NMR were recorded on the same instrument. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants, *J* are reported in hertz. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique, a Bruker maXis 4G mass spectrometer by means of the ESI-TOF technique or the Orbitrap Elite mass spectrometer by means of the ESI technique. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals Adamas-beta or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicalsbook". Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Substituted allylamines were prepared according to the literature procedure. [S1]

2. Optimization reaction conditions

2-1. Optimization reaction conditions of Rh-Catalyzed Allylamine Isomerization/Hydrophosphonylation.[a]

Table S1. Reaction Conditions Screening



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

entry	solvent	catalyst	additive	ligand	time (h)	yield (%)[b]
1	PhMe	$[Rh(COD)Cl]_2$	Ag_2CO_3		20	91
2	DMF	$[Rh(COD)Cl]_2$	Ag_2CO_3		20	trace
3	THF	$[Rh(COD)Cl]_2$	Ag_2CO_3		20	92
4	MeCN	$[Rh(COD)Cl]_2$	Ag_2CO_3		20	0
5	i-PrOH	$[Rh(COD)Cl]_2$	Ag_2CO_3		20	72
6	**dioxane**	**$[Rh(COD)Cl]_2$**	**Ag_2CO_3**		**16**	**97**
7	dioxane	$[Rh(COD)Cl]_2$	Ag_2CO_3	L1	16	96 (race)
8	dioxane	$[Rh(COD)Cl]_2$	Ag_2CO_3	L2	16	97 (race)
9	dioxane	$[Rh(COD)Cl]_2$	Ag_2CO_3	L3	16	84 (race)
10	dioxane	$[Rh(COD)Cl]_2$	Ag_2CO_3	L4	16	97 (race)
11	dioxane		Ag_2CO_3		16	0
12	dioxane	$[Rh(COD)Cl]_2$			16	88
13	dioxane	$[Rh(COD)Cl]_2$	AgOTf		16	33
14	dioxane	$[Rh(COD)Cl]_2$	$AgNO_3$		16	0
15	dioxane	$[Rh(COD)Cl]_2$	Ag_3PO_4		16	0

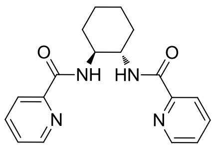
16	dioxane	$[Rh(COD)Cl]_2$	$AgBF_4$	16	66
17	dioxane	$[Rh(COD)Cl]_2$	$AgClO_4$	16	54
18	dioxane	$[Rh(COD)Cl]_2$	AgCl	16	95
19	dioxane	$[Rh(COD)Cl]_2$	Na_2CO_3	16	84
20	dioxane	$[Rh(COD)Cl]_2$	K_2CO_3	16	80
21	dioxane	$[Rh(COD)Cl]_2$	$NaHCO_3$	16	94

tol-BINAP

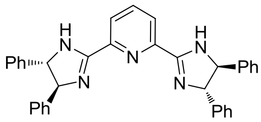
L1

Segphos

L2



L3



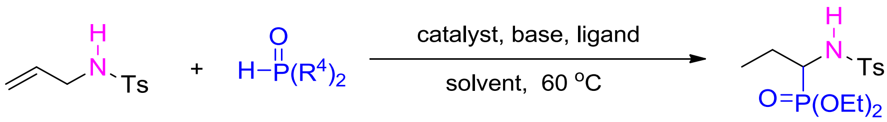
L4

[a] The reaction was carried out with [M] 2.5 mol %, additive 20 mol %, **1a** (0.20 mmol), and **2a** (1.5 equiv.) in solvent (1.0 mL) at 60 °C under argon, unless otherwise noted. [b] Yield of isolated product.

Note: we tried to add some kinds of ligands in this reaction system (entries 7-10; Table S1). However, we find that ligand did not play an important role in this reaction.

2-2. Optimization reaction conditions of Ni-Catalyzed Allylamine Isomerization/Hydrophosphonylation.[a] [S2]

Table S2. Reaction Conditions Screening



4a **5a** **6aa**

entry	solvent	catalyst	base	ligand	yield (%)[b]
1	dioxane	$Ni(PPh_3)_2Cl_2$	K_3PO_4		49
2	THF	$Ni(PPh_3)_2Cl_2$	K_3PO_4		47
3	DMF	$Ni(PPh_3)_2Cl_2$	K_3PO_4		82
4	Et_2O	$Ni(PPh_3)_2Cl_2$	K_3PO_4		40
5	DME	$Ni(PPh_3)_2Cl_2$	K_3PO_4		67
6	toluene	$Ni(PPh_3)_2Cl_2$	K_3PO_4		0
7	DMF	$Ni(PPh_3)_2Cl_2$	Cs_2CO_3		47
8	DMF	$Ni(PPh_3)_2Cl_2$	K_2CO_3		15
9	DMF	$Ni(PPh_3)_2Cl_2$	DABCO		trace
10	DMF	$Ni(PPh_3)_2Cl_2$	Et_3N		trace
11	DMF	$Ni(PPh_3)_2Cl_2$	DMAP		0
12	DMF	$Ni(PPh_3)_2Cl_2$			0

13	DMF	$NiCl_2$	K_3PO_4	PPh_3	86
14	**DMF**	**$NiCl_2$**	**K_3PO_4**		**90**
15	DMF	$Ni(PCy_3)_2Cl_2$	K_3PO_4		70
16	DMF	$Ni(COD)_2$	K_3PO_4		44
17	DMF	Ni(dppe)Cl_2	K_3PO_4		78
18	DMF	$NiBr_2$	K_3PO_4		87
19	DMF	$Ni(OAc)_2$	K_3PO_4		83
20	DMF	$Ni(OTf)_2$	K_3PO_4		65
21	DMF	$Ni(ClO_4)_2$	K_3PO_4		88
22	DMF	$Ni(acac)_2$	K_3PO_4		69
23[c]	DMF	$NiCl_2$	K_3PO_4		0
24[d]	DMF	$NiCl_2$	K_3PO_4		70
25[e]	DMF	$NiCl_2$	K_3PO_4		68
26[f]	DMF	$NiCl_2$	K_3PO_4		60
26[g]	DMF	$NiCl_2$	K_3PO_4		85
27	DMF	Ni(*R*-Binap)Cl_2	K_3PO_4		84 (race)
28	DMF	$NiCl_2$	K_3PO_4	*R*-Binap	40 (race)

[a] The reaction was carried out with catalyst 5 mol %, Base 120 mol %, **4a** (0.20 mmol), and **5a** (1.5 equiv.) in solvent (1.0 mL) at 60 ^{o}C under argon, unless otherwise noted. [b] Yield of isolated product. [c] Under air. [d] at 40 ^{o}C. [e] at 80 ^{o}C. [f] catalyst 2 mol %. [g] catalyst 10 mol %.

3. The experimental procedure

3.1 Rh-Catalyzed Allylamine Isomerization/Hydrophosphonylation.

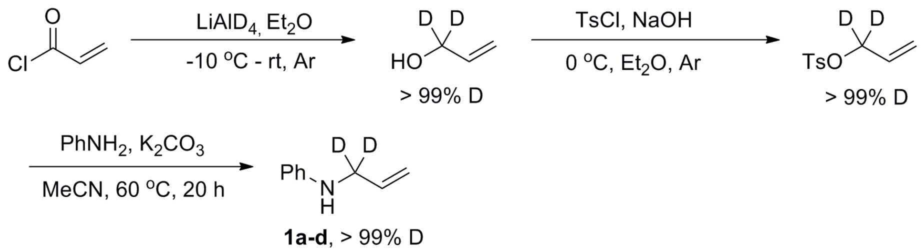
In a Schlenk tube, *N*-allylaniline (0.20 mmol), $[Rh(cod)Cl]_2$ (2.5 mol %), Ag_2CO_3 (20 mol %), $HP(O)Ph_2$ (0.30 mmol) were added and charged with Ar three times. Then anhydrous Dioxane (1.0 mL) was added. The mixture was allowed to stir at 60℃ for 16 hours (monitored by TLC). After substrate was consumed, the reaction was cooled to room temperature and concentrated in vacuo, and the resulting residue was purified by column chromatography to give **3aa** in 97% yield (PE : EA = 3 : 1, then PE : *i*-PrOH = 20 : 1).

3.2 Ni-Catalyzed Allylamine Isomerization/Hydrophosphonylation.

In a Schlenk tube, N-allyl-4-methylbenzenesulfonamide (0.20 mmol), $NiCl_2$ (5 mol %), K_3PO_4 (120 mol %), diethyl phosphonate (0.30 mmol) were added and charged with Ar three times. Then, anhydrous DMF (1.0 mL) were added. The mixture was allowed to stir at 60 ^{o}C for 10 hours (monitored by TLC). After substrate was consumed, the reaction was cooled to room temperature, 5 mL H_2O and 10 mL DCM was added, then the organic layer was separated and aqueous layer was extracted with DCM (10 mL × 2), The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 then concentrated in vacuo, and the resulting residue was purified by column chromatography to give 6**aa** in 90% yield (PE : EA = 3 : 1, then PE : *i*-PrOH = 20 : 1).

4. The preparation of the substrate 1a-*d*, 2a-*d* and 1a-N*d*

4-1 synthesis of 1a-*d*.[S3]



Sheme S1. Synthesis of **1a-*d***

1,1-Dideuterioallyl alcohol:

Under an argon atmosphere , $LiAlD_4$ (0.5 g, 11.9 mmol) and anhydrous ether (20 mL) were added into a 50 mL flame-dried flask fitted with magnetic stirrer bar at -10 ^oC. Then, a solution of acryloyl chloride (1.5 mL, 17.8 mmol) in ether was added dropwise over 10 min, The resulting mixture was warmed to room temperature slowly and stirred for 10 h. The mixture was cooled to -10 ^oC and H_2O (1.0 mL) was slowly added over a 5 min period. After stirring for another 15 min, 15% aqueous NaOH solution (1.0 mL) and then H_2O (1.0 mL) were added. The resulting slurry was stirred for 1 h and then filtered. The filtrate was dried over Na_2SO_4. The solvent was removed carefuly on a rotary evaporator (atmospheric pressure, 37 ^oC) to afford a colorless liquid, which was used in the next step without further purification. **^{1}H NMR (400 MHz, $CDCl_3$)**: 6.01 (1 H, dd), 5.20 (2 H, m).

1,1-Dideuterioallyl tosyl ester:

A 50 mL Schlenk flask was charged with 1,1-dideuterioallyl alcohol (0.5 g, 8.2 mmol, crude product from previous step), tosyl chloride (1.6 g, 8.3 mmol) and anhydrous ether (10 mL). The mixture was cooled to 0 ^oC and powdered NaOH (0.9 g, 22.5 mmol) was added in portions under N_2. The reaction was then warmed to room temperature and stirred for 12 h. The precipitate was filtered and the filtrate concentrated in vacuo. The resulting oil was subjected to column chromatography (silica gel, 90:10 hexane/EtOAc) to the yield pure product (1.5 g, 88%). **^{1}H NMR (300 MHz, $CDCl_3$)**: 7.80 (2 H, d), 7.33 (2 H, d), 5.81 (1 H, dd), 5.28 (1 H, d), 5.16 (1 H, d), 2.46 (3 H, s).

***N*-1-(1,1-Dideuterioallyl)-allylaniline (1a-*d*)**

To a 25 mL Schlenk flask under Ar atmosphere were successively charged, the $PhNH_2$ (4.0 equiv), K_2CO_3 (1.1 equiv) and dry MeCN (2.0 mL). Then, the resulting mixture was heated for 10 min at 60 oC in a preheated oil bath before dropwise addition of 1,1-Dideuterioallyl tosyl ester (1.0 equiv) diluted in dry MeCN (2.0 mL). The resulting mixture was stirred for 20 h at 60 ^oC, The water was added to quench the reaction, 10 mL EtOAc was added, then the organic layer was separated and aqueous layer was extracted with EtOAc (10 mL × 2), The conbined organic layer was washed with brine and dried over anhydrous Na_2SO_4 then concentrated in vacuo, and the resulting residue was purified by column chromatography to give **1a-d** in 58% yield.**^{1}H NMR (400 MHz, $CDCl_3$)** 7.18 (dd, J = 16.7, 9.1 Hz, 2H), 6.74 - 6.65 (m, 1H), 6.61 (d, J = 8.0 Hz, 2H), 5.93 (dt, J = 20.7, 10.3 Hz, 1H), 5.19 (dt, J = 44.8, 25.8 Hz, 2H), 4.05 - 3.26 (m, 1H), **MS : m/z (M+H):** 136.1088.

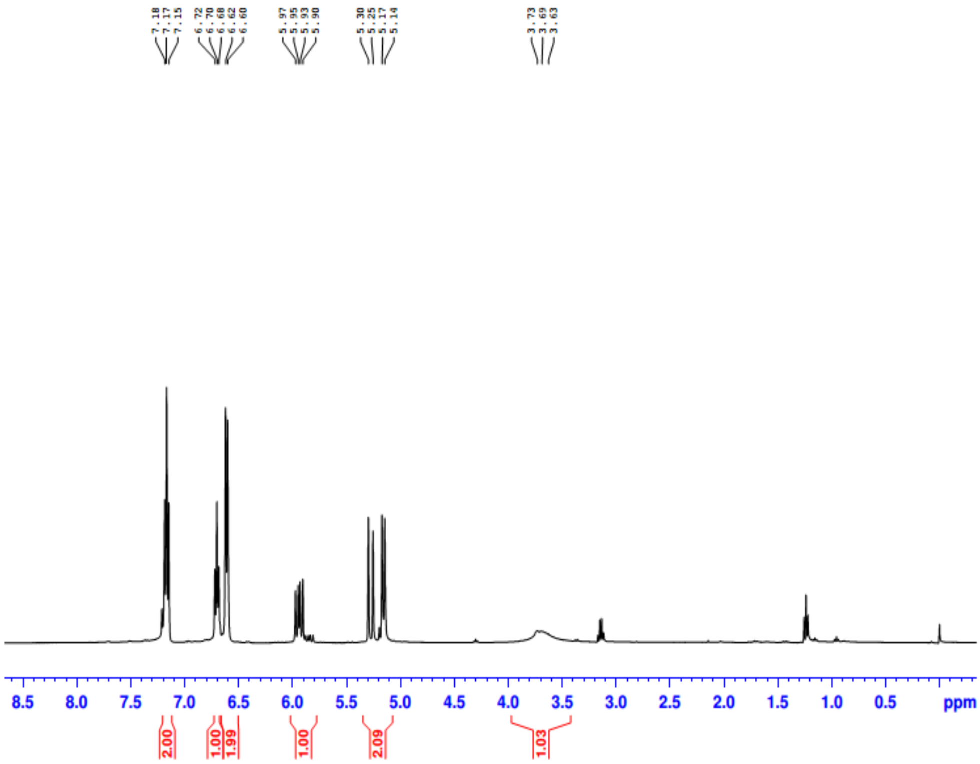
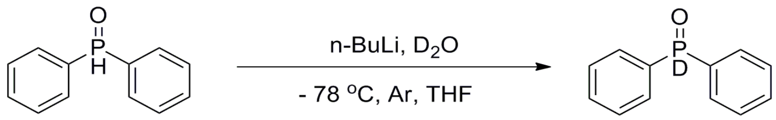


Figure S1. ^{1}H NMR spectra of 1**a-*d***

4-2 synthesis of 2a-*d*



2a-d, 84% D

An oven dried flask (50 mL) was charged with diphenylphosphine oxide (404 mg, 2 mmol) and dried THF (15 mL) at -78 ^{o}C. Then, n-BuLi (2.5 equiv) was added over 5 min, the resulting mixture was warmed to -50 ^{o}C slowly and stirred for 1 h. The mixture was cooled to -78 ^{o}C and D_2O (10 equiv) was slowly added slowly and the mixture was stirred for 1 h and then filtered. The filtrate was dried over $MgSO_4$. The solvent was removed on a rotary evaporator to afford **2a-d** in 100% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** 8.69 (s, 0.08H), 7.77 - 7.64 (m, 4H), 7.58 (m, 2H), 7.54 - 7.43 (m, 4H), 7.28 (s, 0.08H).

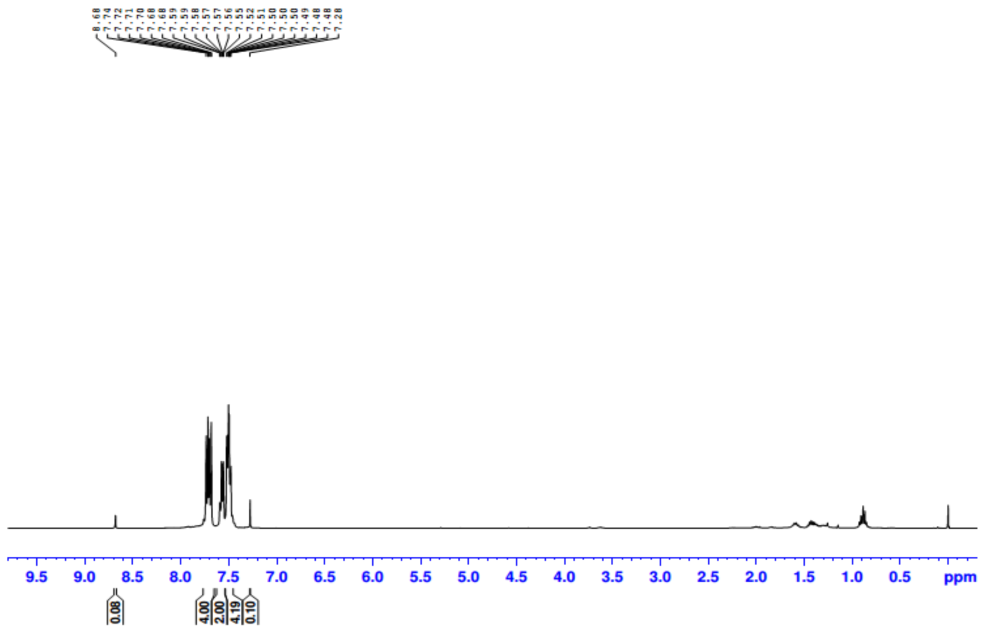
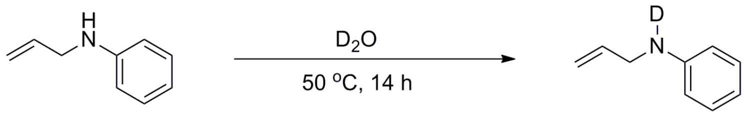


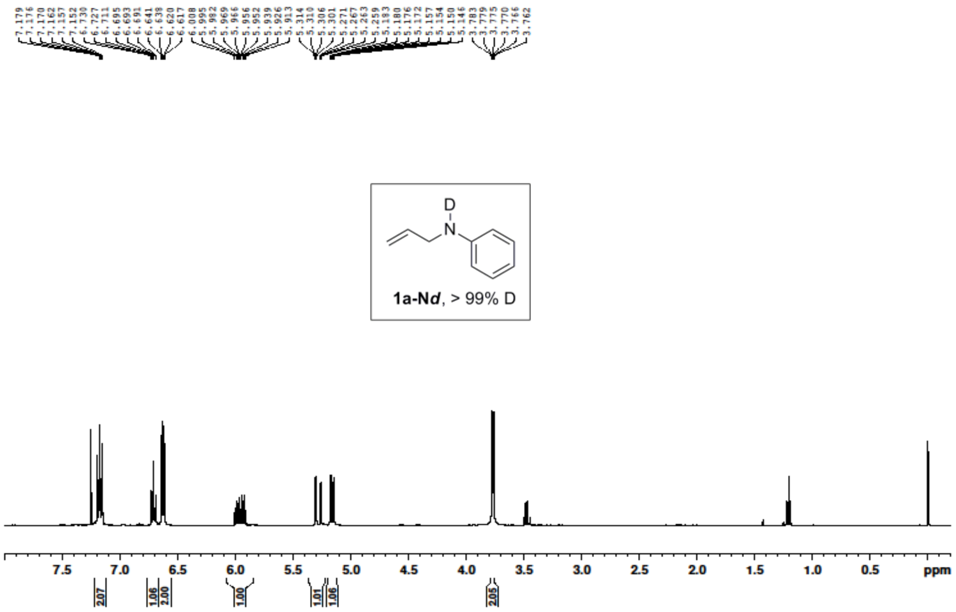
Figure S2. ^{1}H NMR spectra of 2**a-*d***

4-3 synthesis of 1a-N*d*



1a-N*d*, > 99% D

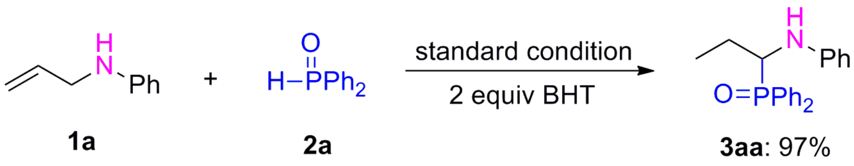
N-allylaniline (200 uL) was stirred in D_2O (4.0 mL) at 50 °C for 14 h, and then the solution was extracted with dry ether (20 mL × 3). The combine organic extracts were dried and evaporated to give **1a-N*d*** (>99% D).



5. Preliminary mechanistic studies

5.1 Radicals Trapping Experiments using BHT

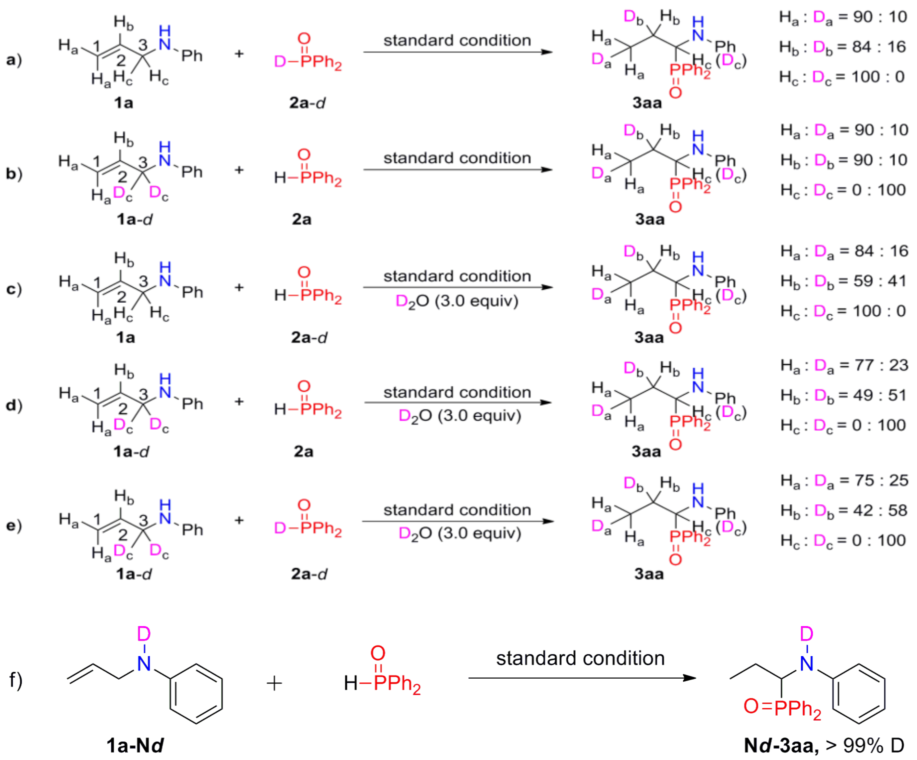
In a Schlenk tube, N-allylaniline (0.20 mmol), $[Rh(cod)Cl]_2$ (2.5 mol %), Ag_2CO_3 (20 mol %), $HP(O)Ph_2$ (0.30 mmol) and BHT (2.0 equiv) were added and charged with Ar three times. Then,anhydrous Dioxane (1.0 mL) were added. The mixture was allowed to stir at 60℃ for 16 hours (monitored by TLC). After substrate was consumed, the reaction was cooled to room temperature and concentrated in vacuo, and the resulting residue was purified by column chromatography to give **3aa** in 97% yield (Scheme S2).



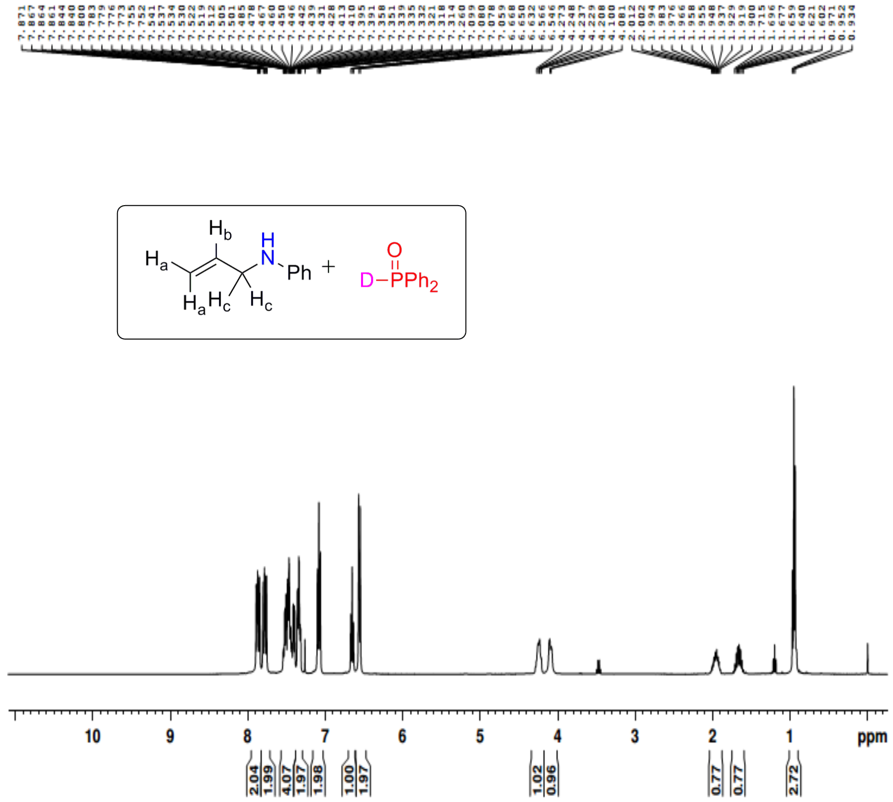
Scheme S2. Radicals Trapping Experiments using BHT

5.2 Deuterium labeling experiment of Rh-Catalyzed Allylamine Isomerization/Hydrophosphonylation.

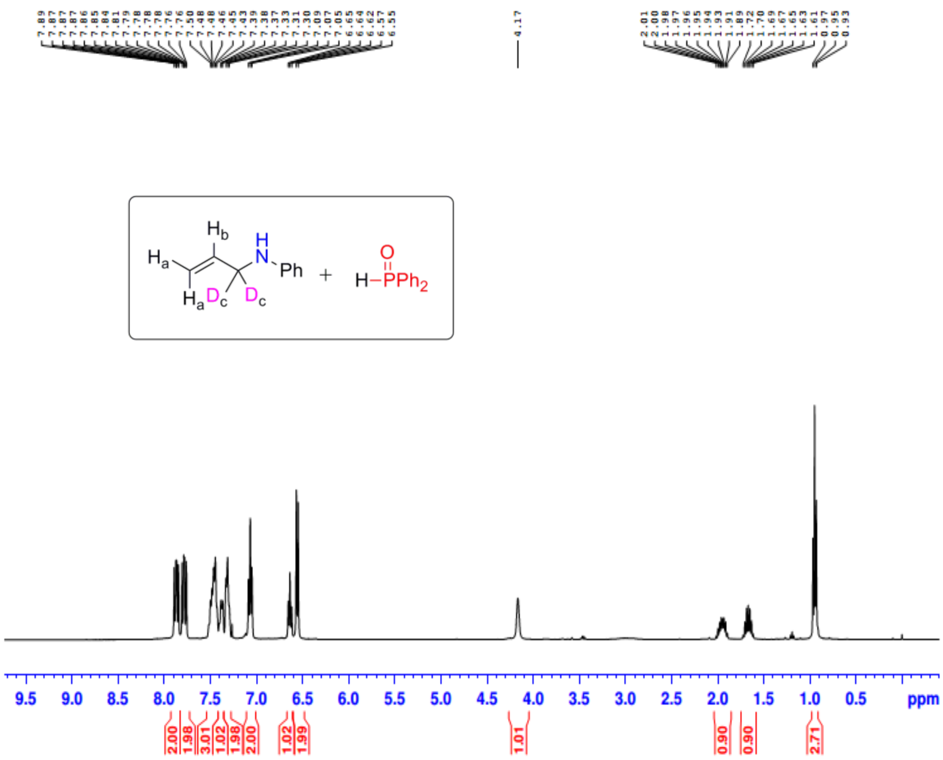
In a Schlenk tube, *N*-allylaniline (deuterated *N*-allylaniline) (0.20 mmol), $[Rh(cod)Cl]_2$ (2.5 mol %), Ag_2CO_3 (20 mol %), $HP(O)Ph_2$ (deuterated $HP(O)Ph_2$) (0.30 mmol) or D_2O (3.0 equiv) were added and charged with Ar three times. Then, anhydrous Dioxane (1.0 mL) was added. The mixture was allowed to stir at 60 °C for 16 hours (monitored by TLC). After substrate was consumed, the reaction was cooled to room temperature and concentrated in vacuo, and the resulting residue was purified by column chromatography to give deuterated product. (Scheme S3). The products were under ^{1}H-NMR analysis.



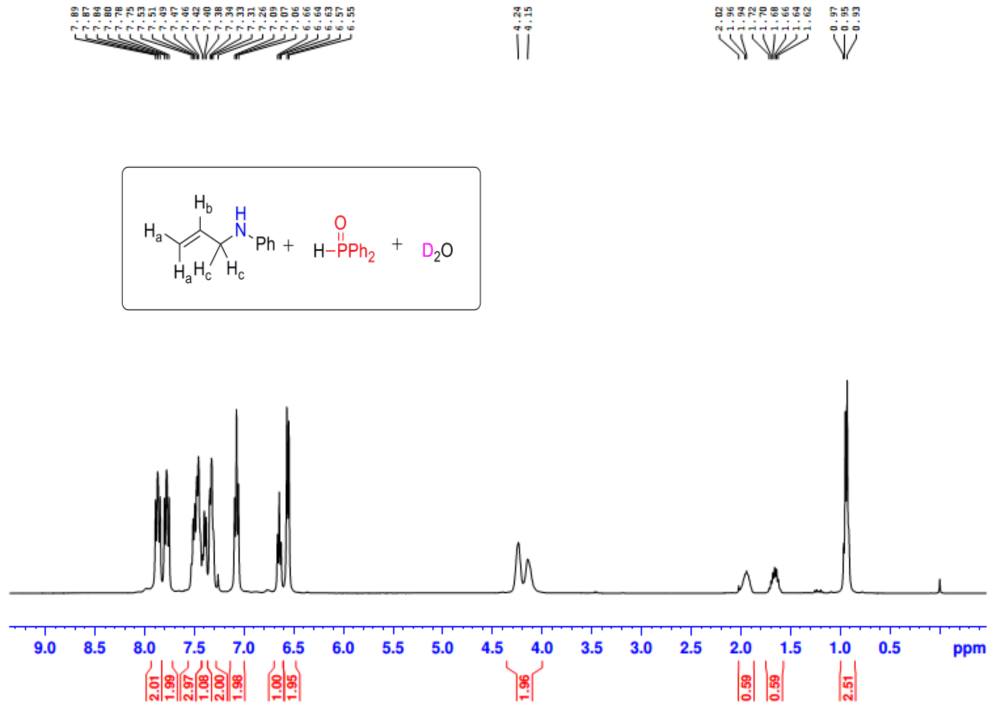
Scheme S3. Deuterium labeling experiment



Hb
Ha
H
N
Ph
Ha Hc
Hc
+
O
D–PPh2
10
9
8
7
6
5
4
3
2
1
ppm
2.04
1.99
4.07
1.97
1.98
1.00
1.97
1.02
0.96
0.77
0.77
2.72



Hb
Ha
H
N
Ph
Ha Dc
Dc
+
O
H–PPh2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.98
3.01
1.02
1.98
2.00
1.02
1.99
1.01
0.90
0.90
2.71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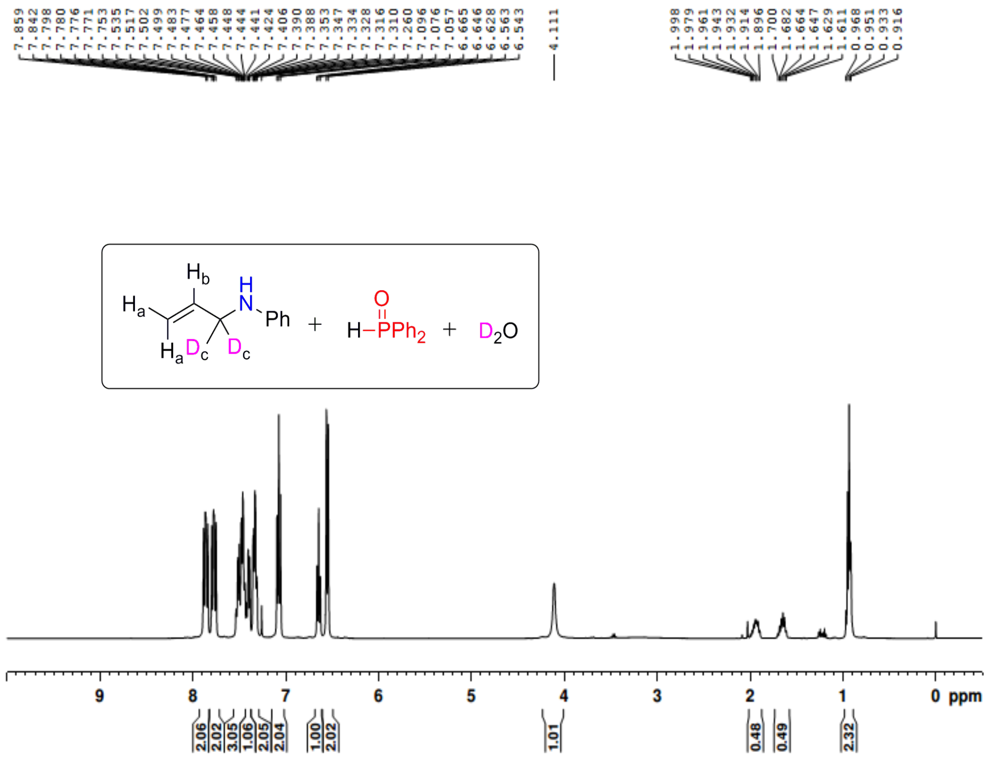
Ha Hc Hc
ppm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Ha Dc Dc
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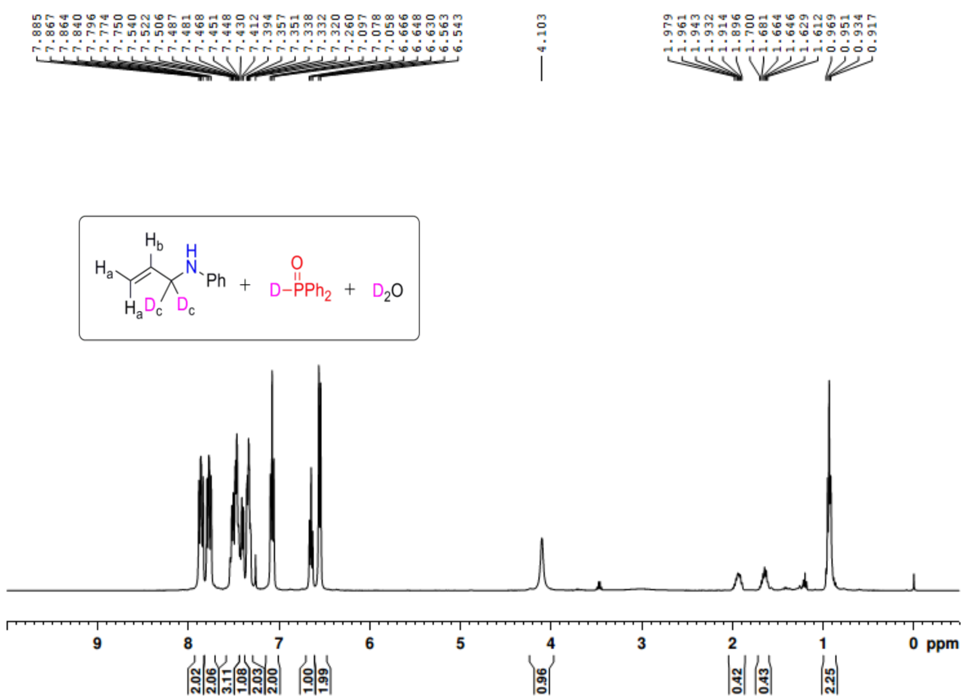
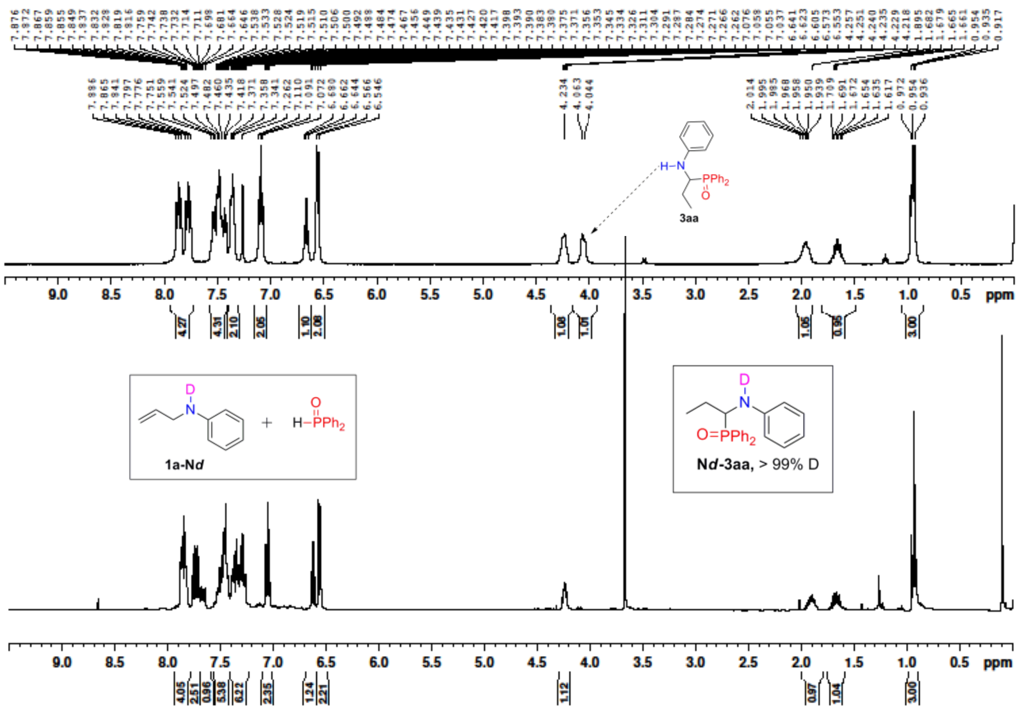
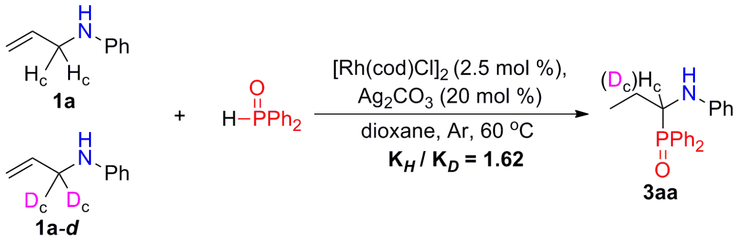




Note: compare the standard ^{1}H NMR with the ^{1}H NMR of N-H deuterated product.

5.3 Experimental procedure for the kinetic isotope effect (KIE) study of Rh-Catalyzed Allylamine Isomerization/Hydrophosphonylation[S4].



Scheme S4. The kinetic isotope effect (KIE) study

In two different Schlenk tube, **1a** (0.30 mmol) or **1a-d** (0.30 mmol), $[Rh(cod)Cl]_2$ (2.5 mol %), Ag_2CO_3 (20 mol %), $HP(O)Ph_2$ **2a** (0.45 mmol) were added and charged with Ar three times. Then, anhydrous dioxane (2.0 mL) was added. The mixture was allowed to stir at 60 °C, The conversions of the reaction were measured carefully after designated time by ^{1}H NMR using 4-Iodotoluene (10 mg) as an internal standard.

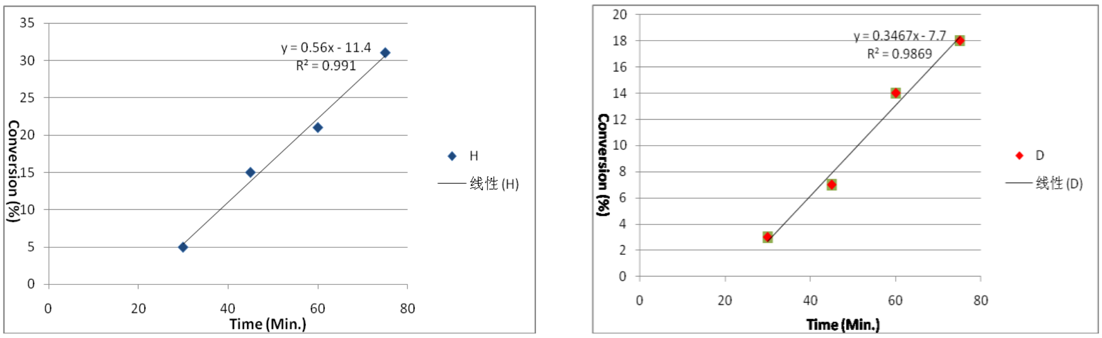
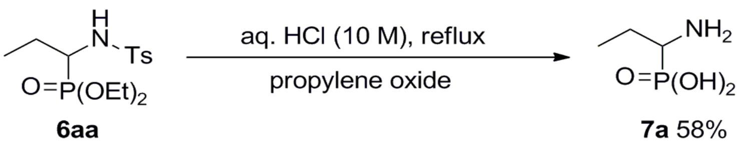


Figure S3 Reaction conversions over time between 1a(1a-d) and diphenylphosphine oxide

K_H/K_D=0.56/0.3467=1.62

6. Procedure for desulfonylation and Hydrolysis reaction of 6aa [S5]

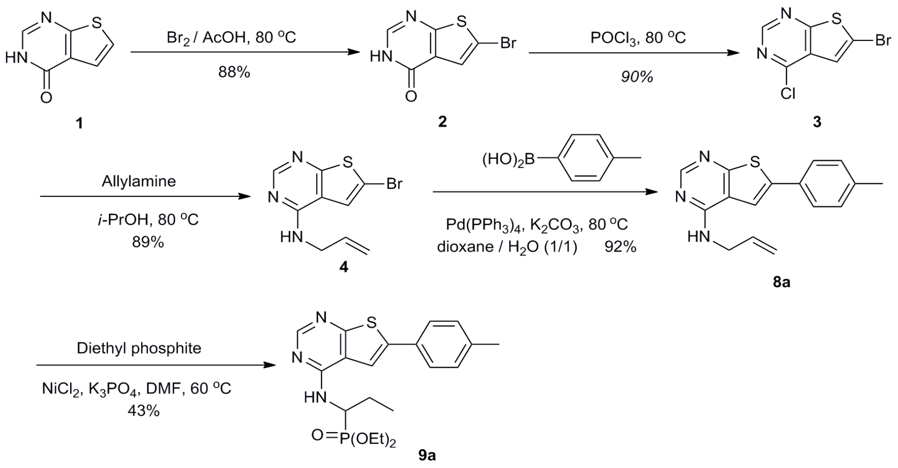
A suspension of α-aminophosphonate **6aa** (349 mg, 1.0 mmol) in HCl (10 M aq., 4 mL) was heated at reflux overnight. The resulting solution was concentrated under vacuum, the residue was dissolved in hot EtOH (2 mL), and an excess of propylene oxide was added to this solution. The mixture was stirred for 3 h at room temperature, and the resulting white solid was collected by filtration to give α-aminophosphonic acid **7a** (80 mg, 58%) (Scheme S5).



Scheme S5. Procedure for desulfonylation and Hydrolysis reaction of 6aa

(1-aminopropyl)phosphonic acid (7a) (58%) White solid; **^{1}H NMR (400 MHz, D_2O)** δ 3.1 – 3.12 (m, 1H), 2.14 – 1.91 (m, 1H), 1.90 – 1.67 (m, 1H), 1.13 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, D_2O)** δ 50.8 (d, *J* = 143.2 Hz), 21.82, 10.2 (d, *J* = 9.4 Hz). **^{31}P NMR (162 MHz, D_2O)** δ 13.48. **MS : m/z (M+H)**: 140.0621.

7. Synthesis of Allosteric Inhibitors of hFPPS 9a [S6]



Scheme S6. Synthesis of Allosteric Inhibitors of hFPPS **9a**

6-Bromothieno[2,3-d]pyrimidin-4(3H)-one (2).

Thieno[2,3-d]pyrimidin-4(3H)-one (1) (0.78 g, 5 mmol) was mixed with acetic acid (12 mL), and bromine (0.52 mL, 1.6 g, 10 mmol) was added slowly before the mixture was heated at 80 °C for 3 h. The reaction mixture was then cooled to rt and filtered to remove insoluble components. The liquid fraction was diluted with ice and neutralised using a saturated aq $NaHCO_3$ solution. The precipitated material was isolated by filtration and washed with water (3×30 mL). Drying gave 1.03 g (4.4 mmol, 88%) of **2** as a light brown solid, **^{1}H NMR (400 MHz, DMSO)** δ 12.63 (s, 1H), 8.17 (s, 1H), 7.54 (s, 1H). **^{13}C NMR (101 MHz, DMSO)** δ 165.4, 156.5, 146.9, 126.0, 125.0, 110.7. **MS : m/z :** 229.91.

6-Bromo-4-chlorothieno[2,3-d]pyrimidine (3)

Compound **2** (0.93 g, 4 mmol) was mixed with $POCl_3$ (3 mL) and heated at 120 °C for 10 h. Then the mixture was quenched into 5 M aq NaOH (30 mL) and ice. The pH was adjusted to 7 using a saturated aq $NaHCO_3$ solution. The formed precipitate was isolated by filtration and washed with water (3×15 mL). Drying gave 0.9 g (3.6 mmol, 90%) of **3** as a brown solid. **^{1}H NMR (400 MHz, DMSO)** δ 9.05 – 8.70 (m, 1H), 7.83 (d, *J* = 4.4 Hz, 1H). **^{13}C NMR (101 MHz, DMSO)** δ 169.3, 153.6, 152.9, 130.6, 123.2, 118.9. **MS : m/z :** 247.88.

N-allyl-6-bromothieno[2,3-d]pyrimidin-4-amine (4)

Compound **3** (0.5 g, 2.0 mmol) was mixed with the Allylamine (3.5 equiv.) and *i*-PrOH (5 mL) and heated at 80 °C for 24 h, under nitrogen atmosphere. Then the mixture was cooled to rt, concentrated in vacuo, diluted with water (30 mL) and diethyl ether (30 mL). After phase separation, the water phase was extracted with more diethyl ether (2 × 30 mL). The combined organic phases were washed with saturated aq NaCl solution (2×30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by column chromatography to give 0.48 g (1.79 mmol, 89%) of **4** as a white soild(PE : EA = 10 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.31 (s, 1H), 8.19 (t, *J* = 5.4 Hz, 1H), 7.83 (s, 1H), 6.08 – 5.80 (m, 1H), 5.28 – 4.96 (m, 2H), 4.28 – 3.96 (m, 2H). **^{13}C NMR (101 MHz, DMSO)** δ 166.8, 155.9, 154.6, 135.4, 123.0, 117.3, 116.1, 110.0, 42.7. **MS : m/z :** 268.90.

N-allyl-6-(p-tolyl)thieno[2,3-d]pyrimidin-4-amine (8a)

Compound **4** (270 mg) was mixed with (4- methylphenyl)boronic acid (1.2 equiv), fine powdered K_2CO_3 (3 eq), $Pd(PPh_3)_4$ (10 mol %) and 1,4-dioxane/water (1/1 by vol. %, 4 mL). The reaction was then stirred at 80 ^oC for 20 h under nitrogen atmosphere. The solvent was removed and the product was diluted with water (30 mL) and extracted with Et_2O (30 mL), the water phase was extracted with more Et_2O (2×30 mL). The combined organic phases were washed with saturated aq NaCl solution (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. And the resulting residue was purified by column chromatography to give 259 mg (0.92 mmol, 92%) of **8a** as a light yellow solid (PE : EA = 8 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.33 (s, 1H), 8.11 (t, *J* = 5.5 Hz, 1H), 7.99 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.99 (m, 1H), 5.19 (m, 2H), 4.17 (t, *J* = 5.4 Hz, 2H), 2.35 (d, *J* = 11.6 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 165.2, 156.8, 154.2, 138.8, 138.6, 135.6, 130.9, 130.3, 125.9, 118.0, 116.1, 115.0, 42.8, 21.2. **MS : m/z :** 281.05.

Diethyl (1-((6-(p-tolyl)thieno[2,3-d]pyrimidin-4-yl)amino)propyl)phosphonate (9a)

In a Schlenk tube, Compound **8a** (0.20 mmol), $NiCl_2$ (5 mol %), K_3PO_4 (120 mol %), diethyl phosphonate (0.30 mmol) were added and charged with Ar three times. Then,anhydrous DMF (1.0 mL) were added. The mixture was allowed to stir at 60℃ for 10 hours (monitored by TLC). After substrate was consumed, the reaction was cooled to room temperature, 5 mL H_2O and 10 mL DCM was added, then the organic layer was separated and aqueous layer was extracted with DCM (10 mL ×2), The conbined organic layer was washed with brine and dried over anhydrous Na_2SO_4 then concentrated in vacuo, and the resulting residue was purified by column chromatography to give 36 mg (0.086 mmol, 43%) of **9a** as a white solid (PE : EA = 4 : 1, then PE : *i*-PrOH = 25 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (s, 1H), 7.56 (d, *J* = 6.2 Hz, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.23 (d, *J* = 9.6 Hz, 1H), 5.33 – 4.83 (m, 1H), 4.35 – 3.87 (m, 4H), 2.39 (s, 3H), 2.20 – 1.96 (m, 1H), 1.97 – 1.72 (m, 1H), 1.32 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H), 1.05 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.1, 156.6, 156.5, 153.4, 141.2, 138.7, 130.8, 129.7, 126.2, 118.0, 112.2, 63.0 (d, *J* = 7.0 Hz), 62.3 (d, *J* = 7.2 Hz), 47.6 (d, *J* = 155.3 Hz), 23.4, 21.2, 16.4 (d, *J* = 6.1 Hz), 10.6 (d, *J* = 13.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 24.98. **MS : m/z (M+H)**: 420.1671.

8. Reference:

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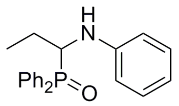
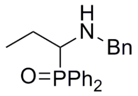
9. Characterization data of products



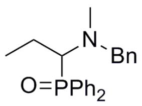
3aa

Diphenyl(1-(phenylamino)propyl)phosphine oxide (3aa) (97%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.92 – 7.83 (m, 2H), 7.82 – 7.72 (m, 2H), 7.55 – 7.37 (m, 4H), 7.33 (m, 2H), 7.08 (dd, *J* = 8.2, 7.6 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 2H), 4.33 – 4.19 (m, 1H), 4.12 (m, 1H), 2.07 – 1.84 (m, 1H), 1.67 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 147.1, 147.1, 131.9, 131.8, 131.8, 131.7, 131.6, 131.2, 131.2, 131.1, 129.1, 128.6 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 11.4 Hz), 117.78, 113.18, 53.6 (d, *J* = 80.1 Hz), 23.3 (d, *J* = 4.3 Hz), 10.9 (d, *J* = 9.8 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 31.71. **HRMS** calc. for $C_{21}H_{22}NOP$ $[M+Na]^+$, 358.1331; found, 358.1334.



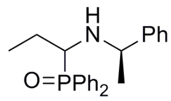
3ab

(1-(benzylamino)propyl)diphenylphosphine oxide (3ab) (55%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.93 (m, 2H), 7.88 – 7.78 (m, 2H), 7.59 – 7.35 (m, 6H), 7.34 – 7.16 (m, 3H), 7.16 – 7.04 (m, 2H), 3.82 – 3.68 (m, 1H), 3.59 (d, *J* = 12.9 Hz, 1H), 3.36 (m, 1H), 1.92 (m, 1H), 1.60 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.6, 133.2, 132.4 (d, *J* = 9.5 Hz), 131.7, 131.6, 131.5, 131.4, 131.2, 131.1, 128.5, 128.4, 128.3, 128.2, 128.1, 127.0, 57.9 (d, *J* = 81.9 Hz), 52.6 (d, *J* = 7.9 Hz), 22.3 (d, *J* = 3.8 Hz), 11.0 (d, *J* = 9.7 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 30.82. **HRMS** calc. for $C_{22}H_{24}NOP$ $[M+Na]^+$, 372.1488; found, 372.1491.



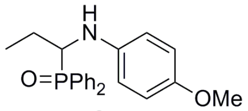
3ac

(1-(benzyl(methyl)amino)propyl)diphenylphosphine oxide (3ac) (80%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.86 (dd, *J* = 27.0, 19.1 Hz, 2H), 7.75 – 7.59 (m, 2H), 7.58 – 7.40 (m, 3H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.27 – 7.17 (m, 2H), 7.13 (t, *J* = 7.7 Hz, 2H), 6.72 – 6.45 (m, 3H), 4.67 – 4.38 (m, 1H), 2.97 (s, 3H), 2.25 (m, 1H), 1.77 (m, 1H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 150.5 (d, *J* = 3.2 Hz), 132.8, 132.0 (d, *J* = 13.2 Hz), 131.6 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 2.7 Hz), 131.1, 130.9, 130.8, 130.7, 130.6, 128.9, 128.7 (d, *J* = 10.9 Hz), 128.1, 127.9, 116.7, 112.4, 60.5 (d, J = 76.6 Hz), 33.0, 19.5 (d, J = 5.5 Hz), 11.5 (d, J = 12.8 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 31.99. **HRMS** calc. for $C_{23}H_{24}NOP$ $[M+Na]^+$, 384.1488; found, 384.1485.



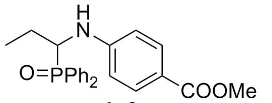
3ad

Diphenyl(1-(((R)-1-phenylethyl)amino)propyl)phosphine oxide (3ad) (65%) (d. r. = 1.0 : 1.2) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 – 7.63 (m, 4H), 7.57 – 7.31 (m, 6H), 7.29 – 7.14 (m,3H), 7.08 (d, J = 7.0 Hz, 1H), 7.02 – 6.92 (m,1H), 3.88 (q, J = 6.4 Hz,0.44H), 3.34 (q, J = 6.5 Hz, 0.52H), 3.23 (dd, J = 11.2, 7.3 Hz, 1H), 2.50 – 2.08 (m, 1H), 2.03 – 1.81 (m, 0.61H), 1.69 – 1.50 (m, 1H), 1.49 – 1.33 (m, 0.64H), 1.24 (m, 1.54H), 1.10 (m, 1.55H), 0.99 – 0.69 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.8, 144.2, 133.3, 132.6, 132.4, 131.5, 131.4, 131.3, 131.2, 131.1, 131.0, 130.9, 128.4, 128.3, 128.2, 128.1,, 128.0, 127.2, 127.0, 126.9, 56.5, 56.4, 56.3, 55.5, 55.2, 55.0, 54.3, 53.4, 24.6, 24.0, 23.8, 23.7, 11.0, 10.9, 10.3, 10.2. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.82, 30.33. (d. r. = 1 : 1.2). **HRMS** calc. for $C_{23}H_{26}NOP$ $[M+Na]^+$, 386.1644; found, 386.1647.



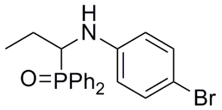
3ae

(1-((4-methoxyphenyl)amino)propyl)diphenylphosphine oxide (3ae) (92%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (m, 2H), 7.83 – 7.73 (m, 2H), 7.55 – 7.37 (m, 4H), 7.37 – 7.29 (m, 2H), 6.67 (d, J = 8.8 Hz, 2H), 6.52 (t, J = 6.2 Hz, 2H), 4.15 (m, 1H), 3.88 (d, J = 10.2 Hz, 1H), 3.69 (s, , 3H), 2.07 – 1.81 (m, 1H), 1.62 (m, 1H), 0.95 (t, J = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.1, 141.2 (d, J = 7.8 Hz), 132.0 (d, J = 13.4 Hz), 131.6 (d, J = 16.5 Hz), 131.2, 131.1, 131.0, 130.9, 128.6, 128.4, 128.3, 128.1, 55.50, 54.9 (d, J = 80.3 Hz), 23.2 (d, J = 4.3 Hz), 10.9 (d, J = 9.7 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 31.61. **HRMS** calc. for $C_{22}H_{24}NO_2P$ $[M+Na]^+$, 388.1437; found, 388.1435.

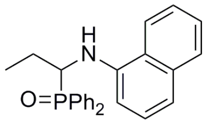


3af

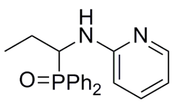
Methyl 4-((1-(diphenylphosphoryl)propyl)amino)benzoate (3af) (84%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 – 7.82 (m, 2H), 7.80 – 7.68 (m, 4H), 7.62 – 7.44 (m, 3H), 7.37 (t, J = 7.2 Hz, 1H), 7.30 (m, 2H), 6.59 (d, J = 8.8 Hz, 2H), 5.32 (s, 1H), 4.48 – 4.20 (m, 1H), 3.81 (s, 3H), 1.99 – 1.84 (m, 1H), 1.83 – 1.67 (m, 1H), 0.97 (t, J = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.94, 151.5 (d, J = 5.5 Hz), 132.00, 131.97, 131.80, 131.77, 131.53, 131.38, 131.24, 131.03, 130.98, 130.94, 130.89, 130.5 (d, J = 10.3 Hz), 128.73, 128.62, 128.3 (d, J = 11.4 Hz), 118.4, 111.7, 53.2 (d, J = 78.9 Hz), 51.3, 23.1 (d, J = 4.0 Hz), 10.8 (d, J = 10.4 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 31.66. **HRMS** calc. for $C_{23}H_{24}NO_3P$ $[M+Na]^+$, 416.1386; found, 416.1382.


3ag

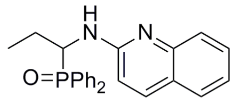
(1-((4-bromophenyl)amino)propyl)diphenylphosphine oxide (3ag) (98%) White solid; **^{1}H NMR (400 MHz,** $CDCl_3$) δ 7.92 – 7.80 (m, 2H), 7.80 – 7.68 (m, 2H), 7.60 – 7.45 (m, 3H), 7.41 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.33 (m, 2H), 7.18 – 7.07 (m, 2H), 6.44 (d, *J* = 8.8 Hz, 2H), 4.36 (dd, *J* = 10.5, 3.8 Hz, 1H), 4.25 – 4.06 (m, 1H), 2.00 – 1.80 (m, 1H), 1.76 – 1.57 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.4 (d, *J* = 6.7 Hz), 132.0, 131.9, 131.8, 131.7, 131.1, 131.0, 130.8, 130.7, 128.7 (d, *J* = 11.3 Hz), 128.4 (d, *J* = 11.4 Hz), 114.6, 109.1, 53.9 (d, *J* = 79.5 Hz), 23.2 (d, *J* = 4.3 Hz), 10.9 (d, *J* = 10.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 31.59. **HRMS** calc. for $C_{21}H_{21}BrNOP$ $[M+Na]^+$, 436.0436; found, 436.0432.


3ah

(1-(naphthalen-1-ylamino)propyl)diphenylphosphine oxide (3ah) (99%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (dd, *J* = 19.2, 9.3 Hz, 2H), 7.83 – 7.68 (m, 4H), 7.52 – 7.29 (m, 6H), 7.28 – 7.20 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 7.4 Hz, 1H), 4.89 (d, *J* = 8.6 Hz, 1H), 4.48 (t, *J* = 21.1 Hz, 1H), 2.18 – 1.95 (m, 1H), 1.80 (m, 1H), 1.05 – 0.89 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.1 (d, *J* = 7.3 Hz), 134.28,131.8 (d, *J* = 18.7 Hz), 131.2, 131.1, 131.0, 130.8 (d, *J* = 11.9 Hz), 128.6, 128.5, 128.4, 128.3, 128.2, 126.1, 125.7, 124.7, 123.3, 119.8, 117.7, 104.8, 53.3 (d, *J* = 79.8 Hz), 23.1 (d, *J* = 3.7 Hz), 10.9 (d, *J* = 9.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.07. **HRMS** calc. for $C_{25}H_{24}NOP$ $[M+Na]^+$, 408.1488; found, 408.1485.

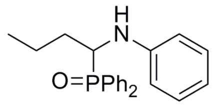

3ai

Diphenyl(1-(pyridin-2-ylamino)propyl)phosphine oxide (3ai) (84%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 4.5 Hz, 1H), 7.86 (m, 4H), 7.57 – 7.40 (m, 3H), 7.37 – 7.30 (m, 1H), 7.29 – 7.17 (m, 3H), 6.54 – 6.32 (m, 2H), 5.51 (s, 1H), 5.43 – 5.29 (m, 1H), 1.78 (m 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.8 (d, *J* = 5.0 Hz), 147.1, 136.7, 132.5, 132.1, 131.6 (d, *J* = 2.4 Hz), 131.4 (d, *J* = 2.6 Hz), 131.2, 131.1, 131.0, 130.9, 130.8, 128.6, 128.4, 128.0 (d, *J* = 11.5 Hz), 112.72, 109.09, 49.4 (d, *J* = 80.2 Hz), 22.7 (d, *J* = 4.8 Hz), 10.6 (d, *J* = 11.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.65. **HRMS** calc. for $C_{20}H_{21}N_2OP$ $[M+Na]^+$, 359.1284; found, 359.1289.



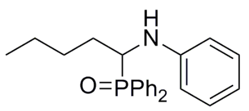
3aj

diphenyl(1-(quinolin-2-ylamino)propyl)phosphine oxide (3aj) (50%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.92 (dd, *J* = 17.6, 9.7 Hz, 4H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.57 – 7.43 (m, 5H), 7.27 – 7.09 (m, 4H), 6.67 (d, *J* = 8.8 Hz, 1H), 5.97 (d, *J* = 9.0 Hz, 1H), 5.74 (d, *J* = 6.8 Hz, 1H), 1.84 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 156.0 (d, *J* = 4.4 Hz), 147.5, 136.7, 132.7, 132.0, 131.8, 131.6 (d, *J* = 30.0 Hz), 131.2, 131.1, 131.0, 130.9, 129.1, 128.6 (d, *J* = 11.3 Hz), 128.0 (d, *J* = 11.6 Hz), 127.3, 126.3, 123.6, 121.9, 112.7, 49.1 (d, *J* = 79.8 Hz), 22.7 (d, *J* = 4.2 Hz), 10.8 (d, *J* = 11.0 Hz) **^{31}P NMR (162 MHz, CDCl$_3$)** δ 34.46. **HRMS** calc. for $C_{24}H_{23}N_2OP$ $[M+H]^+$, 387.1621; found, 387.1626.



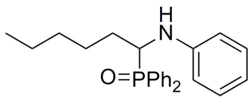
3ak

Diphenyl(1-(phenylamino)butyl)phosphine oxide (3ak) (92%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.96 – 7.83 (m, 2H), 7.83 – 7.72 (m, 2H), 7.55 – 7.42 (m, 3H), 7.39 (m, 1H), 7.35 – 7.28 (m, 2H), 7.06 (dd, *J* = 8.1, 7.6 Hz, 2H), 6.68 – 6.57 (m, 1H), 6.53 (d, *J* = 8.1 Hz, 2H), 4.32 (m, 1H), 4.06 (d, *J* = 10.2 Hz, 1H), 1.97 – 1.76 (m, 1H), 1.73 – 1.58 (m, 1H), 1.58 – 1.43 (m, 1H), 1.37 – 1.16 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 147.1 (d, *J* = 6.6 Hz), 131.92, 131.8 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 2.6 Hz), 131.3, 131.2, 131.1, 131.0, 130.8, 129.0, 128.6, 128.5, 128.3, 128.1, 117.7, 113.0, 52.4 (d, *J* = 80.5 Hz), 32.4 (d, *J* = 4.2 Hz), 19.5 (d, *J* = 10.1 Hz), 13.81. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 31.52. **HRMS** calc. for $C_{22}H_{24}NOP$ $[M+Na]^+$, 372.1488; found, 372.1490.



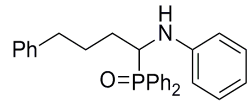
3al

diphenyl(1-(phenylamino)pentyl)phosphine oxide (3al) (60%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.94 – 7.82 (m, 2H), 7.81 – 7.72 (m, 2H), 7.59 – 7.44 (m, 3H), 7.40 (m 1H), 7.32 (m 2H), 7.12 – 6.99 (m, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 2H), 4.38 – 4.14 (m, 1H), 4.04 (dd, *J* = 10.5, 3.5 Hz, 1H), 2.01 – 1.78 (m, 1H), 1.64 (m, 1H), 1.55 – 1.38 (m, 1H), 1.32 – 1.09 (m, 3H), 0.75 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 147.1 (d, *J* = 6.5 Hz), 132.0, 131.9 (d, *J* = 2.8 Hz), 131.7 (d, *J* = 2.7 Hz), 131.4, 131.3, 131.2, 131.1, 131.0, 130.9, 129.1, 128.7, 128.6, 128.4, 128.2, 117.8, 113.2, 52.6 (d, *J* = 80.0 Hz), 29.9 (d, *J* = 4.2 Hz), 28.3 (d, *J* = 9.6 Hz), 22.5, 13.7. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 31.69. **HRMS** calc. for $C_{23}H_{26}NOP$ $[M+Na]^+$, 386.1644; found, 386.1647.



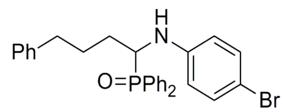
3am

Diphenyl(1-(phenylamino)hexyl)phosphine oxide (3am) (57%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 – 7.82 (m, 2H), 7.82 – 7.72 (m, 2H), 7.59 – 7.43 (m, 3H), 7.43 – 7.36 (m, 1H), 7.32 (m, 2H), 7.12 – 6.99 (m, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.51 (t, *J* = 7.4 Hz, 2H), 4.40 – 4.19 (m, 1H), 4.02 (m, 1H), 2.04 – 1.79 (m, 1H), 1.73 – 1.56 (m, 1H), 1.55 – 1.39 (m, 1H), 1.37 – 1.20 (m, 1H), 1.20 – 1.01 (m, 4H), 0.79 – 0.66 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1 (d, *J* = 6.5 Hz), 132.0, 131.9, 131.7, 131.3 (d, *J* = 8.9 Hz), 131.2 (d, *J* = 9.0 Hz), 131.1, 130.9, 129.1, 128.7, 128.5, 128.3, 128.2, 117.8, 113.2, 52.7 (d, *J* = 80.0 Hz), 31.5, 30.2 (d, *J* = 4.1 Hz), 25.8 (d, *J* = 9.6 Hz), 22.2, 13.8. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 31.61. **HRMS** calc. for $C_{24}H_{28}NOP$ $[M+Na]^+$, 400.1801; found, 400.1797.



3an

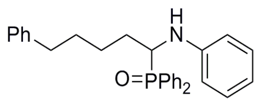
Diphenyl(4-phenyl-1-(phenylamino)butyl)phosphine oxide (3an) (99%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 – 7.77 (m, 2H), 7.77 – 7.66 (m, 2H), 7.45 (dd, *J* = 21.9, 6.2 Hz, 3H), 7.39 – 7.32 (m, 1H), 7.26 (t, *J* = 14.0 Hz, 2H), 7.13 (m, 3H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 7.1 Hz, 2H), 6.62 (t, *J* = 7.1 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 4.67 – 3.96 (m, 2H), 2.63 – 2.31 (m, 2H), 1.97 – 1.78 (m, 2H), 1.66 (dd, *J* = 29.5, 8.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.0 (d, *J* = 6.2 Hz), 141.43, 131.7 (d, *J* = 18.1 Hz), 131.40, 131.27, 131.2 (d, *J* = 9.0 Hz), 131.0(d, *J* = 9.0 Hz), 130.5 (d, *J* = 5.3 Hz), 129.00, 128.5 (d, *J* = 11.3 Hz), 128.25, 128.13, 128.1 (d, *J* = 6.2 Hz), 125.52, 117.63, 113.02, 52.3 (d, *J* = 80.0 Hz), 35.26, 29.5 (d, *J* = 4.4 Hz), 27.6 (d, *J* = 9.7 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.16. **HRMS** calc. for $C_{28}H_{28}NOP$ $[M+Na]^+$, 448.1801; found, 448.1807.



3ao

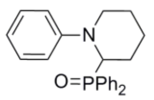
(1-((4-bromophenyl)amino)-4-phenylbutyl)diphenylphosphine oxide (3ao) (99%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 – 7.76 (m, 2H), 7.72 (dd, *J* = 10.6, 7.9 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.45 (dd, *J* = 10.1, 4.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.13 – 7.03 (m, 3H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.38 (d, *J* = 8.6 Hz, 2H), 4.46 (d, *J* = 8.4 Hz, 1H), 4.18 (t, *J* = 19.1 Hz, 1H), 2.58 – 2.33 (m, 2H), 1.94 – 1.79 (m, 2H), 1.71 (dd, *J* = 18.2, 9.0 Hz, 1H), 1.61 (dd, *J* = 14.8, 6.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.2 (d, *J* = 5.9 Hz), 141.3, 131.9 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 2.6 Hz), 131.7, 131.5, 131.3, 131.1, 131.0, 130.9, 130.4 (d, *J* = 13.2 Hz), 128.6 (d, *J* = 11.2 Hz), 128.4, 128.3, 128.1, 125.6, 114.5, 109.0, 52.5 (d, *J* = 79.4 Hz), 35.3, 29.3 (d, *J* = 4.2 Hz), 27.6 (d, *J* = 9.9 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 31.68. **HRMS** calc. for $C_{28}H_{27}BrNOP$ $[M+Na]^+$, 526.0906;

found, 526.0912.



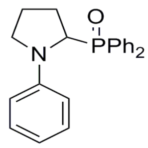
3ap

Diphenyl(5-phenyl-1-(phenylamino)pentyl)phosphine oxide (3ap) (61%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.91 – 7.81 (m, 2H), 7.79 – 7.71 (m, 2H), 7.56 – 7.39 (m, 4H), 7.33 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.04 (dd, *J* = 17.2, 7.7 Hz, 4H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 2H), 4.37 – 4.17 (m, 1H), 4.08 – 3.87 (m, 1H), 2.58 – 2.36 (m, 2H), 2.03 – 1.80 (m, 1H), 1.75 – 1.60 (m, 1H), 1.58 – 1.40 (m, 3H), 1.38 – 1.24 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 147.1 (d, *J* = 6.7 Hz), 142.3, 132.0, 131.8, 131.4 (d, *J* = 9.0 Hz), 131.2 (d, *J* = 9.0 Hz), 129.2, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 125.6, 118.0, 113.3, 52.6 (d, *J* = 79.9 Hz), 35.5, 31.2, 30.1 (d, *J* = 4.2 Hz), 25.9 (d, *J* = 9.5 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 31.62. **HRMS** calc. for $C_{29}H_{30}NOP$ [M+Na]$^+$,462.1957; found, 462.1965.



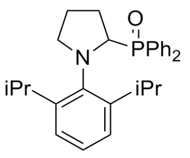
3aq

Diphenyl(1-phenylpiperidin-2-yl)phosphine oxide(3aq) (82%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.87 (m 2H), 7.67 (m, 2H), 7.57 – 7.44 (m, 3H), 7.33 (dd, *J* = 16.0, 8.5 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.07 (dd, *J* = 8.7, 7.2 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 3H), 4.64 (s, 1H), 4.12 – 3.91 (m, 1H), 3.56 (d, *J* = 13.3 Hz, 1H), 2.55 – 2.25 (m, 1H), 2.02 – 1.77 (m, 2H), 1.68 – 1.49 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 150.4 (d, *J* = 5.8 Hz), 133.0, 132.1 (d, *J* = 9.8 Hz), 131.5 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 2.7 Hz), 131.1, 131.0, 130.9, 130.8, 128.9, 128.7, 128.6, 128.1, 127.9, 118.0, 115.8, 56.5 (d, *J* = 77.2 Hz), 45.9, 23.9 (d, *J* = 4.2 Hz), 23.5, 21.0 (d, *J* = 1.6 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 33.63. **HRMS** calc. for $C_{23}H_{24}NOP$ [M+Na]$^+$, 384.1488; found, 384.1483.



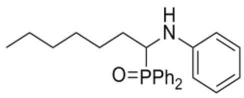
3ar

Diphenyl(1-phenylpyrrolidin-2-yl)phosphine oxide(3ar) (70%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.97 – 7.85 (m, 2H), 7.77 (dd, *J* = 17.1, 8.4 Hz, 2H), 7.45 (m, 4H), 7.35 – 7.24 (m, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.54 (t, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 8.2 Hz, 2H), 4.67 (t, *J* = 8.9 Hz, 1H), 3.60 (t, *J* = 8.3 Hz, 1H), 3.19 (m, 1H), 2.43 (dd, *J* = 18.7, 12.1 Hz, 1H), 2.22 – 2.02 (m, 1H), 2.01 – 1.78 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 147.6, 132.0, 131.9, 131.7 (d, *J* = 9.0 Hz), 131.7, 131.5 (d, *J* = 8.4 Hz), 131.0 (d, *J* = 21.5 Hz), 128.6, 128.4, 128.3, 128.1 (d, *J* = 11.0 Hz), 116.7, 113.1, 60.3 (d, *J* = 86.6 Hz), 50.7, 27.6, 24.0. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 27.50. **HRMS** calc. for $C_{22}H_{22}NOP$ [M+Na]$^+$, 370.1331; found, 370.1335.



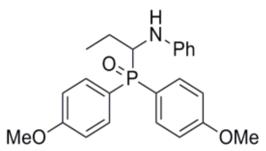
3as

(1-(2,6-diisopropylphenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3as) (55%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.59 (m, 2H), 7.36 (m, 5H), 7.24 (dd, *J* = 14.0, 6.5 Hz, 1H), 7.15 – 6.97 (m, 4H), 6.81 – 6.64 (m, 1H), 4.52 (m, 1H), 3.71 – 3.49 (m, 2H), 3.21 – 2.95 (m, 2H), 2.52 – 2.19 (m, 3H), 2.05 – 1.88 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.36 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 150.6, 146.4, 143.4, 131.1, 131.0, 130.9, 130.5, 130.4, 128.4, 128.3, 127.9, 127.8, 126.6, 124.4, 123.4, 62.7, 61.8, 56.9, 28.1, 28.0, 27.3, 26.7, 26.1, 25.7, 23.6, 21.6. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 28.39. **HRMS** calc. for $C_{28}H_{34}NOP$ $[M+Na]^+$,454.2270; found, 454.2274.



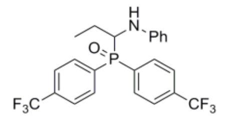
3ax

Diphenyl(1-(phenylamino)heptyl)phosphine oxide (3ax) (63%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.92 – 7.82 (m, 2H), 7.81 – 7.71 (m, 2H), 7.58 – 7.43 (m, 3H), 7.43 – 7.36 (m, 1H), 7.32 (m, 2H), 7.12 – 7.00 (m, 2H), 6.62 (dd, *J* = 17.9, 10.6 Hz, 1H), 6.50 (dd, *J* = 16.4, 5.4 Hz, 2H), 4.36 (d, *J* = 68.9 Hz, 1H), 4.08 (s, 1H), 2.00 – 1.79 (m, 1H), 1.79 – 1.57 (m, 1H), 1.57 – 1.42 (m, 1H), 1.27 (d, *J* = 9.1 Hz, 1H), 1.10 (m 6H), 0.78 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 147.1 (d, *J* = 6.6 Hz), 131.9 (d, *J* = 2.8 Hz), 131.8, 131.7 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 9.0 Hz), 131.2 (d, *J* = 8.9 Hz), 131.0, 129.1, 128.6 (d, *J* = 11.2 Hz), 128.3 (d, *J* = 11.3 Hz), 117.7, 113.1, 52.6 (d, *J* = 80.1 Hz), 31.4, 30.2 (d, *J* = 4.2 Hz), 29.0, 26.1 (d, *J* = 9.6 Hz), 22.4, 13.9. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 31.76. **HRMS** calc. for $C_{25}H_{30}NOP$ $[M+Na]^+$, 414.1957; found, 414.1963.



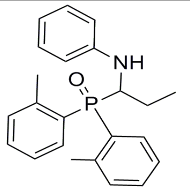
3ba

Bis(4-methoxyphenyl)(1-(phenylamino)propyl)phosphine oxide (3ba) (94%) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.77 (dd, *J* = 10.2, 8.8 Hz, 2H), 7.68 (dd, *J* = 10.2, 8.9 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 7.0 Hz, 2H), 6.85 (d, *J* = 7.1 Hz,2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.20 – 4.03 (m, 2H), 3.81 (s,3H), 3.74 (s, 3H), 2.11 – 1.84 (m, 1H), 1.75 – 1.43 (m, 1H), 0.90 (dt, *J* = 9.3, 7.0 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.2 (d, *J* = 2.7 Hz), 162.10 (d, *J* = 2.8 Hz), 147.2, 147.1, 133.1, 133.0, 132.9, 132.8, 129.1, 123.2 (d, *J* = 11.7 Hz), 122.2 (d, *J* = 8.8 Hz), 117.6, 114.1, 114.0, 113.9, 113.8, 113.1, 55.1, 55.1, 53.7 (d, *J* = 81.3 Hz), 23.3 (d, *J* = 4.2 Hz), 10.9 (d, *J* = 9.7 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 31.89. **HRMS** calc. for $C_{23}H_{26}NO_3P$ $[M+Na]^+$, 418.1543; found, 418.1540.



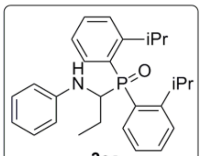
3ca

(1-(phenylamino)propyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ca) (52%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (dd, *J* = 19.0, 9.0 Hz, 2H), 7.91 (dd, *J* = 19.0, 8.7 Hz, 2H), 7.78 (t, *J* = 10.0 Hz, 2H), 7.59 (t, *J* = 13.8 Hz, 2H), 7.09 (t, *J* = 7.9 Hz, 2H), 6.68 (dd, *J* = 16.4, 9.1 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 4.45 – 4.24 (m, 1H), 4.23 – 3.99 (m, 1H), 2.08 – 1.86 (m, 1H), 1.81 – 1.57 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.8 (d, *J* = 6.9 Hz), 135.8 (d, *J* = 21.2 Hz), 134.9 (d, *J* = 26.6 Hz), 134.3, 134.0, 133.7, 131.8, 131.7, 131.6, 129.3, 125.7, 125.6, 125.4, 125.3, 124.7, 122.0, 118.7, 113.6, 54.2 (d, *J* = 80.8 Hz), 23.3 (d, *J* = 4.4 Hz), 10.8 (d, *J* = 10.3 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 29.51. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.31, -63.41. **HRMS** calc. for $C_{23}H_{20}F_6NOP$ $[M+Na]^+$, 494.1079; found, 494.1082.



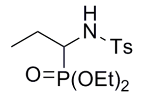
3da

(1-(phenylamino)propyl)di-o-tolylphosphine oxide (3da) (40%) White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (m, 1H), 7.66 – 7.55 (m, 1H), 7.45 – 7.38 (m, 1H), 7.35 – 7.26 (m, 2H), 7.17 (t, *J* = 7.9 Hz, 3H), 7.10 (dd, *J* = 11.1, 5.6 Hz, 2H), 6.75 – 6.63 (m, 3H), 4.59 (m, 1H), 4.54 – 4.39 (m, 1H), 2.26 (d, *J* = 6.3 Hz, 2H), 1.94 – 1.75 (m, 1H), 1.71 – 1.55 (m, 1H), 0.96 – 0.85 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.7 (d, *J* = 8.3 Hz), 142.5 (d, *J* = 7.7 Hz), 140.9, 132.9 (d, *J* = 9.4 Hz), 132.0, 131.9, 131.7 (d, *J* = 2.6 Hz), 131.6, 131.5 (d, *J* = 4.8 Hz), 131.4, 130.9, 130.0 (d, *J* = 5.6 Hz), 129.4, 129.2, 125.8 (d, *J* = 11.2 Hz), 125.5 (d, *J* = 11.7 Hz), 117.9, 117.6, 113.8, 113.1, 50.8 (d, *J* = 78.5 Hz), 23.3 (d, *J* = 4.9 Hz),, 21.2 (d, *J* = 3.9 Hz), 21.0 (d, *J* = 4.6 Hz), 10.8 (d, *J* = 8.6 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.59. **HRMS** calc. for $C_{23}H_{26}NOP$ $[M+Na]^+$, 386.1644; found, 386.1641.



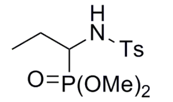
3ea

Bis(2-isopropylphenyl)(1-(phenylamino)propyl)phosphine oxide (3ea) (56%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 – 7.84 (m, 1H), 7.61 – 7.52 (m, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.41 – 7.27 (m, 4H), 7.20 (t, *J* = 7.9 Hz, 2H), 7.13 – 6.98 (m, 1H), 6.72 (m, 3H), 4.72 (dd, *J* = 10.4, 5.8 Hz, 1H), 4.55 – 4.35 (m, 1H), 3.57 (m, 1H), 3.43 – 3.20 (m, 1H), 1.93 – 1.75 (m, 1H), 1.65 (m, 1H), 1.16 (dd, *J* = 6.7, 4.8 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.70 (d, *J* = 6.6 Hz, 3H), 0.52 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.9 (d, *J* = 8.2 Hz), 151.8 (d, *J* = 10.1 Hz), 146.8 (d, *J* = 8.8 Hz), 132.5, 132.4, 132.1 (d, *J* = 2.6 Hz), 131.9 (d, *J* = 2.5 Hz), 131.2, 130.8, 130.5 (d, *J* = 11.2 Hz), 130.2, 129.9, 129.4, 127.5, 127.4, 126.7 (d, *J* = 10.4 Hz), 126.0, 125.9, 125.5 (d, *J* = 11.7 Hz), 117.6, 113.1, 51.2 (d, *J* = 79.1 Hz), 30.9 (d, *J* = 5.2 Hz), 24.3, 23.8, 23.4, 23.3, 23.2, 22.8, 10.6 (d, *J* = 8.5 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.66. **HRMS** calc. for $C_{27}H_{34}NOP$ $[M+Na]^+$, 442.2270; found, 442.2266.



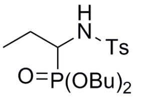
6aa

diethyl (1-(4-methylphenylsulfonamido)propyl)phosphonate (6aa) (91%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.16 – 5.82 (m, 1H), 4.15 – 3.88 (m, 4H), 3.61 (m, 1H), 2.41 (s, 3H), 1.88 – 1.66 (m, 1H), 1.62 – 1.42 (m, 1H), 1.26 (m, 6H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.0, 138.7, 129.3, 126.9, 63.1, 63.1, 62.3, 62.2, 51.5 (d, *J* = 147.2 Hz), 23.6, 23.6, 21.4, 16.3, 16.3, 16.2, 10.3, 10.2. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 23.54. **MS : m/z (M+H)**: 350.1766.



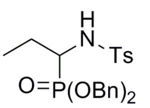
6ab

dimethyl (1-(4-methylphenylsulfonamido)propyl)phosphonate (6ab) (70%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.17 (m, 2H), 5.48 (d, *J* = 6.6 Hz, 1H), 3.63 (m, 7H), 2.42 (s, 3H), 1.81 – 1.68 (m, 1H), 1.64 – 1.48 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.3, 138.4, 129.5, 127.0, 53.6, 53.5, 52.9 (d, *J* = 7.0 Hz), 51.2 (d, *J* = 157.3 Hz), 23.8, 23.8, 21.5, 10.2 (d, *J* = 10.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 26.03. **MS : m/z (M+H)**: 322.1411.



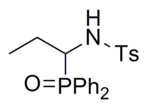
6ac

dibutyl (1-(4-methylphenylsulfonamido)propyl)phosphonate (6ac) (67%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.81 (dd, *J* = 9.4, 2.9 Hz, 1H), 4.11 – 3.82 (m, 4H), 3.76 – 3.49 (m, 1H), 2.41 (s, 3H), 1.75 (m, 1H), 1.69 – 1.50 (m, 5H), 1.34 (m, 2H), 0.98 – 0.73 (m, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.0, 138.7, 129.4, 126.9, 66.8 (d, *J* = 7.4 Hz), 66.0 (d, *J* = 7.3 Hz), 51.6 (d, *J* = 157.4 Hz), 32.5 (d, *J* = 5.5 Hz), 32.4 (d, *J* = 5.8 Hz), 23.81(d, *J* = 3.0 Hz), 21.40, 18.6 (d, *J* = 2.5 Hz), 13.5(d, *J* = 2.8 Hz), 10.2 (d, *J* = 9.6 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 23.56. **MS : m/z (M+H)**: 406.2437.



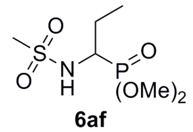
6ad

dibenzyl (1-(4-methylphenylsulfonamido)propyl)phosphonate (6ad) (86%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.28 (m, 6H), 7.24 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.87 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.07 – 4.72 (m, 4H), 3.85 – 3.58 (m, 1H), 2.34 (s, 3H), 1.78 (m, 1H), 1.67 – 1.47 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.1, 138.5, 136.1, 136.0, 135.8, 129.4, 128.6, 128.51, 128.5, 128.4, 128.1, 128.0, 127.0, 68.4 (d, *J* = 7.3 Hz), 67.8 (d, *J* = 7.1 Hz), 51.9 (d, *J* = 157.4 Hz), 23.8, 21.4, 10.2 (d, *J* = 10.5 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 24.67. **MS : m/z (M+H)**: 474.2138.



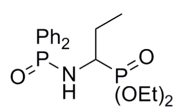
6ae

***N*-(1-(diphenylphosphoryl)propyl)-4-methylbenzenesulfonamide (6ae)** (65%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 – 7.69 (m, 4H), 7.64 – 7.40 (m, 7H), 7.30 (t, *J* = 14.2 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 4.39 (d, *J* = 8.4 Hz, 1H), 2.33 (s, 3H), 1.62 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.34, 139.26, 131.95, 131.92, 131.73, 131.60, 131.57, 131.3 (d, *J* = 9.1 Hz), 131.1, 130.9 (d, *J* = 9.0 Hz), 130.8, 130.2, 129.1, 128.7 (d, *J* = 11.4 Hz), 128.4 (d, *J* = 11.8 Hz), 126.64, 53.9 (d, *J* = 79.4 Hz), 23.0 (d, *J* = 3.9 Hz), 21.39, 10.8 (d, *J* = 9.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.11. **MS : m/z (M+H)**: 414.1887.



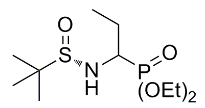
6af

diethyl (1-(methylsulfonamido)propyl)phosphonate (6af) (90%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.17 (d, *J* = 7.6 Hz, 1H), 4.31 – 4.06 (m, 4H), 3.78 – 3.56 (m, 1H), 3.07 (s, 3H), 1.92 (m, 1H), 1.64 (m, 1H), 1.36 (m, 6H), 1.10 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 62.8 (d, *J* = 7.1 Hz), 62.6 (d, *J* = 7.0 Hz), 52.0 (d, *J* = 157.8 Hz), 42.3, 24.01, 23.98, 16.49, 16.45, 16.43, 16.40, 10.4 (d, *J* = 11.7 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 23.91. **MS : m/z (M+H)**: 274.1386.



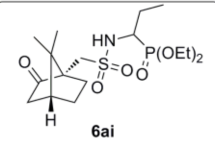
6ag

diethyl (1-((diphenylphosphoryl)amino)propyl)phosphonate (6ag) (87%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 – 7.80 (m, 4H), 7.58 – 7.36 (m, 6H), 4.23 – 4.00 (m, 4H), 3.55 – 3.25 (m, 2H), 1.91 (m, 1H), 1.81 – 1.66 (m, 1H), 1.30 (m, 6H), 1.06 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 133.6, 132.4 (d, *J* = 9.9 Hz), 132.3, 131.9, 131.8, 131.7, 131.0, 128.4 (d, *J* = 5.6 Hz), 128.3 (d, *J* = 5.7 Hz), 62.3 (d, *J* = 7.2 Hz), 62.2 (d, *J* = 7.0 Hz), 49.8, 48.3, 25.6, 16.4 (d, *J* = 3.0 Hz), 16.3 (d, *J* = 3.0 Hz), 10.2 (d, *J* = 8.8 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 26.22, 26.04, 24.00, 23.82. **MS : m/z (M+H)**: 396.2126.



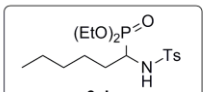
6ah

diethyl (1-((S)-1,1-dimethylethylsulfinamido)propyl)phosphonate (6ah) (82%) (d. r. = 1.0 : 1.0) colourless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.30 – 4.03 (m, 8H), 3.80 (t, *J* = 7.6 Hz, 1H), 3.42 (m 3H), 2.04 (m, 1H), 1.90 (m, 1H), 1.76 (m, 2H), 1.39 – 1.29 (m, 12H), 1.25 (s, 18H), 1.14 (t, *J* = 7.4 Hz, 3H), 1.09 – 1.01 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 63.0, 62.9, 62.3 (d, *J* = 7.0 Hz), 62.2, 62.1 (d, *J* = 2.1 Hz), 56.6, 56.5, 56.4, 54.9, 53.3 (d, *J* = 150.7 Hz), 24.6 (d, *J* = 2.6 Hz), 24.3, 22.5, 22.4, 16.4,16.3 (d, *J* = 5.8 Hz), 16.2 (d, *J* = 5.4 Hz), 16.2, 10.6 (d, *J* = 9.7 Hz), 10.5 (d, *J* = 10.9 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 25.43, 24.56, (d. r. = 1.0 : 1.0). **MS : m/z (M+H)**: 300.1921.



6ai

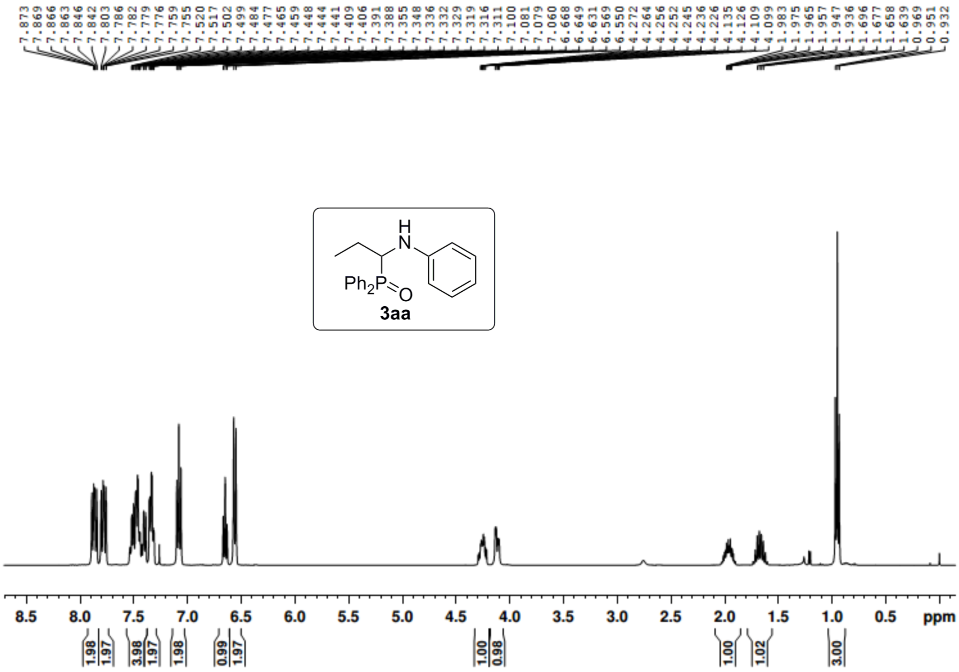
Diethyl (1-(((1S,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methylsulfon-amido)propyl)phosphonate (6ai) (74%) (d. r. = 1.0 : 0.8) colourless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.03 (dd, *J* = 9.8, 4.4 Hz, 1H), 5.50 (dd, *J* = 9.6, 2.7 Hz, 0.80H), 4.28 – 4.05 (m, 7.4H), 3.95 (d, *J* = 15.0 Hz, 1H), 3.77 (m, 1.85H), 3.60 (d, *J* = 15.0 Hz, 1H), 3.18 – 2.97 (m, 0.83H), 2.47 – 2.28 (m, 1.84H), 2.21 – 1.99 (m, 2.82H), 1.98 – 1.79 (m, 7.30H), 1.78 – 1.53 (m, 4.57H), 1.50 – 1.39 (m, 1.96H), 1.35 (m, 1.97H), 1.10 (m, 11H), 1.03 (s, 3H), 0.96 (s, 3H), 0.92 (d, *J* = 7.0 Hz, 2.49H). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 24.37, 23.87, (d. r. = 1.0 : 0.8).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (dd, *J* = 9.7, 4.4 Hz, 1H), 4.25 – 4.08 (m, 4H), 3.96 (d, *J* = 15.0 Hz, 1H), 3.84 – 3.68 (m, 1H), 3.09 (d, *J* = 15.0 Hz, 1H), 2.40 (d, *J* = 19.2 Hz, 1H), 2.20 – 1.98 (m, 4H), 1.96 – 1.85 (m, 2H), 1.69 – 1.53 (m, 1H), 1.45 (m, 1H), 1.34 (m, 6H), 1.10 (t, *J* = 7.3 Hz, 3H), 1.02 (s, 3H), 0.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 216.4, 62.4 (d, *J* = 6.9 Hz), 59.73, 53.13, 52.96, 51.61, 48.72, 42.9 (d, *J* = 13.7 Hz), 27.5, 27.0, 24.5 (d, *J* = 2.9 Hz), 20.05, 19.51, 16.4 (dd, *J* = 5.7, 2.6 Hz), 10.5 (d, *J* = 11.8 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 24.38, (d. r. > 20 : 1). **MS : m/z (M+H)**: 410.1945.



6aj

Diethyl (1-(4-methylphenylsulfonamido)hex-2-en-1-yl)phosphonate (6aj) (18%) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 5.46 (dd, *J* = 9.5, 3.2 Hz, 1H), 4.21 – 3.92 (m, 4H), 3.72 – 3.52 (m, 1H), 2.41 (s, 3H), 1.68 (m, 1H), 1.56 – 1.42 (m, 1H), 1.26 (m, 7H), 1.13 (d, *J* = 7.2 Hz, 5H), 0.80 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.21, 138.57, 129.42, 127.03, 63.1 (d, *J* = 7.2 Hz), 62.4 (d, *J* = 7.0 Hz), 51.2, 49.6, 31.3, 30.6 (d, *J* = 3.0 Hz), 25.2 (d, *J* = 9.7 Hz), 22.2, 21.4, 16.3 (dd, *J* = 9.1, 5.7 Hz), 13.83. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 23.73. **MS : m/z (M+H)**: 392.1817.

10. Copies of NMR spectra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H
N
Ph2P=O
3aa
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 ppm
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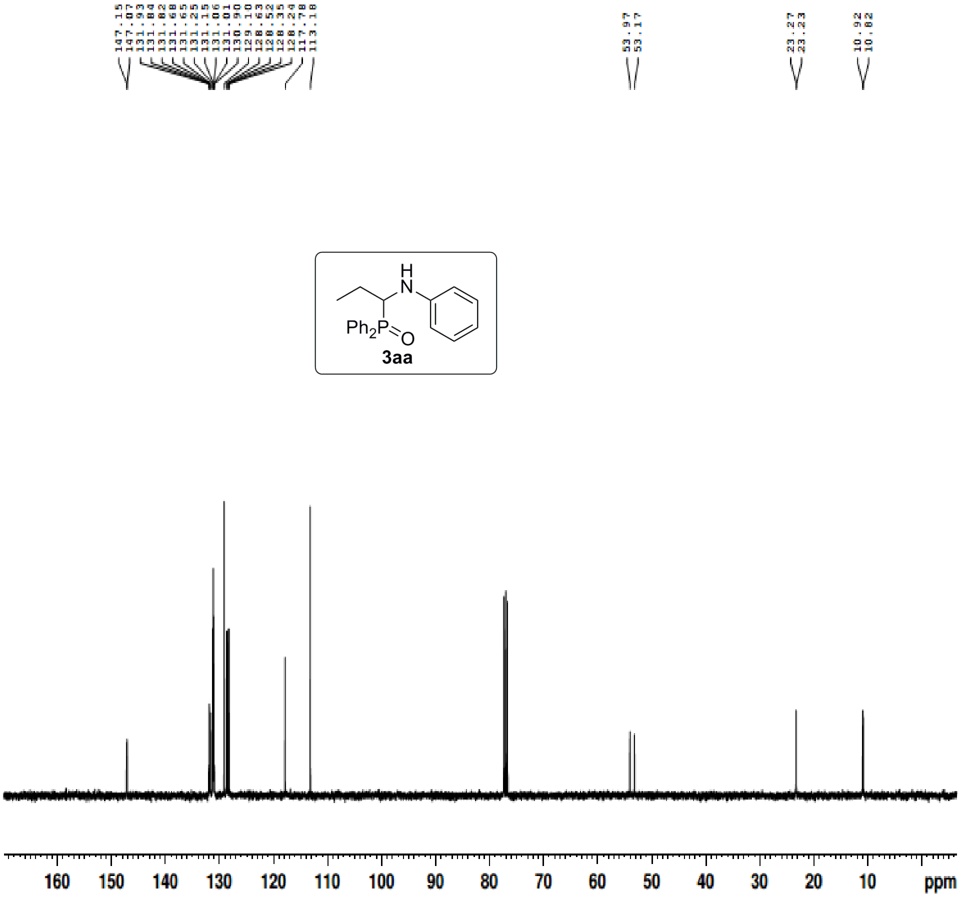
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N
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3aa
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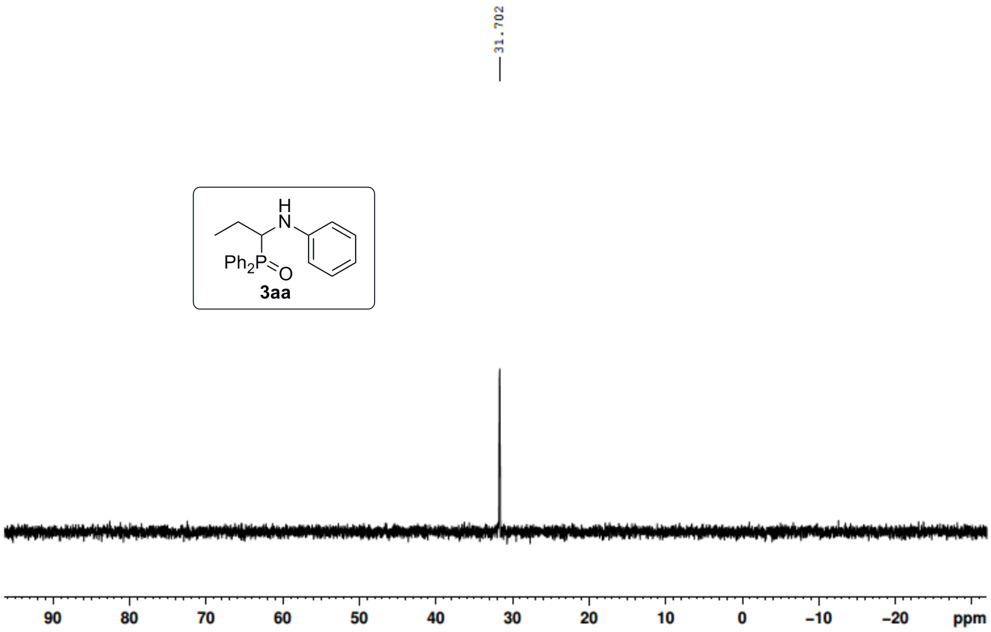
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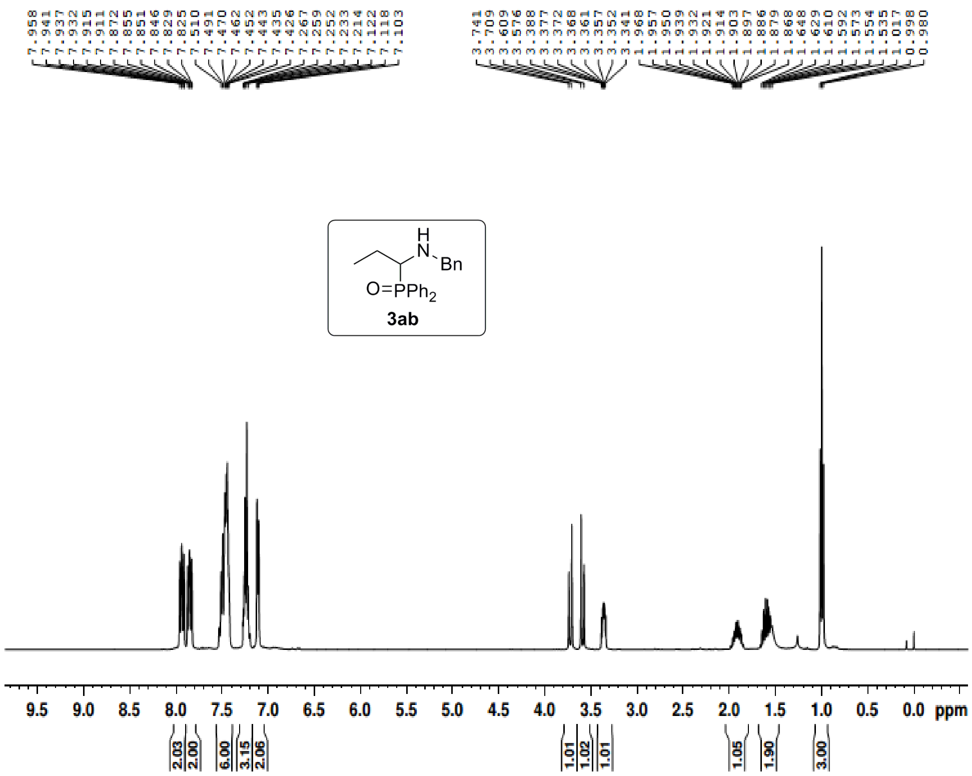
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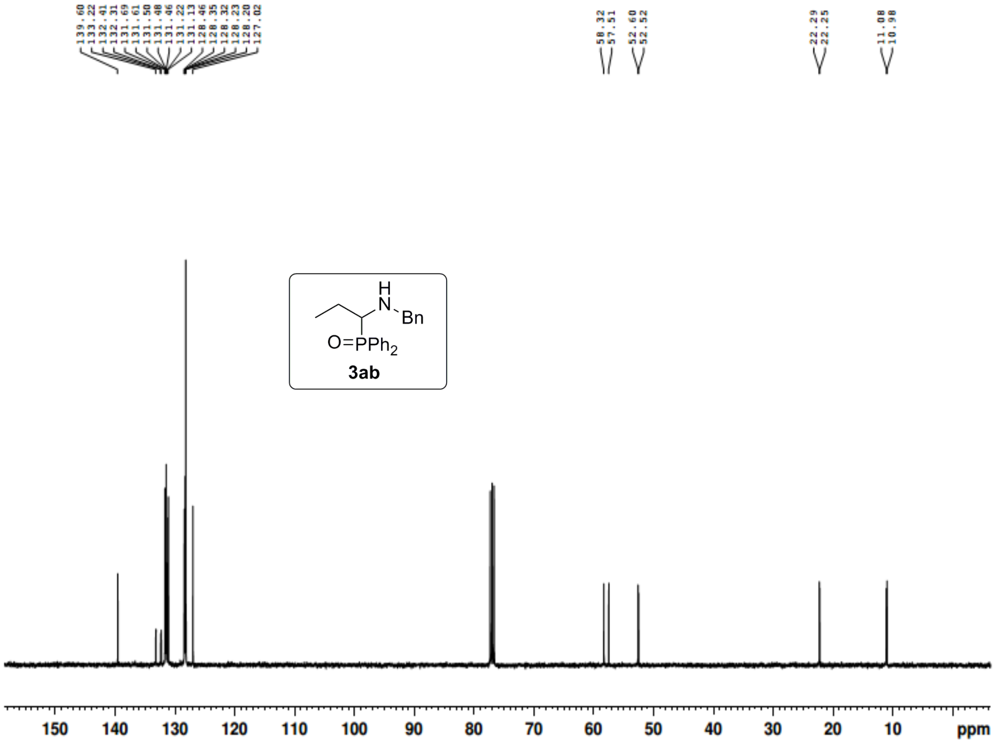
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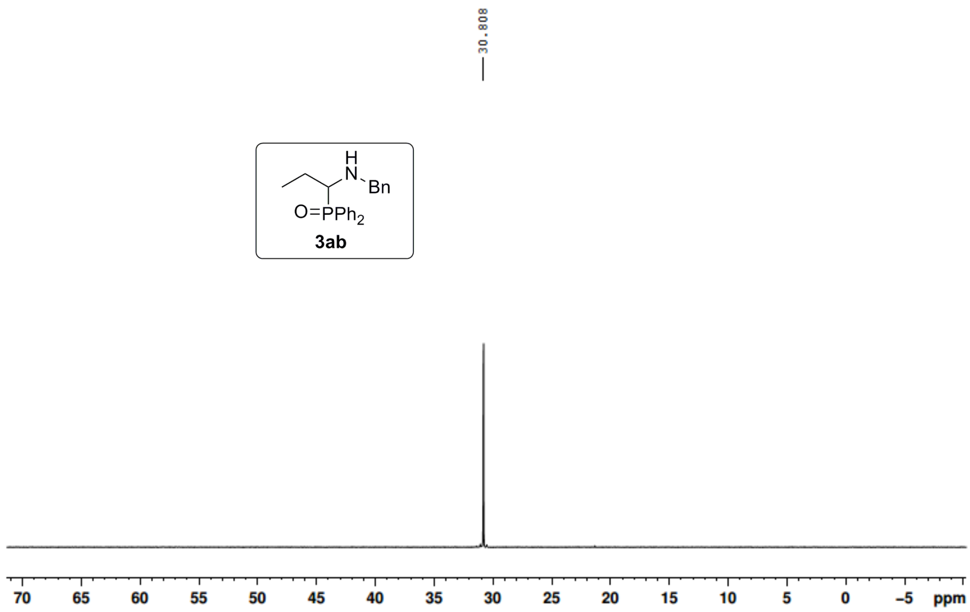
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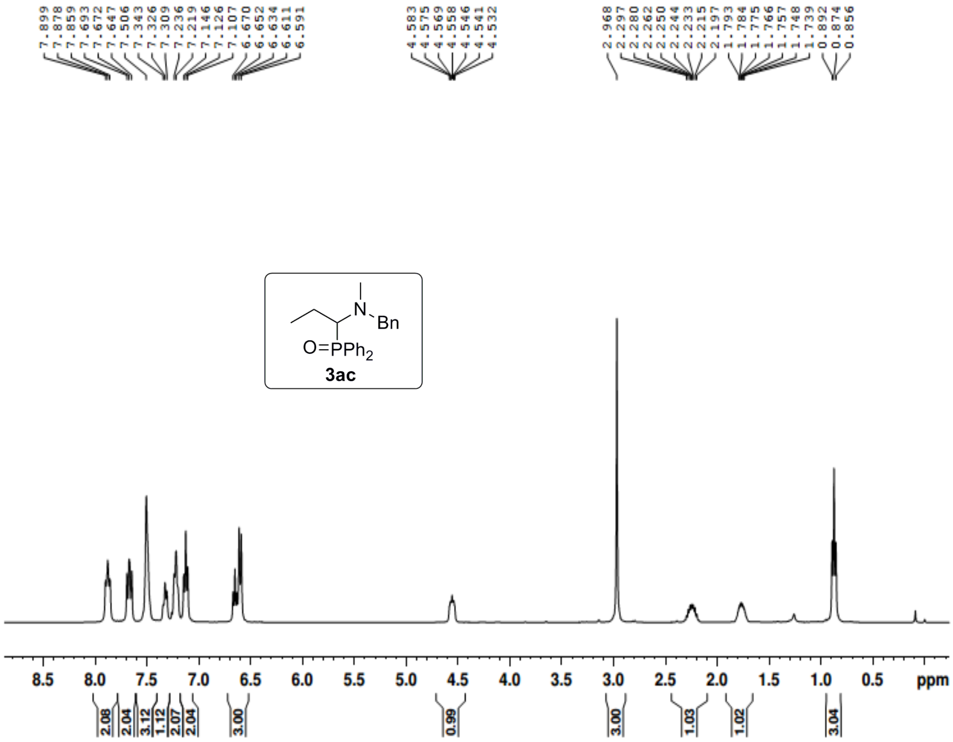

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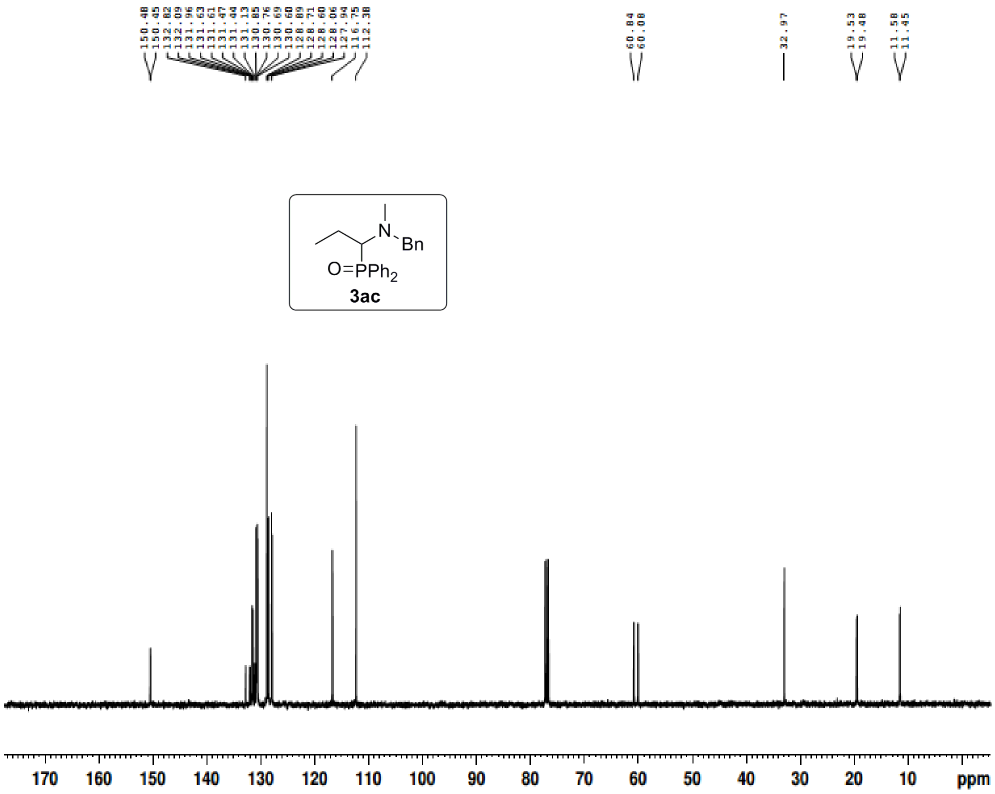
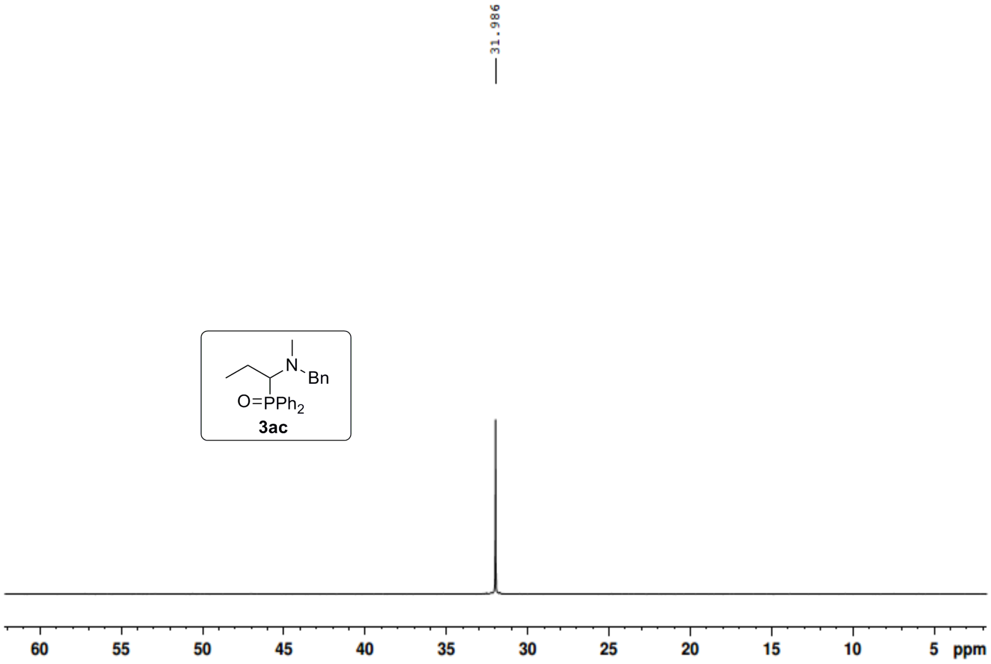
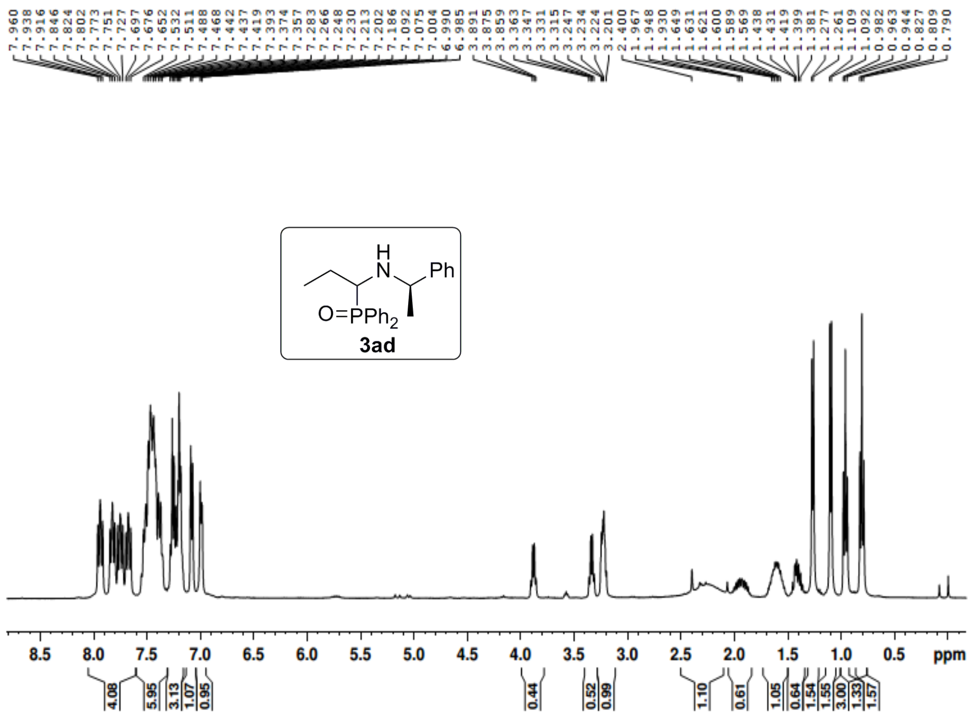
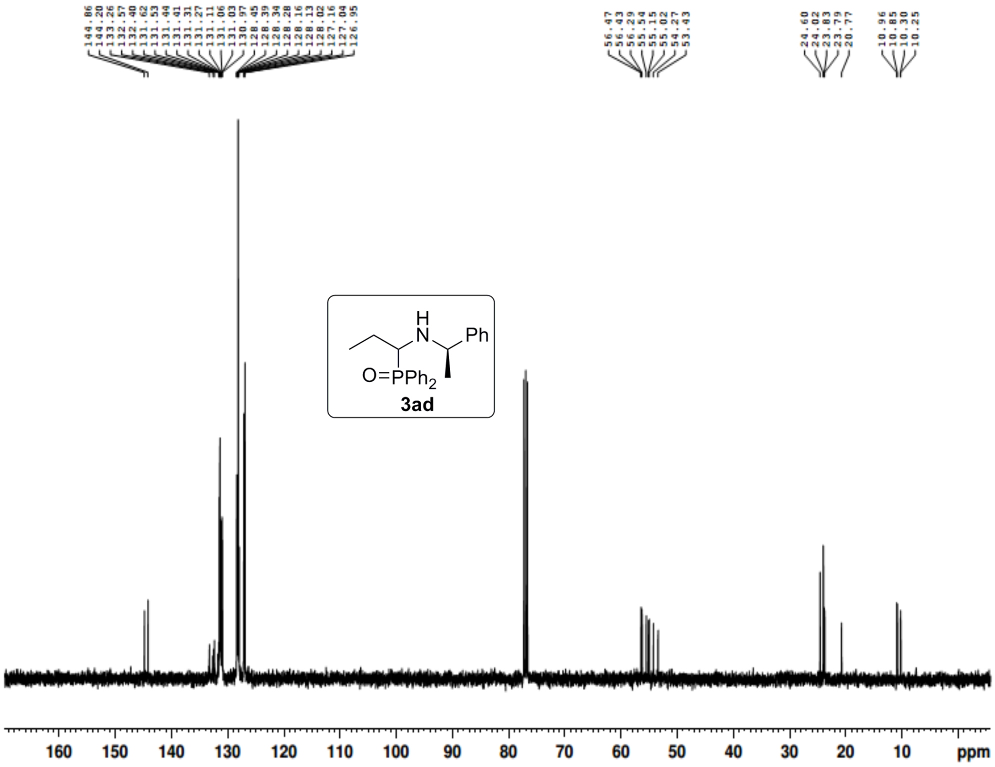
4.583 4.575 4.569 4.558 4.546 4.541 4.532
2.968 2.297 2.280 2.262 2.250 2.244 2.233 2.215 2.197 1.793 1.784 1.775 1.766 1.757 1.748 1.739 0.892 0.874 0.856
N
Bn
O=PPh2
3ac
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.08 2.04 3.12 1.12 2.07 2.04 3.00 0.99 3.00 1.03 1.02 3.04

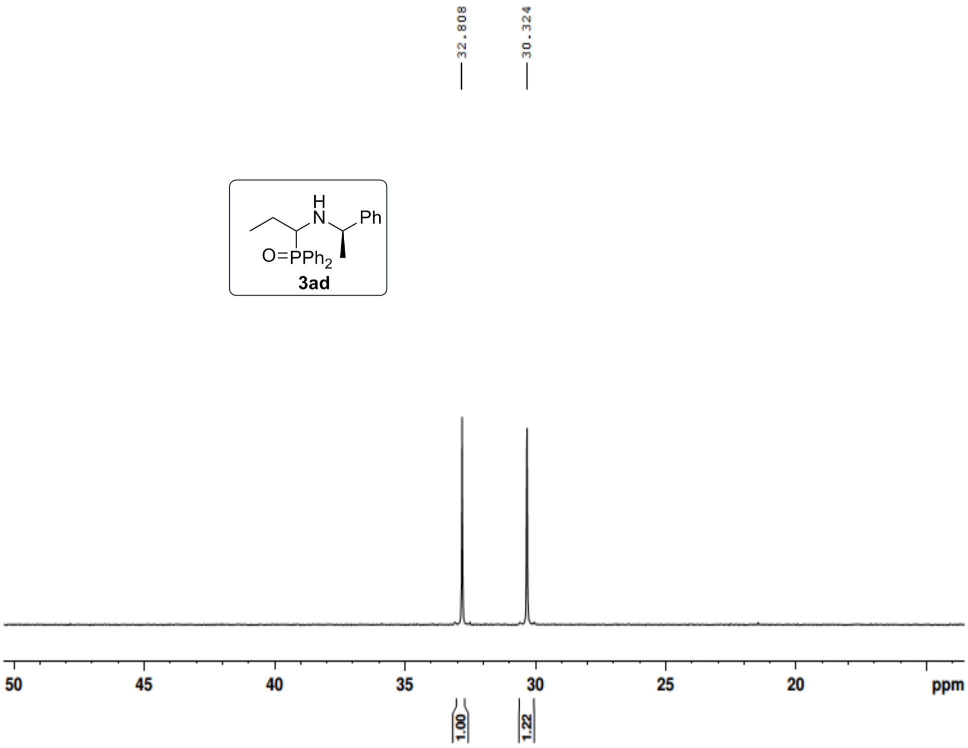


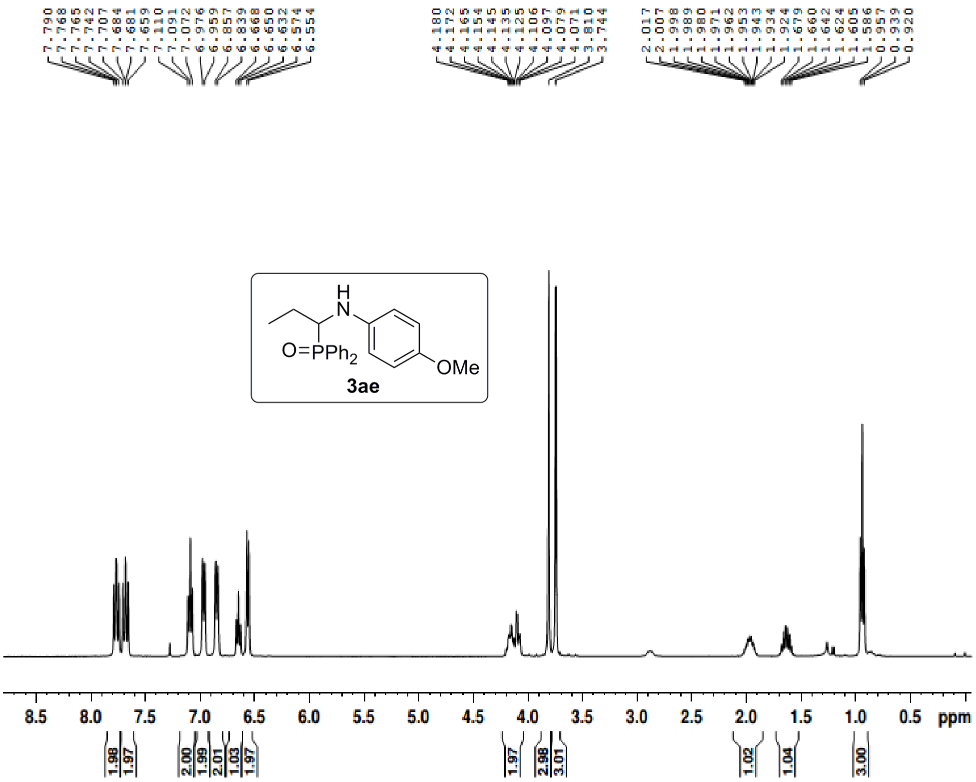
150.48 150.45 132.02 132.09 131.96 131.63 131.61 131.47 131.44 131.13 130.85 130.76 130.69 130.60 128.89 128.71 128.60 128.06 127.94 116.75 112.38
60.84 60.00
32.97
19.53 19.48
11.58 11.45
N
Bn
O=PPh2
3ac
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

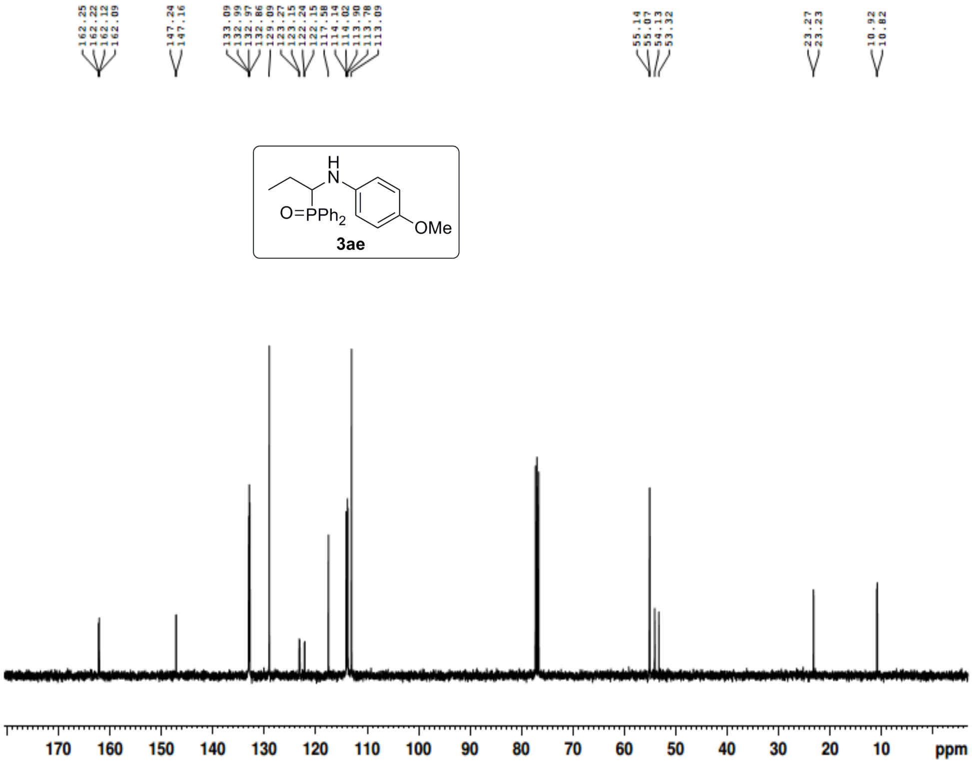

31.986
N
Bn
O=PPh2
3ac
ppm

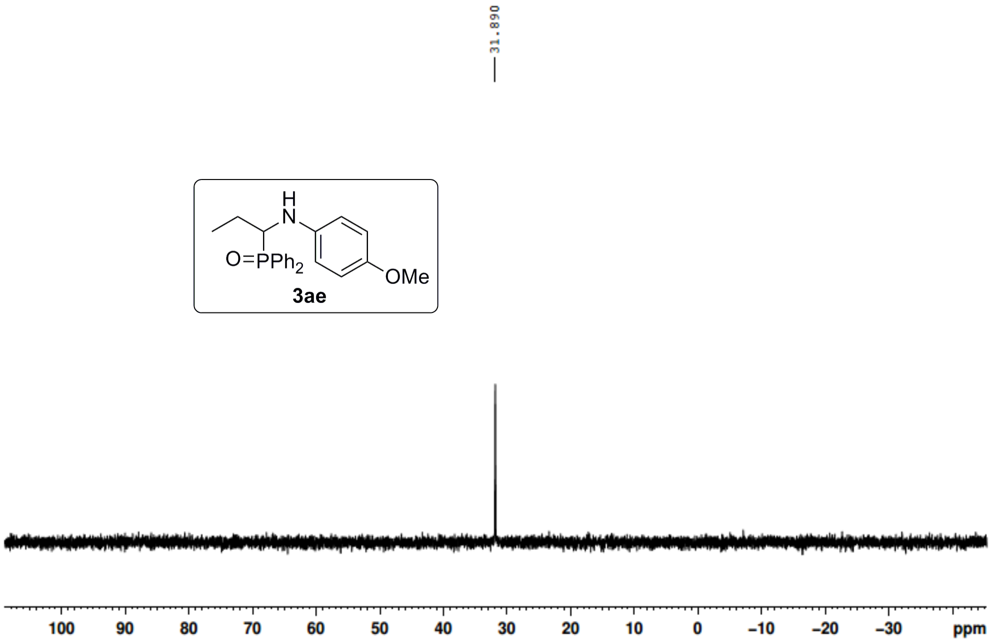

H
N
Ph
O=PPh2
3ad
ppm

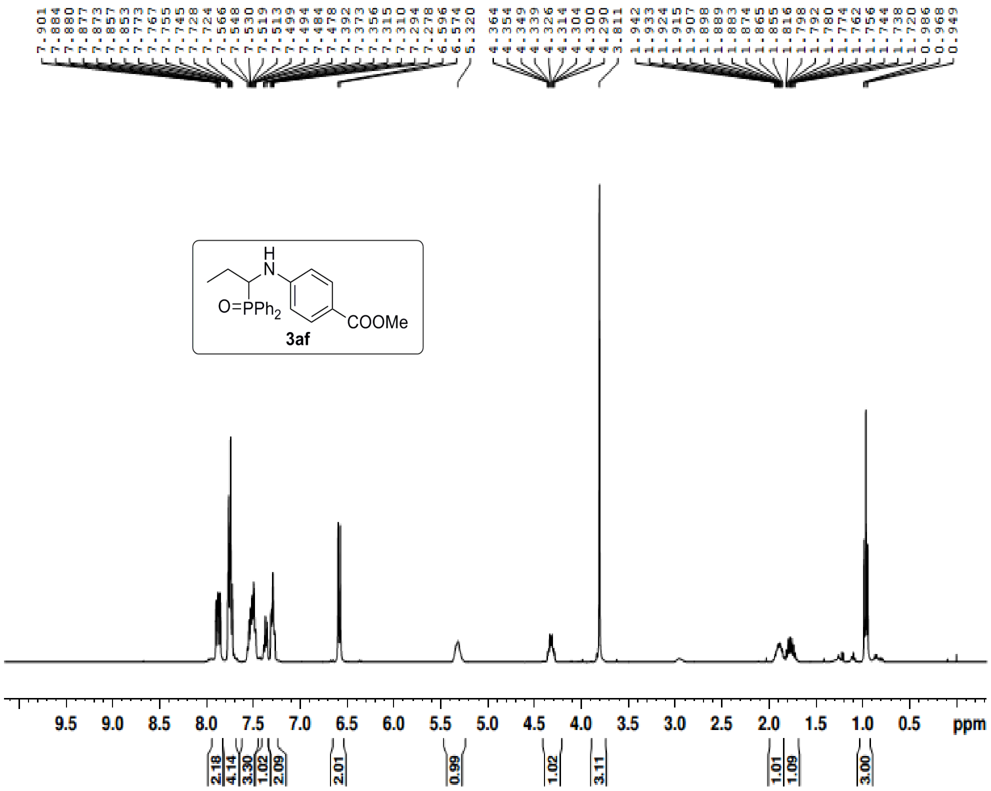

H
N
Ph
O=PPh2
3ad
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

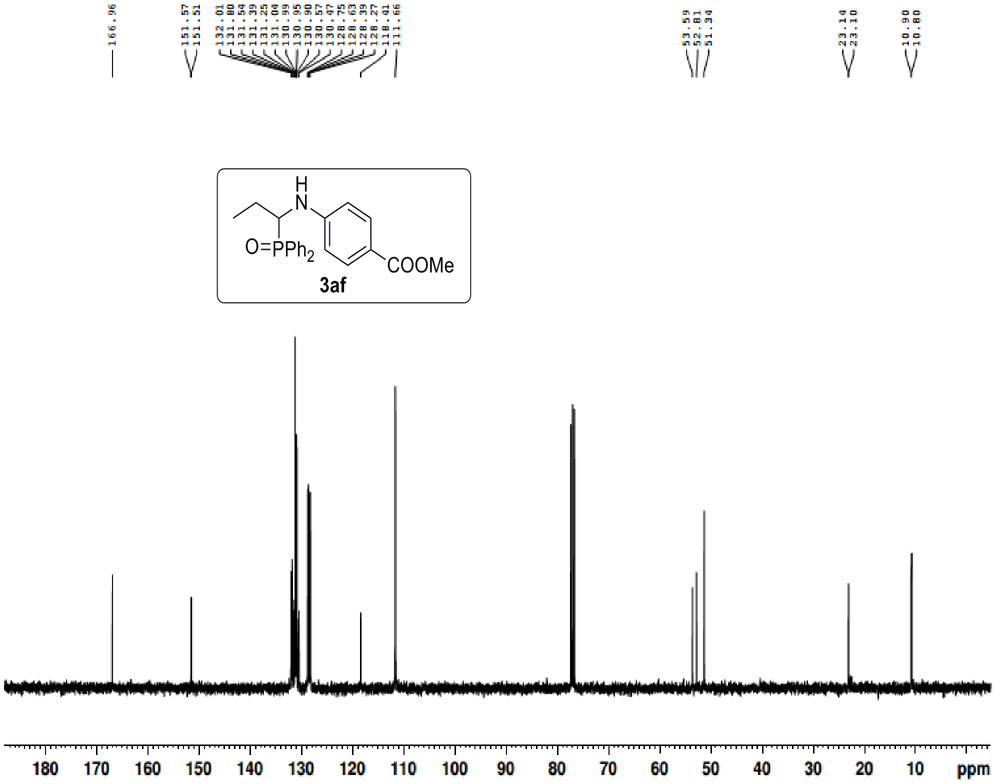

32.808
30.324
H
N
Ph
O=PPh2
3ad
50 45 40 35 30 25 20 ppm
1.00
1.22

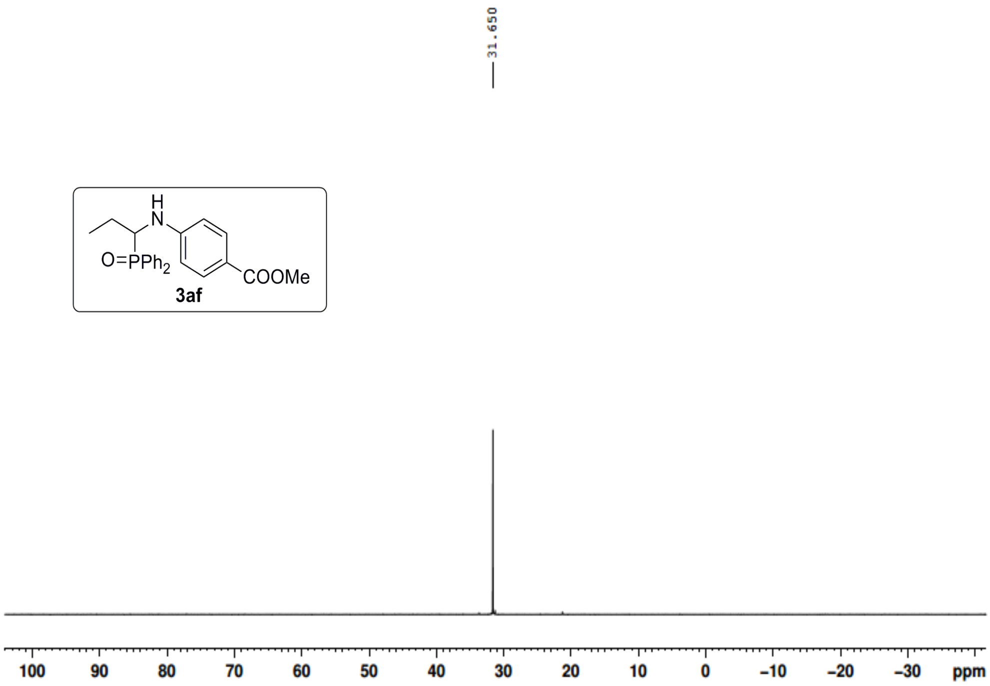

7.790 7.768 7.765 7.742 7.707 7.684 7.681 7.659 7.110 7.091 7.072 6.976 6.959 6.857 6.839 6.668 6.650 6.632 6.574 6.554
4.180 4.172 4.165 4.154 4.145 4.135 4.125 4.106 4.097 4.079 4.071 3.810 3.744
2.017 2.007 1.998 1.989 1.980 1.971 1.962 1.953 1.943 1.934 1.924 1.679 1.660 1.642 1.624 1.605 1.586 0.957 0.939 0.920
H
N
O=PPh2
OMe
3ae
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 ppm
1.98 1.97 2.00 1.99 2.01 1.03 1.97 1.97 2.98 3.01 1.02 1.04 3.00

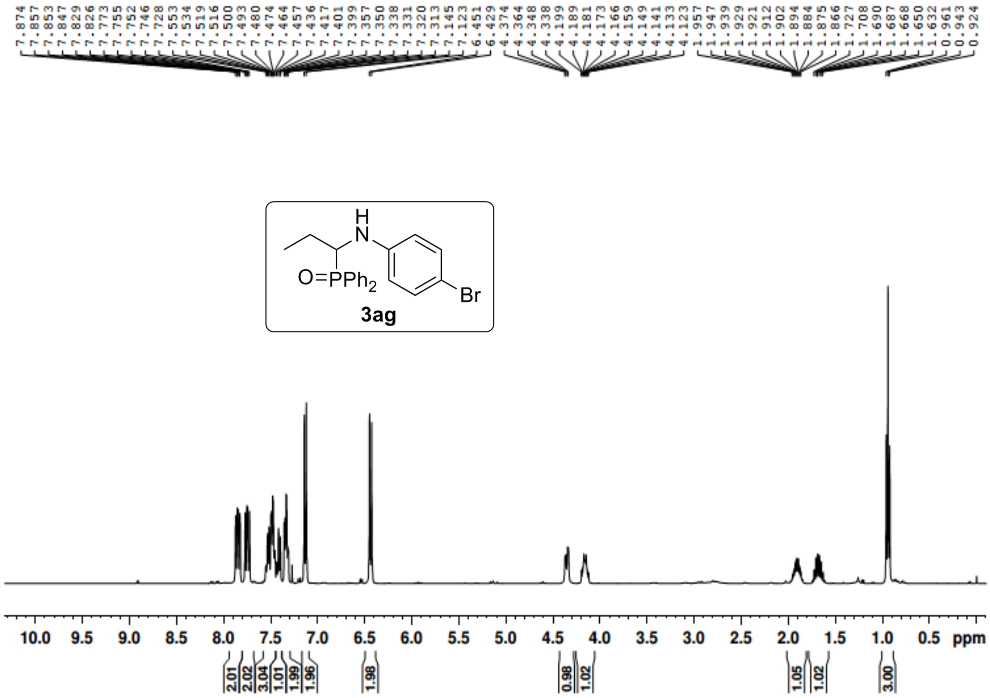

162.25 162.22 162.12 162.09
147.24 147.16
133.09 132.99 132.97 132.86 129.09 123.27 123.15 122.24 122.15 117.58 114.14 114.02 113.90 113.78 113.09
55.14 55.07 54.13 53.32
23.27 23.23
10.92 10.82
H
N
O=PPh2
OMe
3ae
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

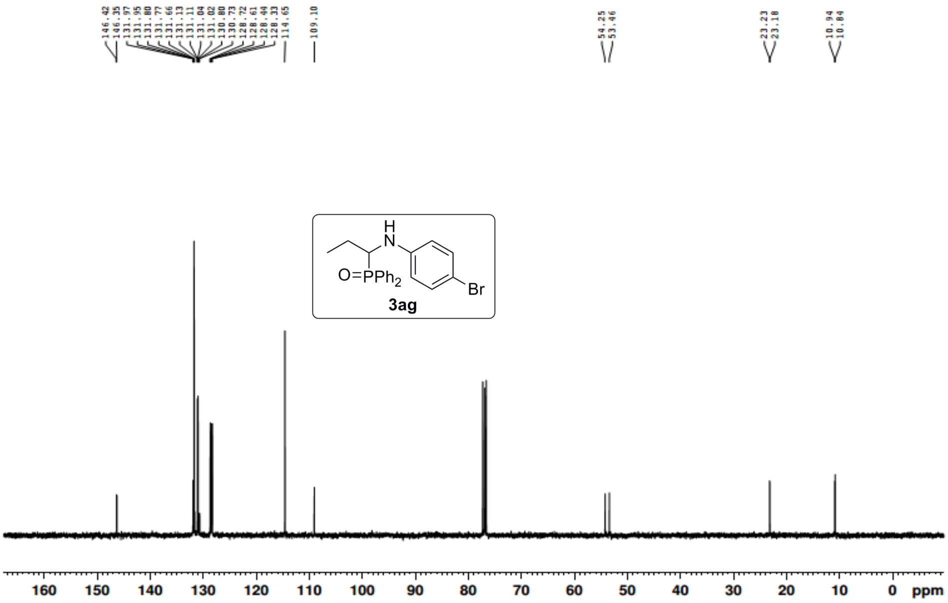

31.890
H
N
O=PPh2
OMe
3ae
100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 ppm

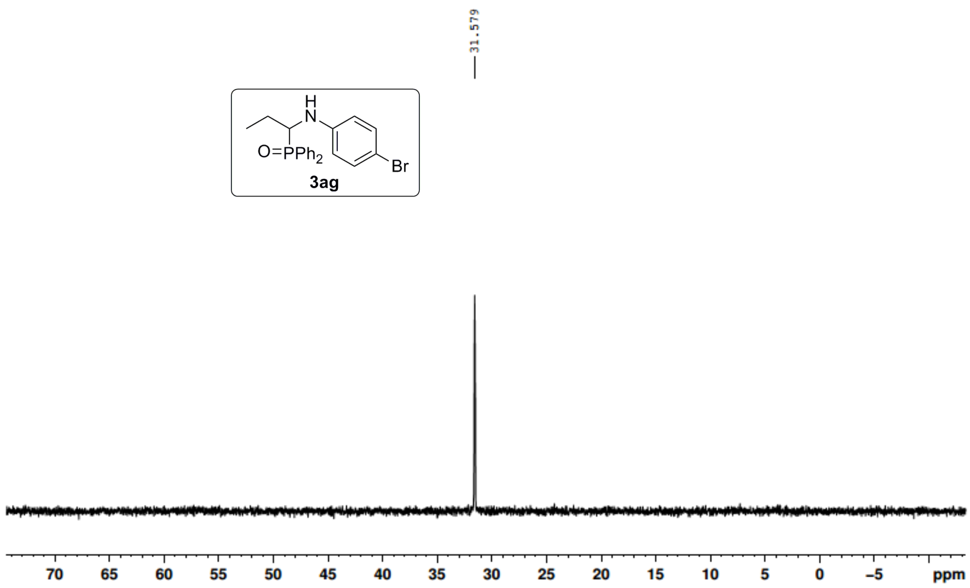

7.901 7.884 7.880 7.877 7.873 7.857 7.853 7.773 7.767 7.755 7.745 7.728 7.724 7.566 7.548 7.530 7.519 7.513 7.499 7.494 7.484 7.478 7.392 7.373 7.356 7.315 7.310 7.294 7.278 6.596 6.574 5.320
4.364 4.354 4.349 4.339 4.326 4.314 4.304 4.300 4.290 3.811
1.942 1.933 1.924 1.915 1.907 1.898 1.889 1.883 1.874 1.865 1.855 1.816 1.798 1.792 1.780 1.774 1.762 1.756 1.744 1.738 1.720 0.986 0.968 0.949
H
N
O=PPh2
COOMe
3af
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.18 4.14 3.30 1.02 2.09 2.01 0.99 1.02 3.11 1.01 1.09 3.00

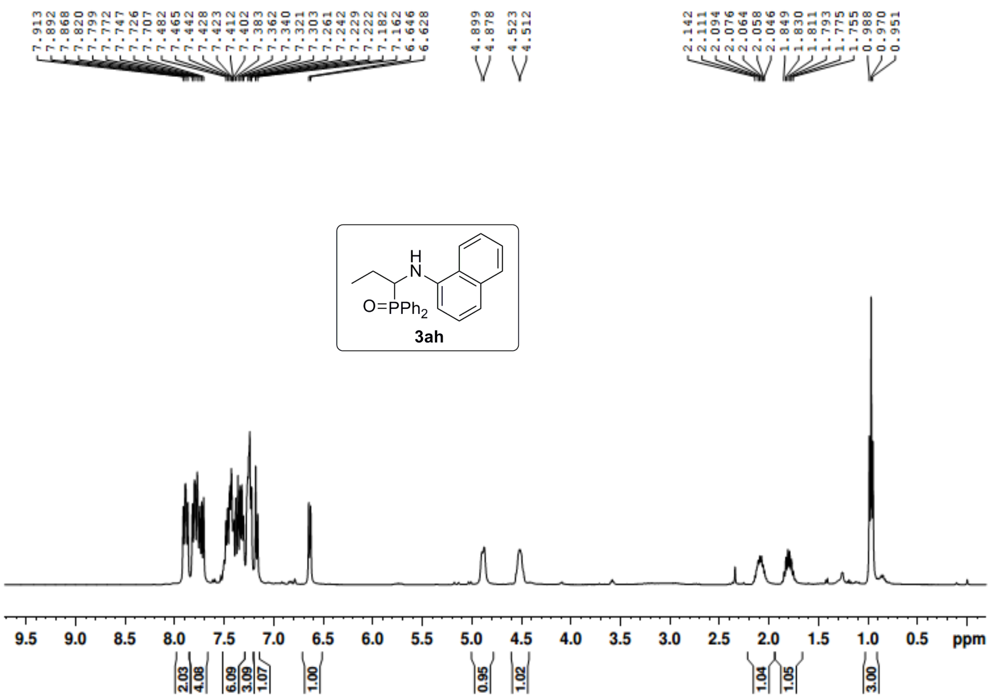

166.96
151.57
151.51
132.01
131.80
131.54
131.39
131.25
131.04
130.99
130.95
130.90
130.57
130.47
128.75
128.63
128.39
128.27
118.41
111.66
53.59
52.81
51.34
23.14
23.10
10.90
10.80
O=PPh2
COOMe
3af
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

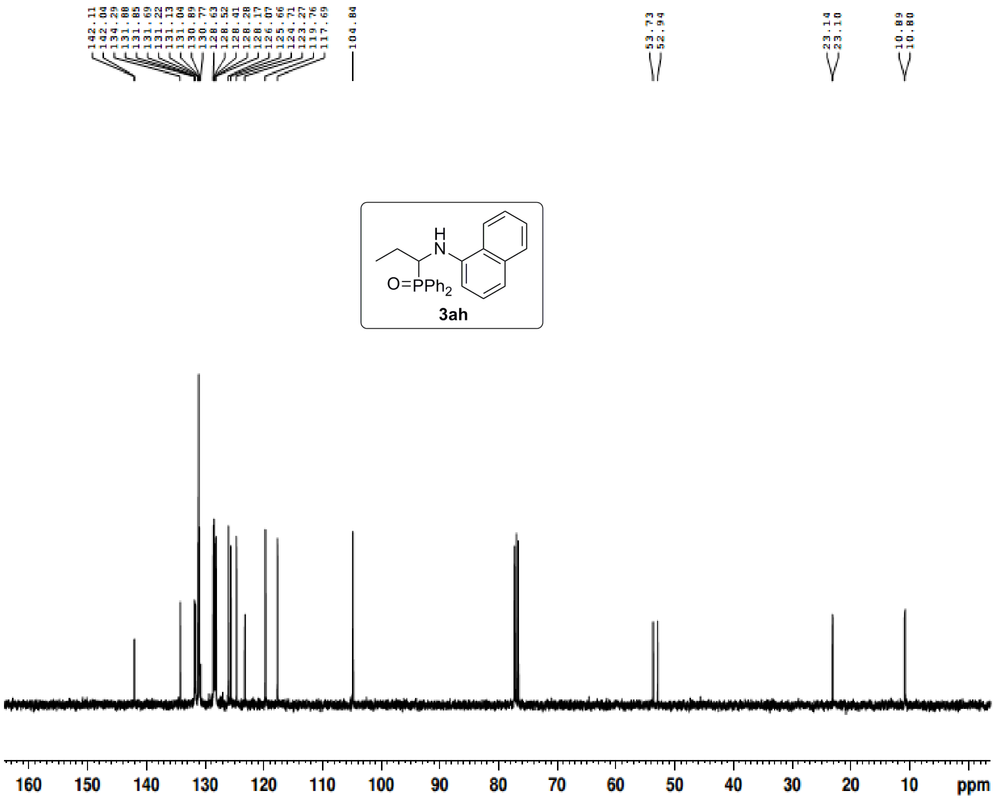

31.650
O=PPh2
COOMe
3af
100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 ppm

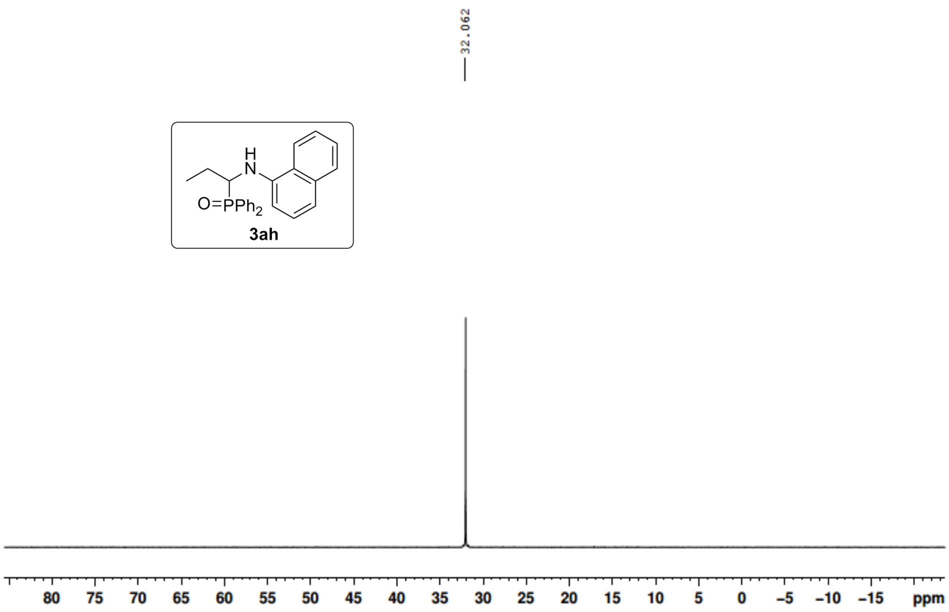

O=PPh2
Br
3ag
ppm

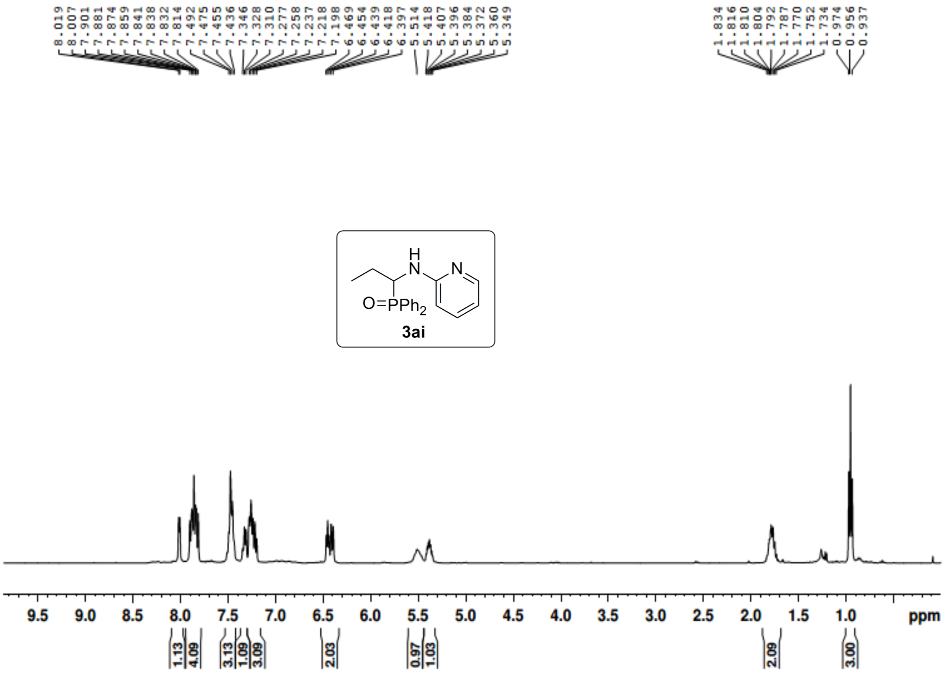

O=PPh2
Br
3ag
ppm

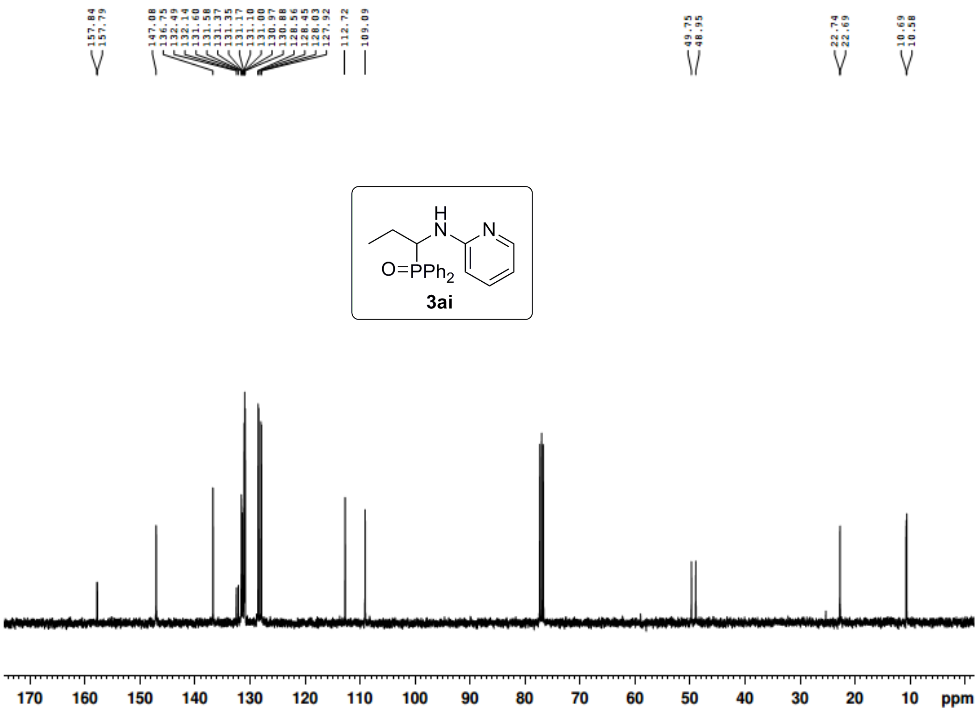

31.579
H
N
O=PPh2
Br
3ag
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
–5
ppm

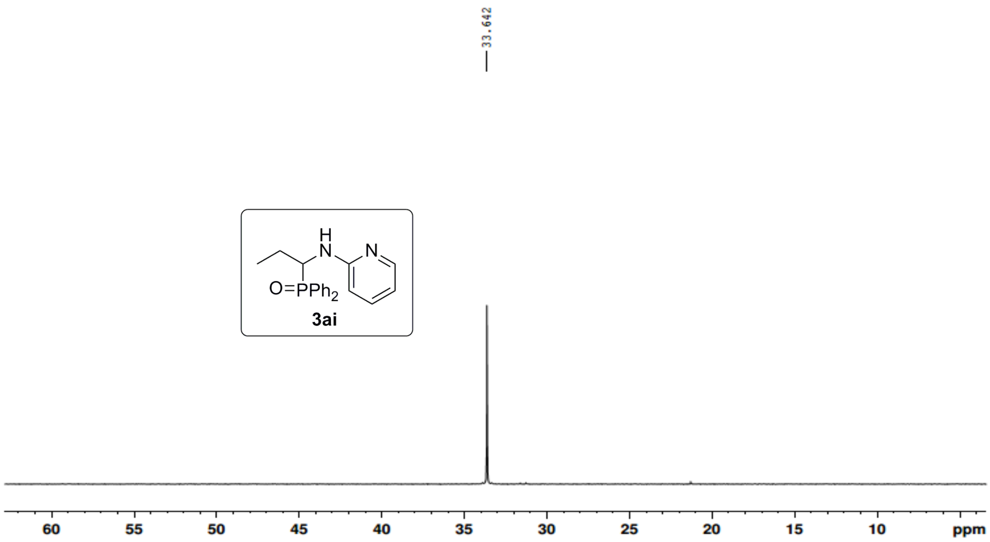

7.913
7.892
7.868
7.820
7.799
7.772
7.747
7.726
7.707
7.482
7.465
7.442
7.428
7.423
7.412
7.402
7.383
7.362
7.340
7.321
7.303
7.261
7.242
7.229
7.222
7.182
7.162
6.646
6.628
4.899
4.878
4.523
4.512
2.142
2.111
2.094
2.076
2.064
2.058
2.046
1.849
1.830
1.811
1.793
1.775
1.755
0.988
0.970
0.951
H
N
O=PPh2
3ah
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
4.08
6.09
3.09
1.07
1.00
0.95
1.02
1.04
1.05
3.00


142.11
142.04
134.29
131.88
131.85
131.69
131.22
131.13
131.04
130.89
130.77
128.63
128.52
128.41
128.28
128.17
126.07
125.66
124.71
123.27
119.76
117.69
104.84
53.73
52.94
23.14
23.10
10.89
10.80
O=PPh2
3ah
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

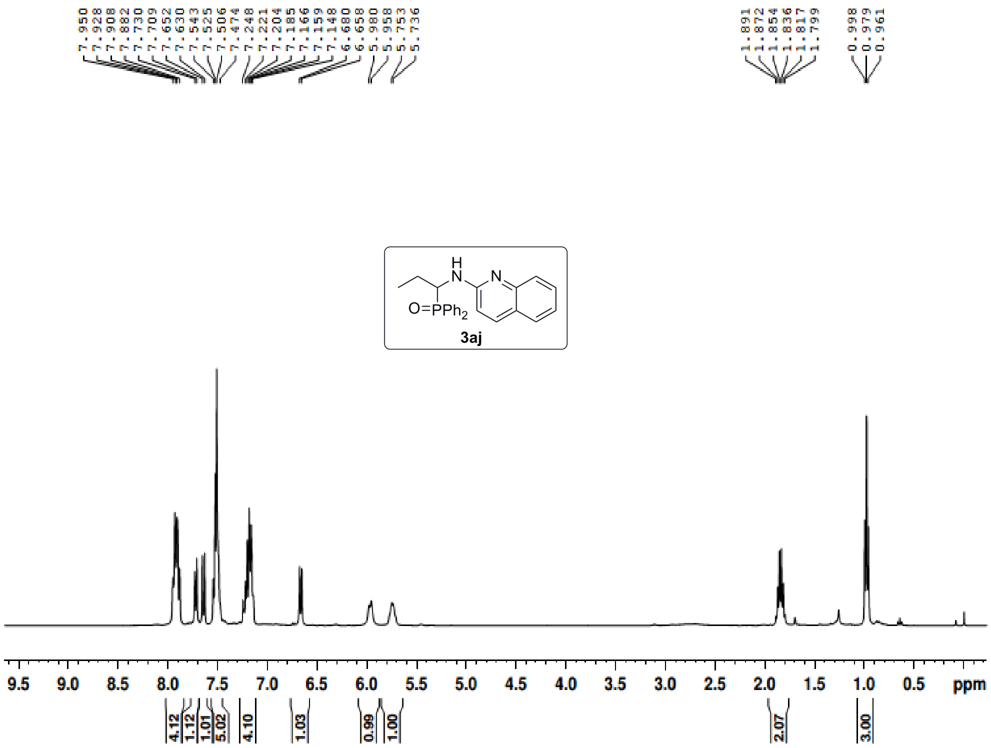

32.062
O=PPh2
3ah
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 ppm


8.019 8.007 7.901 7.881 7.874 7.859 7.841 7.838 7.832 7.814 7.492 7.475 7.455 7.436 7.346 7.328 7.310 7.277 7.258 7.237 7.218 7.198 6.469 6.454 6.439 6.418 6.397 5.514 5.418 5.407 5.396 5.384 5.372 5.360 5.349
1.834 1.816 1.810 1.804 1.792 1.787 1.770 1.752 1.734 0.974 0.956 0.937
H
N
N
O=PPh2
3ai
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.13 4.09 3.13 1.09 3.09 2.03 0.97 1.03 2.09 3.00

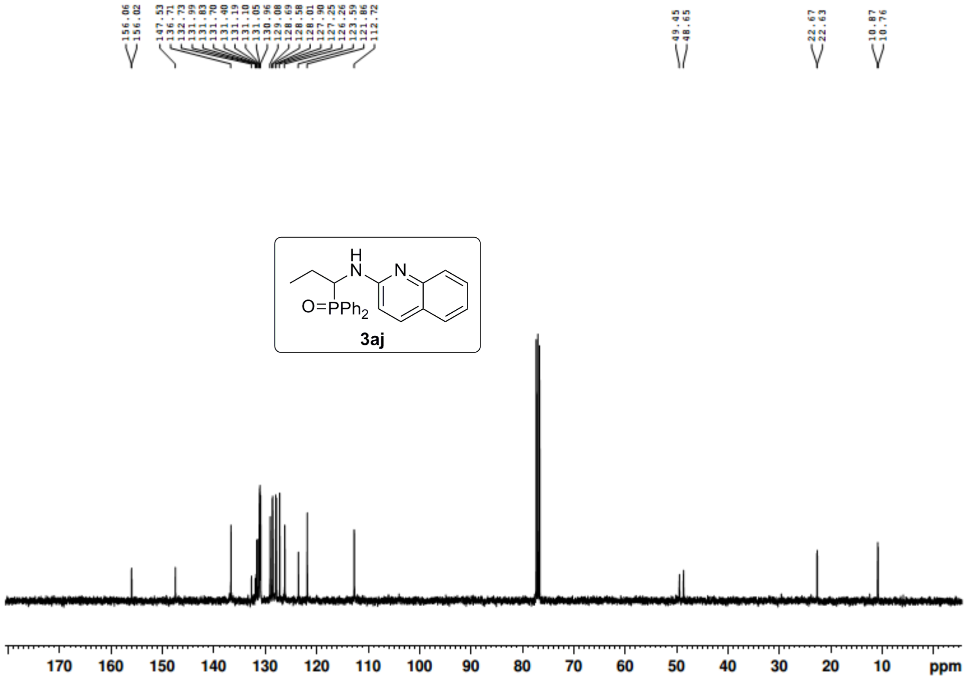

157.84 157.79 147.08 136.75 132.49 132.14 131.60 131.58 131.37 131.35 131.17 131.10 131.00 130.97 130.88 128.56 128.45 128.03 127.92 112.72 109.09
49.75 48.95 22.74 22.69 10.69 10.58
H
N
N
O=PPh2
3ai
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

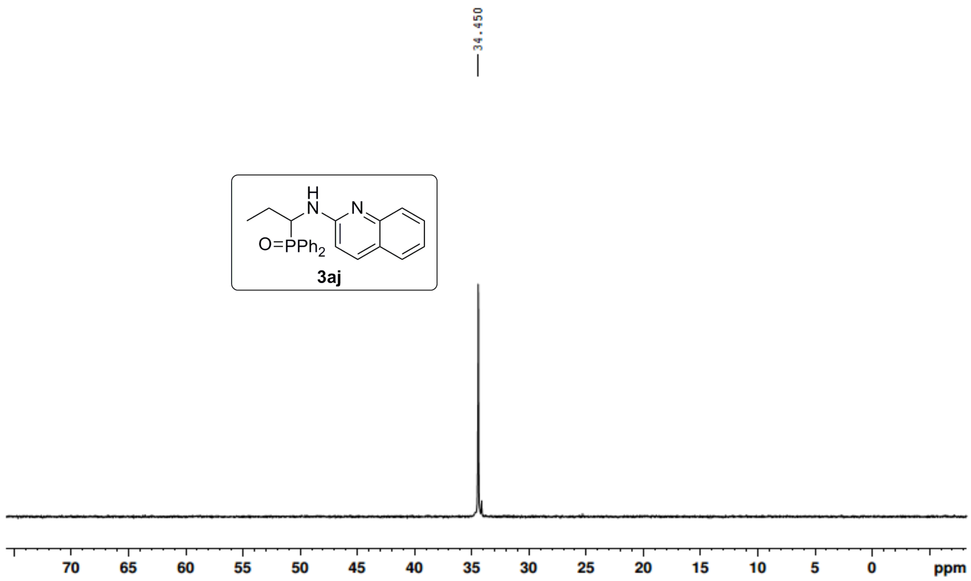


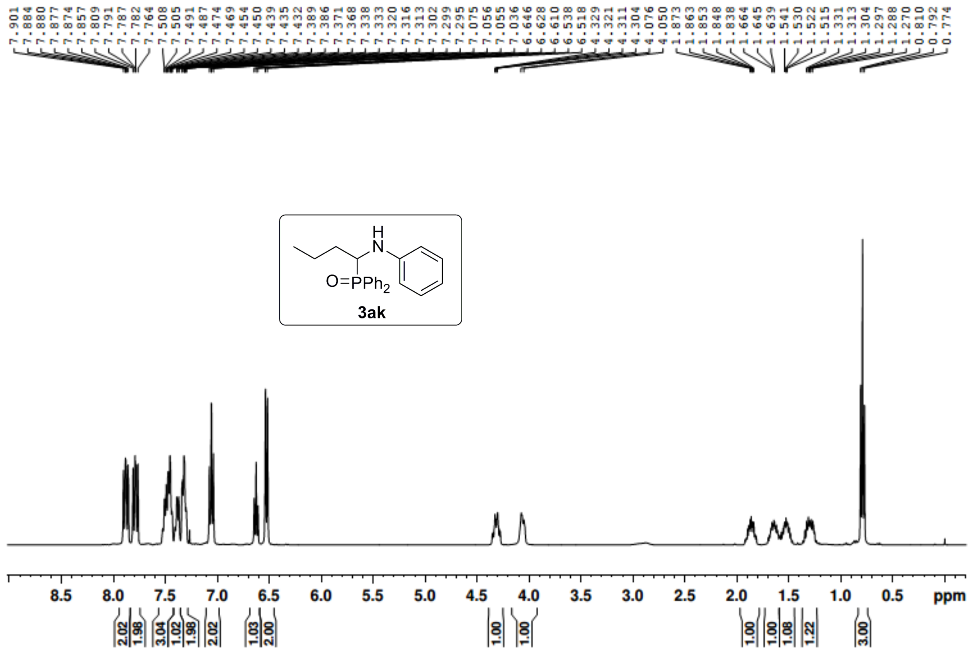
33.642
O=PPh2
3ai
60 55 50 45 40 35 30 25 20 15 10 ppm

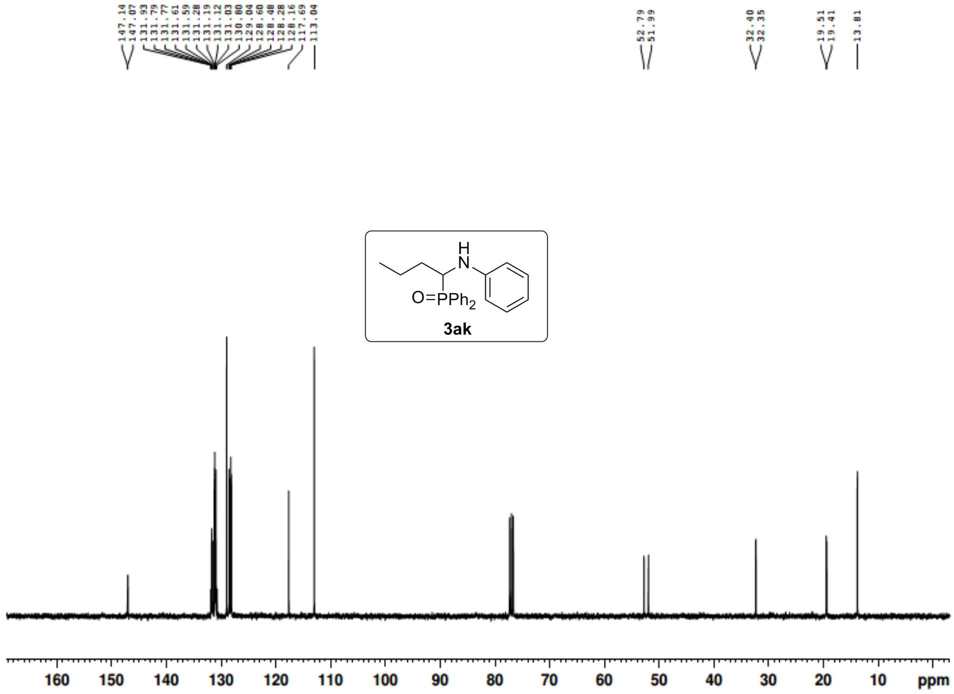


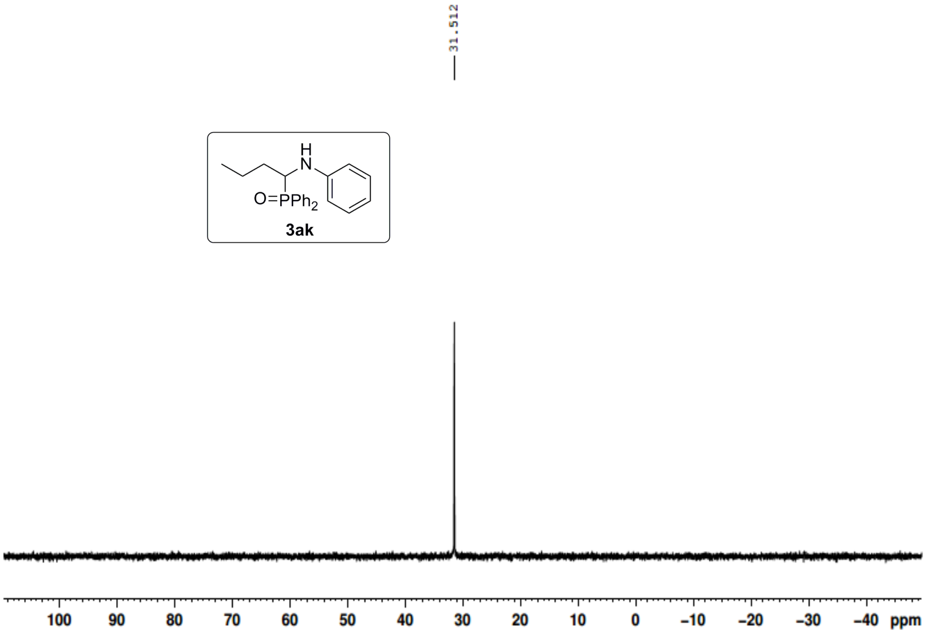
7.950 7.928 7.908 7.882 7.730 7.709 7.652 7.630 7.543 7.525 7.506 7.474 7.248 7.221 7.204 7.185 7.166 7.159 7.148 6.680 6.658 5.980 5.958 5.753 5.736
1.891 1.872 1.854 1.836 1.817 1.799
0.998 0.979 0.961
O=PPh2
3aj
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.12 1.12 1.01 5.02 4.10 1.03 0.99 1.00 2.07 3.00

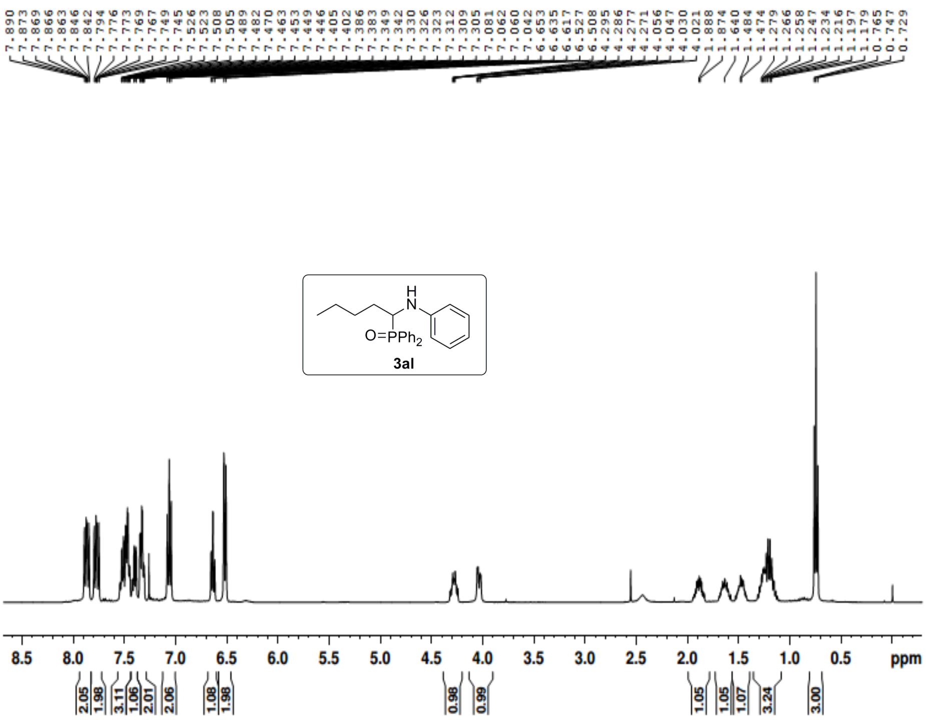

156.06
156.02
147.53
136.71
132.73
131.99
131.83
131.70
131.40
131.19
131.10
131.05
130.96
129.08
128.69
128.58
128.01
127.90
127.25
126.26
123.59
121.86
112.72
49.45
48.65
22.67
22.63
10.87
10.76
H
N
N
O=PPh2
3aj
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

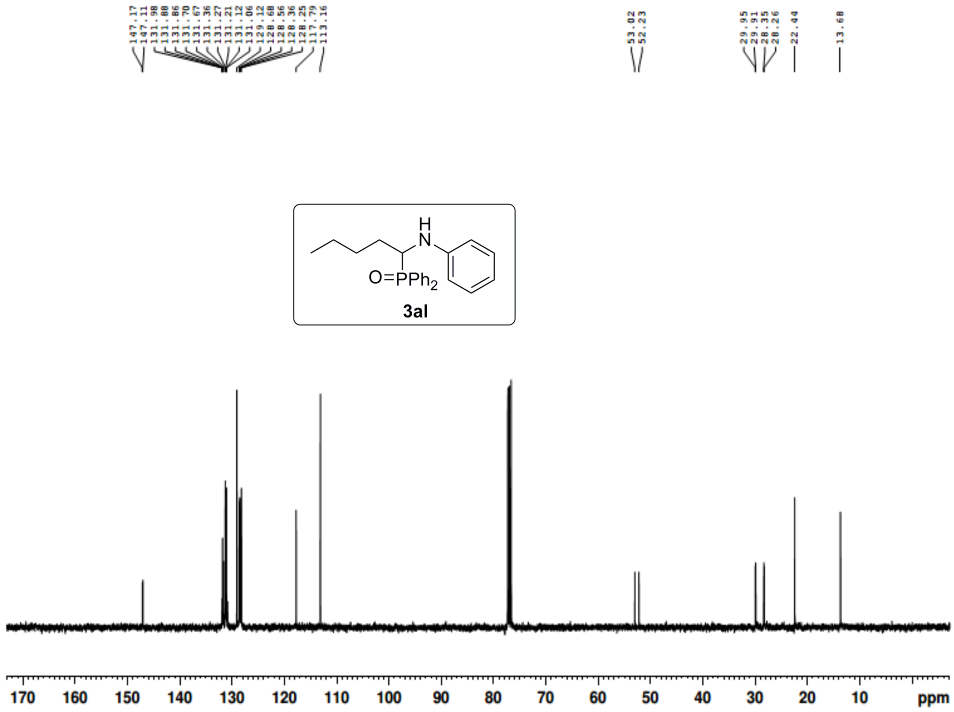

34.450
H
N
N
O=PPh2
3aj
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm

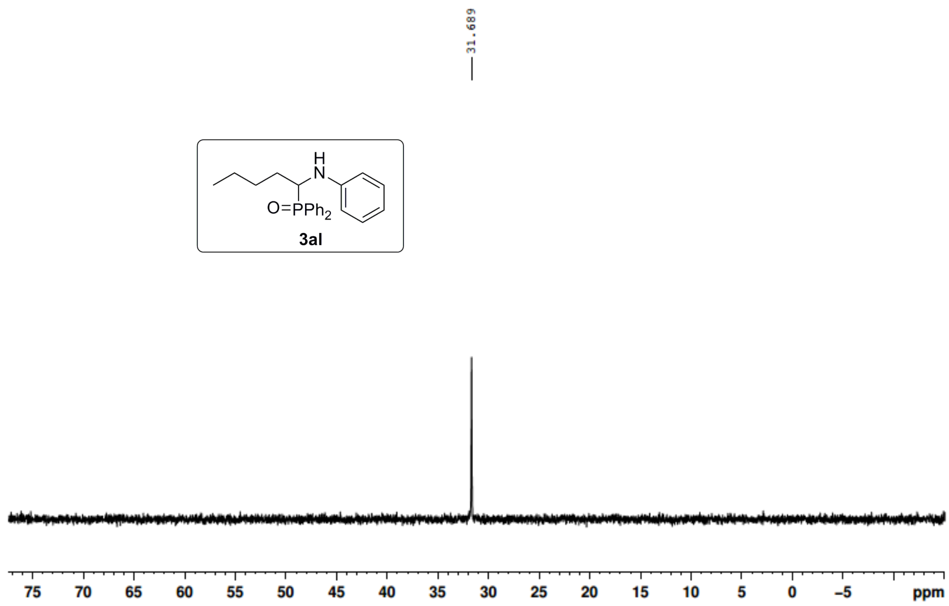

O=PPh2
3ak
ppm

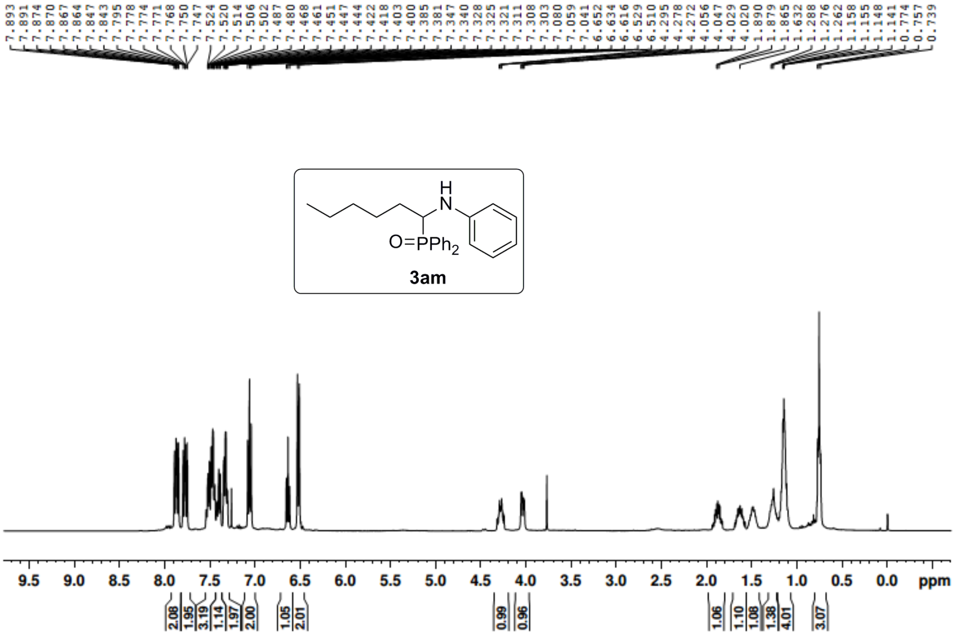

147.14
147.07
131.93
131.79
131.77
131.61
131.59
131.28
131.19
131.12
131.03
130.80
129.04
128.60
128.48
128.28
128.16
117.69
113.04
52.79
51.99
32.40
32.35
19.51
19.41
13.81
O=PPh2
3ak
ppm

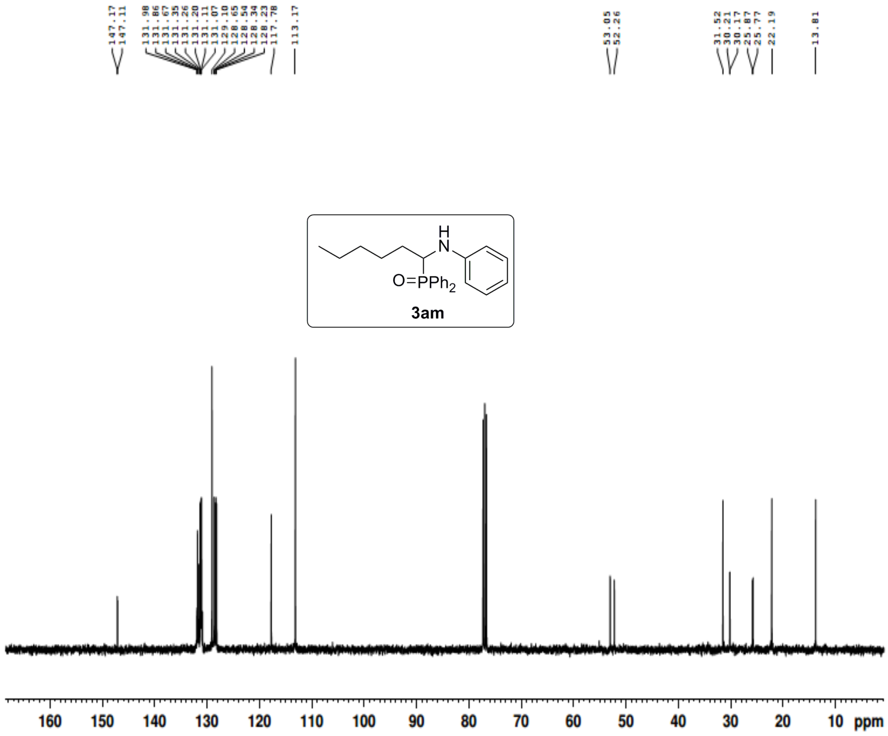

31.512
H
N
O=PPh2
3ak
100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 ppm

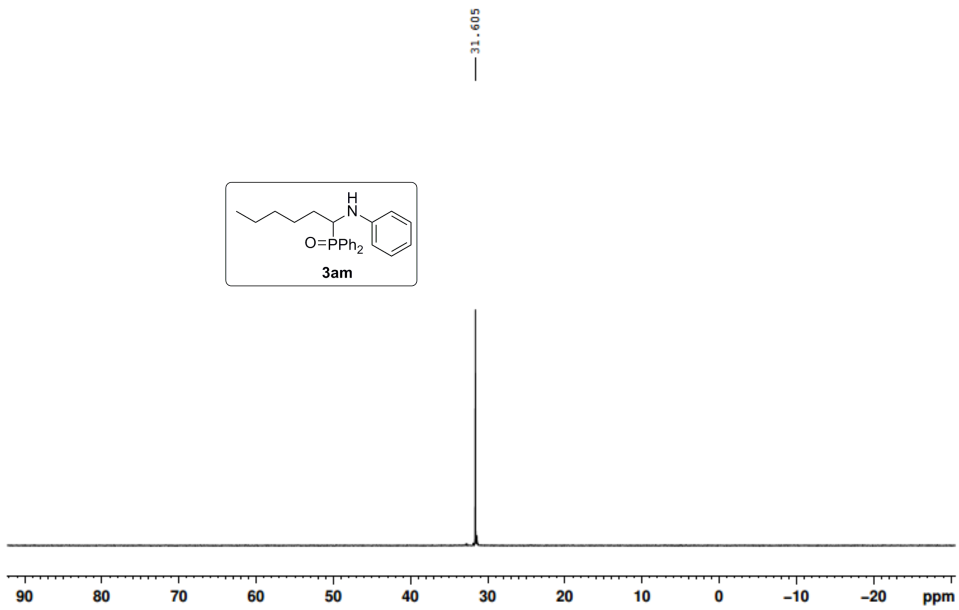

7.890 7.873 7.869 7.866 7.863 7.846 7.842 7.794 7.776 7.773 7.769 7.767 7.749 7.745 7.526 7.523 7.508 7.505 7.489 7.482 7.470 7.463 7.453 7.449 7.446 7.405 7.402 7.386 7.383 7.342 7.330 7.326 7.323 7.312 7.309 7.305 7.081 7.062 7.060 7.042 6.653 6.635 6.617 6.527 6.508 4.295 4.277 4.271 4.056 4.047 4.030 4.021 1.888 1.874 1.640 1.484 1.474 1.279 1.266 1.258 1.247 1.234 1.216 1.197 1.179 0.765 0.747 0.729
H
N
O=PPh2
3al
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 ppm
2.05 1.98 3.11 1.06 2.01 2.06 1.08 1.98 0.98 0.99 1.05 1.05 1.07 3.24 3.00

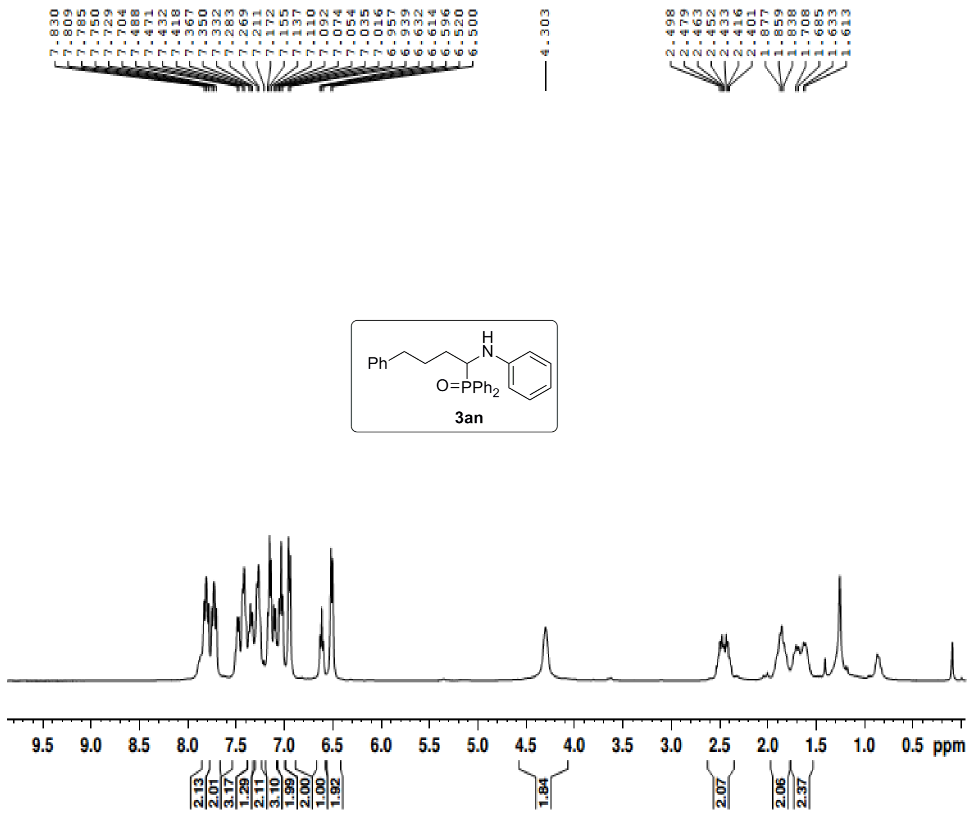

53.02
52.23
22.44
13.68
H
N
O=PPh2
3al
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

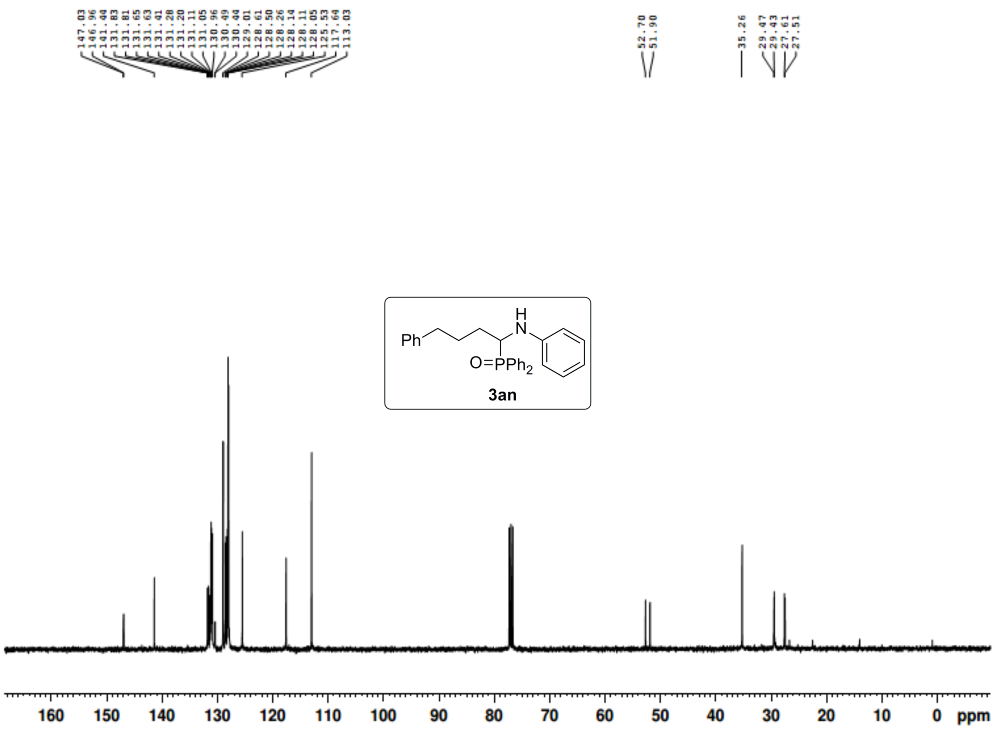

31.689
H
N
O=PPh2
3al
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 –5 ppm

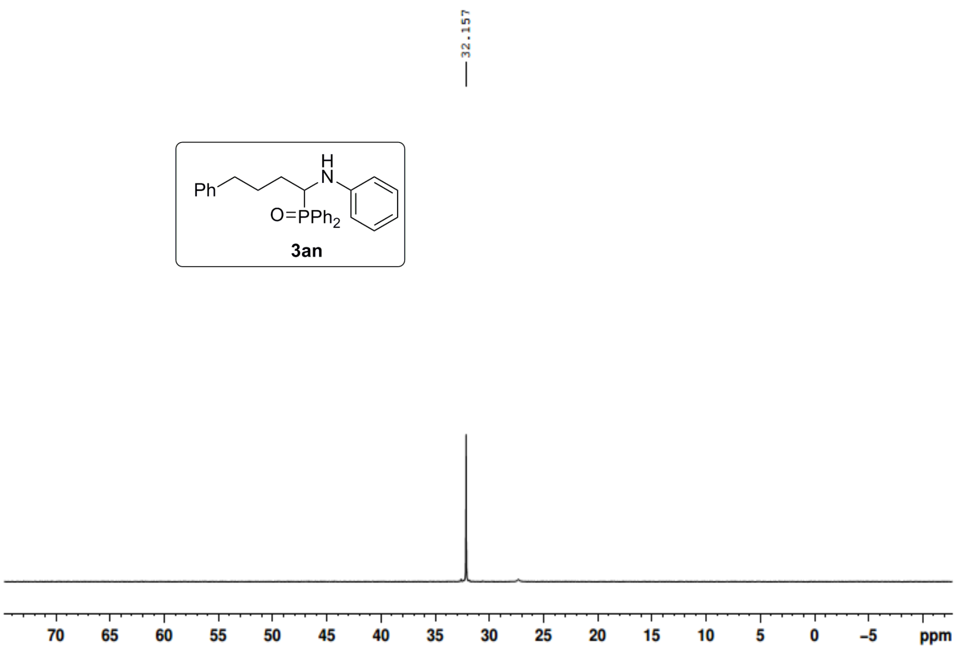

7.893 7.891 7.874 7.870 7.867 7.864 7.847 7.843 7.795 7.778 7.774 7.771 7.768 7.750 7.747 7.524 7.520 7.514 7.506 7.502 7.487 7.480 7.468 7.461 7.451 7.447 7.444 7.422 7.418 7.403 7.400 7.385 7.381 7.347 7.340 7.328 7.325 7.321 7.311 7.308 7.303 7.080 7.059 7.041 6.652 6.634 6.616 6.529 6.510 4.295 4.278 4.272 4.056 4.047 4.029 4.020 1.890 1.879 1.865 1.632 1.288 1.276 1.262 1.158 1.155 1.148 1.141 0.774 0.757 0.739
H
N
O=PPh2
3am
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.08 1.95 3.19 1.14 1.97 2.00 1.05 2.01 0.99 0.96 1.06 1.10 1.08 1.38 4.01 3.07

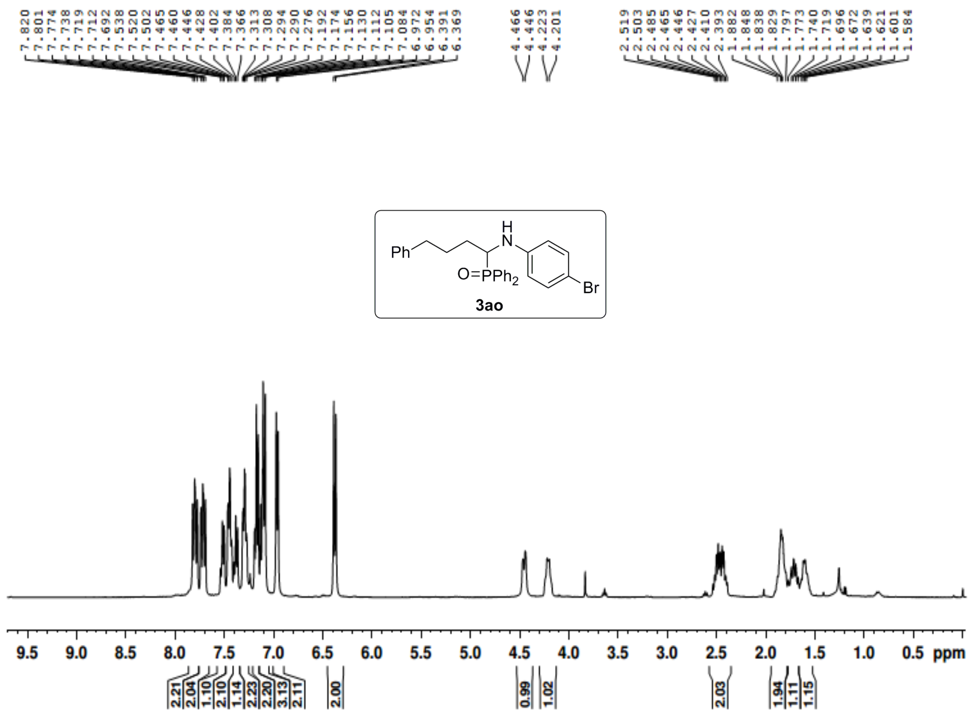

147.17 147.11 131.98 131.86 131.67 131.35 131.26 131.20 131.11 131.07 129.10 128.65 128.54 128.34 128.23 117.78 113.17 53.05 52.26 31.52 30.21 30.17 25.87 25.77 22.19 13.81
H
N
O=PPh2
3am
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

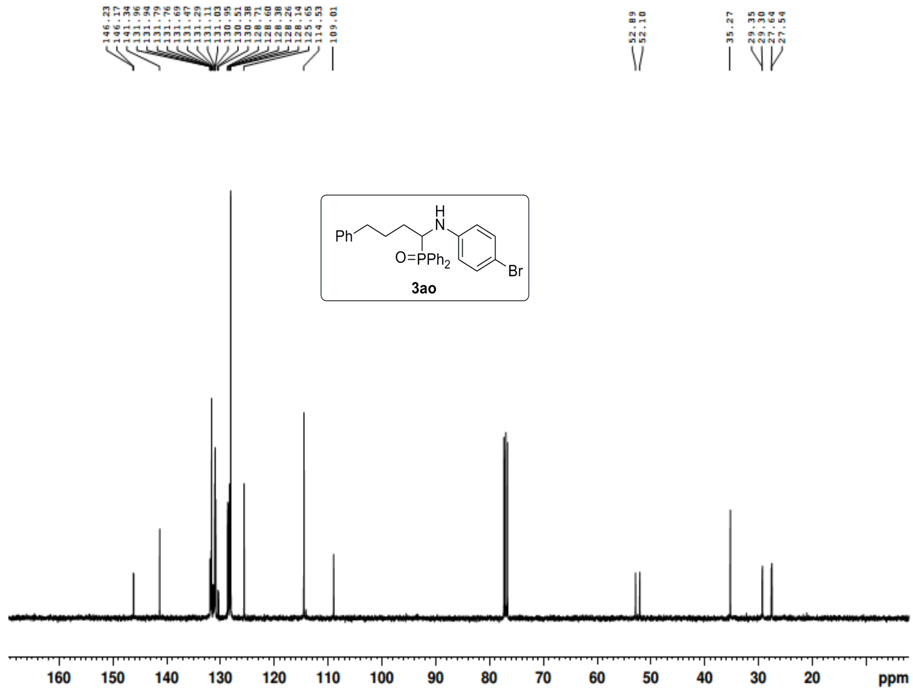

31.605
H
N
O=PPh2
3am
90 80 70 60 50 40 30 20 10 0 −10 −20 ppm

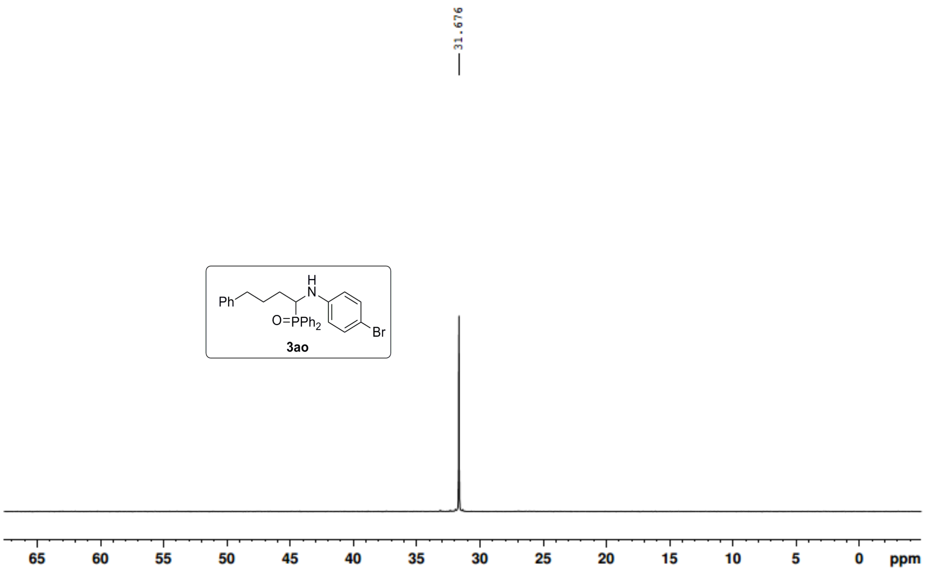

7.830 7.809 7.785 7.750 7.729 7.704 7.488 7.471 7.432 7.418 7.367 7.350 7.332 7.283 7.269 7.211 7.172 7.155 7.137 7.110 7.092 7.074 7.054 7.035 7.016 6.957 6.939 6.632 6.614 6.596 6.520 6.500
4.303
2.498 2.479 2.463 2.452 2.433 2.416 2.401 1.877 1.859 1.838 1.708 1.685 1.633 1.613
Ph
H
N
O=PPh2
3an
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.13 2.01 3.17 1.29 2.11 3.10 1.99 2.00 1.00 1.92
1.84
2.07
2.06 2.37

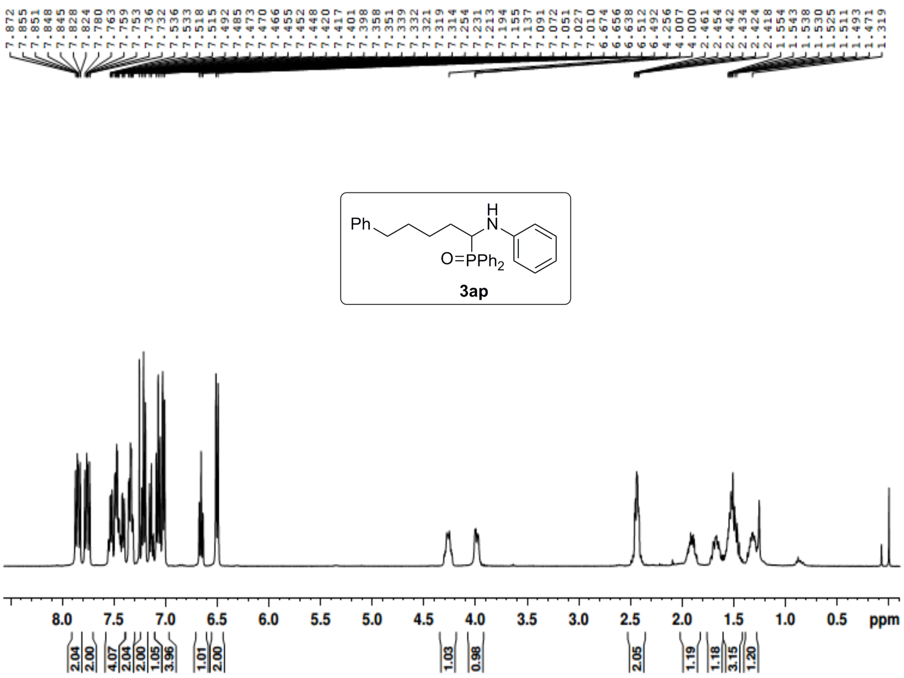

147.03
146.96
141.44
131.83
131.81
131.65
131.63
131.41
131.28
131.20
131.11
131.05
130.96
130.49
130.44
129.01
128.61
128.50
128.26
128.14
128.11
128.05
125.53
117.64
113.03
52.70
51.90
35.26
29.47
29.43
27.61
27.51
Ph
H
N
O=PPh2
3an
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

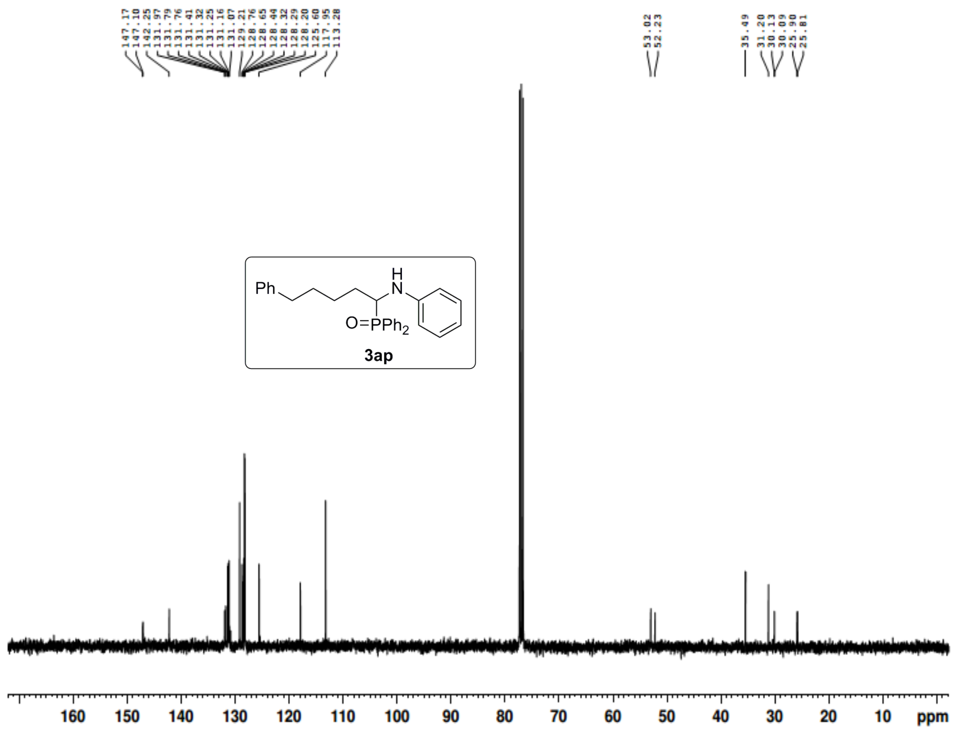

32.157
Ph
H
N
O=PPh2
3an
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
–5
ppm

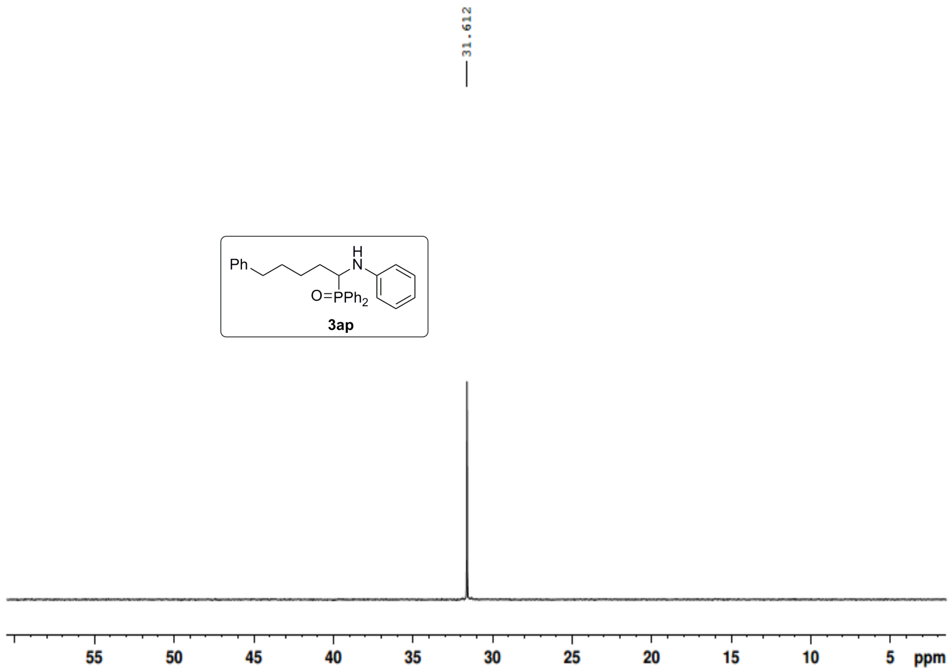

Ph
O=PPh2
Br
3ao
ppm

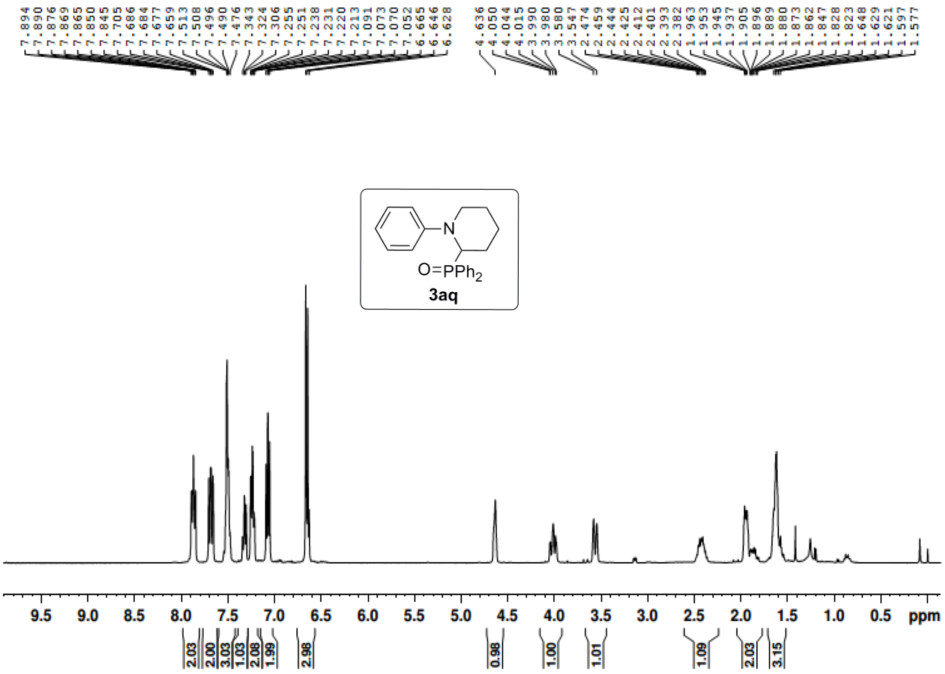

Ph
O=PPh2
Br
3ao
ppm

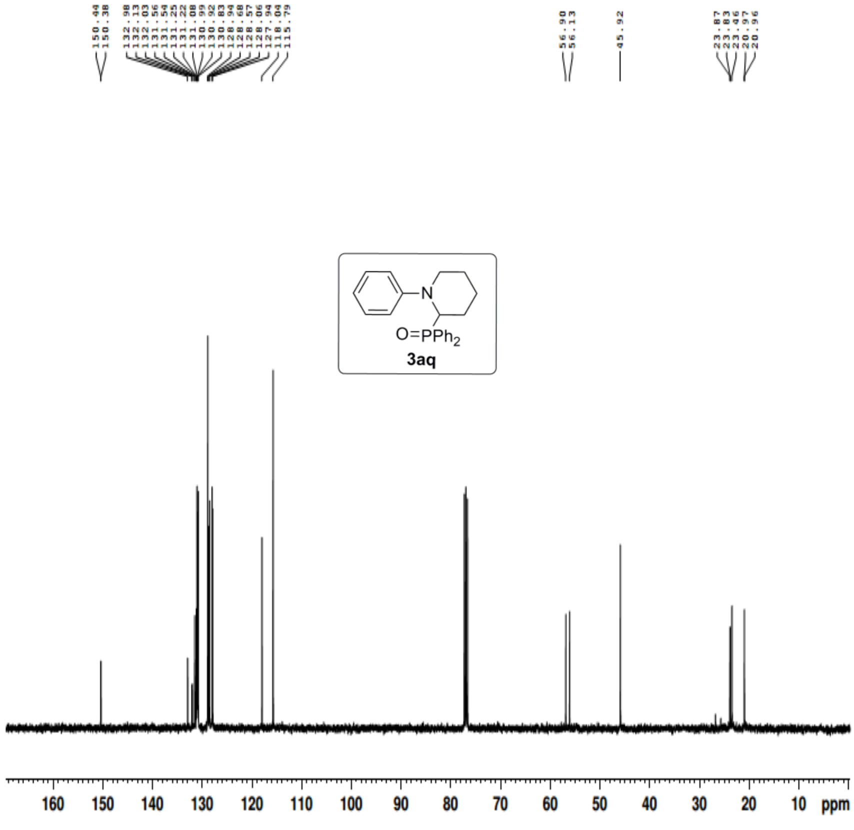


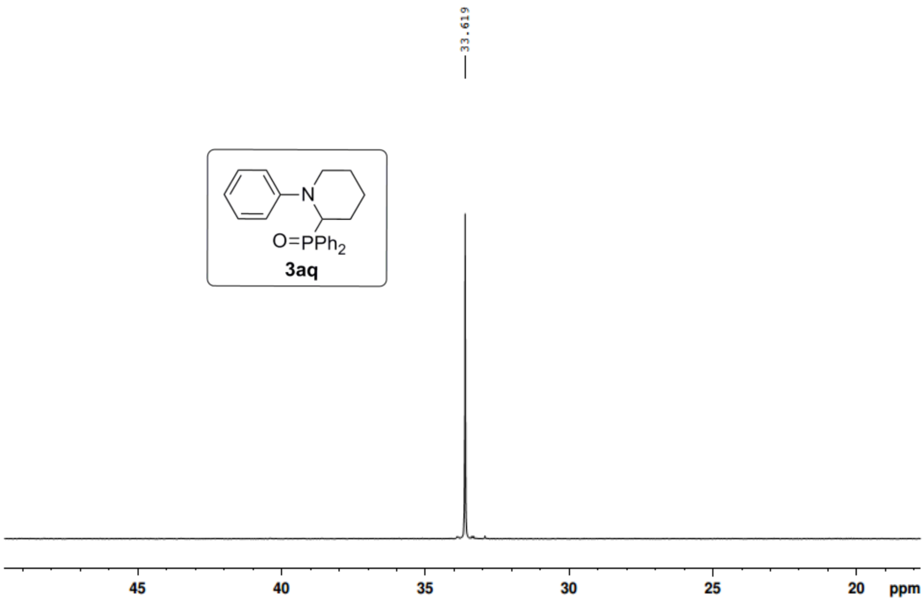


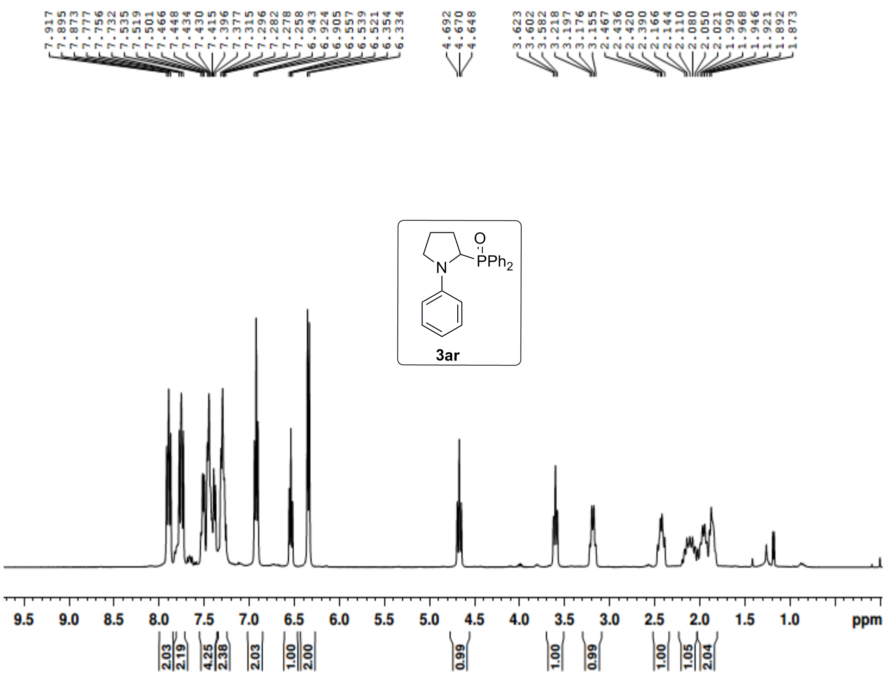

147.17
147.10
142.25
131.97
131.79
131.76
131.41
131.32
131.25
131.16
131.07
129.21
128.76
128.65
128.44
128.32
128.29
128.20
125.60
117.95
113.28
53.02
52.23
35.49
31.20
30.13
30.09
25.90
25.81
Ph
H
N
O=PPh2
3ap
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

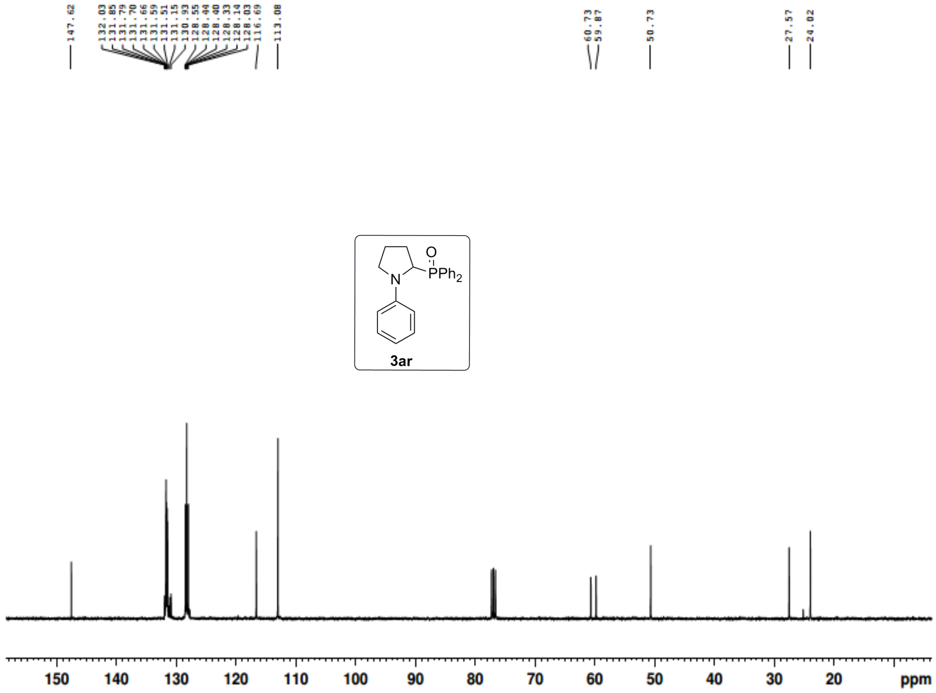

31.612
Ph
H
N
O=PPh2
3ap
55 50 45 40 35 30 25 20 15 10 5 ppm

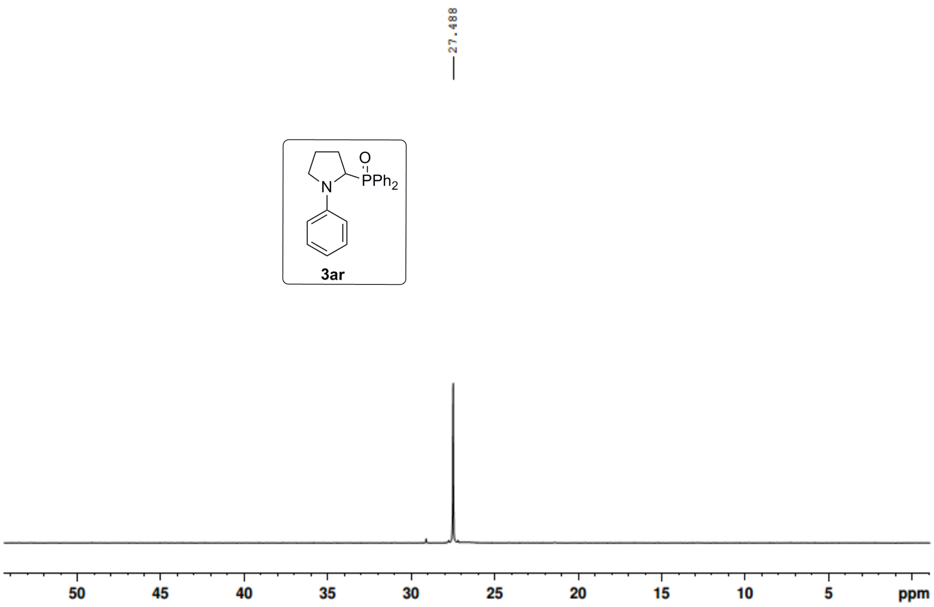


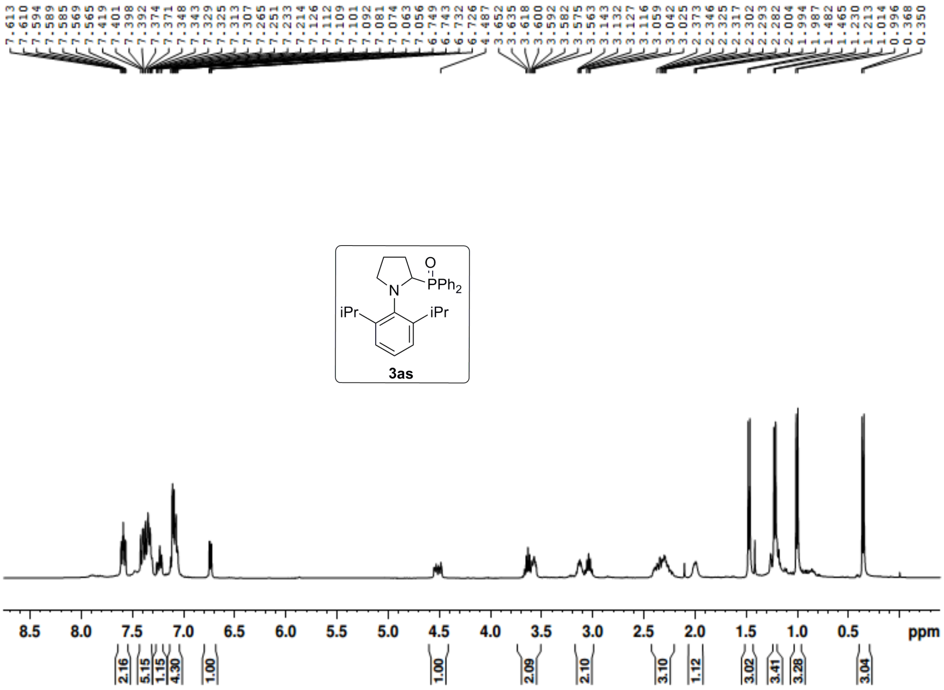


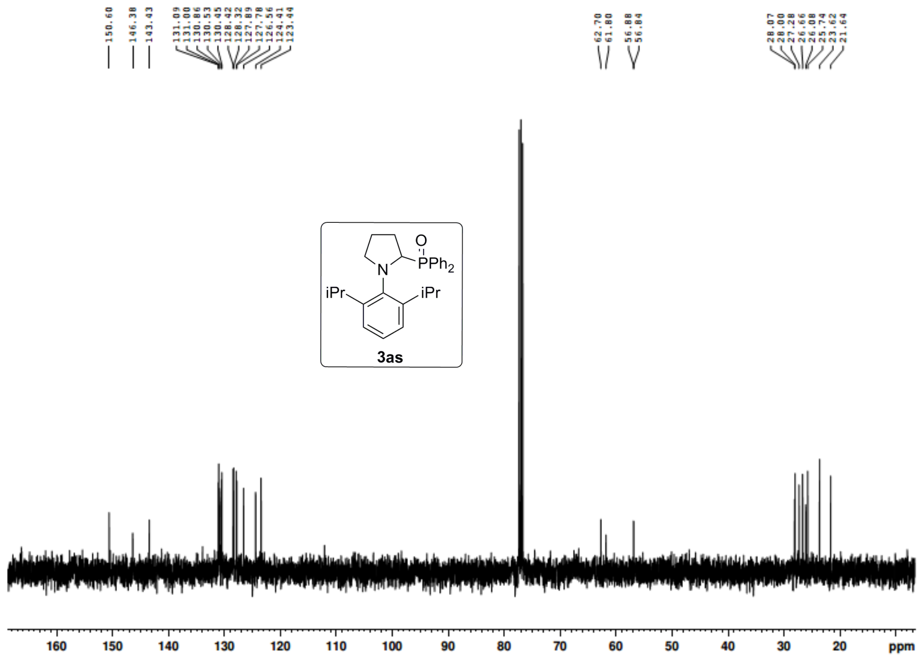


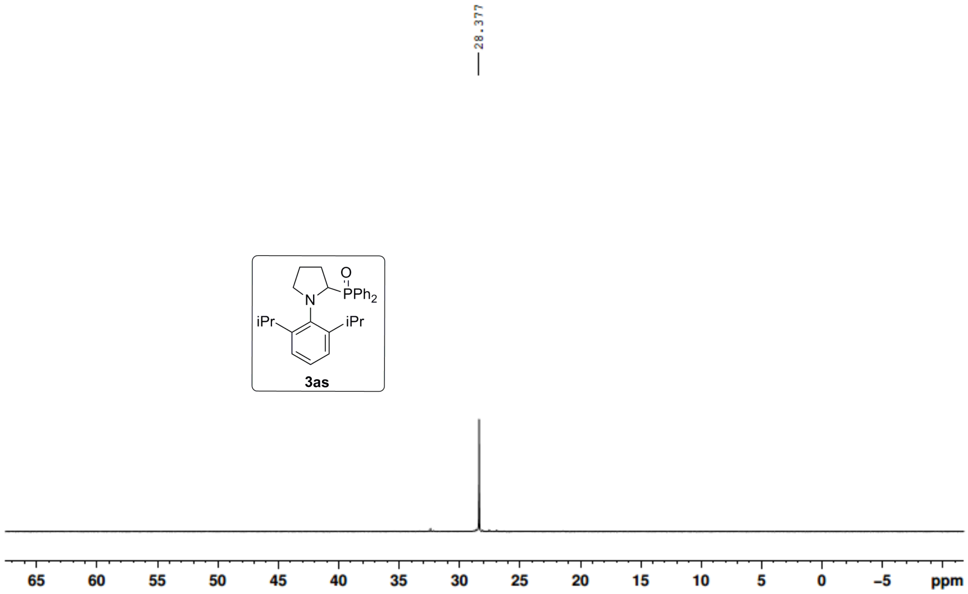


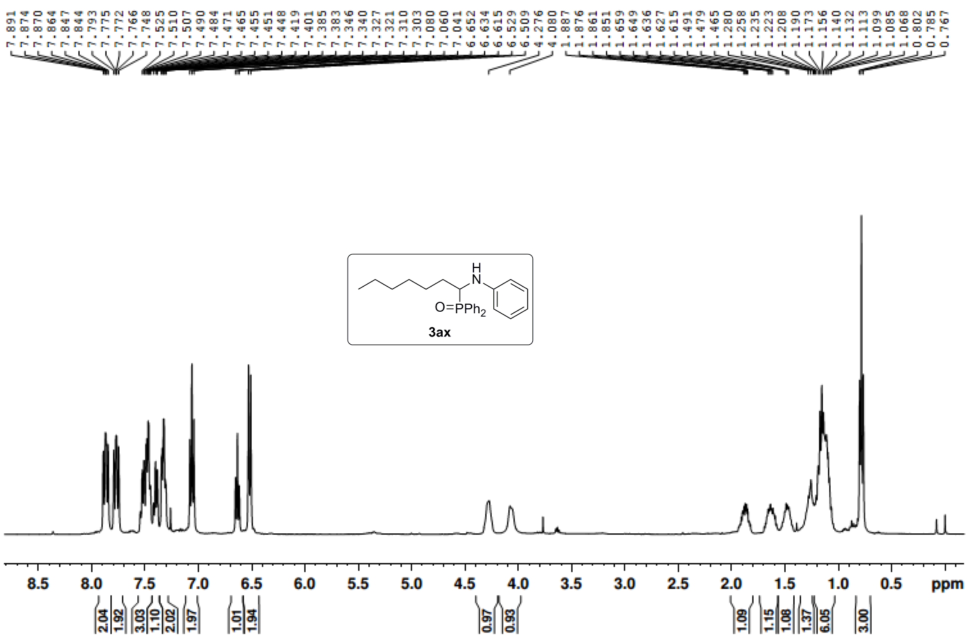

147.62
132.03
131.85
131.79
131.70
131.66
131.59
131.51
131.15
130.93
128.55
128.44
128.40
128.33
128.14
128.03
116.69
113.08
60.73
59.87
50.73
27.57
24.02
PPh2
N
O
3ar
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

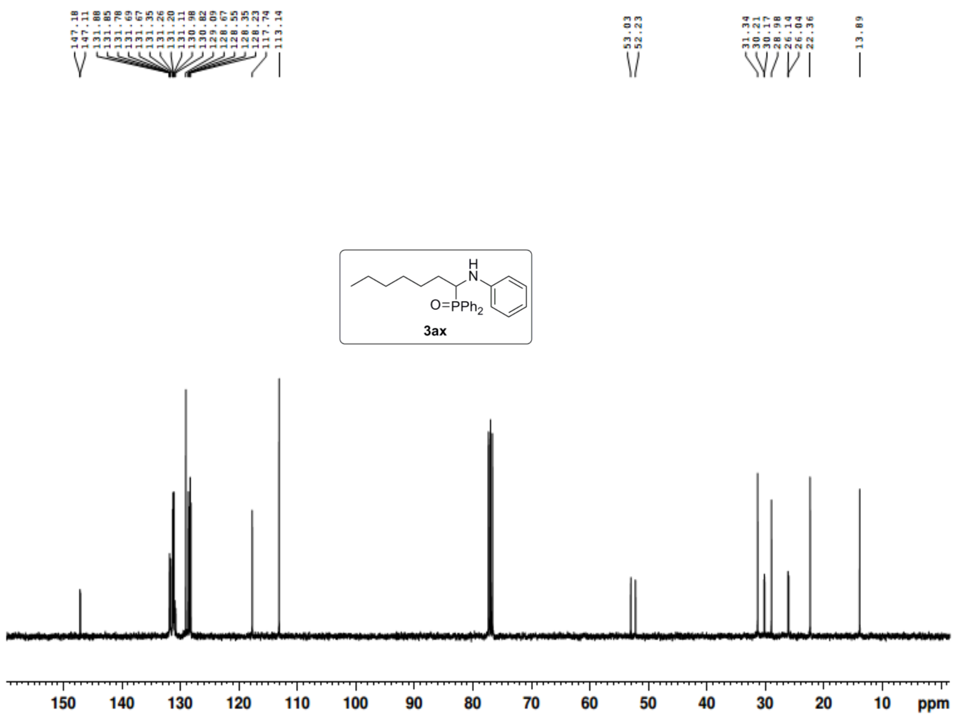

27.488
PPh2
N
O
3ar
50 45 40 35 30 25 20 15 10 5 ppm

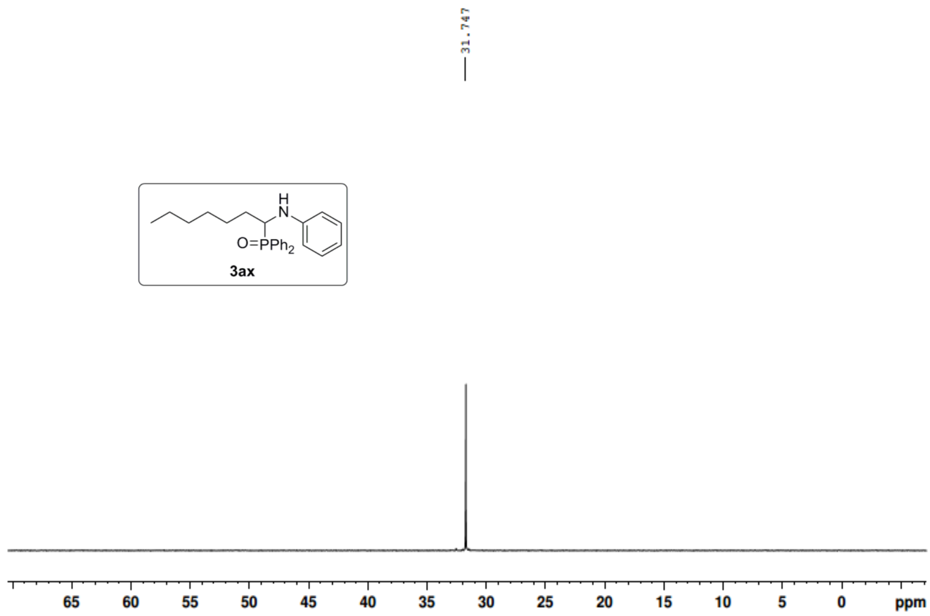


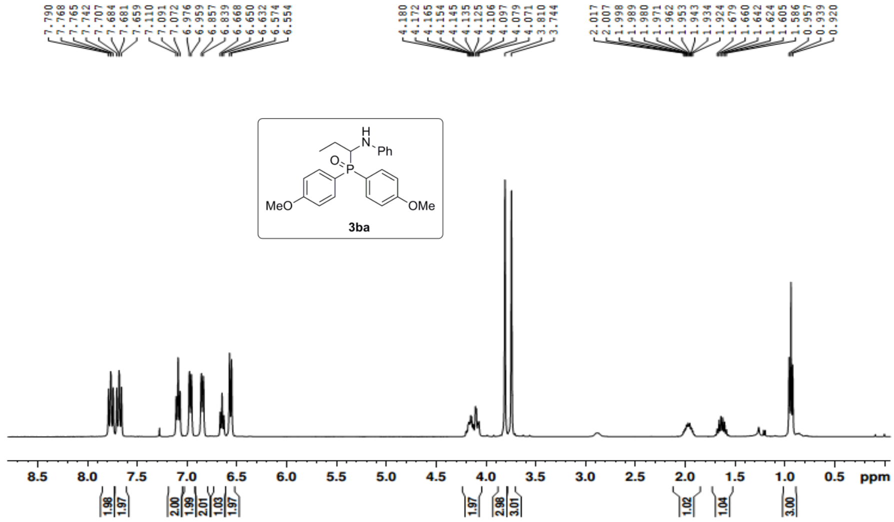


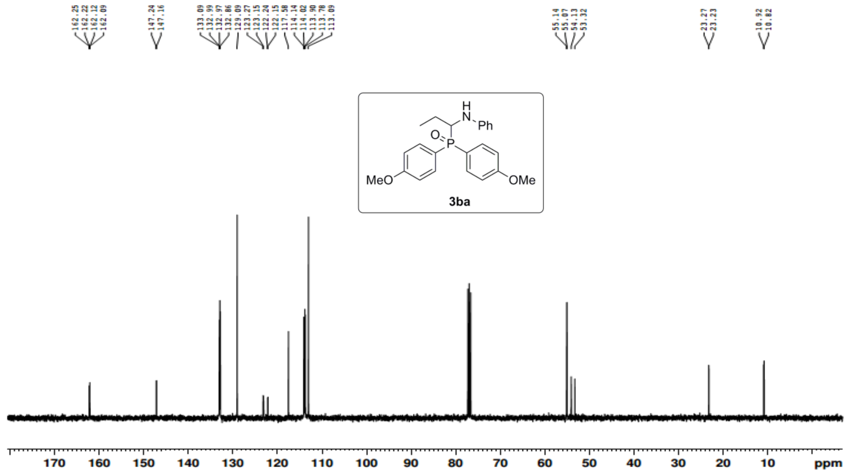

28.377
PPh2
iPr
iPr
3as
ppm

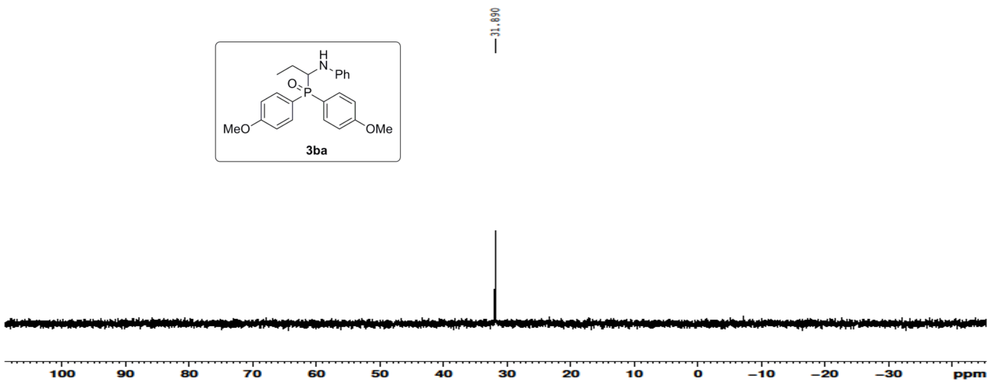

O=PPh2
3ax
ppm

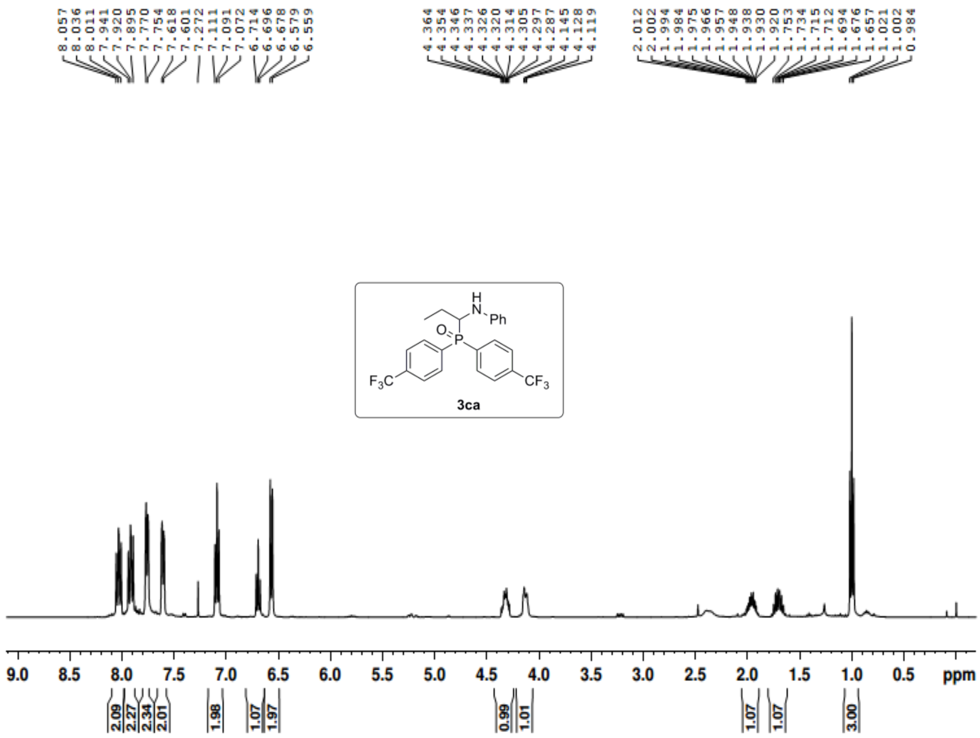

147.18
147.11
131.88
131.85
131.78
131.69
131.67
131.35
131.26
131.20
131.11
130.98
130.82
129.09
128.67
128.55
128.35
128.23
117.74
113.14
53.03
52.23
31.34
30.21
30.17
28.98
26.14
26.04
22.36
13.89
H
N
O=PPh2
3ax
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

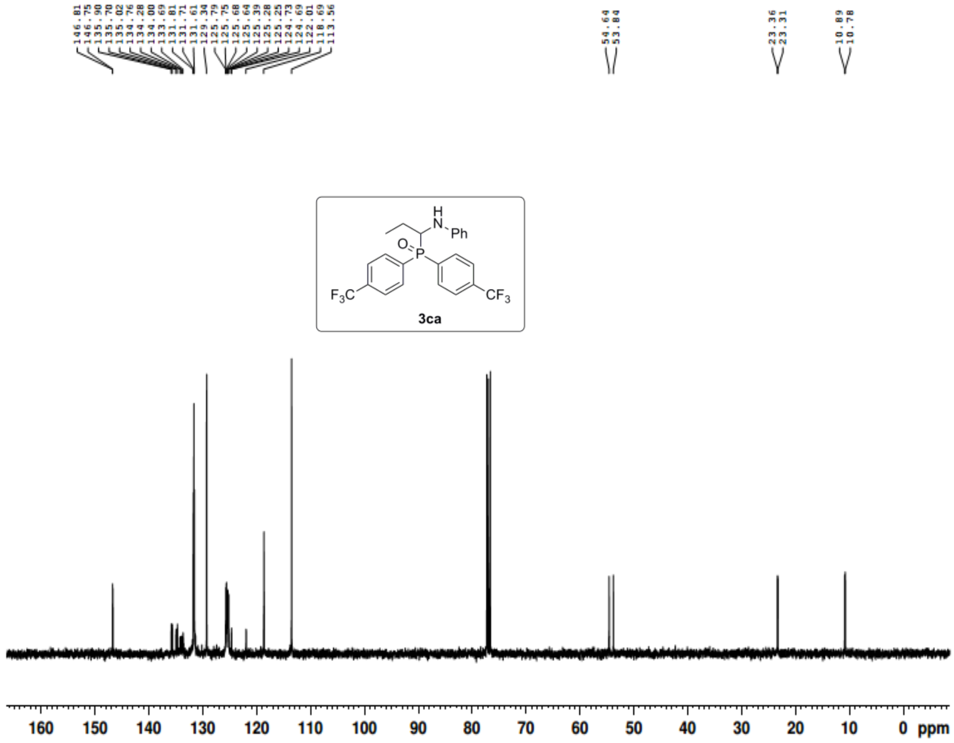

31.747
H
N
O=PPh2
3ax
65
60
55
50
45
40
35
30
25
20
15
10
5
0
ppm

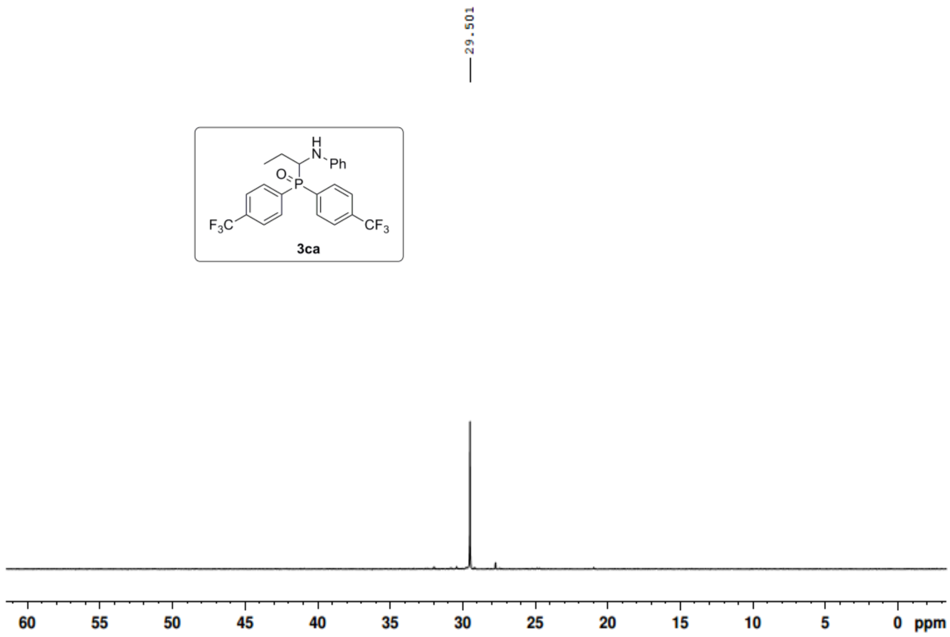


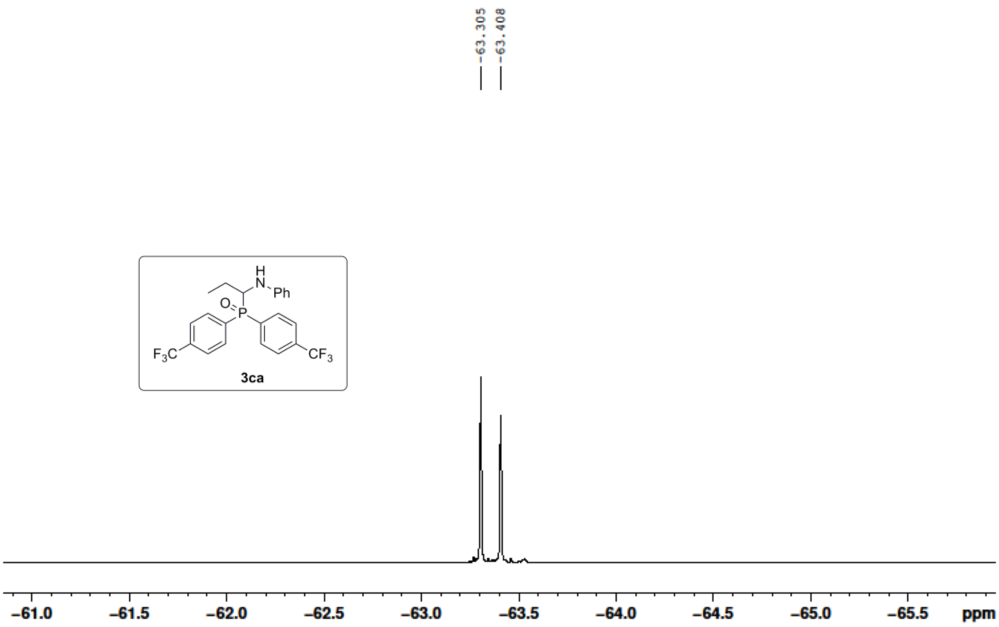


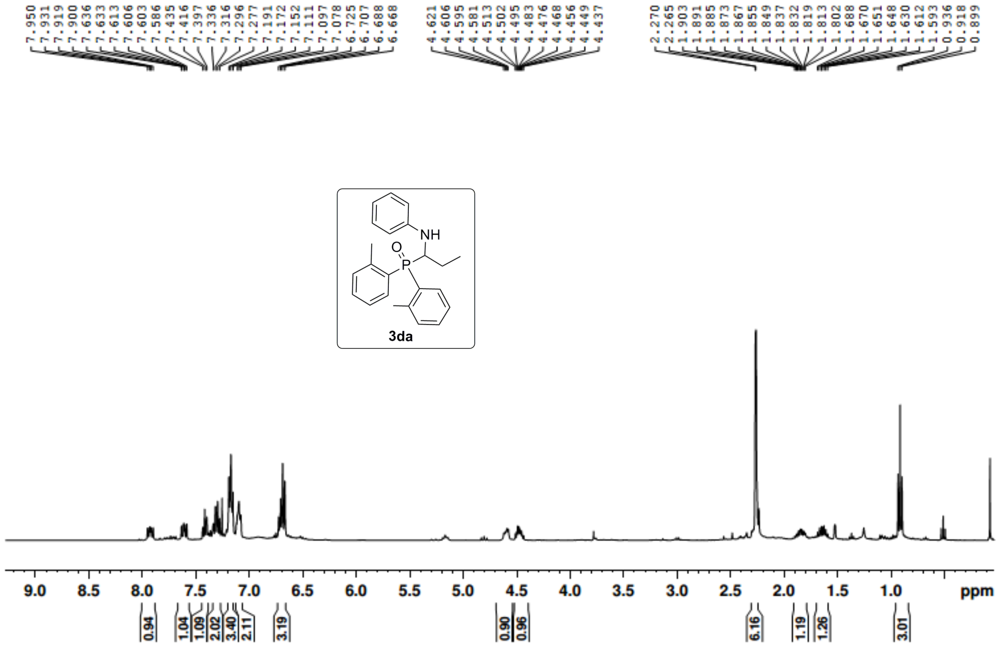


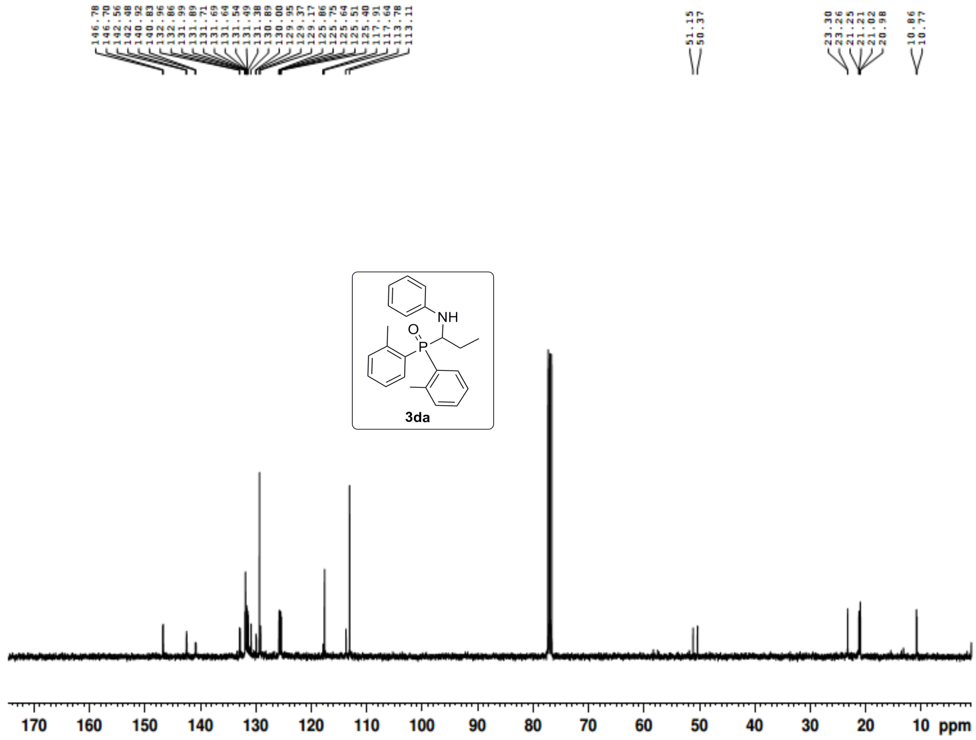

8.057 8.036 8.011 7.941 7.920 7.895 7.770 7.754 7.618 7.601 7.272 7.111 7.091 7.072 6.714 6.696 6.678 6.579 6.559
4.364 4.354 4.346 4.337 4.326 4.320 4.314 4.305 4.297 4.287 4.145 4.128 4.119
2.012 2.002 1.994 1.984 1.975 1.966 1.957 1.948 1.938 1.930 1.920 1.753 1.734 1.715 1.712 1.694 1.676 1.657 1.021 1.002 0.984
3ca
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 ppm
2.09 2.27 2.34 2.01 1.98 1.07 1.97 0.99 1.01 1.07 1.07 3.00

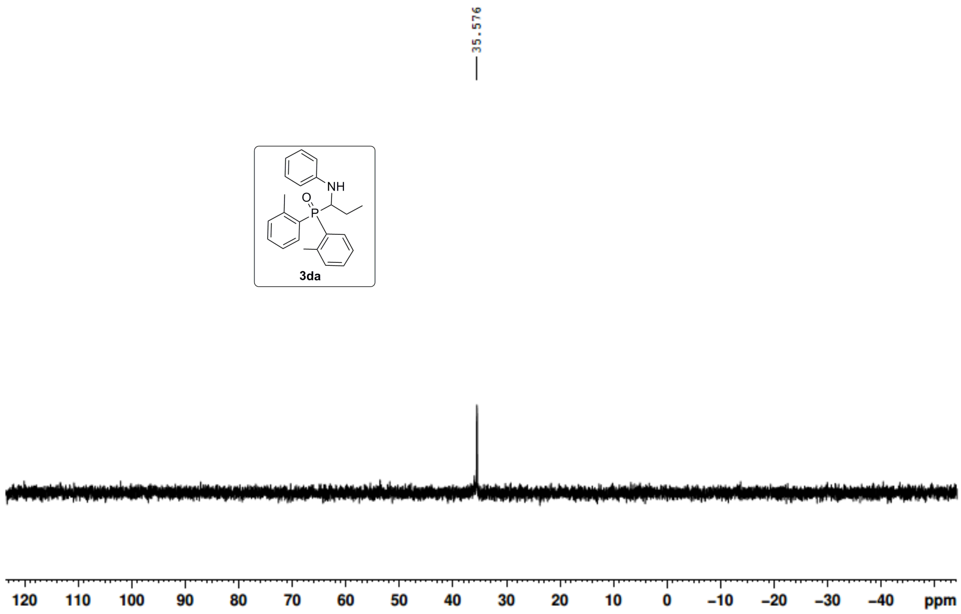

146.81 146.75 135.90 135.70 135.02 134.76 134.28 134.00 133.69 131.81 131.71 131.61 129.34 125.79 125.75 125.68 125.64 125.39 125.28 125.25 124.73 124.69 122.01 118.69 113.56
54.64 53.84
23.36 23.31
10.89 10.78
3ca
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

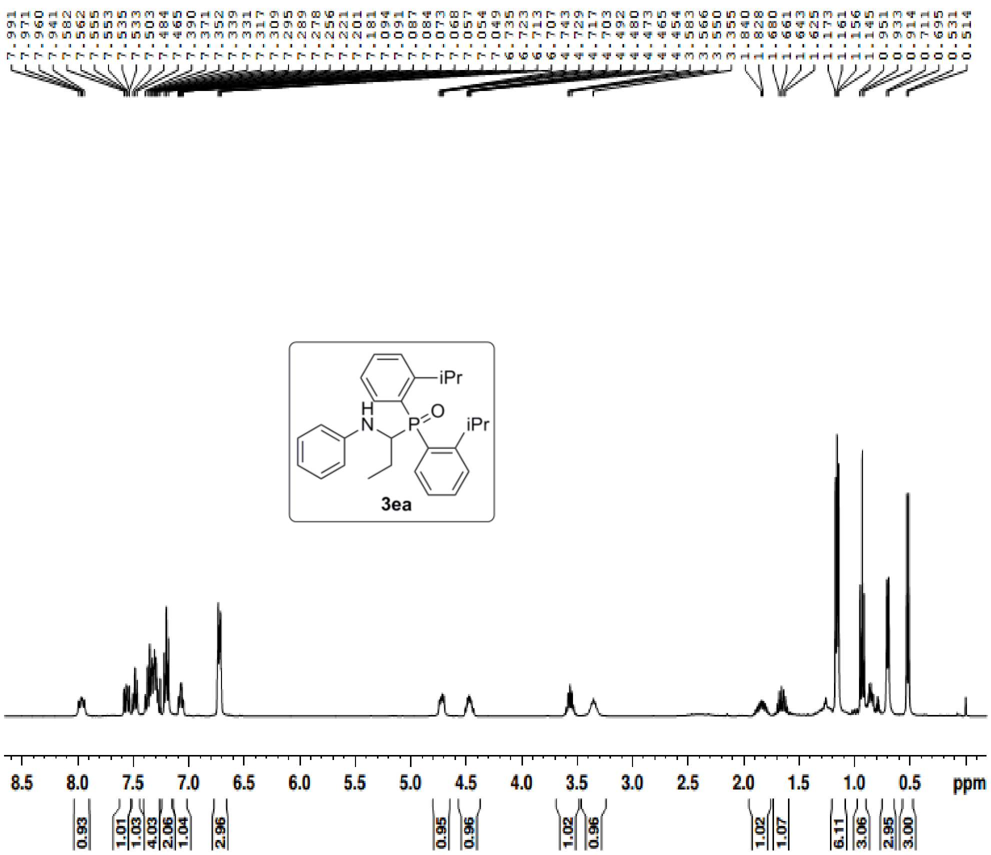

29.501
3ca
60
55
50
45
40
35
30
25
20
15
10
5
0
ppm

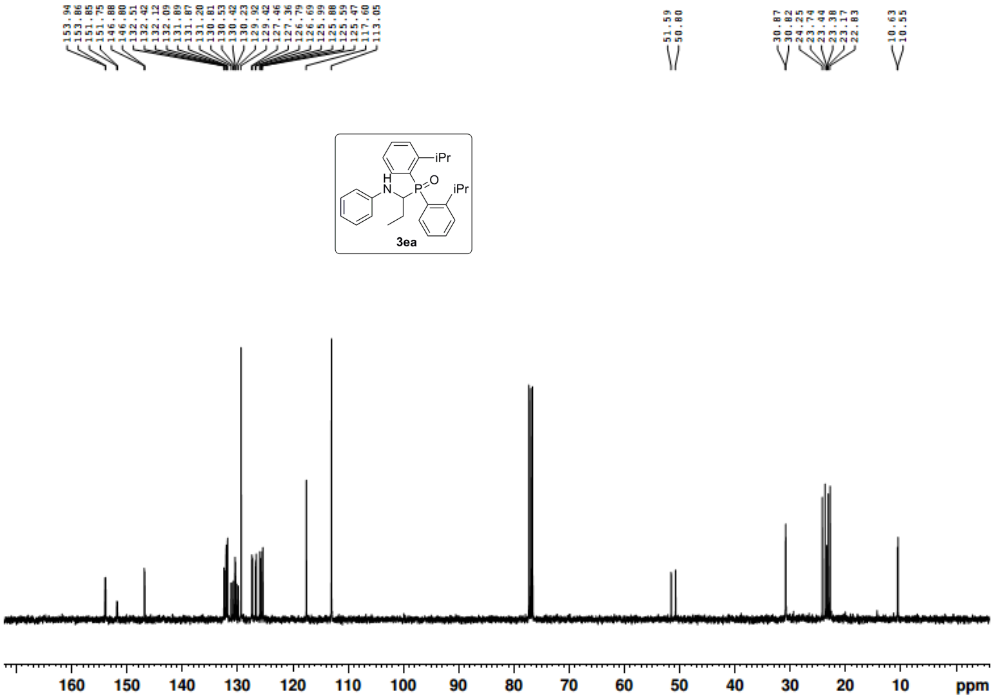

-63.305
-63.408
3ca
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
ppm

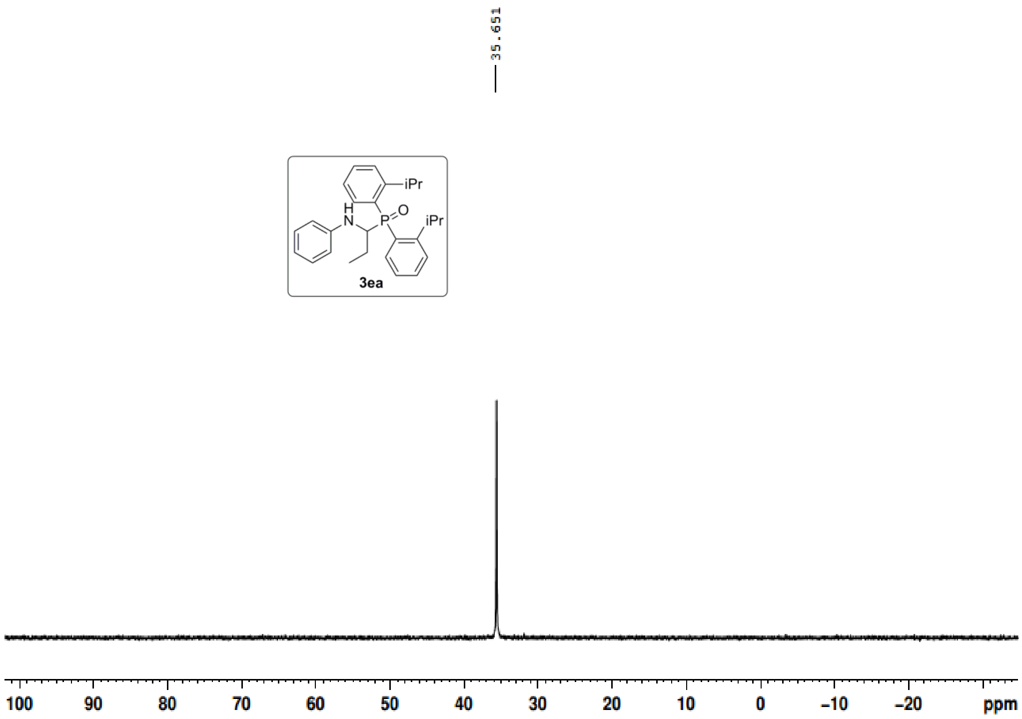

NH
O
P
3da
ppm

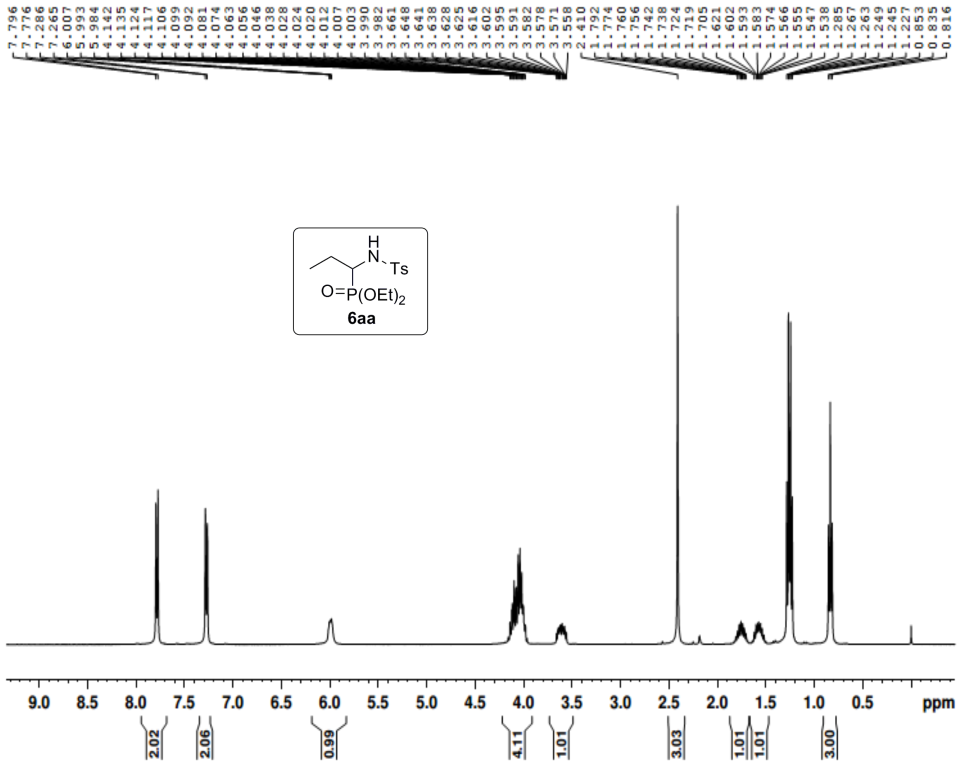

NH
O
P
3da
ppm

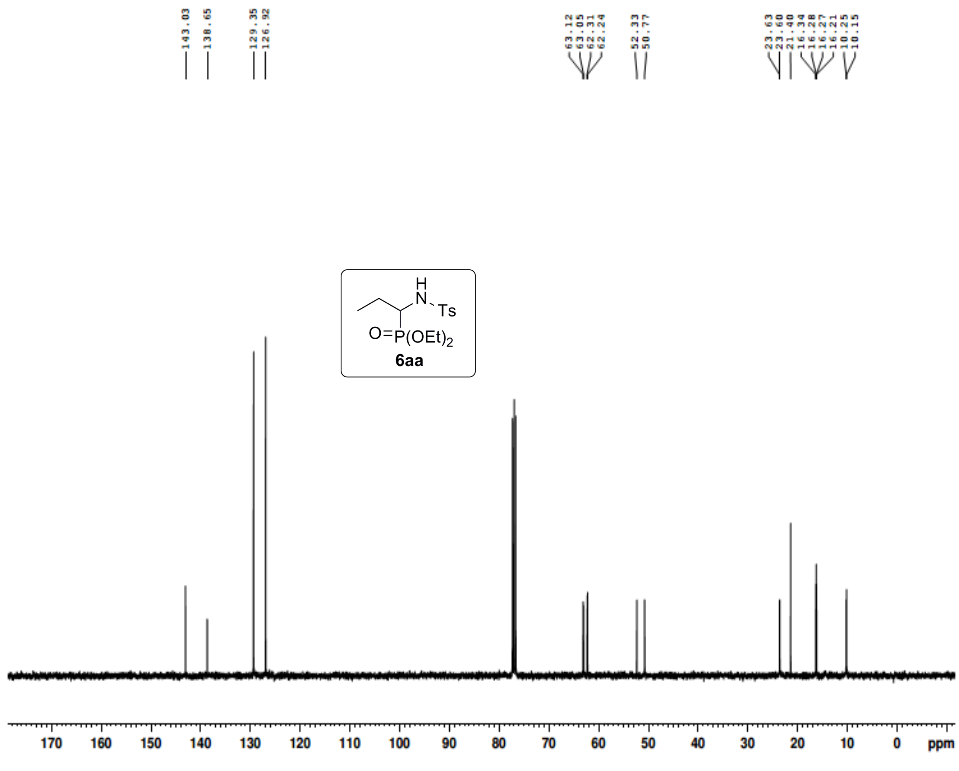

35.576
3da
ppm

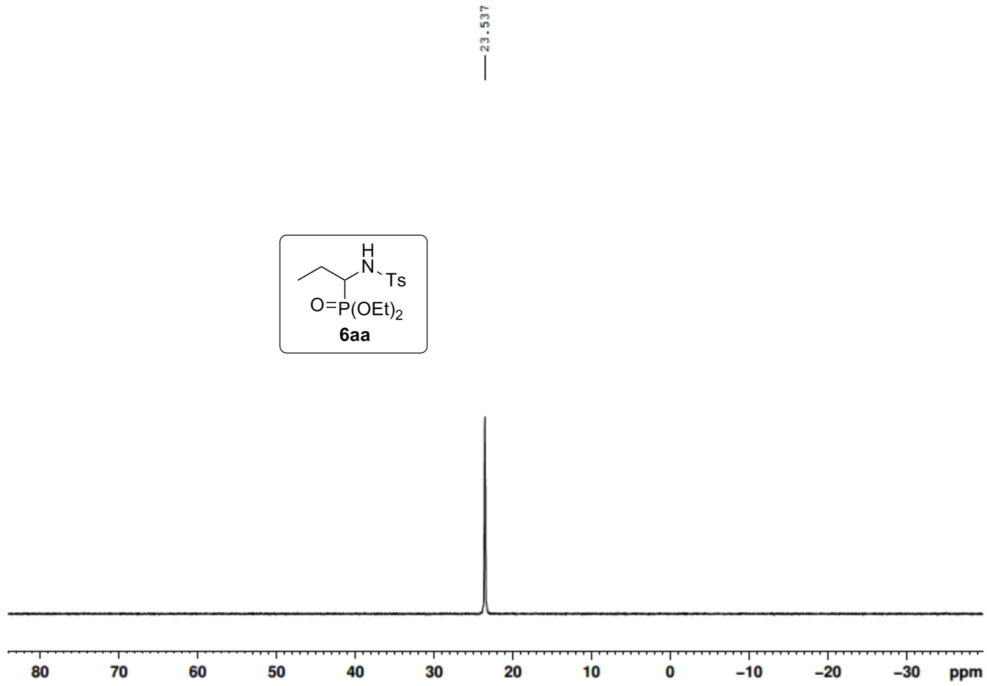

iPr
iPr
3ea
ppm

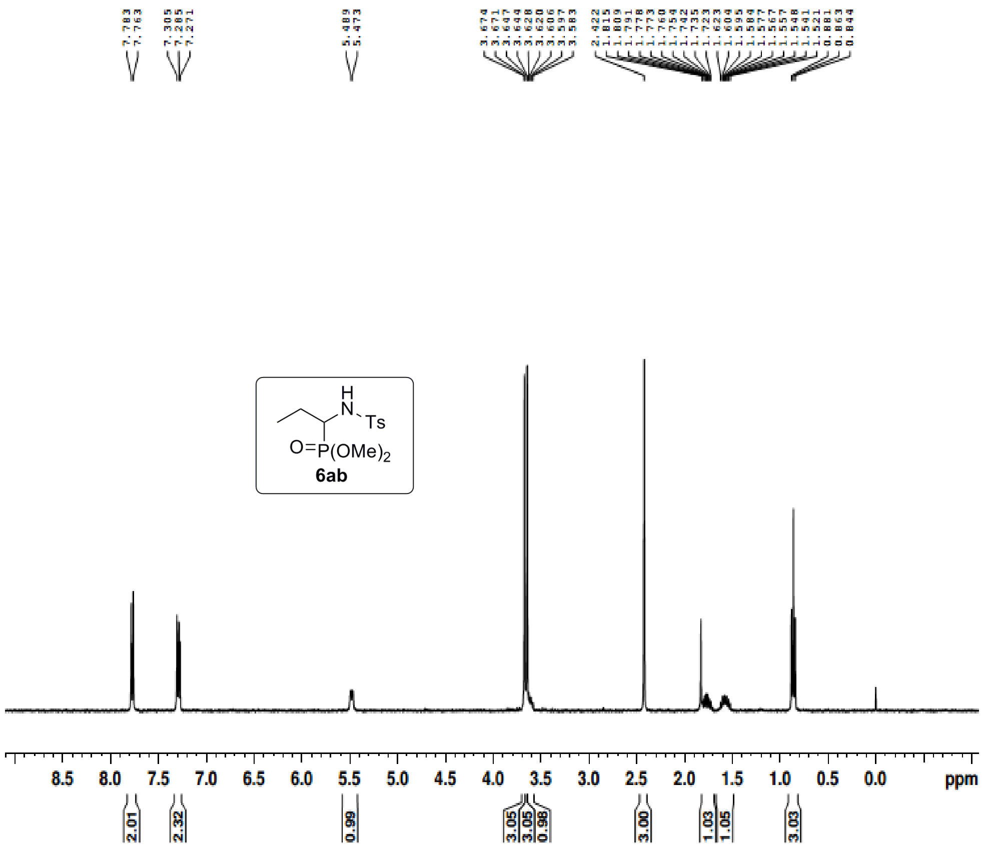

iPr
iPr
H
N
P
O
3ea
ppm

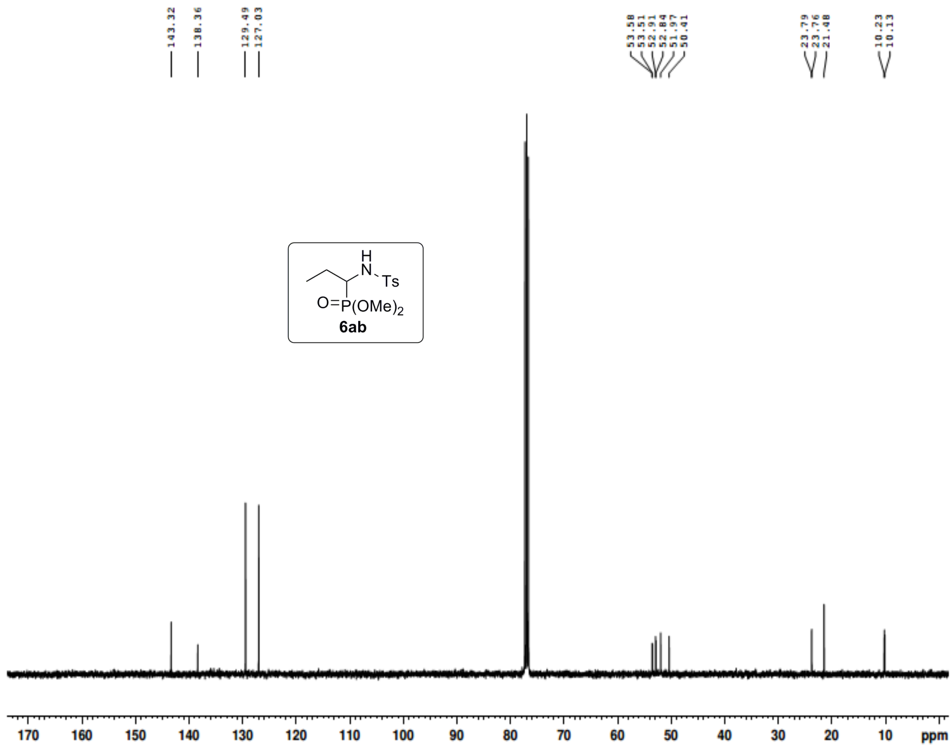

35.651
iPr
iPr
H
N
P
O
3ea
ppm

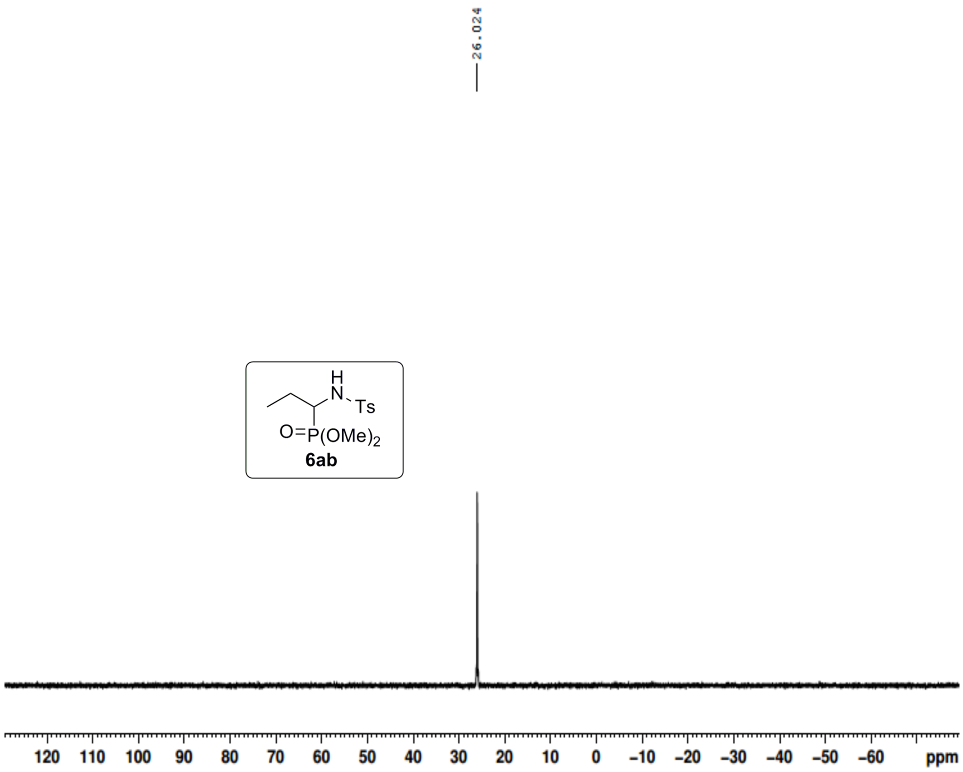

H
N
Ts
O=P(OEt)2
6aa
ppm

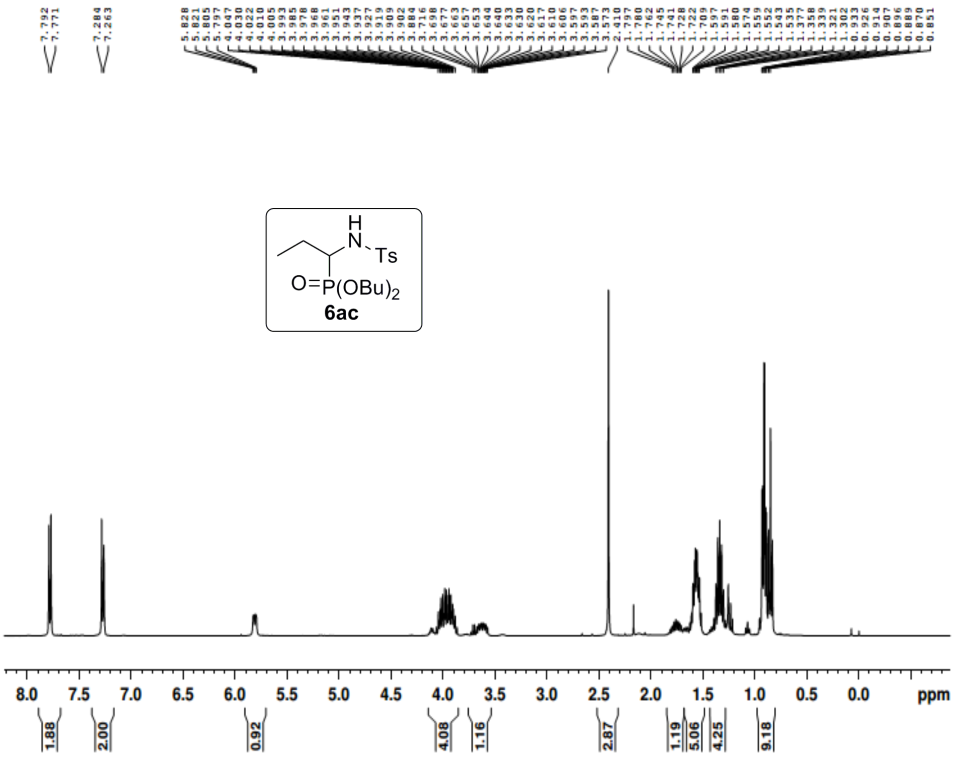

H
N
Ts
O=P(OEt)2
6aa
ppm

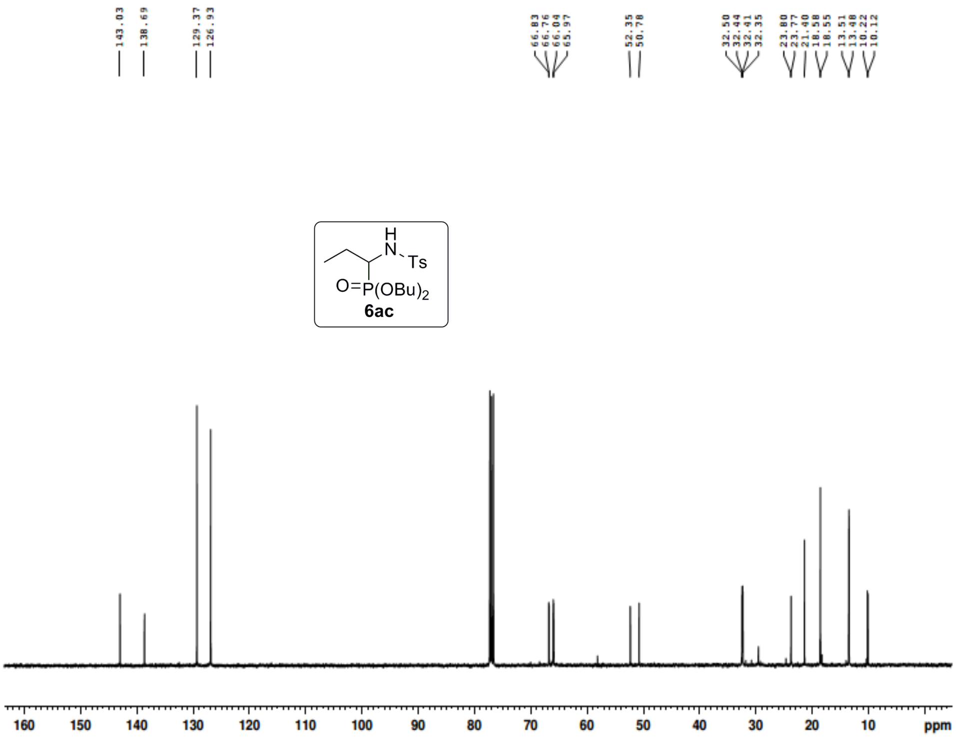

23.537
H
N
Ts
O=P(OEt)2
6aa
80
70
60
50
40
30
20
10
0
−10
−20
−30
ppm

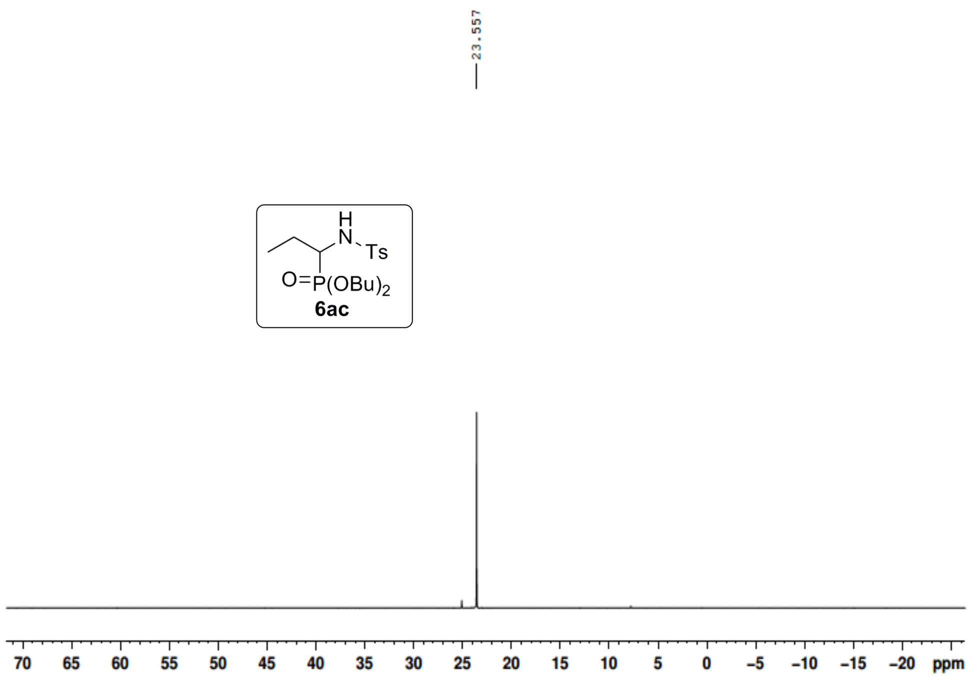

H
N
Ts
O=P(OMe)2
6ab
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
2.32
0.99
3.05
3.05
0.98
3.00
1.03
1.05
3.03

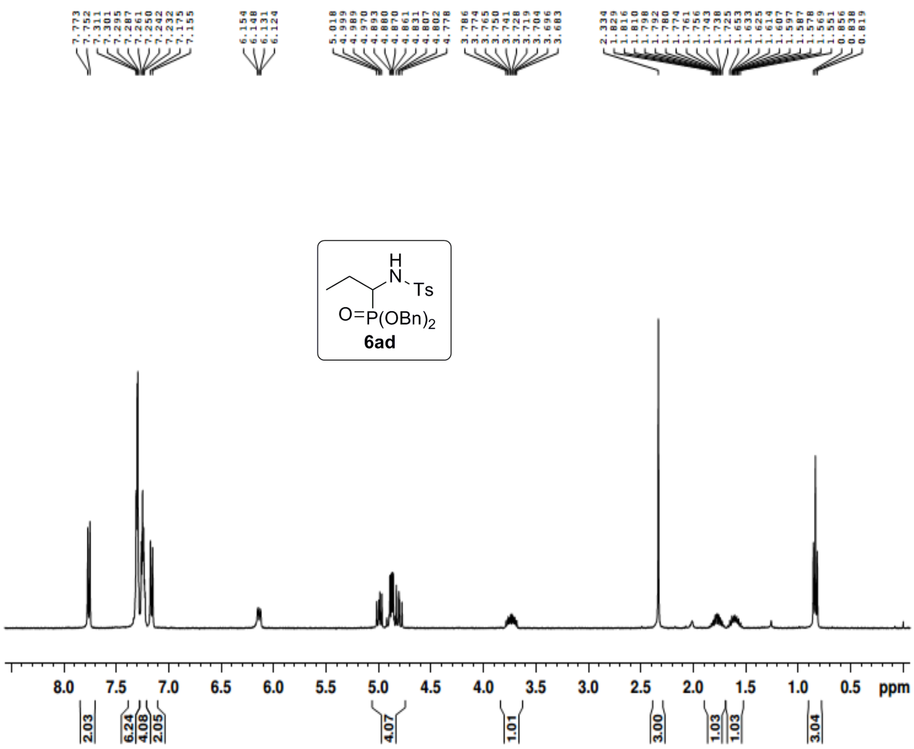

143.32
138.36
129.49
127.03
53.58
53.51
52.91
52.84
51.97
50.41
23.79
23.76
21.48
10.23
10.13
H
N
Ts
O=P(OMe)2
6ab
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

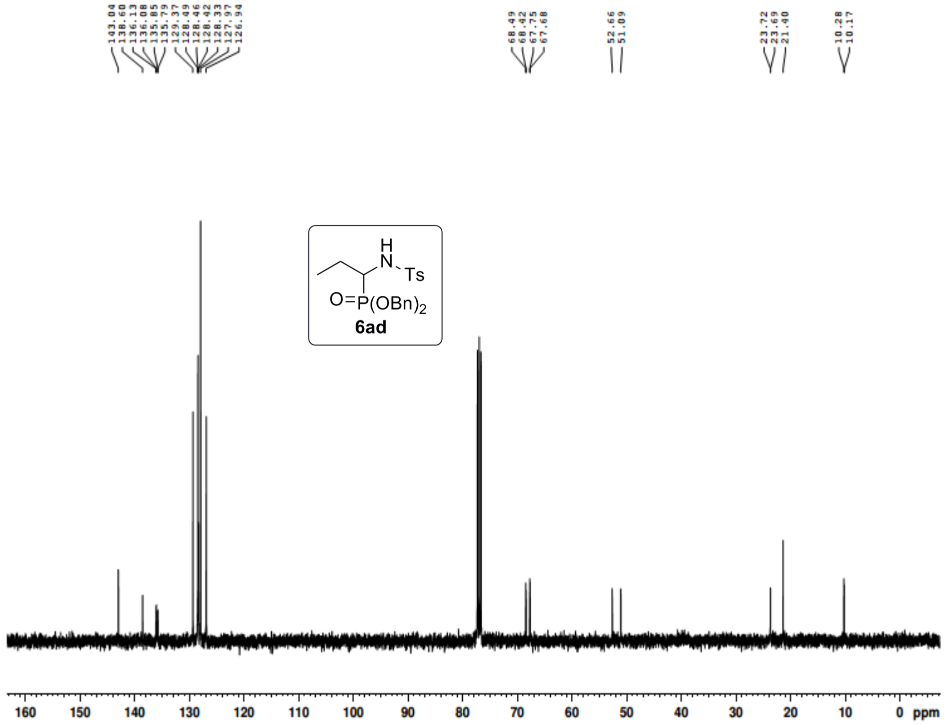

26.024
H
N
Ts
O=P(OMe)2
6ab
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 ppm

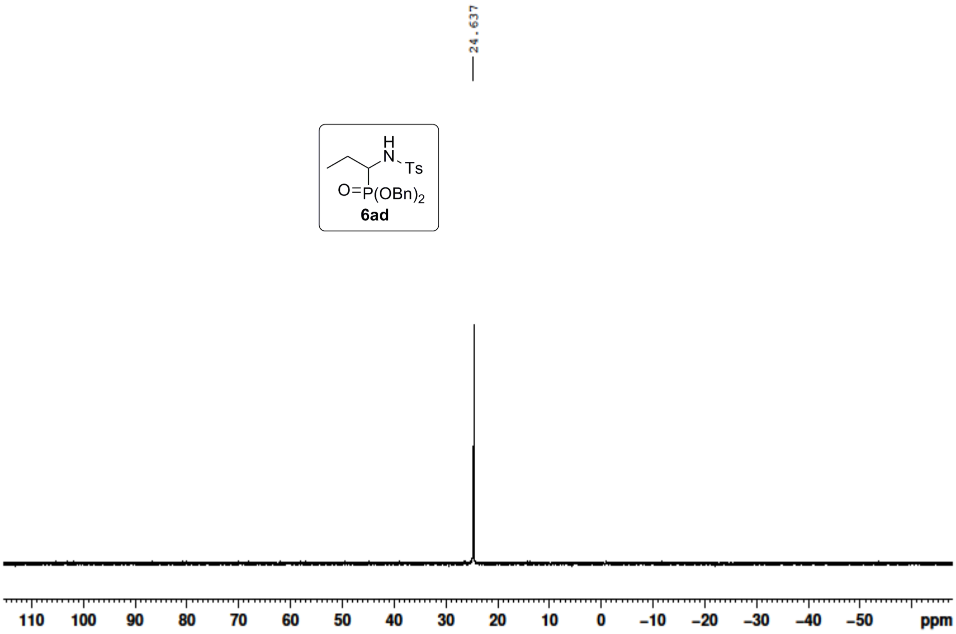

H
N
Ts
O=P(OBu)2
6ac
ppm

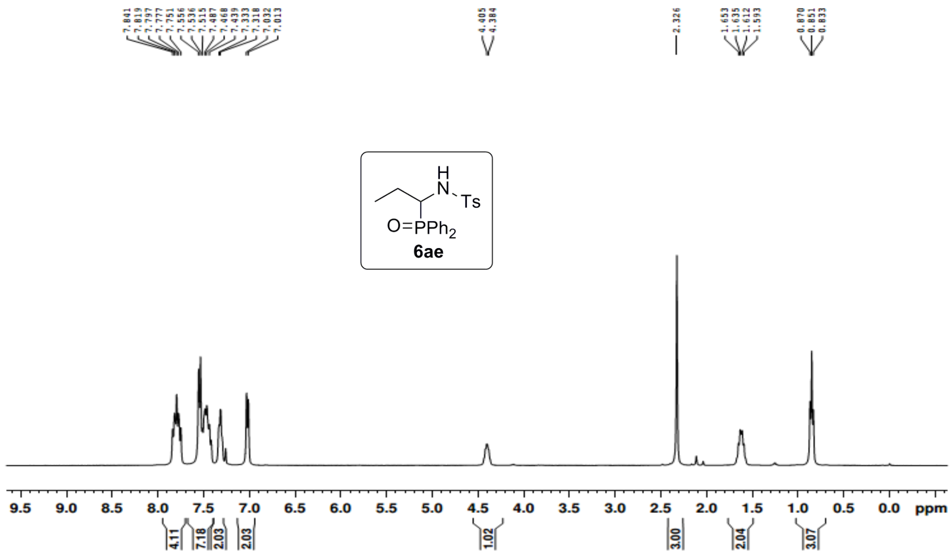

H
N
Ts
O=P(OBu)2
6ac
ppm

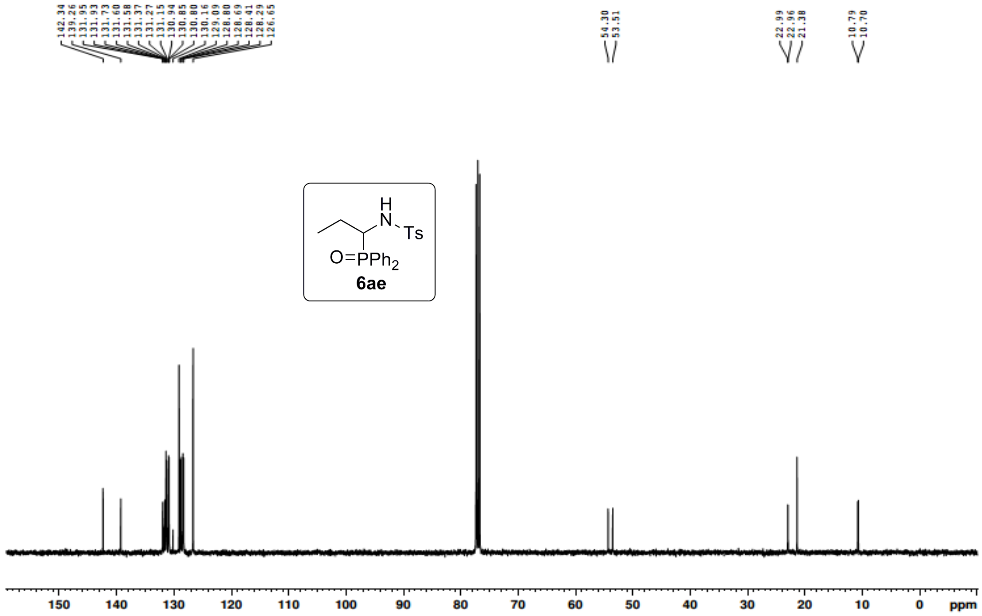

23.557
H
N
Ts
O=P(OBu)2
6ac
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 ppm

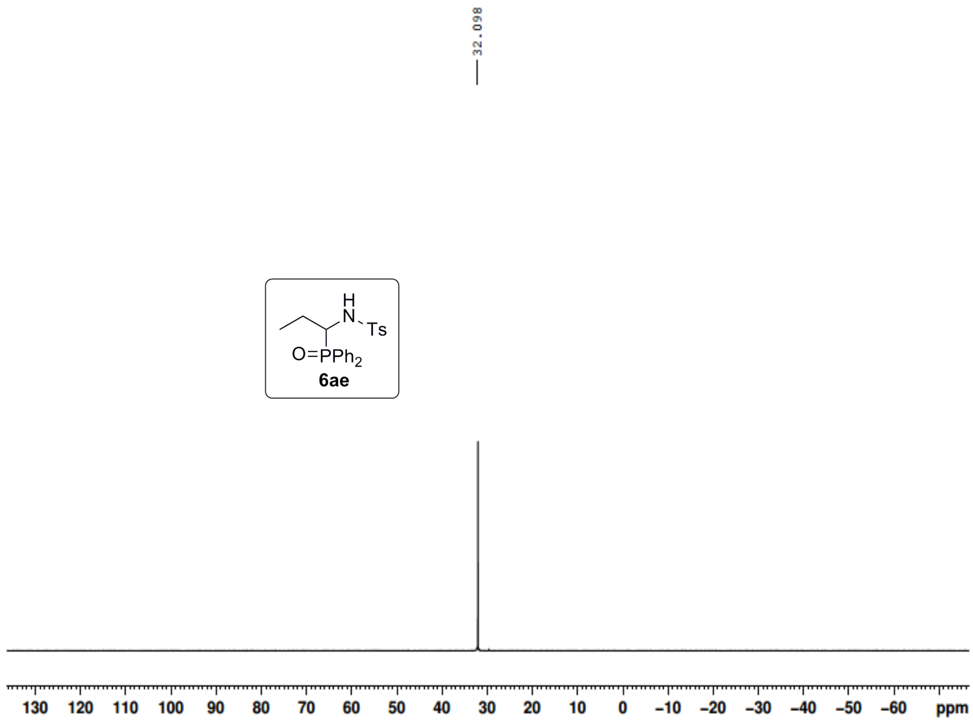

H
N
Ts
O=P(OBn)2
6ad
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.03
6.24
4.08
2.05
4.07
1.01
3.00
1.03
1.03
3.04

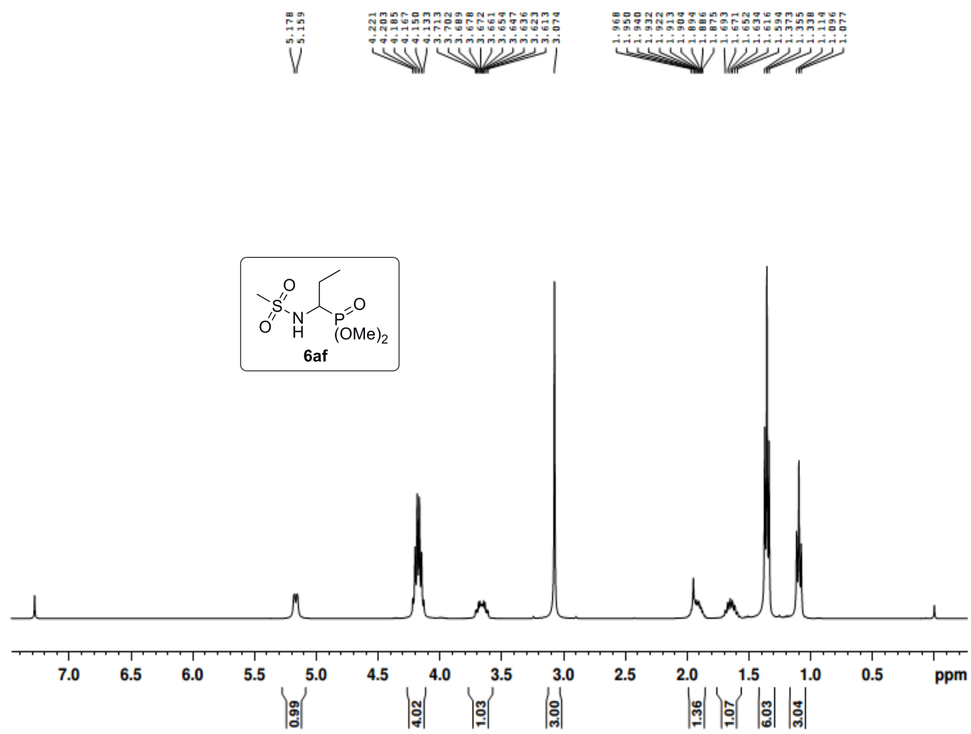

143.04
138.60
136.13
136.08
135.85
135.79
129.37
128.49
128.46
128.42
128.33
127.97
126.94
68.49
68.42
67.75
67.68
52.66
51.09
23.72
23.69
21.40
10.28
10.17
H
N
Ts
O=P(OBn)2
6ad
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

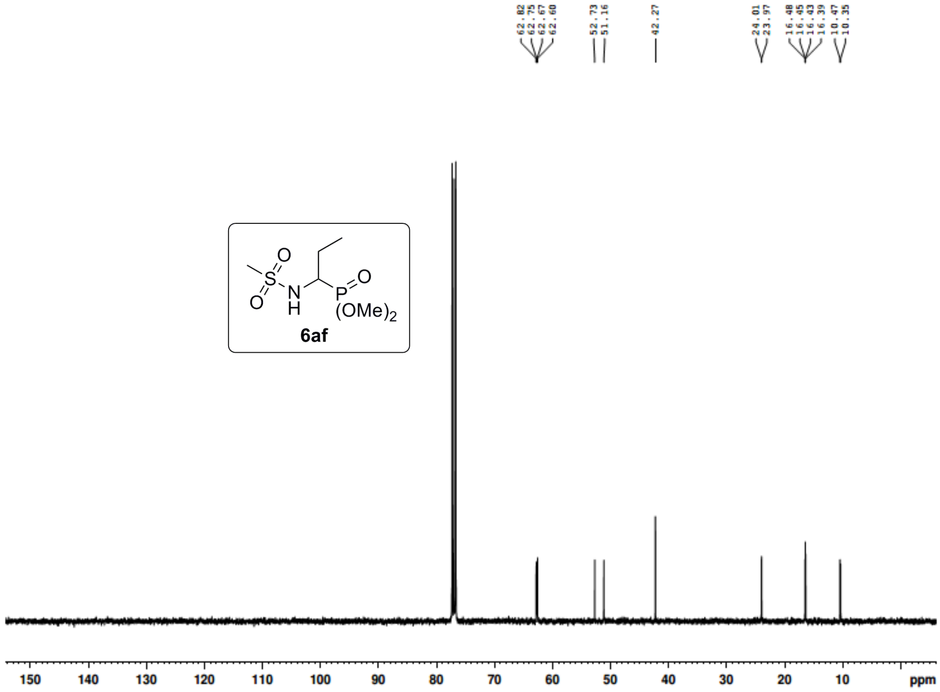

24.637
H
N
Ts
O=P(OBn)2
6ad
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
ppm

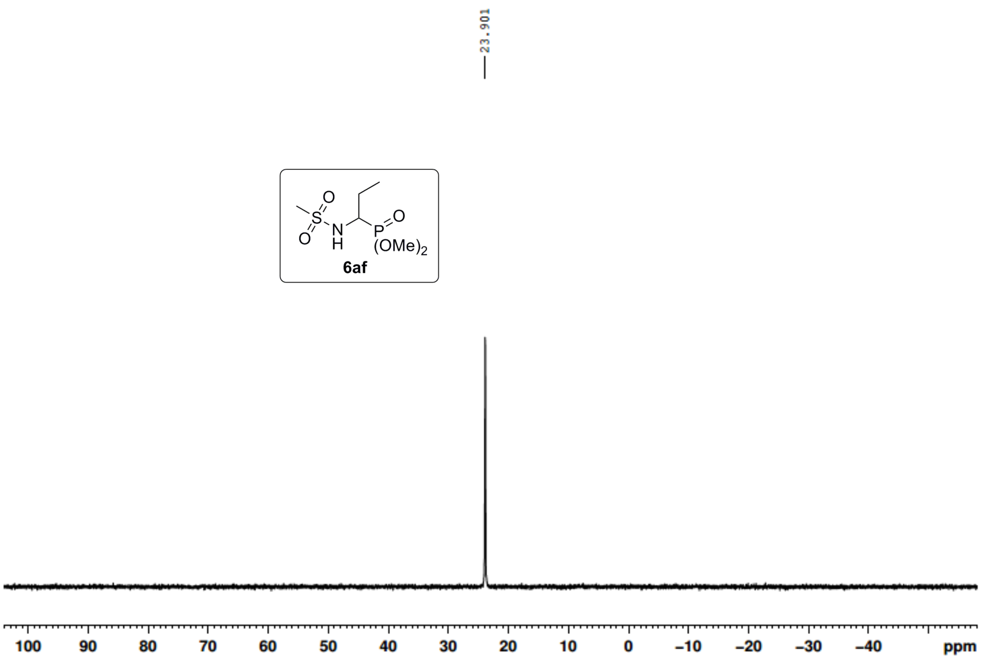

6ae
ppm

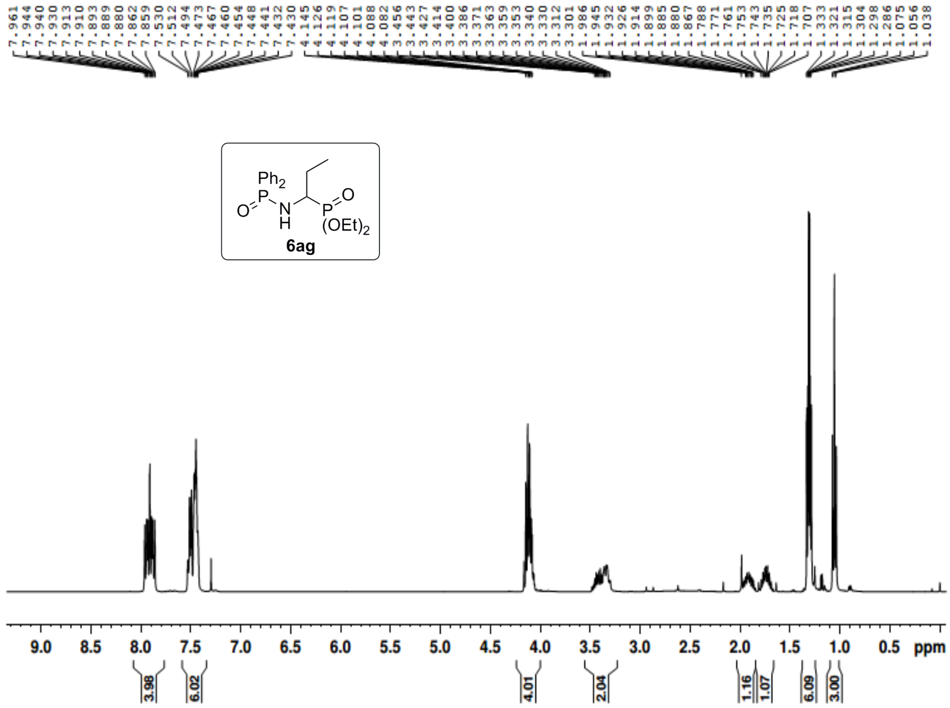

6ae
ppm

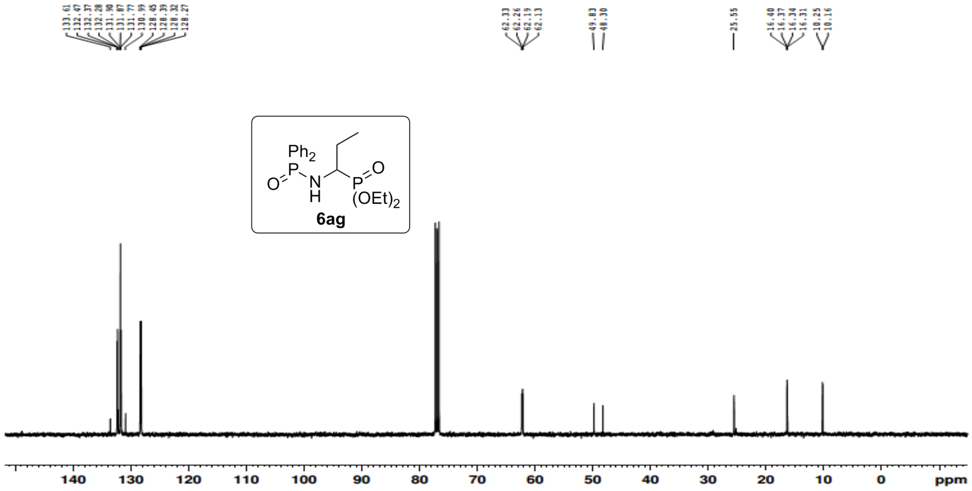

32.098
6ae
ppm

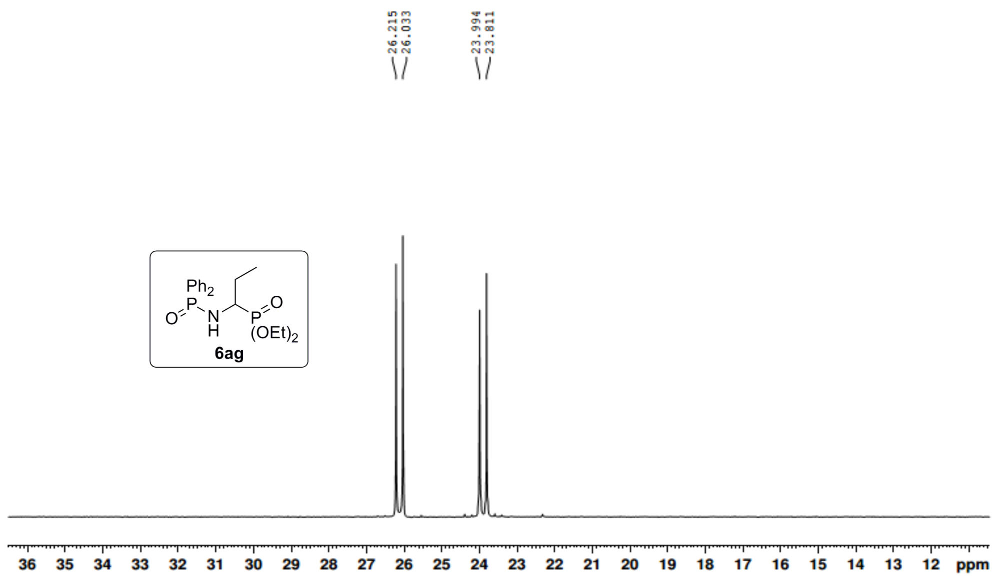

6af
ppm
0.99
4.02
1.03
3.00
1.36
1.07
6.03
3.04

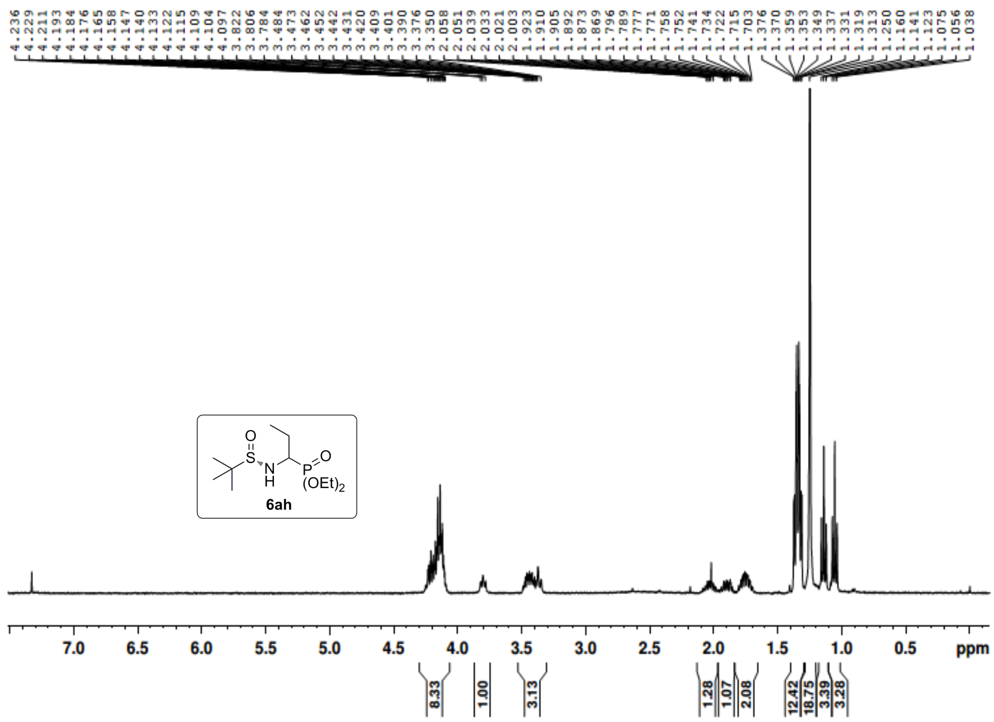

62.82
62.75
62.67
62.60
52.73
51.16
42.27
24.01
23.97
16.48
16.45
16.43
16.39
10.47
10.35
(OMe)2
6af
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

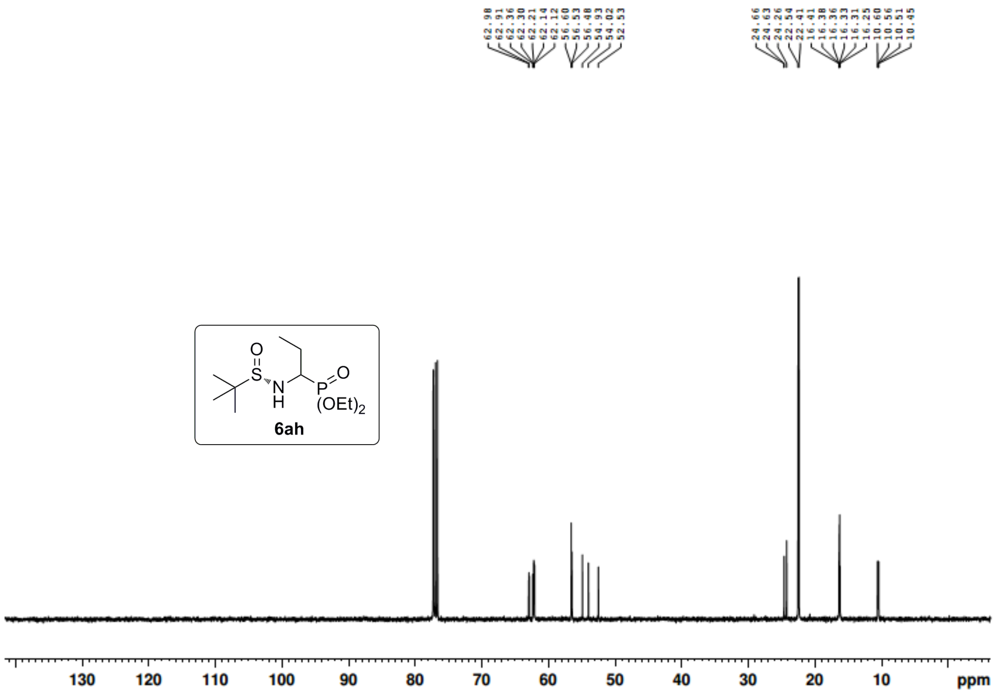

23.901
(OMe)2
6af
100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 ppm

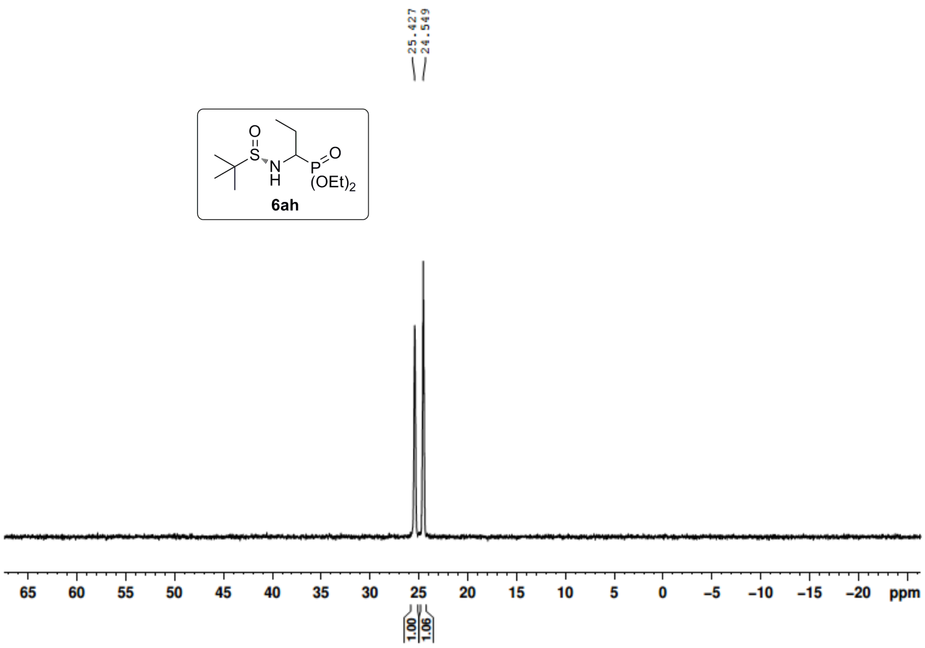


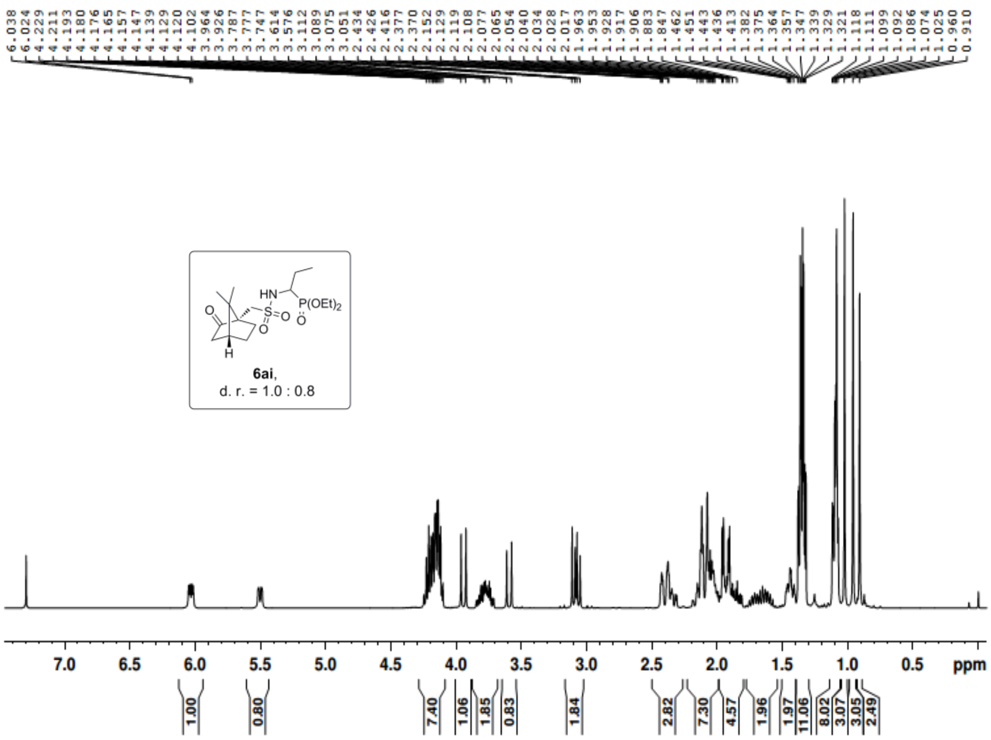


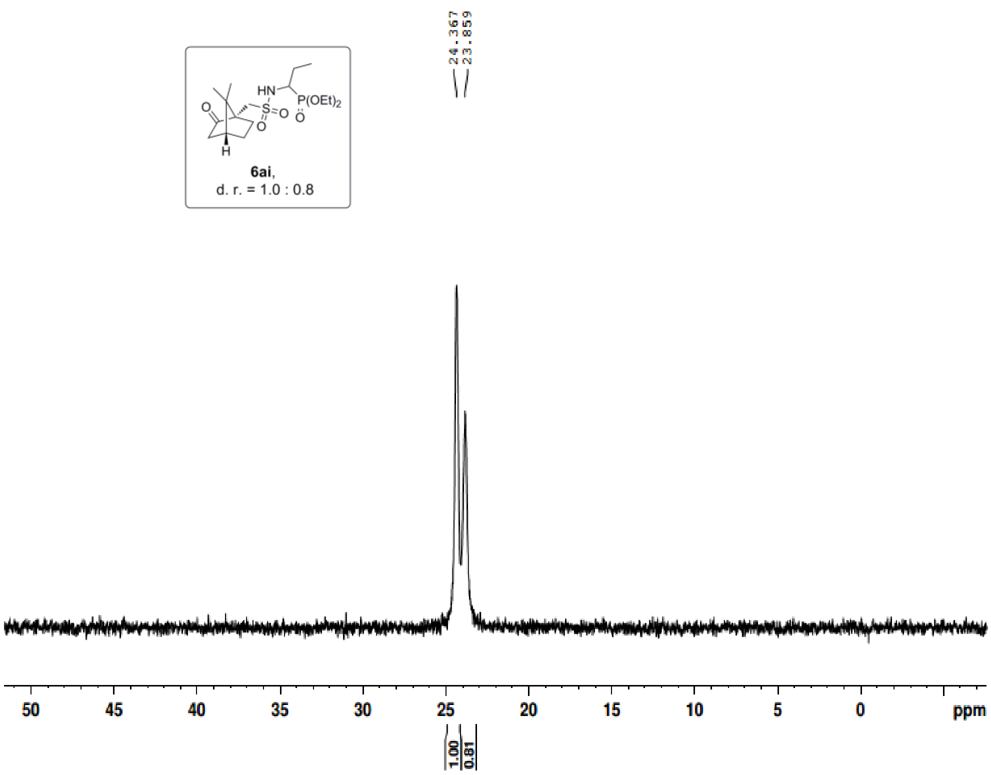

26.215
26.033
23.994
23.811
Ph2
O=P
N
H
P=O
(OEt)2
6ag
ppm

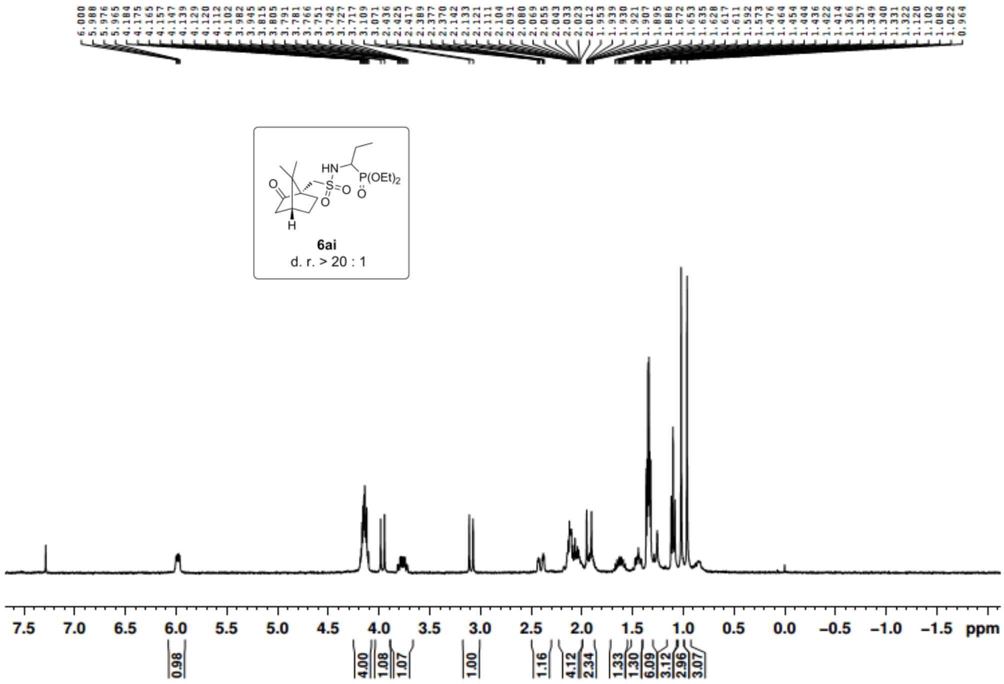

O
S
N
H
P=O
(OEt)2
6ah
ppm
8.33
1.00
3.13
1.28
1.07
2.08
12.42
18.75
3.39
3.28

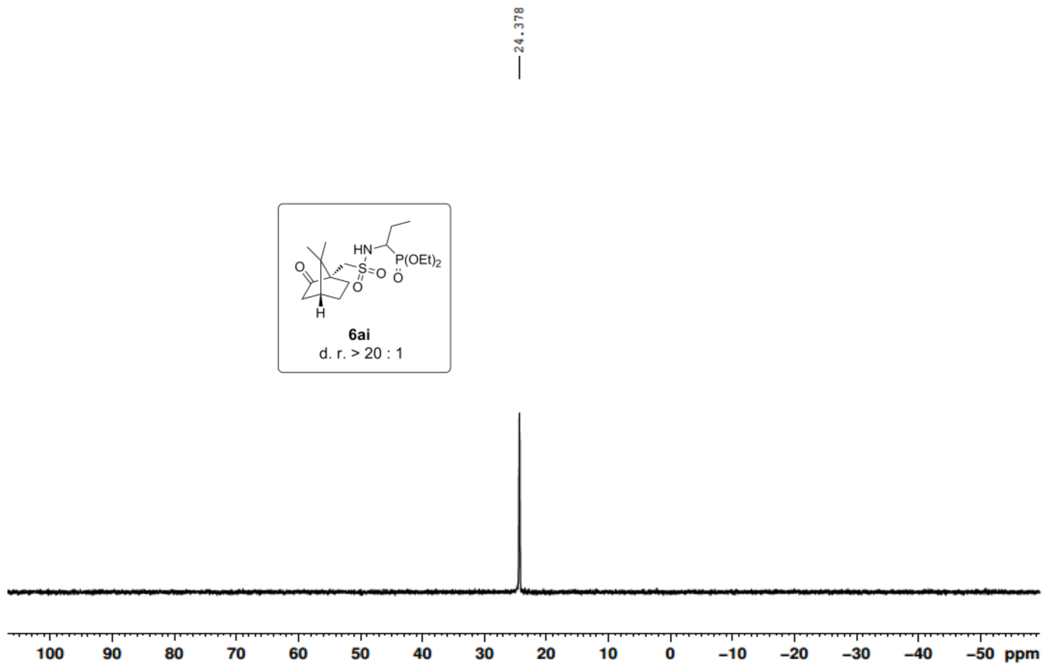

O
S
N
H
P
O
(OEt)2
6ah
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

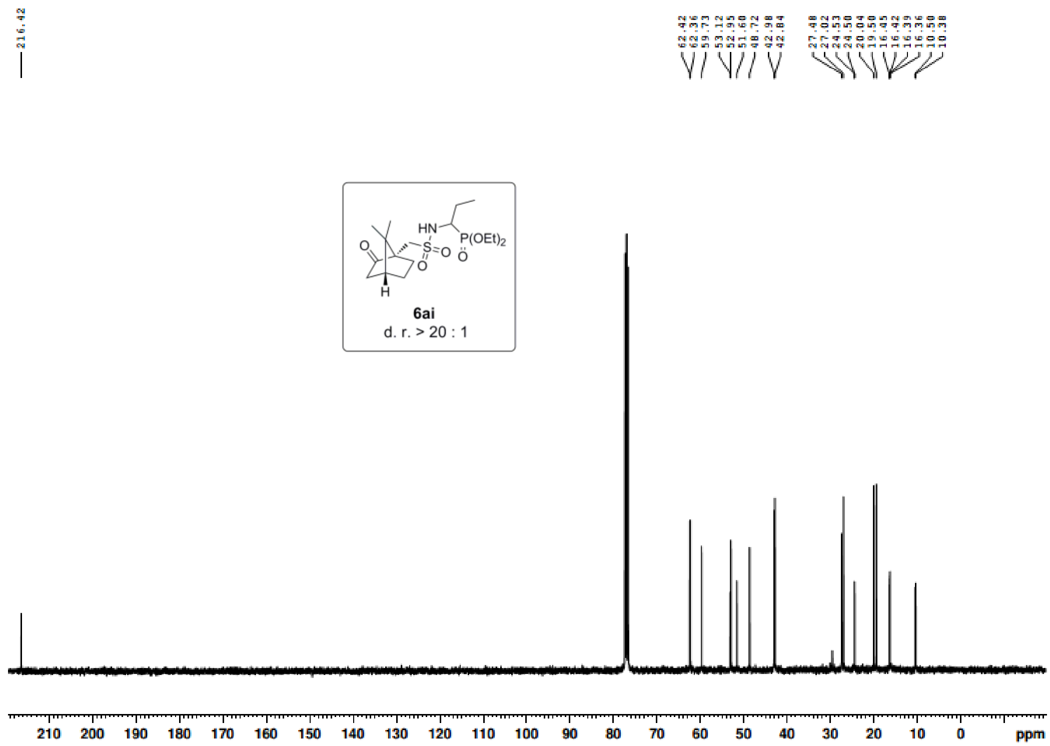

25.427
24.549
O
S
N
H
P
O
(OEt)2
6ah
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
ppm
1.00
1.06


HN
P(OEt)2
O
S=O
O
O
H
6ai,
d. r. = 1.0 : 0.8
ppm

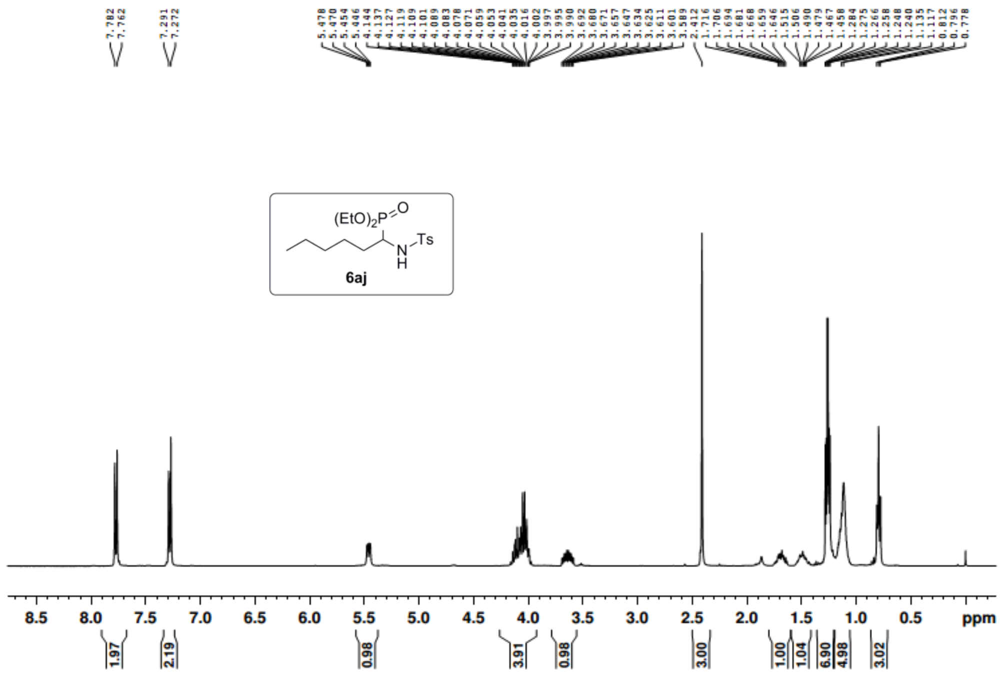

24.367
23.859
HN
P(OEt)2
O
S=O
O
O
H
6ai,
d. r. = 1.0 : 0.8
ppm


HN
P(OEt)2
O
S=O
O
H
6ai
d. r. > 20 : 1
ppm

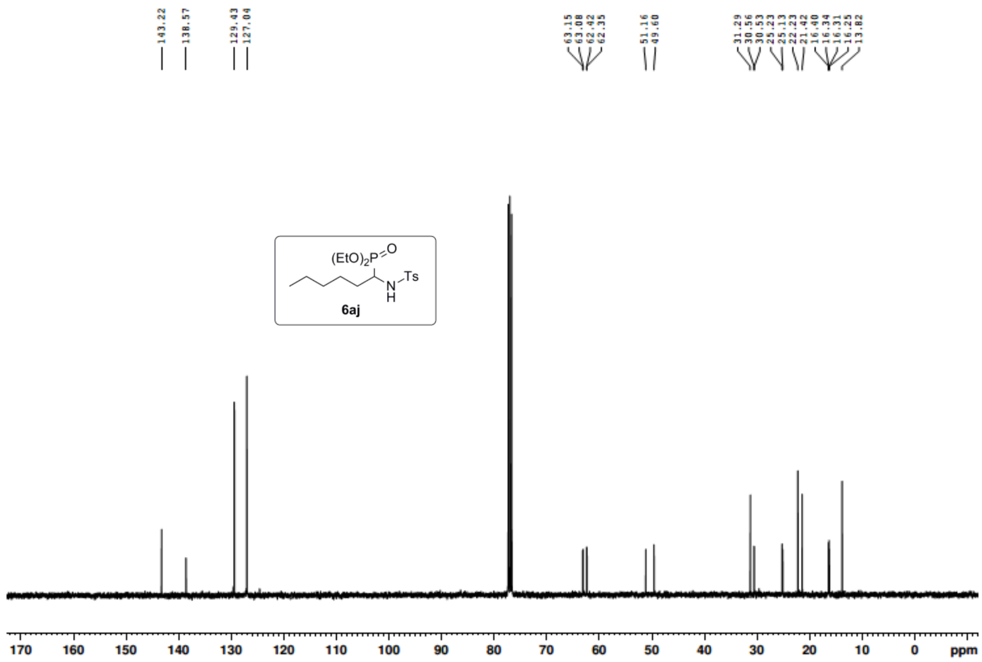

24.378
HN
P(OEt)2
O
S=O
O
H
6ai
d. r. > 20 : 1
ppm

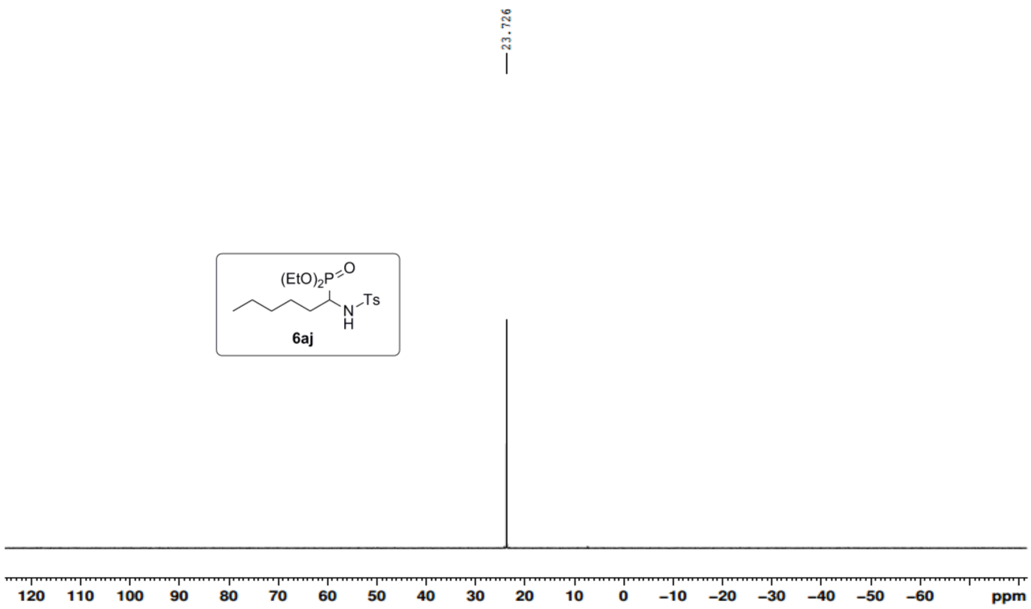


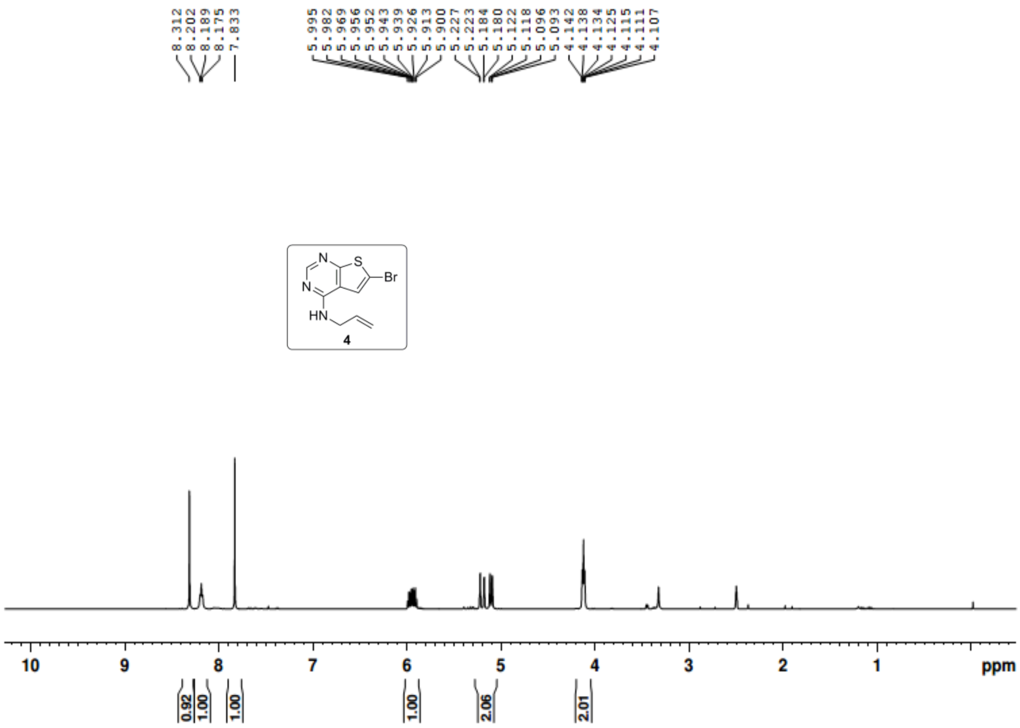
HN
P(OEt)2
S
O
O
O
H
6ai
d. r. > 20 : 1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

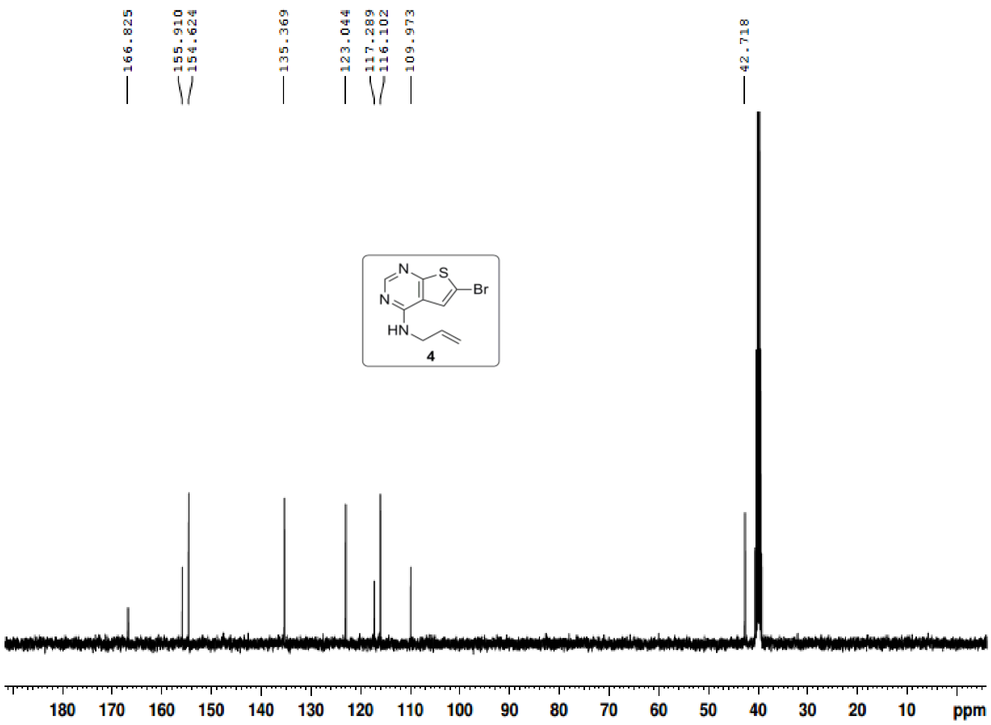


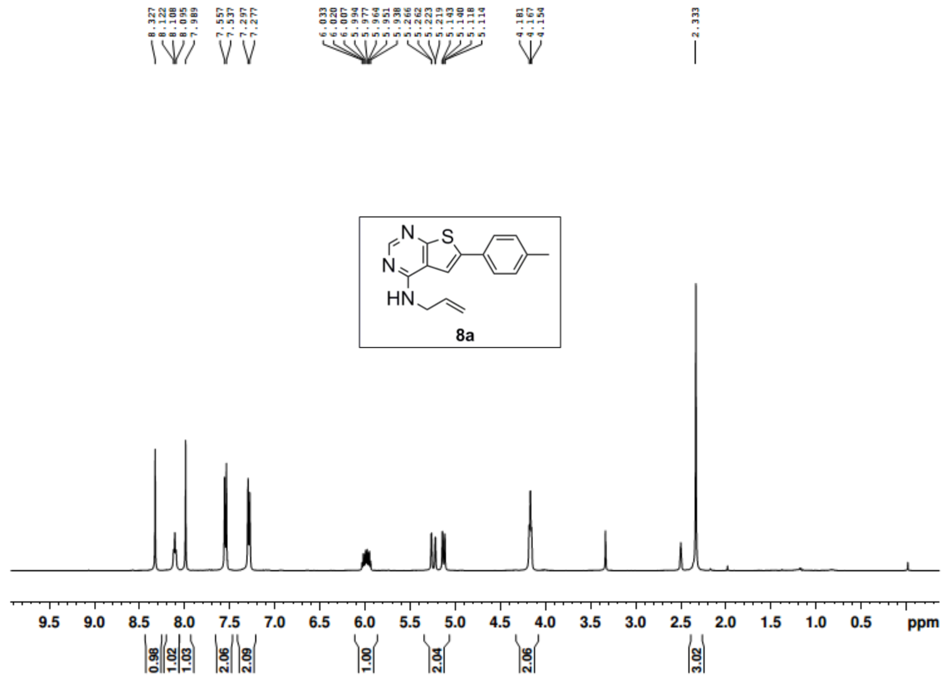
(EtO)2P=O
N
Ts
H
6aj
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.97
2.19
0.98
3.91
0.98
3.00
1.00
1.04
6.90
4.98
3.02

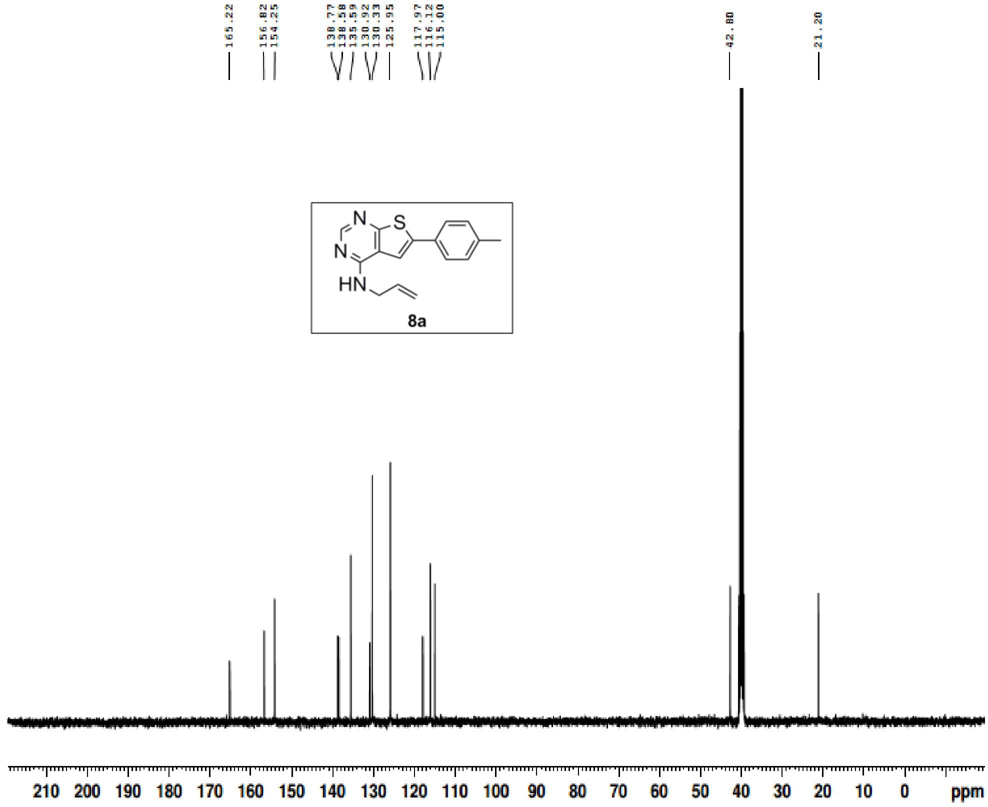

143.22
138.57
129.43
127.04
63.15
63.08
62.42
62.35
51.16
49.60
31.29
30.56
30.53
25.23
25.13
22.23
21.42
16.40
16.34
16.31
16.25
13.82
(EtO)2P=O
NHTs
6aj
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

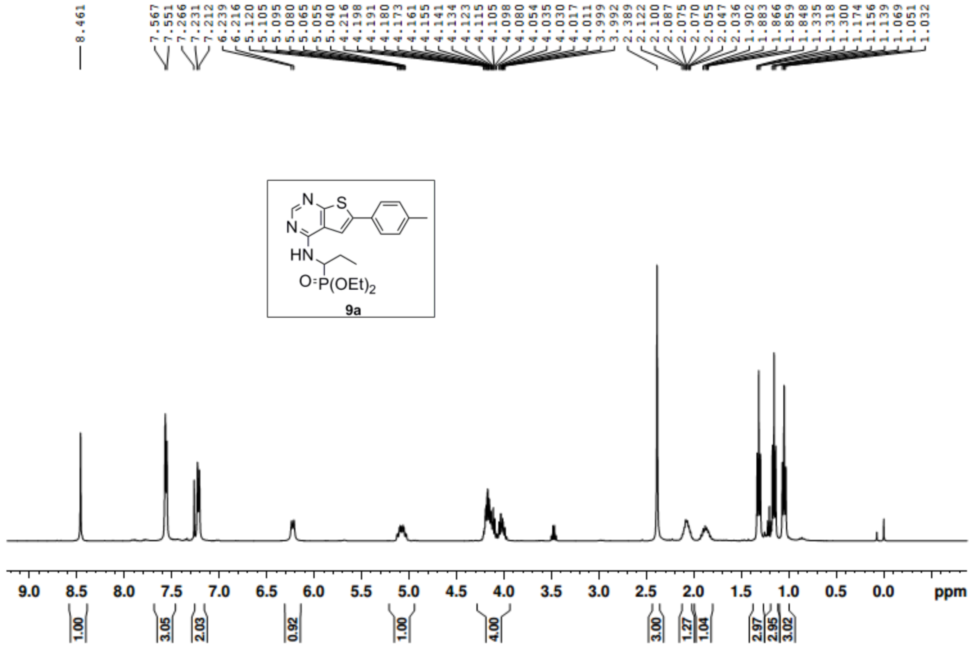

23.726
(EtO)2P=O
NHTs
6aj
120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

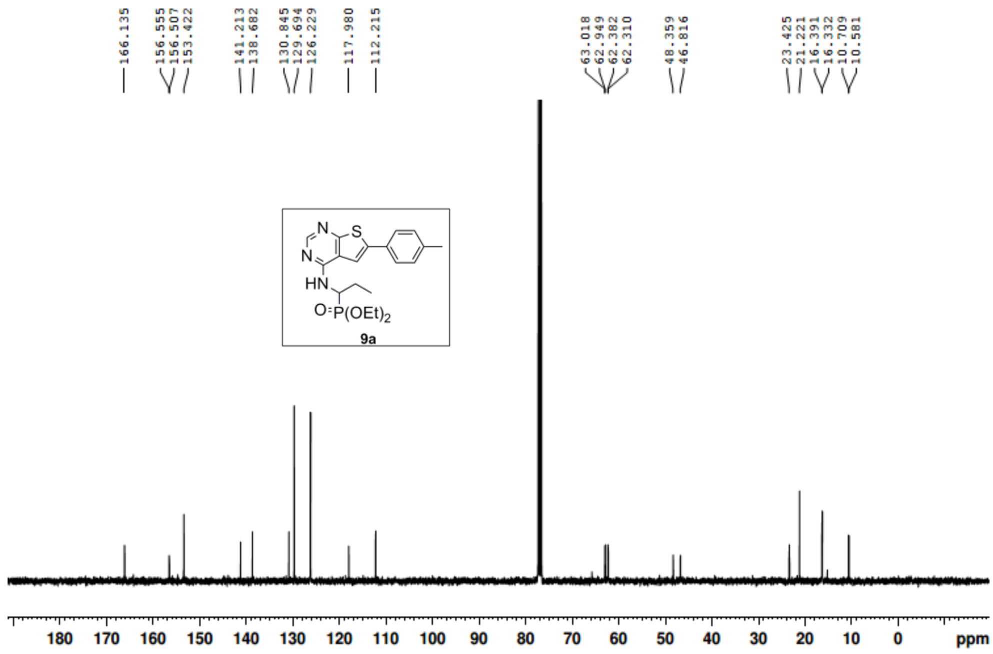

8.312
8.202
8.189
8.175
7.833
5.995
5.982
5.969
5.956
5.952
5.943
5.939
5.926
5.913
5.900
5.227
5.223
5.184
5.180
5.122
5.118
5.096
5.093
4.142
4.138
4.134
4.125
4.115
4.111
4.107
N
S
Br
N
HN
4
10 9 8 7 6 5 4 3 2 1 ppm
0.92
1.00
1.00
1.00
2.06
2.01

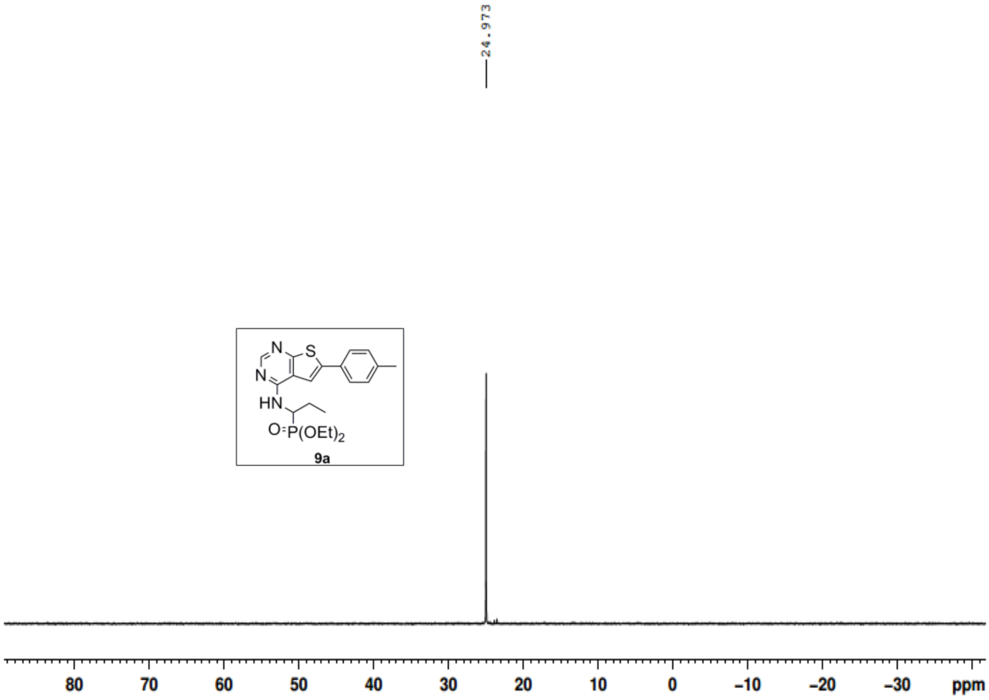

166.825
155.910
154.624
135.369
123.044
117.289
116.102
109.973
42.718
N
S
Br
N
HN
4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

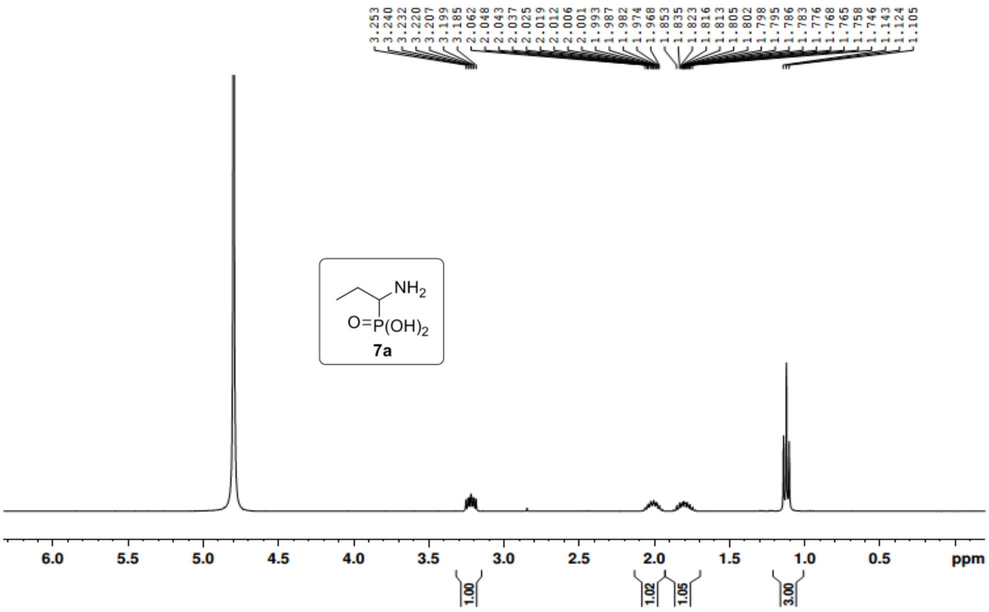

8a
ppm

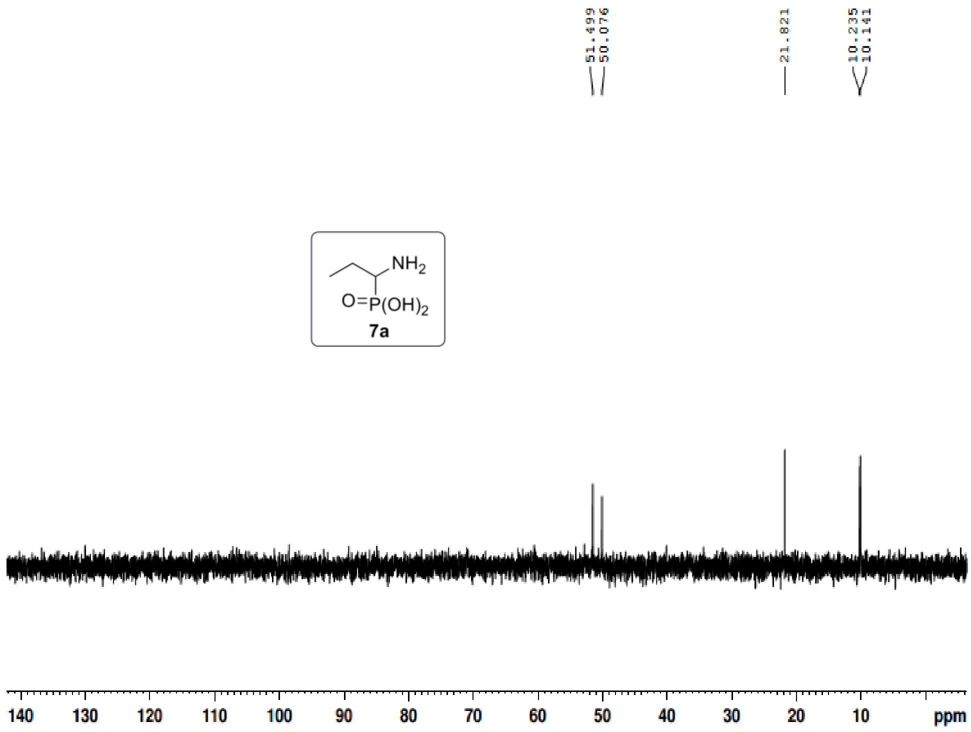

8a
ppm

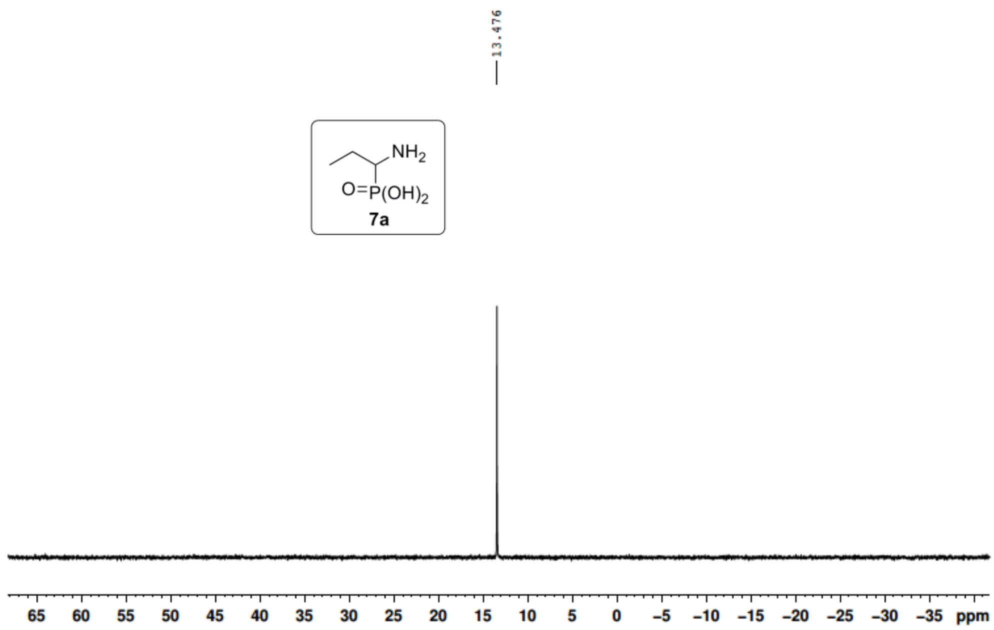

8.461
7.567
7.551
7.266
7.231
7.212
6.239
6.216
5.120
5.105
5.095
5.080
5.065
5.055
5.040
4.216
4.198
4.191
4.180
4.173
4.161
4.155
4.141
4.134
4.123
4.115
4.105
4.098
4.080
4.054
4.035
4.030
4.017
4.011
3.999
3.992
2.389
2.122
2.100
2.087
2.075
2.070
2.055
2.047
2.036
1.902
1.883
1.866
1.859
1.848
1.335
1.318
1.300
1.174
1.156
1.139
1.069
1.051
1.032
N
S
N
HN
O=P(OEt)2
9a
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
1.00
3.05
2.03
0.92
1.00
4.00
3.00
1.27
1.04
2.97
2.95
3.02


166.135
156.555
156.507
153.422
141.213
138.682
130.845
129.694
126.229
117.980
112.215
63.018
62.949
62.382
62.310
48.359
46.816
23.425
21.221
16.391
16.332
10.709
10.581
N
S
N
HN
O=P(OEt)2
9a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


24.973
N
S
N
HN
O=P(OEt)2
9a
80
70
60
50
40
30
20
10
0
−10
−20
−30
ppm


3.253
3.240
3.232
3.220
3.207
3.199
3.185
2.062
2.048
2.043
2.037
2.025
2.019
2.012
2.006
2.001
1.993
1.987
1.982
1.974
1.968
1.853
1.835
1.823
1.816
1.813
1.805
1.802
1.798
1.795
1.786
1.783
1.776
1.768
1.765
1.758
1.746
1.143
1.124
1.105
NH2
O=P(OH)2
7a
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.02
1.05
3.00


51.499
50.076
21.821
10.235
10.141
NH2
O=P(OH)2
7a
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


13.476
NH2
O=P(OH)2
7a
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
ppm