Supporting Information for

Ni-Catalyzed Asymmetric C(sp)−P Cross Coupling Reaction for the Synthesis of *P*-Stereogenic Alkynyl phosphines

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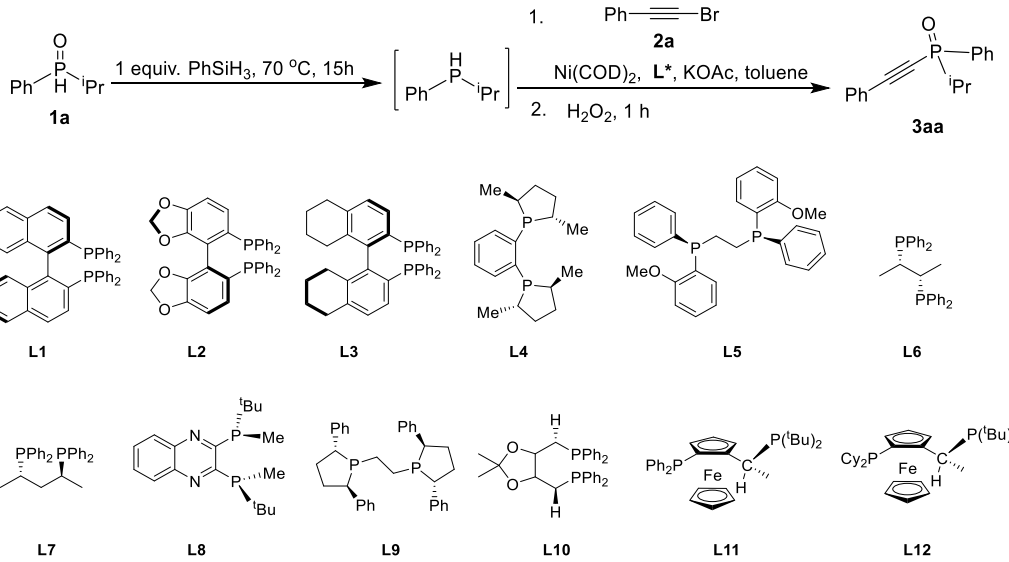
General information

Chemicals and reagents were purchased and used directly unless otherwise stated. Reactions were carried out in a glovebox flushed with N_2 and were monitored by thin-layer chromatography (TLC) on gel F254 plates. Flash column chromatography or preparative thin-layer chromatography was performed using the silica gel (300-400 mesh, GF254, respectively). All reactions were performed in a N_2 flushed glovebox unless otherwise noted. THF and toluene were distilled over sodium and degassed with N_2. Other Super dry solvents were purchased and used directly. NMR spectra (^{1}H, ^{13}C, ^{31}P, ^{19}F) spectra were recorded on Bruker Aescend^{TM} 500 MHz instruments in $CDCl_3$, DMSO-d_6, C_6D_6, acetone-d_6, CD_2Cl_2. The residual solvent peak or tetramethylsilane (TMS) is used as an internal reference. ^{1}H NMR data are reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (Hz), integration. Data for ^{13}C, ^{31}P, and ^{19}F NMR are reported in terms of chemical shifts and multiplicity where appropriate. High-resolution mass spectral analysis (HRMS) data were measured by means of the ESI technique. Enantiomer excess was determined by HPLC analysis using Darcel Chiracel columns (AD-H, OD-H, OJ-H, IA-H, IB-H and IH) and ^{n}hexane/ ^{i}PrOH as eluents. Optical rotations were measured by Perkin-Elmer-343 polarimeter. Fluorescence spectra were measured on a Fluorolog-3-Tau and deltaflex. Circularly polarized luminescence (CPL) was conducted by JASCO CPL-300 in Anhui University.

2. Optimization of reaction conditions.

Table S1. Screening of chiral ligands.[a]



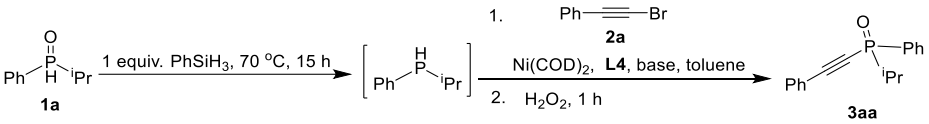
Entry	Ligand	Ee (%)[b]	Yield (%)[c]
1	L1	0	67
2	L2	0	45
3	L3	0	74
4	L4	58	62
5	L5	0	84
6	L6	-14	89
7	L7	0	20
8	L8	26	90
9	L9	4	50
10	L10	0	42
11	L11	0	80
12	L12	0	76

[a]Reaction conditions: 0.1 mmol **1a**, 0.2 mmol **2a**, 5 mol% $Ni(COD)_2$, 6 mol% Ligand and 0.2 mmol KOAc in 1 mL toluene at room temperature for 16 h under nitrogen atmosphere. Quenched with 0.2 mL 30% H_2O_2 aqueous solution.

[b]Determined by chiral HPLC analysis.

[c]NMR yield based on **1a** using $P(O)(OMe)_3$ as an internal standard.

Table S2. Screening of base.[a]



Entry	Base	Ee (%)[b]	Yield (%)[c]
1	no	0	45
2	KOAc	58	62
3	K_2CO_3	2	75
4	K_3PO_4	41	60
5	CH_3OK	56	80
6	K_2HPO_4	50	98
7	CF_3COOK	0	100
8	^tBuCOOK	60	35
9	KOH	54	51
10	DBU	38	90
11	DIEA	16	90
12	NaOAc	64	80
13	CsOAc	63	80
14	LiOAc	6	50
15[d]	NaOAc	64	85

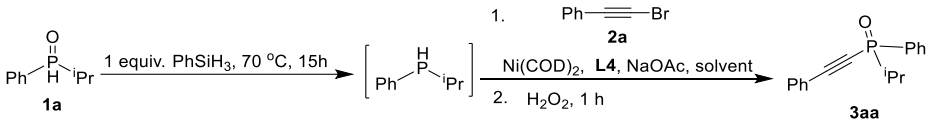
[a]Reaction conditions: 0.1 mmol **1a**, 0.2 mmol **2a**, 5 mol% $Ni(COD)_2$, 6 mol% **L4** and 0.2 mmol base in 1 mL toluene at room temperature for 16 h under nitrogen atmosphere. Quenched with 0.2 mL 30% H_2O_2 aqueous solution.

[b]Determined by chiral HPLC analysis.

[c]NMR yield based on **1a** using $P(O)(OMe)_3$ as an internal standard.

[d]0.25 mmol NaOAc was used.

Table S3. Screening of solvents.[a]



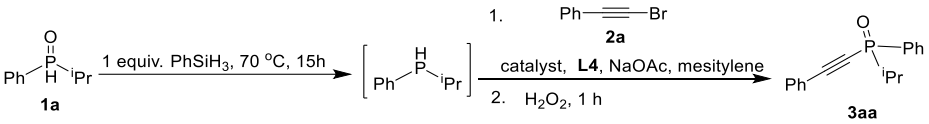
Entry	Solvent	Ee (%)[b]	Yield (%)[c]
1	toluene	64	85
2	mesitylene	66	85
3	*p*-xylene	56	70
4	THF	56	50
5	CPME	55	80
6	acetone	0	10
7	CH_3CN	0	17
8	EtOAc	60	35
9	CH_2Cl_2	2	93

[a]Reaction conditions: 0.1 mmol **1a**, 0.2 mmol **2a**, 5 mol% $Ni(COD)_2$, 6 mol% **L4** and 0.25 mmol NaOAc in 1 mL solvent at room temperature for 16 h under nitrogen atmosphere. Quenched with 0.2 mL 30% H_2O_2 aqueous solution.

[b]Determined by chiral HPLC analysis.

[c]NMR yield based on **1a** using $P(O)(OMe)_3$ as an internal standard.

Table S4. Screening of catalyst.[a]



Entry	Catalyst	Ee (%)[d]	Yield (%)[b]
1	no	0	20
2	$Ni(COD)_2$	66	84
3	$NiBr_2DME$	12	30
4	$NiCl_2DME$	2	28
5	$Ni(acac)_2$	34	36
6	$Ni(COD)_2/Zn$	32	56
7[d]	$Ni(COD)_2$	66	83

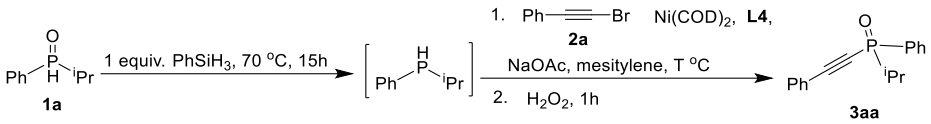
[a]Reaction conditions: 0.1 mmol **1a**, 0.2 mmol **2a**, 5 mol% catalyst, 6 mol% **L4** and 0.25 mmol NaOAc in 1 mL mesitylene at room temperature for 16 h under nitrogen atmosphere. Quenched with 0.2 mL 30% H_2O_2 aqueous solution.

[b]Determined by chiral HPLC analysis.

[c]NMR yield based on **1a** using $P(O)(OMe)_3$ as an internal standard.

[d]10 mol% catalyst and 12 mol% L4 were used.

Table S5. Screening of temperature.[a]



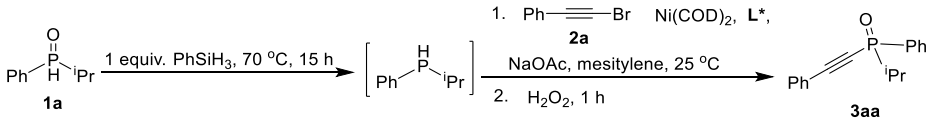
Entry	T °C	Ee (%)[b]	Yield (%)[c]
1	0	42	80
2	-10	30	50
3	25	66	84
4	35	64	87
5	50	7	87

[a]Reaction conditions: 0.1 mmol **1a**, 0.2 mmol **2a**, 5 mol% $Ni(COD)_2$, 6 mol% **L4** and 0.25 mmol NaOAc in 1 mL mesitylene at T °C for 10-50 h under nitrogen atmosphere. Quenched with 0.2 mL 30% H_2O_2 aqueous solution.

[b]Determined by chiral HPLC analysis.

[c]NMR yield based on **1a** using $P(O)(OMe)_3$ as an internal standard.

Table S6. Screening of chiral Duphos ligands.[a]



Entry	L*	Ee (%)[b]	Yield (%)[c]
1	(*S*, *S*)-Me-Duphos	66	84
2	(*S*, *S*)-Et-Duphos	75	83
3	(*S*, *S*)-^{i}Pr-Duphos	3	48
4[d,e]	(*S*, *S*)-Et-Duphos	78	84(80)

[a]Reaction conditions: 0.1 mmol **1a**, 0.2 mmol **2a**, 5 mol% $Ni(COD)_2$, 6 mol% **L*** and 0.25 mmol NaOAc in 1 mL mesitylene at 25 °C for 16 h under nitrogen atmosphere. Quenched with 0.2 mL 30% H_2O_2 aqueous solution.

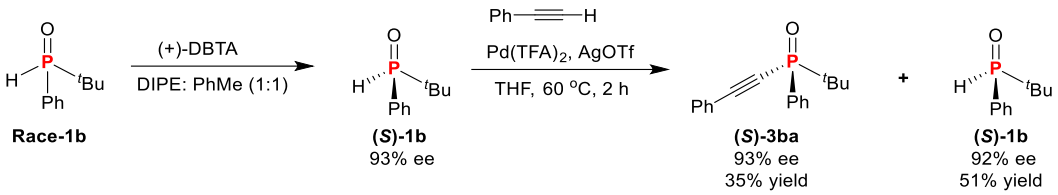
[b]Determined by chiral HPLC analysis.

[c]NMR yield based on **1a** using $P(O)(OMe)_3$ as an internal standard.

[d]0.2 mmol **1a**, 0.1 mmol **2a** were used.

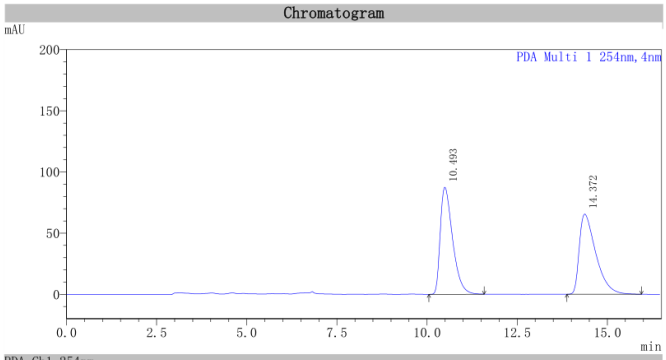
[e]Isolated yields were given in parentheses.

3. The confirmation of absolute configuration.



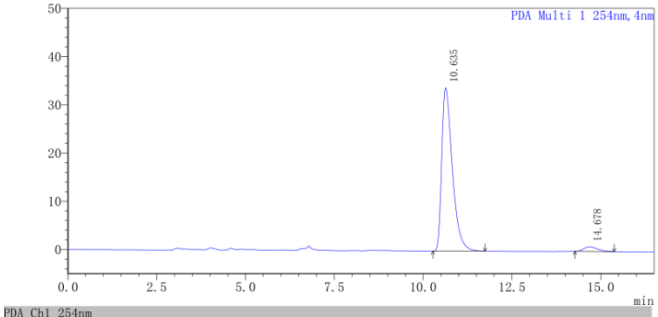
(*S*)-*tert*-butyl(phenyl)phosphine oxide (***S*)-1b** was prepared according to the following procedure[S1]: (+)-(*S*, *S*)-dibenzoyltartaric acid (590 mg, 1.65 mmol) *tert*-butyl(phenyl)phosphine oxide (250 mg, 1.37 mmol) were dissolved in little as possible refluxing diisopropyl ether/toluene (1:1). The mixture was slowly cooled down to r.t. to give the (*S*)-SPO-DBTA complex as colorless crystals. The solid was filtered and re-dissolved in 1 M NaOH (10 mL) and $CHCl_3$ (10 mL). The aqueous phase was extracted with $CHCl_3$ (5 x 5 mL). The combined organic phase was dried and concentrated under reduced pressure to give (*S*)-*tert*-butyl(phenyl)phosphine oxide.

HPLC: **Race-1b**, Chiralpak AD-H, ^{n}hexane/ ^{i}PrOH 90:10, flow: 1.0 mL/min.



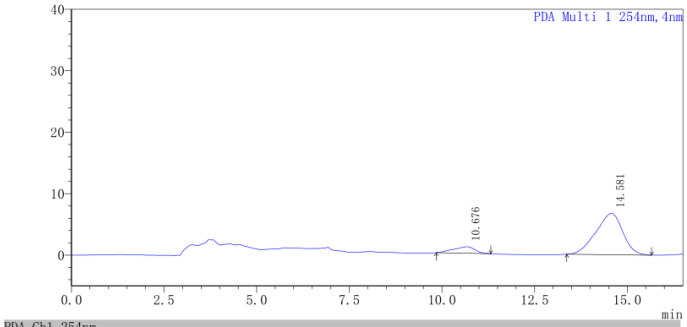
Peak#	Ret. Time	Area	Area%
1	10.493	2082461	49.880
2	14.372	2092480	50.120
Total		4174941	100.000

(*S*)-**1b**, 93% ee, t_1 = 10.6 min, Chiralpak AD-H, ^{n}hexane/ ^{i}PrOH 90:10, flow: 1.0 mL/min.



Peak#	Ret. Time	Area	Area%
1	10.635	703086	96.436
2	14.678	25980	3.564
Total		729066	100.000

(*R*)-**1b**, 78% ee, t_2 = 14.6 min, Chiralpak AD-H, ^{n}hexane/ ^{i}PrOH 90:10, flow: 1.0 mL/min.

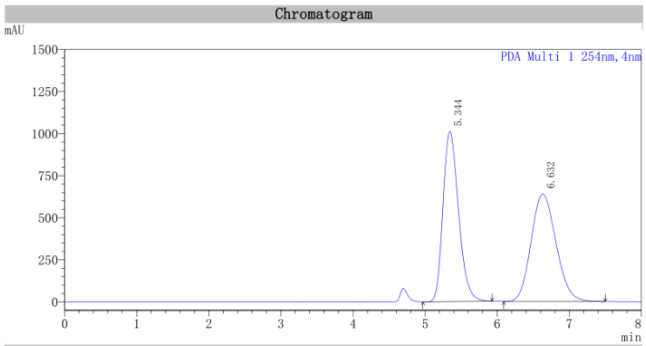


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.676	42421	11.083
2	14.581	340353	88.917
Total		382774	100.000

(*S*)-*tert*-butyl(phenyl)(phenylethynyl)phosphine oxide (***S*)-3ba** was prepared according to the following procedure[9]: Under N_2 atmosphere, 0.1 mmol **(*S*)-3b**, 0.1 mmol phenylacetylene, 10 mol% $Pd(TFA)_2$, 0.4 mmol AgOTf and 1 mL THF were charged into a 4 mL schlenck tube, the mixture was stirred at 60 °C for 2 hours. The ee% of **(*S*)-3b** and **(*S*)-3ba** were monitored by HPLC. The yields were determined by ^{31}P NMR using $P(O)(OMe)_3$ as an internal standard.

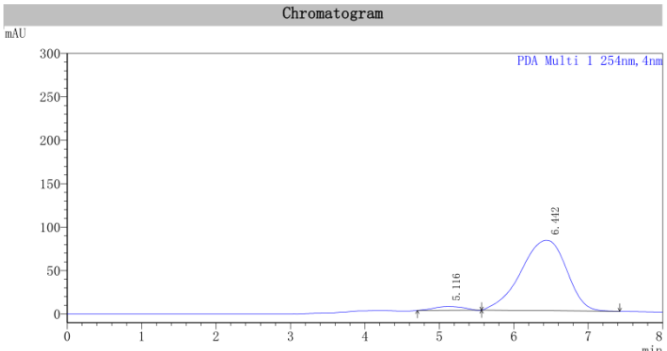
HPLC: **Race-3ba**, Chiralpak OJ-H, ^{n}hexane/ ^{i}PrOH 90:10, flow: 1.0 mL/min.



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.344	15155291	49.686
2	6.632	15346821	50.314
Total		30502112	100.000

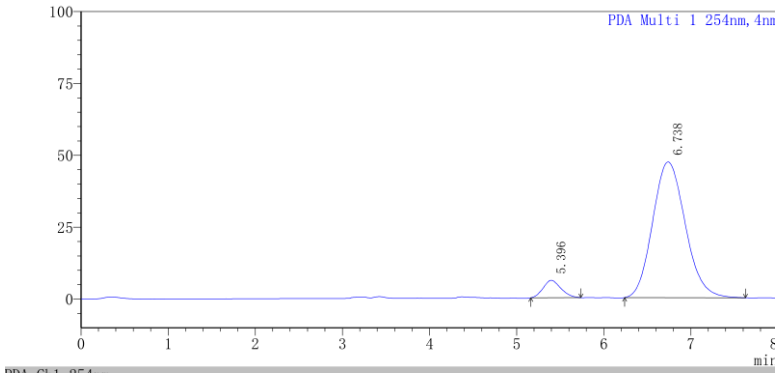
(*S*)-**3ba**, 93% ee, t_2 = 6.4 min, Chiralpak OJ-H, ^{n}hexane/ ^{i}PrOH 90:10, flow: 1.0 mL/min.



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.116	119631	3.346
2	6.442	3455447	96.654
Total		3575077	100.000

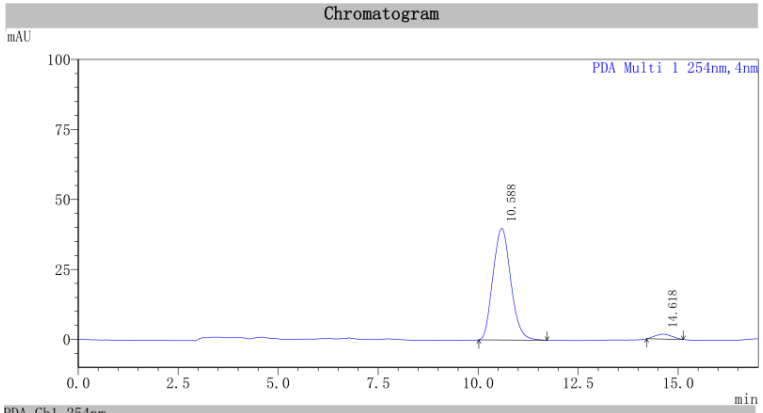
3ba, 86% ee, t_2 = 6.7 min, Chiralpak OJ-H, ^{n}hexane/ ^{i}PrOH 90:10, flow: 1.0 mL/min.



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.396	85918	6.528
2	6.738	1230283	93.472
Total		1316201	100.000

Residual (*S*)-**1b**, 92% ee, t_1 = 10.6 min, Chiralpak AD-H, ^{n}hexane/ ^{i}PrOH 90:10, flow: 1.0 mL/min.



PDA Ch1 254nm

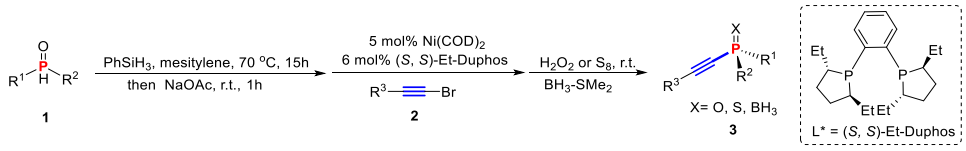
Peak#	Ret. Time	Area	Area%
1	10.588	1231443	95.993
2	14.618	51401	4.007
Total		1282844	100.000

The absolute configuration of *P*-stereogenic alkynyl phosphine oxide **3ba** *via* Ni-catalyzed asymmetric C(sp)−*P* cross coupling was unambiguously determined to be *S* according to above HPLCs.

4. General procedure for the synthesis of substrates.

Secondary phosphine oxides were synthesized according to the previous procedure[S2-S5]. Bromoalkynes were synthesized according to the previous procedure[S6].

5. Asymmetric synthesis of alkynyl phosphines.



1 **2** **3**

General procedure: Under N_2, to a 4 mL vial equipped with a stirrer bar were added secondary phosphine oxide (2 equiv., 0.2 mmol), $PhSiH_3$ (2 equiv., 0.2 mmol, 24 uL) and 0.5 mL mesitylene. Then mixture was stirred for 15 hours at 70 °C and then cooled down to r.t. NaOAc (2.5 equiv., 0.25 mmol, 20.5 mg) was added and the vial was stirred for 1 hour. To the reaction mixture were added a precooled (°C) stock solution of $Ni(COD)_2$ (5 mol%, 1.4 mg), (*S*, *S*)-Et-Duphos (6 mol%, 2.2 mg) in mesitylene (0.5 mL) and bromoalkynes (1 equiv., 0.1 mmol). The reaction was stirred for 72-96 hours at 0 °C until the disappearance of bromoalkynes indicated by TLC. The reaction was quenched with H_2O_2 (0.2 mL, 30% aqueous solution) or S_8 (16 mg, 0.5 mmol) or BH_3-SMe_2 (0.2 mmol), stirred for additional 3 hours (for 3 H_2O_2) or 6 hours (for S_8) at room temperature or 1 hour at 0 °C (for BH_3-SMe_2). The reaction mixture was separated directly by preparative thin-layer chromatography to afford the corresponding product **3**.

Racemic 3 were synthesized according to the following procedure： Under N_2, to a 4 mL vial equipped with a stirrer bar were added secondary phosphine oxide (1 equiv., 0.1 mmol), $PhSiH_3$ (1 equiv., 0.1 mmol, 12 uL) and 1 mL mesitylene. Then vial was stirred for 15 hours at 70 °C and then cooled down to r.t. NaOAc (2.5 equiv., 0.25 mmol, 20.5 mg), $Ni(COD)_2$ (5 mol%, 1.4 mg), DPPP (6 mol%, 2.7 mg), and bromoalkynes (1 equiv., 0.1 mmol) were added to the reaction mixture which was then stirred for 24 hours at r.t. until the disappearance of bromoalkynes indicated by TLC. The reaction was quenched with H_2O_2 (0.2 mL, 30% aqueous solution) or S_8 (16 mg, 0.5 mmol) or BH_3-SMe_2 (0.2 mmol), stirred for additional 3 hours (for 3 H_2O_2) or 6 hours (for S_8) at room temperature BH_3-SMe_2 (0.2 mmol). The reaction mixture was separated directly by preparative thin-layer chromatography to afford the corresponding racemic product.

6. Synthetic applications.

6.1 Gram-scale reaction.

Under N_2, to a 100 mL flask equipped with a stirrer bar were added secondary phosphine oxides **1n** (1 equiv., 5 mmol, 970 mg), $PhSiH_3$ (1 equiv., 5 mmol, 600 uL) and 25 mL mesitylene. Then flask was stirred for 24 hours at 70 °C and then cooled down to r.t. followed by the addition of NaOAc (1.5 equiv., 7.5 mmol, 615 mg). The reaction mixture was stirred for 1 hour and then cooled down to 0 °C. To the reaction mixture were added a precooled (°C) stock solution of $Ni(COD)_2$ (5 mol%, 70 mg), (*S*, *S*)-Et-Duphos (6 mol%, 110 mg) in mesitylene (0.5 mL) and bromoalkynes **2a** (1 equiv., 5 mmol). The reaction was stirred for 96 hours at 0 °C until the disappearance of bromoalkynes indicated by TLC. The reaction was quenched with S_8 (800 mg, 75 mmol), stirred for additional 12 hours at room temperature. The reaction mixture was separated directly by preparative thin-layer chromatography to afford the corresponding product **3na** (842 mg, 54% yield, 87% ee).

6.2 1,2-Addition.

The alkynyl phosphine oxide **3na-O** (0.2 mmol, 59 mg), H_2O (1 mmol, 18 mg) and $PdCl_2$ (0.02 mmol, 3.5 mg) were dissolved in 1,4-dioxane (2 mL) in a 4 mL vial and stirred at 80 °C for 24 h. The resulting mixture was concentrated under vacuum and the crude product was purified by silica gel chromatography with petroleum ether and ethyl acetate as the eluent to afford the corresponding product **4** (45.9 mg, 73% yield, and 84% ee).

6.3 Radical addition/cyclization.

Under N_2, to a 10 mL flask equipped with a stirrer bar was added alkynyl phosphine oxide **3ba** (0.2 mmol, 56 mg), $Ph_2P(O)H$ (0.6 mmol, 122 mg), $K_2S_2O_8$ (1 mmol, 270 mg) and 5 mL CH_3CN. The reaction mixture was stirred at 90 °C for 24 h. The mixture was cooled down to room temperature and subjected to flash chromatography (petroleum ether/ethyl acetate) to afford the corresponding product **5** (56.0 mg, 58% yield, 86% ee, and 3:1 dr).

6.4 Synthesis of *P*-stereogenic phosphepines.

Under N_2, to a mixture of alkynyl phosphine oxide **3wp** (2 mmol, 876 mg) and Na_2HPO_4 (4 mmol, 568 mg) in MeCN (20 mL) was added ICl (6 mmol, 972 mg) dropwise. The reaction was stirred at room temperature for 1 h, and was then quenched by $Na_2S_2O_3$ (10 % aq., 10 mL), diluted with ethyl acetate (10 mL). The organic phase was sequentially washed with water, brine, dried with anhydrous $MgSO_4$ and filtered. The filtration was concentrated under reduced pressure to give the crude product which was used directly without further purification. To the crude product, (4-methoxyphenyl) boronic acid (4 mmol, 608 mg) and K_2CO_3(4 mmol, 553 mg) in degassed solvents (DMF/H_2O= 9 mL/1 mL) was added $Pd(PPh_3)_4$ (0.2 mmol, 115 mg). The reaction mixture was heated at 90 °C under nitrogen for 30 h. The solution was cooled to room temperature and was added saturated aqueous NH_4Cl (10 mL). The mixture was extracted with ethyl acetate (10 mL), the organic phase was washed with water, brine, dried with

anhydrous $MgSO_4$ and filtered. The filtration was concentrated under reduced pressure to give a crude product which was purified by column chromatography on silica gel to give the corresponding product **6** with 560 mg**,** 53% yield, and 64% ee (317 mg, 30% yield, and 99% ee from recrystallization by EA and Et_2O)**.**

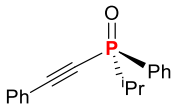
6.5 Measurements of photoluminescence (PL) spectra.

Sample solutions were prepared according to the following procedure： **6** (1.6 mg, 3×10^{-3} mmol) was respectively dissolve in 30 mL 0%, 30%, 60%, and 90% (different water fractions) THF/water mixtures.

6.6 Preparation of chiral composite films.

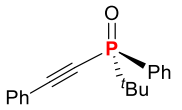
The composite films were prepared as follows. **6** (10 mg) and PMMA (0.5g) were dissolved in 6 mL $CHCl_3$ and cast onto a glass petri dish. The $CHCl_3$ was then evaporated under ambient condition and the film with a uniform thickness of approximately 0.3 mm were obtained.

7. Spectroscopic data of products.



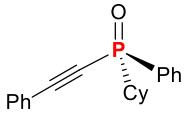
3aa

Colorless oil, R_f = 0.31 (PE/EA = 2:1), 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.60 – 7.53 (m, 3H), 7.53 – 7.47 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 2.29 – 2.17 (m, 1H), 1.27 (dd, *J* = 12.7, 6.2 Hz, 3H), 1.23 (dd, *J* = 12.3, 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.38 (d, *J* = 1.4 Hz), 132.14 (d, *J* = 2.7 Hz), 130.92 (d, *J* = 9.8 Hz), 130.67 (d, *J* = 112.2 Hz), 130.54 (s), 128.54 (s), 128.48 (d, *J* = 13.1 Hz), 119.90 (d, *J* = 3.7 Hz), 104.18 (d, *J* = 25.6 Hz), 81.58 (d, *J* = 152.1 Hz), 31.48 (d, *J* = 84.3 Hz), 15.51 (d, *J* = 1.6 Hz), 15.10 (d, *J* = 2.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.49. HRMS (ESI) calcd for $C_{17}H_{18}OP^+$ $[M+H]^+$ 269.1090, Found 269.1099. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (78% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 7.71 min, *t* (minor) = 6.00 min. $[\alpha]_D^{20}$ = -2.5 (*c* = 0.76, acetone).



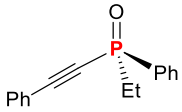
3ba

Colorless oil, R_f = 0.35 (PE/EA = 2:1), 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.60 (dt, *J* = 4.4, 1.9 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.53 – 7.47 (m, 2H), 7.46 (dd, *J* = 6.9, 4.6 Hz, 1H), 7.42 – 7.36 (m, 2H), 1.25 (d, *J* = 16.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.52 (d, *J* = 1.3 Hz), 132.13 (d, *J* = 2.7 Hz), 132.03 (d, *J* = 9.4 Hz), 130.56 (s), 129.55 (d, *J* = 109.3 Hz), 128.62 (s), 128.20 (d, *J* = 12.1 Hz), 120.16 (d, *J* = 3.6 Hz), 104.41 (d, *J* = 24.3 Hz), 81.32 (d, *J* = 149.2 Hz), 34.13 (d, *J* = 83.1 Hz), 23.91 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.30. HRMS (ESI) calcd for $C_{18}H_{20}OP^+$ $[M+H]^+$ 283.1246, Found 283.1259. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (86% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 262 nm, *t* (major) = 6.74 min, *t* (minor) = 5.40 min. $[\alpha]_D^{20}$ = -22.1 (*c* = 0.38, acetone).



3ca

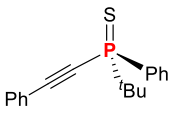
Colorless oil, R_f = 0.3 (PE/EA = 2:1), 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92-7.88 (m, 2H), 7.60-7.58 (m, 2H), 7.57 – 7.54 (m, 1H), 7.54 – 7.48 (m, 2H), 7.47 – 7.41 (m, 1H), 7.40 – 7.35 (m, 2H), 2.06 – 1.91 (m, 3H), 1.88-1.79 (m, 2H), 1.73-1.66 (m, 1H), 1.50 – 1.35 (m, 2H), 1.32 – 1.14 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.49 (d, *J* = 1.5 Hz), 132.09 (d, *J* = 2.7 Hz), 131.03 (d, *J* = 9.9 Hz), 130.85 (d, *J* = 112.2 Hz), 130.52 (s), 128.57 (s), 128.49 (d, *J* = 12.7 Hz), 120.12 (d, *J* = 3.7 Hz), 104.13 (d, *J* = 25.3 Hz), 81.95 (d, *J* = 152.4 Hz), 41.38 (d, *J* = 84.8 Hz), 26.21 (d, *J* = 4.3 Hz), 26.09 (d, *J* = 3.9 Hz), 25.78 (d, *J* = 1.3 Hz), 25.31 (d, *J* = 2.6 Hz), 24.90 (d, *J* = 2.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 22.58. HRMS (ESI) calcd for $C_{20}H_{22}OP^+$ $[M+H]^+$ 309.1403, Found 309.1407. The enantiomeric excess was determined by Daicel Chiralcel IA-H (74% ee), *n*-Hexanes/IPA = 75/25, 1 mL/min, λ = 250 nm, *t* (major) = 16.76 min, *t* (minor) = 12.87 min. $[\alpha]_D^{20}$ = 0.4 (*c* = 1.02, acetone).



3da

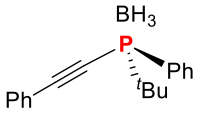
Colorless oil, R_f = 0.2 (PE/EA = 2:1), 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.60 – 7.49 (m, 5H), 7.47 – 7.41 (m, 1H), 7.40 – 7.34 (m, 2H), 2.15 (dq, *J* = 15.1, 7.6 Hz, 2H), 1.25 (dt, *J* = 20.1, 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.47 (d, *J* = 1.6 Hz), 132.22 (d, *J* = 2.7 Hz), 131.86 (d, *J* = 115.2 Hz), 130.56 (d, *J* = 3.6 Hz), 130.46 (s), 128.69 (d, *J* = 12.9 Hz), 128.58 (s), 120.01 (d, *J* = 3.7 Hz), 103.88 (d, *J* = 27.5 Hz), 82.48 (d, *J* = 156.6 Hz), 27.01 (d, *J* = 85.1 Hz), 6.10 (d, *J* = 5.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.93. HRMS (ESI) calcd for $C_{16}H_{16}OP^+$ $[M+H]^+$ 255.0933, Found 255.0943. The enantio-

meric excess was determined by Daicel Chiralcel OJ-H (29% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 262 nm, *t* (major) = 9.14 min, *t* (minor) = 7.80 min. $[\alpha]_D^{20}$ = -2.1 (*c* = 1.02, acetone).



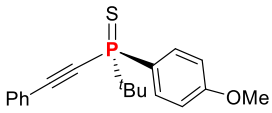
3ea

Colorless oil, R_f = 0.30 (PE/EA = 30:1), 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 13.4, 7.3 Hz, 2H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.57-7.43 (m, 4H), 7.42-7.36 (m, 2H), 1.28 (d, *J* = 18.6 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.45 (d, *J* = 2.1 Hz), 132.35 (d, *J* = 10.4 Hz), 131.84 (d, *J* = 3.2 Hz), 130.51 (s), 129.66 (d, *J* = 83.8 Hz), 128.60 (s), 128.10 (d, *J* = 12.6 Hz), 120.42 (d, *J* = 4.2 Hz), 105.33 (d, *J* = 20.5 Hz), 80.20 (d, *J* = 135.8 Hz), 36.69 (d, *J* = 59.9 Hz), 24.33 (d, *J* = 2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.70. HRMS (ESI) calcd for $C_{18}H_{20}PS^+$ $[M+H]^+$ 299.1018, Found 299.1025. The enantiomeric excess was determined by Daicel Chiralcel AD-H (86% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 6.88 min, *t* (minor) = 5.44 min. $[\alpha]_D^{20}$ = -16.4 (*c* = 1.24, acetone).



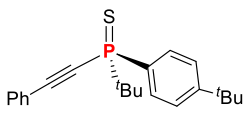
3ea'

Colorless oil, R_f = 0.30 (PE/EA = 10:1), 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.62 – 7.58 (m, 2H), 7.53 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.51 –7.46 (m, 2H), 7.46 – 7.42 (m, 1H), 7.41 – 7.37 (m, 2H), 1.23 (d, *J* = 15.5 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.34 (d, *J* = 9.9 Hz), 132.41 (d, *J* = 1.5 Hz), 131.56 (d, *J* = 2.6 Hz), 130.29 (s), 128.58 (s), 128.39 (d, *J* = 10.6 Hz), 125.98 (d, *J* = 57.0 Hz), 120.81 (d, *J* = 3.0 Hz), 108.05 (d, *J* = 12.9 Hz), 77.85 (d, *J* = 99.9 Hz), 31.36 (d, *J* = 35.3 Hz), 25.27 (d, *J* = 3.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.41 (dd, *J* = 40.4, 17.2 Hz). HRMS (ESI) calcd for $C_{18}H_{22}BNaP^+$ $[M+Na]^+$ 303.1444, Found 303.1459. The enantiomeric excess was determined by Daicel Chiralcel IA-H (84% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 252 nm, *t* (major) = 5.64 min, *t* (minor) = 4.39 min. $[\alpha]_D^{20}$ = 67.5 (*c* = 1.20, acetone).



3fa

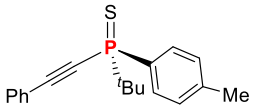
Colorless oil, R_f = 0.30 (PE/EA = 10:1), 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (ddd, *J* = 9.5, 6.8, 2.3 Hz, 2H), 7.61 – 7.58 (m, 2H), 7.47 – 7.42 (m, 1H), 7.41 – 7.36 (m, 2H), 7.02 – 6.97 (m, 2H), 3.86 (s, 3H), 1.27 (d, *J* = 18.6 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.57 (d, *J* = 3.2 Hz), 134.17 (d, *J* = 12.1 Hz), 132.41 (d, *J* = 1.7 Hz), 130.45 (s), 128.59 (s), 120.48 (d, *J* = 93.8 Hz), 120.47 (d, *J* = 4.1 Hz), 113.67 (d, *J* = 13.8 Hz), 104.93 (d, *J* = 20.5 Hz), 80.52 (d, *J* = 134.8 Hz), 55.46 (s), 36.82 (d, *J* = 61.3 Hz), 24.32 (d, *J* = 2.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 44.88. HRMS (ESI) calcd for $C_{19}H_{22}OPS^+$ $[M+H]^+$ 329.1123, Found 329.1127. The enantiomeric excess was determined by Daicel Chiralcel AD-H (76% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 14.92 min, *t* (minor) = 8.47 min. $[\alpha]_D^{20}$ = +3.4 (*c* =0.19, acetone)



3ga

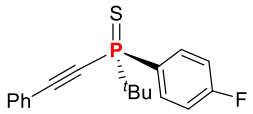
Colorless oil, R_f = 0.30 (PE/EA = 30:1), 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.61 – 7.58 (m, 2H), 7.50 (dd, *J* = 8.5, 2.9 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.38 (dd, *J* = 8.0, 6.7 Hz, 2H), 1.34 (s, 9H), 1.28 (d, *J* = 18.6 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.34 (d, *J* = 3.3 Hz), 132.41 (d, *J* = 1.7 Hz), 132.26 (d, *J* = 10.8 Hz), 130.45 (s), 128.59 (s), 126.31 (d, *J* = 89.8 Hz), 125.17 (d, *J* = 12.9 Hz), 120.49 (d, *J* = 3.8 Hz), 104.99 (d, *J* = 20.7 Hz), 80.49 (d, *J* = 134.6 Hz), 36.69 (d, *J* = 60.1 Hz), 34.98 (s), 31.17 (s), 24.37 (d, *J* = 3.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 45.28. HRMS (ESI) calcd for $C_{22}H_{28}PS^+$ $[M+H]^+$ 355.1644, Found 355.1646. The enantiomeric excess was determined by Daicel

Chiralcel IB-H (90% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 7.29 min, *t* (minor) = 4.48 min. $[\alpha]_D^{20}$ = +3.4 (*c* =4.80, acetone).



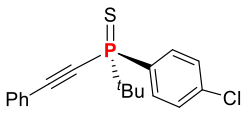
3ha

Colorless oil, R_f = 0.35 (PE/EA = 30:1), 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 13.3, 8.1 Hz, 2H), 7.62 – 7.59 (m, 2H), 7.47 – 7.43 (m, 1H), 7.39 (dd, *J* = 11.5, 4.4 Hz, 2H), 7.30 (dd, *J* = 8.0, 2.7 Hz, 2H), 2.42 (s, 3H), 1.27 (d, *J* = 18.6 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.40 (d, *J* = 3.0 Hz), 132.43 (d, *J* = 2.0 Hz), 132.33 (s), 130.43 (s), 128.86 (d, *J* = 13.1 Hz), 128.58 (s), 126.30 (d, *J* = 89.9 Hz), 120.52 (d, *J* = 3.7 Hz), 105.04 (d, *J* = 20.6 Hz), 80.43 (d, *J* = 134.8 Hz), 36.68 (d, *J* = 60.4 Hz), 24.34 (d, *J* = 2.8 Hz), 21.54 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 45.46. HRMS (ESI) calcd for $C_{19}H_{22}PS^+$ $[M+H]^+$ 313.1174, Found 313.1178. The enantiomeric excess was determined by Daicel Chiralcel OD-H (84% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 9.89 min, *t* (minor) = 5.06 min. $[\alpha]_D^{20}$ = -10.2 (*c* =0.80, acetone).



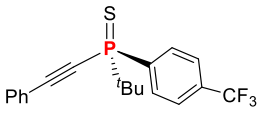
3ia

Colorless oil, R_f = 0.35 (PE/EA = 30:1), 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (ddd, *J* = 12.9, 8.6, 5.5 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.19 (td, *J* = 8.6, 2.0 Hz, 2H), 1.27 (d, *J* = 18.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.14 (dd, *J* = 253.8, 3.6 Hz), 134.81 (dd, *J* = 12.3, 8.9 Hz), 132.45 (d, *J* = 1.9 Hz), 130.63 (s), 128.63 (s), 125.58 (dd, *J* = 90.4, 3.4 Hz), 120.24 (d, *J* = 3.8 Hz), 115.42 (dd, *J* = 21.4, 13.9 Hz), 105.56 (d, *J* = 21.1 Hz), 79.99 (d, *J* = 136.6 Hz), 36.79 (d, *J* = 60.9 Hz), 24.28 (d, *J* = 2.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 44.70. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.33. HRMS (ESI) calcd for $C_{18}H_{19}FPS^+$ $[M+H]^+$ 317.0924, Found 317.0938. The enantiomeric excess was determined by Daicel Chiralcel AD-H (90% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 7.07 min, *t* (minor) = 5.47 min. $[\alpha]_D^{20}$ = -20.2 (*c* = 0.59, acetone).



3ja

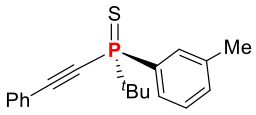
Colorless oil, R_f = 0.25 (PE/EA = 30:1), 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 12.8, 8.4 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.50-7.45 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 2H), 1.27 (d, *J* = 18.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.57 (d, *J* = 3.6 Hz), 133.73 (d, *J* = 11.8 Hz), 132.47 (d, *J* = 1.7 Hz), 130.66 (s), 128.64 (s), 128.41 (d, *J* = 13.4 Hz), 128.39 (d, *J* = 88.4 Hz), 120.18 (d, *J* = 4.1 Hz), 105.71 (d, *J* = 21.2 Hz), 79.79 (d, *J* = 136.8 Hz), 36.81 (d, *J* = 60.6 Hz), 24.27 (d, *J* = 2.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 44.88. HRMS (ESI) calcd for $C_{18}H_{19}ClPS^+$ $[M+H]^+$ 333.0628, Found 333.0631. The enantiomeric excess was determined by Daicel Chiralcel AD-H (83% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 8.18 min, *t* (minor) = 5.61 min. $[\alpha]_D^{20}$ = -16.2 (*c* = 0.63, acetone).



3ka

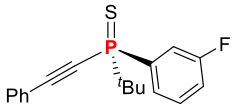
Colorless oil, R_f = 0.35 (PE/EA = 30:1), 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 12.8, 8.1 Hz, 2H), 7.76 (d, *J* = 6.5 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 1.29 (d, *J* = 18.9 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.48 (d, *J* = 84.8 Hz), 133.59 (qd, *J* = 32.9, 3.3 Hz), 132.87 (d, *J* = 11.0 Hz), 132.49 (d, *J* = 2.1 Hz), 130.82 (s), 128.69 (s), 125.10 – 124.81 (m), 123.63 (q, *J* = 273.0 Hz), 119.99 (d, *J* = 4.1 Hz), 106.18 (d, *J* = 21.5 Hz), 79.45 (d, *J* = 138.0 Hz), 36.86 (d, *J* = 60.0 Hz), 24.25 (d, *J* = 2.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 44.96. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.07. HRMS (ESI) calcd for $C_{19}H_{19}F_3PS^+$ $[M+H]^+$367.0892, Found 367.0900. The

enantiomeric excess was determined by Daicel Chiralcel AD-H (84% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 6.10 min, *t* (minor) = 4.53 min. $[\alpha]_D^{20}$ = -22.9 (*c* = 0.70, acetone).



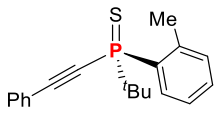
3la

Colorless oil, R_f = 0.3 (PE/EA = 40:1), 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 19.2, 10.9 Hz, 2H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.31 (m, 4H), 2.43 (s, 3H), 1.27 (d, *J* = 18.6 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.00 (d, *J* = 13.0 Hz), 132.75 (d, *J* = 11.5 Hz), 132.68 (d, *J* = 3.4 Hz), 132.44 (d, *J* = 1.6 Hz), 130.44 (s), 129.50 (d, *J* = 10.2 Hz), 129.44 (d, *J* = 87.2 Hz), 128.58 (s), 127.90 (d, *J* = 13.4 Hz), 120.52 (d, *J* = 3.9 Hz), 105.21 (d, *J* = 20.9 Hz), 80.36 (d, *J* = 135.2 Hz), 36.66 (d, *J* = 60.1 Hz), 24.37 (d, *J* = 2.8 Hz), 21.54 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 45.80. HRMS (ESI) calcd for $C_{19}H_{22}PS^+$ $[M+H]^+$ 313.1174, Found 313.1178. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (75% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 254 nm, *t* (major) = 9.84 min, *t* (minor) = 4.67 min. $[\alpha]_D^{20}$ = -14.5 (*c* = 1.00, acetone).



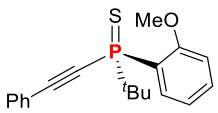
3ma

Colorless oil, R_f = 0.25 (PE/EA = 30:1), 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 12.8, 7.7 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.63 – 7.57 (m, 2H), 7.52 – 7.43 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.20 (m, 1H), 1.32 – 1.24 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.22 (dd, *J* = 249.9, 17.5 Hz), 132.71 (dd, *J* = 86.2, 5.7 Hz).132.46 (d, *J* = 1.7 Hz), 130.75 (s), 129.96 (dd, *J* = 14.6, 7.5 Hz), 128.07 (dd, *J* = 9.9, 2.9 Hz), 120.08 (d, *J* = 3.8 Hz), 119.28 (dd, *J* = 23.3, 12.0 Hz), 119.03 (dd, *J* = 21.3, 2.6 Hz), 105.81 (d, *J* = 21.3 Hz), 79.67 (d, *J* = 137.6 Hz), 36.85 (d, *J* = 59.9 Hz), 24.30 (d, *J* = 2.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 46.14. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.37. HRMS (ESI) calcd for $C_{18}H_{22}PS^+$ $[M+H]^+$ 317.0924, Found 317.0928. The enantiomeric excess was determined by Daicel Chiralcel OD-H (82% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 8.40 min, *t* (minor) = 6.36 min. $[\alpha]_D^{20}$ = -10.73 (*c* = 1.24, acetone).



3na

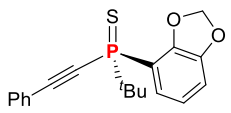
Colorless oil, R_f = 0.30 (PE/EA = 30:1), 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 15.6, 7.6 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.47 – 7.42 (m, 1H), 7.40 (q, *J* = 7.4 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.23 (m, 1H), 2.89 (s, 3H), 1.32 (d, *J* = 18.6 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.79 (d, *J* = 10.8 Hz), 134.77 (d, *J* = 11.8 Hz), 132.85 (d, *J* = 11.8 Hz), 132.21 (d, *J* = 1.7 Hz), 131.71 (d, *J* = 2.8 Hz), 130.36 (s), 128.58 (s), 126.27 (d, *J* = 83.3 Hz), 125.36 (d, *J* = 12.5 Hz), 120.74 (d, *J* = 3.7 Hz), 106.17 (d, *J* = 20.8 Hz), 81.94 (d, *J* = 136.6 Hz), 38.64 (d, *J* = 58.9 Hz), 24.75 (d, *J* = 3.2 Hz), 23.20 (d, *J* = 2.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 46.72. HRMS (ESI) calcd for $C_{19}H_{22}PS^+$ $[M+H]^+$ 313.1174, Found 313.1181. The enantiomeric excess was determined by Daicel Chiralcel AD-H (90% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 7.60 min, *t* (minor) = 5.56 min. $[\alpha]_D^{20}$ = -31.4 (*c* = 0.61, acetone).



3oa

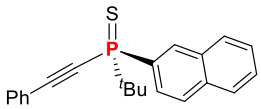
Colorless oil, R_f = 0.30 (PE/EA = 10:1), 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (ddd, *J* = 16.7, 7.8, 1.7 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.51 (ddd, *J* = 8.9, 2.8, 1.4 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.39 – 7.34 (m, 2H), 7.10 (td, *J* = 8.1, 1.4 Hz, 1H), 6.95 (dd, *J* = 8.1, 5.7 Hz, 1H), 3.87 (s, 3H), 1.31 (d, *J* = 19.2 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.68 (d, *J* = 1.8 Hz), 136.40 (d, *J* = 10.8 Hz), 134.03 (d, *J* = 2.1 Hz), 132.20 (d, *J* = 1.7 Hz), 130.02 (s), 128.50 (s), 121.22 (d, *J* = 4.3 Hz), 120.74 (d, *J* = 13.4 Hz), 117.28 (d,

J = 84.5 Hz), 111.87 (d, *J* = 6.4 Hz), 104.21 (d, *J* = 23.0 Hz), 81.40 (d, *J* = 142.7 Hz), 55.47 (s), 38.08 (d, *J* = 61.6 Hz), 24.98 (d, *J* = 3.6 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 41.45. HRMS (ESI) calcd for $C_{19}H_{22}OPS^+$ [M+H] $^+$ 329.1123, Found 329.1128. The enantiomeric excess was determined by Daicel Chiralcel IB-H (76% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 6.97 min, *t* (minor) = 5.93 min. $[\alpha]_D^{20}$ = -31.4 (*c* = 0.61, acetone).



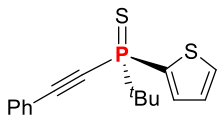
3pa

Colorless oil, R_f = 0.15 (PE/EA = 10:1), 56% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 3H), 7.50 (dd, *J* = 12.6, 1.5 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 6.92 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.05 (s, 2H), 1.27 (d, *J* = 18.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.90 (d, *J* = 2.7 Hz), 147.67 (d, *J* = 19.4 Hz), 132.44 (d, *J* = 1.7 Hz), 130.49 (s), 128.59 (s), 127.87 (d, *J* = 12.0 Hz), 122.64 (d, *J* = 91.7 Hz), 120.39 (d, *J* = 4.1 Hz), 112.04 (d, *J* = 14.1 Hz), 108.17 (d, *J* = 16.0 Hz), 105.18 (d, *J* = 21.1 Hz), 101.78 (s), 80.32 (d, *J* = 135.8 Hz), 36.93 (d, *J* = 60.9 Hz), 24.39 (d, *J* = 2.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 45.96. HRMS (ESI) calcd for $C_{19}H_{20}O_2PS^+$ [M+H] $^+$ 343.0916, Found 343.0919. The enantiomeric excess was determined by Daicel Chiralcel AD-H (86% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 6.88 min, *t* (minor) = 5.44 min. $[\alpha]_D^{20}$ = -1.9 (*c* = 0.30, acetone).



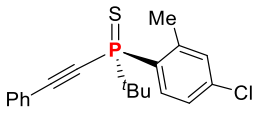
3qa

White solid, R_f = 0.30 (PE/EA = 20:1), 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 15.8 Hz, 1H), 8.09 – 8.02 (m, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.92 (dd, *J* = 8.5, 3.1 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.61 – 7.53 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 1.31 (d, *J* = 18.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.73 (d, *J* = 2.5 Hz), 134.29 (d, *J* = 10.8 Hz), 132.50 (d, *J* = 1.7 Hz), 132.27 (d, *J* = 14.1 Hz), 130.60 (s), 129.09 (s), 128.67 (s), 128.33 (s), 127.80 (s), 127.70 (s), 127.33 (d, *J* = 11.0 Hz), 127.00 (s), 126.82 (d, *J* = 87.4 Hz), 120.42 (d, *J* = 4.2 Hz), 105.55 (d, *J* = 21.0 Hz), 80.35 (d, *J* = 135.4 Hz), 37.08 (d, *J* = 60.4 Hz), 24.47 (d, *J* = 2.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 45.80. HRMS (ESI) calcd for $C_{22}H_{22}PS^+$ [M+H] $^+$ 349.1174, Found 349.1182. The enantiomeric excess was determined by Daicel Chiralcel AD-H (80% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 13.02 min, *t* (minor) = 7.53 min. $[\alpha]_D^{20}$ = -0.7 (*c* = 0.30, acetone).



3ra

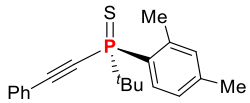
Colorless oil, R_f = 0.20 (PE/EA = 30:1), 41% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.18 (m, 1H), 1.35 (d, *J* = 19.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.94 (d, *J* = 10.1 Hz), 133.94 (s), 132.44 (d, *J* = 1.7 Hz), 132.37 (d, *J* = 97.2 Hz), 130.57 (s), 128.58 (s), 128.20 (d, *J* = 14.6 Hz), 120.24 (d, *J* = 3.9 Hz), 104.67 (d, *J* = 22.1 Hz), 80.80 (d, *J* = 138.8 Hz), 37.16 (d, *J* = 65.0 Hz), 24.30 (d, *J* = 3.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.51. HRMS (ESI) calcd for $C_{16}H_{18}PS_2^+$ [M+H] $^+$ 305.0582, Found 305.0592. The enantiomeric excess was determined by Daicel Chiralcel AD-H (72% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 8.00 min, *t* (minor) = 7.42 min. $[\alpha]_D^{20}$ = -13.0 (*c* = 0.75, acetone).



3sa

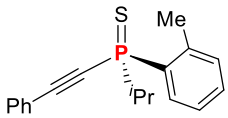
Colorless oil, R_f = 0.2 (PE/EA = 30:1), 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 15.1, 8.4 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.46 (t, *J* = 4.9 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.26 (d, *J* = 3.7 Hz, 1H), 2.87 (s, 3H), 1.31 (d, *J* = 18.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.62 (d, *J* = 11.8 Hz), 137.98 (d, *J* = 3.6 Hz), 136.24 (d, *J* = 12.8 Hz), 132.56 (d, *J* = 12.0 Hz), 132.23 (d, *J* =

2.2 Hz), 130.55 (s), 128.64 (s), 125.63 (d, *J* = 13.5 Hz), 125.03 (d, *J* = 84.6 Hz), 120.47 (d, *J* = 3.8 Hz), 106.61 (d, *J* = 21.5 Hz), 81.48 (d, *J* = 137.9 Hz), 38.75 (d, *J* = 59.3 Hz), 24.68 (d, *J* = 3.2 Hz), 23.09 (d, *J* = 2.6 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 46.04. HRMS (ESI) calcd for $C_{19}H_{21}ClPS^+$ [M+H] $^+$ 347.0785, Found 347.0790. The enantiomeric excess was determined by Daicel Chiralcel AD-H (90% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 8.44 min, *t* (minor) = 5.50 min. $[\alpha]_D^{20}$ = -13.0 (*c* = 0.75, acetone).



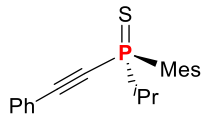
3ta

Colorless oil, R_f = 0.25 (PE/EA = 30:1), 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 16.3 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.10 (m, 1H), 2.83 (s, 3H), 2.36 (s, 3H), 1.32 (d, *J* = 18.6 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.42 (d, *J* = 10.1 Hz), 135.12 (d, *J* = 12.0 Hz), 134.88 (d, *J* = 12.8 Hz), 132.77 (d, *J* = 12.4 Hz), 132.60 (d, *J* = 3.0 Hz), 132.16 (d, *J* = 1.7 Hz), 130.36 (s), 128.61 (s), 125.86 (d, *J* = 82.8 Hz), 120.79 (d, *J* = 4.0 Hz), 106.18 (d, *J* = 21.0 Hz), 82.04 (d, *J* = 136.0 Hz), 38.57 (d, *J* = 59.1 Hz), 24.76 (d, *J* = 2.9 Hz), 22.77 (d, *J* = 2.9 Hz), 21.18 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 46.28. HRMS (ESI) calcd for $C_{20}H_{24}PS^+$ [M+H] $^+$ 327.1331, Found 327.1349. The enantiomeric excess was determined by Daicel Chiralcel OD-H (92% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 4.52 min, *t* (minor) = 5.10 min. $[\alpha]_D^{20}$ = -20.44 (*c* = 3.05, acetone)



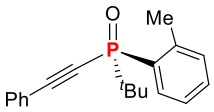
3ua

Colorless oil, R_f = 0.20 (PE/EA = 30:1), 68% yield.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 16.7, 7.7 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.46 – 7.40 (m, 2H), 7.36 (dt, *J* = 15.9, 7.7 Hz, 3H), 7.29 – 7.25 (m, 1H), 2.80 (s, 3H), 2.66 (dq, *J* = 13.9, 6.9 Hz, 1H), 1.32 (dd, *J* = 20.7, 6.9 Hz, 3H), 1.21 (dd, *J* = 21.3, 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.31 (d, *J* = 10.2 Hz), 133.76 (d, *J* = 12.1 Hz), 132.30 (d, *J* = 1.7 Hz), 132.13 (d, *J* = 11.4 Hz), 131.89 (d, *J* = 2.8 Hz), 130.41 (s), 128.54 (s), 128.34 (d, *J* = 88.0 Hz), 125.96 (d, *J* = 13.0 Hz), 120.48 (d, *J* = 4.1 Hz), 105.57 (d, *J* = 22.0 Hz), 80.80 (d, *J* = 136.8 Hz), 32.49 (d, *J* = 62.5 Hz), 21.84 (d, *J* = 3.7 Hz), 17.06 (d, *J* = 2.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 37.80. HRMS (ESI) calcd for $C_{18}H_{20}PS^+$ [M+H] $^+$ 299.1018, Found 299.1028. The enantiomeric excess was determined by Daicel Chiralcel OD-H (88% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 5.44 min, *t* (minor) = 6.78 min. $[\alpha]_D^{20}$ = 7.18(*c* = 1.65, acetone)



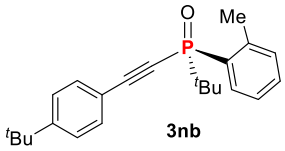
3va

Colorless oil, R_f = 0.20 (PE/EA = 30:1), 50% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.45 – 7.41 (m, 1H), 7.37 (m, 2H), 6.90 (d, *J* = 4.2 Hz, 2H), 2.87 – 2.82 (m, 1H), 2.82 (s, 6H), 2.28 (s, 3H), 1.52 (dd, *J* = 21.3, 6.8 Hz, 3H), 1.20 (dd, *J* = 20.7, 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.27 (d, *J* = 10.9 Hz), 140.89 (d, *J* = 3.0 Hz), 132.00 (s), 131.98 (s), 131.53 (d, *J* = 11.9 Hz), 126.19 (d, *J* = 91.3 Hz), 120.94 (d, *J* = 3.8 Hz), 105.21 (d, *J* = 21.2 Hz), 82.47 (d, *J* = 132.6 Hz), 34.77 (d, *J* = 60.7 Hz), 24.16 (d, *J* = 5.2 Hz), 20.89 (d, *J* = 1.3 Hz), 17.23 (d, *J* = 1.7 Hz), 16.06 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.88. HRMS (ESI) calcd for $C_{20}H_{24}PS^+$ [M+H] $^+$ 327.1331, Found 327.1349. The enantiomeric excess was determined by Daicel Chiralcel AD-H (80% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 9.50 min, *t* (minor) = 8.41 min. $[\alpha]_D^{20}$ = 2.23(*c* = 0.61, acetone)



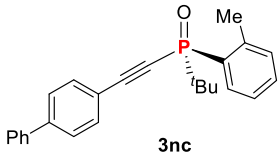
3na-O

Colorless oil, R_f = 0.3 (PE/EA = 1:1), 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (ddd, *J* = 14.6, 8.1, 1.2 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.47 – 7.35 (m, 4H), 7.28-7.26 (m, 2H), 2.79 (s, 3H), 1.27 (d, *J* = 16.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.89 (d, *J* = 10.0 Hz), 133.94 (d, *J* = 11.8 Hz), 132.41 (d, *J* = 1.4 Hz), 132.24 (d, *J* = 11.9 Hz), 131.81 (d, *J* = 2.7 Hz), 130.41 (s), 128.59 (s), 126.59 (d, *J* = 106.0 Hz), 124.91 (d, *J* = 12.6 Hz), 120.42 (d, *J* = 3.6 Hz), 103.99 (d, *J* = 23.4 Hz), 82.78 (d, *J* = 148.7 Hz), 35.71 (d, *J* = 81.9 Hz), 24.29 (d, *J* = 1.3 Hz), 21.97 (d, *J* = 2.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.43. HRMS (ESI) calcd for $C_{19}H_{22}OP^+$ [M+H] $^+$ 297.1403, Found 297.1409. The enantiomeric excess was determined by Daicel Chiralcel IH (90% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 13.04 min, *t* (minor) = 10.34 min. $[\alpha]_D^{20}$ = -3.59 (*c* = 4.00, acetone).



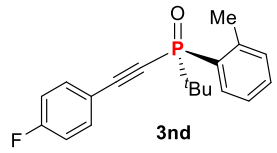
3nb

Colorless oil, R_f = 0.20 (PE/EA = 2:1), 58% yield.^{1}H NMR (500 MHz, DMSO-d_6) δ 7.87 (dd, *J* = 14.3, 7.7 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.55-7.50 (m, 3H), 7.41-7.35 (m, 2H), 2.69 (s, 3H), 1.29 (s, 9H), 1.16 (d, *J* = 16.6 Hz, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.45 (s), 143.50 (d, *J* = 9.5 Hz), 134.03 (d, *J* = 11.6 Hz), 132.67 (d, *J* = 11.8 Hz), 132.57 (s), 132.54 (s), 126.82 (d, *J* = 105.2 Hz), 126.40 (s), 125.73 (d, *J* = 12.5 Hz), 116.83 (d, *J* = 3.5 Hz), 104.05 (d, *J* = 23.1 Hz), 82.63 (d, *J* = 139.8 Hz), 35.56 (d, *J* = 81.9 Hz), 35.26 (s), 31.20 (s), 24.22 (s), 21.66 (d, *J* = 1.9 Hz). ^{31}P NMR (202 MHz, DMSO-d_6) δ 34.17. HRMS (ESI) calcd for $C_{23}H_{30}OP^+$ [M+H] $^+$ 353.2029, Found 353.2035. The enantiomeric excess was determined by Daicel Chiralcel AD-H (93% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 13.24 min, *t* (minor) = 11.64 min. $[\alpha]_D^{20}$ = -49.35 (*c* = 0.43, acetone).



3nc

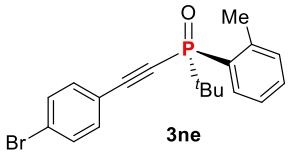
Colorless oil, R_f = 0.2 (PE/EA = 2:1), 62% yield.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 14.7, 7.3 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.56 (m, 4H), 7.48 – 7.40 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.28 (dt, *J* = 7.5, 2.0 Hz, 2H), 2.80 (s, 3H), 1.28 (d, *J* = 16.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.91 (d, *J* = 9.7 Hz), 143.20 (s), 139.83 (s), 133.98 (d, *J* = 11.9 Hz), 132.89 (d, *J* = 1.4 Hz), 132.27 (d, *J* = 11.9 Hz), 131.84 (d, *J* = 2.7 Hz), 129.01 (s), 128.15 (s), 127.20 (d, *J* = 13.9 Hz), 126.64 (d, *J* = 106.4 Hz), 124.94 (d, *J* = 12.8 Hz), 119.15 (d, *J* = 3.7 Hz), 103.99 (d, *J* = 23.5 Hz), 83.42 (d, *J* = 148.4 Hz), 35.75 (d, *J* = 81.9 Hz), 24.33 (s), 22.01 (d, *J* = 2.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.45. HRMS (ESI) calcd for $C_{25}H_{26}OP^+$ [M+H] $^+$ 373.1716, Found 373.1719. The enantiomeric excess was determined by Daicel Chiralcel IB-H (91% ee), n-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 8.65 min, *t* (minor) = 10.08 min. $[\alpha]_D^{20}$ = -34.67 (*c* = 2.96, acetone).



3nd

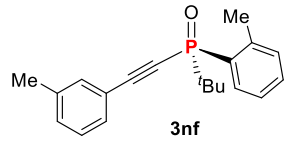
Colorless oil, R_f = 0.3 (PE/EA = 2:1), 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (ddd, *J* = 14.6, 8.1, 1.3 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.43 (ddd, *J* = 9.0, 3.0, 1.5 Hz, 1H), 7.27 (dd, *J* = 6.6, 4.8 Hz, 2H), 7.11 – 7.06 (m, 2H), 2.78 (s, 3H), 1.26 (d, *J* = 16.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.72 (d, *J* = 253.1 Hz), 143.88 (d, *J* = 10.0 Hz), 134.63 (dd, *J* = 9.1, 1.6 Hz), 133.89 (s), 132.29 (d, *J* = 12.0 Hz), 131.91 (d, *J* = 2.7 Hz), 126.33 (d, *J* = 106.4 Hz), 124.93 (d, *J* = 12.8 Hz), 116.49 (t, *J* = 3.6 Hz), 116.10 (d, *J* = 22.2 Hz), 103.06 (d, *J* = 23.8 Hz), 82.56 (d, *J* = 147.7 Hz), 35.68 (d, *J* = 82.0 Hz), 24.24 (d, *J* = 1.2 Hz), 21.94 (d, *J* = 2.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.82. ^{19}F NMR (471 MHz, $CDCl_3$) δ -106.67. HRMS (ESI) calcd for $C_{19}H_{21}FOP^+$ [M+H] $^+$ 315.1309, Found 315.1320. The

enantiomeric excess was determined by Daicel Chiralcel OD-H (86% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 6.62 min, *t* (minor) = 5.98 min. $[\alpha]_D^{20}$ = -5.04 (*c* = 0.60, acetone).



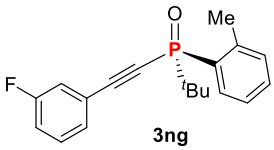
3ne

Colorless oil, R_f = 0.20 (PE/EA = 2:1), 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 14.5, 7.7 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.28 (dd, *J* = 11.2, 4.0 Hz, 2H), 2.78 (s, 3H), 1.26 (d, *J* = 16.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.91 (d, *J* = 9.9 Hz), 133.84 (s), 133.74 (s), 132.30 (d, *J* = 12.0 Hz), 131.96 (s), 131.91 (d, *J* = 2.7 Hz), 126.33 (d, *J* = 106.0 Hz), 125.08 (s), 124.93 (d, *J* = 12.8 Hz), 119.30 (d, *J* = 3.6 Hz), 102.71 (d, *J* = 23.3 Hz), 84.06 (d, *J* = 146.0 Hz), 35.70 (d, *J* = 81.8 Hz), 24.26 (s), 21.94 (d, *J* = 2.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.33. HRMS (ESI) calcd for $C_{19}H_{21}BrOP^+$ $[M+H]^+$ 375.0508, Found 375.0508. The enantiomeric excess was determined by Daicel Chiralcel IB-H (84% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 6.58 min, *t* (minor) = 7.50 min. $[\alpha]_D^{20}$ = -14.43 (*c* = 1.88, acetone).



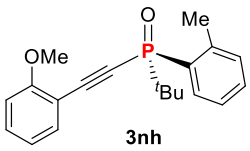
3nf

Colorless oil, R_f = 0.20 (PE/EA = 2:1), 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (ddd, *J* = 14.7, 8.1, 1.2 Hz, 1H), 7.44-7.39 (m, 3H), 7.30 – 7.22 (m, 4H), 2.79 (s, 3H), 2.35 (s, 3H), 1.27 (d, *J* = 16.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.85 (d, *J* = 9.5 Hz), 138.39 (s), 133.96 (d, *J* = 11.7 Hz), 132.82 (d, *J* = 1.4 Hz), 132.21 (d, *J* = 11.9 Hz), 131.78 (d, *J* = 2.7 Hz), 131.33 (s), 129.53 (s), 128.49 (s), 126.64 (d, *J* = 106.4 Hz), 124.90 (d, *J* = 12.7 Hz), 120.20 (d, *J* = 3.6 Hz), 104.30 (d, *J* = 23.7 Hz), 82.37 (d, *J* = 149.7 Hz), 35.69 (d, *J* = 81.9 Hz), 24.29 (s), 21.97 (d, *J* = 2.6 Hz), 21.22 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.3. HRMS (ESI) calcd for $C_{20}H_{24}OP^+$ $[M+H]^+$ 311.1559, Found 311.1563. The enantiomeric excess was determined by Daicel Chiralcel AD-H (90% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 8.58 min, *t* (minor) = 7.64 min. $[\alpha]_D^{20}$ = -14.55 (*c* = 1.00, acetone).



3ng

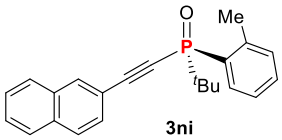
Colorless oil, R_f = 0.20 (PE/EA = 2:1), 57% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (ddd, *J* = 14.6, 8.1, 1.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.30-7.28 (m, 1H), 7.28 – 7.26 (m, 2H), 7.19 – 7.14 (m, 1H), 2.79 (s, 3H), 1.27 (d, *J* = 16.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.20 (d, *J* = 248.2 Hz), 143.91 (d, *J* = 10.0 Hz), 133.76 (d, *J* = 11.9 Hz), 132.29 (d, *J* = 12.0 Hz), 131.92 (d, *J* = 2.7 Hz), 130.38 (d, *J* = 8.5 Hz), 128.36 (d, *J* = 1.9 Hz), 126.25 (d, *J* = 106.5 Hz), 124.94 (d, *J* = 12.6 Hz), 122.12 (dd, *J* = 9.2, 3.6 Hz), 119.13 (dd, *J* = 23.8, 1.4 Hz), 117.91 (d, *J* = 21.1 Hz), 102.23 (dd, *J* = 22.9, 3.4 Hz), 83.72 (d, *J* = 145.3 Hz), 35.71 (d, *J* = 81.8 Hz), 24.22 (s), 21.92 (d, *J* = 2.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.65. ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.74. HRMS (ESI) calcd for $C_{19}H_{21}FOP^+$ $[M+H]^+$ 315.1309, Found 315.1310. The enantiomeric excess was determined by Daicel Chiralcel AD-H (84% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 10.85 min, *t* (minor) = 7.59 min. $[\alpha]_D^{20}$ = -10.73 (*c* = 1.24, acetone).



3nh

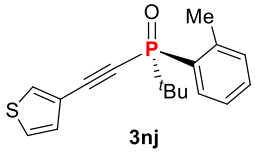
Colorless oil, R_f = 0.15 (PE/EA = 1:1), 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (ddd, *J* = 14.7, 8.1, 1.2 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.28-7.23 (m, 2H), 6.95 – 6.88 (m, 2H), 3.88 (s, 3H), 2.79 (s, 3H), 1.28 (d, *J* = 16.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.56 (s), 143.79 (d, *J* = 9.5 Hz), 134.35 (d, *J* = 11.9 Hz), 133.93 (d, *J* = 1.6 Hz), 132.06 (d, *J* = 11.8 Hz), 131.92 (s), 131.66 (d, *J* = 2.7 Hz), 126.80 (d, *J* = 106.0 Hz), 124.81 (d, *J* = 12.8 Hz), 120.46 (s), 110.79 (s),

109.79 (d, *J* = 3.7 Hz), 100.87 (d, *J* = 24.8 Hz), 86.60 (d, *J* = 152.2 Hz), 55.78 (s), 35.75 (d, *J* = 81.9 Hz), 24.23 (s), 21.97 (d, *J* = 2.6 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.31. HRMS (ESI) calcd for $C_{20}H_{24}O_2P^+$ $[M+H]^+$ 327.1508, Found 327.1508. The enantiomeric excess was determined by Daicel Chiralcel AD (90% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 300 nm, *t* (major) =15.46 min, *t* (minor) = 10.12 min. $[\alpha]_D^{20}$ = -8.83 (*c* = 1.15, acetone).



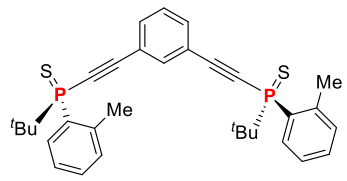
3ni

Colorless oil, R_f = 0.20 (PE/EA = 2:1), 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.96 (dd, *J* = 14.5, 7.7 Hz, 1H), 7.85 – 7.80 (m, 3H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.25 (m, 2H), 2.81 (s, 3H), 1.30 (d, *J* = 16.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.91 (d, *J* = 9.8 Hz), 134.04 (s), 133.94 (s), 133.69 (s), 133.36 (d, *J* = 1.6 Hz), 132.60 (s), 132.32 (s), 132.23 (s), 131.86 (d, *J* = 2.7 Hz), 128.43 (s), 128.08 (s), 127.92 (s), 127.46 (d, *J* = 97.6 Hz), 126.21 (s), 124.96 (d, *J* = 12.8 Hz), 117.56 (d, *J* = 3.7 Hz), 104.47 (d, *J* = 23.7 Hz), 83.00 (d, *J* = 148.3 Hz), 35.77 (d, *J* = 82.0 Hz), 24.35 (d, *J* = 1.1 Hz), 22.01 (d, *J* = 2.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.53. HRMS (ESI) calcd for $C_{23}H_{24}OP^+$ $[M+H]^+$ 347.1559, Found 347.1558. The enantiomeric excess was determined by Daicel Chiralcel AD-H (81% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 254 nm, *t* (major) =17.07 min, *t* (minor) = 12.04 min. $[\alpha]_D^{20}$ = -26.96 (*c* = 3.21, acetone).



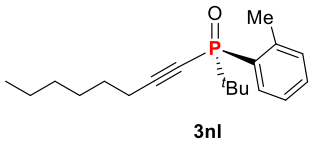
3nj

Colorless oil, R_f = 0.40 (PE/EA = 2:1), 40% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.26 (d, *J* = 1.9 Hz, 1H), 7.85 (dd, *J* = 14.3, 7.7 Hz, 1H), 7.74 (dd, *J* = 4.8, 2.9 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.33 (m, 3H), 2.68 (s, 3H), 1.15 (d, *J* = 16.6 Hz, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 143.51 (d, *J* = 9.9 Hz), 134.84 (d, *J* = 1.4 Hz), 134.05 (d, *J* = 11.6 Hz), 132.66 (d, *J* = 11.8 Hz), 132.53 (d, *J* = 2.4 Hz), 130.20 (s), 128.29 (s), 126.82 (d, *J* = 104.8 Hz), 125.73 (d, *J* = 12.3 Hz), 118.79 (d, *J* = 3.7 Hz), 99.45 (d, *J* = 23.5 Hz), 82.78 (d, *J* = 145.8 Hz), 35.53 (d, *J* = 81.9 Hz), 24.23 (s), 21.65 (d, *J* = 1.8 Hz). ^{31}P NMR (202 MHz, DMSO-d_6) δ 34.36. HRMS (ESI) calcd for $C_{17}H_{20}OPS^+$ $[M+H]^+$ 303.0967, Found 303.0976. The enantiomeric excess was determined by Daicel Chiralcel IB-H (78% ee), *n*-Hexanes/IPA = 97.5/2.5, 1 mL/min, λ = 254 nm, *t* (major) =26.53 min, *t* (minor) = 29.90 min. $[\alpha]_D^{20}$ = -15.08 (*c* = 0.48, acetone).



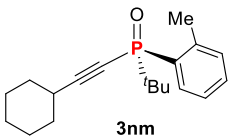
3nk

White solid, R_f = 0.20 (PE/EA = 10:1), 33% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 15.8, 7.8 Hz, 2H), 7.81 (s, 1H), 7.66 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 2H), 2.88 (s, 6H), 1.33 (dd, *J* = 18.8, 1.0 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.83 (d, *J* = 10.9 Hz), 135.53 (d, *J* = 2.0 Hz), 134.65 (d, *J* = 11.4 Hz), 133.70 (s), 132.96 (d, *J* = 11.8 Hz), 131.87 (d, *J* = 2.8 Hz), 129.04 (s), 126.19 (s), 125.46 (d, *J* = 12.9 Hz), 121.51 (d, *J* = 3.7 Hz), 104.16 (d, *J* = 20.1 Hz), 83.42 (d, *J* = 132.4 Hz), 38.73 (d, *J* = 58.6 Hz), 24.75 (d, *J* = 3.2 Hz), 23.23 (d, *J* = 2.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 47.46 (s). HRMS (ESI) calcd for $C_{32}H_{37}P_2S_2^+$ $[M+H]^+$ 547.1806, Found 547.1810. The enantiomeric excess was determined by Daicel Chiralcel IB-H (97% ee, 5:1 dr), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) =7.08 min, t_1 = 7.84 min, t_2 = 8.87 min. $[\alpha]_D^{20}$ = -1.95 (*c* = 0.40, acetone).



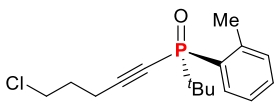
3nl

Colorless oil, R_f = 0.30 (PE/EA = 2:1), 38% yield.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (ddd, *J* = 14.6, 8.0, 1.2 Hz, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.24 (t, *J* = 6.5 Hz, 2H), 2.74 (s, 3H), 2.44 (td, *J* = 7.1, 3.3 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.49 – 1.41 (m, 2H), 1.31 (td, *J* = 7.0, 3.2 Hz, 4H), 1.19 (d, *J* = 16.6 Hz, 9H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.77 (d, *J* = 9.5 Hz), 133.99 (d, *J* = 12.0 Hz), 132.10 (d, *J* = 11.8 Hz), 131.60 (d, *J* = 2.7 Hz), 126.85 (d, *J* = 105.9 Hz), 124.69 (d, *J* = 12.8 Hz), 107.94 (d, *J* = 24.5 Hz), 74.44 (d, *J* = 155.1 Hz), 35.33 (d, *J* = 82.5 Hz), 31.17 (s), 28.58 (s), 27.65 (s), 24.19 (d, *J* = 1.3 Hz), 22.49 (s), 21.89 (d, *J* = 2.5 Hz), 19.67 (d, *J* = 2.7 Hz), 14.00 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.67. HRMS (ESI) calcd for $C_{19}H_{30}OP^+$ $[M+H]^+$ 305.2029, Found 305.2028. The enantiomeric excess was determined by Daicel Chiralcel IH-H (93% ee), n-Hexanes/IPA = 90/10, 1 mL/min, λ = 271 nm, *t* (major) =6.60 min, *t* (minor) = 5.33 min. $[\alpha]_D^{20}$ = 2.63 (*c* = 2.41, acetone).



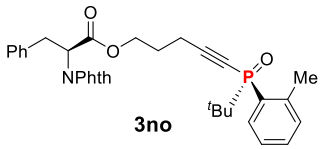
3nm

Colorless oil, R_f = 0.30 (PE/EA = 2:1), 40% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 14.4, 7.6 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.21 (m, 2H), 2.74 (s, 3H), 2.69-2.60 (m, 1H), 1.92-1.83 (m, 2H), 1.79-1.69 (m, 2H), 1.65 – 1.49 (m, 3H), 1.45-1.32 (m, 3H), 1.19 (d, *J* = 16.5 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.76 (d, *J* = 9.7 Hz), 134.02 (d, *J* = 11.8 Hz), 132.08 (d, *J* = 11.9 Hz), 131.57 (d, *J* = 2.7 Hz), 126.94 (d, *J* = 105.8 Hz), 124.71 (d, *J* = 12.7 Hz), 111.28 (d, *J* = 23.5 Hz), 74.21 (d, *J* = 154.8 Hz), 35.36 (d, *J* = 82.6 Hz), 31.52 (s), 29.67 (d, *J* = 1.7 Hz), 25.64 (s), 24.58 (s), 24.23 (d, *J* = 1.2 Hz), 21.94 (d, *J* = 2.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.34. HRMS (ESI) calcd for $C_{19}H_{28}OP^+$ $[M+H]^+$ 303.1872, Found 303.1878. The enantiomeric excess was determined by Daicel Chiralcel AD-H (90% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 271 nm, *t* (major) =7.03 min, *t* (minor) = 6.02 min. $[\alpha]_D^{20}$ = -8.02 (*c* = 1.00, acetone).



3nn

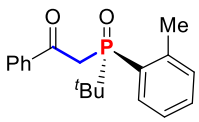
Colorless oil, R_f = 0.30 (PE/EA = 2:1), 35% yield.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 14.7, 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.21 (m, 2H), 3.67 (t, *J* = 6.2 Hz, 2H), 2.74 (s, 3H), 2.66 (td, *J* = 6.9, 3.3 Hz, 2H), 2.11 – 2.05 (m, 2H), 1.19 (d, *J* = 16.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.80 (d, *J* = 9.5 Hz), 133.84 (d, *J* = 11.9 Hz), 132.18 (d, *J* = 11.9 Hz), 131.75 (d, *J* = 2.7 Hz), 126.55 (d, *J* = 106.4 Hz), 124.80 (d, *J* = 12.6 Hz), 105.44 (d, *J* = 23.8 Hz), 75.67 (d, *J* = 151.4 Hz), 43.34 (s), 35.35 (d, *J* = 81.9 Hz), 30.27 (d, *J* = 1.3 Hz), 24.16 (s), 21.87 (d, *J* = 2.1 Hz), 17.09 (d, *J* = 2.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.03. HRMS (ESI) calcd for $C_{16}H_{23}ClOP^+$ $[M+H]^+$ 297.1170, Found 297.1169. The enantiomeric excess was determined by Daicel Chiralcel AD-H (84% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 271 nm, *t* (major) = 8.82 min, *t* (minor) = 7.27 min. $[\alpha]_D^{20}$ = 0.54 (*c* = 0.50, acetone).



3no

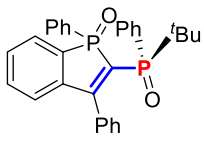
White solid, R_f = 0.20 (PE/EA = 1:1), 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 3H), 7.71 – 7.66 (m, 2H), 7.42 – 7.37 (m, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.11 (m, 5H), 5.17 (dd, *J* = 11.2, 5.3 Hz, 1H), 4.40 – 4.25 (m, 2H), 3.64 – 3.47 (m, 2H), 2.72 (s, 3H), 2.46 (tdd, *J* = 7.1, 3.2, 1.5 Hz, 2H), 2.01 – 1.92 (m, 2H), 1.17 (dd, *J* = 16.7, 2.4 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.73 (s), 167.40 (s), 143.77 (d, *J* = 9.6 Hz), 136.55 (s), 134.23 (s), 133.89 (d, *J* = 11.9 Hz), 132.14 (d, *J* = 11.9 Hz), 131.72 (d, *J* = 2.8 Hz), 131.46 (s), 128.70 (d, *J* = 25.9 Hz), 126.90 (s), 126.50 (d, *J* = 106.2 Hz), 124.83 (d, *J* = 12.8 Hz), 123.50 (s), 105.62 (d, *J* = 23.8 Hz), 77.28 (s), 75.45 (d, *J* =

151.4 Hz), 64.10 (s), 53.25 (s), 35.33 (d, *J* = 82.2 Hz), 34.77 (s), 26.84 (d, *J* = 1.0 Hz), 24.15 (d, *J* = 1.1 Hz), 21.86 (d, *J* = 2.3 Hz), 16.31 (d, *J* = 2.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.09. HRMS (ESI) calcd for $C_{25}H_{31}O_3P^+$ [M+H] $^+$ 410.2005, Found 410.2029. dr = 9:1(δ 38.10: δ 36.09 of ^{31}P NMR). $[\alpha]_D^{20}$ = -61.06 (*c* = 4.15, acetone).



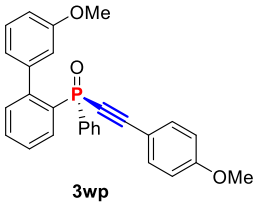
4

Colorless solid, R_f = 0.30 (PE/EA = 1:2), 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.07 (m, 2H), 7.57 – 7.50 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 7.6, 3.8 Hz, 1H), 4.06 (dd, *J* = 15.3, 13.3 Hz, 1H), 3.80 (dd, *J* = 13.2, 10.6 Hz, 1H), 2.67 (s, 3H), 1.23 (d, *J* = 15.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.07 (d, *J* = 6.2 Hz), 144.86 (d, *J* = 7.1 Hz), 137.34 (s), 133.36 (s), 133.05 (d, *J* = 11.8 Hz), 132.59 (d, *J* = 10.6 Hz), 131.67 (d, *J* = 2.7 Hz), 129.61 (s), 128.37 (s), 125.93 (d, *J* = 88.9 Hz), 124.55 (d, *J* = 12.0 Hz), 38.92 (d, *J* = 48.1 Hz), 35.81 (d, *J* = 69.0 Hz), 24.56 (s), 22.00 (d, *J* = 2.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 49.52 (s). HRMS (ESI) calcd for $C_{19}H_{24}O_2P^+$ [M+H] $^+$ 315.1508, Found 315.1506. The enantiomeric excess was determined by Daicel Chiralcel OD-H (84% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 10.11 min, *t* (minor) = 12.33 min. $[\alpha]_D^{20}$ = 1.95 (*c* = 0.40, acetone).



5

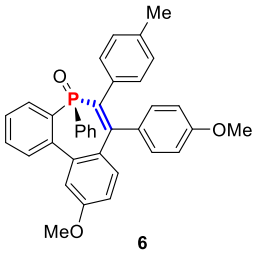
Colorless solid, R_f = 0.30 (EA), 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (ddd, *J* = 12.3, 7.8, 1.6 Hz, 2H), 7.79 (t, *J* = 7.3 Hz, 1H), 7.65 (d, *J* = 4.7 Hz, 1H), 7.54 – 7.41 (m, 7H), 7.29 (s, 1H), 7.13 (ddd, *J* = 10.5, 8.8, 4.4 Hz, 2H), 7.06 – 6.99 (m, 3H), 6.91 (s, 1H), 6.60 (d, *J* = 4.9 Hz, 1H), 1.16 (d, *J* = 16.1 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.57 (dd, *J* = 11.5, 3.9 Hz), 142.65 (dd, *J* = 24.8, 14.7 Hz), 134.76 (d, *J* = 4.9 Hz), 133.91 (d, *J* = 5.0 Hz), 133.06 (dd, *J* = 13.0, 6.5 Hz), 132.68 (s), 132.51 (d, *J* = 9.8 Hz), 131.87 (d, *J* = 2.8 Hz), 131.70 (d, *J* = 5.1 Hz), 131.60 (s), 130.96 (d, *J* = 4.9 Hz), 130.65 (d, *J* = 9.4 Hz), 130.38 (d, *J* = 9.4 Hz), 130.36 (s), 129.47 (d, *J* = 8.8 Hz), 128.91 (s), 127.79 (dd, *J* = 12.5, 5.9 Hz), 127.69 (dd, *J* = 65.3, 3.7 Hz), 126.98 (d, *J* = 60.8 Hz), 125.47 (d, *J* = 10.1 Hz), 34.15 (d, *J* = 68.7 Hz), 24.68 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 64.16 (d, *J* = 31.8 Hz, 1P), 16.61 (d, *J* = 30.4 Hz, 1P). HRMS (ESI) calcd for $C_{30}H_{29}O_2P_2^+$ [M+H] $^+$ 483.1637, Found 483.1645. The enantiomeric excess was determined by Daicel Chiralcel AD-H (86% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 31.22 min, *t* (minor) = 22.36 min. $[\alpha]_D^{20}$ = -4.78 (*c* = 2.25, acetone).



3wp

Colorless solid, R_f = 0.30 (PE/EA = 1: 3), 64% yield. ^{1}H NMR (500 MHz, d_6-acetone) δ 8.15 (dd, *J* = 15.3, 7.7 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.45 (d, *J* = 7.9 Hz, 3H), 7.34 (d, *J* = 6.9 Hz, 3H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 6.80 (d, *J* = 7.4 Hz, 2H), 3.82 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 161.58 (s), 158.93 (s), 146.18 (d, *J* = 10.3 Hz), 141.59 (d, *J* = 4.6 Hz), 134.18 (d, *J* = 1.4 Hz), 133.99 (d, *J* = 122.2 Hz), 132.89 (d, *J* = 11.8 Hz), 132.64 (d, *J* = 119.6 Hz), 132.09 (d, *J* = 2.5 Hz), 131.46 (d, *J* = 1.2 Hz), 131.41 (d, *J* = 6.2 Hz), 130.75 (d, *J* = 11.0 Hz), 128.57 (s), 128.17 (d, *J* = 13.3 Hz), 127.15 (d, *J* = 13.0 Hz), 122.41 (s), 115.36 (s), 114.37 (s), 113.74 (s), 111.73 (d, *J* = 3.9 Hz), 104.85 (d, *J* = 30.0 Hz), 82.91 (d, *J* = 171.1 Hz), 55.08 (s), 54.55 (s). ^{31}P NMR (202 MHz, Acetone) δ 5.83 (s). HRMS (ESI) calcd for $C_{28}H_{24}O_3P^+$ [M+H] $^+$ 439.1458, Found 439.1460. The enantiomeric excess was determined by

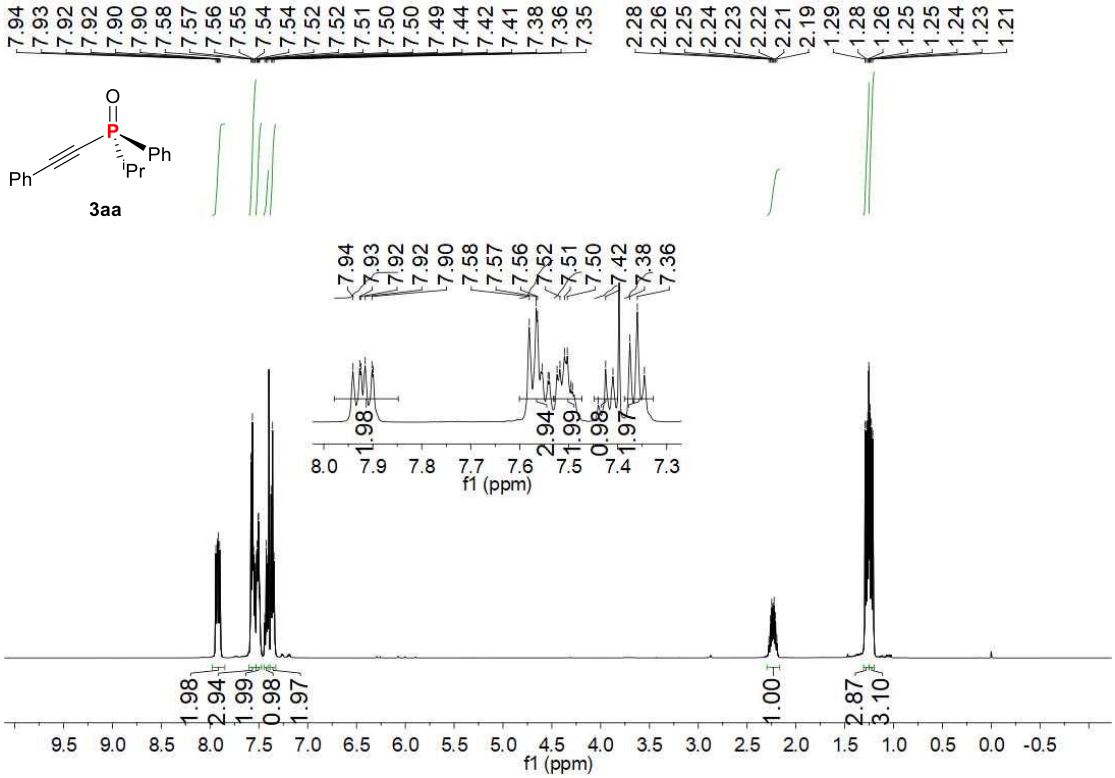
Daicel Chiralcel IB-H (48% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 254 nm, *t* (major) = 23.91 min, *t* (minor) = 29.01 min. $[\alpha]_D^{20}$ = 2.54 (*c* = 0.90, acetone).

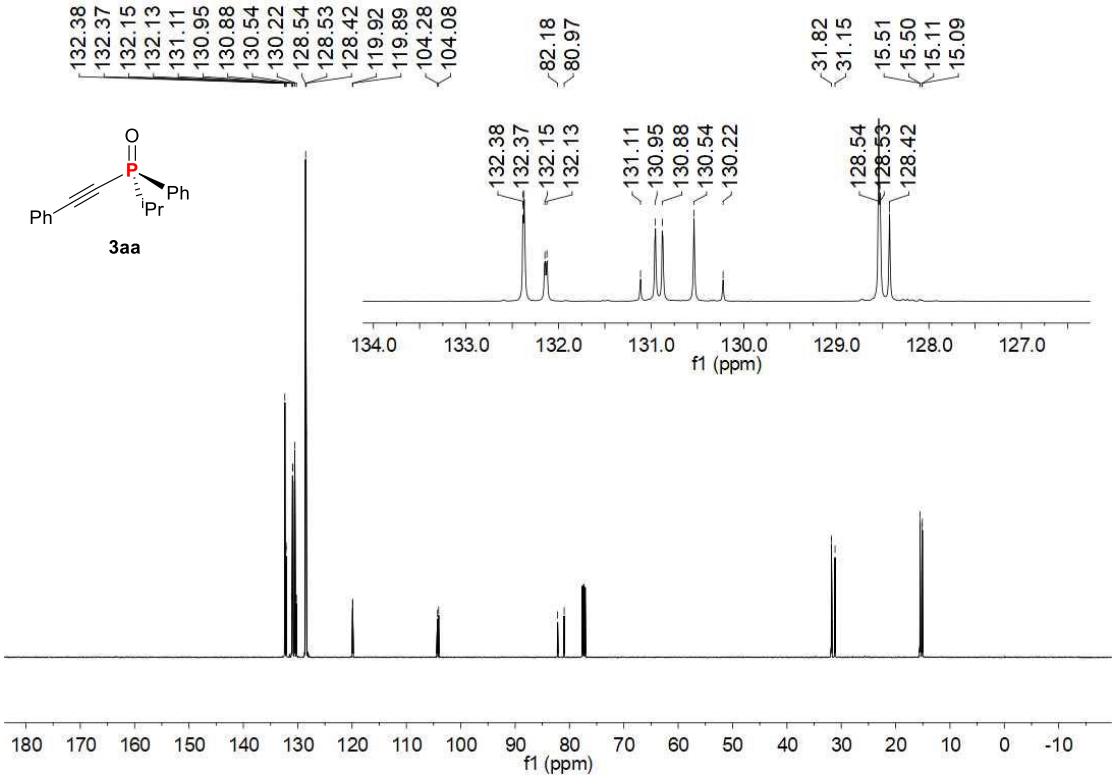


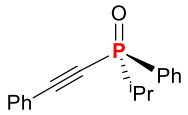
6

Colorless solid, R_f = 0.20 (PE/EA = 1: 3), 53% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.10 (dd, *J* = 11.7, 7.7 Hz, 1H), 7.73 (s, 2H), 7.60 (dt, *J* = 14.5, 10.1 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.38 (dd, *J* = 12.9, 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.0 Hz, 2H), 7.01 (s, 2H), 6.79 (d, *J* = 7.7 Hz, 2H), 6.73 (s, 1H), 6.60 (dd, *J* = 13.9, 8.3 Hz, 3H), 6.42 (d, *J* = 8.8 Hz, 1H), 3.68 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 158.51 (d, *J* = 57.4 Hz), 148.89 (d, *J* = 11.2 Hz), 141.92 (s), 140.89 (d, *J* = 10.6 Hz), 136.59 (d, *J* = 1.2 Hz), 136.24 (d, *J* = 99.2 Hz), 135.91 (d, *J* = 92.5 Hz), 135.12 (d, *J* = 15.1 Hz), 133.93 (d, *J* = 5.7 Hz), 133.33 (s), 133.07 (d, *J* = 51.5 Hz), 132.63 (d, *J* = 49.2 Hz), 132.25 (s), 131.94 (d, *J* = 10.0 Hz), 131.81 (d, *J* = 1.8 Hz), 131.35 (s), 130.91 (d, *J* = 2.4 Hz), 130.43 (d, *J* = 6.2 Hz), 130.09 (d, *J* = 10.3 Hz), 129.80 (d, *J* = 11.3 Hz), 128.51 (d, *J* = 12.2 Hz), 128.40 (s), 127.75 (d, *J* = 12.6 Hz), 127.63 (d, *J* = 10.9 Hz), 113.95 (d, *J* = 76.0 Hz), 112.80 (s), 55.37 (s), 55.08 (s), 20.99 (s). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 19.36. HRMS (ESI) calcd for $C_{35}H_{30}O_3P^+$ $[M+H]^+$ 529.1927, Found 529.1937. The enantiomeric excess was determined by Daicel Chiralcel IB-H (64% ee), *n*-Hexanes/IPA = 70/30, 1 mL/min, λ = 318 nm, *t* (major) = 10.21 min, *t* (minor) = 4.87 min. $[\alpha]_D^{20}$ = -702.44 (*c* = 0.05, acetone). 30% yield, and 99% ee from recrystal.

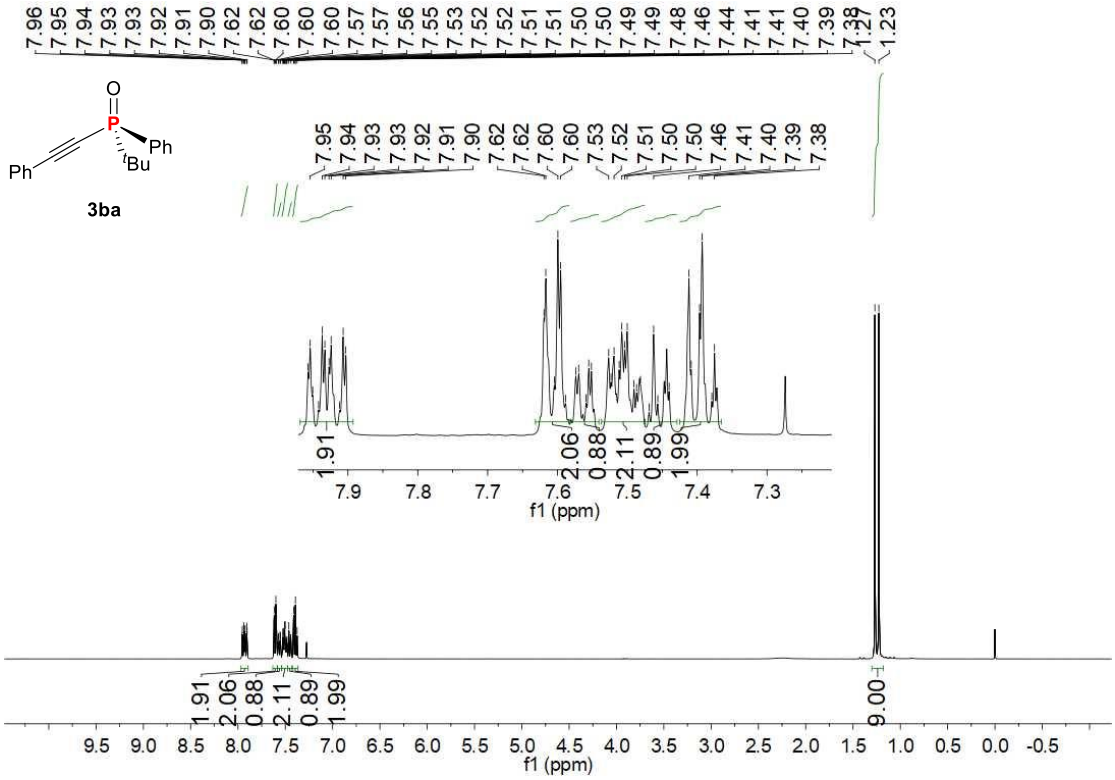
8. Copies of NMR spectroscopy.







3aa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tBu
Ph
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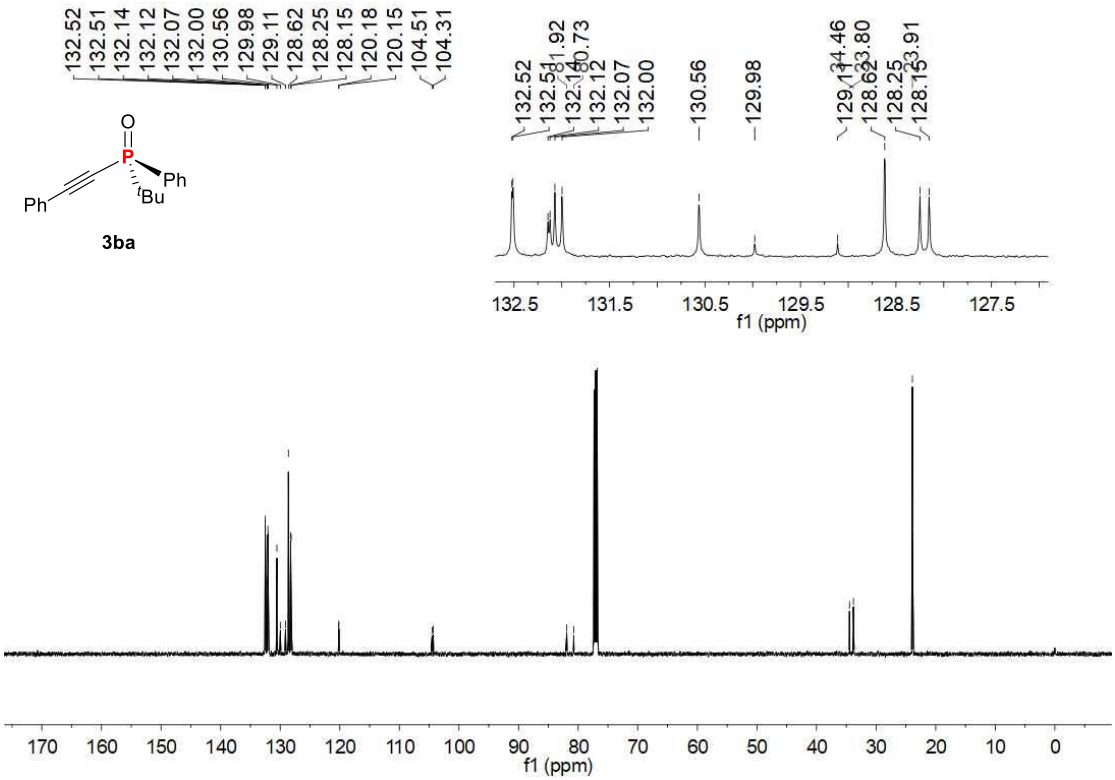
9.00
f1 (ppm)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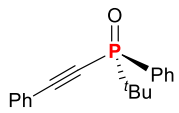
P
Ph
tBu
Ph
3ba
f1 (ppm)



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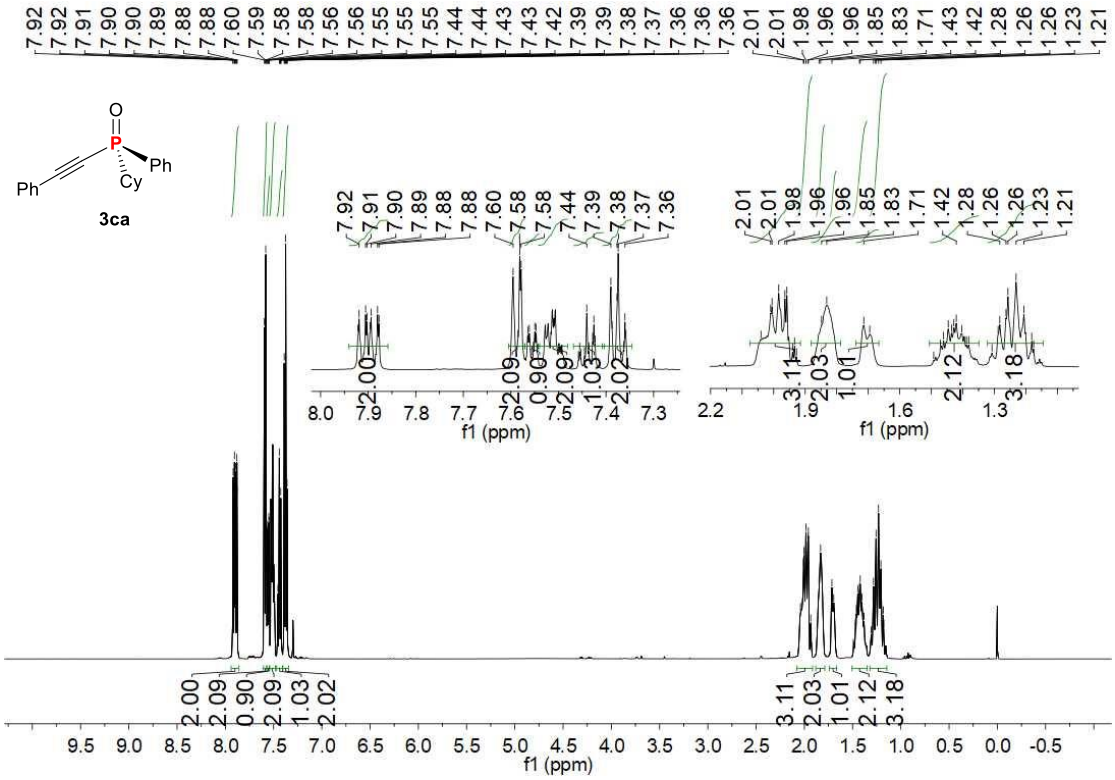
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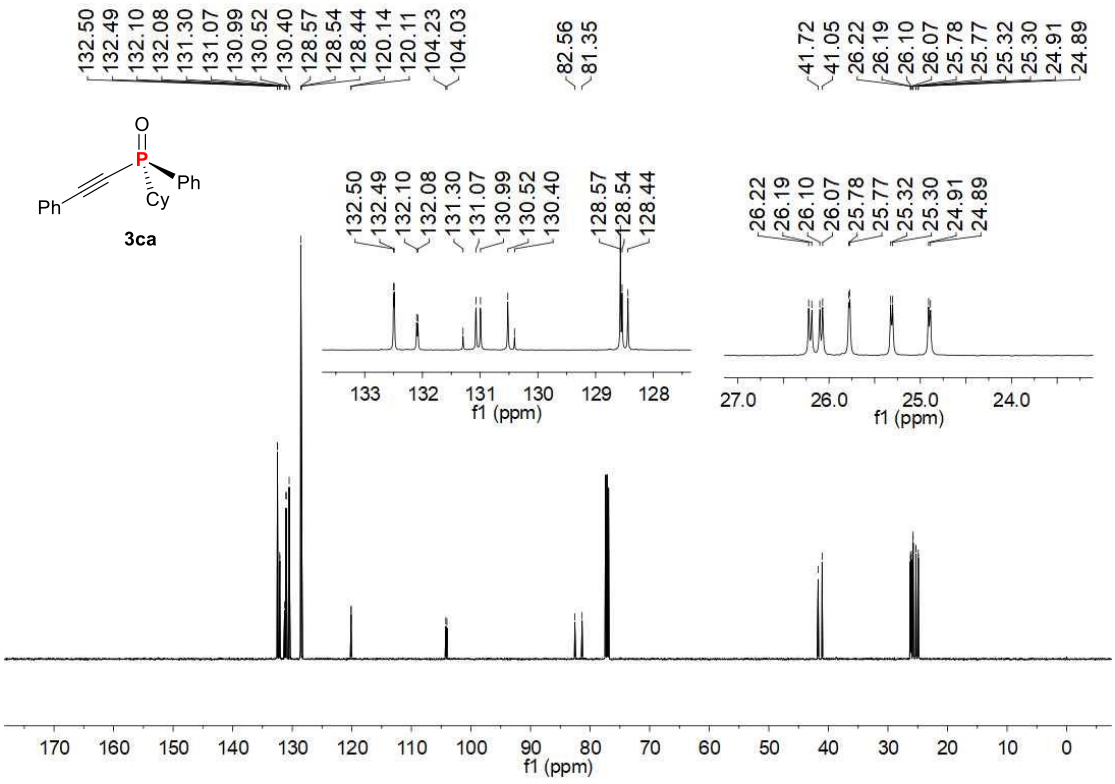
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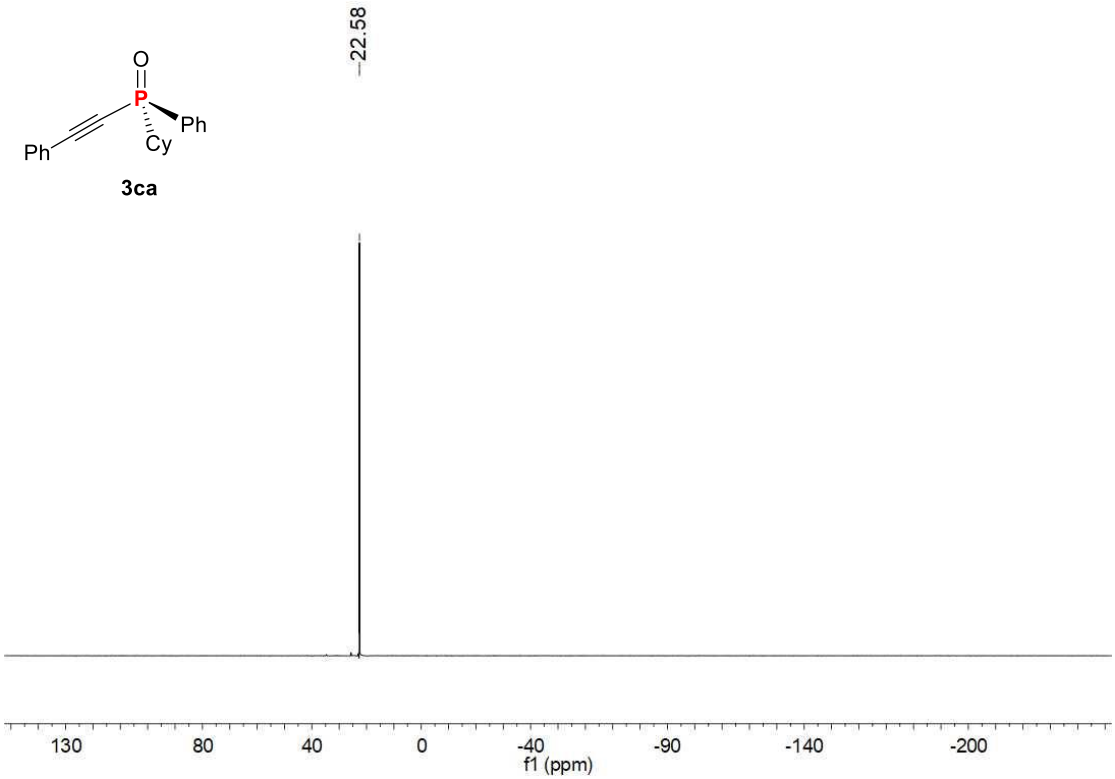

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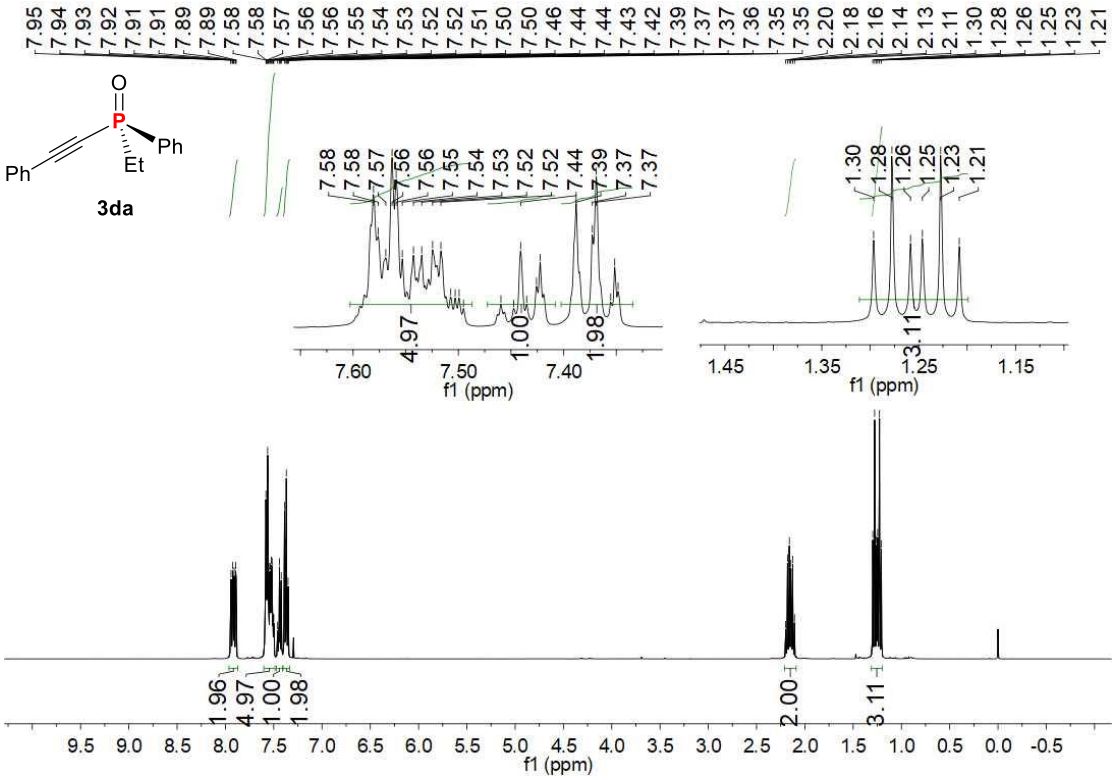
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O
P
Ph
Et
Ph
3da
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f1 (ppm)
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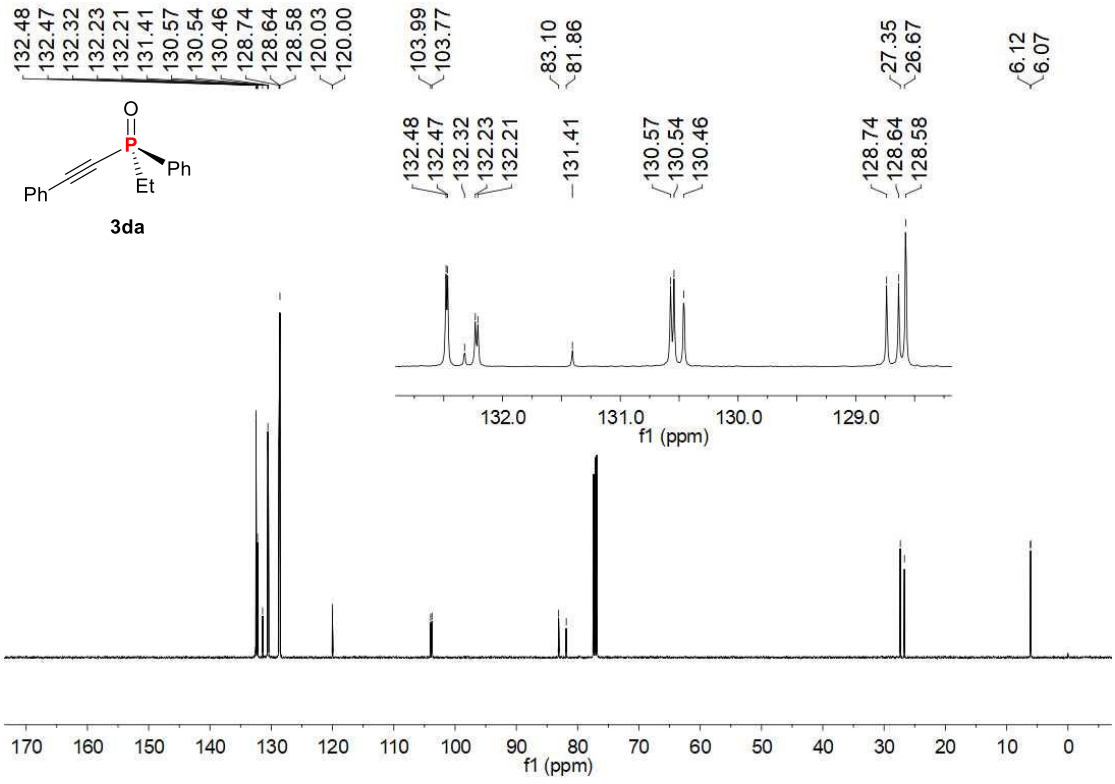
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O
P
Ph
Et
Ph
3da
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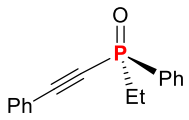
f1 (ppm)



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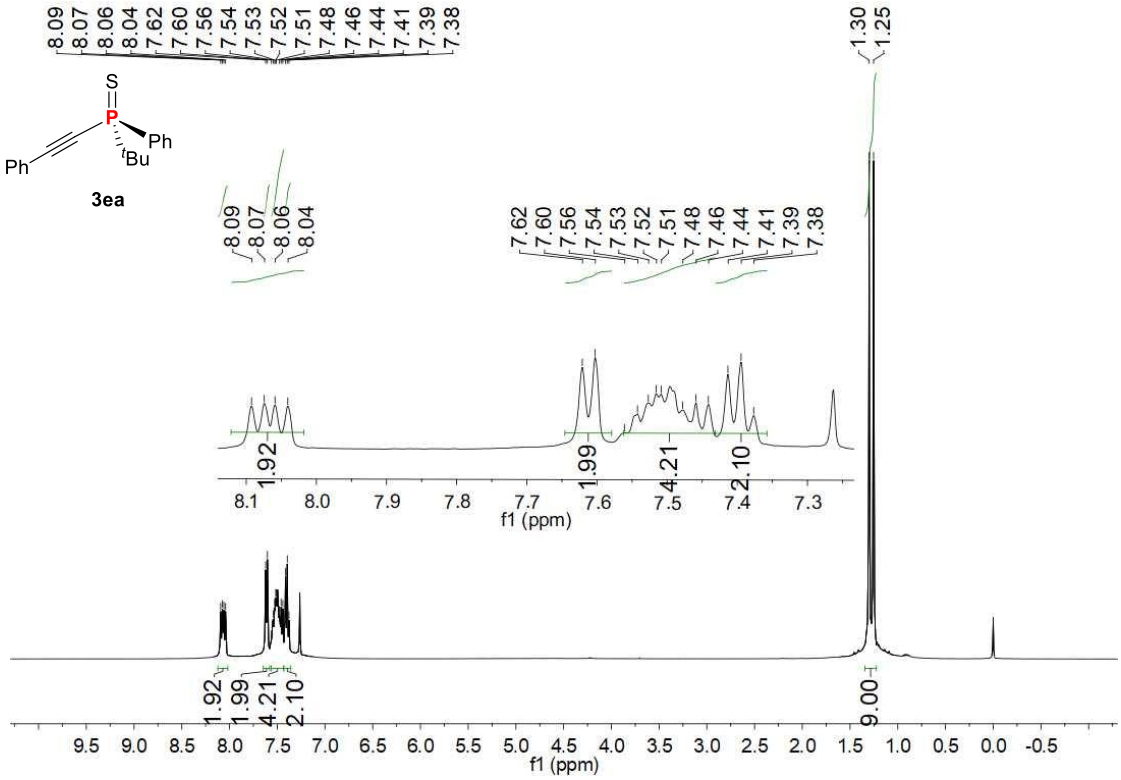
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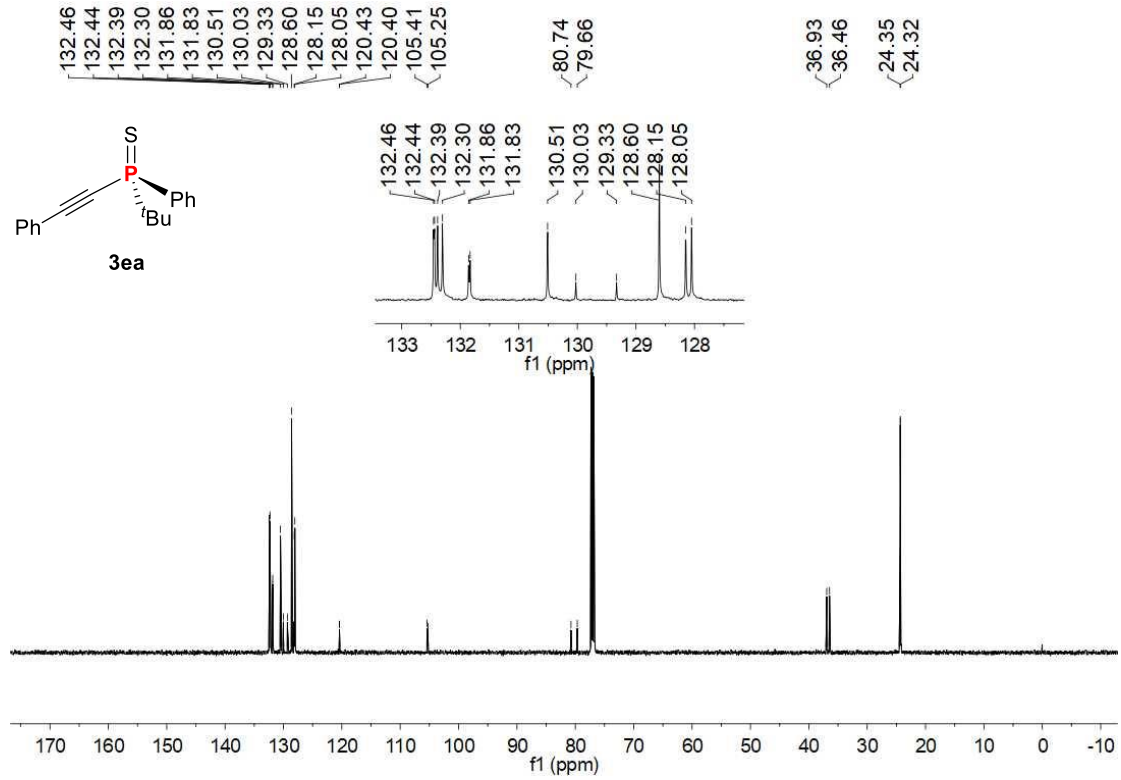
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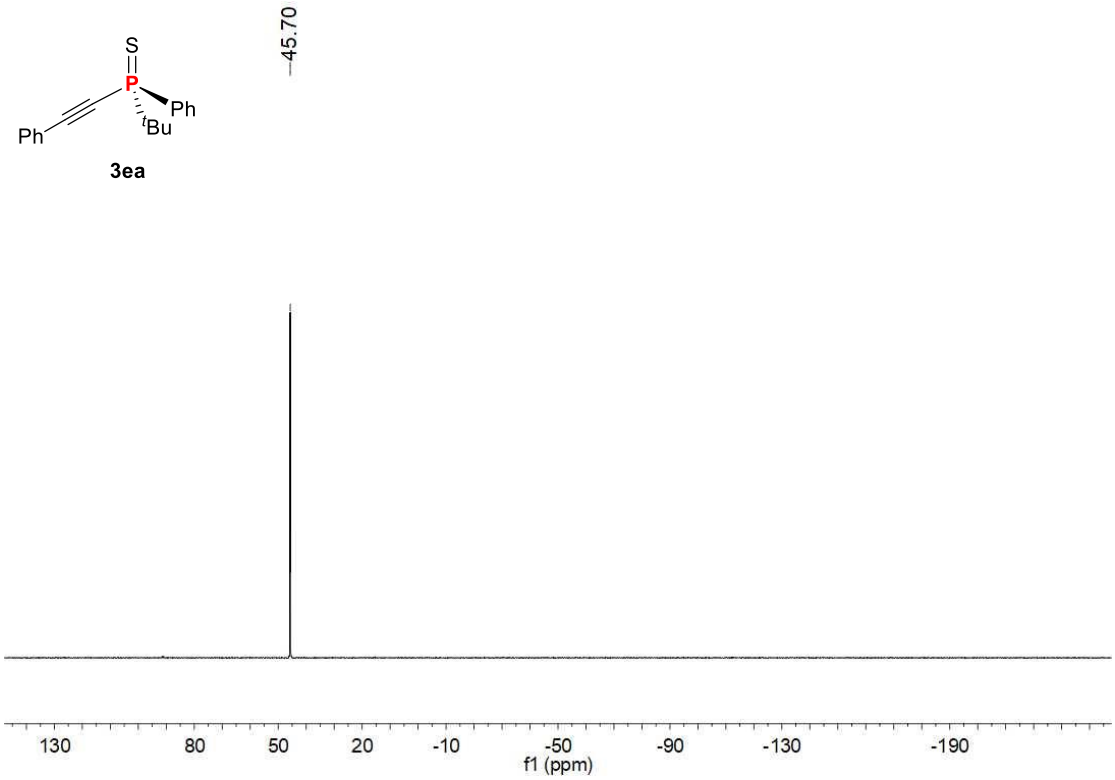
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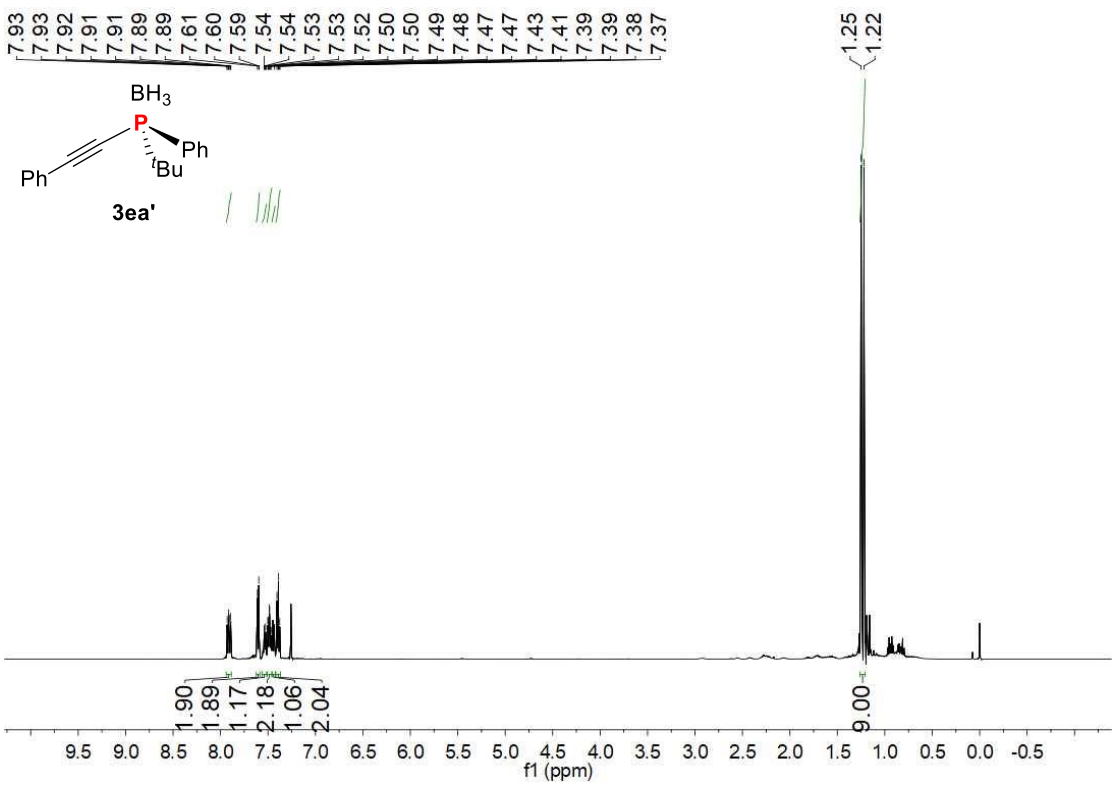
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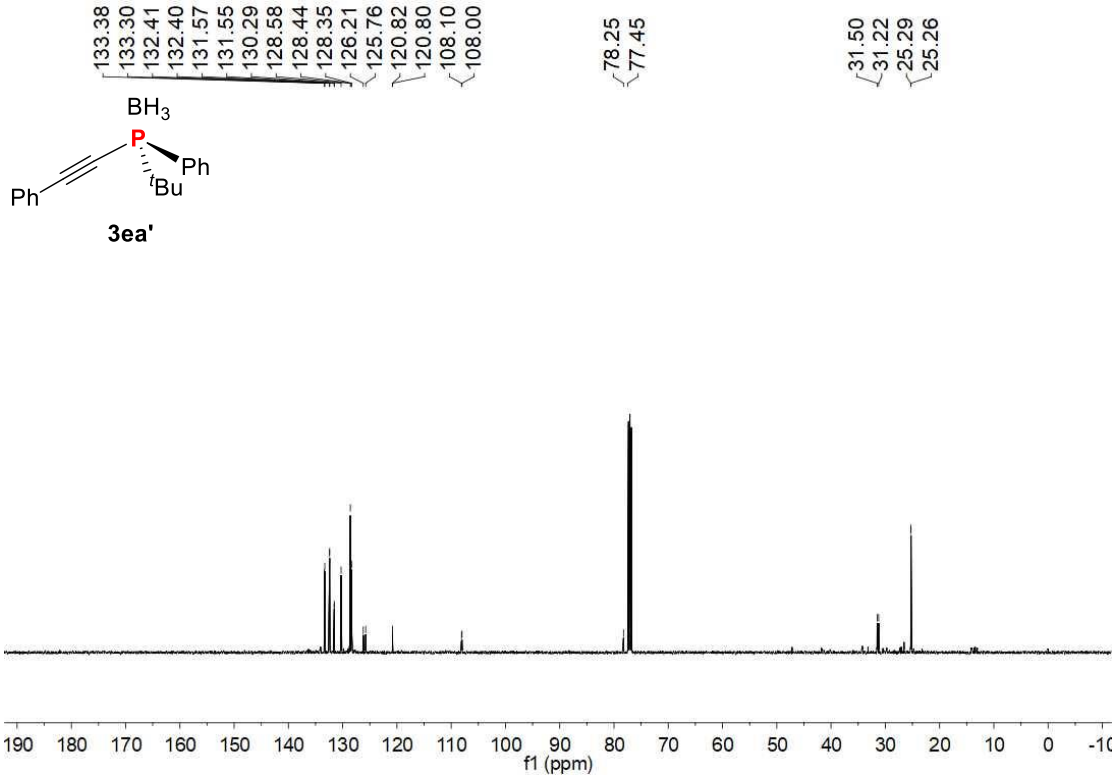
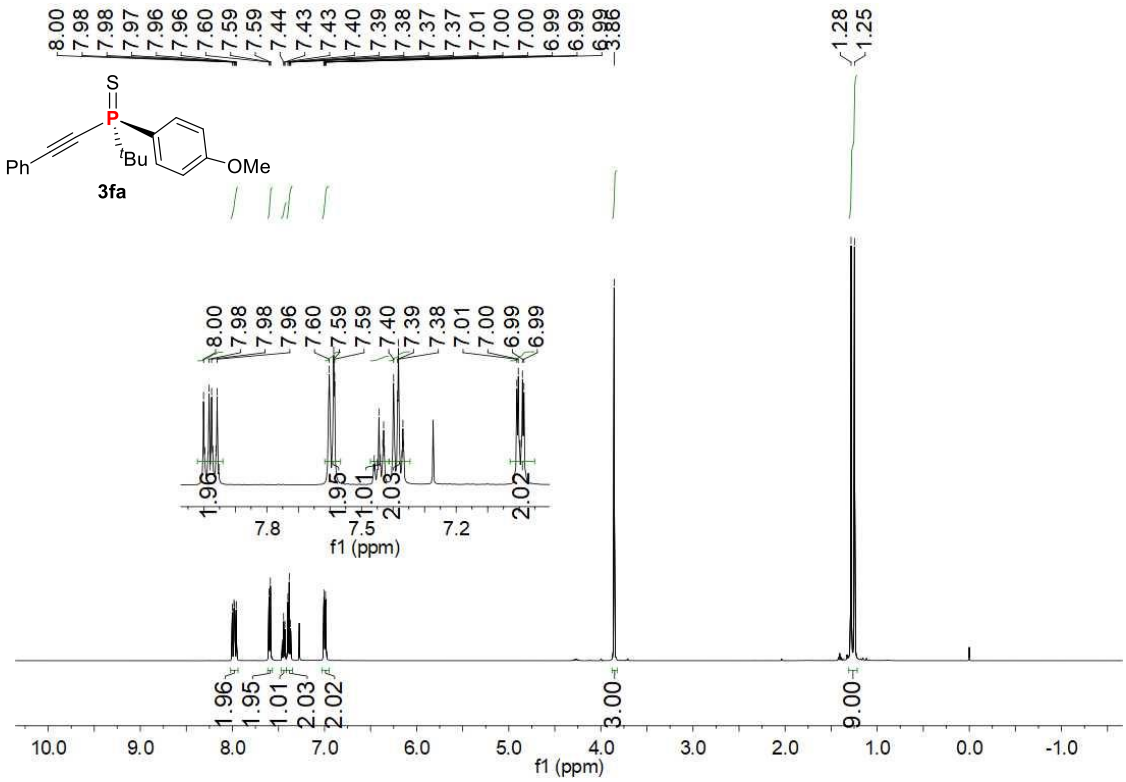
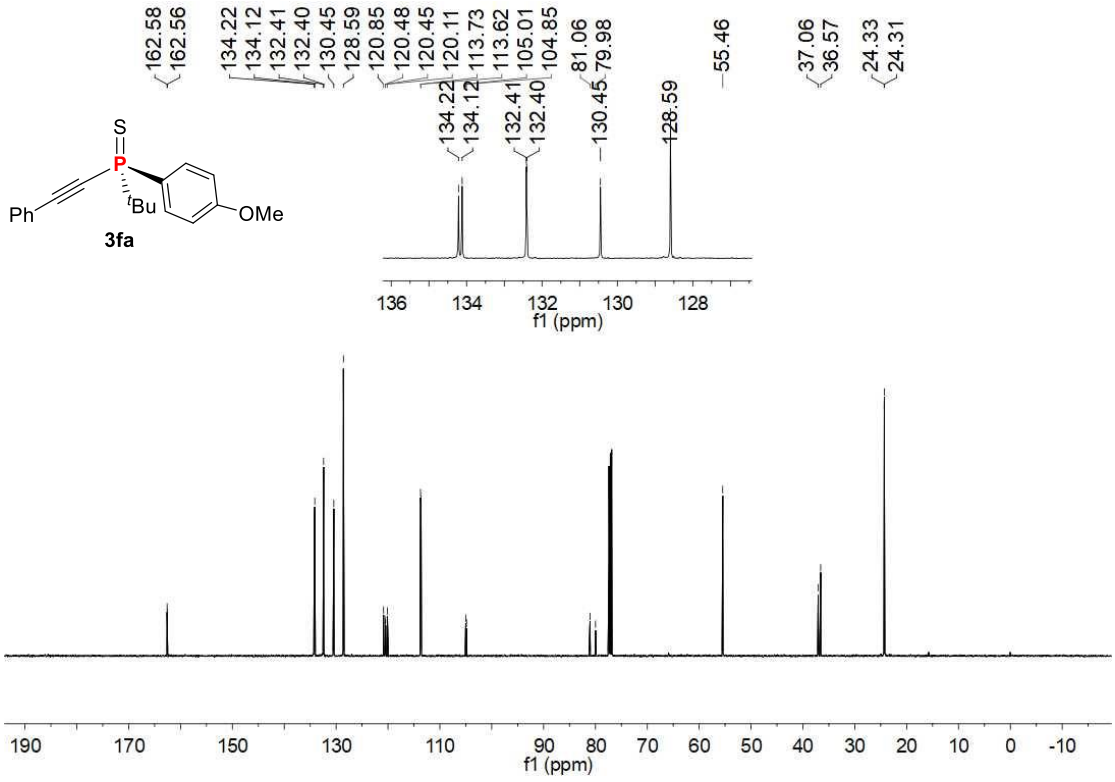
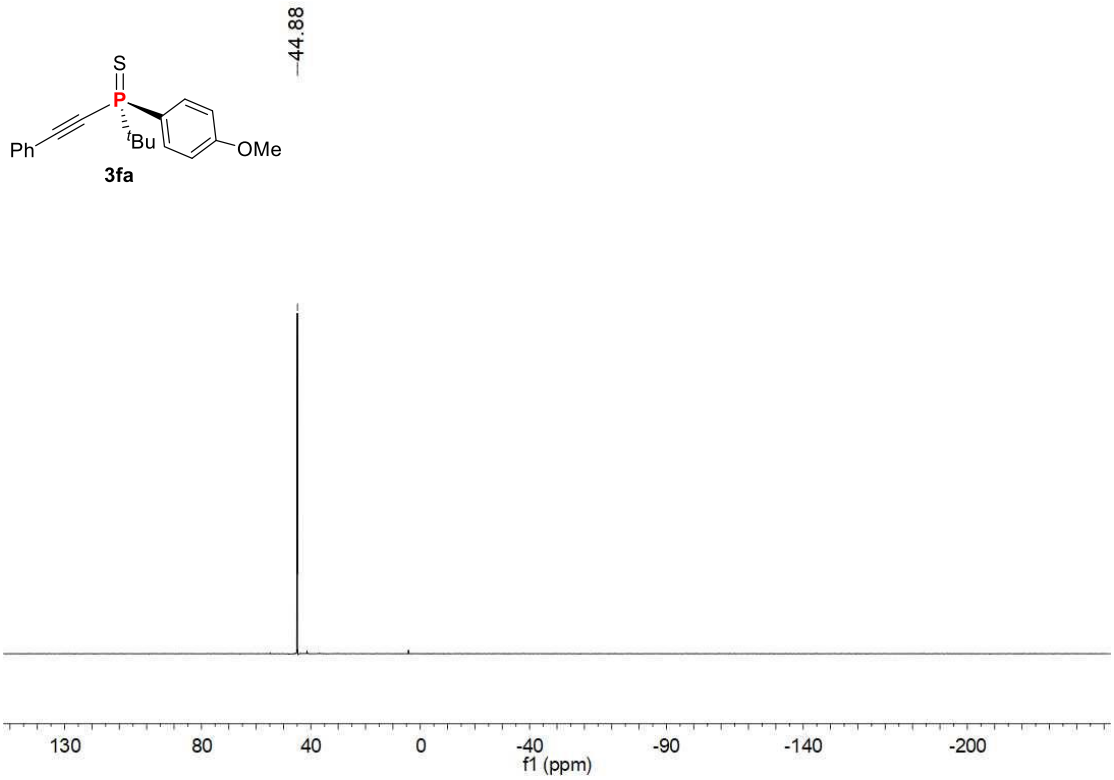
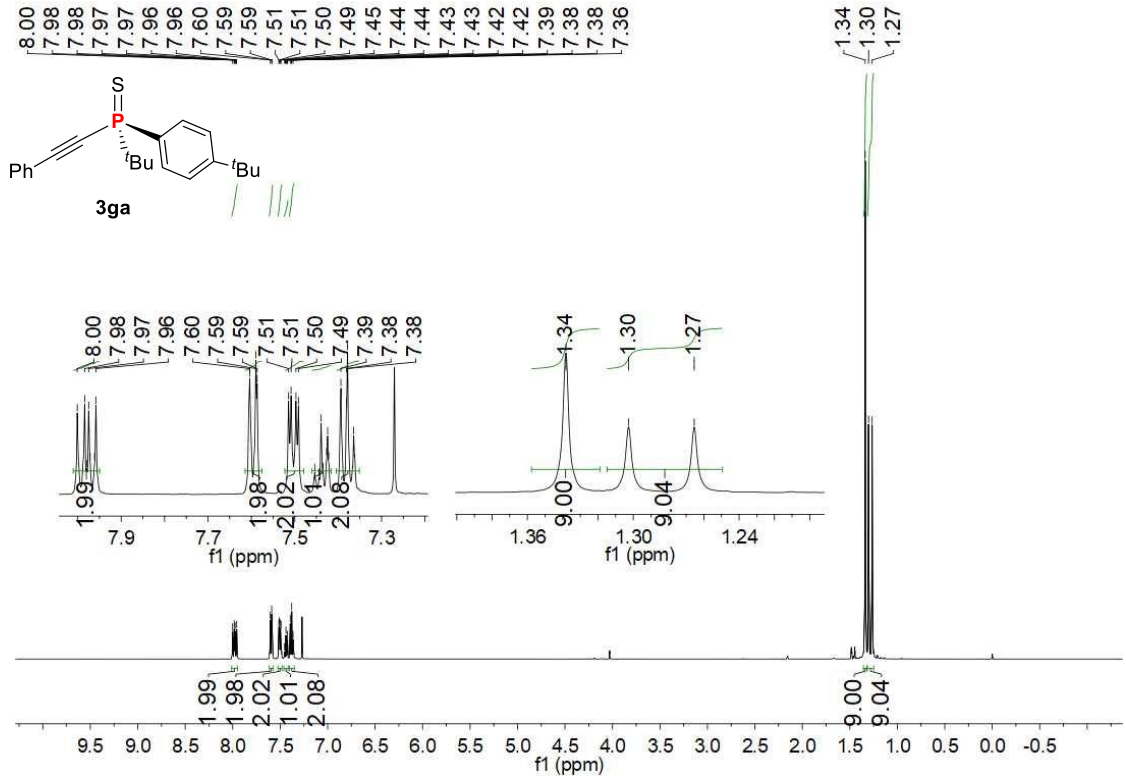
9.00
f1 (ppm)

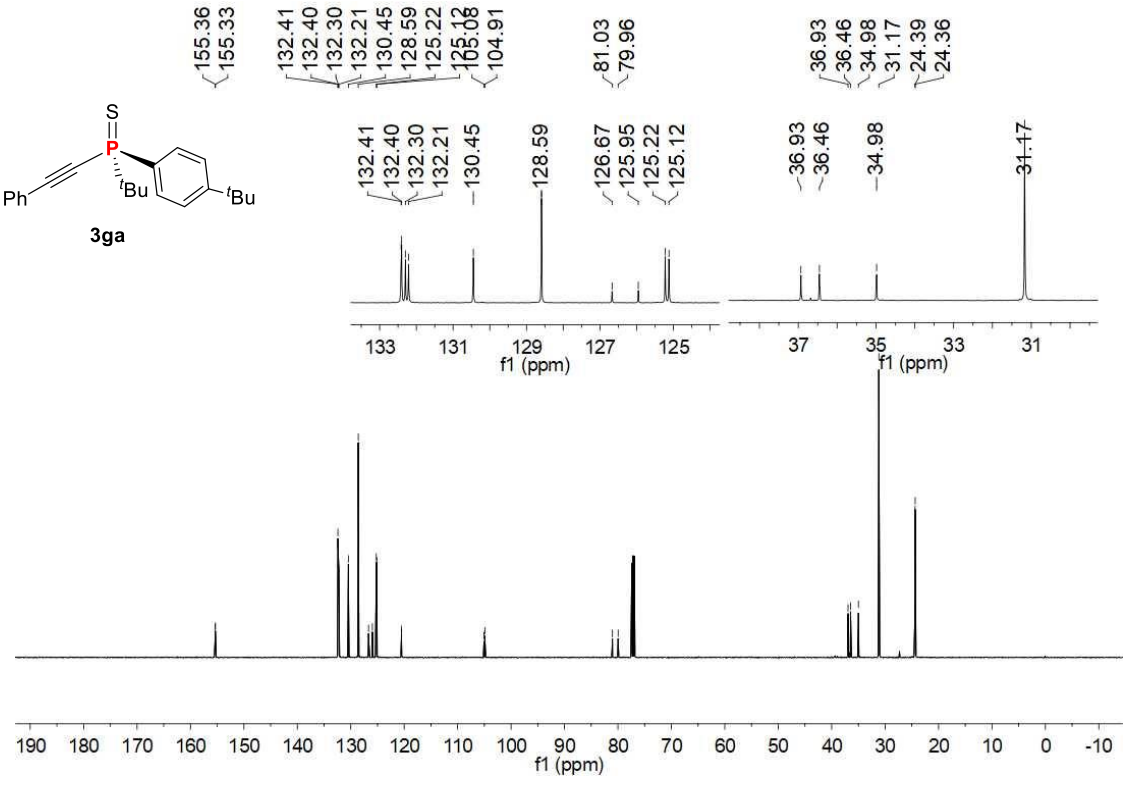

133.38
133.30
132.41
132.40
131.57
131.55
130.29
128.58
128.44
128.35
126.21
125.76
120.82
120.80
108.10
108.00
78.25
77.45
31.50
31.22
25.29
25.26
BH3
P
Ph
tBu
Ph
3ea'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

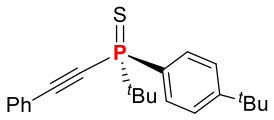

8.00 7.98 7.98 7.97 7.96 7.96 7.60 7.59 7.59 7.44 7.43 7.43 7.40 7.39 7.38 7.37 7.37 7.01 7.00 7.00 6.99 6.99 6.98 3.86
1.28 1.25
S
P
Ph
tBu
OMe
3fa
1.96 1.95 1.01 2.03 2.02
3.00
9.00
f1 (ppm)


162.58 162.56 134.22 134.12 132.41 132.40 130.45 128.59 120.85 120.48 120.45 120.11 113.73 113.62 105.01 104.85 81.06 79.98 55.46 37.06 36.57 24.33 24.31
S
P
Ph
tBu
OMe
3fa
f1 (ppm)

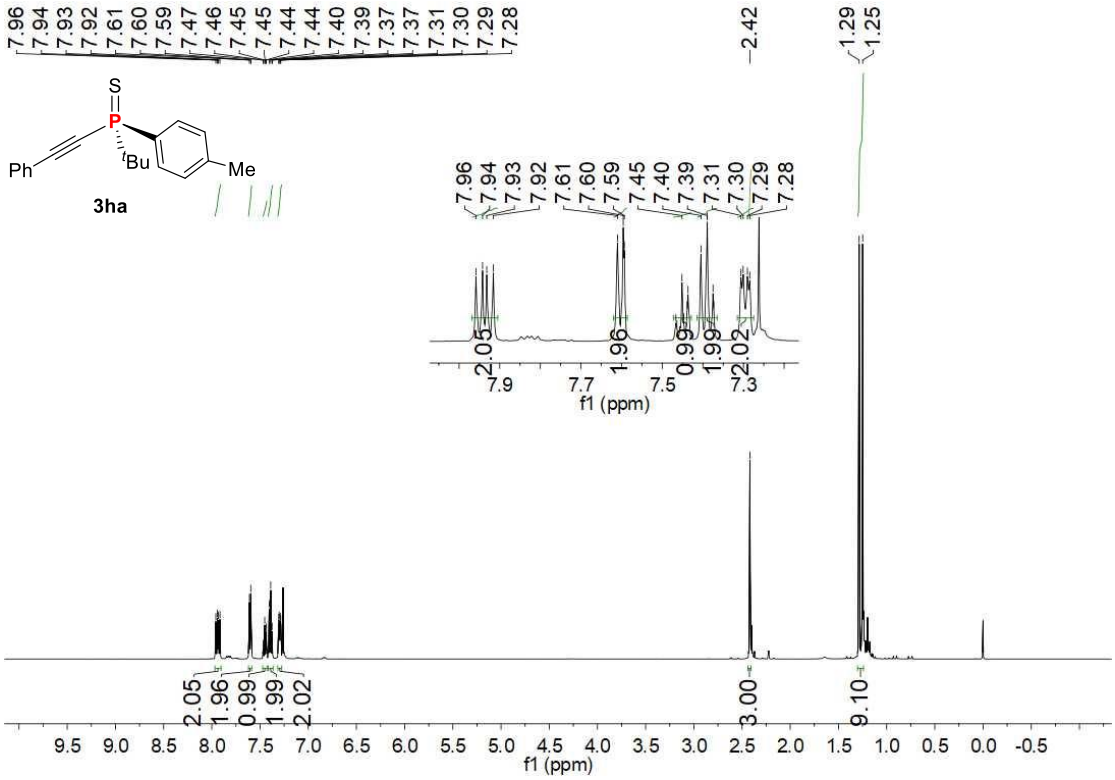

44.88
S
P
Ph
tBu
OMe
3fa
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

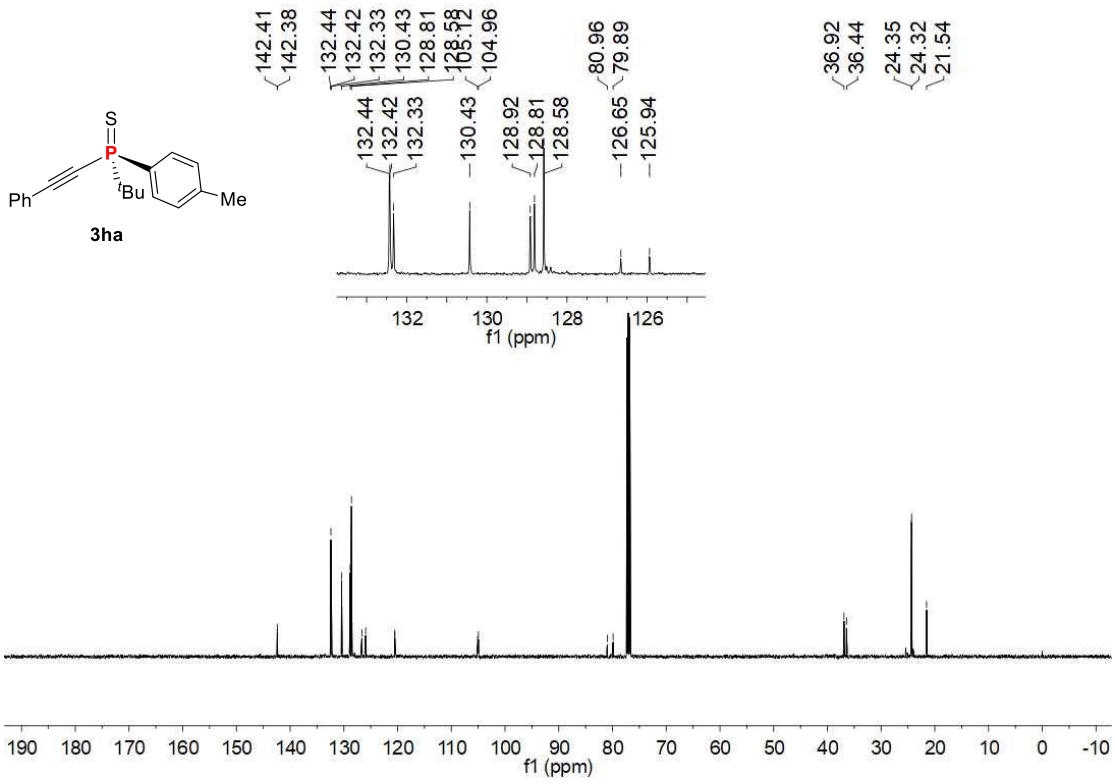

8.00 7.98 7.98 7.97 7.97 7.96 7.96 7.60 7.59 7.59 7.51 7.51 7.50 7.49 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.39 7.38 7.38 7.36
1.34 1.30 1.27
S
P
Ph
tBu
tBu
3ga
1.99 1.98 2.02 1.01 2.08
9.00 9.04
f1 (ppm)

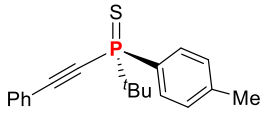

155.36 155.33 132.41 132.40 132.30 132.21 130.45 128.59 125.22 125.12 125.08 104.91 81.03 79.96 36.93 36.46 34.98 31.17 24.39 24.36
S
P
Ph
tBu
tBu
3ga
f1 (ppm)



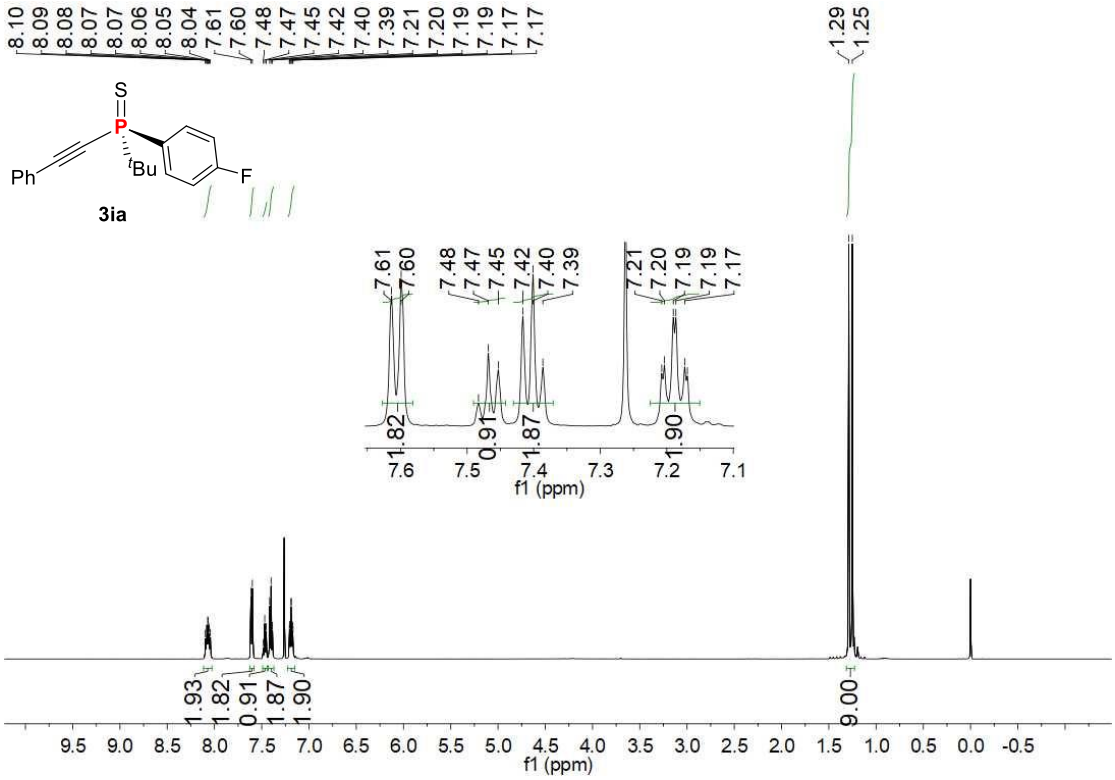
3ga

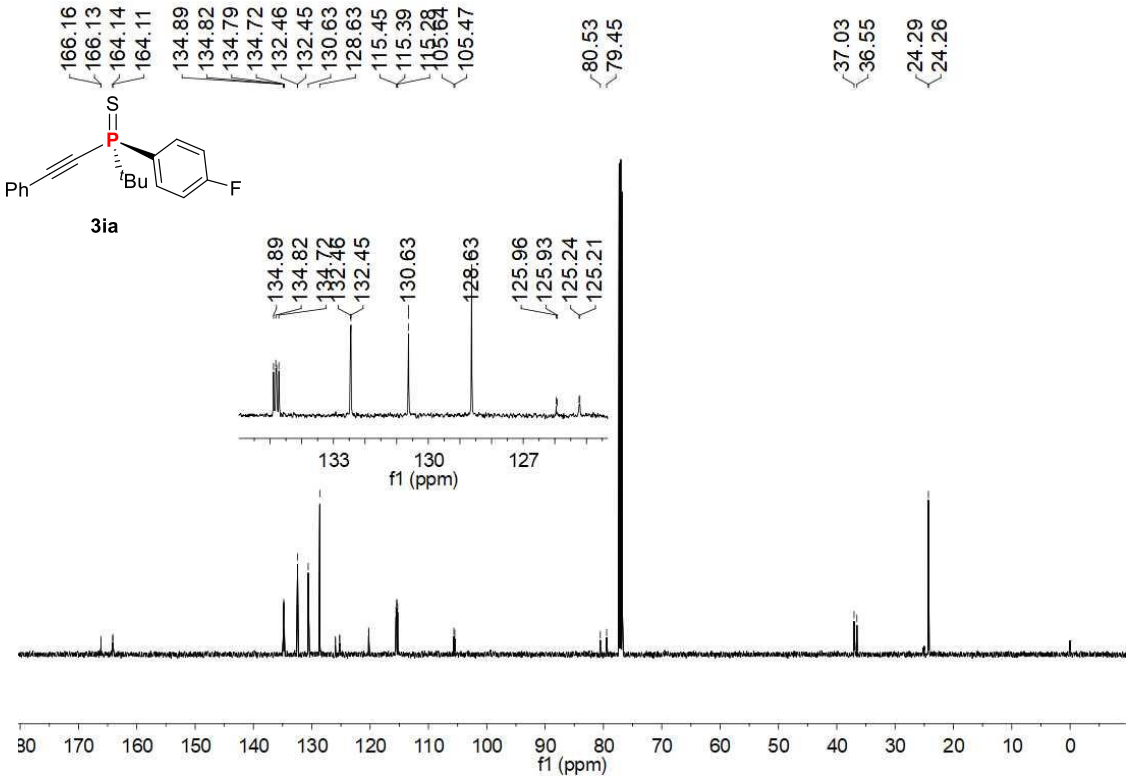

7.96
7.94
7.93
7.92
7.61
7.60
7.59
7.47
7.46
7.45
7.45
7.44
7.44
7.40
7.39
7.37
7.37
7.31
7.30
7.29
7.28
2.42
1.29
1.25
S
P
Ph
tBu
Me
3ha
2.05
1.96
0.99
1.99
2.02
3.00
9.10
f1 (ppm)

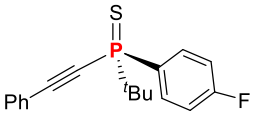

142.41
142.38
132.44
132.42
132.33
130.43
128.81
128.58
128.12
104.96
80.96
79.89
36.92
36.44
24.35
24.32
21.54
126.65
125.94
S
P
Ph
tBu
Me
3ha
f1 (ppm)



3ha

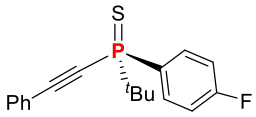

8.10 8.09 8.08 8.07 8.07 8.06 8.05 8.04 7.61 7.60 7.48 7.47 7.45 7.42 7.40 7.39 7.21 7.20 7.19 7.19 7.17 7.17
1.29 1.25
S
P
Ph
tBu
F
3ia
7.61 7.60 7.48 7.47 7.45 7.42 7.40 7.39 7.21 7.20 7.19 7.19 7.17
1.82 0.91 1.87 1.90
7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
1.93 1.82 0.91 1.87 1.90 9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.16 166.13 164.14 164.11 134.89 134.82 134.79 134.72 132.46 132.45 130.63 128.63 115.45 115.39 105.64 105.47
80.53 79.45
37.03 36.55 24.29 24.26
S
P
Ph
tBu
F
3ia
134.89 134.82 132.46 132.45 130.63 128.63 125.96 125.93 125.24 125.21
133 130 127
f1 (ppm)
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


S
P
Ph
tBu
F

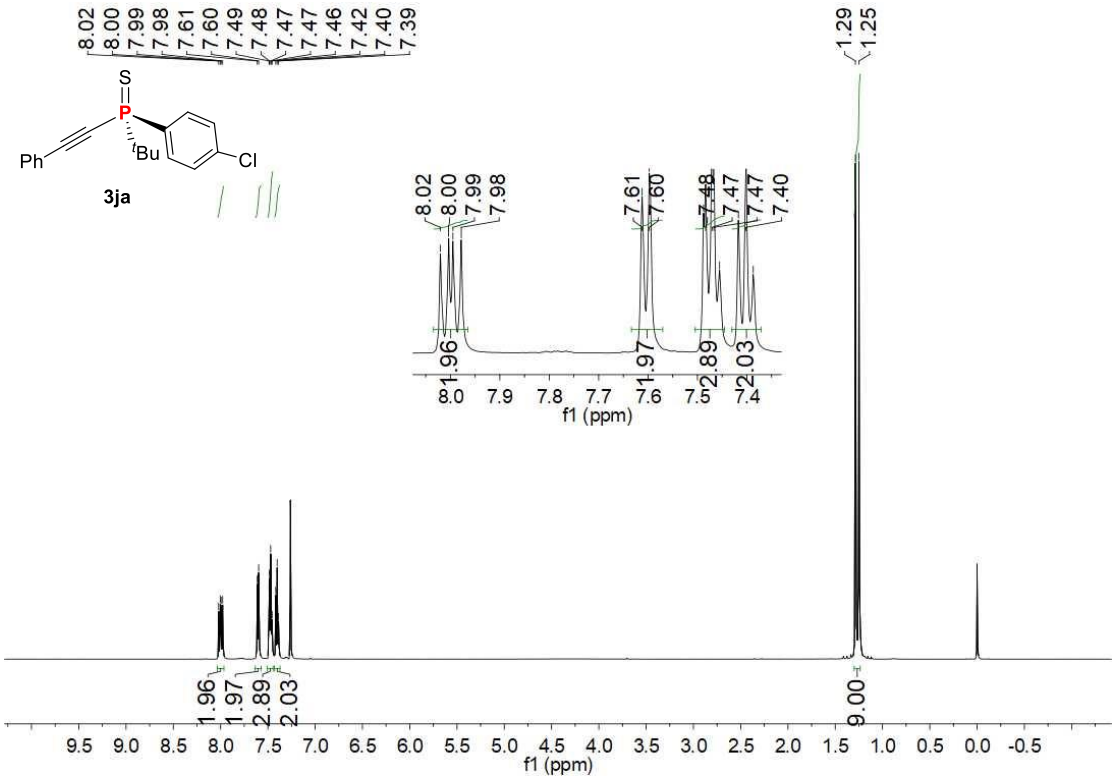
3ia

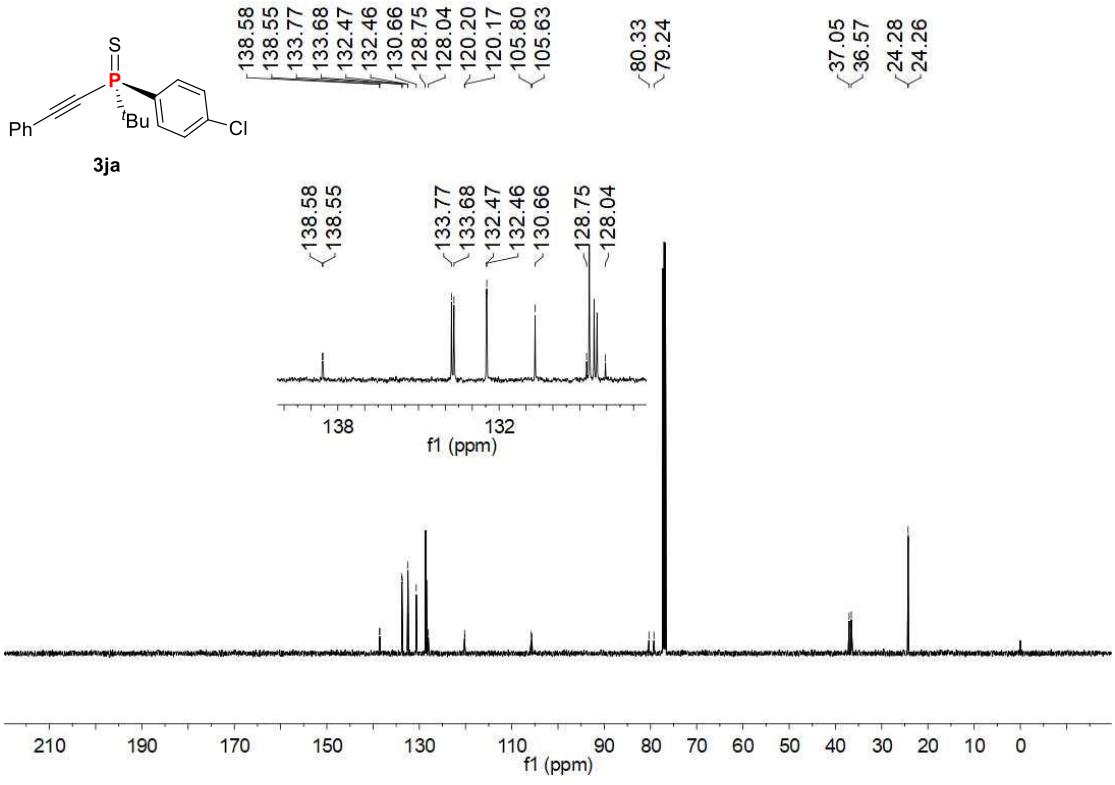
44.70
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

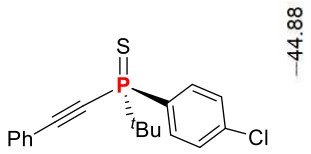

S
P
Ph
tBu
F

3ia

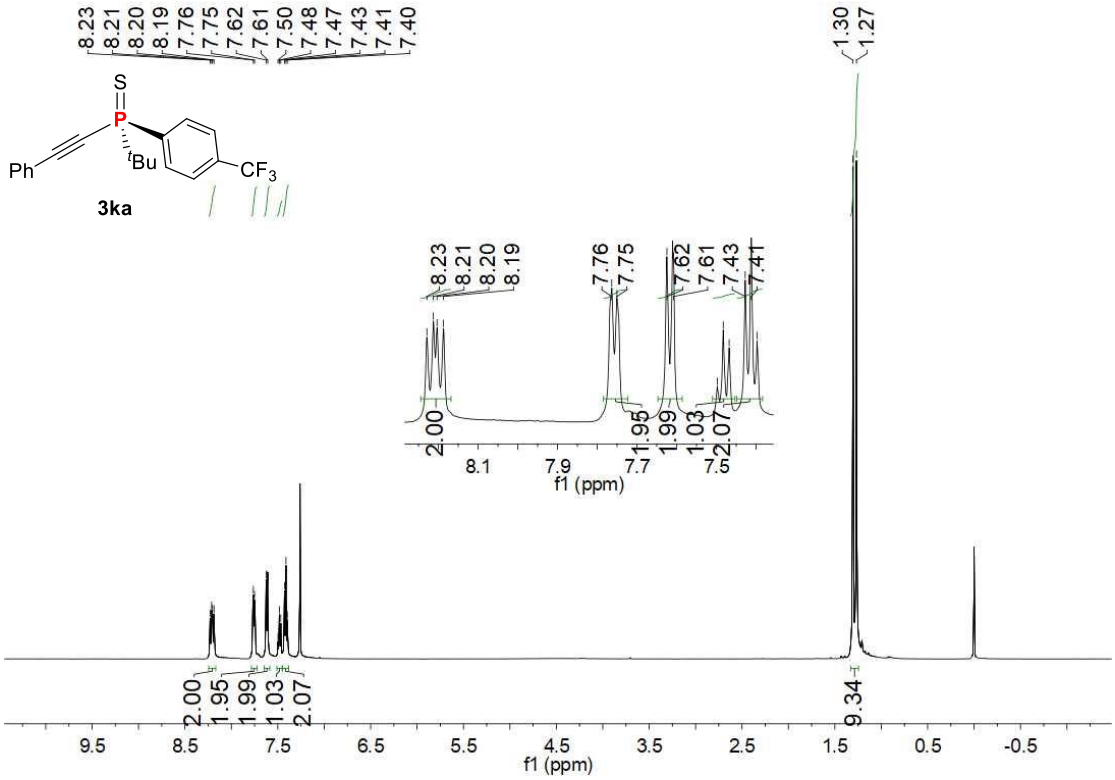
107.33
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

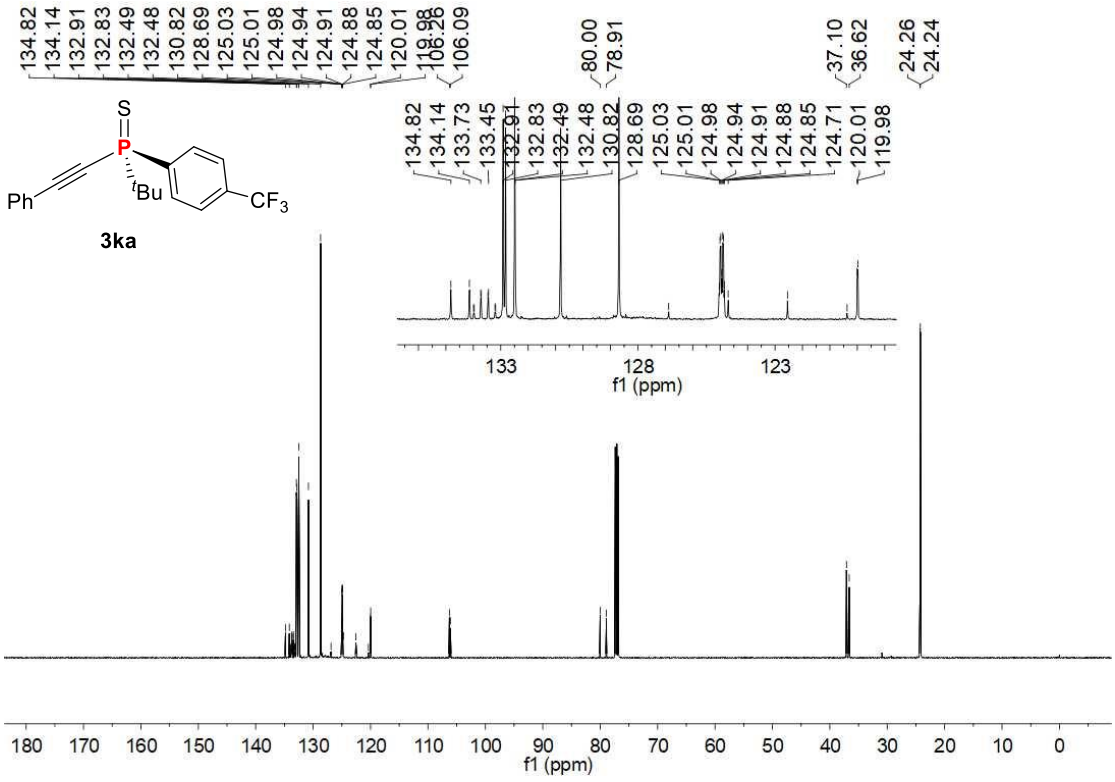

8.02
8.00
7.99
7.98
7.61
7.60
7.49
7.48
7.47
7.47
7.46
7.42
7.40
7.39
1.29
1.25
S
P
Ph
tBu
Cl
3ja
1.96
1.97
2.89
2.03
9.00
f1 (ppm)

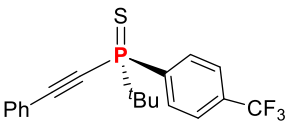

138.58
138.55
133.77
133.68
132.47
132.46
130.66
128.75
128.04
120.20
120.17
105.80
105.63
80.33
79.24
37.05
36.57
24.28
24.26
S
P
Ph
tBu
Cl
3ja
f1 (ppm)



3ja

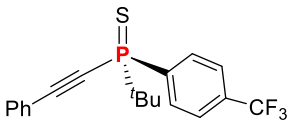

8.23
8.21
8.20
8.19
7.76
7.75
7.62
7.61
7.50
7.48
7.47
7.43
7.41
7.40
1.30
1.27
S
P
Ph
tBu
CF3
3ka
2.00
1.95
1.99
1.03
2.07
9.34
f1 (ppm)


134.82
134.14
132.91
132.83
132.49
132.48
130.82
128.69
125.03
125.01
124.98
124.94
124.91
124.88
124.85
120.01
119.98
106.26
106.09
80.00
78.91
37.10
36.62
24.26
24.24
S
P
Ph
tBu
CF3
3ka
f1 (ppm)


S
P
Ph
tBu
CF3

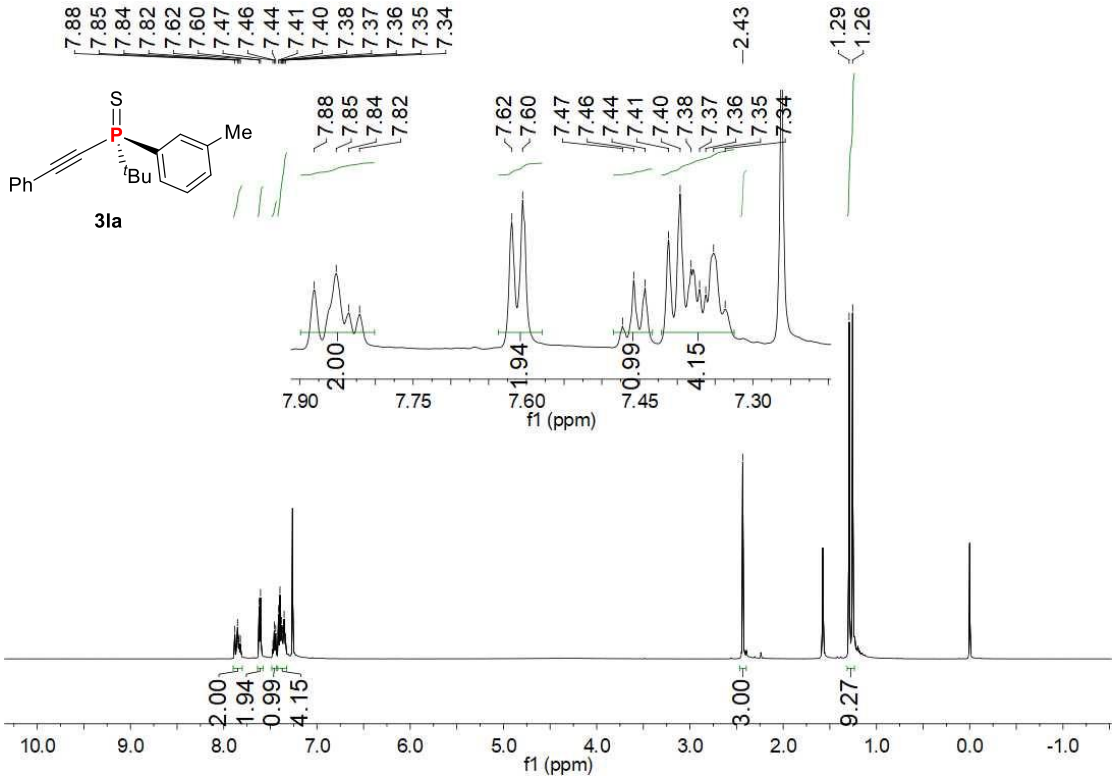
3ka

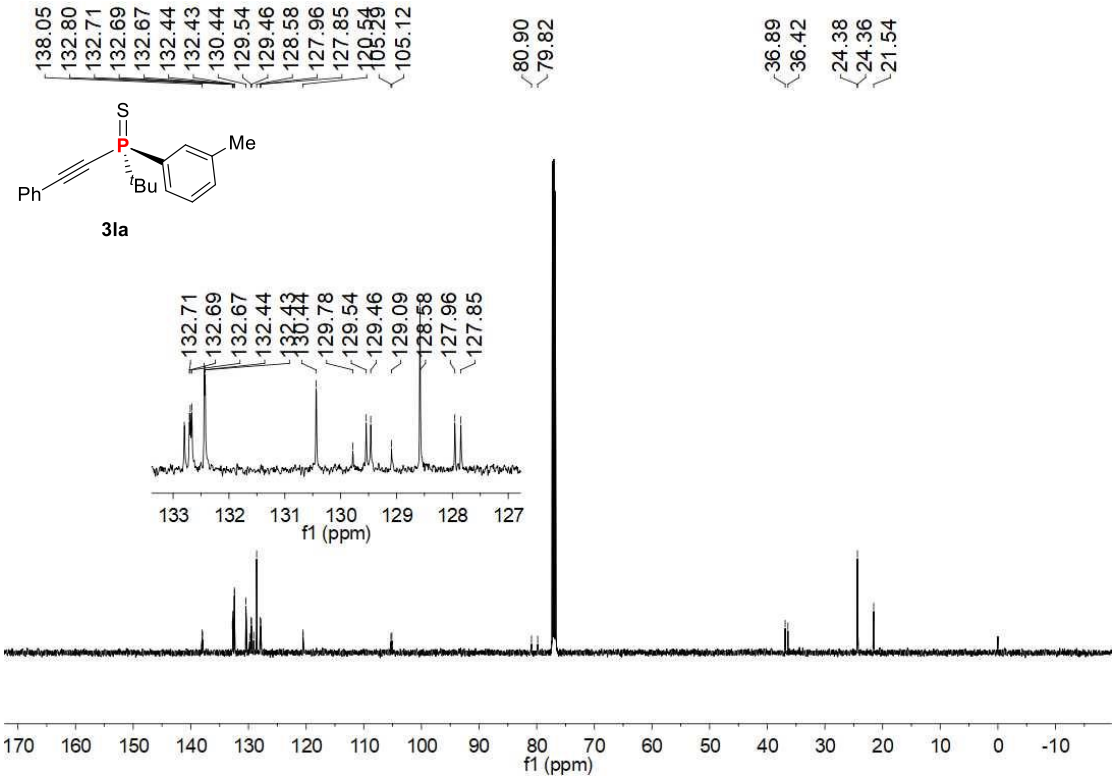
44.95
56
53
50
47
44
41
38
35
32
29
26
23
f1 (ppm)

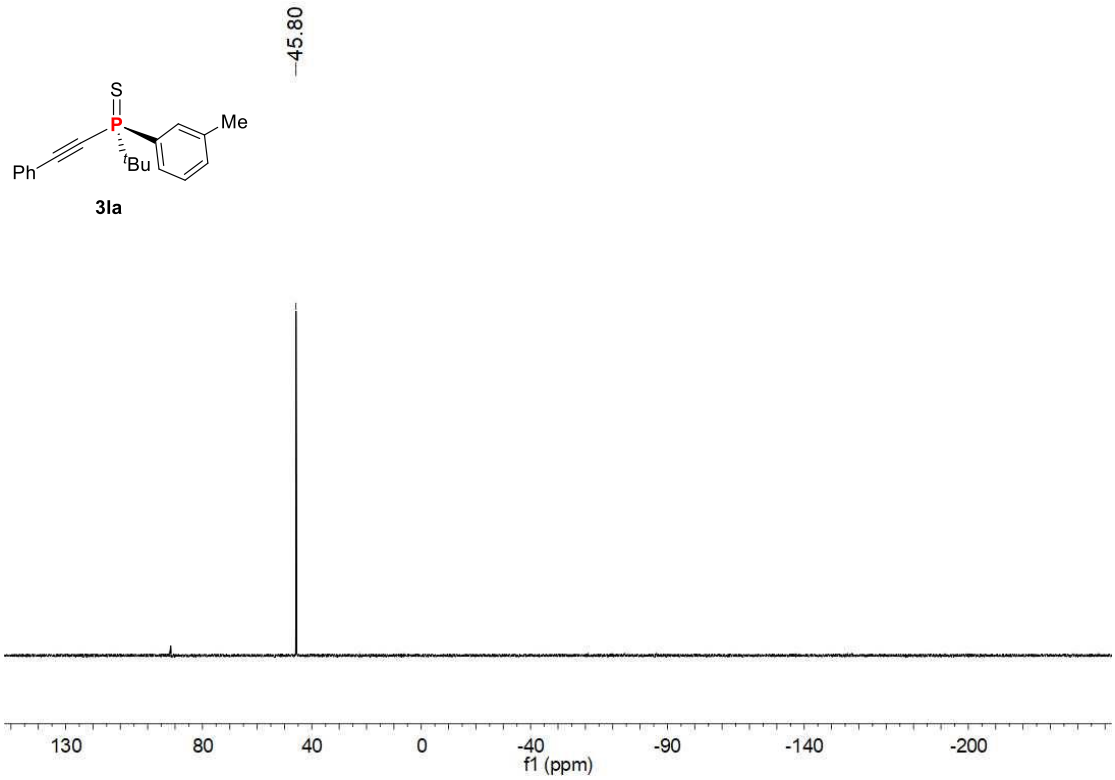

S
P
Ph
tBu
CF3

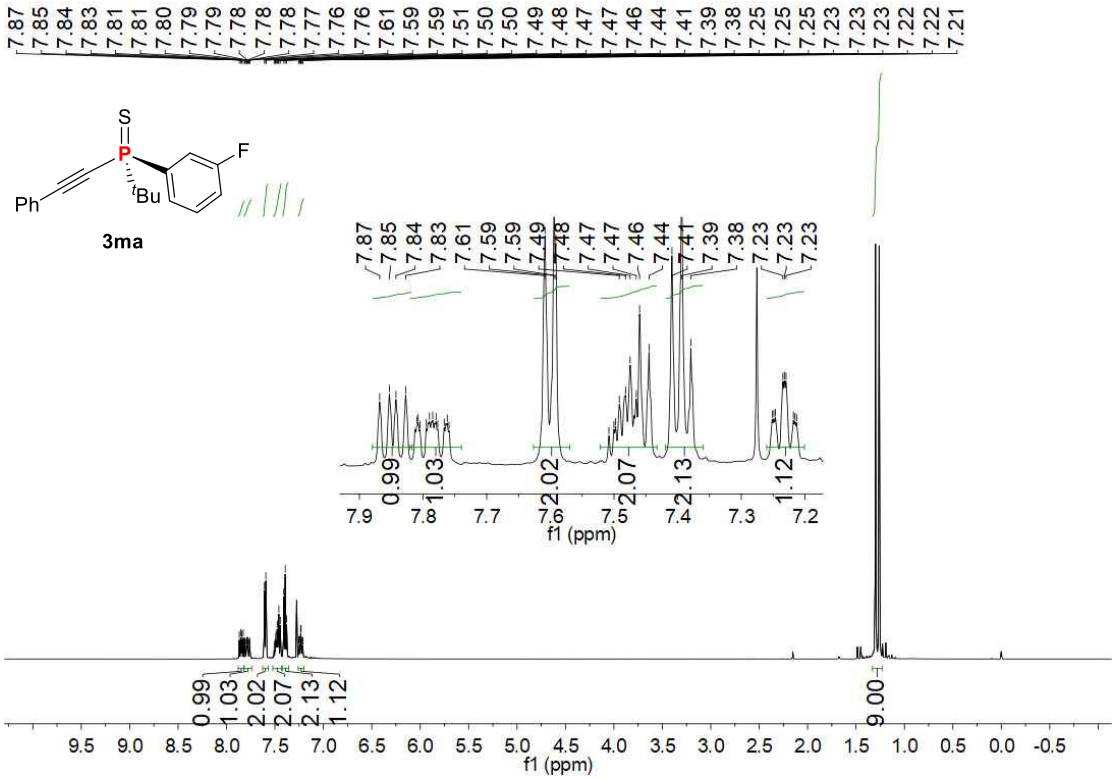
3ka

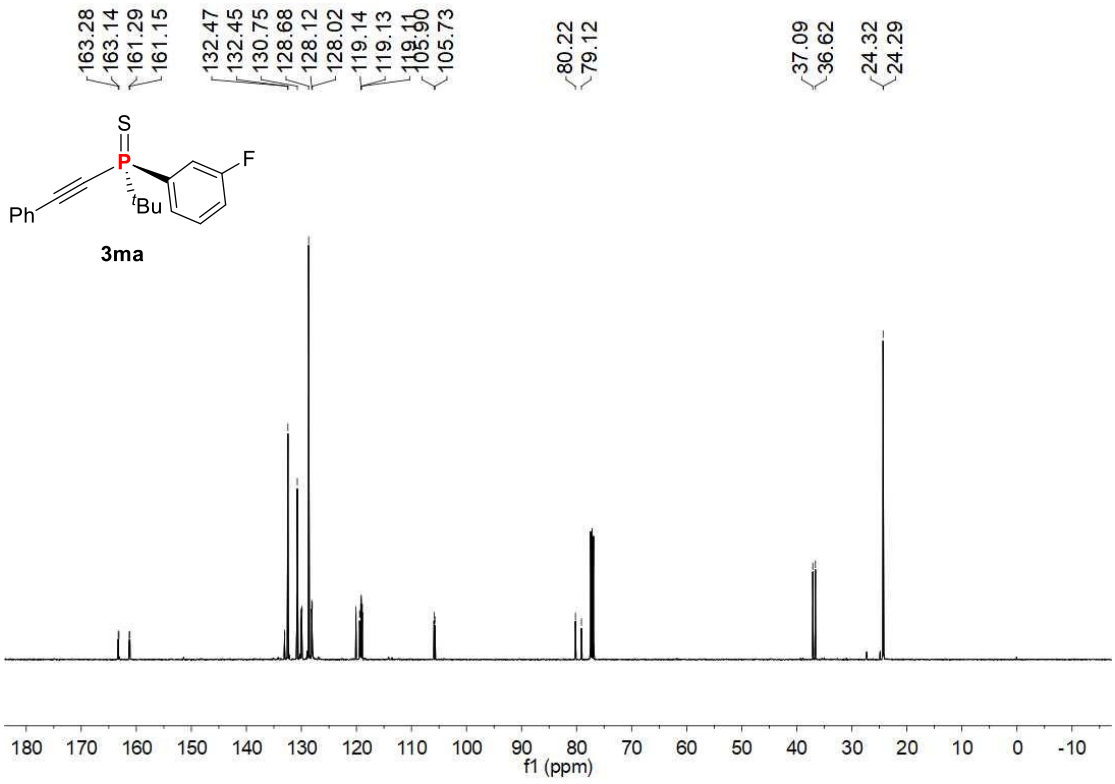
63.07
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

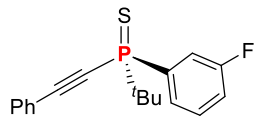

7.88
7.85
7.84
7.82
7.62
7.60
7.47
7.46
7.44
7.41
7.40
7.38
7.37
7.36
7.35
7.34
2.43
1.29
1.26
S
P
Me
Ph
tBu
3la
2.00
1.94
0.99
4.15
3.00
9.27
f1 (ppm)


138.05
132.80
132.71
132.69
132.67
132.44
132.43
130.44
129.54
129.46
128.58
127.96
127.85
120.54
105.29
105.12
80.90
79.82
36.89
36.42
24.38
24.36
21.54
S
P
Me
Ph
tBu
3la
f1 (ppm)


-45.80
S
P
Me
Ph
tBu
3la
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

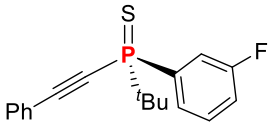

7.87 7.85 7.84 7.83 7.81 7.81 7.80 7.79 7.79 7.78 7.78 7.78 7.77 7.76 7.76 7.61 7.59 7.59 7.51 7.50 7.50 7.49 7.48 7.47 7.47 7.46 7.44 7.41 7.39 7.38 7.25 7.25 7.23 7.23 7.23 7.22 7.22 7.21
S
P
F
Ph
tBu
3ma
0.99 1.03 2.02 2.07 2.13 1.12
9.00
f1 (ppm)


163.28 163.14 161.29 161.15 132.47 132.45 130.75 128.68 128.12 128.02 119.14 119.13 119.11 105.90 105.73 80.22 79.12 37.09 36.62 24.32 24.29
S
P
F
Ph
tBu
3ma
f1 (ppm)


S
P
F
Ph
tBu

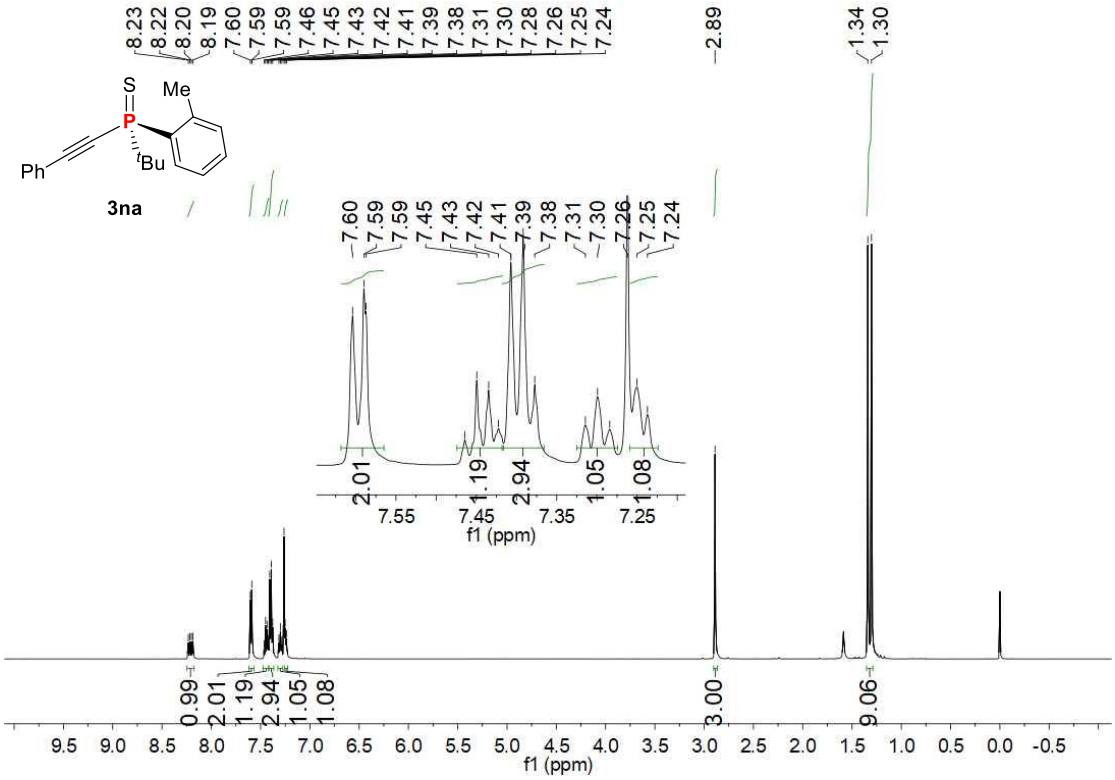
3ma

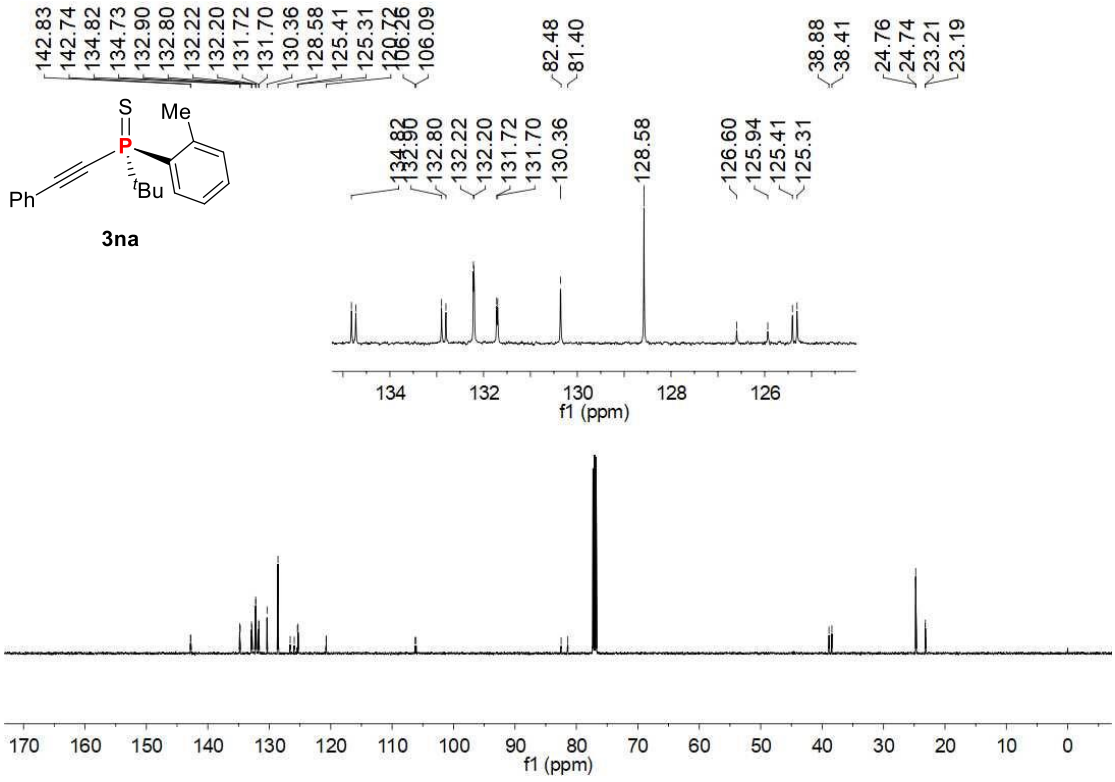
-46.14
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

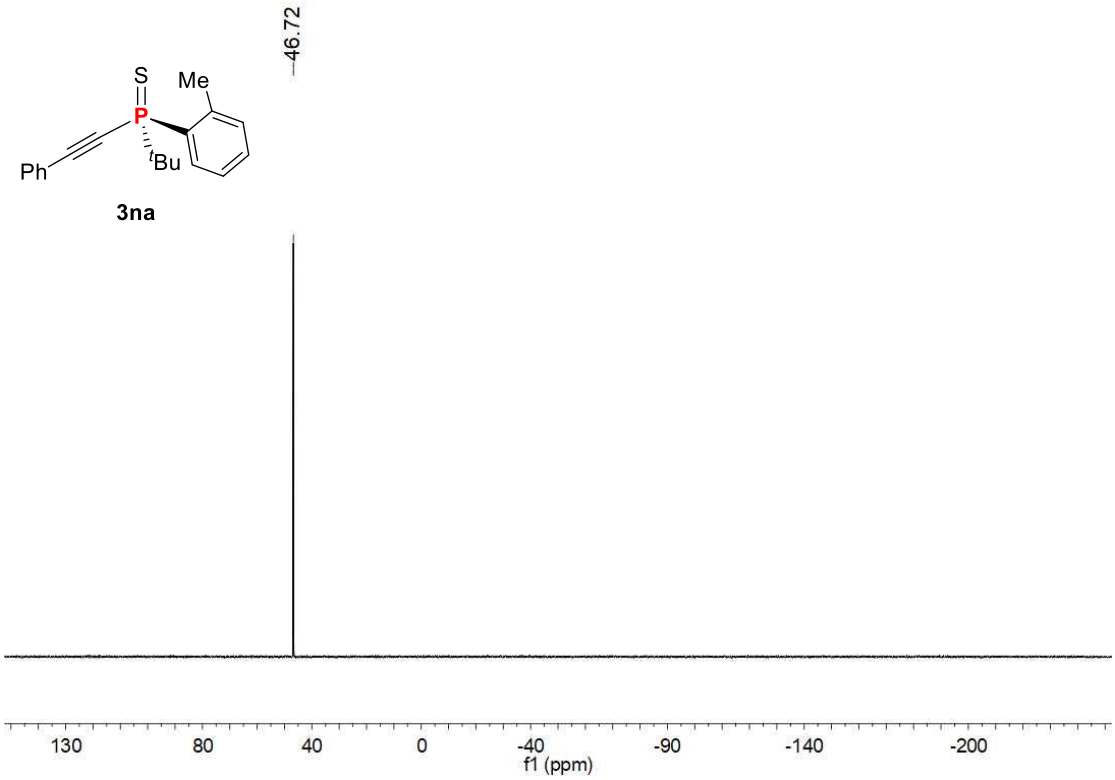

S
P
F
Ph
tBu

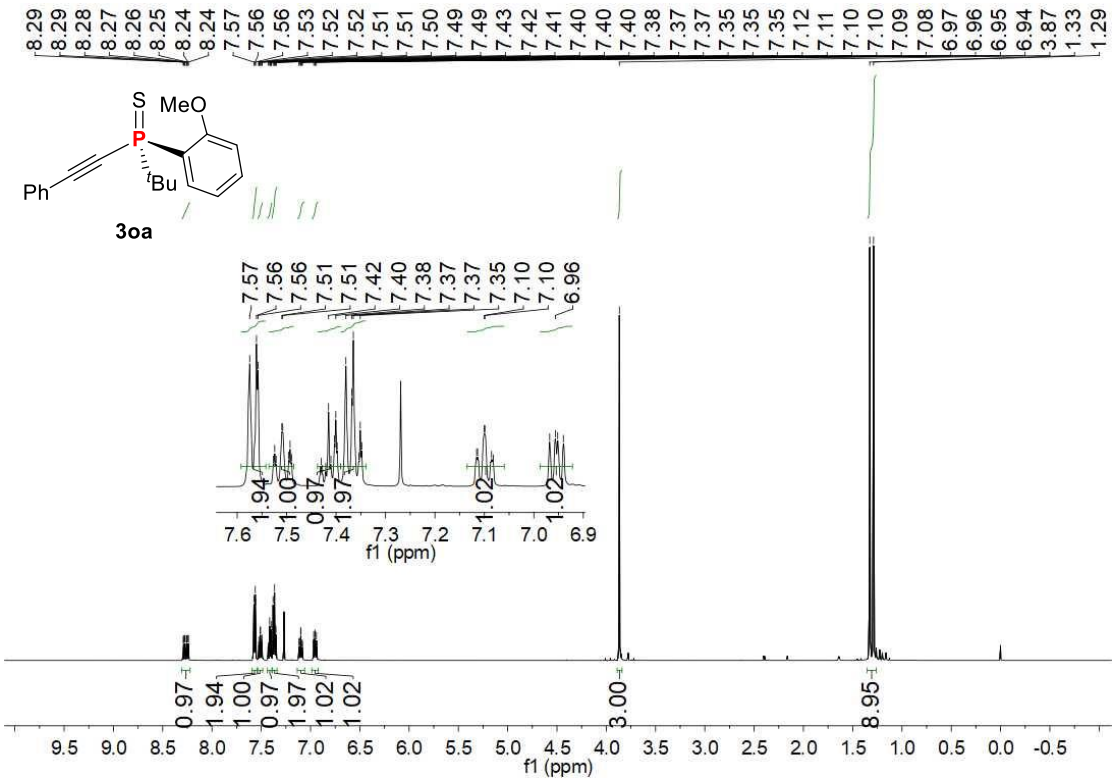
3ma

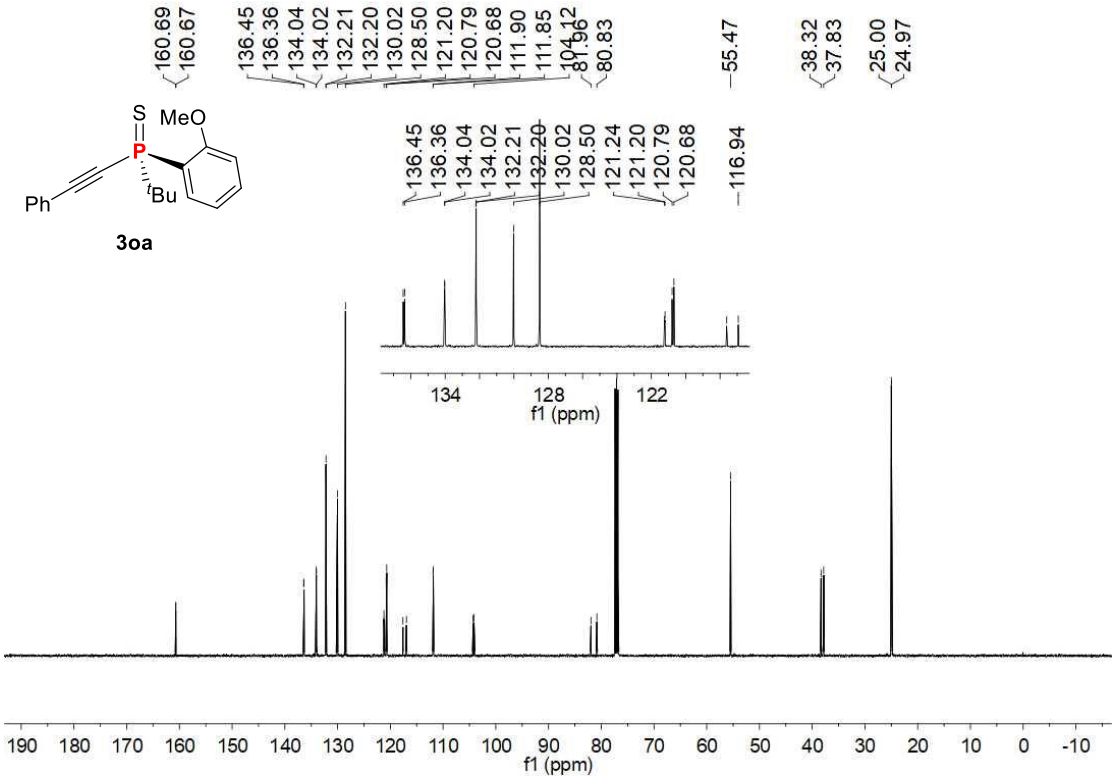
-111.37
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

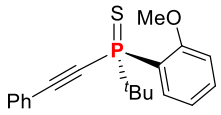

8.23
8.22
8.20
8.19
7.60
7.59
7.59
7.46
7.45
7.43
7.42
7.41
7.39
7.38
7.31
7.30
7.28
7.26
7.25
7.24
2.89
1.34
1.30
S
Me
P
Ph
tBu
3na
2.01
1.19
2.94
1.05
1.08
7.55
7.45
7.35
7.25
f1 (ppm)
0.99
3.00
9.06
f1 (ppm)


142.83
142.74
134.82
134.73
132.90
132.80
132.22
132.20
131.72
131.70
130.36
128.58
125.41
125.31
106.09
82.48
81.40
38.88
38.41
24.76
24.74
23.21
23.19
S
Me
P
Ph
tBu
3na
128.58
126.60
125.94
125.41
125.31
134
132
130
128
126
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

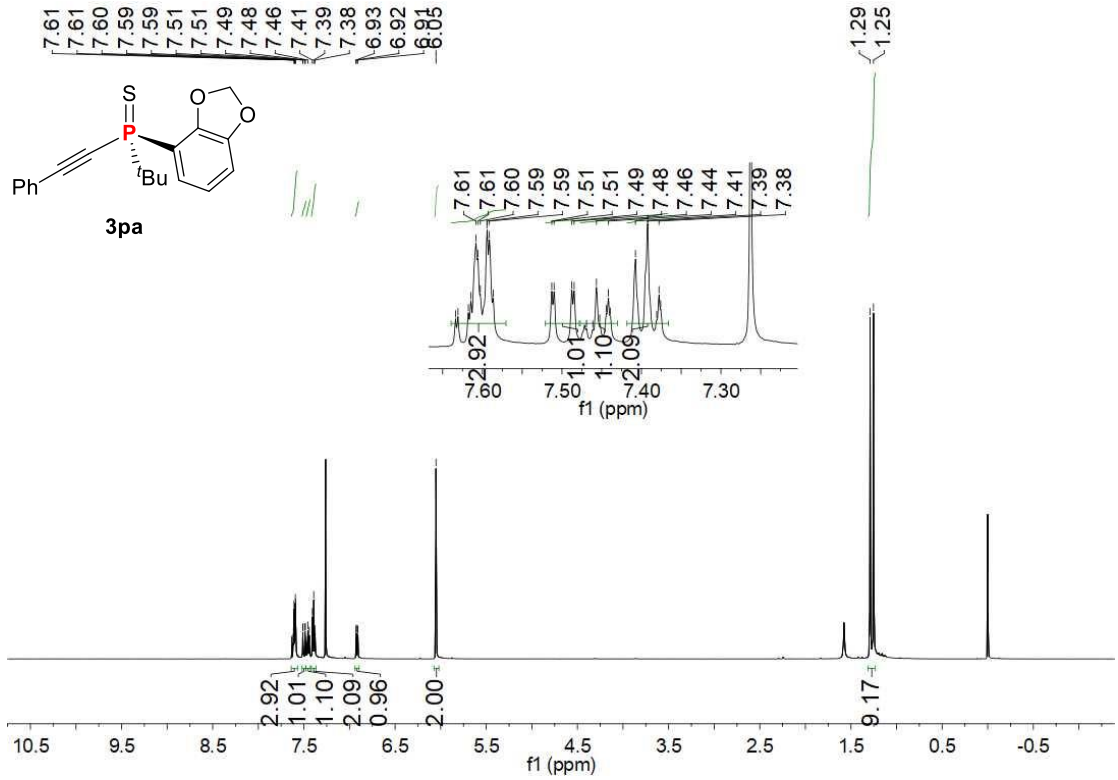

46.72
S
Me
P
tBu
Ph
3na
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

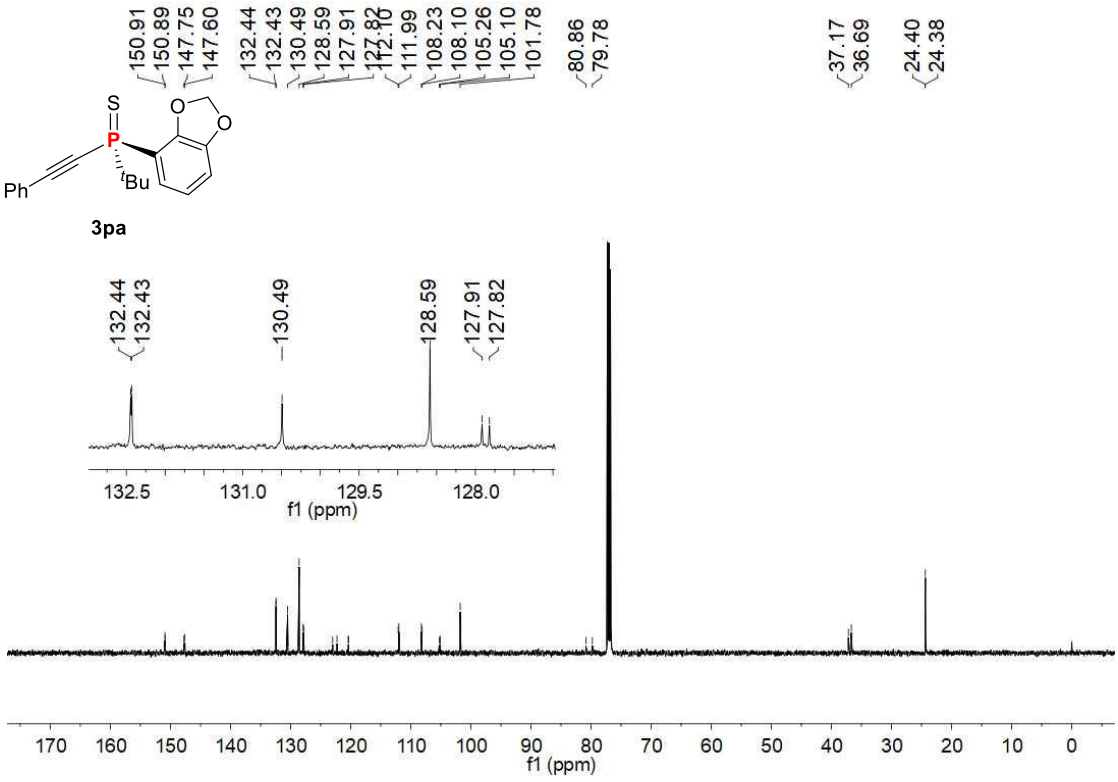

8.29 8.29 8.28 8.27 8.26 8.25 8.24 8.24 7.57 7.56 7.56 7.53 7.52 7.52 7.51 7.51 7.50 7.49 7.49 7.43 7.42 7.41 7.40 7.40 7.40 7.38 7.37 7.37 7.35 7.35 7.12 7.11 7.10 7.10 7.09 7.08 6.97 6.96 6.95 6.94 3.87 1.33 1.29
S
MeO
P
tBu
Ph
3oa
7.57 7.56 7.56 7.51 7.51 7.42 7.40 7.38 7.37 7.37 7.35 7.10 7.10 6.96
1.94 1.00 0.97 1.97 1.02 1.02
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
0.97 1.94 1.00 0.97 1.97 1.02 1.02 3.00 8.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

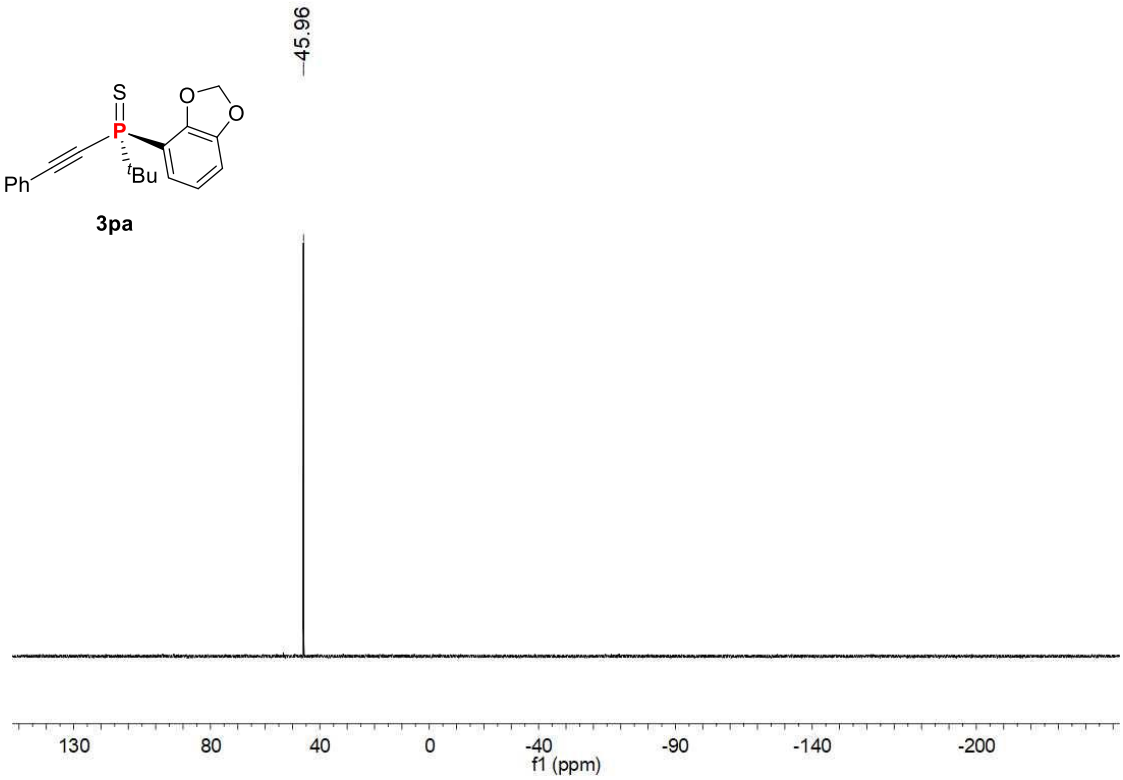

160.69 160.67 136.45 136.36 134.04 134.02 132.21 132.20 130.02 128.50 121.20 120.79 120.68 111.90 111.85 104.12 81.96 80.83 55.47 38.32 37.83 25.00 24.97
S
MeO
P
tBu
Ph
3oa
136.45 136.36 134.04 134.02 132.21 132.20 130.02 128.50 121.24 121.20 120.79 120.68 116.94
134 128 122
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



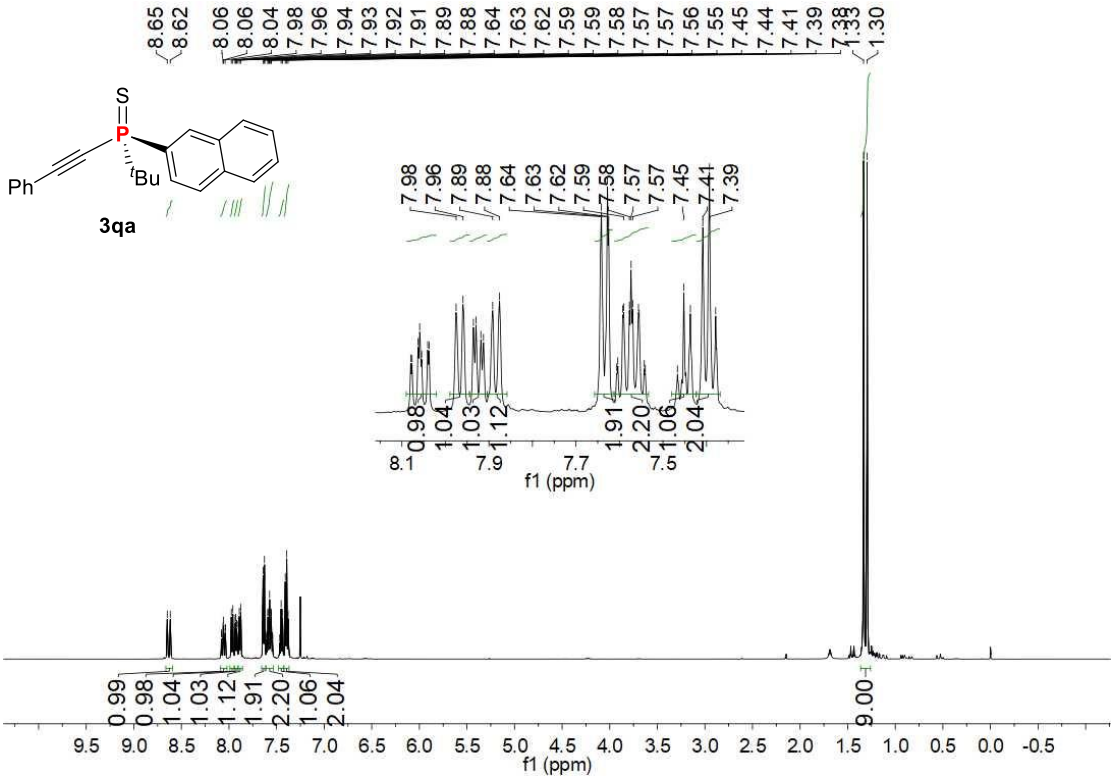
3oa

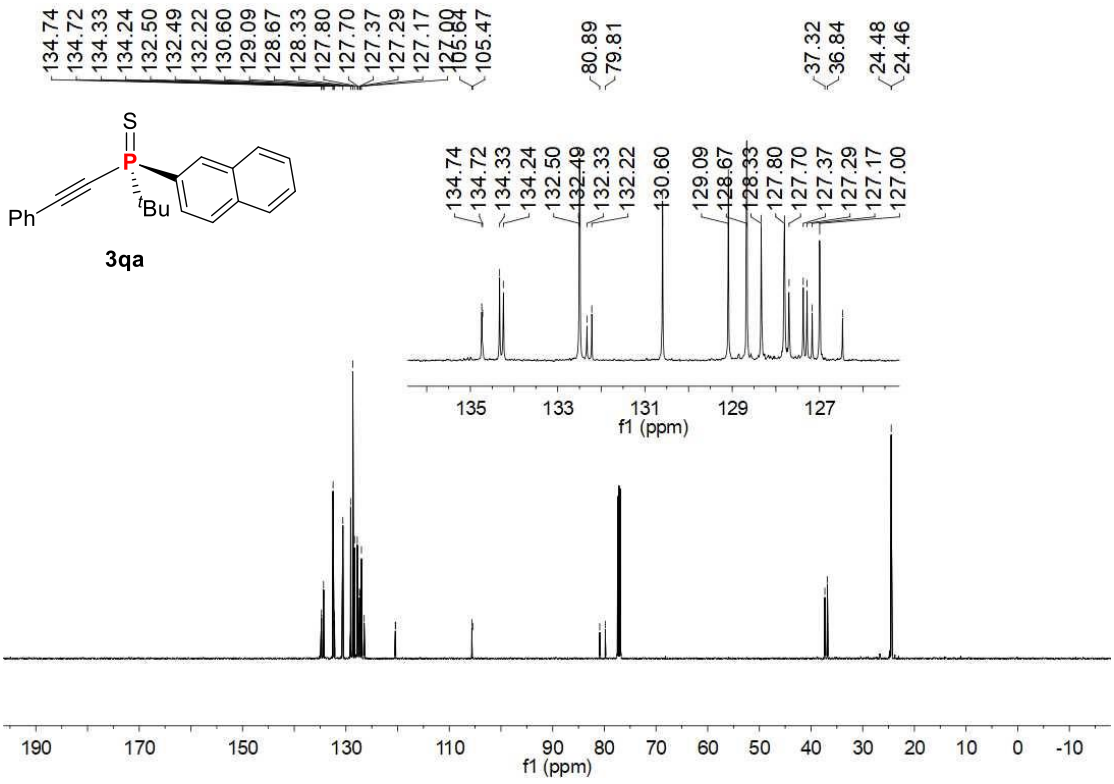

7.61
7.61
7.60
7.59
7.59
7.51
7.51
7.49
7.48
7.46
7.41
7.39
7.38
6.93
6.92
6.85
1.29
1.25
S
O
O
P
Ph
tBu
3pa
2.92
1.01
1.10
2.09
0.96
2.00
9.17
f1 (ppm)

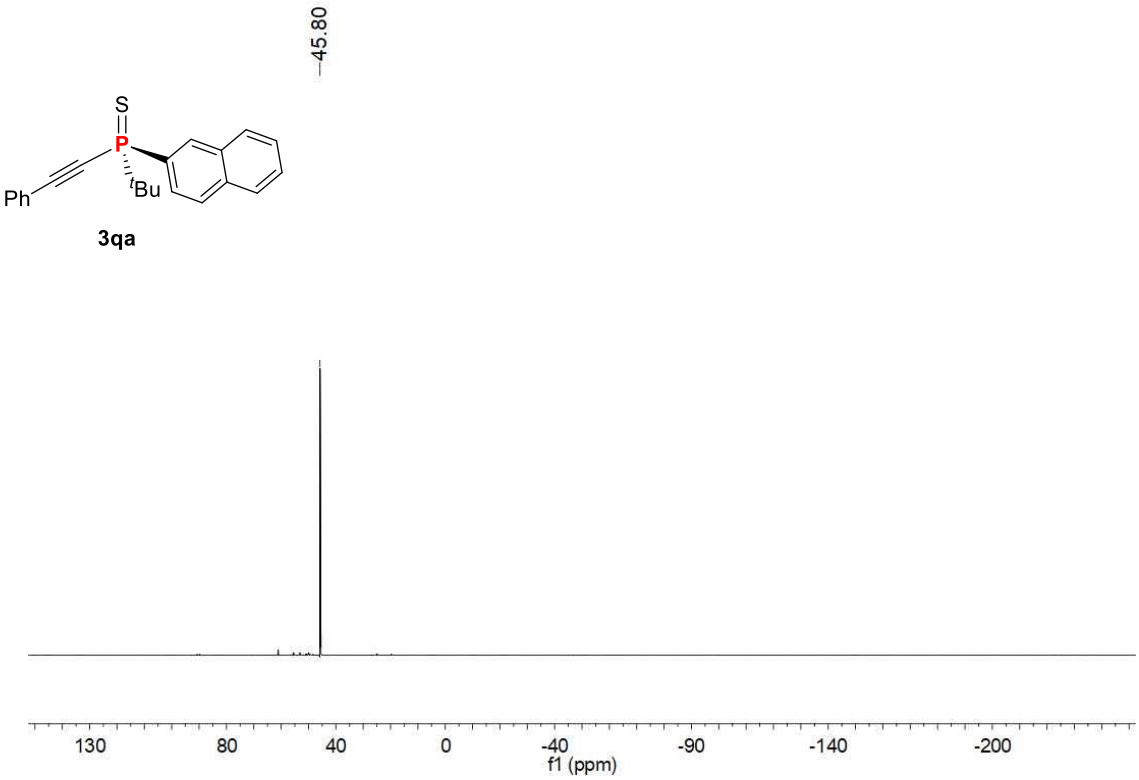

150.91
150.89
147.75
147.60
132.44
132.43
130.49
128.59
127.91
127.82
112.10
111.99
108.23
108.10
105.26
105.10
101.78
80.86
79.78
37.17
36.69
24.40
24.38
S
O
O
P
Ph
tBu
3pa
f1 (ppm)



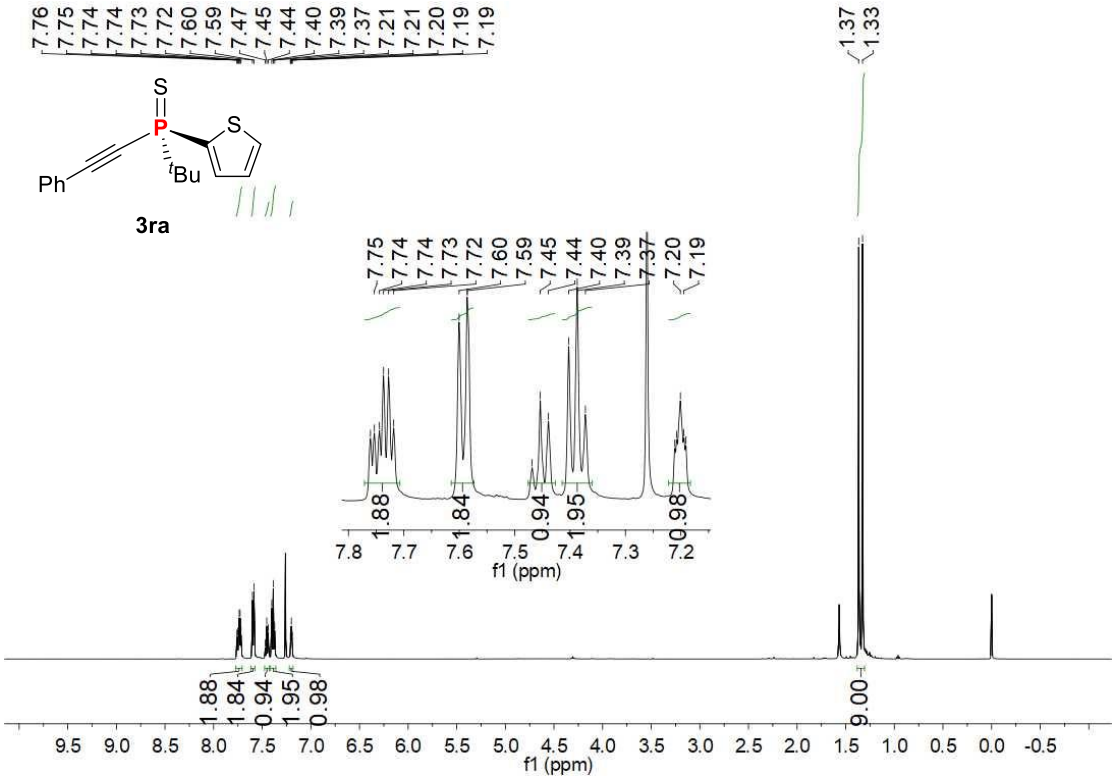
3pa

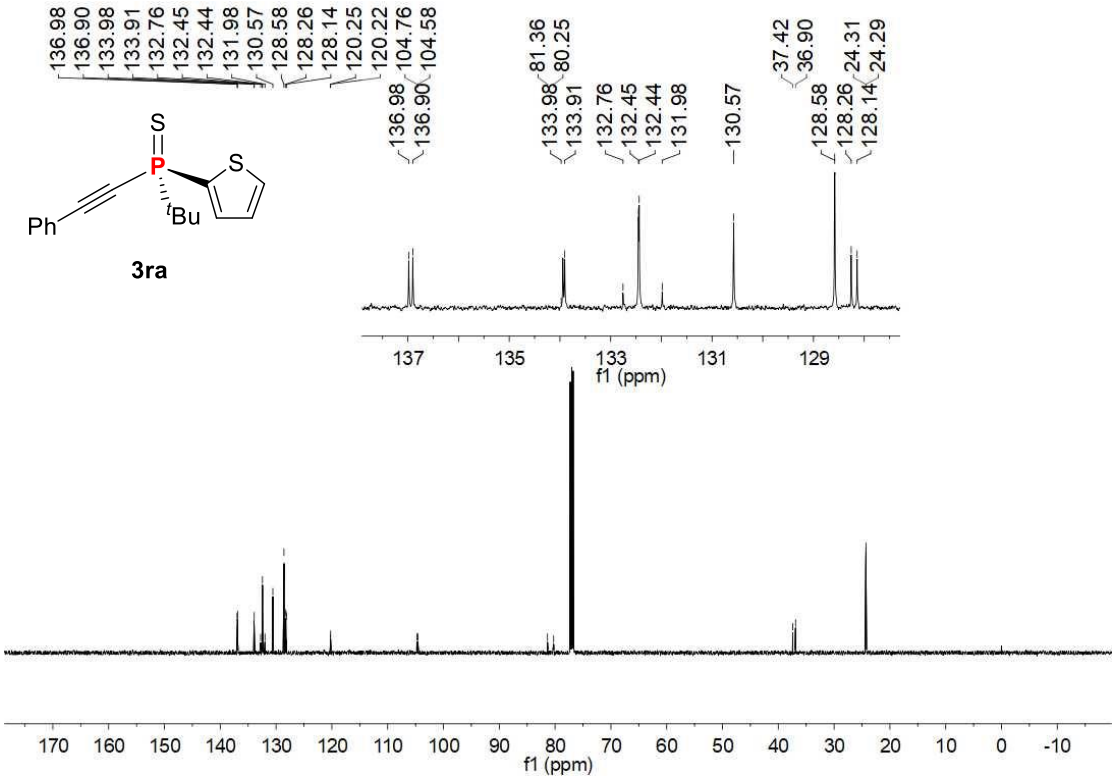

8.65 8.62 8.06 8.06 8.04 7.98 7.96 7.94 7.93 7.92 7.91 7.89 7.88 7.64 7.63 7.62 7.59 7.59 7.58 7.57 7.57 7.56 7.55 7.45 7.44 7.41 7.39 1.33 1.30
S
P
Ph
tBu
3qa
7.98 7.96 7.89 7.88 7.64 7.63 7.62 7.59 7.58 7.57 7.57 7.45 7.41 7.39
0.98 1.04 1.03 1.12 1.91 2.20 1.06 2.04
8.1 7.9 7.7 7.5
f1 (ppm)
0.99 0.98 1.04 1.03 1.12 1.91 2.20 1.06 2.04 9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

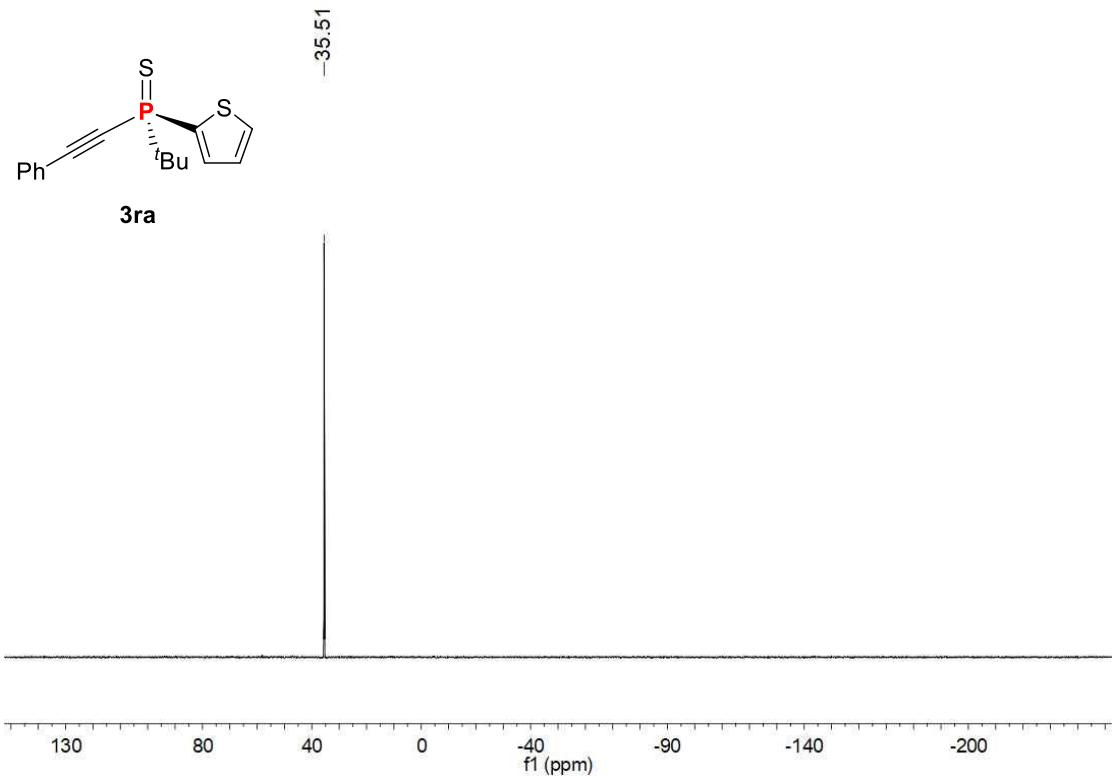

134.74 134.72 134.33 134.24 132.50 132.49 132.22 130.60 129.09 128.67 128.33 127.80 127.70 127.37 127.29 127.17 127.00 105.47
80.89 79.81
37.32 36.84
24.48 24.46
S
P
Ph
tBu
3qa
134.74 134.72 134.33 134.24 132.50 132.49 132.33 132.22 130.60 129.09 128.67 128.33 127.80 127.70 127.37 127.29 127.17 127.00
135 133 131 129 127
f1 (ppm)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



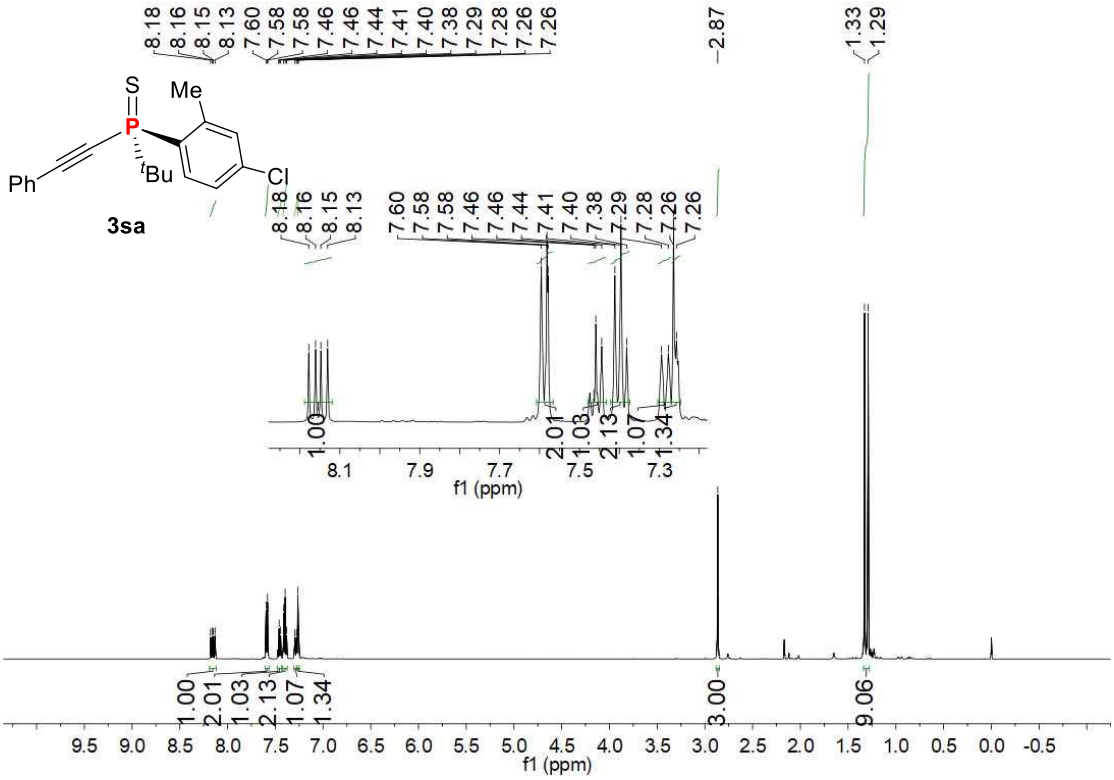
3qa

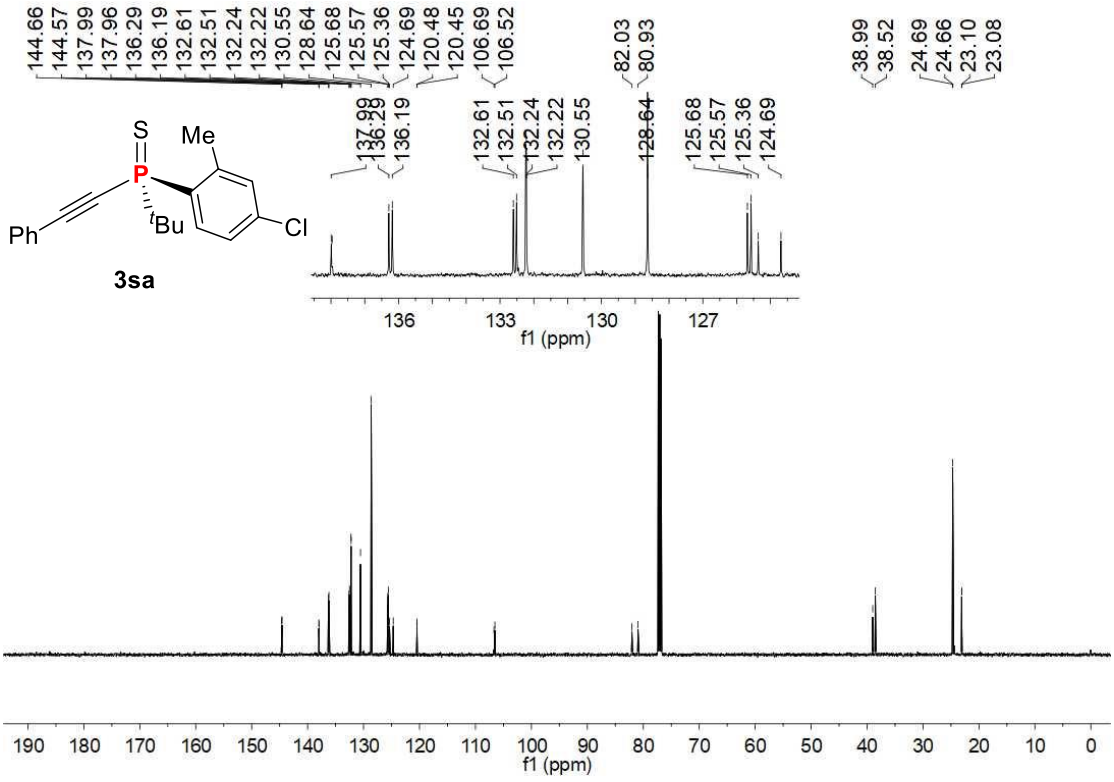

7.76
7.75
7.74
7.74
7.73
7.72
7.60
7.59
7.47
7.45
7.44
7.40
7.39
7.37
7.21
7.21
7.20
7.19
7.19
1.37
1.33
S
P
S
Ph
tBu
3ra
1.88
1.84
0.94
1.95
0.98
9.00
f1 (ppm)

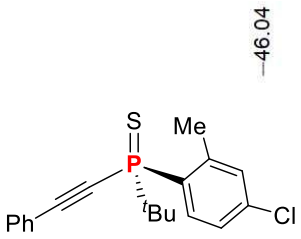

136.98
136.90
133.98
133.91
132.76
132.45
132.44
131.98
130.57
128.58
128.26
128.14
120.25
120.22
104.76
104.58
81.36
80.25
37.42
36.90
24.31
24.29
S
P
S
Ph
tBu
3ra
f1 (ppm)



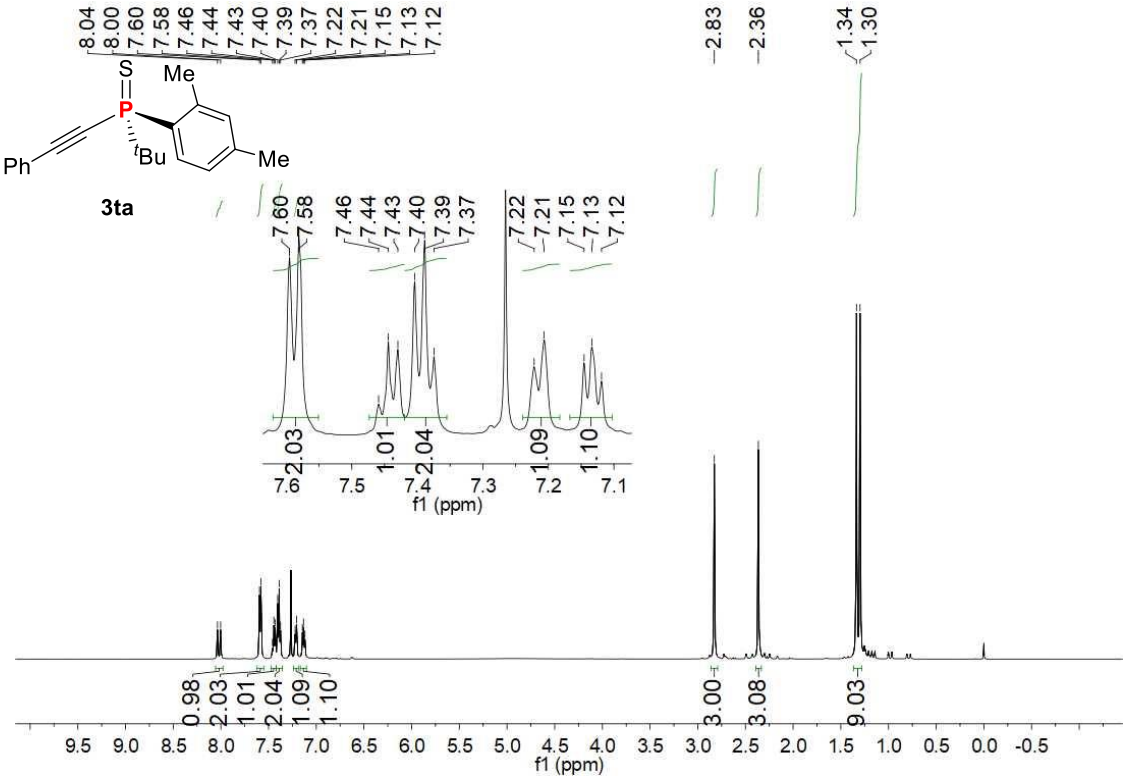
3ra

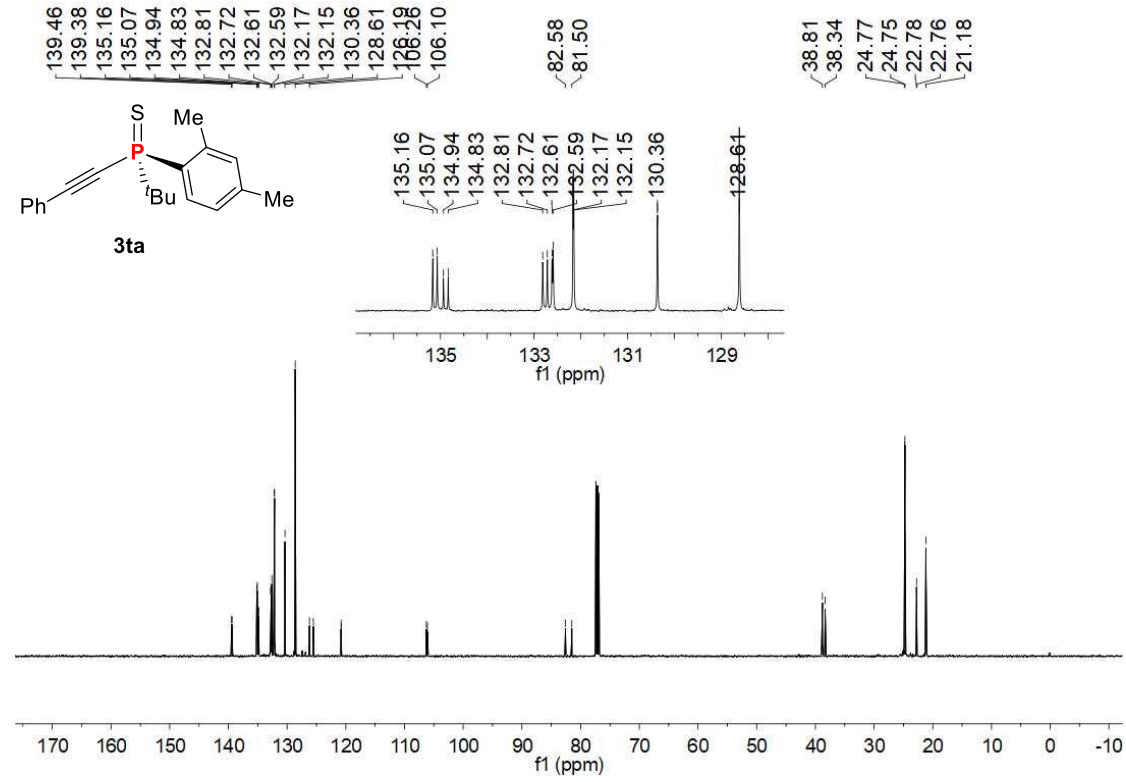

8.18
8.16
8.15
8.13
7.60
7.58
7.58
7.46
7.46
7.44
7.41
7.40
7.38
7.29
7.28
7.26
7.26
2.87
1.33
1.29
S
Me
P
Ph
tBu
Cl
3sa
1.00
2.01
1.03
2.13
1.07
1.34
3.00
9.06
f1 (ppm)

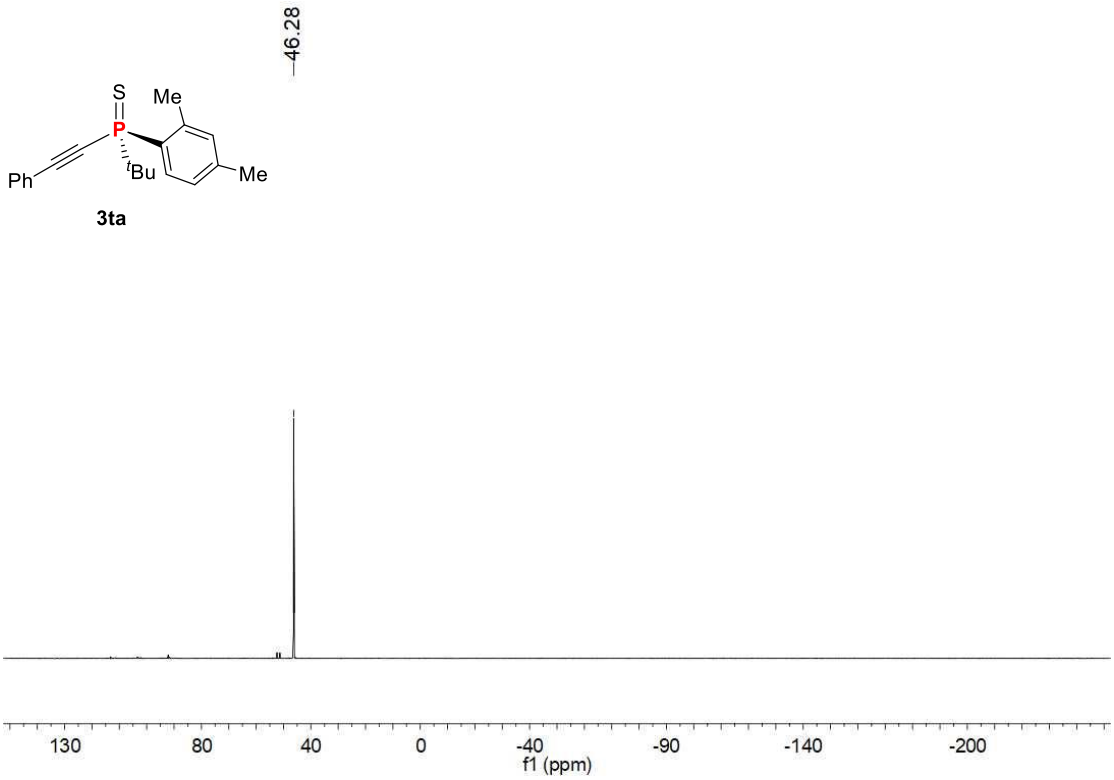

144.66
144.57
137.99
137.96
136.29
136.19
132.61
132.51
132.24
132.22
130.55
128.64
125.68
125.57
125.36
124.69
120.48
120.45
106.69
106.52
82.03
80.93
38.99
38.52
24.69
24.66
23.10
23.08
S
Me
P
Ph
tBu
Cl
3sa
f1 (ppm)

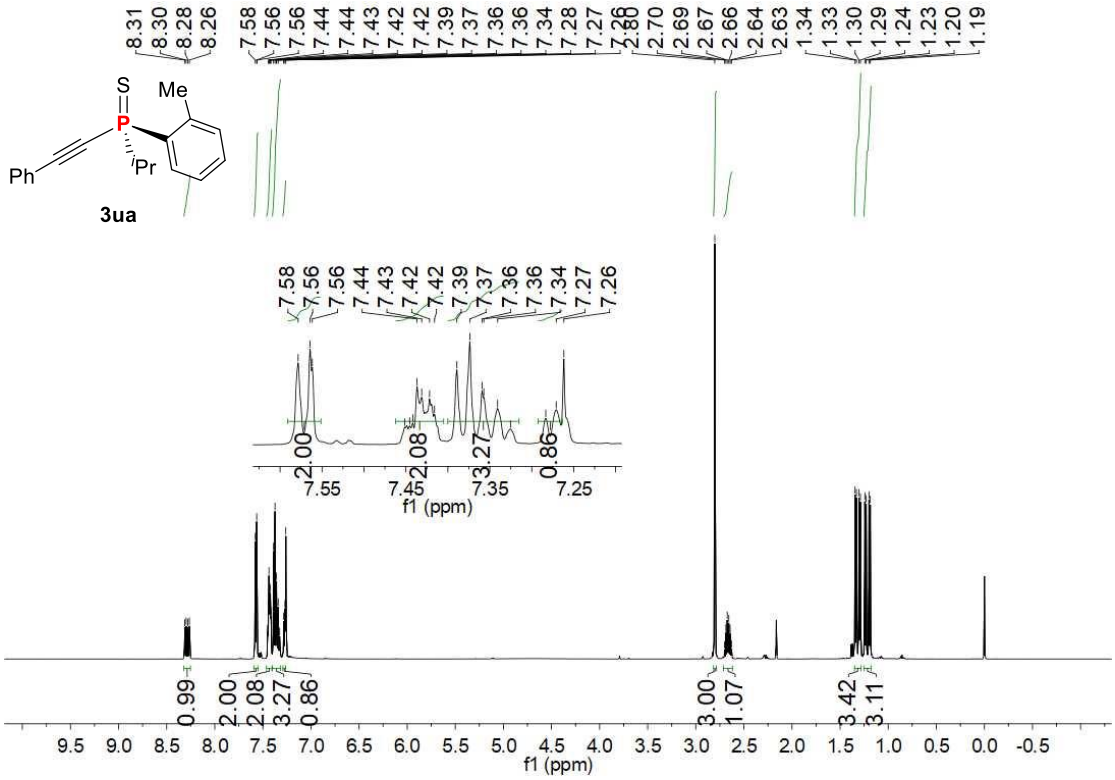


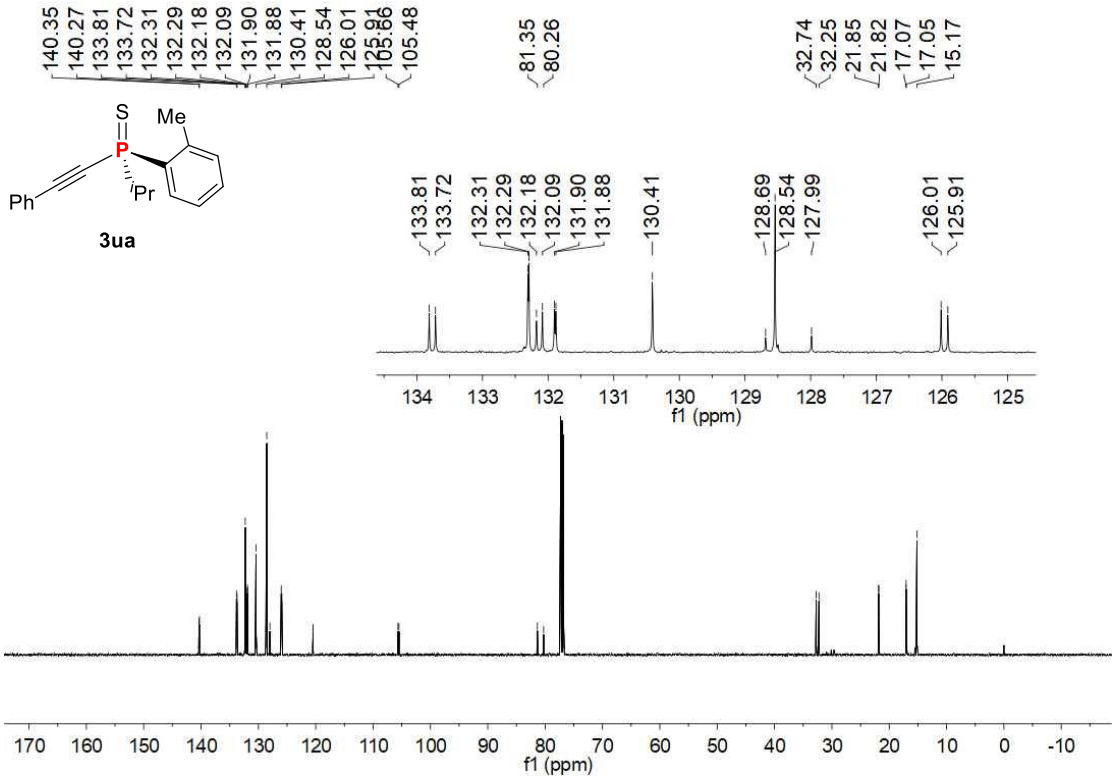
3sa

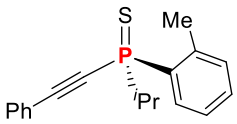

8.04
8.00
7.60
7.58
7.46
7.44
7.43
7.40
7.39
7.37
7.22
7.21
7.15
7.13
7.12
2.83
2.36
1.34
1.30
S
P
Me
Ph
tBu
Me
3ta
2.03
1.01
2.04
1.09
1.10
f1 (ppm)
0.98
2.03
1.01
2.04
1.09
1.10
3.00
3.08
9.03
f1 (ppm)


139.46
139.38
135.16
135.07
134.94
134.83
132.81
132.72
132.61
132.59
132.17
132.15
130.36
128.61
106.10
82.58
81.50
38.81
38.34
24.77
24.75
22.78
22.76
21.18
S
P
Me
Ph
tBu
Me
3ta
f1 (ppm)
f1 (ppm)


46.28
S
Me
P
Ph
tBu
Me
3ta
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

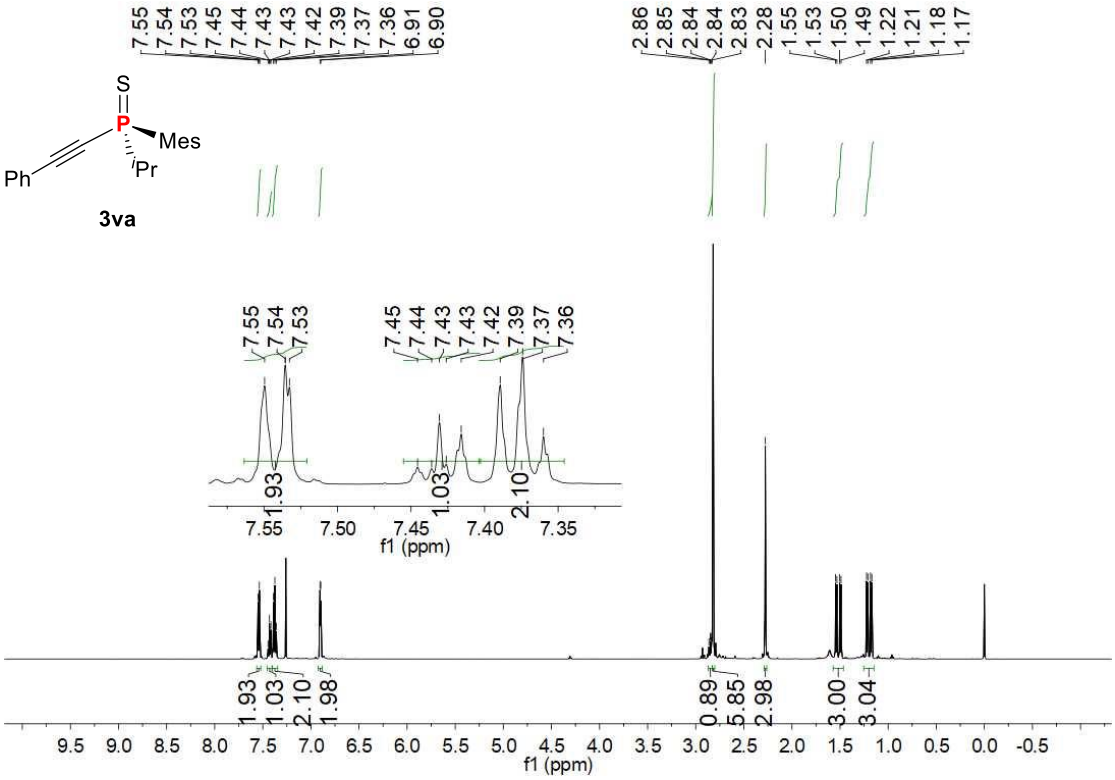

8.31 8.30 8.28 8.26 7.58 7.56 7.56 7.44 7.44 7.43 7.42 7.42 7.39 7.37 7.36 7.36 7.34 7.28 7.27 2.70 2.69 2.67 2.66 2.64 2.63 1.34 1.33 1.30 1.29 1.24 1.23 1.20 1.19
S
Me
P
Ph
iPr
3ua
7.58 7.56 7.56 7.44 7.43 7.42 7.42 7.39 7.37 7.36 7.36 7.34 7.27 7.26
2.00 2.08 3.27 0.86
7.55 7.45 7.35 7.25
f1 (ppm)
0.99 2.00 2.08 3.27 0.86 3.00 1.07 3.42 3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

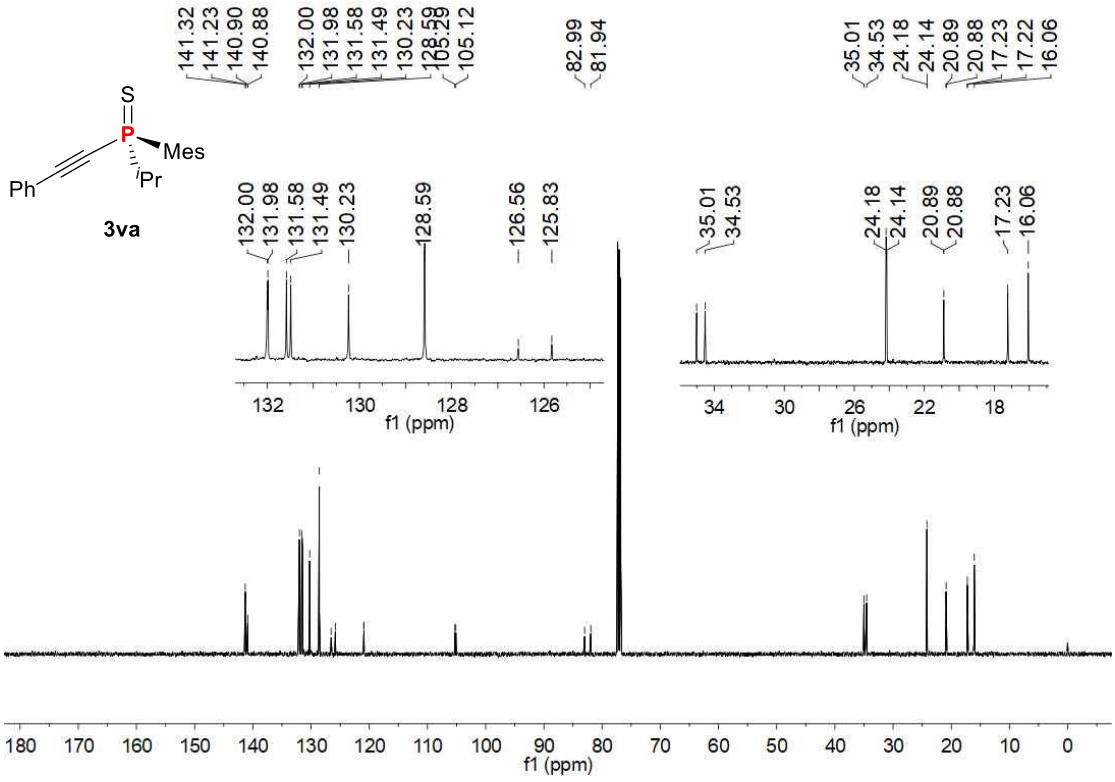

140.35 140.27 133.81 133.72 132.31 132.29 132.18 132.09 131.90 131.88 130.41 128.54 126.01 125.91 105.66 105.48
81.35 80.26
32.74 32.25 21.85 21.82 17.07 17.05 15.17
S
Me
P
Ph
iPr
3ua
133.81 133.72 132.31 132.29 132.18 132.09 131.90 131.88 130.41 128.69 128.54 127.99 126.01 125.91
134 133 132 131 130 129 128 127 126 125
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

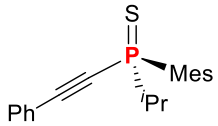

S
Me
P
Ph
iPr

3ua

-37.80
45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23
f1 (ppm)

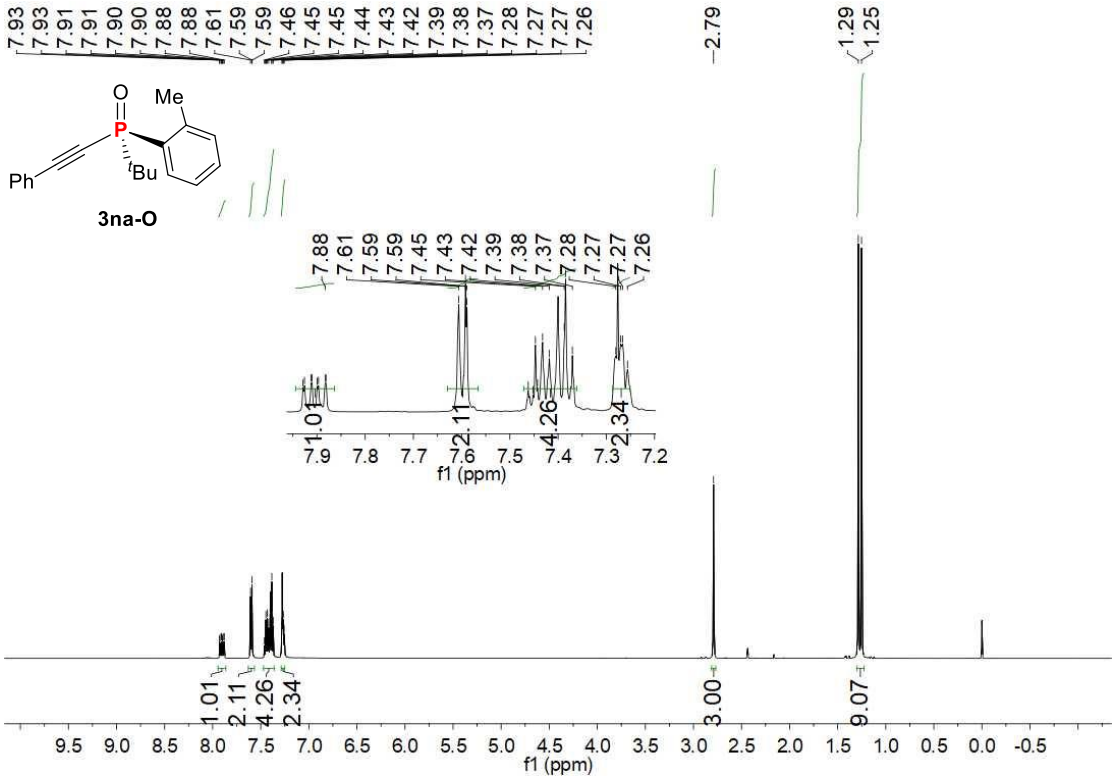

7.55
7.54
7.53
7.45
7.44
7.43
7.43
7.42
7.39
7.37
7.36
6.91
6.90
2.86
2.85
2.84
2.84
2.83
2.28
1.55
1.53
1.50
1.49
1.22
1.21
1.18
1.17
S
P
Mes
iPr
Ph
3va
1.93
1.03
2.10
1.98
0.89
5.85
2.98
3.00
3.04
f1 (ppm)

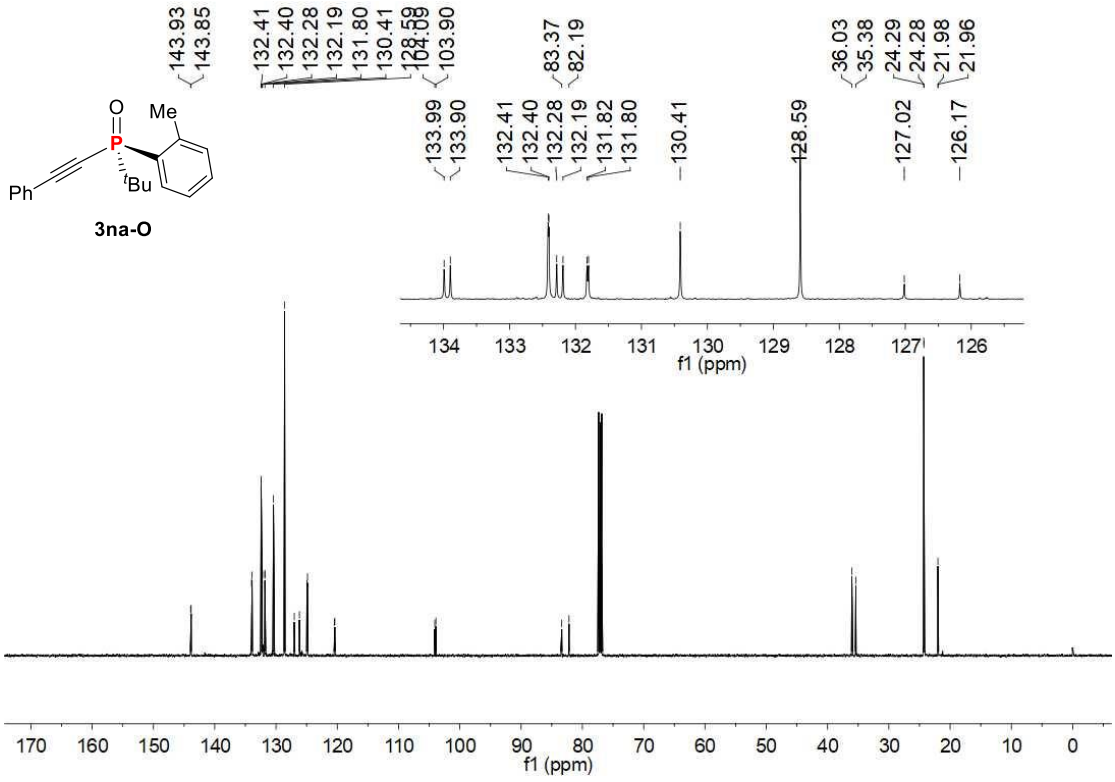

141.32
141.23
140.90
140.88
132.00
131.98
131.58
131.49
130.23
128.59
105.12
82.99
81.94
35.01
34.53
24.18
24.14
20.89
20.88
17.23
17.22
16.06
S
P
Mes
iPr
Ph
3va
f1 (ppm)

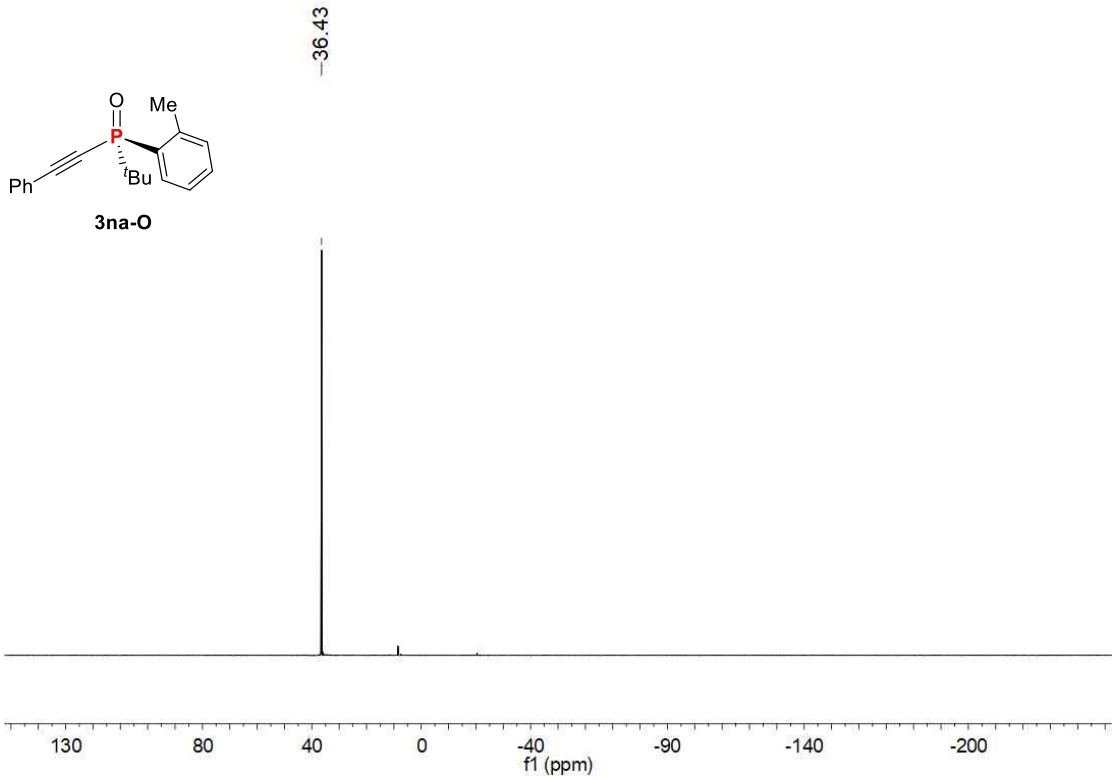

S
P
Mes
Ph
iPr

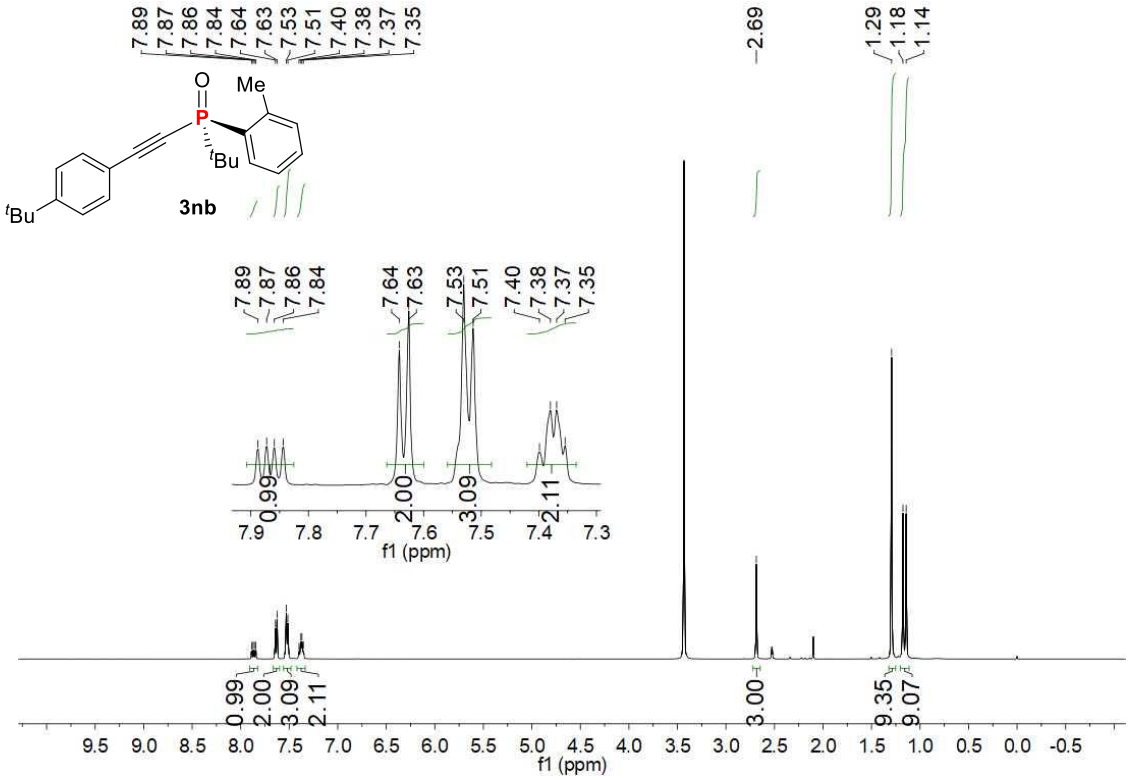
3va

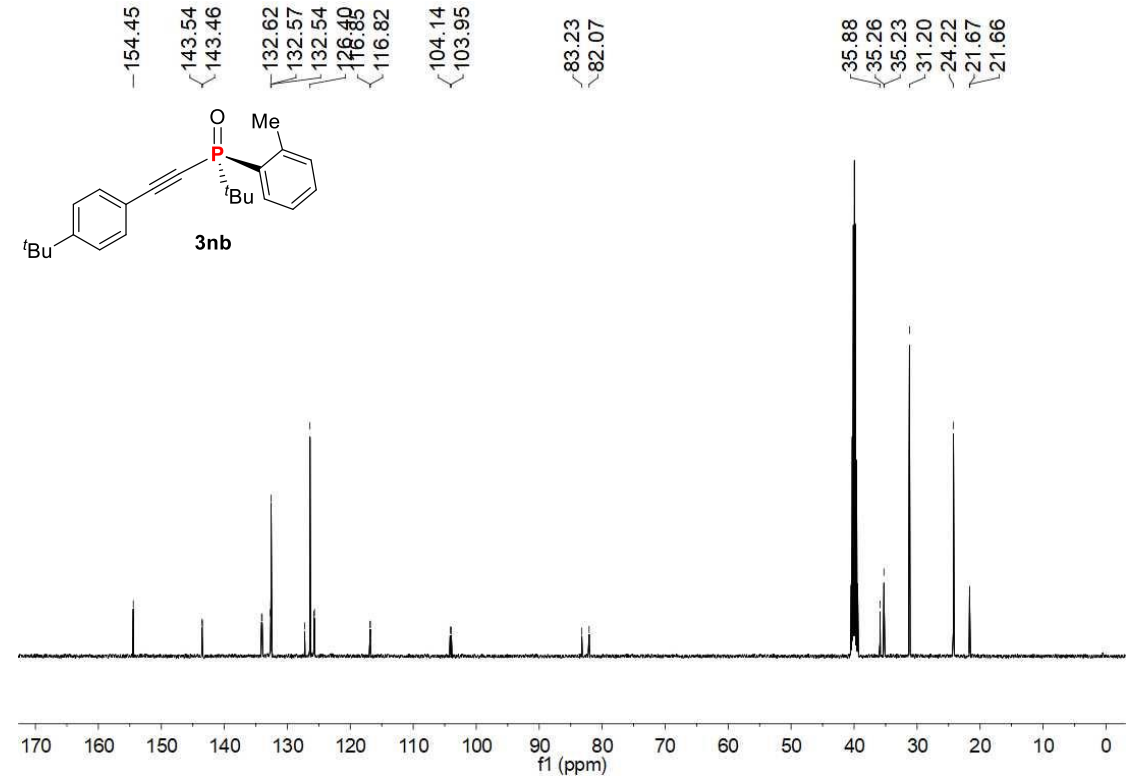
-34.88
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
f1 (ppm)

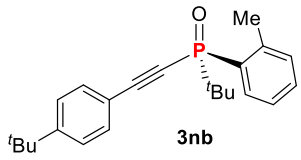

7.93 7.93 7.91 7.91 7.90 7.90 7.88 7.88 7.61 7.59 7.59 7.46 7.45 7.45 7.44 7.43 7.42 7.39 7.38 7.37 7.28 7.27 7.27 7.26
2.79
1.29 1.25
O
Me
P
Ph
tBu
3na-O
7.88 7.61 7.59 7.59 7.45 7.43 7.42 7.39 7.38 7.37 7.28 7.27 7.27 7.26
1.01 2.11 4.26 2.34
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
1.01 2.11 4.26 2.34 3.00 9.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


143.93 143.85 132.41 132.40 132.28 132.19 131.80 130.41 128.59 104.09 103.90 83.37 82.19 36.03 35.38 24.29 24.28 21.98 21.96
O
Me
P
Ph
tBu
3na-O
133.99 133.90 132.41 132.40 132.28 132.19 131.82 131.80 130.41 128.59 127.02 126.17
134 133 132 131 130 129 128 127 126
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


36.43
O
Me
P
tBu
Ph
3na-O
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

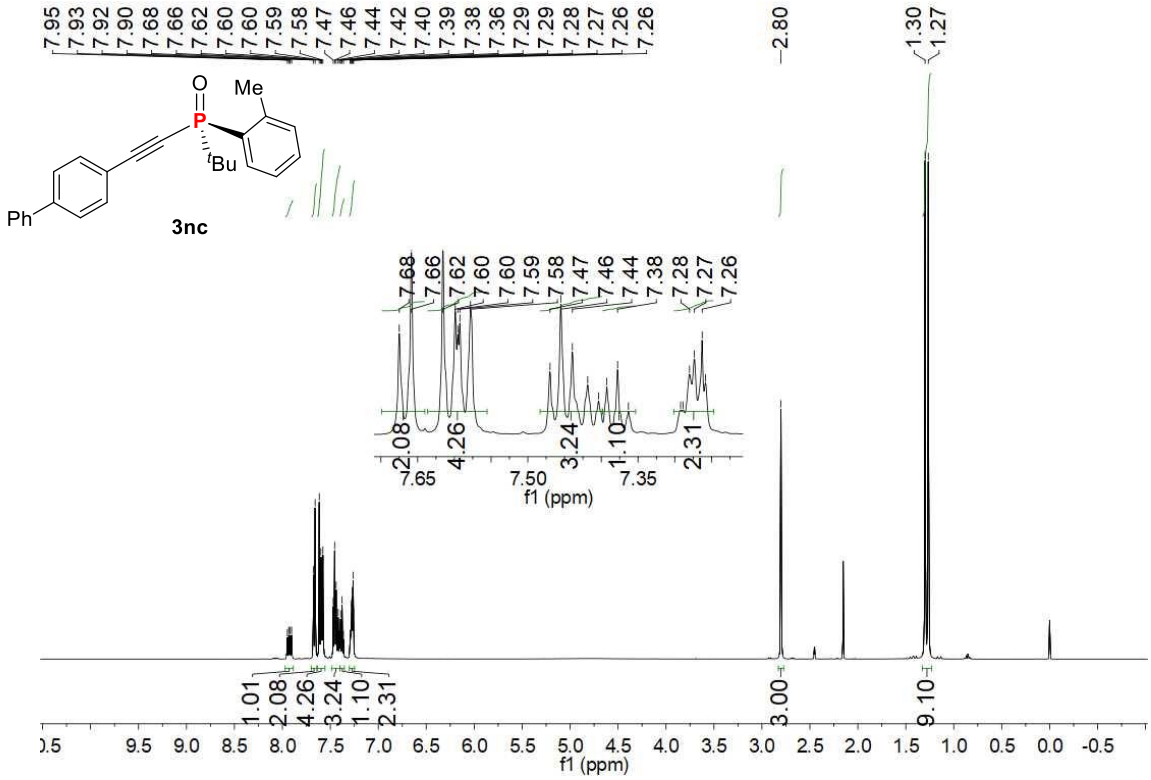

7.89
7.87
7.86
7.84
7.64
7.63
7.53
7.51
7.40
7.38
7.37
7.35
2.69
1.29
1.18
1.14
O
P
Me
tBu
tBu
3nb
0.99
2.00
3.09
2.11
3.00
9.35
9.07
f1 (ppm)

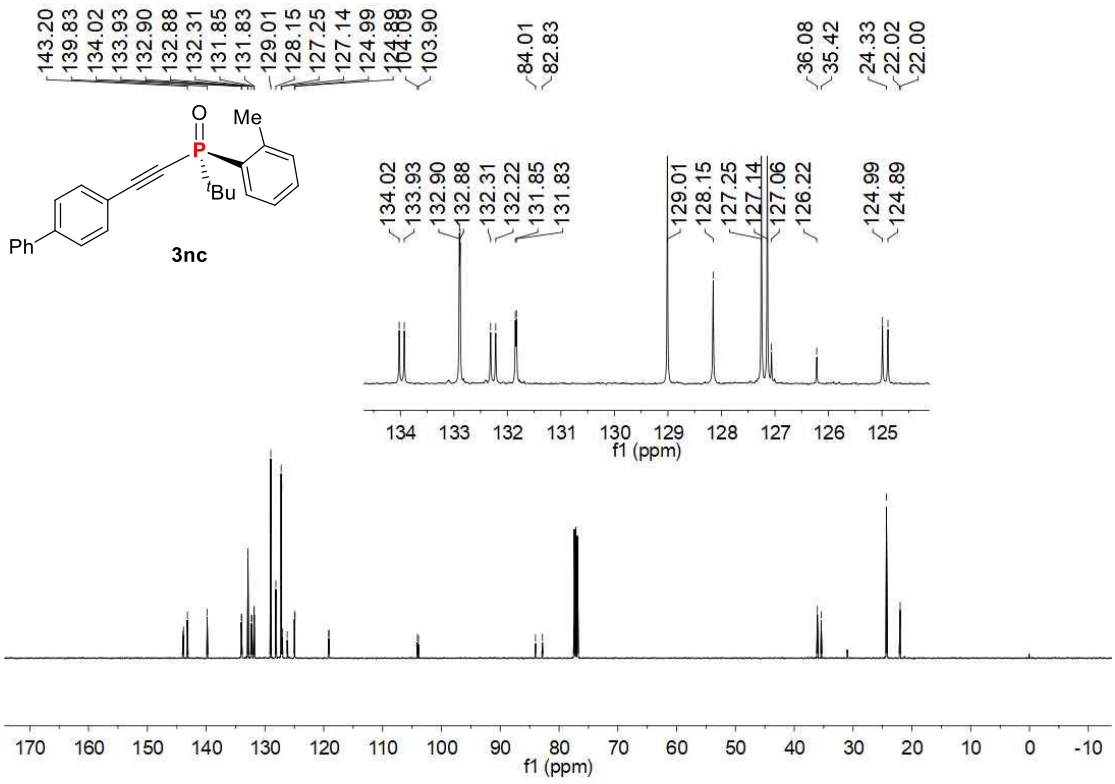

154.45
143.54
143.46
132.62
132.57
132.54
116.82
104.14
103.95
83.23
82.07
35.88
35.26
35.23
31.20
24.22
21.67
21.66
O
P
Me
tBu
tBu
3nb
f1 (ppm)

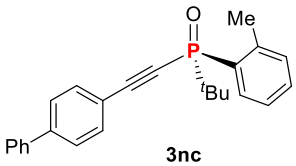

O
Me
P
tBu
tBu

3nb

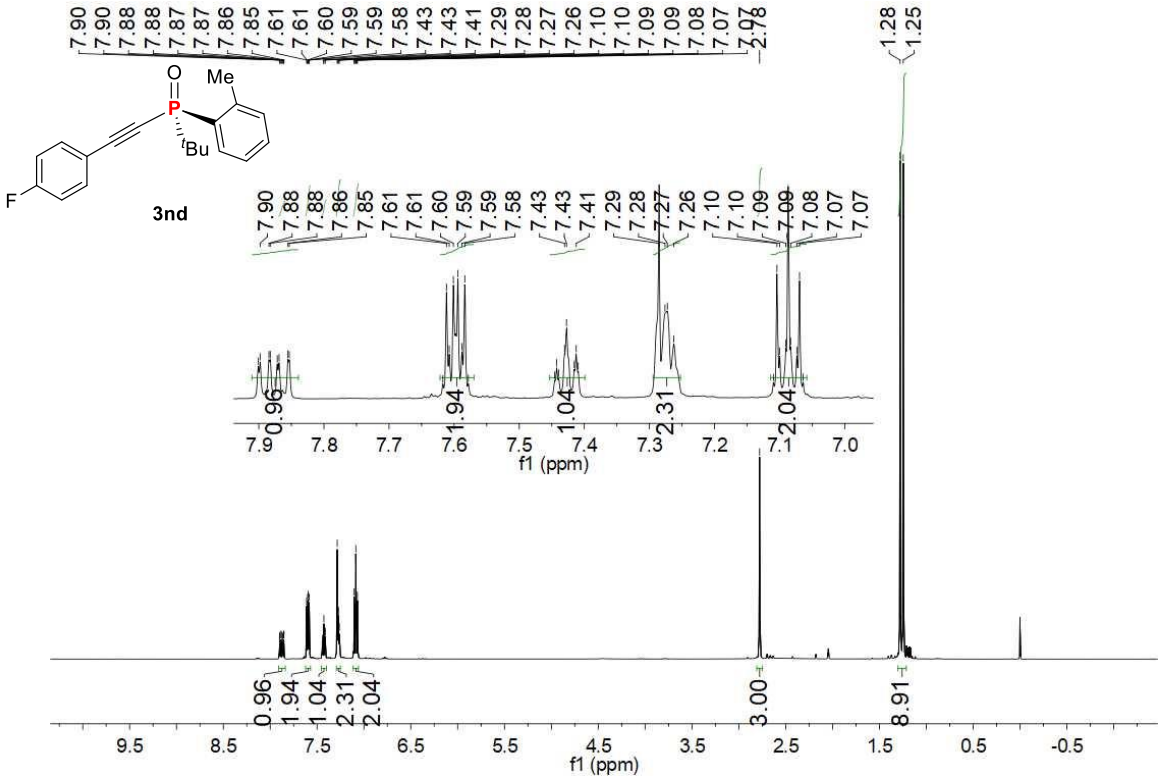
34.17
42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21
f1 (ppm)

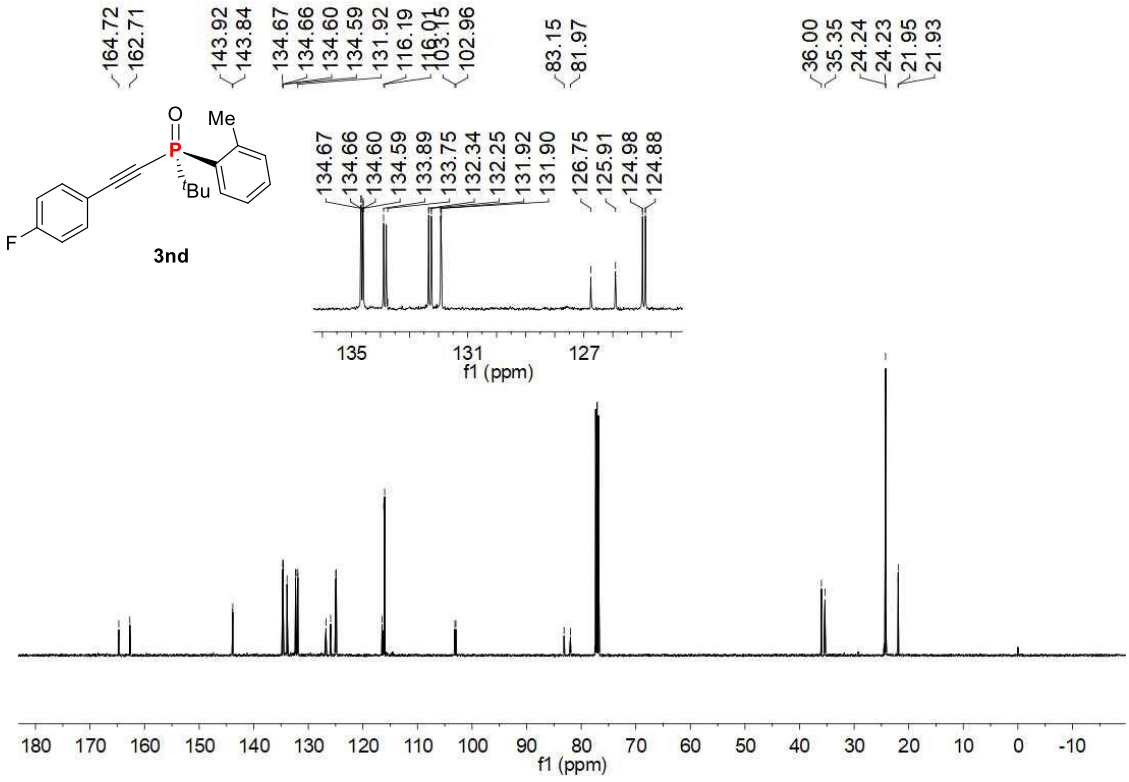

7.95 7.93 7.92 7.90 7.68 7.66 7.62 7.60 7.60 7.59 7.58 7.47 7.46 7.44 7.42 7.40 7.39 7.38 7.36 7.29 7.29 7.28 7.27 7.26 7.26
2.80
1.30 1.27
O
P
Me
tBu
Ph
3nc
7.68 7.66 7.62 7.60 7.60 7.59 7.58 7.47 7.46 7.44 7.38 7.28 7.27 7.26
2.08 4.26 3.24 1.10 2.31
7.65 7.50 7.35
f1 (ppm)
1.01 2.08 4.26 3.24 1.10 2.31 3.00 9.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

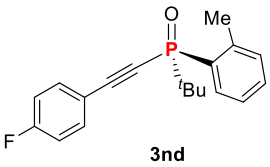

143.20 139.83 134.02 133.93 132.90 132.88 132.31 131.85 131.83 129.01 128.15 127.25 127.14 124.99 124.89 103.90
84.01 82.83
36.08 35.42 24.33 22.02 22.00
O
P
Me
tBu
Ph
3nc
134.02 133.93 132.90 132.88 132.31 132.22 131.85 131.83 129.01 128.15 127.25 127.14 127.06 126.22 124.99 124.89
134 133 132 131 130 129 128 127 126 125
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3nc

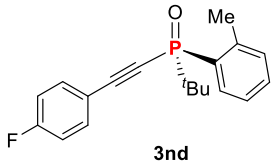

3nd
f1 (ppm)


3nd
f1 (ppm)


O
Me
P
tBu
F

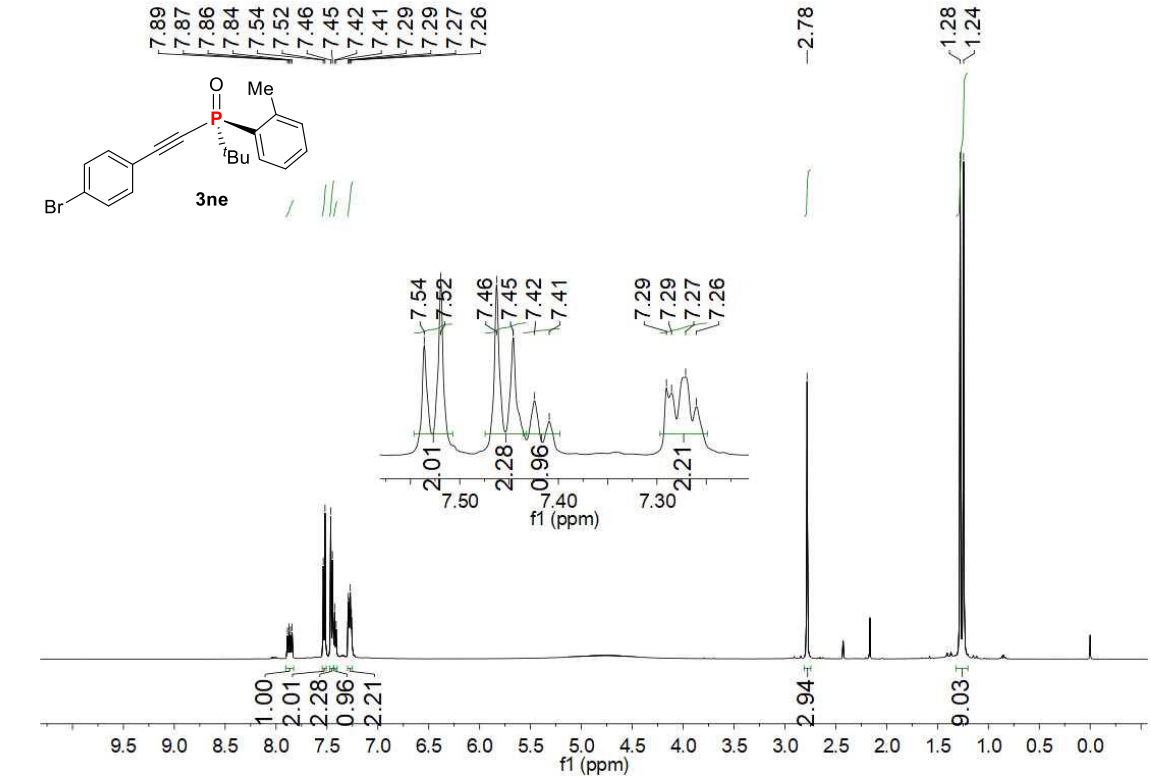
3nd

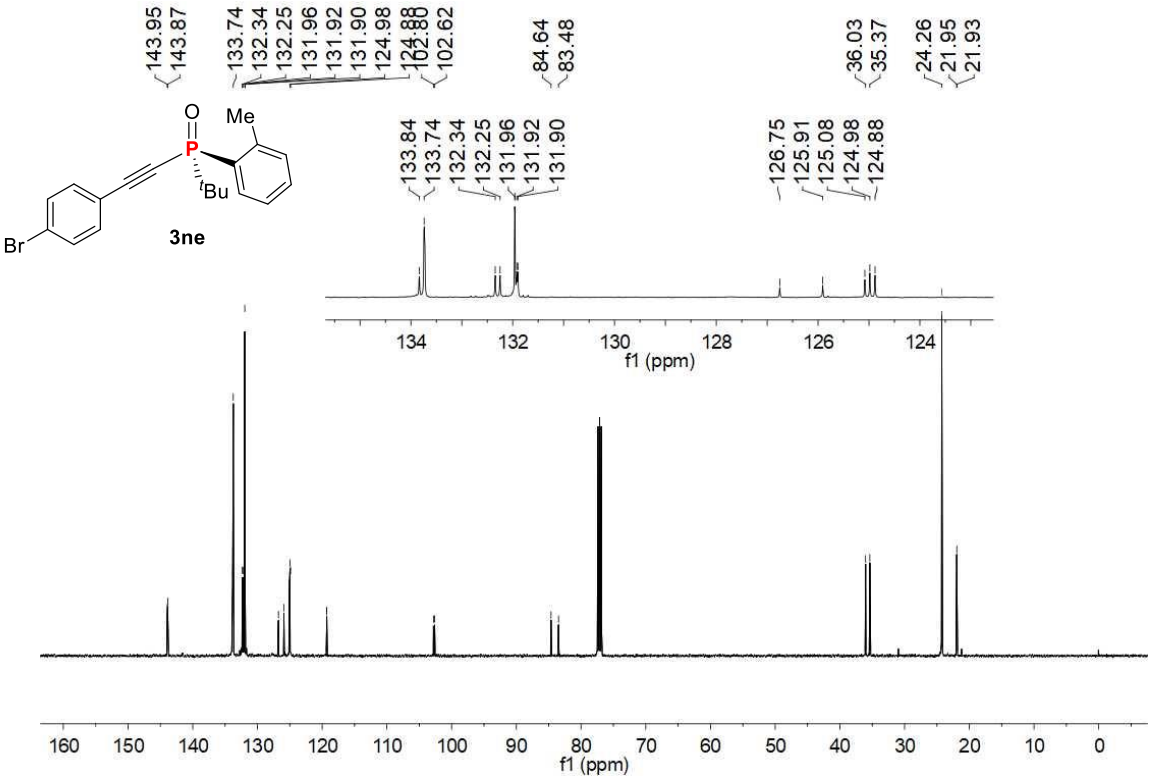
36.82
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

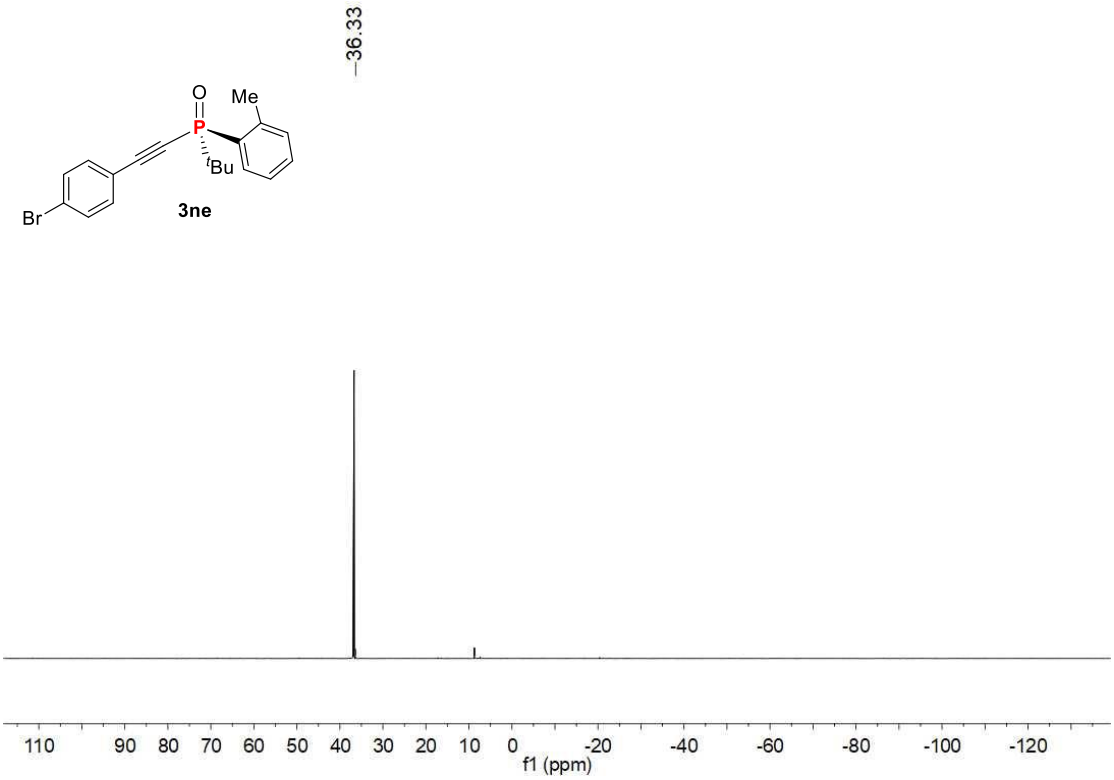

O
Me
P
tBu
F

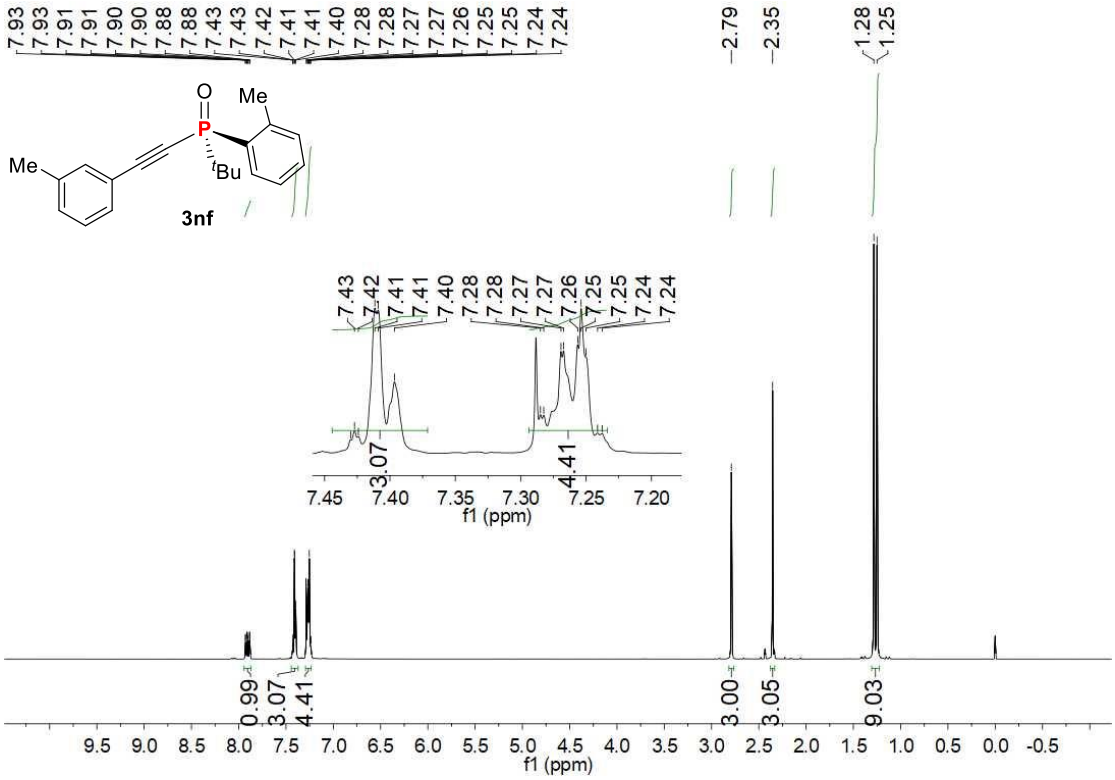
3nd

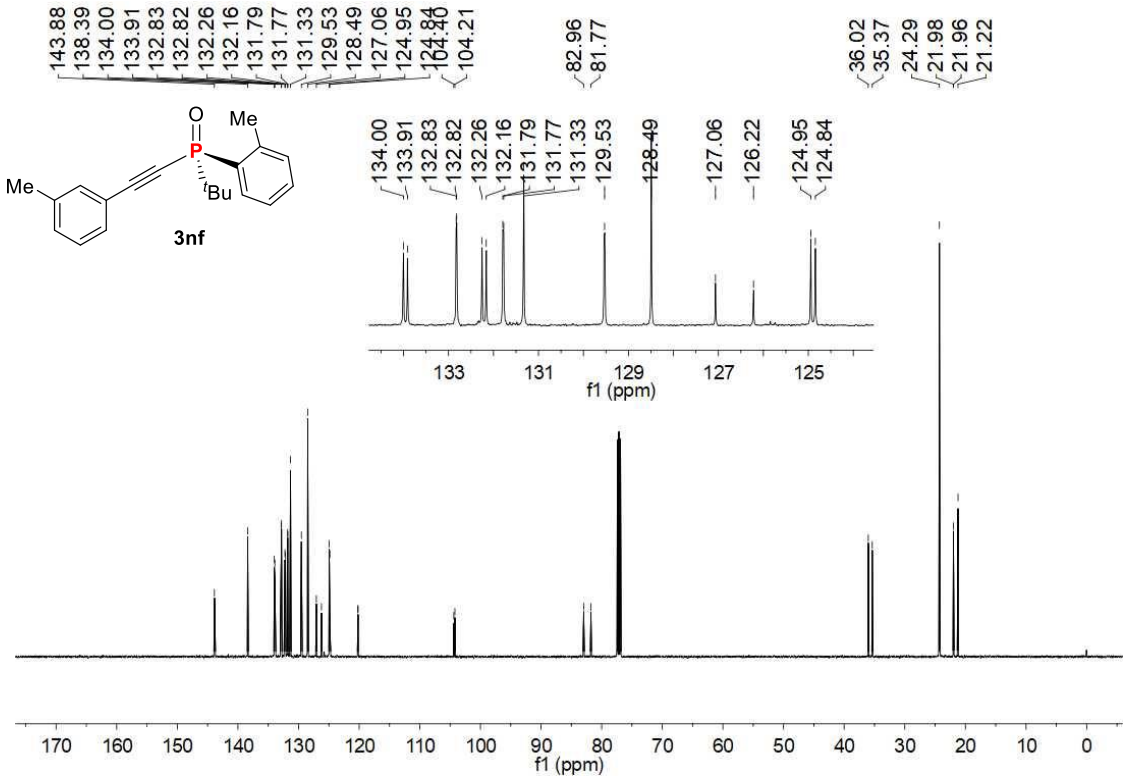
-106.67
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

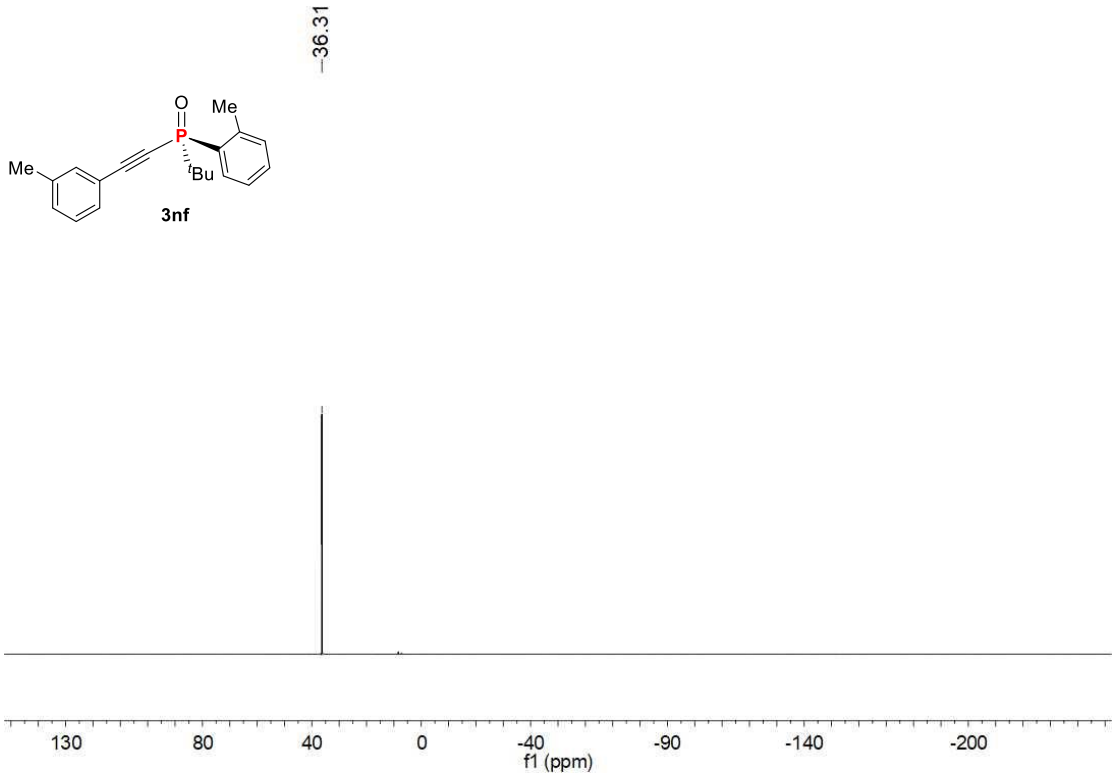

7.89
7.87
7.86
7.84
7.54
7.52
7.46
7.45
7.42
7.41
7.29
7.29
7.27
7.26
2.78
1.28
1.24
O
P
Me
tBu
Br
3ne
7.54
7.52
7.46
7.45
7.42
7.41
7.29
7.29
7.27
7.26
2.01
2.28
0.96
2.21
7.50
7.40
7.30
f1 (ppm)
1.00
2.01
2.28
0.96
2.21
2.94
9.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

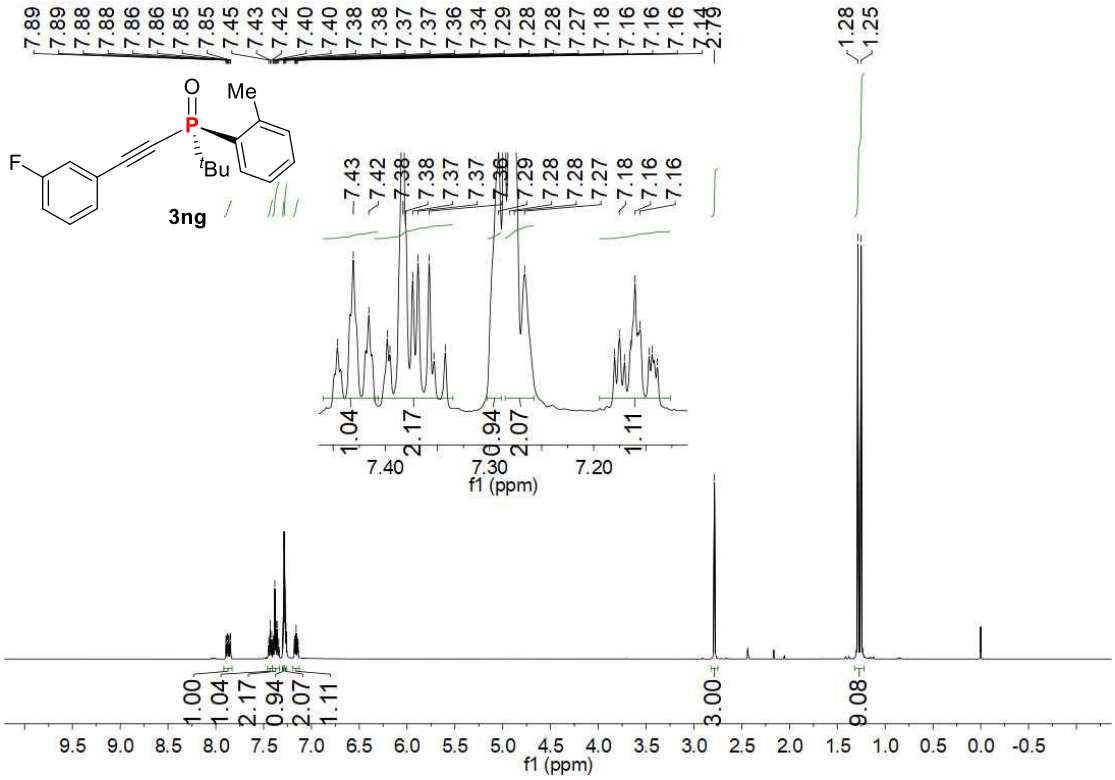

143.95
143.87
133.74
132.34
132.25
131.96
131.92
131.90
124.98
102.62
84.64
83.48
36.03
35.37
24.26
21.95
21.93
O
P
Me
tBu
Br
3ne
133.84
133.74
132.34
132.25
131.96
131.92
131.90
126.75
125.91
125.08
124.98
124.88
134
132
130
128
126
124
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

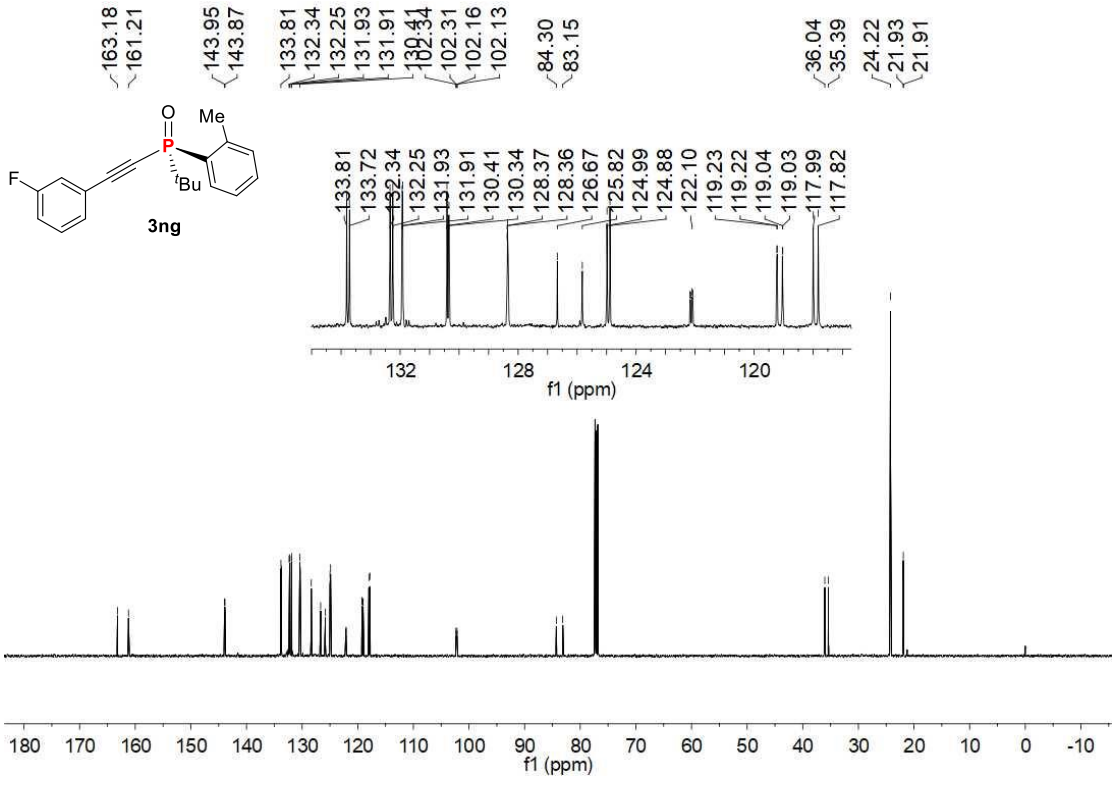

36.33
O
Me
P
tBu
Br
3ne
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
f1 (ppm)

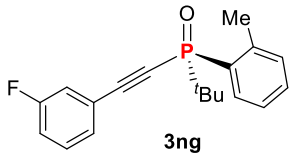

7.93
7.93
7.91
7.91
7.90
7.90
7.88
7.88
7.43
7.43
7.42
7.41
7.41
7.40
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.24
2.79
2.35
1.28
1.25
O
P
Me
Me
tBu
3nf
3.07
4.41
f1 (ppm)
0.99
3.07
4.41
3.00
3.05
9.03
f1 (ppm)


143.88
138.39
134.00
133.91
132.83
132.82
132.26
132.16
131.79
131.77
131.33
129.53
128.49
127.06
124.95
124.84
104.21
82.96
81.77
36.02
35.37
24.29
21.98
21.96
21.22
O
P
Me
Me
tBu
3nf
f1 (ppm)
f1 (ppm)


36.31
O
Me
P
Me
tBu
3nf
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

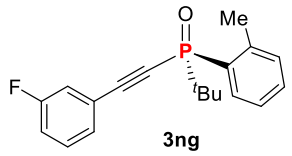

7.89 7.89 7.88 7.88 7.86 7.86 7.85 7.85 7.45 7.43 7.42 7.40 7.40 7.38 7.38 7.37 7.37 7.36 7.34 7.29 7.28 7.28 7.27 7.18 7.16 7.16 7.16 7.14 2.79
1.28 1.25
O
Me
P
F
tBu
3ng
7.43 7.42 7.38 7.38 7.37 7.37 7.36 7.29 7.28 7.28 7.27 7.18 7.16 7.16
1.04 2.17 0.94 2.07 1.11
7.40 7.30 7.20
f1 (ppm)
1.00 1.04 2.17 0.94 2.07 1.11 3.00 9.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.18 161.21 143.95 143.87 133.81 132.34 132.25 131.93 131.91 130.41 130.34 102.31 102.16 102.13 84.30 83.15 36.04 35.39 24.22 21.93 21.91
O
Me
P
F
tBu
3ng
133.81 133.72 132.34 132.25 131.93 131.91 130.41 130.34 128.37 128.36 126.67 125.82 124.99 124.88 122.10 119.23 119.22 119.04 119.03 117.99 117.82
132 128 124 120
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Me
P
F
tBu

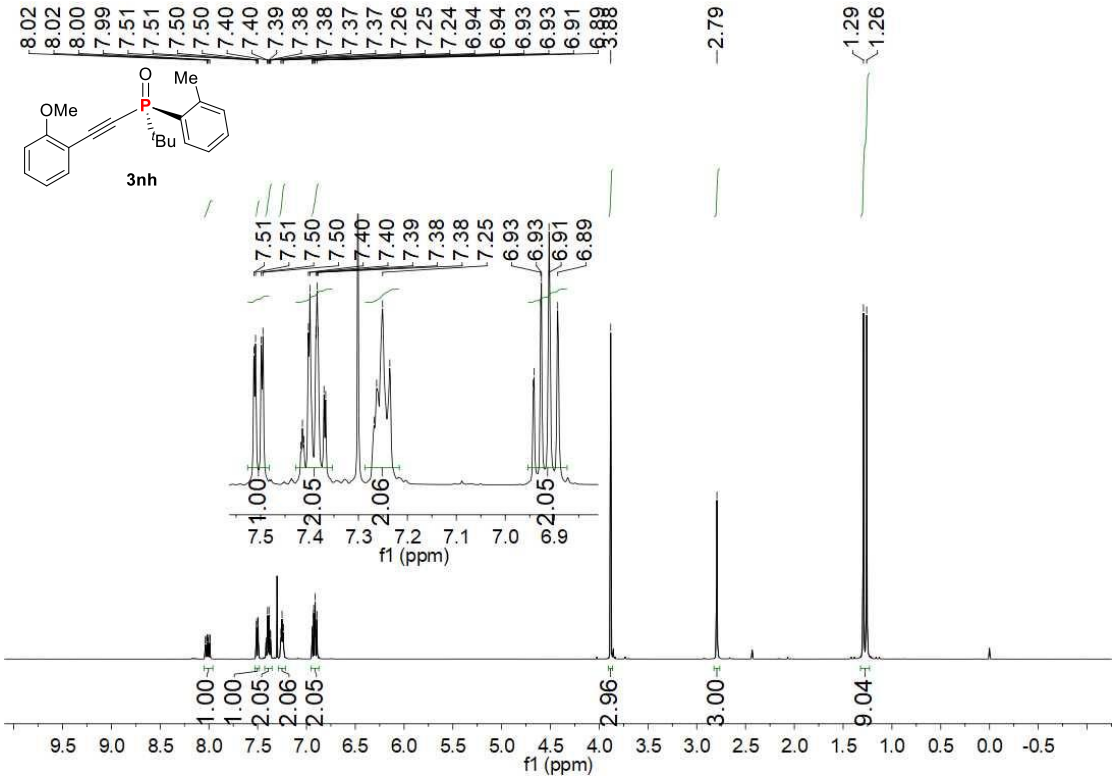
3ng

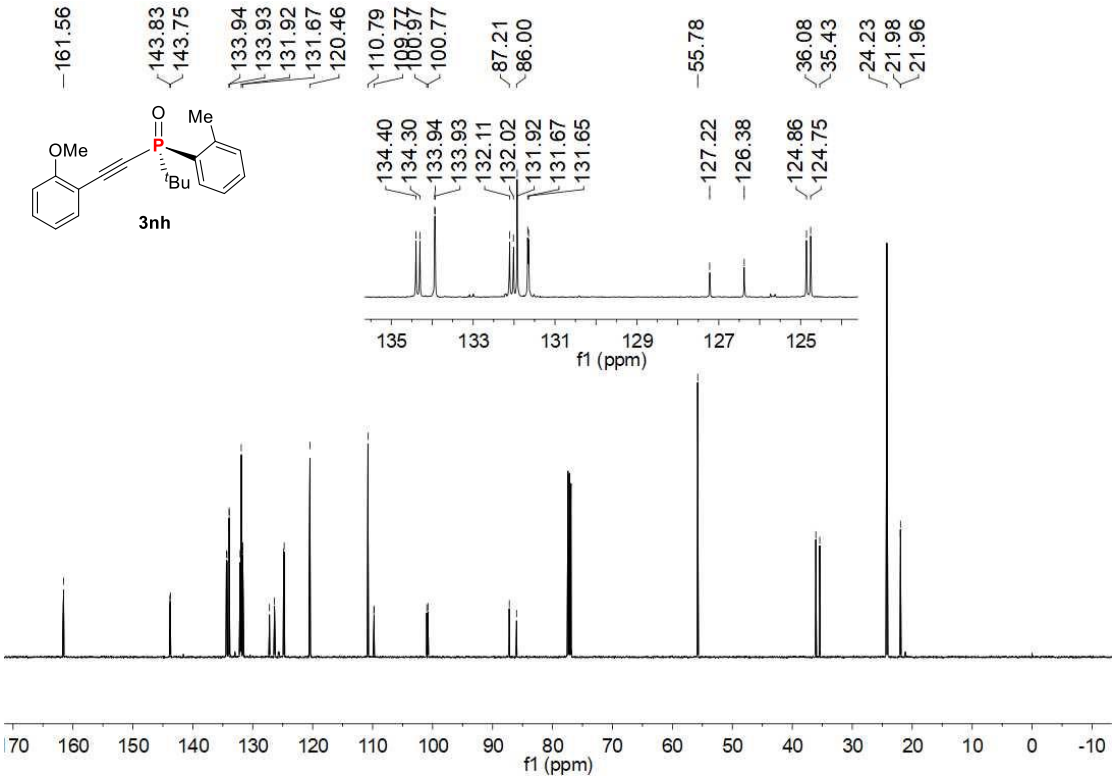
36.74
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

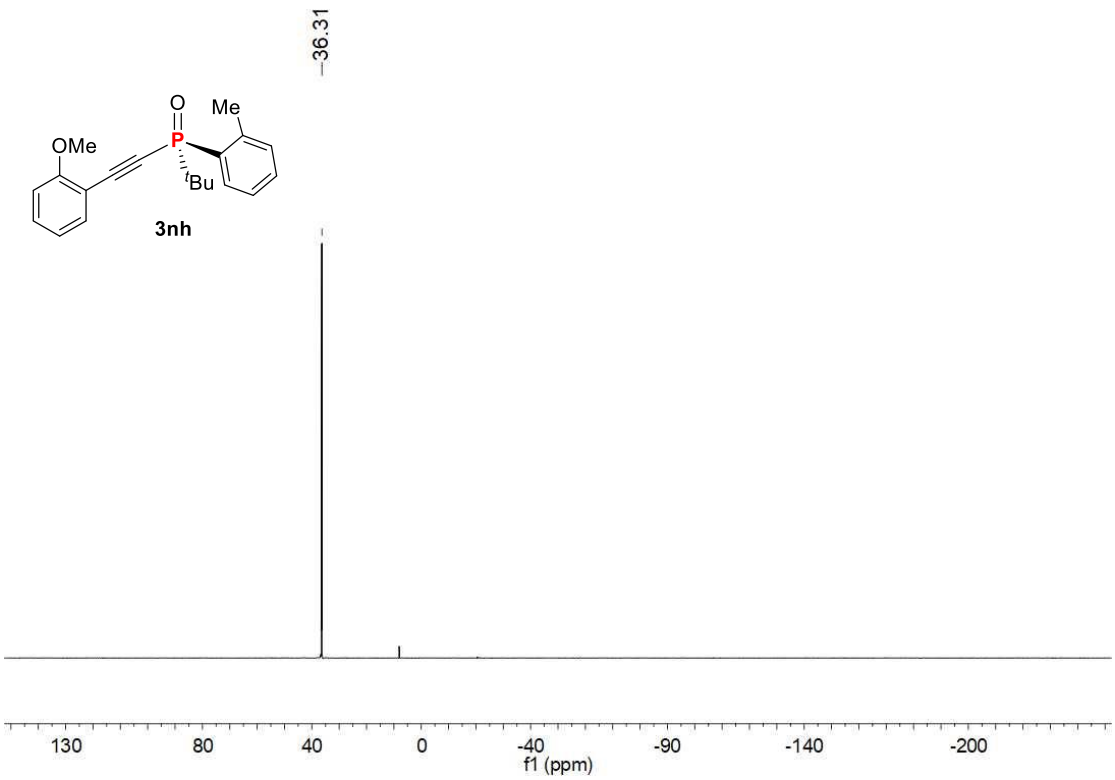

O
Me
P
F
tBu

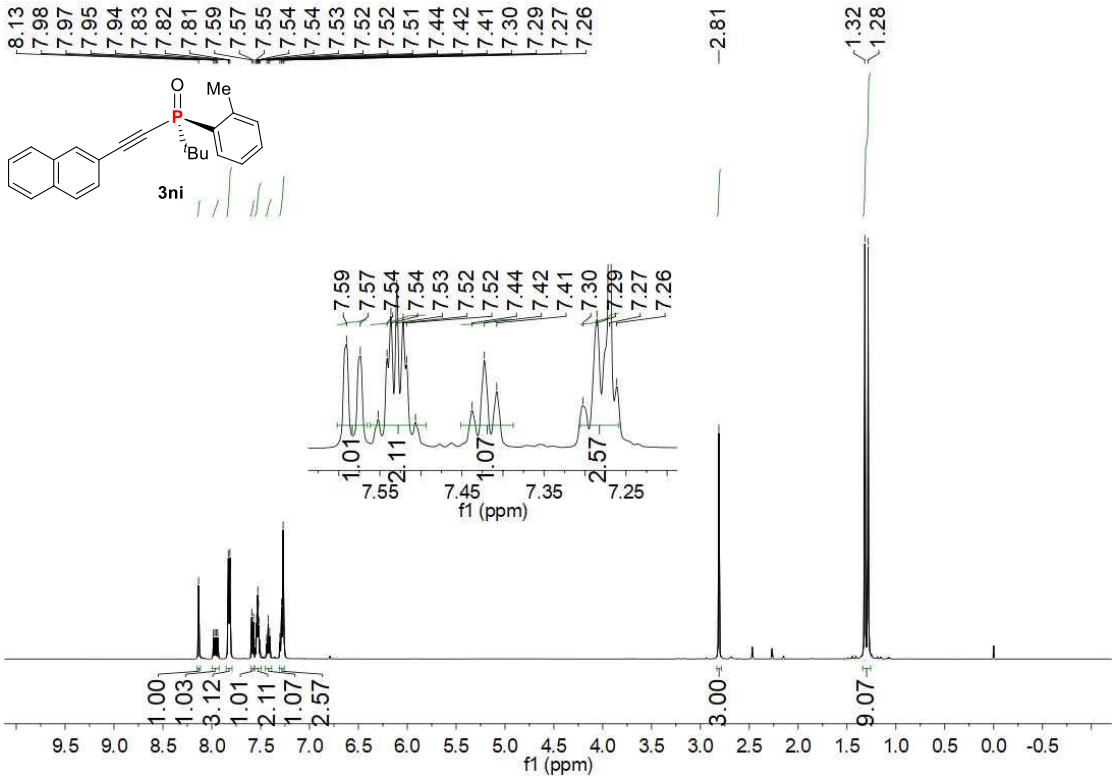
3ng

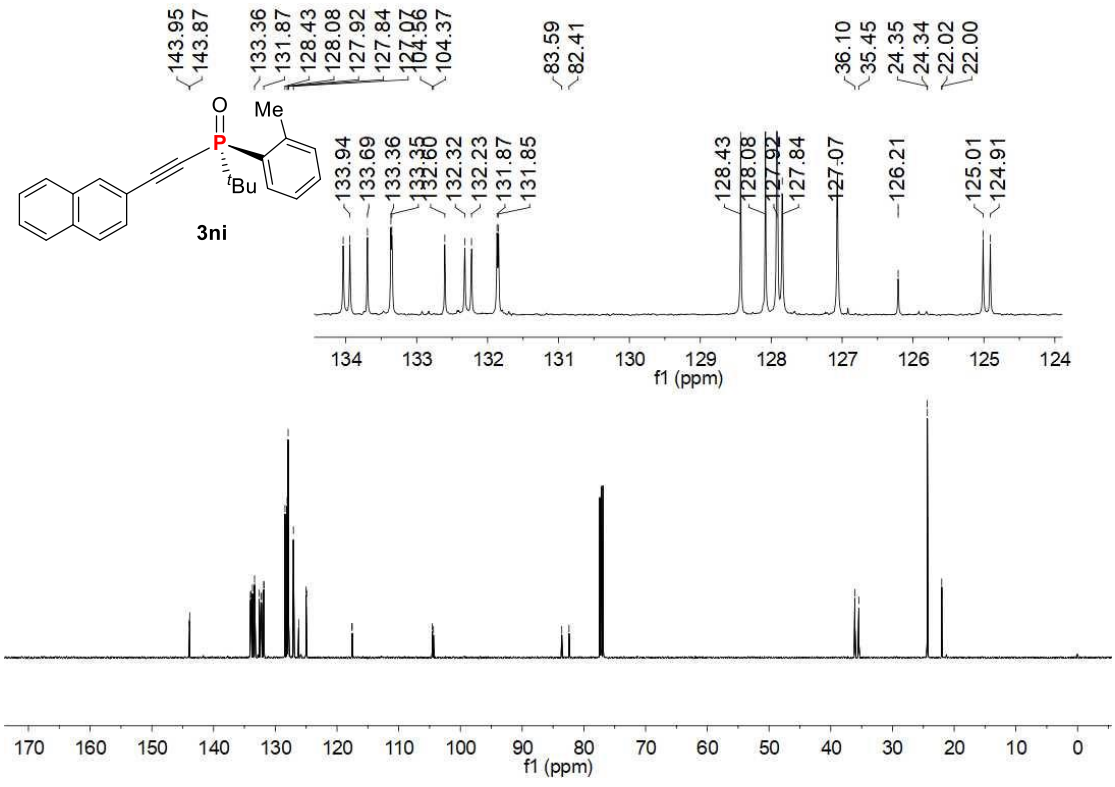
111.65
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

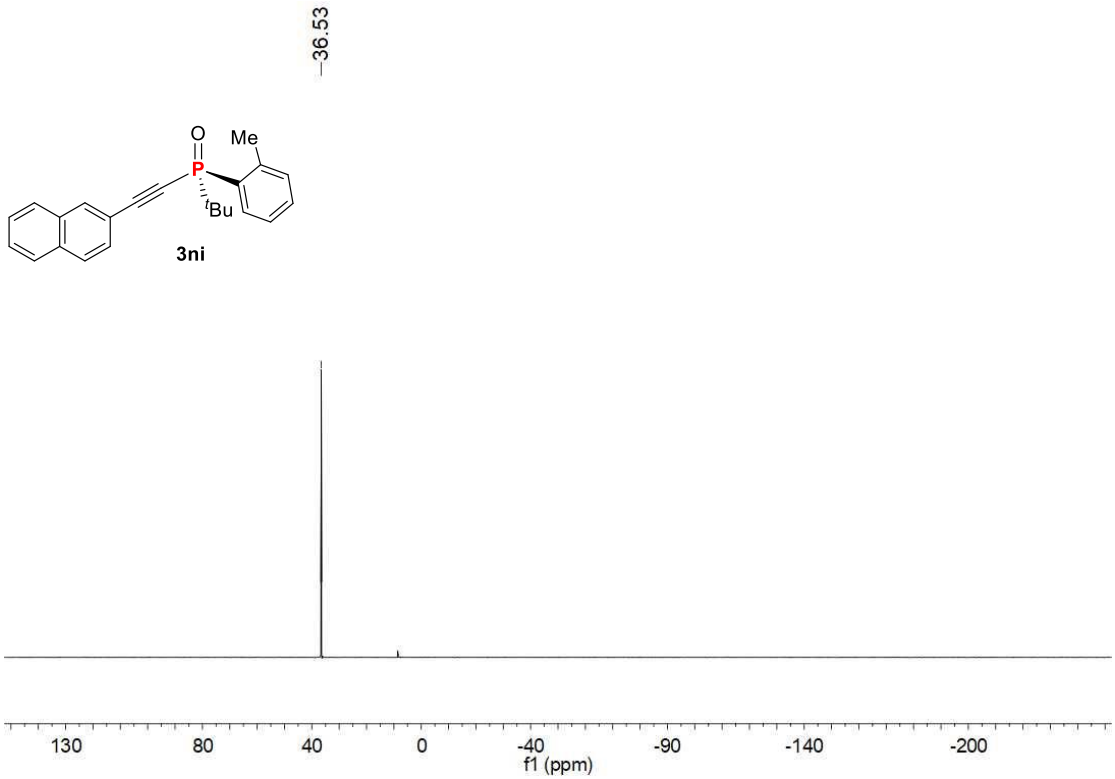

3nh
f1 (ppm)

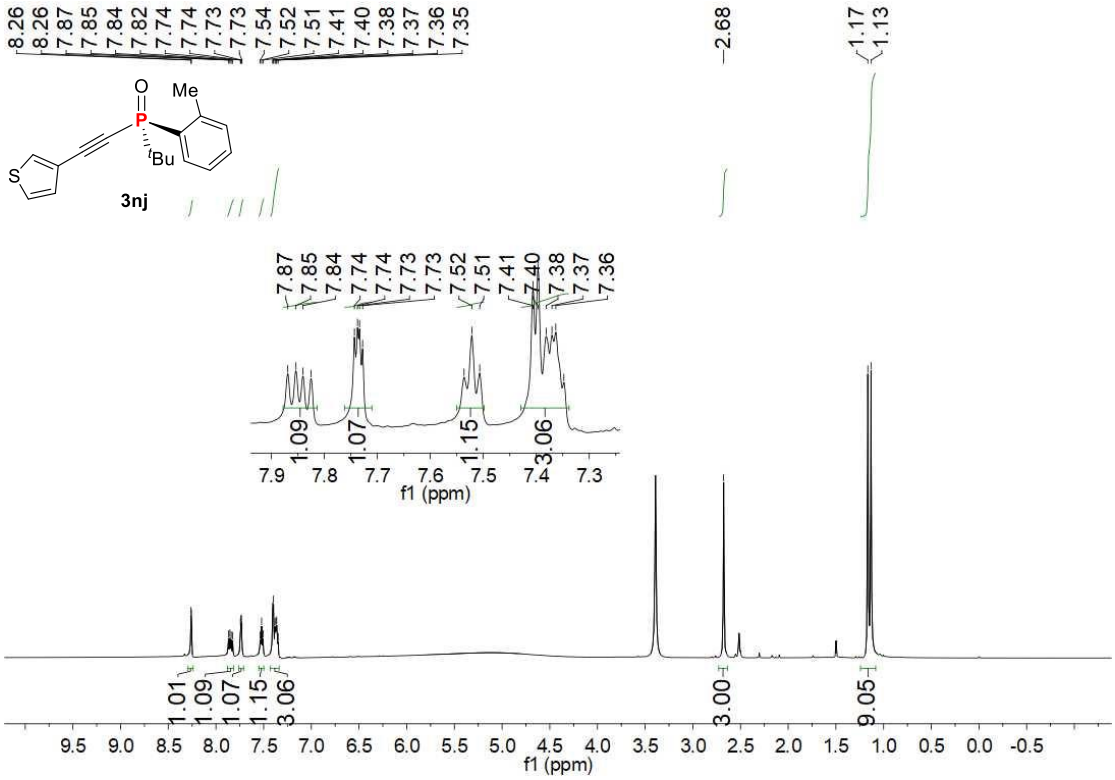

3nh
f1 (ppm)

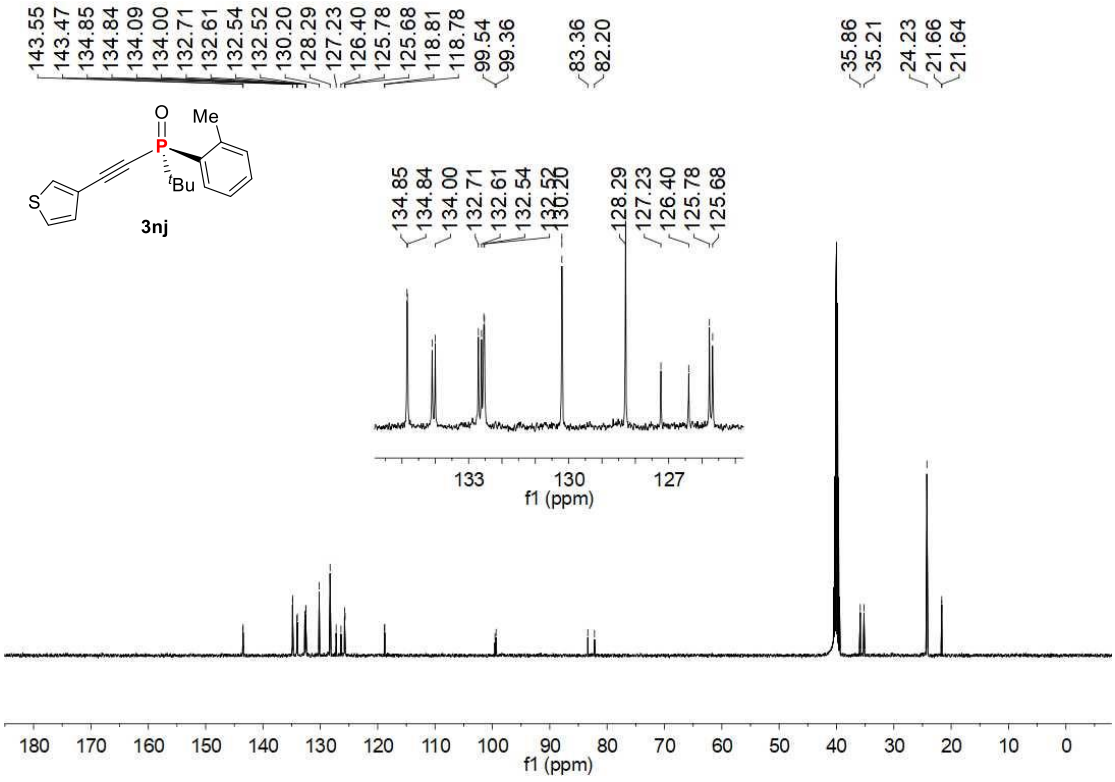

36.31
O
Me
OMe
P
tBu
3nh
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

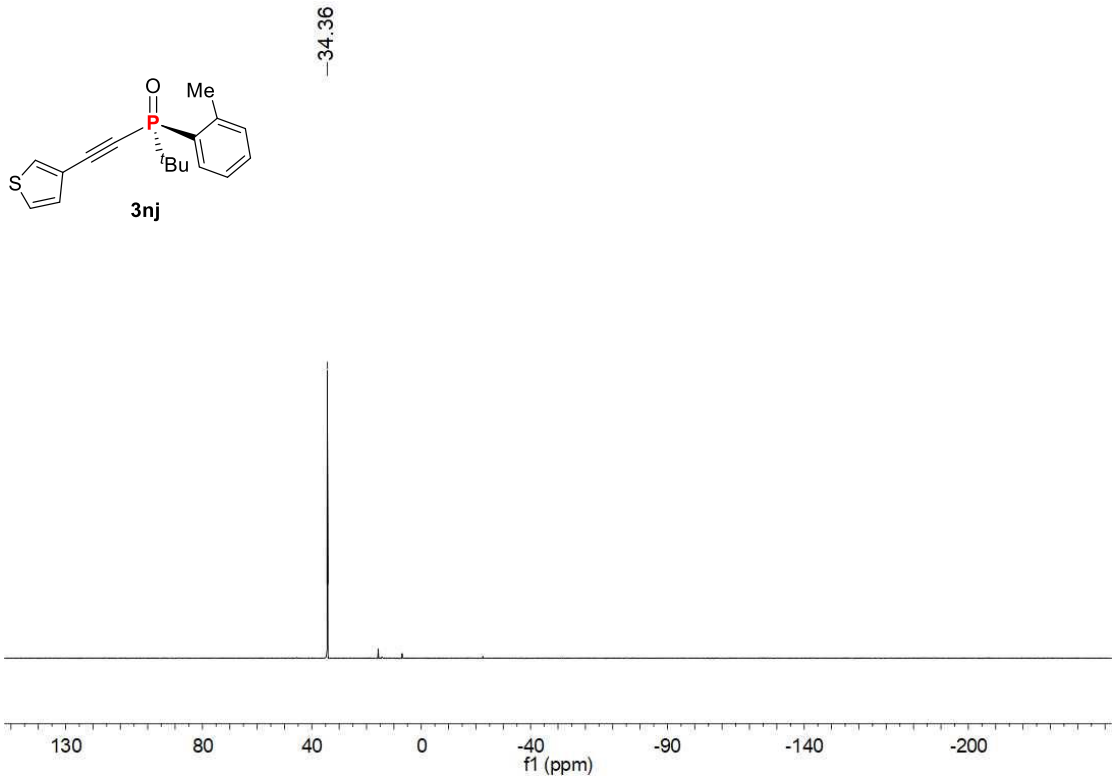

8.13 7.98 7.97 7.95 7.94 7.83 7.82 7.81 7.59 7.57 7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.44 7.42 7.41 7.30 7.29 7.27 7.26
2.81
1.32 1.28
O
Me
P
tBu
3ni
7.59 7.57 7.54 7.54 7.53 7.52 7.52 7.44 7.42 7.41 7.30 7.29 7.27 7.26
1.01 2.11 1.07 2.57
7.55 7.45 7.35 7.25
f1 (ppm)
1.00 1.03 3.12 1.01 2.11 1.07 2.57
3.00
9.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

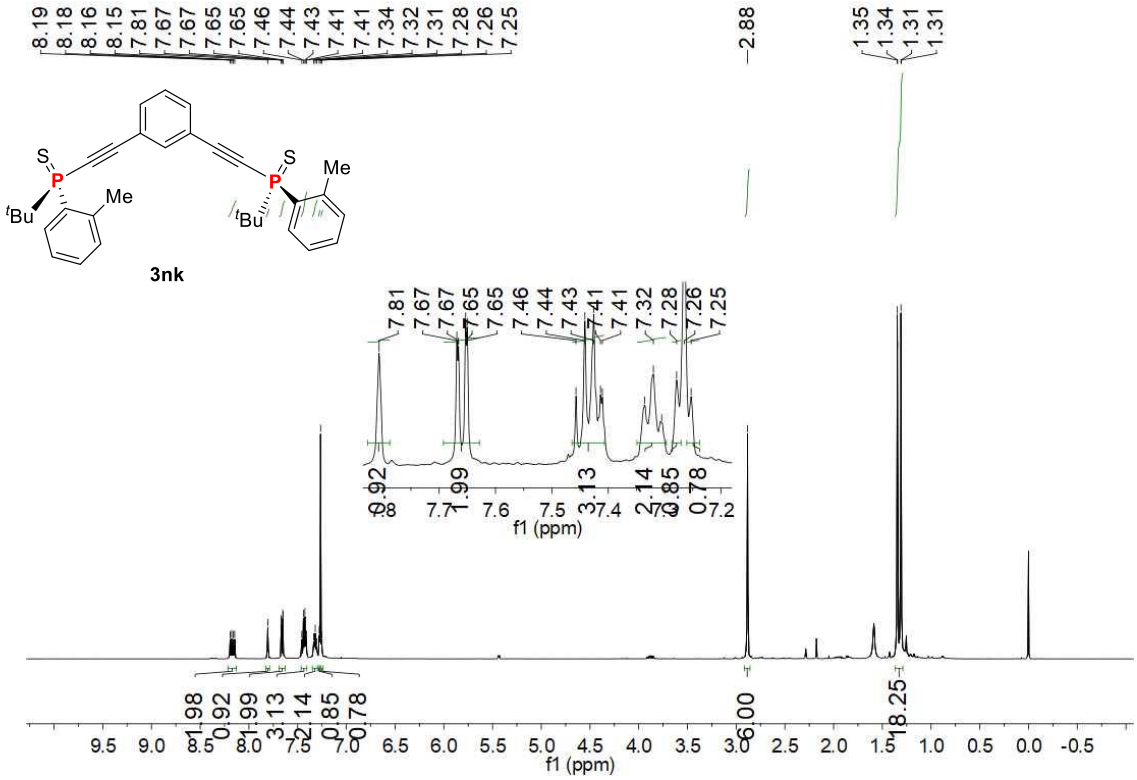

143.95 143.87 133.36 131.87 128.43 128.08 127.92 127.84 127.07 104.56 104.37
83.59 82.41
36.10 35.45 24.35 24.34 22.02 22.00
O
Me
P
tBu
3ni
133.94 133.69 133.36 133.35 132.60 132.32 132.23 131.87 131.85
128.43 128.08 127.92 127.84 127.07 126.21 125.01 124.91
134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

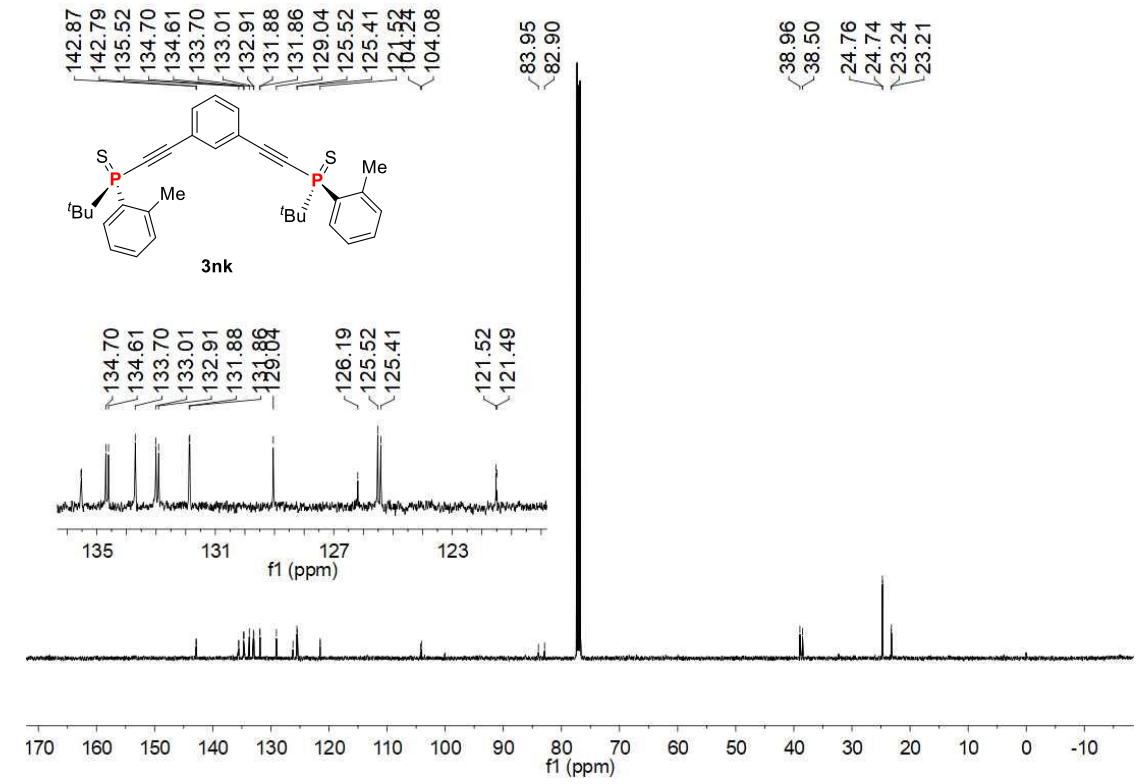

36.53
O
Me
P
tBu
3ni
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

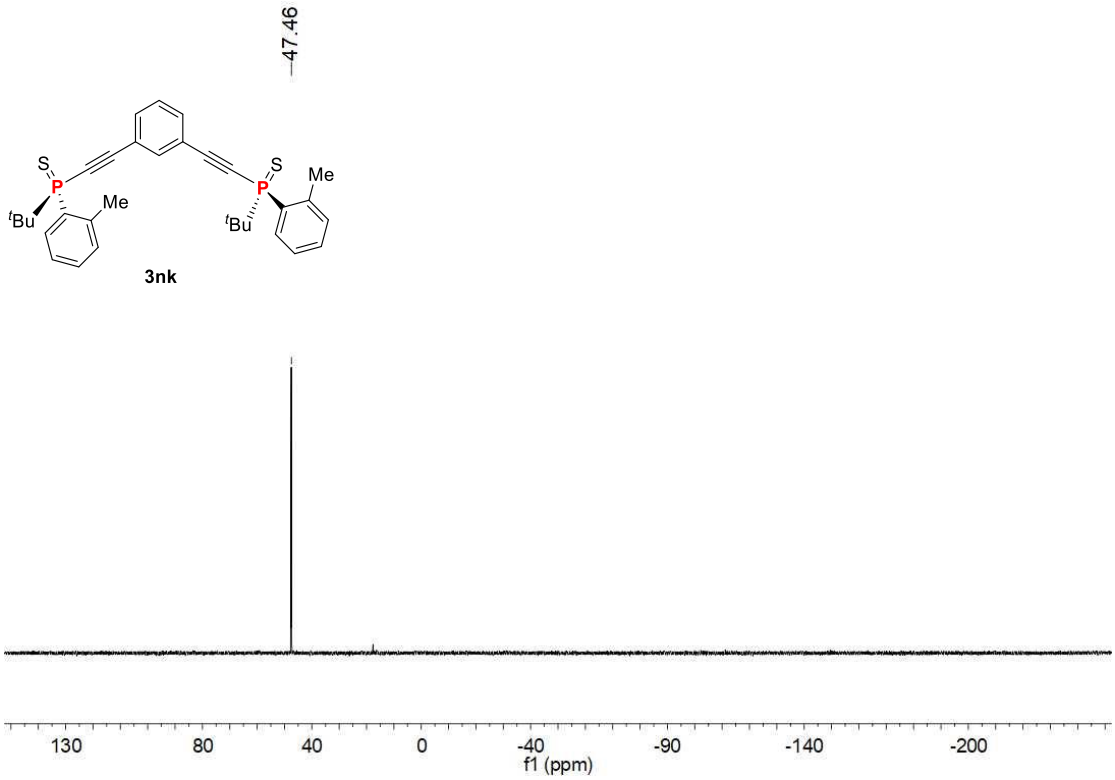

8.26
8.26
7.87
7.85
7.84
7.82
7.74
7.74
7.73
7.73
7.54
7.52
7.51
7.41
7.40
7.38
7.37
7.36
7.35
2.68
1.17
1.13
O
Me
P
tBu
S
3nj
7.87
7.85
7.84
7.74
7.74
7.73
7.73
7.52
7.51
7.41
7.40
7.38
7.37
7.36
1.09
1.07
1.15
3.06
7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
1.01
1.09
1.07
1.15
3.06
3.00
9.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

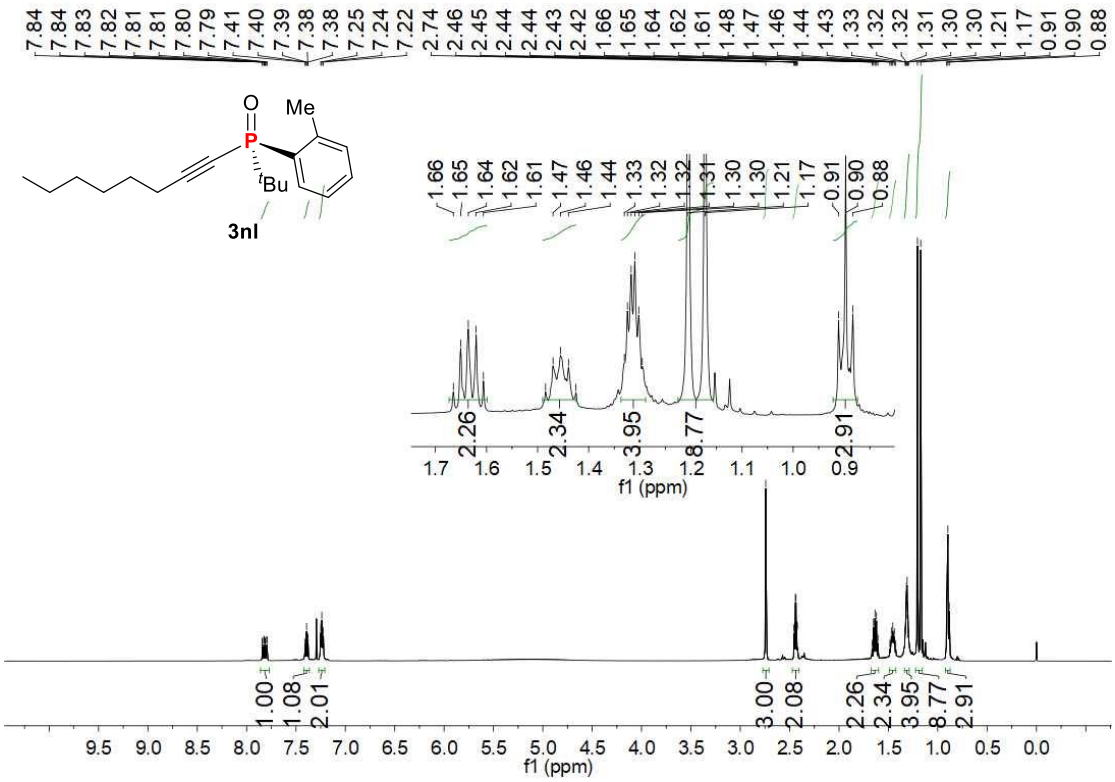

143.55
143.47
134.85
134.84
134.09
134.00
132.71
132.61
132.54
132.52
130.20
128.29
127.23
126.40
125.78
125.68
118.81
118.78
99.54
99.36
83.36
82.20
35.86
35.21
24.23
21.66
21.64
O
Me
P
tBu
S
3nj
134.85
134.84
134.00
132.71
132.61
132.54
132.52
130.20
128.29
127.23
126.40
125.78
125.68
133 130 127
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

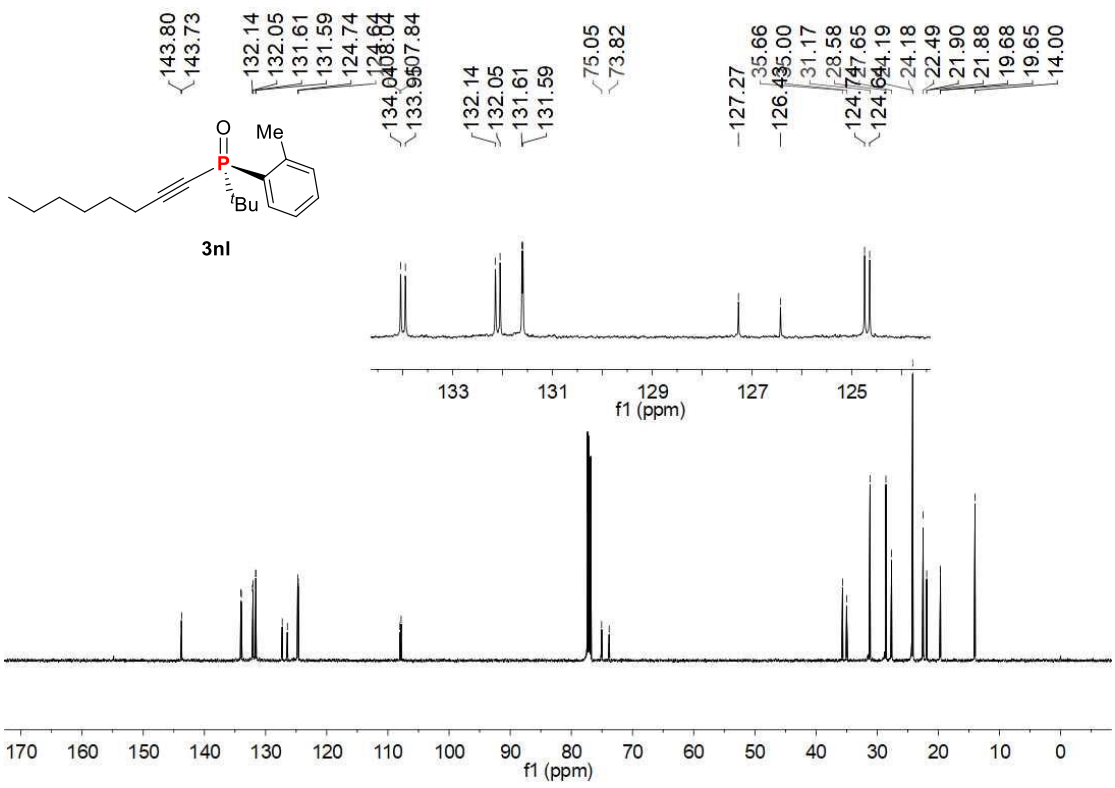

34.36
O
Me
P
tBu
S
3nj
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

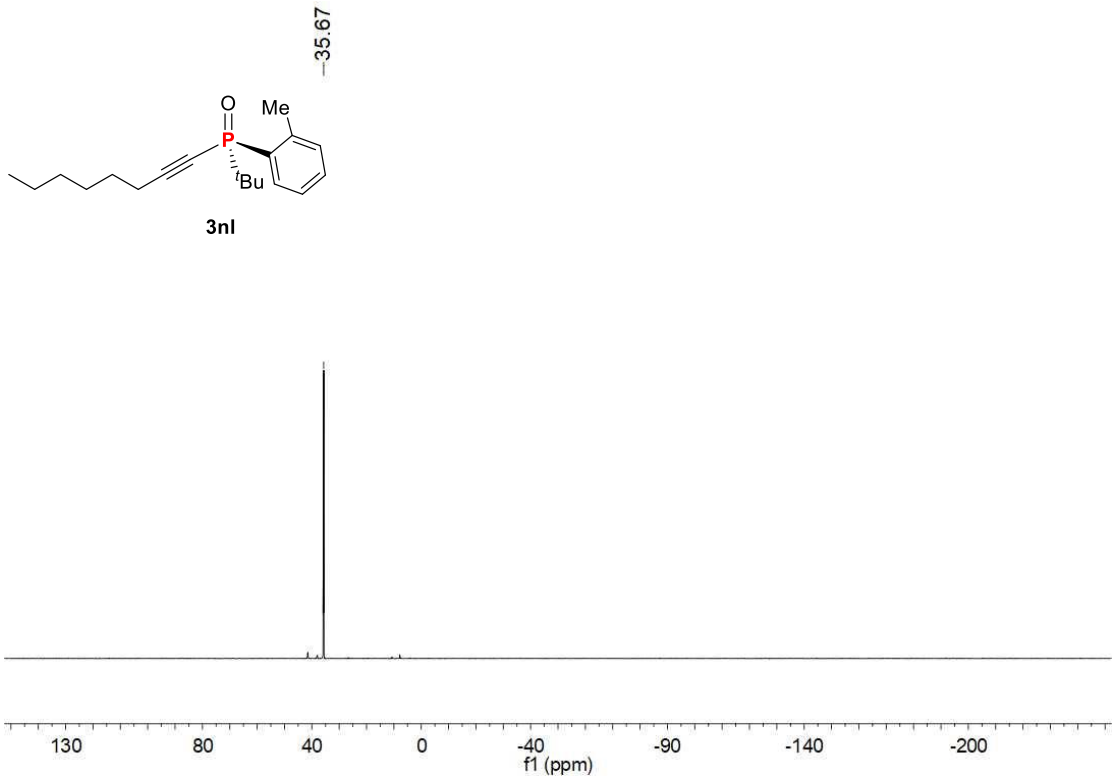

8.19 8.18 8.16 8.15 7.81 7.67 7.67 7.65 7.65 7.46 7.44 7.43 7.41 7.41 7.34 7.32 7.31 7.28 7.26 7.25
2.88
1.35 1.34 1.31 1.31
S P Me
tBu
tBu
S P Me
3nk
7.81 7.67 7.67 7.65 7.65 7.46 7.44 7.43 7.41 7.41 7.32 7.28 7.26 7.25
0.92 1.99 3.13 2.14 0.85 0.78
f1 (ppm)
1.98 0.92 1.99 3.13 2.14 0.85 0.78 6.00 18.25
f1 (ppm)

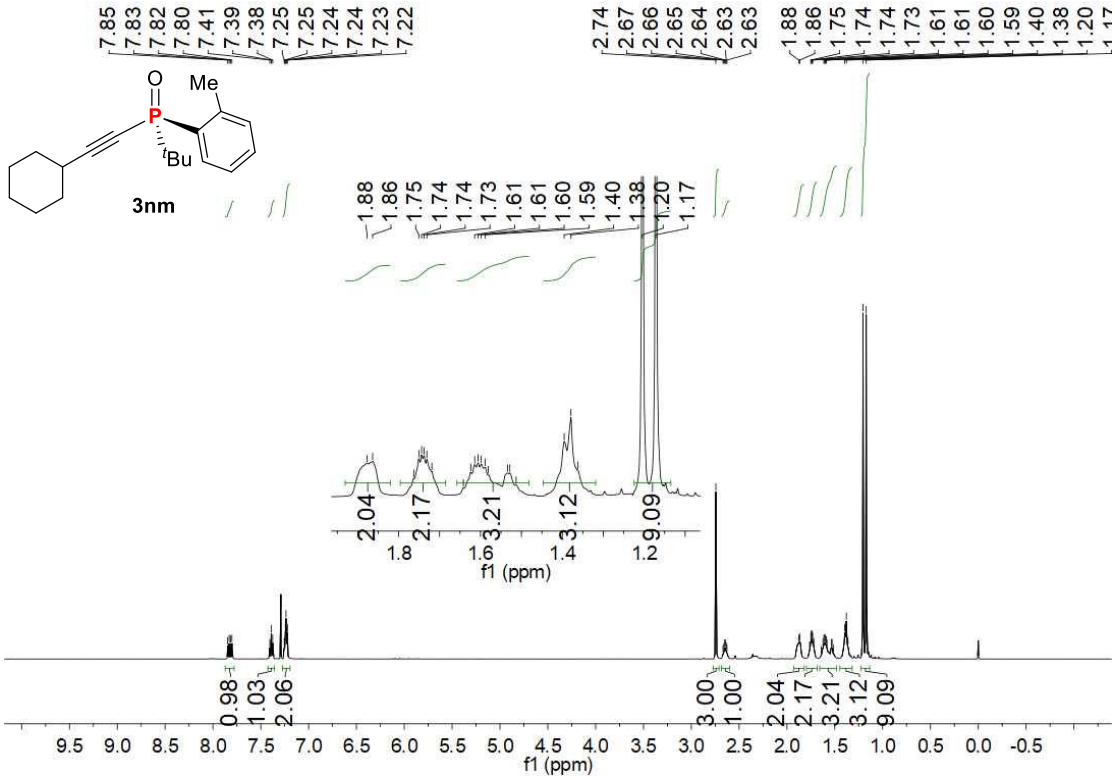

142.87 142.79 135.52 134.70 134.61 133.70 133.01 132.91 131.88 131.86 129.04 125.52 125.41 121.52 121.24 104.08
83.95 82.90
38.96 38.50
24.76 24.74 23.24 23.21
S P Me
tBu
tBu
S P Me
3nk
134.70 134.61 133.70 133.01 132.91 131.88 131.86 129.04 126.19 125.52 125.41 121.52 121.49
135 131 127 123
f1 (ppm)
f1 (ppm)

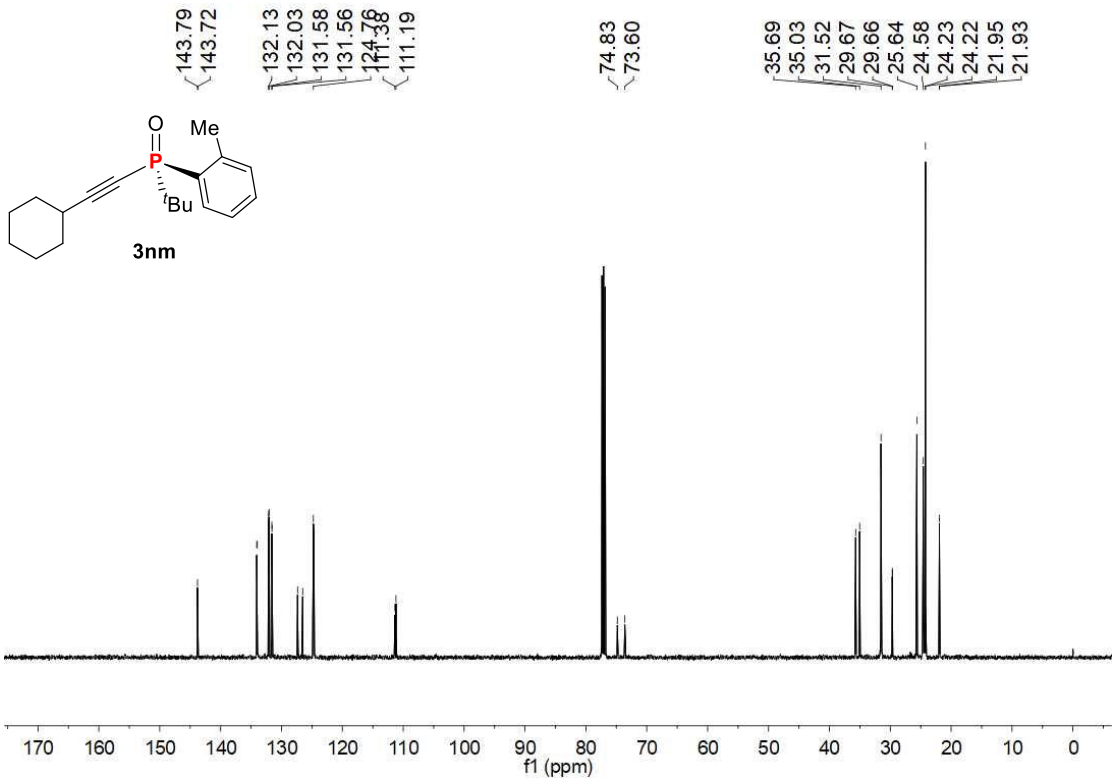

47.46
S
P
Me
tBu
S
P
Me
tBu
3nk
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

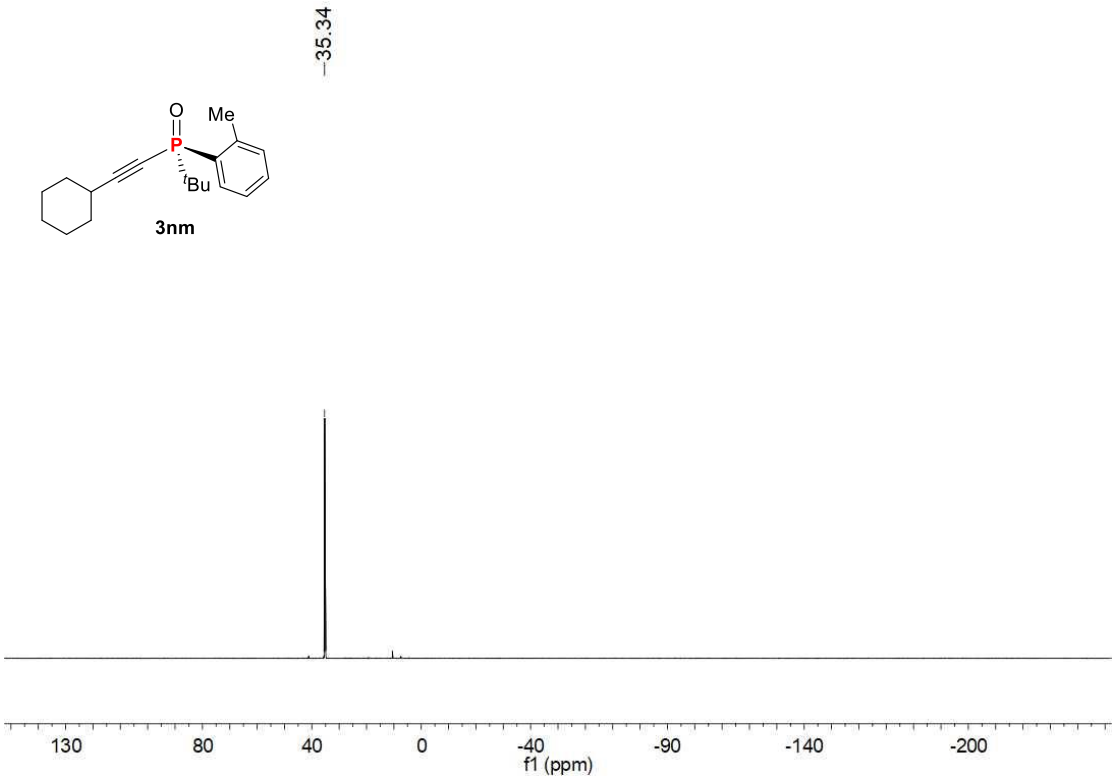

7.84 7.84 7.83 7.82 7.81 7.81 7.80 7.79 7.41 7.40 7.39 7.38 7.38 7.25 7.24 7.22
2.74 2.46 2.45 2.44 2.44 2.43 2.42 1.66 1.65 1.64 1.62 1.61 1.48 1.47 1.46 1.44 1.43 1.33 1.32 1.32 1.31 1.30 1.30 1.21 1.17 0.91 0.90 0.88
O
P
Me
tBu
3nl
1.66 1.65 1.64 1.62 1.61 1.47 1.46 1.44 1.33 1.32 1.32 1.31 1.30 1.30 1.21 1.17 0.91 0.90 0.88
2.26 2.34 3.95 8.77 2.91
1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9
f1 (ppm)
1.00 1.08 2.01 3.00 2.08 2.26 2.34 3.95 8.77 2.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

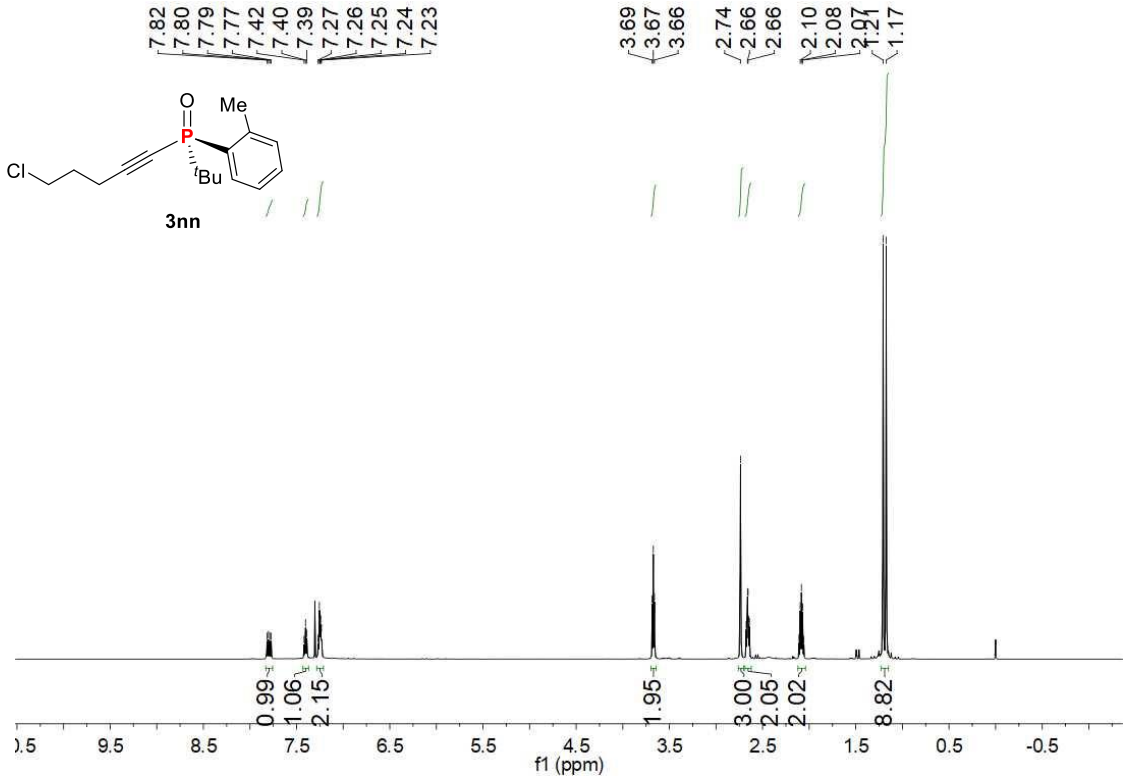

143.80 143.73 132.14 132.05 131.61 131.59 124.74 124.64 108.04 107.84 75.05 73.82 127.27 35.66 35.00 31.17 28.58 24.18 22.49 21.90 21.88 19.68 19.65 14.00
O
P
Me
tBu
3nl
133 131 129 127 125
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

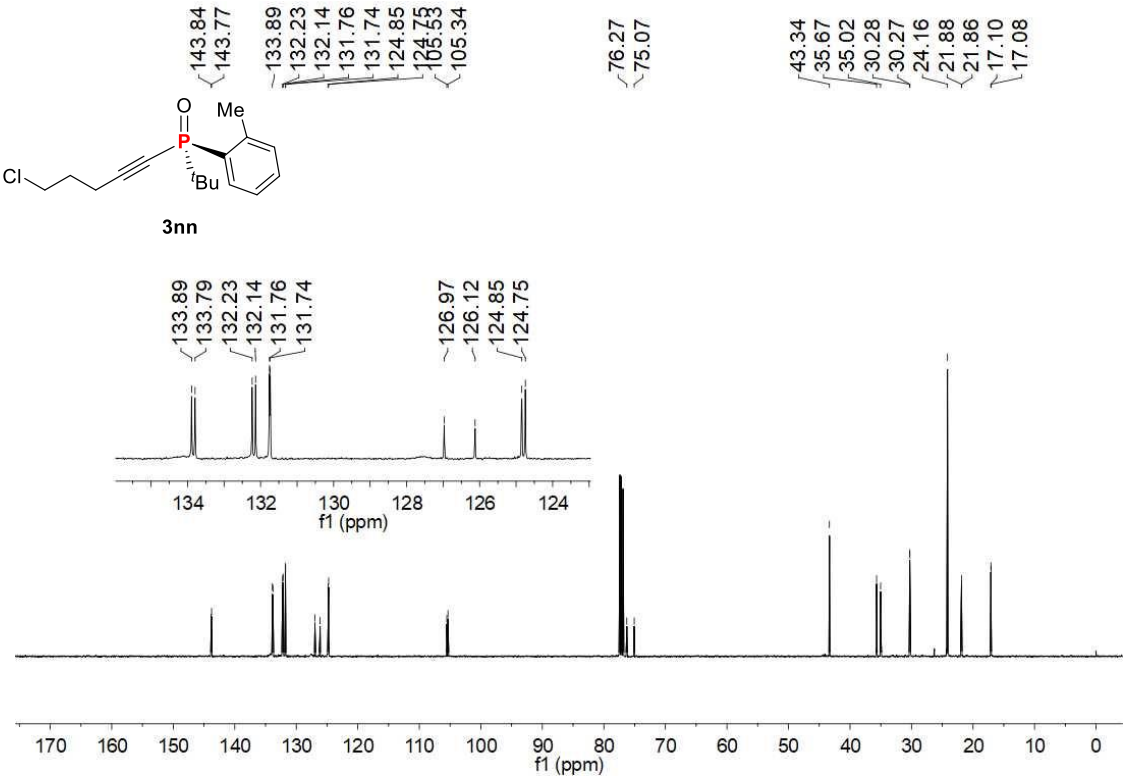

35.67
O
P
Me
tBu
3nl
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

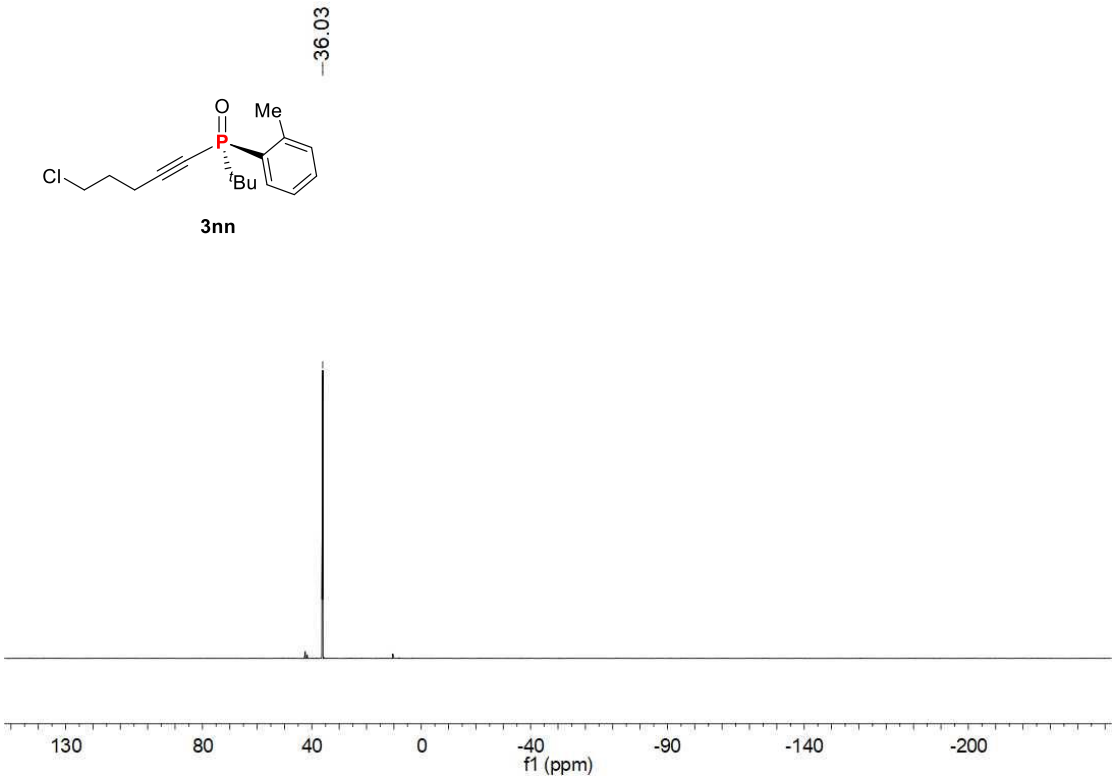

7.85 7.83 7.82 7.80 7.41 7.39 7.38 7.25 7.25 7.24 7.24 7.23 7.22
2.74 2.67 2.66 2.65 2.64 2.63 2.63
1.88 1.86 1.75 1.74 1.74 1.73 1.61 1.61 1.60 1.59 1.40 1.38 1.20 1.17
O
P
Me
tBu
3nm
2.04 2.17 3.21 3.12 9.09
f1 (ppm)
0.98 1.03 2.06 3.00 1.00 2.04 2.17 3.21 3.12 9.09
f1 (ppm)

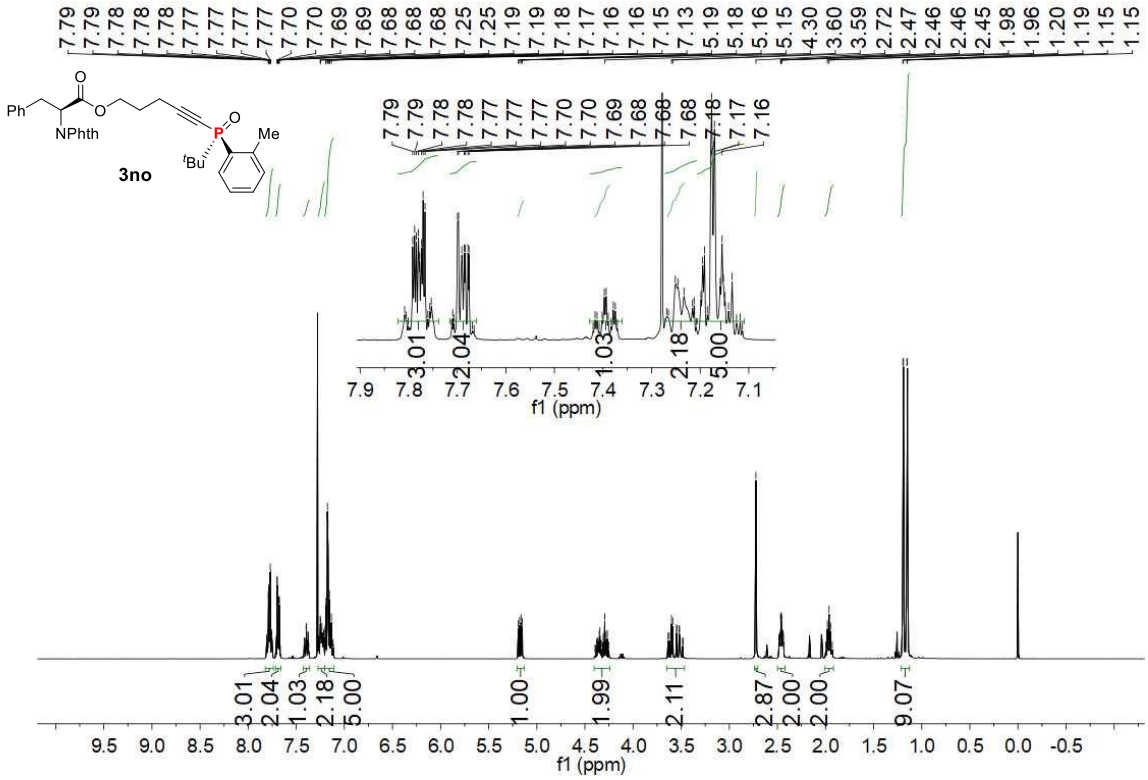

143.79 143.72 132.13 132.03 131.58 131.56 111.19 74.83 73.60 35.69 35.03 31.52 29.67 29.66 25.64 24.58 24.23 24.22 21.95 21.93
O
P
Me
tBu
3nm
f1 (ppm)

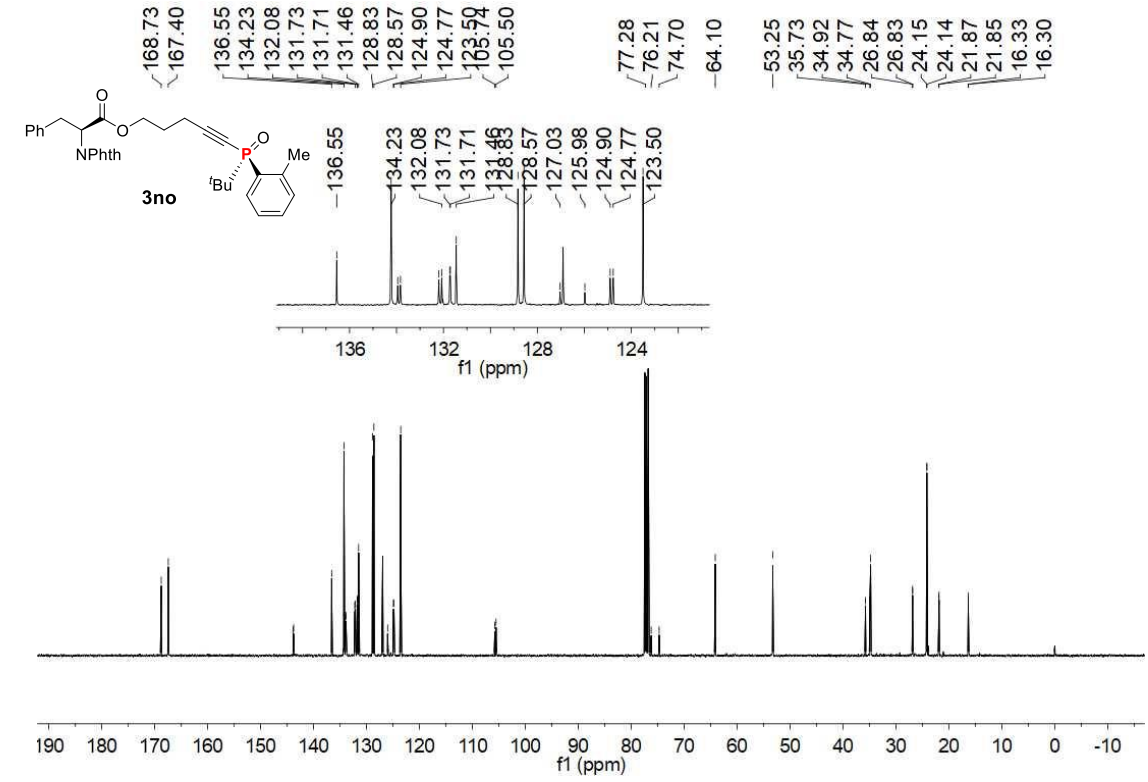

35.34
O
Me
P
tBu
3nm
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

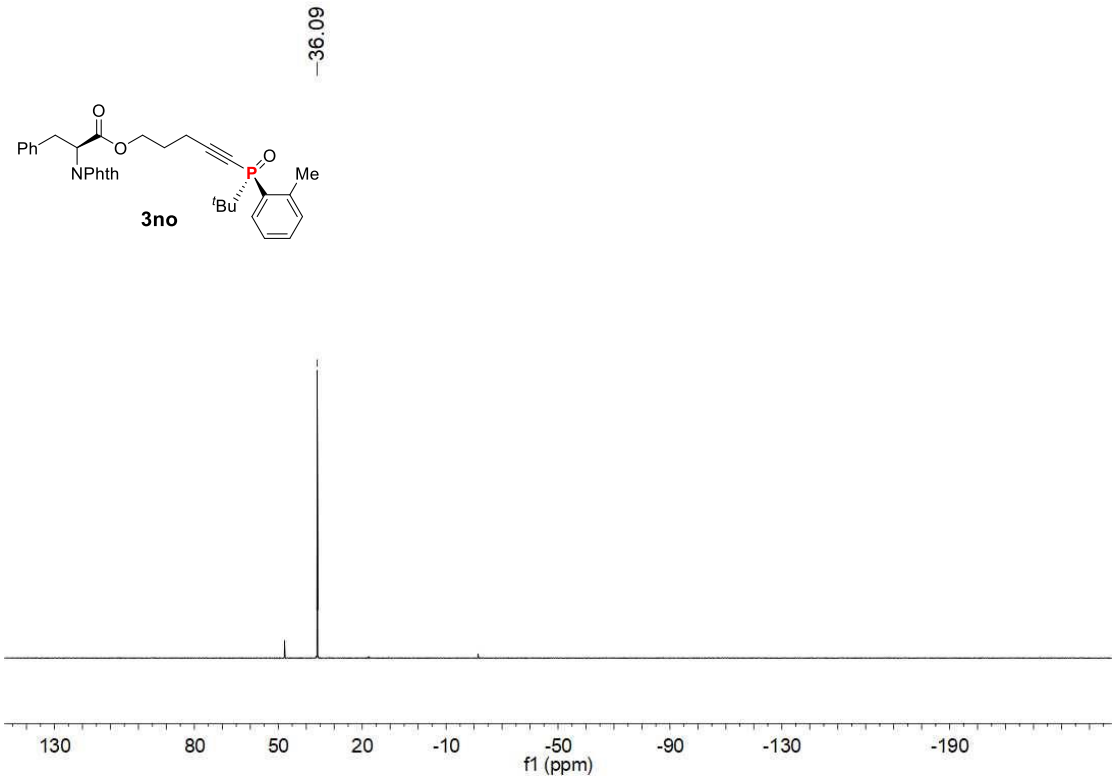

7.82
7.80
7.79
7.77
7.42
7.40
7.39
7.27
7.26
7.25
7.24
7.23
3.69
3.67
3.66
2.74
2.66
2.66
2.10
2.08
1.17
O
Me
P
Cl
tBu
3nn
0.99
1.06
2.15
1.95
3.00
2.05
2.02
8.82
f1 (ppm)

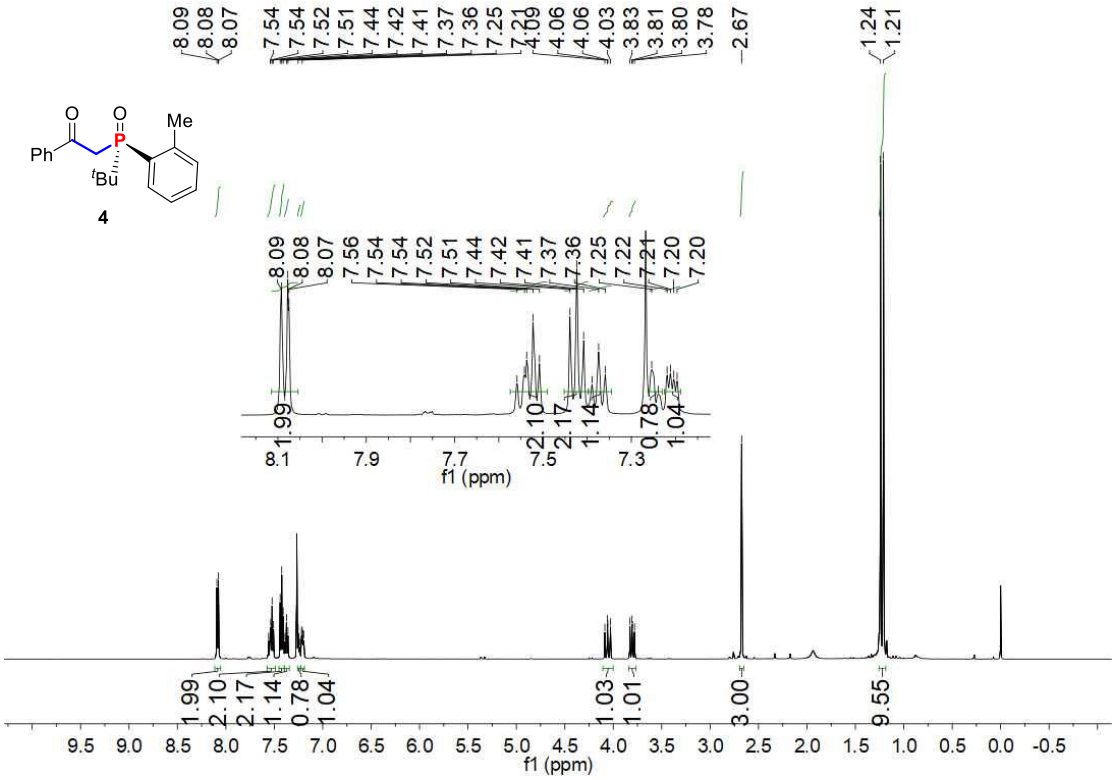

143.84
143.77
133.89
132.23
132.14
131.76
131.74
124.85
105.34
76.27
75.07
43.34
35.67
35.02
30.28
30.27
24.16
21.88
21.86
17.10
17.08
O
Me
P
Cl
tBu
3nn
133.89
133.79
132.23
132.14
131.76
131.74
126.97
126.12
124.85
124.75
f1 (ppm)
f1 (ppm)

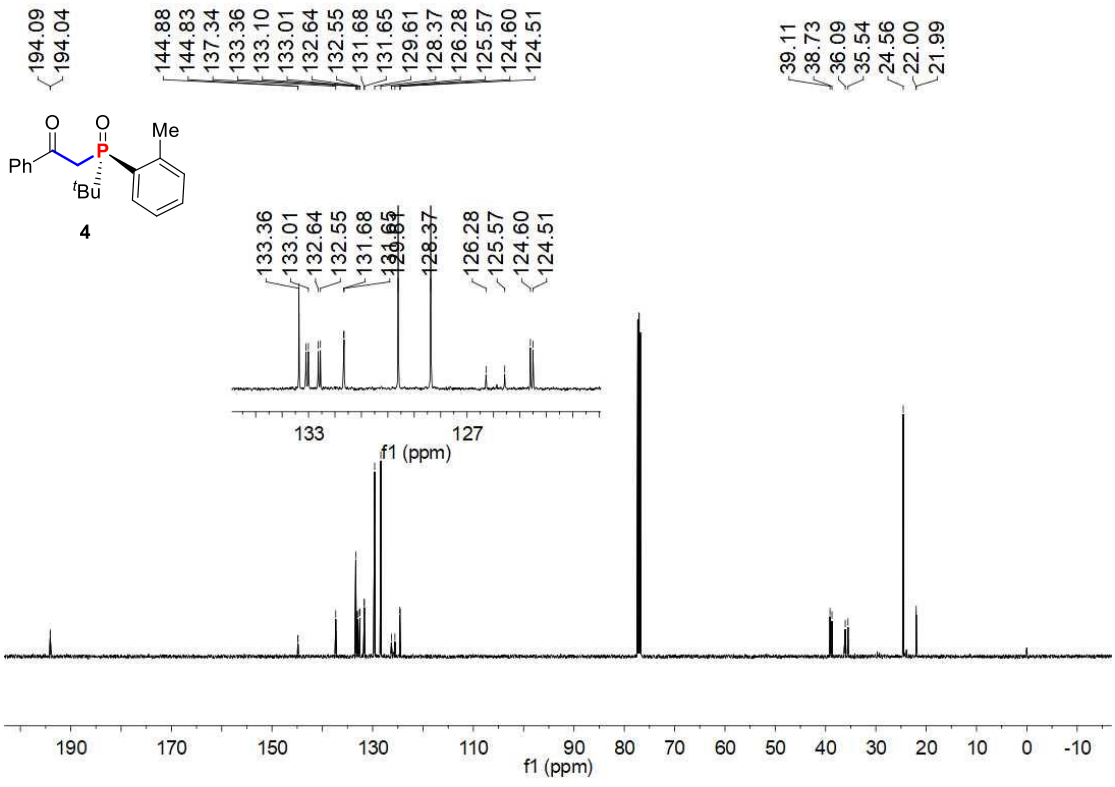

36.03
O
Me
P
Cl
tBu
3nn
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

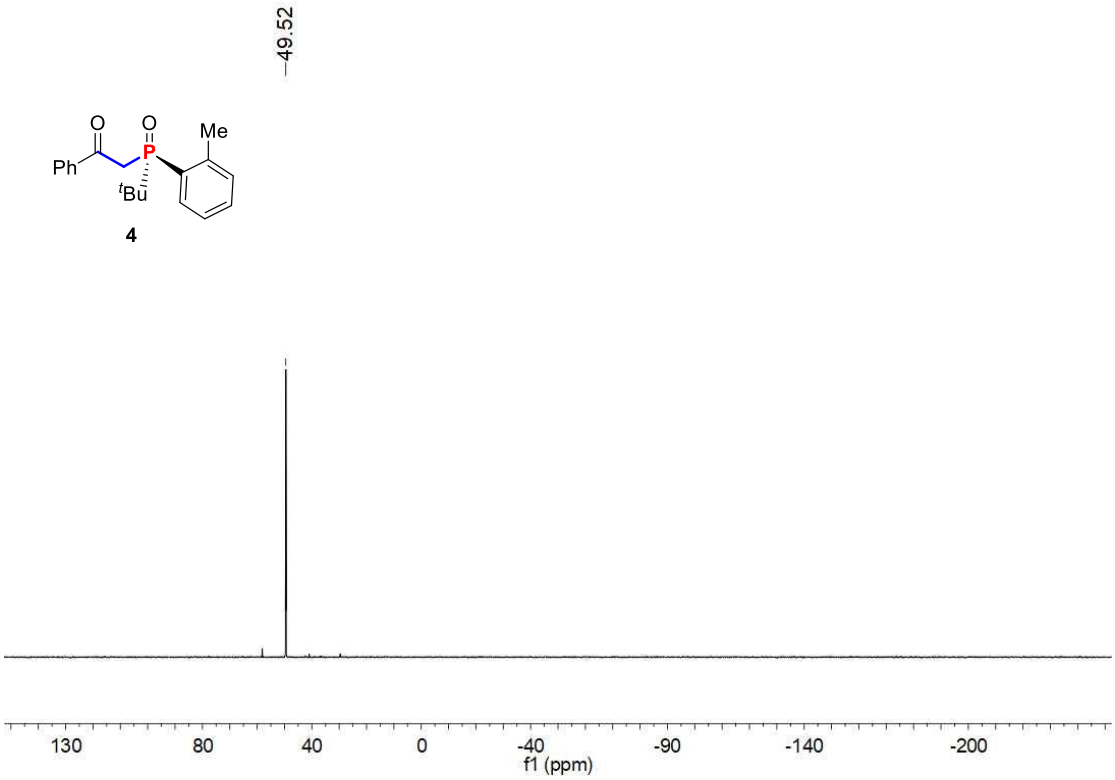

3no
f1 (ppm)

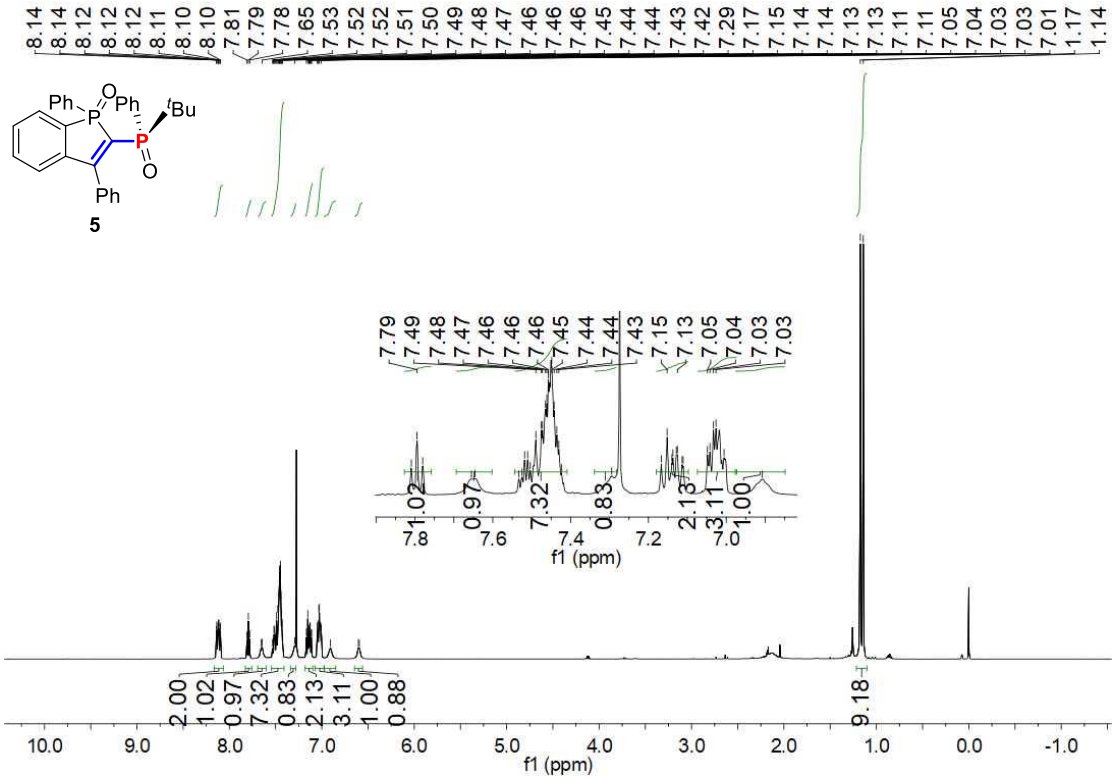

3no
f1 (ppm)

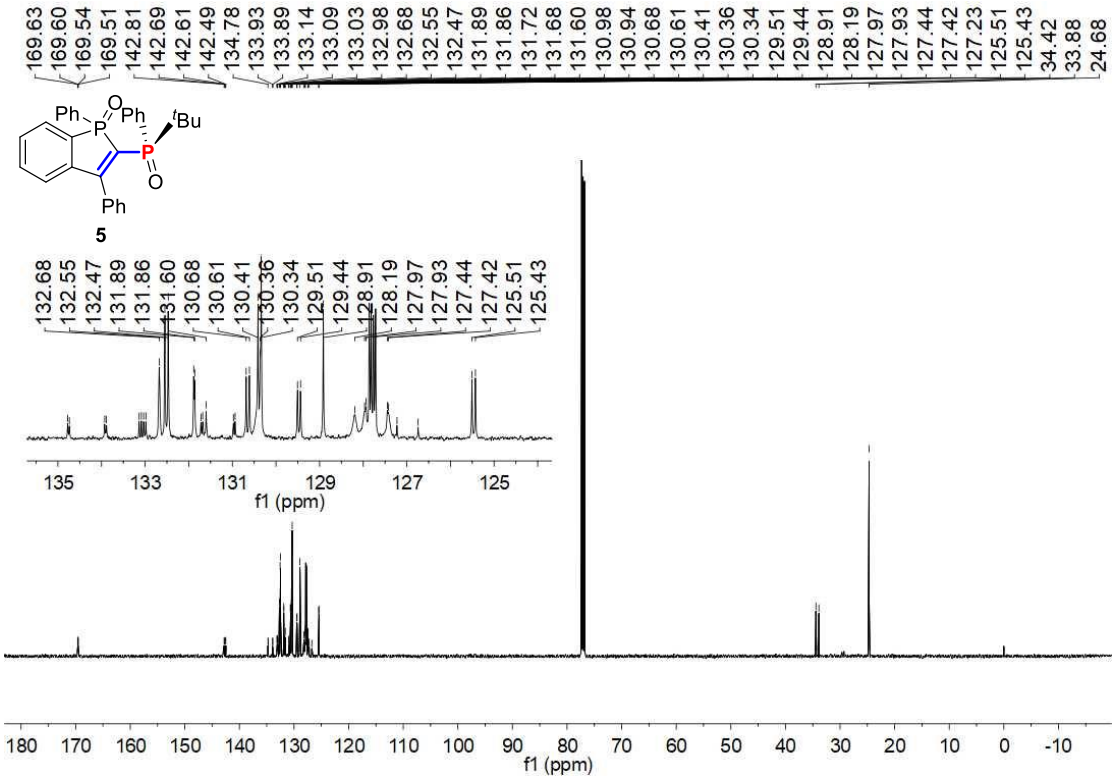

36.09
Ph
O
O
NPhth
P
O
Me
tBu
3no
130
80
50
20
-10
-50
-90
-130
-190
f1 (ppm)

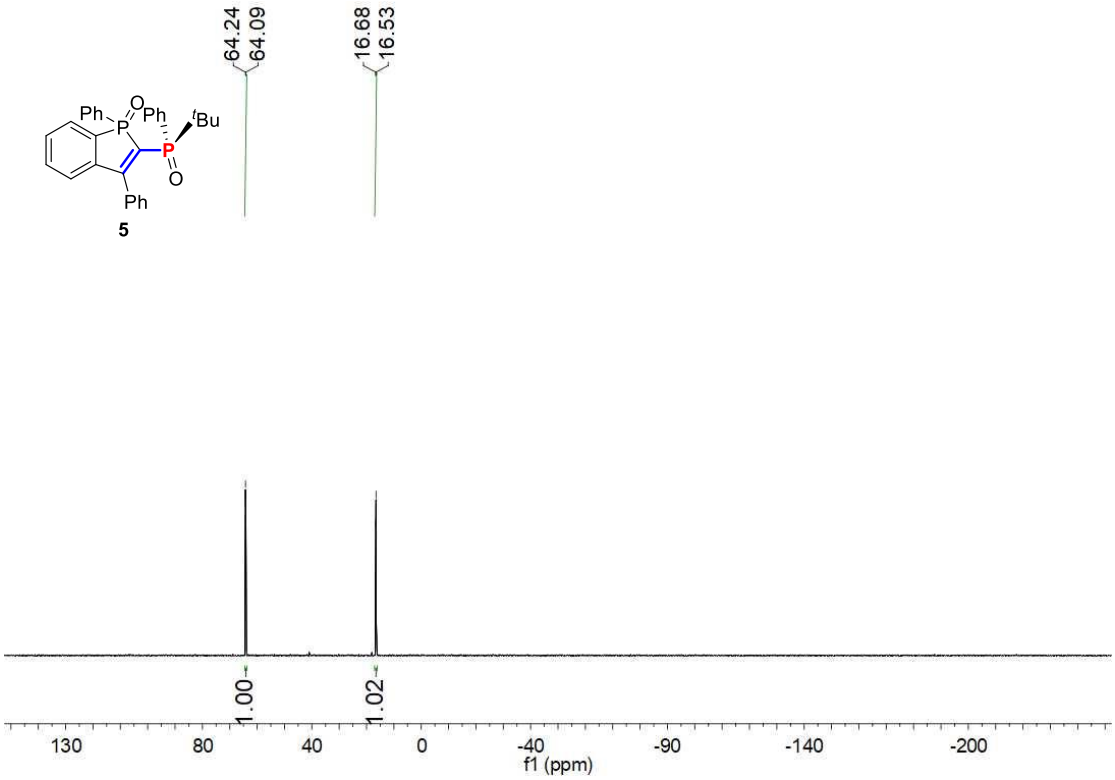

8.09
8.08
8.07
7.54
7.54
7.52
7.51
7.44
7.42
7.41
7.37
7.36
7.25
7.21
4.09
4.06
4.06
4.03
3.83
3.81
3.80
3.78
2.67
1.24
1.21
Ph
O
O
P
Me
tBu
4
1.99
2.10
2.17
1.14
0.78
1.04
1.03
1.01
3.00
9.55
f1 (ppm)

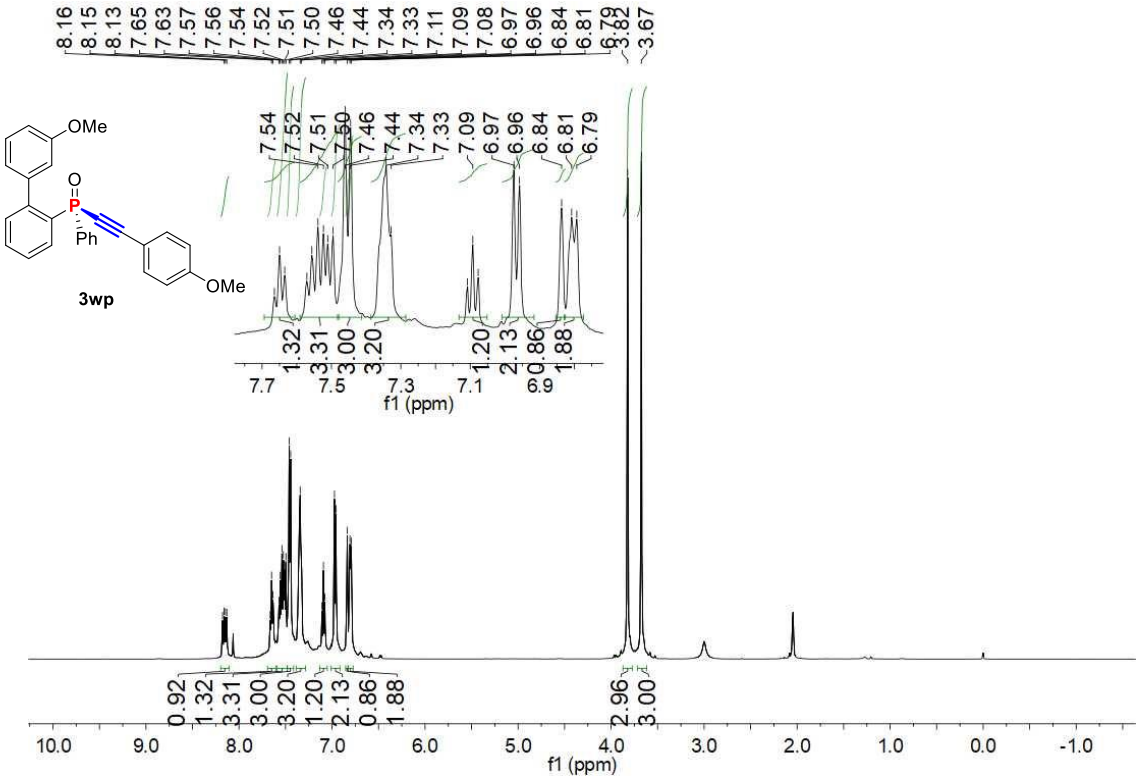

194.09
194.04
144.88
144.83
137.34
133.36
133.10
133.01
132.64
132.55
131.68
131.65
129.61
128.37
126.28
125.57
124.60
124.51
39.11
38.73
36.09
35.54
24.56
22.00
21.99
Ph
O
O
P
Me
tBu
4
f1 (ppm)

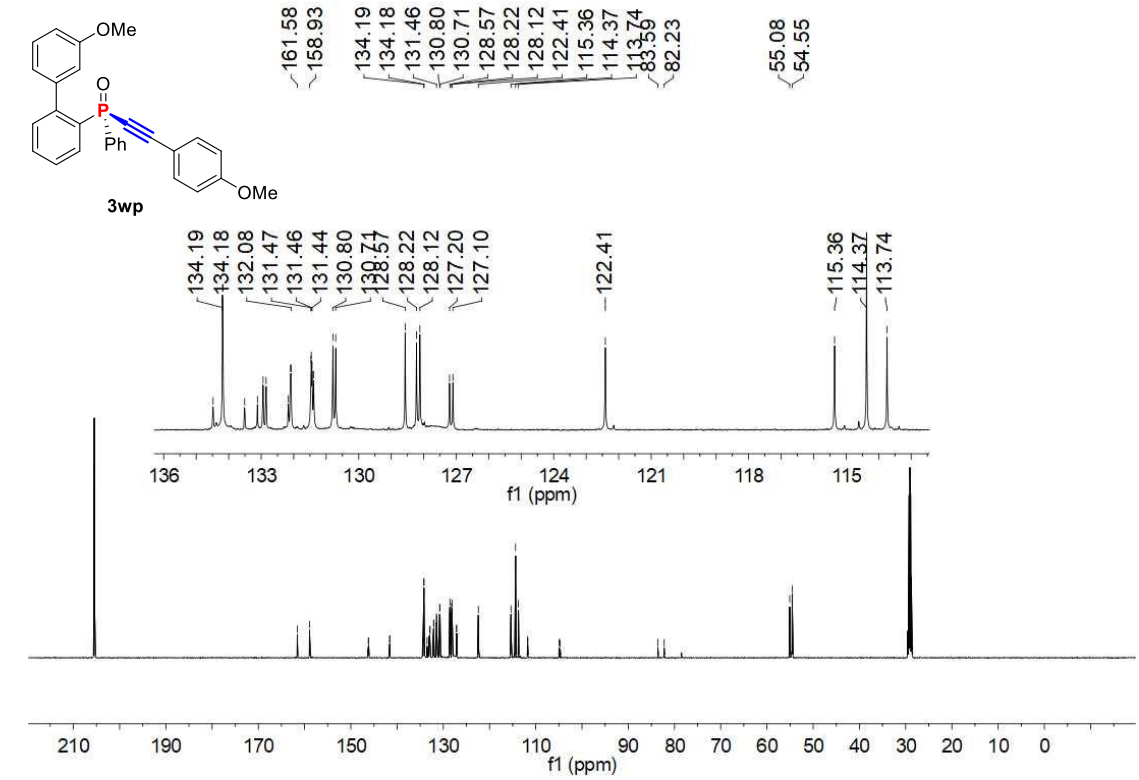

49.52
O
O
Me
Ph
P
tBu
4
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

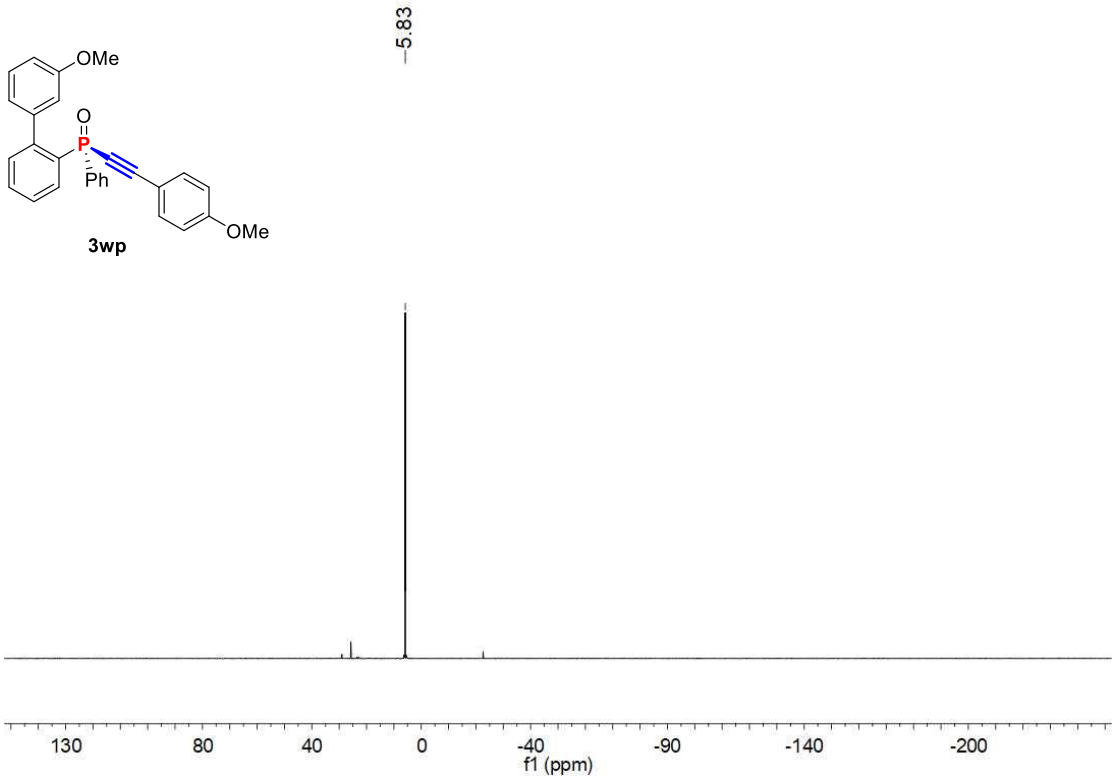

8.14 8.14 8.12 8.12 8.12 8.11 8.10 8.10 7.81 7.79 7.78 7.65 7.53 7.52 7.52 7.51 7.50 7.49 7.48 7.47 7.46 7.46 7.45 7.44 7.44 7.43 7.42 7.29 7.17 7.15 7.14 7.14 7.13 7.13 7.11 7.11 7.05 7.04 7.03 7.03 7.01 1.17 1.14
Ph
O
Ph
P
tBu
P
O
Ph
5
7.79 7.49 7.48 7.47 7.46 7.46 7.46 7.45 7.44 7.44 7.43 7.15 7.13 7.05 7.04 7.03 7.03
1.02 0.97 7.32 0.83 2.13 3.11 1.00
7.8 7.6 7.4 7.2 7.0
f1 (ppm)
2.00 1.02 0.97 7.32 0.83 2.13 3.11 1.00 0.88
9.18
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

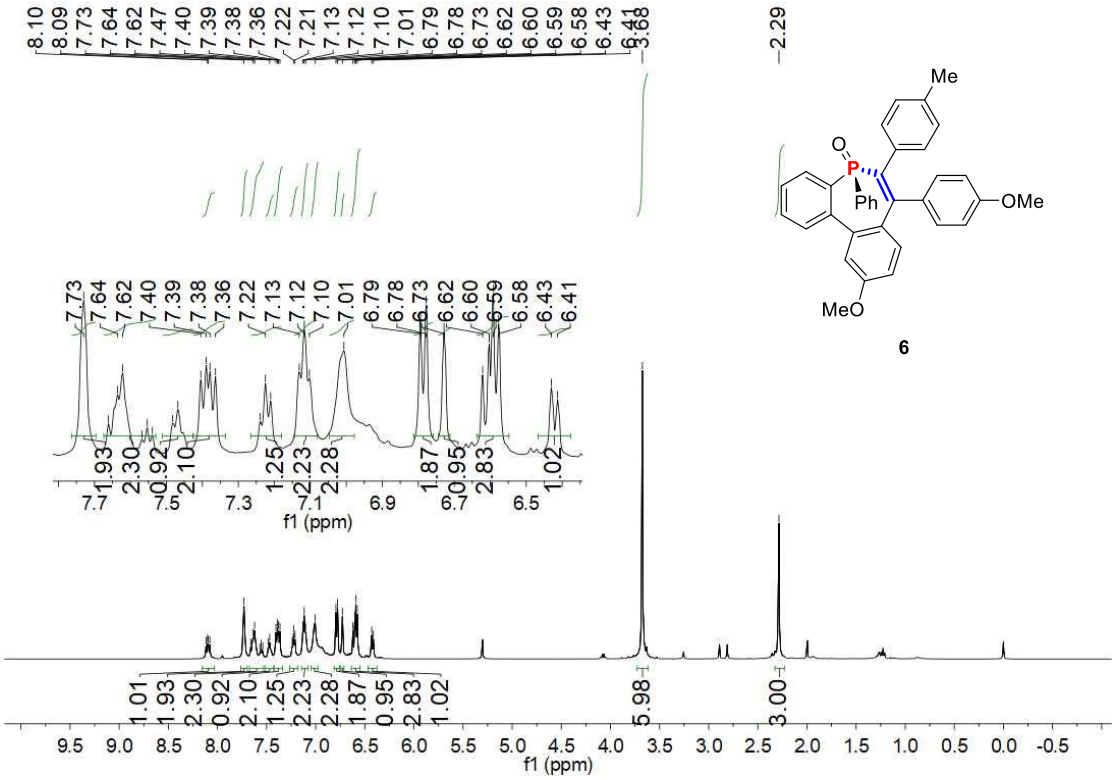

169.63 169.60 169.54 169.51 142.81 142.69 142.61 142.49 134.78 133.93 133.89 133.14 133.09 133.03 132.98 132.68 132.55 132.47 131.89 131.86 131.72 131.68 131.60 130.98 130.94 130.68 130.61 130.41 130.36 130.34 129.51 129.44 128.91 128.19 127.97 127.93 127.44 127.42 127.23 125.51 125.43 34.42 33.88 24.68
Ph
O
Ph
P
tBu
P
O
Ph
5
132.68 132.55 132.47 131.89 131.86 131.60 130.68 130.61 130.41 130.36 130.34 129.51 129.44 128.91 128.19 127.97 127.93 127.44 127.42 125.51 125.43
135 133 131 129 127 125
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

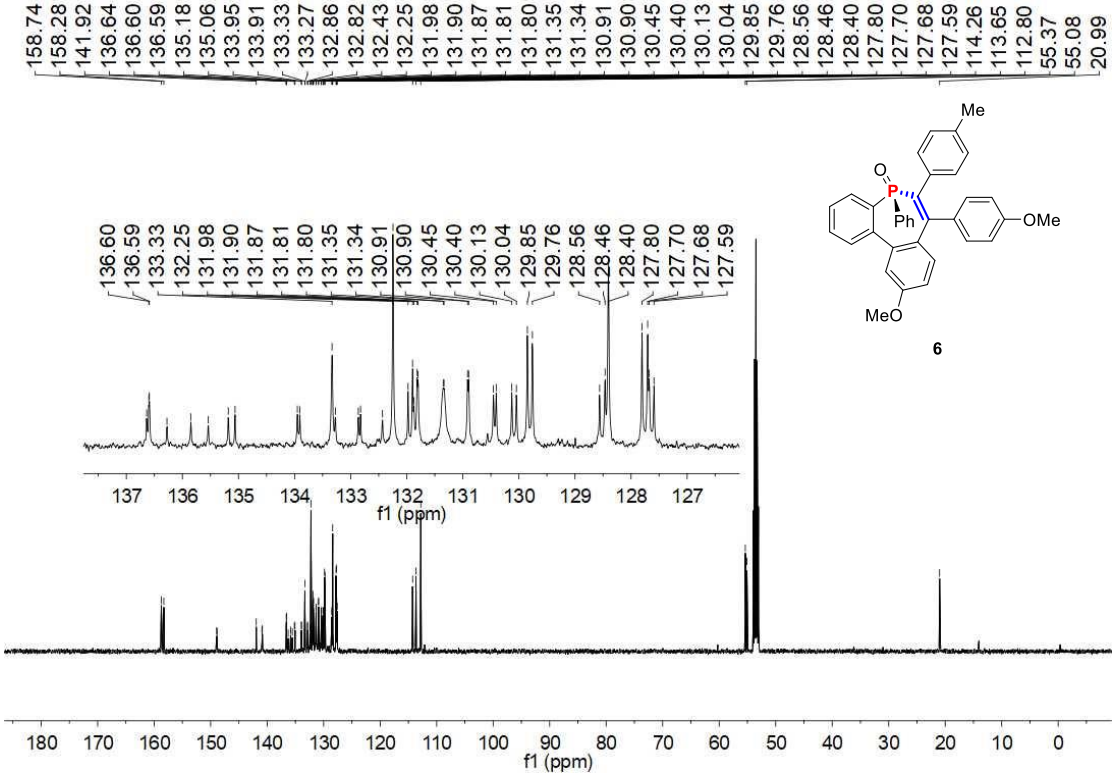

64.24
64.09
16.68
16.53
Ph
O
Ph
P
tBu
P
O
Ph
5
1.00
1.02
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

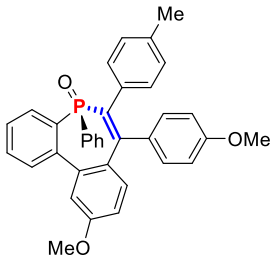

8.16
8.15
8.13
7.65
7.63
7.57
7.56
7.54
7.52
7.51
7.50
7.46
7.44
7.34
7.33
7.11
7.09
7.08
6.97
6.96
6.84
6.81
6.79
3.82
3.67
OMe
O
P
Ph
OMe
3wp
0.92
1.32
3.31
3.00
3.20
1.20
2.13
0.86
1.88
2.96
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


161.58
158.93
134.19
134.18
131.46
130.80
130.71
128.57
128.22
128.12
122.41
115.36
114.37
113.74
83.59
82.23
55.08
54.55
OMe
O
P
Ph
OMe
3wp
134.19
134.18
132.08
131.47
131.46
131.44
130.80
128.57
128.22
128.12
127.20
127.10
122.41
115.36
114.37
113.74
136
133
130
127
124
121
118
115
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
O
P
Ph
OMe
3wp
-5.83
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

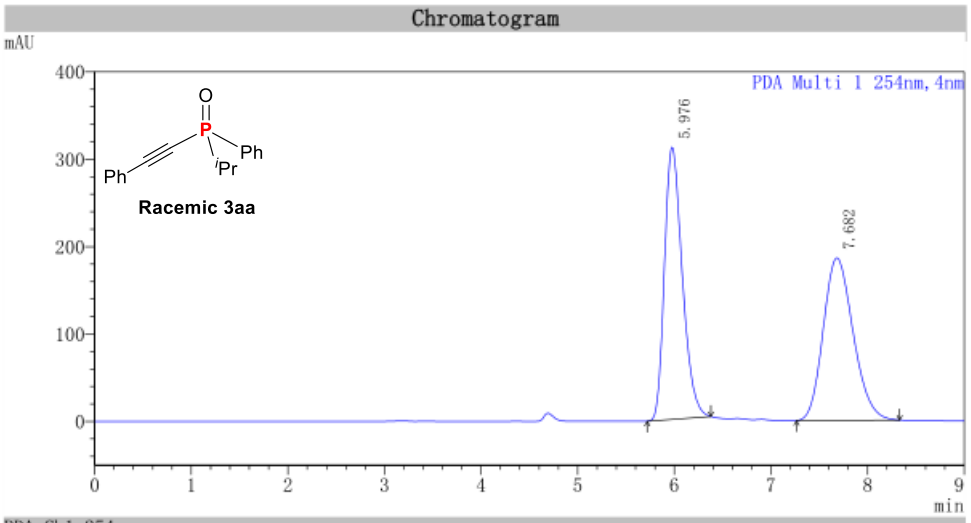

8.10 8.09 7.73 7.64 7.62 7.47 7.40 7.39 7.38 7.36 7.22 7.21 7.13 7.12 7.10 7.01 6.79 6.78 6.73 6.62 6.60 6.59 6.58 6.43 6.41 3.68
2.29
Me
O
P
Ph
OMe
MeO
6
1.01 1.93 2.30 0.92 2.10 1.25 2.23 2.28 1.87 0.95 2.83 1.02 5.98 3.00
f1 (ppm)


158.74 158.28 141.92 136.64 136.60 136.59 135.18 135.06 133.95 133.91 133.33 133.27 132.86 132.82 132.43 132.25 131.98 131.90 131.87 131.81 131.80 131.35 131.34 130.91 130.90 130.45 130.40 130.13 130.04 129.85 129.76 128.56 128.46 128.40 127.80 127.70 127.68 127.59 114.26 113.65 112.80 55.37 55.08 20.99
Me
O
P
Ph
OMe
MeO
6
f1 (ppm)



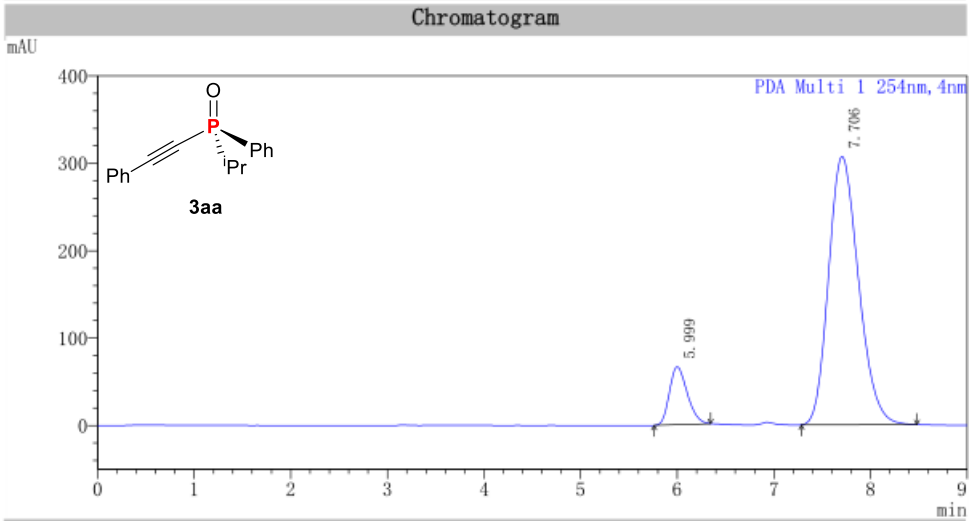
6

9. Copies of HPLC



PDA Ch1 254nm

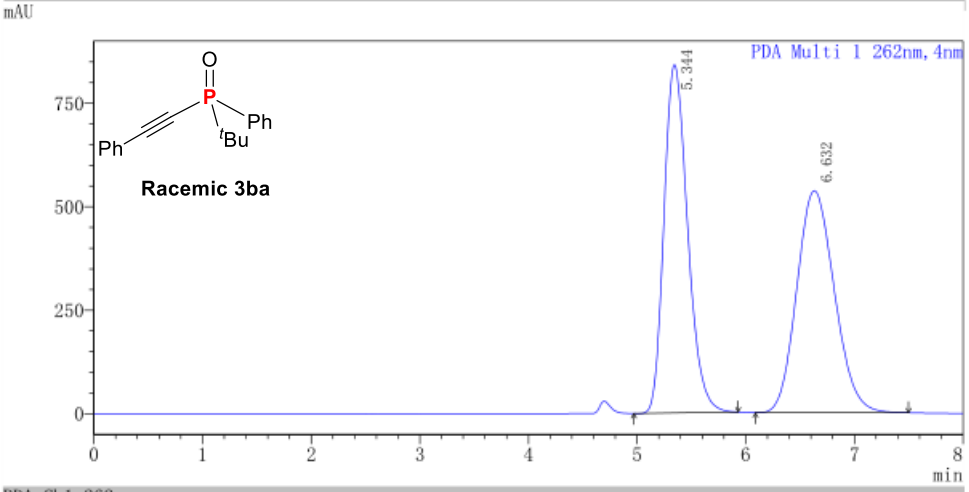
Peak#	Ret. Time	Area	Area%
1	5.976	3994111	49.921
2	7.682	4006746	50.079
Total		8000857	100.000



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.999	850984	11.377
2	7.706	6628918	88.623
Total		7479903	100.000

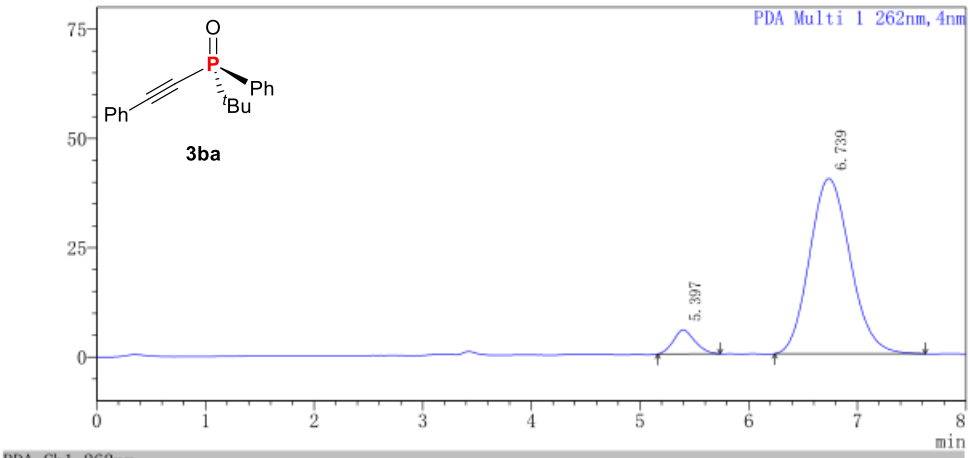
Chromatogram



PDA Ch1 262nm

Peak#	Ret. Time	Area	Area%
1	5.344	12713930	49.547
2	6.632	12946206	50.453
Total		25660135	100.000

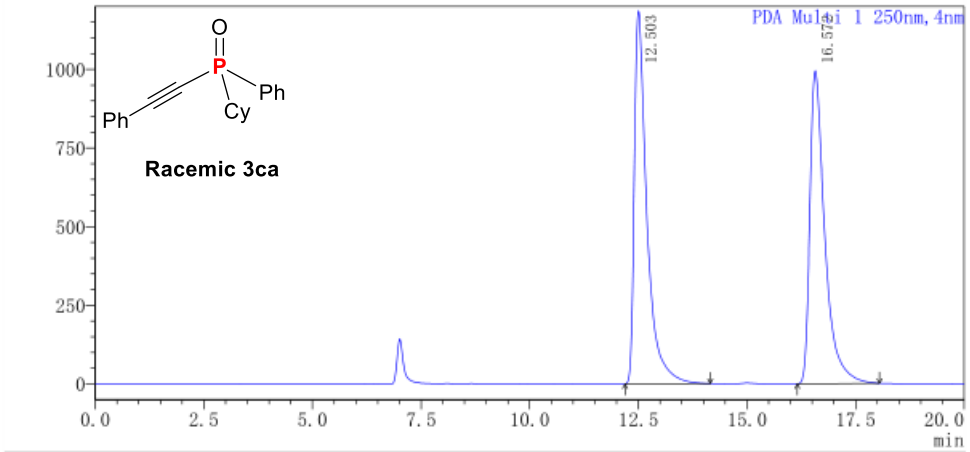
Chromatogram



PDA Ch1 262nm

Peak#	Ret. Time	Area	Area%
1	5.397	76230	6.806
2	6.739	1043886	93.194
Total		1120116	100.000

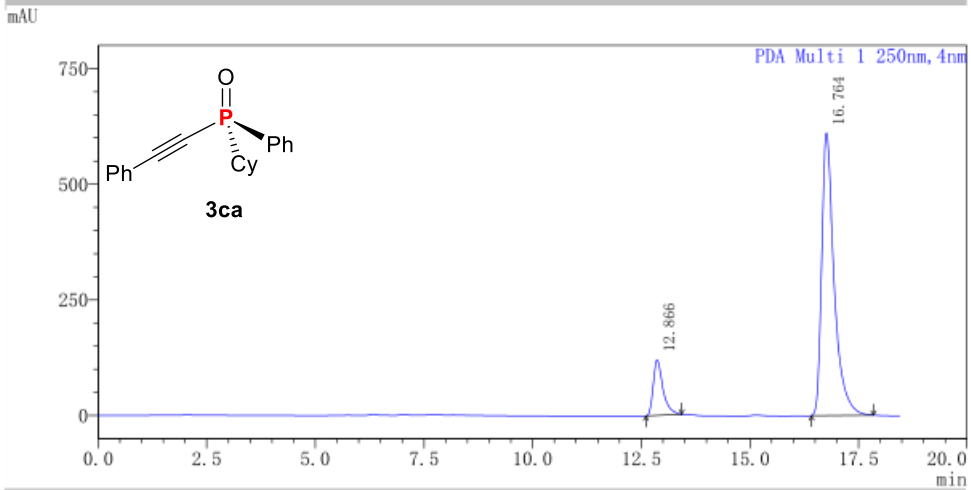
Chromatogram



PDA Ch1 250nm

Peak#	Ret. Time	Area	Area%
1	12.503	23847672	49.994
2	16.572	23853365	50.006
Total		47701037	100.000

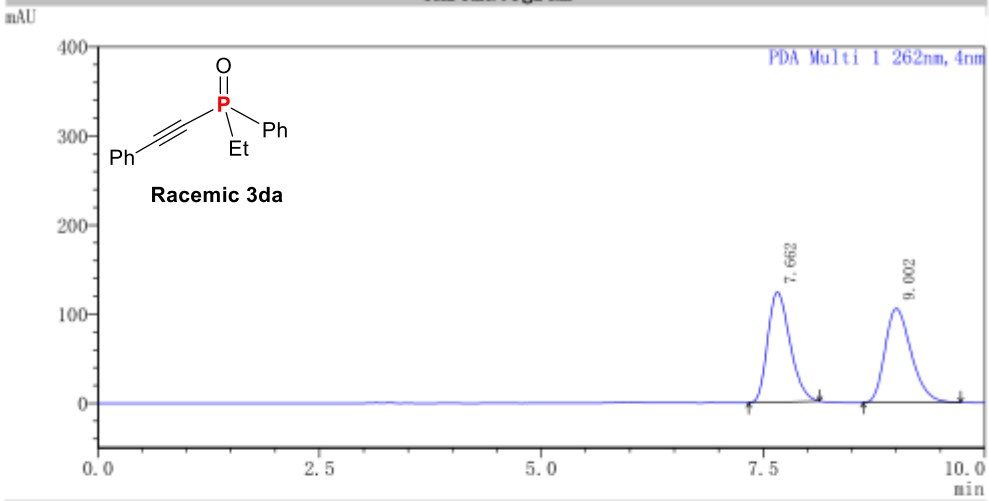
Chromatogram



PDA Ch1 250nm

Peak#	Ret. Time	Area	Area%
1	12.866	1876013	13.369
2	16.764	12156042	86.631
Total		14032055	100.000

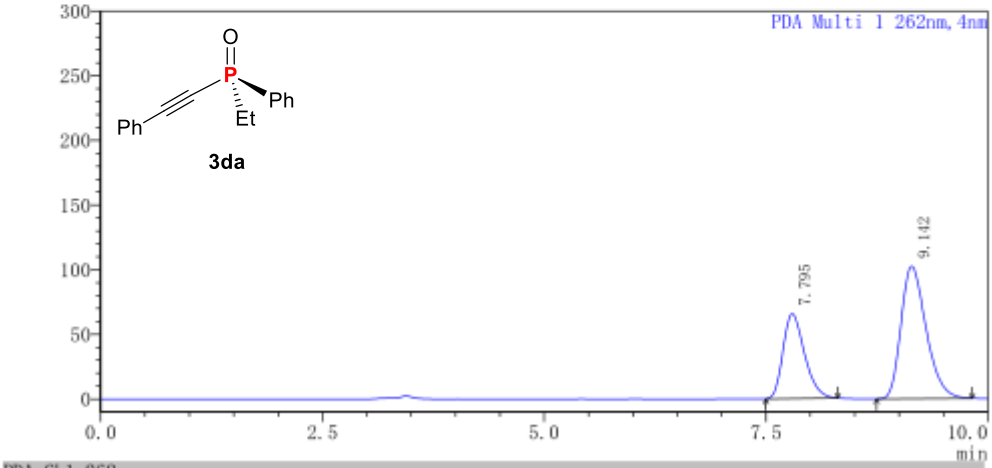
Chromatogram



PDA Ch1 262nm

Peak#	Ret. Time	Area	Area%
1	7.662	2171944	49.923
2	9.002	2178618	50.077
Total		4350562	100.000

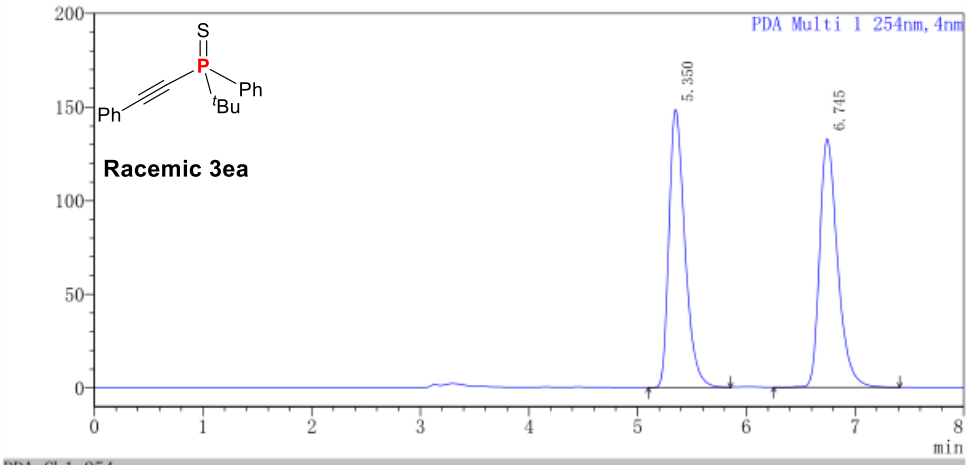
Chromatogram



PDA Ch1 262nm

Peak#	Ret. Time	Area	Area%
1	7.795	1109470	35.437
2	9.142	2021352	64.563
Total		3130822	100.000

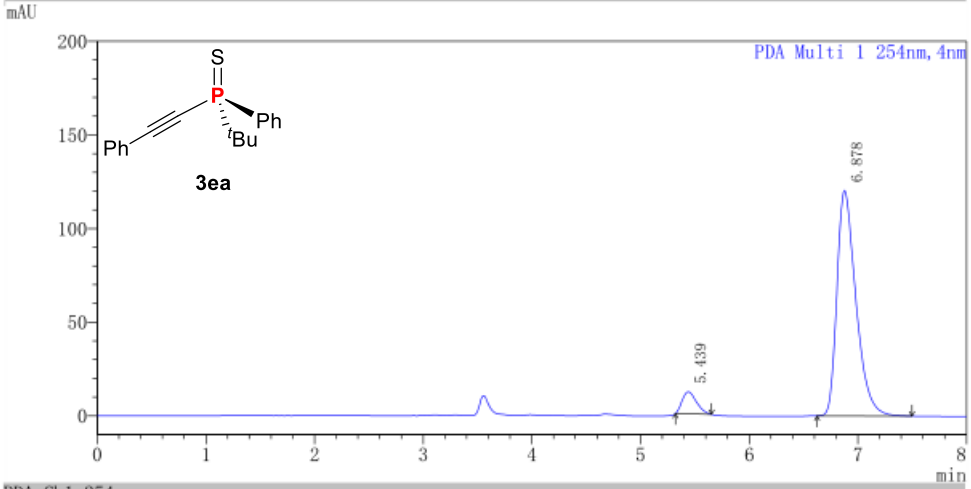
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.350	1514165	49.813
2	6.745	1525557	50.187
Total		3039722	100.000

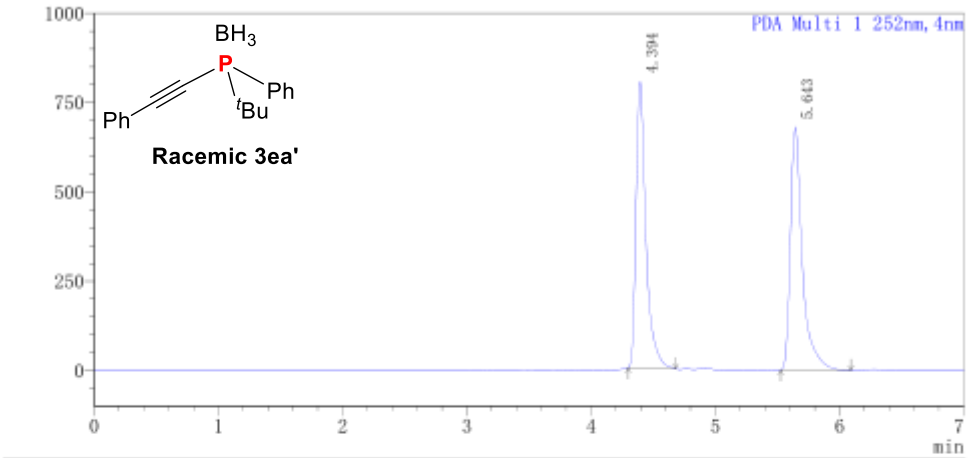
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.439	107193	6.827
2	6.878	1462995	93.173
Total		1570188	100.000

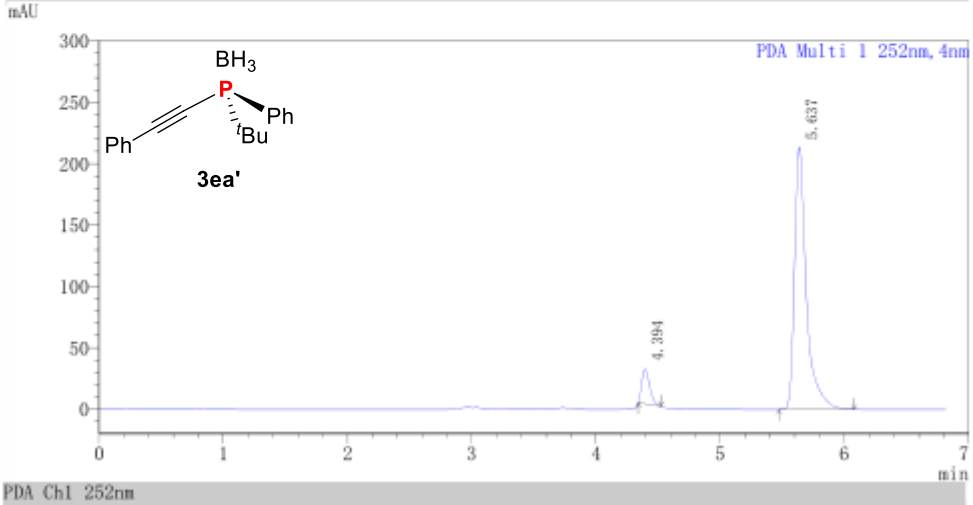
Chromatogram



PDA Ch1 252nm

Peak#	Ret. Time	Area	Area%
1	4.394	4450554	49.424
2	5.643	4554299	50.576
Total		9004853	100.000

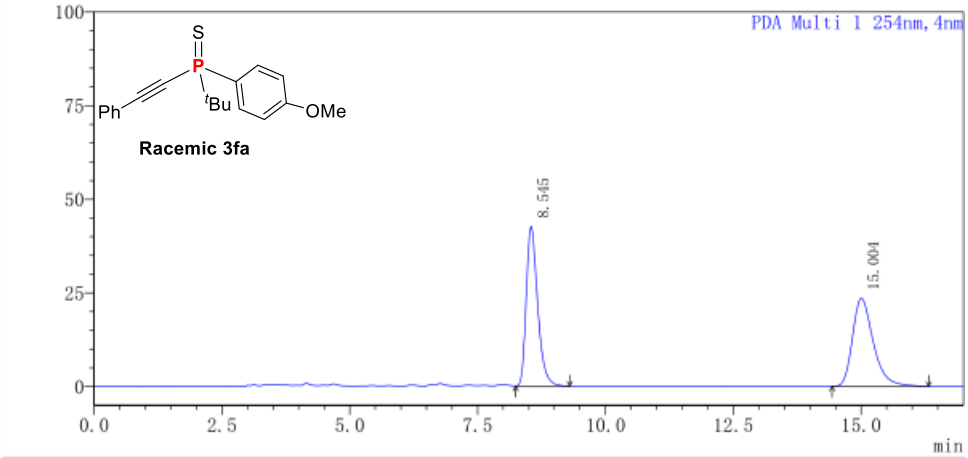
Chromatogram



PDA Ch1 252nm

Peak#	Ret. Time	Area	Area%
1	4.394	124076	8.062
2	5.637	1415008	91.938
Total		1539084	100.000

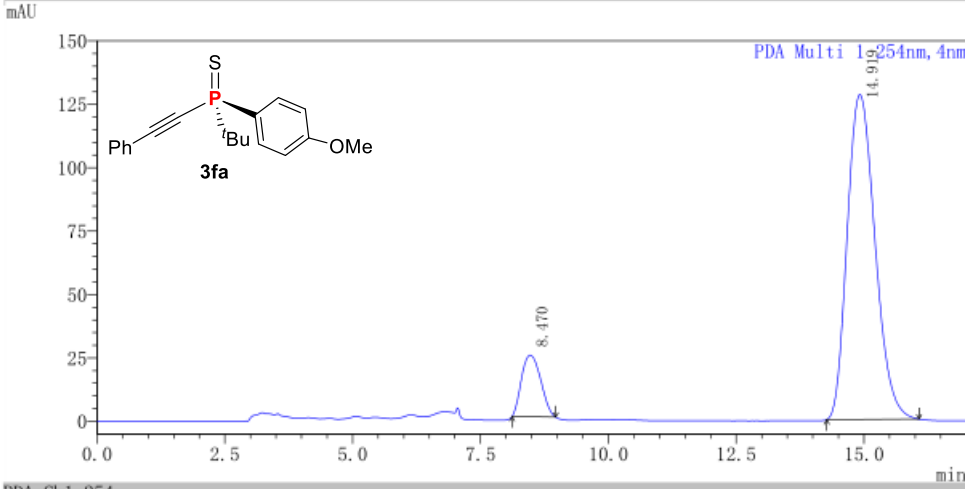
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.545	662691	49.904
2	15.004	665247	50.096
Total		1327937	100.000

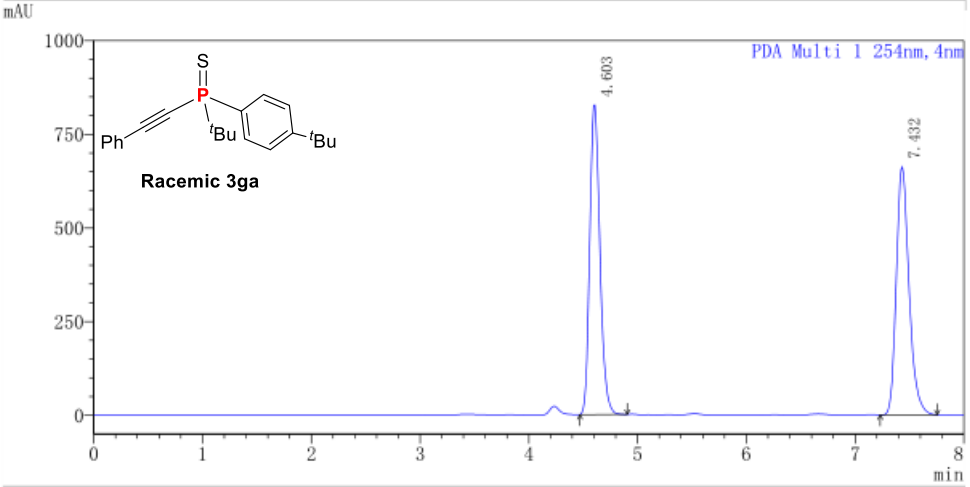
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.470	636598	11.604
2	14.919	4849454	88.396
Total		5486052	100.000

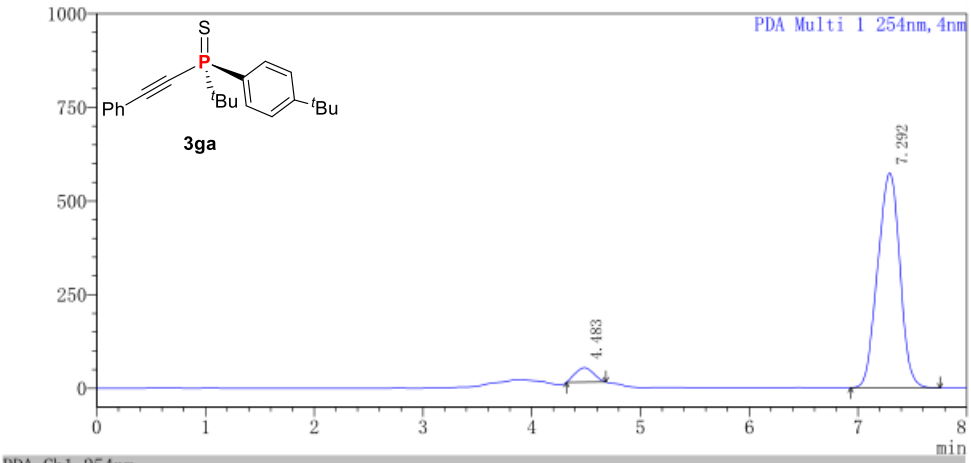
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.603	5375367	49.893
2	7.432	5398402	50.107
Total		10773769	100.000

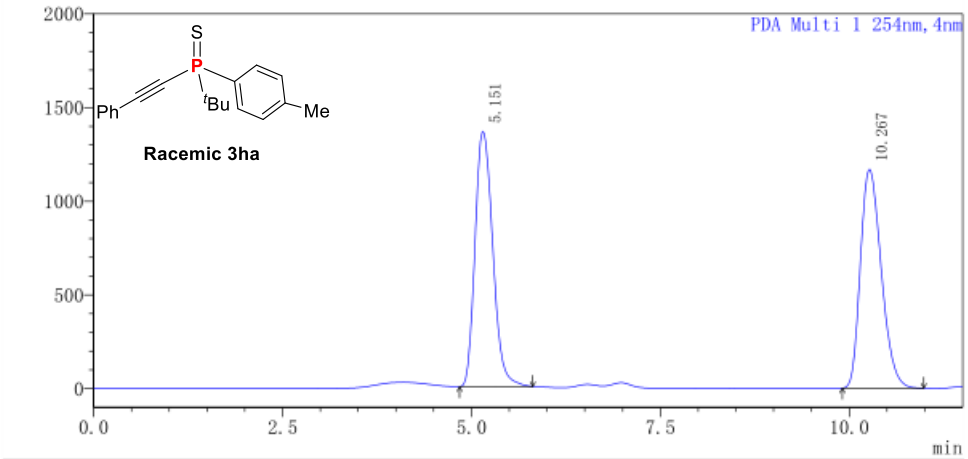
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.483	456239	5.303
2	7.292	8147739	94.697
Total		8603978	100.000

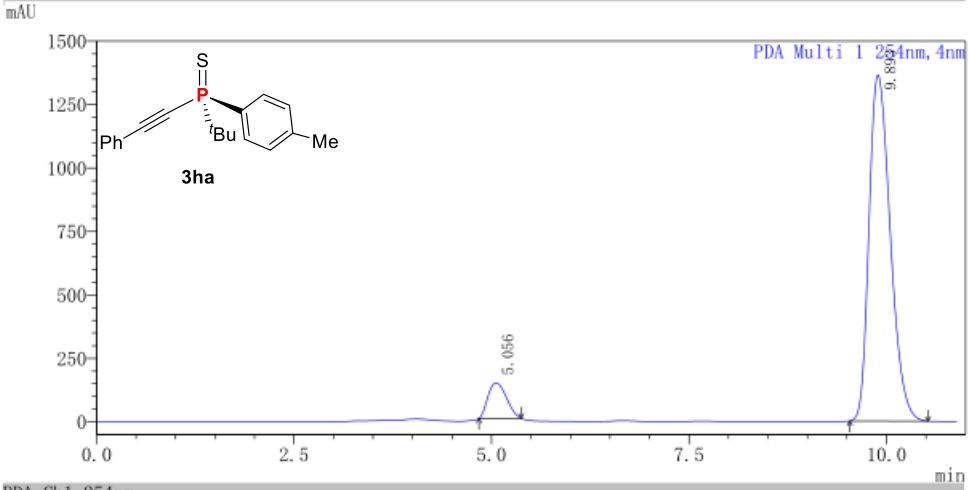
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.151	22293660	49.796
2	10.267	22476466	50.204
Total		44770126	100.000

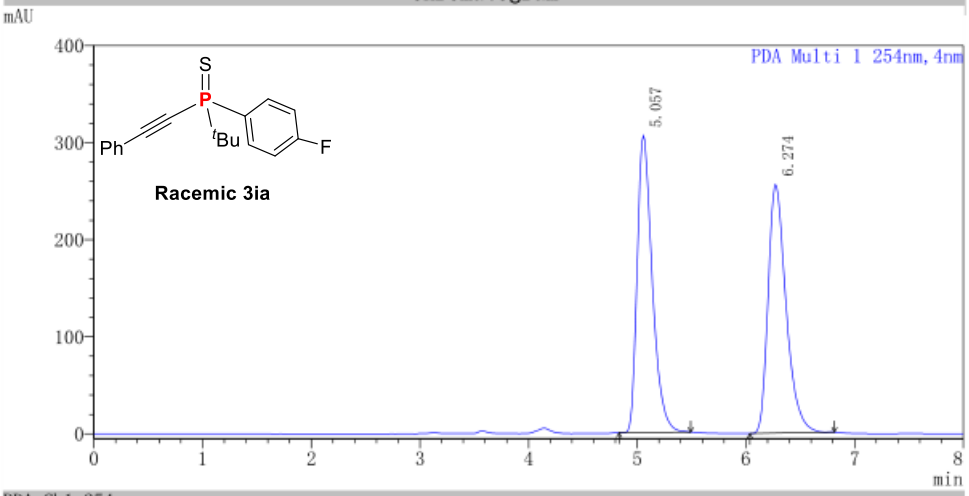
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.056	2260201	8.175
2	9.893	25388648	91.825
Total		27648850	100.000

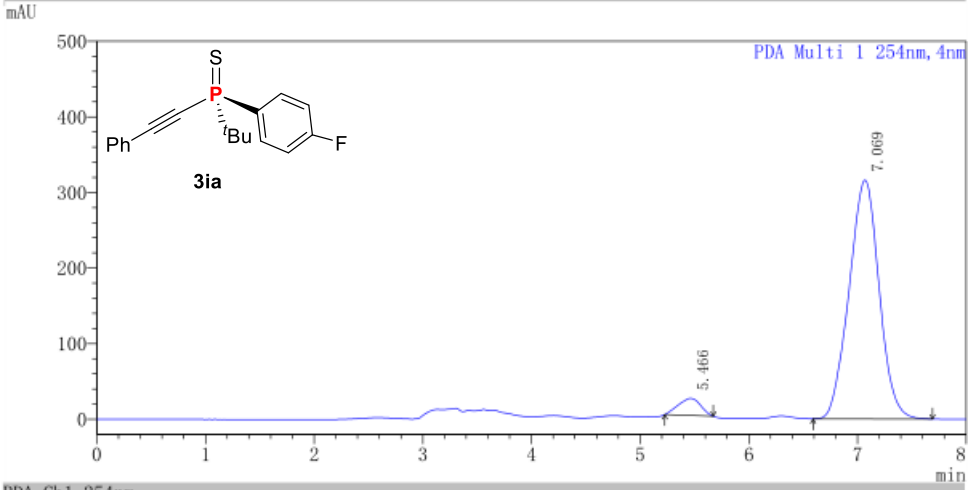
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.057	2946747	50.002
2	6.274	2946523	49.998
Total		5893271	100.000

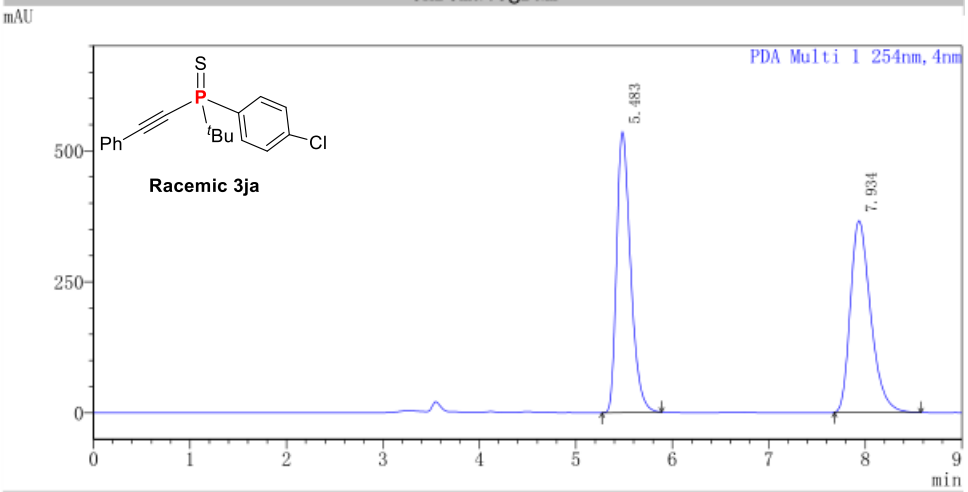
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.466	323529	5.046
2	7.069	6087791	94.954
Total		6411319	100.000

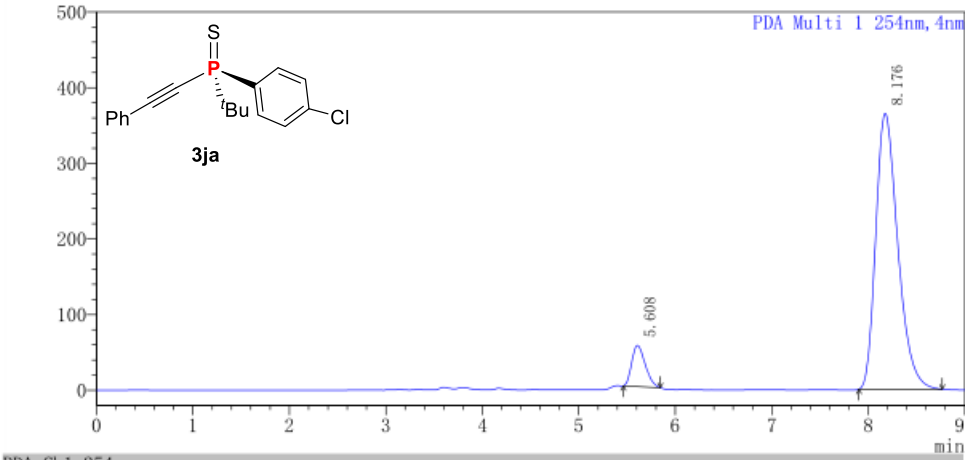
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.483	5385011	50.080
2	7.934	5367825	49.920
Total		10752836	100.000

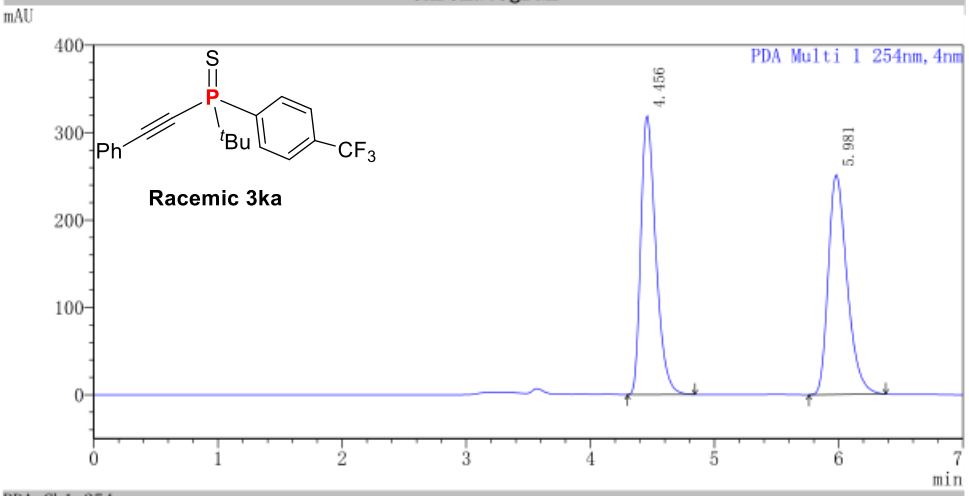
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.608	529205	8.360
2	8.176	5800778	91.640
Total		6329983	100.000

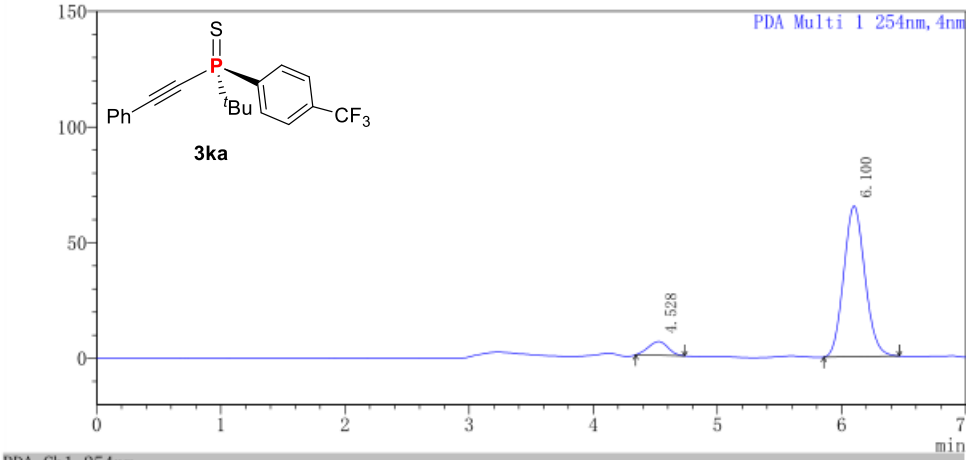
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.456	2686211	50.262
2	5.981	2658176	49.738
Total		5344387	100.000

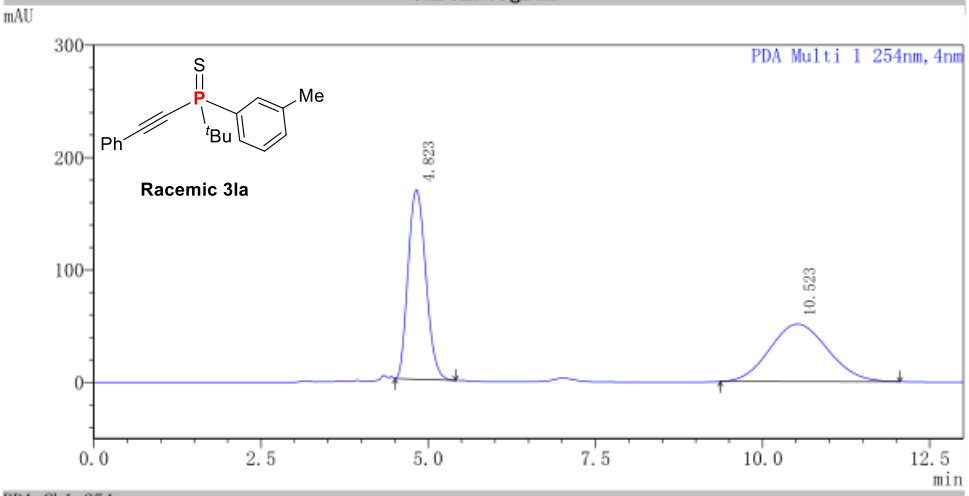
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.528	65497	7.772
2	6.100	777252	92.228
Total		842749	100.000

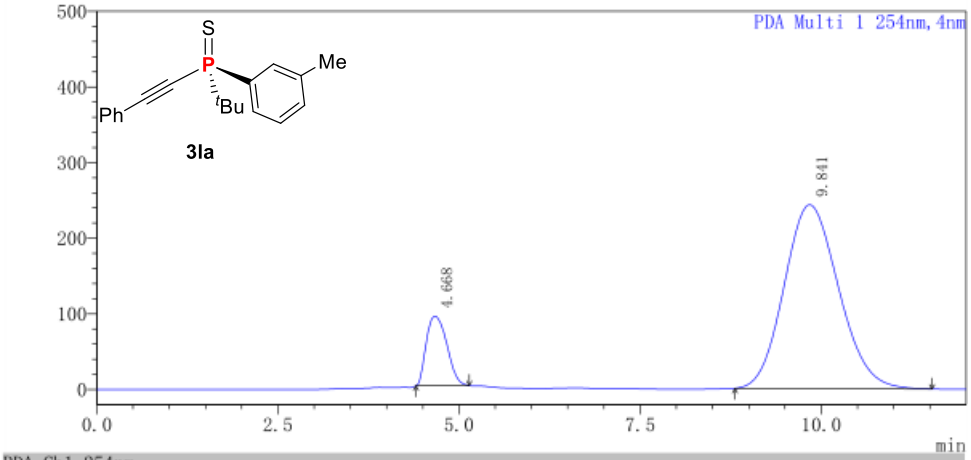
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.823	3121522	50.071
2	10.523	3112639	49.929
Total		6234161	100.000

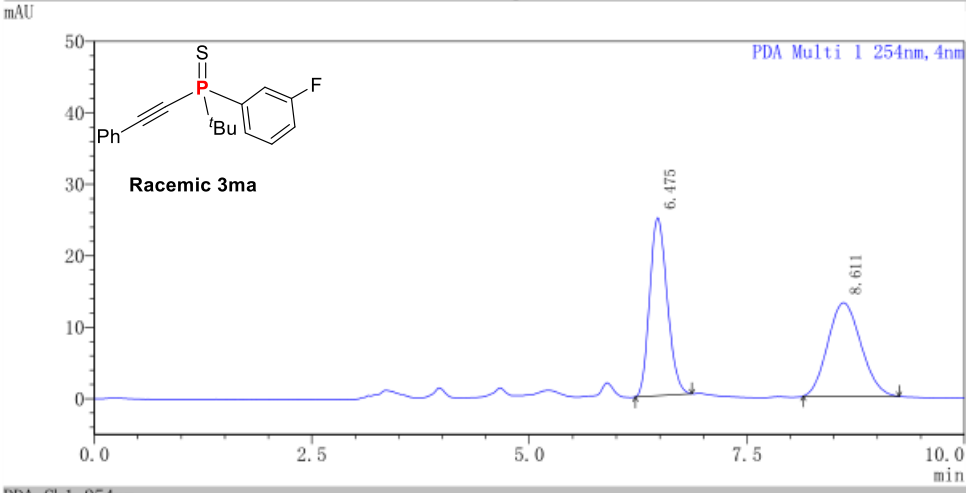
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.668	1819577	12.499
2	9.841	12738059	87.501
Total		14557636	100.000

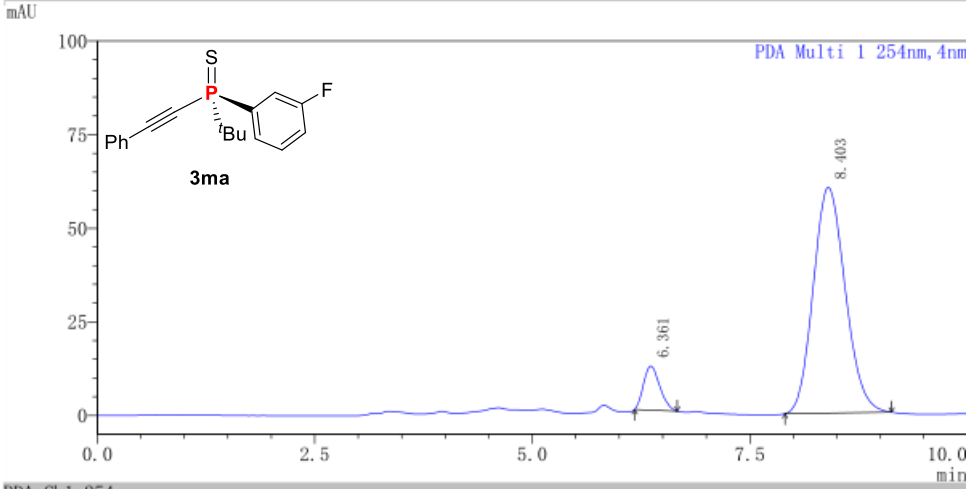
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.475	350293	50.163
2	8.611	348016	49.837
Total		698309	100.000

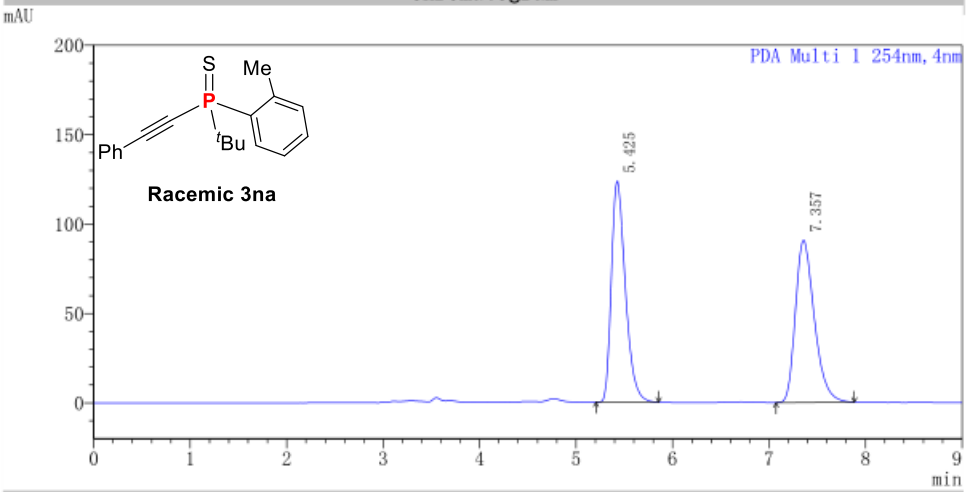
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.361	153561	9.033
2	8.403	1546341	90.967
Total		1699902	100.000

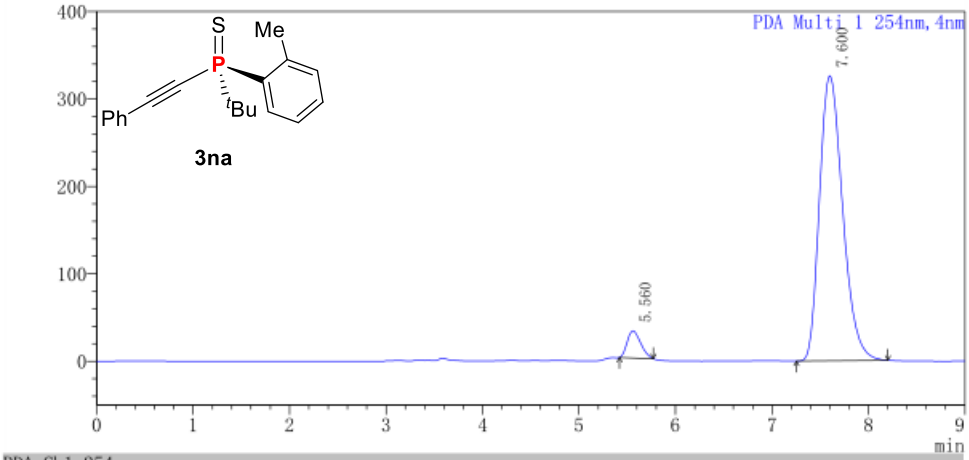
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.425	1248079	50.157
2	7.357	1240269	49.843
Total		2488348	100.000

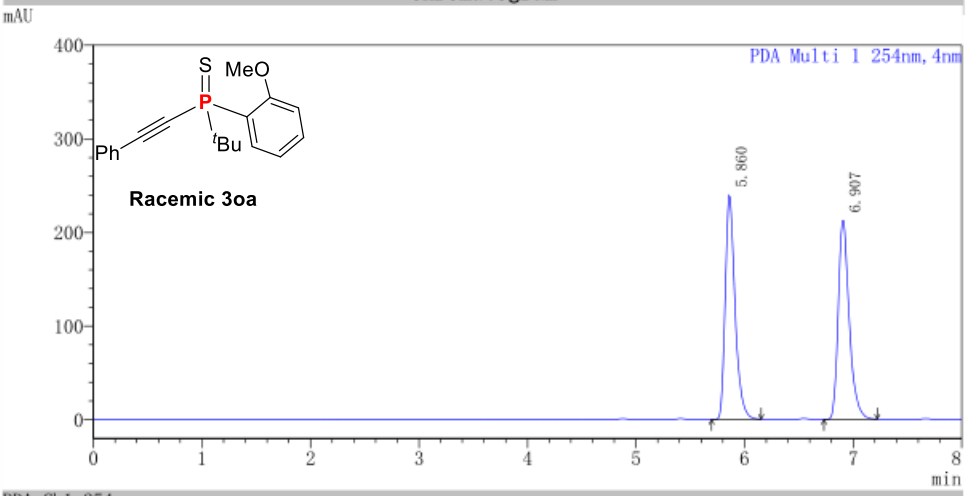
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.560	300611	5.227
2	7.600	5450738	94.773
Total		5751349	100.000

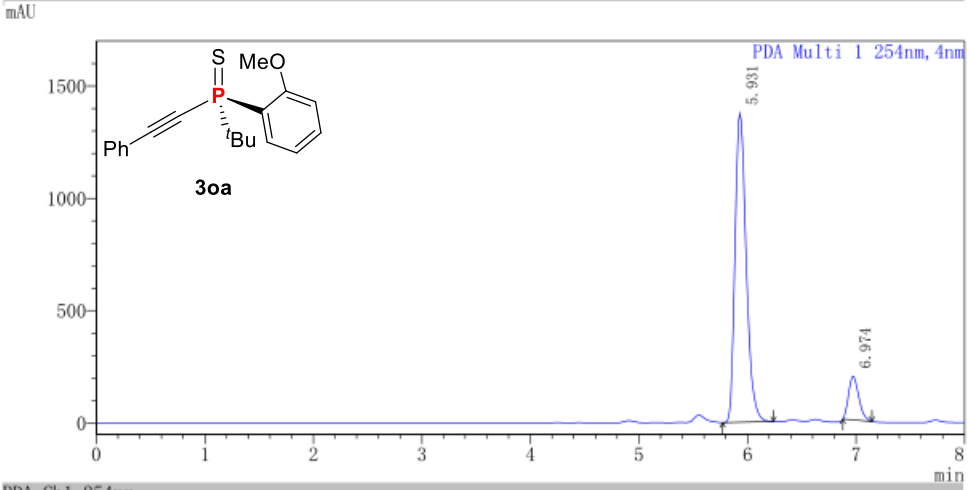
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.860	1503345	49.960
2	6.907	1505781	50.040
Total		3009126	100.000

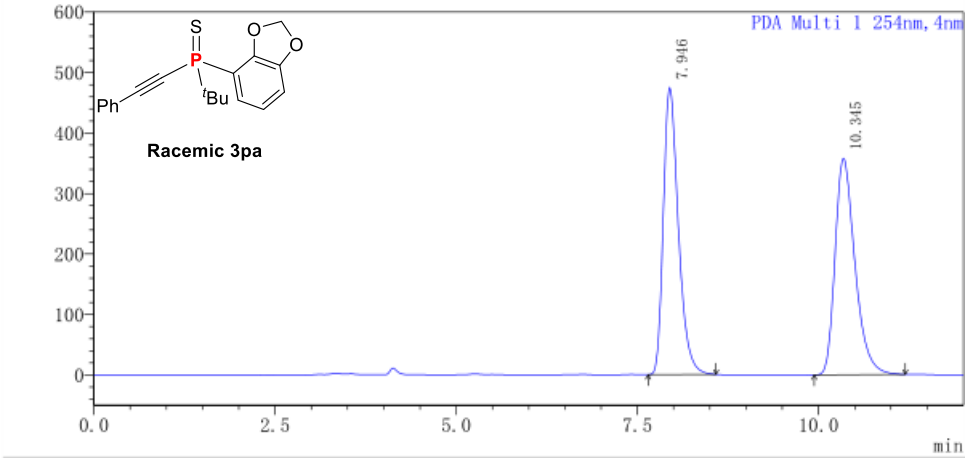
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.931	9856850	88.629
2	6.974	1264563	11.371
Total		11121414	100.000

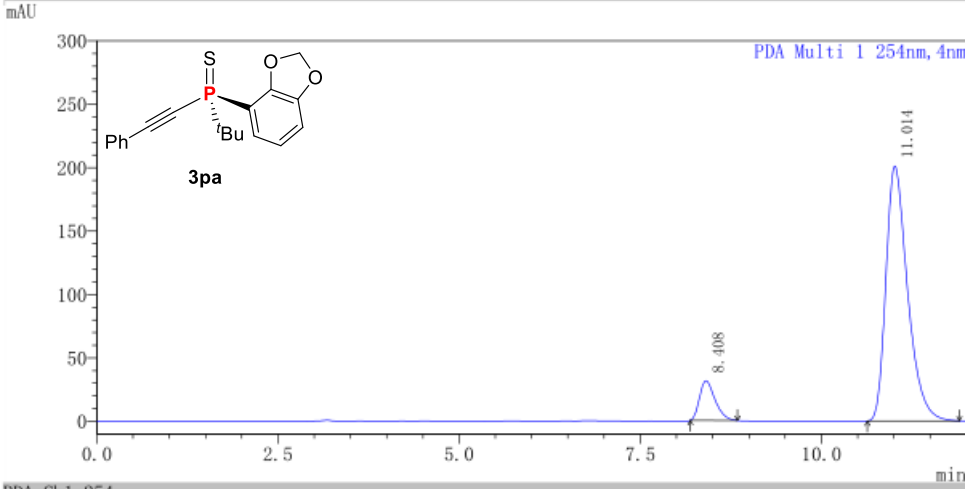
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.946	6847136	50.022
2	10.345	6841125	49.978
Total		13688261	100.000

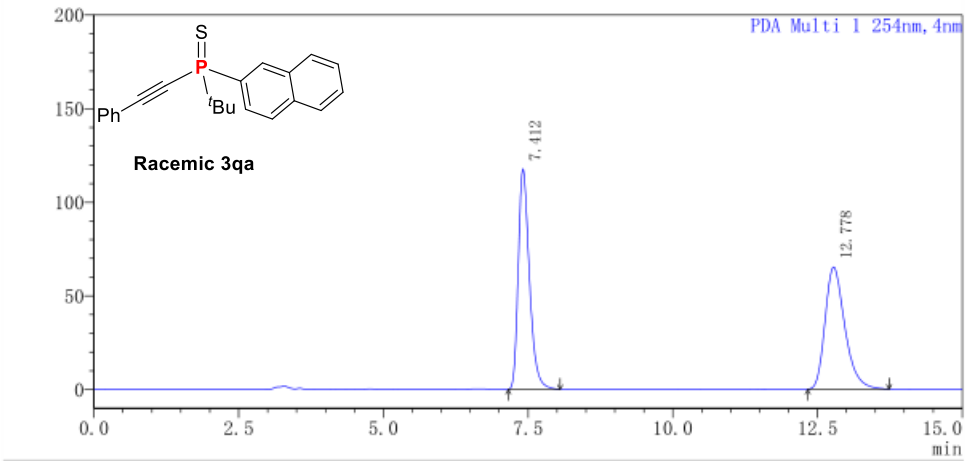
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.439	107193	6.827
2	6.878	1462995	93.173
Total		1570188	100.000

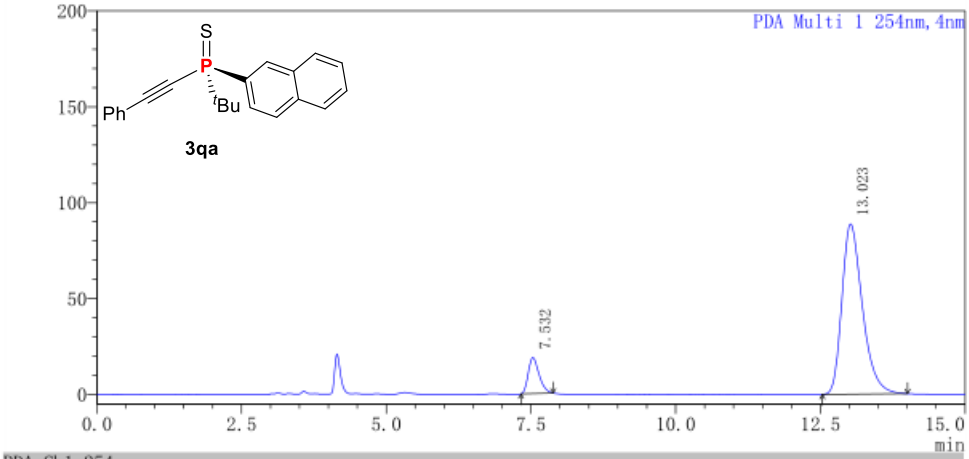
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.412	1574867	50.276
2	12.778	1557579	49.724
Total		3132446	100.000

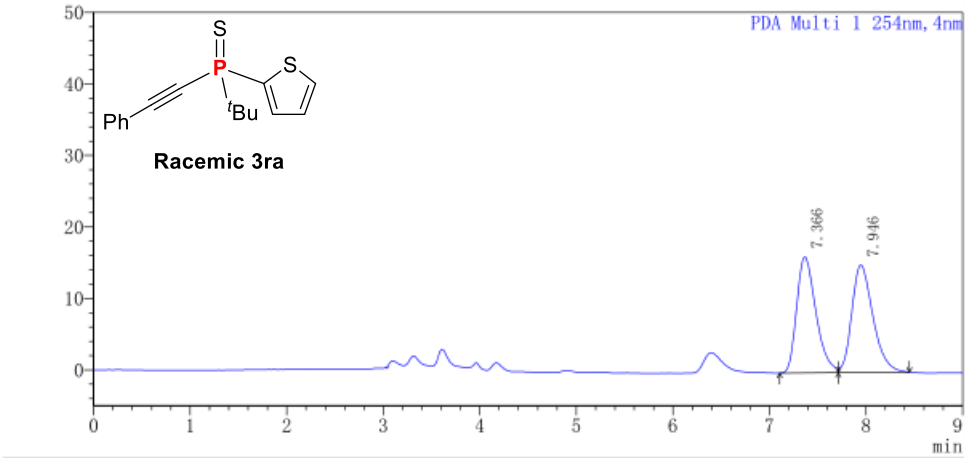
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.532	245616	10.098
2	13.023	2186775	89.902
Total		2432391	100.000

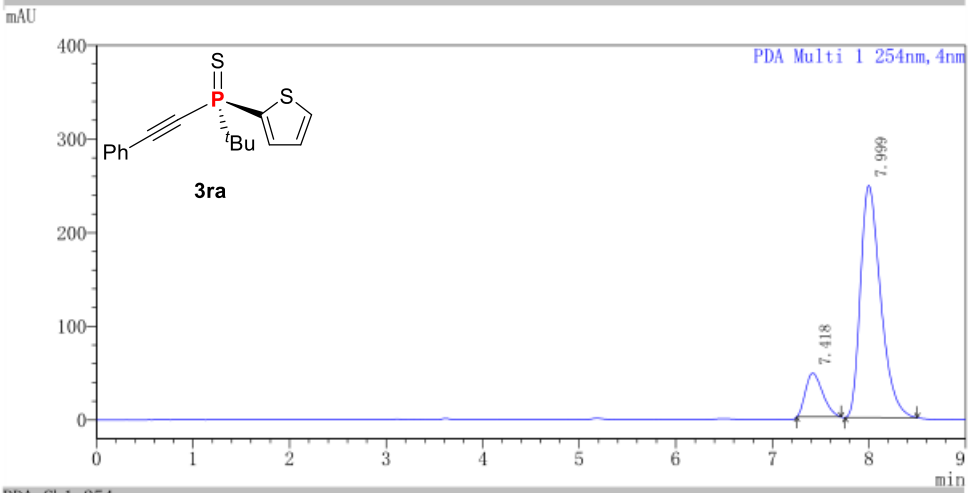
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.366	225586	49.593
2	7.946	229293	50.407
Total		454879	100.000

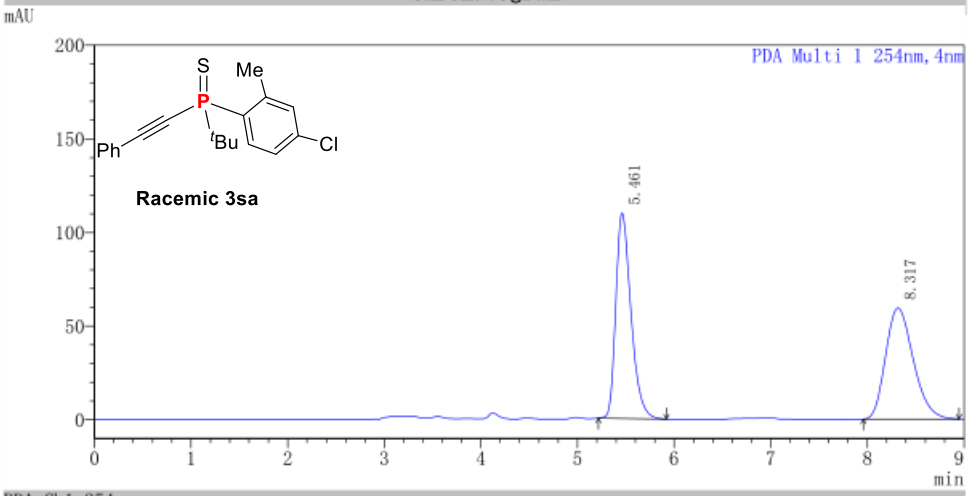
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.418	580494	13.845
2	7.999	3612422	86.155
Total		4192916	100.000

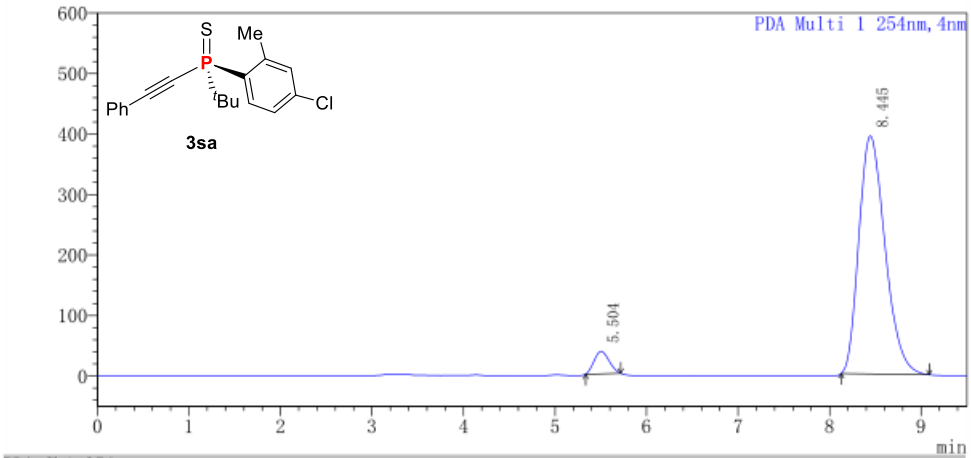
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.461	1196940	50.255
2	8.317	1184809	49.745
Total		2381750	100.000

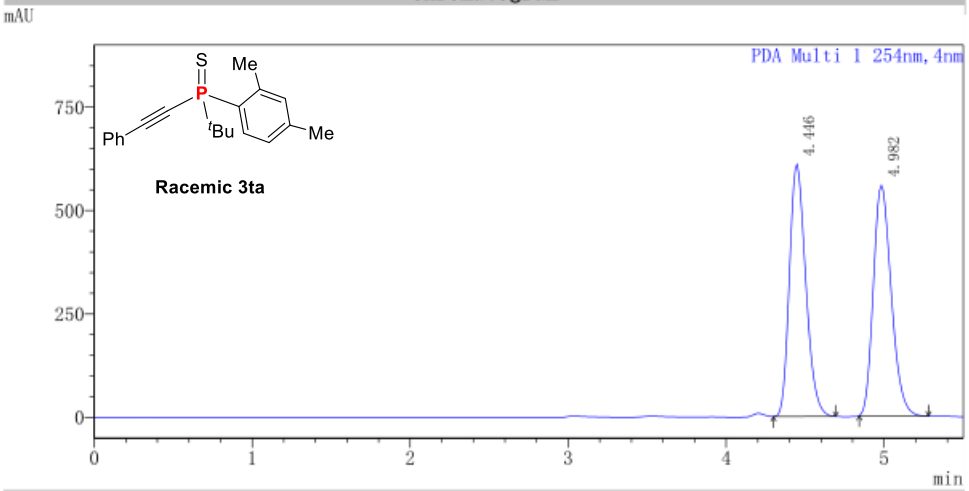
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.504	420344	5.094
2	8.445	7831845	94.906
Total		8252189	100.000

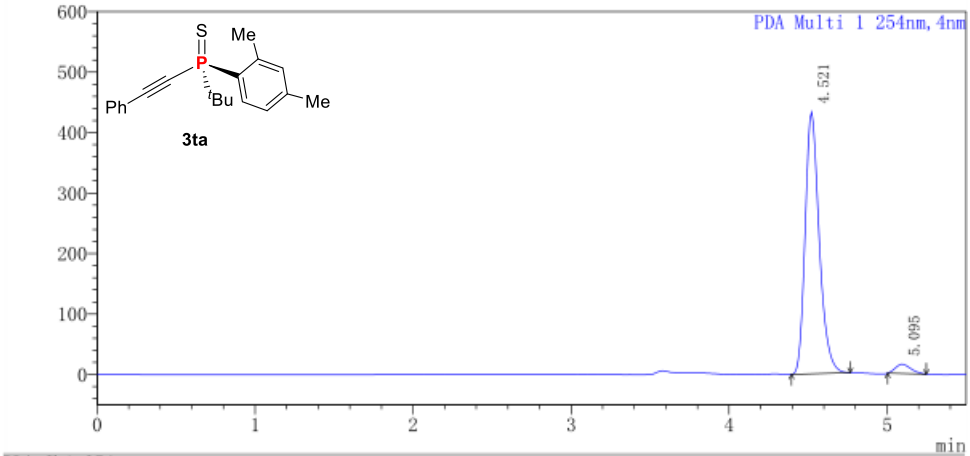
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.446	4397573	50.272
2	4.982	4349959	49.728
Total		8747532	100.000

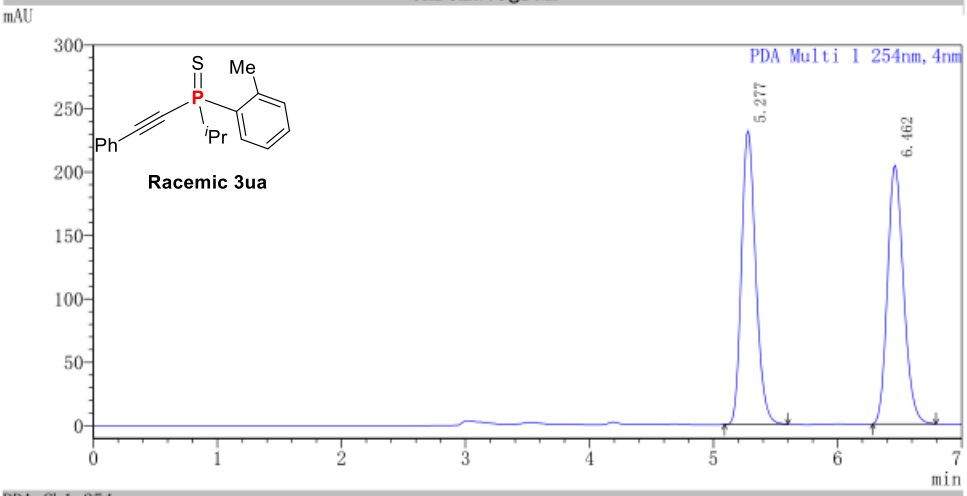
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.521	2691931	96.315
2	5.095	102979	3.685
Total		2794909	100.000

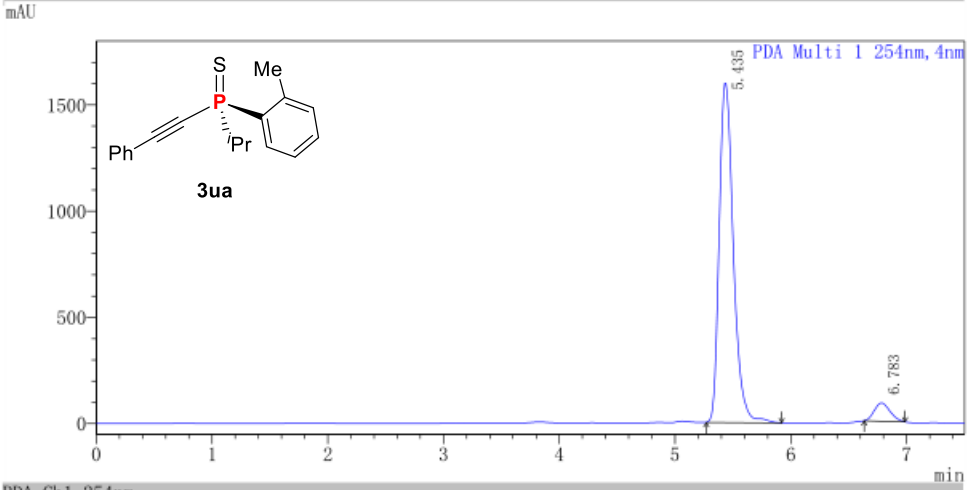
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.277	1839717	50.045
2	6.462	1836377	49.955
Total		3676095	100.000

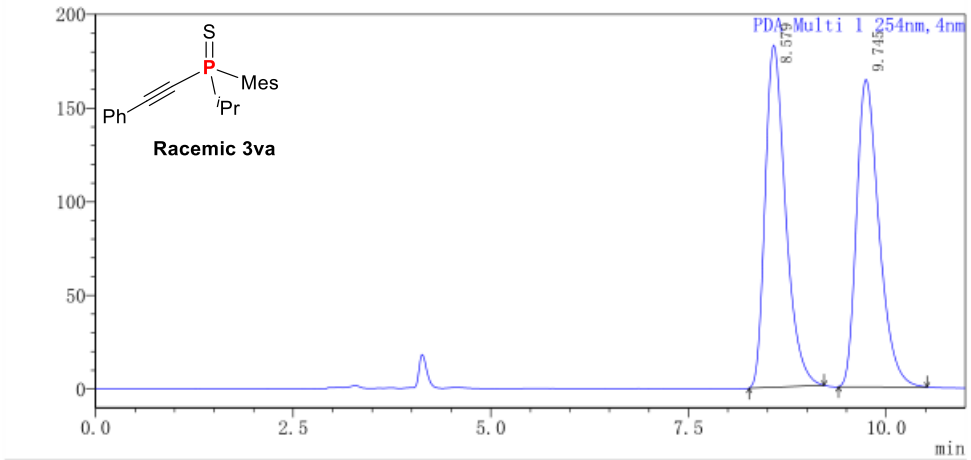
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.435	13559353	94.379
2	6.783	807545	5.621
Total		14366898	100.000

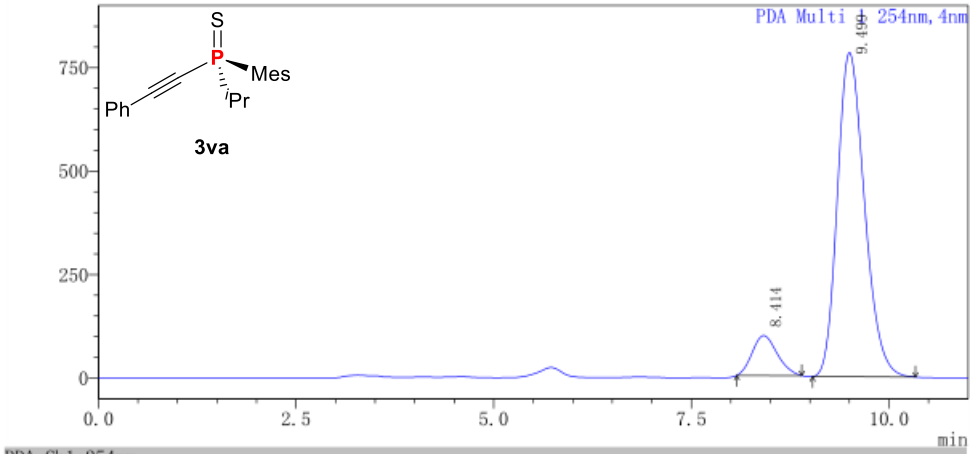
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.579	3305537	50.432
2	9.745	3248901	49.568
Total		6554438	100.000

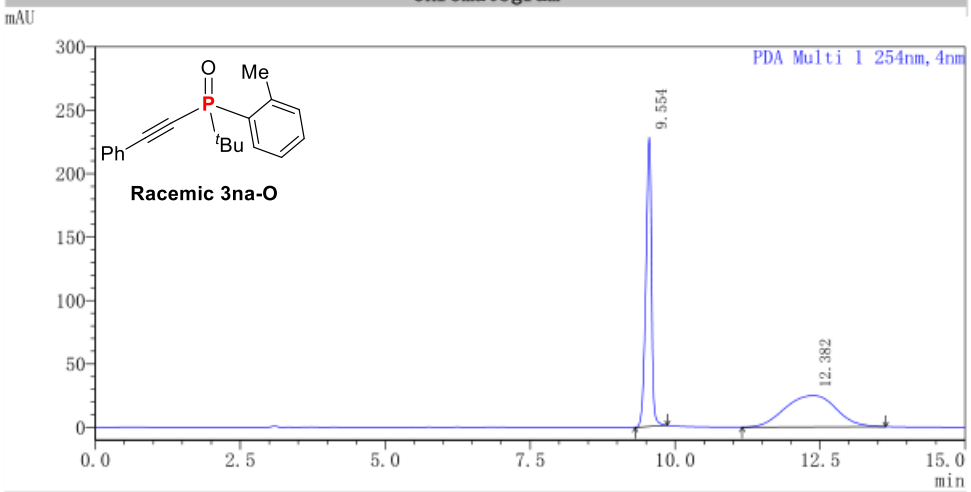
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.414	2120876	10.147
2	9.499	18781580	89.853
Total		20902456	100.000

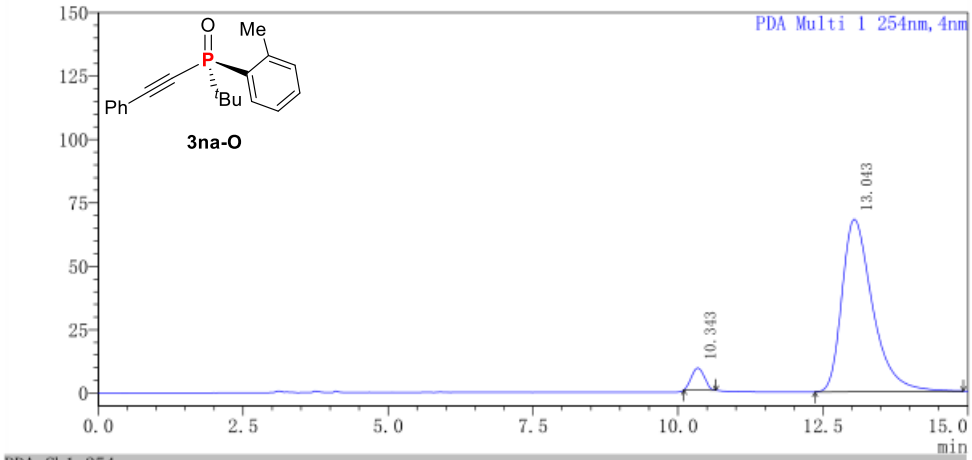
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.554	1545648	50.448
2	12.382	1518169	49.552
Total		3063816	100.000

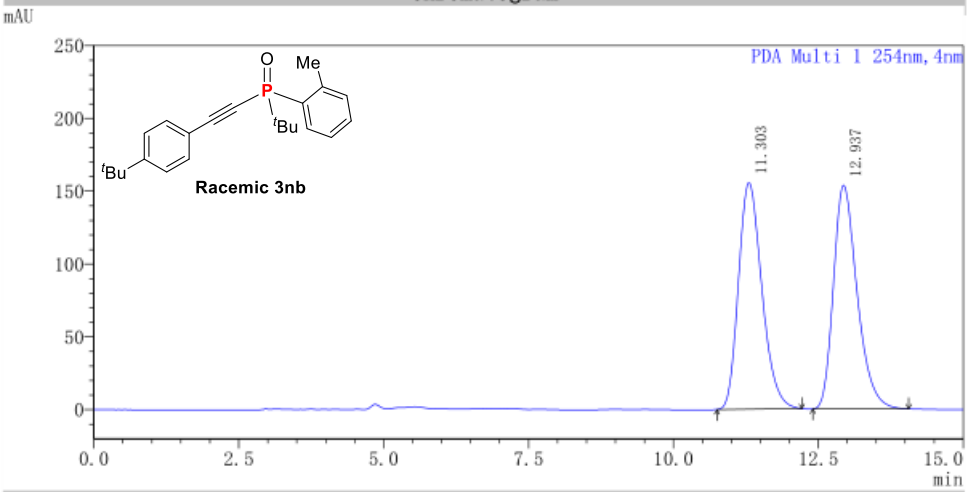
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.343	135265	5.127
2	13.043	2503146	94.873
Total		2638410	100.000

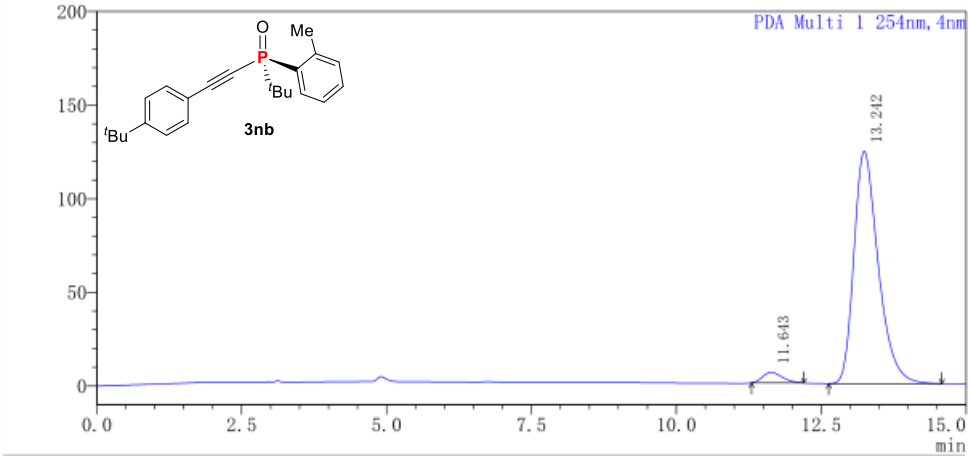
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.303	4377882	49.980
2	12.937	4381358	50.020
Total		8759240	100.000

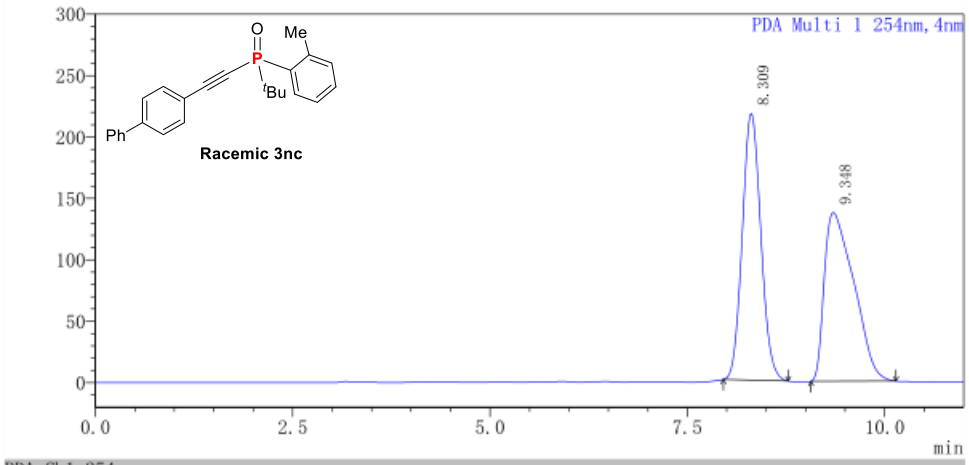
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.643	133740	3.558
2	13.242	3624896	96.442
Total		3758635	100.000

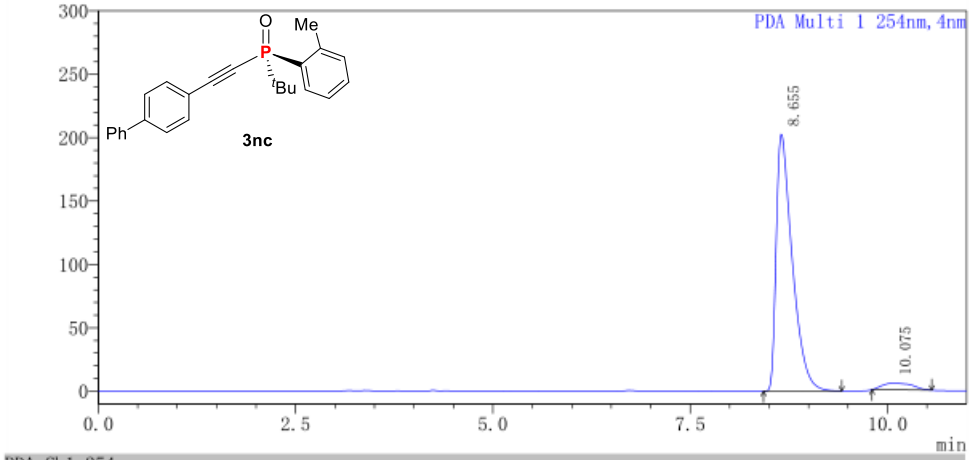
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.309	3541938	49.723
2	9.348	3581464	50.277
Total		7123403	100.000

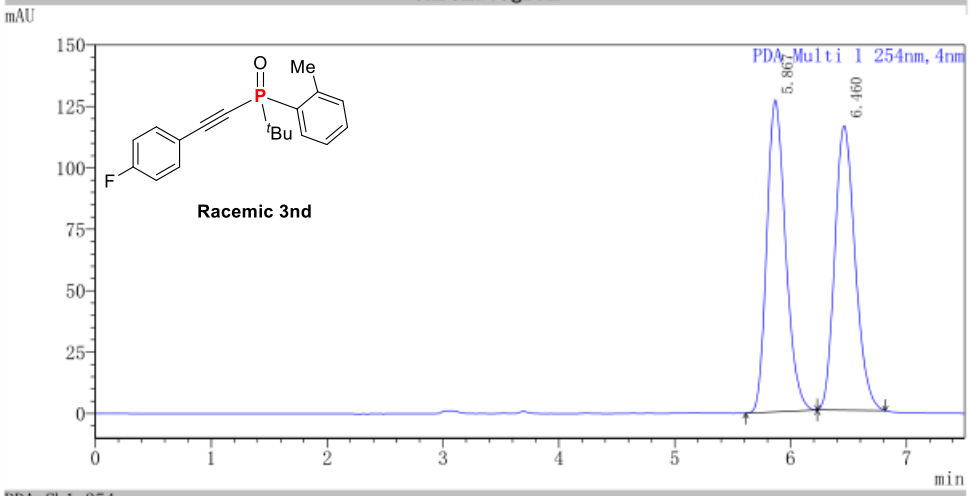
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.655	2877125	95.293
2	10.075	142115	4.707
Total		3019240	100.000

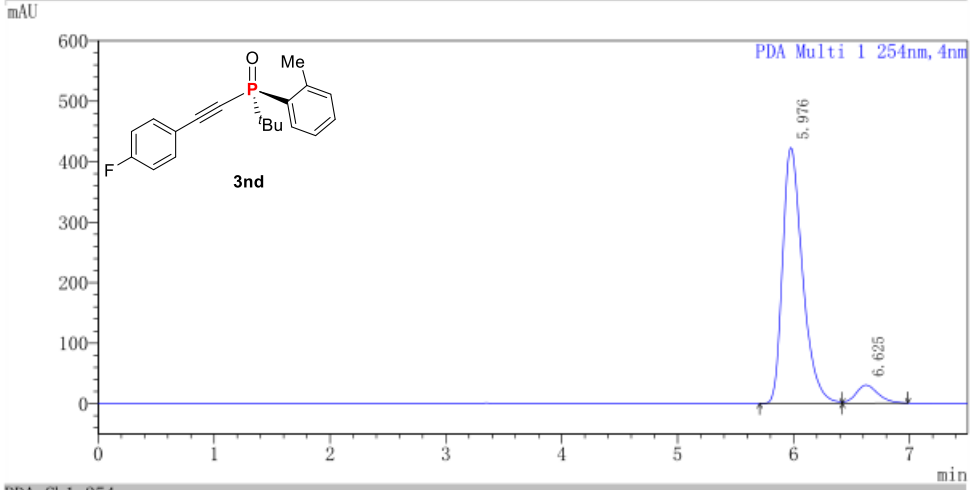
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.867	1433372	50.300
2	6.460	1416255	49.700
Total		2849627	100.000

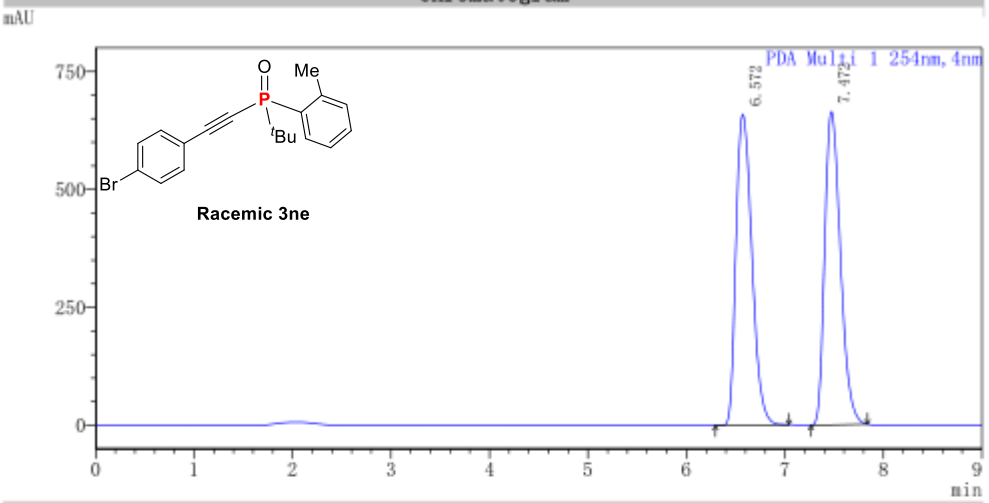
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.976	5072523	92.743
2	6.625	396923	7.257
Total		5469446	100.000

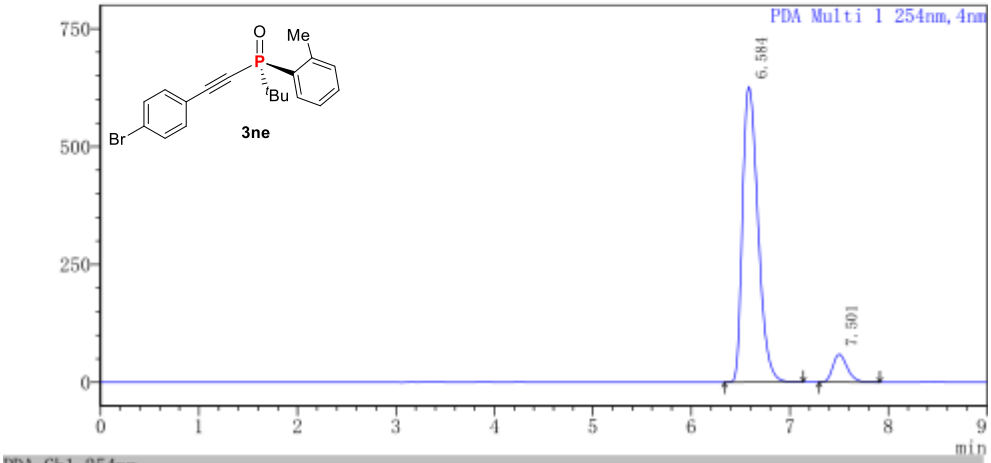
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.572	7413945	50.130
2	7.472	7375376	49.870
Total		14789320	100.000

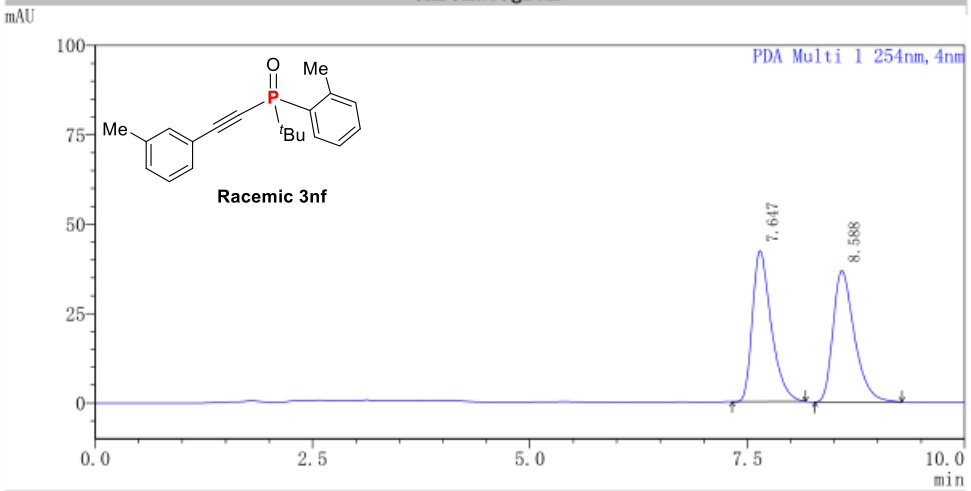
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.584	6853538	91.847
2	7.501	608388	8.153
Total		7461926	100.000

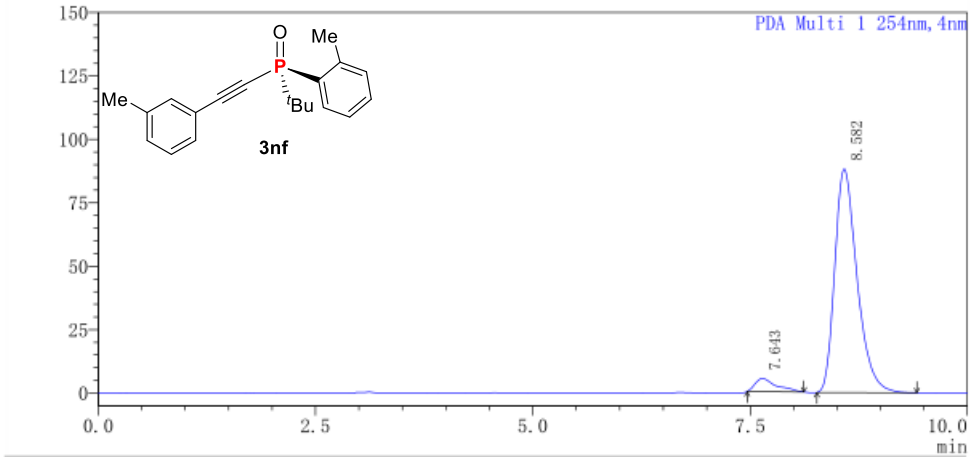
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.647	637585	50.207
2	8.588	632340	49.793
Total		1269924	100.000

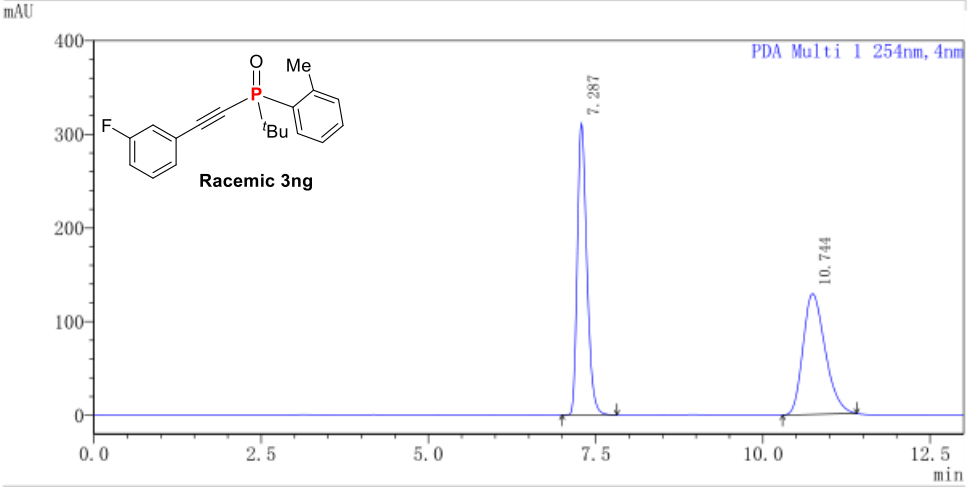
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.643	88391	5.310
2	8.582	1576261	94.690
Total		1664652	100.000

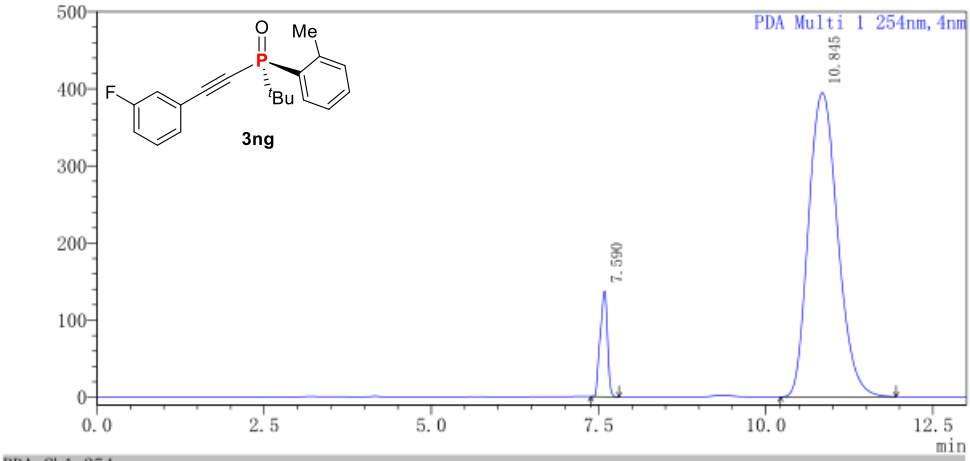
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.287	3053228	50.533
2	10.744	2988861	49.467
Total		6042089	100.000

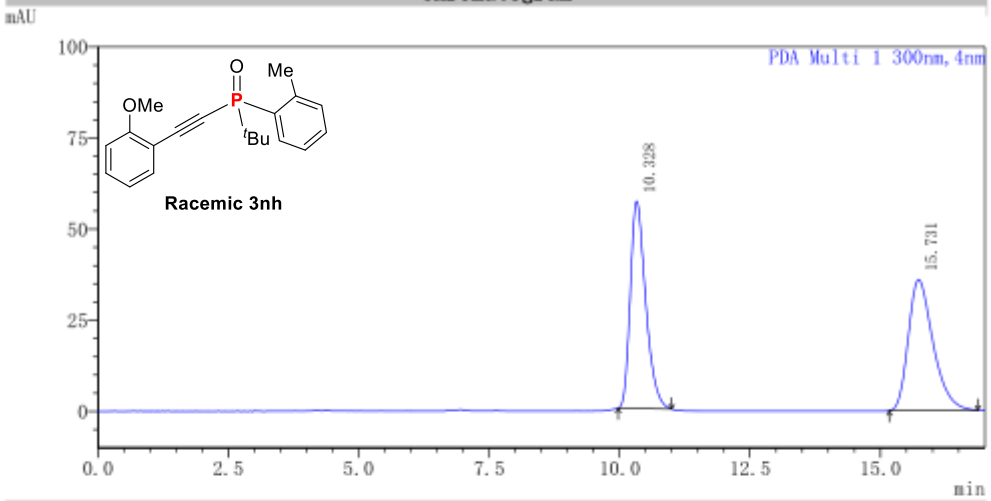
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.590	1025828	7.896
2	10.845	11966533	92.104
Total		12992361	100.000

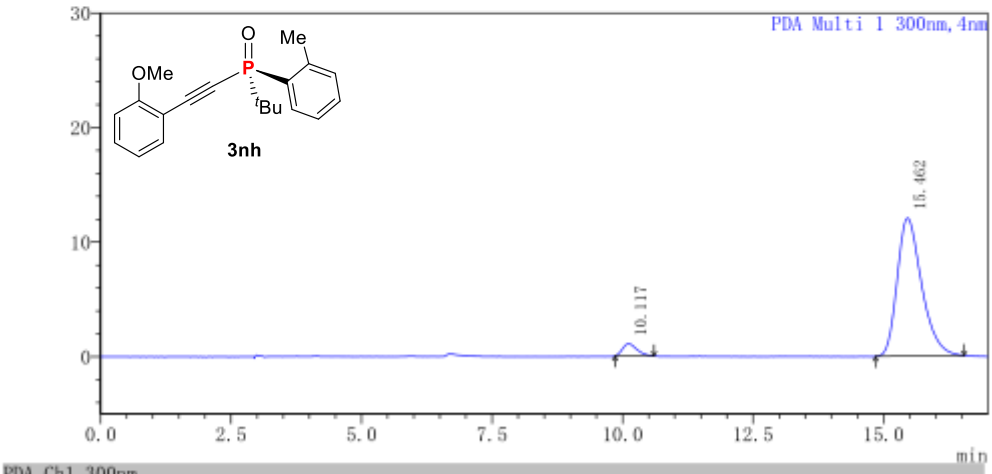
Chromatogram



PDA Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	10.328	1170860	49.656
2	15.731	1187104	50.344
Total		2357964	100.000

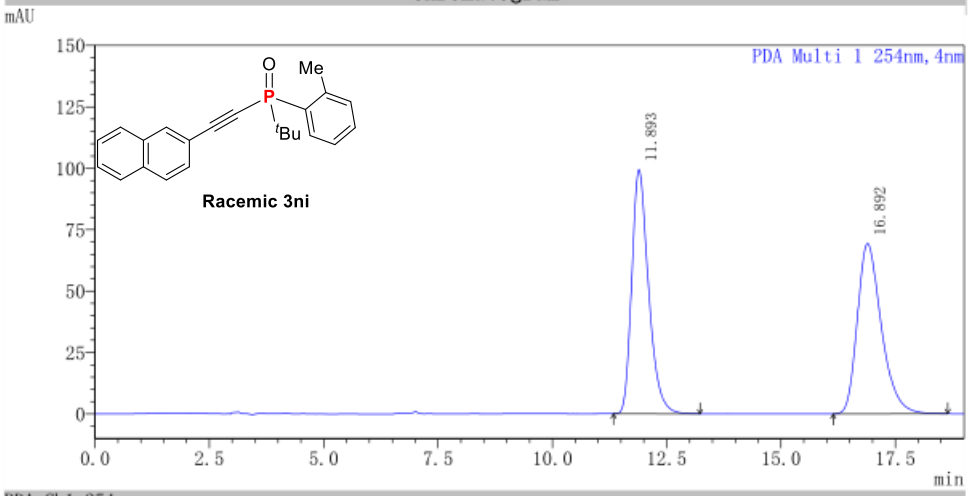
Chromatogram



PDA Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	10.117	20596	4.975
2	15.462	393351	95.025
Total		413947	100.000

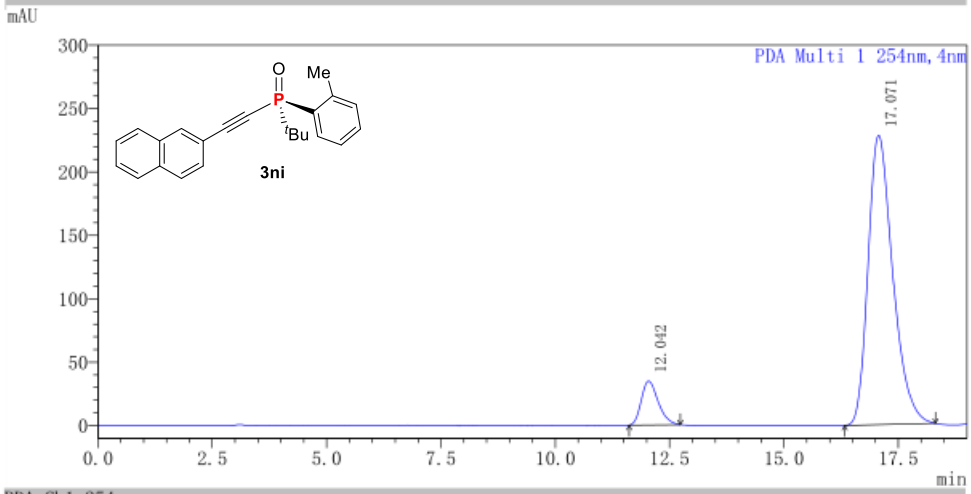
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.893	2545418	49.983
2	16.892	2547106	50.017
Total		5092523	100.000

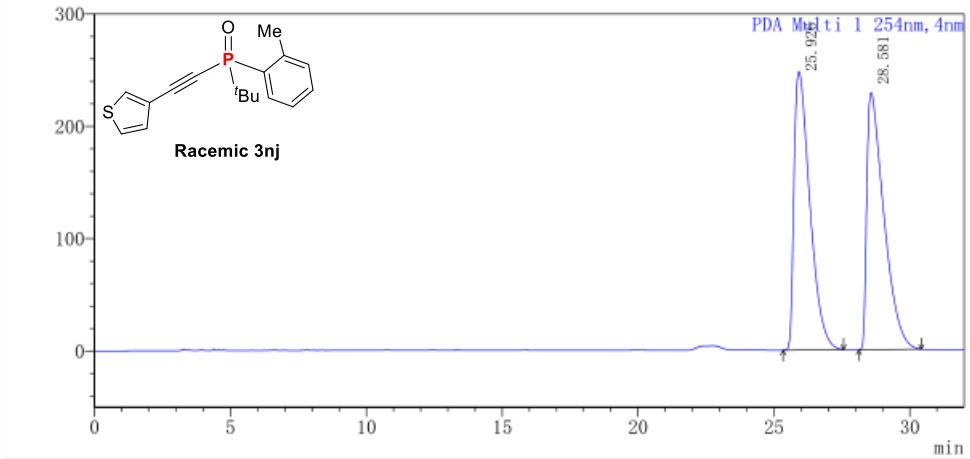
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.042	892433	9.402
2	17.071	8599713	90.598
Total		9492146	100.000

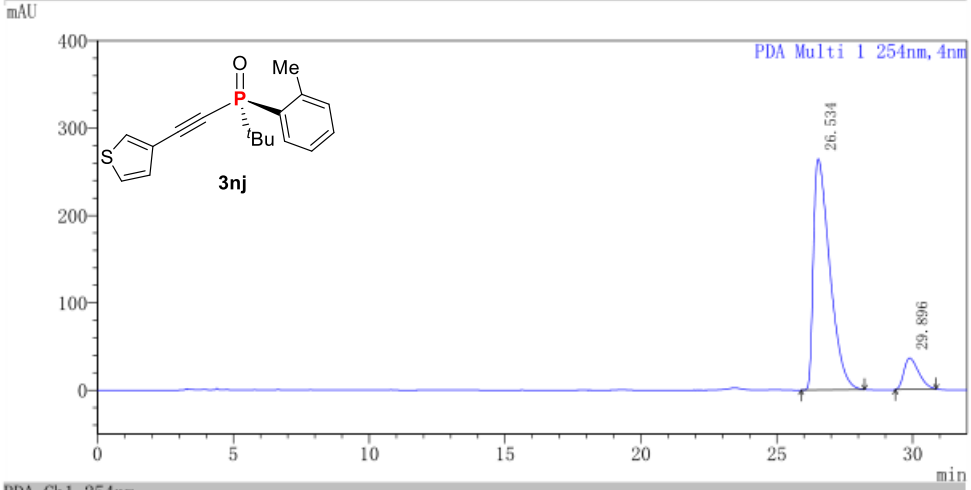
Chromatogram



PDA Ch1 254nm

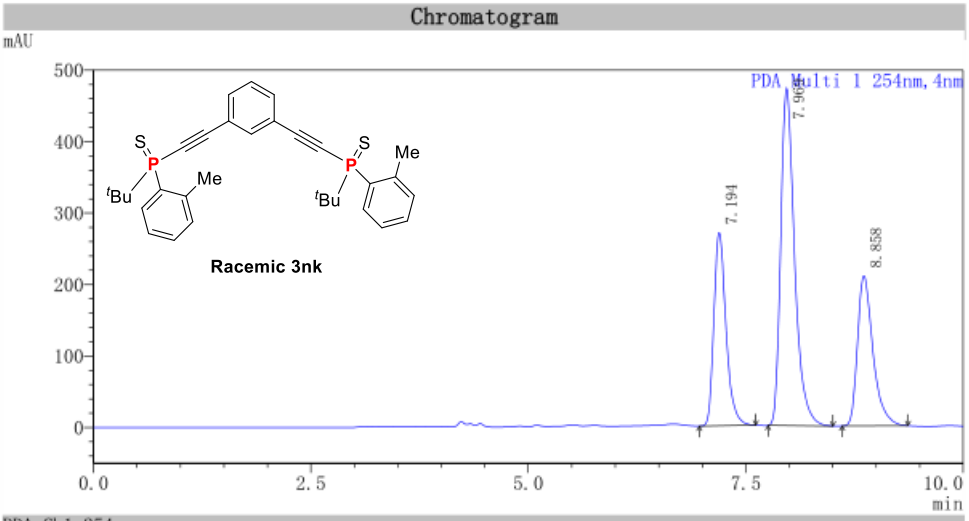
Peak#	Ret. Time	Area	Area%
1	25.926	10070978	50.107
2	28.581	10027876	49.893
Total		20098855	100.000

Chromatogram



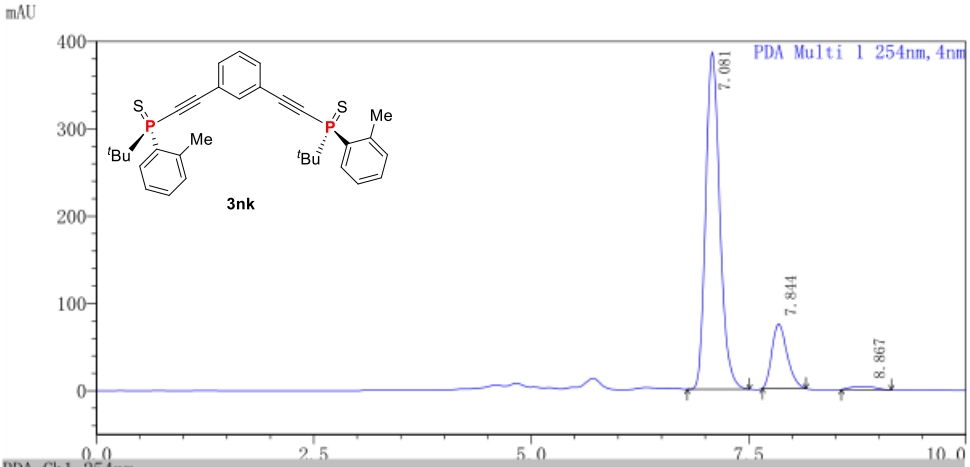
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	26.534	11099600	89.105
2	29.896	1357164	10.895
Total		12456764	100.000



PDA Ch1 254nm

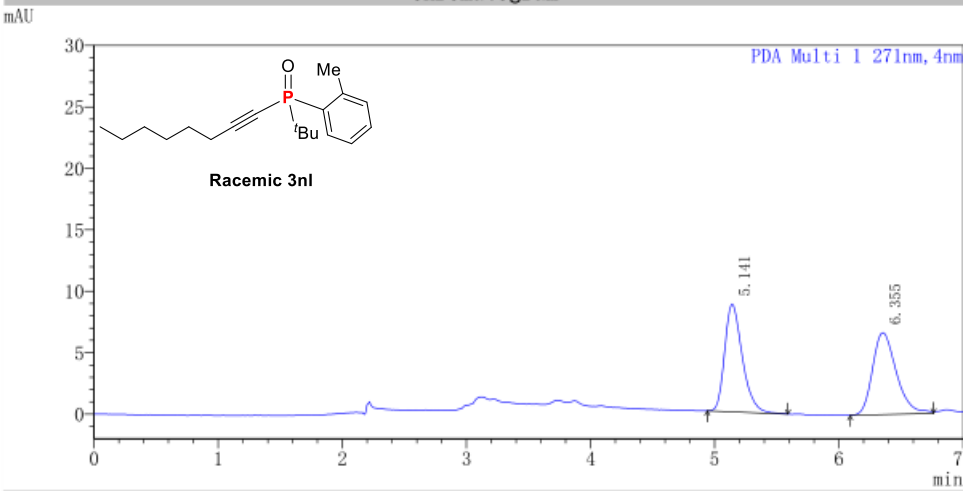
Peak#	Ret. Time	Area	Area%
1	7.194	2631640	25.140
2	7.969	5227836	49.942
3	8.858	2608329	24.918
Total		10467805	100.000



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.081	4362942	81.850
2	7.844	897717	16.841
3	8.867	69735	1.308
Total		5330393	100.000

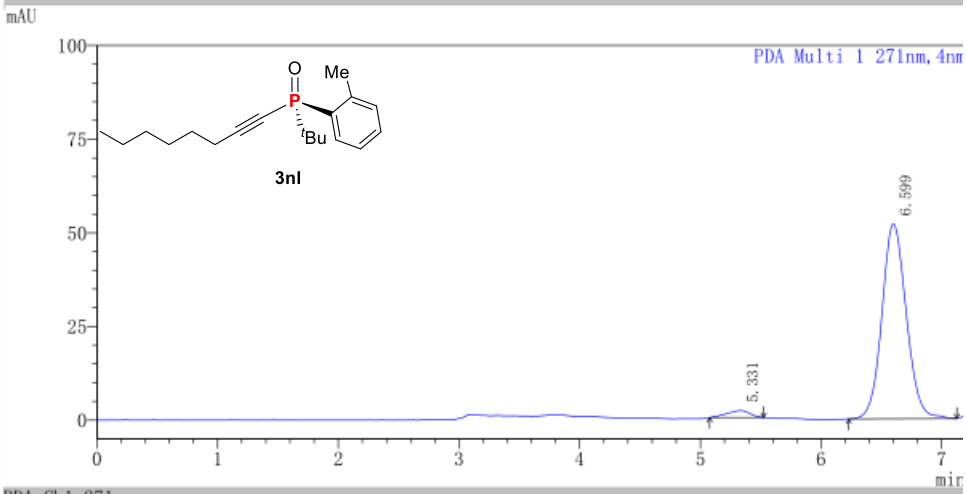
Chromatogram



PDA Ch1 271nm

Peak#	Ret. Time	Area	Area%
1	5.141	87137	49.492
2	6.355	88925	50.508
Total		176062	100.000

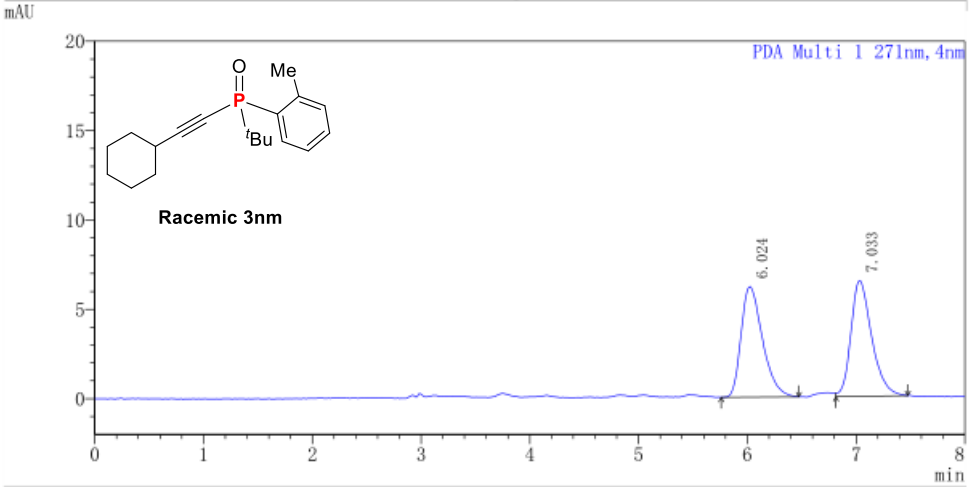
Chromatogram



PDA Ch1 271nm

Peak#	Ret. Time	Area	Area%
1	5.331	24697	3.266
2	6.599	731378	96.734
Total		756074	100.000

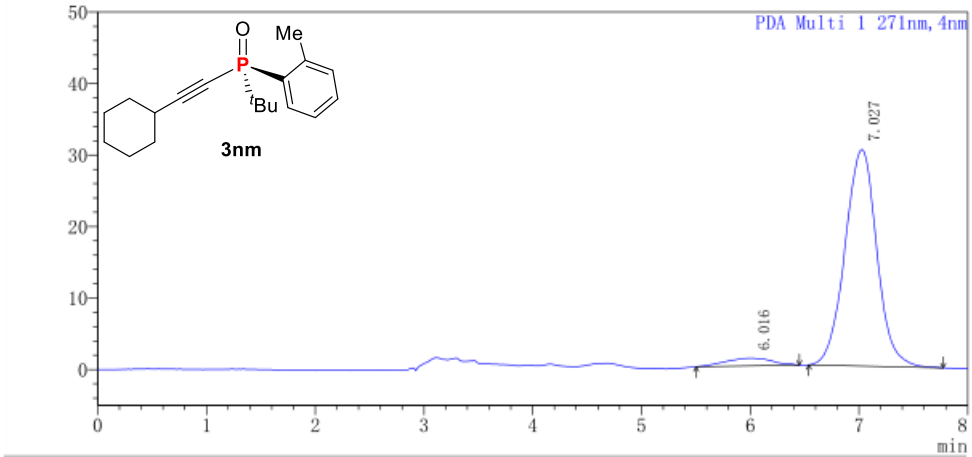
Chromatogram



PDA Ch1 271nm

Peak#	Ret. Time	Area	Area%
1	6.024	84971	49.776
2	7.033	85737	50.224
Total		170708	100.000

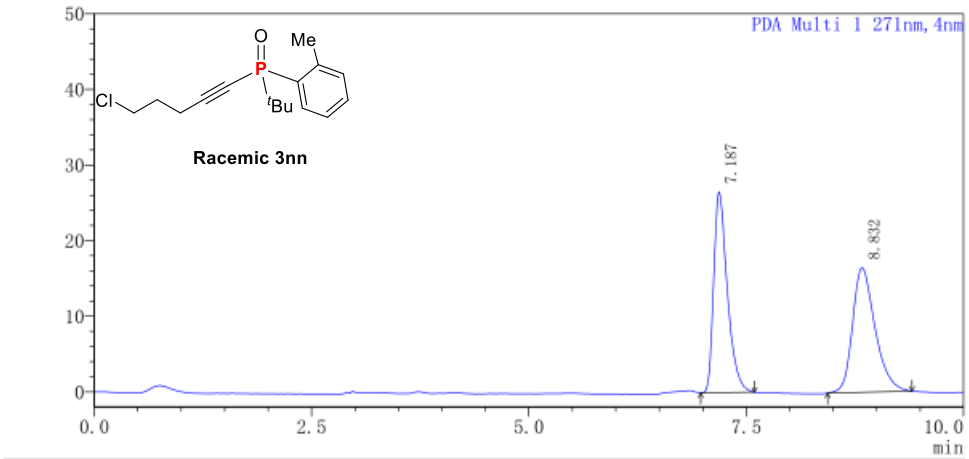
Chromatogram



PDA Ch1 271nm

Peak#	Ret. Time	Area	Area%
1	6.016	31351	4.827
2	7.027	618093	95.173
Total		649444	100.000

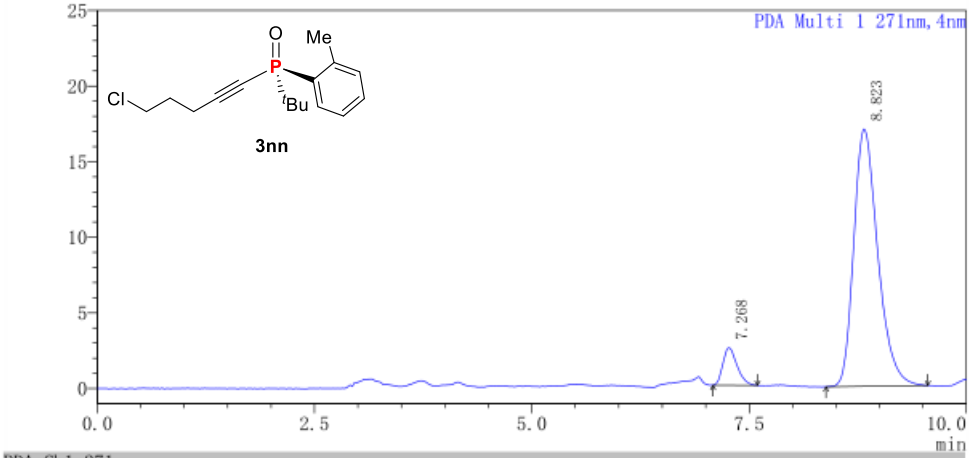
Chromatogram



PDA Ch1 271nm

Peak#	Ret. Time	Area	Area%
1	7.187	289978	49.365
2	8.832	297442	50.635
Total		587420	100.000

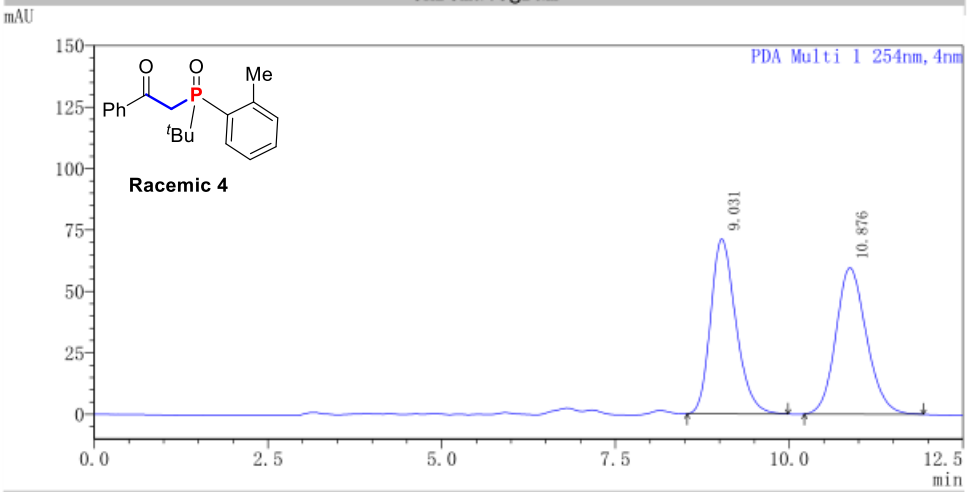
Chromatogram



PDA Ch1 271nm

Peak#	Ret. Time	Area	Area%
1	7.268	28156	7.919
2	8.823	327394	92.081
Total		355550	100.000

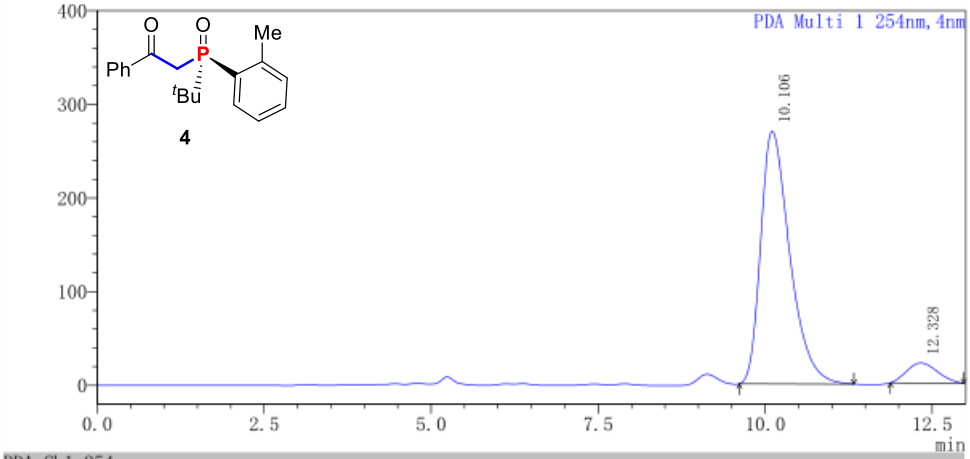
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.031	1808830	49.609
2	10.876	1837373	50.391
Total		3646203	100.000

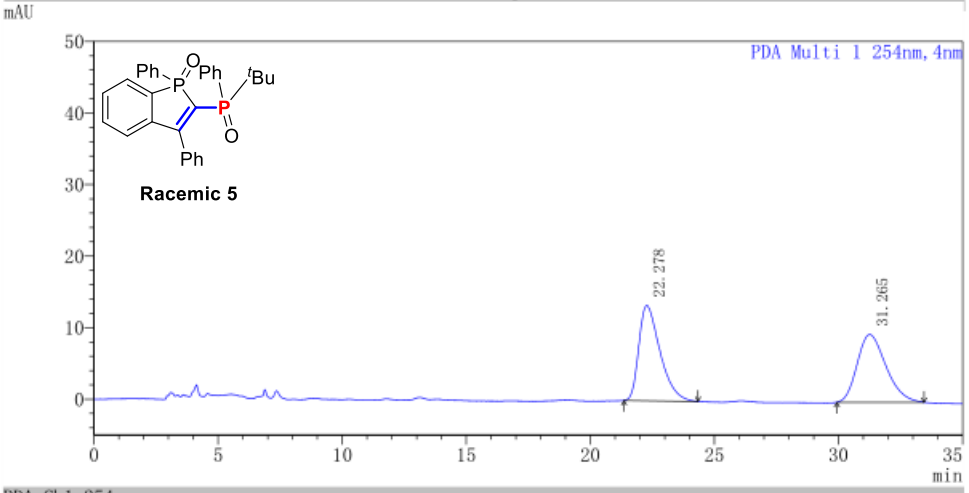
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.106	8191052	92.265
2	12.328	686736	7.735
Total		8877788	100.000

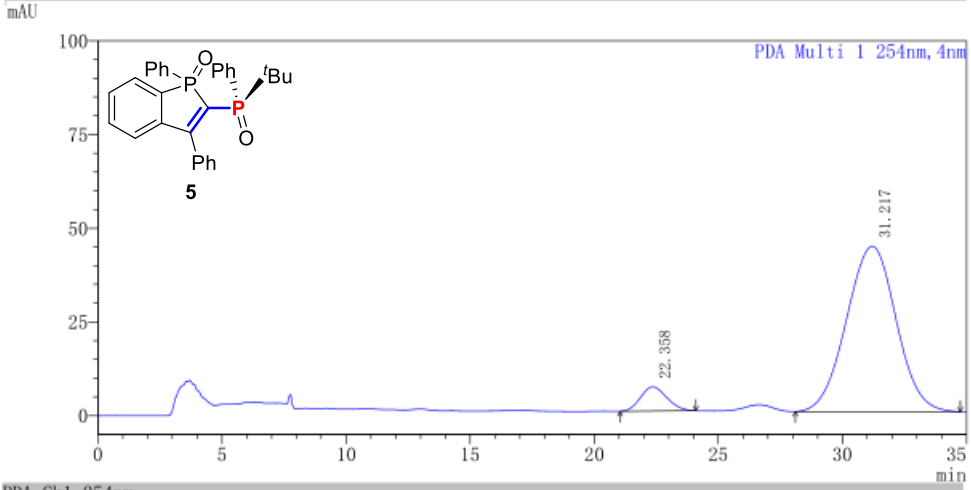
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.278	793293	50.826
2	31.265	767500	49.174
Total		1560793	100.000

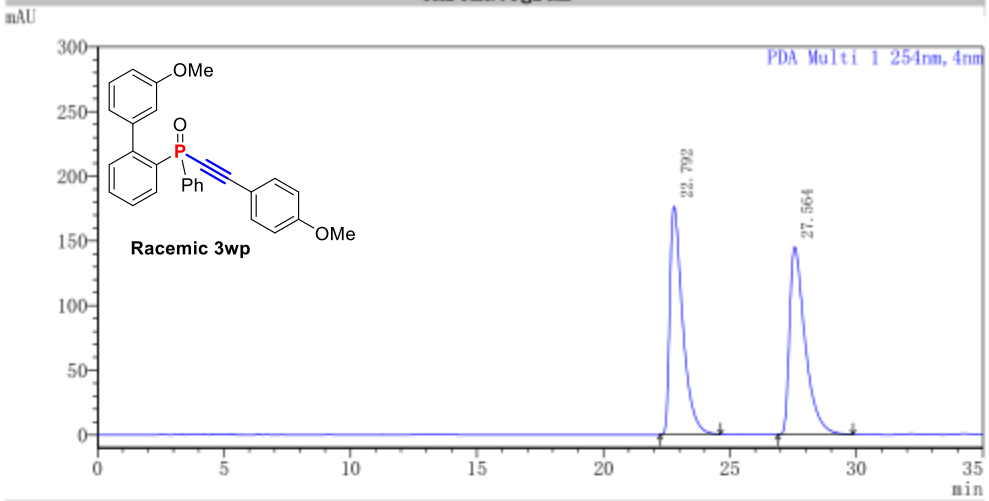
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.358	475237	7.167
2	31.217	6155899	92.833
Total		6631136	100.000

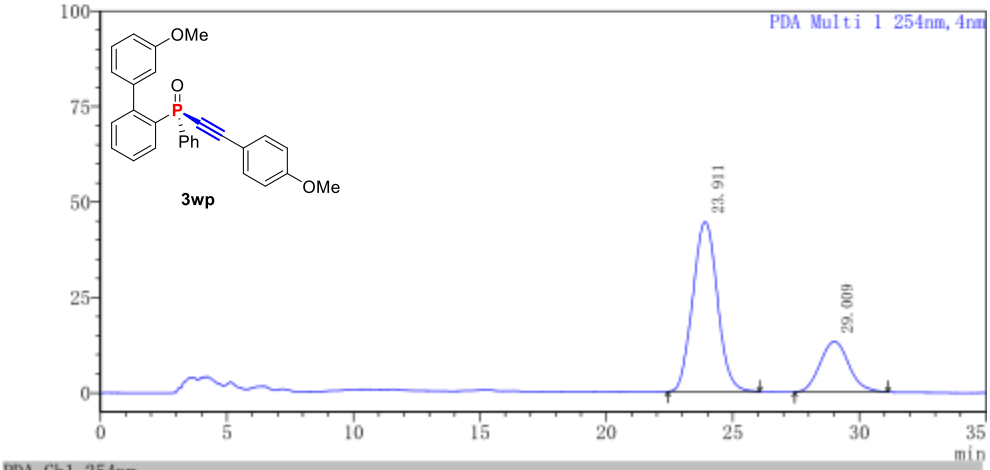
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.792	6242698	49.973
2	27.564	6249568	50.027
Total		12492267	100.000

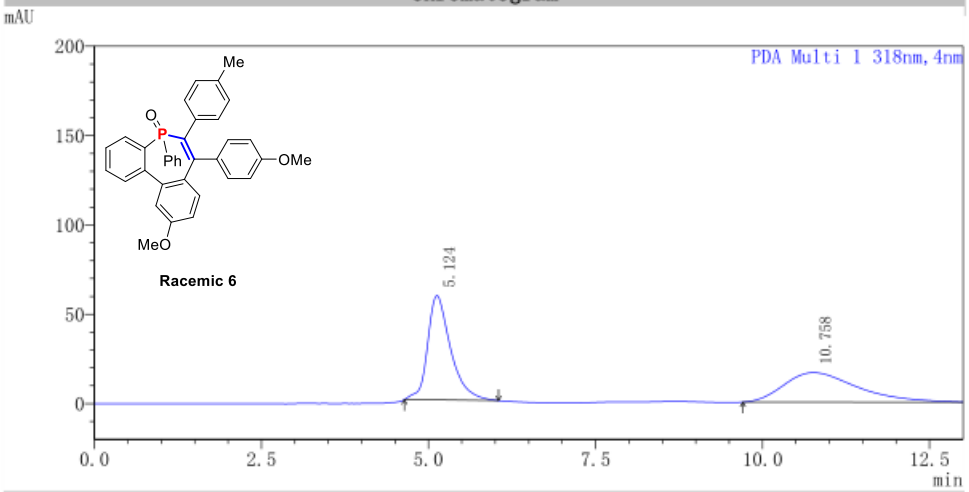
Chromatogram



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.911	3020277	74.122
2	29.009	1054438	25.878
Total		4074714	100.000

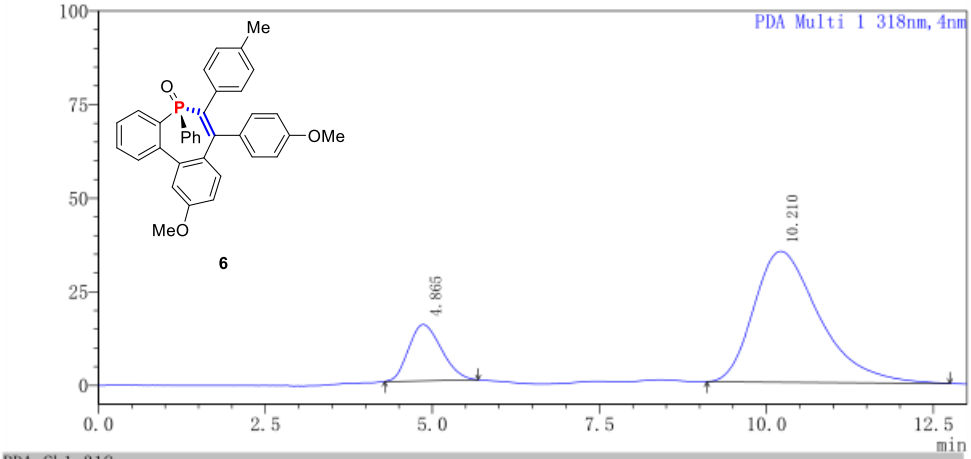
Chromatogram



PDA Ch1 318nm

Peak#	Ret. Time	Area	Area%
1	5.124	1406334	52.605
2	10.758	1267027	47.395
Total		2673361	100.000

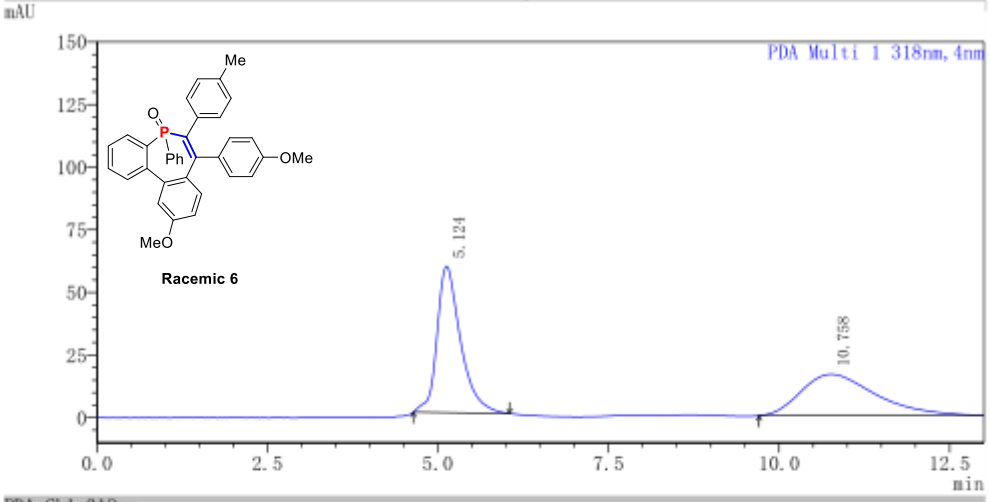
Chromatogram



PDA Ch1 318nm

Peak#	Ret. Time	Area	Area%
1	4.865	513696	17.670
2	10.210	2393469	82.330
Total		2907165	100.000

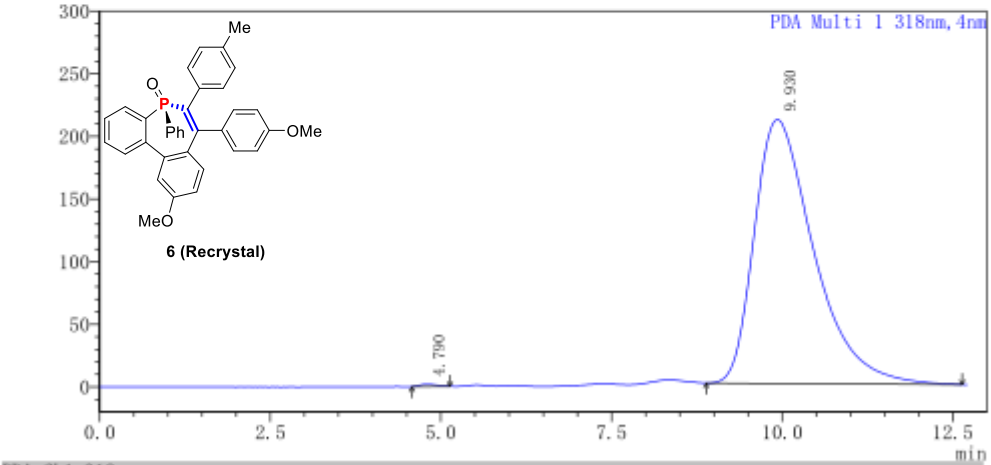
Chromatogram



PDA Ch1 318nm

Peak#	Ret. Time	Area	Area%
1	5.124	1406334	52.605
2	10.758	1267027	47.395
Total		2673361	100.000

Chromatogram



PDA Ch1 318nm

Peak#	Ret. Time	Area	Area%
1	4.790	31351	0.244
2	9.930	12810222	99.756
Total		12841574	100.000

10. References

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