Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

for

Metal-free visible-light-induced phosphorylation of unactivated alkyl iodides with white phosphorus as the P-atom source

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1. General information.

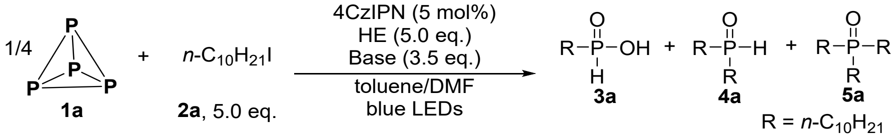
All reactions were carried out under dry argon (unless otherwise noted). All glassware was oven-dried (120 °C, 6 h) prior to use. Toluene was freshly distilled over sodium with the use of diphenyl ketone as an indicator then stored over molecular sieve (3 Å). *N*,*N*-dimethylformamide, dimethyl sulfoxide, *N*,*N*-dimethylacetamide, tetrahydrofuran, acetone and acetonitrile were purchased from Energy Chemical (99.5%, with molecular sieves, water ≤ 50 ppm) and used as the solvent. Methanol, dichloromethane, petroleum ether and ethyl acetate are all ACS grade were obtained commercially and used as eluent without further purification. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were measured on Bruker AV 500M spectrometers with $CDCl_3$ as solvent. Data were reported relative to solvent peaks $CDCl_3$ (7.26 ppm) for ^{1}H and $CDCl_3$ (77.26 ppm) for ^{13}C. 85% H_3PO_4 as external standard for $^{31}P\{^1H\}$ NMR spectra, $^{19}F\{^1H\}$ chemical shifts were un-calibrated. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constants in Hertz (Hz). The products were purified by column chromatography on silica gel 300-400 mesh. The CAS number of the known compound was listed. All products were further characterized by HRMS (FT-ICR-MS) and an electrospray ionization source in positive-ion mode. The Uv-vis absorption were recorded by Shimadzu UV-2550. Alkyl iodides, Hantzsch ester (HE), Cesium fluoride, and other commercial reagents were purchased from TCI, Energy Chemical and Aldrich and used without further purification.

Safety note for P_4: White phosphorus is spontaneously flammable; it should be stored in water or glove box. White phosphorus-toluene solution should be sealed in argon and stored away from light.
Preparation of P_4-toluene solution: A piece of P_4 was taken out of water and then put in ethanol under argon. Two minutes later, P_4 was taken out and the ethanol on the surface of P_4 was blown away by the argon. Then, the dry P_4 was put in a conical flask containing toluene. The mixture was stirred intensely with a magnetic stirrer until P_4 was completely dissolved in the toluene. (the concentration of P_4 was determined by ^{31}P NMR analysis using triphenyl phosphate $(C_6H_5O)_3P(O)$ as an internal standard, D1 = 20 s, zg30, LB = 1).

2. Tables for optimization of the reaction conditions

Yield of product determined by $^{31}P\{^{1}H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard. After confirming the yield of **4a** and **5a**, (*di-tert*-butyl peroxide DTBP, 0.1 mL) was added and stirred at room temperature for 5 h in air, and the yield of **3a** was determined by $^{31}P\{^{1}H\}$ NMR analysis. A control experiment was performed to confirm the content of the internal standard did not decrease during the oxidation process (DTBP and $(C_6H_5O)_3P(O)$ in a mixture of DMF and toluene were stirred at rt. for 5 h in air). Yield of **3a** was analyzed by $^{31}P\{^{1}H\}$ spectra (D1 = 20 s, zgig30, LB = 1). Yield of **4a** were analyzed by ^{31}P spectra (D1 = 20 s, zg30, LB = 1).[1]

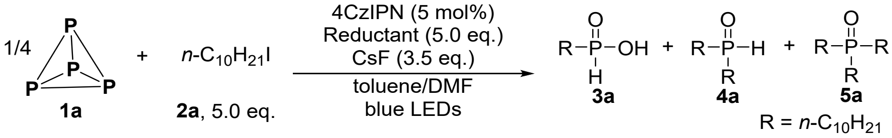
Supplementary Table 1 Photochemical functionalization of P_4: screening of **bases**.[a]



Entry	Different Base	Yield (%)[b]			Full conversion of P_4?
		3a	**4a**	**5a**	
1	NaOH	0	35	0	√
2	Na_2CO_3	12	43	0	√
3	$NaHCO_3$	13	52	0	√
4	K_2CO_3	0	57	0	√
5	Cs_2CO_3	0	45	0	√
6	DBU	0	33	0	√
7	**CsF**	**<5**	**86**	**0**	√

[a]Reaction conditions: P_4 (9.30 mg, 0.30 mmol of P atom, 0.67 M solution of P_4 in toluene, 0.45 mL), **2a** (1.50 mmol), HE (1.50 mmol), **base** (1.05 mmol), 4CzIPN (5 mol%) in DMF (3.00 mL) and toluene (2.55 mL) irradiated by blue LEDs (2 x 3 W, 450–470 nm) at room temperature for 12 h under argon, and subsequently stirred at room temperature for 1 h in air (oxidation of R_2PH by air afforded DAPOs). [b]The yield of products was determined by ^{31}P NMR analysis using $(PhO)_3P(O)$ (δ: -16 ppm) as an internal standard. After confirming the yield of **4a**, (*di-tert*-butylperoxide DTBP, 0.1 mL) was added and stirred at room temperature for 5 h in air, and the yield of **3a** was determined by $^{31}P\{^{1}H\}$ NMR analysis. Yield based on the P atom unless otherwise specified.

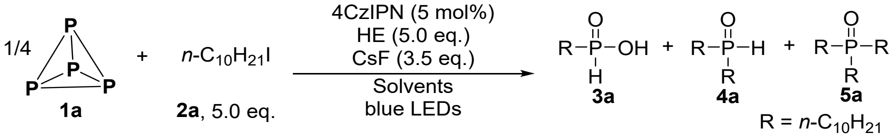
Supplementary Table 2 Photochemical functionalization of P_4: screening of **reductants**.[a]



Entry	Different reductants	Yield (%)[b]			Full conversion of P_4?
		3a	**4a**	**5a**	
1	NEt_3	0	26	12	√
2	DIPEA	0	14	0	√
3	**HE**	**<5**	**86**	**0**	√

[a]Reaction conditions: P_4 (9.30 mg, 0.30 mmol of P atom, 0.67 M solution of P_4 in toluene, 0.45 mL), **2a** (1.50 mmol), **reductant** (1.50 mmol), CsF (1.05 mmol), 4CzIPN (5 mol%) in DMF (3.00 mL) and toluene (2.55 mL) irradiated by blue LEDs (2 x 3 W, 450–470 nm) at room temperature for 12 h under argon, and subsequently stirred at room temperature for 1 h in air (oxidation of R_2PH by air afforded DAPOs). [b]The yield of products was determined by ^{31}P NMR analysis using $(PhO)_3P(O)$ (δ: -16 ppm) as an internal standard. After confirming the yield of **4a**, (*di-tert*-butylperoxide DTBP, 0.1 mL) was added and stirred at room temperature for 5 h in air, and the yield of **3a** was determined by $^{31}P\{^1H\}$ NMR analysis. Yield based on the P atom unless otherwise specified.

Supplementary Table 3 Photochemical functionalization of P_4: screening of **solvents**.[a]

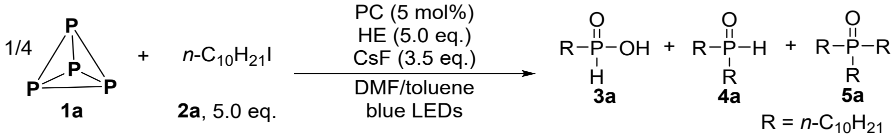


Entry	Different solvents	Yield (%)[b]			Full conversion of P_4?
		3a	**4a**	**5a**	
1	DMSO : toluene (3 mL : 3 mL)	<5	61	0	√
2	DMAc : toluene (3 mL : 3 mL)	0	19	0	√
3	THF : toluene (3 mL : 3 mL)	0	<5	0	×
4	acetone : toluene (3 mL : 3 mL)	8	9	0	√
5	MeCN : toluene (3 mL : 3 mL)	15	29	0	√
6	**DMF : toluene (3 mL : 3 mL)**	**<5**	**86**	**0**	√

[a]Reaction conditions: P_4 (9.30 mg, 0.30 mmol of P atom, 0.67 M solution of P_4 in toluene, 0.45 mL), **2a** (1.50 mmol), HE (1.50 mmol), CsF (1.05 mmol), 4CzIPN (5 mol%) in **solvents** (3.00 mL) and toluene (2.55 mL) irradiated by blue LEDs (2 x 3 W, 450–470 nm) at room temperature for 12 h under argon, and subsequently stirred at room temperature for 1 h in air (oxidation of R_2PH by air afforded DAPOs). [b]The yield of products was determined by ^{31}P

NMR analysis using (PhO)$_3$P(O) (δ: -16 ppm) as an internal standard. After confirming the yield of **4a**, (*di-tert*-butylperoxide DTBP, 0.1 mL) was added and stirred at room temperature for 5 h in air, and the yield of **3a** was determined by ^{31}P{^{1}H} NMR analysis. Yield based on the P atom unless otherwise specified.

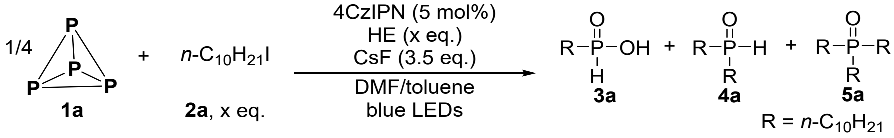
Supplementary Table 4 Photochemical functionalization of P$_4$: screening of **photocatalyst**.[a]



Entry	Photocatalyst	Yield (%)[b]			Full conversion of P$_4$?
		3a	**4a**	**5a**	
1	-	<5	48	0	√
2	Eosin Y	<5	42	0	√
3	Eosin B	0	0	0	×
4	Rhodamine B	<5	48	0	√
6	Fluorescein	<5	52	0	√
7	3DPAFIN	<5	49	0	√
8	**4CzIPN**	**<5**	**86**	**0**	√

[a]Reaction conditions: P$_4$ (9.30 mg, 0.30 mmol of P atom, 0.67 M solution of P$_4$ in toluene, 0.45 mL), **2a** (1.50 mmol), HE (1.50 mmol), CsF (1.05 mmol), photocatalyst (5 mol%) in DMF (3.00 mL) and toluene (2.55 mL) irradiated by blue LEDs (2 x 3 W, 450–470 nm) at room temperature for 12 h under argon, and subsequently stirred at room temperature for 1 h in air (oxidation of R$_2$PH by air afforded DAPOs). [b]The yield of products was determined by ^{31}P NMR analysis using (PhO)$_3$P(O) (δ: -16 ppm) as an internal standard. After confirming the yield of **4a**, (*di-tert*-butylperoxide DTBP, 0.1 mL) was added and stirred at room temperature for 5 h in air, and the yield of **3a** was determined by ^{31}P{^{1}H} NMR analysis. Yield based on the P atom unless otherwise specified.

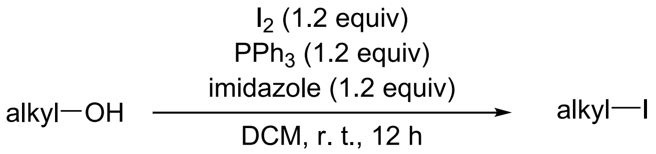
Supplementary Table 5 Photochemical functionalization of P_4: screening of **loading amount of alkyl iodides and HE**.[a]



Entry	**2a** and HE (x eq.)	Yield (%)[b]			Full conversion of P_4?
		3a	**4a**	**5a**	
1	3	<5	37	0	√
2	4	<5	56	0	√
3	**5**	**<5**	**86**	**0**	√
4	6	0	84	6	√
5	8	0	76	9	√

[a] Reaction conditions: P_4 (9.30 mg, 0.30 mmol of P atom, 0.67 M solution of P_4 in toluene, 0.45 mL), **2a** (x mmol), HE (x mmol), CsF (1.05 mmol), 4CzIPN (5 mol%) in DMF (3.00 mL) and toluene (2.55 mL) irradiated by blue LEDs (2 x 3 W, 450–470 nm) at room temperature for 12 h under argon, and subsequently stirred at room temperature for 1 h in air (oxidation of R_2PH by air afforded DAPOs). [b] The yield of products was determined by ^{31}P NMR analysis using $(PhO)_3P(O)$ (δ: -16 ppm) as an internal standard. After confirming the yield of **4a**, (*di-tert*-butylperoxide DTBP, 0.1 mL) was added and stirred at room temperature for 5 h in air, and the yield of **3a** was determined by $^{31}P\{^1H\}$ NMR analysis. Yield based on the P atom unless otherwise specified.

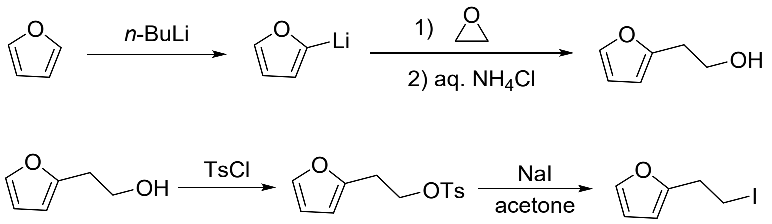
3. General experimental procedures



$$\text{alkyl—OH} \xrightarrow[\text{DCM, r. t., 12 h}]{\substack{I_2\ (1.2\ \text{equiv}) \\ PPh_3\ (1.2\ \text{equiv}) \\ \text{imidazole}\ (1.2\ \text{equiv})}} \text{alkyl—I}$$

Supplementary Scheme 1 Procedure for preparation of alkyl iodides (method A).

To a round bottom flask containing triphenylphosphine (12.0 mmol, 1.2 eq.), iodine (12.0 mmol, 1.2 eq.) was evacuated and purged with argon three times. Then DCM (50.0 mL) was added and stirred at room temperature. The reaction mixture was stirred at room temperature for 10 minutes, subsequently, the solution of imidazole (12.0 mmol, 1.2 eq.) in DCM (15 mL) was added dropwise into the flask at the same temperature and the result mixture was stirred at room temperature for 10 minutes. Solution of alkyl alcohol in DCM (15 mL) was added and stirred at room temperature until the alcohol was consumed (reaction time 15~20 h, monitored by TLC). The reaction was quenched with solution of Na_2SO_3 (sat. aq.) and extracted with DCM. The combined organic layers were washed with brine and dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the desired products (**2d**, **2i** and **2j**).[2]



Supplementary Scheme 2 Procedure for preparation of alkyl iodides (method B).

To a solution of furan (20.0 mmol, 1.0 eq.) in THF (20.0 mL) at –25 °C was added *n*-BuLi (1.02 equiv, 20.4 mmol, 2.5 M in THF) dropwise, with vigorous stirring. After 4 h, ethylene oxide (24 mmol, 3.0 M in THF) was added to the reaction mixture, After the addition was complete the reaction was stirred vigorously for 12 h, and the reaction system allowed to warm to room temperature. After 12 h, The reaction was quenched with solution of NH_4Cl (sat. aq.) and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4, filtered, and concentrated in vacuo. And the 2-(furan-2-yl)ethan-1-ol was purified by flash chromatography.

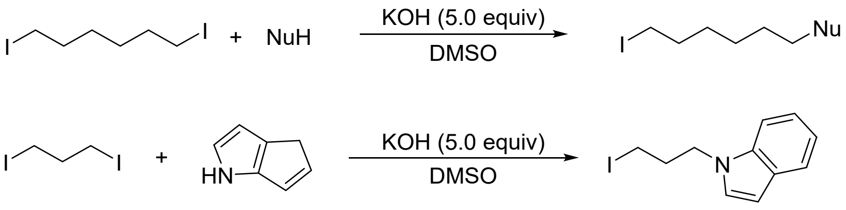
To a stirred solution of 2-(furan-2-yl)ethan-1-ol in DCM (50.0 mL) were added Et_3N (3. 0 eq.) and TsCl (1.0 eq. in DCM) and the mixture was stirred at room temperature. After 12 h, The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography to afford 2-(furan-2-yl)ethyl-4-methylbenzenesulfonate. The resulting product and NaI (3.0 eq.) were refluxed in acetone (30.0 mL) for 12 h. Then the solvent was removed under vacuum and the residue was diluted with H_2O (50.0 mL) and extracted with

DCM. The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude residue was purified by columnchromatography over silica gel using petroleum ether/ethyl acetate (50:1, v/v) as the eluent to afford the desired product **2l**.[3]

$$\text{Alkyl—Cl} \xrightarrow[\text{acetone}]{\text{NaI (3.0 equiv)}} \text{Alkyl—I}$$

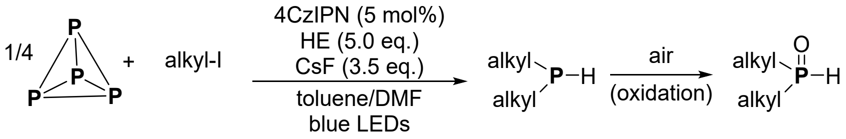
Supplementary Scheme 3 Procedure for preparation of alkyl iodides (method C).

A schlenk tube containing alkyl chlorines (10.0 mmol, 1.0 eq.) and NaI (30.0 mmol, 3.0 eq.) was evacuated and purged with argon three times. Acetone (50.0 mL) was added to the system and the mixture was refluxed for 12 h. Then the solvent was removed under vacuum and the residue was diluted with H_2O (50.0 mL) and extracted with DCM. The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude residue was purified by columnchromatography over silica gel using petroleum ether/ethyl acetate (50:1, v/v) as the eluent to afford the desired products **2e** and **2g**.[2]



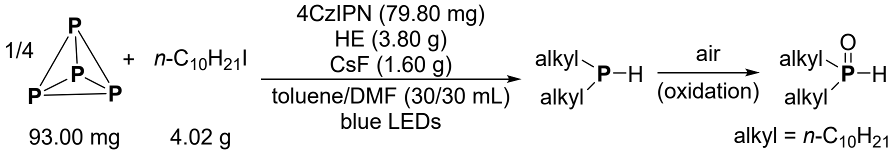
Supplementary Scheme 4 Procedure for preparation of alkyl iodides (method D).

To a stirred suspension of phenol or iodole (10 mmol, 1.0 equiv) in DMSO, KOH (50 mmol, 5.0 equiv) was added at room temperature. The reaction was stirred for additional 0.5 hours at room temperature, 1,6-diiodohexane or 1,3-diiodopropane were added. The mixture was stirred at room temperature for 12 h, extracted with EA, washed with saturated sodium chloride solution, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting mixture was isolated by flash chromatography using petroleum ether/ethyl acetate (50:1, v/v) as the eluent to afford **2k**, **2m**–**2p** and **2q**–**2w**.[2]



Supplementary Scheme 5 General preparation of dialkylphosphine oxides.

A schlenk tube containing alkyl iodides (2, 1.50 mmol, 5.0 eq.), HE (1.50 mmol, 5.0 eq.), CsF (1.05 mmol, 3.5 eq.) and 4CzIPN (5 mol%) were evacuated and purged with argon three times. DMF (3.0 mL), toluene (2.55 mL) and P_4 (9.30 mg, 0.30 mmol of P atom, 0.67 M solution of P_4 in toluene, 0.45 mL) were sequentially added to the system at room temperature. And the reaction mixture was stirred at room temperature under the irradiation of 2 x 3 W blue LEDs (450–470) for 12 h. Afterwards, reaction mixture was stirred at room temperature for 1 h under air. Quenched with addition of saturated brine (3*10.0 mL), extracted with ethyl acetate (3*10 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and then removed in vacuum. And the residue was purified by flash chromatography using DCM/MeOH (from 200:1 to 40:1, v/v) as the eluent to afford the desired dialkyl phosphine Oxides.

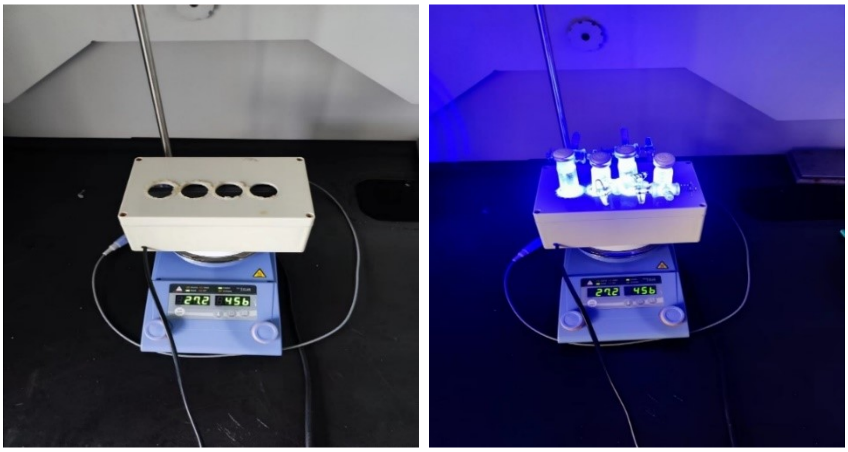


Supplementary Scheme 6 Gram-scale synthesis of **4a**.

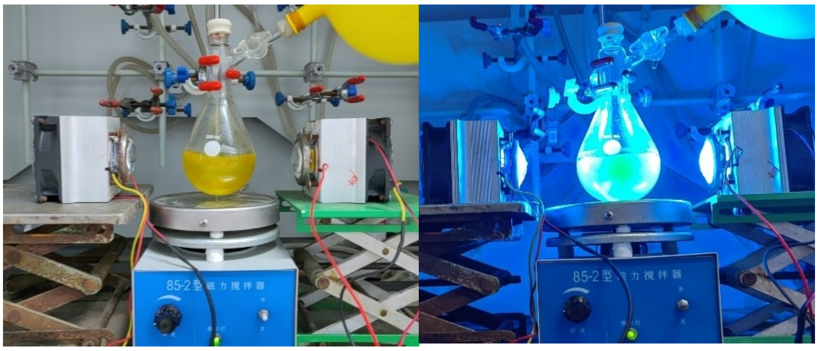
A round flask containing 1-decyl iodide **2a** (15.0 mmol, 4.02 g), HE (15.0 mmol, 3.80 g), CsF (10.5 mmol, 1.60 g) and 4CzIPN (0.1 mmol, 78.9 mg) were evacuated and purged with argon three times, DMF (30.0 mL) and P_4 (93 mg dissolved in toluene 30 mL) were added to the system at room temperature. Then the reaction mixture was stirred at room temperature under the irradiation of 2 x 30 W blue LEDs for 36 hours. Then the system was quenched with addition of saturated brine (3*100.0 mL), extracted with ethyl acetate (3*100 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and then removed in vacuum. The residue was purified by flash chromatography using DCM/MeOH (from 200:1 to 40:1, v/v) as the eluent to afford the desired phosphorylation products.

4. Photograph of photoreactor

LED bulb purchased from GeAo Chem (24 W, broad spectral range of 450–470 nm，1 W for every bulb, every schlenk tube was irradiated by 6 light bulbs from the side) was used in our research. In each case, the light source was placed around 3 cm from the reaction vessel. The reaction was maintained at room temperature (around 25–30 ^{o}C) without using additional cooling. Gram-scale reaction was performed under the irradiation of blue LEDs (30W, 450 nm), which is bought from Xinxingyuan.



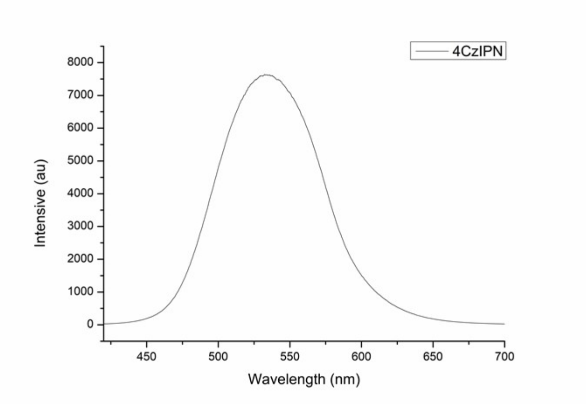
Supplementary figure 1 Photoreactor used in this research (2 x 3 W, 450-470 nm).



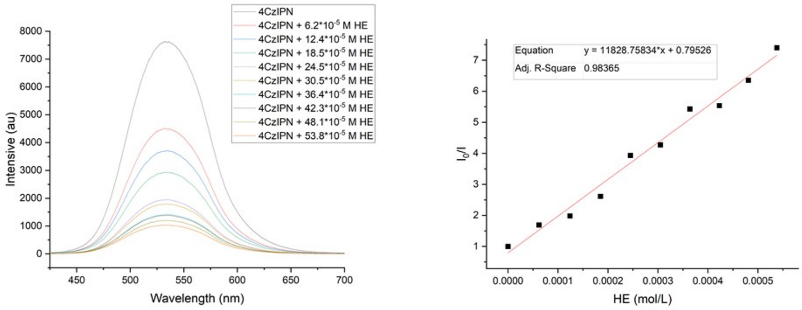
Supplementary figure 2 Photoreactor used in gram-scale synthesis (2 x 30W, 450 nm).

5. Luminescence quenching experiments

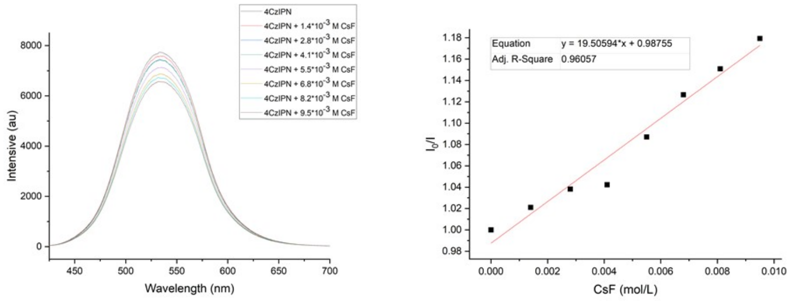
Emission intensities were recorded on a Hitachi F-7000 Fluorescent Spectrophoto-meter in a 4.5 cm quartz cuvette. Series 4CzIPN solutions were excited at 532 nm and the emissions intensities were collected at 400-700 nm.



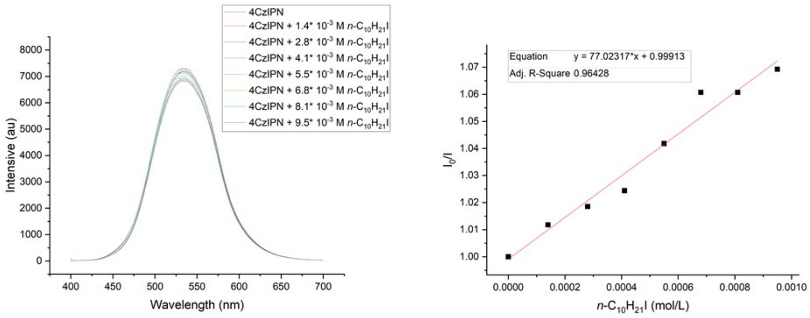
Supplementary figure 3 the emission spectra of a 3.75×10^{-4} M solution of 4CzIPN in degassed DMF: touluene = 1:1 excited at 532 nm



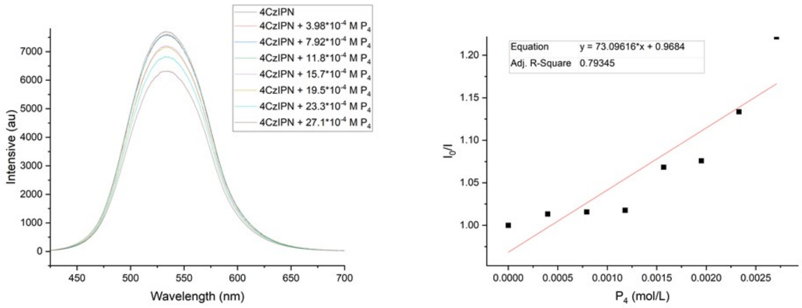
Supplementary figure 4 the emission spectra of a 3.75×10^{-4} M solution of 4CzIPN with various concentrations of HE in degassed DMF: touluene = 1:1 (left); corresponding Stern-Volmer plot (right).



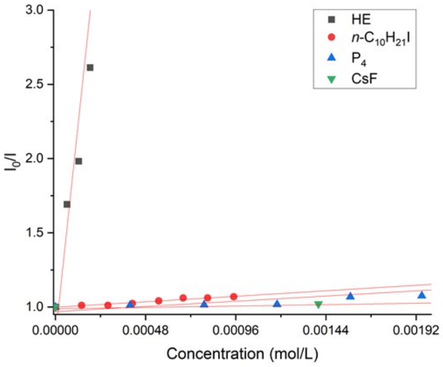
Supplementary figure 5 the emission spectra of a 3.75×10^{-4} M solution of 4CzIPN with various concentrations of CsF in degassed DMF: touluene = 1:1(left); corresponding Stern-Volmer plot (right).



Supplementary figure 6 the emission spectra of a 3.75×10^{-4} M solution of 4CzIPN with various concentrations of n-$C_{10}H_{21}I$ in degassed DMF: touluene = 1:1(left); corresponding Stern-Volmer plot (right).



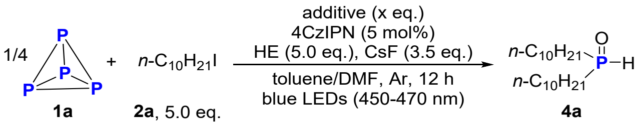
Supplementary figure 7 the emission spectra of a 3.75×10^{-4} M solution of 4CzIPN with various concentrations of P_4 in degassed DMF: touluene = 1:1(left); corresponding Stern-Volmer plot (right).



Supplementary figure 8 Stern-Volmer plot

6. Control experiments.

Supplementary Table 6 Radical inhibition experiments[a]



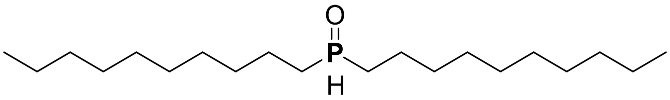
Entry	Additive	^{31}P NMR yield of **4a** (%)[b]
1	-	86
2	TEMPO (10.0 eq.)	0
3	1,1-Diphenylethene (10.0 eq.)	18
4	BHT (10.0 eq.)	55
5	BHT (15.0 eq.)	48

TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, BHT = 2,6-*di*-*tert*-butyl-4-methylpheno.

Experimental Procedures: [a]A schlenk tube containing alkyl iodides (2, 1.50 mmol, 5.0 eq.), HE (1.50 mmol, 5.0 eq.), CsF (1.05 mmol, 3.5 eq.) and 4CzIPN (5 mol%) were evacuated and purged with argon three times. DMF (3.0 mL), toluene (2.55 mL) and P_4 (9.30 mg, 0.30 mmol of P atom, 0.67 M solution of P_4 in toluene, 0.45 mL) were sequentially added to the system at room temperature. And the reaction mixture was stirred at room temperature under the irradiation of 2 x 3 W blue LEDs (450–470) for 12 h. Afterwards, reaction mixture was stirred at room temperature for 1 h under air. Then triphenyl phosphate 97.8 mg was added as internal standard. Resulting mixture was transferred to a NMR tube by a syringe and the resulting solution was monitored by ^{31}P NMR. [b]Yield of **4a** determined by ^{31}P NMR using $(PhO)_3P(O)$ as internal standard (D1 = 20 s, zg30, LB = 1).

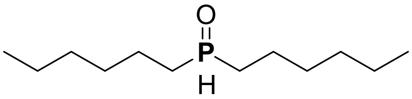
7. Characterization for products.

Didecylphosphine oxide (4a, CAS NO. 74038-18-9)



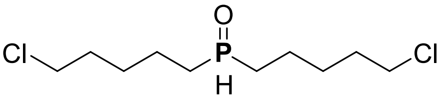
White solid; 75.6 mg, 76% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 6.84 (d, *J* = 446.0 Hz, 1H), 1.85-1.68 (m, 4H), 1.67-1.53 (m, 4H), 1.44-1.35 (m, 4H), 1.29-1.20 (m, 24H), 0.86 (t, *J* = 7.0 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 32.1, 30.9 (d, *J* = 13.6 Hz), 29.7, 29.6, 29.5, 29.3, 28.5 (d, *J* = 65.1 Hz), 22.9, 22.0 (d, *J* = 4.4 Hz), 14.3; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 35.04 (d, *J* = 446.0 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{22}H_{43}OPNa^+$ 353.2943, found 353.2942.

Dihexylphosphine oxide (4b, CAS NO. 17529-42-9)



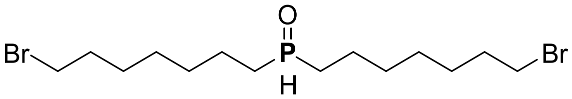
Colorless oil; 46.5 mg, 71% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 6.85 (d, *J* = 446.0 Hz, 1H), 1.85-1.71 (m, 4H), 1.70-1.54 (m, 4H), 1.45-1.38 (m, 4H), 1.33-1.29 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 31.5, 30.6 (d, *J* = 14.3 Hz), 28.5 (d, *J* = 65.2 Hz), 22.6, 22.0 (d, *J* = 3.8 Hz), 14.2; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 35.00 (d, *J* = 446.0 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{12}H_{27}OPNa^+$ 241.1691, found 241.1691.

Bis(5-chloropentyl)phosphine oxide (4c, CAS NO. 2891619-81-9)



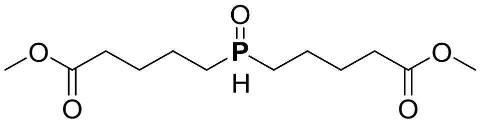
Colorless oil; 51.9 mg, 67% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 6.87 (d, *J* = 451.6 Hz, 1H), 3.49 (t, *J* = 6.4 Hz, 4H), 1.85-1.49 (m, 16H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 44.7, 32.1, 28.3 (d, *J* = 65.2 Hz), 28.0 (d, *J* = 13.8 Hz), 21.3 (d, *J* = 3.4 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 34.10 (d, *J* = 450.7 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{10}H_{21}C1_2OPNa^+$ 281.0599, found 281.0603.

Bis(7-bromoheptyl)phosphine oxide (4d, new compound)



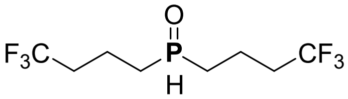
Colorless oil; 43.4 mg, 36% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 6.86 (d, *J* = 446.7 Hz, 1H), 3.96 (t, *J* = 6.7 Hz, 4H), 1.87-1.61 (m, 12H), 1.46-1.41 (m, 8H), 1.38-1.33 (m, 4H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 34.0, 32.8, 30.7 (d, *J* = 13.7 Hz), 28.7, 28.5 (d, *J* = 65.2 Hz), 28.1, 29.1 (d, *J* = 3.6 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.64 (d, *J* = 450.0 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{14}H_{29}Br_2OPNa^+$ 425.0215, found 425.0222.

Dimethyl 5,5'-(oxo-l5-phosphanediyl)dipentanoate (4e, new compound)



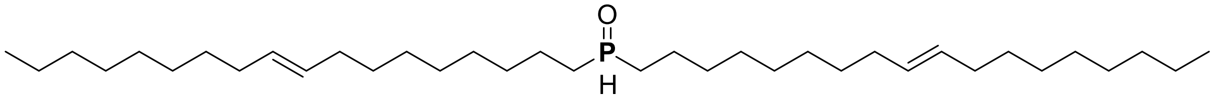
Colorless oil; 35.0 mg, 42% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 6.88 (d, *J* = 446.0 Hz, 1H), 3.67 (s, 6H), 2.35 (t, *J* = 7.2 Hz, 4H), 1.89-1.60 (m, 12H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 173.7, 51.9, 33.7, 28.3 (d, *J* = 65.3 Hz), 26.1 (d, *J* = 15.5 Hz), 21.6 (d, *J* = 3.2 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 33.37 (d, *J* = 451.41 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{12}H_{23}O_5PNa^+$ 301.1175, found 301.1170.

Bis(4,4,4-trifluorobutyl)phosphine oxide (4f, new compound)



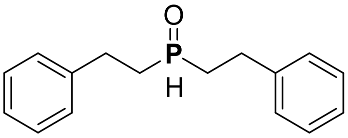
Colorless oil; 60.0 mg, 74% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 6.97 (d, *J* = 454.0 Hz, 1H), 2.32-2.22 (m, 4H), 2.04-1.76 (m, 8H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 126.7 (q, *J* = 276.6 Hz), 34.4 (dq, J_1 = 29.0 Hz, J_2 = 13.3 Hz), 27.5 (d, *J* = 65.7 z), 15.4 (dq, J_1 = 4.3 Hz, J_2 = 3.0 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.54 (d, *J* = 454.0 Hz); **^{19}F{^{1}H} NMR (CDCl$_3$, 471 MHz):** δ -66.00; **HRMS:** [M+Na]$^+$ m/z calcd for $C_8H_{13}F_6OPNa^+$ 293.0500, found 293.0500.

Di((E)-octadec-9-en-1-yl)phosphine oxide (4g, new compound)



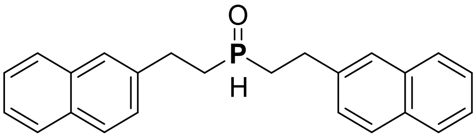
Colorless oil; 118.9 mg, 72% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 6.83 (d, *J* = 446.2 Hz, 1H), 5.37-5.30 (m, 4H), 2.00-1.93 (m, 8H), 1.84-1.69 (m, 8H), 1.67-1.52 (m, 8H), 1.43-1.37 (m, 4H), 1.32-1.24 (m, 40H), 0.86 (t, *J* = 7.3 Hz, 6H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 130.2, 129.9, 32.1, 30.9 (d, *J* = 13.5 Hz), 30.0, 29.9, 29.7, 29.52 (overlap, 2C), 29.46, 29.4, 29.3, 28.4 (d, *J* = 65.1 Hz), 27.42, 27.37, 22.9, 22.0 (d, *J* = 3.5 Hz), 14.3; **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.53 (d, *J* = 446.9 Hz); **HRMS:** [M+K]$^+$ m/z calcd for $C_{36}H_{71}OPK^+$ 573.5132, found 573.5132.

Diphenethylphosphine oxide (4h, CAS NO. 27440-52-4)



Colorless oil; 60.4 mg, 78% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.32-7.30 (m, 4H), 7.27-7.20 (m, 6H), 6.89 (d, *J* = 458.4 Hz, 1H), 3.05-2.98 (m, 2H), 2.96-2.89 (m, 2H), 2.20-2.12 (m, 2H), 2.07-2.00 (m, 2H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 140.3 (d, *J* = 12.3 Hz), 129.0, 128.4, 126.9, 30.4 (d, *J* = 64.1 Hz), 28.1 (d, *J* = 3.0 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.67 (d, *J* = 457.9 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{16}H_{19}OPNa^+$ 281.1065, found 281.1063.

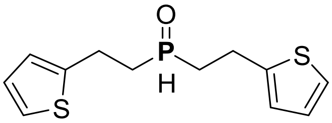
Bis(2-(naphthalen-2-yl)ethyl)phosphine oxide (4i, CAS NO. 473721-94-7)



Pale yellow oil; 79.5 mg, 74% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.55-7.47 (m, 4H), 7.39 (t, *J*= 7.8 Hz, 2H), 7.33 (d, *J* = 6.9 Hz, 2H), 6.93 (d, *J* = 448.6 Hz, 1H), 3.53-3.43 (m, 2H), 3.39-3.29 (m, 2H), 2.31-2.20 (m, 2H), 2.16-2.06 (m, 2H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 136.2 (d, *J* = 12.7 Hz), 134.1, 131.3, 129.2, 127.7, 126.5, 126.3, 126.0, 125.7, 123.3, 29.5 (d, *J* = 63.8 Hz), 25.2 (d, *J* = 3.6 Hz); **^{31}P{^{1}H} NMR**

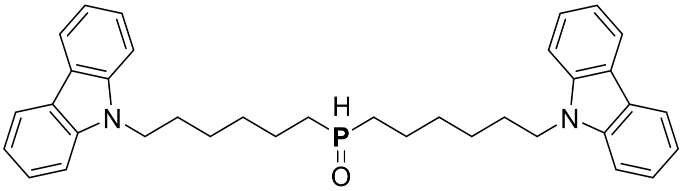
($CDCl_3$, 202 MHz): δ 31.16 (d, *J* = 448.7 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{24}H_{23}OPNa^+$ 381.1379, found 381.1378.

Bis(2-(thiophen-2-yl)ethyl)phosphine oxide (4j, new compound)



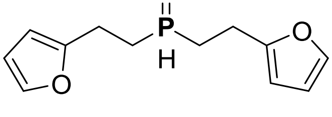
Colorless oil; 51.8 mg, 64% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.15 (d, *J* = 5.2 Hz, 2H), 6.92 (t, *J* = 4.5 Hz, 4H), 6.90 (d, *J* = 460.2 Hz, 1H), 6.86 (d, *J* = 3.8 Hz, 2H), 3.28-3.13 (m, 4H), 2.26-2.16 (m, 2H), 2.13-2.03 (m, 2H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 142.7 (d, *J* = 12.9 Hz), 127.3, 125.4, 124.3, 30.7 (d, *J* = 66.1 Hz), 22.5 (d, *J* = 2.7 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 29.58 (d, *J* = 455.8 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{12}H_{15}OPS_2Na^+$ 293.0194, found 293.0198.

Bis(6-(9H-carbazol-9-yl)hexyl)phosphine oxide (4k, new compound)



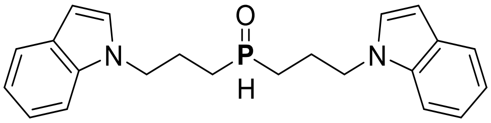
White solid; 88.8 mg, 54% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.06 (d, *J* = 7.6 Hz, 4H), 7.42 (dt, J_1 = 8.5 Hz, J_2 = 1.2, 4H), 7.33 (d, *J* = 8.2 Hz, 4H), 7.19 (dt, J_1 = 6.7 Hz, J_2 = 1.0, 4H), 6.65 (d, *J* = 454.8 Hz, 1H), 4.23 (t, *J* = 7.0 Hz, 4H), 1.86-1.79 (m, 4H), 1.62-1.41 (m, 8H), 1.36-1.27 (m, 8H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 140.5, 125.8, 122.9, 120.5, 118.9, 108.8, 43.0, 30.5 (d, *J* = 13.5 Hz), 28.8, 28.1 (d, *J* = 65.3 Hz), 26.9, 21.7 (d, *J* = 3.6 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 34.27 (d, *J* = 452.7 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{36}H_{41}N_2OPNa^+$ 571.2849, found 571.2840.

Bis(2-(furan-2-yl)ethyl)phosphine oxide (4l, CAS NO. 1919036-23-9)



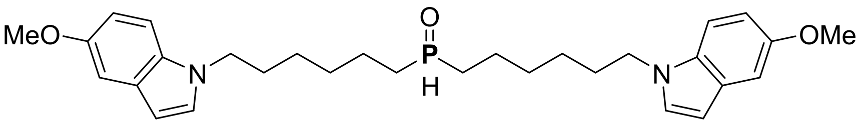
Colorless oil; 40.0 mg, 56% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.31 (d, J = 2.0 Hz, 2H), 6.83 (d, J = 453.7 Hz, 1H), 6.28 (dd, J_1 = 2.0 Hz, J_2 = 1.9 Hz, 2H), 6.07 (dd, J_1 = 2.5 Hz, J_2 = 1.9 Hz, 2H), 3.06-2.92 (m, 4H), 2.19-1.99 (m, 4H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 153.3 (d, J = 12.3 Hz), 141.8, 110.6, 106.4, 26.9 (d, J = 65.2 Hz), 20.7 (d, J = 2.7 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 31.21 (d, J = 457.9 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{12}H_{16}O_3PNa^+$ 261.0651, found 261.0647.

Bis(3-(1H-indol-1-yl)propyl)phosphine oxide (4m, new compound)



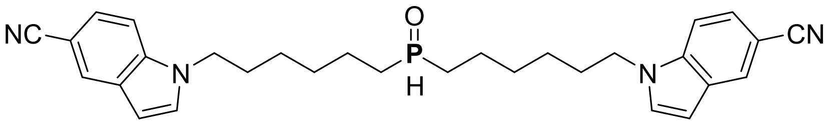
Colorless oil; 71.0 mg, 65% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.64 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 7.0 Hz, 2H), 7.13 (d, J = 7.7 Hz, 2H), 7.03 (d, J = 3.3 Hz, 2H), 6.63 (d, J = 456.7 Hz, 1H), 6.51 (d, J = 2.9 Hz, 2H), 4.15 (dt, J_1 = 6.6 Hz, J_2 = 4.1 Hz, 4H), 2.21-1.98 (m, 4H), 1.62-1.55 (m, 2H), 1.51-1.42 (m, 2H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 135.9, 128.8, 127.8, 121.9, 121.3, 119.7, 109.4, 101.9, 46.3 (d, J = 14.1 Hz), 25.4 (d, J = 65.6 Hz), 22.8 (d, J = 3.4 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 33.43 (d, J = 457.5 Hz); **HRMS:** [M+H]$^+$ m/z calcd for $C_{22}H_{25}N_2OPNa^+$ 387.1597, found 387.1590.

bis(6-(5-methoxy-1H-indol-1-yl)hexyl)phosphine oxide (4n, new compound)



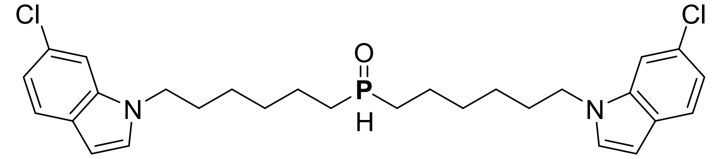
Colorless oil; 94.5 mg, 62% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.21 (d, J = 9.6 Hz, 2H), 7.09 (d, J = 3.1 Hz, 2H), 7.05 (d, J = 2.9 Hz, 2H), 6.88 (t, J = 2.0 Hz, 1H), 6.86 (t, J = 2.2 Hz, 1H), 6.77 (d, J = 448.9 Hz, 1H), 6.40 (t, J = 2.6 Hz, 2H), 4.07 (t, J = 6.8 Hz, 4H), 3.85 (s, 6H), 1.85-1.79 (m, 4H), 1.76-1.49 (m, 8H), 1.44-1.38 (m, 4H), 1.33-1.26 (m, 4H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 154.1, 131.4, 129.1, 128.5, 111.9, 110.2, 102.7, 100.7, 56.0, 46.6, 30.4 (d, J = 13.6 Hz), 30.1, 28.3 (d, J = 65.2 Hz), 26.7, 21.8 (d, J = 3.6 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.31 (d, J = 448.9 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{30}H_{41}N_2O_3PNa^+$ 531.2747, found 531.2735.

1,1'-((oxo-l5-phosphanediyl)bis(hexane-6,1-diyl))bis(1H-indole-5-carbonitrile) (4o, new compound)



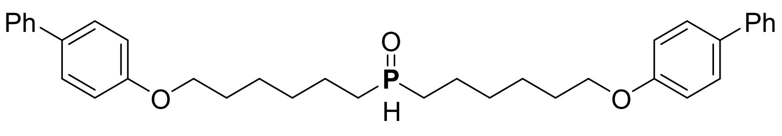
Colorless oil; 101.7 mg, 68% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.96 (d, *J* = 0.8 Hz, 2H), 7.41 (d, *J* = 9.3 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 3.2 Hz, 2H), 6.79 (d, *J* = 446.7 Hz, 1H), 6.56 (d, *J* = 4.1 Hz, 2H), 4.14 (t, *J* = 6.7 Hz, 4H), 1.87-1.82 (m, 4H), 1.77-1.52 (m, 8H), 1.46-1.40 (m, 4H), 1.34-1.27 (m, 4H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 137.5, 130.2, 128.3, 126.6, 124.3, 120.9, 110.3, 102.3, 102.2, 46.5, 30.2 (d, *J* = 13.4 Hz), 29.9, 28.2 (d, *J* = 65.1 Hz), 26.5, 21.8 (d, *J* = 3.6 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 33.99 (d, *J* = 448.5 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for C$_{30}$H$_{35}$N$_4$OPNa$^+$ 521.2441, found 521.2438.

Bis(6-(6-chloro-1H-indol-1-yl)hexyl)phosphine oxide (4p, new compound)



White solid; 99.1 mg, 64% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 2H), 7.08-7.05 (m, 4H), 6.47 (d, *J* = 3.2 Hz, 2H), 6.78 (d, *J* = 447.6 Hz, 1H), 4.04 (t, *J* = 7.0 Hz, 4H), 1.84-1.79 (m, 4H), 1.77-1.68 (m, 2H), 1.67 – 1.48 (m, 6H), 1.46-1.38 (m, 4H), 1.34-1.26 (m, 4H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 136.40, 128.64, 127.40, 127.17, 121.89, 119.95, 109.42, 101.36, 46.36, 30.23 (d, *J* = 13.8 Hz), 29.90, 28.14 (d, *J* = 65.2 Hz), 26.49, 21.74 (d, *J* = 3.8 Hz).; **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.27 (d, *J* = 447.6 Hz) **HRMS:** [M+Na]$^+$ m/z calcd for C$_{28}$H$_{35}$Cl$_2$OPNa$^+$ 539.1756, found 539.1748.

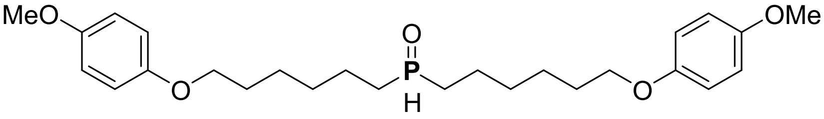
Bis(6-([1,1'-biphenyl]-4-yloxy)hexyl)phosphine oxide (4q, new compound)



White solid; 73.2 mg, 44% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.56-7.51 (m, 8H), 7.41 (t, *J* =

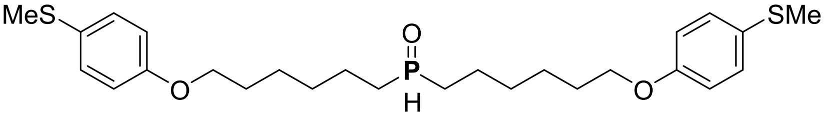
7.8 Hz, 4H), 7.30 (t, *J* = 7.3 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 4H), 6.89 (d, *J* = 448.2 Hz, 1H), 4.00 (t, *J* = 6.1 Hz, 4H), 1.90-1.65 (m, 12H), 1.59-1.47 (m, 8H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 158.8, 141.0, 133.9, 128.9, 128.4, 126.93, 126.86, 115.0, 68.0, 30.6 (d, *J* = 13.7 Hz), 29.2, 28.5 (d, *J* = 65.1 Hz), 25.9, 22.0 (d, *J* = 3.6 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.55 (d, *J* = 446.1 Hz); **HRMS:** [M+H]$^+$ m/z calcd for $C_{36}H_{44}O_3P^+$ 577.2842, found 577.2832.

Bis(6-(4-methoxyphenoxy)hexyl)phosphine oxide (4r, new compound)



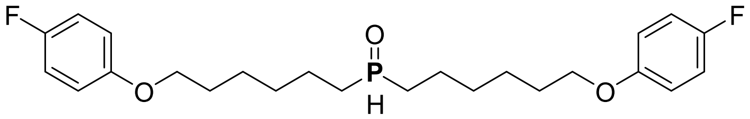
White solid; 73.5 mg, 53% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 6.87 (d, *J* = 445.7 Hz, 1H), 6.82 (s, 8H), 3.90 (t, *J* = 6.3 Hz, 4H), 3.76 (s, 6H), 1.89-1.64 (m, 12H), 1.59-1.49 (m, 8H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 154.0, 153.4, 115.6, 114.9, 68.5, 56.0, 30.7 (d, *J* = 13.8 Hz), 29.3, 28.5 (d, *J* = 64.8 Hz), 25.9, 22.0 (d, *J* = 3.4 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.27 (d, *J* = 446.5 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{26}H_{39}O_5PNa^+$ 485.2427, found 485.2427.

Bis(6-(4-(methylthio)phenoxy)hexyl)phosphine oxide (4s, new compound)



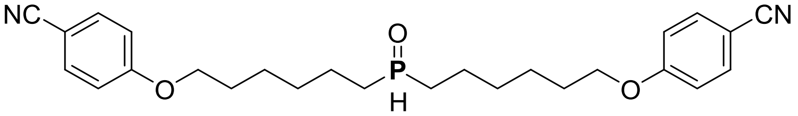
Colorless oil; 69.7 mg, 47% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.24 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 447.6 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 4H), 3.91 (t, *J* = 8.5 Hz, 4H), 2.42 (s, 6H), 1.89-1.58 (m, 12H), 1.57-1.45 (m, 8H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 157.8, 130.3, 128.8, 115.3, 68.0, 30.6 (d, *J* = 13.6 Hz), 29.1, 28.4 (d, *J* = 65.1 Hz), 25.8, 21.9 (d, *J* = 3.7 Hz), 18.2; **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 33.86 (d, *J* = 446.6 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{26}H_{39}O_3PS_2Na^+$ 517.1970, found 517.1965.

Bis(6-(4-fluorophenoxy)hexyl)phosphine oxide (4t, new compound)



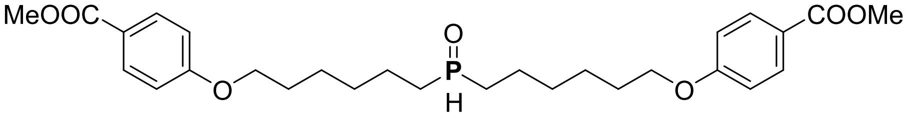
Colorless oil; 81.5 mg, 62% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 6.96-6.92 (m, 4H), 6.85 (d, *J* = 446.4 Hz, 1H), 6.81-6.78 (m, 4H), 3.89 (t, *J* = 6.5 Hz, 4H), 1.87-1.72 (m, 8H), 1.70-1.59 (m, 4H), 1.52-1.45 (m, 8H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 157.3 (d, *J* = 237.7 Hz), 155.3 (d, *J* = 2.2 Hz), 115.9 (d, *J* = 23.1 Hz), 115.5 (d, *J* = 7.6 Hz), 68.5, 30.6 (d, *J* = 14.3 Hz), 29.2, 28.4 (d, *J* = 65.2 Hz), 25.8, 22.0 (d, *J* = 4.4 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.42 (d, *J* = 446.5 Hz); **^{19}F{^{1}H} NMR (CDCl$_3$, 471 MHz):** δ -124.28; **HRMS:** [M+Na]$^+$ m/z calcd for $C_{24}H_{33}F_2O_3PNa^+$ 461.2028, found 461.2020.

4,4'-(((oxo-l5-phosphanediyl)bis(hexane-6,1-diyl))bis(oxy))dibenzonitrile (4u, new compound)



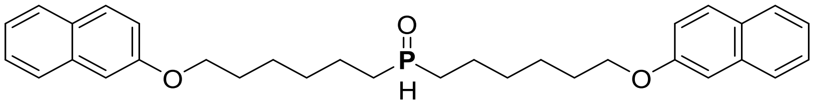
Colorless oil; 92.2 mg, 68% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.53 (d, *J* = 7.8 Hz, 4H), 6.89 (d, *J* = 8.2 Hz, 4H), 6.86 (d, *J* = 445.1 Hz, 1H), 3.96 (t, *J* = 6.2 Hz, 4H), 1.89-1.59 (m, 12H), 1.52-1.43 (m, 8H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 162.3, 133.9, 119.3, 115.2, 103.6, 68.1, 30.3 (d, *J* = 13.6 Hz), 28.7, 28.1 (d, *J* = 65.3 Hz), 25.5, 21.7 (d, *J* = 3.6 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.57 (d, *J* = 448.0 Hz); **HRMS:** [M+H]$^+$ m/z calcd for $C_{26}H_{34}N_2O_3P^+$ 475.2021, found 475.2021

Dimethyl 4,4'-(((oxo-l5-phosphanediyl)bis(hexane-6,1-diyl))bis(oxy))dibenzoate (4v, new compound)



Colorless oil; 79.3 mg, 51% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.97 (d, *J* = 8.5 Hz, 4H), 6.89 (d, *J* = 9.2 Hz, 4H), 6.88 (d, *J* = 445.7 Hz, 1H), 4.00 (t, *J* = 6.3 Hz, 4H), 3.87 (s, 6H), 1.88-1.62 (m, 12H), 1.54-1.48 (m, 8H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 167.1, 163.0, 131.8, 122.7, 114.3, 68.1, 30.6 (d, *J* = 13.4 Hz), 29.1, 28.5 (d, *J* = 65.3 Hz), 25.9, 22.0 (d, *J* = 3.6 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.26 (d, *J* = 447.6 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{28}H_{39}O_7PNa^+$ 541.2326, found 541.2322.

Bis(6-(naphthalen-2-yloxy)hexyl)phosphine oxide (4w, new compound)

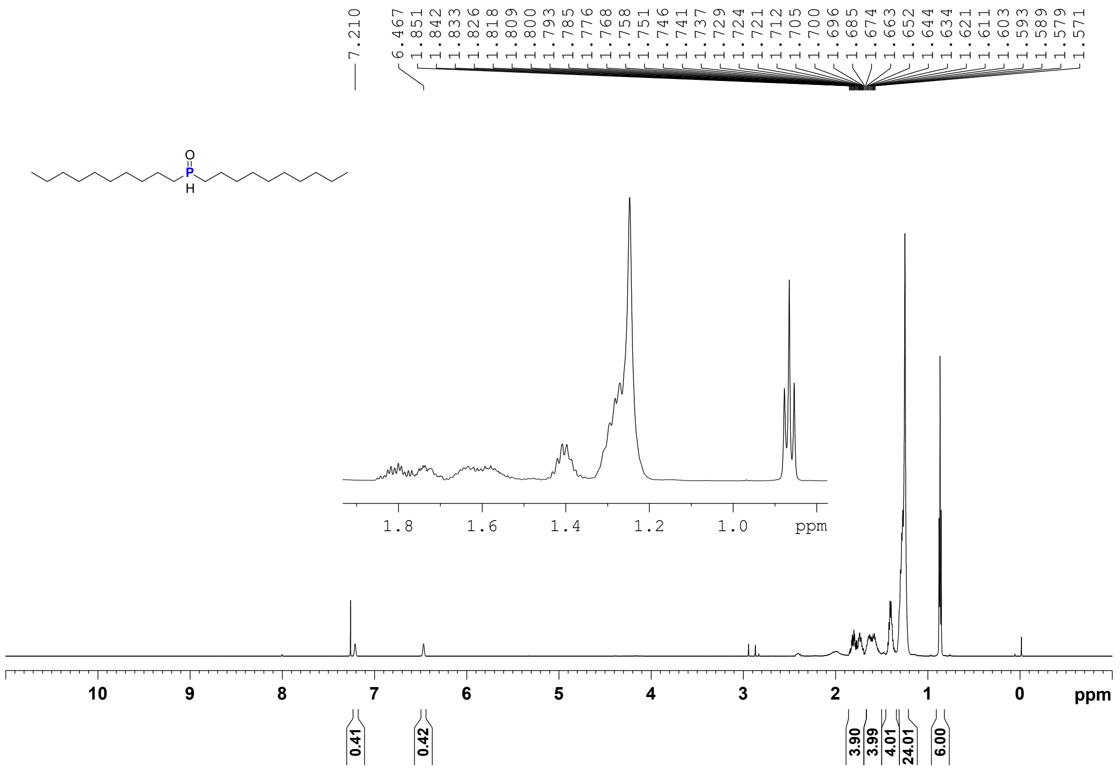


White solid; 107.0 mg, 71% yield; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 7.76-7.71 (m, 6H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.15-7.12 (m, 4H), 6.86 (d, *J* = 447.1 Hz, 1H), 4.07 (t, *J* = 6.6 Hz, 4H), 1.88-1.81 (m, 6H), 1.78-1.69 (m, 4H), 1.67-1.61 (m, 2H), 1.58-1.49 (m, 8H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 157.2, 134.8, 129.5, 129.1, 127.8, 126.9, 126.5, 123.7, 119.1, 106.7, 67.8, 30.6 (d, *J* = 14.0 Hz), 29.1, 28.4 (d, *J* = 65.0 Hz), 25.9, 22.0 (d, *J* = 4.4 Hz); **^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz):** δ 34.55 (d, *J* = 447.1 Hz); **HRMS:** [M+Na]$^+$ m/z calcd for $C_{32}H_{39}O_3PNa^+$ 525.2529, found 525.2529.

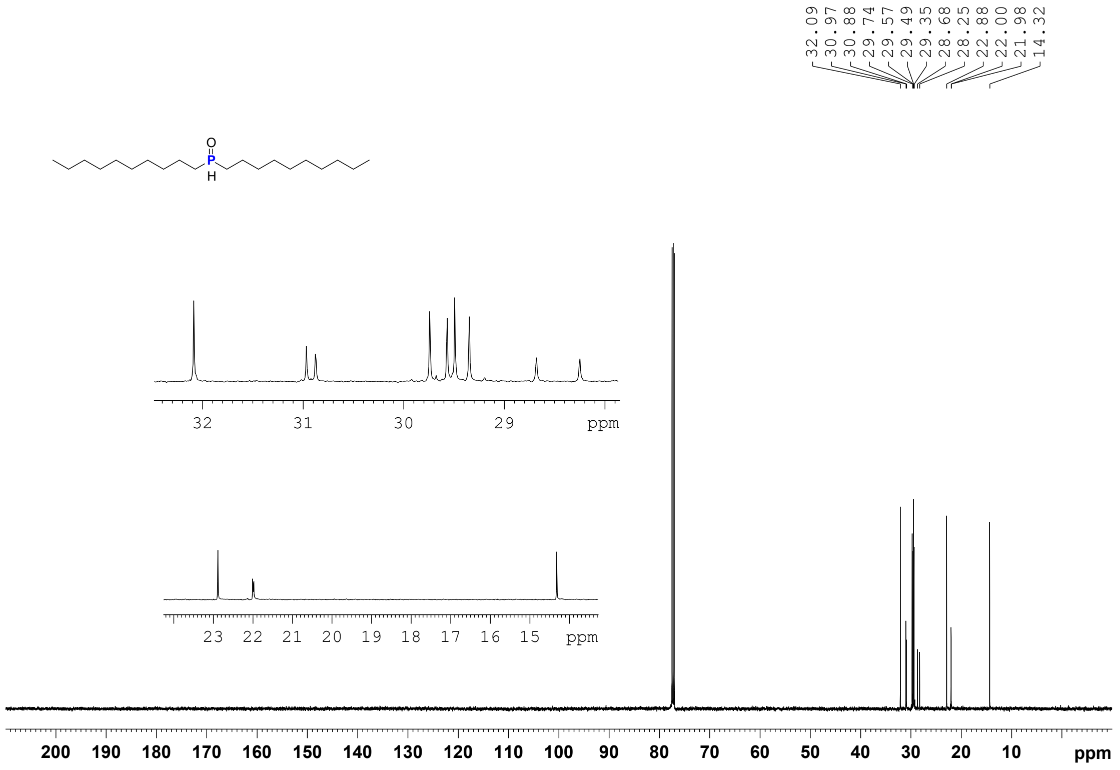
8. Supplementary Reference

1. F. Chen, M. Bai, Y. Zhang, W. Liu, X. Huangfu, Y. Liu, G. Tang and Y. Zhao, *Angew. Chem. Int. Ed*. 2022, **61**, doi.org/10.1002/anie.202210334.
2. H.-Q. Geng and X.-F. Wu, *Org. Lett*. 2021, **23**, 8062–8066.
3. M. Harmata, C. B. Gamlath, C. L. Barnes and D. E. Jones, *J. Org. Chem*. 1995, **60**, 5077–6092.

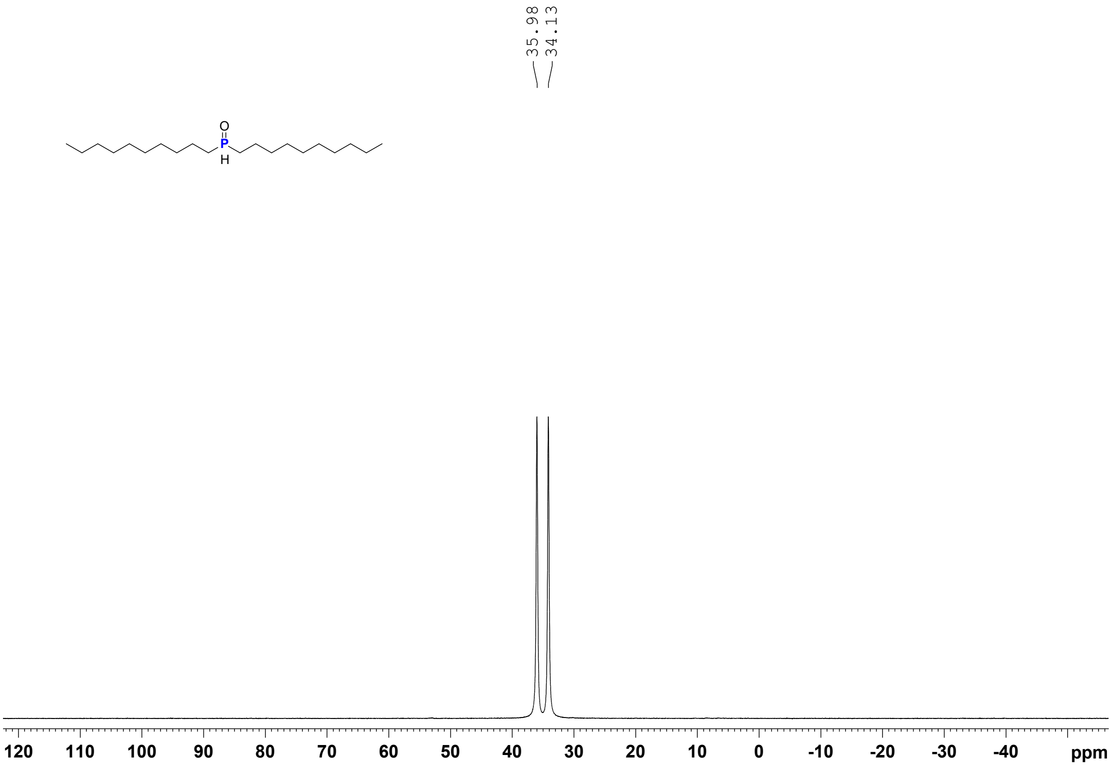
9. NMR spectrum of isolated products.



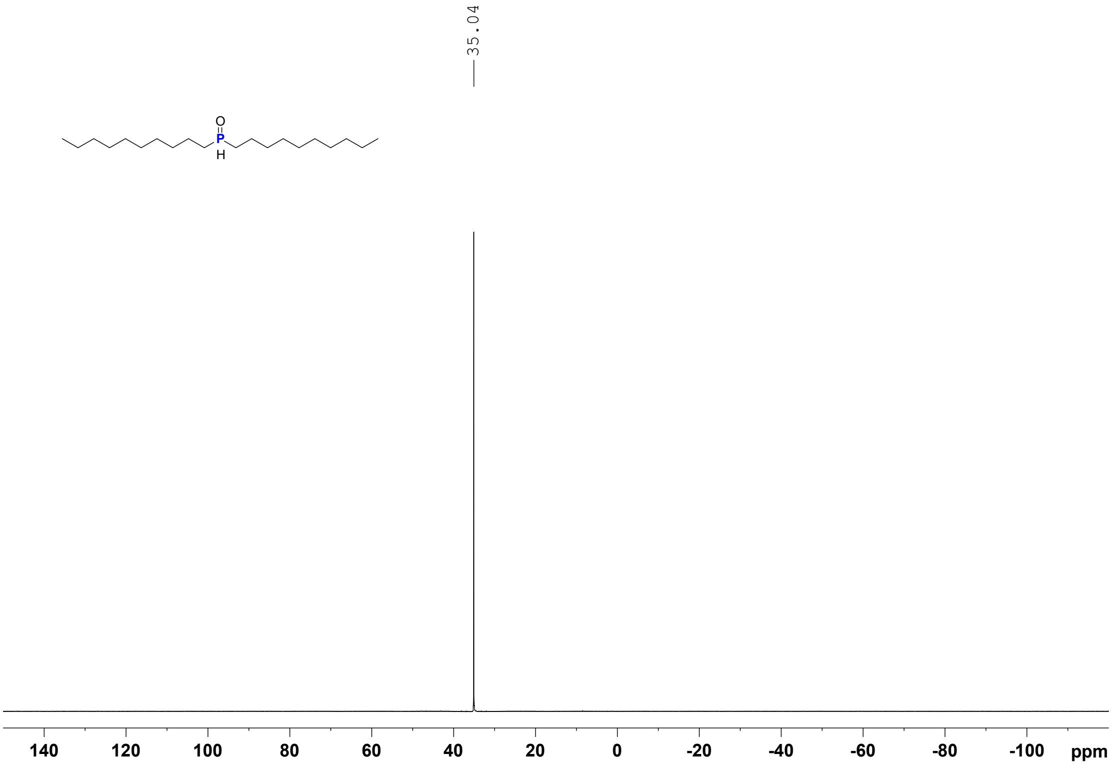
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4a**



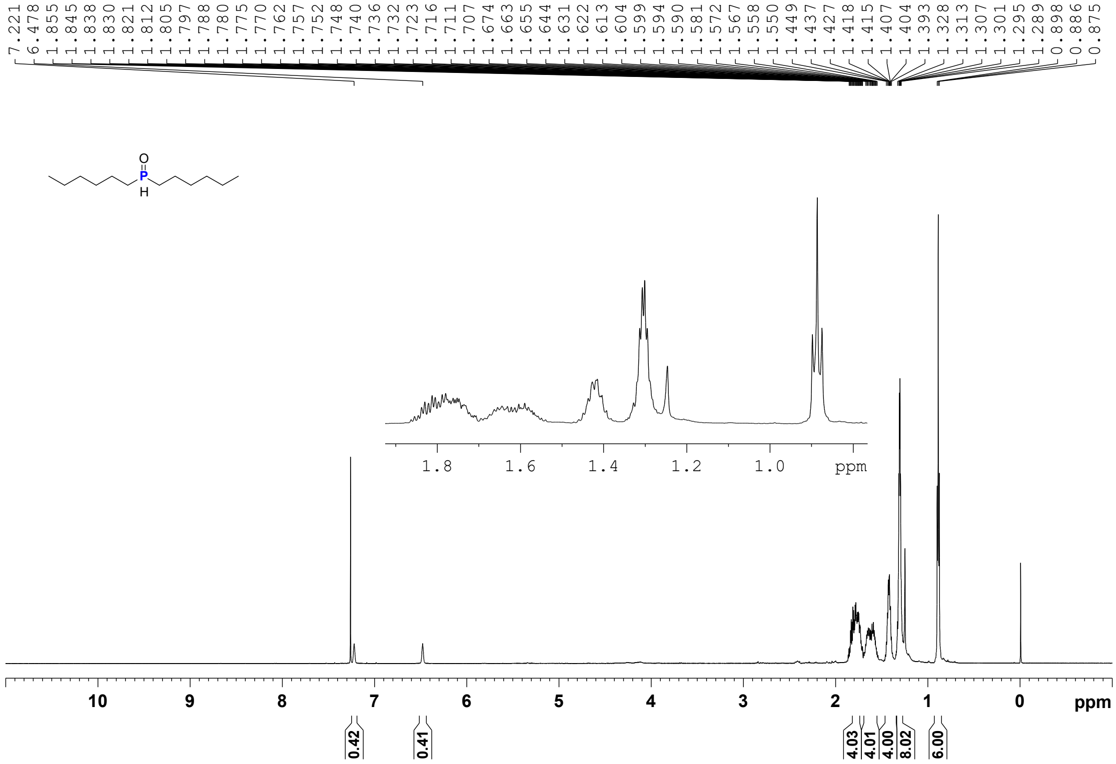
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4a**



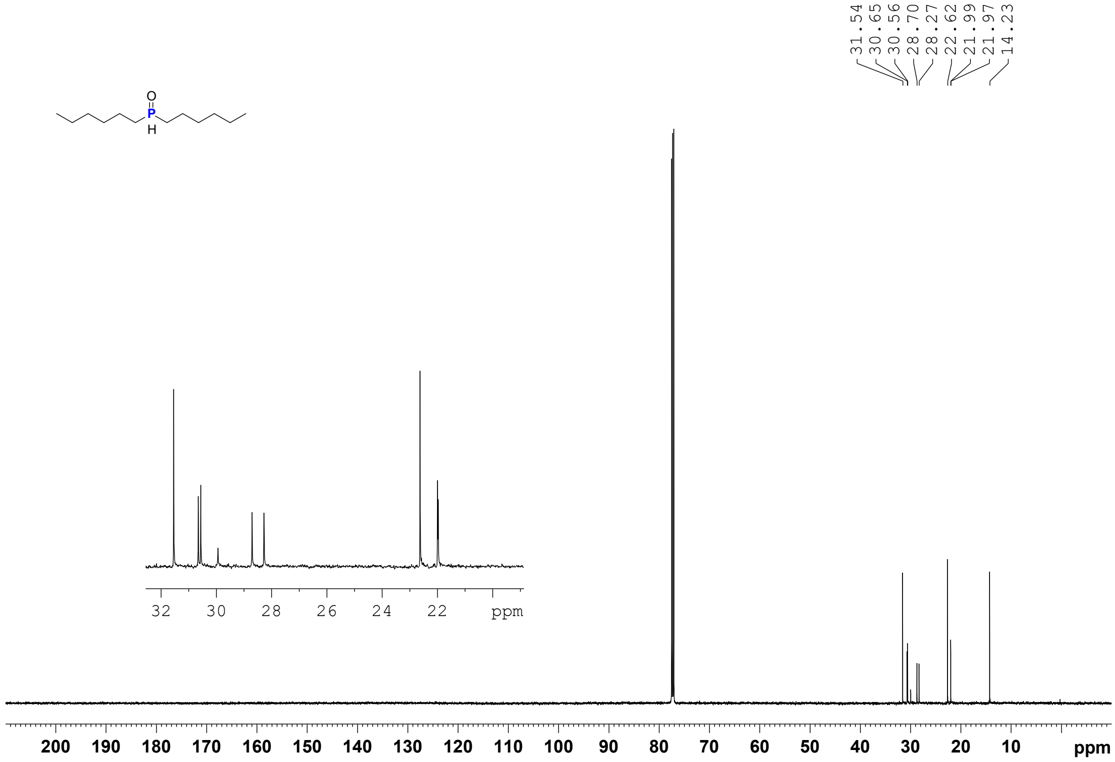
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4a**



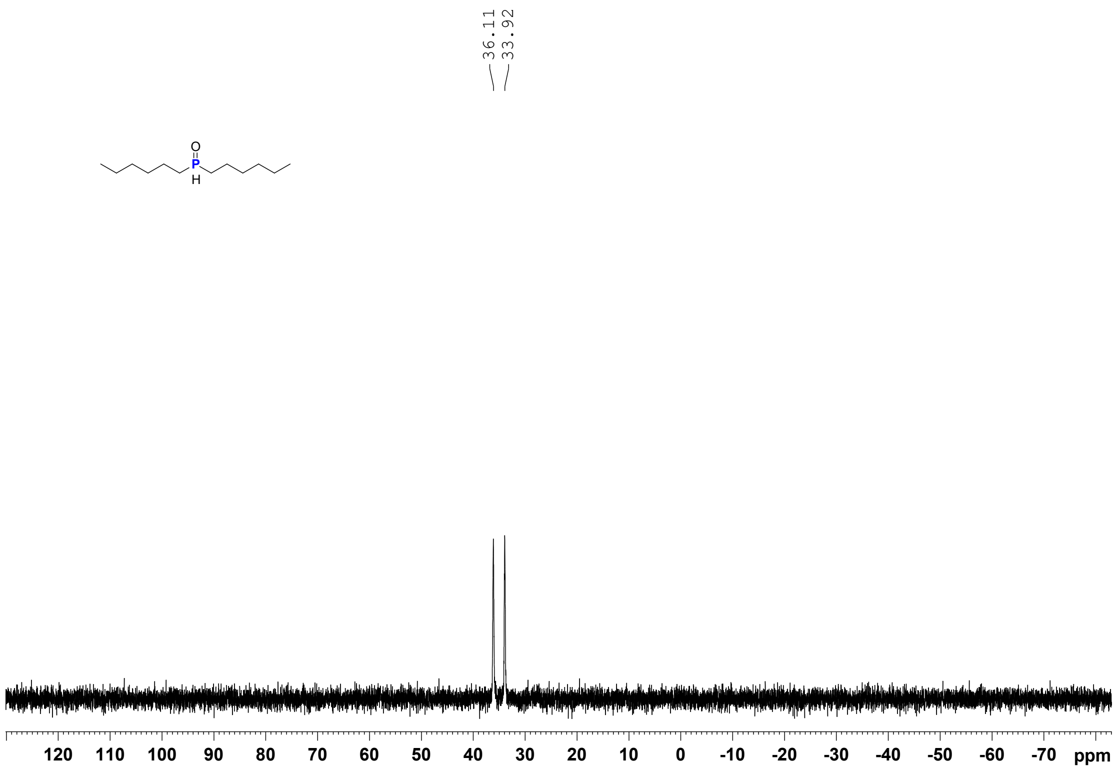
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4a**



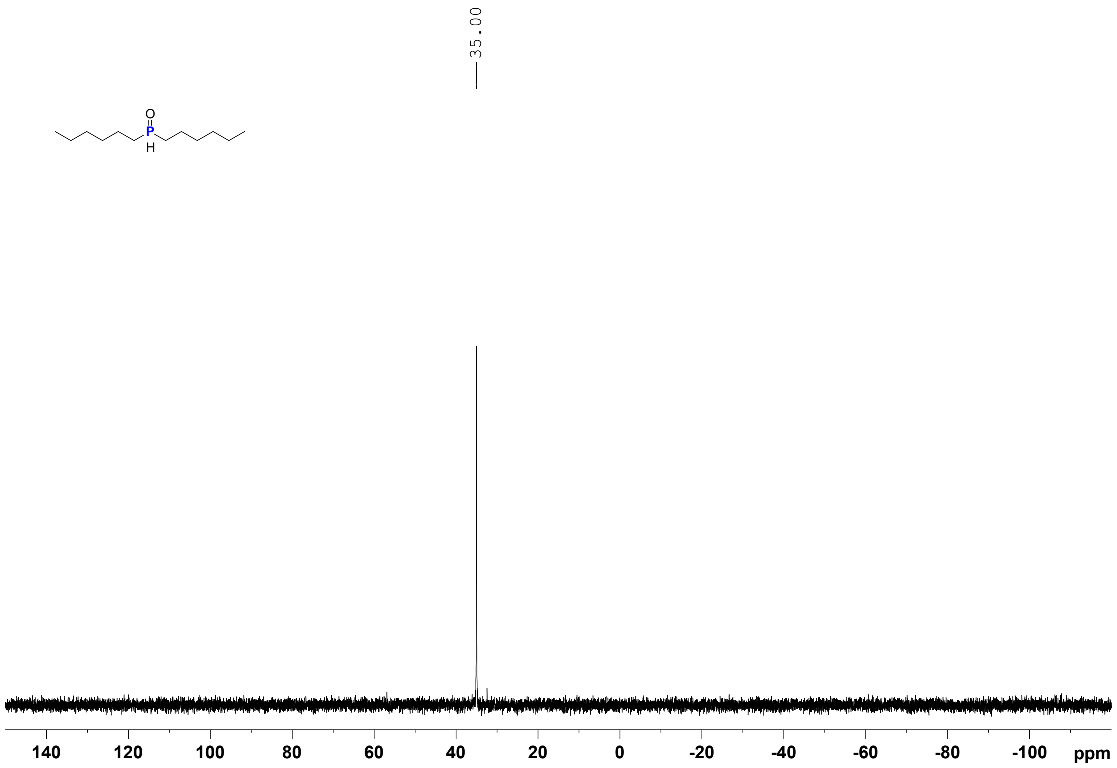
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4b**



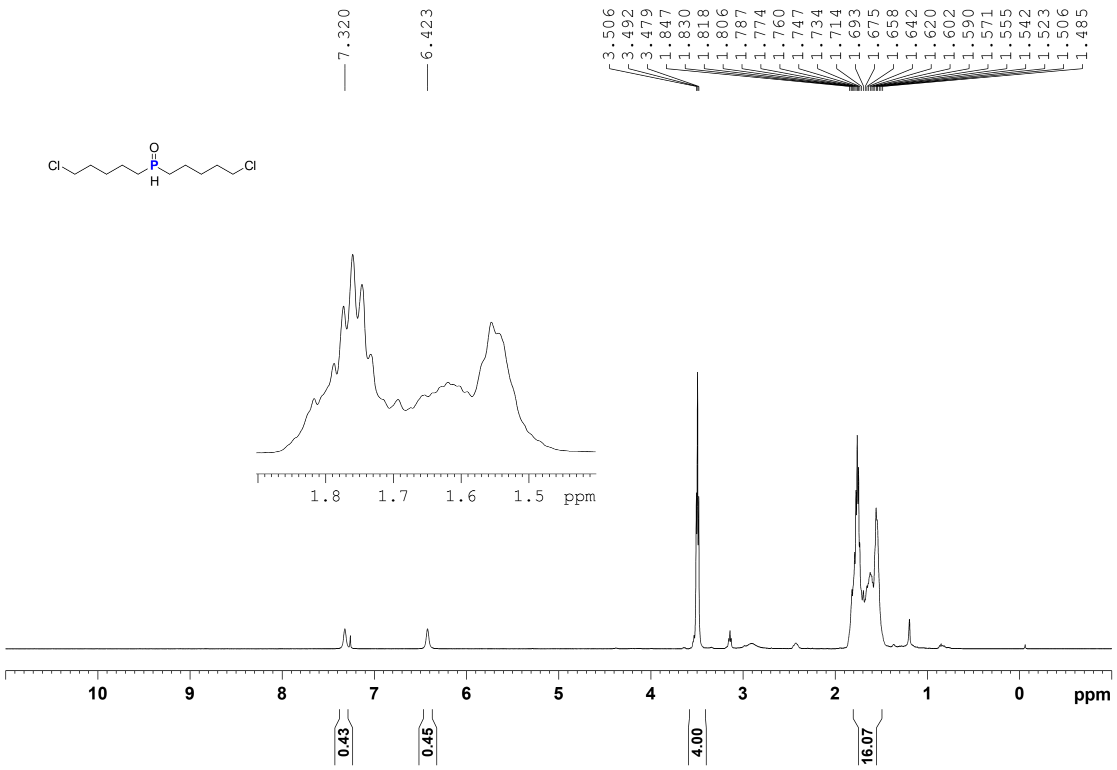
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4b**



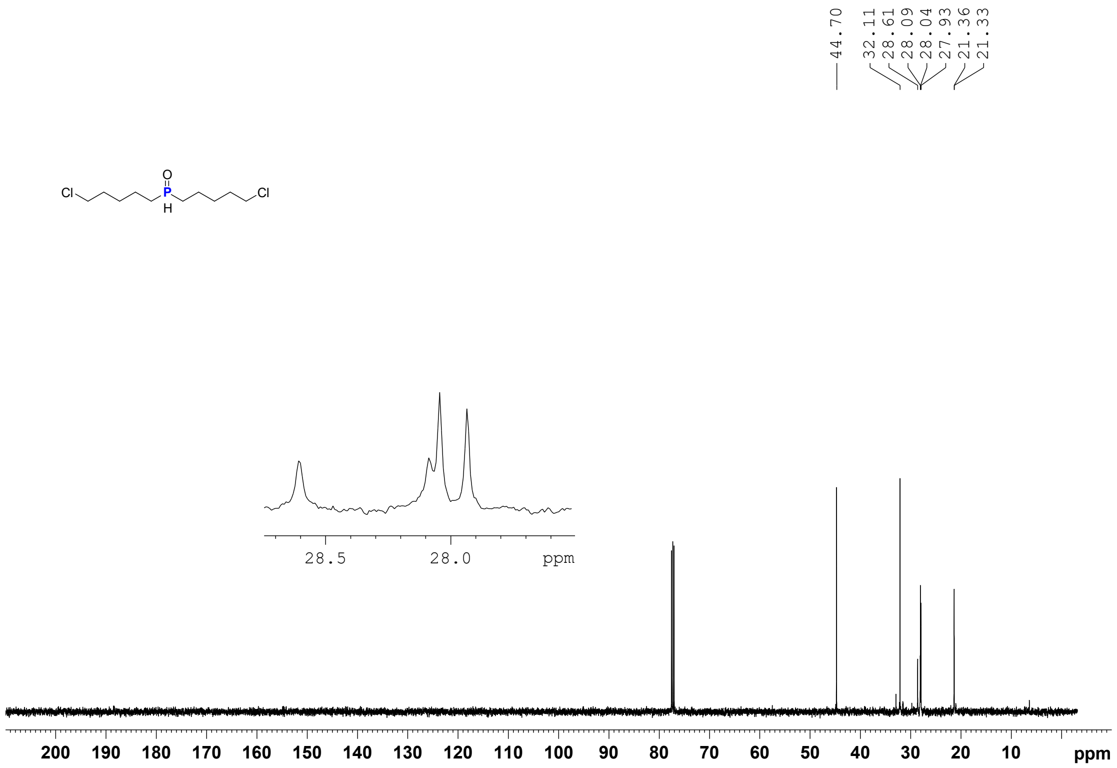
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **4b**



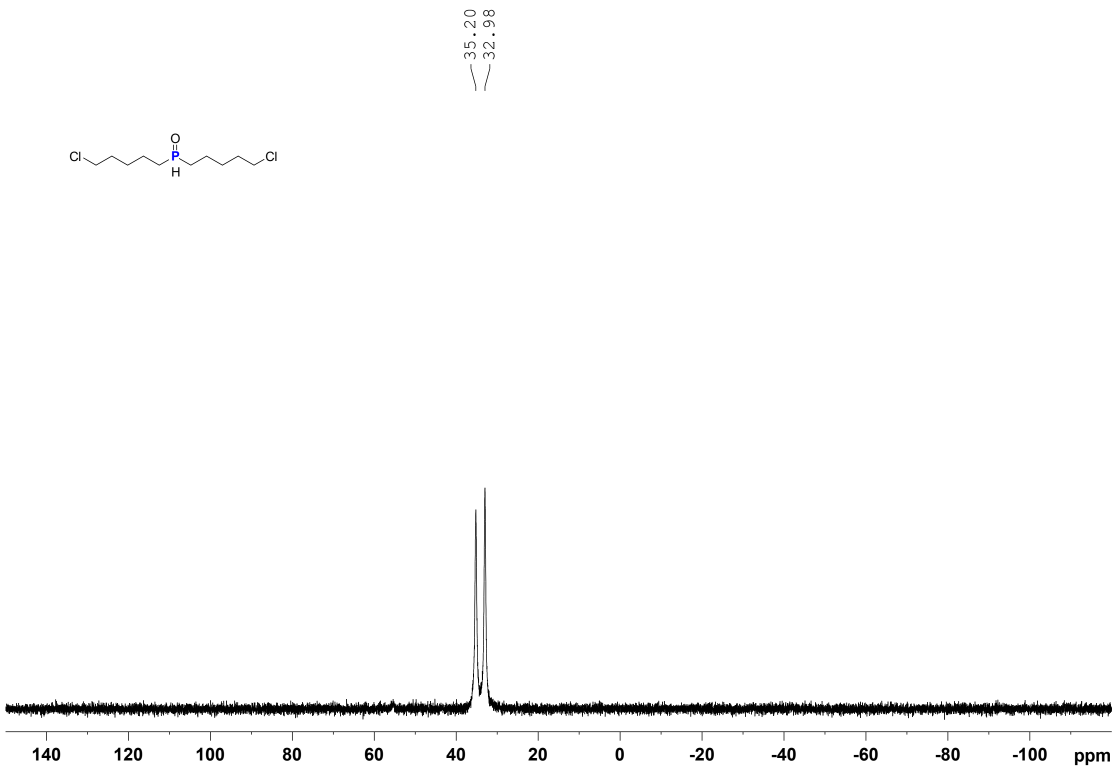
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) spectrum of compound **4b**



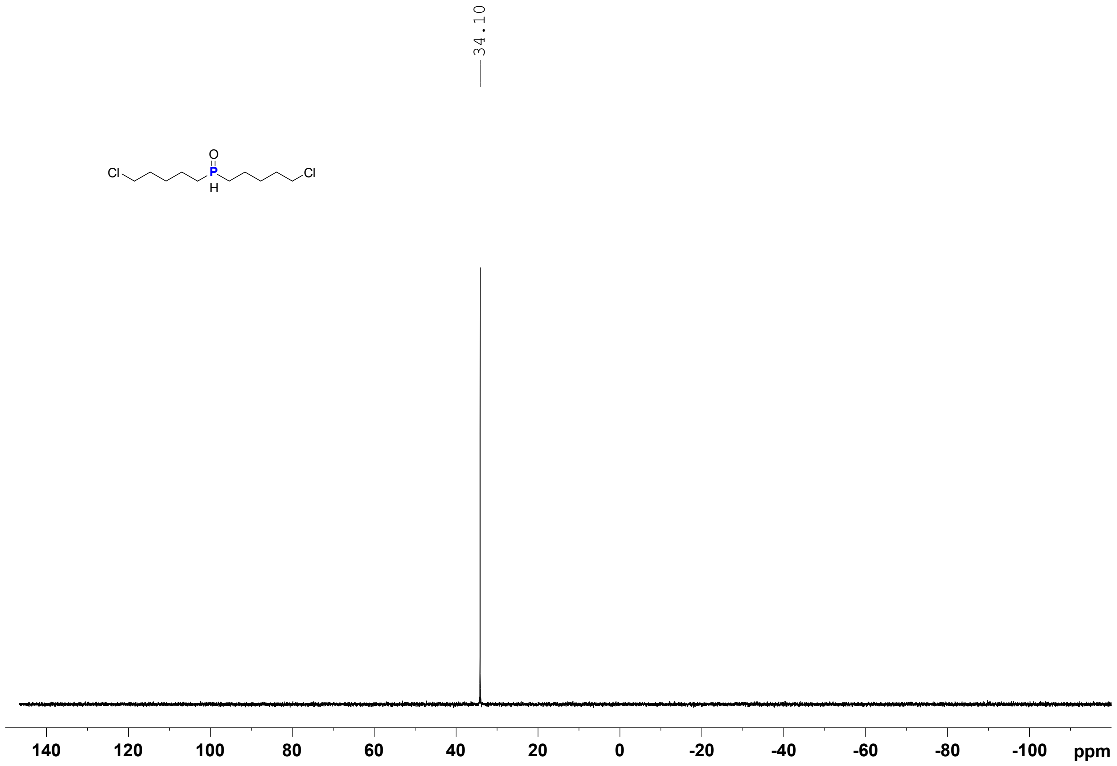
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4c**



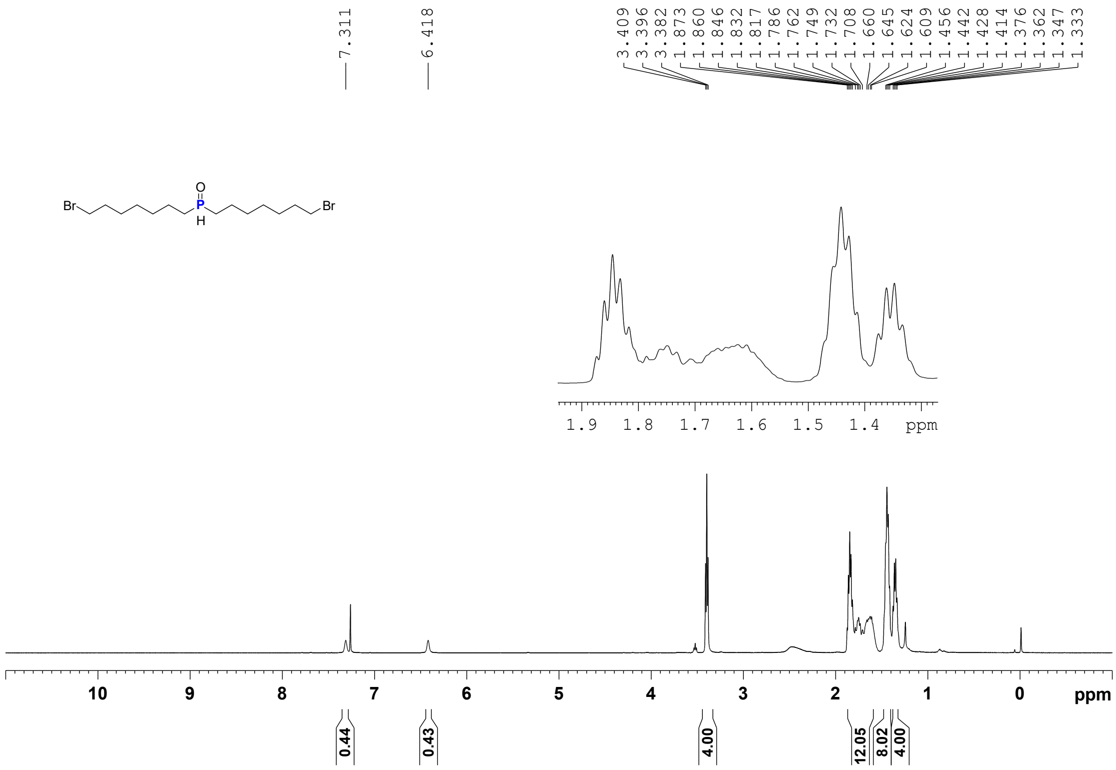
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4c**



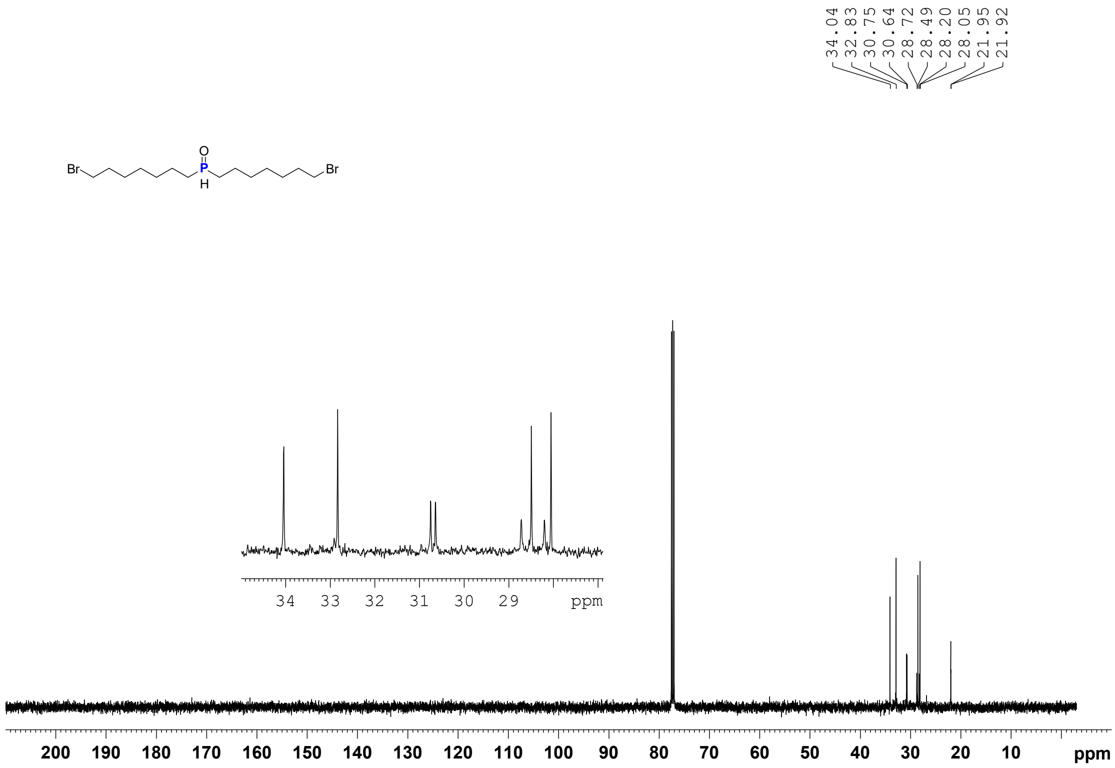
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4c**



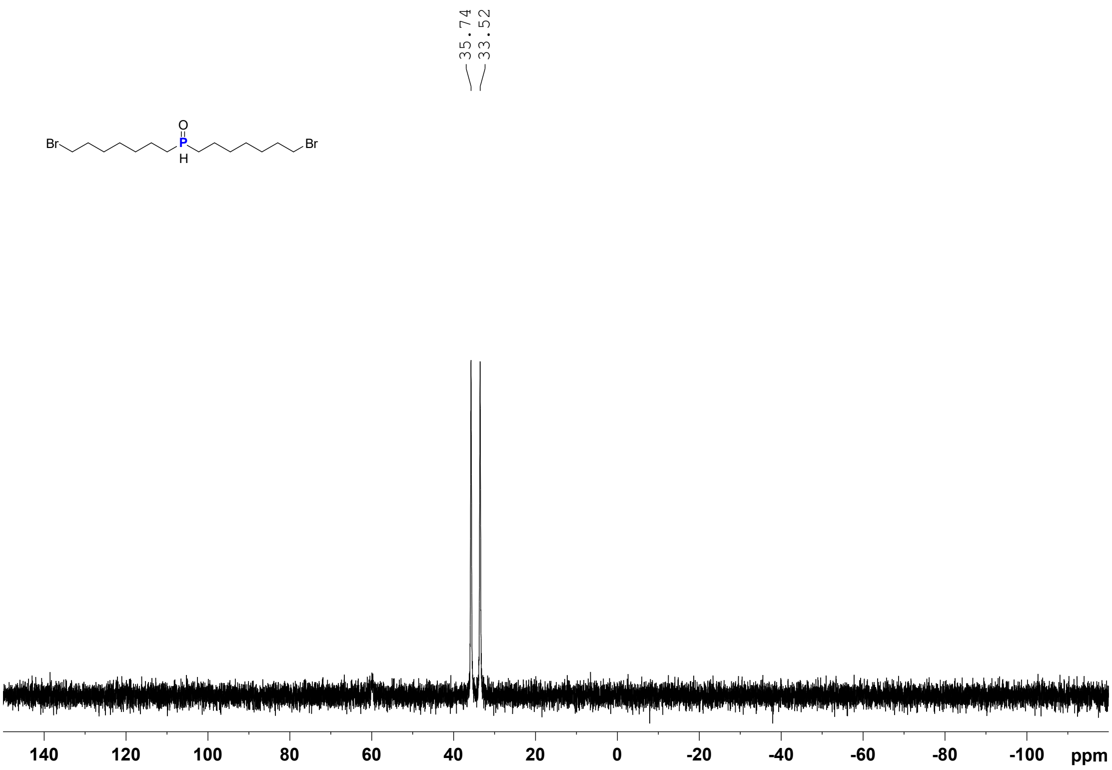
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4c**



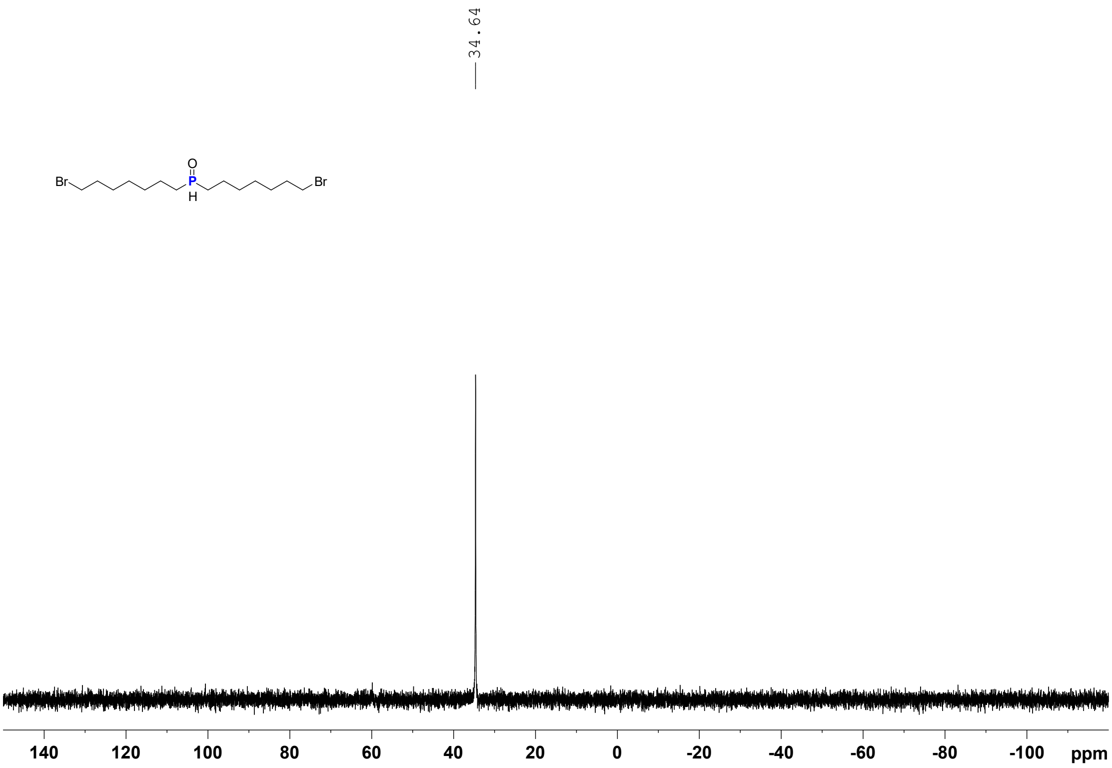
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4d**



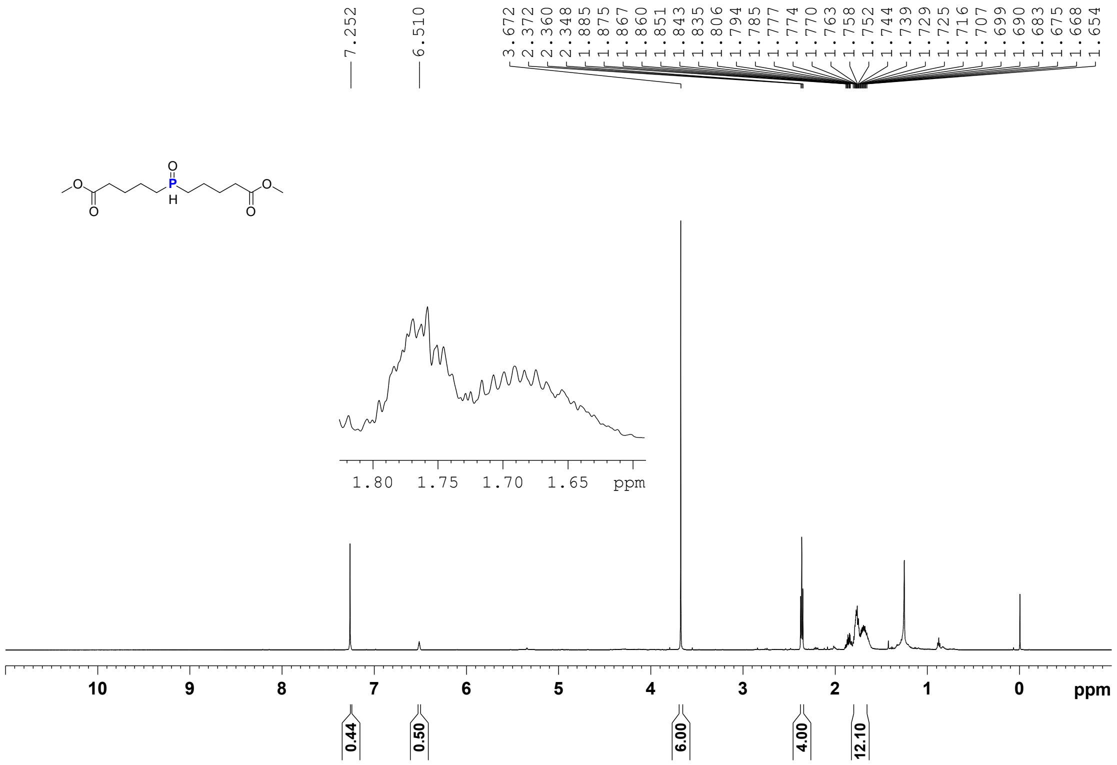
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4d**



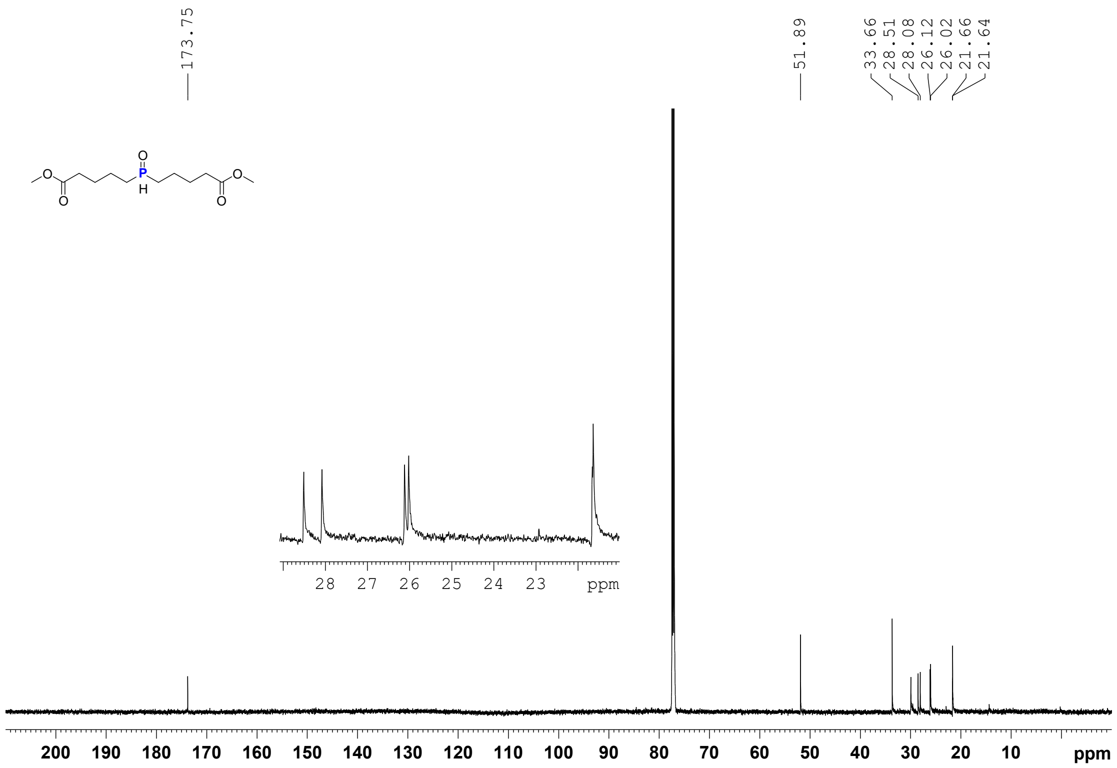
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4d**



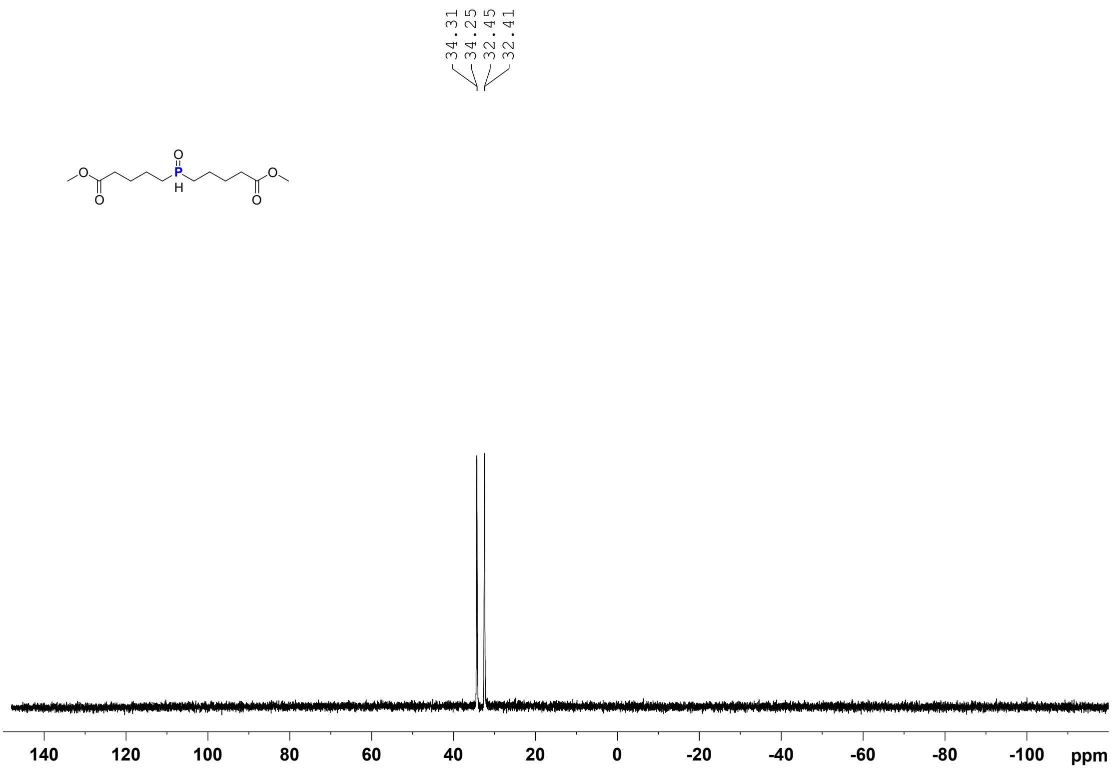
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4d**



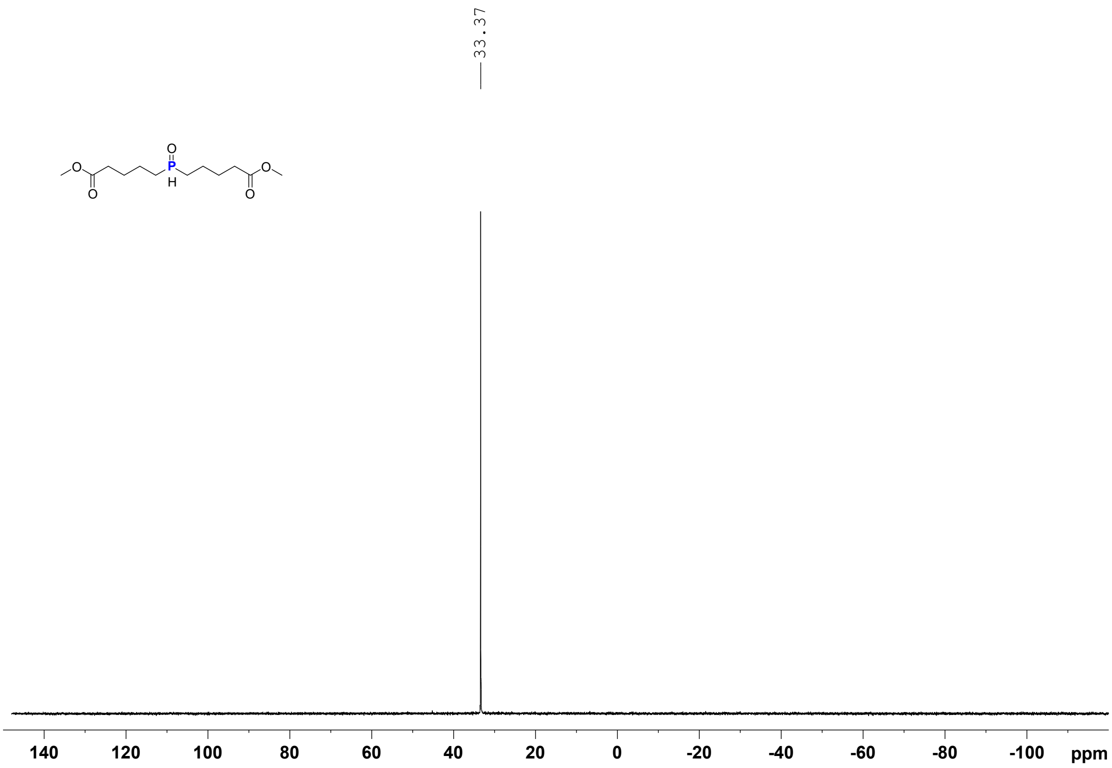
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4e**



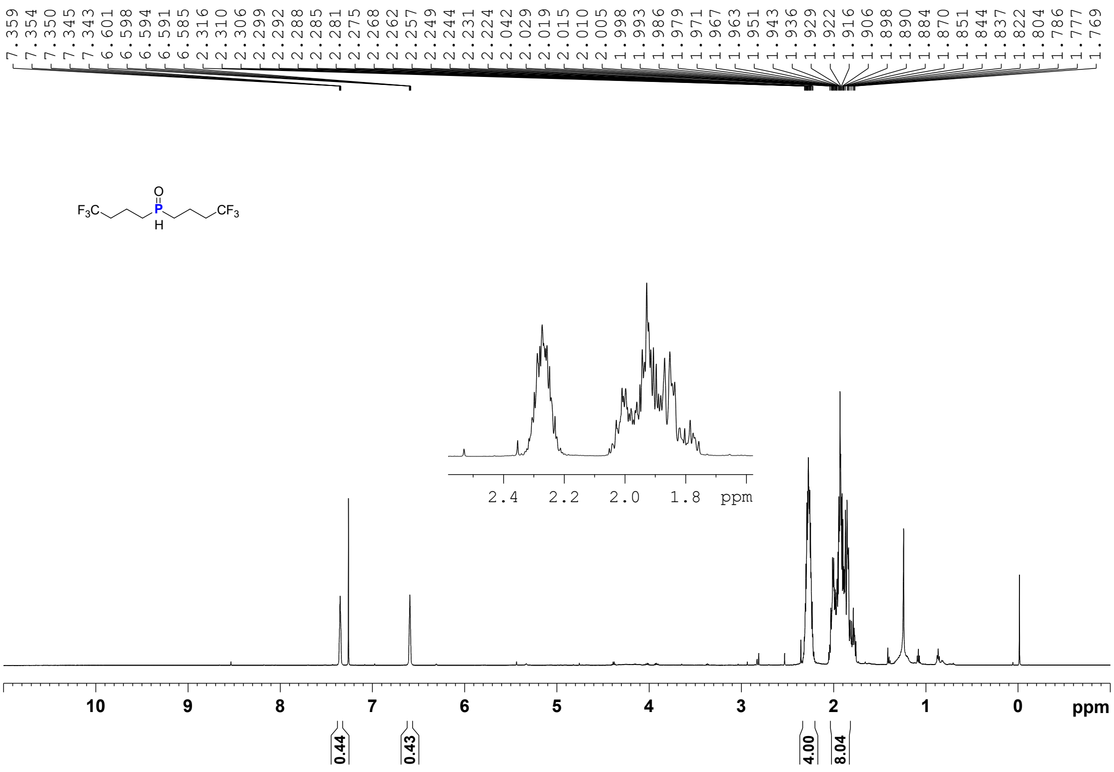
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4e**



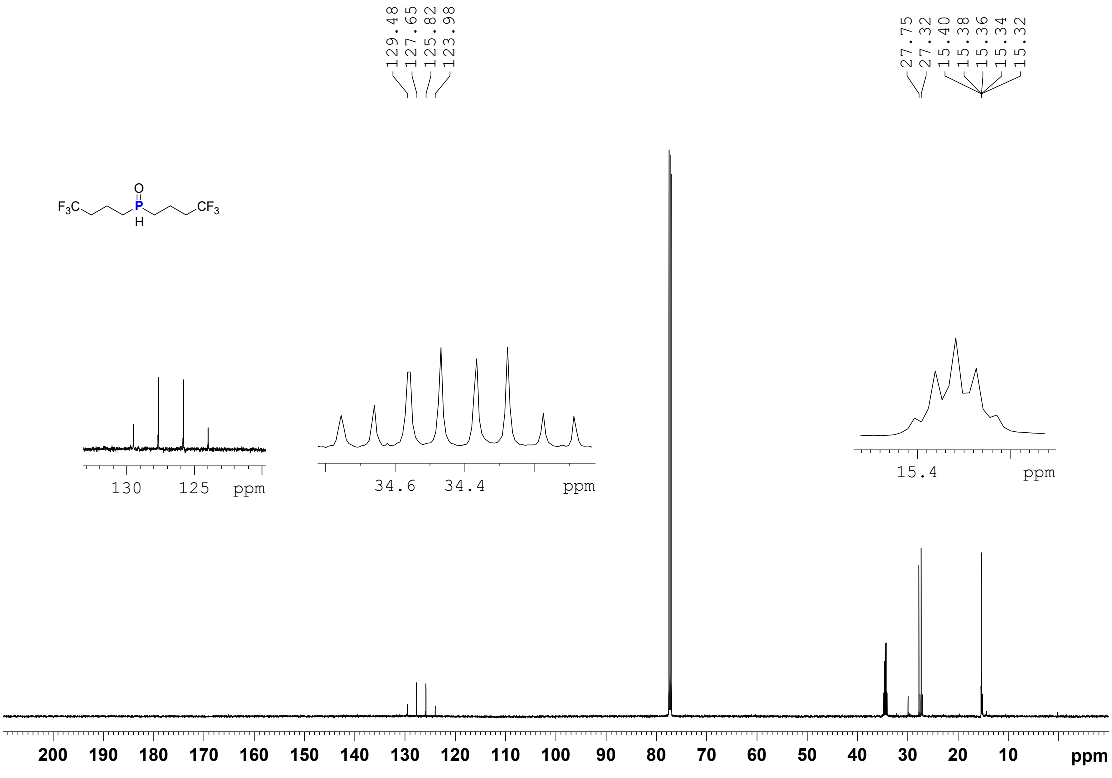
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **4e**



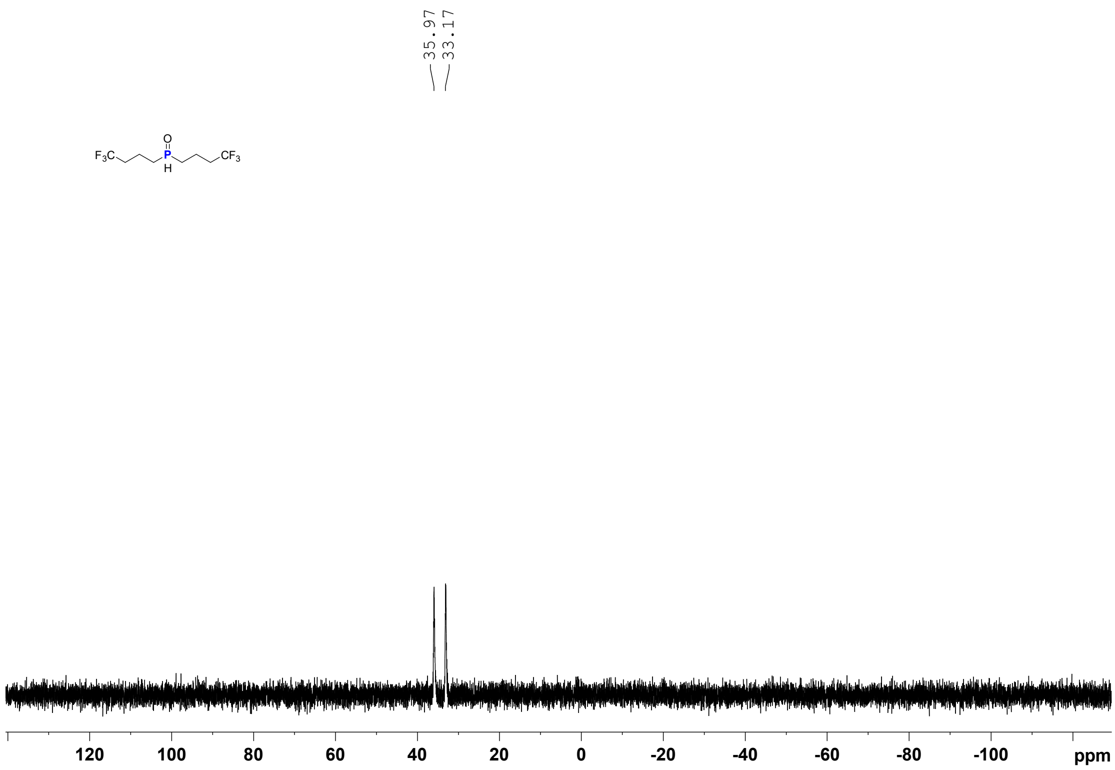
$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4e**



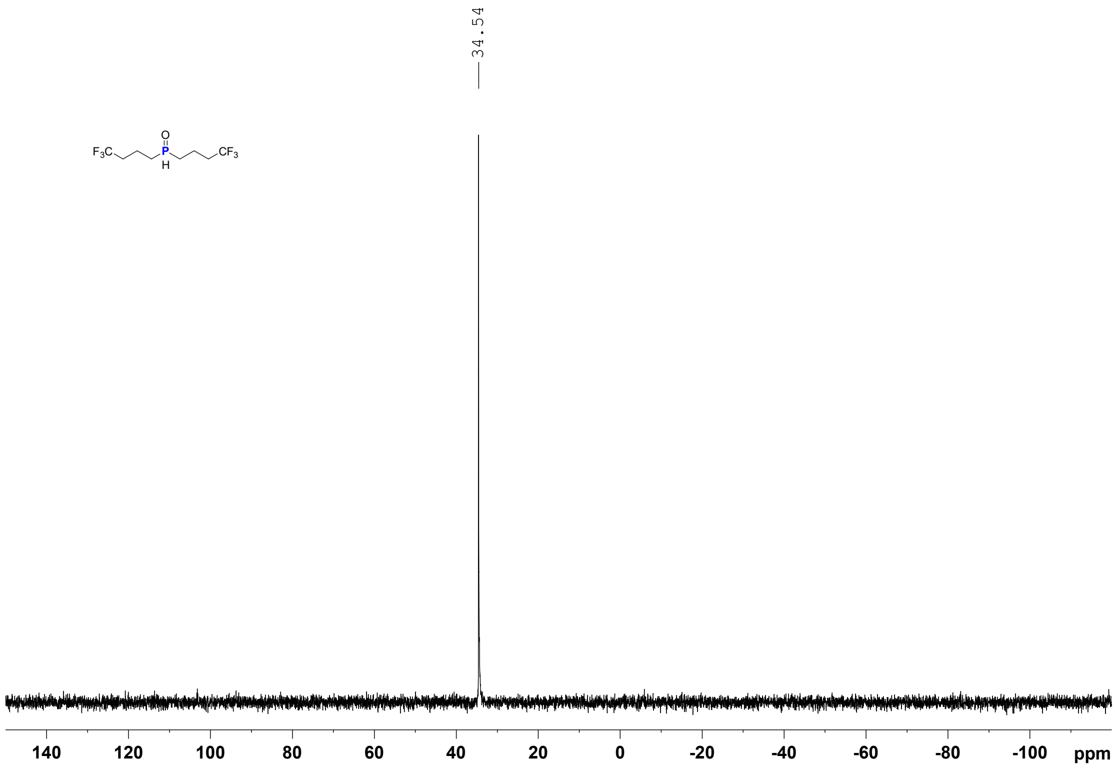
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4f**



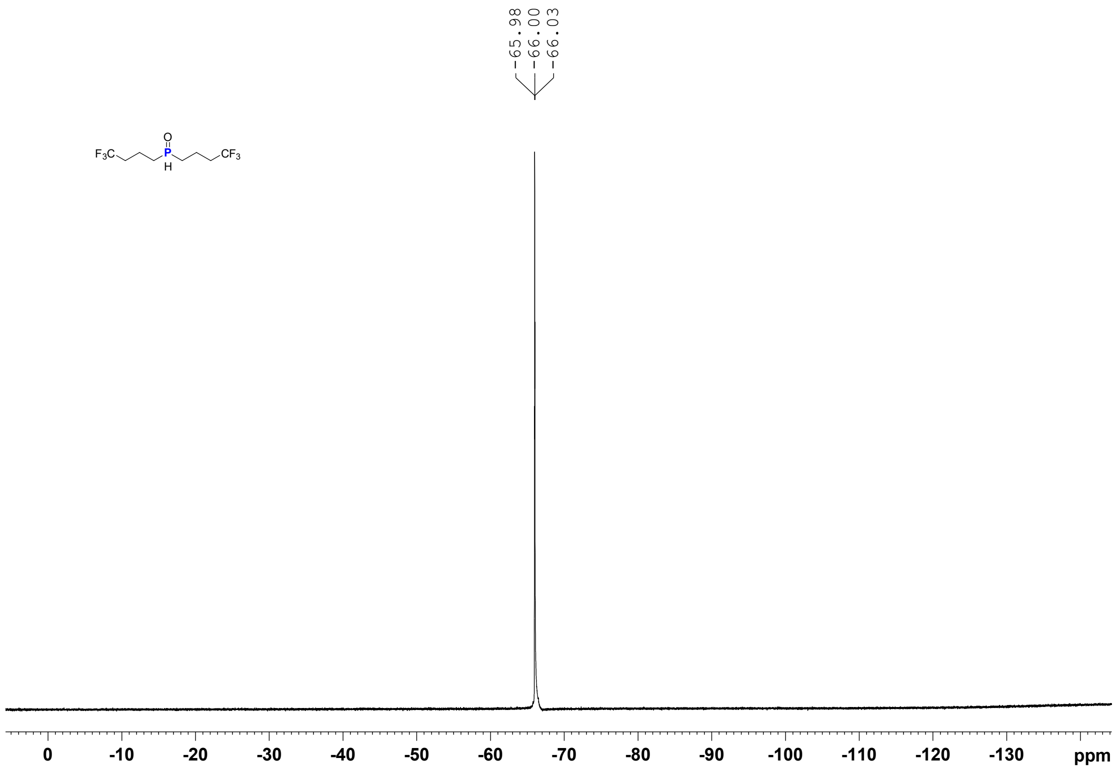
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4f**



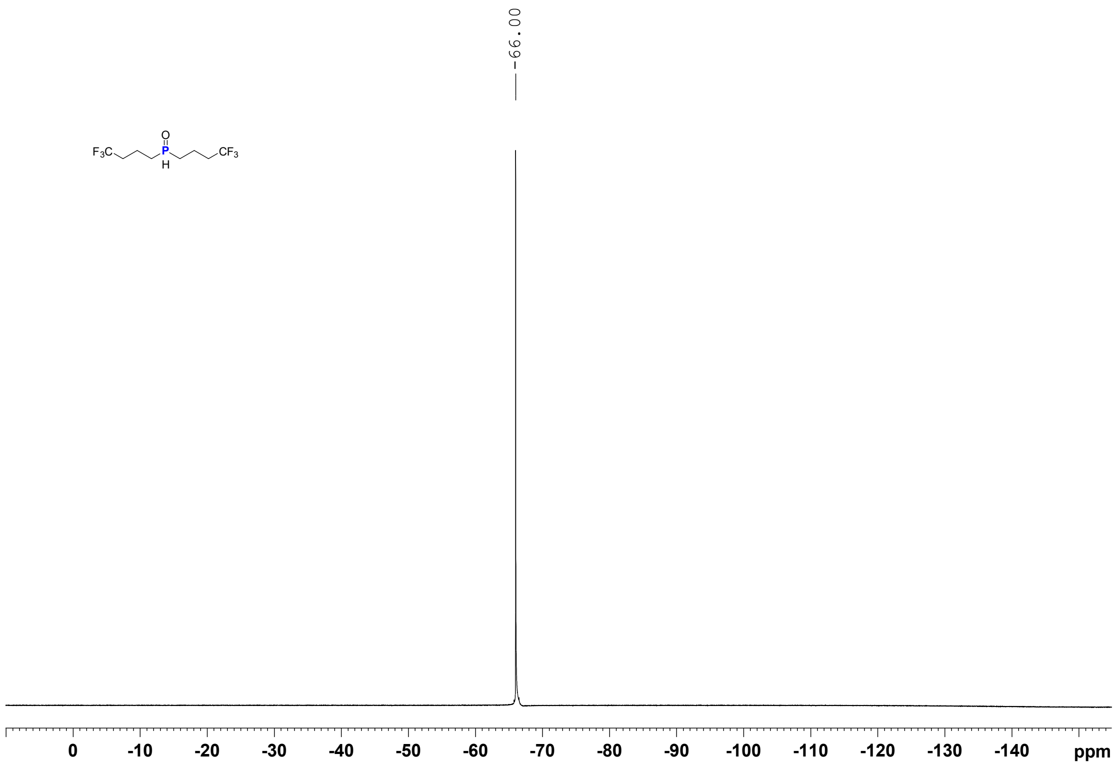
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4f**



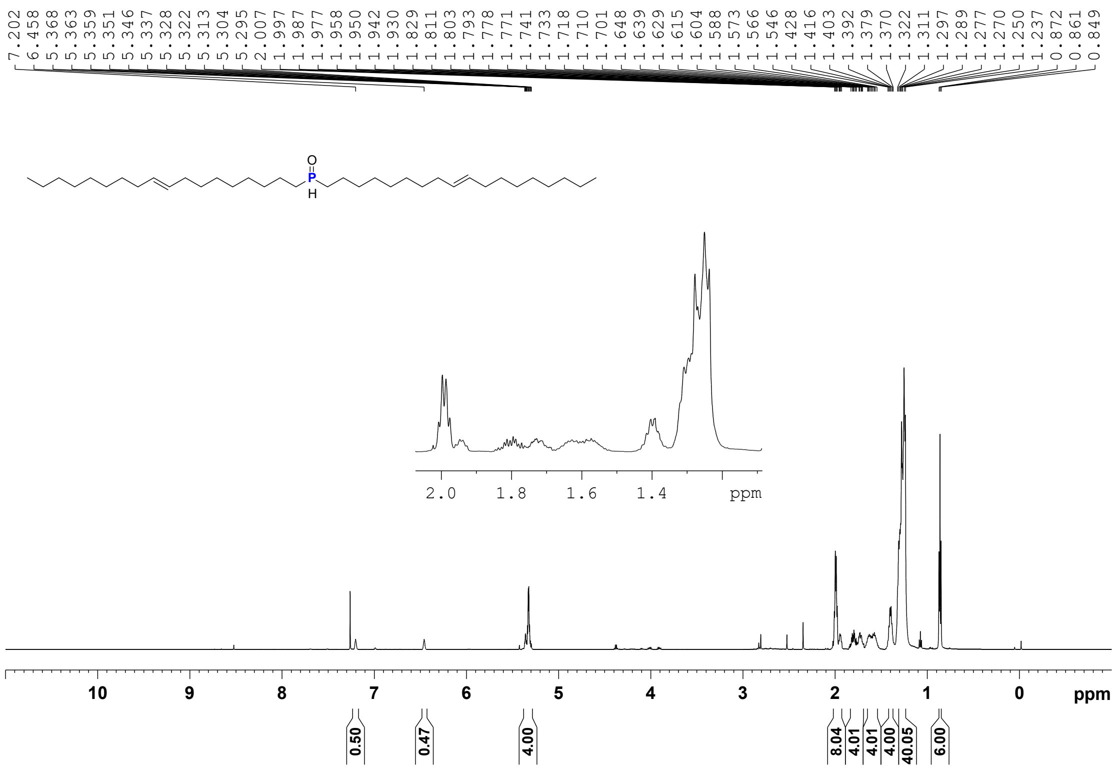
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4f**



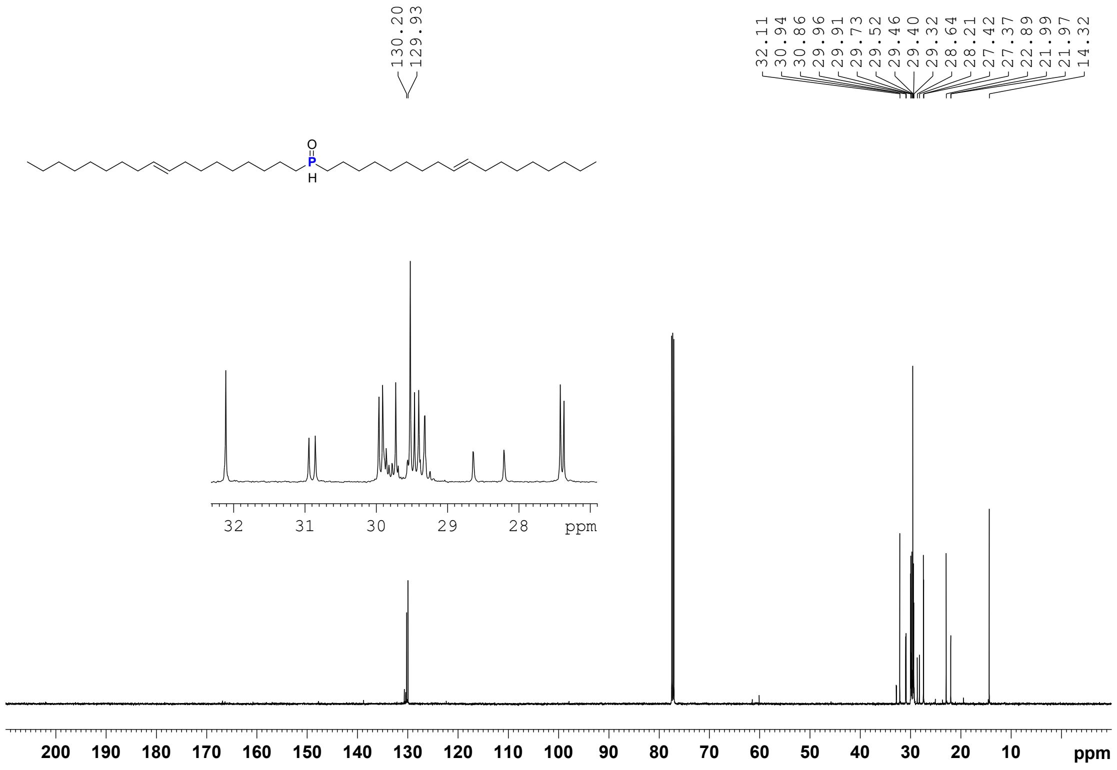
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound **4f**



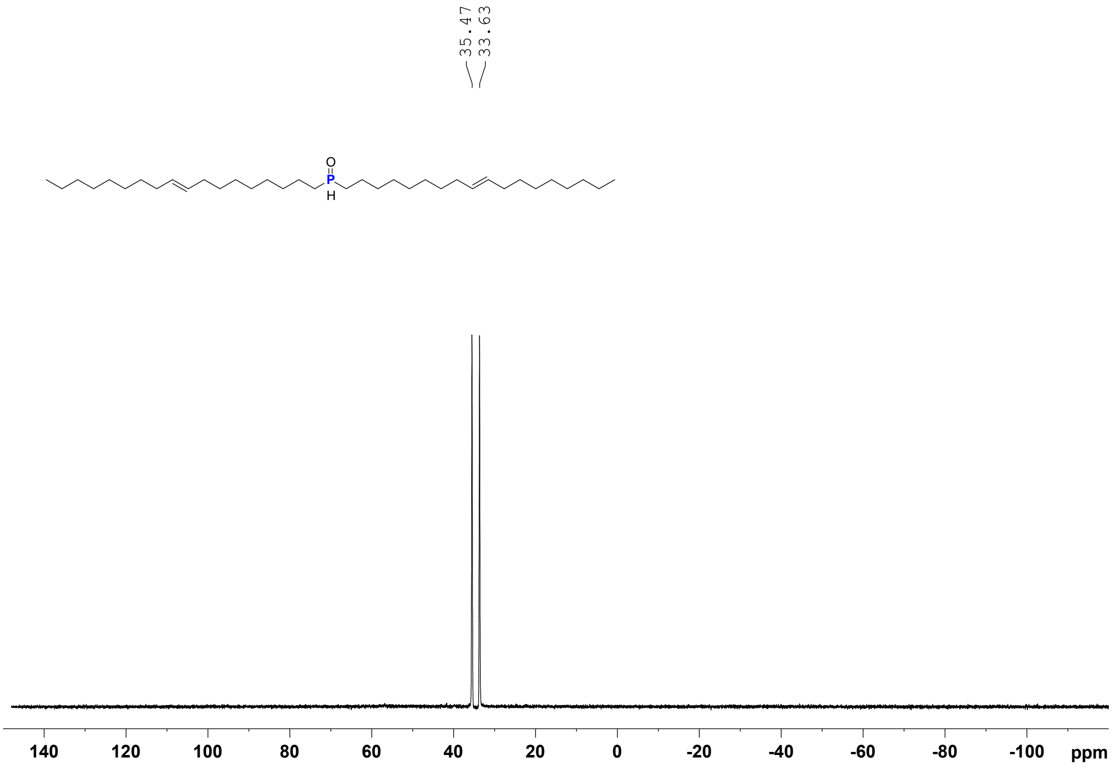
$^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$) spectrum of compound **4f**



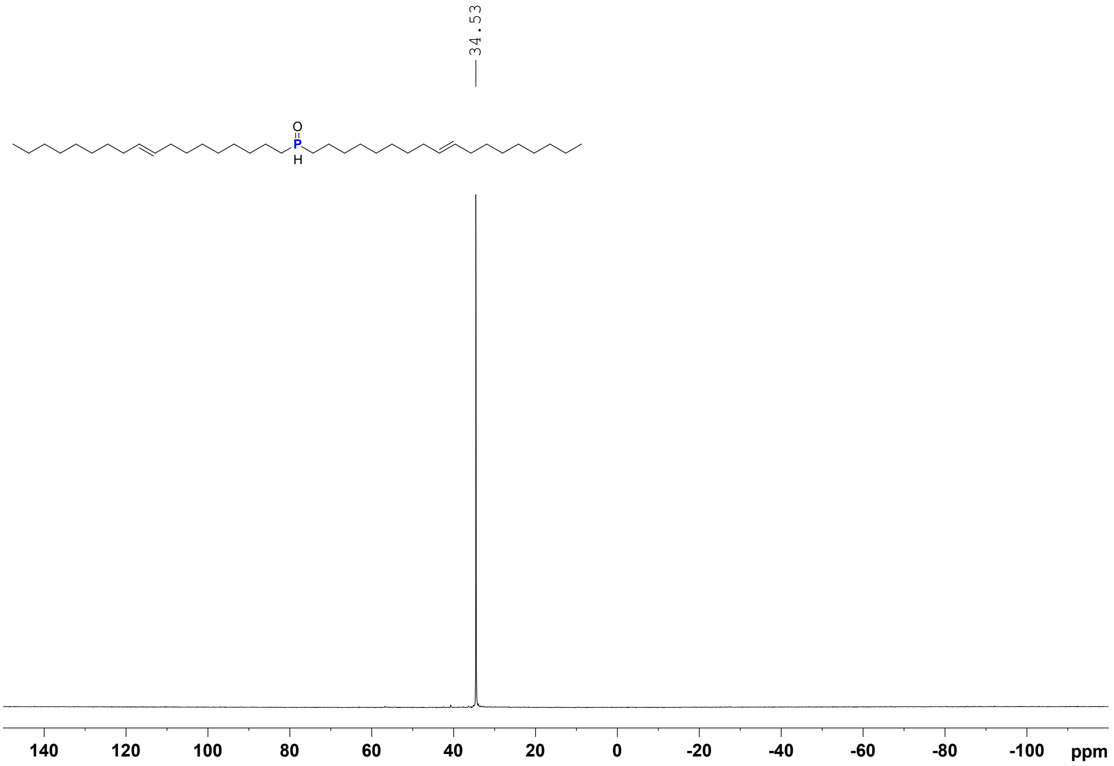
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4g**



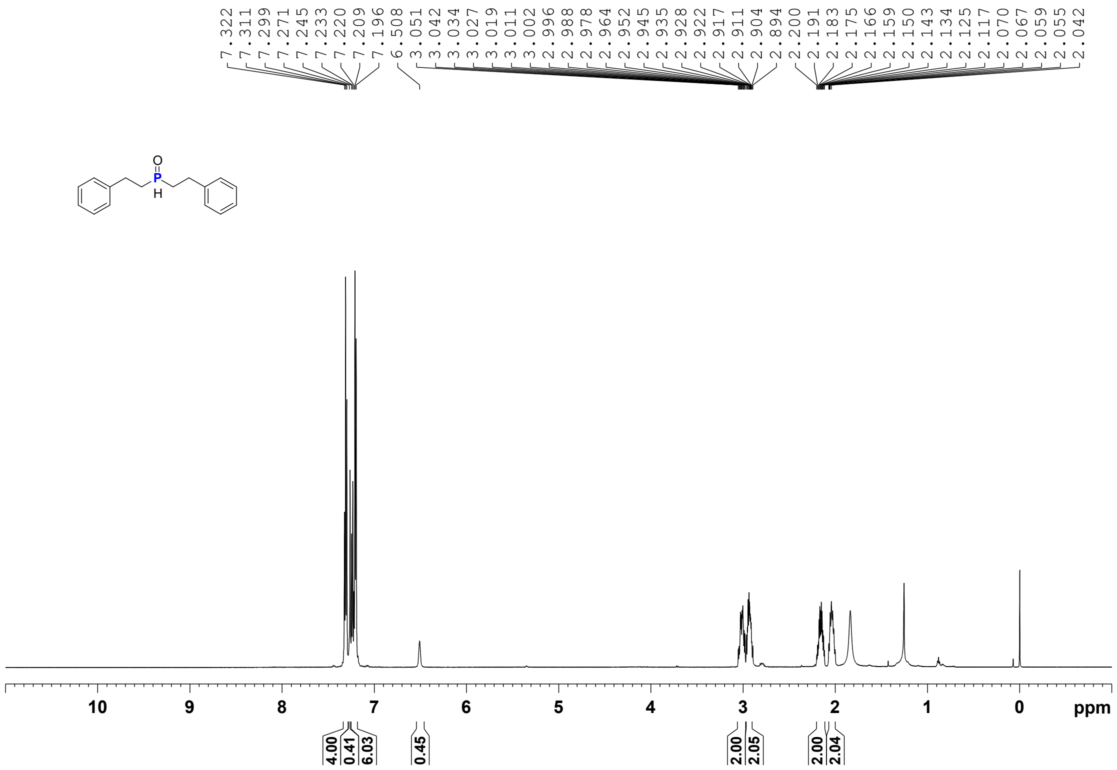
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4g**



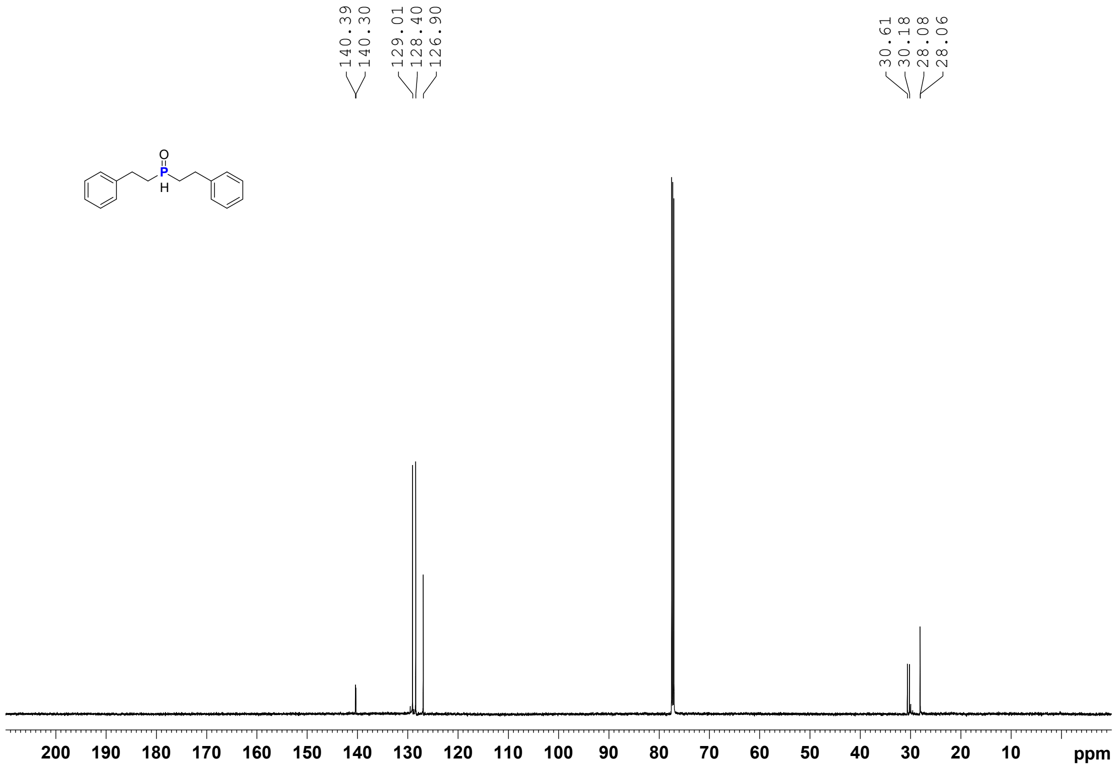
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4g**



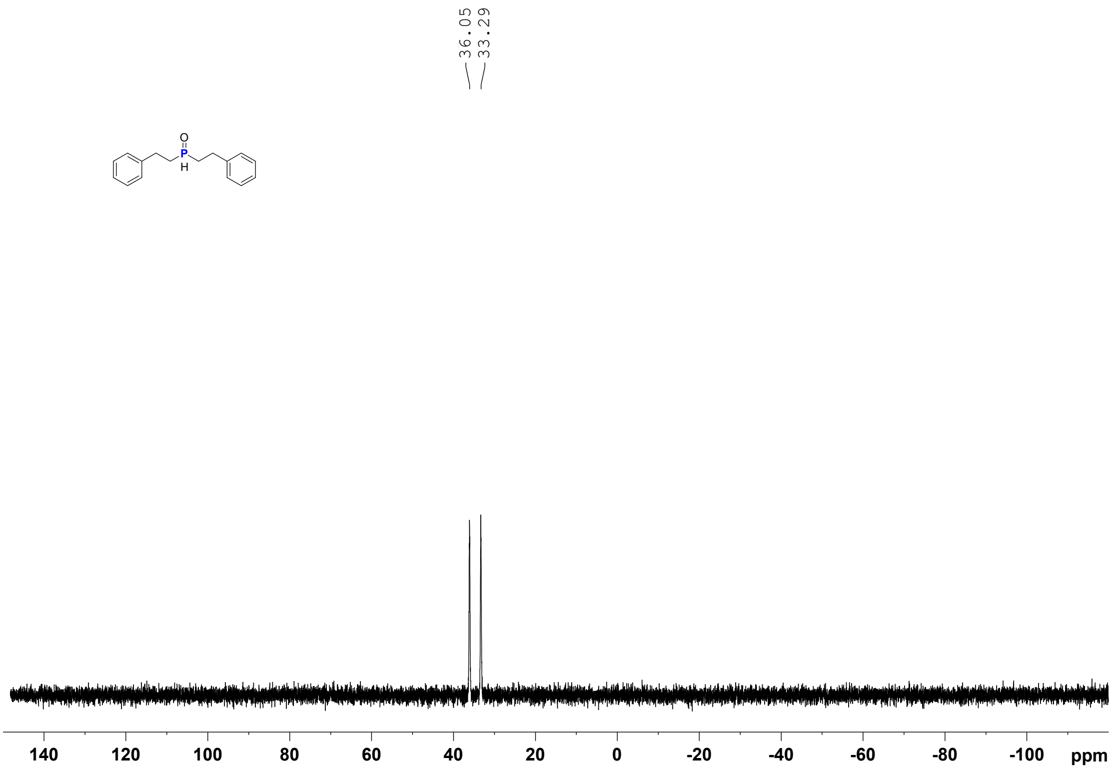
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4g**



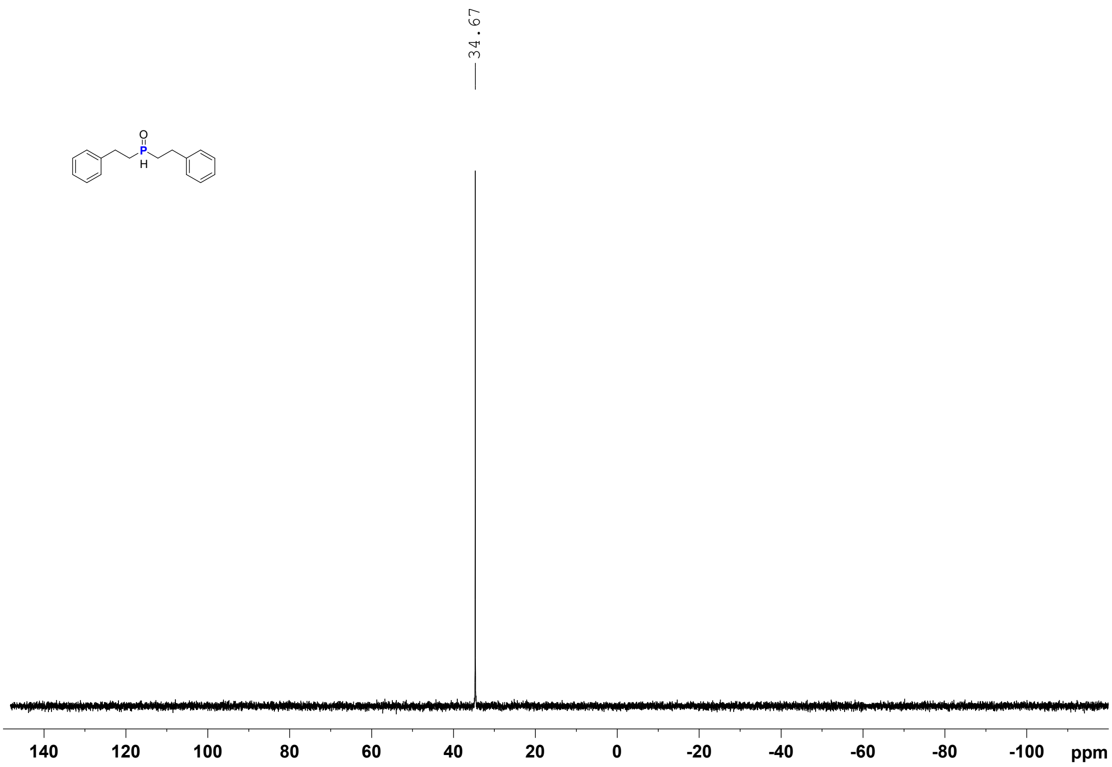
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4h**



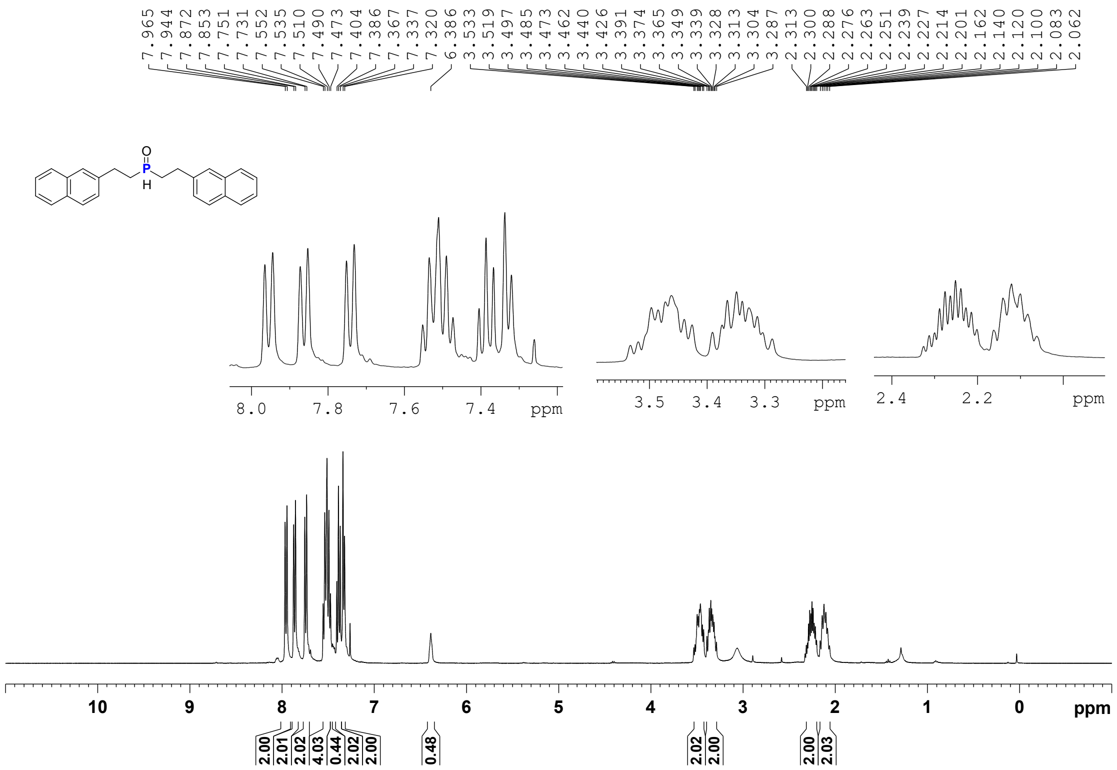
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4h**



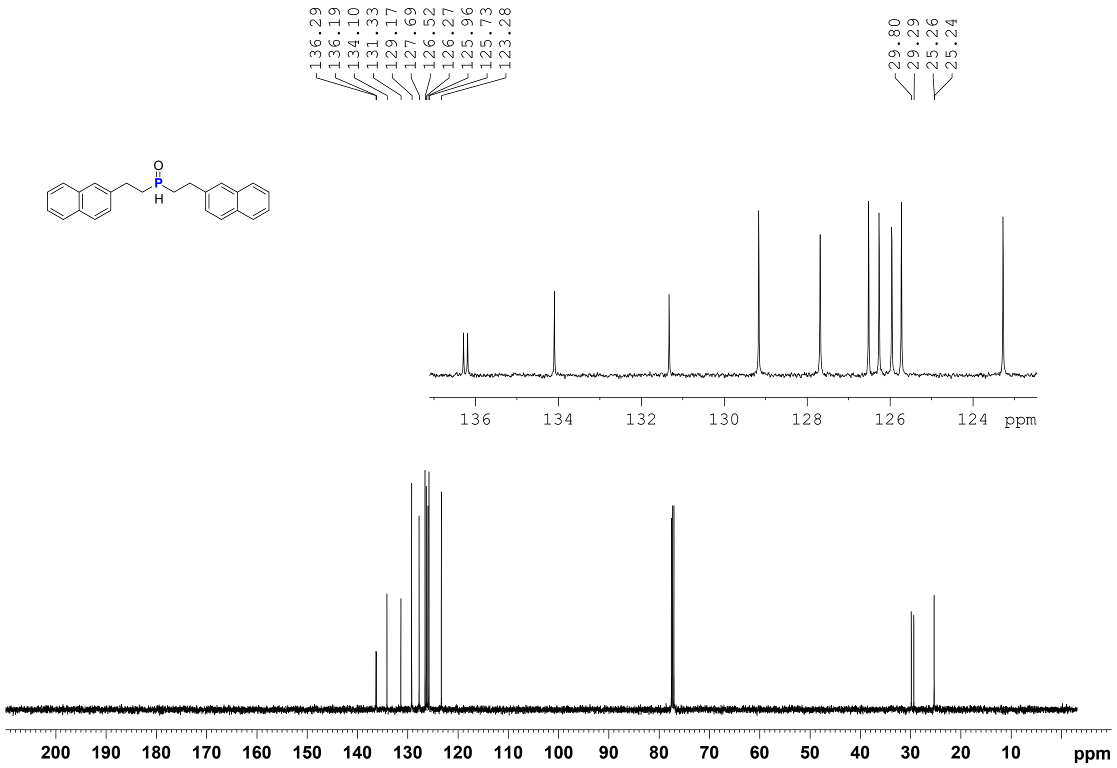
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4h**



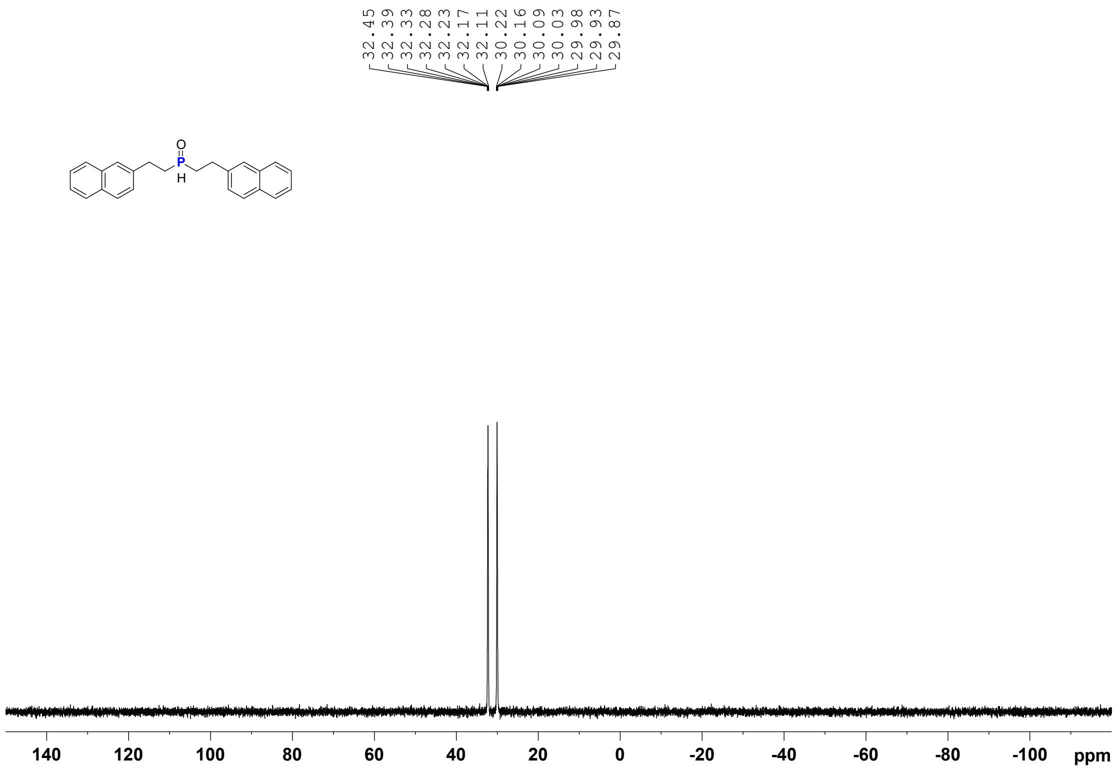
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4h**



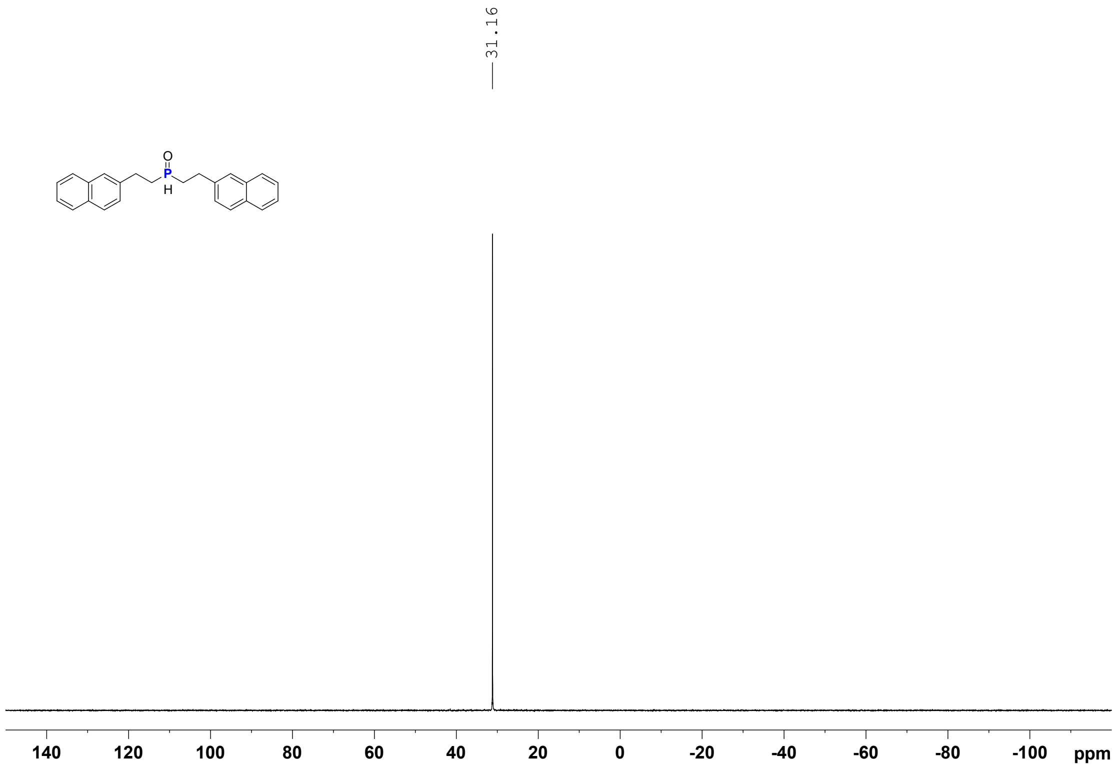
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4i**



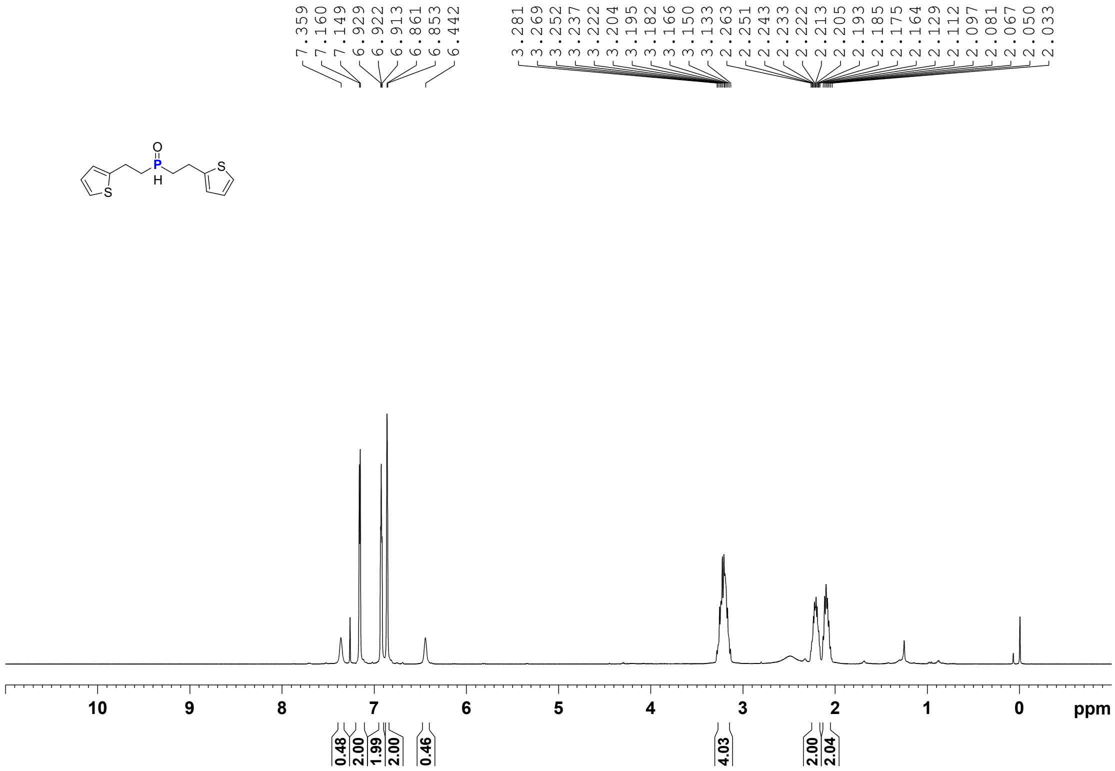
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4i**



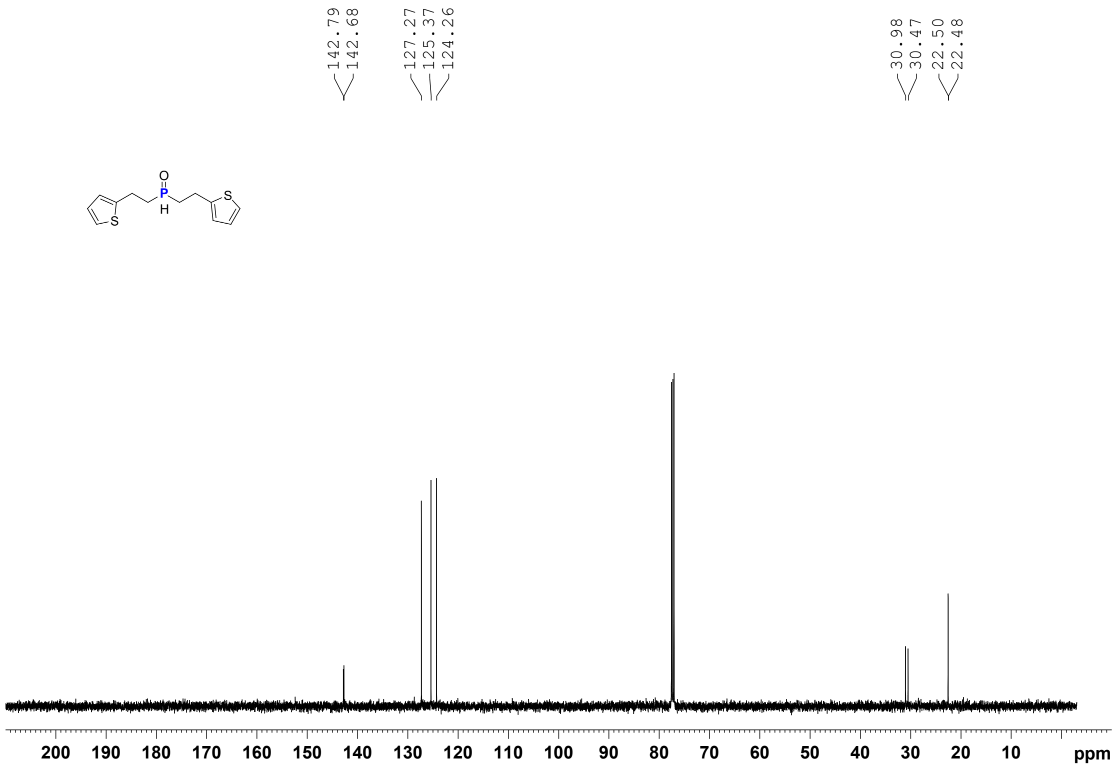
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4i**



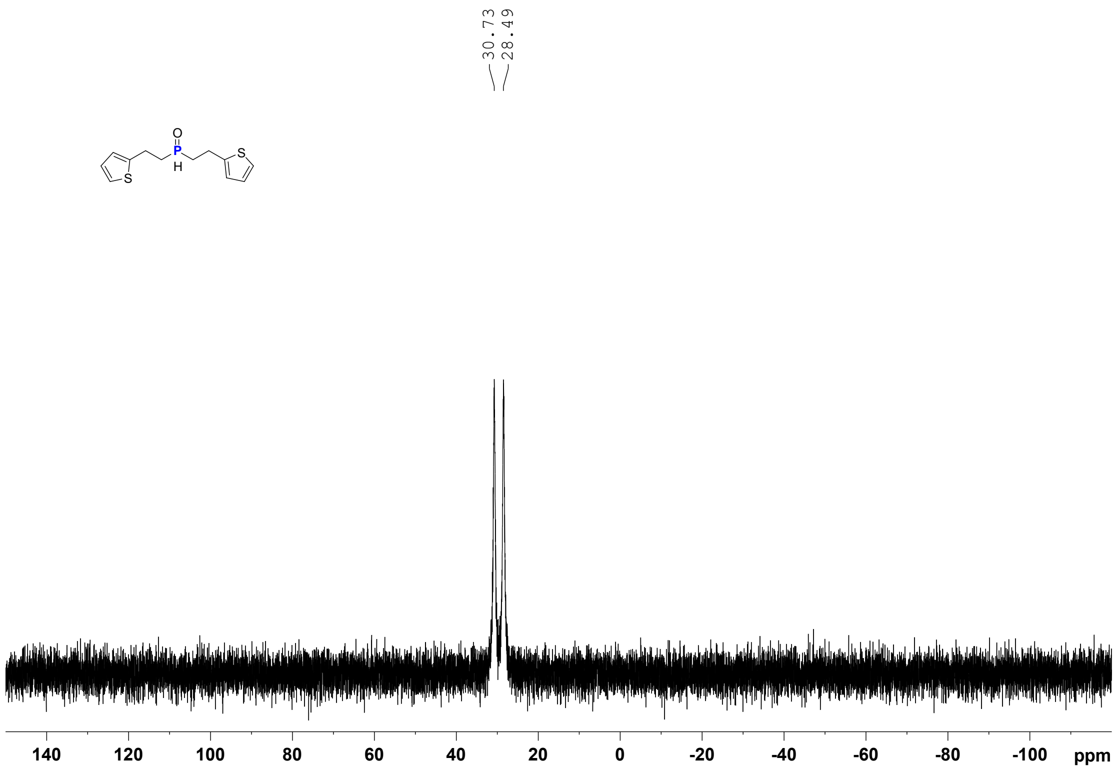
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4i**



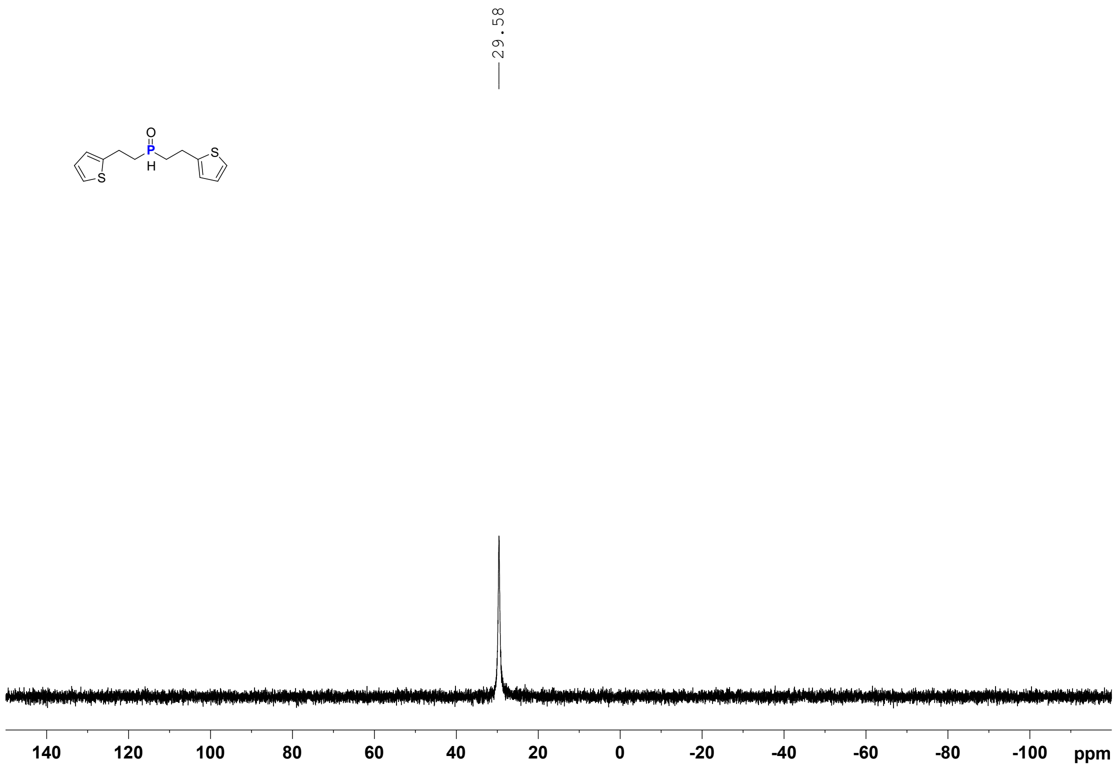
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4j**



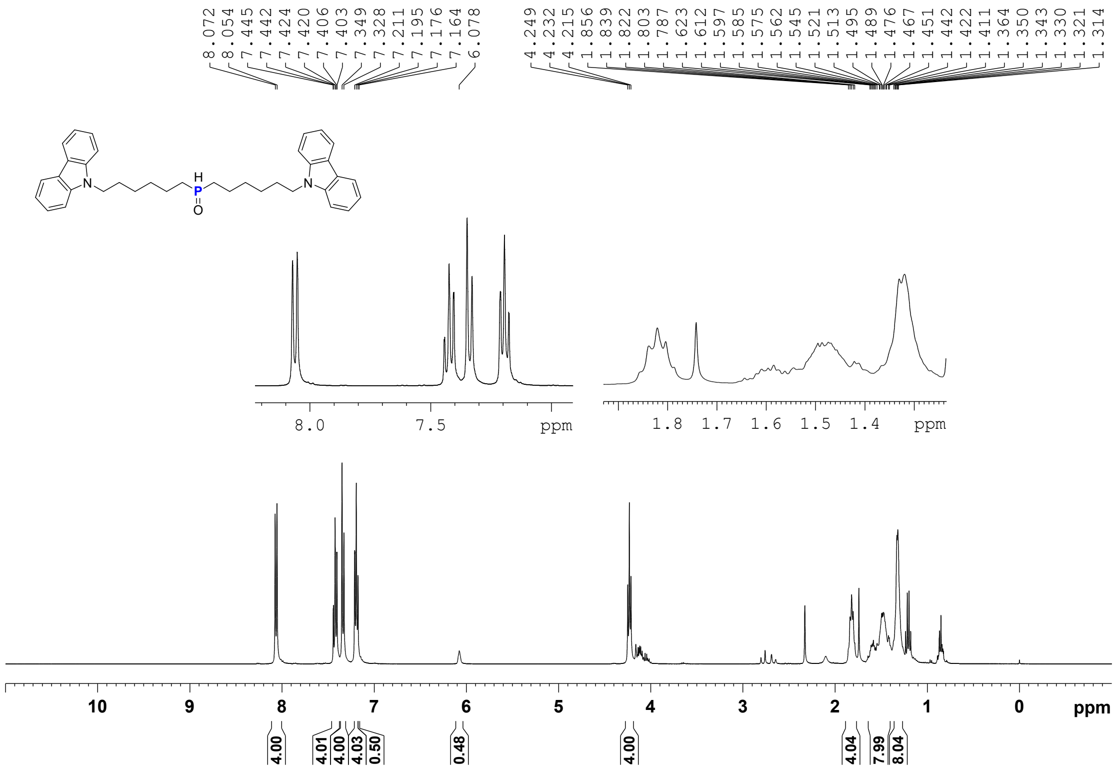
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4j**



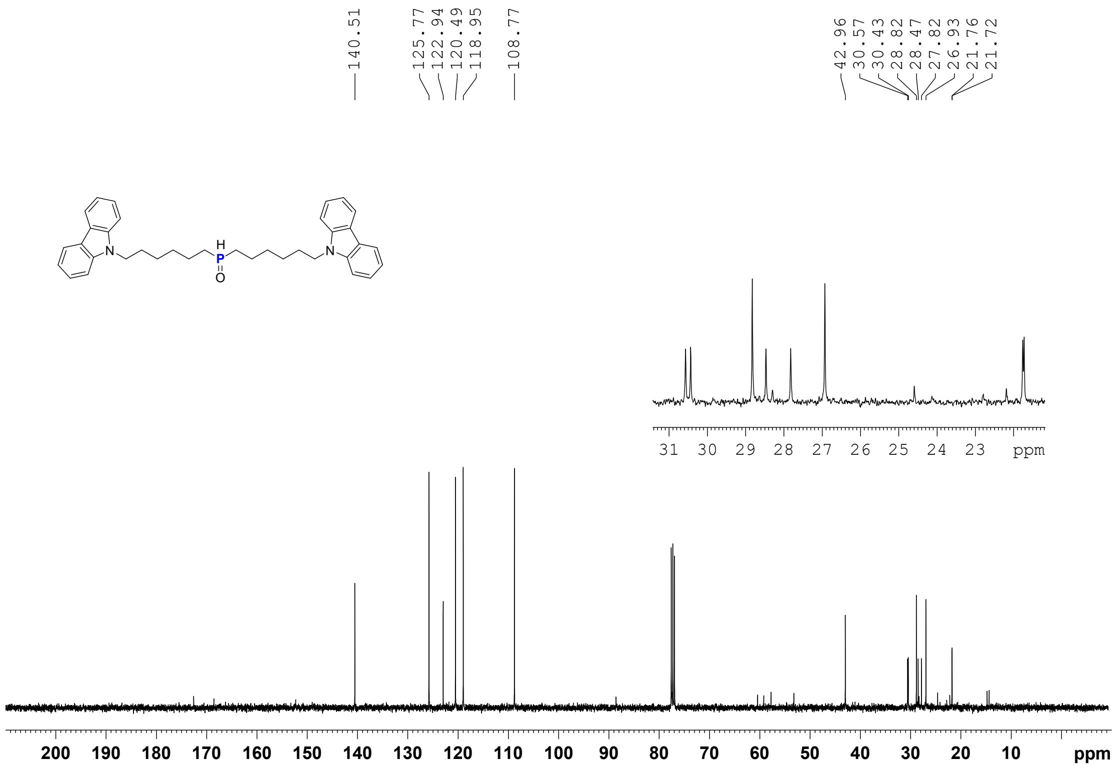
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4j**



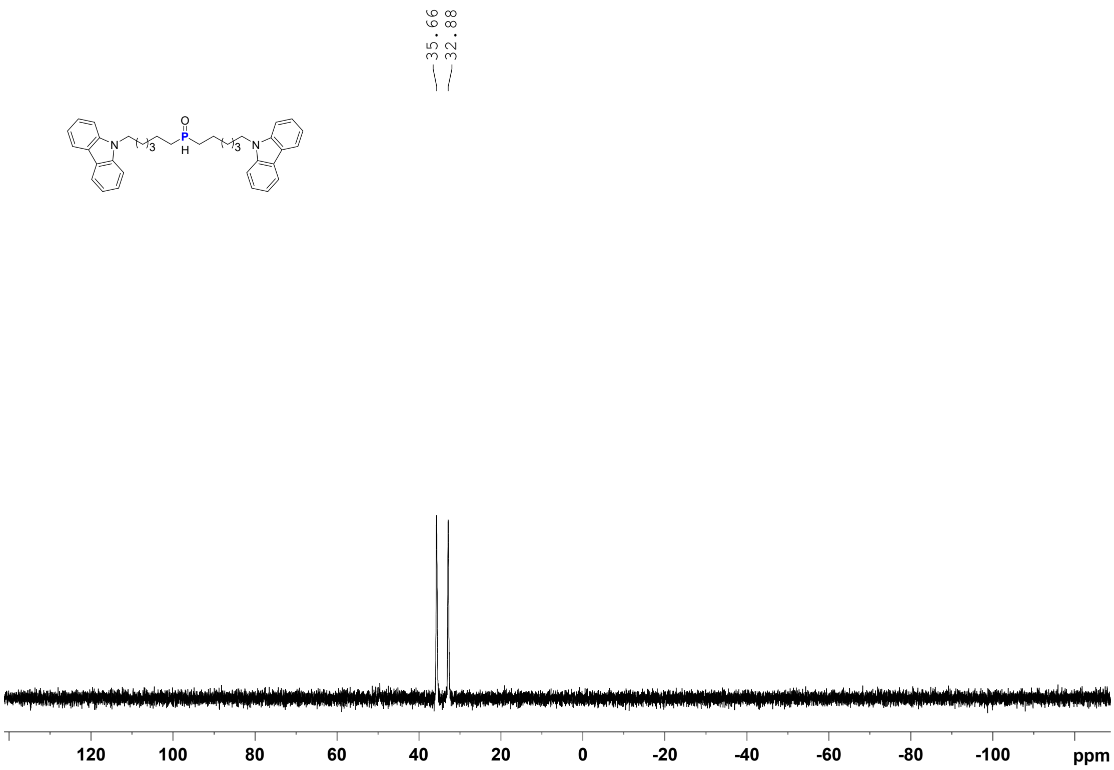
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4j**



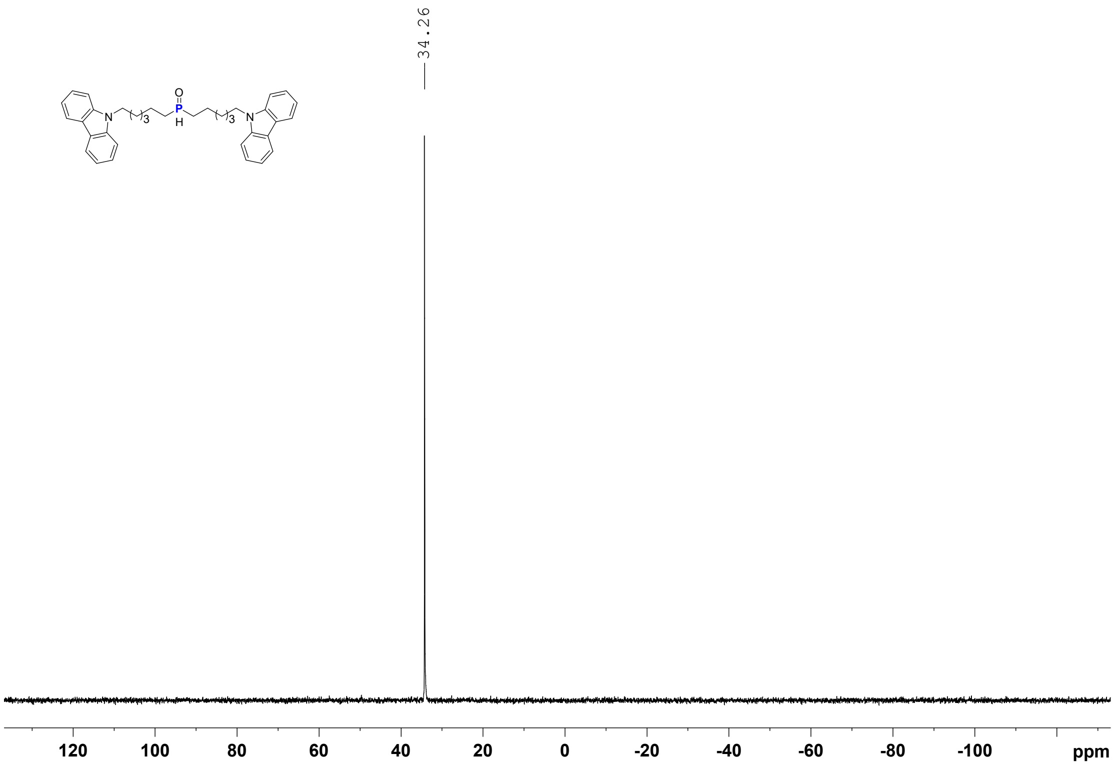
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4k**



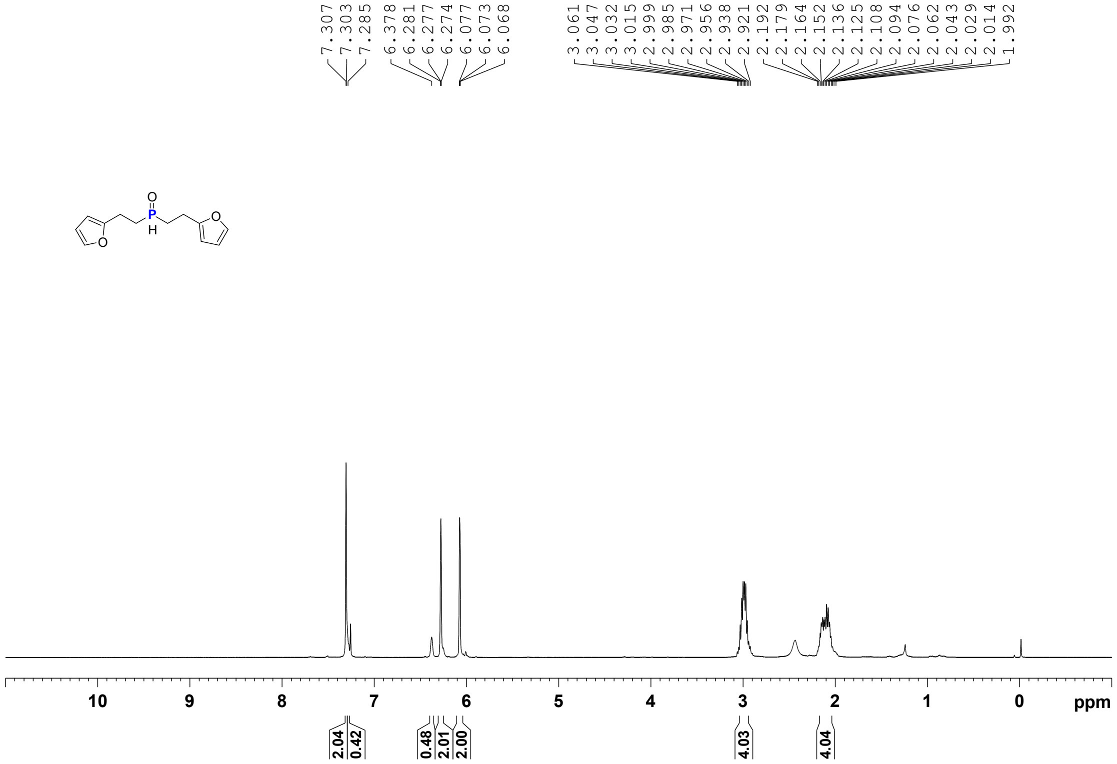
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **4k**



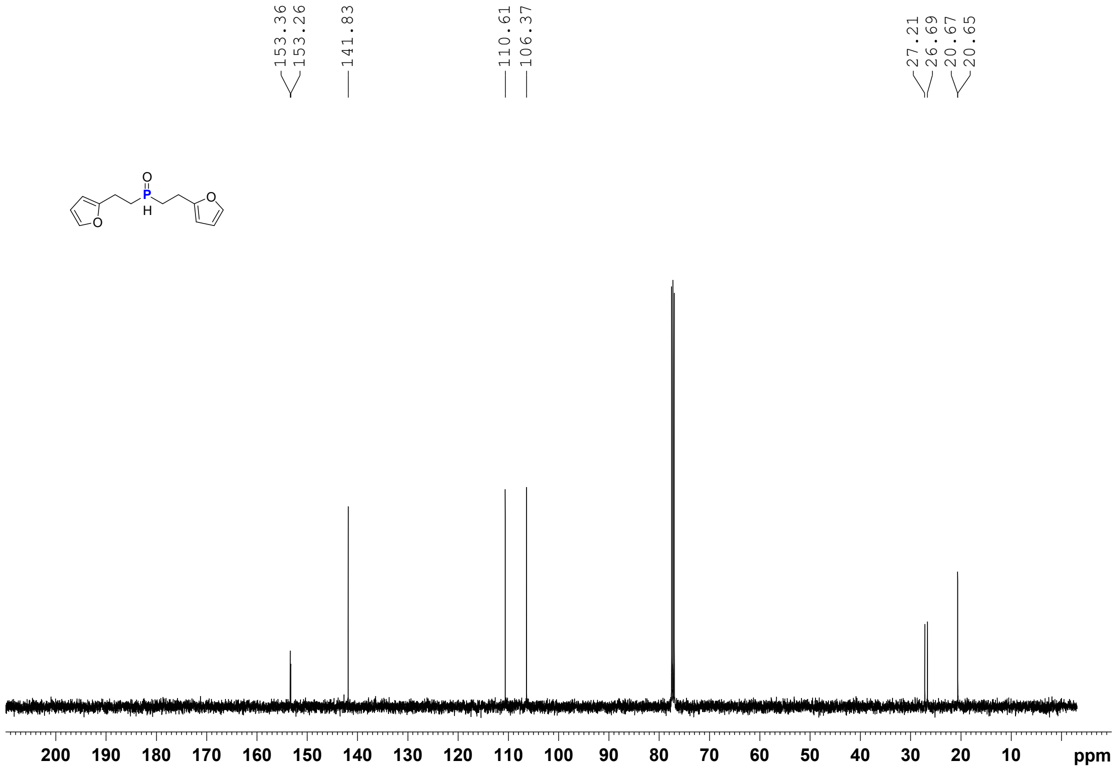
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4k**



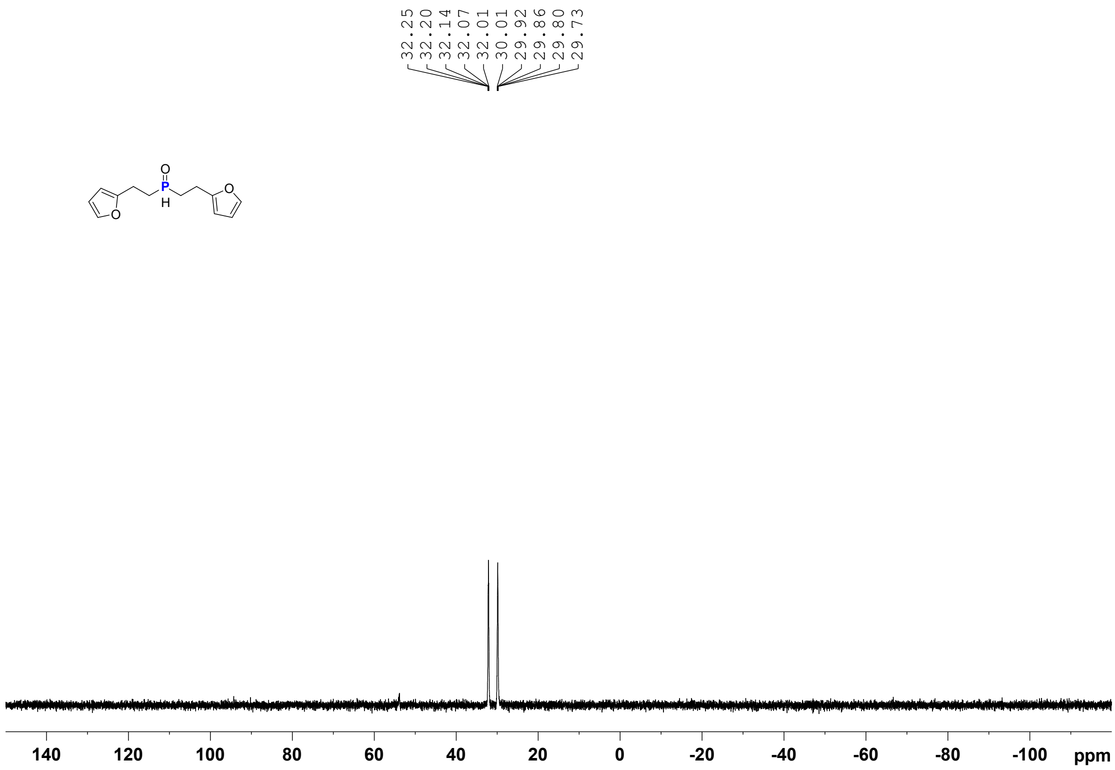
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4k**



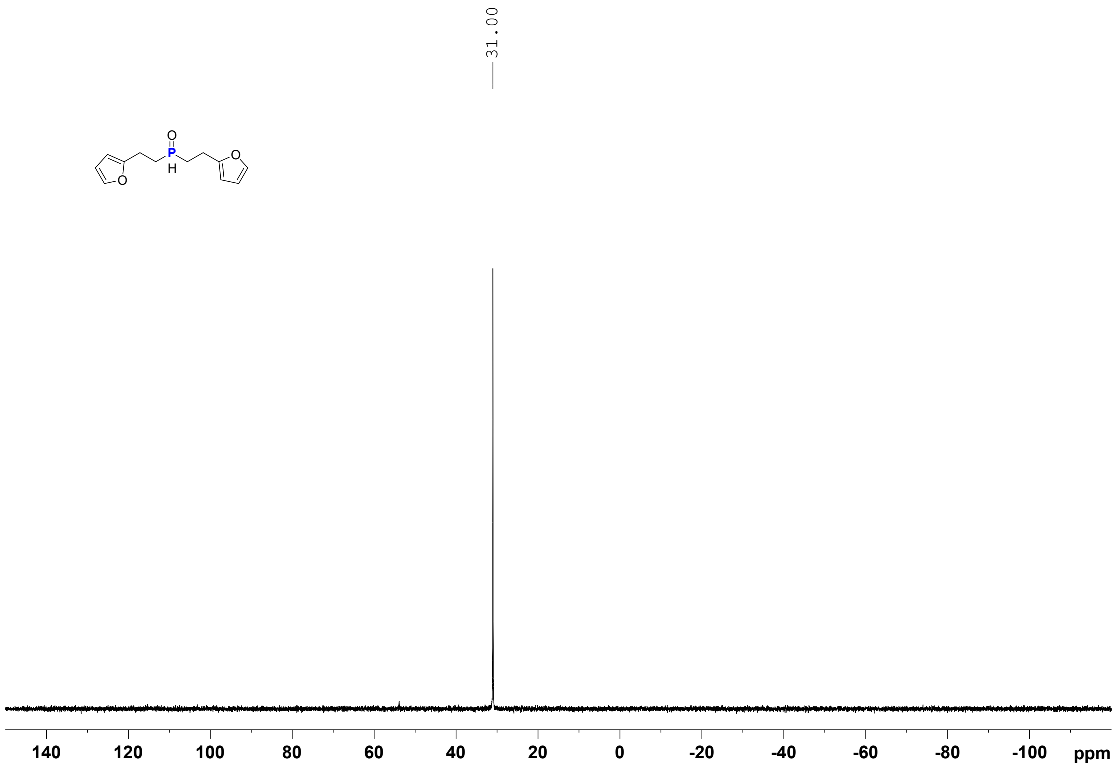
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4l**



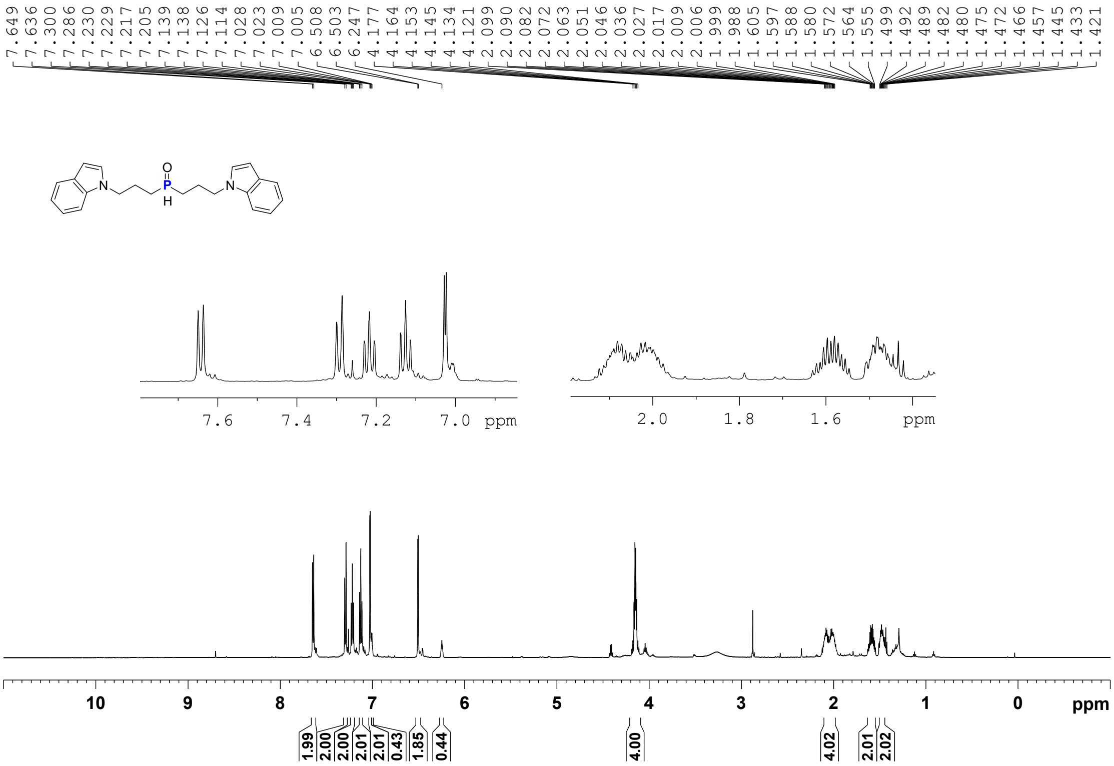
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4l**



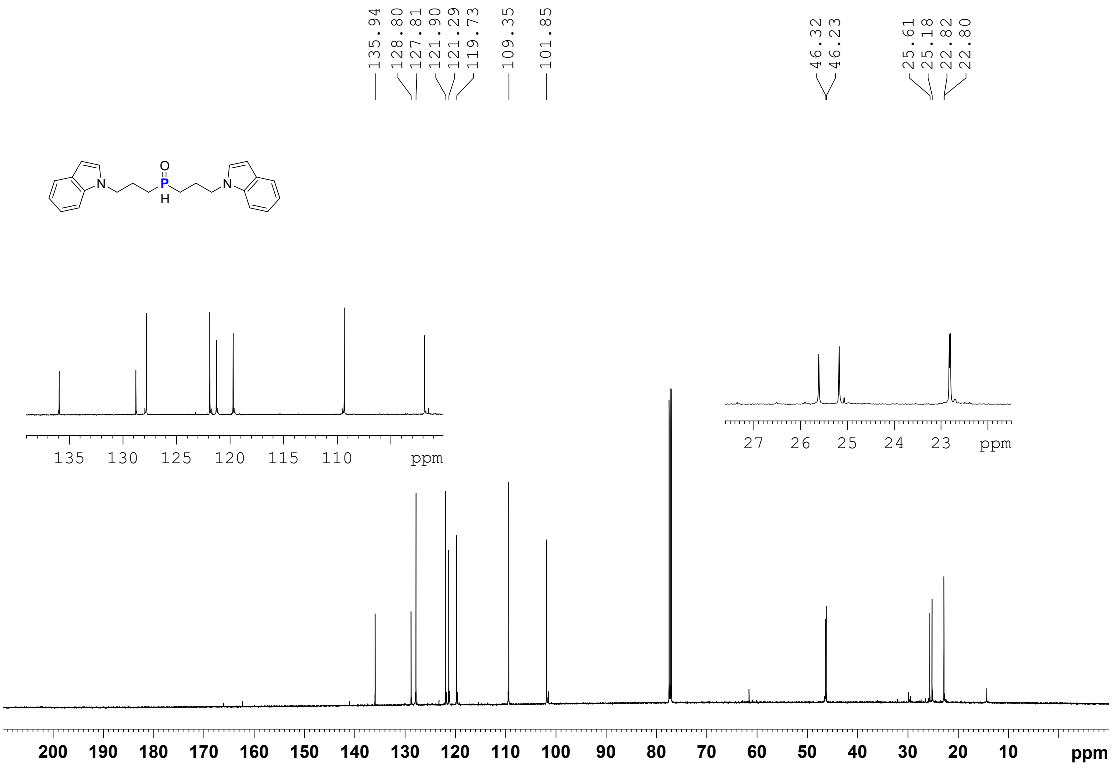
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4l**



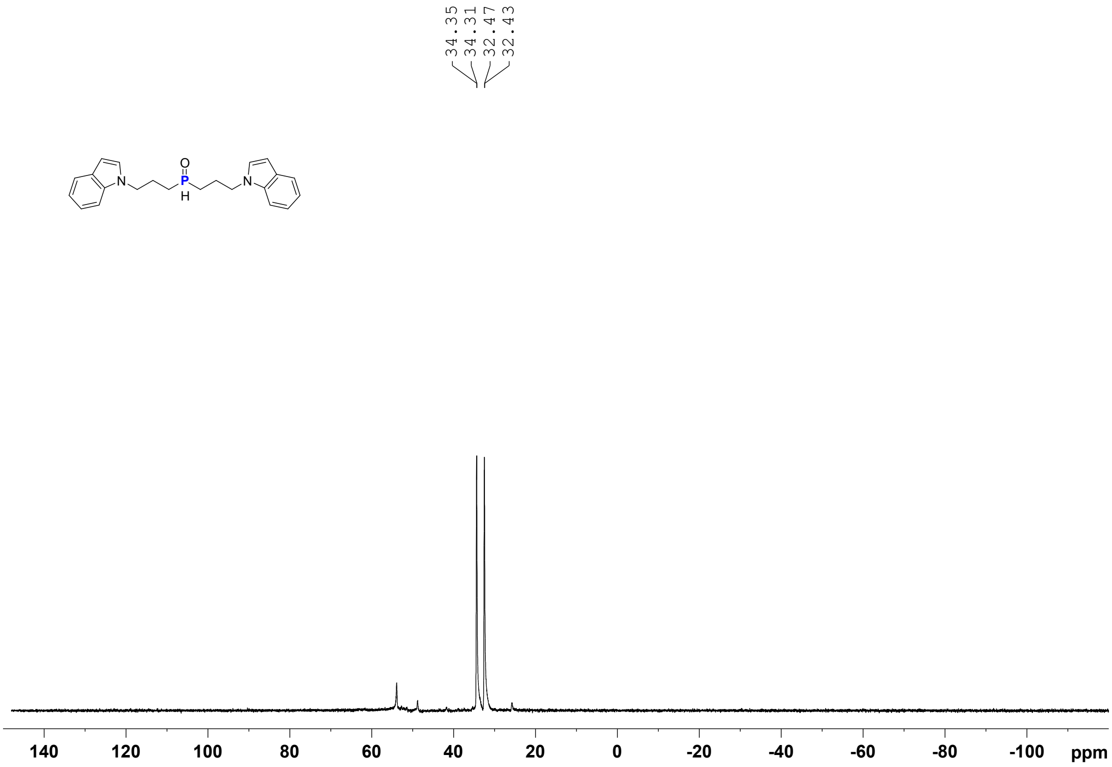
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4l**



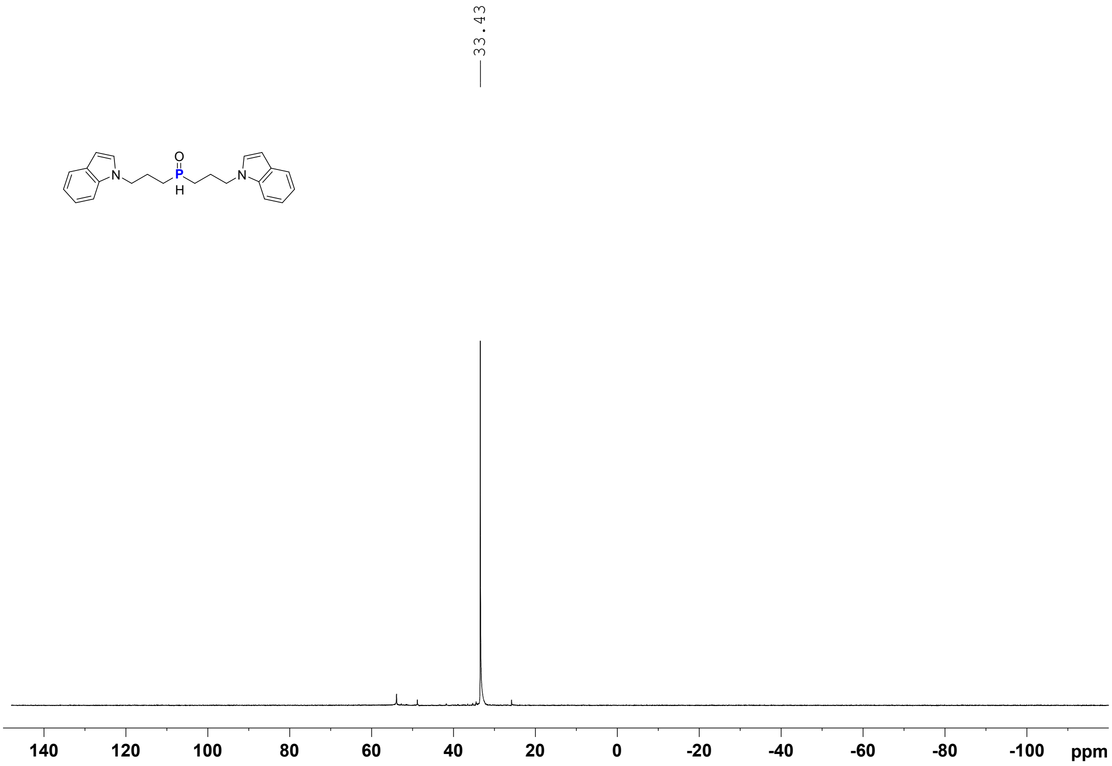
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4m**



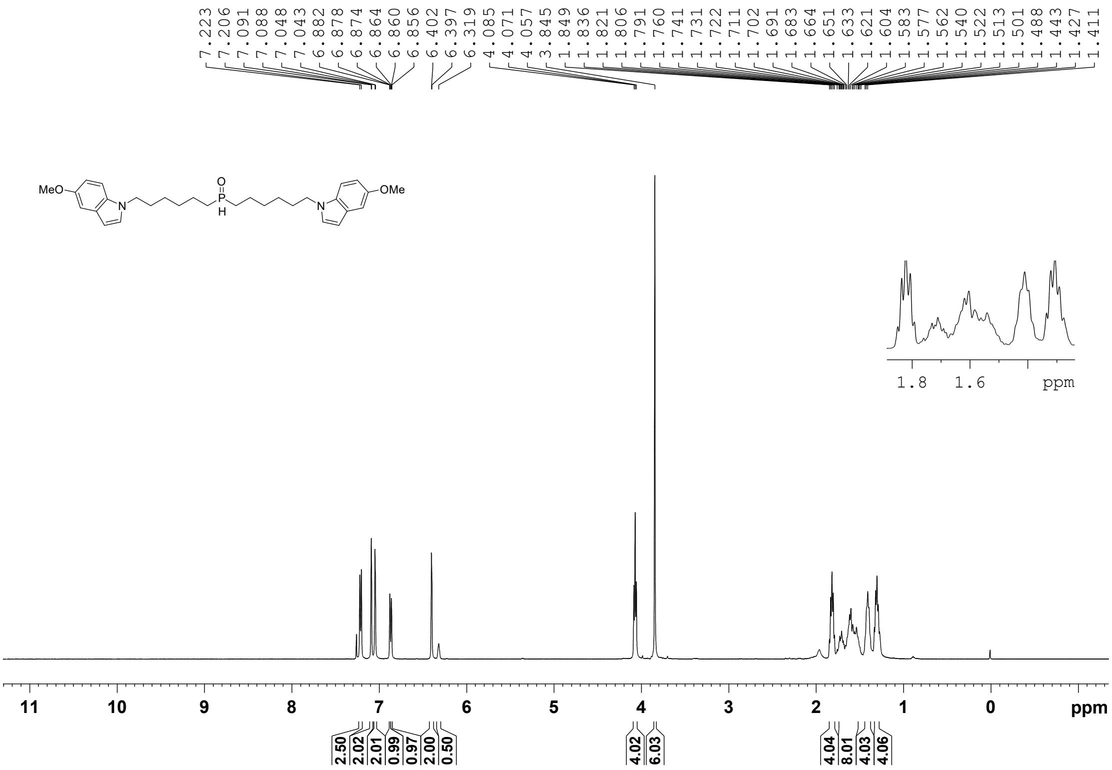
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4m**



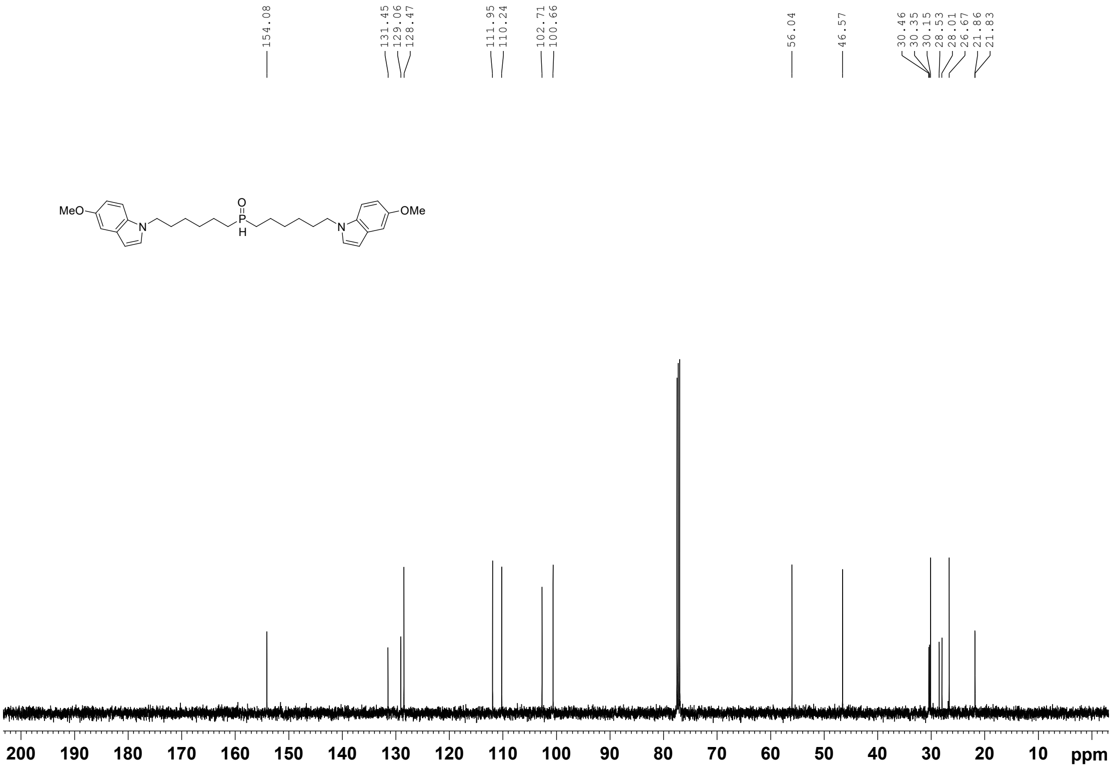
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4m**



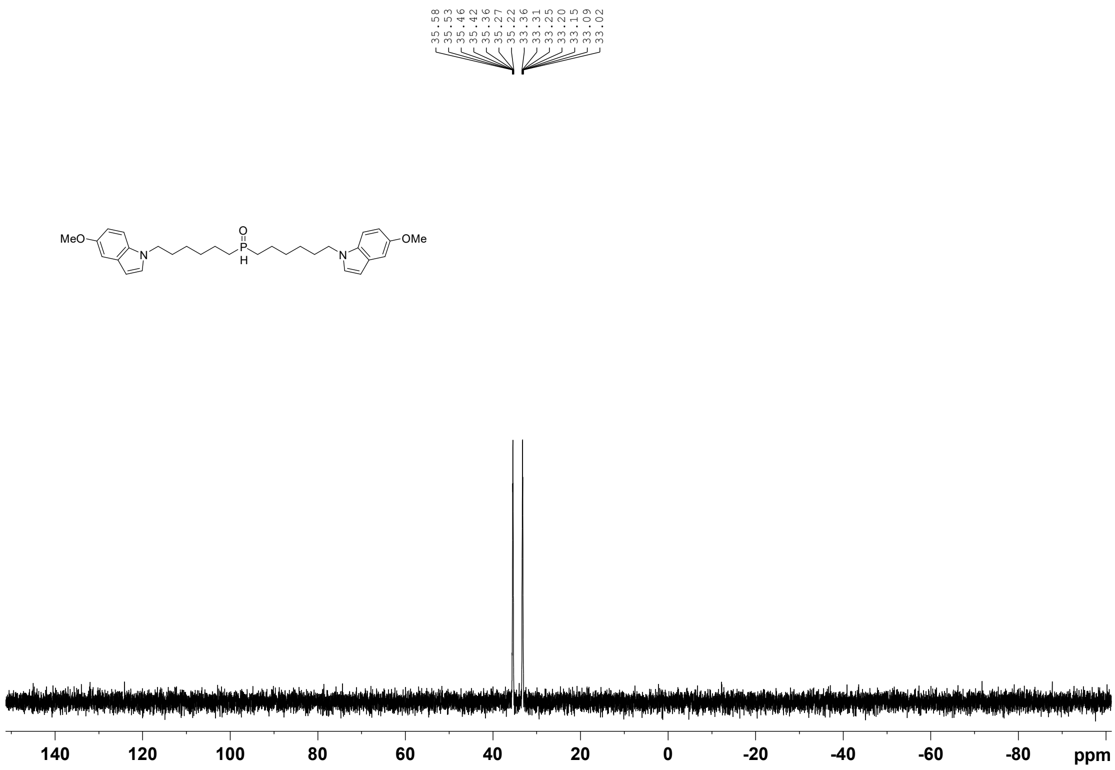
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4m**



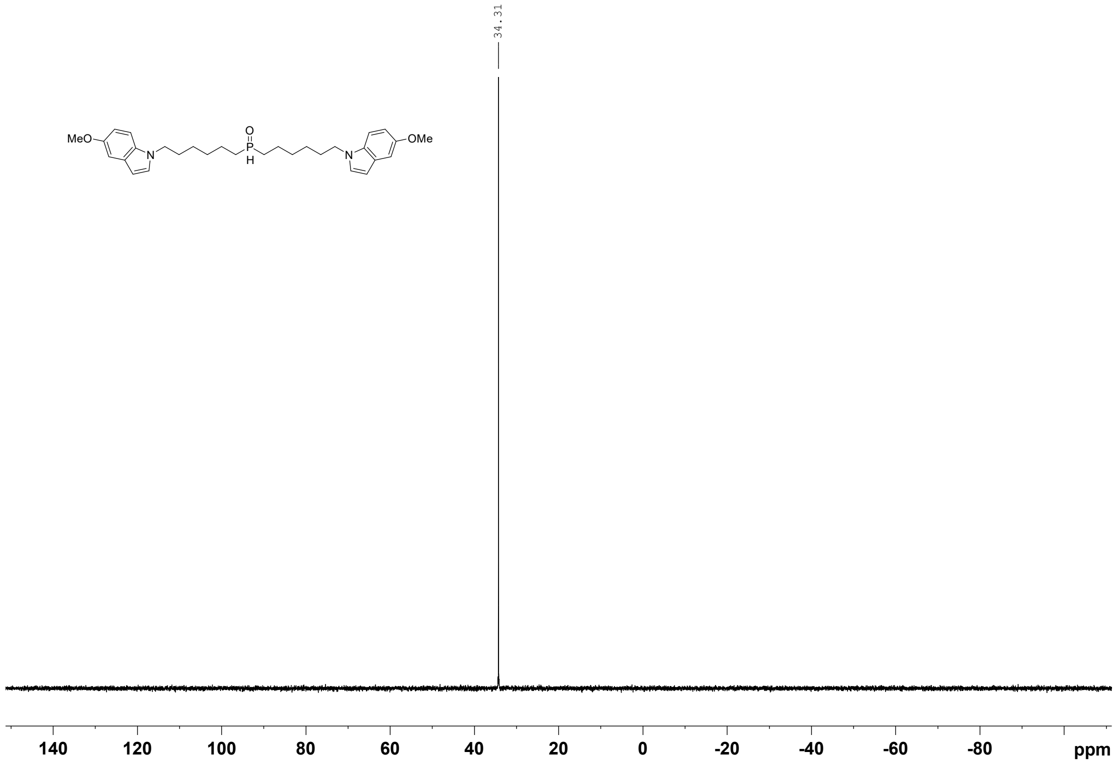
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4n**



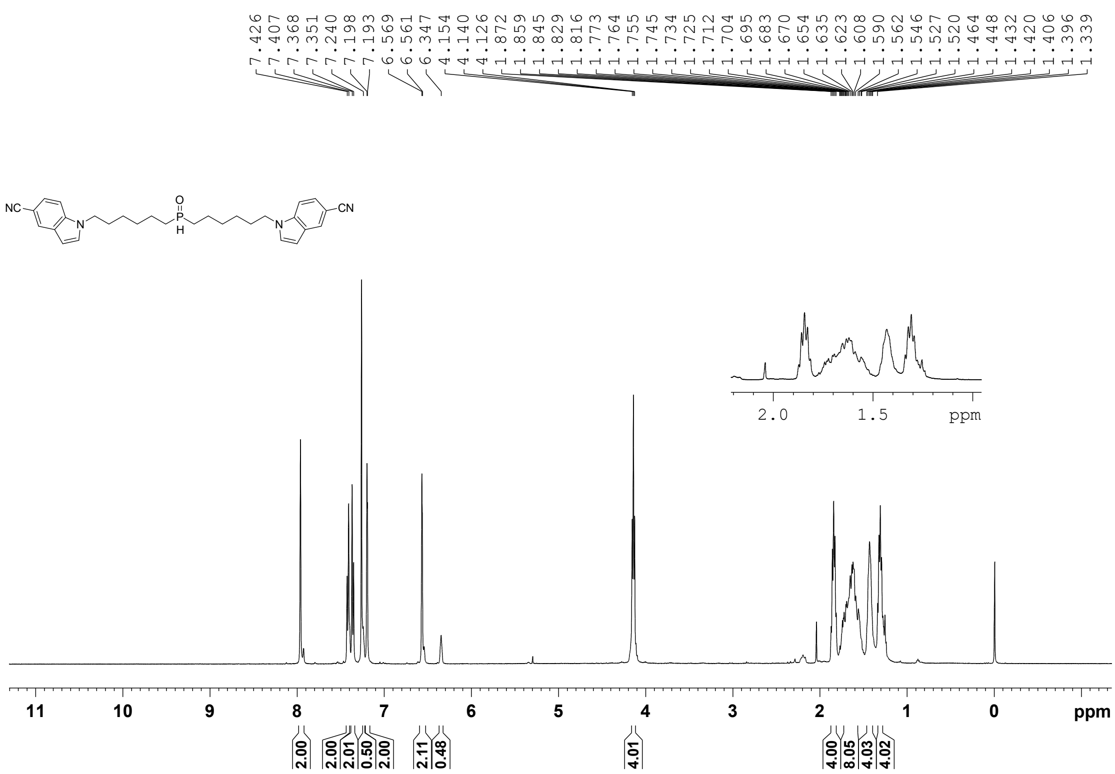
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4n**



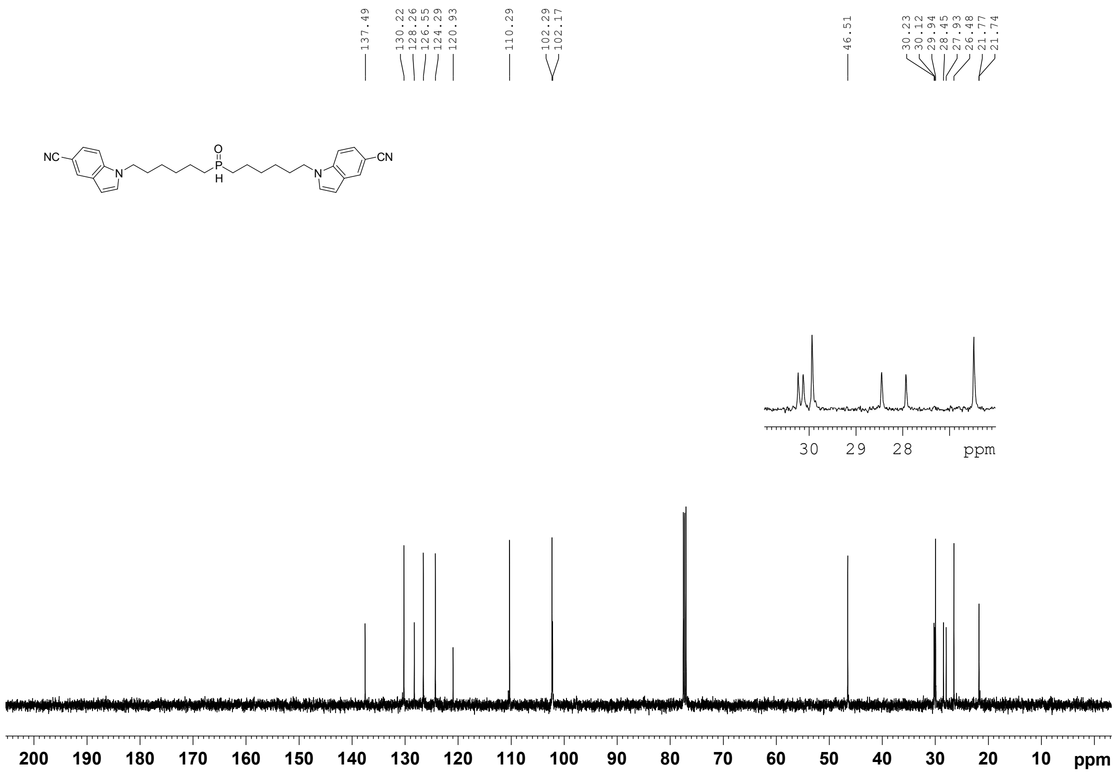
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4n**



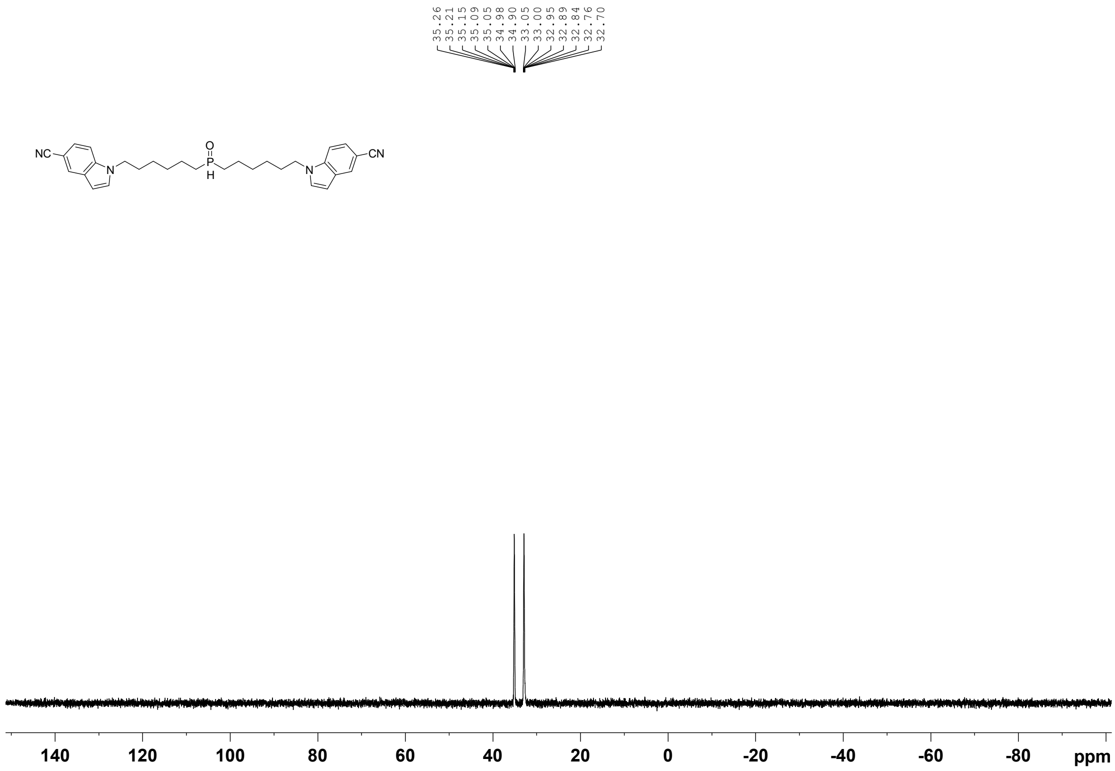
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4n**



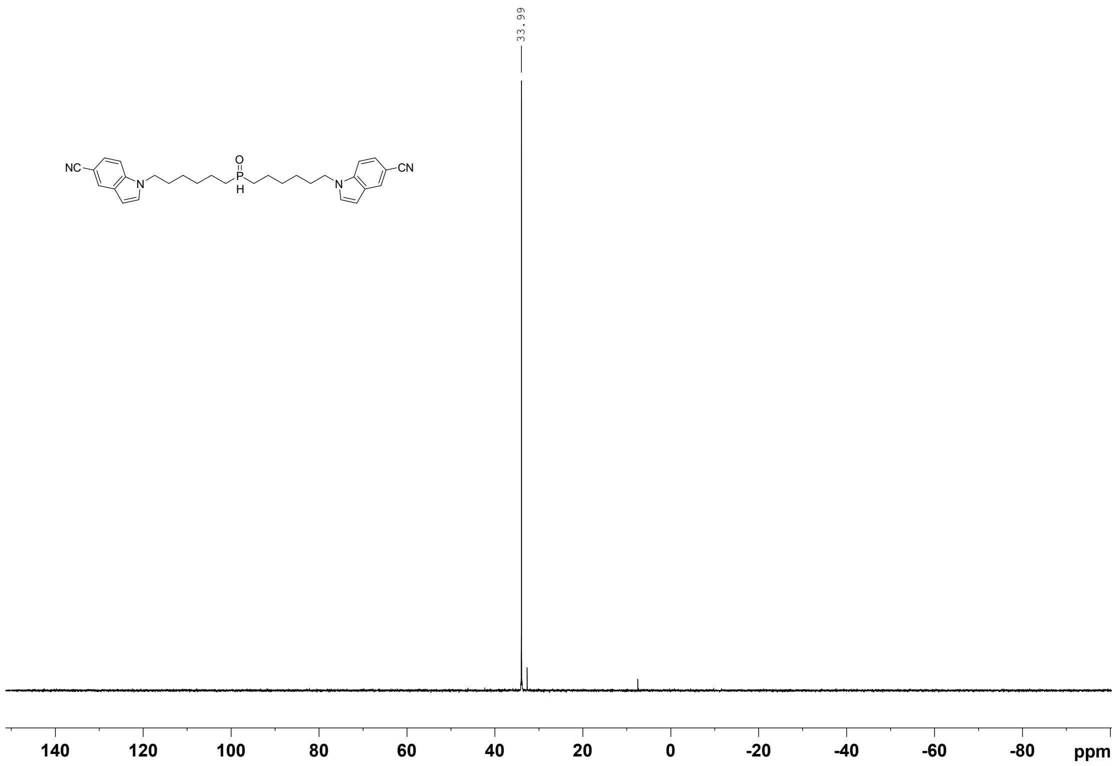
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4o**



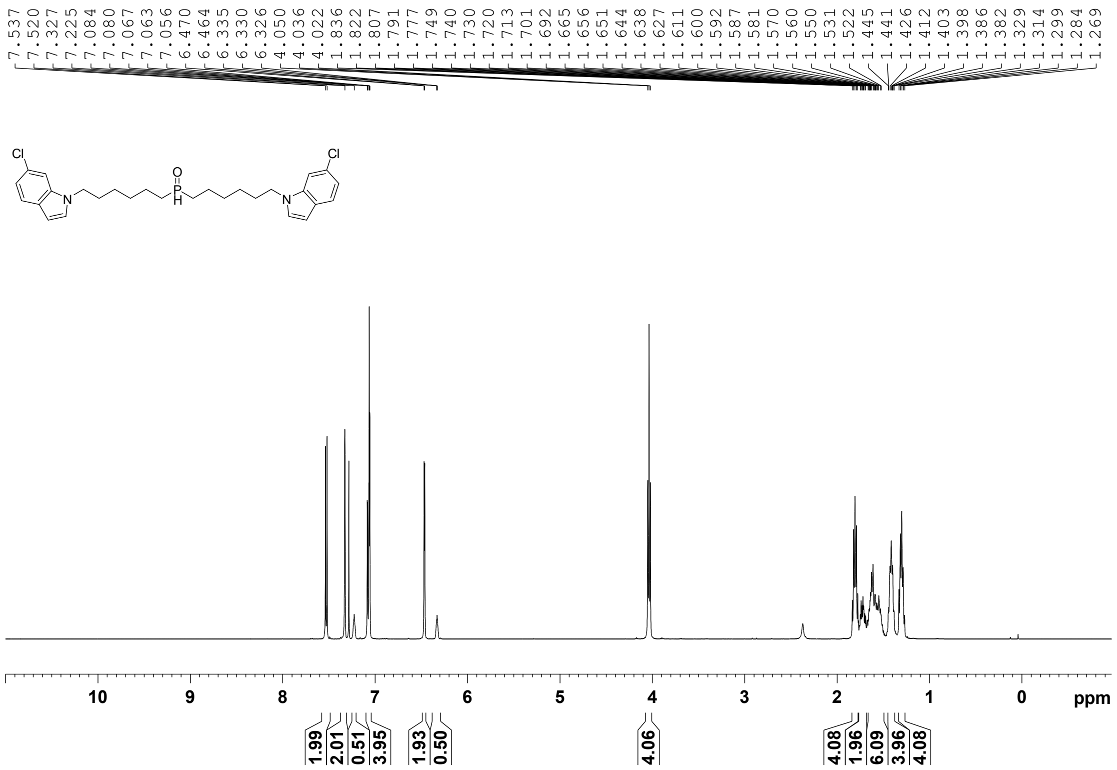
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4o**



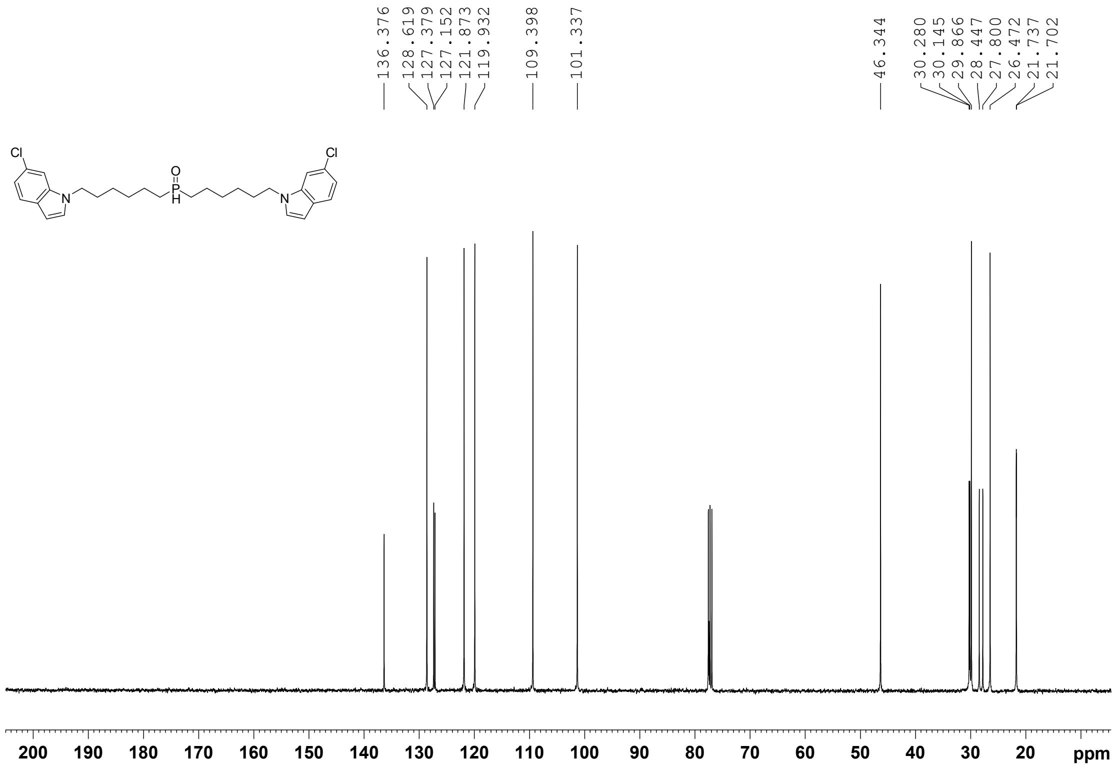
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4o**



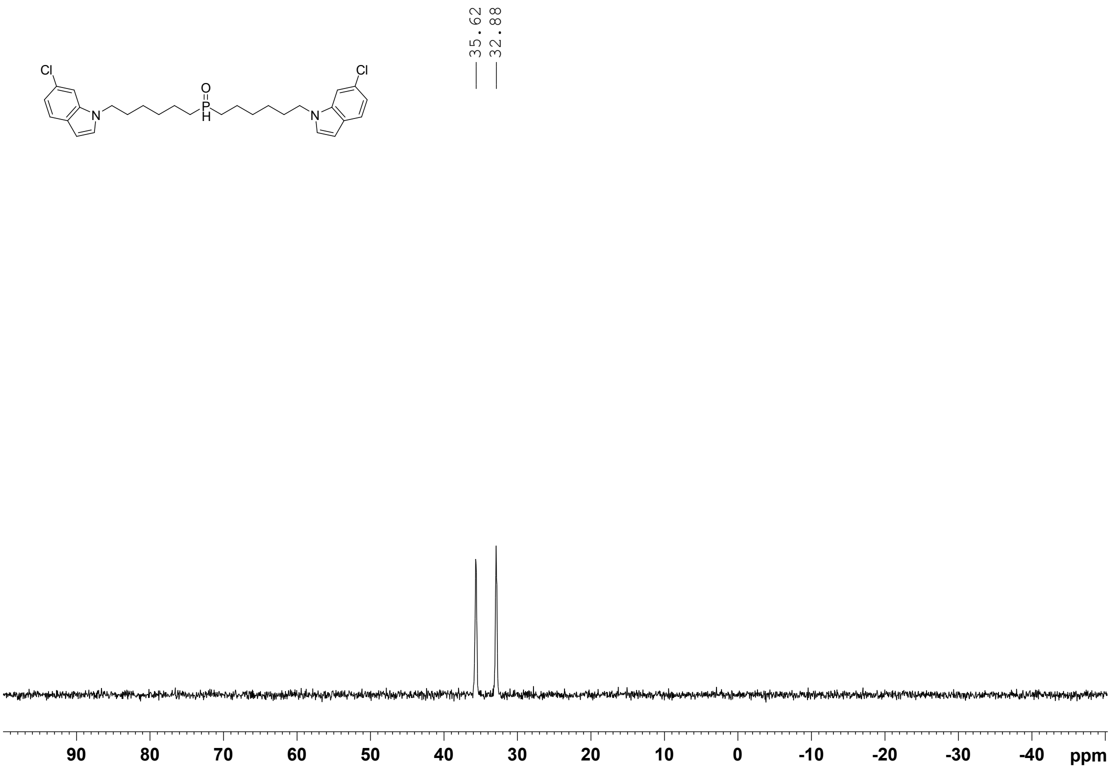
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4o**



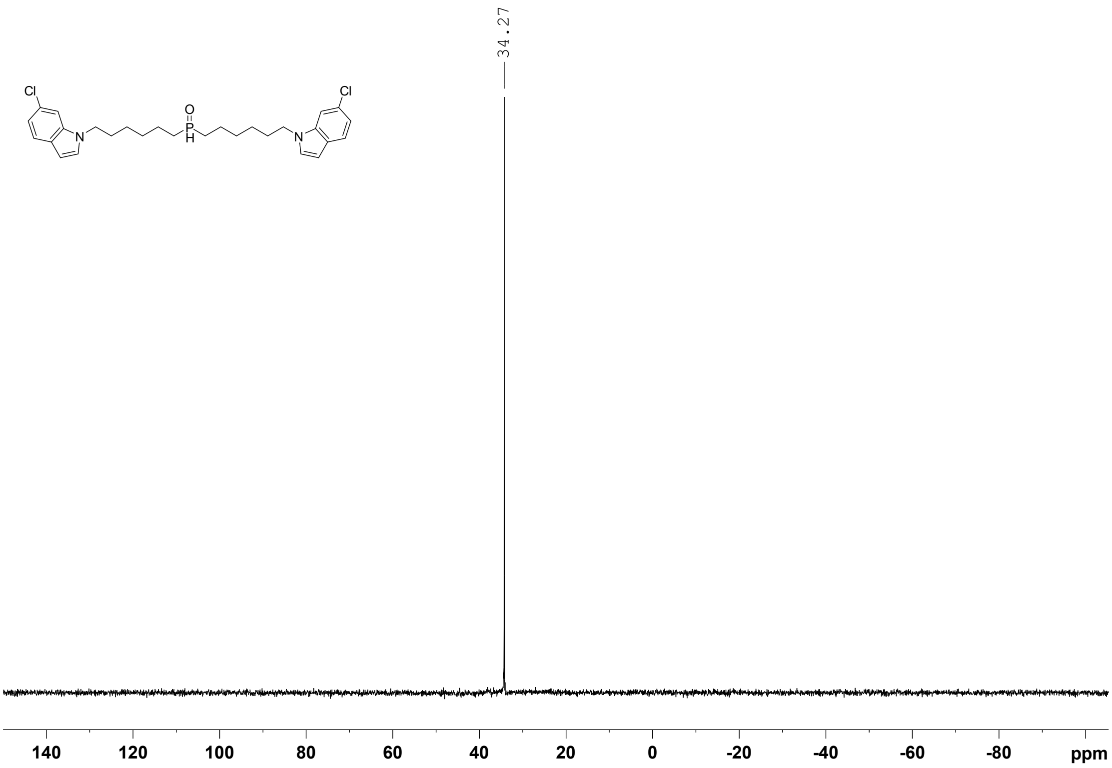
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4p**



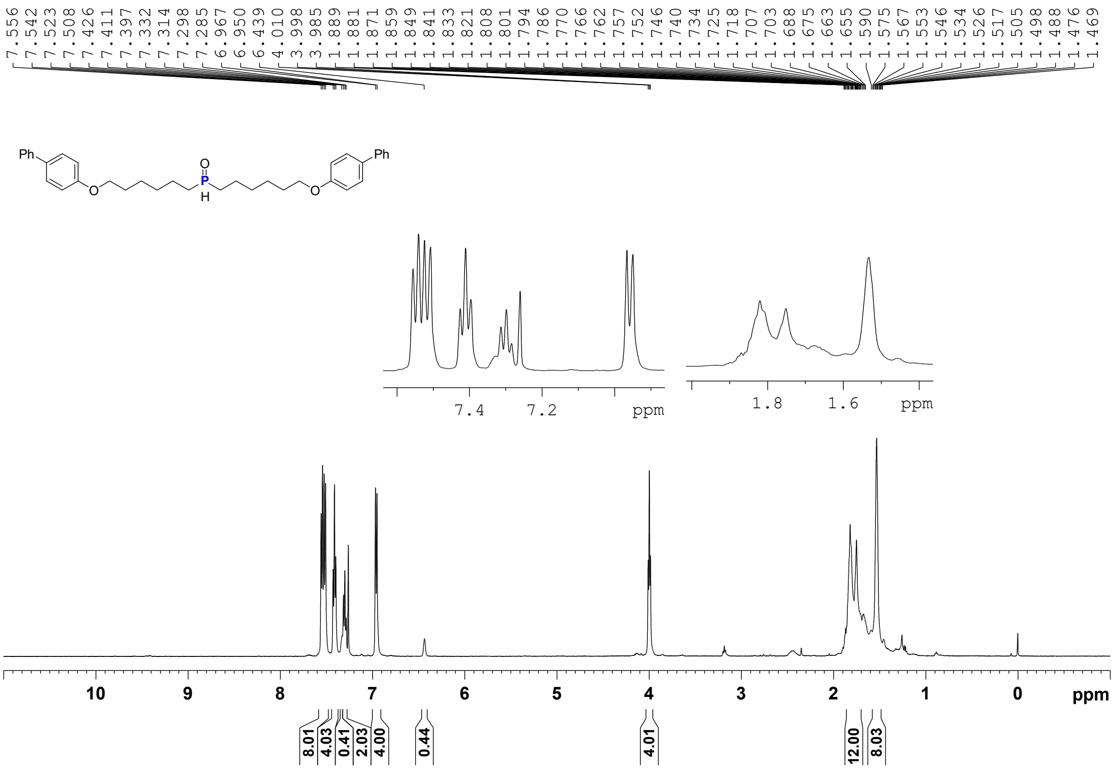
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4p**



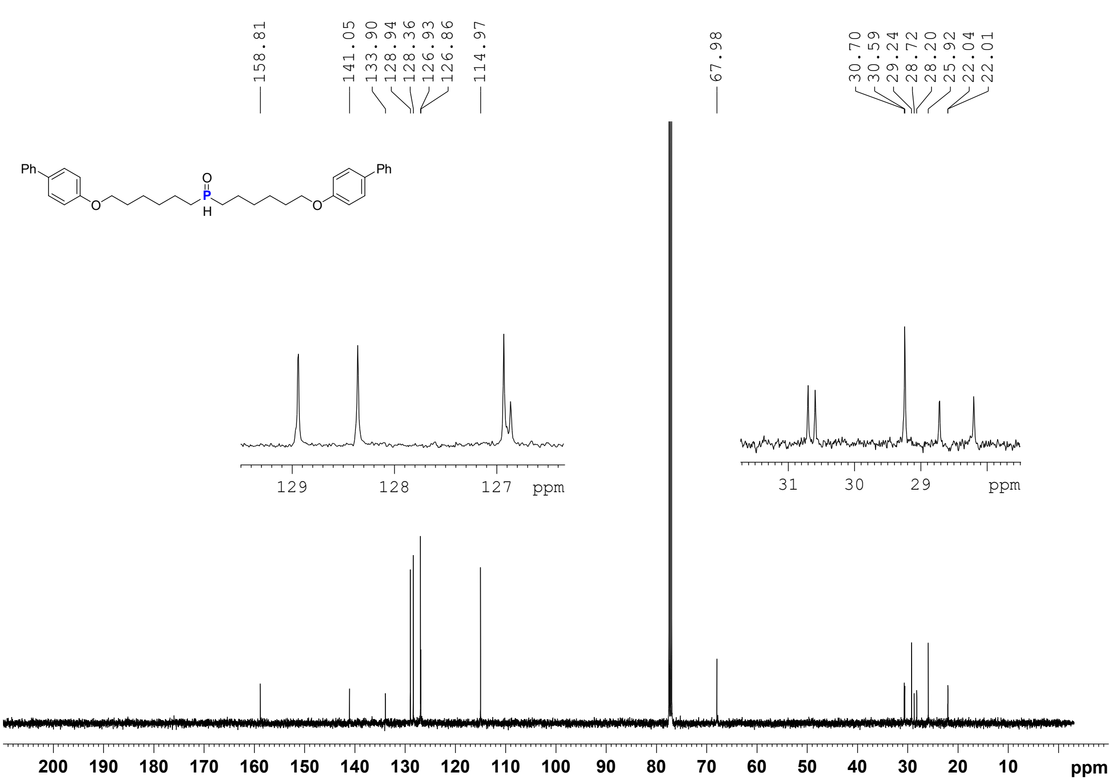
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4p**



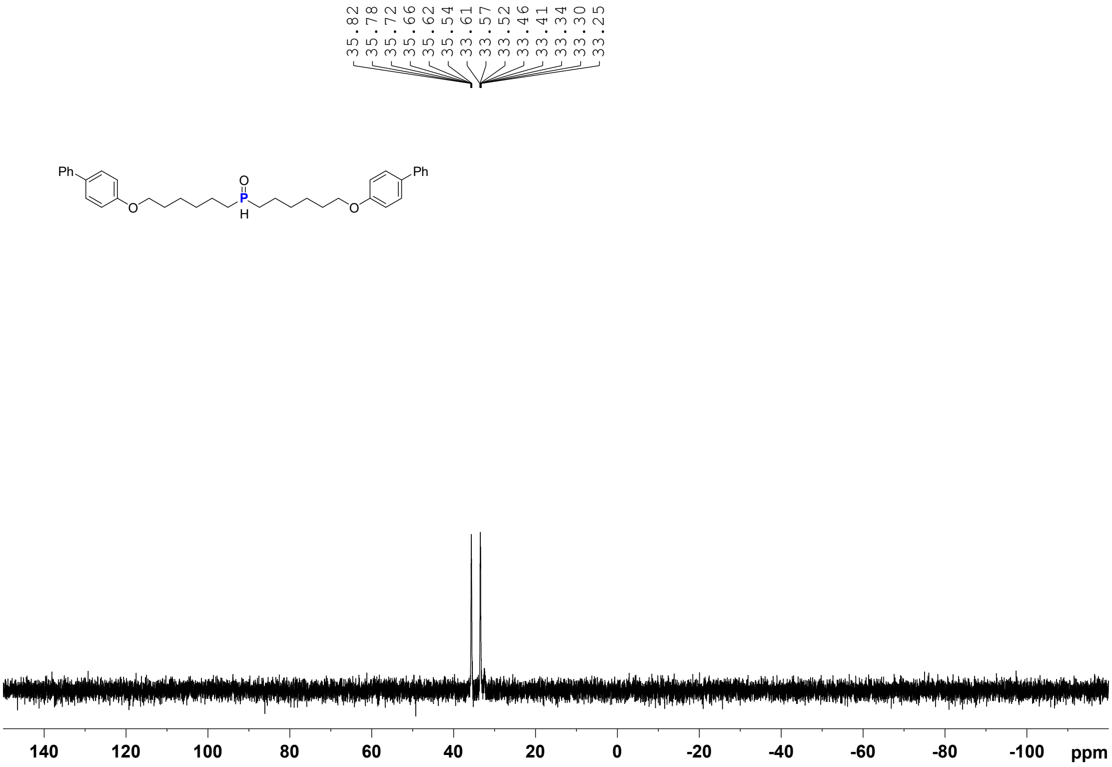
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4p**



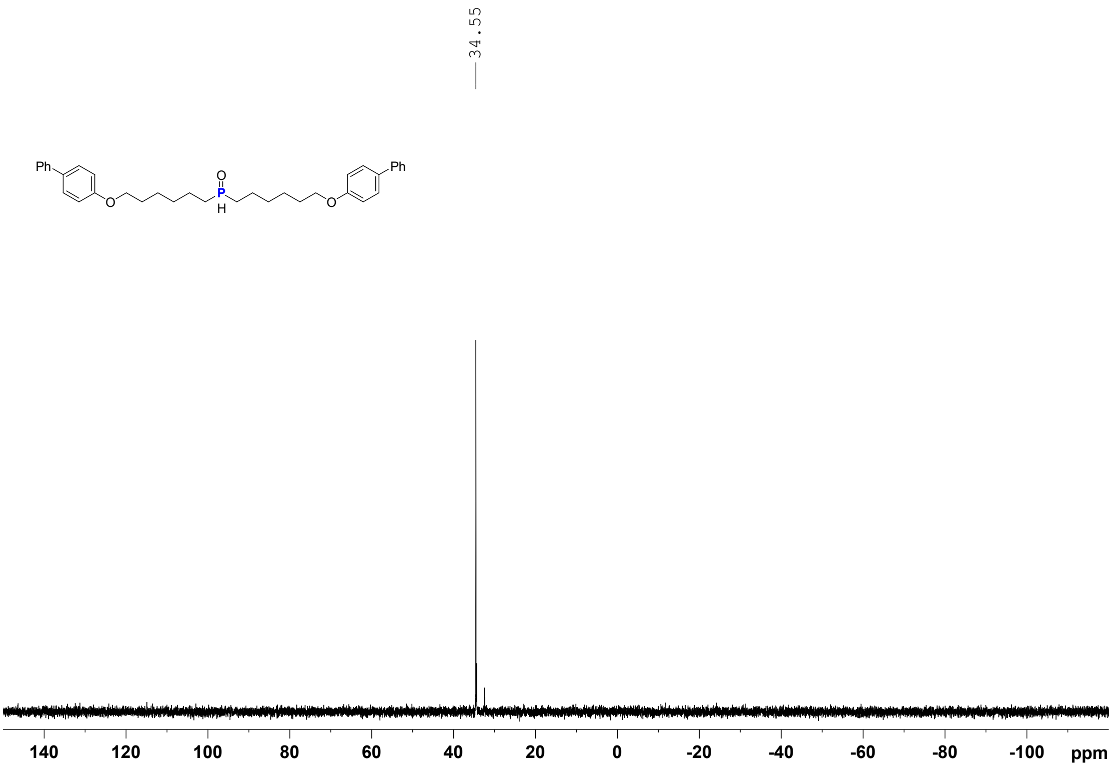
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4q**



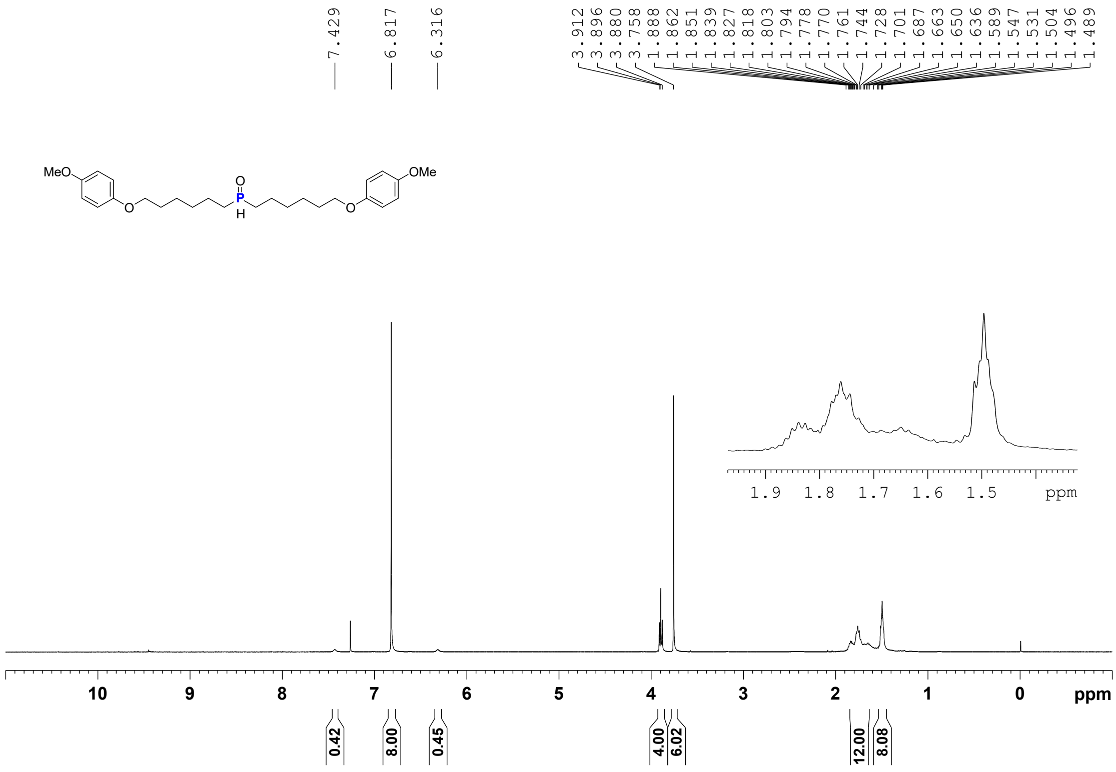
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4q**



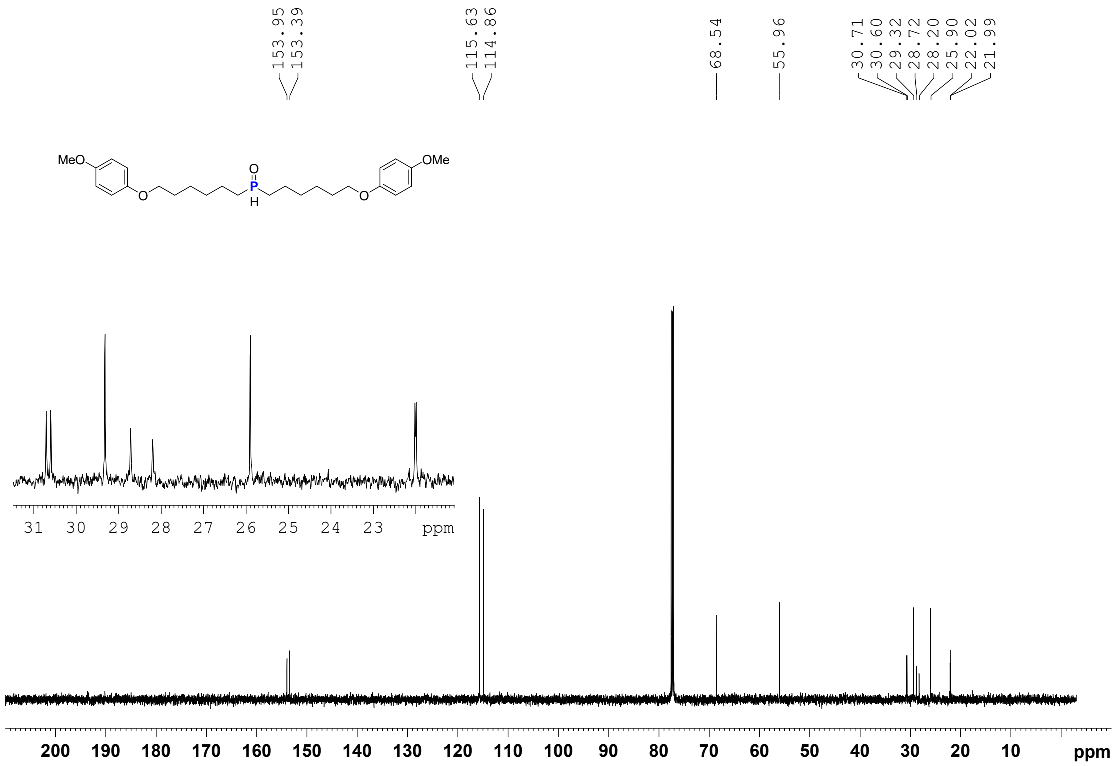
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4q**



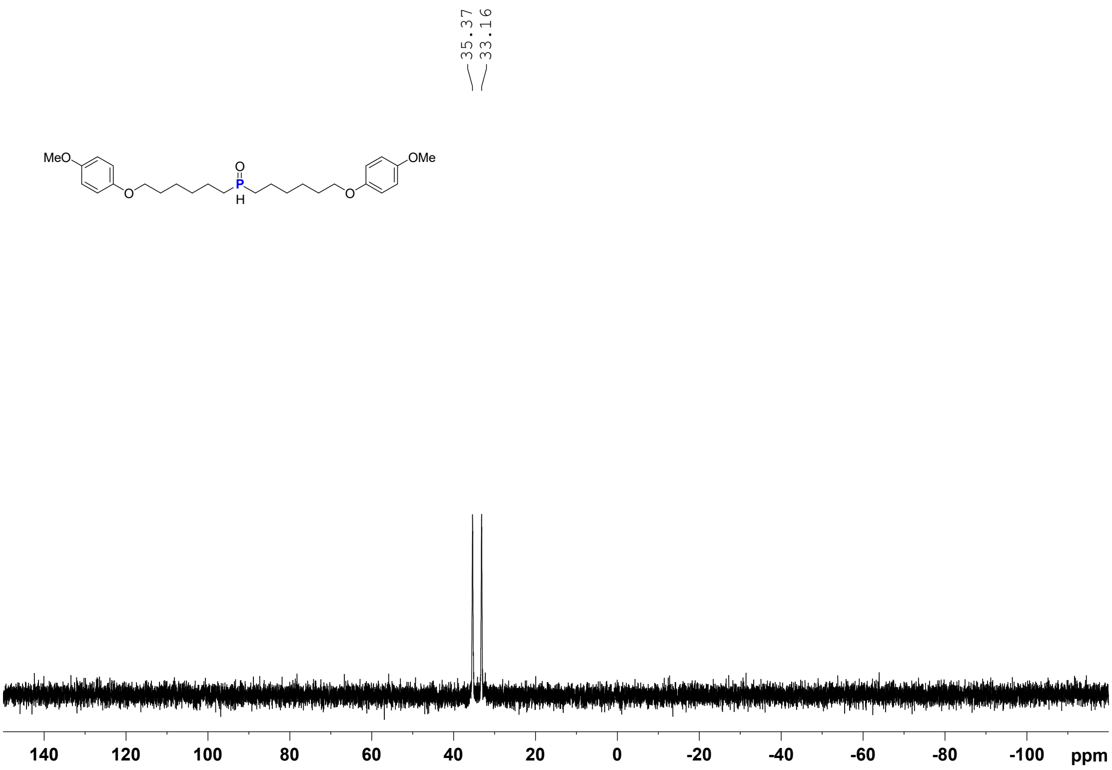
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4q**



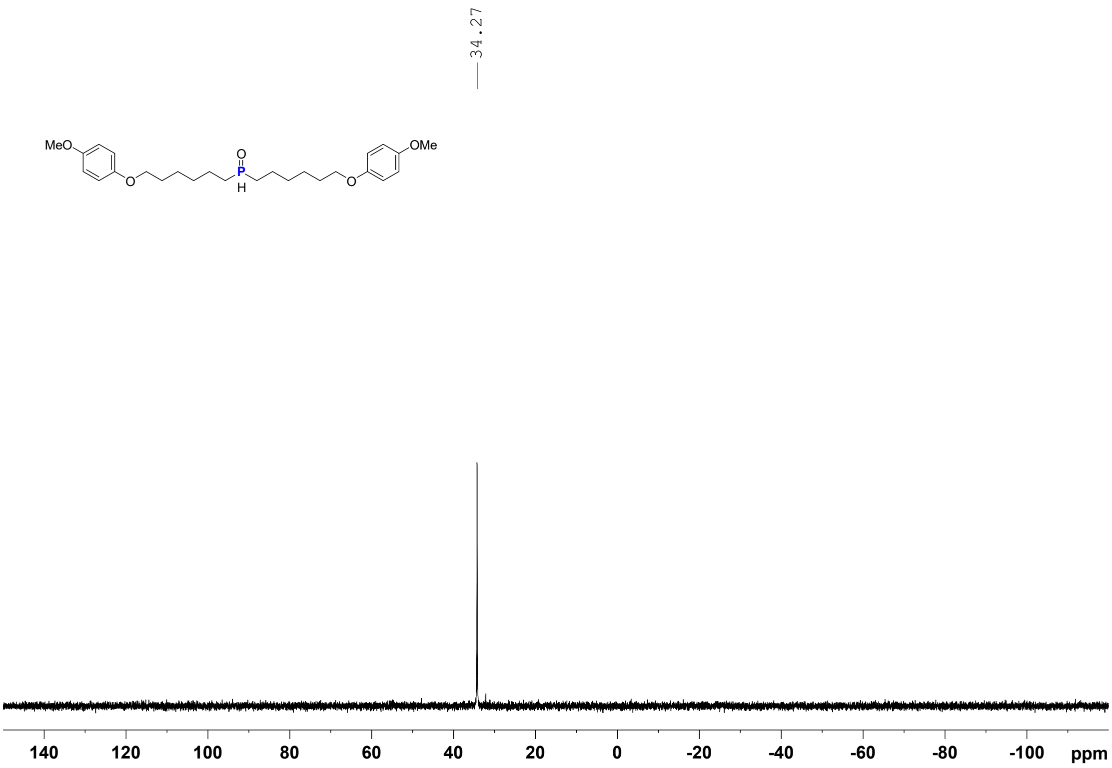
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4r**



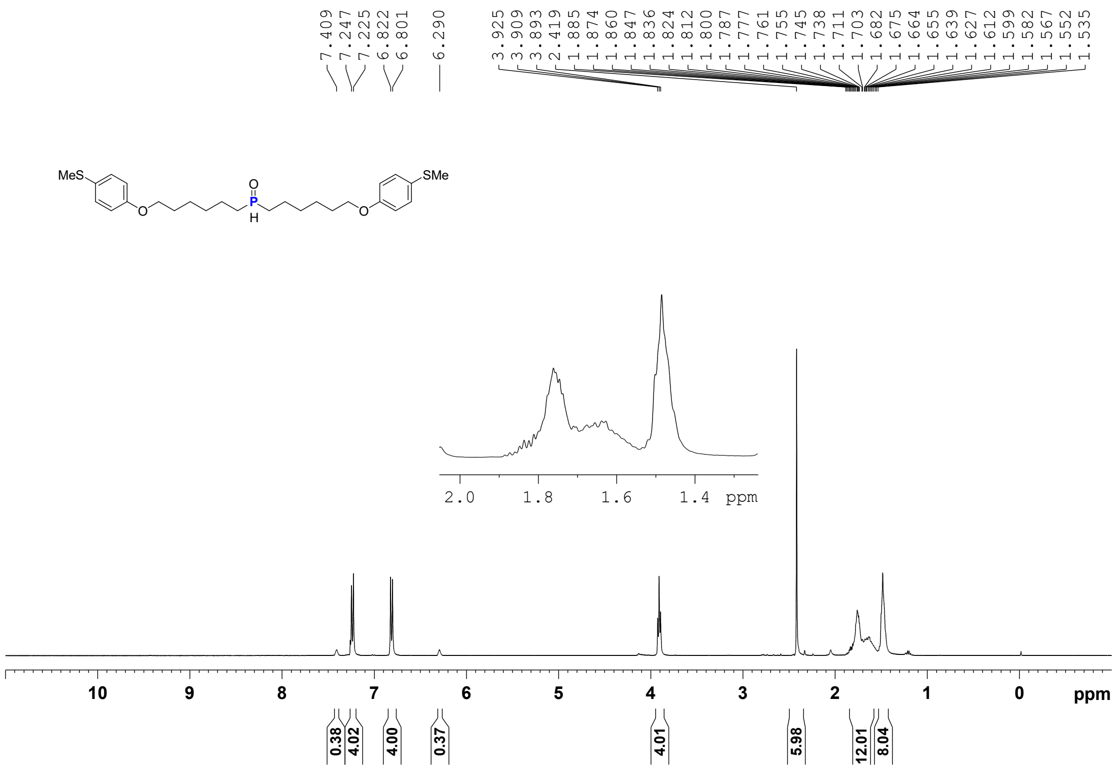
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4r**



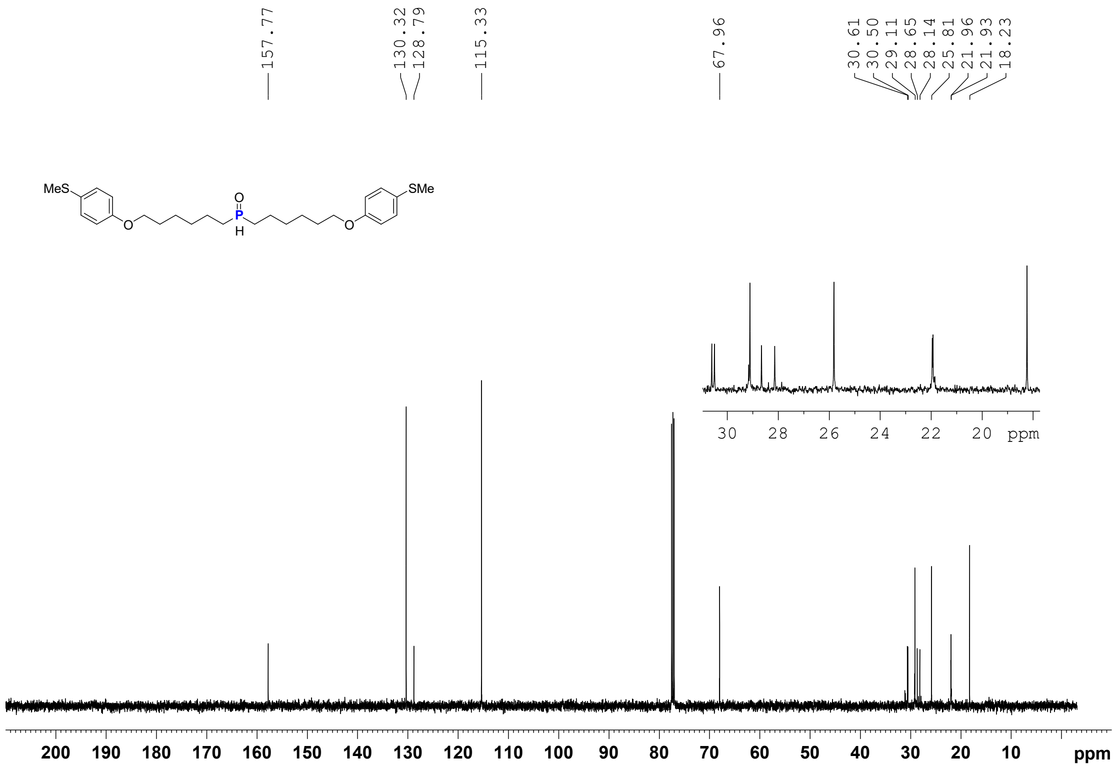
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4r**



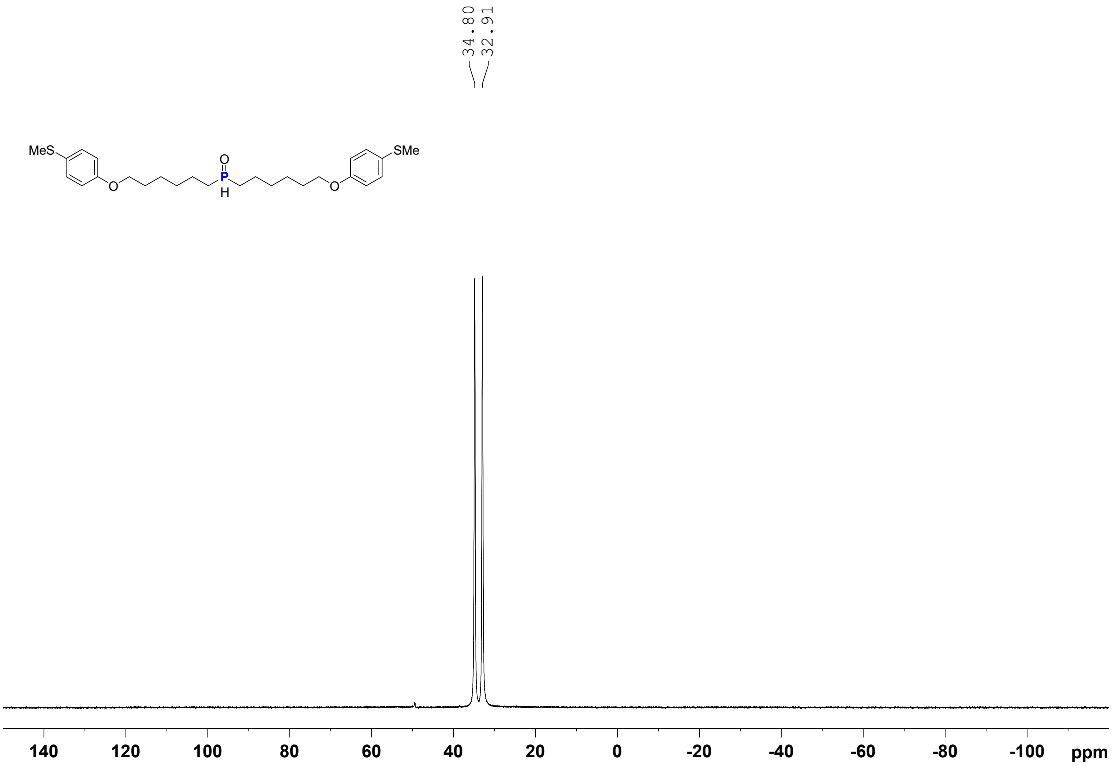
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4r**



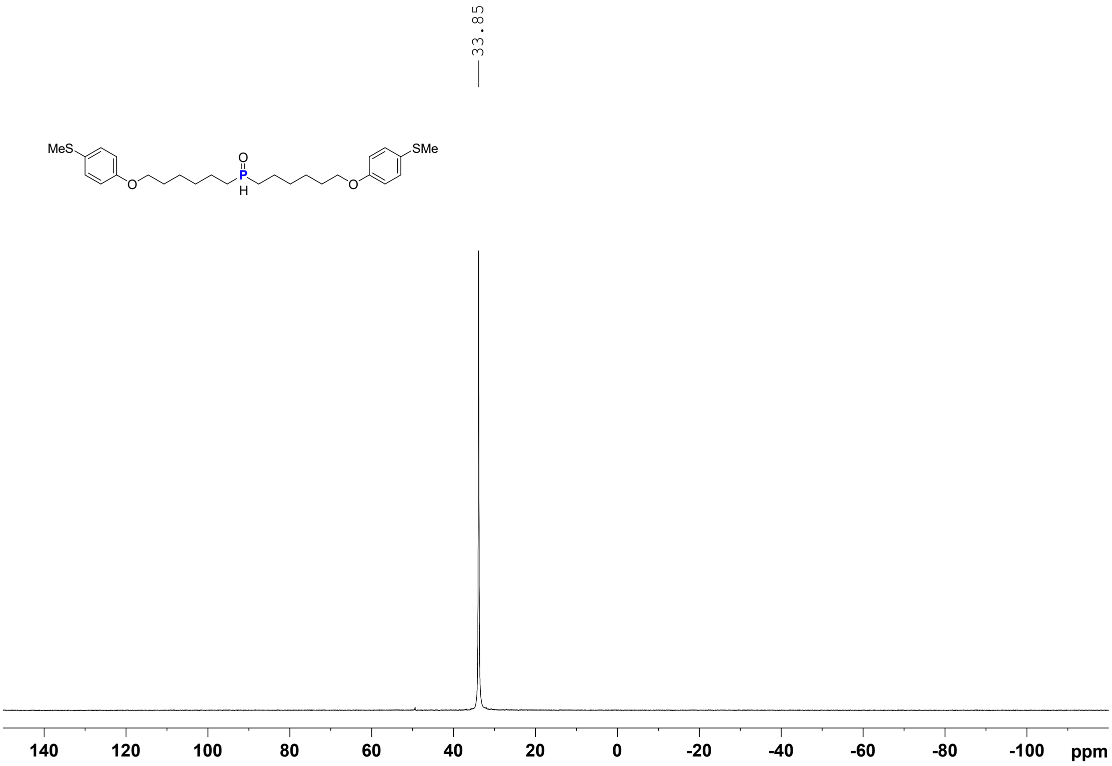
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4s**



^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4s**



^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4s**



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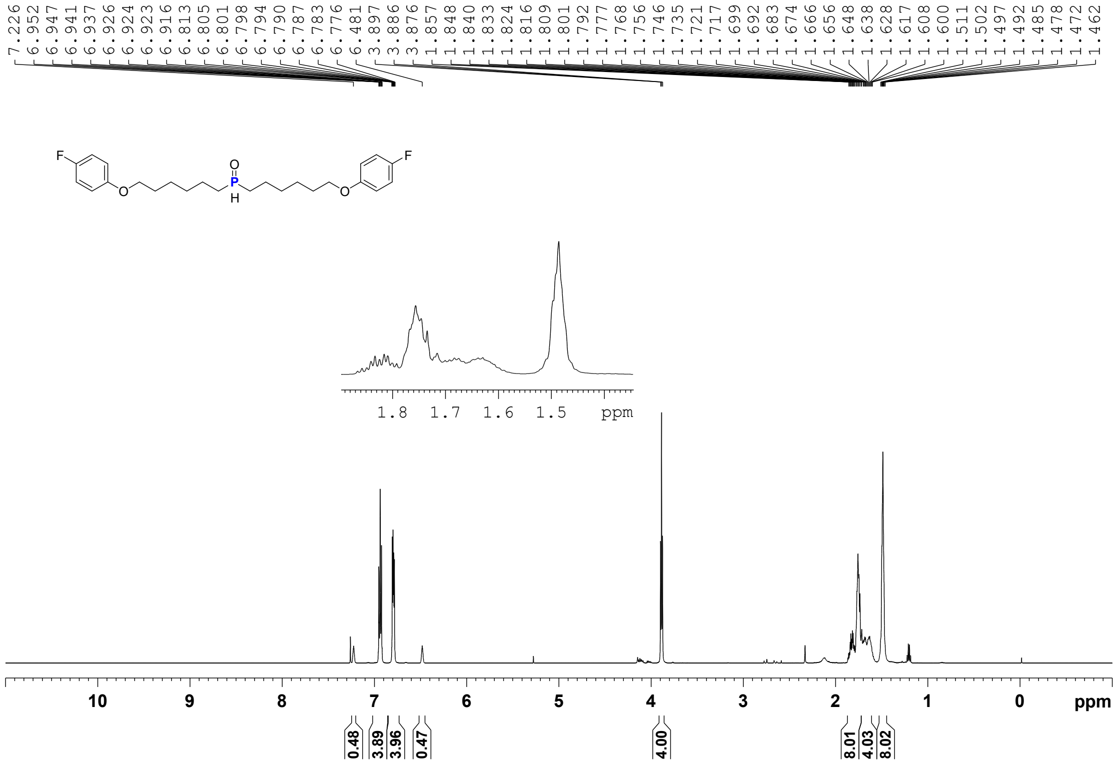
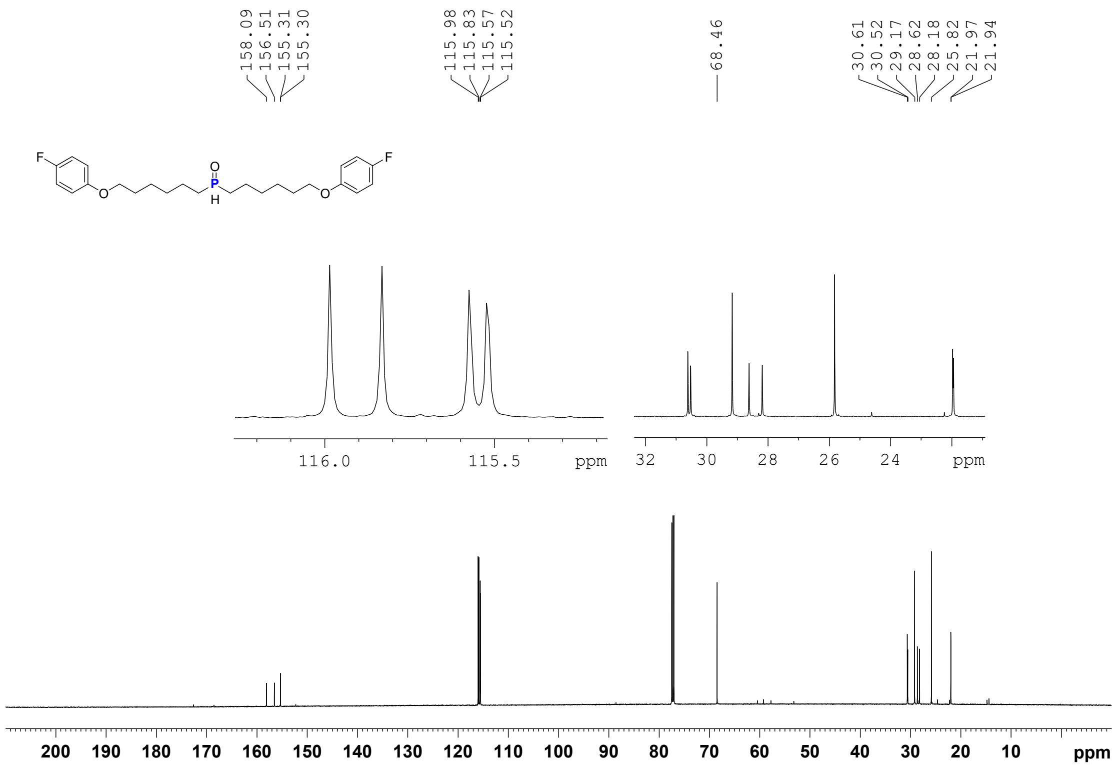
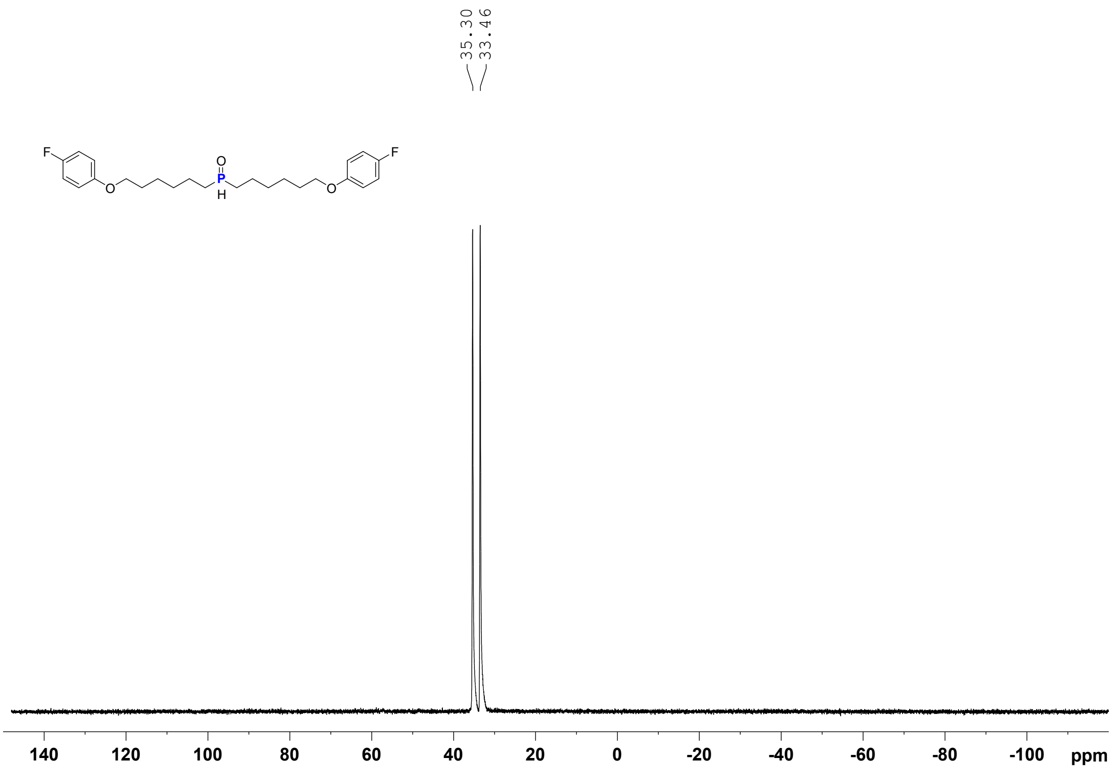


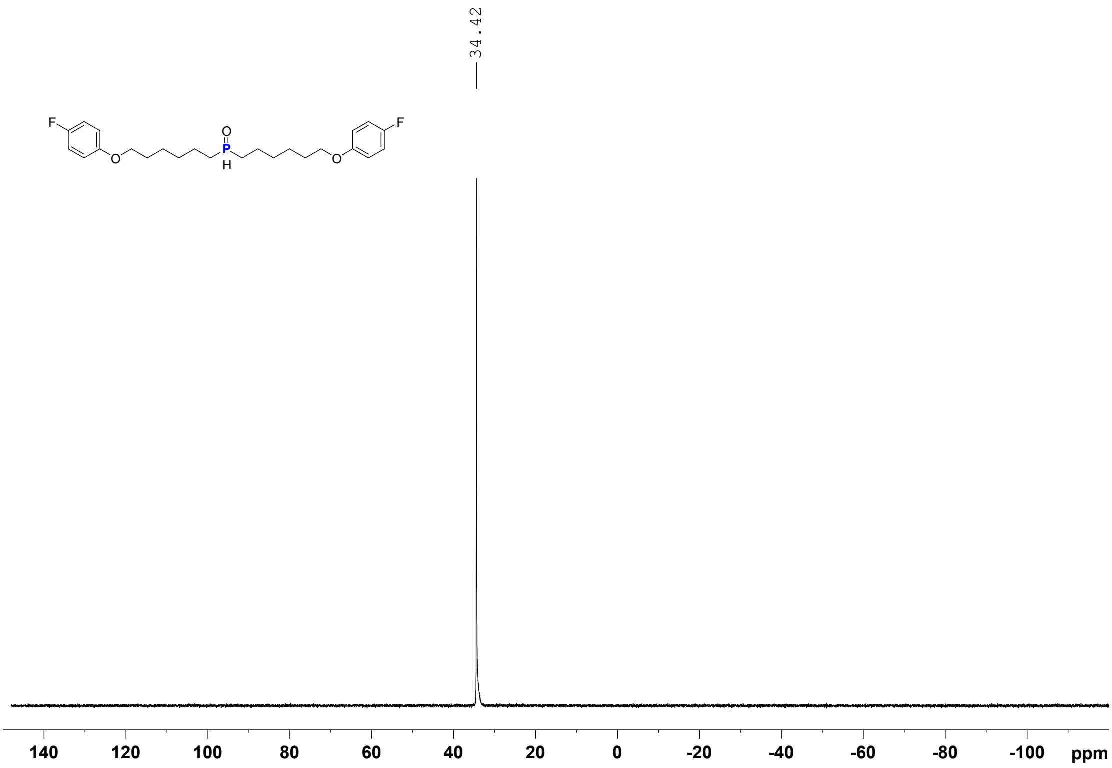
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4t**



^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4t**

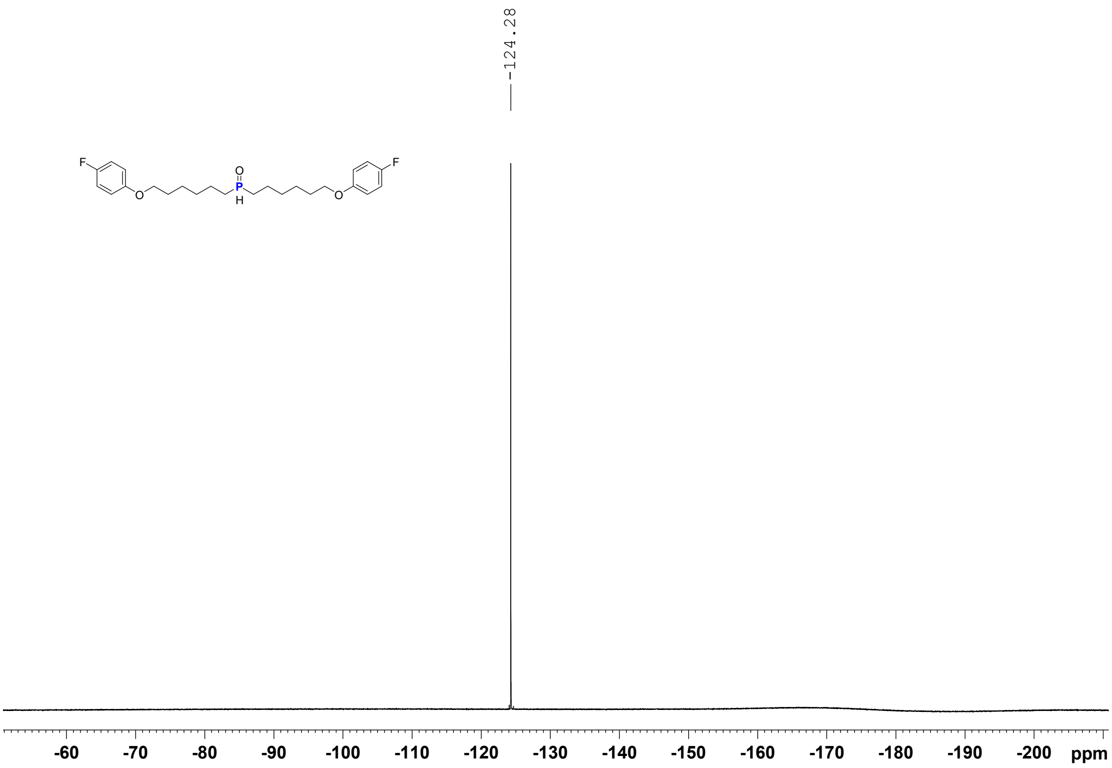


^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4t**

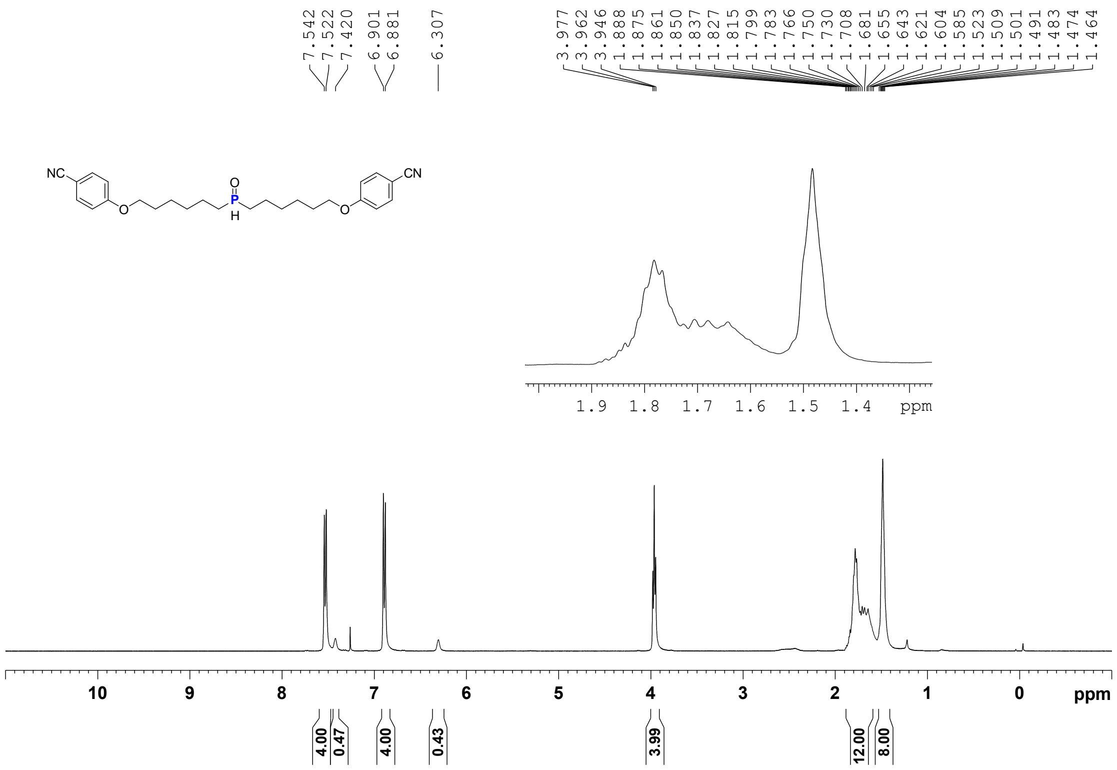


^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4t**

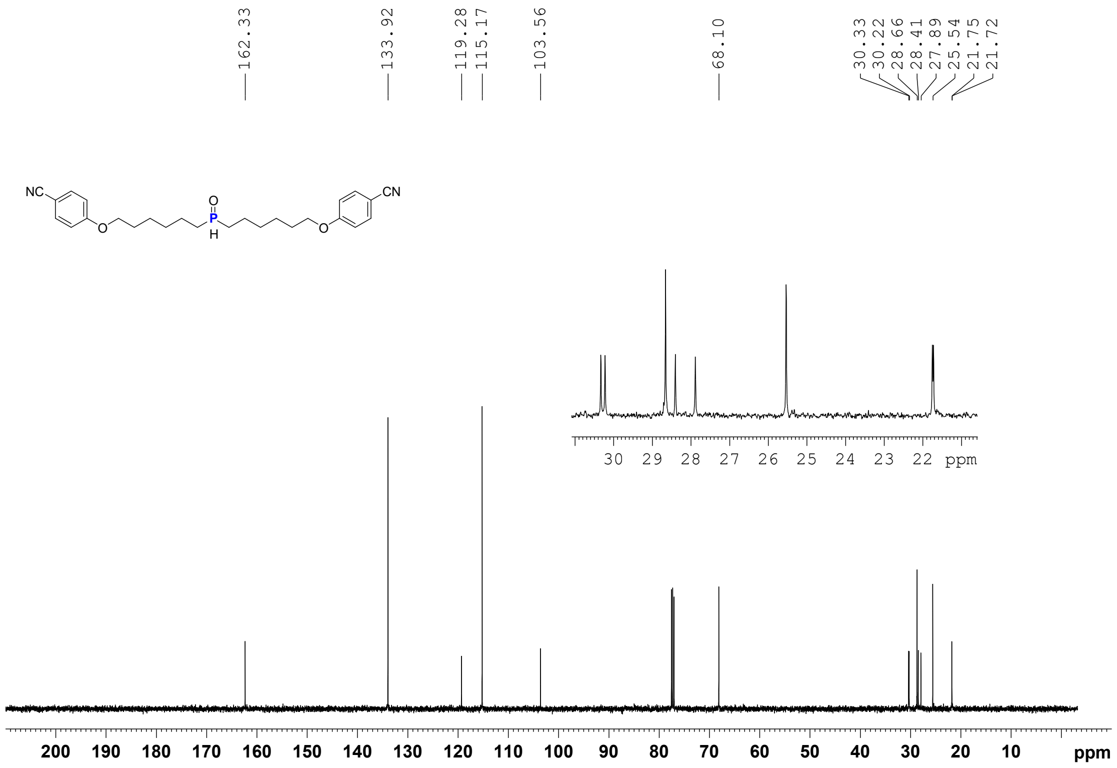
^{19}F NMR (471 MHz, CDCl$_3$) spectrum of compound **4t**



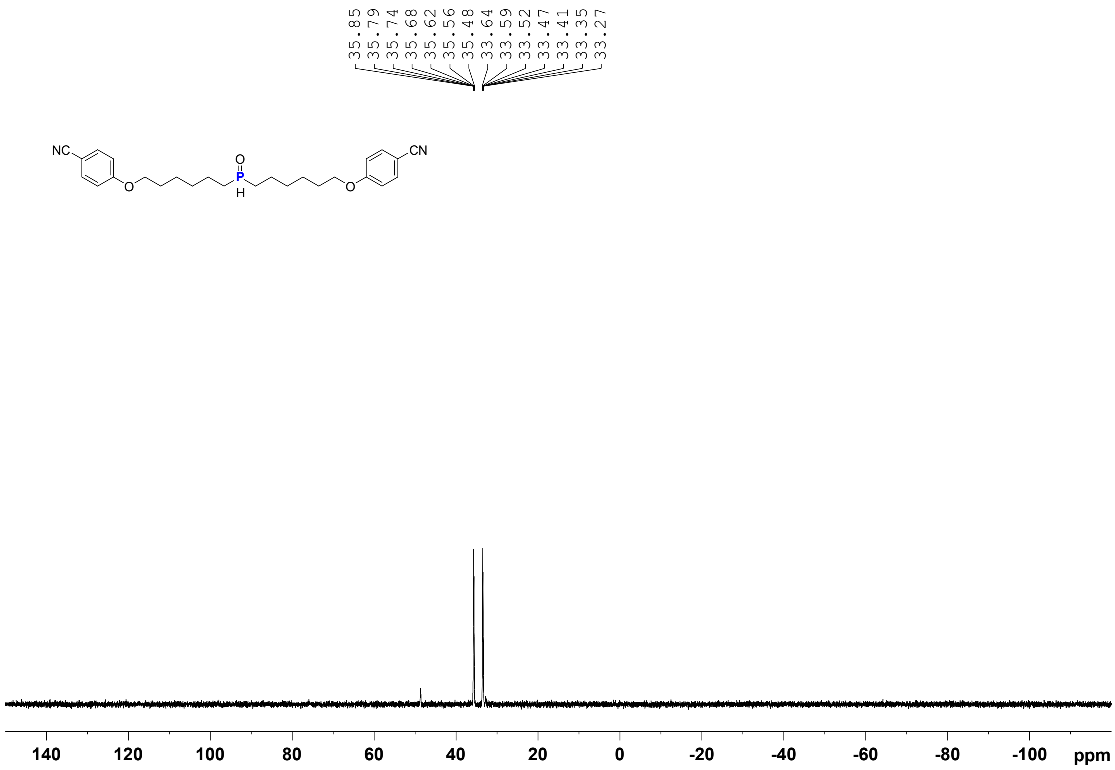
^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$) spectrum of compound **4t**



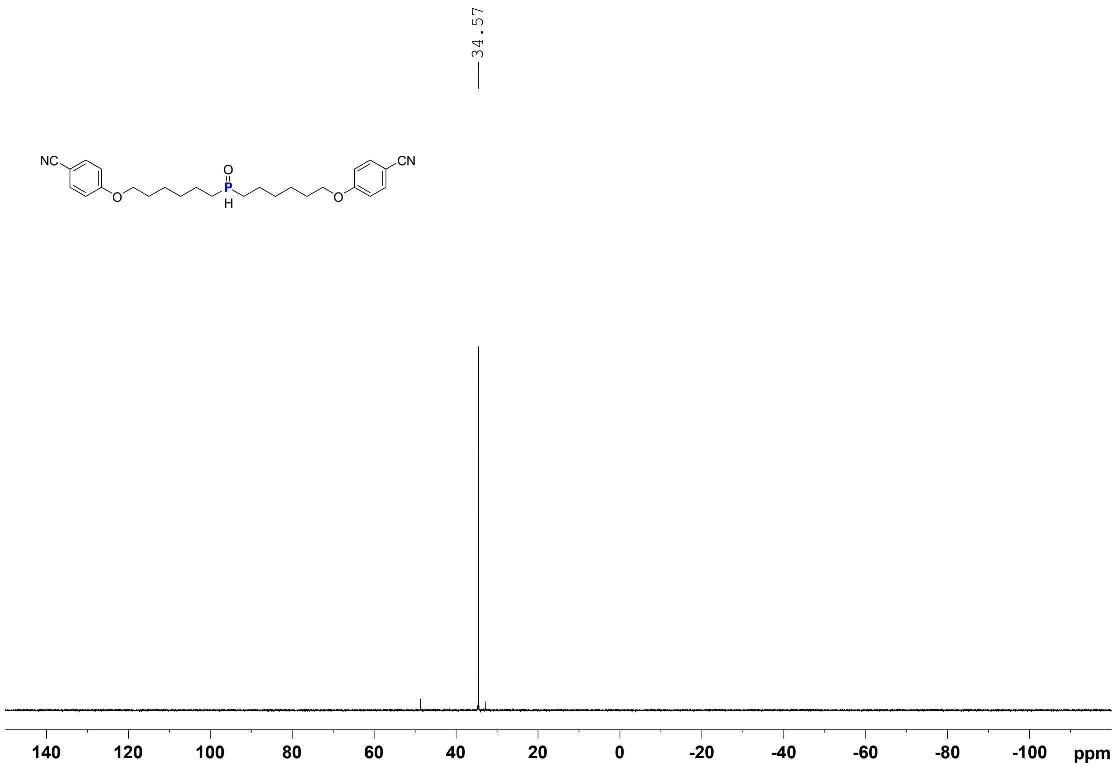
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4u**



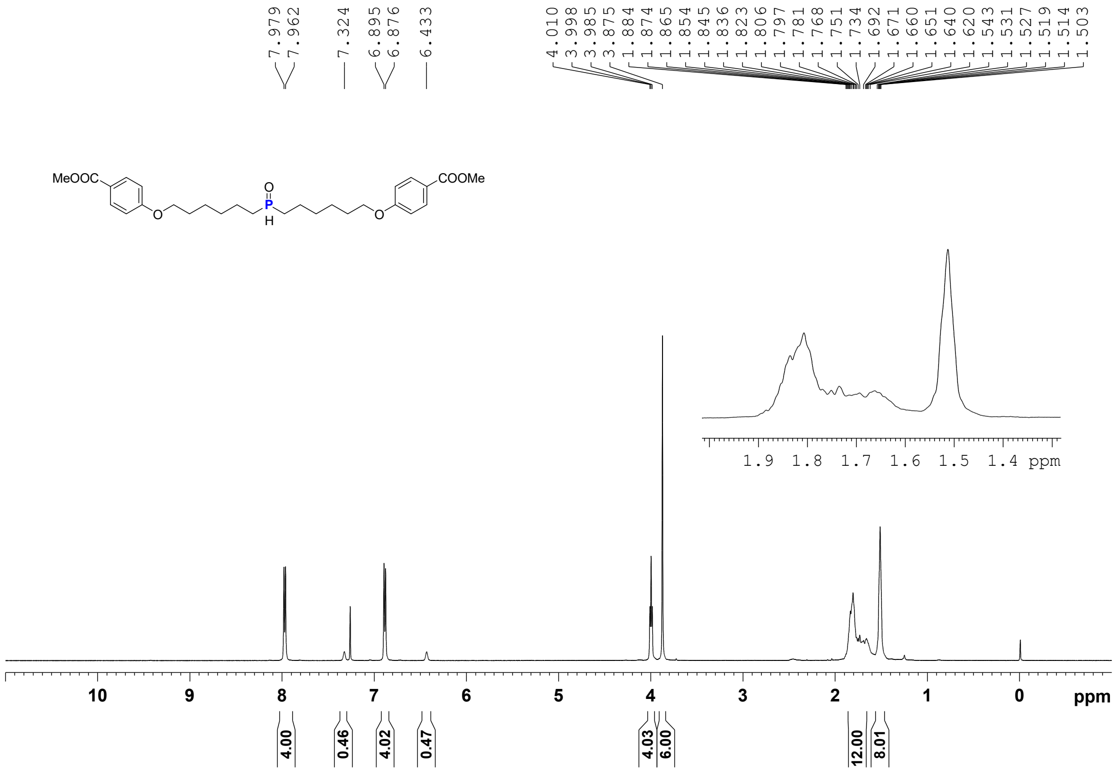
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4u**



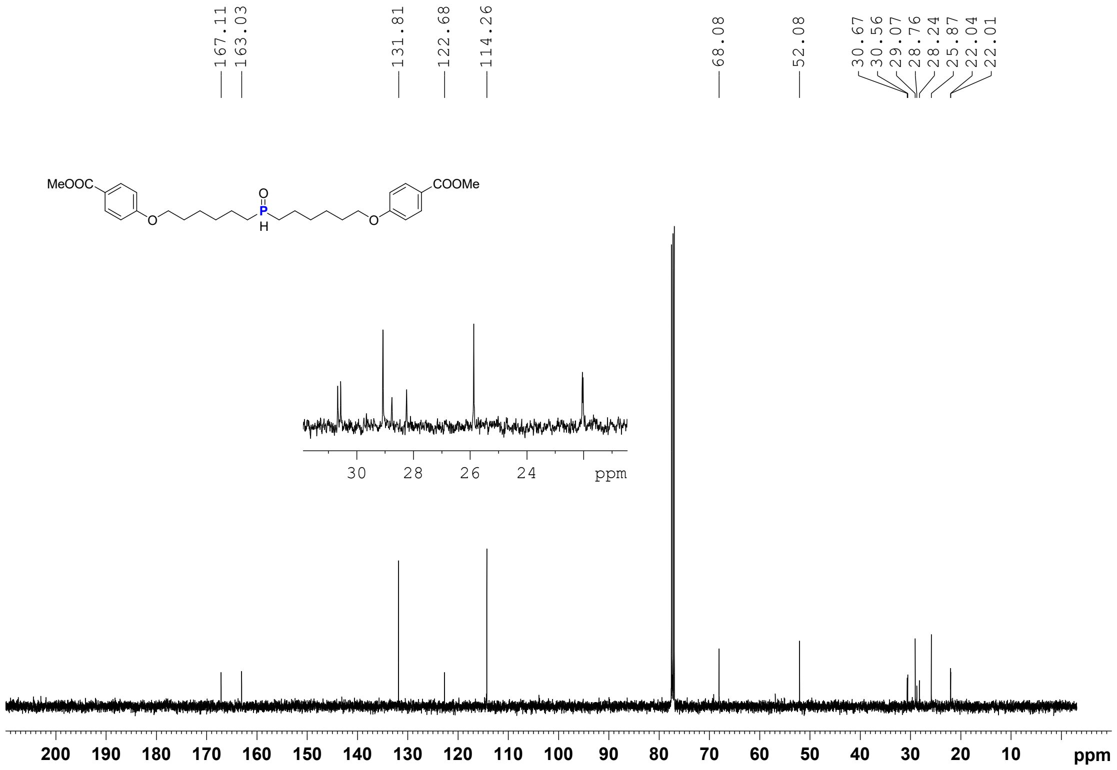
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4u**



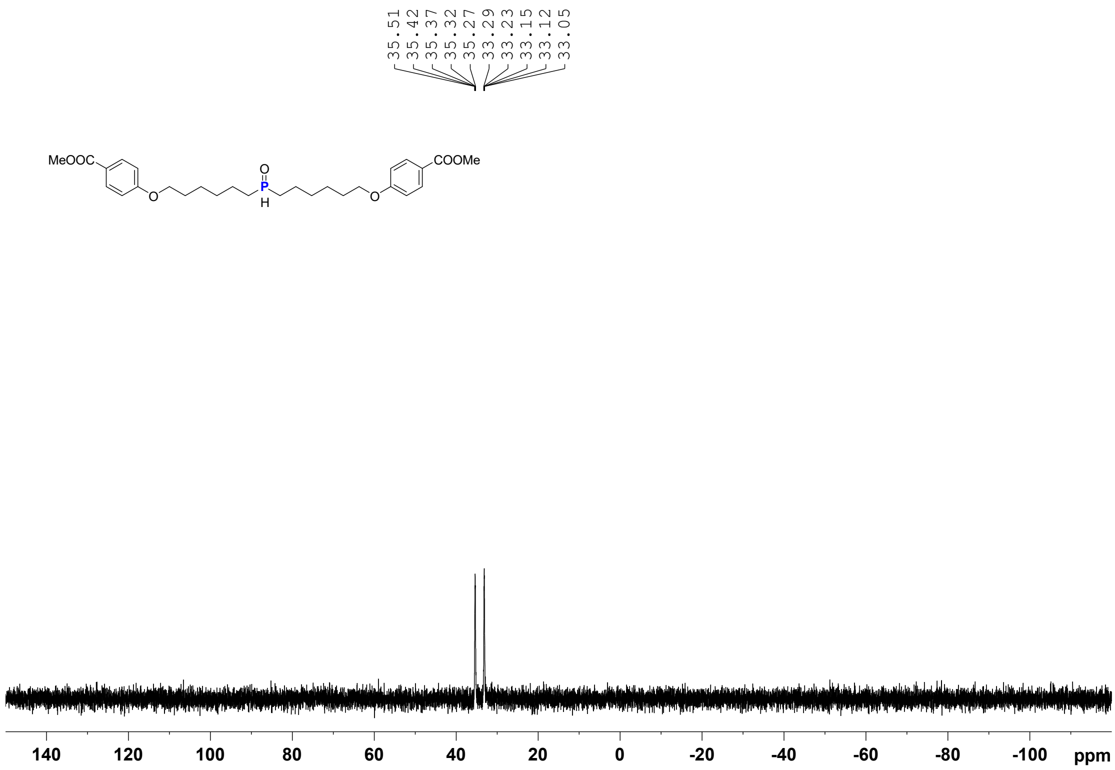
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4u**



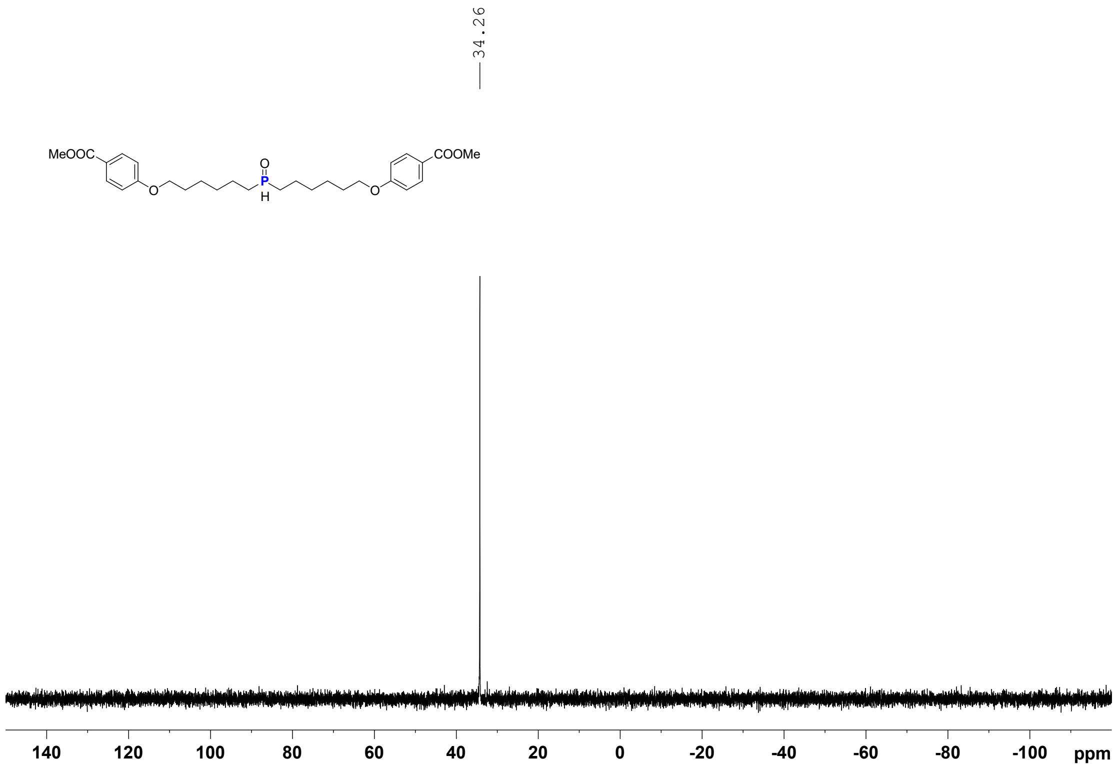
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4v**



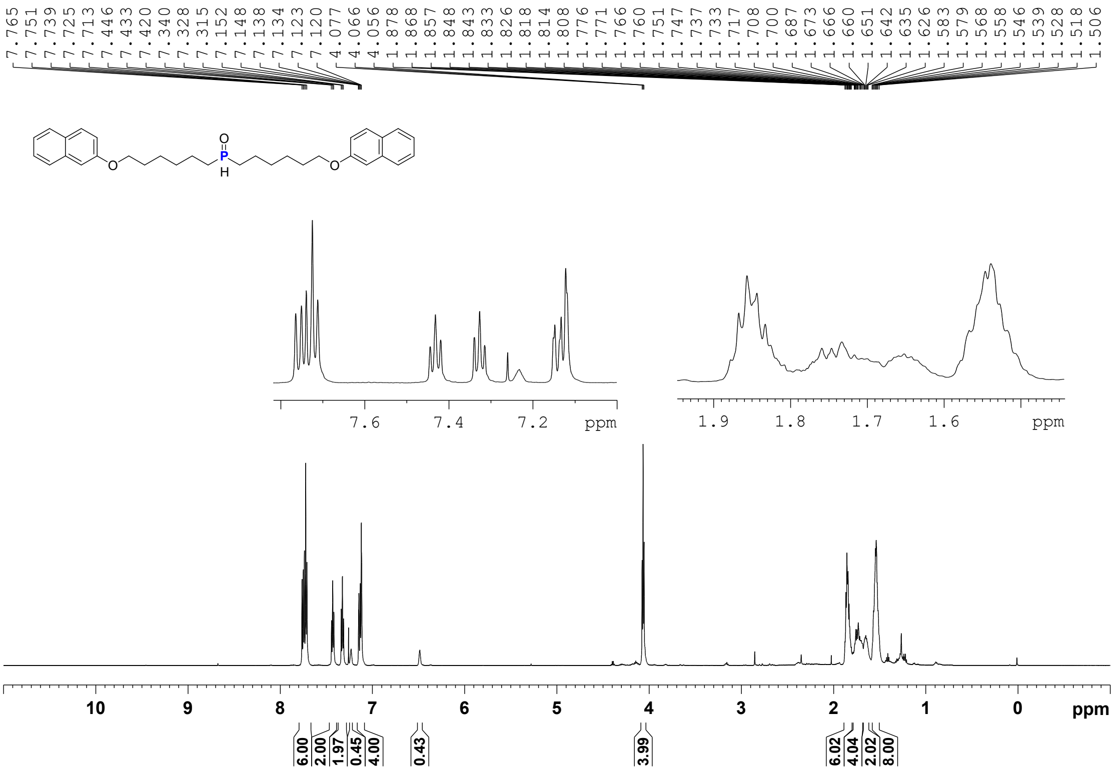
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4v**



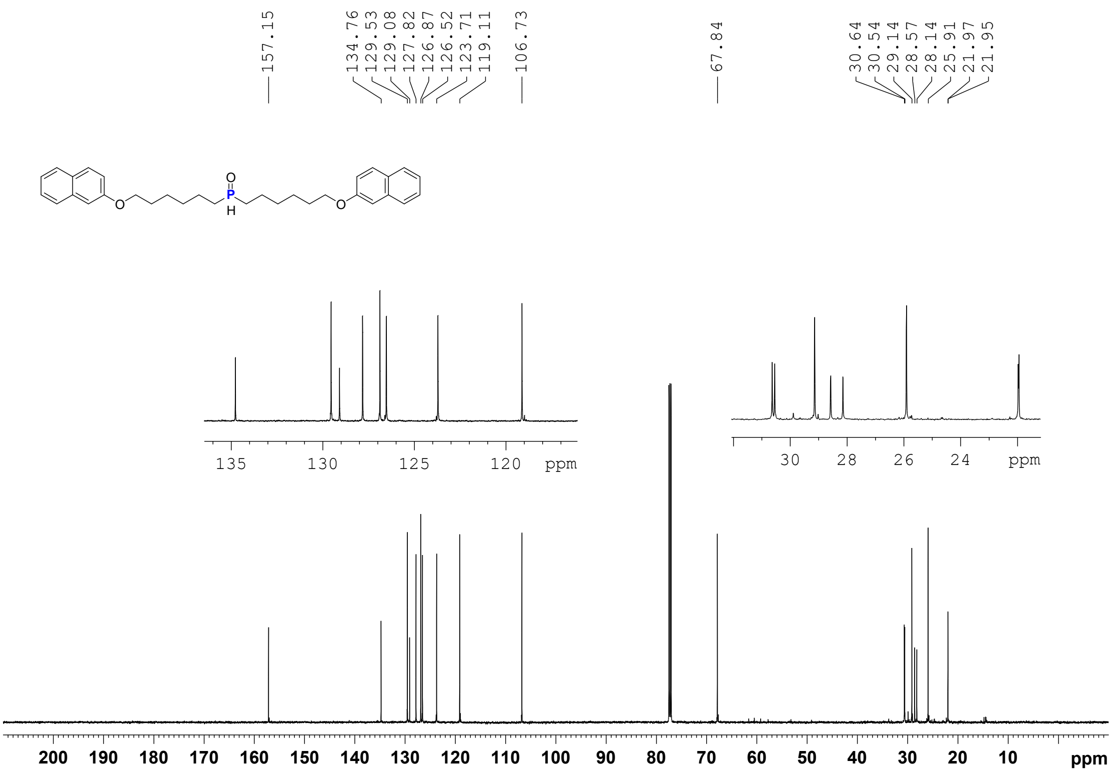
^{31}P NMR (202 MHz, CDCl$_3$) spectrum of compound **4v**



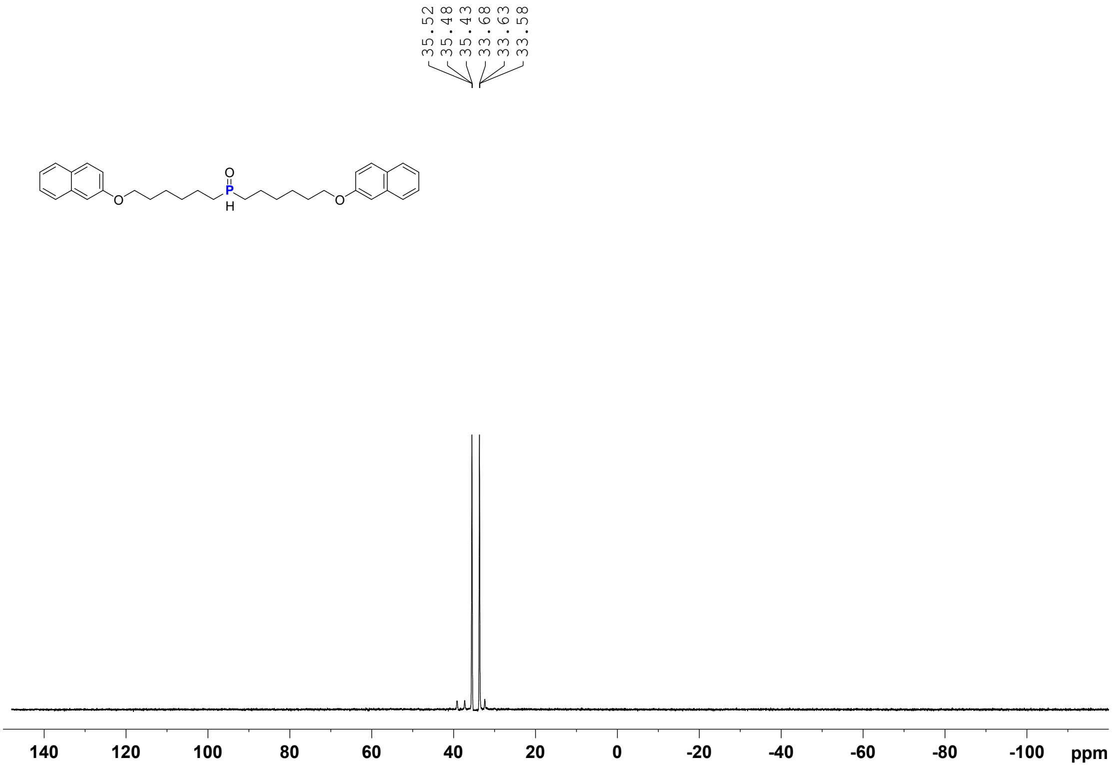
^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) spectrum of compound **4v**



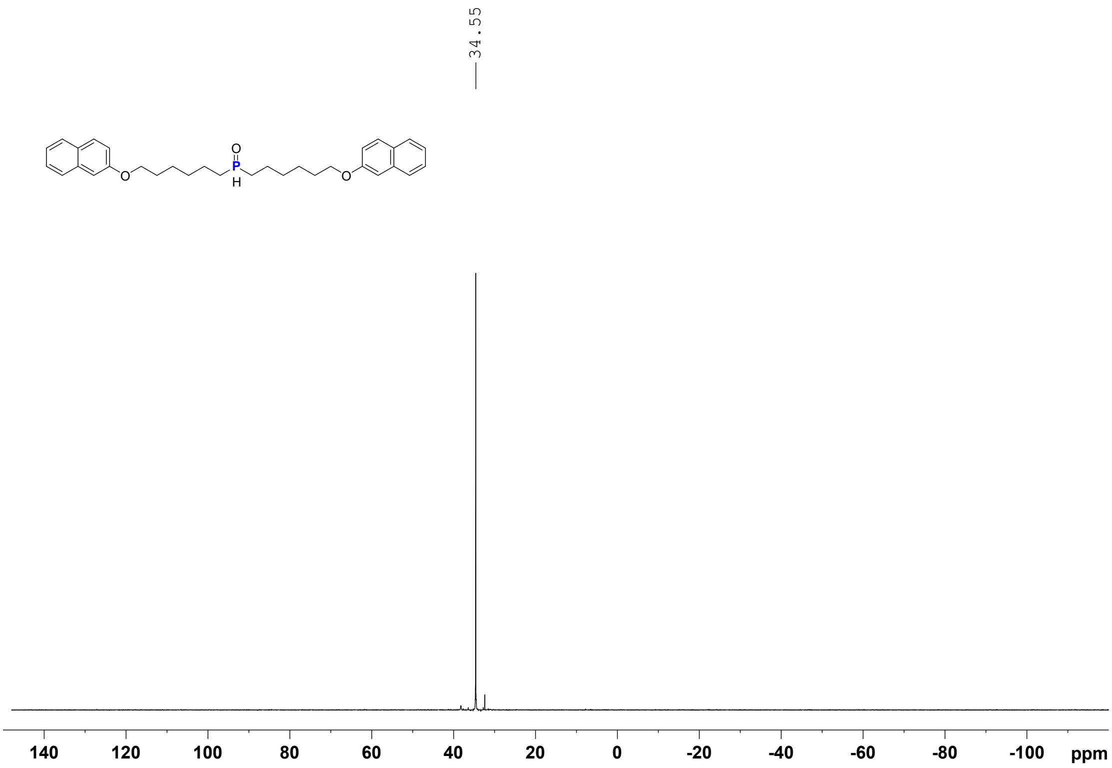
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **4w**



^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of compound **4w**



^{31}P NMR (202 MHz, $CDCl_3$) spectrum of compound **4w**



^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) spectrum of compound **4w**