Supporting Information

Synthesis of 1,2,4-Diazaphospholes via Base-Promoted Cyclization Reaction of Hydrazonoyl Chlorides and $[Bu_4N][P(SiCl_3)_2]$

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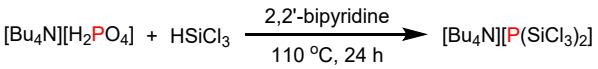
1. General Information

All manipulations are performed in a MO-40M glove box under a vacuum with an argon atmosphere or using standard Schlenk techniques. Unless otherwise stated, commercially available reagents and solvents were used without further purification. Deuterated solvents were purchased from Adamas. ^{1}H NMR, ^{31}P NMR, ^{19}F NMR spectra were recorded on a Varian Mercury-400 Plus in $CDCl_3$, and ^{13}C NMR was recorded on Agilent Technologies DD2 (600 MHz) spectrometers in $CDCl_3$. The chemical shifts (ppm) were recorded using tetramethylsilane (TMS) as the internal reference standard, and the solvent peak was 7.26 ppm for ^{1}H and 77.00 ppm for ^{13}C in $CDCl_3$. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets), or m (multiplet). Coupling constants (J) are reported in hertz (Hz). High-Resolution Mass Spectrometry (HRMS) was obtained using a Q-Exactive instrument equipped with an ESI source from the thermofisher, and the type of mass analyzer used for HRMS measurements was a quadrupole mass filter. X-ray single crystal diffraction data were collected on a Bruker D8 VENTURE diffractometer equipped with a liquid nitrogen cryogenic device. Melting points (m.p.) were measured on an X-4 apparatus (uncorrected). Reactions were monitored by thin-layer chromatography (TLC) using pre-coated silica gel plates (GF254). Visualization on TLC was achieved by use of UV light (254 nm). Column chromatography was performed using Yantai Xinnuo silica gel (200-300 mesh) using ethyl acetate/petroleum ether.

2. Preparation of Starting Materials

2.1 Preparation of $[Bu_4N][P(SiCl_3)_2]$

$[Bu_4N][P(SiCl_3)_2]$ was synthesized, and it was pre-treated and post-treated as described in the literature.[1]

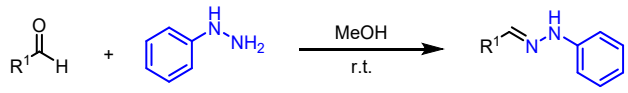


In a glove box, 2,2'-bipyridine (32 mg, 0.2 mmol, 0.1 equiv.) was added into a reaction tube with a magnetic stir bar. Subsequently, an excess of $HSiCl_3$ (6.7 mL, 66 mmol, 33 equiv.) was carefully added via a syringe. The reaction tube was immediately sealed and stirred at room temperature for 15-30 minutes, followed by

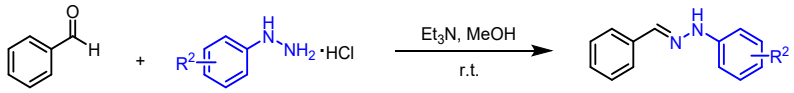
the addition of [TBA][H_2PO_4] (679 mg, 2.0 mmol, 1.0 equiv.), and the mixture was heated to 110 °C for 24 hours. After completion of the reaction, the reaction tube was cooled to room temperature and then immersed in cold hydrazine (-78 °C) for 10 minutes, and the resulting gas was subsequently vented to an oil bubbler and then to a water bubbler in series to remove the toxic gas. The volatile materials were removed in vacuo over a period of 2 hours on the Schlenk line. The reaction tube was then brought into the glovebox. The white solid was washed with ether (3 × 5 ml) and filtered through diatomaceous earth (fine pores, 1 cm) to eliminate most of the microsoluble material and insoluble impurities. The obtained white solid was collected and dried under a vacuum at a constant temperature. The ^{1}H NMR and ^{31}P NMR spectra of the obtained [Bu_4N][$P(SiCl_3)_2$] were consistent with the data reported in the literature. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.30 (t, J = 8.4 Hz, 8H), 1.7 (m, 8H), 1.5 (m, 8H), 1.0 (t, J = 7.2 Hz, 12H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -171.03.

2.2 Preparation of hydrazones

Hydrazones were synthesized according to the reported methods.[2]



Methanol (50 mL), aldehyde (20 mmol, 1 equiv.), and phenylhydrazine (20 mmol, 1 equiv., 1.97 mL) were sequentially added to a 100 mL round bottom flask. The reaction was carried out at room temperature, and a large amount of pale yellow solid was precipitated, which was monitored by TLC. After the reaction was completed, the methanol was evaporated under reduced pressure, and the crude product was directly used in the preparation of the next raw material.

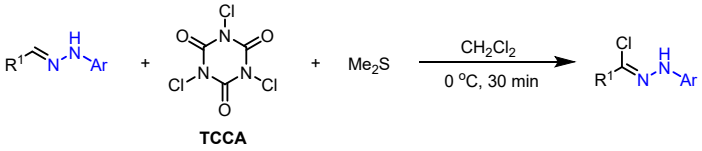


The substituted phenylhydrazine hydrochloride derivatives (20 mmol, 1 equiv.), methanol (50 mL), triethylamine (30 mmol, 1.5 equiv., 4.17 mL) were sequentially added to a 100 mL round bottom flask. The mixture was stirred until the substituted phenylhydrazine hydrochloride derivatives solid disappeared, then benzaldehyde (30 mmol, 1.5 equiv., 3.05 mL) was added, and the reaction was carried out under room temperature conditions and monitored by TLC. After completion of the reaction, methanol was evaporated under reduced pressure. The reaction mixture was treated with saturated salt solution, and the resulting mixture extracted three times. The

combined organic phases were dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. Finally, the crude product was directly used in the preparation of the next raw material.

2.3 Preparation of hydrazonoyl chlorides

All hydrazonoyl chlorides were prepared according to the methods provided in the literature and their spectra were consistent with those reported in the literature.[3]



The reaction was carried out in a 250 mL round-bottomed flask. TCCA (22 mmol, 1.1 equiv., 5.11 g) was added, followed by dichloromethane (60 mL), and dimethyl sulfide (66 mmol, 3.3 equiv., 4.85 mL) sequentially under an ice bath. The mixture was stirred for 10 minutes, and a large amount of white turbidity appeared rapidly. Then, the hydrazone (20 mmol, 1 equiv.) was dissolved in dichloromethane (60 mL) and added to the above mixture, and the reaction was continued to be stirred in an ice bath for 20 min, and monitored by TLC. After the reaction was complete, distilled water (50 mL) was added to the flask to quench the reaction, and the reaction mixture was extracted with dichloromethane three times. The combined organic phases were dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. Then the residue was purified by column chromatography (petroleum ether/ethyl acetate or petroleum ether/dichloromethane) to afford the pure substituted hydrazonoyl chlorides.

3. Optimization of Reaction Conditions

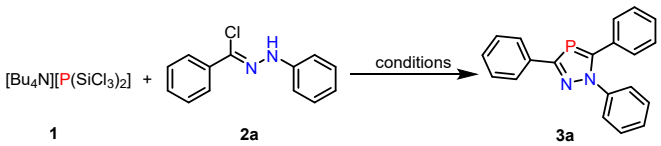


Table S1. Screening of Solvent [a]

Entry	Solvent	Yield (**4aa**)/(%) [b]
1	CH_3CN	30
2	**toluene**	**43**
3	THF	35
4	CH_2Cl_2	38

5	CH_3OH	N.D.
6	1,4-dioxane	<10
7	MTBE	28

[a] Reaction conditions: **1** (0.2 mmol, 1 equiv.), **2a** (0.2 mmol, 1 equiv.), Et_3N (0.4 mmol, 2.0 equiv.), Solvent (2 mL), 60 ℃, Ar, 17 h. [b] Isolated yield. N.D. = Not Detected.

Table S2. Screening of Molar Ratio [a]

Entry	**1** (x mmol)	**2a** (y mmol)	Yield (**4aa**)/(%) [b]
1	0.2	0.15	40
2	0.2	0.24	50
3	**0.2**	**0.3**	**73**
4	0.2	0.4	56
5	0.2	0.5	55

[a] Reaction conditions: **1** (x mmol), **2a** (y mmol), Et_3N (0.4 mmol, 2.0 equiv.), toluene (2 mL), 60 ℃, Ar, 17 h. [b] Isolated yield.

Table S3. Screening of Base [a]

Entry	Base	Yield (**4aa**)/(%) [b]
1	**Et_3N**	**73**
2	DIPEA	69
3	DBU	47
4	Na_2CO_3	N.D.
5	K_2CO_3	trace
6	Cs_2CO_3	N.D.
7	K_3PO_4	trace
8	DABCO	65
9	NaOH	trace
10	DMAP	36
11	$(^iPr)_2HN$	53
12	NaHMDS	<10
13	-	19

[a] Reaction conditions: **1** (0.2 mmol, 1 equiv.), **2a** (0.3 mmol, 1.5 equiv.), Base (2 equiv.), toluene (2 mL), 60 ℃, Ar, 17 h. [b] Isolated yield.

Table S4. Screening of Temperature [a]

Entry	T (℃)	Yield (**4aa**) (%) [b]
1	25	67
2	40	71
3	60	75
4	80	81
5	100	76
6	110	61

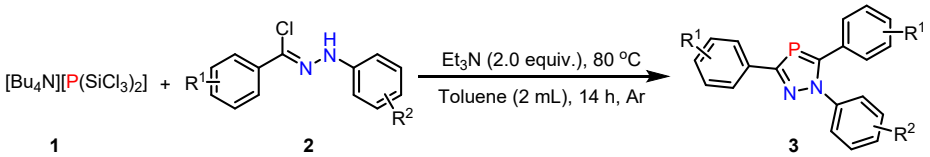
[a] Reaction conditions: **1** (0.2 mmol, 1 equiv.), **2a** (0.3 mmol, 1.5 equiv.), Et_3N (2 equiv.), toluene (2 mL), T (℃), Ar, 17 h. [b] Isolated yield.

Table S5. Screening of Time [a]

Entry	Time (x h)	Yield (**4aa**) (%) [b]
1	6	72
2	10	76
3	14	86
4	17	83
5	20	81
6	24	80

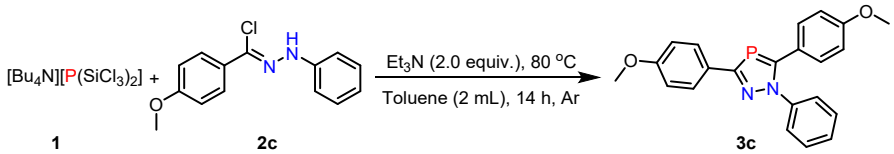
[a] Reaction conditions: **1** (0.2 mmol, 1 equiv.), **2a** (0.3 mmol, 1.5 equiv.), Et_3N (2 equiv.), toluene (2 mL), 80 ℃, Ar, x h. [b] Isolated yield.

4. General Procedure for Synthesis of Substrates



Hydrazonoyl chlorides **2** (0.3 mmol, 1.5 equiv.), $[Bu_4N][P(SiCl_3)_2]$ **1** (0.2 mmol, 1 equiv., 108 mg), and toluene (0.1 M, 2 mL) were added sequentially into a 15 mL Schlenk reaction tube in a glove box. Subsequently, Et_3N (0.4 mmol, 2 equiv., 55.60 μL) was added to the reaction tube using a microsyringe. The reaction was carried out at 80 °C for 14 h and monitored by TLC. After the reaction was cooled to room temperature, the reaction mixture was treated with saturated salt solution, and the resulting mixture extracted three times. The combined organic phases were dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. Then the residue was purified by column chromatography (petroleum ether/ethyl acetate) to obtain the corresponding product **3**.

5. Procedure for Gram-Scale Synthesis of 3c

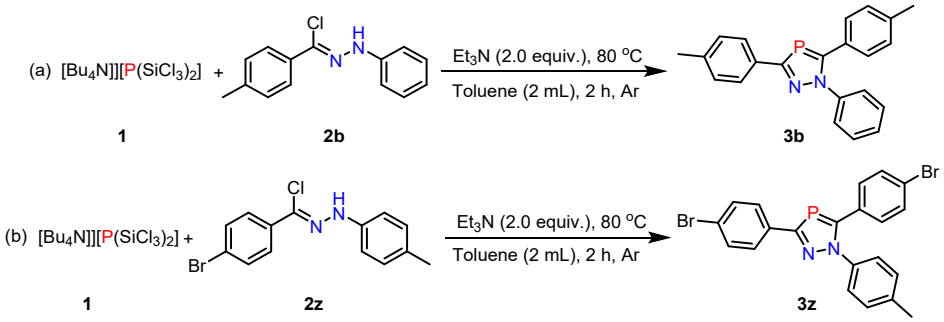


(Z)-4-methoxy-*N*-phenylbenzohydrazonoyl chloride **2c** (3.85 mmol, 1.0 g, 1.5 equiv.), $[Bu_4N][P(SiCl_3)_2]$ **1** (2.56 mmol, 1.3842 g, 1 equiv.), and toluene (0.1 M, 25.6

ml) were added sequentially into a 100 ml round-bottomed flask in a glove box. Then Et_3N (5.12 mmol, 0.71 mL, 2 equiv.) was added to the above reaction solution using a syringe. The reaction was carried out at 80 °C for 14 h (monitored by TLC). The reaction mixture was cooled to room temperature, and extracted with ethyl acetate and saturated salt solution for three times. The combined organic phases were dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. Then the residue was purified by column chromatography (petroleum ether/ethyl acetate = 15/1, R_f = 0.36) to obtain the compound **3c** (1.33 mmol, 0.50 g, 69%).

6. Control Experiment

In order to further understand the reaction mechanism, eliminated diazenyl aryl compound was successfully detected by high-resolution mass spectrometry (HRMS), laying the data support for the proposed mechanism.



Eq (a): (Z)-4-methyl-*N*-phenylbenzohydrazonoyl chloride **2b** (0.3 mmol, 73.22 mg, 1.5 equiv.), $[Bu_4N][P(SiCl_3)_2]$ **1** (0.2 mmol, 108 mg, 1 equiv.), and toluene (0.1 M, 2 ml) were added sequentially into a 15 mL Schlenk reaction tube in a glove box. Subsequently, Et_3N (0.4 mmol, 2 equiv., 55.60 μL) was added to the reaction tube using a microsyringe. The reaction was carried out at 80 °C for 2 h. After two hours, the sample of the reactions was tested by high-resolution mass spectrometry (HRMS). The possible diazenyl benzene could be successfully detected by HRMS.

Eq (b): (Z)-4-bromo-*N*-(*p*-tolyl)benzohydrazonoyl chloride **2z** (0.3 mmol, 96.60 mg, 1.5 equiv.), $[Bu_4N][P(SiCl_3)_2]$ **1** (0.2 mmol, 108 mg, 1 equiv.), and toluene (0.1 M, 2 ml) were added sequentially into a 15 mL Schlenk reaction tube in a glove box. Subsequently, Et_3N (0.4 mmol, 2 equiv., 55.60 μL) was added to the reaction tube using a microsyringe. The reaction was carried out at 80 °C for 2 h. After two hours, the sample of the reactions was tested by high-resolution mass spectrometry (HRMS). The possible diazenyl toluene could be successfully detected by HRMS.

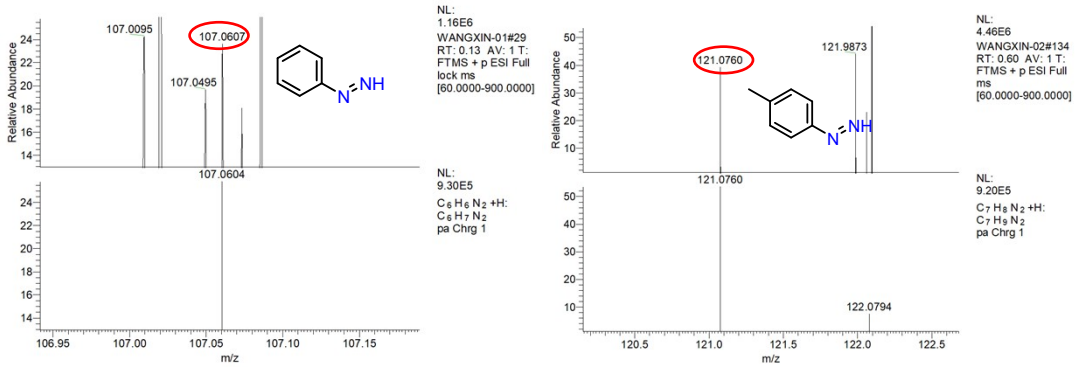


Figure S1. Eliminated diazenyl aryl compound was detected by HRMS

7. X-ray Crystallographic Data of Compounds 3a

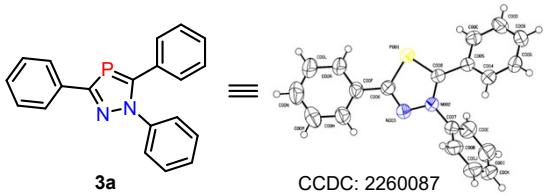


Table S6. X-ray Crystallographic Data of Compounds **3a**

Bond precision:	C-C = 0.0054 A	Wavelength=0.71073
Cell:	a=6.0016(4)	b=11.8760(7) c=11.5703(8)
	alpha=90	beta=90.548(2) gamma=90
Temperature:	298 K	
	Calculated	Reported
Volume	824.64(9)	824.64(9)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C20 H15 N2 P	C20 H15 N2 P
Sum formula	C20 H15 N2 P	C20 H15 N2 P
Mr	314.31	314.31
Dx,g cm-3	1.266	1.266
Z	2	2
Mu (mm-1)	0.167	0.167
F000	328.0	328.0
F000'	328.30	
h,k,lmax	8,16,16	8,16,15
Nref	4613[2411]	3887
Tmin,Tmax	0.968,0.975	0.671,0.746
Tmin'	0.967	

Correction method= # Reported T Limits: Tmin=0.671 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.61/0.84 Theta(max)= 29.513

R(reflections)= 0.0435(2740) wR2(reflections)= 0.1008(3887)

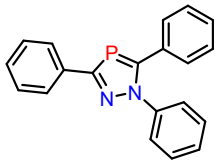
S = 1.034 Npar= 208

Sample preparation: A saturated solution of compound **3a** (40 mg) in ethyl acetate was placed in a vial (5 mL). Petroleum ether was added to the vial with a dropper until a small amount of solid precipitation. Then, ethyl acetate was added to the vial with a dropper until the solution clarification. The single crystal **3a** was obtained by

slowly evaporating mixed solvent at room temperature under the air conditions.

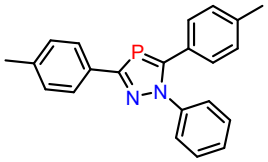
8. Characterization Data of the Corresponding Products[4]

1,3,5-triphenyl-1*H*-1,2,4-diazaphosphole (3a)



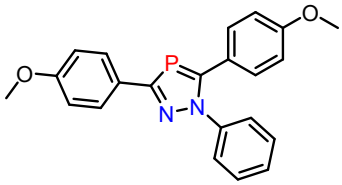
40.6 mg, Yield: 86%. Pale Yellow solid, m.p. 135-137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.2, 1.6 Hz, 2 H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.34 (s, 5H), 7.27 (s, 5H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.6 (d, *J* = 57.0 Hz), 175.4 (d, *J* = 49.5 Hz), 141.2 (d, *J* = 3.0 Hz), 135.8 (d, *J* = 19.5 Hz), 132.7 (d, *J* = 18.0 Hz), 129.2 (d, *J* = 6.0 Hz), 128.8, 128.7, 128.6 (d, *J* = 1.5 Hz), 128.5, 128.4, 128.1, 126.4 (d, *J* = 10.5 Hz), 126.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 94.40. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{20}H_{16}N_2P^+$: 315.1046; found: 315.1045.

1-phenyl-3,5-di-*p*-tolyl-1*H*-1,2,4-diazaphosphole (3b)



41.2 mg, Yield: 80%. Pale yellow solid, m.p. 116-118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.34 (s, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.5 (d, *J* = 57.0 Hz), 175.5 (d, *J* = 48.0 Hz), 141.3, 138.5 (d, *J* = 4.5 Hz), 133.2 (d, *J* = 19.5 Hz), 129.8 (d, *J* = 16.5 Hz), 129.4, 129.1, 129.0, 128.97, 128.8, 128.0, 126.2 (d, *J* = 9.0 Hz), 126.1, 21.33, 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 92.75. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{22}H_{20}N_2P^+$: 343.1359; found: 343.1358.

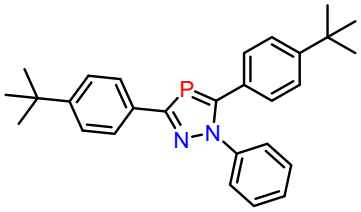
3,5-bis(4-methoxyphenyl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3c)



40.1 mg, Yield: 71%. Pale yellow solid, m.p. 128-129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.34 (s, 5H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.79 (s, 3H). **^{13}C NMR** (151 MHz,

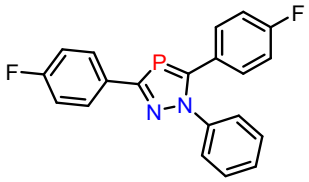
$CDCl_3$) δ 177.1 (d, *J* = 57.0 Hz), 175.2 (d, *J* = 49.5 Hz), 160.1 (d, *J* = 1.5 Hz), 159.8, 141.3 (d, *J* = 1.5 Hz), 130.4 (d, *J* = 7.5 Hz), 128.8, 128.0, 127.62, 127.6, 126.1, 125.1 (d, *J* = 18.0 Hz), 114.0, 113.8, 55.3, 55.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 90.03. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{22}H_{20}N_2O_2P^+$: 375.1257; found: 375.1257.

3,5-bis(4-(*tert*-butyl)phenyl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3d)



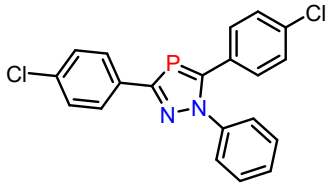
41.6 mg, Yield: 65%. Pale yellow solid, m.p. 174-175 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.33 (m, 5H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 1.35 (s, 9H), 1.29 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.4 (d, *J* = 57.0 Hz), 175.4 (d, *J* = 48.0 Hz), 151.87, 141.4, 133.2 (d, *J* = 19.5 Hz), 129.7 (d, *J* = 18.0 Hz), 128.8, 128.7 (d, *J* = 7.5 Hz), 128.0, 126.08, 126.1 (d, *J* = 9.0 Hz), 125.6, 125.3, 34.68, 34.7, 31.3, 31.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 93.20. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{28}H_{32}N_2P^+$: 427.2298; found: 427.2299.

3,5-bis(4-fluorophenyl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3e)



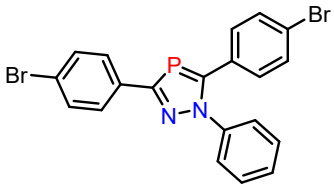
35.3 mg, Yield: 67%. Pale yellow solid, m.p. 144-146 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.36 – 7.29 (m, 5H), 7.22 (dd, *J* = 8.4, 5.6 Hz, 2 H), 7.10 (t, *J* = 8.4 Hz, 2H), 6.96 (t, *J* = 8.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.4 (d, *J* = 57.0 Hz), 174.3 (d, *J* = 49.5 Hz), 163.2 (dd, *J* = 247.5, 3.0 Hz), 162.8 (dd, *J* = 247.5, 1.5 Hz), 140.9 (d, *J* = 1.5 Hz), 132.0 (dd, *J* = 19.5, 3.0 Hz), 130.9 (q, *J* = 7.5 Hz), 129.0, 128.6 (dd, *J* = 18.0, 3.0 Hz), 128.4, 128.0 (q, *J* = 9.0 Hz), 126.0, 115.7 (d, *J* = 12.0 Hz), 115.5 (d, *J* = 10.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 93.44. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.19 – -112.27 (m), -113.09 – -113.17 (m). **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{20}H_{14}F_2N_2P^+$: 351.0857; found: 351.0856.

3,5-bis(4-chlorophenyl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3f)



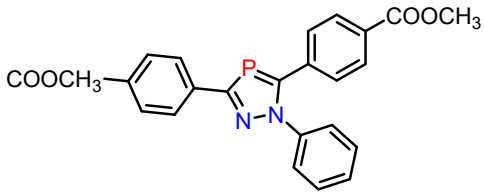
42.8 mg, Yield: 75%. Pale yellow solid, m.p. 161-162 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.37 (m, 5H), 7.33 – 7.30 (m, 2H), 7.25 (d, *J* = 4.8 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.3 (d, *J* = 57.0 Hz), 174.1 (d, *J* = 49.5 Hz), 140.8, 134.8 (d, *J* = 1.5 Hz), 134.6 (d, *J* = 1.5 Hz), 134.2 (d, *J* = 19.5 Hz), 130.9 (d, *J* = 18.0 Hz), 130.3 (d, *J* = 6.0 Hz), 129.1, 128.9, 128.7, 128.5, 127.5 (d, *J* = 9.0 Hz), 126.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 95.57. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{20}H_{14}Cl_2N_2P^+$: 383.0266; found: 383.0266.

3,5-bis(4-bromophenyl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3g)



50.5 mg, Yield: 71%. White solid, m.p. 156-157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.34 (m, 5H), 7.30 – 7.28 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.3 (d, *J* = 57.0 Hz), 174.0 (d, *J* = 49.5 Hz), 140.8 (d, *J* = 1.5 Hz), 134.6 (d, *J* = 19.5 Hz), 131.8, 131.6, 131.3 (d, *J* = 18.0 Hz), 130.5 (d, *J* = 7.5 Hz), 129.0, 128.5, 127.8 (d, *J* = 10.5 Hz), 125.9, 123.1 (d, *J* = 1.5 Hz), 122.8 (d, *J* = 3.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 96.01. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{20}H_{14}Br_2N_2P^+$: 472.9235; found: 472.9235.

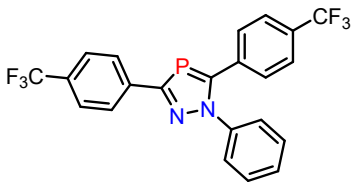
dimethyl 4,4'-(1-phenyl-1*H*-1,2,4-diazaphosphole-3,5-diyl)dibenzoate (3h)



32.7 mg, Yield: 51%. White solid, m.p. 205-207 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 8.09 (m, 2H), 8.08 – 8.05 (m, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.32 (m, 7H), 3.94 (s, 3H), 3.91 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.4 (d, *J* = 57.0 Hz), 174.2 (d, *J* = 49.5 Hz), 166.8, 166.4, 140.8 (d, *J* = 1.5 Hz), 139.8 (d, *J* = 19.5 Hz),

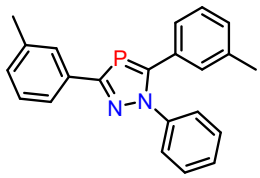
136.8 (d, J = 18.0 Hz), 130.1, 129.7, 129.11, 129.1, 129.05, 128.7, 126.2, 126.1, 126.0, 52.3, 52.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 100.01. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}N_2O_4P^+$: 431.1155; found: 431.1156.

1-phenyl-3,5-bis(4-(trifluoromethyl)phenyl)-1*H*-1,2,4-diazaphosphole (3i)



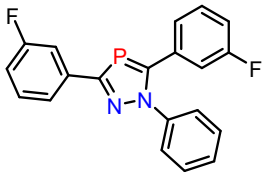
48.6 mg, Yield: 72%. Pale yellow solid, m.p. 148 – 150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.41 – 7.37 (m, 5H), 7.34 – 7.32 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.1 (d, J = 57.0 Hz), 173.8 (d, J = 49.5 Hz), 140.7 (d, J = 1.5 Hz), 138.9 (d, J = 19.5 Hz), 135.9 (d, J = 18.0 Hz), 130.7 (q, J = 33.0 Hz), 130.6 (q, J = 33.0 Hz), 129.4 (d, J = 7.5 Hz), 129.2, 128.8, 126.5 (d, J = 10.5 Hz), 126.0, 125.8 (q, J = 3.0 Hz), 125.5 (q, J = 3.0 Hz), 124.2 (q, J = 270.0 Hz), 123.8 (q, J = 271.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 99.67. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.57, -62.79. **HRMS (ESI)** *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{14}F_6N_2P^+$ 451.0793, Found 451.0794.

1-phenyl-3,5-di-*m*-tolyl-1*H*-1,2,4-diazaphosphole (3j)



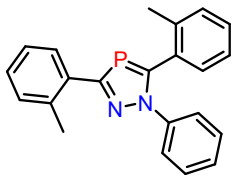
38.5 mg, Yield: 75%. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.35 – 7.29 (m, 6H), 7.18 – 7.08 (m, 4H), 6.98 (d, J = 6.8 Hz, 1H), 2.41 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.7 (d, J = 55.5 Hz), 175.6 (d, J = 49.5 Hz), 141.3 (d, J = 1.5 Hz), 138.3, 138.1, 135.7 (d, J = 19.5 Hz), 132.5 (d, J = 18.0 Hz), 129.9 (d, J = 7.5 Hz), 129.4 (d, J = 1.5 Hz), 129.2, 128.8, 128.6, 128.2, 128.1, 126.8 (d, J = 9.0 Hz), 126.1 (d, J = 7.5 Hz), 126.0, 123.7 (d, J = 10.5 Hz), 21.4, 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 94.01. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{22}H_{20}N_2P^+$: 343.1359; found: 343.1359.

3,5-bis(3-fluorophenyl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3k)



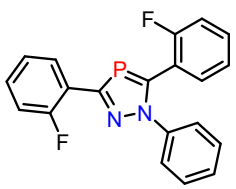
40.4 mg, Yield: 77%. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 10.0 Hz, 1H), 7.41 – 7.32 (m, 6H), 7.28 – 7.22 (m, 1H), 7.09 – 6.95 (m, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.3 (dd, *J* = 57.0, 3.0 Hz), 174.0 (dd, *J* = 49.5, 3.0 Hz), 163.1 (d, *J* = 244.5 Hz), 162.4 (d, *J* = 246.0 Hz), 140.8 (d, *J* = 1.5 Hz), 137.8 (dd, *J* = 19.5, 7.5 Hz), 134.5 (dd, *J* = 19.5, 9.0 Hz), 130.2 (d, *J* = 9.0 Hz), 130.0 (d, *J* = 9.0 Hz), 129.1, 128.6, 125.9, 125.0 (dd, *J* = 7.5, 3.0 Hz), 122.2 (dd, *J* = 10.5, 3.0 Hz), 116.1 (dd, *J* = 22.5, 7.5 Hz), 115.6 (d, *J* = 16.5 Hz), 115.5 (d, *J* = 16.5 Hz), 112.9 (dd, *J* = 22.5, 9.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 97.07. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.14 – -112.20 (m), -112.94 – -113.01 (m). **HRMS (ESI)** *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{14}F_2N_2P^+$ 351.0857, Found 351.0856.

1-phenyl-3,5-di-*o*-tolyl-1*H*-1,2,4-diazaphosphole (3l)



33.1 mg, Yield: 64%. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (t, *J* = 4.8 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.19 (m, 10H), 7.12 (d, *J* = 7.6 Hz, 1H), 2.64 (s, 3H), 1.99 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.9 (d, *J* = 60.0 Hz), 174.0 (d, *J* = 49.5 Hz), 141.2 (d, *J* = 1.5 Hz), 136.4 (d, *J* = 4.5 Hz), 135.9 (d, *J* = 3.0 Hz), 135.3 (d, *J* = 18.0 Hz), 132.3 (d, *J* = 16.5 Hz), 131.0, 130.9 (d, *J* = 4.5 Hz), 130.4, 129.8 (d, *J* = 7.5 Hz), 129.0, 128.6, 128.1, 127.7, 125.9, 125.7, 124.9, 21.9 (d, *J* = 6.0 Hz), 20.2 (d, *J* = 1.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 103.90. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{22}H_{20}N_2P^+$: 343.1359; found: 343.1358.

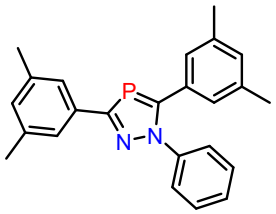
3,5-bis(2-fluorophenyl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3m)



41.6 mg, Yield: 79%. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.30 (m, 7H), 7.24 – 7.13 (m, 3H), 6.96 (t, *J*

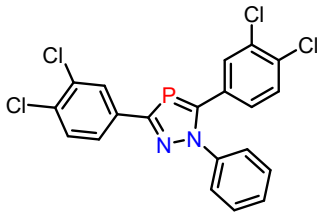
= 9.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3 (dd, *J* = 64.5, 6.0 Hz), 168.4 (dd, *J* = 49.5, 12.0 Hz), 160.5 (d, *J* = 249.0 Hz), 158.5 (dd, *J* = 249.0, 4.5 Hz), 141.3, 131.9 (dd, *J* = 7.5, 3.0 Hz), 131.0 (d, *J* = 7.5 Hz), 129.7 (d, *J* = 7.5 Hz), 128.7, 128.3, 128.1 (q, *J* = 3.0 Hz), 125.2, 124.3 (d, *J* = 3.0 Hz), 124.2 (d, *J* = 4.5 Hz), 123.6 (dd, *J* = 16.5, 12.0 Hz), 120.8 (dd, *J* = 19.5, 16.5 Hz), 116.0 (d, *J* = 6.0 Hz), 115.9 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 110.65, 110.58, 109.83, 109.75. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.13 – -111.23 (m), -111.79 – -111.85 (m), -112.15 – -112.21 (m). **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{14}F_2N_2P^+$ 351.0857, Found 351.0856.

3,5-bis(3,5-dimethylphenyl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3n)



33.2 mg, Yield: 60%. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.34 – 7.29 (m, 5H), 6.99 (s, 1H), 6.90 (s, 1H), 6.86 (s, 2H), 2.36 (s, 6H), 2.19 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.7 (d, *J* = 57.0 Hz), 175.7 (d, *J* = 48.0 Hz), 141.3 (d, *J* = 1.5 Hz), 138.1, 137.8, 135.7 (d, *J* = 18.0 Hz), 132.4 (d, *J* = 16.5 Hz), 130.3 (d, *J* = 1.5 Hz), 130.1, 128.7, 128.0, 126.9 (d, *J* = 7.5 Hz), 126.0, 124.1 (d, *J* = 9.0 Hz), 21.3, 21.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 93.68. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{24}H_{24}N_2P^+$: 371.1672; found: 371.1673.

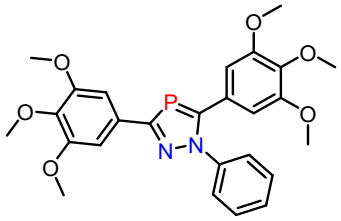
3,5-bis(3,4-dichlorophenyl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3o)



55.4 mg, Yield: 82%. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (t, *J* = 2.0 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.40 (m, 4H), 7.34 – 7.31 (m, 3H), 7.02 – 6.99 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.1 (d, *J* = 58.5 Hz), 172.7 (d, *J* = 51.0 Hz), 140.5 (d, *J* = 1.5 Hz), 135.5 (d, *J* = 21.0 Hz), 133.2 (d, *J* = 1.5 Hz), 133.0, 132.8, 132.7 (d, *J* = 3.0 Hz), 132.2 (d, *J* = 18.0 Hz), 130.8 (d, *J* = 7.5 Hz), 130.7, 130.4, 129.3, 128.9, 128.1 (d, *J* = 7.5 Hz), 127.8 (d, *J* = 9.0 Hz), 125.9, 125.6 (d, *J* = 10.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 98.04. **HRMS (ESI)** *m/z*:

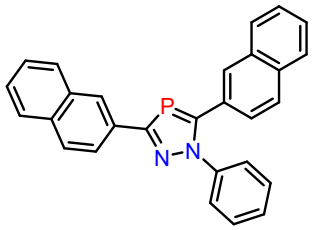
$[M+H]^+$ Calcd for $C_{20}H_{12}Cl_4N_2P^+$ 452.9457, Found 452.9456.

1-phenyl-3,5-bis(3,4,5-trimethoxyphenyl)-1*H*-1,2,4-diazaphosphole (3p)



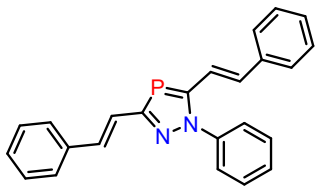
47.4 mg, Yield: 64%. Pale yellow solid, m.p. 156 – 158 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 5H), 7.21 (s, 2H), 6.45 (s, 2H), 3.95 (s, 6H), 3.90 (s, 3H), 3.85 (s, 3H), 3.65 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.3 (d, *J* = 57.0 Hz), 175.4 (d, *J* = 48.0 Hz), 153.4, 152.9, 141.3 (d, *J* = 1.5 Hz), 138.5 (d, *J* = 55.5 Hz), 131.5 (d, *J* = 19.5 Hz), 128.9, 128.3, 127.6 (d, *J* = 18.0 Hz), 126.1, 106.5 (d, *J* = 9.0 Hz), 103.5 (d, *J* = 9.0 Hz), 60.9, 56.2, 55.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 91.43. **HRMS (ESI)** *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{28}N_2O_6P^+$ 495.1679, Found 495.1680.

3,5-di(naphthalen-2-yl)-1-phenyl-1*H*-1,2,4-diazaphosphole (3q)



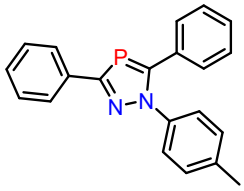
41.6 mg, Yield: 67%. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.76 (m, 6H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.45 (m, 4H), 7.42 – 7.40 (m, 2H), 7.35 – 7.29 (m, 3H), 7.22 – 7.19 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.5 (d, *J* = 57.0 Hz), 175.4 (d, *J* = 49.5 Hz), 141.3, 133.62, 133.6, 133.3 (d, *J* = 19.5 Hz), 133.0, 132.9, 130.0 (d, *J* = 16.5 Hz), 129.0, 128.7 (d, *J* = 7.5 Hz), 128.42, 128.4, 128.3, 128.2, 128.0, 127.72, 127.7, 126.8, 126.6, 126.3 (d, *J* = 6.0 Hz), 126.3, 126.1, 126.0, 125.2 (d, *J* = 10.5 Hz), 124.5 (d, *J* = 9.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 96.20. **HRMS (ESI)** *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{20}N_2P^+$ 415.1359, Found 415.1359.

1-phenyl-3,5-di((*E*)-styryl)-1*H*-1,2,4-diazaphosphole (3r)



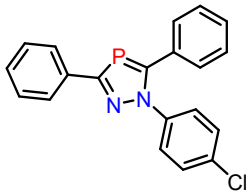
21.3 mg, Yield: 39%. Pale yellow solid, m.p. 207-209 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 7H), 7.43 – 7.28 (m, 11H), 6.93 (dd, *J* = 16.0, 9.6 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.4 (d, *J* = 55.5 Hz), 172.9 (d, *J* = 49.5 Hz), 140.4, 136.8, 136.2, 134.8 (d, *J* = 16.5 Hz), 132.6 (d, *J* = 15.0 Hz), 129.3, 128.9, 128.8, 128.67, 128.65, 128.0, 126.9, 126.7, 126.1, 124.2 (d, *J* = 19.5 Hz), 119.2 (d, *J* = 13.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 83.97. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{24}H_{20}N_2P^+$: 367.1359; found: 367.1359.

3,5-diphenyl-1-(*p*-tolyl)-1*H*-1,2,4-diazaphosphole (3s)



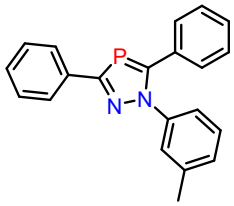
37.4 mg, Yield: 76%. Pale yellow solid, m.p. 134-135 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.38 – 7.34 (m, 1H), 7.28 (s, 5H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.4 (d, *J* = 57.0 Hz), 175.3 (d, *J* = 49.5 Hz), 138.8 (d, *J* = 3.0 Hz), 138.1, 135.9 (d, *J* = 19.5 Hz), 132.8 (d, *J* = 18.0 Hz), 129.4, 129.1 (d, *J* = 7.5 Hz), 128.7, 128.6 (d, *J* = 1.5 Hz), 128.4, 128.3, 126.3 (d, *J* = 9.0 Hz), 125.8, 21.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 93.69. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{18}N_2P^+$: 329.1202; found: 329.1202.

1-(4-chlorophenyl)-3,5-diphenyl-1*H*-1,2,4-diazaphosphole (3t)



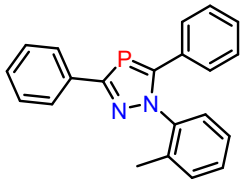
31.4 mg, Yield: 60%. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.32 – 7.26 (m, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.7 (d, *J* = 57.0 Hz), 175.5 (d, *J* = 49.5 Hz), 139.6 (d, *J* = 1.5 Hz), 135.6 (d, *J* = 19.5 Hz), 133.9, 132.4 (d, *J* = 18.0 Hz), 129.1 (d, *J* = 7.5 Hz), 129.0, 128.8 (d, *J* = 1.5 Hz), 128.75, 128.6, 127.2, 126.4, 126.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 96.01. **HRMS (ESI)** *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{15}ClN_2P^+$ 349.0656, Found 349.0656.

3,5-diphenyl-1-(*m*-tolyl)-1*H*-1,2,4-diazaphosphole (3u)



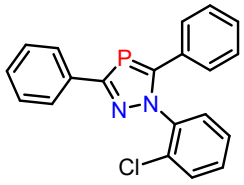
39.4 mg, Yield: 80%. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 6.8 Hz, 2H), 7.42 (t, *J* = 6.8 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.25 (m, 5H), 7.20 – 7.12 (m, 3H), 7.03 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.5 (d, *J* = 57.0 Hz), 175.4 (d, *J* = 49.5 Hz), 141.1 139.1, 135.9 (d, *J* = 19.5 Hz), 132.7 (d, *J* = 18.0Hz), 129.1 (d, *J* = 7.5 Hz), 128.9, 128.7, 128.6 (d, *J* = 1.5 Hz), 128.50, 128.47, 128.3, 126.6, 126.4 (d, *J* = 9.0 Hz), 123.2, 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 93.87. **HRMS (ESI)** *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{18}N_2P^+$ 329.1202, Found 329.1203.

3,5-diphenyl-1-(*o*-tolyl)-1*H*-1,2,4-diazaphosphole (3v)



38.4 mg, Yield: 78%. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 6.8 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.32 – 7.19 (m, 9H), 2.04 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.6 (d, *J* = 57.0 Hz), 176.7 (d, *J* = 49.5 Hz), 140.7 (d, *J* = 3.0 Hz), 135.9 (d, *J* = 18.0 Hz), 135.1, 132.3 (d, *J* = 18.0 Hz), 131.1, 129.2, 128.8 (d, *J* = 9.0 Hz), 128.7, 128.6 (d, *J* = 1.5 Hz), 128.5, 128.2, 127.7, 126.5, 126.3 (d, *J* = 9.0 Hz), 17.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 87.84. **HRMS (ESI)** *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{18}N_2P^+$ 329.1202, Found 329.1201.

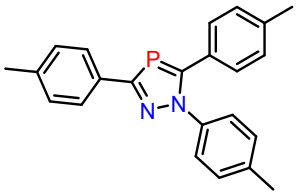
1-(2-chlorophenyl)-3,5-diphenyl-1*H*-1,2,4-diazaphosphole (3w)



33.9 mg, Yield: 65%. White solid, m.p. 133 – 135 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.8 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 4H), 7.38 – 7.22 (m, 8H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.9 (d, *J* = 57.0 Hz), 177.6 (d, *J* = 49.5 Hz), 139.2 (d, *J* = 1.5 Hz), 135.7 (d, *J* = 19.5 Hz), 132.1 (d, *J* = 18.0 Hz), 131.9, 130.42, 130.39, 129.5, 128.9,

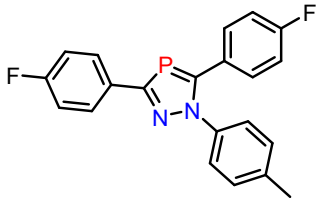
128.8, 128.7, 128.3, 127.4, 126.5, 126.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 89.11. **HRMS (ESI)** *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{15}ClN_2P^+$ 349.0656, Found 349.0657.

1,3,5-tri-*p*-tolyl-1*H*-1,2,4-diazaphosphole (3x)



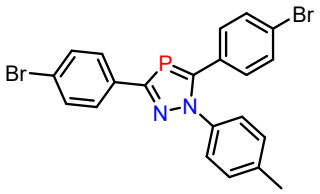
30.3 mg, Yield: 57%. White solid, m.p. 153-155 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.23 – 7.20 (m, 4H), 7.14 (t, *J* = 8.8 Hz, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.4 (d, *J* = 57.0 Hz), 175.3 (d, *J* = 48.0 Hz), 139.0 (d, *J* = 1.5 Hz), 138.4, 138.0, 133.2 (d, *J* = 19.5 Hz), 129.9 (d, *J* = 18.0 Hz), 129.4, 129.3, 129.03, 128.99, 128.95, 126.2 (d, *J* = 9.0 Hz), 125.8, 21.3, 21.2, 21.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 92.08. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{23}H_{22}N_2P^+$: 357.1515; found: 357.1515.

3,5-bis(4-fluorophenyl)-1-(*p*-tolyl)-1*H*-1,2,4-diazaphosphole (3y)



33.4 mg, Yield: 61%. White solid, m.p. 125-126 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.22 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.08 (t, *J* = 8.4 Hz, 2H), 6.95 (t, *J* = 8.4 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.2 (d, *J* = 57.0 Hz), 174.1 (d, *J* = 49.5 Hz), 163.1 (dd, *J* = 247.5, 3.0 Hz), 162.7 (dd, *J* = 247.5, 1.5 Hz), 138.5 (d, *J* = 1.5 Hz), 138.4, 132.0 (dd, *J* = 19.5, 3.0 Hz), 130.9 (q, *J* = 7.5 Hz), 129.5, 128.7 (dd, *J* = 18.0, 4.5 Hz), 128.0 (q, *J* = 7.5 Hz), 125.7, 115.6 (d, *J* = 13.5 Hz), 115.4 (d, *J* = 15.0 Hz), 21.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 92.75. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.29 – -112.37 (m), -113.16 – -113.24 (m). **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{21}H_{16}F_2N_2P^+$: 365.1014; found: 365.1015.

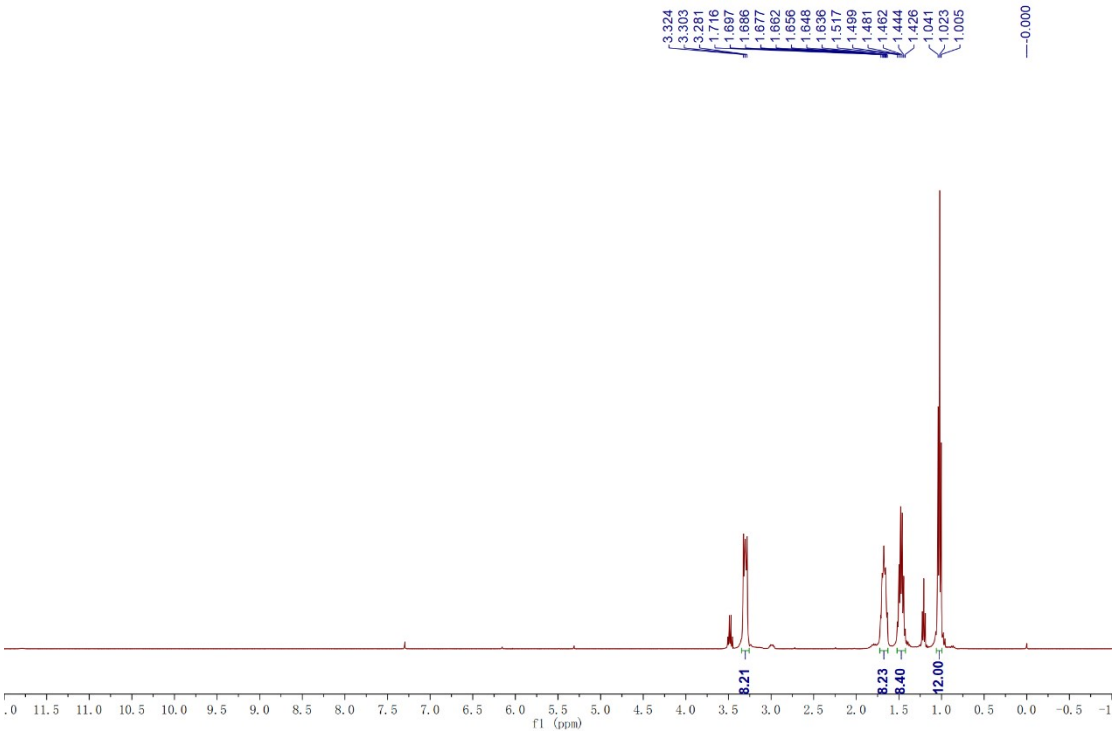
3,5-bis(4-bromophenyl)-1-(*p*-tolyl)-1*H*-1,2,4-diazaphosphole (3z)



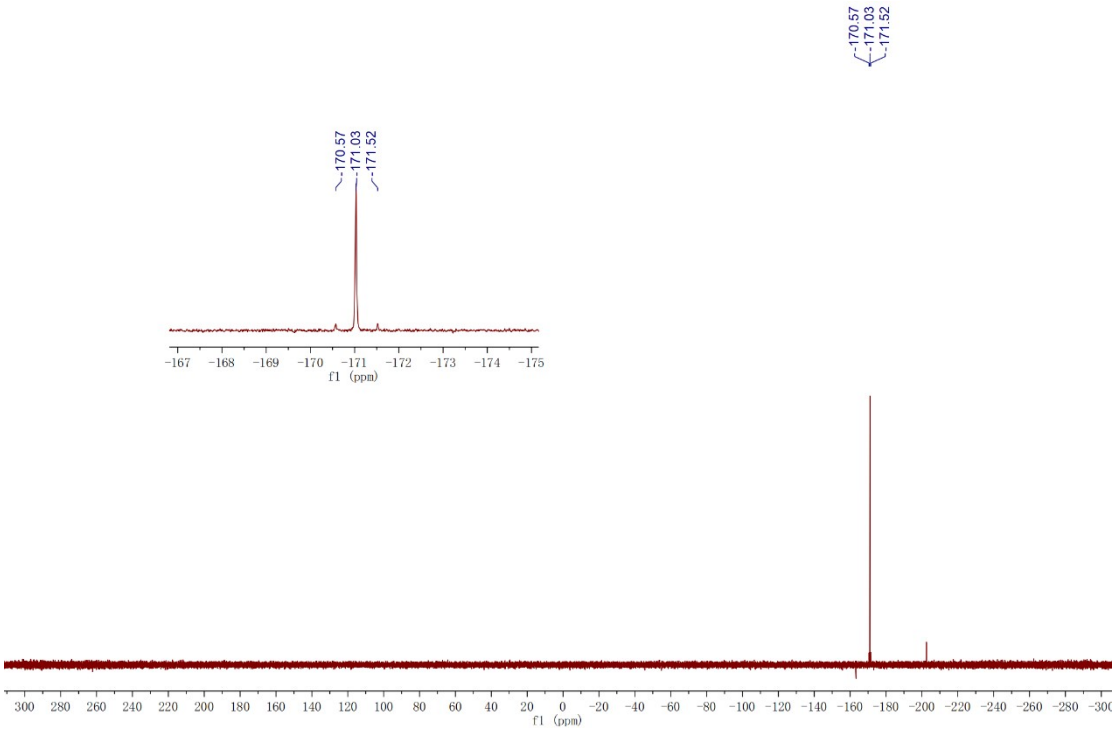
54.4 mg, Yield: 75%. Yellow solid, m.p. 190 – 192 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.14 (m, 4H), 7.11 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.2 (d, *J* = 57.0 Hz), 174.0 (d, *J* = 49.5 Hz), 138.6, 138.4 (d, *J* = 3.0 Hz), 134.7 (d, *J* = 21.0 Hz), 131.8, 131.6, 131.5 (d, *J* = 18.0 Hz), 130.5 (d, *J* = 7.5 Hz), 129.6, 127.8 (d, *J* = 10.5 Hz), 125.7, 123.0 (d, *J* = 1.5 Hz), 122.7 (d, *J* = 3.0 Hz), 21.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 95.15. **HRMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{21}H_{16}Br_2N_2P^+$ 486.9392, Found 486.9393.

9. Copies of NMR Spectra

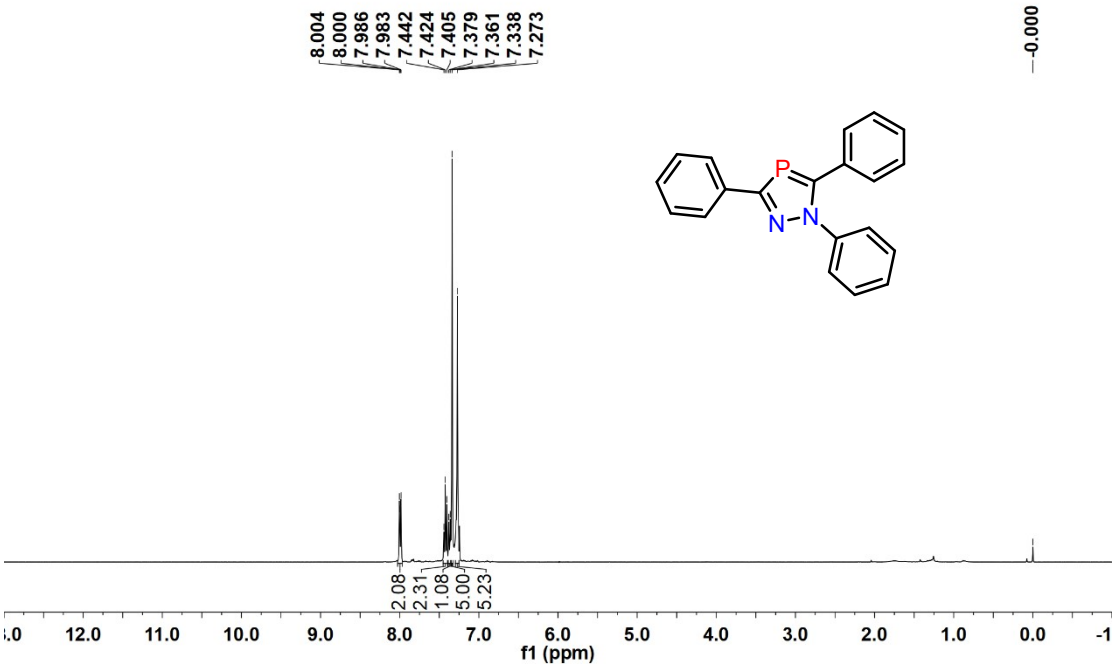
^{1}H NMR (400 MHz, $CDCl_3$) of **$[Bu_4N][P(SiCl_3)_2]$**



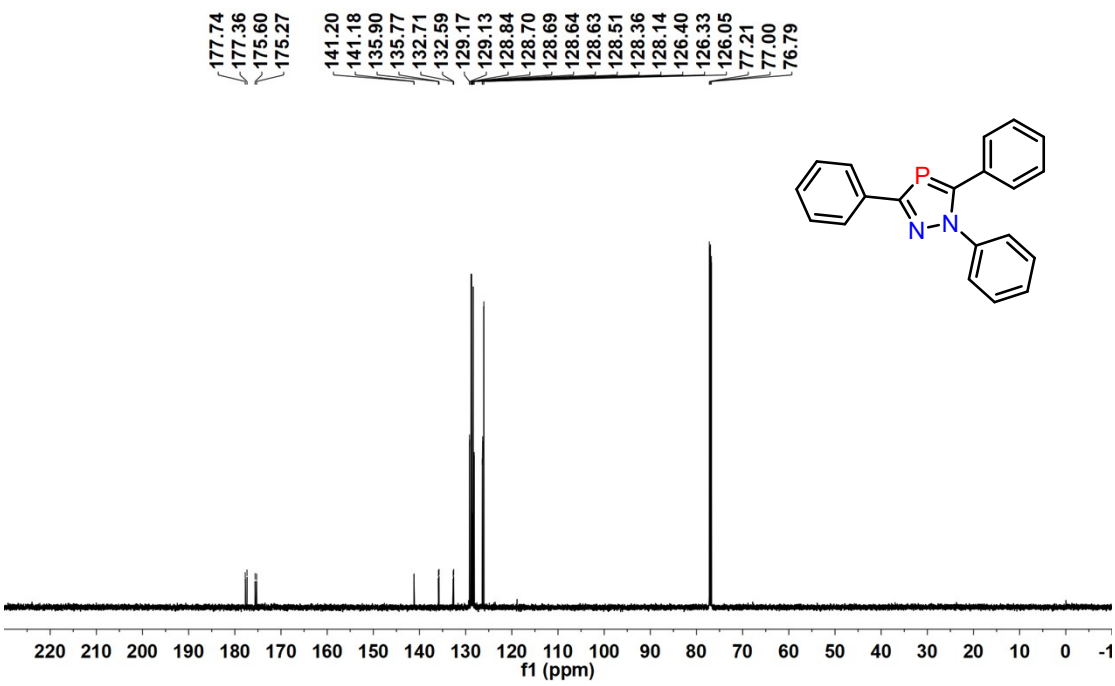
^{31}P NMR (162 MHz, $CDCl_3$) of **$[Bu_4N][P(SiCl_3)_2]$**



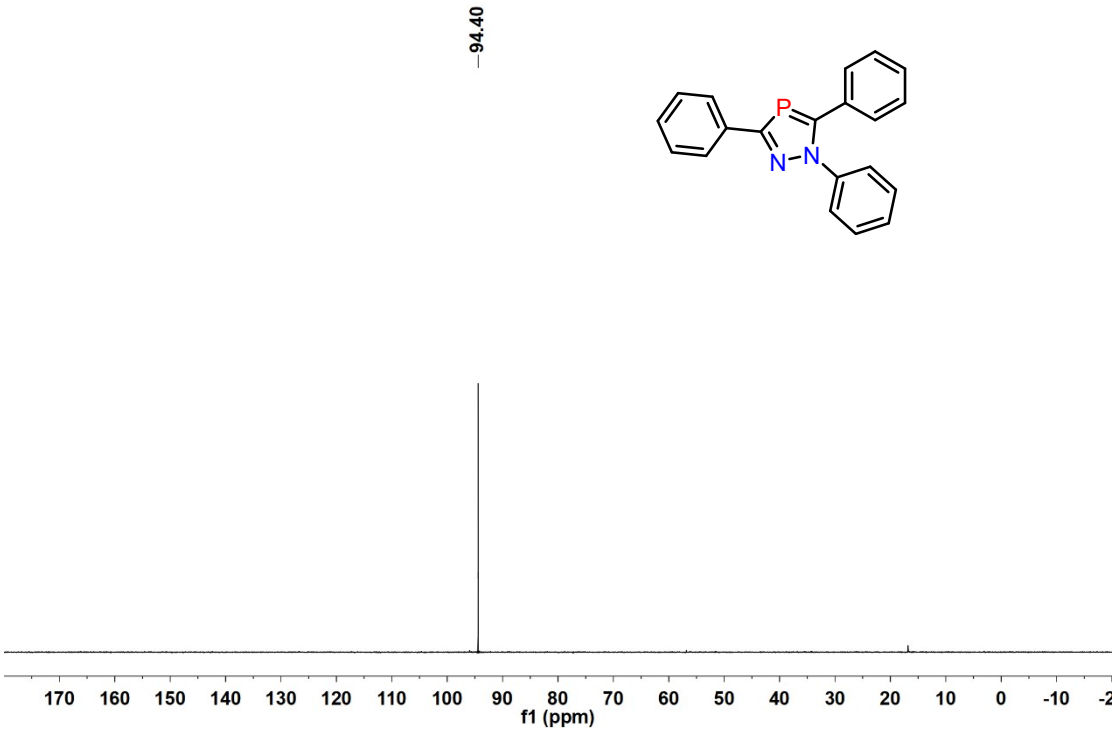
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



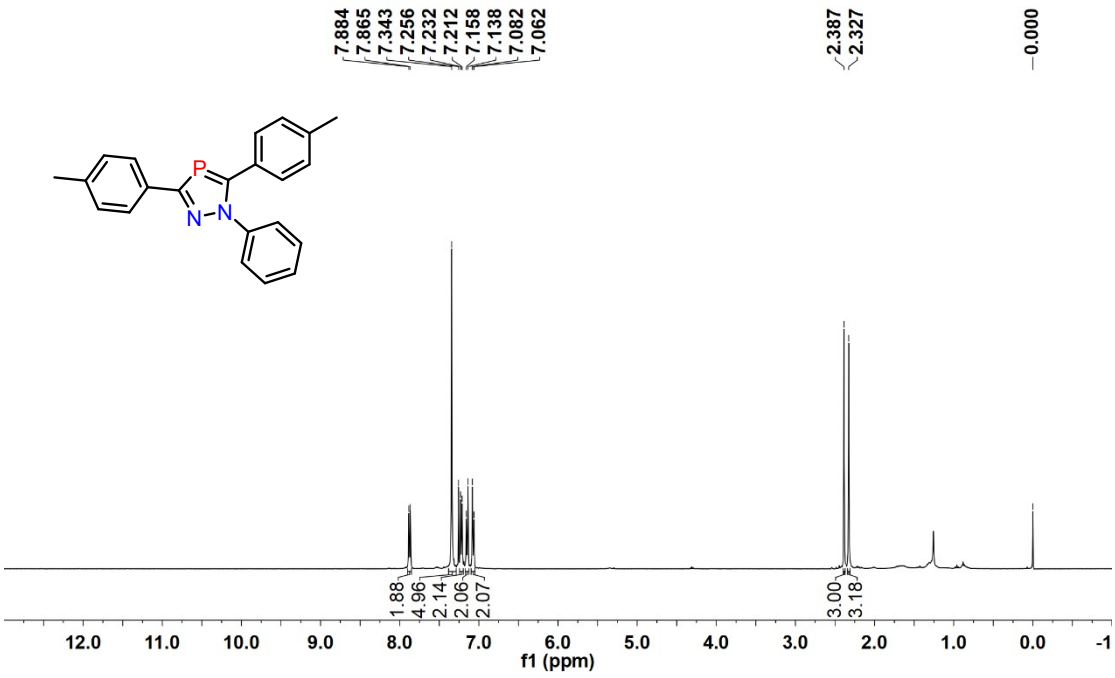
^{13}C NMR (151 MHz, $CDCl_3$) of **3a**



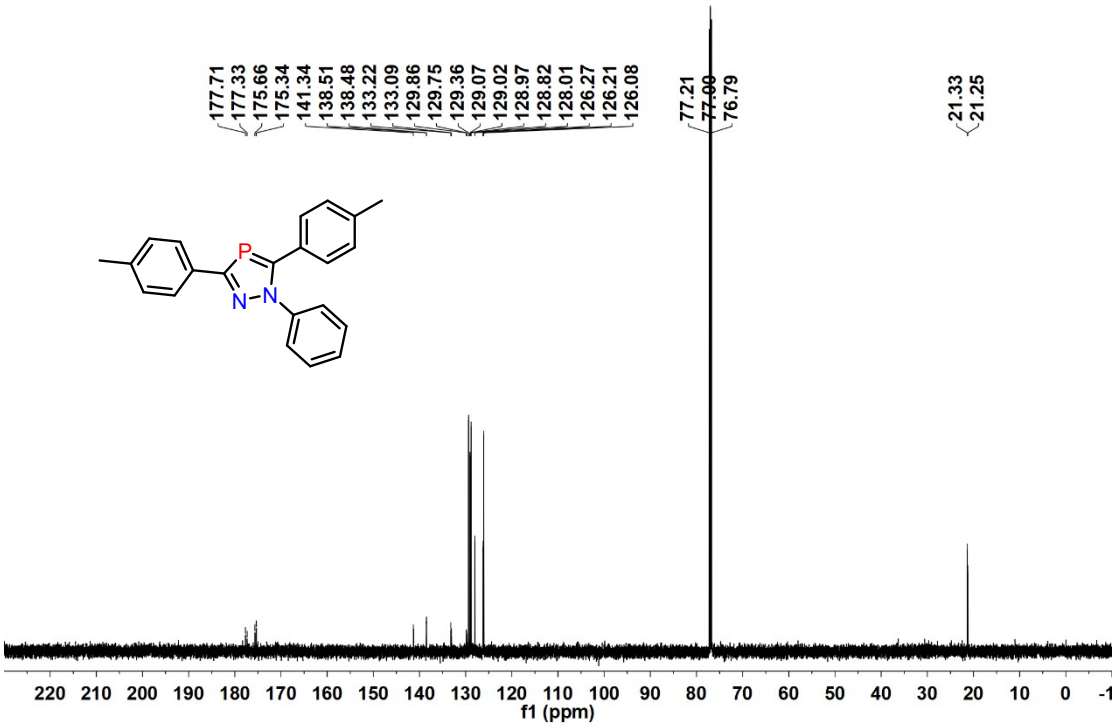
^{31}P NMR (162 MHz, $CDCl_3$) of **3a**



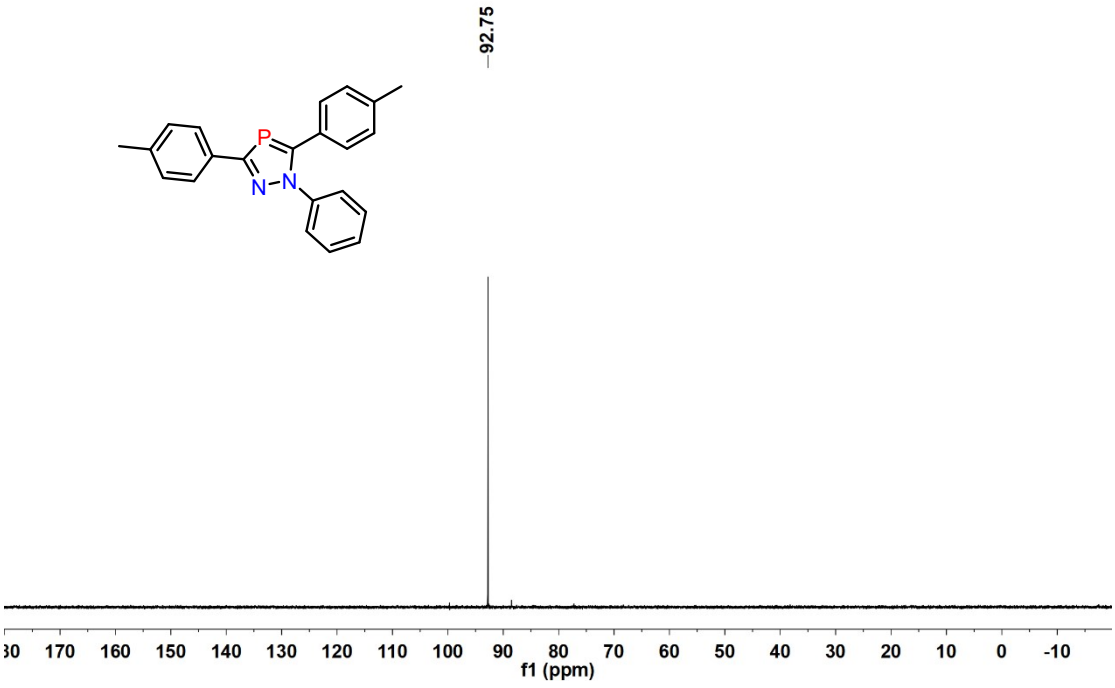
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



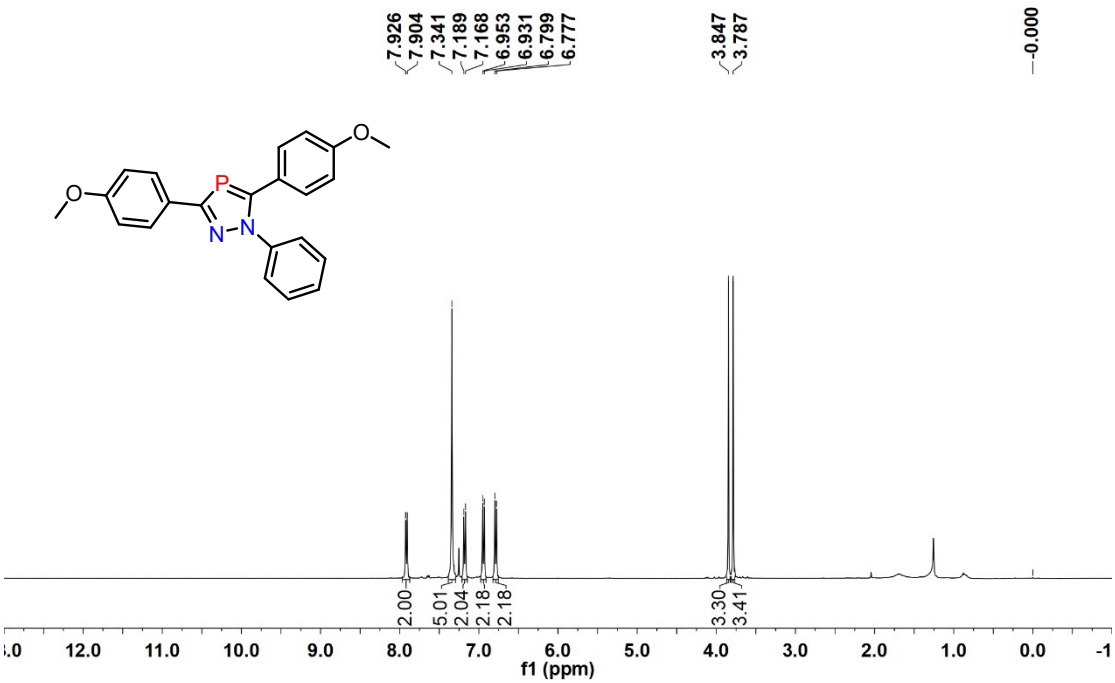
^{13}C NMR (151 MHz, $CDCl_3$) of **3b**



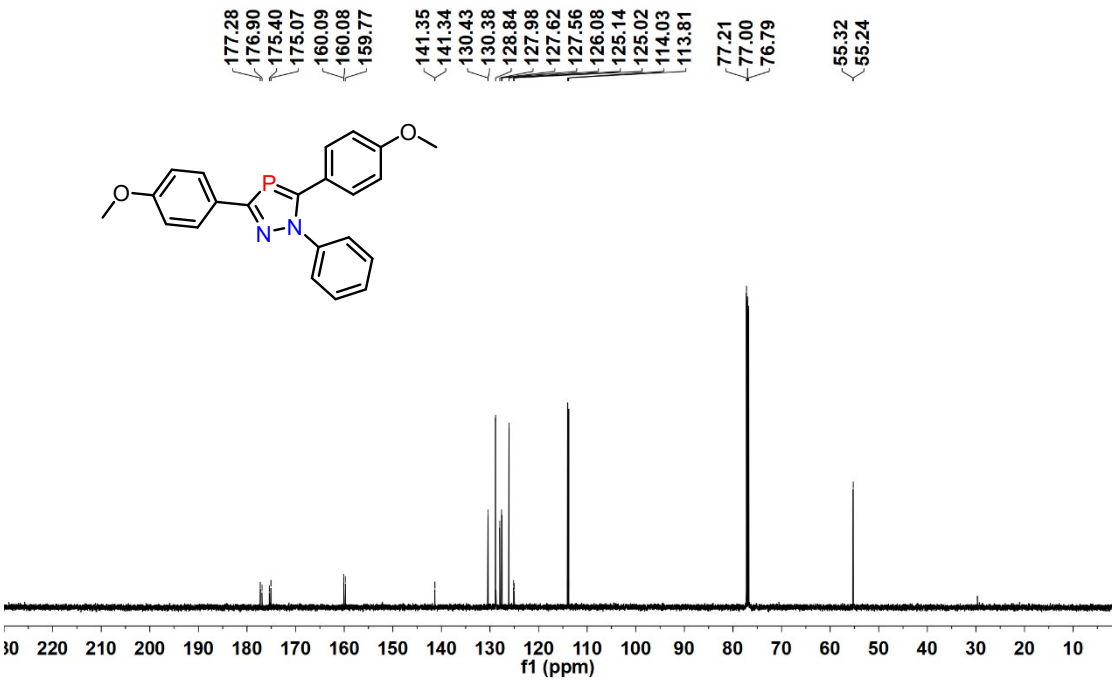
^{31}P NMR (162 MHz, $CDCl_3$) of **3b**



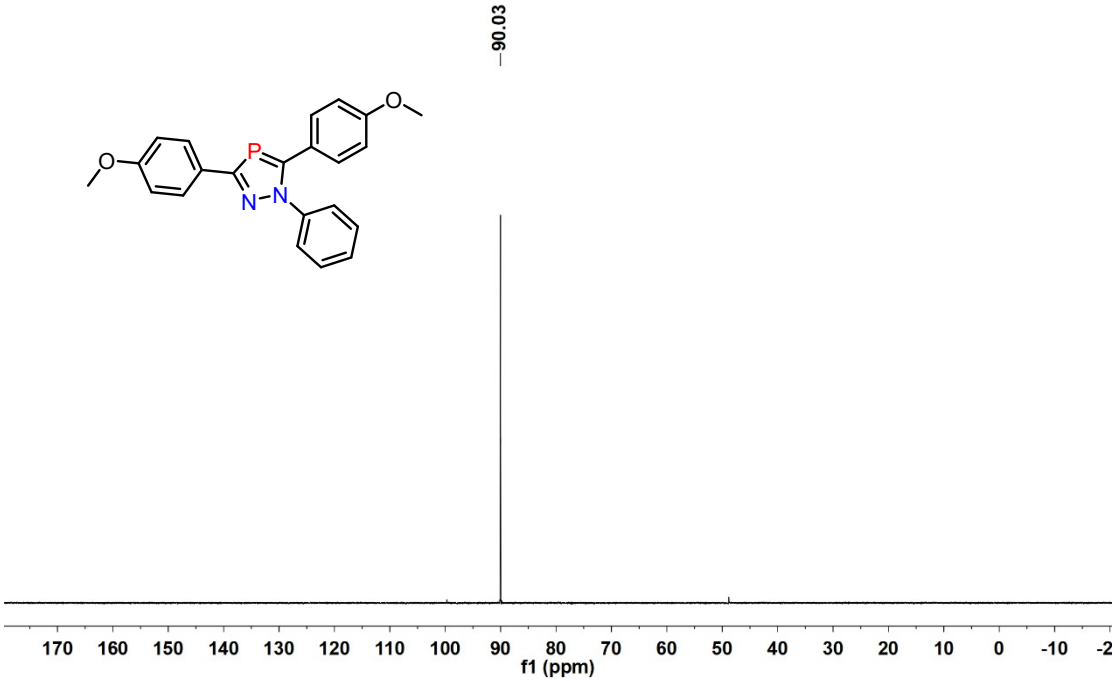
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



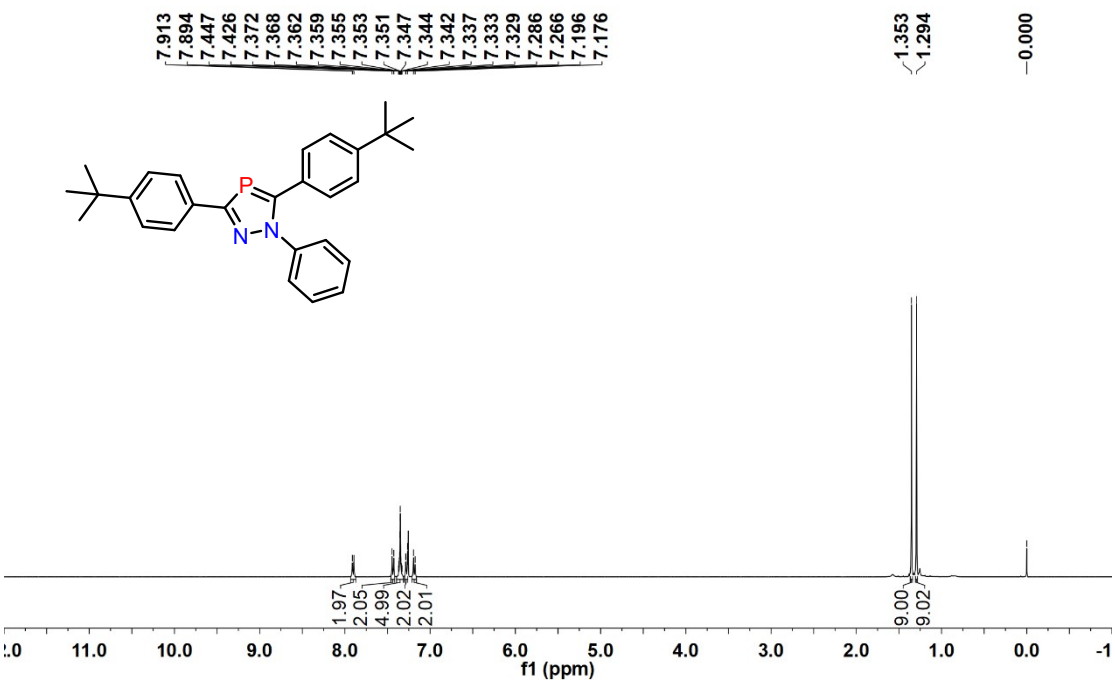
^{13}C NMR (151 MHz, $CDCl_3$) of **3c**



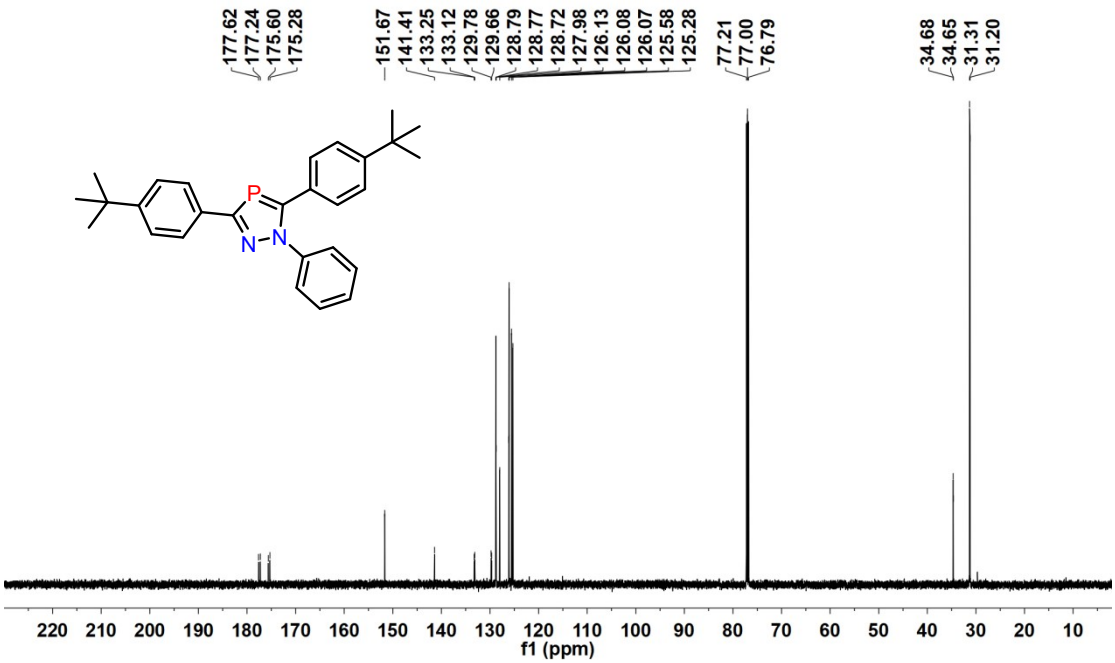
^{31}P NMR (162 MHz, $CDCl_3$) of **3c**



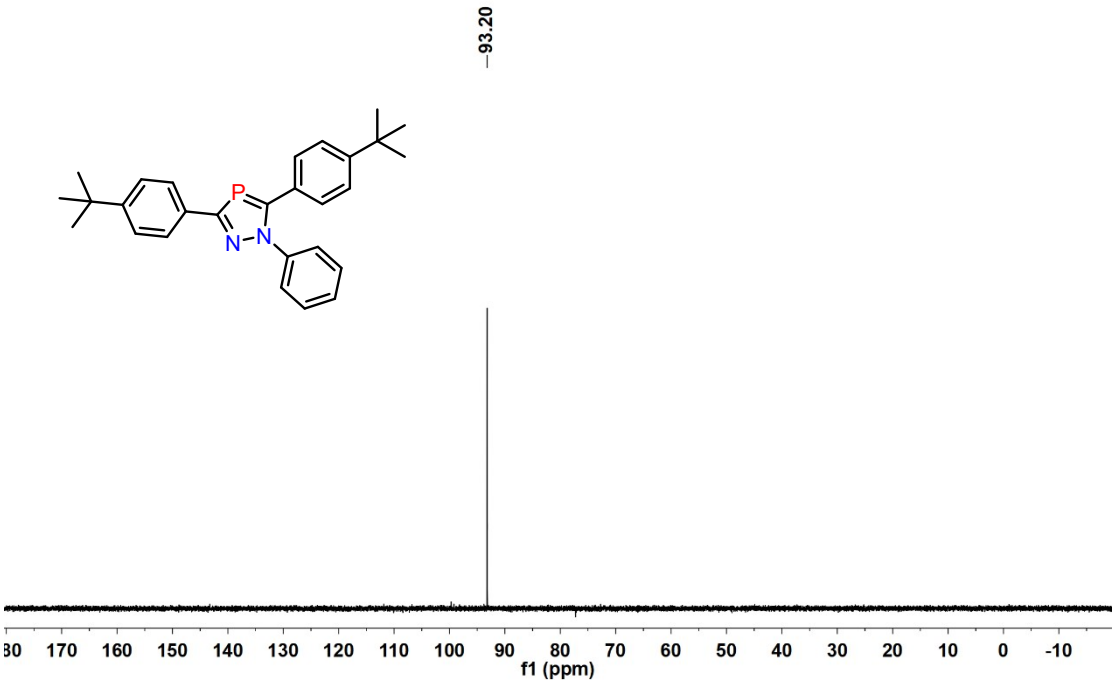
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



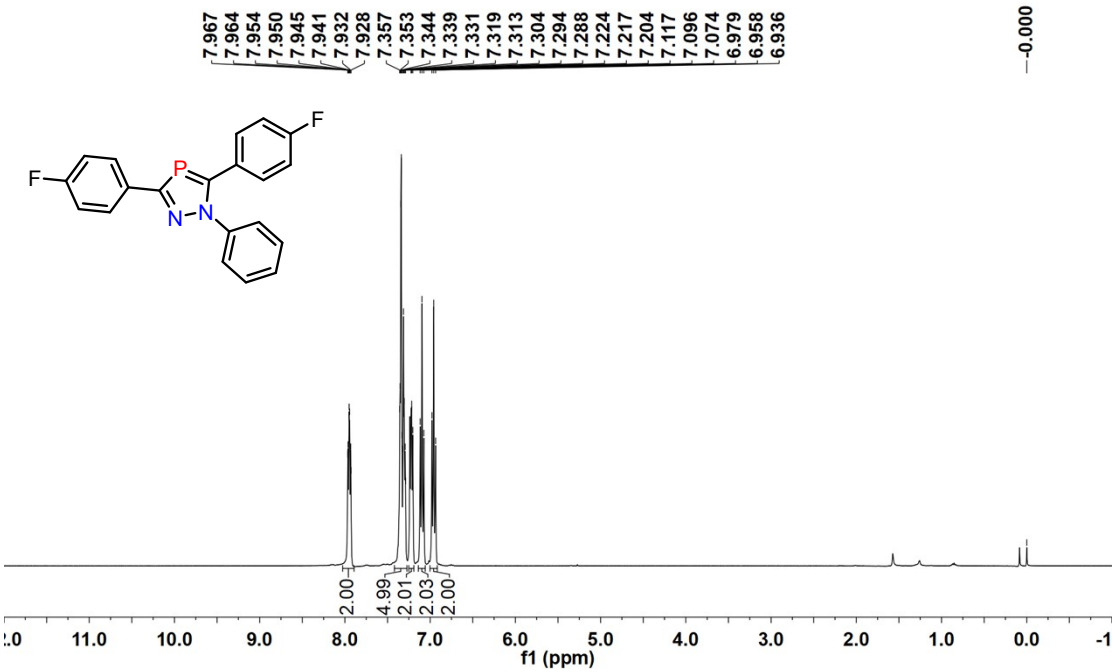
^{13}C NMR (151 MHz, $CDCl_3$) of **3d**



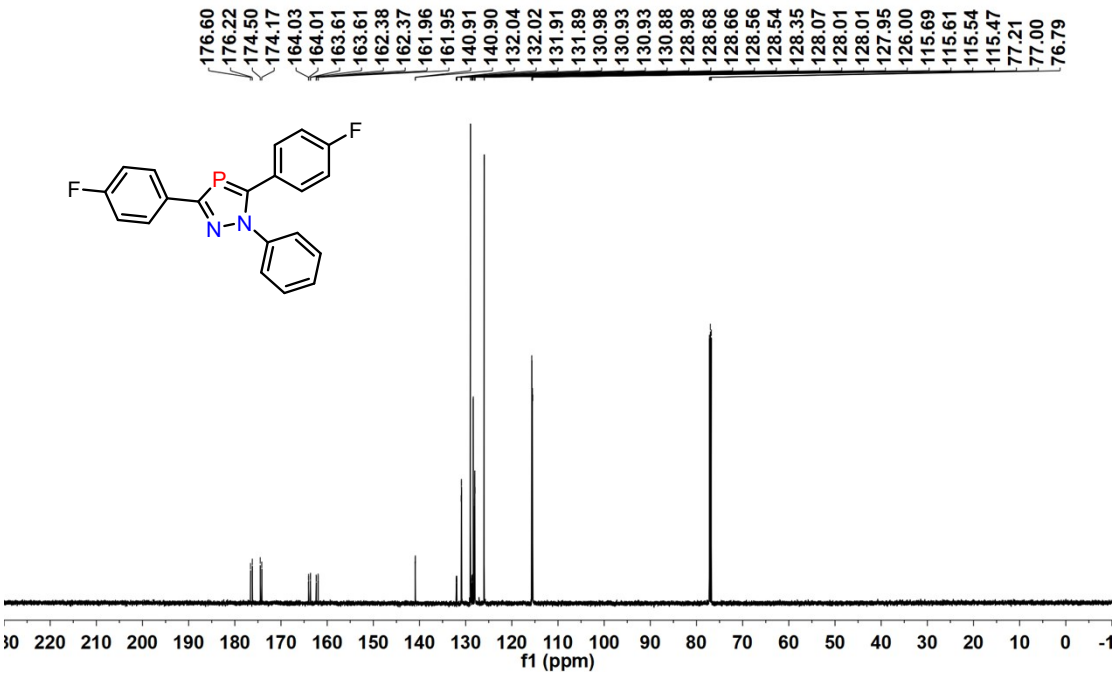
^{31}P NMR (162 MHz, $CDCl_3$) of **3d**



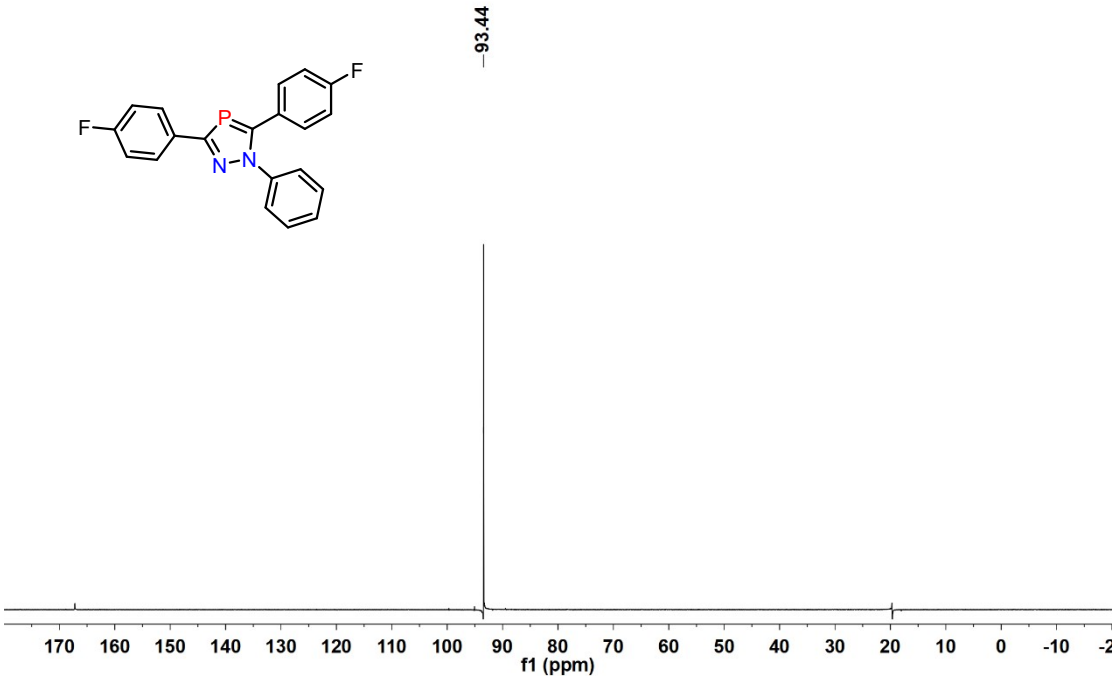
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



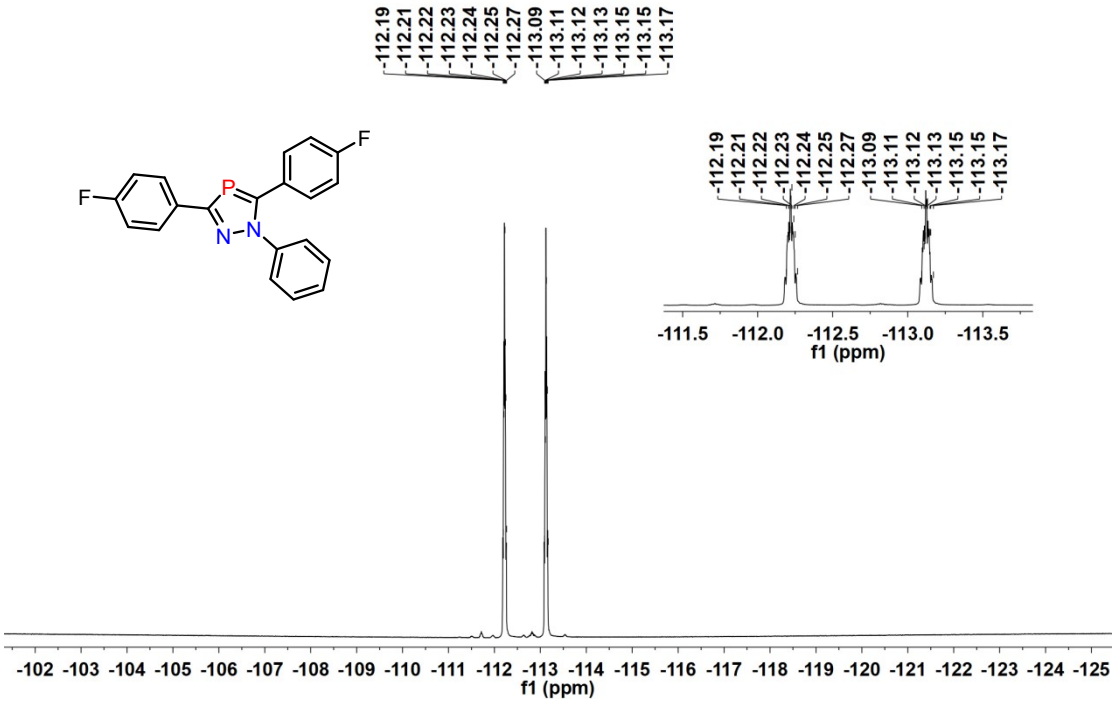
^{13}C NMR (151 MHz, $CDCl_3$) of **3e**



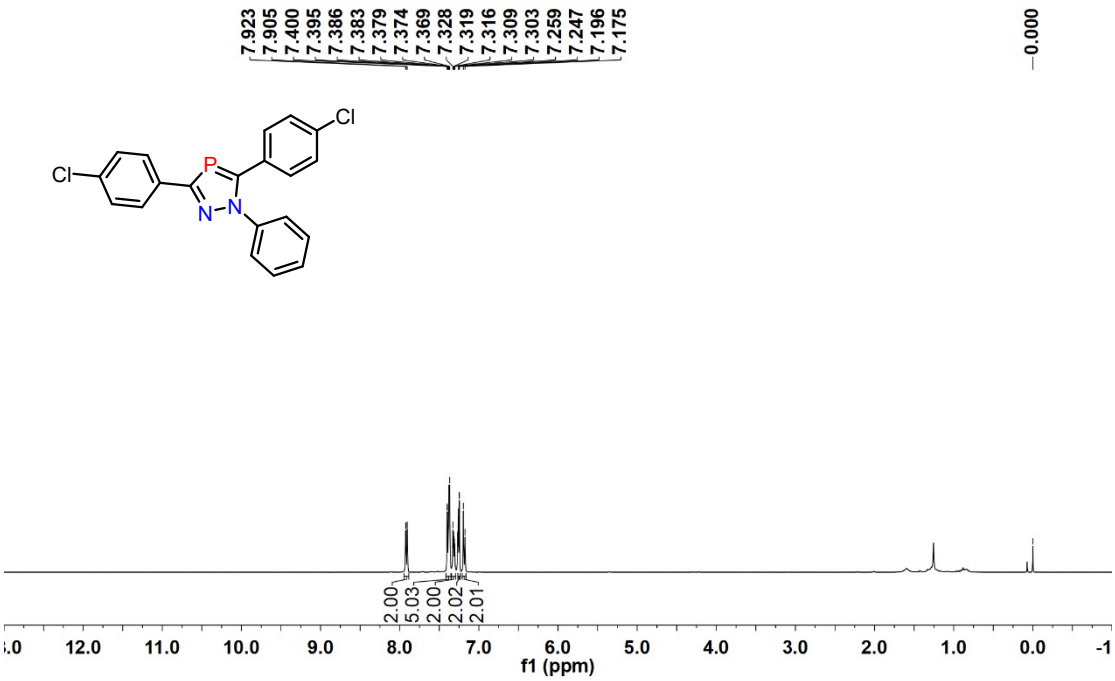
^{31}P NMR (162 MHz, $CDCl_3$) of **3e**



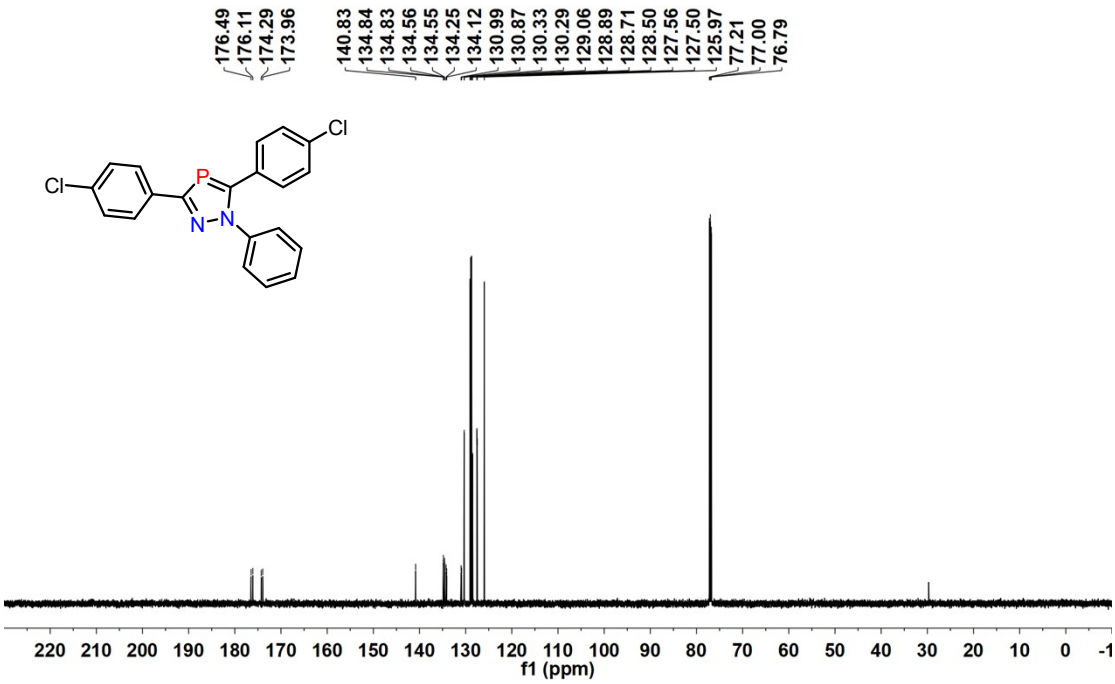
^{19}F NMR (376 MHz, $CDCl_3$) of **3e**



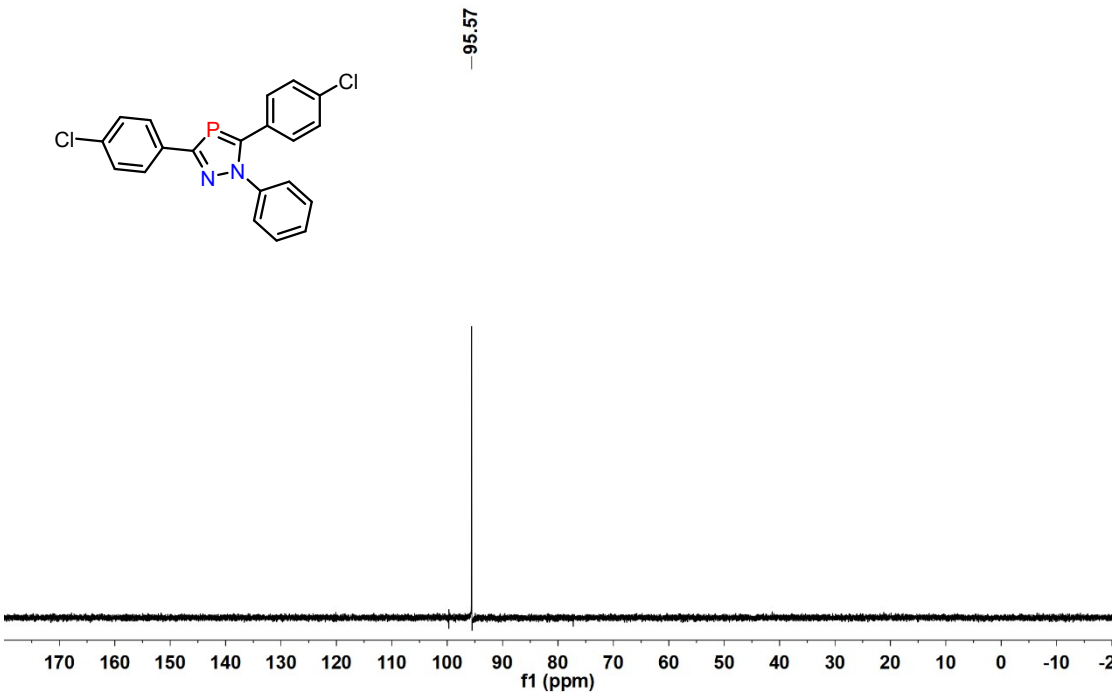
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



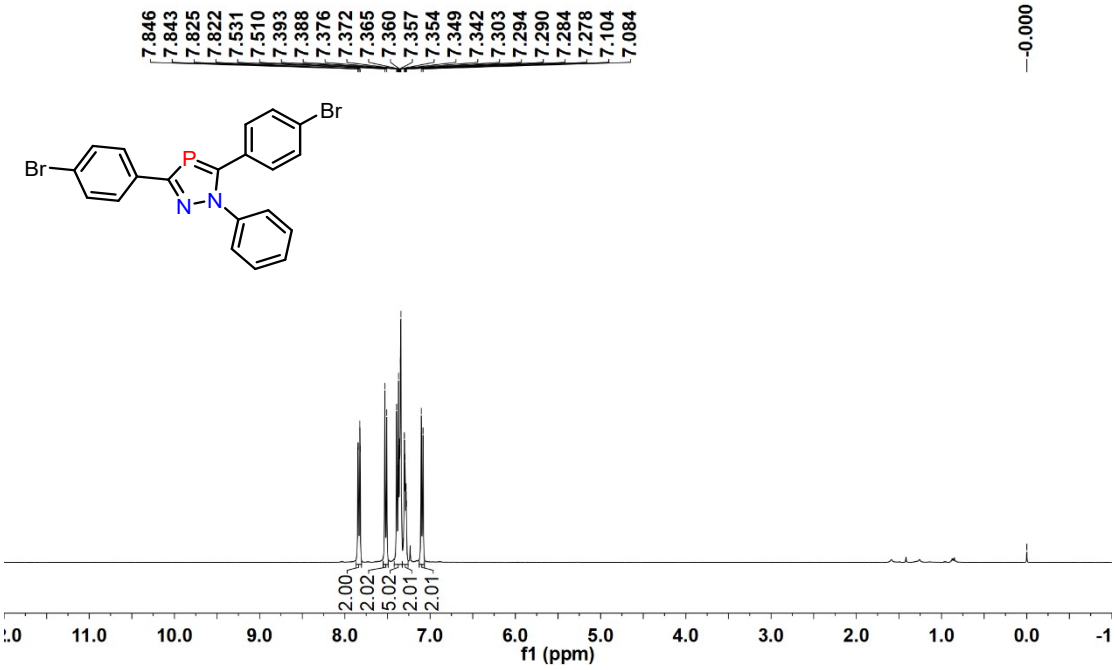
^{13}C NMR (151 MHz, $CDCl_3$) of **3f**



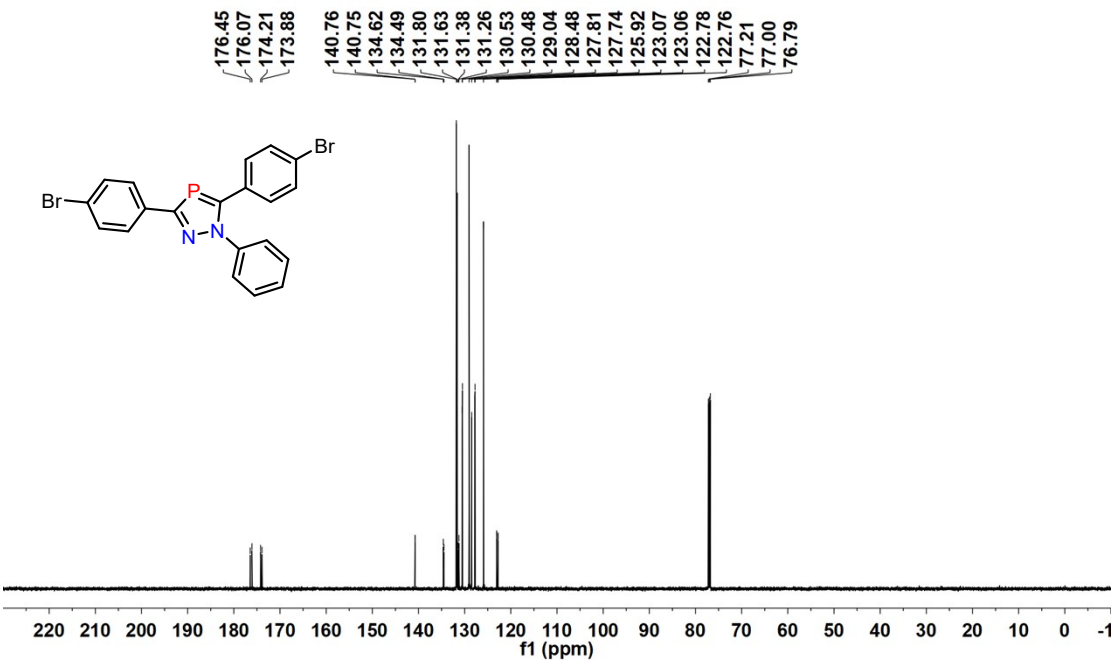
^{31}P NMR (162 MHz, $CDCl_3$) of **3f**



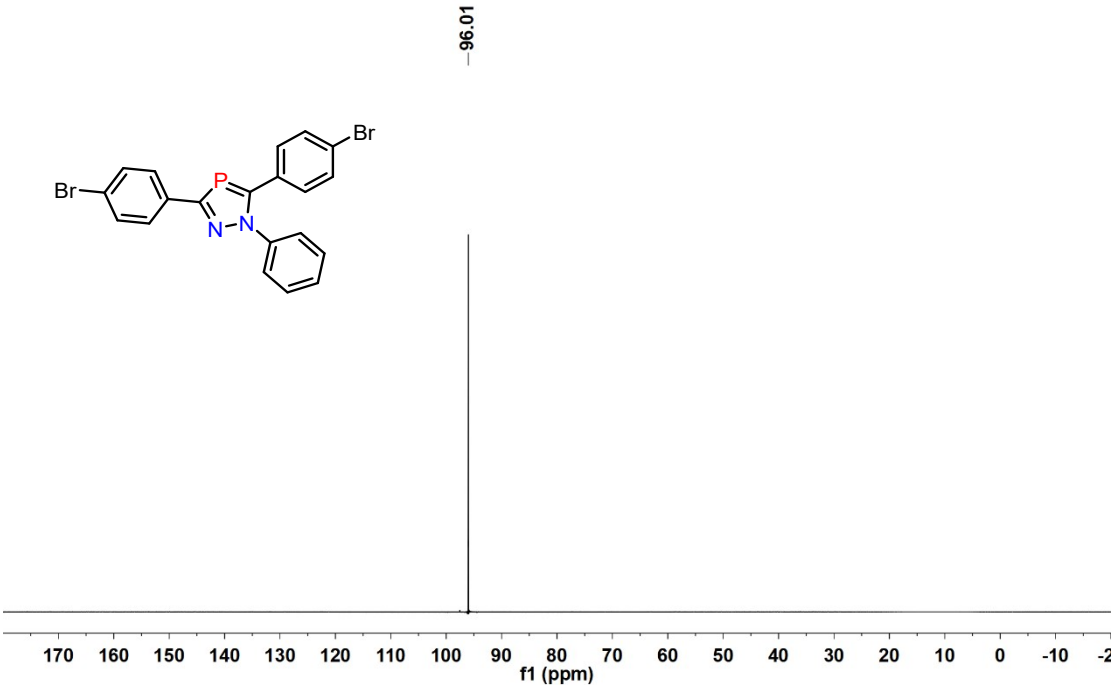
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



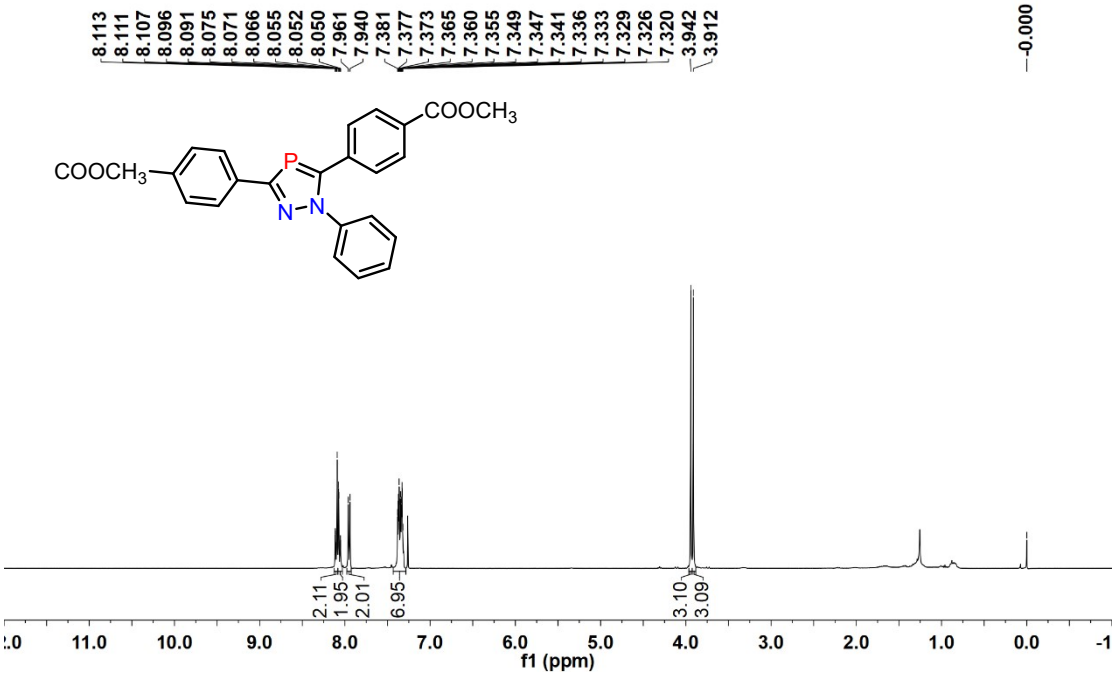
^{13}C NMR (151 MHz, $CDCl_3$) of **3g**



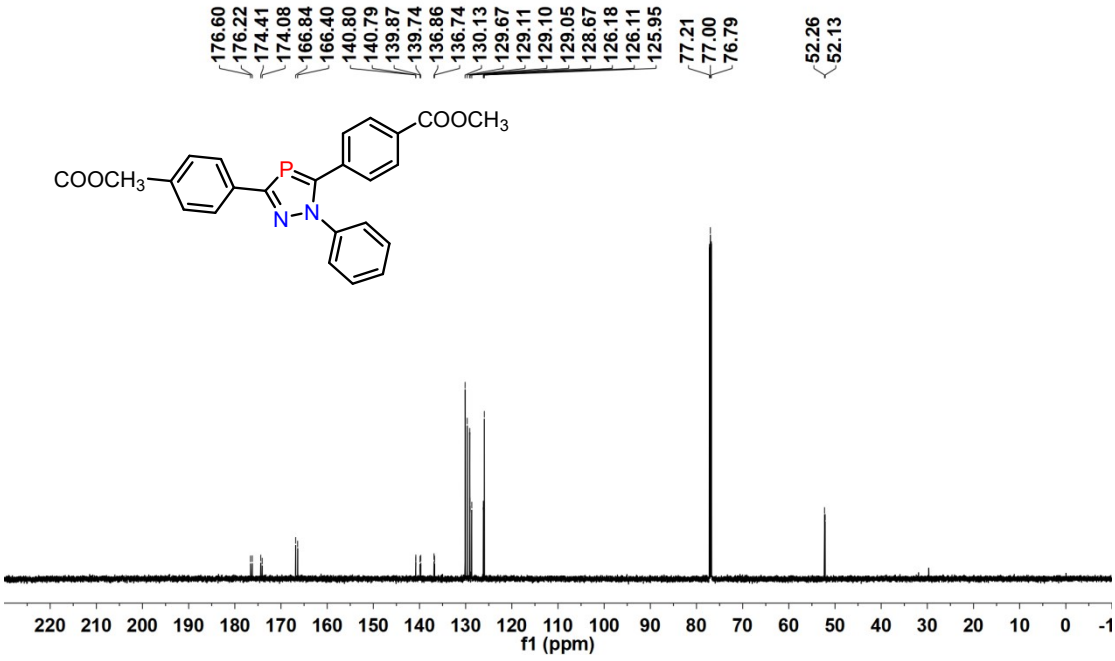
^{31}P NMR (162 MHz, $CDCl_3$) of **3g**



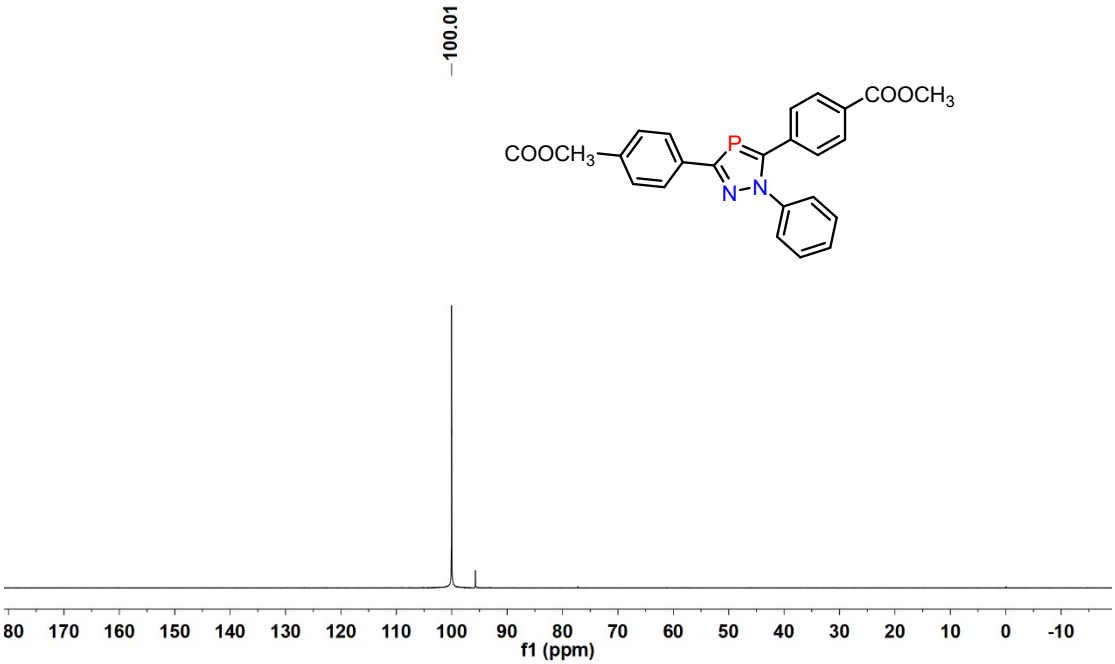
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



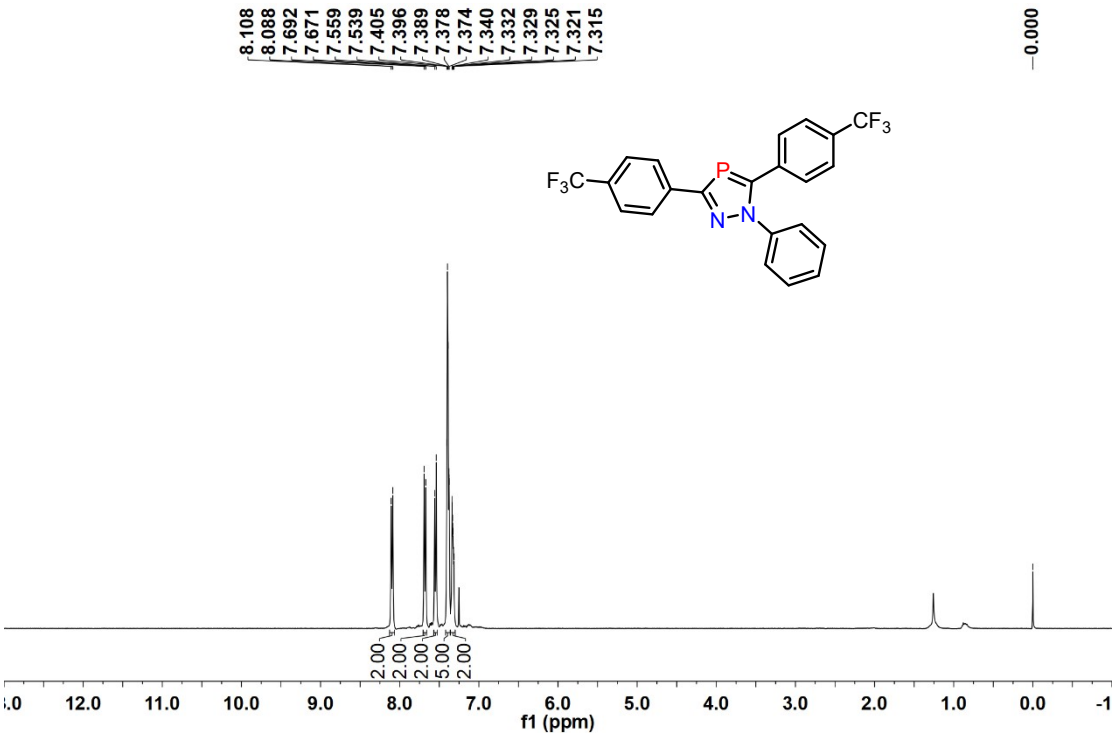
^{13}C NMR (151 MHz, $CDCl_3$) of **3h**



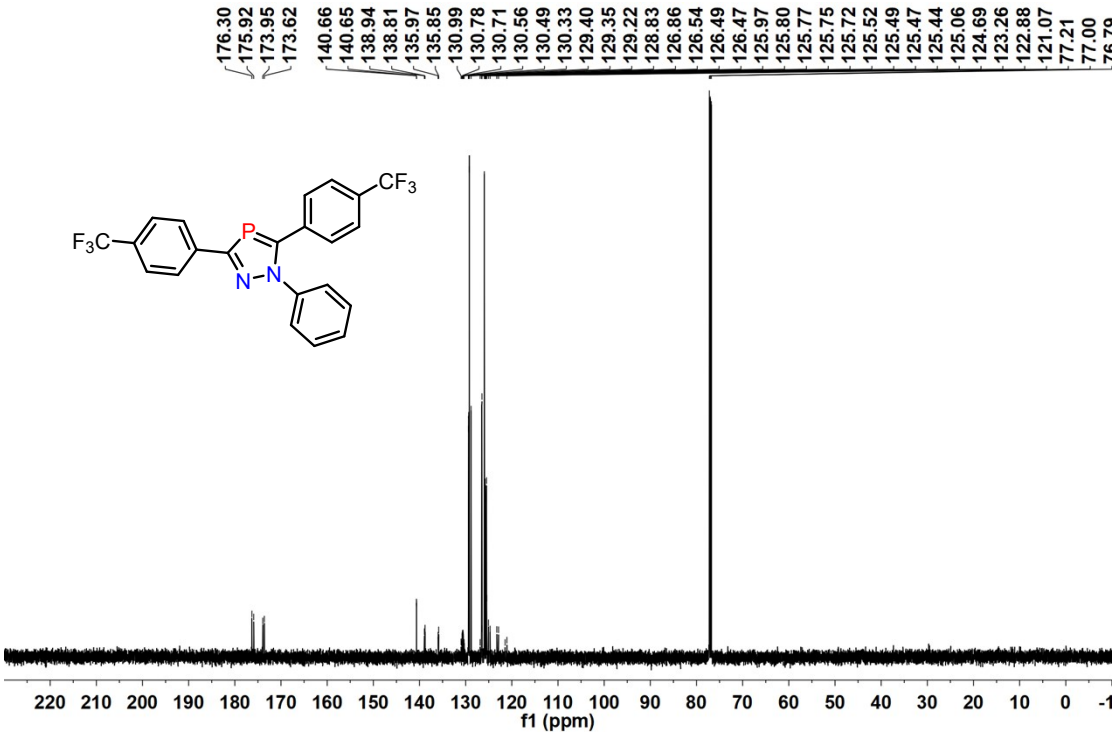
^{31}P NMR (162 MHz, $CDCl_3$) of **3h**



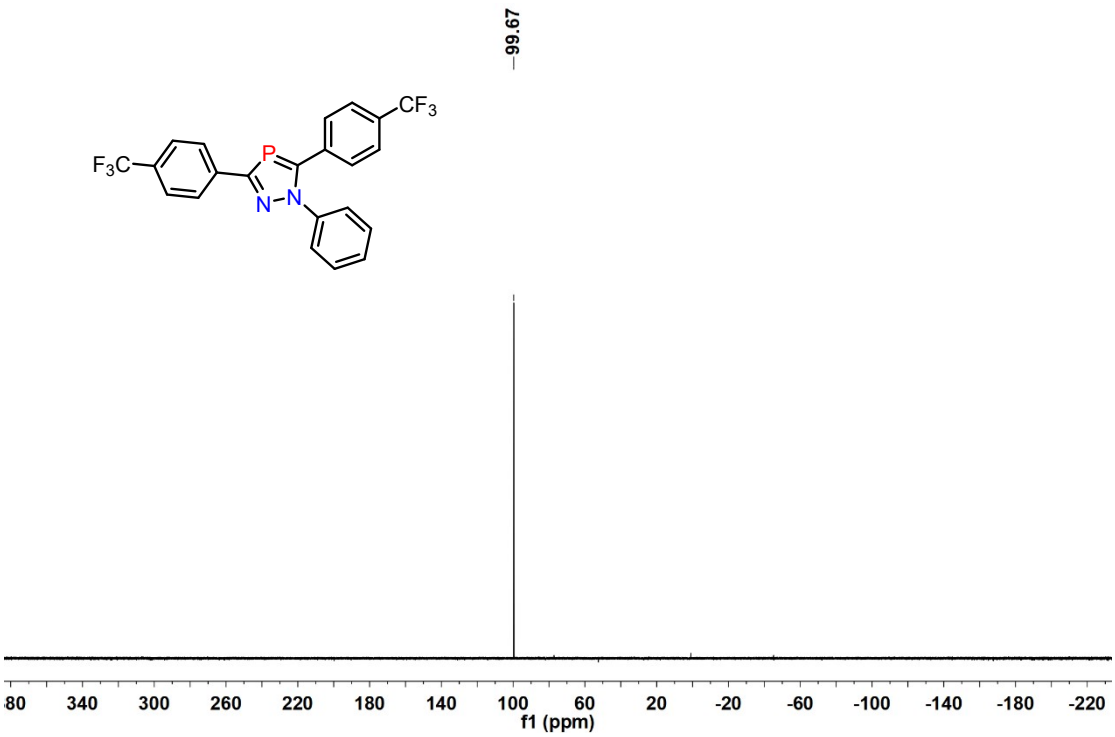
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



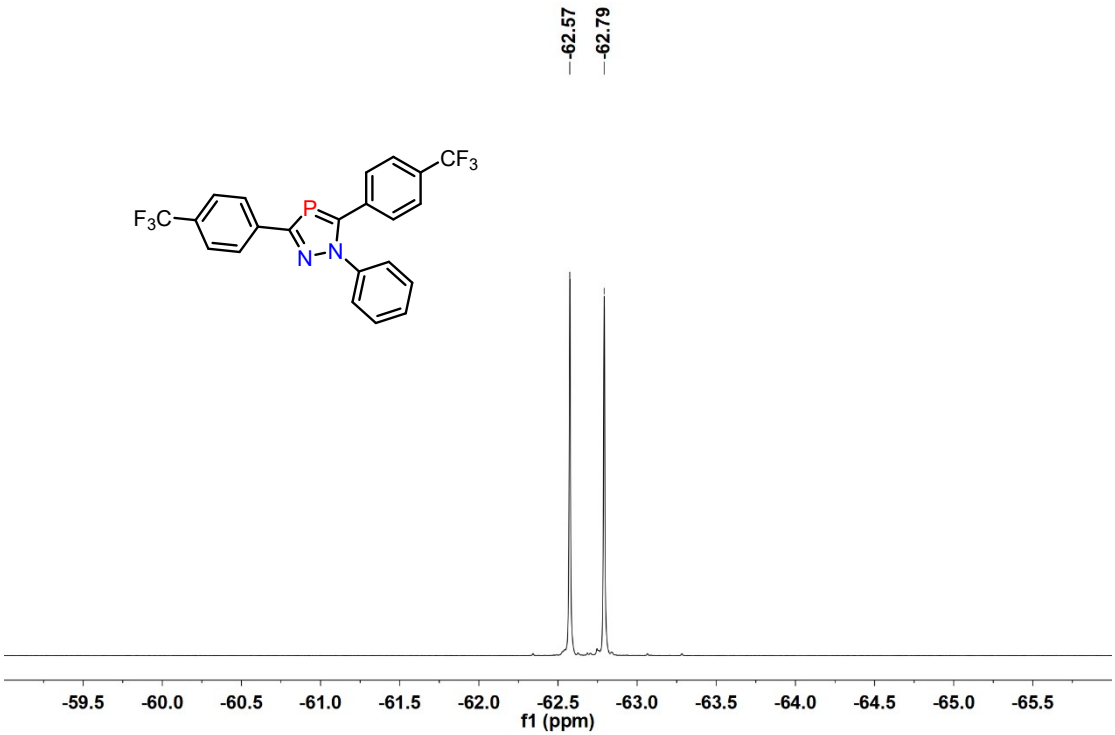
^{13}C NMR (151 MHz, $CDCl_3$) of **3i**



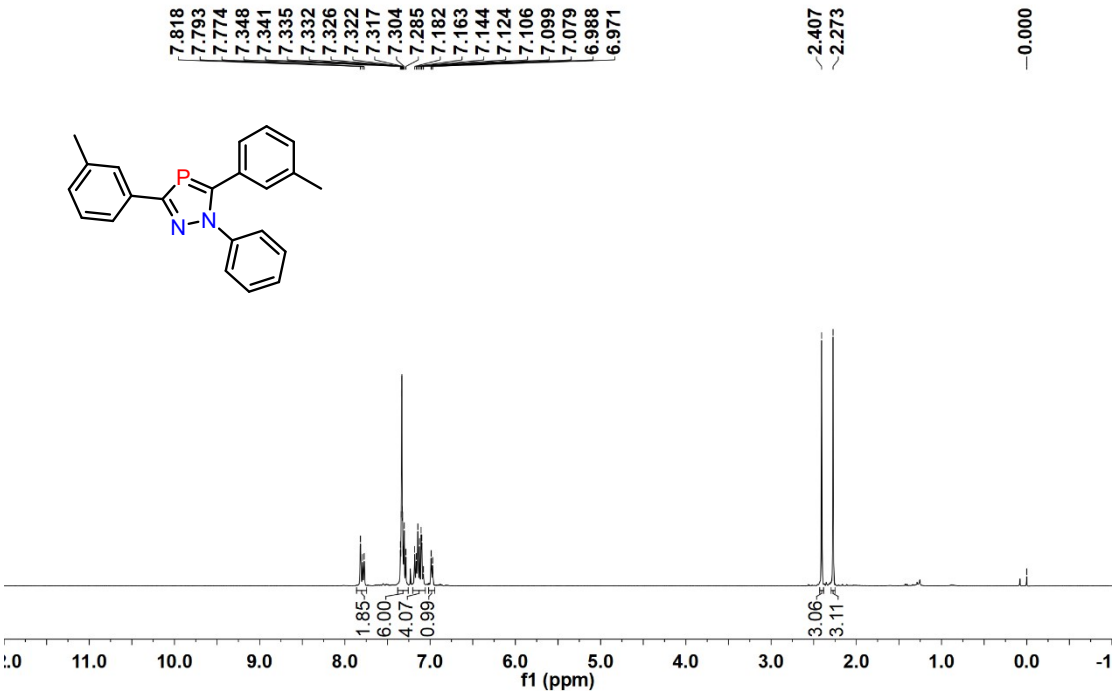
^{31}P NMR (162 MHz, $CDCl_3$) of **3i**



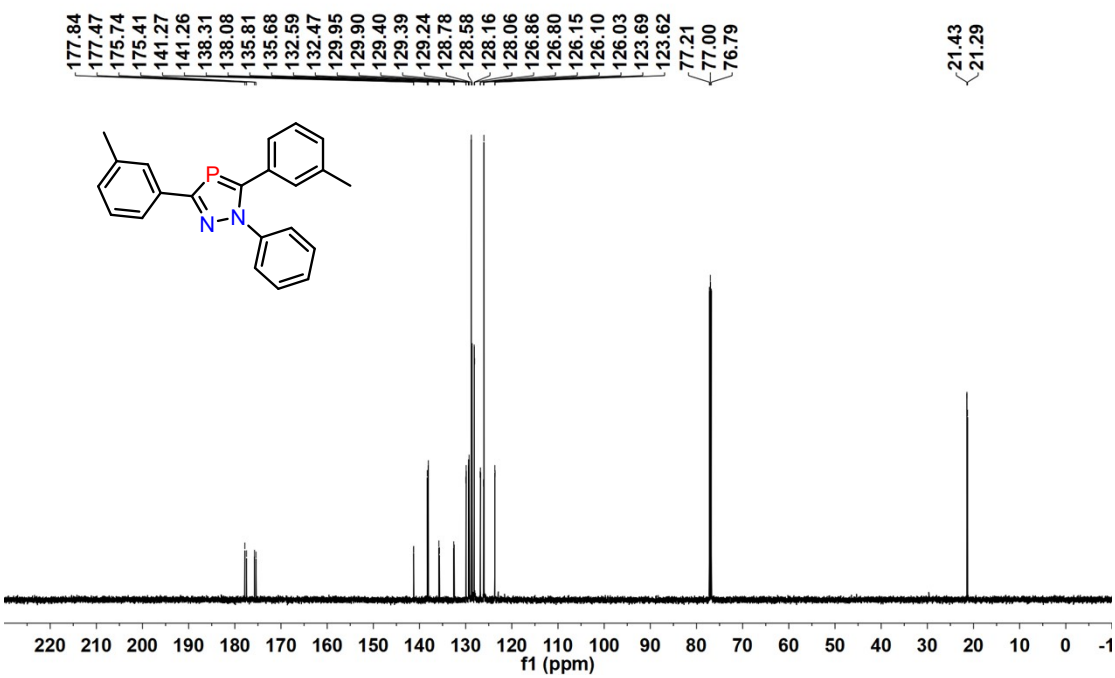
^{19}F NMR (376 MHz, $CDCl_3$) of **3i**



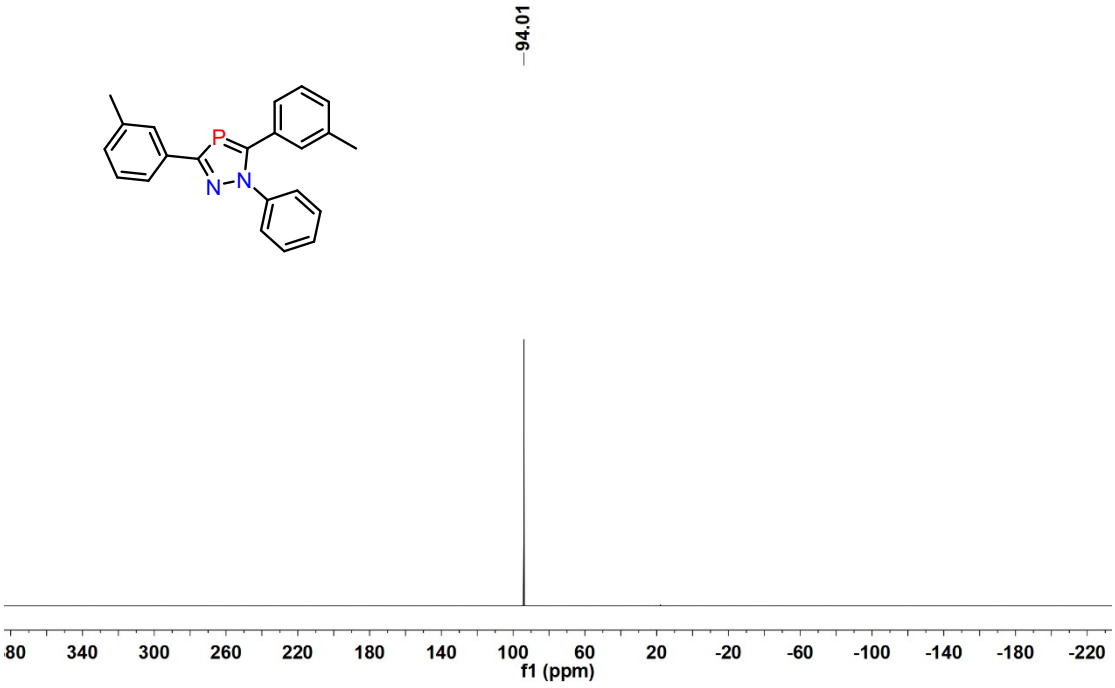
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



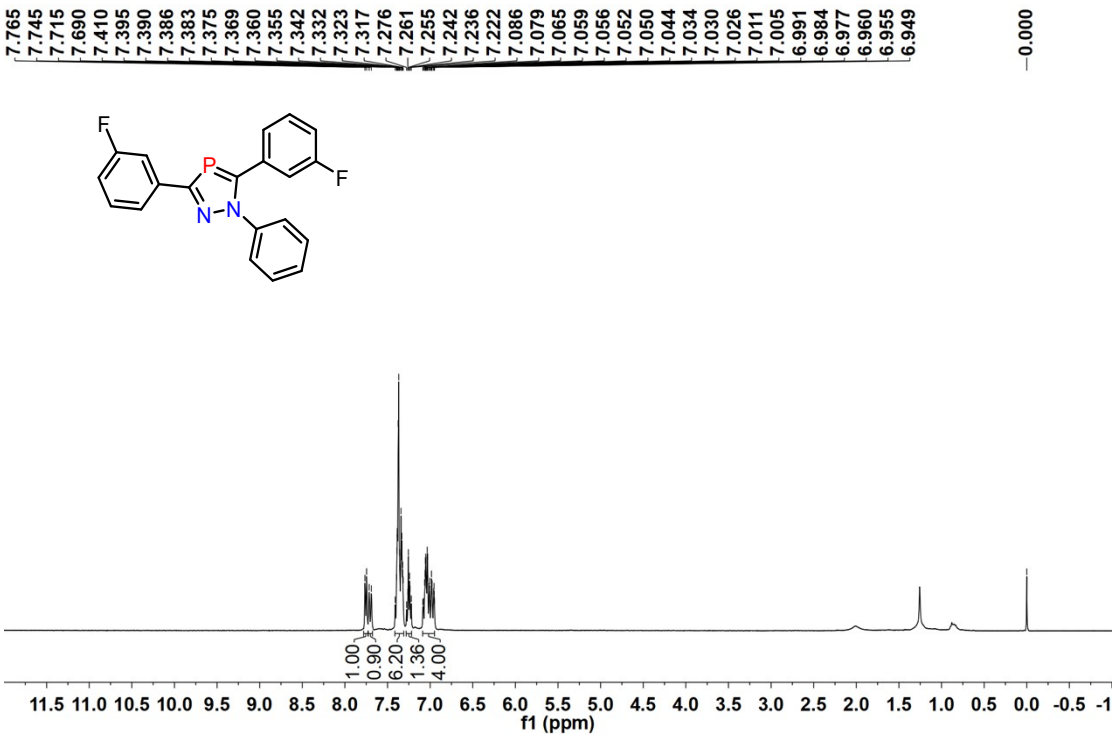
^{13}C NMR (151 MHz, $CDCl_3$) of **3j**



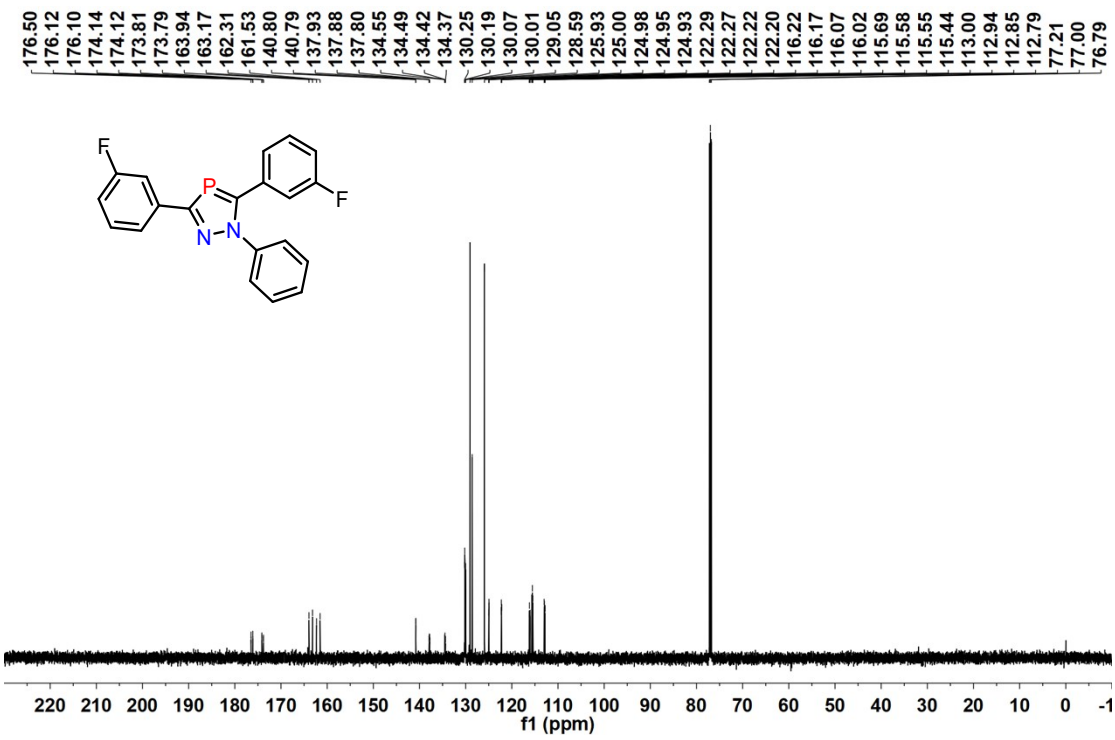
^{31}P NMR (162 MHz, $CDCl_3$) of **3j**



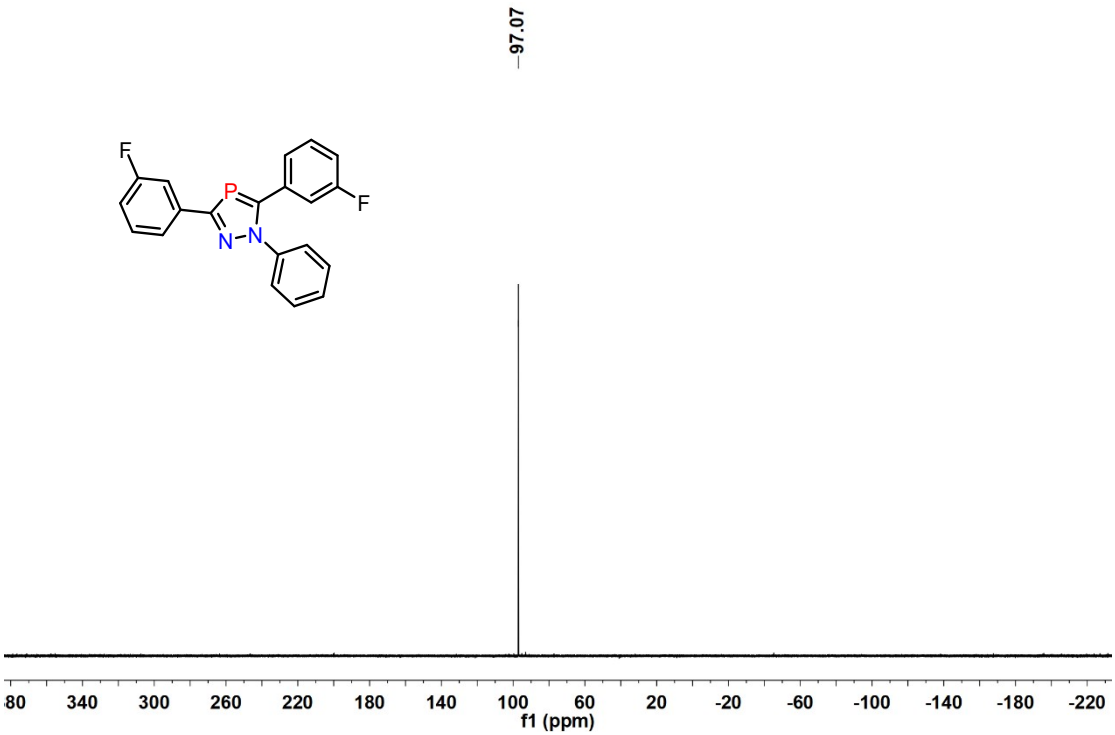
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



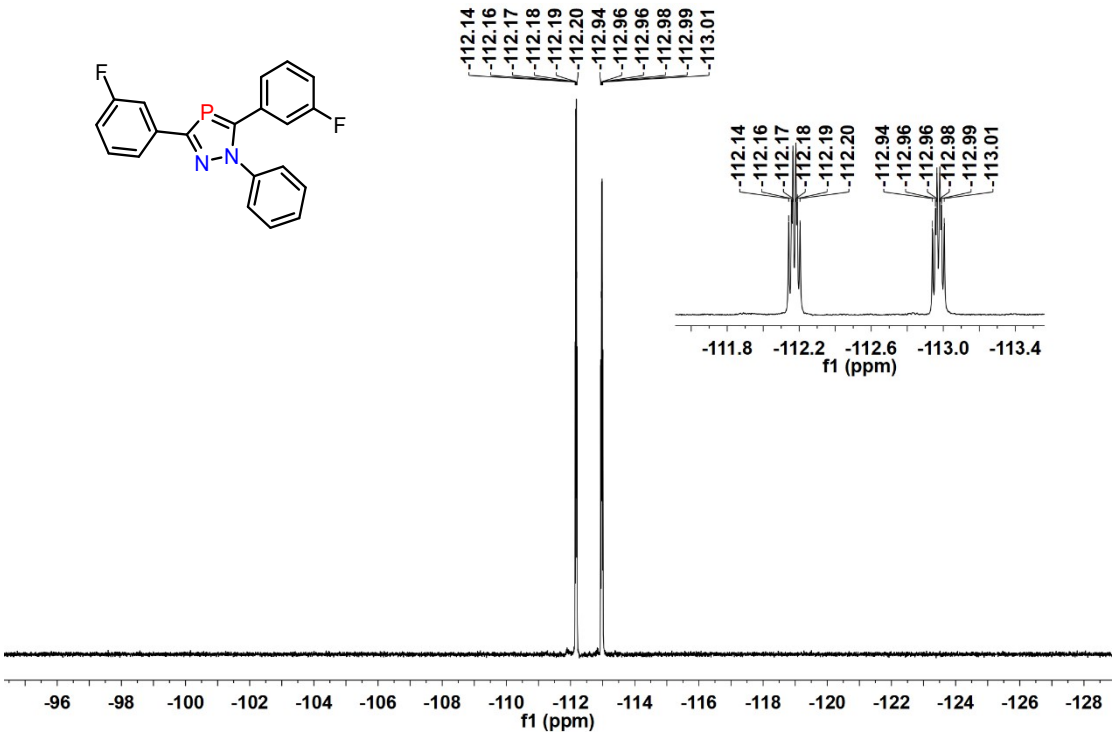
^{13}C NMR (151 MHz, $CDCl_3$) of **3k**



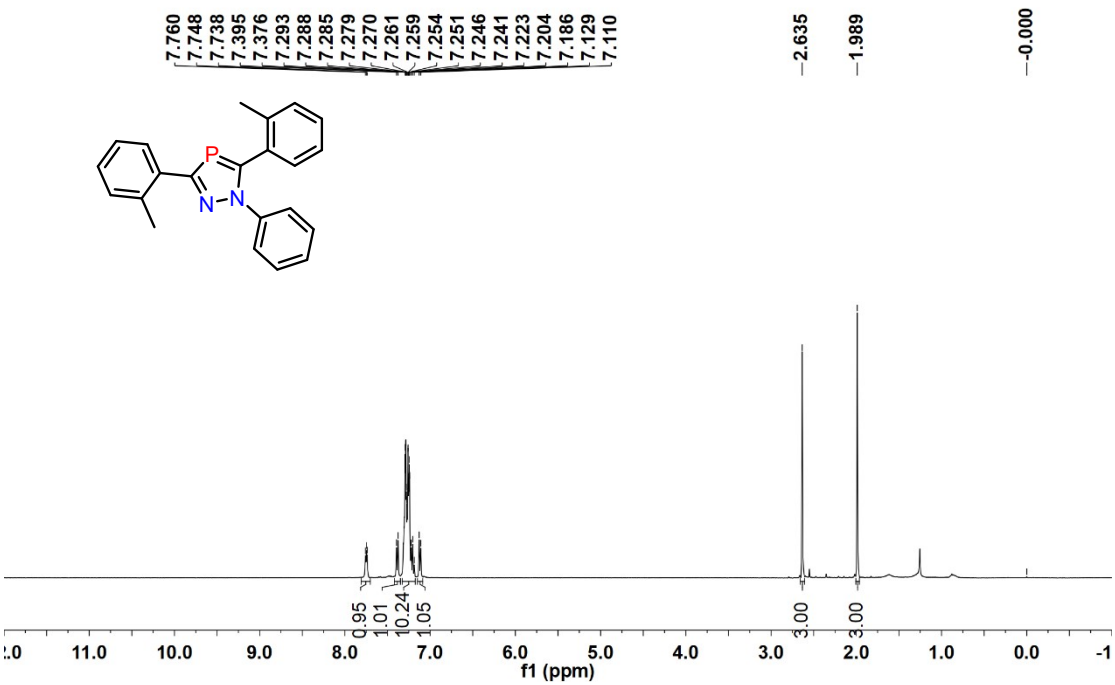
^{31}P NMR (162 MHz, $CDCl_3$) of **3k**



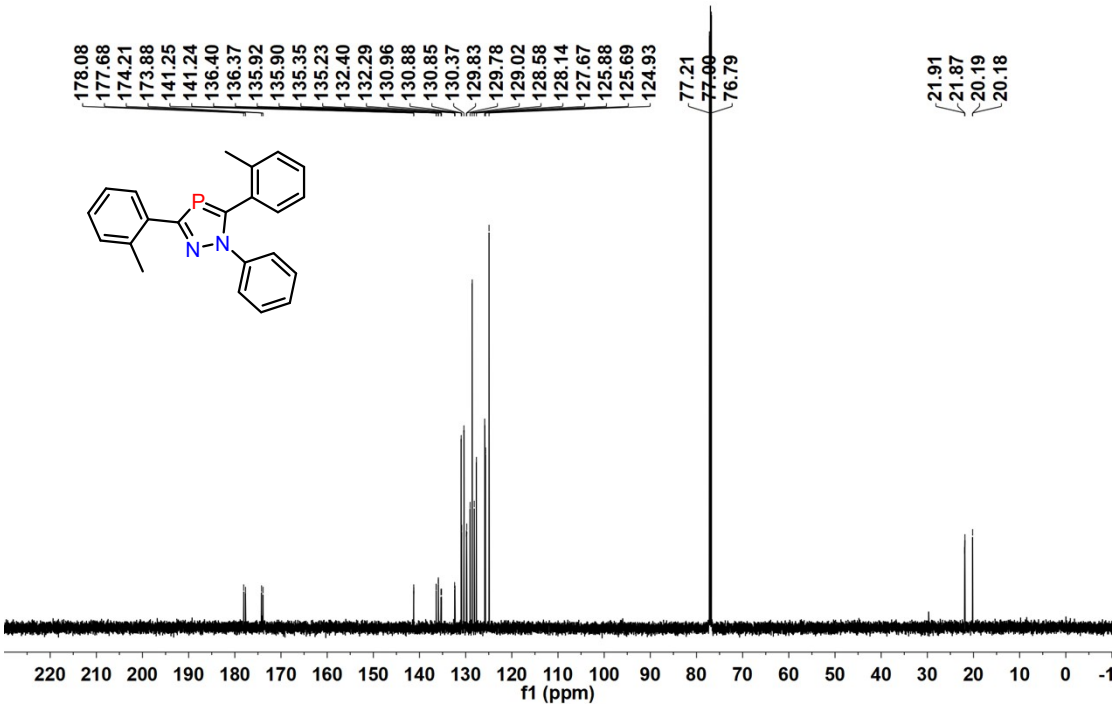
^{19}F NMR (376 MHz, $CDCl_3$) of **3k**



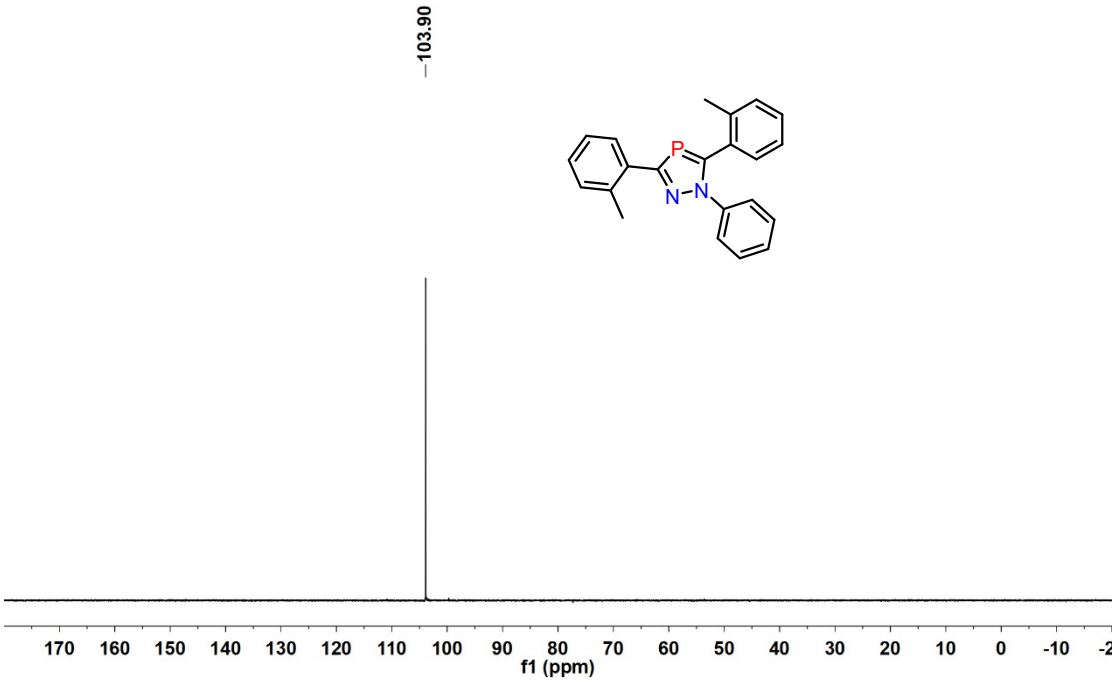
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



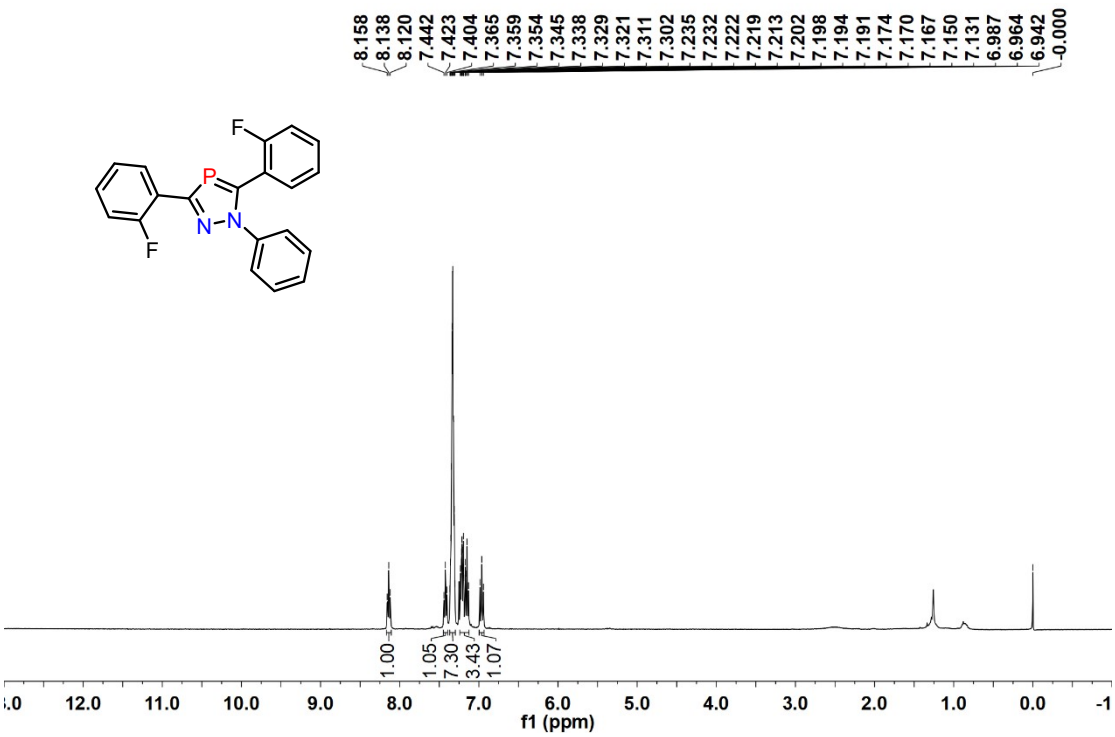
^{13}C NMR (151 MHz, $CDCl_3$) of **3l**



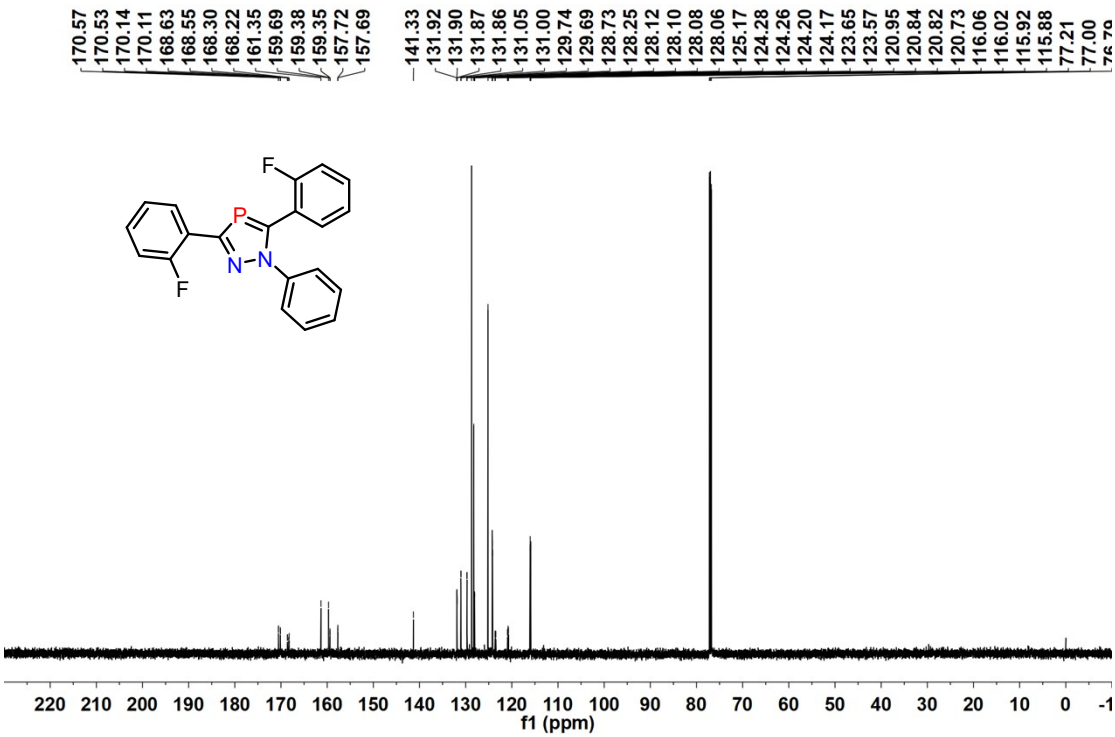
^{31}P NMR (162 MHz, $CDCl_3$) of **3l**



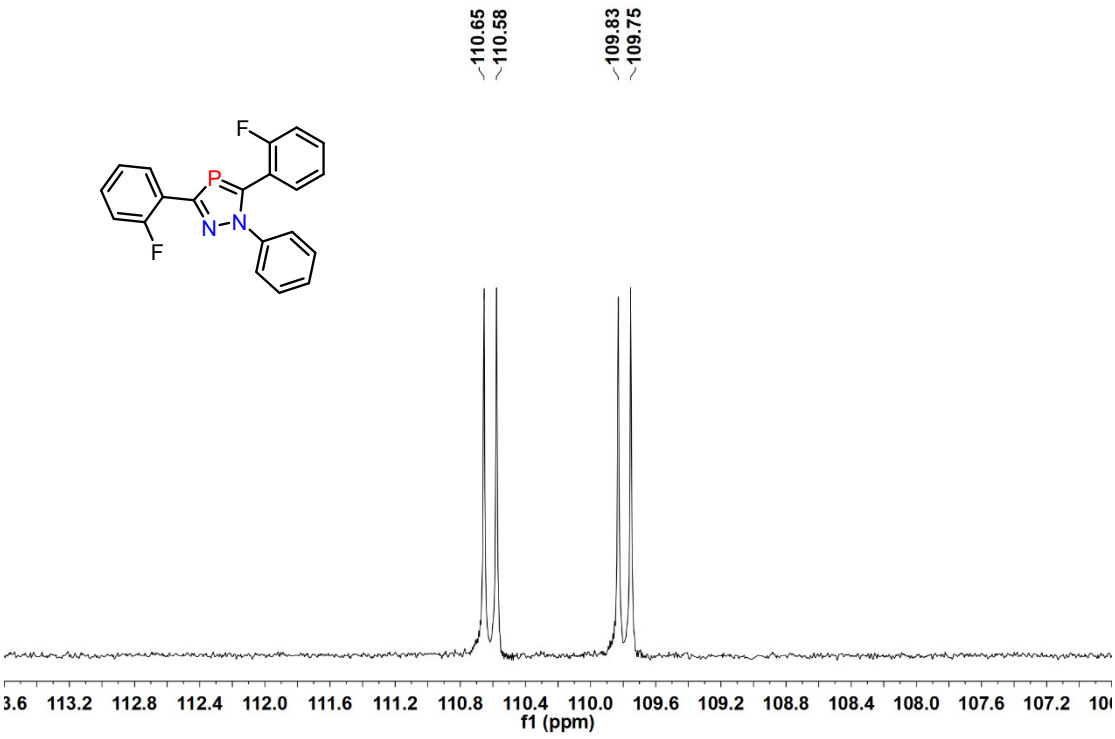
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



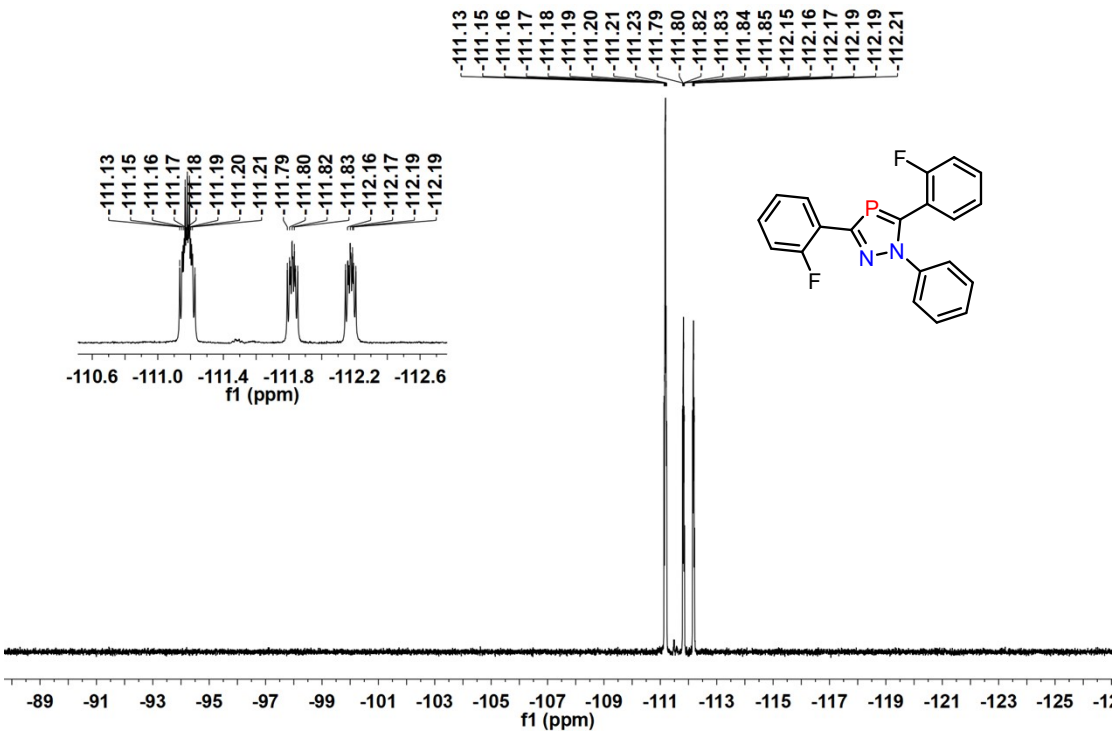
^{13}C NMR (151 MHz, $CDCl_3$) of **3m**



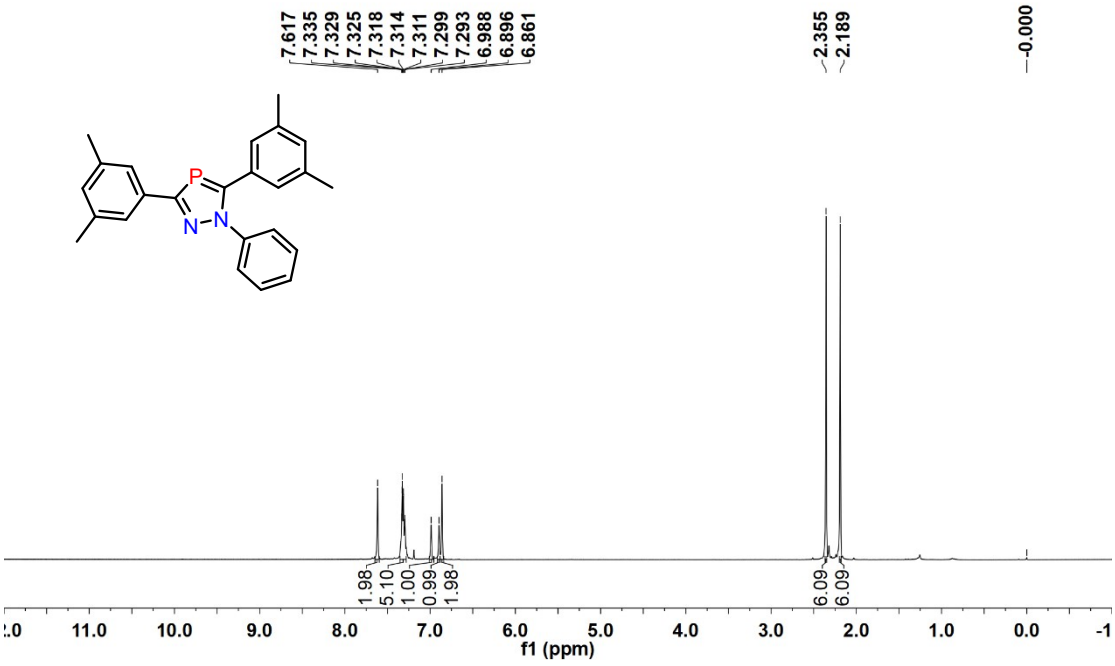
^{31}P NMR (162 MHz, $CDCl_3$) of **3m**



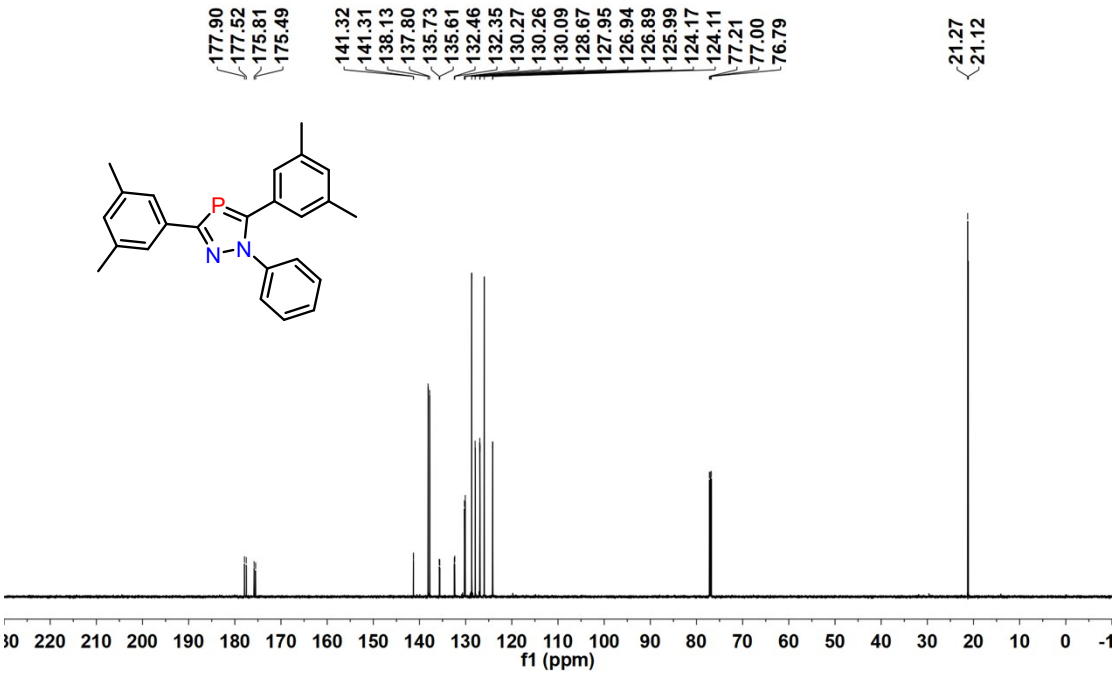
^{19}F NMR (376 MHz, $CDCl_3$) of **3m**



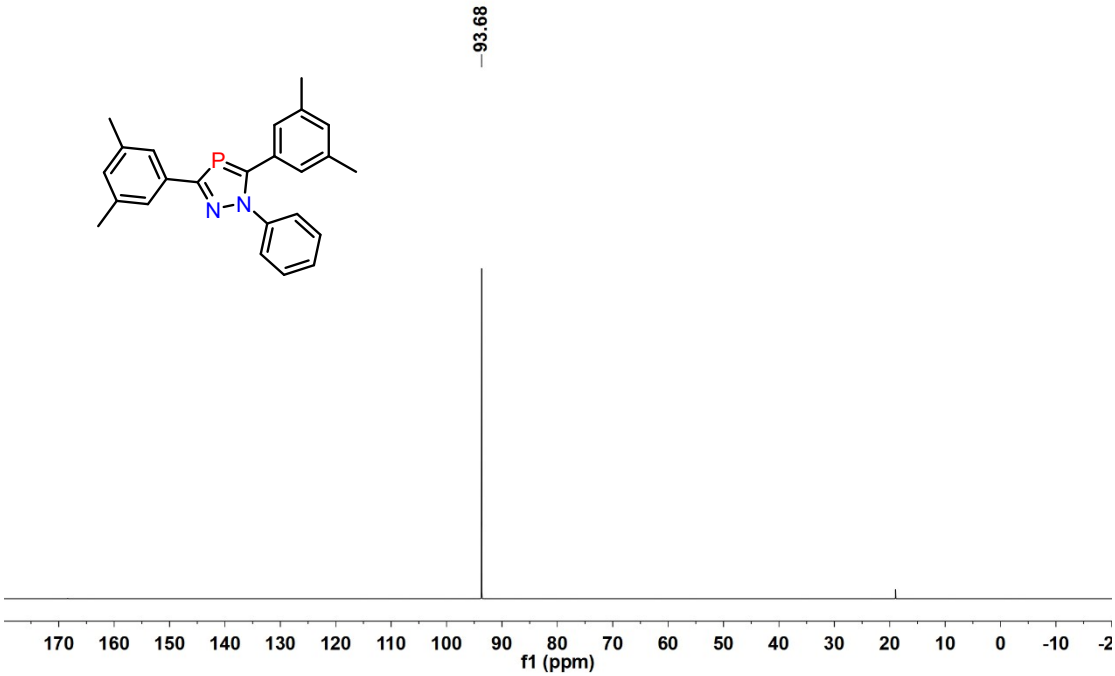
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



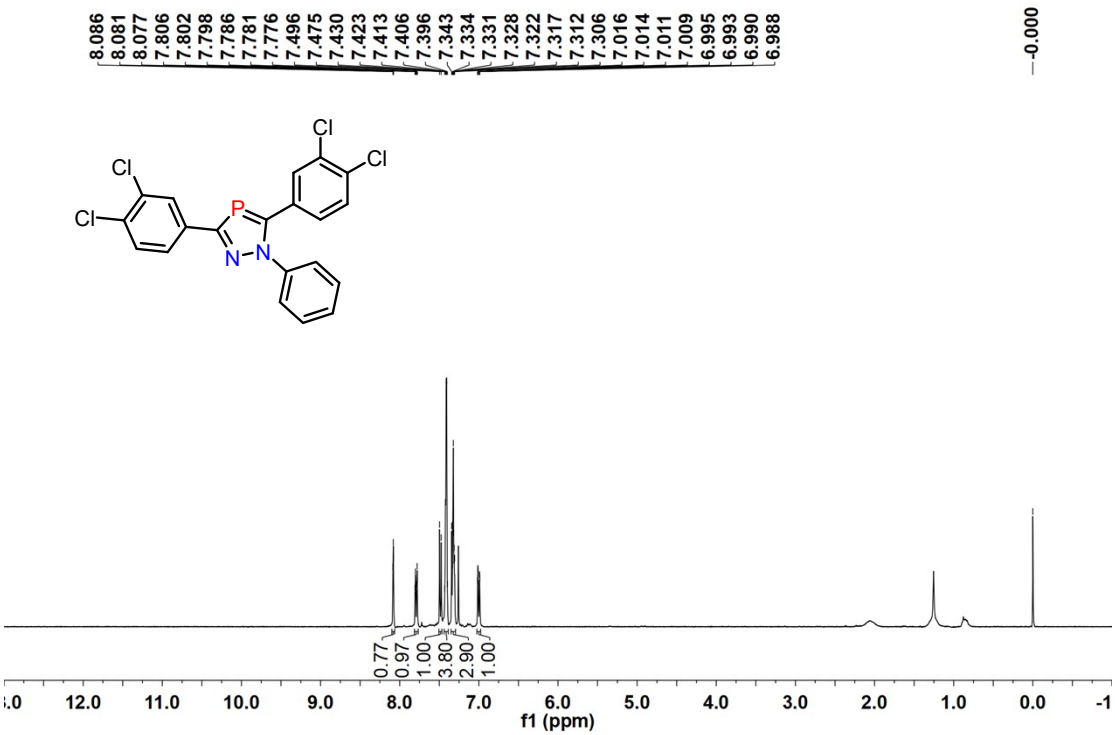
^{13}C NMR (151 MHz, $CDCl_3$) of **3n**



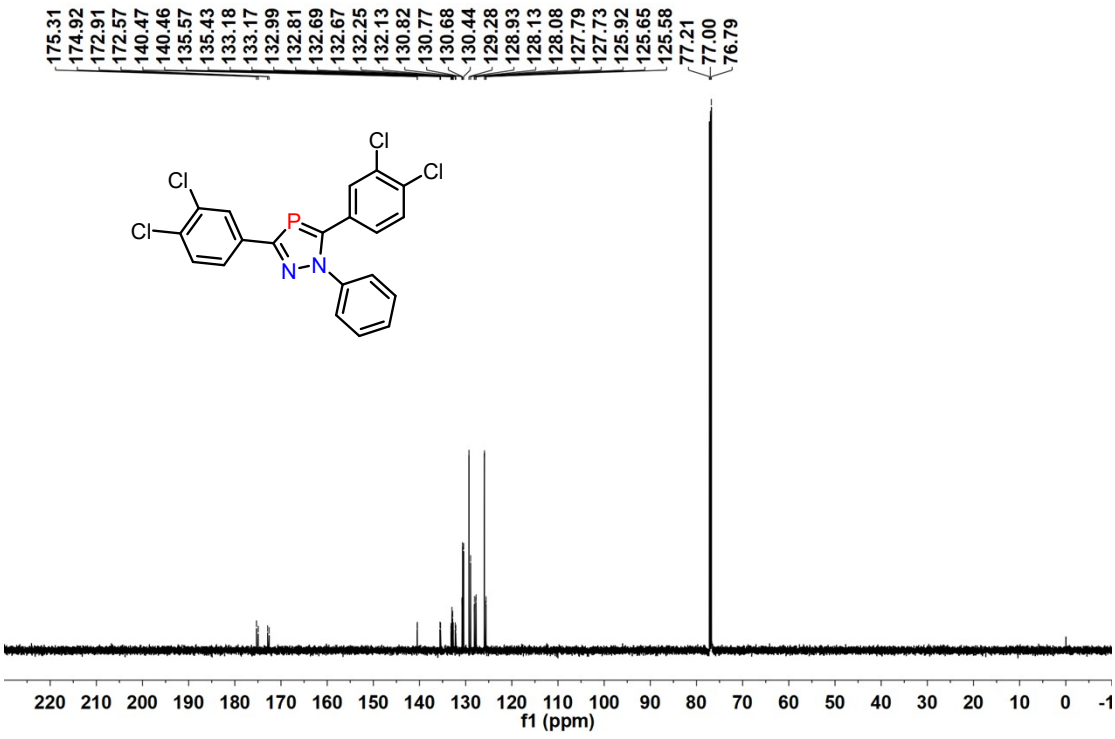
^{31}P NMR (162 MHz, $CDCl_3$) of **3n**



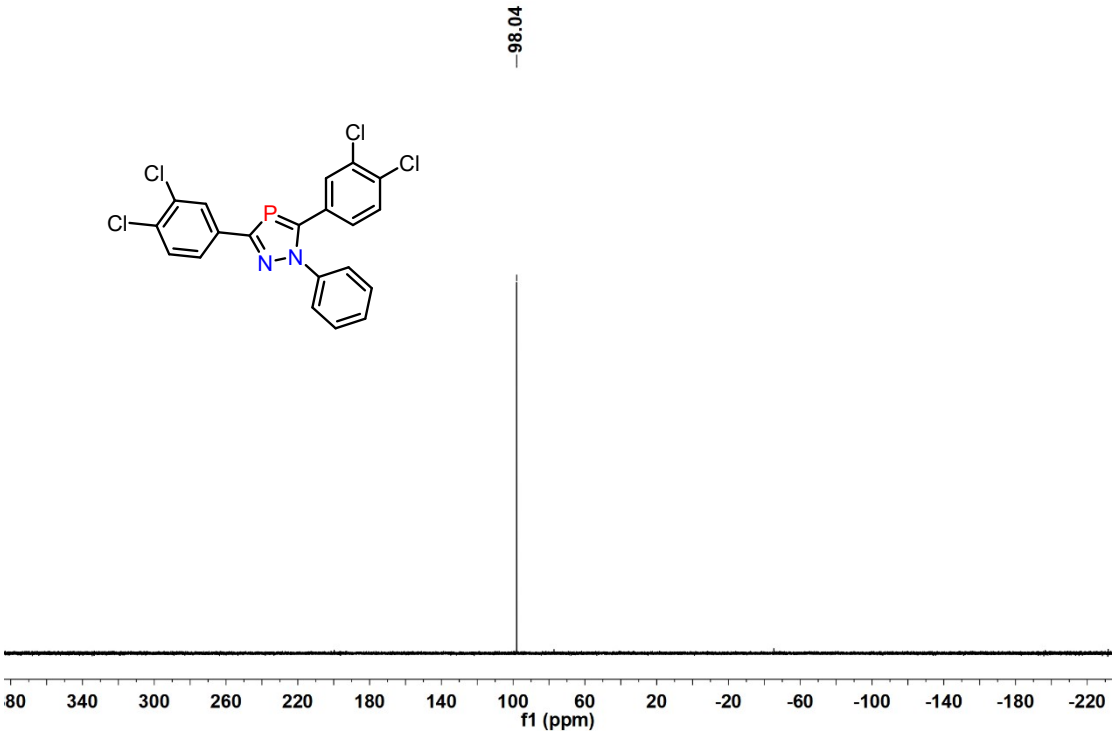
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



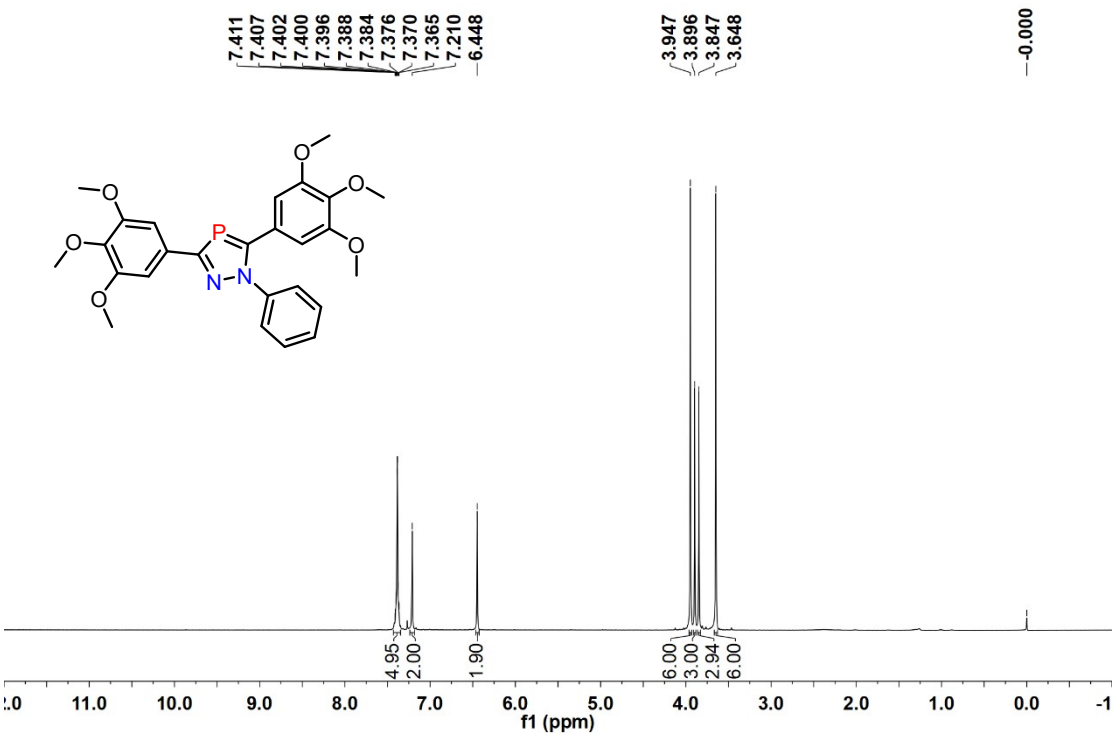
^{13}C NMR (151 MHz, $CDCl_3$) of **3o**



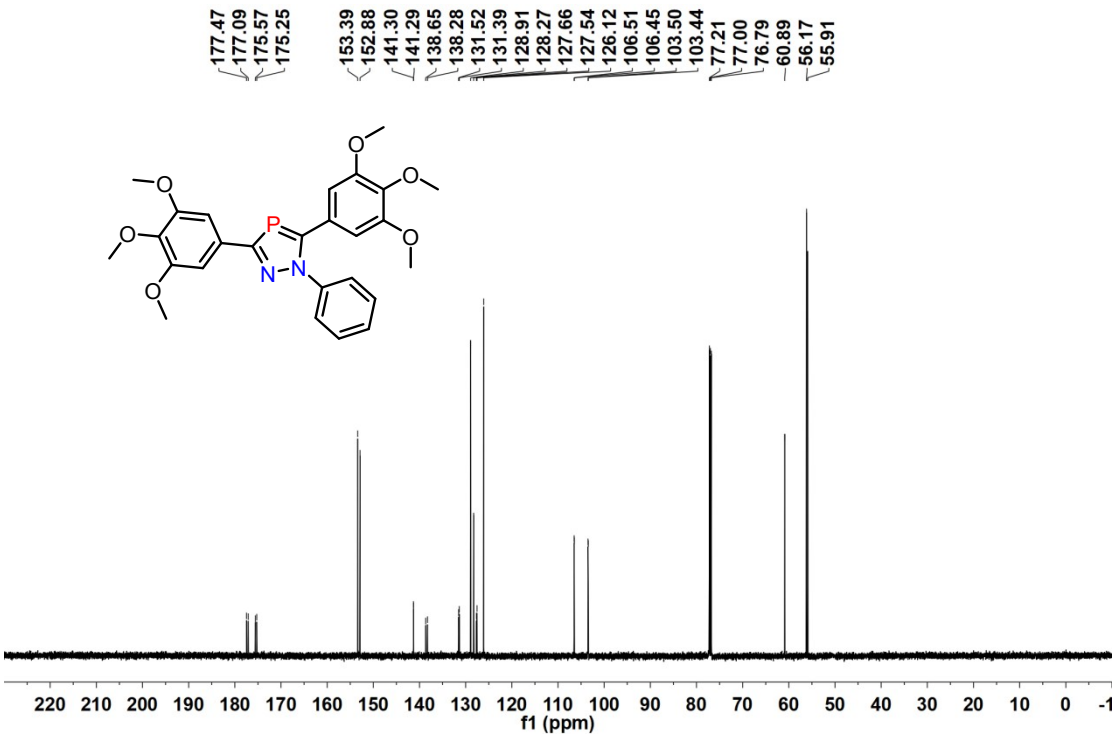
^{31}P NMR (162 MHz, $CDCl_3$) of **3o**



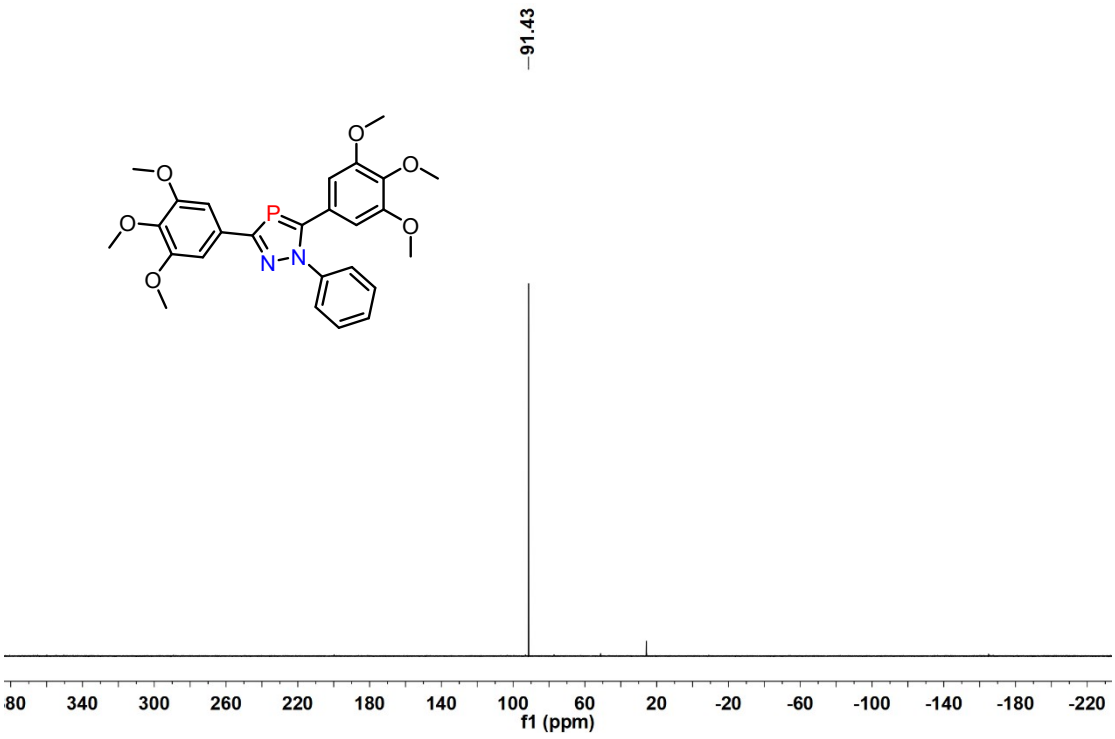
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



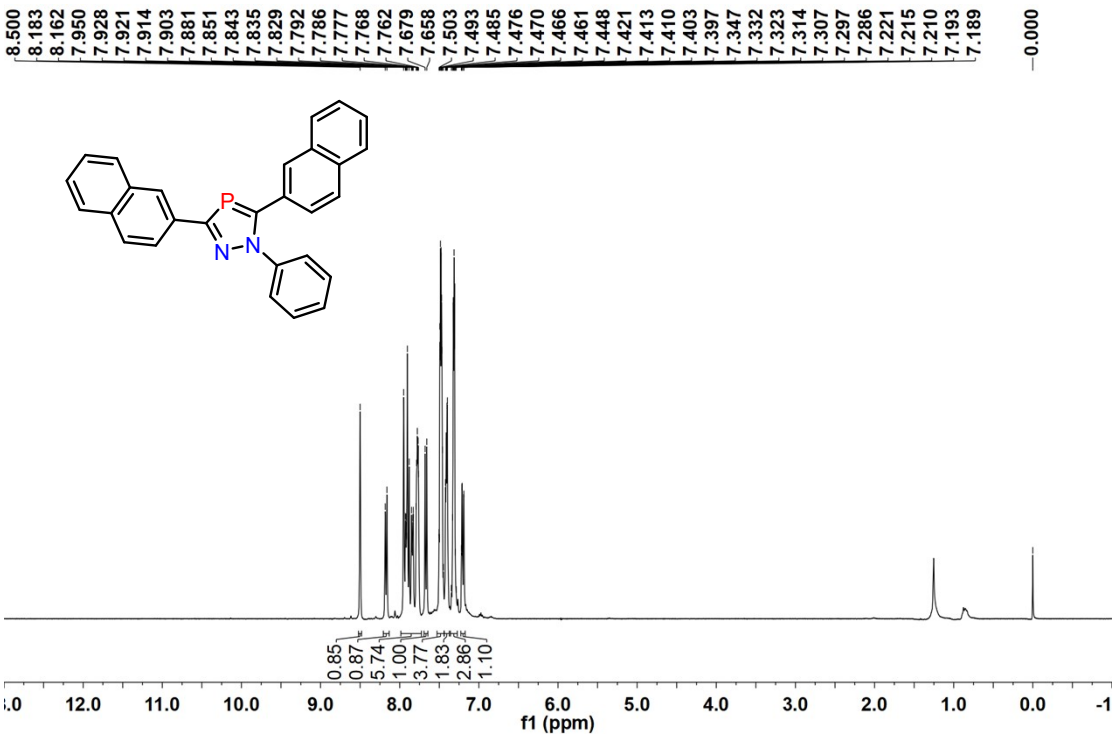
^{13}C NMR (151 MHz, $CDCl_3$) of **3p**



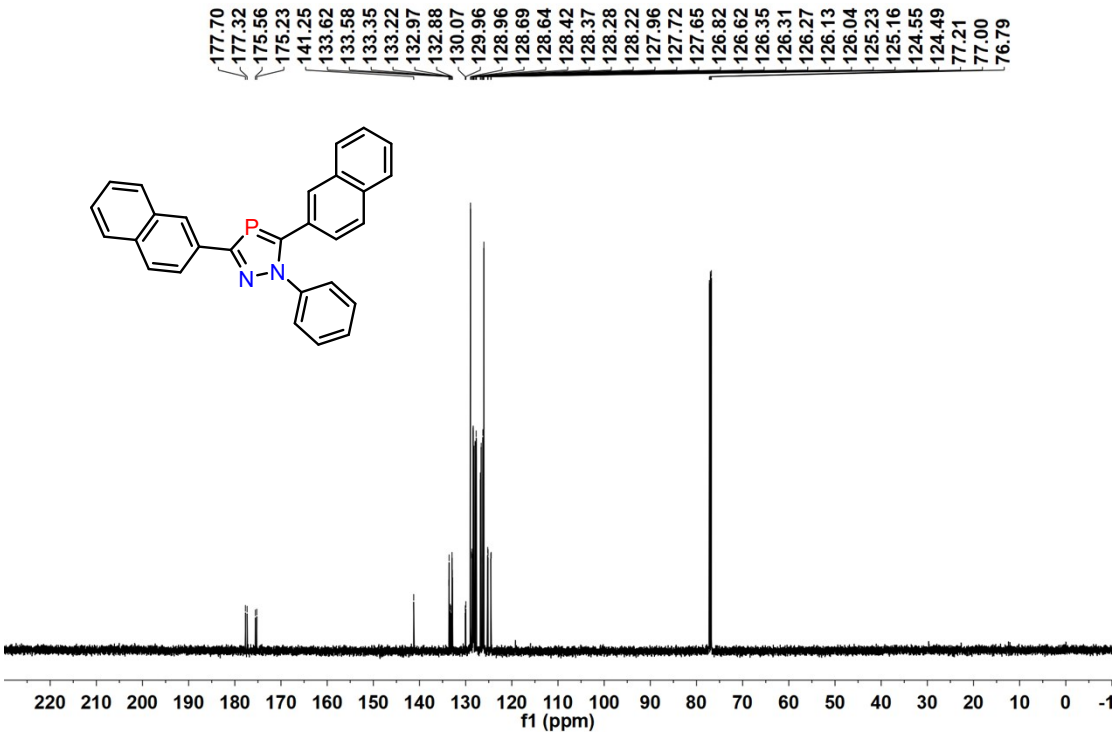
^{31}P NMR (162 MHz, $CDCl_3$) of **3p**



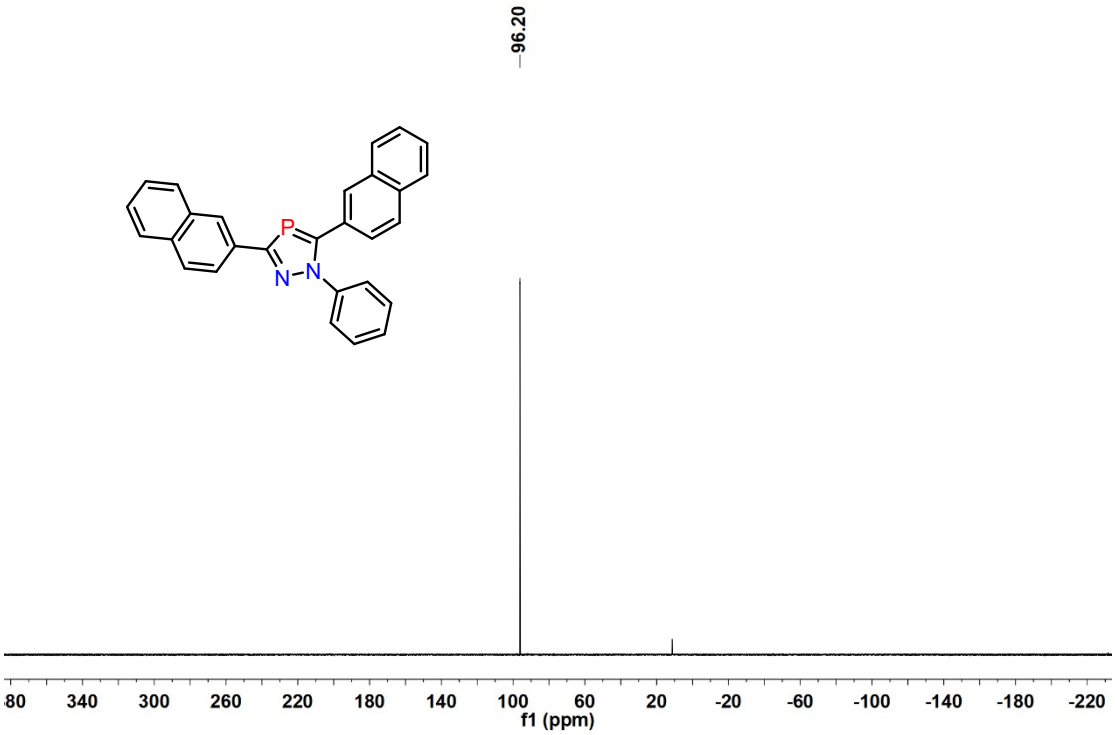
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



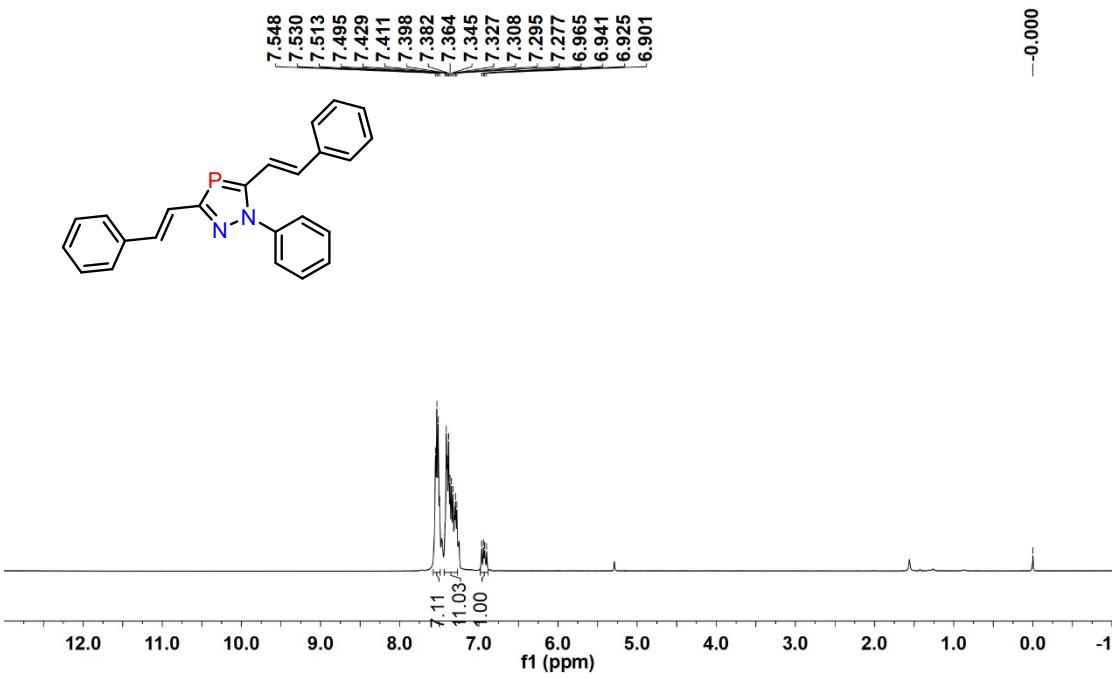
^{13}C NMR (151 MHz, $CDCl_3$) of **3q**



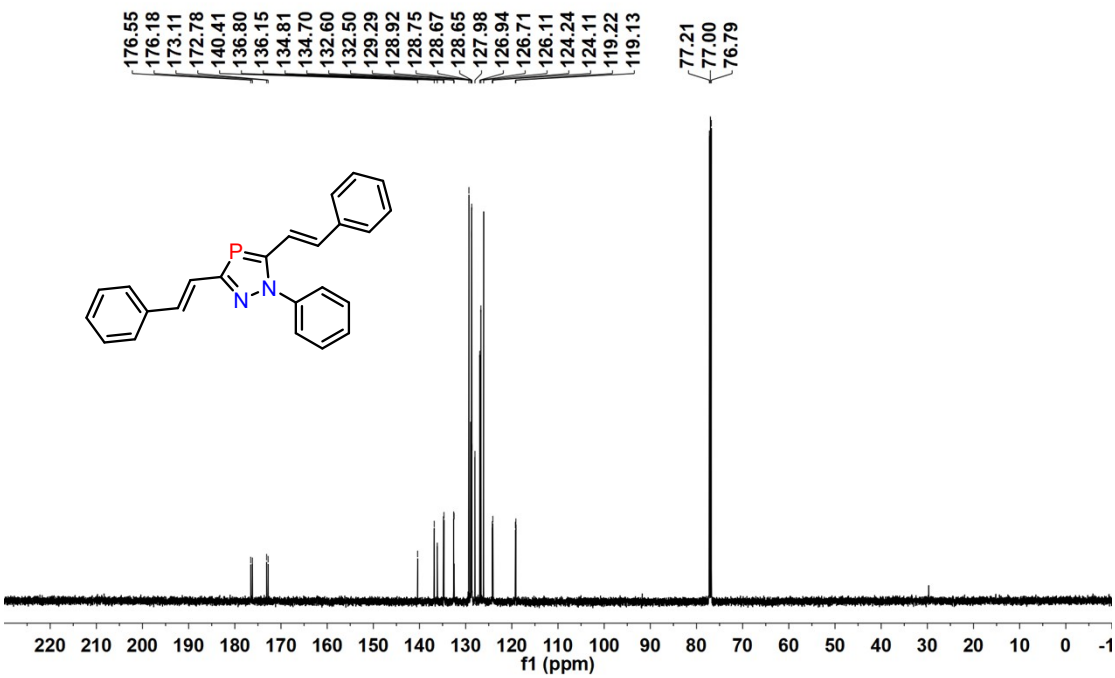
^{31}P NMR (162 MHz, $CDCl_3$) of **3q**



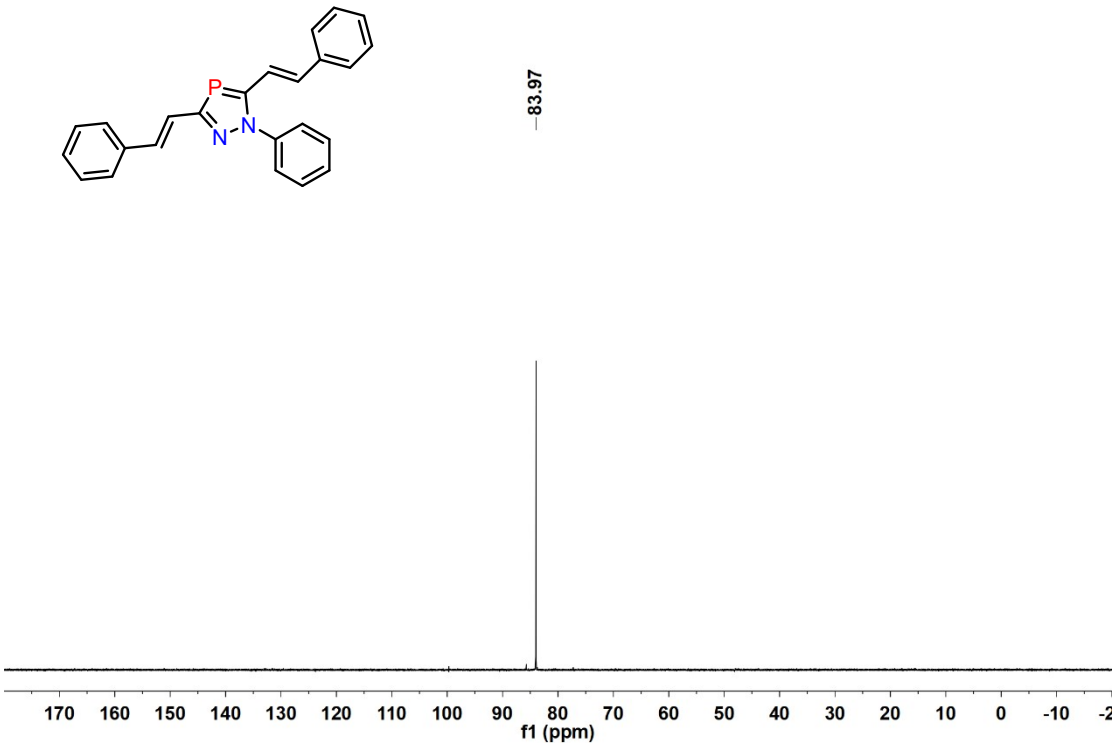
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



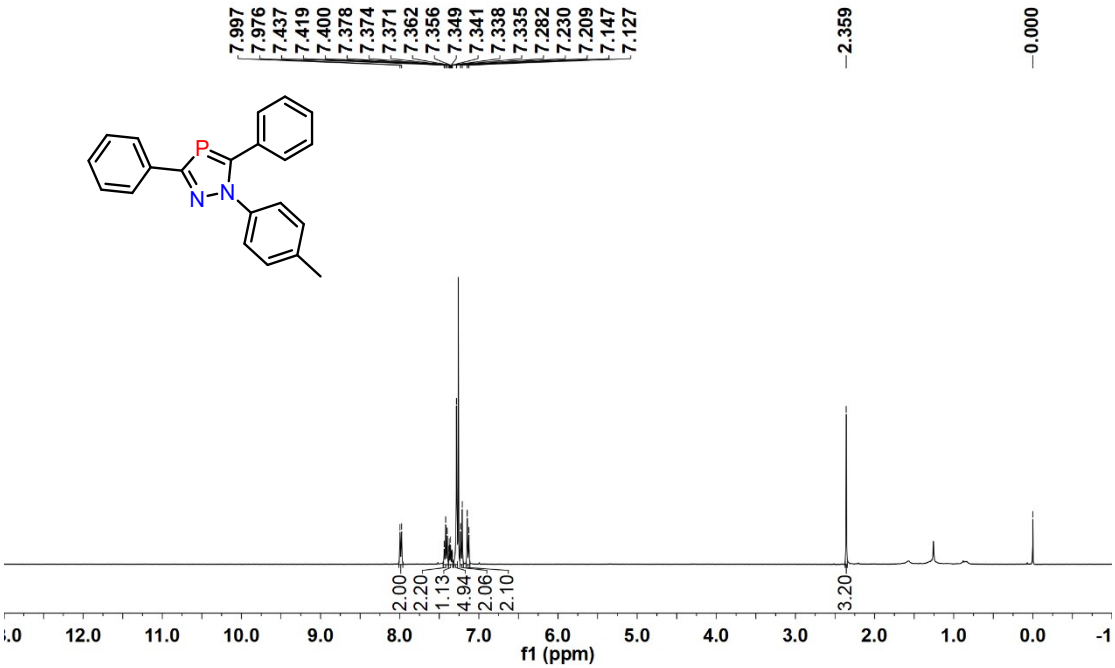
^{13}C NMR (151 MHz, $CDCl_3$) of **3r**



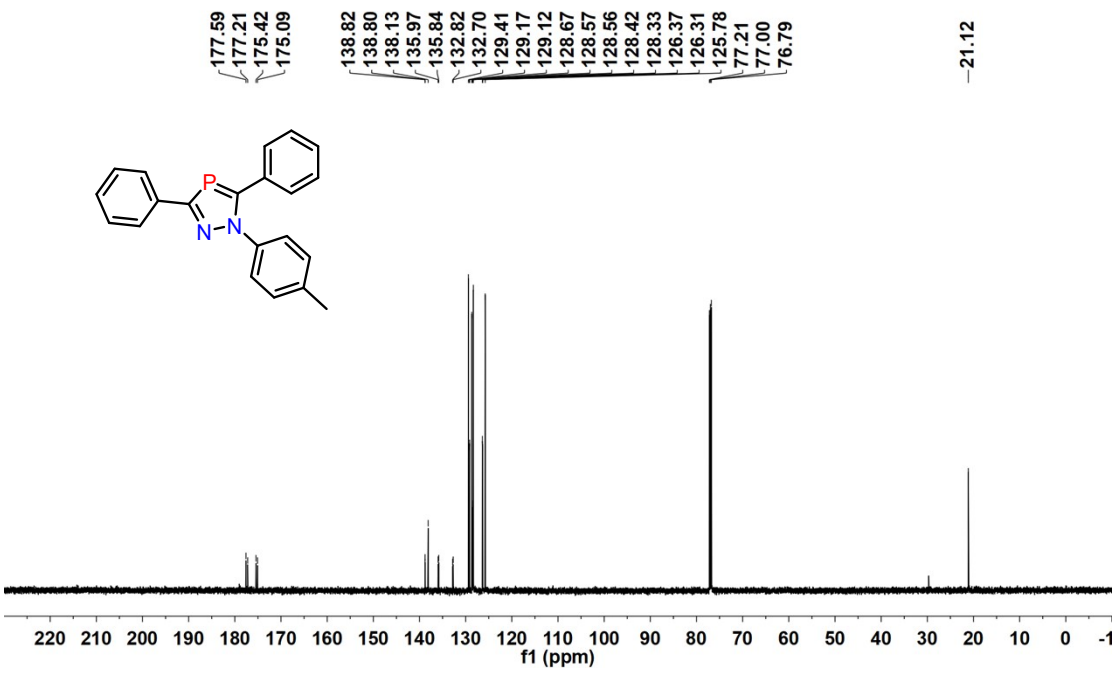
^{31}P NMR (162 MHz, $CDCl_3$) of **3r**



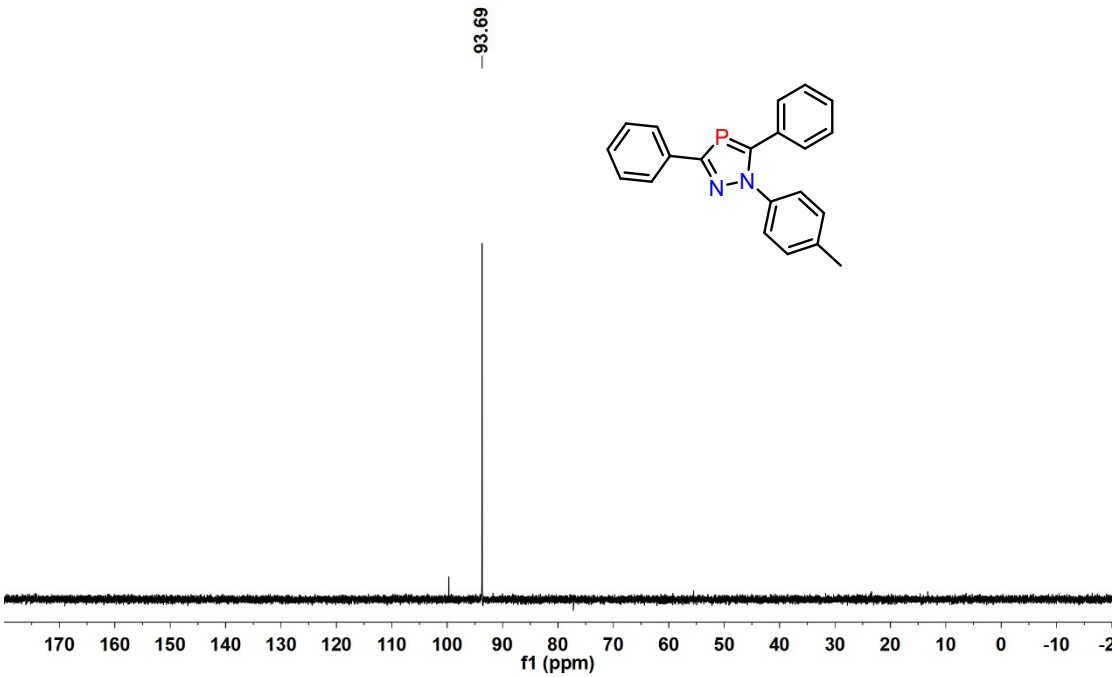
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



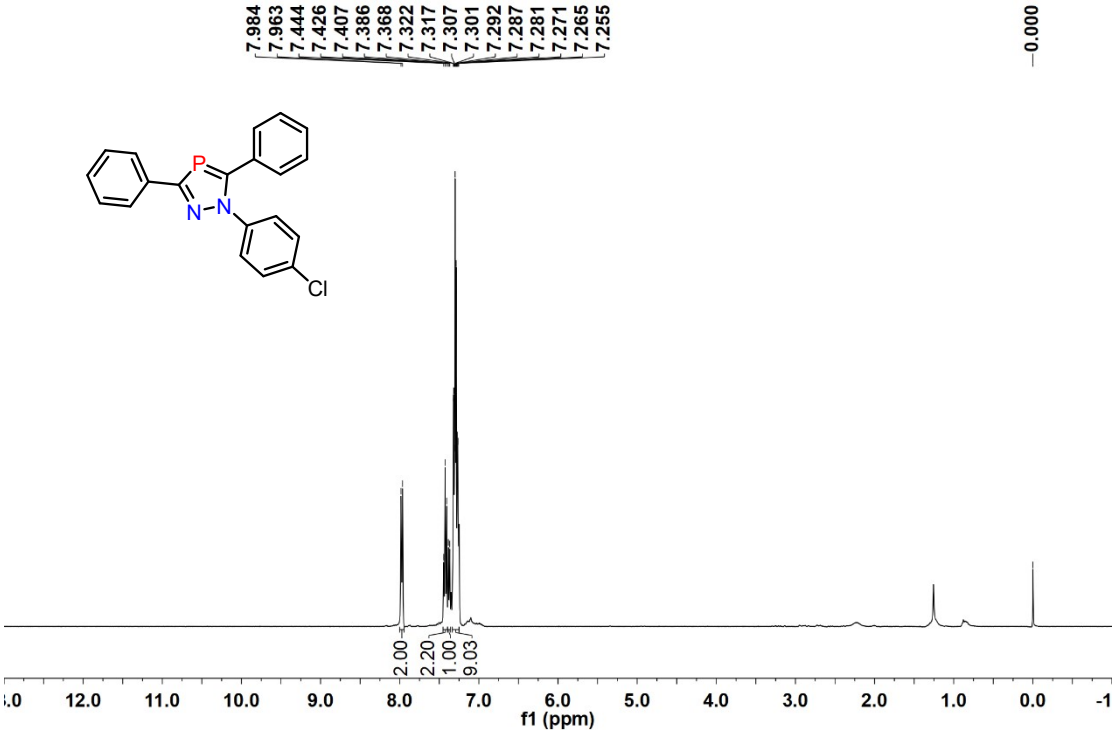
^{13}C NMR (151 MHz, $CDCl_3$) of **3s**



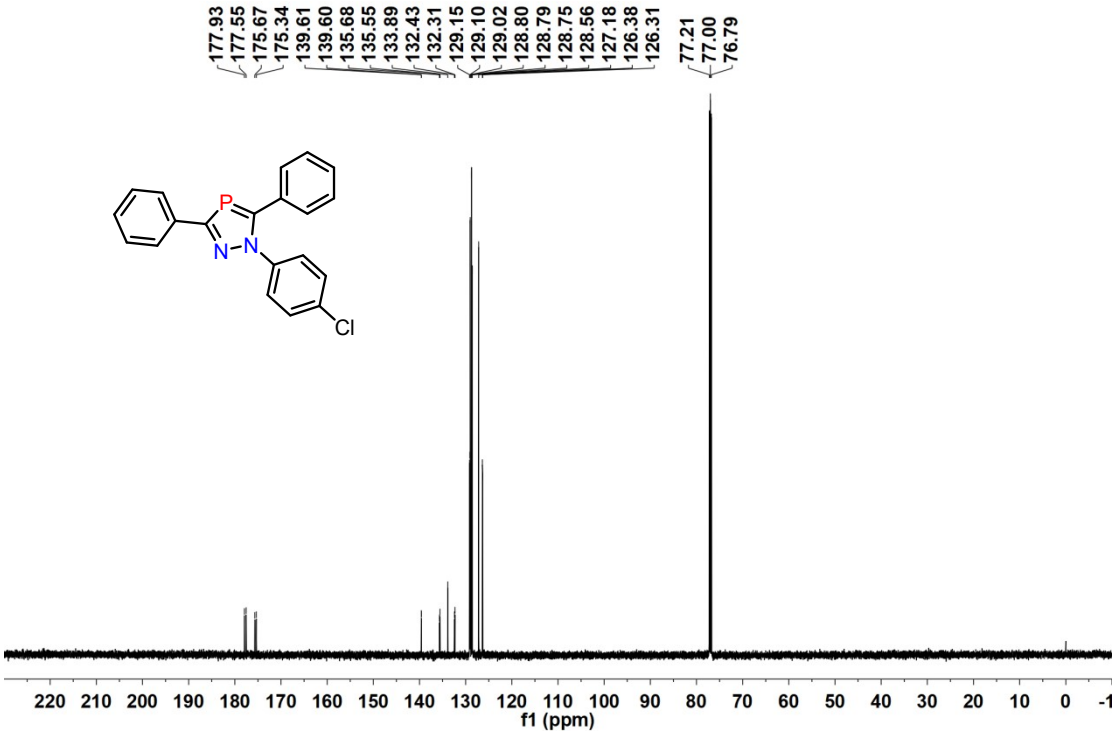
^{31}P NMR (162 MHz, $CDCl_3$) of **3s**



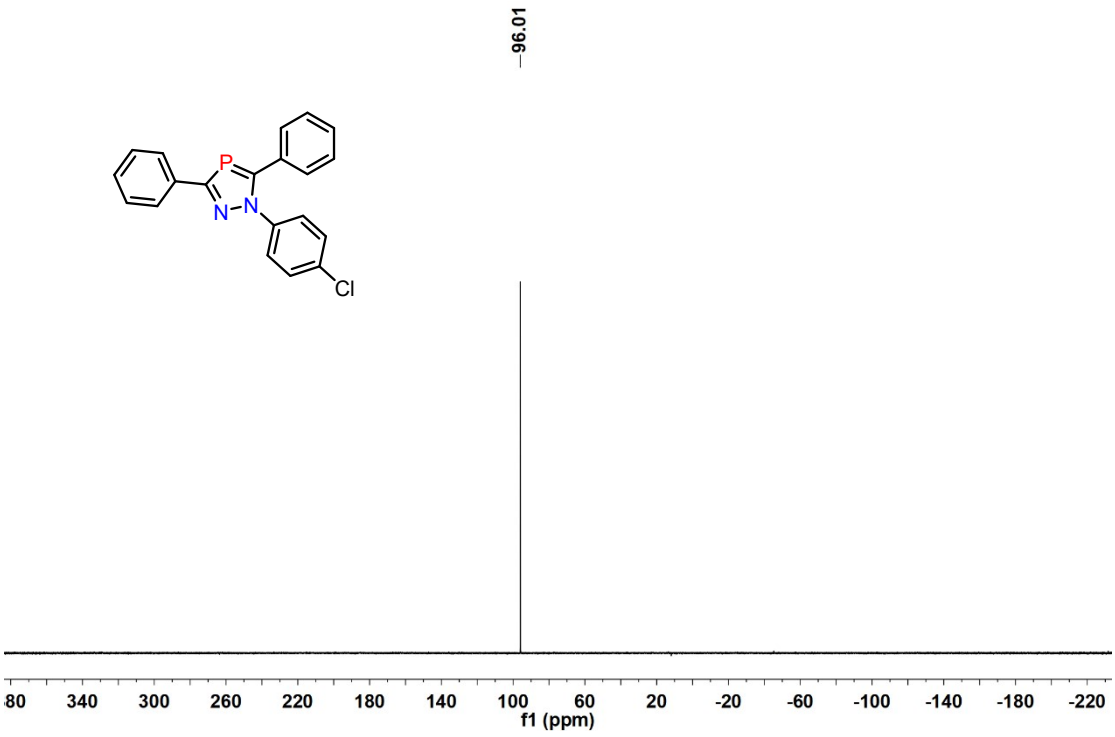
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



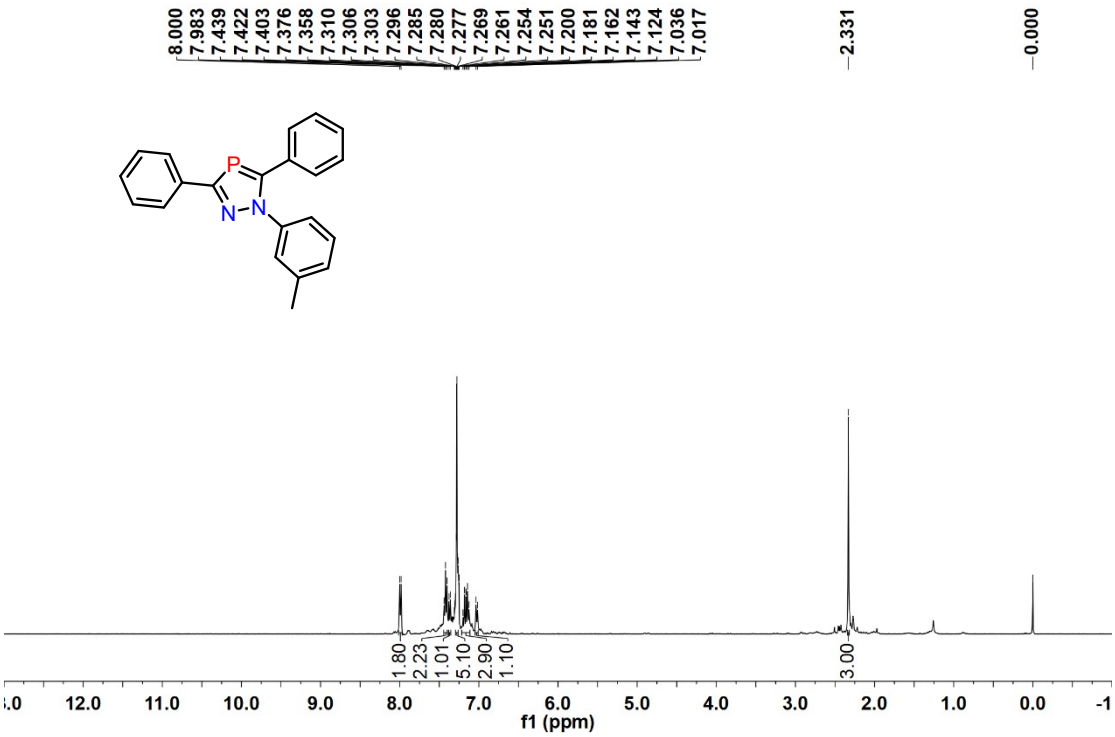
^{13}C NMR (151 MHz, $CDCl_3$) of **3t**



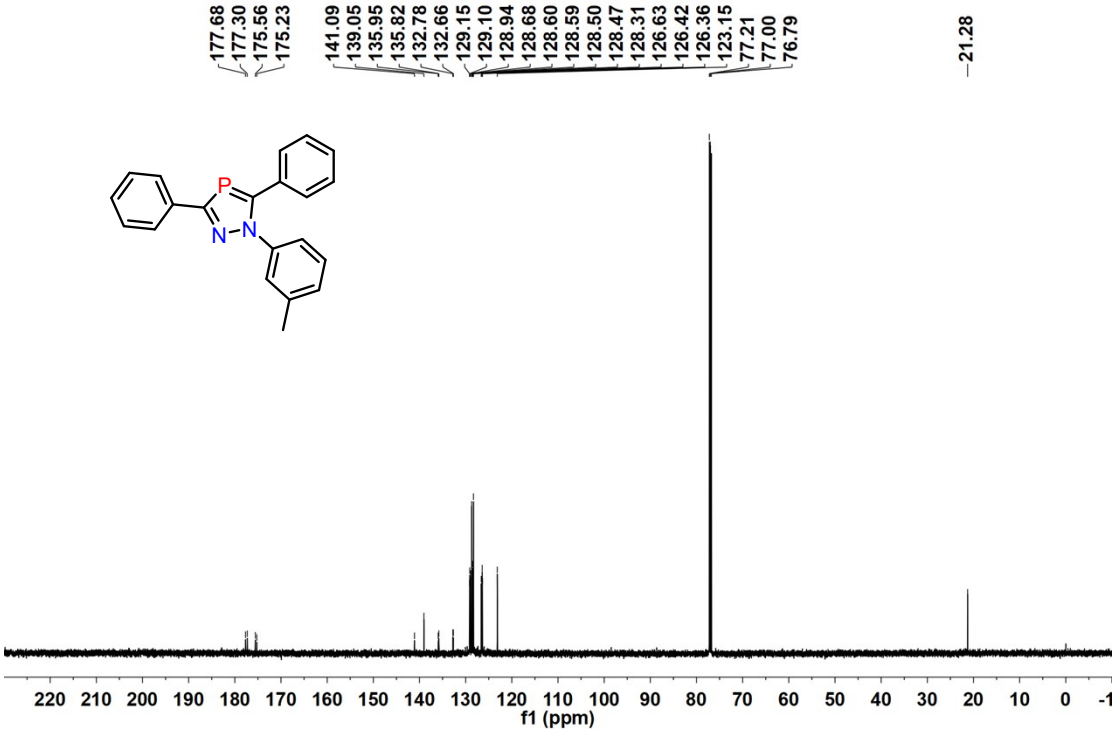
^{31}P NMR (162 MHz, $CDCl_3$) of **3t**



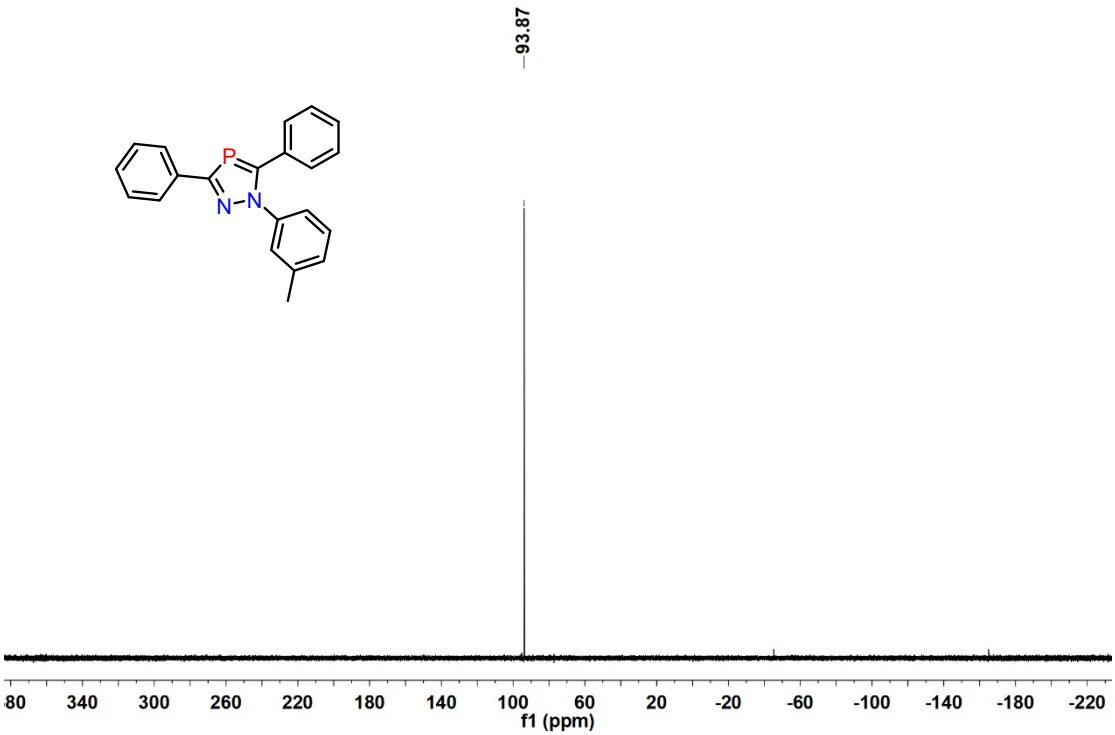
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



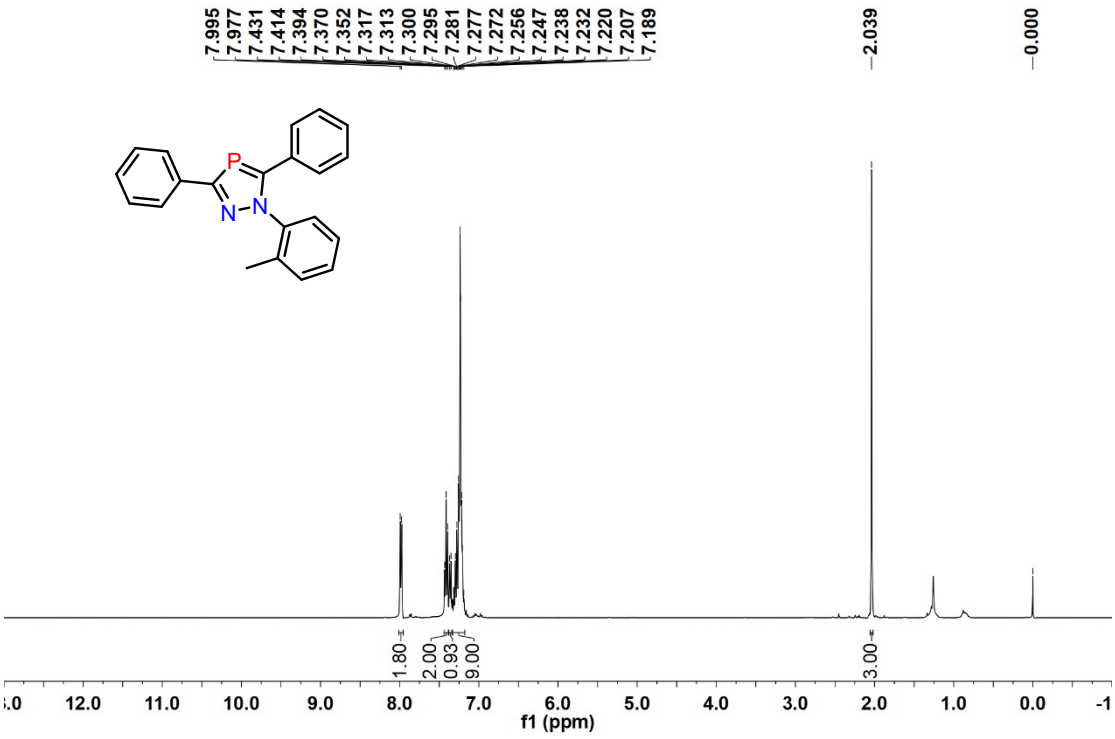
^{13}C NMR (151 MHz, $CDCl_3$) of **3u**



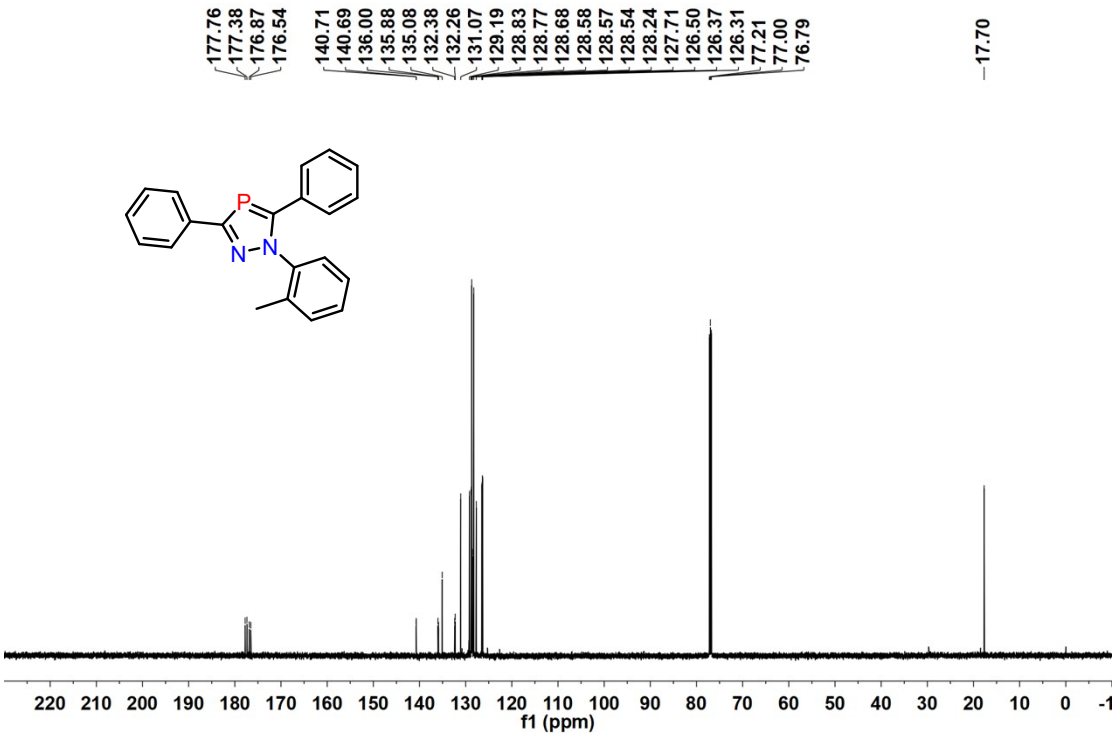
^{31}P NMR (162 MHz, $CDCl_3$) of **3u**



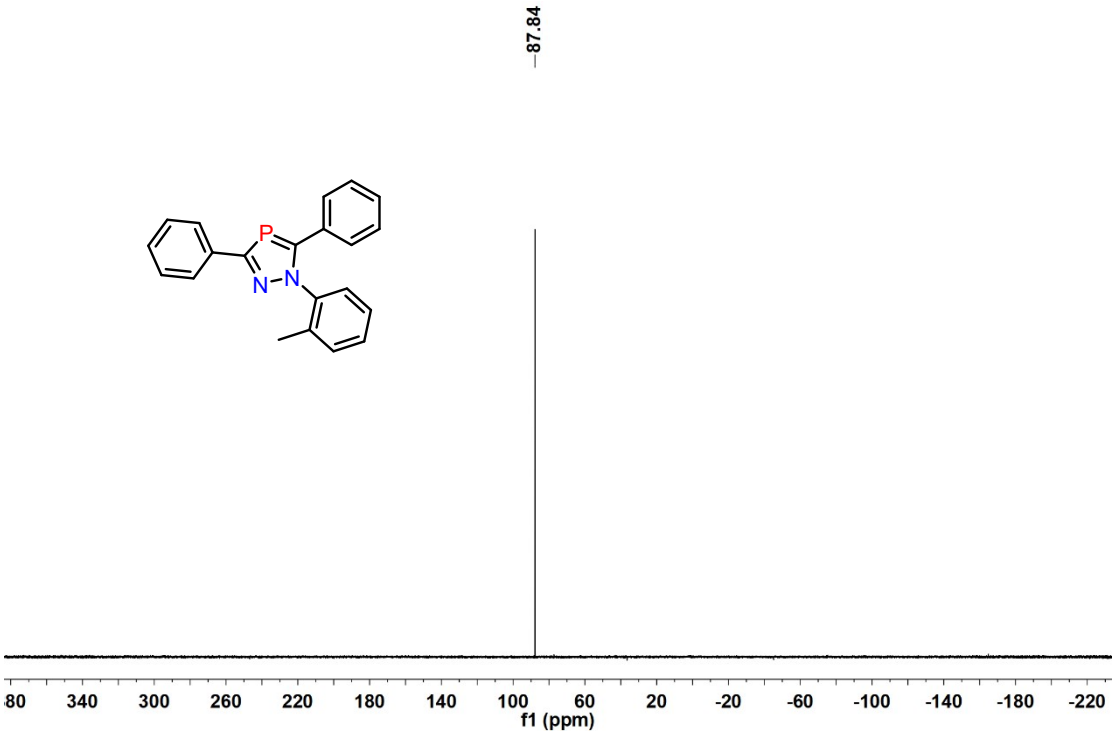
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



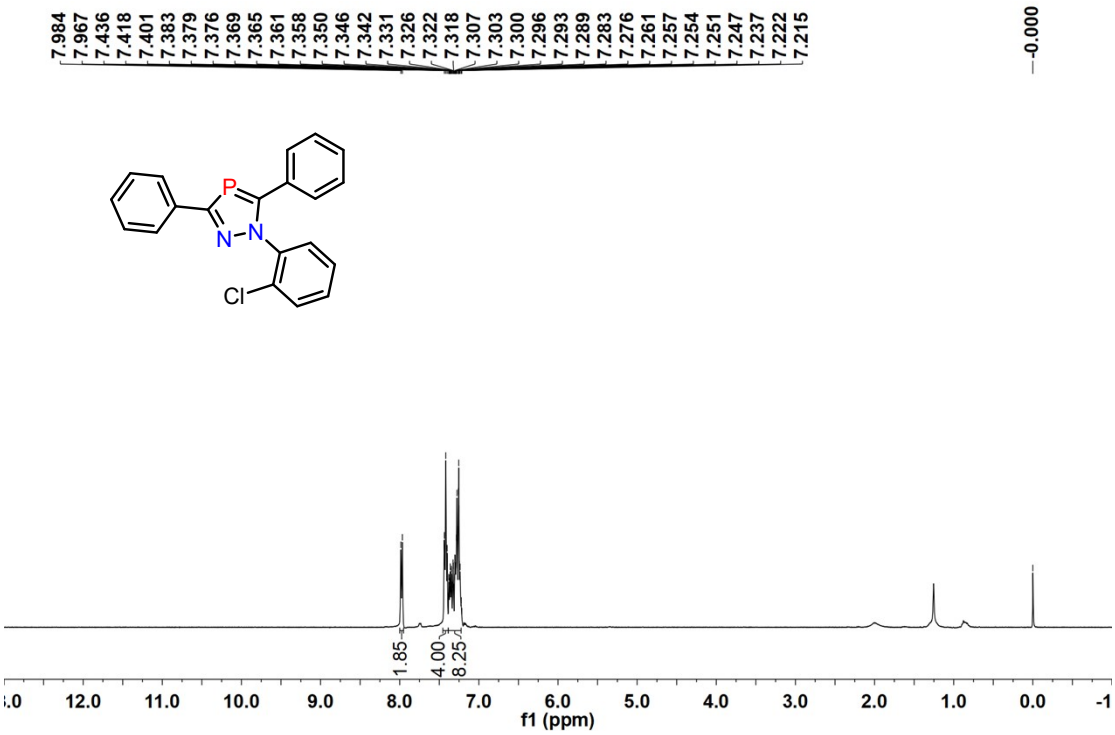
^{13}C NMR (151 MHz, $CDCl_3$) of **3v**



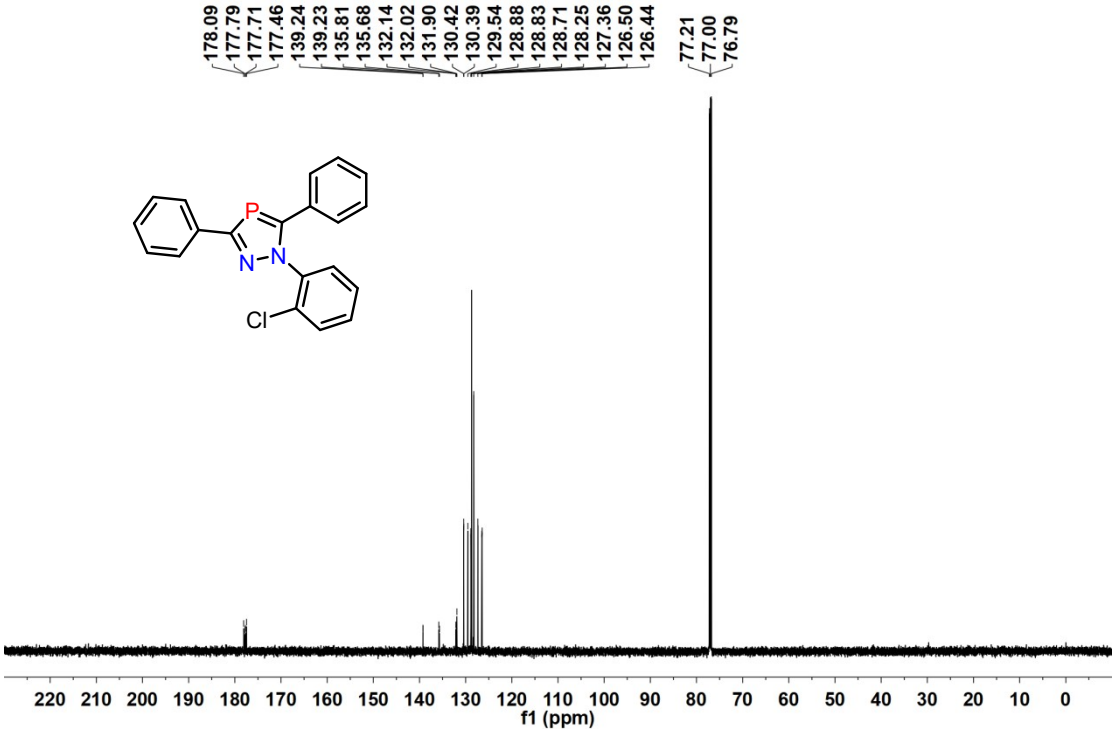
^{31}P NMR (162 MHz, $CDCl_3$) of **3v**



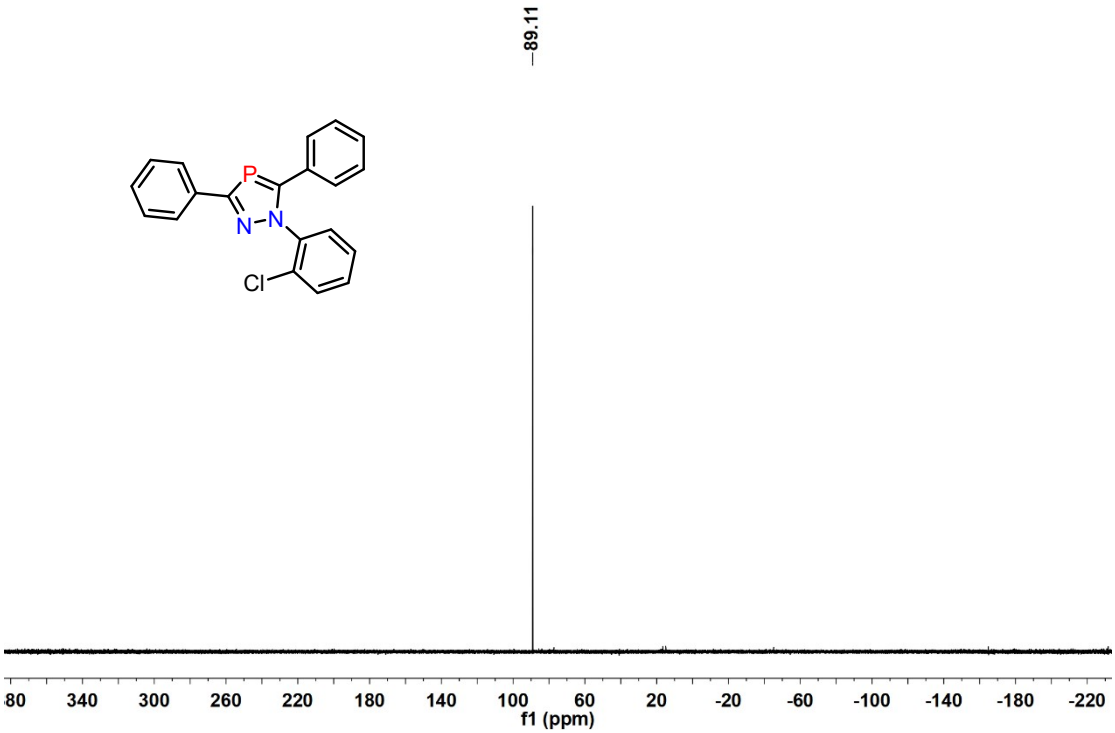
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



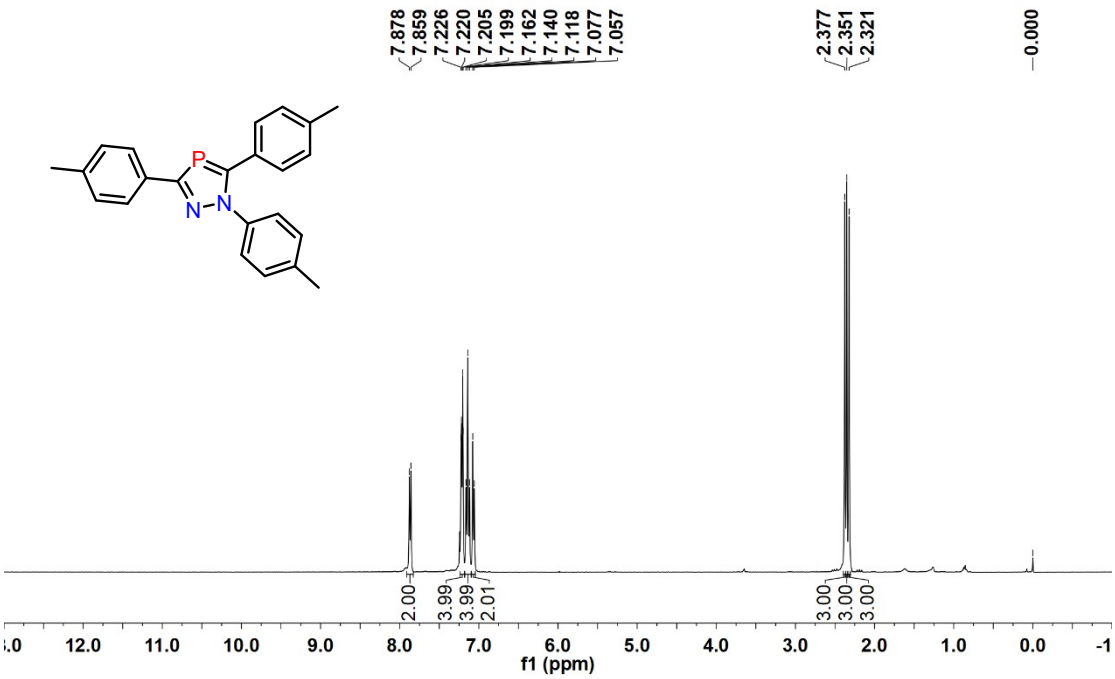
^{13}C NMR (151 MHz, $CDCl_3$) of **3w**



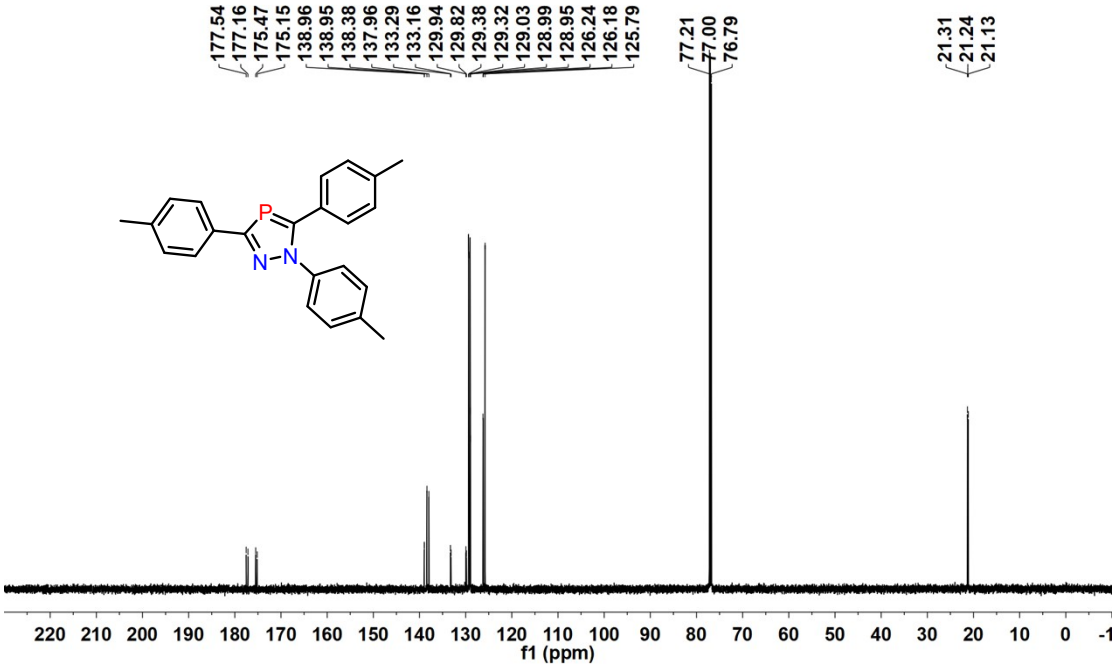
^{31}P NMR (162 MHz, $CDCl_3$) of **3w**



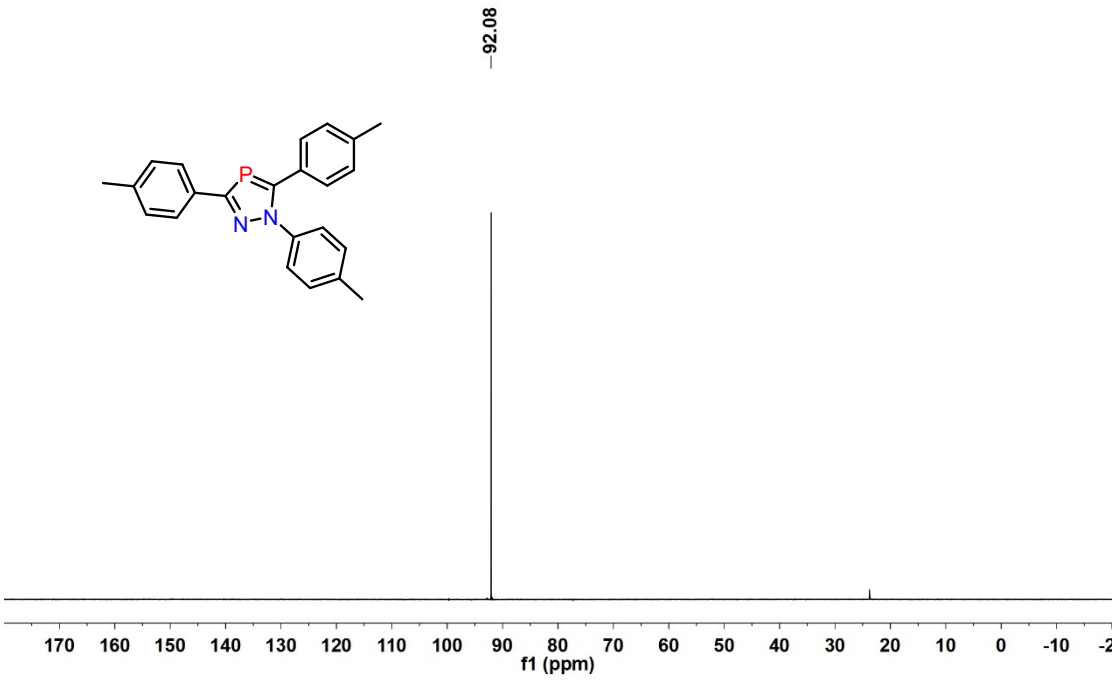
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



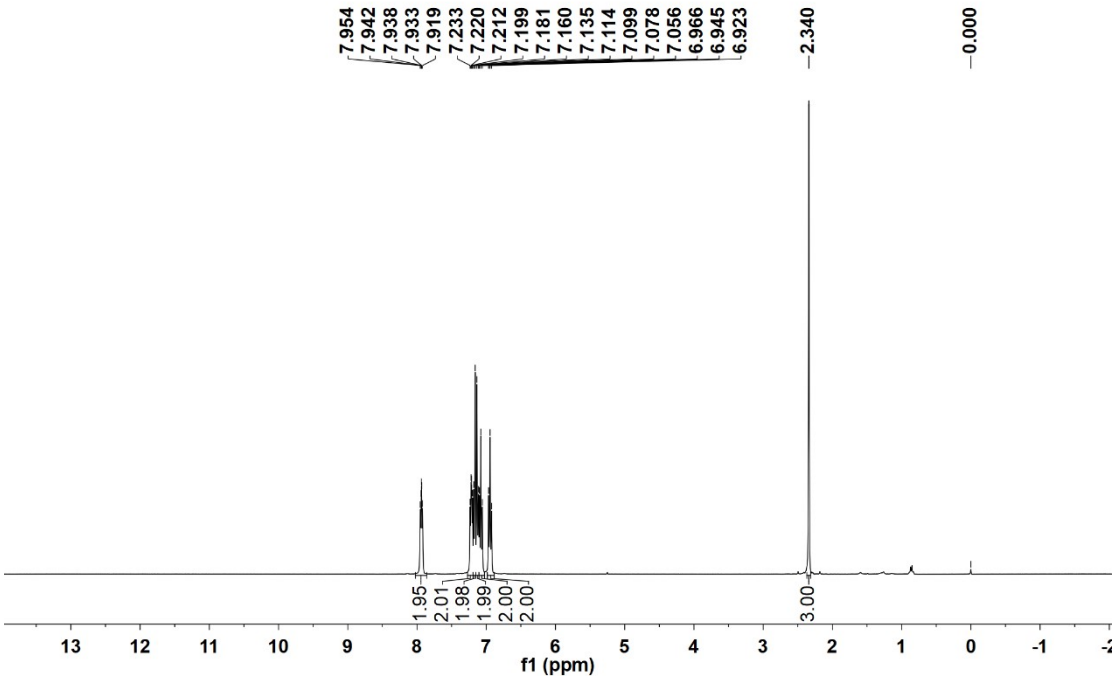
^{13}C NMR (151 MHz, $CDCl_3$) of **3x**



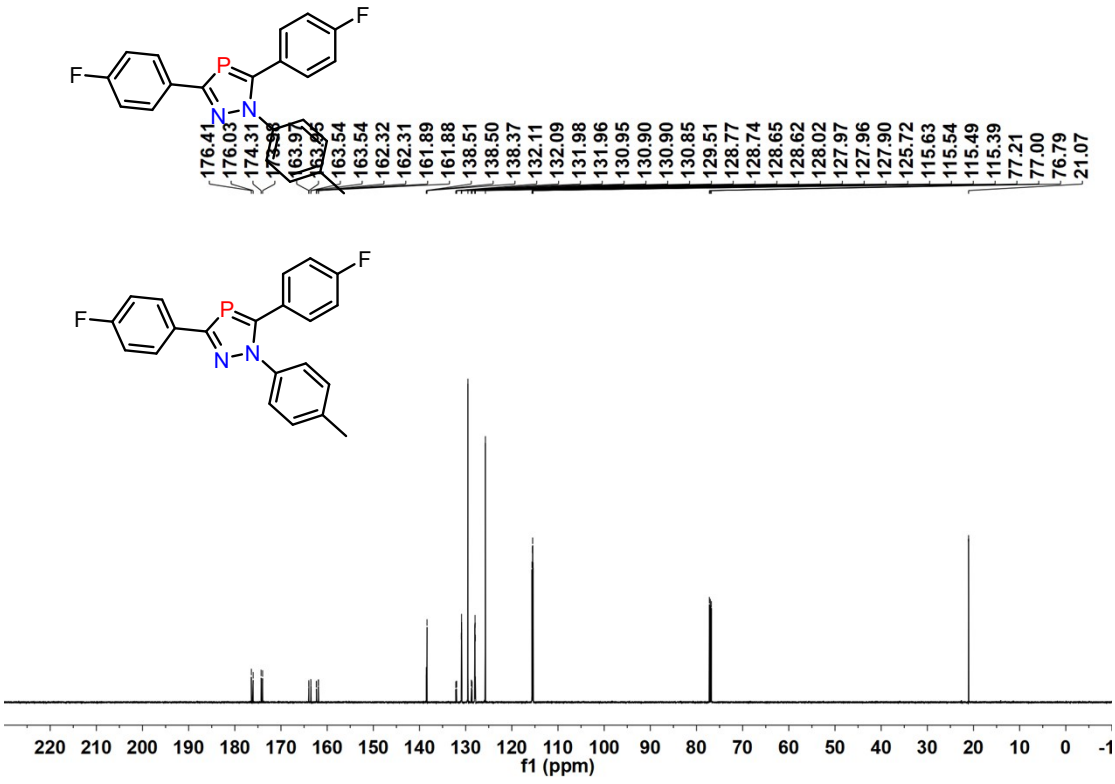
^{31}P NMR (162 MHz, $CDCl_3$) of **3x**



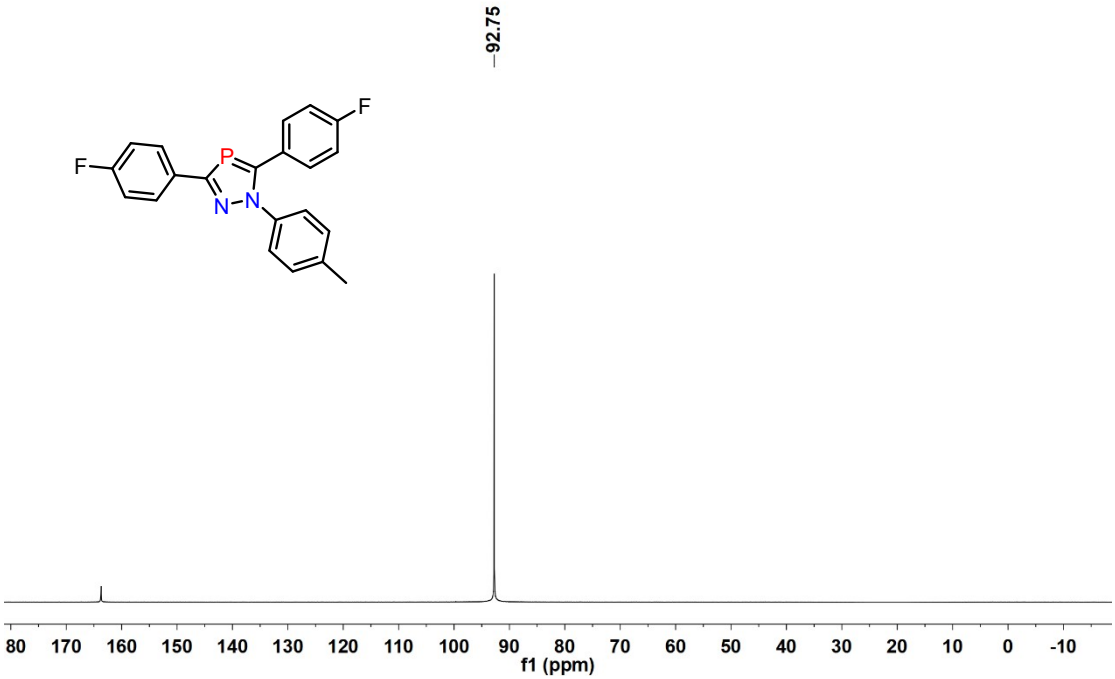
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



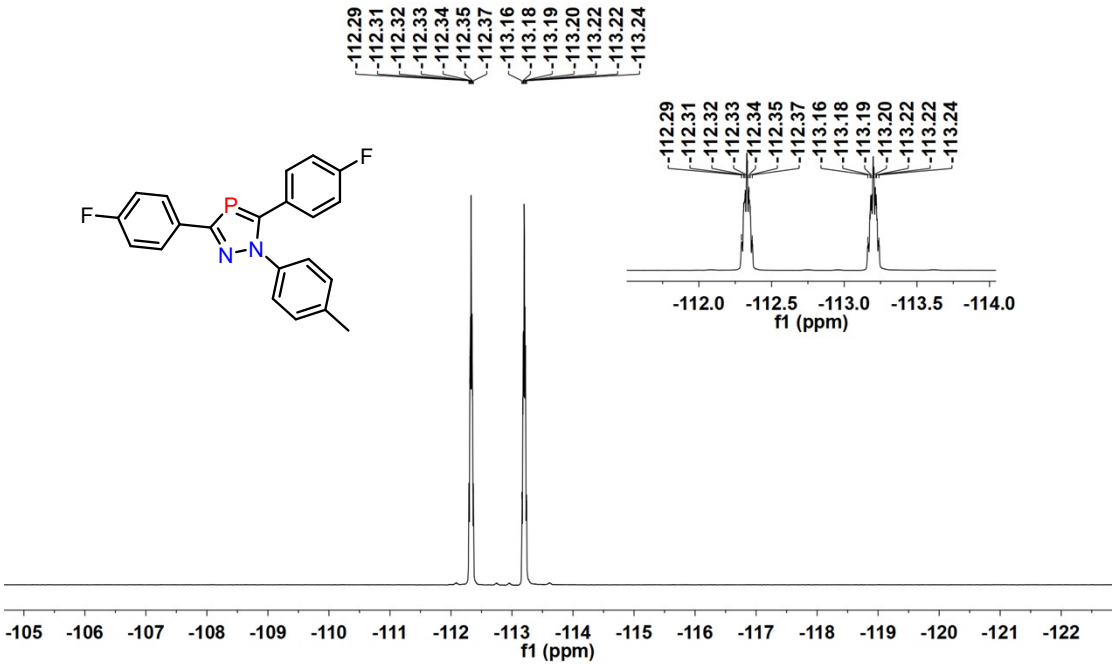
^{13}C NMR (151 MHz, $CDCl_3$) of **3y**



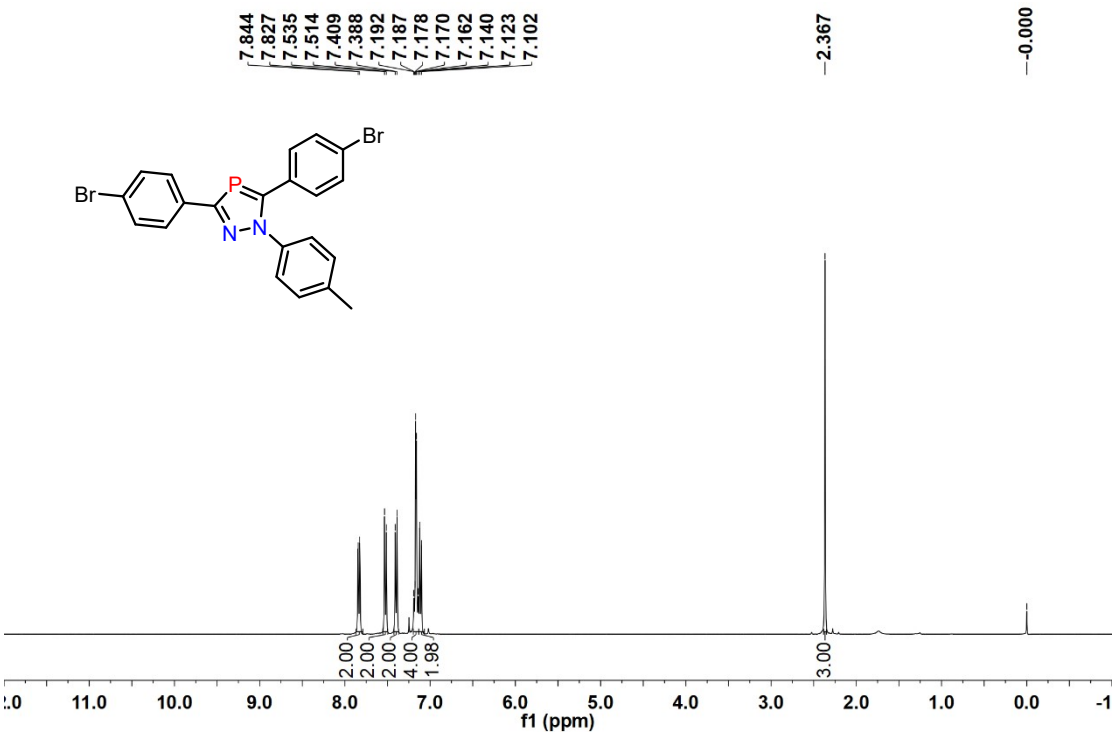
^{31}P NMR (162 MHz, $CDCl_3$) of **3y**



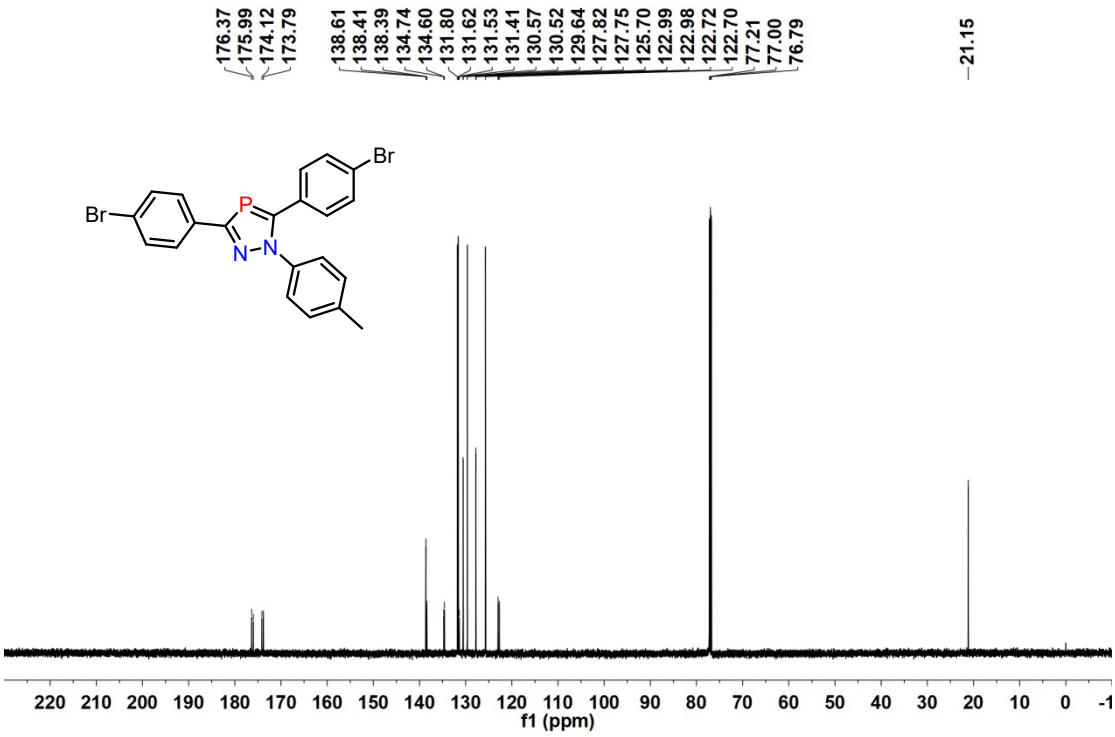
^{19}F NMR (376 MHz, $CDCl_3$) of **3y**



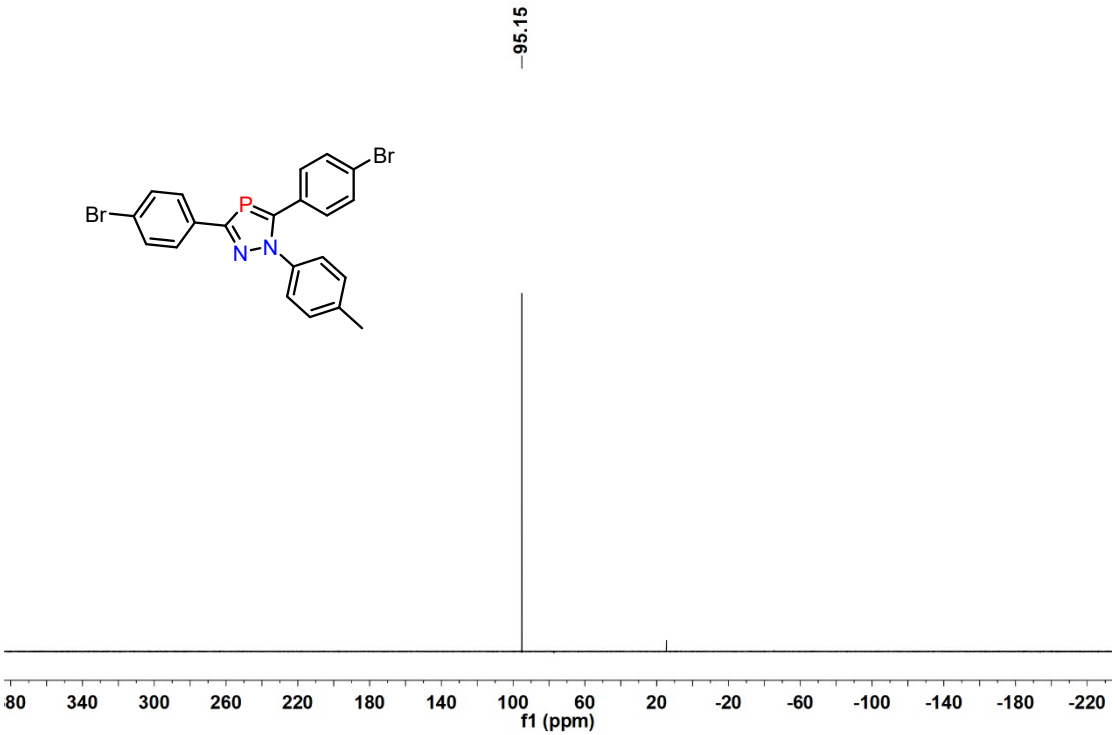
^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



^{13}C NMR (151 MHz, $CDCl_3$) of **3z**



^{31}P NMR (162 MHz, $CDCl_3$) of **3z**



10. References

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