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Supporting Information

Palladium-catalyzed coupling of aryl sulfonium salts with [TBA][P(SiCl$_3$)$_2$] for the construction of tertiary Phosphines

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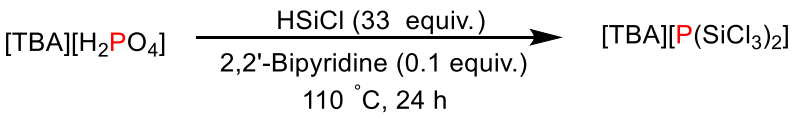
1. General Information

Unless otherwise stated, commercially available reagents and solvents were used without further purification. Deuterated solvents were purchased from Adamas. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and ^{19}F NMR spectra were recorded on a Varian Mercury 400 Plus, Agilent Technologies DD2 (600 MHz) in $CDCl_3$. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard, and the solvent peak was 7.26 ppm for 1H 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. UV-visible absorption spectra were recorded on a Shimadzu 2450 spectrophotometer. Melting points (m.p.) were measured on an X-4 apparatus (uncorrected). Reactions were monitored by thinlayer 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 General procedure for the synthesis of 1[1]

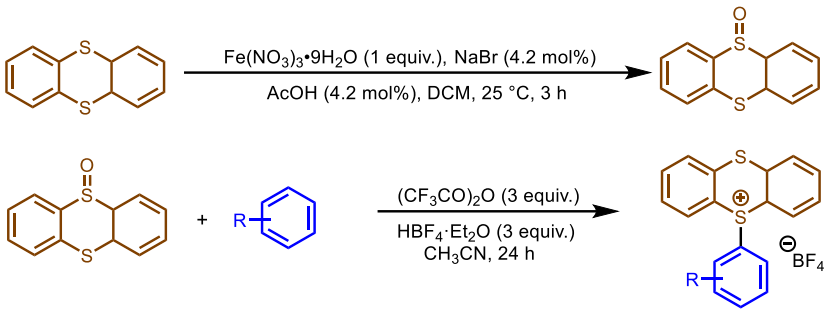


The dried and cooled 50 mL pressure tube, 10 mL syringe, $HSiCl_3$, 2,2'-bipyridine, and $[TBA][H_2PO_4]$ were placed in the glove box for standby use, and all weighing operations were completed within the glove box. In the pressure tube, 2,2'-bipyridine (32 mg, 0.2 mmol) was weighed, and then $HSiCl_3$ (6.7 mL, 66 mmol, 33 equivalents) was added using the syringe. After sealing, the mixture was stirred at room temperature for 15-30 minutes. $[TBA][H_2PO_4]$ (679 mg, 2.0 mmol, 1.0 equivalent) was added to the system. After re-sealing, the reaction was carried out at

110 °C for 24 hours. After the reaction had cooled to room temperature, it was immersed in cold hydrazine at -78 °C for approximately 10 minutes. Volatile substances were removed under vacuum on a Schlenk line. The resulting white solid was mixed with ether and filtered through a 1 cm pore size celite filter to remove most of the impurities, yielding the final target product [TBA][$P(SiCl_3)_2$] with a yield of 57%.

^{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 General procedure for the synthesis of 2a-2g[2]

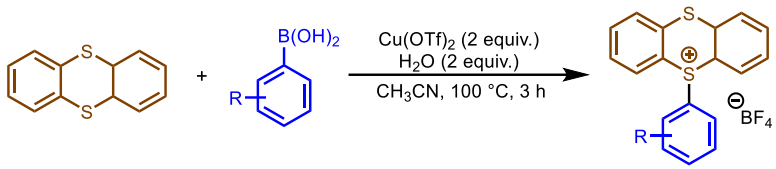


Initially, under atmospheric conditions, thiophene (5.0 g, 23 mmol, 1 equiv.) is added to a 100 mL round-bottom flask, followed by sodium bromide (0.1 g, 0.97 mmol) and ferric nitrate nonahydrate (9.3 g, 23 mmol, 1 equiv.). DCM (50 mL) is then introduced, and acetic acid (1 mL, 17 mmol, 0.76 equiv.) is added dropwise using a Pasteur pipette. The reaction mixture is stirred at room temperature for 3 hours. The progress of the reaction is monitored by TLC. Upon completion, the reaction mixture is diluted with 50 mL of water, transferred to a separatory funnel, and extracted three times with DCM and water. The organic layers are combined, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to obtain the crude product, which is recrystallized from ethanol to afford the pure oxidized product, thiophene oxide.

Subsequently, in a 200 mL round-bottom flask, an aromatic hydrocarbon (20 mmol, 1 equiv.) is combined with 25 mL of CH_3CN. The mixture is stirred at room temperature, and boron trifluoride etherate (60 mmol, 3 equiv.) is added. After complete addition, the mixture is stirred at 0 °C, and upon cooling, the oxidized thiophene (4.64 g, 20 mmol, 1 equiv.) is introduced, followed by trifluoroacetic anhydride (8.3 mL, 60 mmol, 3 equiv.). The solution's color gradually intensifies to a deep purple. The reaction is then allowed to proceed at room temperature with stirring. After

approximately 6 hours, the color becomes lighter, and the intensity of the purple diminishes. Once the reaction is complete, the reaction mixture is diluted with DCM, and saturated sodium bicarbonate aqueous solution is added. The organic layer is separated, and the aqueous phase is extracted three times with saturated sodium tetrafluoroborate solution and DCM. The combined organic layers are dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to yield the crude product, which is recrystallized from ethanol to obtain the final ArTTs.

2.3 General procedure for the synthesis of 2h-2r[3]



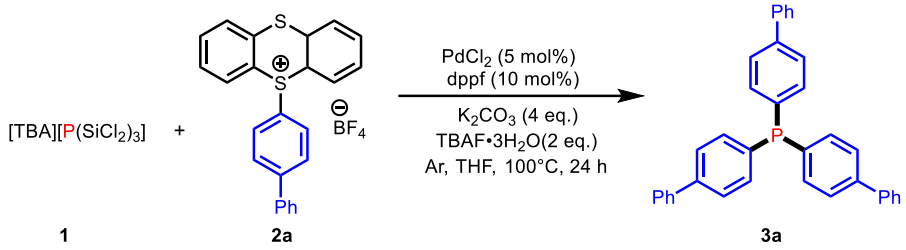
Inside the glove box, accurately weigh aryl boronic acid (10 mmol, 1.0 equiv.), thiophene (3.27 g, 15 mmol, 1.5 equiv.), and $Cu(OTf)_2$ (7.23 mg, 20 mmol, 2.0 equiv.) into a pressure-resistant tube. Then, add H_2O (0.36 mL, 20 mmol, 2.0 equiv.) and CH_3CN (10 mL) to the tube. After sealing, place the tube under stirring at 100 °C for 3.0 hours. Once cooled to room temperature, transfer the reaction mixture to an aqueous ammonia solution (100 mL, 25%-28%) and extract the aqueous phase with DCM. Dry the combined organic layers over anhydrous Na_2SO_4, filter, and then concentrate under reduced pressure to obtain the crude product. Dissolve the crude product in DCM and subsequently add the solution to stirred Et_2O to precipitate the product. Filter and collect the solid to obtain the final aryl thiophene salt product, without further purification.

3. Optimization of reaction conditions for the preparation of 3a

3.1 Screening of reaction temperature

Temperature generally has a significant impact on metal-catalyzed reactions. Based on this, we screened the reaction temperature (Table 1). Encouragingly, increasing the temperature was found to favor the formation of the product. When the temperature was raised to 100 °C, the desired target product was obtained with a yield of 48%. Upon further increasing the temperature to 110 °C, the yield did not show a significant improvement, hovering around 46%. Therefore, the optimal reaction

temperature was determined to be 110 °C.



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

Table 1 Screening of reaction temperature [a]

Entry	T/°C	Yield (**3a**)/(%)[b]
1	60	Trace
2	70	Trace
3	80	13
4	90	35
5	**100**	**48**
6	110	46

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3 equiv.), $Pd(OAc)_2$ (2.5 mol%), dppf (5 mol%), K_2CO_3 (4 equiv.), THF (2 mL), $TBAF{\cdot}3H_2O$(2 equiv.), at T °C for 24 h. [b] Isolated yields.

3.2 Screening of reaction solvent

After determining the optimal temperature, we conducted a screening of the reaction solvents (Table 2). With common solvents such as dichloromethane, acetone, methanol, and hexafluoroisopropanol, the reaction did not proceed, leaving a large amount of starting material unreacted. Although product formation was observed when using toluene as the solvent, the yield was much lower compared to tetrahydrofuran, reaching only 23%. The yield in acetonitrile was slightly lower than that in tetrahydrofuran. Therefore, tetrahydrofuran was chosen as the solvent for the reaction.

Table 2 Optimization of reaction solvent[a]

Entry	Solvent/mL	Yield (**3a**)/(%)[b]
1	DCM	nr
2	Acetone	nr
3	MeOH	nr
4	HFIP	nr
5	Tol	23

6	**THF**	**48**
7	CH_3CN	39

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3 equiv.), [M] (2.5 mol%), dppf (5 mol%), K_2CO_3 (4 equiv.), solvent (2 mL), TBAF·3H_2O(2 equiv.), at 100 °C for 24 h. [b] Isolated yields.

3.3 Screening of reaction catalyst

After experimenting with different metal catalysts (Table 3), it was found that $PdCl_2$ was more effective than $Pd(OAc)_2$, yielding the target product at a 52% rate. In contrast, $Pd_2(dba)_3$ or $Pd(acac)_2$ were not as effective as $PdCl_2$, and the complex $Pd(dppf)Cl_2$ also achieved a 47% yield. Other catalysts did not exhibit any catalytic activity. Therefore, we chose to use $PdCl_2$ as the catalyst for this approach.

Table 3 screening of catalyst[a]

Entry	[M]/mg	Yield (**3a**)/(%)[b]
1	$Pd(OAc)_2$	48
2	**$PdCl_2$**	**52**
3	$Pd_2(dba)_3$	41
4	$Pd(acac)_2$	36
5	$Pd(dppf)Cl_2$[c]	47
6	$NiCl_2$	nr
7	CuCl	nr

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3 equiv.), [M] (2.5 mol%), dppf (5 mol%), K_2CO_3 (4 equiv.), THF (2 mL), TBAF·3H_2O(2 equiv.), at 100 °C for 24 h. [b] Isolated yields. [c] without L.

3.4 Screening of reaction catalyst molar amount

Subsequently, we conducted a screening of the molar amount of $PdCl_2$ (Table 4). We found that reducing the loading of the catalyst led to a decrease in yield. Conversely, increasing the amount of catalyst resulted in a higher yield, reaching up to 61%. Therefore, we determined that the optimal molar amount of $PdCl_2$ should be 5 mol%.

Table 4 Screening of catalyst molar amount[a]

Entry	x/mol%	Yield (**3a**)/(%)[b]
1	1	30
2	2.5	52
3	**5**	**61**

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3 equiv.), $PdCl_2$ (x mol%), dppf (5 mol%), K_2CO_3 (4 equiv.), THF (2 mL), TBAF·$3H_2O$(2 equiv.), at 100 °C for 24 h. [b] Isolated yields. [c] without L.

3.5 Screening of the molar amount of ligands

Next, we performed a simple screening of the ligand molar amount (Table 5). Previously, when the ligand was added in a 1:1 ratio with the catalyst, the yield was 61%. When the ligand concentration was increased to 10 mol%, the yield rose to 70%. Further increasing the ligand amount to 15 mol% did not result in a significant change in yield. Therefore, we established that the molar amount of the ligand dppf should be 10 mol%, with the catalyst and ligand added to the system in a 1:1 ratio.

Table 5 Screening of the molar amount of ligands[a]

Entry	y/mol%	Yield (**3a**)/(%)[b]
1	5	61
2	**10**	**70**
3	15	67

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3 equiv.), $PdCl_2$ (5 mol%), dppf (y mol%), K_2CO_3 (4 equiv.), THF (2 mL), TBAF·$3H_2O$(2 equiv.), at 100 °C for 24 h. [b] Isolated yields.

3.6 Screening of alkali

We systematically optimized various inorganic and organic bases (Table 6) and found that organic bases were less effective, while inorganic bases showed relatively better performance. Specifically, carbonates such as Na_2CO_3 or Cs_2CO_3 yielded the target product at 52% and 47% respectively, but the overall comparison indicated that K_2CO_3 was the most effective, yielding the target product at the highest rate.

Table 6 Screening of alkali[a]

Entry	Base	Yield (**3a**)/(%)[b]
1	**K_2CO_3**	**70**
2	Na_2CO_3	52
3	Cs_2CO_3	47
4	$NaHCO_3$	trace
5	K_3PO_4	39
6	NaOH	33
7	DMAP	trace

8	DBU	trace
9	DABCO	nr
10	DIPEA	trace
11	Et_3N	trace

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3 equiv.), $PdCl_2$ (5 mol%), dppf (10 mol%), base (4 equiv.), THF (2 mL), TBAF·$3H_2O$(2 equiv.), at 100 °C for 24 h. [b] Isolated yields.

3.7 Screening the equivalent of alkali

The equivalents of K_2CO_3 were optimized (Table 7), and it was found that the reaction did not proceed effectively when the amount of base was below 2.5 equivalents. As the amount of base increased, the yield also gradually increased, reaching the highest yield when the base was at 4 equivalents. Therefore, it was determined that the optimal amount of base should be 4 equivalents.

Table 7 Screening the equivalent of alkali[a]

Entry	z/equiv.	Yield (**3a**)/(%)[b]
1	1	\
2	1.5	\
3	2	\
4	2.5	trace
6	3	34
7	3.5	41
8	**4**	**70**

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3 equiv.), $PdCl_2$ (5 mol%), dppf (10 mol%), K_2CO_3 (z equiv.), THF (2 mL), TBAF·$3H_2O$(2 equiv.), at 100 °C for 24 h. [b] Isolated yields.

3.8 Screening of reaction time

The reaction was carried out under argon atmosphere, so initially, we set the reaction time to 24 hours. After determining the key factors such as the reaction solvent, temperature, catalyst, ligand, and base, we attempted to shorten the reaction time. Unfortunately, when the reaction time was reduced to 18 hours, the yield decreased to 63%. Therefore, it was concluded that a reaction time of 24 hours was still necessary (Table 8).

Table 8 Screening of reaction time[a]

Entry	**t/h**	Yield (**3a**)/(%)[b]
1	3	trace
2	6	35
3	9	47
4	12	56
5	18	63
6	**24**	**76**

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3 equiv.), $PdCl_2$ (5 mol%), dppf (10 mol%), K_2CO_3 (4 equiv.), THF (2 mL), TBAF·$3H_2O$(2 equiv.), at 100 °C for t h. [b] Isolated yields.

3.9 Screening of alkali

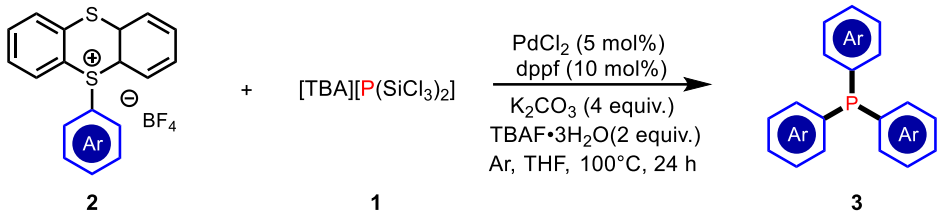
Next, we optimized the molar ratio of [TBA][$P(SiCl_3)_2$] **1** to ArTTs **2a** (Table 9). When [TBA][$P(SiCl_3)_2$] and ArTTs were added in a 1:3.2 ratio, the target product6aa was obtained with a yield of 76%. When the ratio of **1** to **2a** was increased from 1:3.2 to 1:3.5 or 1:4, the yield remained largely unchanged. Additionally, based on our previous research results on reactions involving [TBA][$P(SiCl_3)_2$], we noted that the addition of TBAF·$3H_2O$ typically promotes the occurrence of the reaction. Through literature research, we speculated that TBAF·$3H_2O$ could accelerate the cleavage of the P-Si bond. In summary, we determined the optimal reaction conditions to be: ArTTs **2a** (3.2 equiv.), $PdCl_2$ (5 mol%) as the catalyst, dppf (10 mol%) as the ligand, K_2CO_3 (4 equiv.) as the base, and TBAF·$3H_2O$ (2 equiv.) as an additive, reacting in tetrahydrofuran at 100 °C for 24 hours.

Table 3.9 Screening the equivalent of alkali[a]

Entry	**N_4** : N_{5aa}	Yield (**6aa**)/(%)[b]
1	1 : 3	70
2	**1 : 3.2**	**76**
3	1 : 3.5	73
4	1 : 4	71

[a] Reaction conditions: N_4 : N_{5aa}, $PdCl_2$ (5 mol%), dppf (10 mol%), K_2CO_3 (4 equiv.), THF (2 mL), TBAF·$3H_2O$(2 equiv.), at T °C for 24 h. [b] Isolated yields.

4. Procedure for Synthesis of 3

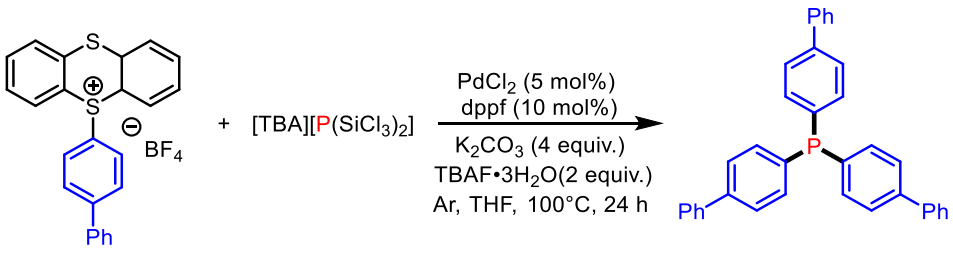


2 **1** **3**

All reagents and dried pressure-resistant tubes required for weighing were placed inside the glove box for standby use. In a 10 mL pressure-resistant tube, [TBA][$P(SiCl_3)_2$] (108 mg, 0.2 mmol), ArTTs (0.64 mmol, 3.2 equiv.), $PdCl_2$ (1.77 mg, 0.01 mmol), dppf (5.54 mg, 0.02 mmol), K_2CO_3 (110.4 mg, 0.8 mmol, 4 equiv.), and TBAF·$3H_2O$ (126.2 mg, 0.4 mmol, 2 equiv.) were added. Subsequently, THF (2 mL) was introduced, and the tube was sealed and heated at 100 °C for 12 h. After the reaction was completed, the mixture was cooled to room temperature, diluted with DCM, and then extracted three times with a DCM-water mixture. The organic phases were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to yield the crude product. The crude product was purified by silica gel column chromatography using a mixture of petroleum ether and ethyl acetate as the eluent, resulting in the final target compound **3**.

5. Procedure for Gram-Scale Synthesis of 3a

Under standard conditions, using 1.08 g of **2a** and 2.93 g of [TBA][$P(SiCl_3)_2$], the reaction was conducted for 24 hours under an argon atmosphere, yielding the target compound at a 61% yield. This result suggests the potential applicability and value of the reaction system.

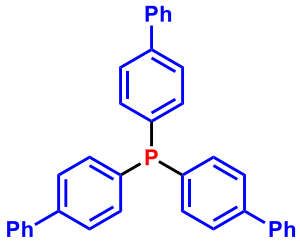


5aa 6.4 mmol 2.93 g

4 2 mmol 1.08 g

6aa 0.6 g 61%

6. Characterization Data of the Corresponding Products



3a

tri([1,1'-biphenyl]-4-yl)phosphane

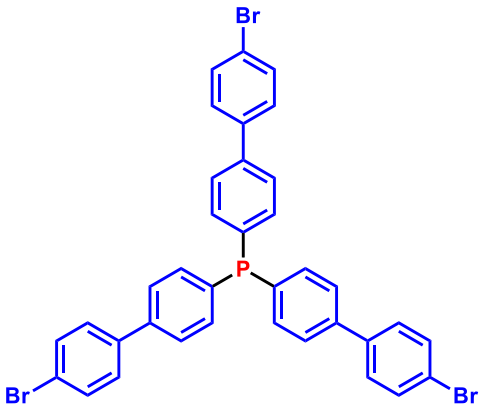
PE/EA = 5:1; Yield: 76% (74.5 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.8 Hz, 12H), 7.52 – 7.43 (m, 12H), 7.42 - 7.32 (m, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.6, 140.5, 136.0 (d, *J* = 10.5 Hz), 134.2 (d, *J* = 19.5 Hz), 128.8, 127.5, 127.2 (d, *J* = 7.5 Hz), 127.1.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -7.59.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{36}H_{28}P^{+}$: 491.1923; Found 491.1925.



3b

tris(4'-bromo-[1,1'-biphenyl]-4-yl)phosphane

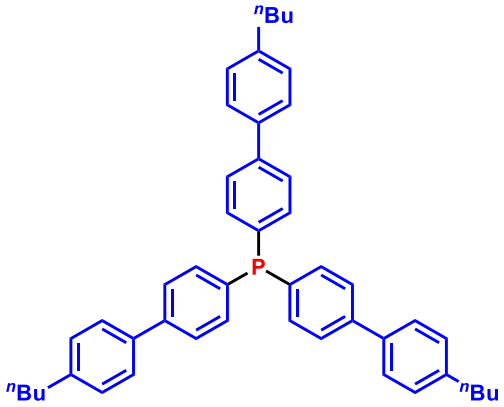
PE/EA = 5:1; Yield: 51% (73.8 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.34 (m, 24H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.4, 141.4, 137.8, 134.2, 134.0, 128.8, 127.0 (d, *J* = 7.3 Hz), 126.8, 35.2, 33.5, 22.3, 13.9.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -7.50.

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{36}H_{25}Br_3P^+$: 724.9239; Found 724.9241.



3c

tris(4'-butyl-[1,1'-biphenyl]-4-yl)phosphane

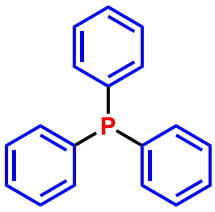
PE/EA = 5:1; Yield: 57% (70.0 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, J = 8.4, 1.6 Hz, 5H), 7.54 – 7.50 (m, 6H), 7.43 (t, J = 8.0 Hz, 5H), 7.28 - 7.21 (m, 8H), 2.65 (t, J = 8.0 Hz, 6H), 1.69 – 1.60 (m, 6H), 1.45 – 1.32 (m, 6H), 0.94 (t, J = 7.3 Hz, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.4, 139.3, 136.3 (d, *J* = 11.3 Hz), 134.3 (d, *J* = 19.5 Hz), 131.9, 128.6, 127.0 (d, *J* = 6.9 Hz), 121.95.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -7.63.

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{48}H_{52}P^+$: 659.3801; Found 659.3803.



3d

triphenylphosphane

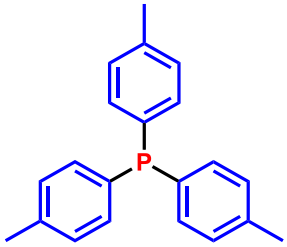
PE; Yield: 61% (40.0 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.11 (m, 15H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.4 (d, *J* = 12.0 Hz), 133.9 (d, *J* = 19.5 Hz), 128.9, 128.7 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ -5.35.

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{18}H_{16}P^+$: 263.0984; Found 263.0980.



3e

tri-*p*-tolylphosphane

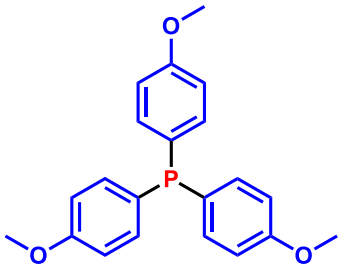
PE; Yield: 66% (40.1 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.6 Hz, 6H), 7.15 (d, *J* = 7.6 Hz, 6H), 2.36 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.5, 134.1 (d, *J* = 9.0 Hz), 133.6 (d, *J* = 19.5 Hz), 129.2 (d, *J* = 7.5 Hz), 21.3.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -8.02.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{21}H_{22}P^{+}$: 305.1454; Found 305.1456.



3f

tris(4-methoxyphenyl)phosphane

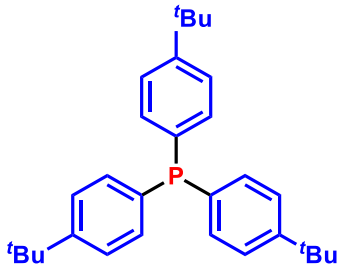
PE/EA = 5:1; Yield: 58% (40.8 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.6 Hz, 6H), 7.15 (d, *J* = 7.6 Hz, 6H), 2.36 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.1, 135.0 (d, *J* = 21.0 Hz), 129.0 (d, *J* = 7.5 Hz), 114.2 (d, *J* = 7.5 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ -10.30.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{21}H_{22}O_3P^{+}$: 353.1301; Found 353.1305.



3g

tris(4-(*tert*-butyl)phenyl)phosphane

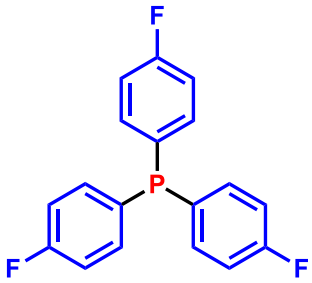
PE; Yield: 52% (47.5 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 6H), 7.28 (t, *J* = 8.0 Hz, 6H), 1.34 (s, 27H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.6, 133.8 (d, *J* = 9.0 Hz), 133.4 (d, *J* = 19.5 Hz), 125.4 (d, *J* = 7.5 Hz), 34.6, 31.2.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -8.91.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{30}H_{40}P^{+}$: 431.2862; Found 431.2859.



3h

tris(4-fluorophenyl)phosphane

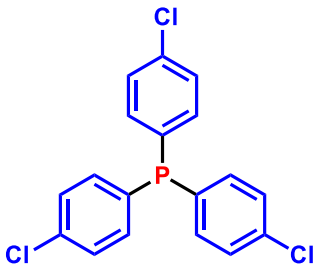
PE; Yield: 59% (37.2 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 6H), 7.04 (t, *J* = 8.4 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.2, 162.6, 135.4 (dd, *J* = 21.0, 9.0 Hz), 132.5 (dd, *J* = 10.5, 3.0 Hz), 115.9 (dd, *J* = 21.0, 7.5 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ -2.26.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{18}H_{13}F_3P^{+}$: 317.0701; Found 317.0703.



3i

tris(4-chlorophenyl)phosphane

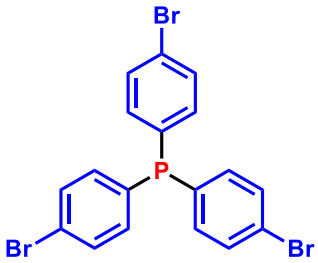
PE; Yield: 64% (46.6 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 6H), 7.24 – 7.18 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 135.5, 134.9, 134.7, 129.0 (d, *J* = 7.5 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ -8.64.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{18}H_{13}Cl_3P^{+}$: 364.9815; Found 364.9815.



3j

tris(4-bromophenyl)phosphane

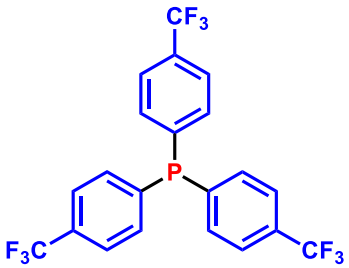
PE; Yield: 49% (48.6 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 6H), 7.24 – 7.18 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 135.2 (d, *J* = 12.0 Hz), 135.0 (d, *J* = 21.0 Hz), 131.9 (d, *J* = 7.5 Hz), 123.9.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -8.50.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{18}H_{13}Br_3P^{+}$: 496.8300; Found 496.8297.



3k

tris(4-(trifluoromethyl)phenyl)phosphane

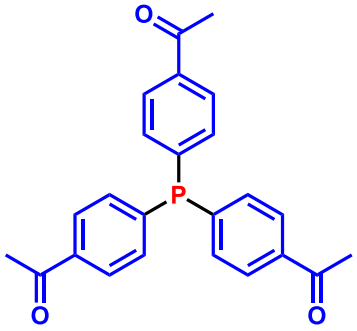
PE/EA = 5:1; Yield: 54% (50.3 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 6H), 7.46 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.3 (d, *J* = 15.0 Hz), 133.9 (d, *J* = 19.5 Hz), 131.5 (q, *J* = 33.0 Hz), 126.0 – 125.4 (m), 123.8 (q, *J* = 270.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ -6.18.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{21}H_{13}F_9P^{+}$: 467.0606; Found 467.0605.



3l

1,1',1''-(phosphanetriyltris(benzene-4,1-diyl))tris(ethan-1-one)

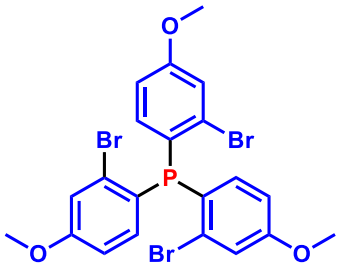
PE/EA = 5:1; Yield: 67% (52.0 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 6H), 7.37 (t, *J* = 7.2 Hz, 6H), 2.58 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.5, 141.8 (d, *J* = 13.8 Hz), 137.5, 133.8 (d, *J* = 19.5 Hz), 128.3 (d, *J* = 6.9 Hz), 26.6.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -5.54.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{24}H_{22}O_3P^{+}$: 389.1301; Found 389.1305.



3m

tris(2-bromo-4-methoxyphenyl)phosphane

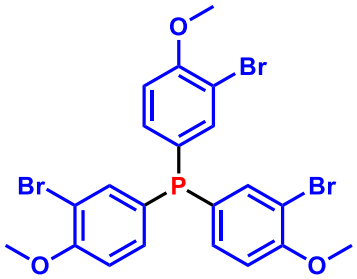
PE/EA = 5:1; Yield: 65% (76.2 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 3.2 Hz, 3H), 6.79 (dd, *J* = 8.4, 2.8 Hz, 3H), 6.66 (dd, *J* = 8.4, 2.0 Hz, 3H), 3.81 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.8, 135.3 (d, *J* = 36.0 Hz), 130.6 (d, *J* = 10.0 Hz), 118.5 (d, *J* = 3.0 Hz), 114.1, 55.4.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -7.50 (d, *J* = 15.2 Hz).

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{21}H_{19}Br_3O_3P^+$: 586.8616; Found 586.8612.



3n

tris(3-bromo-4-methoxyphenyl)phosphane

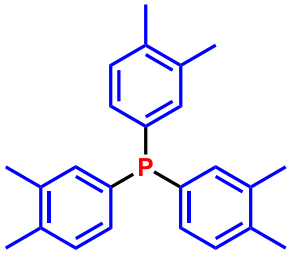
PE/EA = 5:1; Yield: 70% (82.0 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 7.2, 2.0 Hz, 3H), 7.20 – 7.15 (m, 3H), 6.89 (d, *J* = 8.4 Hz, 3H), 3.90 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.6, 137.9 (d, *J* = 22.5 Hz), 133.8 (d, *J* = 21.0 Hz), 129.8 (d, *J* = 13.5 Hz), 112.6 (d, *J* = 7.5 Hz), 112.2 (d, *J* = 7.5 Hz), 56.2.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -8.94.

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{21}H_{19}Br_3O_3P^+$: 586.8616; Found 586.8615.



3o

tris(3,4-dimethylphenyl)phosphane

PE; Yield: 66% (45.7 mg).

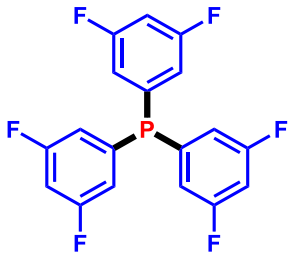
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 4.8 Hz, 1H), 7.17 – 7.00 (m, 8H), 2.26 (d, *J* = 4.4 Hz, 9H), 2.22 (d, *J* = 4.4 Hz, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.27, 136.61 (d, *J* = 8.2 Hz), 134.98 (d, *J* =

22.7 Hz), 131.09 (d, J = 16.0 Hz), 129.77 (d, J = 6.9 Hz), 128.41.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -7.68.

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{24}H_{28}P^+$: 347.1923; Found 347.1926.



3p

tris(3,5-difluorophenyl)phosphane

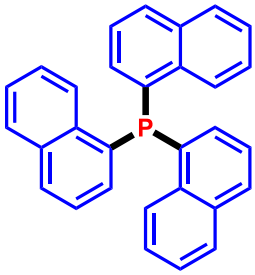
PE; Yield: 41% (30.3 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.92 - 6.81 (m, 3H), 6.85 – 6.74 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.7 – 161.2 (m), 141.0 – 137.7 (m), 117.8 – 114.8 (m), 105.5 (t, J = 25.7 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ -1.79.

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{18}H_{10}F_6P^+$: 371.0419; Found 371.0422.



3q

tri(naphthalen-1-yl)phosphane

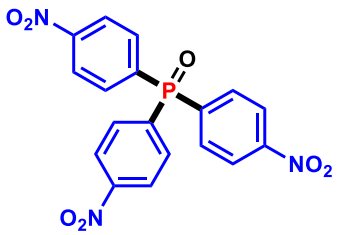
PE/EA = 10:1; Yield: 43% (35.4 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, J = 7.2, 2.0 Hz, 3H), 7.20 – 7.15 (m, 3H), 6.89 (d, J = 8.4 Hz, 3H), 3.90 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 135.68 (d, J = 22.7 Hz), 133.53 (d, J = 4.5 Hz), 133.41, 132.77 (d, J = 12.1 Hz), 129.6, 128.6 (d, J = 3.0 Hz), 126.5, 126.3, 126.3 (d, J = 3.0 Hz), 125.9 (d, J = 30.2 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ -33.12.

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{30}H_{22}P^+$: 413.1454; Found 413.1457.



3r

tris(4-nitrophenyl)phosphine oxide

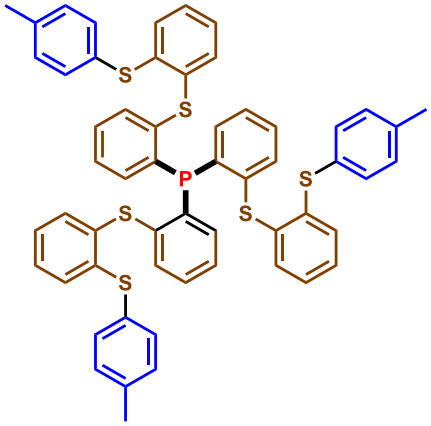
PE/EA = 3:1; Yield: 66% (47.0 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (dd, *J* = 9.2, 2.4 Hz, 6H), 7.95 – 7.85 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 133.2, 133.1, 124.0, 123.9.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 23.98.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{18}H_{13}N_3O_7P^{+}$: 414.0491; Found 414.0487.



4a

tris(2-((2-(*p*-tolylthio)phenyl)thio)phenyl)phosphane

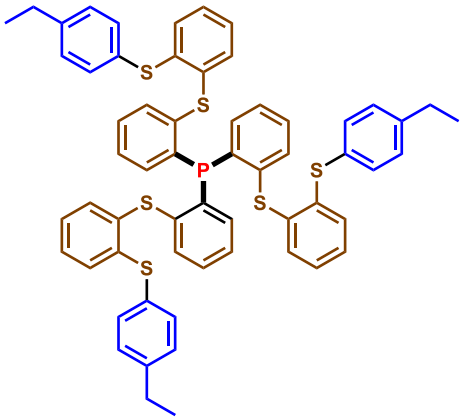
PE/EA = 8:1; Yield: 14% (26.7 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.20 (m, 14H), 7.19 – 7.08 (m, 10H), 7.00 – 6.91 (m, 12H), 2.33 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.3, 141.09, 140.05 (d, *J* = 11.9 Hz), 139.0, 137.7, 136.6 (d, *J* = 5.7 Hz), 134.4, 132.9, 132.6 (d, *J* = 3.9 Hz), 130.7, 130.1, 130.0, 129.5 (d, *J* = 8.8 Hz), 127.7, 127.2, 126.8, 21.1.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -22.83.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{57}H_{46}PS_6^{+}$: 953.1656; Found 953.1655.



4b

tris(2-((2-((4-ethylphenyl)thio)phenyl)thio)phenyl)phosphane

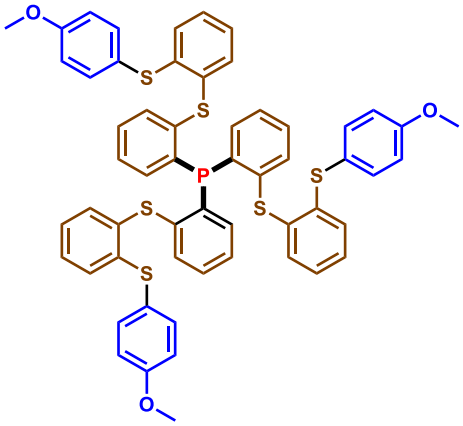
PE/EA = 8:1; Yield: 11% (21.9 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.24 (m, 14H), 7.18 – 7.07 (m, 10H), 7.02 – 6.84 (m, 12H), 2.61 (m, 6H), 1.22 (t, *J* = 7.6 Hz, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.9, 140.0, 138.9, 136.7 (d, *J* = 7.0 Hz), 134.4, 133.97, 132.93, 132.69, 132.65, 130.9, 129.6 (d, *J* = 7.7 Hz), 129.0, 128.8, 127.7, 127.2, 126.8, 28.49, 15.34.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -22.75.

HRMS (ESI) m/z: ([M+H]$^{+}$) Calcd for $C_{60}H_{52}PS_6^{+}$: 995.2125; Found 995.2127.



4c

tris(2-((2-((4-methoxyphenyl)thio)phenyl)thio)phenyl)phosphane

PE/EA = 3:1; Yield: 17% (34.0 mg).

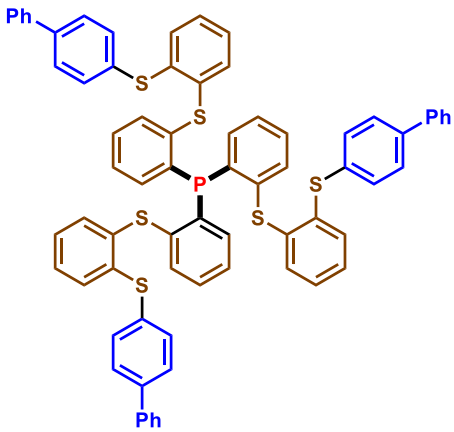
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 6.53 (m, 36H), 3.79 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.87, 141.68, 141.47, 141.23, 139.34 (d, *J* =

10.6 Hz), 135.90, 134.75 (d, J = 6.0 Hz), 134.43, 133.18, 131.99, 129.58, 128.07, 127.49 (d, J = 9.1 Hz), 126.21, 124.02, 115.00, 55.32.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -23.45.

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{57}H_{46}O_3PS_6^+$: 1001.1503; Found 1001.1504.



4d

tris(2-((2-([1,1'-biphenyl]-4-ylthio)phenyl)thio)phenyl)phosphane

PE/EA = 3:1; Yield: 10% (22.8 mg).

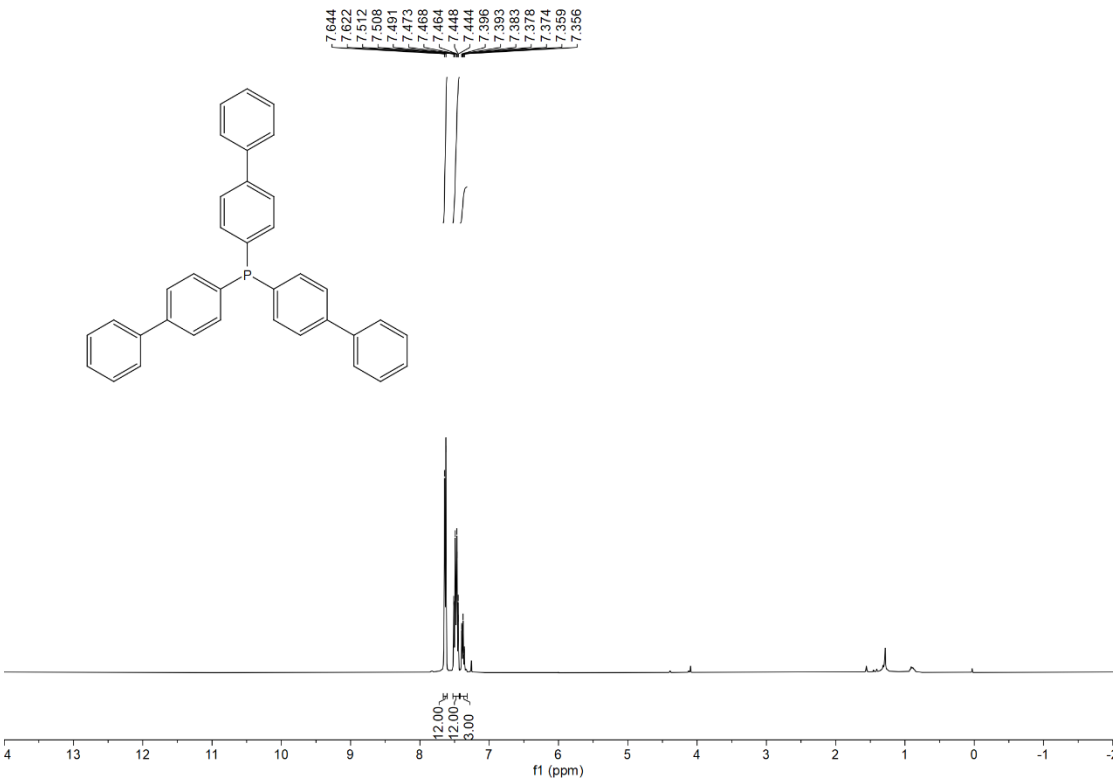
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, J = 7.2 Hz, 6H), 7.47 (d, J = 8.4 Hz, 6H), 7.41 (t, J = 7.6 Hz, 6H), 7.35 - 7.26 (m, 14H), 7.21 – 7.16 (m, 6H), 7.11 – 7.05 (m, 4H), 7.02 – 6.96 (m, 6H), 6.92 (d, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.7, 140.6, 140.3, 140.0, 138.4, 136.9, 134.5, 134.1, 133.2, 132.2, 132.0, 131.1, 129., 128.7, 128.0, 127.8, 127.6, 127.3, 127.19, 126.9.

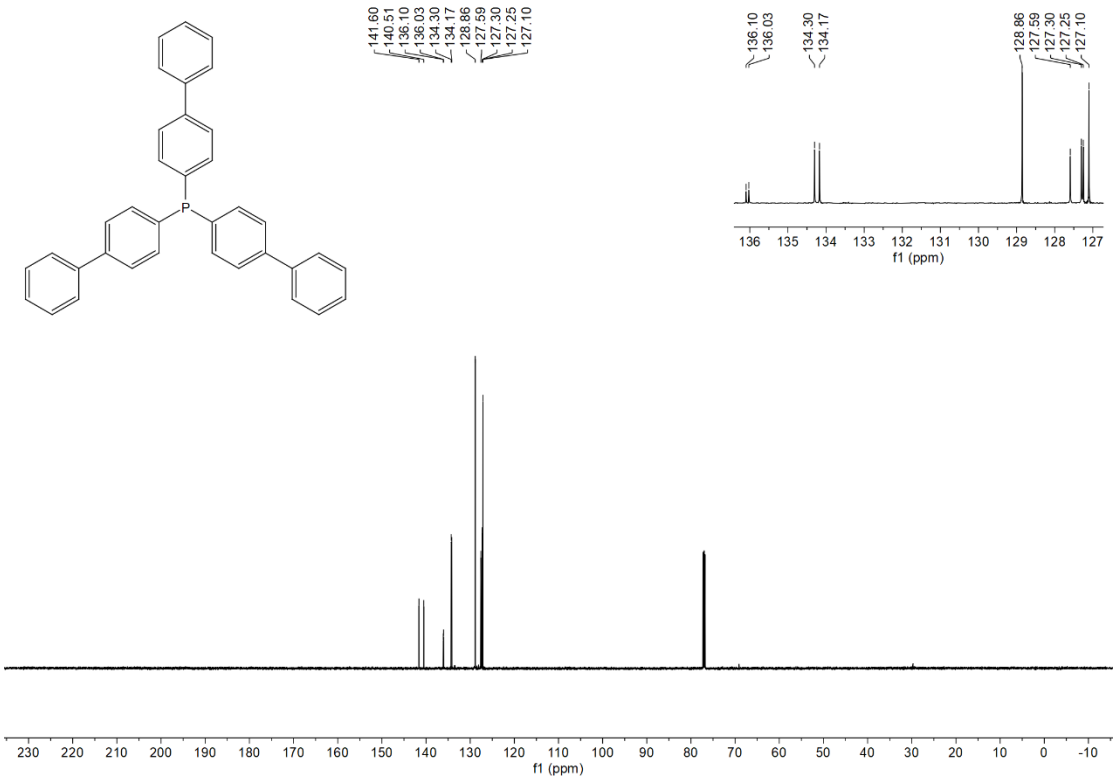
^{31}P NMR (162 MHz, Chloroform-*d*) δ -22.67.

HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{72}H_{52}PS_6^+$: 1139.2125; Found 1139.2121.

7. Copies of NMR Spectra

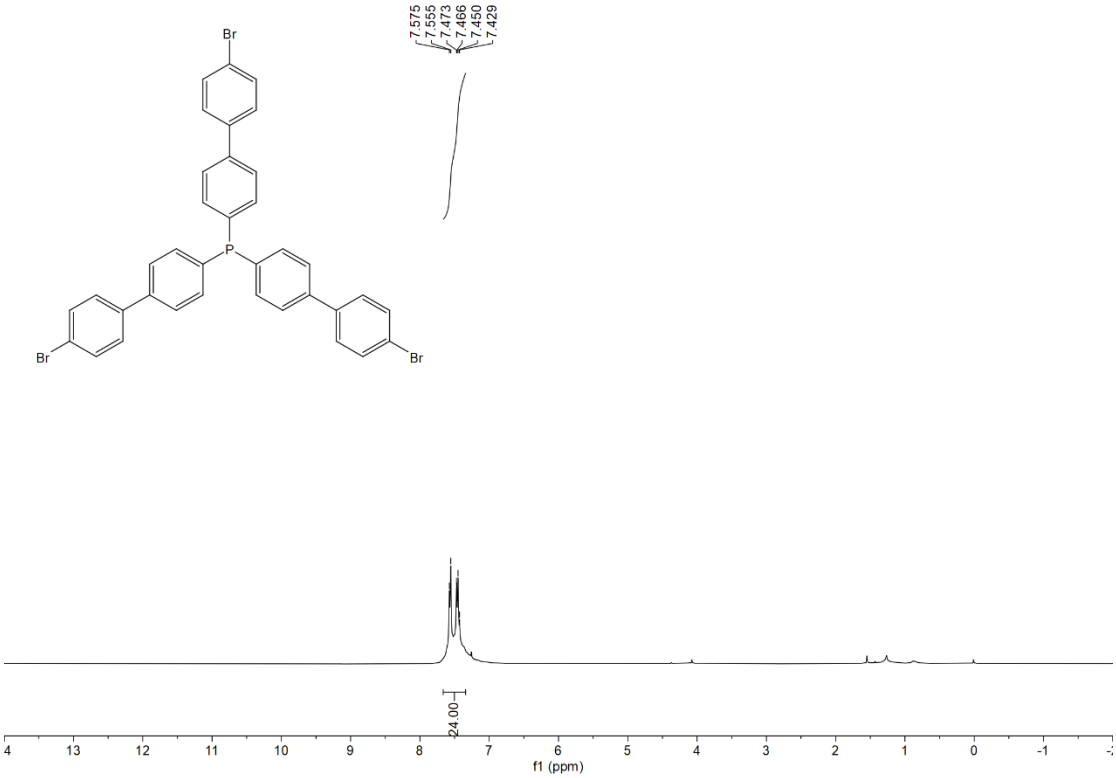


^{1}H NMR spectrum of **3a** (400 MHz, Chloroform-*d*)

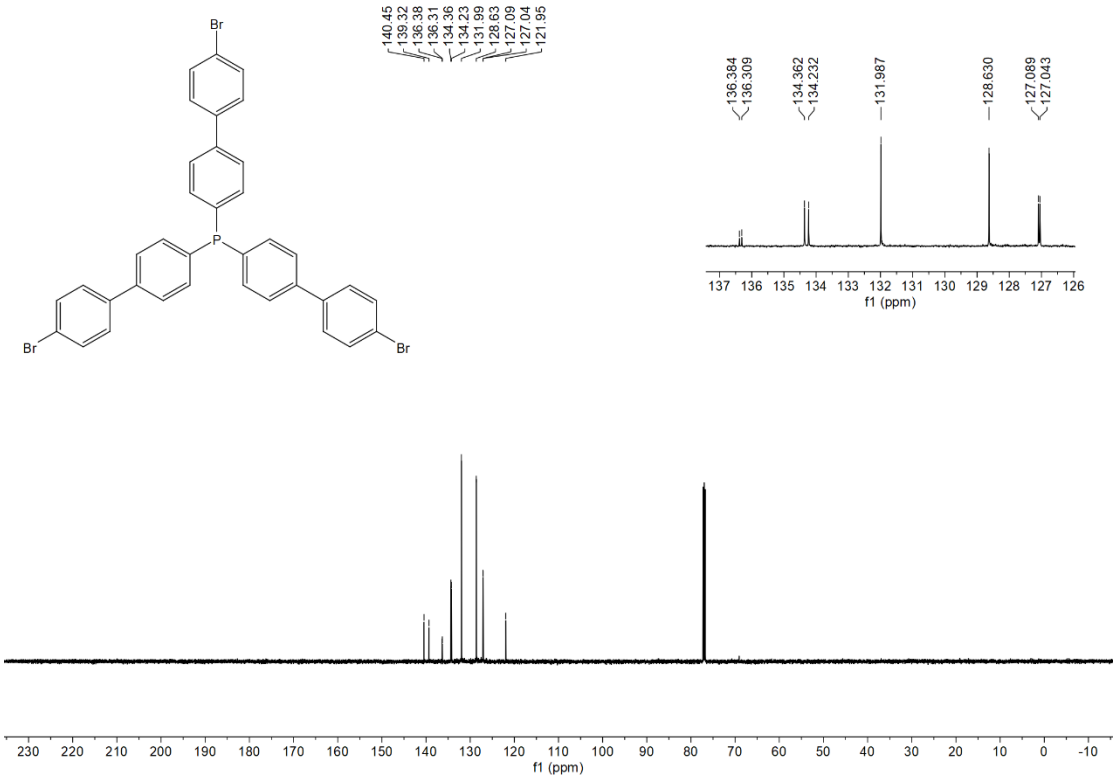


^{13}C spectrum of **3a** (151 MHz, Chloroform-*d*)

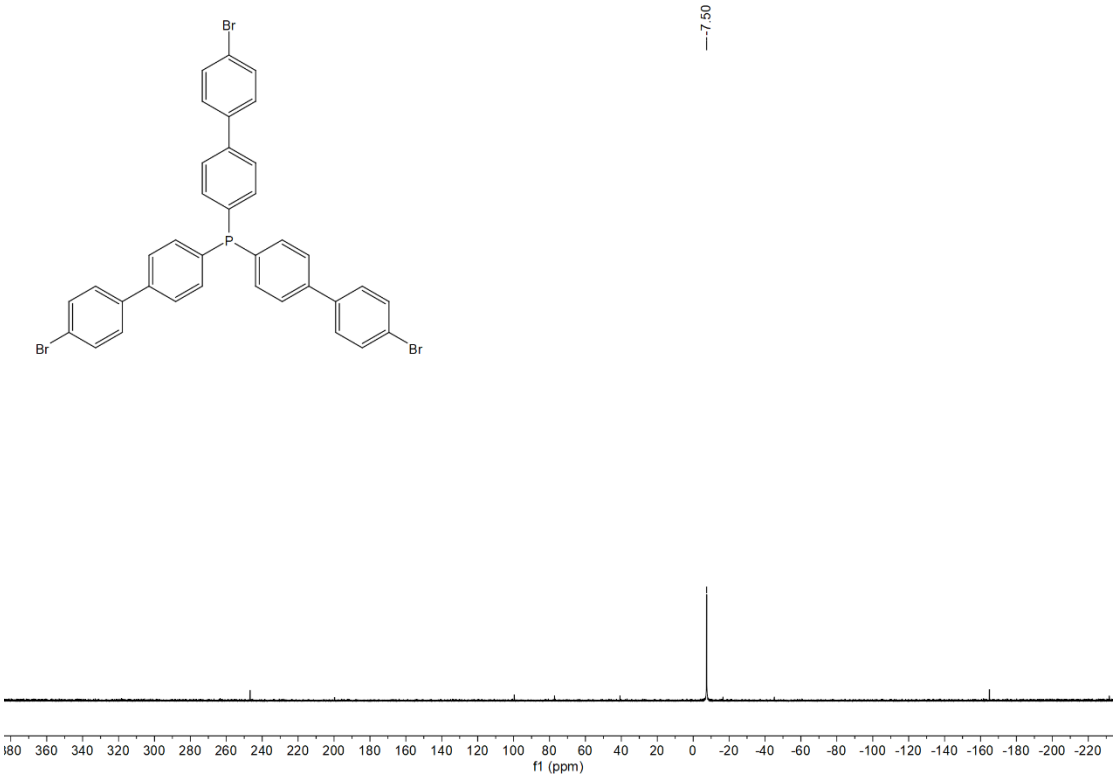
^{31}P NMR spectrum of **3a** (162 MHz, Chloroform-*d*)



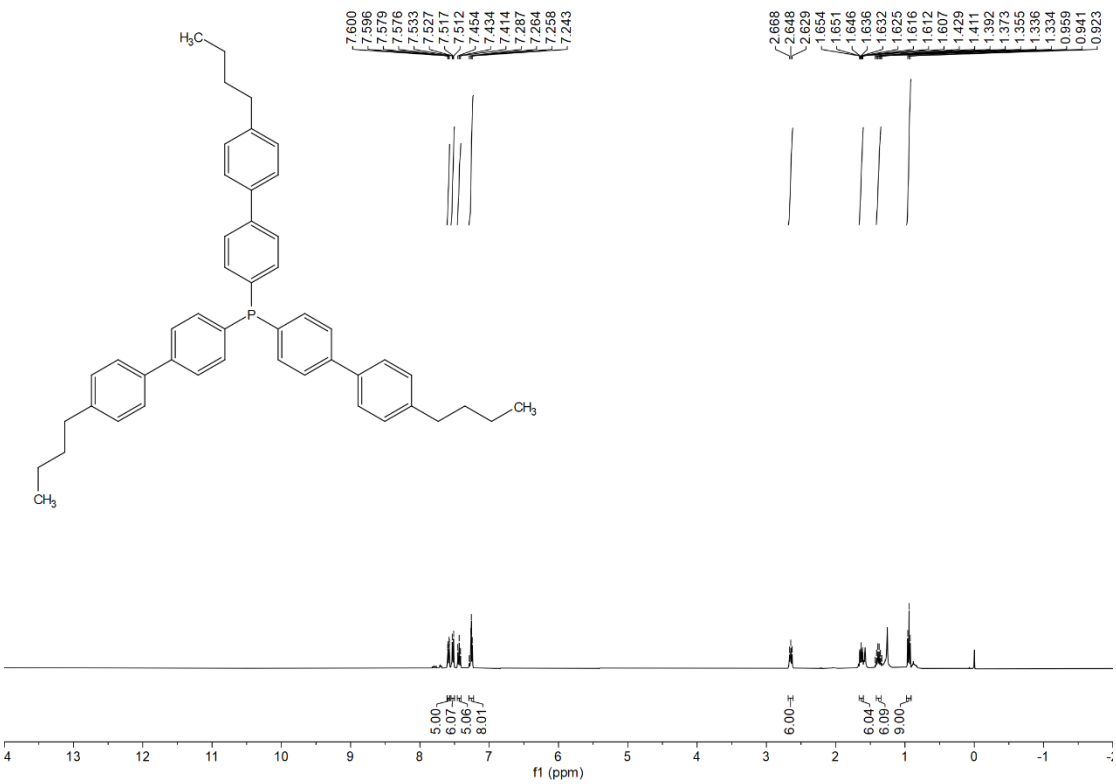
^{1}H NMR spectrum of **3b** (400 MHz, Chloroform-*d*)



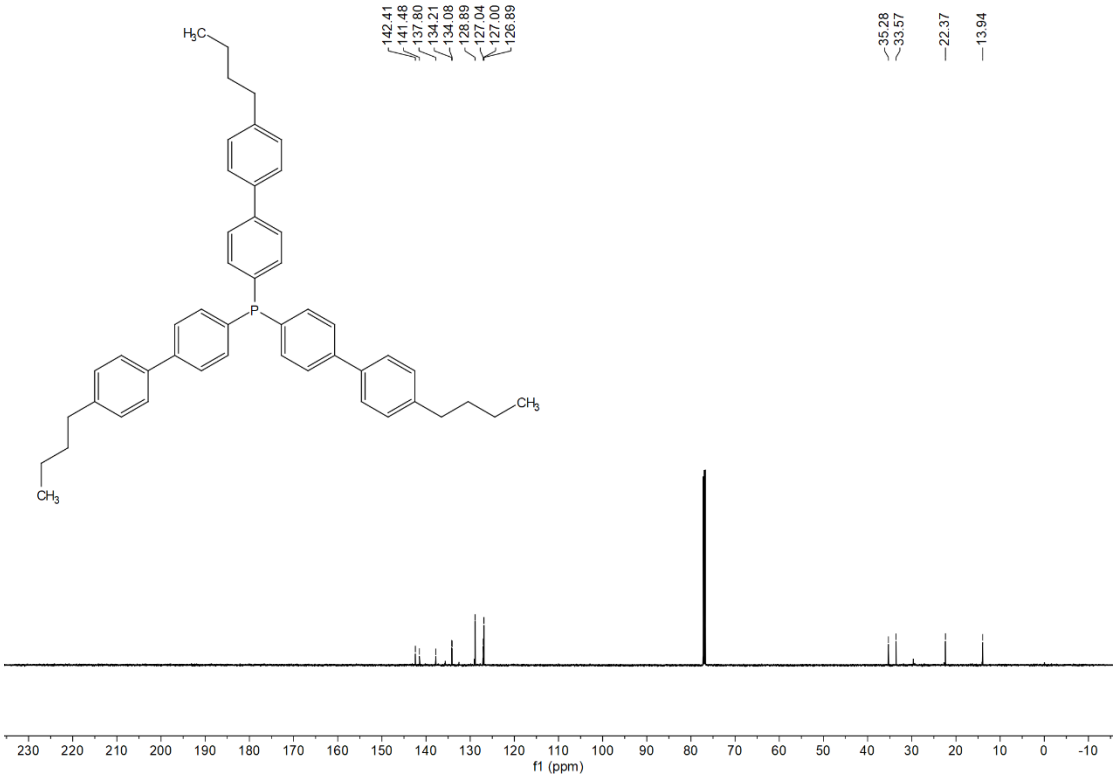
^{13}C spectrum of **3b** (151 MHz, Chloroform-*d*)



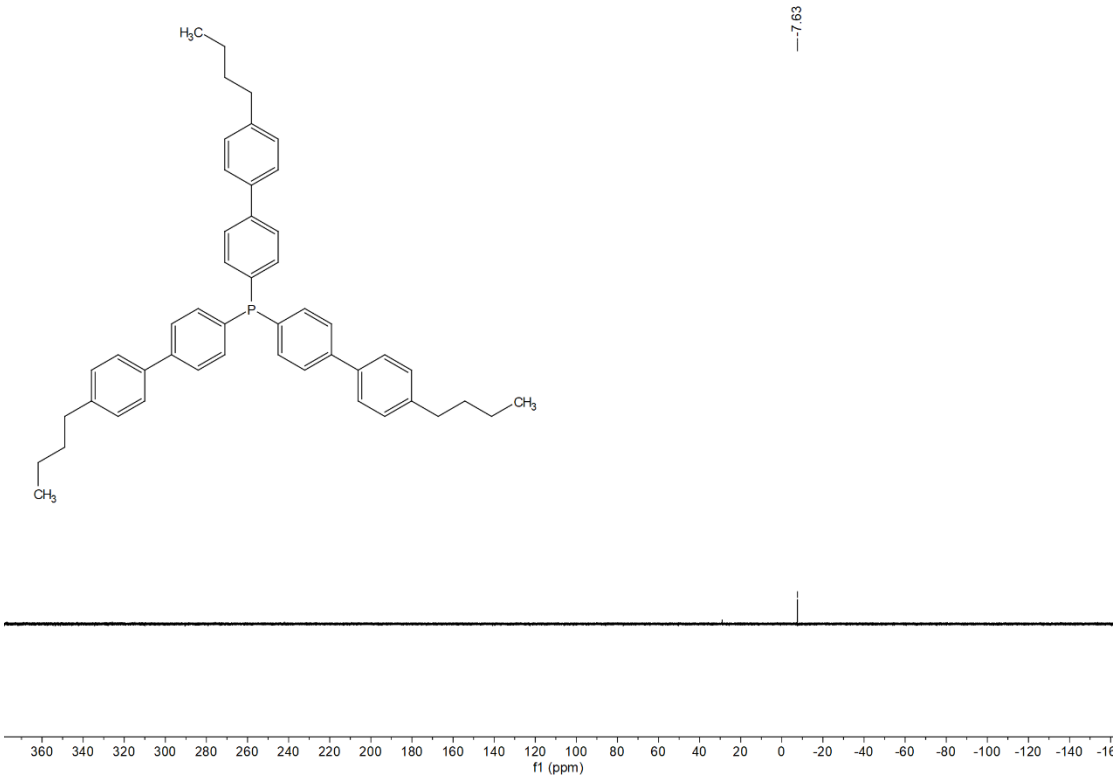
^{31}P NMR spectrum of **3b** (162 MHz, Chloroform-*d*)



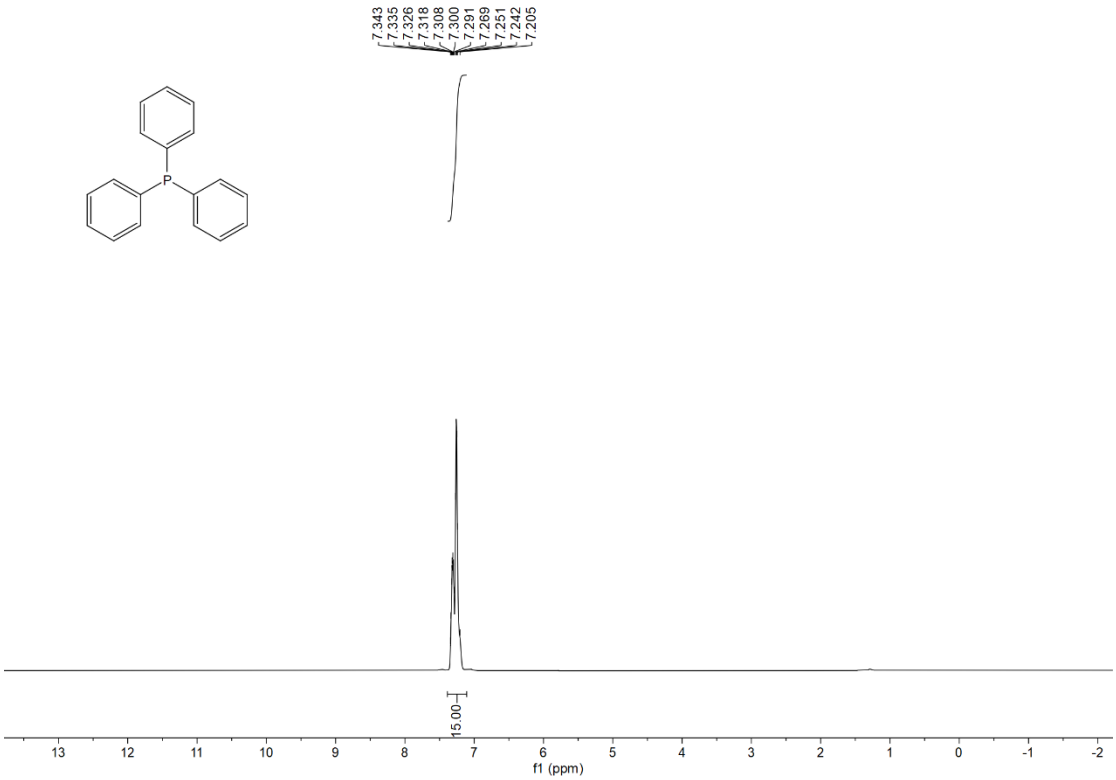
^{1}H NMR spectrum of **3c** (400 MHz, Chloroform-*d*)



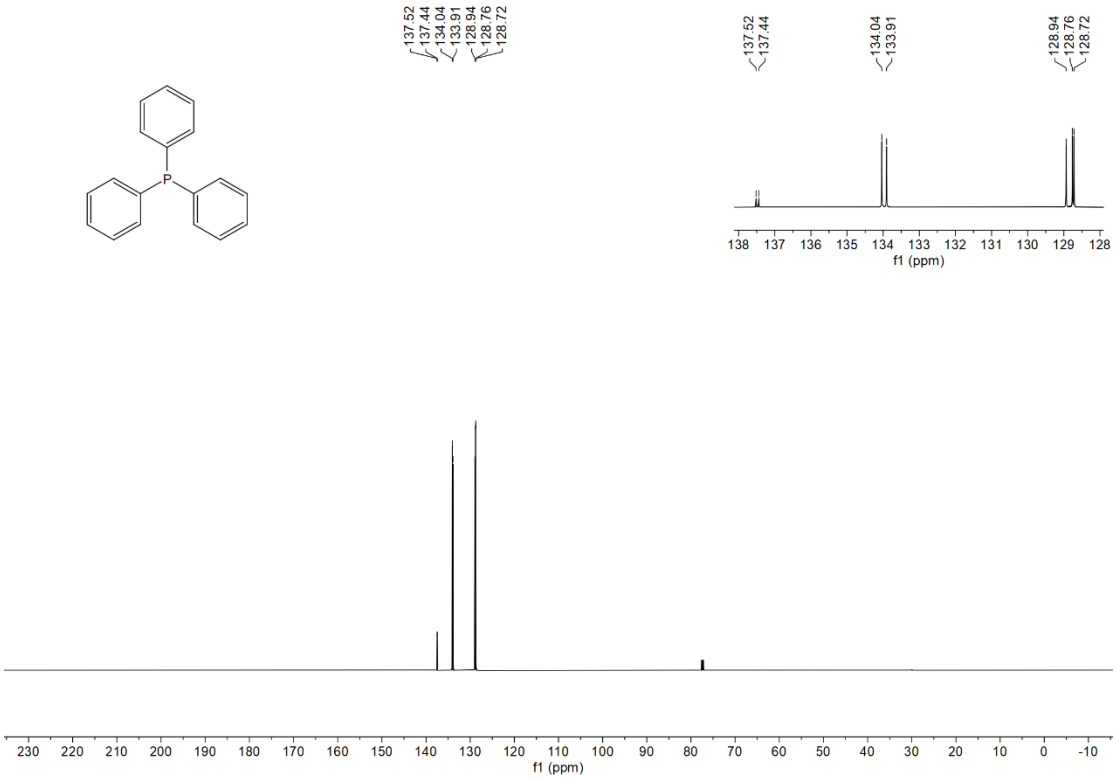
^{13}C spectrum of **3c** (151 MHz, Chloroform-*d*)



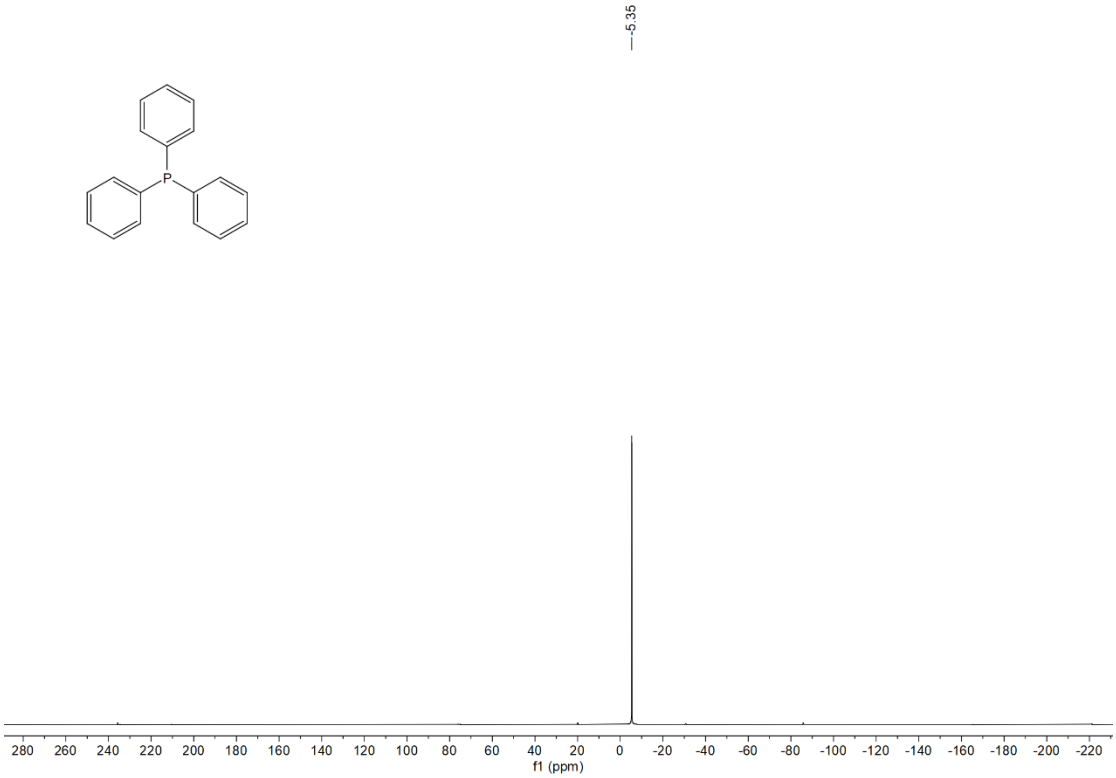
^{31}P NMR spectrum of **3c** (162 MHz, Chloroform-*d*)



^{1}H NMR spectrum of **3d** (400 MHz, Chloroform-*d*)

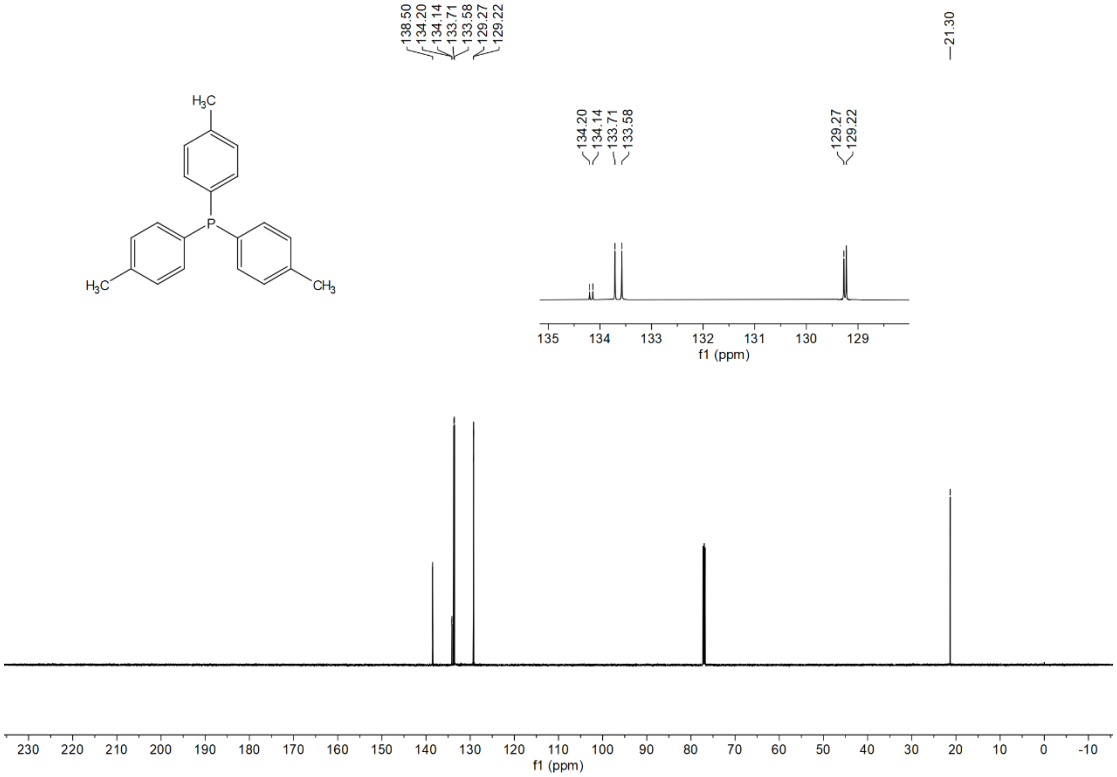


^{13}C spectrum of **3d** (151 MHz, Chloroform-*d*)

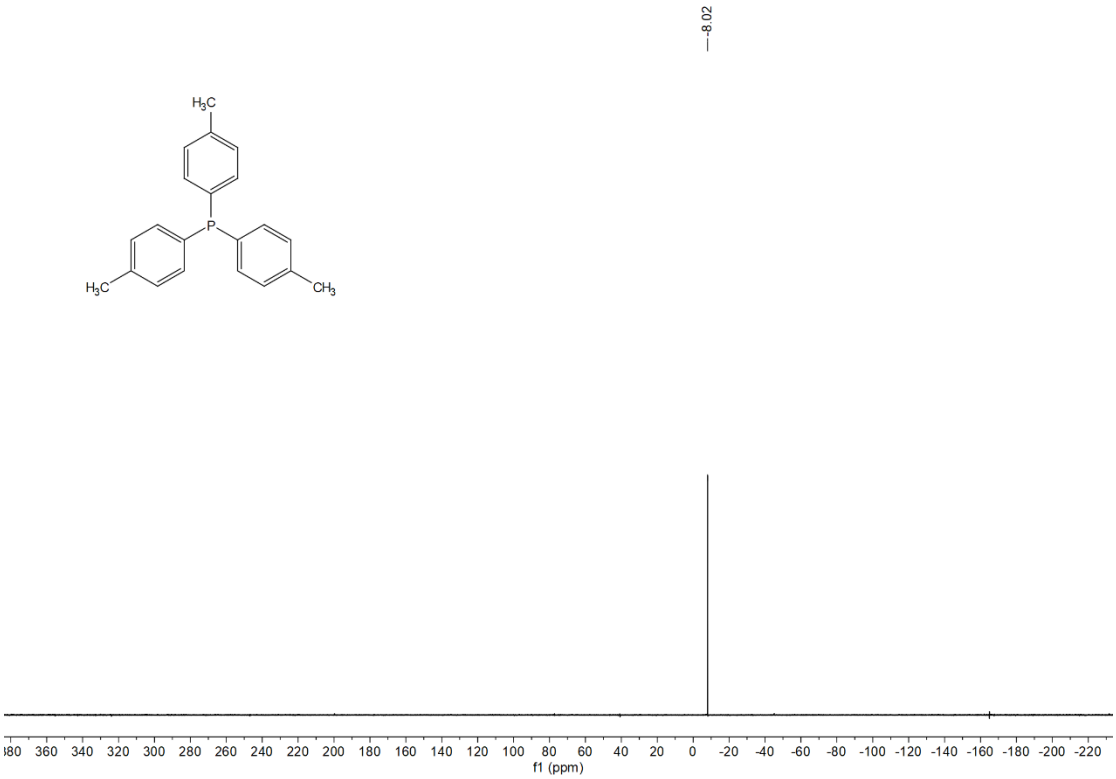


^{31}P NMR spectrum of **3d** (162 MHz, Chloroform-*d*)

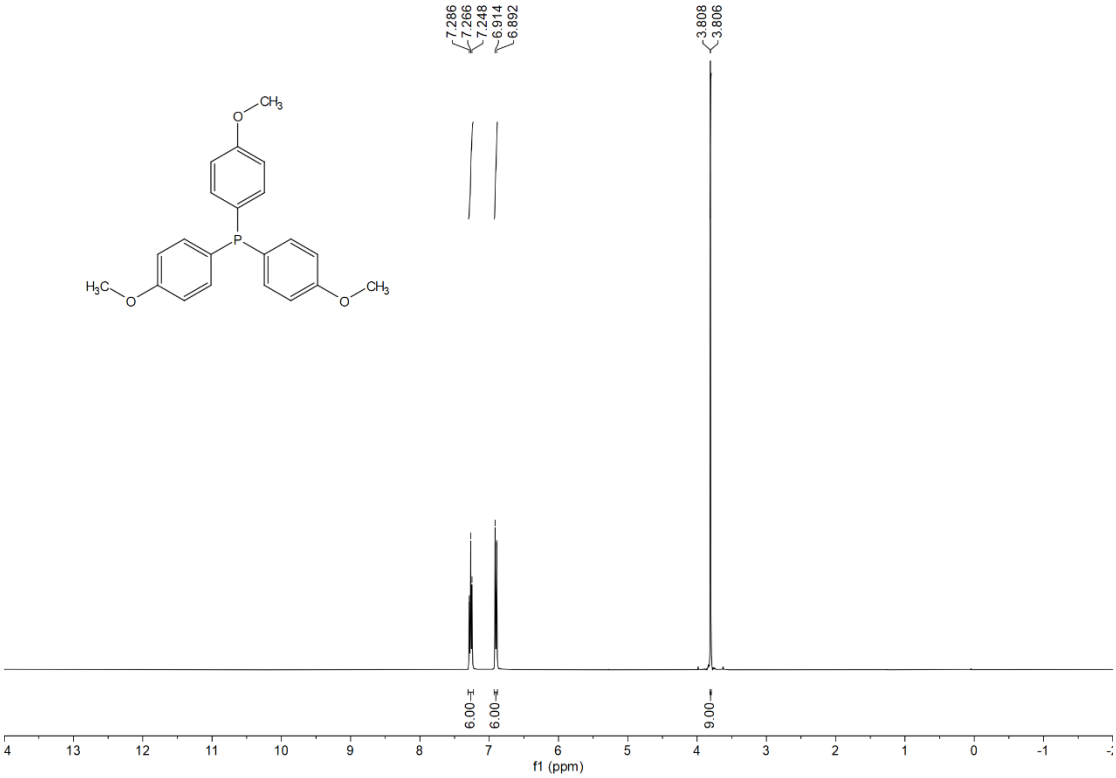
^{1}H NMR spectrum of **3e** (400 MHz, Chloroform-*d*)



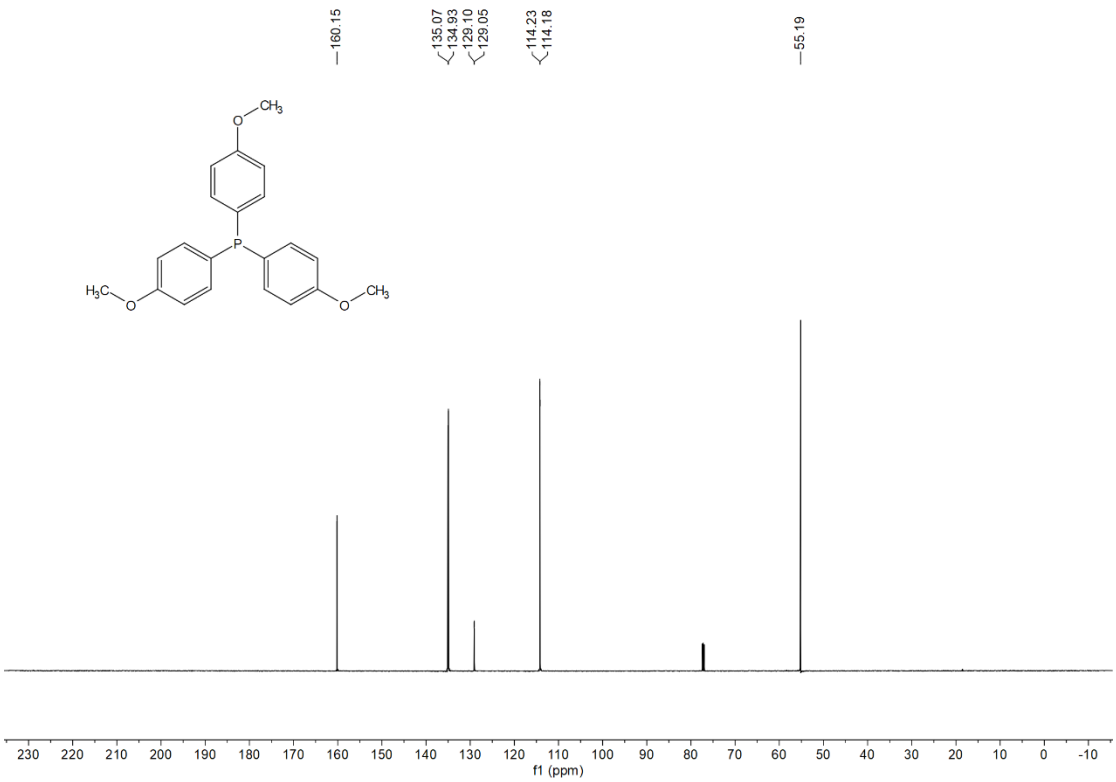
^{13}C spectrum of **3e** (151 MHz, Chloroform-*d*)



^{31}P NMR spectrum of **3e** (162 MHz, Chloroform-*d*)

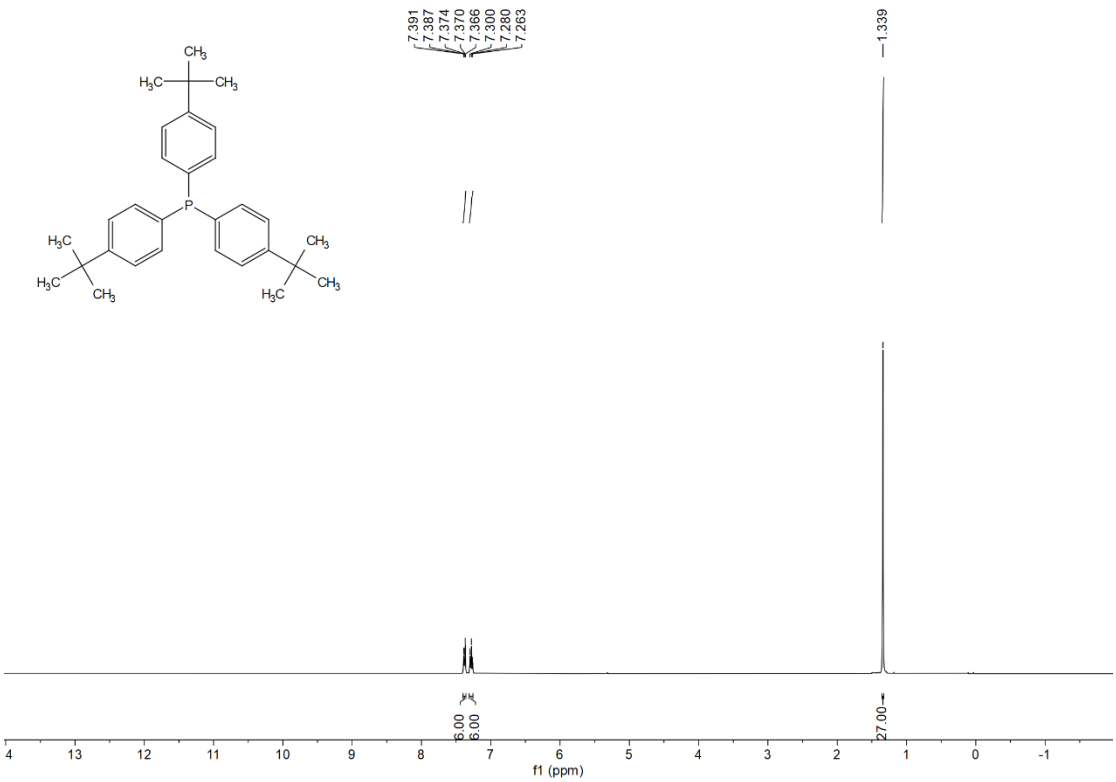


^{1}H NMR spectrum of **3f** (400 MHz, Chloroform-*d*)

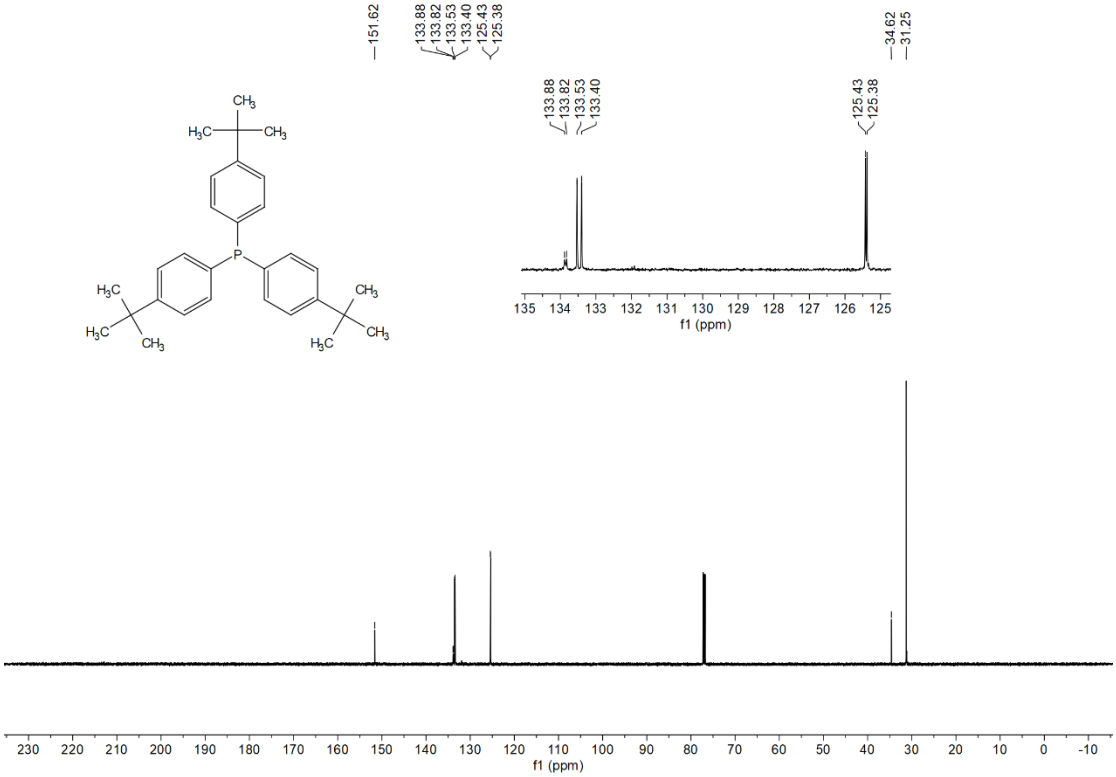


^{13}C spectrum of **3f** (151 MHz, Chloroform-*d*)

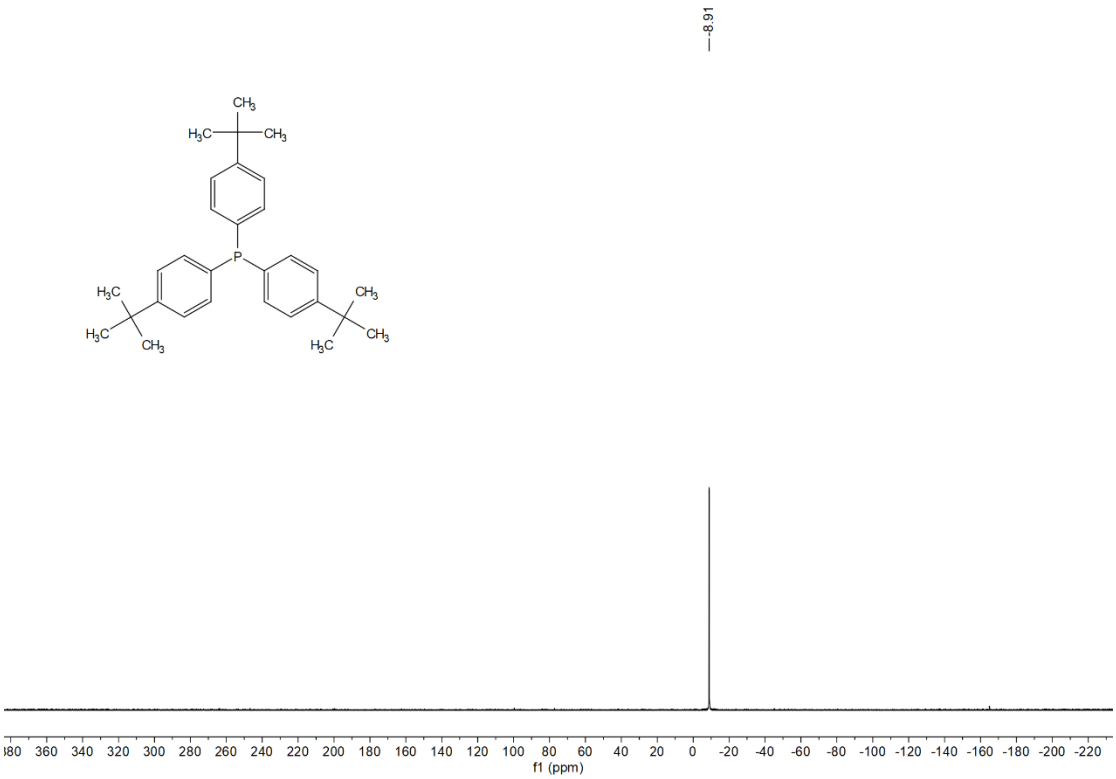
^{31}P NMR spectrum of **3f** (162 MHz, Chloroform-*d*)



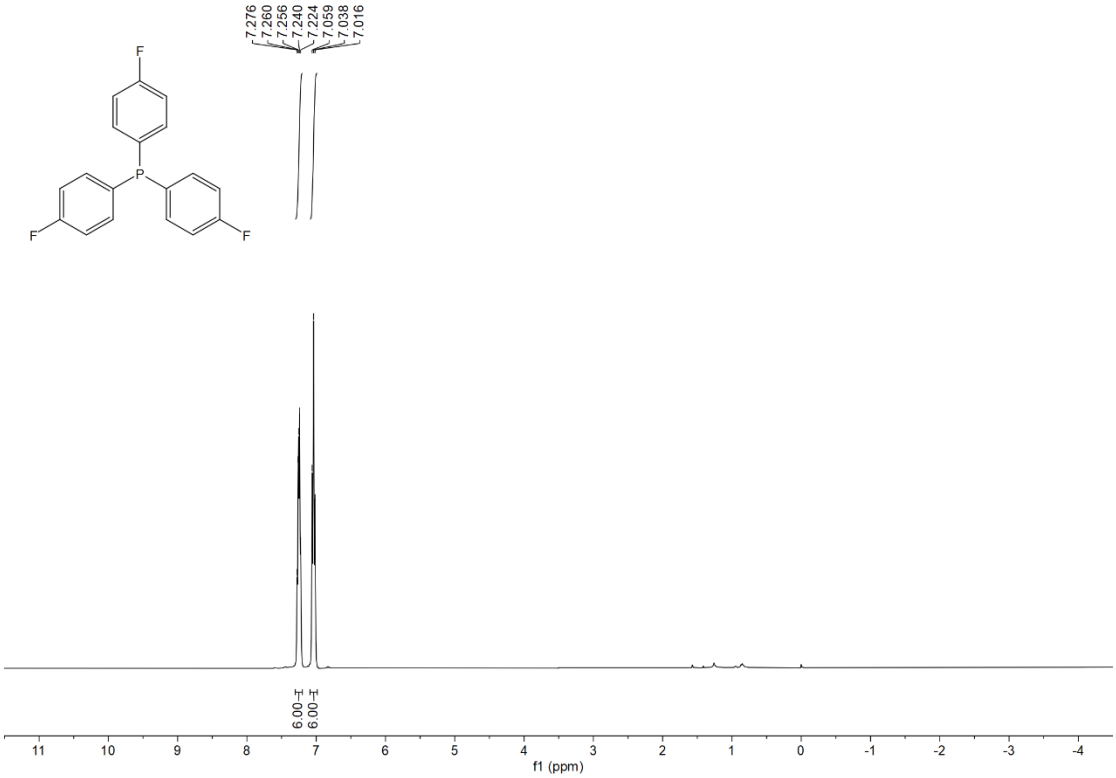
^{1}H NMR spectrum of **3g** (400 MHz, Chloroform-*d*)



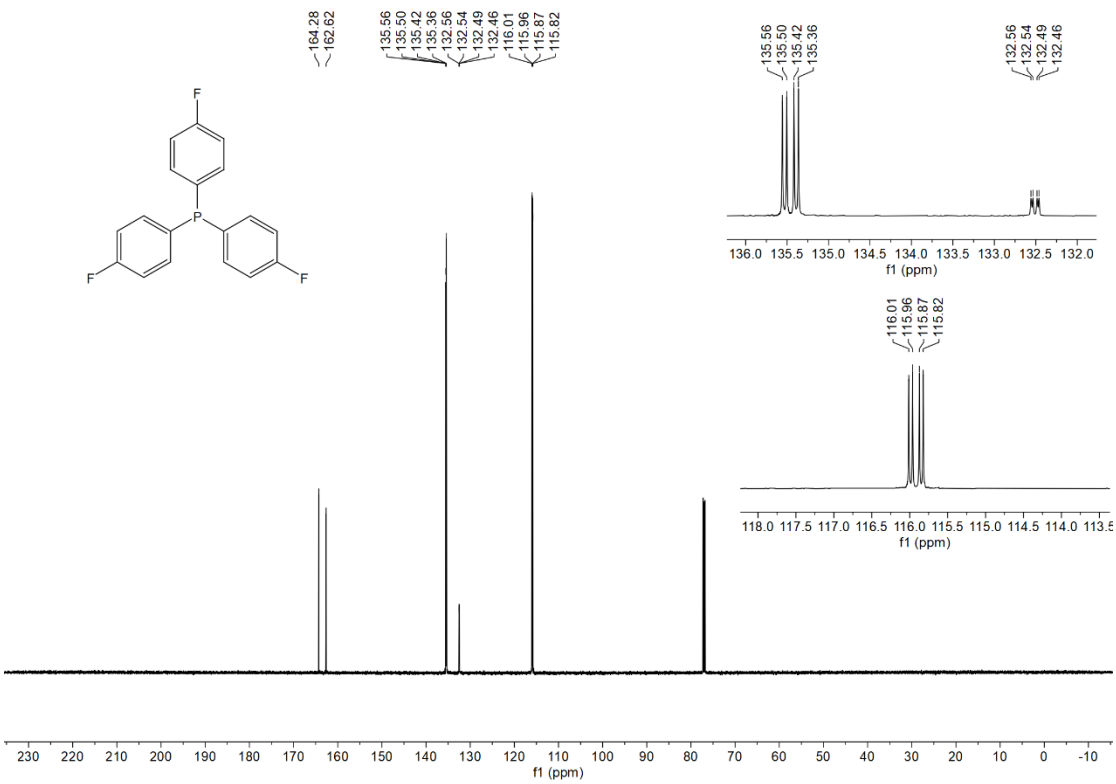
^{13}C spectrum of **3g** (151 MHz, Chloroform-*d*)



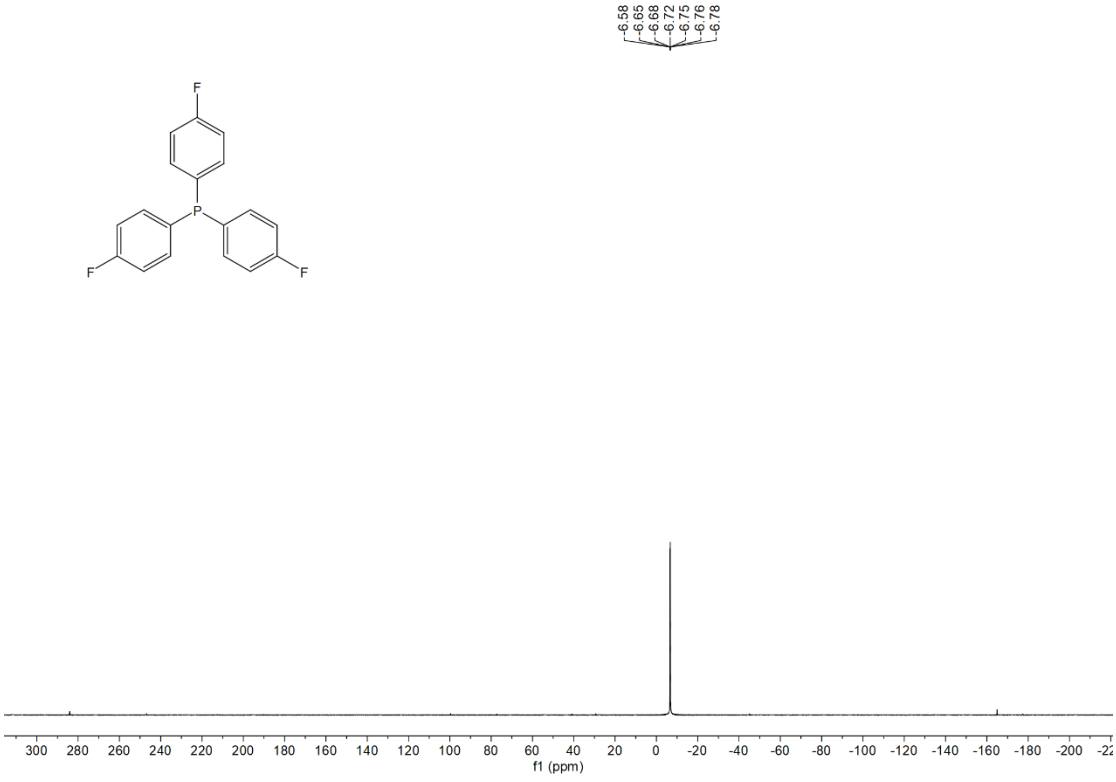
^{31}P NMR spectrum of **3g** (162 MHz, Chloroform-*d*)



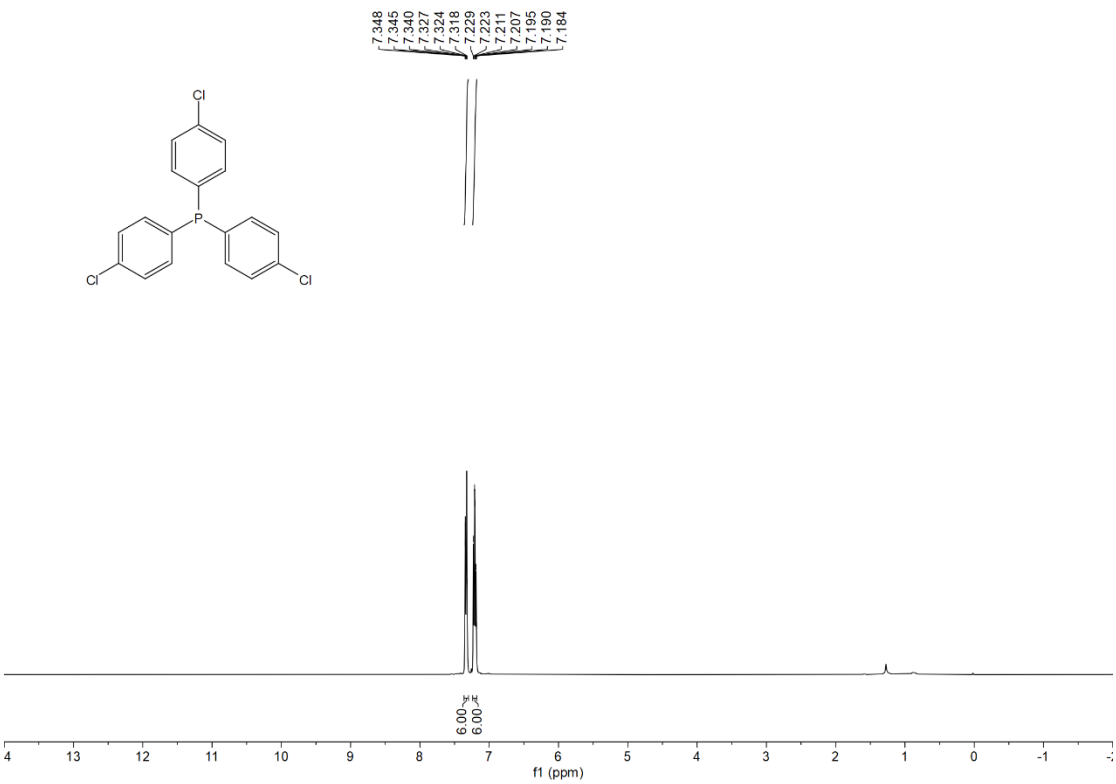
^{1}H NMR spectrum of **3h** (400 MHz, Chloroform-*d*)



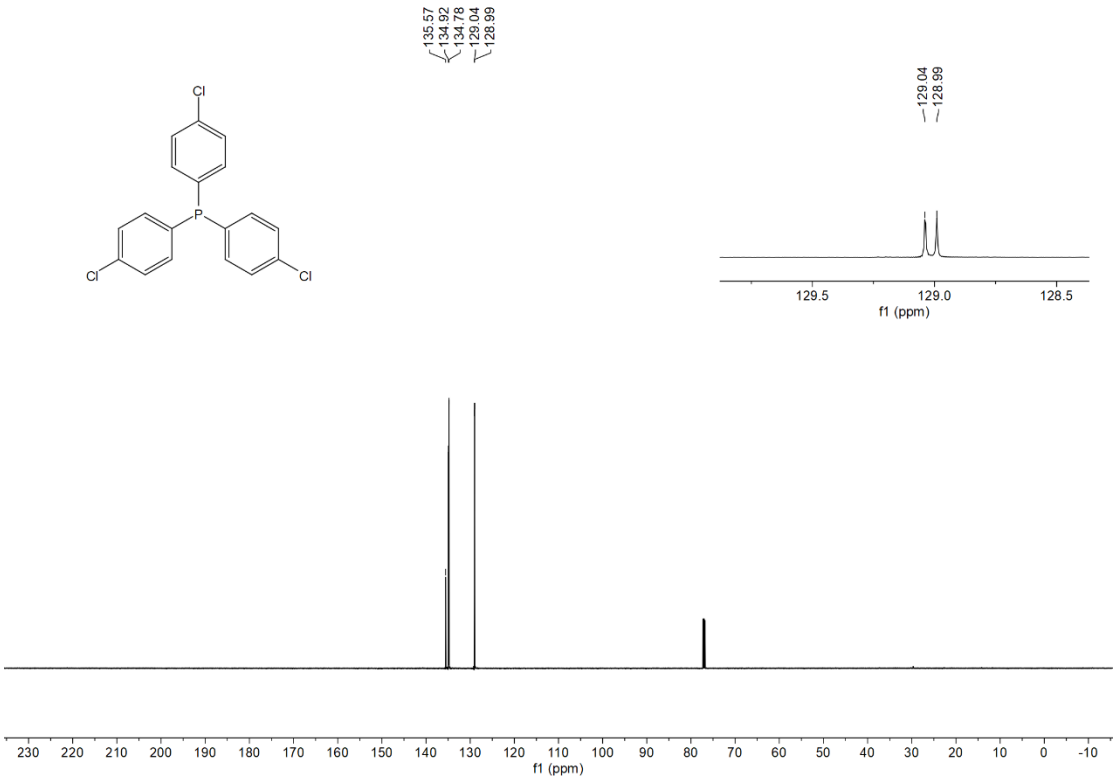
^{13}C spectrum of **3h** (151 MHz, Chloroform-*d*)



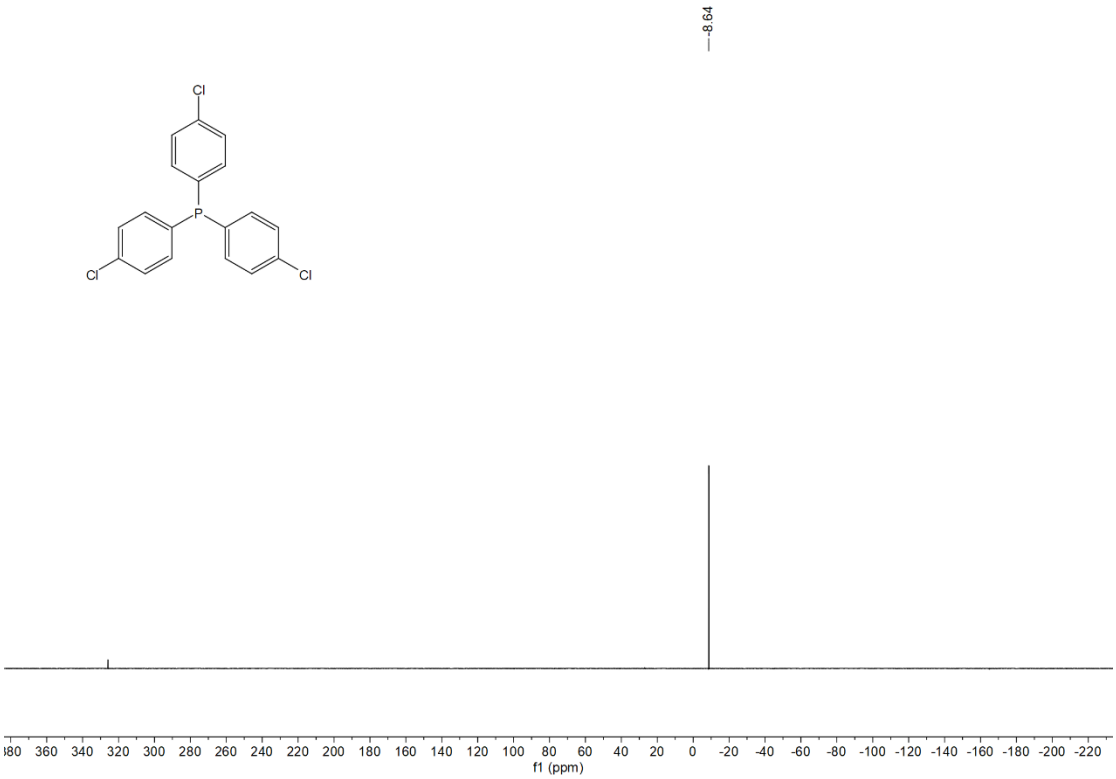
^{31}P NMR spectrum of **3h** (162 MHz, Chloroform-*d*)



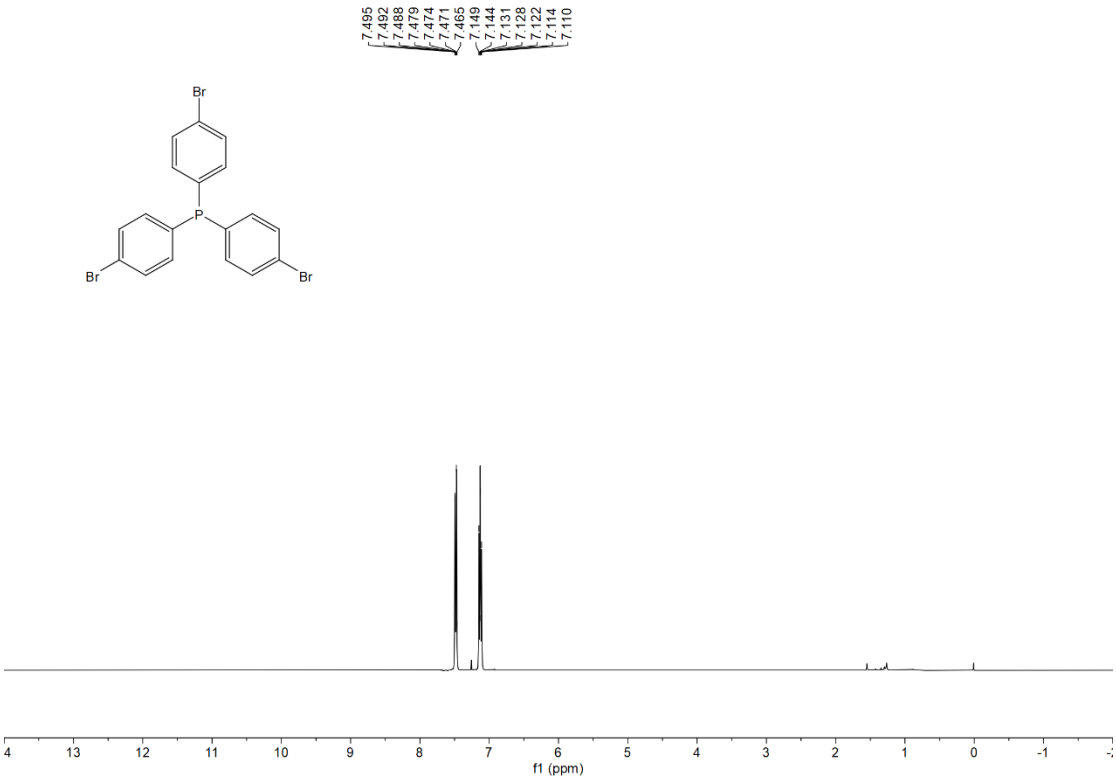
^{1}H NMR spectrum of **3i** (400 MHz, Chloroform-*d*)



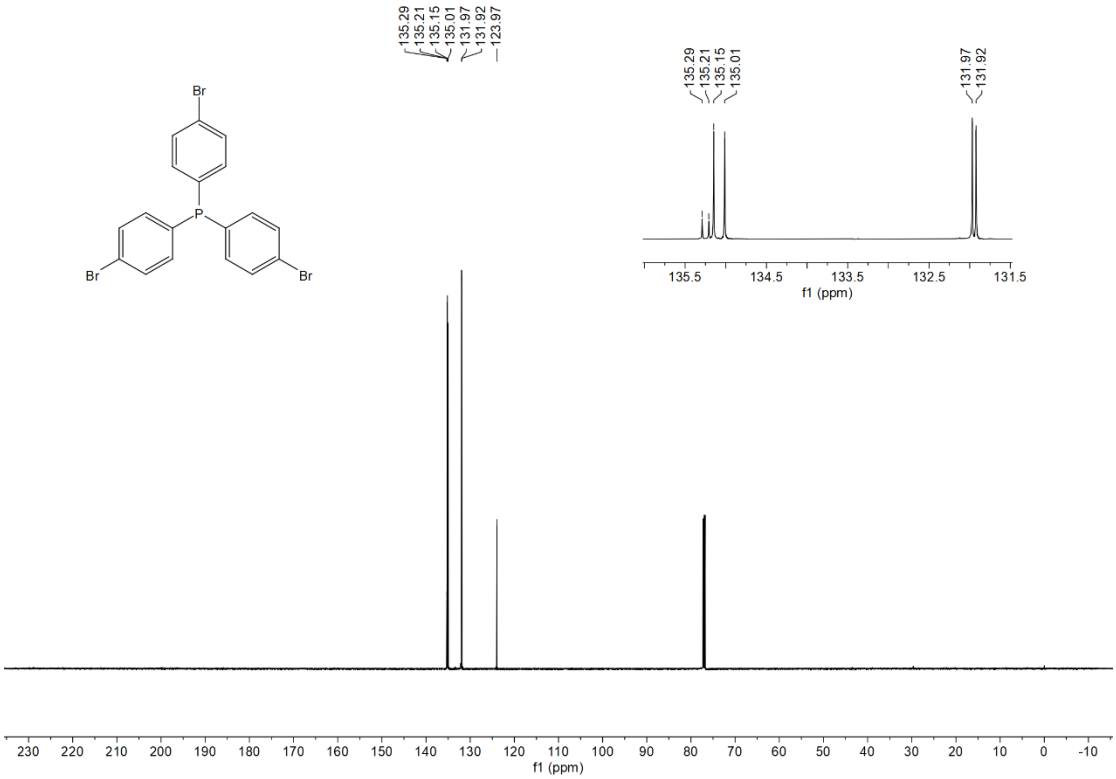
^{13}C spectrum of **3i** (151 MHz, Chloroform-*d*)



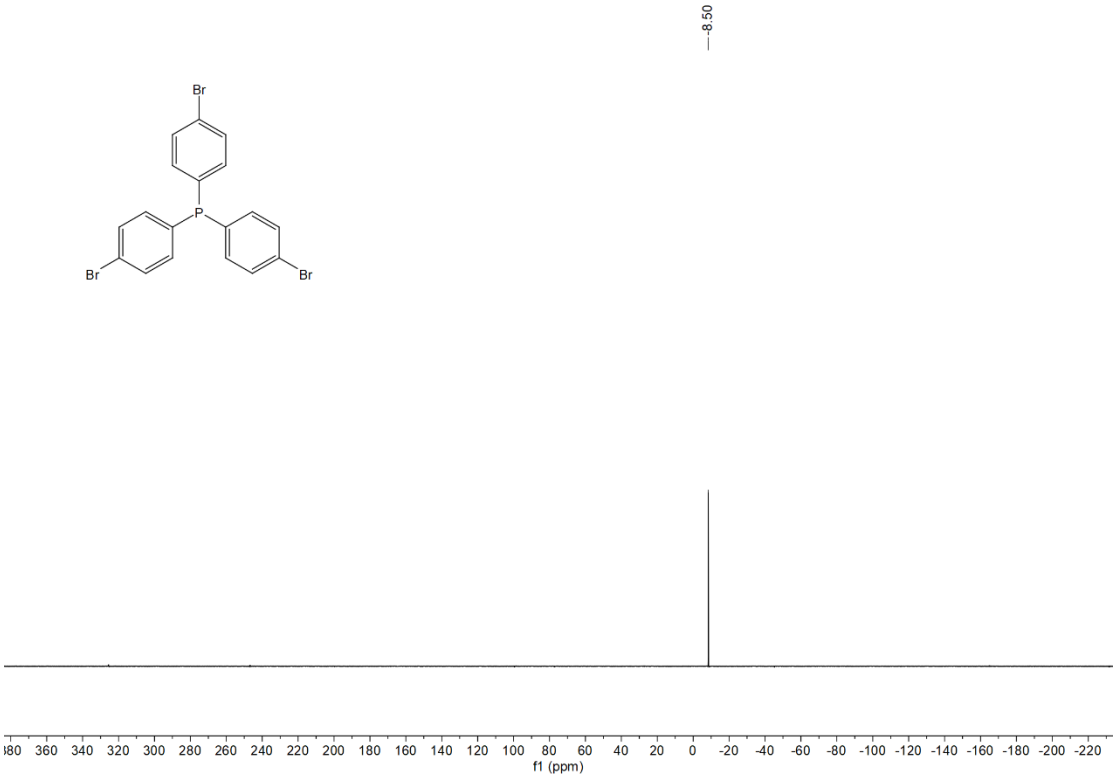
^{31}P NMR spectrum of **3i** (162 MHz, Chloroform-*d*)



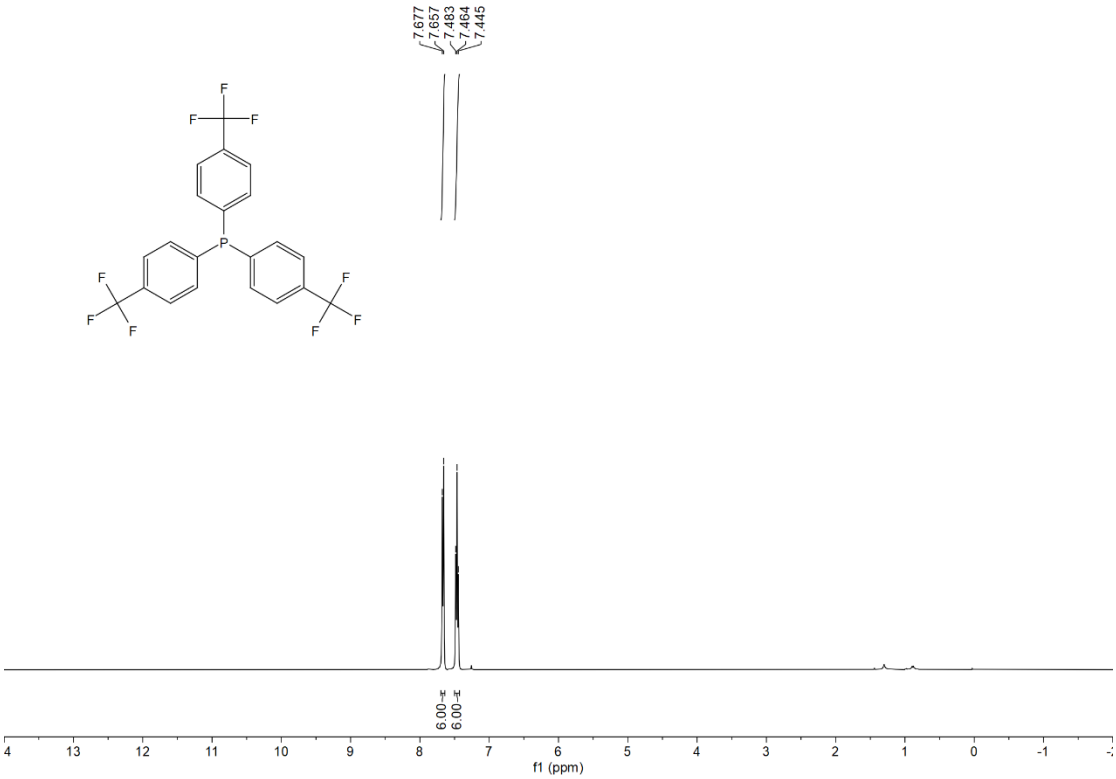
^{1}H NMR spectrum of **3j** (400 MHz, Chloroform-*d*)



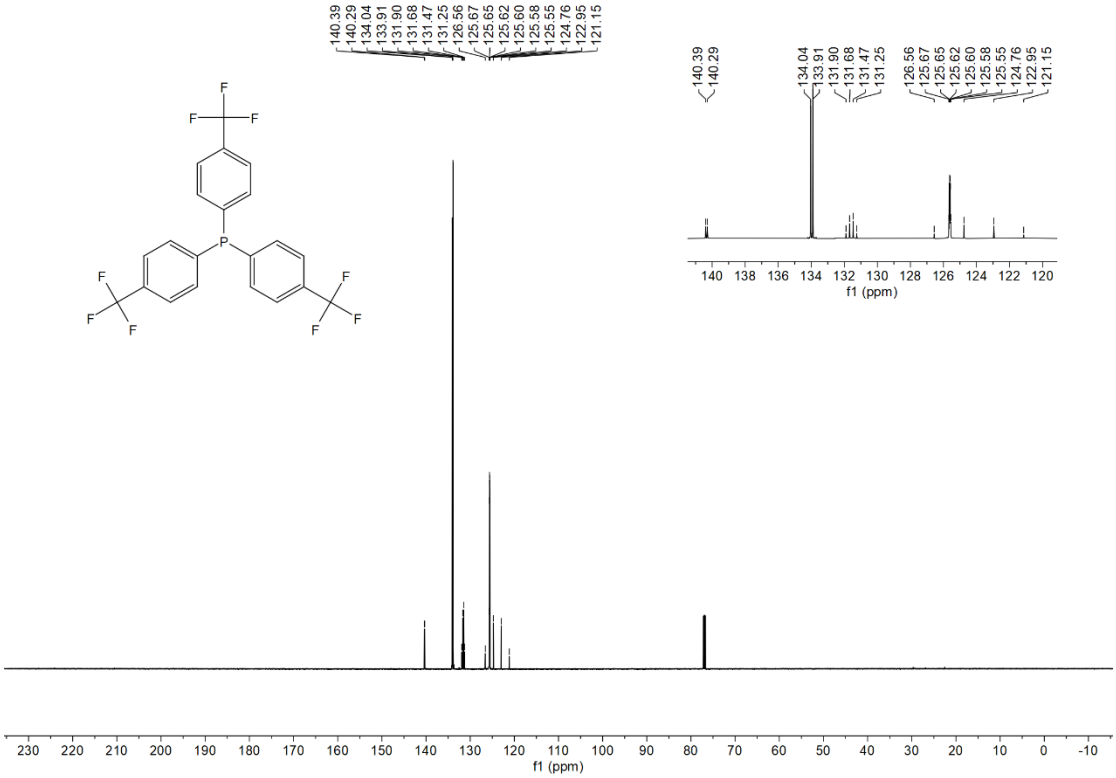
^{13}C spectrum of **3j** (151 MHz, Chloroform-*d*)



^{31}P NMR spectrum of **3j** (162 MHz, Chloroform-*d*)

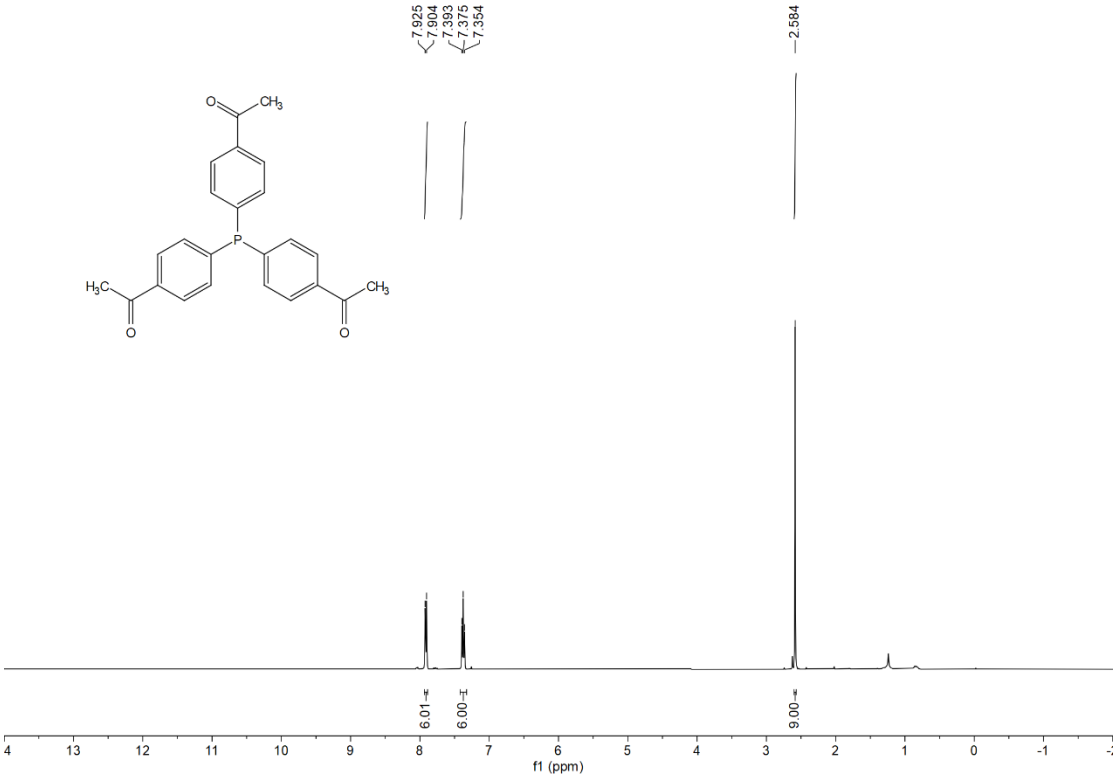


^{1}H NMR spectrum of **3k** (400 MHz, Chloroform-*d*)

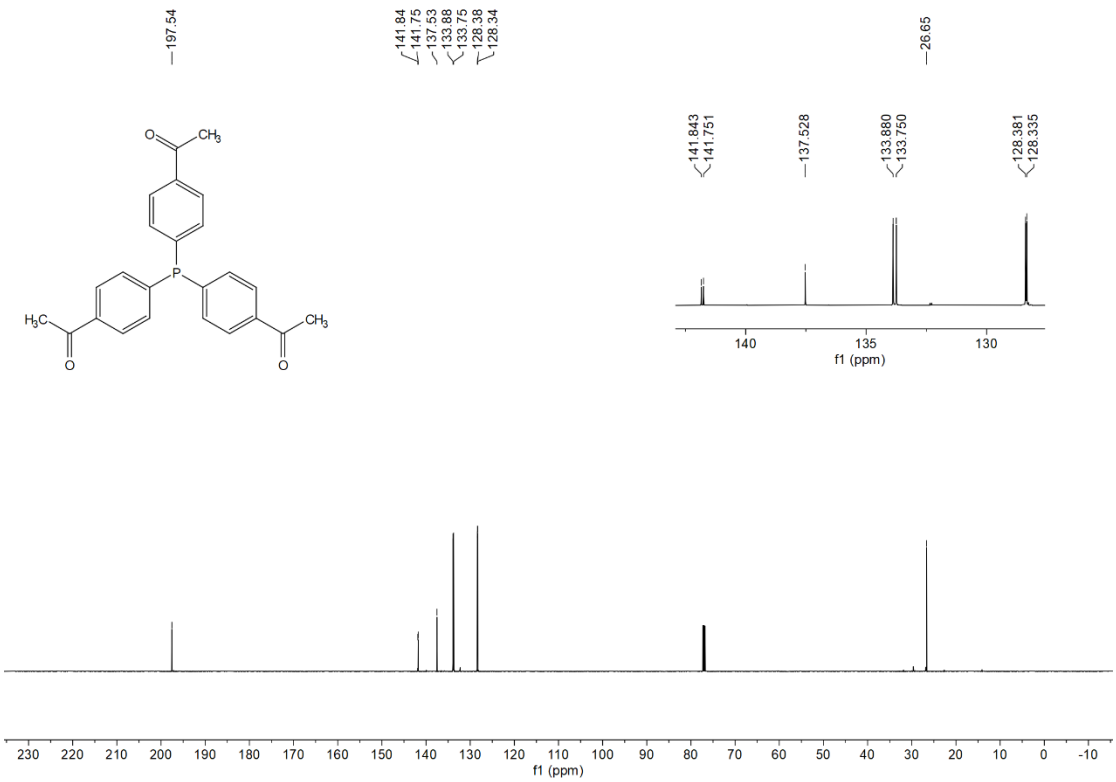


^{13}C spectrum of **3k** (151 MHz, Chloroform-*d*)

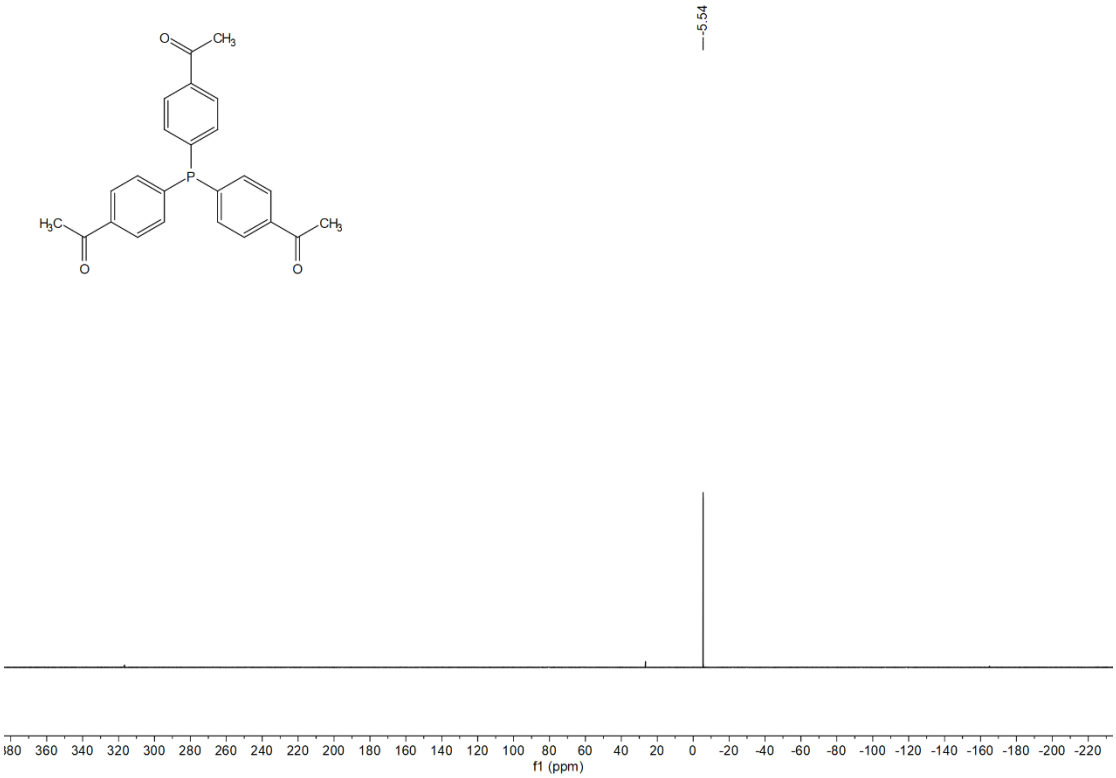
^{31}P NMR spectrum of **3k** (162 MHz, Chloroform-*d*)



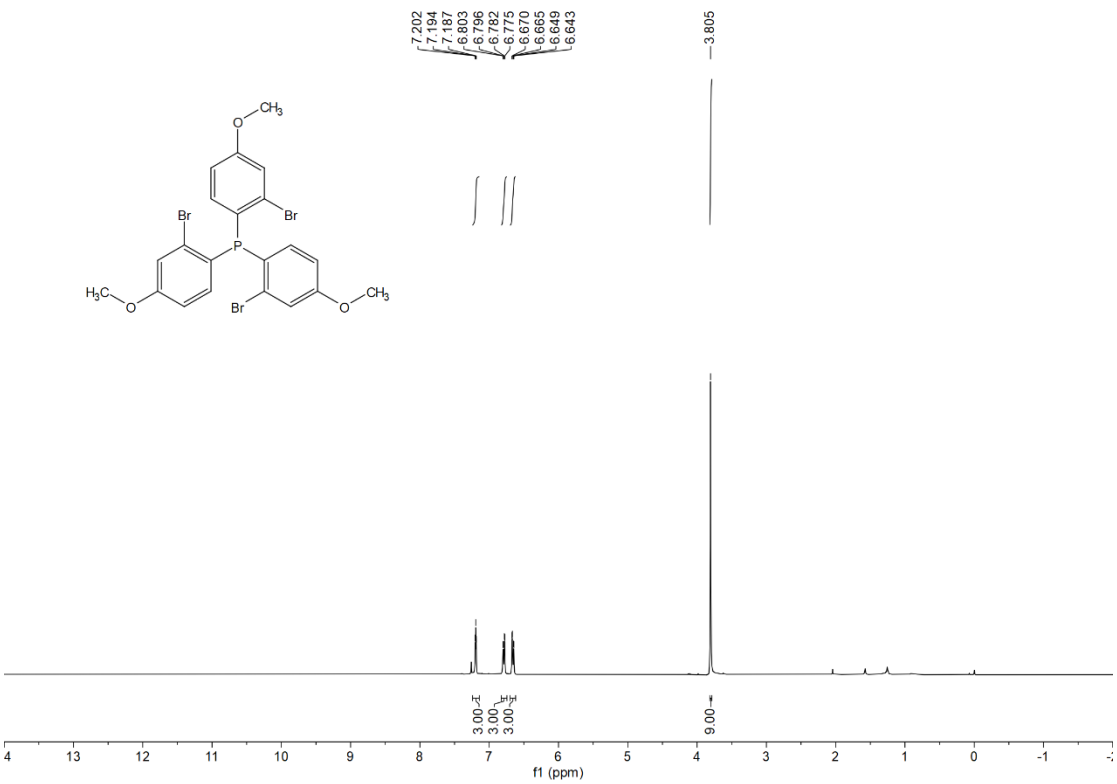
^{1}H NMR spectrum of **3l** (400 MHz, Chloroform-*d*)



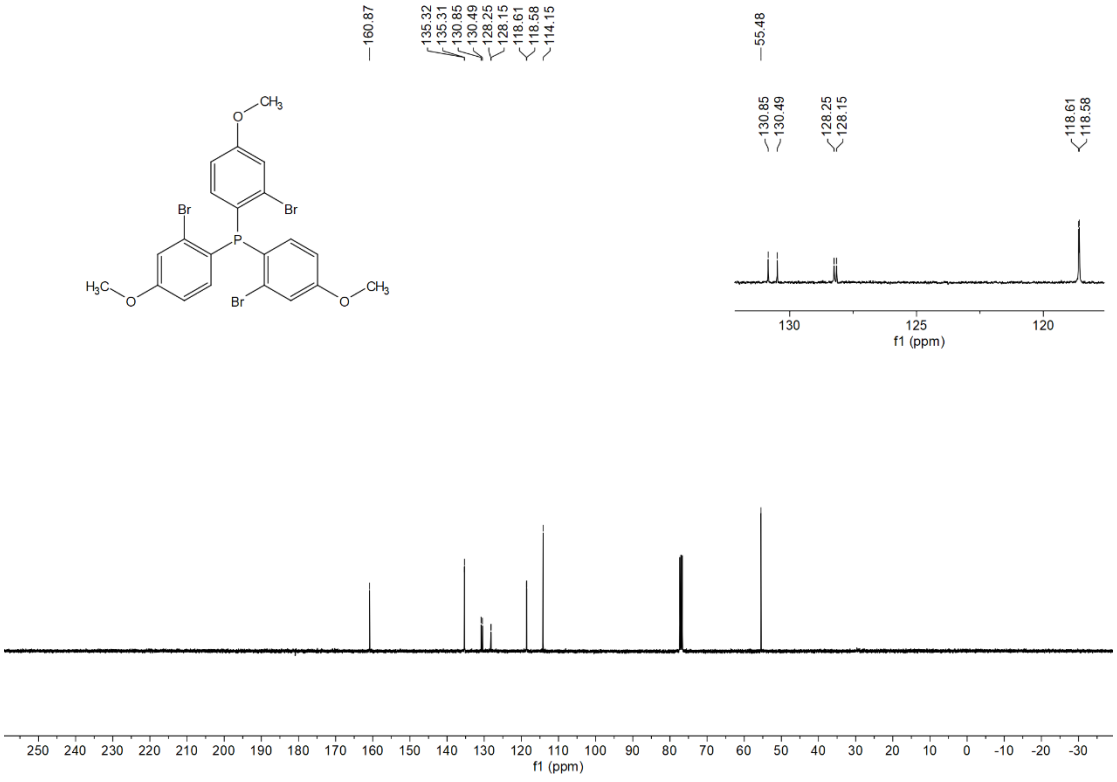
^{13}C spectrum of **3l** (151 MHz, Chloroform-*d*)



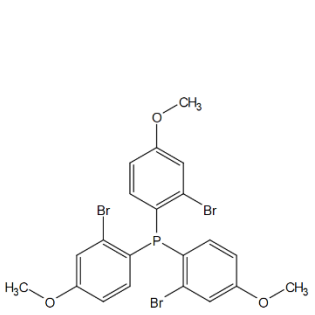
^{31}P NMR spectrum of **3l** (162 MHz, Chloroform-*d*)

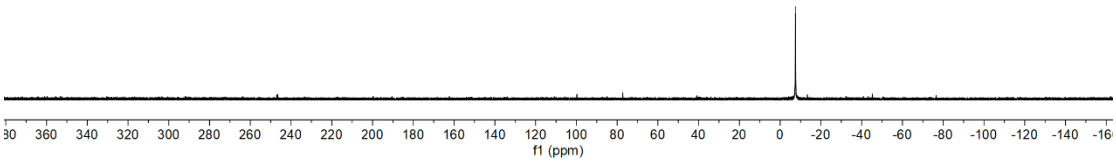


^{1}H NMR spectrum of **3m** (400 MHz, Chloroform-*d*)

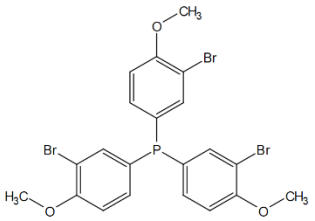


^{13}C spectrum of **3m** (151 MHz, Chloroform-*d*)

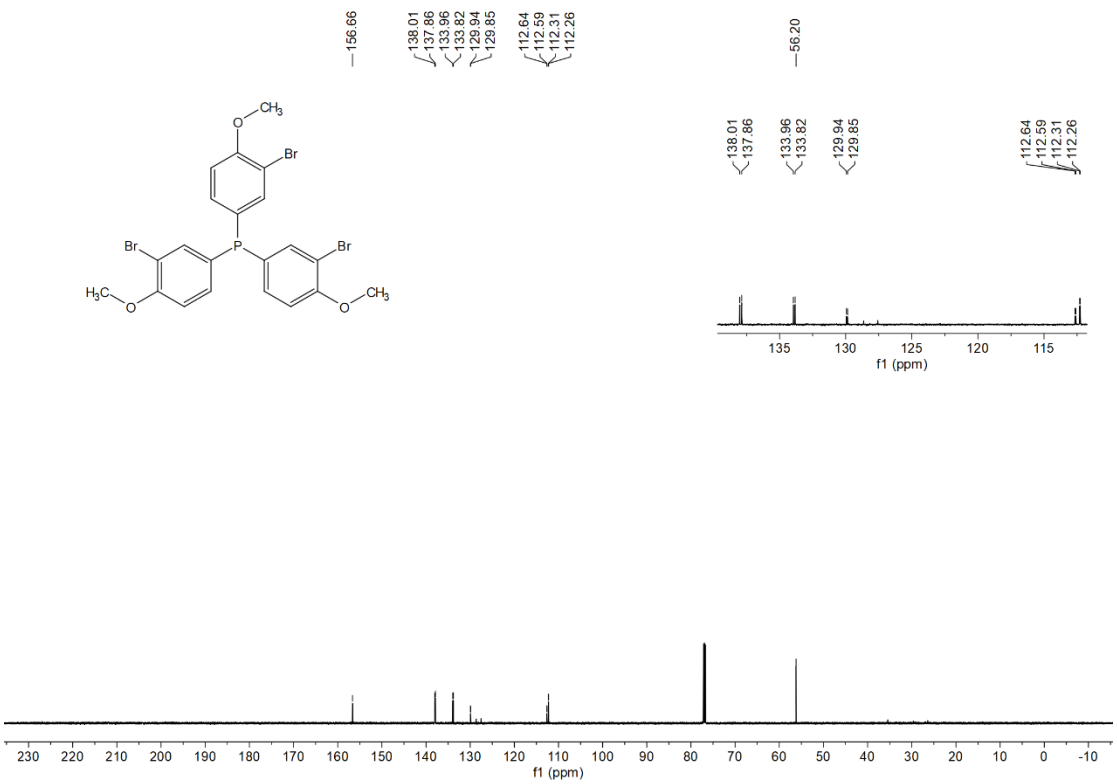




^{31}P NMR spectrum of **3m** (162 MHz, Chloroform-*d*)

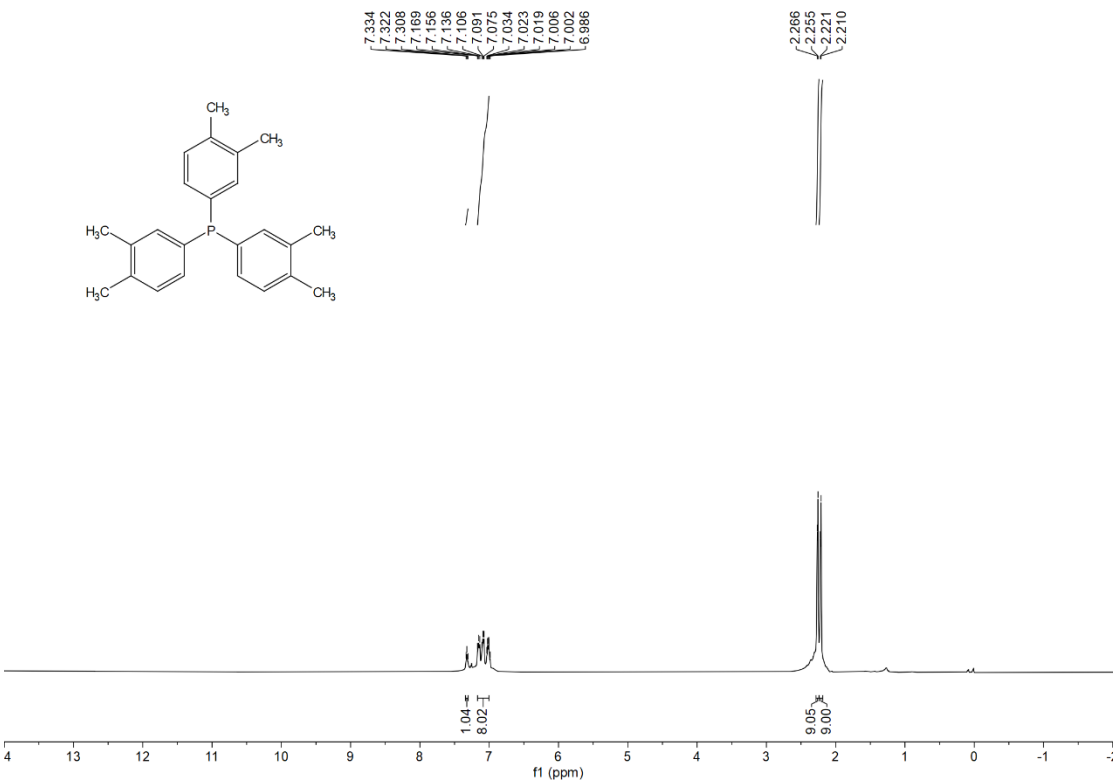


^{1}H NMR spectrum of **3n** (400 MHz, Chloroform-*d*)

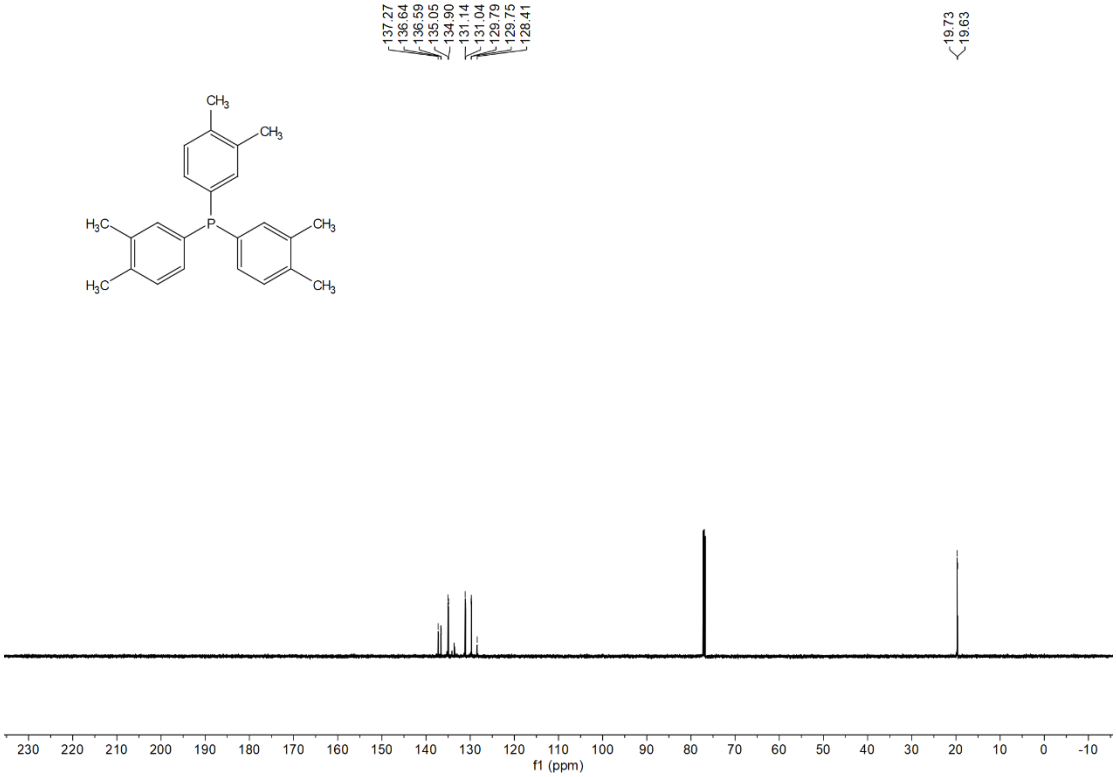


^{13}C spectrum of **3n** (151 MHz, Chloroform-*d*)

^{31}P NMR spectrum of **3n** (162 MHz, Chloroform-*d*)

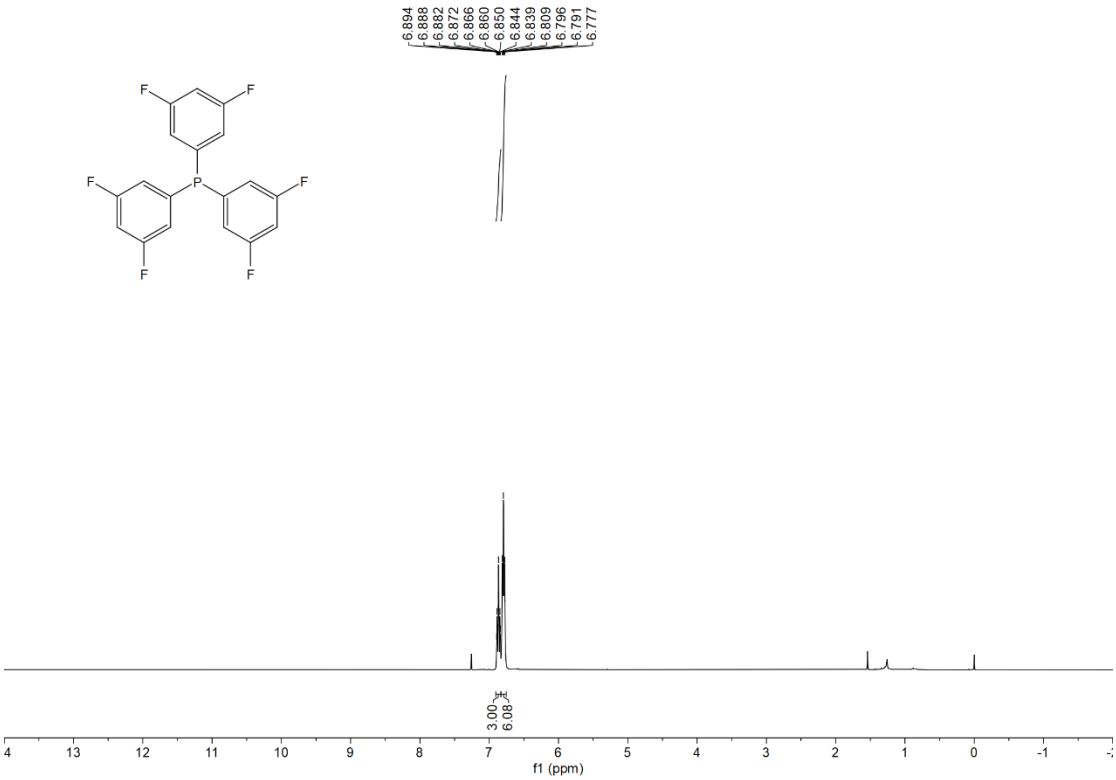


^{1}H NMR spectrum of **3o** (400 MHz, Chloroform-*d*)

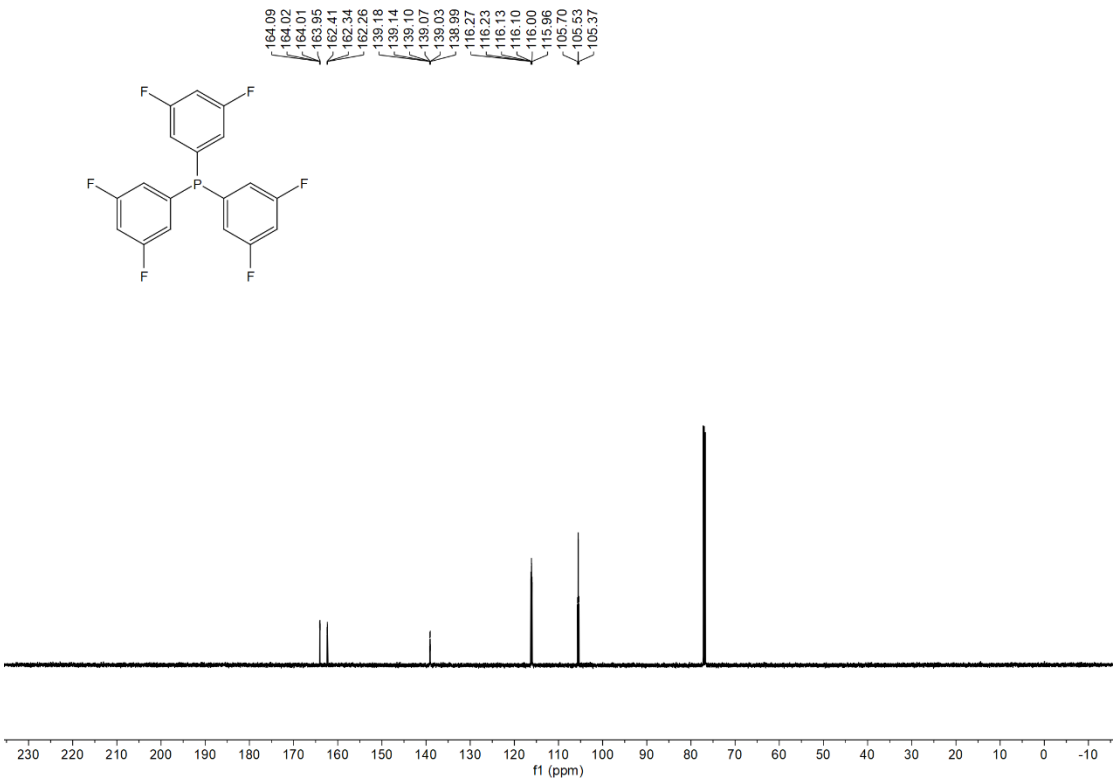


^{13}C spectrum of **3o** (151 MHz, Chloroform-*d*)

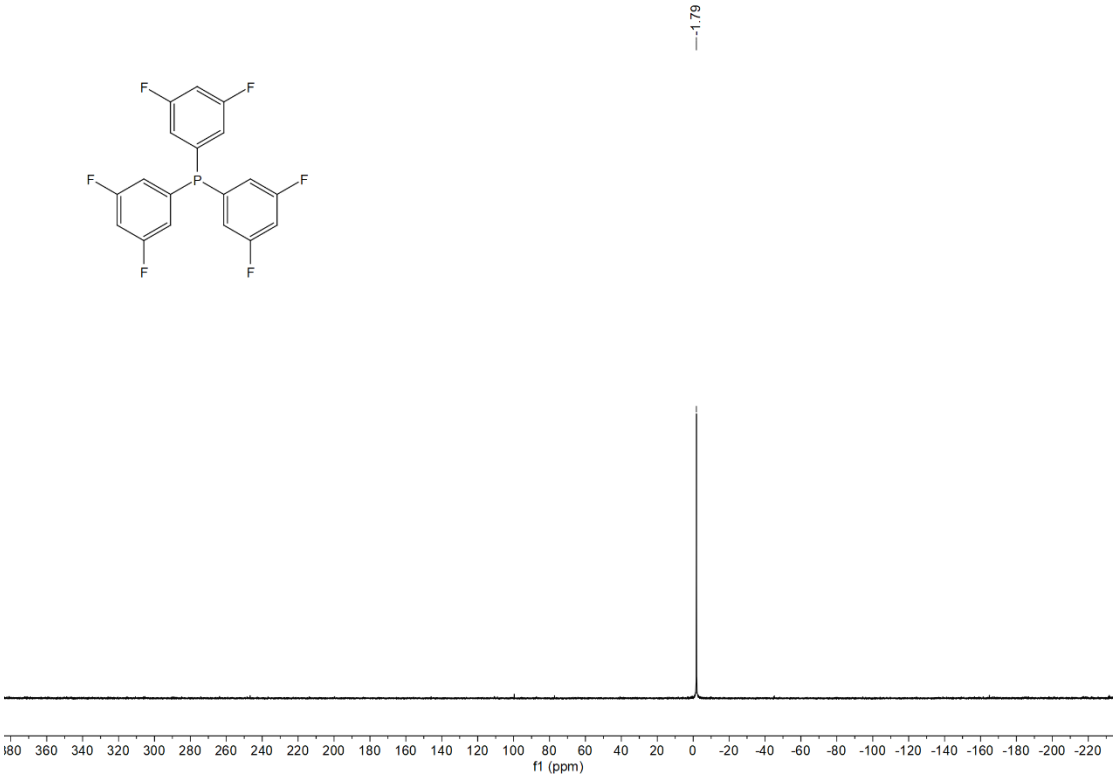
^{31}P NMR spectrum of **3o** (162 MHz, Chloroform-*d*)



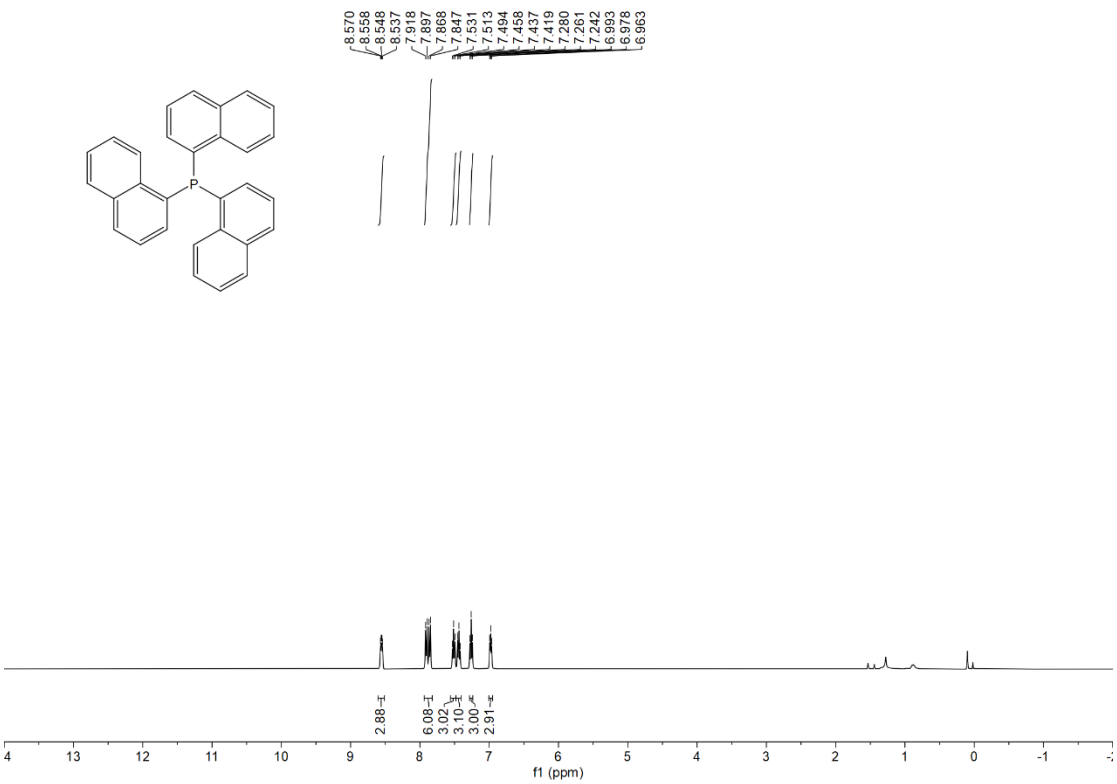
^{1}H NMR spectrum of **3p** (400 MHz, Chloroform-*d*)



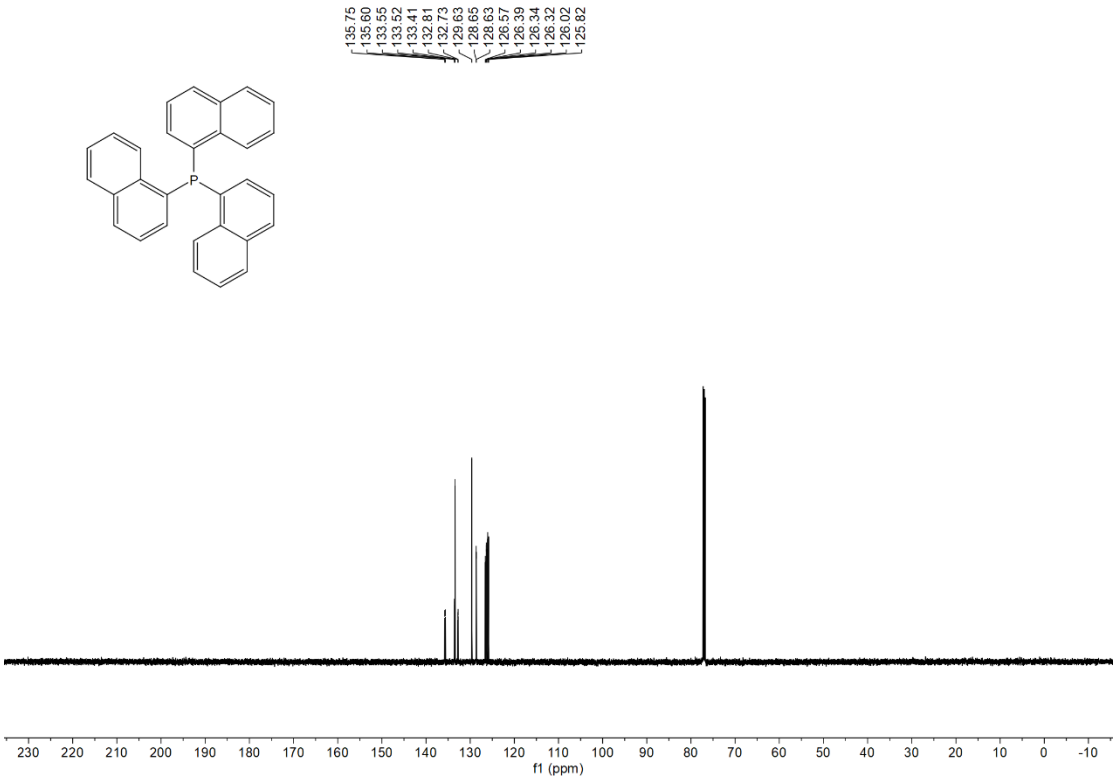
^{13}C spectrum of **3p** (151 MHz, Chloroform-*d*)



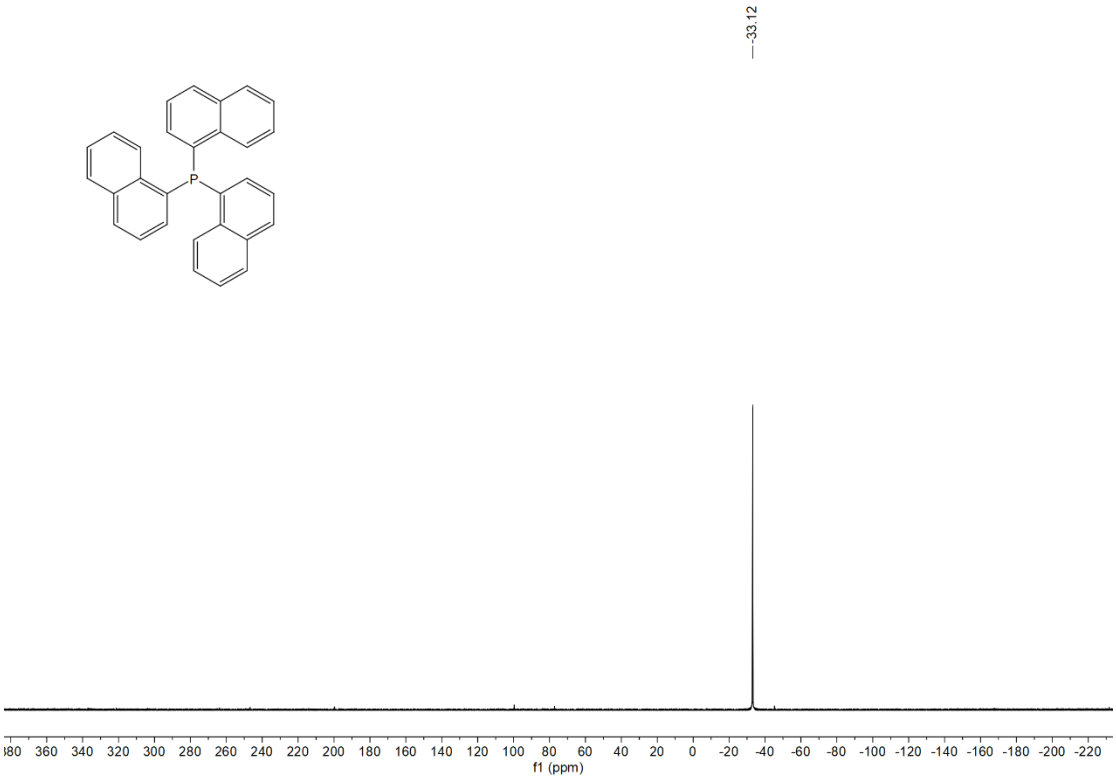
^{31}P NMR spectrum of **3p** (162 MHz, Chloroform-*d*)



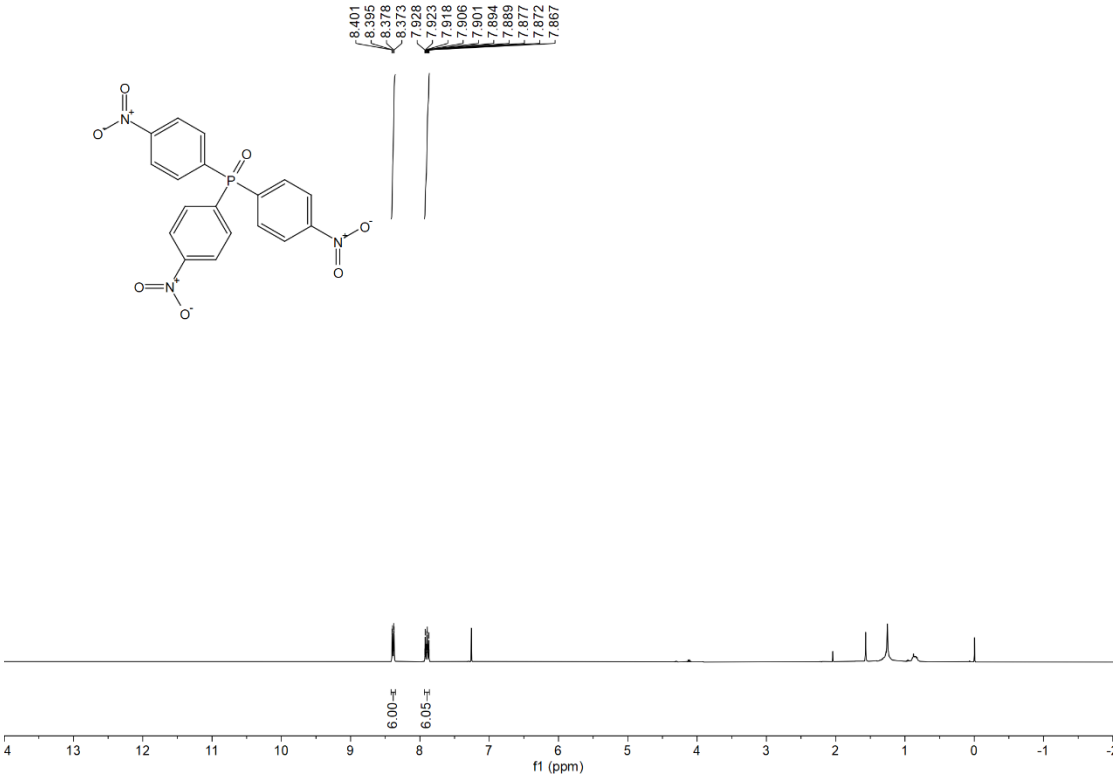
^{1}H NMR spectrum of **3q** (400 MHz, Chloroform-*d*)



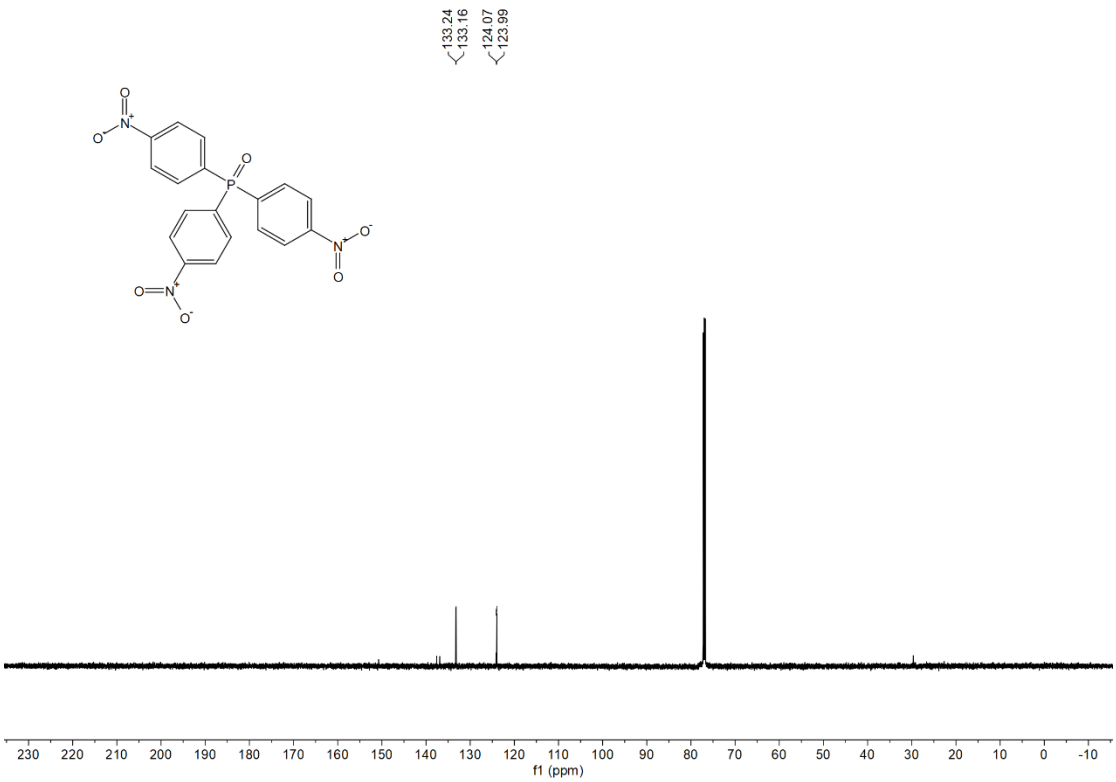
^{13}C spectrum of **3q** (151 MHz, Chloroform-*d*)



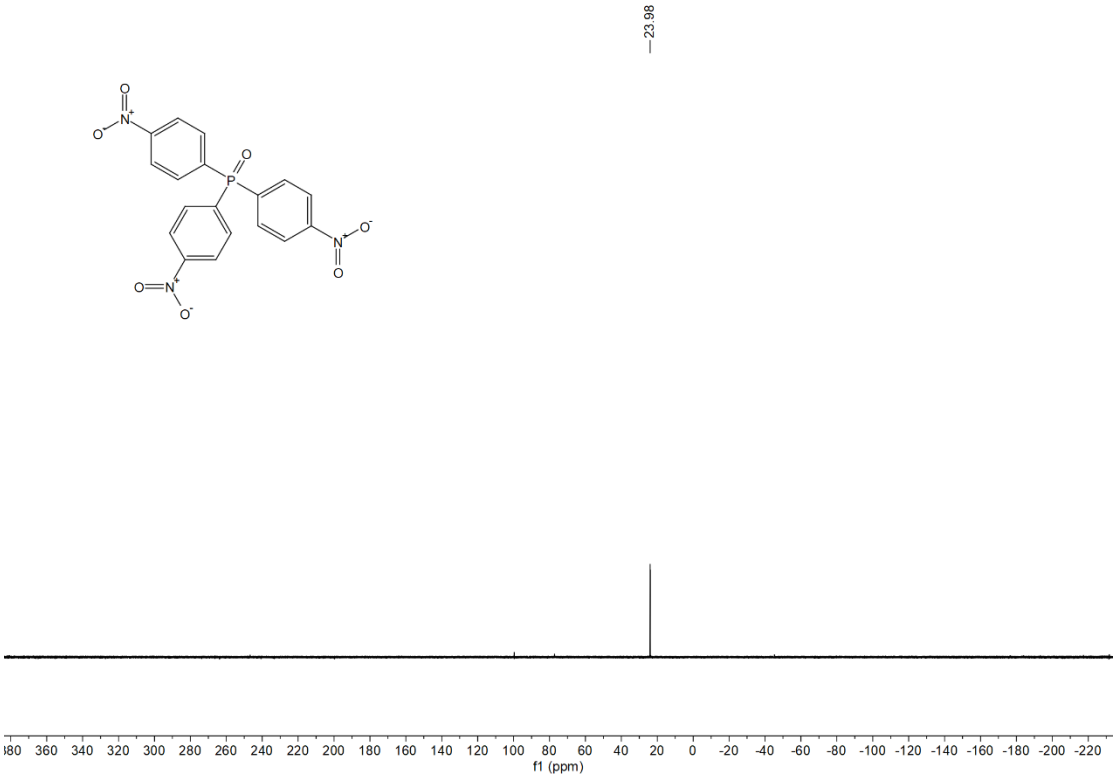
^{31}P NMR spectrum of **3q** (162 MHz, Chloroform-*d*)



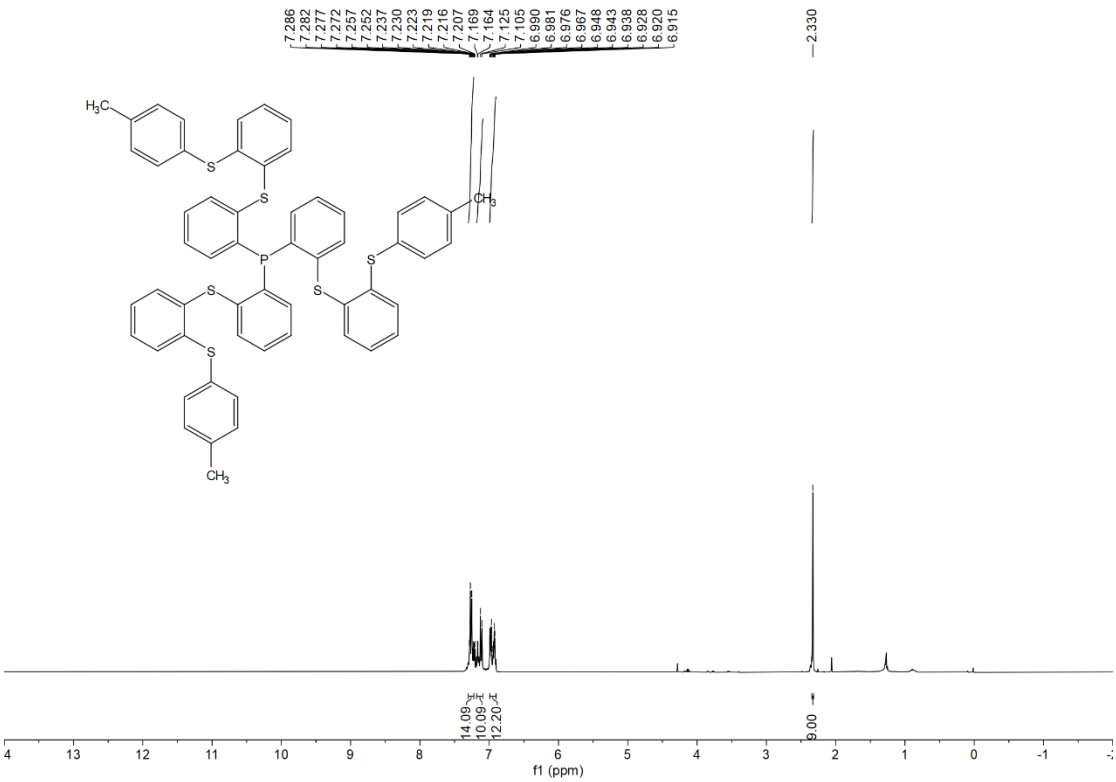
^{1}H NMR spectrum of **3r** (400 MHz, Chloroform-*d*)



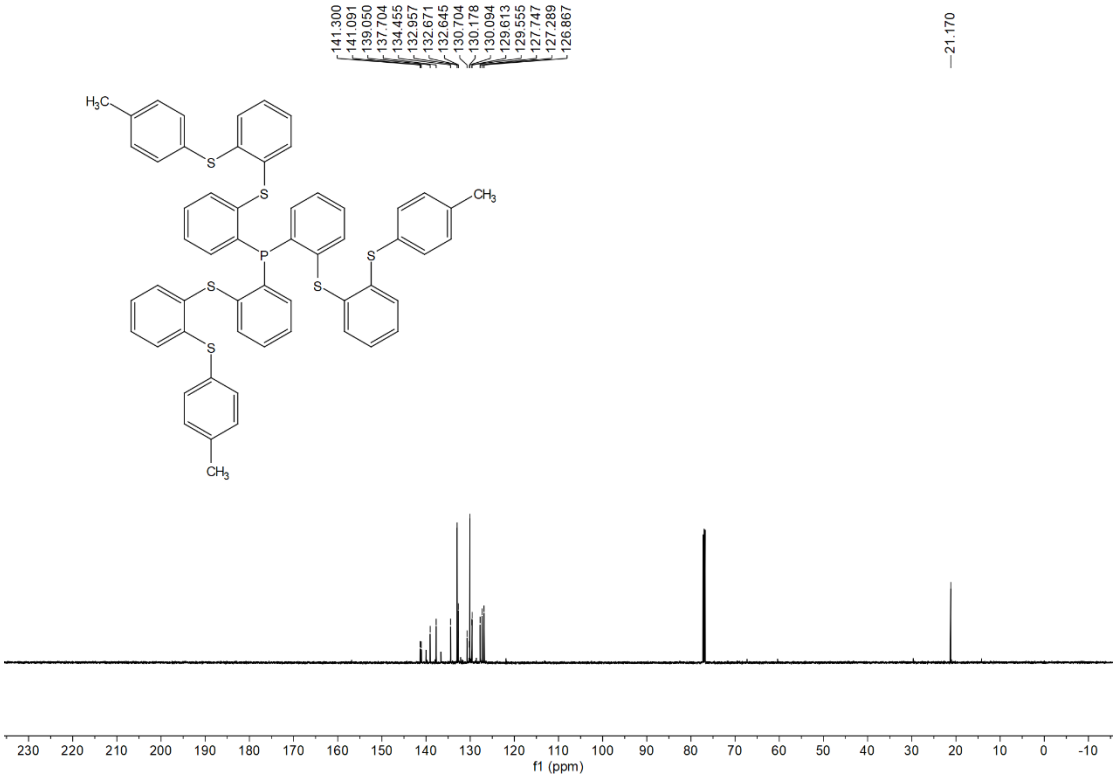
^{13}C spectrum of **3r** (151 MHz, Chloroform-*d*)



^{31}P NMR spectrum of **3r** (162 MHz, Chloroform-*d*)

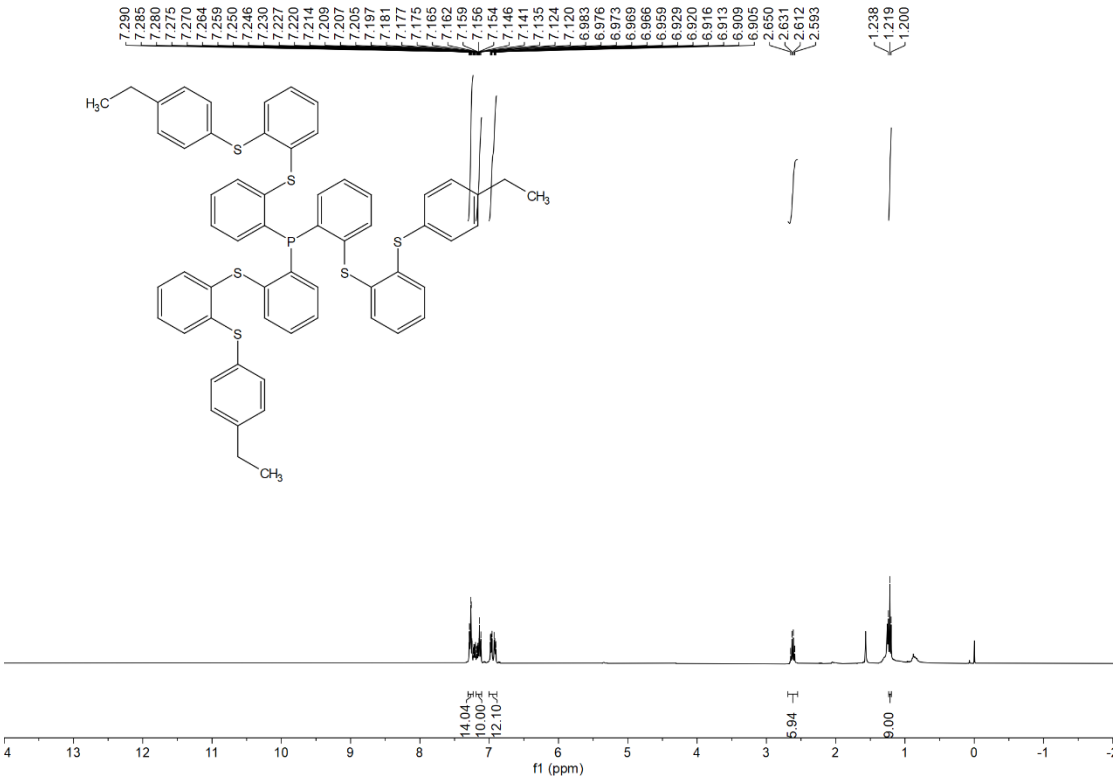


^{1}H NMR spectrum of **4a** (400 MHz, Chloroform-*d*)

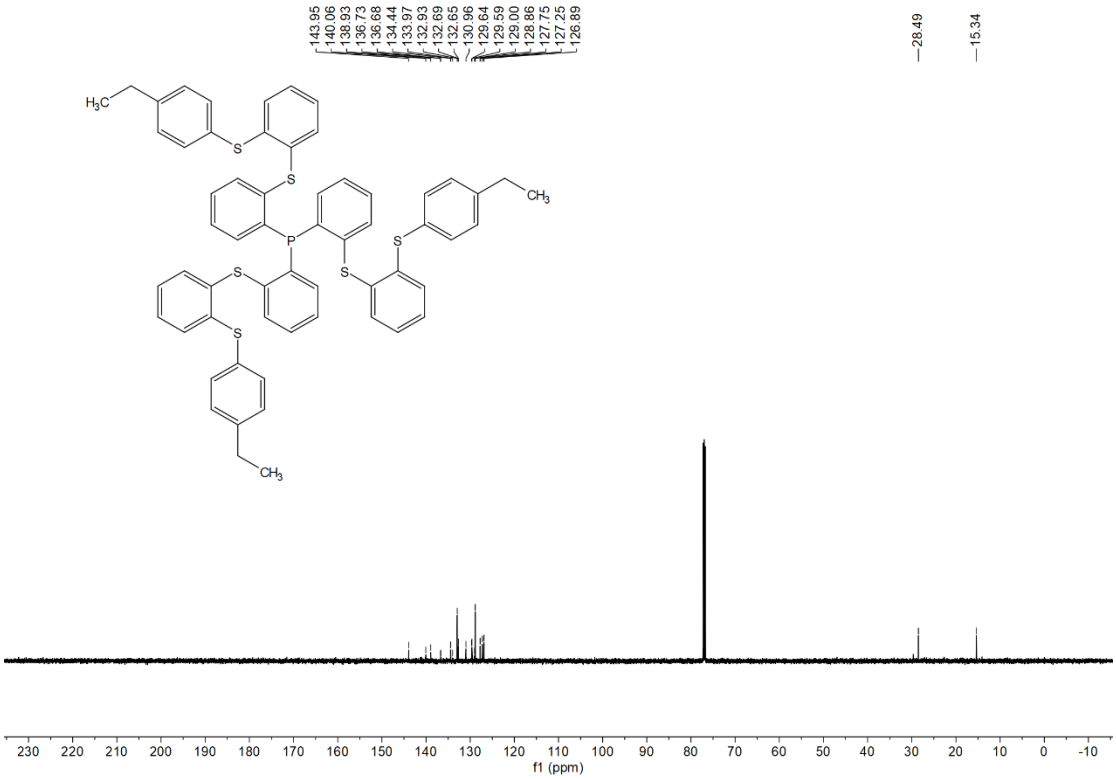


^{13}C spectrum of **4a** (151 MHz, Chloroform-*d*)

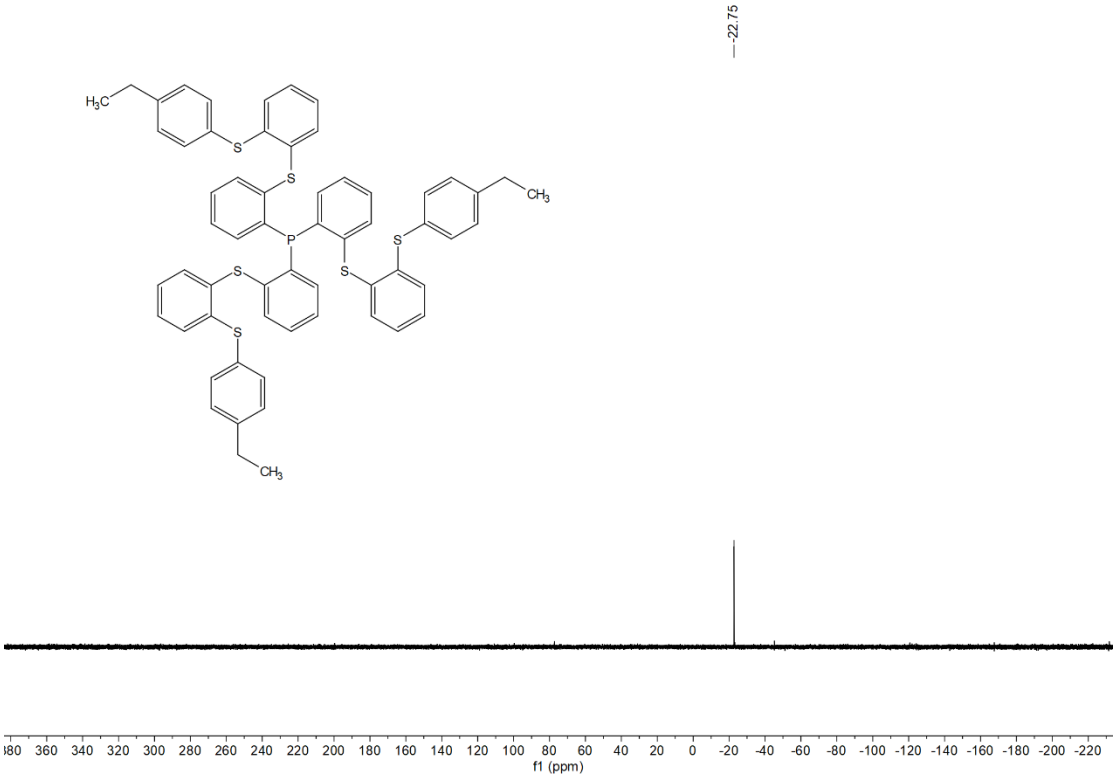
^{31}P NMR spectrum of **4a** (162 MHz, Chloroform-*d*)



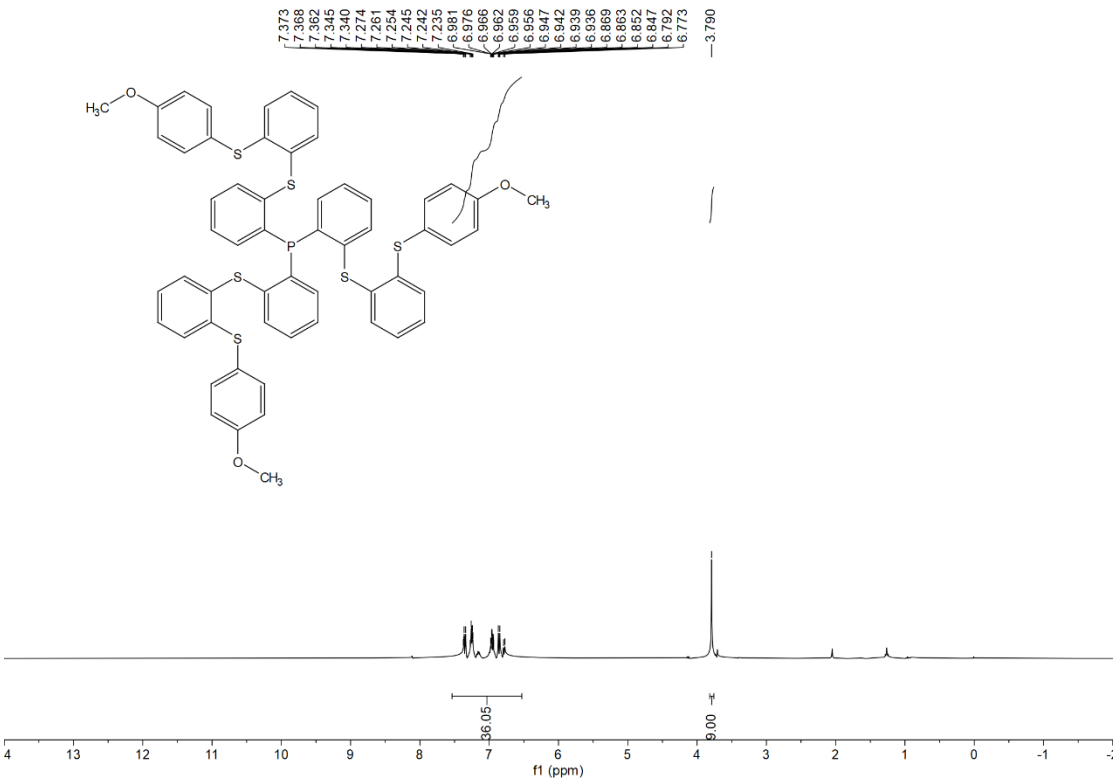
^{1}H NMR spectrum of **4b** (400 MHz, Chloroform-*d*)



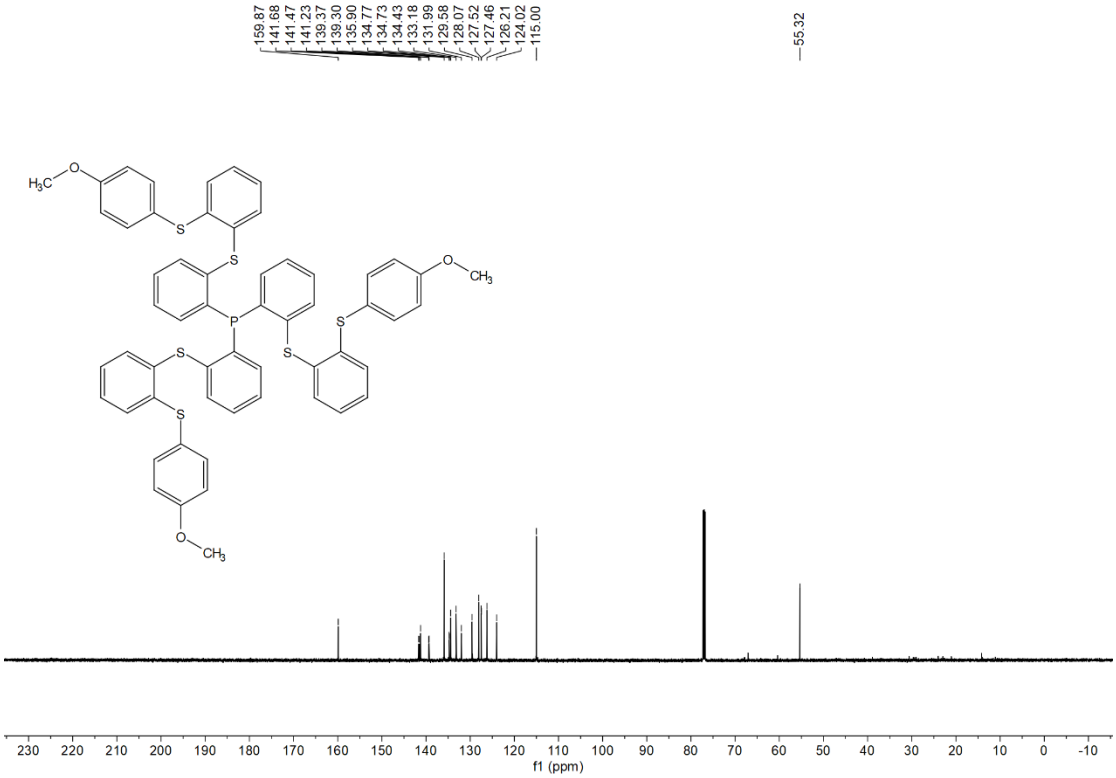
^{13}C spectrum of **4b** (151 MHz, Chloroform-*d*)



^{31}P NMR spectrum of **4b** (162 MHz, Chloroform-*d*)

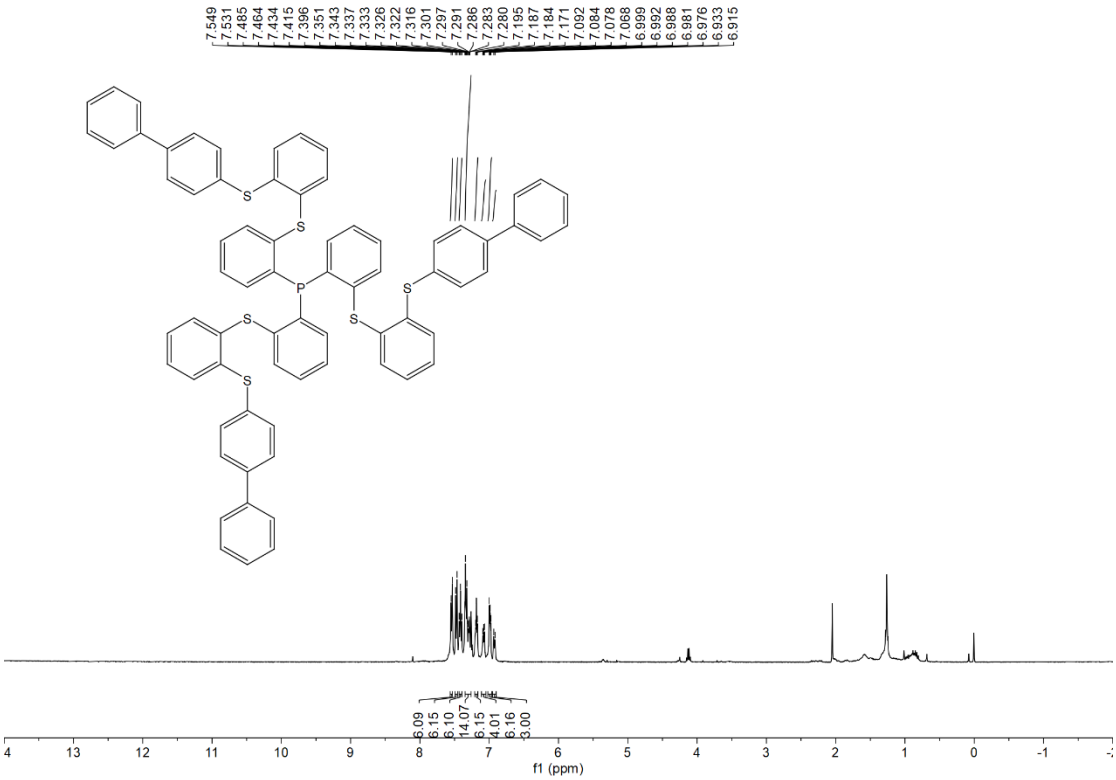


^{1}H NMR spectrum of **4c** (400 MHz, Chloroform-*d*)

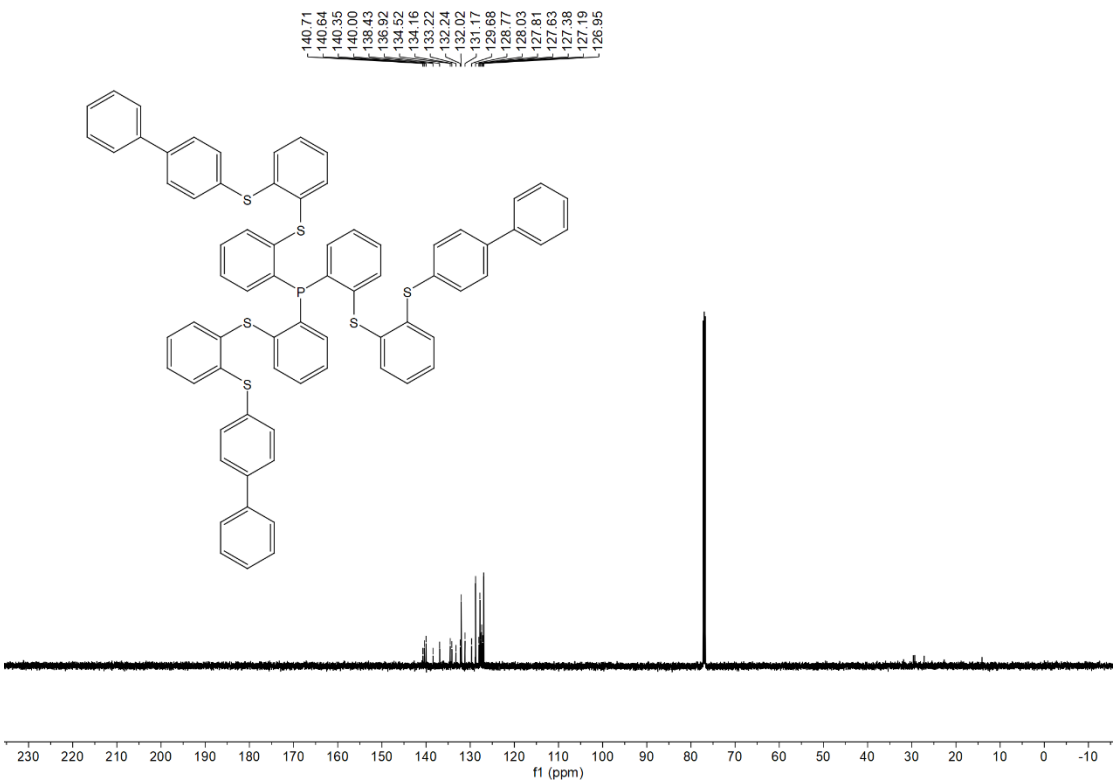


^{13}C spectrum of **4c** (151 MHz, Chloroform-*d*)

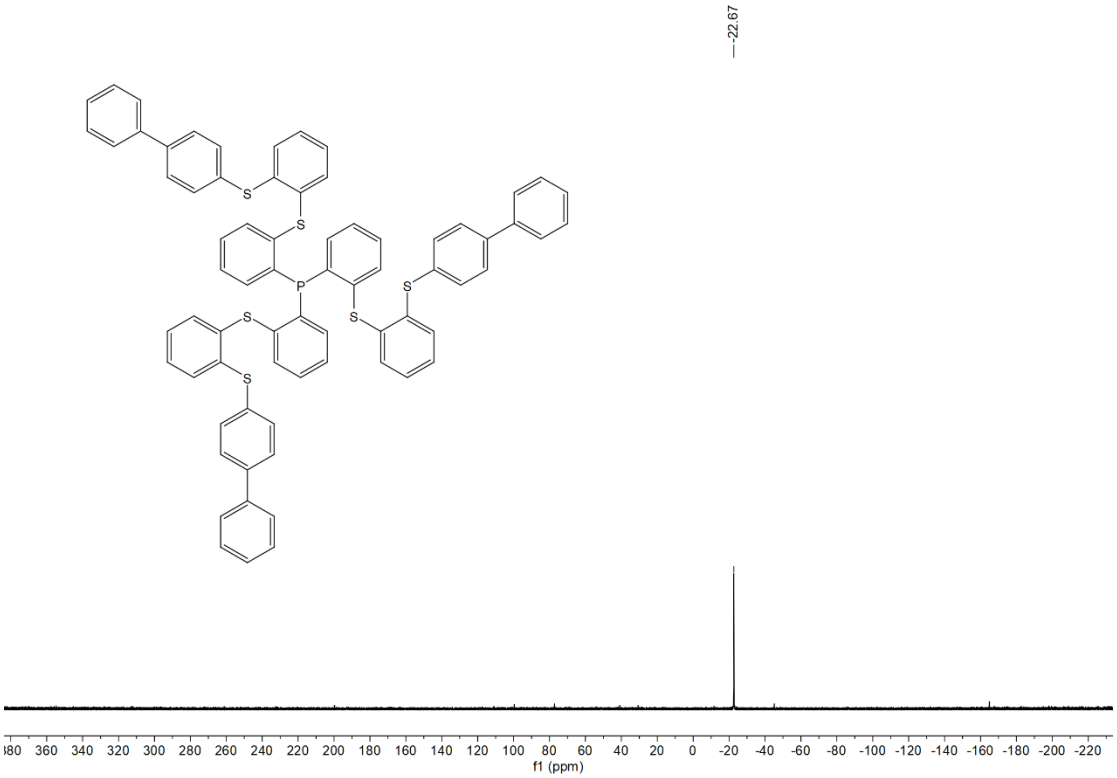
^{31}P NMR spectrum of **4c** (162 MHz, Chloroform-*d*)



^{1}H NMR spectrum of **4d** (400 MHz, Chloroform-*d*)



^{13}C spectrum of **4d** (151 MHz, Chloroform-*d*)



^{31}P NMR spectrum of **4d** (162 MHz, Chloroform-*d*)

8. References

1. H. Luo, M. Li, X. C. Wang, Z. J. Quan. *Org Biomol Chem.* 2023, **21**, 2499.

2. F. Berger, M. B. Plutschack, J. Riegger, W. Yu, S. Speicher, M. Ho, N. Frank, T. Ritter. *Nature*. 2019, **567**, 223.

3. X.-Y. Chen, Y.-N. Li, Y. Wu, J. Bai, Y. Guo, P. Wang. *J. Am. Chem. Soc.,* 2023, **145**, 10431.