Supplementary Information

Palladium-catalysed C–H arylation of benzophospholes with aryl halides

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Contents

Instrumentation and Chemicals

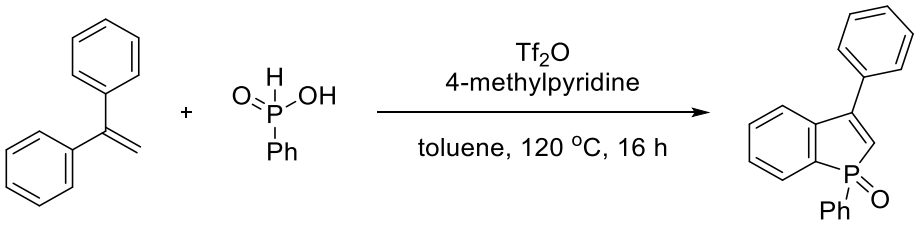
^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded at 400 MHz, 100 MHz, 376 MHz, and 162 MHz, respectively, for $CDCl_3$ solutions. HRMS data were obtained by APCI using TOF. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or CBP capillary column (i. d. 0.5 mm x 25 m). TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakosil C-200, Wako Pure Chemical Co.) was used for column chromatography. Flash silica gel column chromatography was performed by Isolera One (Biotage). Gel permeation chromatography (GPC) was performed by LC-20AR (pump, SHIMADZU, 7.5 mL/min $CHCl_3$ or EtOAc) 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. Cyclic voltammograms and differential pulse voltammograms were recorded on ALS Electrochemical Analyzer Model 600E equipped with SVC-3 Voltammetry cell. Counter and working electrodes were made of Pt, and the reference electrode was Ag/Ag^{+}. The measurements were conducted in MeCN solvent containing tetrabutylammonium hexafluorophosphate as a supporting electrolyte at an indicated scan rate. All the potentials were calibrated with the standard ferrocene/ferrocenium (Fc/Fc^{+}) redox couple measured in identical conditions. Microwave irradiation

was conducted with Initiator^{+} (Biotage), and the reaction temperature was measured by an internal probe. The crystal measurement was performed with XtaLAB Synergy-S/Cu (Rigaku).

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was dried on a Glass Contour Solvent dispensing system (Nikko Hansen & Co., Ltd.) prior to use. The 1,1-diarylethylene (**1a**) was commercially available from TCI, and others **1b-d** and **1f-j** were prepared from the commercially available corresponding benzophenones by the Wittig reaction with methyltriphenylphosphonium bromide. The **1e** was prepared according to the literature method.[S1] 4-Bromo-3-chloro-*N*,*N*-diphenylaniline was synthesized from 1-bromo-2-chloro-4-iodobenzene and diphenylamine by the Buchwald-Hartwig amination reaction.[S2] Unless otherwise noted, all reaction were performed under nitrogen atmosphere.

Experimental Procedures

1. Procedures for the synthesis of benzophosphole 2 (Scheme 3)



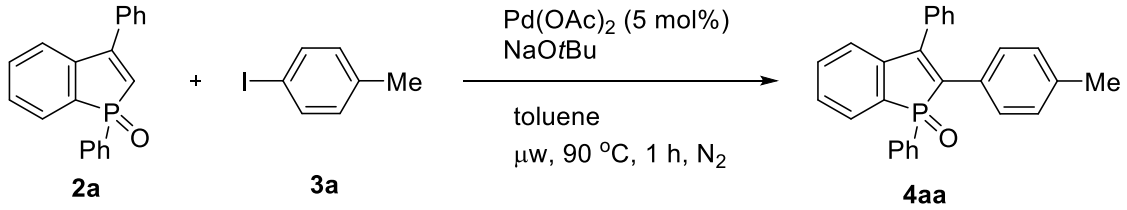
1a **2a**

A 0.1 mmol scale reaction of **1a**: In a Schlenk tube with pressure resistance, phenylphosphinic acid (0.20 mmol, 28.4 mg) was dissolved in toluene (1.5 mL), and 1,1-diphenylethylene (**1a**, 0.10 mmol, 18.0 mg) and 4-methylpyridine (0.48 mmol, 44.7 mg) were subsequently added under N_2. Tf_2O (0.48 mmol, 80 μL) was then added, and the mixture was heated at 120 ˚C in an oil bath for 16 h. After cooling, the resulting mixture was quenched with aqueous HCl (1 M, 1 mL) and extracted with $CHCl_3$ (3 x 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash silica gel column chromatography with hexane/EtOAc (1:2, v/v) to give the desired product **2a** (98%, 29.6 mg).

A 7.3 mmol scale reaction of **1a**: In a Schlenk tube with pressure resistance, phenylphosphinic acid (14.6 mmol, 2.073 g) was dissolved in toluene (15 mL), and 1,1-diphenylethylene (**1a**, 7.3 mmol, 1.314 g) and 4-methylpyridine (35.04 mmol, 3.263 g) were subsequently added under N_2. The tube was cooled to 0 °C with an ice bath, and Tf_2O (35.04 mmol, 5.8 mL) was added. The mixture was heated at 120 ˚C in an oil bath for 22 h. After cooling, the resulting mixture was quenched with aqueous HCl (1 M, 10 mL) and extracted with $CHCl_3$ (3 x 25 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography with hexane/EtOAc (1:2, v/v) and GPC ($CHCl_3$) subsequently to give the desired product **2a** (64%, 1.41 g).

2. Procedures for palladium-catalysed C–H arylation of benzophospholes

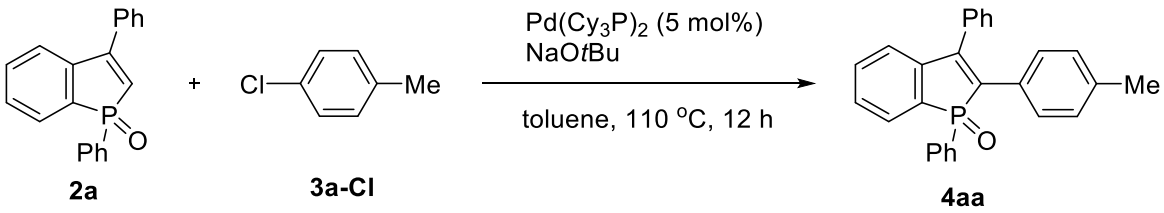
Procedure for the reaction with aryl iodides or bromides (Scheme 4)



A 0.2 mmol scale reaction of **2a**: To a 10 mL microwave vessel were added **2a** (0.20 mmol, 60.4 mg), 4-iodotoluene (**3a**, 0.30 mmol, 65.4 mg), and $Pd(OAc)_2$ (0.010 mmol, 2.3 mg). The vessel was moved to a glovebox filled with N_2, and NaO*t*Bu (0.40 mmol, 38.4 mg) was added. The vessel was sealed and taken out from the glovebox. Toluene (2.0 mL) was then added by syringe, and the reaction mixture was irradiated under microwave reactor conditions at 90 °C for 1 hour. The reaction was allowed to cool to room temperature, and the mixture was filtered through a short plug of activated alumina (EtOAc as eluent) and concentrated in vacuo. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (1:2, v/v) as eluent to give the desired product **4aa** (79%, 61.9 mg).

A 2.0 mmol scale reaction of **2a**: To a 30 mL microwave vessel were added **2a** (2.0 mmol, 604.0 mg), 4-iodotoluene (**3a**, 3.0 mmol, 654.0 mg), and $Pd(OAc)_2$ (0.10 mmol, 22.5 mg). The vessel was moved to a glovebox filled with N_2, and NaO*t*Bu (4.0 mmol, 384.0 mg) was added. The vessel was sealed and taken out from the glovebox. Toluene (15 mL) was then added by syringe, and the reaction mixture was irradiated under microwave reactor conditions at 90 °C for 1 hour. The reaction was allowed to cool to room temperature, and the mixture was filtered through a short plug of activated alumina (EtOAc as eluent) and concentrated in vacuo. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (1:2, v/v) as eluent to give the desired product **4aa** (65%, 510.0 mg).

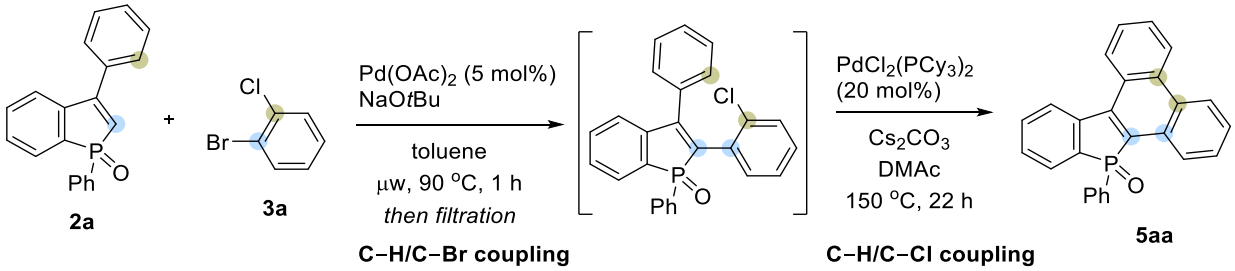
Procedure for the reaction with aryl chlorides (Scheme 8a)



A 0.1 mmol scale reaction of **2a**: To a 10 mL microwave vessel were added **2a** (0.10 mmol, 30.2 mg) and 4-chlorotoluene (**3a-Cl**, 0.30 mmol, 38.0 mg). The vessel was moved to a glovebox filled with N_2, and $Pd(Cy_3P)_2$ (0.0050 mmol, 3.3 mg) and NaO*t*Bu (0.20 mmol, 19.2 mg) were added. The vessel was sealed and taken out from the glovebox. Toluene (1.0 mL) was then added by

syringe, and the reaction mixture was stirred at 110 °C (oil bath) for 12 hour. The reaction was allowed to cool to room temperature, and the mixture was filtered through a short plug of activated alumina (EtOAc as eluent) and concentrated in vacuo. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (1:2, v/v) as eluent to give the desired product **4aa** (69%, 27.1 mg).

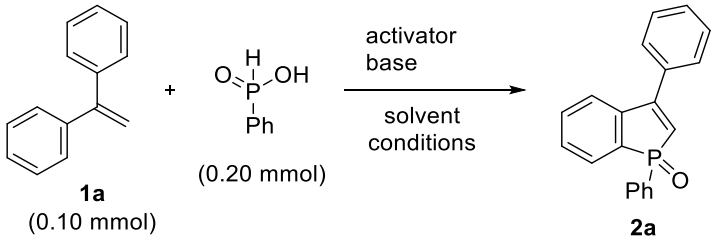
Procedure for the synthesis of 5 (Scheme 8b)



Synthesis of **5aa**: To a 10 mL microwave vessel were added **2a** (0.20 mmol, 60.4 mg), 1-bromo-2-chlorobenzene (**3**, 0.30 mmol, 57.4 mg), and $Pd(OAc)_2$ (0.010 mmol, 2.3 mg). The vessel was moved to a glovebox filled with N_2, and NaO*t*Bu (0.40 mmol, 38.4 mg) was added. The vessel was sealed and taken out from the glovebox. Toluene (2.0 mL) was then added by syringe, and the reaction mixture was irradiated under microwave reactor conditions at 90 °C for 1 hour. The reaction was allowed to cool to room temperature, and the mixture was filtered through a short plug of activated alumina (EtOAc as eluent) and concentrated in vacuo. The residue was transferred to a 20 mL two-neck round-bottom flask, and $PdCl_2(PCy_3)_2$ (0.040 mmol, 29.6 mg), Cs_2CO_3 (0.4 mmol, 130.4 mg), and DMAc (1.0 mL) were added. The mixture was stirred at 150 °C (oil bath) for 22 hour under N_2. The resulting mixture was then quenched with brine and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with hexane/ethyl acetate (1:1, v/v) gave the desired product **5aa** (75%, 56.3 mg).

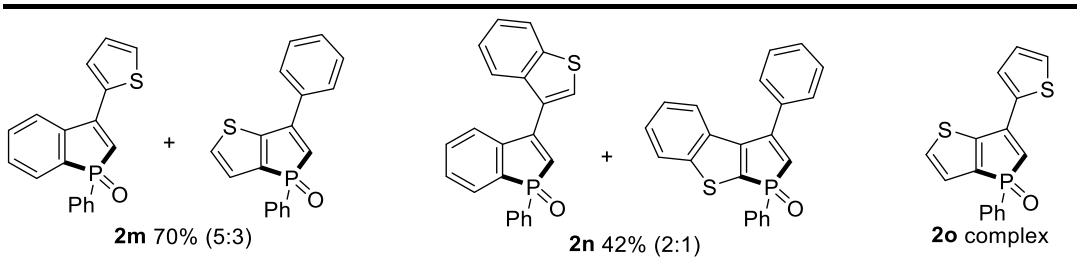
Detailed Optimization Studies

Table S1. Optimization Studies for the Synthesis of Starting Benzophosphole **2a** from 1,1-Diphenylethylene **1a** and Phenylphosphinic Acid[a]



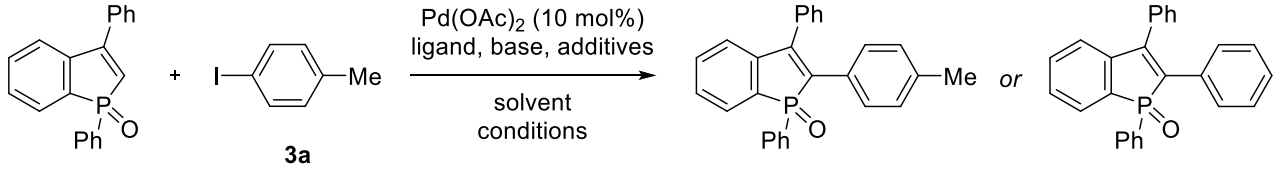
Entry	Activator (mmol)	Base (mmol)	Solvent	Conditions	Yield of 2a (%)[b]
1	Tf_2O (0.48)	DMAP (0.48)	DCE	120 °C, 16 h	(69)
2	Tf_2O (0.48)	DMAP (0.48)	DCE	90 °C, 16 h	trace
3	$PhNTf_2$ (0.48)	DMAP (0.48)	DCE	120 °C, 16 h	n.d.
4	TfOH (0.96)	none	DCE	120 °C, 16 h	n.d.
5	Tf_2O (0.48)	2,6-lutidine (0.48)	DCE	120 °C, 16 h	1
6	Tf_2O (0.48)	4-methylpyridine (0.48)	DCE	120 °C, 16 h	76
7	Tf_2O (0.48)	pyridine (0.48)	DCE	120 °C, 16 h	60
8	Tf_2O (0.48)	Et_3N (0.48)	DCE	120 °C, 16 h	1
9	Tf_2O (0.48)	K_2CO_3 (0.48)	DCE	120 °C, 16 h	21
10	Tf_2O (0.48)	none	DCE	120 °C, 16 h	n.d.
11	**Tf_2O (0.48)**	**4-methylpyridine (0.48)**	**touene**	**120 °C, 16 h**	**92(98)**
12	Tf_2O (0.48)	4-methylpyridine (0.48)	toluene	110 °C, 16 h	81
13	Tf_2O (0.48)	4-methylpyridine (0.48)	$PhCF_3$	120 °C, 16 h	78
14	Tf_2O (0.48)	4-methylpyridine (0.48)	dioxane	120 °C, 16 h	n.d.
15	Tf_2O (0.48)	4-methylpyridine (0.48)	HFIP	120 °C, 16 h	1

[a]Reaction conditions: **1a** (0.10 mmol), phenylphosphinic acid (0.20 mmol), activator (0.48 mmol), base (0.48 mmol), solvent (1.5 mL), N_2. [b]Determined by ^{31}P NMR using triethylphosphate as an internal standard. Isolated yield is in parentheses.



Scheme S1 Unsuccessful heterocyclic systems in starting material preparation.

Table S2. Optimization Studies for Palladium-Catalysed C–H Arylation of Benzophosphole **2a** with 4-Iodotoluene **3a**[a]



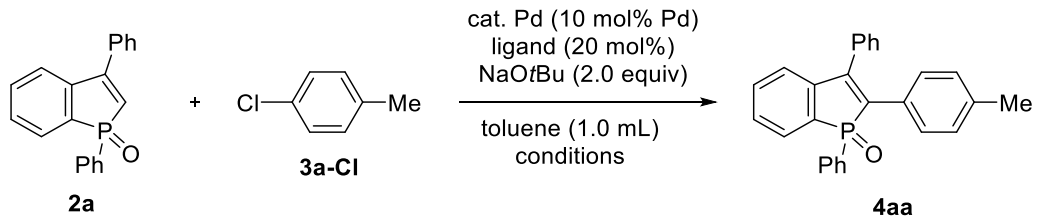
2a **3a** **4aa** **4aa'**

Entry	Ligand (mol%)	Base (equiv)	Additives (equiv)	Solvent (mL)	Conditions	Yield of 4aa or 4aa' (%)[b]
1		NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 16 h	66
2		NaO*t*Bu (2.0)		toluene (1.5)	110 °C, 16 h	32
3[c]		NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 22 h	60(66)
4[c]		NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 11 h	42
5[c]		NaO*t*Bu (2.0)		toluene (1.5)	80 °C, 22 h	55
6[d]		NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 16 h	n.d.
7	SPhos (20)	NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 16 h	21
8	XPhos (20)	NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 16 h	19
9	PPh_2Cy (20)	NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 16 h	56
10	PPh_3 (20)	NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 16 h	39
11[e]		NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 16 h	49
12[f]		NaO*t*Bu (2.0)		toluene (1.5)	110 °C, 16 h	0
13[g]		NaO*t*Bu (2.0)		toluene (1.5)	90 °C, 16 h	trace
14		KO*t*Bu (2.0)		toluene (1.5)	90 °C, 16 h	68
15		LiO*t*Bu (2.0)		toluene (1.5)	110 °C, 16 h	21
16		LiO*t*Bu (2.0)		DMF (1.5)	90 °C, 18 h	13
17		NaO*t*Amyl (2.0)		toluene (1.5)	90 °C, 16 h	28
18		Cs_2CO_3 (2.0)		toluene (1.5)	110 °C, 16 h	0
19		NaO*t*Bu (1.5)		toluene (1.5)	90 °C, 16 h	39
20		NaO*t*Bu (1.0)		toluene (1.5)	110 °C, 16 h	23
21		NaO*t*Bu (1.5)	DIPEA (1.0)	toluene (1.5)	90 °C, 16 h	43
22		NaO*t*Bu (1.5)	DIPEA (1.0)	toluene (1.5)	100 °C, 11 h	46
23		NaO*t*Bu (2.0)		mesitylene (1.5)	90 °C, 16 h	44
24		NaO*t*Bu (2.0)		*o*-xylene (1.5)	90 °C, 16 h	61
25		NaO*t*Bu (2.0)		benzene (1.5)	90 °C, 16 h	58
26[c]		NaO*t*Bu (2.0)		$PhCF_3$ (1.5)	90 °C, 18 h	61
27[c]		NaO*t*Bu (2.0)		MeCN (1.5)	90 °C, 16 h	complex
28[c]		NaO*t*Bu (2.0)		octane (1.5)	90 °C, 16 h	9

29	NaO*t*Bu (2.0)	LiCl (1.0)	toluene (1.5)	90 °C, 16 h	67
30	NaO*t*Bu (2.0)	TBAI (1.0)	toluene (1.5)	90 °C, 16 h	59
31	NaO*t*Bu (2.0)	TBAB (1.0)	toluene (1.5)	90 °C, 16 h	22
32	NaO*t*Bu (2.0)	Ag_2CO_3 (0.5)	toluene (1.5)	90 °C, 12 h	42
33	NaO*t*Bu (1.5)	Ag_2CO_3 (0.5)	toluene (1.5)	90 °C, 18 h	32
34	NaO*t*Bu (2.0)	AgOAc (1.0)	toluene (1.5)	90 °C, 12 h	54
35	NaO*t*Bu (2.0)	AgTFA (1.0)	toluene (1.5)	90 °C, 16 h	46
36	NaO*t*Bu (2.0)	$Cu(OAc)_2$ (2.0)	toluene (1.5)	90 °C, 16 h	43
37	NaO*t*Bu (2.0)	CuOAc (2.0)	toluene (1.5)	90 °C, 16 h	51
38	NaO*t*Bu (2.0)		toluene (2.0)	90 °C, 16 h	73(76)
39	NaO*t*Bu (2.0)		toluene (2.0)	100 °C, 8 h	70
40	NaO*t*Bu (2.0)		toluene (3.0)	90 °C, 16 h	43
41	NaO*t*Bu (2.0)		toluene (2.0)	μw, 100 °C, 2 h	71
42	NaO*t*Bu (2.0)		toluene (1.5)	μw, 100 °C, 1 h	78
43	NaO*t*Bu (2.0)		toluene (1.5)	μw, 90 °C, 2 h	78
44	NaO*t*Bu (2.0)		toluene (1.5)	μw, 80 °C, 2 h	35
45	NaO*t*Bu (2.0)		toluene (1.5)	μw, 90 °C, 1 h	72
46	NaO*t*Bu (2.0)		toluene (1.0)	μw, 90 °C, 1 h	83
47	NaO*t*Bu (2.0)		toluene (0.5)	μw, 90 °C, 1 h	76
48[h]	**NaO*t*Bu (2.0)**		**toluene (2.0)**	**μw, 90 °C, 1 h**	**81(79)**
49[e]	NaO*t*Bu (2.0)		toluene (1.0)	μw, 90 °C, 1 h	74
50[i]	NaO*t*Bu (2.0)		toluene (1.0)	μw, 90 °C, 1 h	n.d.
51[j]	NaO*t*Bu (2.0)		toluene (1.0)	μw, 90 °C, 1 h	trace

[a]Reaction conditions: $Pd(OAc)_2$ (0.010 mmol), **2a** (0.10 mmol), **3a** (0.15 mmol), solvent (1.5 mL), N_2. [b]Determined by ^1H NMR using triethylphosphate as an internal standard. Isolated yields are in parentheses. [c]With 0.20 mmol of **2a**. [d]Without $Pd(OAc)_2$. [e]4-Bromotoluene was used instead of **3a**. [f]PhOTf was used instead of **3a**. The targeted product was **4aa'**. [g]Ph_2IOTf was used instead of **3a**. The targeted product was **4aa'**. [h]On a 0.20 mmol scale with $Pd(OAc)_2$ (0.010 mmol, 5 mol %). [i]PhOTs was used instead of **3a**. The targeted product was **4aa'**. [j]4-Chlorotoluene was used instead of **3a**.

Table S3. Optimization Studies for Palladium-Catalysed C–H Arylation of Benzophosphole **2a** with 4-Chlorotoluene **3a-Cl**[a]

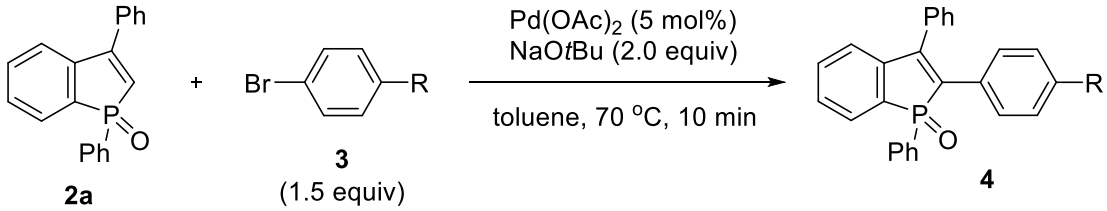


Entry	Cat. Pd	Ligand (20 mol%)	Conditions	Yield of 4aa (%)[b]
1	$Pd_2(dba)_3$	XPhos	μw, 100 °C, 1 h	15
2	$Pd_2(dba)_3$	XPhos	μw, 140 °C, 1 h	11
3	$Pd_2(dba)_3$		μw, 100 °C, 1 h	trace
4[c]	$PdCl_2(Cy_3P)_2$		μw, 110 °C, 1 h	11
5	**$Pd_2(dba)_3$**	**XPhos**	**110 °C, 12 h**	**45**
6[d]	$Pd_2(dba)_3$	XPhos	90 °C, 20 h	42
7	$Pd_2(dba)_3$	XPhos	70 °C, 16 h	33
8	$Pd_2(dba)_3$	$PCy_3H{\cdot}BF_4$	90 °C, 16 h	complex
9	$Pd_2(dba)_3$	PCy_3	100 °C, 16 h	32
10	$Pd(OAc)_2$	XPhos	110 °C, 12 h	6
11	$Pd(OAc)_2$	SPhos	110 °C, 12 h	complex
12[c]	XPhos Pd G4		110 °C, 6 h	16
13[c]	XPhos Pd G4		110 °C, 18 h	14
14[c, e]	XPhos Pd G4		110 °C, 10 h	24
15[c]	RuPhos Pd G3		110 °C, 10 h	trace
16	CpPd(π-allyl)	XPhos	110 °C, 17 h	n.d.
17	$(cod)Pd(CH_2TMS)_2$	XPhos	110 °C, 17 h	n.d.
18	$Pd_2(dba)_3{\cdot}CHCl_3$	XPhos	110 °C, 12 h	n.d.
19[c,d]	$Pd(tBu_3P)_2$		100 °C, 15 h	51
20[c,d]	$Pd(Cy_3P)_2$		100 °C, 15 h	62
21[c,d]	$Pd(Ph_3P)_4$		100 °C, 15 h	n.d.
22[c,d]	$Pd(Cy_3P)_2$		μw, 100 °C, 1 h	33
23[c,d]	**$Pd(Cy_3P)_2$**		**110 °C, 12 h**	**69(69)**
24[f]	$Pd(Cy_3P)_2$		110 °C, 12 h	40
25[g]	$Pd(Cy_3P)_2$		110 °C, 12 h	11

[a]Reaction conditions: Pd catalyst (0.010 mmol, based on Pd), **2a** (0.10 mmol), **3a-Cl** (0.15 mmol), solvent (1.0 mL), N_2. [b]Determined by ^1H NMR using triethylphosphate as an internal standard. Isolated yield is in parentheses. [c]With 5 mol % Pd loading. [d]With 0.30 mmol of **3a-Cl**. [e]Dioxane

(1.0 mL) was used instead of toluene. [f]With 0.30 mmol of 4-iodotoluene. [g]With 0.30 mmol of 4-bromotoluene.

Hammett Studies



Yields of **4** (NMR)

R = OPh: 6% R = OMe: 9% R = Me: 13% R = H: 15%

R = F: 7% R = Cl: 6% R = CF_3: 2%

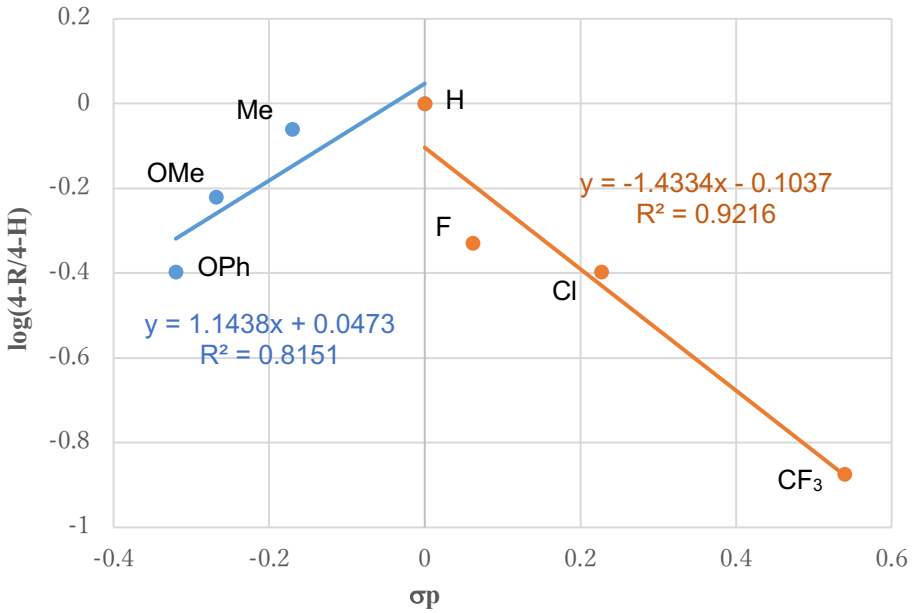


Figure S1. Hammett plot with *para*-substituted aryl bromides **3**.

Cyclic Voltammetry and Differential Pulse Voltammetry

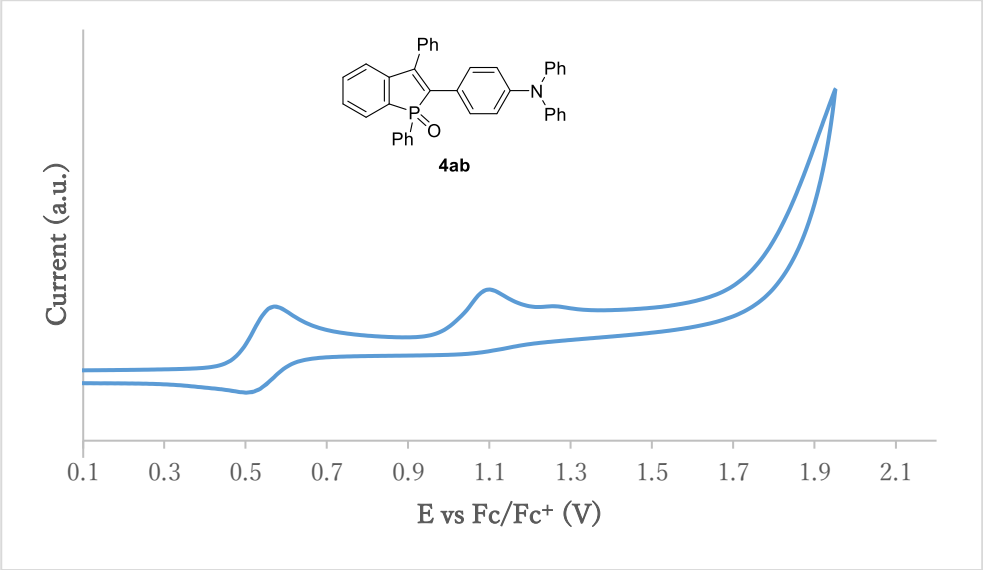


Figure S2. Cyclic voltammograms of **4ab** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.05 V/s.

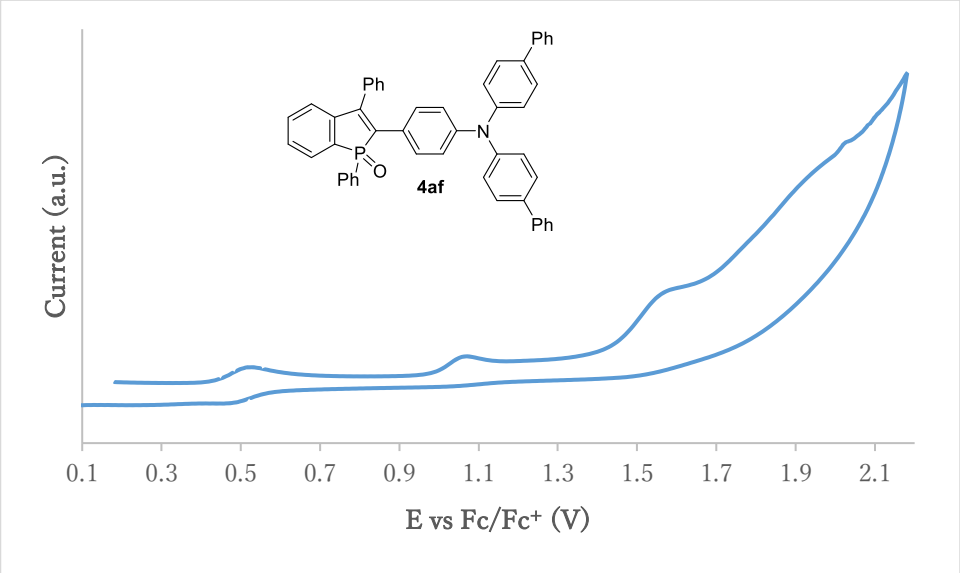


Figure S3. Cyclic voltammograms of **4af** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.05 V/s.

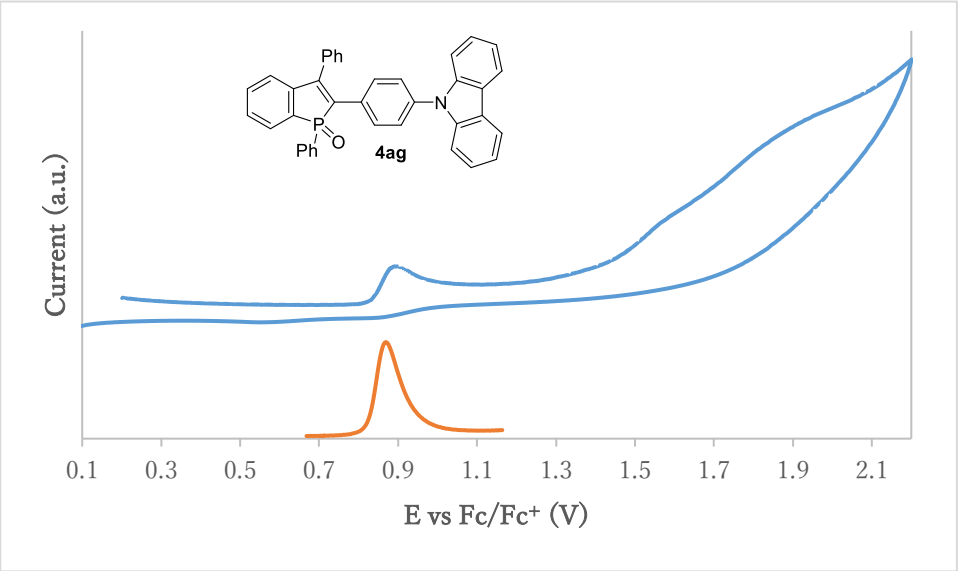


Figure S4. Cyclic voltammograms (blue line) and differential pulse voltammograms (orange line) of **4ag** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.1 V/s.

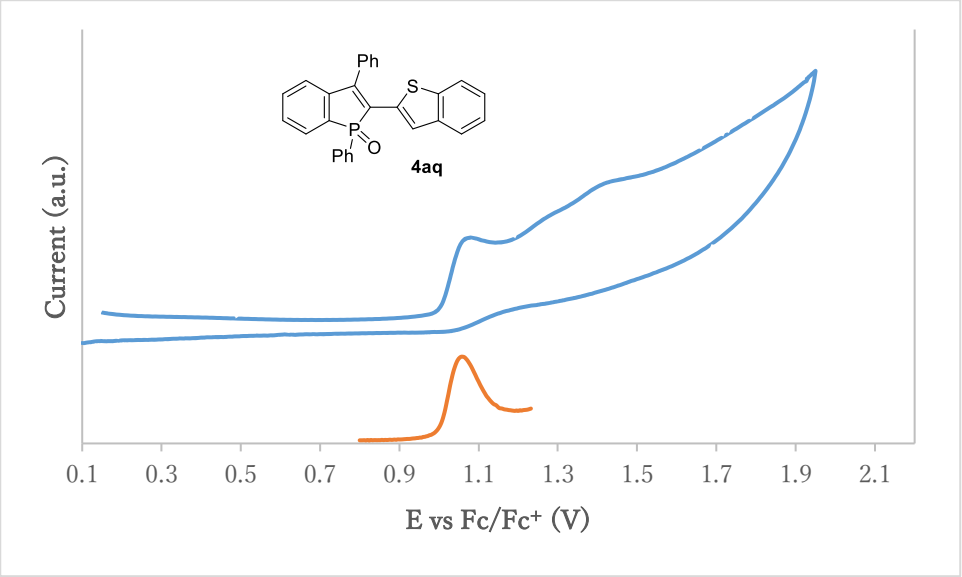


Figure S5. Cyclic voltammograms (blue line) and differential pulse voltammograms (orange line) of **4aq** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.05 V/s.

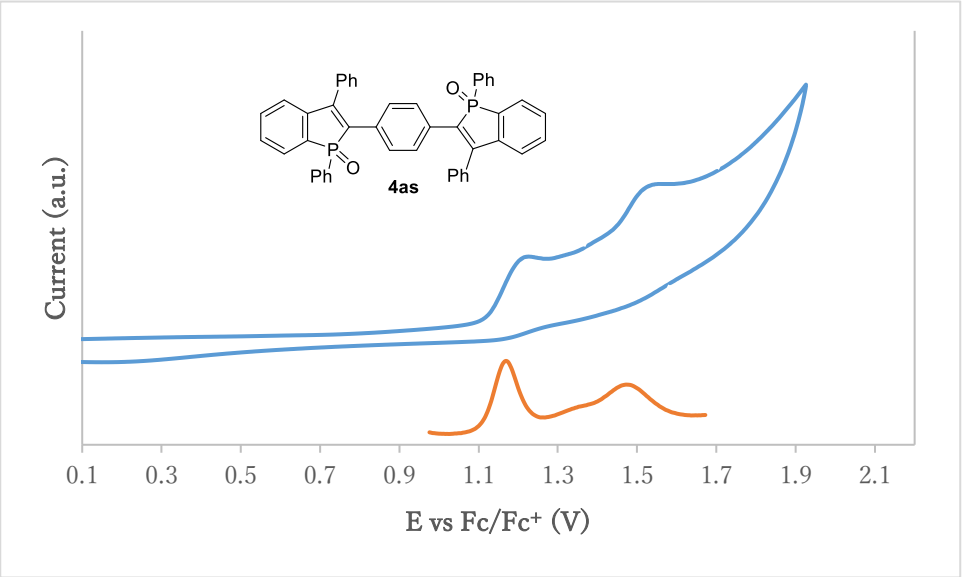


Figure S6. Cyclic voltammograms (blue line) and differential pulse voltammograms (orange line) of **4as** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.05 V/s.

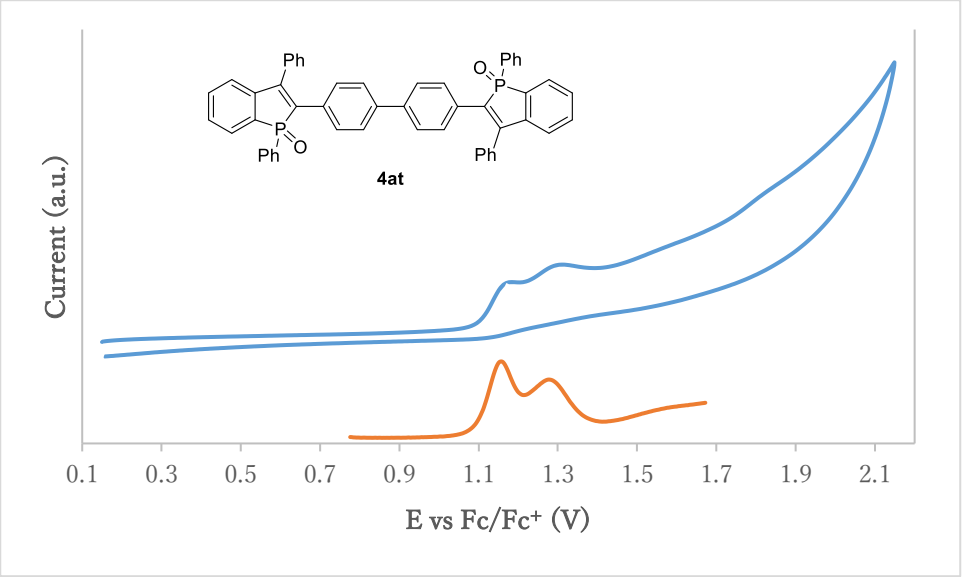


Figure S7. Cyclic voltammograms (blue line) and differential pulse voltammograms (orange line) of **4at** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.03 V/s.

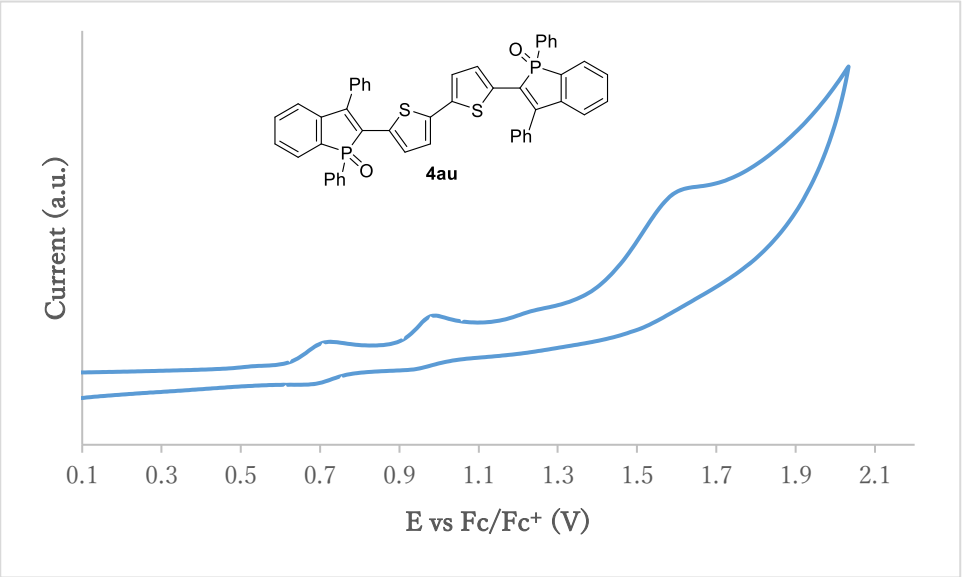


Figure S8. Cyclic voltammograms of **4au** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.05 V/s.

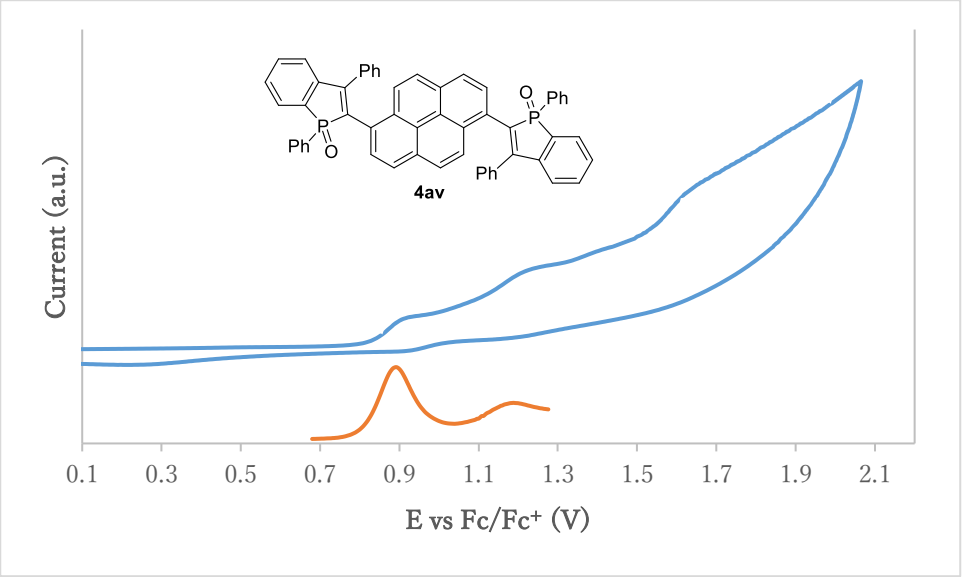


Figure S9. Cyclic voltammograms (blue line) and differential pulse voltammograms (orange line) of **4av** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.05 V/s.

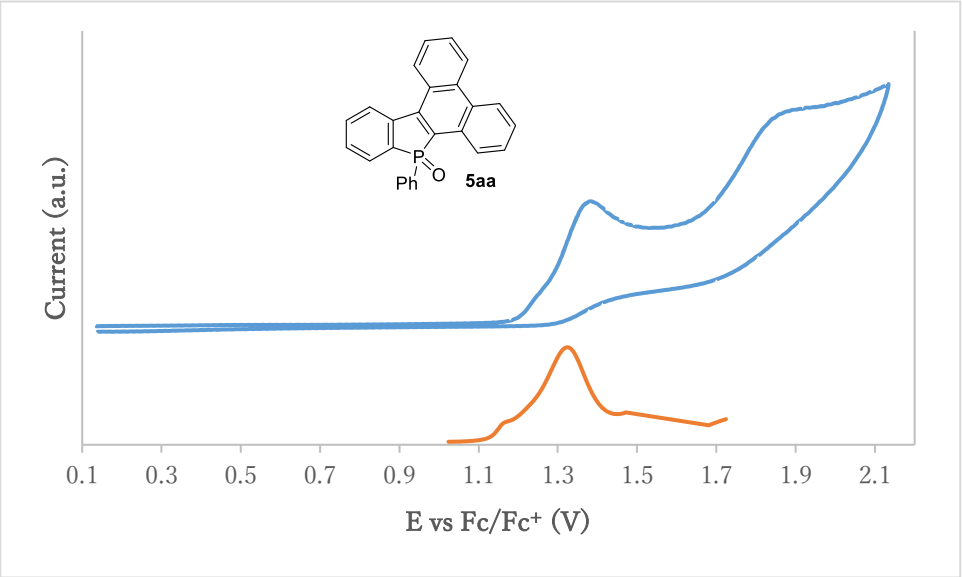


Figure S10. Cyclic voltammograms (blue line) and differential pulse voltammograms (orange line) of **5aa** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.05 V/s.

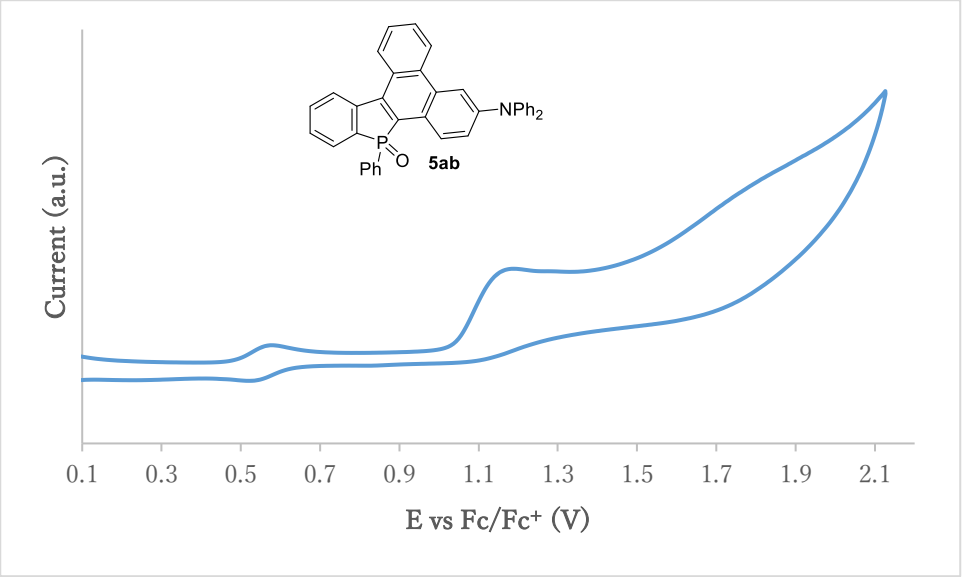


Figure S11. Cyclic voltammograms of **5ab** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.03 V/s.

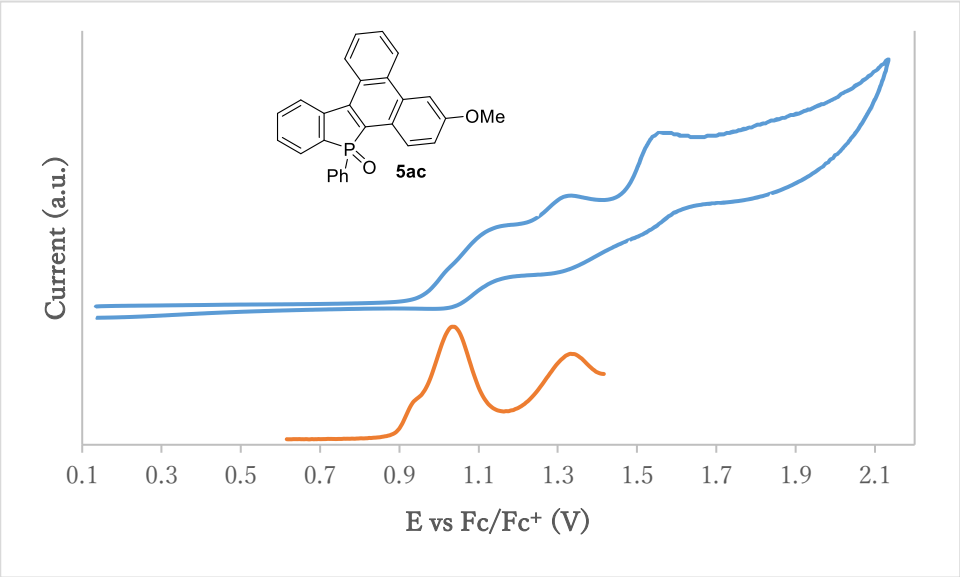


Figure S12. Cyclic voltammograms (blue line) and differential pulse voltammograms (orange line) of **5ac** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.03 V/s.

Absorption and Fluorescence Spectra

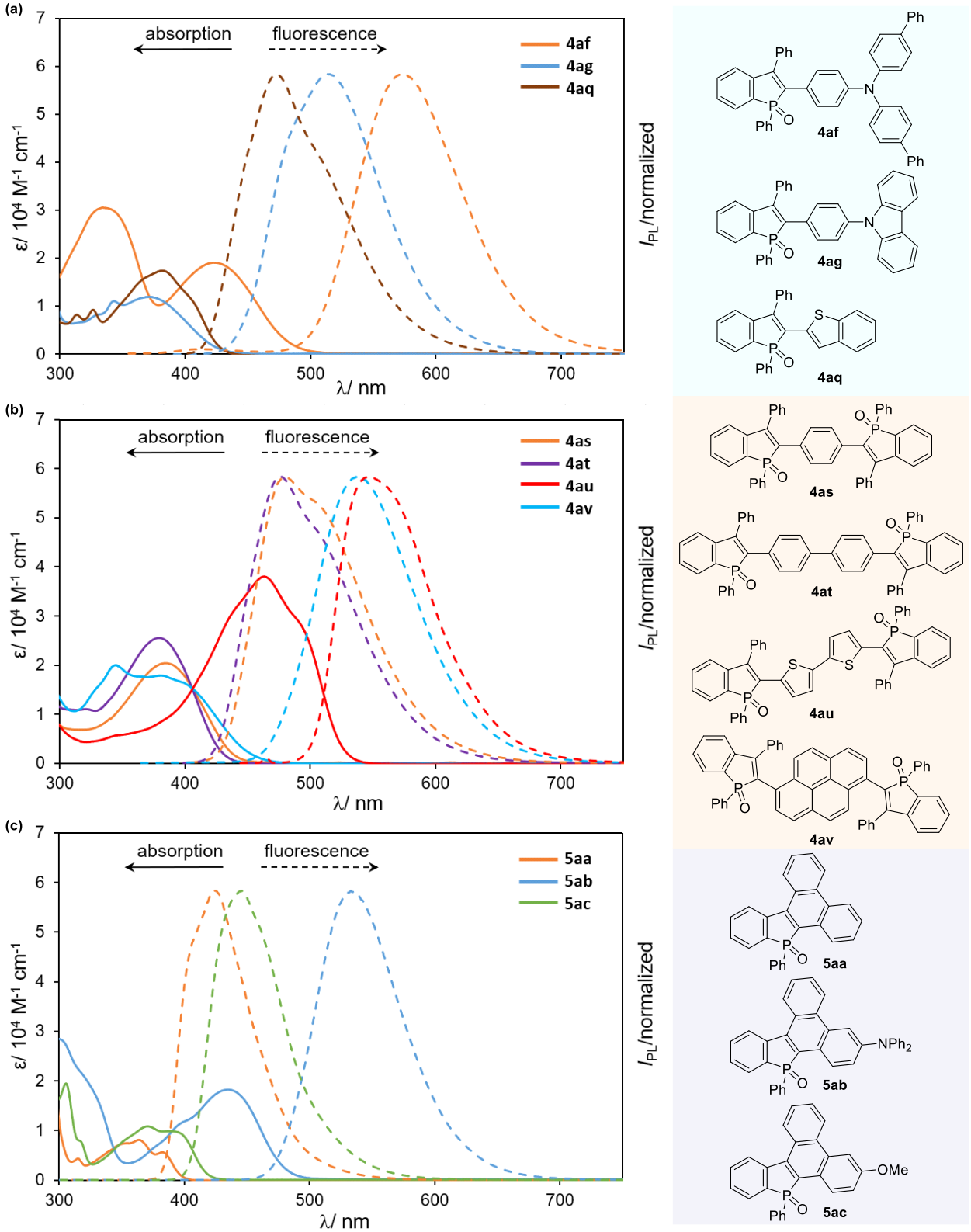


Figure S13. UV-vis absorption (solid line) and fluorescence spectra (dashed line; excited at the absorption maxima) of (a) **4af-ag**, and **4aq**, (b) **4as-av**, and **5aa-ac** in CH_2Cl_2 (c = 10^{-5} M).

Theoretical Calculations

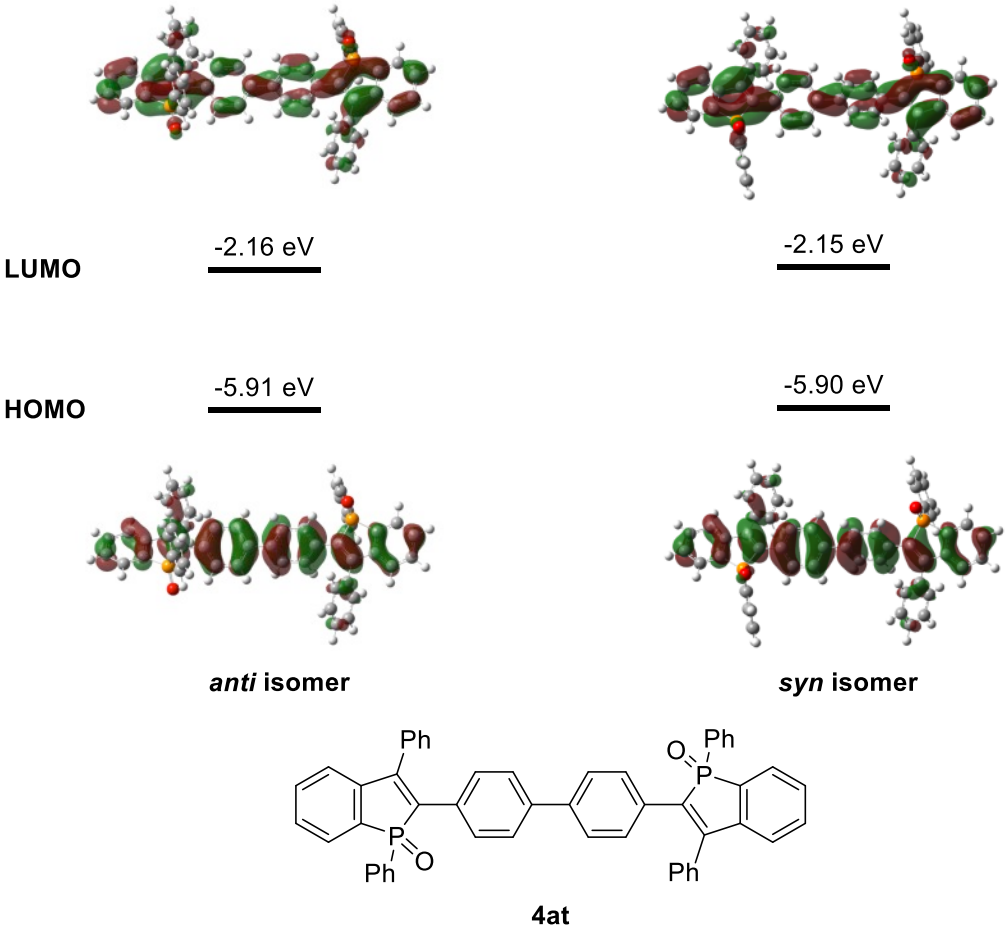


Figure S14. Kohn-Sham molecular orbitals of **4at** calculated at the PBE0/6-31 +G(d) level of theory, implemented in the Gaussian 16 program.

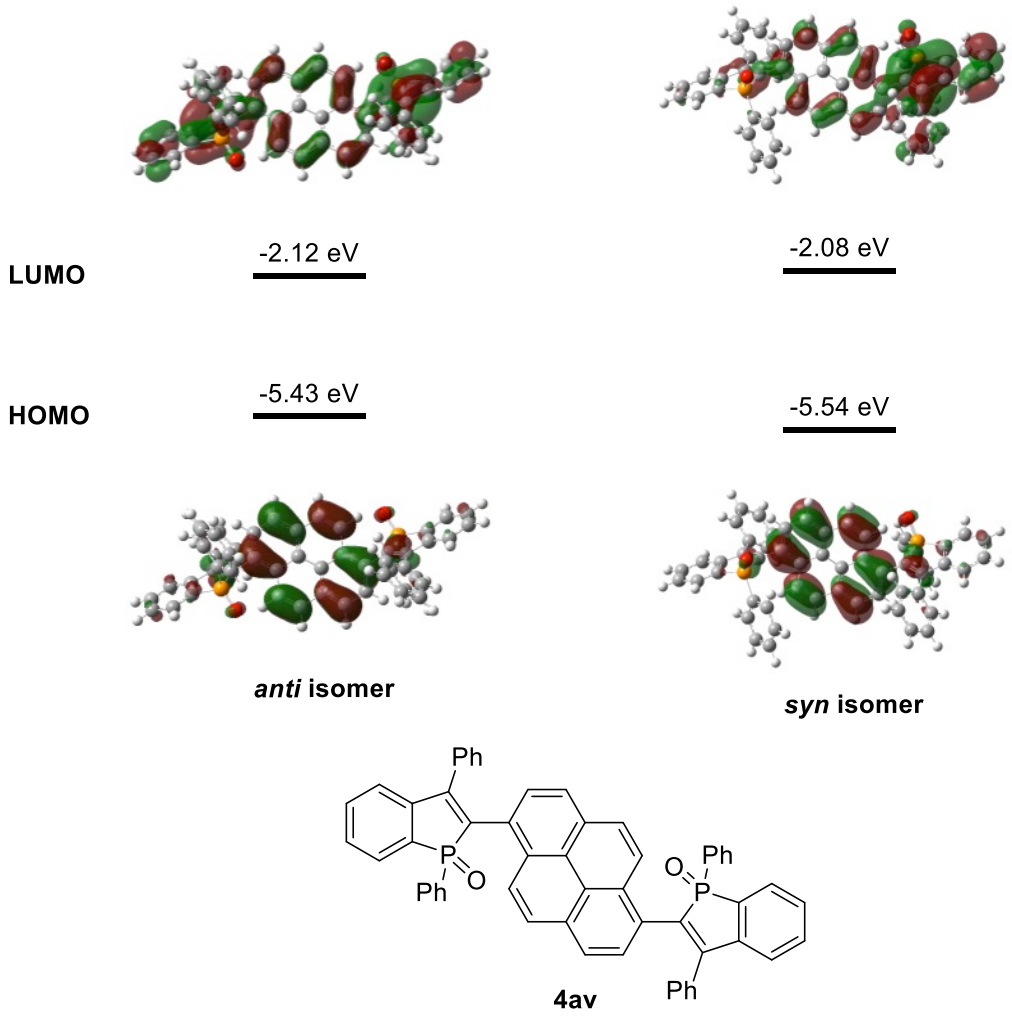


Figure S15. Kohn-Sham molecular orbitals of **4av** calculated at the PBE0/6-31 +G(d) level of theory, implemented in the Gaussian 16 program.

X-Ray Analysis

The single crystals of **2b** suitable for X-ray analysis were grown from $CHCl_3$/hexane. The structure was refined by full-matrix least-squares method using SHELXL-2017/1.

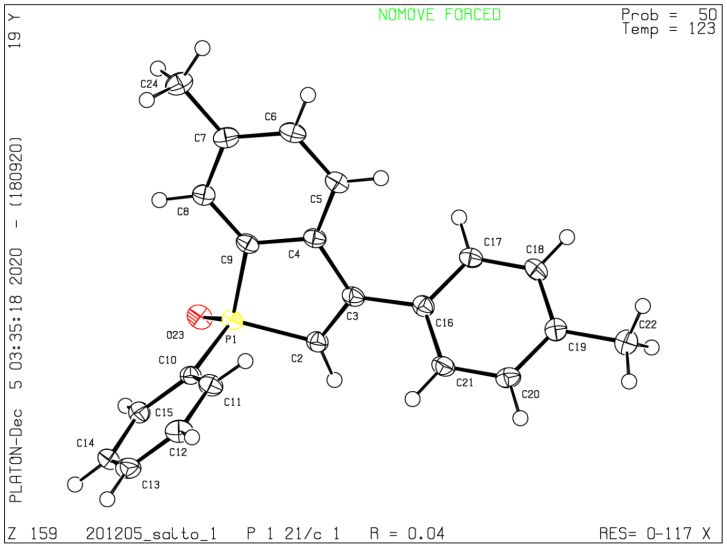


Figure S16. ORTEP drawing of **2b** (CCDC 2174057, 50% thermal probability).

Table S4. Crystal Data for **2b**

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	12.5743(3)
Cell length b	11.3680(2)
Cell length c	11.7601(2)
Cell angle alpha	90
Cell angle beta	93.369(2)
Cell angle gamma	90
Cell volume	1678.14(6)
Cell formula units Z	4
Refine ls R factor all	0.0435
Refine ls R factor gt	0.0403
Refine ls wR factor gt	0.1064
Refine ls wR factor ref	0.1094
Refine ls goodness of fit ref	1.064

The single crystals of **4av** suitable for X-ray analysis were grown from $CHCl_3$/EtOAc/hexane. The structure was refined by full-matrix least-squares method using SHELXL-2017/1.

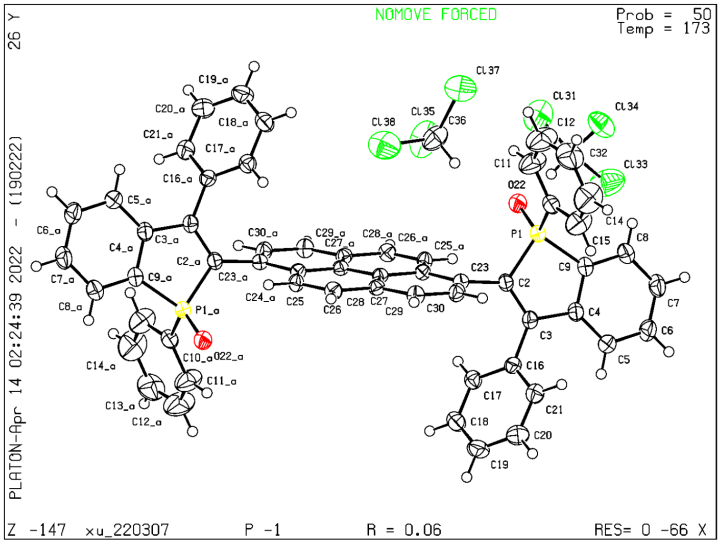


Figure S17. ORTEP drawing of **4av** (CCDC 2166424, 50% thermal probability).

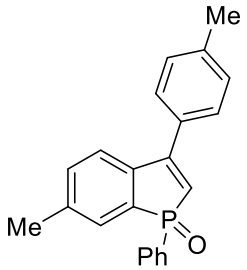
Table S5. Crystal Data for **4av**

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	10.0941(3)
Cell length b	10.4249(3)
Cell length c	15.3161(3)
Cell angle alpha	73.955(2)
Cell angle beta	87.469(2)
Cell angle gamma	73.633(3)
Cell volume	1485.17(7)
Cell formula units Z	2
Refine ls R factor all	0.0877
Refine ls R factor gt	0.0633
Refine ls wR factor gt	0.1680
Refine ls wR factor ref	0.1847
Refine ls goodness of fit ref	1.113

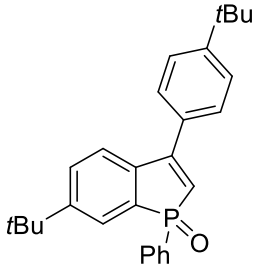
Characterization Data for Substrates and Products

The characterization data for **2a** is consistent with that reported in our previous work.[S3]

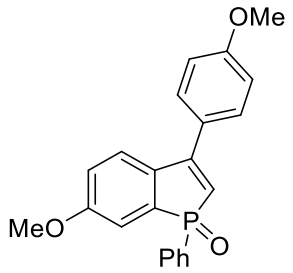
^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra for all compounds are attached in the last part.



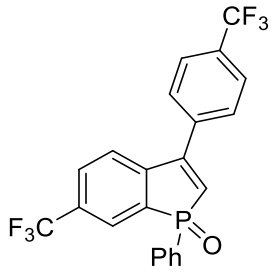
6-Methyl-1-phenyl-3-(*p*-tolyl)phosphindole 1-oxide (2b) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 28 mg (85%, 0.10 mmol scale); pale yellow solid; m.p. 157.6 – 158.7 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.76 (m, 2H), 7.55-7.42 (m, 6H), 7.37 (dd, J = 3.0, 7.8 Hz, 1H), 7.30 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 10.4 Hz, 1H), 6.26 (d, J = 24.2 Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.3 (d, $^{2}J_{CP}$ = 15.4 Hz, 1C), 140.0 (d, $^{3}J_{CP}$ = 10.5 Hz, 1C), 139.8 (1C), 139.7 (d, $^{2}J_{CP}$ = 27.0 Hz, 1C), 134.4 (d, $^{1}J_{CP}$ = 104.1 Hz, 1C), 133.0 (1C), 132.5 (d, $^{3}J_{CP}$ = 16.4 Hz, 1C), 132.3 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 131.1 (d, $^{2}J_{CP}$ = 10.8 Hz, 2C), 130.2 (d, $^{2}J_{CP}$ = 9.8 Hz, 1C), 130.1 (d, $^{1}J_{CP}$ = 101.4 Hz, 1C), 129.6 (2C), 128.9 (d, $^{3}J_{CP}$ = 12.4 Hz, 2C), 127.9 (2C), 124.0 (d, $^{3}J_{CP}$ = 11.9 Hz, 1C), 121.3 (d, $^{1}J_{CP}$ = 99.9 Hz, 1C), 21.6 (1C), 21.4 (1C); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz): δ 36.92; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{22}H_{20}OP$: 331.1246, found: 331.1224.



6-(*tert*-Butyl)-3-(4-(*tert*-butyl)phenyl)-1-phenylphosphindole 1-oxide (2c) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 29 mg (70%, 0.10 mmol scale); pale yellow solid; m.p. 180.4 – 181.6 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.72 (m, 3H), 7.52-7.49 (m, 6H), 7.47-7.42 (m, 3H), 6.29 (d, J = 24.2 Hz, 1H), 1.38 (s, 9H), 1.30 (s, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz); δ 157.9 (d, $^{2}J_{CP}$ = 15.3 Hz, 1C), 153.3 (d, $^{3}J_{CP}$ = 9.7 Hz, 1C), 153.0 (1C), 139.7 (d, $^{2}J_{CP}$ = 27.6 Hz, 1C), 134.1 (d, $^{1}J_{CP}$ = 104.3 Hz, 1C), 132.4 (d, $^{3}J_{CP}$ = 16.1 Hz, 1C), 132.2 (d, $^{4}J_{CP}$ = 2.6 Hz, 1C), 131.2 (d, $^{2}J_{CP}$ = 10.8 Hz, 2C), 130.2 (d, $^{1}J_{CP}$ = 101.9 Hz, 1C), 129.5 (1C), 128.9 (d, $^{3}J_{CP}$ = 12.3 Hz, 2C), 127.8 (2C), 126.6 (d, $^{2}J_{CP}$ = 10.1 Hz, 1C), 125.8 (2C), 124.0 (d, $^{3}J_{CP}$ = 11.9 Hz, 1C), 121.9 (d, $^{1}J_{CP}$ = 100.7 Hz, 1C), 35.2 (1C), 35.0 (1C), 31.4-31.3 (overlapped, 6C); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz): δ 37.31; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{28}H_{32}OP$: 415.2185, found: 415.2205.

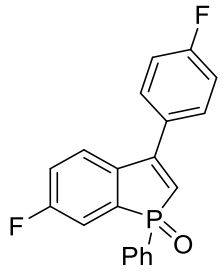


6-Methoxy-3-(4-methoxyphenyl)-1-phenylphosphindole 1-oxide (2d) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 14 mg (40%, 0.10 mmol scale); pale yellow solid; m.p. 61.6 – 62.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81-7.76 (m, 2H), 7.54-7.51 (m, 3H), 7.47-7.41 (m, 3H), 7.22 (dd, J = 2.5, 11.0 Hz, 1H), 7.02-7.00 (m, 2H), 6.95 (dd, J = 2.5, 8.5 Hz, 1H), 6.16 (d, J = 24.5 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 161.1 (d, $^{3}J_{CP}$ = 13.6 Hz, 1C), 160.8 (1C), 158.0 (d, $^{2}J_{CP}$ = 15.2 Hz, 1C), 136.5 (d, $^{1}J_{CP}$ = 103.0 Hz, 1C), 134.7 (d, $^{2}J_{CP}$ = 26.9 Hz, 1C), 132.3 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 131.1 (d, $^{2}J_{CP}$ = 10.8 Hz, 2C), 130.1 (d, $^{1}J_{CP}$ = 102.2 Hz, 1C), 129.4 (2C), 129.0 (d, $^{3}J_{CP}$ = 12.4 Hz, 2C), 127.8 (d, $^{3}J_{CP}$ = 17.0 Hz, 1C), 125.4 (d, $^{3}J_{CP}$ = 13.2 Hz, 1C), 119.2 (d, $^{1}J_{CP}$ = 101.6 Hz, 1C), 117.4 (d, $^{4}J_{CP}$ = 1.6 Hz, 1C), 115.2 (d, $^{2}J_{CP}$ = 10.9 Hz, 1C), 114.3 (2C), 55.8 (1C), 55.6 (1C); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 36.59; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{22}H_{20}O_3P$: 363.1145, found:363.1115.

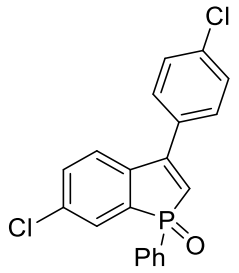


1-Phenyl-6-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)phosphindole 1-oxide (2e): colorless solid (0.1 mmol scale, 17.9 mg, 41% yield; 1.0 mmol scale, 113.9 mg, 26% yield); m.p. 142.8-143.7 °C (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (dd, J = 9.5, 0.5 Hz, 1H), 7.84-7.78 (m, 5H), 7.69 (d, J = 8.0 Hz, 2H), 7.64-7.59 (m, 1H), 7.56-7.49 (m, 3H), 6.61 (d, J = 23.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 155.5 (d, $^{2}J_{CP}$ = 14.3 Hz, 1C), 142.1, 144.6 (d, $^{2}J_{CP}$ = 27.1 Hz, 1C), 137.8 (d, $^{3}J_{CP}$ = 16.0 Hz, 1C), 135.6, 134.5, 133.0 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 132.5, 132.4, 132.2, 132.1, 131.8, 131.7, 131.5, 131.4, 130.9 (d, $^{2}J_{CP}$ = 11.0 Hz, 2C), 130.19, 130.18, 130.16, 129.2 (d, $^{3}J_{CP}$ = 12.6 Hz, 2C), 128.2, 128.1, 127.8, 127.5, 127.1, 126.5, 126.34, 126.31, 126.27, 126.23, 126.19, 126.17, 126.13, 126.10, 126.0, 125.1, 124.8, 124.79, 123.9 (d, $^{3}J_{CP}$ = 11.0 Hz, 1C), 122.3, 122.09, 122.07, 119.7, 119.4 (All observed signals are just shown because of complexity associated with C–F and C–P couplings.); ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ -62.7, -62.8. ^{31}P{^{1}H}

NMR ($CDCl_3$, 162 MHz) δ 35.8; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{22}H_{14}F_6OP$: 439.0681, Found: 439.0667.

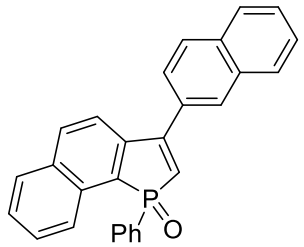


6-Fluoro-3-(4-fluorophenyl)-1-phenylphosphindole 1-oxide (2f) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 26 mg (78%, 0.10 mmol scale); pale yellow solid; m.p. 51.6 – 53.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.74 (m, 2H), 7.59-7.50 (m, 3H), 7.49-7.44 (m, 2H), 7.42-7.35 (m, 2H), 7.23-7.14 (m, 3H), 6.33 (d, J = 24.1 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 163.9 (dd, $^3J_{CP}/^1J_{CF}$ = 15.2, 252.3 Hz, 1C), 163.7 (d, $^1J_{CF}$ = 248.7 Hz, 1C), 156.6 (d, $^2J_{CP}$ = 14.5 Hz, 1C), 137.8 (dd, $^4J_{CF}/^2J_{CP}$ = 3.0, 26.4 Hz, 1C), 137.1 (dd, $^3J_{CF}/^1J_{CP}$ = 7.0, 103.1 Hz, 1C), 132.8 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 131.0 (d, $^2J_{CP}$ = 10.9 Hz, 2C), 130.9 (dd, $^4J_{CF}/^3J_{CP}$ = 3.5, 16.8 Hz, 1C), 129.8 (d, $^3J_{CF}$ = 8.6 Hz, 2C), 129.2 (d, $^3J_{CP}$ = 12.5 Hz, 2C), 128.9 (d, $^1J_{CP}$ = 103.6 Hz, 1C), 125.6 (dd, $^3J_{CF}/^3J_{CP}$ = 7.9, 13.1 Hz, 1C), 122.8 (dd, $^5J_{CF}/^1J_{CP}$ = 3.7, 100.0 Hz, 1C), 119.2 (dd, $^4J_{CP}/^2J_{CF}$ = 1.2, 22.5 Hz, 1C), 117.3 (dd, $^2J_{CP}/^2J_{CF}$ = 10.7, 23.7 Hz, 1C), 116.2 (d, $^2J_{CF}$ = 21.7 Hz, 2C); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.3 (d, J = 5.4 Hz), -110.5; ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 35.44 (d, J = 4.6 Hz); HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{20}H_{14}F_2OP$: 339.0745, found: 339.0763.

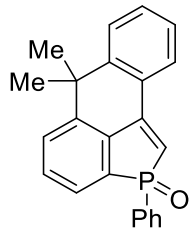


6-Chloro-3-(4-chlorophenyl)-1-phenylphosphindole 1-oxide (2g) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 21 mg (55%, 0.10 mmol scale); pale yellow solid; m.p. 75.6 – 76.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.74 (m, 2H), 7.63 (dd, J = 1.7, 9.9 Hz, 1H), 7.60-7.55 (m, 1H), 7.50-7.45 (m, 7H), 7.34 (dd, J = 3.2, 8.2 Hz, 1H), 6.37 (d, J = 23.9 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.4 (d, $^2J_{CP}$ = 14.6 Hz, 1C), 140.1 (d, $^2J_{CP}$ = 26.7 Hz, 1C), 136.5 (d, $^3J_{CP}$ = 13.9 Hz, 1C), 136.3 (d, $^1J_{CP}$ = 102.3 Hz, 1C), 136.1 (1C), 133.1 (d, $^3J_{CP}$ = 16.5 Hz, 1C), 132.9 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 132.7 (d, $^4J_{CP}$ = 1.4 Hz, 1C), 131.0 (d, $^2J_{CP}$ = 10.8 Hz, 2C), 129.8 (d, $^2J_{CP}$ = 10.5 Hz, 1C), 129.4 (2C), 129.23 (d, $^3J_{CP}$ = 12.5 Hz, 2C), 129.23 (2C), 128.6 (d, $^1J_{CP}$ = 103.9 Hz, 1C), 125.0 (d, $^3J_{CP}$ = 12.2 Hz, 1C), 123.6 (d, $^1J_{CP}$ = 98.9 Hz, 1C); ^{31}P{^{1}H} NMR ($CDCl_3$,

162 MHz): δ 35.84; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{20}H_{14}Cl_2OP$: 371.0154, found: 371.0142.

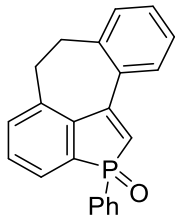


3-(Naphthalen-2-yl)-1-phenylbenzo[*g*]phosphindole 1-oxide (2h) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 25 mg (62%, 0.10 mmol scale); pale yellow solid; m.p. 125.7 – 126.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11-8.09 (m, 2H), 8.05-7.99 (dd, J = 8.5, 14.2 Hz, 2H), 7.95-7.85 (m, 5H), 7.69 (dd, J = 2.0, 8.5 Hz, 2H), 7.60-7.57 (m, 2H), 7.53-7.43 (m, 5H), 6.55 (d, J = 25.3 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.8 (d, $^2J_{CP}$ = 16.6 Hz, 1C), 141.6 (d, $^2J_{CP}$ = 26.1 Hz, 1C), 133.9 (d, $^3J_{CP}$ = 8.6 Hz, 1C), 133.8 (1C), 133.7 (1C), 133.3 (1C), 132.7 (d, $^3J_{CP}$ = 16.7 Hz, 1C), 132.4 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 132.2 (d, $^2J_{CP}$ = 9.2 Hz, 1C), 131.1 (d, $^2J_{CP}$ = 10.9 Hz, 2C), 129.77 (d, $^1J_{CP}$ = 103.2 Hz, 1C), 129.76 (d, $^1J_{CP}$ = 101.0 Hz, 1C), 129.2 (d, $^3J_{CP}$ = 12.4 Hz, 2C), 128.84 (d, $^4J_{CP}$ = 2.0 Hz, 1C), 128.79 (1C), 128.6 (1C), 128.5 (1C), 128.0 (1C), 127.5 (1C), 127.2 (2C), 127.0 (1C), 126.0 (d, $^3J_{CP}$ = 5.0 Hz, 1C), 125.6 (1C), 124.0 (d, $^1J_{CP}$ = 99.1 Hz, 1C), 121.5 (d, $^3J_{CP}$ = 12.8 Hz, 1C); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 38.09; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{28}H_{20}OP$: 403.1246, found: 403.1250.

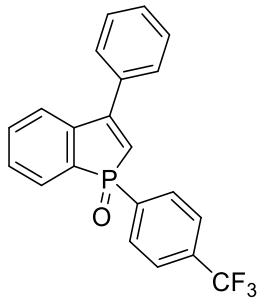


6,6-Dimethyl-2-phenyl-6*H*-naphtho[1,2,3-*cd*]phosphindole 2-oxide (2i): pale yellow solid (0.1 mmol scale, 23.9 mg, 70% yield; 3.04 mmol scale, 488.8 mg, 47% yield); m.p. 194.8-195.8 °C (from hexane); TLC R_f 0.20 (hexane/EtOAc, 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (dd, J = 7.9, 1.3 Hz, 1H), 7.80-7.75 (m, 2H), 7.69-7.66 (m, 2H), 7.59-7.34 (m, 7H), 6.60 (d, J = 23.2 Hz, 1H), 1.75 (s, 3H), 1.70 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 148.2 (d, $^2J_{CP}$ = 17.0 Hz, 1C), 146.3 (1C), 141.7 (d, $^3J_{CP}$ = 11.3 Hz, 1C), 135.6 (d, $^2J_{CP}$ = 29.5 Hz, 1C), 132.4 (d, $^1J_{CP}$ = 105.8 Hz, 1C), 132.1 (d, $^4J_{CP}$ = 2.5 Hz, 1C), 131.4 (1C), 131.0 (d, $^2J_{CP}$ = 10.8 Hz, 2C), 130.6 (d, $^1J_{CP}$ = 102.9 Hz, 1C), 130.4 (1C), 130.3 (d, $^4J_{CP}$ = 1.9 Hz, 1C), 128.7 (d, $^3J_{CP}$ = 12.2 Hz, 1C), 127.8 (1C), 127.1 (d, $^2J_{CP}$ = 9.6 Hz, 1C), 126.8 (1C), 126.6 (d, $^1J_{CP}$ = 96.8 Hz, 1C), 126.0 (1C), 112.0 (d, $^3J_{CP}$ = 9.7 Hz, 1C), 110.9 (d, $^3J_{CP}$ = 9.1 Hz, 1C), 38.6 (d, $^5J_{CP}$ = 1.0 Hz, 1C), 33.3 (d, $^4J_{CP}$ = 3.4 Hz, 1C), 32.5 (d, $^5J_{CP}$ = 1.9 Hz, 1C). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 40.6; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{23}H_{20}OP$:

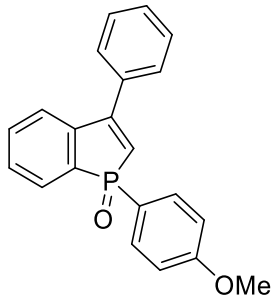
343.1247, Found: 343.1234.



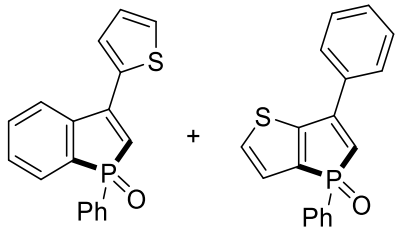
6-Phenyl-10,11-dihydrobenzo[6,7]cyclohepta[1,2,3-*cd*]phosphindole 6-oxide (2j): pale yellow solid (6.0 mmol scale, 905.6 mg, 46% yield); m.p. 157.8-158.8 °C (from hexane); TLC R_f 0.20 (hexane/EtOAc, 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (dd, J = 12.6, 7.4 Hz, 2H), 7.68 (bs, 1H), 7.54-7.50 (m, 2H), 7.43 (td, J = 7.7, 2.4 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.30-7.23 (m, 4H), 6.57 (d, J = 21.6 Hz, 1H), 3.12 (bs, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 158.4 (d, $^2J_{CP}$ = 11.8 Hz, 1C), 142.1 (1C), 140.5 (d, $^3J_{CP}$ = 10.6 Hz, 1C), 139.2 (d, $^2J_{CP}$ = 26.9 Hz, 1C), 135.0 (d, $^4J_{CP}$ = 1.8 Hz, 1C), 134.9 (d, $^3J_{CP}$ = 16.1 Hz, 1C), 132.1 (d, $^4J_{CP}$ = 2.7 Hz, 1C), 131.1 (d, $^2J_{CP}$ = 10.7 Hz, 2C), 130.6 (1C), 129.9 (1C), 129.8 (d, $^1J_{CP}$ = 104.1 Hz, 1C), 129.4 (d, $^1J_{CP}$ = 90.0 Hz, 1C), 129.1 (d, $^3J_{CP}$ = 11.5 Hz, 1C), 129.0 (1C), 128.8 (d, $^3J_{CP}$ = 12.5 Hz, 2C), 127.2 (d, $^2J_{CP}$ = 9.8 Hz, 1C), 126.9 (1C), 122.9 (d, $^1J_{CP}$ = 98.2 Hz, 1C), 35.4 (1C), 34.9 (d, $^4J_{CP}$ = 2.1 Hz, 1C). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 34.07; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{22}H_{18}OP$: 329.1090, Found: 329.1073.



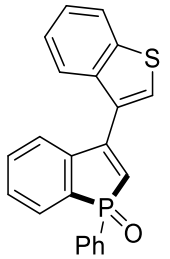
3-Phenyl-1-(4-(trifluoromethyl)phenyl)phosphindole 1-oxide (2k) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 37 mg (99%, 0.10 mmol scale); pale yellow solid; m.p. 43.2 – 44.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93-7.88 (m, 2H), 7.71-7.66 (m, 3H), 7.57-7.49 (m, 7H), 7.46-7.43 (m, 1H), 6.36 (d, J = 24.3 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.1 (d, $^2J_{CP}$ = 15.8 Hz, 1C), 142.1 (d, $^2J_{CP}$ = 27.7 Hz, 1C), 134.8 (d, $^3J_{CP}$ = 16.6 Hz, 1C), 134.6 (d, $^1J_{CP}$ = 99.5 Hz, 1C), 134.2 (qd, $^4J_{CP}/^2J_{CF}$ = 3.0, 32.9 Hz, 1C), 133.3 (d, $^1J_{CP}$ = 105.6 Hz, 1C), 133.2 (d, $^4J_{CP}$ = 1.9 Hz, 1C), 131.7 (d, $^2J_{CP}$ = 11.1 Hz, 2C), 129.98 (1C), 129.97 (d, $^2J_{CP}$ = 10.6 Hz, 1C), 129.5 (d, $^3J_{CP}$ = 9.6 Hz, 1C), 129.0 (2C), 127.9 (2C), 125.8 (qd, $^3J_{CF}/^3J_{CP}$ = 3.7, 12.4 Hz, 2C), 124.5 (d, $^3J_{CP}$ = 11.3 Hz, 1C), 123.7 (q, $^1J_{CF}$ = 273.2 Hz, 1C), 122.1 (d, $^1J_{CP}$ = 100.0 Hz, 1C); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -63.2; ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 35.38; HRMS (APCI) m/z (M+H)$^+$ calcd for $C_{21}H_{15}F_3OP$: 371.0807, found: 371.0783.



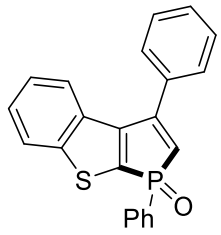
1-(4-Methoxyphenyl)-3-phenylphosphindole 1-oxide (2l) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 18 mg (55%, 0.10 mmol scale); pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.65 (m, 3H), 7.55-7.52 (m, 2H), 7.51-7.39 (m, 6H), 6.97-6.94 (m, 2H), 6.34 (d, J = 23.9 Hz, 1H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 163.1 (d, $^{4}J_{CP}$ = 2.9 Hz, 1C), 157.7 (d, $^{2}J_{CP}$ = 15.3 Hz, 1C), 142.1 (d, $^{2}J_{CP}$ = 27.0 Hz, 1C), 135.3 (d, $^{3}J_{CP}$ = 16.1 Hz, 1C), 134.4 (d, $^{1}J_{CP}$ = 104.6 Hz, 1C), 133.0 (d, $^{2}J_{CP}$ = 12.0 Hz, 2C), 132.60 (d, $^{4}J_{CP}$ = 1.7 Hz, 1C), 129.63 (1C), 129.5 (d, $^{2}J_{CP}$ = 9.9 Hz, 1C), 129.3 (d, $^{3}J_{CP}$ = 9.7 Hz, 1C), 128.9 (2C), 128.0 (2C), 124.1 (d, $^{3}J_{CP}$ = 11.3 Hz, 1C), 123.5 (d, $^{1}J_{CP}$ = 99.3 Hz, 1C), 120.2 (d, $^{1}J_{CP}$ = 108.7 Hz, 1C), 114.7 (d, $^{3}J_{CP}$ = 13.6 Hz, 2C), 55.5 (1C); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 37.19; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{21}H_{18}O_2P$: 333.1039, found: 333.1022.



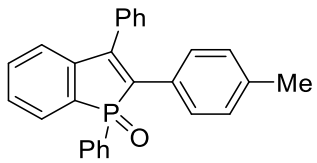
1-Phenyl-3-(thiophen-2-yl)phosphindole 1-oxide + 4,6-Diphenylphospholo[3,2-*b*]thiophene 4-oxide (2m + 2m', 5:3 mixture) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 22 mg (70%, 0.10 mmol scale); pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81-7.63 (m, 5.2H), 7.57-7.52 (1.6H), 7.49-7.40 (m, 4.2H), 7.35 (dd, J = 1.3, 5.0 Hz, 1H), 6.40 (d, J = 23.6 Hz, 0.6H), 6.29 (dd, J = 1.0, 26.2 Hz, 0.4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz); δ 152.6, 142.2, 135.9, 135.7, 134.3, 133.3, 132.9, 132.5, 131.2, 131.1, 130.2, 129.9, 129.8, 129.6, 129.5, 129.2, 129.1, 129.02, 128.96, 127.6, 127.5, 126.8, 125.4, 124.1, 124.0, 122.2, 121.2 (All observed signals are just shown because of complexity associated with C–P couplings and structural isomers.); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) for mixture: δ 37.49, 28.99; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{18}H_{14}OPS$:309.0497, found: 309.0475.



3-(Benzo[*b*]thiophen-3-yl)-1-phenylphosphindole 1-oxide (2n) : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 10 mg (28%, 0.10 mmol scale); pale yellow solid; m.p. 67.9 – 69.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97-7.94 (m, 1H), 7.87-7.81 (m, 3H), 7.75-7.71 (m, 1H), 7.69 (s, 1H), 7.58-7.54 (m, 1H), 7.75-7.39 (m, 7H), 6.56 (d, J = 24.1 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.7 (d, $^{2}J_{CP}$ = 15.9 Hz, 1C), 142.4 (d, $^{2}J_{CP}$ = 27.0 Hz, 1C), 140.5 (1C), 137.7 (1C), 133.6 (d, $^{1}J_{CP}$ = 104.4 Hz, 1C), 132.9 (d, $^{4}J_{CP}$ = 1.6 Hz, 1C), 132.5 (d, $^{4}J_{CP}$ = 2.9 Hz, 1C), 131.1 (d, $^{2}J_{CP}$ = 10.8 Hz, 2C), 130.8 (d, $^{3}J_{CP}$ = 17.3 Hz, 1C), 130.0 (d, $^{2}J_{CP}$ = 10.6 Hz, 1C), 129.6 (d, $^{1}J_{CP}$ = 102.7 Hz, 1C), 129.4 (d, $^{3}J_{CP}$ = 9.6 Hz, 1C), 129.1 (d, $^{3}J_{CP}$ = 12.4 Hz, 2C), 126.7 (1C), 125.3 (1C), 124.9 (1C), 124.3 (d, $^{1}J_{CP}$ = 97.9 Hz, 1C), 124.2 (d, $^{3}J_{CP}$ = 11.0 Hz, 1C), 123.3 (1C), 123.1 (1C); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 37.42; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{22}H_{16}OPS$: 359.0654, found: 359.0631.

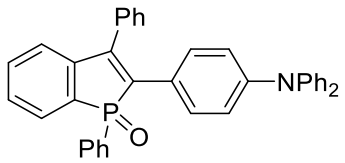


1,3-Diphenylbenzo[*b*]phospholo[3,2-*d*]thiophene 1-oxide (2n') : Purified by flash chromatography with hexane/ethyl acetate (1/2, v/v): 5 mg (14%, 0.10 mmol scale); pale yellow solid; m.p. 115.3 – 116.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.89 (m, 1H), 7.85-7.79 (m, 2H), 7.59-7.52 (m, 6H), 7.49-7.44 (m, 2H), 7.40-7.36 (m, 2H), 7.26 (dd, J = 1.1, 15.3 Hz, 1H), 6.24 (d, J = 26.8 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): The clear spectra was not obtained because of a small amount of the sample.; ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 29.76; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{22}H_{16}OPS$: 359.0654, found: 359.0658.

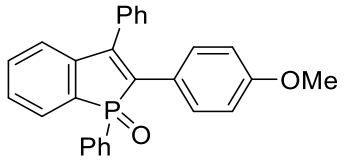


1,3-Diphenyl-2-(*p*-tolyl)phosphindole 1-oxide (4aa): pale yellow solid (0.2 mmol scale, 61.9 mg, 79% yield; 2.0 mmol scale, 510.0 mg, 65% yield); m.p. 159.7-161.0 °C (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80-7.75 (m, 2H), 7.71-7.67 (m, 1H), 7.48-7.32

(m, 10H), 7.18 (dd, J = 7.6, 2.9 Hz, 1H), 7.14 (d, J = 7.6 Hz, 2H), 6.89 (d, J = 8.2 Hz, 2H), 2.18 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 149.3 (d, $^{2}J_{CP}$ = 21.8 Hz, 1C), 143.9 (d, $^{2}J_{CP}$ = 27.2 Hz, 1C), 137.8 (1C), 134.5 (d, $^{3}J_{CP}$ = 15.4 Hz, 1C), 134.1 (d, $^{1}J_{CP}$ = 95.7 Hz, 1C), 132.9 (d, $^{4}J_{CP}$ = 1.8 Hz, 1C), 132.1 (d, $^{4}J_{CP}$ = 2.5 Hz, 1C), 132.1 (d, $^{1}J_{CP}$ = 105.6 Hz, 1C), 131.0 (d, $^{2}J_{CP}$ = 10.7 Hz, 2C), 130.1 (d, $^{1}J_{CP}$ = 99.6 Hz, 1C), 129.7 (d, $^{2}J_{CP}$ = 10.1 Hz, 1C), 129.1 (4C), 129.0 (2C), 128.9 (2C), 128.89 (2C), 128.85 (d, $^{3}J_{CP}$ = 12.2 Hz, 2C), 128.6 (1C), 123.9 (d, $^{2}J_{CP}$ = 10.9 Hz, 1C), 21.2 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.2; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{27}H_{22}OP$: 393.1408, Found: 393.1407.

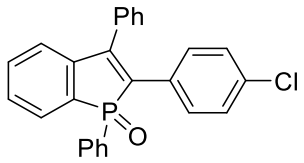


2-(4-(Diphenylamino)phenyl)-1,3-diphenylphosphindole 1-oxide (4ab): yellow solid (0.2 mmol scale, 94.8 mg, 87% yield; 1.0 mmol scale, 430.7 mg, 79% yield); TLC R_f 0.20 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85-7.80 (m, 2H), 7.68-7.64 (m, 1H), 7.52-7.29 (m, 10H), 7.21-7.17 (m, 4H), 7.10 (dd, J = 7.5, 2.8 Hz, 1H), 7.07-6.97 (m, 8H), 6.72 (d, J = 8.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 147.8 (d, $^{2}J_{CP}$ = 21.8 Hz, 1C), 147.4 (1C), 147.1 (2C), 144.3 (d, $^{2}J_{CP}$ = 27.2 Hz, 1C), 135.0 (d, $^{3}J_{CP}$ = 15.4 Hz, 1C), 133.5 (d, $^{1}J_{CP}$ = 95.7 Hz, 1C), 132.9 (d, $^{4}J_{CP}$ = 1.8 Hz, 1C), 132.1 (d, $^{4}J_{CP}$ = 2.7 Hz, 1C), 131.8 (d, $^{1}J_{CP}$ = 106.1 Hz, 1C), 131.0 (d, $^{2}J_{CP}$ = 10.5 Hz, 2C), 130.7 (d, $^{1}J_{CP}$ = 98.6 Hz, 1C), 129.9 (d, $^{3}J_{CP}$ = 6.4 Hz, 2C), 129.3 (4C), 129.1 (2C), 128.95 (2C), 128.93 (d, $^{3}J_{CP}$ = 12.0 Hz, 2C), 128.91 (1C), 128.8 (d, $^{3}J_{CP}$ = 10.5 Hz, 1C), 128.6 (1C), 125.7 (d, $^{2}J_{CP}$ = 10.3 Hz, 1C), 125.1 (4C), 123.6 (d, $^{2}J_{CP}$ = 10.9 Hz, 1C), 123.4 (2C), 121.6 (2C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.3; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{38}H_{29}NOP$: 546.1982, Found: 546.2011.

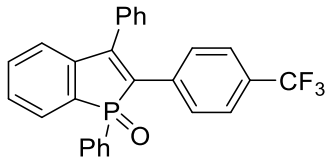


2-(4-Methoxyphenyl)-1,3-diphenylphosphindole 1-oxide (4ac): pale yellow solid (0.2 mmol, 60.6 mg, 74% yield); TLC R_f 0.24 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80-7.75 (m, 2H), 7.70-7.66 (m, 1H), 7.48-7.30 (m, 10H), 7.21-7.19 (m, 2H), 7.15 (dd, J = 7.6, 2.9 Hz, 1H), 6.62 (d, J = 8.8 Hz, 2H), 3.67 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 159.2 (1C), 148.3 (d, $^{2}J_{CP}$ = 21.9 Hz, 1C), 144.1 (d, $^{2}J_{CP}$ = 27.2 Hz, 1C), 134.7 (d, $^{3}J_{CP}$ = 15.4 Hz, 1C), 133.6 (d, $^{1}J_{CP}$ = 96.0 Hz, 1C), 132.9 (d, $^{4}J_{CP}$ = 1.5 Hz, 1C), 132.1 (d, $^{4}J_{CP}$ = 2.7 Hz, 1C), 131.8 (d, $^{1}J_{CP}$ = 105.6 Hz, 1C), 130.9 (d, $^{2}J_{CP}$ = 10.5 Hz, 2C), 130.4 (d, $^{3}J_{CP}$ = 6.0 Hz, 2C), 130.3 (d, $^{1}J_{CP}$ = 99.2 Hz, 1C), 129.09 (2C), 129.06 (2C), 128.9 (d, $^{3}J_{CP}$ = 9.8 Hz, 1C), 128.8 (d, $^{3}J_{CP}$ = 12.0 Hz, 2C), 128.7 (d, $^{3}J_{CP}$ = 10.4 Hz, 1C), 128.6 (1C),

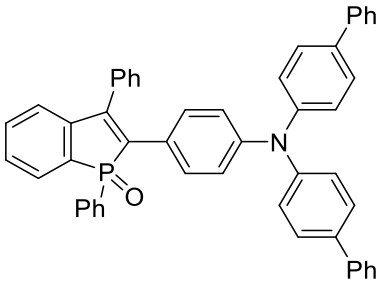
125.1 (d, $^{2}J_{CP}$ = 10.3 Hz, 1C), 123.7 (d, $^{2}J_{CP}$ = 10.9 Hz, 1C), 113.8 (2C), 55.1 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.2; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{27}H_{22}O_2P$: 409.1352, Found: 409.1367.



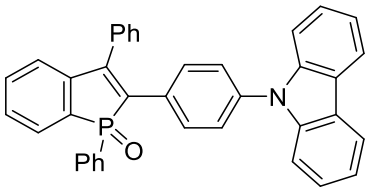
2-(4-Chlorophenyl)-1,3-diphenylphosphindole 1-oxide (4ad): colorless solid (0.2 mmol, 66.7 mg, 81% yield); m.p. 104.6-105.9 ºC (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77-7.69 (m, 3H), 7.51-7.36 (m, 8H), 7.32-7.30 (m, 2H), 7.21 (dd, *J* = 7.5, 2.9 Hz, 1H), 7.19-7.16 (m, 2H), 7.07-7.05 (m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 150.5 (d, $^{2}J_{CP}$ = 21.1 Hz, 1C), 143.6 (d, $^{2}J_{CP}$ = 26.7 Hz, 1C), 133.9 (d, $^{3}J_{CP}$ = 14.7 Hz, 1C), 133.8 (1C), 133.1 (d, $^{1}J_{CP}$ = 95.7 Hz, 1C), 133.0 (d, $^{4}J_{CP}$ = 1.9 Hz, 1C), 132.4 (1C), 132.3 (d, $^{4}J_{CP}$ = 2.9 Hz, 1C), 131.9 (d, $^{1}J_{CP}$ = 105.3 Hz, 1C), 131.3 (1C), 130.9 (d, $^{2}J_{CP}$ = 10.8 Hz, 2C), 130.6 (d, $^{1}J_{CP}$ = 112.6 Hz, 1C), 130.3 (d, $^{3}J_{CP}$ = 5.7 Hz, 2C), 129.3 (d, $^{2}J_{CP}$ = 10.7 Hz, 1C), 129.15 (d, $^{3}J_{CP}$ = 9.7 Hz, 1C), 129.14 (2C), 128.96 (d, $^{3}J_{CP}$ = 12.2 Hz, 2C), 128.93 (2C), 128.6 (2C), 124.2 (d, $^{2}J_{CP}$ = 10.7 Hz, 1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.0; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{26}H_{19}ClOP$: 413.0857, Found: 413.0878.



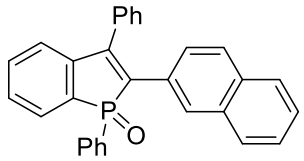
1,3-Diphenyl-2-(4-(trifluoromethyl)phenyl)phosphindole 1-oxide (4ae): colorless solid (0.2 mmol, 45.5 mg, 51% yield); m.p. 94.3-95.6 ºC (from hexane); TLC R_f 0.23 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78-7.71 (m, 3H), 7.53-7.39 (m, 8H), 7.34-7.31 (m, 6H), 7.25 (dd, *J* = 6.5, 1.8 Hz, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 151.8 (d, $^{2}J_{CP}$ = 20.9 Hz, 1C), 143.3 (d, $^{2}J_{CP}$ = 26.4 Hz, 1C), 136.5 (d, $^{2}J_{CP}$ = 10.2 Hz, 1C), 133.6 (d, $^{3}J_{CP}$ = 14.5 Hz, 1C), 133.1 (d, $^{4}J_{CP}$ = 1.8 Hz, 1C), 133.0 (d, $^{1}J_{CP}$ = 95.8 Hz, 1C), 132.5 (d, $^{4}J_{CP}$ = 2.9 Hz, 1C), 132.0 (d, $^{1}J_{CP}$ = 106.3 Hz, 1C), 130.9 (d, $^{2}J_{CP}$ = 10.7 Hz, 2C), 129.6 (d, $^{3}J_{CP}$ = 10.8 Hz, 1C), 129.5 (q, $^{2}J_{CF}$ = 32.2 Hz, 1C), 129.4 (1C), 129.3 (d, $^{1}J_{CP}$ = 99.9 Hz, 1C), 129.2 (2C), 129.18 (2C), 129.10 (2C), 128.93 (d, $^{3}J_{CP}$ = 12.4 Hz, 2C), 128.90 (1C), 125.2 (q, $^{3}J_{CF}$ = 3.8 Hz, 2C), 124.5 (d, $^{2}J_{CP}$ = 10.9 Hz, 1C), 124.0 (q, $^{1}J_{CF}$ = 272.1 Hz, 1C). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz) δ -62.8. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.0; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{27}H_{19}F_3OP$: 447.1121, Found: 447.1131.



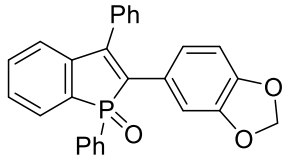
2-(4-(Di([1,1'-biphenyl]-4-yl)amino)phenyl)-1,3-diphenylphosphindole 1-oxide (4af): orange solid (0.2 mmol, 92.1 mg, 66% yield); m.p. 151.7-153.0 °C (from hexane); TLC R_f 0.20 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87-7.82 (m, 2H), 7.66 (dd, *J* = 9.2, 7.3 Hz, 1H), 7.54-7.52 (m, 4H), 7.50-7.37 (m, 17H), 7.33-7.27 (m, 3H), 7.13-7.08 (m, 7H), 6.83 (d, *J* = 8.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 148.1 (d, $^2J_{CP}$ = 22.0 Hz, 1C), 147.4 (1C), 146.2 (2C), 144.3 (d, $^2J_{CP}$ = 27.1 Hz, 1C), 140.5 (2C), 136.2 (2C), 135.0 (d, $^3J_{CP}$ = 15.2 Hz, 1C), 133.4 (d, $^1J_{CP}$ = 95.7 Hz, 1C), 133.0 (d, $^4J_{CP}$ = 1.6 Hz, 1C), 132.2 (d, $^4J_{CP}$ = 2.5 Hz, 1C), 131.9 (d, $^1J_{CP}$ = 106.2 Hz, 1C), 131.0 (d, $^2J_{CP}$ = 10.7 Hz, 2C), 130.7 (d, $^1J_{CP}$ = 98.6 Hz, 1C), 130.1 (d, $^3J_{CP}$ = 6.3 Hz, 2C), 129.2 (2C), 129.0 (d, $^3J_{CP}$ = 12.2 Hz, 2C), 128.97 (2C), 128.92 (d, $^3J_{CP}$ = 10.3 Hz, 1C), 128.79 (4C), 128.78 (1C), 128.73 (d, $^3J_{CP}$ = 9.5 Hz, 1C), 127.9 (4C), 127.0 (2C), 126.8 (4C), 126.3 (d, $^2J_{CP}$ = 10.0 Hz, 1C), 125.1 (4C), 123.7 (d, $^2J_{CP}$ = 10.7 Hz, 1C), 122.2 (2C). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 39.3; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{50}H_{37}NOP$: 698.2608, Found: 698.2635.



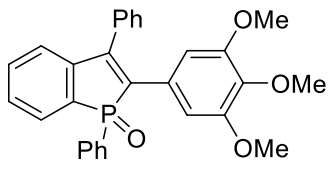
2-(4-(9*H*-Carbazol-9-yl)phenyl)-1,3-diphenylphosphindole 1-oxide (4ag): yellow solid (0.2 mmol, 76.0 mg, 70% yield); m.p. 135.7-137.0 °C (from hexane); TLC R_f 0.22 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.90-7.84 (m, 2H), 7.74 (dd, *J* = 9.4, 7.2 Hz, 1H), 7.56-7.38 (m, 12H), 7.37-7.30 (m, 6H), 7.25-7.21 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 150.6 (d, $^2J_{CP}$ = 21.2 Hz, 1C), 143.7 (d, $^2J_{CP}$ = 26.7 Hz, 1C), 140.4 (2C), 137.2 (1C), 134.2 (d, $^3J_{CP}$ = 14.8 Hz, 1C), 133.4 (d, $^1J_{CP}$ = 96.2 Hz, 1C), 133.1 (d, $^4J_{CP}$ = 1.7 Hz, 1C), 132.4 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 132.1 (d, $^1J_{CP}$ = 106.1 Hz, 1C), 131.6 (d, $^2J_{CP}$ = 10.0 Hz, 1C), 131.0 (d, $^2J_{CP}$ = 10.8 Hz, 2C), 130.5 (d, $^3J_{CP}$ = 6.0 Hz, 2C), 130.0 (d, $^1J_{CP}$ = 98.5 Hz, 1C), 129.4 (d, $^3J_{CP}$ = 10.8 Hz, 1C), 129.2 (2C), 129.1 (d, $^3J_{CP}$ = 12.7 Hz, 2C), 129.09 (1C), 129.03 (3C), 126.5 (2C), 125.9 (2C), 124.3 (d, $^2J_{CP}$ = 10.8 Hz, 1C), 123.5 (2C), 120.3 (2C), 120.1 (2C), 109.9 (2C). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 39.1; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{38}H_{27}NOP$: 544.1825, Found: 544.1850.



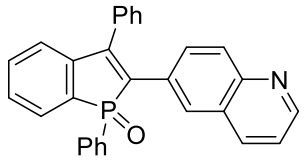
2-(Naphthalen-2-yl)-1,3-diphenylphosphindole 1-oxide (4ah): colorless solid (0.2 mmol, 69.3 mg, 81% yield); m.p. 92.7-94.3 °C (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (bs, 1H), 7.83-7.72 (m, 3H), 7.66-7.63 (m, 2H), 7.50-7.34 (m, 13H), 7.26 (dd, J = 7.6, 2.9 Hz, 1H), 7.14 (dd, J = 8.6, 0.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 150.3 (d, $^2J_{CP}$ = 21.1 Hz, 1C), 143.7 (d, $^2J_{CP}$ = 26.8 Hz, 1C), 134.3 (d, $^3J_{CP}$ = 14.8 Hz, 1C), 134.1 (d, $^1J_{CP}$ = 96.2 Hz, 1C), 133.1 (1C), 133.0 (d, $^4J_{CP}$ = 1.9 Hz, 1C), 132.6 (1C), 132.2 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 132.1 (d, $^1J_{CP}$ = 106.0 Hz, 1C), 130.9 (d, $^2J_{CP}$ = 10.3 Hz, 2C), 130.4 (1C), 129.9 (d, $^1J_{CP}$ = 90.1 Hz, 1C), 129.19 (2C), 129.18 (d, $^2J_{CP}$ = 10.5 Hz, 1C), 129.10 (1C), 129.05 (2C), 128.9 (d, $^3J_{CP}$ = 12.5 Hz, 2C), 128.8 (1C), 128.7 (d, $^3J_{CP}$ = 5.4 Hz, 1C), 128.5 (1C), 127.7 (1C), 127.4 (1C), 126.6 (d, $^3J_{CP}$ = 6.2 Hz, 1C), 126.4 (1C), 126.0 (1C), 124.1 (d, $^2J_{CP}$ = 11.0 Hz, 1C). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 39.2; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{30}H_{22}OP$: 429.1403, Found: 429.1419.



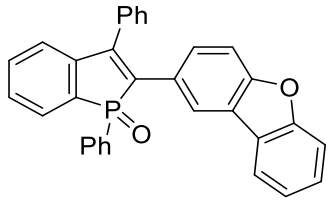
2-(Benzo[*d*][1,3]dioxol-5-yl)-1,3-diphenylphosphindole 1-oxide (4ai): pale yellow solid (0.2 mmol, 57.4 mg, 68% yield); m.p. 209.1-210.5 °C (from hexane); TLC R_f 0.22 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79-7.74 (m, 2H), 7.70-7-66 (m, 1H), 7.51-7.38 (m, 7H), 7.35-7.32 (m, 3H), 7.16 (dd, J = 7.5, 2.9 Hz, 1H), 6.91 (dt, J = 8.2, 1.6 Hz, 1H), 6.61 (dd, J = 1.3, 1.0 Hz, 1H), 6.57 (d, J = 8.2 Hz, 1H), 5.81 (d, J = 1.5 Hz, 1H), 5.80 (d, J = 1.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 148.9 (d, $^2J_{CP}$ = 21.6 Hz, 1C), 147.4 (1C), 147.3 (1C), 143.9 (d, $^2J_{CP}$ = 26.7 Hz, 1C), 134.4 (d, $^3J_{CP}$ = 14.9 Hz, 1C), 133.8 (d, $^1J_{CP}$ = 96.4 Hz, 1C), 132.9 (d, $^4J_{CP}$ = 1.8 Hz, 1C), 132.2 (d, $^4J_{CP}$ = 2.7 Hz, 1C), 131.8 (d, $^1J_{CP}$ = 106.0 Hz, 1C), 130.9 (d, $^2J_{CP}$ = 10.8 Hz, 2C), 130.0 (d, $^1J_{CP}$ = 99.7 Hz, 1C), 129.1 (1C), 129.05 (1C), 129.0 (2C), 128.95 (2C), 128.90 (1C), 128.8 (d, $^3J_{CP}$ = 10.1 Hz, 2C), 126.5 (d, $^2J_{CP}$ = 10.4 Hz, 1C), 123.8 (d, $^2J_{CP}$ = 11.0 Hz, 1C), 123.5 (d, $^3J_{CP}$ = 5.8 Hz, 1C), 109.2 (d, $^3J_{CP}$ = 6.3 Hz, 1C), 108.3 (1C), 100.9 (1C) . ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 39.1; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{27}H_{20}O_3P$: 423.1145, Found: 423.1155.



1,3-Diphenyl-2-(3,4,5-trimethoxyphenyl)phosphindole 1-oxide (4aj): pale yellow solid (0.2 mmol, 64.6 mg, 69% yield); m.p. 197.1-198.4 °C (from hexane); TLC R_f 0.20 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85-7.80 (m, 2H), 7.69 (dd, J = 9.2, 7.1 Hz, 1H), 7.54-7.40 (m, 7H), 7.39-7.34 (m, 3H), 7.17 (dd, J = 7.5, 2.9 Hz, 1H), 6.45 (d, J = 0.7 Hz, 2H), 3.74 (s, 3H), 3.44 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 152.7 (2C), 149.2 (d, $^2J_{CP}$ = 21.5 Hz, 1C), 144.0 (d, $^2J_{CP}$ = 26.8 Hz, 1C), 137.7 (1C), 134.8 (d, $^3J_{CP}$ = 14.8 Hz, 1C), 134.0 (d, $^1J_{CP}$ = 96.5 Hz, 1C), 133.0 (d, $^4J_{CP}$ = 1.5 Hz, 1C), 132.2 (d, $^4J_{CP}$ = 2.6 Hz, 1C), 131.7 (d, $^1J_{CP}$ = 106.3 Hz, 1C), 131.0 (d, $^2J_{CP}$ = 10.7 Hz, 2C), 130.4 (d, $^1J_{CP}$ = 99.0 Hz, 1C), 129.2 (2C), 129.1 (d, $^3J_{CP}$ = 10.1 Hz, 1C), 129.0 (1C), 128.97 (2C), 128.95 (d, $^3J_{CP}$ = 12.2 Hz, 2C), 128.6 (1C), 127.8 (d, $^2J_{CP}$ = 10.4 Hz, 1C), 123.9 (d, $^2J_{CP}$ = 10.9 Hz, 1C), 106.4 (d, $^3J_{CP}$ = 6.4 Hz, 2C), 60.7 (1C), 55.5 (2C). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 38.7; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{29}H_{26}O_4P$: 469.1564, Found: 469.1543.

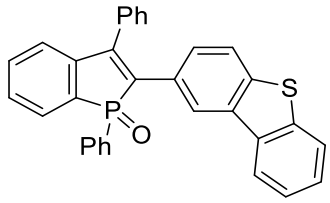


1,3-Diphenyl-2-(quinolin-6-yl)phosphindole 1-oxide (4ak): orange solid (0.2 mmol, 53.2 mg, 62% yield); m.p. 111.4-112.7 °C (from hexane); TLC R_f 0.24 (hexane/EtOAc, 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.80 (dd, J = 4.1, 1.5 Hz, 1H), 8.03 (s, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.82-7.72 (m, 4H), 7.52-7.36 (m, 10H), 7.32-7.28 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 151.0 (d, $^2J_{CP}$ = 20.8 Hz, 1C), 150.7 (1C), 147.5 (1C), 143.5 (d, $^2J_{CP}$ = 26.7 Hz, 1C), 136.4 (1C), 133.9 (d, $^3J_{CP}$ = 14.5 Hz, 1C), 133.5 (d, $^1J_{CP}$ = 95.7 Hz, 1C), 133.1 (d, $^4J_{CP}$ = 1.6 Hz, 1C), 132.4 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 132.0 (d, $^4J_{CP}$ = 1.9 Hz, 1C), 132.2 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 132.0 (d, $^1J_{CP}$ = 106.2 Hz, 1C), 131.3 (1C), 130.9 (d, $^2J_{CP}$ = 10.5 Hz, 2C), 130.7 (d, $^1J_{CP}$ = 108.4 Hz, 1C), 130.3 (d, $^3J_{CP}$ = 6.1 Hz, 1C), 129.4 (d, $^2J_{CP}$ = 10.8 Hz, 1C), 129.3 (1C), 129.2 (2C), 129.1 (1C), 129.0 (1C), 128.9 (d, $^3J_{CP}$ = 12.3 Hz, 2C), 128.3 (d, $^3J_{CP}$ = 5.2 Hz, 1C), 128.1 (1C), 124.3 (d, $^2J_{CP}$ = 10.8 Hz, 1C), 121.3 (1C). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 39.1; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{29}H_{21}NOP$: 430.1356, Found: 430.1362.

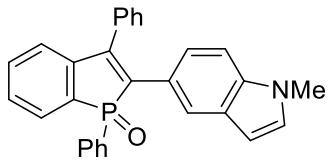


2-(Dibenzo[*b*,*d*]furan-2-yl)-1,3-diphenylphosphindole 1-oxide (4al): pale yellow solid (0.2 mmol, 67.4 mg, 72% yield); m.p. 108.9-109.6 °C (from hexane); TLC R_f 0.22 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (s, 1H), 7.83-7.70 (m, 4H), 7.50-7.36 (m, 12H), 7.31-7.24 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 156.4 (1C), 155.6 (1C), 149.6 (d, $^2J_{CP}$ = 21.7 Hz, 1C), 143.8 (d, $^2J_{CP}$ = 26.8 Hz, 1C), 134.3 (d, $^3J_{CP}$ = 14.9 Hz, 1C), 134.2 (d, $^1J_{CP}$ = 96.2 Hz, 1C), 133.0 (d, $^4J_{CP}$ = 1.9 Hz,

1C), 132.2 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 131.9 (d, $^{1}J_{CP}$ = 106.1 Hz, 1C), 131.0 (d, $^{2}J_{CP}$ = 10.6 Hz, 2C), 129.9 (d, $^{1}J_{CP}$ = 99.8 Hz, 1C), 129.18 (2C), 129.17 (d, $^{3}J_{CP}$ = 9.6 Hz, 1C), 129.09 (2C), 129.06 (1C), 128.9 (d, $^{3}J_{CP}$ = 12.3 Hz, 2C), 128.7 (1C), 128.5 (d, $^{3}J_{CP}$ = 5.9 Hz, 1C), 127.5 (d, $^{2}J_{CP}$ = 10.0 Hz, 1C), 127.3 (1C), 124.3 (1C), 124.0 (d, $^{2}J_{CP}$ = 10.7 Hz, 1C), 123.9 (1C), 122.8 (1C), 121.3 (d, $^{4}J_{CP}$ = 5.6 Hz, 1C), 120.8 (1C), 111.6 (2C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.1; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{32}H_{22}O_2P$: 469.1352, Found: 469.1366.

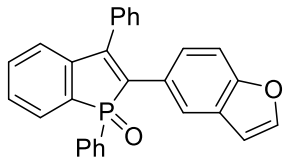


2-(Dibenzo[*b*,*d*]thiophen-2-yl)-1,3-diphenylphosphindole 1-oxide (4am): yellow solid (0.2 mmol, 66.8 mg, 69% yield); m.p. 108.0-109.3 °C (from hexane); TLC R_f 0.22 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (s, 1H), 7.86-7.81 (m, 2H), 7.78-7.74 (m, 3H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.51-7.34 (m, 13H), 7.27 (dd, *J* = 7.5, 3.0 Hz, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 149.9 (d, $^{2}J_{CP}$ = 21.7 Hz, 1C), 143.9 (d, $^{2}J_{CP}$ = 26.9 Hz, 1C), 139.5 (1C), 139.1 (1C), 135.5 (1C), 135.3 (1C), 134.4 (d, $^{3}J_{CP}$ = 14.9 Hz, 1C), 134.1 (d, $^{1}J_{CP}$ = 96.0 Hz, 1C), 133.0 (d, $^{4}J_{CP}$ = 1.8 Hz, 1C), 132.3 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 132.0 (d, $^{1}J_{CP}$ = 106.3 Hz, 1C), 131.0 (d, $^{2}J_{CP}$ = 10.6 Hz, 2C), 130.0 (d, $^{1}J_{CP}$ = 99.6 Hz, 1C), 129.2 (2C), 129.16 (d, $^{2}J_{CP}$ = 10.8 Hz, 1C), 129.11 (d, $^{3}J_{CP}$ = 9.7 Hz, 1C), 129.10 (3C), 128.9 (d, $^{3}J_{CP}$ = 12.3 Hz, 2C), 128.8 (1C), 127.6 (d, $^{3}J_{CP}$ = 5.6 Hz, 1C), 126.8 (1C), 124.4 (1C), 124.1 (d, $^{2}J_{CP}$ = 10.7 Hz, 1C), 122.7 (1C), 122.6 (1C), 122.1 (d, $^{3}J_{CP}$ = 6.2 Hz, 1C), 121.6 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.1; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{32}H_{22}OPS$: 485.1124, Found: 485.1130.

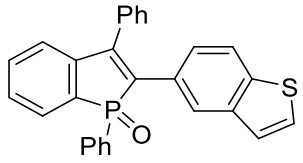


2-(1-Methyl-1*H*-indol-5-yl)-1,3-diphenylphosphindole 1-oxide (4an): yellow solid (0.2 mmol, 56.0 mg, 65% yield); m.p. 121.4-122.7 °C (from hexane); TLC R_f 0.24 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82-7.77 (m, 2H), 7.72-7.68 (m, 2H), 7.44-7.30 (m, 10H), 7.19 (dd, *J* = 7.6, 2.8 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.91 (d, *J* = 3.0 Hz, 1H), 6.31 (d, *J* = 3.0 Hz, 1H), 3.63 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 147.8 (d, $^{2}J_{CP}$ = 22.2 Hz, 1C), 144.2 (d, $^{2}J_{CP}$ = 27.6 Hz, 1C), 136.1 (1C), 135.1 (d, $^{1}J_{CP}$ = 95.6 Hz, 1C), 135.0 (d, $^{3}J_{CP}$ = 15.1 Hz, 1C), 132.8 (d, $^{4}J_{CP}$ = 1.3 Hz, 1C), 132.1 (d, $^{1}J_{CP}$ = 105.4 Hz, 1C), 131.9 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 131.0 (d, $^{2}J_{CP}$ = 10.6 Hz, 2C), 130.5 (d, $^{1}J_{CP}$ = 99.7 Hz, 1C), 129.3 (2C), 129.1 (1C), 129.0 (2C), 128.9 (d, $^{3}J_{CP}$ = 9.5 Hz, 1C), 128.7 (d, $^{3}J_{CP}$ = 12.2 Hz, 2C), 128.5 (d, $^{2}J_{CP}$ = 10.4 Hz, 1C), 128.4 (1C), 128.2 (1C),

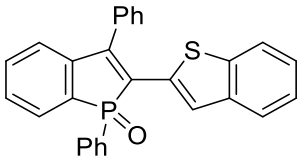
123.8 (d, $^{3}J_{CP}$ = 10.2 Hz, 1C), 123.6 (d, $^{2}J_{CP}$ = 11.0 Hz, 1C), 123.1 (d, $^{3}J_{CP}$ = 6.3 Hz, 1C), 122.1 (d, $^{3}J_{CP}$ = 5.9 Hz, 1C), 109.1 (1C), 101.7 (1C), 32.8 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.3; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{29}H_{23}NOP$: 432.1512, Found: 432.1534.



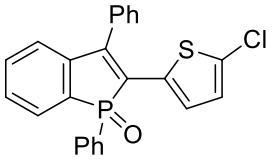
2-(Benzofuran-5-yl)-1,3-diphenylphosphindole 1-oxide (4ao): pale yellow solid (0.2 mmol, 46.8 mg, 56% yield); m.p. 202.8-204.1 °C (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80-7.70 (m, 3H), 7.66 (s, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.47-7.33 (m, 10H), 7.23 (dd, *J* = 7.5, 2.9 Hz, 1H), 7.18 (dd, *J* = 8.7, 0.6 Hz, 1H), 7.07 (dt, *J* = 8.7, 1.4 Hz, 1H), 6.59 (dd, *J* = 2.2, 0.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 154.4 (1C), 149.4 (d, $^{2}J_{CP}$ = 21.6 Hz, 1C), 145.2 (1C), 143.8 (d, $^{2}J_{CP}$ = 27.1 Hz, 1C), 134.4 (d, $^{1}J_{CP}$ = 95.6 Hz, 1C), 134.3 (d, $^{3}J_{CP}$ = 15.4 Hz, 1C), 132.9 (d, $^{4}J_{CP}$ = 1.7 Hz, 1C), 132.2 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 132.0 (d, $^{1}J_{CP}$ = 105.5 Hz, 1C), 131.0 (d, $^{2}J_{CP}$ = 10.6 Hz, 2C), 129.9 (d, $^{1}J_{CP}$ = 99.5 Hz, 1C), 129.2 (2C), 129.1 (1C), 129.05 (1C), 129.01 (2C), 128.9 (1C), 128.8 (d, $^{3}J_{CP}$ = 12.2 Hz, 2C), 128.6 (1C), 127.4 (d, $^{2}J_{CP}$ = 10.0 Hz, 1C), 125.7 (d, $^{3}J_{CP}$ = 6.2 Hz, 1C), 123.9 (d, $^{2}J_{CP}$ = 10.9 Hz, 1C), 122.1 (d, $^{3}J_{CP}$ = 5.3 Hz, 1C), 111.3 (1C), 106.9 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.1; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{28}H_{20}O_2P$: 419.1196, Found: 419.1197.



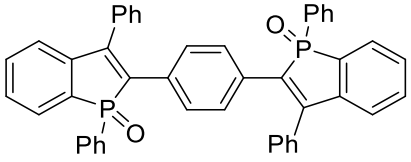
2-(Benzo[*b*]thiophen-5-yl)-1,3-diphenylphosphindole 1-oxide (4ap): pale yellow solid (0.2 mmol, 53.8 mg, 62% yield); m.p. 200.1-201.5 °C (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (s, 1H), 7.81-7.71 (m, 3H), 7.54 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.49-7.34 (m, 10H), 7.32 (d, *J* = 5.5 Hz, 1H), 7.24 (dd, *J* = 7.5, 2.9 Hz, 1H), 7.16 (dd, *J* = 5.5, 0.6 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 149.8 (d, $^{2}J_{CP}$ = 21.5 Hz, 1C), 143.8 (d, $^{2}J_{CP}$ = 27.0 Hz, 1C), 139.6 (1C), 139.2 (1C), 134.3 (d, $^{3}J_{CP}$ = 15.2 Hz, 1C), 134.2 (d, $^{1}J_{CP}$ = 95.7 Hz, 1C), 132.9 (d, $^{4}J_{CP}$ = 1.7 Hz, 1C), 132.2 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 132.1 (d, $^{1}J_{CP}$ = 105.7 Hz, 1C), 130.9 (d, $^{2}J_{CP}$ = 10.8 Hz, 2C), 129.8 (d, $^{1}J_{CP}$ = 100.2 Hz, 1C), 129.2 (3C), 129.0 (3C), 128.93 (d, $^{2}J_{CP}$ = 10.6 Hz, 1C), 128.90 (d, $^{3}J_{CP}$ = 12.4 Hz, 2C), 128.7 (1C), 126.6 (1C), 125.2 (d, $^{3}J_{CP}$ = 6.4 Hz, 1C), 124.3 (1C), 124.2 (d, $^{3}J_{CP}$ = 5.3 Hz, 1C), 124.0 (d, $^{2}J_{CP}$ = 10.8 Hz, 1C), 122.2 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.2; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{28}H_{20}OPS$: 435.0967, Found: 435.0970.



2-(Benzo[*b*]thiophen-2-yl)-1,3-diphenylphosphindole 1-oxide (4aq): yellow solid (0.2 mmol, 41.6 mg, 48% yield); m.p. 125.4-126.7 °C (from hexane); TLC R_f 0.22 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91-7.85 (m, 2H), 7.74 (s, 1H), 7.73-7.69 (m, 1H), 7.64-7.58 (m, 4H), 7.52-7.48 (m, 2H), 7.46-7.41 (m, 5H), 7.38-7.33 (m, 1H), 7.23-7.15 (m, 2H), 7.02 (dd, J = 7.5, 2.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 148.8 (d, $^2J_{CP}$ = 20.2 Hz, 1C), 144.2 (d, $^2J_{CP}$ = 26.1 Hz, 1C), 140.4 (1C), 138.8 (1C), 135.3 (d, $^3J_{CP}$ = 14.8 Hz, 1C), 133.7 (1C), 133.5 (1C), 133.2 (d, $^4J_{CP}$ = 1.9 Hz, 1C), 132.4 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 131.5 (d, $^1J_{CP}$ = 107.3 Hz, 1C), 130.8 (d, $^2J_{CP}$ = 10.6 Hz, 2C), 130.1 (d, $^1J_{CP}$ = 100.5 Hz, 1C), 129.5 (1C), 129.4 (1C), 129.3 (2C), 129.2 (1C), 129.1 (d, $^3J_{CP}$ = 12.6 Hz, 2C), 128.96 (d, $^1J_{CP}$ = 95.7 Hz, 1C), 128.91 (d, $^2J_{CP}$ = 10.1 Hz, 1C), 126.6 (d, $^3J_{CP}$ = 4.6 Hz, 1C), 125.1 (1C), 124.3 (1C), 124.2 (d, $^2J_{CP}$ = 10.4 Hz, 1C), 124.1 (1C), 121.7 (1C). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 38.7; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{28}H_{20}OPS$: 435.0967, Found: 435.0968.

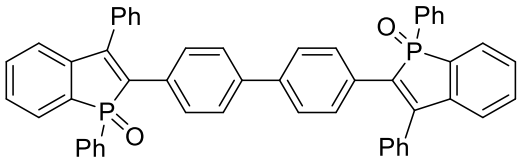


2-(5-Chlorothiophen-2-yl)-1,3-diphenylphosphindole 1-oxide (4ar): pale yellow solid (0.2 mmol, 35.9 mg, 43% yield); m.p. 175.8-177.1 °C (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85-7.80 (m, 2H), 7.68-7.64 (m, 1H), 7.60-7.51 (m, 4H), 7.48-7.42 (m, 3H), 7.40-7.30 (m, 3H), 7.20 (dd, J = 4.0, 1.0 Hz, 1H), 6.96 (dd, J = 7.5, 2.9 Hz, 1H), 6.65 (d, J = 4.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 146.5 (d, $^2J_{CP}$ = 20.3 Hz, 1C), 144.2 (d, $^2J_{CP}$ = 25.8 Hz, 1C), 134.2 (d, $^3J_{CP}$ = 15.7 Hz, 1C), 133.6 (1C), 133.3 (d, $^4J_{CP}$ = 1.9 Hz, 1C), 132.9 (d, $^1J_{CP}$ = 98.3 Hz, 1C), 132.5 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 131.0 (d, $^1J_{CP}$ = 107.3 Hz, 1C), 130.8 (d, $^2J_{CP}$ = 10.6 Hz, 2C), 130.5 (1C), 130.0 (d, $^1J_{CP}$ = 100.2 Hz, 1C), 129.8 (1C), 129.6 (1C), 129.1 (d, $^3J_{CP}$ = 12.4 Hz, 2C), 129.0 (d, $^3J_{CP}$ = 10.6 Hz, 1C), 129.0 (1C), 128.9 (1C), 128.88 (2C), 128.85 (d, $^2J_{CP}$ = 10.3 Hz, 1C), 126.0 (1C), 123.9 (d, $^2J_{CP}$ = 10.9 Hz, 1C). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 38.5; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{24}H_{17}ClOPS$: 419.0421, Found: 419.0437.

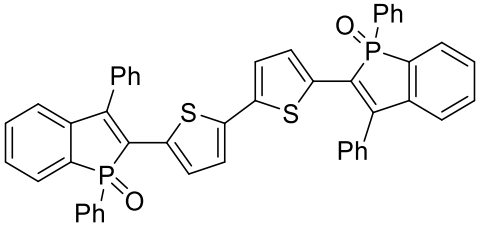


2,2'-(1,4-Phenylene)bis(1,3-diphenylphosphindole 1-oxide) (4as, *syn* + *anti*, ca. 1:1 mixture):

yellow solid (0.08 mmol scale, 28.7 mg, 53% yield); m.p. 267.6-268.6 °C (from hexane); TLC R_f 0.20 (hexane/EtOAc, 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71-7.62 (m, 6H), 7.51-7.45 (m, 2H), 7.43-7.31 (m, 14H), 7.23-7.19 (m, 4H), 7.15 (dd, J = 7.5, 2.9 Hz, 2H), 6.93 (d, J = 10.7 Hz, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 150.2 (d, $^2J_{CP}$ = 21.5 Hz, 1C), 150.1 (d, $^2J_{CP}$ = 21.3 Hz, 1C), 143.7 (d, $^2J_{CP}$ = 27.0 Hz, 1C), 143.6 (d, $^2J_{CP}$ = 27.0 Hz, 1C), 134.1 (d, $^3J_{CP}$ = 14.8 Hz, 1C), 134.0 (d, $^3J_{CP}$ = 14.8 Hz, 1C), 133.6 (d, $^1J_{CP}$ = 95.6 Hz, 1C), 133.5 (d, $^1J_{CP}$ = 95.6 Hz, 1C), 132.9 (2H), 132.3 (d, $^3J_{CP}$ = 4.7 Hz, 1C), 132.2 (d, $^3J_{CP}$ = 4.7 Hz, 1C), 132.1 (d, $^4J_{CP}$ = 2.7 Hz, 2C), 132.0 (d, $^1J_{CP}$ = 106.4 Hz, 1C), 131.9 (d, $^1J_{CP}$ = 106.4 Hz, 1C), 130.9 (d, $^2J_{CP}$ = 10.8 Hz, 2C), 130.8 (d, $^2J_{CP}$ = 10.8 Hz, 2C), 129.97 (d, $^1J_{CP}$ = 99.3 Hz, 1C), 129.95 (d, $^1J_{CP}$ = 99.3 Hz, 1C), 129.2, 129.07, 129.05, 129.01, 128.9, 128.8, 128.79, 128.74, 124.1 (d, $^2J_{CP}$ = 10.9 Hz, 2C) (All observed signals are just shown because of complexity associated with C–P couplings and diastereomers.); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 39.04, 38.97; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{46}H_{33}O_2P_2$: 679.1951, Found: 679.1956.

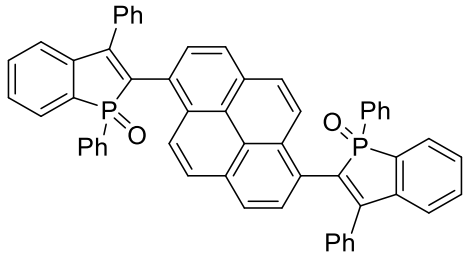


2,2'-([1,1'-Biphenyl]-4,4'-diyl)bis(1,3-diphenylphosphindole 1-oxide) (4at, *syn* + *anti*, ca. 1:1 mixture): yellow solid (0.08 mmol scale, 29.6 mg, 49% yield); m.p. 190.5-191.8 °C (from hexane); TLC R_f 0.20 (hexane/EtOAc, 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78-7.73 (m, 4H), 7.72-7.68 (m, 2H), 7.48-7.31 (m, 20H), 7.26-7.18 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 149.93 (d, $^2J_{CP}$ = 21.5 Hz, 1C), 149.91 (d, $^2J_{CP}$ = 21.5 Hz, 1C), 143.8 (d, $^2J_{CP}$ = 26.8 Hz, 2C), 139.4, 134.3 (d, $^3J_{CP}$ = 15.1 Hz, 2C), 133.71 (d, $^1J_{CP}$ = 98.7 Hz, 1C), 133.74 (d, $^1J_{CP}$ = 93.8 Hz, 1C), 132.9, 132.2, 132.0 (d, $^1J_{CP}$ = 106.2 Hz, 2C), 131.9 (d, $^2J_{CP}$ = 9.9 Hz, 2C), 130.9 (d, $^2J_{CP}$ = 10.8 Hz, 4C), 129.9 (d, $^1J_{CP}$ = 99.8 Hz, 2C), 129.4, 129.07, 129.01, 128.8, 128.7, 126.5, 124.1, 124.0, 123.99 (All observed signals are just shown because of complexity associated with C–P couplings and diastereomers.); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 39.18, 39.15; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{52}H_{37}O_2P_2$: 755.2264, Found: 755.2282.

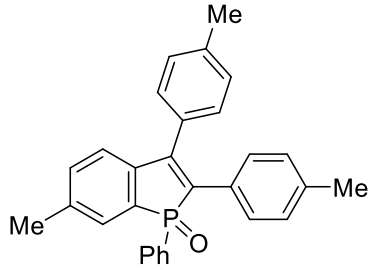


2,2'-([2,2'-Bithiophene]-5,5'-diyl)bis(1,3-diphenylphosphindole 1-oxide) (4au, *syn* + *anti*, ca. 1:1 mixture): dark orange solid (0.08 mmol scale, 42.2 mg, 69% yield); m.p. 179.8-181.1 °C (from hexane); TLC R_f 0.20 (hexane/EtOAc, 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82-7.77 (m, 4H), 7.64

(dd, J = 9.9, 7.1 Hz, 2H), 7.56-7.54 (m, 6H), 7.52-7.47 (m, 2H), 7.44-7.27 (m, 12H), 7.21-7.19 (m, 2H), 6.95 (dt, J = 7.7, 1.4 Hz, 2H), 6.65 (d, J = 4.0 Hz, 1H), 6.63 (d, J = 4.0 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 146.4, 146.2, 144.6, 144.3, 138.7, 135.0, 134.8, 133.9, 133.7, 133.2, 132.4, 132.3, 131.7, 130.9, 130.8, 130.7, 130.65, 130.62, 130.5, 130.4, 129.7, 129.6, 129.4, 129.1, 129.0, 128.95, 128.90, 128.79, 128.07, 128.04, 123.85, 123.80, 123.7 (All observed signals are just shown because of complexity associated with C–P couplings and diastereomers.); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 38.47, 38.41; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{48}H_{33}O_2P_2S_2$: 767.1392, Found: 767.1388.

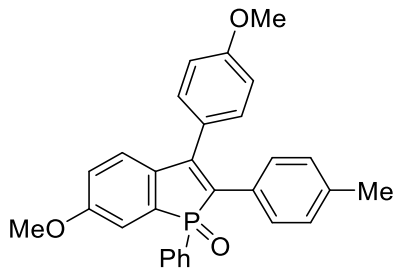


2,2'-(Pyrene-1,6-diyl)bis(1,3-diphenylphosphindole 1-oxide) (4av, *syn* + *anti*, the ratio was not determined): yellow solid (0.08 mmol scale, 23.1 mg, 36% yield); m.p. over 270 °C (from hexane); TLC R_f 0.22 (hexane/EtOAc, 1:3). ^1H NMR ($CDCl_3$, 400 MHz) δ 8.51 (bs, 2H), 7.86-7.30 (m, 23H), 7.20 (bs, 4H), 7.10 (bs, 7H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 152.5, 143.8, 143.6, 133.7, 133.5, 133.1, 132.7, 132.3, 131.7, 131.3, 131.2, 129.8, 129.7, 129.5, 129.4, 129.3, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.7, 127.6, 127.5, 124.7, 124.4, 124.3 (All observed signals are just shown because of complexity associated with C–P couplings and diastereomers.); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.1; HRMS (APCI) m/z ([M+H]$^+$) Calcd for $C_{56}H_{37}O_2P_2$: 803.2264, Found: 803.2275.

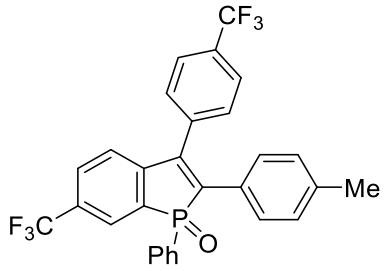


6-Methyl-1-phenyl-2,3-di-*p*-tolylphosphindole 1-oxide (4ba): colorless solid (0.2 mmol scale, 65.5 mg, 78% yield); m.p. 84.9-86.3 °C (from hexane); TLC R_f 0.24 (hexane/EtOAc, 1:2). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81-7.75 (m, 2H), 7.50-7.43 (m, 2H), 7.40-7.35 (m, 2H), 7.24-7.20 (m, 5H), 7.14 (d, J = 7.5 Hz, 2H), 7.08 (dd, J = 7.8, 3.1 Hz, 1H), 6.88 (d, J = 8.3 Hz, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 2.18 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 149.6 (d, $^2J_{CP}$ = 22.0 Hz, 1C), 141.4 (d, $^2J_{CP}$ = 27.2 Hz, 1C), 139.2 (d, $^3J_{CP}$ = 10.4 Hz, 1C), 138.4 (1C), 137.5 (1C), 133.2 (d, $^4J_{CP}$ = 1.5 Hz, 1C), 132.6 (d, $^1J_{CP}$ = 96.9 Hz, 1C), 132.2 (d, $^1J_{CP}$ = 105.4 Hz, 1C), 132.0 (d, $^4J_{CP}$ = 2.8 Hz, 1C), 131.6 (d, $^3J_{CP}$ = 15.3 Hz, 1C), 131.0 (d, $^2J_{CP}$ = 10.5 Hz, 2C), 130.5 (d, $^1J_{CP}$ = 98.0 Hz, 1C), 130.1 (1C), 129.7

(d, $^{2}J_{CP}$ = 9.7 Hz, 1C), 129.6 (2C), 129.0 (2C), 128.9 (2C), 128.89 (d, $^{3}J_{CP}$ = 6.0 Hz, 2C), 128.80 (d, $^{3}J_{CP}$ = 12.1 Hz, 2C), 123.8 (d, $^{2}J_{CP}$ = 11.6 Hz, 1C), 21.5 (1C), 21.26 (1C), 21.24 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.2; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{29}H_{26}OP$: 421.1716, Found: 421.1720.

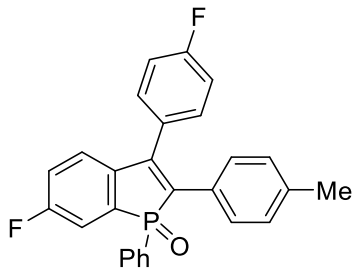


6-Methoxy-3-(4-methoxyphenyl)-1-phenyl-2-(*p*-tolyl)phosphindole 1-oxide (4da): colorless solid (0.2 mmol scale, 69.6 mg, 77% yield); m.p. 89.9-91.2 °C (from hexane); TLC R_f 0.22 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80-7.75 (m, 2H), 7.48-7.44 (m, 1H), 7.41-7.36 (m, 2H), 7.27-7.22 (m, 3H), 7.16 (dd, *J* = 8.5, 3.6 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 2H), 6.96-6.88 (m, 5H), 3.85 (s, 3H), 3.79 (s, 3H), 2.19 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 160.5 (d, $^{3}J_{CP}$ = 13.4 Hz, 1C), 159.7 (1C), 149.3 (d, $^{2}J_{CP}$ = 21.3 Hz, 1C), 137.2 (1C), 136.4 (d, $^{2}J_{CP}$ = 27.0 Hz, 1C), 134.2 (d, $^{1}J_{CP}$ = 104.5 Hz, 1C), 132.0 (d, $^{4}J_{CP}$ = 2.7 Hz, 1C), 131.2 (d, $^{1}J_{CP}$ = 98.1 Hz, 1C), 131.0 (d, $^{2}J_{CP}$ = 10.7 Hz, 2C), 130.4 (2C), 130.3 (d, $^{1}J_{CP}$ = 99.1 Hz, 1C), 130.1 (d, $^{2}J_{CP}$ = 10.3 Hz, 1C), 129.0 (2C), 128.83 (d, $^{3}J_{CP}$ = 12.2 Hz, 2C), 128.82 (d, $^{3}J_{CP}$ = 5.9 Hz, 2C), 126.7 (d, $^{3}J_{CP}$ = 15.6 Hz, 1C), 125.1 (d, $^{3}J_{CP}$ = 12.8 Hz, 1C), 117.8 (1C), 114.5 (d, $^{2}J_{CP}$ = 10.6 Hz, 1C), 114.3 (2C), 55.7 (1C), 55.3 (1C), 21.2 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 38.7; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{29}H_{26}O_3P$: 453.1615, Found: 453.1613.

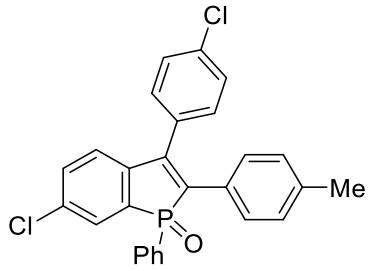


1-Phenyl-2-(*p*-tolyl)-6-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)phosphindole 1-oxide (4ea): colorless solid (0.2 mmol scale, 53.8 mg, 51% yield); m.p. 151.3-152.6 °C (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, *J* = 9.7 Hz, 1H), 7.79-7.70 (m, 5H), 7.56-7.42 (m, 5H), 7.23 (dd, *J* = 8.0, 2.7 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 2.22 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 146.6, 146.4, 146.3, 146.1, 139.1, 138.7, 137.8, 137.7, 133.6, 132.84, 132.81, 132.5, 131.2, 131.1, 131.0, 130.95, 130.93, 130.8, 130.34, 130.32, 130.30, 129.5, 129.4, 129.3, 129.1, 128.9, 128.8, 128.6, 128.5, 127.8, 126.33, 126.30, 126.2, 126.1,

126.06, 126.03, 125.2, 124.9, 123.7, 123.6, 122.5, 21.3. (All observed signals are just shown because of complexity associated with C–F and C–P couplings.); $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz) δ -62.6, -62.7. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 37.9; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{29}H_{20}F_6OP$: 529.1151, Found: 529.1154.

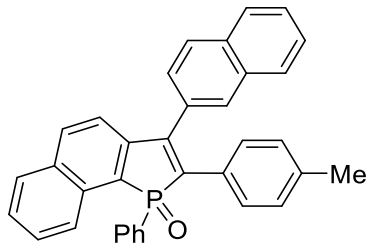


6-Fluoro-3-(4-fluorophenyl)-1-phenyl-2-(*p*-tolyl)phosphindole 1-oxide (4fa): pale yellow solid (0.2 mmol scale, 60.7 mg, 71% yield); m.p. 218.1-219.4 °C (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78-7.73 (m, 2H), 7.53-7.48 (m, 1H), 7.43-7.37 (m, 3H), 7.33-7.29 (m, 2H), 7.17-7.09 (m, 6H), 6.92 (d, J = 8.5 Hz, 2H), 2.21 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 164.6, 164.5, 164.1, 162.1, 162.0, 161.6, 147.66, 147.65, 147.45, 147.44, 139.64, 139.62, 139.38, 139.35, 138.1, 135.38, 135.31, 134.9, 134.3, 134.27, 133.9, 132.5, 132.48, 131.3, 131.2, 131.0, 130.9, 130.89, 130.84, 130.6, 130.2, 130.17, 130.05, 130.01, 129.7, 129.4, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4, 125.4, 125.3, 125.2, 125.1, 119.5, 119.3, 117.0, 116.9, 116.7, 116.6, 116.5, 116.2, 21.2 (All observed signals are just shown because of complexity associated with C–F and C–P couplings.); $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz) δ -111.1 (d, J_{FP} = 5.3 Hz, 1F), -111.7. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 37.7 (d, J_{PF} = 5.3 Hz); HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{27}H_{20}F_2OP$: 429.1215, Found: 429.1229.

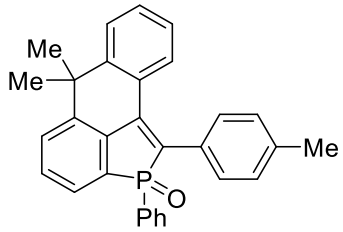


6-Chloro-3-(4-chlorophenyl)-1-phenyl-2-(*p*-tolyl)phosphindole 1-oxide (4ga): pale yellow solid (0.2 mmol scale, 60.7 mg, 66% yield); m.p. 107.2-108.6 °C (from hexane); TLC R_f 0.25 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77-7.72 (m, 2H), 7.64 (dd, J = 9.8, 2.0 Hz, 1H), 7.53-7.48 (m, 1H), 7.44-7.39 (m, 5H), 7.26 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 7.09 (dd, J = 8.1, 3.3 Hz, 1H), 6.92 (d, J = 8.1 Hz, 2H), 2.21 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 147.1 (d, $^{2}J_{CP}$ = 21.1 Hz, 1C), 141.7 (d, $^{2}J_{CP}$ = 26.5 Hz, 1C), 138.4 (1C), 135.5 (d, $^{3}J_{CP}$ = 13.6 Hz, 1C), 135.0 (d, $^{1}J_{CP}$ = 95.6 Hz, 1C), 134.9 (1C), 134.2 (d, $^{1}J_{CP}$ = 103.3 Hz, 1C), 132.8 (d, $^{4}J_{CP}$ = 1.2

Hz, 1C), 132.6 (d, $^4J_{CP}$ = 2.5 Hz, 1C), 132.4 (1C), 130.9 (d, $^2J_{CP}$ = 10.7 Hz, 2C), 130.4 (2C), 129.5 (2C), 129.4 (d, $^2J_{CP}$ = 10.0 Hz, 1C), 129.3 (2C), 129.2 (d, $^3J_{CP}$ = 15.3 Hz, 1C), 129.1 (d, $^3J_{CP}$ = 12.2 Hz, 2C), 128.9 (d, $^1J_{CP}$ = 100.8 Hz, 1C), 128.8 (d, $^3J_{CP}$ = 5.9 Hz, 2C), 124.7 (d, $^2J_{CP}$ = 11.7 Hz, 1C), 21.3 (1C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 38.0; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{27}H_{20}Cl_2OP$: 461.0629, Found: 461.0657.

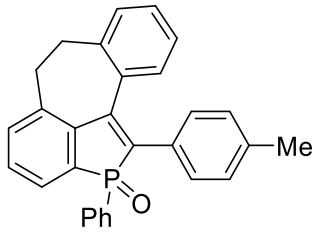


3-(Naphthalen-2-yl)-1-phenyl-2-(*p*-tolyl)benzo[*g*]phosphindole 1-oxide (4ha): yellow solid (0.2 mmol scale, 64.9 mg, 66% yield); m.p. 135.3-136.6 ºC (from hexane); TLC R_f 0.20 (hexane/EtOAc, 1:2). ^1H NMR ($CDCl_3$, 400 MHz) δ 8.13 (dd, *J* = 8.2, 0.5 Hz, 1H), 7.93-7.85 (m, 7H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.58-7.51 (m, 2H), 7.50-7.33 (m, 7H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 2.16 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 148.5 (d, $^2J_{CP}$ = 23.2 Hz, 1C), 143.3 (d, $^2J_{CP}$ = 26.2 Hz, 1C), 137.9 (1C), 135.0 (d, $^1J_{CP}$ = 95.6 Hz, 1C), 133.6 (d, $^4J_{CP}$ = 2.1 Hz, 1C), 133.5 (d, $^3J_{CP}$ = 7.9 Hz, 1C), 133.4 (1C), 133.2 (1C), 132.3 (d, $^3J_{CP}$ = 15.7 Hz, 1C), 132.1 (d, $^4J_{CP}$ = 2.7 Hz, 1C), 131.8 (d, $^2J_{CP}$ = 9.2 Hz, 1C), 130.9 (d, $^2J_{CP}$ = 10.4 Hz, 2C), 129.6 (d, $^2J_{CP}$ = 10.6 Hz, 1C), 129.4 (d, $^1J_{CP}$ = 95.1 Hz, 1C), 129.1 (1C), 129.08 (1C), 129.07 (d, $^3J_{CP}$ = 12.5 Hz, 2C), 129.02 (d, $^3J_{CP}$ = 6.1 Hz, 2C), 128.9 (1C), 128.7 (d, $^4J_{CP}$ = 1.5 Hz, 1C), 128.5 (1C), 128.3 (1C), 128.2 (1C), 128.0 (1C), 127.4 (d, $^1J_{CP}$ = 102.2 Hz, 1C), 126.9 (1C), 126.76 (1C), 126.75 (1C), 126.6 (1C), 125.7 (d, $^3J_{CP}$ = 4.9 Hz, 1C), 121.3 (d, $^3J_{CP}$ = 12.5 Hz, 1C), 21.3 (1C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.9; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{35}H_{26}OP$: 493.1716, Found: 493.1723.

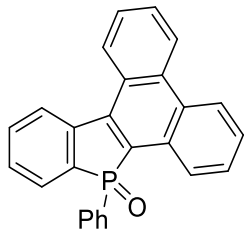


6,6-Dimethyl-2-phenyl-1-(*p*-tolyl)-6*H*-naphtho[1,2,3-*cd*]phosphindole 2-oxide (4ia): colorless solid (0.2 mmol scale, 54.4 mg, 63% yield); m.p. 131.3-132.6 ºC (from hexane); TLC R_f 0.22 (hexane/EtOAc, 1:2). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.67-7.57 (m, 5H), 7.48-7.42 (m, 2H), 7.39-7.33 (m, 3H), 7.12 (bs, 4H), 6.96 (td, *J* = 7.5, 1.2 Hz, 1H), 2.33 (d, *J* = 1.1 Hz, 3H), 1.77 (s, 3H), 1.72 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 146.9 (1C), 141.5 (d, $^3J_{CP}$ = 11.6 Hz, 1C), 139.0 (d, $^2J_{CP}$ = 23.2 Hz, 1C), 137.7 (d, $^4J_{CP}$ = 2.1 Hz, 1C), 137.4 (d, $^2J_{CP}$ = 29.3 Hz, 1C), 132.0 (d, $^4J_{CP}$ = 2.7 Hz, 1C), 131.3 (d, $^2J_{CP}$ = 10.8 Hz, 2C), 131.28 (1C), 130.8 (d, $^1J_{CP}$ = 98.9

Hz, 1C), 130.5 (d, $^{4}J_{CP}$ = 1.6 Hz, 1C), 130.4 (1C), 130.3 (d, $^{1}J_{CP}$ = 103.9 Hz, 1C), 130.0 (2C), 128.9 (d, $^{1}J_{CP}$ = 100.7 Hz, 1C), 129.5 (d, $^{3}J_{CP}$ = 11.1 Hz, 1C), 128.6 (d, $^{3}J_{CP}$ = 12.2 Hz, 2C), 128.5 (1C), 128.4 (1C), 128.3 (1C), 127.5 (1C), 127.4 (d, $^{2}J_{CP}$ = 9.0 Hz, 1C), 127.2 (d, $^{2}J_{CP}$ = 17.0 Hz, 1C), 125.9 (1C), 38.6 (d, $^{4}J_{CP}$ = 1.1 Hz, 1C), 33.4 (1C), 33.0 (1C), 21.4 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 39.8; HRMS (APCI) m/z ([M+H]$^{+}$) Calcd for $C_{30}H_{26}OP$: 433.1716, Found: 433.1738.

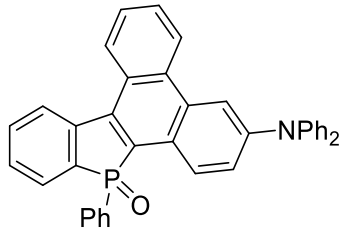


6-Phenyl-5-(*p*-tolyl)-10,11-dihydrobenzo[6,7]cyclohepta[1,2,3-*cd*]phosphindole 6-oxide (4ja): colorless solid (0.2 mmol scale, 46.0 mg, 55% yield); m.p. 126.4-127.7 °C (from hexane); TLC R_f 0.24 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (bs, 2H), 7.53 (ddd, *J* = 10.2, 6.4, 1.7 Hz, 1H), 7.43-7.36 (m, 3H), 7.25-7.18 (m, 7H), 6.93-6.87 (m, 3H), 3.20-3.07 (m, 4H), 2.21 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 150.1 (d, $^{2}J_{CP}$ = 19.5 Hz, 1C), 143.3 (1C), 140.2 (d, $^{2}J_{CP}$ = 28.2 Hz, 1C), 139.5 (d, $^{3}J_{CP}$ = 10.6 Hz, 1C), 137.6 (1C), 135.6 (d, $^{4}J_{CP}$ = 1.5 Hz, 1C), 134.1 (d, $^{3}J_{CP}$ = 15.0 Hz, 1C), 133.2 (1C), 131.9 (d, $^{4}J_{CP}$ = 2.5 Hz, 1C), 131.4 (d, $^{1}J_{CP}$ = 93.9 Hz, 1C), 131.3 (d, $^{2}J_{CP}$ = 8.7 Hz, 1C), 131.0 (d, $^{2}J_{CP}$ = 10.3 Hz, 2C), 130.3 (d, $^{1}J_{CP}$ = 102.5 Hz, 1C), 129.8 (1C), 129.3 (d, $^{3}J_{CP}$ = 5.4 Hz, 2C), 129.2 (2C), 128.8 (d, $^{3}J_{CP}$ = 11.9 Hz, 2C), 128.3 (1C), 128.1 (d, $^{3}J_{CP}$ = 11.5 Hz, 1C), 127.5 (d, $^{1}J_{CP}$ = 98.5 Hz, 1C), 126.9 (d, $^{2}J_{CP}$ = 9.6 Hz, 1C), 125.8 (1C), 35.4 (1C), 34.7 (1C), 21.3 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 35.5; HRMS (APCI) m/z ([M+H]$^{+}$) Calcd for $C_{29}H_{24}OP$: 419.1560, Found: 419.1562.

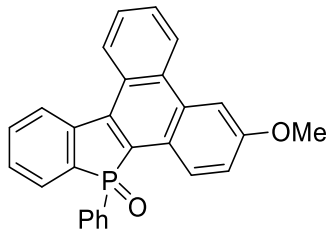


9-Phenyltribenzo[*b*,*e*,*g*]phosphindole 9-oxide (5aa): colorless solid (0.2 mmol scale, 56.3 mg, 75% yield); TLC R_f 0.28 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.97-8.95 (m, 1H), 8.80-8.78 (m, 1H), 8.64 (d, *J* = 8.5 Hz, 1H), 8.51 (dd, *J* = 8.0, 3.5 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.85-7.72 (m, 5H), 7.68-7.60 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.40 (m, 2H), 7.36-7.32 (m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 142.5 (d, $^{2}J_{CP}$ = 23.4 Hz, 1C), 139.5 (d, $^{2}J_{CP}$ = 20.0 Hz, 1C), 134.6 (d, $^{1}J_{CP}$ = 106.5 Hz, 1C), 133.9 (d, $^{4}J_{CP}$ = 1.9 Hz, 1C), 133.1 (d, $^{4}J_{CP}$ = 2.0 Hz, 1C), 132.2 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 131.1 (d, $^{2}J_{CP}$ = 10.8 Hz, 2C), 130.8 (d, $^{1}J_{CP}$ = 102.1 Hz, 1C), 130.6 (d, $^{3}J_{CP}$ = 14.4 Hz, 1C), 130.09 (d, $^{3}J_{CP}$ = 9.9 Hz, 1C), 130.05 (d, $^{1}J_{CP}$ = 108.8 Hz, 1C), 129.3 (d, $^{2}J_{CP}$ = 8.9 Hz, 1C), 128.9 (d,

$^{3}J_{CP}$ = 11.4 Hz, 1C), 128.8 (d, $^{3}J_{CP}$ = 12.5 Hz, 2C), 128.6 (1C), 128.0 (1C), 127.9 (d, $^{3}J_{CP}$ = 13.9 Hz, 1C), 127.8 (1C), 127.4 (1C), 127.0 (d, $^{3}J_{CP}$ = 5.4 Hz, 1C), 125.9 (1C), 125.6 (d, $^{2}J_{CP}$ = 10.9 Hz, 1C), 124.1 (1C), 123.1 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 34.0; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{26}H_{18}OP$: 377.1089, Found: 377.1091.



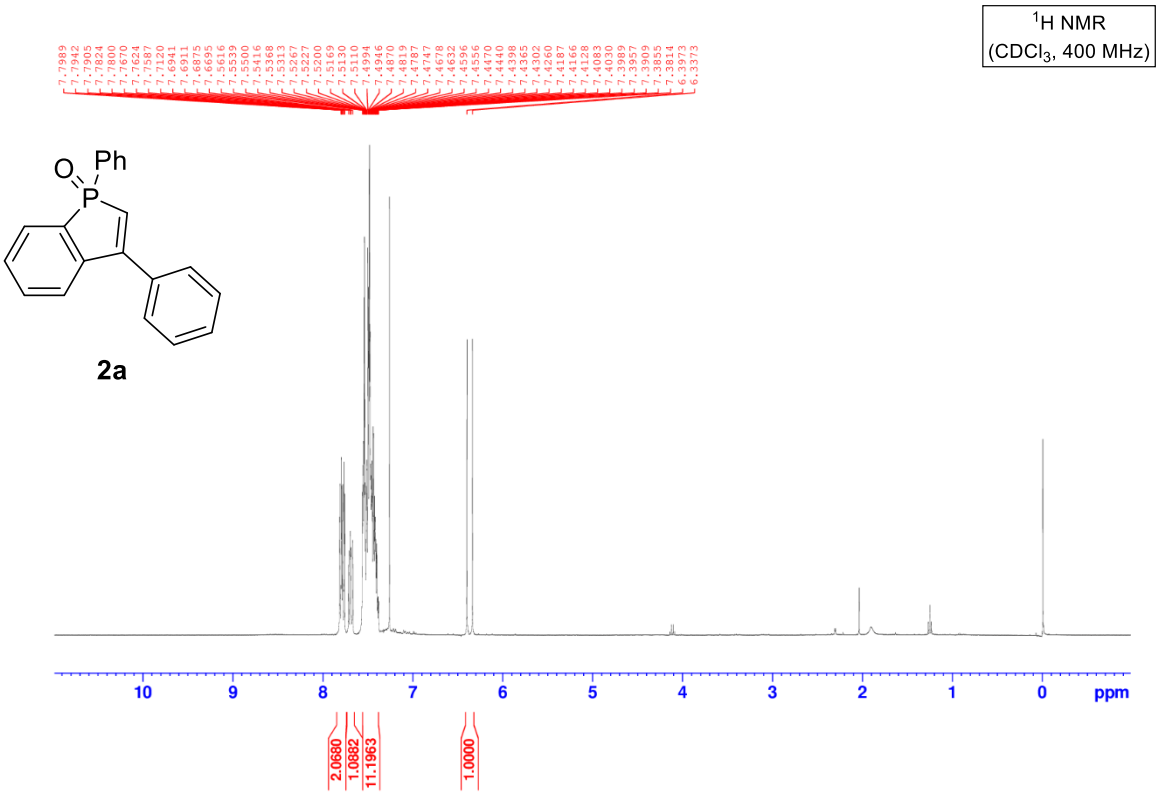
6-(Diphenylamino)-9-phenyltribenzo[*b*,*e*,*g*]phosphindole 9-oxide (5ab): yellow solid (0.2 mmol scale, 64.1 mg, 59% yield); m.p. 225.9-226.9 °C (from hexane); TLC R_f 0.20 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.93 (d, *J* = 7.8 Hz, 1H), 8.48 (dd, *J* = 8.0, 3.4 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.25 (s, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.82-7.70 (m, 4H), 7.68-7.63 (m, 2H), 7.48-7.34 (m, 4H), 7.30-7.25 (m, 5H), 7.17-7.15 (m, 4H), 7.08 (t, *J* = 7.3 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 147.6 (1C), 147.3 (2C), 142.9 (d, $^{2}J_{CP}$ = 23.5 Hz, 1C), 137.1 (d, $^{2}J_{CP}$ = 20.0 Hz, 1C), 134.4 (d, $^{1}J_{CP}$ = 106.5 Hz, 1C), 133.1 (d, $^{4}J_{CP}$ = 2.5 Hz, 1C), 132.1 (d, $^{4}J_{CP}$ = 2.9 Hz, 1C), 132.0 (d, $^{3}J_{CP}$ = 9.5 Hz, 1C), 131.1 (d, $^{2}J_{CP}$ = 10.8 Hz, 2C), 130.9 (d, $^{1}J_{CP}$ = 102.0 Hz, 1C), 130.1 (d, $^{3}J_{CP}$ = 9.7 Hz, 1C), 130.0 (d, $^{1}J_{CP}$ = 102.2 Hz, 1C), 129.5 (4C), 128.8 (d, $^{3}J_{CP}$ = 11.4 Hz, 1C), 128.8 (d, $^{3}J_{CP}$ = 12.5 Hz, 2C), 128.5 (1C), 128.4 (d, $^{4}J_{CP}$ = 2.7 Hz, 1C), 128.1 (1C), 127.8 (d, $^{3}J_{CP}$ = 5.6 Hz, 1C), 127.4 (1C), 125.6 (1C), 125.2 (d, $^{2}J_{CP}$ = 10.9 Hz, 1C), 125.0 (4C), 124.7 (d, $^{2}J_{CP}$ = 8.9 Hz, 1C), 124.6 (1C), 124.2 (1C), 123.7 (2C), 115.2 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 34.0; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{38}H_{27}NOP$: 544.1825, Found: 544.1853.

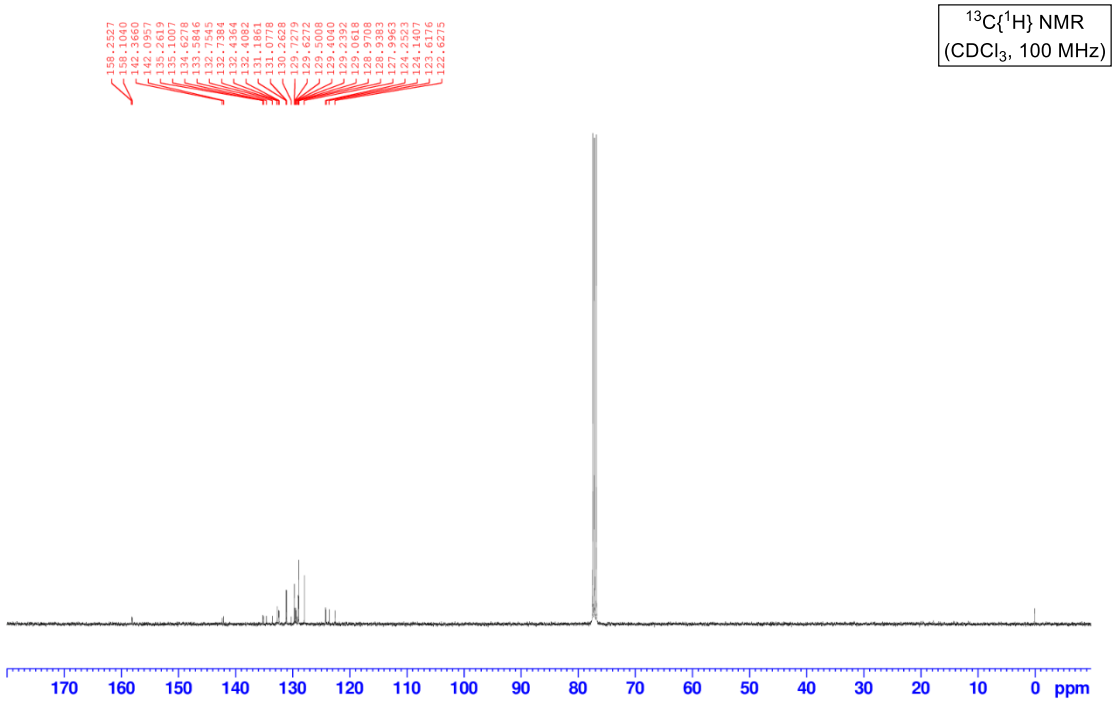


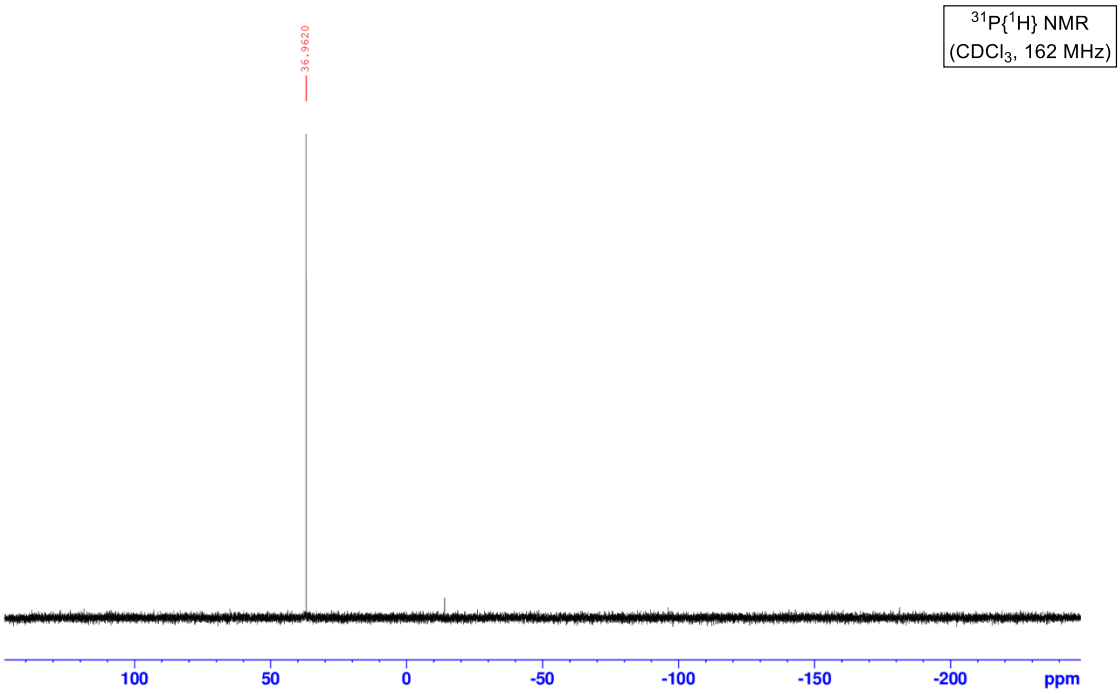
6-Methoxy-9-phenyltribenzo[*b*,*e*,*g*]phosphindole 9-oxide (5ac): yellow solid (0.2 mmol scale, 53.6 mg, 66% yield); m.p. 215.3-216.3 °C (from hexane); TLC R_f 0.24 (hexane/EtOAc, 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.94 (dd, *J* = 5.2, 4.1 Hz, 1H), 8.70 (dd, *J* = 5.2, 4.1 Hz, 1H), 8.47 (dd, *J* = 7.8, 3.4 Hz, 1H), 8.23 (d, *J* = 8.9 Hz, 1H), 8.00 (s, 1H), 7.83-7.70 (m, 5H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.46-7.32 (m, 4H), 7.19 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.96 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 159.3 (1C), 142.8 (d, $^{2}J_{CP}$ = 22.9 Hz, 1C), 136.8 (d, $^{2}J_{CP}$ = 20.0 Hz, 1C), 134.3 (d, $^{1}J_{CP}$ = 106.5 Hz, 1C), 133.2 (d, $^{4}J_{CP}$ = 1.9 Hz, 1C), 133.1 (d, $^{4}J_{CP}$ = 1.9 Hz, 1C), 132.4 (d, $^{2}J_{CP}$ = 8.6 Hz, 1C), 132.1 (d, $^{4}J_{CP}$ = 2.8 Hz, 1C), 131.05 (d, $^{2}J_{CP}$ = 10.9 Hz, 2C), 131.03 (d, $^{1}J_{CP}$ = 102.1 Hz, 1C), 130.02 (d, $^{3}J_{CP}$ = 9.7

Hz, 1C), 130.0 (d, $^{1}J_{CP}$ = 102.8 Hz, 1C), 128.8 (d, $^{3}J_{CP}$ = 12.5 Hz, 2C), 128.5 (d, $^{3}J_{CP}$ = 5.6 Hz, 1C), 128.4 (d, $^{3}J_{CP}$ = 10.8 Hz, 1C), 128.3 (d, $^{3}J_{CP}$ = 12.1 Hz, 1C), 128.1 (1C), 127.5 (1C), 125.7 (1C), 125.2 (d, $^{2}J_{CP}$ = 10.9 Hz, 1C), 124.1 (1C), 123.9 (d, $^{3}J_{CP}$ = 9.2 Hz, 1C), 117.9 (1C), 104.7 (1C), 55.5 (1C). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ 34.0; HRMS (APCI) m/z ($[M+H]^+$) Calcd for $C_{27}H_{20}O_2P$: 407.1196, Found: 407.1182.

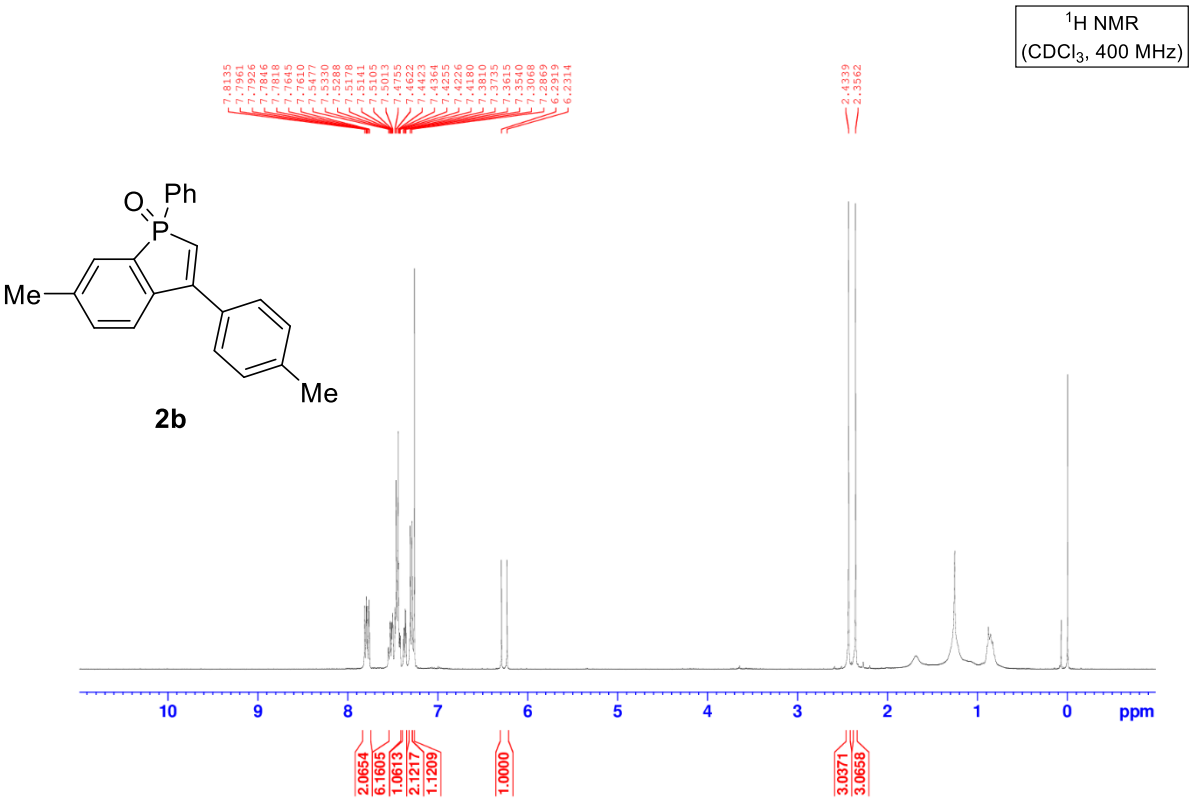
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2a**]

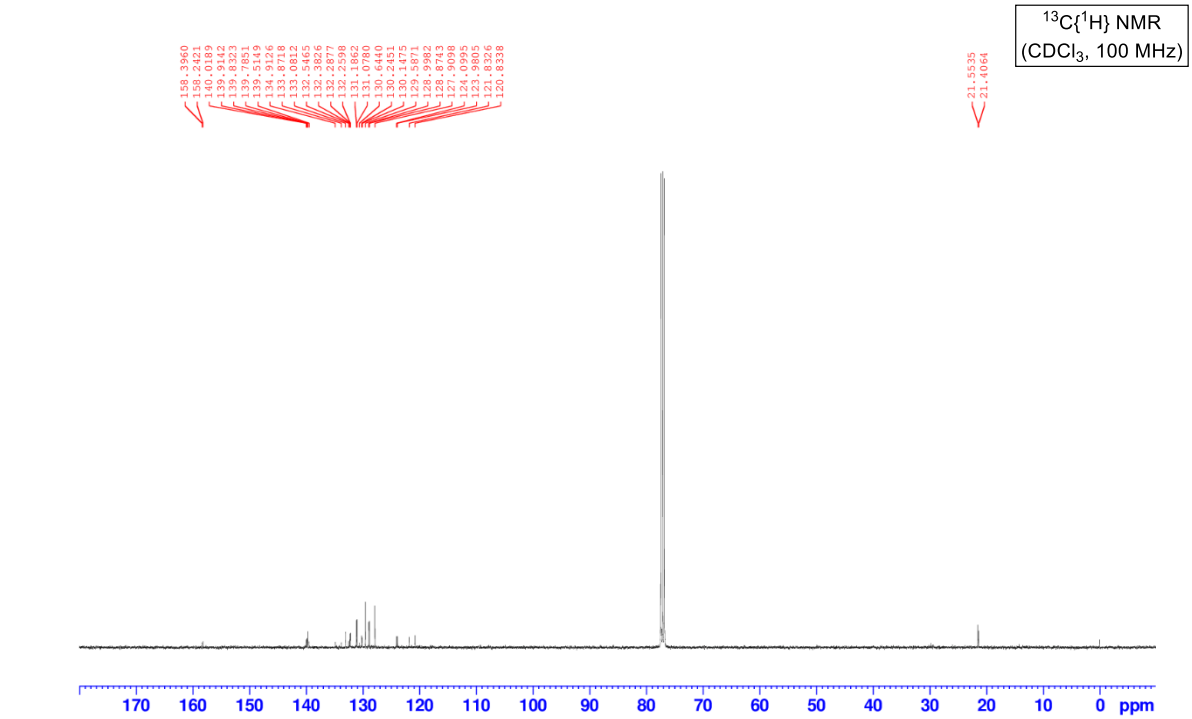


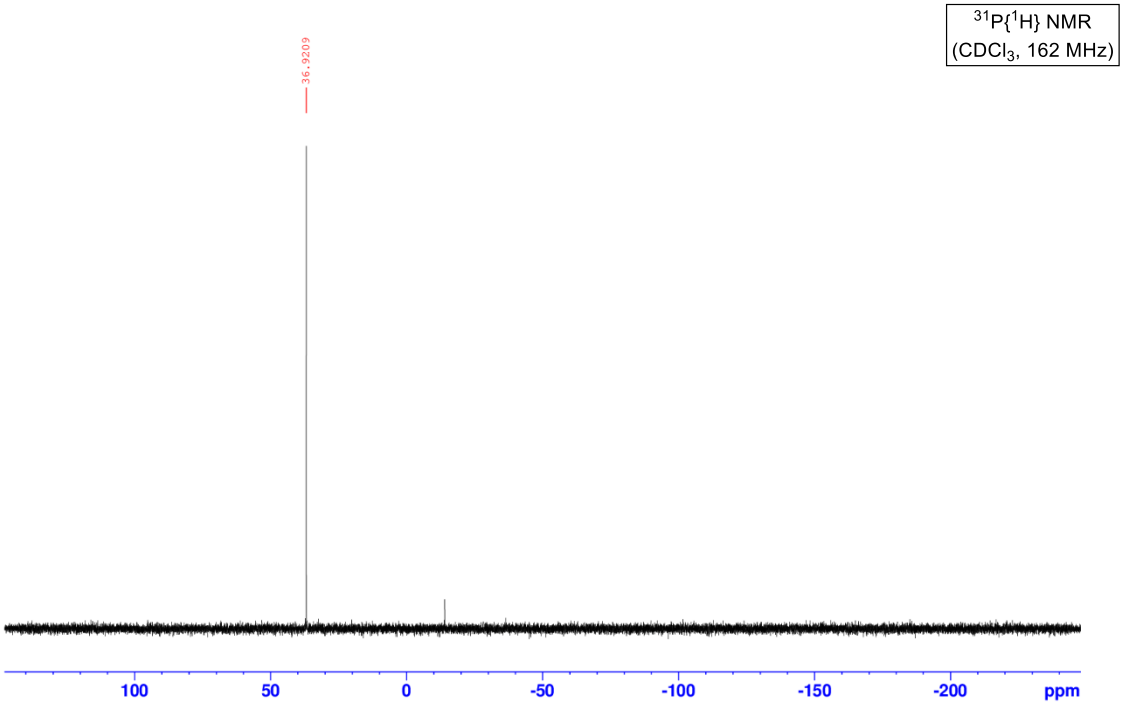



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
36.9620
100
50
0
-50
-100
-150
-200
ppm

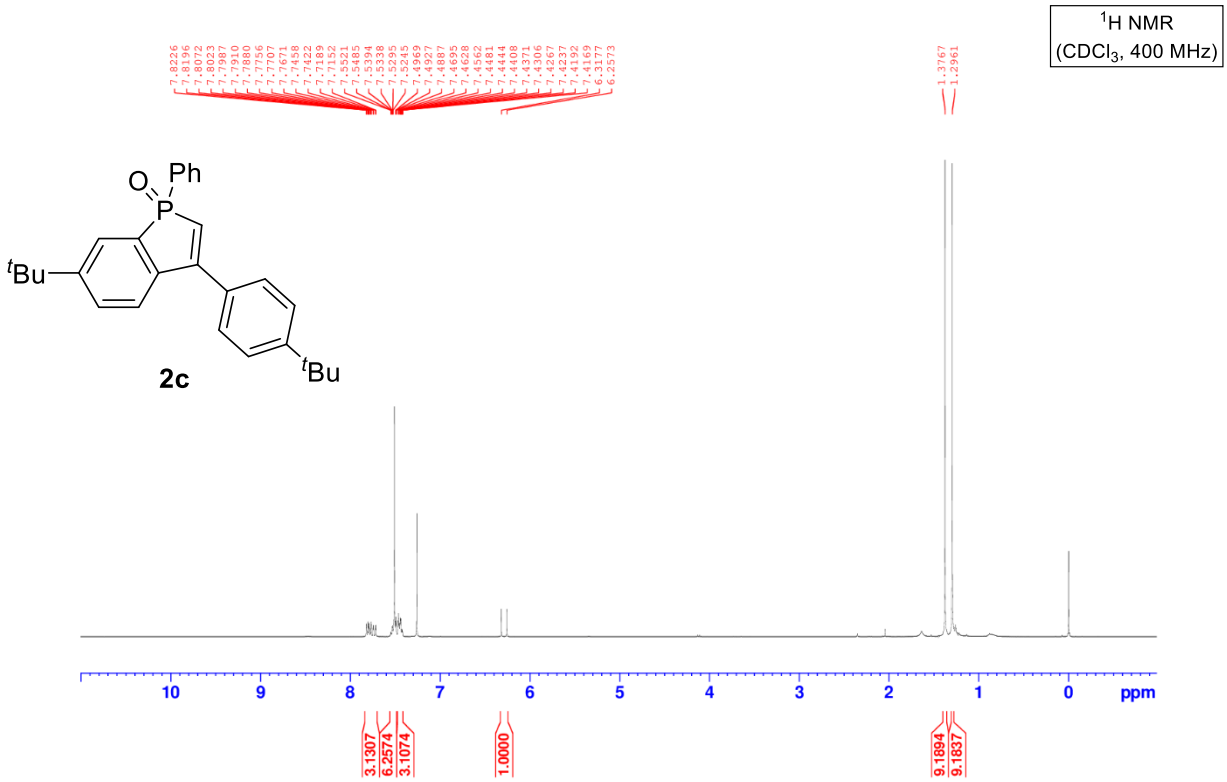
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2b**]

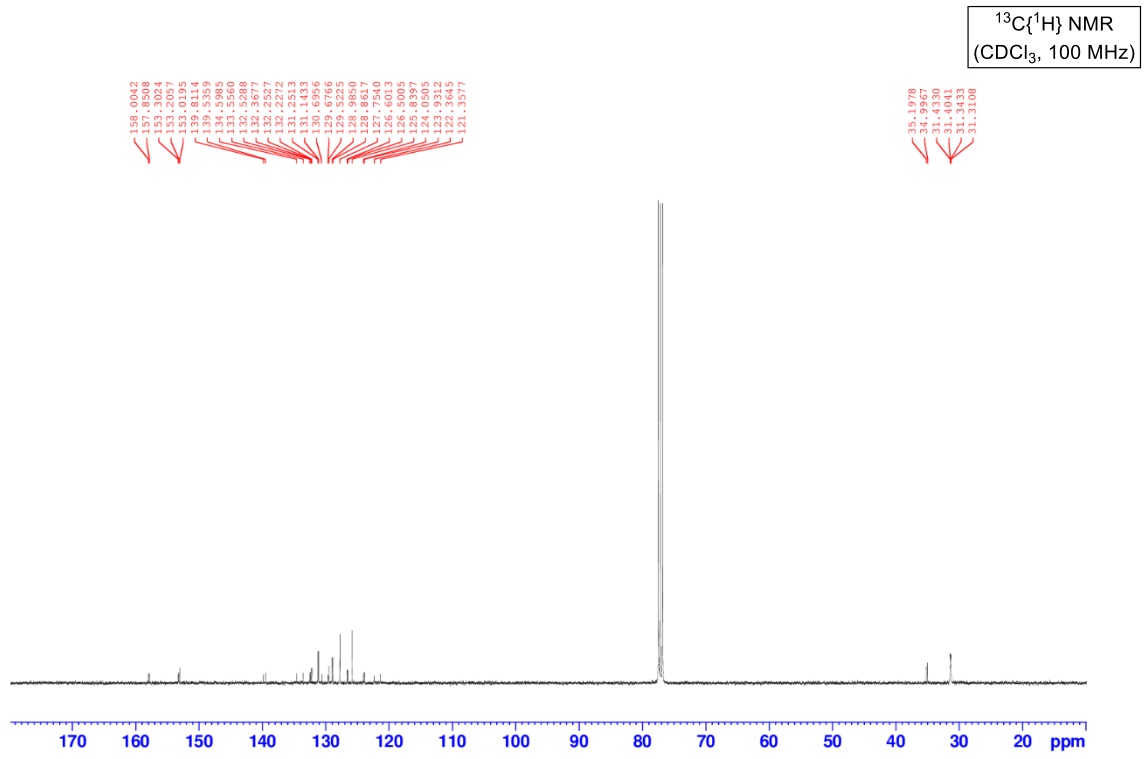


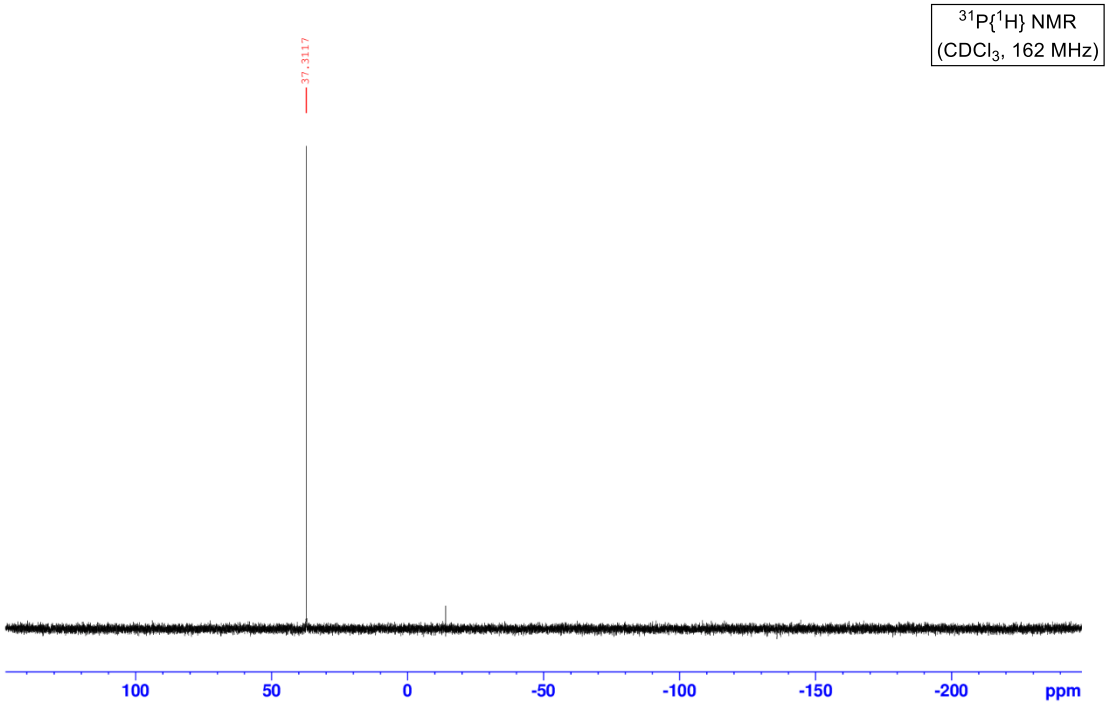



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
36.9209
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2c**]

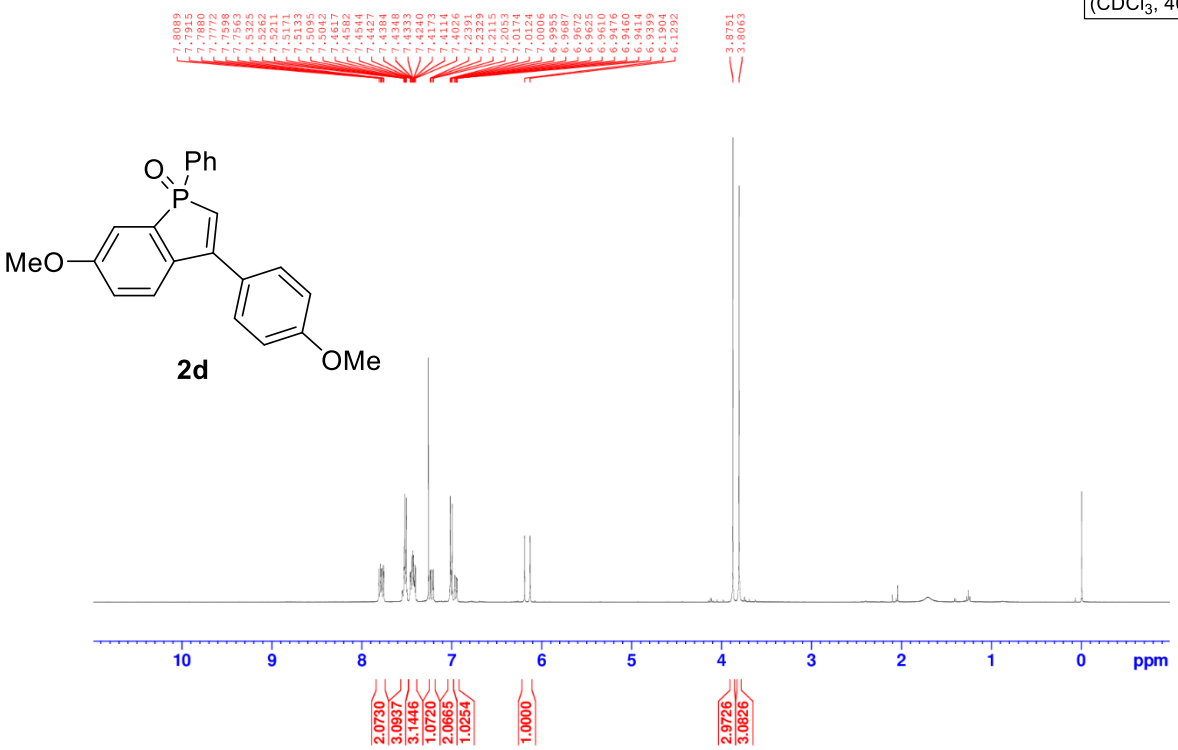




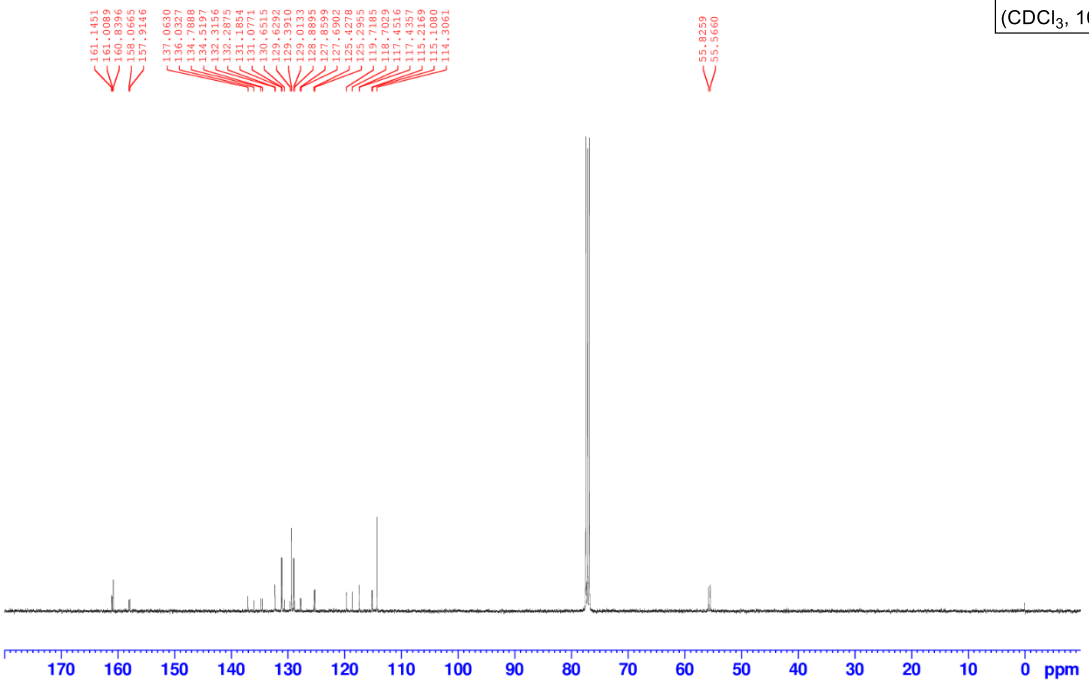

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
37.3117
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR of **2d**]

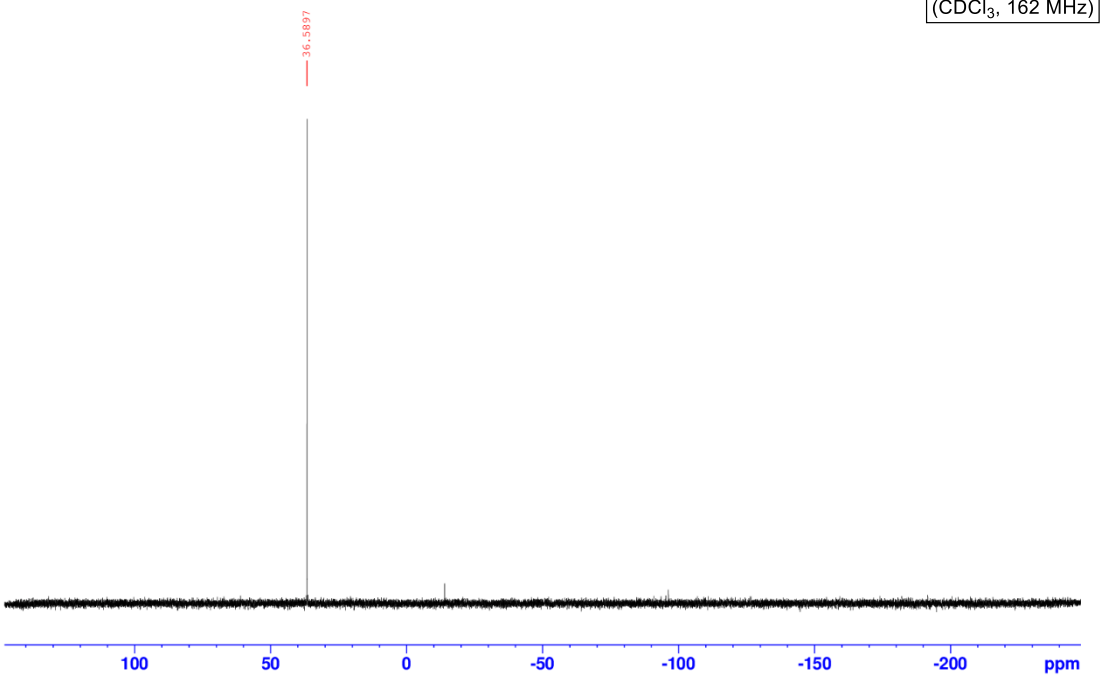
^{1}H NMR
($CDCl_3$, 400 MHz)



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

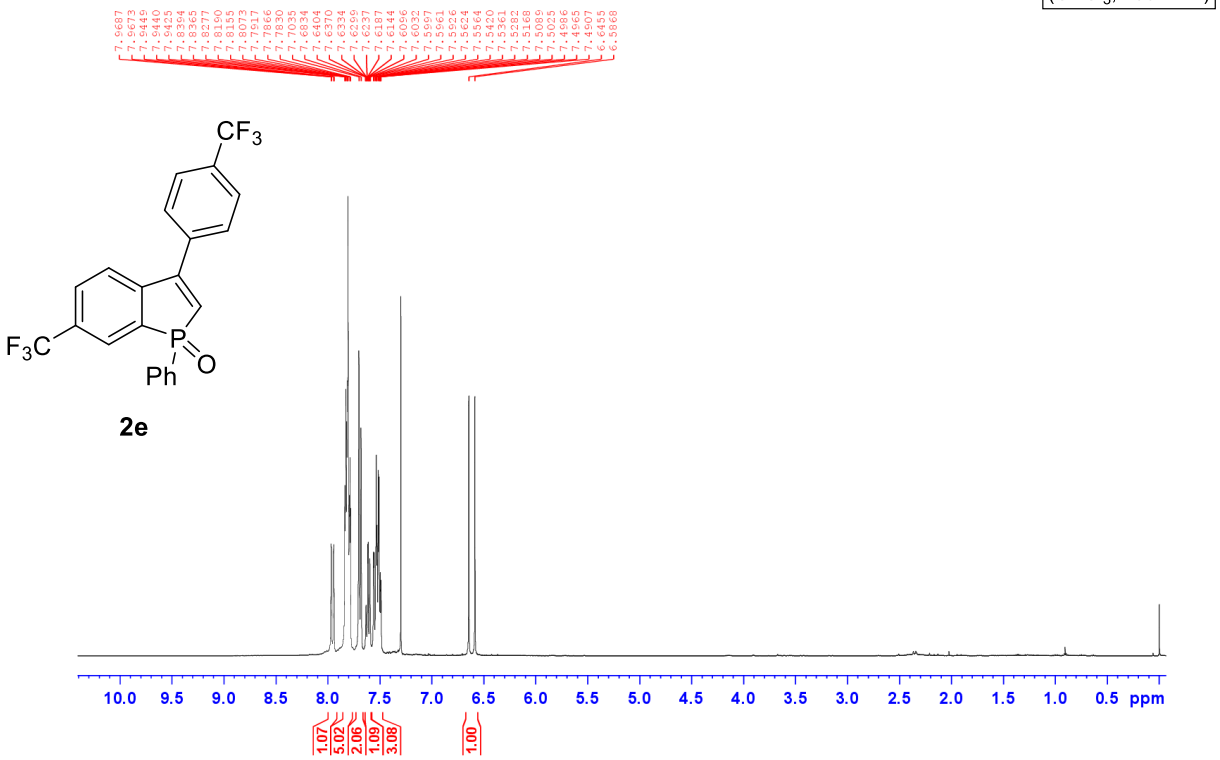


$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)

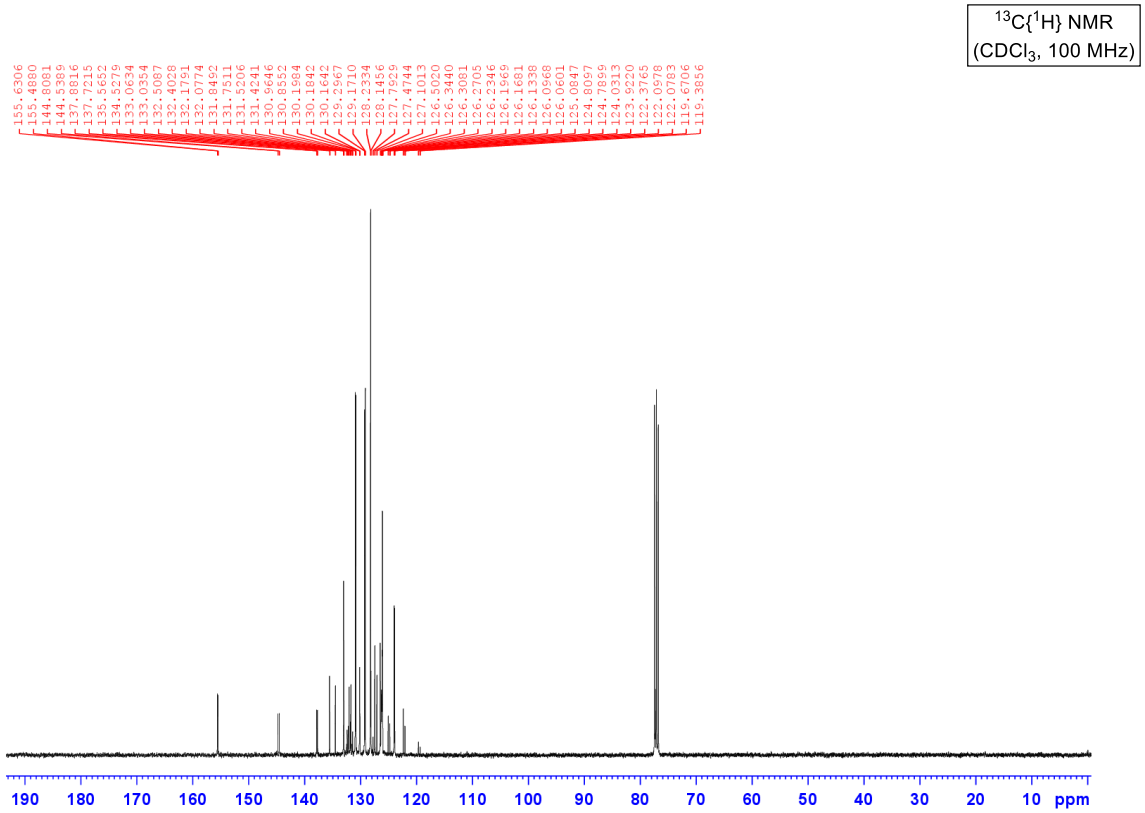


[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2e**]

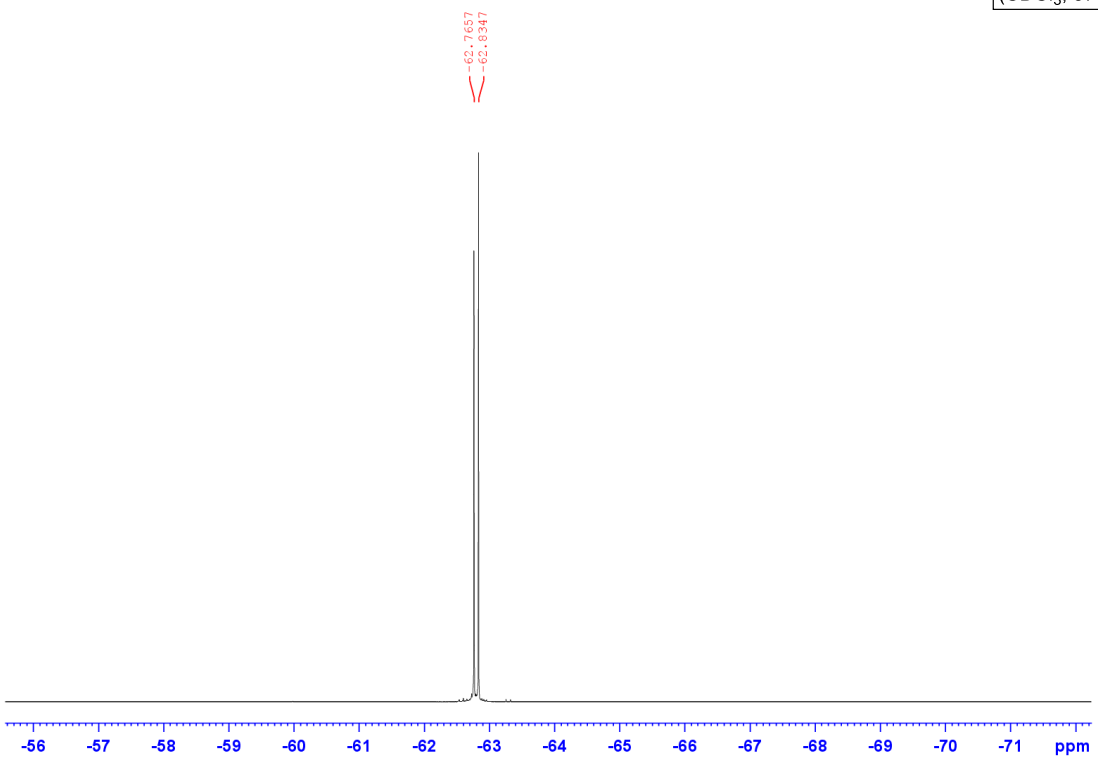
^{1}H NMR
($CDCl_3$, 400 MHz)



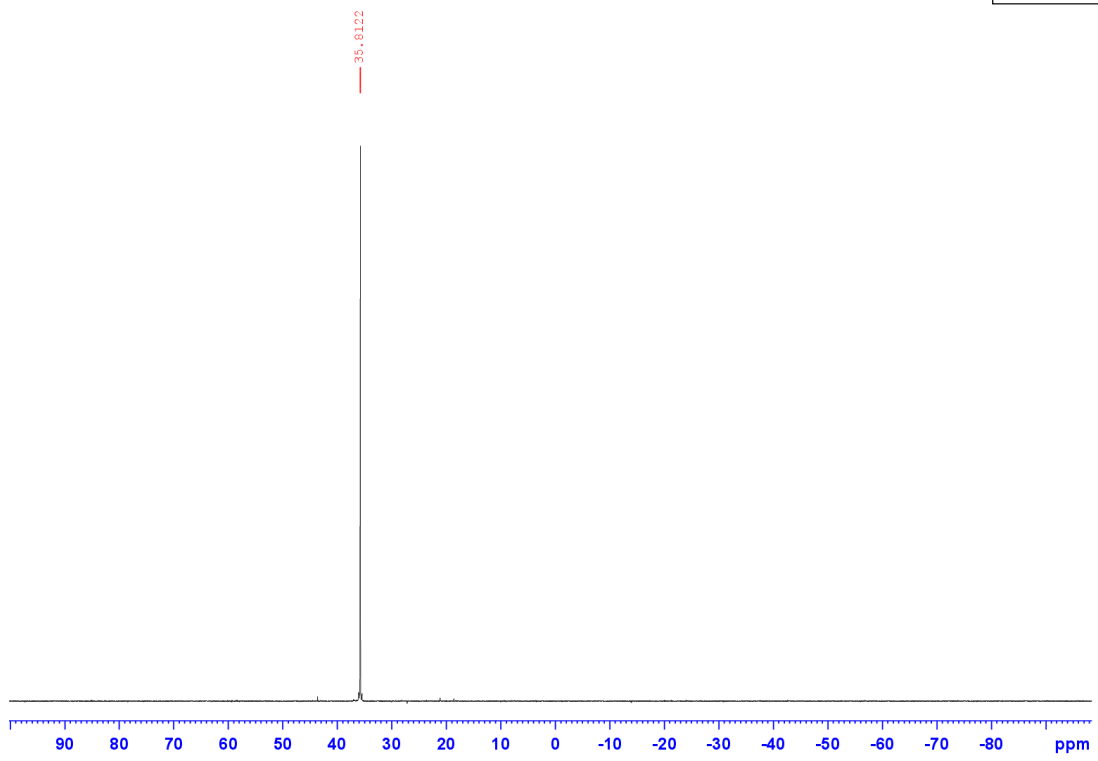
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



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

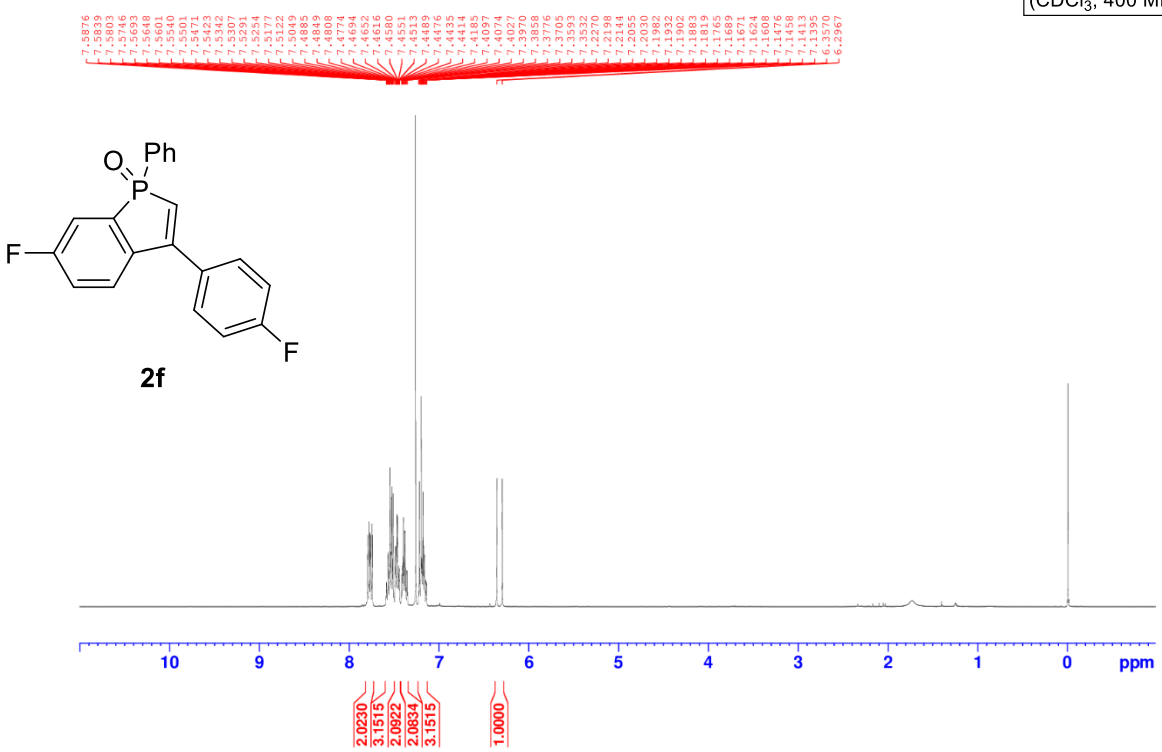


$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)

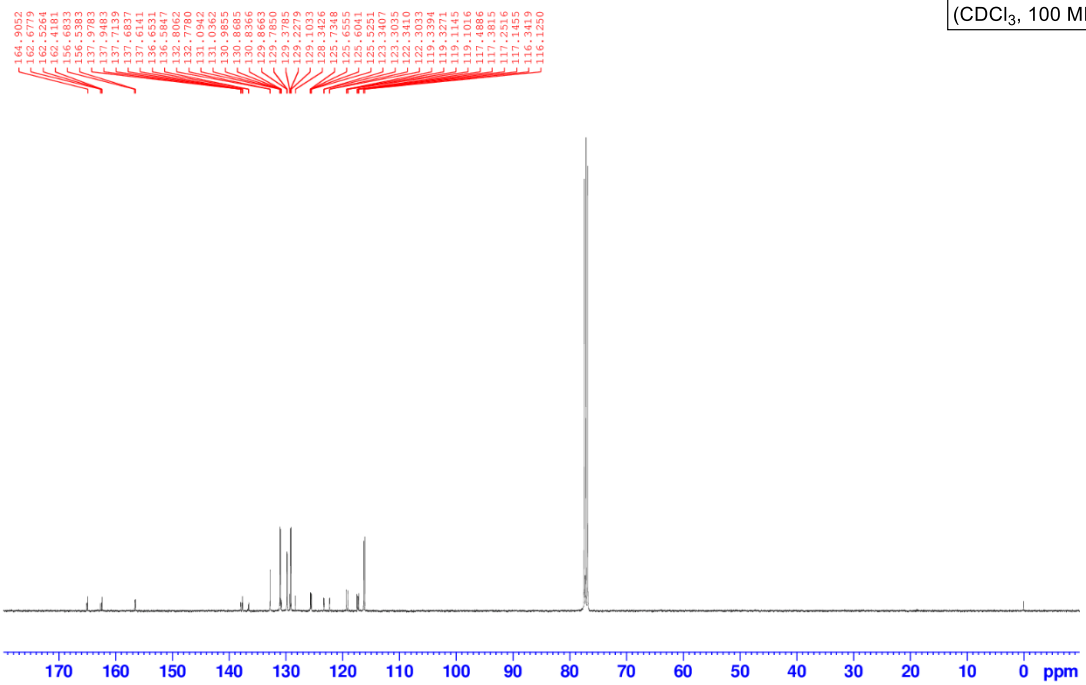


[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2f**]

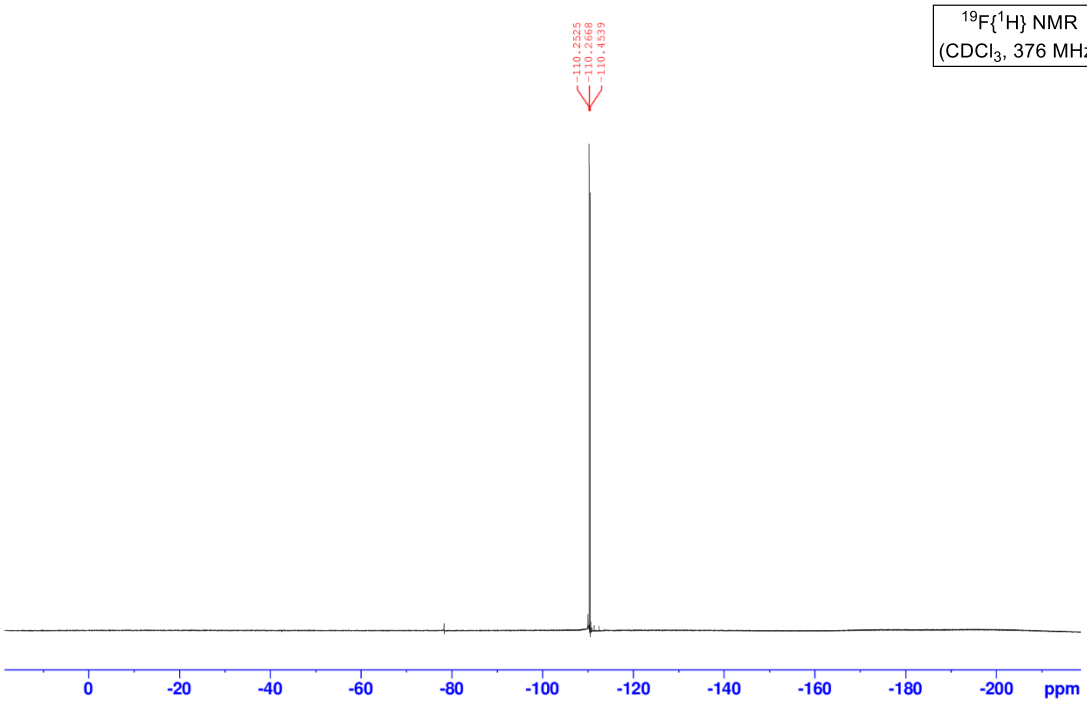
^{1}H NMR
($CDCl_3$, 400 MHz)



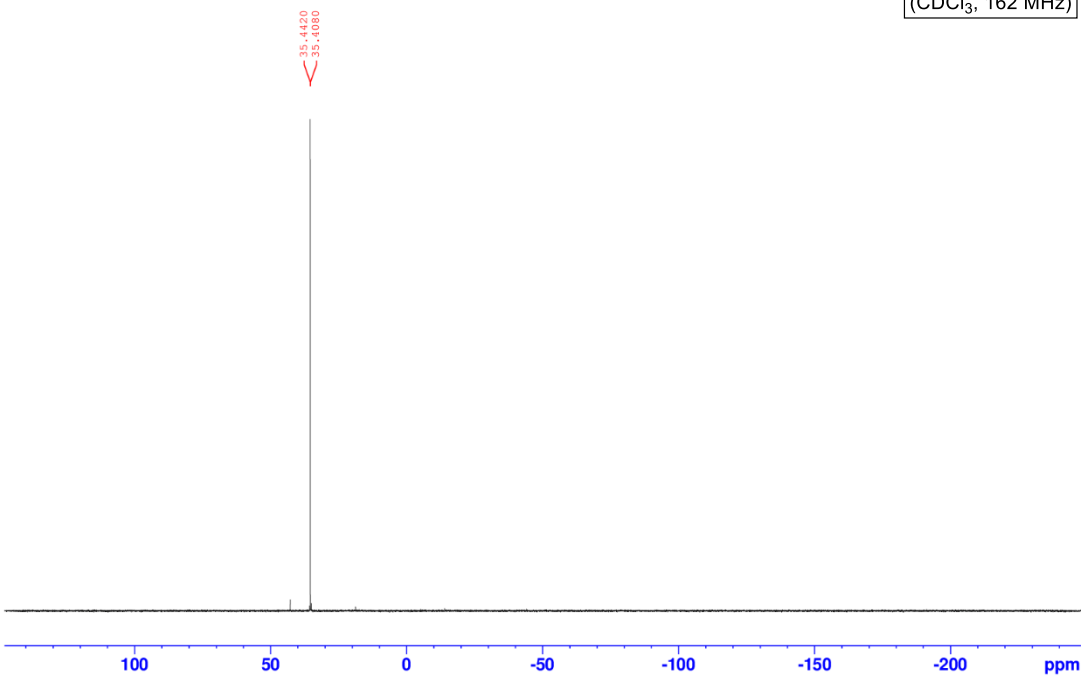
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



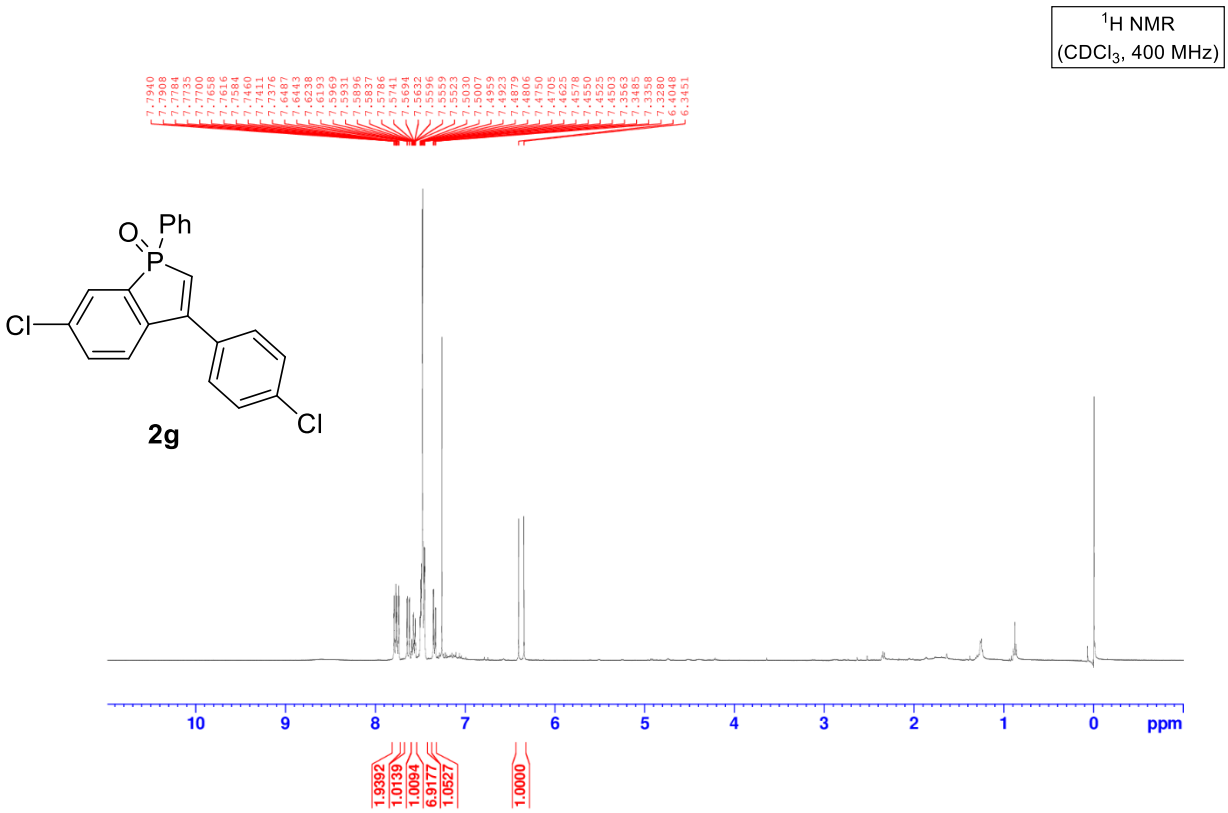
$^{19}F\{^{1}H\}$ NMR
($CDCl_3$, 376 MHz)

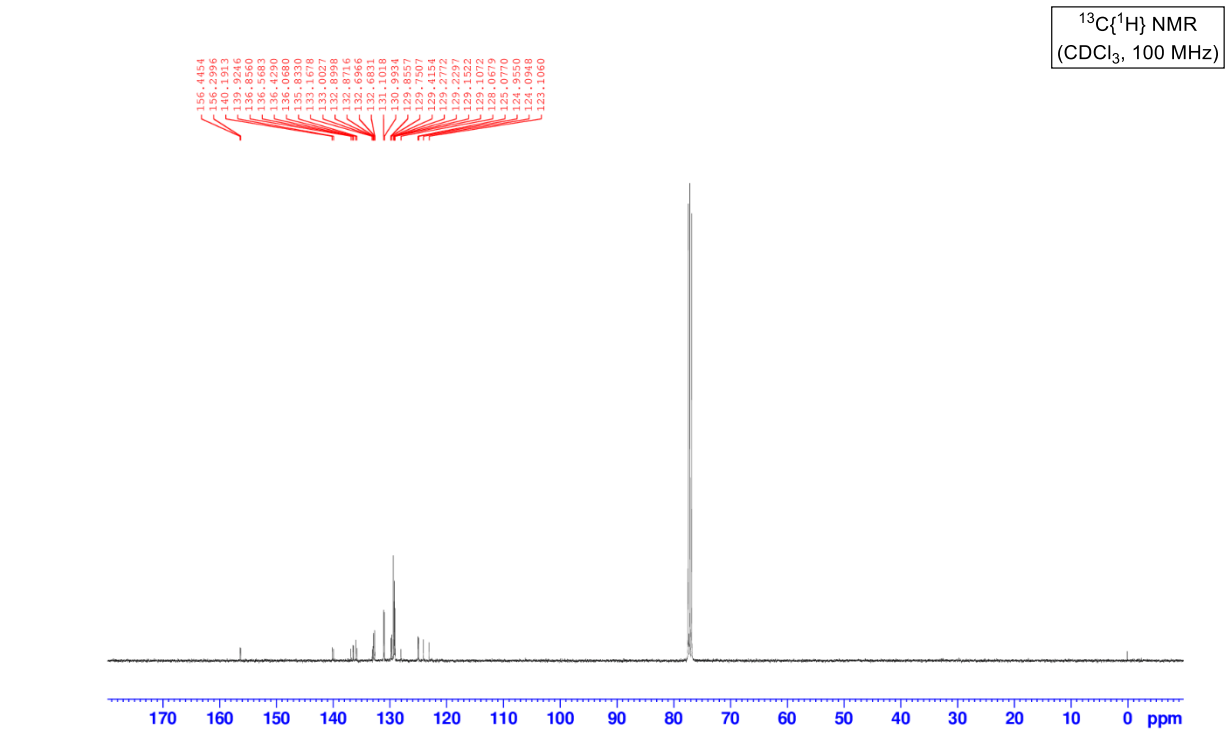


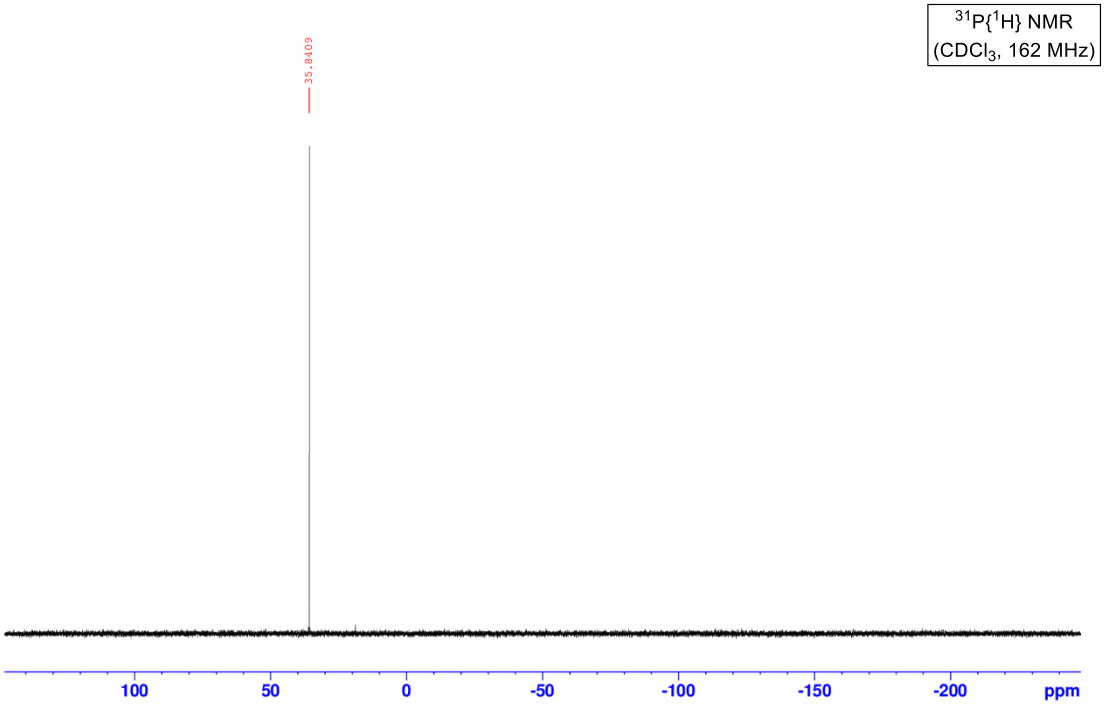
$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)



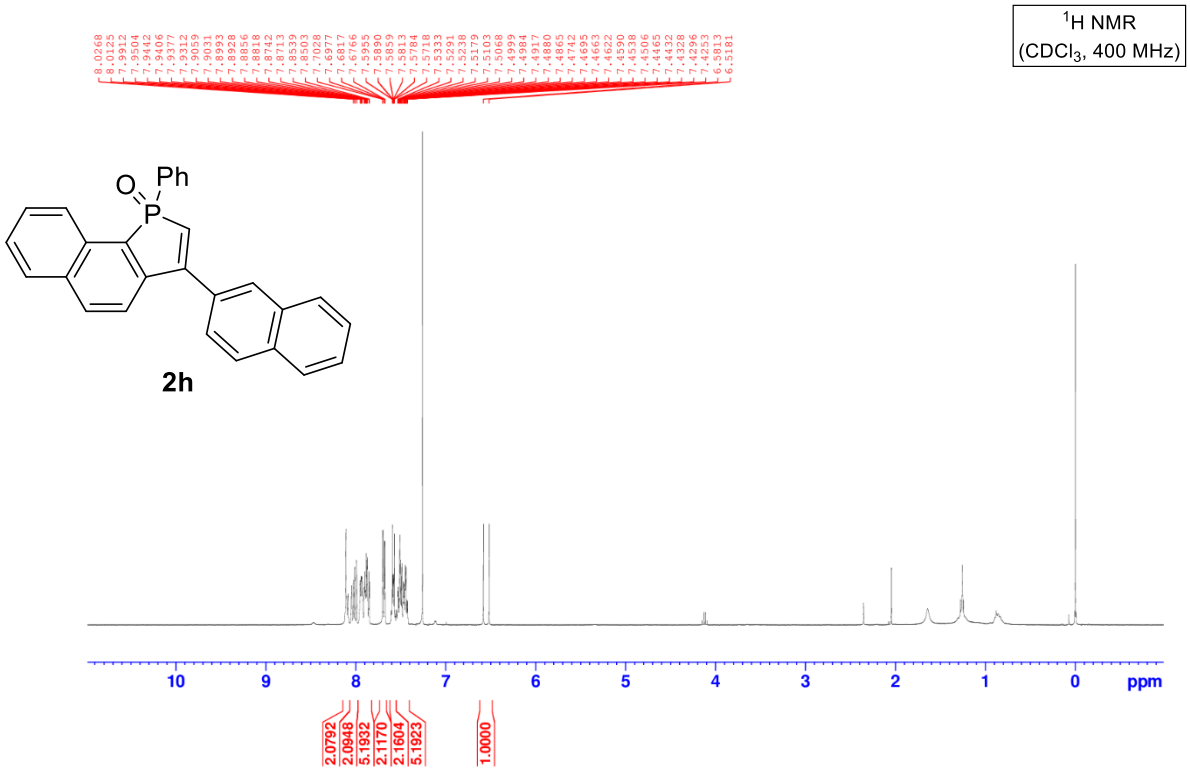
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2g**]

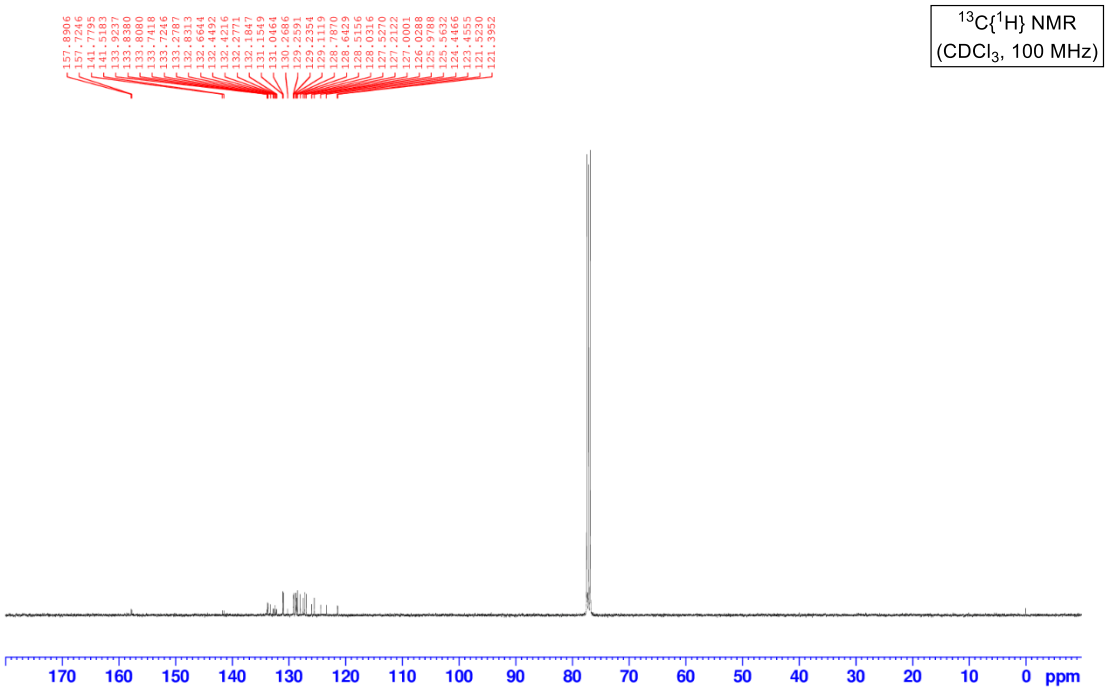


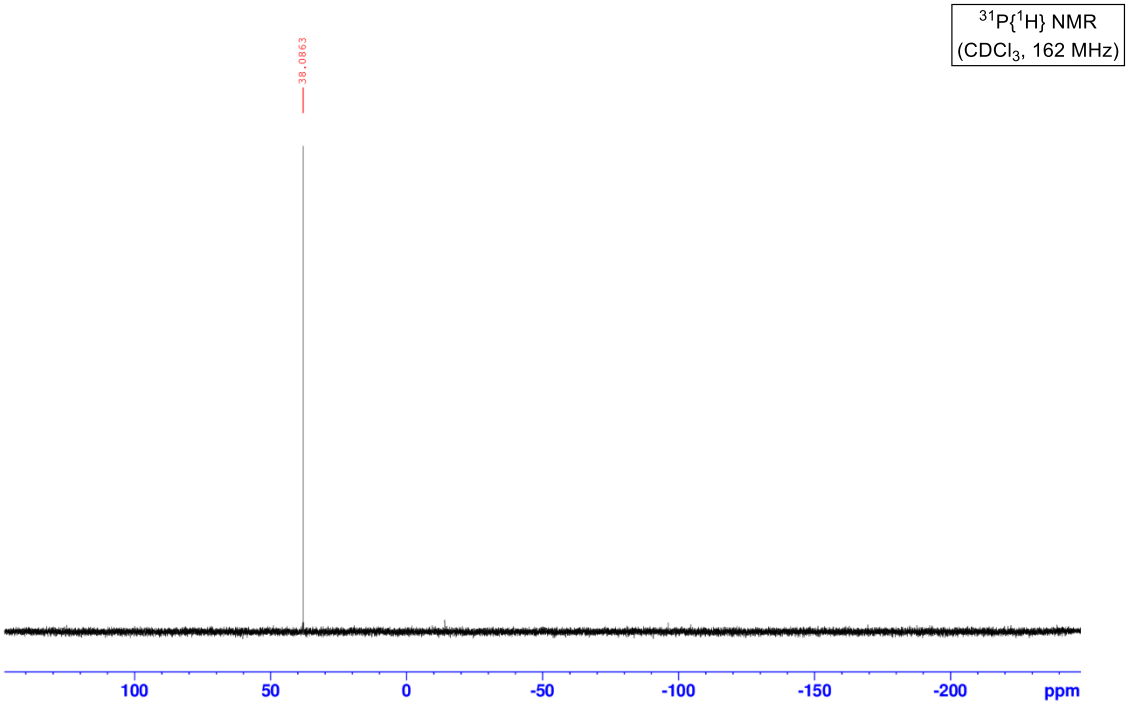



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
35.8409
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2h**]

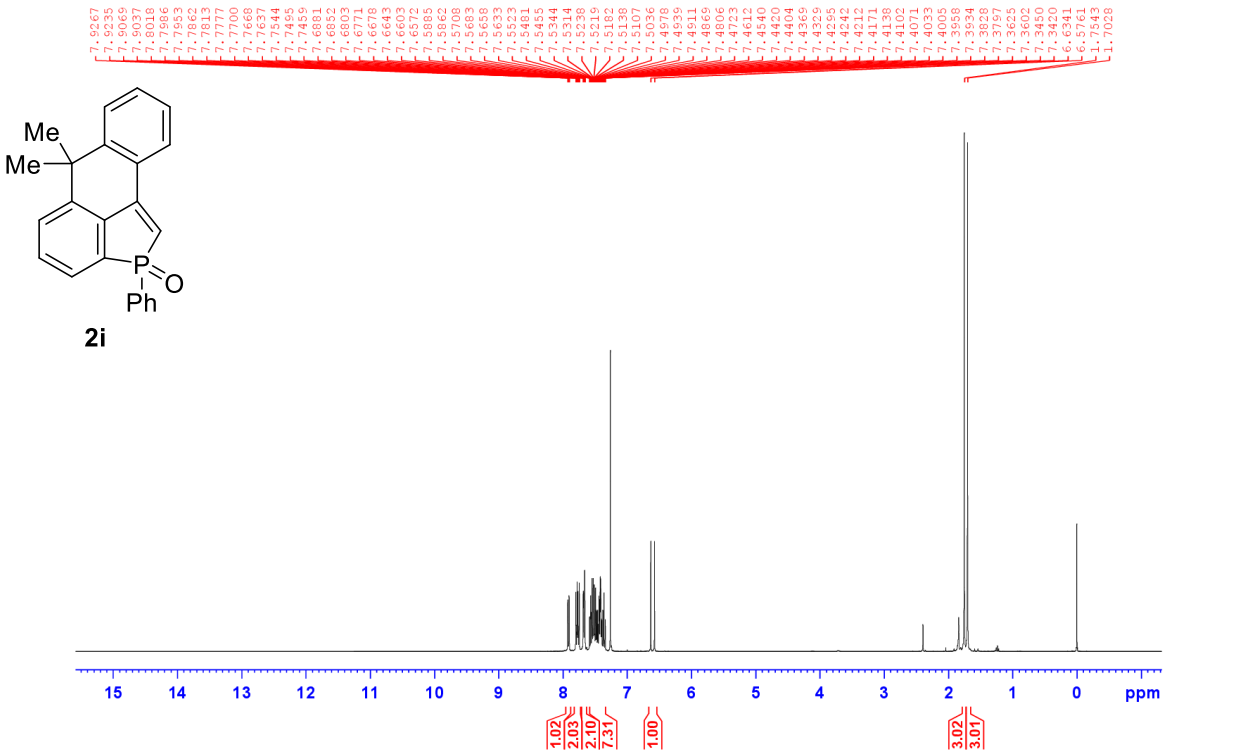





$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
38.0863
100
50
0
-50
-100
-150
-200
ppm

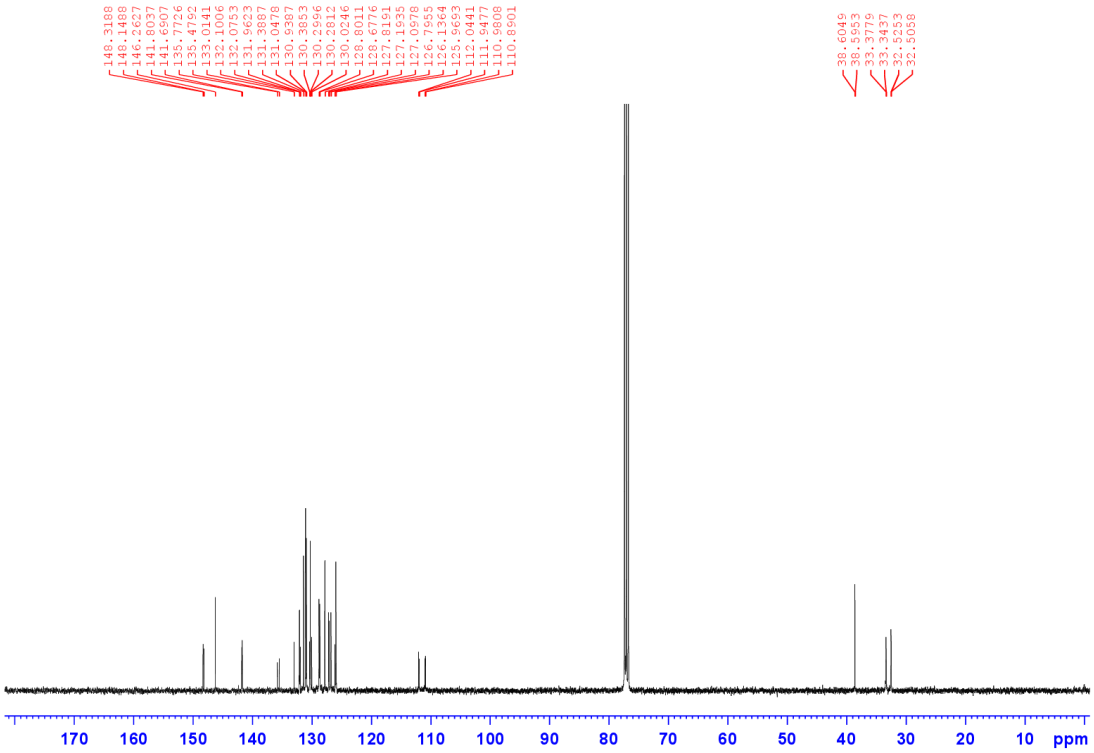
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2i**]

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

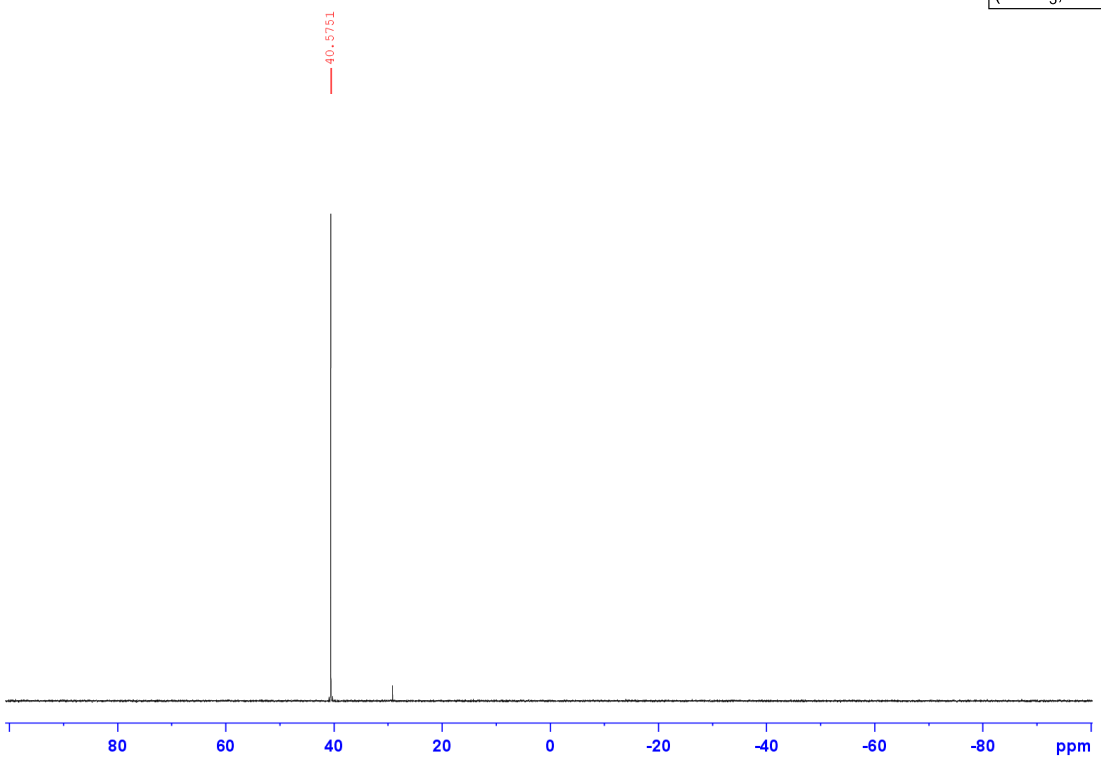


2i

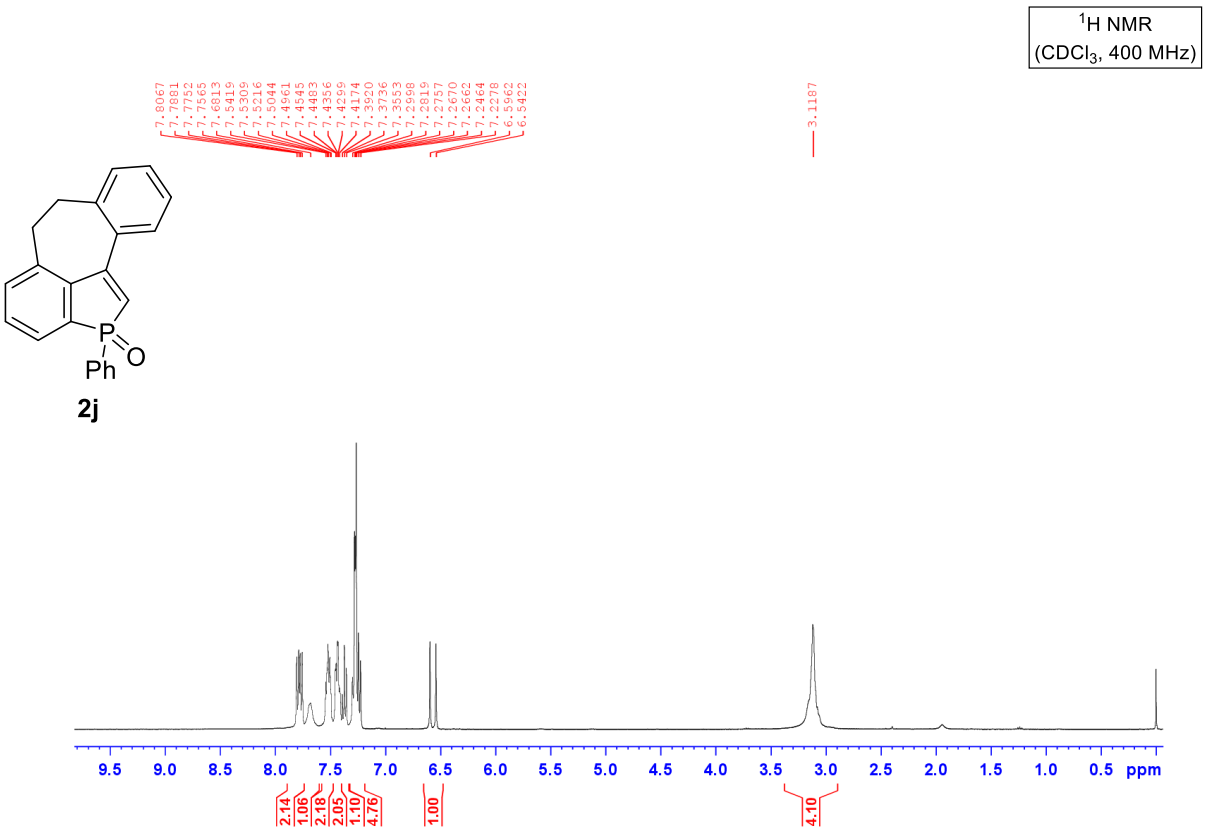
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)

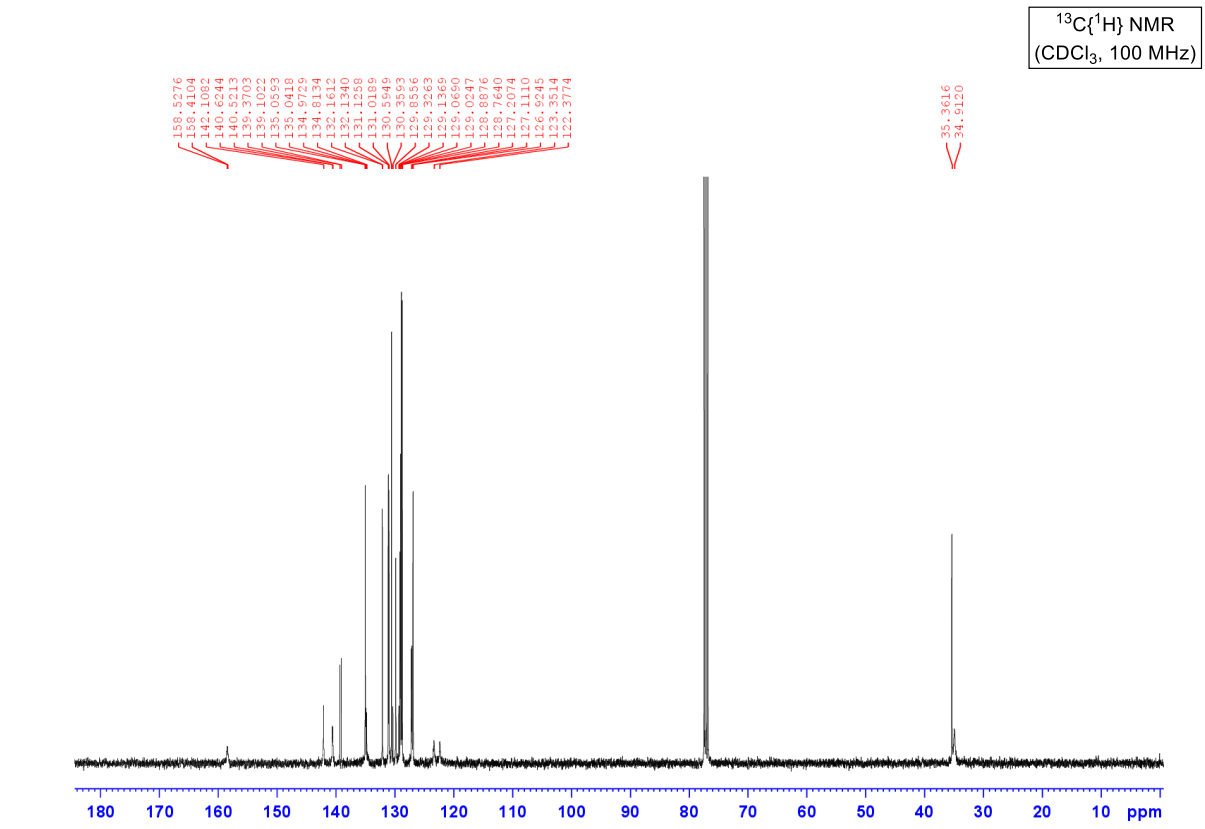


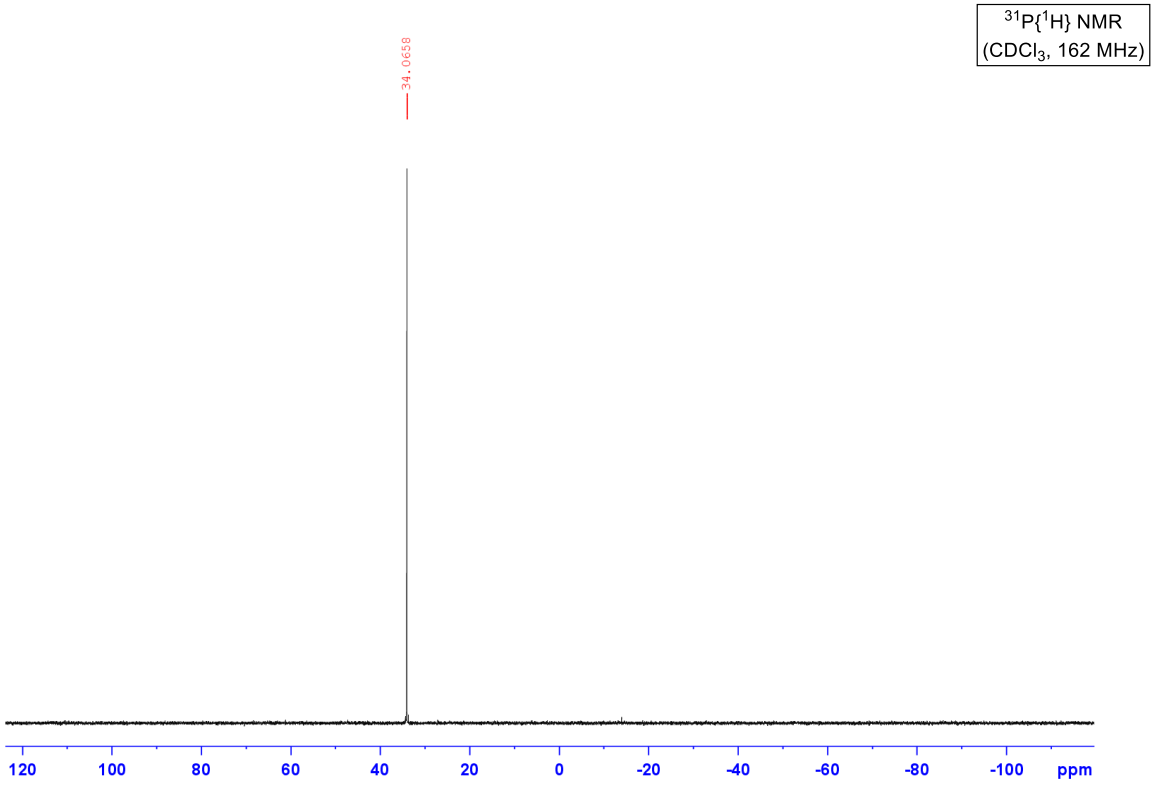
$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)



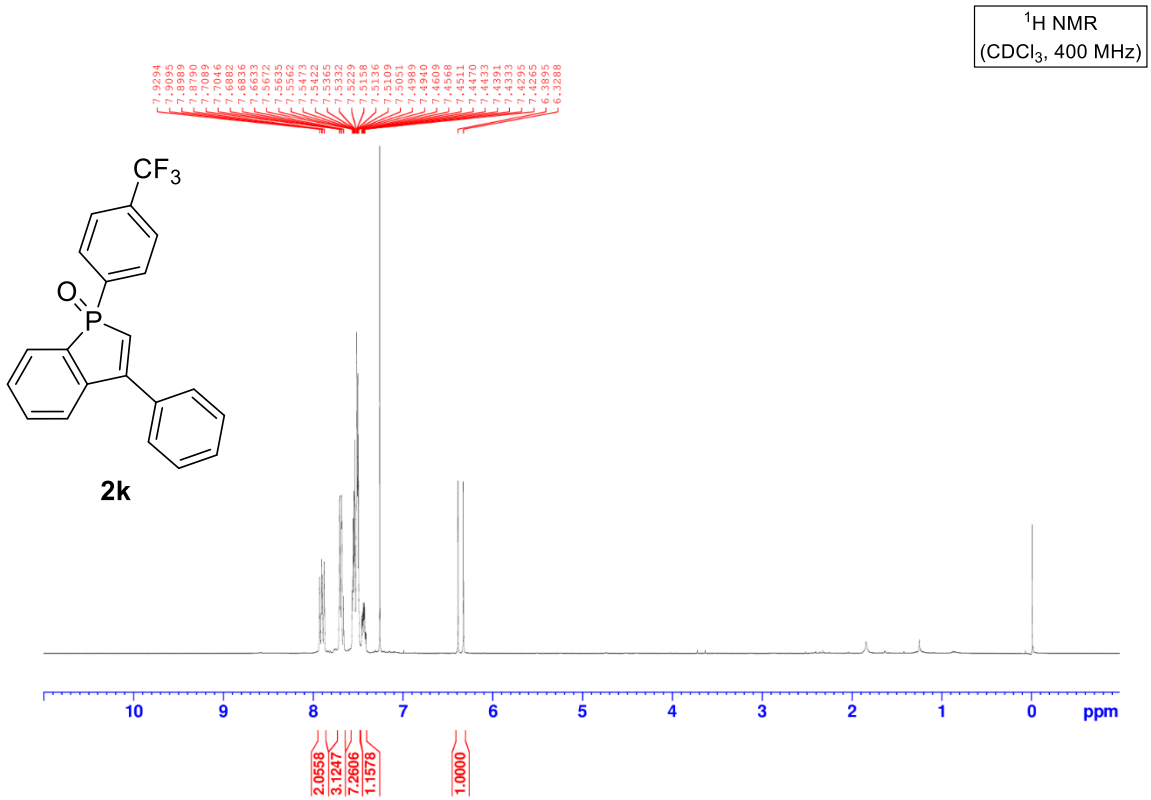
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2j**]

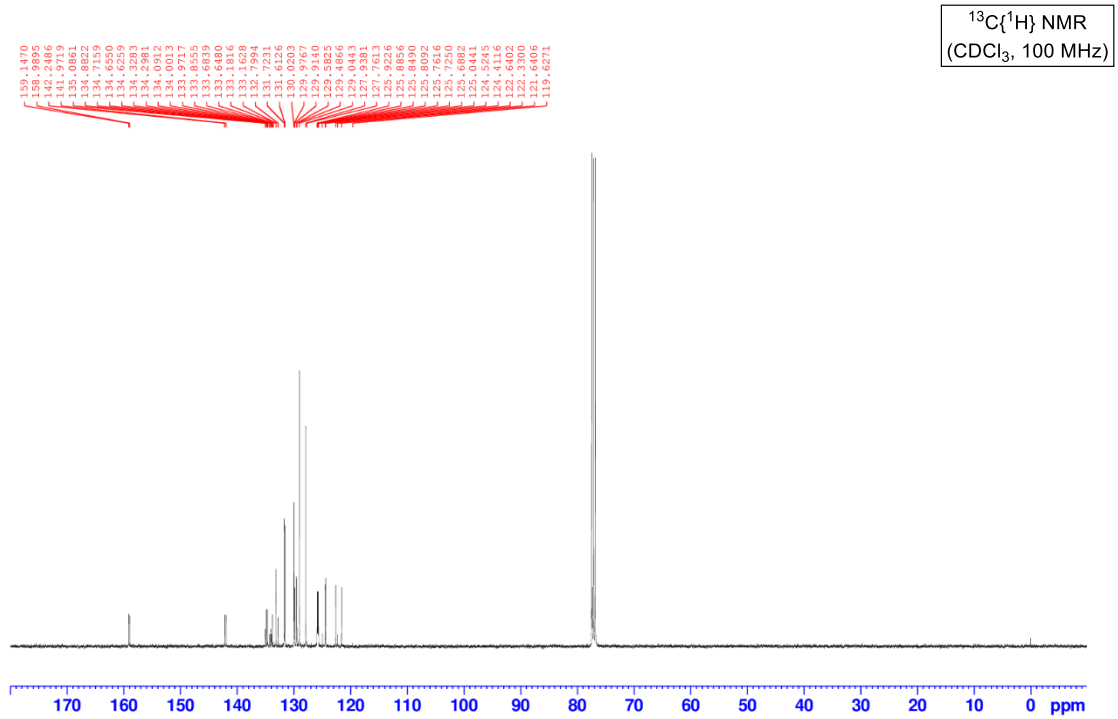




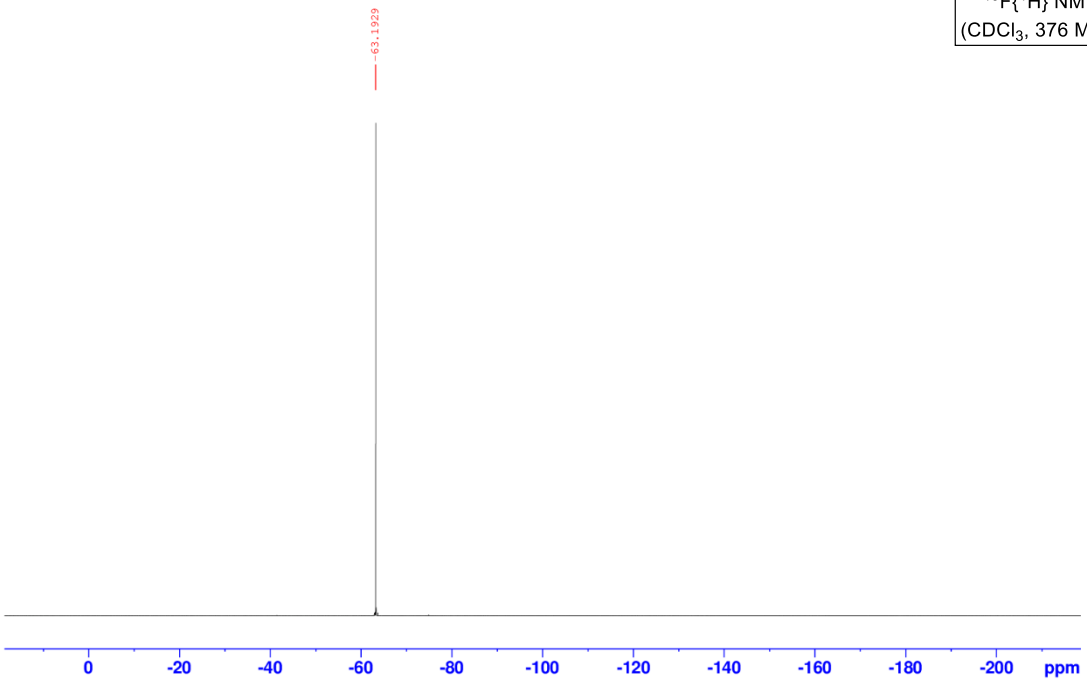

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
34.0658
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2k**]

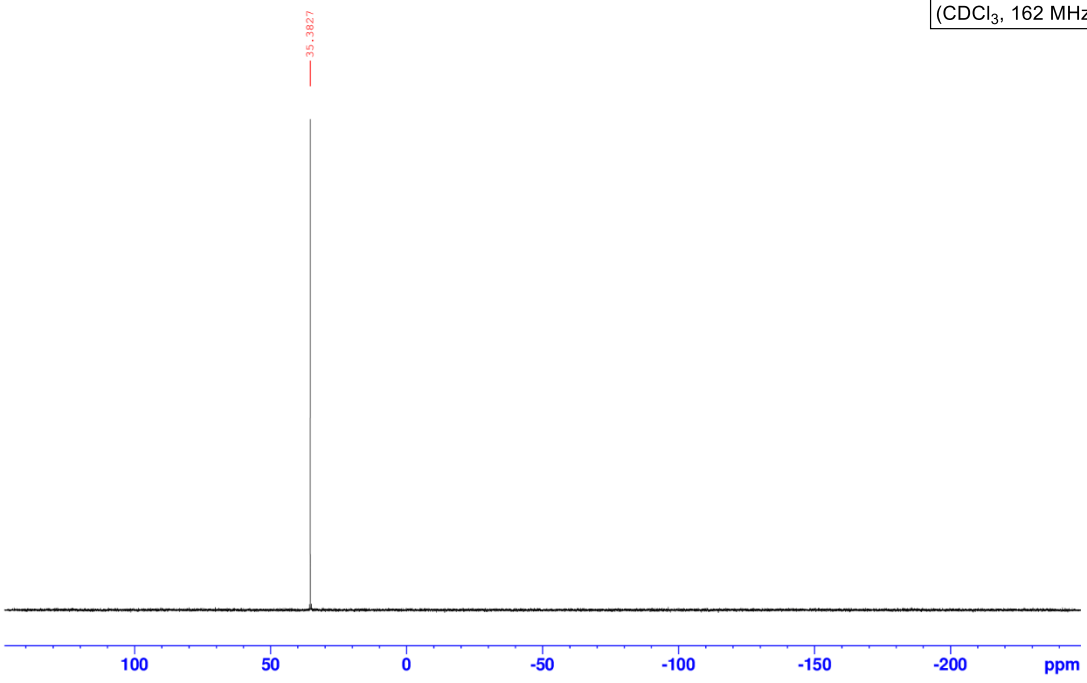




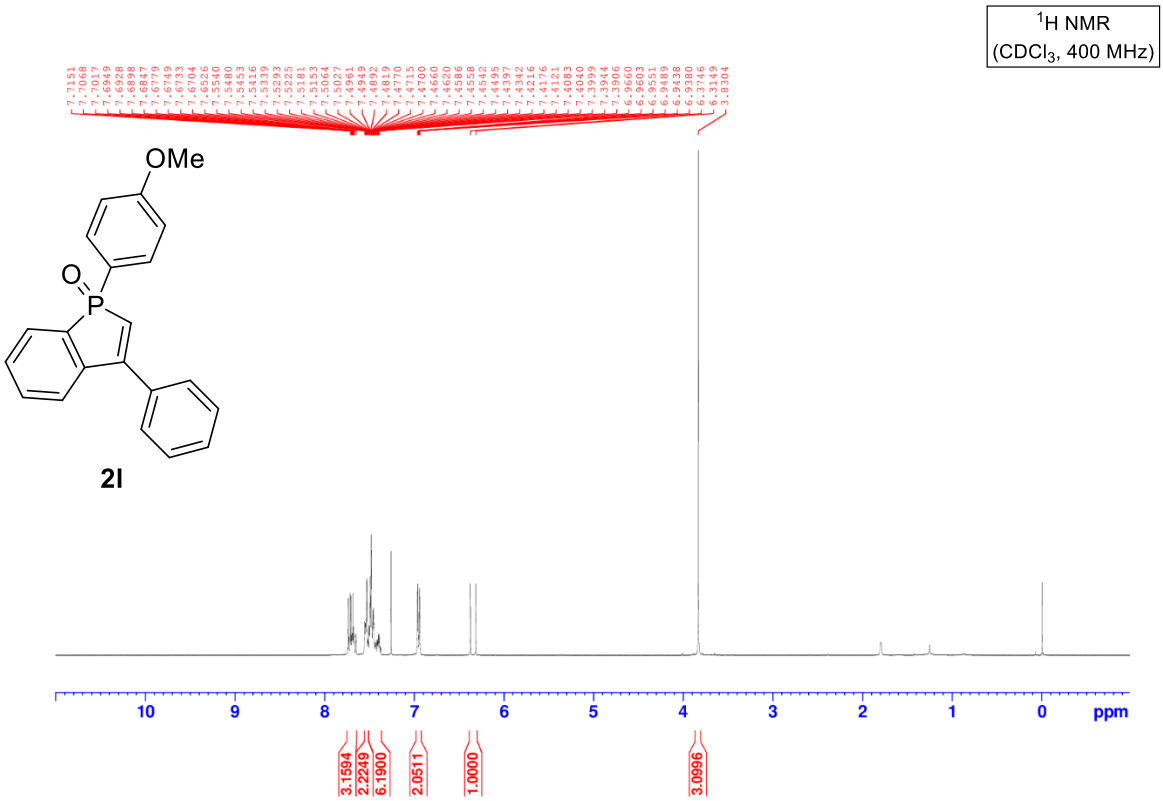
$^{19}F\{^{1}H\}$ NMR
($CDCl_3$, 376 MHz)

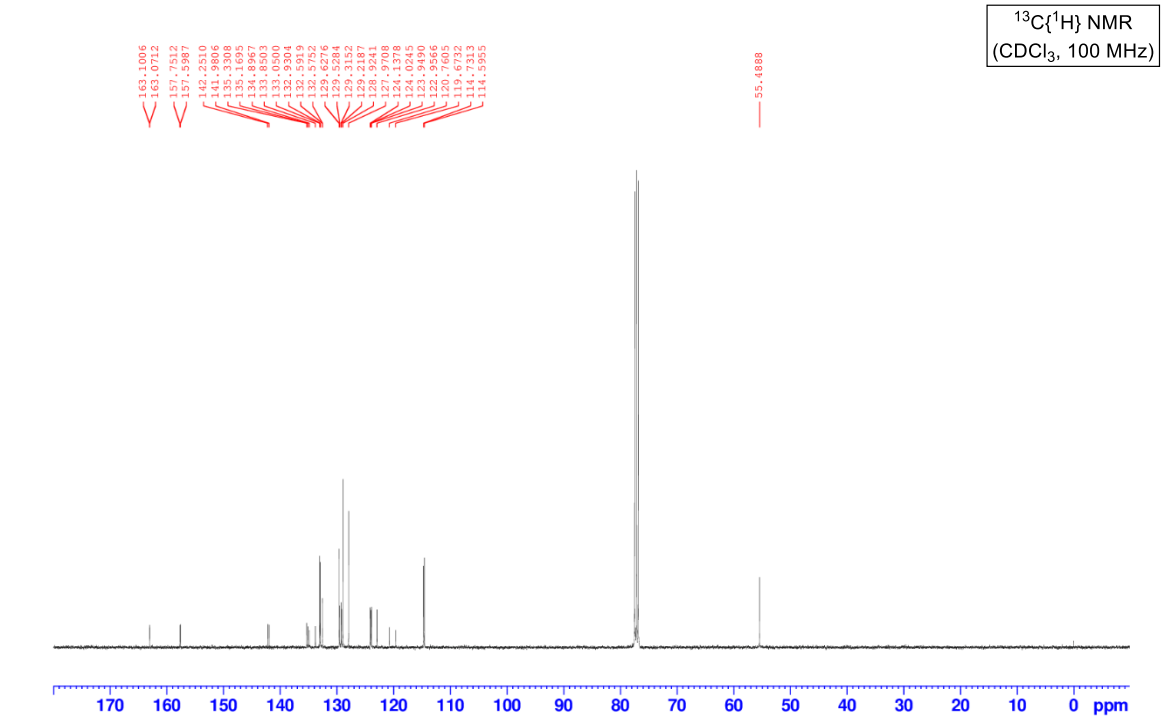


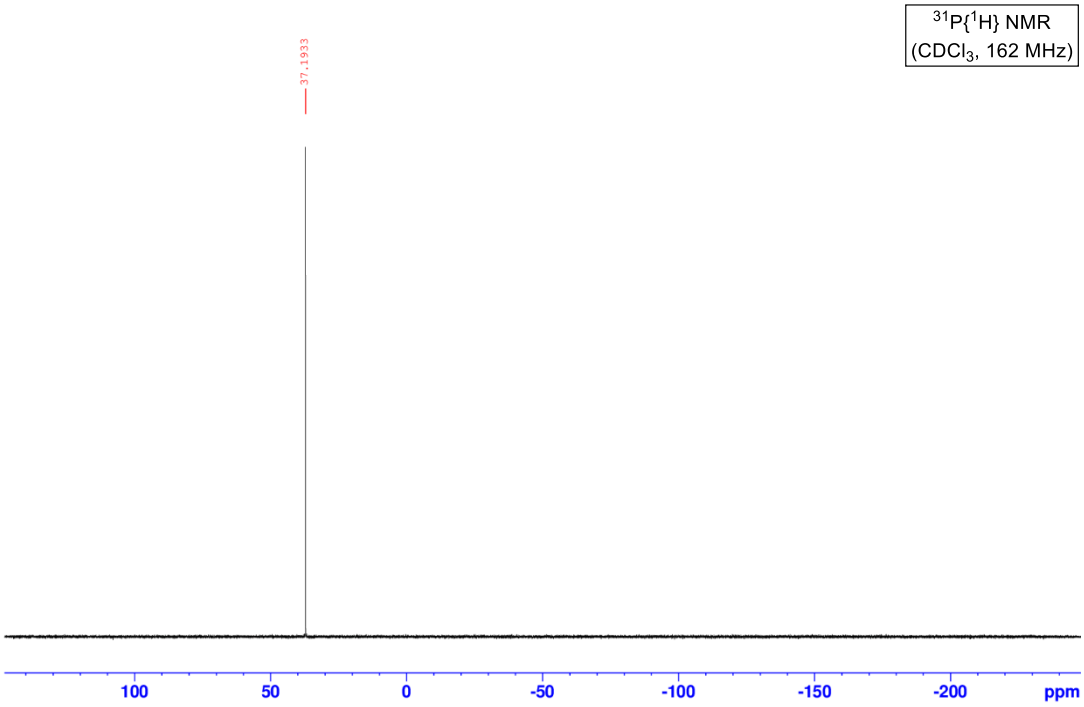
$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)



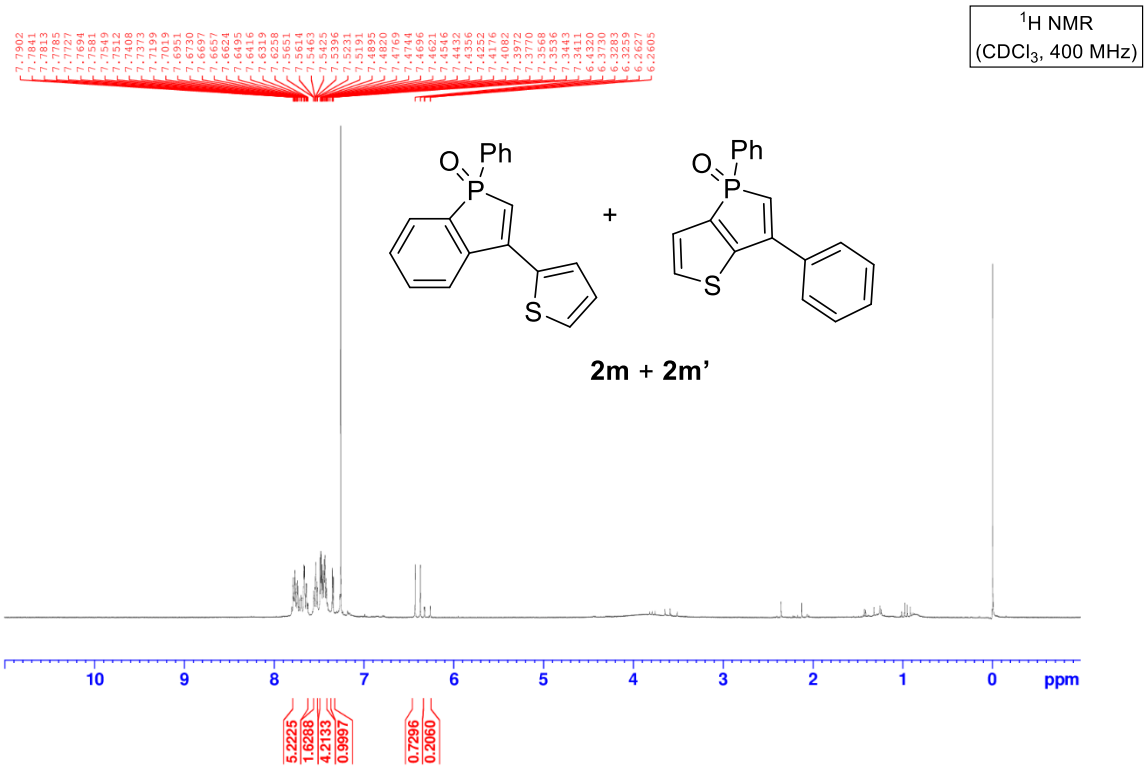
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2l**]

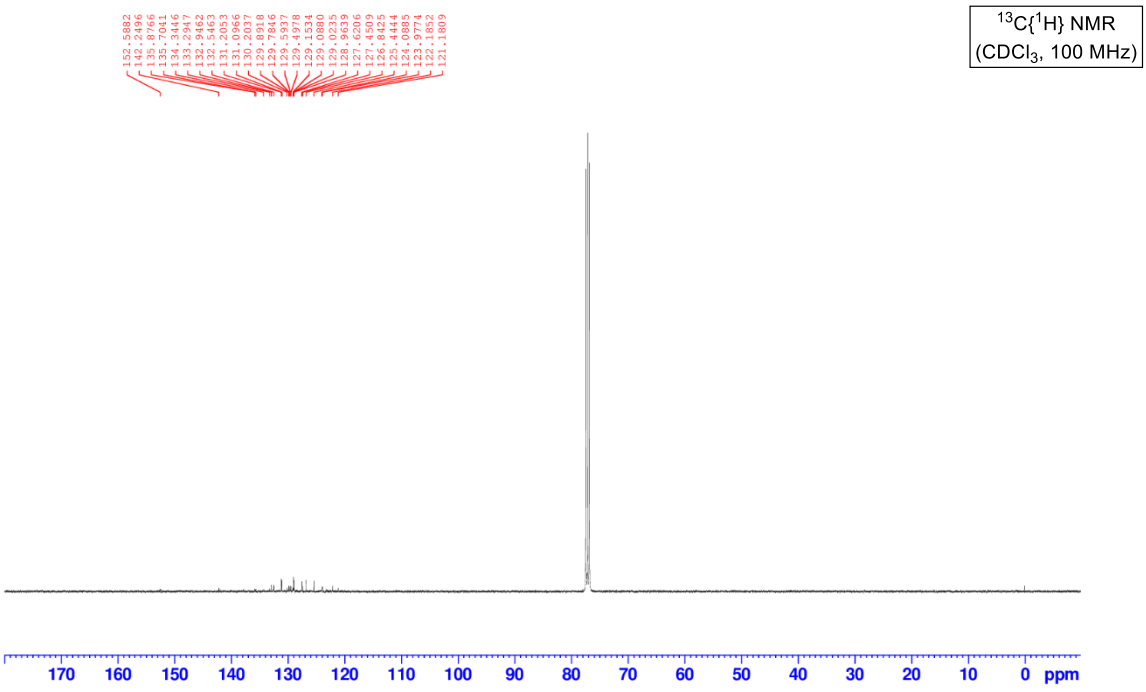




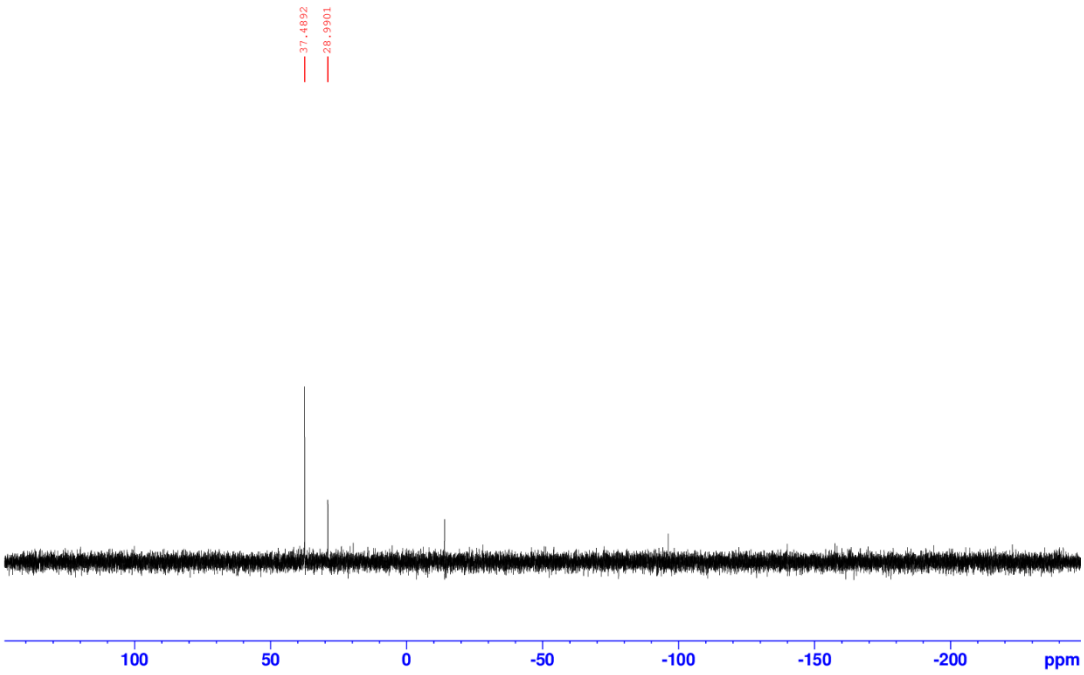

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
37.1933
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2m** + **2m'**]



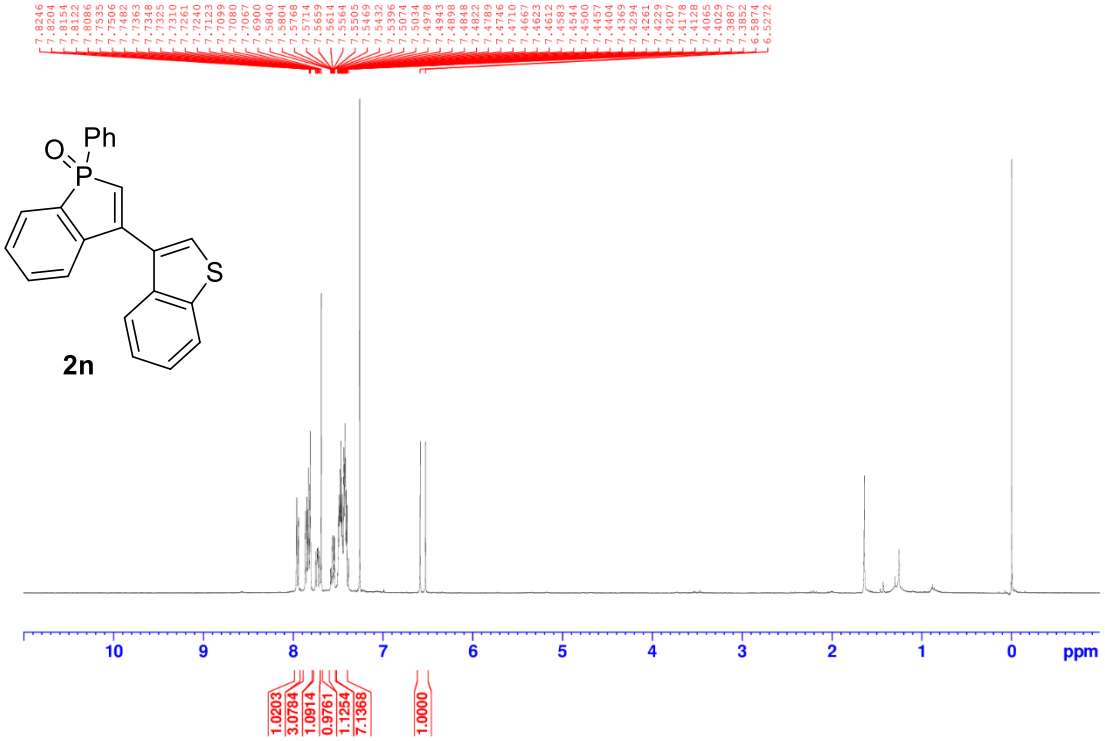


$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)

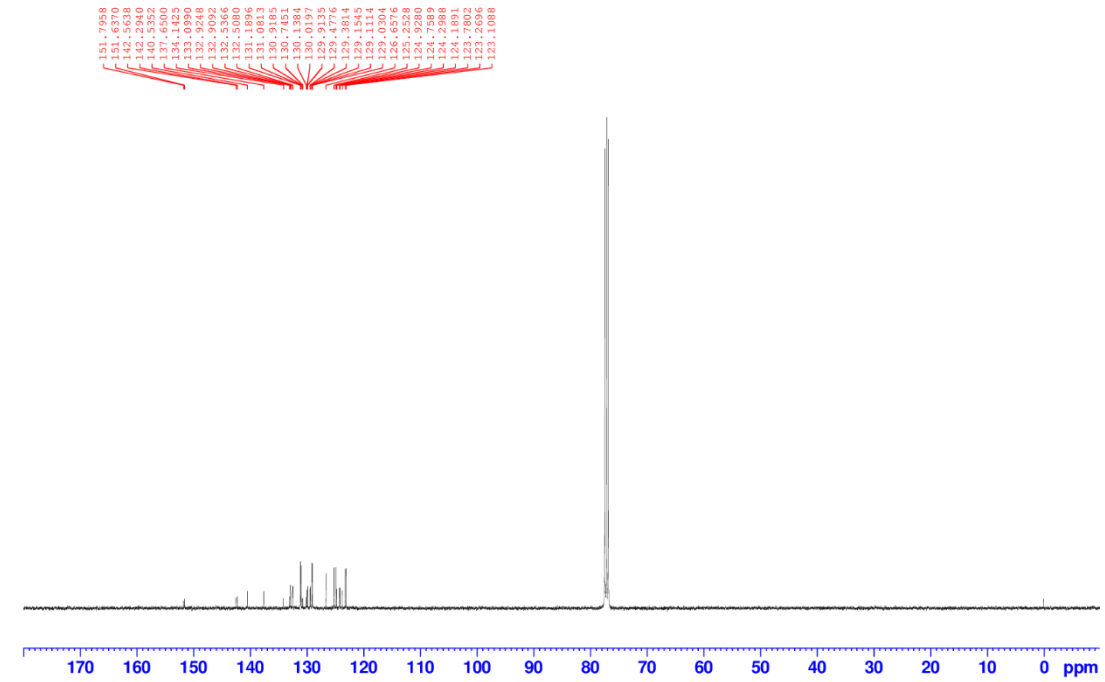


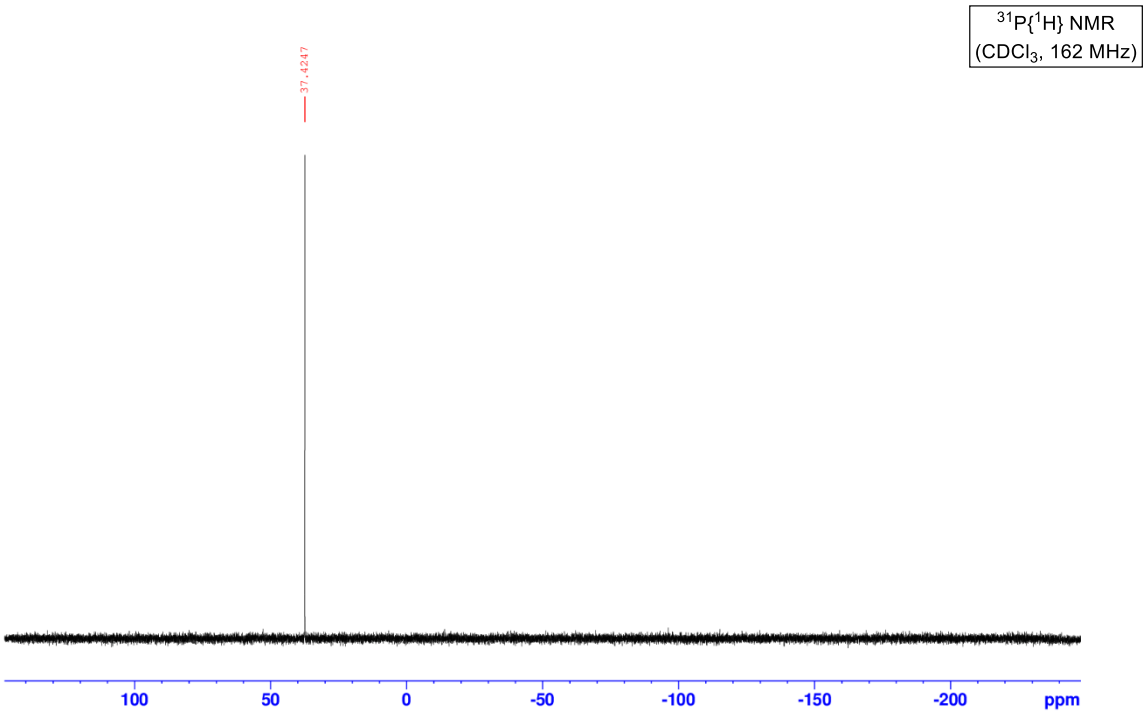
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2n**]

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



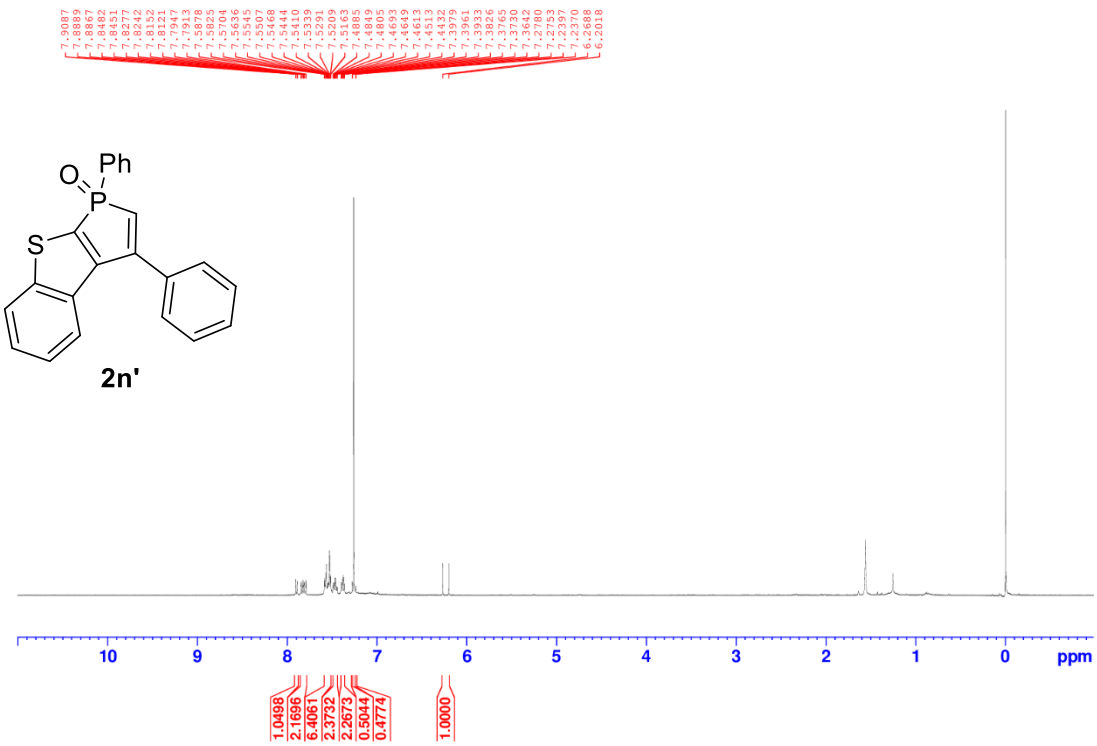
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



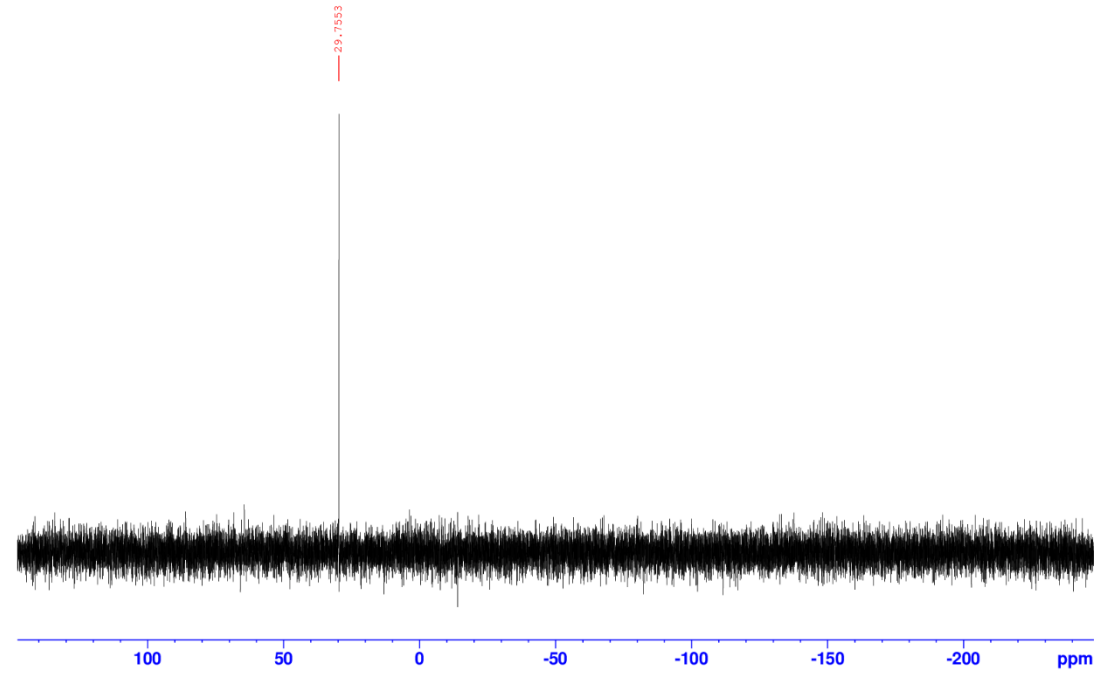

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
37.4247
100
50
0
-50
-100
-150
-200
ppm

[^{1}H and ^{31}P{^{1}H} NMR Spectra of **2n'**]

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

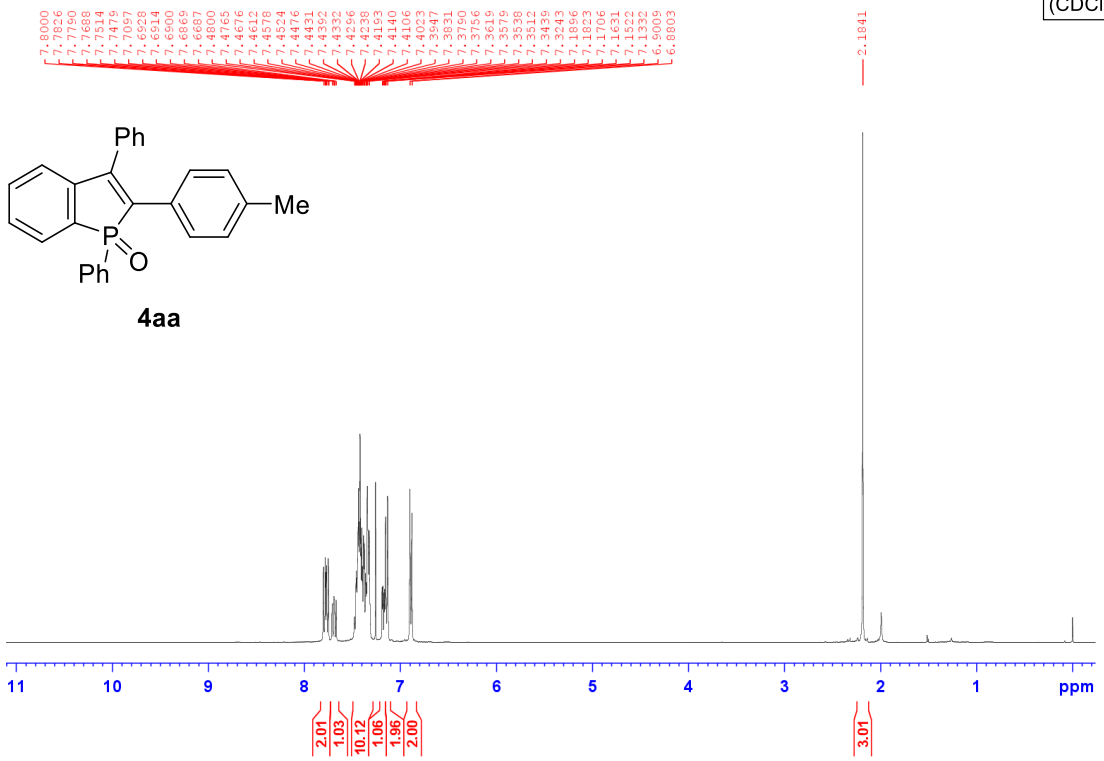


^{31}P{^{1}H} NMR
($CDCl_3$, 162 MHz)

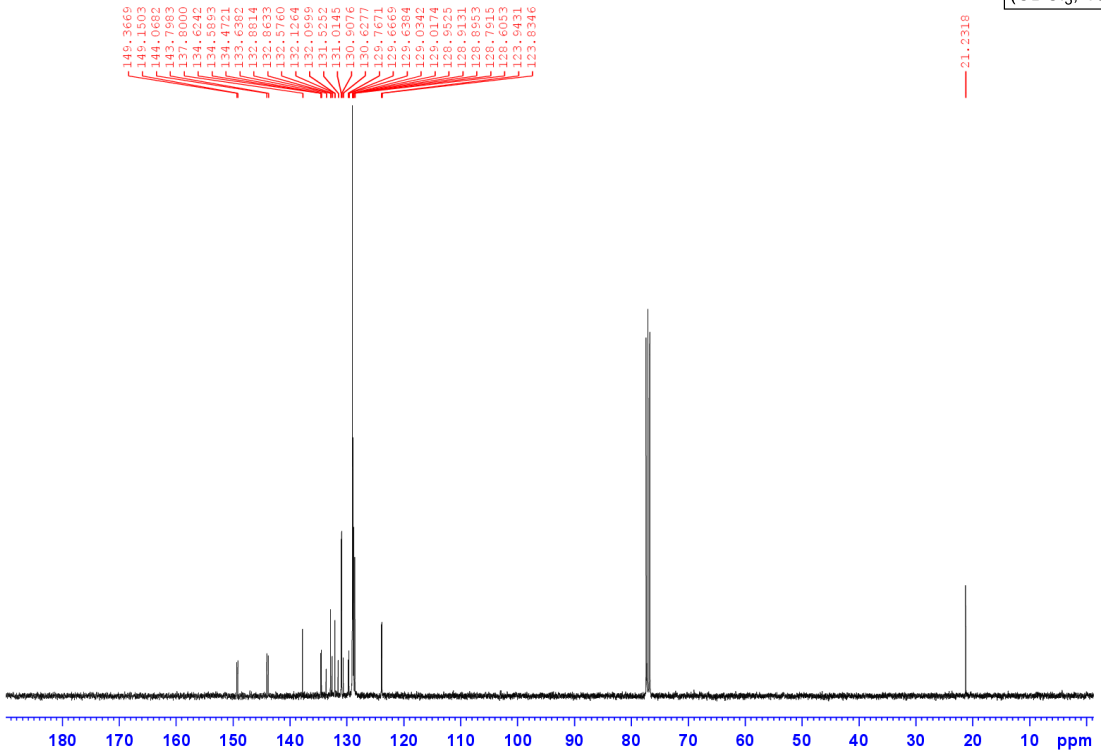


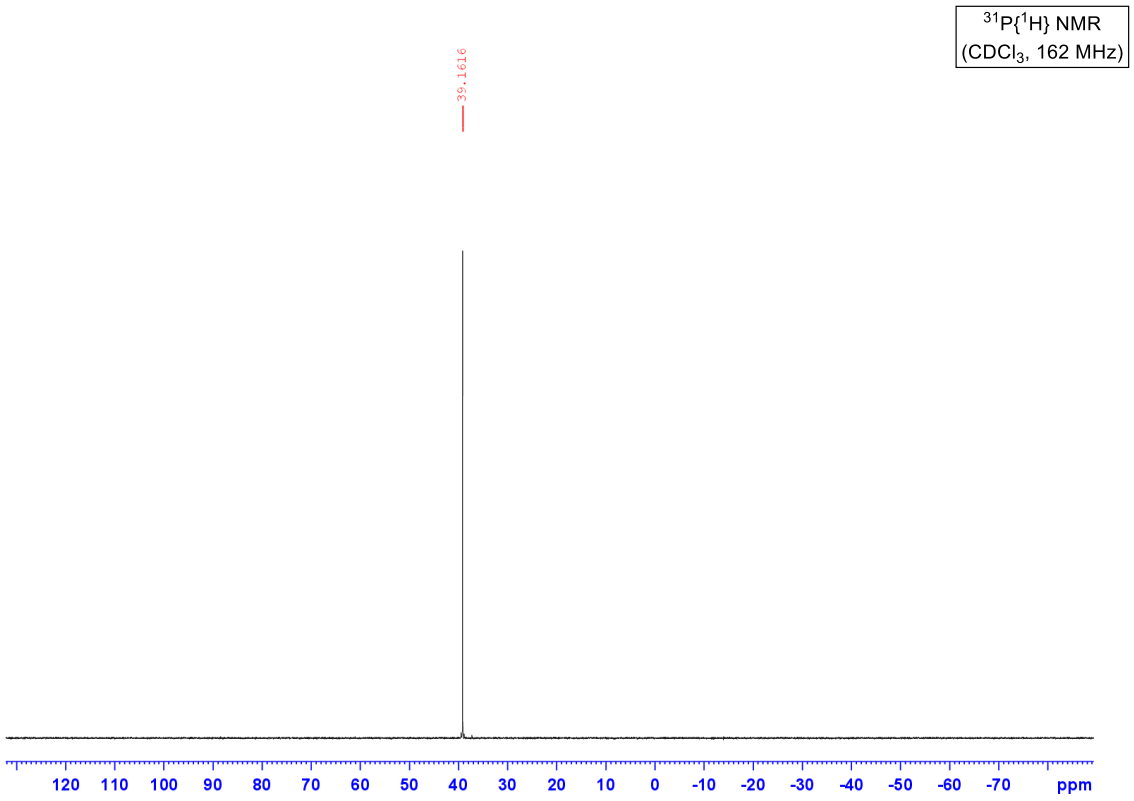
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4aa**]

^{1}H NMR
(CDCl$_3$, 400 MHz)



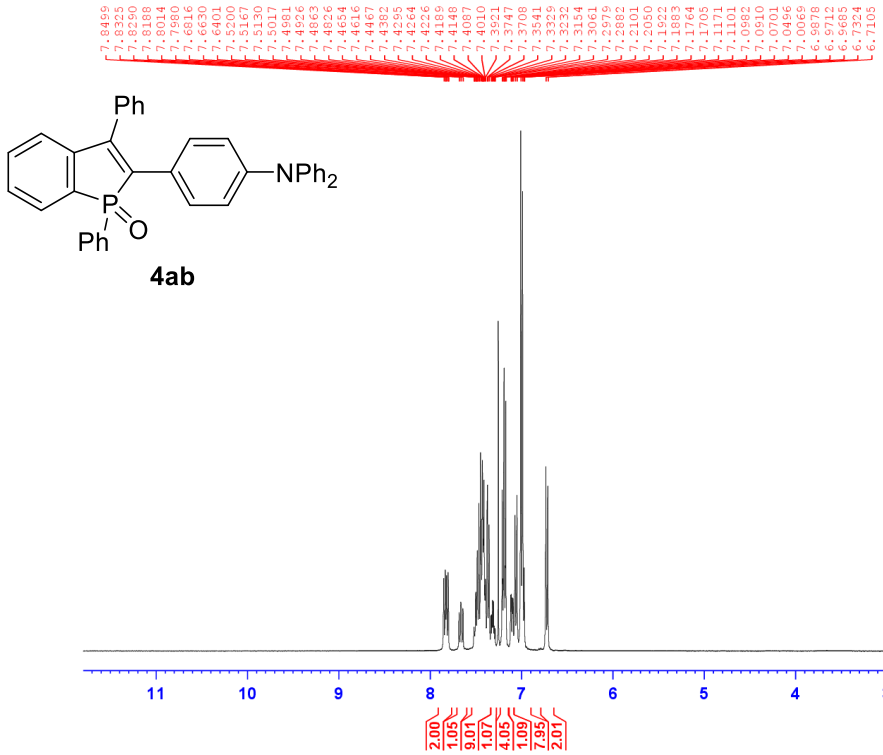
^{13}C{^{1}H} NMR
(CDCl$_3$, 100 MHz)



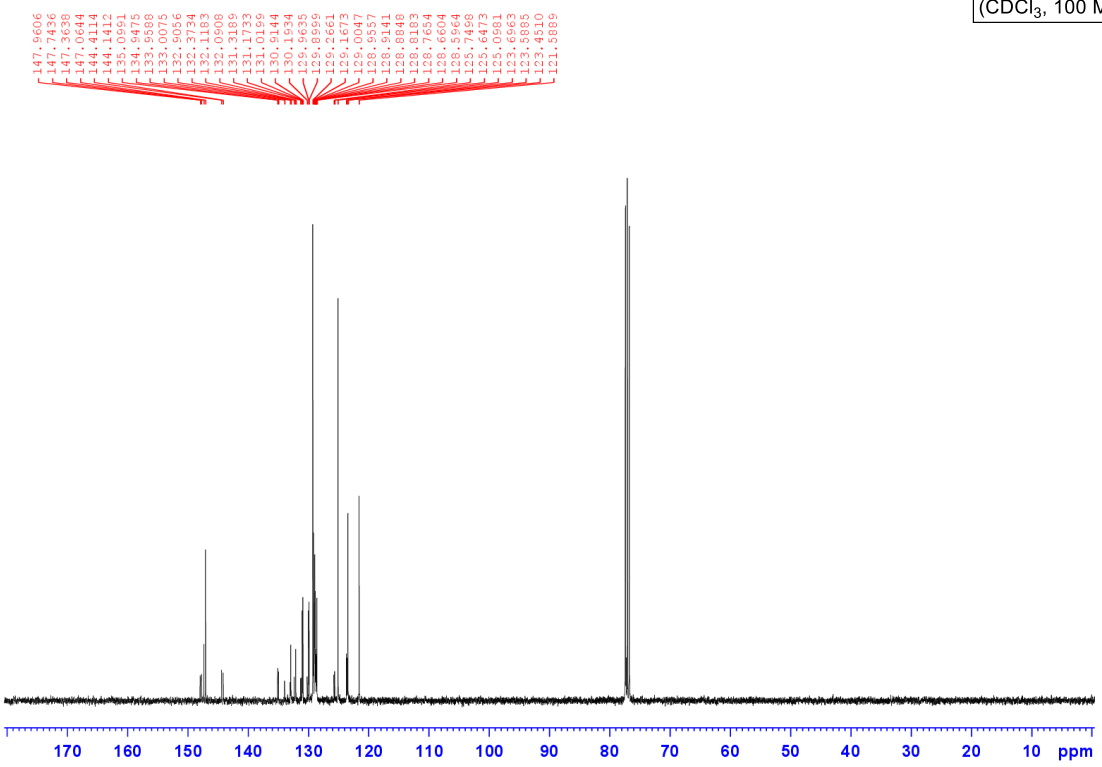

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.1616
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm

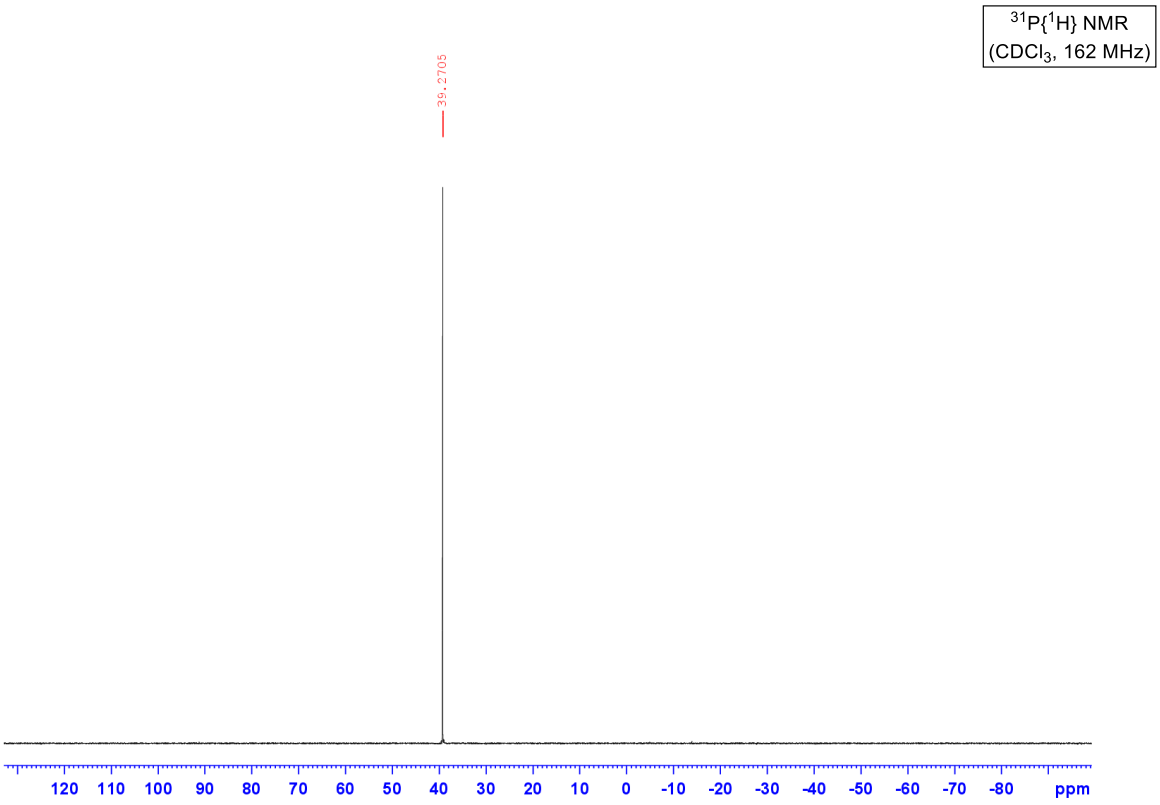
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ab**]

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

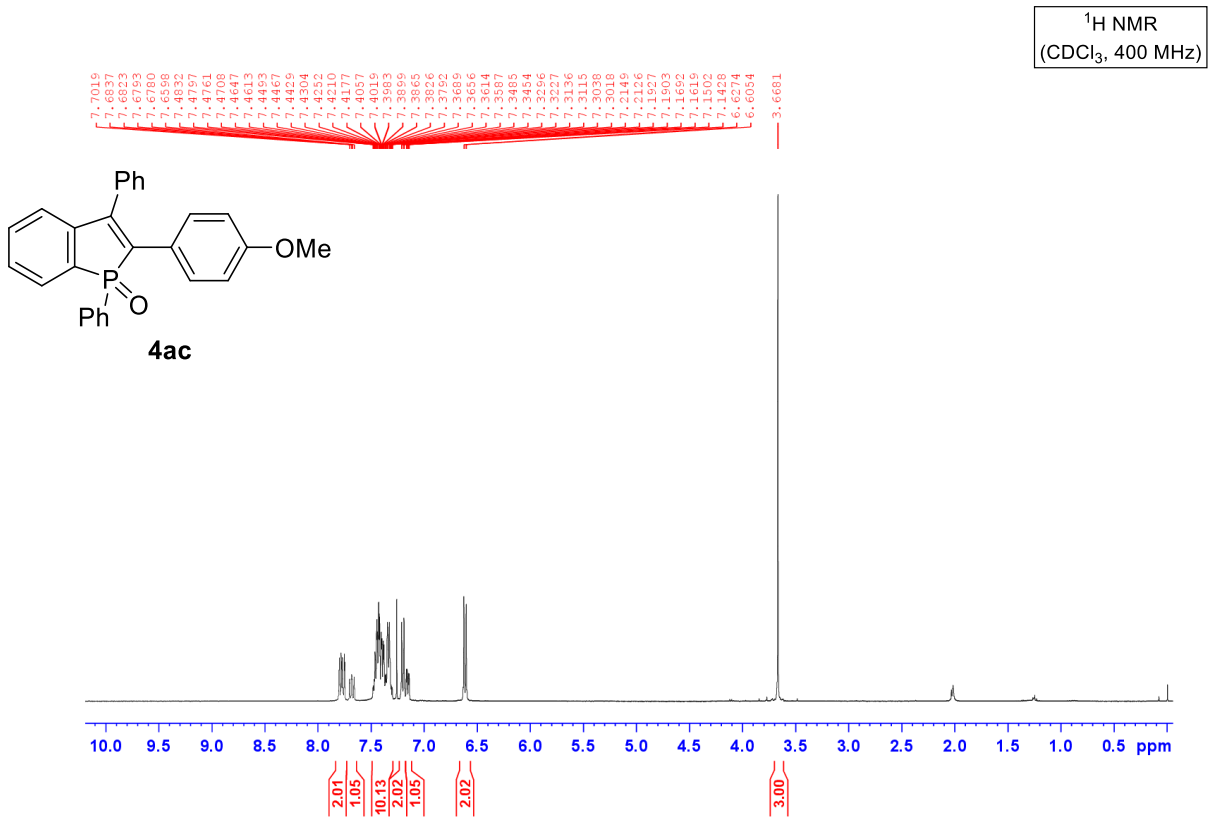


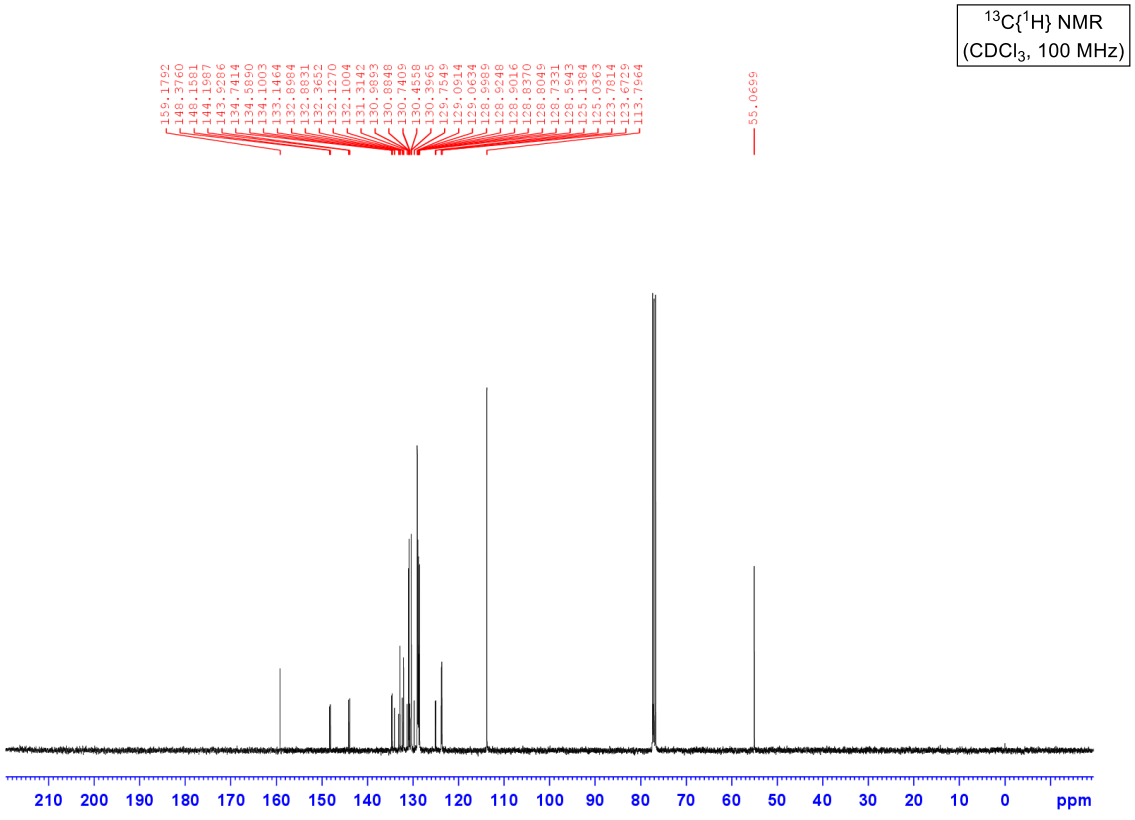
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)

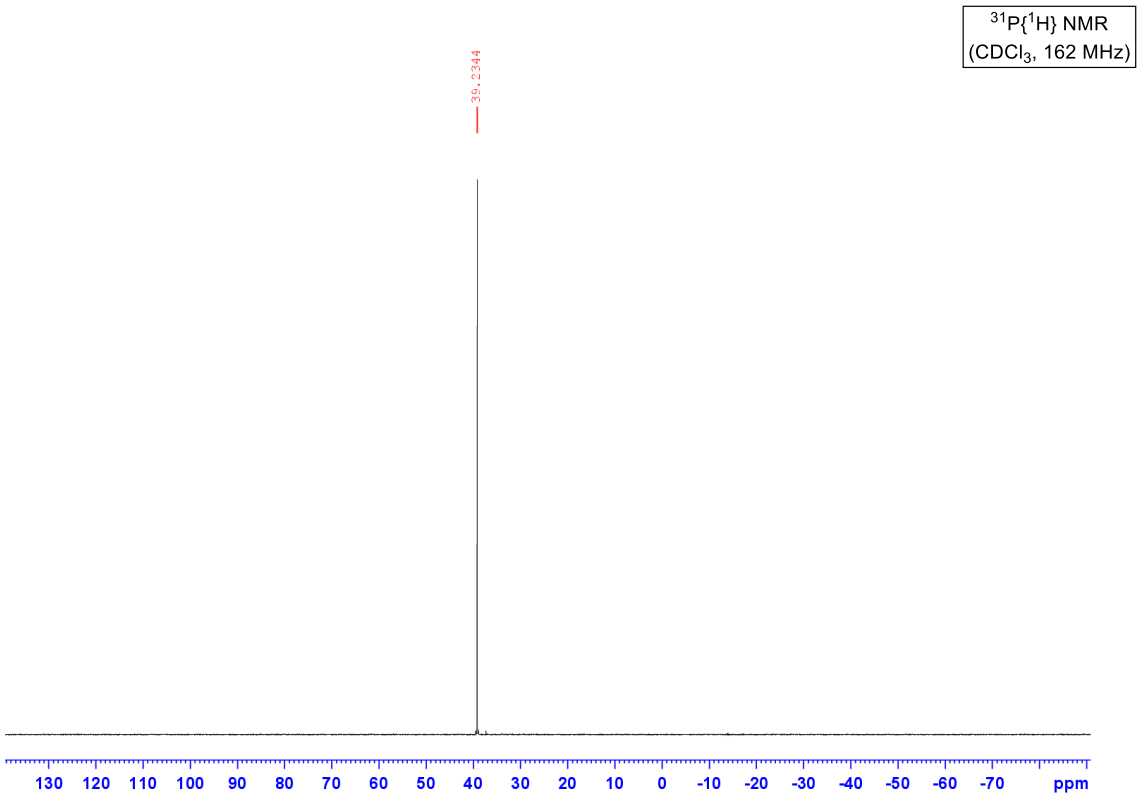



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.2705
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ac**]

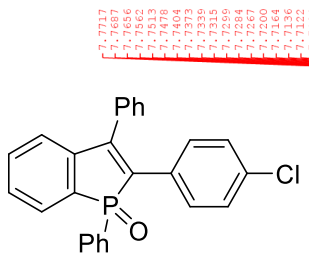




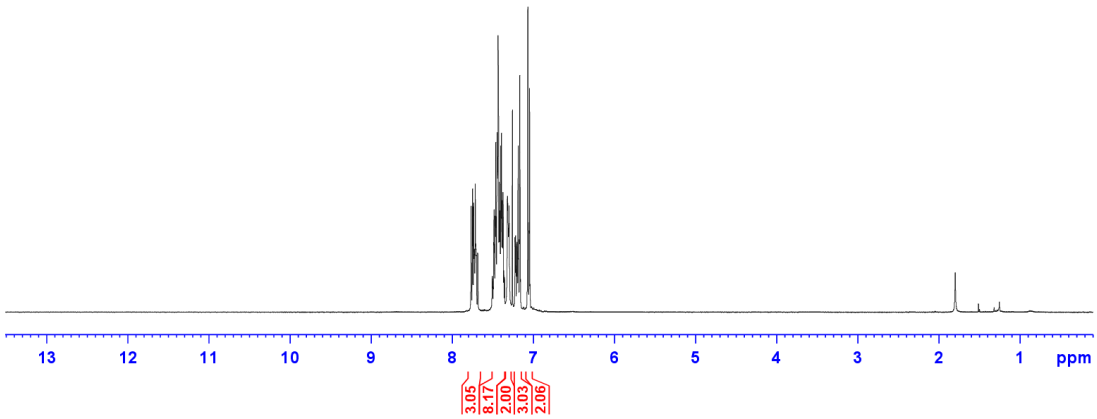

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.2344
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ad**]

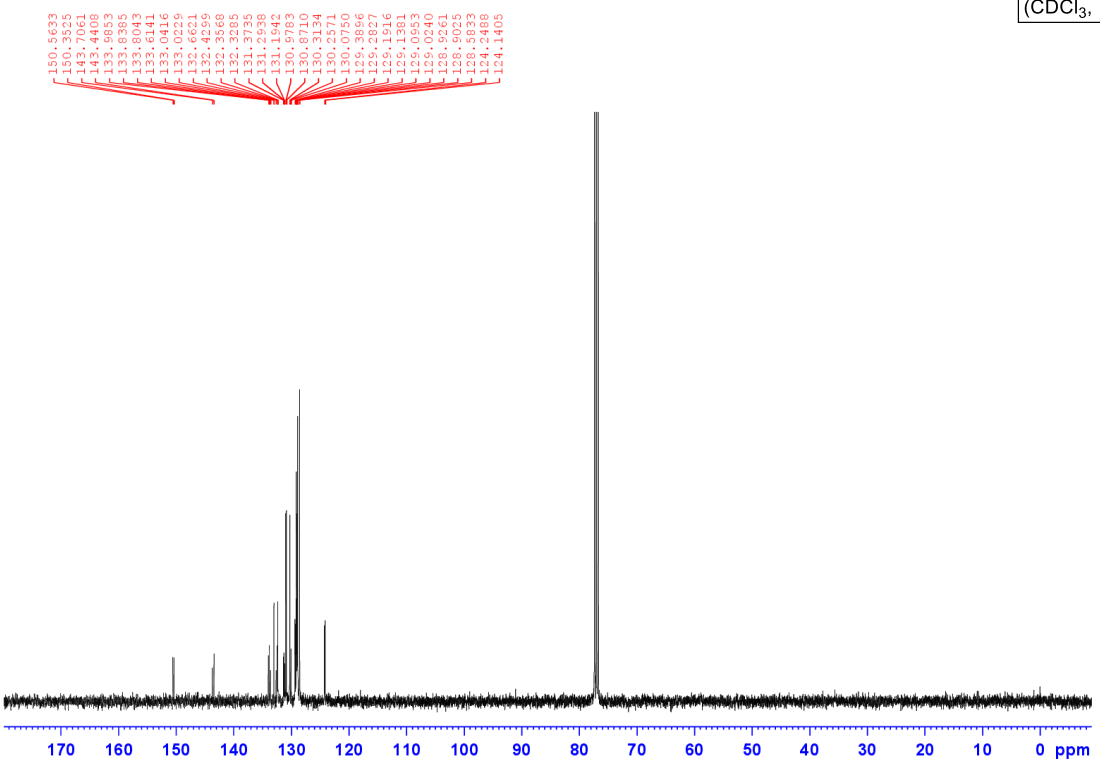
^{1}H NMR
($CDCl_3$, 400 MHz)

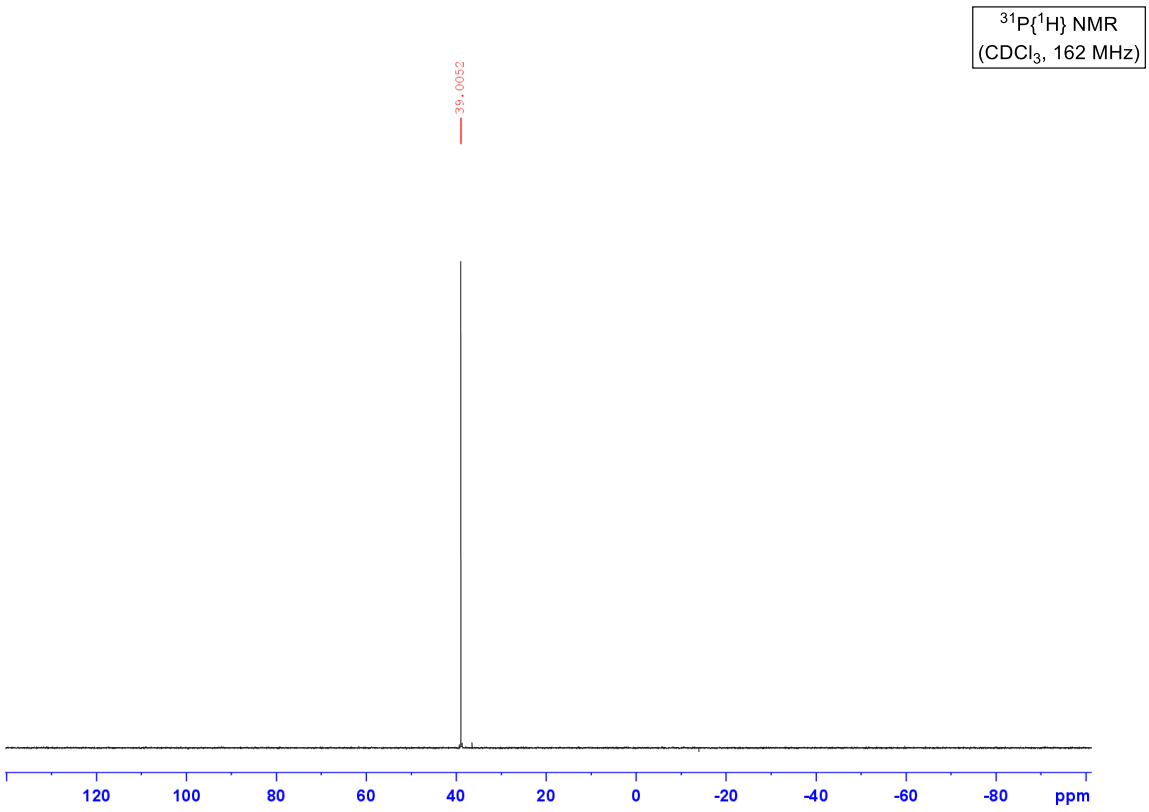


4ad



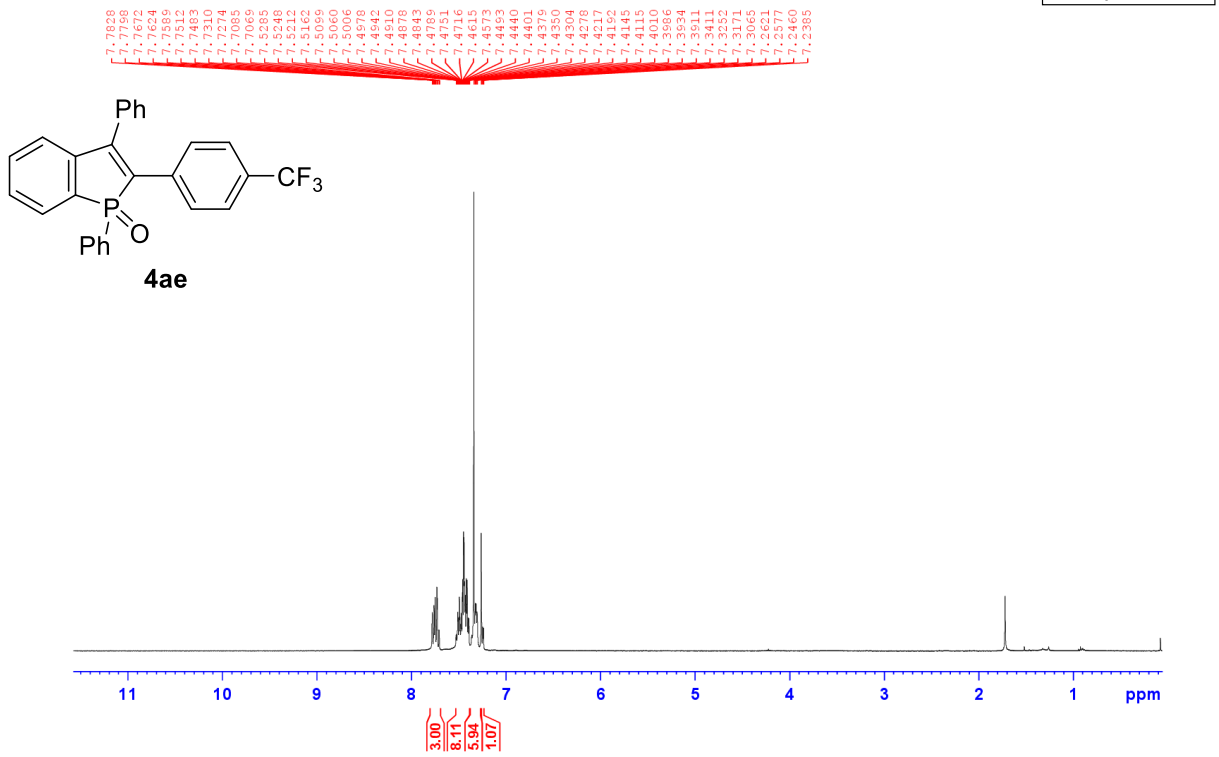
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



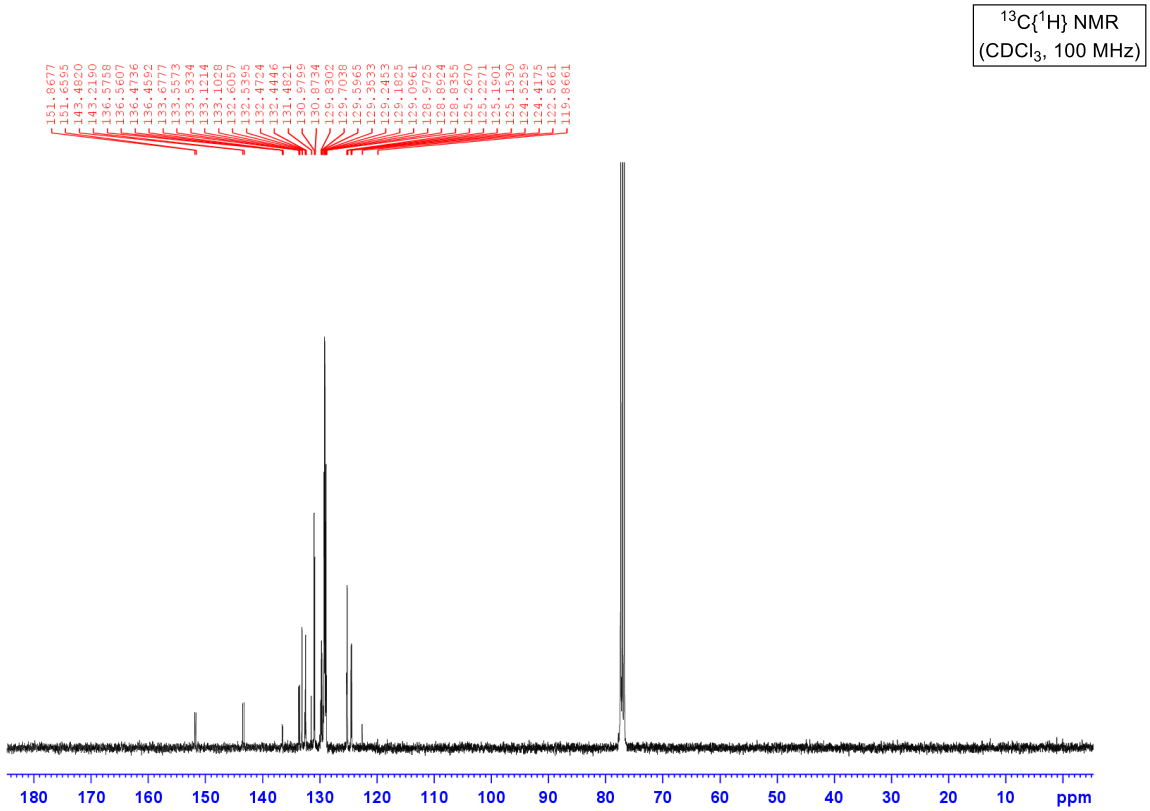

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.0052
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm

[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ae**]

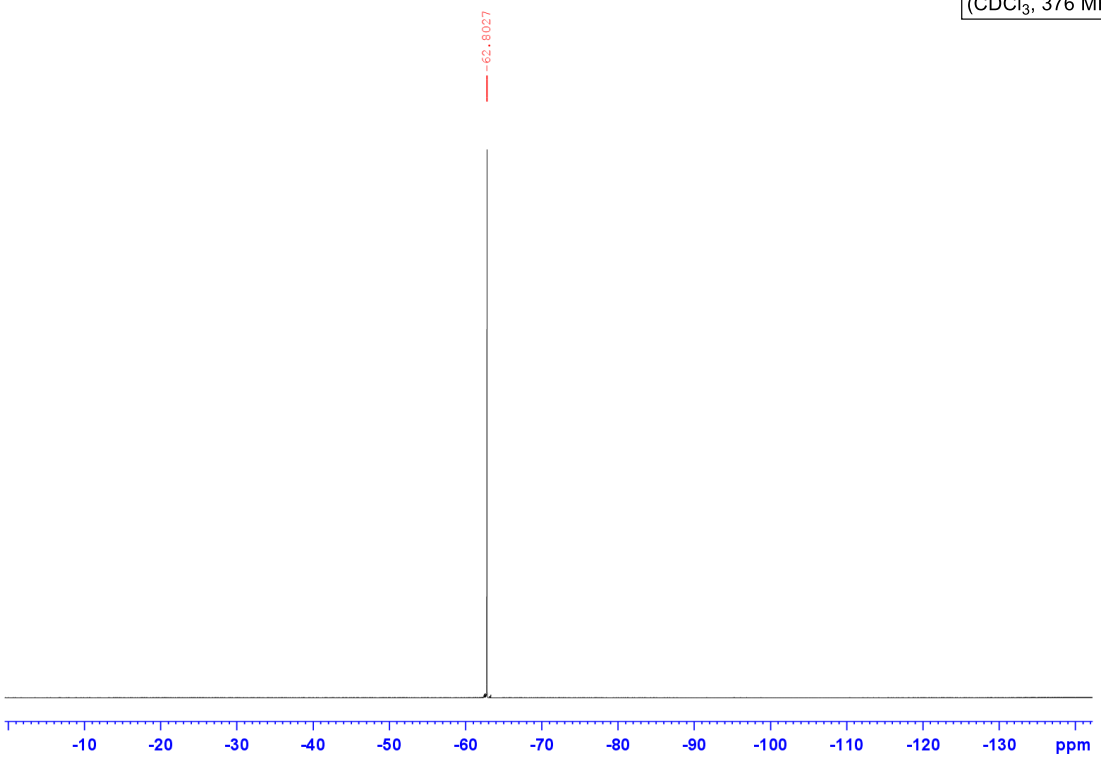
^{1}H NMR
($CDCl_3$, 400 MHz)



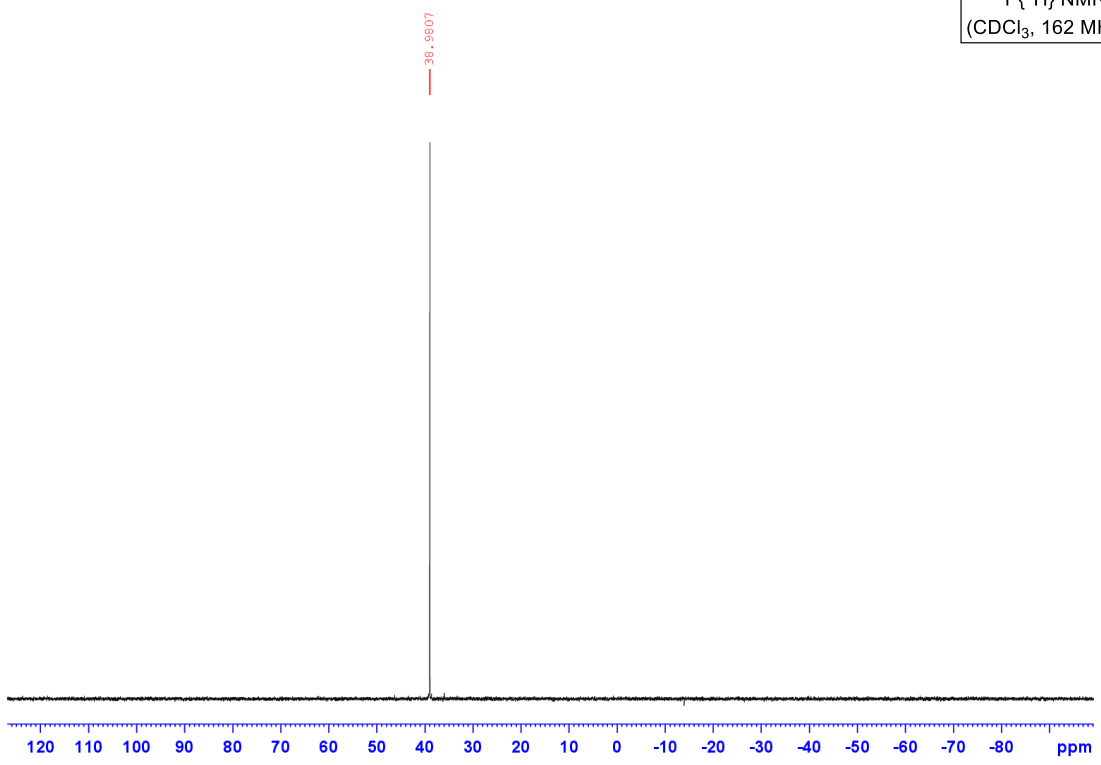
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



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

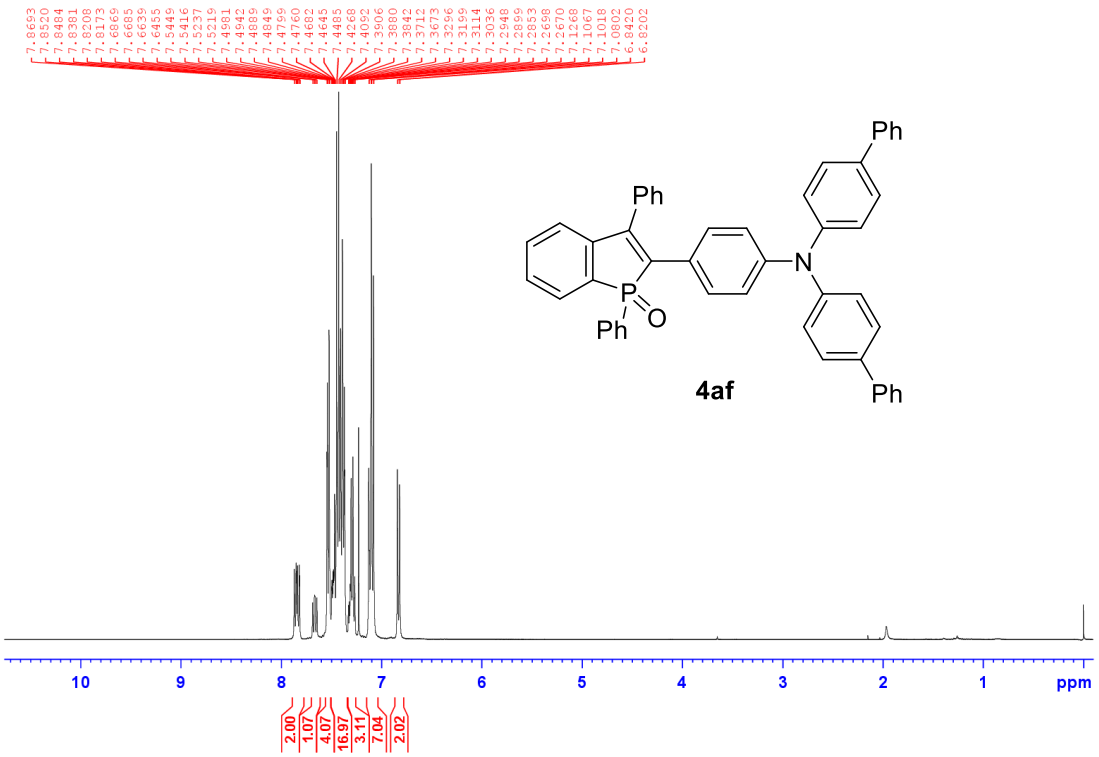


$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)

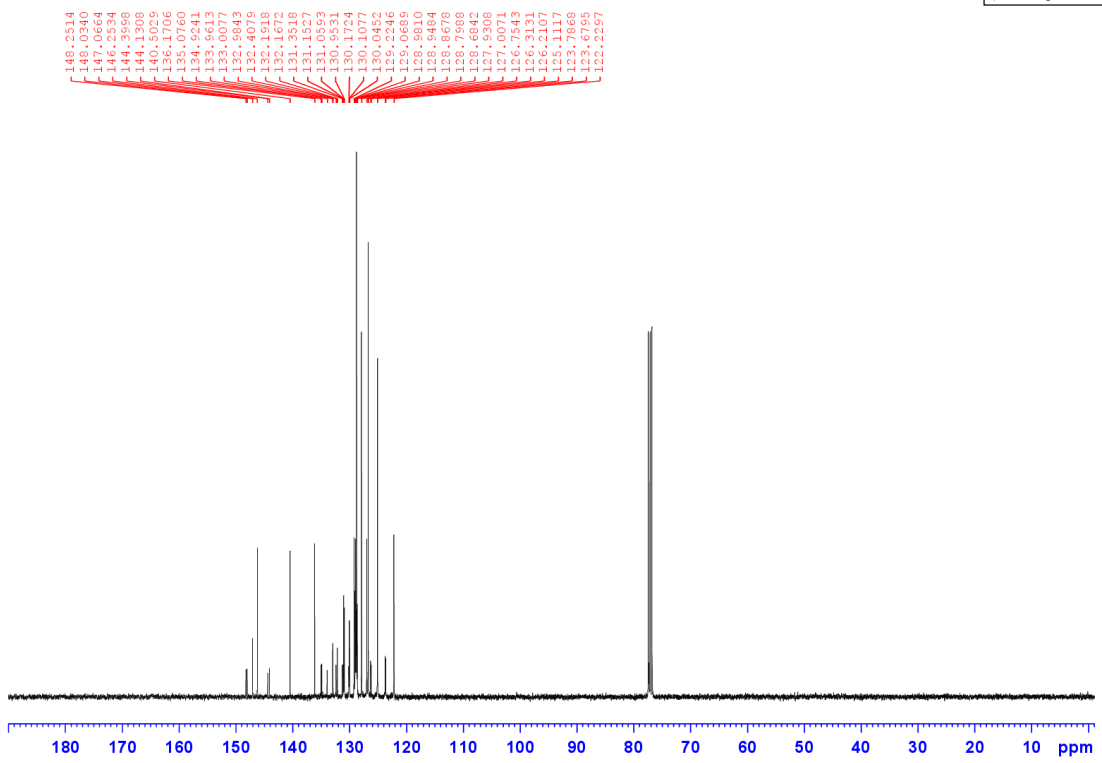


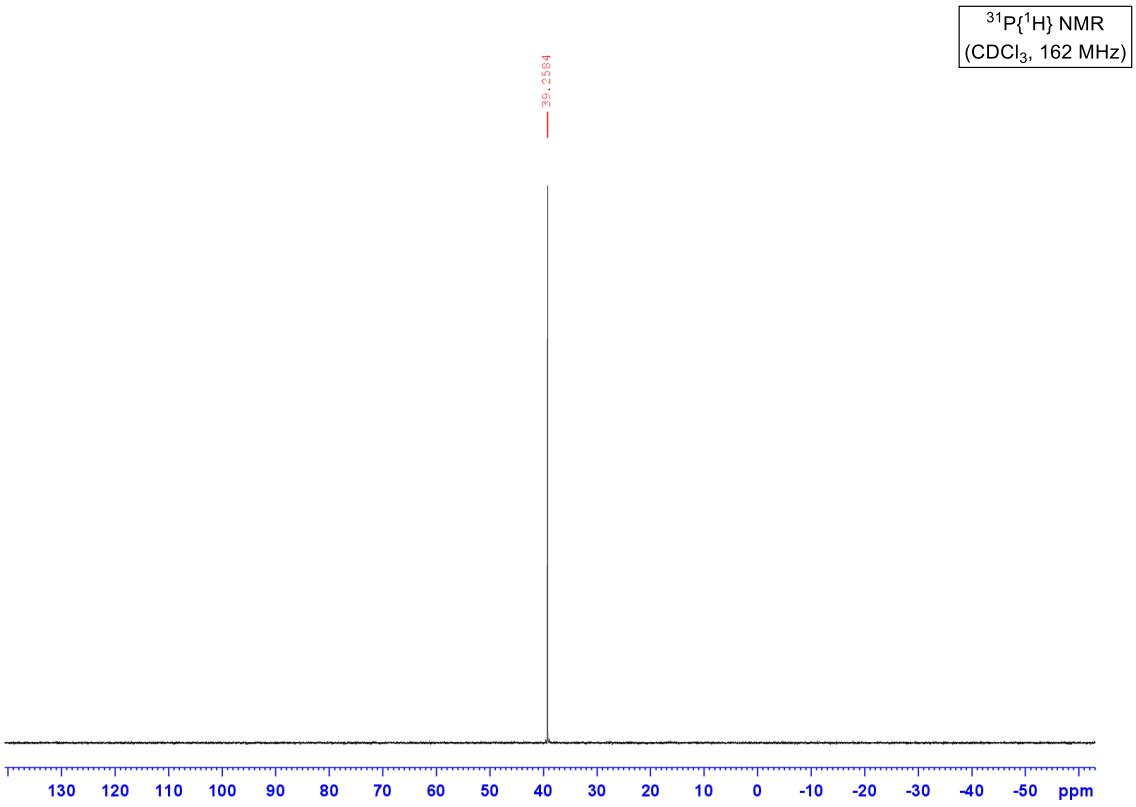
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4af**]

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



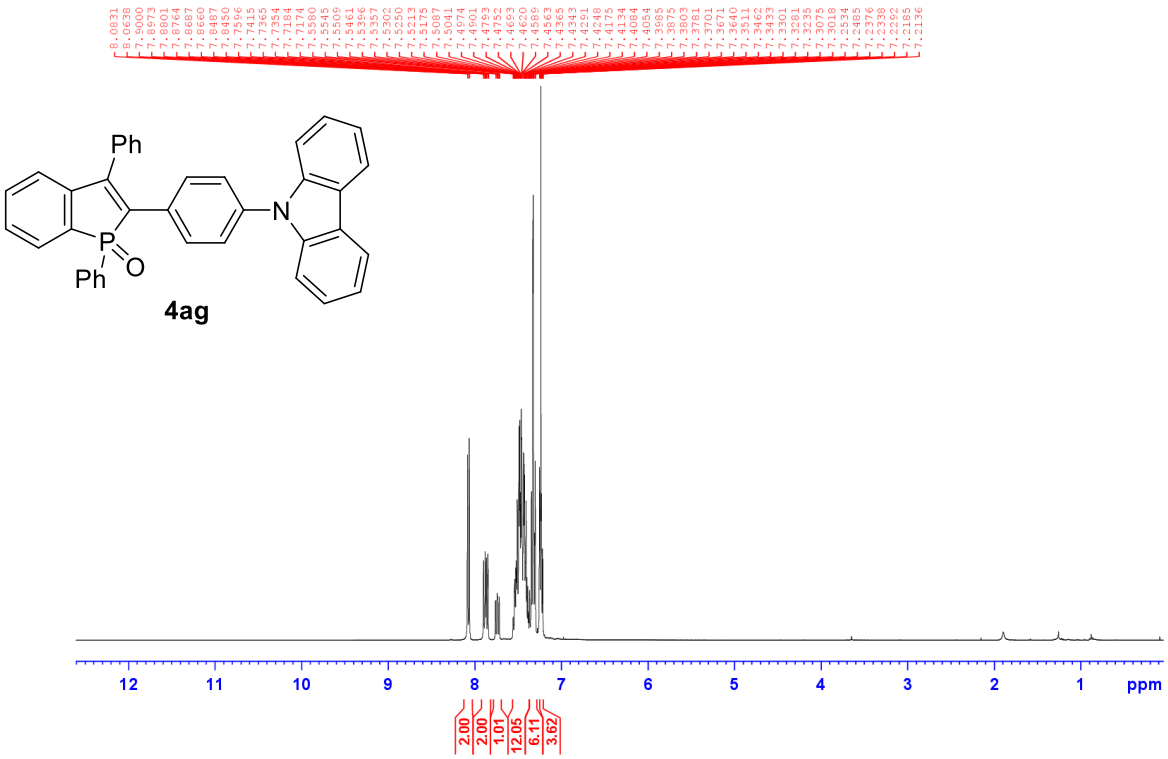
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



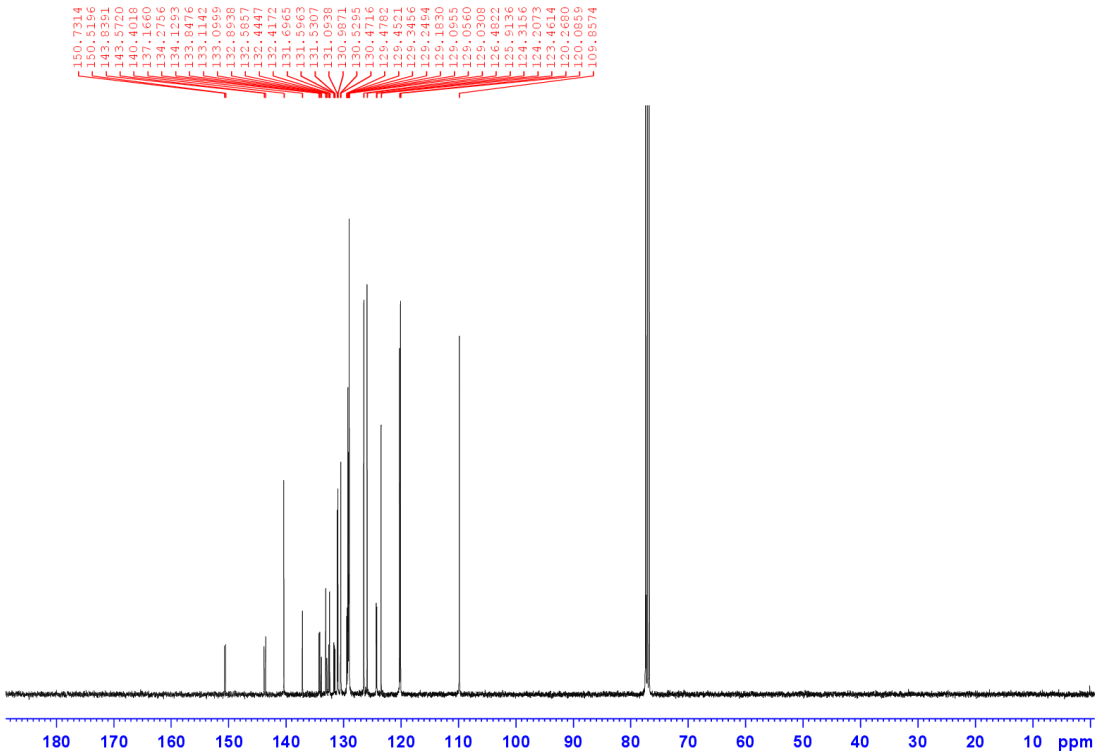

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.2584
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 ppm

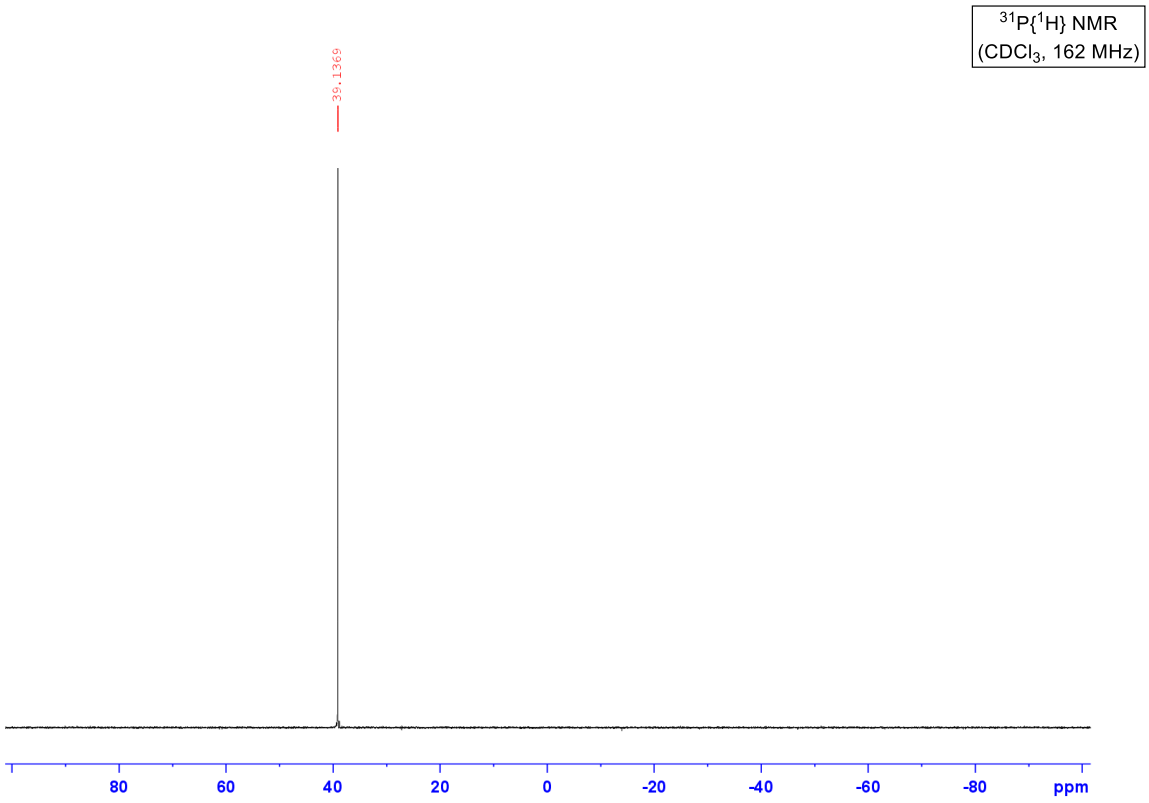
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ag**]

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



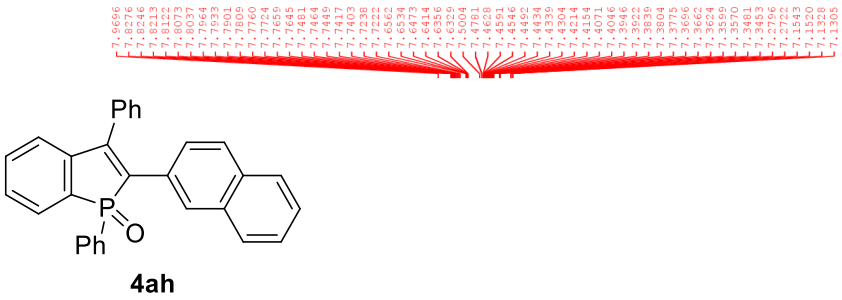
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



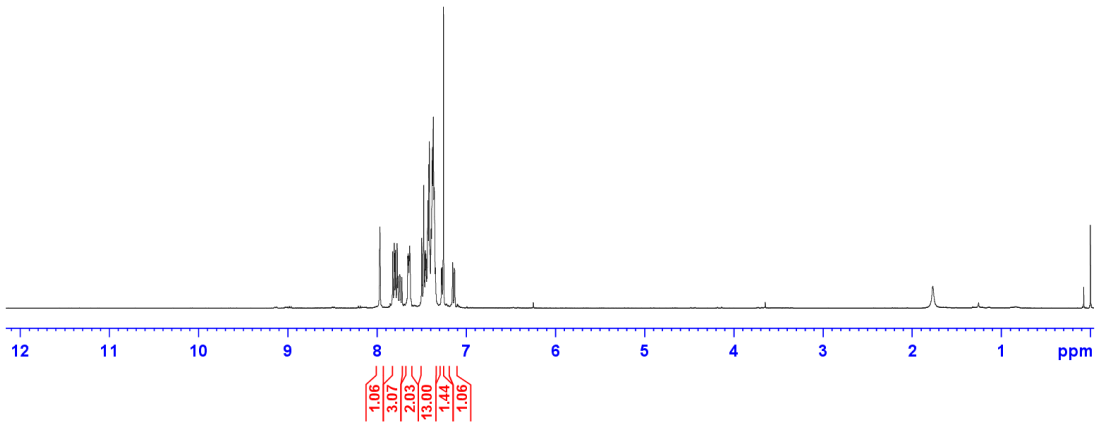

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.1369
80
60
40
20
0
-20
-40
-60
-80
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ah**]

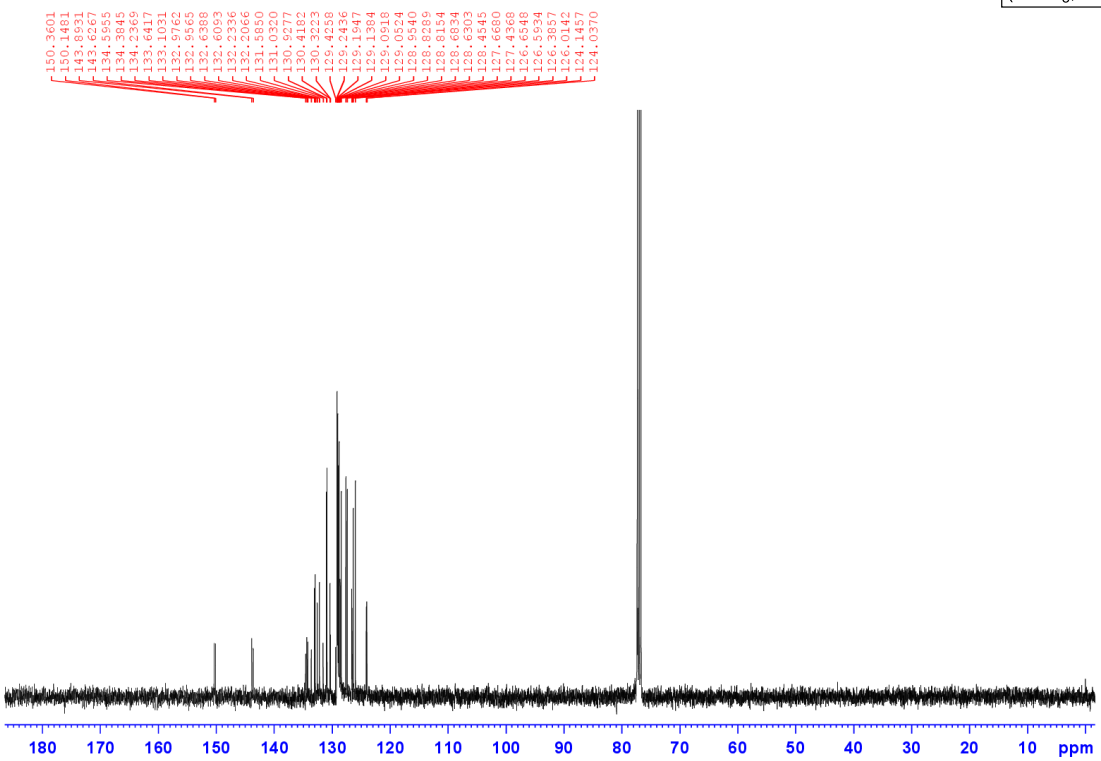
^{1}H NMR
($CDCl_3$, 400 MHz)

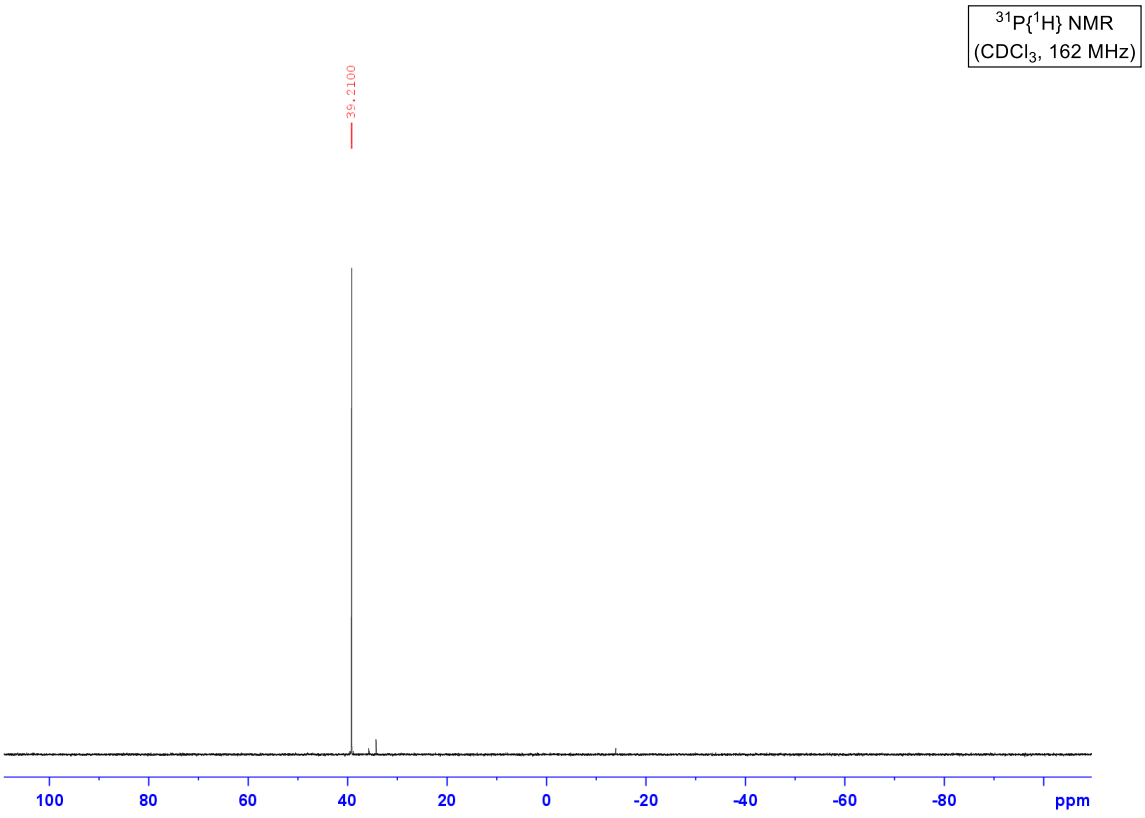


4ah



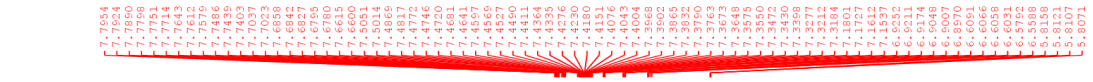
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)

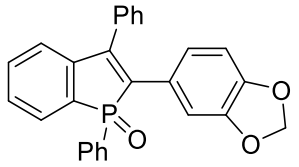



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.2100
100
80
60
40
20
0
-20
-40
-60
-80
ppm

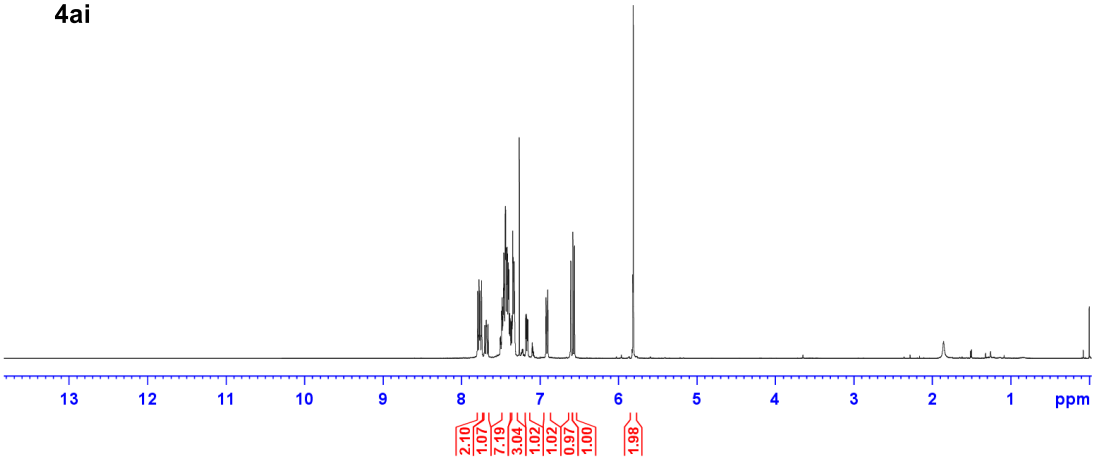
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ai**]

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

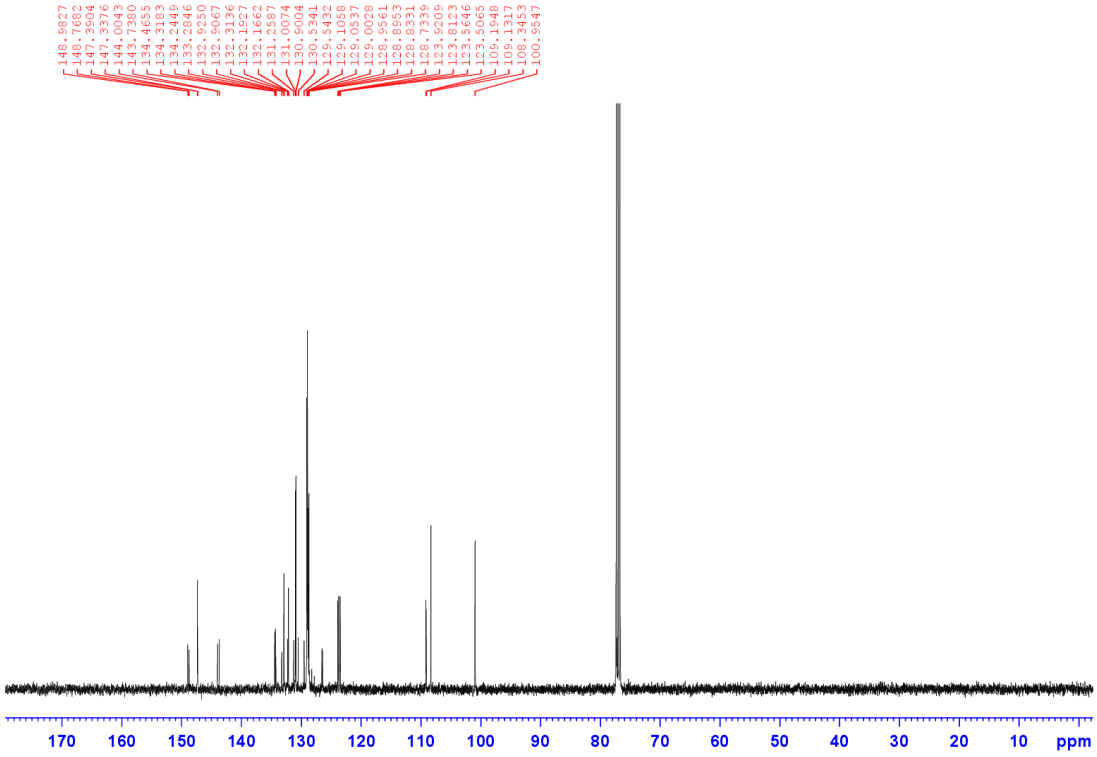


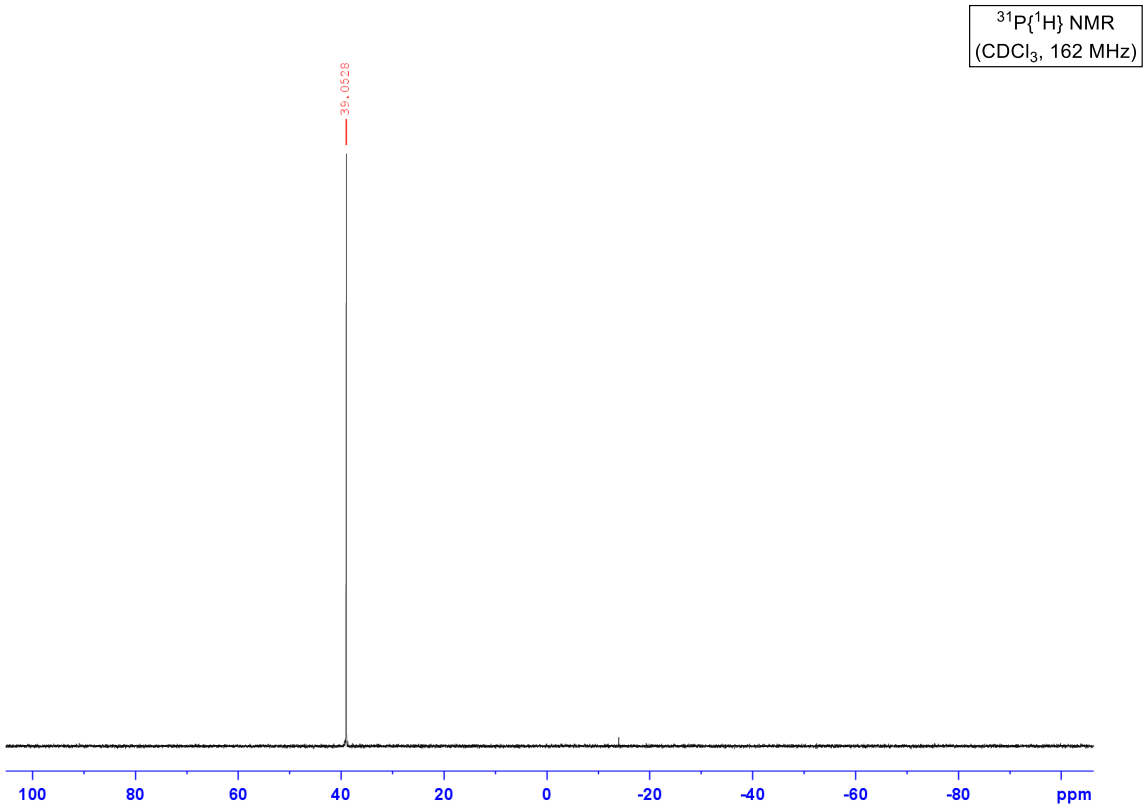


4ai

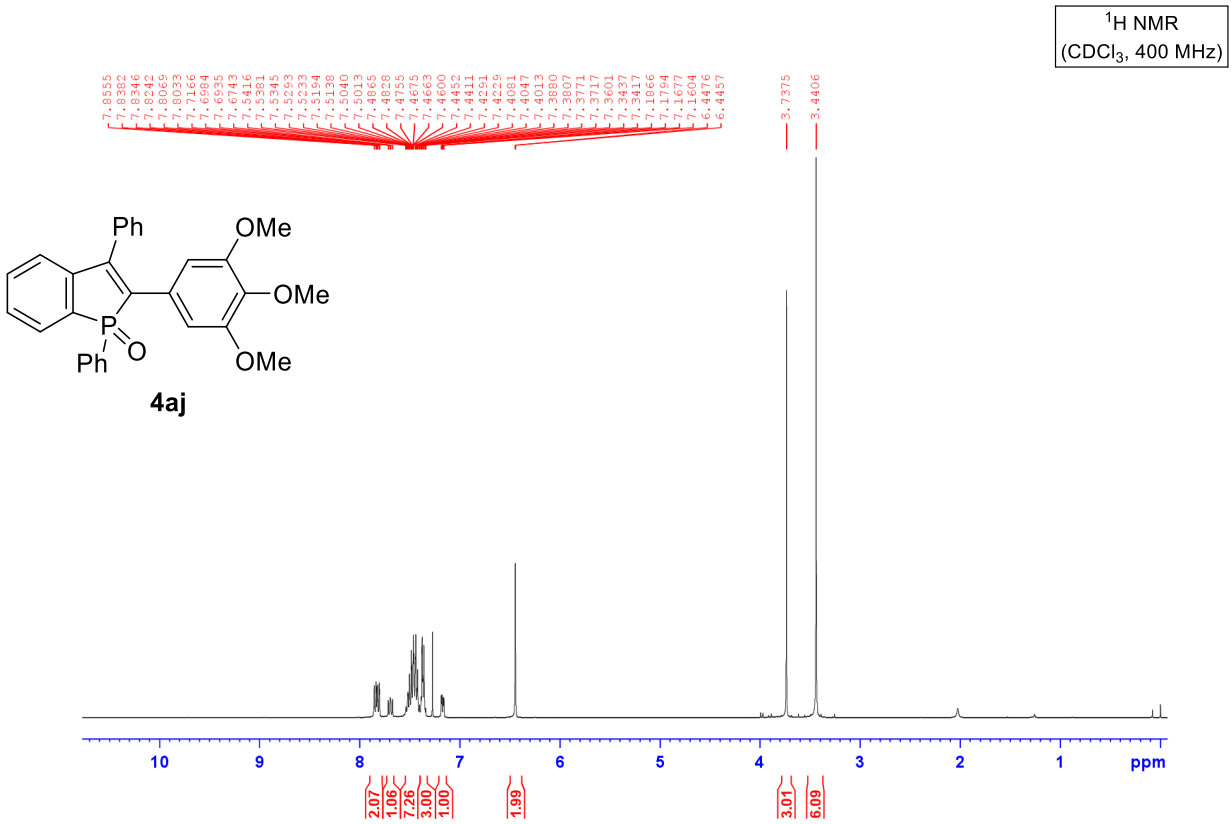


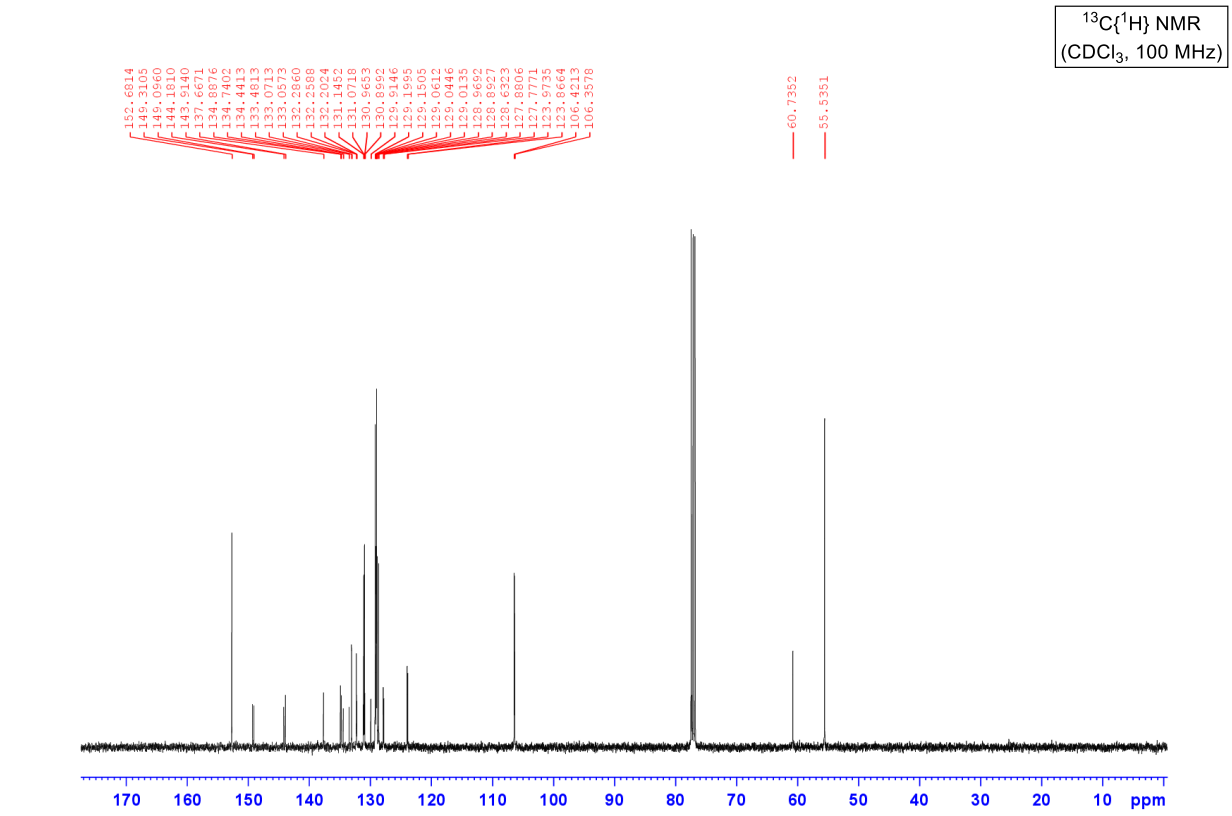
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)

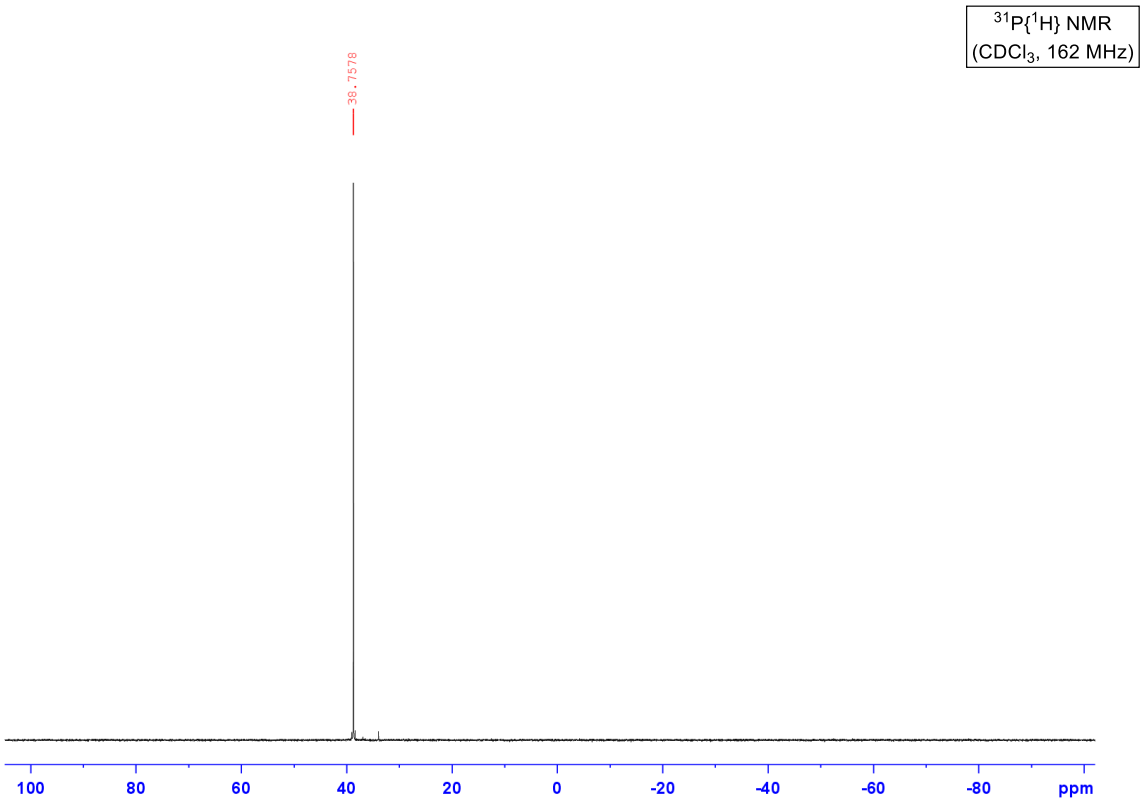



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.0528
100
80
60
40
20
0
-20
-40
-60
-80
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4aj**]

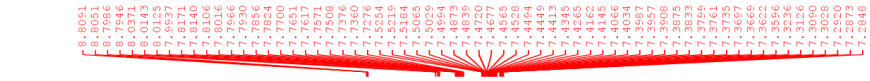


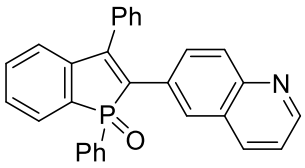



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
38.7578
100
80
60
40
20
0
-20
-40
-60
-80
ppm

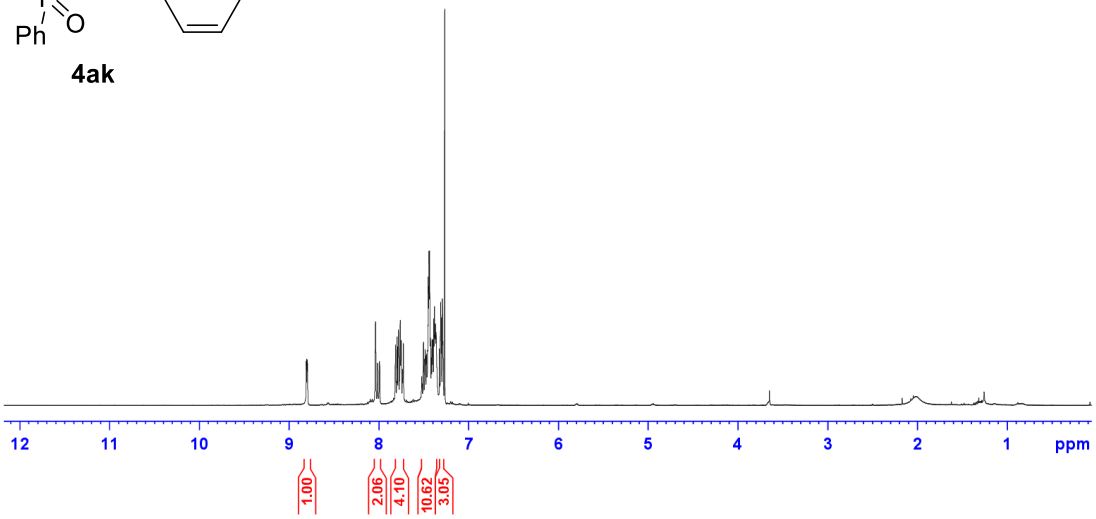
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ak**]

^{1}H NMR
(CDCl$_3$, 400 MHz)

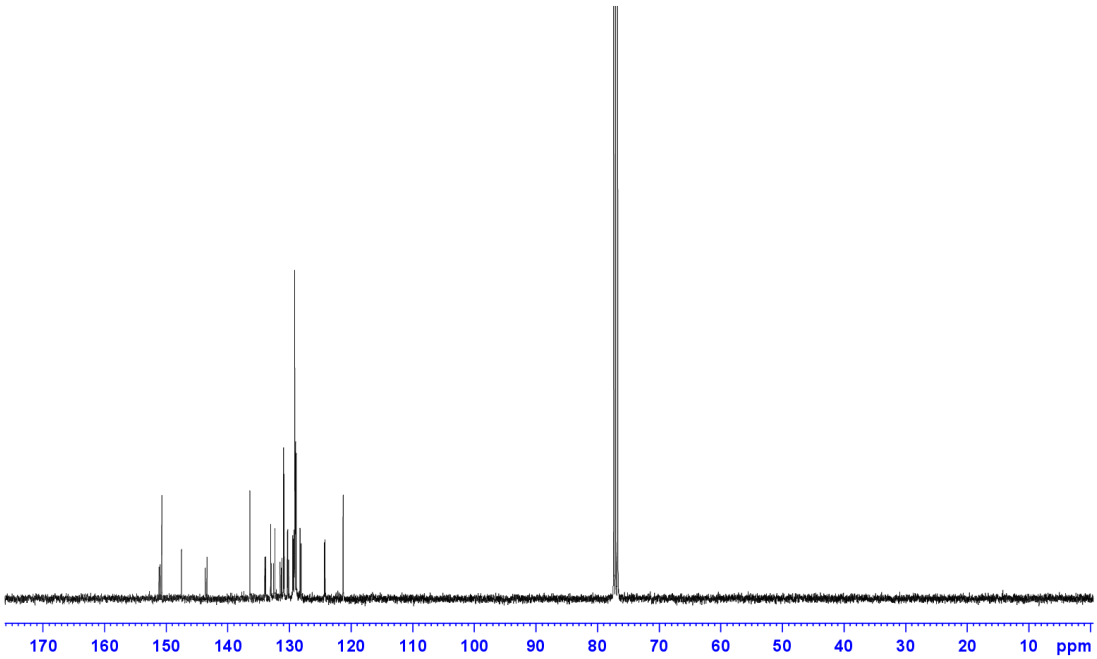


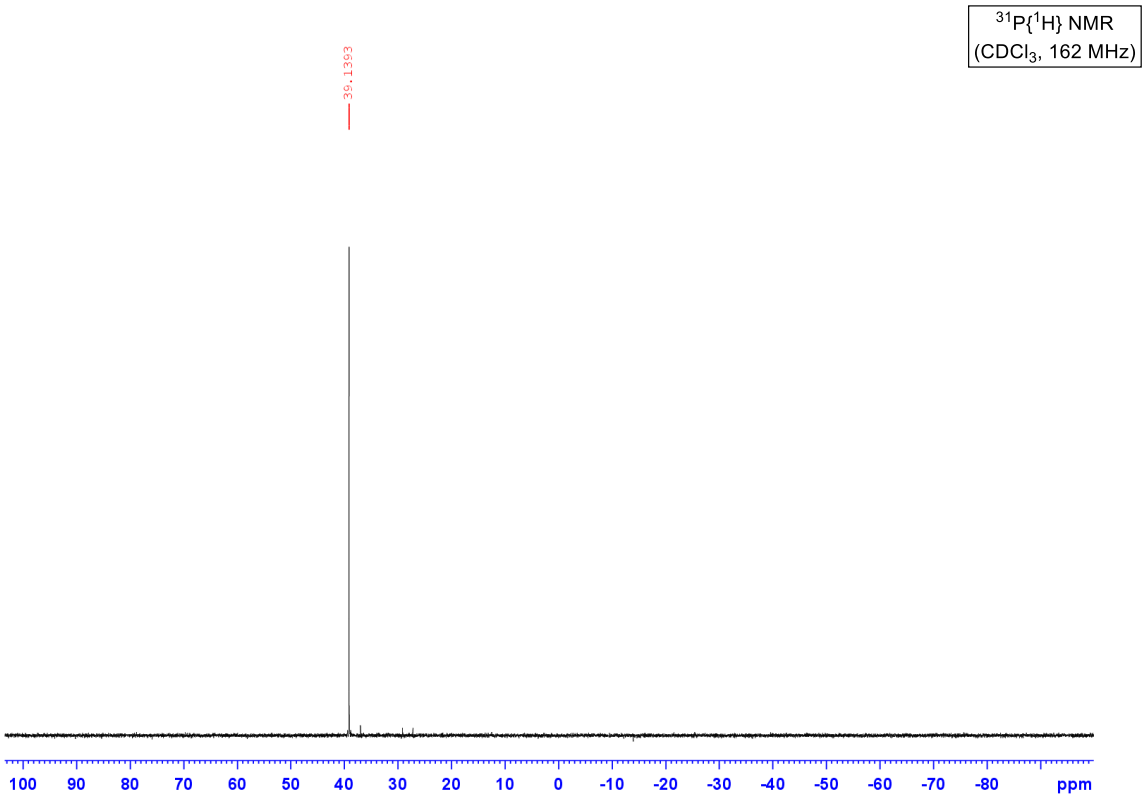


4ak



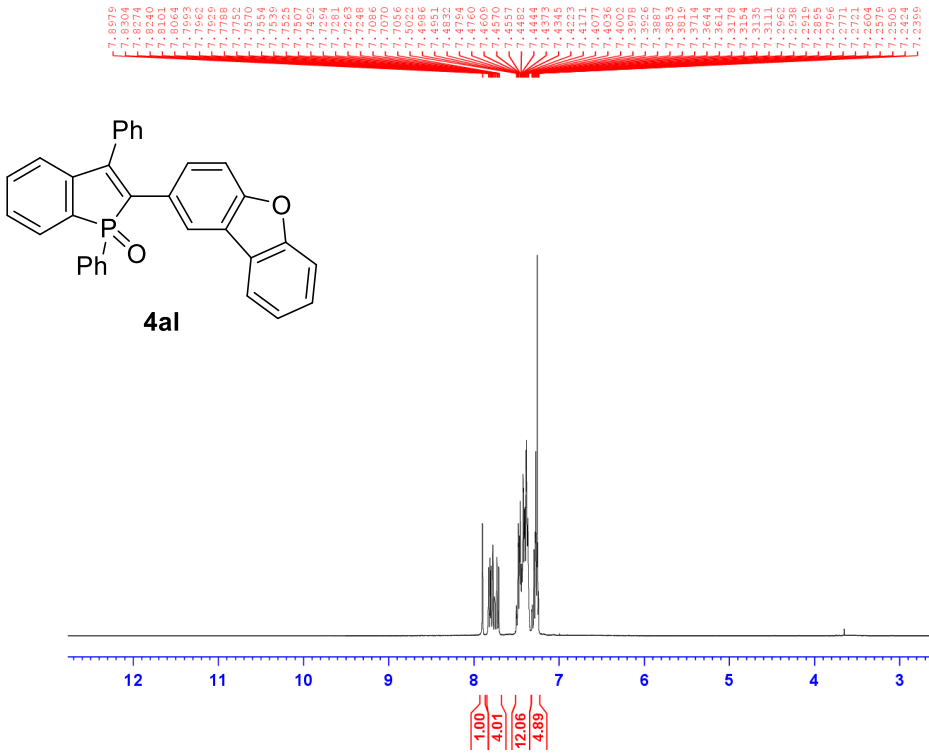
^{13}C{^{1}H} NMR
(CDCl$_3$, 100 MHz)



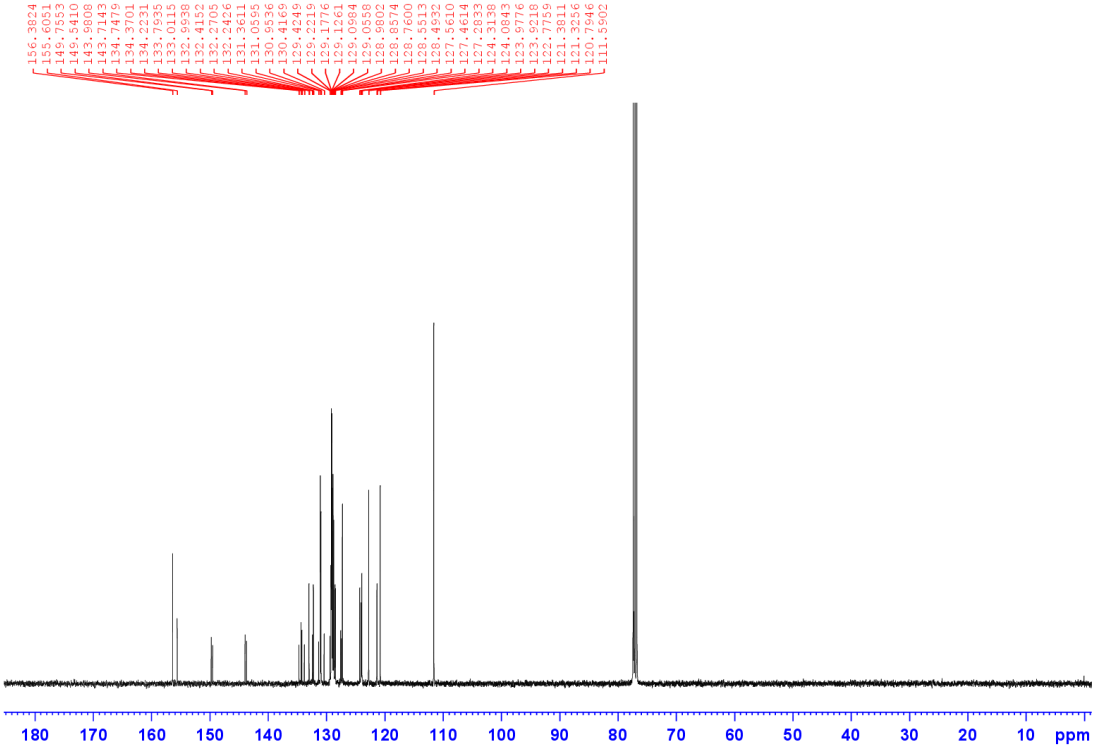

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.1393
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

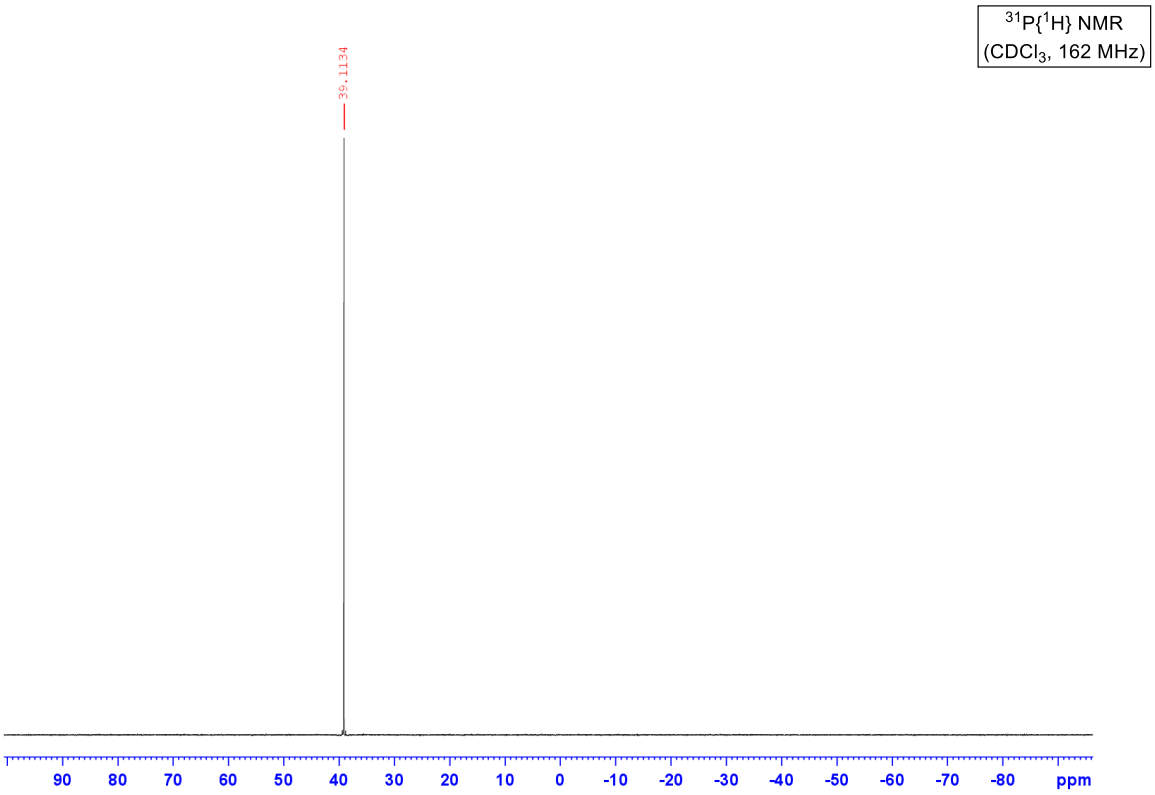
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4al**]

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



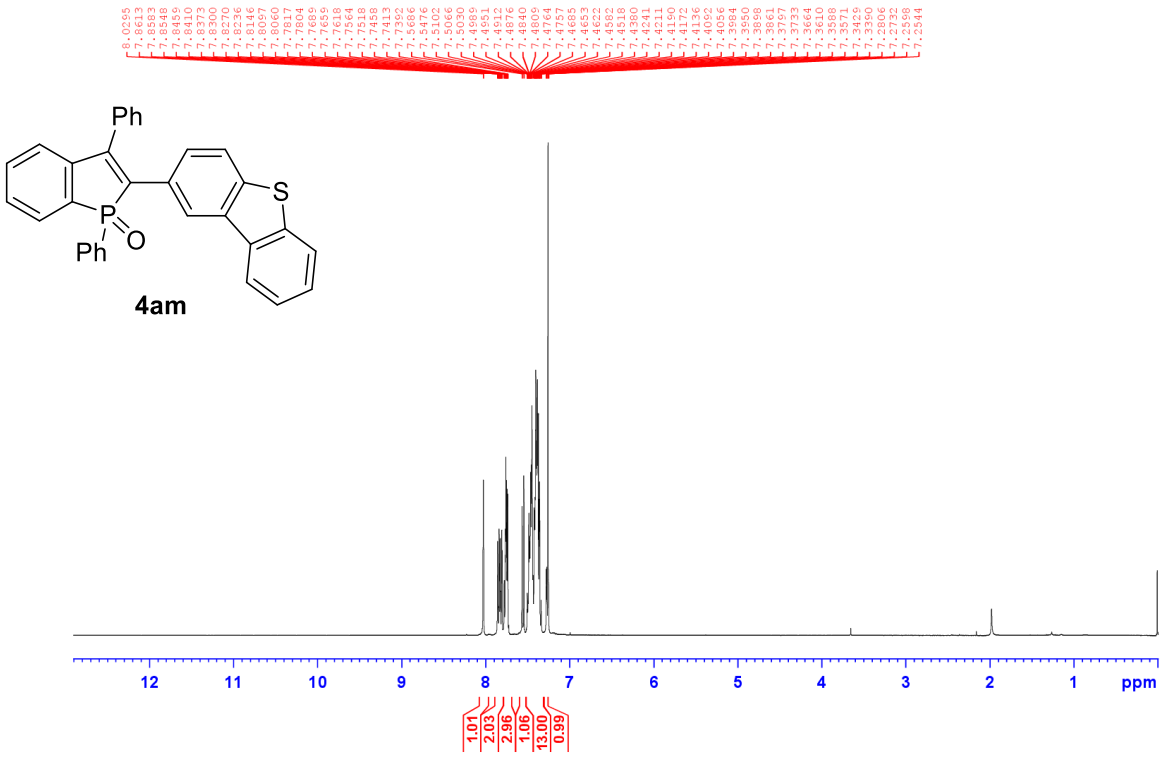
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



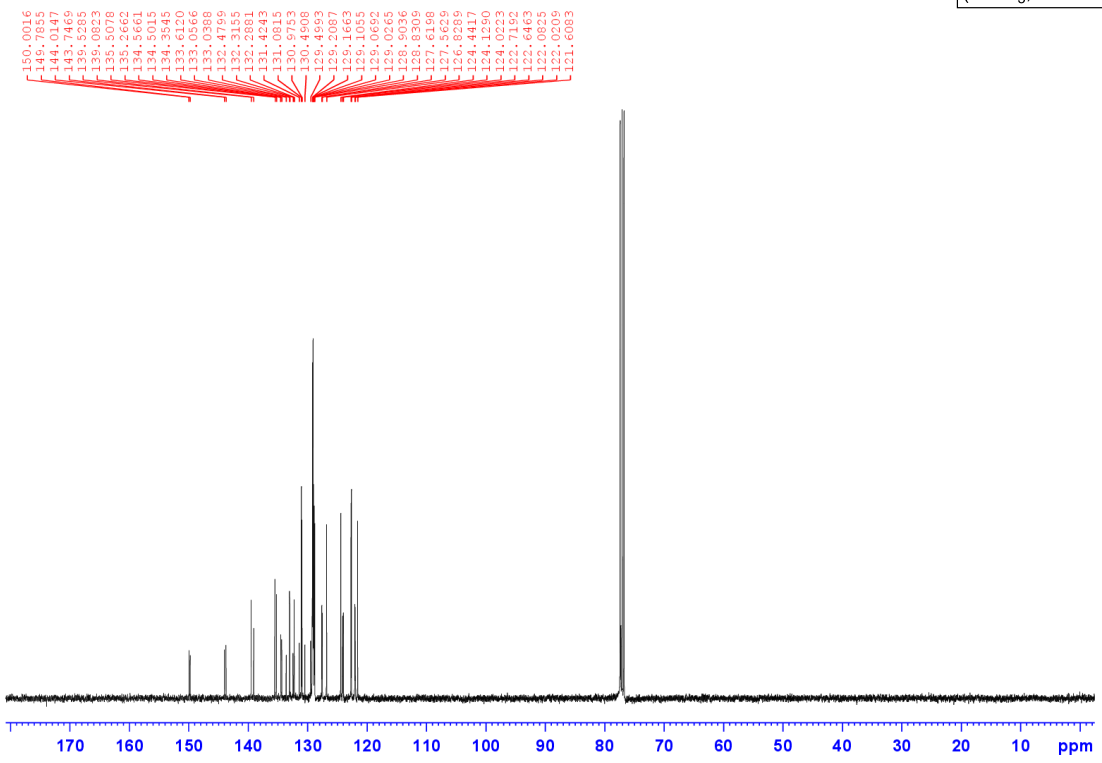

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.1134
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

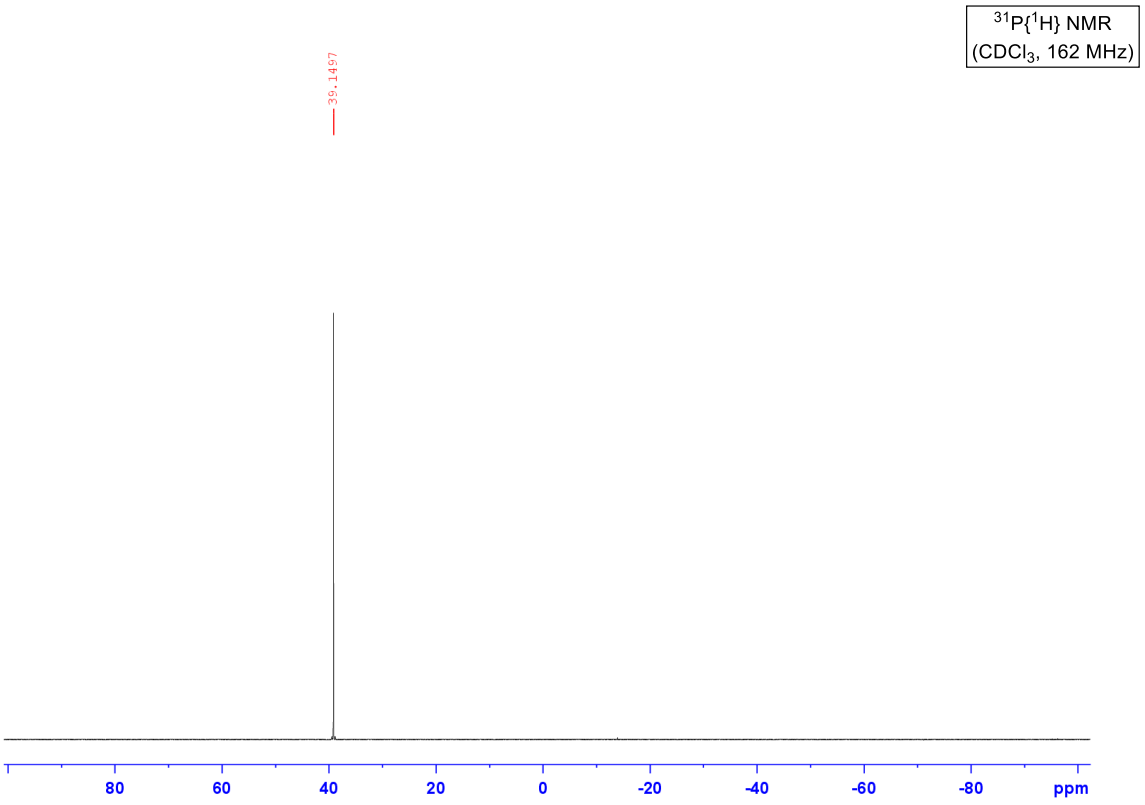
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4am**]

^{1}H NMR
(CDCl$_3$, 400 MHz)

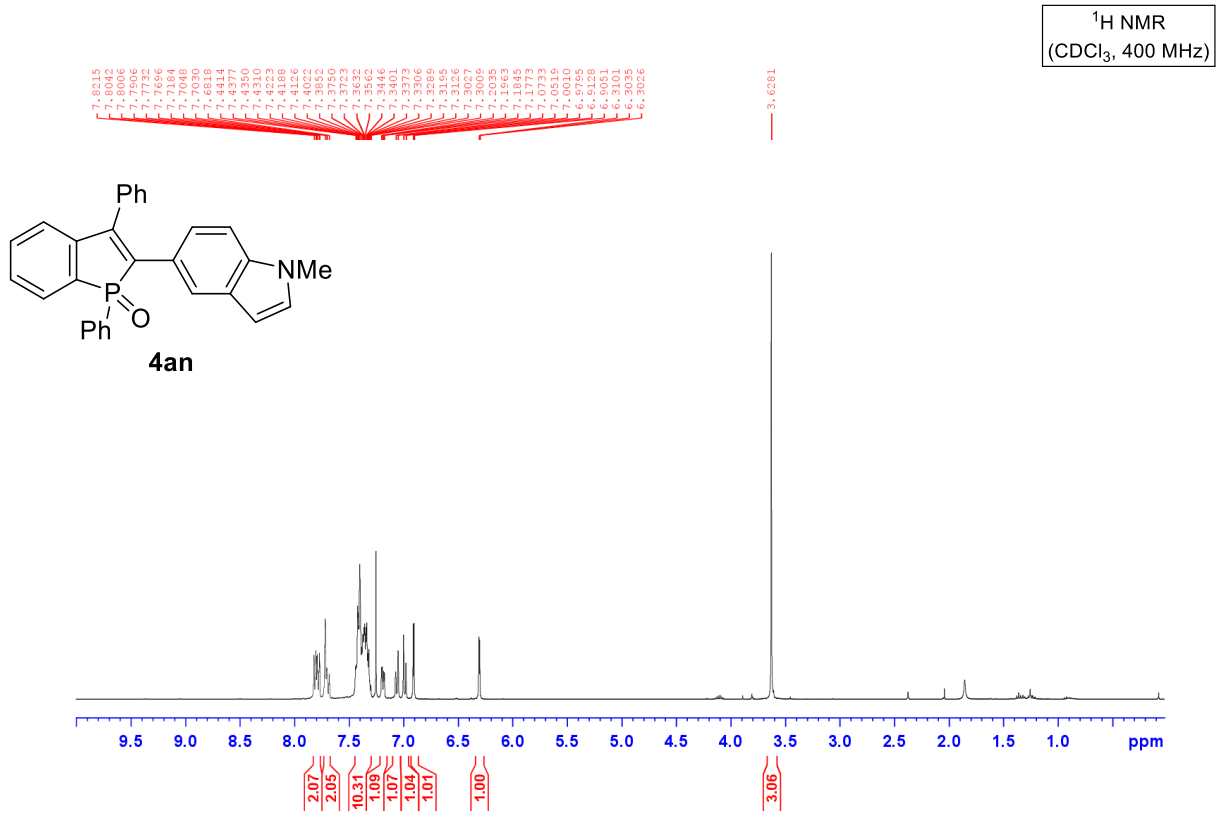


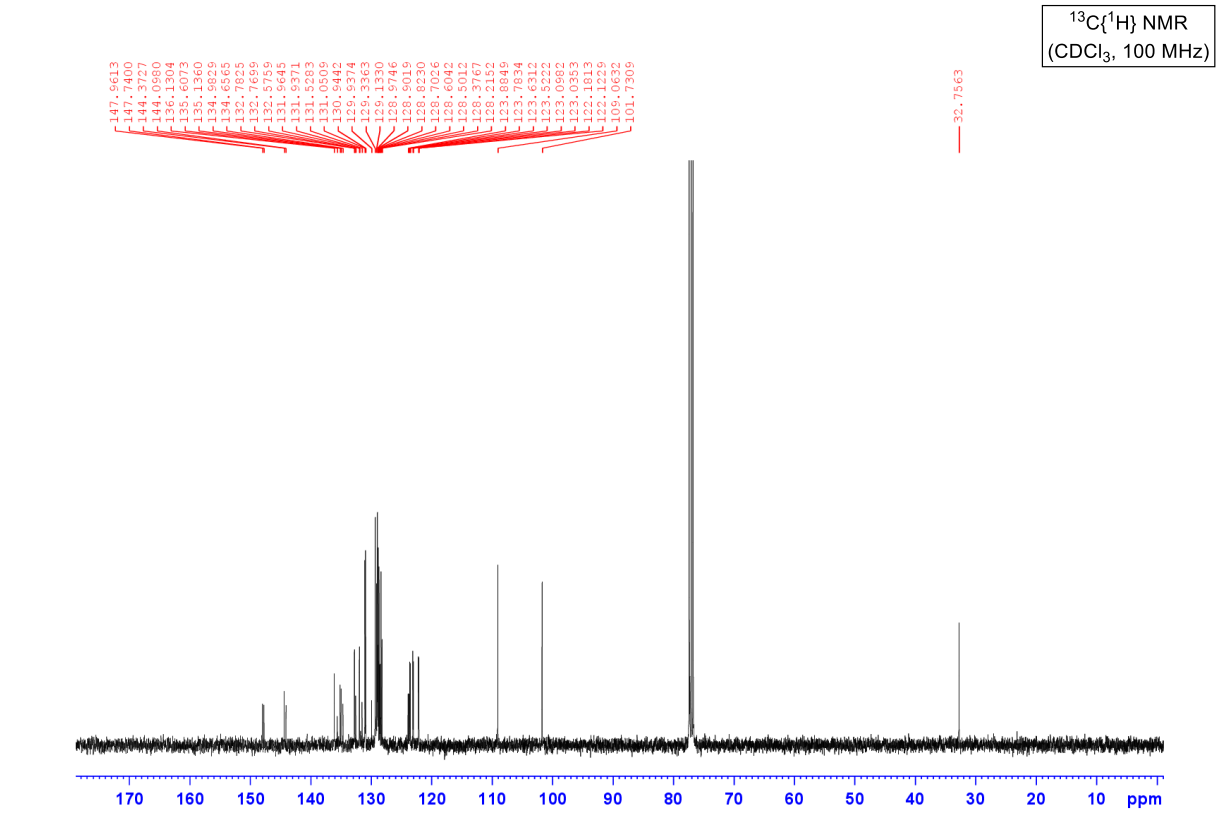
^{13}C{^{1}H} NMR
(CDCl$_3$, 100 MHz)

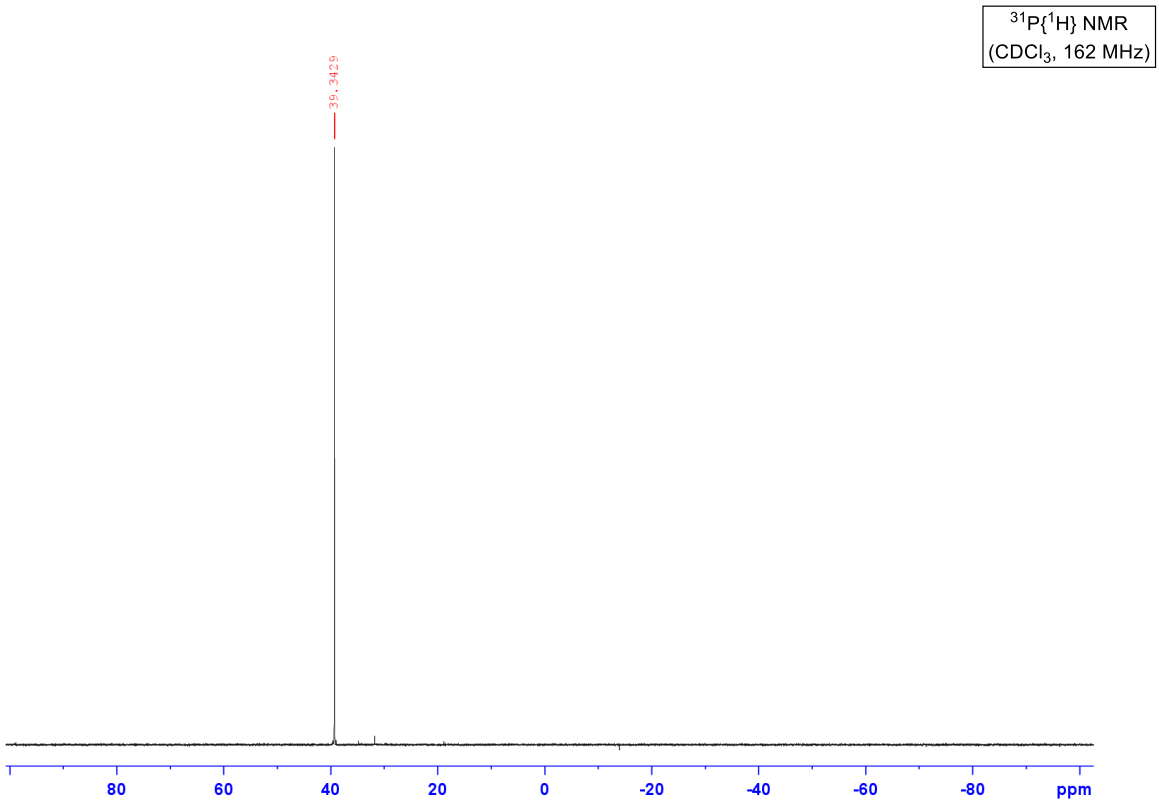



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.1497
80
60
40
20
0
-20
-40
-60
-80
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4an**]

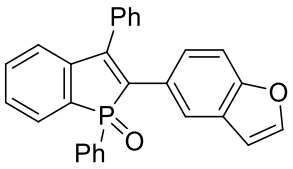




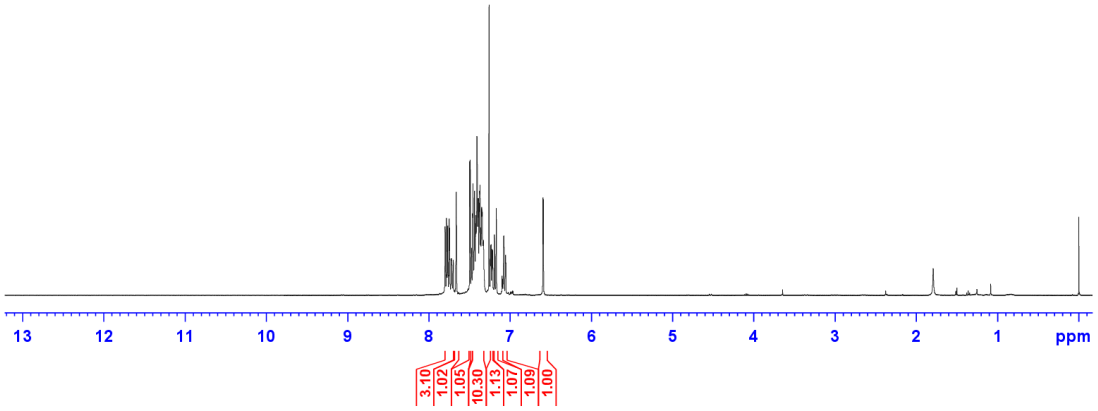

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.3429
80
60
40
20
0
-20
-40
-60
-80
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ao**]

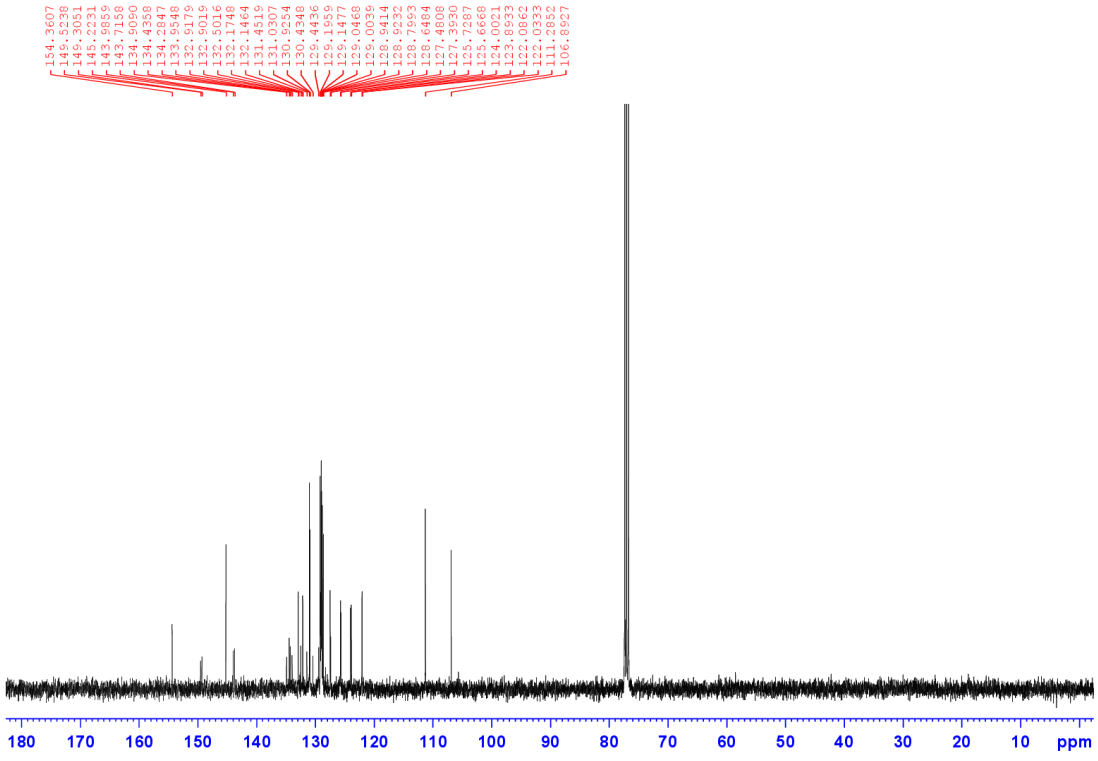
^{1}H NMR
($CDCl_3$, 400 MHz)

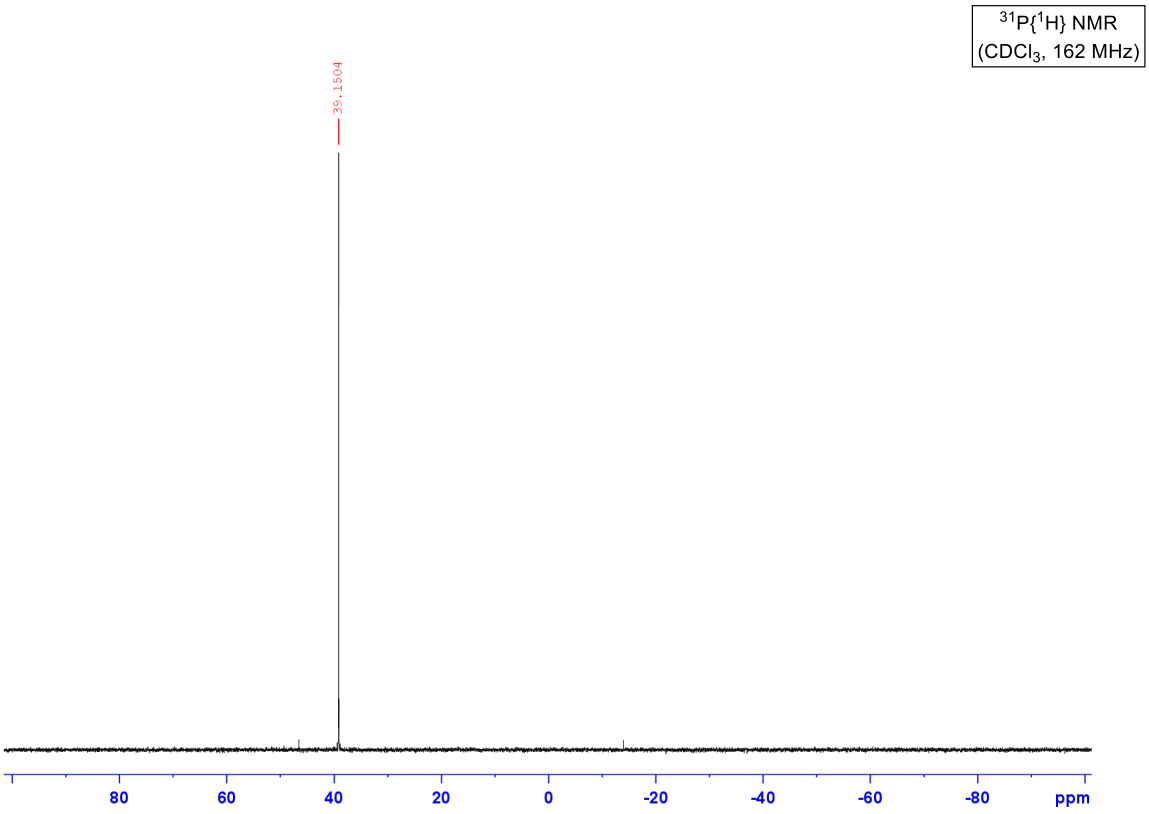


4ao



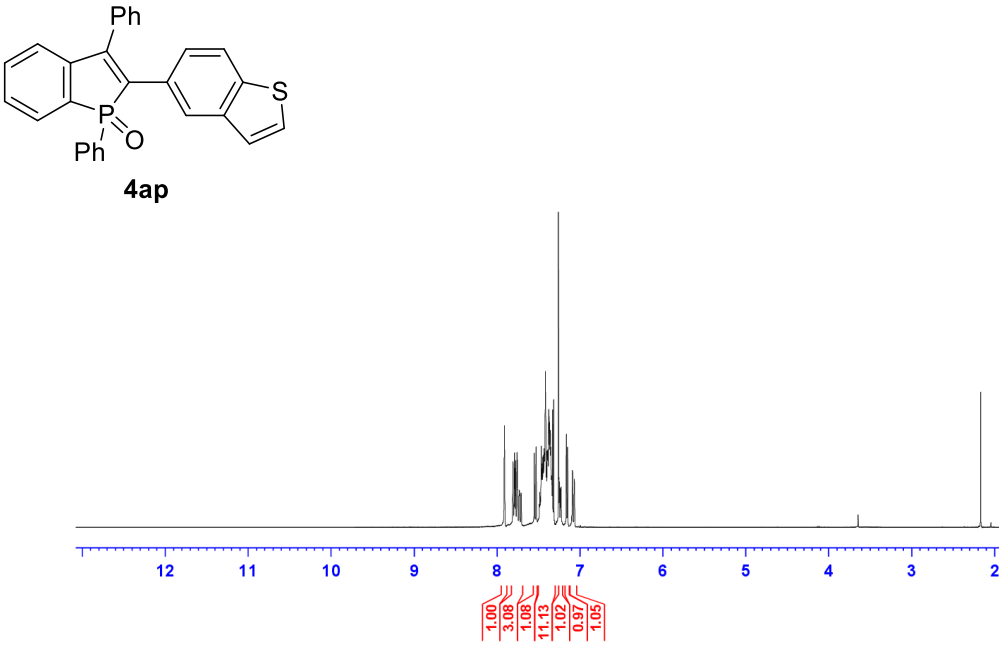
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



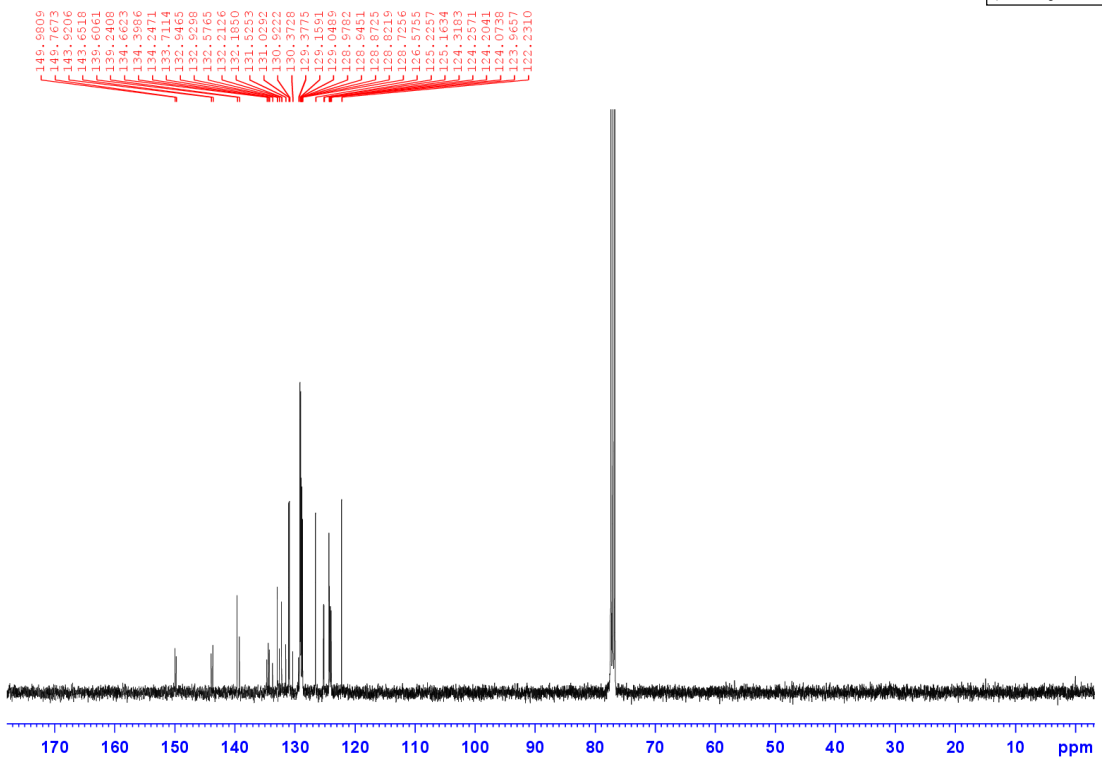

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.1504
80
60
40
20
0
-20
-40
-60
-80
ppm

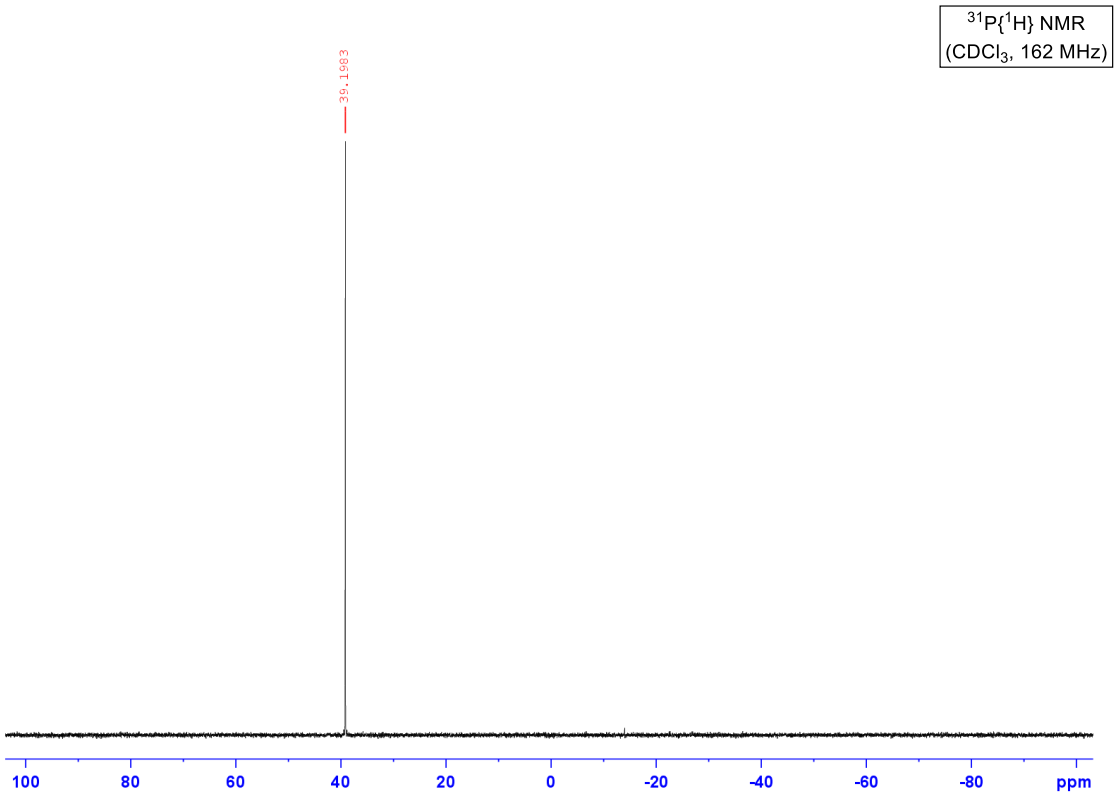
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ap**]

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



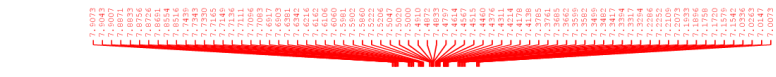
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)

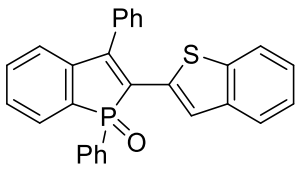



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.1983
100
80
60
40
20
0
-20
-40
-60
-80
ppm

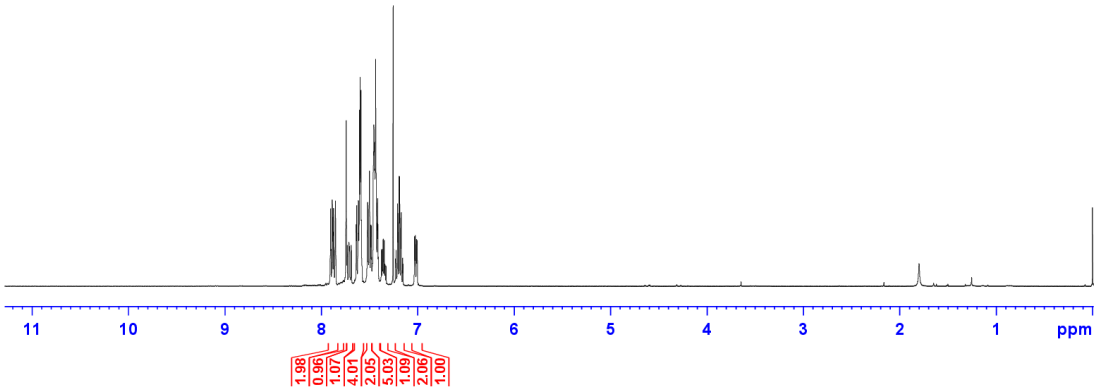
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4aq**]

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

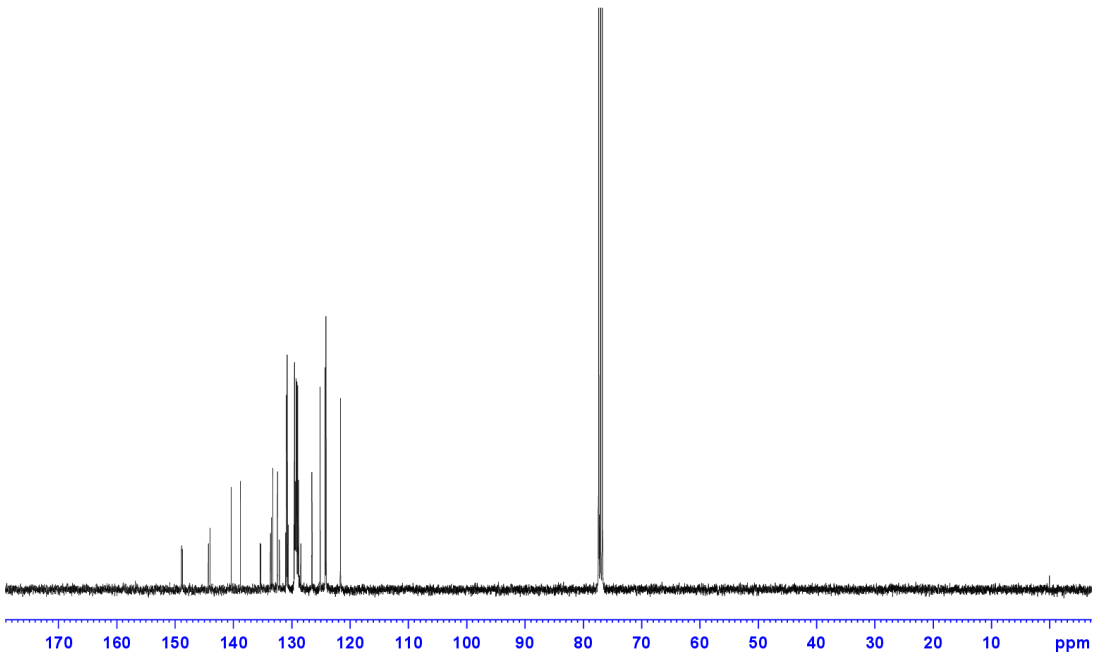


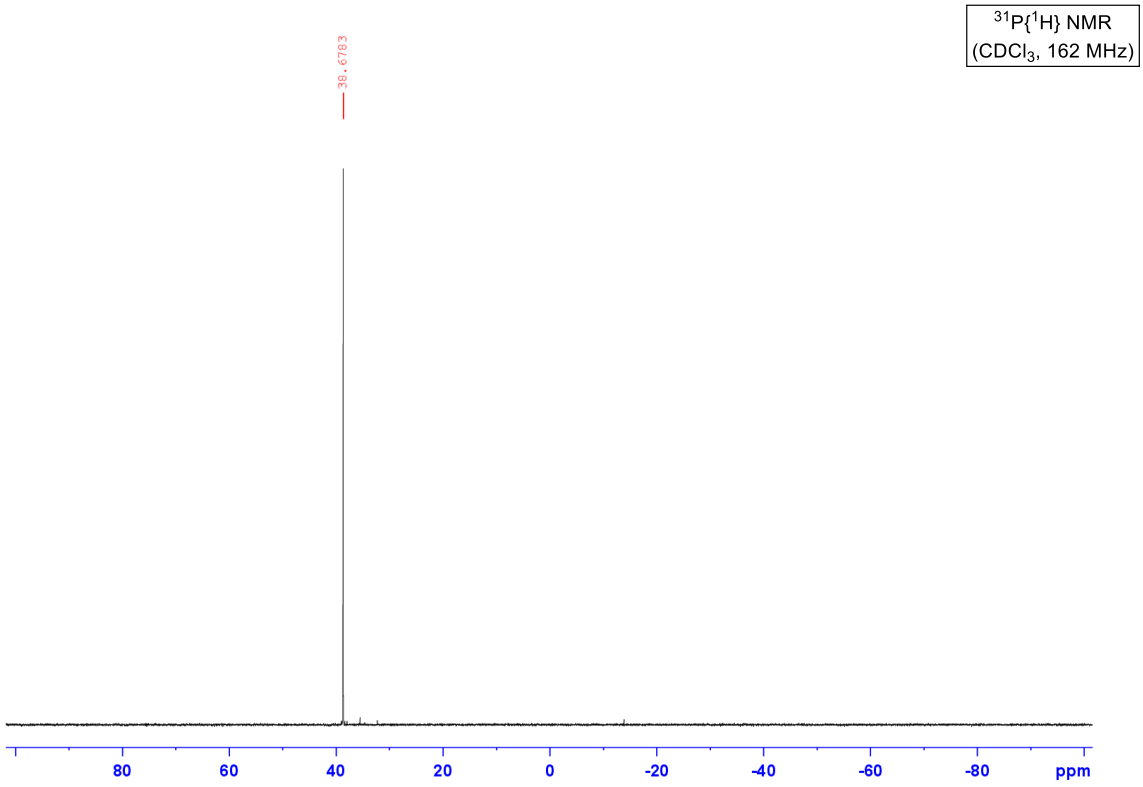


4aq



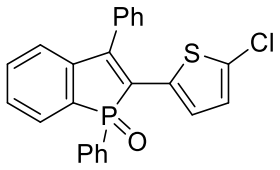
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



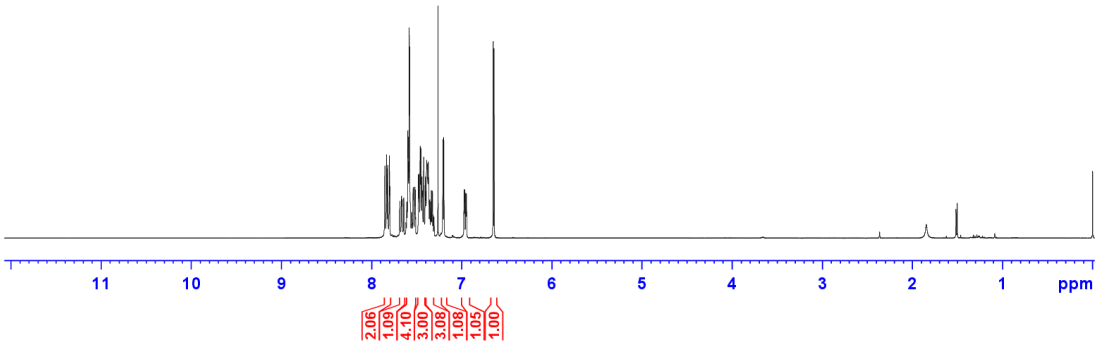

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
38.6783
80
60
40
20
0
-20
-40
-60
-80
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ar**]

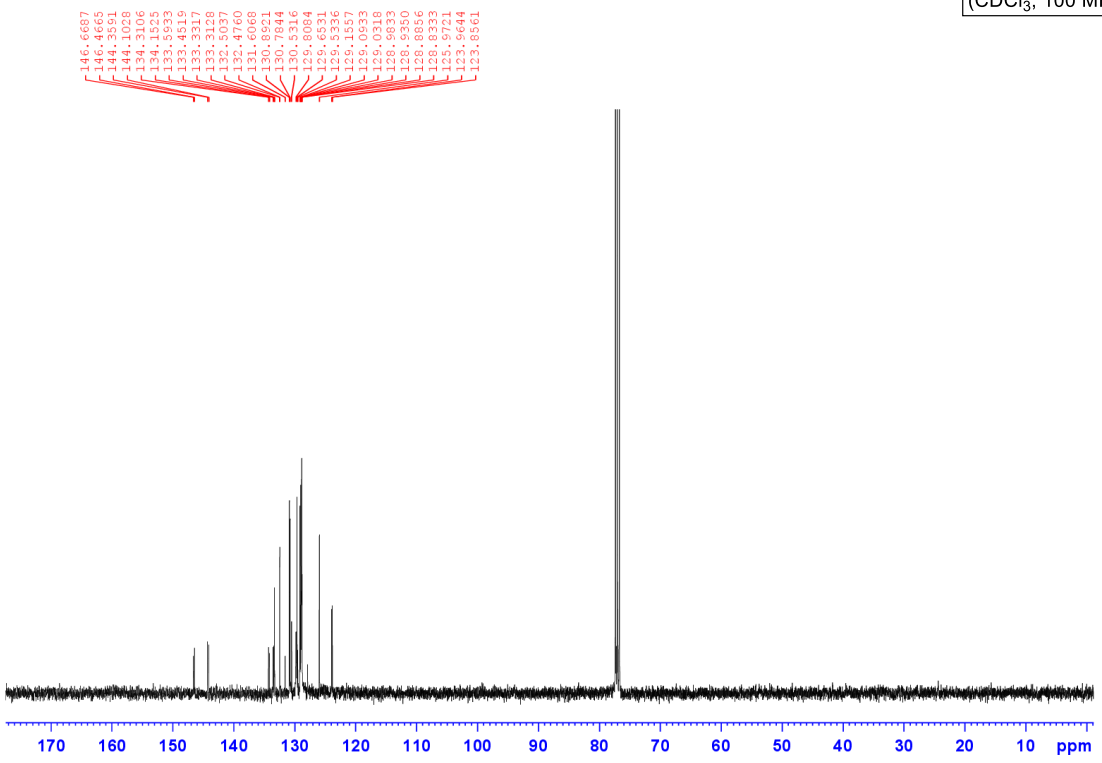
^{1}H NMR
($CDCl_3$, 400 MHz)

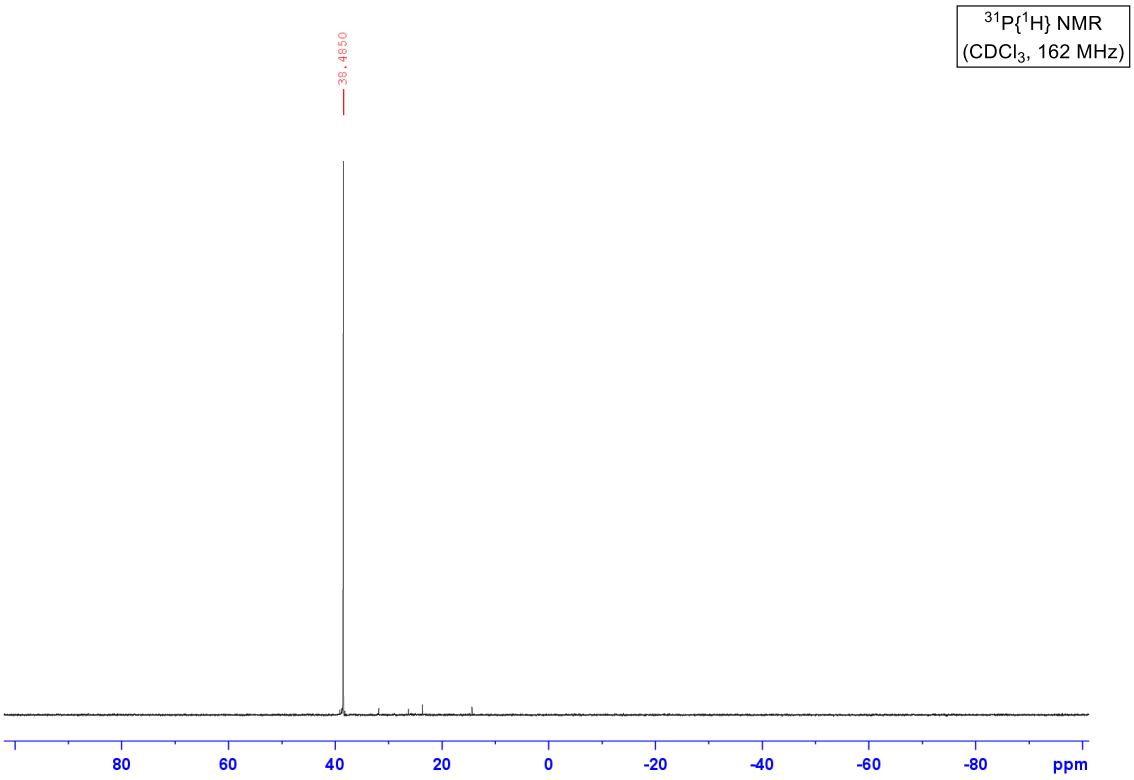


4ar



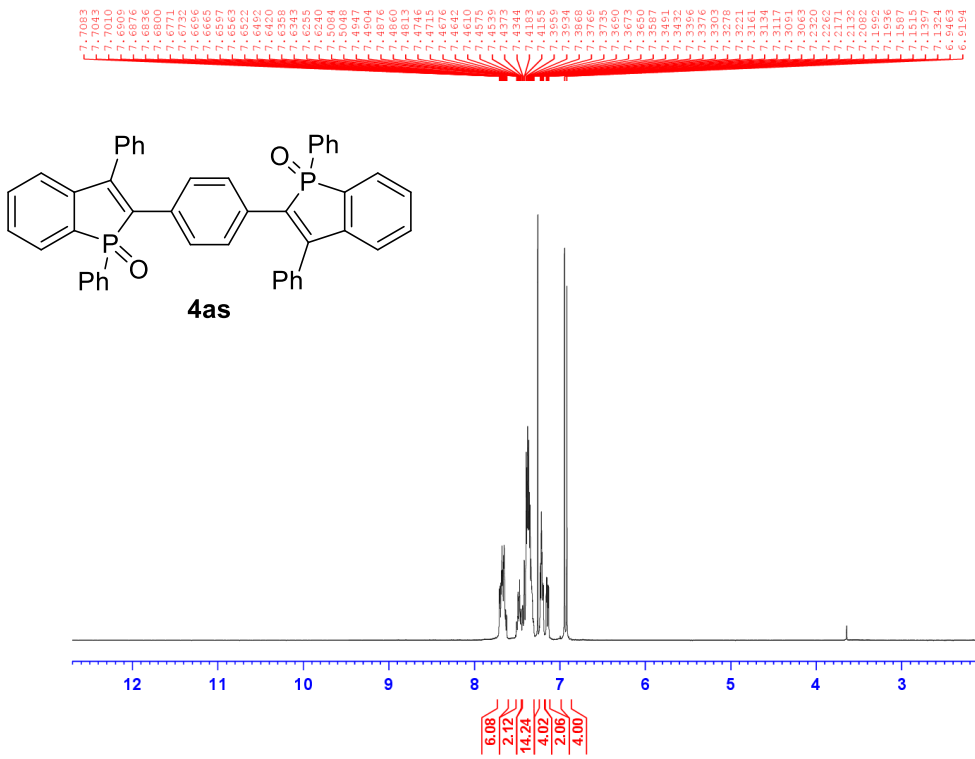
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



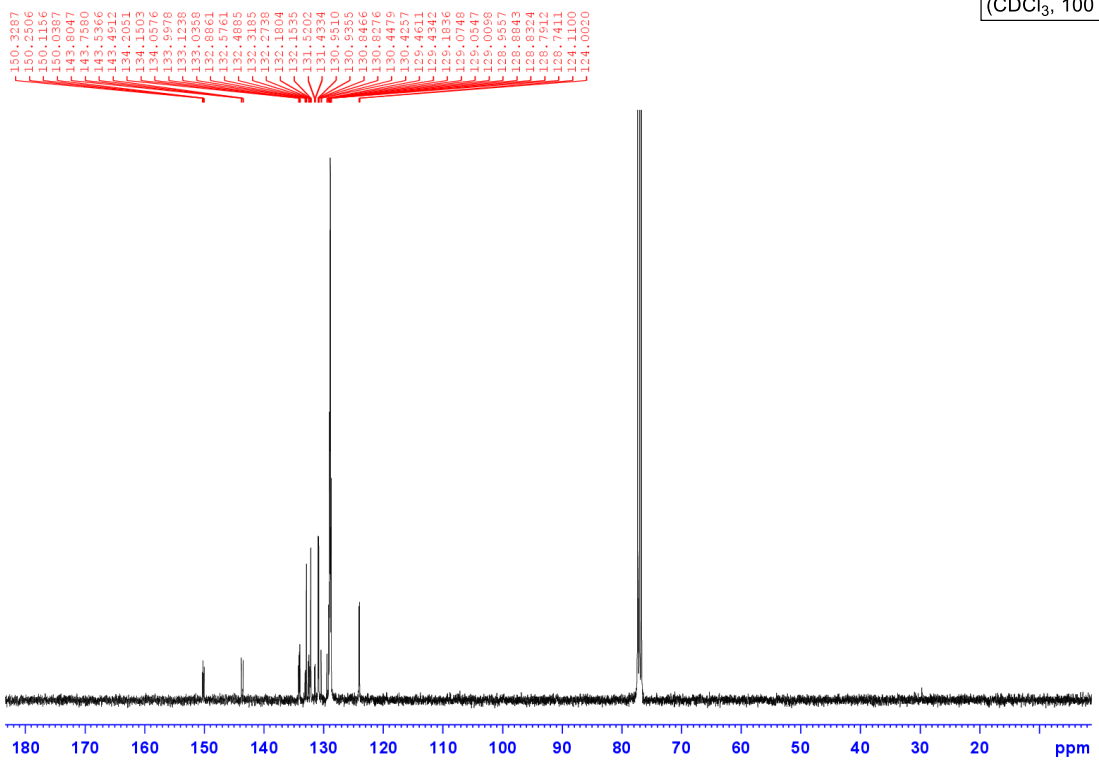

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
38.4650
80
60
40
20
0
-20
-40
-60
-80
ppm

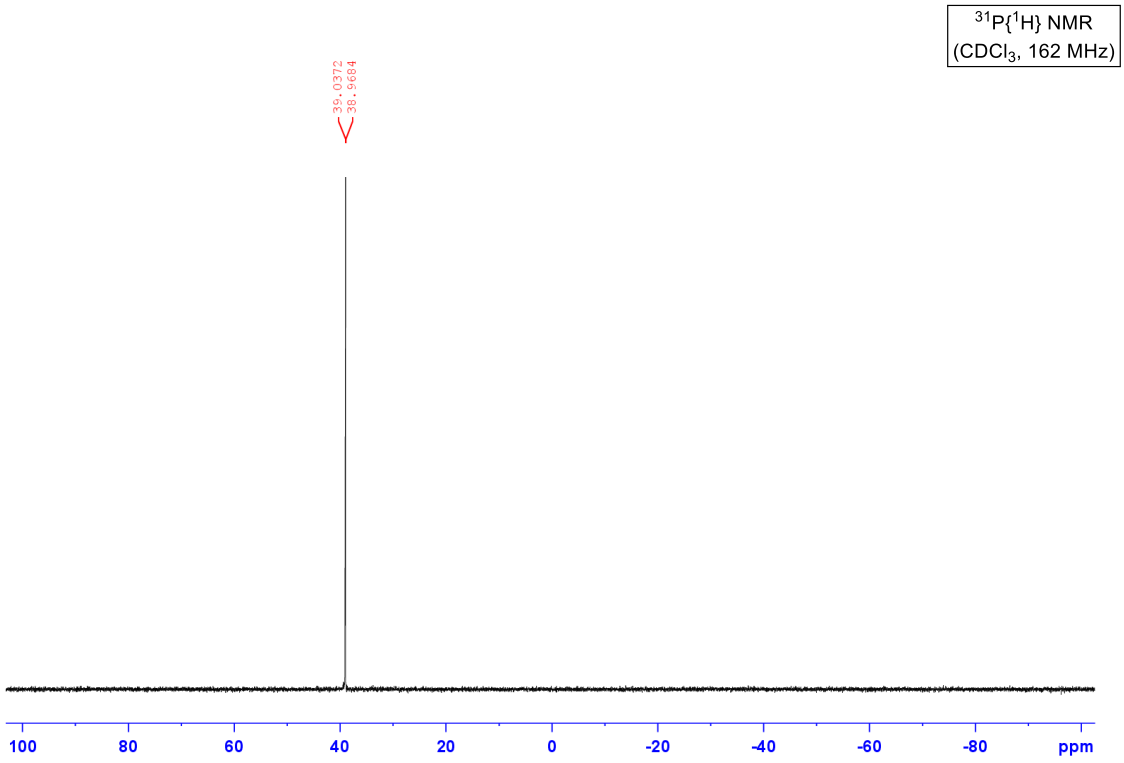
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4as**]

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



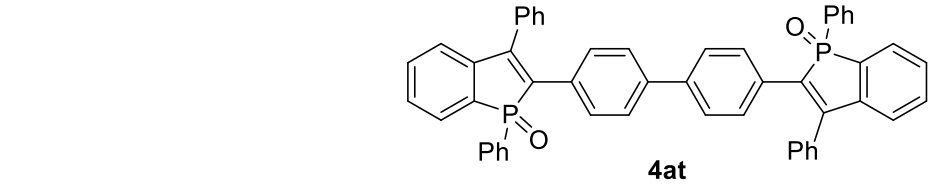
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



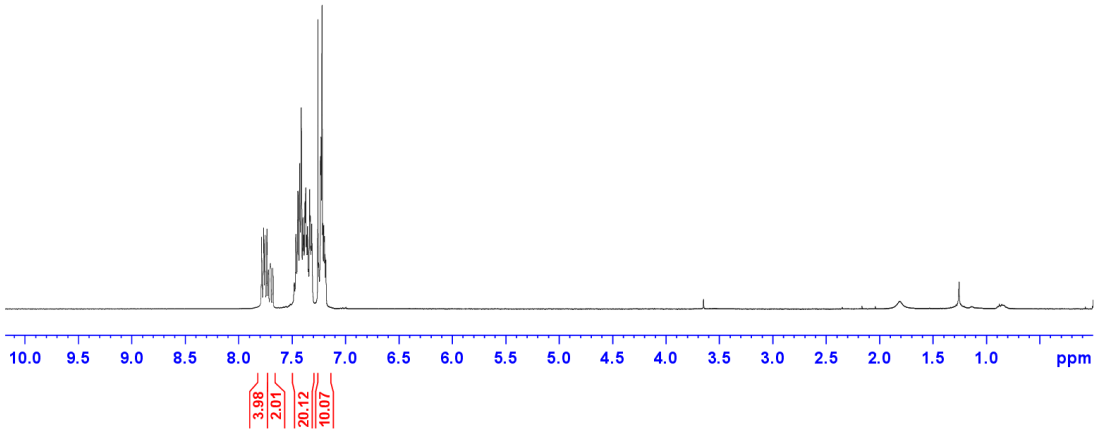

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.0372
38.9684
100
80
60
40
20
0
-20
-40
-60
-80
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4at**]

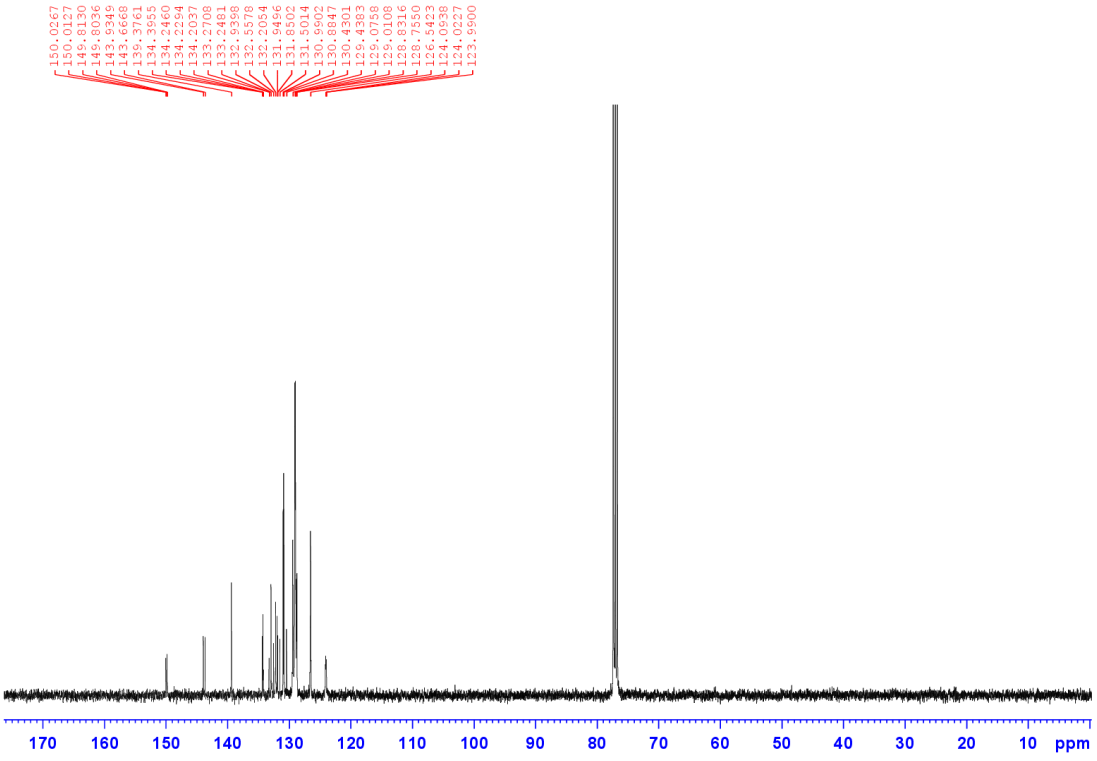
^{1}H NMR
($CDCl_3$, 400 MHz)

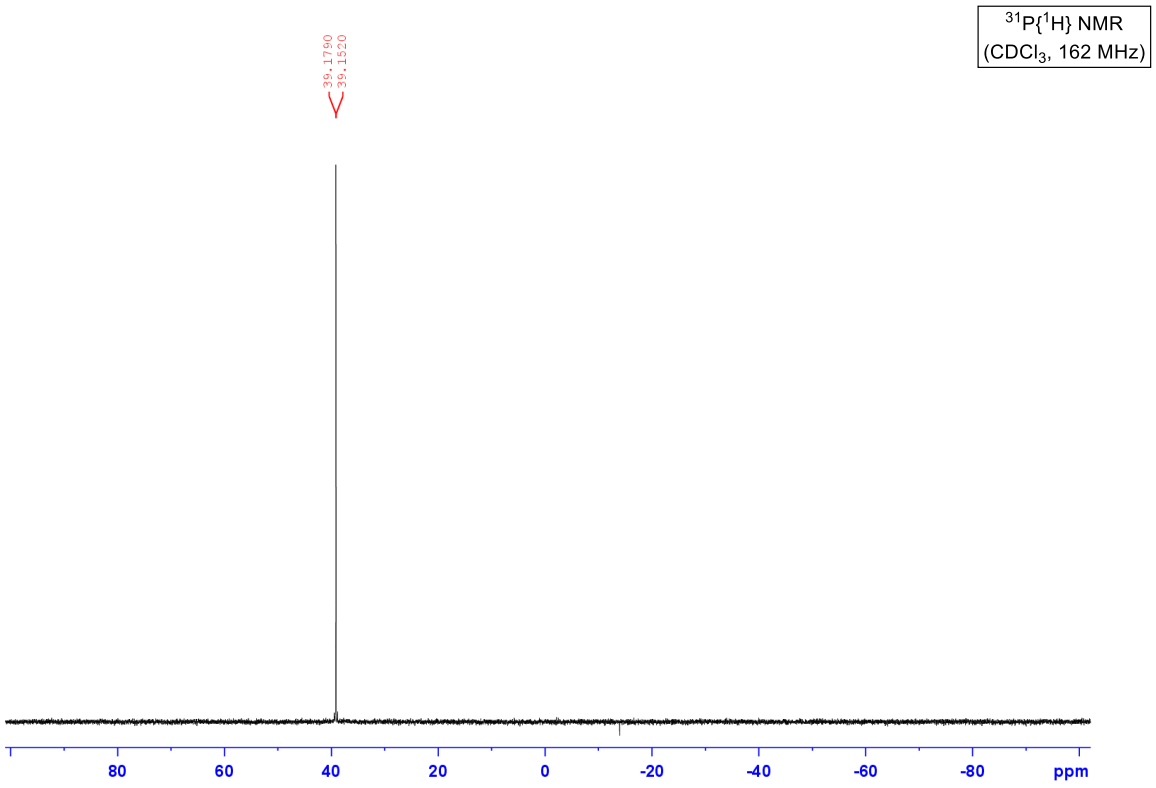


4at

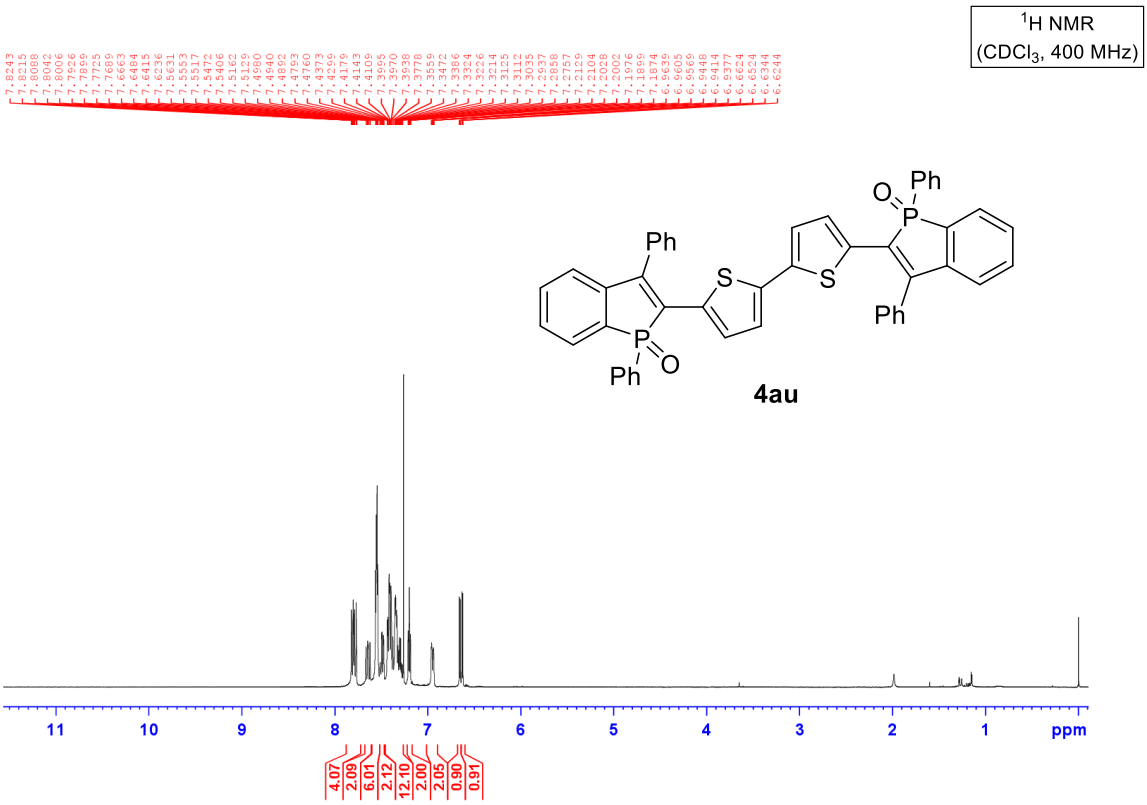


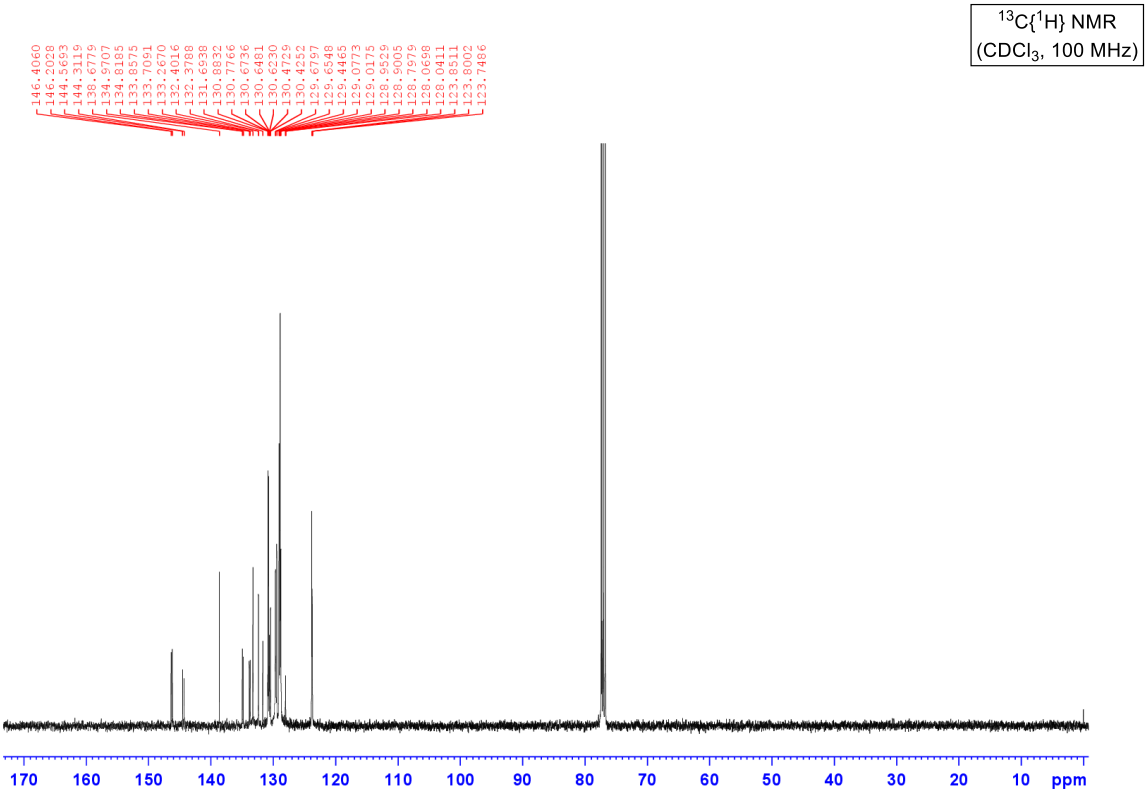
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)

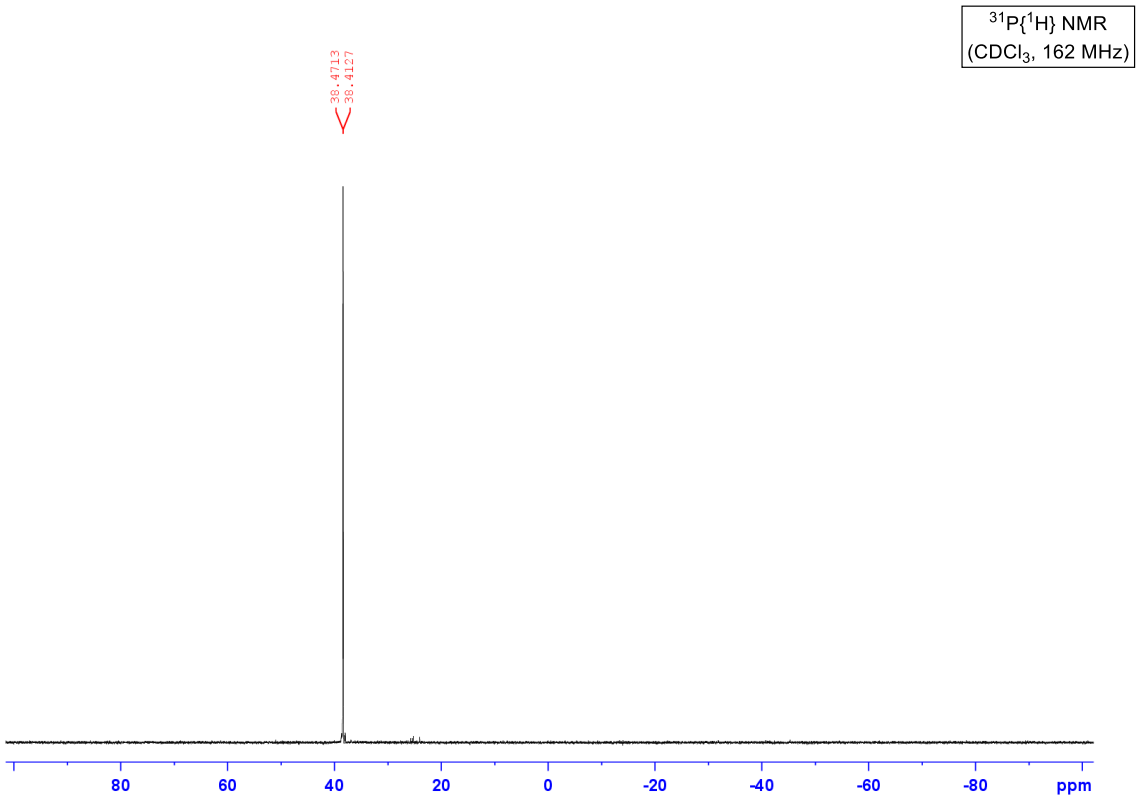



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.1790
39.1520
80
60
40
20
0
-20
-40
-60
-80
ppm

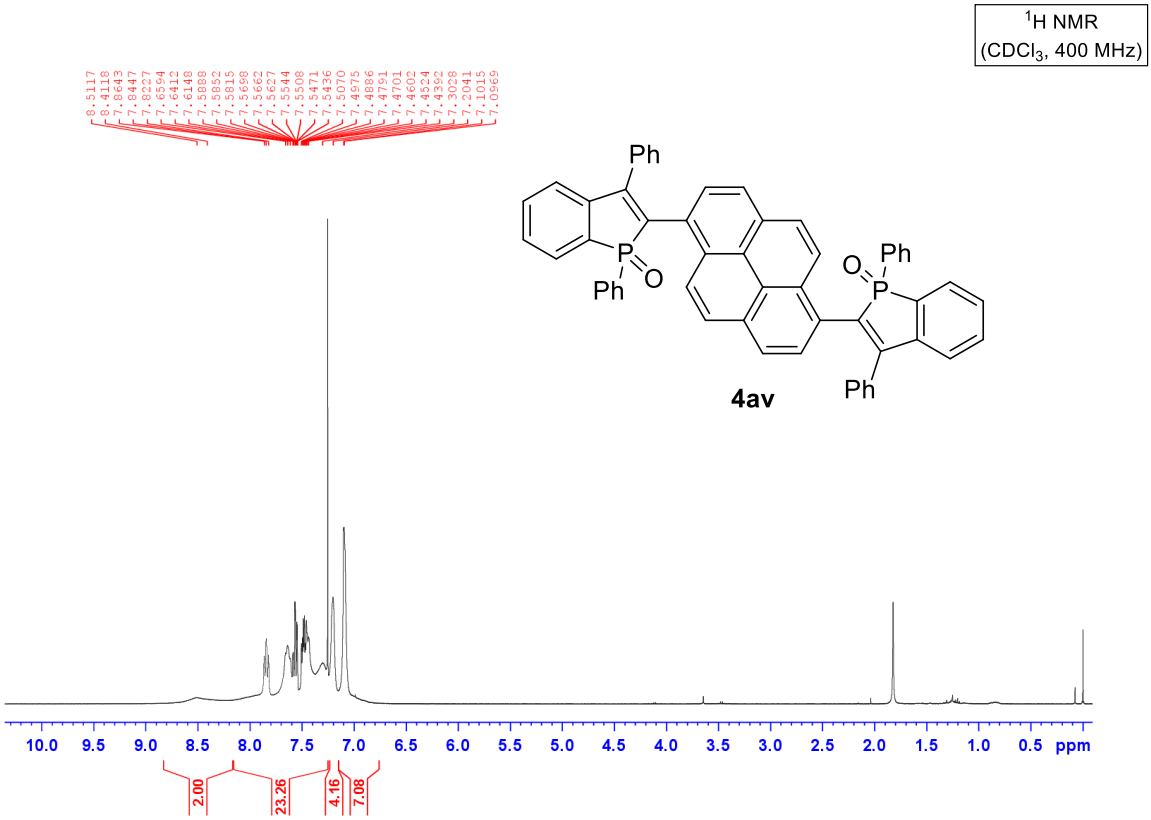
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4au**]

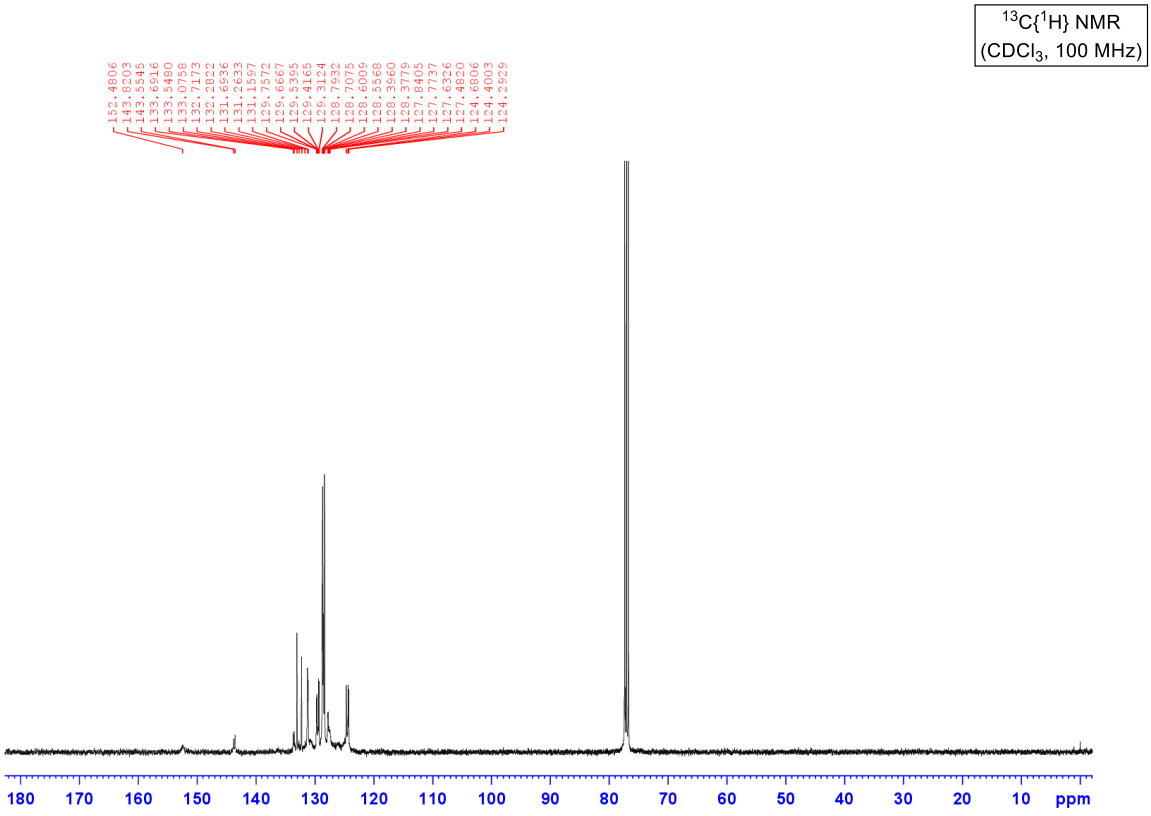


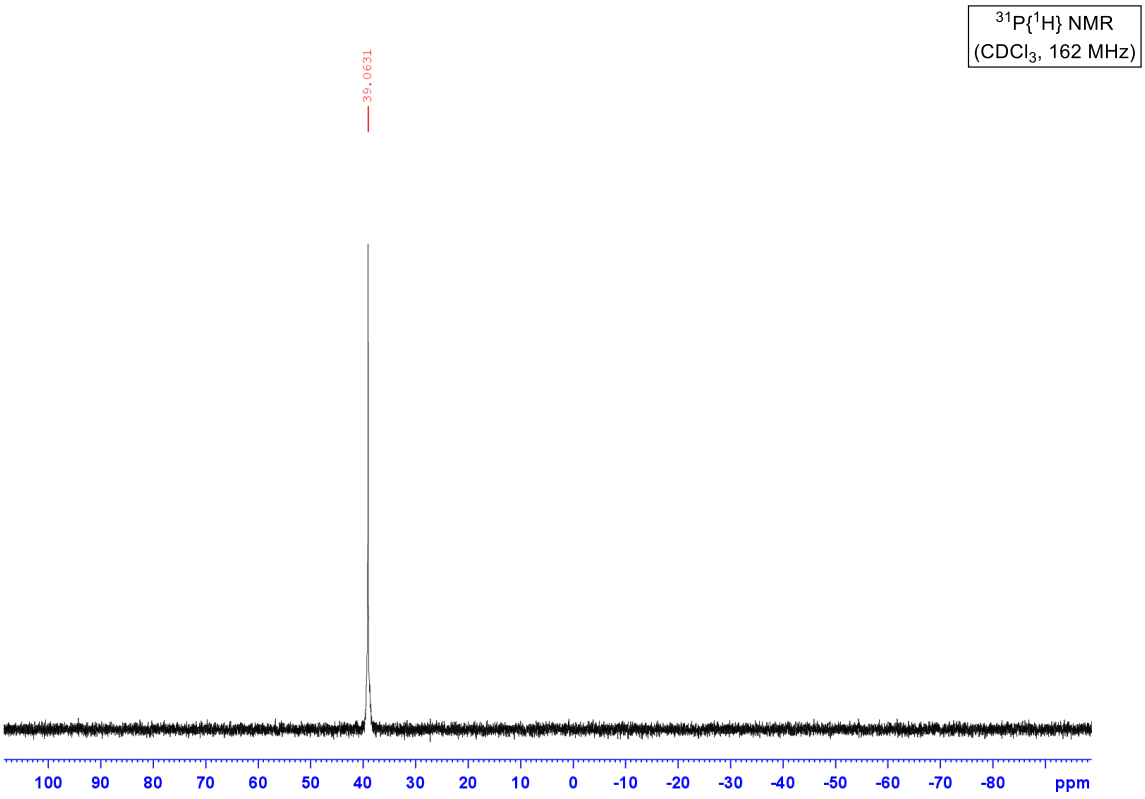



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
38.4713
38.4127
80
60
40
20
0
-20
-40
-60
-80
ppm

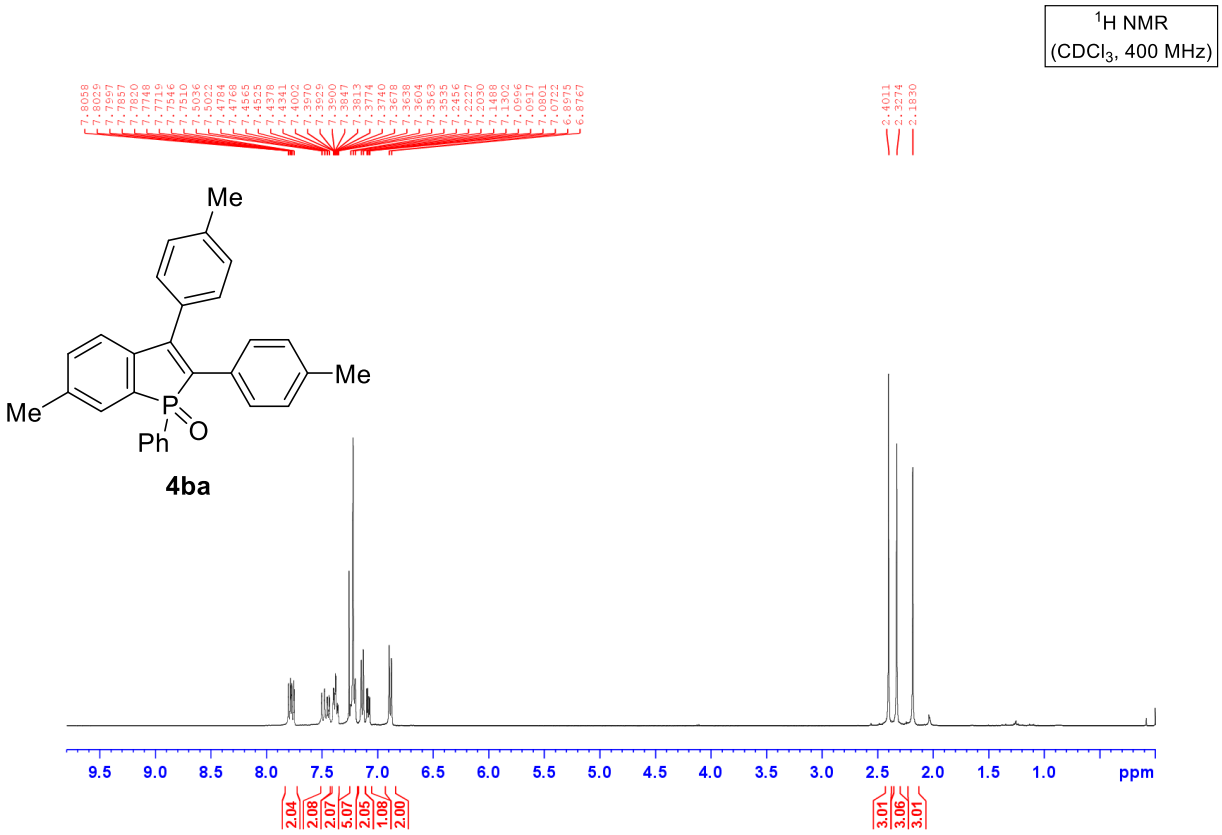
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4av**]

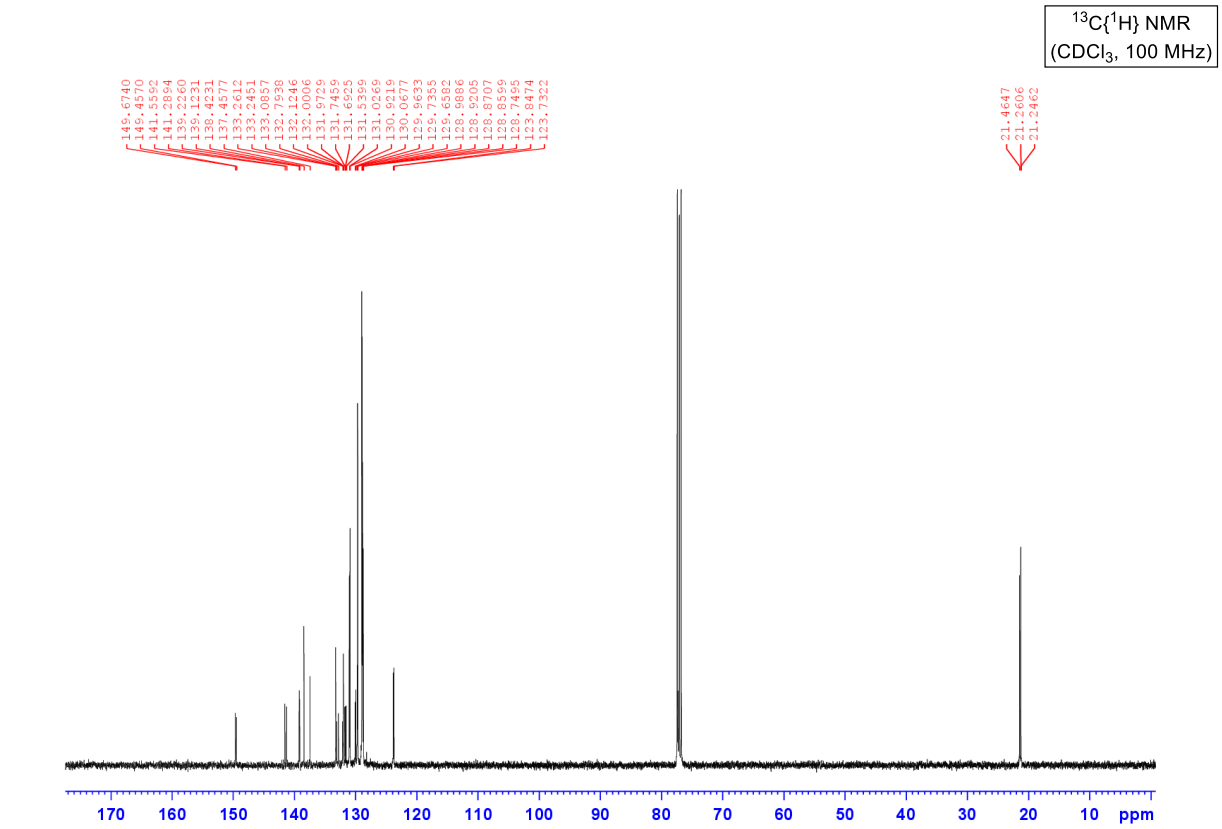


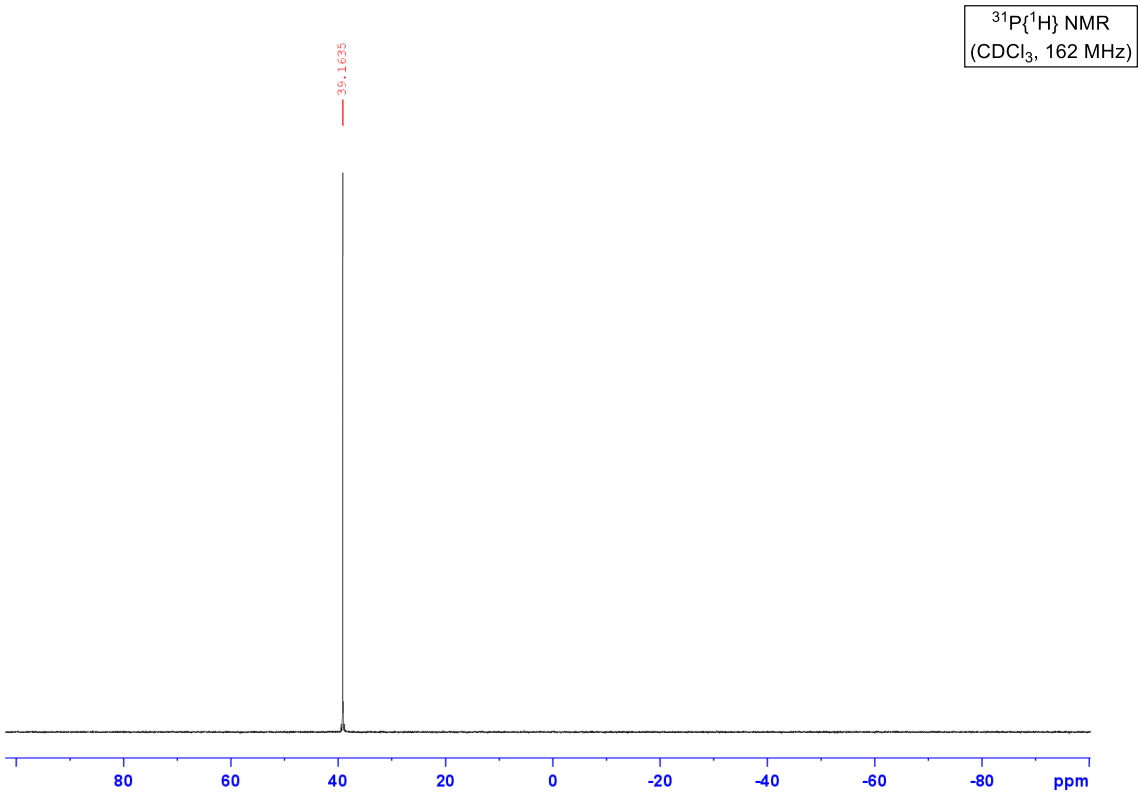



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
35.0631
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ba**]

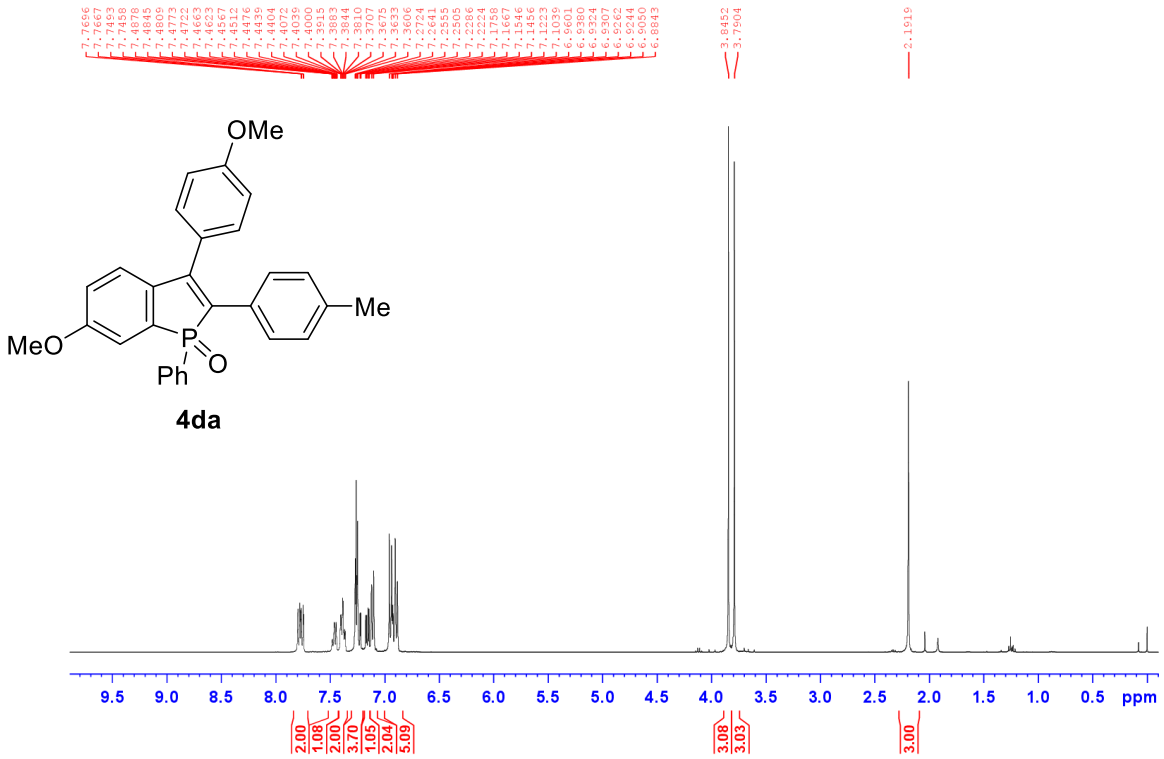




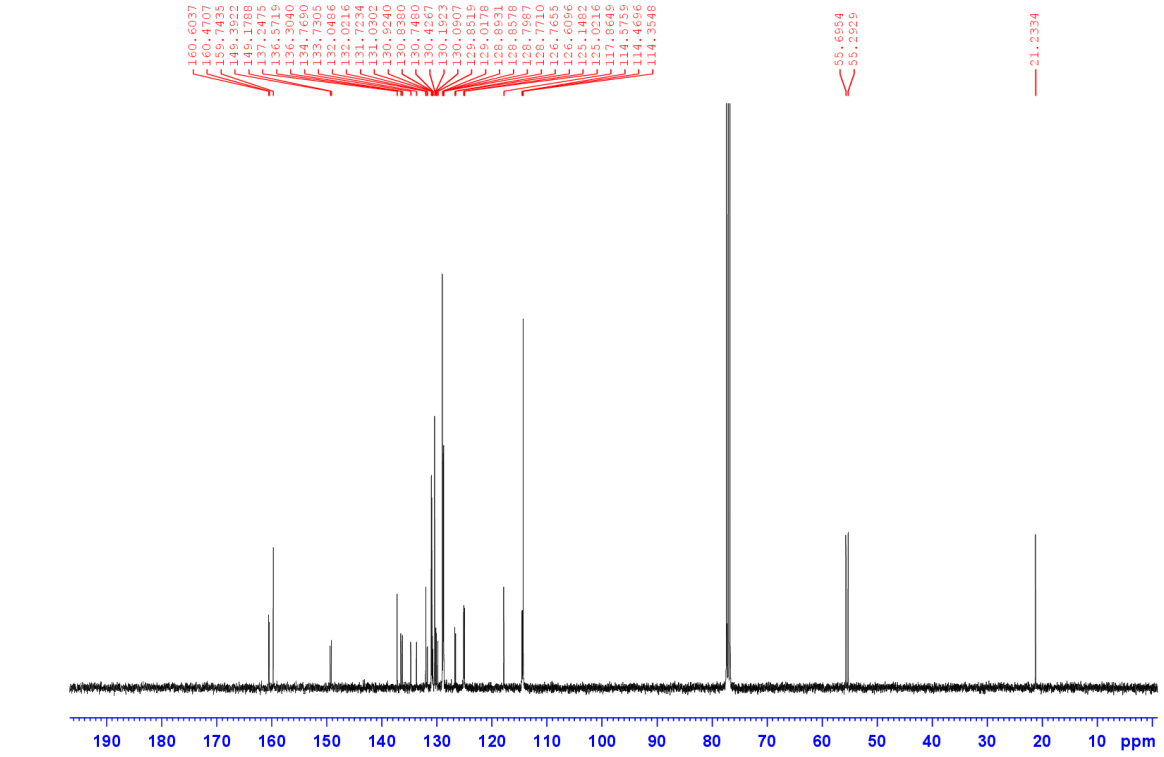

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.1635
80
60
40
20
0
-20
-40
-60
-80
ppm

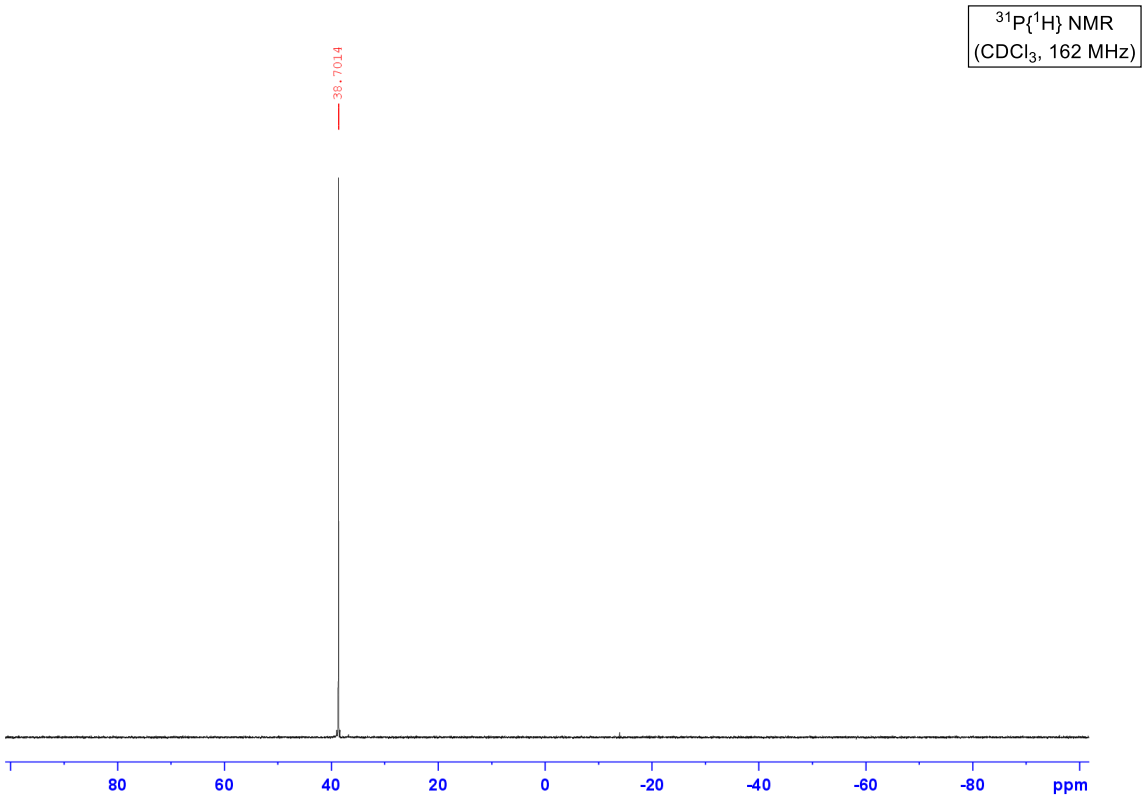
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4da**]

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



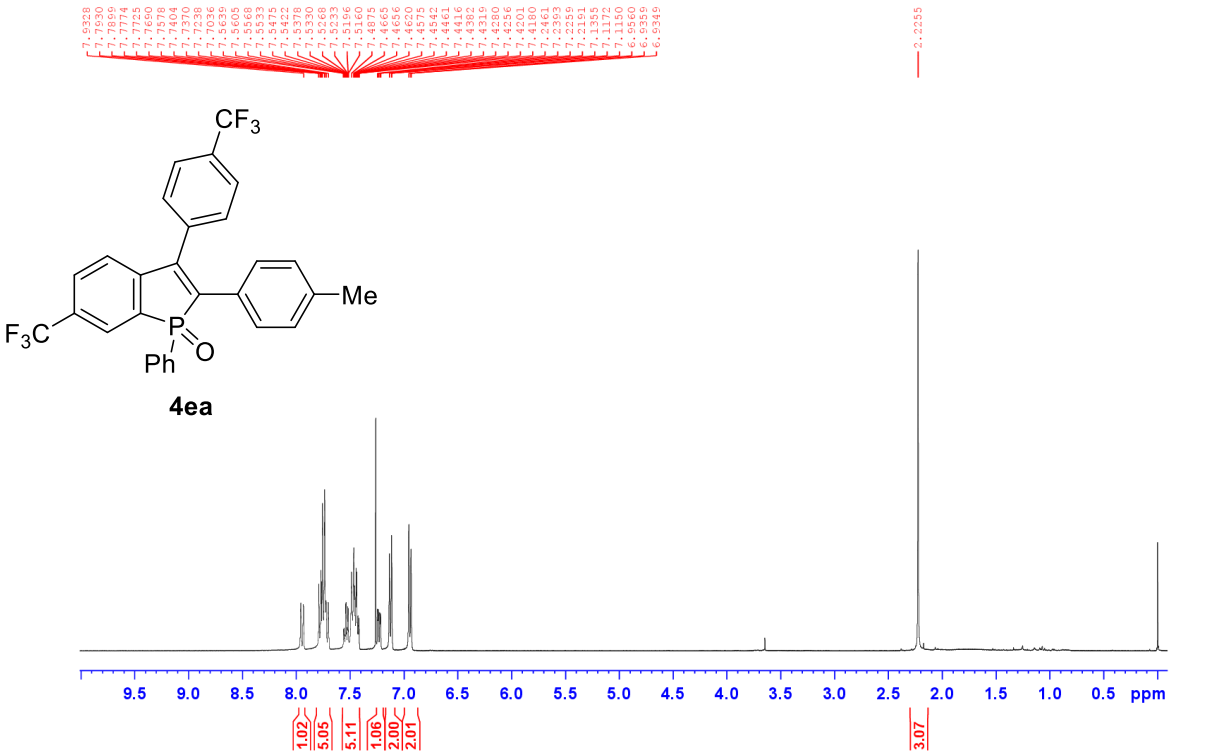
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



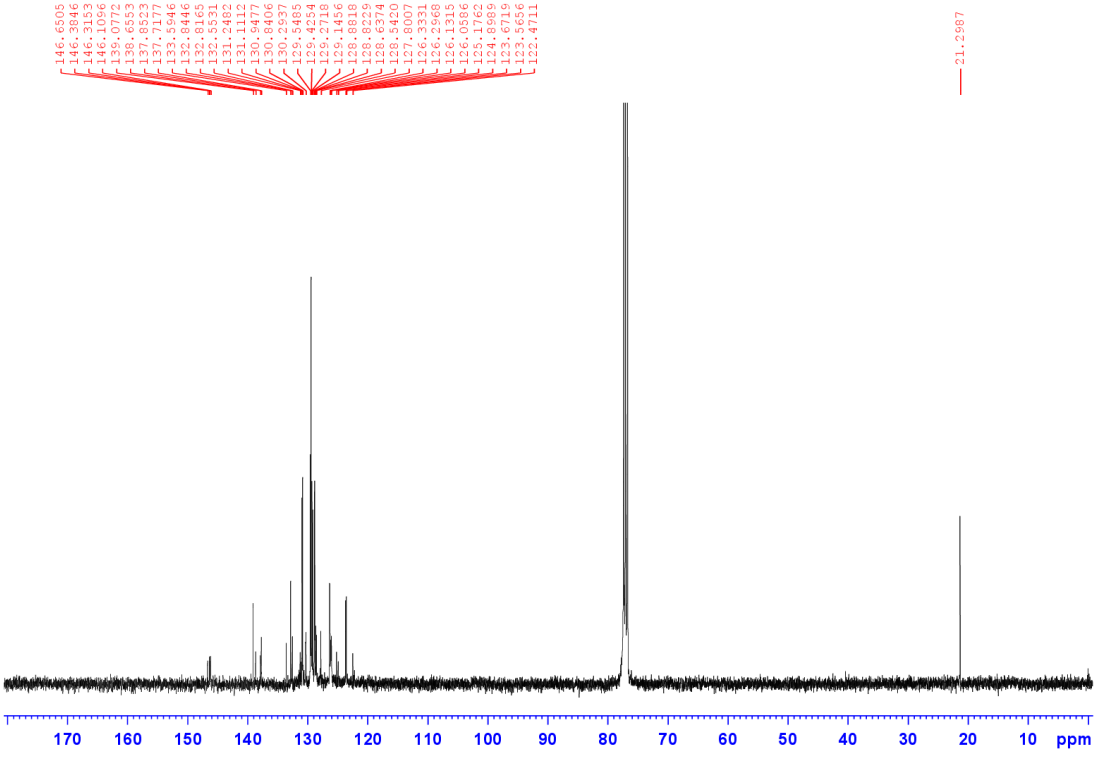

$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
38.7014
80
60
40
20
0
-20
-40
-60
-80
ppm

[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ea**]

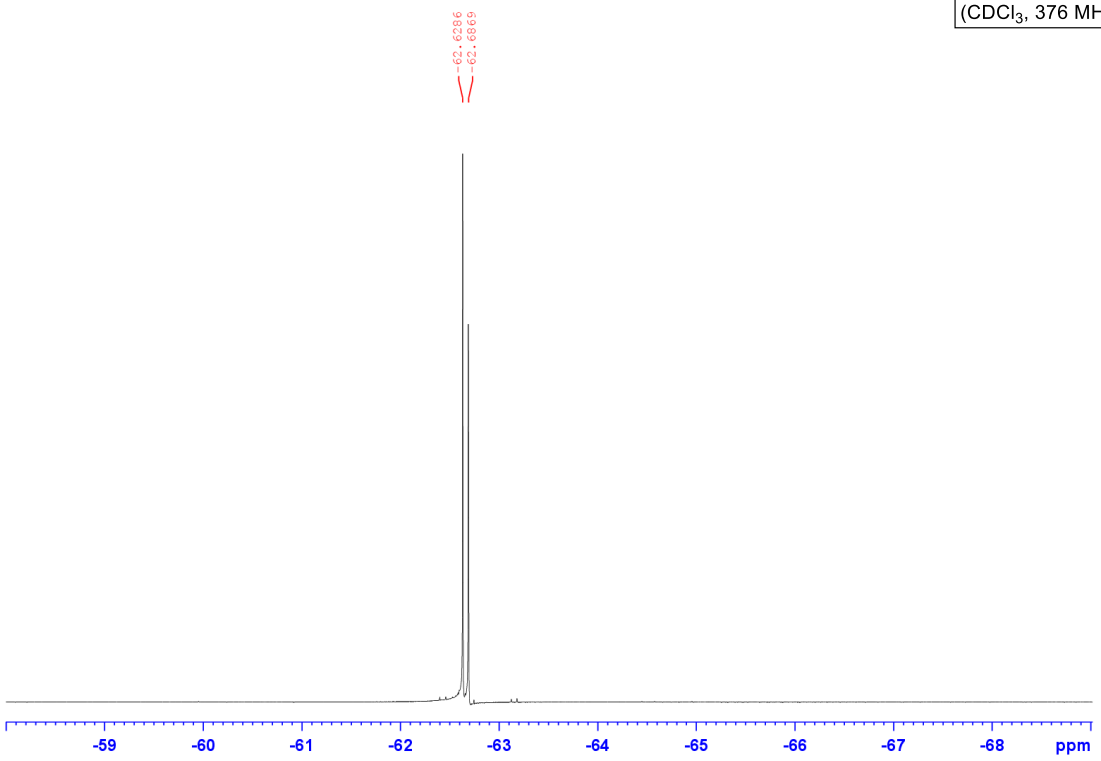
^{1}H NMR
($CDCl_3$, 400 MHz)



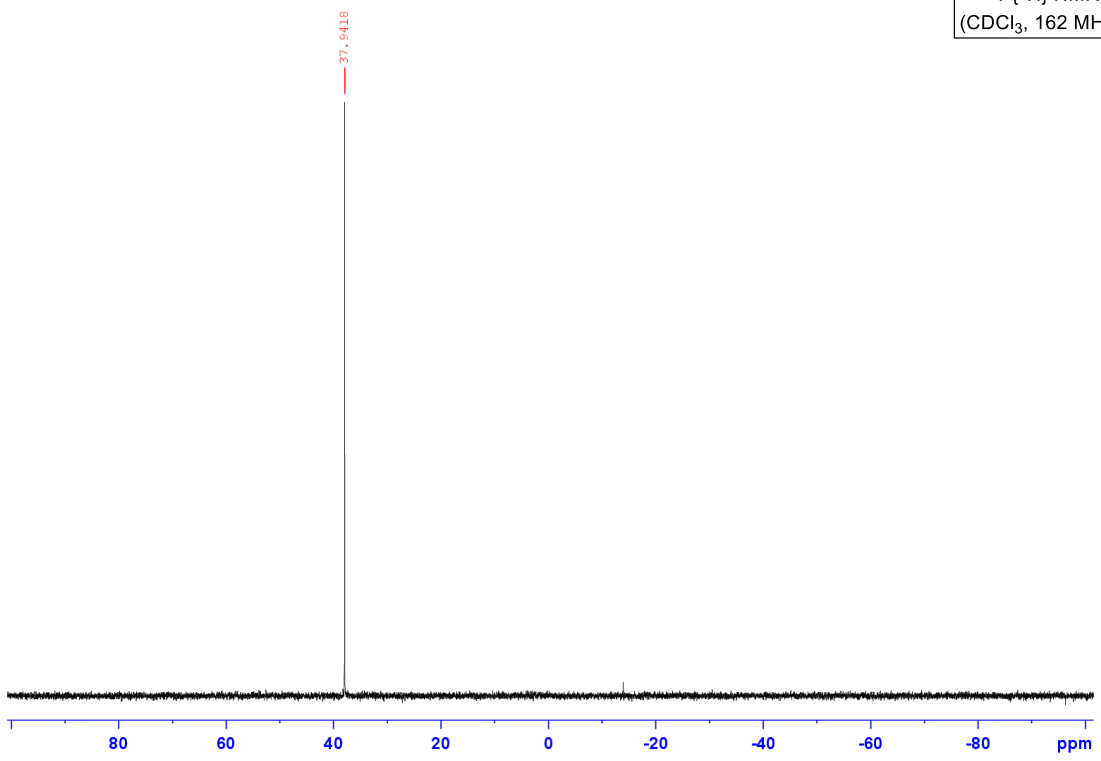
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



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

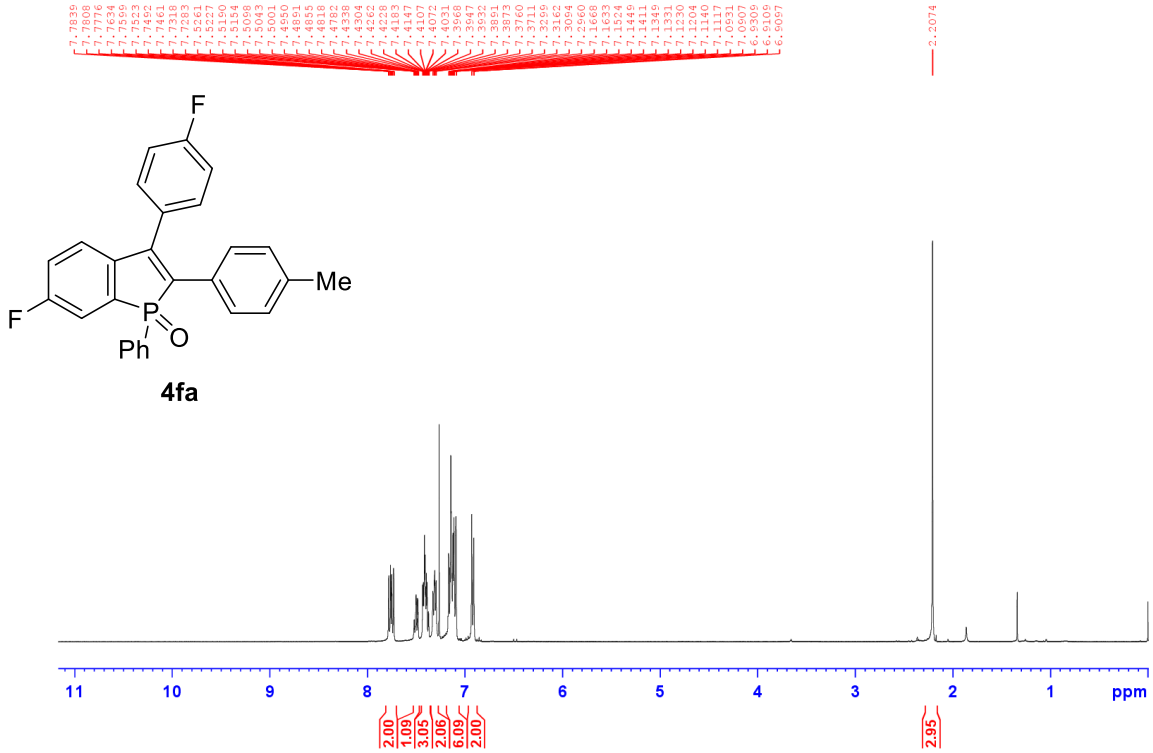


$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)

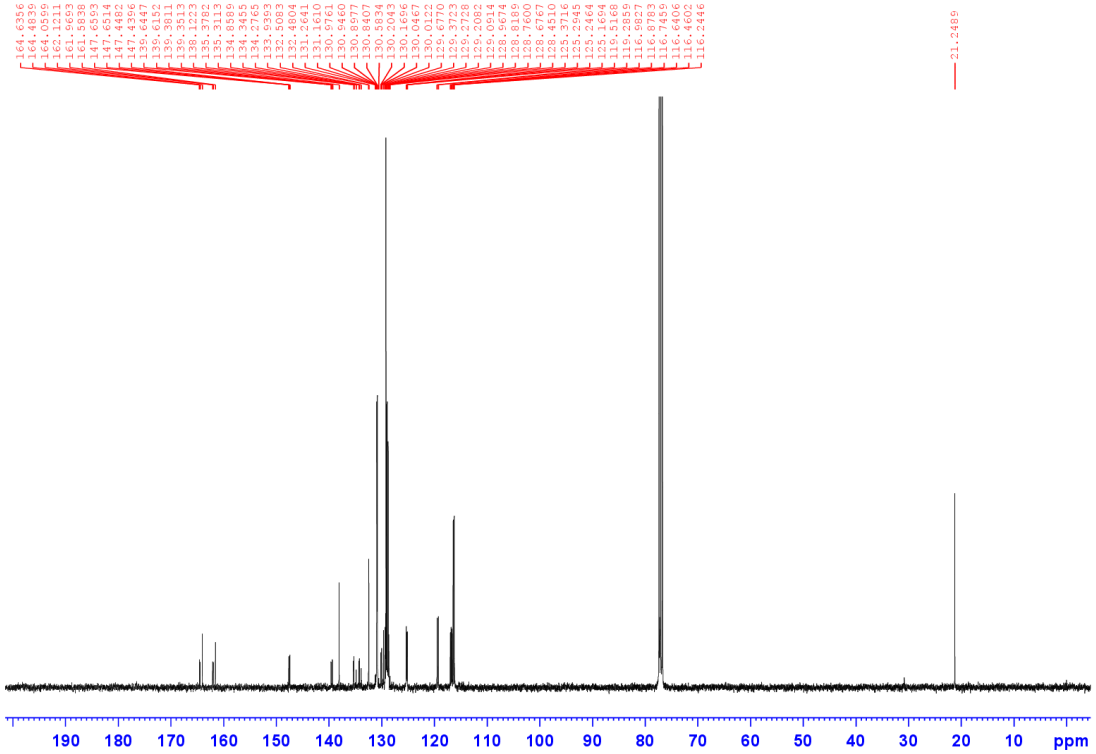


[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4fa**]

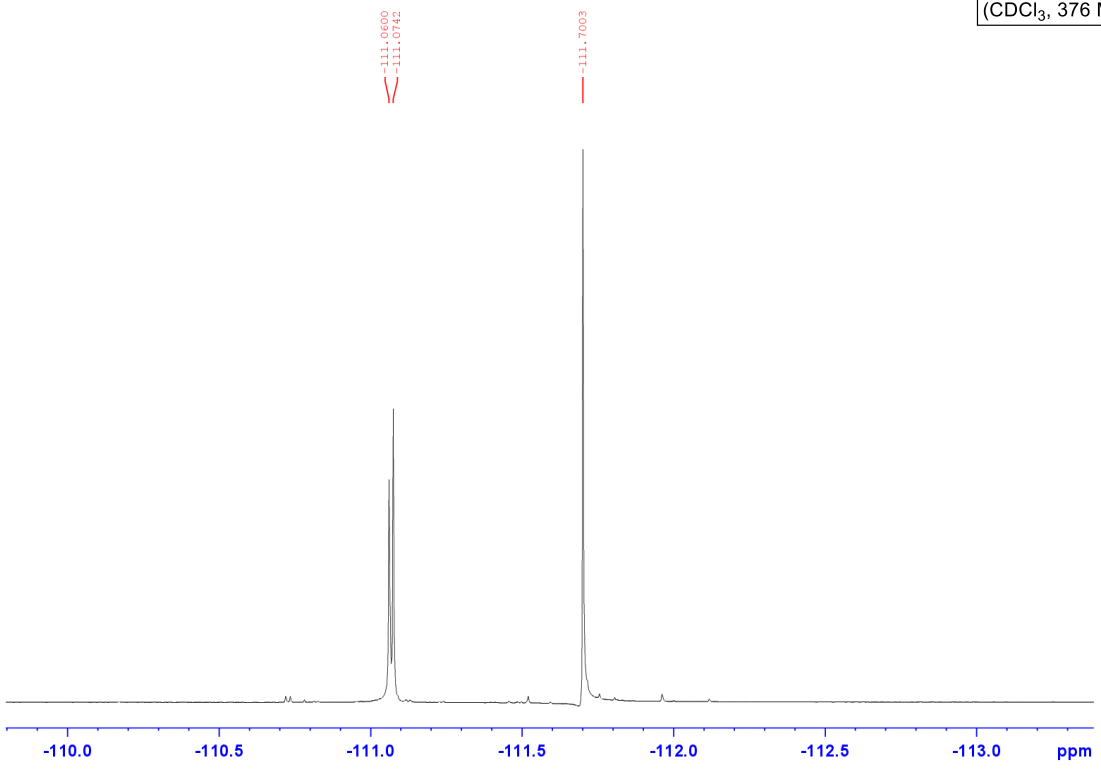
^{1}H NMR
($CDCl_3$, 400 MHz)



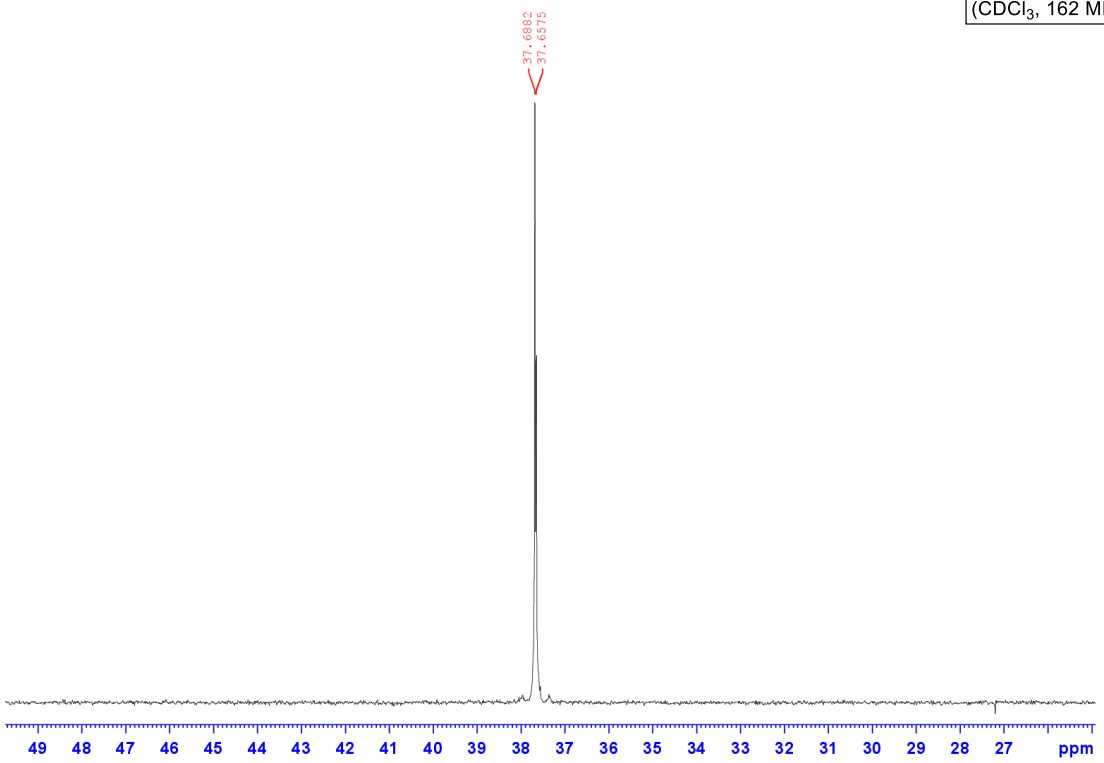
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)



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

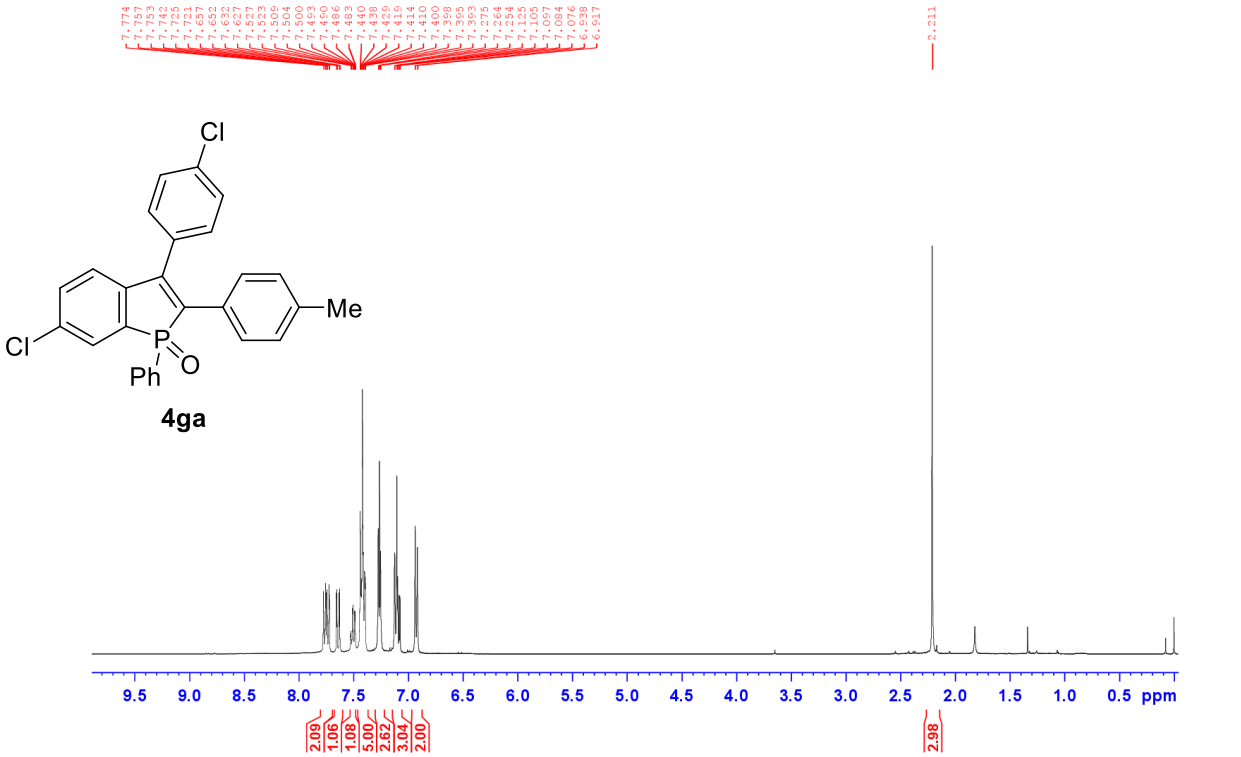


$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)

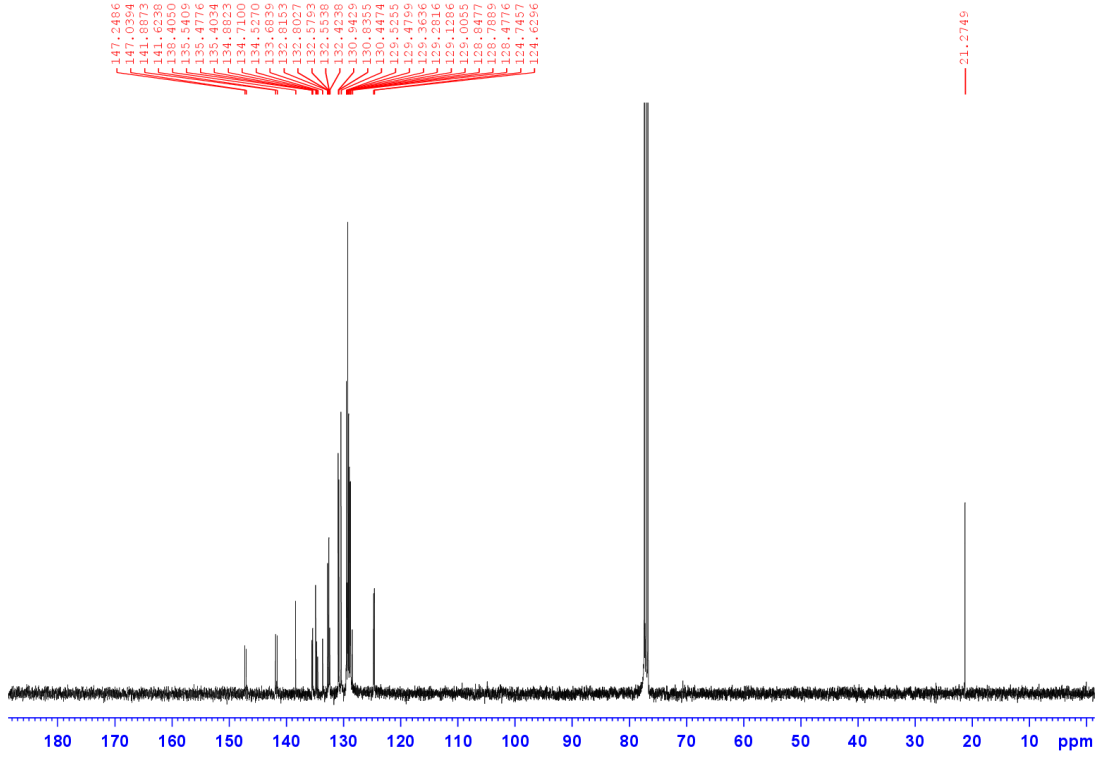


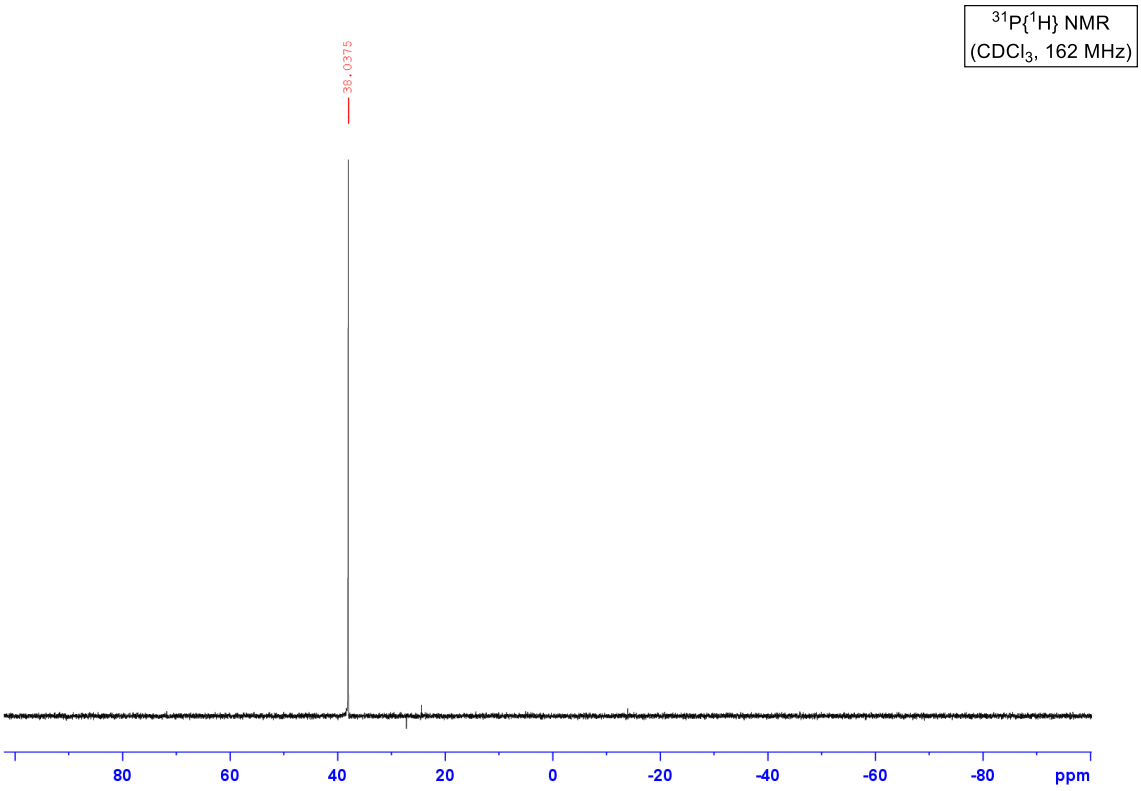
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ga**]

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



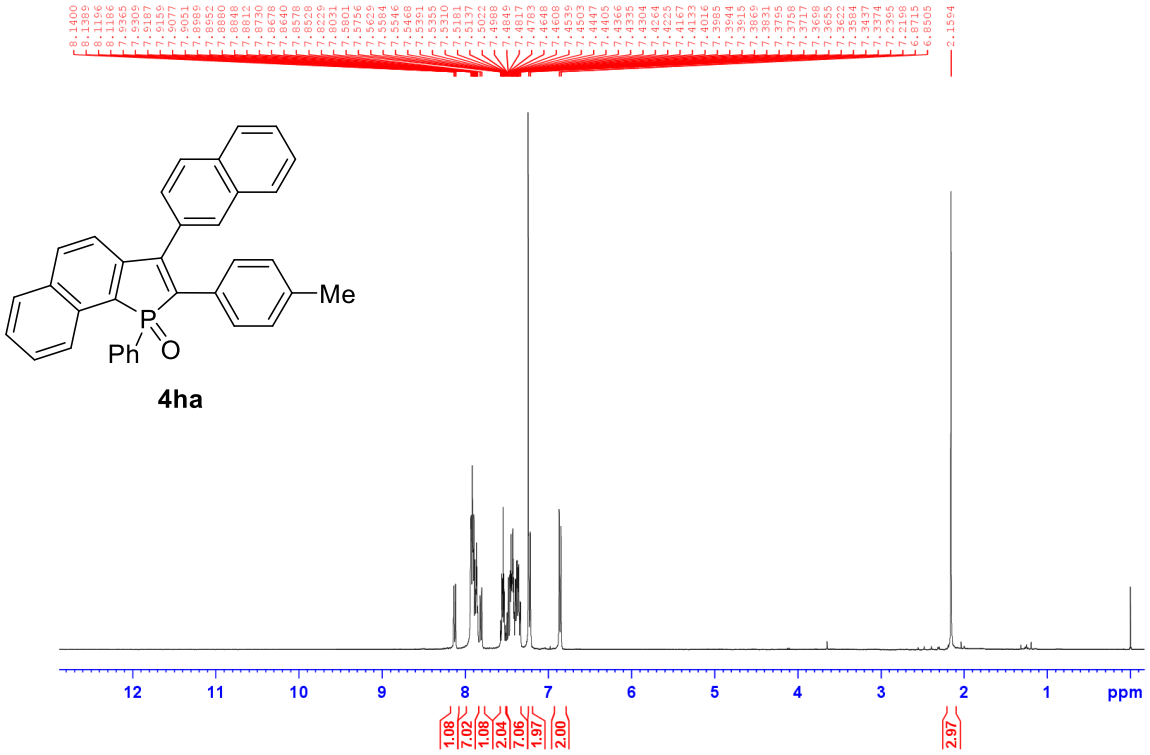
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)




$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
38.0375
80
60
40
20
0
-20
-40
-60
-80
ppm

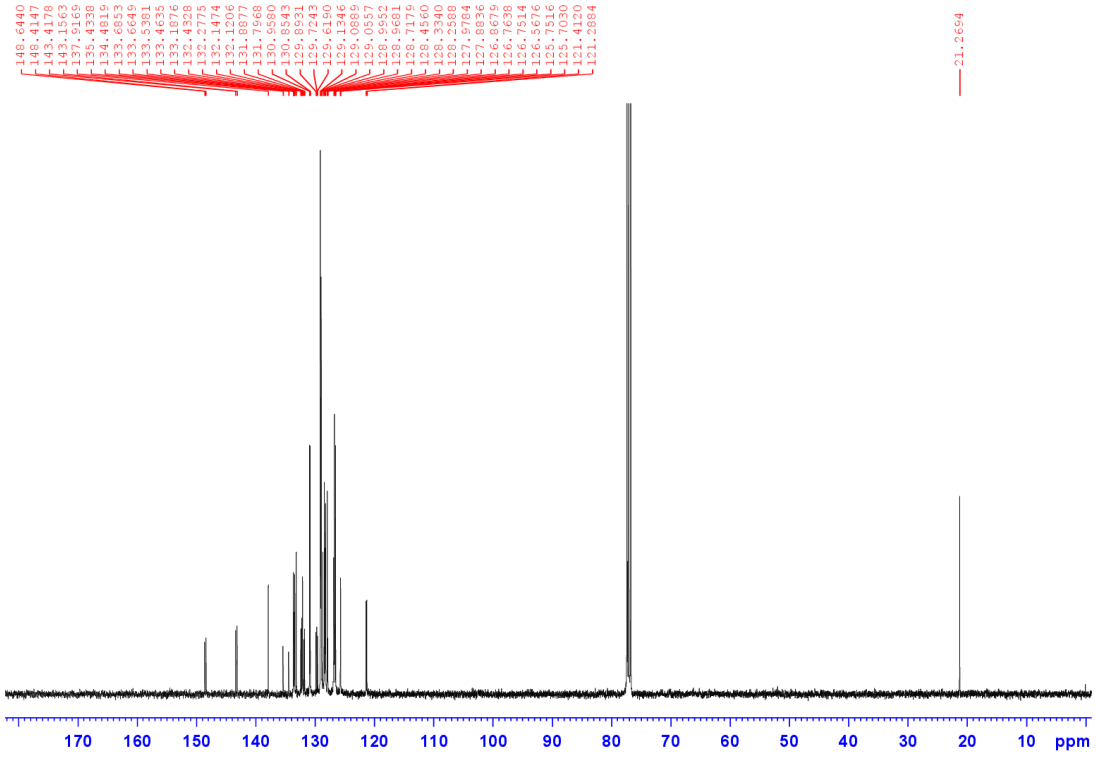
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ha**]

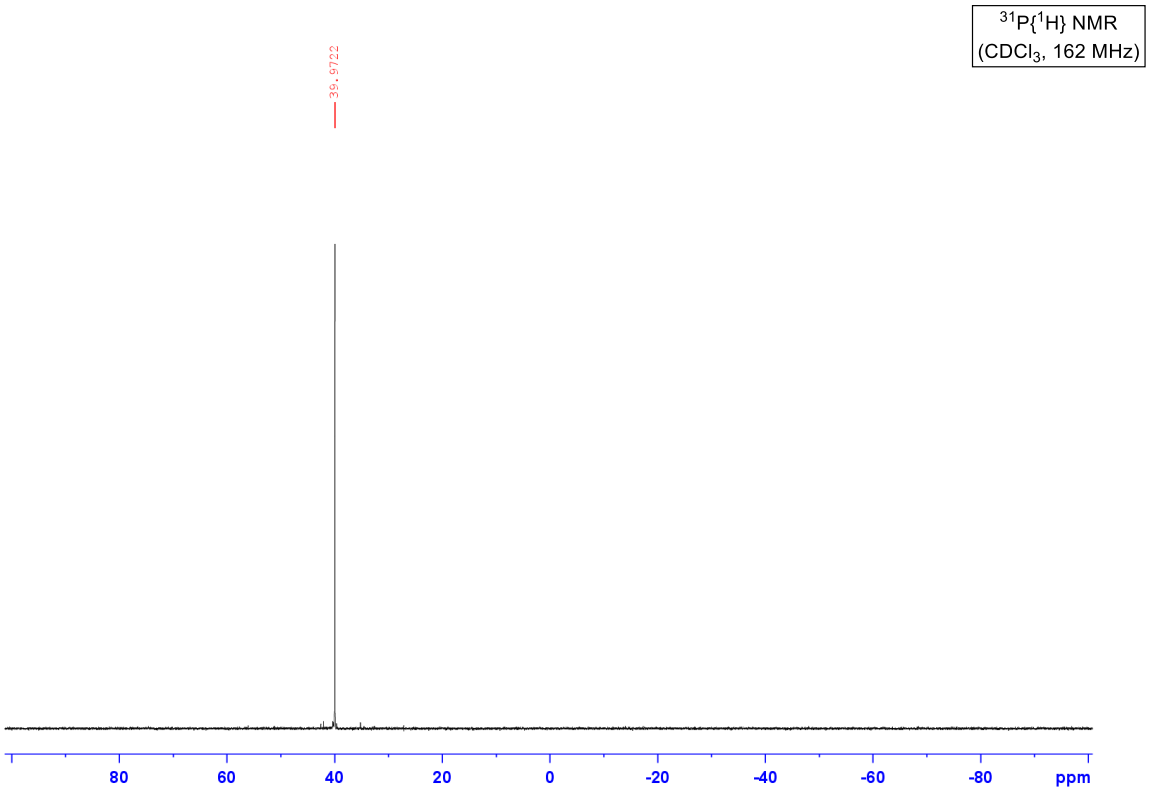
^{1}H NMR
($CDCl_3$, 400 MHz)



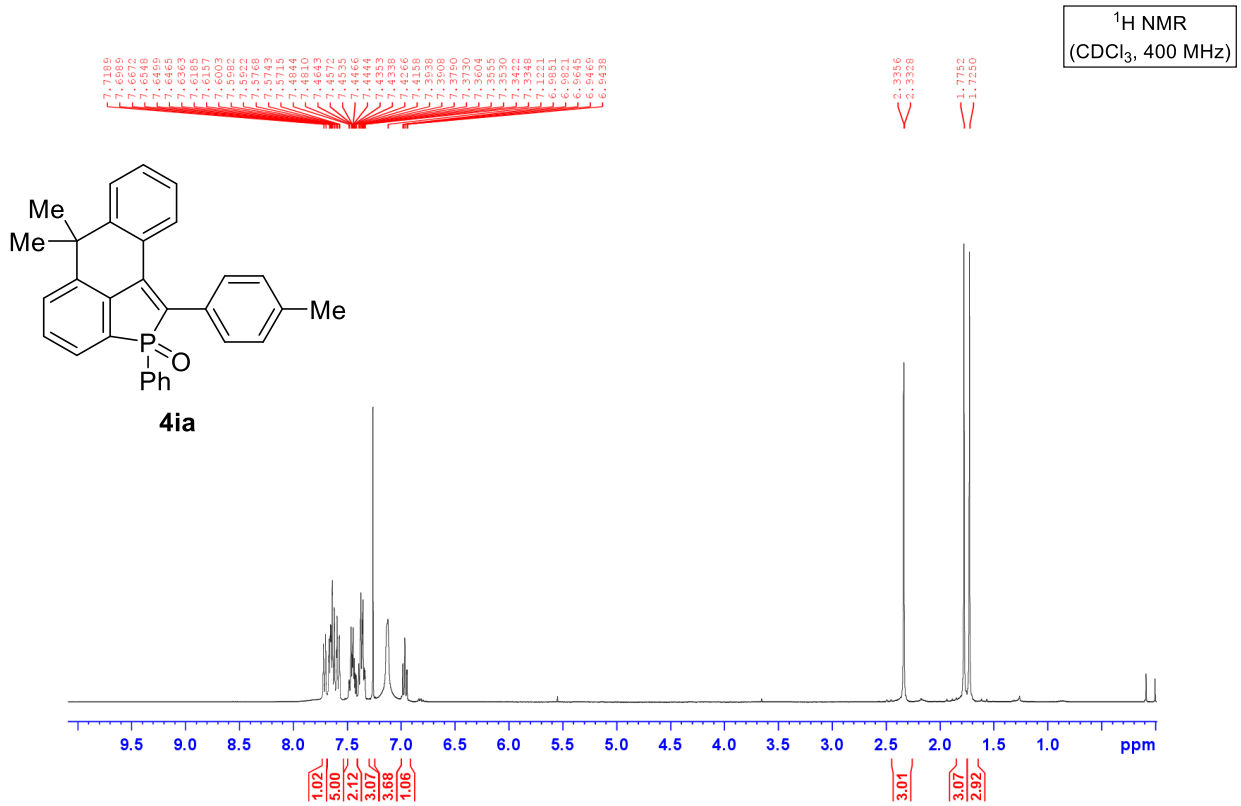
4ha

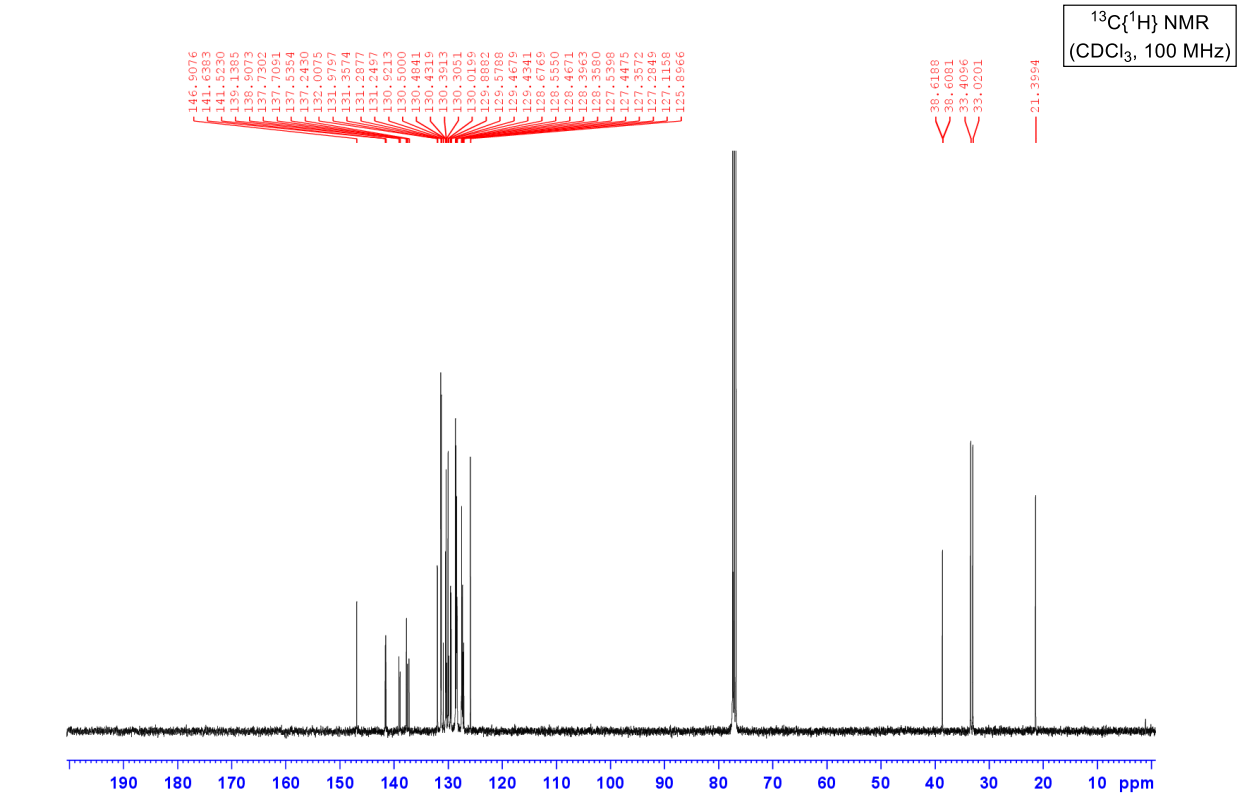
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)

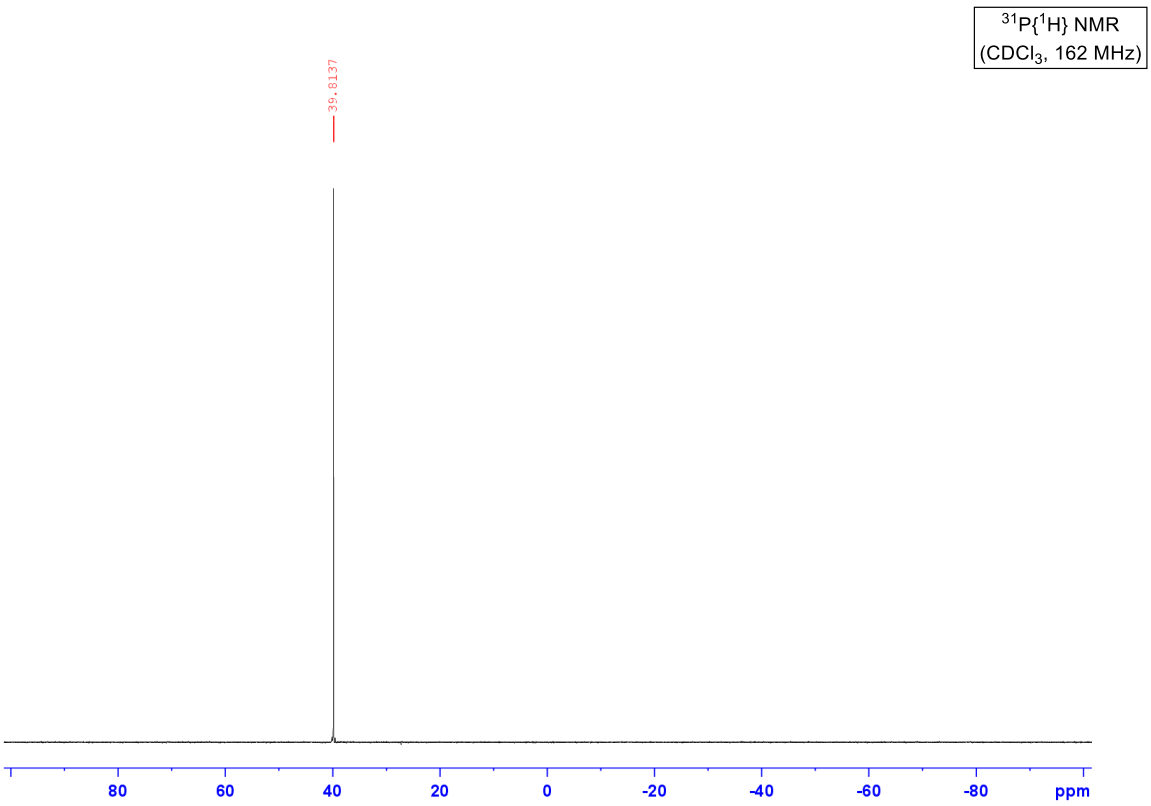



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.9722
80
60
40
20
0
-20
-40
-60
-80
ppm

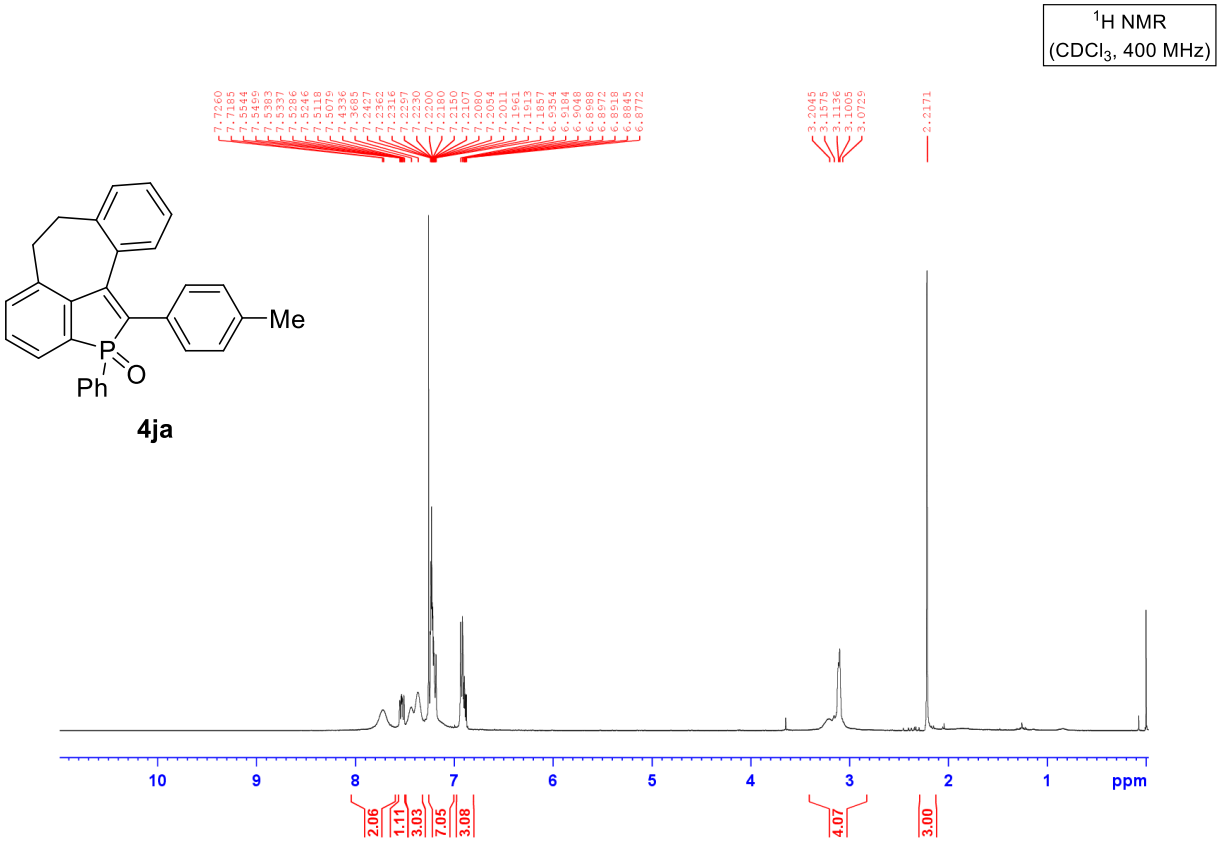
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ia**]

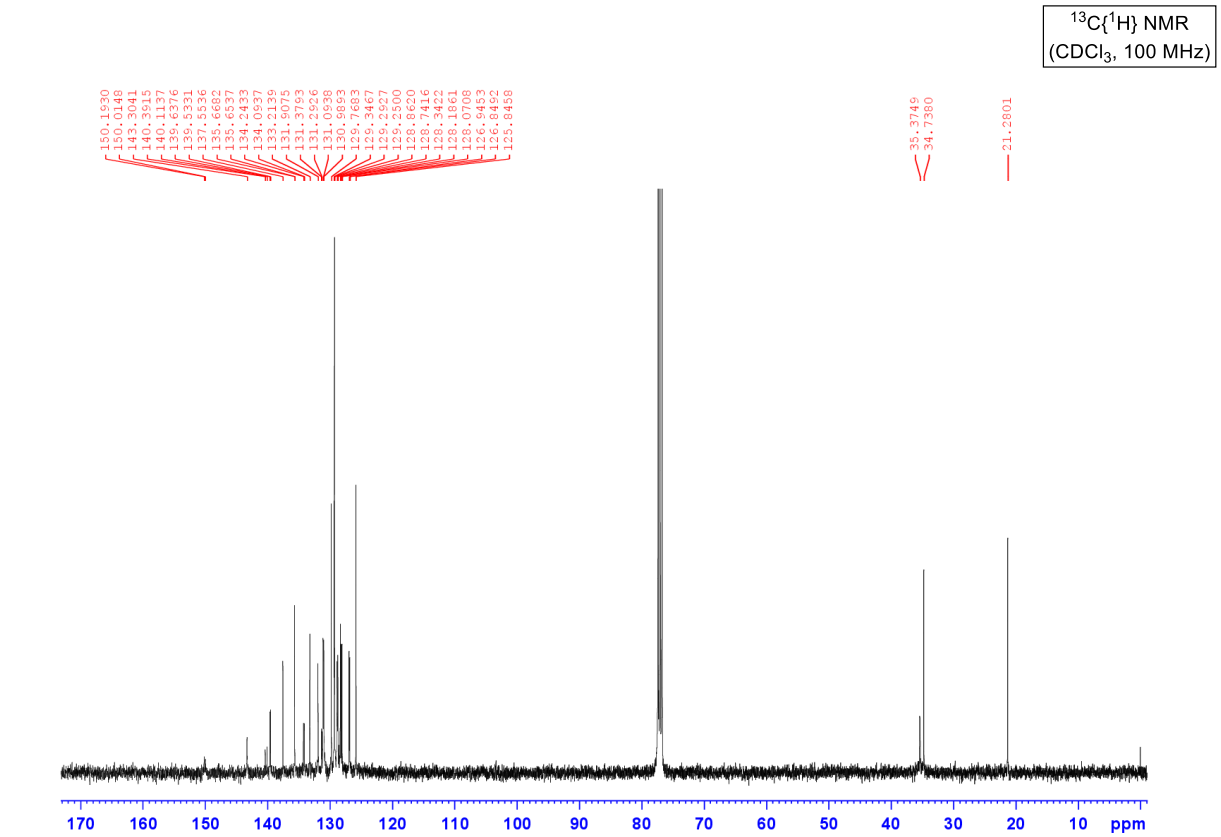


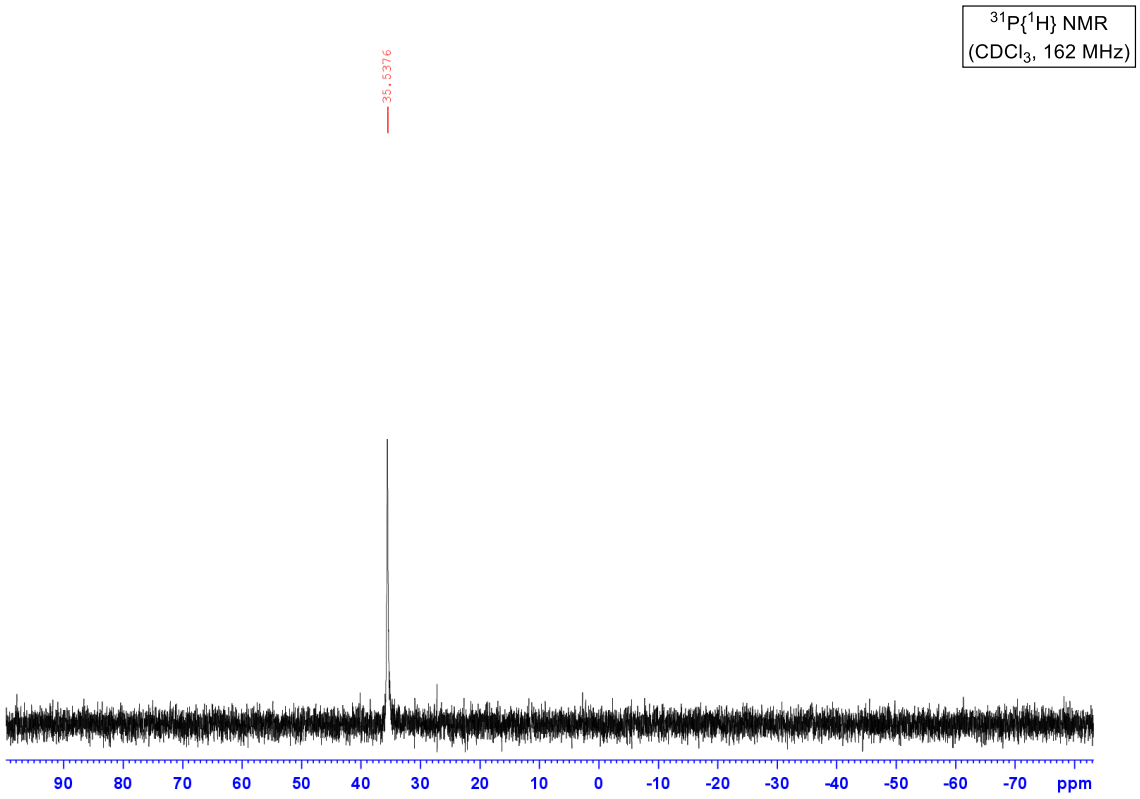



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
39.8137
80
60
40
20
0
-20
-40
-60
-80
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4ja**]

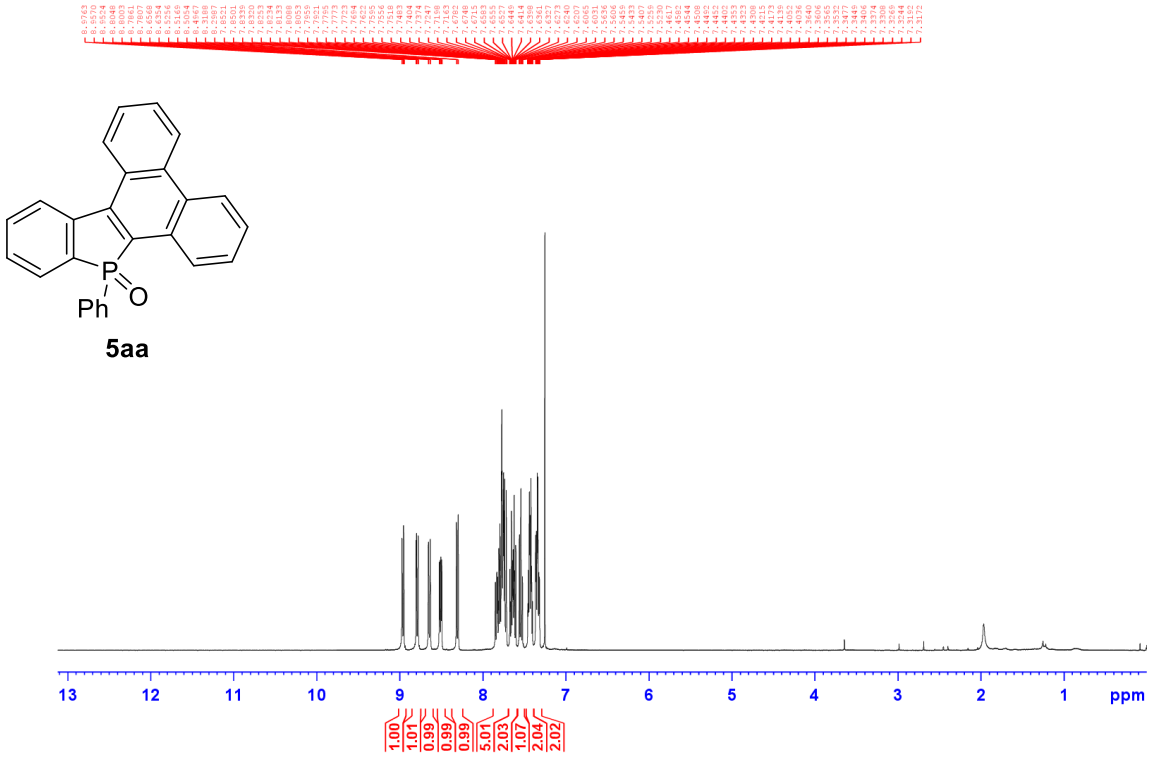





$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
35.5376
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm

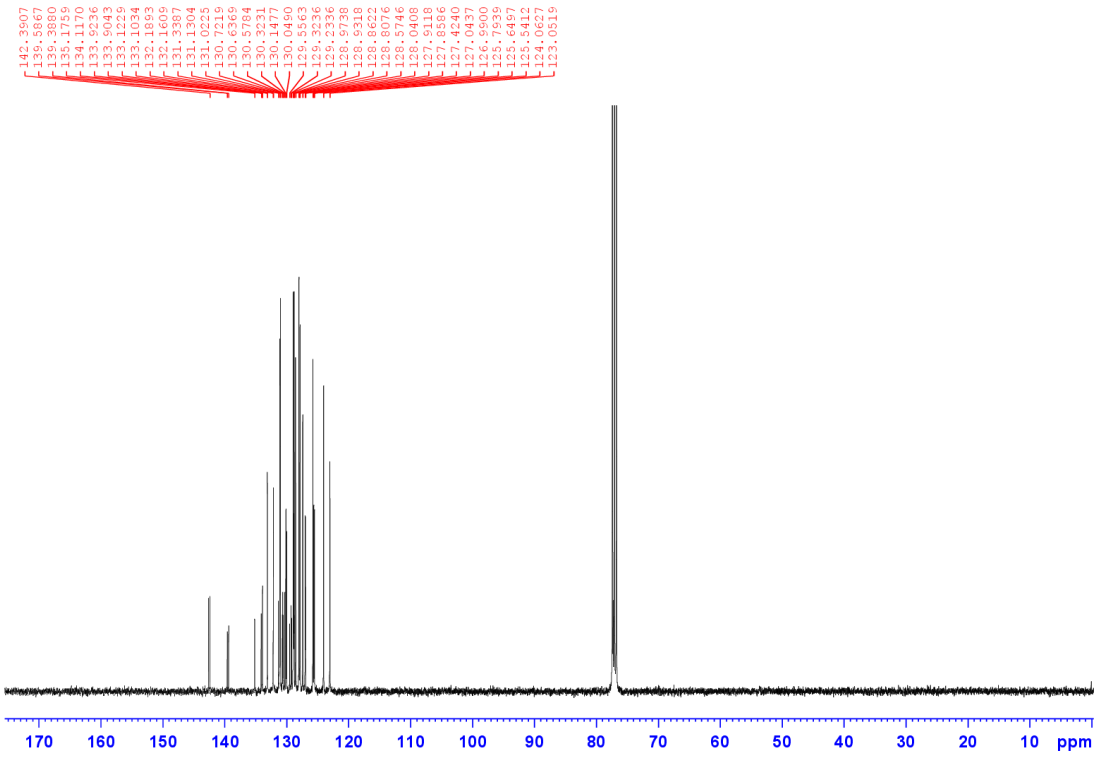
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **5aa**]

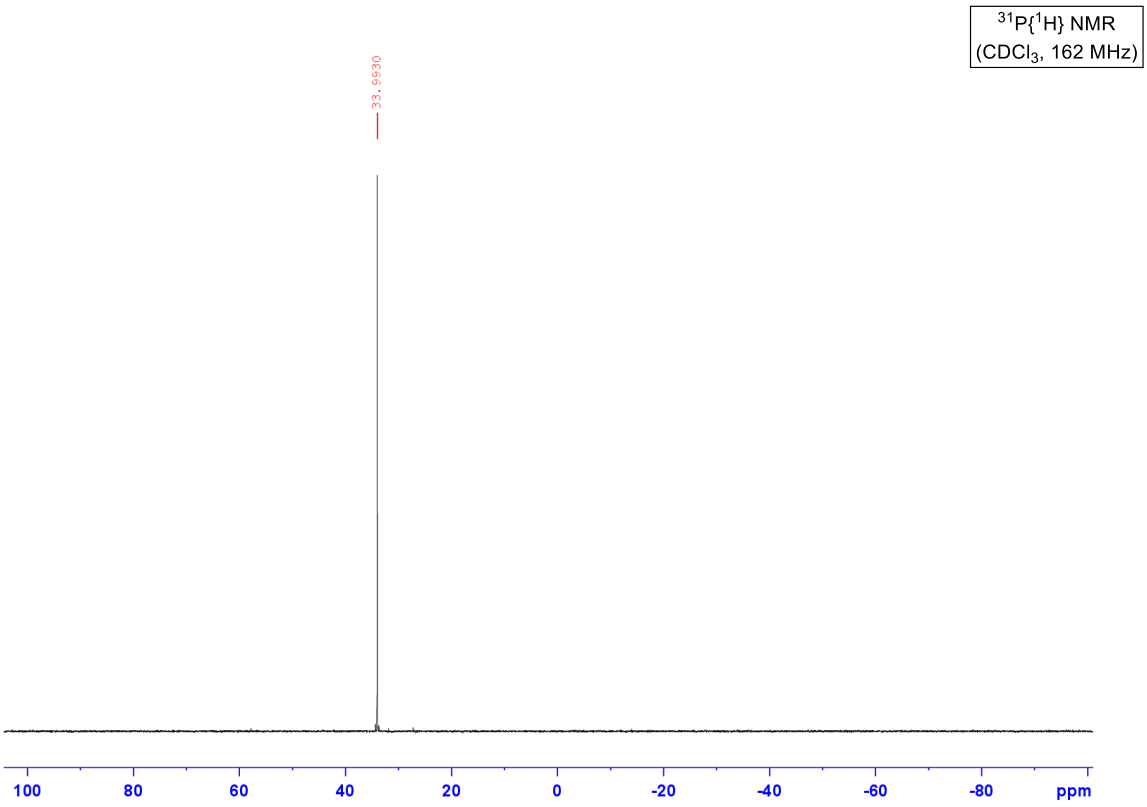
^{1}H NMR
($CDCl_3$, 400 MHz)



5aa

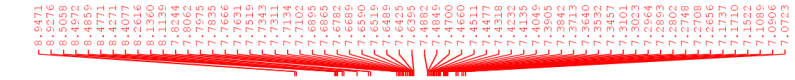
^{13}C{^{1}H} NMR
($CDCl_3$, 100 MHz)

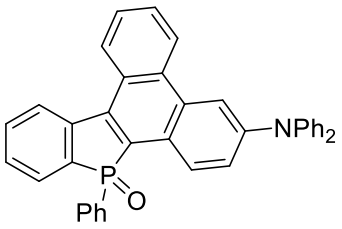



$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
33.9930
100
80
60
40
20
0
-20
-40
-60
-80
ppm

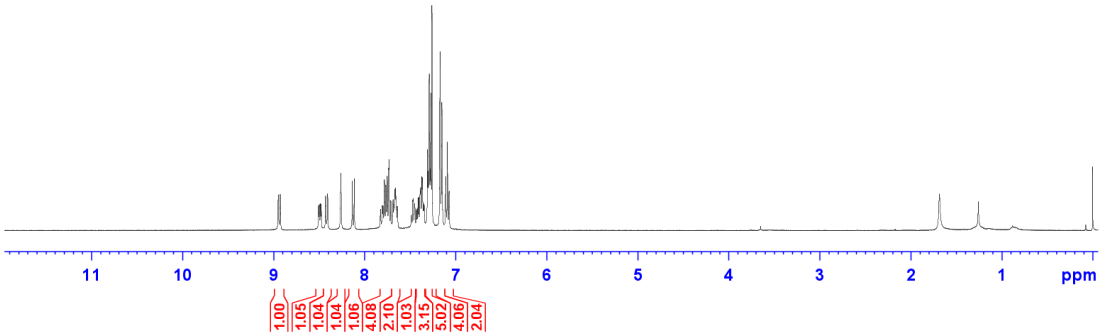
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **5ab**]

^{1}H NMR
(CDCl$_3$, 400 MHz)

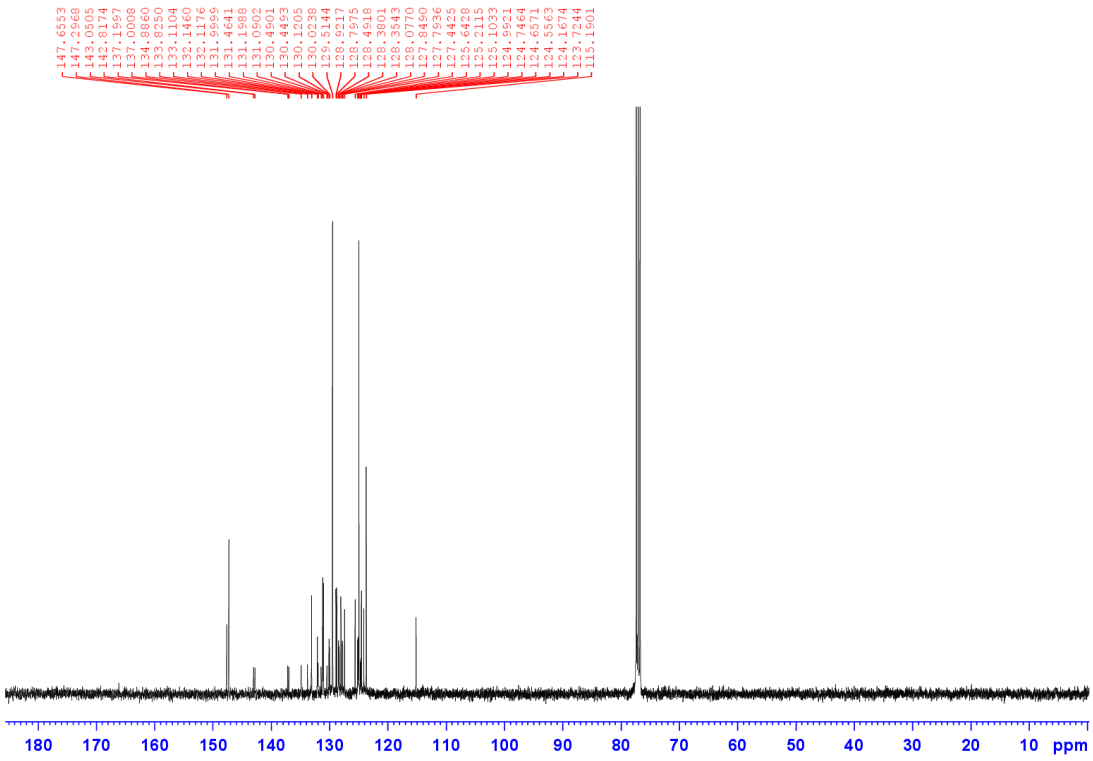


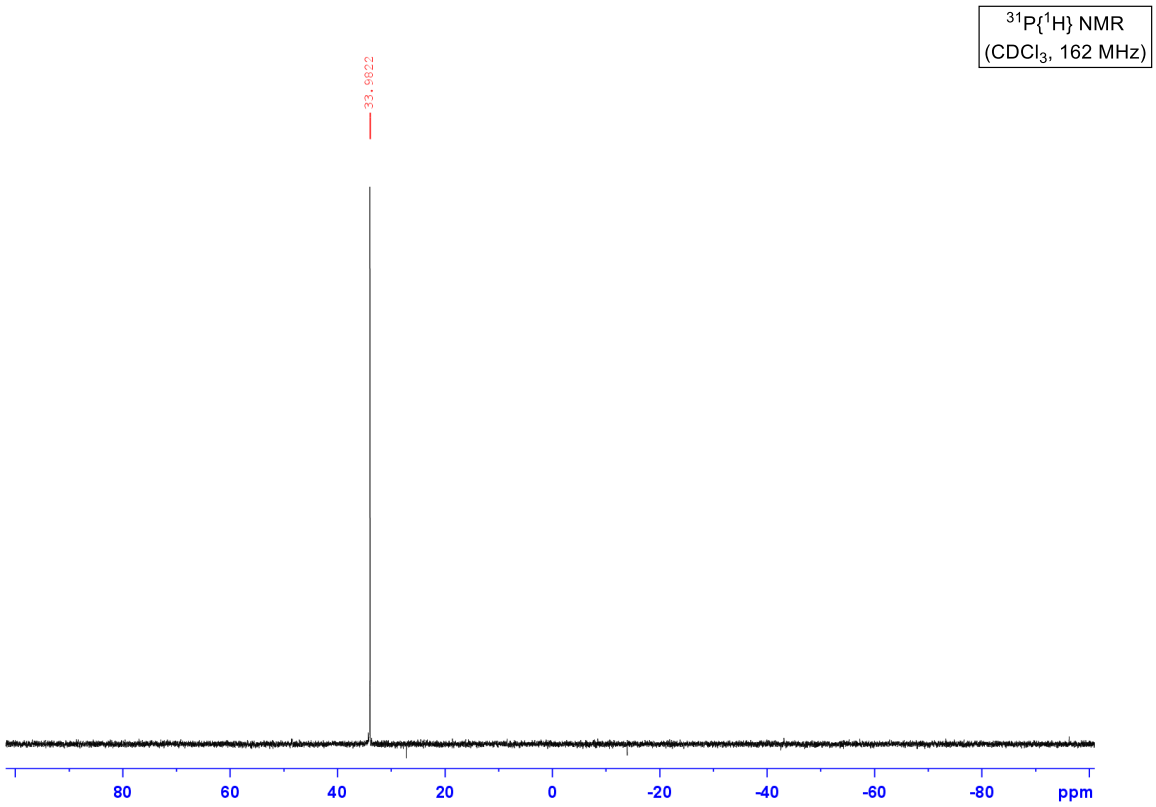


5ab



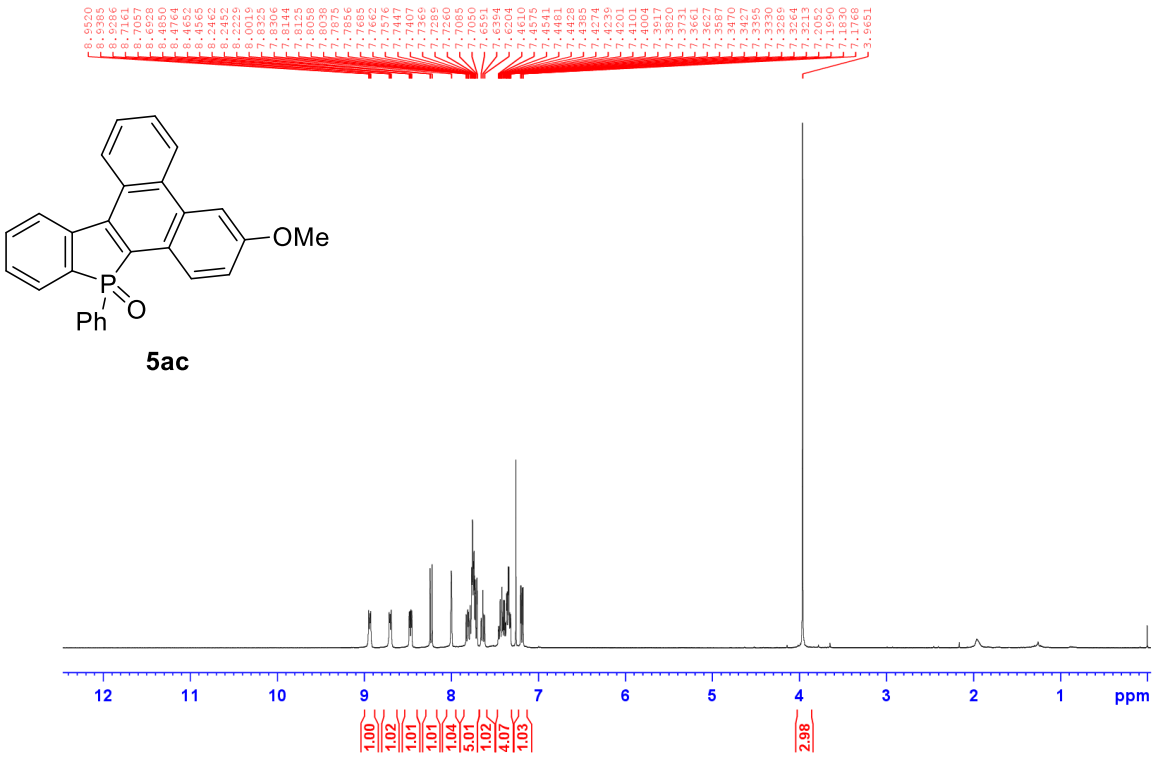
^{13}C{^{1}H} NMR
(CDCl$_3$, 100 MHz)




$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
33.9822
80
60
40
20
0
-20
-40
-60
-80
ppm

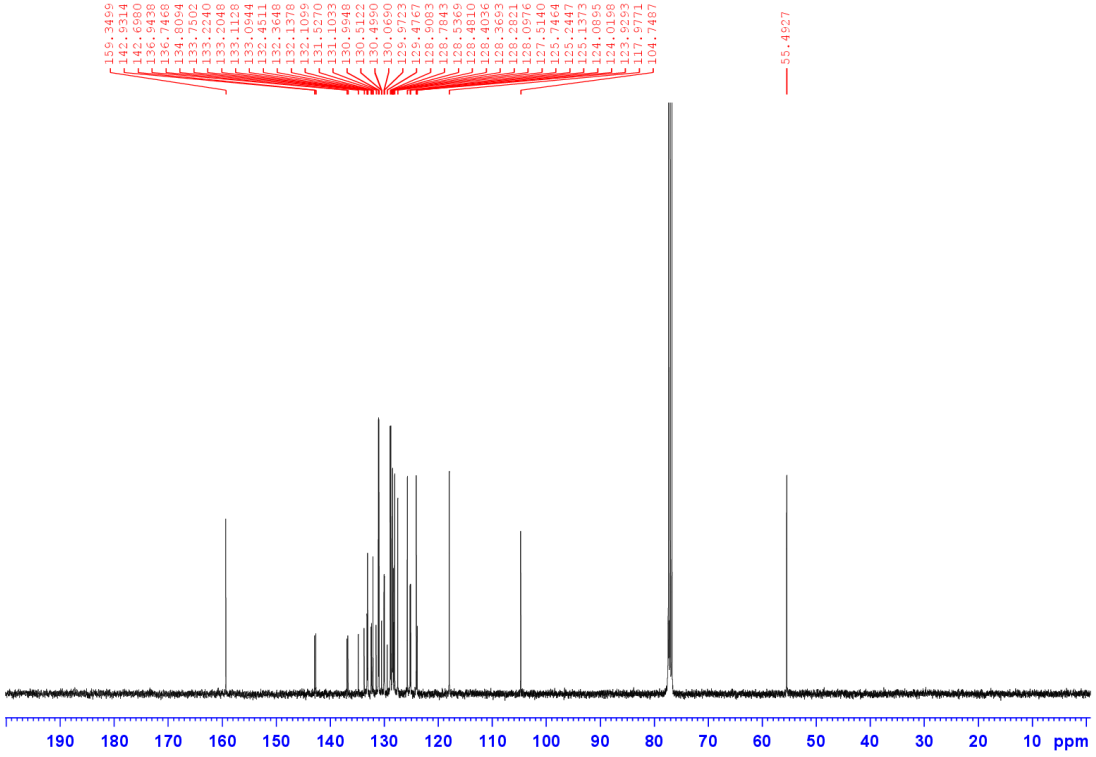
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **5ac**]

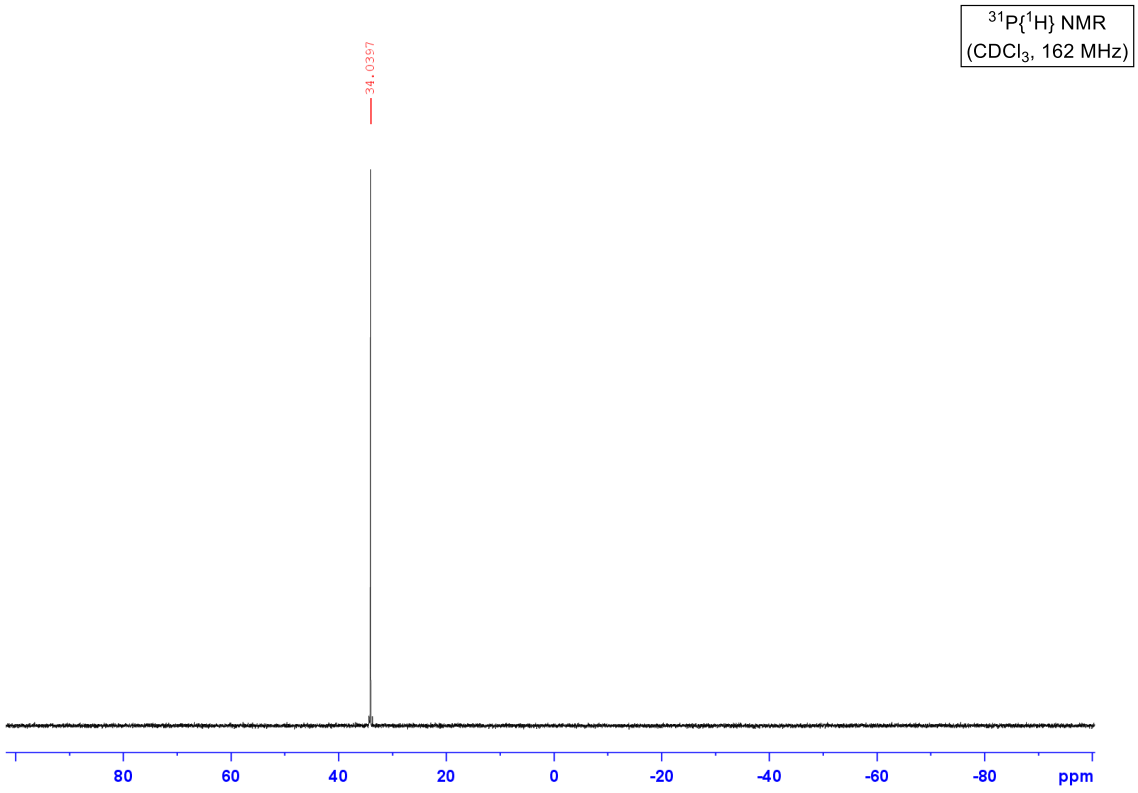
^{1}H NMR
($CDCl_3$, 400 MHz)



5ac

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




$^{31}P\{^{1}H\}$ NMR
($CDCl_3$, 162 MHz)
34.0397
80
60
40
20
0
-20
-40
-60
-80
ppm

References

(S1) T. H.H. Hsieh and V. M. Dong, *Tetrahedron,* 2009, **65**, 3062–3068.

(S2) Y. Kanazawa, T. Yokota, H. Ogasa, H. Watanabe, T. Hanakawa, S. Soga and M. Kawatsura, *Tetrahedron,* 2015, **71**, 1395–1402.

(S3) K. Nishimura, K. Hirano and M. Miura, *Org. Lett.,* 2020, **22**, 3185–3189.