Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Pd-catalysed, Ag-assisted C2–H alkenylation of benzophospholes

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Contents

Instrumentation and Chemicals

^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded at 400 MHz, 100 MHz, 376 MHz, and 162 MHz, respectively, for $CDCl_3$ solutions. HRMS data were obtained by APCI using TOF. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel $60F_{254}$. Silica gel (60 N, spherical neutral, Kanto Chemical Co.) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-20AR (pump, SHIMADZU, 7.5 mL/min $CHCl_3$) and SPD-20A (UV detector, SHIMADZU, 254 nm) with two in-line YMC-GPC T2000 (20 x 600 mm, particle size: 10 μm) (preparative columns, YMC). UV-vis spectra were acquired with JASCO V-750 spectrometer. Photoluminescence spectra and quantum yield measurements were conducted with JASCO FP-8500 spectrometer equipped with an integration sphere system. The crystal measurement was performed with XtaLAB Synergy-S/Mo or Cu (Rigaku).

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 1,4-Dioxane was dried on a Glass Contour Solvent dispensing system (Nikko Hansen & Co., Ltd.) prior to use. $Pd(OAc)_2$, AgTFA, and $NaHCO_3$ were purchased from FUJIFILM Wako Pure Chemical Co. The C2-H benzophospholes **1** were prepared from the corresponding 1,1-diarylethenes and phenylphosphinic acid according to the literature method.[S1]

Experimental Procedures

Pd-Catalysed C2-H Alkenylation of Benzophospholes (Scheme 2)

A 0.10 mmol scale synthesis of **3aa**: 1,3-Diphenylbenzophosphole oxide (**1a**; 30 mg, 0.10 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), AgTFA (44 mg, 0.20 mmol), $NaHCO_3$ (16 mg, 0.20 mmol), and 1,4-dioxane (1.0 mL) were placed in a 15 mL screw cap test tube, and styrene (**2a**; 21 mg, 0.20 mmol) was finally added. The tube was sealed with a cap and heated at 110 ºC for 20 h (oil bath). The resulting mixture was cooled to room temperature and then quenched with water and brine. Extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4, and evaporation under reduced pressure formed a crude material. Triethyl phosphate (10 mg) was added as an internal standard, and the resulting mixture was analyzed by ^1H and $^{31}P\{^1H\}$ NMR in $CDCl_3$ solution. The conversion of **1a** was estimated to be 90% by comparison with integrated intensity of triethyl phosphate. After the above NMR analysis, the volatiles were evaporated, and residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1:2, v/v) then GPC ($CHCl_3$) to give (*E*)-1,3-Diphenyl-2-styrylphosphindole 1-oxide (**3aa**; 35 mg, 0.086 mmol) in 85% yield.

A 1.0 mmol scale synthesis of **3aa**: 1,3-Diphenylbenzophosphole oxide (**1a**; 303 mg, 1.0 mmol), $Pd(OAc)_2$ (23 mg, 0.10 mmol), AgTFA (443 mg, 2.0 mmol), $NaHCO_3$ (169 mg, 2.0 mmol), and 1,4-dioxane (10 mL) were placed in a 100 mL screw cap test tube, and styrene (**2a**; 208 mg, 2.0 mmol) was finally added. The tube was sealed with a cap and heated at 110 ºC for 20 h (oil bath). The resulting mixture was cooled to room temperature and then quenched with water and brine. Extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4, and evaporation under reduced pressure formed a crude material. The residue was purified by column chromatography on silica gel with MeOH then GPC ($CHCl_3$) to give (*E*)-1,3-Diphenyl-2-styrylphosphindole 1-oxide (**3aa**; 262 mg, 0.65 mmol) in 65% yield.

A 0.050 mmol scale synthesis of **3am**: 1,3-Diphenylbenzophosphole oxide (**1a**; 30 mg, 0.10 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), AgTFA (44 mg, 0.20 mmol), $NaHCO_3$ (16 mg, 0.20 mmol), and 1,4-dioxane (1.0 mL) were placed in a 15 mL screw cap test tube, and 1,4-di(vinyl)benzene (**2m**; 6.8 mg, 0.050 mmol) was finally added. The tube was sealed with a cap and heated at 110 ºC for 20 h (oil bath). The resulting mixture was cooled to room temperature and then quenched with water and brine. Extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4, and evaporation

under reduced pressure formed a crude material. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1:2, v/v) then GPC ($CHCl_3$) to give 2,2'-((1*E*,1'*E*)-1,4-phenylenebis(ethene-2,1-diyl))bis(1,3-diphenylphosphindole 1-oxide) (**3am**; 18 mg, 0.024 mmol) in 47% yield.

A 0.10 mmol scale synthesis of **3an**: 1,3-Diphenylbenzophosphole oxide (**1a**; 30 mg, 0.10 mmol), $Pd(OAc)_2$ (4.8 mg, 0.020 mmol), AgTFA (66 mg, 0.30 mmol), $NaHCO_3$ (17 mg, 0.20 mmol), and 1,4-dioxane (1.0 mL) were placed in a 15 mL screw cap test tube, and methyl vinyl ketone (**2n**; 14.5 mg, 0.20 mmol) was finally added. The tube was sealed with a cap and heated at 110 ºC for 20 h (oil bath). The resulting mixture was cooled to room temperature and then quenched with water and brine. Extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4, and evaporation under reduced pressure formed a crude material. The residue was purified by GPC ($CHCl_3$) to give (*E*)-4-(1-oxido-1,3-diphenylphosphindol-2-yl)but-3-en-2-one (**3an**; 26 mg, 0.071 mmol) in 71% yield.

X-Ray Analysis

The single X-ray quality crystals of **3al** were grown from hexane/$CHCl_3$ by slow evaporation at room temperature. The structure was refined by full-matrix least-squares method using SHELXL-2017/1.

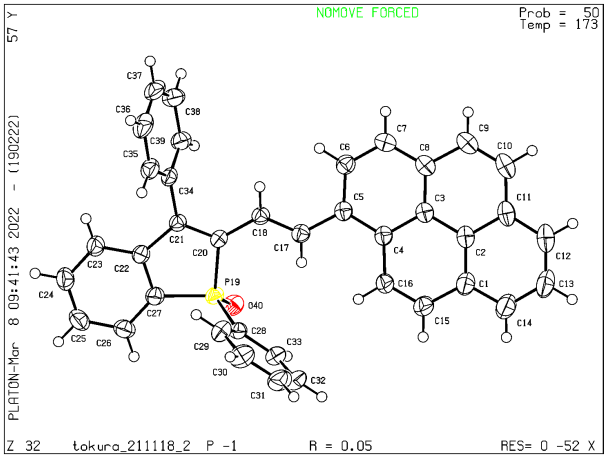


Figure S1. ORTEP drawing of **3al** (CCDC 2180994, 50% thermal probability).

Table S1. Crystal data for **3al**

Crystal system	triclinic
Space group IT number	2
Space group name H-M alt	P -1
Space group name Hall	-P 1
Cell length a	8.4130(3)
Cell length b	10.9151(5)
Cell length c	16.0946(7)
Cell angle alpha	81.509(4)
Cell angle beta	81.007(3)
Cell angle gamma	86.633(4)
Cell volume	1442.82(11)
Cell formula units Z	2
Refine ls R factor all	0.0645
Refine ls R factor gt	0.0461
Refine ls wR factor gt	0.1152
Refine ls wR factor ref	0.1241
Refine ls goodness of fit ref	1.085

The single X-ray quality crystals of **3aq** were grown from hexane/$CHCl_3$ by slow evaporation at room temperature. The structure was refined by full-matrix least-squares method using SHELXL-2017/1.

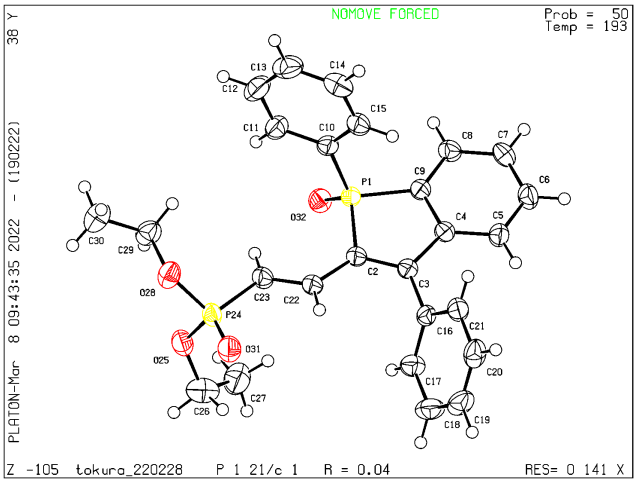


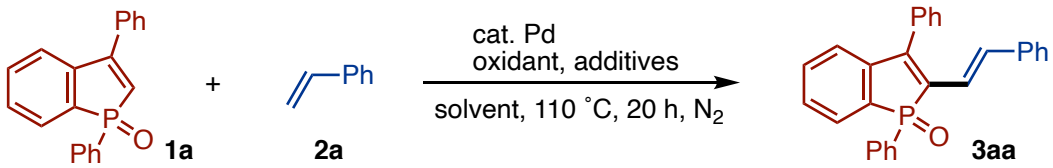
Figure S2. ORTEP drawing of **3aq** (CCDC 2180995, 50% thermal probability).

Table S2. Crystal data for **3aq**

Crystal system	monoclinic
Space group IT number	14
Space group name H-M alt	P 1 21/c 1
Space group name Hall	-P 2ybc
Cell length a	8.7292(2)
Cell length b	12.4540(2)
Cell length c	21.6161(3)
Cell angle alpha	90
Cell angle beta	92.026(2)
Cell angle gamma	90
Cell volume	2348.49(7)
Cell formula units Z	4
Refine ls R factor all	0.0448
Refine ls R factor gt	0.0403
Refine ls wR factor gt	0.1116
Refine ls wR factor ref	0.1157
Refine ls goodness of fit ref	1.097

Detailed Optimization Studies

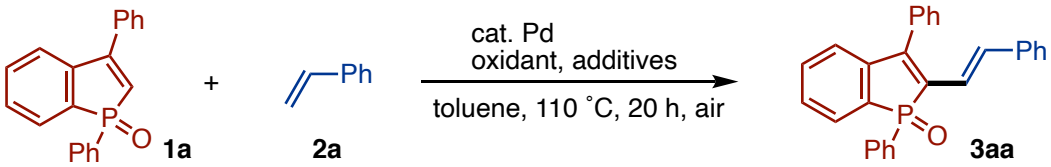
Table S3. Pd-Catalysed C2–H Alkenylation of **1a** with **2a**: Initial Screening under N_2.[a]



entry	Pd	oxidant	additives (equiv)	solvent	**1a**:**3aa**[b]
1	$Pd(OAc)_2$	AgTFA	phenanthroline (0.15)	toluene	100:0
2	***$Pd(OAc)_2$***	***AgTFA***	***none***	***toluene***	***53:57***
3	$Pd(OPiv)_2$	AgTFA	none	toluene	45:55
4	$Pd(TFA)_2$	AgTFA	none	toluene	50:50
5	$Pd(OAc)_2$	AgOAc	none	toluene	69:31
6	$Pd(OAc)_2$	Ag_2CO_3	none	toluene	97:3
7	$Pd(OAc)_2$	Ag_2O	none	toluene	95:5
8	$Pd(OAc)_2$	Ag_3PO_4	none	toluene	100:0
9	$Pd(OAc)_2$	$AgNO_3$	none	toluene	90:10
10	$Pd(OAc)_2$	$Cu(OAc)_2$	none	toluene	92:8
11	$Pd(OAc)_2$	$Cu(TFA)_2$	none	toluene	95:5
12	$Pd(OAc)_2$	AgTFA	none	MeCN	95:5
13	$Pd(OAc)_2$	AgTFA	none	DMSO	100:0
14	$Pd(OAc)_2$	AgTFA	none	DMF	95:5
15	$Pd(OAc)_2$	AgTFA	none	PivOH	55:45
16[c]	$Pd(OAc)_2$	AgTFA	none	HFIP	100:0
17[d]	$Pd(OAc)_2$	AgTFA	none	*o*-xylene	78:22
18	$Pd(OAc)_2$	AgTFA	pyridine (1.0)	toluene	88:12
19	$Pd(OAc)_2$	AgTFA	PivOH (1.0)	toluene	64:36
20	$Pd(OAc)_2$	AgTFA	CsOPiv (1.0)	toluene	60:40
21[e]	***$Pd(OAc)_2$***	***AgTFA***	***none***	***toluene***	***37:63***

[a] Reaction conditions: Pd (0.010 mmol), oxidant (0.20 mmol), additives, **1a** (0.10 mmol), **2a** (0.50 mmol), solvent (1.0 mL), 110 ˚C, 20 h, N_2. [b] Ratios of **1a**:**3aa** estimated by ^1H and $^{31}P\{^1H\}$ NMR with $P(O)(OEt)_3$ as the internal standard. [c] At 50 ˚C. [d] At 140 ˚C. [e] With **2a** (0.20 mmol).

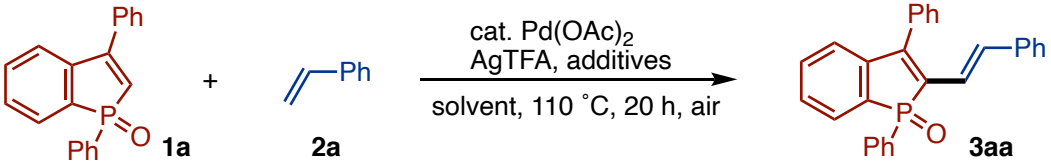
Table S4. Pd-Catalysed C2–H Alkenylation of **1a** with **2a**: Screening under Air.[a]



entry	Pd	oxidant	additives (equiv)	**1a**:**3aa**[b]
1	***$Pd(OAc)_2$***	***AgTFA***	***none***	***37:63***
2	$Pd(OPiv)_2$	AgTFA	none	38:62
3	$Pd(OAc)_2$	$AgBF_4$	none	100:0
4	$Pd(OAc)_2$	AgOTf	none	100:0
5	$Pd(OAc)_2$	$AgPF_6$	none	97:3
6	$Pd(OAc)_2$	AgTFA	CF_3COOH (1.0)	38:62
7	$Pd(OAc)_2$	AgTFA	$Cy_3P{=}O$ (0.10)	38:62

[a] Reaction conditions: Pd (0.010 mmol), oxidant (0.20 mmol), additives, **1a** (0.10 mmol), **2a** (0.20 mmol), toluene (1.0 mL), 110 ˚C, 20 h, air. [b] Ratios of **1a**:**3aa** estimated by ^{1}H and $^{31}P\{1H\}$ NMR with $P(O)(OEt)_3$ as the internal standard.

Table S5. Pd-Catalysed C2–H Alkenylation of **1a** with **2a**: Base Screening and Reinvestigation of Solvent.[a]



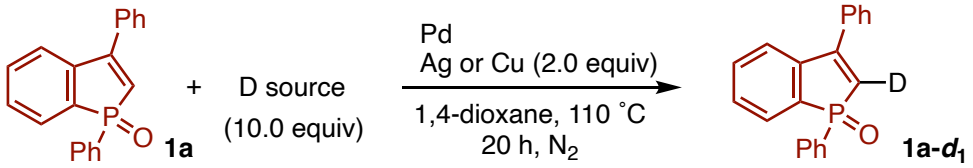
entry	additives (equiv)	solvent	**1a**:**3aa**[b]
1	MgO (2.0)	toluene	35:65
2	Li_2CO_3 (2.0)	toluene	24:76
3	Na_2CO_3 (2.0)	toluene	23:77
4	K_2CO_3 (2.0)	toluene	34:66
5	Cs_2CO_3 (2.0)	toluene	88:12
6	***$NaHCO_3$ (2.0)***	***toluene***	***21:79***
7	$KHCO_3$ (2.0)	toluene	34:66
8	K_3PO_4 (2.0)	toluene	21:79
9	K_2HPO_4 (2.0)	toluene	62:38

10	$K_4P_2O_7$ (2.0)	toluene	85:15
11	LiOAc (2.0)	toluene	28:72
12	NaOAc (2.0)	toluene	31:69
13	KOAc (2.0)	toluene	35:65
14	CsOAc (2.0)	toluene	46:54
15	***none***	***1,4-dioxane***	***22:78***
16	none	THF	41:59
17	none	*i*-Pr_2O	28:72
18	***none***	***CPME***	***26:74***
19	***none***	***MTBE***	***18:82***
20	none	AcOH	61:39
21	***$NaHCO_3$ (2.0)***	***1,4-dioxane***	***10:90 (85%)***
22	$NaHCO_3$ (2.0)	CPME	23:77
23	$NaHCO_3$ (2.0)	MTBE	9:91
24	$NaHCO_3$ (2.0), $Cy_3P{=}O$ (0.10)	1,4-dioxane	11:89
25	$NaHCO_3$ (2.0), Ph_3P (0.20)	1,4-dioxane	64:46
26	$NaHCO_3$ (2.0), phenanthroline (0.10)	1,4-dioxane	44:56
27[c]	$NaHCO_3$ (2.0)	1,4-dioxane	14:86
28[d]	$NaHCO_3$ (2.0)	1,4-dioxane	8:92
29[e]	$NaHCO_3$ (2.0)	1,4-dioxane	13:87
30[f]	$NaHCO_3$ (2.0)	1,4-dioxane	100:0
31[g]	$NaHCO_3$ (2.0)	1,4-dioxane	98:2

[a] Reaction conditions: $Pd(OAc)_2$ (0.010 mmol), AgTFA (0.20 mmol), additives, **1a** (0.10 mmol), **2a** (0.20 mmol), solvent (1.0 mL), 110 °C, 20 h, air. [b] Ratios of **1a**:**3aa** estimated by ^1H and $^{31}P\{1H\}$ NMR with $P(O)(OEt)_3$ as the internal standard. Isolated yield of **3aa** is in parentheses. [c] With $Pd(OAc)_2$ (0.0050 mmol). [d] With $Pd(OAc)_2$ (0.015 mmol). [e] With **2a** (0.30 mmol). [f] Without $Pd(OAc)_2$. [g] With benzoquinone instead of AgTFA.

Control Experiments

Table S6. H/D Exchange Reaction of **1a**.[a]



entry	D source	Pd (mol %)	Ag or Cu	% D of **1a-*d*$_1$**[b]
1	acetic acid-d_4	$Pd(OAc)_2$ (10)	AgTFA	70
2	acetic acid-d_4	$Pd(OAc)_2$ (10)	none	0
3	acetic acid-d_4	$Pd(OAc)_2$ (100)	none	37
4	acetic acid-d_4	$Pd(TFA)_2$ (10)	none	0
5	acetic acid-d_4	$Pd(TFA)_2$ (100)	none	0
6	acetic acid-d_4	none	AgTFA	64
7	acetic acid-d_4	none	AgOAc	12
8	acetic acid-d_4	none	Ag_2CO_3	21
9	acetic acid-d_4	none	AgOTf	10
10	acetic acid-d_4	none	$Cu(OAc)_2$	0
11	D_2O	none	AgTFA	87
12	D_2O	none	AgOAc	14

[a] Reaction conditions: Pd, Ag or Cu (0.20 mmol), D source (1.0 mmol), **1a** (0.10 mmol), 1,4-dioxane (1.0 mL), 110 ˚C, 20 h, N_2. [b] Estimated by ^1H and ^2H NMR analysis.

Optical Properties of Products

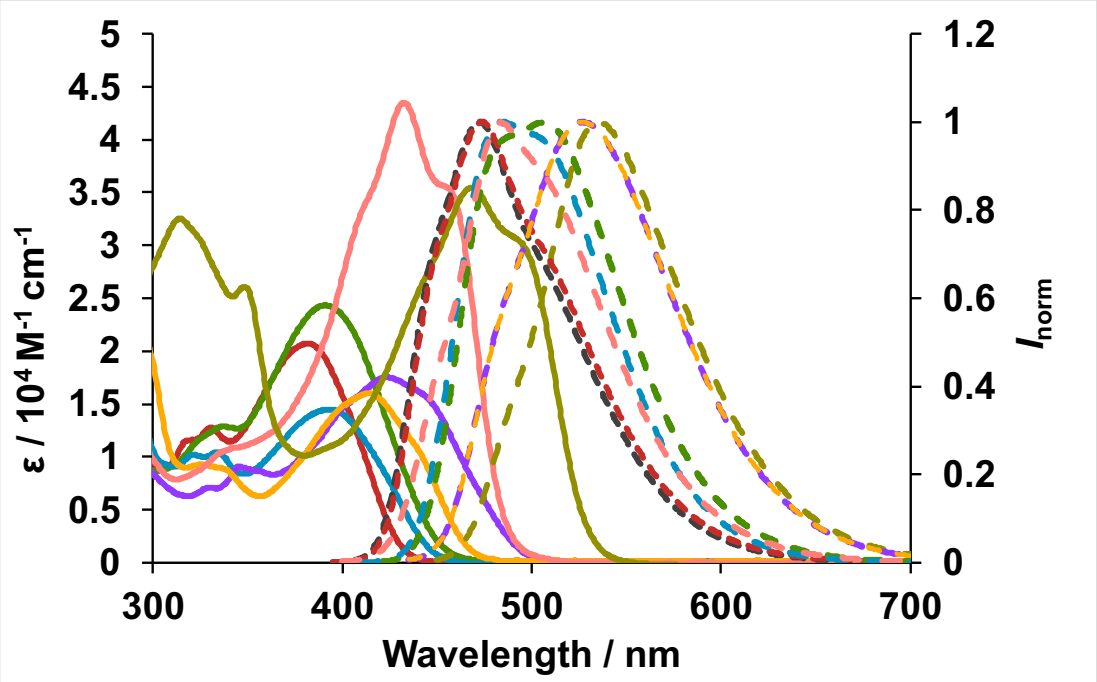


Figure S3. UV-vis absorption (solid line) and emission (dotted line) spectra of **3aa**, **3ac**, **3ae**, **3ak**, **3al**, **3ga**, **3am**, and **3hm** (1.0 x 10^{-5} M in CH_2Cl_2). Excited at the absorption maxima for the emission spectrum.

Table S7. Optical properties for selected compounds.

compd	λ_{abs} (nm)	λ_{em} (nm)	Φ_F
3aa	380	473	0.82
3ac	382	474	0.82
3ae	394	485	0.78
3ak	382	506	0.56
3al	423	535	0.81
3ga	415	527	0.52
3am	432	510	0.14
3hm	468	536	0.05

DFT Calculations

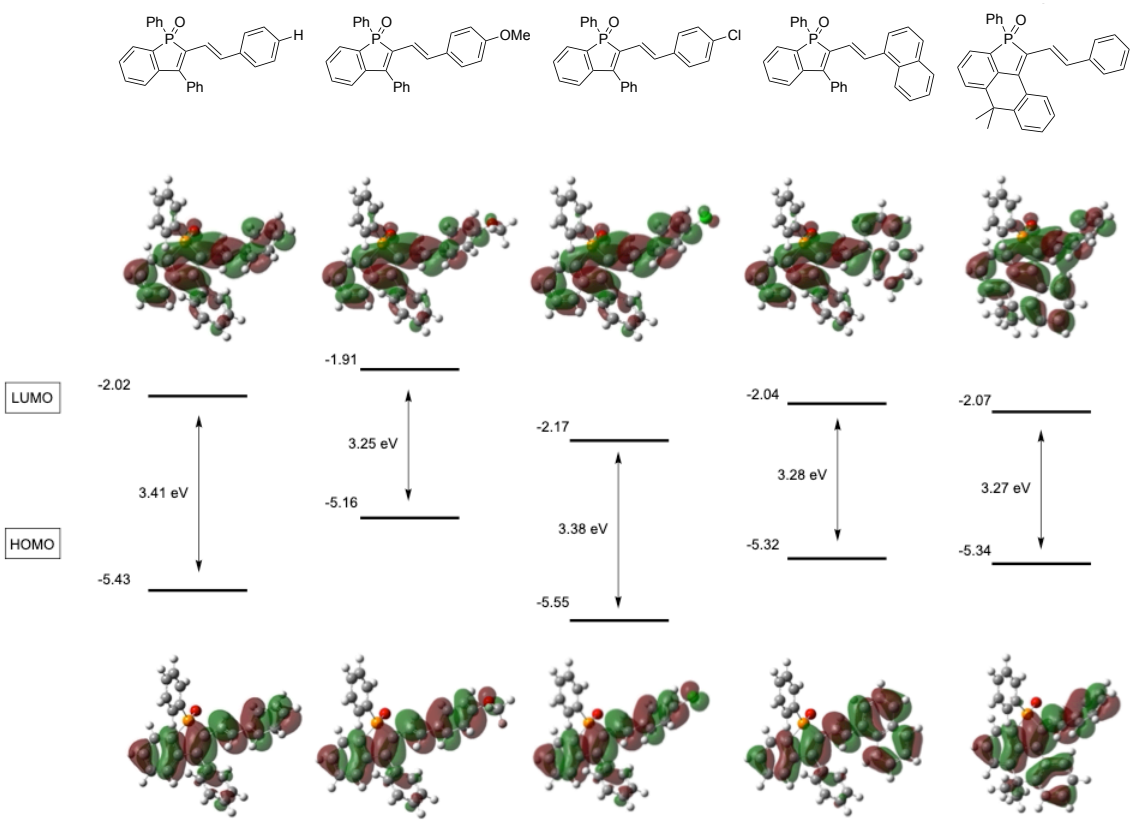
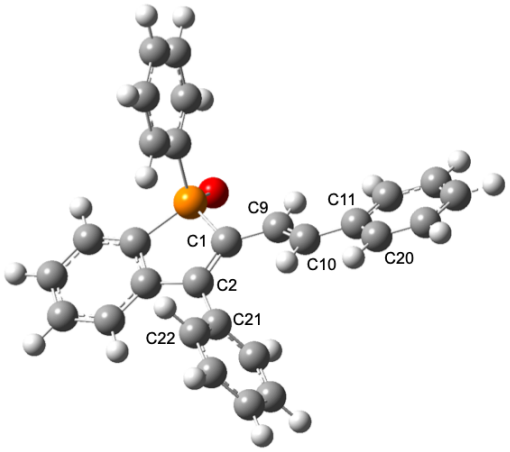
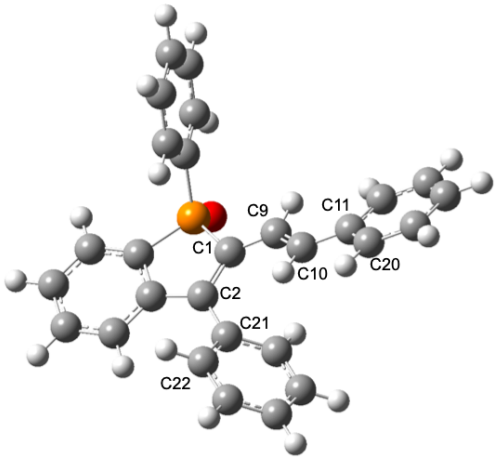


Figure S4. HOMOs and LUMOs and their energies calculated at the B3LYP/6-31G* level of theory.

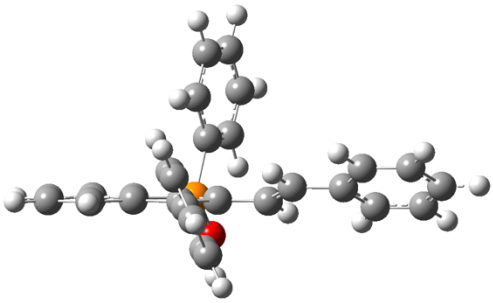
(a) Top views of **3aa** (S0)



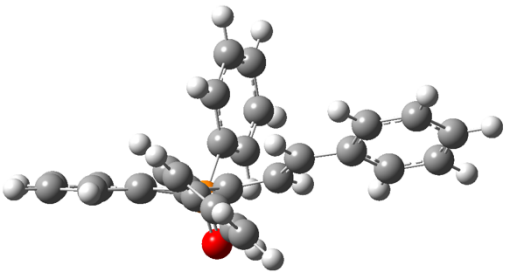
(b) Top views of **3aa** (S1)



(c) Side views of **3aa** (S0)



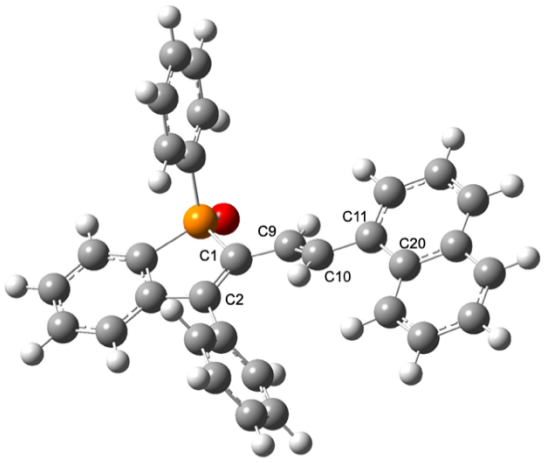
(d) Side views of **3aa** (S1)



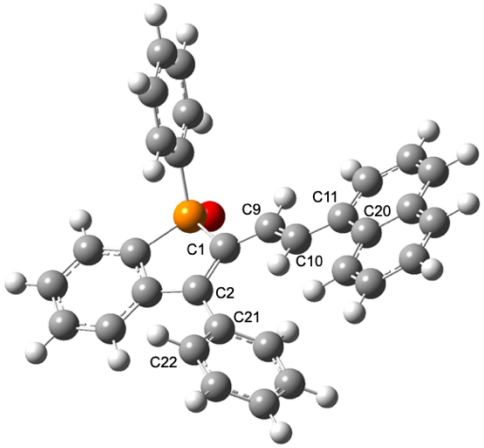
	C2-C1-C9-C10	C1-C9-C10-C11	C9-C10-C11-C20	C1-C2-C21-C22
3aa (S0)	-25.6	-179.1	174.9	116.8
3aa (S1)	-11.5	175.9	171.9	141.6

Figure S5. Optimized structures of (a) and (c) **3aa** (S0), (b) and (d) **3aa** (S1): Top views (upper) and side views (lower). Selected torsion angles (deg) of **3aa** (S0) and **3aa** (S1) calculated at the B3LYP/6-31G* level of theory.

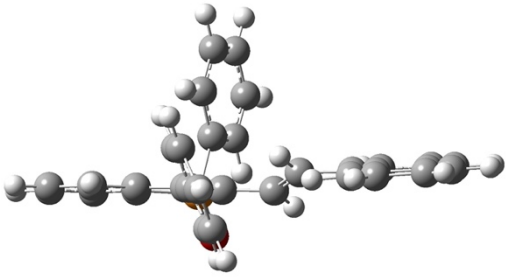
(a) Top views of **3ak** (S0)



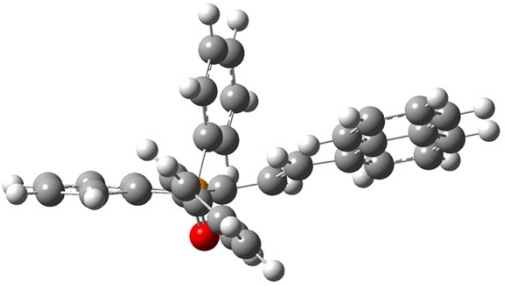
(b) Top views of **3ak** (S1)



(c) Side views of **3ak** (S0)



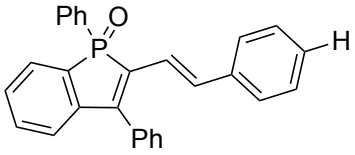
(d) Side views of **3ak** (S1)



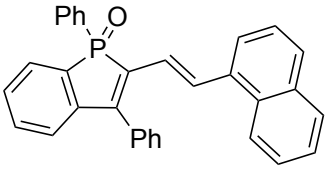
	C2-C1-C9-C10	C1-C9-C10-C11	C9-C10-C11-C20	C1-C2-C21-C22
3ak (S0)	-25.7	-175.8	-152.4	116.1
3ak (S1)	-9.9	-178.9	-179.8	139.4

Figure S6. Optimized structures of (a) and (c) **3ak** (S0), (b) and (d) **3ak** (S1): Top views (upper) and side views (lower). Selected torsion angles (deg) of **3ak** (S0) and **3ak** (S1) calculated at the B3LYP/6-31G* level of theory.

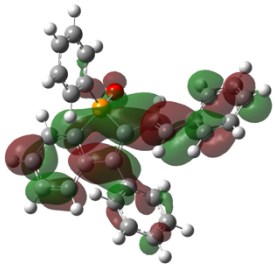
3aa



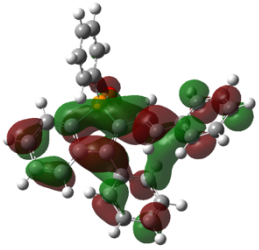
3ak



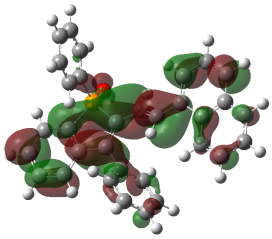
S0 LUMO



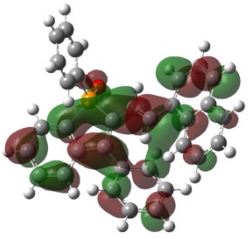
S1 LUMO



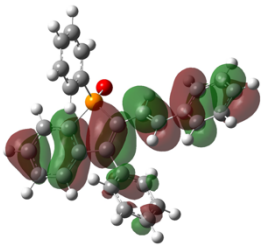
S0 LUMO



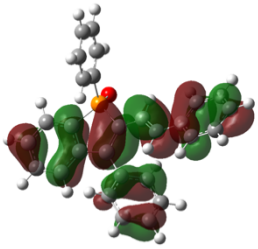
S1 LUMO



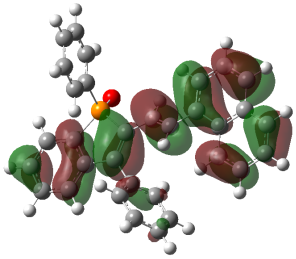
S0 HOMO



S1 HOMO



S0 HOMO



S1 HOMO

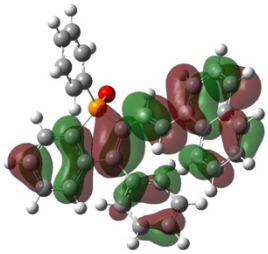
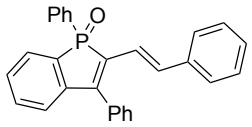


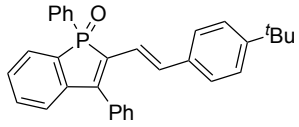
Figure S7. HOMOs and LUMOs (S0 and S1) of **3aa** and **3ak**.

Characterization Data for Products

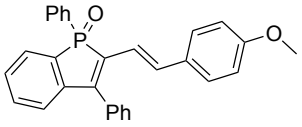
Copy of ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra for all compounds are attached in the last part.



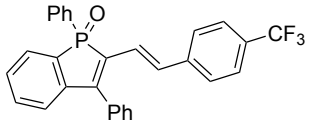
(*E*)-1,3-Diphenyl-2-styrylphosphindole 1-oxide (3aa): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 35 mg (85%, 0.10 mmol scale); Yellow solid; m.p. 96.2-97.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 2H), 7.68 (dd, *J* = 9.3, 7.4 Hz, 1H), 7.59-7.55 (m, 2H), 7.53-7.49 (m, 2H), 7.47-7.41 (m, 5H), 7.33, (td, *J* = 7.5, 3.9 Hz, 1H), 7.27-7.14 (m, 7H), 6.88 (dd, *J* = 23.6, 16.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 149.6 (d, *J* = 21.2 Hz, 1C), 143.5 (d, *J* = 25.8 Hz, 1C), 136.9 (1C), 135.3 (d, *J* = 5.2 Hz, 1C), 133.6 (d, *J* = 14.3 Hz, 1C), 133.0 (d, *J* = 1.8 Hz, 1C), 132.8 (d, *J* = 95.4 Hz, 1C), 132.4 (d, *J* = 106.0 Hz, 1C), 132.2 (d, *J* = 2.8 Hz, 1C), 130.8 (d, *J* = 10.7 Hz, 2C), 130.69 (d, *J* = 98.9, 1C), 129.2 (2C), 129.1 (d, *J* = 3.0 Hz, 1C), 129.02 (1C), 128.99 (1C), 128.96 (1C), 128.9 (2C+1C), 128.5 (2C), 128.2 (1C), 126.8 (2C), 123.8 (d, *J* = 10.5 Hz, 1C), 120.9 (d, *J* = 9.3 Hz, 1C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 37.58; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{28}H_{22}OP$: 405.1403, found: 405.1393.



(*E*)-2-(4-(*tert*-Butyl)styryl)-1,3-diphenylphosphindole 1-oxide (3ab): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 33 mg (70%, 0.10 mmol scale); Yellow solid; m.p. 106.3-107.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, 2H), 7.68 (dd, *J* = 9.7, 6.8 Hz, 1H), 7.58-7.54 (m, 2H), 7.53-7.47 (m, 2H), 7.46-7.40 (m, 5H), 7.32 (td, *J* = 7.4, 3.8 Hz, 1H), 7.26-7.16 (m, 6H), 6.85 (dd, *J* = 23.8, 16.4 Hz, 1H), 1.25 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 151.5 (1C), δ 149.0 (d, *J* = 21.2 Hz, 1C), 143.6 (d, *J* = 26.0 Hz, 1C), 135.2 (d, *J* = 5.2 Hz, 1C), 134.2 (1C), 133.7 (d, *J* = 14.4 Hz, 1C), 133.0 (d, *J* = 95.4 Hz, 1C), 132.9 (d, *J* = 1.9 Hz, 1C), 132.4 (d, *J* = 107.4 Hz, 1C), 132.2 (d, *J* = 2.7 Hz, 1C), 130.80 (d, *J* = 10.6 Hz, 2C), 130.78 (d, *J* = 99.0 Hz, 1C), 129.3 (2C), 129.03 (1C), 128.97 (1C), 128.93 (1C), 128.91 (1C), 128.85 (2C+1C), 126.6 (2C), 125.5 (2C), 123.7 (d, *J* = 10.6 Hz, 1C), 120.3 (d, *J* = 9.3 Hz, 1C), 34.6 (1C), 31.2 (3C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 37.66; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{32}H_{30}OP$: 461.2029, found: 461.2038.

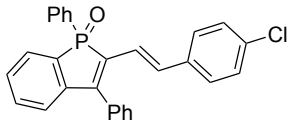


(*E*)-2-(4-Methoxystyryl)-1,3-diphenylphosphindole 1-oxide (3ac): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 30 mg (69%, 0.10 mmol scale); Yellow solid; m.p. 91.2-92.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 2H), 7.67 (dd, *J* = 9.3, 7.2 Hz, 1H), 7.59-7.55 (m, 2H), 7.54-7.48 (m, 2H), 7.47-7.40 (m, 5H), 7.32 (td, *J* = 7.4, 3.9 Hz, 1H), 7.22-7.16 (m, 3H), 7.12 (d, *J* = 16.4 Hz, 1H), 6.76 (dd, *J* = 23.9, 16.3 Hz, 1H), 6.77-6.74 (m, 2H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.8 (1C), 148.4 (d, *J* = 21.3 Hz, 1C), 143.7 (d, *J* = 26.0 Hz, 1C), 135.0 (d, *J* = 5.4 Hz, 1C), 133.8 (d, *J* = 14.4 Hz, 1C), 133.1 (d, *J* = 95.0 Hz, 1C), 132.9 (d, *J* = 1.2 Hz, 1C), 132.3 (d, *J* = 105.8 Hz, 1C), 132.2 (d, *J* = 2.8 Hz, 1C), 130.9 (d, *J* = 98.8 Hz, 1C), 130.8 (d, *J* = 10.8 Hz, 2C), 129.8 (1C), 129.3 (2C), 129.0 (2C), 128.89 (1C), 128.86 (1C), 128.84 (1C), 128.80 (1C), 128.7 (1C), 128.2 (2C), 123.6 (d, *J* = 10.4 Hz, 1C), 118.9 (d, *J* = 9.2 Hz, 1C), 114.0 (2C), 55.3 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.70; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{29}H_{24}O_2P$: 435.1508, found: 435.1499.

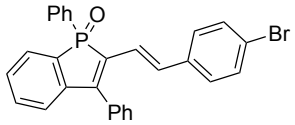


(*E*)-1,3-Diphenyl-2-(4-(trifluoromethyl)styryl)phosphindole 1-oxide (3ad): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 29 mg (61%, 0.10 mmol scale); Yellow solid; m.p. 194.7-196.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.81 (m, 2H), 7.70 (dd, *J* = 9.9, 7.2 Hz, 1H), 7.62-7.58 (m, 2H), 7.56-7.52 (m, 2H), 7.49-7.44 (m, 7H), 7.37 (td, *J* = 7.4, 3.9 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.23 (dd, *J* = 7.6, 3.0 Hz, 1H), 7.17 (d, *J* = 16.4 Hz, 1H), 6.94 (dd, *J* = 23.2, 16.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.3 (d, *J* = 21.0 Hz, 1C), δ 143.2 (d, *J* = 22.9 Hz, 1C), 140.3 (1C), 133.4 (d, *J* = 4.8 Hz, 1C), 133.3 (d, *J* = 13.8 Hz, 1C), 133.1 (d, *J* = 1.8 Hz, 1C), 132.41 (d, *J* = 106.1 Hz, 1C), 132.40 (d, *J* = 2.8 Hz, 1C), 132.3 (d, *J* = 95.5 Hz, 1C), 130.8 (d, *J* = 10.8 Hz, 2C), 130.4 (d, *J* = 99.1 Hz, 1C), 129.6 (q, *J* = 32.2 Hz, 1C), 129.4 (d, *J* = 10.8 Hz, 1C), 129.3 (1C), 129.2 (2C), 129.11 (1C), 129.06 (1C), 129.0 (2C+1C), 126.9 (2C), 125.4 (q, *J* = 3.8 Hz, 2C), 124.1714 (d, *J* = 10.5 Hz, 1C), 124.0 (q, *J* = 279.7 Hz, 1C), 123.3 (d, *J* = 9.3 Hz, 1C); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.61; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.36; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for

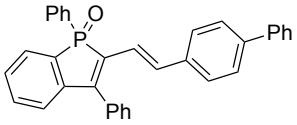
$C_{29}H_{21}F_3OP$: 473.1277, found: 473.1253.



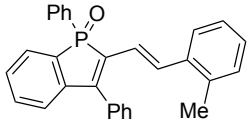
(*E*)-2-(4-Chlorostyryl)-1,3-diphenylphosphindole 1-oxide (3ae): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 36 mg (80%, 0.10 mmol scale); Yellow solid; m.p. 104.6-106.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.81 (m, 2H), 7.68 (dd, *J* = 9.9, 7.2 Hz, 1H), 7.60-7.50 (m, 4H), 7.48-7.42 (m, 5H), 7.34 (td, *J* = 7.5, 3.9 Hz, 1H), 7.20 (dd, *J* = 7.6, 3.0 Hz, 1H), 7.17 (s, 4H), 7.11 (d, *J* = 16.4 Hz, 1H), 6.84 (dd, *J* = 23.4, 16.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.1 (d, *J* = 21.1 Hz, 1C), 143.4 (d, *J* = 25.6 Hz, 1C), 135.4 (1C), 133.820 (d, *J* = 5.1 Hz, 1C), 133.816 (1C), 133.4 (d, *J* = 14.0 Hz, 1C), 133.0 (d, *J* = 1.8 Hz, 1C), 132.6 (d, *J* = 98.1 Hz, 1C), 132.35 (d, *J* = 2.8 Hz, 1C), 132.34 (d, *J* = 106.2 Hz, 1C), 130.8 (d, *J* = 10.6 Hz, 2C), 130.5 (d, *J* = 98.8 Hz, 1C), 129.3 (1C), 129.2 (d, *J* = 3.0 Hz, 1C), 129.15 (1C), 129.11 (1C), 129.08 (1C), 128.99 (1C), 128.96 (3C), 128.7 (2C), 128.0 (2C), 124.0 (d, *J* = 10.7 Hz, 1C), 121.4 (d, *J* = 9.4 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.52; HRMS (APCI) m/z ([M+H]$^+$) calcd for $C_{28}H_{21}ClOP$: 439.1013, found: 439.0991.



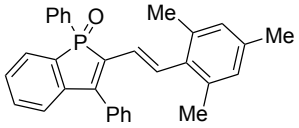
(*E*)-2-(4-Bromostyryl)-1,3-diphenylphosphindole 1-oxide (3af): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v) and GPC ($CHCl_3$): 19 mg (38%, 0.10 mmol scale); Yellow solid; m.p. 106.2-107.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 2H), 7.68 (dd, *J* = 9.8, 7.1 Hz, 1H) 7.60-7.56 (m, 2H), 7.54-7.51 (m, 2H), 7.48-7.42 (m, 5H), 7.38-7.35 (m,1H), 7.34-7.31 (m, 2H), 7.20 (dd, *J* = 7.6, 3.0 Hz, 1H), 7.12-7.07 (m, 3H), 6.85 (dd, *J* = 23.4, 16.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.2 (d, *J* = 21.0 Hz, 1C), 143.4 (d, *J* = 25.7 Hz, 1C), 135.8 (1C), 133.9 (d, *J* = 5.2 Hz, 1C), 133.4 (d, *J* = 14.0 Hz, 1C), 133.0 (d, *J* = 2.6 Hz, 1C), 132.6 (d, *J* = 95.3 Hz, 1C), 132.4 (d, *J* = 103.4 Hz, 1C), 132.3 (d, *J* = 2.8 Hz, 1C), 131.6 (2C), 130.8 (d, *J* = 10.7 Hz, 2C), 130.5 (d, *J* = 99.0 Hz, 1C), 129.3 (1C), 129.2 (2C), 129.11 (2C), 129.07 (1C), 129.0 (1C), 128.94 (2C), 128.2 (2C), 124.0 (d, *J* = 10.7 Hz, 1C), 122.1 (1C), 121.5 (d, *J* = 9.4 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.46; HRMS (APCI) m/z ([M+H]$^+$) calcd for $C_{28}H_{21}BrOP$: 483.0508, found: 483.0516.



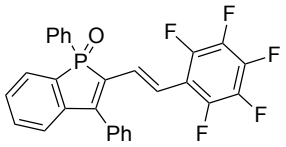
(*E*)-2-(2-([1,1'-Biphenyl]-4-yl)vinyl)-1,3-diphenylphosphindole 1-oxide (3ag): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 39 mg (80%, 0.10 mmol scale); Yellow solid; m.p. 106.2-107.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.83 (m, 2H), 7.68 (dd, *J* = 9.8, 7.2 Hz, 1H), 7.61-7.57 (m, 2H), 7.55-7.50 (m, 4H), 7.48-7.44 (m, 7H), 7.43-7.38 (m, 2H), 7.37-7.29 (m, 4H), 7.23-7.19 (m, 2H), 6.93 (dd, *J* = 23.7, 16.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6 (d, *J* = 21.3 Hz, 1C), δ 143.5 (d, *J* = 25.8 Hz, 1C), 140.9 (1C), 140.5 (1C), 136.0 (1C), 134.9 (1C), 134.8 (1C), 133.6 (d, *J* = 14.4 Hz, 1C), 133.0 (d, *J* = 1.1 Hz, 1C), 132.9 (d, *J* = 95.4 Hz, 1C), 132.4 (d, *J* = 105.8 Hz, 1C), 132.3 (d, *J* = 2.8 Hz, 1C), 130.8 (d, *J* = 10.6 Hz, 2C), 130.7 (d, *J* = 99.0 Hz, 1C), 129.3 (2C), 129.10 (1C), 129.08 (1C), 129.05 (1C), 129.02 (1C), 128.99 (1C), 128.92 (2C), 128.80 (2C), 127.4 (1C), 127.3 (1C), 127.2 (2C), 126.9 (2C), 123.8 (d, *J* = 10.6 Hz, 1C), 121.0 (d, *J* = 9.2 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.58; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{34}H_{26}OP$: 481.1716, found: 481.1735.



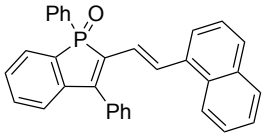
(*E*)-2-(2-Methylstyryl)-1,3-diphenylphosphindole 1-oxide (3ah): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2v/v): 34 mg (81%, 0.10 mmol scale); Yellow solid; m.p. 184.6-186.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.83 (m, 2H), 7.68 (dd, *J* = 9.9, 7.2 Hz, 1H), 7.58-7.54 (m, 2H), 7.53-7.50 (m, 2H), 7.48-7.42 (m,5H), 7.36-7.32 (m, 2H), 7.27-7.25 (m, 1H), 7.21 (dd, *J* = 7.6, 3.0 Hz, 1H), 7.09-7.01 (m, 3H), 6.76 (dd, *J* = 23.6, 16.2 Hz, 1H), 2.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.2 (d, *J* = 21.0 Hz, 1C), δ 143.8 (d, *J* = 25.7 Hz, 1C), 136.4 (1C), 135.9 (1C), 133.6334 (d, *J* = 5.6 Hz, 1C), 133.61165 (d, *J* = 14.3 Hz, 1C), 133.61165 (d, *J* = 14.3 Hz, 1C), 133.5 (d, *J* = 97.5 Hz, 1C), 132.3 (d, *J* = 105.8 Hz, 1C), 132.2 (d, *J* = 2.8 Hz, 1C), 130.9 (d, *J* = 10.6 Hz, 2C), 130.8 (d, *J* = 98.3 Hz, 1C), 130.3 (1C), 129.2 (2C), 129.06 (d, *J* = 6.9 Hz, 1C), 129.0 (2C), 128.94 (1C), 128.92 (1C), 128.88 (2C), 128.1 (1C), 125.9 (1C), 124.9 (1C), 123.8 (d, *J* = 10.5 Hz, 1C), 121.7 (d, *J* = 9.3 Hz, 1C), 19.5 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.58; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{29}H_{24}OP$: 419.1559, found: 419.1568.



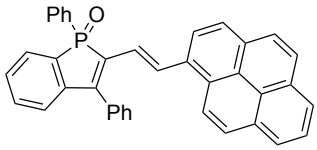
(*E*)-1,3-Diphenyl-2-(2,4,6-trimethylstyryl)phosphindole 1-oxide (3ai): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v) and GPC ($CHCl_3$): 14 mg (31%, 0.10 mmol scale); Yellow solid; m.p. 89.5-91.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.84 (m, 2H), 7.69 (dd, *J* = 9.9, 7.2 Hz, 1H), 7.54-7.41 (m, 9H), 7.33 (td, *J* = 7.2, 3.8, Hz, 1H), 7.22 (dd, *J* = 7.6, 3.0 Hz, 1H), 7.13 (d, *J* = 16.7 Hz, 1H), 6.73 (s, 2H), 6.37 (dd, *J* = 23.8, 16.7 Hz, 1H), 2.18 (s, 3H), 1.97 (6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.0 (d, *J* = 21.1 Hz, 1C), 143.6 (d, *J* = 26.0 Hz, 1C), 136.8 (1C), 136.0 (2C), 134.7 (d, *J* = 5.7 Hz, 1C), 133.561 (d, *J* = 14.6 Hz, 1C), 133.557 (1C), 133.2 (d, *J* = 95.3 Hz, 1C), 132.9 (d, *J* = 1.3 Hz, 1C), 132.5 (d, *J* = 105.7 Hz, 1C), 132.2 (d, *J* = 2.8 Hz, 1C), 131.0 (d, *J* = 10.7 Hz, 2C), 130.7 (d, *J* = 98.9 Hz, 1C), 129.1 (1C), 129.0 (3C), 128.86 (1C), 128.85 (2C), 128.7 (4C), 125.8 (d, *J* = 9.0 Hz, 1C), 123.7 (d, *J* = 10.4 Hz, 1C), 20.9 (1C), 20.7 (2C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.39; HRMS (APCI) m/z ([M+H]$^+$) calcd for $C_{31}H_{28}OP$: 447.1872, found: 447.1854.



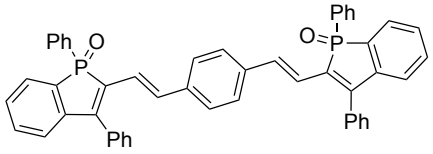
(*E*)-2-(2-(Perfluorophenyl)vinyl)-1,3-diphenylphosphindole 1-oxide (3aj): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 37 mg (74%, 0.10 mmol scale); Yellow solid; m.p. 193.0-194.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.79 (m, 2H), 7.71 (dd, *J* = 10.0, 7.2 Hz, 1H), 7.59-7.38 (m, 10H), 7.28 (dd, *J* = 7.6, 3.0 Hz, 1H), 7.15 (dd, *J* = 22.4, 16.8 Hz, 1H), 7.00 (d, *J* = 16.9 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.5 (d, *J* = 20.8 Hz, 1C), 144.6 (dm, *J* = 253.7 Hz, 2C), 142.2 (d, *J* = 25.3 Hz, 1C), 140.0 (dm, *J* = 259.0 Hz, 1C), 137.6 (dm, *J* = 249.3 Hz, 2C), 133.2 (d, *J* = 1.6 Hz, 1C), 132.850 (d, *J* = 13.8 Hz, 1C), 132.848 (d, *J* = 95.4 Hz, 1C), 132.49 (d, *J* = 106.2 Hz, 1C), 132.48 (d, *J* = 2.9 Hz, 1C), 130.7 (d, *J* = 10.7 Hz, 2C) , 130.0 (d, *J* = 99.2 Hz, 1C), 129.8 (d, *J* = 10.9 Hz, 1C), 129.4 (1C), 129.3 (d, *J* = 9.8 Hz, 1C), 129.1 (2C), 129.0 (1C+1C+1C), 128.9 (2C), 124.5 (d, *J* = 10.6 Hz, 1C), 118.9 (dt, *J* = 3.0, 2.5 Hz, 1C), 112.2 (td, *J* = 13.3, 4.0 Hz 1C); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -141.86 (d, *J* = 21.5 Hz), -141.88 (d, *J* = 21.5 Hz), -155.3 (t, *J* = 20.7 Hz), -162.8 (t, *J* = 20.9 Hz), -162.9 (t, *J* = 20.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 36.80; HRMS (APCI) m/z ([M+H]$^+$) calcd for $C_{28}H_{17}F_5OP$: 495.0932, found: 495.0953.



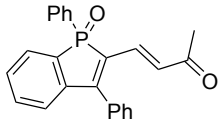
(*E*)-2-(2-(Naphthalen-1-yl)vinyl)-1,3-diphenylphosphindole 1-oxide (3ak): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 42 mg (91%, 0.10 mmol scale); Yellow solid; m.p. 233.0-234.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.91 (m, 3H), 7.77-7.69 (m, 4H), 7.59-7.55 (m, 3H), 7.53-7.35 (m, 10H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.23 (dd, *J* = 7.6, 3.0 Hz, 1H), 6.91 (dd, *J* = 23.6, 16.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6 (d, *J* = 21.1 Hz, 1C), 143.7 (d, *J* = 25.8 Hz, 1C), 134.5 (1C), 133.6 (d, *J* = 14.6 Hz, 1C), 135.5 (1C), 133.4 (d, *J* = 95.3 Hz, 1C), 133.0 (1C), 132.9 (d, *J* = 7.6 Hz, 1C), 132.31 (d, *J* = 2.8 Hz, 1C), 132.30 (d, *J* = 105.8 Hz, 1C), 131.1 (1C), 131.0 (d, *J* = 10.6 Hz, 2C), 130.9 (d, *J* = 98.5 Hz, 1C), 129.2 (2C), 129.15 (1C), 129.12 (1C), 129.05 (1C), 129.0 (2C), 128.9 (2C), 128.6 (1C), 128.4 (1C), 126.2 (1C), 125.9 (1C), 125.4 (1C), 123.9 (d, *J* = 10.6 Hz, 1C), 123.7 (1C), 123.37 (1C), 123.36 (d, *J* = 9.1 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.39; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{32}H_{24}OP$: 455.1559, found: 455.1548.



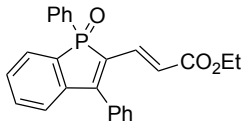
(*E*)-1,3-Diphenyl-2-(2-(pyren-1-yl)vinyl)phosphindole 1-oxide (3al): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 28 mg (%, 0.10 mmol scale); Orange solid; m.p. 214.7-216.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 16.1 Hz, 1H), 8.14 (dd, *J* = 7.6, 3.0 Hz, 2H), 8.04-7.93 (m, 9H), 7.75 (dd, *J* = 9.9, 7.2 Hz, 1H), 7.62-7.52 (m, 8H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38 (td, *J* = 7.4, 3.8 Hz, 1H), 7.26 (dd, *J* = 7.6, 3.0 Hz, 1H), 7.1 (dd, *J* = 23.6, 16.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.5 (d, *J* = 21.1 Hz, 1C), 143.8 (d, *J* = 25.6 Hz, 1C), 133.7 (d, *J* = 14.0 Hz, 1C), 133.6 (d, *J* = 95.3 Hz, 1C), 133.1 (d, *J* = 1.9 Hz, 1C), 132.8 (d, *J* = 5.0 Hz, 1C), 132.4 (d, *J* = 2.8 Hz, 1C), 132.3 (d, *J* = 106.8 Hz, 1C), 131.4 (1C), 131.31 (1C), 131.28 (1C), 131.0 (d, *J* = 10.7 Hz, 2C), 130.94 (d, *J* = 98.8 Hz, 1C), 130.88 (1C), 129.3 (2C), 129.21 (1C), 129.18 (1C), 129.13 (d, *J* = 4.5 Hz, 1C), 129.06 (1C), 129.04 (1C), 128.98 (2C), 128.6 (1C), 127.8 (1C), 127.6 (1C), 127.3 (1C), 126.0 (1C), 125.4 (1C), 125.2 (1C), 124.9 (1C), 124.8 (1C),124.7 (1C), 123.9 (d, *J* = 10.6 Hz, 1C),123.4 (d, *J* = 9.3 Hz, 1C), 123.2 (1C), 123.0 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.52; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{38}H_{26}OP$: 529.1716, found: 529.1701.



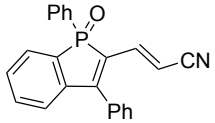
2,2'-((1*E*,1'*E*)-1,4-Phenylenebis(ethene-2,1-diyl))bis(1,3-diphenylphosphindole 1-oxide) (a 1:1 mixture of diastereomers) (3am): Purified by GPC ($CHCl_3$): 18 mg (47%, 0.050 mmol scale); Yellow solid; m.p. 194.7-196.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.78 (m, 4H), 7.66 (dd, *J* = 9.8, 7.0 Hz, 2H), 7.57-7.48 (m, 8H), 7.45-7.40 (m, 10H), 7.33 (td, *J* = 7.4, 3.8 Hz, 2H), 7.19 (dd, *J* = 7.7, 2.7 Hz, 2H), 7.10 (d, *J* = 2.5 Hz, 4H), 7.06 (dd, *J* = 16.4, 2.9 Hz, 2H), 6.83 (dd, *J* = 23.6, 16.3 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.7 (d, *J* = 21.2 Hz, 2C), 143.5 (d, *J* = 25.6 Hz, 2C), 136.8 (2C), 134.6 (d, *J* = 5.1 Hz, 2C), 133.5 (d, *J* = 14.2 Hz, 2C), 132.8 (d, *J* = 94.8 Hz, 2C), 133.0 (2C), 132.4 (d, *J* = 104.3 Hz, 2C), 132.2 (2C), 130.8 (d, *J* = 10.7 Hz, 4C), 130.6 (d, *J* = 98.4 Hz, 2C), 129.2 (4C), 129.1 (d, *J* = 4.0 Hz, 2C), 129.00 (4C), 128.97 (2C), 128.90 (2C), 128.88 (4C), 126.9 (4C), 123.8 (d, *J* = 10.4 Hz, 2C), 121.2 (d, *J* = 9.2 Hz, 2C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.46, 37.44; HRMS (APCI) m/z ([M+H]$^+$) calcd for $C_{50}H_{37}O_2P_2$: 731.2263, found: 731.2250.



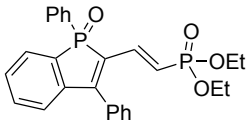
(*E*)-4-(1-Oxido-1,3-diphenylphosphindol-2-yl)but-3-en-2-one (3an): Purified by GPC ($CHCl_3$): 26 mg (71%, 0.10 mmol scale); Pale yellow solid; m.p. 166.3-168.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.68 (m, 2H), 7.71 (dd, *J* = 9.9, 7.2 Hz, 1H), 7.60-7.54 (m, 4H), 7.50-7.40 (m, 6H), 7.29 (dd, *J* = 7.8, 3.0 Hz, 1H), 7.25 (dd, *J* = 23.4, 16.0 Hz, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.7 (1C), 157.8 (d, *J* = 22.2 Hz, 1C), 142.6 (d, *J* = 24.9 Hz, 1C), 133.8 (d, *J* = 9.3 Hz, 1C), 133.2 (d, *J* = 1.9 Hz, 1C), 133.0 (d, *J* = 106.0 Hz, 1C), 132.6 (d, *J* = 2.8 Hz, 1C), 132.4 (d, *J* = 13.6 Hz, 1C), 130.824 (d, *J* = 4.0 Hz, 1C), 130.76 (d, *J* = 11.3 Hz, 2C), 130.77 (d, *J* = 96.5 Hz, 1C), 130.6 (d, *J* = 10.7 Hz, 1C), 129.8 (1C), 129.5 (d, *J* = 102.0 Hz, 1C), 129.3 (d, *J* = 9.4 Hz, 1C), 129.2 (1C), 129.09 (2C), 129.08 (1C), 129.0 (2C), 125.2 (d, *J* = 10.3 Hz, 1C), 28.8 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 36.36; HRMS (APCI) m/z ([M+H]$^+$) calcd for $C_{24}H_{20}O_2P$: 371.1195, found: 371.1195.



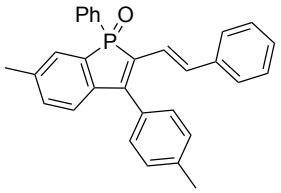
Ethyl (*E*)-3-(1-oxido-1,3-diphenylphosphindol-2-yl)acrylate (3ao): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 25 mg (62%, 0.10 mmol scale); Pale yellow solid; m.p. 144.6-146.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.74(m, 2H), 7.70 (dd, *J* = 9.9, 7.2 Hz, 1H), 7.59-7.53 (m, 4H), 7.52-7.40 (m, 6H), 7.39 (dd, *J* = 23.7, 16.1 Hz, 1H), 7.28 (dd, *J* = 7.4, 2.8 Hz, 1H), 6.43 (dd, *J* = 16.0, 1.1 Hz, 1H), 4.14 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.06 (dq, *J* = 10.9, 7.1 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6 (1C), 156.7 (d, *J* = 20.6 Hz, 1C), 142.5 (d, *J* = 25.2 Hz, 1C), 135.5 (d, *J* = 9.1 Hz, 1C), 133.0 (d, *J* = 105.5 Hz, 1C), 133.1 (d, *J* = 1.5 Hz, 1C), 132.5 (d, *J* = 3.1 Hz, 1C), 132.5 (d, *J* = 13.4 Hz, 1C), 130.8 (d, *J* = 10.9 Hz, 2C), 130.6 (d, *J* = 96.4 Hz, 1C), 130.4 (d, *J* = 10.7 Hz, 1C), 129.7 (1C), 129.5 (d, *J* = 105.6 Hz, 1C), 129.23 (d, *J* = 8.8 Hz, 1C), 129.18 (1C), 129.1 (2C), 129.0 (2C+1C), 125.1 (d, *J* = 10.5 Hz, 1C), 123.6 (d, *J* = 4.6 Hz, 1C), 60.5 (1C), 14.2 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 36.43; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{25}H_{22}O_3P$: 401.1301, found: 401.1298.



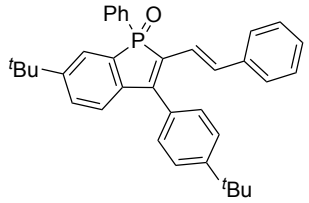
A 92:8 mixture of (*E*)-3-(1-Oxido-1,3-diphenylphosphindol-2-yl)acrylonitrile ((*E*)-3ap) and (*Z*)-3-(1-Oxido-1,3-diphenylphosphindol-2-yl)acrylonitrile ((*Z*)-3ap): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 25 mg (62%, 0.10 mmol scale); Pale yellow solid; m.p. 82.8-84.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) for (*E*)-**3ap**: δ 7.76-7.69 (m, 3H), 7.62-7.45 (m, 8H), 7.40-7.38 (m, 2H), 7.32 (dd, *J* = 7.3, 2.8 Hz, 1H), 7.07 (dd, *J* = 22.2, 16.5 Hz, 1H), 5.90 (dd, *J* = 16.6, 1.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) for (*E*)-**3ap**: δ 157.4 (d, *J* = 19.8 Hz, 1C), 142.1 (d, *J* = 24.6 Hz, 1C), 141.8 (d, *J* = 9.2 Hz, 1C), 133.4 (d, *J* = 2.0 Hz, 1C), 133.0 (d, *J* = 2.9 Hz, 1C), 132.7 (d, *J* = 106.3 Hz, 1C), 131.8 (d, *J* = 12.9 Hz, 1C), 131.0 (d, *J* = 11.0 Hz, 1C), 130.7 (d, *J* = 10.9 Hz, 2C), 130.2 (1C), 130.0 (d, *J* = 96.8 Hz, 1C), 129.42 (d, *J* = 10.0 Hz, 1C), 129.41 (1C), 129.3 (1C), 129.2 (2C), 128.9 (2C), 128.8 (d, *J* = 96.2 Hz, 1C), 125.7 (d, *J* = 10.5 Hz, 1C), 117.9 (1C), 101.3 (d, *J* = 5.6 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) for (*E*)-**3ap**: δ 36.01; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{23}H_{17}NOP$: 354.1042, found: 354.1044.



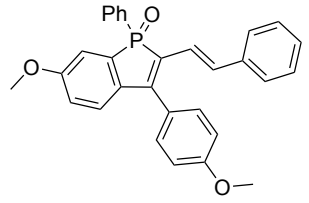
Diethyl (E)-(2-(1-oxido-1,3-diphenylphosphindol-2-yl)vinyl)phosphonate (3aq): Purified by GPC ($CHCl_3$): 29 mg (62%, 0.10 mmol scale); Yellow solid; m.p. 129.5-131.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (m, 2H), 7.7 (dd, *J* = 9.7, 7.5 Hz, 1H), 7.58-7.39 (m, 10H), 7.28 (dd, *J* = 7.5, 2.9 Hz, 1H), 7.19 (ddd, *J* = 22.8, 21.7, 17.4 Hz, 1H), 6.33 (dd, *J* = 17.4, 17.4 Hz, 1H), 3.99 (qd, *J* = 7.2, 7.1 Hz, 2H), 3.78 (dqd, *J* = 10.1, 7.6, 7.1 Hz, 1H), 3.68 (dqd, *J* = 10.1, 7.3, 7.1 Hz, 1H), 1,25 (t, *J* = 7.0 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.0 (d, *J* = 20.6 Hz, 1C), 142.5 (dd, *J* = 25.7, 2.2 Hz, 1C), 139.7 (dd, *J* = 9.1, 7.6 Hz, 1C), 133.2 (d, *J* = 1.8 Hz, 1C), 132.8 (d, *J* = 105.6 Hz, 1C), 132.3 (d, *J* = 13.6 Hz, 1C), 132.5 (d, *J* = 2.8 Hz, 1C), 131.0 (dd, *J* = 96.9, 26.4 Hz, 1C), 130.8 (d, *J* = 10.8 Hz, 2C), 130.4 (d, *J* = 10.5 Hz, 1C), 129.8 (1C), 129.6 (d, *J* = 105.7 Hz, 1C), 129.2 (d, *J* = 9.9 Hz, 1C), 129.1 (3C), 129.0 (3C), 125.2 (d, *J* = 10.6 Hz, 1C), 120.7 (dd, *J* = 185.7, 4.7 Hz, 1C), 61.9 (d, *J* = 5.3 Hz, 1C), 61.7 (d, 5.2 Hz, 1C), 16.3 (d, *J* = 6.6 Hz, 1C), 16.1 (d, *J* = 6.4 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 36.66 (d, *J* = 3.9 Hz), 17.52 (d, *J* = 3.9 Hz); HRMS (APCI) m/z ([M+H]$^+$) calcd for $C_{26}H_{27}O_4P_2$: 465.1379, found: 465.1399.



(*E*)-6-Methyl-1-phenyl-2-styryl-3-(*p*-tolyl)phosphindole 1-oxide (3ba): Purified by silica gel column chromatography with hexane/ethyl acetate (1/1, v/v): 36 mg (80%, 0.10 mmol scale); Yellow solid; m.p. 101.1-102.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 2H), 7.54-7.42 (m, 4H), 7.38-7.33 (m, 4H), 7.27-7.10 (m, 8H), 6.90 (dd, *J* = 23.7, 16.4 Hz, 1H), 2.48 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.0 (d, *J* = 21.4 Hz, 1C), 141.0 (d, *J* = 26.0 Hz, 1C), 139.4 (d, *J* = 10.5 Hz, 1C), 138.9 (1C), 137.1 (1C), 134.4 (d, *J* = 5.2 Hz, 1C), 133.4 (d, *J* = 1.6 Hz, 1C), 132.6 (d, *J* = 105.5 Hz, 1C), 132.1 (d, *J* = 2.7 Hz, 1C), 131.5 (d, *J* = 96.2 Hz, 1C), 131.0 (d, *J* = 98.7 Hz, 1C), 130.8 (d, *J* = 10.5 Hz, 2C), 130.7 (d, *J* = 13.7 Hz, 1C), 129.7 (d, *J* = 9.7 Hz, 1C), 129.5 (2C), 129.2 (2C), 129.0 (1C), 128.9 (1C), 128.4 (2C), 128.0 (1C), 126.7 (2C), 123.7 (d, *J* = 11.1 Hz, 1C), 121.2 (d, *J* = 9.4 Hz, 1C), 21.5 (1C), 21.3 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.60; HRMS (APCI) m/z ([M+H]$^+$) calcd for $C_{30}H_{26}OP$: 433.1716, found: 433.1713.

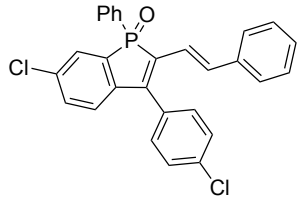


(*E*)-6-(*tert*-Butyl)-3-(4-(*tert*-butyl)phenyl)-1-phenyl-2-styrylphosphindole 1-oxide (3ca): Purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v): 30 mg (58%, 0.10 mmol scale); Yellow solid; m.p. 124.5-126.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.82 (m, 2H), 7.72 (dd, *J* = 10.8, 1.72 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.51-7.44 (m, 4H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.29-7.12 (m, 7H), 6.94 (dd, *J* = 23.6, 16.4 Hz, 1H), 1.42 (s, 9H), 1.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.7 (d, *J* = 9.3 Hz, 1C), 152.1 (1C), 149.6 (d, *J* = 21.2 Hz, 1C), 141.1 (d, *J* = 26.1 Hz, 1C), 137.2 (1C), 134.5 (d, *J* = 5.3 Hz, 1C), 132.3 (d, *J* = 105.5 Hz, 1C), 132.1 (d, *J* = 2.8 Hz, 1C), 131.8 (d, *J* = 96.3 Hz, 1C), 131.1 (d, *J* = 98.4 Hz, 1C), 130.9 (d, *J* = 10.9 Hz, 2C), 130.6 (d, *J* = 14.4 Hz, 1C), 129.9 (d, *J* = 1.6 Hz, 1C), 129.0 (2C), 128.9 (1C), 128.8 (1C), 128.4 (2C), 127.9 (1C), 126.8 (2C), 126.0 (d, *J* = 10.0 Hz, 1C), 125.7 (2C), 123.7 (d, *J* = 11.4 Hz, 1C), 121.3 (d, *J* = 9.4 Hz, 1C), 35.1 (1C), 34.9 (1C), 31.4 (3C), 31.2 (3C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 38.09; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{36}H_{38}OP$: 517.2655, found: 517.2662.

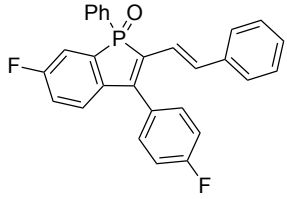


(*E*)-6-Methoxy-3-(4-methoxyphenyl)-1-phenyl-2-styrylphosphindole 1-oxide (3da): Purified by silica gel column chromatography with hexane/ethyl acetate (1/1, v/v): 35 mg (74%, 0.10 mmol scale); Yellow solid; m.p. 94.5-96.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 2H), 7.54-7.42 (m, 3H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.27-7.13 (m, 7H), 7.083 (d, *J* = 8.8 Hz, 2H), 7.078 (d, *J* = 16.3 Hz, 1H), 6.92 (dd, *J* = 8.6, 0.76 Hz, 1H), 6.89 (dd, *J* = 24.0, 16.4 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.7 (d, *J* = 13.4 Hz, 1C), 160.1 (1C), 149.7 (d, *J* = 21.2 Hz, 1C), 137.2 (1C), 136.1 (d, *J* = 25.7 Hz, 1C), 134.6 (d, *J* = 104.4 Hz, 1C), 133.5 (d, *J* = 5.3 Hz, 1C), 132.2 (d, *J* = 2.8 Hz, 1C), 130.9 (d, *J* = 98.6 Hz, 1C), 130.8 (d, *J* = 10.8 Hz, 2C), 130.6 (2C), 130.1 (d, *J* = 97.9 Hz, 1C), 129.0 (1C), 128.9 (1C), 128.5 (2C), 127.8 (1C), 126.6 (2C), 125.9 (d, *J* = 14.7 Hz, 1C), 125.0 (d, *J* = 12.5 Hz, 1C), 121.3 (d, *J* = 9.7 Hz, 1C), 118.1 (d, *J* = 1.4 Hz, 1C), 114.5 (d, *J* = 11.0 Hz, 1C), 114.2

(2C), 55.7 (1C), 55.4 (1C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 37.29; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{30}H_{26}O_3P$: 465.1614, found: 465.1614.

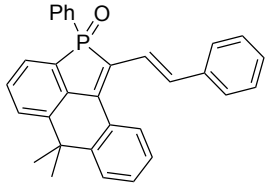


(*E*)-6-Chloro-3-(4-chlorophenyl)-1-phenyl-2-styrylphosphindole 1-oxide (3ea): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 42 mg (86%, 0.10 mmol scale); Yellow solid; m.p. 181.3-183.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.80 (m, 2H), 7.62 (dd, *J* = 10.0, 2.0 Hz, 1H), 7.58-7.53 (m, 3H), 7.50-7.46 (m, 2H), 7.41-7.38 (m, 3H), 7.28-7.19 (m, 5H), 7.17 (dd, *J* = 16.3, 0.72 Hz, 1H), 7.09 (dd, *J* = 8.2, 3.3 Hz, 1H), 6.81 (dd, *J* = 24.0, 16.3 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2 (d, *J* = 20.1 Hz, 1C), 141.4 (d, *J* = 25.3 Hz, 1C), 136.5 (1C), 136.4 (d, *J* = 5.3 Hz, 1C), 135.5 (d, *J* = 14.3 Hz, 1C), 135.3 (1C), 134.4 (d, *J* = 103.6 Hz, 1C), 133.6 (d, *J* = 95.0 Hz, 1C), 132.9 (d, *J* = 1.7 Hz, 1C), 132.7 (d, *J* = 2.8 Hz, 1C), 131.6 (d, *J* = 14.5 Hz, 1C), 130.7 (d, *J* = 10.9 Hz, 2C), 130.6 (2C), 129.7 (d, *J* = 100.1 Hz, 1C),129.4 (2C), 129.4 (1C), 129.3 (1C), 129.1 (1C), 128.6 (3C), 126.9 (2C), 124.5 (d, *J* = 11.4 Hz, 1C), 120.2 (d, *J* = 9.1 Hz, 1C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 36.60; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{28}H_{20}Cl_2OP$: 473.0623, found: 473.0632.

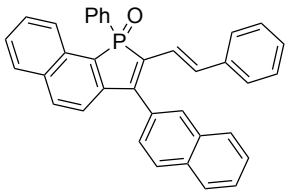


(*E*)-6-Fluoro-3-(4-fluorophenyl)-1-phenyl-2-styrylphosphindole 1-oxide (3fa): Purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v) and GPC ($CHCl_3$): 21 mg (47%, 0.10 mmol scale); Yellow solid; m.p. 234.7-236.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.80 (m, 2H), 7.58-7.53 (m, 1H), 7.50-7.41 (m, 4H), 7.40-7.36 (m, 1H), 7.30-7.09 (m, 10H), 6.80 (dd, *J* = 24.1, 16.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.4 (dd, *J* = 251.7, 15.4 Hz, 1C), 163.1 (d, *J* = 248.0 Hz, 1C), 147.7 (dd, *J* = 20.8, 1.7 Hz, 1C), 139.2 (dd, *J* = 25.3, 3.1 Hz, 1C), 136.7 (1C), 135.6 (d, *J* = 5.8 Hz, 1C), 135.0 (dd, *J* = 104.4, 6.6 Hz, 1C), 133.1 (dd, *J* = 96.5, 3.6 Hz, 1C), 132.6 (d, *J* = 2.9 Hz, 1C), 131.1 (d, *J* = 7.9 Hz, 2C), 130.7 (d, *J* = 10.8 Hz, 2C), 129.8 (d, *J* = 99.8 Hz, 1C), 129.3 (dd, *J* = 15.7, 2.4 Hz, 1C), 129.2 (1C), 129.1 (1C), 128.6 (2C), 128.4 (1C), 126.8 (2C), 125.1 (dd, *J* = 12.3, 7.7

Hz, 1C), 120.5 (d, J = 9.4 Hz, 1C), 119.6 (d, J = 22.3 Hz, 1C), 116.8 (dd, J = 23.8, 10.6 Hz, 1C), 116.3 (d, J = 21.4 Hz, 2C); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -110.8 (d, J = 5.4 Hz), -111.2; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 36.32 (d, J = 5.4 Hz); HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{26}H_{20}F_2OP$: 441.1214, found: 441.1221.

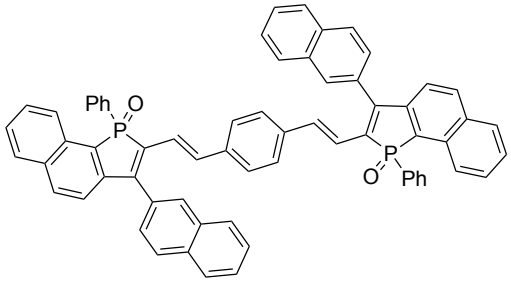


(*E*)-6,6-Dimethyl-2-phenyl-1-styryl-6*H*-naphtho[1,2,3-*cd*]phosphindole 2-oxide (3ga): Purified by GPC ($CHCl_3$): 36 mg (80%, 0.10 mmol scale); Yellow solid; m.p. 119.5-121.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.5 Hz, 1H), 7.80-7.73 (m, 3H), 7.67 (dd, J = 8.0 Hz, 1H), 7.59 (dd, J = 22.5, 16.3 Hz, 1H), 7.56 (dd, J = 9.44, 7.2 Hz, 1H), 7.53-7.45 (m, 3H), 7.43-7.38 (m, 5H), 7.31 (m, 3H), 7.24 (t, J = 7.3 Hz, 1H), 1.75 (s, 3H), 1.71 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2 (1C), 141.3 (d, J = 11.1 Hz, 1C), 139.1 (d, J = 22.1 Hz, 1C), 137.9 (d, J = 28.2 Hz, 1C), 137.2 (d, J = 1.1 Hz, 1C), 135.0 (d, J = 6.5 Hz, 1C), 132.0 (d, J = 2.7 Hz, 1C), 131.5 (d, J = 98.4 Hz, 1C), 130.9 (d, J = 10.4 Hz, 2C), 130.7 (d, J = 105.7 Hz, 1C), 130.3 (1C), 130.0 (d, J = 1.8 Hz, 1C), 129.5 (d, J = 11.4 Hz, 1C), 129.0 (1C), 128.9 (1C), 128.8 (1C), 128.6 (2C), 128.5 (d, J = 16.6 Hz, 1C), 128.1 (1C), 127.8 (d, J = 99.0 Hz, 1C), 127.4 (1C), 127.1 (d, J = 9.4 Hz, 1C), 126.8 (2C), 126.6 (1C), 122.1 (d, J = 8.0 Hz, 1C), 39.0 (d, J = 1.1 Hz, 1C), 33.1 (1C), 32.7 (1C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 39.56; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{31}H_{26}OP$: 445.1716, found: 445.1731.



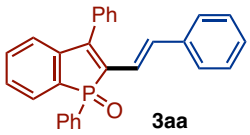
(*E*)-3-(Naphthalen-2-yl)-1-phenyl-2-styrylbenzo[*g*]phosphindole 1-oxide (3ha): Purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v): 47 mg (92%, 0.10 mmol scale); Yellow solid; m.p. 152.9-154.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.00-7.92 (m, 6H), 7.81 (d, J = 7.9 Hz, 1H), 7.64-7.58 (m, 3H), 7.52-7.42 (m, 5H), 7.38 (dd, J = 8.5, 2.6 Hz, 1H), 7.31-7.13 (m, 6H), 6.96 (dd, J = 24.1, 16.3 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 149.0 (d, J = 22.5 Hz, 1C), 143.0 (d, J = 24.8 Hz, 1C), 136.9 (1C), 135.2 (d, J = 5.1 Hz,

1C), 134.1 (d, J = 95.2 Hz, 1C), 133.8 (d, J = 2.0 Hz, 1C), 133.6 (d, J = 8.4 Hz, 1C), 133.4 (2C), 132.2 (d, J = 2.7 Hz, 1C), 131.9 (d, J = 9.3 Hz, 1C), 131.3 (d, J = 14.6 Hz, 1C), 130.9 (d, J = 97.3 Hz, 1C), 130.7 (d, J = 10.8 Hz, 2C), 129.2 (1C), 129.1 (1C), 128.77 (1C), 128.76 (1C), 128.72 (1C), 128.5 (4C), 128.2 (1C), 128.0 (1C), 127.7 (d, J = 100.0 Hz, 1C), 127.0 (1C), 126.9 (2C), 126.8 (3C), 125.6 (d, J = 5.0 Hz, 1C), 121.3 (d, J = 12.2 Hz, 1C), 120.9 (d, J = 10.3 Hz, 1C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 38.34; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{36}H_{26}OP$: 505.1716, found: 505.1733.



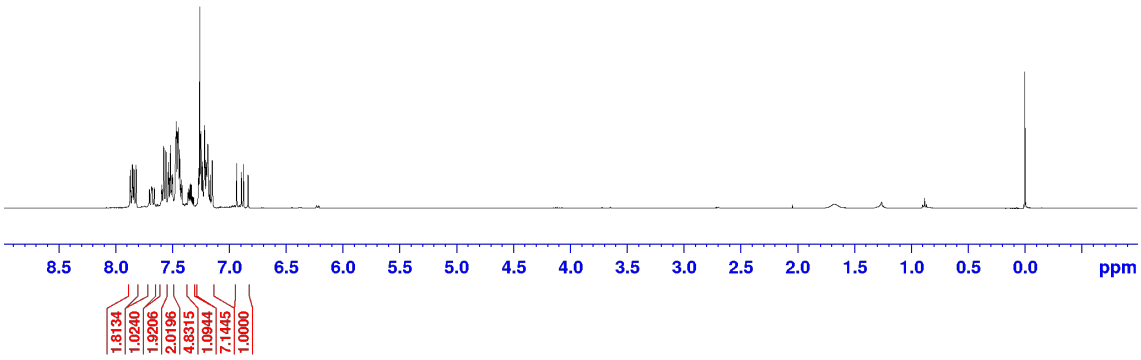
2,2'-((1*E*,1'*E*)-1,4-Phenylenebis(ethene-2,1-diyl))bis(3-(naphthalen-2-yl)-1-phenylbenzo[*g*]phosphindole 1-oxide) (a 1:1 mixture of diastereomers) (3hm): Purified by GPC ($CHCl_3$): 29 mg (61%, 0.050 mmol scale); Red solid; m.p. 229.8-230.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2H), 8.03 (dd, J = 8.4, 2.8 Hz, 2H), 7.98-7.89 (m, 12H), 7.80 (d, J = 7.9 Hz, 2H), 7.63-7.54 (m, 6H), 7.49-7.41 (m, 10H), 7.36 (dd, J = 8.5, 1.8 Hz, 2H), 7.17 (d, J = 16.2 Hz, 2H), 7.07 (d, J = 2.2 Hz, 4H), 6.89 (dd, J = 24.1, 16.3 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 149.2 (d, J = 22.5 Hz, 2C), 143.0 (d, J = 24.8 Hz, 2C), 136.9 (2C), 134.5 (d, J = 5.4 Hz, 2C), 134.1 (d, J = 94.4 Hz, 2C), 133.8 (2C), 133.6 (d, J = 9.0 Hz, 2C), 133.34 (2C), 133.30 (2C), 132.3 (2C), 131.9 (d, J = 9.1 Hz, 2C), 131.2 (d, J = 14.7 Hz, 2C), 130.9 (d, J = 97.6 Hz, 2C), 130.7 (d, J = 10.8 Hz, 4C), 129.2 (2C), 129.1 (2C), 128.8 (4C), 128.7 (2C), 128.5 (2C), 128.3 (2C), 128.0 (2C), 127.7 (d, J = 103.9 Hz, 2C), 127.0 (6C), 126.8 (4C), 126.7 (2C), 125.5 (d, J = 4.9 Hz, 2C), 121.3 (d, J = 12.1 Hz, 2C), 121.2 (d, J = 9.8 Hz, 2C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 38.23, 38.21; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{66}H_{45}O_2P_2$: 931.2889, found: 931.2889.

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3aa**]

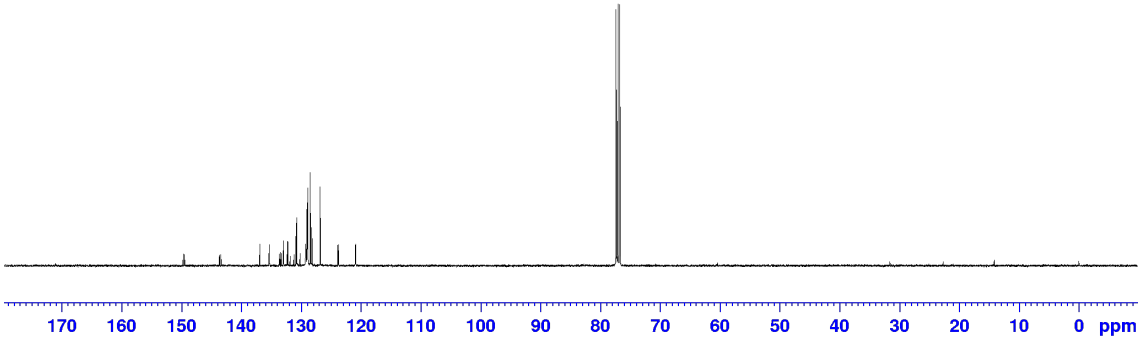


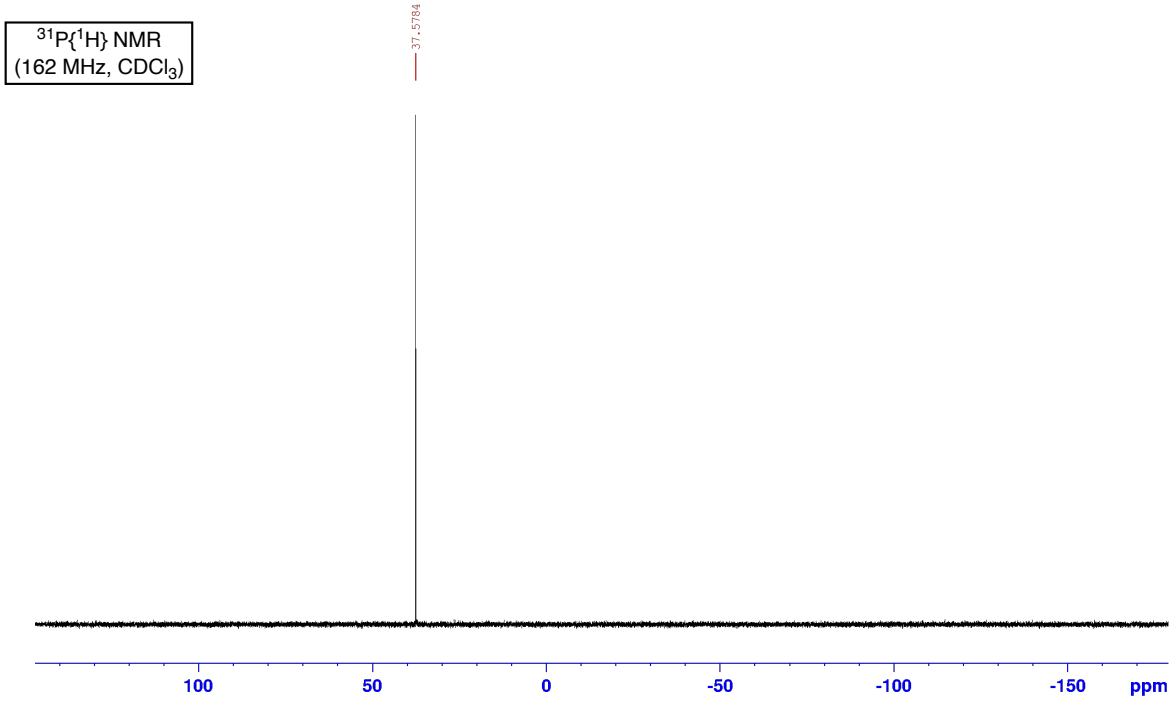
3aa

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

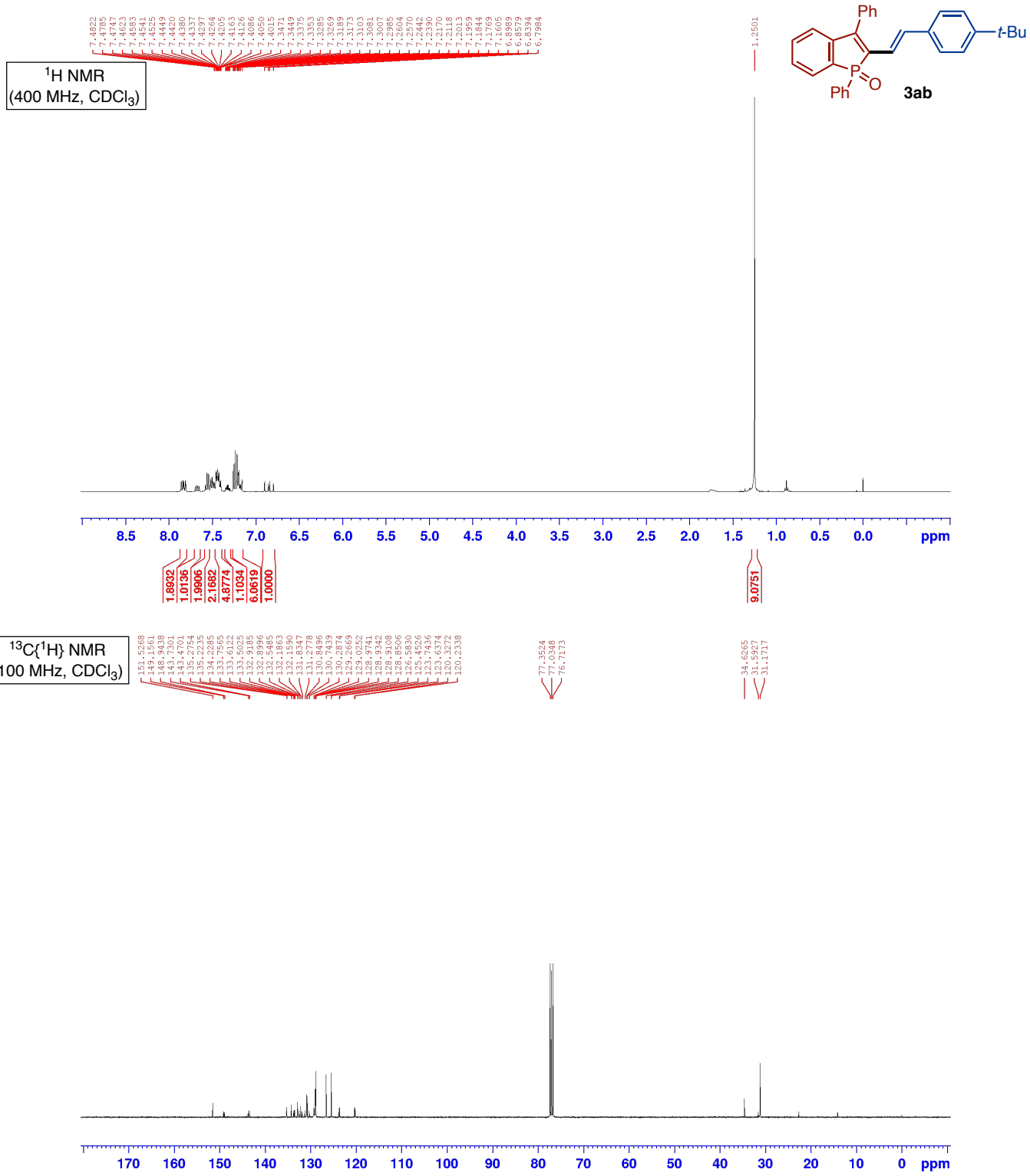


^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)

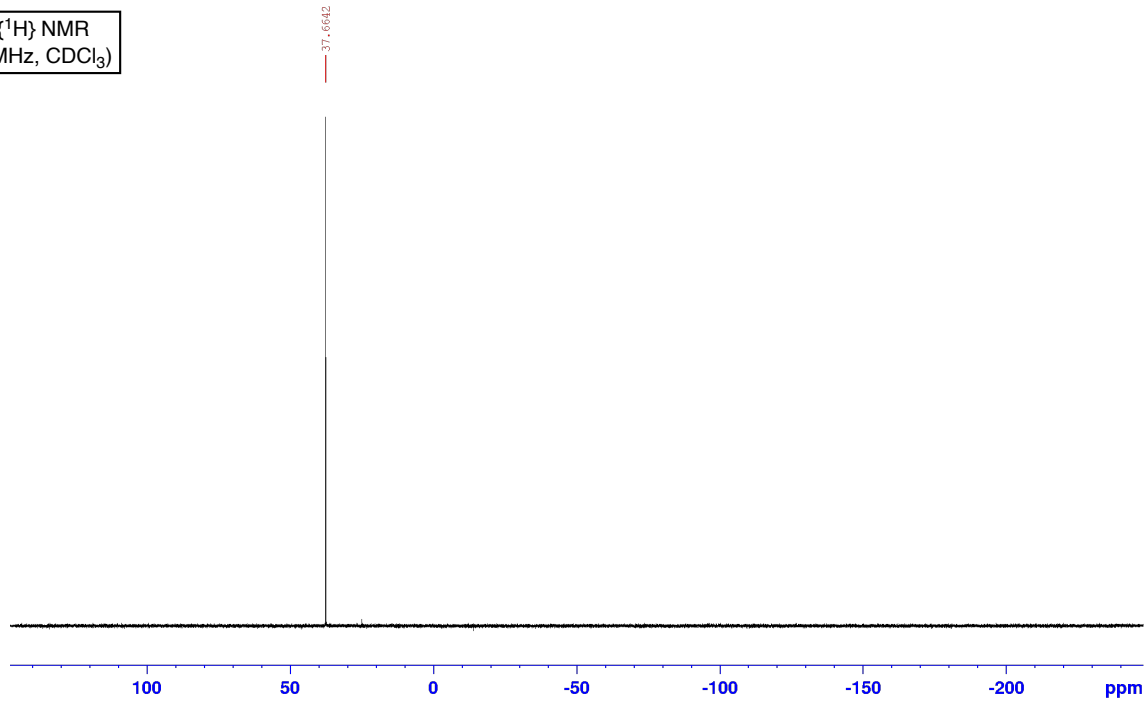



31P{1H} NMR
(162 MHz, CDCl3)
37.5784
100
50
0
-50
-100
-150
ppm

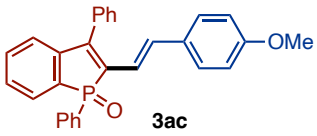
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ab**]



$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

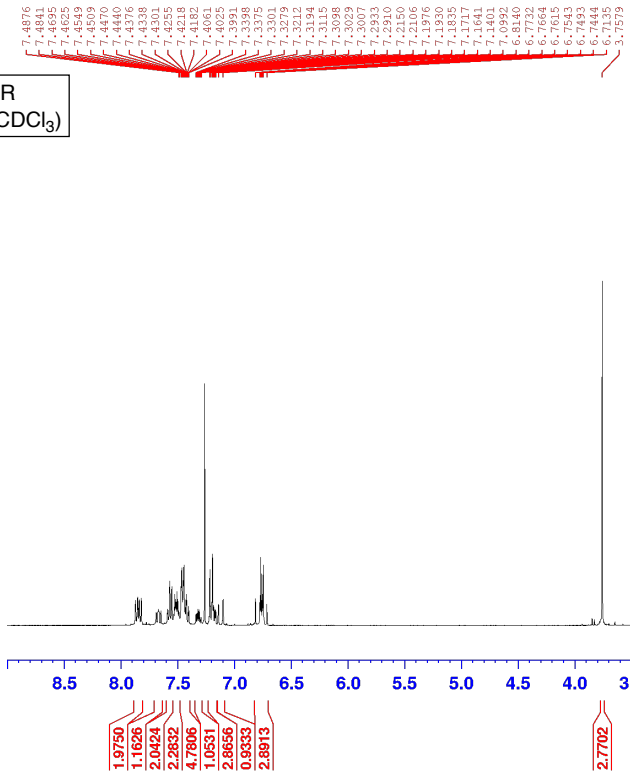


[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ac**]

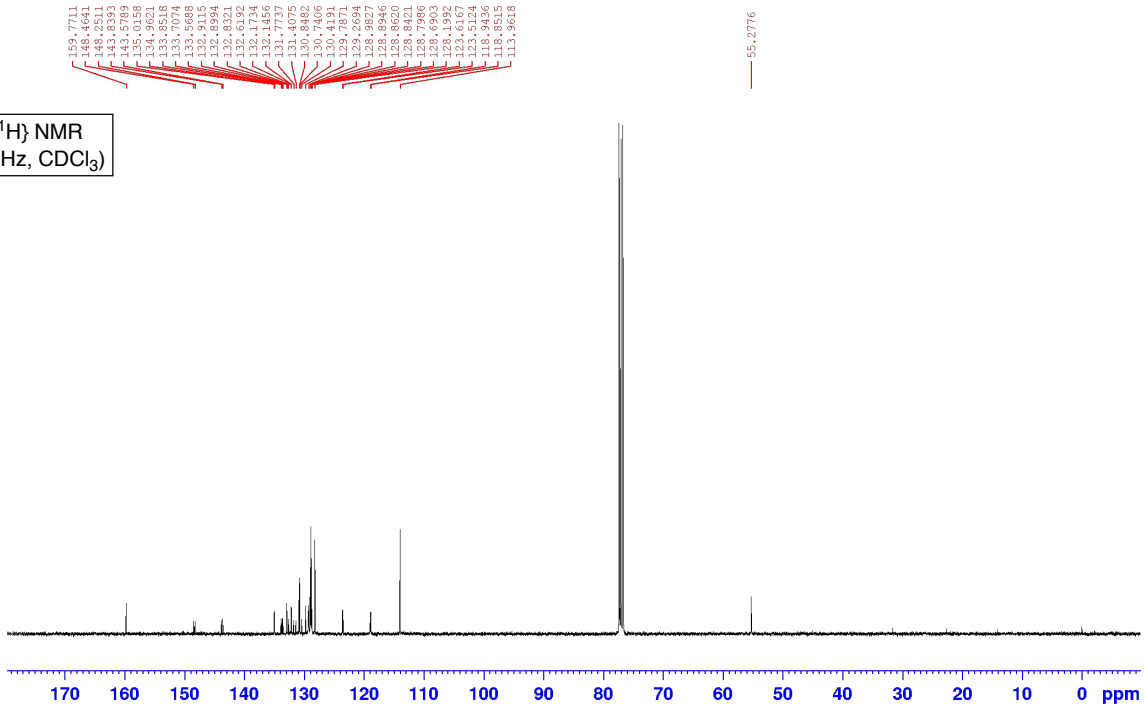


3ac

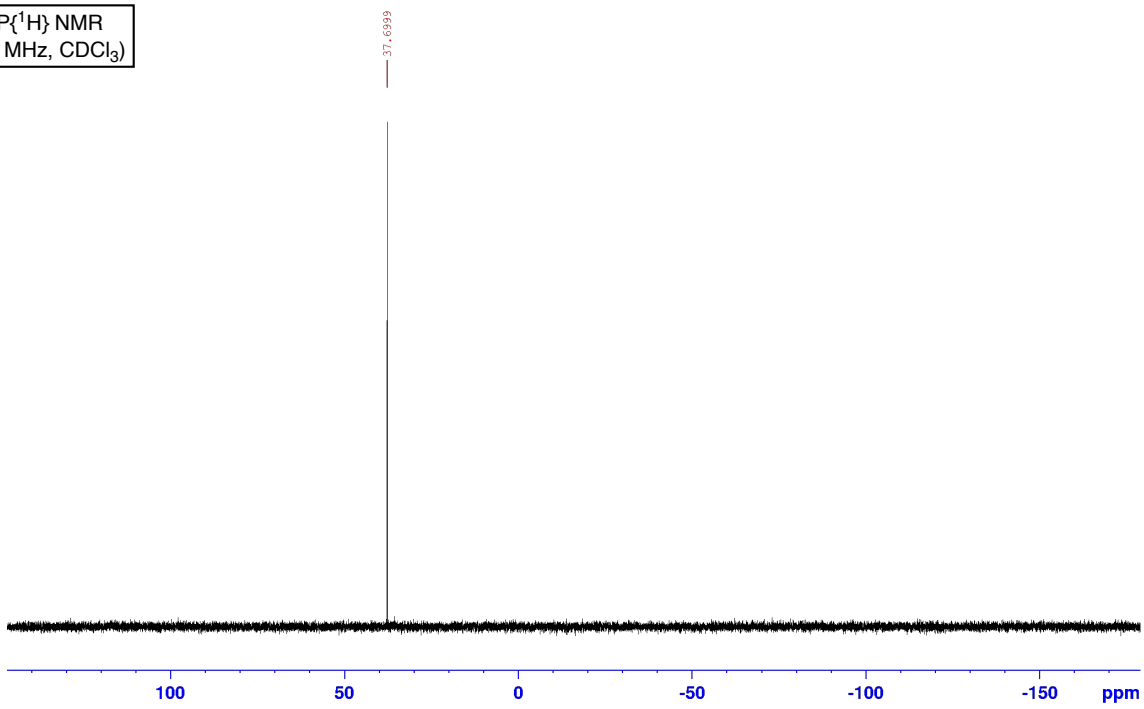
^{1}H NMR
(400 MHz, $CDCl_3$)



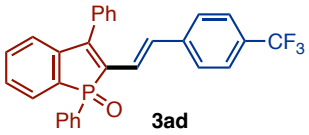
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

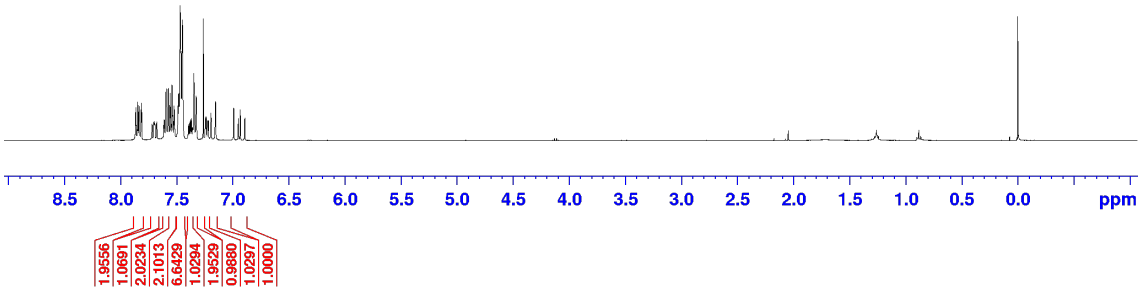


[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ad**]

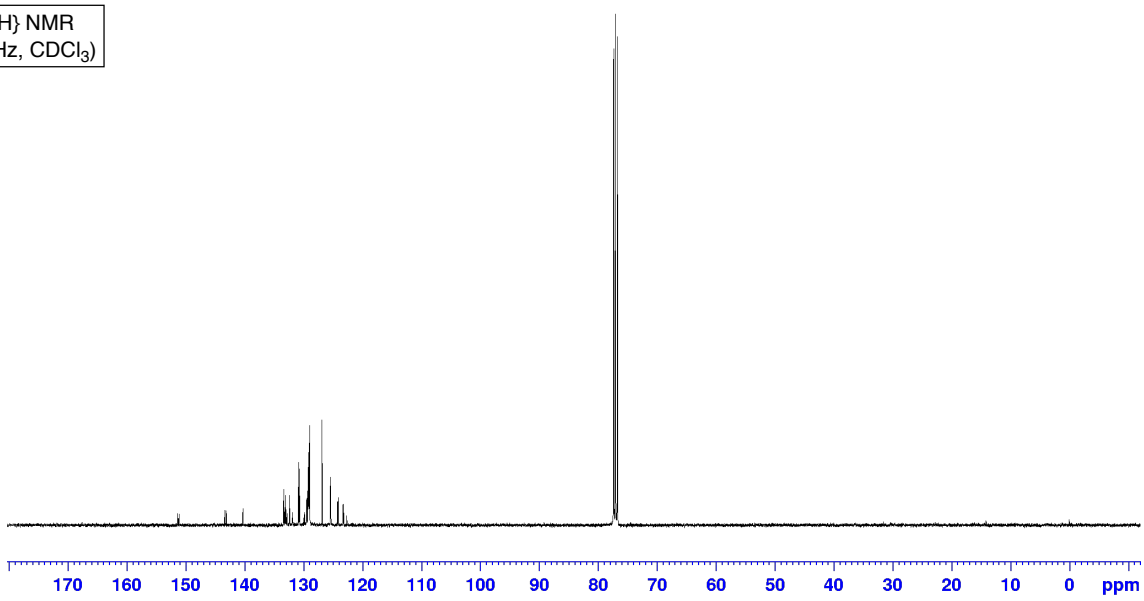


3ad

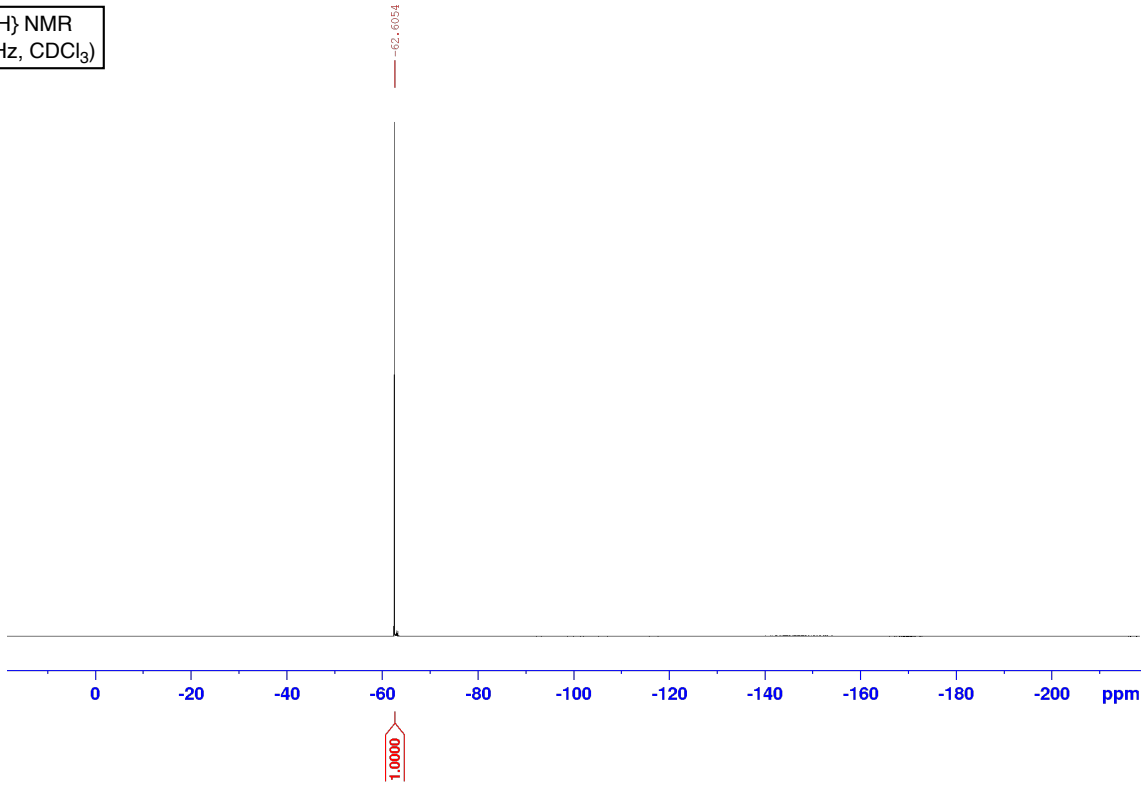
^{1}H NMR
(400 MHz, $CDCl_3$)



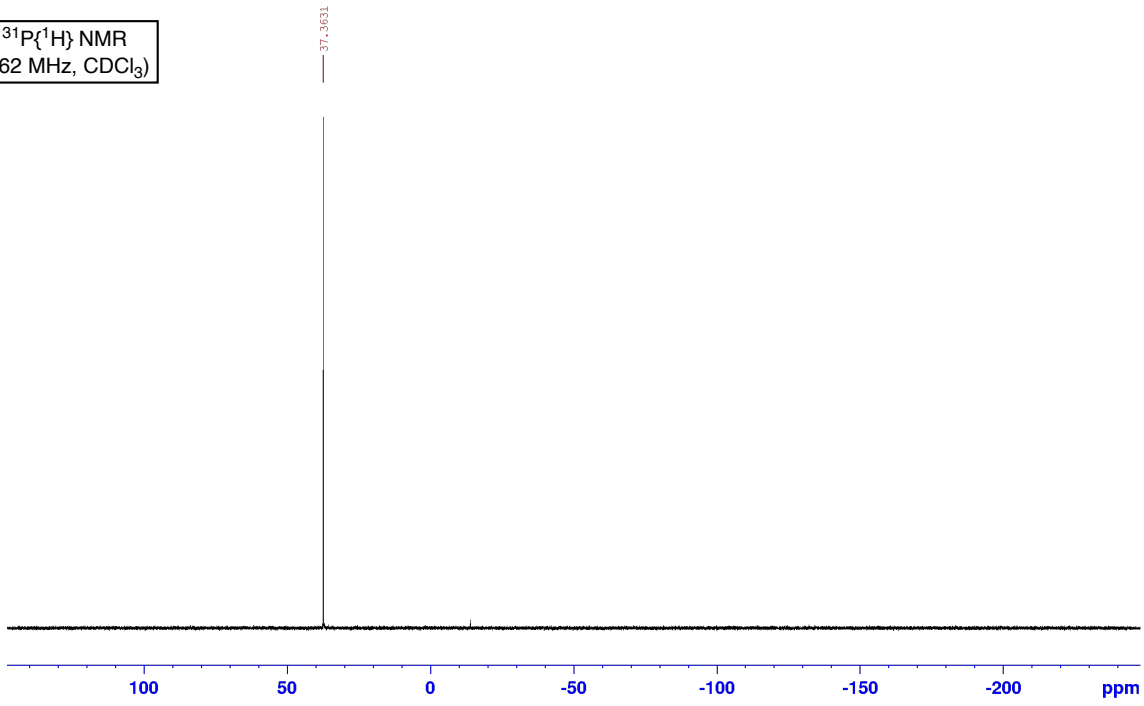
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



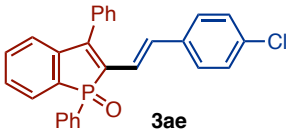
$^{19}F\{^{1}H\}$ NMR
(376 MHz, $CDCl_3$)



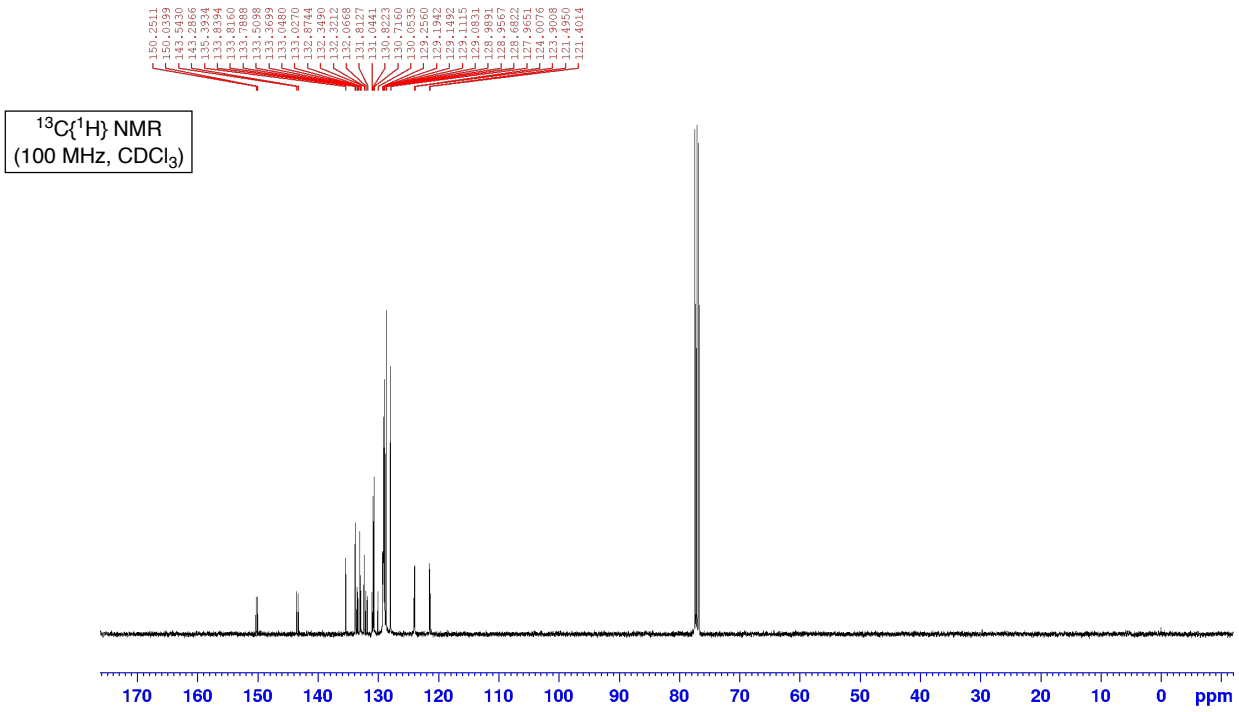
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

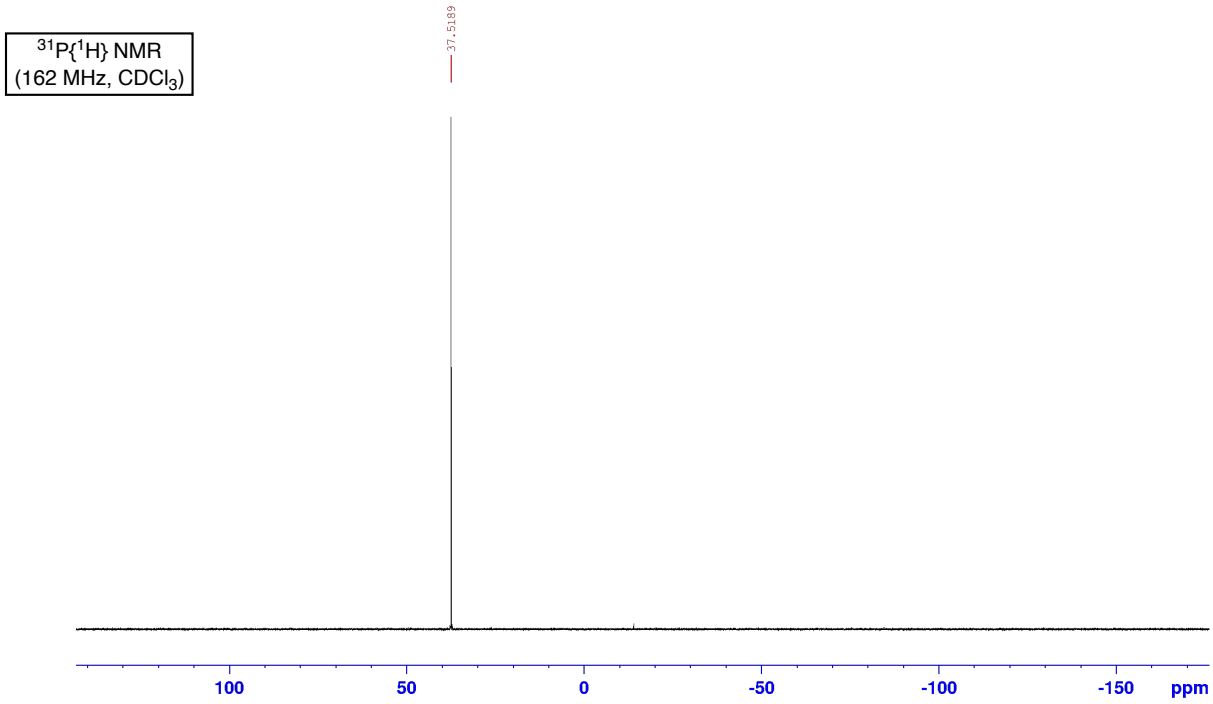


[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ae**]

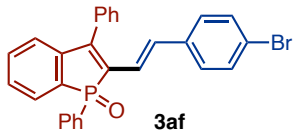


3ae



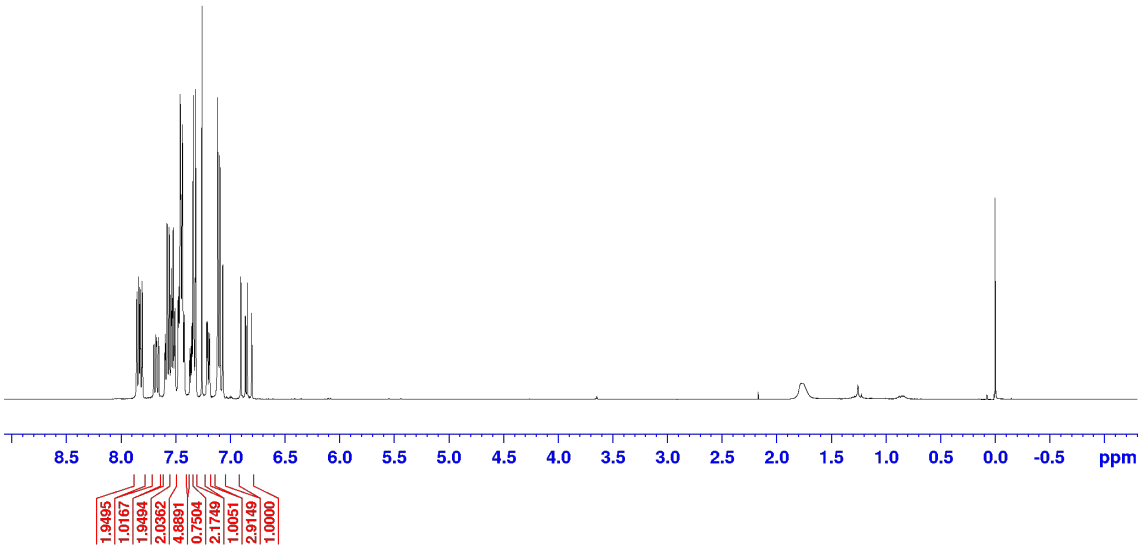

$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)
37.5189
100
50
0
-50
-100
-150
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3af**]

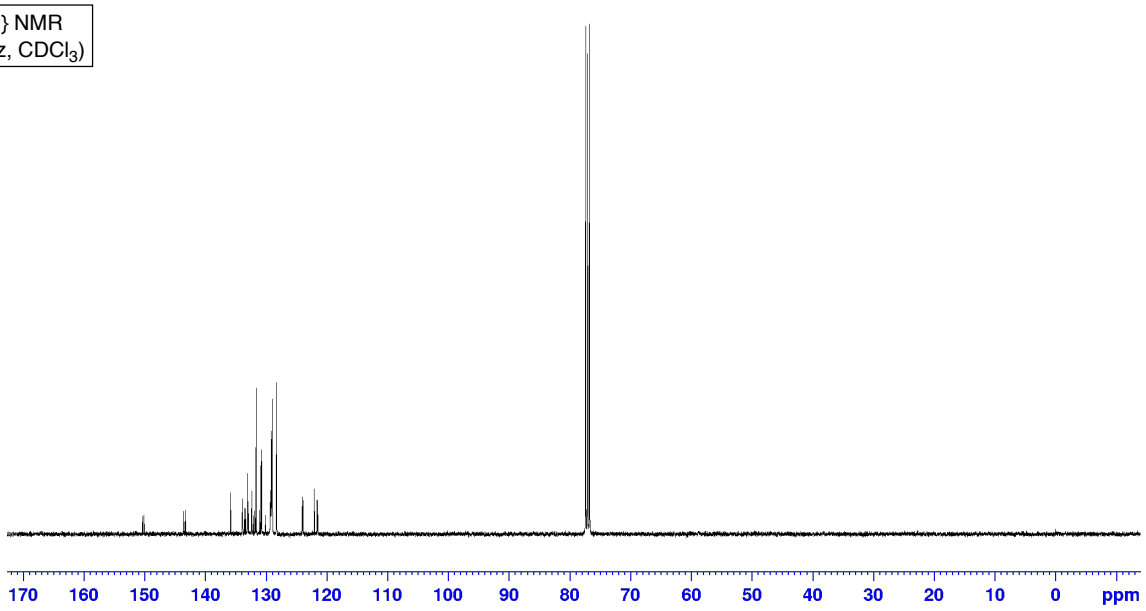


3af

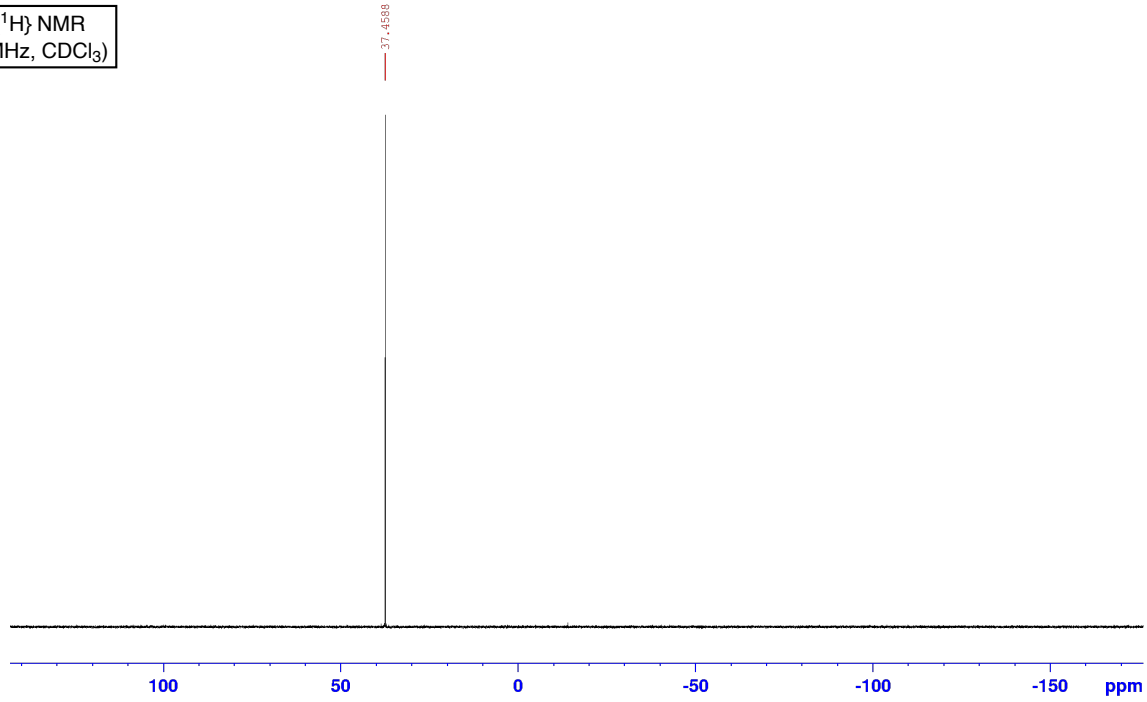
^{1}H NMR
(400 MHz, $CDCl_3$)



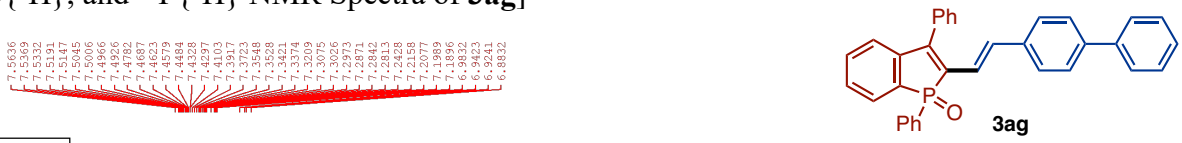
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



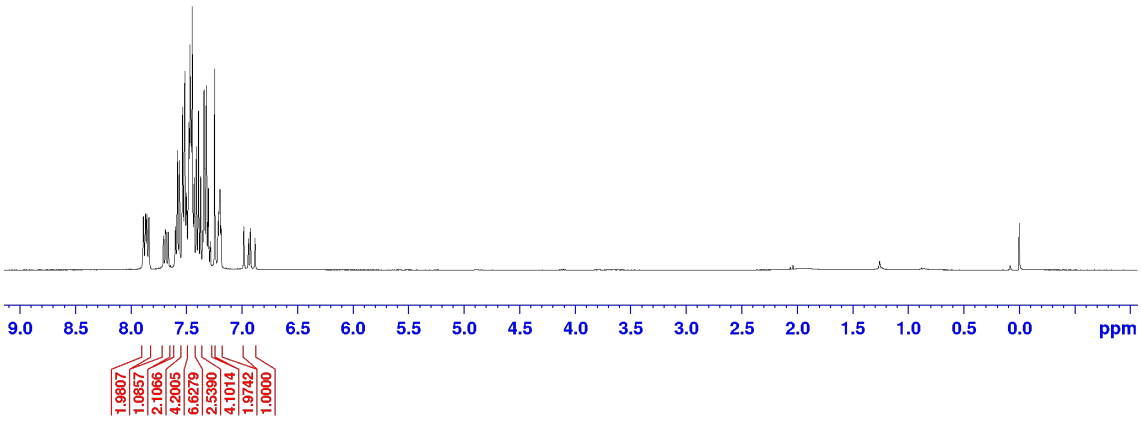
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



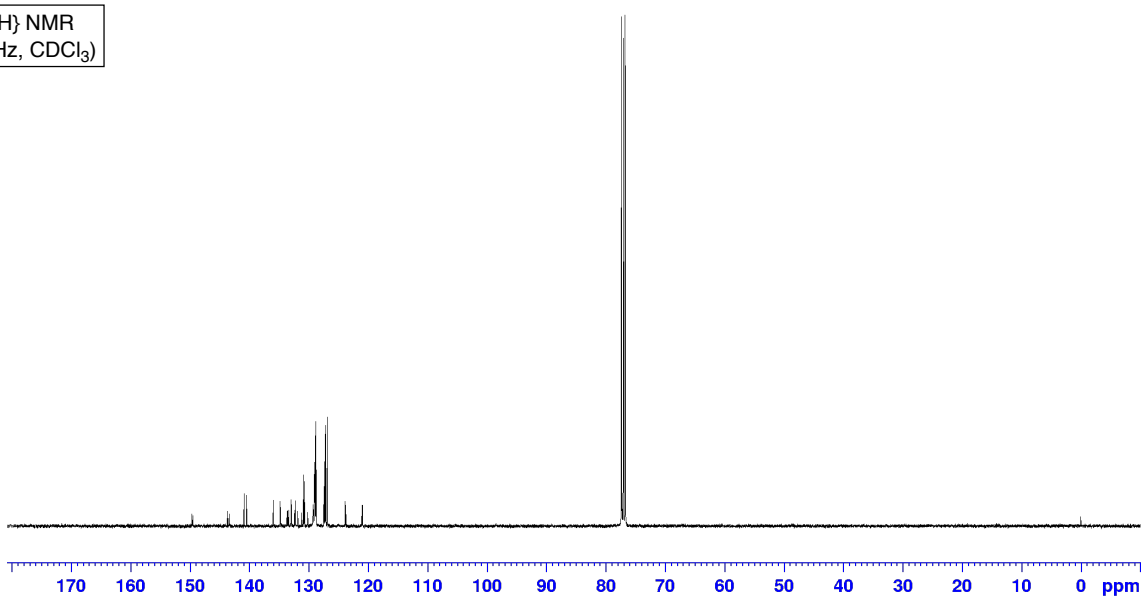
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ag**]

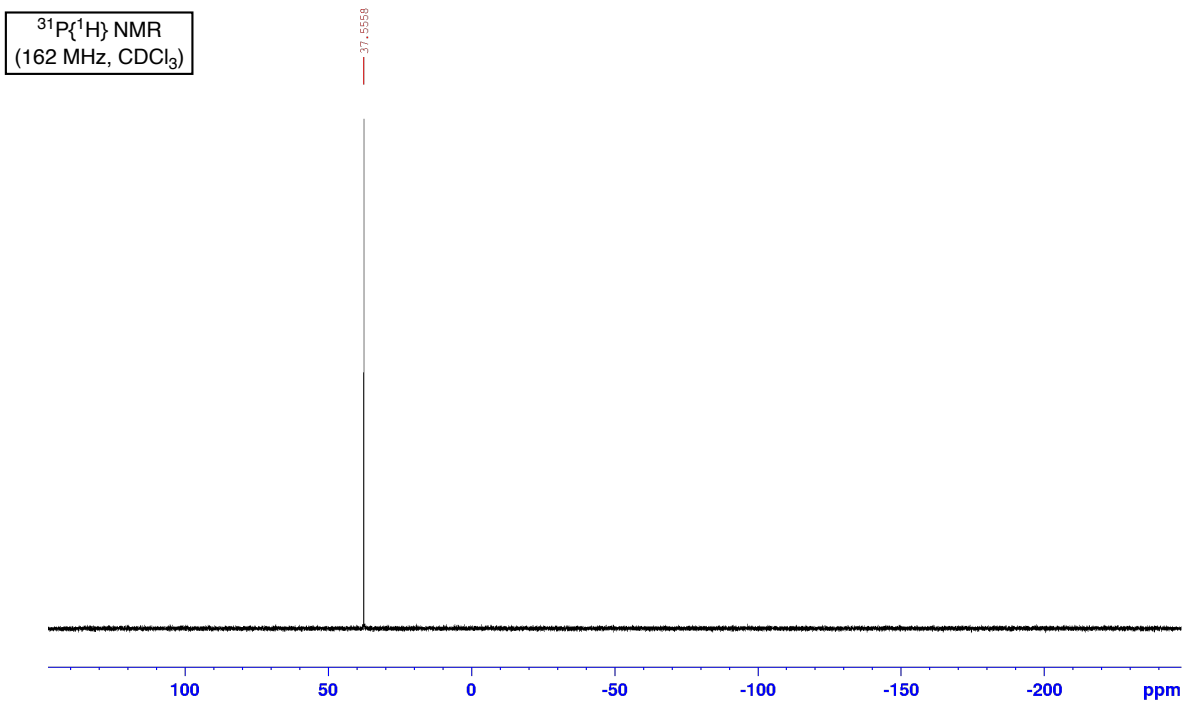


^{1}H NMR
(400 MHz, $CDCl_3$)

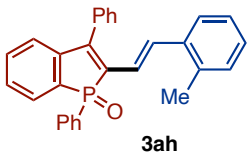


^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)




$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)
37.5558
100
50
0
-50
-100
-150
-200
ppm

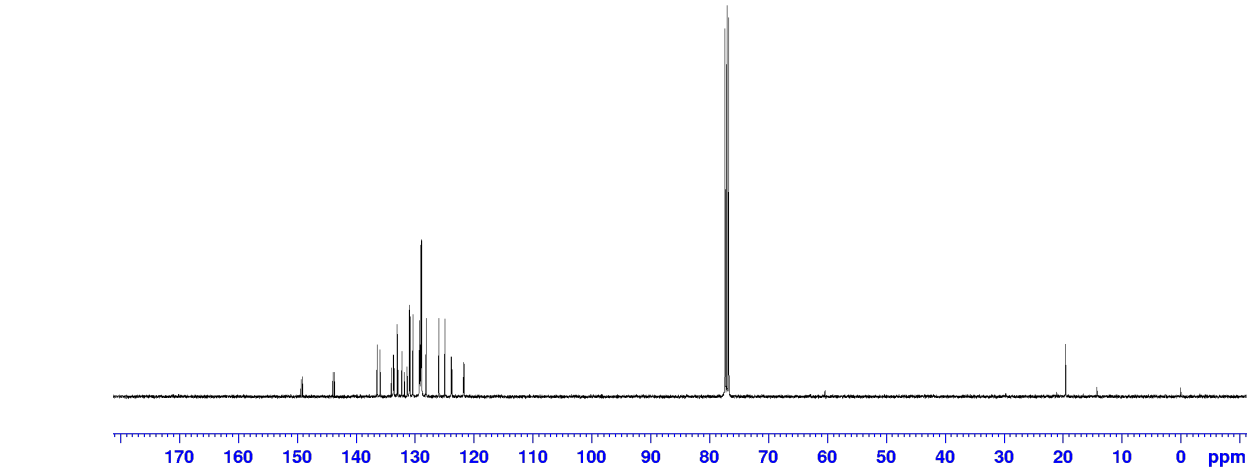
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ah**]

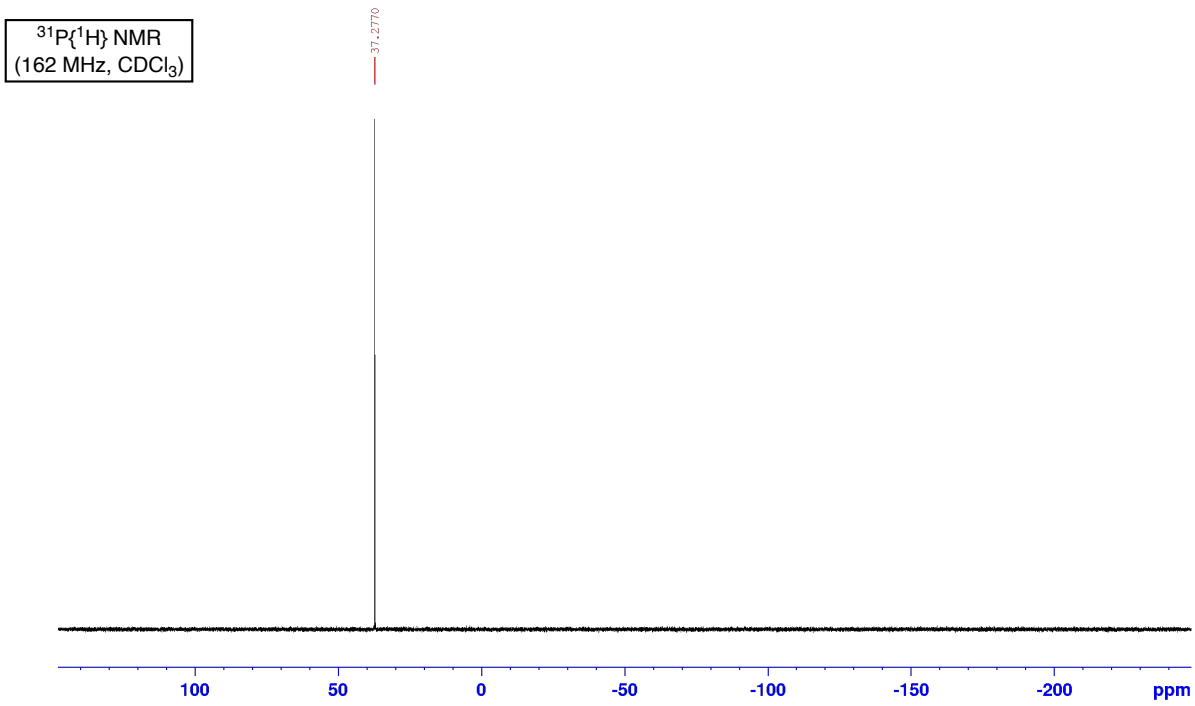


3ah

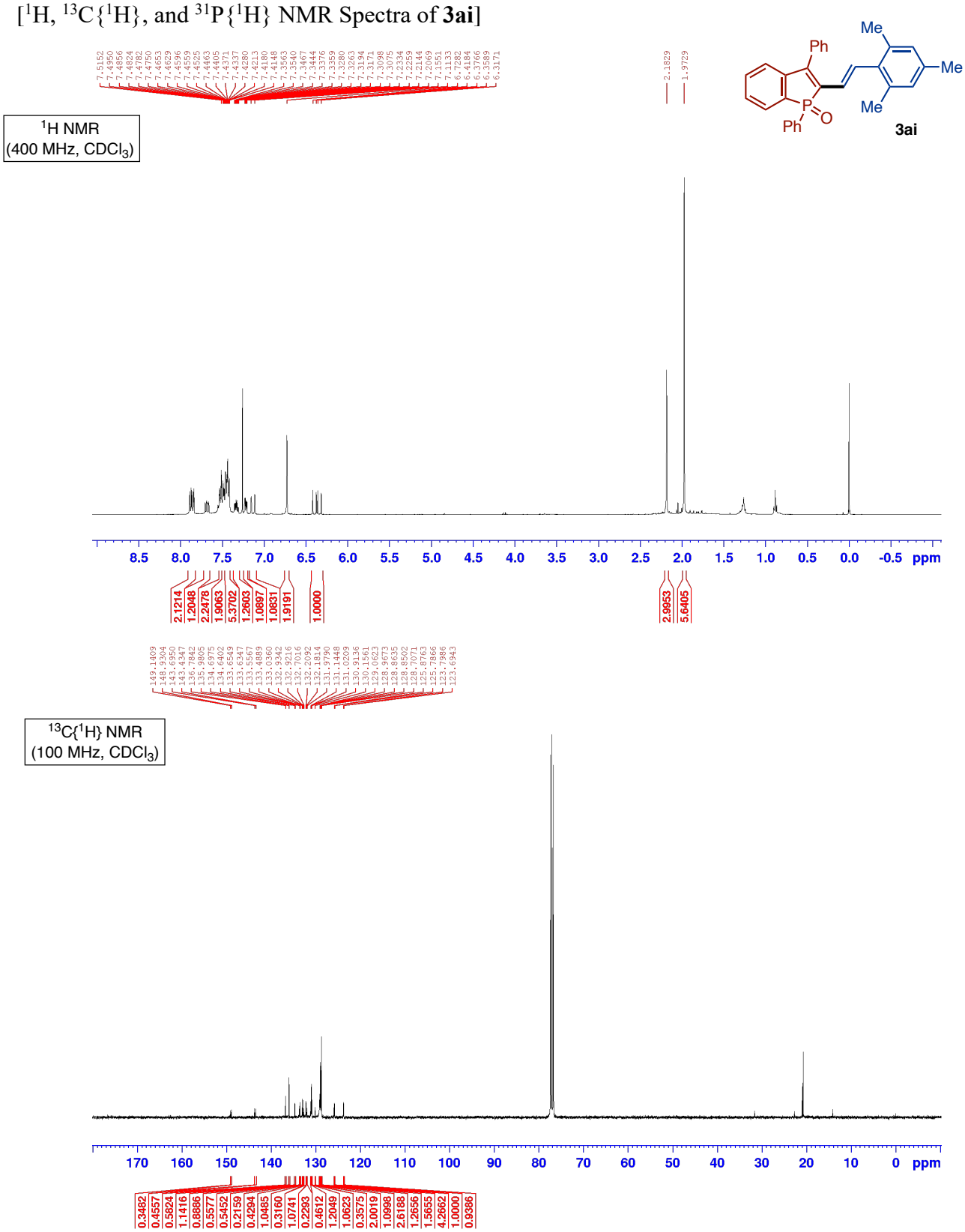
^{1}H NMR
(400 MHz, $CDCl_3$)

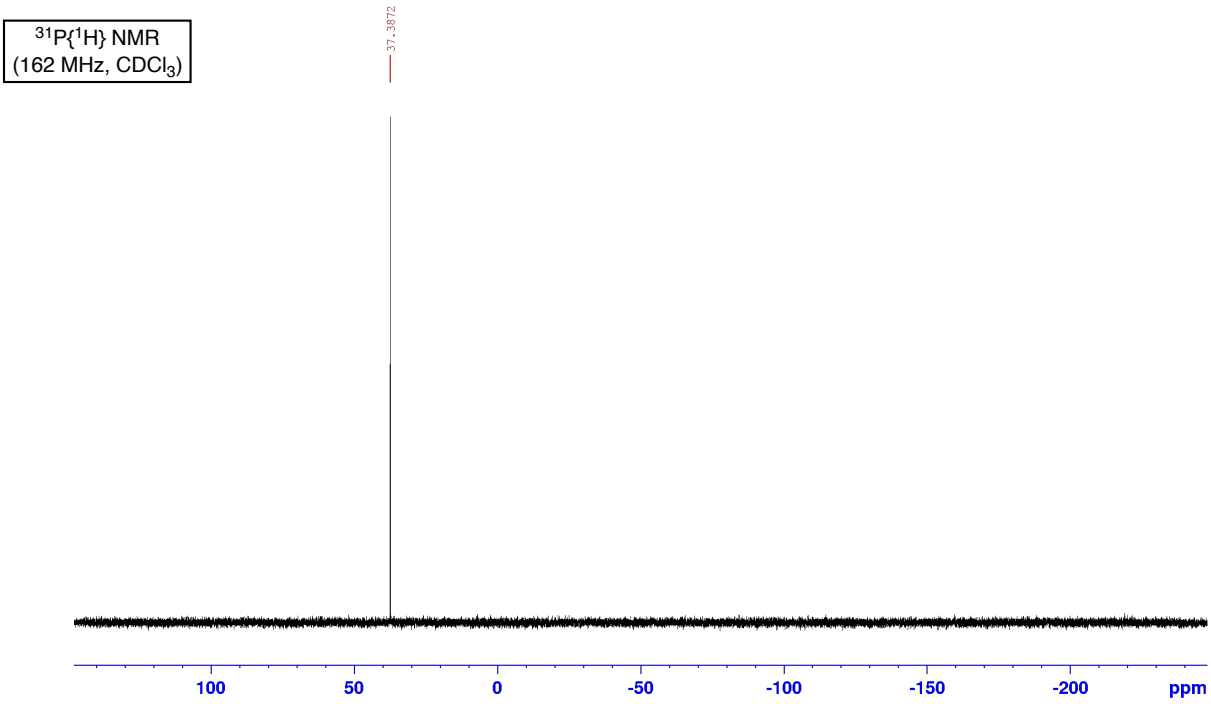
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



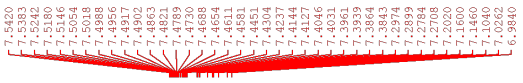

$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)
37.2770
100
50
0
-50
-100
-150
-200
ppm

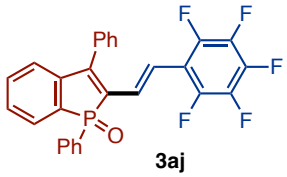
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ai**]




31P{1H} NMR
(162 MHz, CDCl3)
37.3872
100
50
0
-50
-100
-150
-200
ppm

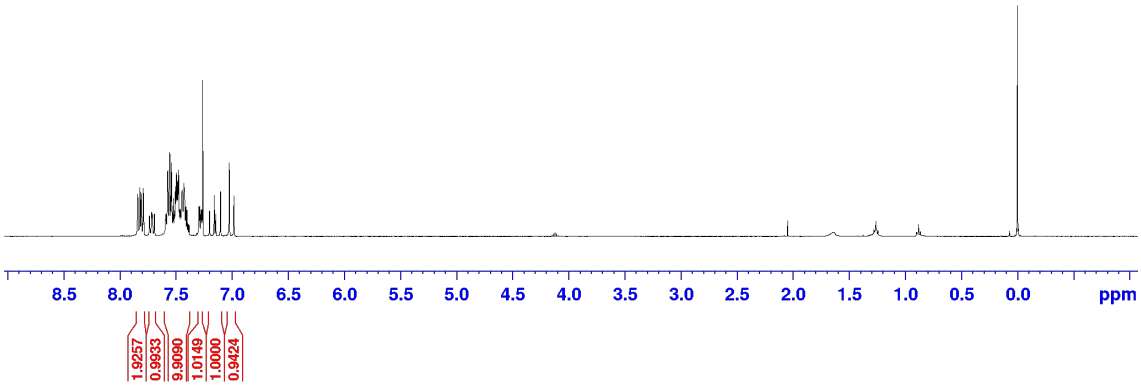
[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3aj**]

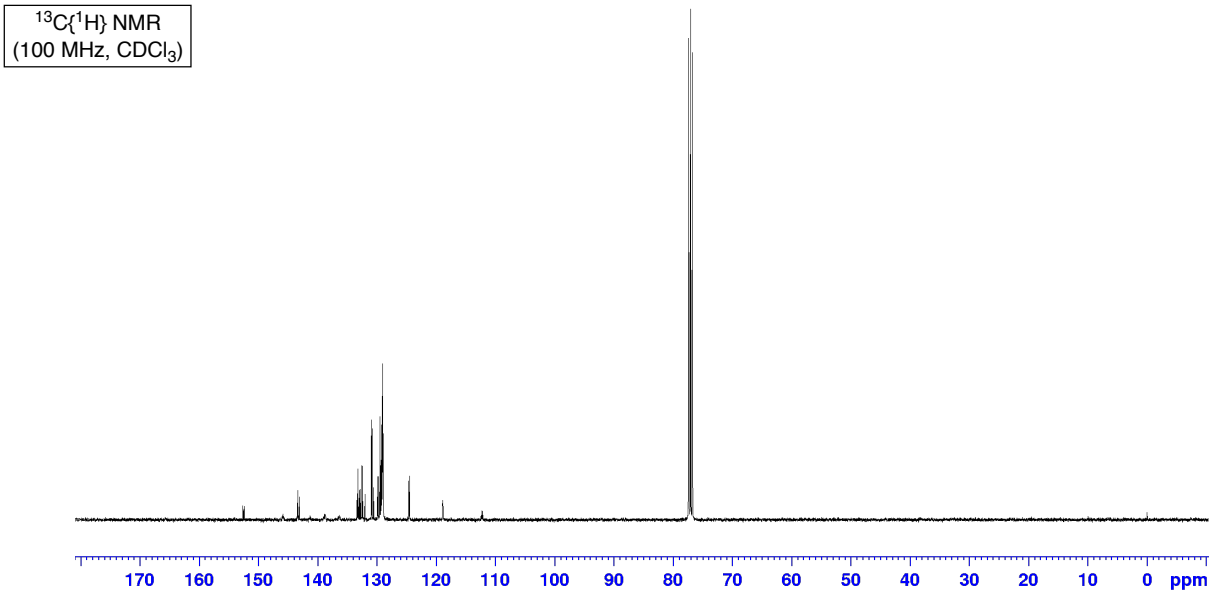




3aj

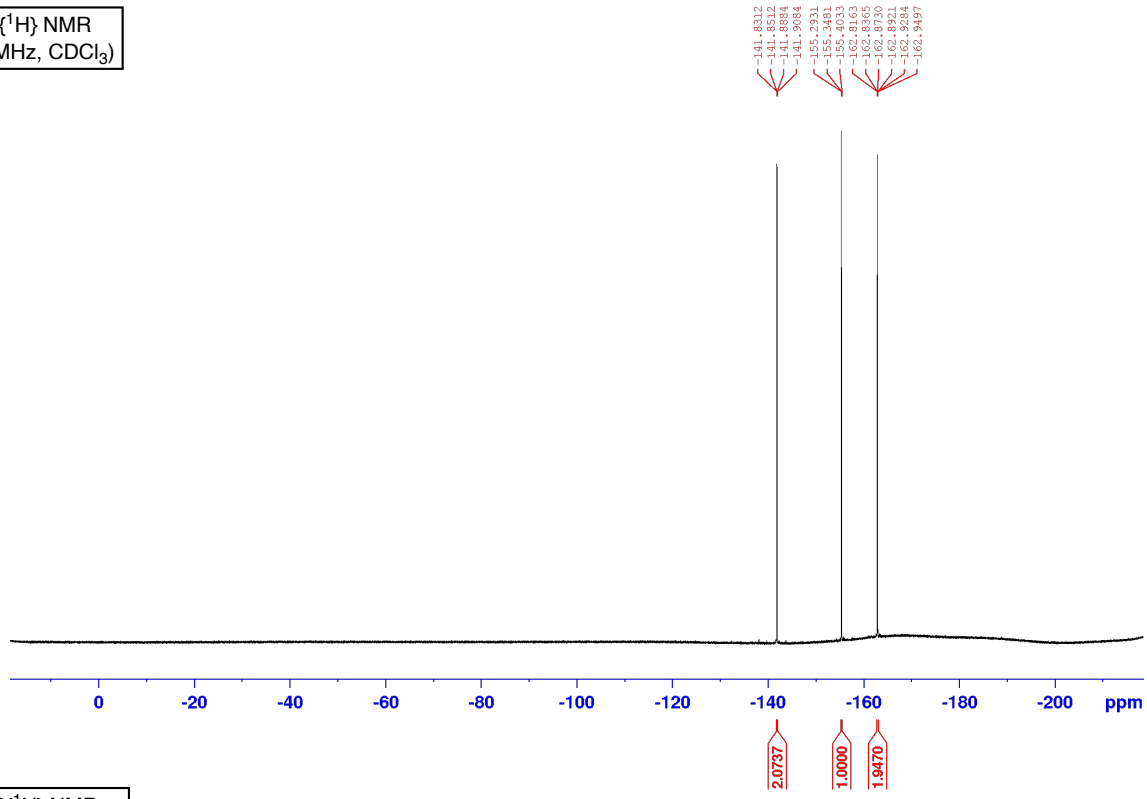
^{1}H NMR
(400 MHz, $CDCl_3$)



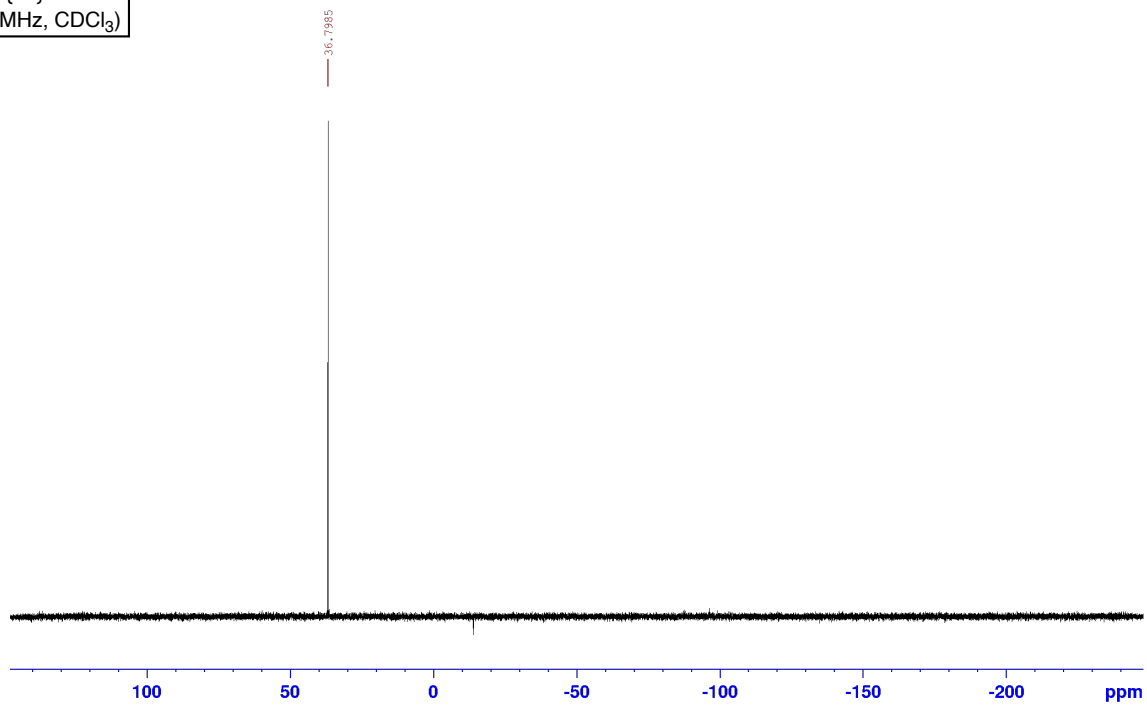


^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)

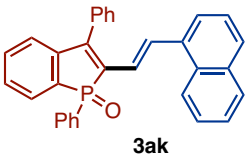
$^{19}F\{^{1}H\}$ NMR
(376 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

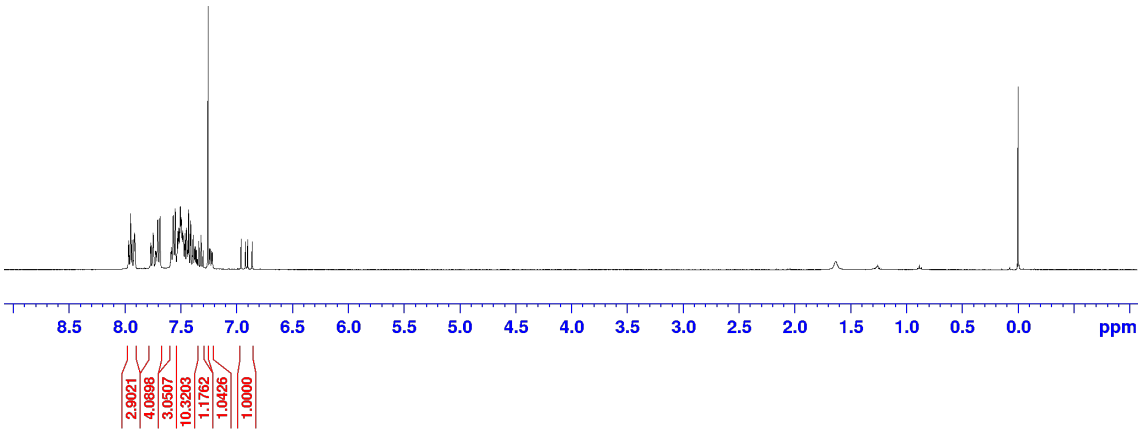


[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ak**]

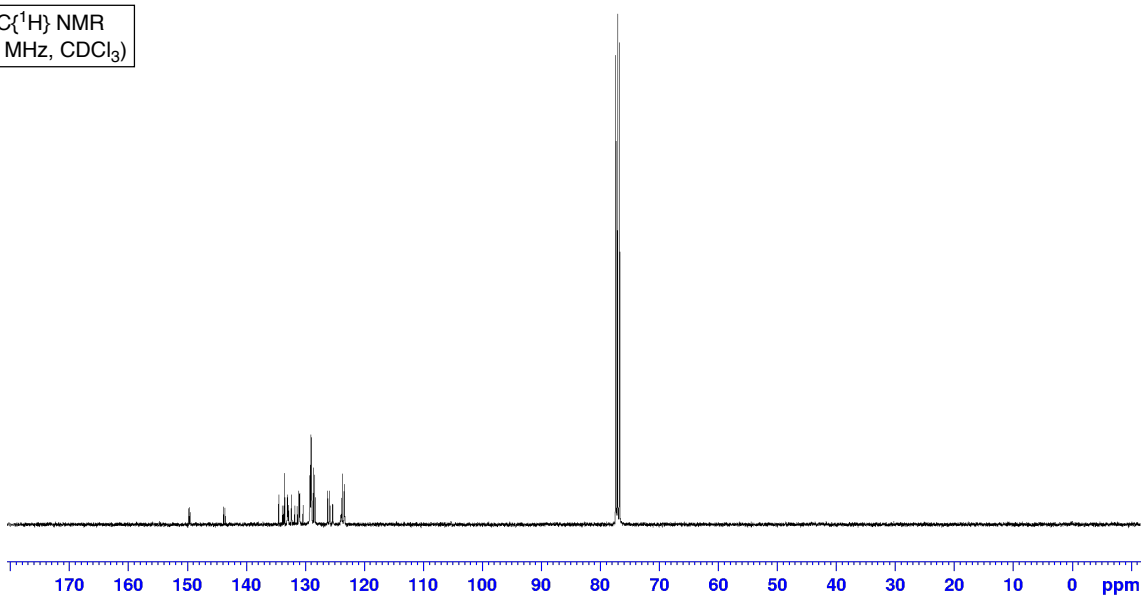


3ak

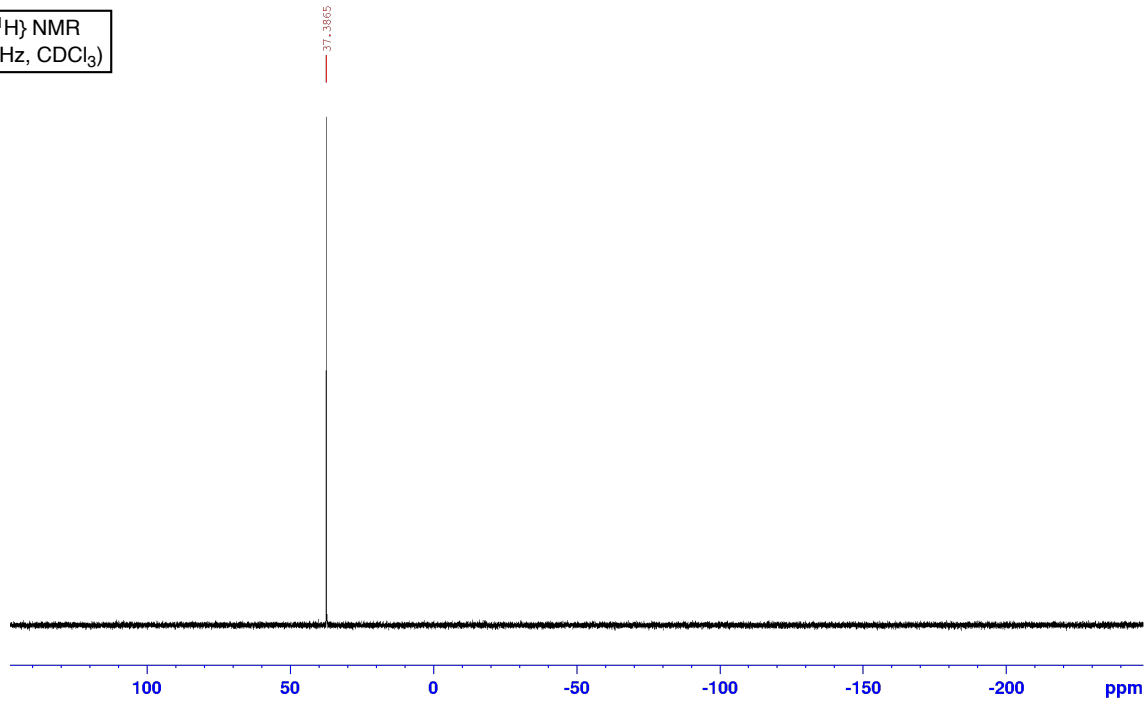
^{1}H NMR
(400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)

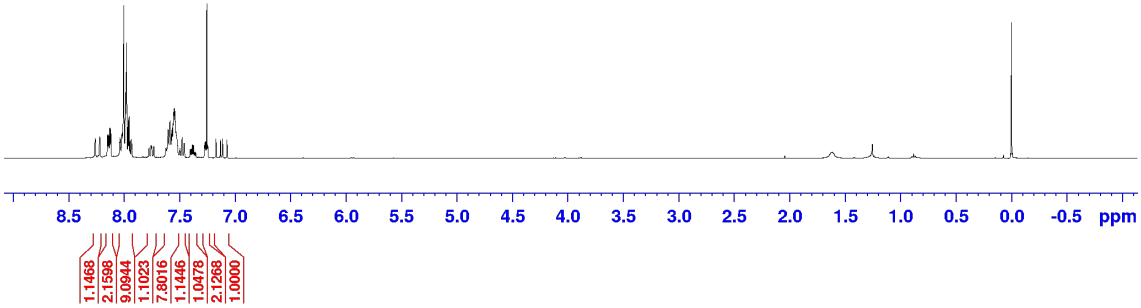


$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

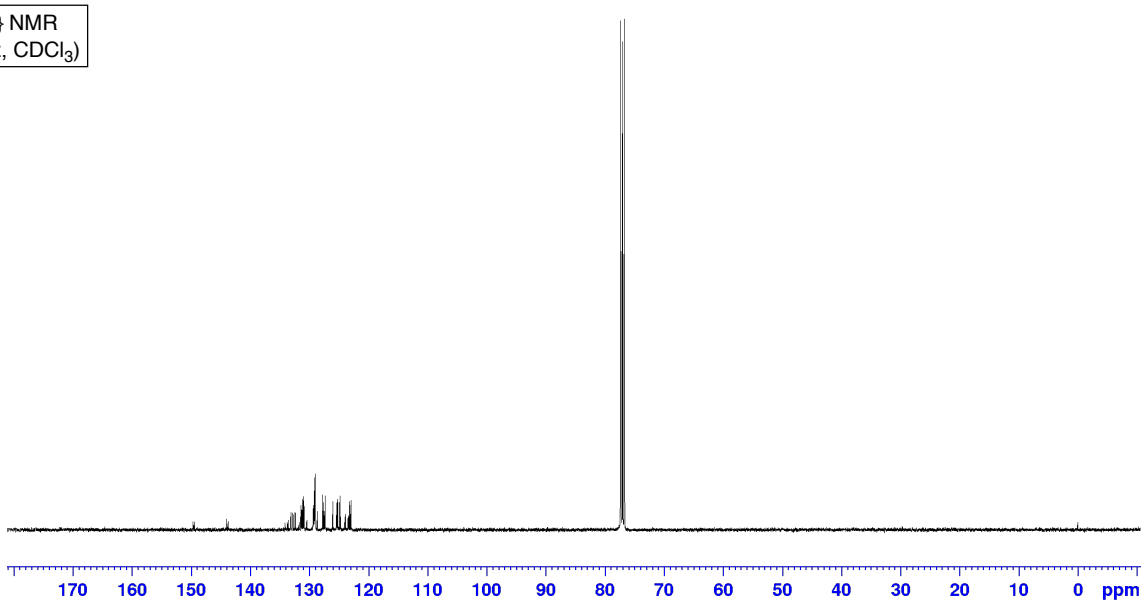


[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3al**]

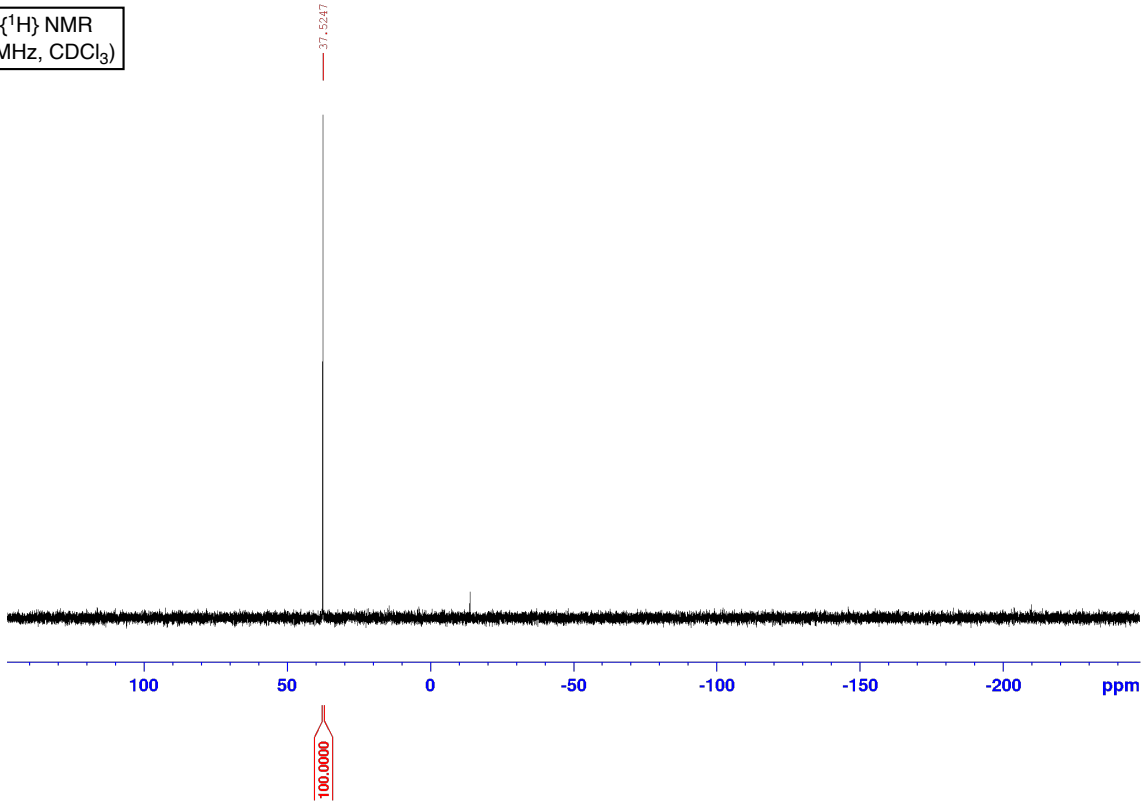
^{1}H NMR
(400 MHz, $CDCl_3$)



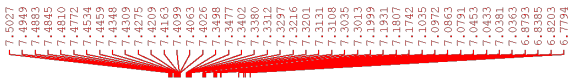
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



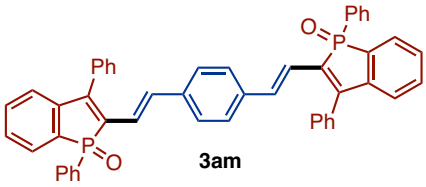
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



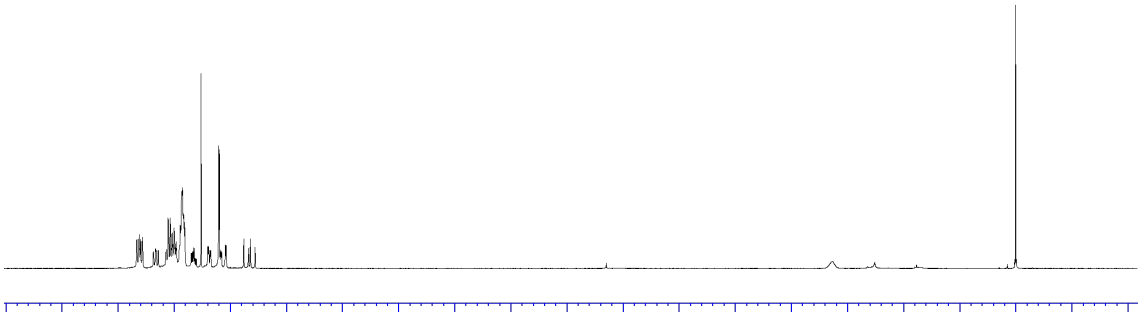
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3am**]

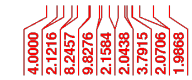


^{1}H NMR
(400 MHz, $CDCl_3$)

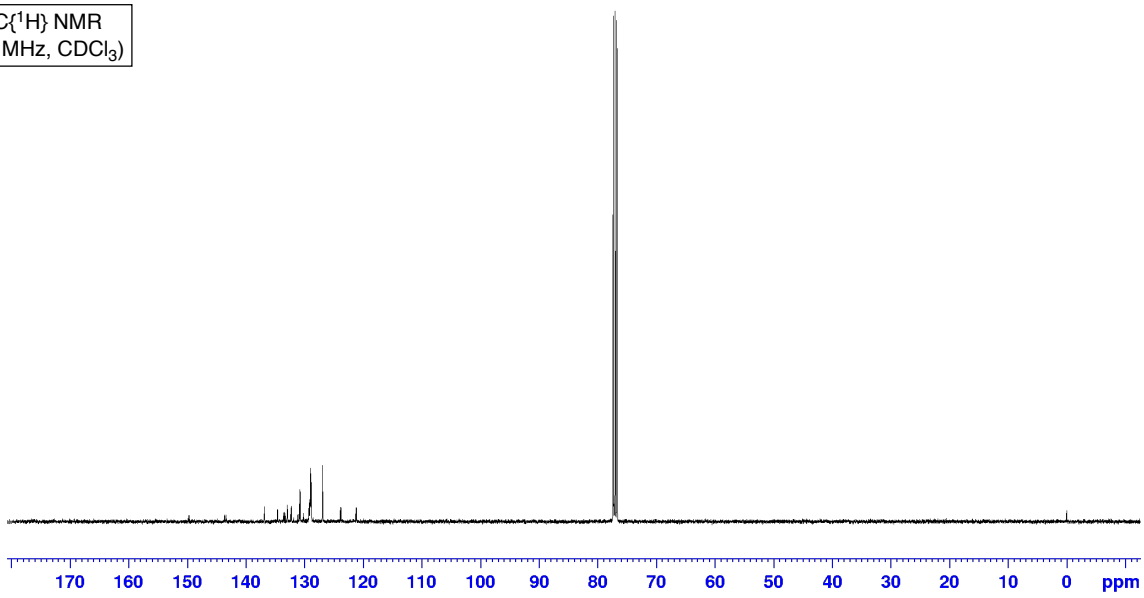


3am

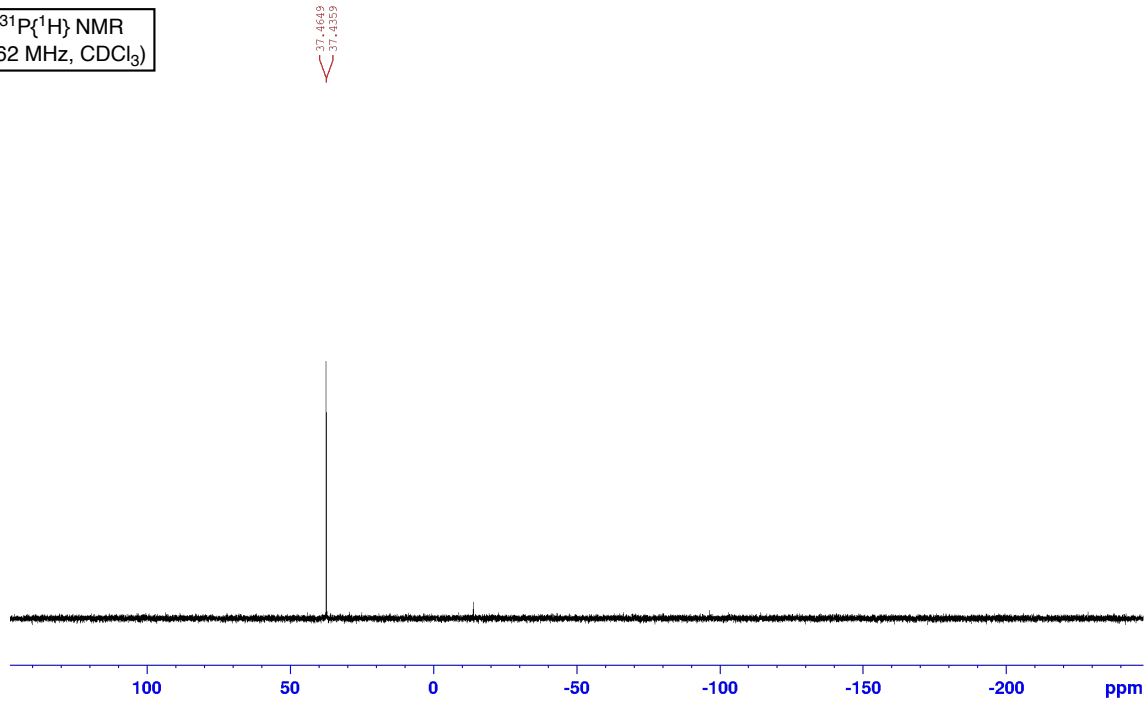




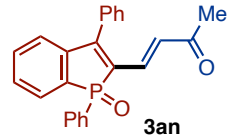
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



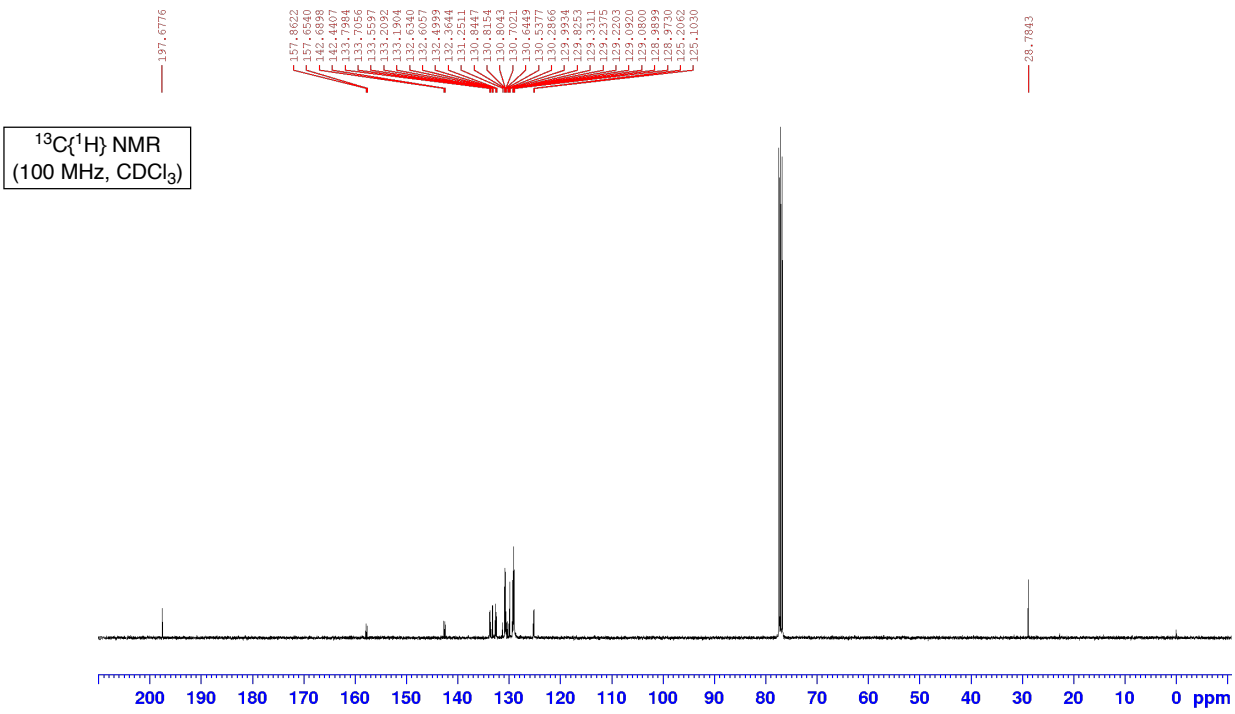
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3an**]

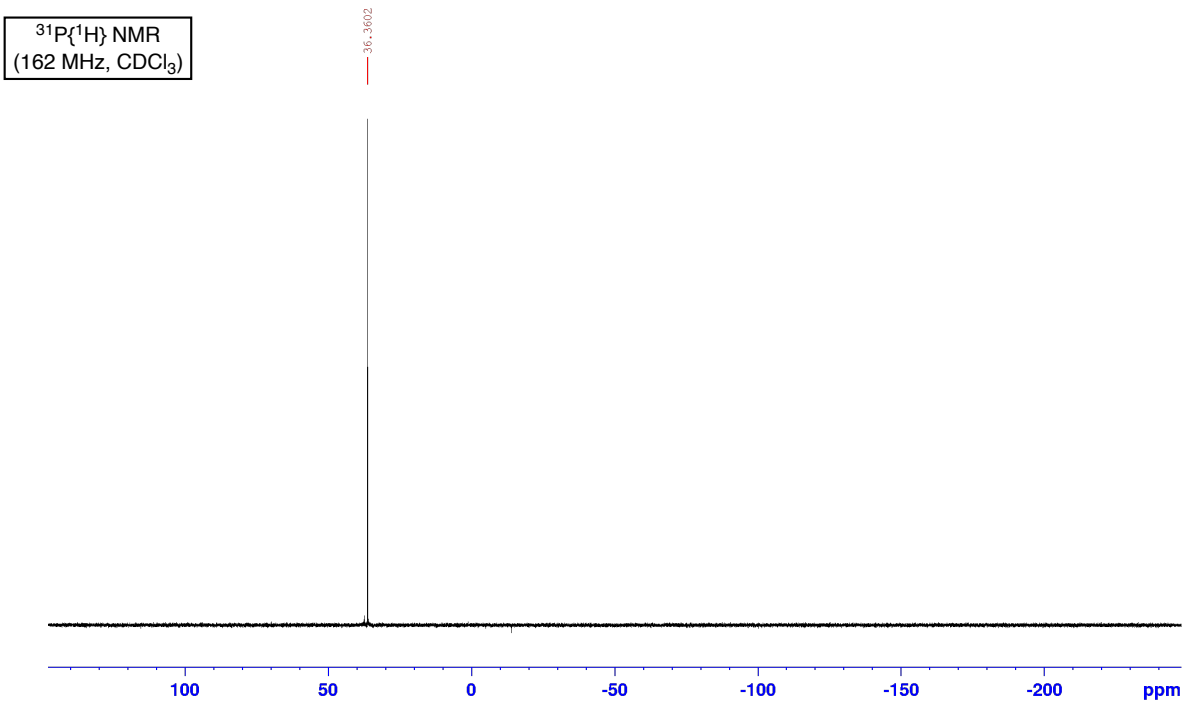


3an

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

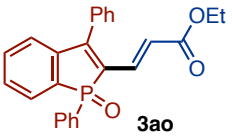
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



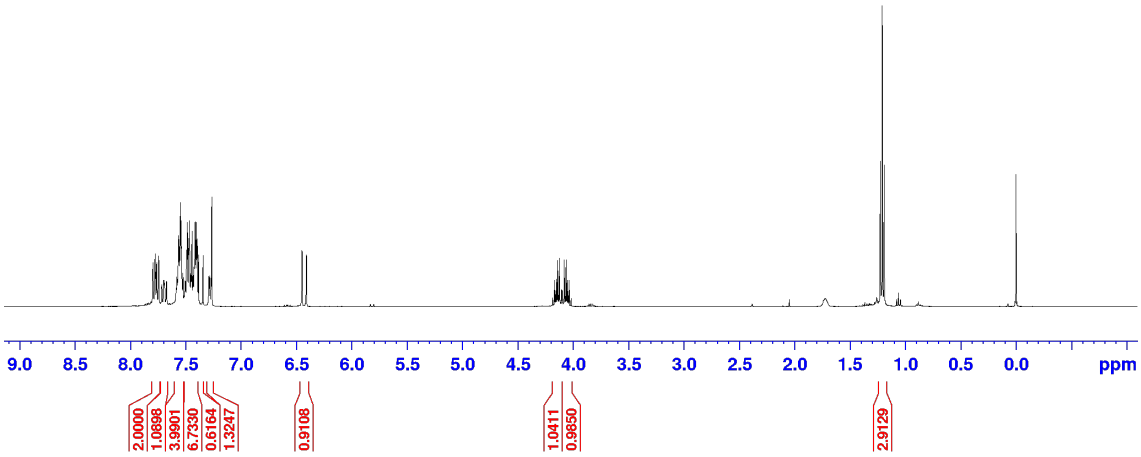

31P{1H} NMR
(162 MHz, CDCl3)
36.3602
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ao**]

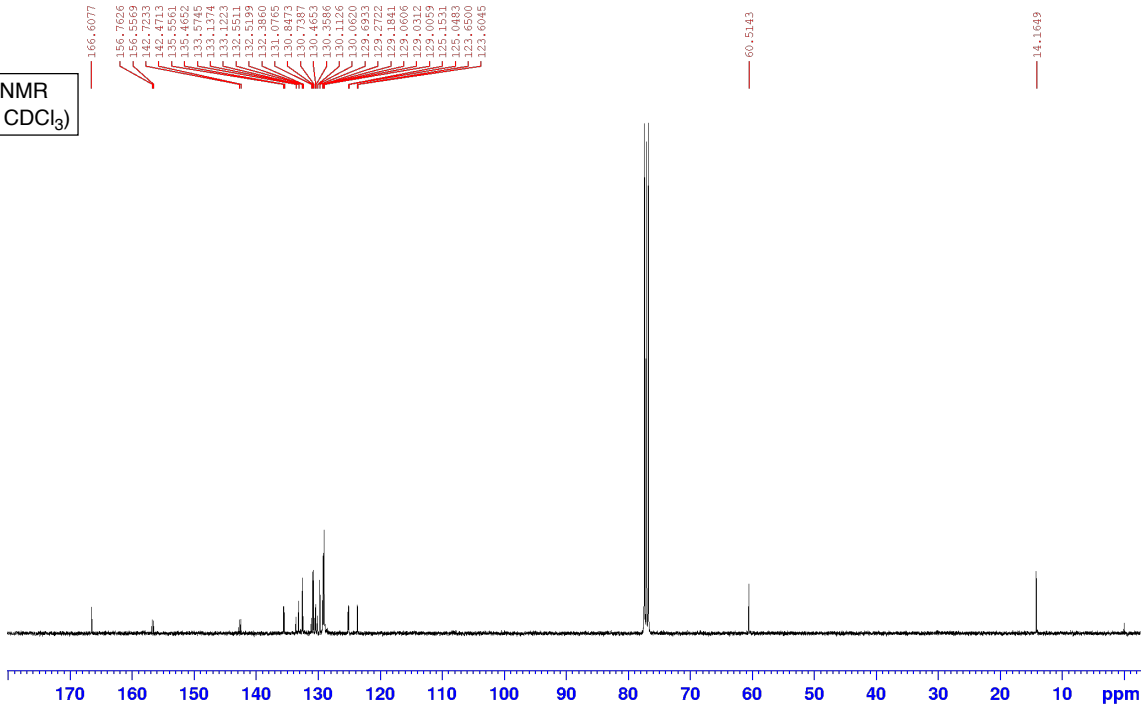
^{1}H NMR
(400 MHz, $CDCl_3$)



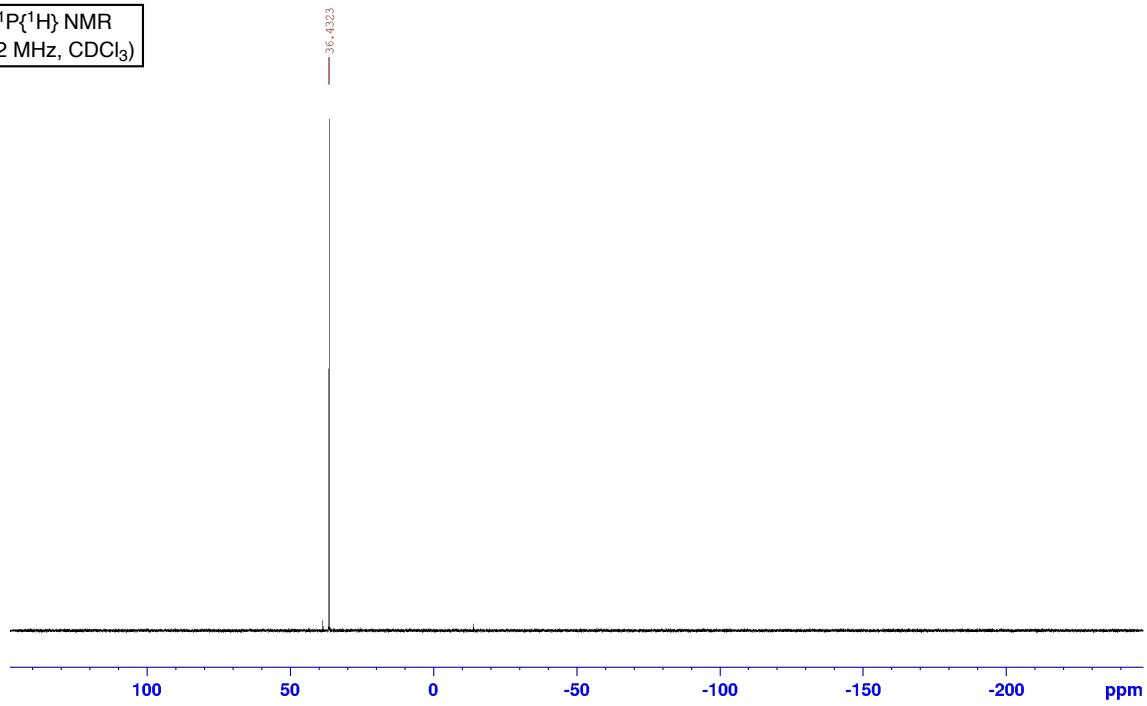
3ao



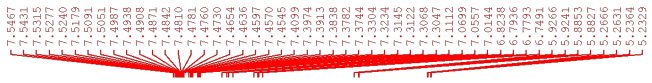
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)

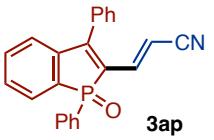


$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ap**]

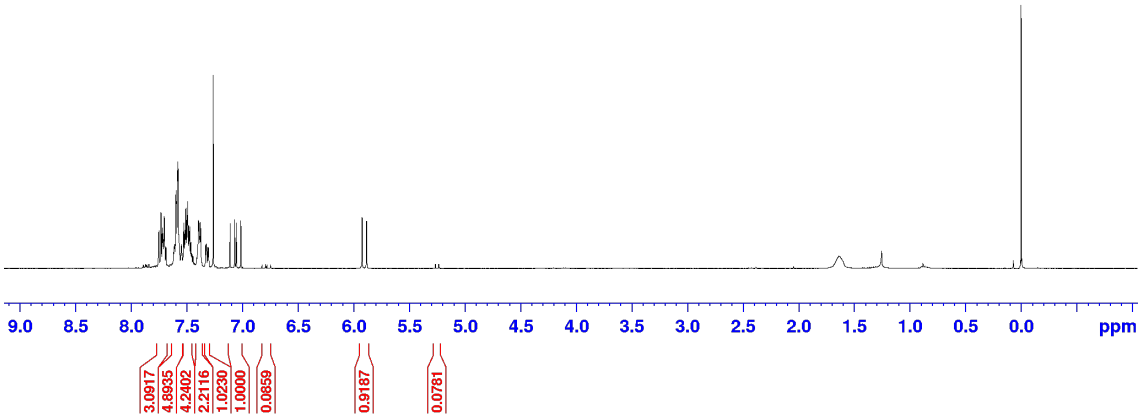




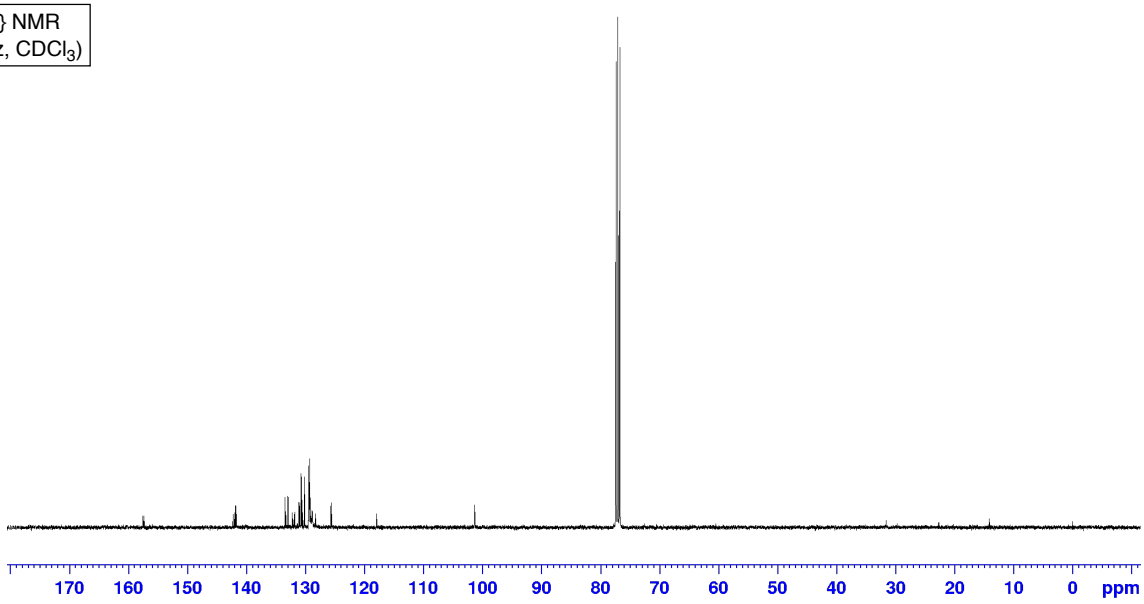
3ap

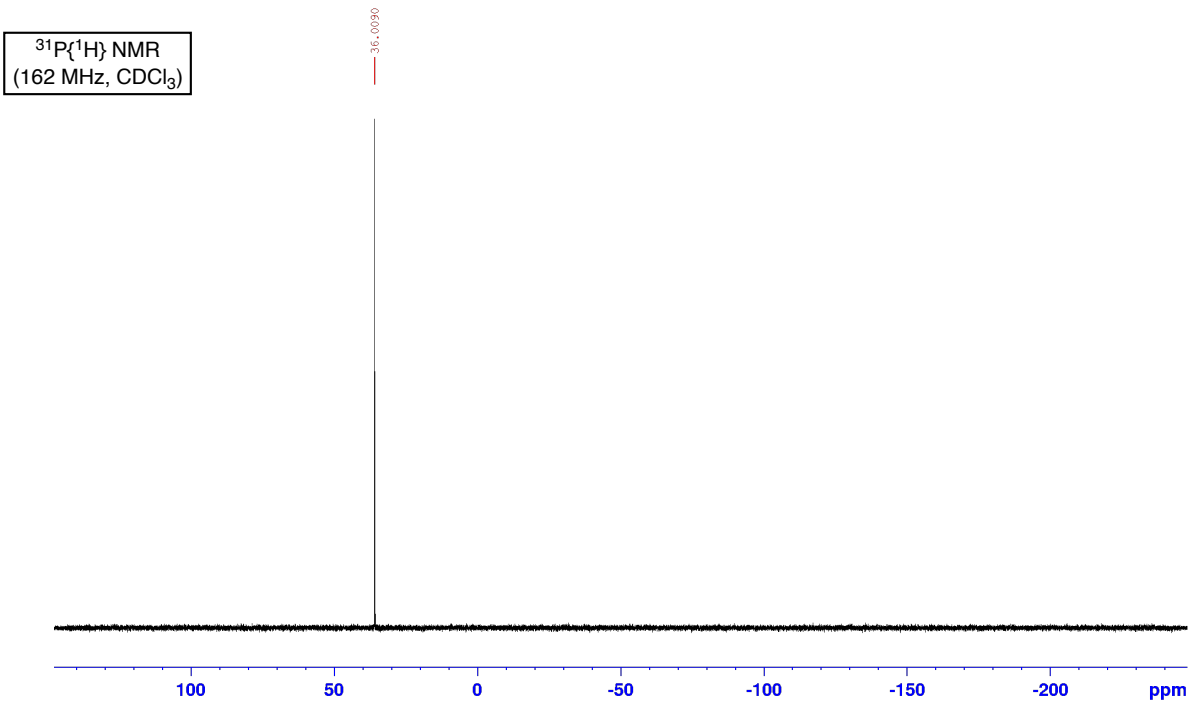
E/*Z* = 92:8

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



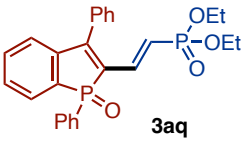
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



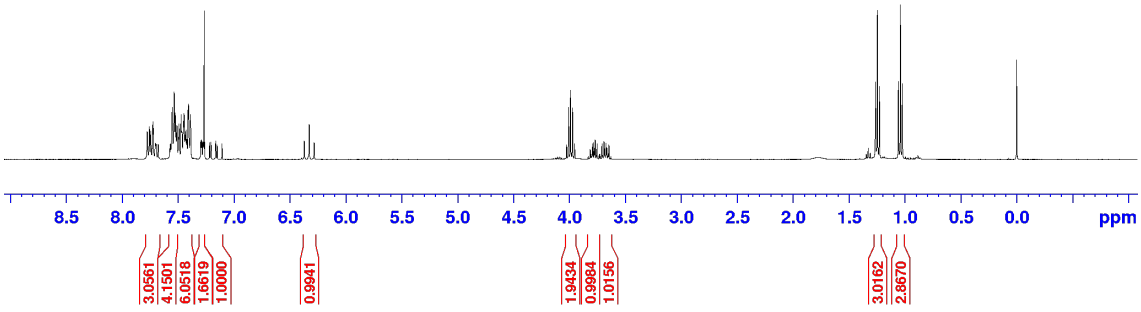

31P{1H} NMR
(162 MHz, CDCl3)
36.0090
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3aq**]

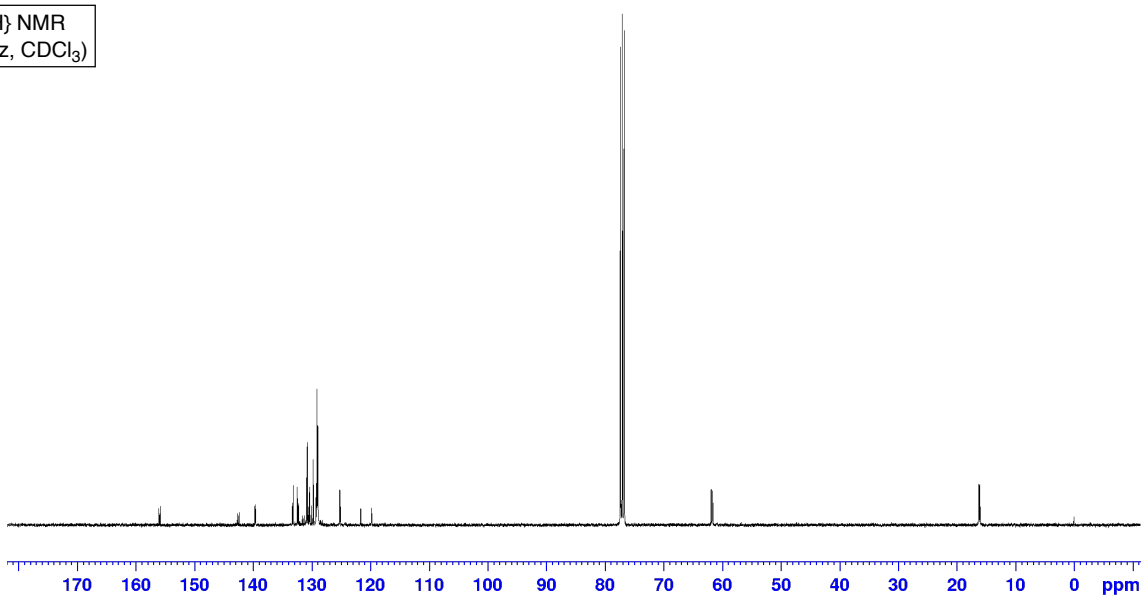
^{1}H NMR
(400 MHz, $CDCl_3$)

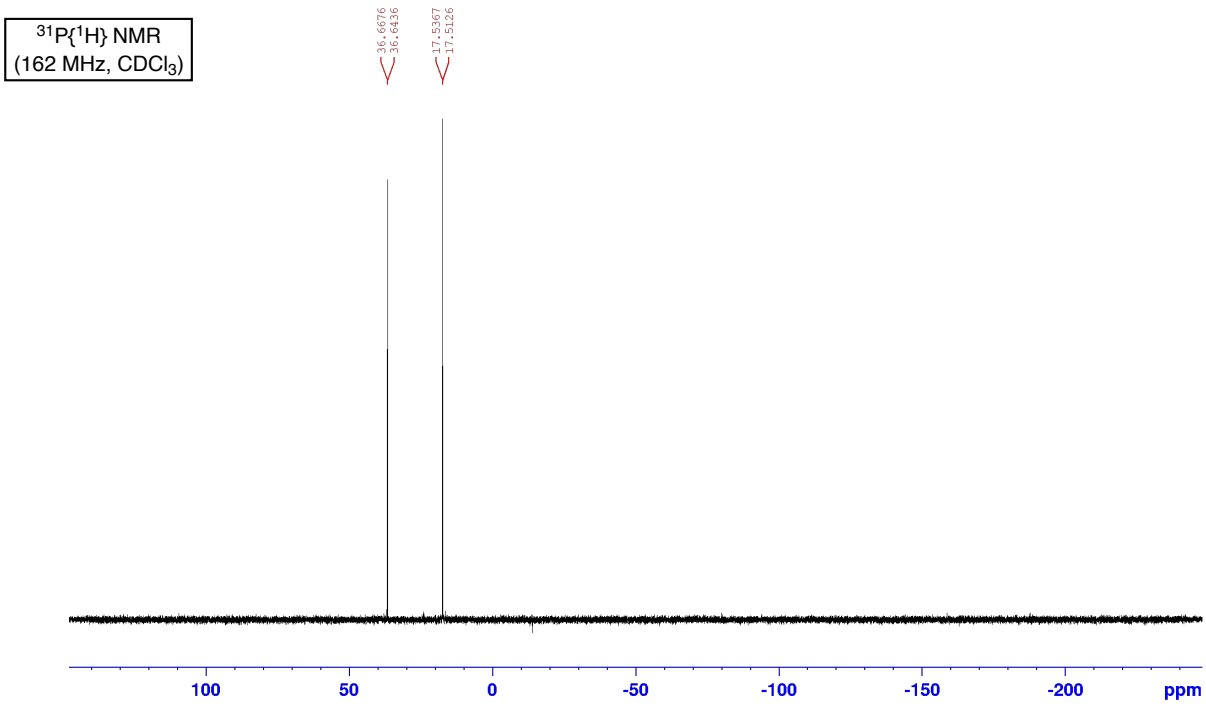


3aq

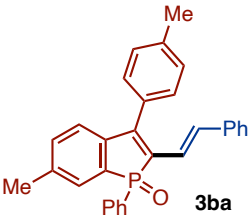


^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



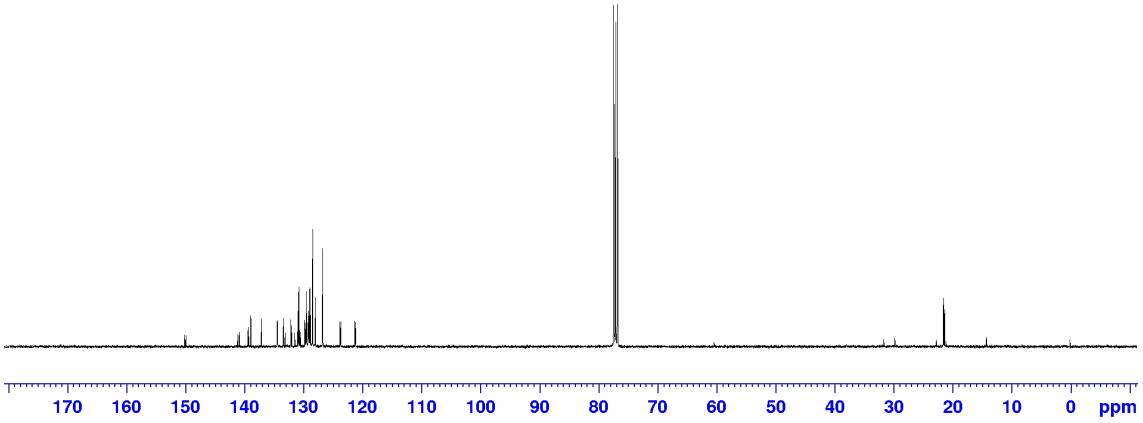

31P{1H} NMR
(162 MHz, CDCl3)
36.6676
36.6436
17.5367
17.5126
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ba**]

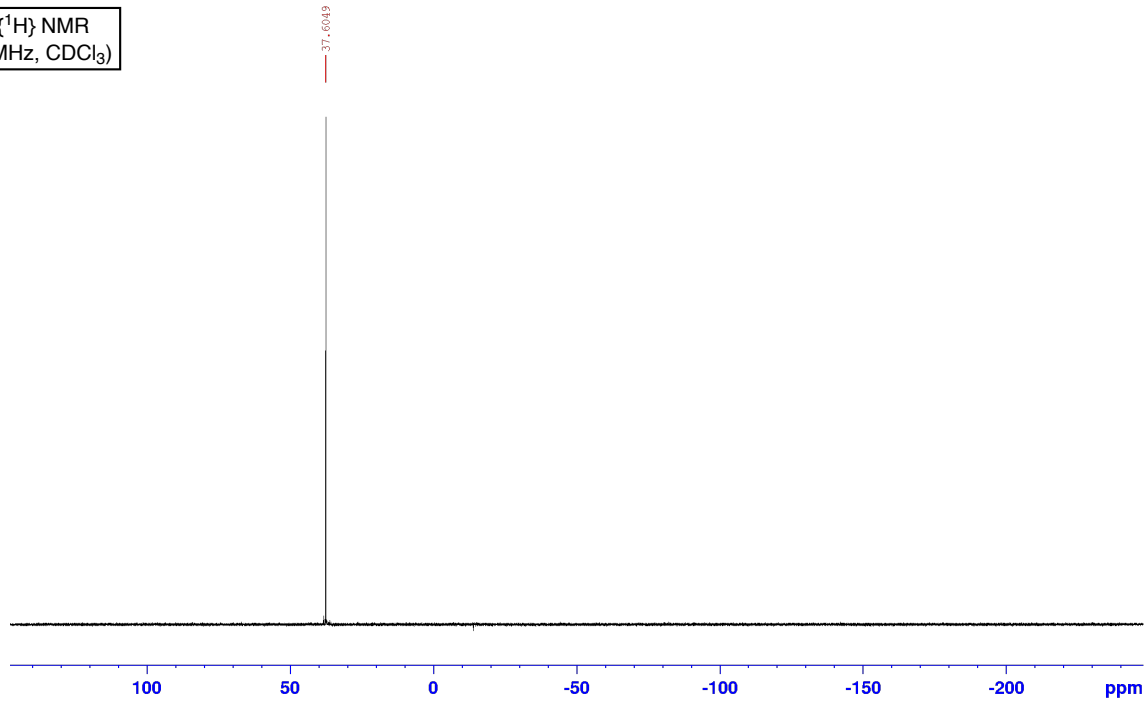


^{1}H NMR
(400 MHz, $CDCl_3$)

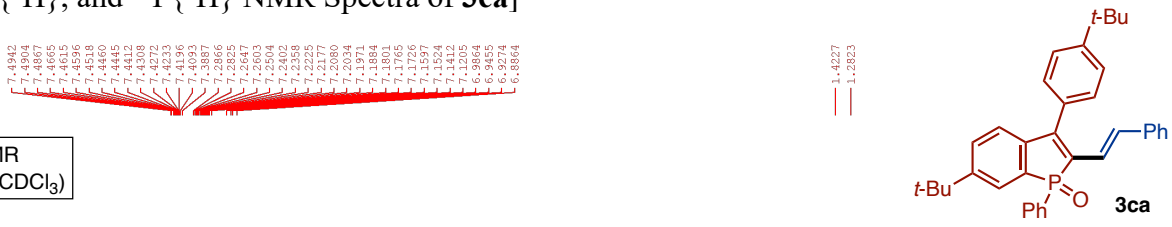
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



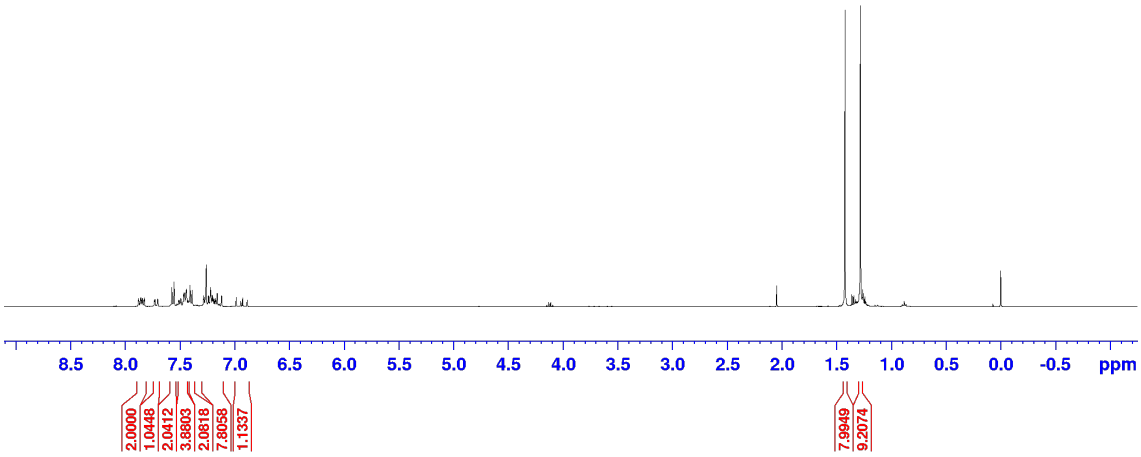
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



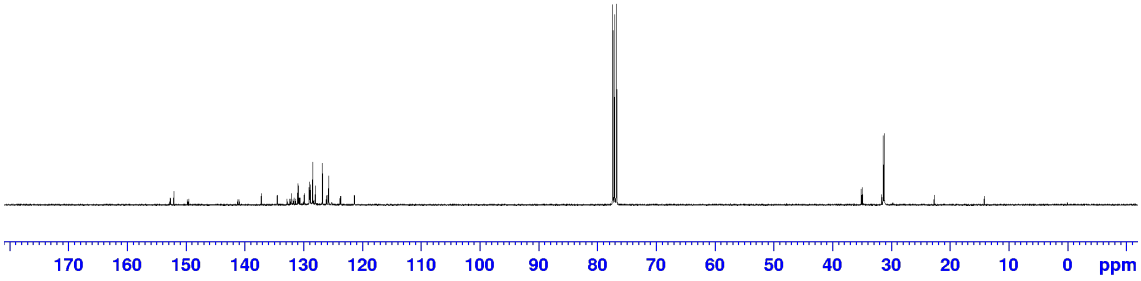
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ca**]



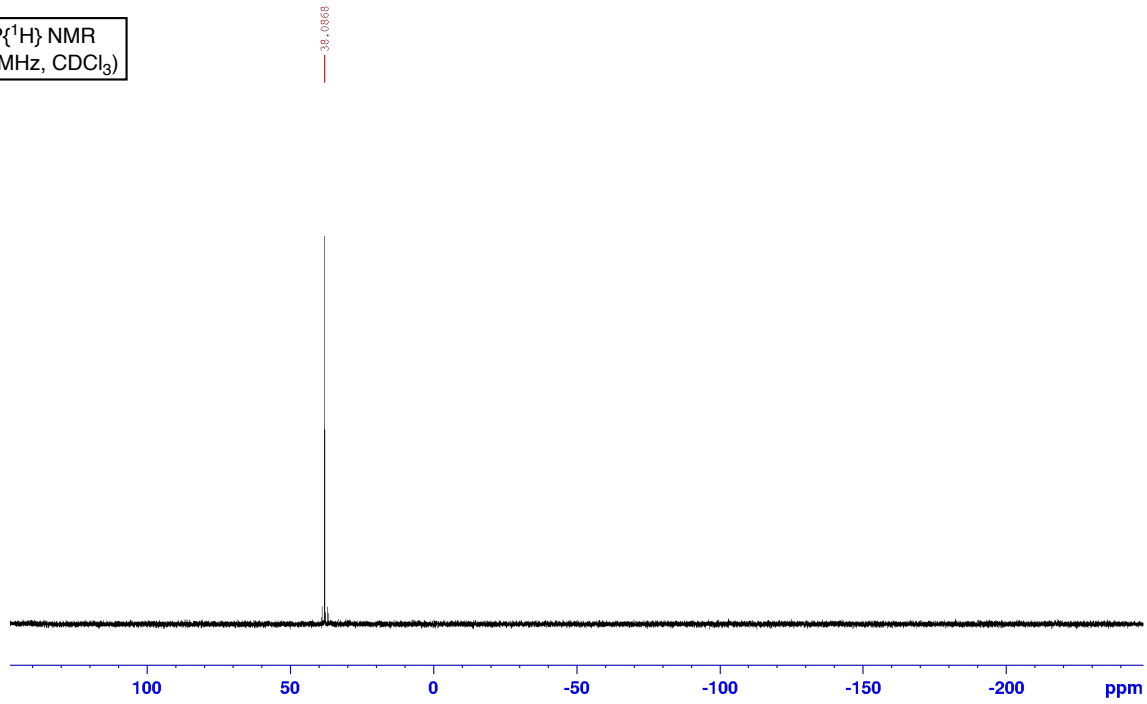
^{1}H NMR
(400 MHz, $CDCl_3$)



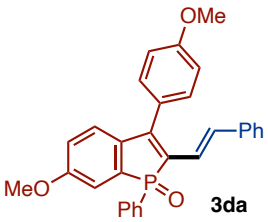
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)

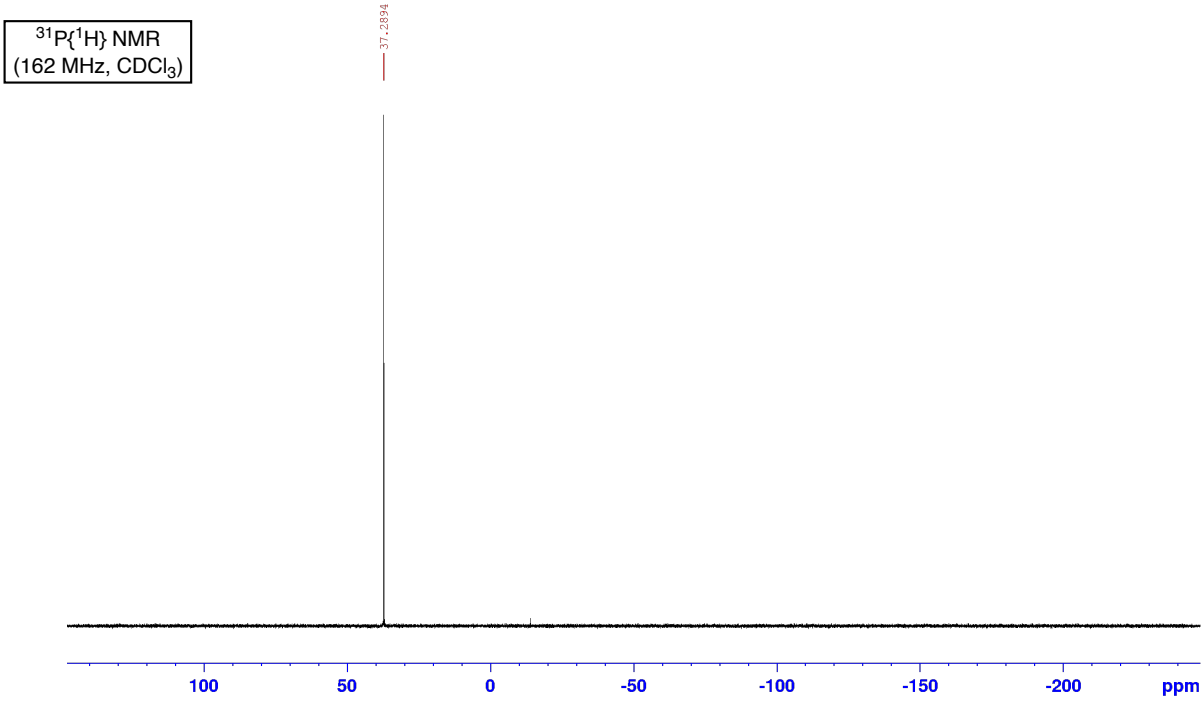


$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

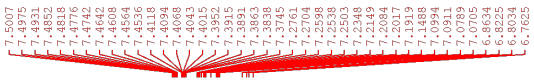


[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3da**]

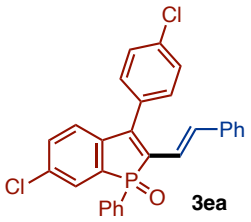



31P{1H} NMR
(162 MHz, CDCl3)
37.2894
100
50
0
-50
-100
-150
-200
ppm

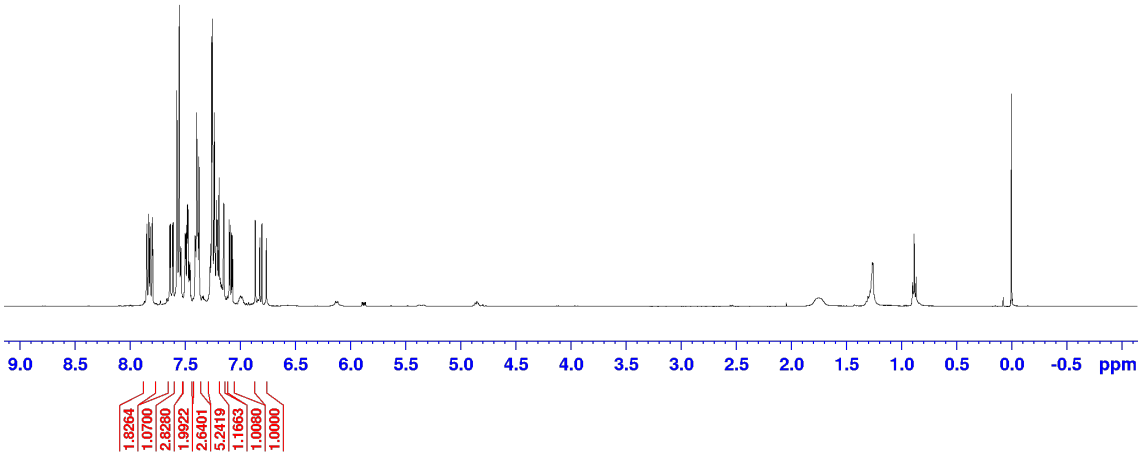
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ea**]



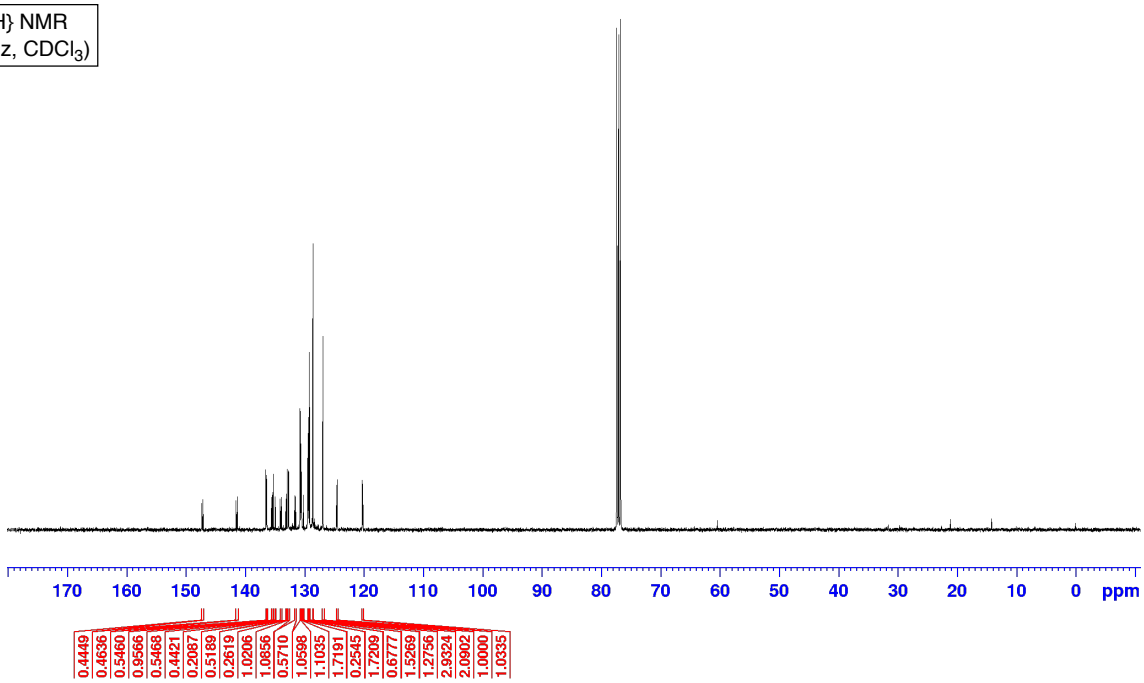
^{1}H NMR
(400 MHz, $CDCl_3$)

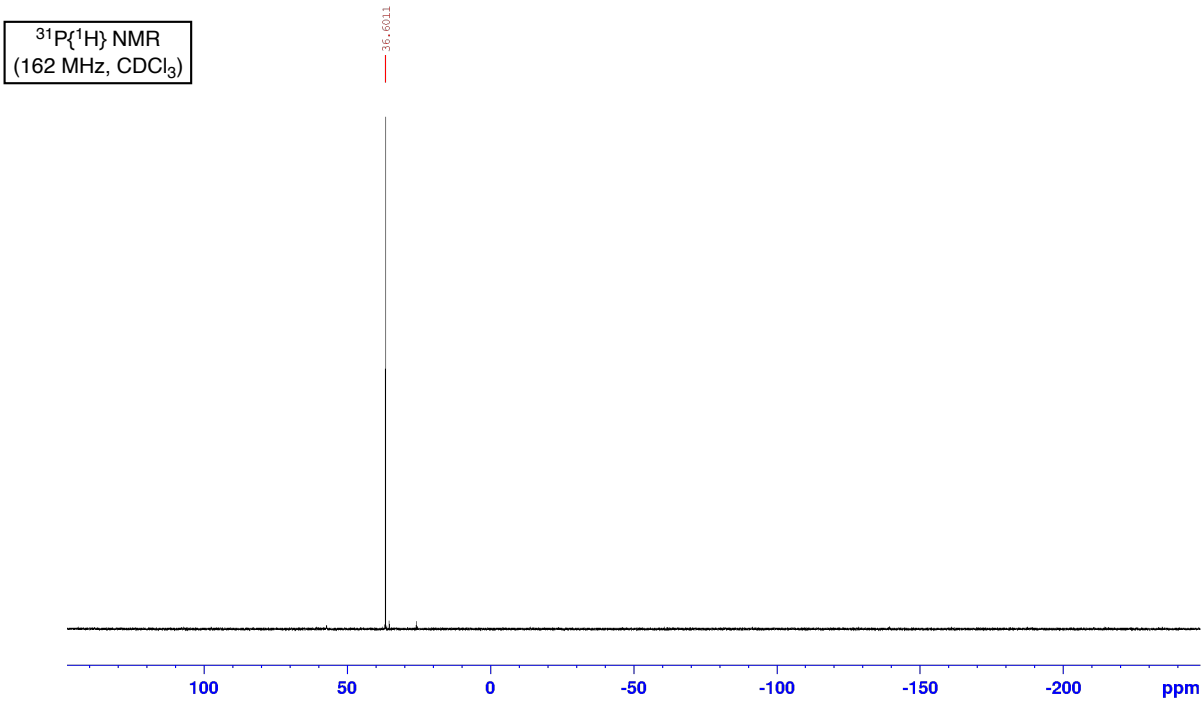


3ea

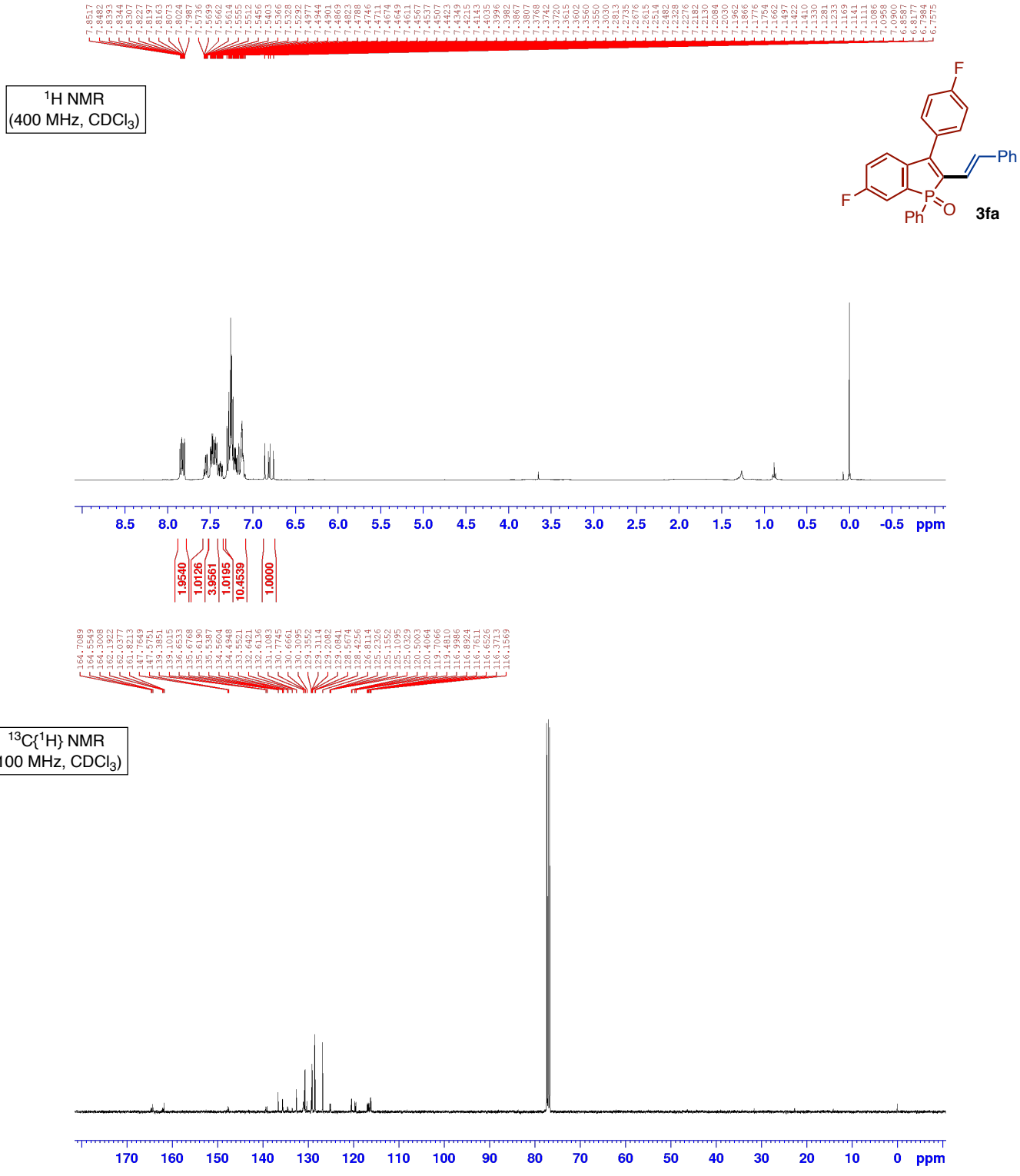


^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)

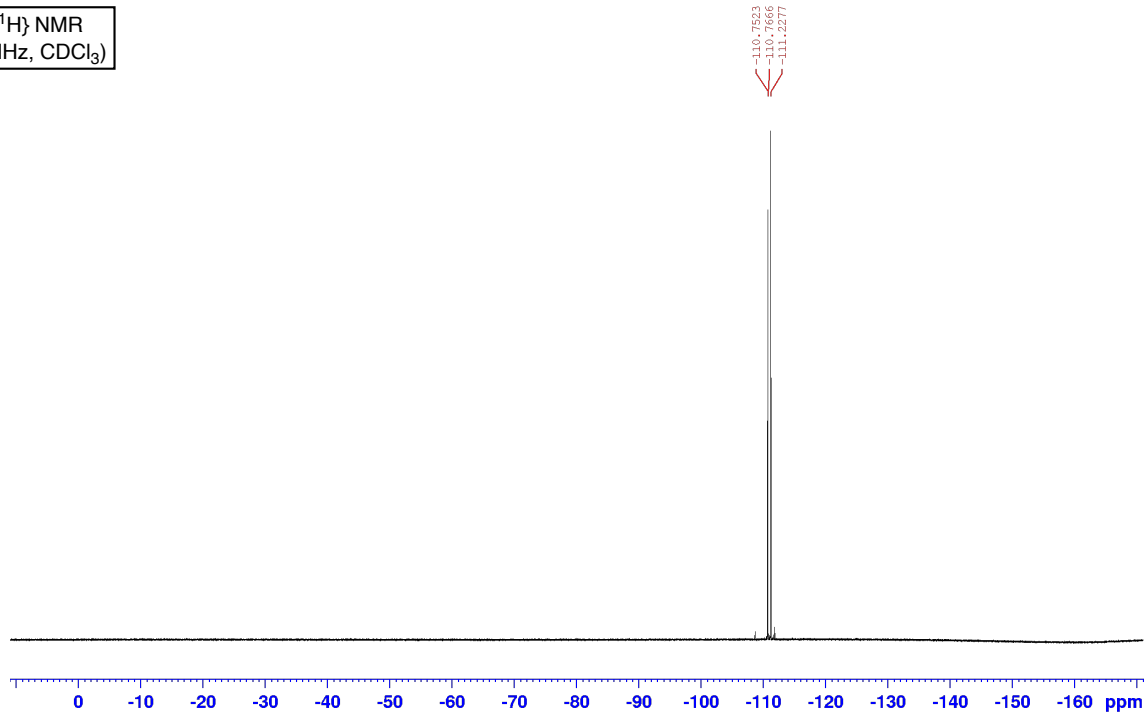



31P{1H} NMR
(162 MHz, CDCl3)
36.6011
100
50
0
-50
-100
-150
-200
ppm

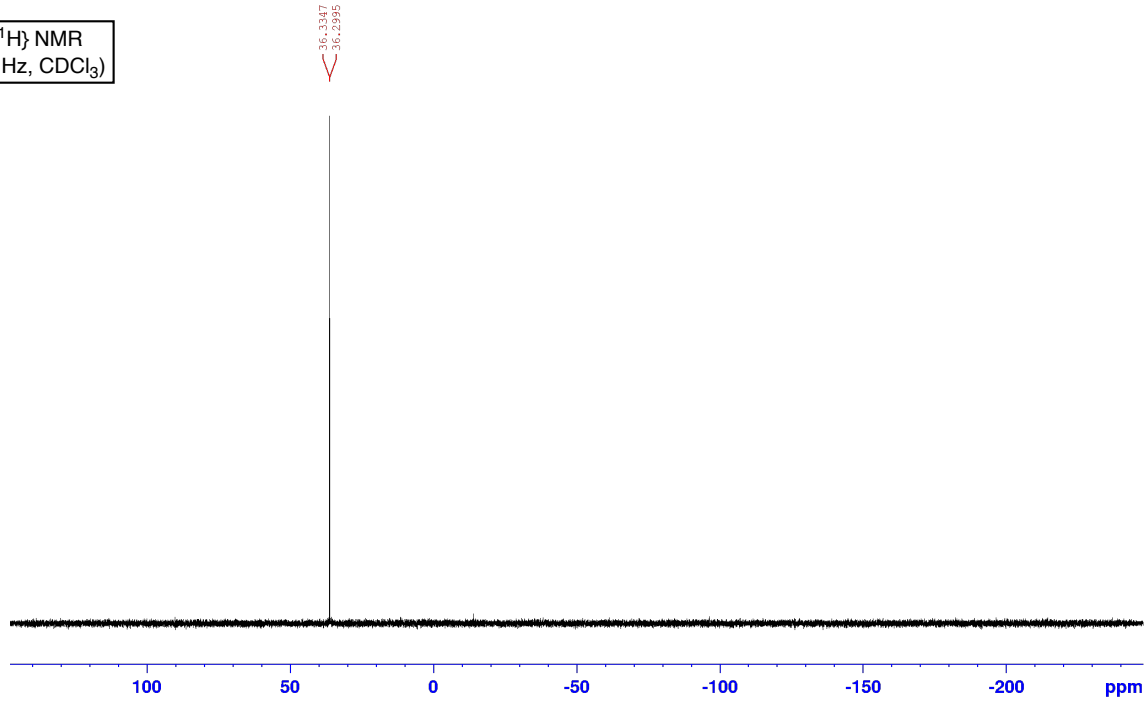
[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3fa**]



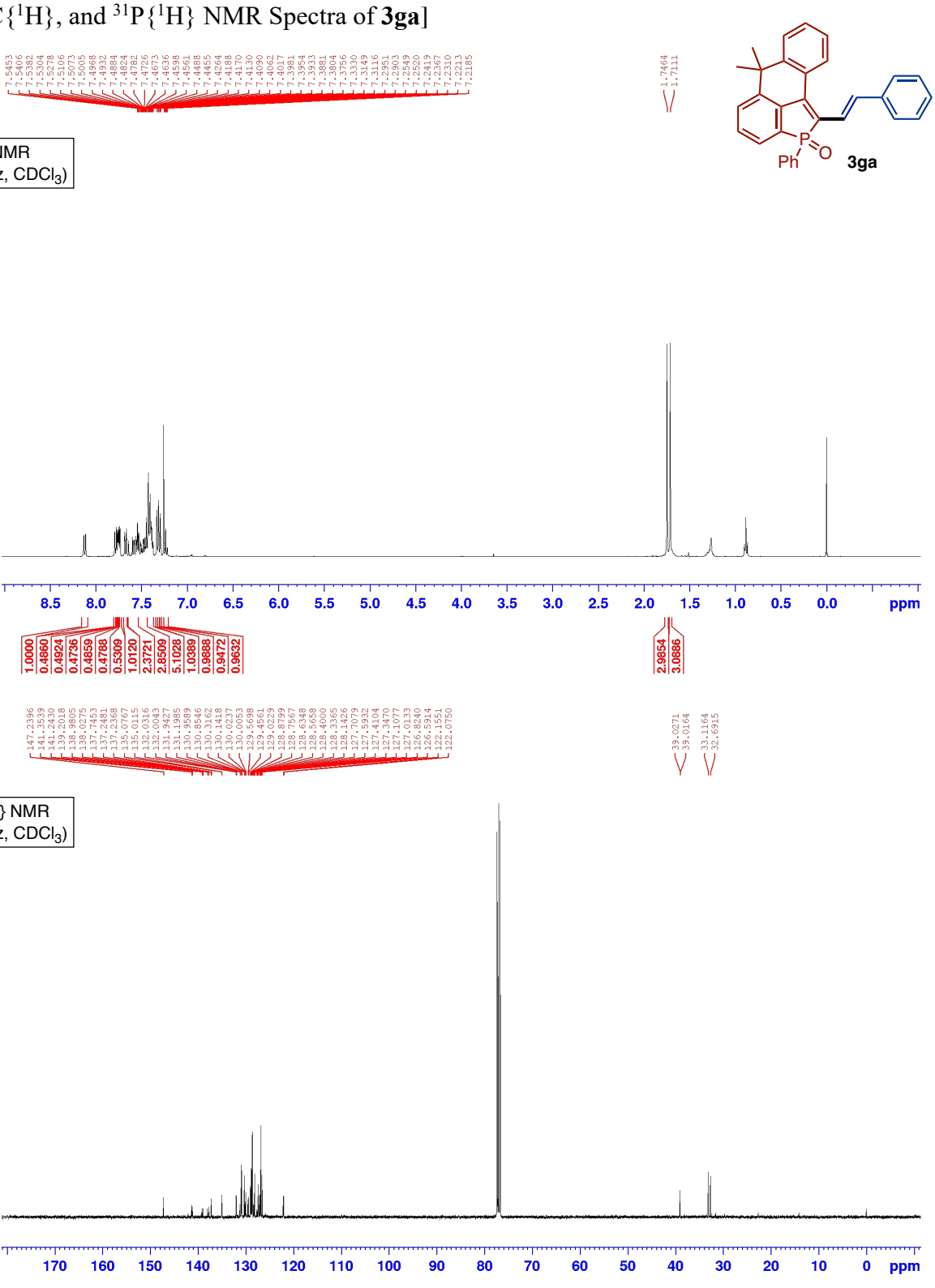
$^{19}F\{^{1}H\}$ NMR
(376 MHz, $CDCl_3$)



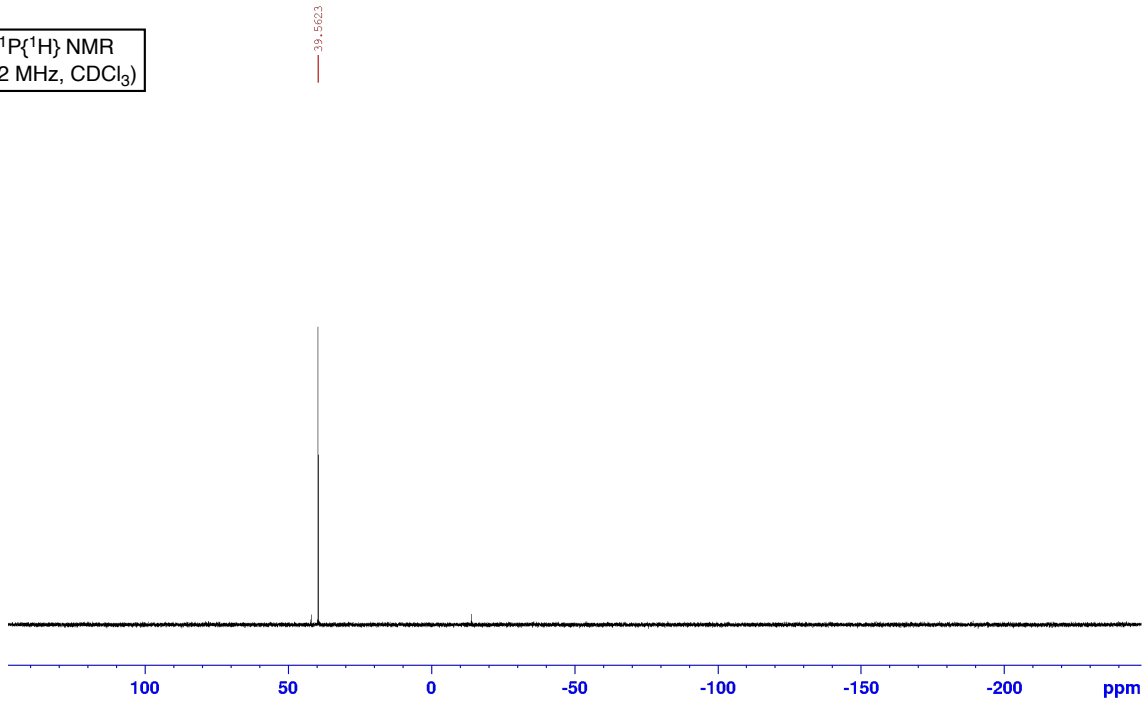
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



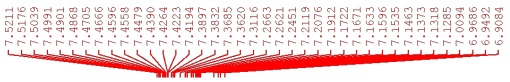
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ga**]



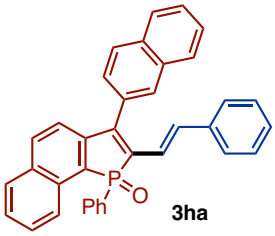
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



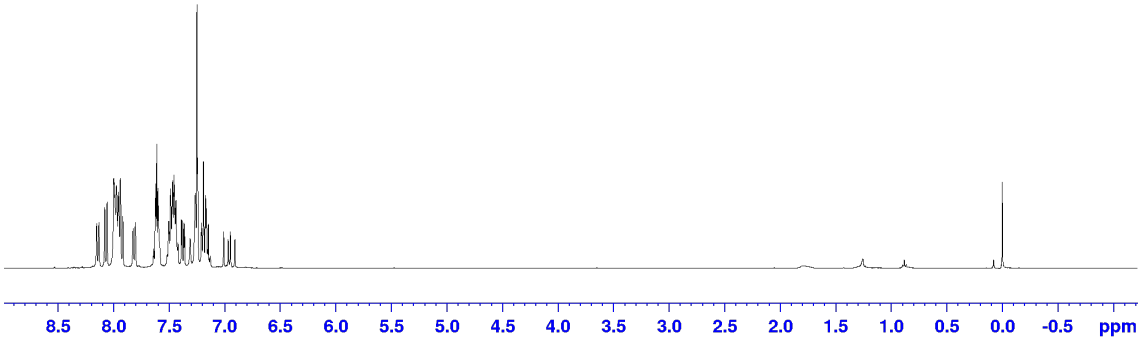
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ha**]

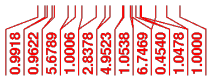


^{1}H NMR
(400 MHz, $CDCl_3$)

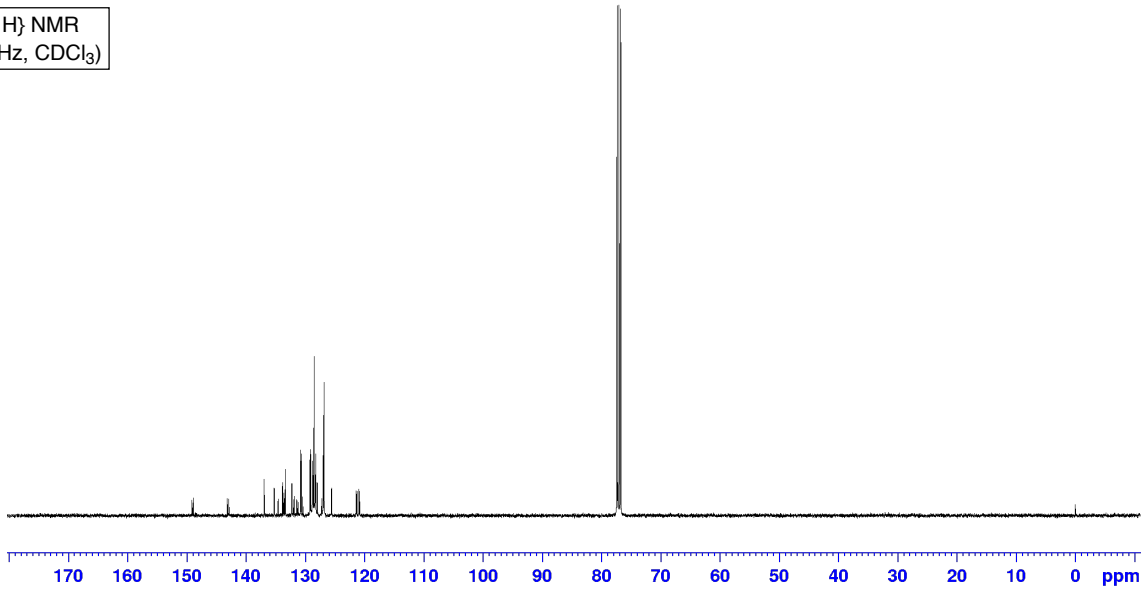


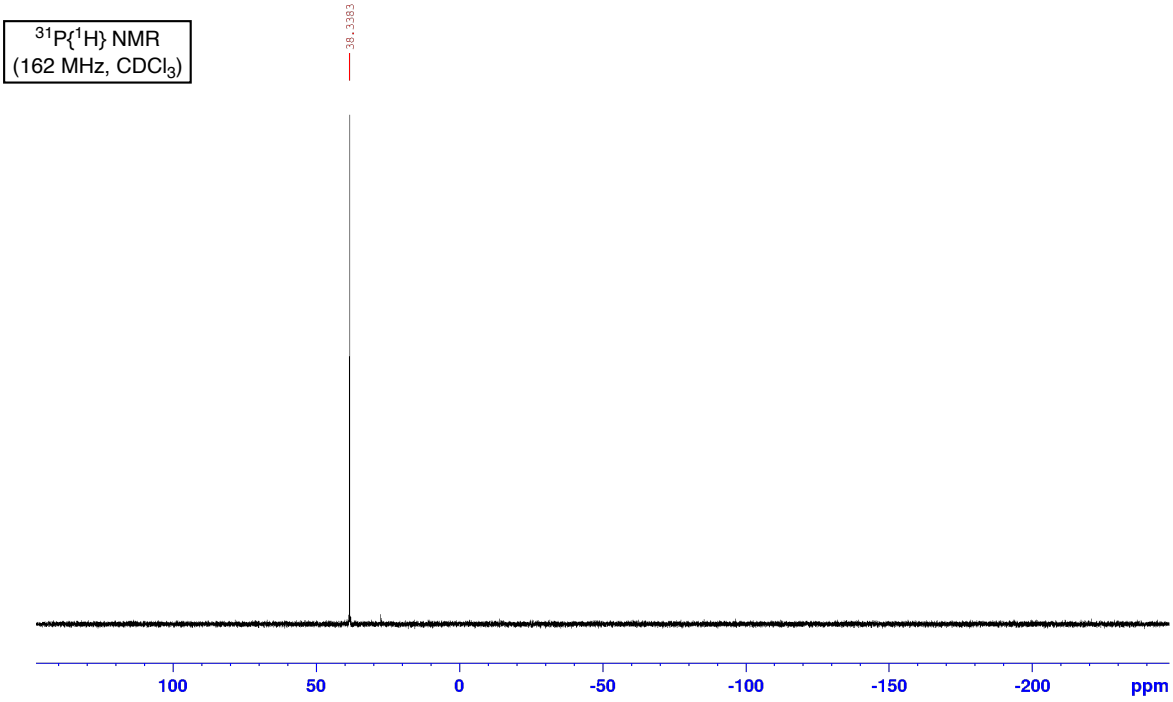
3ha



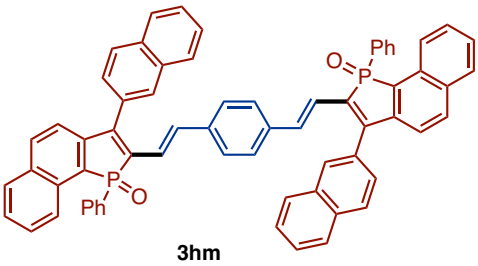


^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)

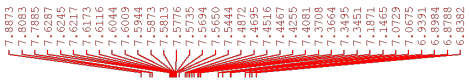



31P{1H} NMR
(162 MHz, CDCl3)
38.3383
100
50
0
-50
-100
-150
-200
ppm

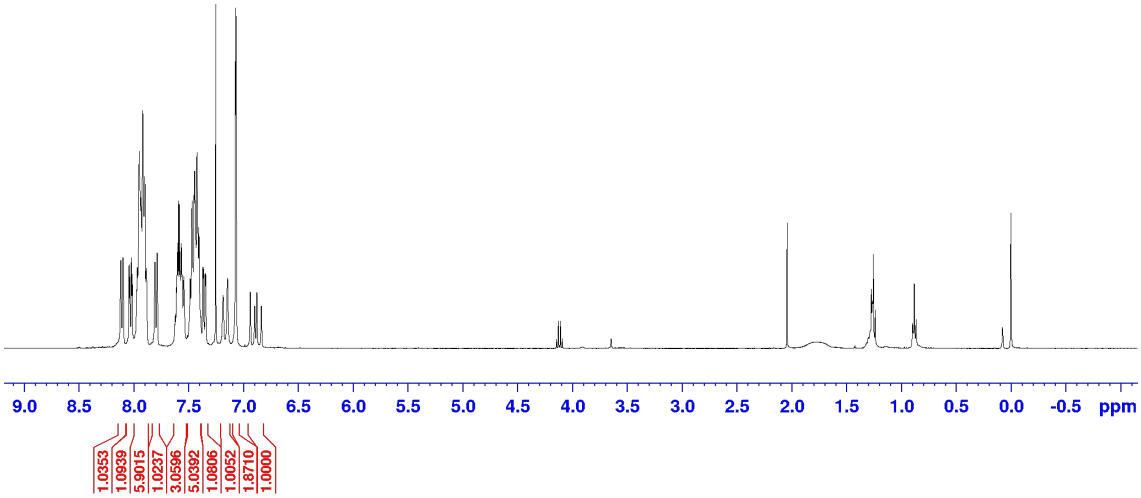
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3hm**]



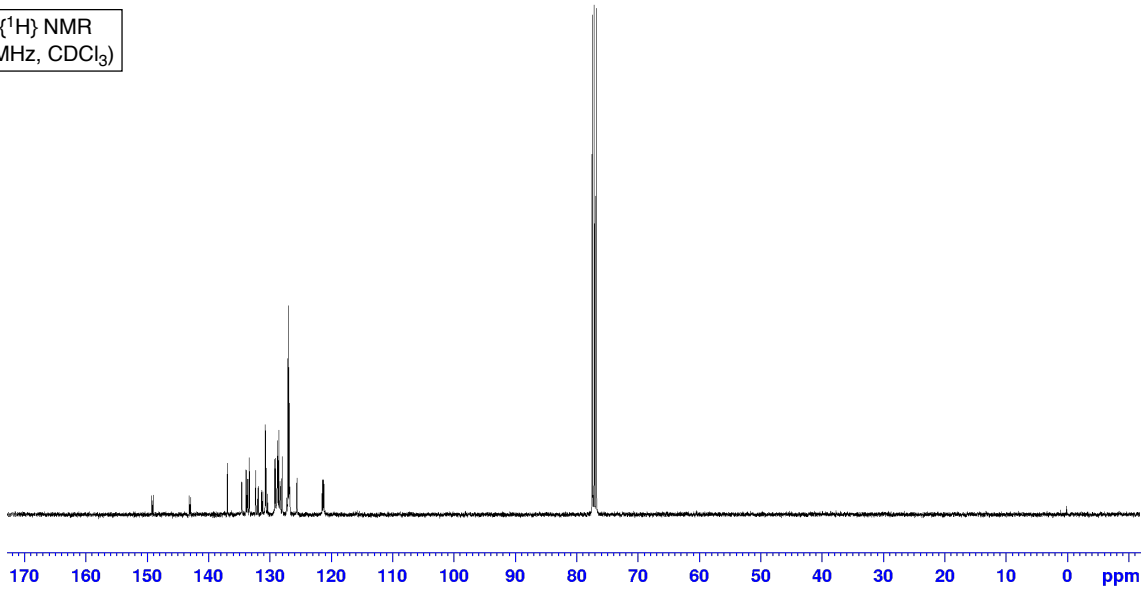
3hm

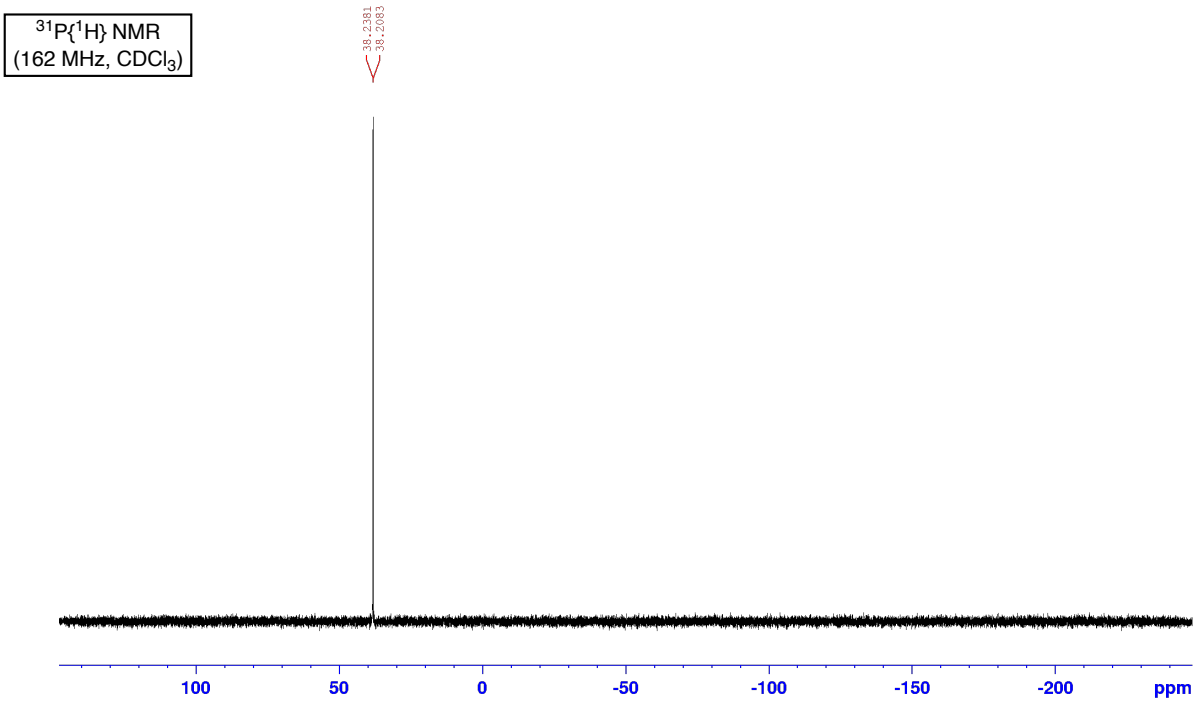


^{1}H NMR
(400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)




31P{1H} NMR
(162 MHz, CDCl3)
38.2381
38.2083
100
50
0
-50
-100
-150
-200
ppm

References

(S1) S. Xu, K. Nishimura, K. Saito, K. Hirano and M. Miura, *Chem. Sci.,* doi: 10.1039/D2SC04311D.