Supplemental Experimental Procedures

General Methods

Commercial solvents and reagents were used as supplied. Unless otherwise stated, all reactions were monitored by TLC on Polygram® SIL/G_{25} plates, visualized using UV light, and stained using basic $KMnO_4$. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on either a Bruker Ascend™ 400 (400 MHz) or an Ultrashield™ 500 PLUS (500 MHz) instrument as dilute solutions in the stipulated solvent. All chemical shifts (δ) are reported in parts per million (ppm) with ^{1}H and ^{13}C NMR referenced to solvent signals [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.16)] and ^{31}P and ^{19}F NMR referenced to internal standards [^{31}P NMR: Ph_3P (-5.3); ^{19}F NMR: $PhCF_3$ (-63.0)]. Coupling constants (*J*) are reported in Hertz (Hz) and recorded after averaging. The multiplicity of the ^{1}H NMR signals are designated by one of the following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, hept=heptet, m=multiplet, br=broad signal. Diastereomeric ratios were assigned by ^{31}P NMR analysis. HRMS were obtained using an Agilent 6530 accurate-mass Q-TOF LC/MS in electrospray ionization (ESI) mode or a Thermo Fisher Scientific Q Exactive HF utilizing a heated electrospray ionization (HESI-II) probe. Flash column chromatography was performed using a Biotage® Selekt™ on Biotage® Sfär Silica D - Duo cartridges.

Comments on Safety

The work described involves the synthesis and handling of organophosphorus compounds, including agents with electrophilic P–X bonds. While offering immense potential scope for development, organophosphorus compounds can be highly toxic. For example, as with other electrophiles, compounds containing P(V)–F bonds can function as covalent nerve agents, reacting with the active site serine residues of acetylcholinesterase (AChE) and ablating enzyme function. AChE is essential in the termination of synaptic transmission, and inhibition leads to muscle paralysis, seizures, and fatal respiratory failure.

As with all potentially toxic/dangerous reagents (cf. azides used in CuAAC and the fumigant SO_2F_2 gas employed in SuFEx), the authors strongly advise caution when handling organophosphorus compounds. Before preparing any organophosphorus compound, it is recommended that colleagues acquaint themselves with the extensive literature on the toxicological properties of known representative compounds[1] and adhere to strict safety protocols. Readers should also refer to the American Chemical Society's policy on risk assessment as a helpful guide for chemical management and safety (https://www.acs.org/policy/publicpolicies/sustainability/chemicalsmanagement.html).

Nomenclature

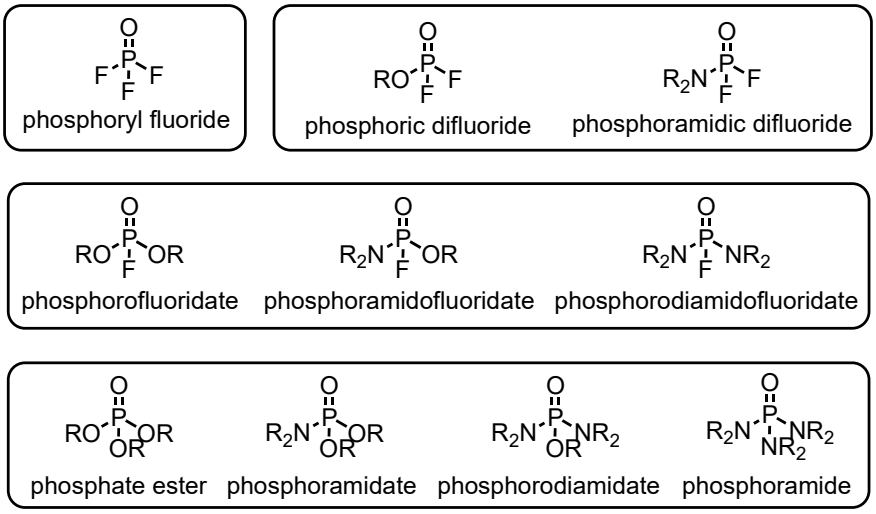
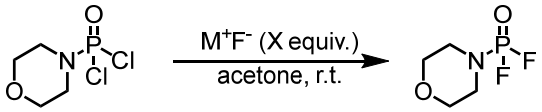


Figure S1: Naming conventions for organophosphorus(V) compounds.

PFEx Substrate Synthesis and Reactivity

Table S1. Conversion of phosphoramidic dichloride **7a** to phosphoramidic difluoride **9a**.



7a **9a**

Entry	M^+F^- (equiv)	Time (h)	Conversion[a] (Yield)
1	NaF (2.00)	16	0%
2[b]	KF (4.00)	4	Complex mixture
3	KF (4.00)	2	50%
5	KF (4.00)	16	Degradation
6[c]	KF (2.00)	2	70%
7[c]	KF (4.00)	2	50%
8[d]	KF (4.00)	2	50%
9[c]	KF (8.00)	2	90%
10[c]	KF (8.00)	3	100% (92%)

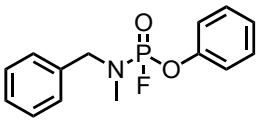
Reactions performed on 0.50 mmol scale at 0.5 M. [a]Conversion determined by ^{31}P NMR and ^{19}F NMR. [b]Water included as an additive. [c]Reaction performed at 0.125 M. [d]Reaction performed at 60 °C.

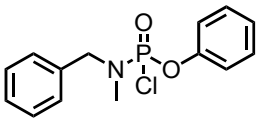
Stability Tests:

Aqueous buffers:
Stability tests were conducted in a 1:1 mixture of MeCN (to aid solubility) and the appropriate aqueous phosphate buffer (i.e., pH = 4.8, 7.4, or 8.8) at a concentration of 0.05 M. Reactions were stirred vigorously at room temperature to ensure a homogenous solution. Aliquots (50 µL) were taken immediately and at regular intervals (1 h, 3 h, 6 h, and 24 h), added to 650 µL of MeCN, filtered to remove solid material (i.e., phosphates), and analyzed by LCMS. Compound peak areas were quantified, and the formation of new peaks was noted.

Ethanol:
Solutions were prepared in anhydrous ethanol at a concentration of 0.05 M. Sampling and analysis were carried out as outlined above.

Table S2. Stability tests for phosphoramidofluoridate **12a** and chloridate **11a**.

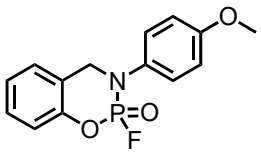


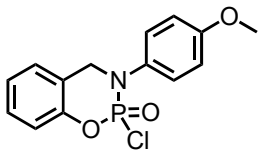


Solution	0 h	1 h	3 h	24 h	0 h	1 h	3 h	24 h
MeCN:buffer (pH = 4.8)								
MeCN:buffer (pH = 7.4)								
MeCN:buffer (pH = 8.8)								
EtOH								

Remaining substrate: >90% 25–90% <25%

Table S3. Stability tests for cyclic phosphoramidofluoridate **10c** and chloridate **8c**.

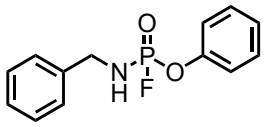


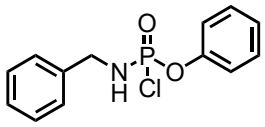


Solution	0 h	1 h	3 h	24 h	0 h	1 h	3 h	24 h
MeCN:buffer (pH = 4.8)								
MeCN:buffer (pH = 7.4)								
MeCN:buffer (pH = 8.8)								
EtOH								

Remaining substrate: >90% 25–90% <25%

Table S4. Stability tests for phosphoramidofluoridate **12c** and chloridate **11c**.

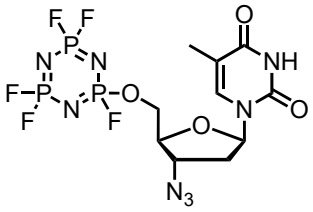




Solution	0 h	1 h	3 h	24 h	0 h	1 h	3 h	24 h
MeCN:buffer (pH = 4.8)								
MeCN:buffer (pH = 7.4)								
MeCN:buffer (pH = 8.8)								
EtOH								

Remaining substrate: >90% 25–90% <25%

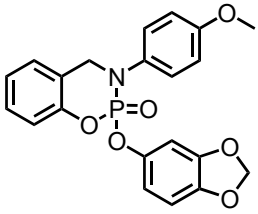
Table S5. Stability tests for HFP-adduct **17d**.



Solution	0 h	1 h	3 h	24 h
MeCN:buffer (pH = 4.8)				
MeCN:buffer (pH = 7.4)				
MeCN:buffer (pH = 8.8)				
EtOH				

Remaining substrate: >90% 25–90% <25%

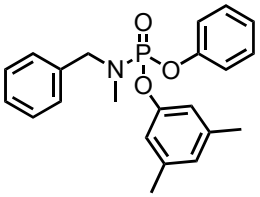
Table S6. Stability tests for phosphoramidate **15d**.



Solution	0 h	1 h	3 h	24 h
MeCN:buffer (pH = 4.8)				
MeCN:buffer (pH = 7.4)				
MeCN:buffer (pH = 8.8)				
EtOH				

Remaining substrate: >90% 25–90% <25%

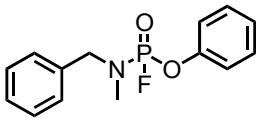
Table S7. Stability tests for phosphoramidate **16a**.

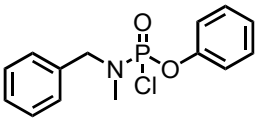


Solution	0 h	1 h	3 h	24 h
MeCN:buffer (pH = 4.8)				
MeCN:buffer (pH = 7.4)				
MeCN:buffer (pH = 8.8)				
EtOH				

Remaining substrate: >90% 25–90% <25%

Table S8. Additional stability tests for phosphoramidofluoridate **12a** and chloridate **11a**.





Conditions	Outcome	Outcome
CrO_3, AcOH, r.t.	Degraded after 30 min	Degraded after 30 min
PPh_3 (3 equiv), toluene, 90 °C	No reaction after 1 h	No reaction after 1 h
aniline, 80 °C	No reaction after 4 h	**11a** completely consumed after 1 h, P–Cl exchange product identified
aniline, r.t.	No reaction after 10 days	-
aniline-water (50:50 v/v), r.t.	No reaction after 24 h	-

Remaining substrate: >90% 25–90% <25%

Acetylcholinesterase (AChE) Inhibition Assay:

Representative PFEx substrates were evaluated using an Attogene "Acetylcholinesterase Inhibition Assay" kit (catalog number: EZ2018) that uses recombinant insect-derived enzyme. Stock solutions were prepared in DMSO prior to dilution with the provided buffer. The known reversible AChE inhibitor tacrine (trade name: Cognex) was used as a positive control. "No inhibitor" and "no enzyme" wells were used to give 0% and 100% AChE inhibition values, respectively. The absorbance at 412 nm of each well was measured after 5 minutes of incubation at room temperature. Each concentration was carried out in duplicate, and averaged results are presented.

Results: Compounds **8a**, **12c**, and **17d** showed no enzyme inhibition up to a concentration of 150 nM (Figure S3), whereas the cyclic phosphoramidofluoridate **10a** was found to be a potent inhibitor of AChE (estimated IC_{50} = 5 nM, Figure S2). The PFEx product phosphoramidate **15h** also inhibited enzyme activity over the evaluated concentration range (Figure S4). *Note:* Phosphoramidofluoridate **10a** and chloridate **8a** also absorbed at 412 nm resulting in a slight absorbance increase when tested at a concentration of 150 nM. Phosphoramidate **15h** absorbed significantly at 412 nm – results in Figure S4 are corrected to account for this.

Figure S2. AChE inhibition results, tacrine and phosphoramidofluoridate **10a**.

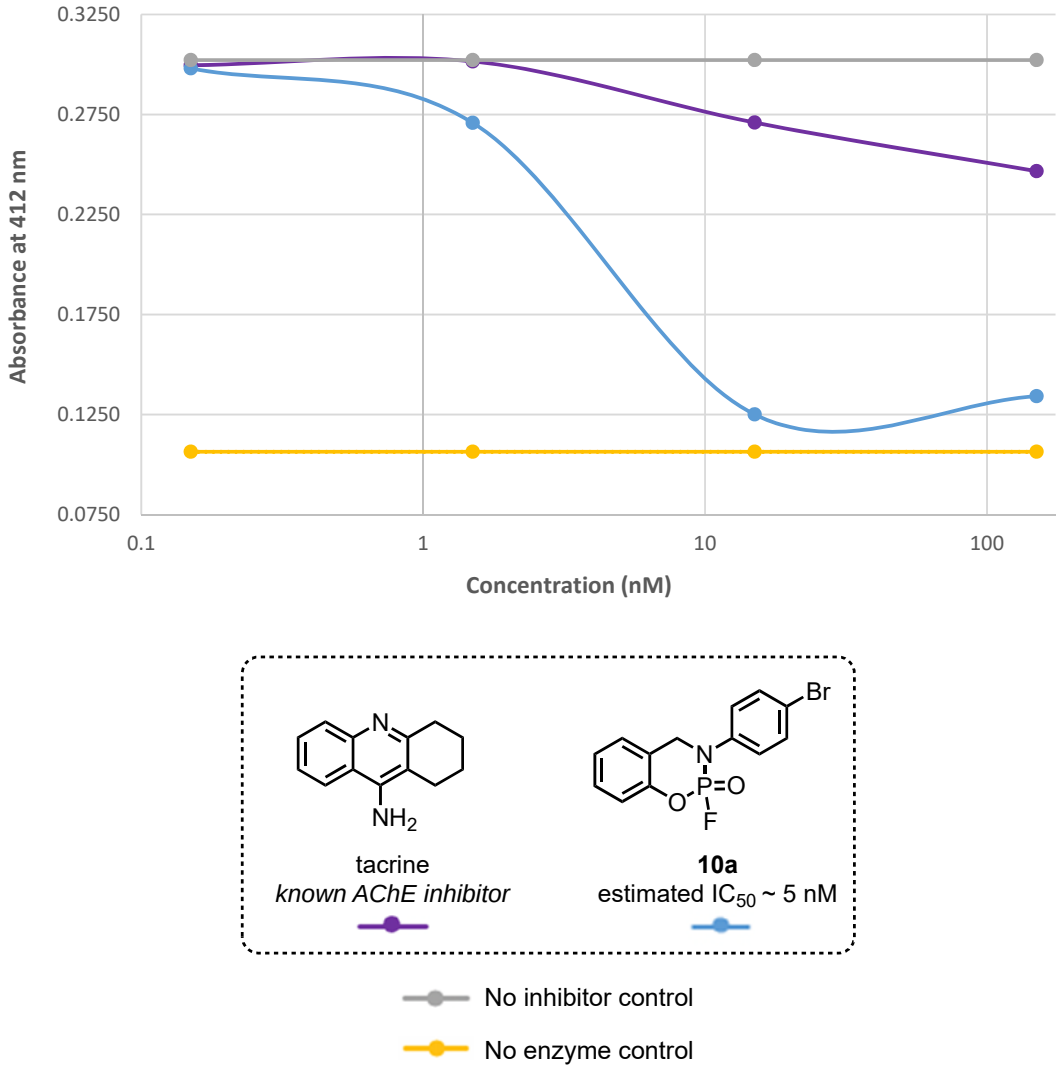


Figure S3. AChE inhibition results, phosphoramidochloridate **8a** and phosphamidofluoridates **12c** and **17d.**

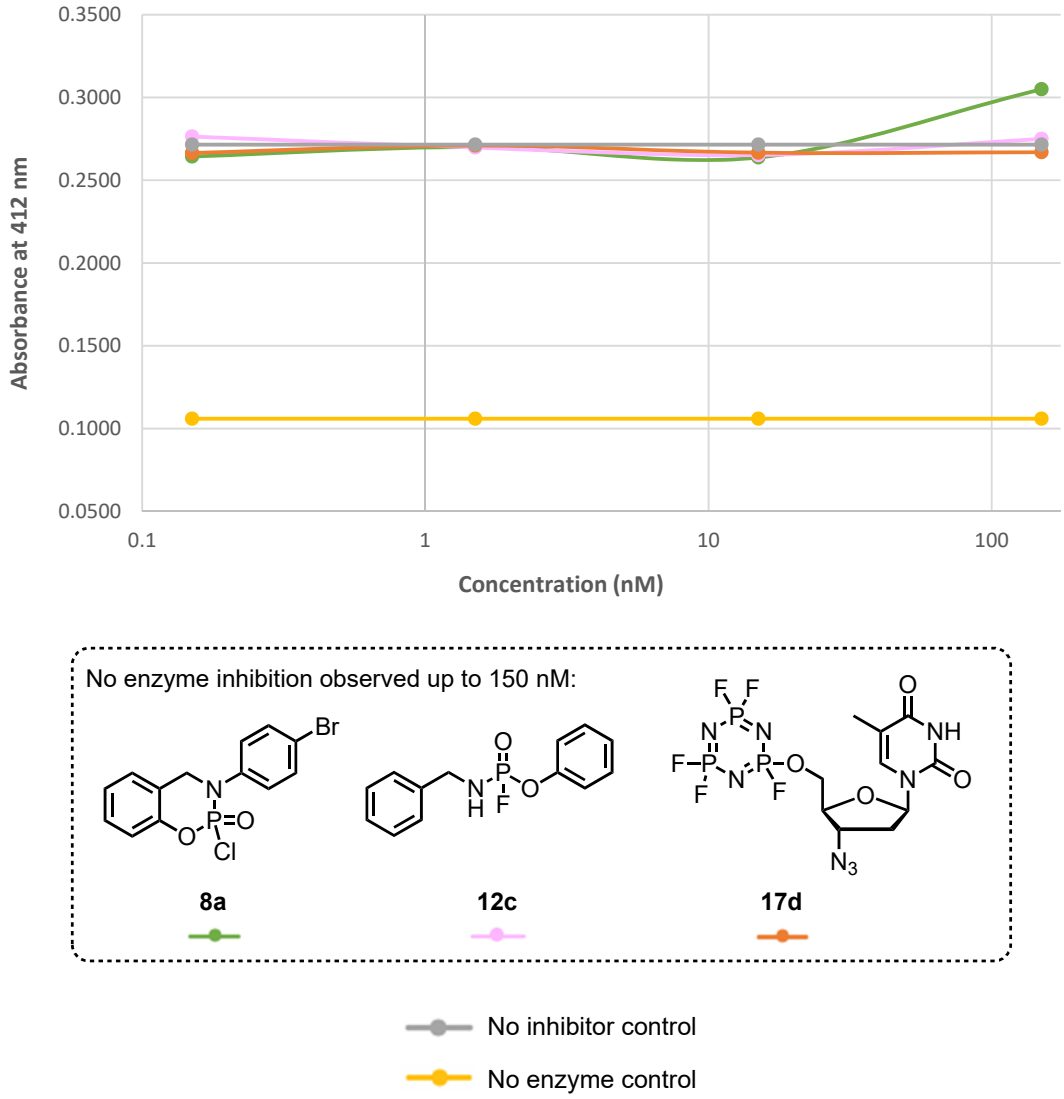
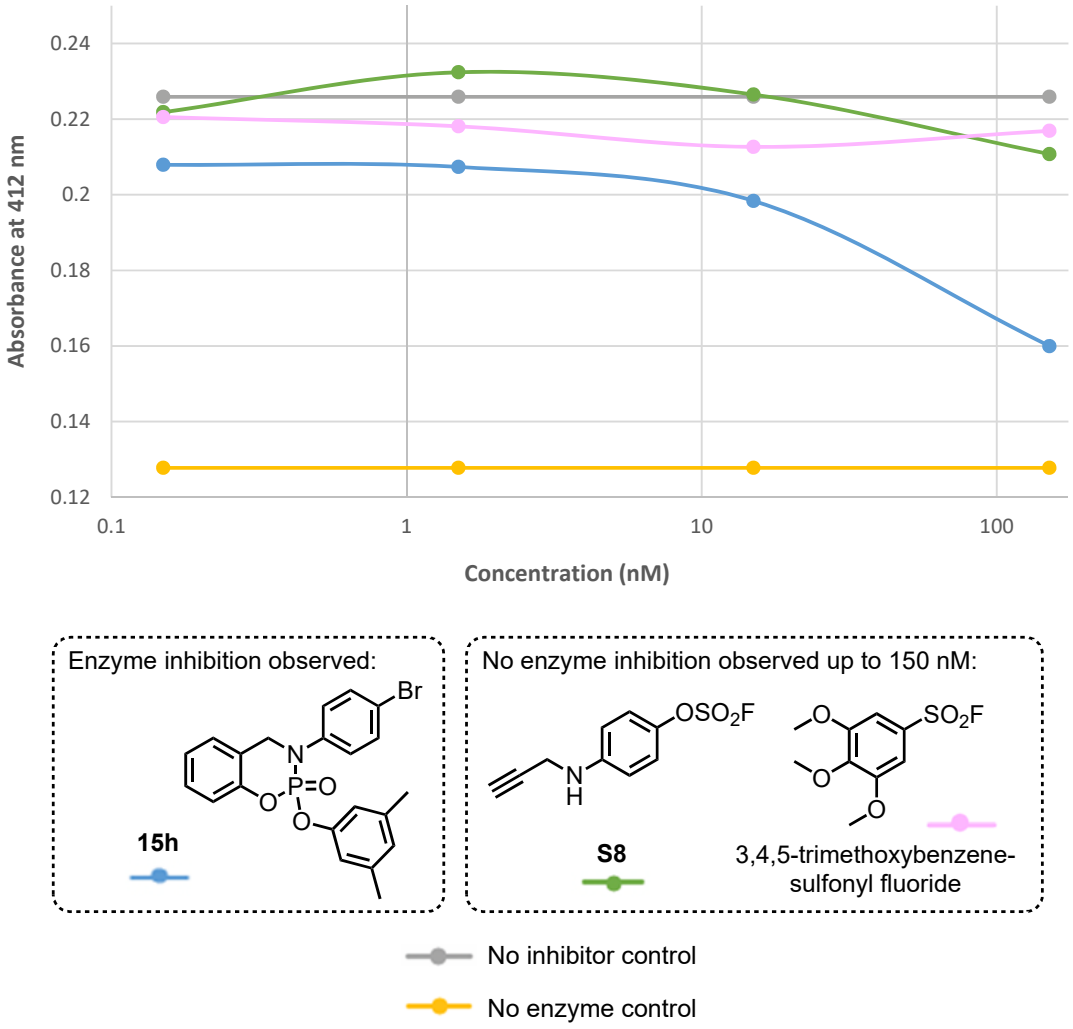
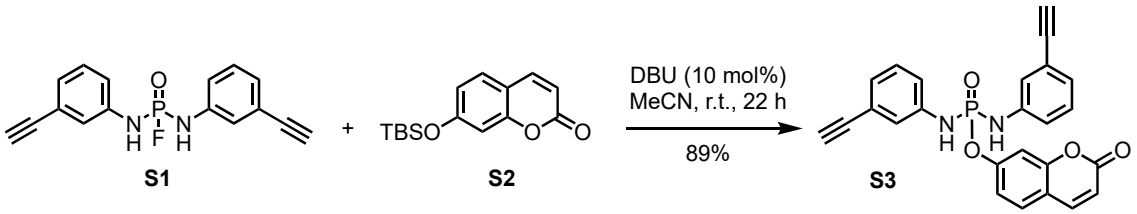


Figure S4. AChE inhibition results, phosphoramidate **15h**, fluorosulfate **S8,** and 3,4,5-trimethoxybenzenesulfonyl fluoride.



PFEx Reaction Development

Preliminary PFEx Reaction:



S1 **S2** **S3**

To a stirred solution of *N,N*'-di(3-ethynyl)phenylphosphorodiamidofluoridate (30 mg, 0.1 mmol, **S1**) and TBS-protected 7-hydroxycoumarin (28 mg, 0.1 mmol, **S2**) in acetonitrile (0.5 mL, 0.2 M), was added DBU (20 µL, 10 mol%). The reaction was maintained at room temperature for 22 h. The reaction mixture was extracted with dichloromethane (3 x 10 mL), and the combined organic layer was washed with water (10 mL), brine (10 mL), and dried over anhydrous $MgSO_4$ before being concentrated *in vacuo*. The resulting crude was purified by flash column chromatography on silica gel eluting with methanol-dichloromethane (1:40 v/v) to afford the 7-coumarinyl *N,N*′-di(3-ethynyl)phenylphosphorodiamidate (39 mg, 89%, **S3**) as a white solid. $\mathbf{R_f}$ = 0.3 (1:10 methanol/dichloromethane). **mp** 170–172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 4 Hz, 2H), 7.38 (d, *J* = 4 Hz, 1H), 7.1–7.2 (m, 9H), 6.61 (d, *J* = 4 Hz, 2H), 6.31 (d, *J* = 4 Hz, 2H), 5.32 (s, 1H), 3.05 (s, 2H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.81 (t, J_{NP} = 10 Hz); **LRMS** (ESI^+) calculated for $C_{25}H_{18}N_2O_4P$ $[M+H]^+$: m/z = 441.1006, m/z found 441.0.

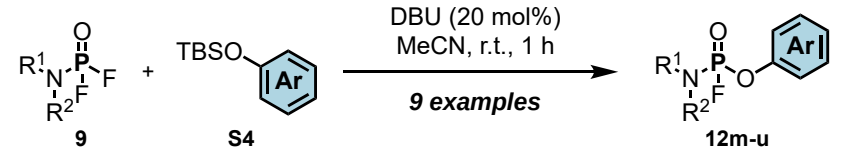
Table S9. Phosphorus fluoride exchange between phosphoramidic difluoride **9b** and TBS ether **13a**.

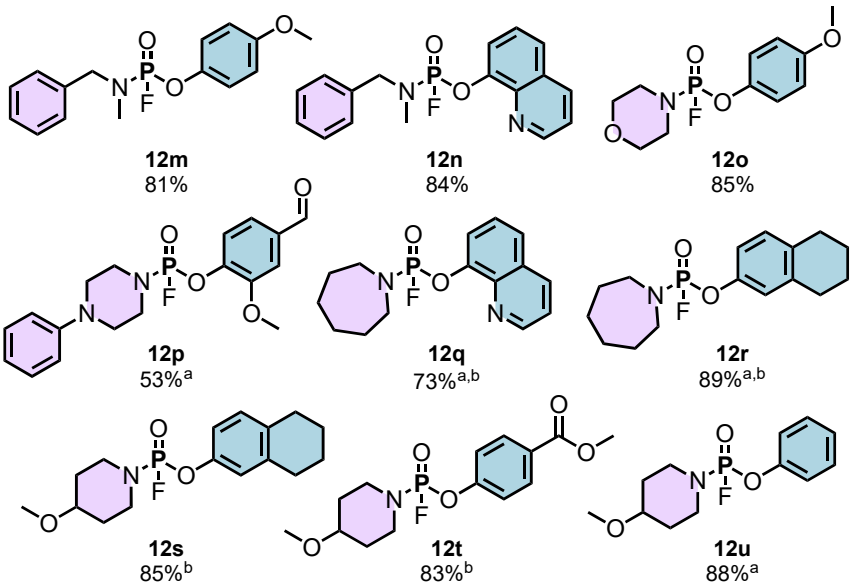
9b **S4** **12m**

Entry	**9b** (equiv)	**S4** (equiv)	DBU (mol%)	Yield
1	1.50	1.00	10	82%
2	1.50	1.00	20	87%
3	1.50	1.00	30	85%
4	1.20	1.00	20	81%
5	1.00	1.00	20	60%
6	1.00	1.00	0	0%

Reactions performed on 0.20 mmol scale at 0.4 M.

Scheme S1. PFEx reaction of phosphoamidic difluorides with TBS aryl ethers.



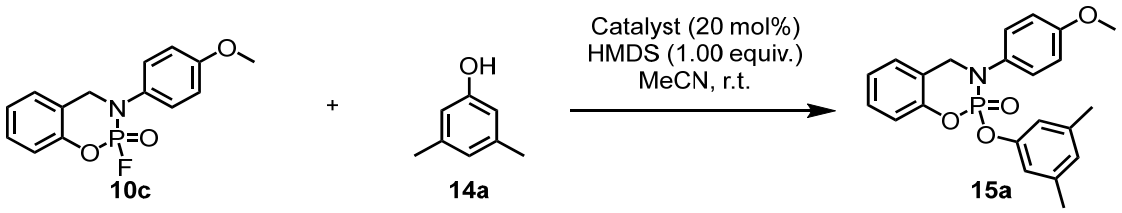


General reaction conditions: P(V)–F derivative (1.2 equiv) and aromatic TBS-ether (1.0 equiv) were stirred in acetonitrile (0.4 M) in the presence of DBU (20 mol%) for 1 h at room temperature. Isolated yields are reported. Reactions were conducted on a 1.20 mmol scale unless otherwise stated.

[a]An additional 20 mol% of DBU was added, and the reaction was stirred for a further 1 h.

[b]Reaction performed on 0.5 mmol of TBS ether.

Table S10. Catalyst screen for PFEx between cyclic phosphoramidofluoridate **10c** and 3,5-xylenol (**14a**).



10c + **14a** → **15a**

Entry	Catalyst	Time (h)	Conversion (%)[a]
1	P_4-^{t}Bu	0.5	>99
2	TBD	0.5	>99
3	BTMG	0.5	86
4	P_1-^{t}Bu	2	>99
5	TMG	2	83
6	DPG	2	Trace
7	BEMP	2	>99
8	MTBD	2	>99
9[b]	TBD	0.25	>99

Reactions were conducted on a 0.10 mmol scale in acetonitrile (0.25 M) using 1.00 equiv of both **10c** and **14a**. [a]Conversion was determined by ^{31}P NMR and ^{19}F NMR. [b]1.20 equiv HMDS and **14a** in MeCN (0.5 M).

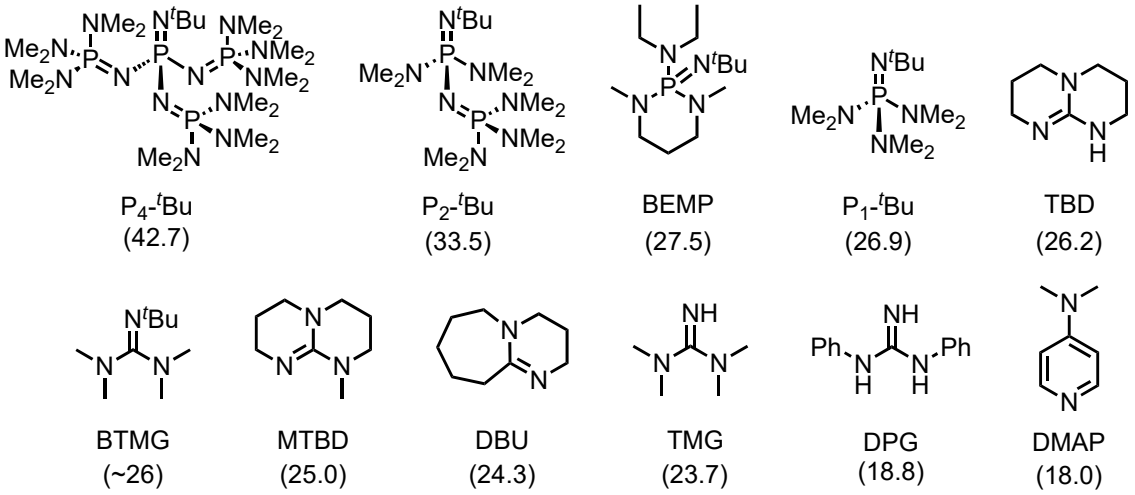
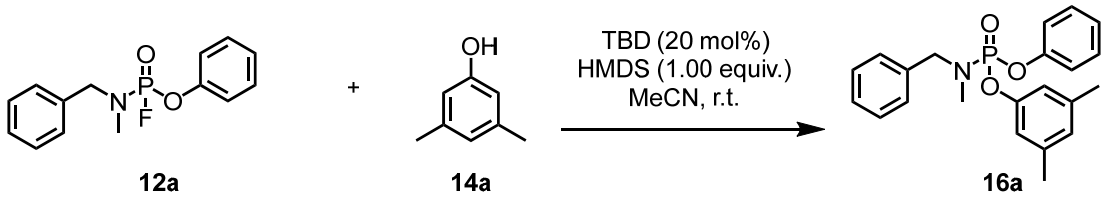


Figure S5. Bases screened in PFEx reaction (pK_aH values in MeCN).

Table S11. Catalyst screen for PFEx between phosphoramidofluoridate **12a** and 3,5-xylenol (**14a**).

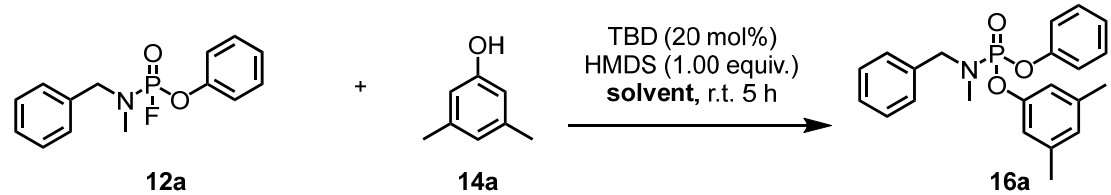


12a **14a** **16a**

Entry	Catalyst	Time (h)	Conversion (%)[a]
1	P_4-*t*Bu	1	>99
2	P_2-*t*Bu	1.5	>99
3	TBD	5	>99
4	BTMG	14	91
5	DBU	14	80
6	P_1-*t*Bu	14	10
7	TMG	14	9
8	DPG	14	Trace
9	BEMP	14	66
10	MTBD	14	64
11	DMAP	14	0
12[b]	TBD	2	>99
13[c]	TBD	7	16
14[d]	TBD	7	20

Reactions were conducted on a 0.10 mmol scale in acetonitrile (0.25 M). [a]Conversions were determined by ^{31}P NMR and ^{19}F NMR. [b]1.20 equiv HMDS and **14a** in MeCN (0.5 M). [c]Replaced HMDS with Et_3N (1.00 equiv). [d]Without HMDS.

Table S12. Solvent screen for PFEx between phosphoramidofluoridate **12a** and 3,5-xylenol (**14a**).



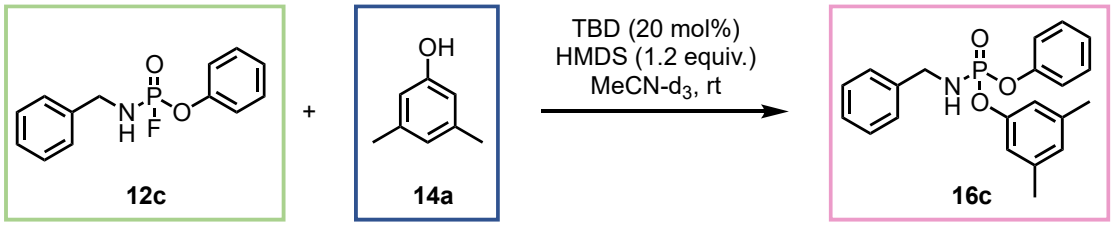
12a **14a** **16a**

Entry	Solvent	Conversion (%)[a]
1	MeCN	>99
2	DMF	85
3	THF	69
4	CH_2Cl_2	73
5	Toluene	68
6	DMSO	25
7	MeOH	0
8	Ether	62
9[b]	Water	13

Reactions were conducted on a 0.10 mmol scale (0.25 M). [a]Conversions were determined by ^{31}P NMR and ^{19}F NMR. [b]Carried out for 7 h.

NMR Experiments:

PFEx reaction between phosphoramidofluoridate **12c** and phenol **14a**:



Phosphoramidofluoridate **12c** (0.07 mmol) and phenol **14a** (0.07 mmol) were added to MeCN-d_3 (0.5 mL) in an NMR tube and vortexed. An initial ^{1}H NMR spectrum was obtained. A solution of TBD (20 mol%) and HMDS (1.2 equiv) was added and vortexed. ^{1}H NMR spectra were taken immediately and at 15-minute intervals until the reaction reached completion – this was noted at 60 min. Colored boxes match annotation on following spectra.

Figure S6. ^{1}H NMR spectrum for the PFEx reaction between phosphoramidofluoridate **12c** and phenol **14a** (400 MHz, MeCN-d_3)

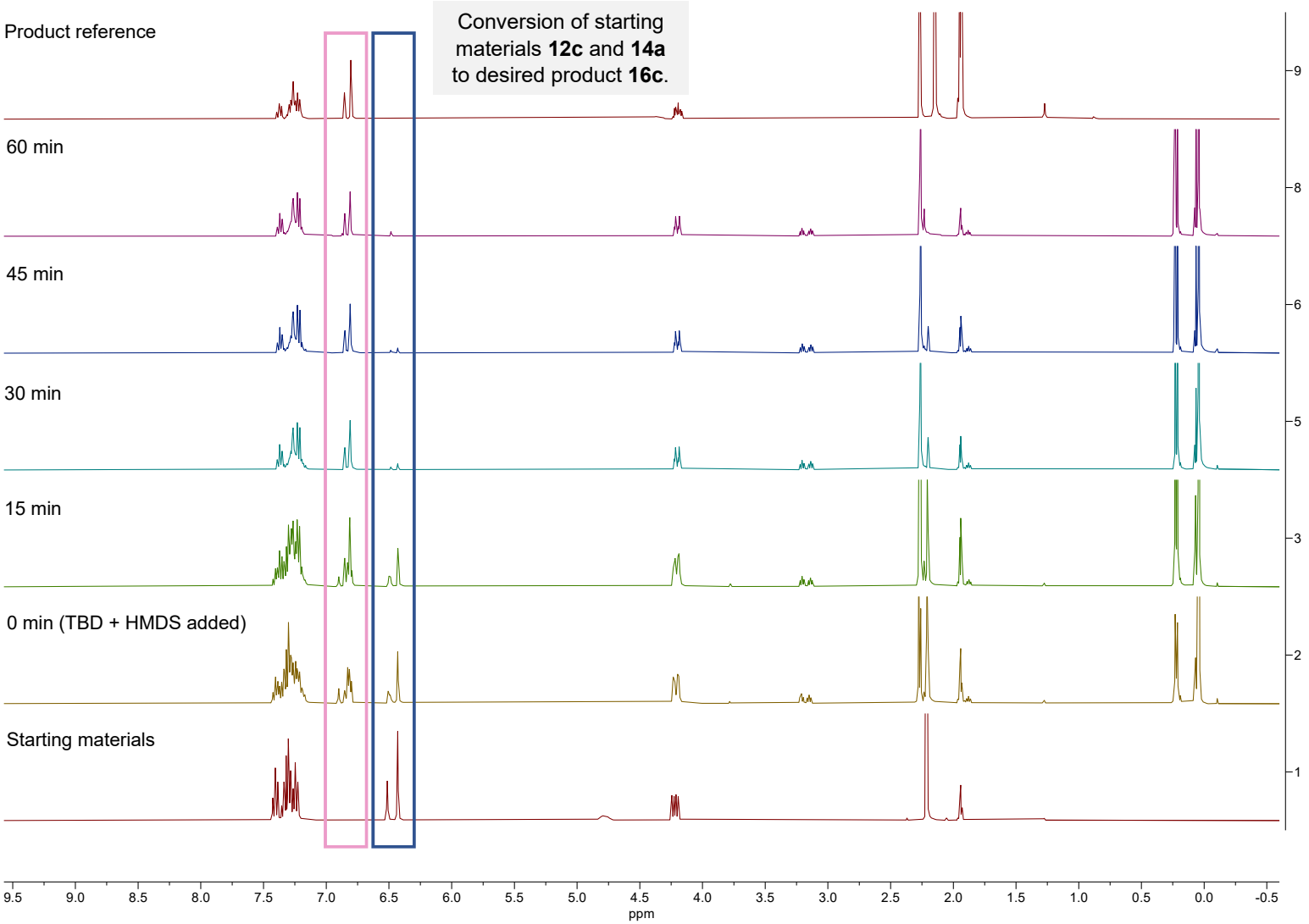
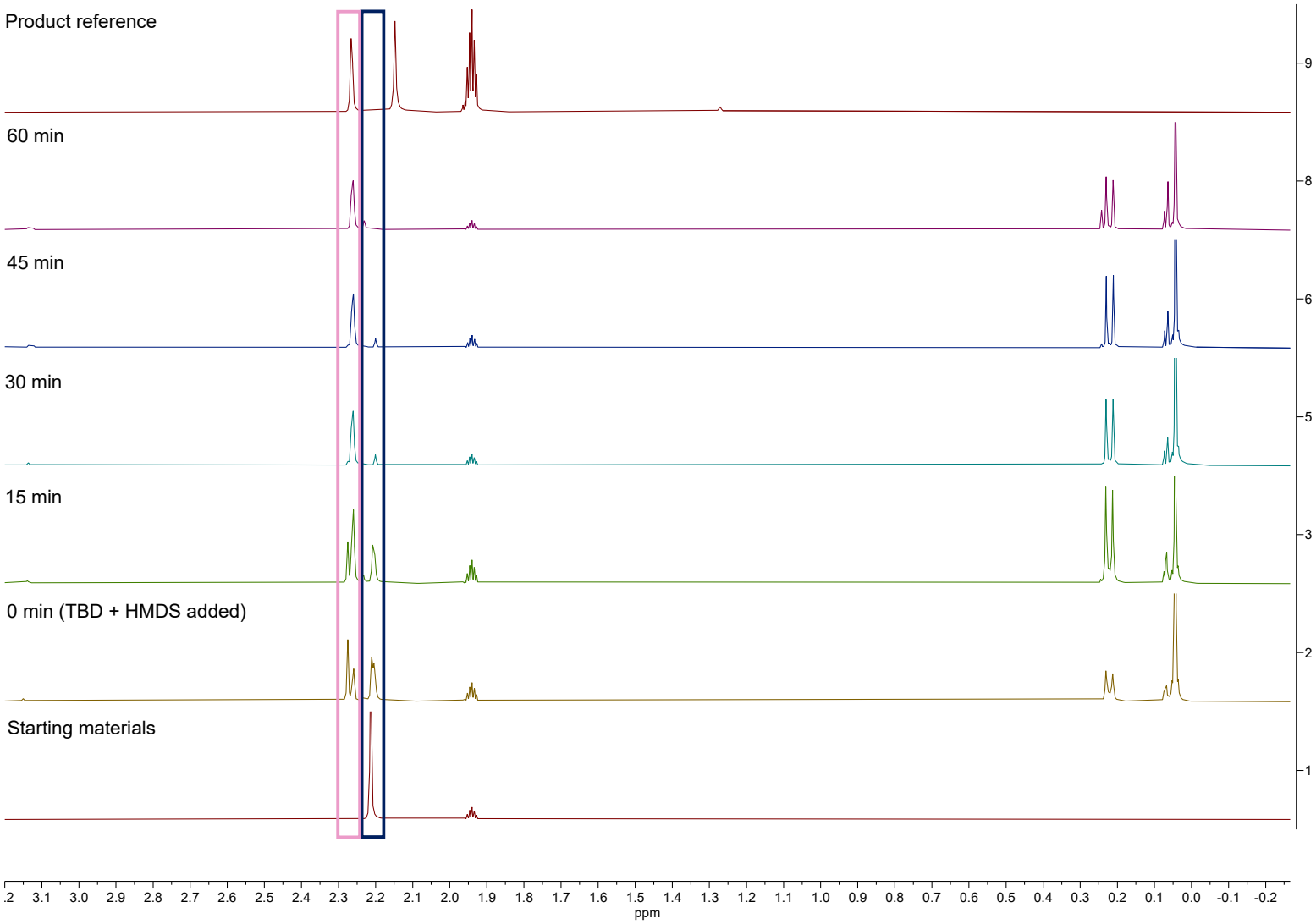
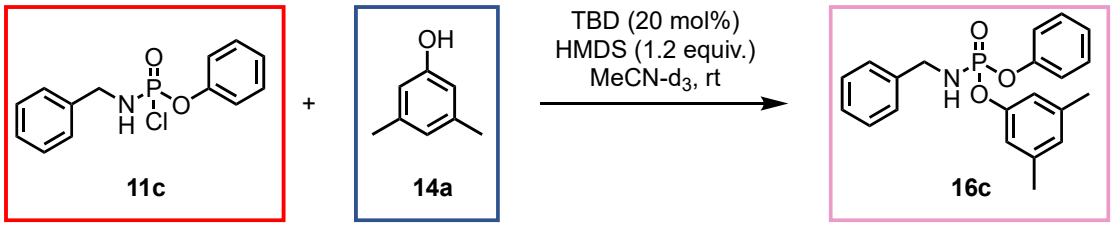


Figure S7. ^{1}H NMR spectrum (-0.2–3.1 ppm) for the PFEx reaction between phosphoramidofluoridate **12c** and phenol **14a** (400 MHz, MeCN-d_3)



PFEx reaction between phosphoramidofluoridate **11c** and phenol **14a**:



Phosphoramidofluoridate **11c** (0.07 mmol) and phenol **14a** (0.07 mmol) were added to MeCN-d_3 (0.5 mL) in an NMR tube and vortexed. An initial ^{1}H NMR spectrum was obtained. A solution of TBD (20 mol%) and HMDS (1.2 equiv) was added and vortexed. ^{1}H NMR spectra were taken immediately and at 15-minute intervals until the reaction reached completion – this was noted at 60 min. Colored boxes match annotation on following spectra.

Figure S8. ^{1}H NMR spectrum for the exchange reaction between phosphoramidochloridate **11c** and phenol **14a** (400 MHz, MeCN-d_3)

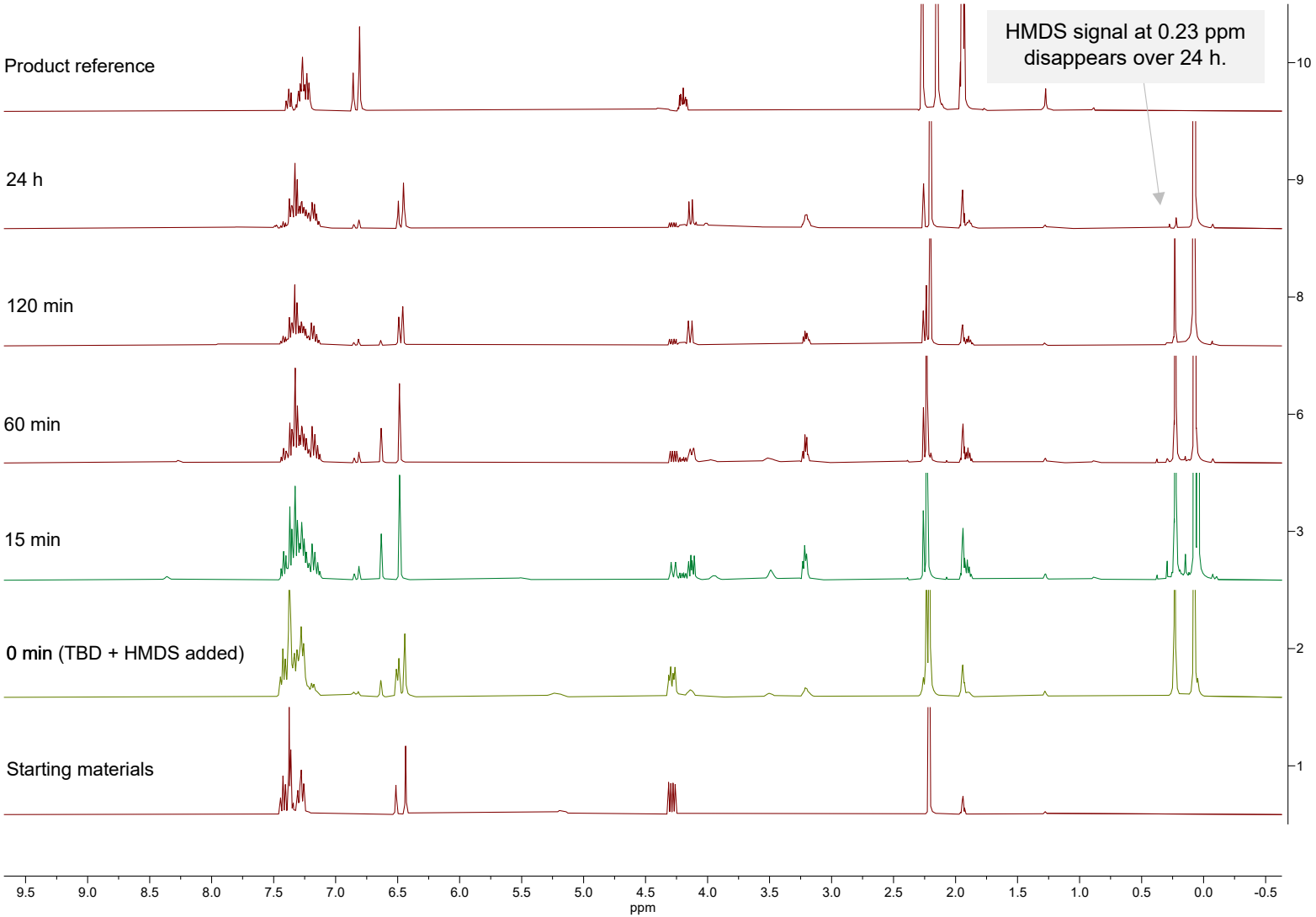


Figure S9: ^{1}H NMR spectrum (5.9–8.5 ppm) for the exchange reaction between phosphoramidochloridate **11c** and phenol **14a** (400 MHz, MeCN-d_3)

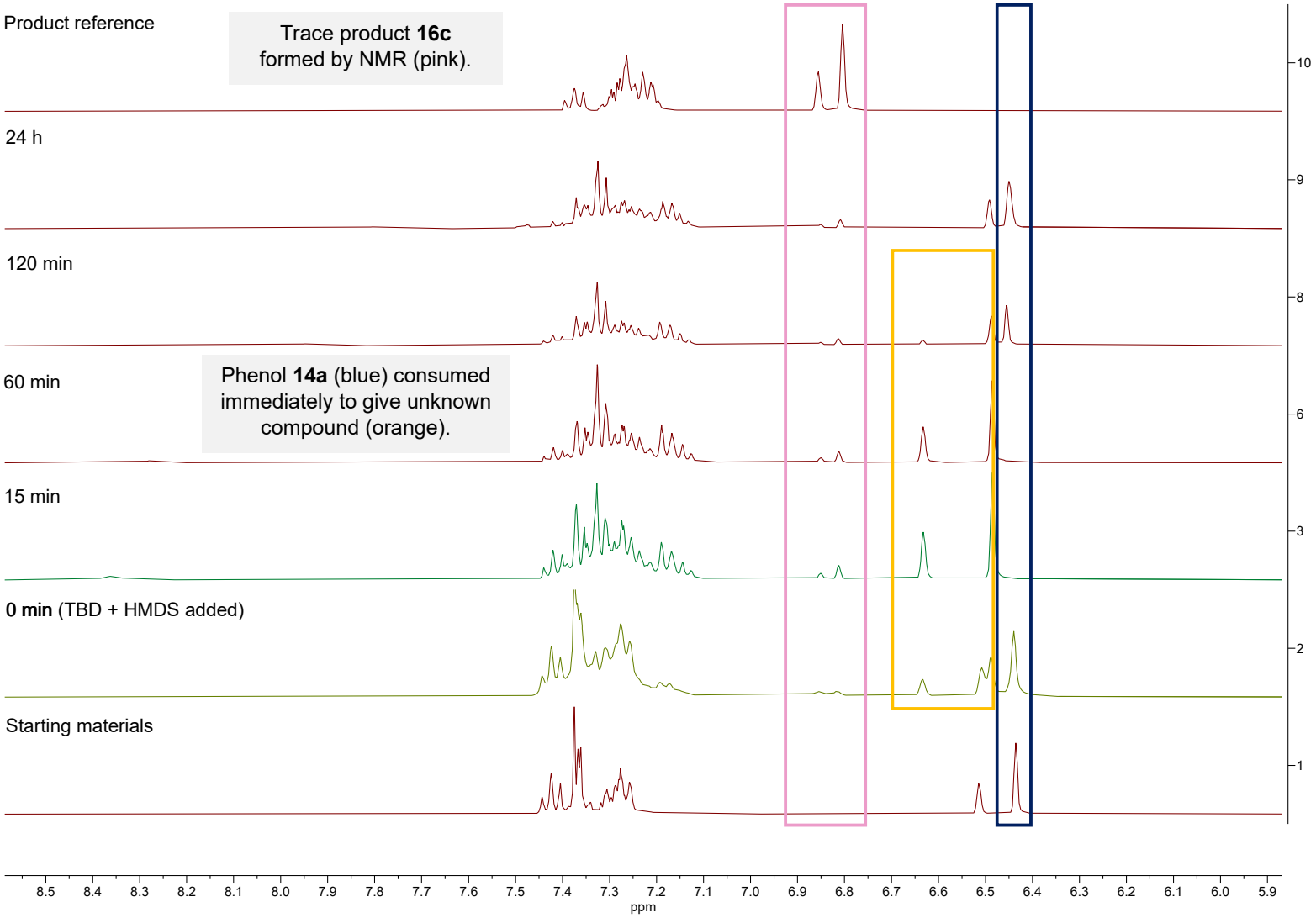


Figure S10. ^{1}H NMR spectrum (5.9–8.5 ppm) for the exchange reaction between phosphoramidochloridate **11c** and phenol **14a** (400 MHz, MeCN-d_3)

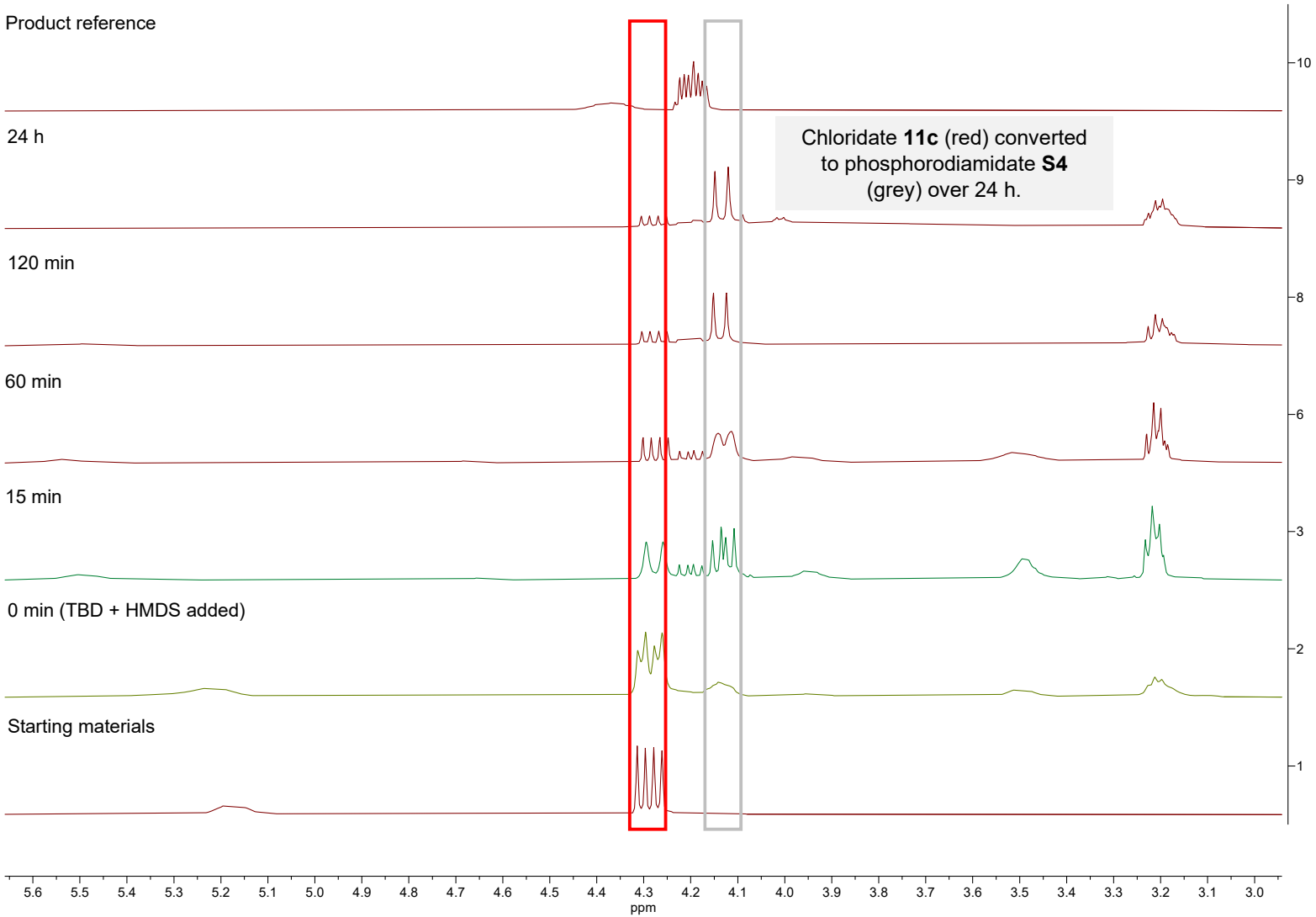
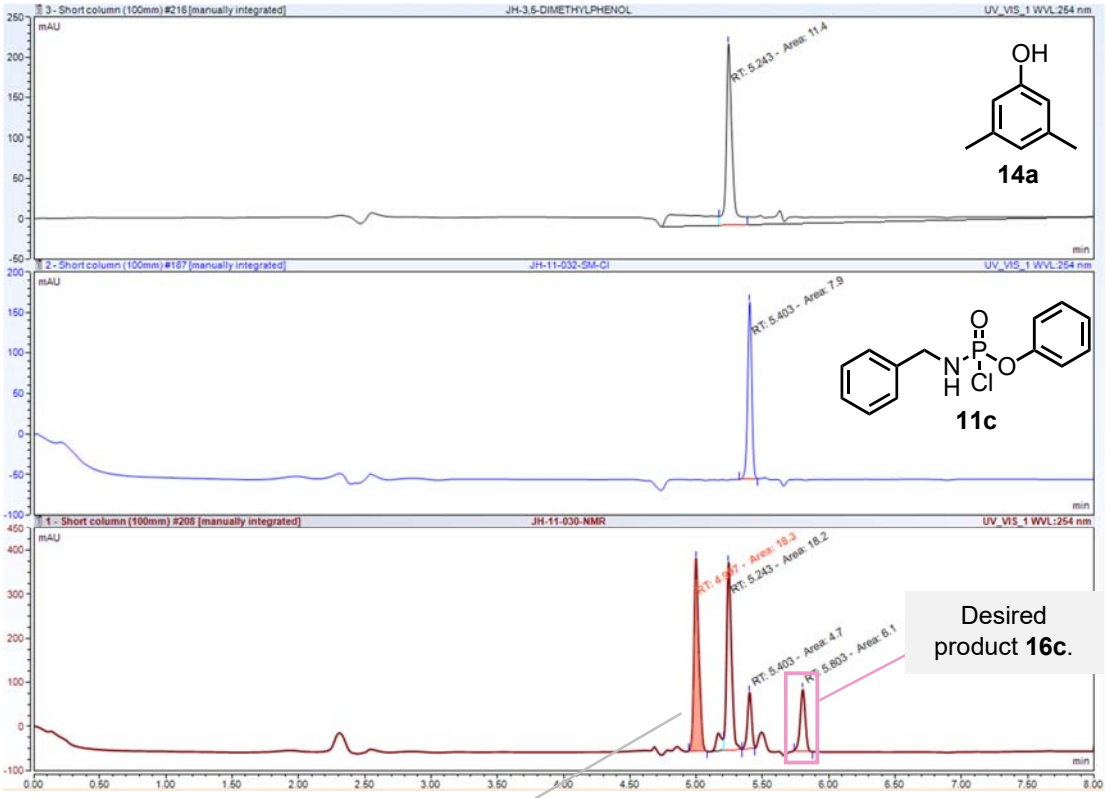
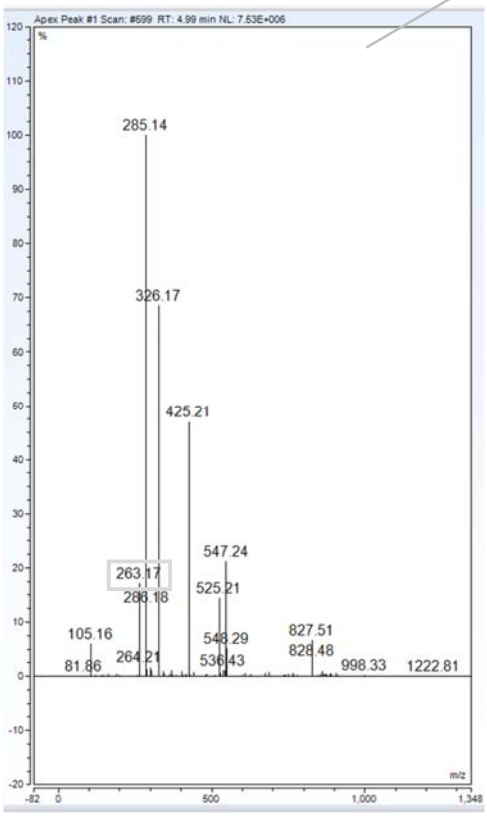
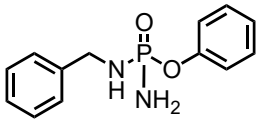


Figure S11. LCMS analysis of exchange reaction between **11c** and **14a**.







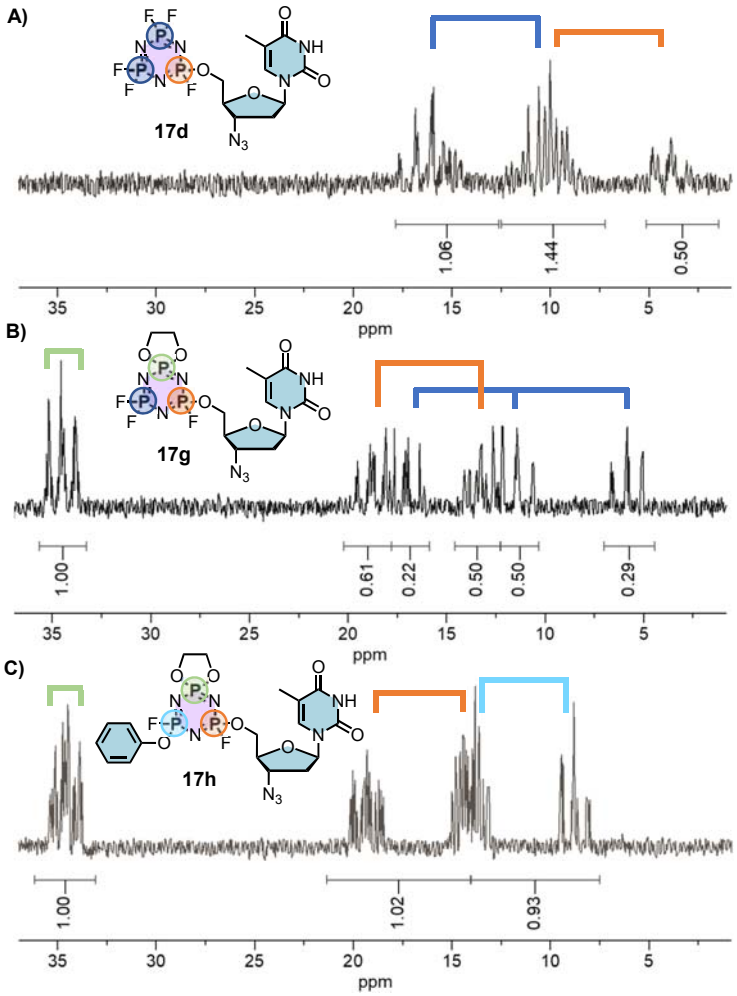
Chemical Formula: $C_{13}H_{15}N_2O_2P$
Exact Mass: 262.09

Phosphorodiamidate **S5** side product suspected to form via HMDS reaction with chloridate **11c** and subsequent cleavage of the TMS groups.

HFP-product NMR Analysis

Products **17g**–**17i** were obtained as diastereomeric mixtures that were inseparable by either flash column chromatography or LCMS. Representative ^{31}P NMR spectra for compounds **17d**, **17g**, and **17h** are presented in Figure S12 to highlight the changes in multiplicity observed following serial phosphorus-fluoride exchange reactions. PFEx of HFP with AZT affords **17d** with two distinct phosphorus environments (Figure S12A), one doublet of multiplets (dm) integrating to 2 P (dark blue) and one dm integrating to 1 P (orange). The reaction of **17d** with ethylene glycol to give spirocyclophosphazene **17g** (Figure S12B) breaks symmetry through the phosphazene ring, creating three unique phosphorus environments; a multiplet shifted upfield correlating to increased electron density at the spirocyclic phosphorus (green), a triplet of multiplets due to two chemically distinct fluorine atoms now bonded to phosphorus (dark blue), and an upfield shifted dm (orange). Finally, following reaction with phenol, **17h** was found to have three chemically unique phosphorus environments, a multiplet (green) and two doublets of multiplets (orange and light blue).

Figure S12. Comparison of ^{31}P NMR spectra for compounds A) **17d**, B) **17g**, and C) **17h**.

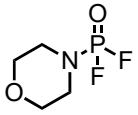


Synthesis and Experimental Data for Substituted Phosphoramidic Difluorides 9a–9g

General Procedure A:

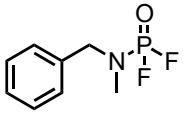
To a solution of the desired substituted phosphoramidic dichloride[2] (1.00 equiv) in acetone (0.125 M) was added KF (8.00 equiv). The reaction mixture was rapidly stirred at room temperature for 3 h and then filtered through Celite®. The solvent was removed under reduced pressure to give the desired phosphoramidic difluoride, as determined by crude NMR analysis. The shelf-life of these compounds is limited (several hours at room temperature or up to 3 days at −20 °C) and so they should be converted to the more stable phosphoramidofluoridates as soon as possible.

Morpholinophosphonic difluoride (**9a**)



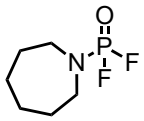
Following General Procedure A using morpholinophosphonic dichloride (1.01 g, 5.00 mmol), the title compound was isolated as a yellow oil (787 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.73 – 3.71 (m, 4H), 3.31 – 3.26 (m, 4H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -7.1 (t, *J* = 1005.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.0 (d, *J* = 1006.0 Hz). Limited stability precluded full characterization.

Benzyl(methyl)phosphoramidic difluoride (**9b**)



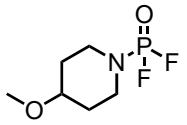
Following General Procedure A using benzyl(methyl)phosphoramidic dichloride (1.19 g, 5.00 mmol), the title compound was isolated as a yellow oil (868 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 4.29 (d, *J* = 11.3 Hz, 2H), 2.67 (appt. dt, *J* = 10.8, 1.4 Hz, 3H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.4 – -10.1 (m).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.3 (d, *J* = 1004.9 Hz). Limited stability precluded full characterization.

Azepan-1-ylphosphonic difluoride (**9c**)



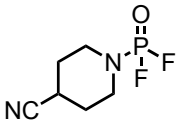
Following General Procedure A using azepan-1-ylphosphonic dichloride (1.08 g, 5.00 mmol), the title compound was isolated as a colourless oil (811 mg, 89%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.32 – 3.26 (m, 4H), 1.78 – 1.73 (m, 4H), 1.66 – 1.62 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 47.8 (d, *J* = 5.0 Hz), 29.7 (d, *J* = 3.4 Hz), 26.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -3.8 (t, *J* = 1002.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.8 (d, *J* = 1002.7 Hz). Limited stability precluded full characterization.

(4-Methoxypiperidin-1-yl)phosphonic difluoride (**9d**)



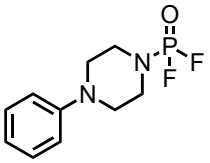
Following General Procedure A using (4-methoxypiperidin-1-yl)phosphonic dichloride (928 mg, 4.00 mmol), the title compound was isolated as a yellow oil (778 mg, 98%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.50 – 3.39 (m, 3H), 3.35 (s, 3H), 3.15 – 3.07 (m, 2H), 1.91 – 1.83 (m, 2H), 1.68 – 1.62 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 74.3, 55.9, 41.9 (d, *J* = 4.2 Hz), 30.5 (d, *J* = 3.9 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -5.9 (t, *J* = 1003.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.0 (d, *J* = 1003.1 Hz). Limited stability precluded full characterization.

(4-Cyanopiperidin-1-yl)phosphonic difluoride (**9e**)



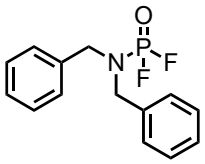
Following General Procedure A using (4-cyanopiperidin-1-yl)phosphonic dichloride (908 mg, 4.00 mmol), the title compound was isolated as a colourless oil (630 mg, 81%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.52 – 3.42 (m, 2H), 3.34 – 3.29 (m, 2H), 2.96 – 2.93 (m, 1H), 2.01 – 1.87 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 120.2, 42.6 (d, *J* = 4.2 Hz), 28.4 (d, *J* = 3.9 Hz), 25.9 (d, *J* = 1.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -7.0 (t, *J* = 1006.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.7 (d, *J* = 1007.0 Hz). Limited stability precluded full characterization.

(4-Phenylpiperazin-1-yl)phosphonic difluoride (**9f**)



Following General Procedure A using (4-phenylpiperazin-1-yl)phosphonic dichloride (1.40 g, 5.00 mmol), the title compound was isolated as a pink oil (852 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 6.95 – 6.90 (m, 3H), 3.47 – 3.43 (m, 4H), 3.21 – 3.19 (m, 4H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -0.6 – -3.0 (m). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.3 (d, *J* = 1004.9 Hz). Limited stability precluded full characterization.

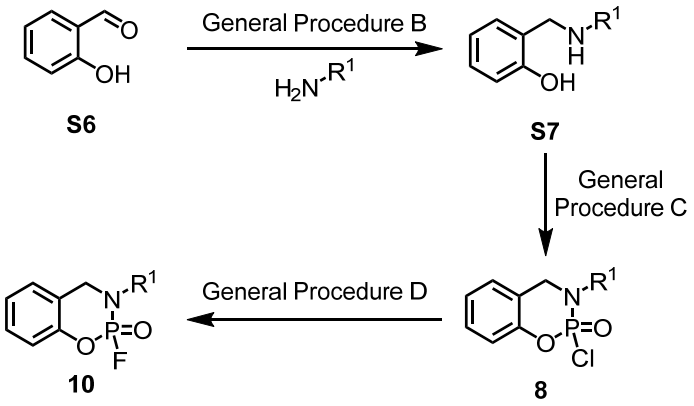
Dibenzylphosphoramidic difluoride (**9g**)



Following General Procedure A using dibenzylphosphoramidic dichloride (1.57 g, 5.00 mmol), the title compound was isolated as a yellow gum (1.397 g, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m,

6H), 7.26 – 7.22 (m, 4H), 4.17 – 4.11 (m, 4H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.2 – -10.4 (m).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.4 (d, *J* = 1005.6 Hz). Limited stability precluded full characterization.

Synthesis and Experimental Data for Cyclic Phosphoramidofluoridates 10a–10g



General Procedure B:

To a solution of amine or aniline (1.00 equiv) in MeOH (0.8 M) at room temperature was added salicylaldehyde (**S6**, 1.00 equiv). The resulting reaction was stirred at room temperature and monitored by ^{1}H NMR. When completed, the reaction was diluted with methanol to 0.4 M and cooled to 0 °C. Sodium borohydride (1.00 equiv) was added in one portion. The resulting mixture was stirred for 10 min at 0 °C and then warmed to room temperature. When completed as determined by ^{1}H NMR, the reaction was poured into ice-cold water and extracted with ethyl acetate three times. The crude material was purified by flash column chromatography on silica gel to afford the desired aminophenol **S7**.

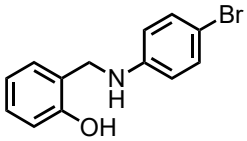
General Procedure C:

To a solution of aminophenol **S7** (1.00 equiv) or diamine (in the instance of compound **10g** 1.00 equiv) in CH_2Cl_2 (0.2 M) cooled to –78 °C was slowly added phosphorus oxychloride or thiophosphoryl chloride (1.00 equiv) followed by Et_3N (2.00 equiv). The reaction warmed to room temperature and stirred for 1 h, diluted with CH_2Cl_2, and washed with NH_4Cl (sat. aqueous). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the desired cyclic phosphoramidochloridate **8**.

General Procedure D:

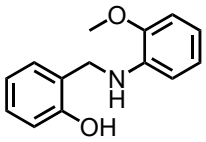
To a solution of cyclic phosphoramidochloridate **8** (1.00 equiv) in acetone (0.15 M) was added potassium fluoride (8.00 equiv) and tetrabutylammonium chloride (10 mol%). The resultant suspension was vigorously stirred for 16 h. The solvent was removed under a stream of nitrogen, the residue suspended in ethyl acetate, and filtered through a plug of Celite®. The filtrate was concentrated under reduced pressure to yield the desired cyclic phosphoramidofluoridate **10**.

2-(((4-Bromophenyl)amino)methyl)phenol (**S7a**)



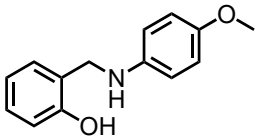
Following the General Procedure B using salicylaldehyde (2.13 mL, 20.0 mmol) and 4-bromoaniline (3.44 mL, 20.0 mmol), the title compound was isolated as a white solid (5.36 g, 96%). **m.p.** 124.8 – 126.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.88 (m, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 4.38 (d, *J* = 5.6 Hz, 2H), 3.98 (br, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.5, 146.4, 132.3, 129.5, 128.9, 122.7, 120.4, 117.4, 116.7, 112.8, 48.4. **HRMS** (ESI^+) calculated for $C_{13}H_{12}BrNO$ $[M+H]^+$: m/z = 278.0175, m/z found 278.0167. **IR** ν_{max} (ATR)/cm^{-1} 3253, 1593, 1487, 1452, 1230, 845, 825, 754, 645, 511.

2-(((2-Methoxyphenyl)amino)methyl)phenol (**S7b)**



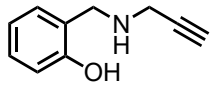
Following the General Procedure B using salicylaldehyde (2.13 mL, 20.0 mmol) and *o*-anisidine (2.26 mL, 20.0 mmol), the title compound was isolated as a white solid (4.32 g, 94%). **m.p.** 68.7 – 71.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.26 – 7.22 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.93 – 6.88 (m, 5H), 6.86 – 6.83 (m, 1H), 4.58 (br, 1H), 4.43 (s, 2H), 3.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 148.6, 137.1, 129.2, 128.7, 123.3, 121.3, 120.4, 120.0, 116.8, 114.0, 109.9, 55.6, 48.7. **HRMS** (ESI^+) calculated for $C_{14}H_{15}NO_2$ $[M+H]^+$: m/z = 230.1175, m/z found 230.1175. **IR** ν_{max} (ATR)/cm^{-1} 3337, 1588, 1506, 1489, 1243, 1229, 1123, 1026, 735, 581.

2-(((4-Methoxyphenyl)amino)methyl)phenol (**S7c**)



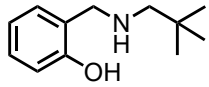
Following the General Procedure B using salicylaldehyde (1.07 mL, 10.0 mmol) and *p*-anisidine (1.23 mL, 10.0 mmol), the title compound was isolated as a white solid (2.20 g, 96%). **m.p.** 128.5 – 130.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.83 (s, 4H), 4.38 (s, 2H), 3.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.3, 154.7, 140.6, 129.2, 128.6, 122.9, 119.9, 117.9, 116.8, 114.9, 55.7, 50.3. **HRMS** (ESI^+) calculated for $C_{14}H_{15}NO_2$ $[M+H]^+$: m/z = 230.1175, m/z found 230.1169. **IR** ν_{max} (ATR)/cm^{-1} 3252, 1593, 1508, 1457, 1247, 1222, 1032, 828, 758, 741, 527.

2-(Propargylaminomethyl)phenol (**S7d**)



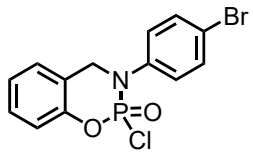
Following the General Procedure B using salicylaldehyde (2.13 mL, 20.0 mmol) and propargylamine (1.28 mL, 20.0 mmol), the title compound was isolated as a white solid (3.10 g, 95%). **m.p.** 62.5 – 64.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.2 Hz, 1H), 4.10 (s, 2H), 3.47 (s, 2H), 2.30 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 129.1, 129.0, 121.7, 119.4, 116.5, 80.3, 72.9, 50.9, 36.6. **HRMS** (ESI^+) calculated for $C_{10}H_{11}NO$ $[M+H]^+$: m/z = 162.0913, m/z found 162.0909. **IR** ν_{max} (ATR)/cm^{-1} 3297, 3267, 1595, 1458, 1342, 1250, 1116, 1084, 749, 616.

2-(Neopentylaminomethyl)phenol (**S7e**)



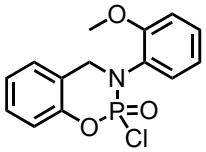
Following the General Procedure B using salicylaldehyde (1.07 mL, 10.0 mmol) and neopentylamine (1.17 mL, 10.0 mmol), the title compound was isolated as a colorless oil (1.53 g, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 6.8 Hz, 1H), 6.78 (t, *J* = 6.8 Hz, 1H), 3.98 (s, 2H), 2.45 (s, 2H), 0.96 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 128.8, 128.3, 122.9, 119.0, 116.4, 61.6, 53.6, 31.3, 27.8. **HRMS** (ESI^+) calculated for $C_{12}H_{19}NO$ $[M+H]^+$: m/z = 194.1539, m/z found 194.1534. **IR** ν_{max} (ATR)/cm^{-1} 2955, 1590, 1474, 1400, 1255, 1098, 1034, 751, 720.

3-(4-Bromophenyl)-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**8a**)



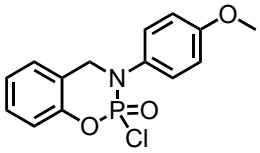
Following the General Procedure C using 2-(((4-bromophenyl)amino)methyl)phenol (2.78 g, 10.0 mmol), the title compound was isolated as a colorless solid (2.76 g, 81%). **m.p.** 105.6 – 108.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.24 – 7.19 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.95 (dd, *J* = 14.8, 6.8 Hz, 1H), 4.59 (dd, *J* = 25.6, 14.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2 (d, *J* = 9.7 Hz), 139.3, 132.8 (d, *J* = 1.7 Hz), 142.8 (d, *J* = 1.7 Hz), 127.0 (d, *J* = 1.2 Hz), 126.5 (d, *J* = 4.5 Hz), 125.4, 121.1 (d, *J* = 7.4 Hz), 120.8 (d, *J* = 2.6 Hz), 119.2 (d, *J* = 9.7 Hz), 52.6 (d, *J* = 1.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.3 (d, *J* = 25.2 Hz). **HRMS** (ESI^+) calculated for $C_{13}H_{10}BrClNO_2P$ $[M+H]^+$: m/z = 357.9394, m/z found 357.9391. **IR** ν_{max} (ATR)/cm^{-1} 1587, 1488, 1454, 1295, 1215, 1190, 1084, 968, 829, 753, 540.

3-(2-Methoxylphenyl)-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**8b**)



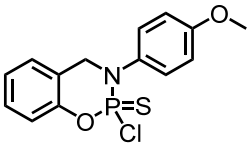
Following the General Procedure C using 2-(((2-methoxyphenyl)amino)methyl)phenol (1.15 g, 5.00 mmol), the title compound was isolated as a colorless solid (824 mg, 99%). **m.p.** 137.1 – 139.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.00 (m, 2H), 6.98 – 6.95 (m, 2H), 4.92 (dd, *J* = 15.2, 7.2 Hz, 1H), 4.51 (dd, *J* = 23.2, 15.2 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2 (d, *J* = 4.5 Hz), 149.6 (d, *J* = 9.6 Hz), 129.5 (d, *J* = 3.5 Hz), 129.5 (d, *J* = 0.8 Hz), 129.1 (d, *J* = 1.2 Hz), 128.1 (d, *J* = 1.9 Hz), 126.6 (d, *J* = 0.9 Hz), 124.9, 122.4 (d, *J* = 7.8 Hz), 121.2 (d, *J* = 1.5 Hz), 119.2 (d, *J* = 9.4 Hz), 112.4, 55.7, 52.7 (d, *J* = 2.9 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.3 (dd, *J* = 23.3, 7.1 Hz). **HRMS** (ESI^+) calculated for $C_{14}H_{13}ClNO_3P$ $[M+H]^+$: m/z = 310.0394, m/z found 310.0392. **IR** ν_{max} (ATR)/cm^{-1} 1497, 1453, 1306, 1288, 1188, 927, 966, 923, 757, 700, 568, 524,

3-(4-Methoxylphenyl)-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**8c**)



Following the General Procedure C using 2-(((4-methoxyphenyl)amino)methyl)phenol (0.962 mL, 4.20 mmol), the title compound was isolated as a colorless solid (1.01 g, 78%). **m.p.** 106.8 – 108.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 8.8 Hz, 1H), 4.89 (dd, *J* = 26.0, 7.2 Hz, 1H), 4.53 (dd, *J* = 26.0, 15.2 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9 (d, *J* = 2.0 Hz), 149.4 (d, *J* = 9.5 Hz), 132.6, 129.5 (d, *J* = 1.5 Hz), 127.1 (d, *J* = 4.2 Hz), 126.9 (d, *J* = 0.9 Hz), 125.2, 121.5 (d, *J* = 7.4 Hz), 119.2 (d, *J* = 29.8 Hz), 115.0 (d, *J* = 1.7 Hz), 55.7, 53.5 (d, *J* = 4.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.2 (dd, *J* = 26.4, 3.4 Hz). **HRMS** (ESI^+) calculated for $C_{14}H_{13}ClNO_3P$ $[M+H]^+$: m/z = 310.0394, m/z found 310.0392. **IR** ν_{max} (ATR)/cm^{-1} 1585, 1513, 1457, 1293, 1222, 1184, 1026, 966, 939, 751, 542.

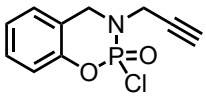
3-(4-Methoxylphenyl)-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine -2-thione (**8d**)



Following the General Procedure C using 2-(((4-methoxyphenyl)amino)methyl)phenol (1.14 g, 5.00 mmol) and thiophosphoryl chloride (508 uL), the title compound was isolated as a yellow solid (1.49 g, 96%), **m.p.** 99.1-100.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 3H), 7.17 (td, *J* = 7.2, 1.2 Hz, 1H), 7.14 – 7.09 (m, 2H), 6.93 (dd, *J* = 9.2, 0.8 Hz, 2H), 4.90 (dd, *J* = 15.2, 7.2 Hz, 1H), 4.54 (dd, *J* = 26.0, 15.2 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 149.4 (d, *J* = 12.6 Hz), 134.4 (d, *J* = 2.1 Hz), 129.4, 128.7 (d, *J* = 4.3 Hz), 127.0, 125.0, 121.6 (d, *J* = 7.8 Hz), 119.4 (d, *J* = 9.7 Hz), 114.9 (d, *J* = 1.9 Hz), 55.6, 54.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 58.43 (dd, *J* = 25.4, 7.0 Hz); **HRMS (ESI):** m/z

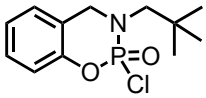
calcd for $C_{14}H_{14}ClNO_2PS$: 326.0178 $[M+H]^+$; found: 326.0166; **IR** ν_{max} (ATR)/cm^{-1} 2843, 1503, 1455, 1278, 1183, 1099, 936, 828, 752, 509, 481.

3-Propargyl-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**8e**)



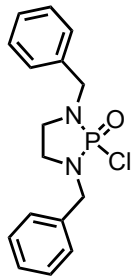
Following the General Procedure C using 2-(propargylaminomethyl)phenol (806 mg, 5.00 mmol), the title compound was isolated as a colorless solid (858 mg, 71%). **m.p.** 110.2 – 113.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.04 (t, *J* = 8.0 Hz, 1H), 4.50 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.37 (dd, *J* = 26.8, 15.2 Hz, 1H), 4.24 (dd, *J* = 6.4, 2.4 Hz, 1H), 4.19 (dd, *J* = 26.8, 2.4 Hz, 1H), 2.40 (t, *J* = 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.0 (d, *J* = 9.4 Hz), 129.4 (d, *J* = 1.6 Hz), 127.1 (d, *J* = 1.0 Hz), 115.2, 120.6 (d, *J* = 19.2 Hz), 119.3 (d, *J* = 9.9 Hz), 76.2 (d, *J* = 6.8 Hz), 74.8, 49.2, 37.4 (d, *J* = 3.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.4 (dd, *J* = 23.3, 7.1 Hz). **HRMS** (ESI^+) calculated for $C_{10}H_9ClNO_2P$ 242.0130 $[M+H]^+$: m/z = 242.0132, m/z found 242.0130. **IR** ν_{max} (ATR)/cm^{-1} 3230, 2118, 1490, 1457, 1314, 1287, 1186, 1116, 1097, 959, 758, 707.

3-Neopentyl-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**8f**)



Following the General Procedure C using 2-(neopentylaminomethyl)phenol (966 mg, 5.00 mmol), the title compound was isolated as a colorless solid (1.03 g, 75%). **m.p.** 95.4 – 97.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.2 Hz, 1H), 7.14 (td, *J* = 7.2, 0.8 Hz, 1H), 7.08 (d, *J* = 6.4 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.46 (dd, *J* = 15.2, 7.2 Hz, 1H), 4.33 (dd, *J* = 30.0, 7.2 Hz, 1H), 3.25 (dd, *J* = 18.4, 14.4 Hz, 1H), 2.73 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.01 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2 (d, *J* = 9.2 Hz), 129.3 (d, *J* = 1.6 Hz), 126.8 (d, *J* = 0.8 Hz), 124.9, 121.6 (d, *J* = 8.7 Hz), 119.1 (d, *J* = 9.9 Hz), 60.5, 53.0, 33.8 (d, *J* = 4.3 Hz), 28.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 8.2 (ddd, *J* = 31.3, 16.5, 7.6 Hz). **HRMS** (ESI^+) calculated for $C_{12}H_{17}ClNO_2P$ $[M+H]^+$: m/z = 274.0758, m/z found 274.0753. **IR** ν_{max} (ATR)/cm^{-1} 2962, 1585, 1490, 1457, 1332, 1294, 1185, 1087, 948, 934, 793, 752, 716, 523.

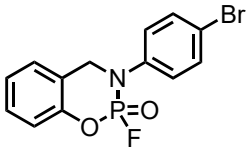
2-Chloro-2-oxo-1, 3-dibenzyl-1,3,2-diazaphospholidine (**8g**)



Following the General Procedure C using *N*, *N*'-dibenzylethylenediamine (1.20 g, 5.00 mmol), the title compound was isolated as a colorless oil (1.48 g, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 10H), 4.37 (dd, *J* = 14.8, 9.2 Hz, 2H), 4.00 (dd, *J* = 14.8, 6.8 Hz, 2H), 3.15 – 3.07 (m, 2H), 2.97 – 2.91 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0 (d, *J* = 8.3 Hz), 128.8, 128.5, 128.0, 49.0 (d, *J* = 4.9

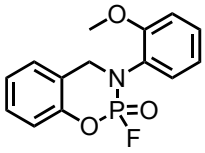
Hz), 42.9 (d, *J* = 14.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.3. **HRMS** (ESI^+) calculated for $C_{16}H_{18}ClN_2OP$ $[M+H]^+$: m/z = 321.0918, m/z found 321.0920. **IR** ν_{max} (ATR)/cm^{-1} 2856, 1455, 1360, 1279, 1146, 1066, 794, 717, 696, 589, 534, 489.

3-(4-Bromophenyl)-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**10a**)



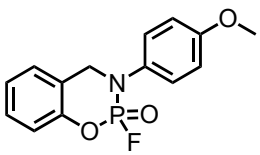
Following the General Procedure D using 3-(4-bromophenyl)-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (1.71 g, 5.00 mmol), the title compound was isolated as a colorless solid (1.55 g, 91%). **m.p.** 116.9 – 119.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.15 (m, 5H), 4.90 (dd, *J* = 15.2, 6.4 Hz, 1H), 4.68 – 4.59 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9 (d, *J* = 8.3 Hz), 140.1 (dd, *J* = 4.1, 1.7 Hz), 132.8, 129.9 (d, *J* = 1.4 Hz), 126.8, 126.1 (dd, *J* = 3.9, 1.5 Hz), 125.3, 122.0 (d, *J* = 7.2 Hz), 120.0 (d, *J* = 1.5 Hz), 119.1 (d, *J* = 9.1 Hz), 52.4 (d, *J* = 2.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -9.5 (ddd, *J* = 1016.7, 19.1, 6.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.08 (d, *J* = 1016.6 Hz). **HRMS** (ESI^+) calculated for $C_{13}H_{10}BrFNO_2P$ $[M+H]^+$: m/z = 341.9689, m/z found 341.9680. **IR** ν_{max} (ATR)/cm^{-1} 1585, 1489, 1456, 1317, 1225, 1183, 1104, 972, 936, 840, 822, 761, 540, 468.

2-Fluoro-3-(2-methoxyphenyl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**10b**)



Following the General Procedure D using 3-(2-methoxylphenyl)-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (0.65 g, 2.10 mmol), the title compound was isolated as a colorless solid (510 mg, 85%). **m.p.** 106.9 – 109.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 3H), 7.18 – 7.09 (m, 3H), 6.97 – 6.73 (m, 2H), 4.90 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.47 (ddd, *J* = 20.0, 15.2, 1.2 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9 (dd, *J* = 3.5, 2.1 Hz), 150.3 (d, *J* = 8.1 Hz), 129.3 (dd, *J* = 3.5, 2.1 Hz), 129.2, 129.0 (dd, *J* = 3.4, 1.3 Hz), 126.6, 124.7, 123.0 (d, *J* = 7.2 Hz), 121.3, 119.0 (d, *J* = 8.9 Hz), 112.4, 55.9, 52.8 (d, *J* = 2.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -9.1 (ddd, *J* = 1012.8, 20.0, 4.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -69.33 (d, *J* = 1012.8 Hz). **HRMS** (ESI^+) calculated for $C_{14}H_{13}FNO_3P$ $[M+H]^+$: m/z = 294.0690, m/z found 294.0687. **IR** ν_{max} (ATR)/cm^{-1}: 2927, 1491, 1316, 1191, 1105, 970, 945, 838, 755, 570.

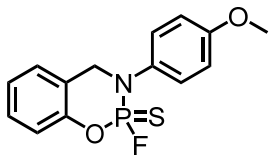
2-Fluoro-3-(4-methoxyphenyl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**10c**)



Following the General Procedure D using 3-(4-methoxylphenyl)-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (1.01 g, 3.26 mmol), the title compound was isolated

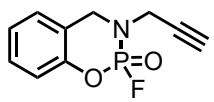
as a colorless solid (870 mg, 91%). **m.p.** 110.1 – 112.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.6 Hz, 1H), 7.26 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.20 – 7.13 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.88 (dd, *J* = 15.2, 6.4 Hz, 1H), 4.89 (ddd, *J* = 19.6, 15.2, 2.0 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6 (d, *J* = 1.2 Hz), 150.0 (d, *J* = 8.1 Hz), 133.4 (d, *J* = 3.2, 1.9 Hz), 129.5 (d, *J* = 1.4 Hz), 127.1 (d, *J* = 3.7, 1.5 Hz), 126.8, 125.0, 122.3 (d, *J* = 7.3 Hz), 119.1 (d, *J* = 9.1 Hz), 115.0 (d, *J* = 1.7 Hz), 55.6, 53.5 (d, *J* = 2.7 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -8.3 (dd, *J* = 21016.4, 19.9, 5.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.43 (d, *J* = 1014.8 Hz). **HRMS** (ESI^+) calculated for $C_{14}H_{13}FNO_3P$ $[M+H]^+$: m/z = 294.0690, m/z found 294.0680. **IR** ν_{max} (ATR)/cm^{-1} 2562, 1509, 1456, 1301, 1218, 1182, 972, 828, 776, 476.

3-(4-Methoxylphenyl)-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine -2-thione (**10d**)



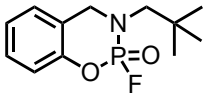
Following the General Procedure D using 3-(4-Methoxylphenyl)-2-chloro-3,4-dihydrobenzo[e][1,3,2]oxazaphosphinine -2-thione (1.20 g, 3.68 mmol), the title compound was isolated as a yellow solid (1.04 g, 90%), **m.p.** 80.7-82.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 9.6, 2.0 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.11 (dd, *J* = 7.6, 2.0 Hz, 1H), 4.85 (dd, *J* = 15.2, 6.8 Hz, 1H), 4.60 – 4.52 (m, 1H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9 (d, *J* = 1.2 Hz), 150.0 (d, *J* = 11.1 Hz), 134.9, 129.5, 128.9 (dd, *J* = 4.3, 2.1 Hz), 126.8, 124.9, 122.8 (d, *J* = 7.6 Hz), 119.1 (d, *J* = 8.7 Hz), 114.9 (d, *J* = 1.5 Hz), 55.6, 53.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 58.76 (ddd, *J* = 1109.4, 18.5, 6.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -35.97 (d, *J* = 1109.4 Hz); **HRMS** (ESI^+) calculated for $C_{14}H_{13}FNO_2PS$ $[M+H]^+$: m/z = 310.0461, m/z found 310.0461. **IR** ν_{max} (ATR)/cm^{-1}: 2964, 1509, 1455, 1188, 1099, 1027, 940, 823, 760, 622, 545.

2-Fluoro-3-(prop-2-yn-1-yl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**10e**)



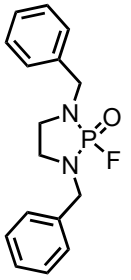
Following the General Procedure D using 3-propargyl-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (0.85 g, 3.50 mmol), the title compound was isolated as a colorless solid (680 mg, 86%). **m.p.** 49.5 – 51.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 1H), 7.18 – 7.14 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 4.61 (dd, *J* = 15.2, 4.0 Hz, 1H), 4.34 (ddd, *J* = 21.2, 15.2, 1.6 Hz, 1H), 4.25 (ddd, *J* = 18.0, 8.0, 2.8 Hz, 1H), 4.02 – 3.92 (m, 1H), 2.36 (t, *J* = 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7 (d, *J* = 8.0 Hz), 129.4 (d, *J* = 1.7 Hz), 127.1 (d, *J* = 0.7 Hz), 125.1, 121.1 (d, *J* = 8.5 Hz), 119.1 (d, *J* = 9.4 Hz), 77.4 (dd, *J* = 7.6, 4.9 Hz), 74.1, 48.7, 37.6 (dd, *J* = 5.2, 1.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -5.3 (d, *J* = 1012.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.57 (d, *J* = 1012.8 Hz). **HRMS** (ESI^+) calculated for $C_{10}H_9FNO_2P$ $[M+H]^+$: m/z = 226.0428, m/z found 226.0427. **IR** ν_{max} (ATR)/cm^{-1} 3206, 2115, 1491, 1458, 1315, 1292, 1187, 1099, 971, 839, 751, 499.

2-Fluoro-3-neopentyl-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**10f**)



Following the General Procedure D using 3-neopentyl-2-chloro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (0.82 g, 3.00 mmol), the title compound was isolated as a colorless solid (643 mg, 83%). **m.p.** 100.5 – 102.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 6.4 Hz, 1H), 7.14 – 7.06 (m, 3H), 4.66 (dd, *J* = 14.4, 4.0 Hz, 1H), 4.13 (dd, *J* = 23.6, 8.0 Hz, 1H), 3.28 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.92 – 2.83 (m, 1H), 0.99 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.6 Hz), 129.4 (d, *J* = 1.8 Hz), 126.7, 124.6, 122.3 (d, *J* = 8.0 Hz), 119.0 (dd, *J* = 9.2, 0.9 Hz), 61.9 (d, *J* = 3.8 Hz), 52.2 (d, *J* = 2.0 Hz), 33.9, 27.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -2.4 (d, *J* = 987.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.45 (d, *J* = 987.8 Hz). **HRMS** (ESI^+) calculated for $C_{12}H_{17}FNO_2P$ $[M+H]^+$: m/z = 258.1054, m/z found 258.1052. **IR** ν_{max} (ATR)/cm^{-1} 2953, 1488, 1300, 1188, 1140, 1100, 930, 846, 747, 475.

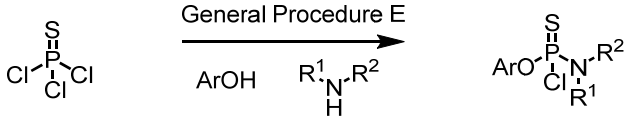
2-Fluoro-2-oxo-1, 3-dibenzyl-1, 3, 2-diazaphospholidine (**10g**)



Following the General Procedure D using 2-chloro-2-oxo-1,3-dibenzyl-1,3,2-diazaphospholidine (1.33 g, 4.15 mmol), the title compound was isolated as a colorless oil (1.2 g, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 10H), 4.23 – 4.19 (m, 4H), 3.07 – 3.02 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.6 (d, *J* = 5.8 Hz), 128.8, 128.3, 127.9, 49.0 (d, *J* = 5.2 Hz), 43.0 (d, *J* = 15.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.6 (d, *J* = 992.6 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.76 (d, *J* = 992.6 Hz). **HRMS** (ESI^+) calculated for $C_{16}H_{18}FN_2OP$ $[M+H]^+$: m/z = 305.1213, m/z found 305.1208. **IR** ν_{max} (ATR)/cm^{-1} 2862, 1455, 1360, 1283, 1150, 1070, 817, 801, 696, 474.

Synthesis and Experimental Data for Phosphoramidofluoridates 12a–12l

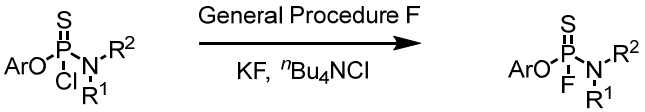
General Procedure E:



To a solution of the required phenol (1.00 equiv) in CH_2Cl_2 (0.25 M) was added thiophosphoryl chloride (1.00 equiv) dropwise at -78 °C, followed by the slow addition of Et_3N (1.00 equiv). The resulting reaction was warmed to room temperature and stirred overnight. Next, the required amine (1.00 equiv) was added, followed by the slow addition of Et_3N (1.00 equiv) at -78 °C. The reaction was warmed to room temperature slowly and monitored by ^{31}P NMR. When completed, the reaction was filtered through

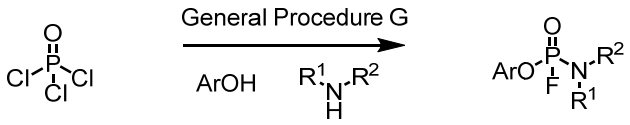
Celite® and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel.

General Procedure F:



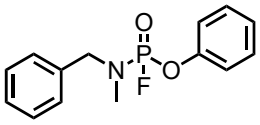
The required thiophosphoramidochloridate was taken up in acetone (0.25 M) and stirred at room temperature. Potassium fluoride (8.00 equiv) and tetrabutylammonium chloride (0.10 equiv) were added. When completed (as determined by ^{31}P NMR), the reaction was again filtered through Celite® and concentrated. The crude material was purified by flash column chromatography on silica gel.

General Procedure G:



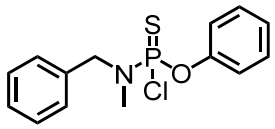
To a solution of the required phenol (1.00 equiv) in CH_2Cl_2 (0.25 M) was added phosphorus oxychloride (1.00 equiv) dropwise at –78 °C, followed by the slow addition of Et_3N (1.00 equiv). The resulting reaction was warmed to room temperature and stirred overnight. Next, the required amine (1.00 equiv) was added, followed by the slow addition of Et_3N (1.00 equiv) at -78 °C. The reaction was warmed to room temperature slowly and monitored by ^{31}P NMR. When completed, the reaction was filtered through Celite® and concentrated *in vacuo*. The crude was taken up in acetone (0.25 M) and stirred at room temperature. Potassium fluoride (8.00 equiv) and tetrabutylammonium chloride (0.10 equiv) were added. When completed (as determined by ^{31}P NMR), the reaction was again filtered through Celite® and concentrated. The crude material was purified by flash column chromatography on silica gel.

Phenyl *N*-methyl-*N*-benzylphosphoramidofluoridate (**12a**)



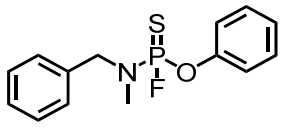
Following the General Procedure G using phenol (0.47 g, 5.00 mmol) and *N*-methylbenzylamine (665 µL, 5.00 mmol), the title compound was isolated as a colorless oil (965 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.0 Hz, 2H), 7.23 – 7.18 (m, 3H), 7.16 – 7.10 (m, 5H), 4.21 – 4.18 (m, 2H), 2.56 (d, *J* = 10.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1 (d, *J* = 6.0 Hz), 136.3, 130.1, 128.8, 128.2, 128.0, 125.7, 120.0 (d, *J* = 5.1 Hz), 53.1 (d, *J* = 5.6 Hz), 33.1 (d, *J* = 4.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 0.3 (d, *J* = 973.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.41 (d, *J* = 973.5 Hz). **HRMS** (ESI^+) calculated for $C_{14}H_{15}FNO_2P$ $[M+H]^+$: m/z = 280.0897, m/z found 280.0895. **IR** ν_{max} (ATR)/cm^{-1} 2919, 1594, 1489, 1290, 1193, 1018, 943, 867, 788, 762, 690, 509, 459.

Phenyl *N*-methyl-*N*-benzylphosphoramidochloridothioate (**11b**)



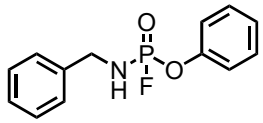
Following the General Procedure E using phenol (0.47 g, 5.00 mmol) and *N*-methylbenzylamine (665 µL, 5.00 mmol), the title compound was isolated as a colorless oil (1.20 g, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 10H), 4.59 – 4.55 (m, 2H), 2.85 (d, *J* = 14.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 8.6 Hz), 136.5 (d, *J* = 6.9 Hz), 129.8 (d, *J* = 1.9 Hz), 128.8, 128.4, 128.0, 126.1 (d, *J* = 2.4 Hz), 121.5 (d, *J* = 5.3 Hz), 54.4 (d, *J* = 5.6 Hz), 34.5 (d, *J* = 2.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 72.8; **HRMS** (ESI^+) calculated for $C_{14}H_{15}ClNOPS$ $[M+H]^+$: m/z = 312.0373, m/z found 312.0370. **IR** ν_{max} (ATR)/cm^{-1} 2909, 1591, 1488, 1184, 1160, 1007, 924, 752, 658, 496.

Phenyl *N*-methyl-*N*-benzylthiophosphoramidofluoridothioate (**12b**)



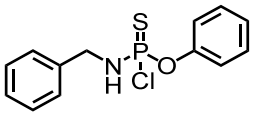
Following the General Procedure F using phenyl *N*-methyl-*N*-benzylthiophosphoramidochloridate (0.935 g, 3.00 mmol), potassium fluoride (1.39 g, 24.00 mmol), the title compound was isolated as a colorless oil (585 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 7H), 7.26 – 7.22 (m, 3H), 4.51 (dd, *J* = 13.2, 2.0 Hz, 2H), 2.82 (dd, *J* = 11.2, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 6.9 Hz), 136.6 (dd, *J* = 4.5, 2.0 Hz), 130.0 (d, *J* = 1.5 Hz), 128.8, 128.2, 128.0, 125.7 (d, *J* = 2.0 Hz), 120.9 (d, *J* = 5.3 Hz), 54.2 (dd, *J* = 7.3, 5.5 Hz), 33.8 (d, *J* = 3.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 69.6 (d, *J* = 1053.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -46.9 (d, *J* = 1053.8 Hz). **HRMS** (ESI^+) calculated for $C_{14}H_{15}FNOPS$ $[M+H]^+$: m/z = 296.0669, m/z found 296.0667. **IR** ν_{max} (ATR)/cm^{-1} 1592, 1490, 1190, 1014, 930, 848, 798, 754, 733, 687.

Phenyl *N*-benylphosphoramidofluoridate (**12c**)



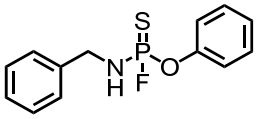
Following the General Procedure G using phenol (0.47 g, 5.00 mmol) and benzylamine (546 µL, 5.00 mmol), the title compound was isolated as a colorless oil (704 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.21 (m, 10H), 4.27 – 4.22 (m, 2H), 3.87 – 3.79 (br, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0 (d, *J* = 6.4 Hz), 138.2, 130.1, 128.8, 128.0, 127.4, 125.7, 120.0 (d, *J* = 4.9 Hz), 45.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -0.3 (d, *J* = 972.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.34 (d, *J* = 972.7 Hz). **HRMS** (ESI^+) calculated for $C_{13}H_{13}FNO_2P$ $[M+H_3O]^+$: m/z = 284.0846, m/z found 284.0839. **IR** ν_{max} (ATR)/cm^{-1} 3225, 1592, 1489, 1278, 1200, 1100, 949, 889, 688, 498.

Phenyl *N*-benzylphosphoramidochloridothioate (**11d**)



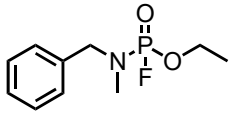
Following the General Procedure E using phenol (0.47 g, 5.00 mmol) and benzylamine (546 µL, 5.00 mmol), the title compound was isolated as a colorless oil (1.32 g, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 10H), 4.45 – 4.39 (m, 2H), 4.01 (br, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3 (d, *J* = 8.8 Hz), 137.5 (d, *J* = 9.0 Hz), 129.8 (d, *J* = 2.0 Hz), 129.0, 128.1, 127.9, 126.1 (d, *J* = 2.4 Hz), 121.4 (d, *J* = 5.4 Hz), 47.2 (d, *J* = 3.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 66.2; **HRMS** (ESI^+) calculated for $C_{13}H_{13}ClNOPS$ $[M-H]^-$: m/z = 296.0071, m/z found 264.0372. **IR** ν_{max} (ATR)/cm^{-1} 3361, 1589, 1487, 1399, 1189, 1068, 926, 751, 671, 497.

Phenyl *N*-benzylthiophosphoramidofluoridothioate (**12d**)



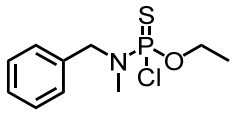
Following the General Procedure F using Phenyl benzylthiophosphoramidochloridate (0.893 g, 3.00 mmol), potassium fluoride (1.39 g, 24.00 mmol), the title compound was isolated as a colorless oil (635 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 7H), 7.26 – 7.22 (m, 3H), 4.44 – 4.34 (m, 2H), 3.81 (br, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3 (d, *J* = 6.8 Hz), 138.0 (d, *J* = 6.7 Hz), 130.0 (d, *J* = 1.5 Hz), 129.0, 128.1, 127.7, 125.8 (d, *J* = 1.8 Hz), 120.9 (d, *J* = 5.1 Hz), 46.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.6 (d, *J* = 1059.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -44.9 (d, *J* = 1059.3 Hz). **HRMS** (ESI^+) calculated for $C_{13}H_{13}FNOPS$ $[M+H]^+$: m/z = 280.0367, m/z found 280.0367. **IR** ν_{max} (ATR)/cm^{-1} 3374, 1591, 1459, 1406, 1195, 1070, 935, 940, 752, 665.

Ethyl benzyl(methyl)phosphoramidofluoridate (**12e**)



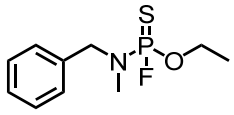
Following the General Procedure G using ethanol (292 µL, 5.00 mmol) and *N*-methylbenzylamine (665 µL, 5.00 mmol), the title compound was isolated as a colorless oil (560 mg, 48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 4.25 – 4.19 (m, 4H), 2.60 (d, *J* = 11.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8 (d, *J* = 2.4 Hz), 128.7, 128.2, 127.8, 64.0 (d, *J* = 5.3 Hz), 52.9 (d, *J* = 5.4 Hz), 33.0 (d, *J* = 4.5 Hz), 16.2 (d, *J* = 7.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.3 (d, *J* = 967.1 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.26 (d, *J* = 967.1 Hz). **HRMS** (ESI^+) calculated for $C_{10}H_{15}FNO_2P$ $[M+H]^+$: m/z = 232.0897, m/z found 232.0898. **IR** ν_{max} (ATR)/cm^{-1} 2987, 1352, 1276, 1033, 1014, 959, 847, 801, 698, 579, 457.

Ethyl *N*-methyl-*N*-benzylphosphoramidochloridothioate (**11f**)



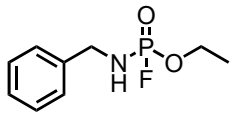
Following the General Procedure E using ethanol (0.292 mL, 5.00 mmol) and *N*-methylbenzylamine (665 µL, 5.00 mmol), the title compound was isolated as a colorless oil (978 mg, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 4.47 – 4.40 (m, 2H), 4.35 – 4.23 (m, 2H), 2.71 (d, *J* = 14.4 Hz, 3H), 1.41 (td, *J* = 7.2, 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7 (d, *J* = 7.7 Hz), 128.7, 128.4, 127.8, 64.6 (d, *J* = 5.7 Hz), 54.0 (d, *J* = 5.7 Hz), 34.1 (d, *J* = 2.1 Hz), 15.8 (d, *J* = 9.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 77.9; **HRMS** (ESI^+) calculated for $C_{10}H_{15}ClNOPS$ $[M+H]^+$: m/z = 264.0373, m/z found 264.0371. **IR** ν_{max} (ATR)/cm^{-1} 2909, 1591, 1488, 1184, 1160, 1007, 924, 752, 658, 496.

Ethyl *N*-methyl-*N*-benzylthiophosphoramidofluoridothioate (**12f**)



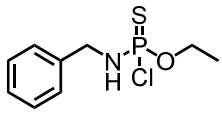
Following the General Procedure F using ethyl benzyl(methyl)phosphoramidochloridate (0.743 g, 3.00 mmol), potassium fluoride (1.39 g, 24.00 mmol), the title compound was isolated as a colorless oil (540 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 4.41 (dd, *J* = 12.8, 2.0 Hz, 2H), 4.26 – 4.16 (m, 2H), 2.69 (dd, *J* = 14.4, 1.6 Hz, 3H), 1.38 (tt, *J* = 6.8, 0.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.0 (dd, *J* = 4.5, 2.1 Hz), 128.7, 128.1, 127.8, 64.4 (d, *J* = 4.9 Hz), 53.8 (dd, *J* = 7.2, 1.6 Hz), 33.6 (d, *J* = 3.8 Hz), 15.9 (d, *J* = 7.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 75.2 (d, *J* = 1047.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -47.2 (d, *J* = 1047.2 Hz). **HRMS** (ESI^+) calculated for $C_{10}H_{15}FNOPS$ $[M+H]^+$: m/z = 248.0669, m/z found 248.0668. **IR** ν_{max} (ATR)/cm^{-1} 2985, 1455, 1133, 1032, 1011, 952, 811, 786, 734, 698.

Ethyl benzylphosphoramidofluoridate (**12g**)



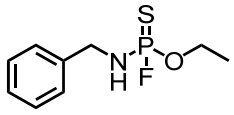
Following the General Procedure G using ethanol (292 µL, 5.00 mmol) and benzylamine (546 µL, 5.00 mmol), the title compound was isolated as a colorless oil (570 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 4.19 – 4.14 (m, 4H), 3.66 – 3.32 (m, 1H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 128.9, 127.9, 127.4, 64.2, 45.5, 16.2 (d, *J* = 6.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 3.4 (d, *J* = 962.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -73.35 (d, *J* = 962.9 Hz). **HRMS** (ESI^+) calculated for $C_9H_{13}FNO_2P$ $[M-H]^-$: m/z = 216.0595, m/z found 216.0589. **IR** ν_{max} (ATR)/cm^{-1} 2988, 1455, 1266, 1104, 1039, 885, 837, 732, 697, 483.

Ethyl *N*-benzylphosphoramidochloridothioate (**11h**)



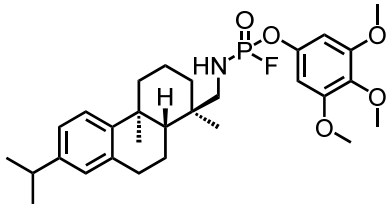
Following the General Procedure E using phenol (0.292 mL, 5.00 mmol) and benzylamine (546 µL, 5.00 mmol), the title compound was isolated as a colorless oil (562 mg, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 4H), 7.33 – 7.30 (m, 1H), 4.39 – 4.15 (m, 4H), 3.82 (br, 1H), 1.41 (td, *J* = 7.2, 0.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.9 (d, *J* = 9.0 Hz), 128.9, 128.0, 127.9, 64.5 (d, *J* = 5.5 Hz), 46.8 (d, *J* = 3.5 Hz), 15.7 (d, *J* = 9.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 71.6. **HRMS** (ESI^+) calculated for $C_9H_{13}ClNOPS$ $[M-H]^-$: m/z = 248.0071, m/z found 248.0062. **IR** ν_{max} (ATR)/cm^{-1} 3357, 2984, 1391, 1019, 961, 789, 697, 649, 471.

Ethyl *N*-benzylthiophosphoramidofluoridothioate (**12h**)



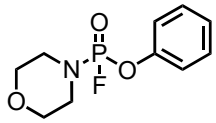
Following the General Procedure F using ethyl benzylthiophosphoramidochloridate (0.35 g, 1.50 mmol), potassium fluoride (697 g, 12.00 mmol), the title compound was isolated as a colorless oil (298 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 4.27 – 4.16 (m, 4H), 3.61 (br, 1H), 1.41 (tt, *J* = 7.2, 0.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.5 (d, *J* = 6.5 Hz), 128.9, 127.9, 127.6, 64.5 (d, *J* = 4.5 Hz), 46.1, 15.9 (d, *J* = 7.9 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 73.6 (d, *J* = 1047.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -46.2 (d, *J* = 1047.5 Hz). **HRMS** (ESI^+) calculated for $C_9H_{13}FNOPS$ $[M+H]^+$: m/z = 232.0367, m/z found 232.0367. **IR** ν_{max} (ATR)/cm^{-1} 3328, 1455, 1407, 1026, 969, 812, 734, 697, 659.

3,4,5-Trimethoxyphenyl (((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)phosphoramidofluoridate (**12i**)



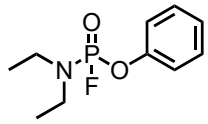
Following the General Procedure G using 3,4,5-trimethoxyphenol (921 mg, 5.00 mmol) and (+)-dehydroabietylamine (1.43 g, 5.00 mmol), the title compound was isolated as a colorless solid (1.57 g, 59% yield, dr = 1:1). **m.p.** 54.3 – 55.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.4 Hz, 1H), 7.00 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.88 – 6.87 (m, 1H), 6.47 (s, 2H), 3.81 (s, 3H), 3.80 (s, 6H), 3.21 – 2.97 (m, 2H), 2.93 – 2.79 (m, 4H), 2.31 – 2.27 (m, 1H), 1.77 – 1.67 (m, 4H), 1.53 – 1.46 (m, 1H), 1.42 – 1.33 (m, 3H), 1.23 – 1.20 (m, 9H), 0.94 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.8, 147.0 (d, *J* = 2.5 Hz), 146.2 (d, *J* = 5.9 Hz), 135.6, 134.5 (d, *J* = 5.2 Hz), 126.9 (d, *J* = 3.5 Hz), 124.3 (d, *J* = 3.0 Hz), 124.1 (d, *J* = 2.7 Hz), 97.6 (d, *J* = 5.2 Hz), 97.5 (d, *J* = 5.4 Hz), 61.1, 56.3 (d, *J* = 1.3 Hz), 52.8, 44.9, 38.4, 37.9, 37.3 (d, *J* = 2.5 Hz), 37.2 (d, *J* = 3.0 Hz), 35.5 (d, *J* = 11.5 Hz), 33.6, 30.0, 25.3 (d, *J* = 4.9 Hz), 24.1, 18.9 (d, *J* = 2.0 Hz), 18.6, 18.4 (d, *J* = 3.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -0.7 (d, *J* = 973.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.78 (dd, *J* = 973.5, 22.6 Hz). **HRMS** (ESI^+) calculated for $C_{29}H_{41}FNO_5P$ $[M+H]^+$: m/z = 532.2634, m/z found 532.2634. **IR** ν_{max} (ATR)/cm^{-1} 2934, 1605, 1502, 1463, 1275, 1224, 1104, 1129, 883, 820, 492.

Phenyl morpholinophosphonofluoridate (**12j**)



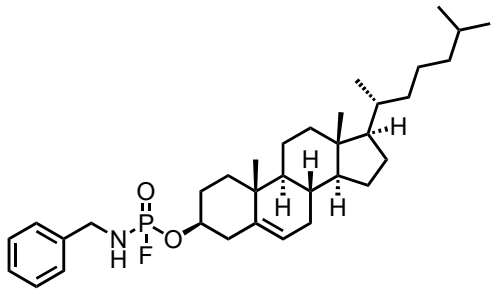
Following the General Procedure G using phenol (0.47 g, 5.00 mmol), and morpholine (437 µL, 5.00 mmol), the title compound was isolated as a colorless oil (859 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.24 – 7.21 (m, 3H), 3.66 – 3.64 (m, 4H), 3.32 – 3.27 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0 (d, *J* = 6.2 Hz), 130.1, 125.8, 119.9 (d, *J* = 5.2 Hz), 66.8 (d, *J* = 5.0 Hz), 44.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -3.4 (d, *J* = 977.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.65 (d, *J* = 977.8 Hz). **HRMS** (ESI^+) calculated for $C_{10}H_{13}FNO_3P$ $[M+H]^+$: m/z = 246.0690, m/z found 246.0688. **IR** ν_{max} (ATR)/cm^{-1} 2861, 1489, 1299, 1203, 1142, 1114, 978, 940, 862, 770, 689, 514.

O-Phenyl diethylphosphoramidofluoridate (**12k**)



Following the General Procedure G using phenol (0.47 g, 5.00 mmol) and diethylamine (517 µL, 5 mmol), the title compound was isolated as a colorless oil (683 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 8.0 Hz, 2H), 7.24 – 7.17 (m, 3H), 3.29 – 3.12 (m, 4H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2 (d, *J* = 5.9 Hz), 130.1, 125.4 (d, *J* = 0.7 Hz), 120.0 (d, *J* = 5.3 Hz), 40.3 (d, *J* = 5.1 Hz), 14.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -0.4 (d, *J* = 973.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.65 (d, *J* = 973.8 Hz). **HRMS** (ESI^+) calculated for $C_{10}H_{15}FNO_2P$ $[M+H]^+$: m/z = 232.0897, m/z found 232.0895. **IR** ν_{max} (ATR)/cm^{-1} 2979, 1490, 1291, 1199, 1166, 1041, 968, 935, 769, 689, 516, 484.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl benzylphosphoramidofluoridate (**12l**)

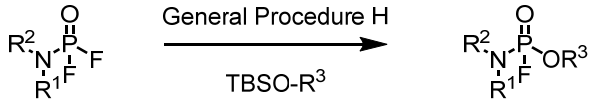


Following the General Procedure G using cholesterol (1.93 g, 5.00 mmol) and benzylamine (546 µL, 5.00 mmol) the title compound was isolated as a colorless solid (1.3 g, 47% yield, dr = 4:1). **m.p.** 118.9 – 121.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 5H), 5.40 – 5.34 (m, 1H), 4.35 – 4.27 (m,1H), 4.17 (dd, *J* = 10.4, 6.8 Hz, 2H), 3.56 – 3.37 (m, 1H), 2.47 – 2.41 (m, 2H), 2.31 – 2.20 (m, 1H), 2.04 – 1.96 (m, 4H), 1.88 – 1.76 (m, 3H), 1.75 – 1.66 (m, 1H), 1.61 – 1.42 (m, 6H), 1.40 – 1.22 (m, 4H), 1.16 – 1.04 (m, 7H), 1.00 (s, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.86 (dd, *J* = 6.8, 1.6 Hz, 6H), 0.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 139.0, 138.8, 138.7, 128.9, 127.8, 127.4, 123.5, 121.8, 79.2 (d, *J* =

5.7 Hz), 71.9, 56.9, 56.8, 56.2, 50.2, 50.0, 45.5, 42.4, 39.9 (d, *J* = 4.4 Hz), 37.4, 37.0, 36.6, 36.5, 36.3, 35.9, 32.0 (d, *J* = 9.6 Hz), 29.7 (d, *J* = 4.8 Hz), 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.8, 12.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.4 (d, *J* = 964.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.93 (d, *J* = 964.1 Hz). **HRMS** (ESI^+) calculated for $C_{34}H_{53}FNO_2P$ [M-H]$^-$: m/z = 556.3725, m/z found 556.3715. **IR** ν_{max} (ATR)/cm^{-1} 2936, 1457, 1272, 1023, 878, 698, 548, 624, 494, 463.

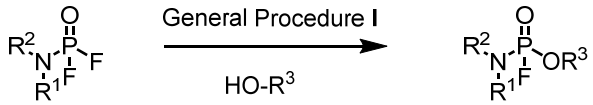
Phosphorus(V) Fluoride Exchange Reactions with TBS-ethers (Phosphoramidofluoridates 12m–12u)

General Procedure H



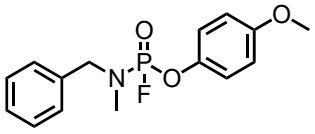
To a solution of the desired TBS ether (1.00 equiv) and phosphoramidic difluoride (1.20 equiv) in MeCN (0.4 M) was added DBU (20 mol%) and the resulting reaction was stirred at room temperature for 1 h. (To the incomplete reaction mixture (monitored by TLC) was added an extra aliquot of DBU (20 mol%) and the reaction mixture was stirred for a further 1 h, when didn't complete in an hour.) The reaction mixture was then concentrated under reduced pressure and purified by flash column chromatography to give the desired product.

General Procedure I



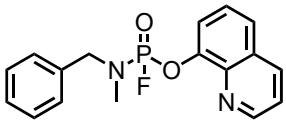
To a solution of the desired desired phosphoramidic difluoride (1.00 equiv) and phenols (1.00 equiv) in MeCN (0.4 M) was added HMDS (1.00 equiv) and BTMG (20 mol%) and the resulting reaction was stirred at room temperature for 15 min. The reaction mixture was then concentrated under reduced pressure and purified by flash column chromatography to give the desired product

4-Methoxyphenyl benzyl(methyl)phosphoramidofluoridate (**12m**)



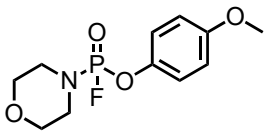
Following General Procedure I using benzyl(methyl)phosphoramidic difluoride (41 mg, 0.20 mmol) and 4-methoxyphenol (24.2 mg, 0.2 mmol), the title compound was isolated as a yellow oil (56 mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 3H), 7.27 – 7.22 (m, 2H), 7.21 – 7.15 (m, 2H), 6.88 (appt. d, *J* = 9.2 Hz, 2H), 4.38 – 4.19 (m, 2H), 3.81 (s, 3H), 2.68 (dd, *J* = 10.4, 1.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.2 (d, *J* = 1.0 Hz), 143.7 (d, *J* = 6.5 Hz), 136.4 (dd, *J* = 3.9, 1.6 Hz), 128.8, 128.2, 127.9, 121.0 (d, *J* = 4.8 Hz), 115.0, 55.8, 53.2 (d, *J* = 5.5 Hz), 33.1 (d, *J* = 4.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 0.0 (ddd, *J* = 973.9, 20.0, 9.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.9 (d, *J* = 974.4 Hz). **HRMS** (ESI^+): calculated for $C_{15}H_{18}FNO_3P$ [M+H]$^+$: m/z = 310.1003, m/z found 310.1003. **IR** ν_{max} (ATR)/cm^{-1} 2954, 1505, 1292, 1191, 1019, 1009, 945, 864, 831, 731.

Quinolin-8-yl benzyl(methyl)phosphoramidofluoridate (**12n**)



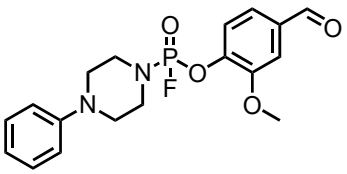
Following General Procedure I using benzyl(methyl)phosphoramidic difluoride (41 mg, 0.20 mmol) and 8-quinoline (29 mg, 0.20 mmol), the title compound was isolated as a yellow oil (56 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.83 – 7.80 (m, 1H), 7.72 (appt. dt, *J* = 8.2, 1.0 Hz, 1H), 7.54 (appt. t, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.30 – 7.26 (m, 5H), 4.50 – 4.38 (m, 2H), 2.81 (dd, *J* = 10.6, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 146.1 (d, *J* = 6.6 Hz), 140.7 (d, *J* = 5.6 Hz), 136.5 (dd, *J* = 4.1, 1.2 Hz), 135.9, 129.7, 128.5, 128.1, 127.6, 126.3 (d, *J* = 1.6 Hz), 125.3 (d, *J* = 1.3 Hz), 122.0, 119.4 (d, *J* = 3.7 Hz), 53.0 (dd, *J* = 12.1, 5.3 Hz), 33.3 (d, *J* = 4.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 0.0 (ddd, *J* = 974.5, 19.8, 9.7 Hz).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -74.1 (d, *J* = 975.3 Hz). **HRMS** (ESI^+): calculated for $C_{17}H_{17}FN_2O_2P$ $[M+H]^+$: m/z = 331.1006, m/z found 331.1010. **IR** ν_{max} (ATR)/cm^{-1} 2921, 1499, 1289, 1246, 1092, 1019, 933, 843, 755.

4-Methoxyphenyl morpholinophosphonofluoridate (**12o**)



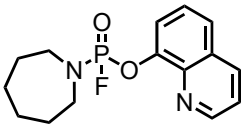
Following General Procedure I using morpholinophosphonic difluoride (34.2 mg, 0.20 mmol) and 4-methoxyphenol (24.8 mg, 0.20 mmol), the title compound was isolated as a colourless oil (47 mg, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (appt. d, *J* = 8.1 Hz, 2H), 6.87 (appt. d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.65 (appt. t, *J* = 4.7 Hz, 4H), 3.31 – 3.26 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1 (d, *J* = 1.0 Hz), 143.4 (d, *J* = 6.4 Hz), 120.7 (d, *J* = 4.9 Hz), 114.9, 66.6 (d, *J* = 4.9 Hz), 55.6, 44.5 (d, *J* = 1.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -3.1 (d, *J* = 976.3 Hz).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.1 (d, *J* = 977.1 Hz). **HRMS** (ESI^+): calculated for $C_{11}H_{16}FNO_4P$ $[M+H]^+$: m/z = 276.0795, m/z found 276.0789. **IR** ν_{max} (ATR)/cm^{-1} 2859, 1504, 1291, 1260, 1198, 1143, 1114, 979, 944, 833.

4-Formyl-2-methoxyphenyl (4-phenylpiperazin-1-yl)phosphonofluoridate (**12p**)



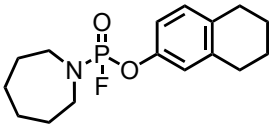
Following General Procedure I using (4-phenylpiperazin-1-yl)phosphonic difluoride (49.2 mg, 0.20 mmol) and vanillin (30.4 mg, 0.20 mmol), the title compound was isolated as a colourless oil (73 mg, 96%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.56 – 7.53 (m, 1H), 7.49 – 7.48 (m, 1H), 7.44 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.28 – 7.24 (m, 2H), 6.92 – 6.88 (m, 3H), 3.93 (s, 3H), 3.52 – 3.44 (m, 4H), 3.14 (appt. t, *J* = 4.9 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 151.2 (d, *J* = 5.9 Hz), 151.1, 143.9 (d, *J* = 6.5 Hz), 134.6 (d, *J* = 1.0 Hz), 129.3, 125.1 (d, *J* = 1.3 Hz), 121.6 (d, *J* = 3.1 Hz), 120.8, 116.9, 111.0, 56.2, 49.8 (d, *J* = 4.8 Hz), 44.7 (d, *J* = 2.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 0.0 – -6.9 (m).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -74.1 (d, *J* = 985.2 Hz). **HRMS** (ESI^+): calculated for $C_{18}H_{21}FN_2O_4P$ $[M+H]^+$: m/z = 379.1217, m/z found 379.1216. **IR** ν_{max} (ATR)/cm^{-1} 2824, 1693, 1598, 1504, 1268, 1140, 981, 862, 754, 693.

Quinolin-8-yl azepan-1-ylphosphonofluoridate (**12q**)



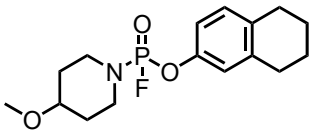
Following General Procedure I using azepan-1-ylphosphonic difluoride (36.6 mg, 0.20 mmol) and 8-quinoline (29 mg, 0.20 mmol), the title compound was isolated as a yellow oil (53 mg, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.00 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.70 (appt. d, *J* = 8.3 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.47 – 3.42 (m, 4H), 1.72 – 1.68 (m, 4H), 1.57 – 1.53 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 146.2 (d, *J* = 5.6 Hz), 140.5 (d, *J* = 6.2 Hz), 136.2, 129.8, 126.4 (d, *J* = 1.5 Hz), 125.0 (d, *J* = 1.1 Hz), 122.0, 119.2 (d, *J* = 3.5 Hz), 47.8 (d, *J* = 4.6 Hz), 29.8 (d, *J* = 3.6 Hz), 26.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 3.1 – -3.5 (m). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -73.0 (d, *J* = 975.7 Hz). **HRMS** (ESI^+): calculated for $C_{15}H_{19}FN_2O_2P$ $[M+H]^+$: m/z = 309.1163, m/z found 309.1171. **IR** ν_{max} (ATR)/cm^{-1} 2922, 1497, 1282, 1231, 1072, 922, 828, 771, 483.

5,6,7,8-Tetrahydronaphthalen-2-yl azepan-1-ylphosphonofluoridate (**12r**)



Following General Procedure I using azepan-1-ylphosphonic difluoride (36.6 mg, 0.20 mmol) and *5,6,7,8*-tetrahydro-2-naphthol (30 mg, 0.20 mmol), the title compound was isolated as a colourless oil (58 mg, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.1 Hz, 1H), 6.97 – 6.92 (m, 2H), 3.31 – 3.26 (m, 4H), 2.75 – 2.70 (m, 4H), 1.79 – 1.75 (m, 4H), 1.74 – 1.70 (m, 4H), 1.61 – 1.58 (m, 4H**^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9 (d, *J* = 6.4 Hz), 139.0, 134.3, 130.4, 119.9 (d, *J* = 5.0 Hz), 117.0 (d, *J* = 5.2 Hz), 47.8 (d, *J* = 4.4 Hz), 29.9 (d, *J* = 3.1 Hz), 29.6 (d, *J* = 5.7 Hz), 28.9, 26.8, 23.2, 23.0.. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.6 – -3.8 (m). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -74.3 (d, *J* = 973.3 Hz). **HRMS** (ESI^+): calculated for $C_{16}H_{24}FNO_2P$ $[M+H]^+$: m/z = 312.1523, m/z found 312.1528. **IR** ν_{max} (ATR)/cm^{-1} 2924, 1497, 1296, 1122, 1147, 1071, 996, 967, 859.

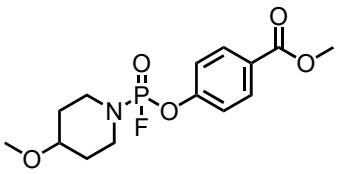
5,6,7,8-Tetrahydronaphthalen-2-yl (4-methoxypiperidin-1-yl)phosphonofluoridate (**12s**)



Following General Procedure I using (4-methoxypiperidin-1-yl)phosphonic difluoride (40 mg, 0.20 mmol) and *5,6,7,8*-tetrahydro-2-naphthol (30 mg, 0.20 mmol), the title compound was isolated as a colourless oil (62 mg, 94%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 9.3 Hz, 1H), 6.93 – 6.90 (m, 2H), 3.56 – 3.47 (m, 2H), 3.40 – 3.35 (m, 1H), 3.34 (s, 3H), 3.14 – 3.02 (m, 2H), 2.76 – 2.69 (m, 4H), 1.89 – 1.81 (m, 2H), 1.80 – 1.74 (m, 4H), 1.61 – 1.51 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.8 (d, *J* = 6.5 Hz), 139.1, 134.5, 130.4, 120.0 (d, *J* = 5.0 Hz), 116.9 (d, *J* = 5.0 Hz), 75.2, 55.8, 42.2 (dd, *J* = 5.9, 3.6 Hz), 30.9 – 30.6 (m), 29.6, 28.9, 23.2, 22.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -2.3 (d, *J* = 974.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.4 (d, *J* = 974.9 Hz). **HRMS** (ESI^+): calculated for $C_{16}H_{24}FNO_3P$ $[M+H]^+$:

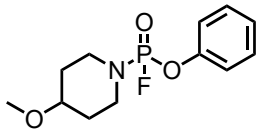
m/z = 328.1472, m/z found 328.1476. . **IR** ν_{max} (ATR)/cm^{-1} 2929, 1497, 1291, 1223, 1137, 1067, 965, 862, 823, 752.

Methyl 4-((fluoro(4-methoxypiperidin-1-yl)phosphoryl)oxy)benzoate (**12t**)



Following General Procedure I using (4-methoxypiperidin-1-yl)phosphonic difluoride (40 mg, 0.20 mmol) and methyl 4-hydroxybenzoate (30.4 mg, 0.20 mmol), and stirred at room temperature for 1 h, the title compound was isolated as a yellow oil (48 mg, 73%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.30 – 7.26 (m, 2H), 3.91 (s, 3H), 3.53 – 3.46 (m, 2H), 3.40 – 3.35 (m, 1H), 3.33 (s, 3H), 3.12 – 3.08 (m, 2H), 1.86 – 1.79 (m, 2H), 1.60 – 1.52 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 153.8 (d, *J* = 6.1 Hz), 131.9, 131.9, 127.6, 119.8 (d, *J* = 5.5 Hz), 74.8 (d, *J* = 0.6 Hz), 55.9, 52.4, 42.1 (dd, *J* = 6.5, 3.6 Hz), 30.8 – 30.6 (m). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -3.2 (d, *J* = 980.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.2 (d, *J* = 975.5 Hz). **HRMS** (ESI$^+$): calculated for $C_{14}H_{19}FNNaO_5P$ $[M+Na]^+$: m/z = 354.0877, m/z found 354.0884. **IR** ν_{max} (ATR)/cm^{-1} 2953, 1722, 1607, 1506, 1277, 1217, 1098, 1068, 932, 861, 772.

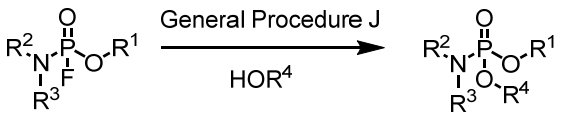
Phenyl (4-methoxypiperidin-1-yl)phosphonofluoridate (**12u**)



Following General Procedure I using (4-methoxypiperidin-1-yl)phosphonic difluoride (40 mg, 0.20 mmol) and phenol (18.8 mg, 0.20 mmol), the title compound was isolated as a colourless oil (45 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.26 – 7.18 (m, 3H), 3.58 – 3.46 (m, 2H), 3.41 – 3.31 (m, 4H), 3.15 – 3.02 (m, 2H), 1.89 – 1.78 (m, 2H), 1.63 – 1.50 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1 (d, *J* = 6.1 Hz), 129.9, 125.5 (d, *J* = 0.9 Hz), 119.8 (d, *J* = 5.2 Hz), 74.9 (d, *J* = 0.6 Hz), 55.7, 42.0 (dd, *J* = 5.2, 3.8 Hz), 30.61 (dd, *J* = 3.5, 2.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -2.6 (d, *J* = 975.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.2 (d, *J* = 976.0 Hz). **HRMS** (ESI$^+$): calculated for $C_{12}H_{18}FNO_3P$ $[M+H]^+$: m/z = 274.1003, m/z found 279.0997. **IR** ν_{max} (ATR)/cm^{-1} 2930, 1592, 1489, 1290, 1194, 1138, 1069, 935, 858, 771, 689.

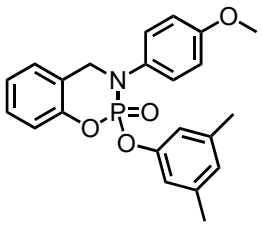
Phosphorus(V) Fluoride Exchange Reactions with Phenols (Phosphoramidofluoridates 15a–15q and 16a–16m)

General Procedure J



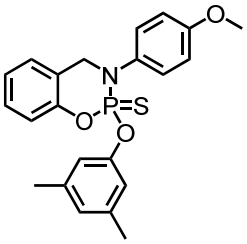
To a solution of phosphoramidofluoridate (0.10 mmol) and phenol (0.12 mmol) in acetonitrile (0.25 mL) was added hexamethyldisilazane (25 µL, 0.12 mmol), followed by TBD (2.8 mg, 0.02 mmol). The resulting solution was stirred at room temperature and monitored by ^{31}P NMR and ^{19}F NMR. When completed, the reaction was diluted with ethyl acetate (5 mL), passed through a short silica pad, and concentrated. The crude was purified by flash column chromatography to give the desired product.

2-(3,5-Dimethylphenoxy)-3-(4-methoxyphenyl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15a**)



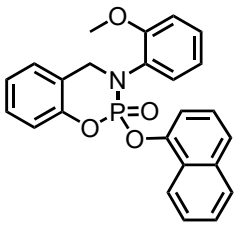
Following General Procedure J using 3-(4-methoxylphenyl)-2-fluoro -3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (29.3 mg, 0.10 mmol) and 3,5-dimethylphenol (14.7 mg, 0.12 mmol), the title compound was isolated as a colorless oil (37 mg, 93%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 1H), 7.26 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.15 (d, *J* = 6.0 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.78 – 6.76 (m, 3H), 4.90 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.55 (dd, *J* = 18.8, 15.2 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9 (d, *J* = 1.7 Hz), 150.6 (d, *J* = 8.1 Hz), 150.5 (d, *J* = 8.1 Hz), 139.6, 134.9 (d, *J* = 3.0 Hz), 129.1 (d, *J* = 1.4 Hz), 126.9 (d, *J* = 1.4 Hz), 126.8, 126.6 (d, *J* = 3.5 Hz), 124.4, 123.0(d, *J* = 7.2 Hz), 119.1 (d, *J* = 8.6 Hz), 118.0 (d, *J* = 4.7 Hz), 114.7, 55.6, 53.4 (d, *J* = 2.2 Hz), 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -7.4 (d, *J* = 18.0, 5.0 Hz). **HRMS** (ESI^+) calculated for $C_{22}H_{22}NO_4P$ $[M+H]^+$: m/z = 396.1359, m/z found 396.1355. **IR** ν_{max} (ATR)/cm^{-1} 2919, 1587, 1509, 1457, 1286, 1223, 1138, 1030, 925, 757.

2-(3,5-Dimethylphenoxy)-3-(4-methoxyphenyl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-thione (**15b**)



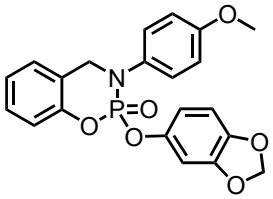
Following the General Procedure J using 3-(4-Methoxylphenyl)-2-fluoro-3,4-dihydrobenzo[e][1,3,2]oxazaphosphinine -2-thione (31 mg, 0.10 mmol) and 3,5-dimethylphenol (14.6, 0.12 mmol), the title compound was isolated as a yellow solid (37 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 3H), 7.17 – 7.11 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.81 (s, 1H), 6.76 (s, 2H), 4.95 (dd, *J* = 14.8, 6.4 Hz, 1H), 4.60 (dd, *J* = 17.6, 15.2 Hz, 1H), 3.82 (s, 3H), 2.28 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5 (d, *J* = 1.7 Hz), 150.9 (d, *J* = 8.8 Hz), 150.4 (d, *J* = 10.9 Hz), 139.4 (d, *J* = 1.7 Hz), 136.0 (d, *J* = 4.6 Hz), 129.1, 128.9 (d, *J* = 4.1 Hz), 127.1 (d, *J* = 1.8 Hz), 124.3, 123.4 (d, *J* = 7.5 Hz), 119.2 (d, *J* = 8.3 Hz), 118.7 (d, *J* = 4.7 Hz), 114.7 (d, *J* = 1.5 Hz), 55.6, 53.8, 21.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.77. **HRMS (ESI):** m/z calculated for $C_{22}H_{23}NO_3PS$: 412.1116 $[M+H]^+$; found: 412.1131. **IR** ν_{max} (ATR)/cm^{-1} 2919, 1588, 1509, 1456, 1246, 1218, 1188, 1135, 1028, 918, 825, 754, 573.

3-(2-Methoxyphenyl)-2-(naphthalen-1-yloxy)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15c**)



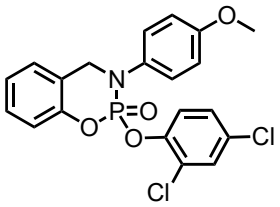
Following General Procedure J using 3-(2-methoxylphenyl)-2-fluoro -3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (29.3 mg, 0.10 mmol) and 1-naphthol (17.4 mg, 0.12 mmol), the title compound was isolated as a colorless oil (39 mg, 94%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 6.8 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.28 – 7.22 (m, 2H), 7.15 – 7.08 (m, 3H), 6.93 – 6.84 (m, 2H), 4.97 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.46 (dd, *J* = 18.8, 15.2 Hz, 1H), 3.55 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0 (d, *J* = 4.0 Hz), 150.9 (d, *J* = 8.0 Hz), 146.9 (d, *J* = 7.7 Hz), 134.7, 130.0 (d, *J* = 4.0 Hz), 129.8 (d, *J* = 2.6 Hz), 128.9, 128.7 (d, *J* = 1.3 Hz), 127.7, 126.7, 126.6, 126.5, 125.7(d, *J* = 1.5 Hz), 124.6, 124.2, 123.9 (d, *J* = 7.3 Hz), 121.6, 121.0, 119.2 (d, *J* = 8.3 Hz), 115.2 (d, *J* = 3.0 Hz), 112.1, 55.4, 52.9 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -7.9 (d, *J* = 21.0, 6.3 Hz). **HRMS** (ESI^+) calculated for $C_{24}H_{20}NO_4P$ $[M+H]^+$: m/z = 418.1203, m/z found 418.1202. **IR** ν_{max} (ATR)/cm^{-1} 2924, 1500, 1456, 1391, 1297, 1223, 1081, 926, 751, 478.

2-(Benzo[*d*][1,3]dioxol-5-yloxy)-3-(4-methoxyphenyl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15d**)



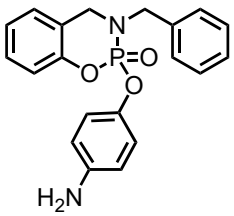
Following General Procedure J using 3-(4-methoxylphenyl)-2-fluoro -3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (29.3 mg, 0.10 mmol) and seamol (16.6 mg, 0.12 mmol), the title compound was isolated as a colorless solid (37 mg, 90%). **m.p.** 114.3–117.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 1H), 7.27 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.14 (d, *J* = 4.4 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.69 – 6.66 (m, 2H), 6.60 – 5.71 (m, 1H), 5.94 (s, 2H), 4.89 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.56 (dd, *J* = 18.8, 15.2 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0 (d, *J* = 1.2 Hz), 150.5 (d, *J* = 8.1 Hz), 148.2, 145.1 (d, *J* = 8.6 Hz), 145.0 (d, *J* = 1.6 Hz), 134.7 (d, *J* = 3.5 Hz), 129.2 (d, *J* = 1.2 Hz), 126.8, 126.6 (d, *J* = 3.8 Hz), 124.5, 123.0 (d, *J* = 3.3 Hz), 119.1 (d, *J* = 9.6 Hz), 114.8 (d, *J* = 0.9 Hz), 112.9 (d, *J* = 4.8 Hz), 108.1 (d, *J* = 1.1 Hz), 103.0 (d, *J* = 4.5 Hz), 101.8, 55.6, 53.4 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -7.1 (dd, *J* = 18.6, 5.0 Hz). **HRMS** (ESI^+) calculated for $C_{21}H_{18}NO_6P$ $[M+H]^+$: m/z = 412.0944, m/z found 412.0942. **IR** ν_{max} (ATR)/cm^{-1} 2915, 1516, 1484, 1456, 1289, 1244, 1122, 1093, 928, 759.

2-(2,4-Dichlorophenoxy)-3-(4-methoxyphenyl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15e**)



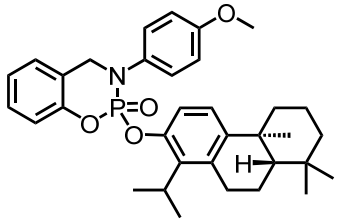
Following General Procedure J using 3-(4-methoxylphenyl)-2-fluoro -3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (29.3 mg, 0.10 mmol) and 2, 6-dichlorophenol (19.6 mg, 0.12 mmol), the product was isolated as a colorless oil (39 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.35 (dd, *J* = 2.4, 0.8 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.18 (dd, *J* = 8.8, 2.4 Hz, 2H), 7.14 (d, *J* = 4.4 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.04 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.58 (dd, *J* = 18.8, 15.2 Hz, 1H), 3.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3 (d, *J* = 1.3 Hz), 150.1 (d, *J* = 8.1 Hz), 145.7 (d, *J* = 7.5 Hz), 145.0 (d, *J* = 1.6 Hz), 134.0 (d, *J* = 2.6 Hz), 130.6 (d, *J* = 1.3 Hz), 130.3, 129.2 (d, *J* = 1.2 Hz), 128.1 (d, *J* = 1.3 Hz), 127.2 (d, *J* = 3.6 Hz), 126.8, 126.4 (d, *J* = 7.5 Hz), 124.6, 122.8 (d, *J* = 1.5 Hz), 122.7 (d, *J* = 7.1 Hz), 119.0 (d, *J* = 8.8 Hz), 114.8, 112.9 (d, *J* = 4.8 Hz), 55.6, 53.6 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -7.5 (dd, *J* = 19.7, 5.2 Hz). **HRMS** (ESI^+) calculated for $C_{20}H_{16}Cl_2NO_4P$ $[M+H]^+$: m/z = 436.0267, m/z found 436.0265. **IR** ν_{max} (ATR)/cm^{-1} 2838, 1509, 1490, 1256, 1221, 1098, 1033, 927, 811, 755, 563.

2-(4-Aminophenoxy)-3-benzyl-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15f**)



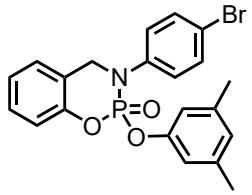
Following General Procedure J using 3-benzyl-2-fluoro -3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (27.7 mg, 0.10 mmol) and 4-aminophenol (13.1 mg, 0.12 mmol), the title compound was isolated as a colorless oil (32 mg, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 7.23 – 7.21 (m, 1H), 7.07 – 7.00 (m, 2H), 6.98 – 6.92 (m, 3H), 6.59 (d, *J* = 6.8 Hz, 1H), 4.50 (dd, *J* = 15.2, 4.0 Hz, 1H), 4.33 – 4.26 (m, 2H), 4.11 (dd, *J* = 23.6, 8.0 Hz, 1H), 3.62 (br, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.6 Hz), 143.8 (d, *J* = 1.6 Hz), 142.9 (d, *J* = 8.2 Hz), 136.6 (d, *J* = 5.4 Hz), 128.8 (d, *J* = 1.6 Hz), 128.7, 128.4, 127.8, 127.0, 124.1, 122.2 (d, *J* = 8.8 Hz), 121.2 (d, *J* = 4.3 Hz), 119.2 (d, *J* = 8.6 Hz), 115.9 (d, *J* = 1.2 Hz), 51.7 (d, *J* = 3.6 Hz), 48.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -3.2. **HRMS** (ESI^+) calculated for $C_{20}H_{19}N_2O_3P$ $[M+H]^+$: m/z = 367.1206, m/z found 367.1205. **IR** ν_{max} (ATR)/cm^{-1} 3442, 3361, 1506, 1454, 1267, 1181, 1097, 933, 742, 492

2-(((4b*S*,8a*S*)-1-*iso*-Propyl-4b,8,8-trimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)oxy)-3-(4-methoxyphenyl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15g**)



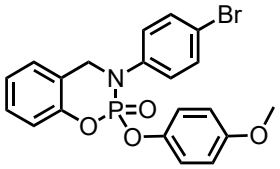
Following General Procedure J using 3-propargyl-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (22.5 mg, 0.10 mmol) and (+)-totarol (34.4 mg, 0.12 mmol), the title compound was isolated as a colorless solid (51 mg, 91%, 1:1 dr). **m.p.** 144.5 – 145.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 3H), 7.23 – 7.18 (m, 1H), 7.17 – 7.06 (m, 3H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.00 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.62 – 4.52 (m 1H), 3.80 (s, 3H), 3.23 (s, 1H), 2.90 (d, *J* = 17.2, 6.0 Hz, 1H), 2.75 – 2.63 (m, 1H), 2.23 (d, *J* = 9.2 Hz, 1H), 1.92 – 1.87 (m, 1H), 1.74 – 1.57 (m, 3H), 1.48 – 1.46 (m, 1H), 1.35 – 1.11 (m, 12H), 0.92 (d, *J* = 12.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7, 150.6 (d, *J* = 4.0 Hz), 150.5 (d, *J* = 4.0 Hz), 146.9, 135.0, 134.7, 129.1, 126.6, 126.5, 124.2, 123.4, 122.9 (d, *J* = 7.1 Hz), 122.8 (d, *J* = 7.2 Hz), 119.1 (d, *J* = 8.7 Hz), 117.1, 114.6, 77.4, 55.6, 53.1, 49.5, 41.6, 39.5 (d, *J* = 3.2 Hz), 38.0, 33.4, 33.3, 28.9, 25.1, 21.7, 20.7, 20.6, 19.5, 19.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -8.4 (d, *J* = 16.8 Hz). **HRMS** (ESI^+) calculated for $C_{34}H_{42}NO_4P$ $[M+H]^+$: m/z = 560.2924, m/z found 560.2923. **IR** ν_{max} (ATR)/cm^{-1} 2926, 1510, 1457, 1294, 1226, 1181, 951, 925, 829, 753, 479.

3-(4-Bromophenyl)-2-(3,5-dimethylphenoxy)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15h**)



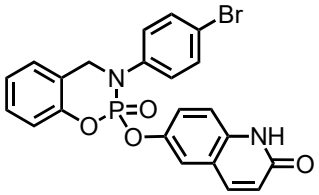
Following General Procedure J using 3-(4-bromophenyl)-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (34.2 mg, 0.10 mmol) and 3, 5-dimethoxylphenol (14.7 mg, 0.12 mmol), the title compound was isolated as a colorless oil (40 mg, 91%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.22 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.19 – 7.16 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 1H), 6.74 (s, 2H), 4.91 (dd, *J* = 15.2, 5.6 Hz, 1H), 4.59 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.25 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3 (d, *J* = 8.0 Hz), 150.2 (d, *J* = 8.0 Hz), 141.5 (d, *J* = 3.7 Hz), 139.7, 132.4, 129.4 (d, *J* = 1.4 Hz), 127.1 (d, *J* = 1.4 Hz), 126.8, 125.3 (d, *J* = 2.9 Hz), 124.6, 122.6 (d, *J* = 7.7 Hz), 119.1 (d, *J* = 8.6 Hz), 118.7 (d, *J* = 1.6 Hz), 117.8 (d, *J* = 4.8 Hz), 52.2 (d, *J* = 1.5 Hz), 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -8.0 (dd, *J* = 18.6, 6.0 Hz). **HRMS** (ESI^+) calculated for $C_{21}H_{19}BrNO_3P$ $[M+H]^+$: m/z = 444.0359, m/z found 444.0357. **IR** ν_{max} (ATR)/cm^{-1} 2920, 1587, 1488, 1457, 1284, 1225, 1137, 1030, 958, 927, 625, 754

3-(4-Bromophenyl)-2-(4-methoxyphenoxy)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15i**)



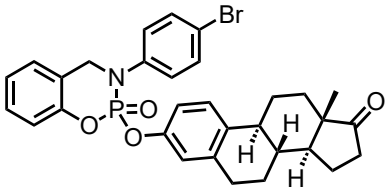
Following General Procedure J using 3-(4-bromophenyl)-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (34.2 mg, 0.10 mmol) and 4-methoxylphenol (14.9 mg, 0.12 mmol), the title compound was isolated as a colorless solid (43 mg, 97%). **m.p.** 99.7 – 101.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.22 (dd, *J* = 4.8, 0.8 Hz, 2H), 7.19 – 7.16 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.04 (dd, *J* = 8.8, 5.2 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.90 (dd, *J* = 15.2, 5.6 Hz, 1H), 4.59 (dd, *J* = 18.0, 15.2 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 150.4 (d, *J* = 1.8 Hz), 144.0 (d, *J* = 8.1 Hz), 141.4 (d, *J* = 3.9 Hz), 132.4, 129.5, 126.8, 125.4 (d, *J* = 3.8 Hz), 124.7, 122.7 (d, *J* = 7.4 Hz), 121.3 (d, *J* = 4.5 Hz), 119.2 (d, *J* = 8.5 Hz), 118.8, 114.8 (d, *J* = 0.9 Hz), 55.7, 52.3 (d, *J* = 1.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -8.00 (dd, *J* = 18.1, 5.2 Hz). **HRMS** (ESI$^+$) calculated for $C_{20}H_{17}BrNO_4P$ $[M+H]^+$: m/z = 446.0151, m/z found 446.0147. **IR** ν_{max} (ATR)/cm^{-1} 2921, 1507, 1484, 1301, 1180, 1093, 936, 912, 826, 756, 528.

6-((3-(4-Bromophenyl)-2-oxido-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinin-2-yl)oxy)quinolin-2(1*H*)-one (**15j**)



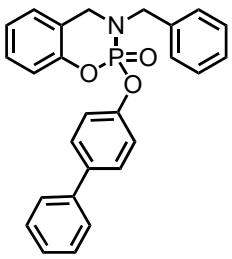
Following the General Procedure J using 3-(4-bromophenyl)-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (34.2 mg, 0.10 mmol) and 6-hydroxyquinolin-2(1H)-one (19.3 mg, 0.12 mmol), the title compound was isolated as a white solid (46 mg, 94%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.78 (s, 1H), 7.56 (d, *J* = 9.6 Hz, 1H), 7.33-7.30 (m, 2H), 7.27 – 7.17 (m, 3H), 7.13 – 7.10 (m, 3H), 7.07 – 7.04 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.81 (dd, *J* = 15.2, 5.6 Hz, 1H), 4.50 (dd, *J* = 18.0, 15.2 Hz, 1H. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 150.4 (d, *J* = 1.8 Hz), 144.0 (d, *J* = 8.1 Hz), 141.4 (d, *J* = 3.9 Hz), 132.4, 129.5, 126.8, 125.4 (d, *J* = 3.8 Hz), 124.7, 122.7 (d, *J* = 7.4 Hz), 121.3 (d, *J* = 4.5 Hz), 119.2 (d, *J* = 8.5 Hz), 118.8, 114.8 (d, *J* = 0.9 Hz), 55.7, 52.3 (d, *J* = 1.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -8.00 (dd, *J* = 18.1, 5.8 Hz). **HRMS** (ESI$^+$) calculated for $C_{22}H_{16}BrN_2O_4P$ $[M+H]^+$: m/z = 483.0104, m/z found 483.0101. **IR** ν_{max} (ATR)/cm^{-1} 2921, 1656, 1488, 1427, 1221, 965, 932, 819, 753, 464.

(8*R*,9*S*,13*S*,14*S*)-3-((3-(4-Bromophenyl)-2-oxido-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinin-2-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**15k**)



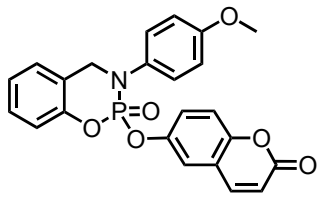
Following General Procedure J using 3-(4-bromophenyl)-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (34.2 mg, 0.10 mmol) and estrone (32.4 mg, 0.12 mmol), the title compound was isolated as a colorless oil (57 mg, 95%, 1:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.16 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.87 – 6.85 (m, 2H), 4.92 (dd, *J* = 15.2, 3.2 Hz, 1H), 4.60 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.84 – 2.81 (m, 2H), 2.49 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.38 – 2.34 (m, 1H), 2.25 – 2.21 (m 1H), 2.16 – 1.93 (m, 4H), 1.61 – 1.46 (m, 6H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3 (d, *J* = 8.0 Hz), 148.2 (dd, *J* = 12.8, 1.8 Hz), 141.4 (d, *J* = 3.8 Hz), 138.5, 137.0, 132.4, 129.4, 126.8 (d, *J* = 8.3 Hz), 125.3 (d, *J* = 2.8 Hz), 124.6, 122.6 (d, *J* = 7.3 Hz), 120.4 (d, *J* = 4.6 Hz), 120.3 (d, *J* = 4.6 Hz), 119.1 (d, *J* = 8.6 Hz), 118.7, 117.4 (d, *J* = 4.6 Hz), 77.4, 52.2, 50.5, 48.0, 44.1 (d, *J* = 1.7 Hz), 38.1, 35.9, 31.6, 29.4, 26.4, 25.9, 21.7,13.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -8.2 (dd, *J* = 18.0, 3.6 Hz). **HRMS** (ESI^+) calculated for $C_{31}H_{31}BrNO_4P$ $[M+H]^+$: m/z = 592.1247, m/z found 592.1243. **IR** ν_{max} (ATR)/cm^{-1} 2927, 1734, 1489, 1293, 1223, 1150, 955, 824, 752, 622.

2-([1,1'-Biphenyl]-4-yloxy)-3-benzyl-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15l**)



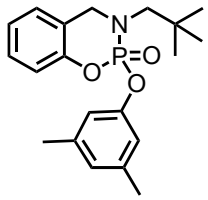
Following General Procedure J using 3-benzyl-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (27.7 mg, 0.10 mmol) and 4-phenylphenol (20.4 mg, 0.12 mmol), the title compound was isolated as a colorless solid (41 mg, 95%). **m.p.** 144.3 – 146.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 5.2 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.29 (m, 6H), 7.27 – 7.24 (m, 2H), 7.09 – 6.99 (m, 3H), 4.53 (dd, *J* = 15.2, 4.0 Hz, 1H), 4.42 – 4.33 (m, 2H), 4.11 (dd, *J* = 23.6, 8.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.7 Hz), 150.2 (d, *J* = 8.0 Hz), 140.4, 138.4 (d, *J* = 1.5 Hz), 136.5 (d, *J* = 5.4 Hz), 129.0 (d, *J* = 1.6 Hz), 129.0, 128.9, 128.5, 128.4, 128.0, 127.4, 127.1, 124.3, 122.2 (d, *J* = 8.8 Hz), 120.8 (d, *J* = 4.7 Hz), 119.2 (d, *J* = 8.8 Hz), 51.8 (d, *J* = 4.7 Hz), 48.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -3.4 (dd, *J* = 18.6, 5.3 Hz). **HRMS** (ESI^+) calculated for: $C_{26}H_{22}NO_3P$ $[M+H]^+$: m/z = 428.1410, m/z found 428.1402. **IR** ν_{max} (ATR)/cm^{-1} 2922, 2855, 1485, 1457, 1294, 1184, 1117, 1092, 929, 844, 757, 688.

6-((3-(4-Methoxyphenyl)-2-oxido-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinin-2-yl)oxy)-2*H*-chromen-2-one (**15m**)



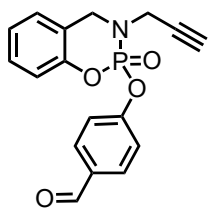
Following General Procedure J using 3-(4-methoxylphenyl)-2-fluoro -3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (29.3 mg, 0.10 mmol) and 6-hydroxy-2H-chromen-2-one (19.5 mg, 0.12 mmol), the title compound was isolated as a colorless solid (40 mg, 93%). **m.p.** 48.9 – 50.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 9.6 Hz, 2H), 7.27 – 7.16 (m, 6H), 7.10 (d, *J* = 4.4 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 9.2 Hz, 2H), 6.35 (d, *J* = 9.2 Hz, 2H), 4.86 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.54 (d, *J* = 18.8, 15.2 Hz, 1H), 3.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 158.2 (d, *J* = 1.3 Hz), 151.1, 150.2 (d, *J* = 8.1 Hz), 146.9 (d, *J* = 7.1 Hz), 128.0, 134.1 (d, *J* = 3.0 Hz), 129.4, 126.9, 126.8 (d, *J* = 3.1 Hz), 124.7, 124.2 (d, *J* = 5.1 Hz), 122.8 (d, *J* = 7.3 Hz), 119.4, 119.0, 118.9 (d, *J* = 2.0 Hz), 118.8, 118.6, 117.6, 114.9, 55.6, 53.5 (d, *J* = 2.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -7.3 (dd, *J* = 18.5, 5.7 Hz). **HRMS** (ESI^+) calculated for $C_{23}H_{18}NO_6P$ $[M+H]^+$: m/z = 436.0944, m/z found 436.0942. **IR** ν_{max} (ATR)/cm^{-1} 2925, 1724, 1568, 1509, 1437, 1292, 1244, 1096, 964, 926, 819, 757.

2-(3,5-Dimethylphenoxy)-3-neopentyl-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15n**)



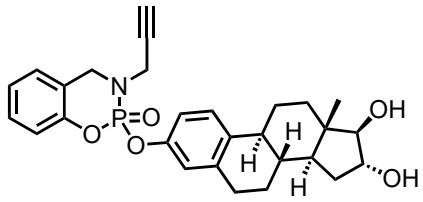
Following General Procedure J using 3-neopentyl-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (25.7 mg, 0.10 mmol) and 3,5-dimethylphenol (14.7 mg, 0.12 mmol), the title compound was isolated as a colorless oil (33 mg, 92%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 1H), 7.08 (d, *J* = 4.4 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 2H), 6.78 (s, 1H), 4.71 (dd, *J* = 15.6, 3.2 Hz, 1H), 4.17 (dd, *J* = 22.0, 15.2 Hz, 1H), 3.17 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.91 (t, *J* = 14.0 Hz, 1H), 2.26 (s, 6H), 0.97 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.2 (d, *J* = 7.5 Hz), 151.1 (d, *J* = 3.7 Hz), 139.6, 128.9 (d, *J* = 1.7 Hz), 126.8 (d, *J* = 1.6 Hz), 123.8, 122.8 (d, *J* = 8.5 Hz), 119.1 (d, *J* = 8.8 Hz), 118.0 (d, *J* = 4.7 Hz), 61.1 (d, *J* = 3.0 Hz), 52.8, 34.1 (d, *J* = 3.4 Hz), 27.9, 21.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -1.8. **HRMS** (ESI^+) calculated for : $C_{20}H_{26}NO_3P$ $[M+H]^+$: m/z = 360.1723, m/z found 360.1720. **IR** ν_{max} (ATR)/cm^{-1} 2956, 1594, 1457, 1289, 1219, 1189, 1137, 1026, 930, 832, 754.

4-((2-Oxido-3-(prop-2-yn-1-yl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinin-2-yl)oxy)benzaldehyde (**15o**)



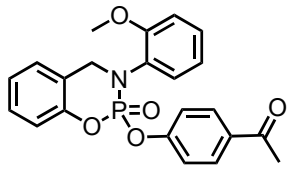
Following General Procedure J using 3-propargyl-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (22.5 mg, 0.10 mmol), 4-hydroxybenzaldehyde (14.7 mg, 0.12 mmol), the title compound was isolated as a colorless oil (30 mg, 91%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.72 – 7.69 (m, 1H), 7.66 (s, 1H), 7.53 – 7.49 (m, 2H), 7.31 – 7.26 (m, 1H), 7.20 – 7.14 (m, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 4.66 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.21 – 4.26 (m, 2H), 4.02 – 3.93 (m, 1H), 2.31 (t, *J* = 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.2, 151.2 (d, *J* = 7.7 Hz), 150.7 (d, *J* = 7.8 Hz), 138.0, 130.6, 129.2 (d, *J* = 1.7 Hz), 127.2, 126.6 (d, *J* = 1.5 Hz), 124.6, 121.6 (d, *J* = 8.5 Hz), 121.0 (d, *J* = 8.5 Hz), 119.1 (d, *J* = 8.5 Hz), 77.8 (d, *J* = 4.7 Hz), 73.7, 49.1, 37.6 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -5.0. **HRMS** (ESI^+) calculated for $C_{17}H_{14}NO_4P$ $[M+H]^+$: m/z = 328.0733, m/z found 328.0731. **IR** ν_{max} (ATR)/cm^{-1} 3291, 1698, 1585, 1497, 1315, 1285, 1221, 1189, 1098, 944, 855, 756, 644.

2-(((8*R*,9*S*,13*S*,14*S*,16*R*,17*R*)-16,17-Dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-3-(prop-2-yn-1-yl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (**15p**)



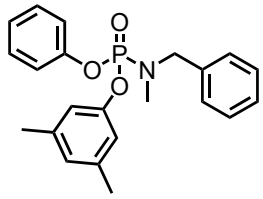
Following General Procedure J using 3-propargyl-2-fluoro-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (22.5 mg, 0.10 mmol) and (+)-estriol (34.6 mg, 0.12 mmol), the title compound was isolated as a colorless solid (41 mg, 82%, 1:1 dr). **m.p.** 89.9 – 92.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.24 (m, 1H), 7.17 – 7.09 (m, 3H), 7.01 (d, *J* = 15.2, 8.0 Hz, 1H), 6.89 – 6.86 (m, 2H), 4.59 (dd, *J* = 15.2, 3.2 Hz, 1H), 4.33 (dd, *J* = 20.0, 15.2 Hz, 1H), 4.20 – 4.14 (m, 2H), 4.02 – 3.95 (m, 1H), 3.58 (br, 1H), 3.57 (d, *J* = 9.6 Hz, 1H), 2.88 (s, 2H), 2.30 (s, 1H), 2.24 – 2.15 (m, 2H), 1.90 – 1.79 (m 3H), 1.65 – 1.60 (m, 1H), 1.56 – 1.25 (m, 6H), 0.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2 (d, *J* = 7.8 Hz), 148.2 (d, *J* = 9.0 Hz), 138.6, 137.3, 129.0, 127.1, 126.5, 124.3, 121.9 (d, *J* = 8.5 Hz), 120.3, 119.1 (d, *J* = 8.6 Hz), 117.4, 89.7, 78.4, 78.0 (d, *J* = 5.5 Hz), 77.4, 73.5, 49.0, 43.9 (d, *J* = 7.8 Hz), 38.0, 37.6 (d, *J* = 4.9 Hz), 36.6, 33.5, 29.8, 29.5, 27.1, 25.8, 12.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -4.7. **HRMS** (ESI^+) calculated for $C_{28}H_{32}NO_5P$ $[M+H]^+$: m/z = 494.2091, m/z found 494.2089. **IR** ν_{max} (ATR)/cm^{-1} 3298, 2923, 1490, 1220, 1190, 1098, 944, 754, 662, 499.

1-(4-((3-(2-Methoxyphenyl)-2-oxido-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinin-2-yl)oxy)phenyl)ethan-1-one (**15q**)



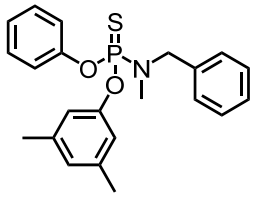
Following General Procedure J using 3-(2-methoxylphenyl)-2-fluoro -3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine 2-oxide (29.3 mg, 0.10 mmol) and 1-(4-hydroxyphenyl)ethan-1-one (16.3 mg, 0.12 mmol), the title compound was isolated as a colorless solid (37 mg, 90%). **m.p.** 93.7 – 96.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.8 Hz, 2H), 7.32 – 7.24 (m, 5H), 7.16 – 7.09 (m, 3H), 6.94 – 6.90 (m, 2H), 4.93 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.47 (dd, *J* = 18.8, 15.2 Hz, 1H), 3.69 (s, 3H), 2.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 155.9 (d, *J* = 4.0 Hz), 154.8 (d, *J* = 7.1 Hz), 150.7 (d, *J* = 8.1 Hz), 133.9, 130.3, 129.7 (d, *J* = 3.9 Hz), 129.5 (d, *J* = 2.5 Hz), 129.0 (d, *J* = 1.1 Hz), 128.8 (d, *J* = 1.3 Hz), 126.6, 124.4, 123.6 (d, *J* = 7.5 Hz), 121.2, 120.5 (d, *J* = 6.3 Hz), 119.0 (d, *J* = 8.7 Hz), 112.2, 55.6, 52.8 (d, *J* = 2.4 Hz), 26.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -8.5 (dd, *J* = 18.1, 5.0 Hz). **HRMS** (ESI^+) calculated for: $C_{22}H_{20}NO_5P$ $[M+H]^+$: m/z = 410.1152, m/z found 410.1147. **IR** ν_{max} (ATR)/cm^{-1} 1677, 1570, 1500, 1300, 1267, 1212, 1189, 925, 901, 778, 534.

3,5-Dimethylphenyl phenyl benzyl(methyl)phosphoramidate (**16a**)



Following General Procedure J using phenyl *N*-benylphosphoramidofluoridate (26.5 mg, 0.10 mmol) and 3, 5-dimethylphenol (14.7 mg, 0.12 mmol) for 15 min, the title compound was isolated as a colorless solid (35 mg, 93%). **m.p.** 71.9–74.5 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.18 – 7.13 (m, 5H), 7.10 – 7.04 (m, 3H), 6.78 (s, 2H), 6.71 (s, 1H), 4.21 – 4.17 (m, 2H), 2.56 (d, *J* = 10.4 Hz, 3H), 2.19 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0 (d, *J* = 7.0 Hz), 150.7 (d, *J* = 7.0 Hz), 139.6, 137.1 (d, *J* = 4.6 Hz), 129.8, 128.5, 128.3, 127.5, 126.7, 125.0, 120.4 (d, *J* = 4.9 Hz), 117.9 (d, *J* = 4.9 Hz), 113.2, 53.3(d, *J* = 4.9 Hz), 33.4 (d, *J* = 3.6 Hz), 21.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -1.1. **HRMS** (ESI^+) calculated for $C_{22}H_{24}NO_3P$ $[M+H]^+$: m/z = 382.1566, m/z found 382.1565. **IR** ν_{max} (ATR)/cm^{-1} 3191, 2917, 1592, 1489, 1494, 1235, 1141, 1030, 932, 854, 682, 553.

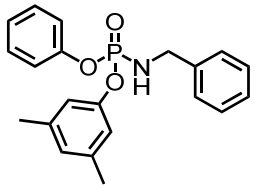
3,5-Dimethylphenyl phenyl benzyl(methyl)phosphoramidatothioate (**16b**)



Following General Procedure H using phenyl *N*-methyl-*N*-benzylthiophosphoramidofluoridothioate (29.50 mg, 0.10 mmol) and 3,5-dimethylphenol (14.7 mg, 0.12 mmol), the title compound was isolated as a colorless oil (38 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 10H), 6.86 (s, 1H), 6.85

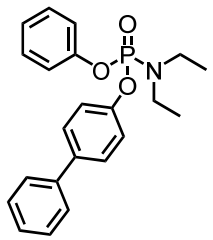
(s, 2H), 4.64 – 4.46 (m, 2H), 2.88 (d, *J* = 6.8 Hz, 3H), 2.32 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.3 (d, *J* = 7.6 Hz), 151.0 (d, *J* = 7.5 Hz), 139.4, 139.3, 137.4 (d, *J* = 5.1 Hz), 129.6 (d, *J* = 1.5 Hz), 128.5 (d, *J* = 3.3 Hz), 127.6, 126.9 (d, *J* = 1.8 Hz), 125.1 (d, *J* = 1.6 Hz), 121.3 (d, *J* = 4.9 Hz), 118.8 (d, *J* = 5.1 Hz), 54.5 (d, *J* = 7.0 Hz), 33.8 (d, *J* = 2.1 Hz), 21.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 68.2. **HRMS** (ESI^+) calculated for $C_{22}H_{24}NO_2PS$ $[M+H]^+$: m/z = 398.1338, m/z found 398.1335. **IR** ν_{max} (ATR)/cm^{-1} 2919, 1590, 1489, 1454, 1290, 1204, 1133, 1010, 950, 915, 752, 687.

3,5-Dimethylphenyl phenyl benzylphosphoramidate (**16c**)



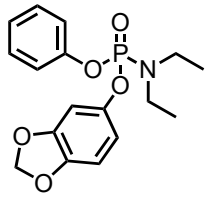
Following the General Procedure H using phenyl *N*-benylphosphoramidofluoridate (26.5 mg, 0.10 mmol) and 3, 5-dimethylphenol (14.7 mg, 0.12 mmol) for 15 min, the title compound was isolated as a colorless oil (35 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 10H), 6.85 (s, 2H), 6.80 (s, 1H), 4.26 (dd, *J* = 9.6 7.2 Hz, 2H), 3.48 – 3.39 (br, 1H), 2.23 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0 (d, *J* = 7.0 Hz), 150.7 (d, *J* = 7.0 Hz), 139.6, 137.1 (d, *J* = 4.6 Hz), 129.8, 128.5, 128.3, 127.5, 126.7, 125.0, 120.4 (d, *J* = 4.9 Hz), 117.9 (d, *J* = 4.9 Hz), 113.2, 53.3(d, *J* = 4.9 Hz), 33.4 (d, *J* = 3.6 Hz), 21.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -1.14. **HRMS** (ESI^+) calculated for $C_{21}H_{22}NO_3P$ $[M+H]^+$: m/z = 368.1410, m/z found 368.1409. **IR** ν_{max} (ATR)/cm^{-1} 3191, 2917, 1592, 1489, 1454, 1235, 1141, 1030, 932, 854, 682.

[1,1'-Biphenyl]-4-yl phenyl diethylphosphoramidate (**16d**)



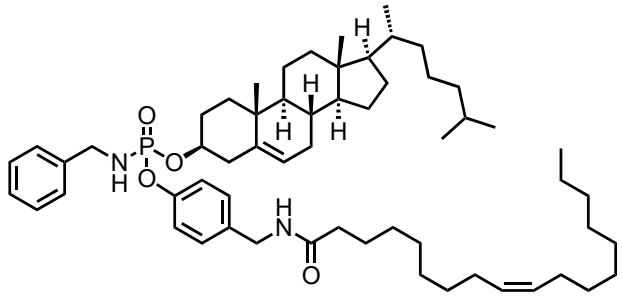
Following General Procedure J using *O*-phenyl diethylphosphoramidofluoridate (23.1 mg, 0.10 mmol) and 4-phenylphenol (20.4 mg, 0.12 mmol) for 2 h, the title compound was isolated as a colorless oil (36 mg, 93%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 4H), 7.30 (td, *J* = 7.6, 1.6 Hz, 2H), 7.32 – 7.12 (m, 7H), 7.05 – 4.01 (m, 1H), 3.19 – 3.09 (m, 4H), 1.01 – 0.91 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.2 (d, *J* = 6.7 Hz), 150.6 (d, *J* = 6.7 Hz), 140.5, 137.9, 129.7, 128.9, 128.4, 127.3, 127.1, 124.8, 120.6 (d, *J* = 5.2 Hz), 120.3 (d, *J* = 5.1 Hz), 39.9 (d, *J* = 4.8 Hz), 13.9 (d, *J* = 2.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 0.9. **HRMS** (ESI^+) calculated for $C_{22}H_{24}NO_3P$ $[M+H]^+$: m/z = 382.1566, m/z found 382.1567. **IR** ν_{max} (ATR)/cm^{-1} 2974, 1591, 1485, 1269, 1196, 1165, 1038, 963, 914, 762, 690, 600.

Benzo[*d*][1,3]dioxol-5-yl phenyl diethylphosphoramidate (**16e**)



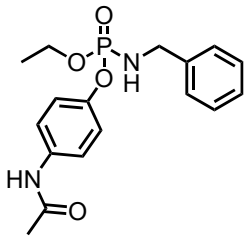
Following General Procedure J using *O*-phenyl diethylphosphoramidofluoridate (23.1 mg, 0.10 mmol) and sesamol (16.6 mg, 0.12 mmol) for 3 h, the title compound was isolated as a colorless oil (31 mg, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.15 (dd, *J* = 7.2, 0.8 Hz, 2H), 6.79 – 6.78 (m, 1H), 6.73 – 6.69 (m, 2H), 5.95 (s, 2H), 3.26 – 3.18 (m, 4H), 1.08 – 1.03 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0 (d, *J* = 6.8 Hz), 148.1, 145.4 (d, *J* = 7.0 Hz), 144.6, 129.7, 124.8, 120.3 (d, *J* = 4.9 Hz), 112.7 (d, *J* = 5.0 Hz), 108.1, 102.8 (d, *J* = 4.7 Hz), 101.7, 39.8 (d, *J* = 4.4 Hz), 13.9 (d, *J* = 2.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.2. **HRMS** (ESI^+) calculated for $C_{17}H_{20}NO_5P$ $[M+H]^+$: m/z = 350.1152, m/z found 350.1151. **IR** ν_{max} (ATR)/cm^{-1} 2976, 1593, 1482, 1245, 1167, 1121, 1034, 920, 875, 770, 690, 498.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (4-(oleamidomethyl)phenyl) benzylphosphoramidate (**16f**)



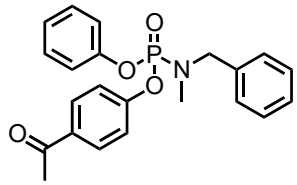
Following General Procedure J using (-)-cholesterol substrate (55.8 mg, 0.10 mmol) and 4-(oleamidomethyl)phenol (46.5 mg, 0.12 mmol) in 0.25 mL acetonitrile and 0.25 mL CH_2Cl_2 for 1 h, the title compound was isolated as a colorless oil (89 mg, 95% yield, 2:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.19 – 6.14 (br, 1H), 5.35 – 5.29 (m, 3H), 4.35 (d, *J* = 5.6 Hz, 2H), 4.29 – 4.25 (m, 1H), 4.16 – 4.12 (m, 2H), 3.38 – 3.31 (br, 1H), 2.40 (d, *J* = 14.0 Hz, 2H), 2.18 (d, *J* = 8.0 Hz, 2H), 2.02 – 1.92 (m, 8H), 1.85 – 1.80 (m, 2H), 1.65 – 1.61 (m, 4H), 1.55 – 1.41 (m, 6H), 1.32 – 1.26 (m, 25H), 1.16 – 1.05 (m, 6H), 1.02 – 0.97 (m, 1H), 0.99 (s, 3H), 0.92 – 0.85 (m, 12H), 0.67 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 150.4 (d, *J* = 6.5 Hz), 139.5, 139.3 (d, *J* = 6.1 Hz), 135.0, 130.1, 129.8, 129.1 (d, *J* = 2.2 Hz), 128.6, 127.4, 123.1, 120.5, 115.8, 78.1, 77.9, 56.8, 56.3, 50.1, 45.7, 42.9, 42.4, 40.1, 39.8, 39.6, 37.0, 36.8, 36.5, 36.3, 35.9, 32.0, 31.9, 29.9, 29.8, 29.7, 29.6, 29.4, 29.4, 29.4, 29.3, 28.3, 28.1, 27.3, 27.2, 25.9, 25.8, 24.4, 23.9, 22.9, 22.8, 22.7, 21.1, 19.4, 18.8, 14.2, 11.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.8. **HRMS** (ESI^+) calculated for: $C_{59}H_{93}N_2O_4P$ $[M+H]^+$: m/z = 925.6946, m/z found 925.6943; **IR** ν_{max} (ATR)/cm^{-1} 3274, 2925, 2853, 1647, 1548, 1508, 1456, 1217, 1018, 928, 732, 697, 497.

4-Acetamidophenyl ethyl benzylphosphoramidate (**16g**)



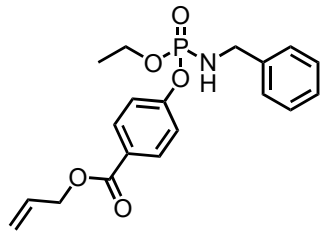
Following General Procedure J using ethyl benzylphosphoramidofluoridate (21.7 mg, 0.10 mmol) and 4-acetaminophenol (15.0 mg, 0.12 mmol) for 1 h, the title compound was isolated as a colorless oil (34 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (br, 1H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.04 (dd, *J* = 8.8, 1.2 Hz, 2H), 4.18 – 4.11 (m, 4H), 3.71-3.65 (m, 1H), 2.11 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 146.8 (d, *J* = 6.8 Hz), 139.2 (d, *J* = 6.4 Hz), 135.3, 128.7, 127.6, 127.4, 121.5, 120.5 (d, *J* = 4.7 Hz), 63.3 (d, *J* = 5.6 Hz), 45.5, 24.2, 16.2 (d, *J* = 7.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 3.9. **HRMS** (ESI^+) calculated for $C_{17}H_{21}N_2O_4P$ $[M+H]^+$: m/z = 349.1312, m/z found 349.1310. **IR** ν_{max} (ATR)/cm^{-1} 3257, 3144, 2931, 1672, 1552, 1508, 1244, 1203, 1027, 917, 840, 700.

4-Acetylphenyl phenyl benzyl(methyl)phosphoramidate (**16h**)



Following General Procedure J using *N*-methyl-*N*-benzylphosphoramidofluoridate (28.0 mg, 0.10 mmol) and 4-hydroxyacetophenone (16.3 mg, 0.12 mmol) for 3 h, the title compound was isolated as a colorless oil (36 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.40 – 7.36 (m, 4H), 7.31 – 7.26 (m, 5H), 7.25 – 7.17 (m, 3H), 4.40 – 4.28 (m, 2H), 2.72 (d, *J* = 10.4 Hz, 3H), 2.62 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.9, 154.7 (d, *J* = 6.7 Hz), 150.6 (d, *J* = 6.7 Hz), 136.7 (d, *J* = 4.3 Hz), 133.9, 130.5, 129.9, 128.6, 128.2, 127.7, 125.3, 120.3 (d, *J* = 3.8 Hz), 120.2 (d, *J* = 3.4 Hz), 53.3 (d, *J* = 5.0 Hz), 33.3 (d, *J* = 3.7 Hz), 26.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 0.7. **HRMS** (ESI^+) calculated for $C_{22}H_{22}NO_4P$ $[M+H]^+$: m/z = 396.1359, m/z found 396.1359. **IR** ν_{max} (ATR)/cm^{-1} 2916, 1683, 1597, 1489, 1265, 1192, 1162, 1012, 914, 843, 690, 593.

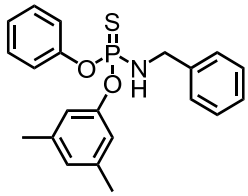
Allyl 4-(((benzylamino)(ethoxy)phosphoryl)oxy)benzoate (**16i**)



Following General Procedure J using ethyl benzylphosphoramidofluoridate (21.7 mg, 0.10 mmol) and allyl 4-hydroxybenzoate (21.4 mg, 0.12 mmol) for 1 h, the title compound was isolated as a colorless oil (34 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.24 (m, 7H), 6.09 – 5.99 (m, 1H), 5.41 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.29 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.82 (d, *J* = 5.6 Hz, 1H),

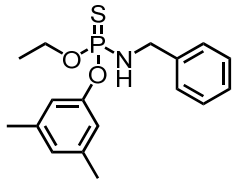
4.23 – 4.12 (m, 4H), 3.60 – 3.53 (br, 1H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 155.0 (d, *J* = 6.4 Hz), 139.1 (d, *J* = 6.4 Hz), 132.3, 131.6, 128.7, 127.6, 127.5, 126.6, 120.1 (d, *J* = 5.1 Hz), 118.4, 65.7, 63.5 (d, *J* = 5.4 Hz), 45.6, 16.2 (d, *J* = 6.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 3.3. **HRMS** (ESI$^+$) calculated for $C_{19}H_{22}NO_5P$ [M+H]$^+$: m/z = 376.1308, m/z found 376.1302. **IR** ν_{max} (ATR)/cm^{-1} 3216, 2932, 1718, 1604, 1455, 1266, 1095, 1038, 917, 770, 696.

3,5-Dimethylphenyl phenyl benzylphosphoramidatothioate (**16j**)



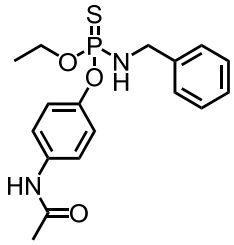
Following General Procedure J using Phenyl benzylthiophosphoramidofluoridothioate (28.10 mg, 0.10 mmol) and 3,5-dimethylphenol (14.7 mg, 0.12 mmol), the title compound was isolated as a colorless oil (35 mg, 92%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 10H), 6.87 – 6.84 (m, 3H), 4.44 – 4.39 (m, 2H), 3.70 (br, 1H), 2.31 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.2 (d, *J* = 7.6 Hz), 150.9 (d, *J* = 7.3 Hz), 139.4 (d, *J* = 1.7 Hz), 139.3 (d, *J* = 1.5 Hz), 138.7 (d, *J* = 7.2 Hz), 129.6, 128.8, 127.7, 127.0 (dd, *J* = 5.5, 1.8 Hz), 125.2 (d, *J* = 1.8 Hz), 121.3 (d, *J* = 4.8 Hz), 118.8 (dd, *J* = 5.9, 5.1 Hz), 46.5 (d, *J* = 2.8 Hz), 21.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 62.7. **HRMS** (ESI$^+$) calculated for $C_{21}H_{22}NO_2PS$ [M+H]$^+$: m/z = 384.1182, m/z found 384.1181. **IR** ν_{max} (ATR)/cm^{-1} 2921, 1590, 1289, 1202, 1134, 1026, 919, 851, 773, 686.

3,5-Dimethylphenyl ethyl benzylphosphoramidatothioate (**16k**)



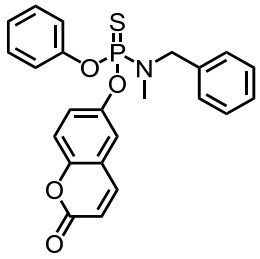
Following General Procedure J using Phenyl benzylthiophosphoramidofluoridothioate (21.70 mg, 0.10 mmol) and 3,5-dimethylphenol (14.7 mg, 0.12 mmol), the title compound was isolated as a colorless oil (31 mg, 92%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 6.83 (s, 2H), 6.81 (s, 1H), 4.30 – 4.25 (m, 2H), 4.24 – 4.11 (m, 2H), 2.30 (s, 6H), 1.35 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0 (d, *J* = 7.5 Hz), 139.3, 139.1 (d, *J* = 6.9 Hz), 128.7, 127.7, 127.6, 126.8 (d, *J* = 1.7 Hz), 118.8 (d, *J* = 2.9 Hz), 63.7 (d, *J* = 5.6 Hz), 46.1 (d, *J* = 2.4 Hz), 21.4, 16.0 (d, *J* = 8.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 67.2. **HRMS** (ESI$^+$) calculated for $C_{17}H_{22}NO_2PS$ [M+H]$^+$: m/z = 336.1186, m/z found 336.1182. **IR** ν_{max} (ATR)/cm^{-1} 2921, 1615, 1592, 1292, 1141, 1023, 954, 850, 827, 697.

4-Acetamidophenyl ethyl benzylphosphoramidothioate (**16l**)



Following General Procedure J using Phenyl benzylthiophosphoramidofluoridothioate (21.70 mg, 0.10 mmol) and 4-acetaminophenol (18.1 mg, 0.12 mmol), the title compound was isolated as a colorless oil (32 mg, 89%). **m.p.** 132.5 – 135.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.35 – 7.25 (m, 5H), 7.14 (dd, *J* = 8.8, 2.2 Hz, 2H), 4.26 – 4.22 (m, 2H), 4.21 – 4.07 (m, 2H), 2.14 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 147.4 (d, *J* = 7.6 Hz), 138.9 (d, *J* = 6.9 Hz), 135.0 (d, *J* = 2.0 Hz), 128.8, 127.7, 121.6 (d, *J* = 4.8 Hz), 121.1, 63.8 (d, *J* = 5.1 Hz), 46.1 (d, *J* = 2.5 Hz), 24.6, 16.0 (d, *J* = 8.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 67.7. **HRMS** (ESI^+) calculated for $C_{17}H_{21}N_2O_3PS$ $[M+H]^+$: m/z = 365.1083, m/z found 365.1085. **IR** ν_{max} (ATR)/cm^{-1} 3065, 1661, 1503, 1207, 1035, 905, 847, 804, 746, 697, 601.

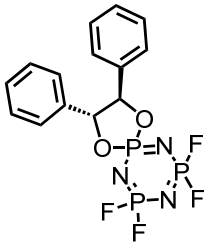
2*H*-Chromen-2-one-6-hydroxyl phenyl benzylphosphoramidothioate (**16m**)



Following General Procedure J using Phenyl *N*-methyl-*N*-benzylthiophosphoramidofluoridothioate (29.50 mg, 0.10 mmol) and 6-hydroxy-2H-chromen-2-one (19.5 mg, 0.12 mmol), the title compound was isolated as a colorless oil (38 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 9.6 Hz, 1H), 7.39 – 7.26 (m, 10H), 7.25 – 7.20 (m, 3H), 6.46 (d, *J* = 9.6 Hz, 1H), 4.62 – 4.44 (m, 2H), 2.90 (d, *J* = 10.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 151.2, 150.9, 147.2 (d, *J* = 7.3 Hz), 143.0, 137.1 (d, *J* = 4.6 Hz), 129.8, 128.7, 128.5, 127.9, 125.5 (d, *J* = 1.7 Hz), 125.4 (d, *J* = 4.6 Hz), 121.4 (d, *J* = 4.9 Hz), 119.9 (d, *J* = 4.8 Hz), 119.4, 118.0, 117.6, 54.5 (d, *J* = 7.1 Hz), 34.0 (d, *J* = 2.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 69.1; **HRMS** (ESI^+) calculated for $C_{23}H_{20}NO_4PS$ $[M+H]^+$: m/z = 438.0923, m/z found 438.0926. **IR** ν_{max} (ATR)/cm^{-1} 2913, 1727, 1567, 1485, 1436, 1155, 1097, 914, 819, 733, 688.

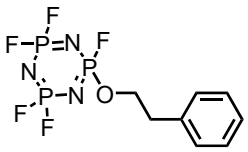
Phosphorus(V) Fluoride Exchange Reactions with Hexafluorophosphazene (HFP)

(±)-Hydrobenzoinotetrafluorocyclotriphosphazene (**17a**)



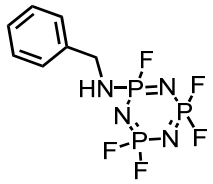
2,2,4,4,6,6-Hexafluoro-1,3,5,2λ^5,4λ^5,6λ^5-triazatriphosphinine (hexafluorocyclotriphosphazene, **HFP**, 107 mg, 0.43 mmol, 1.00 equiv), (±)-hydrobenzoin (92.1 mg, 0.43 mmol, 1.00 equiv), acetonitrile (MeCN, 4 mL), and triethylamine (120 µL, 0.86 mmol, 2.00 equiv) were sequentially introduced into a 12 mL vial. The resulting mixture was stirred at room temperature for 16 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate = 10:1→2:1) to afford the title compound as a colorless oil (126 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 6H), 7.28 – 7.24 (m, 4H), 5.39 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.8 (d, *J* = 10.0 Hz), 3129.9, 129.1, 126.9, 87.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.1 – 29.8 (m, 1.0 P), 17.7 – 15.9 (m, 0.5 P), 12.2 – 10.1 (m, 1.0 P), 6.4 – 4.6 (m, 0.5 P), **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.0 – -67.4 (m, 2.0 F), -69.5 – -69.9 (m, 2.0 F). **HRMS** (ESI$^+$) calculated for $C_{14}H_{12}F_4N_3O_2P_3$ $[M+H]^+$: m/z = 424.0151, m/z found 424.0155. **IR** ν_{max} (ATR)/cm^{-1} 2929, 1257, 1023, 923, 897, 825, 696, 637, 524, 490.

2-Phenylethanoxypentafluorocyclotriphosphazene (**17b**)



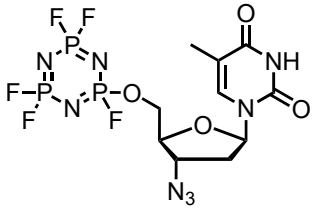
HFP (125 mg, 0.5 mmol, 1.00 equiv), 2-phenylethanol (60.2 µL, 0.5 mmol, 1.00 equiv), acetonitrile (MeCN, 5 mL), and triethylamine (69.5 µL, 0.5 mmol, 1.00 equiv) were sequentially introduced into a 12 mL vial. The resulting mixture was stirred at room temperature for 1 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate = 10:1→2:1) to afford the title compound as a yellow oil (110 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 2H), 4.30 (t, *J* = 8.0 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0, 129.1, 128.9, 127.3, 69.93 (d, *J* = 6.9 Hz), 36.4 (d, *J* = 7.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.5 – 14.5 (m, 1.0 P), 10.8 – 8.6 (m, 1.5 P), 4.9 – 3.0 (m, 0.5 P). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.0 – -63.5 (m, 0.5 F), -65.4 – -66.1 (m, 0.5 F), -67.1 – -68.3 (m, 0.5 F), -69.4 – -70.8 (m, 0.5 F). **HRMS** (ESI$^+$) calculated for $C_8H_{10}F_4N_3O_2P_3$ $[M-F+O]^-$: m/z = 347.9849, m/z found 347.9860. *Note***:** Due to the presence of the 5F in the ^{19}F NMR, we suspect exchange of F^- with O^- occurs during ionization. **IR** ν_{max} (ATR)/cm^{-1} 2929, 1264, 1070, 940, 836, 799, 781, 748, 698, 512.

N-Benzylaminopentafluorocyclotriphosphazene (**17c**)



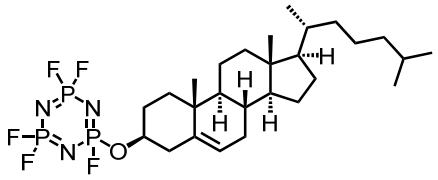
HFP (83 mg, 0.33 mmol, 1.00 equiv), benzylamine (36.4 µL, 0.33 mmol, 1.00 equiv), acetonitrile (MeCN, 3.5 mL), and triethylamine (46.4 µL, 0.33 mmol, 1.00 equiv) were sequentially introduced into a 12 mL vial. The resulting mixture was stirred at room temperature for 16 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate = 10:1→2:1) to afford the title compound as a yellow oil (87 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 5H), 4.25 – 4.20 (m, 2H), 3.34 (br, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.8 (d, *J* = 7.3 Hz), 129.0, 128.2, 127.6, 44.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.6 – 23.1 (m, 0.5 P), 19.0 – 17.4 (m, 0.5 P), 15.6 – 13.8 (m, 0.5 P), 9.9 – 8.0 (m, 1.0 P), 4.2 – 2.3 (m, 0.5 P), **^{19}F NMR** (376 MHz, $CDCl_3$) δ -53.0 – -53.3 (m, 0.5 F), -55.4 – -55.7 (m, 0.5 F), -66.9 – -66.2 (m, 1.0 F), -69.4 – -70.7 (m, 1.0 F). **HRMS** (ESI^+) calculated for $C_7H_8F_5N_4P_3$ [M-H]$^-$: m/z = 334.9809, m/z found 334.9816. **IR** ν_{max} (ATR)/cm^{-1} 2927, 1259, 1076, 936, 824, 733, 698, 611, 462.

1-((2*R*,4*S*,5*S*)-4-Azido-5-(((2,4,4,6,6-pentafluoro-1,3,5,2λ^5,4λ^5,6λ^5-triazatriphosphinin-2-yl)oxy)methyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (**17d**)



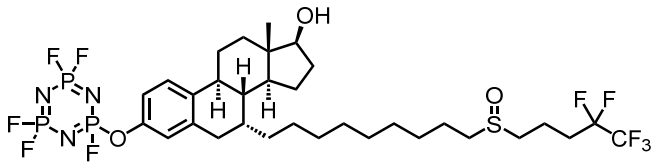
HFP (2.49 g, 10.0 mmol, 1.00 equiv), 1-((2*R*,4*S*,5*S*)-4-azido-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (azidothymidine, AZT, 2.67 g, 10.0 mmol, 1.00 equiv), acetonitrile (MeCN, 50 mL), and triethylamine (1.01 g, 10.0 mmol, 1.00 equiv) were sequentially introduced into a 100 mL flask. The resulting mixture was stirred at room temperature for 0.5 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate = 3:1→1:3) to afford the title compound as a light yellow solid (3.33 g, 6.7 mmol, 67% yield). **m.p.** 36 – 38 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.04 (br s, 1H), 7.17 (d, *J* = 1.2 Hz, 1H), 6.08 (t, *J* = 6.4 Hz, 1H), 4.47 – 4.32 (m, 3H), 4.04 – 4.00 (m, 1H), 2.48 (t, *J* = 6.8 Hz, 2H), 1.90 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 150.5, 136.1, 117.9, 86.3, 81.9 (d, *J* = 7.6 Hz), 67.9 (d, *J* = 5.1 Hz), 59.8, 37.3, 12.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.7 – 14.5 (m, 1.0 P), 12.2 – 8.9 (m, 1.5 P), 4.9 – 3.0 (m, 0.5 P). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.5 – -63.8 (m, 0.5 F), -66.0 – -66.2 (m, 0.5 F), -66.7 – -67.4 (m, 1.0 F), -68.0 – -68.6 (m, 1.0 F), -69.3 – -70.0 (s, 1.0 F), -70.5 – -71.0 (s, 1.0 F). **HRMS** (ESI^+) calculated for $C_{10}H_{12}F_5N_8O_4P_3$ [M+H]$^+$: m/z = 497.0188, m/z found 497.0180. **IR** ν_{max} (ATR)/cm^{-1} 3216, 2932, 1718, 1604, 1455, 1266, 1095, 1038, 917, 770, 696.

Cholesteroloxypentafluorocyclotriphosphazene (**17e**)



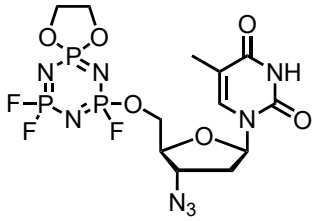
HFP (67 mg, 0.27 mmol, 1.00 equiv), cholesterol (104 mg, 0.27 mmol, 1.00 equiv), CH_2Cl_2 (2.5 mL), and triethylamine (37.4 µL, 0.33 mmol, 1.00 equiv) were sequentially introduced into a 12 mL vial. The resulting mixture was stirred at room temperature for 16 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate = 10:1→2:1) to afford the title compound as a yellow oil (105 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.44 – 5.32 (m, 1H), 4.37 – 4.07 (m, 1H), 2.57 – 2.40 (m, 2H), 2.05 – 1.95 (m, 3H), 1.91 – 1.80 (m, 2H), 1.79 – 1.65 (m, 1H), 1.64 – 1.43 (m, 6H), 1.41 – 1.25 (m, 4H), 1.24 – 1.04 (m, 7H), 1.03 – 0.97 (m, 5H), 0.96 – 0.93 (m, 1H), 0.92 (d, *J* = 6.4Hz, 3H), 0.87 (dd, *J* = 6.4, 2.0 Hz, 6H), 0.68 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 124.1, 81.9 (d, *J* = 6.4 Hz), 56.8, 56.3, 50.1, 42.5, 42.5, 39.8, 39.7, 36.9, 36.5, 36.3, 35.9, 32.0, 32.0, 29.4 (d, *J* = 4.5 Hz), 28.5, 28.4, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4 (d, *J* = 5.7 Hz), 18.9, 12.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.4 – 13.8 (m, 1.0 P), 10.6 – 6.5 (m, 1.5 P), 4.91 – 2.95 (m, 0.5 P); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.4 – -60.9 (m, 0.5 F), -62.4 – -63.3 (m, 0.5 F), -66.9 – -68.2 (m, 2.0 F), -69.4 – -70.9 (m, 2.0 F). **HRMS** (ESI^+) calculated for $C_{27}H_{46}F_4N_3O_2P_3$ $[M-H]^-$: m/z = 613.2667, m/z found 612.2676. *Note***:** Due to the presence of 5F in the ^{19}F NMR, we suspect exchange of F^- with O^- occurs during ionization. **IR** ν_{max} (ATR)/cm^{-1} 2940, 1270, 1252, 1021, 1004, 942, 920, 843, 821, 617.

Fulvestrantoxypentafluorocyclotriphosphazene (**17f**)



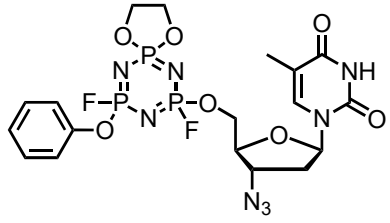
HFP (12.4 mg, 0.05 mmol, 1.00 equiv), fulvestrant (30.5 mg, 0.05 mmol, 1.00 equiv), ACN (1.0 mL), HMDS (10.4 µL, 0.05 mmol, 1.00 equiv), and DMAP (5.2 mg, 0.01 mmol, 0.20 equiv) were sequentially introduced into a 6 mL vial. The resulting mixture was stirred at room temperature for 3 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate = 5:1→1:1) to afford the title compound as a colorless oil (34 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 6.96 – 6.84 (m, 2H), 3.77 – 3.63 (m, 1H), 2.91 – 2.59 (m, 1H), 2.79 – 2.59 (m, 4H), 2.35 – 2.08 (m, 6H), 1.98 – 1.83 (m, 2H), 1.64 – 1.40 (m, 11H), 1.39 – 1.13 (m, 8H), 1.12 – 0.92 (m, 8H), 0.82 – 0.71 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.3, 138.2, 127.7, 121.2, 117.7, 117.5, 81.9, 52.7, 51.0, 16.5, 43.3, 41.7, 38.3, 34.6, 33.0, 31.9, 30.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.8, 27.1, 22.7, 22.6, 22.5, 14.1, 11.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.4 – 15.3 (m, 0.5 P), 12.5 – 9.3 (m, 1.5 P), 7.4 – 4.0 (m, 0.5 P); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.8 – -66.1 (m, 1.0 F), -67.4 – -68.5 (m, 2.0 F), -69.8 – -71.1 (m, 2.0 F), -85.5 (s, 3.0 F), -118.1 (s, 2.0 F). **HRMS** (ESI^+) calculated for $C_{32}H_{46}F_{10}N_3O_3P_3S$ $[M+H]^+$: m/z = 836.2386, m/z found 836.2387. **IR** ν_{max} (ATR)/cm^{-1} 2927, 2856, 1277, 1195, 1007, 962, 843, 745, 720, 513.

1-((2*R*,4*S*,5*S*)-4-Azido-5-(((7,9,9-trifluoro-1,4-dioxa-6,8,10-triaza-5λ^5,7λ^5,9λ^5-triphosphaspiro[4.5]deca-5,7,9-trien-7-yl)oxy)methyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (**17g**)



Compound **17d** (2.48 g, 5.0 mmol, 1.00 equiv), ethane-1,2-diol (0.31 g, 5.0 mmol, 1.00 equiv), acetonitrile (MeCN, 25 mL), and triethylamine (Et_3N, 1.01 g, 10.0 mmol, 2.00 equiv) were sequentially introduced into a 50 mL flask. The resulting mixture was stirred at room temperature for 0.5 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate = 3:1→1:3) to afford the title compound as a white solid (2.13 g, 4.1 mmol, 82% yield). **m.p.** 45 – 47 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.41 (d, *J* = 10.4 Hz, 1H), 7.29 (dd, *J* = 6.4, 1.2 Hz, 1H), 6.22 – 6.16 (m, 1H), 4.49 – 4.40 (m, 4H), 4.39 – 4.26 (m, 3H), 4.04 – 4.01 (m, 1H), 2.50 – 2.34 (m, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.0 (d, *J* = 6.5 Hz), 150.4, 135.4 (d, *J* = 28.8 Hz), 111.7 (d, *J* = 4.3 Hz), 85.5, 85.1, 82.1 (d, *J* = 8.3 Hz), 82.0 (d, *J* = 8.4 Hz), 66.9 (d, *J* = 4.7 Hz), 66.7, 66.6 (d, *J* = 4.9 Hz), 60.0, 59.9, 37.8, 37.7, 12.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.3 – 33.7 (m, 1.0 P), 19.6 – 16.2 (m, 1.8 P), 14.1 – 10.2 (m, 1.0 P), 6.8 – 5.1 (m, 0.2 P). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.8 – -64.0 (m, 0.5 F), -66.2 – -66.5 (m, 0.5 F), -66.7 – -67.1 (m, 0.5 F), -67.4 – -68.0 (s, 0.5 F), -69.2 – -69.6 (s, 0.5 F), -69.8 – -70.4 (s, 0.5 F). **HRMS** (ESI^+) calculated for $C_{12}H_{16}F_3N_8O_6P_3$ $[M+H]^+$: m/z = 519.0431, m/z found 519.0424. **IR** ν_{max} (ATR)/cm^{-1} 3216, 2932, 1718, 1604, 1455, 1266, 1095, 1038, 917, 770, 696.

1-((2*R*,4*S*,5*S*)-4-Azido-5-(((7,9-difluoro-9-phenoxy-1,4-dioxa-6,8,10-triaza-5λ^5,7λ^5,9λ^5-triphosphaspiro[4.5]deca-5,7,9-trien-7-yl)oxy)methyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (**17h**)



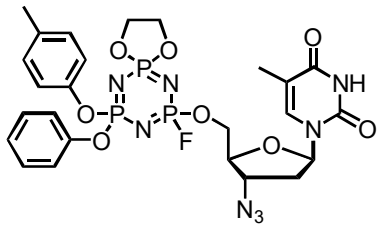
Compound **17g** (26 mg, 0.05 mmol, 1.00 equiv), phenol (4.7 mg, 0.05 mmol, 1.00 equiv), HMDS (10.4 μL, 0.05 mmol, 1.00 equiv) in acetonitrile (0.5 mL), and BTMG (2 μL, 0.01 mmol, 20 mol%) were sequentially introduced into a 5 mL vial. The resulting mixture was stirred at room temperature for 0.5 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate = 3:1→1:3) to afford the title compound as a white solid (28 mg, 89% yield). **m.p.** 52 – 54 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.38 (br, 1H), 7.37 – 7.27 (m, 3H), 7.24 – 7.18 (m, 3H), 6.25 – 6.20 (m, 1H), 4.48 – 4.32 (m, 5H), 4.29 – 4.13 (m, 1H), 4.07 – 3.76 (m, 2H), 2.46 – 2.12 (m, 2H), 1.89 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.0, 163.9, 150.5, 149.8, 149.6, 135.2 (d, *J* = 12.0 Hz), 135.0 (d, *J* = 5.4 Hz), 130.0 (d, *J* = 7.7 Hz), 126.2 (d, *J* = 7.7 Hz), 120.9 (d, *J* = 4.4 Hz), 120.8 (d, *J* = 4.6 Hz), 120.7 (d, *J* = 4.7 Hz), 111.8 (d, *J* = 4.0 Hz), 85.0, 84.9, 84.7 (d, *J* = 2.3 Hz), 82.0, 66.6 (d, *J* = 4.8 Hz), 66.5, 66.2 (d, *J* = 4.9 Hz), 60.3, 60.1 (d, *J* = 2.6 Hz), 60.0, 37.8 (d, *J* = 4.9 Hz), 37.7, 12.5, 12.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.4–33.8 (m, 1.0 P), 20.2–18.5 (m, 0.5 P),

15.0–13.1 (m, 1.0 P), 9.6–8.0 (m, 0.5 P), **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.6 – -64.5 (m, 1.0 F), -66.0 – -66.9 (m, 1.0 F). **HRMS** (ESI^+) calculated for $C_{18}H_{21}F_2N_8O_7P_3$ $[M+H]^+$: m/z = 593.0787, m/z found 593.0778. **IR** ν_{max} (ATR)/cm^{-1} 3216, 2932, 1718, 1604, 1455, 1266, 1095, 1038, 917, 770, 696.

*One-pot synthesis of Compound **17h**:*

HFP (1.00 g, 4.0 mmol, 1.00 equiv), 1-((2*R*,4*S*,5*S*)-4-azido-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (1.07 g, 4.0 mmol, 1.00 equiv), acetonitrile (20 mL), and triethylamine (0.41 g, 4.0 mmol, 1.00 equiv) were sequentially introduced into a 50 mL flask, and the resulting mixture was stirred at room temperature for 0.5 h. Next, ethane-1,2-diol (0.25 g, 4.0 mmol, 1.00 equiv) and triethylamine (0.81 g, 8.0 mmol, 2.00 equiv) were sequentially introduced into the flask, and the resulting mixture was stirred at room temperature for 0.5 h. Finally, *tert*-butyldimethyl(phenoxy)silane (0.84 g, 4.0 mmol, 1.00 equiv), acetonitrile (20 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.06 g, 0.4 mmol, 10 mol%) were sequentially introduced into the flask. The resulting mixture was stirred at room temperature for 6 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexanes/ethyl acetate = 3:1→1:3) to afford the title compound as a white solid (1.78 g, 3.0 mmol, 75% yield).

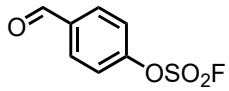
1-((2*R*,4*S*,5*S*)-4-Azido-5-(((7,9-difluoro-9-phenoxy-9-*p*-cresoxy-1,4-dioxa-6,8,10-triaza-5λ^5,7λ^5,9λ^5-triphosphaspiro[4.5]deca-5,7,9-trien-7-yl)oxy)methyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (**17i**)



Compound **17h** (63 mg, 0.11 mmol, 1.00 equiv), *p*-cresol (11.5 mg, 0.11 mmol, 1.00 equiv), Cs_2CO_3 (69.1 mg, 0.22 mmol, 2.00 equiv), acetonitrile (2 mL) were sequentially introduced into a 50 mL flask. The resulting mixture was stirred at room temperature for 16 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate = 3:1→1:3) to afford the title compound as a white solid (56 mg, 78% yield). **m.p.** 61.5 – 63.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.21 (br, 1H), 7.56 – 7.25 (m, 3H), 7.25 – 6.72 (m, 7H), 6.30 – 6.20 (m, 1H), 4.47 – 4.24 (m, 5H), 4.19 – 4.04 (m, 1H), 3.99 – 3.60 (m, 2H), 2.47 – 2.46 (m, 4H), 2.25 – 2.03 (m, 1H), 1.90 – 1.85 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.9, 150.4, 135.2, 135.0, 130.4, 130.2, 129.8, 129.7, 125.6, 120.9, 120.8, 120.7, 111.7, 84.6, 82.2, 66.3, 60.6, 60.0, 37.9, 37.7, 20.9 12.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.6 – 33.9 (m, 1.0 P), 20.5 – 18.6 (m, 0.5 P), 16.0 – 13.6 (m, 1.0 P), 11.3 – 8.2 (m, 0.5 P), **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.1 – -64.5 (m, 0.5 F), -66.2 – -66.9 (m, 0.5 F). **HRMS** (ESI^+) calculated for $C_{25}H_{28}FN_8O_8P_3$ $[M+H]^+$: m/z = 681.1299, m/z found 681.1299. **IR** ν_{max} (ATR)/cm^{-1} 2925, 2106, 1507, 1246, 1183, 1042, 944, 913, 821, 774, 690.

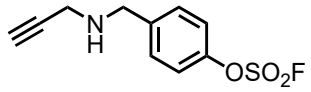
Orthogonality of PFEx, SuFEx, and CuAAC Catalysis

4-Formylphenyl fluorosulfate (**S8**)



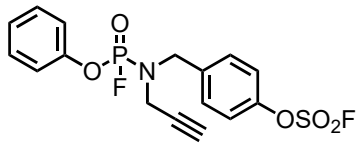
To a solution of 4-hydroxybenzaldehyde (2.44 g, 20.00 mmol) in CH_2Cl_2 (50 mL) was added Et_3N (3.4 mL, 24.00 mmol). The resulting reaction was stirred at room temperature under an atmosphere of SO_2F_2 gas. Upon completion, as determined by TLC (1 h), the reaction was concentrated *in vacuo*. The crude was purified by flash column chromatography on silica gel (ethyl acetate-hexane, 1:10 v/v) to afford the title compound as a colorless oil (3.2 g, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.2, 153.6, 136.2, 132.0, 121.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 38.84. **IR** ν_{max} (ATR)/cm^{-1} 2837, 1702, 1449, 1232, 1141, 910, 802, 581, 539, 494.

4-((Prop-2-yn-1-ylamino)methyl)phenyl fluorosulfate (**S9**)



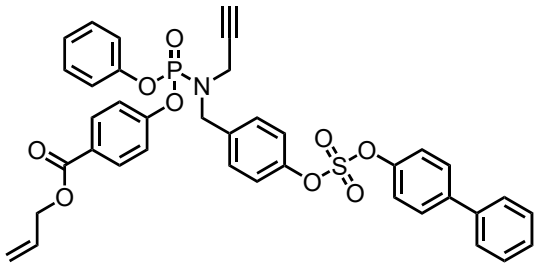
Following General Procedure B using 4-formylphenyl fluorosulfate (2.04 g, 10 mmol) and propargylamine (640 µL, 10 mmol), the title compound was isolated as a colorless oil (2.1 g, 88% yield) after purification by flash column chromatography on silica gel (ethyl acetate-hexane, 1:3 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 2H), 3.42 (d, *J* = 2.4 Hz, 2H), 2.27 (d, *J* = 2.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 140.5, 130.3, 121.0, 51.3, 37.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 37.1. **HRMS** (ESI^+) calculated for $C_{10}H_{10}FNO_3S$ $[M+H]^+$: m/z = 244.0438, m/z found 244.0439. **IR** ν_{max} (ATR)/cm^{-1} 3301, 1501, 1445, 1231, 1138, 910, 799, 637, 683, 541.

4-(((Fluoro(phenoxy)phosphoryl)(prop-2-yn-1-yl)amino)methyl)phenyl sulfurofluoridate (**18**)



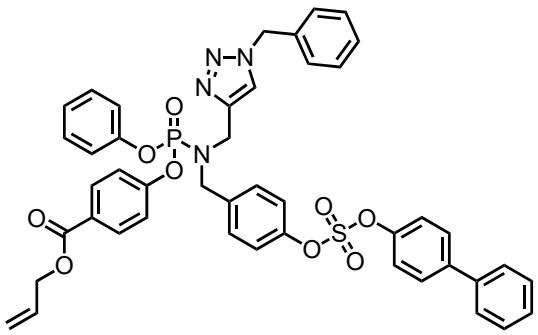
Following General Procedure G using phenol (470 mg, 5.00 mmol) and 4-((prop-2-yn-1-ylamino)methyl)phenyl fluorosulfate (1.22 g, 5.00 mmol), the title compound was isolated as a colorless oil (597 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 4H), 7.34 – 7.26 (m, 5H), 4.57 – 4.45 (m, 2H), 3.91 – 3.73 (m, 2H), 2.35 (d, *J* = 2.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7 (d, *J* = 6.2 Hz), 136.4 (d, *J* = 4.6 Hz), 130.6, 130.2, 126.1, 121.4, 120.1 (d, *J* = 5.1 Hz), 74.1, 48.4 (d, *J* = 5.1 Hz), 35.1 (d, *J* = 6.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ -2.1 (d, *J* = 982.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ 37.49 (s, 1.0 F), -73.87 (d, *J* = 982.5 Hz, 1.0 F). **HRMS** (ESI^+) calculated for $C_{16}H_{14}F_2NO_5PS$ $[M+H]^+$: m/z = 402.0371, m/z found 402.0370. **IR** ν_{max} (ATR)/cm^{-1} 3302, 1503, 1448, 1293, 1233, 1201, 1120, 911, 759, 688, 522.

Allyl 4-((((4-(((([1,1'-biphenyl]-4-yloxy)sulfonyl)oxy)benzyl)(prop-2-yn-1-yl)amino)(phenoxy)phosphoryl)-oxy)benzoate (**20**)



To a solution of compound **18** (40.10 mg, 0.10 mmol, 1.00 equiv) in acetonitrile (0.5 mL), was added 4-phenylphenol (17.0 mg, 0.10 mmol, 1.00 equiv), HMDS (21 µL, 0.10 mmol, 1.00 equiv), and BTMG (4 µL, 0.02 mmol, 20%). The resulting reaction was stirred at room temperature and monitored by ^{19}F NMR and TLC. After 0.5 h, 10 mL ethyl acetate was added, and the organic phase was washed with sodium carbonate (aqueous, saturated), brine, dried over sodium sulfate, and concentrated *in vacuo*. The crude was dissolved in acetonitrile (0.25 mL). Allyl 4-hydroxybenzoate (21 mg, 0.12 mmol), HMDS (25 µL, 0.12 mmol) and TBD (2.80 mg, 0.02 mmol) were then added. The reaction was stirred at room temperature and monitored by ^{31}P NMR, ^{19}F NMR, and TLC. After 2 hours, the reaction was diluted with 10 mL ethyl acetate, and the organic phase was washed with sodium carbonate (aqueous, saturated), brine, dried over sodium sulfate, and concentrated *in vacuo*. The crude product was purified by silica column (ethyl acetate-hexane = 1:3 v/v) to afford the title compound as a colorless oil (61 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.57 – 7.55 (m, 2H), 7.48 – 7.43 (m, 2H), 7.40 – 7.31 (m, 9H), 7.30 – 7.25 (m, 5H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.08 – 5.99 (m, 1H), 5.41 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.29 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.82 (dd, *J* = 5.6, 1.2 Hz, 2H), 4.56 – 4.44 (m, 2H), 3.86 (d, *J* = 12.0 Hz, 2H), 2.26 – 2.24 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 154.4, 150.5 (d, *J* = 8.0 Hz), 150.0 (d, *J* = 22.2 Hz), 149.9, 141.1, 139.7, 135.7 (d, *J* = 4.5 Hz), 132.3, 131.8, 130.4, 130.0, 129.1, 128.8, 128.0, 127.3, 121.4, 120.4 (d, *J* = 5.2 Hz), 120.3, 118.5, 78.0, 73.7, 65.8, 48.6, 35.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -1.3 (d, *J* = 982.5 Hz). **HRMS** (ESI^+) calculated for $C_{38}H_{32}NO_9PS$ $[M+H]^+$: m/z = 710.1608, m/z found 710.1595. **IR** ν_{max} (ATR)/cm^{-1} 3297, 1718, 1485, 1404, 1269, 1148, 1094, 877, 762, 690, 571.

Allyl 4-((((4-((([1,1'-biphenyl]-4-yloxy)sulfonyl)oxy)benzyl)((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-amino)(phenoxy)phosphoryl)oxy)benzoate (**21**)



To a solution of **20** (55.0 mg, 0.075 mmol, 1.00 equiv) in DMF (0.2 mL) was added benzyl azide (10.3 µL, 0.085 mmol, 1.10 equiv) and sodium ascorbate (5.9 mg, 0.03 mmol, 0.40 equiv), $CuSO_4 \cdot 5H_2O$ (1.9 mg, 8.5 µmol, 0.10 equiv) was added and the resulting reaction was stirred at room temperature. After completed (3 h), water (10 mL) was added and then extracted with ethyl acetate three times. The organic phases were combined, washed with brine, dried over sodium sulfate, and then concentrated *in vacuo.* The crude product was purified by silica column (ethyl acetate-hexane = 1:3 v/v) to afford the

title compound as a colorless oil (54 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.57 – 7.54 (m, 2H), 7.47 – 7.44 (m, 2H), 7.40 – 7.33 (m, 9H), 7.31 – 7.28 (m, 2H), 7.25 – 7.23 (m, 2H), 7.21 – 7.13 (m, 6H), 7.02 (s, 1H), 6.09 – 5.99 (m, 1H), 5.44 – 5.28 (m, 4H), 4.83 (d, *J* = 6.0 Hz, 2H), 4.45 – 4.28 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 154.4, 150.4, 150.0 149.9, 144.4, 141.0, 139.7, 136.2, 134.4, 132.2, 131.7, 130.7, 130.0, 129.9, 129.3, 129.1, 129.0, 128.9, 128.2, 128.0, 127.3, 125.5, 122.7, 121.5, 121.3, 120.3 (d, *J* = 5.2 Hz), 120.2 (d, *J* = 5.2 Hz), 118.6, 65.9, 54.3, 48.8, 40.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -0.3. **HRMS** (ESI^+) calculated for: $C_{45}H_{39}N_4O_9PS$ $[M+H]^+$: m/z = 843.2248, m/z found 843.2224. **IR** ν_{max} (ATR)/cm^{-1} 3068, 2929, 1717, 1603, 1485, 1268, 1192, 1148, 920, 877, 763, 691.

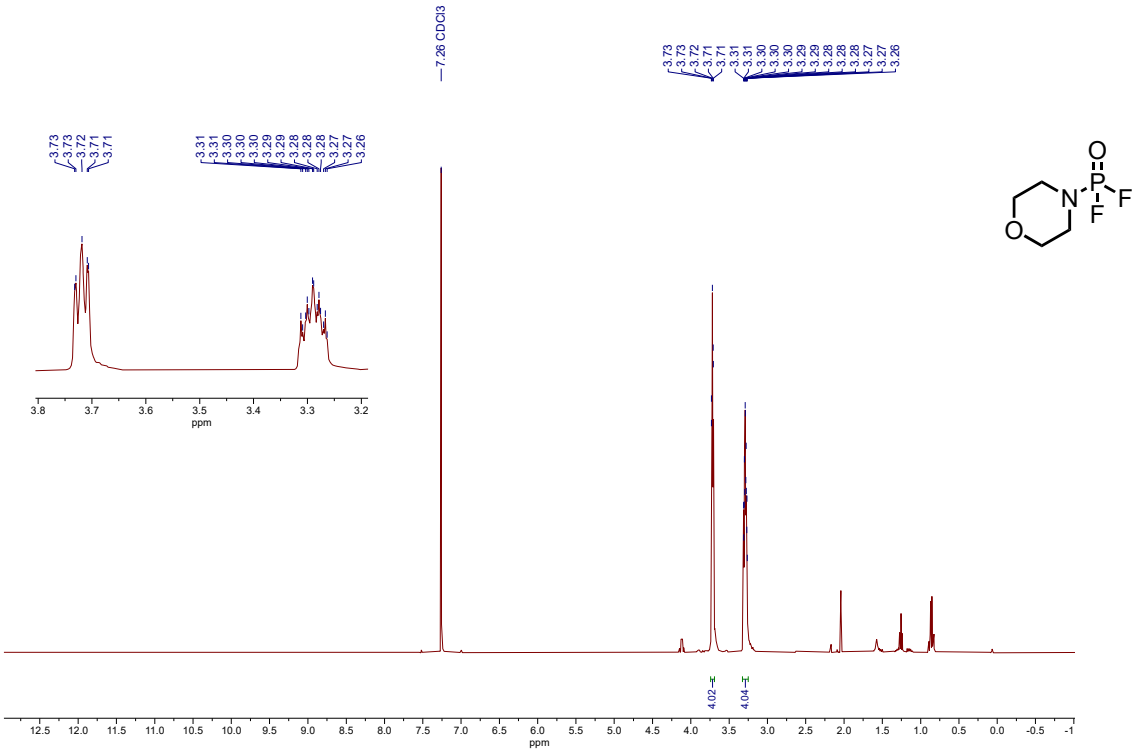
References

1. Timperley, C. (2014). Best Synthetic Methods: Organophosphorus (V) Chemistry (Newnes).

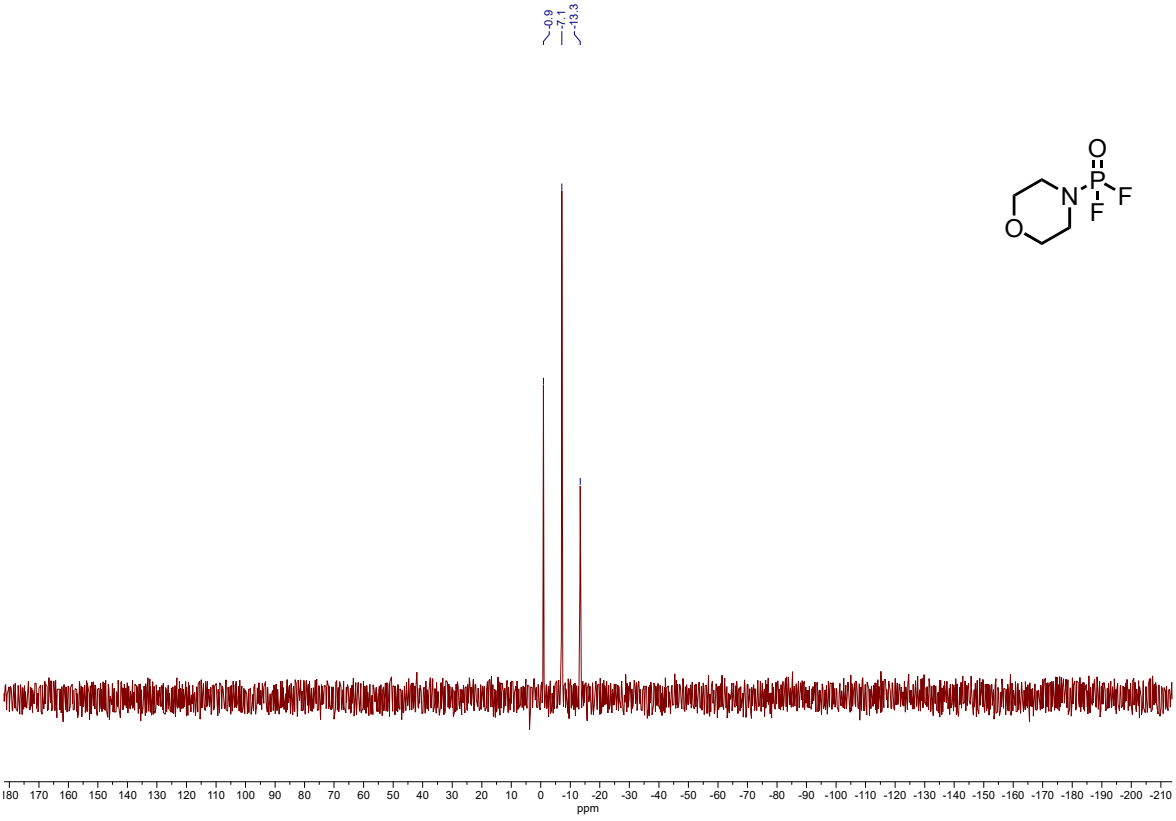
2. Flader, C., Liu, J. & Borch, R. F. (2000). Development of Novel Quinone Phosphorodiamidate Prodrugs Targeted to DT-Diaphorase. J. Med. Chem. *43*, 3157–3167.

Data S1: NMR Spectra

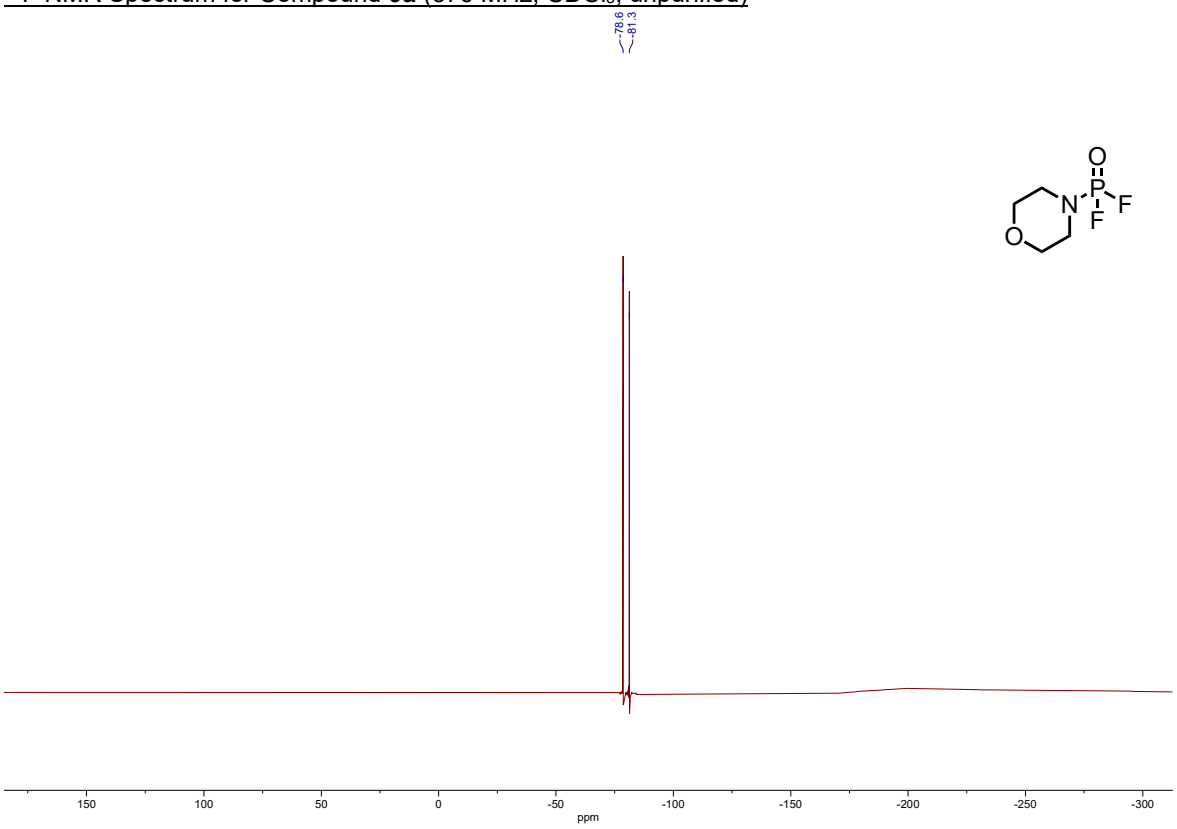
^{1}H NMR Spectrum for Compound **9a** (400 MHz, $CDCl_3$, unpurified)



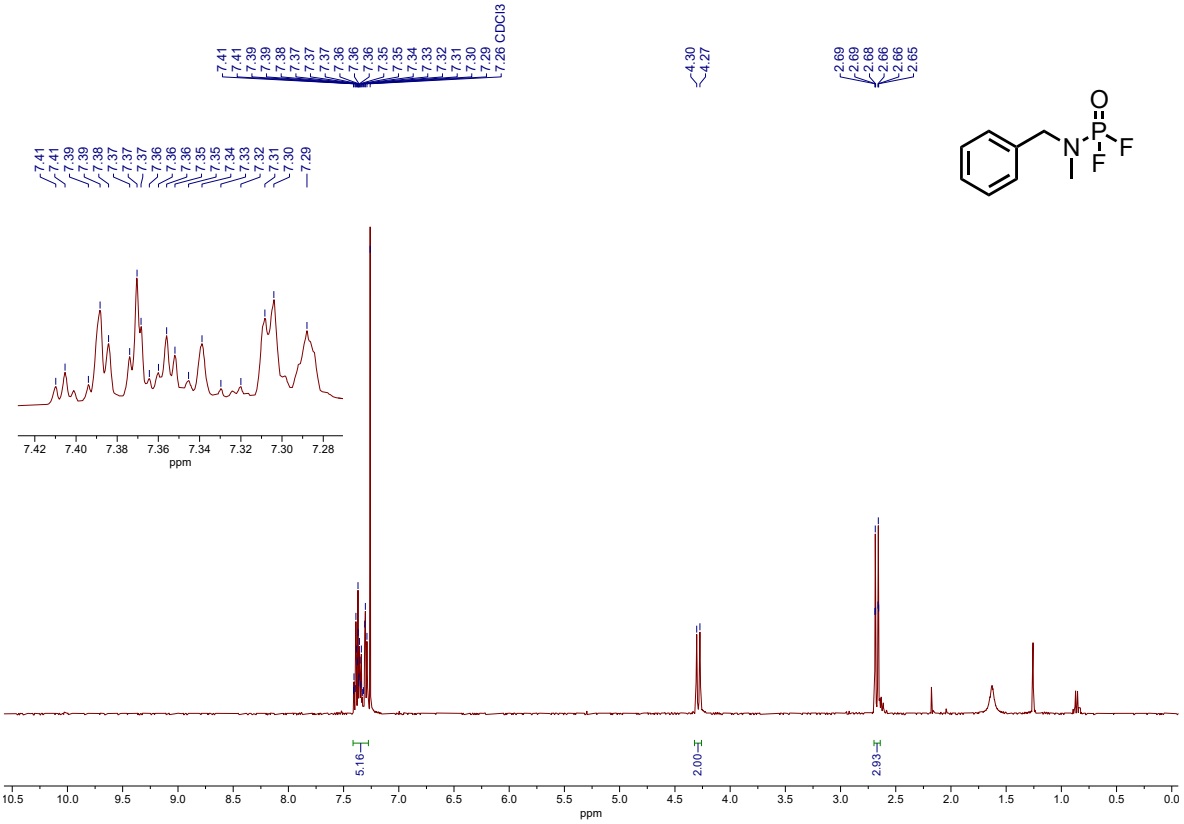
^{31}P NMR Spectrum for Compound **9a** (162 MHz, $CDCl_3$, unpurified)



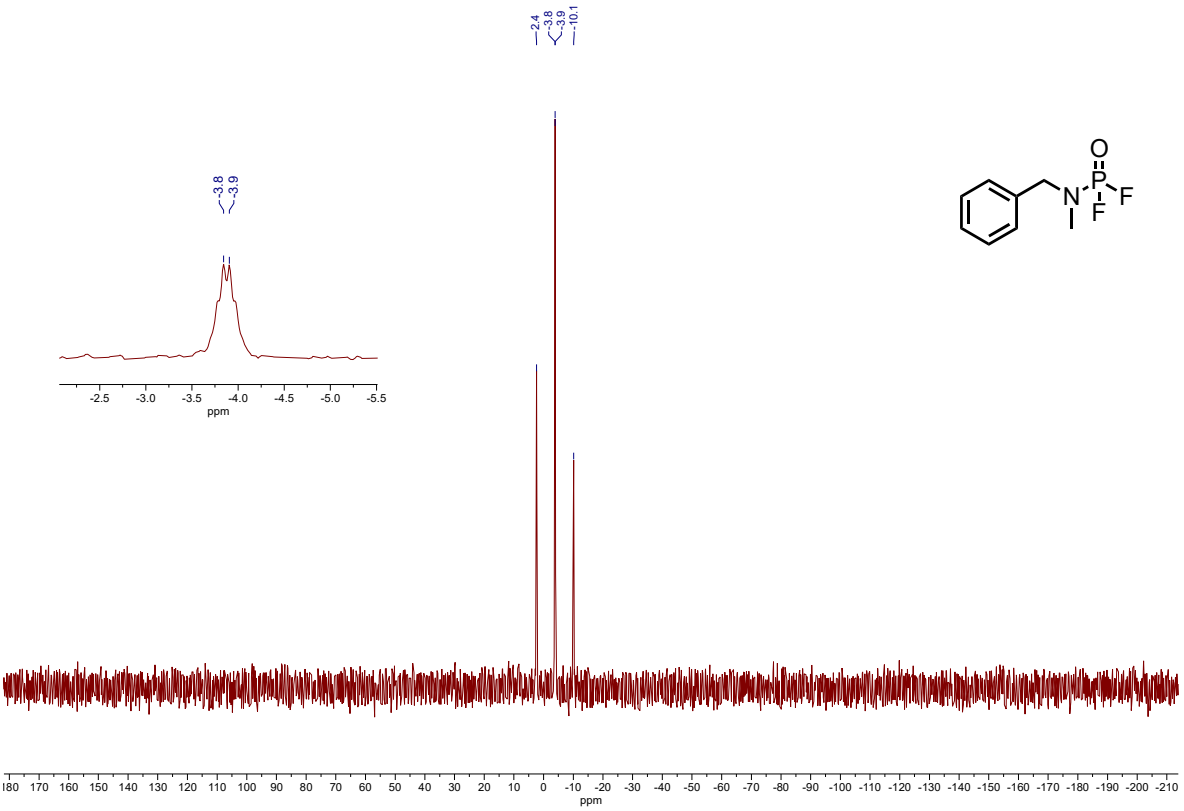
^{19}F NMR Spectrum for Compound **9a** (376 MHz, $CDCl_3$, unpurified)



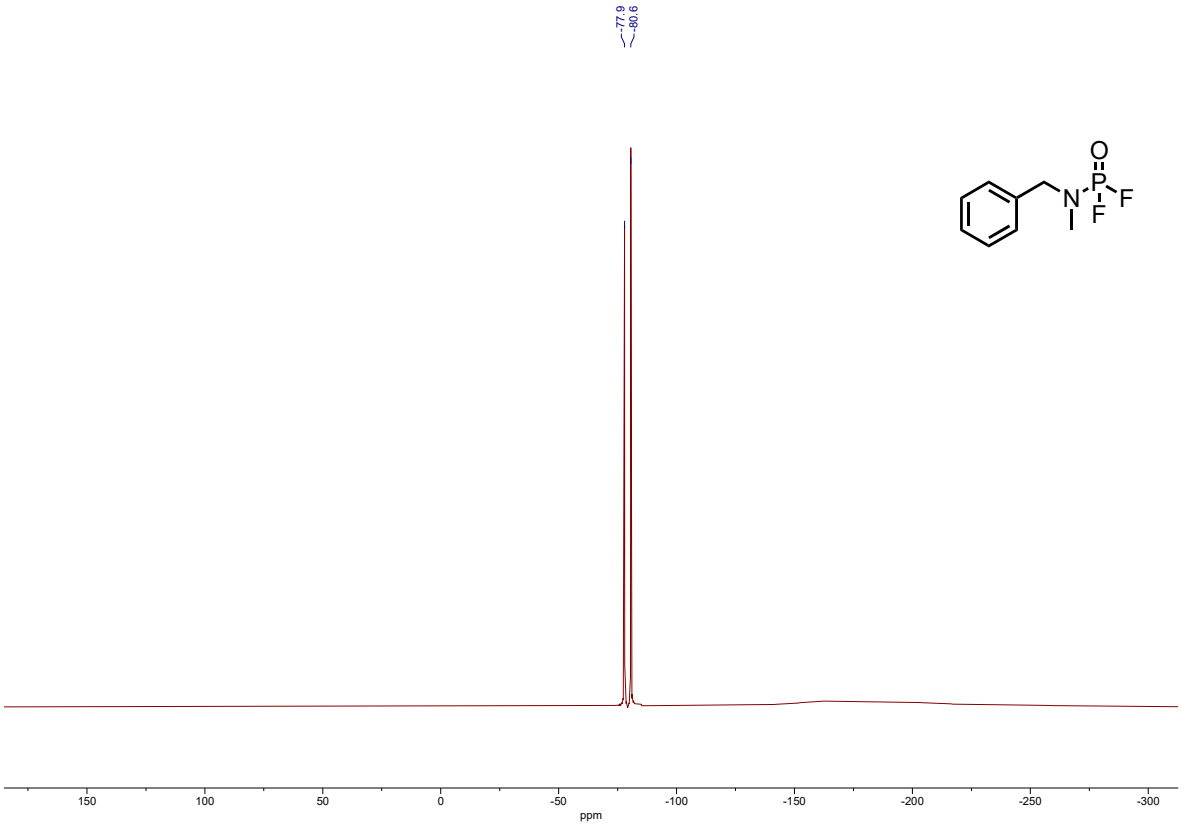
^{1}H NMR Spectrum for Compound **9b** (400 MHz, $CDCl_3$, unpurified)



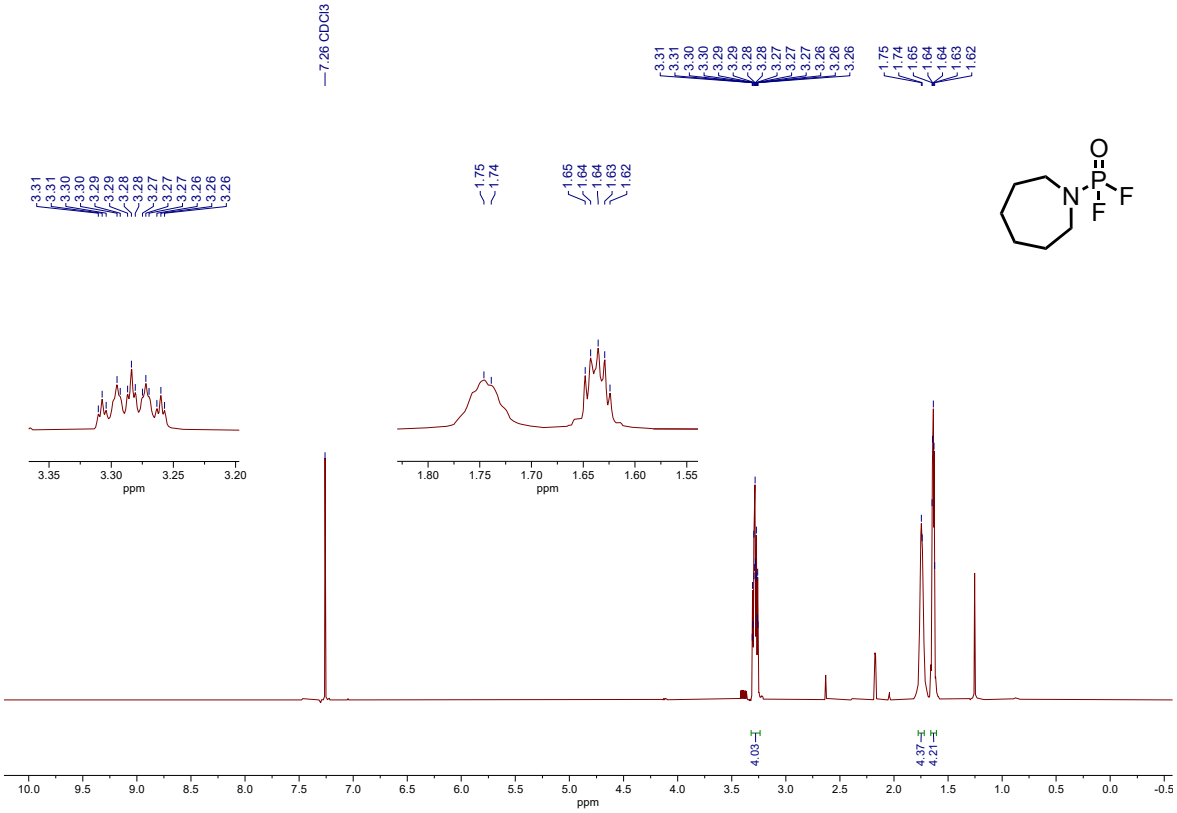
^{31}P NMR Spectrum for Compound **9b** (162 MHz, $CDCl_3$, unpurified)



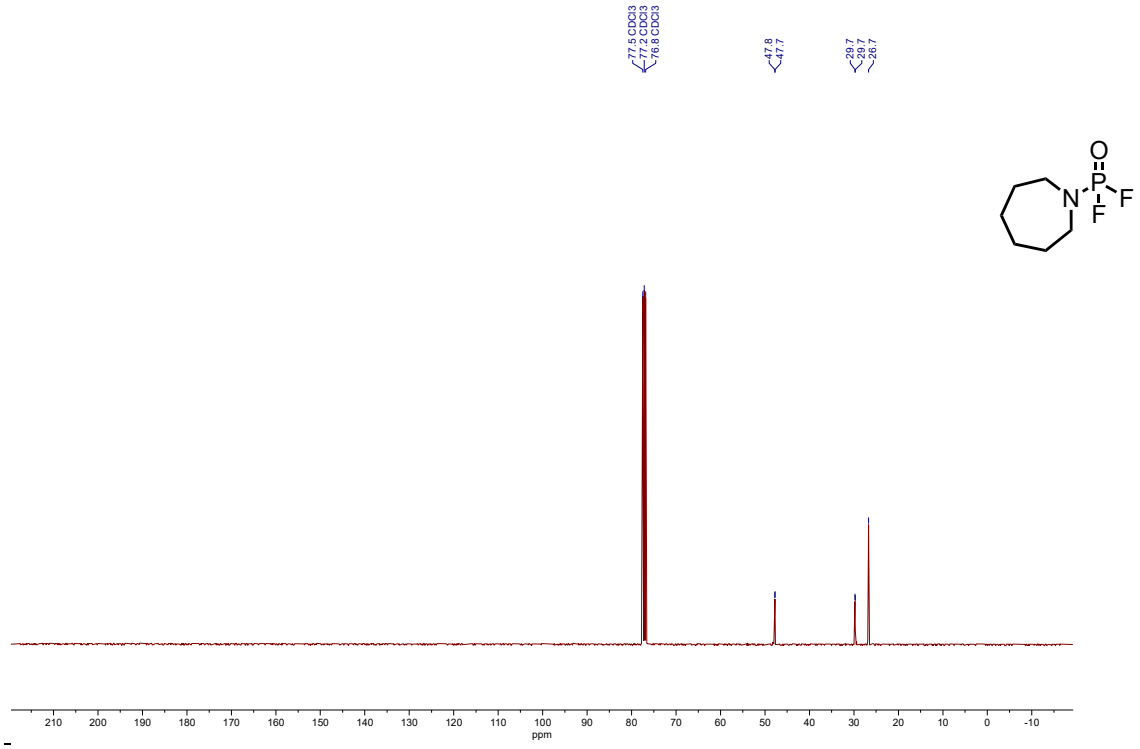
^{19}F NMR Spectrum for Compound **9b** (376 MHz, $CDCl_3$, unpurified)



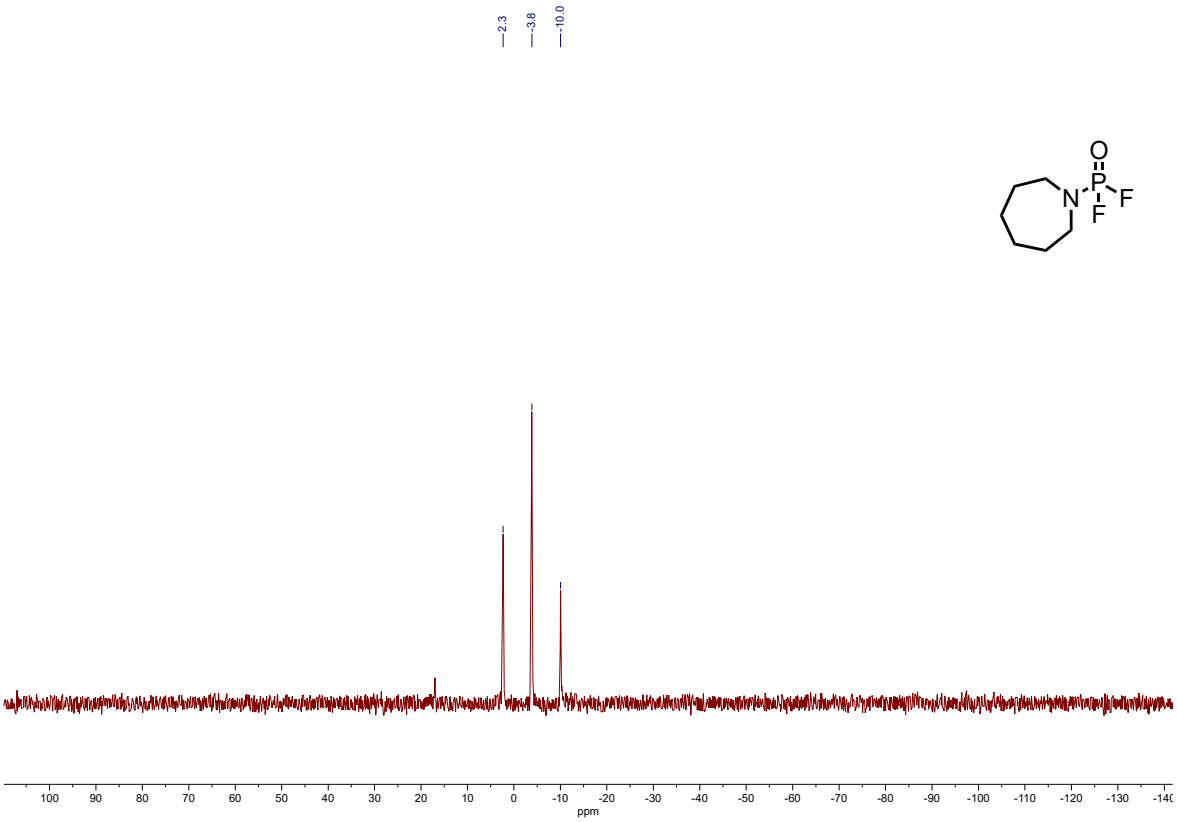
^{1}H NMR Spectrum for Compound **9c** (400 MHz, $CDCl_3$, unpurified)



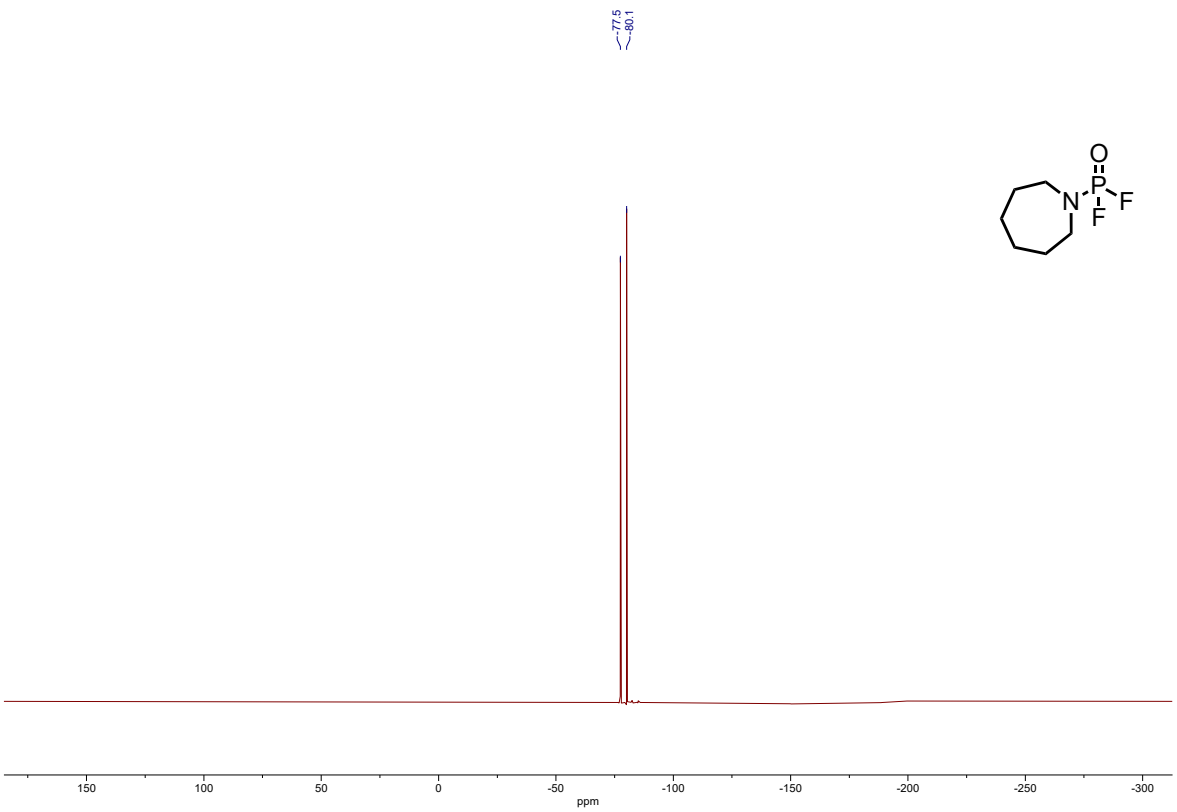
^{13}C NMR Spectrum for Compound **9c** (101 MHz, $CDCl_3$, unpurified)



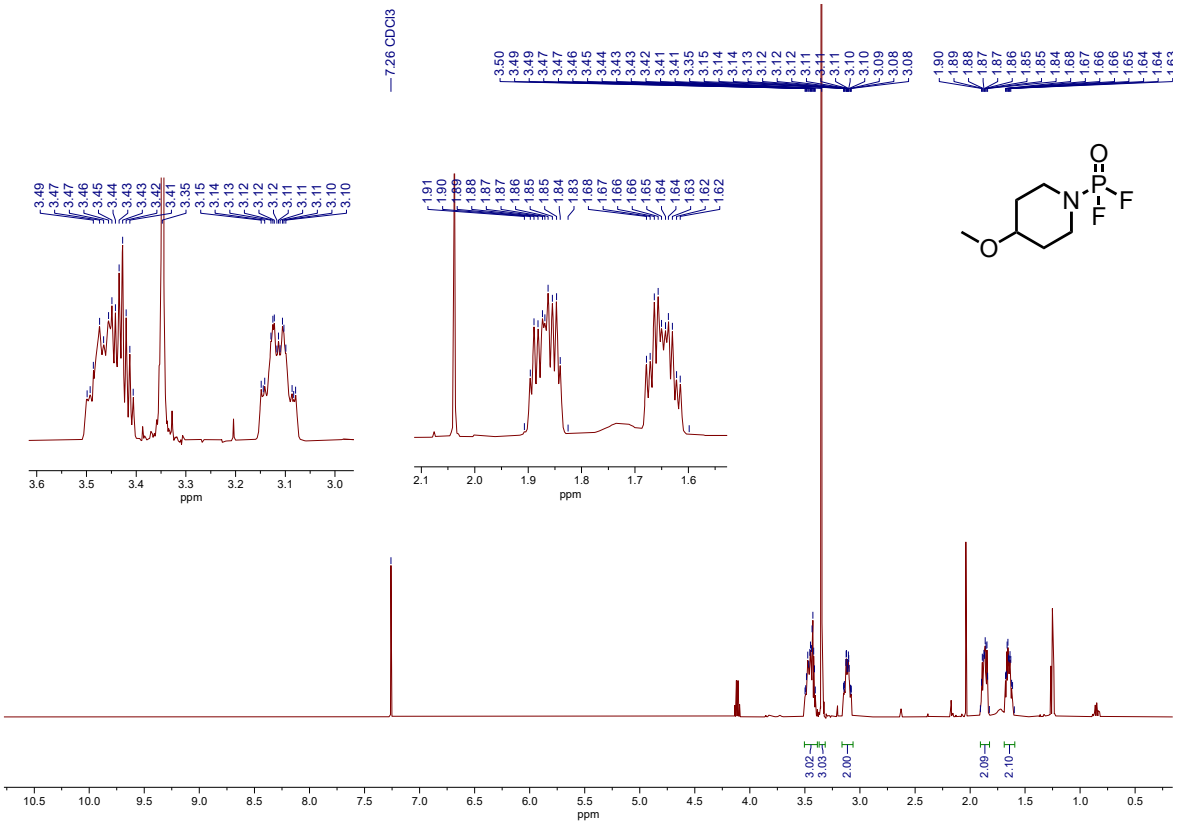
^{31}P NMR Spectrum for Compound **9c** (162 MHz, $CDCl_3$, unpurified)



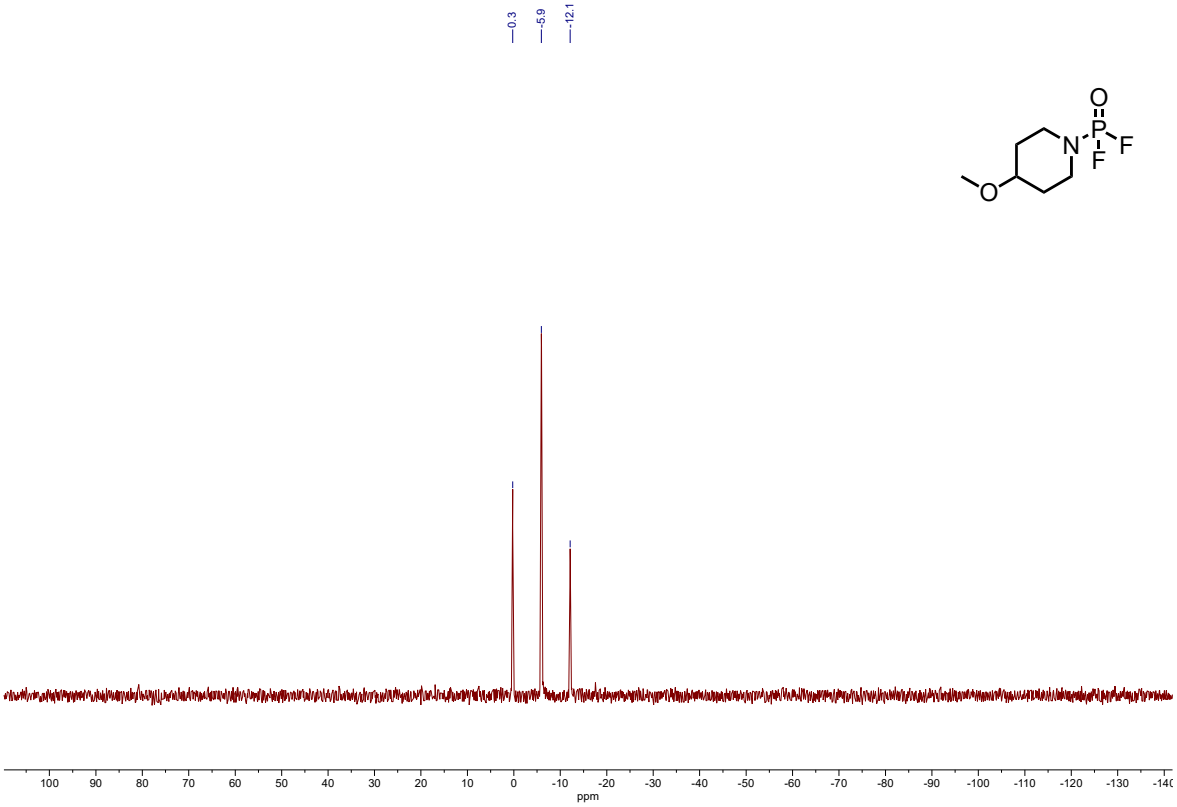
^{19}F NMR Spectrum for Compound **9c** (376 MHz, $CDCl_3$, unpurified)



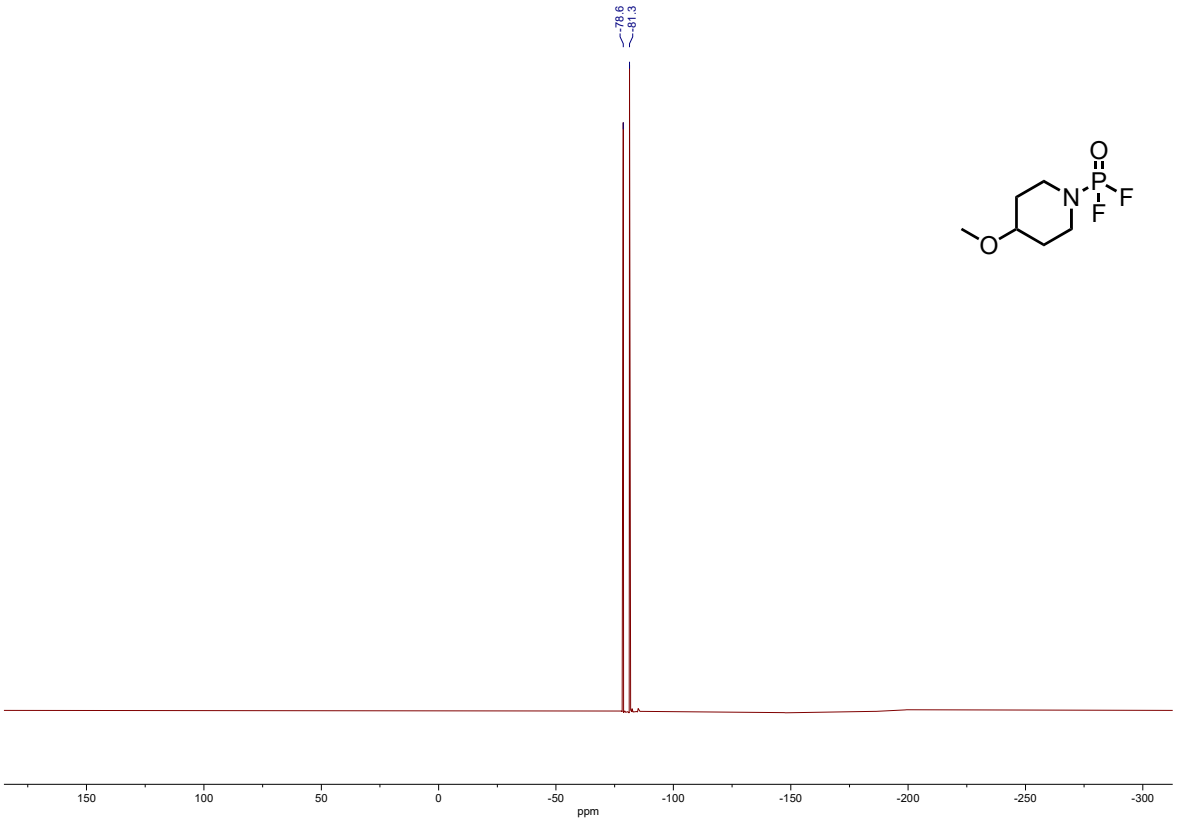
^{1}H NMR Spectrum for Compound **9d** (400 MHz, $CDCl_3$, unpurified)



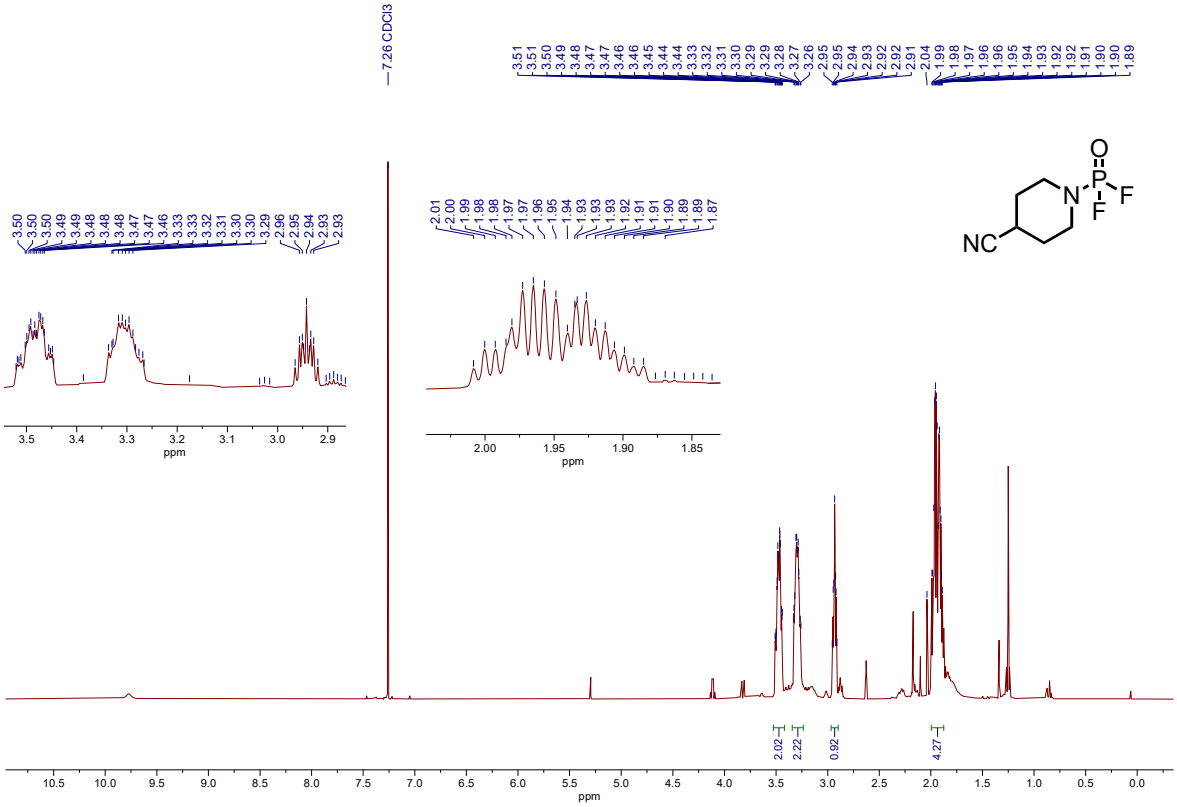
^{31}P NMR Spectrum for Compound **9d** (162 MHz, $CDCl_3$, unpurified)



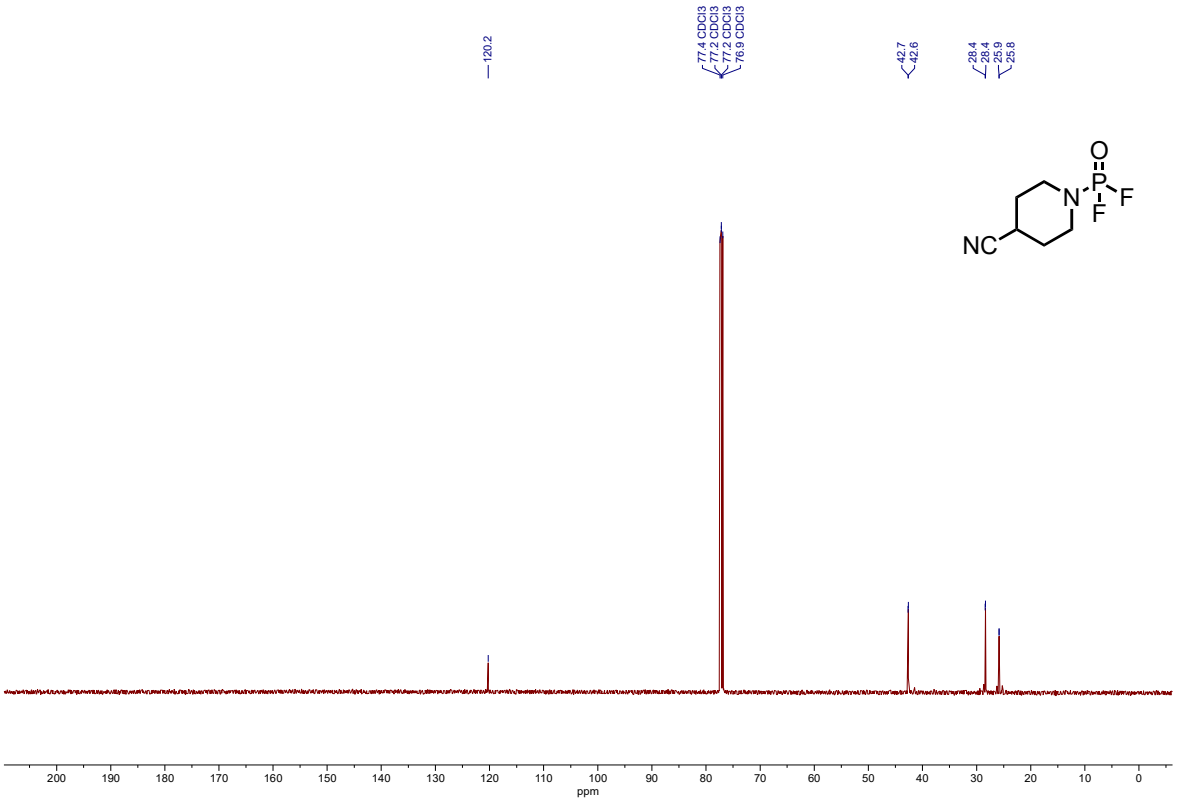
^{19}F NMR Spectrum for Compound **9d** (376 MHz, $CDCl_3$, unpurified)



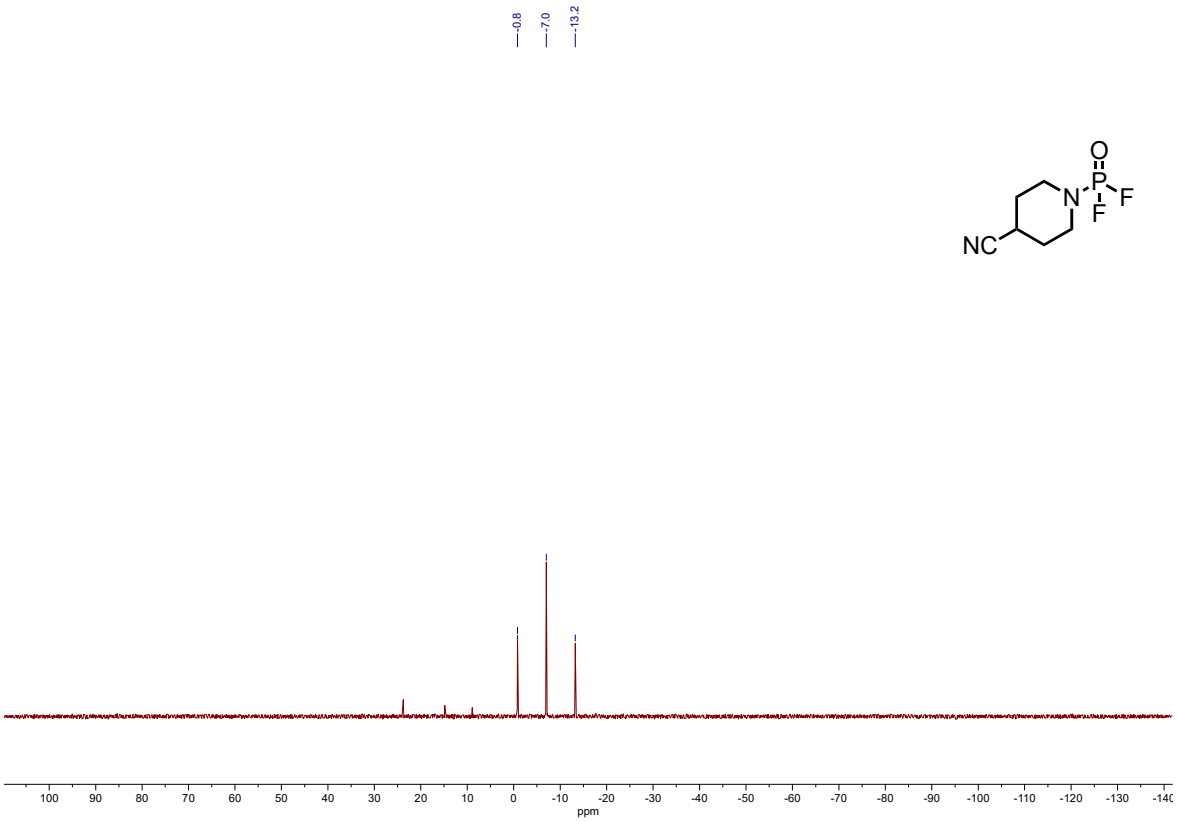
^{1}H NMR Spectrum for Compound **9e** (400 MHz, $CDCl_3$, unpurified)



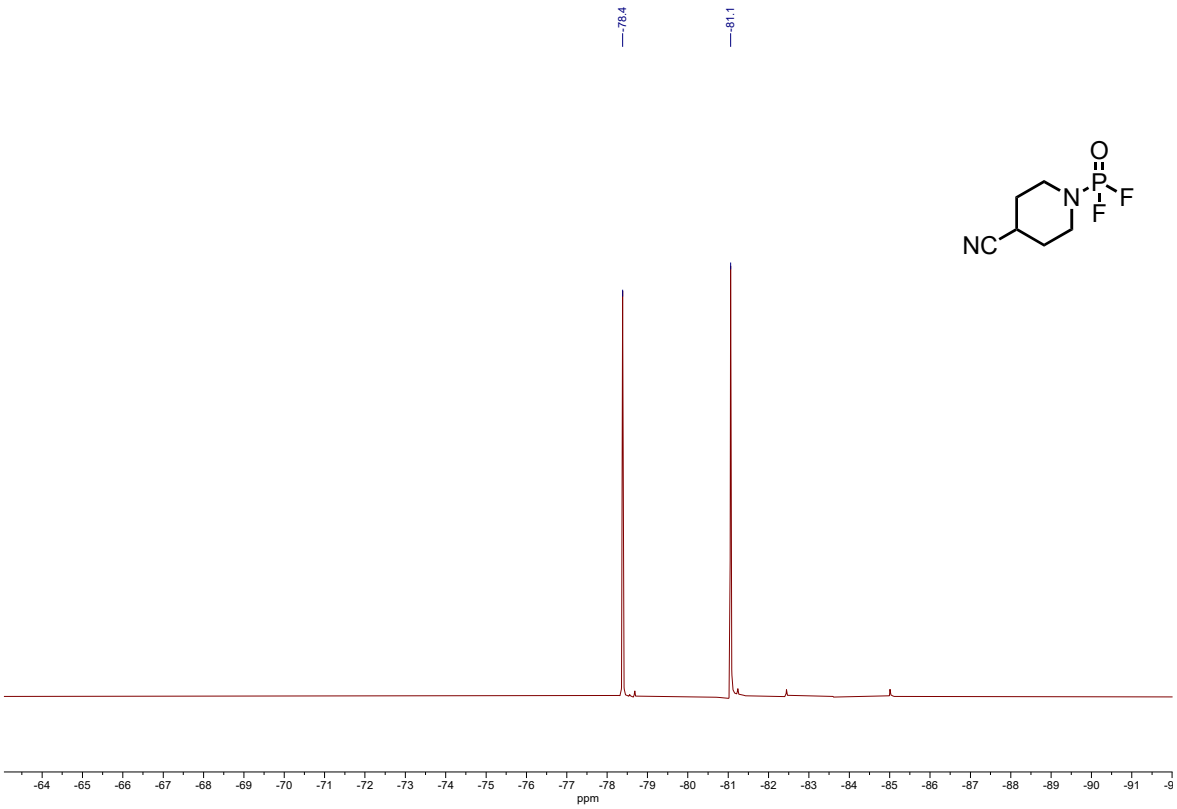
^{13}C NMR Spectrum for Compound **9e** (101 MHz, $CDCl_3$, unpurified)



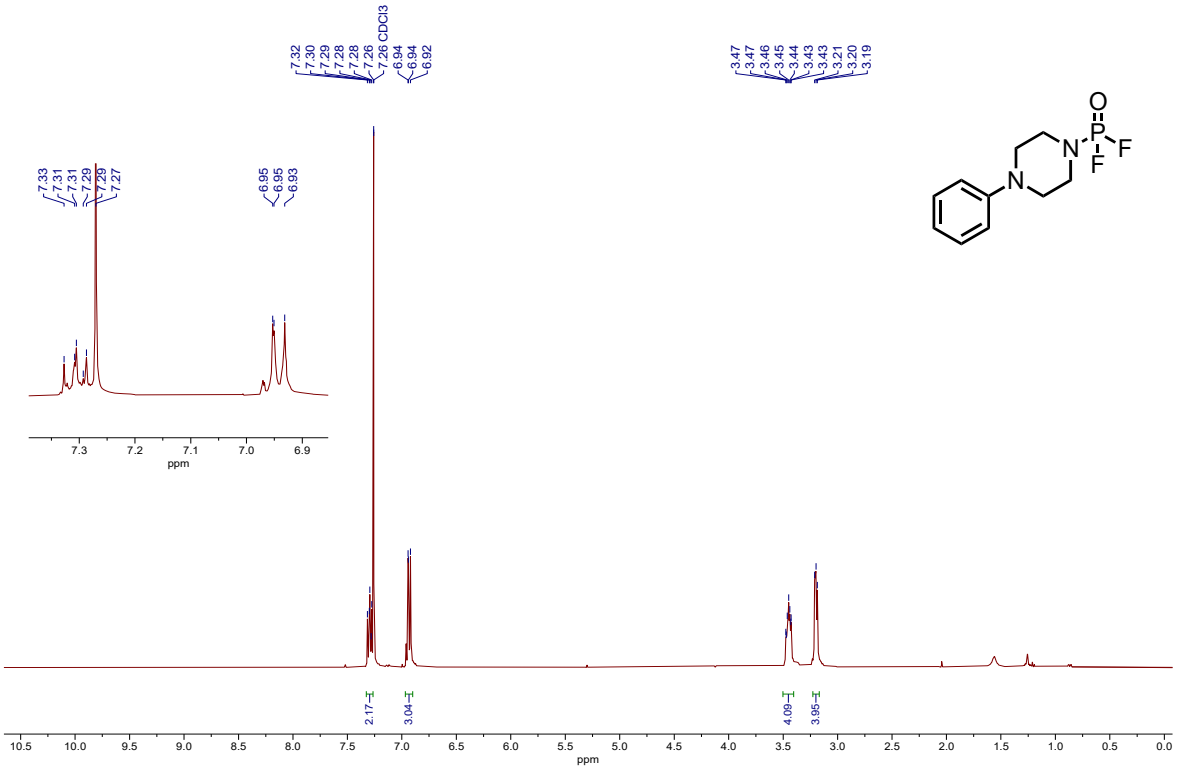
^{31}P NMR Spectrum for Compound **9e** (162 MHz, $CDCl_3$, unpurified)



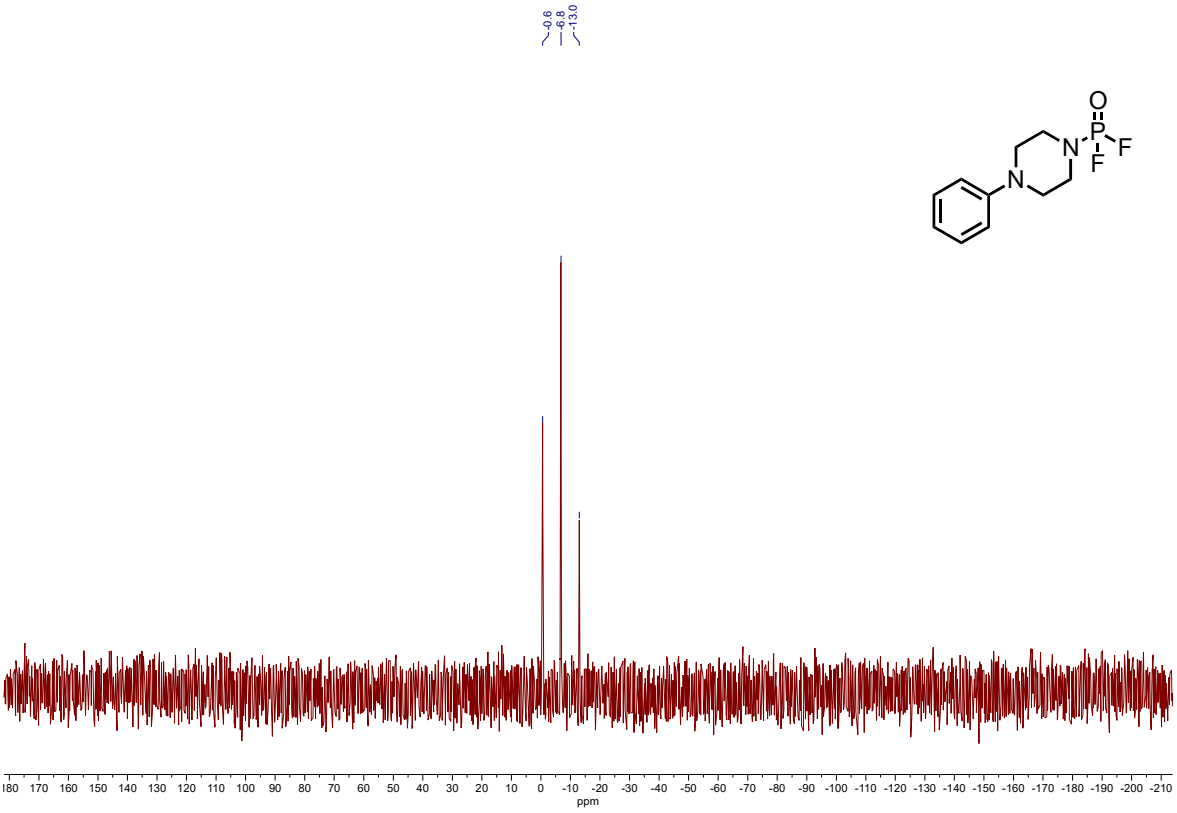
^{19}F NMR Spectrum for Compound **9e** (376 MHz, $CDCl_3$, unpurified)



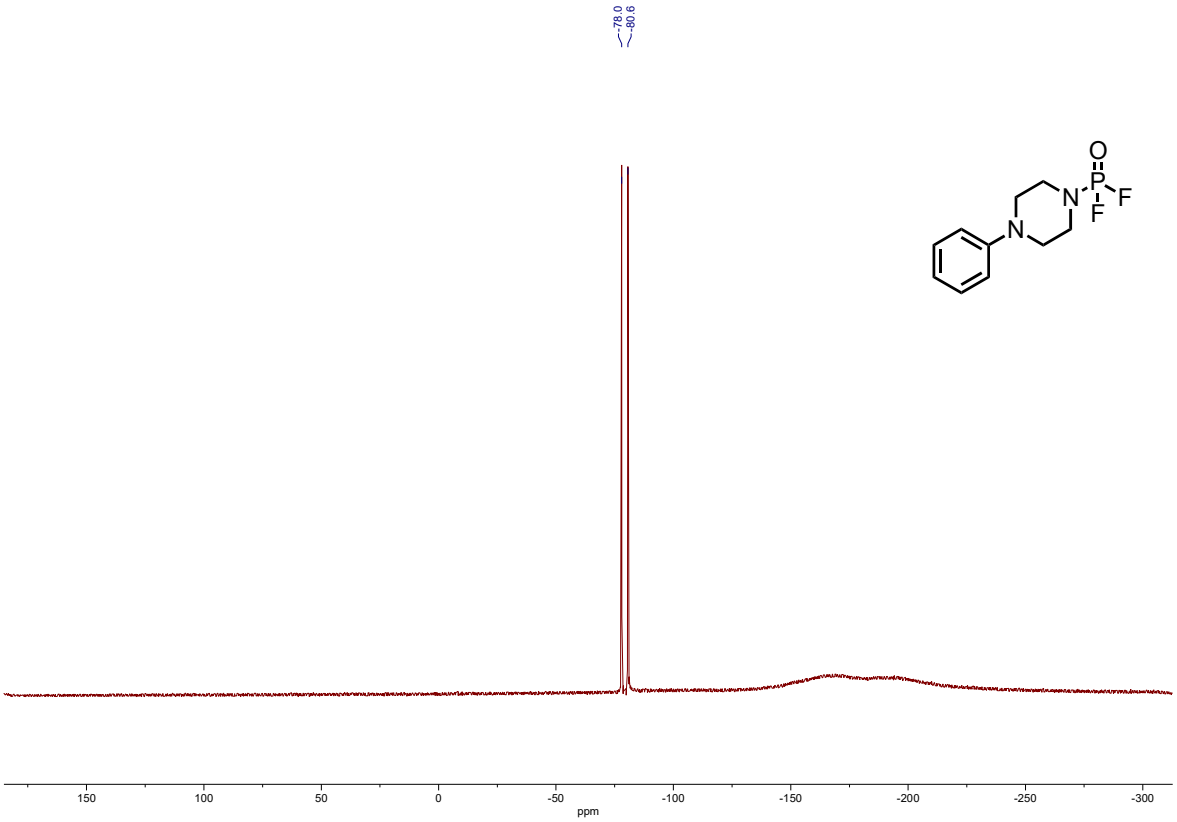
^{1}H NMR Spectrum for Compound **9f** (400 MHz, $CDCl_3$, unpurified)



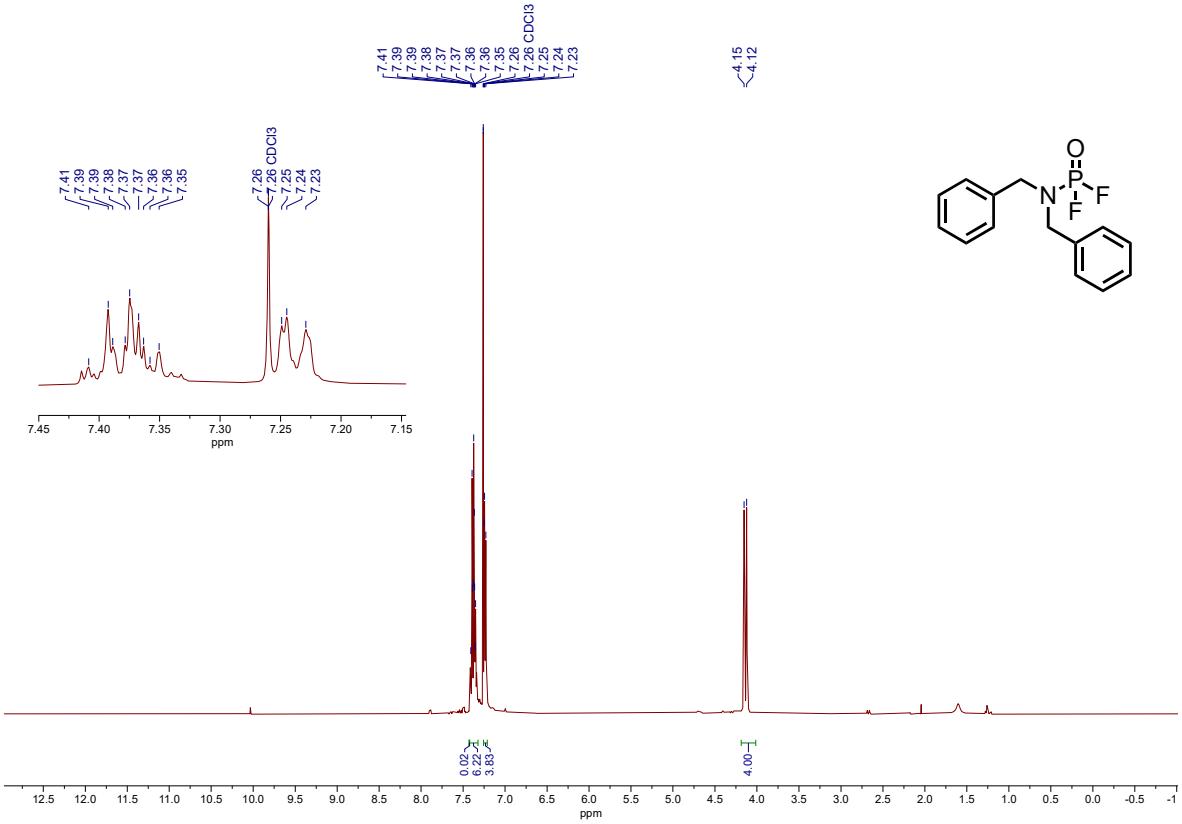
^{31}P NMR Spectrum for Compound **9f** (162 MHz, $CDCl_3$, unpurified)



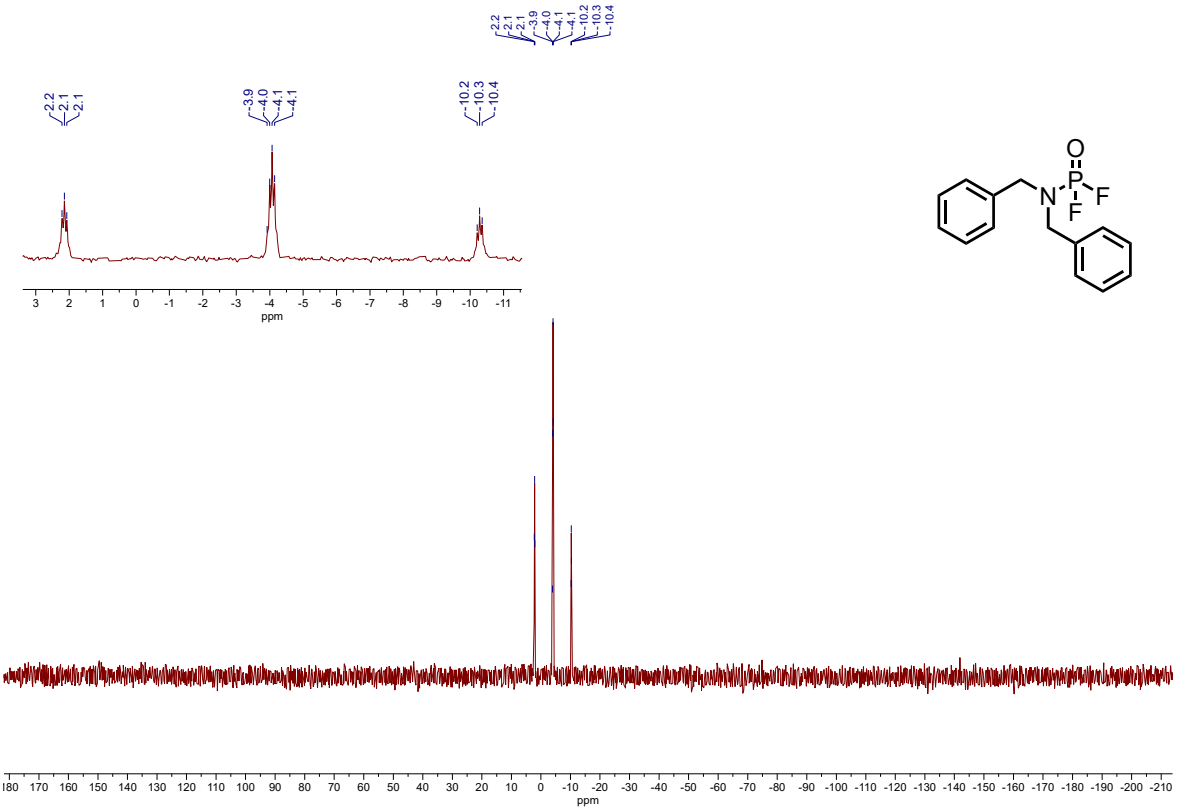
^{19}F NMR Spectrum for Compound **9f** (376 MHz, $CDCl_3$, unpurified)



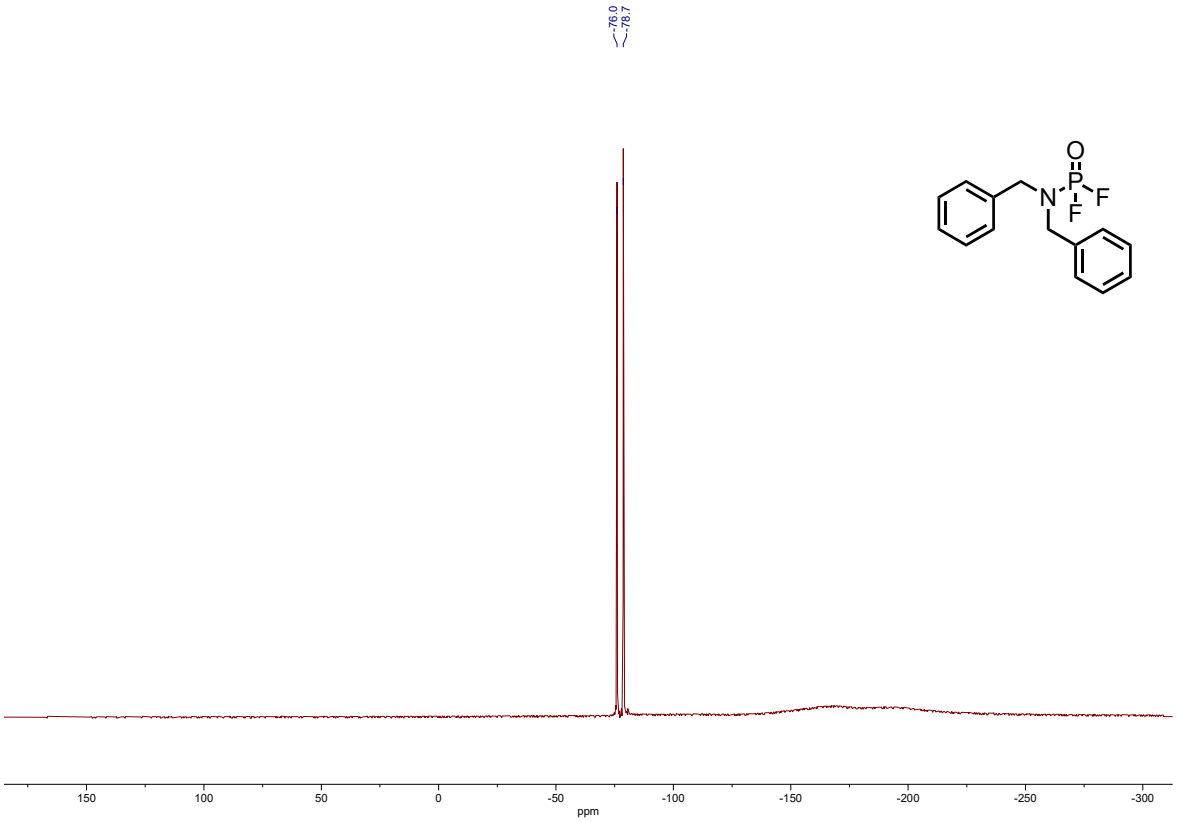
^{1}H NMR Spectrum for Compound **9g** (400 MHz, $CDCl_3$, unpurified)



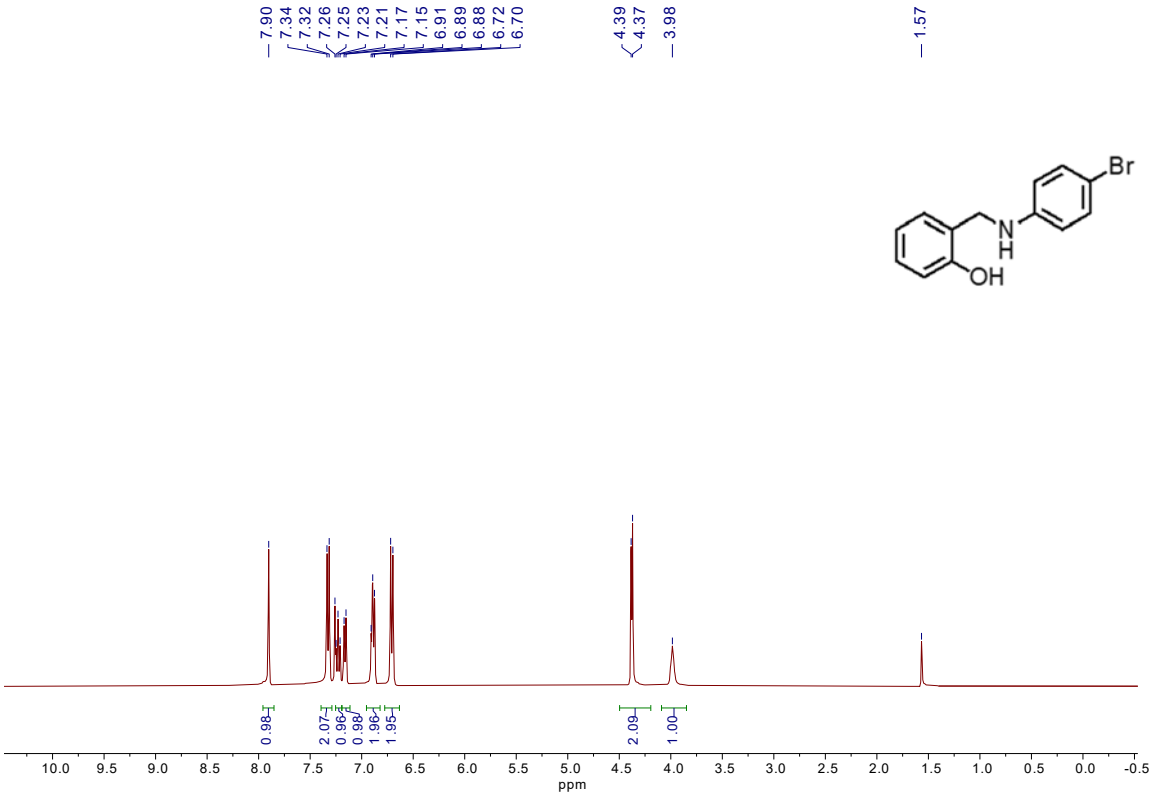
^{31}P NMR Spectrum for Compound **9g** (162 MHz, $CDCl_3$, unpurified)



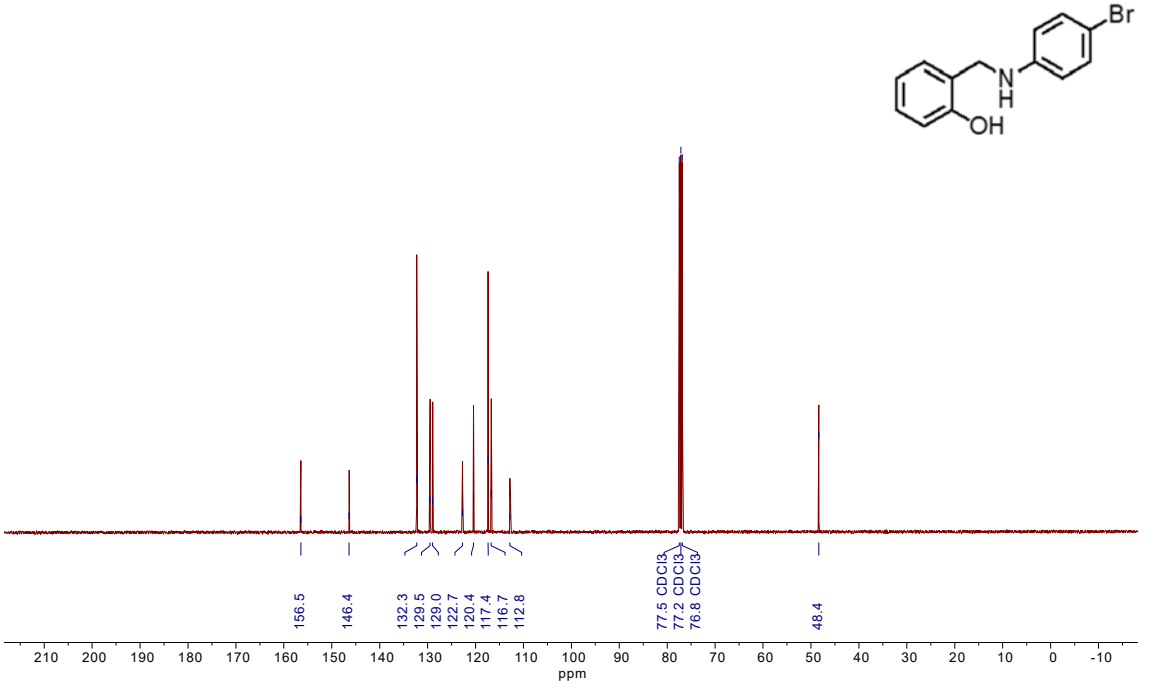
^{19}F NMR Spectrum for Compound **9g** (376 MHz, $CDCl_3$, unpurified)



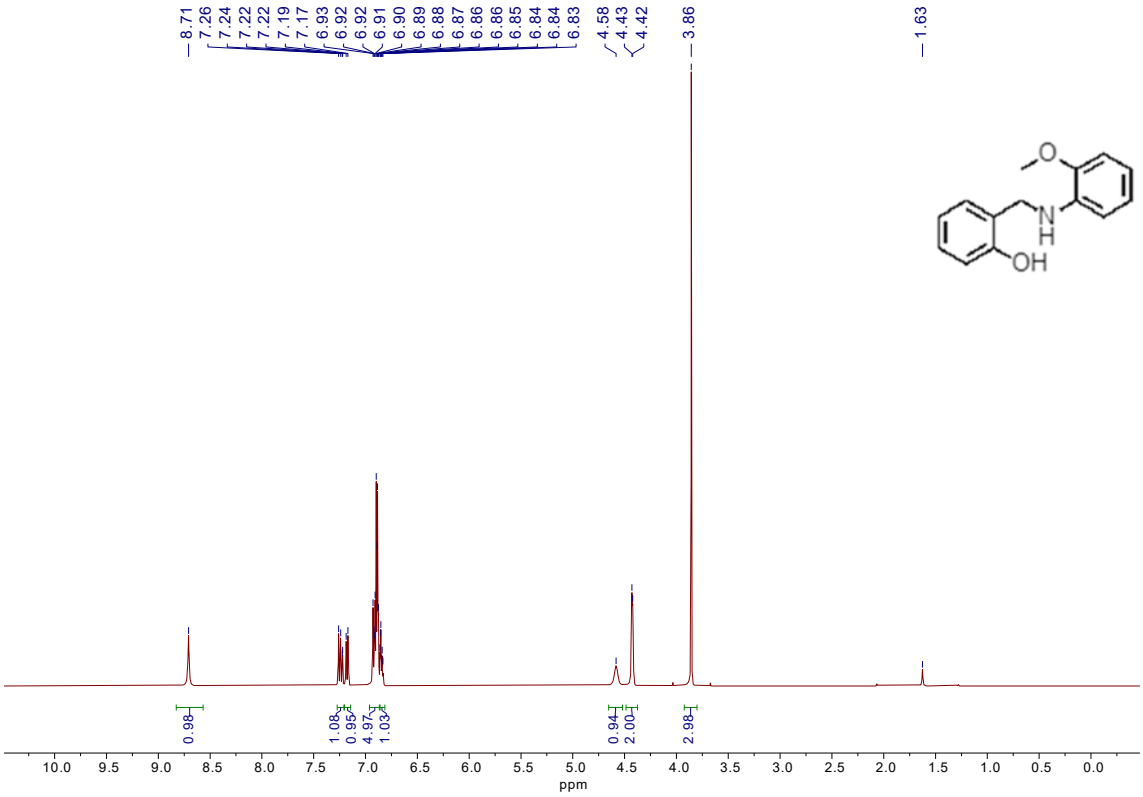
^{1}H NMR Spectrum for Compound **S7a** (400 MHz, $CDCl_3$)



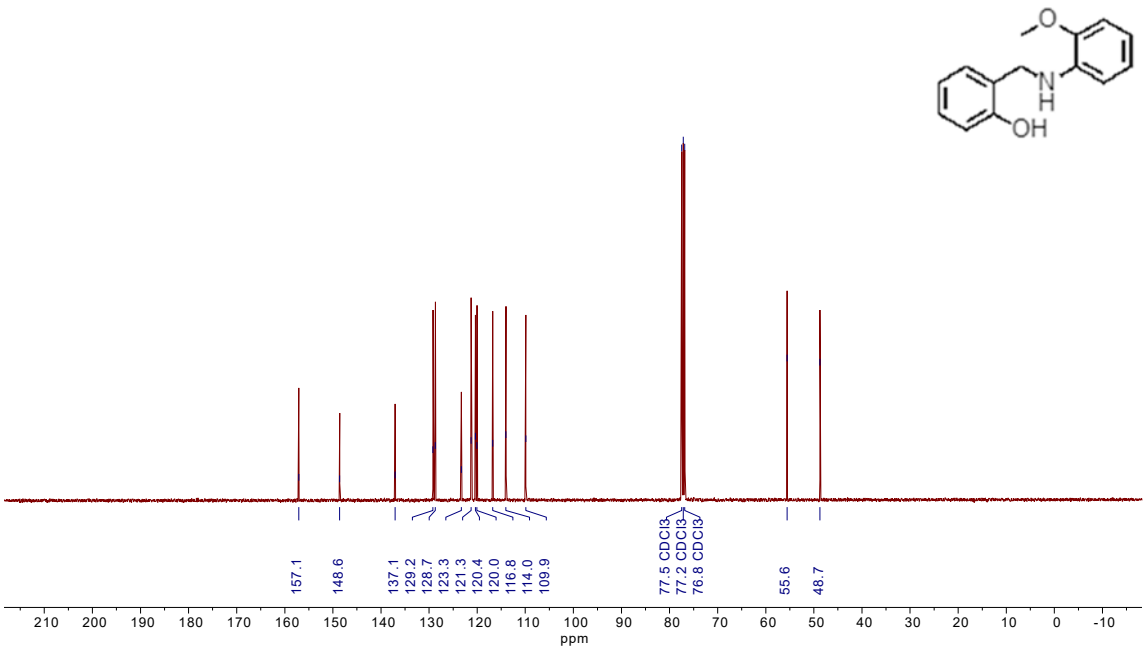
^{13}C NMR Spectrum for Compound **S7a** (101 MHz, $CDCl_3$)



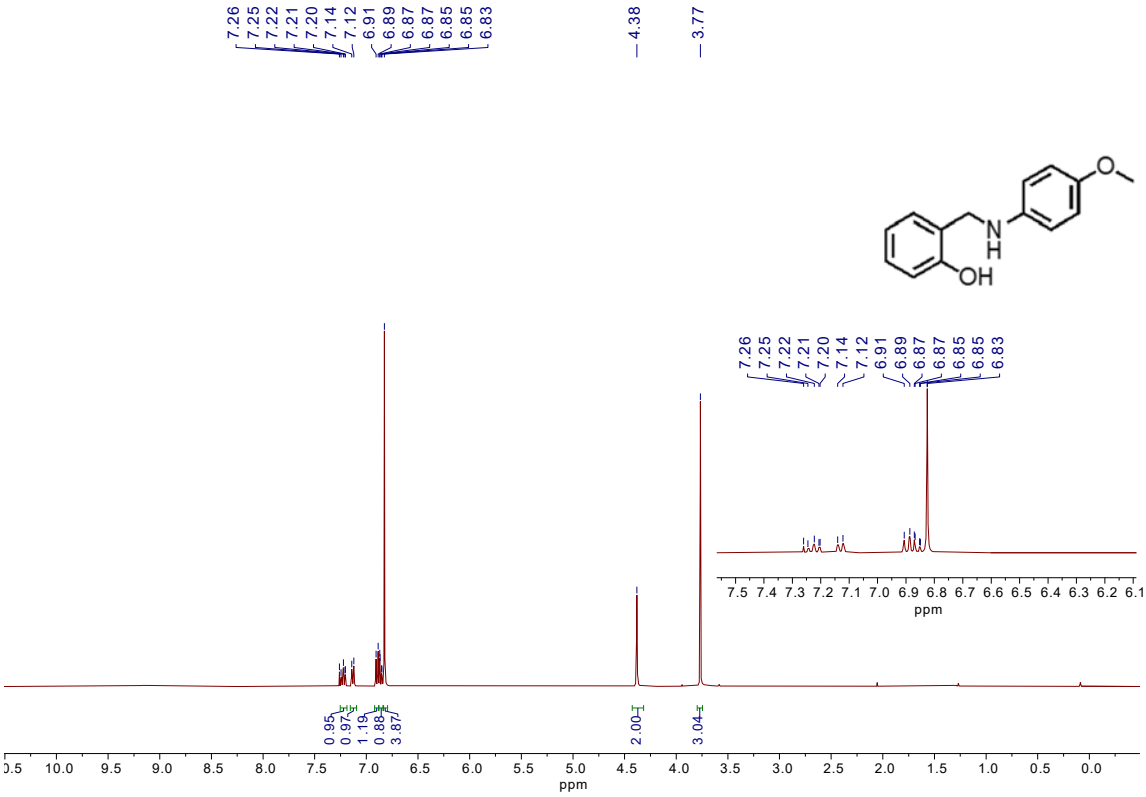
^{1}H NMR Spectrum for Compound **S7b** (400 MHz, $CDCl_3$)



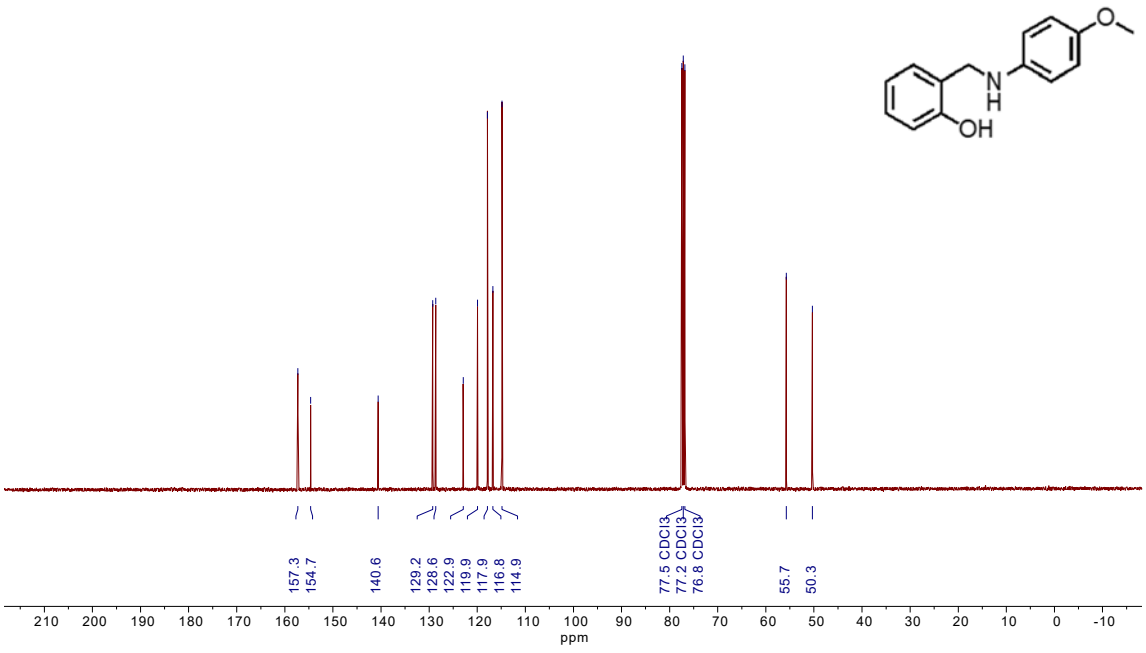
^{13}C NMR Spectrum for Compound **S7b** (101 MHz, $CDCl_3$)



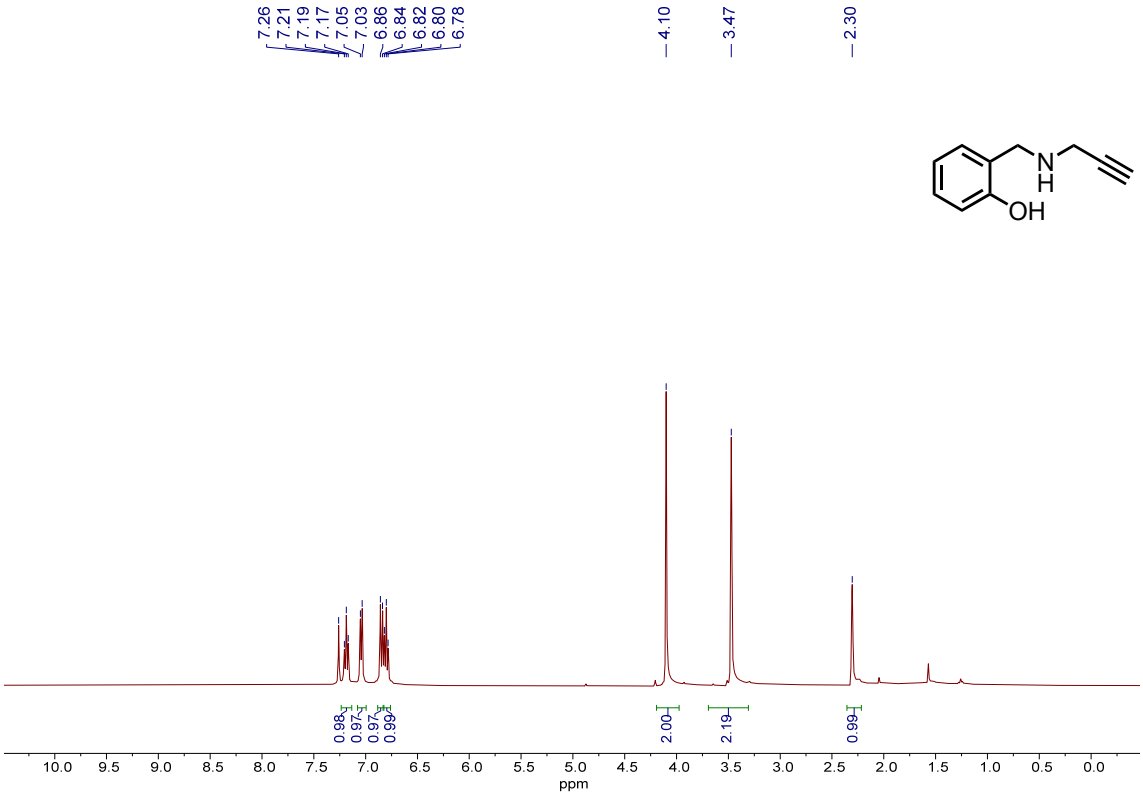
^{1}H NMR Spectrum for Compound **S7c** (400 MHz, $CDCl_3$)



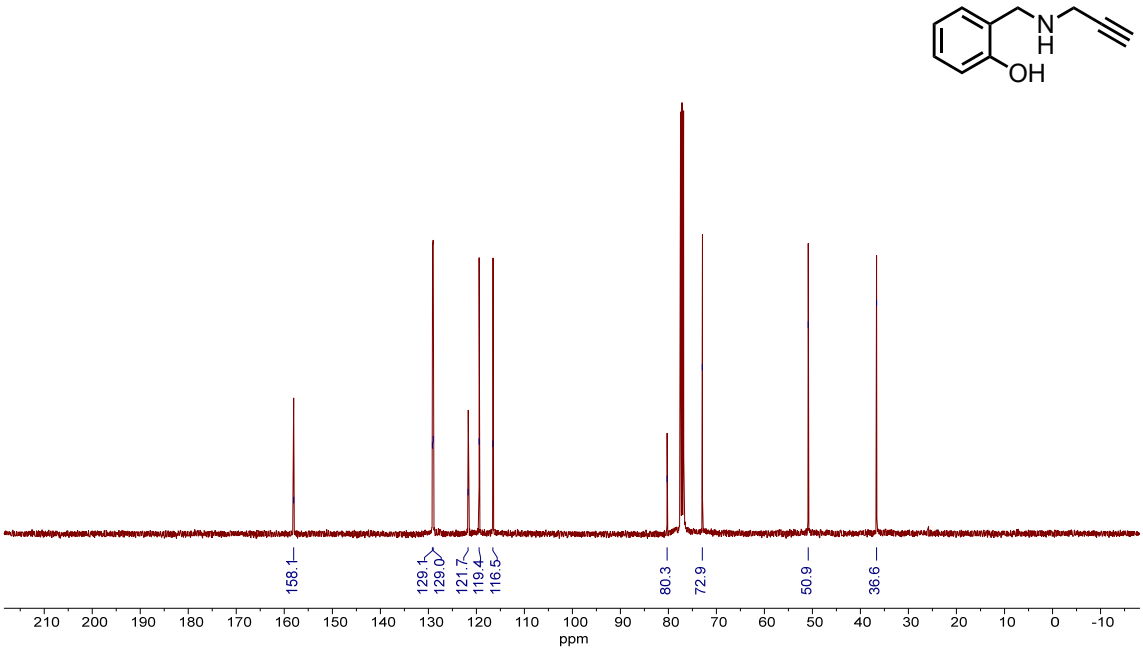
^{13}C NMR Spectrum for Compound **S6c** (101 MHz, $CDCl_3$)



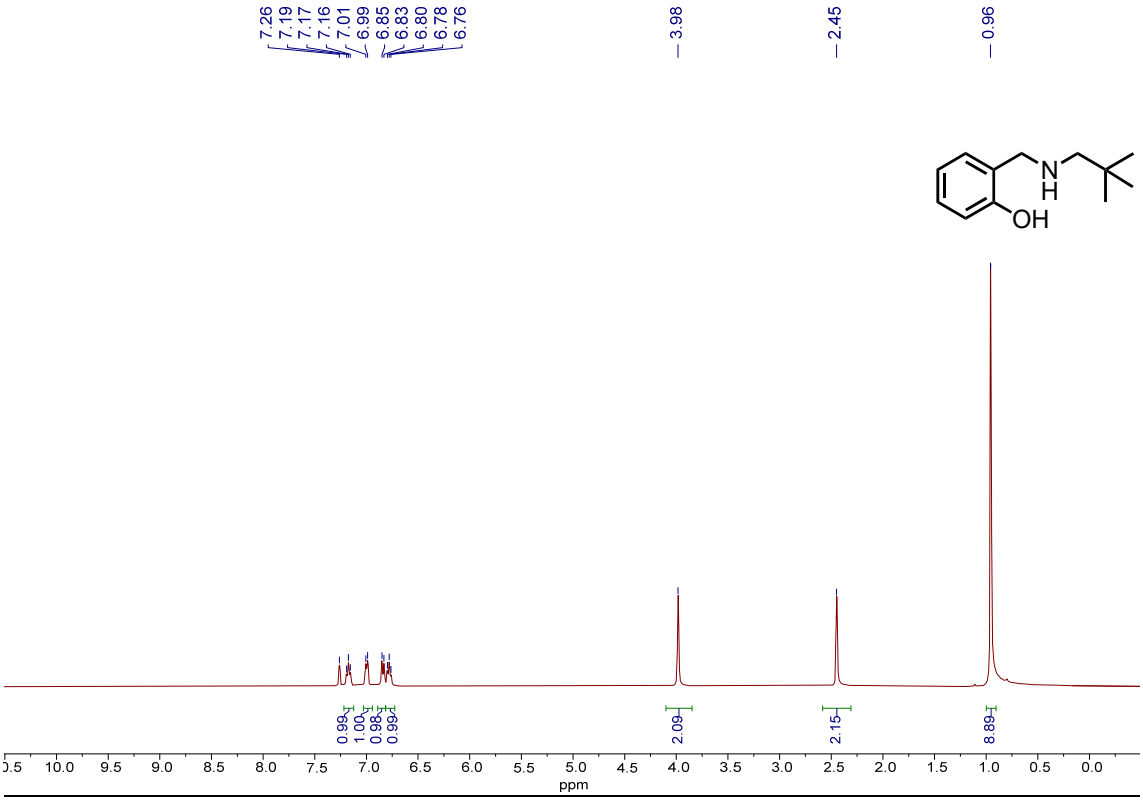
^{1}H NMR Spectrum for Compound **S7d** (400 MHz, $CDCl_3$)



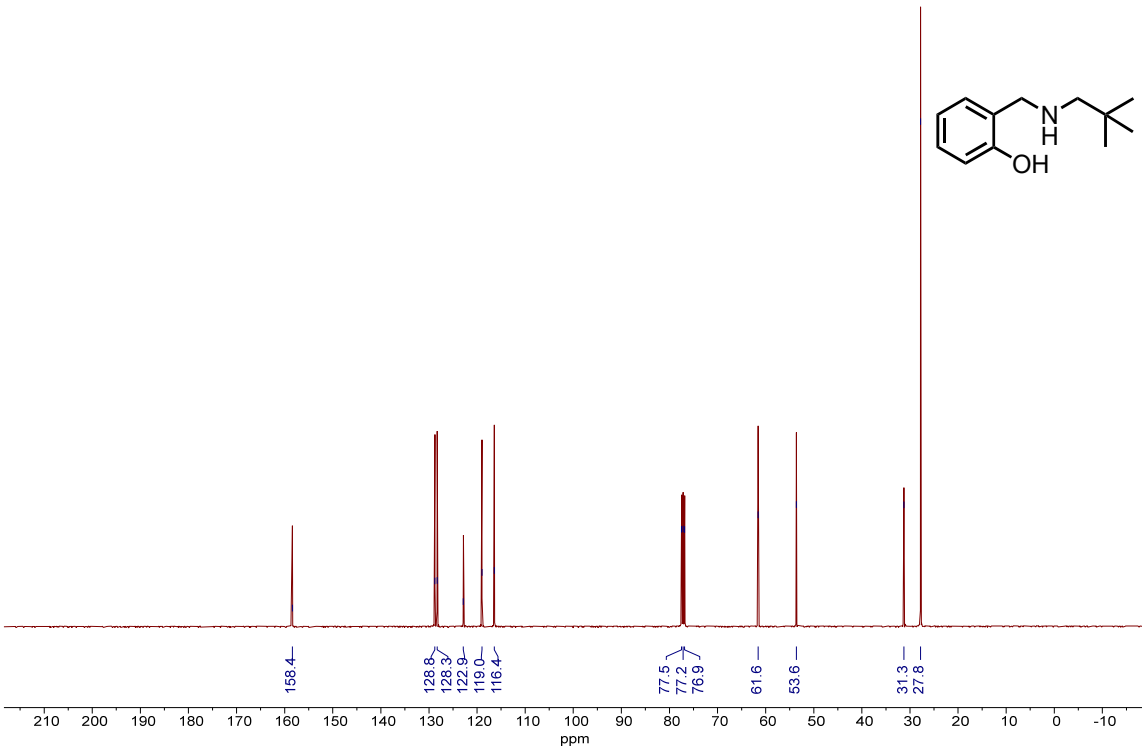
^{13}C NMR Spectrum for Compound **S6d** (101 MHz, $CDCl_3$)



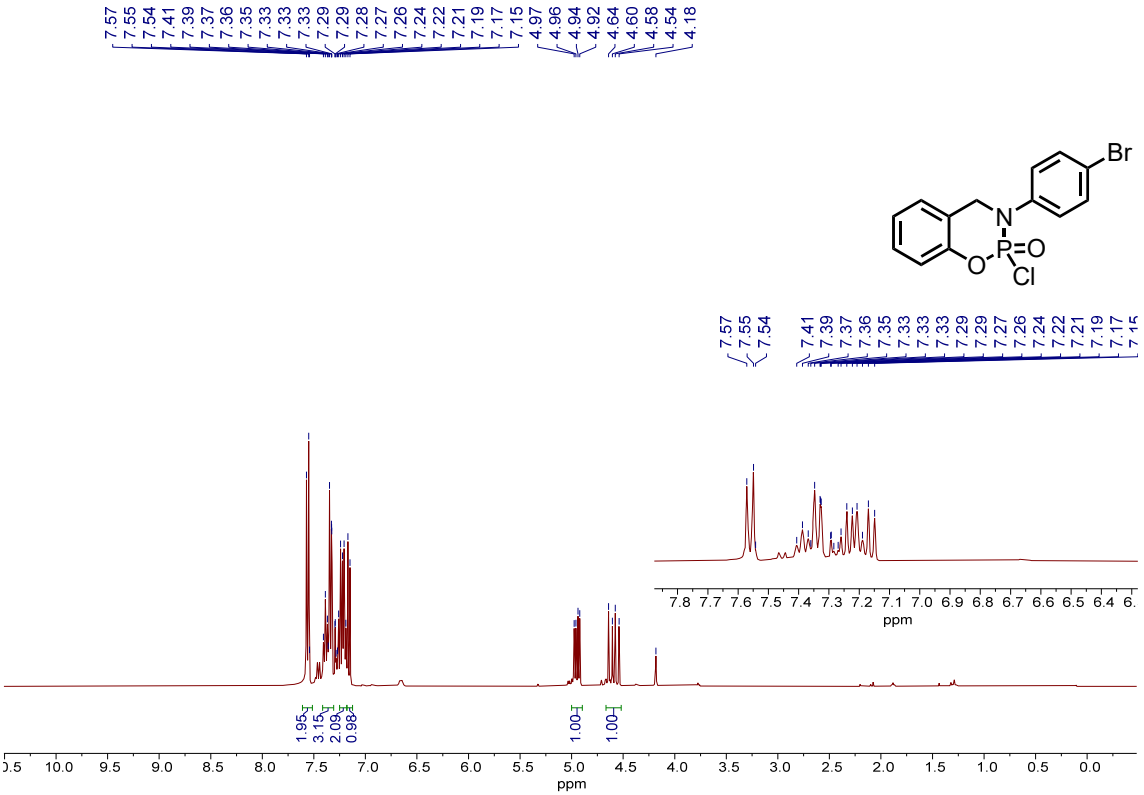
^{1}H NMR Spectrum for Compound **S7e** (400 MHz, $CDCl_3$)



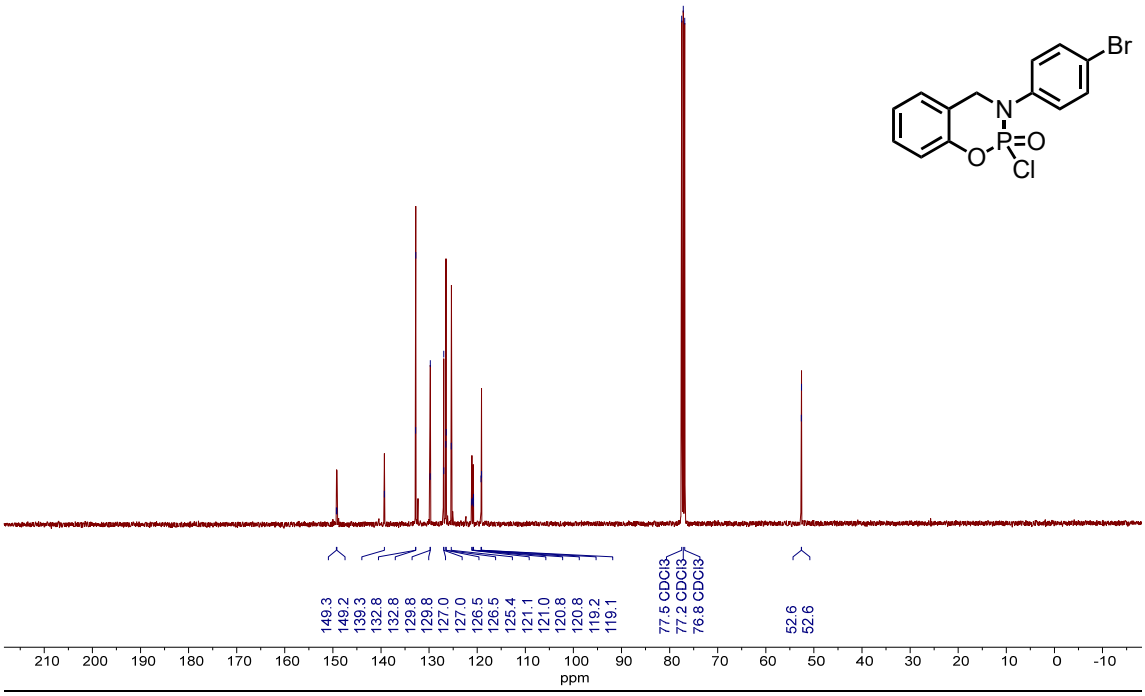
^{13}C NMR Spectrum for Compound **S7e** (101 MHz, $CDCl_3$)



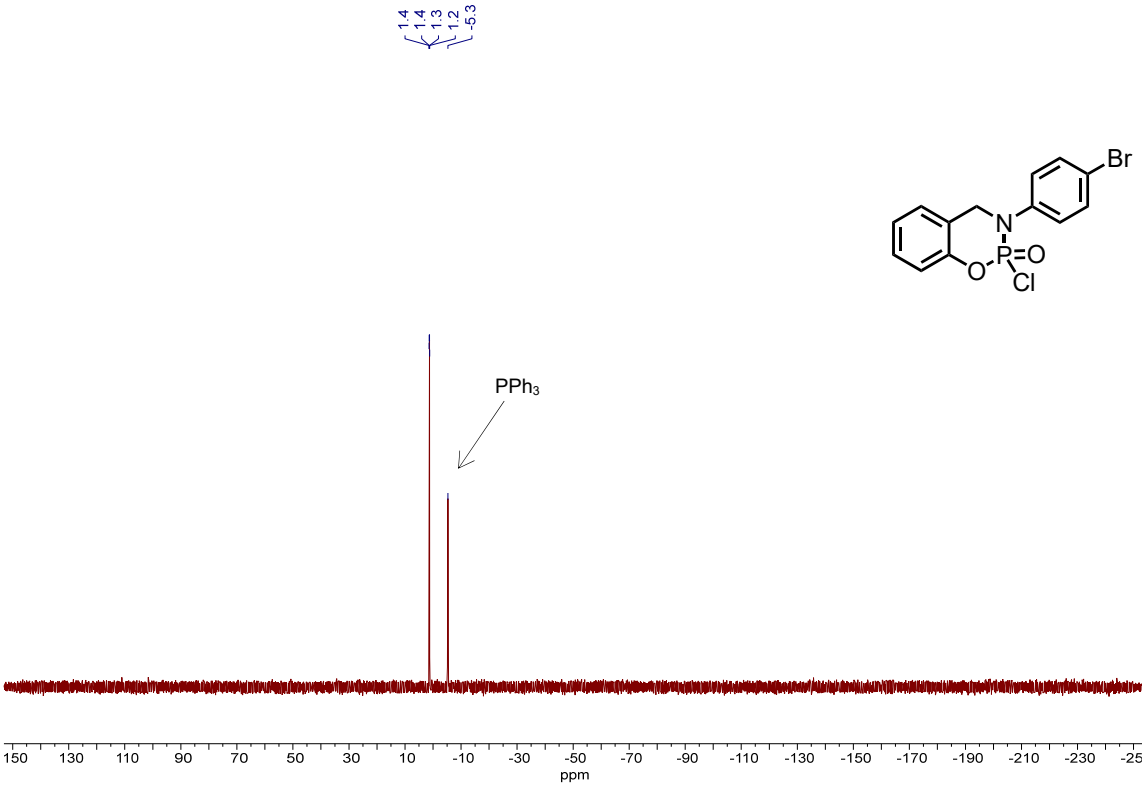
^{1}H NMR Spectrum for Compound **8a** (400 MHz, $CDCl_3$)



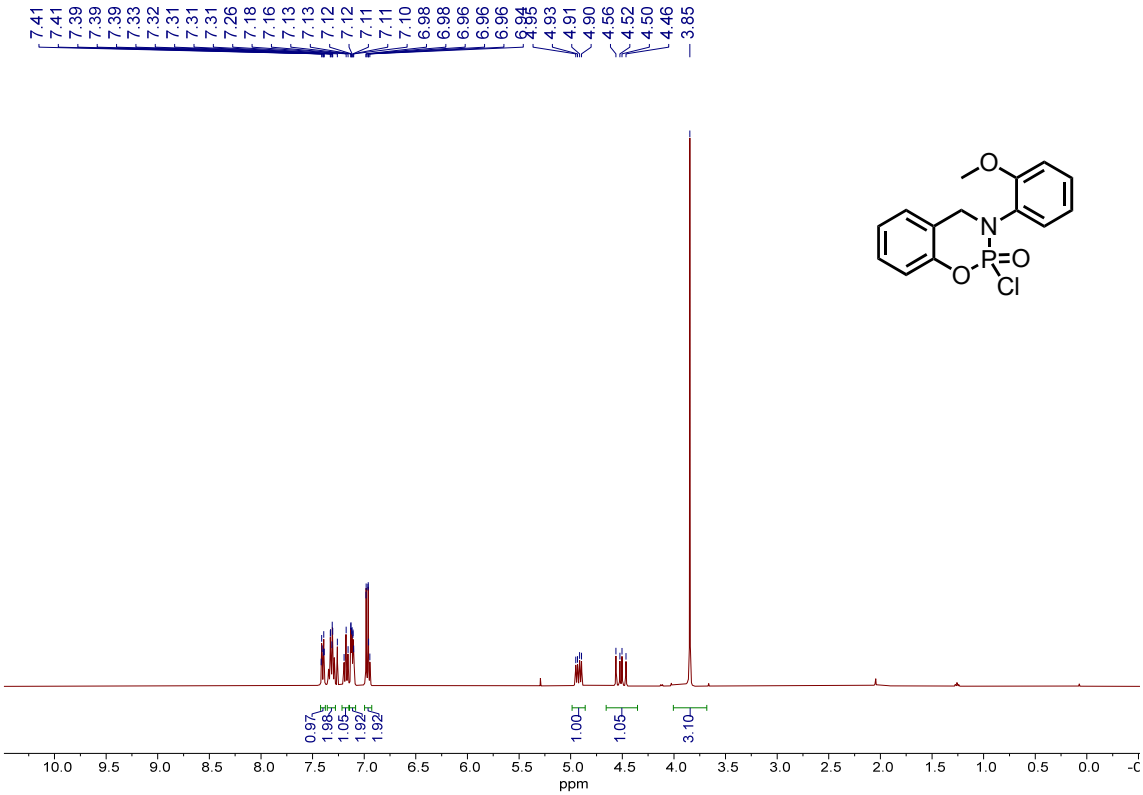
^{13}C NMR Spectrum for Compound **8a** (101 MHz, $CDCl_3$)



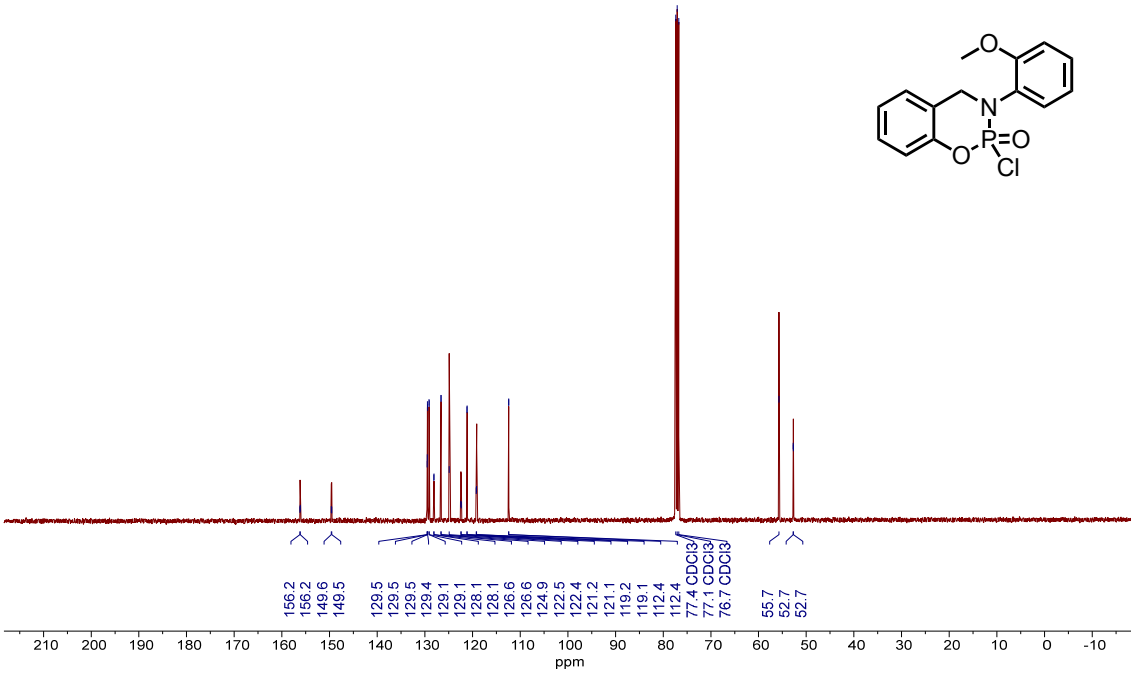
^{31}P NMR Spectrum for Compound **8a** (162 MHz, $CDCl_3$)



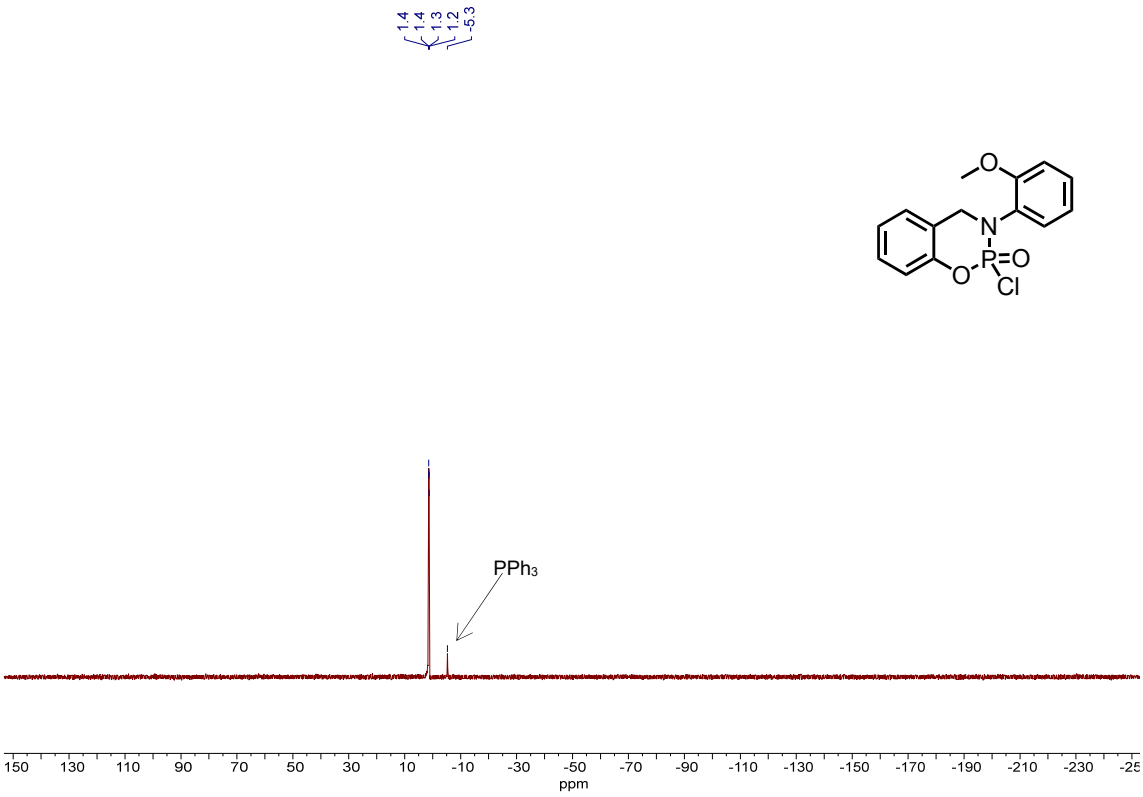
^{1}H NMR Spectrum for Compound **8b** (400 MHz, $CDCl_3$)



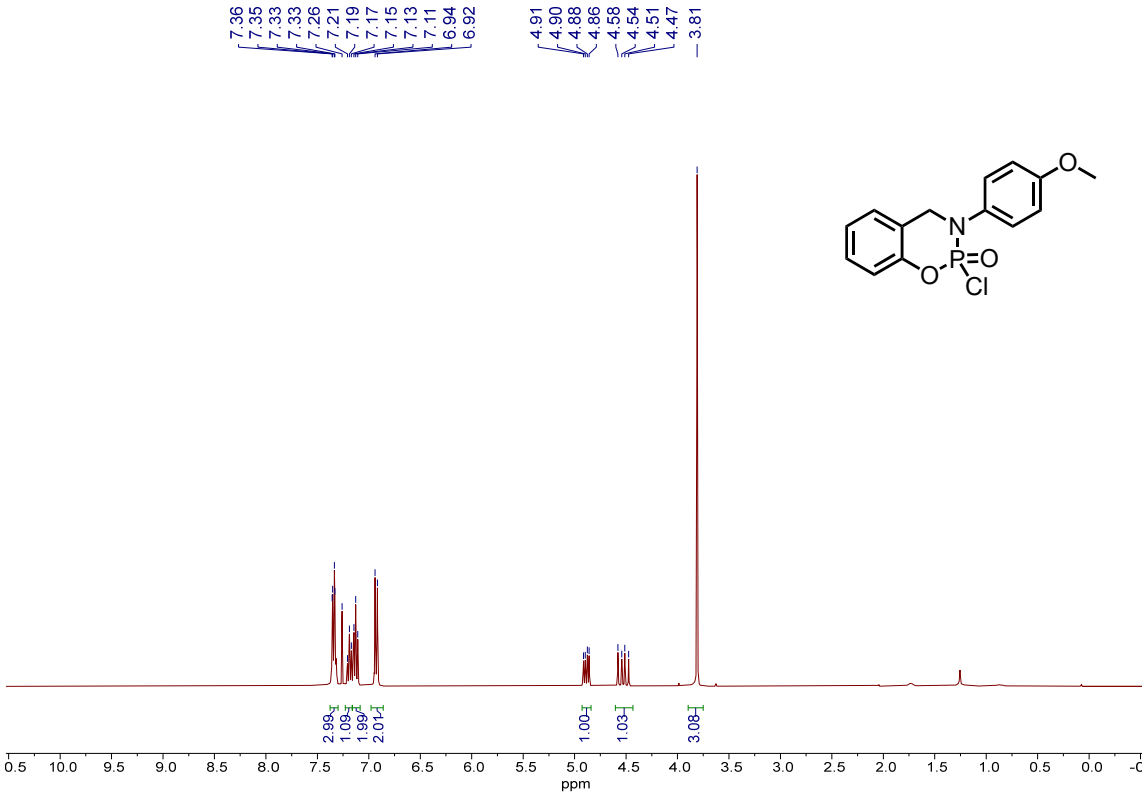
^{13}C NMR Spectrum for Compound **8b** (101 MHz, $CDCl_3$)



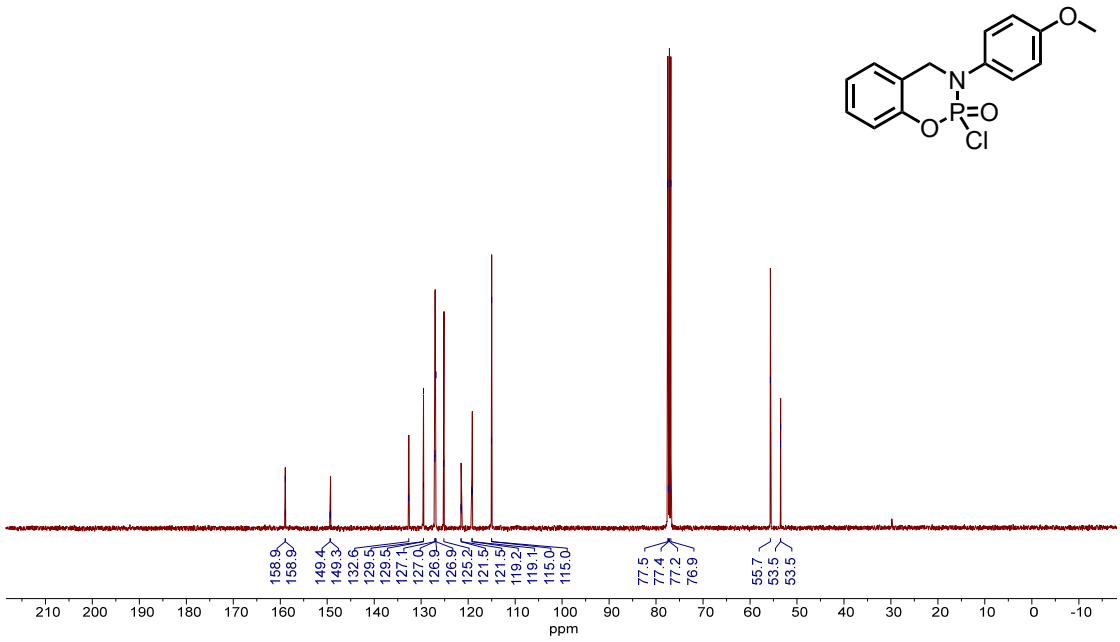
^{31}P NMR Spectrum for Compound **8b** ($CDCl_3$)



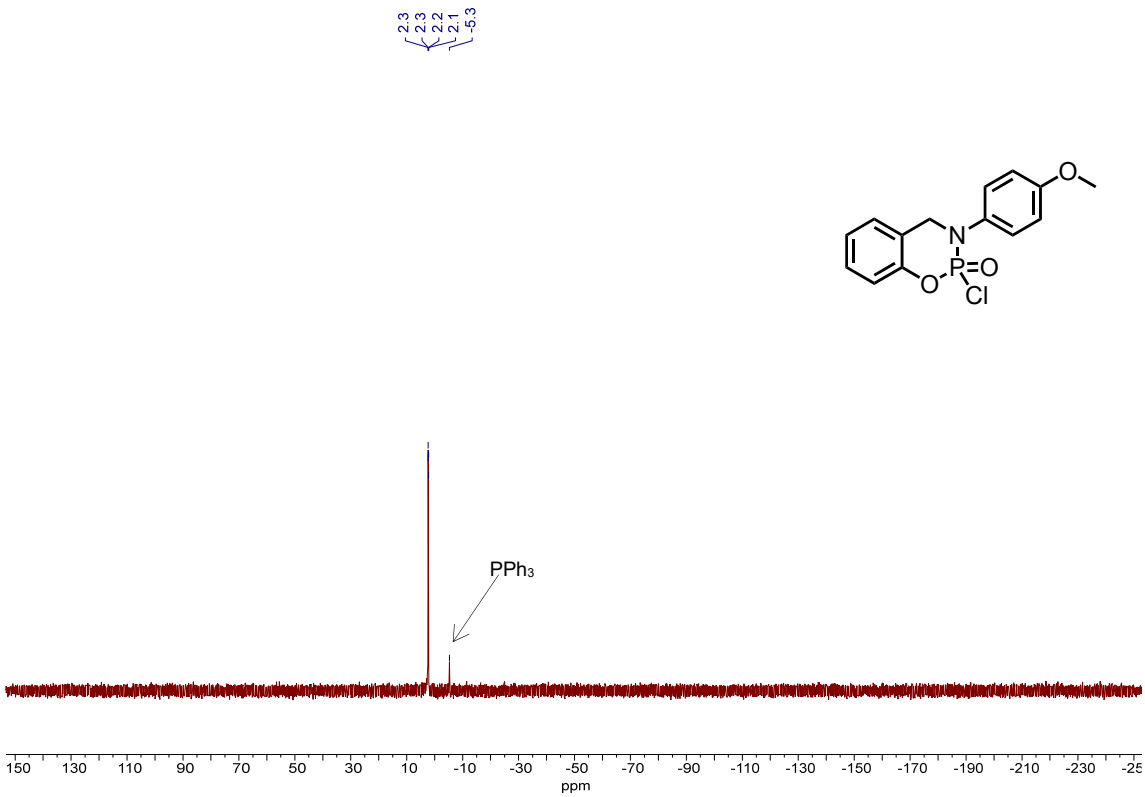
[1]H NMR Spectrum for Compound **8c** (400 MHz, $CDCl_3$)



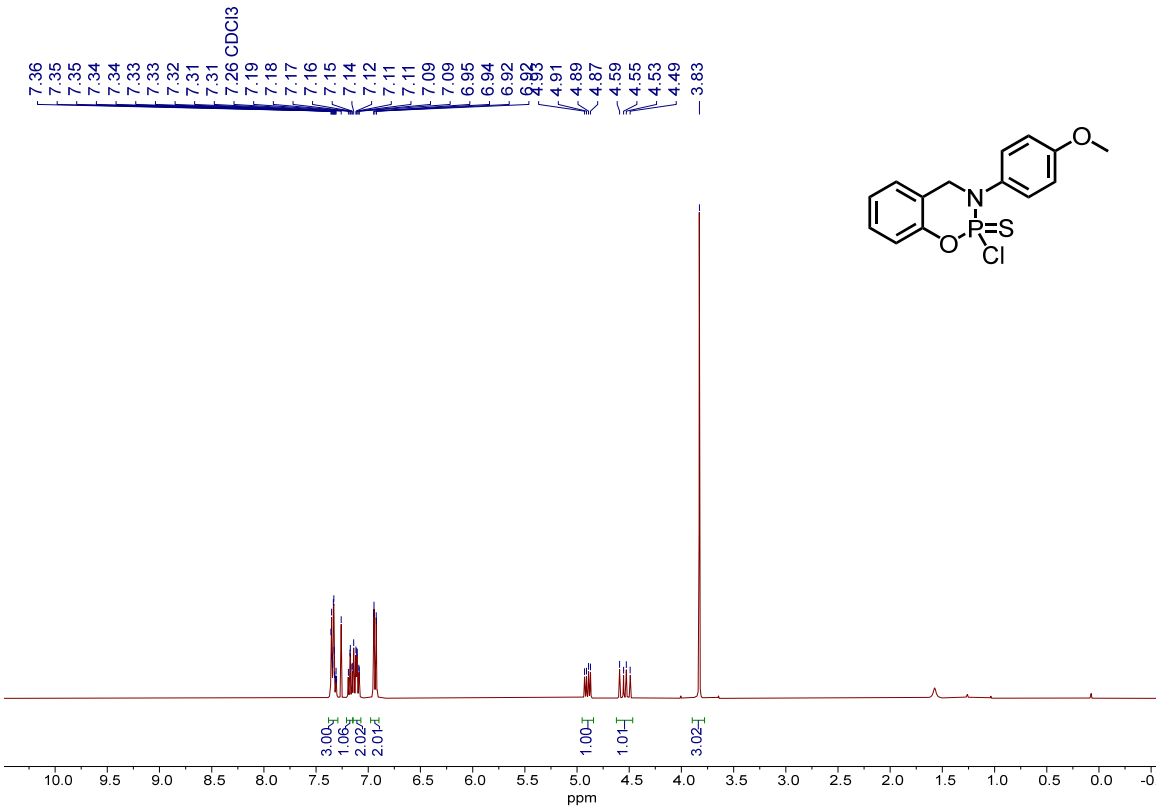
[13]C NMR Spectrum for Compound **8c** (101 MHz, $CDCl_3$)



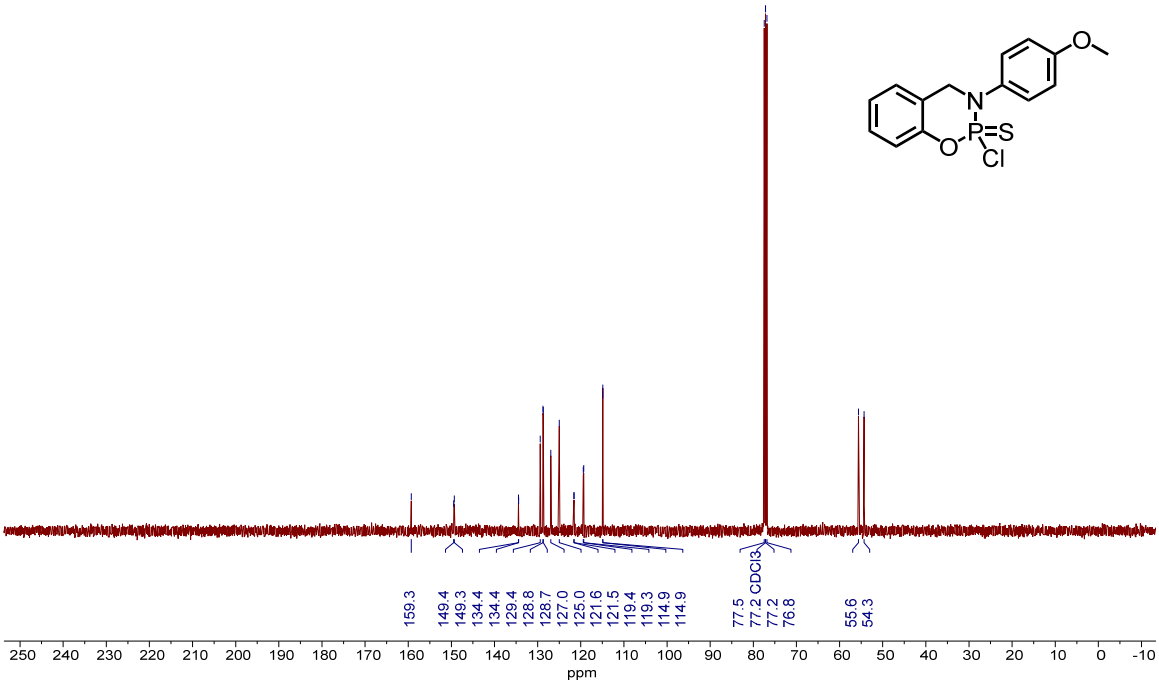
^{31}P NMR Spectrum for Compound **8c** (162 MHz, $CDCl_3$)



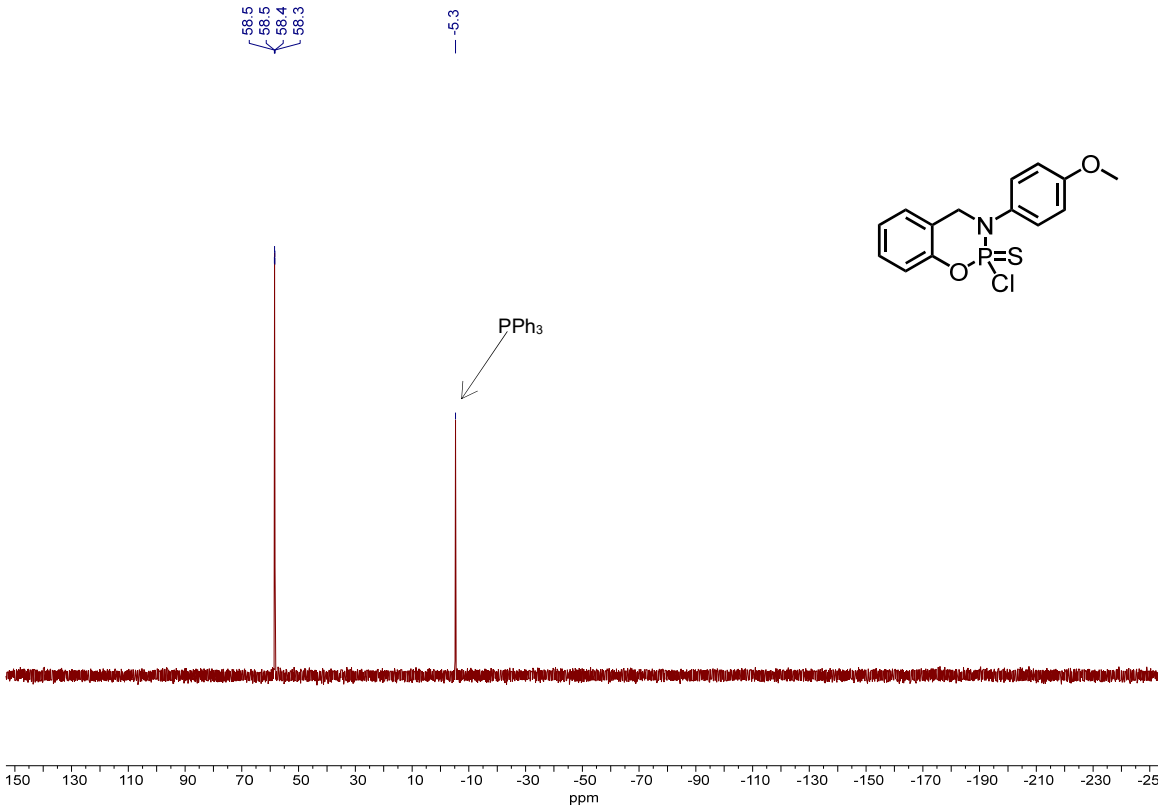
^{1}H NMR Spectrum for Compound **8d** (400 MHz, $CDCl_3$)



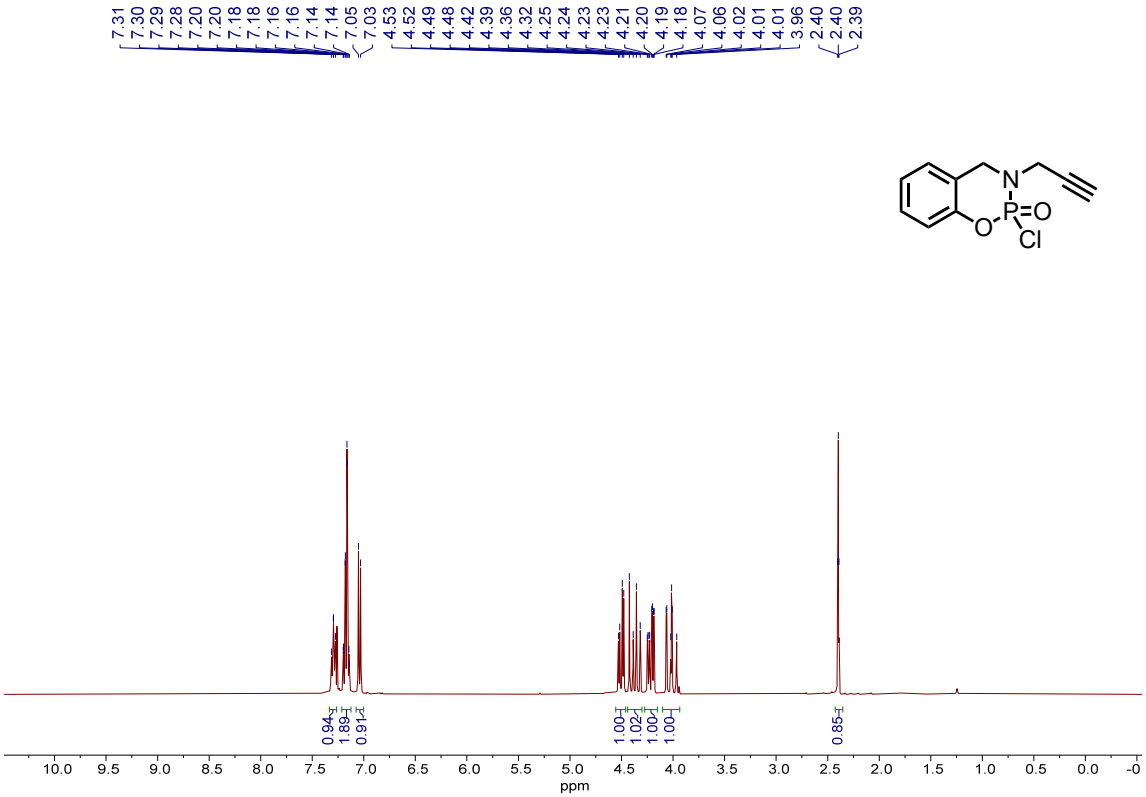
^{13}C NMR Spectrum for Compound **8d** (101 MHz, $CDCl_3$)



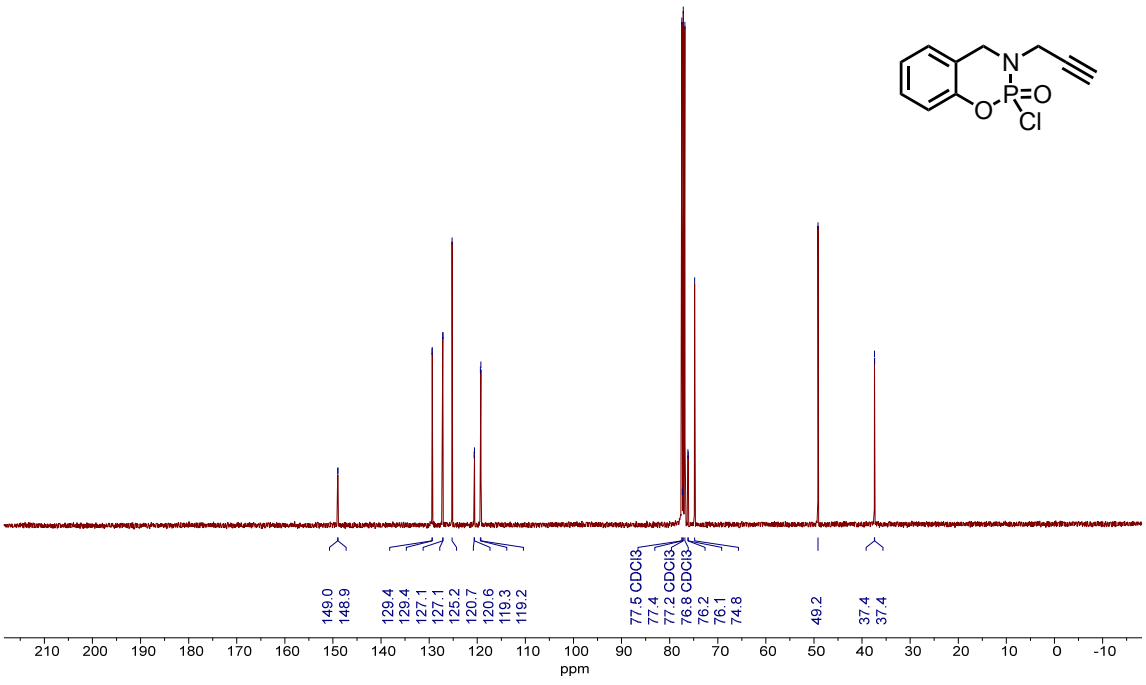
^{31}P NMR Spectrum for Compound **8d** (162 MHz, $CDCl_3$)



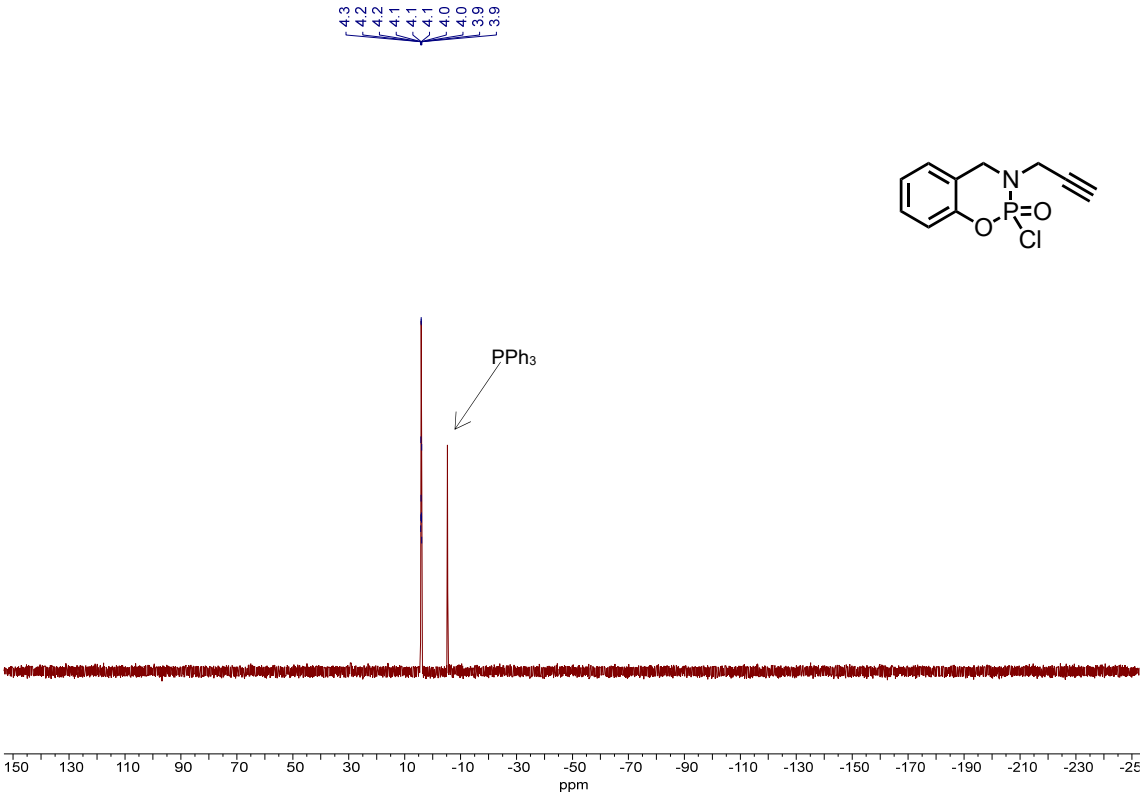
^{1}H NMR Spectrum for Compound **8e** (400 MHz, $CDCl_3$)



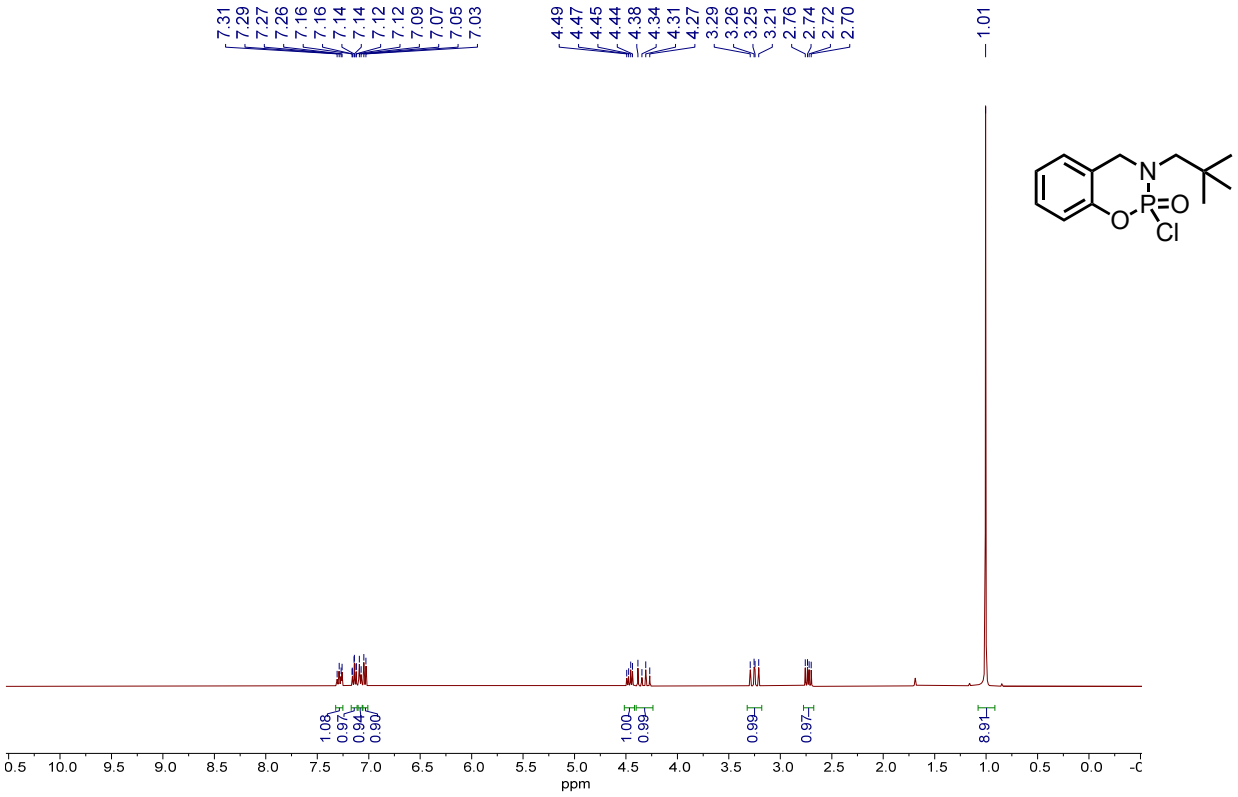
^{13}C NMR Spectrum for Compound **8e** (101 MHz, $CDCl_3$)



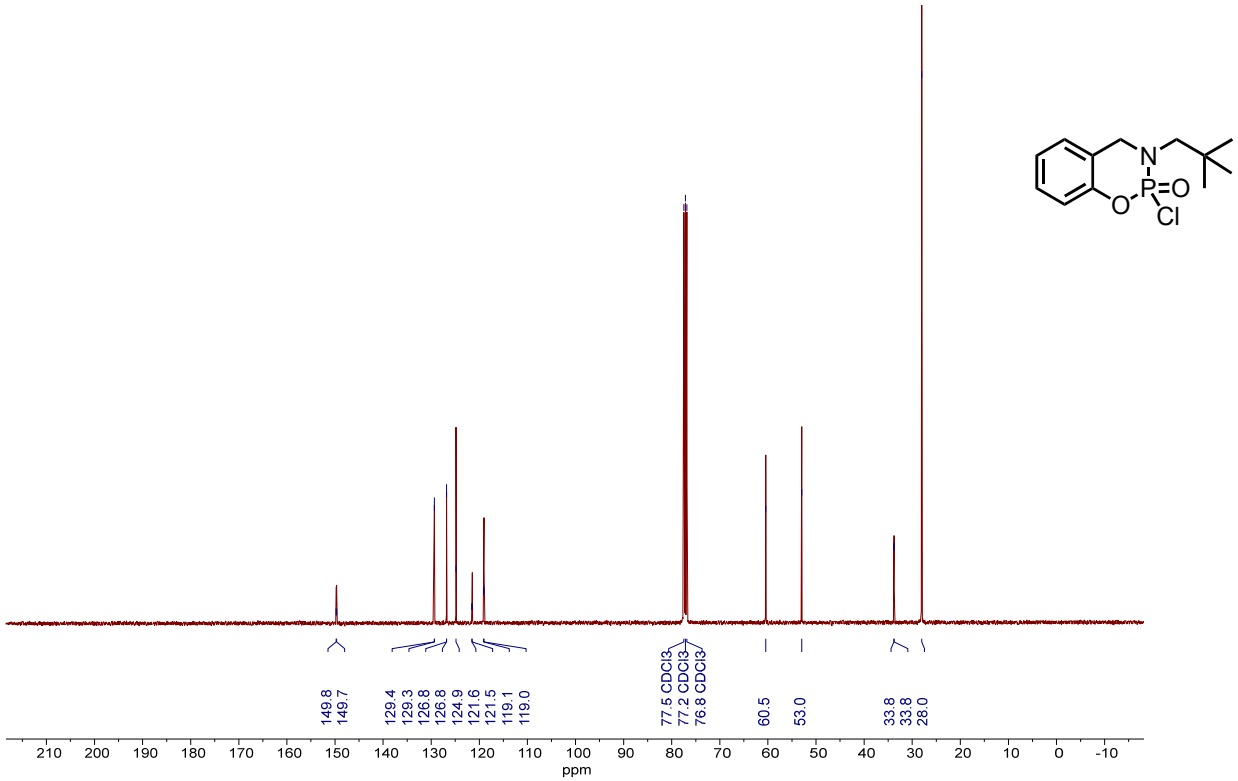
^{31}P NMR Spectrum for Compound **8e** (162 MHz, $CDCl_3$)



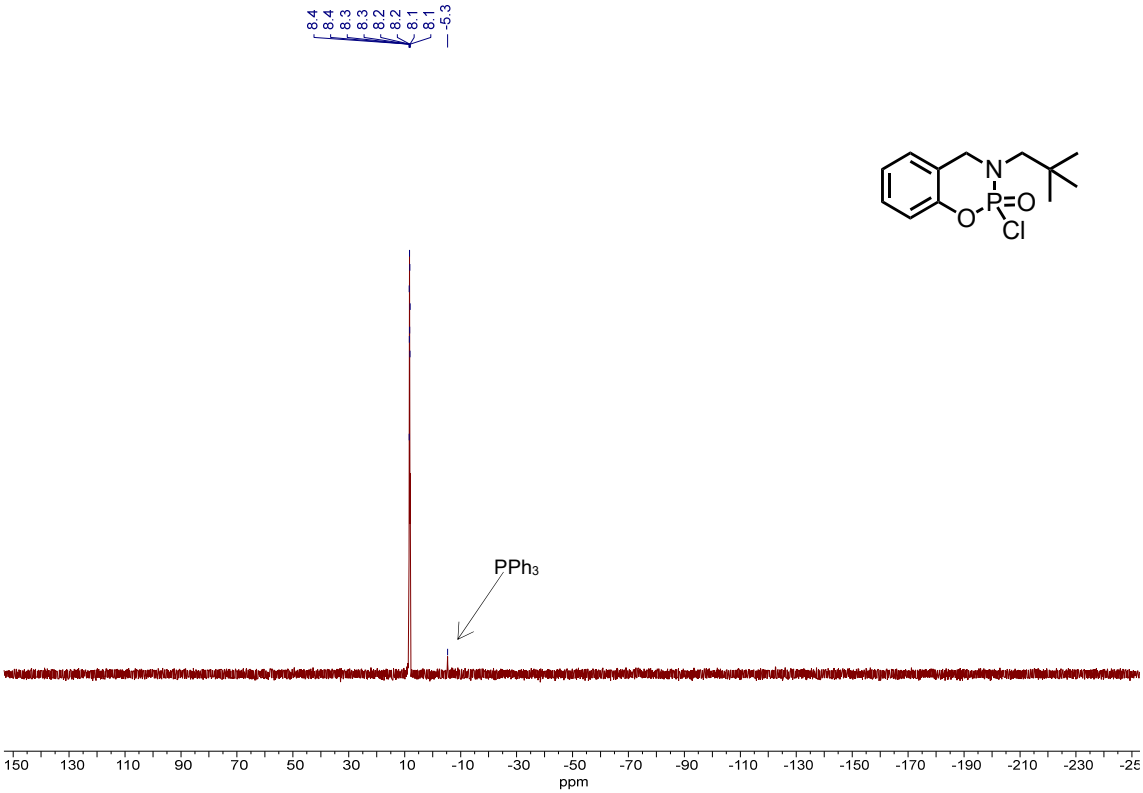
^{1}H NMR Spectrum for Compound **8f** (400 MHz, $CDCl_3$)



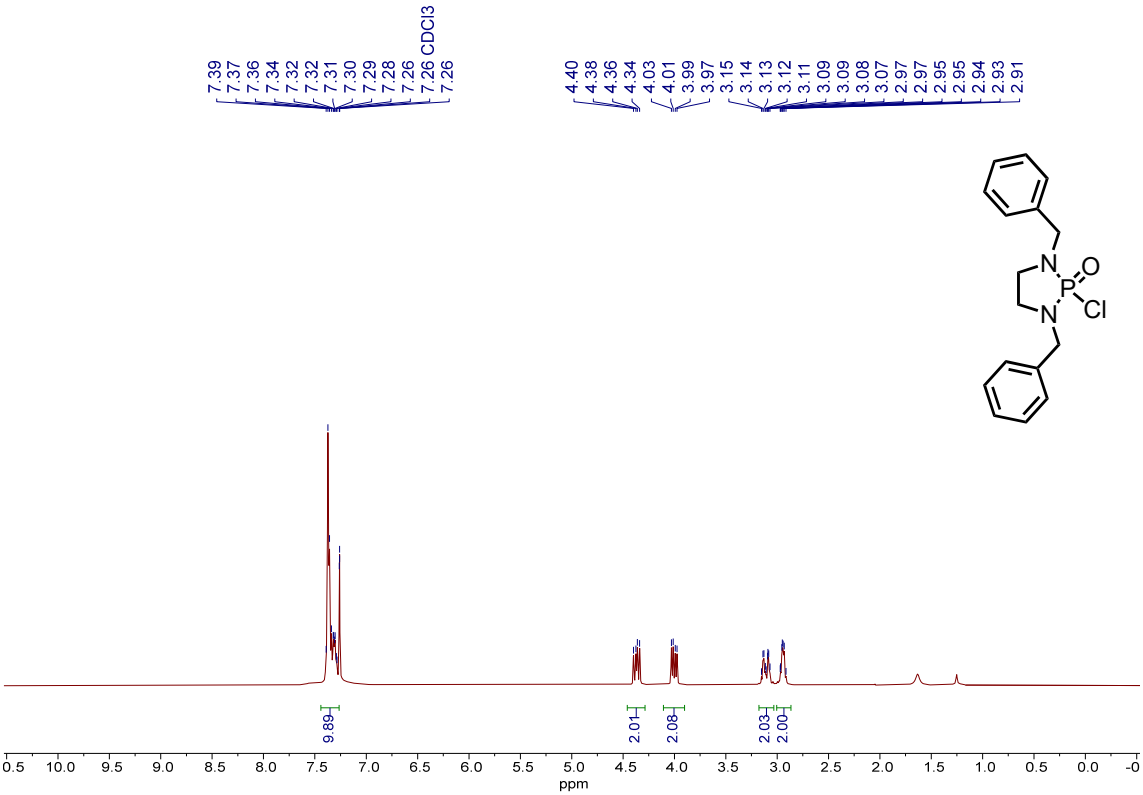
^{13}C NMR Spectrum for Compound **8f** (101 MHz, $CDCl_3$)



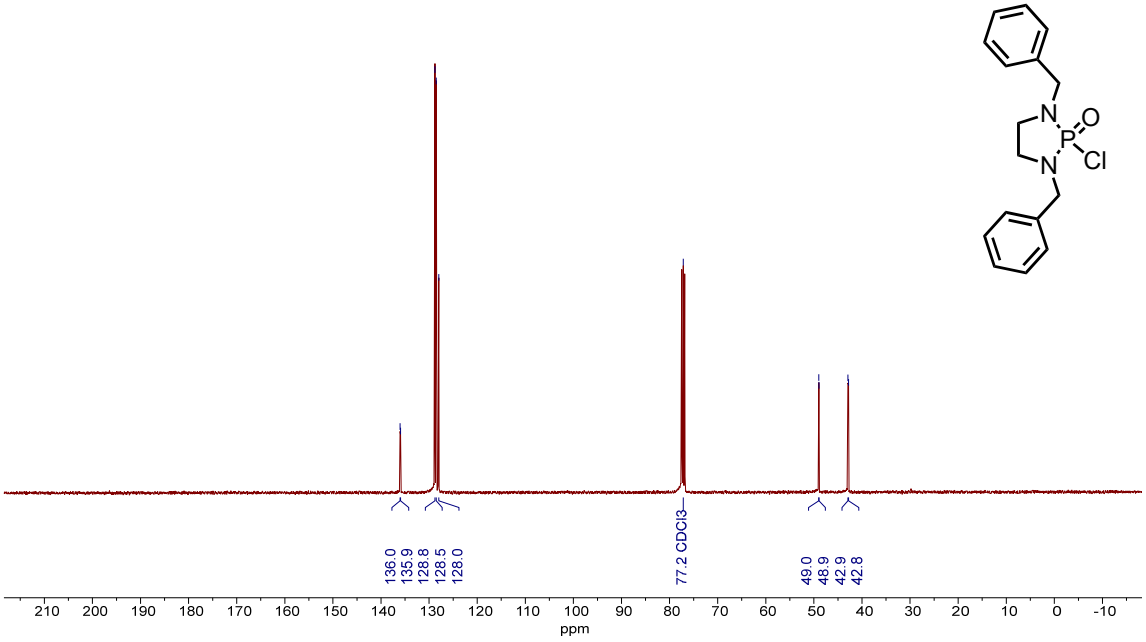
^{31}P NMR Spectrum for Compound **8f** (162 MHz, $CDCl_3$)



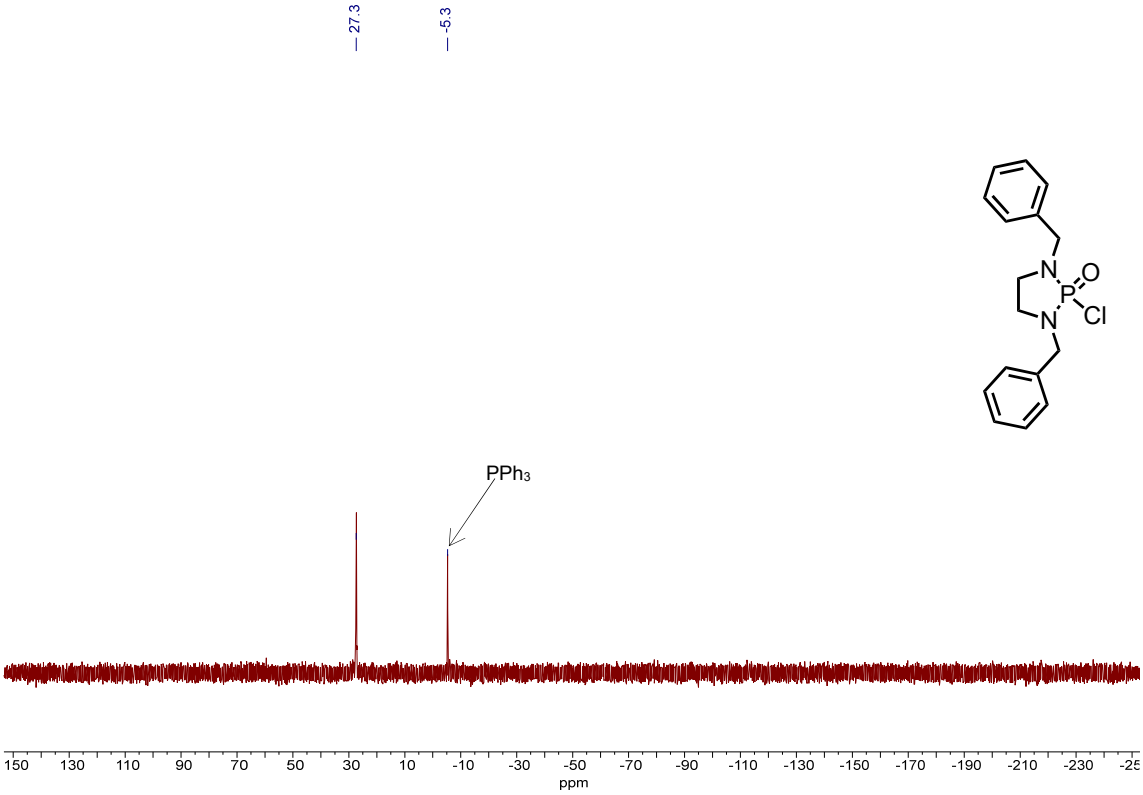
^{1}H NMR Spectrum for Compound **8g**(400 MHz, $CDCl_3$)



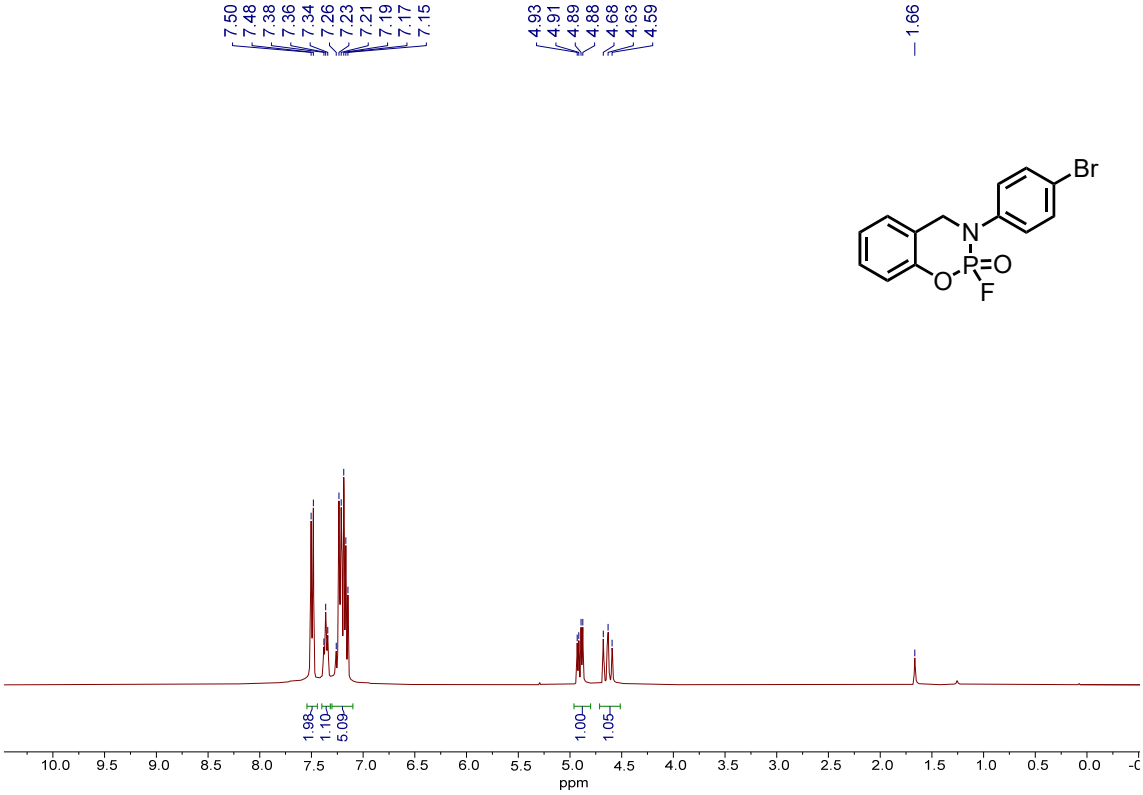
^{13}C NMR Spectrum for Compound **8g** (101 MHz, $CDCl_3$)



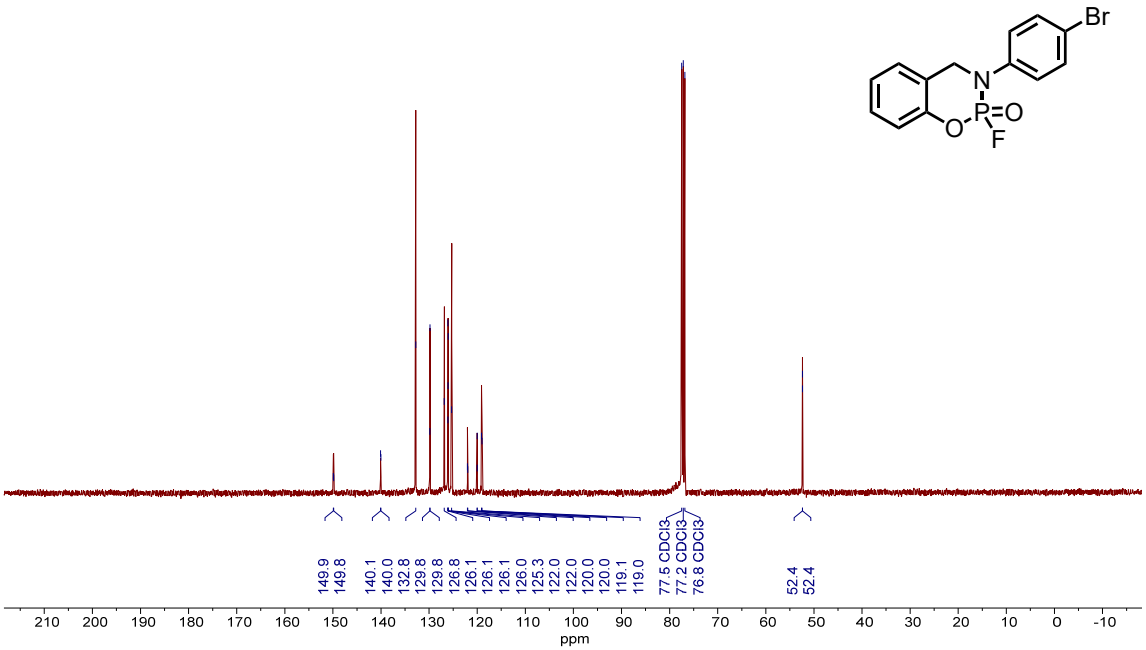
^{31}P NMR Spectrum for Compound **8g** (162 MHz, $CDCl_3$)



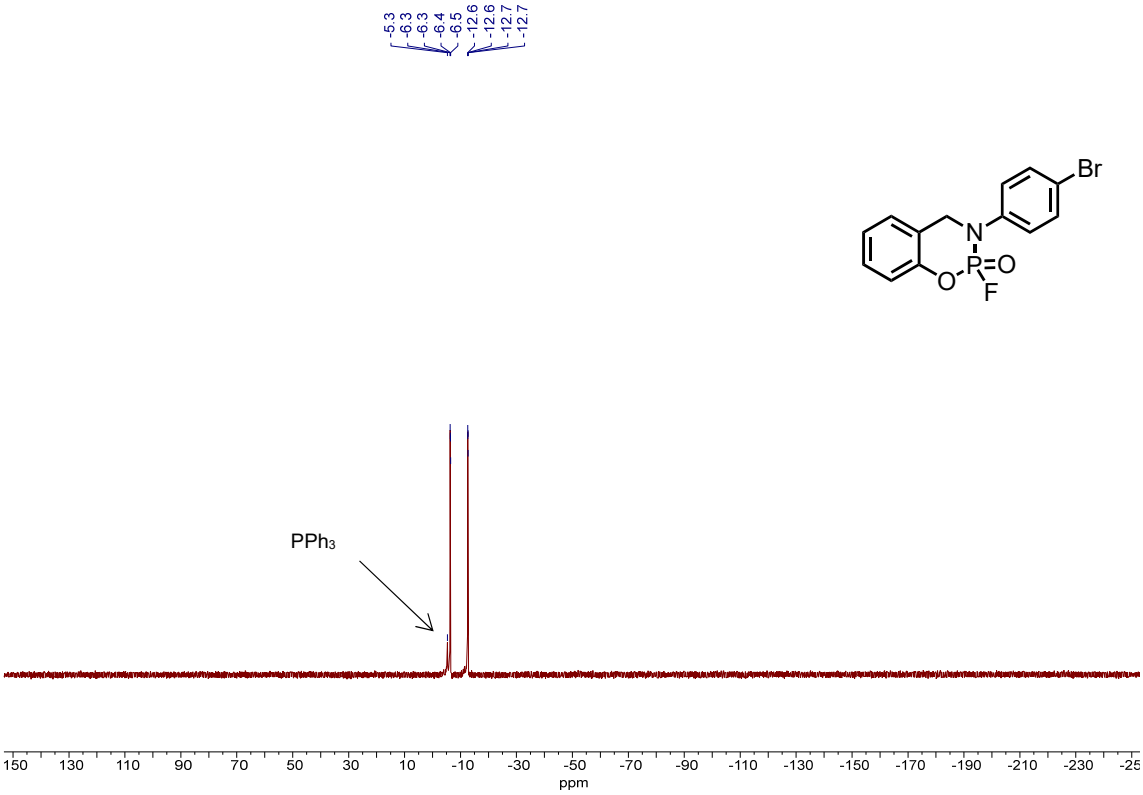
^{1}H NMR Spectrum for Compound **10a** (400 MHz, $CDCl_3$)



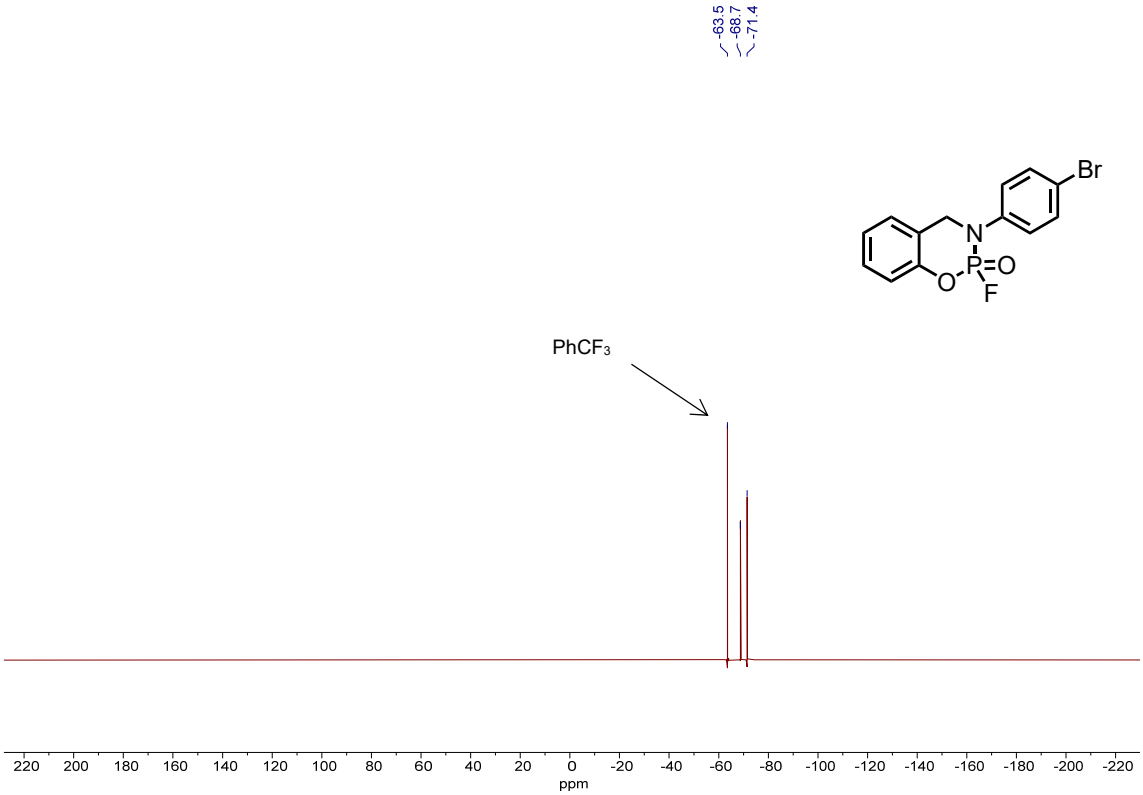
^{13}C NMR Spectrum for Compound **10a** (101 MHz, $CDCl_3$)



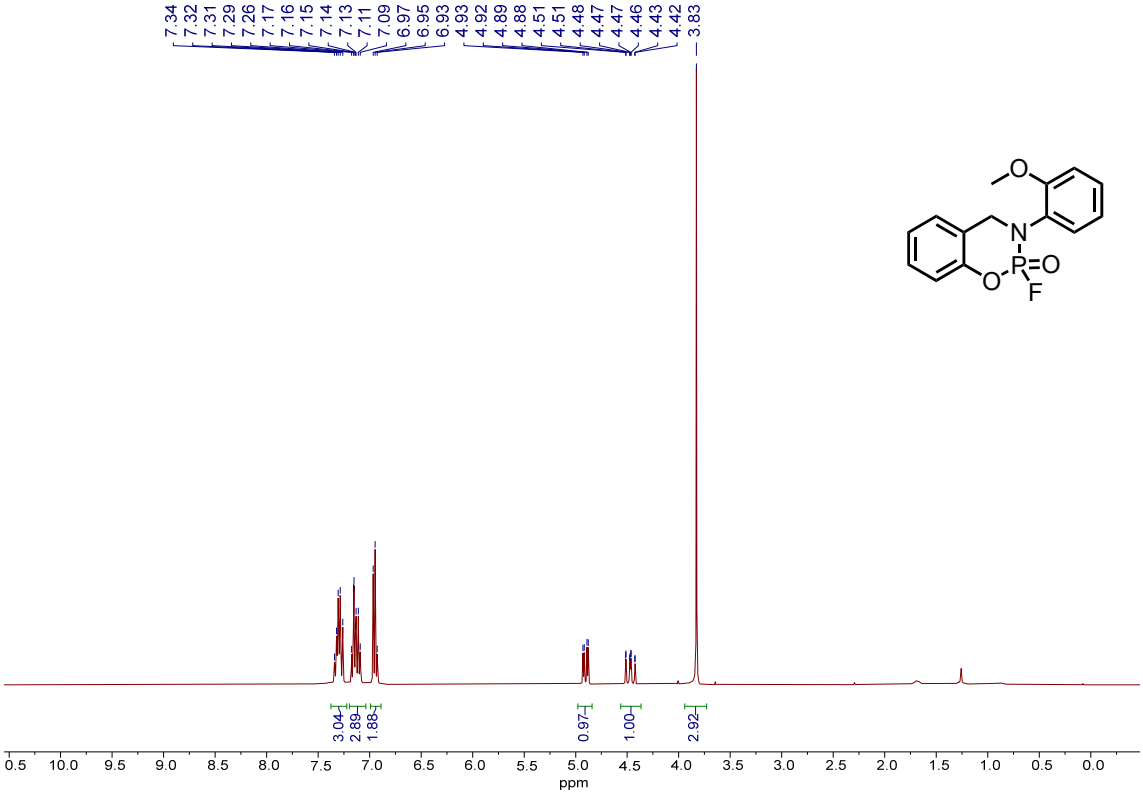
^{31}P NMR Spectrum for Compound **10a** (162 MHz, $CDCl_3$)



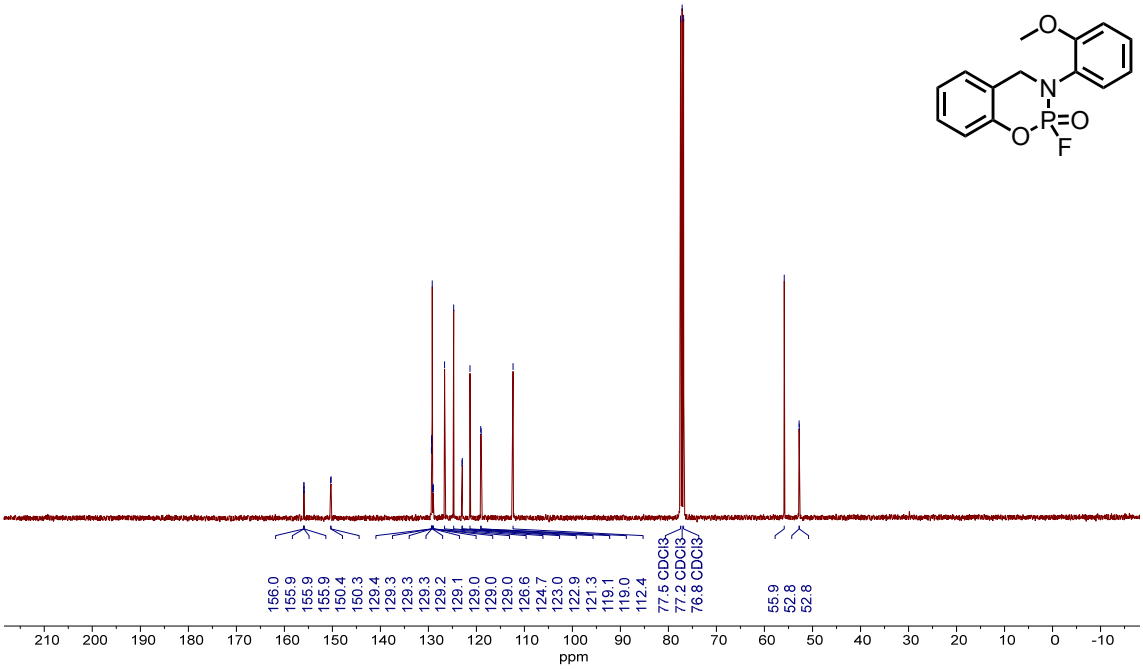
^{19}F NMR Spectrum for Compound **10a** (376 MHz, $CDCl_3$)



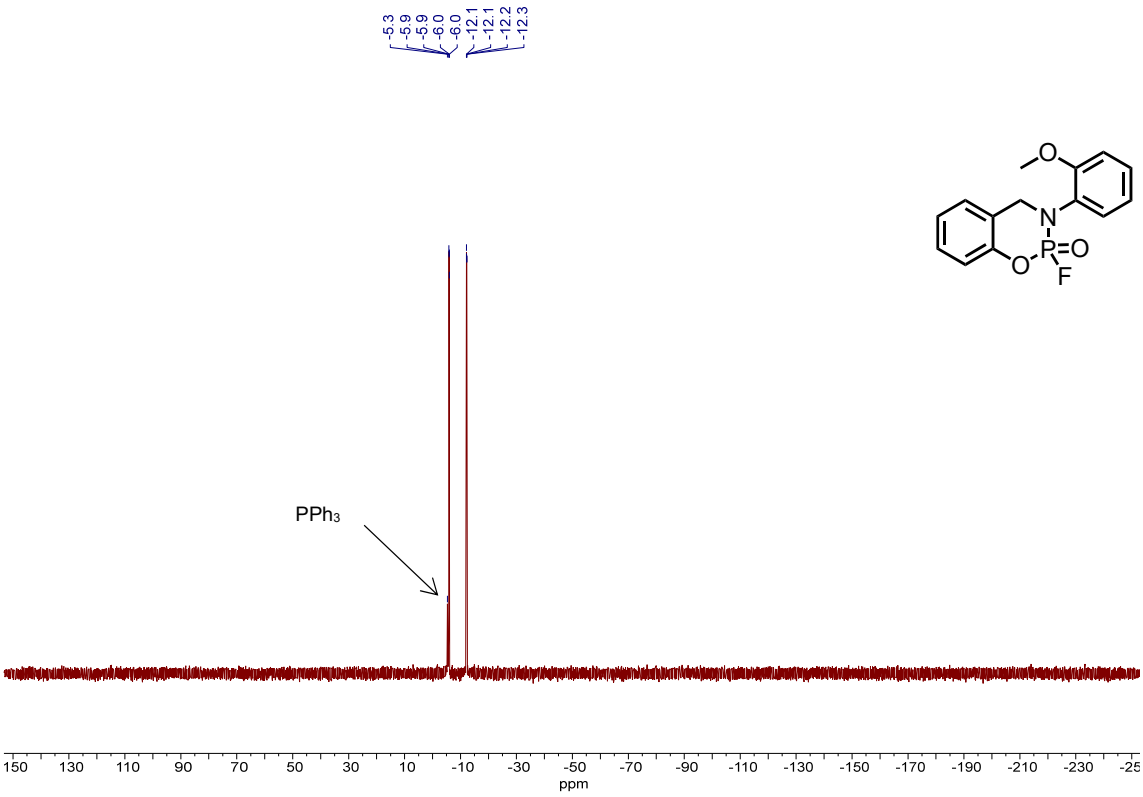
^{1}H NMR Spectrum for Compound **10b** (400 MHz, $CDCl_3$)



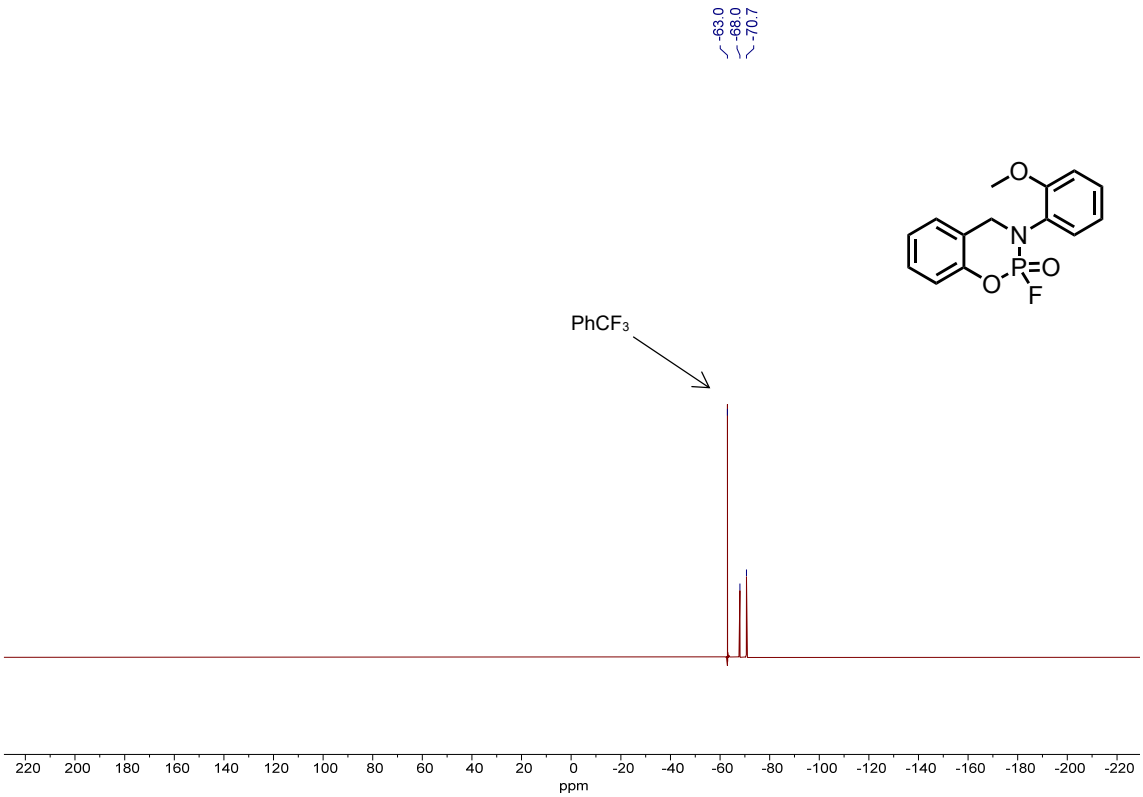
^{13}C NMR Spectrum for Compound **10b** (101 MHz, $CDCl_3$)



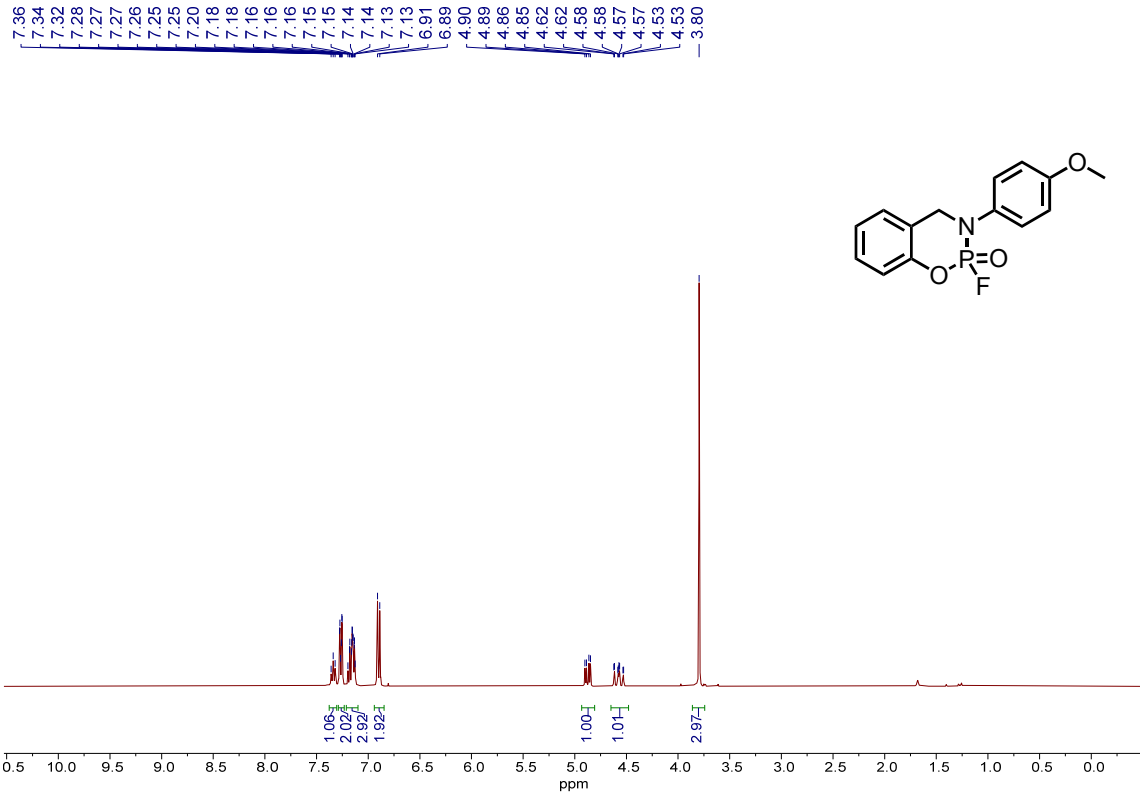
^{31}P NMR Spectrum for Compound **10b** (162 MHz, $CDCl_3$)



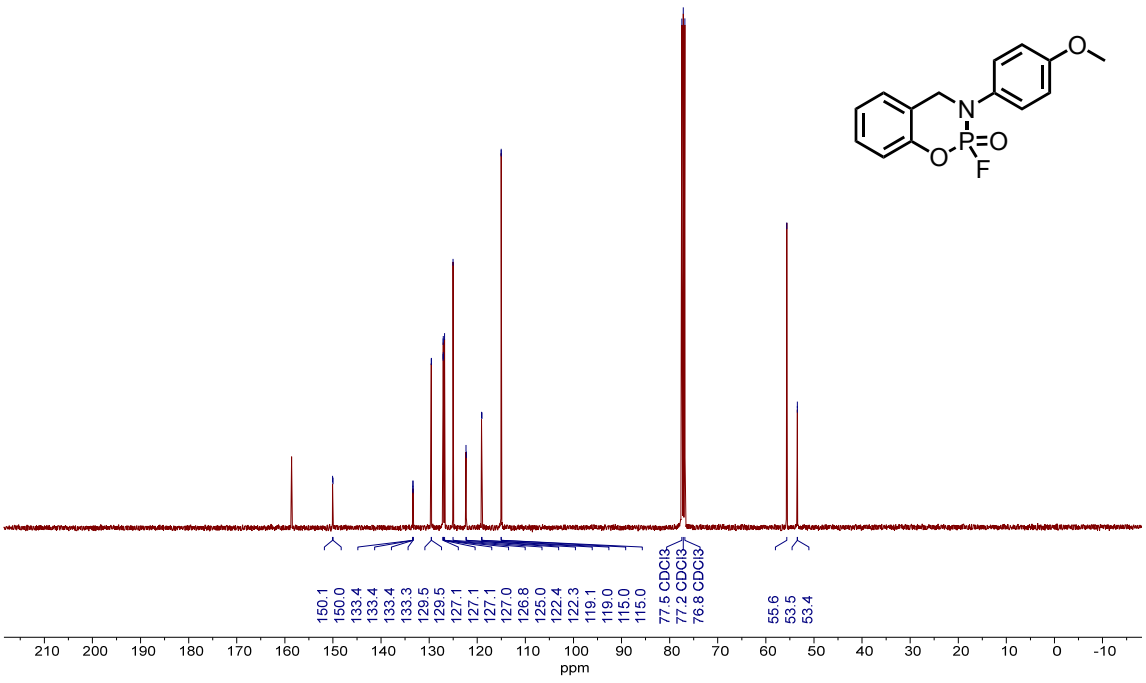
^{19}F NMR Spectrum for Compound **10b** (376 MHz, $CDCl_3$)



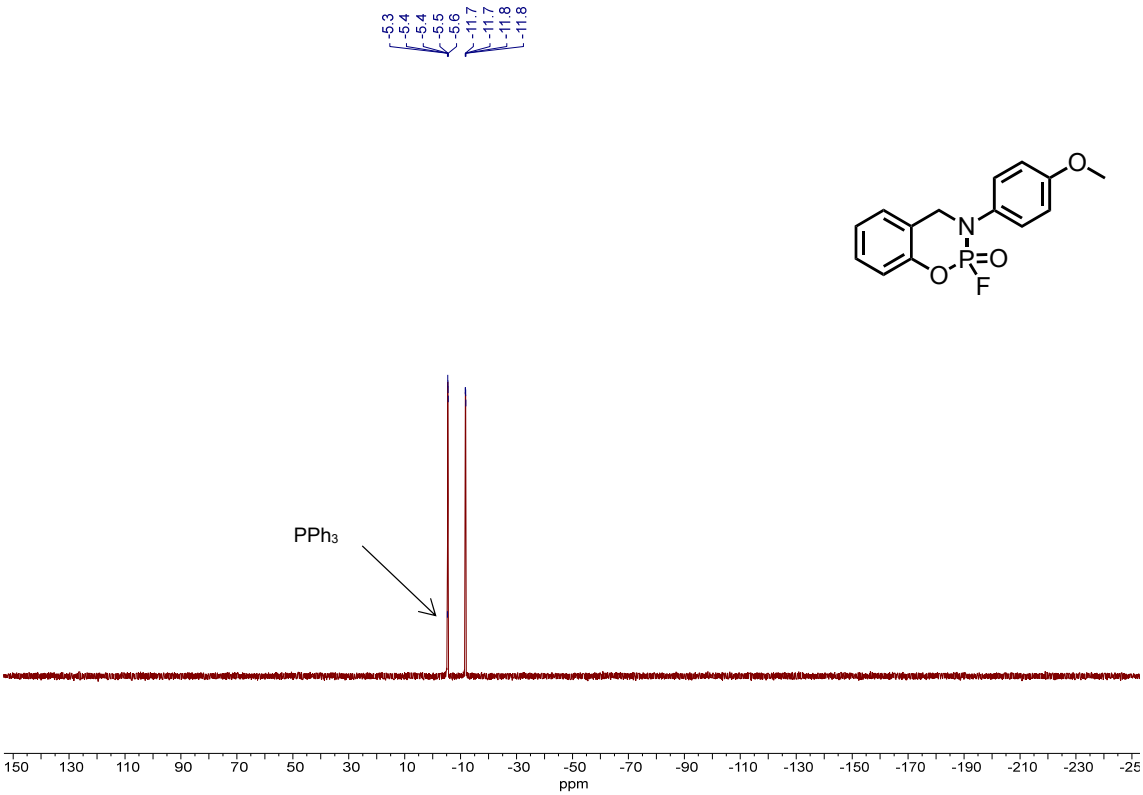
[1]H NMR Spectrum for Compound **10c** (400 MHz, $CDCl_3$)



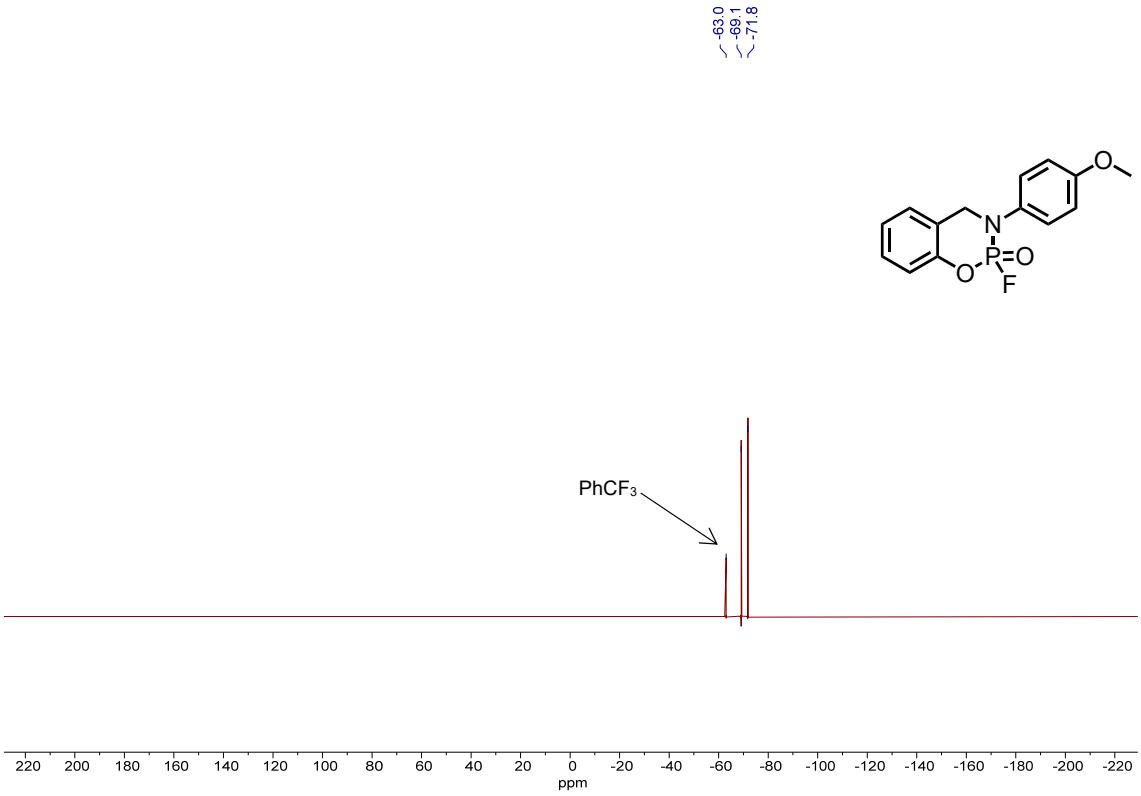
[13]C NMR Spectrum for Compound **10c** (101 MHz, $CDCl_3$)



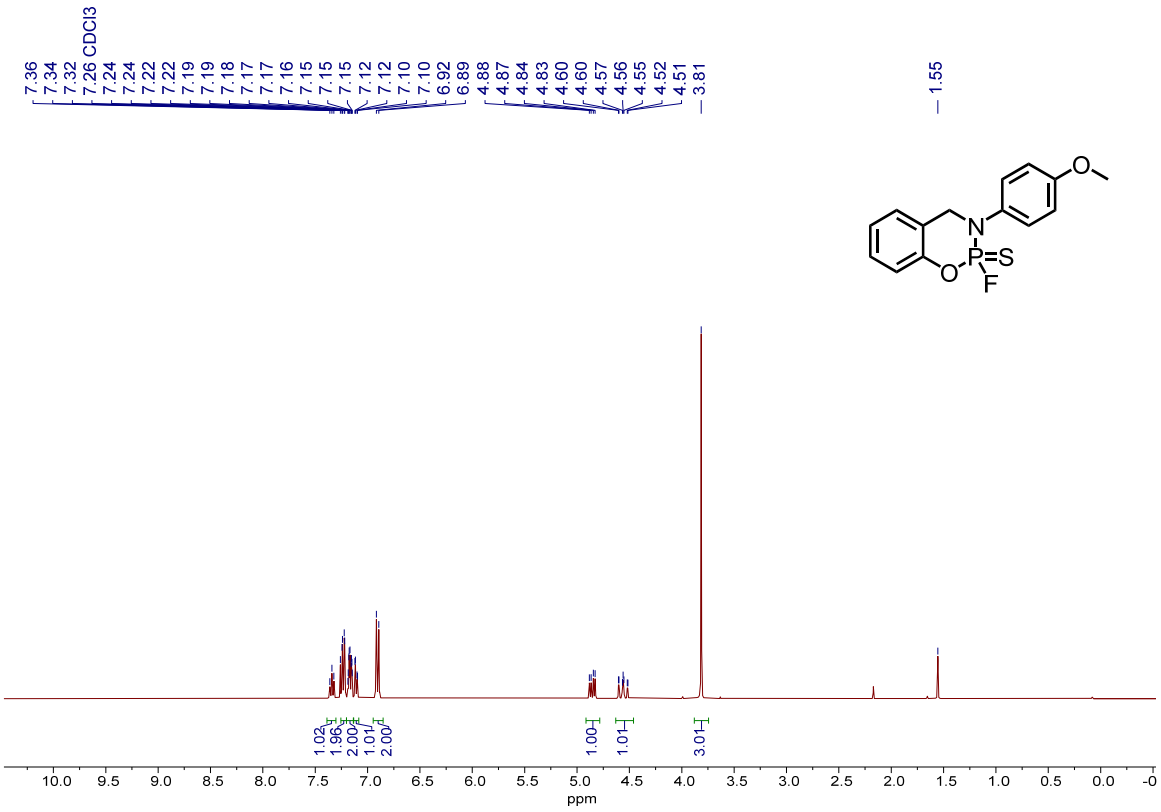
^{31}P NMR Spectrum for Compound **10c** (162 MHz, $CDCl_3$)



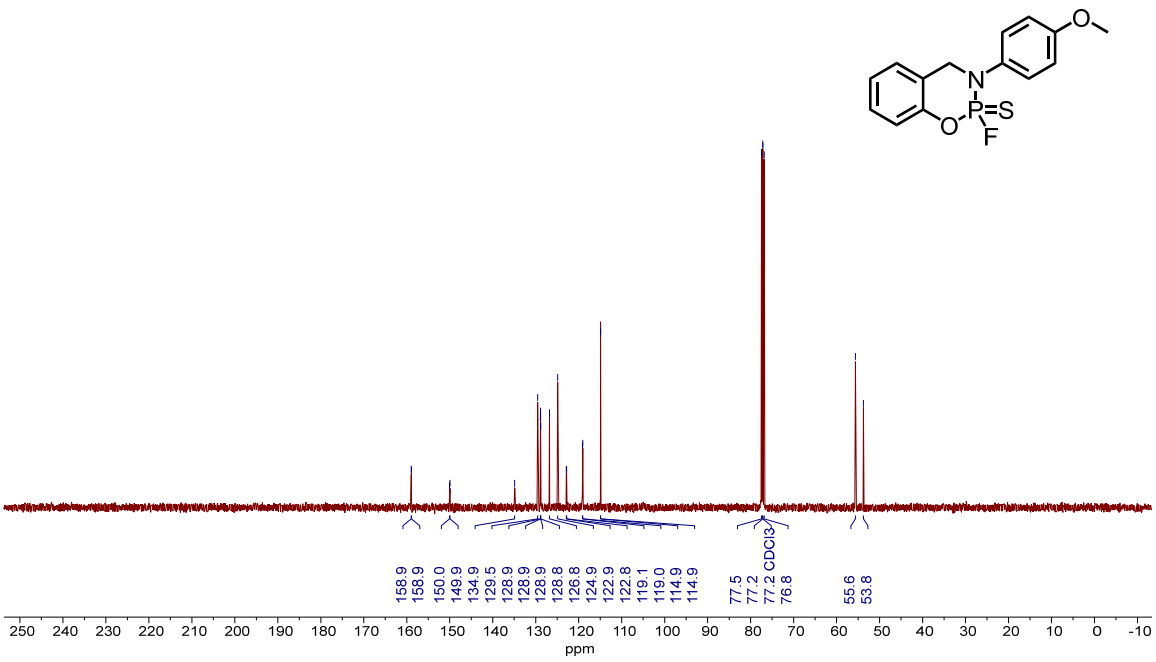
^{19}F NMR Spectrum for Compound **10c** (376 MHz, $CDCl_3$)



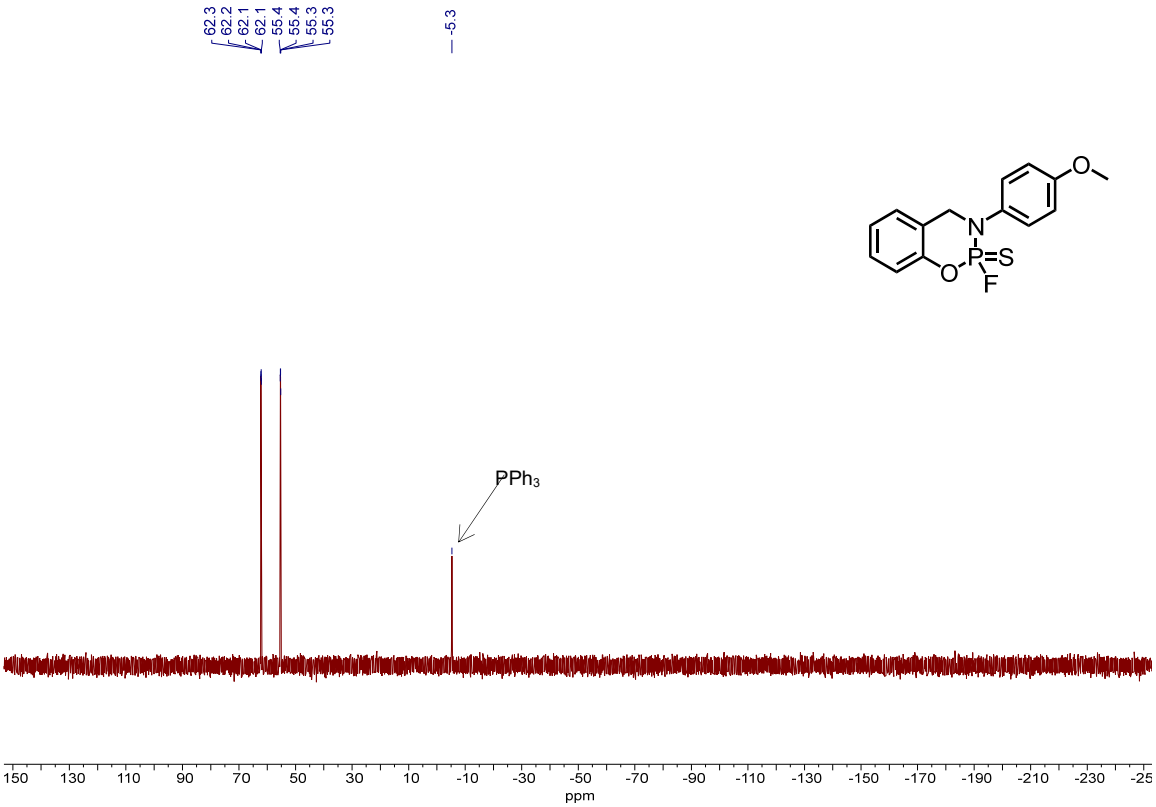
^{1}H NMR Spectrum for Compound **10d** (400 MHz, $CDCl_3$)



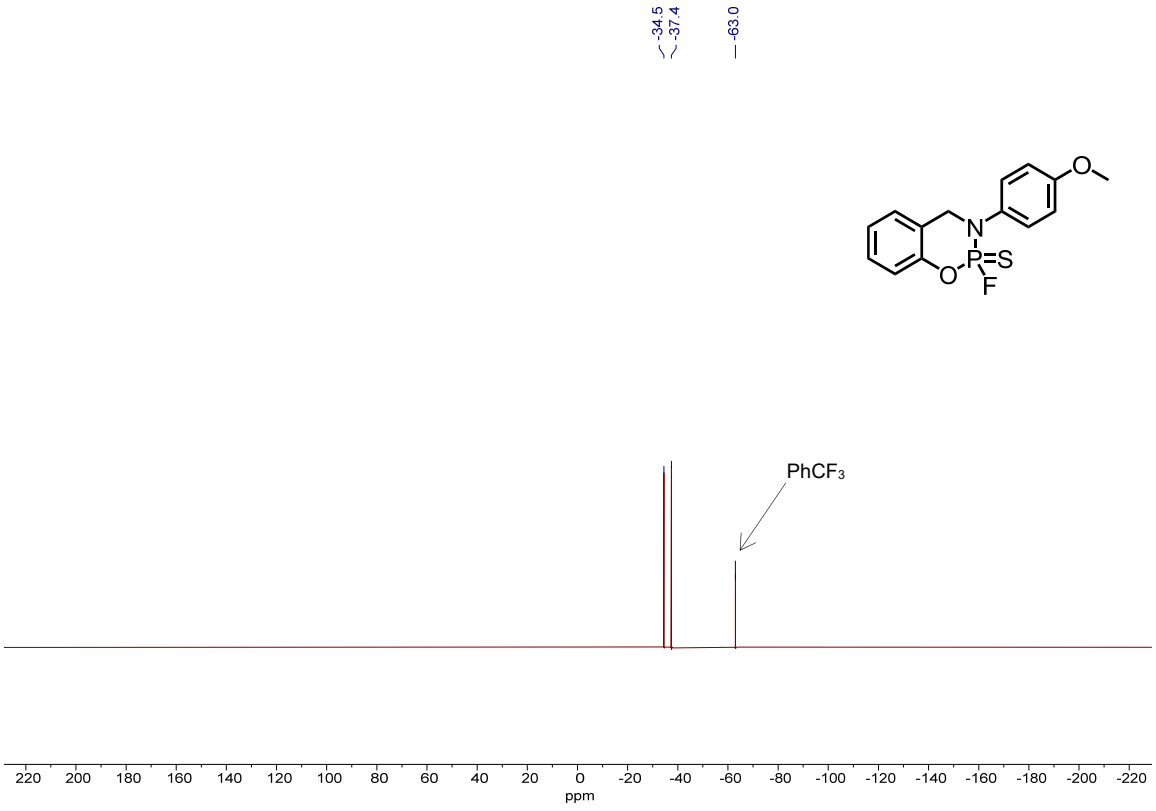
^{13}C NMR Spectrum for Compound **10d** (101 MHz, $CDCl_3$)



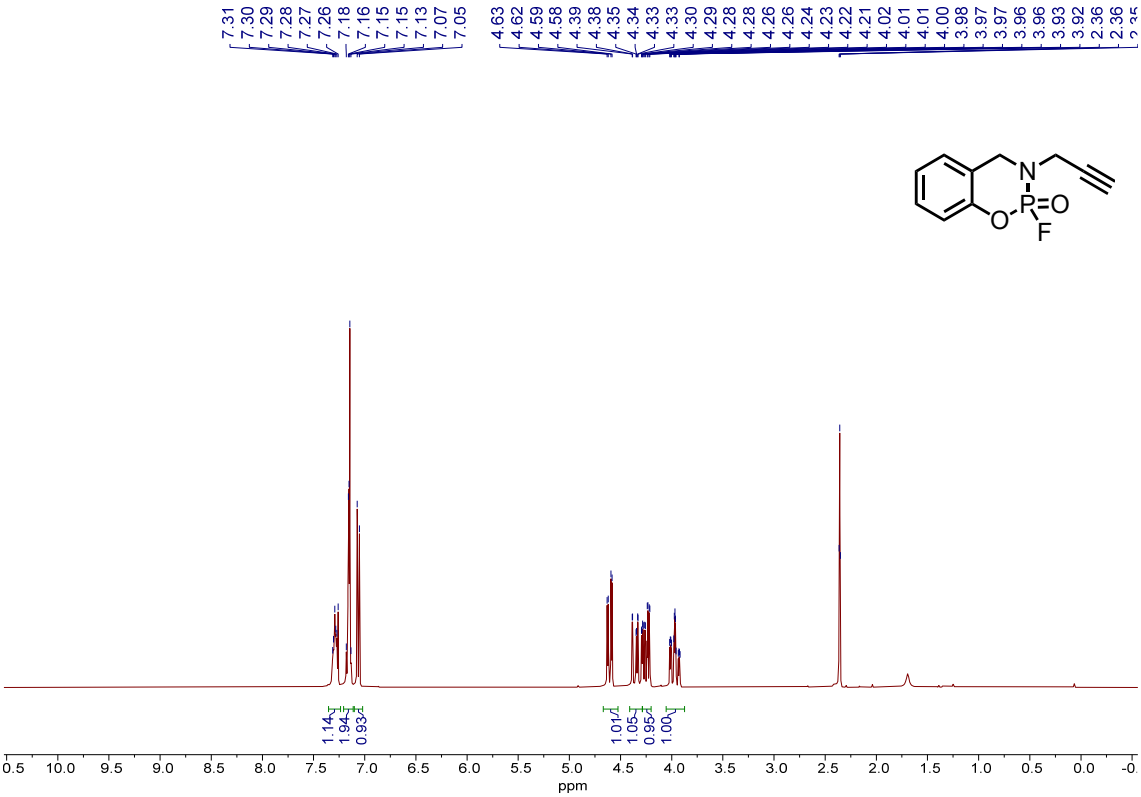
^{31}P NMR Spectrum for Compound **10d** (162 MHz, $CDCl_3$)



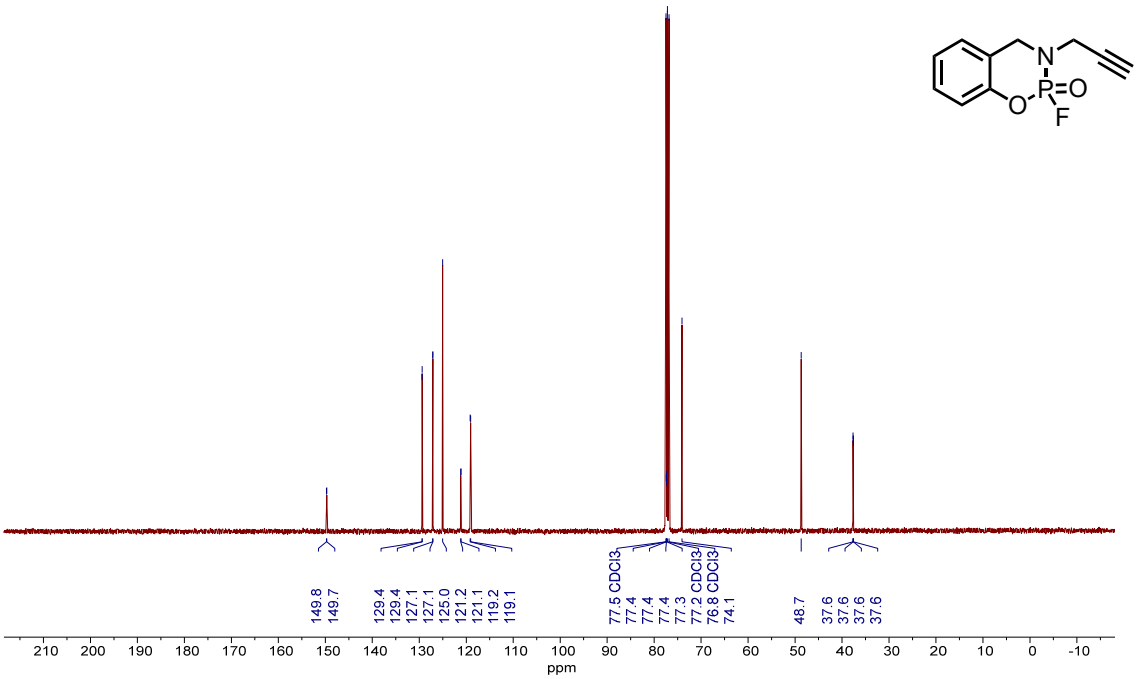
^{19}F NMR Spectrum for Compound **10d** (376 MHz, $CDCl_3$)



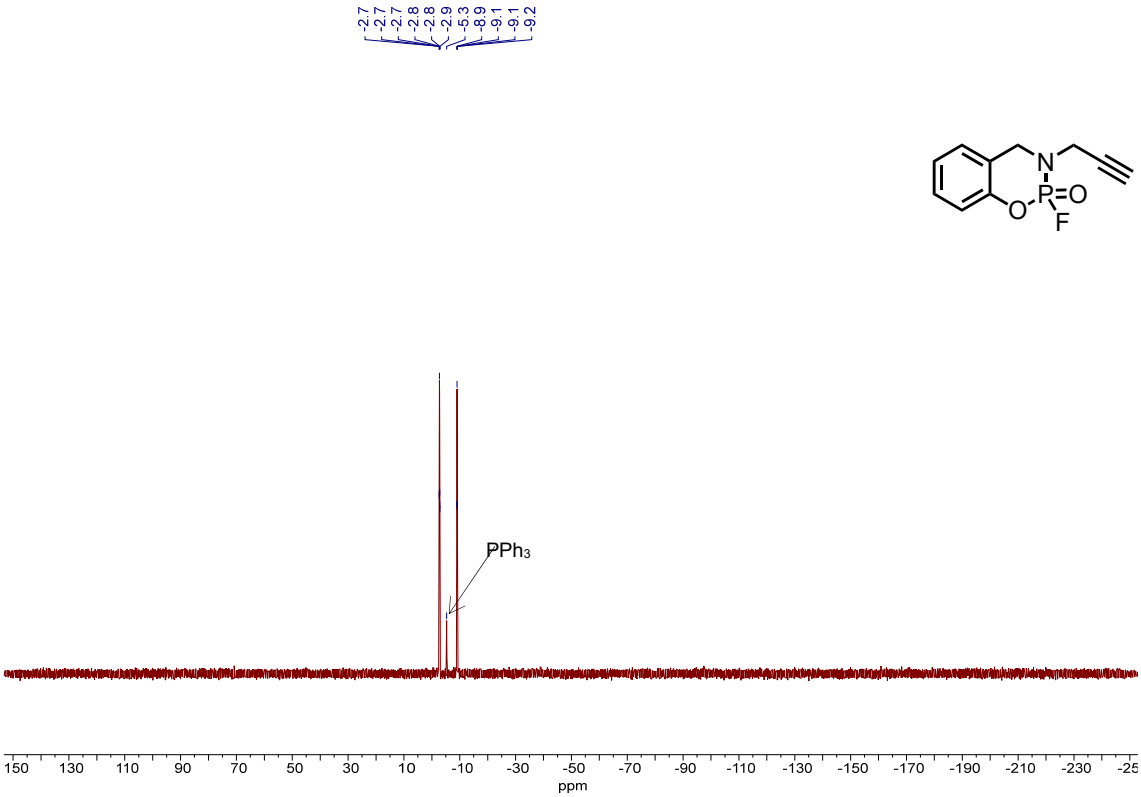
^{1}H NMR Spectrum for Compound **10e** (400 MHz, $CDCl_3$)



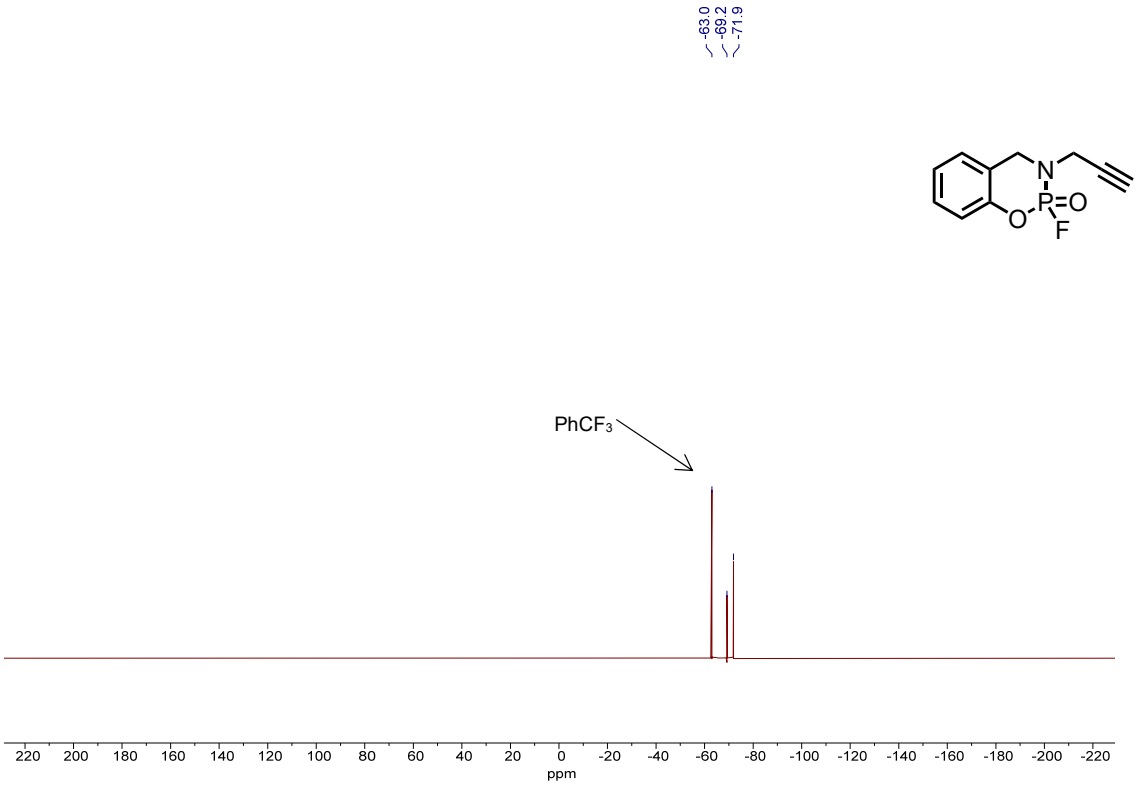
^{13}C NMR Spectrum for Compound **10e** (101 MHz, $CDCl_3$)



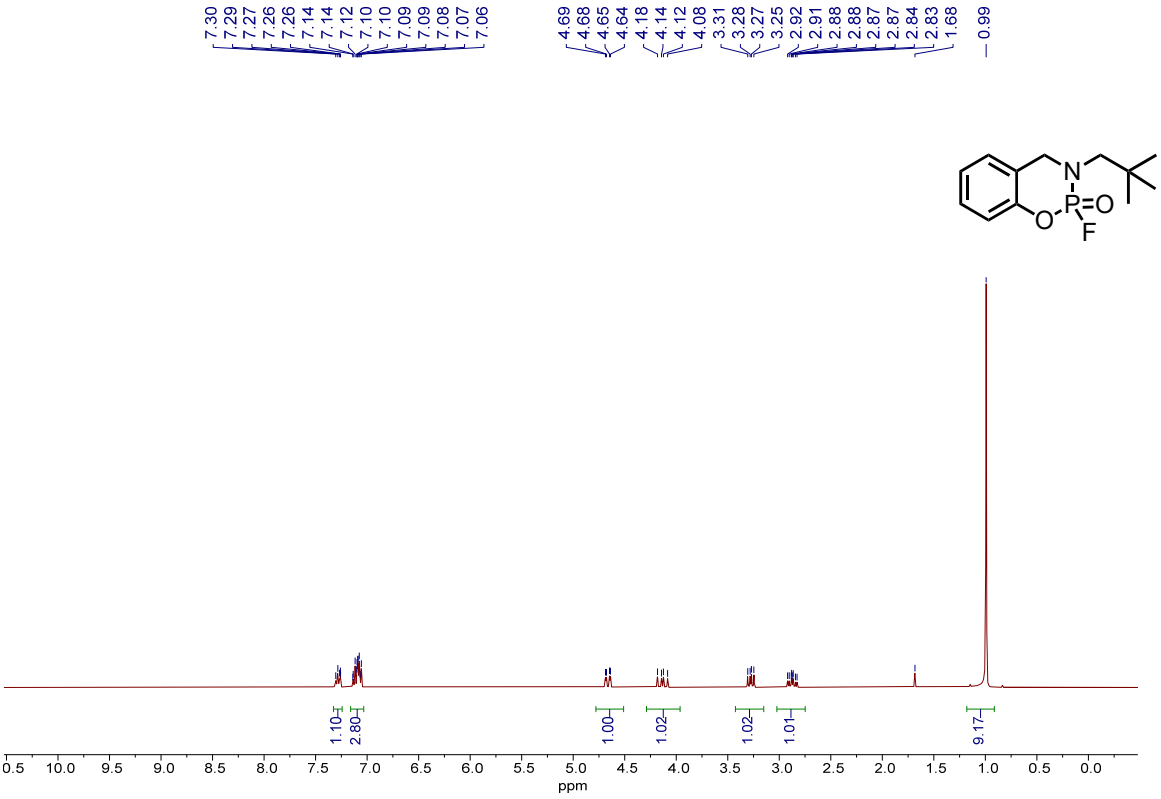
^{31}P NMR Spectrum for Compound **10e** (162 MHz, $CDCl_3$)



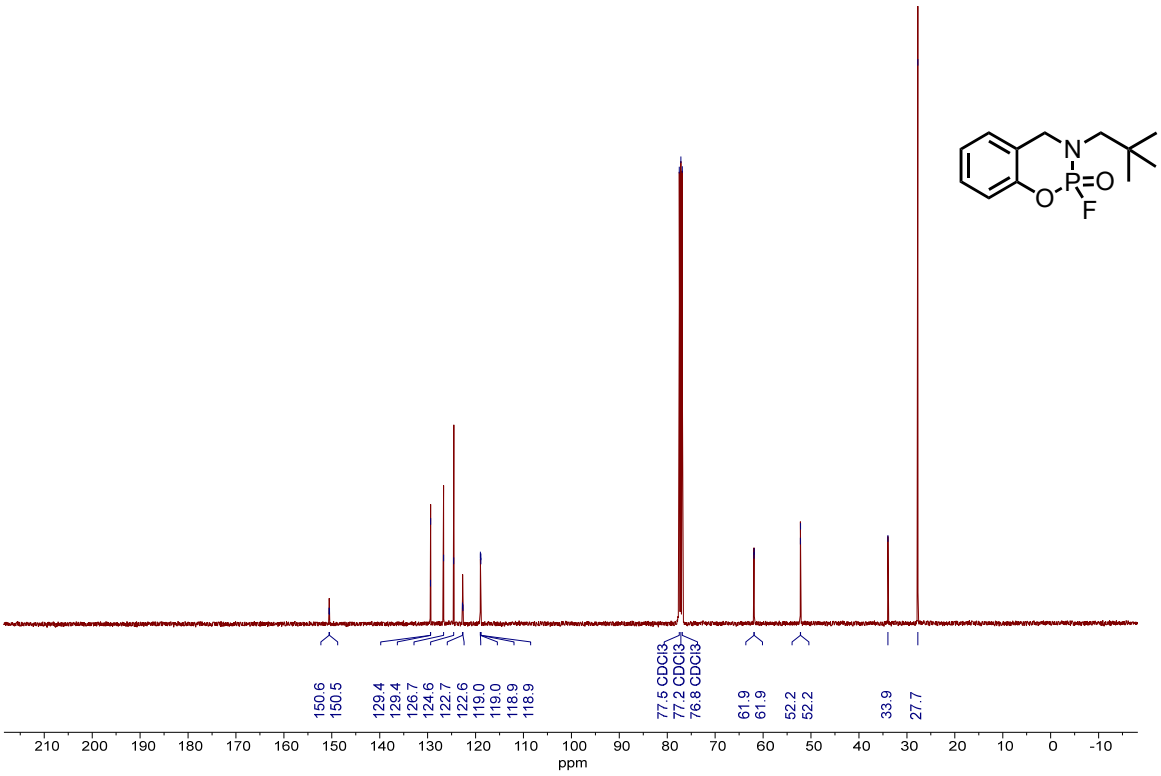
^{19}F NMR Spectrum for Compound **10e** (376 MHz, $CDCl_3$)



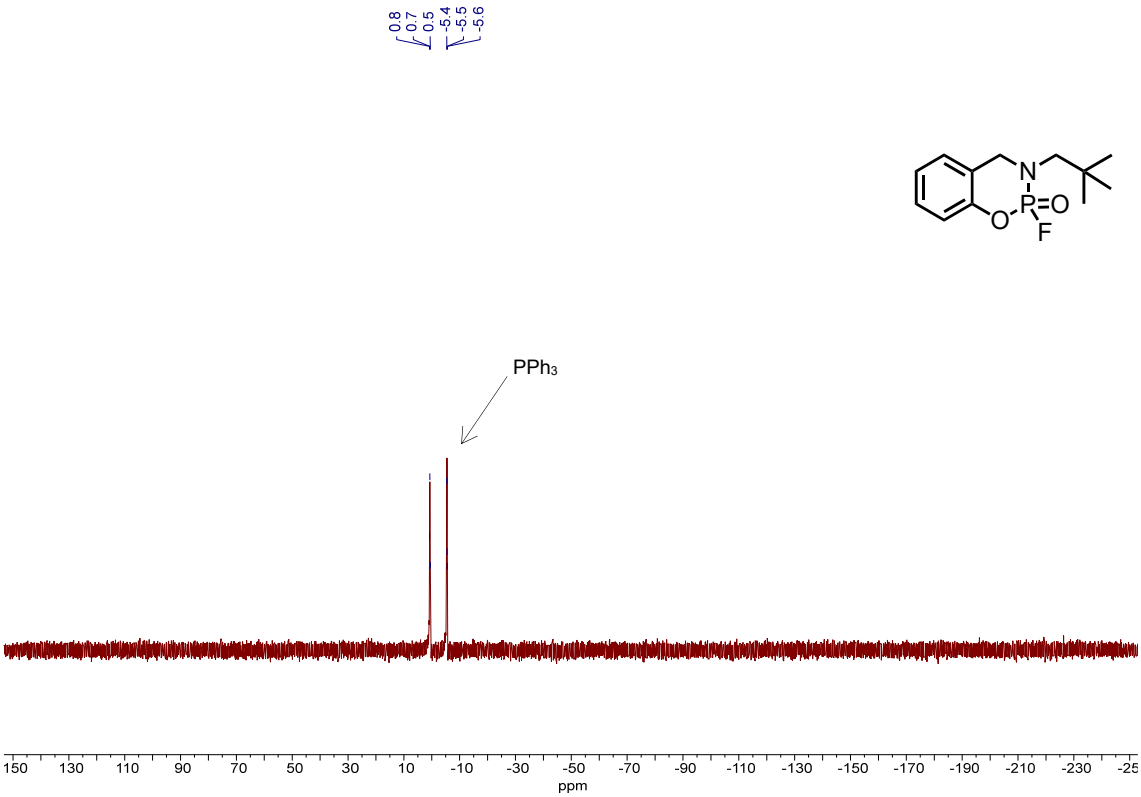
^{1}H NMR Spectrum for Compound **10f** (400 MHz, $CDCl_3$)



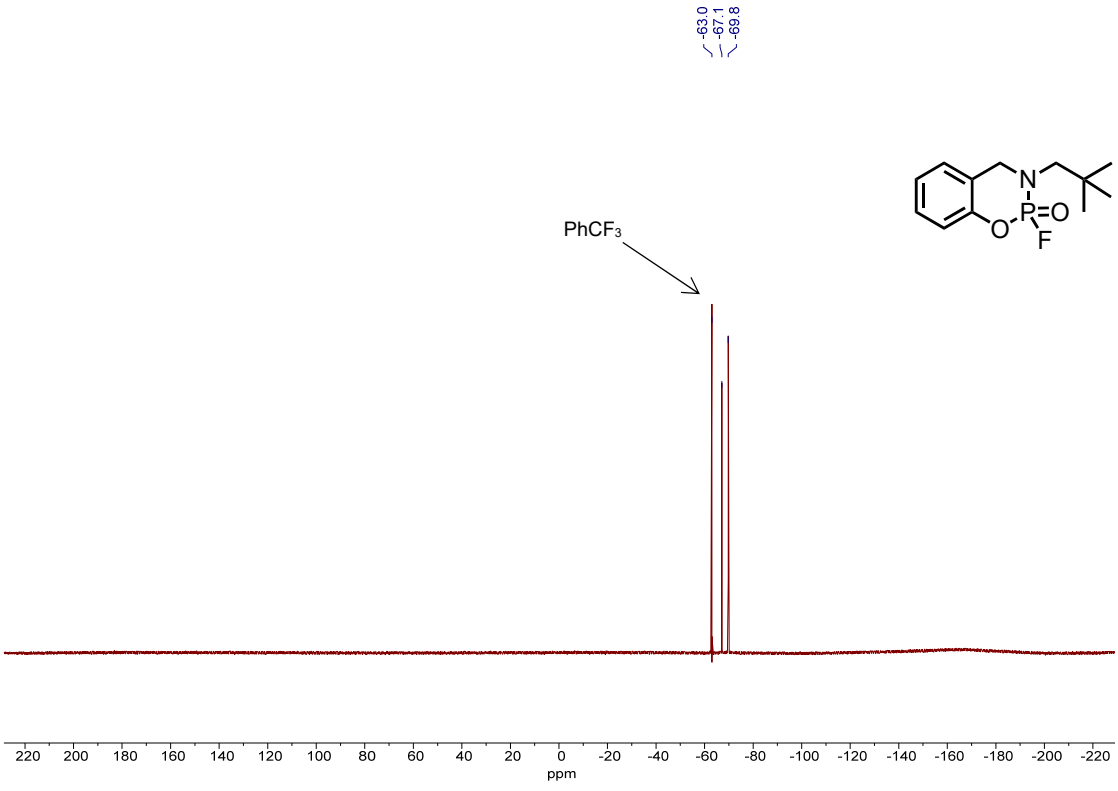
^{13}C NMR Spectrum for Compound **10f** (101 MHz, $CDCl_3$)



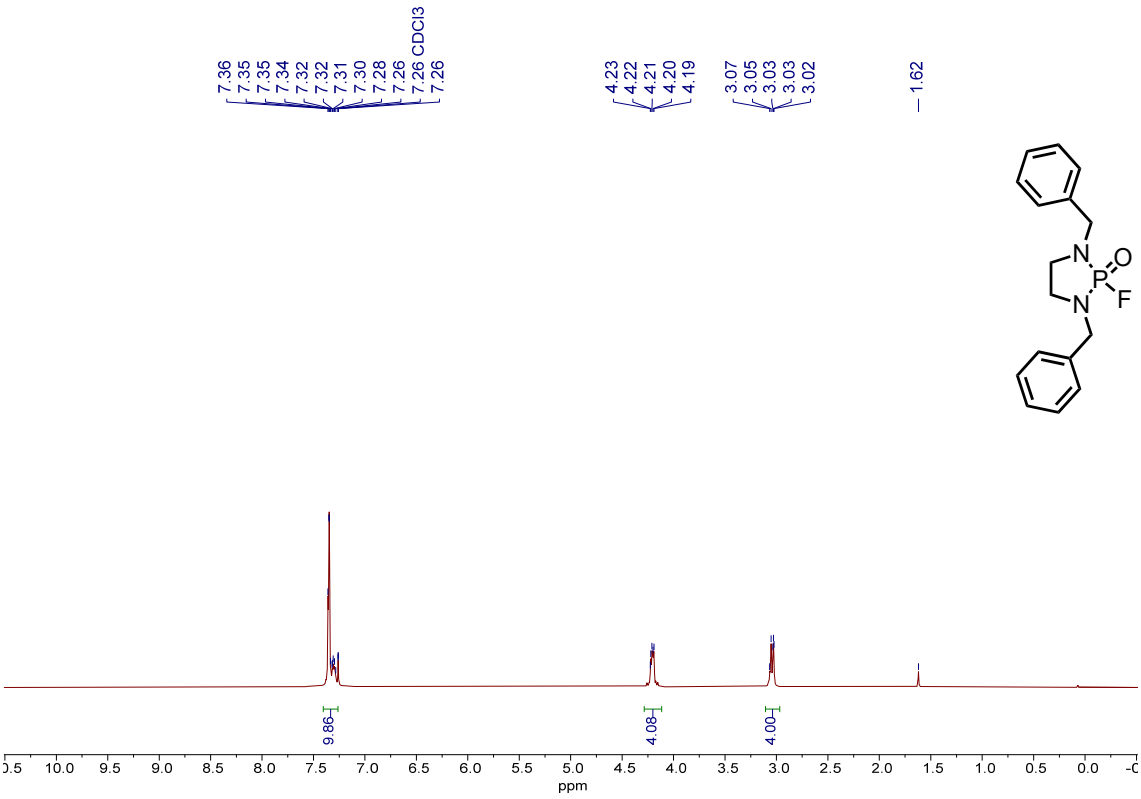
^{31}P NMR Spectrum for Compound **10f** (162 MHz, $CDCl_3$)



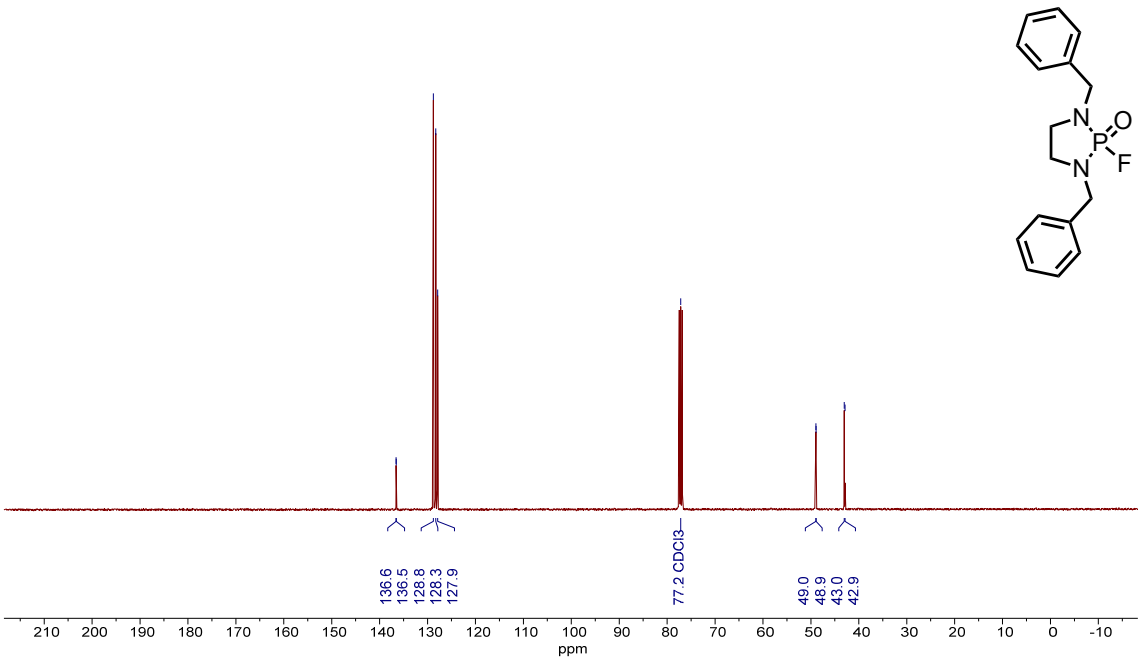
^{19}F NMR Spectrum for Compound **10f** (376 MHz, $CDCl_3$)



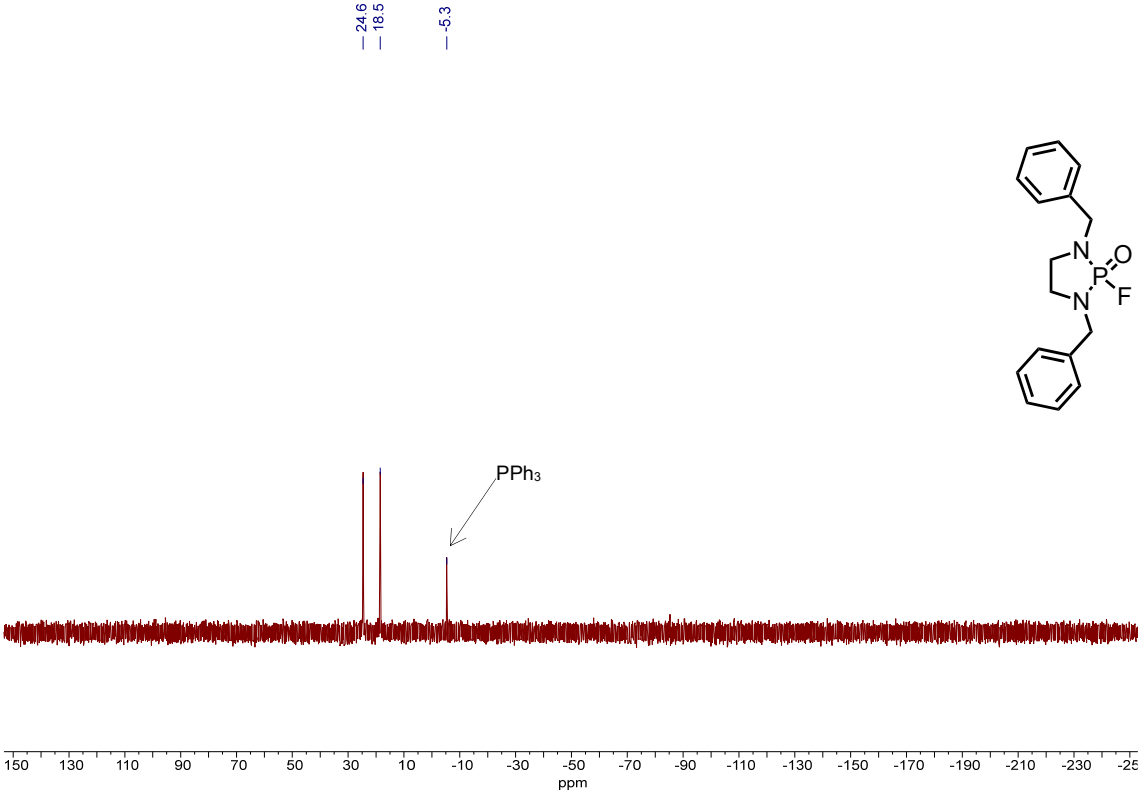
^{1}H NMR Spectrum for Compound **10g** (400 MHz, $CDCl_3$)



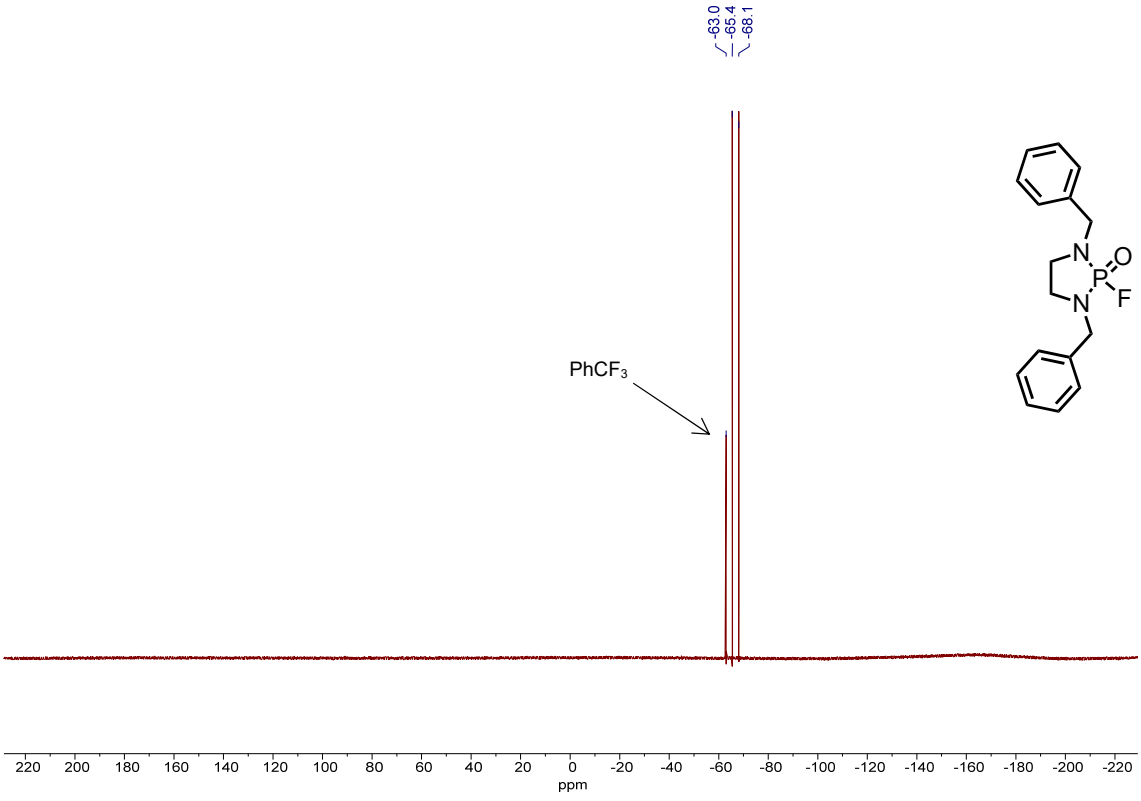
^{13}C NMR Spectrum for Compound **10g** (101 MHz, $CDCl_3$)



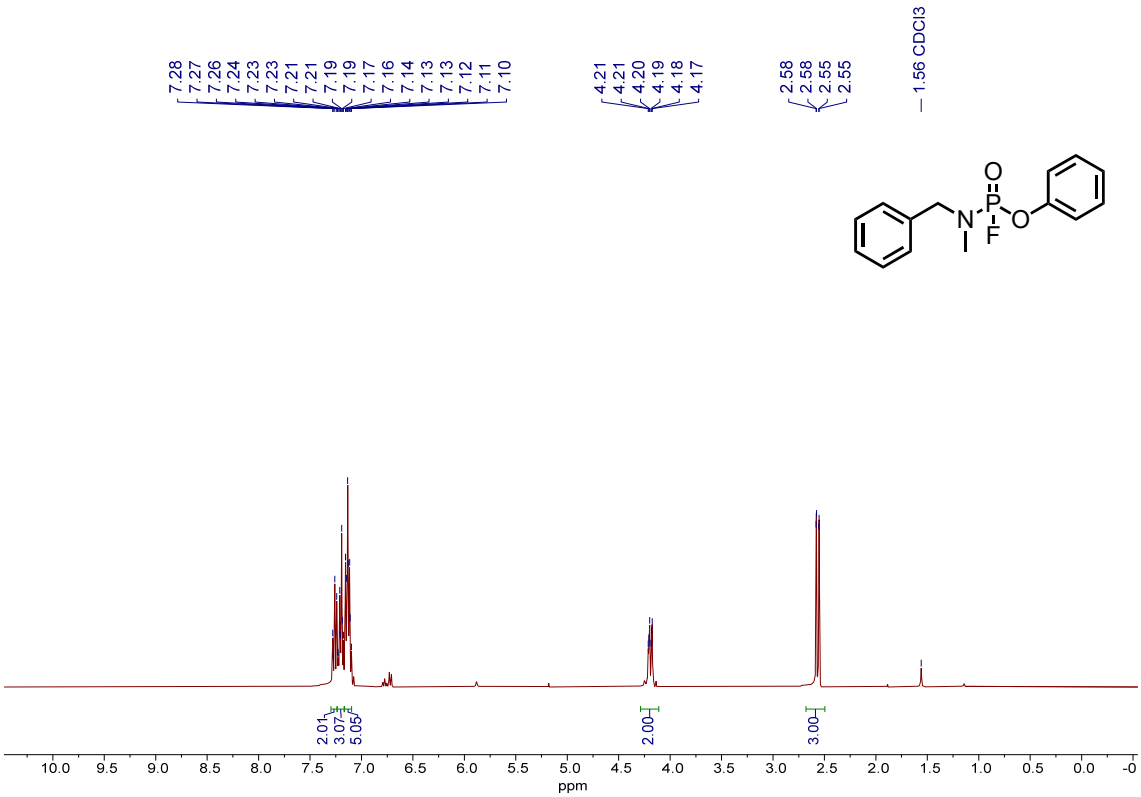
^{31}P NMR Spectrum for Compound **10g** (162 MHz, $CDCl_3$)



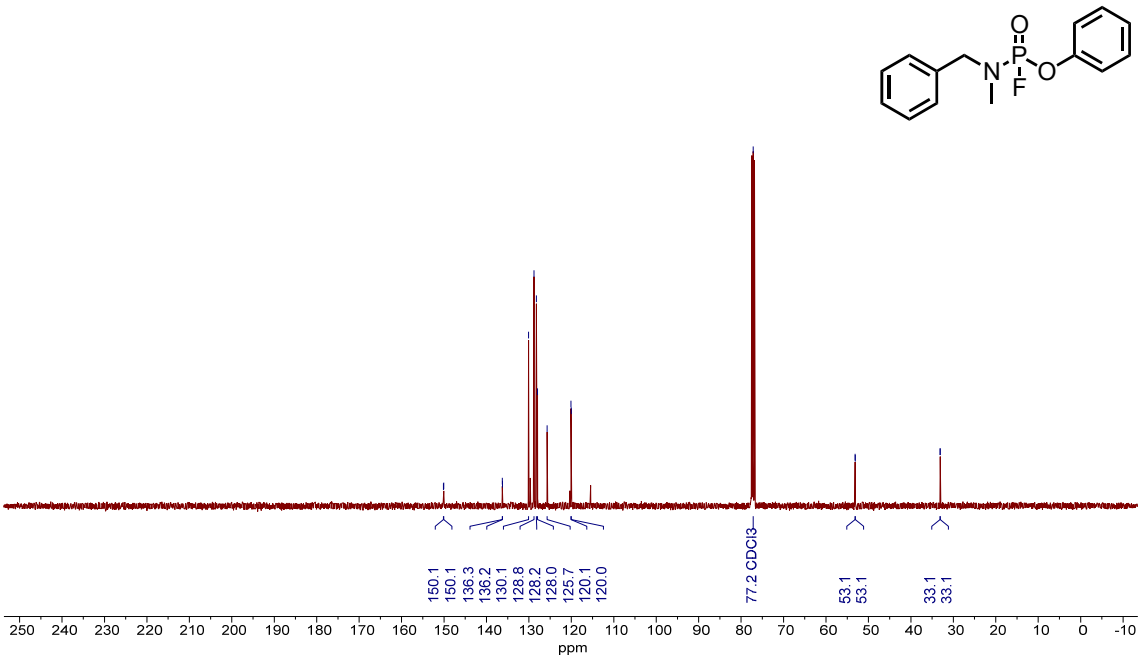
^{19}F NMR Spectrum for Compound **10g** (376 MHz, $CDCl_3$)



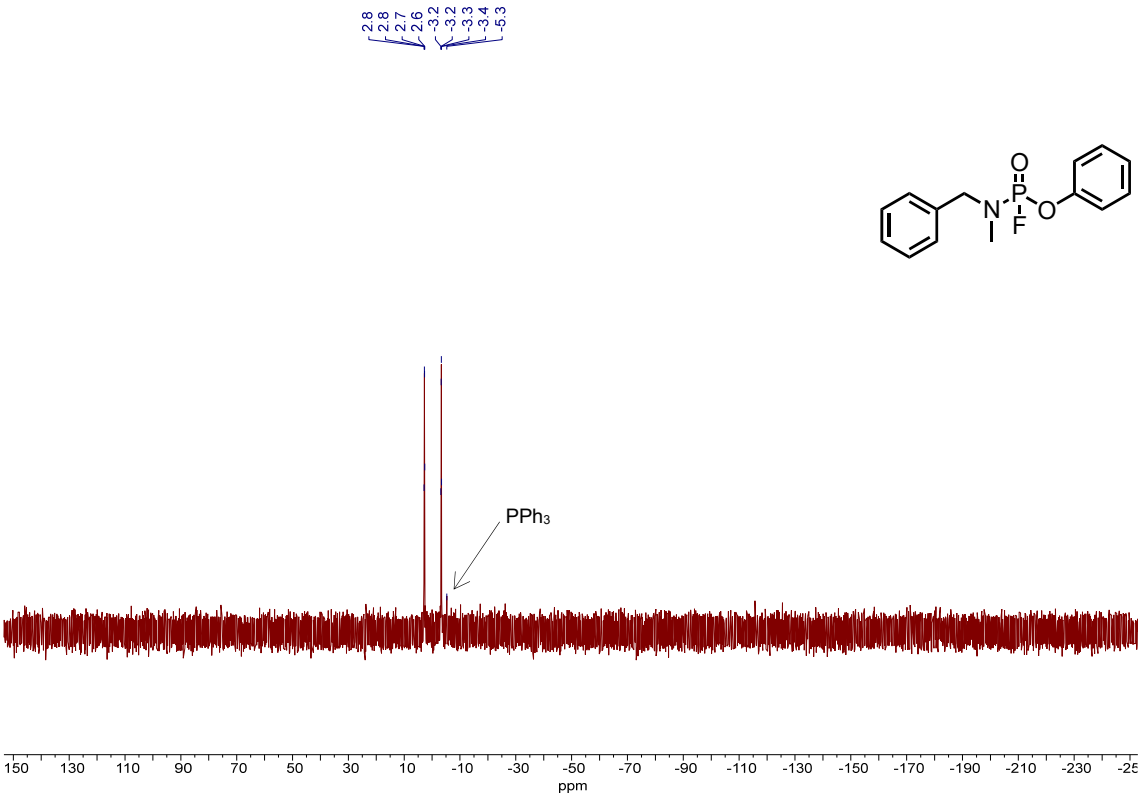
^{1}H NMR Spectrum for Compound **12a** (400 MHz, $CDCl_3$)



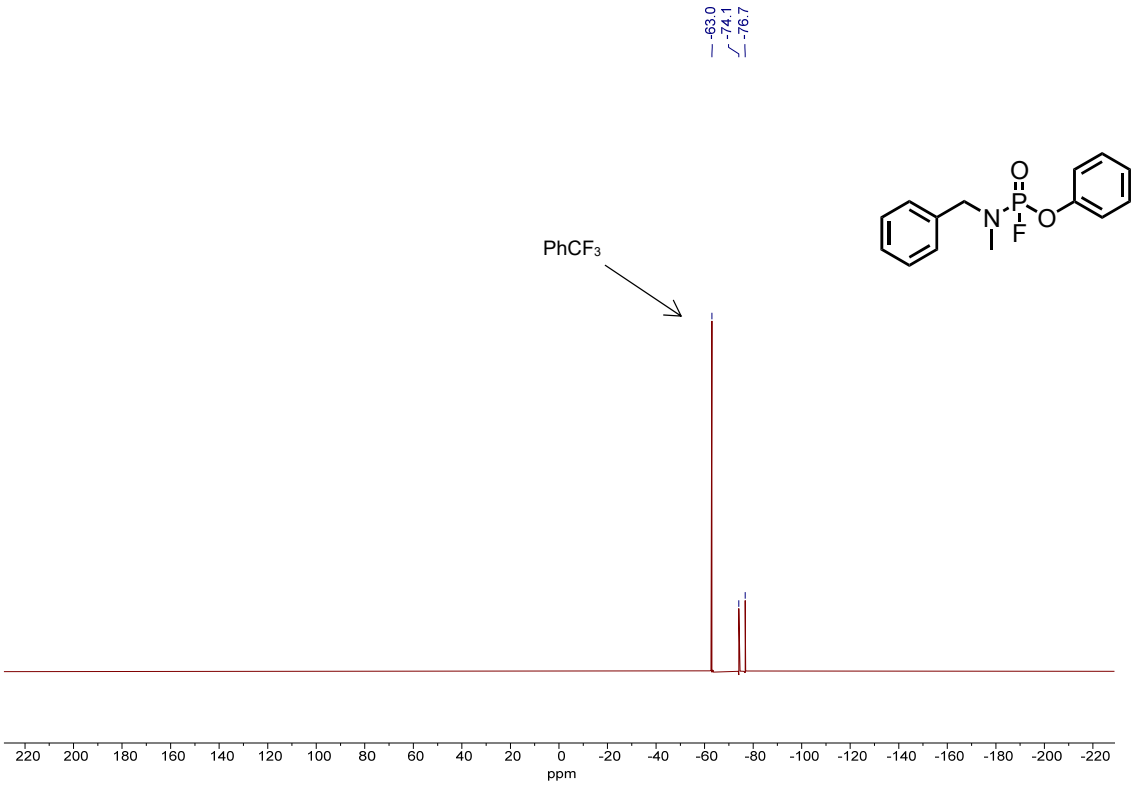
^{13}C NMR Spectrum for Compound **12a** (101 MHz, $CDCl_3$)



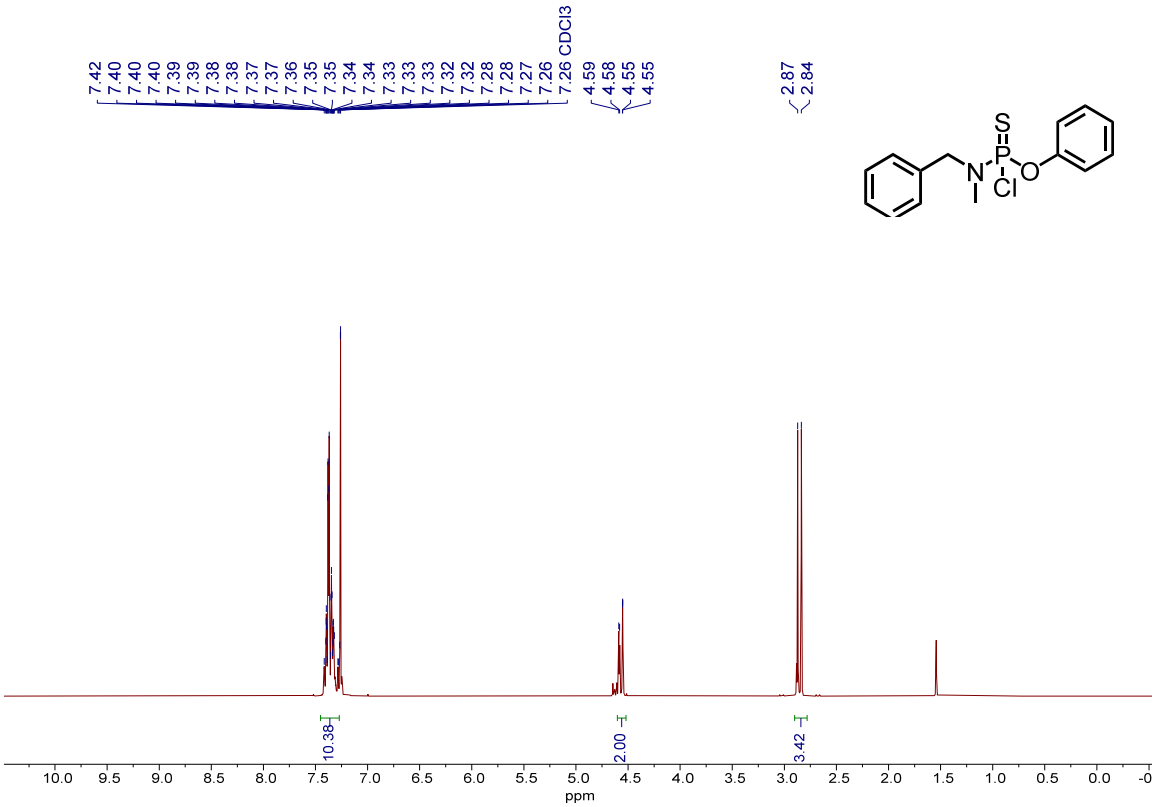
^{31}P NMR Spectrum for Compound **12a** (162 MHz, $CDCl_3$)



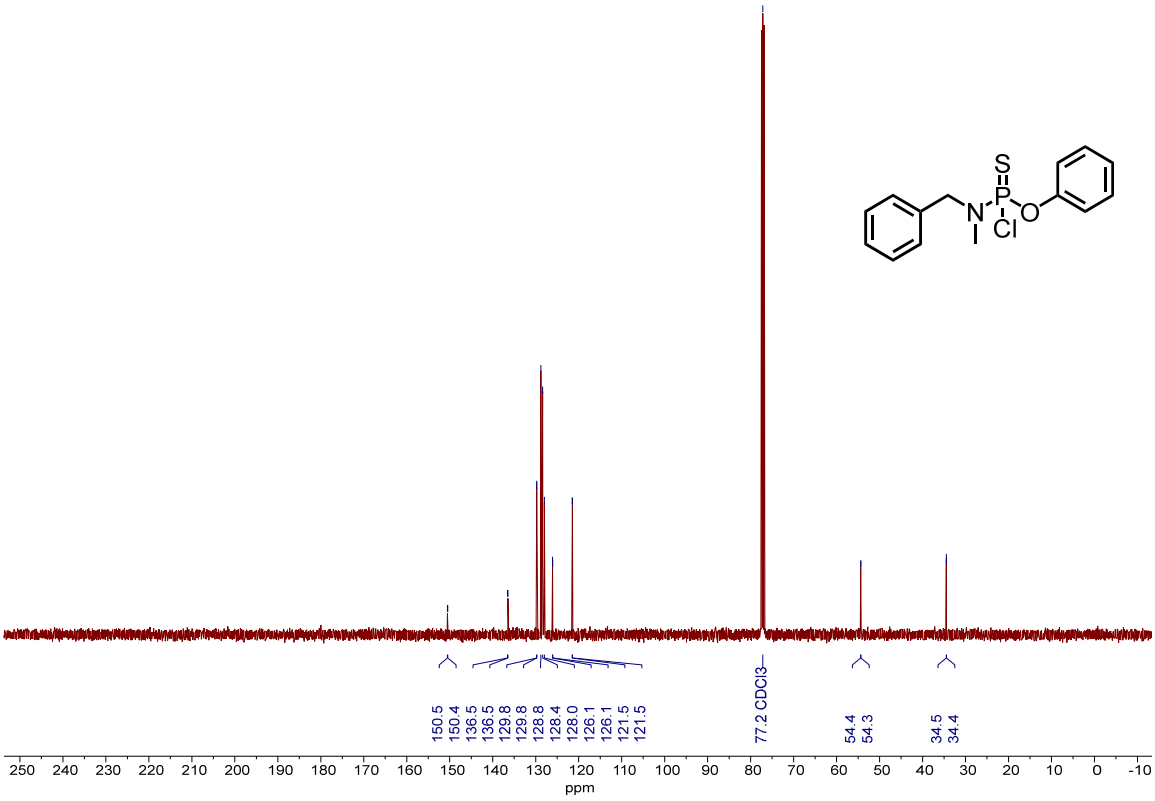
^{19}F NMR Spectrum for Compound **12a** (376 MHz, $CDCl_3$)



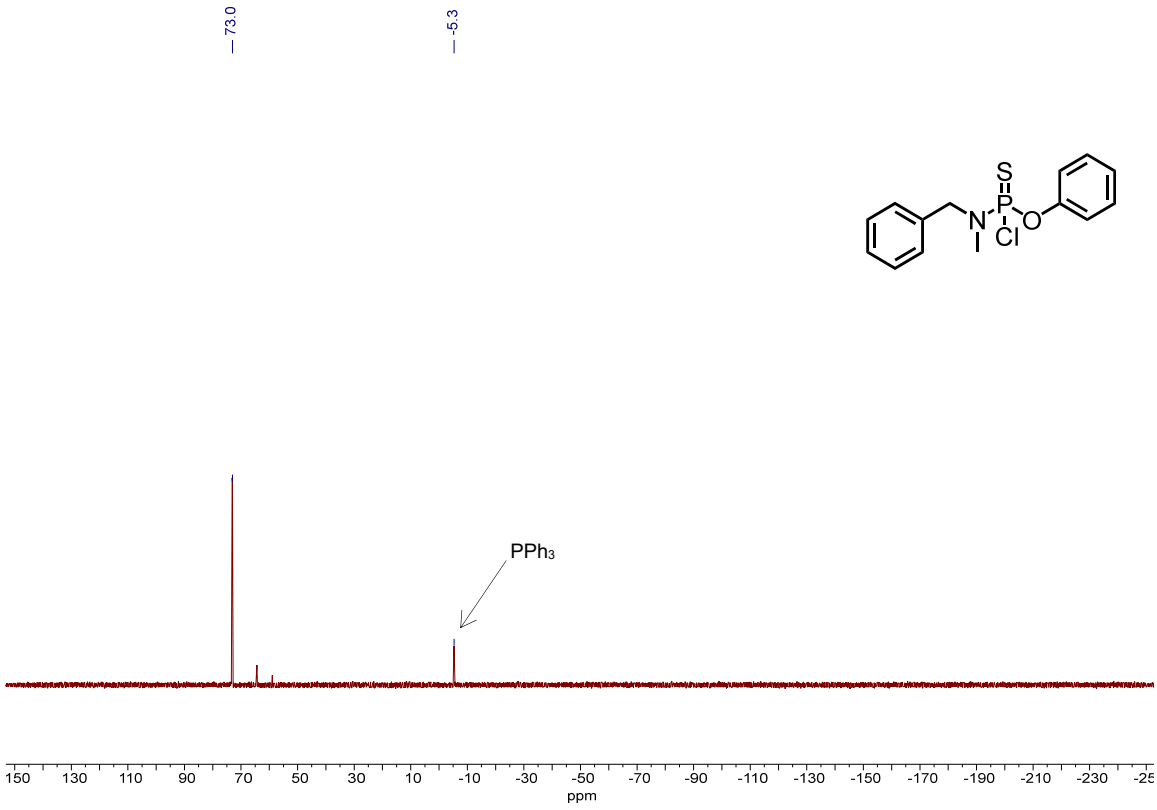
^{1}H NMR Spectrum for Compound **11b** (400 MHz, $CDCl_3$)



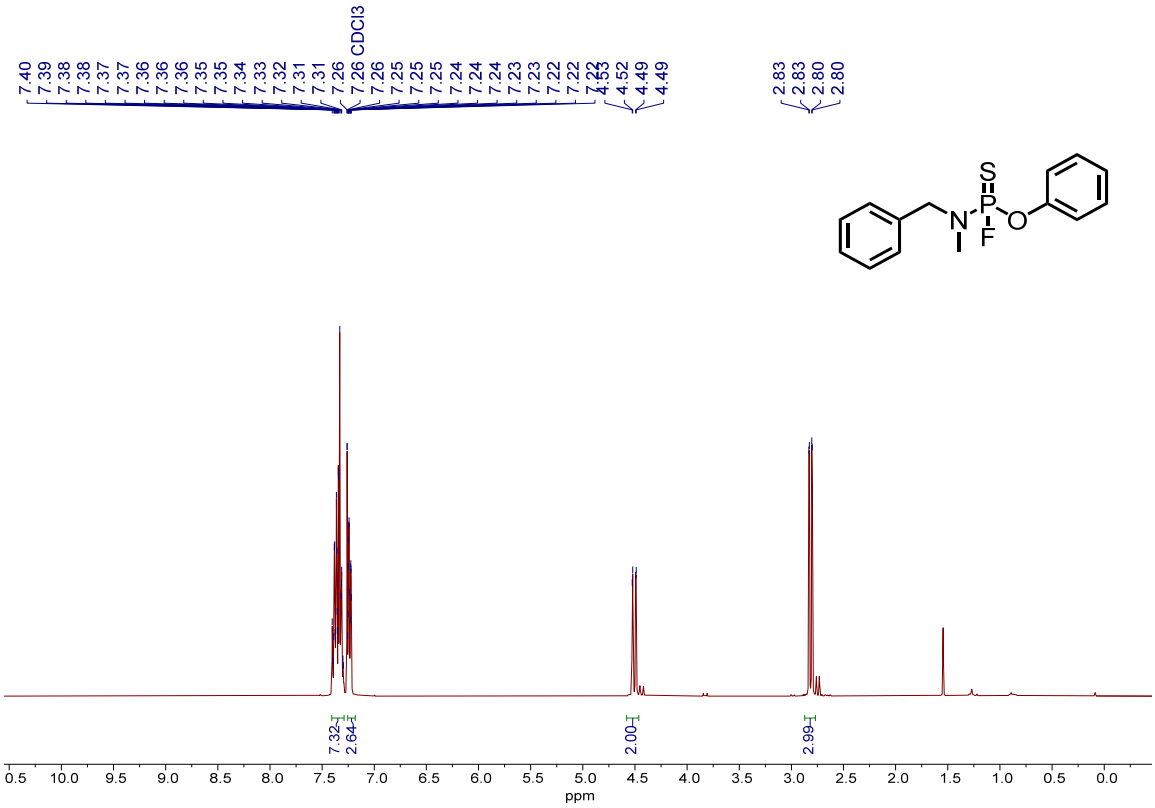
^{13}C NMR Spectrum for Compound **11b** (101 MHz, $CDCl_3$)



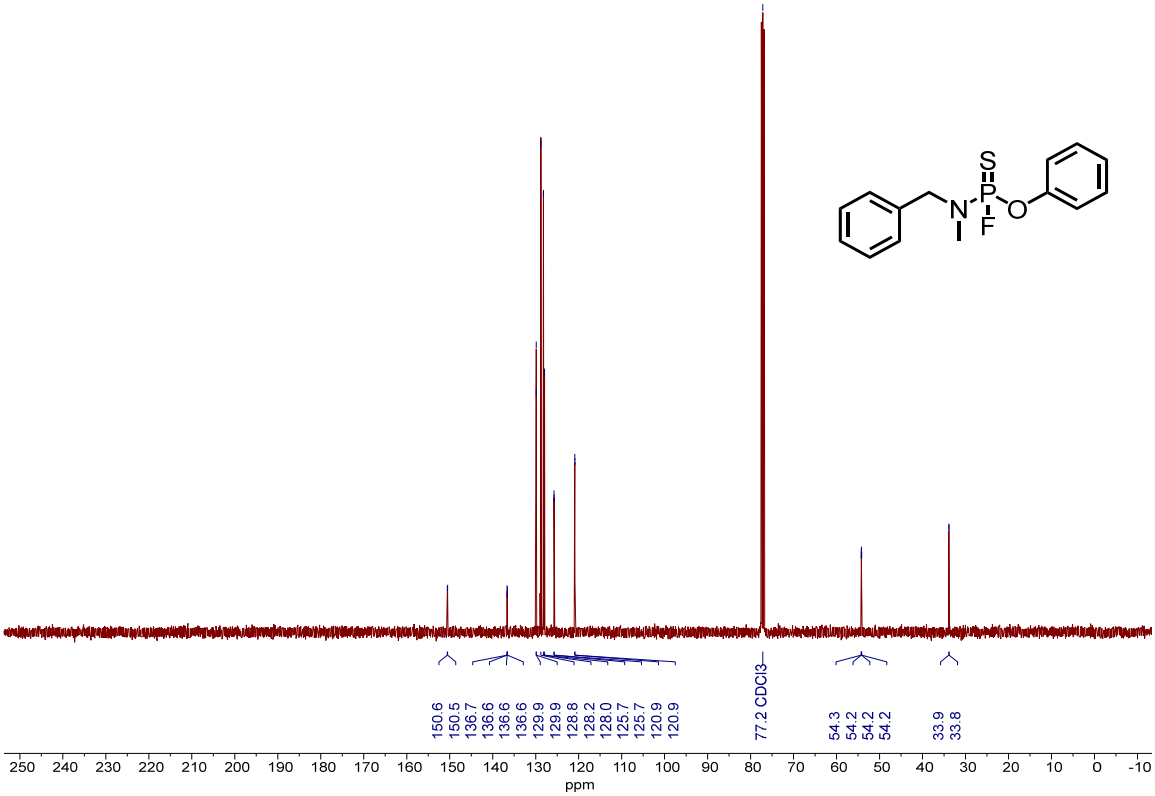
^{31}P NMR Spectrum for Compound **11b** (162 MHz, $CDCl_3$)



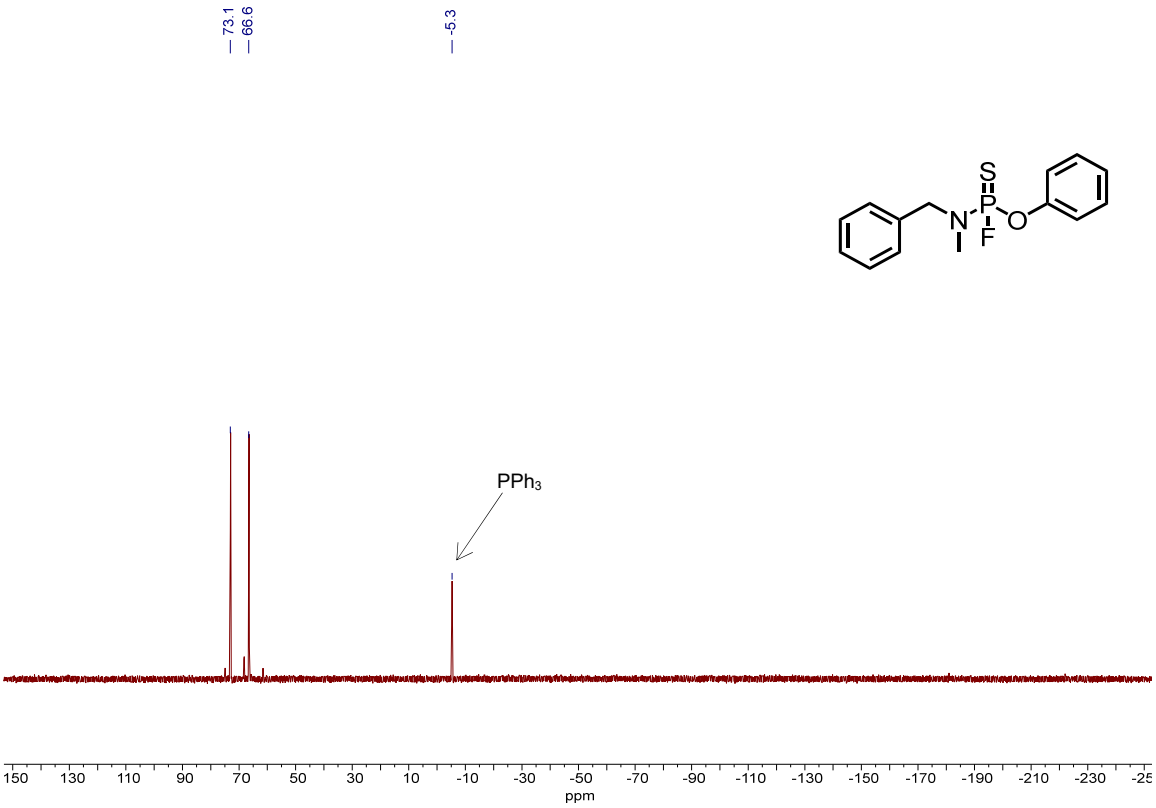
^{1}H NMR Spectrum for Compound **12b** (400 MHz, $CDCl_3$)



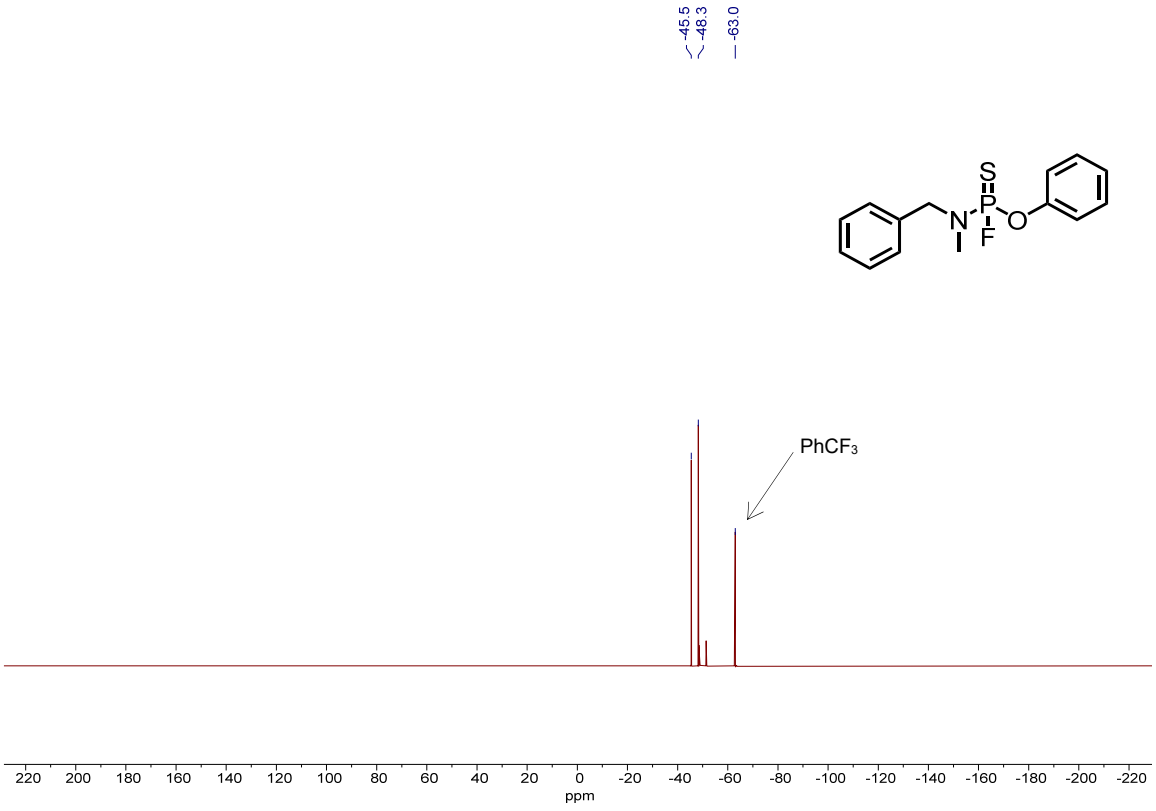
^{13}C NMR Spectrum for Compound **12b** (101 MHz, $CDCl_3$)



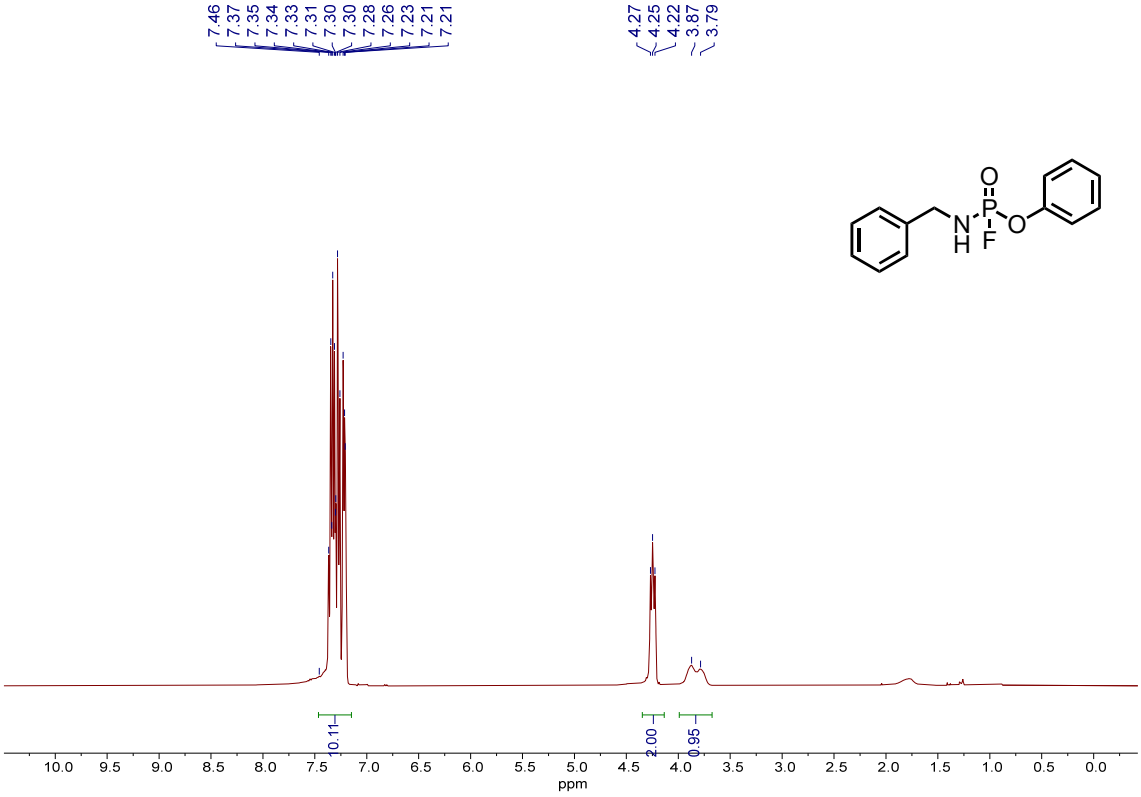
^{31}P NMR Spectrum for Compound **12b** (162 MHz, $CDCl_3$)



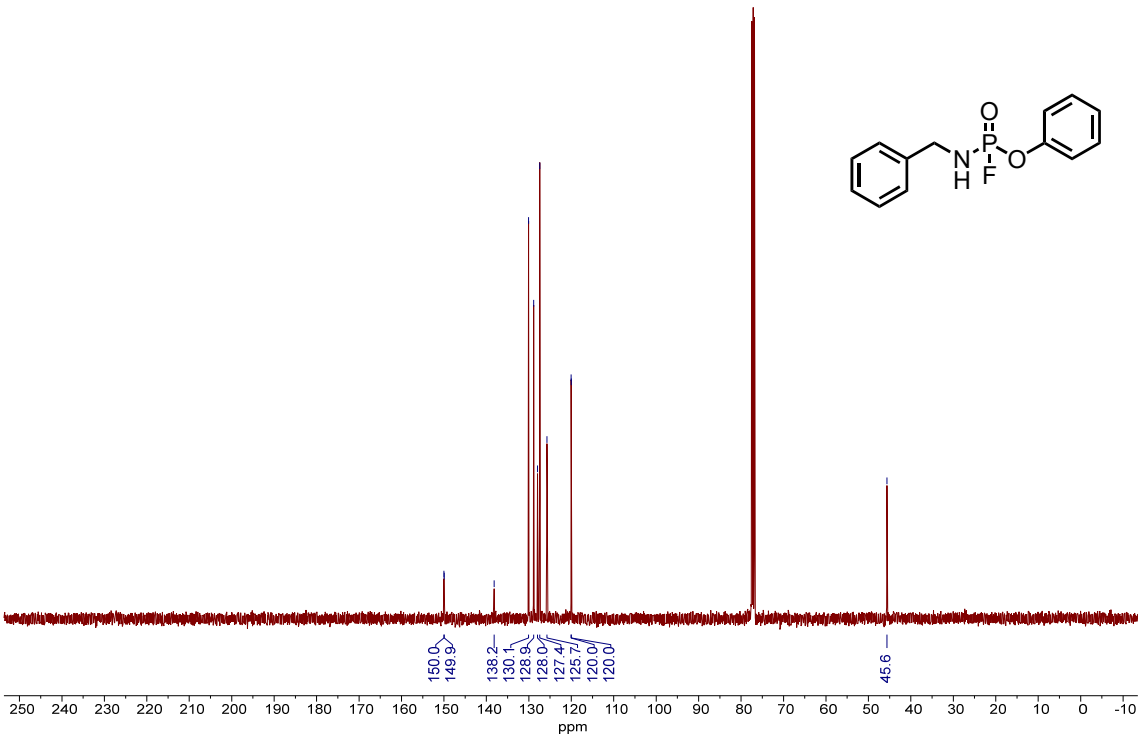
^{19}F NMR Spectrum for Compound **12b** (376 MHz, $CDCl_3$)



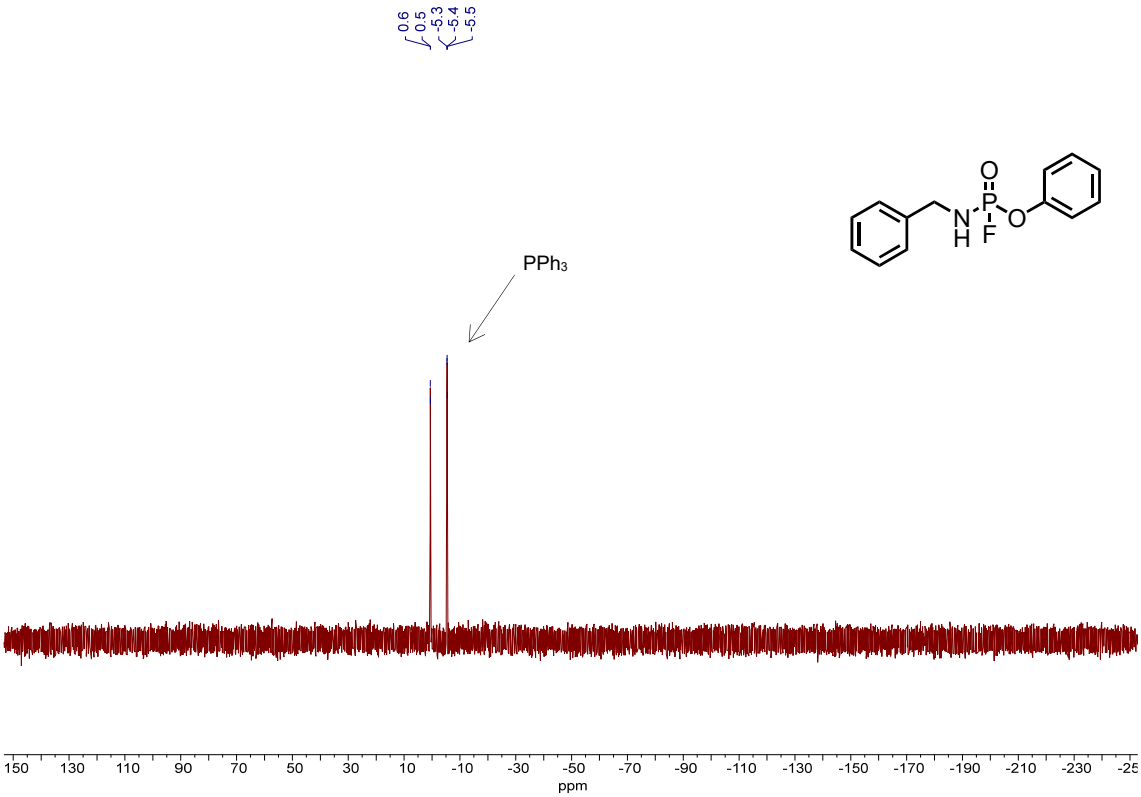
^{1}H NMR Spectrum for Compound **12c** (400 MHz, $CDCl_3$)



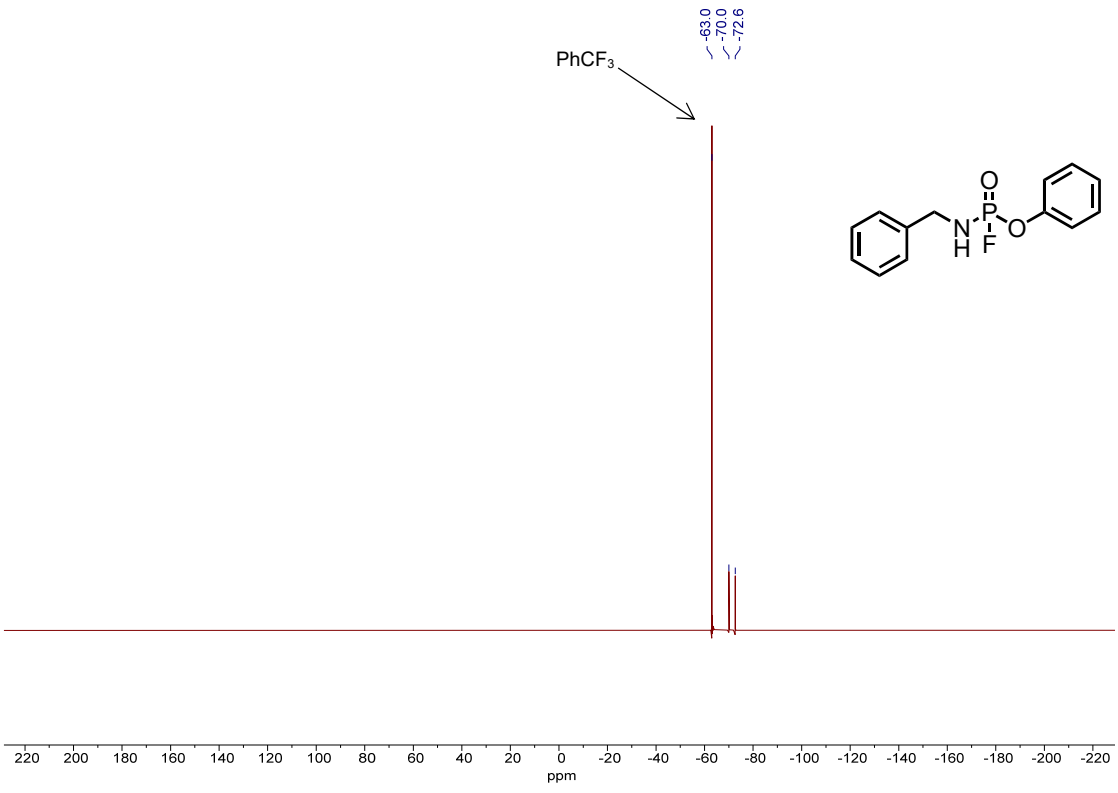
^{13}C NMR Spectrum for Compound **12c** (101 MHz, $CDCl_3$)



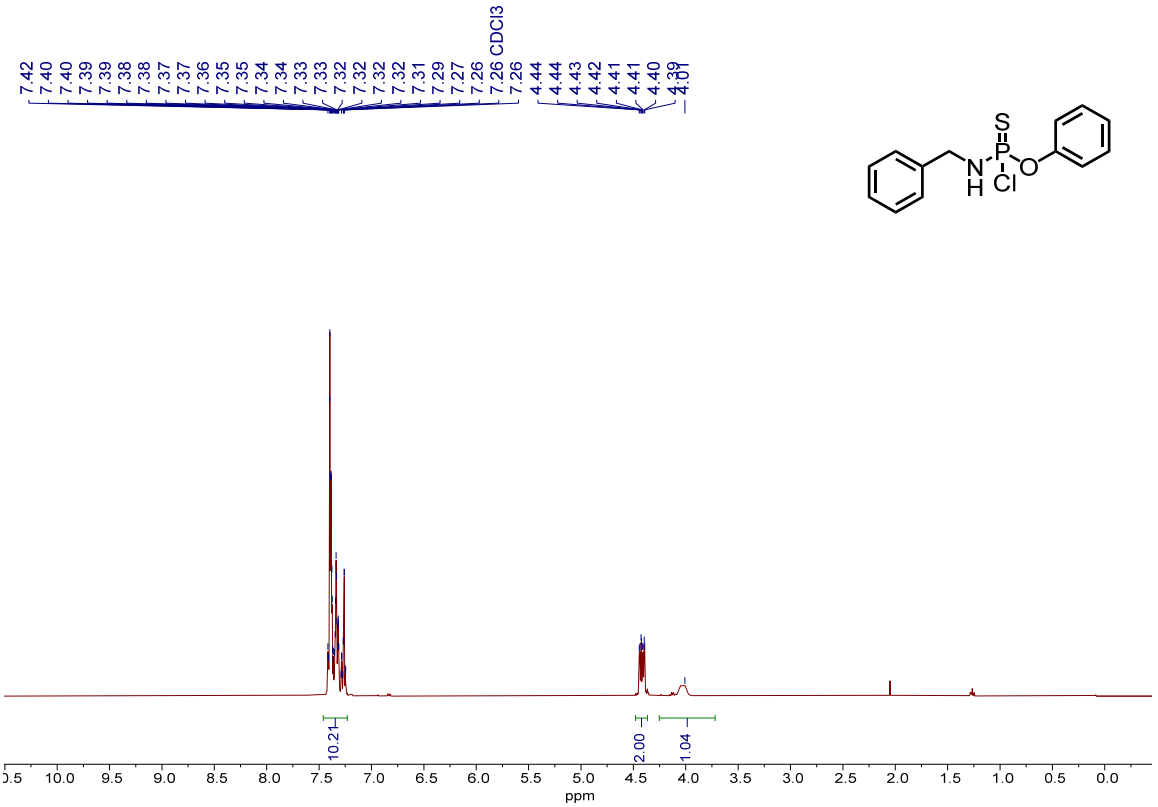
^{31}P NMR Spectrum for Compound **12c** (162 MHz, $CDCl_3$)



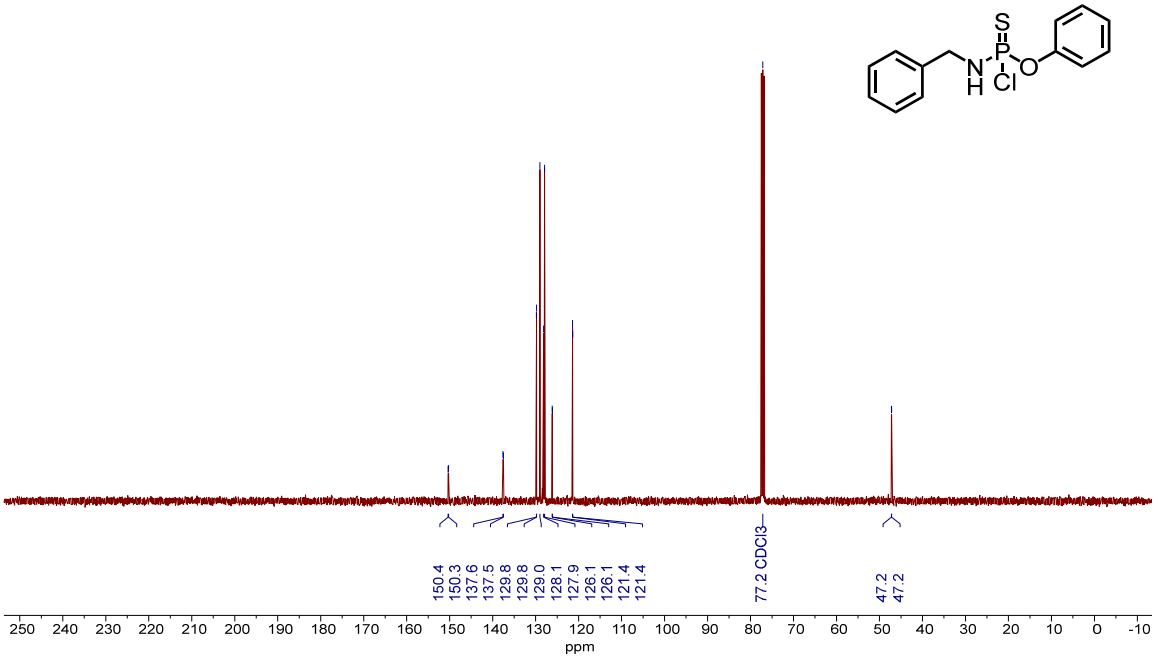
^{19}F NMR Spectrum for Compound **12c** (376 MHz, $CDCl_3$)



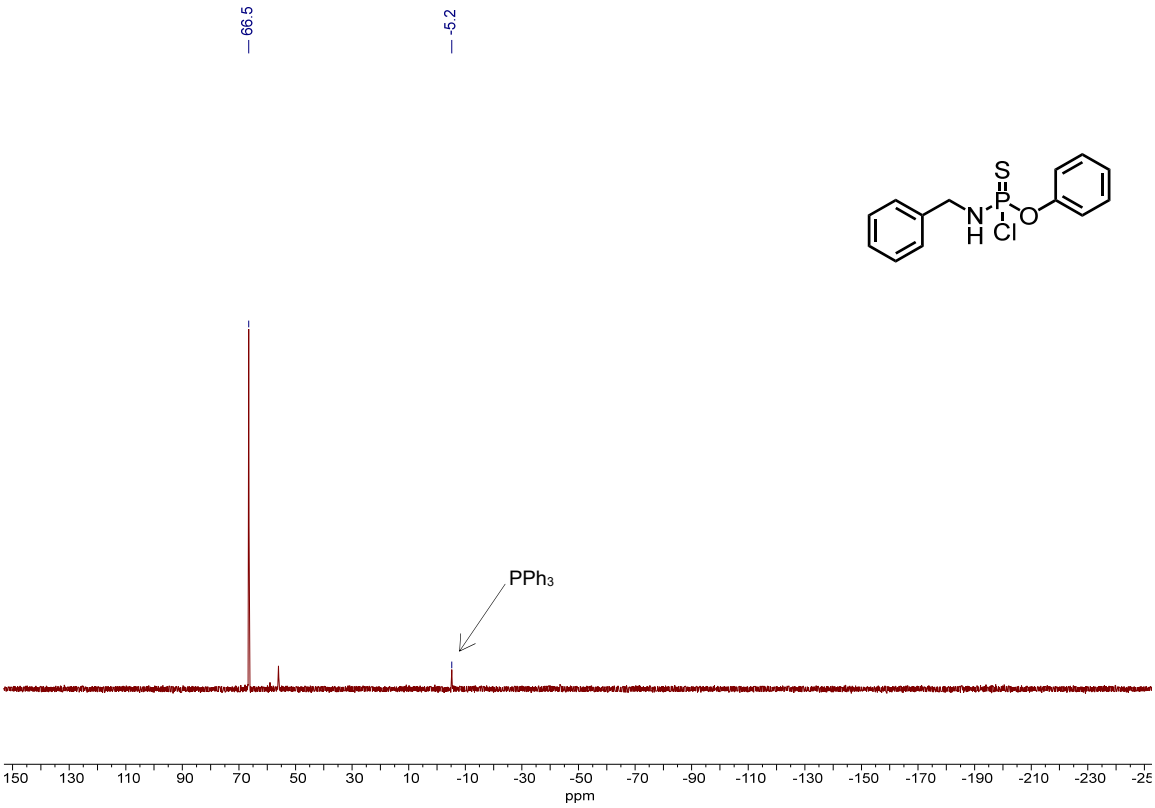
^{1}H NMR Spectrum for Compound **11d** (400 MHz, $CDCl_3$)



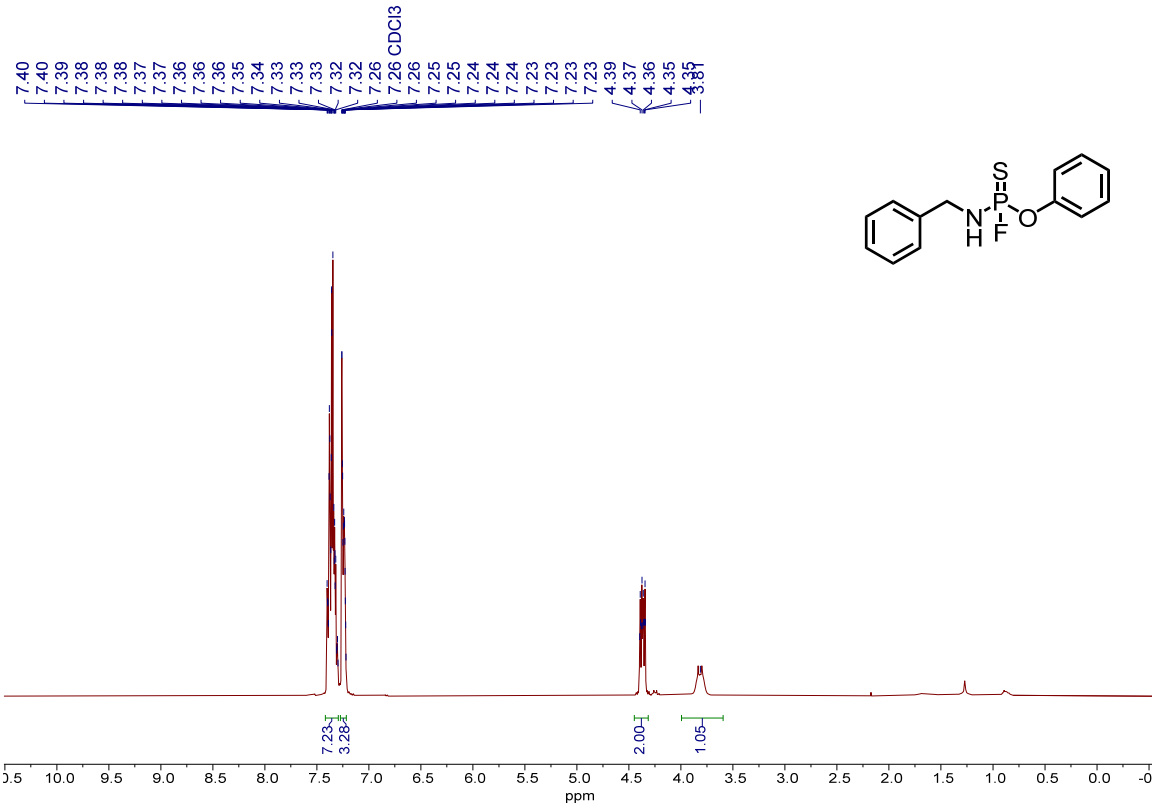
^{13}C NMR Spectrum for Compound **11d** (101 MHz, $CDCl_3$)



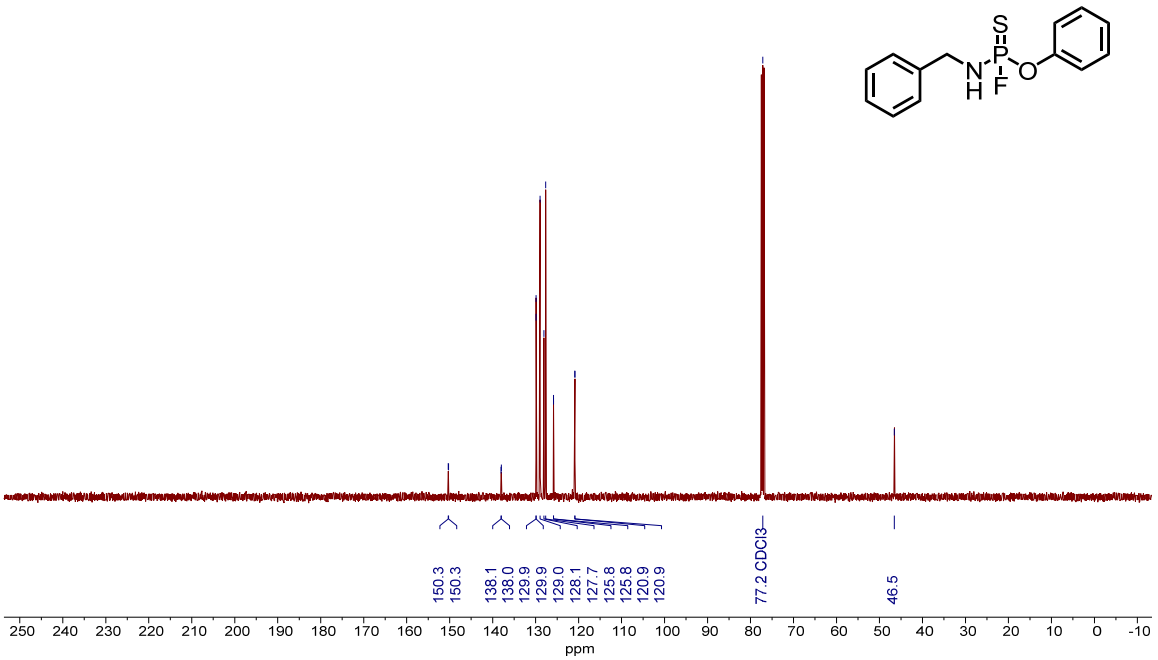
^{31}P NMR Spectrum for Compound **11d** (162 MHz, $CDCl_3$)



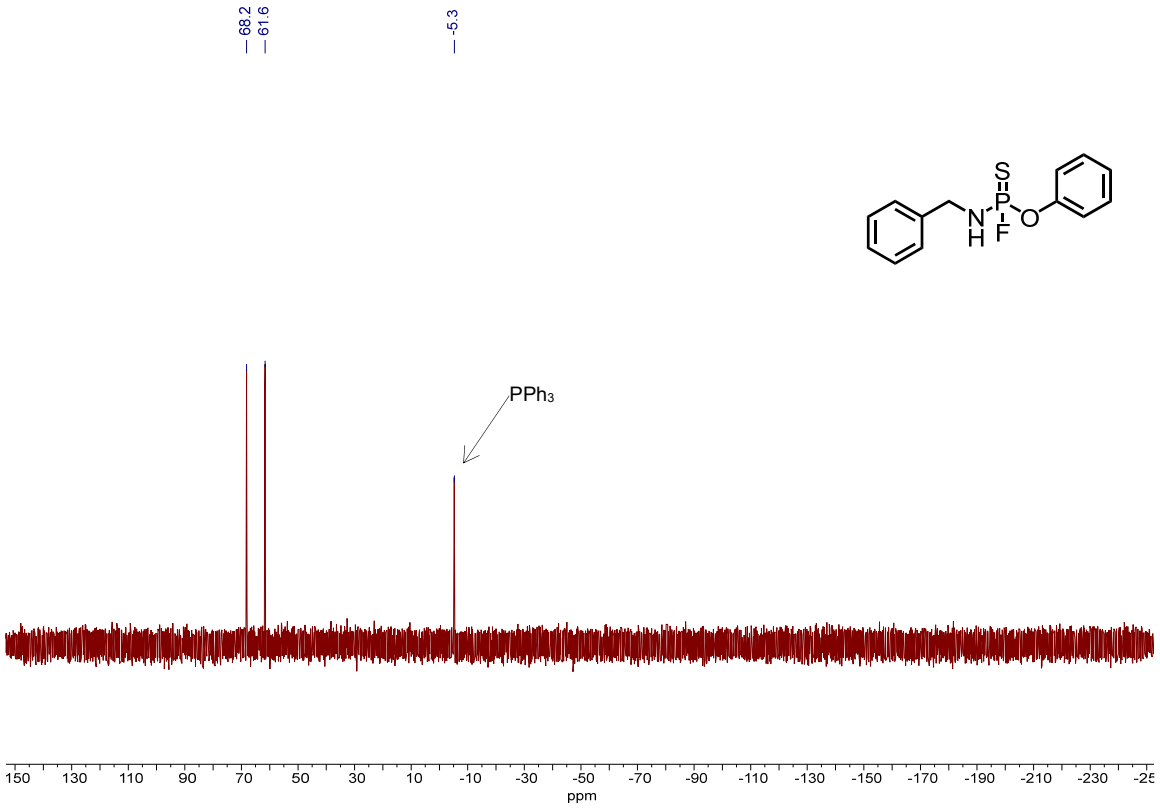
^{1}H NMR Spectrum for Compound **12d** (400 MHz, $CDCl_3$)



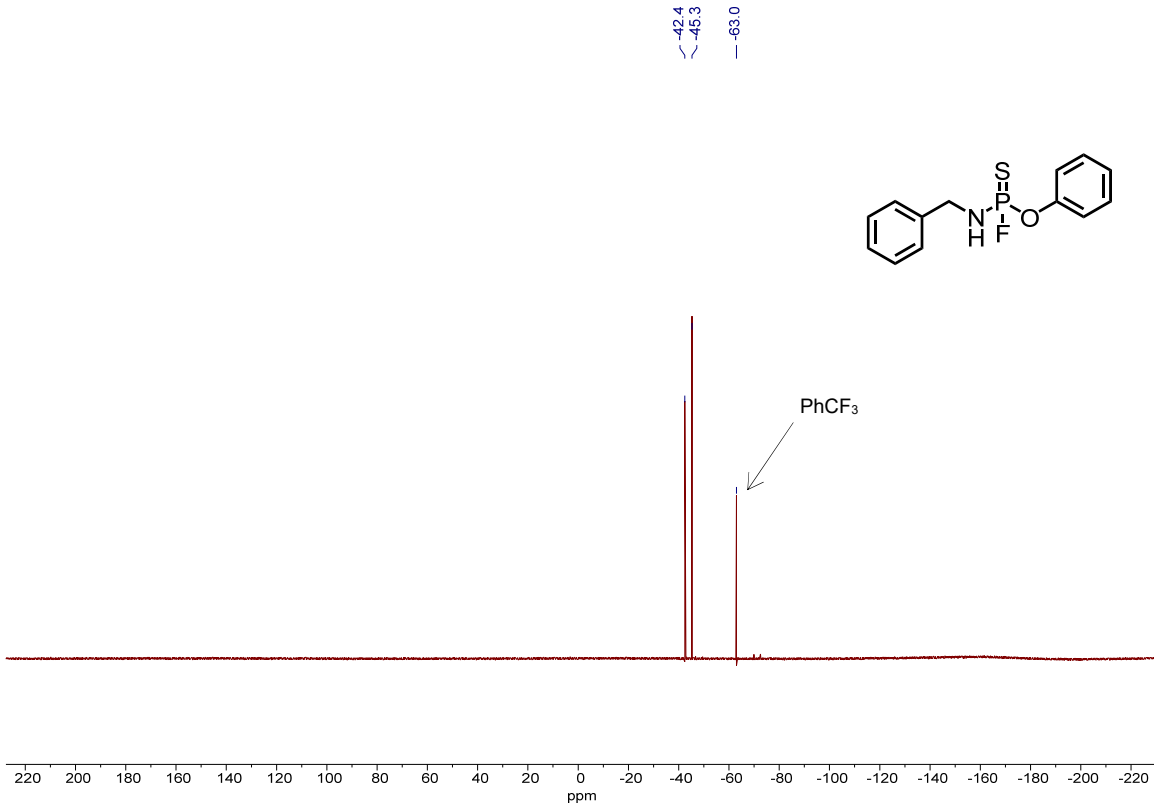
^{13}C NMR Spectrum for Compound **12d** (101 MHz, $CDCl_3$)



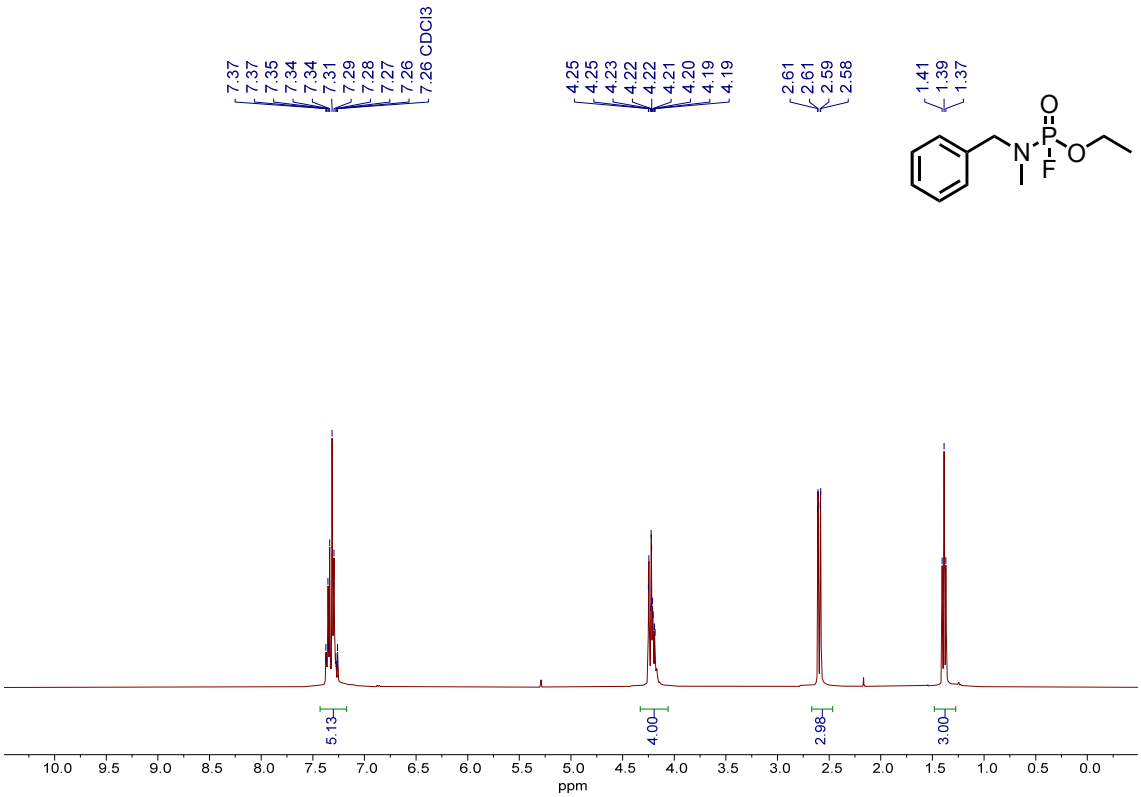
^{31}P NMR Spectrum for Compound **12d** (162 MHz, $CDCl_3$)



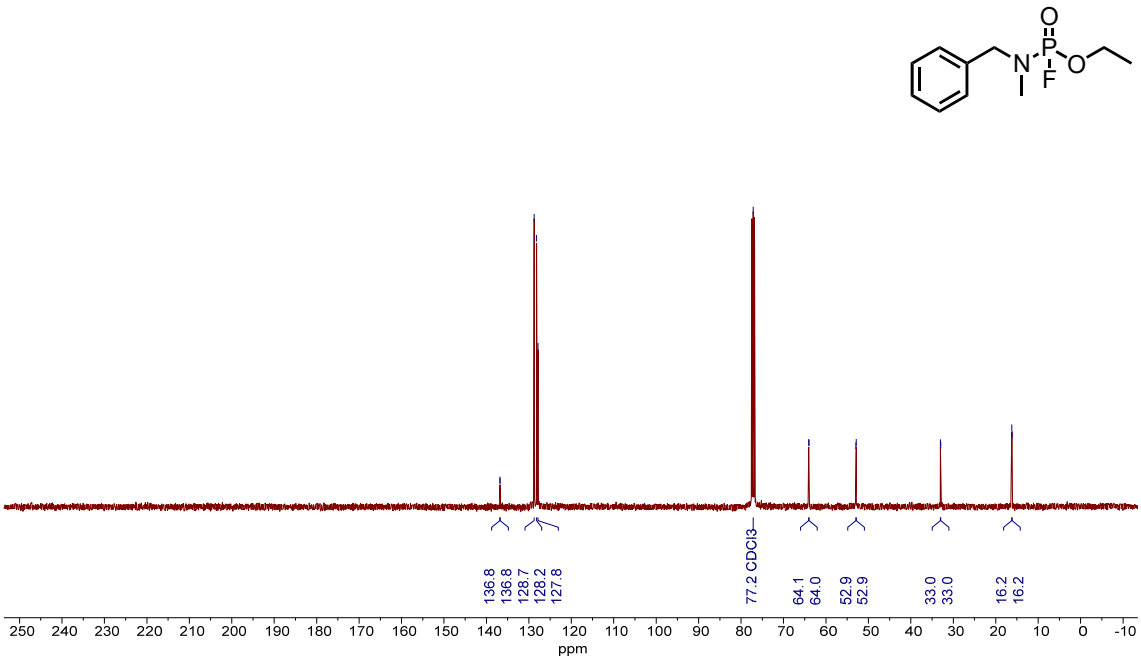
^{19}F NMR Spectrum for Compound **12d** (376 MHz, $CDCl_3$)



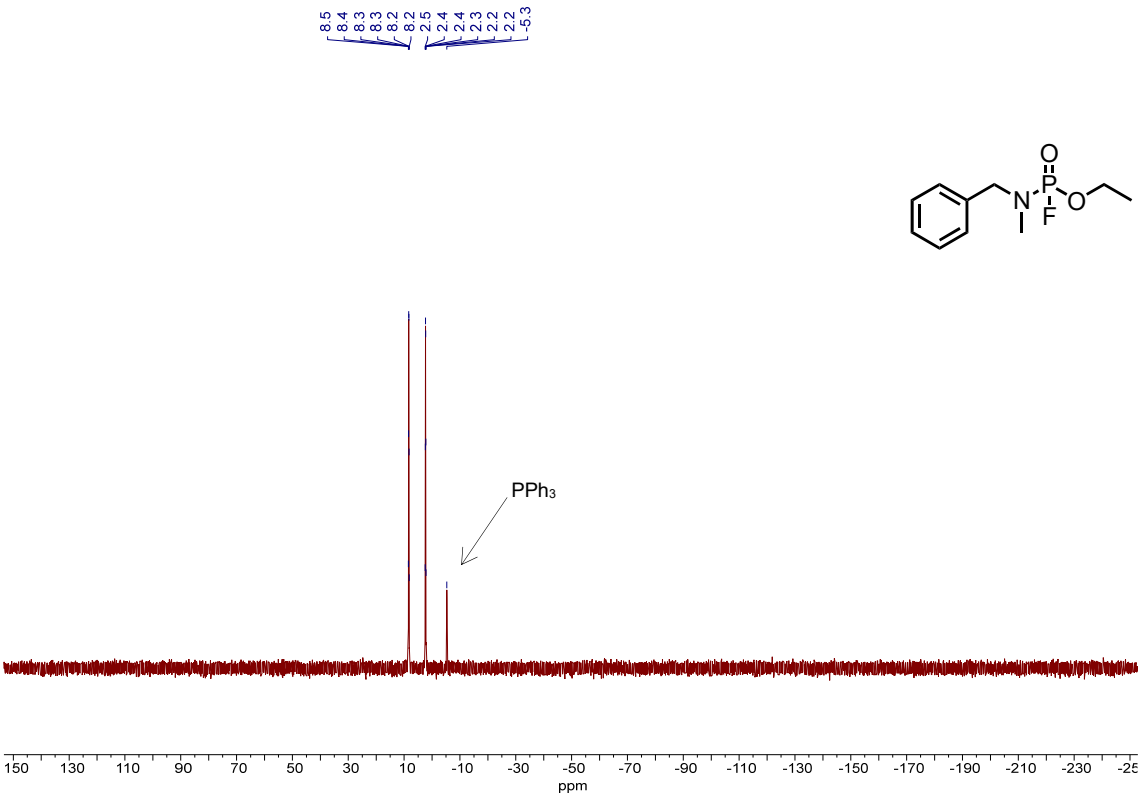
^{1}H NMR Spectrum for Compound **12e** (400 MHz, $CDCl_3$)



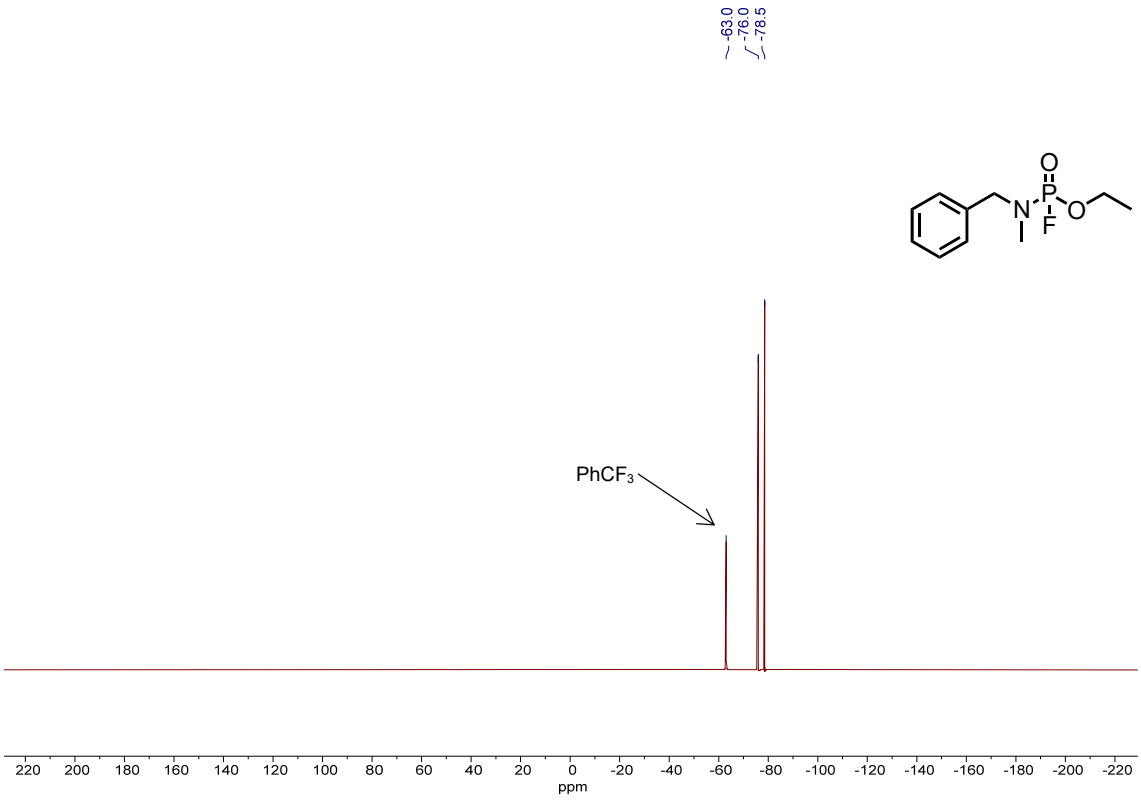
^{13}C NMR Spectrum for Compound **12e** (101 MHz, $CDCl_3$)



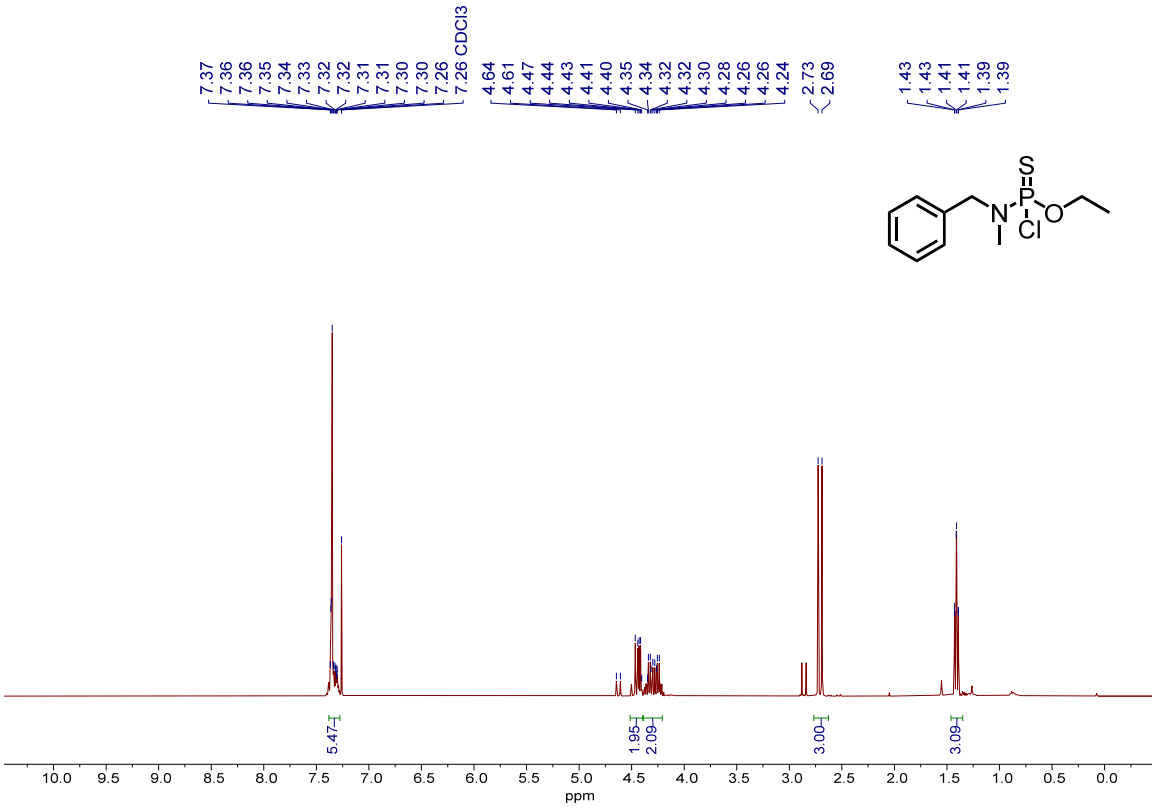
^{31}P NMR Spectrum for Compound **12e** (162 MHz, $CDCl_3$)



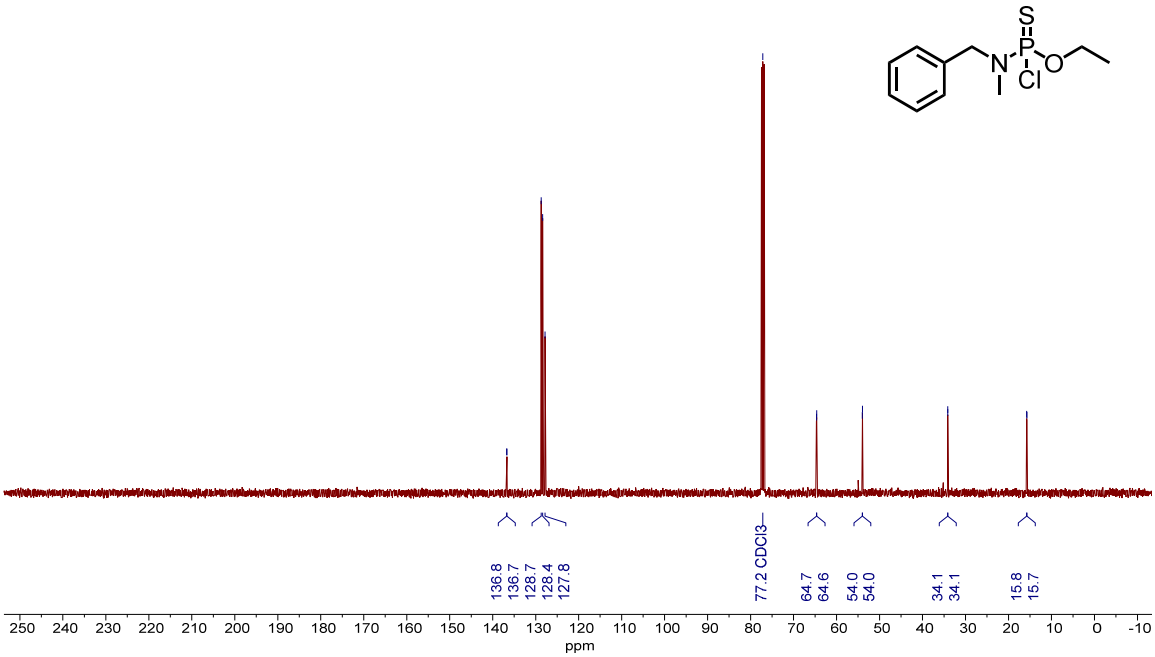
^{19}F NMR Spectrum for Compound **12e** (376 MHz, $CDCl_3$)



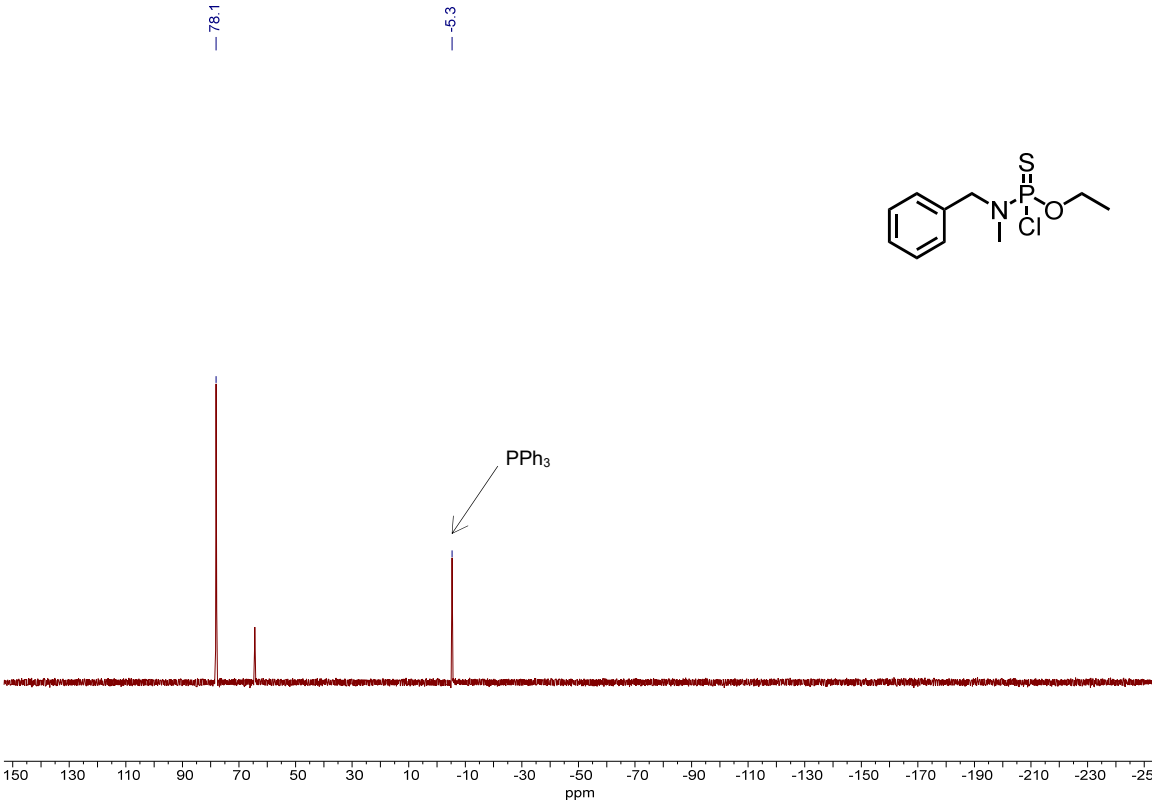
^{1}H NMR Spectrum for Compound **11f** (400 MHz, $CDCl_3$)



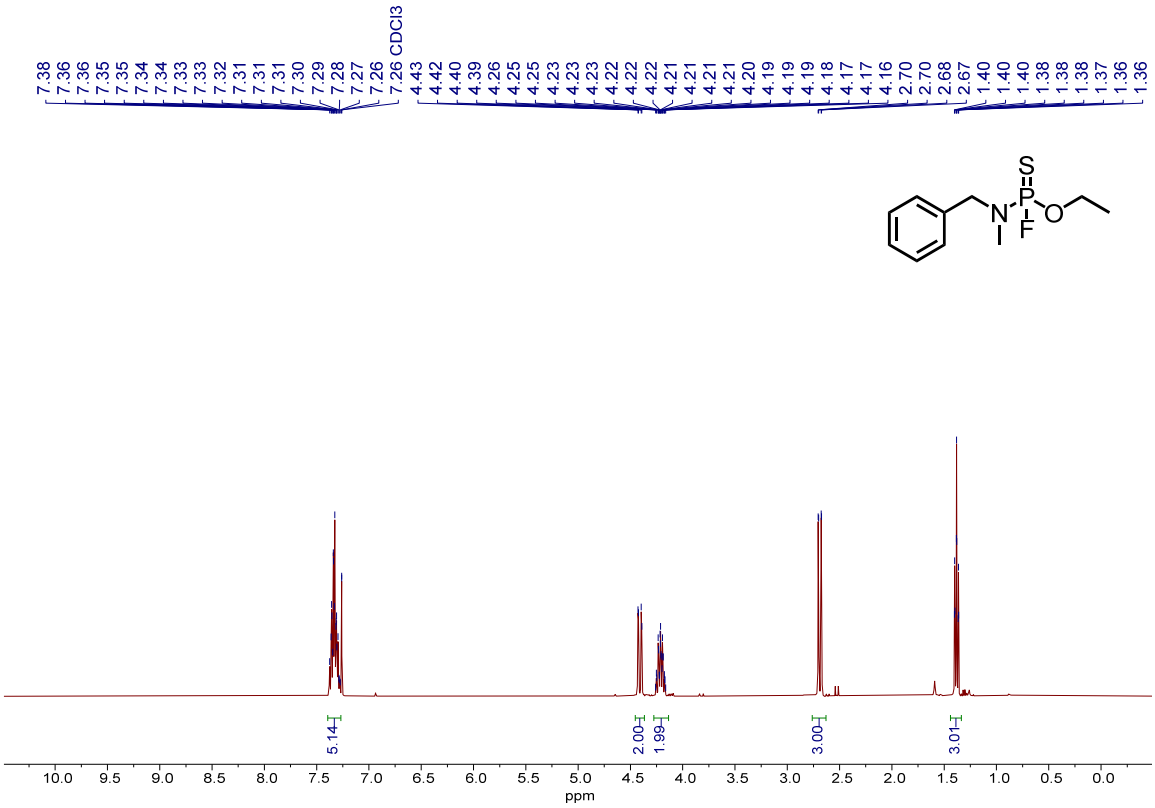
^{13}C NMR Spectrum for Compound **11f** (101 MHz, $CDCl_3$)



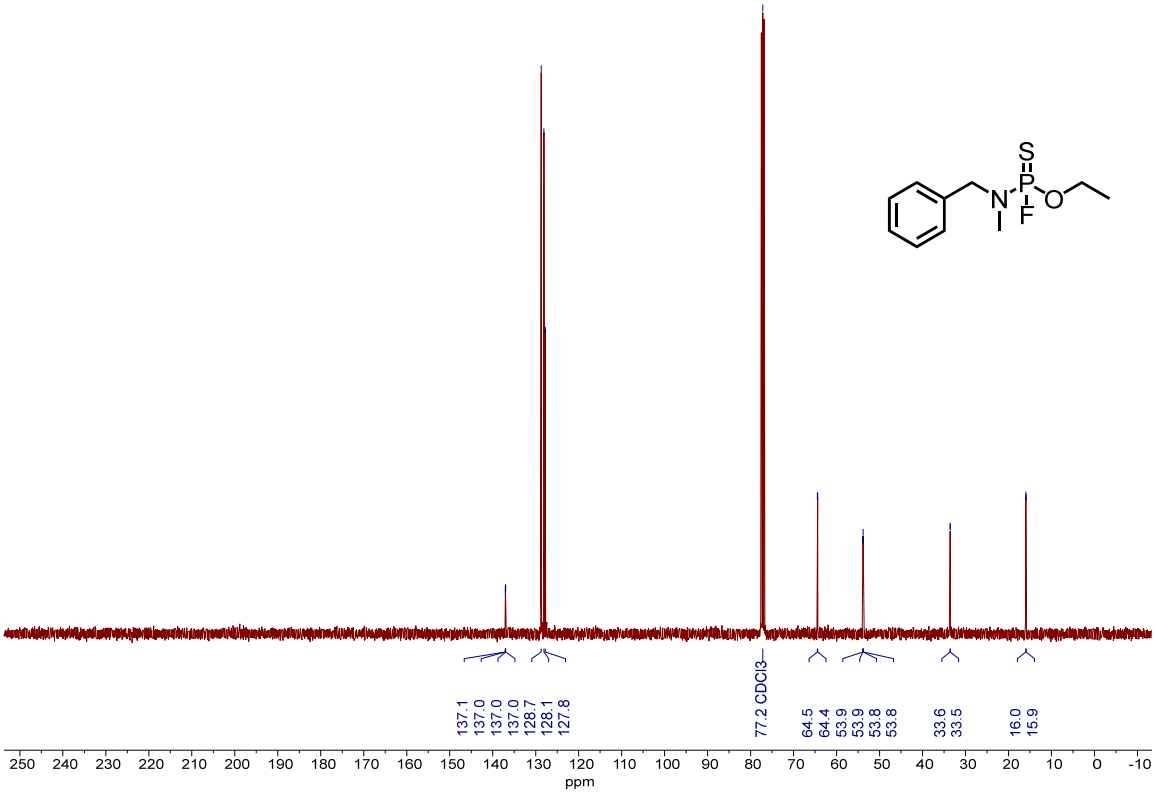
^{31}P NMR Spectrum for Compound **11f** (162 MHz, $CDCl_3$)



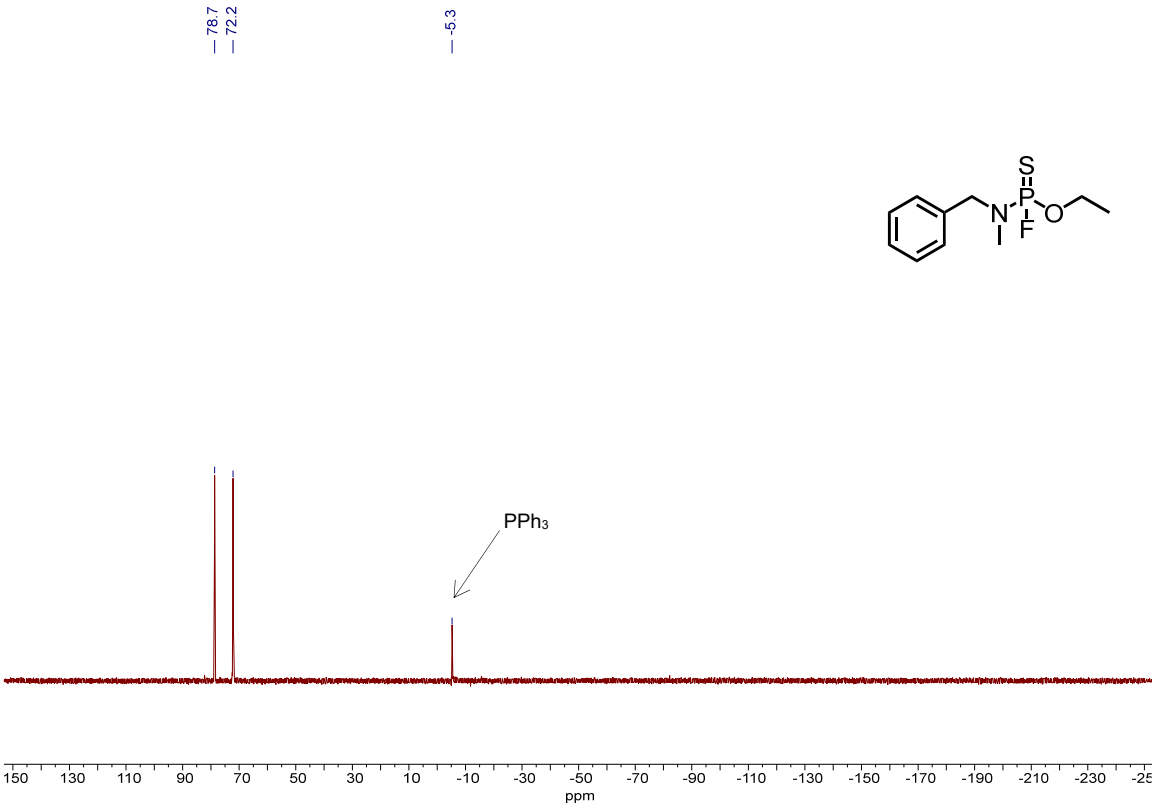
^{1}H NMR Spectrum for Compound **12f** (400 MHz, $CDCl_3$)



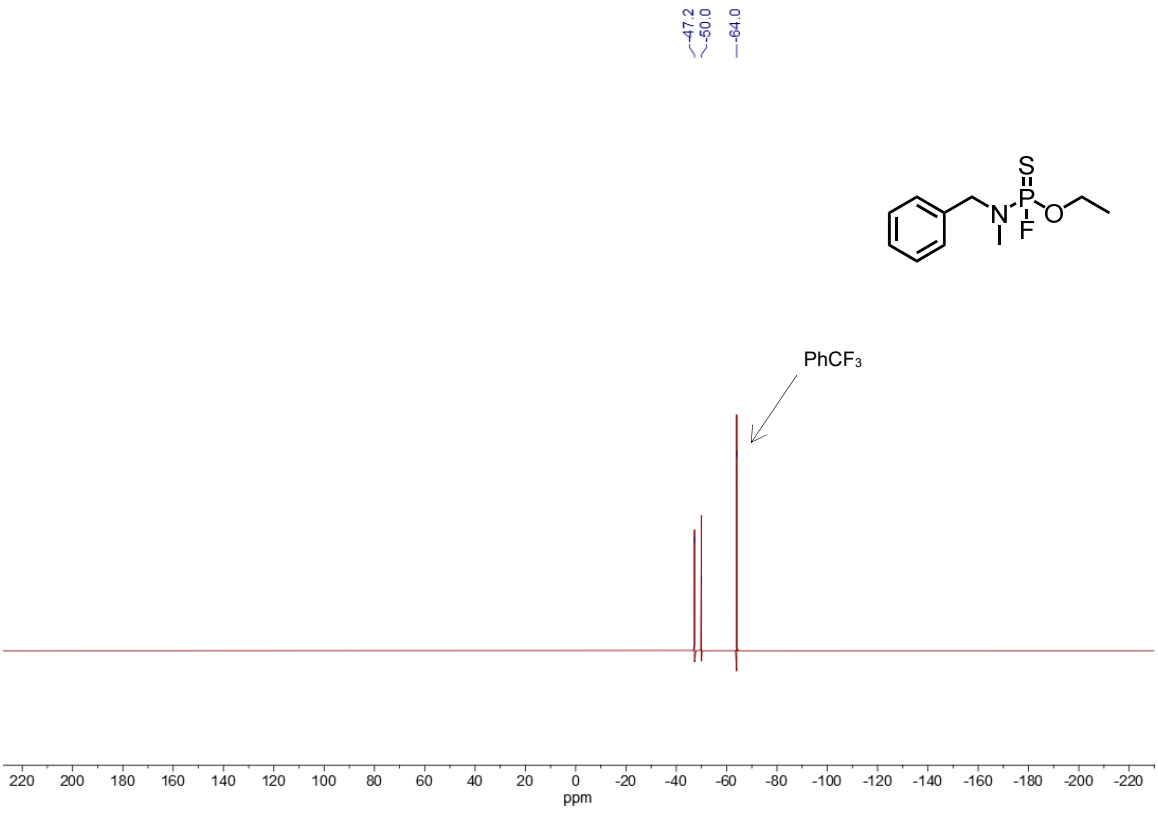
^{13}C NMR Spectrum for Compound **12f** (101 MHz, $CDCl_3$)



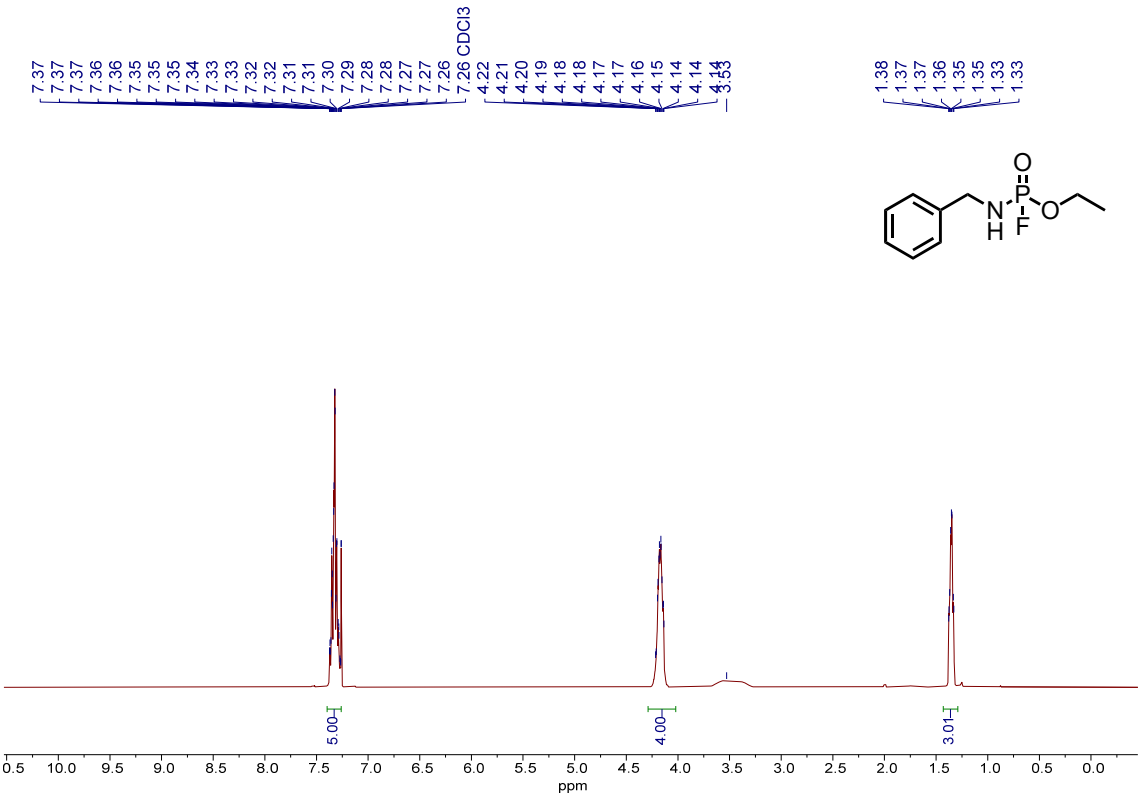
^{31}P NMR Spectrum for Compound **12f** (162 MHz, $CDCl_3$)



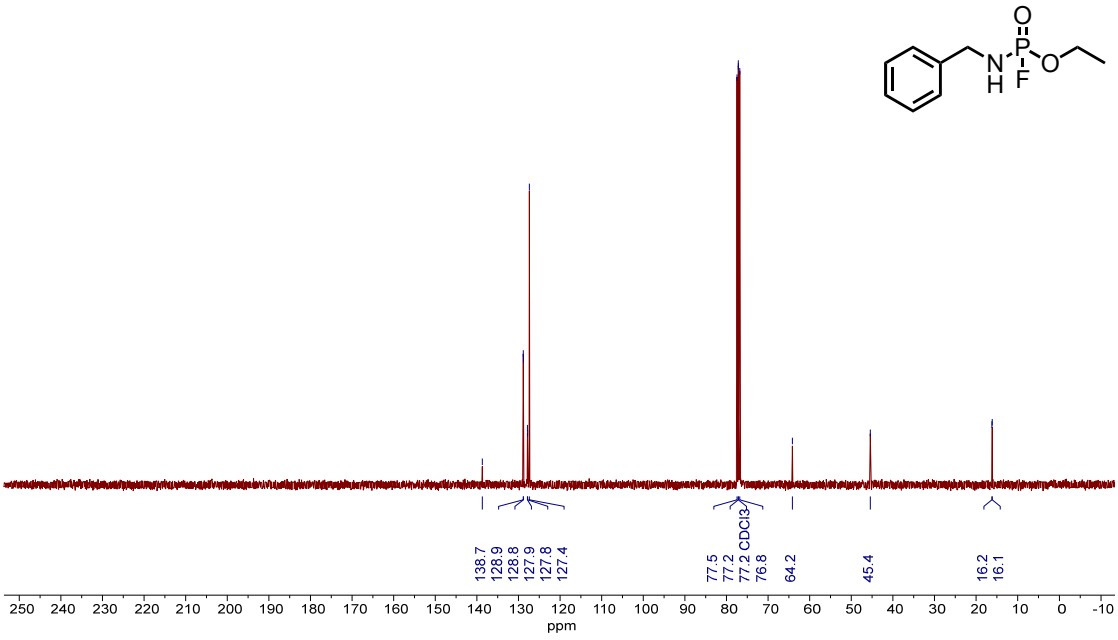
^{19}F NMR Spectrum for Compound **12f** (376 MHz, $CDCl_3$)



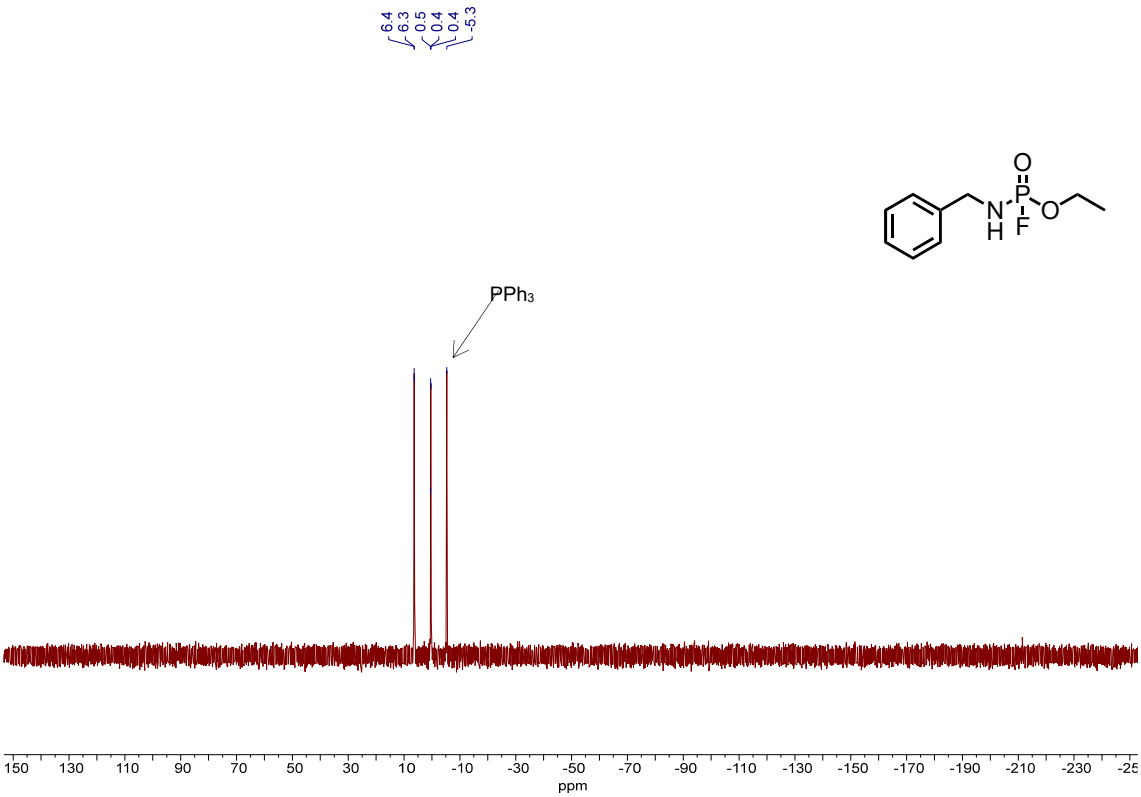
^{1}H NMR Spectrum for Compound **12g** (400 MHz, $CDCl_3$)



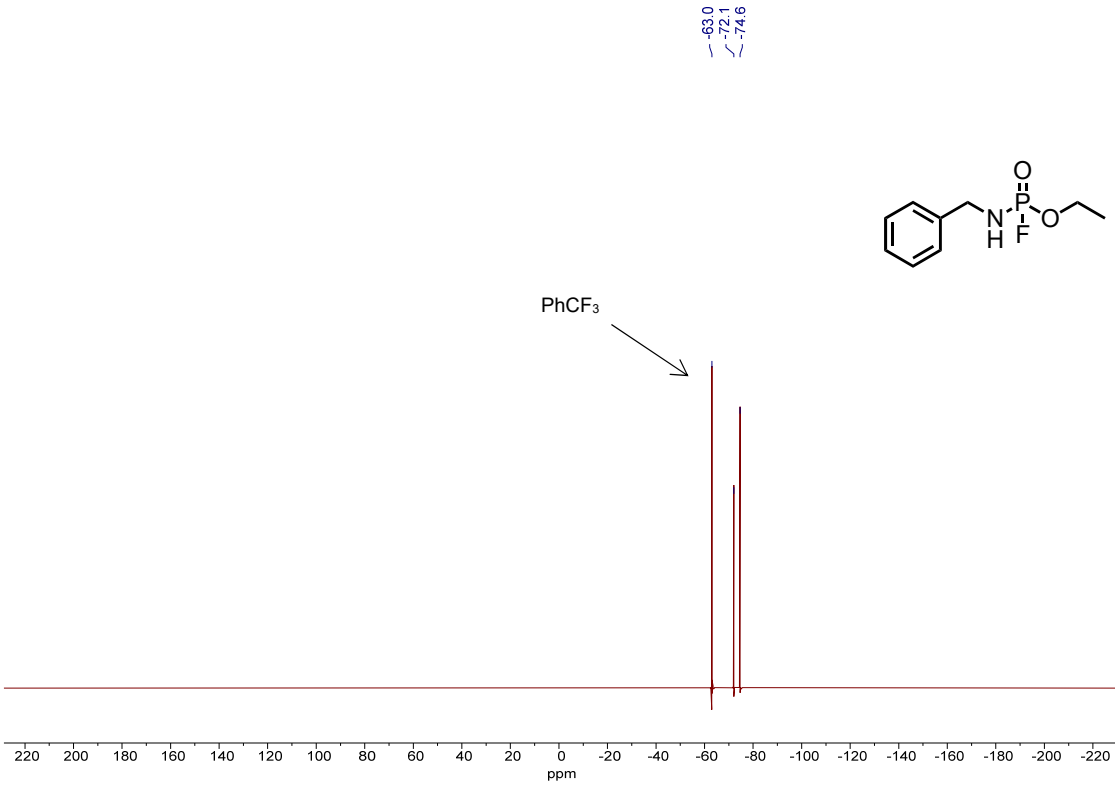
^{13}C NMR Spectrum for Compound **12g** (101 MHz, $CDCl_3$)



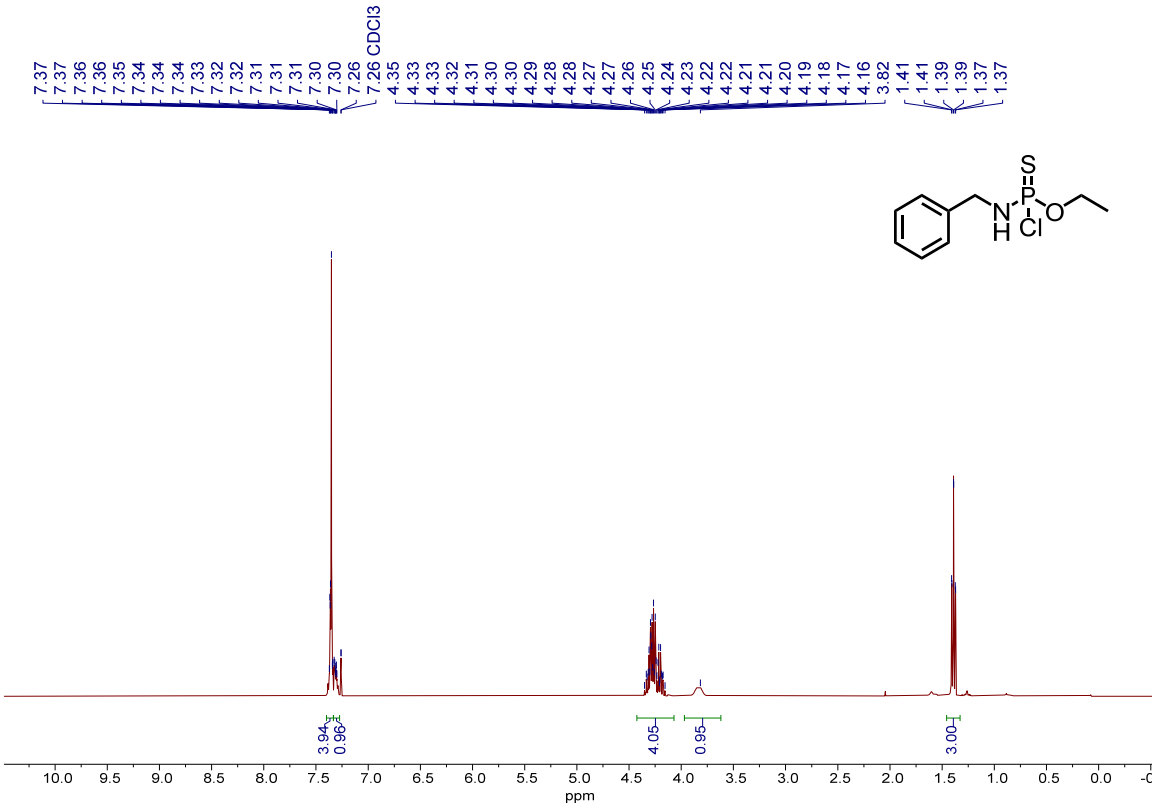
^{31}P NMR Spectrum for Compound **12g** (162 MHz, $CDCl_3$)



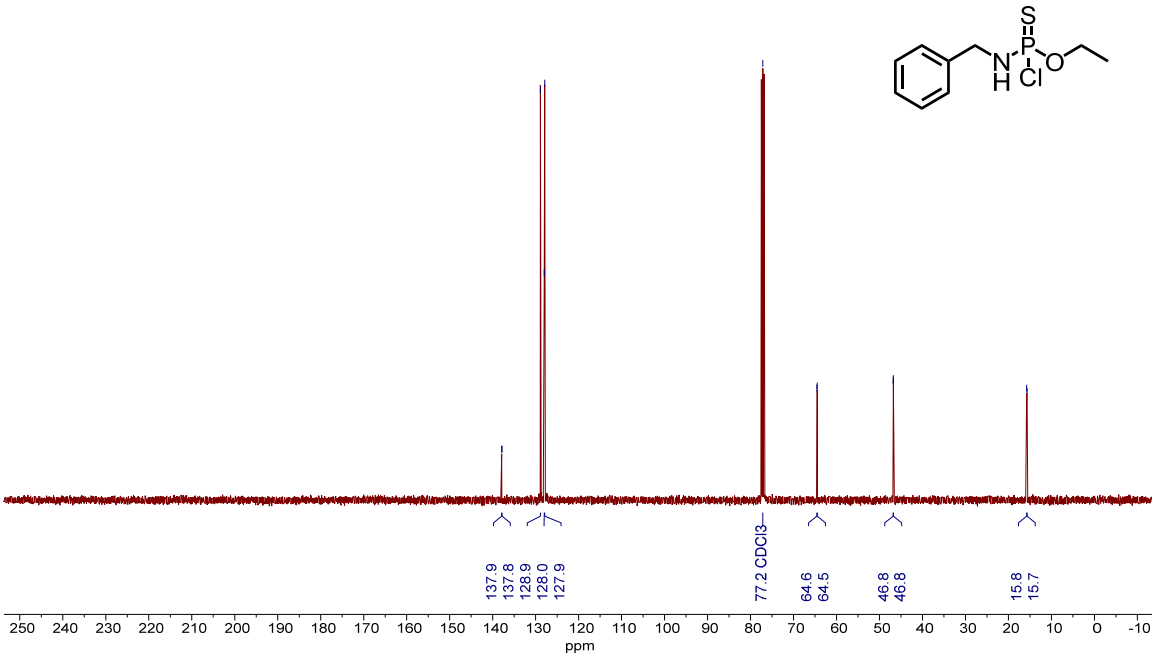
^{19}F NMR Spectrum for Compound **12g** (376 MHz, $CDCl_3$)



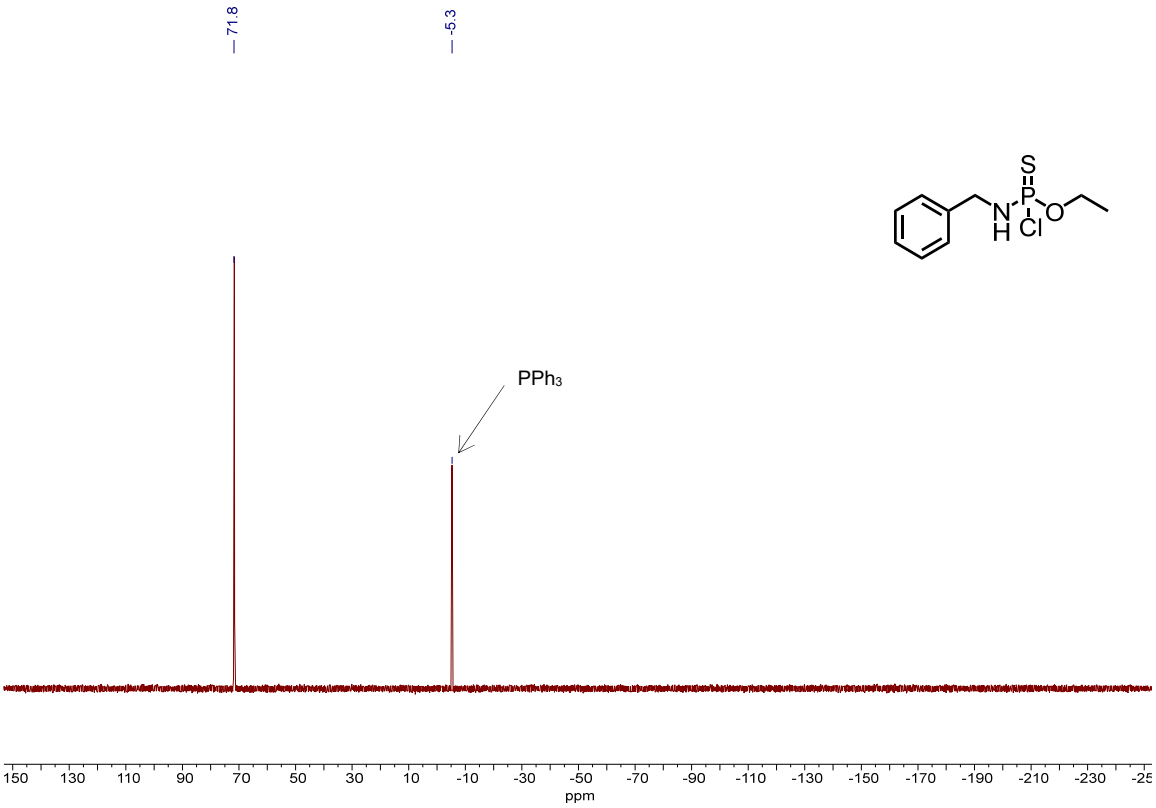
^{1}H NMR Spectrum for Compound **11h** (400 MHz, $CDCl_3$)



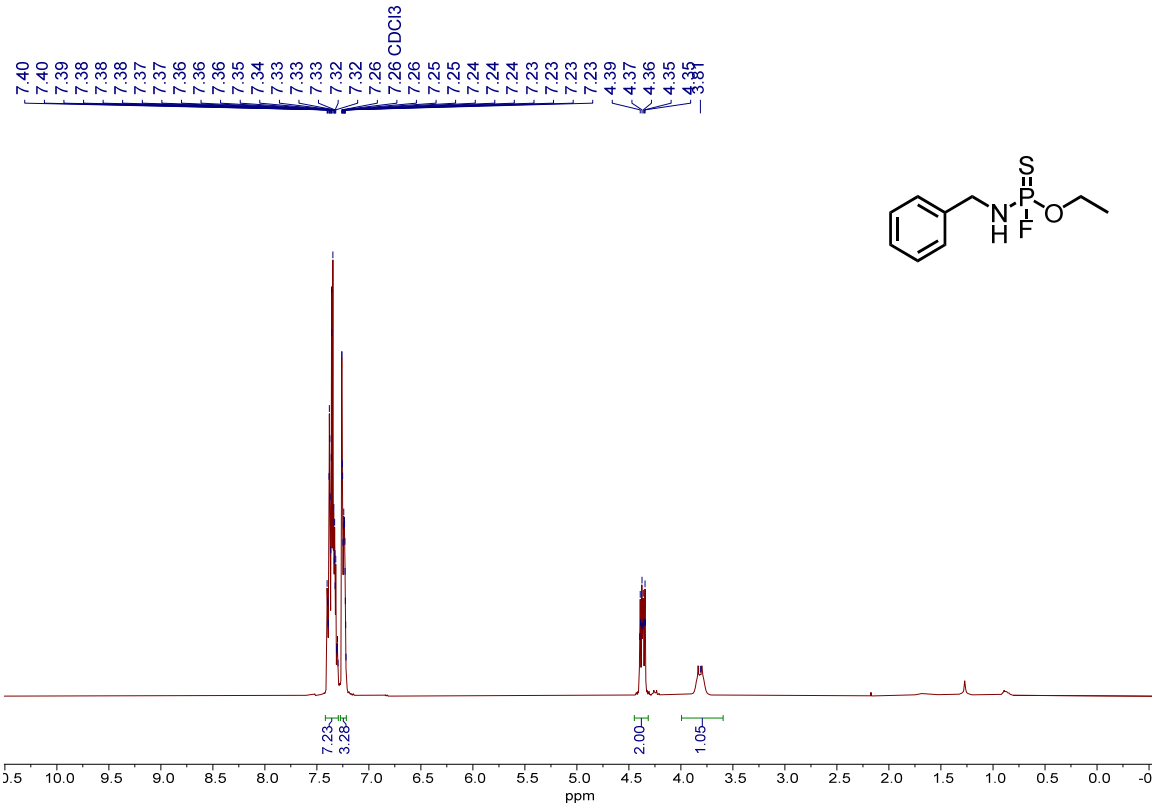
^{13}C NMR Spectrum for Compound **12c** (101 MHz, $CDCl_3$)



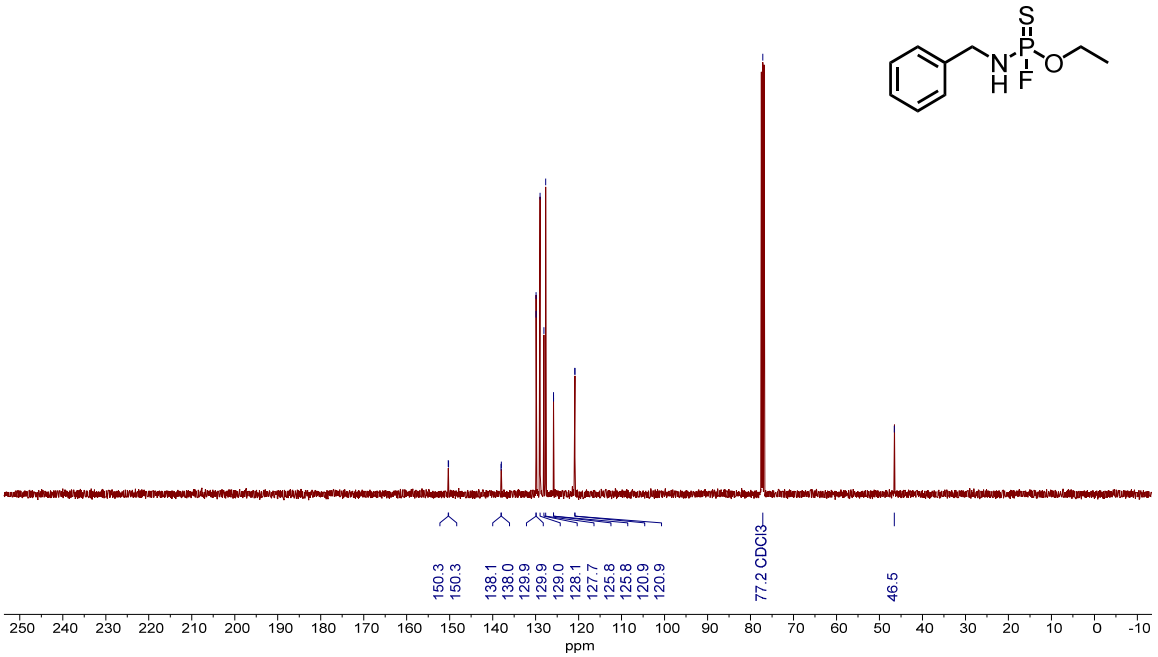
^{31}P NMR Spectrum for Compound **11h** (162 MHz, $CDCl_3$)



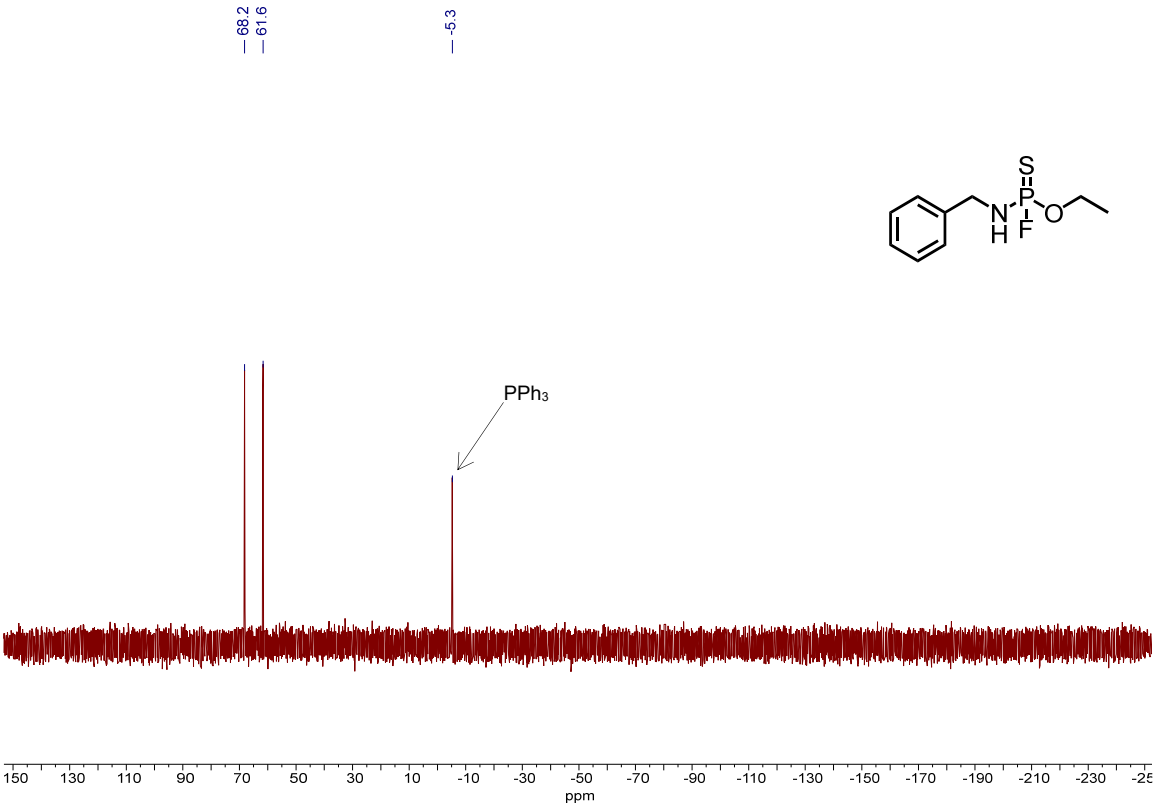
^{1}H NMR Spectrum for Compound **12h** (400 MHz, $CDCl_3$)



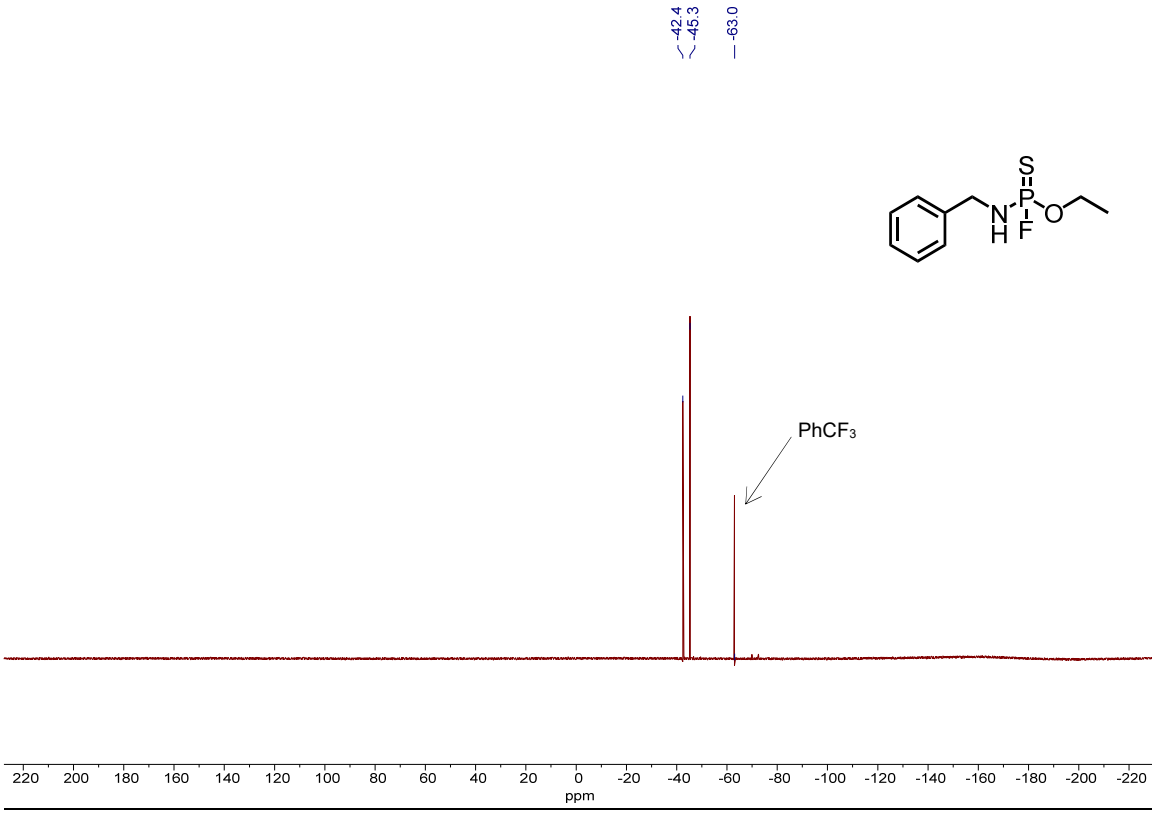
^{13}C NMR Spectrum for Compound **12h** (101 MHz, $CDCl_3$)



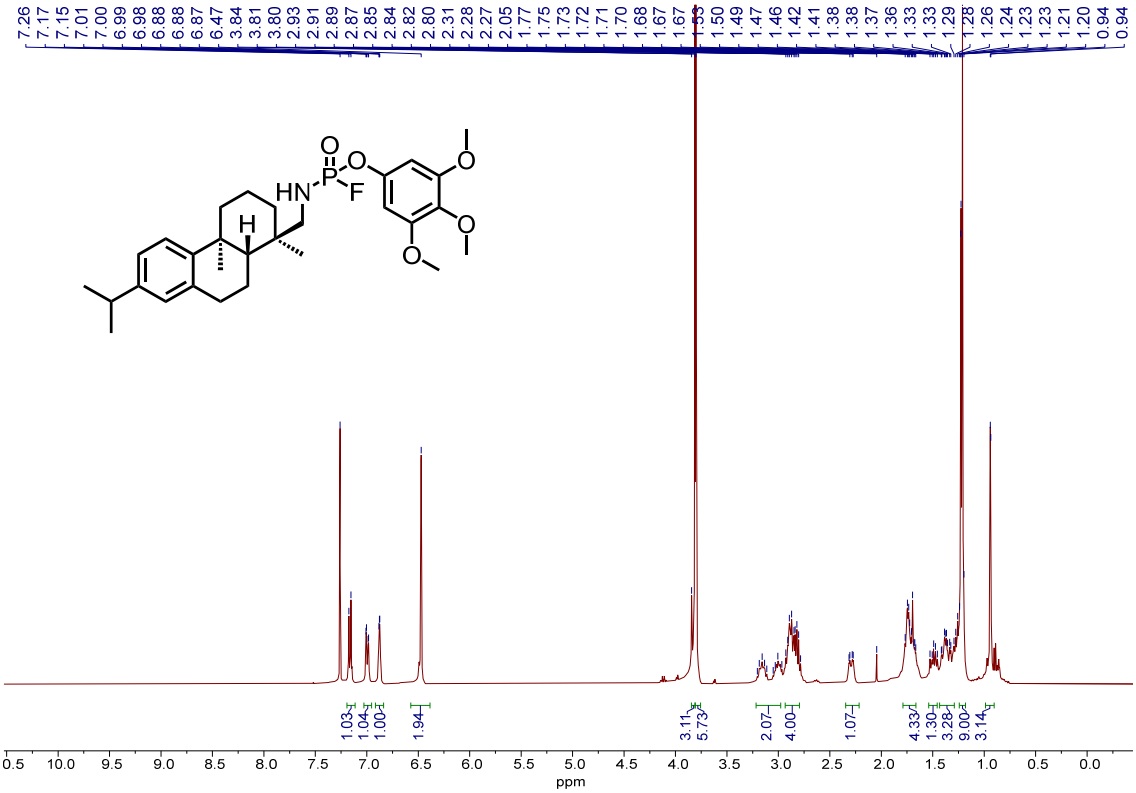
^{31}P NMR Spectrum for Compound **12h** (162 MHz, $CDCl_3$)



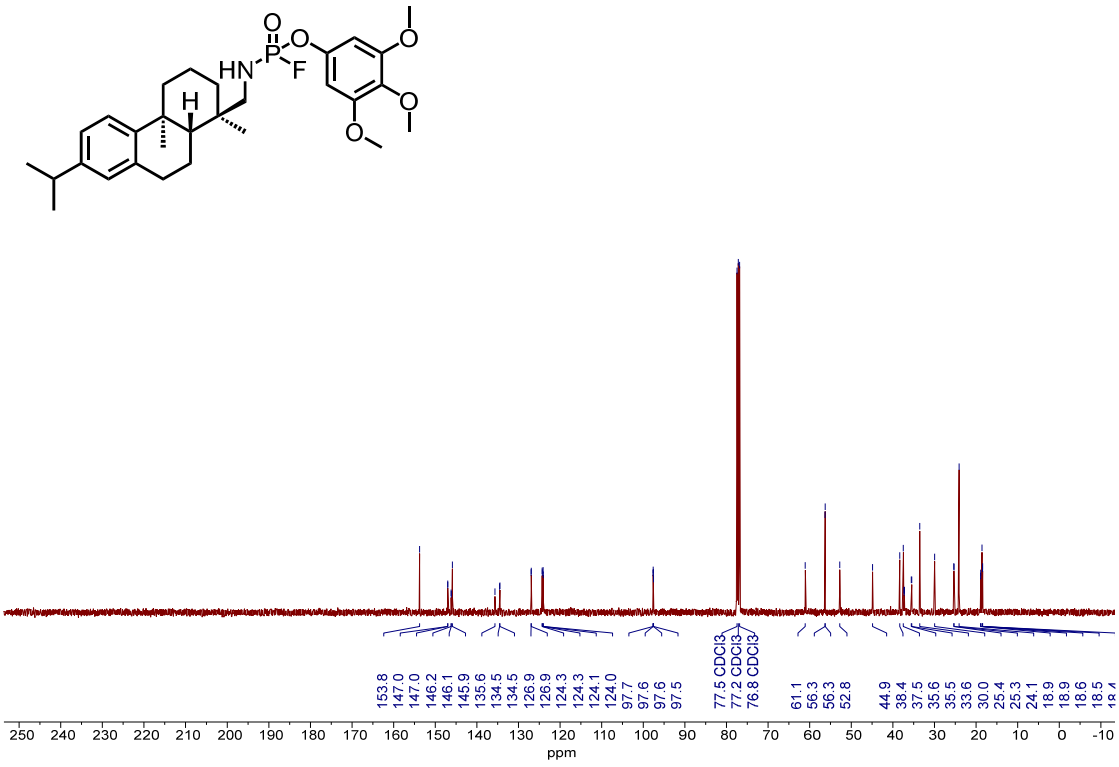
^{19}F NMR Spectrum for Compound **12h** (376 MHz, $CDCl_3$)



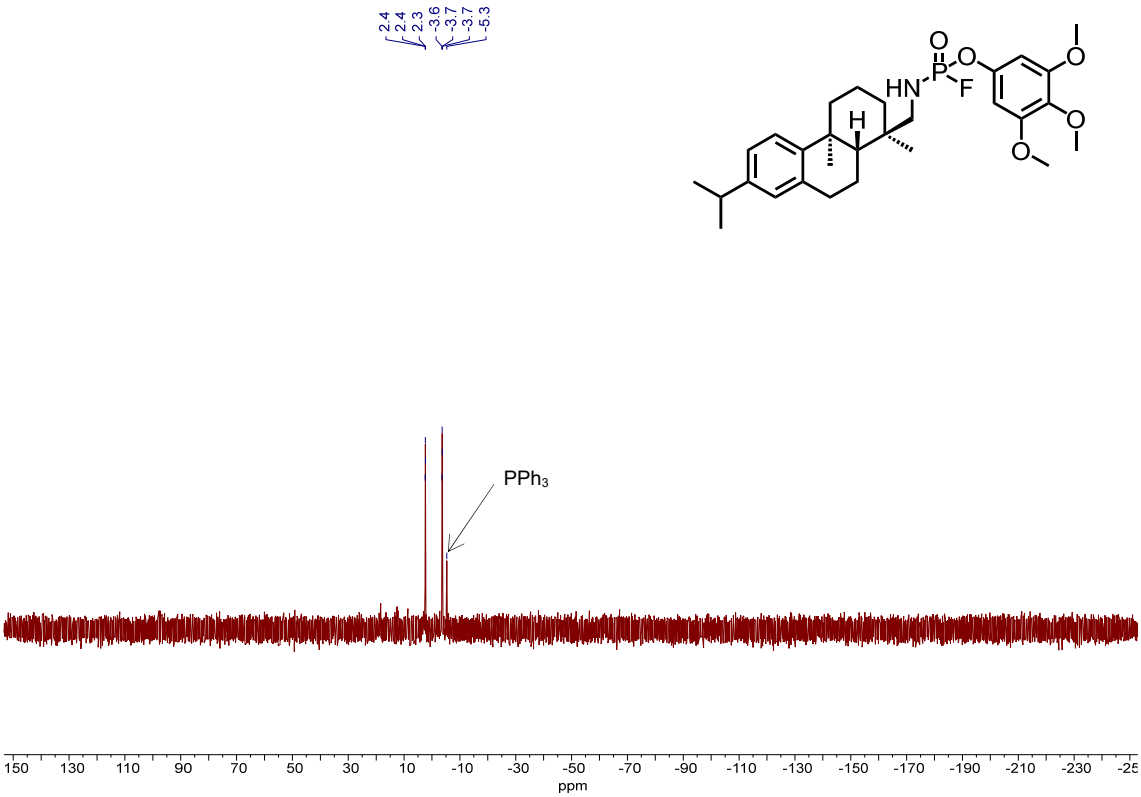
^{1}H NMR Spectrum for Compound **12i** (400 MHz, $CDCl_3$)



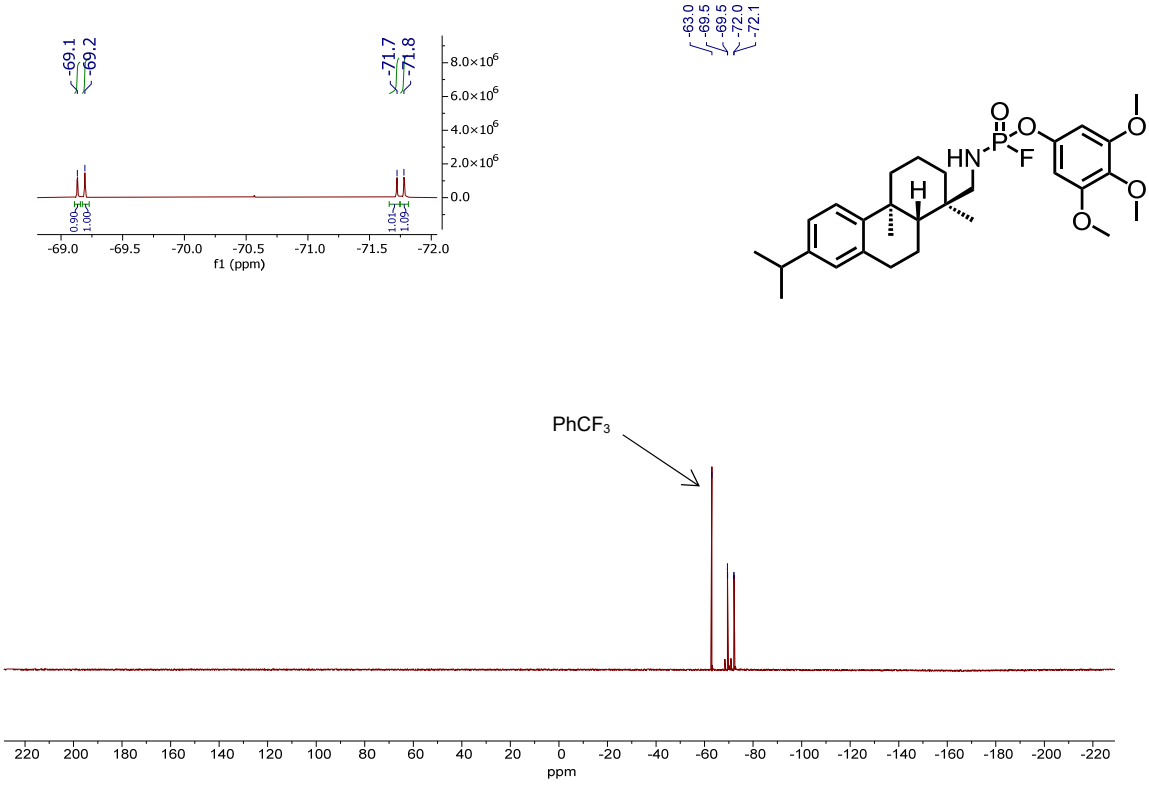
^{13}C NMR Spectrum for Compound **12i** (101 MHz, $CDCl_3$)



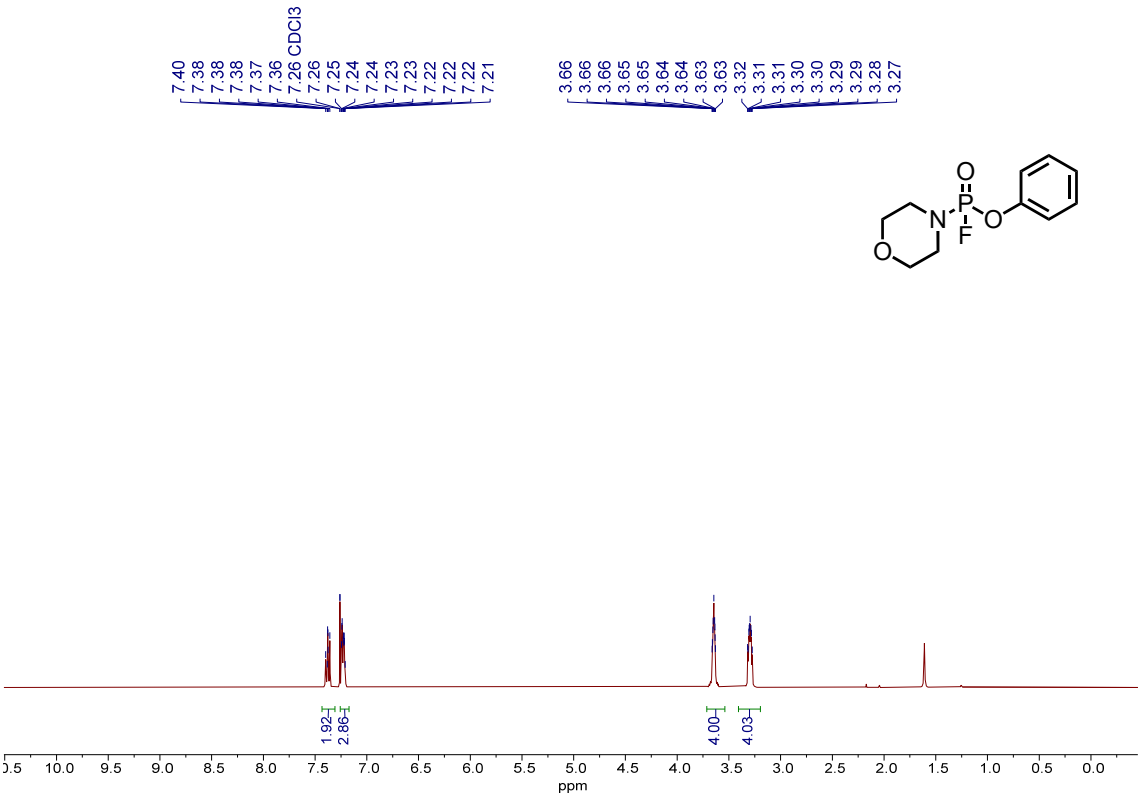
^{31}P NMR Spectrum for Compound **12i** (162 MHz, $CDCl_3$)



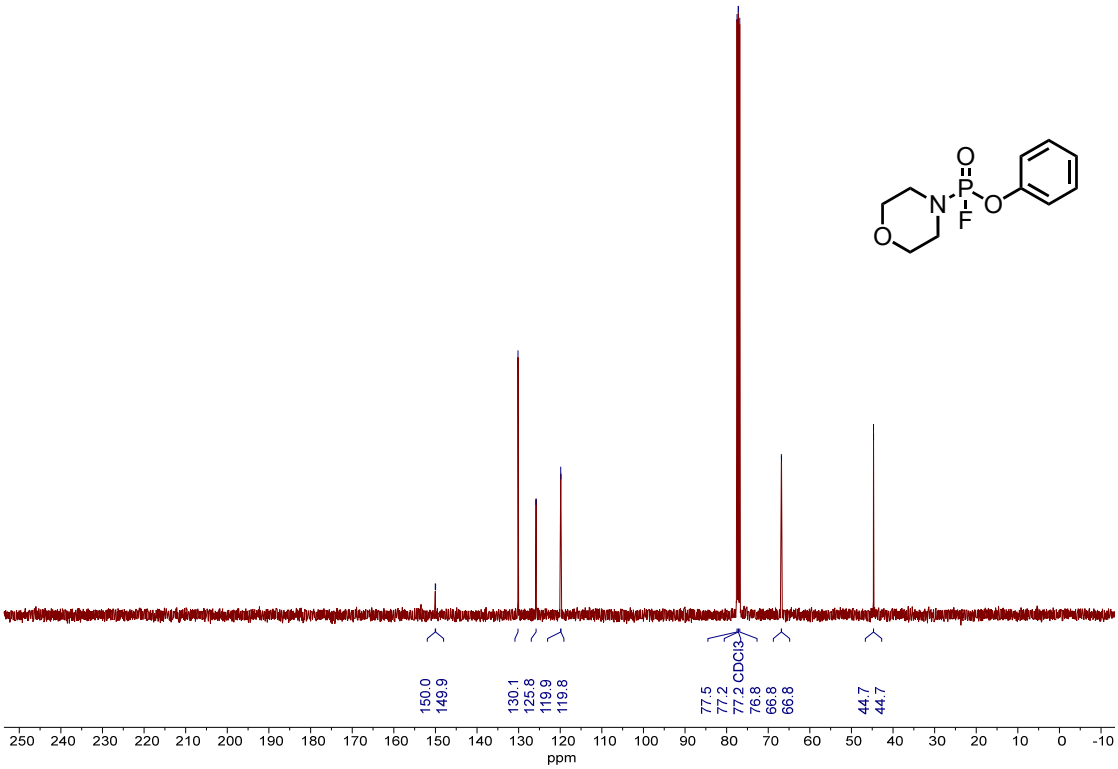
^{19}F NMR Spectrum for Compound **12i** (376 MHz, $CDCl_3$)



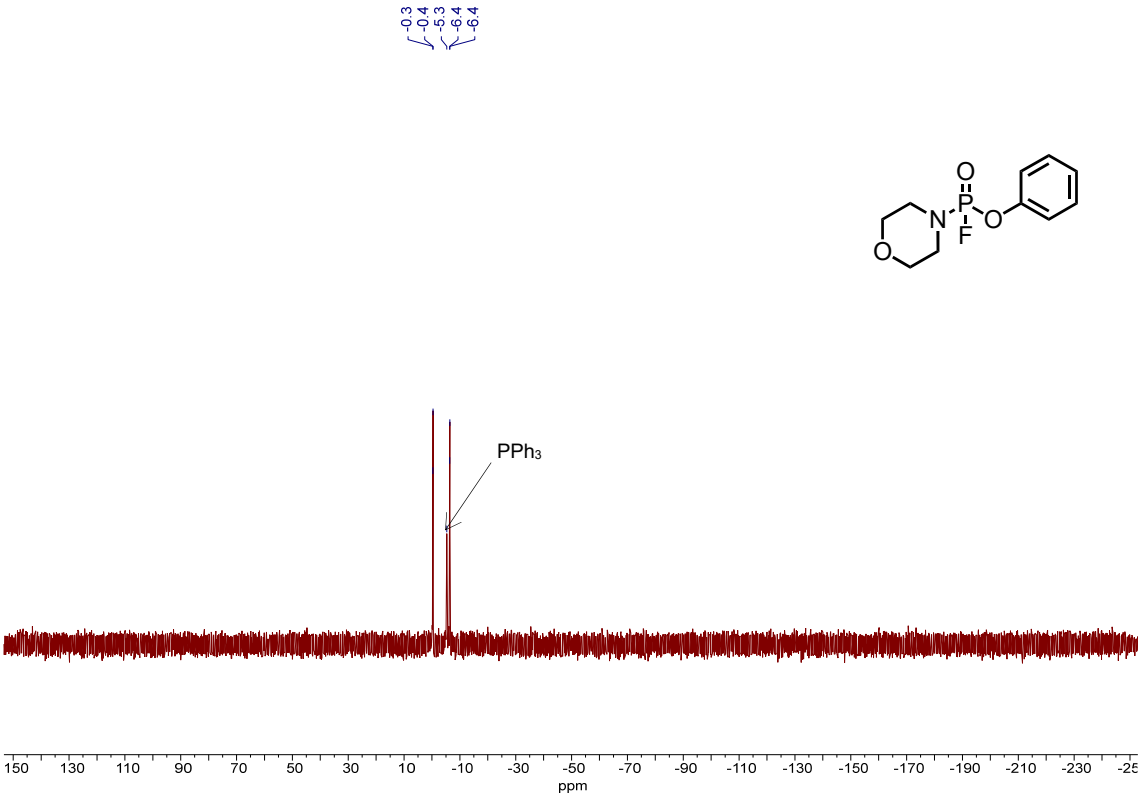
^{1}H NMR Spectrum for Compound **12j** (400 MHz, $CDCl_3$)



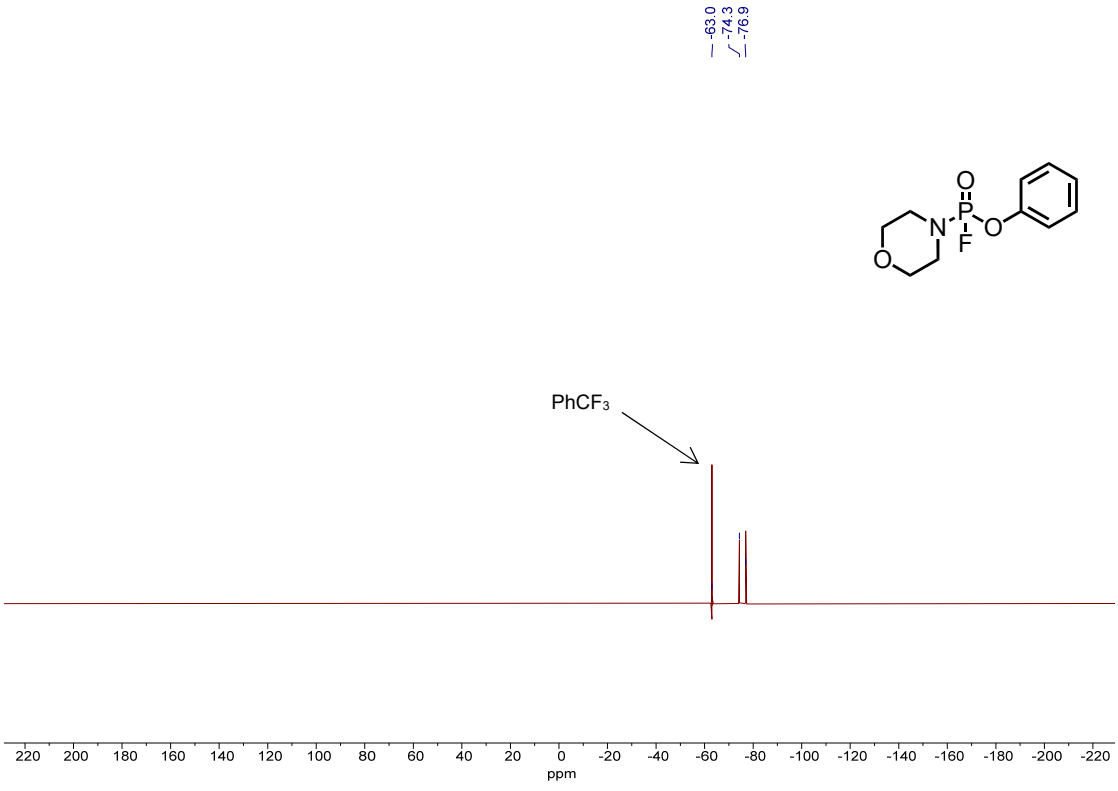
^{13}C NMR Spectrum for Compound **12j** (101 MHz, $CDCl_3$)



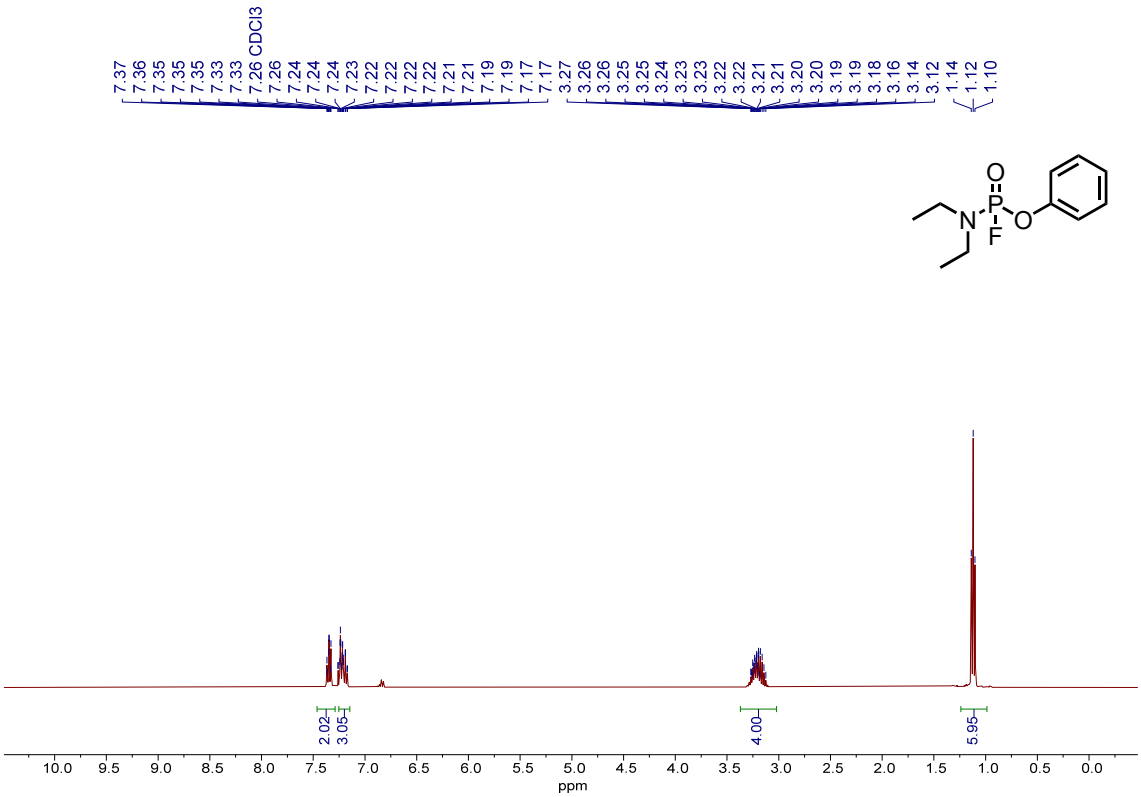
^{31}P NMR Spectrum for Compound **12j** (162 MHz, $CDCl_3$)



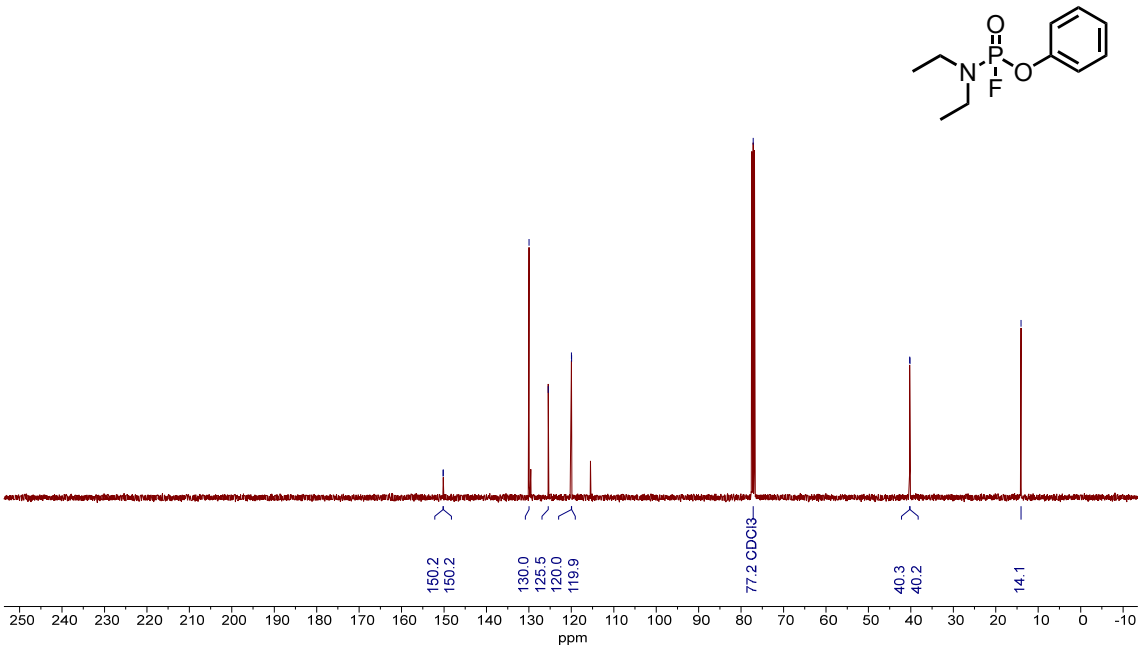
^{19}F NMR Spectrum for Compound **12j** (376 MHz, $CDCl_3$)



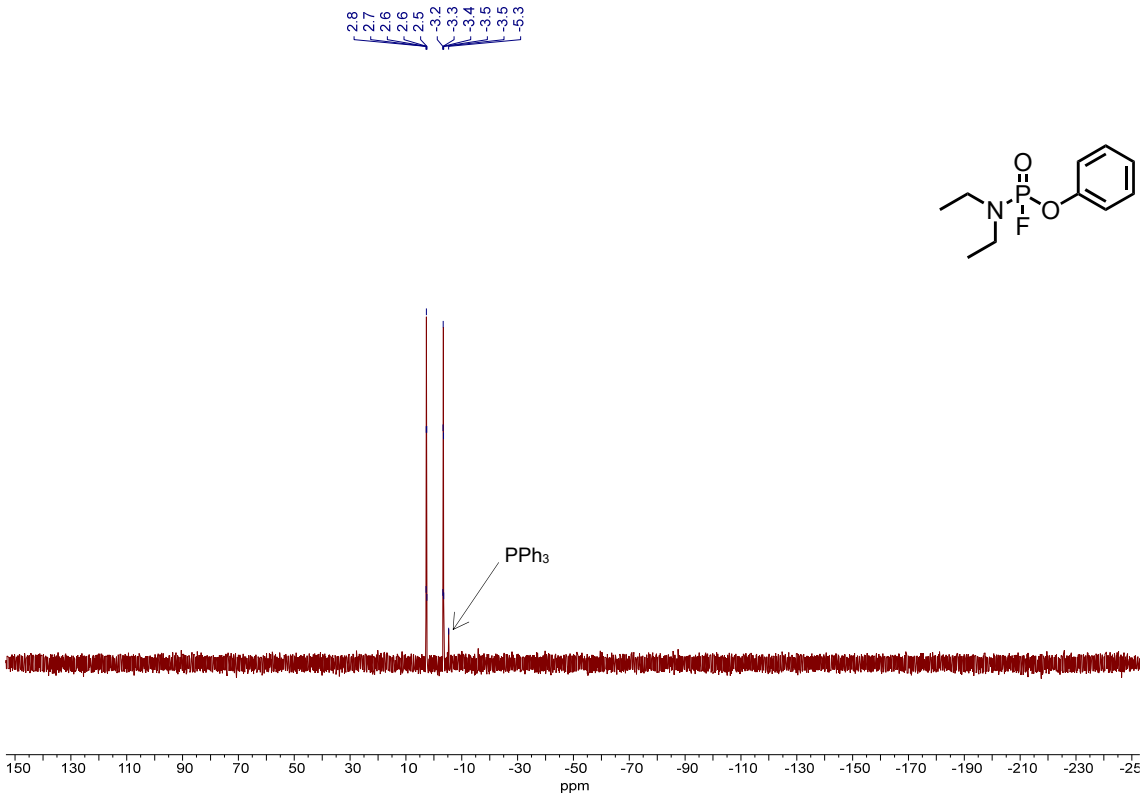
^{1}H NMR Spectrum for Compound **12k** (400 MHz, $CDCl_3$)



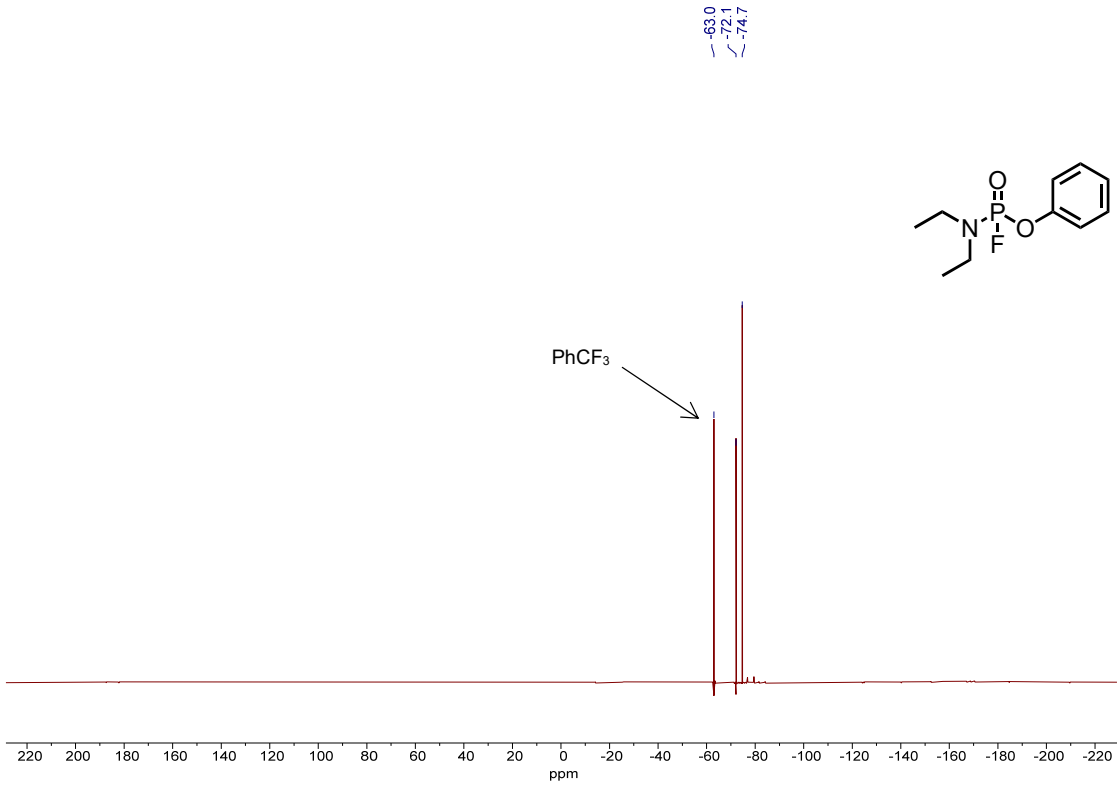
^{13}C NMR Spectrum for Compound **12k** (101 MHz, $CDCl_3$)



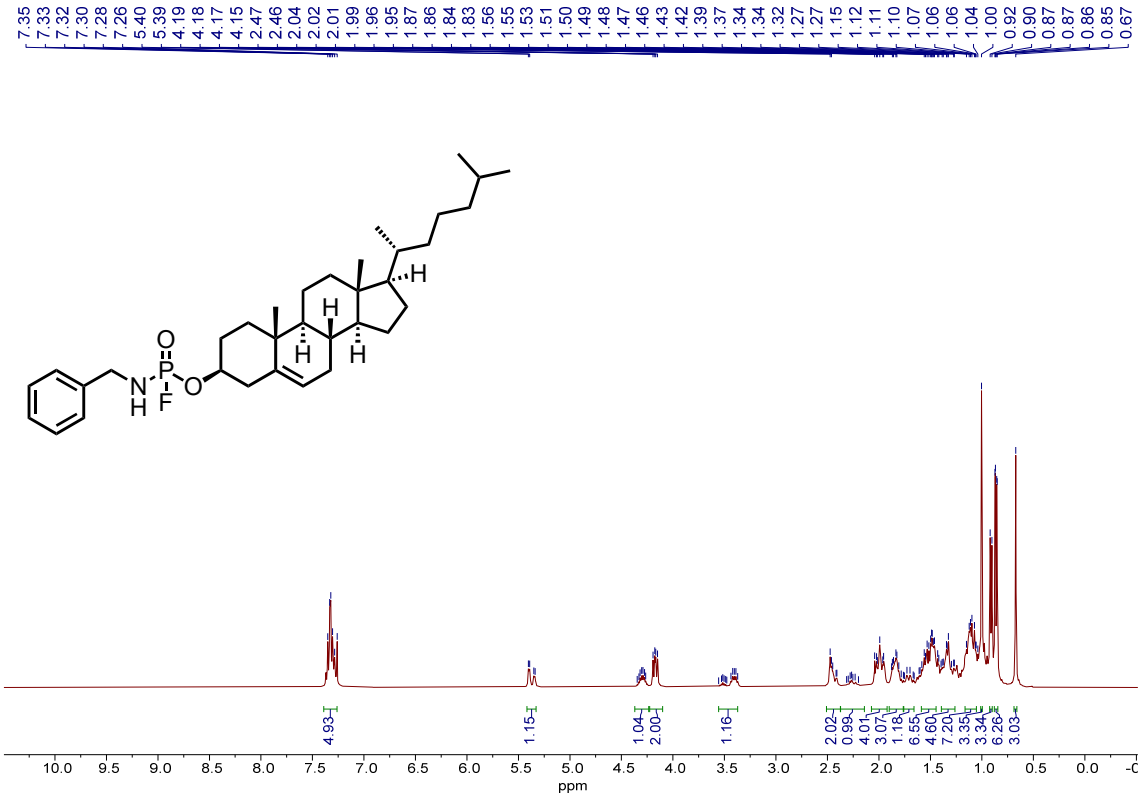
^{31}P NMR Spectrum for Compound **12k** (162 MHz, $CDCl_3$)



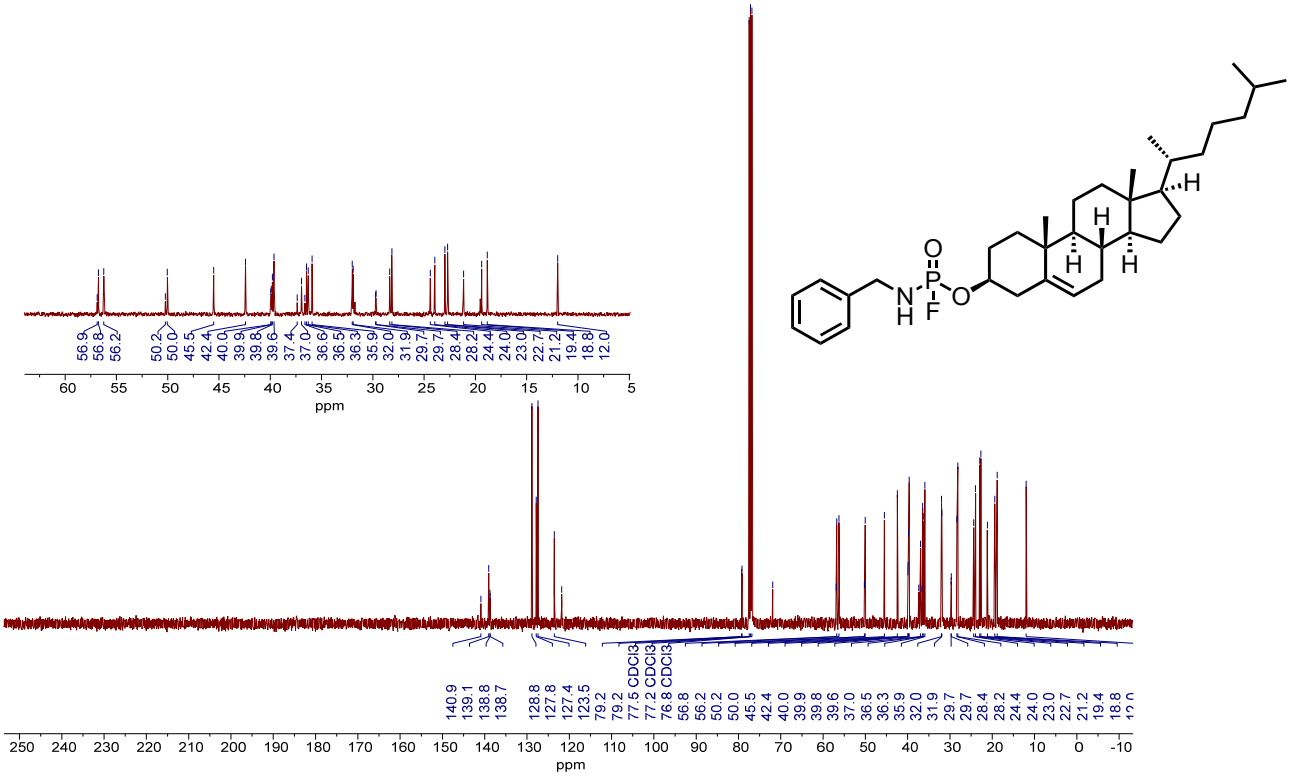
^{19}F NMR Spectrum for Compound **12k** (376 MHz, $CDCl_3$)



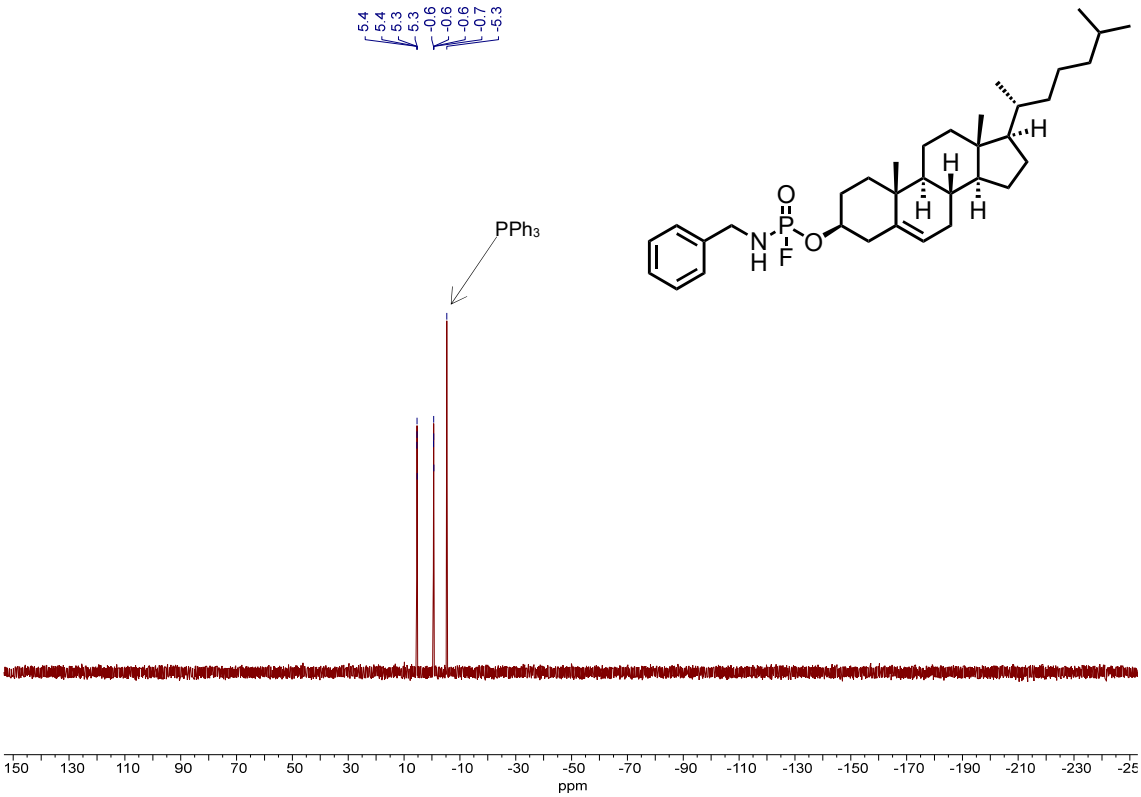
^{1}H NMR Spectrum for Compound **12l** (400 MHz, $CDCl_3$)



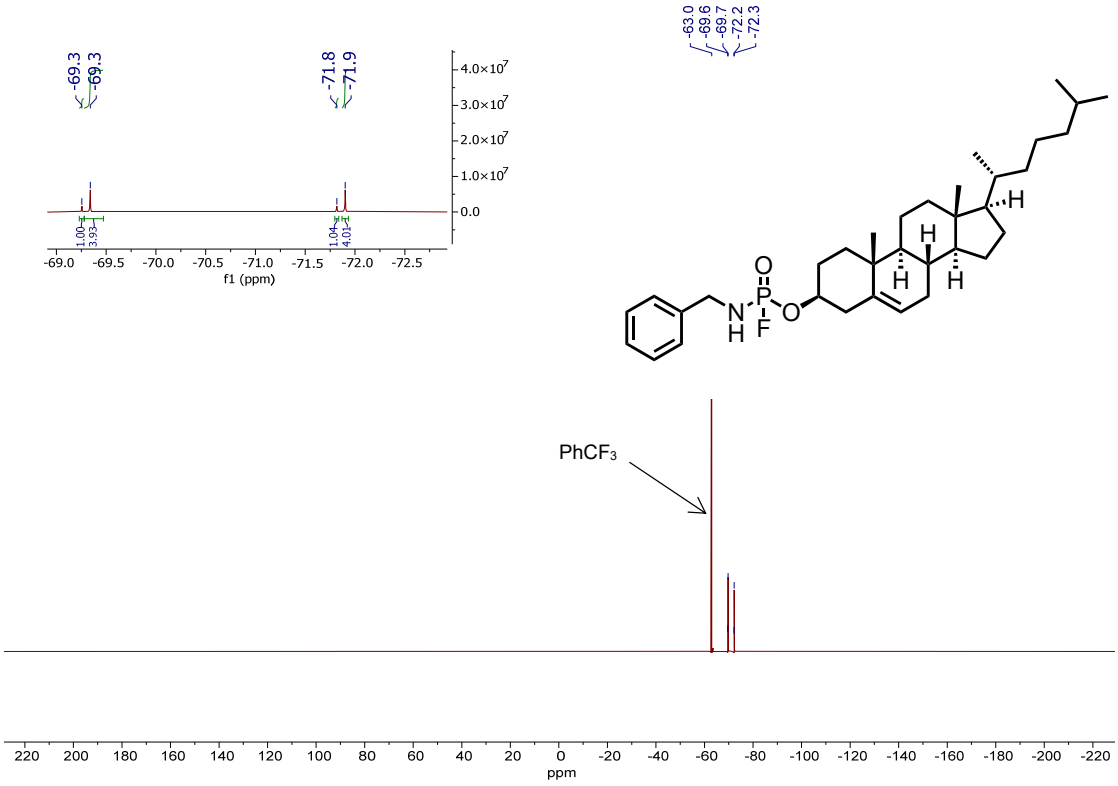
^{13}C NMR Spectrum for Compound **12l** (101 MHz, $CDCl_3$)



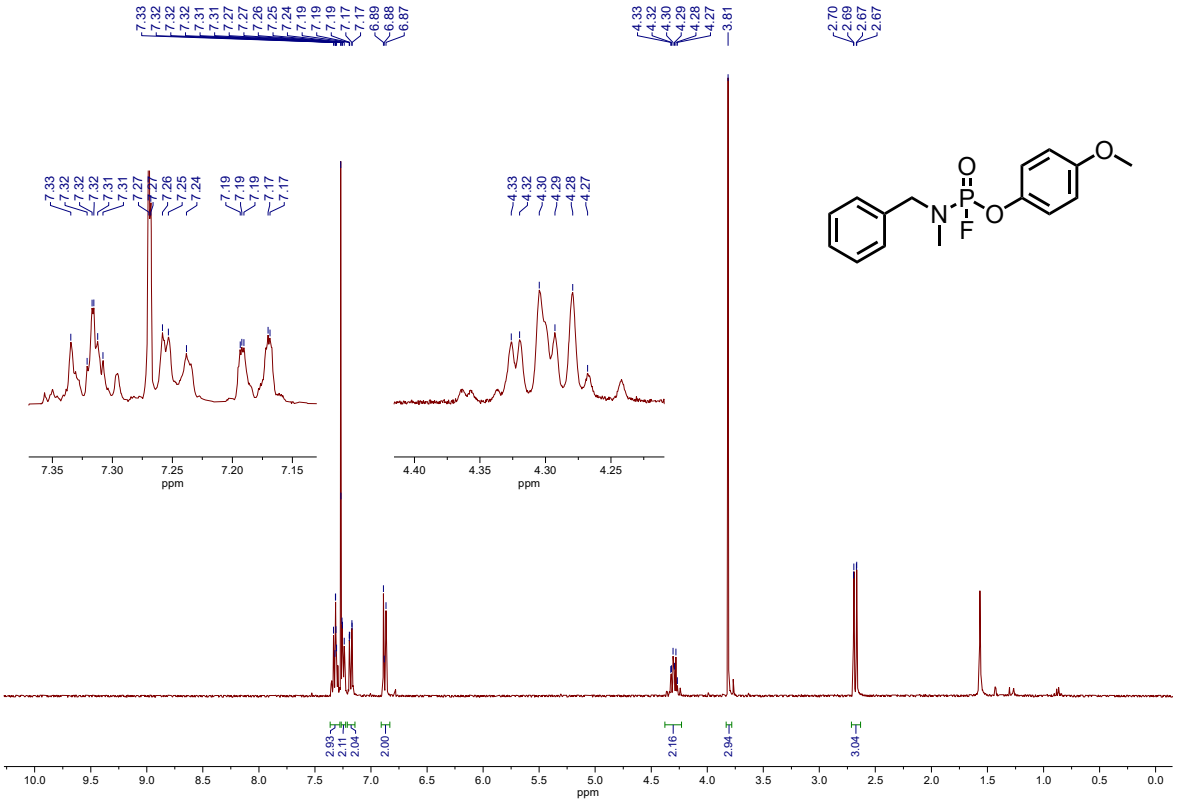
^{31}P NMR Spectrum for Compound **12l** (162 MHz, $CDCl_3$)



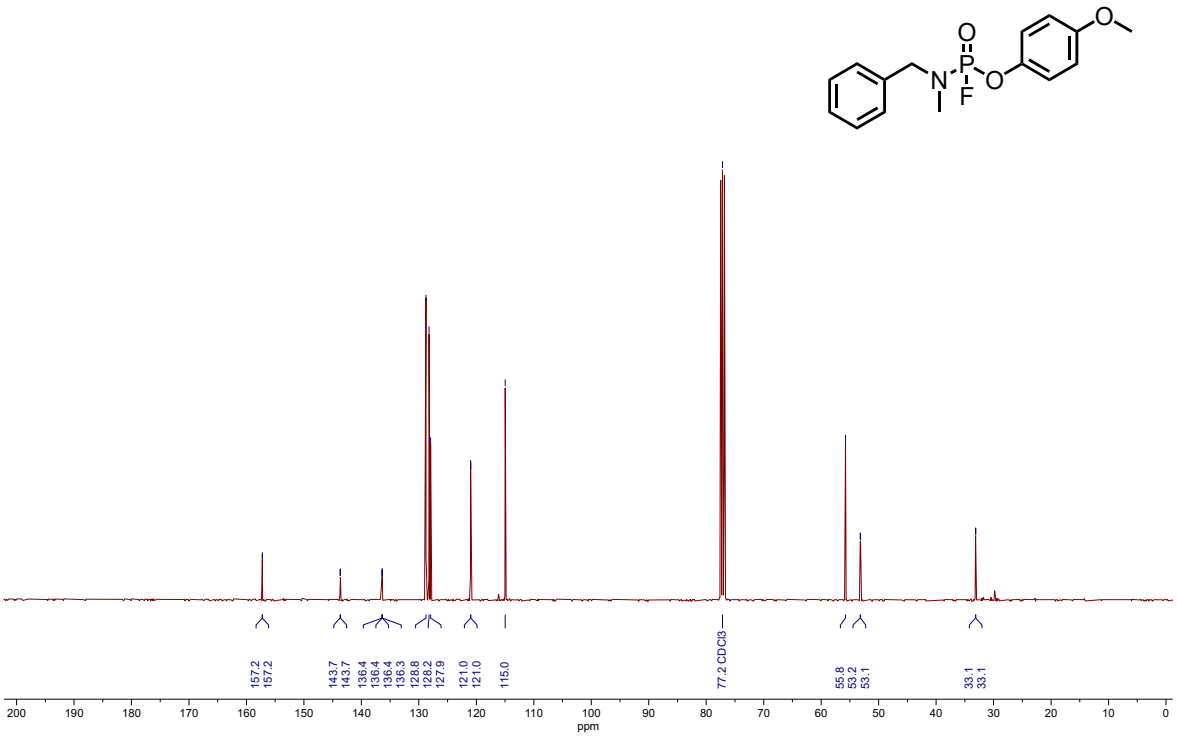
^{19}F NMR Spectrum for Compound **12l** (376 MHz, $CDCl_3$)



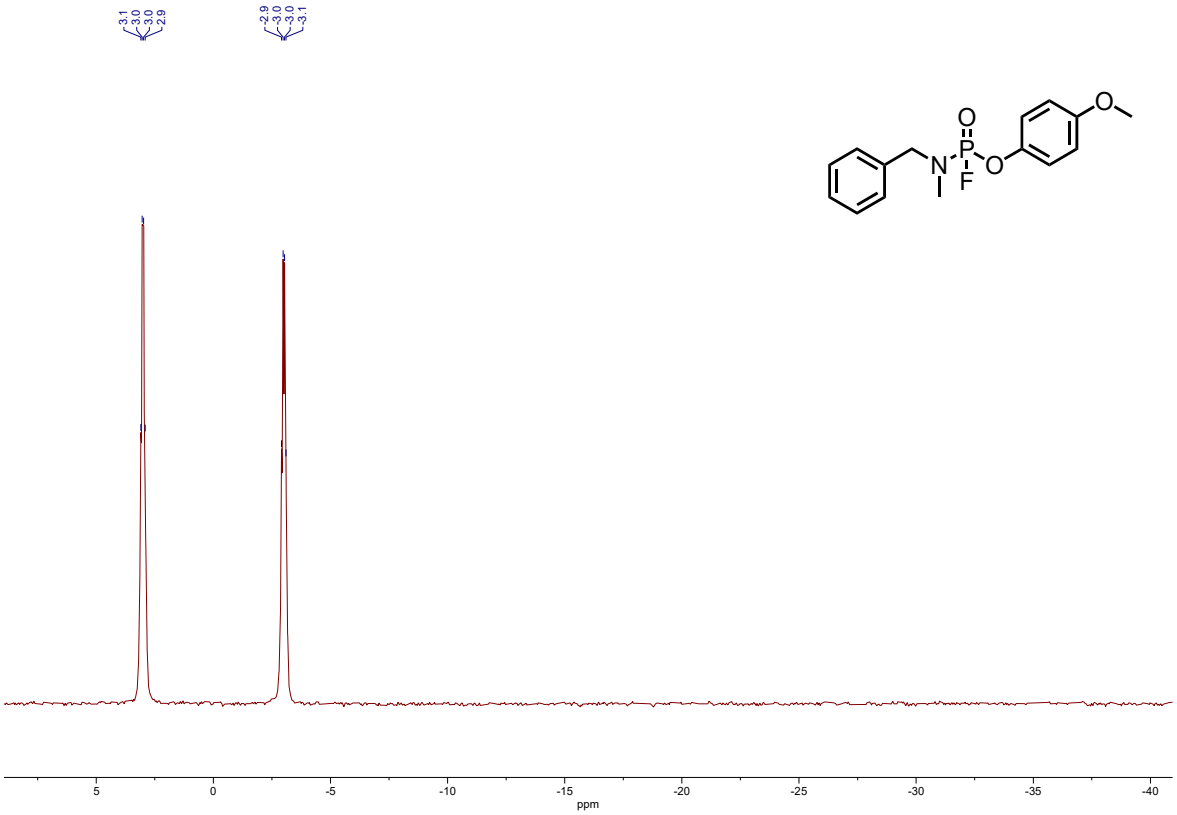
^{1}H NMR Spectrum for Compound **12m** (400 MHz, $CDCl_3$)



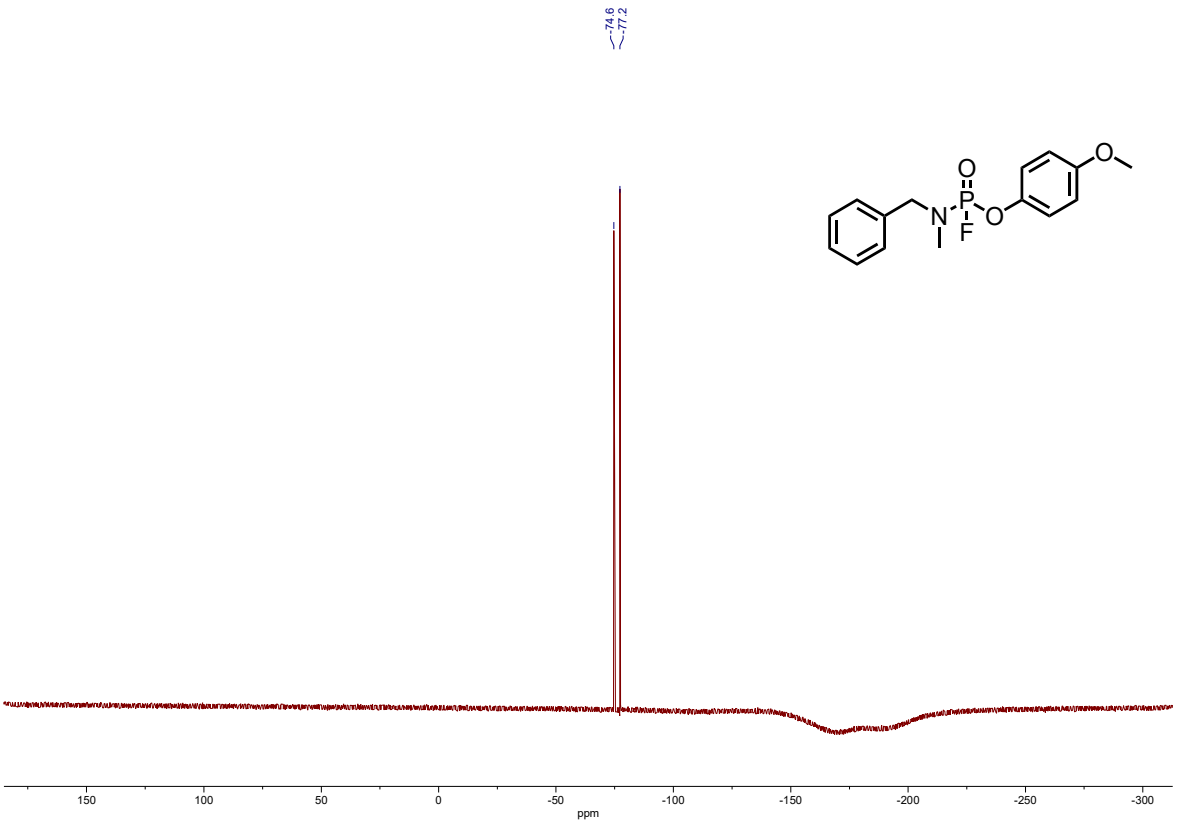
^{13}C NMR Spectrum for Compound **12m** (101 MHz, $CDCl_3$)



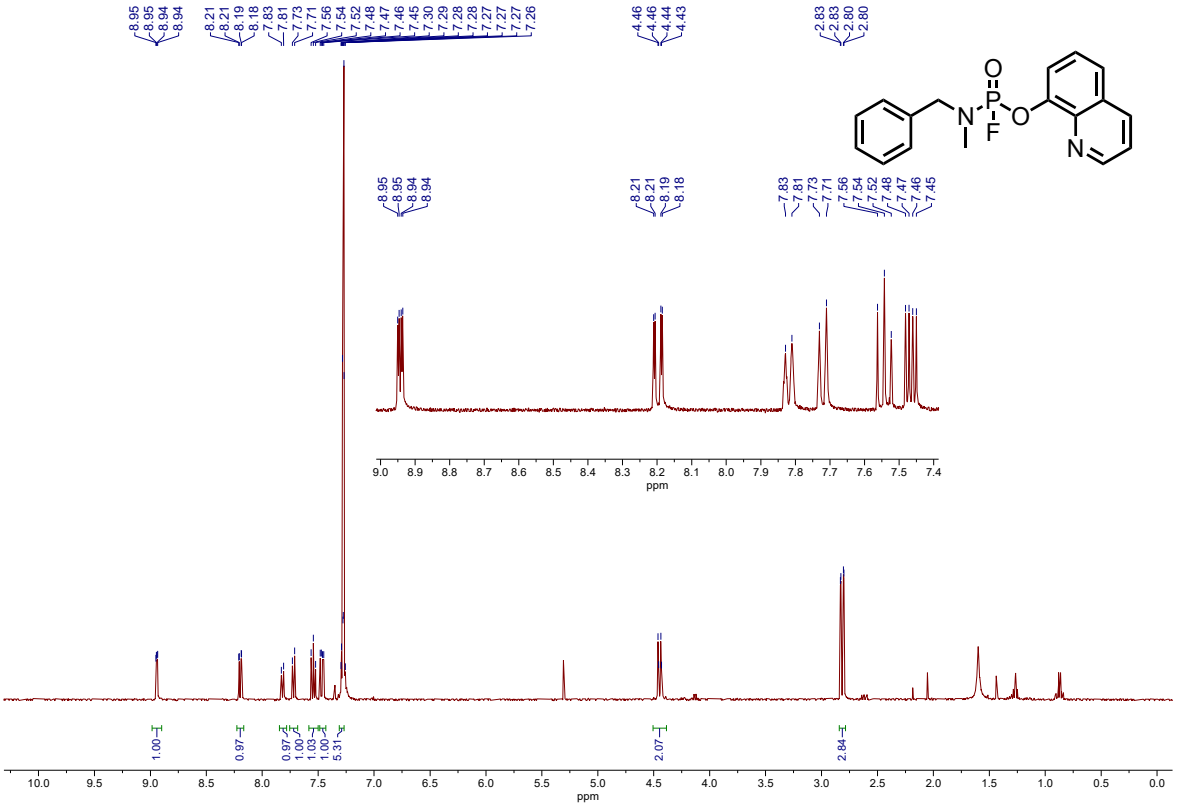
^{31}P NMR Spectrum for Compound **12m** (162 MHz, $CDCl_3$)



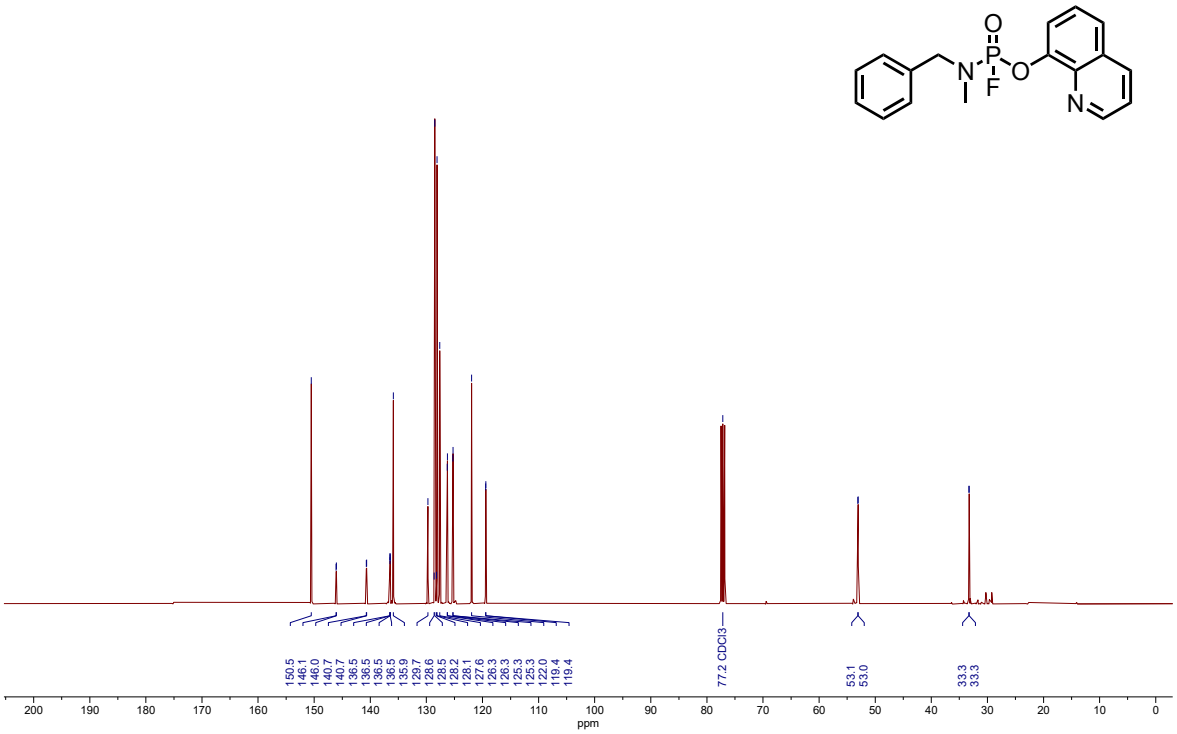
^{19}F NMR Spectrum for Compound **12m** (376 MHz, $CDCl_3$)



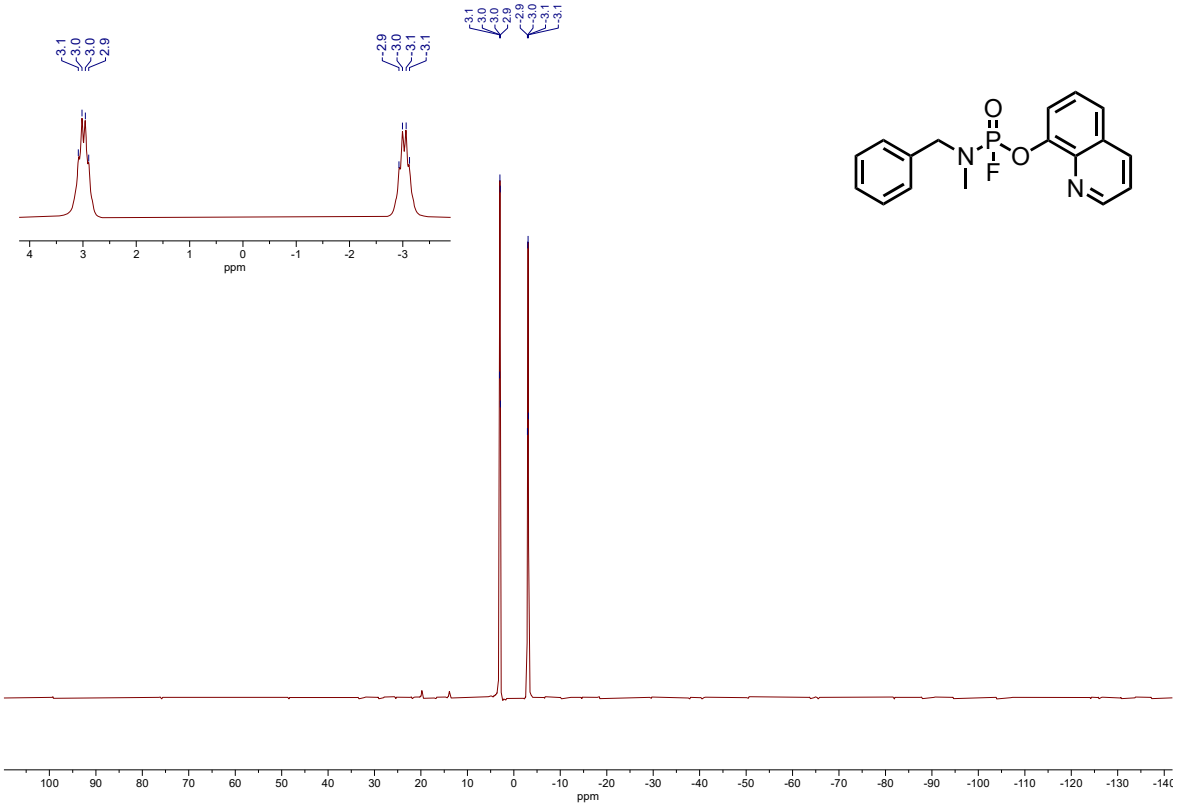
^{1}H NMR Spectrum for Compound **12n** (400 MHz, $CDCl_3$)



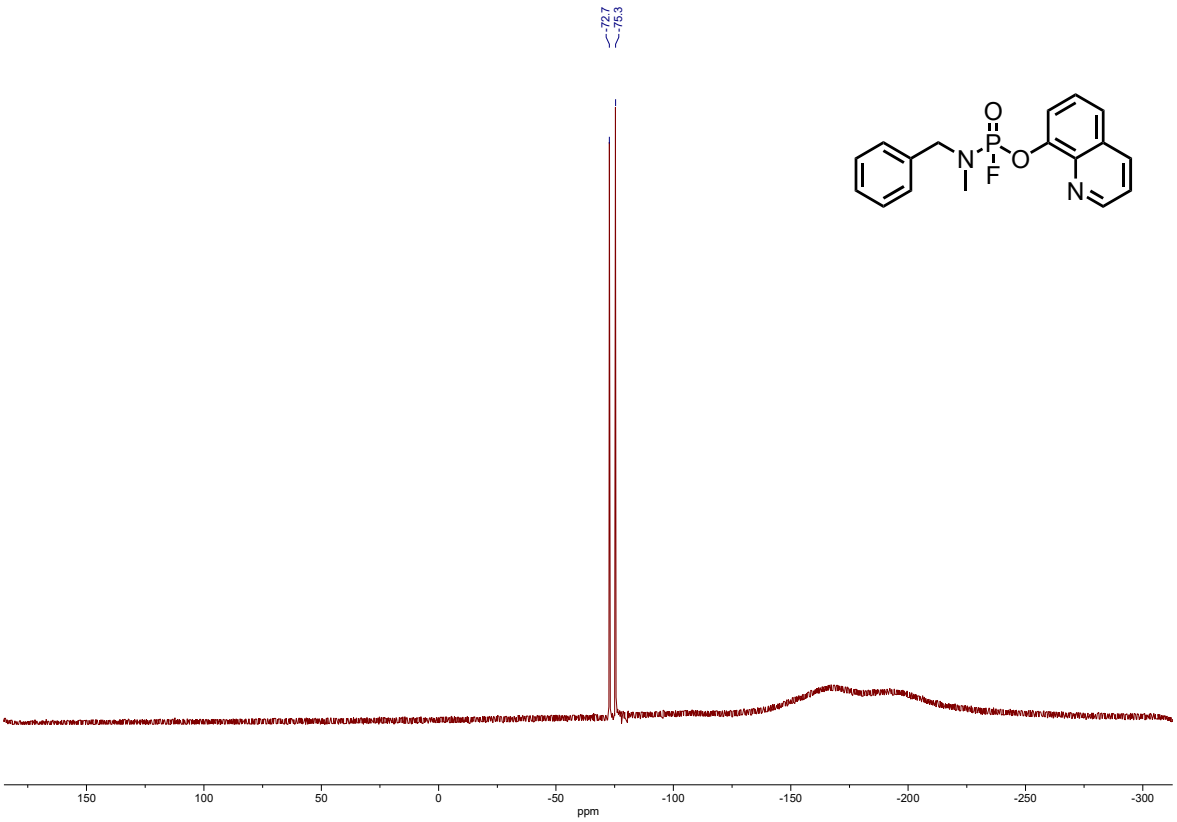
^{13}C NMR Spectrum for Compound **12n** (101 MHz, $CDCl_3$)



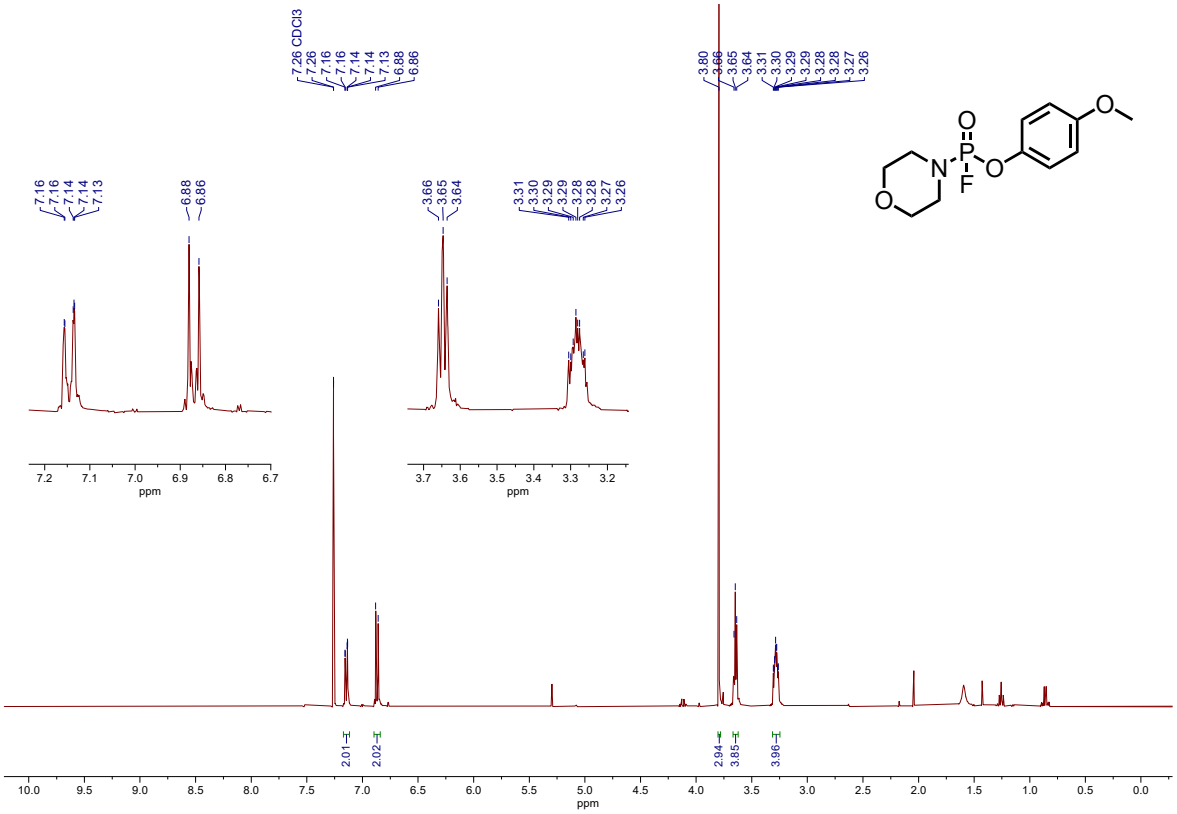
^{31}P NMR Spectrum for Compound **12n** (162 MHz, $CDCl_3$)



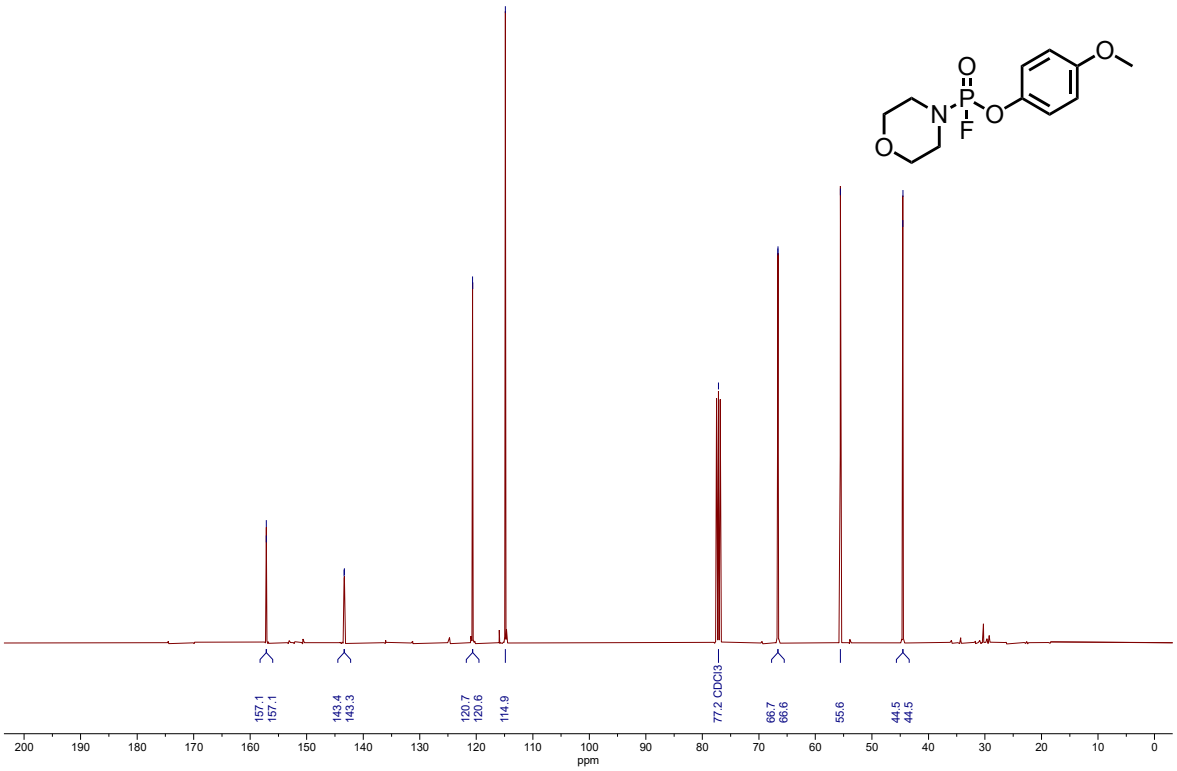
^{19}F NMR Spectrum for Compound **12n** (376 MHz, $CDCl_3$)



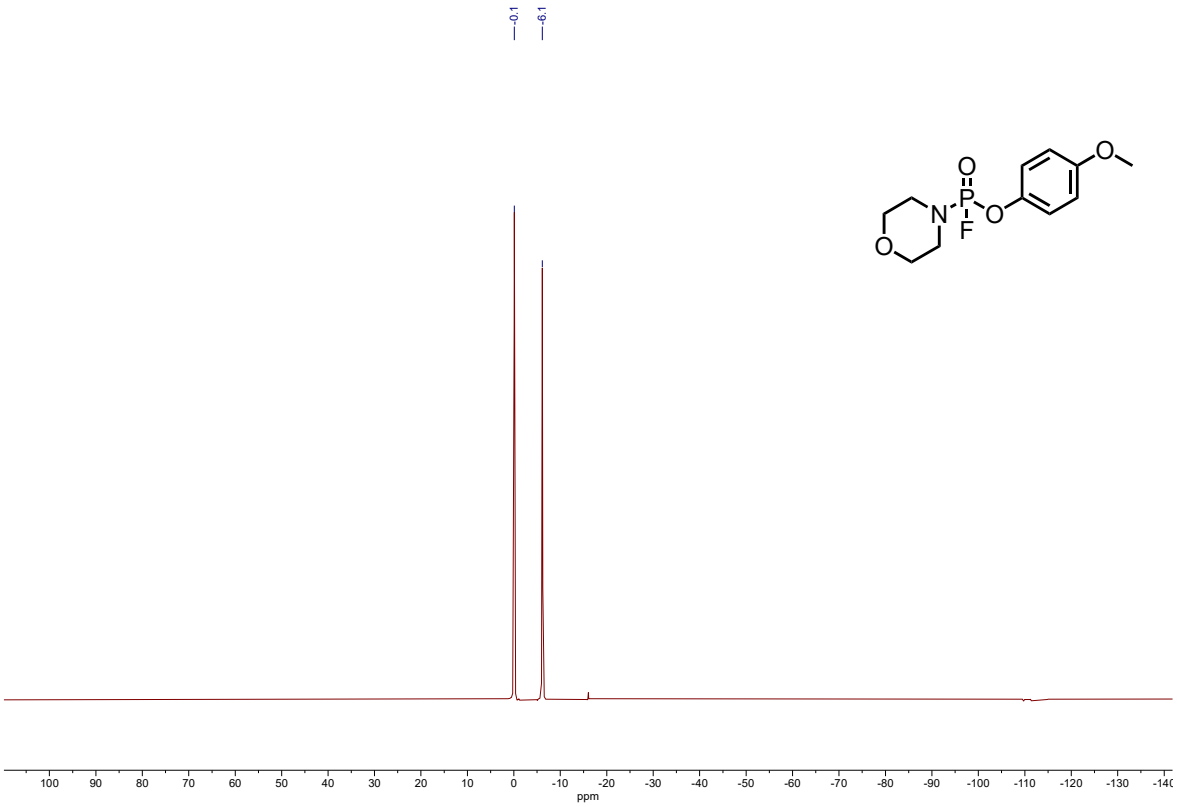
^{1}H NMR Spectrum for Compound **12o** (400 MHz, $CDCl_3$)



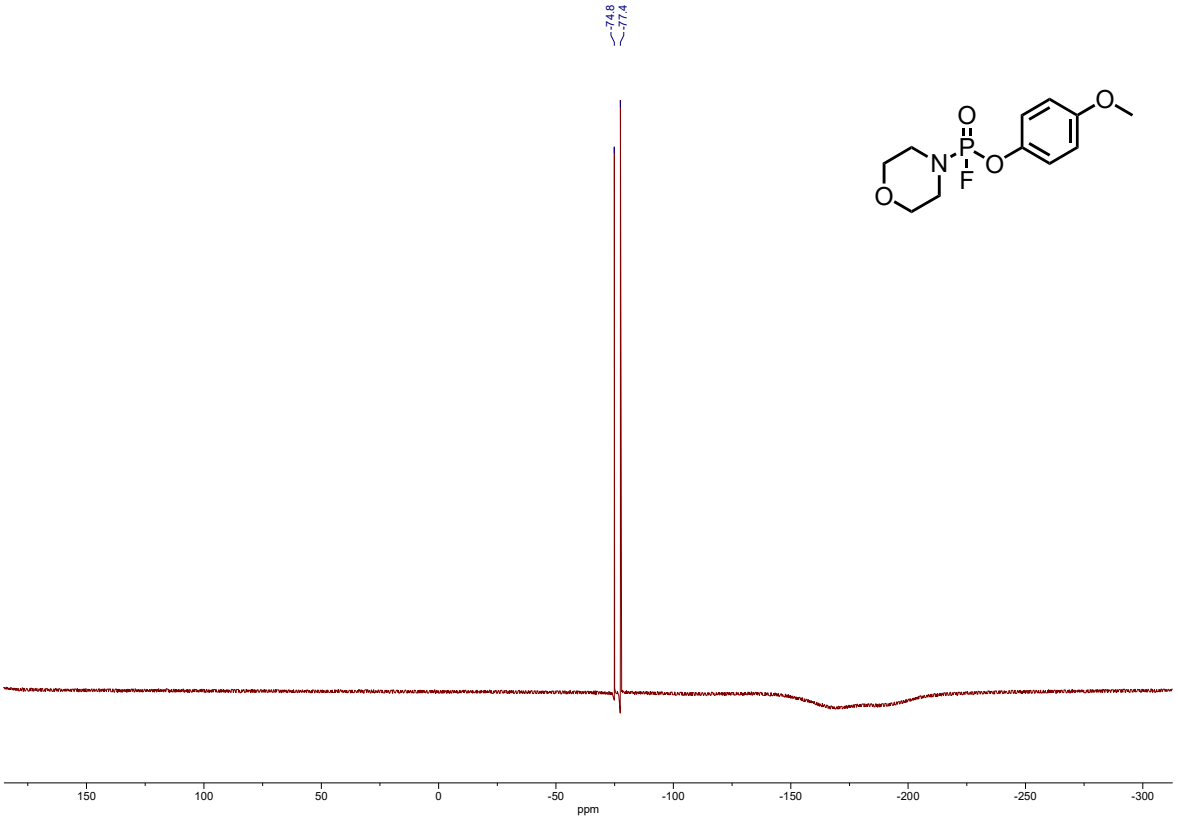
^{13}C NMR Spectrum for Compound **12o** (101 MHz, $CDCl_3$)



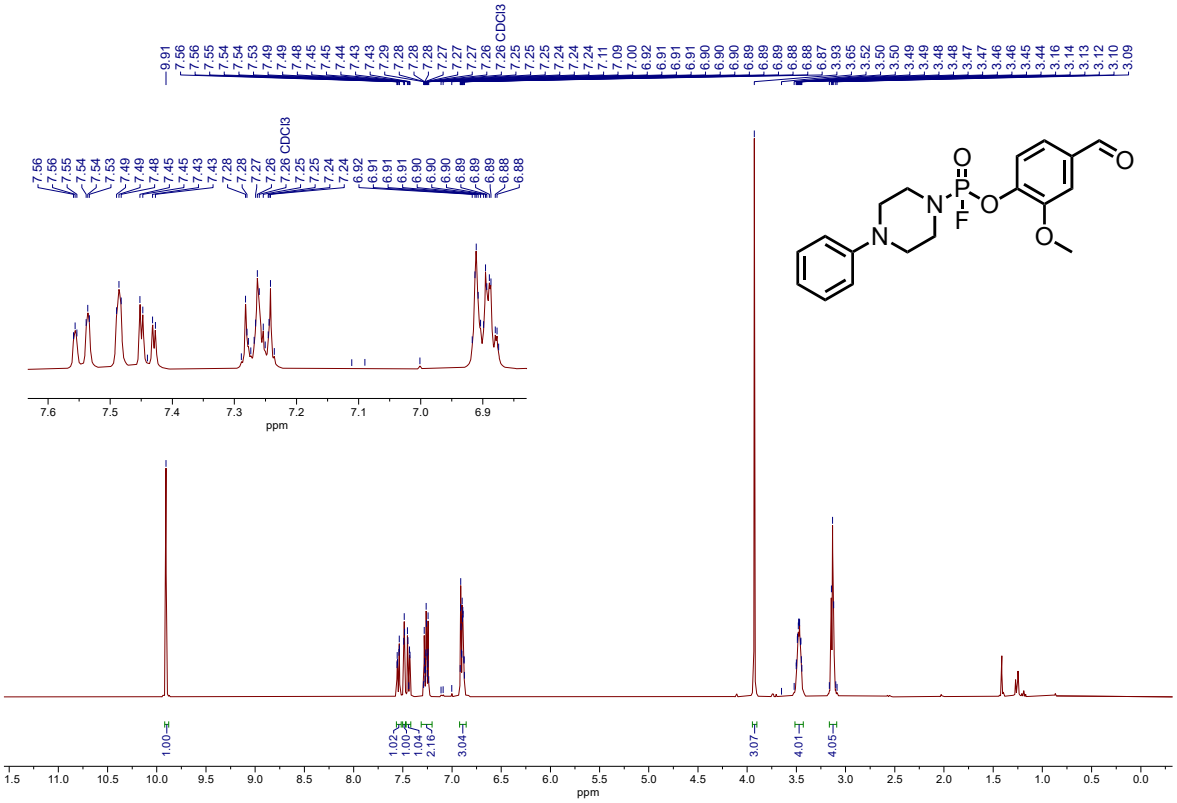
^{31}P NMR Spectrum for Compound **12o** (162 MHz, $CDCl_3$)



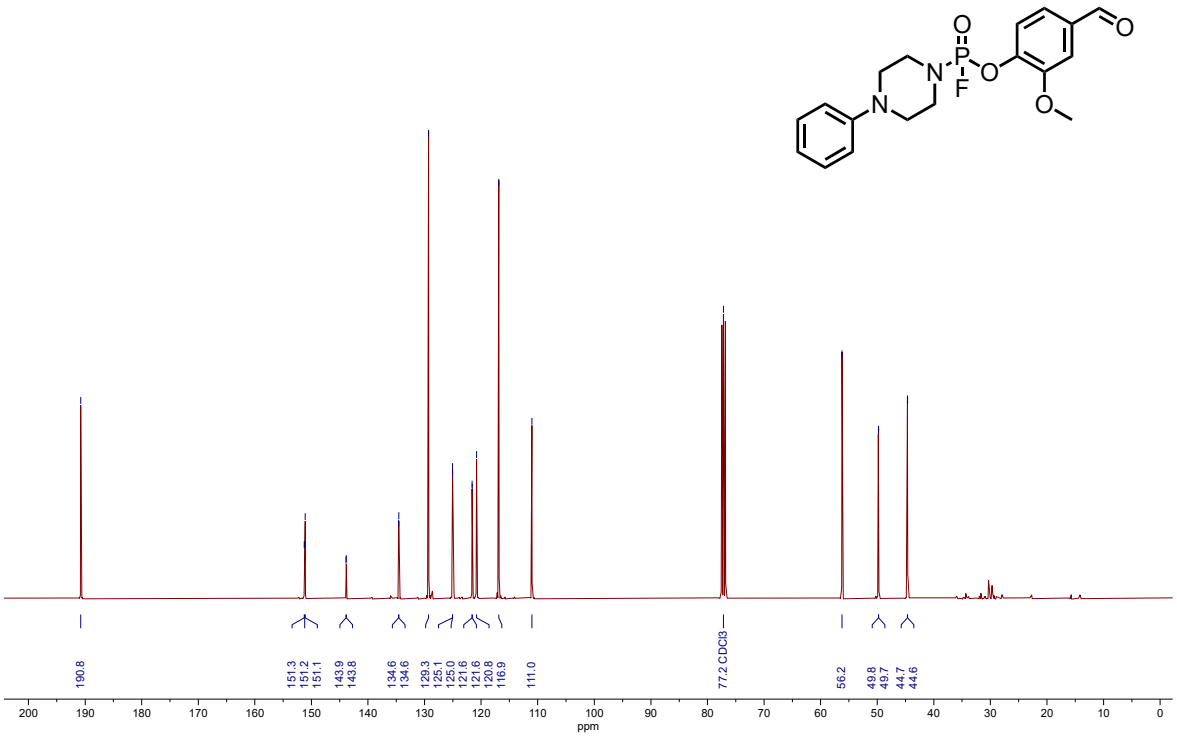
^{19}F NMR Spectrum for Compound **12o** (376 MHz, $CDCl_3$)



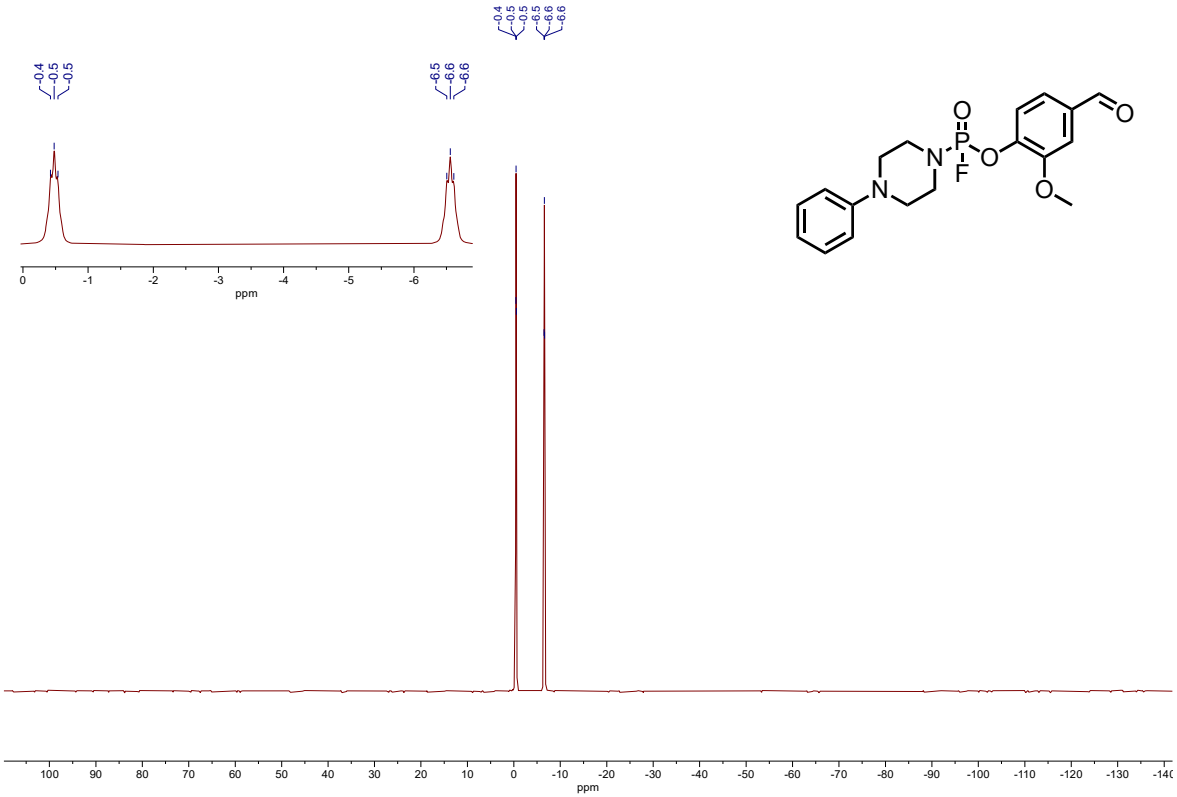
^{1}H NMR Spectrum for Compound **12p** (400 MHz, $CDCl_3$)



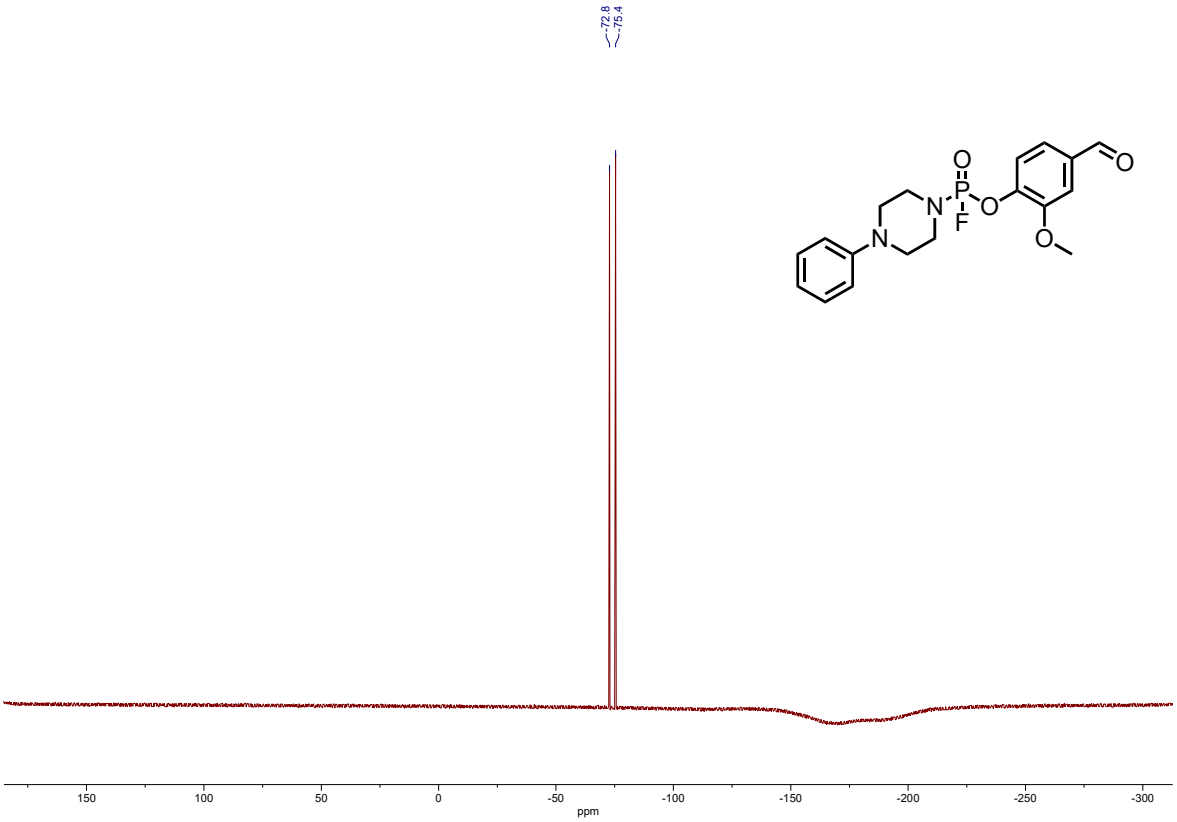
^{13}C NMR Spectrum for Compound **12p** (101 MHz, $CDCl_3$)



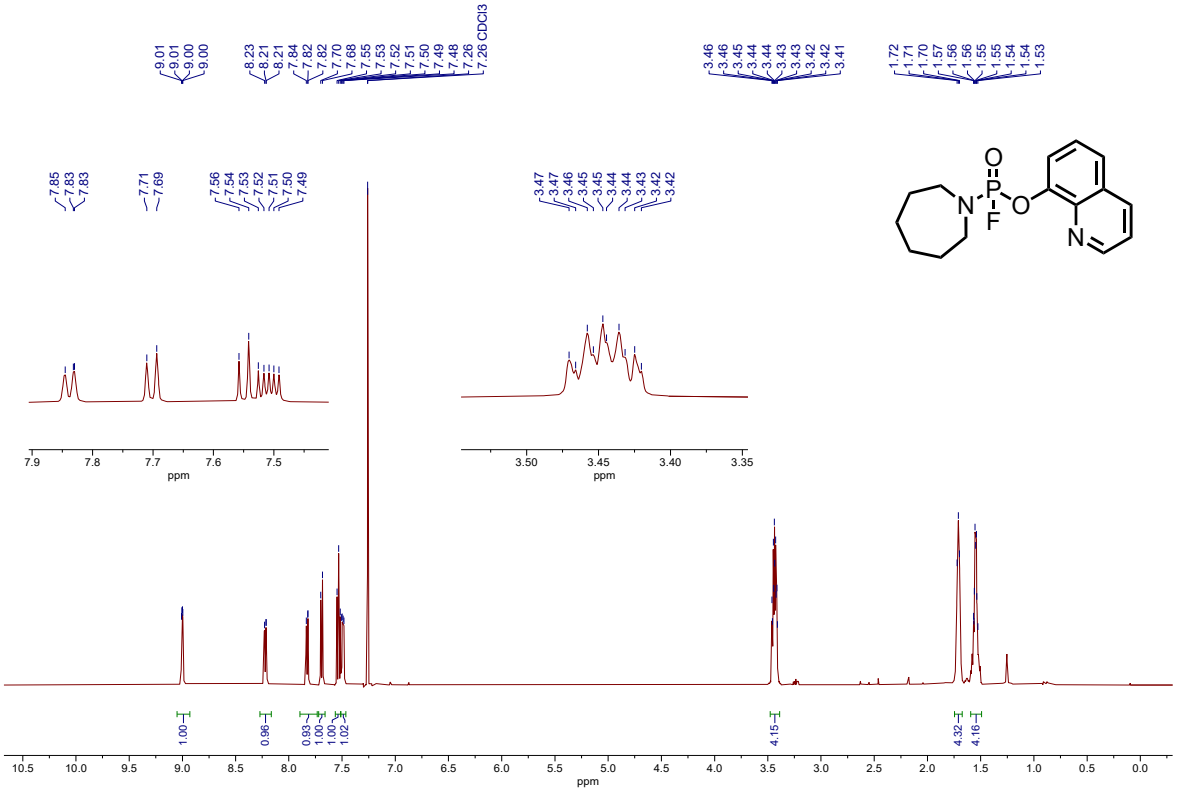
^{31}P NMR Spectrum for Compound **12p** (162 MHz, $CDCl_3$)



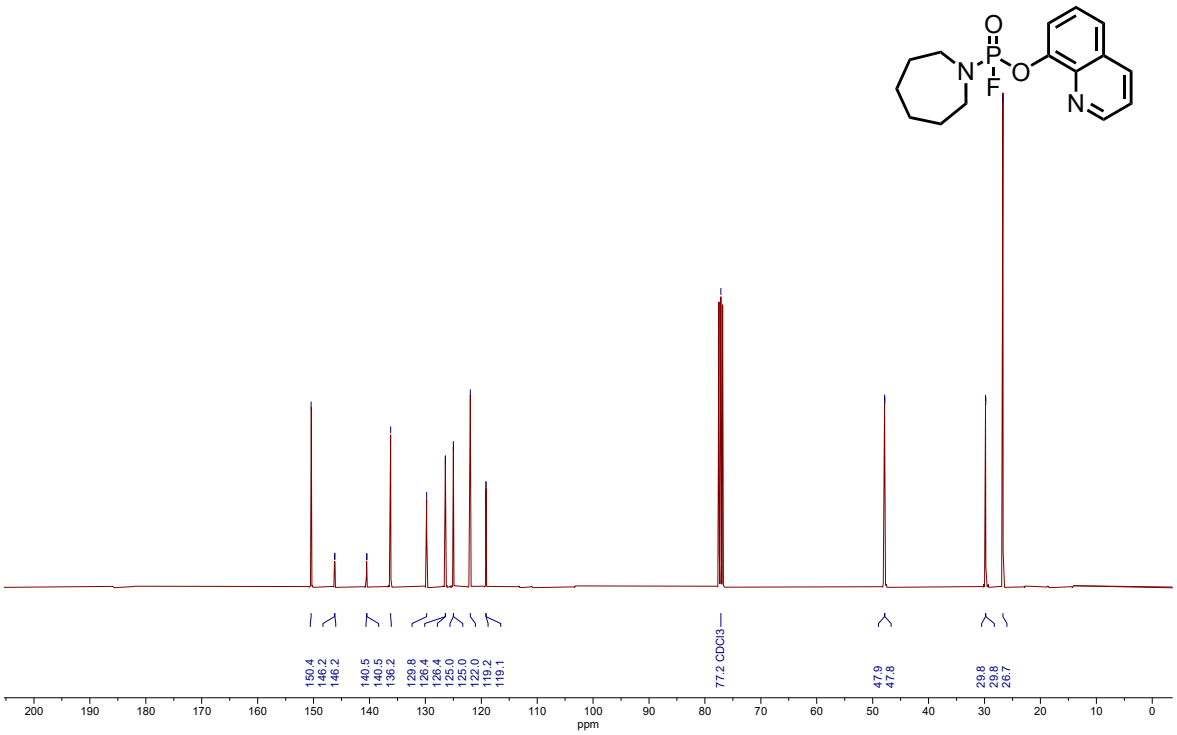
^{19}F NMR Spectrum for Compound **12p** (376 MHz, $CDCl_3$)



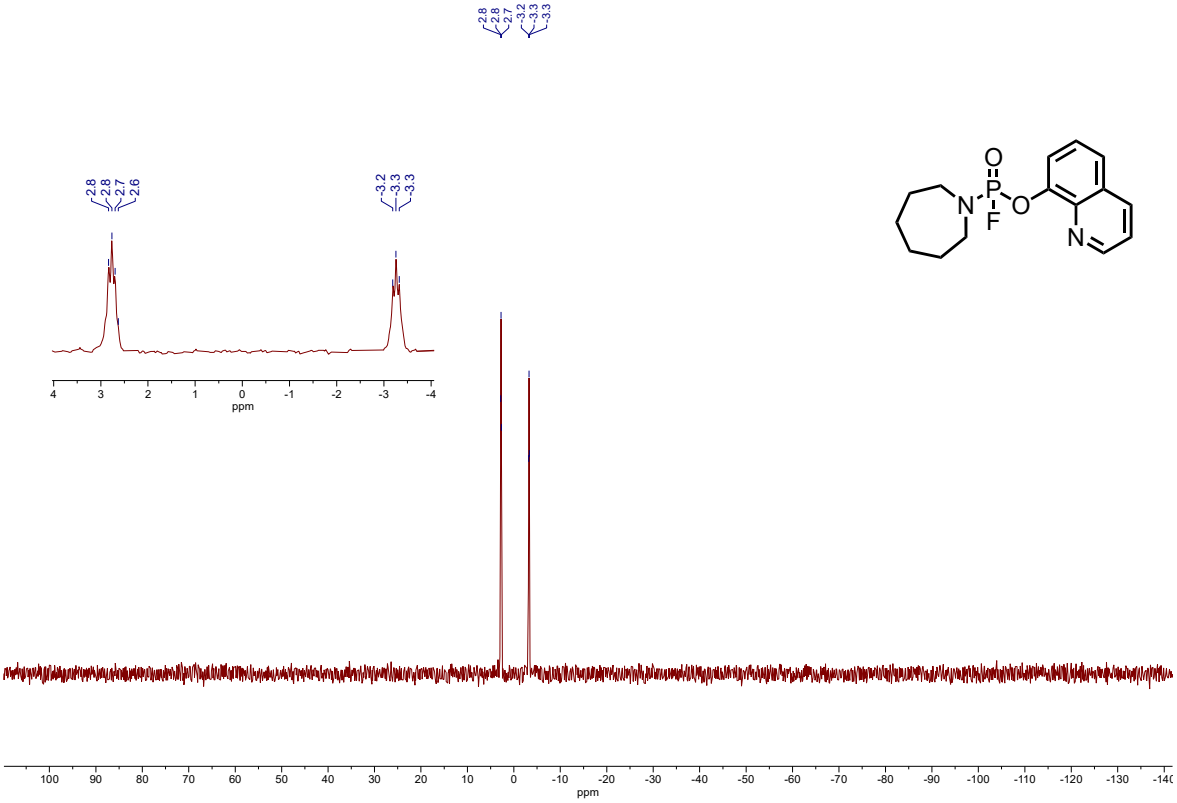
^{1}H NMR Spectrum for Compound **12q** (400 MHz, $CDCl_3$)



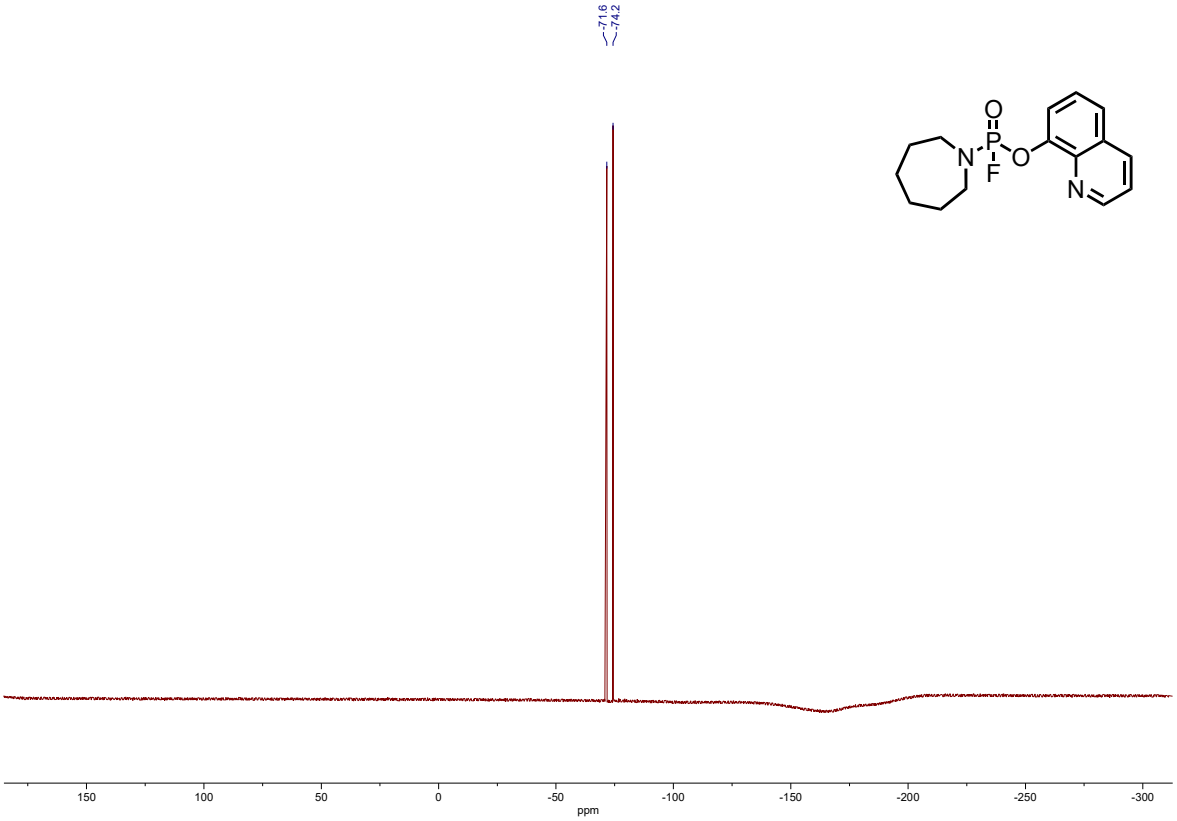
^{13}C NMR Spectrum for Compound **12q** (101 MHz, $CDCl_3$)



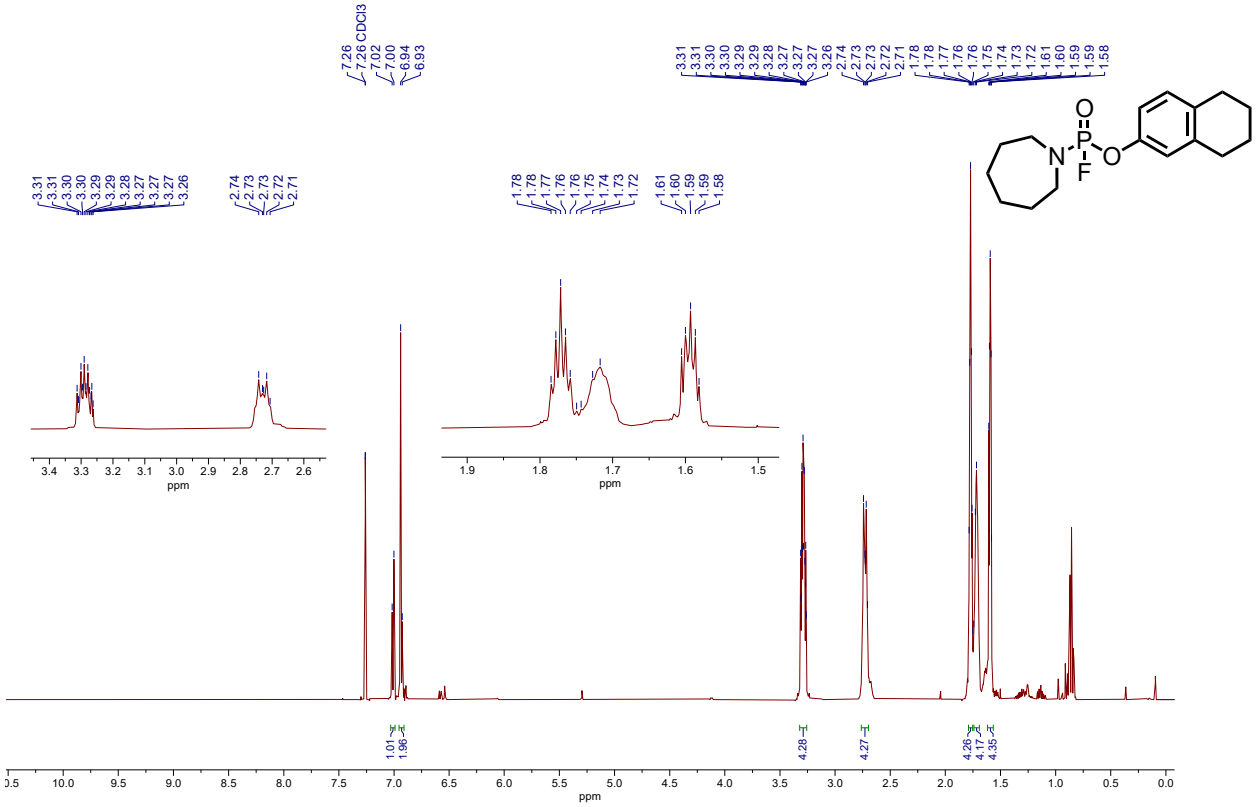
^{31}P NMR Spectrum for Compound **12q** (162 MHz, $CDCl_3$)



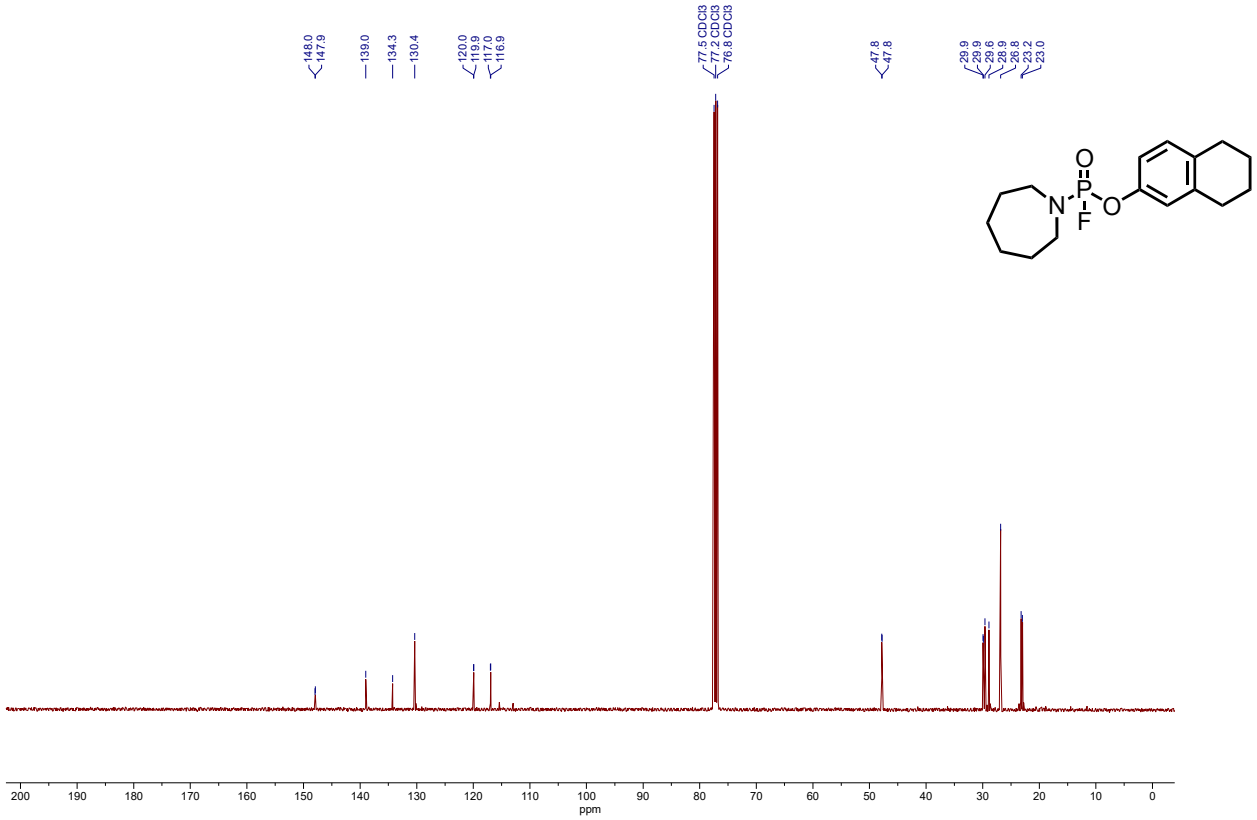
^{19}F NMR Spectrum for Compound **12q** (376 MHz, $CDCl_3$)



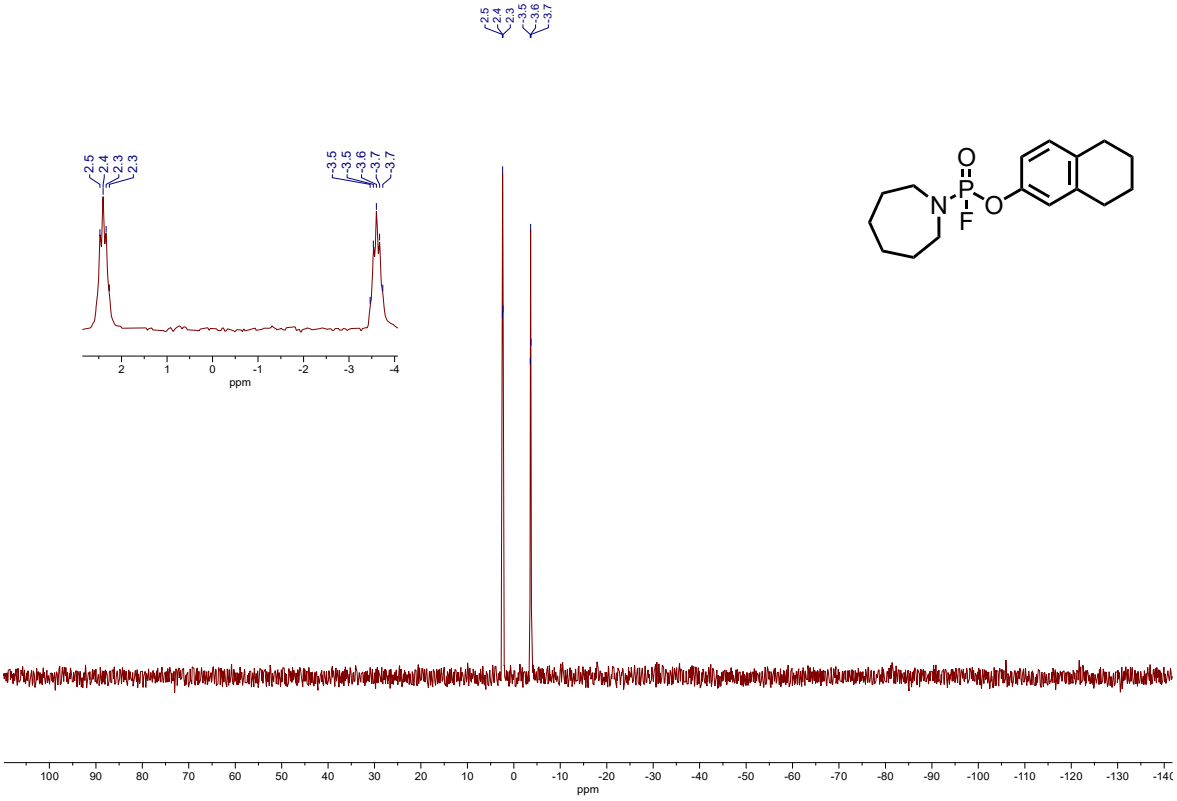
^{1}H NMR Spectrum for Compound **12r** (400 MHz, $CDCl_3$)



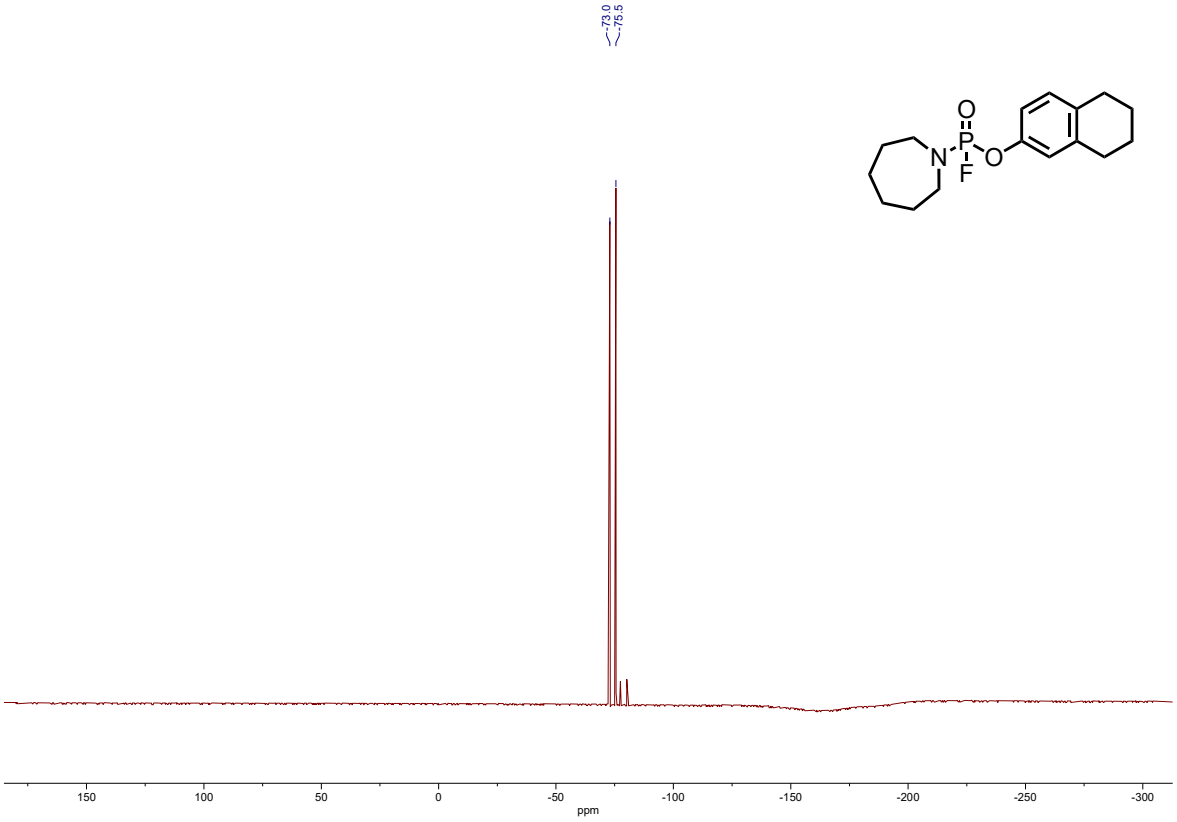
^{13}C NMR Spectrum for Compound **12r** (101 MHz, $CDCl_3$)



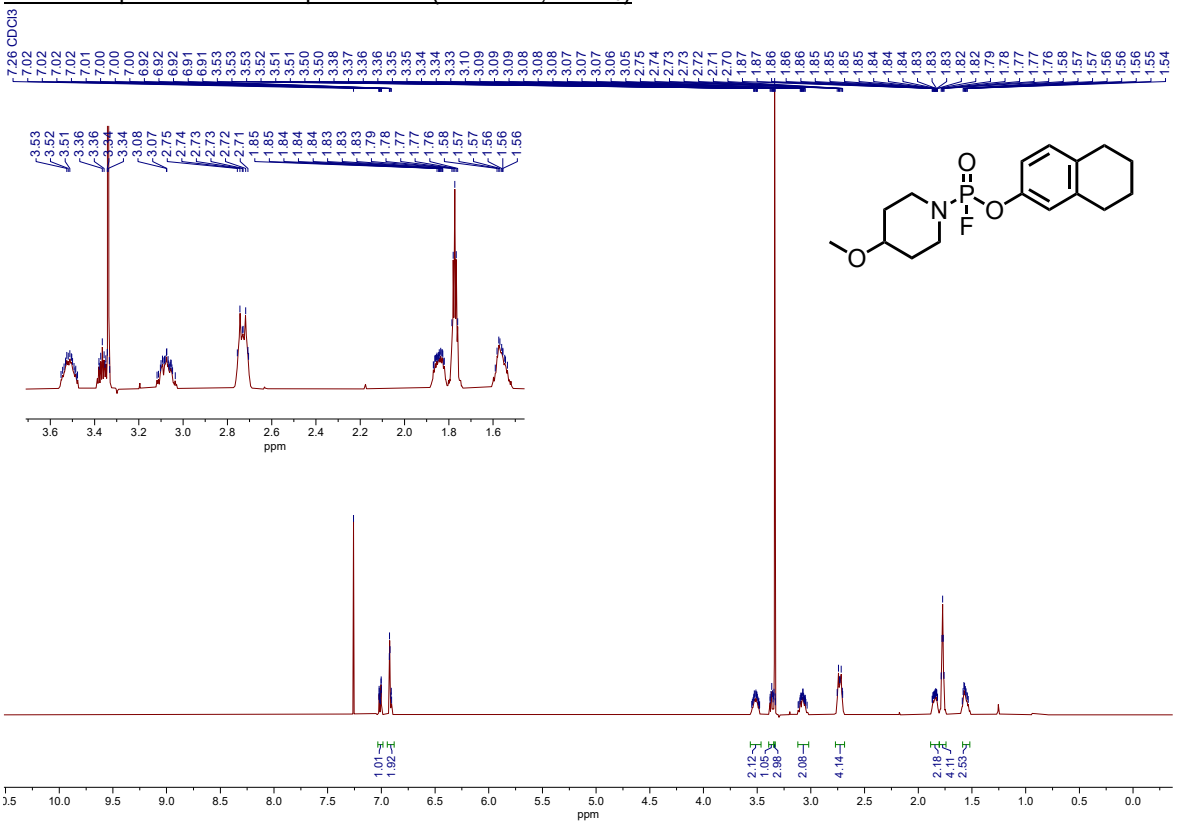
^{31}P NMR Spectrum for Compound **12r** (162 MHz, $CDCl_3$)



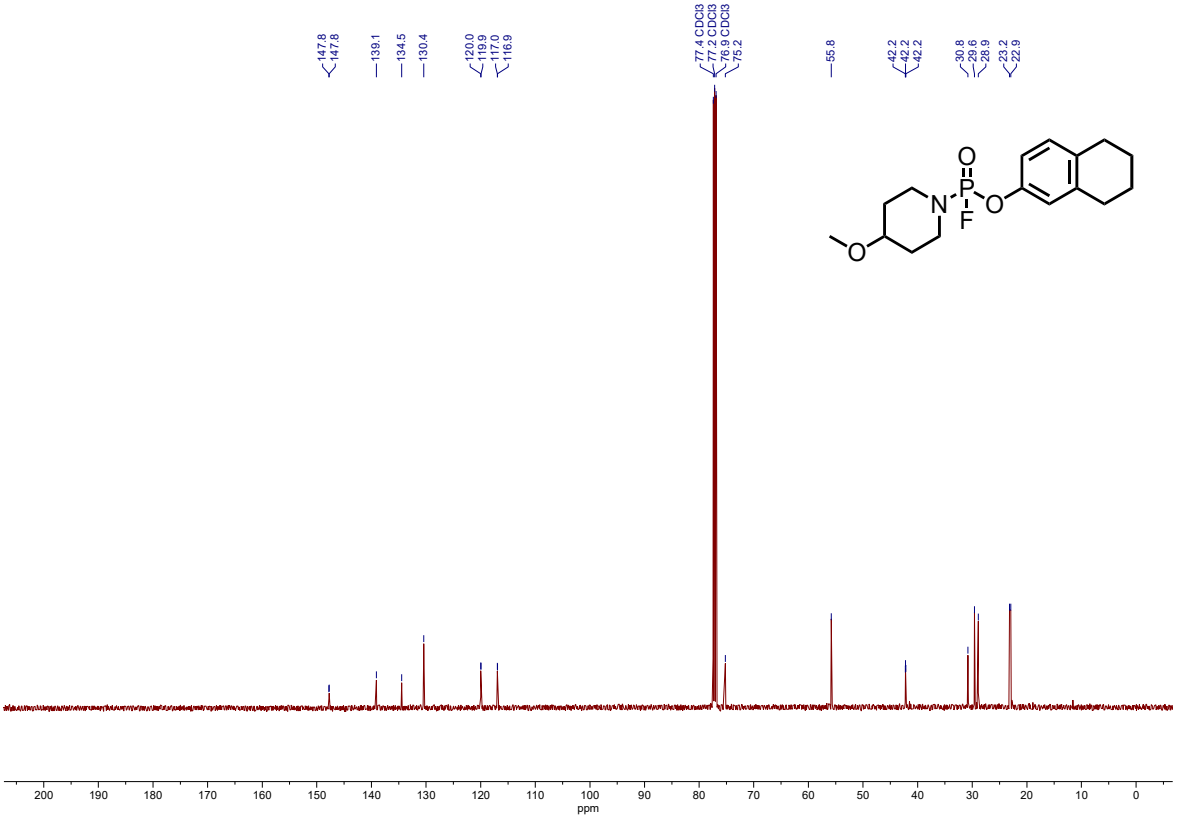
^{19}F NMR Spectrum for Compound **12r** (376 MHz, $CDCl_3$)



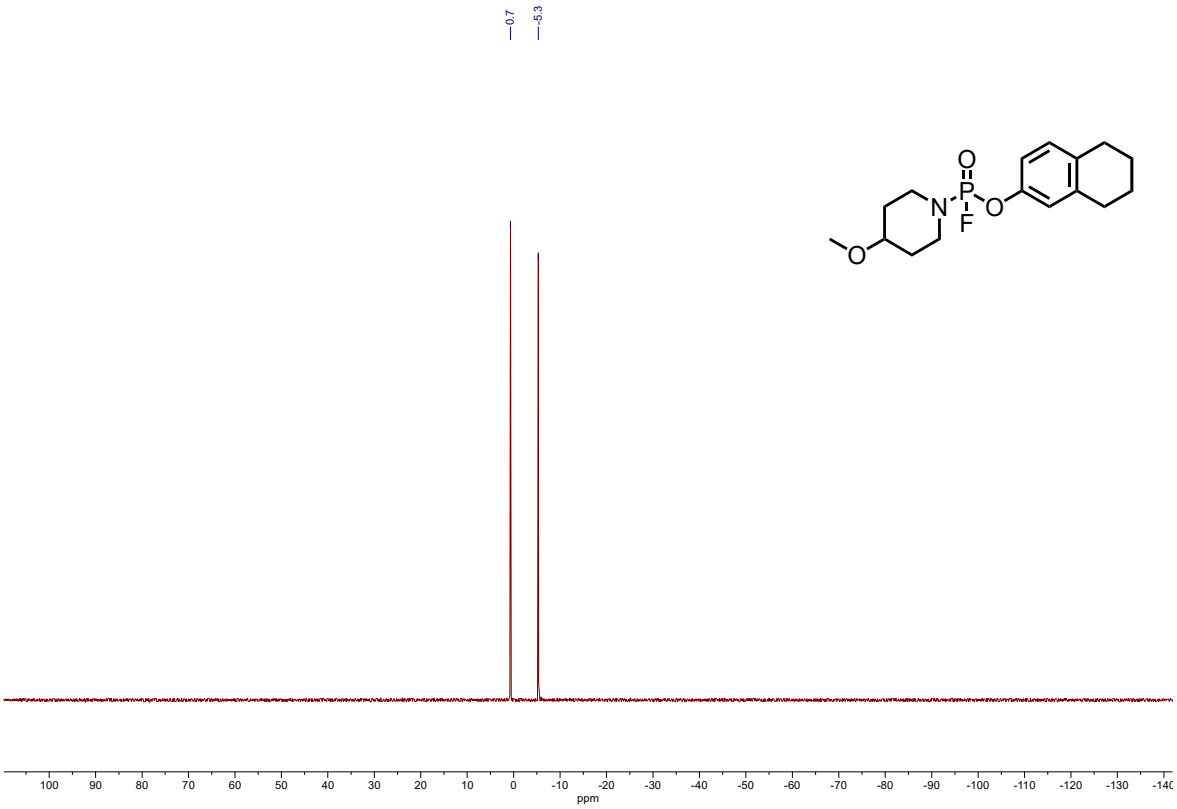
^{1}H NMR Spectrum for Compound **12s** (400 MHz, $CDCl_3$)



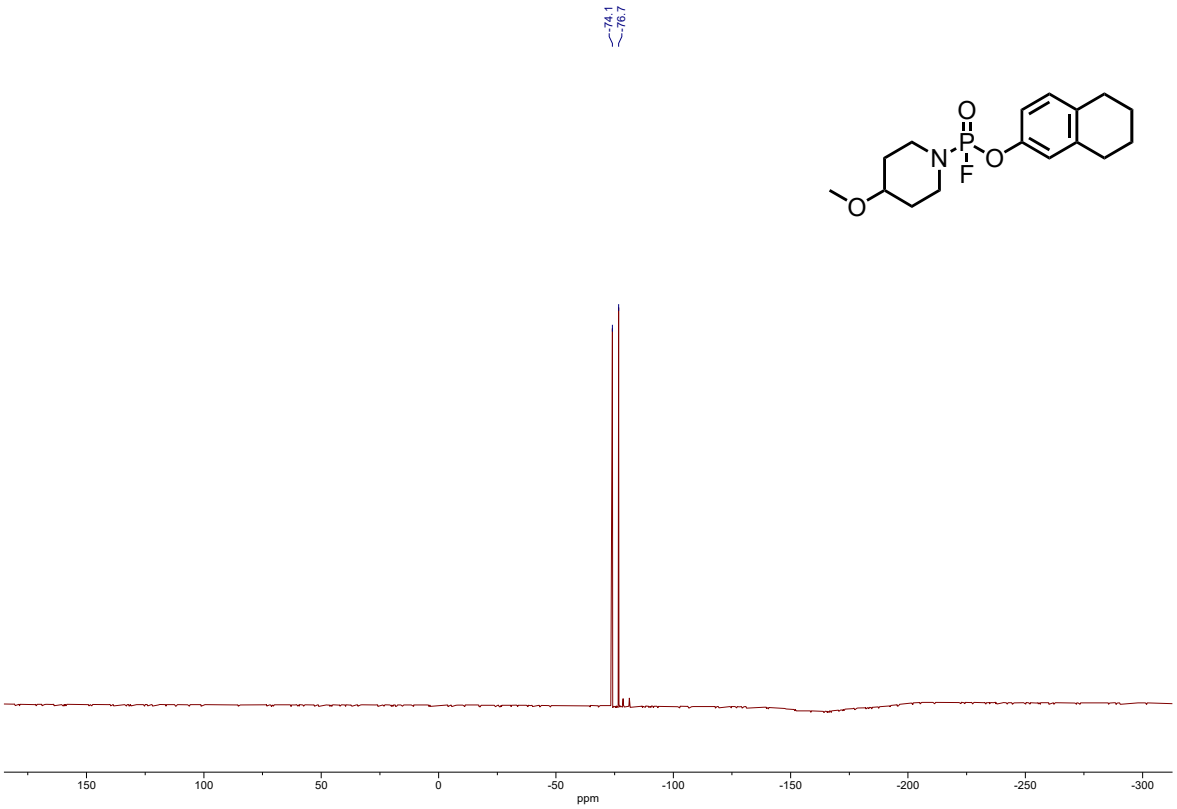
^{13}C NMR Spectrum for Compound **12s** (101 MHz, $CDCl_3$)



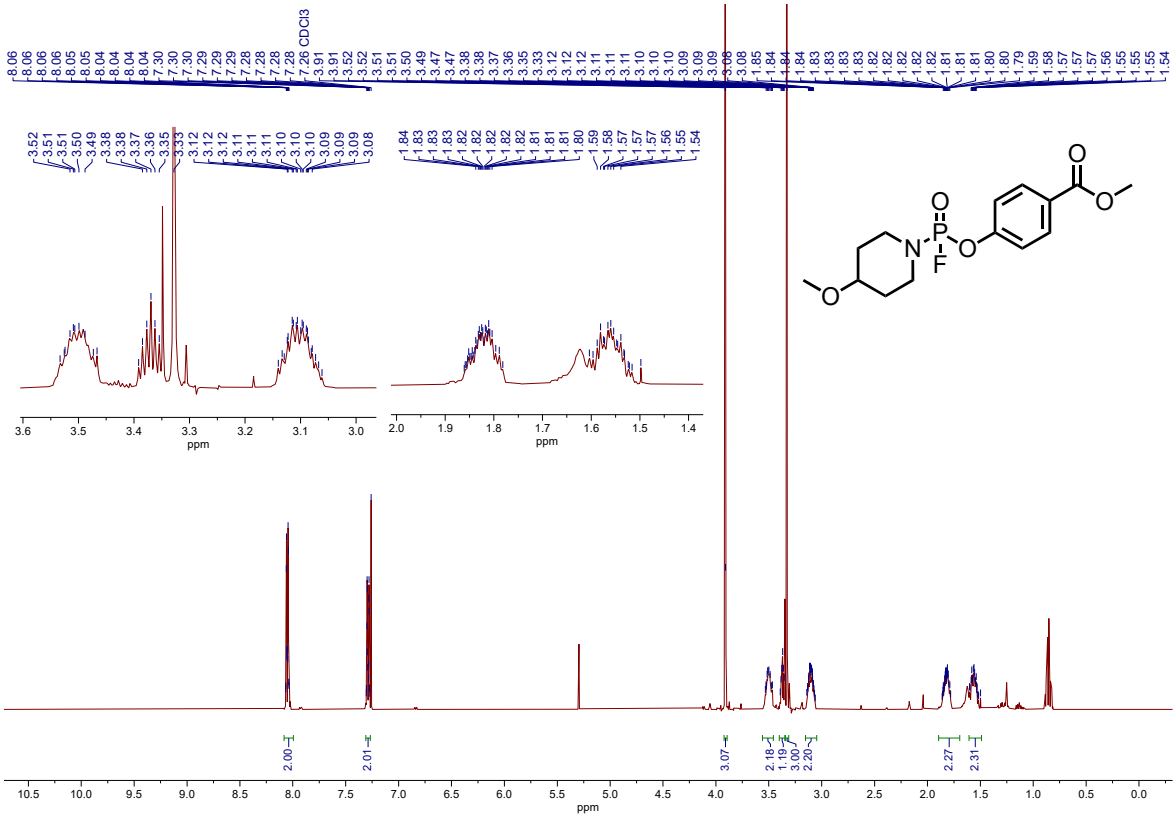
^{31}P NMR Spectrum for Compound **12s** (162 MHz, $CDCl_3$)



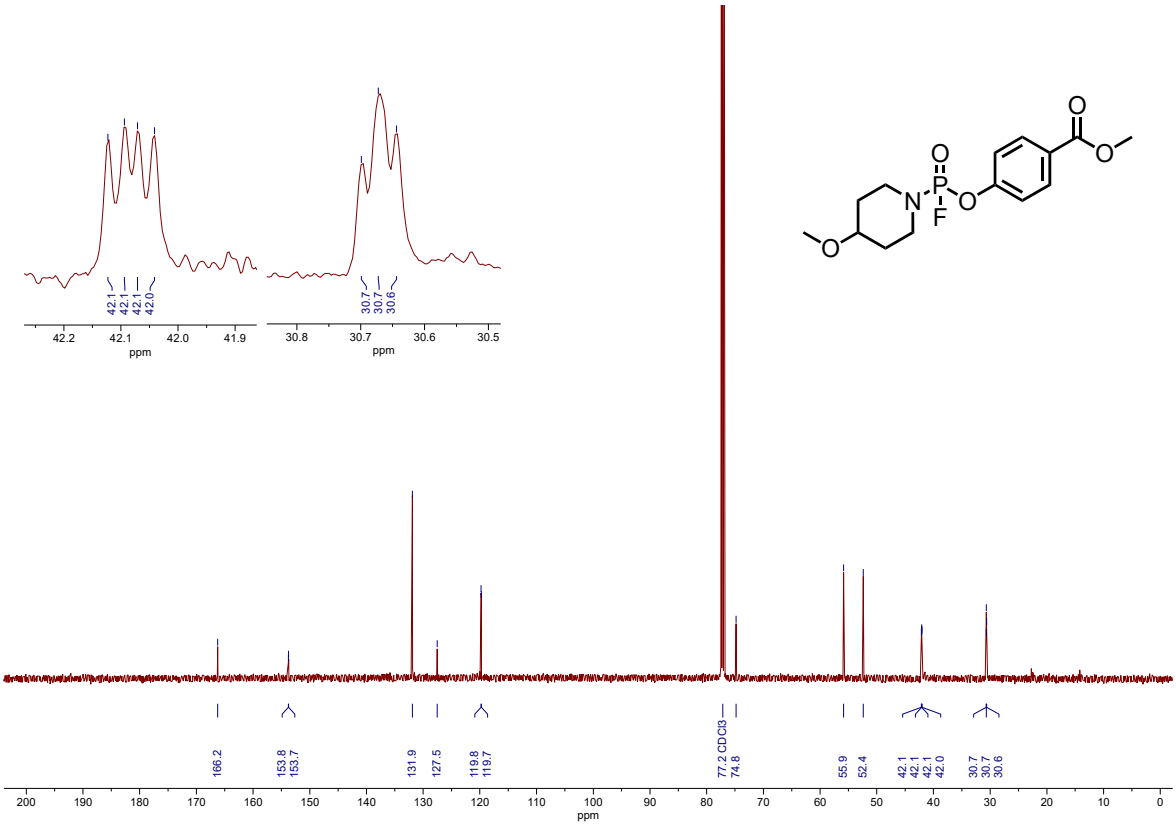
^{19}F NMR Spectrum for Compound **12s** (376 MHz, $CDCl_3$)



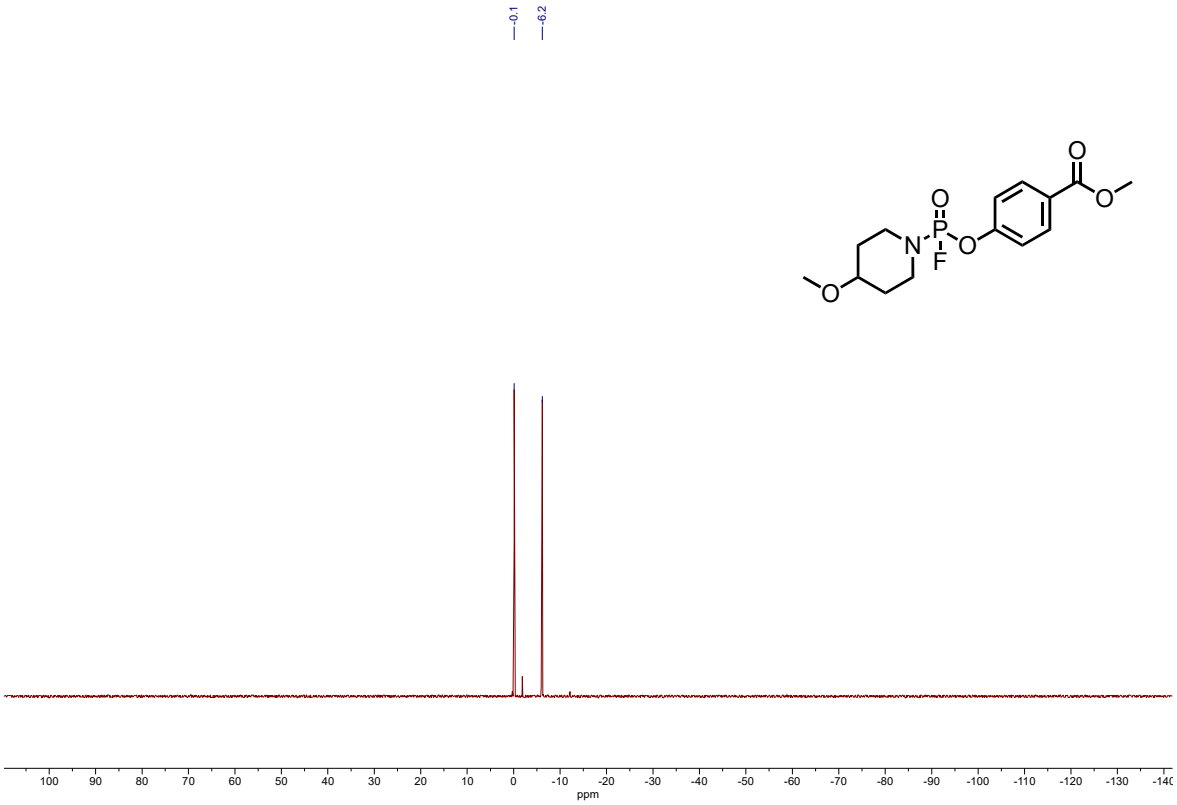
^{1}H NMR Spectrum for Compound **12t** (400 MHz, $CDCl_3$)



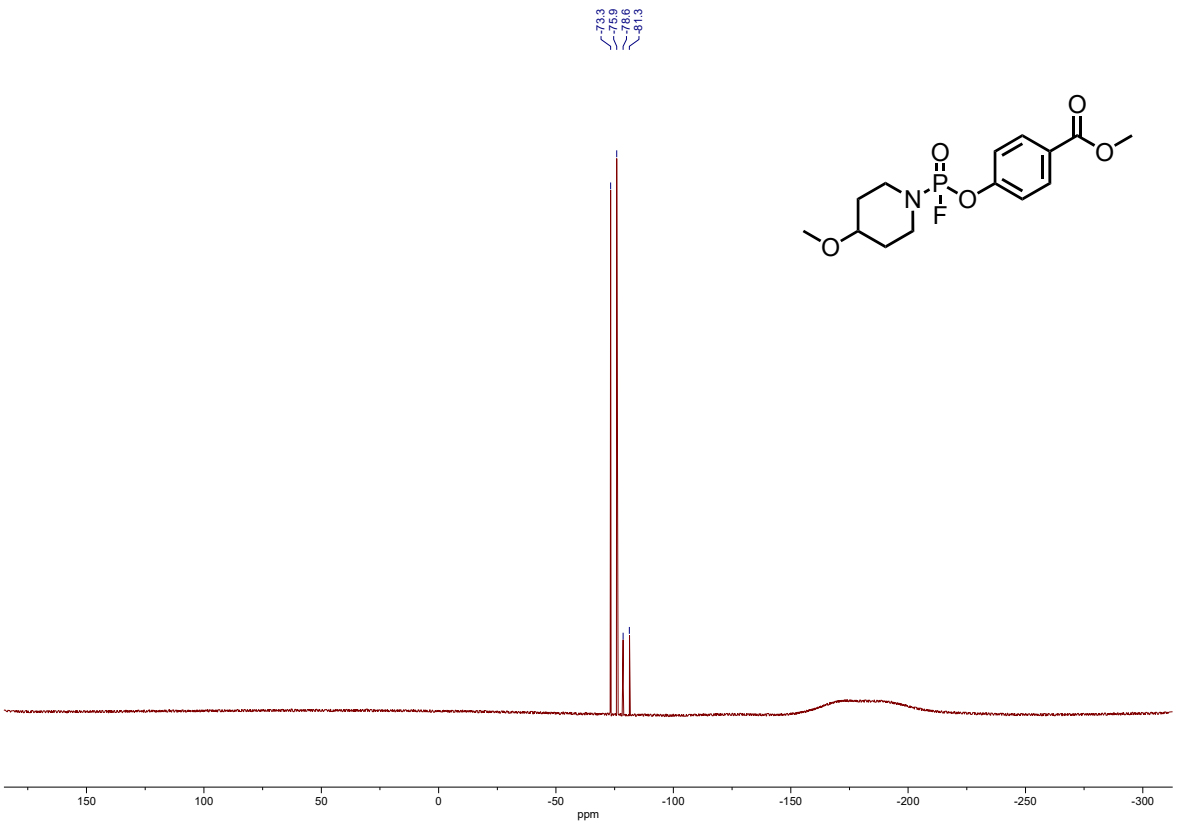
^{13}C NMR Spectrum for Compound **12t** (101 MHz, $CDCl_3$)



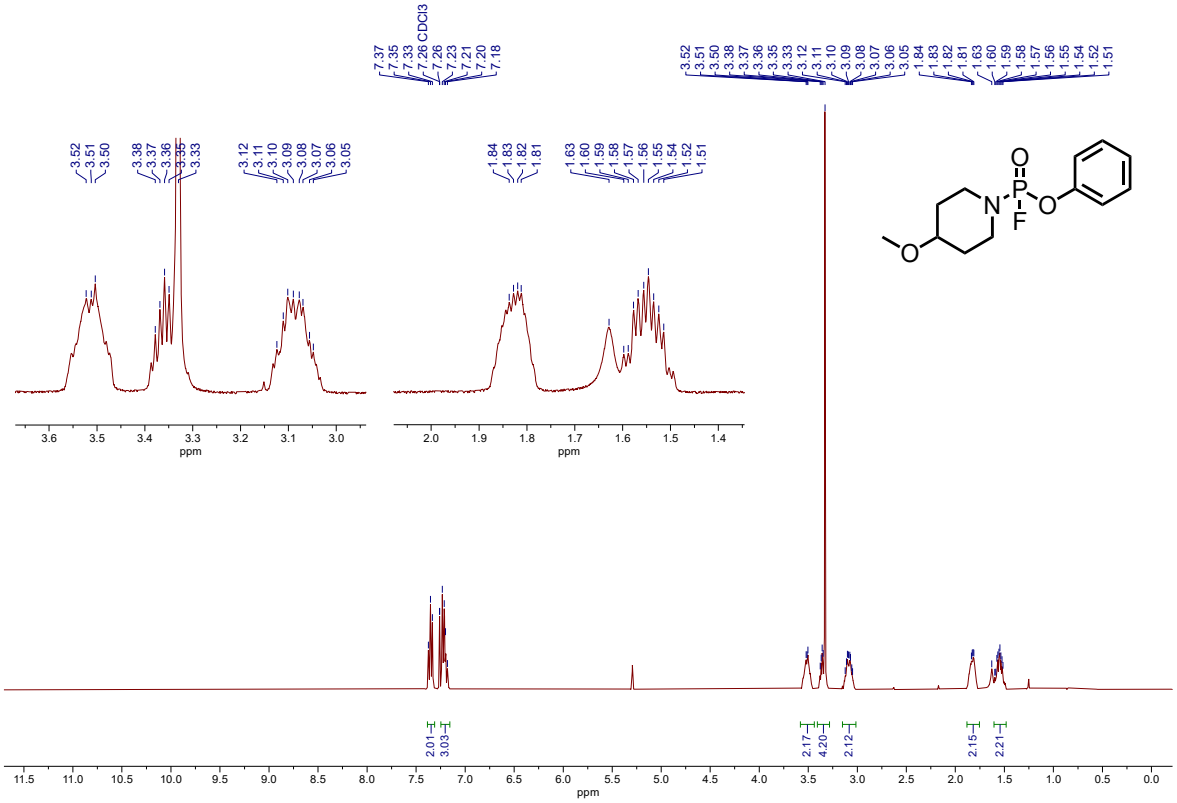
^{31}P NMR Spectrum for Compound **12t** (162 MHz, $CDCl_3$)



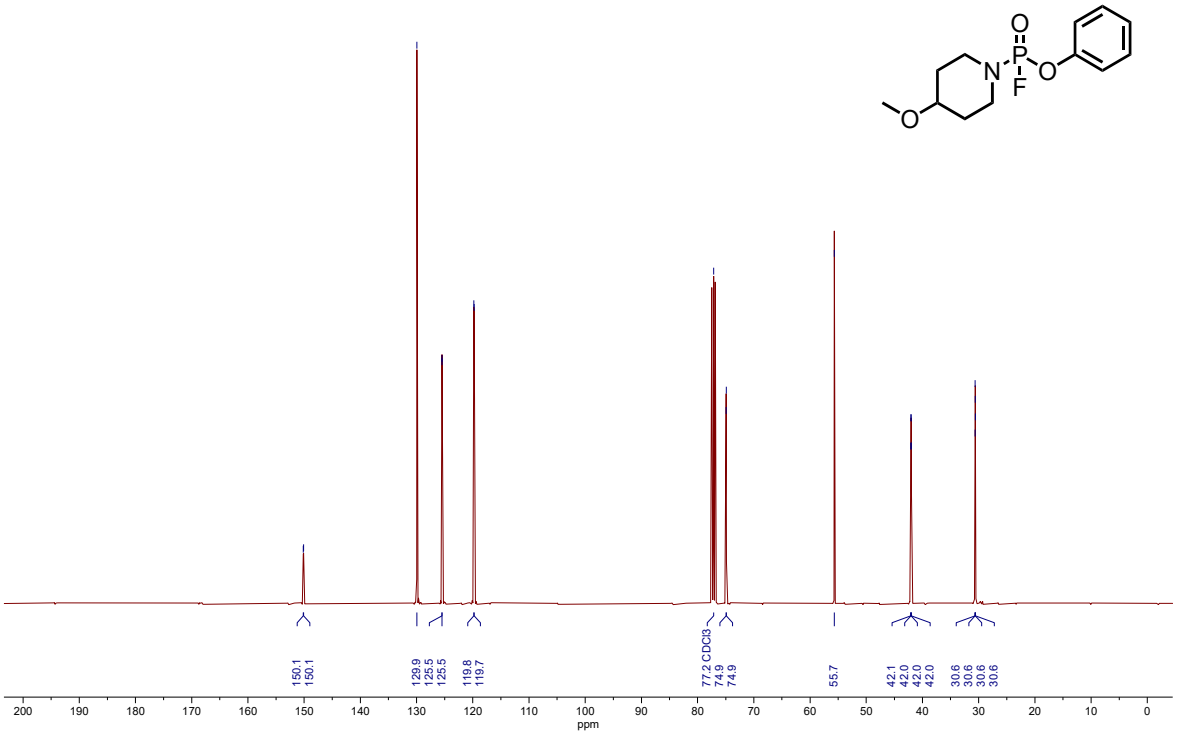
^{19}F NMR Spectrum for Compound **12t** (376 MHz, $CDCl_3$)



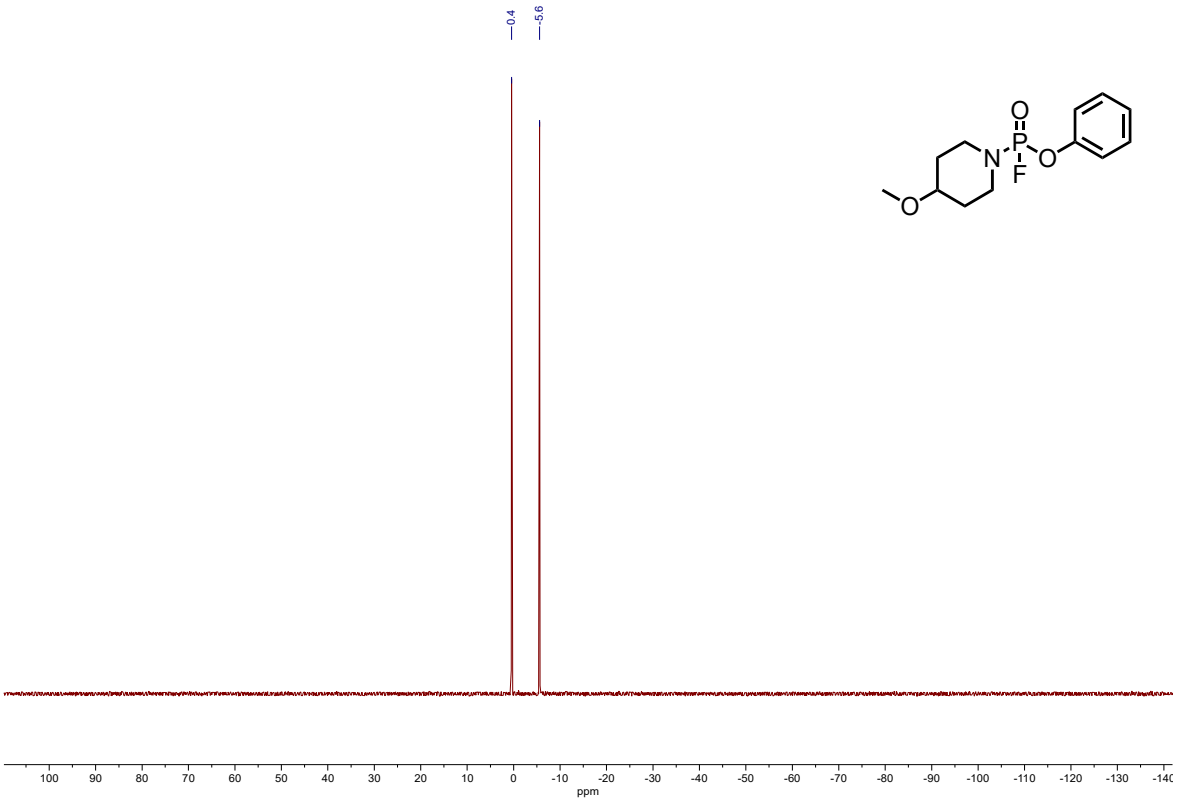
^{1}H NMR Spectrum for Compound **12u** (400 MHz, $CDCl_3$)



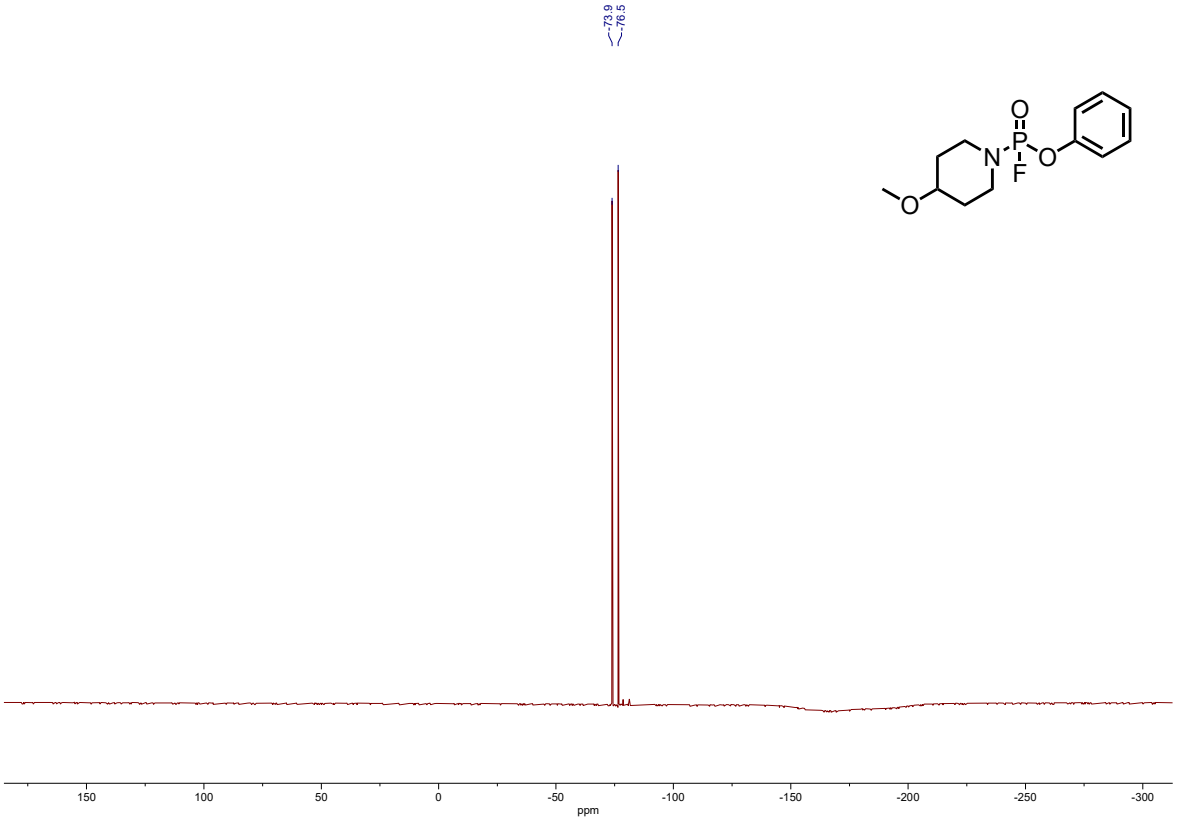
^{13}C NMR Spectrum for Compound **12u** (101 MHz, $CDCl_3$)



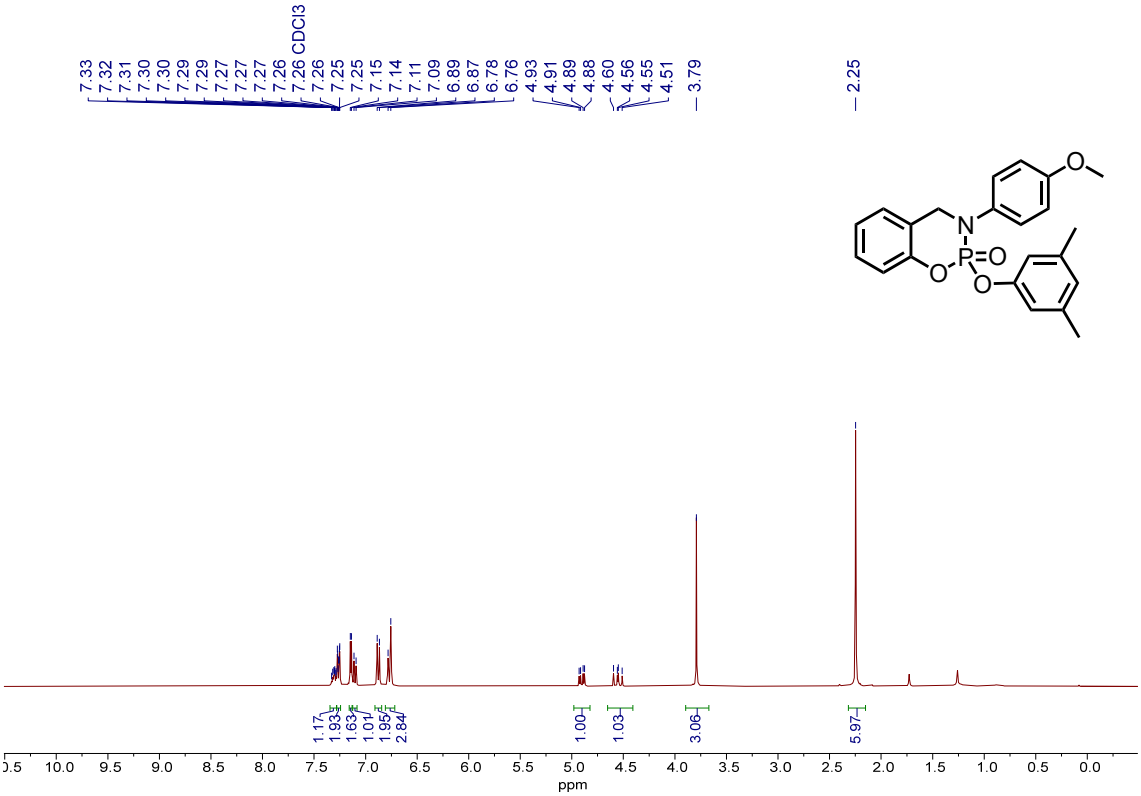
^{31}P NMR Spectrum for Compound **12u** (162 MHz, $CDCl_3$)



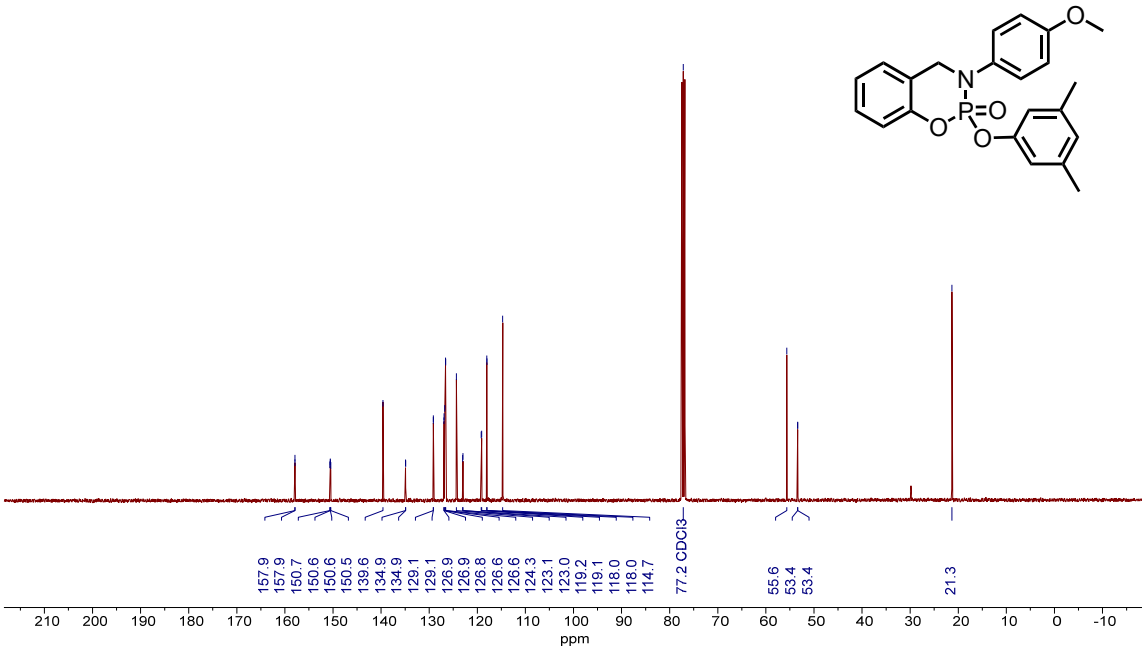
^{19}F NMR Spectrum for Compound **12u** (376 MHz, $CDCl_3$)



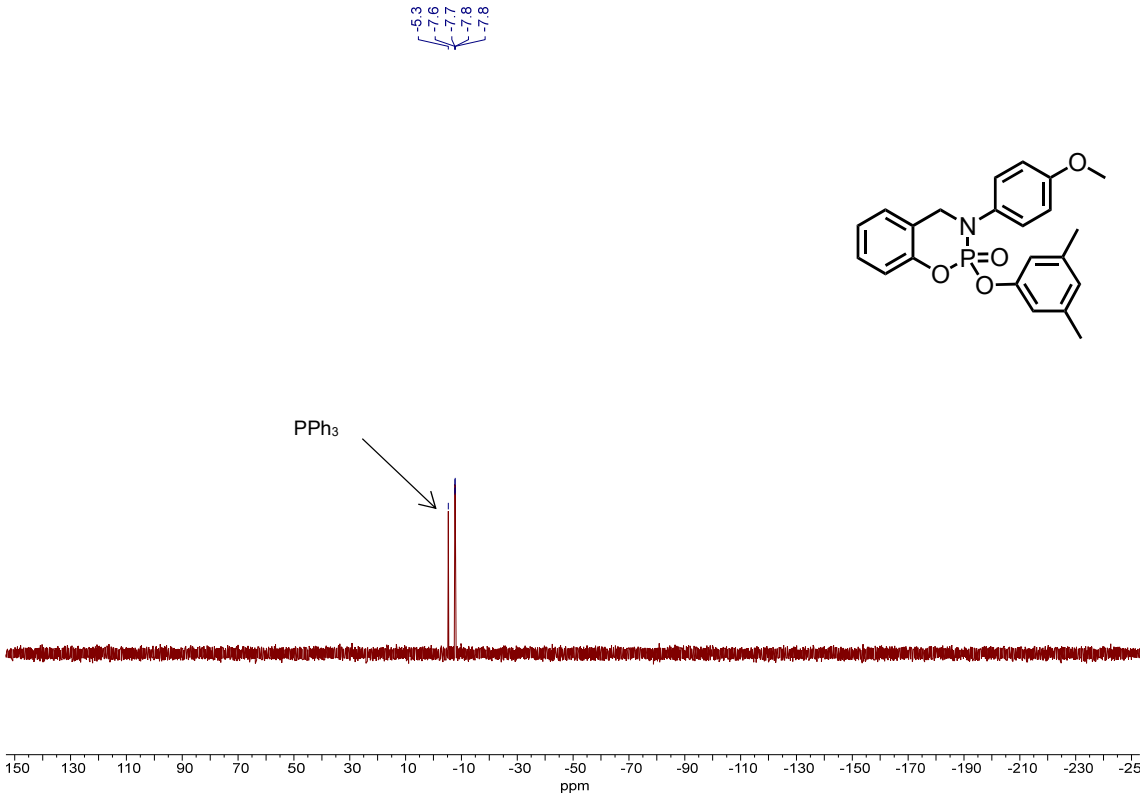
^{1}H NMR Spectrum for Compound **15a** (400 MHz, $CDCl_3$)



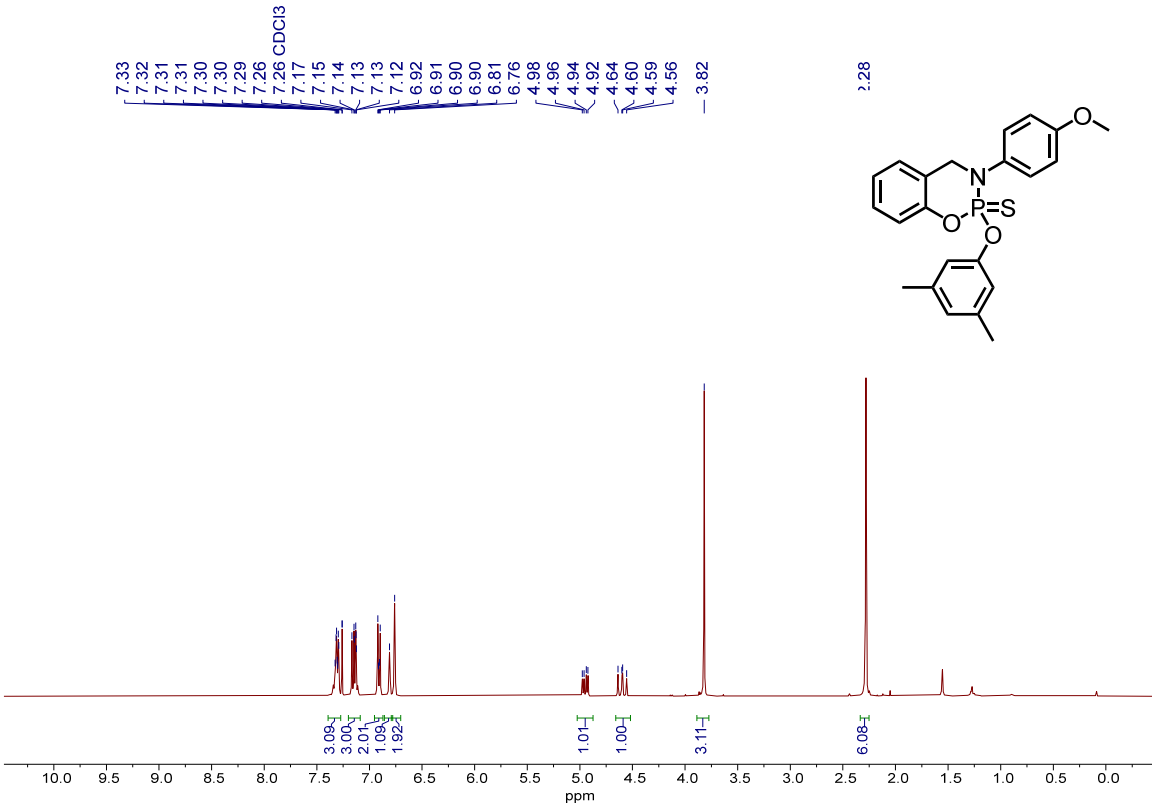
^{13}C NMR Spectrum for Compound **15a** (101 MHz, $CDCl_3$)



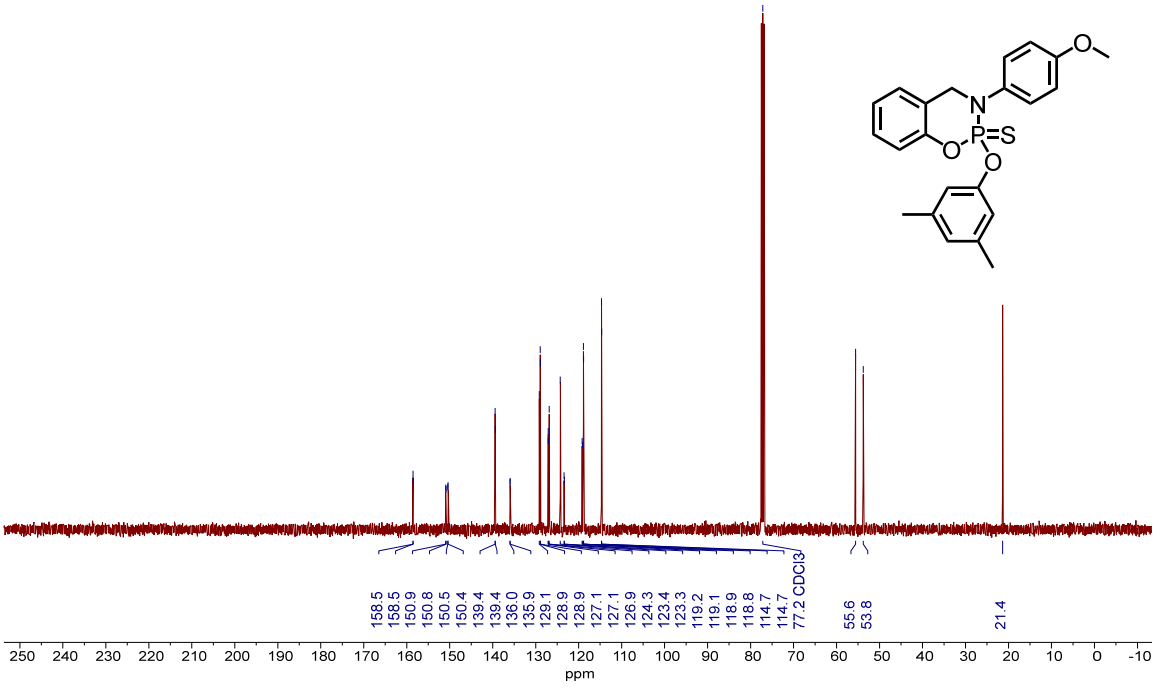
^{31}P NMR Spectrum for Compound **15a** (162 MHz, $CDCl_3$)



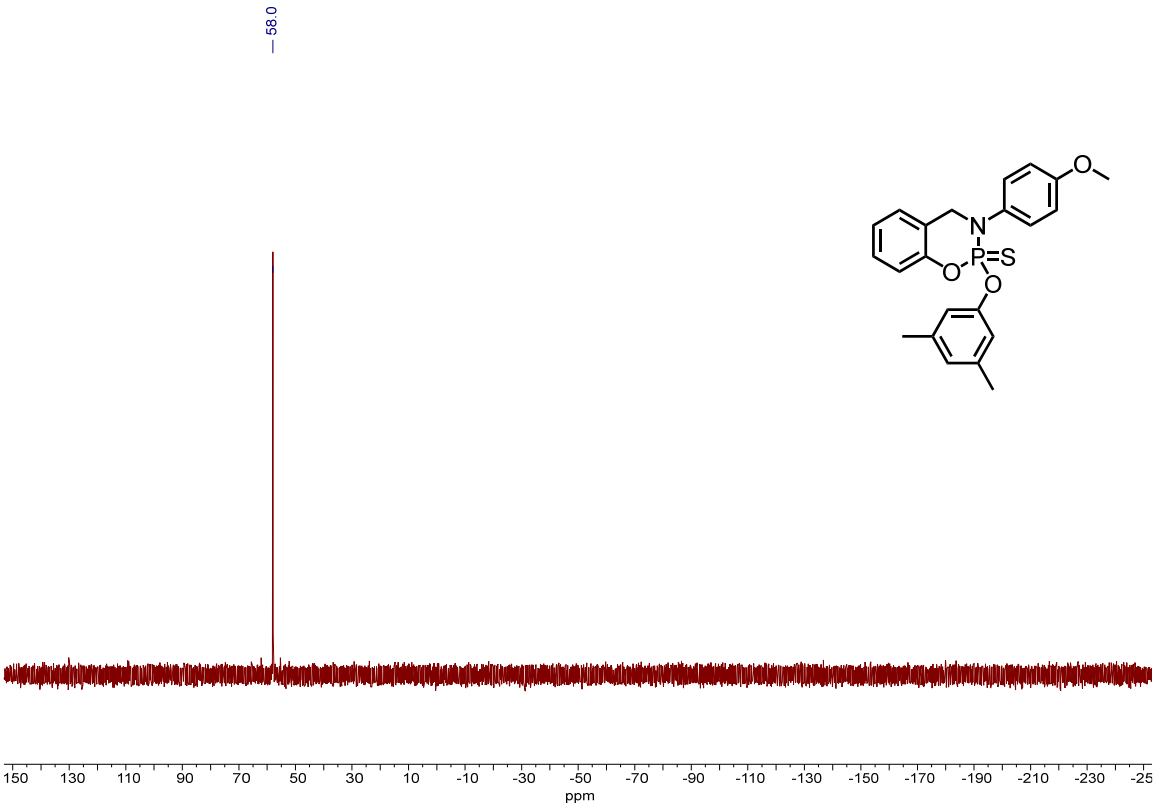
^{1}H NMR Spectrum for Compound **15b** (400 MHz, $CDCl_3$)



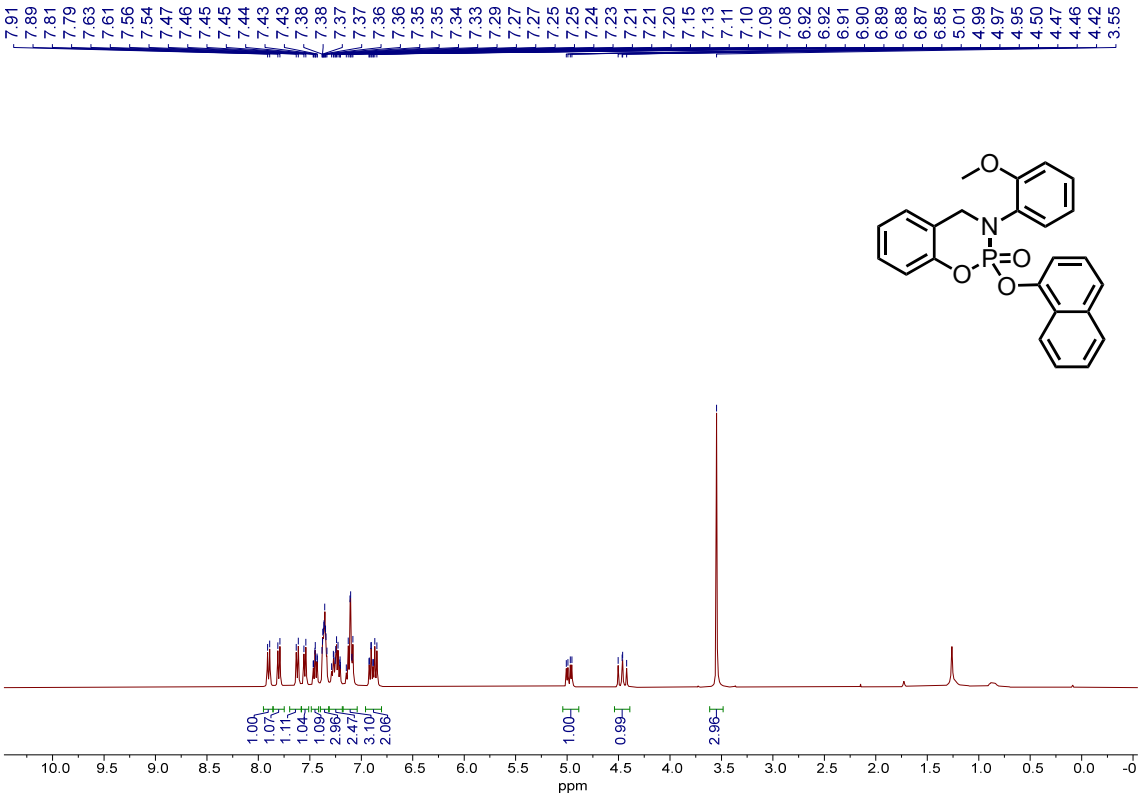
^{13}C NMR Spectrum for Compound **15b** (101 MHz, $CDCl_3$)



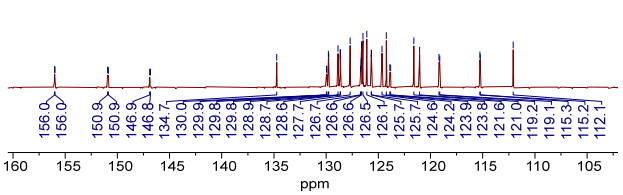
^{31}P NMR Spectrum for Compound **15b** (162 MHz, $CDCl_3$)

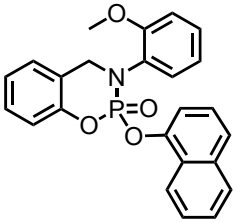


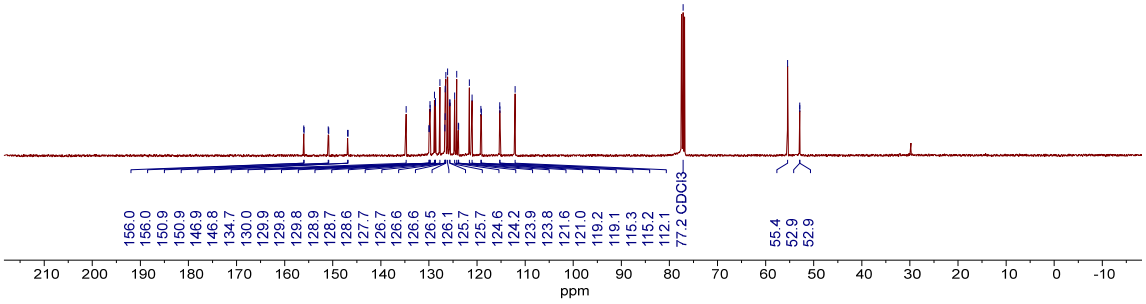
^{1}H NMR Spectrum for Compound **15c** (400 MHz, $CDCl_3$)



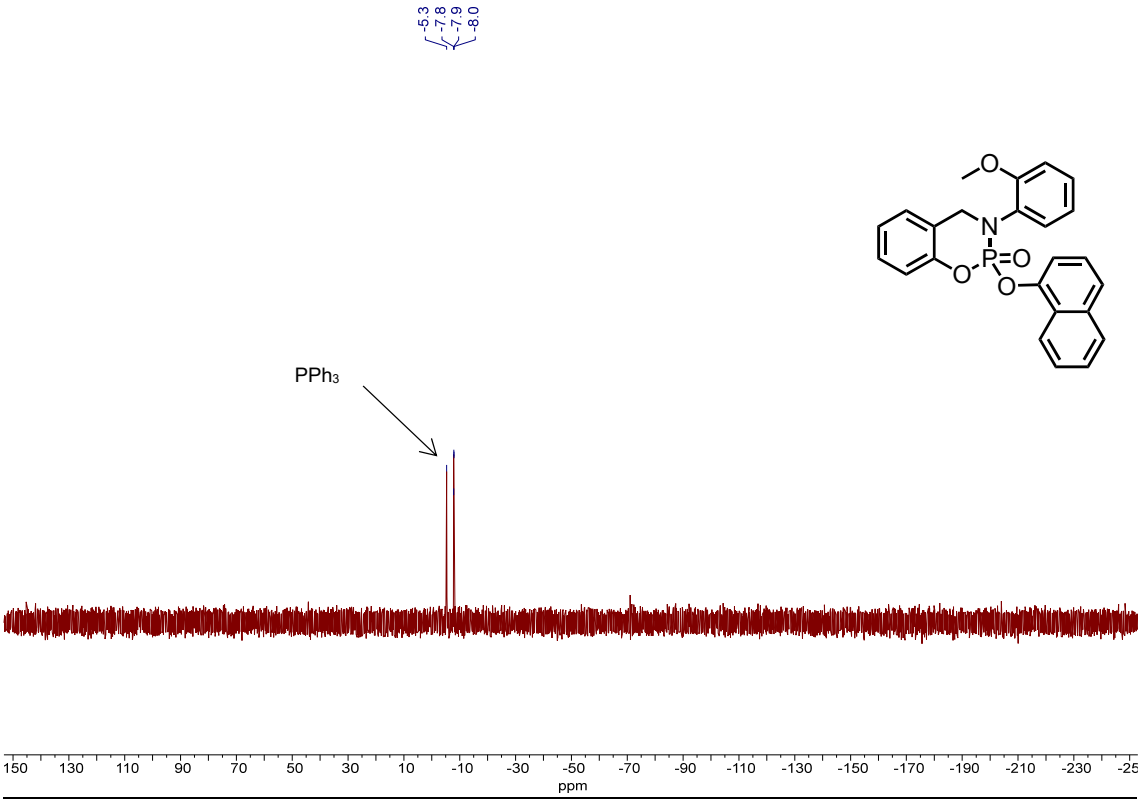
^{13}C NMR Spectrum for Compound **15c** (101 MHz, $CDCl_3$)



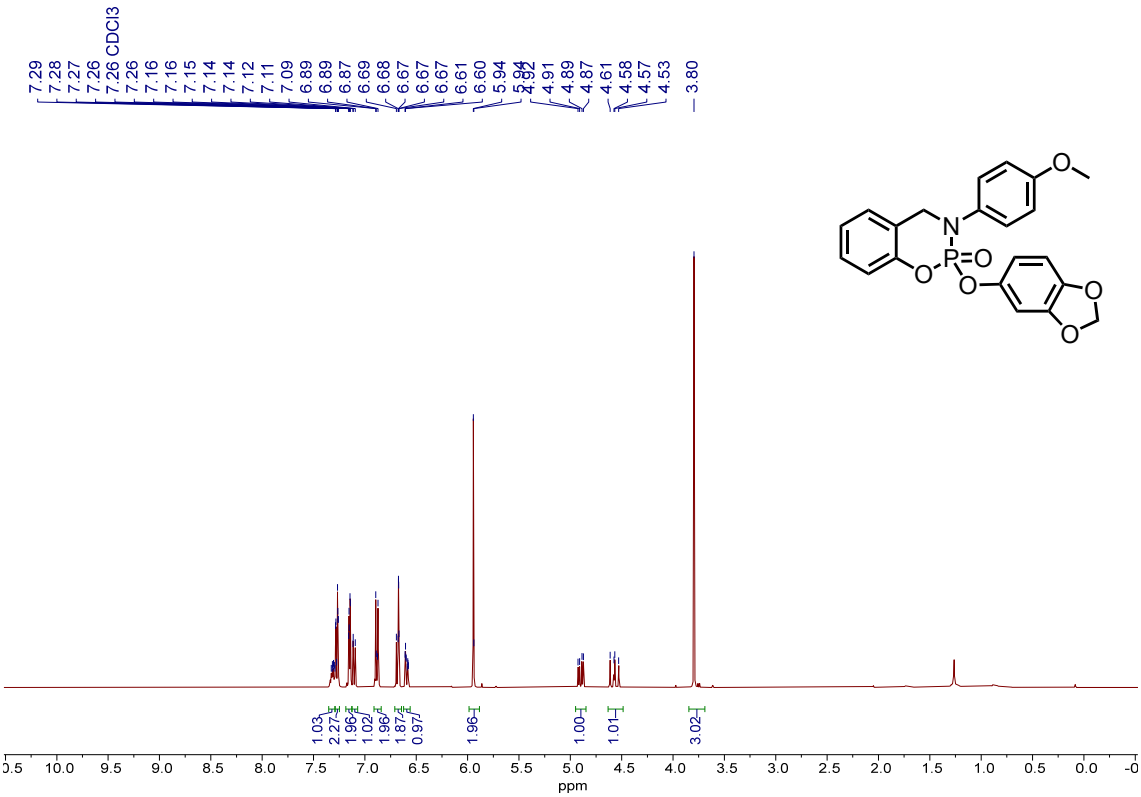




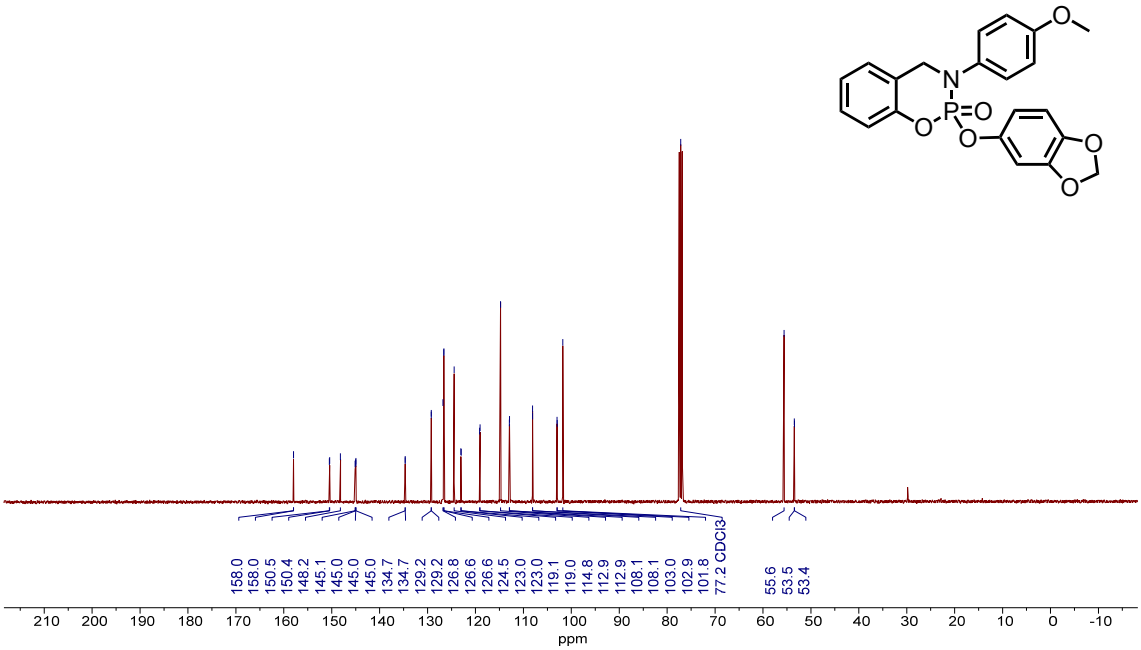
^{31}P NMR Spectrum for Compound **15c** (162 MHz, $CDCl_3$)



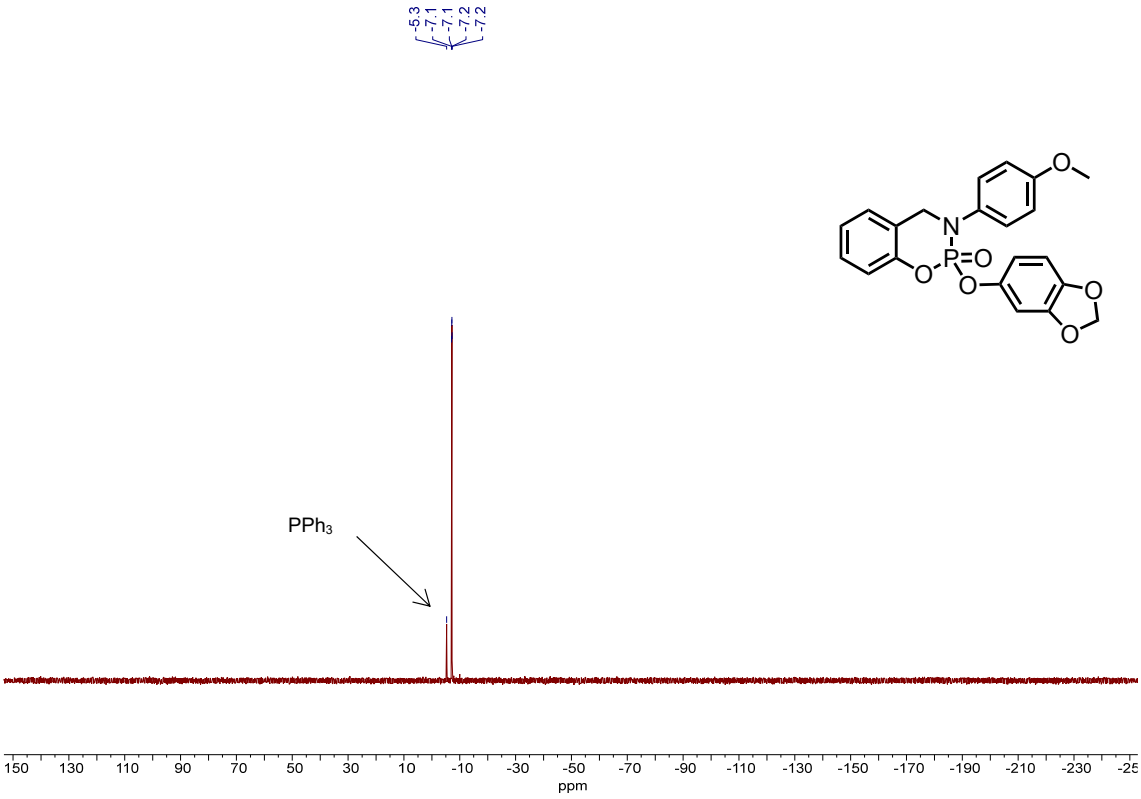
^{1}H NMR Spectrum for Compound **15d** (400 MHz, $CDCl_3$)



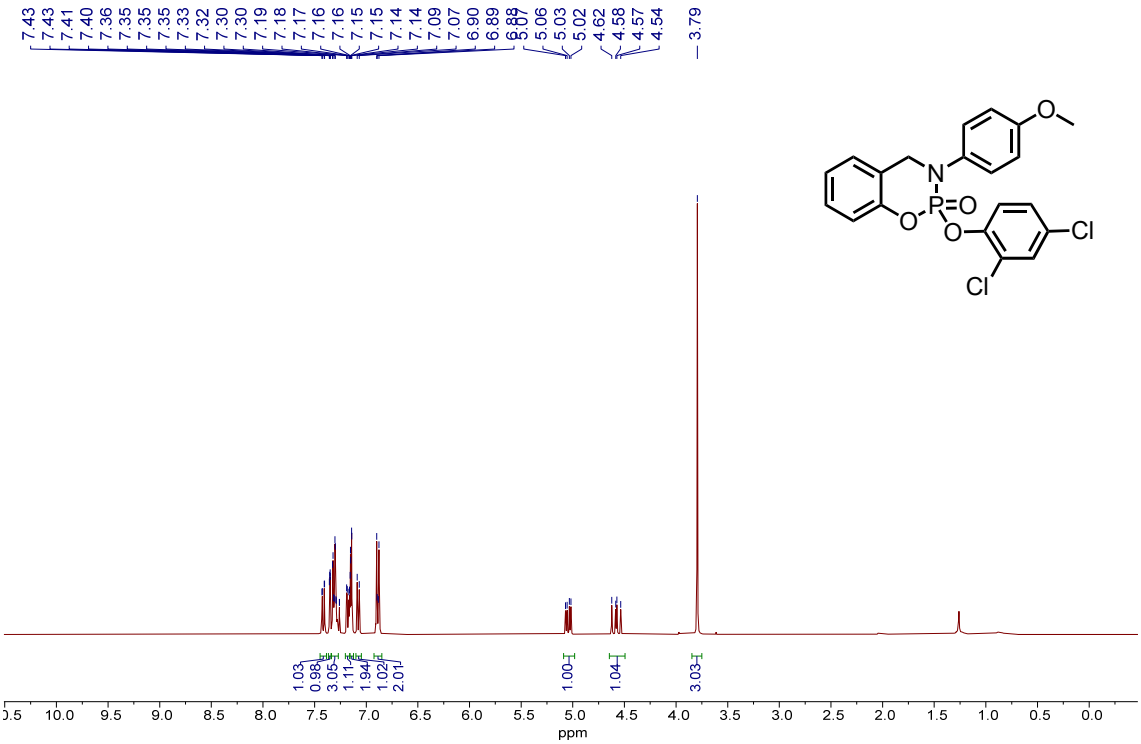
^{13}C NMR Spectrum for Compound **15d** (101 MHz, $CDCl_3$)



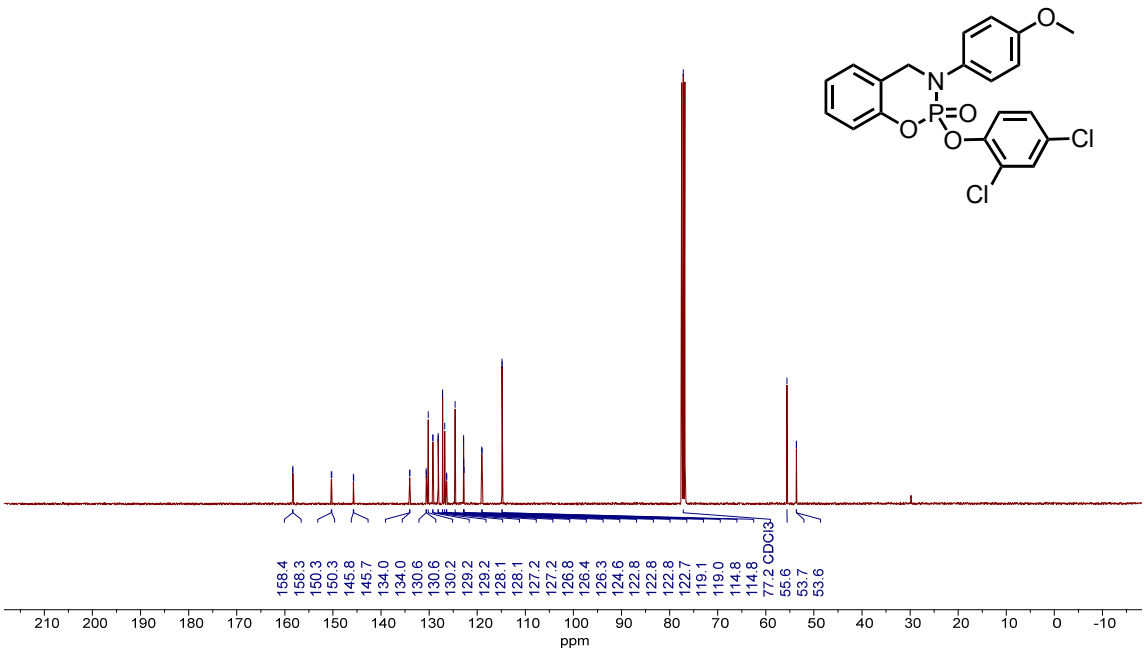
^{31}P NMR Spectrum for Compound **15d** (162 MHz, $CDCl_3$)



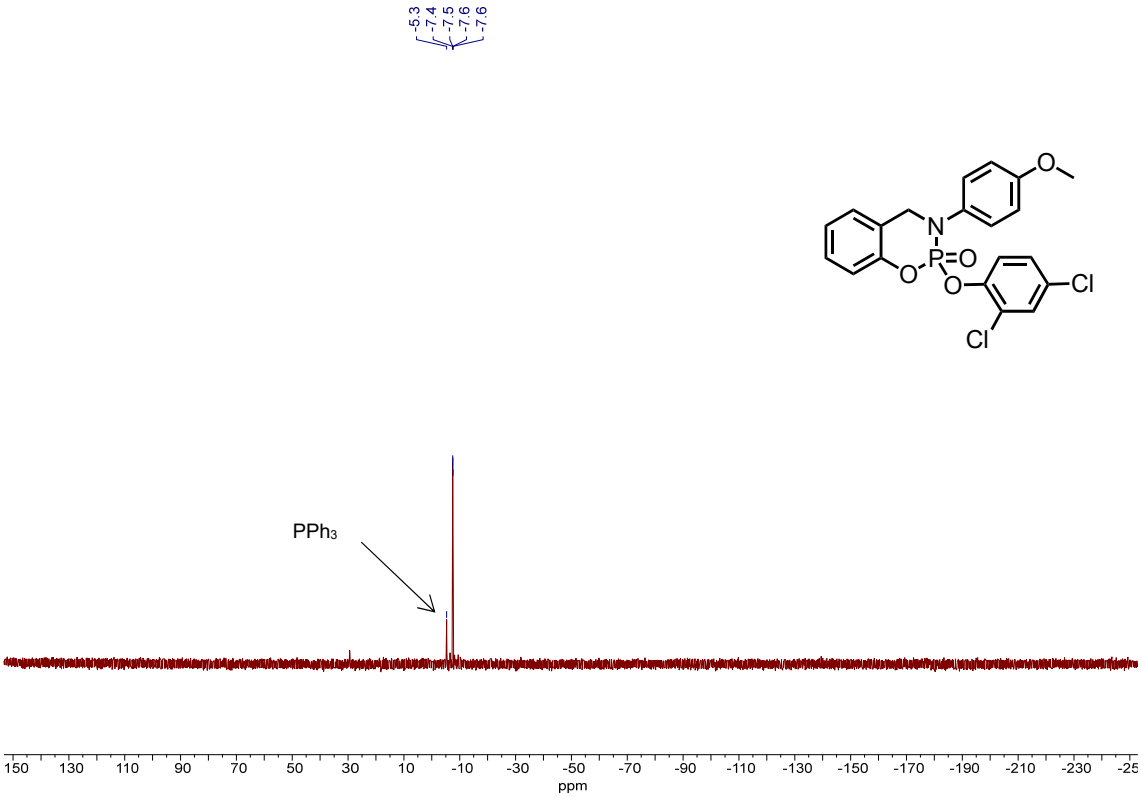
^{1}H NMR Spectrum for Compound **15e** (400 MHz, $CDCl_3$)



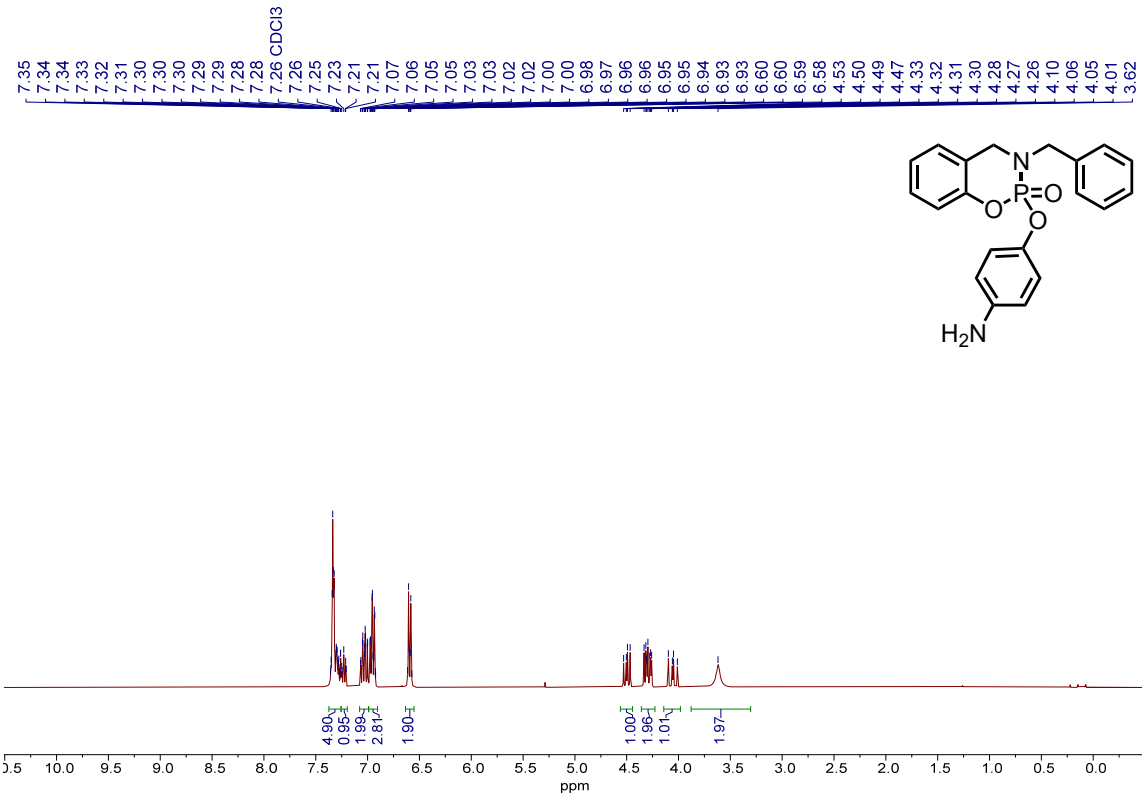
^{13}C NMR Spectrum for Compound **15e** (101 MHz, $CDCl_3$)



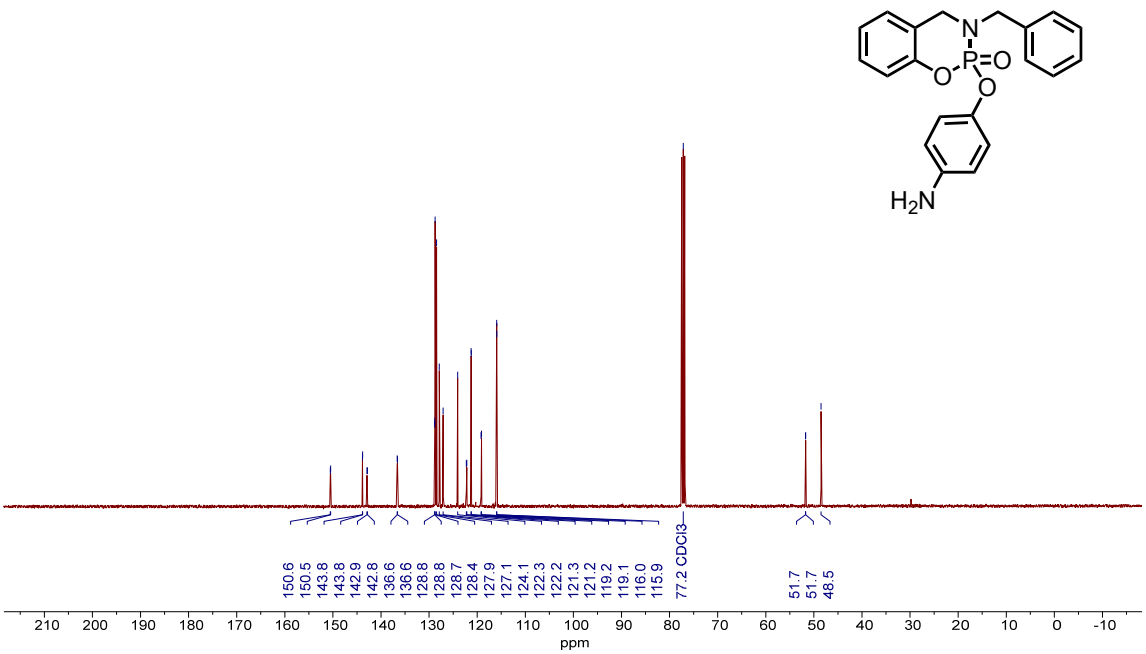
^{31}P NMR Spectrum for Compound **15e** (162 MHz, $CDCl_3$)



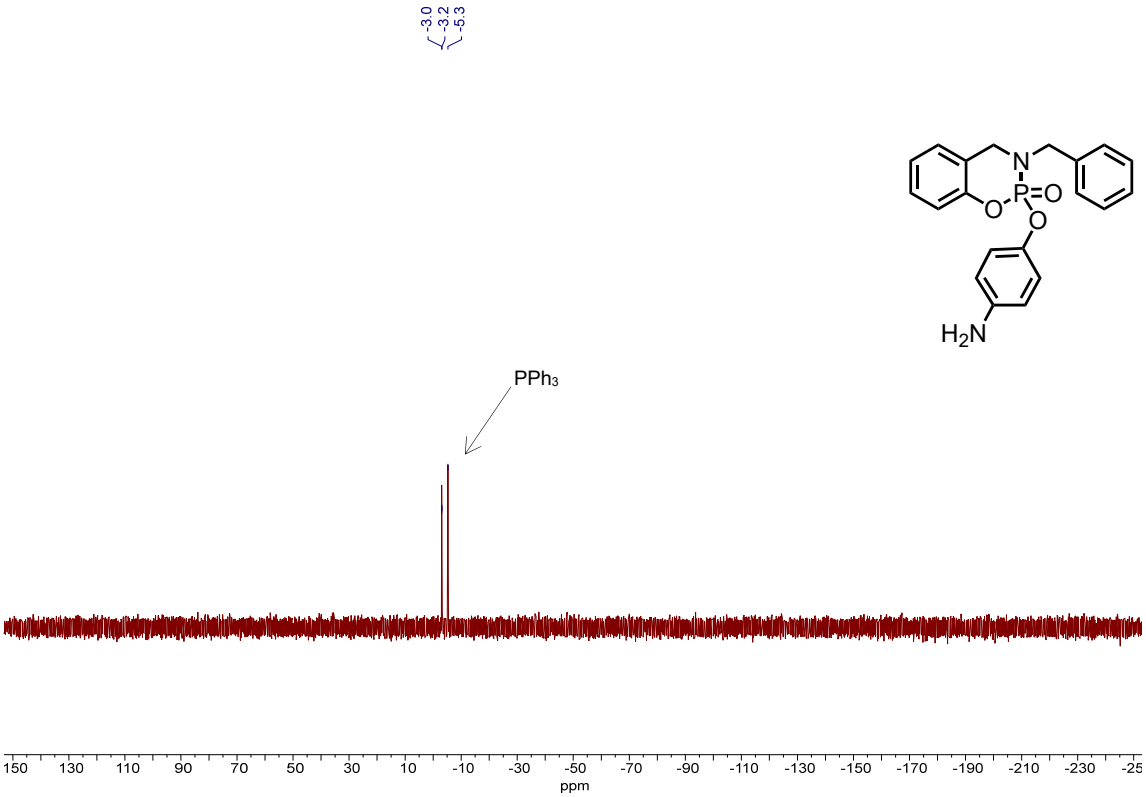
^{1}H NMR Spectrum for Compound **15f** (400 MHz, $CDCl_3$)



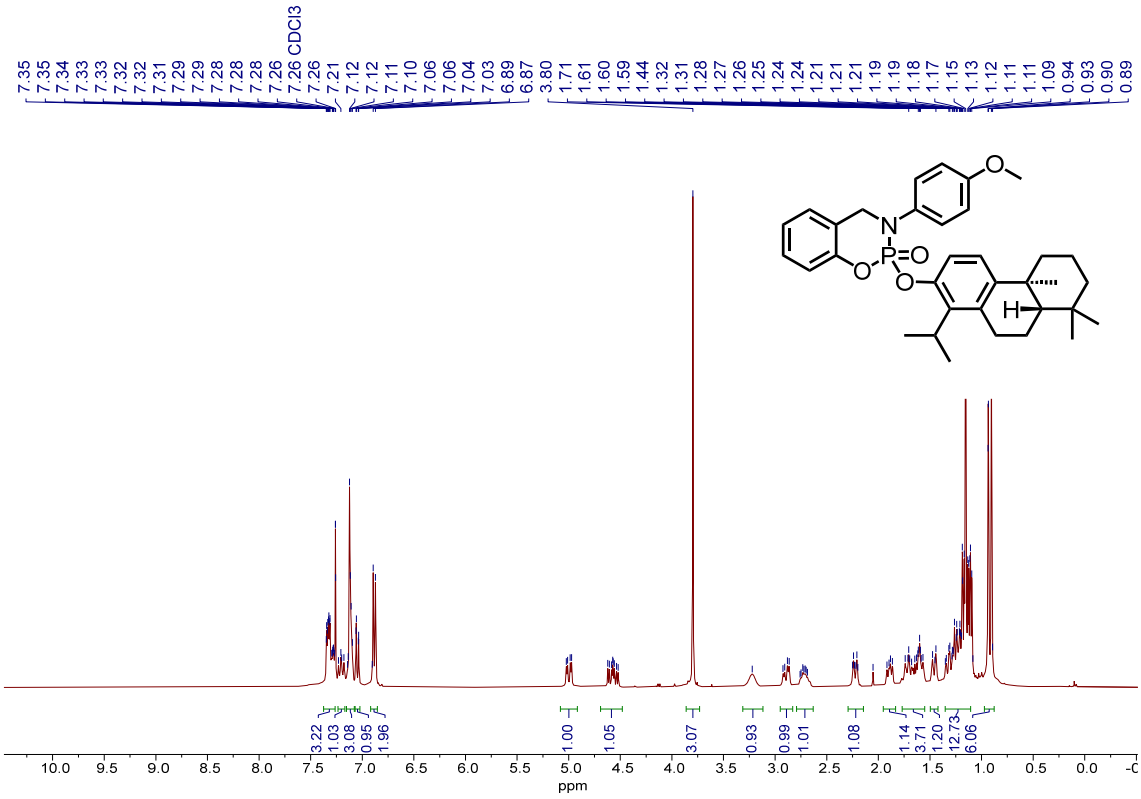
^{13}C NMR Spectrum for Compound **15f** (101 MHz, $CDCl_3$)



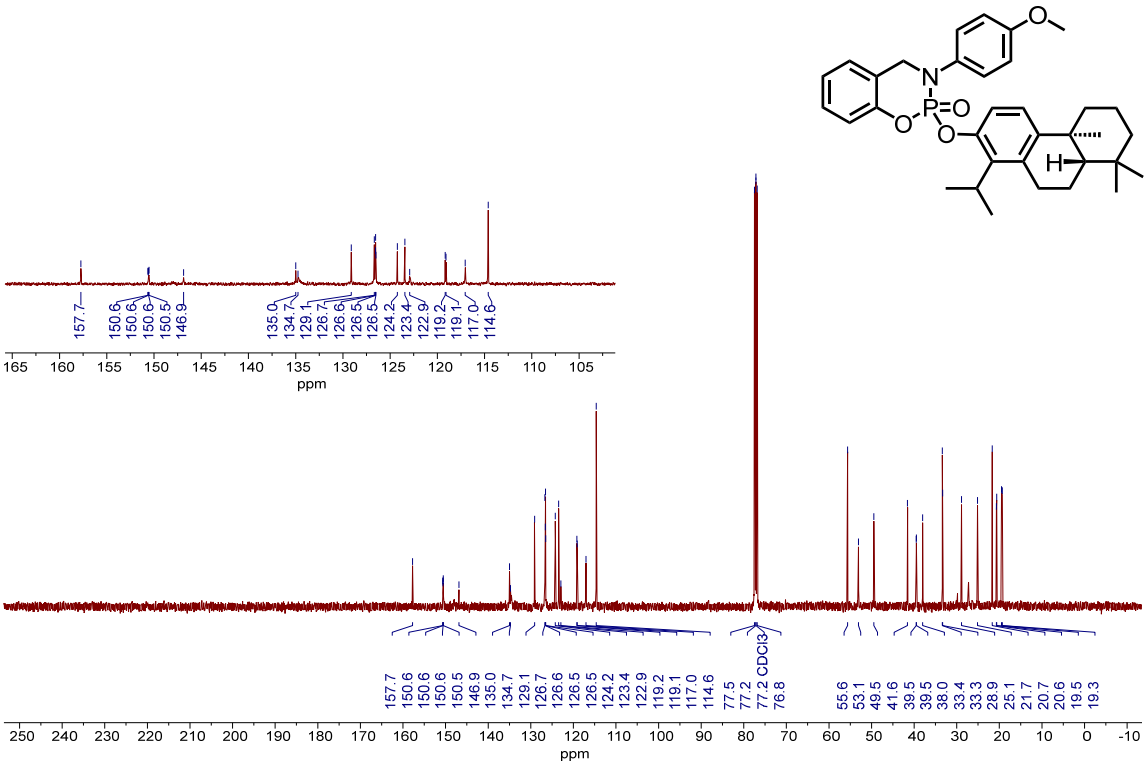
^{31}P NMR Spectrum for Compound **15f** (162 MHz, $CDCl_3$)



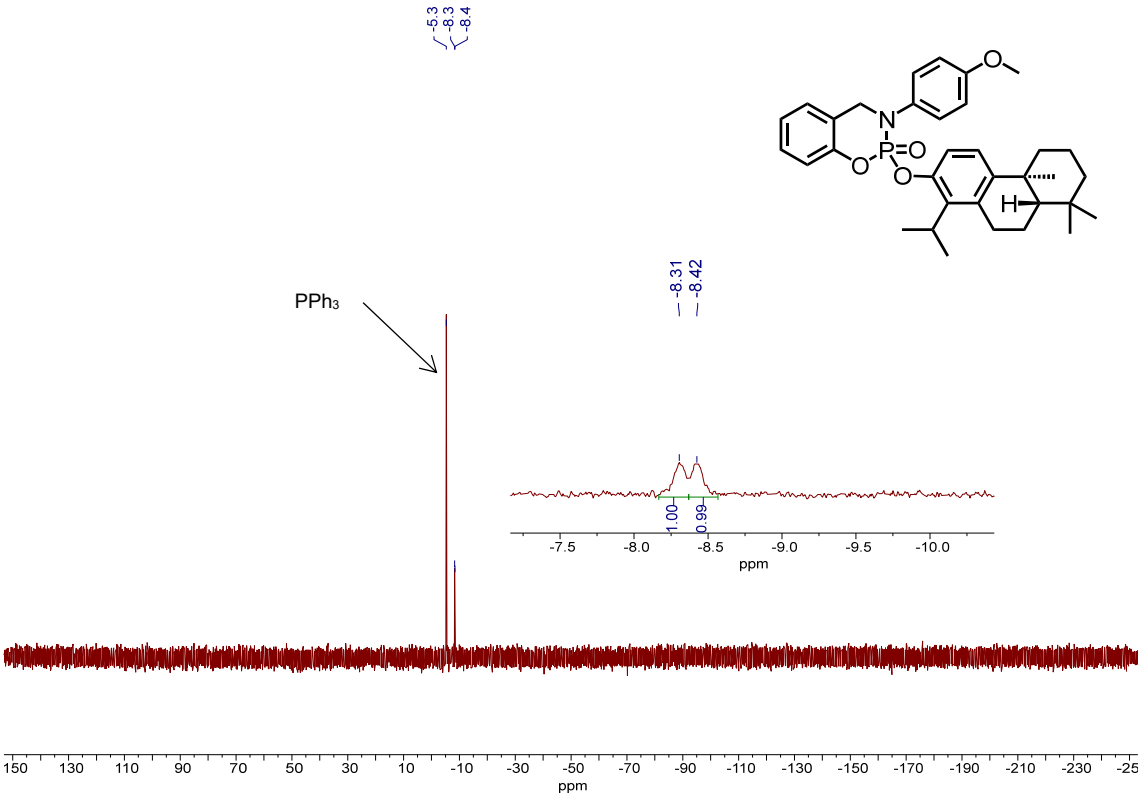
^{1}H NMR Spectrum for Compound **15g** (400 MHz, $CDCl_3$)



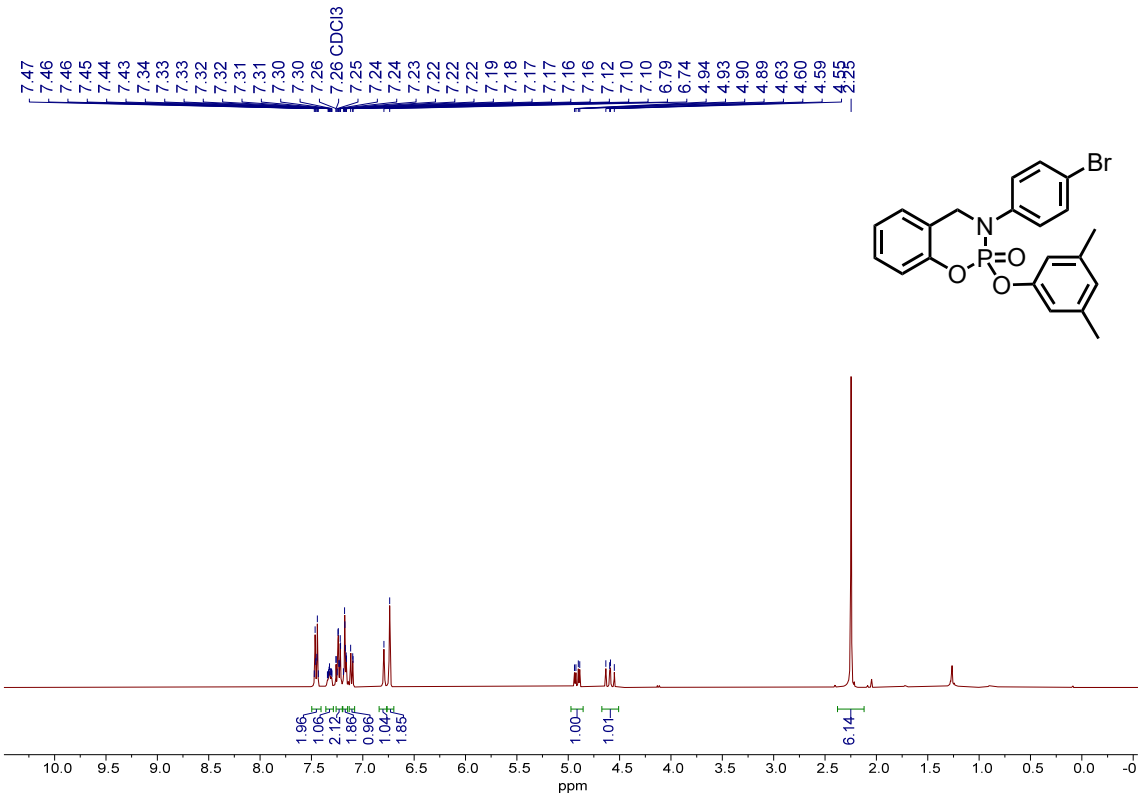
^{13}C NMR Spectrum for Compound **15g** (101 MHz, $CDCl_3$)



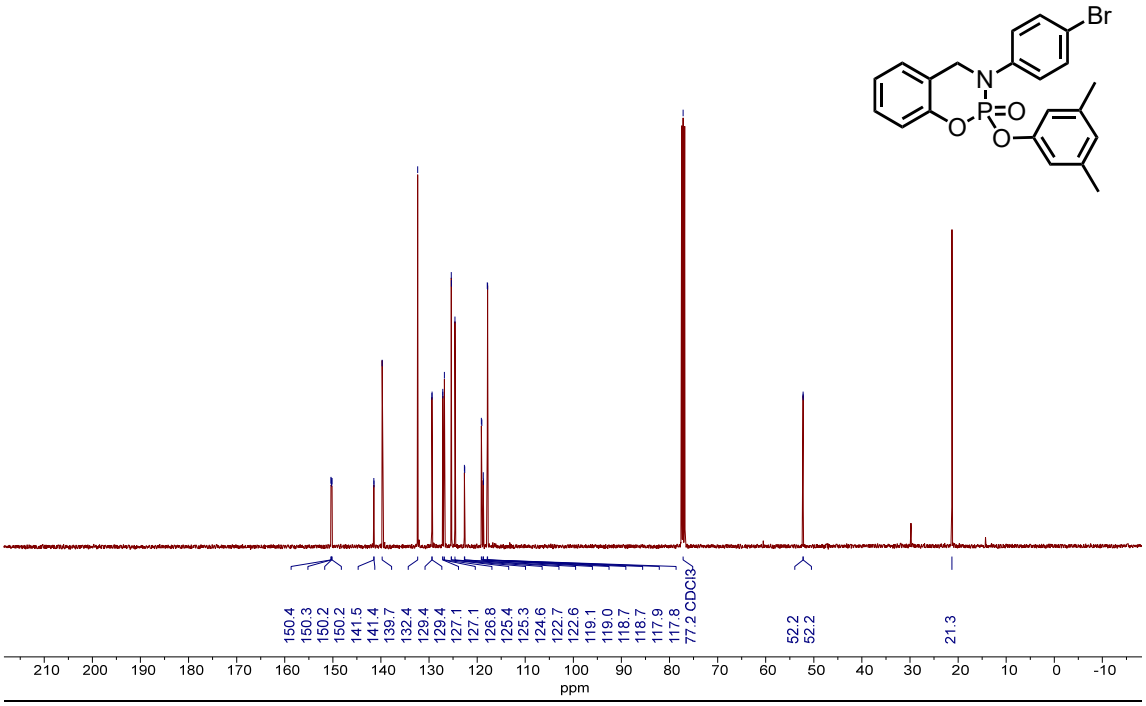
^{31}P NMR Spectrum for Compound **15g** (162 MHz, $CDCl_3$)



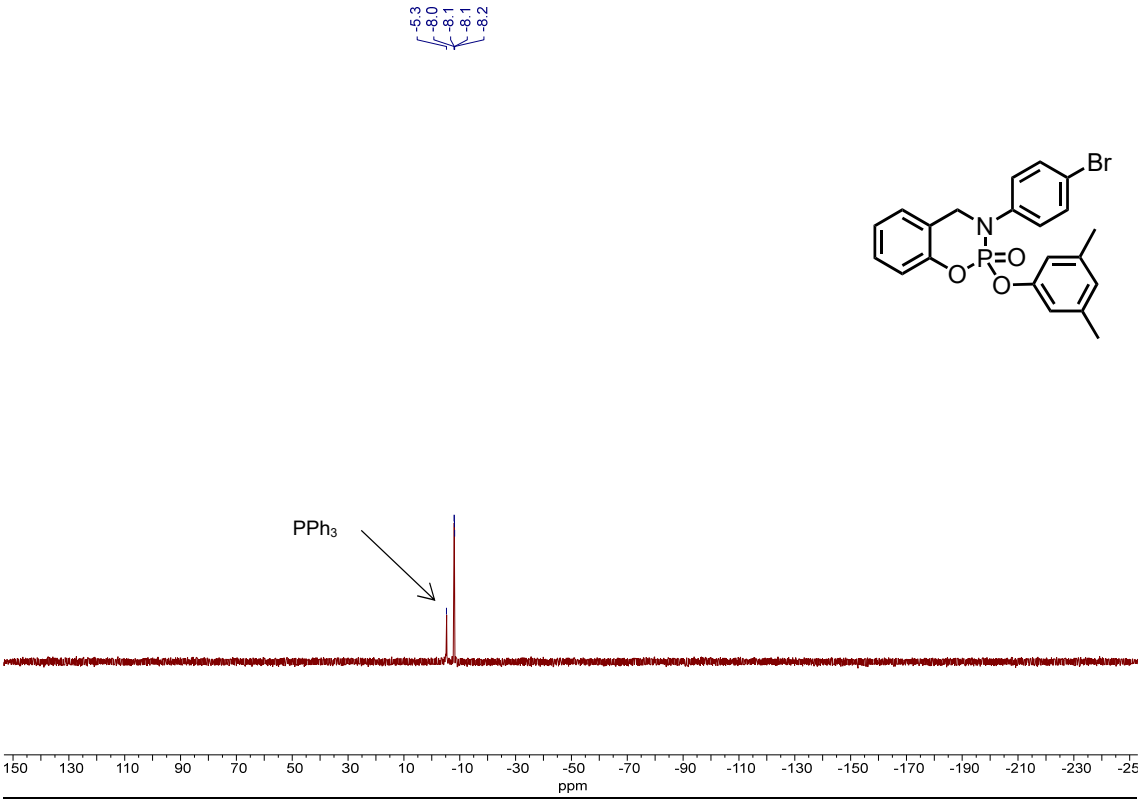
^{1}H NMR Spectrum for Compound **15h** (400 MHz, $CDCl_3$)



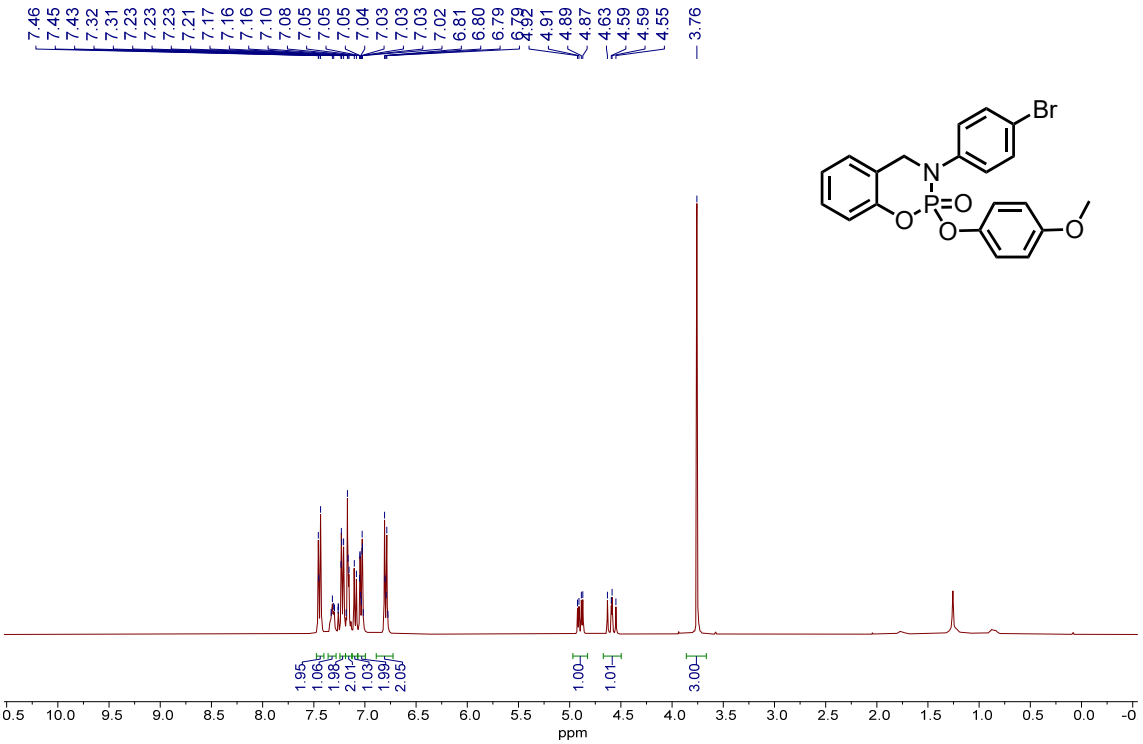
^{13}C NMR Spectrum for Compound **15h** (101 MHz, $CDCl_3$)



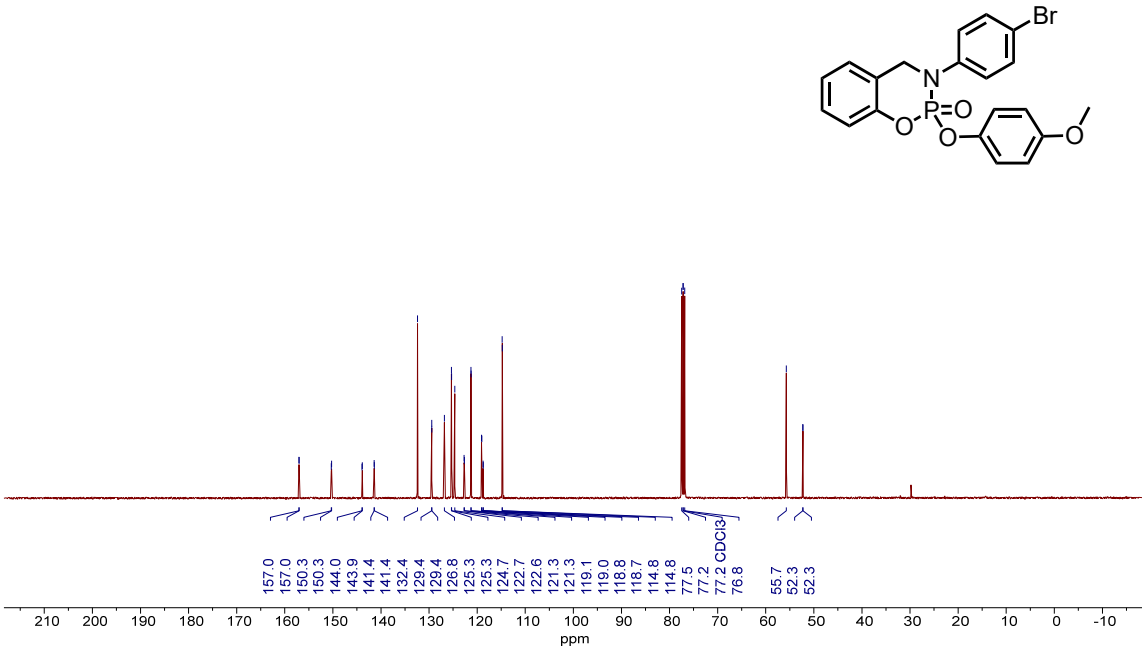
^{31}P NMR Spectrum for Compound **15h** (162 MHz, $CDCl_3$)



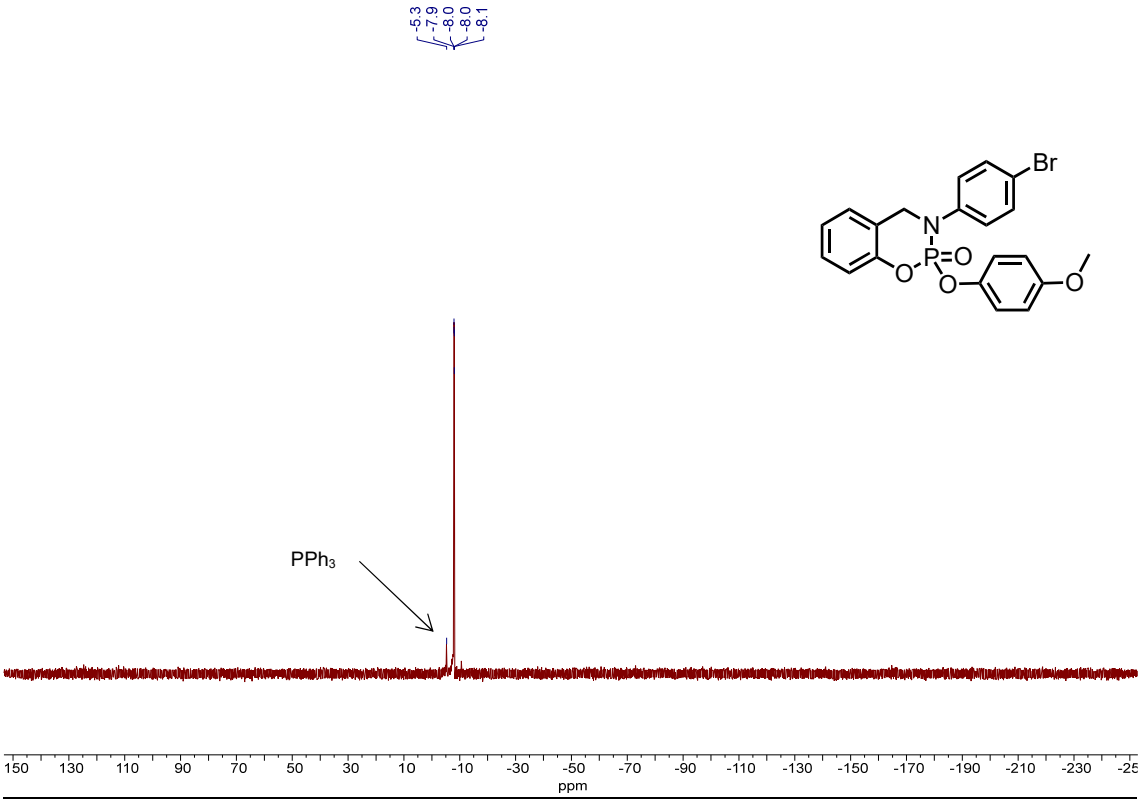
^{1}H NMR Spectrum for Compound **15i** (400 MHz, $CDCl_3$)



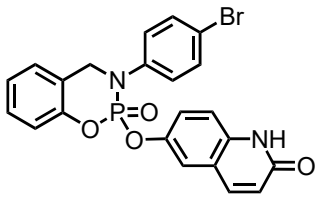
^{13}C NMR Spectrum for Compound **15i** (101 MHz, $CDCl_3$)

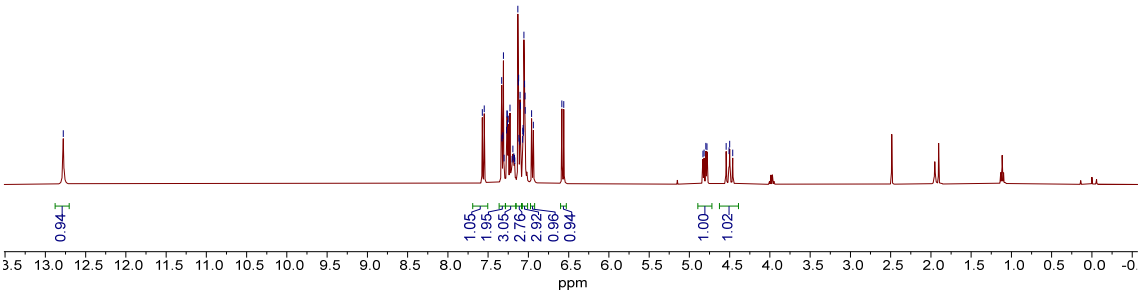


^{31}P NMR Spectrum for Compound **15i** (162 MHz, $CDCl_3$)

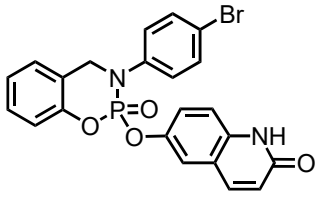


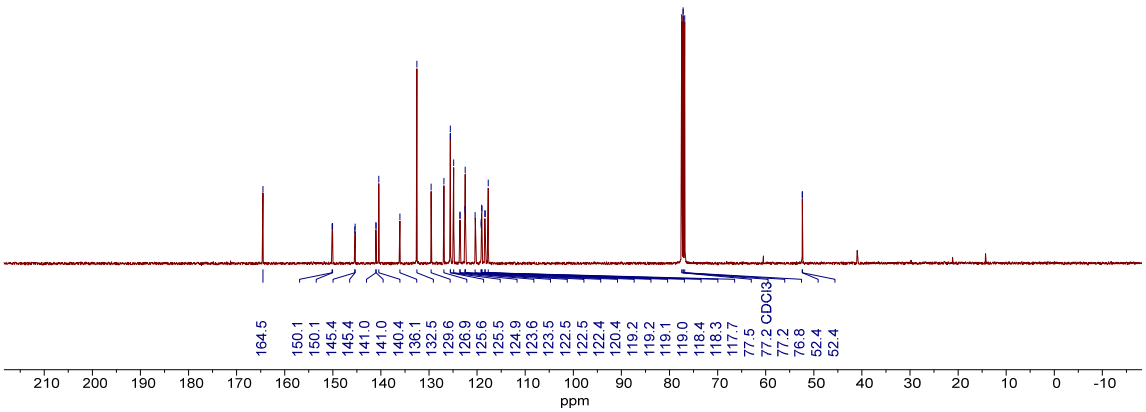
^{1}H NMR Spectrum for Compound **15j** (400 MHz, $CDCl_3$)



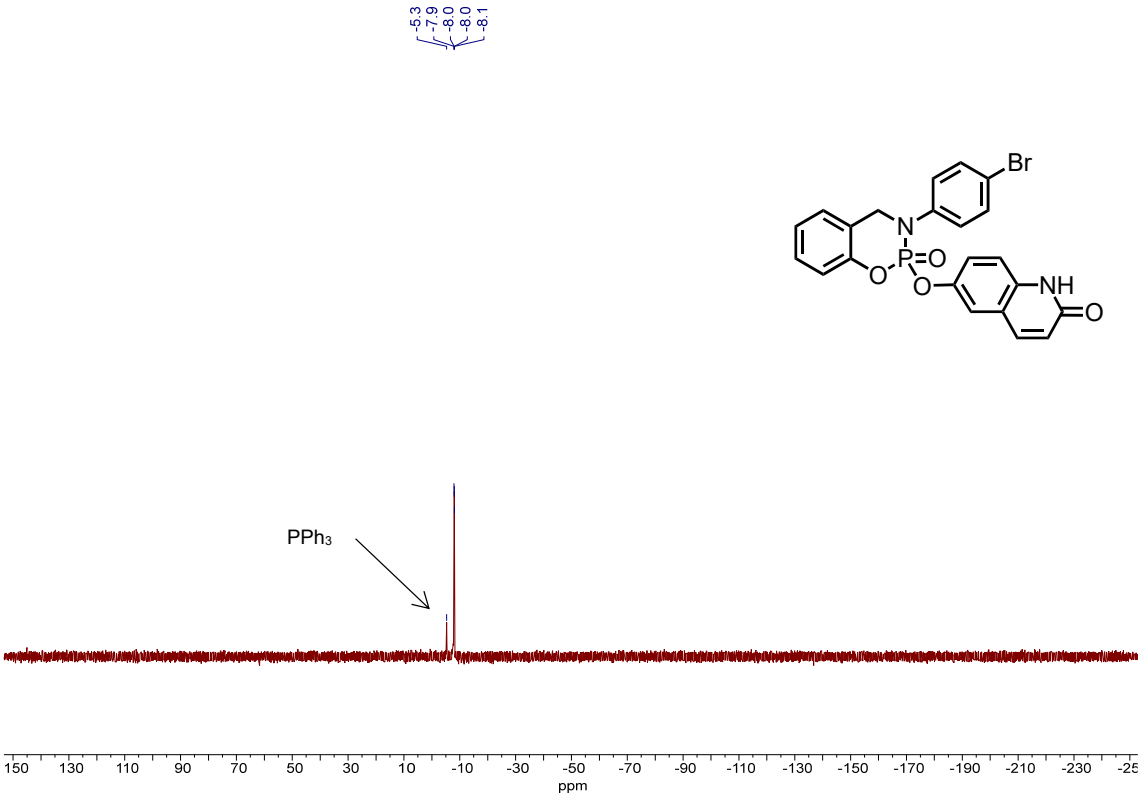


^{13}C NMR Spectrum for Compound **15j** (101 MHz, $CDCl_3$)

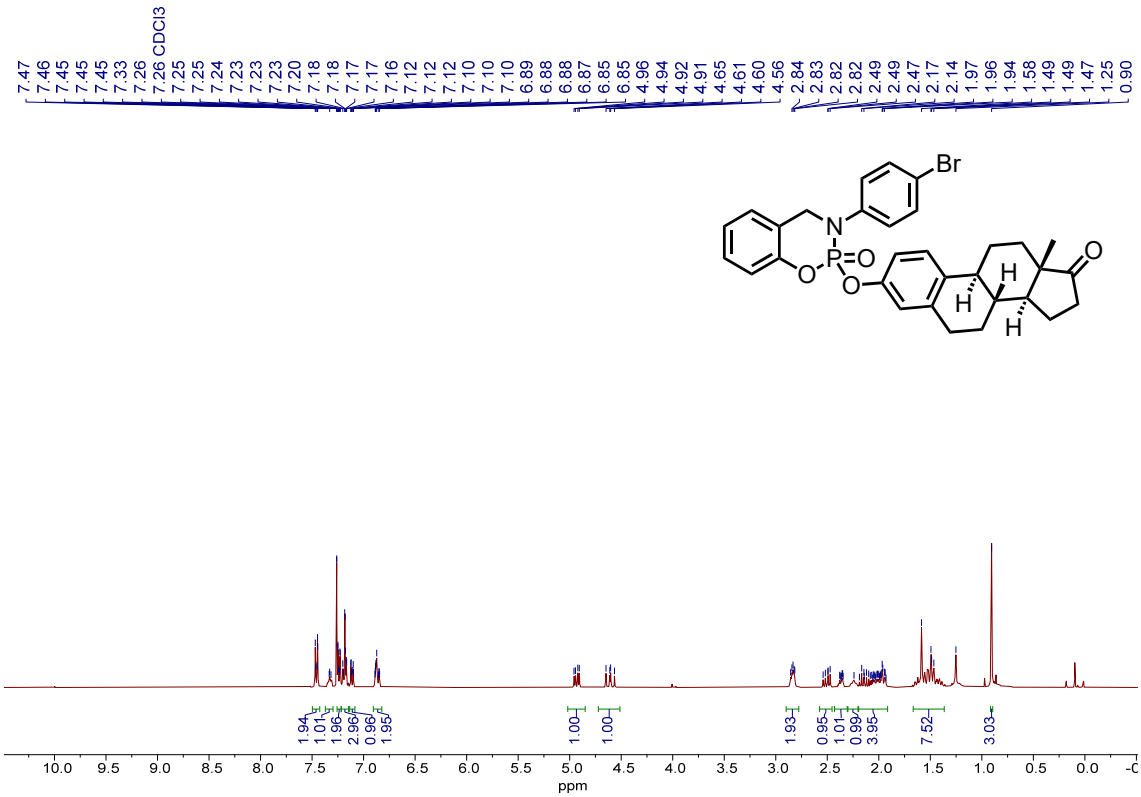




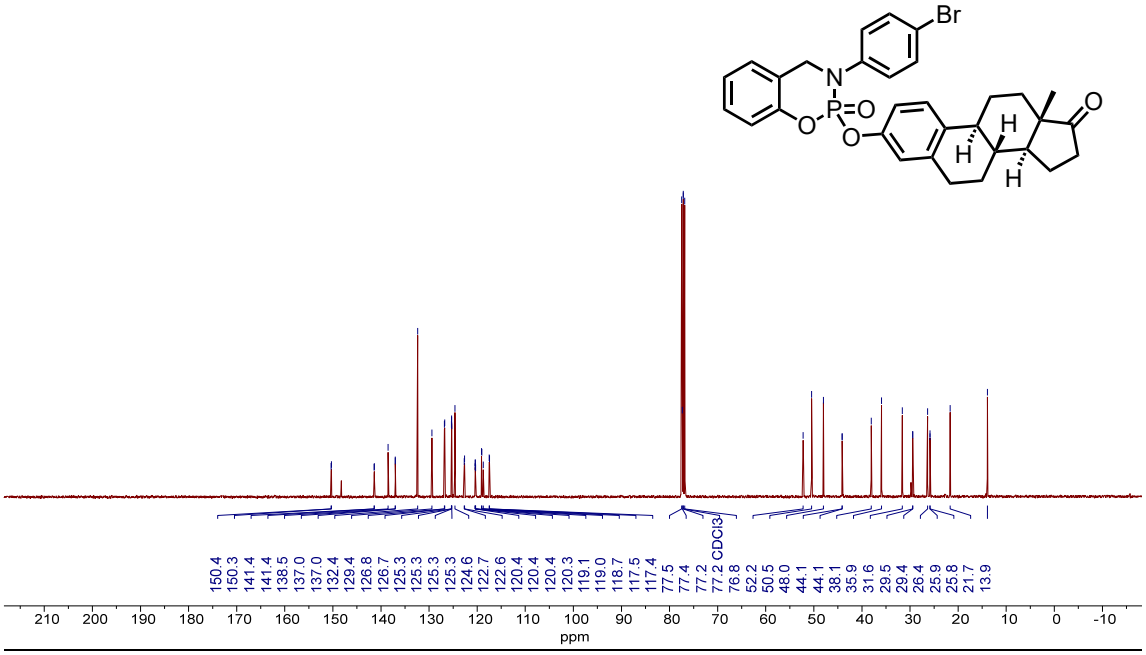
^{31}P NMR Spectrum for Compound **15j** (162 MHz, $CDCl_3$)



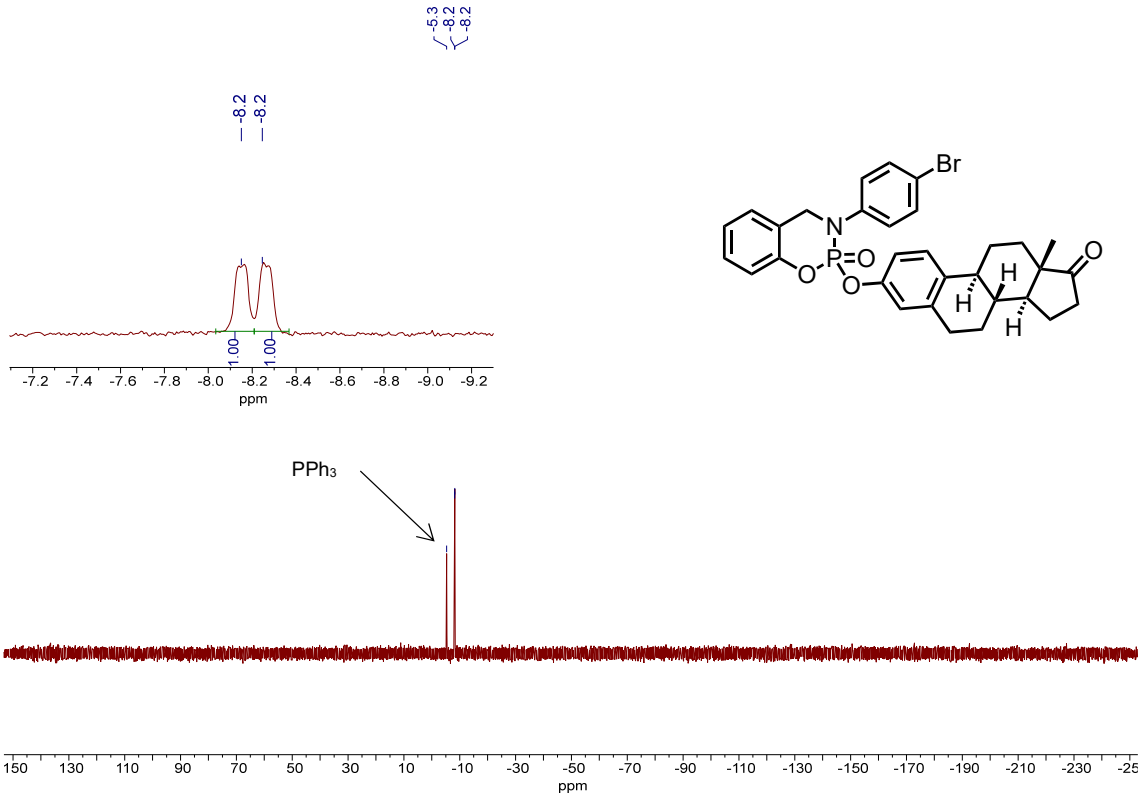
^{1}H NMR Spectrum for Compound **15k** (400 MHz, $CDCl_3$)



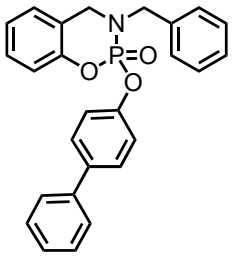
^{13}C NMR Spectrum for Compound **15k** (101 MHz, $CDCl_3$)

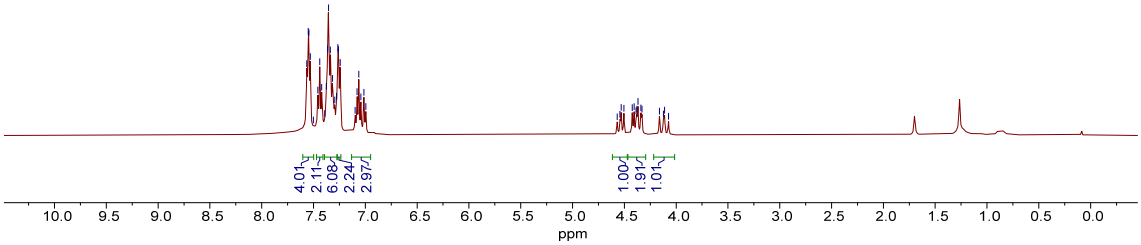


^{31}P NMR Spectrum for Compound **15k** (162 MHz, $CDCl_3$)

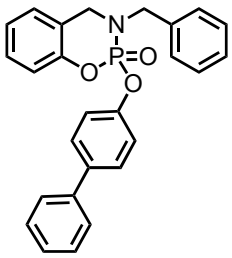


^{1}H NMR Spectrum for Compound **15l** (400 MHz, $CDCl_3$)

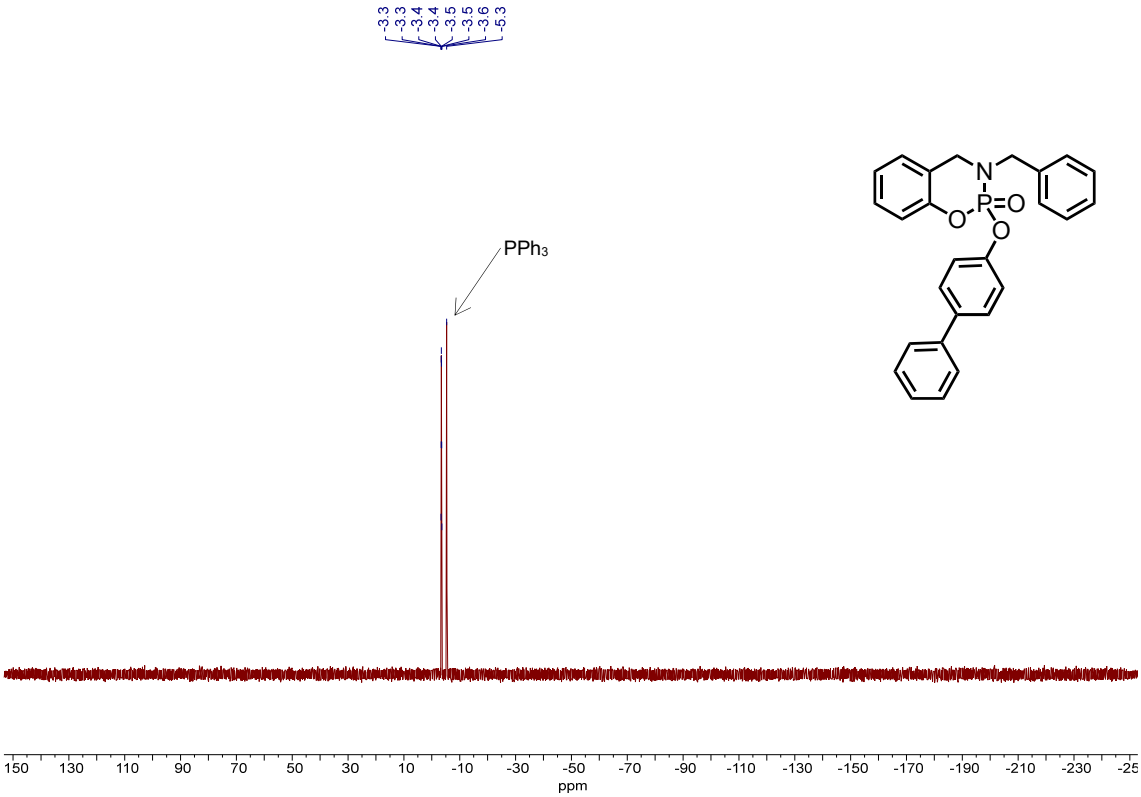




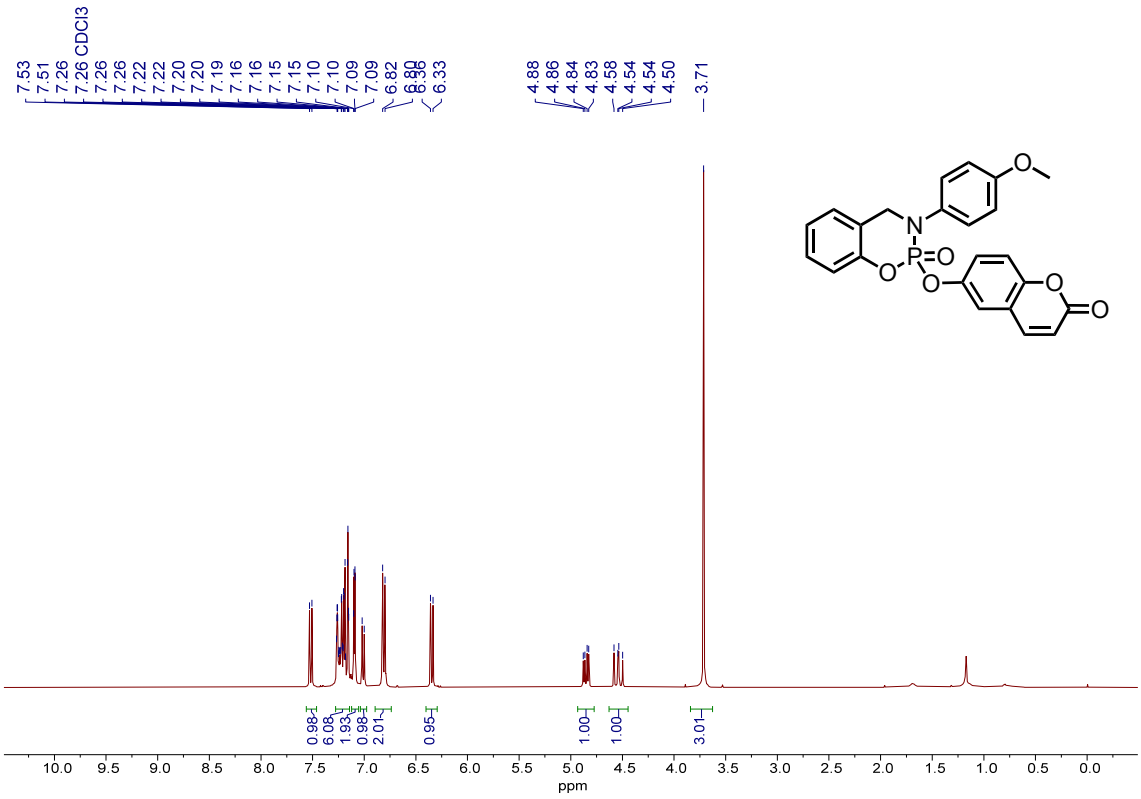
^{13}C NMR Spectrum for Compound **15l** (101 MHz, $CDCl_3$)



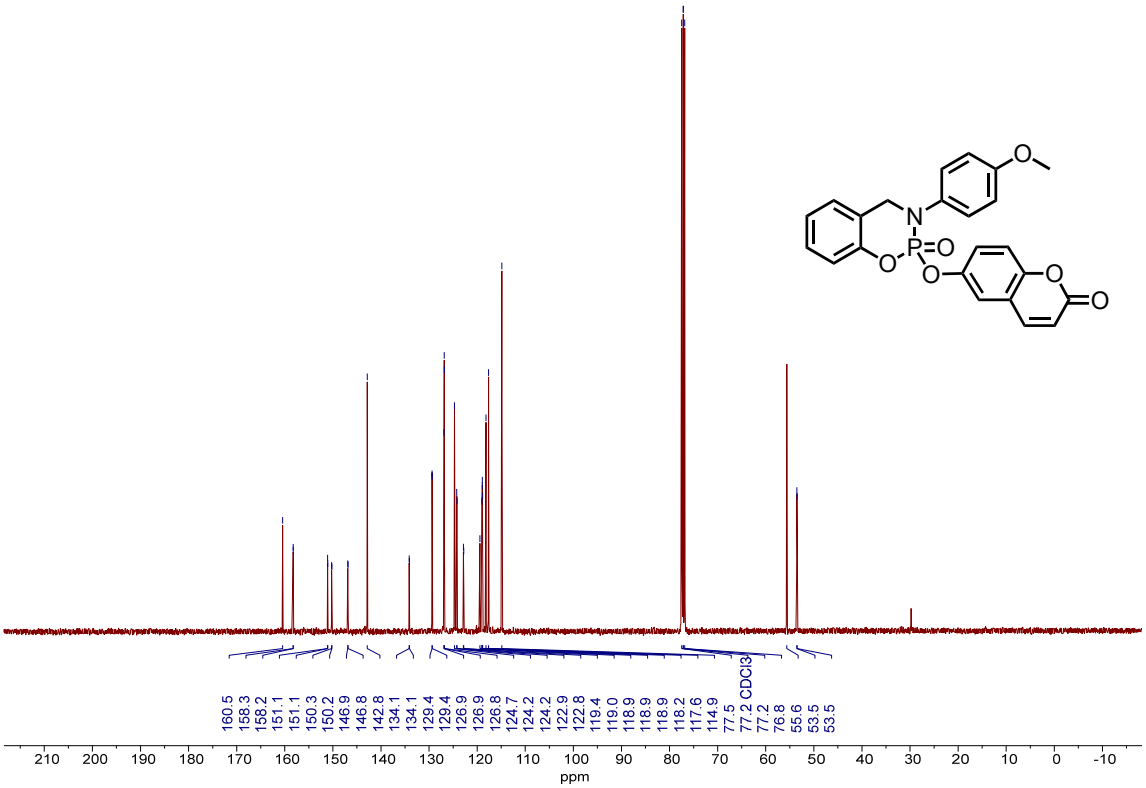
^{31}P NMR Spectrum for Compound **15l** (162 MHz, $CDCl_3$)



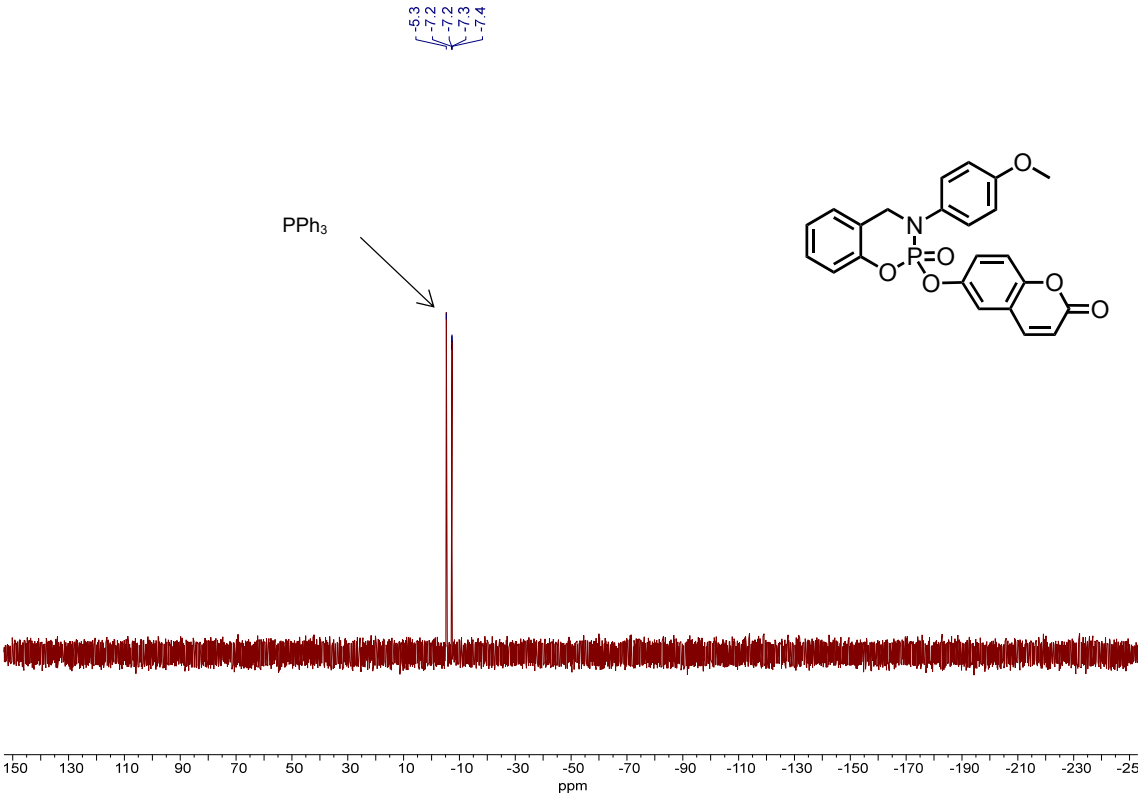
^{1}H NMR Spectrum for Compound **15m** (400 MHz, $CDCl_3$)



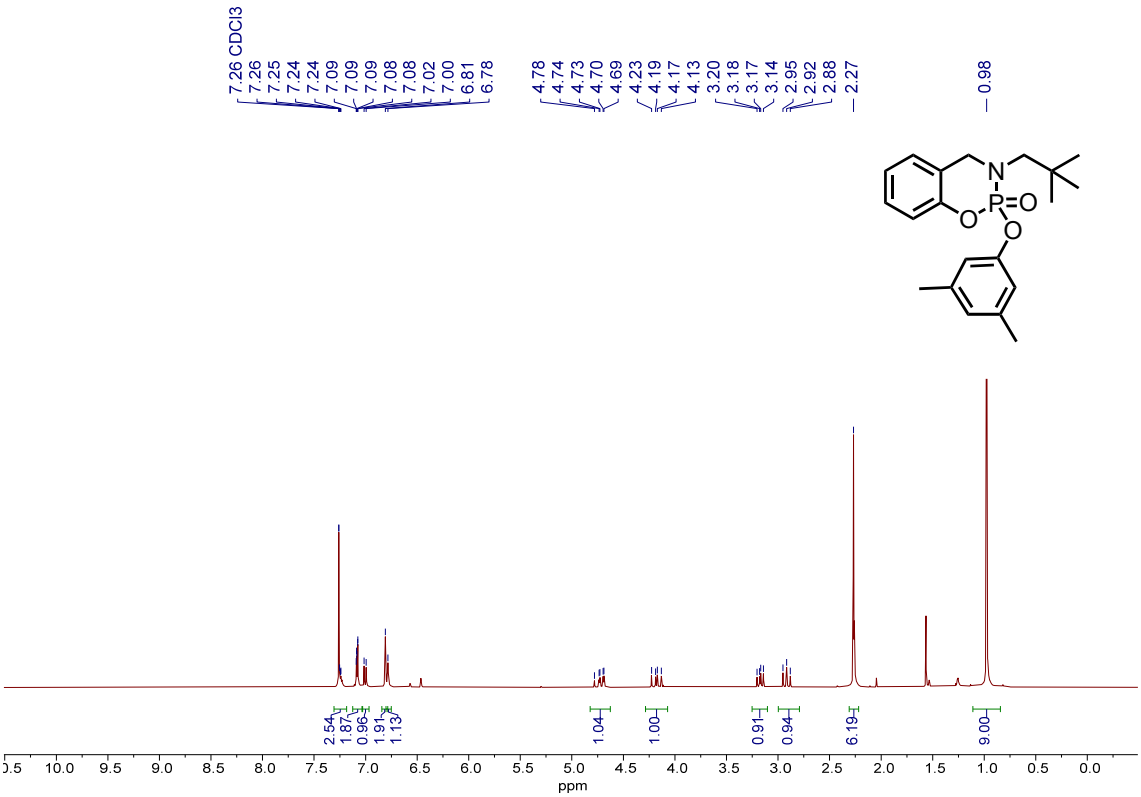
^{13}C NMR Spectrum for Compound **15m** (101 MHz, $CDCl_3$)



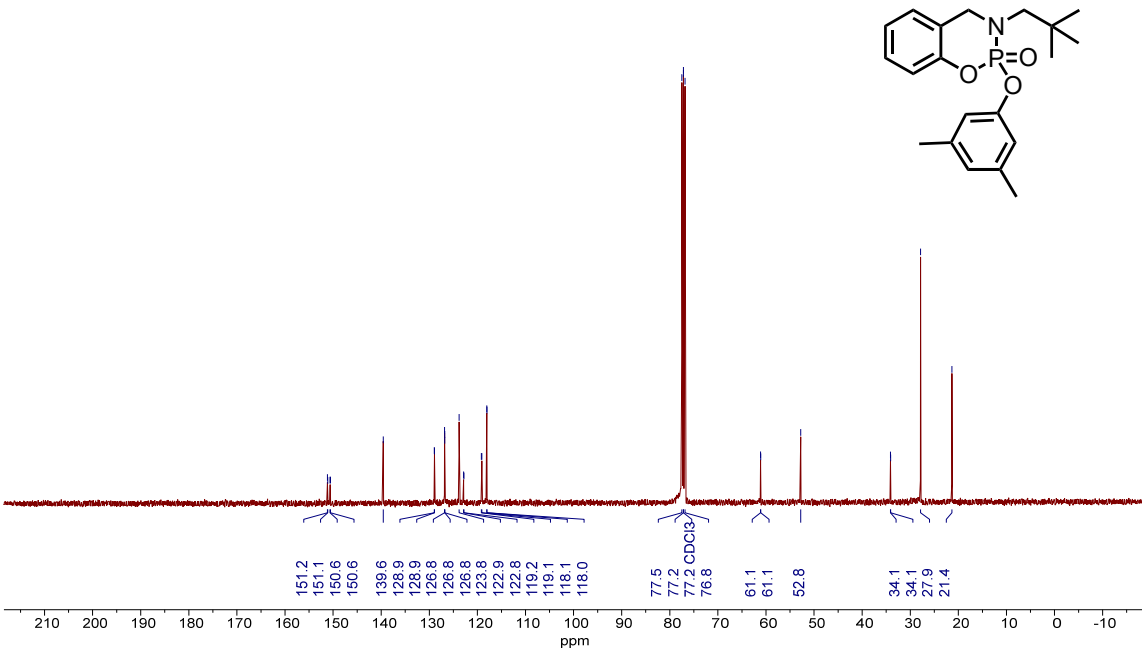
^{31}P NMR Spectrum for Compound **15m** (162 MHz, $CDCl_3$)



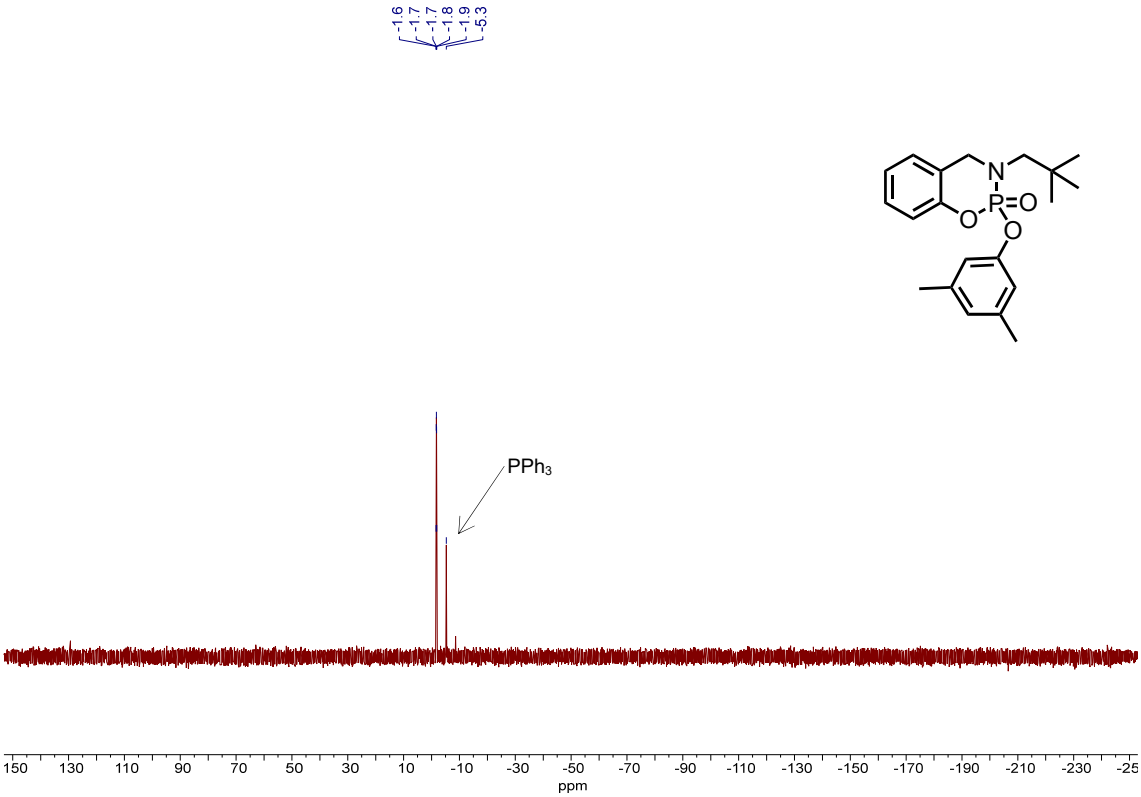
^{1}H NMR Spectrum for Compound **15n** (400 MHz, $CDCl_3$)



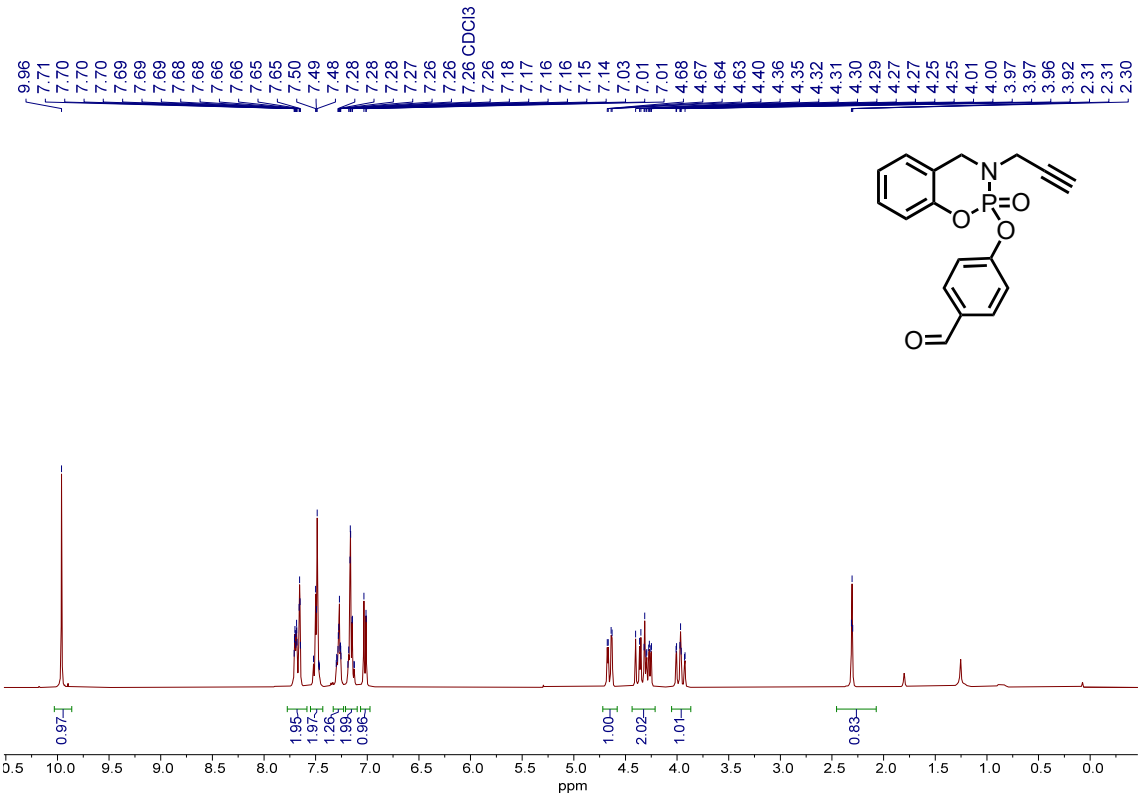
^{13}C NMR Spectrum for Compound **15n** (101 MHz, $CDCl_3$)



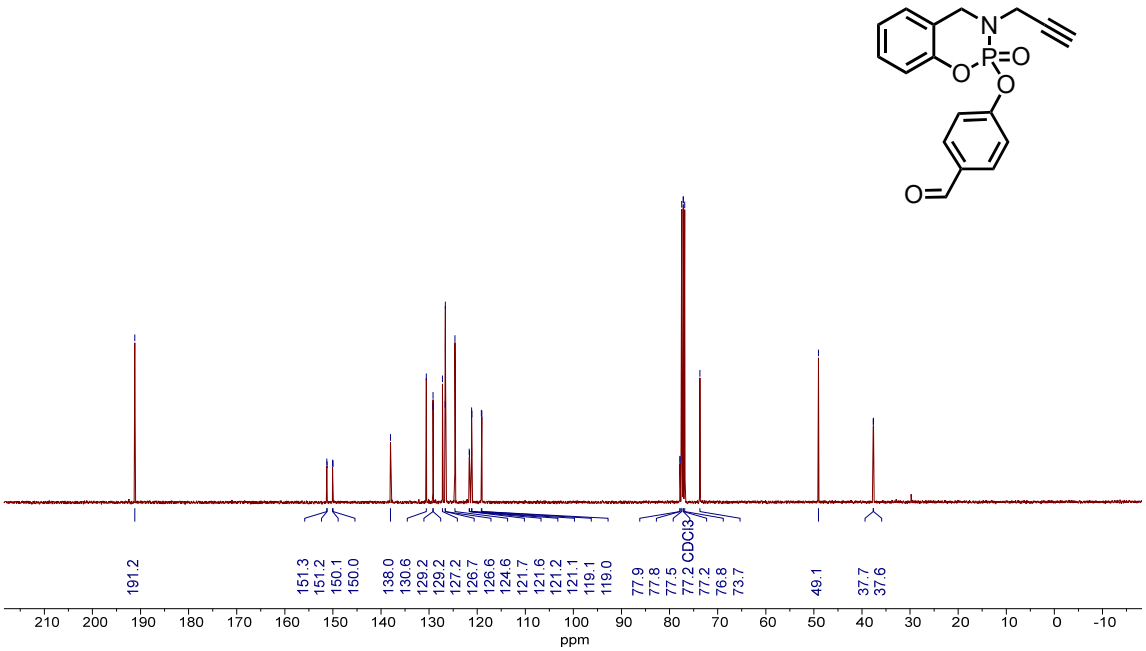
^{31}P NMR Spectrum for Compound **15n** (162 MHz, $CDCl_3$)



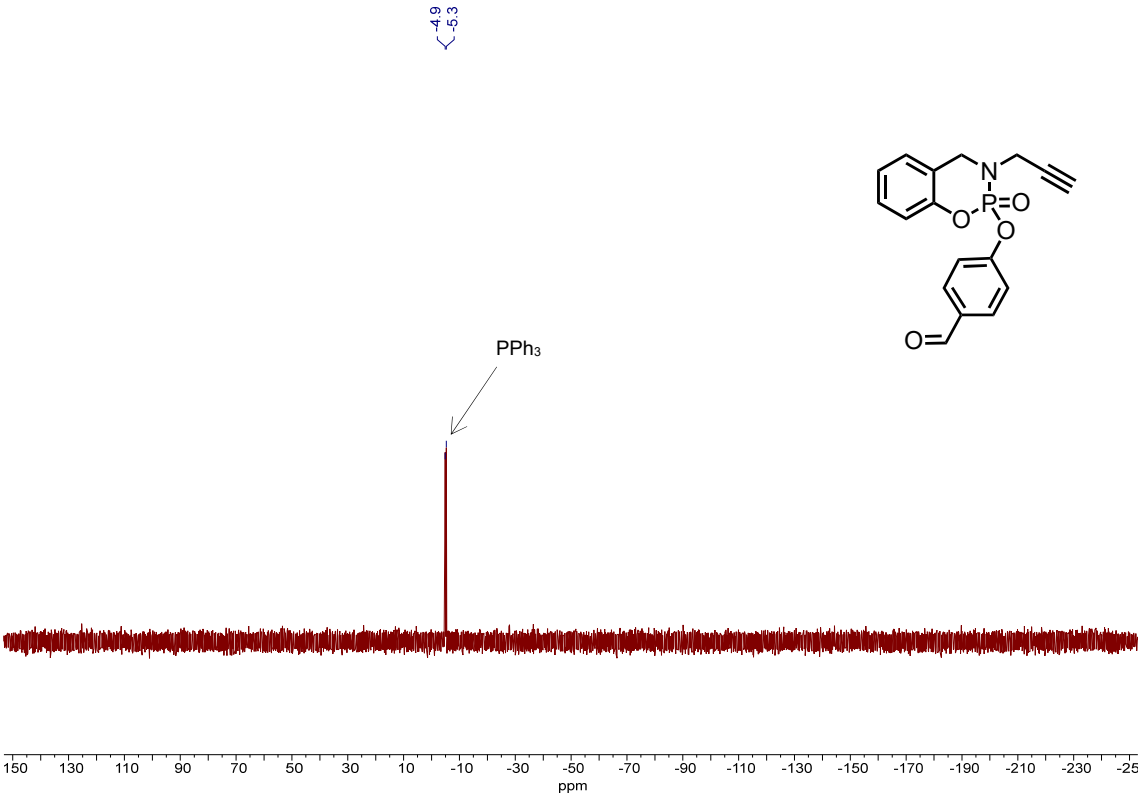
^{1}H NMR Spectrum for Compound **15o** (400 MHz, $CDCl_3$)



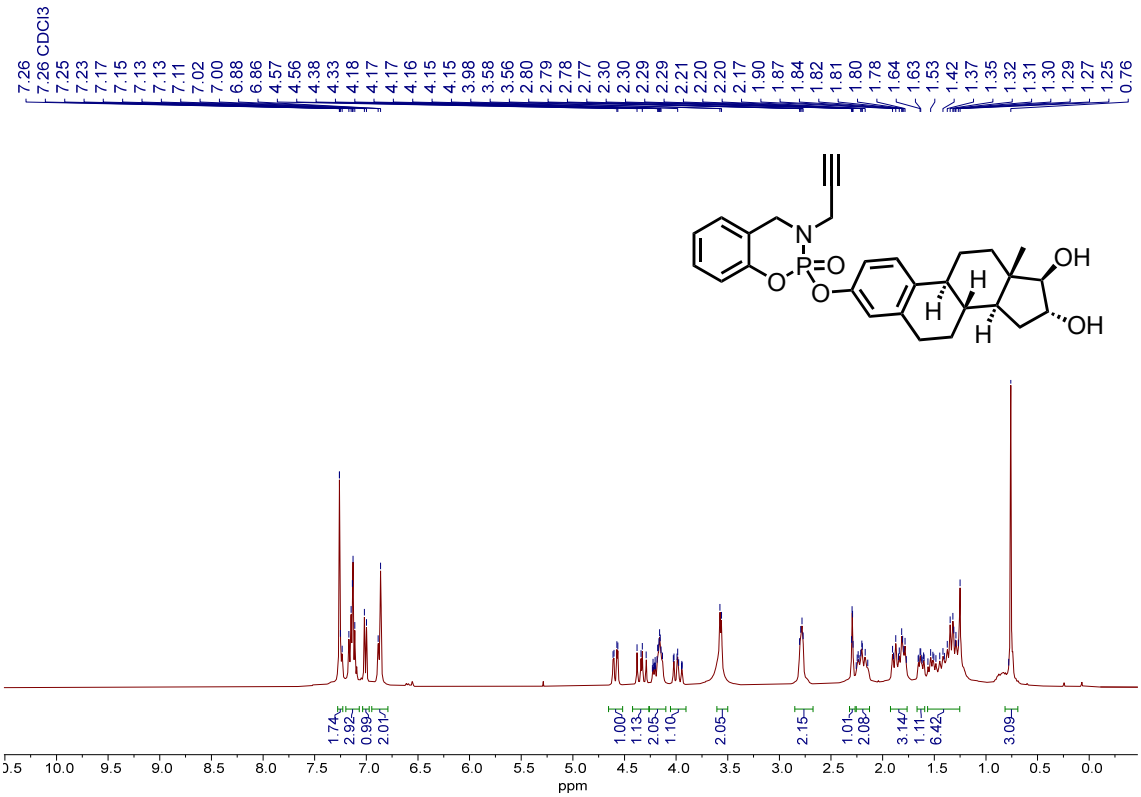
^{13}C NMR Spectrum for Compound **15o** (101 MHz, $CDCl_3$)



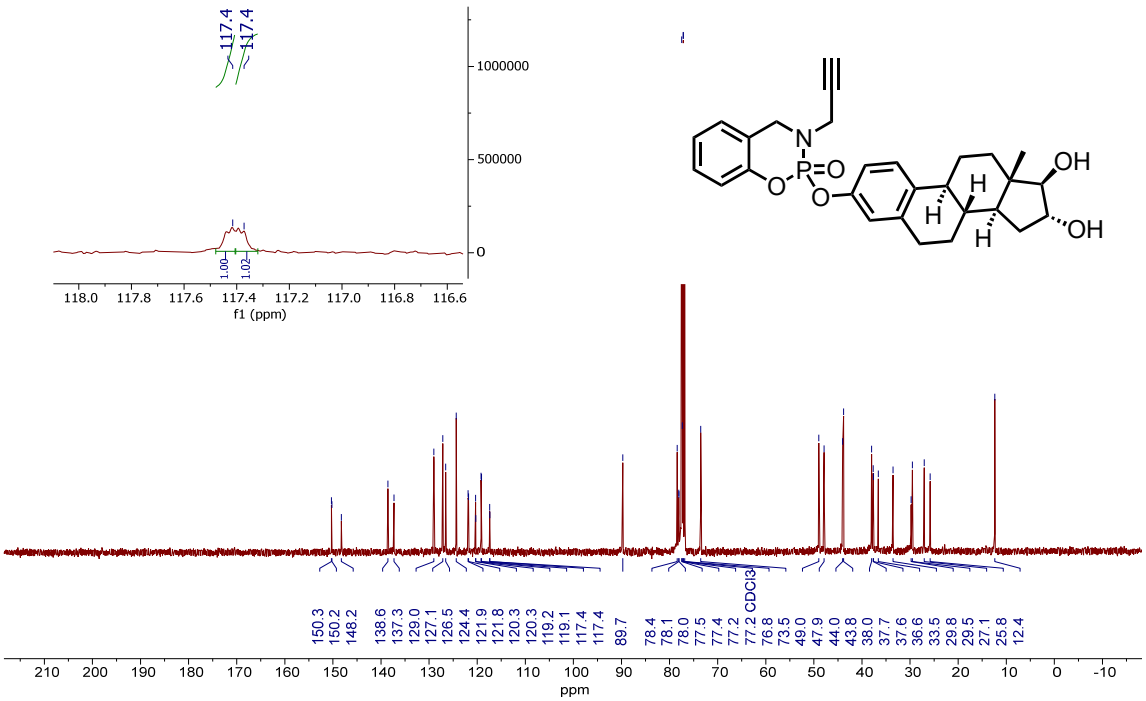
^{31}P NMR Spectrum for Compound **15o** (162 MHz, $CDCl_3$)



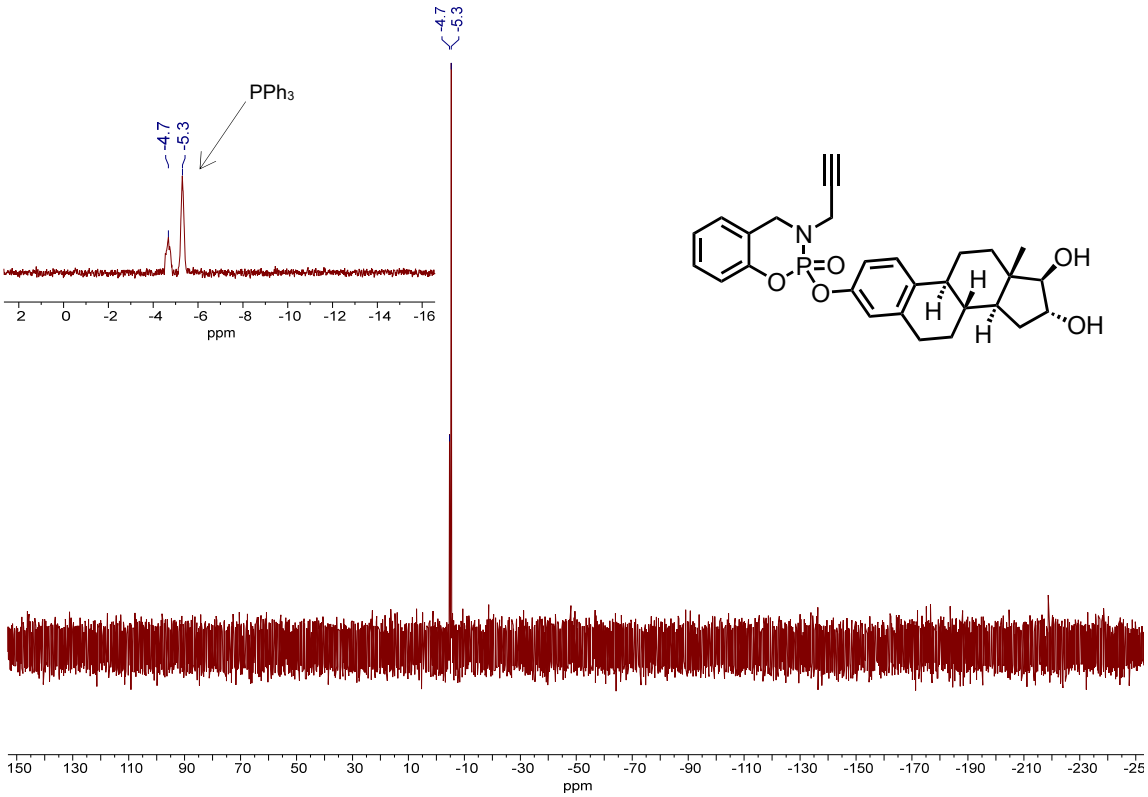
^{1}H NMR Spectrum for Compound **15p** (400 MHz, $CDCl_3$)



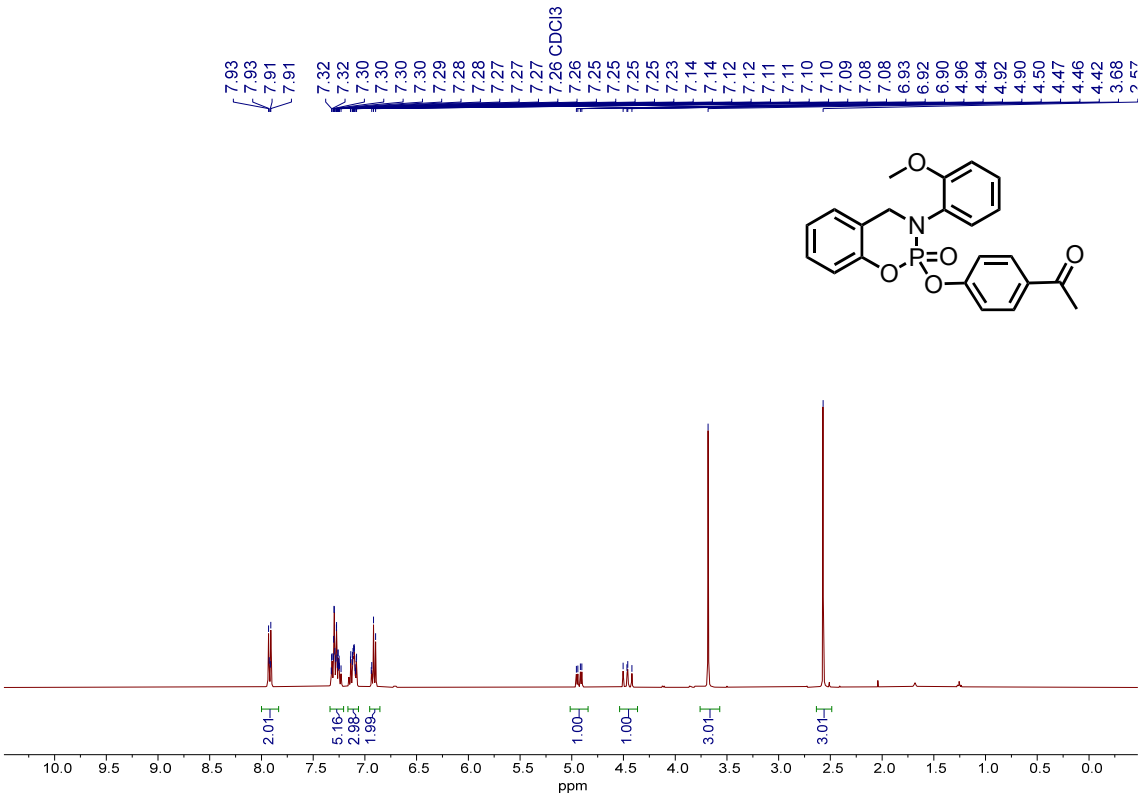
^{13}C NMR Spectrum for Compound **15p** (101 MHz, $CDCl_3$)



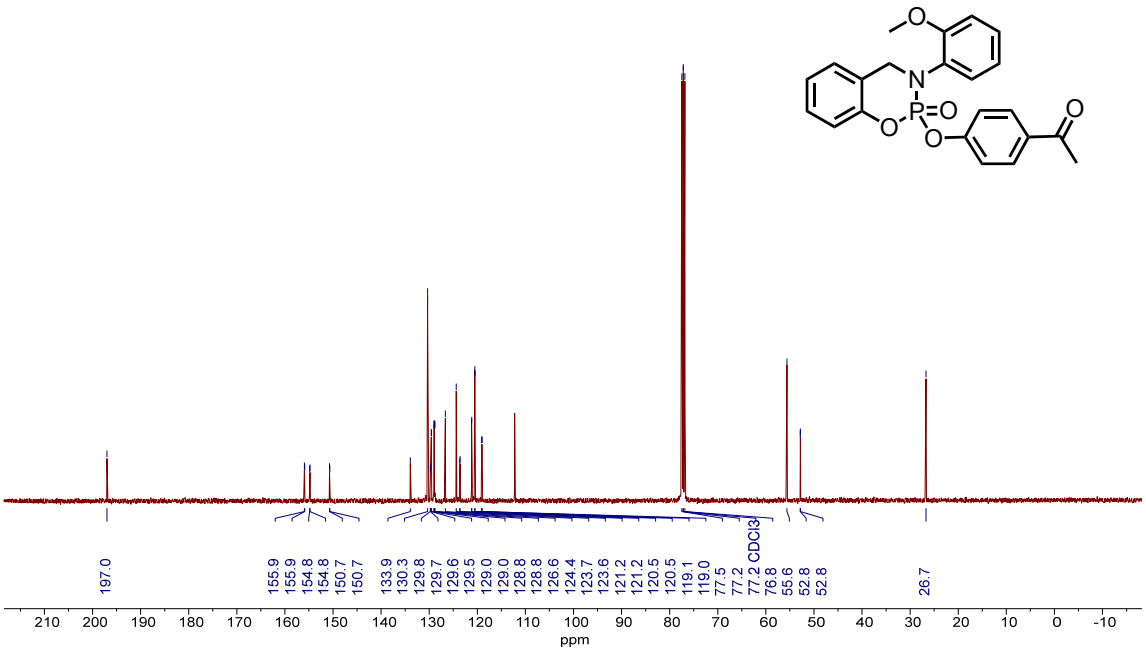
^{31}P NMR Spectrum for Compound **15p** (162 MHz, $CDCl_3$)



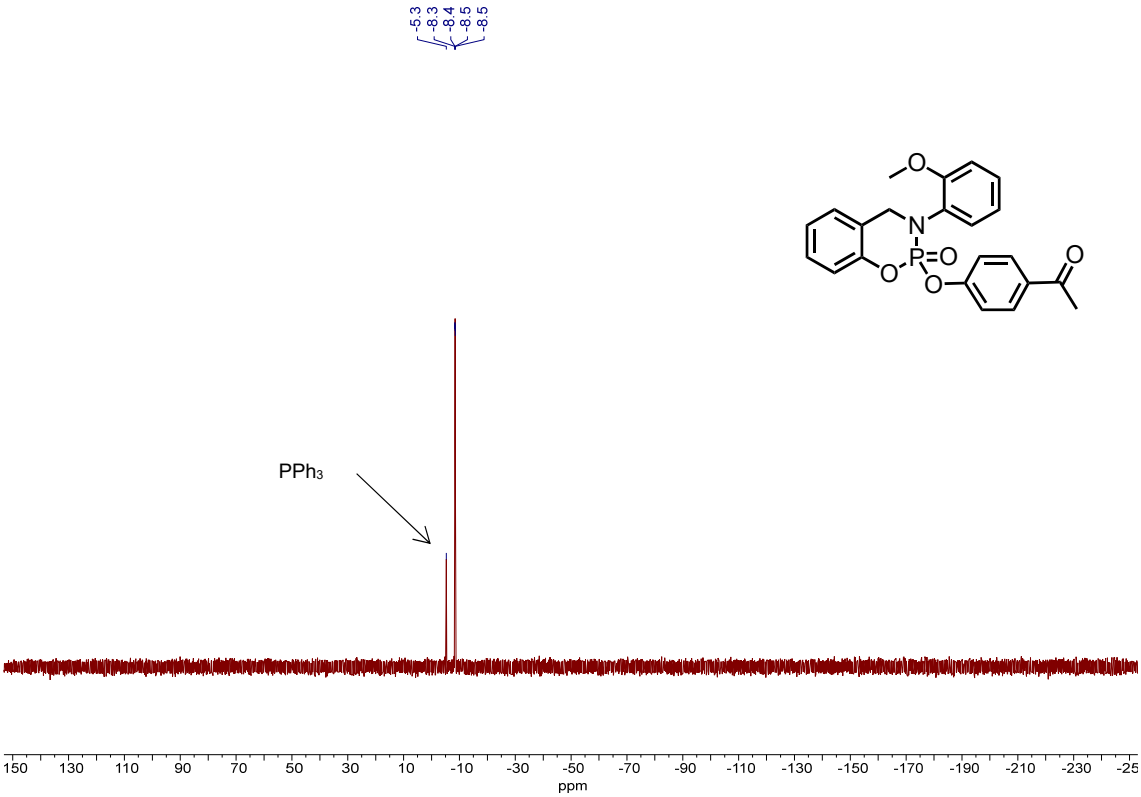
^{1}H NMR Spectrum for Compound **15q** (400 MHz, $CDCl_3$)



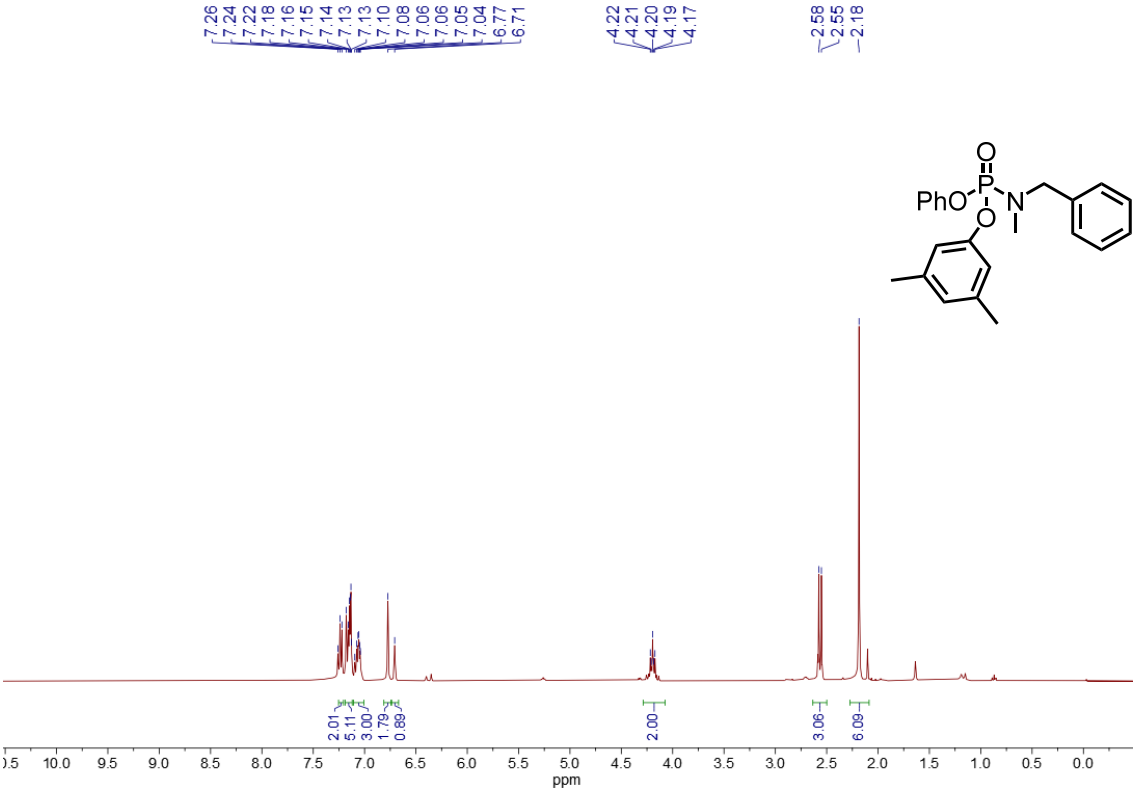
^{13}C NMR Spectrum for Compound **15q** (101 MHz, $CDCl_3$)



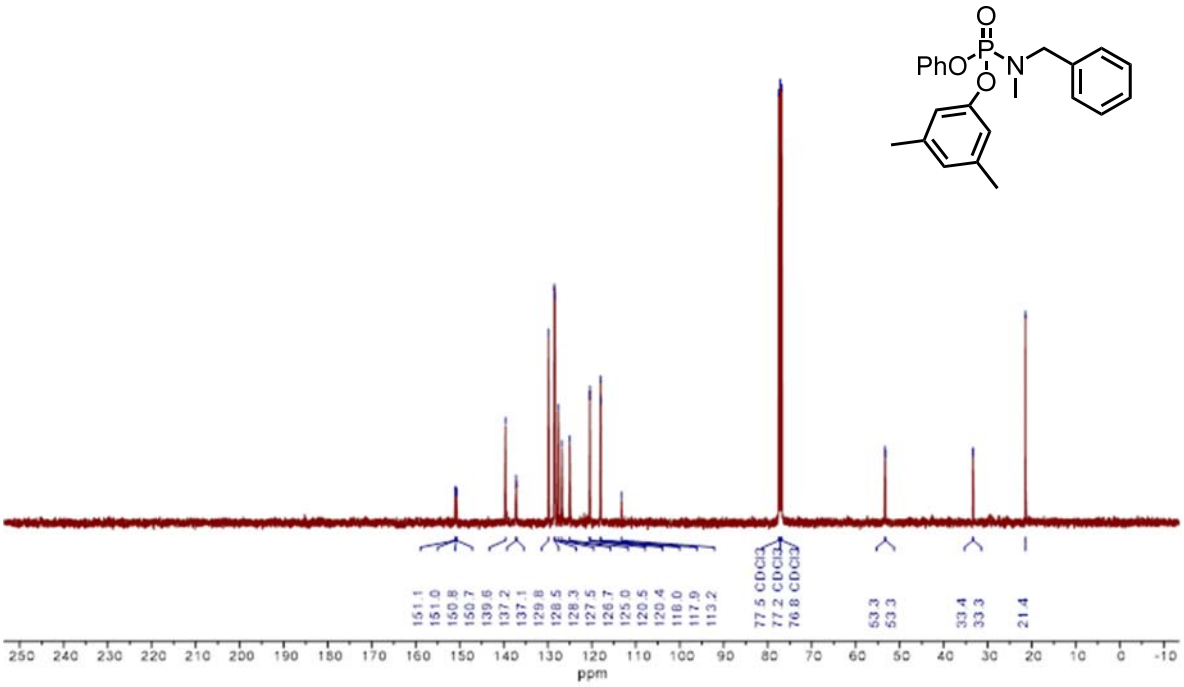
^{31}P NMR Spectrum for Compound **15q** (162 MHz, $CDCl_3$)



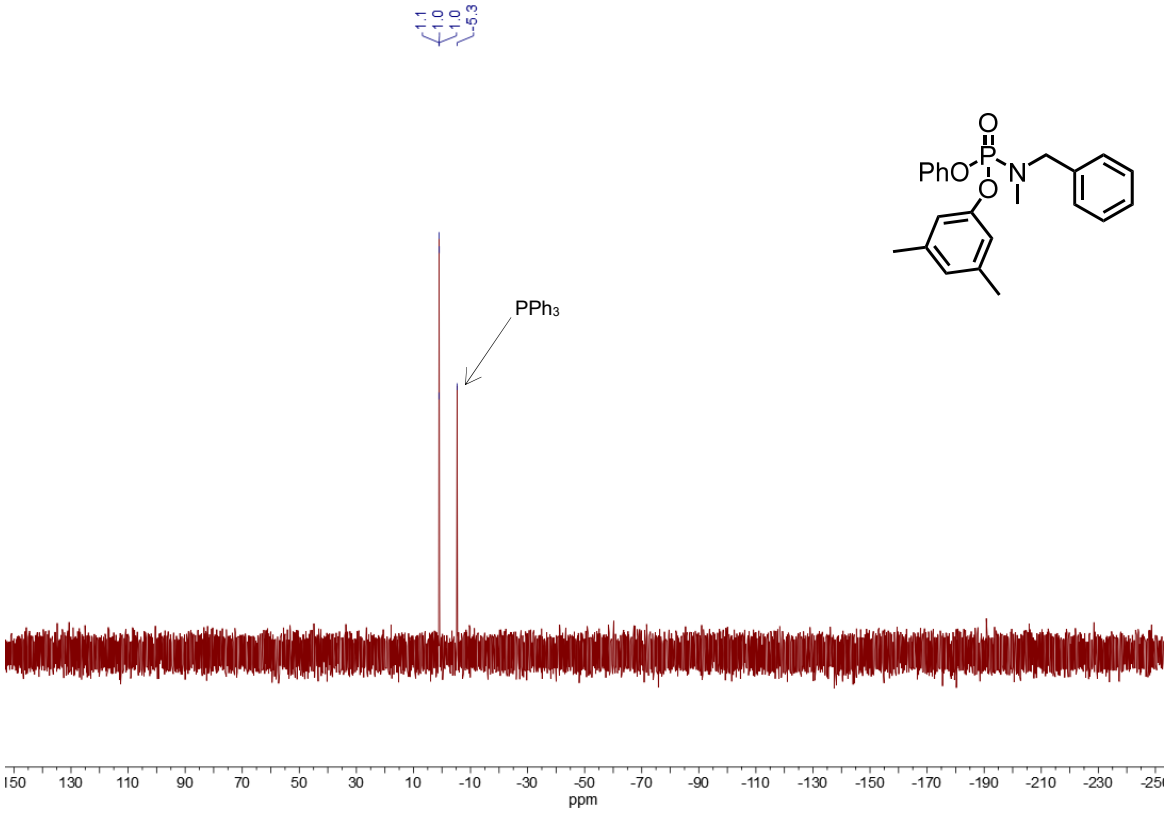
^{1}H NMR Spectrum for Compound **16a** (400 MHz, $CDCl_3$)



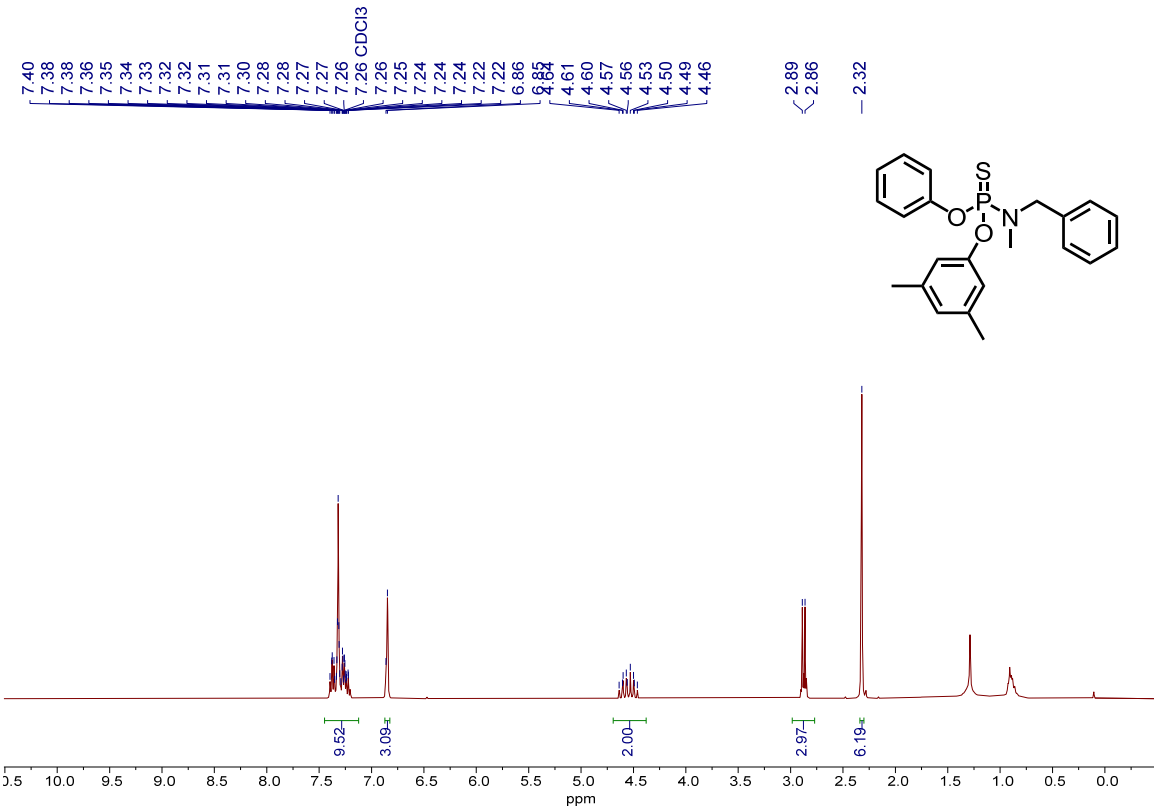
^{13}C NMR Spectrum for Compound **16a** (101 MHz, $CDCl_3$)



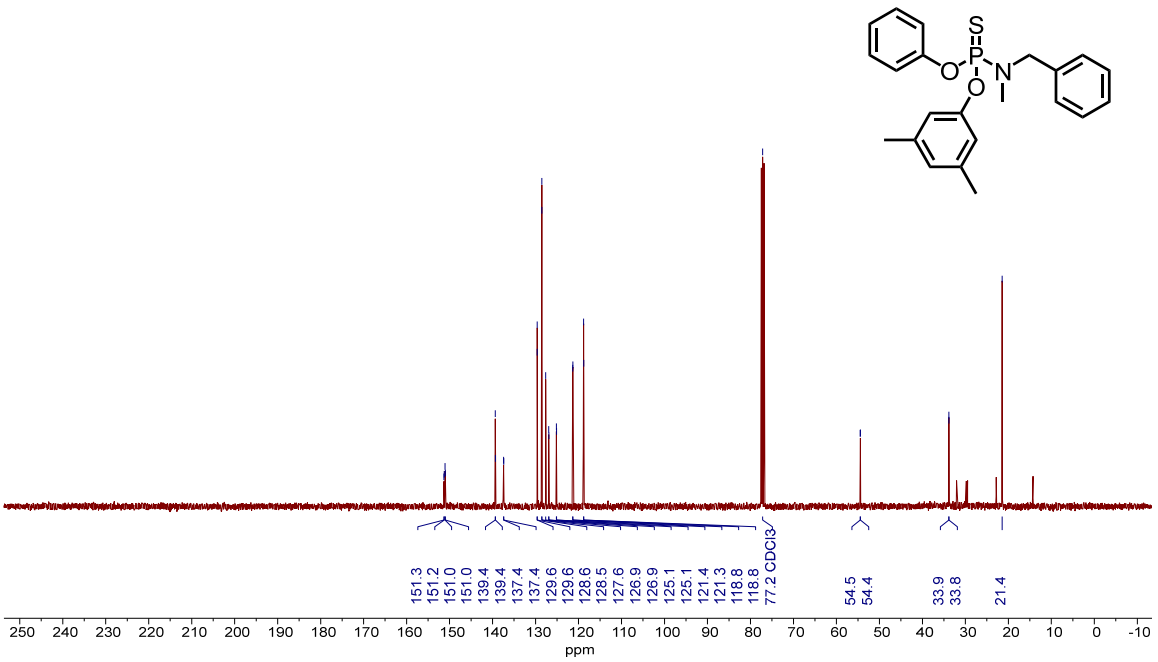
^{31}P NMR Spectrum for Compound **16a** (162 MHz, $CDCl_3$)



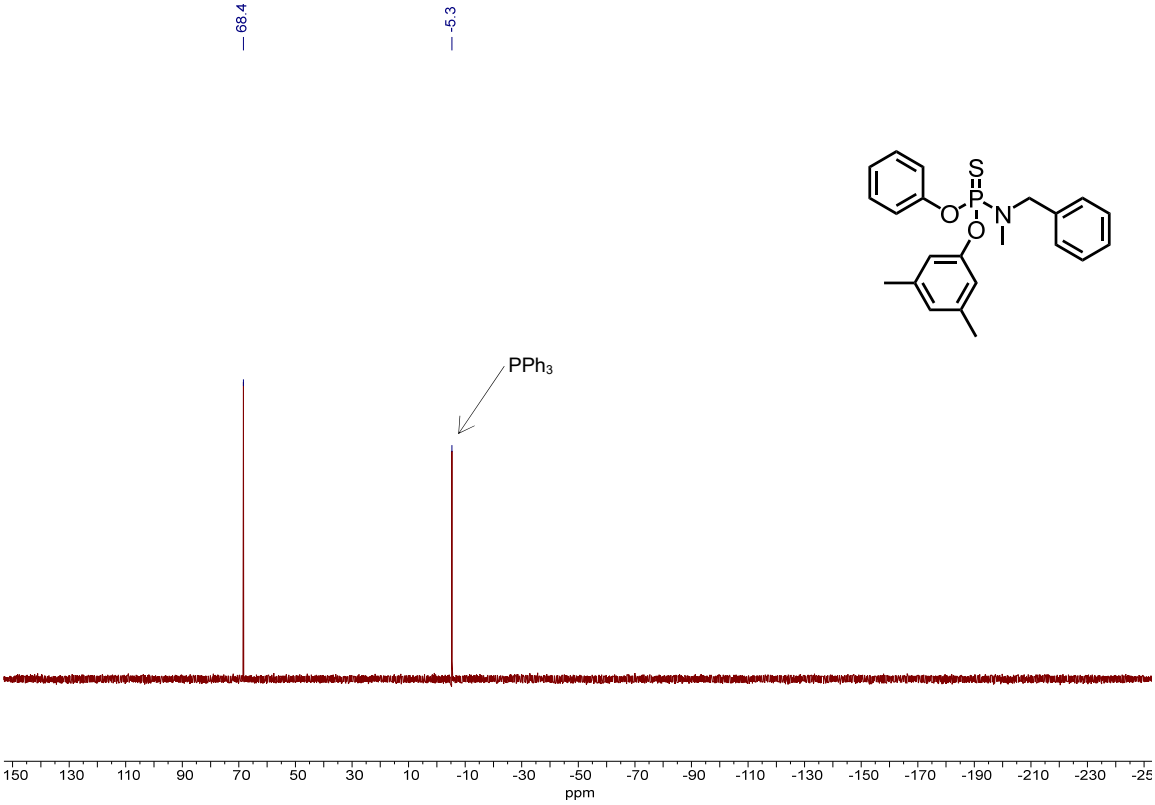
^{1}H NMR Spectrum for Compound **16b** (400 MHz, $CDCl_3$)



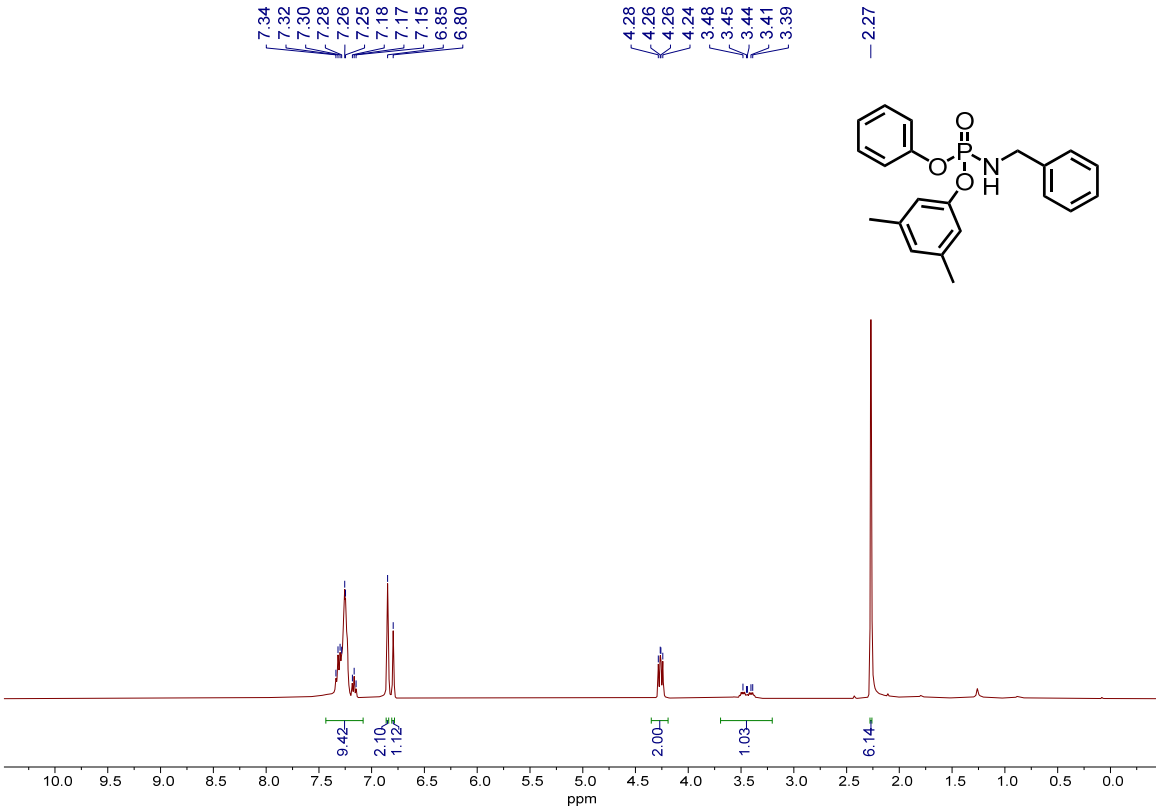
^{13}C NMR Spectrum for Compound **16b** (101 MHz, $CDCl_3$)



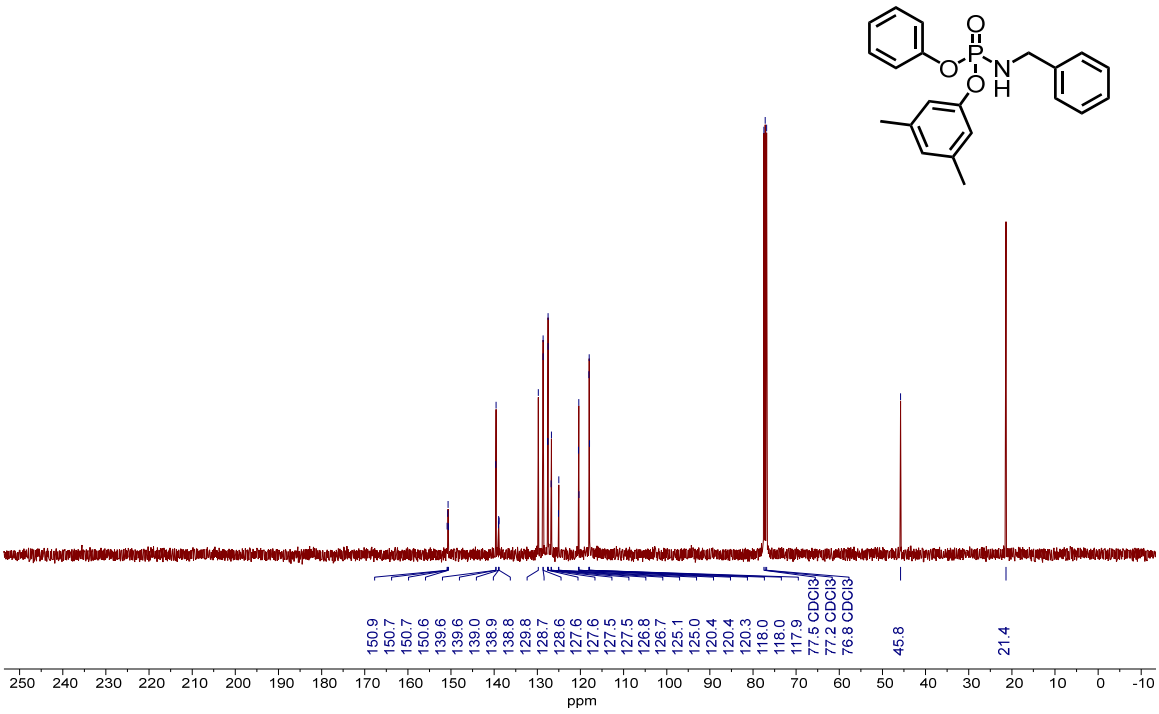
^{31}P NMR Spectrum for Compound **16b** (162 MHz, $CDCl_3$)



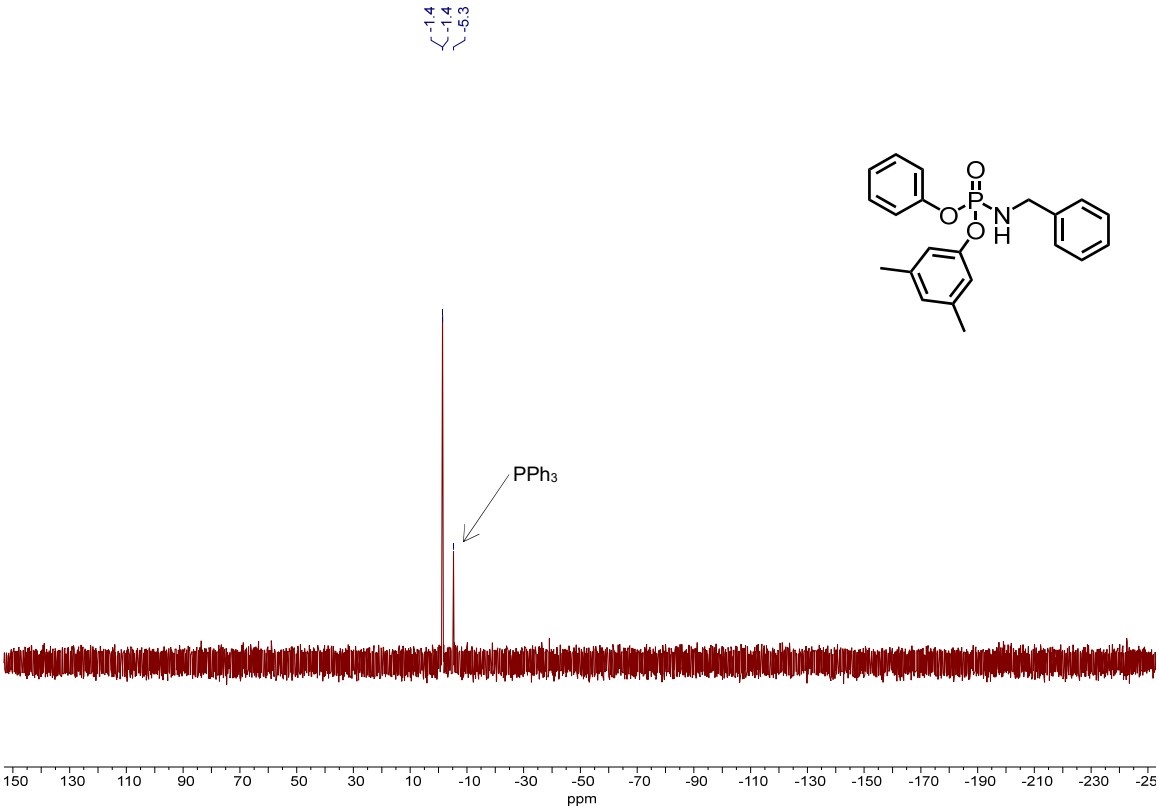
^{1}H NMR Spectrum for Compound **16c** (400 MHz, $CDCl_3$)



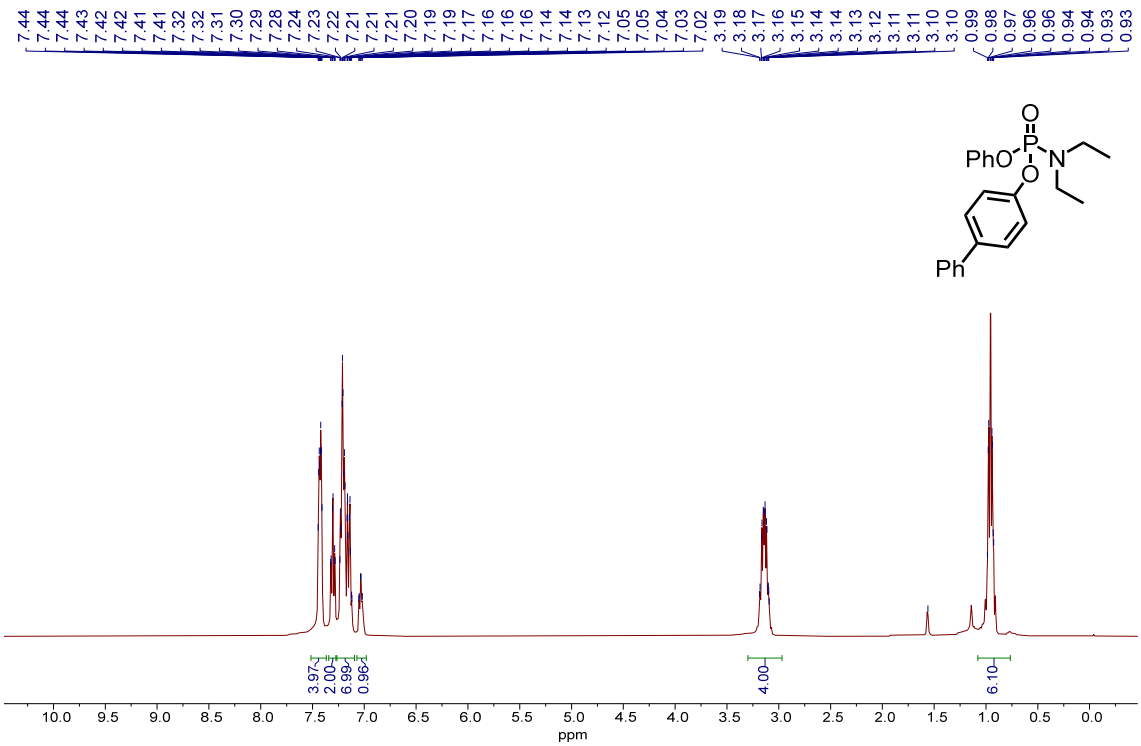
^{13}C NMR Spectrum for Compound **16c** (101 MHz, $CDCl_3$)



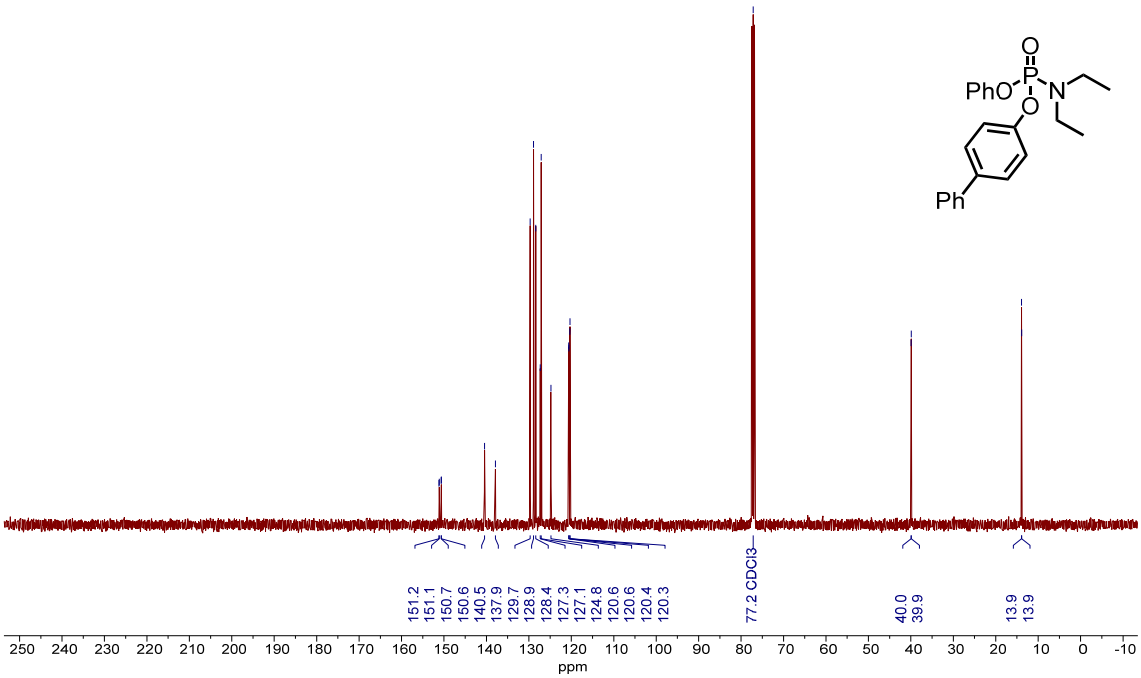
^{31}P NMR Spectrum for Compound **16c** (162 MHz, $CDCl_3$)



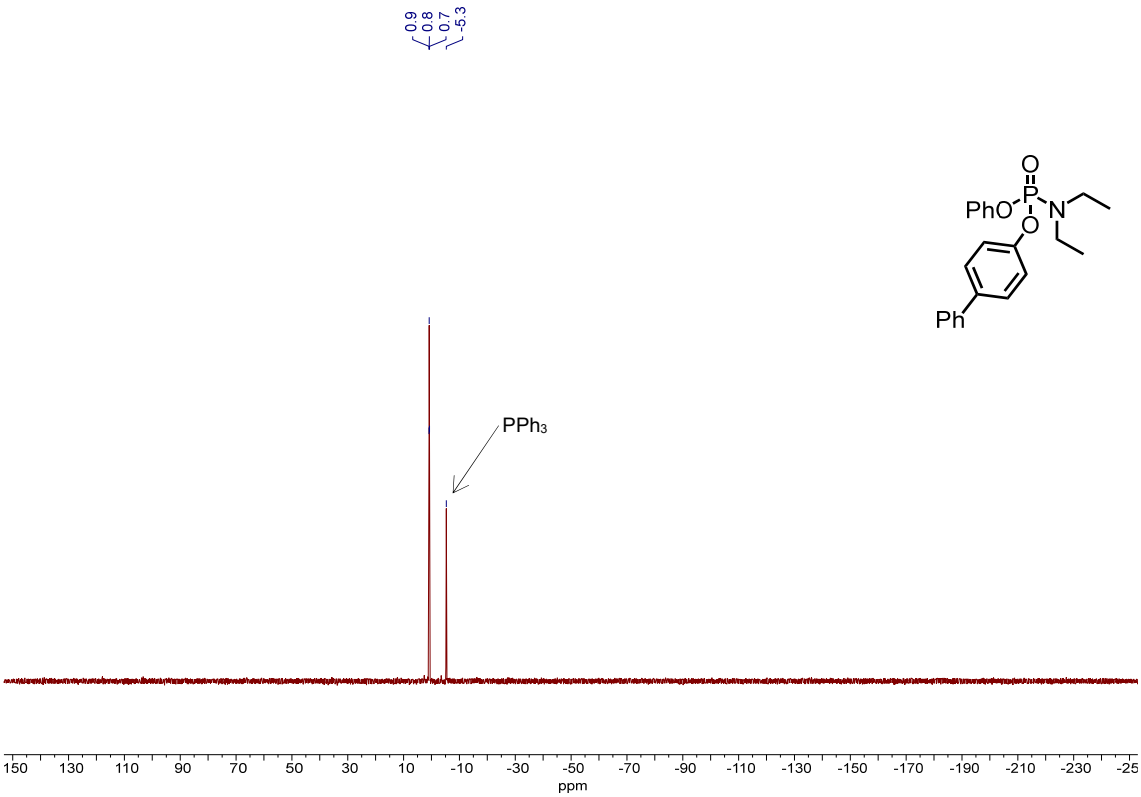
^{1}H NMR Spectrum for Compound **16d** (400 MHz, $CDCl_3$)



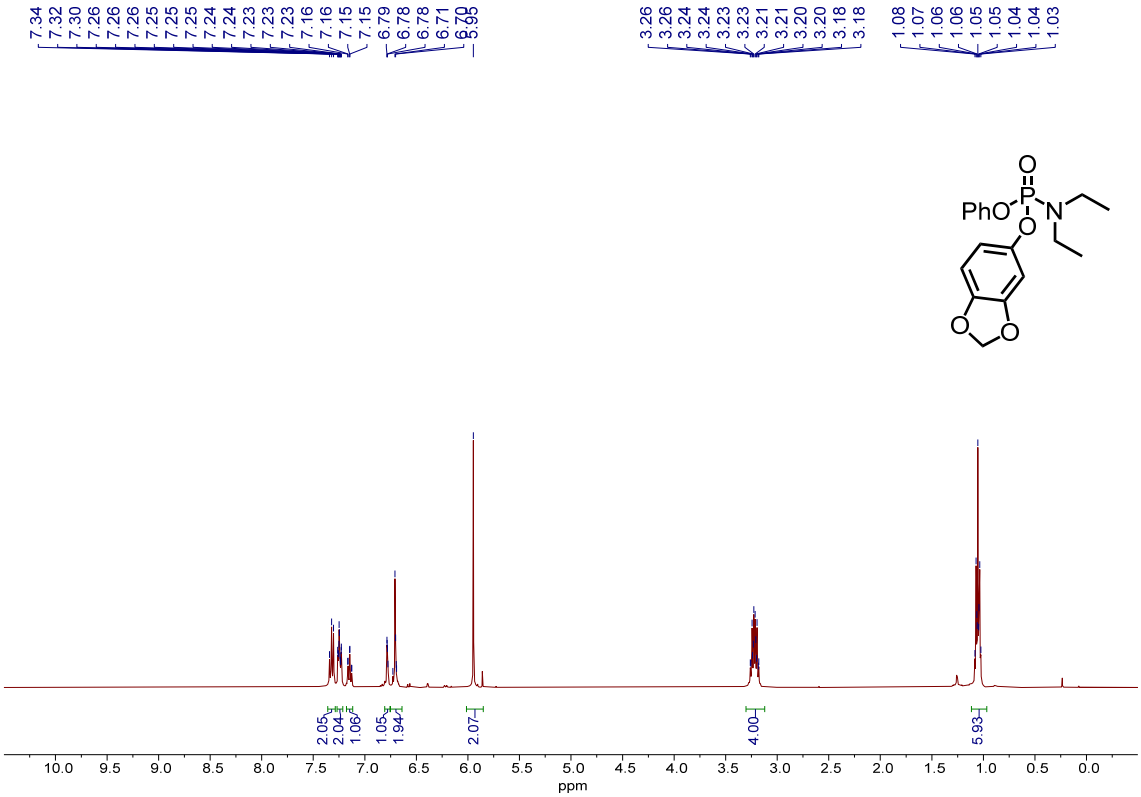
^{13}C NMR Spectrum for Compound **16d** (101 MHz, $CDCl_3$)



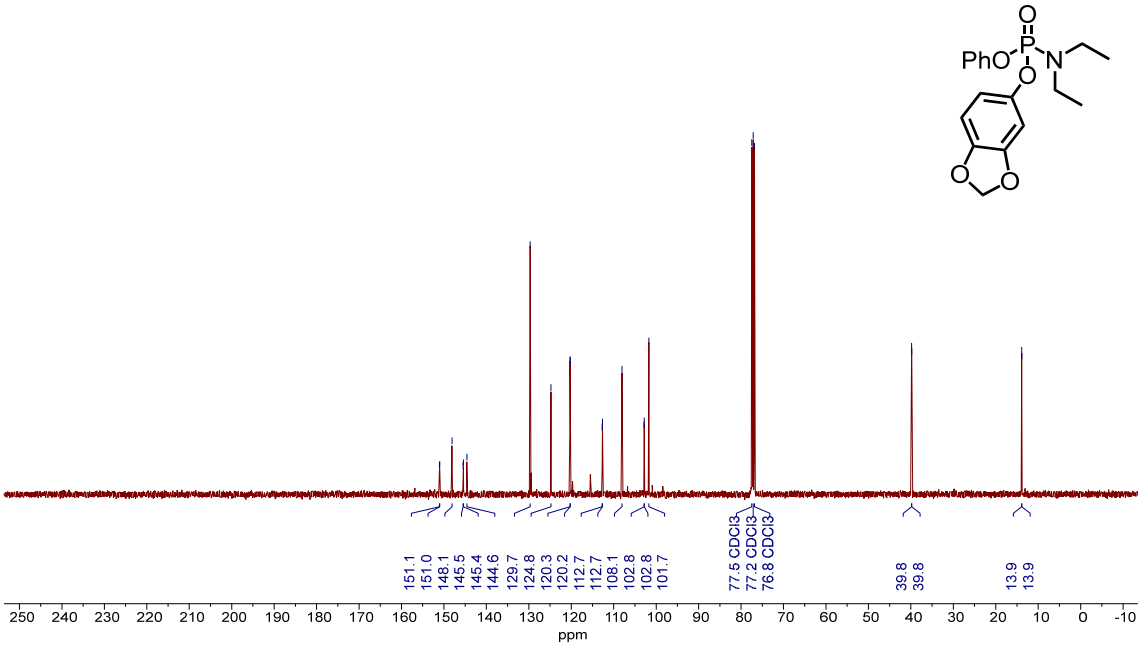
^{31}P NMR Spectrum for Compound **16d** (162 MHz, $CDCl_3$)



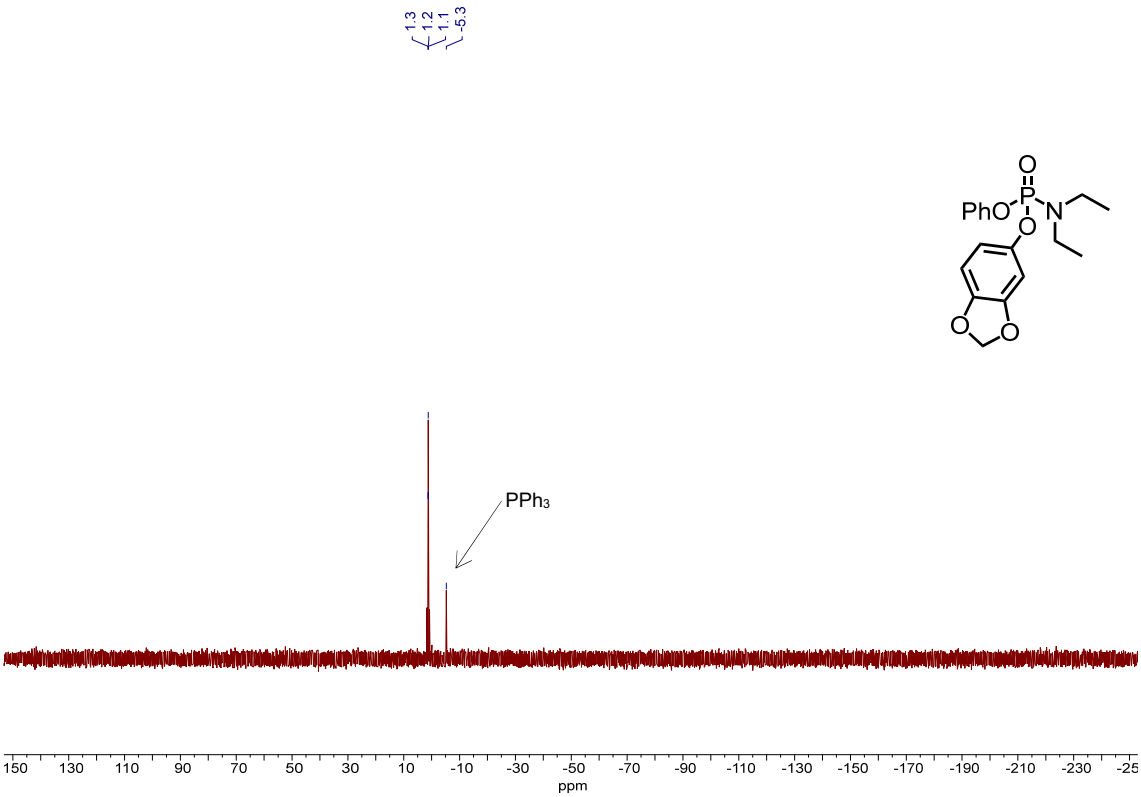
^{1}H NMR Spectrum for Compound **16e** (400 MHz, $CDCl_3$)



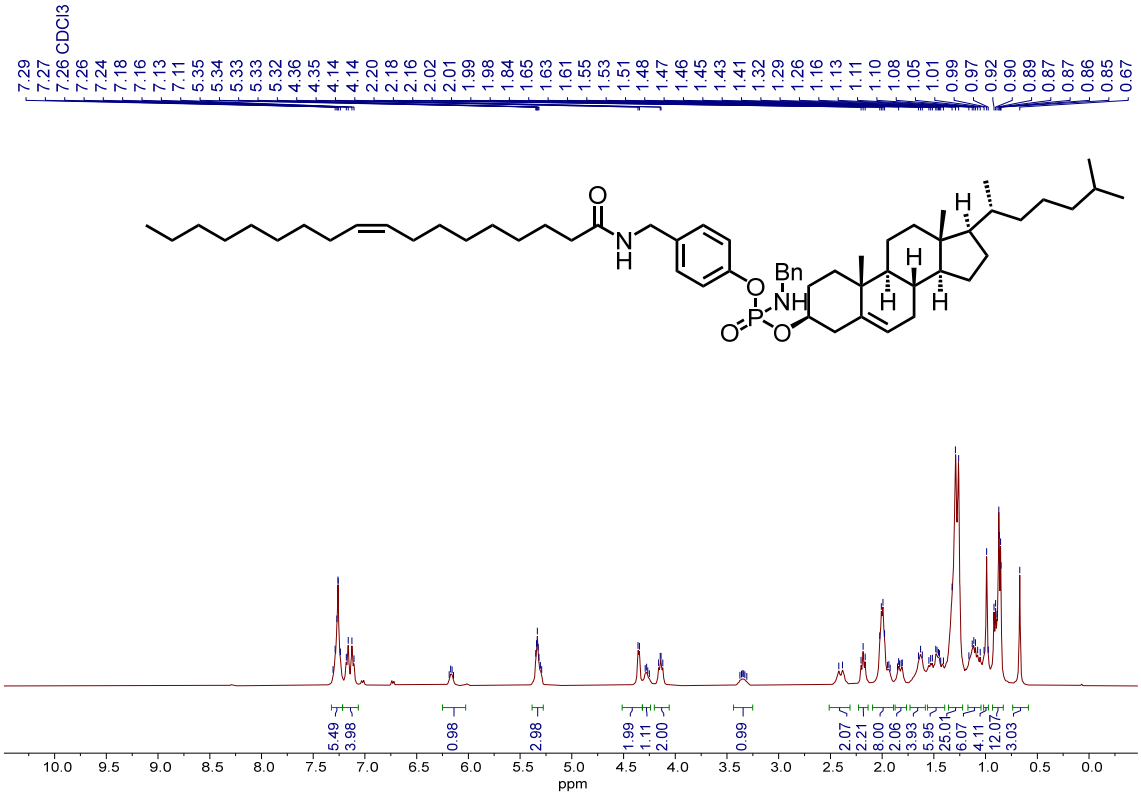
^{13}C NMR Spectrum for Compound **16e** (101 MHz, $CDCl_3$)



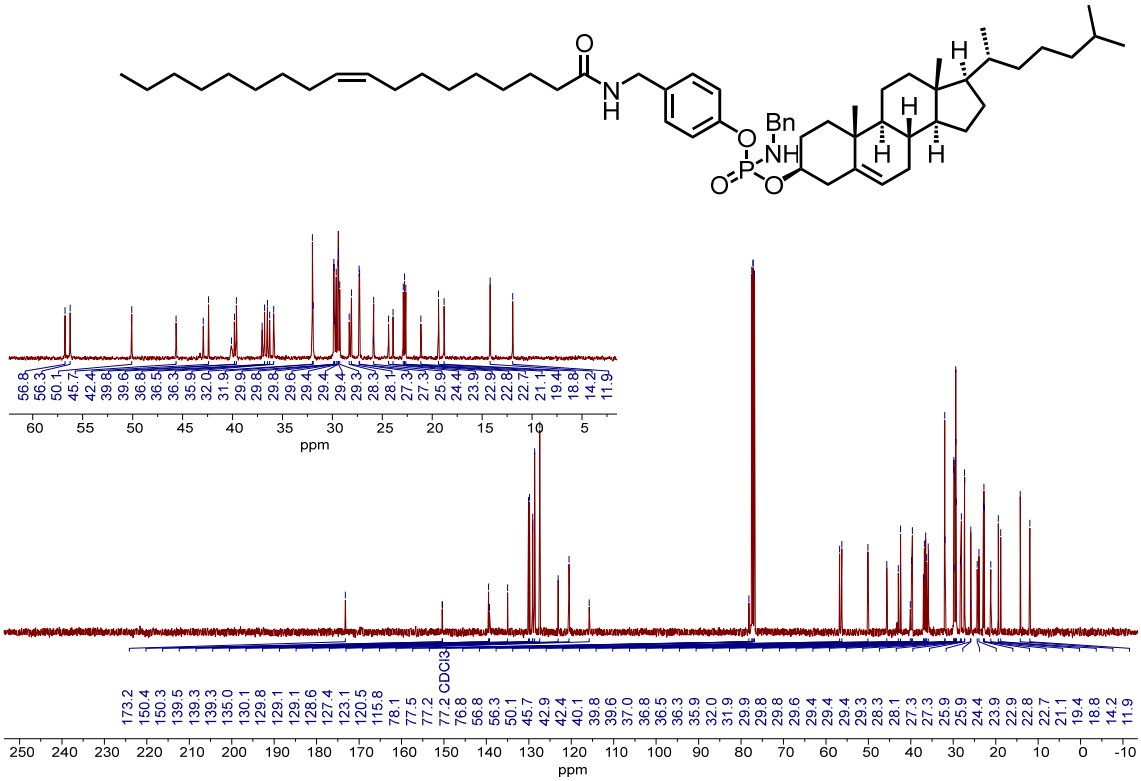
^{31}P NMR Spectrum for Compound **16e** (162 MHz, $CDCl_3$)



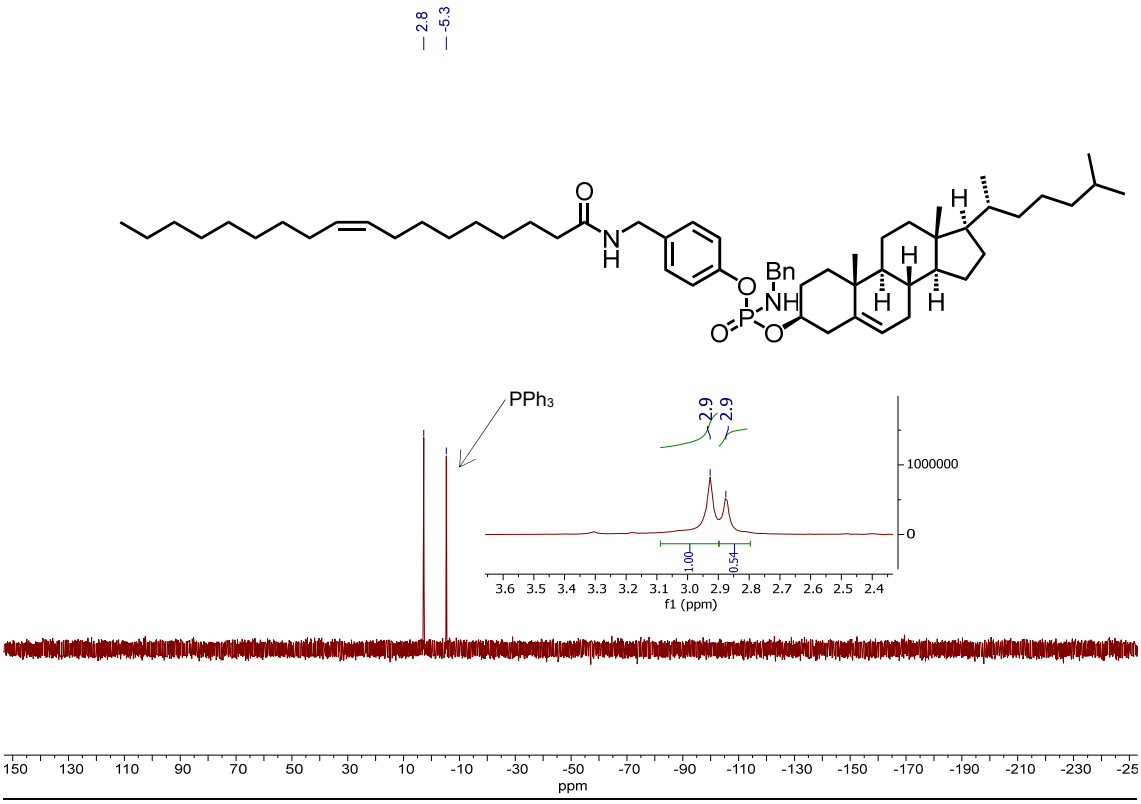
^{1}H NMR Spectrum for Compound **16f** (400 MHz, $CDCl_3$)



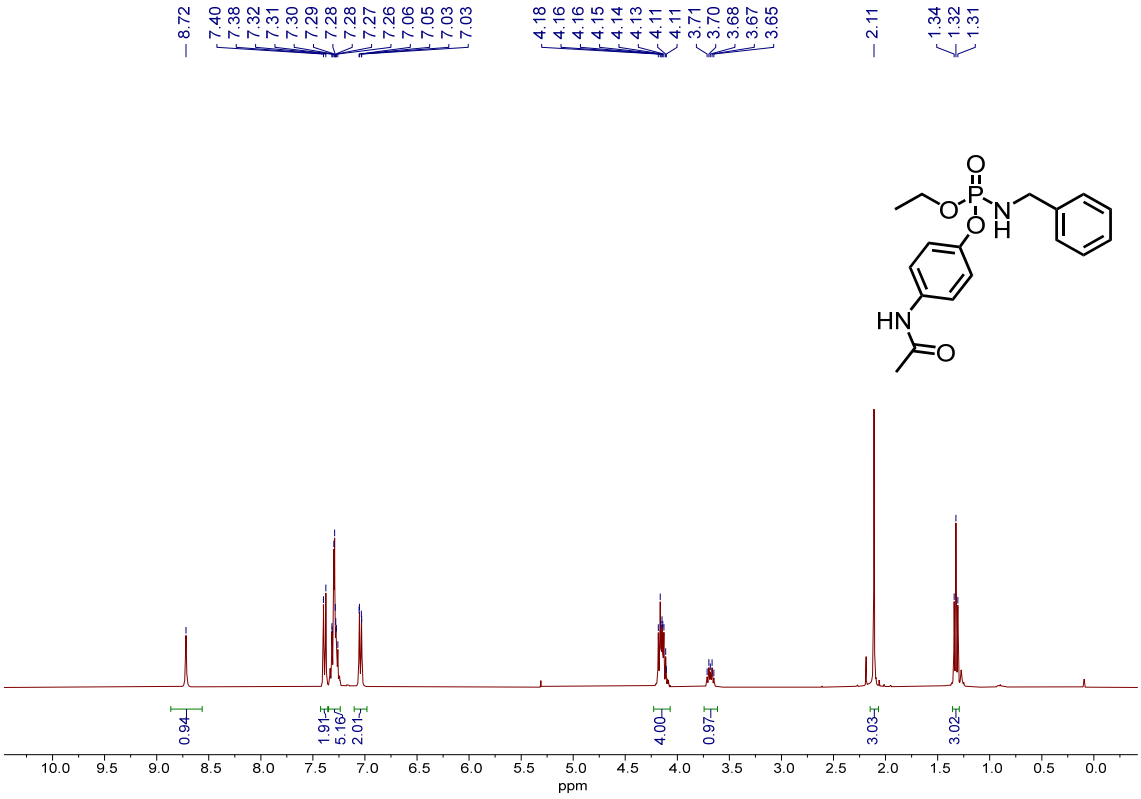
^{13}C NMR Spectrum for Compound **16f** (101 MHz, $CDCl_3$)



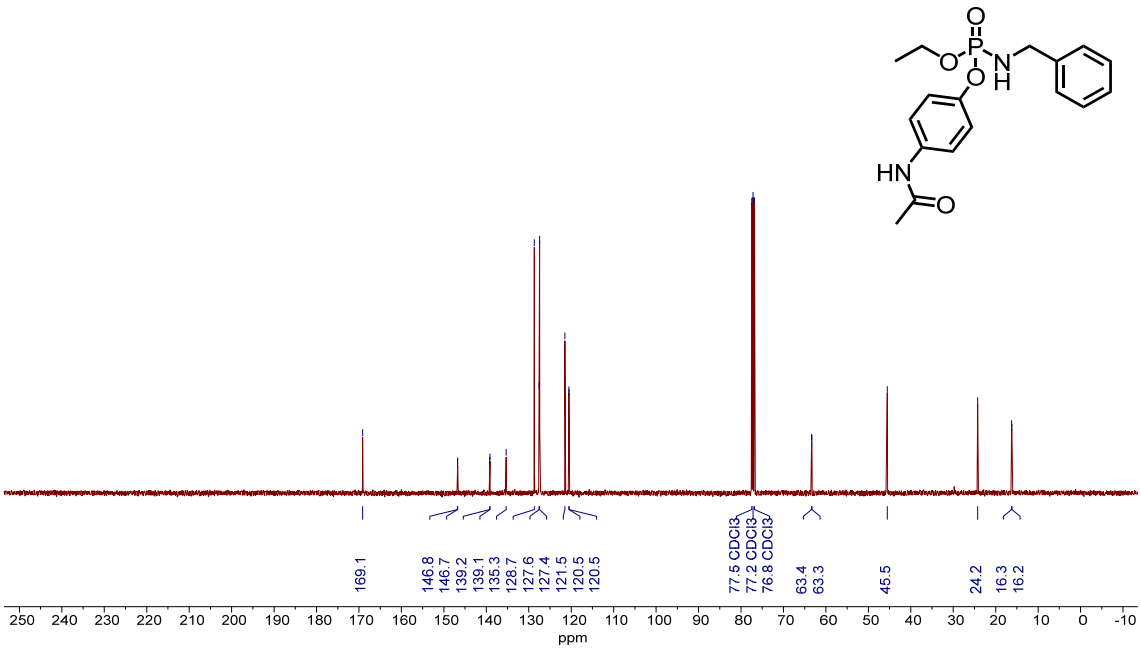
^{31}P NMR Spectrum for Compound **16f** (162 MHz, $CDCl_3$)



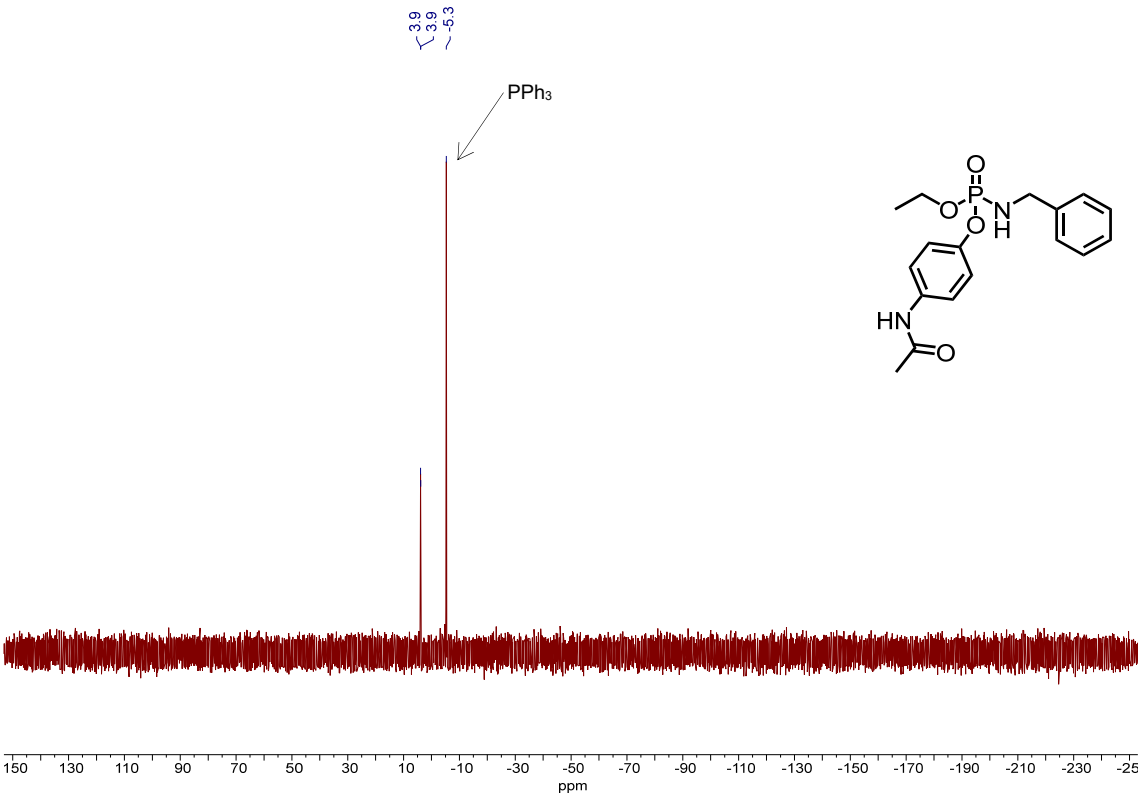
^{1}H NMR Spectrum for Compound **16g** (400 MHz, $CDCl_3$)



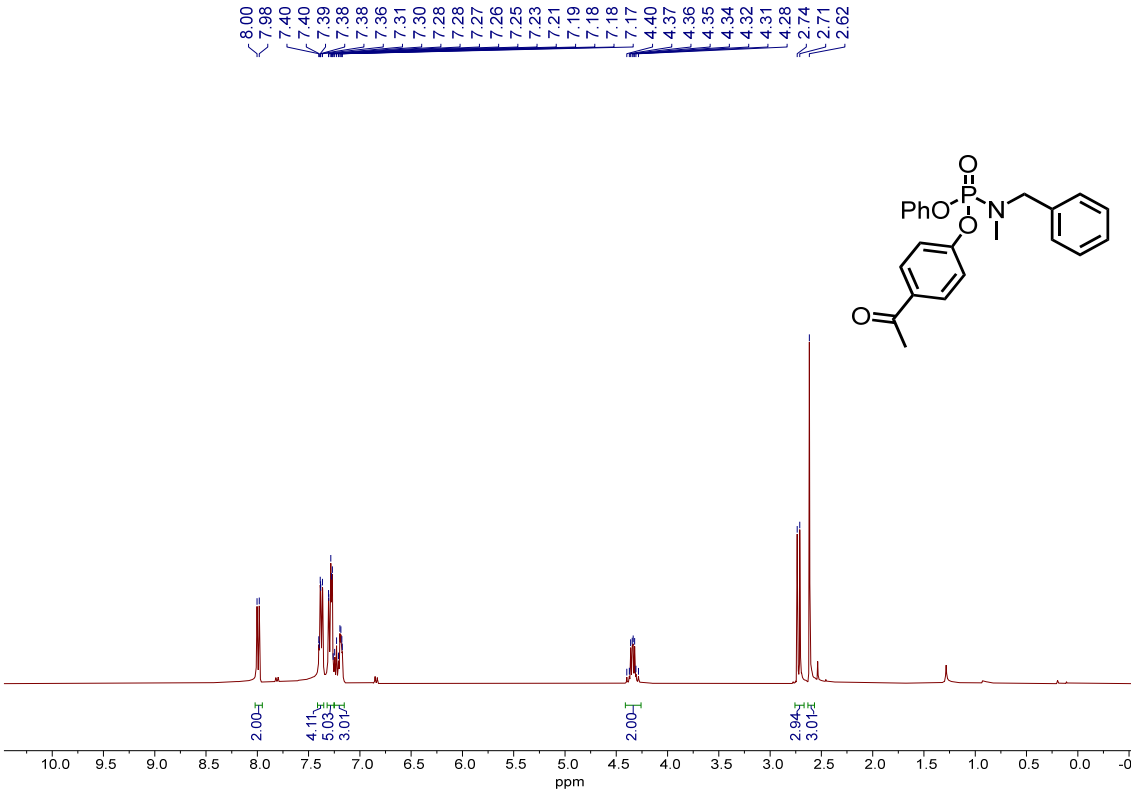
^{13}C NMR Spectrum for Compound **16g** (101 MHz, $CDCl_3$)



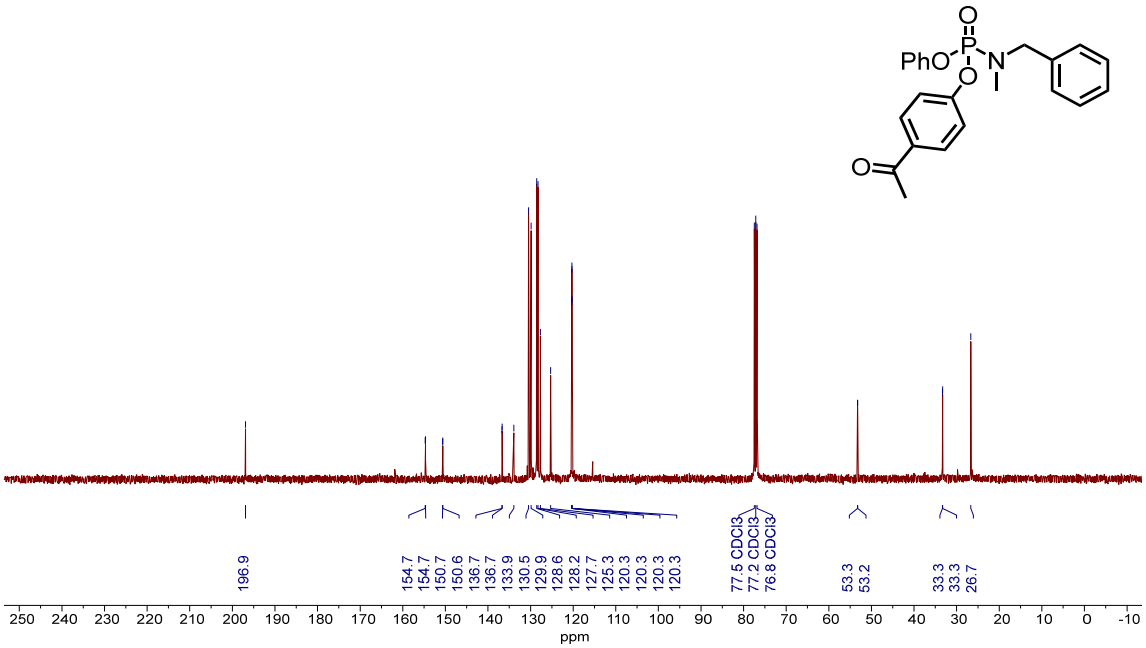
^{31}P NMR Spectrum for Compound **16g** (162 MHz, $CDCl_3$)



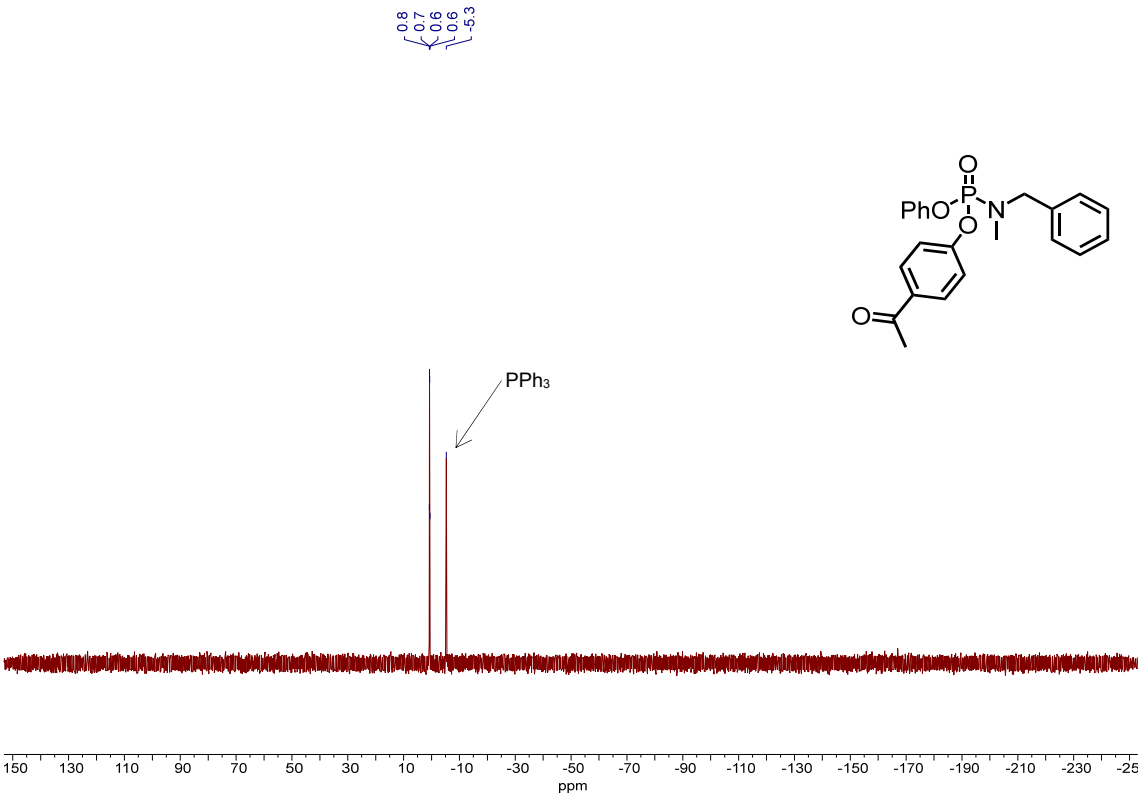
^{1}H NMR Spectrum for Compound **16h** (400 MHz, $CDCl_3$)



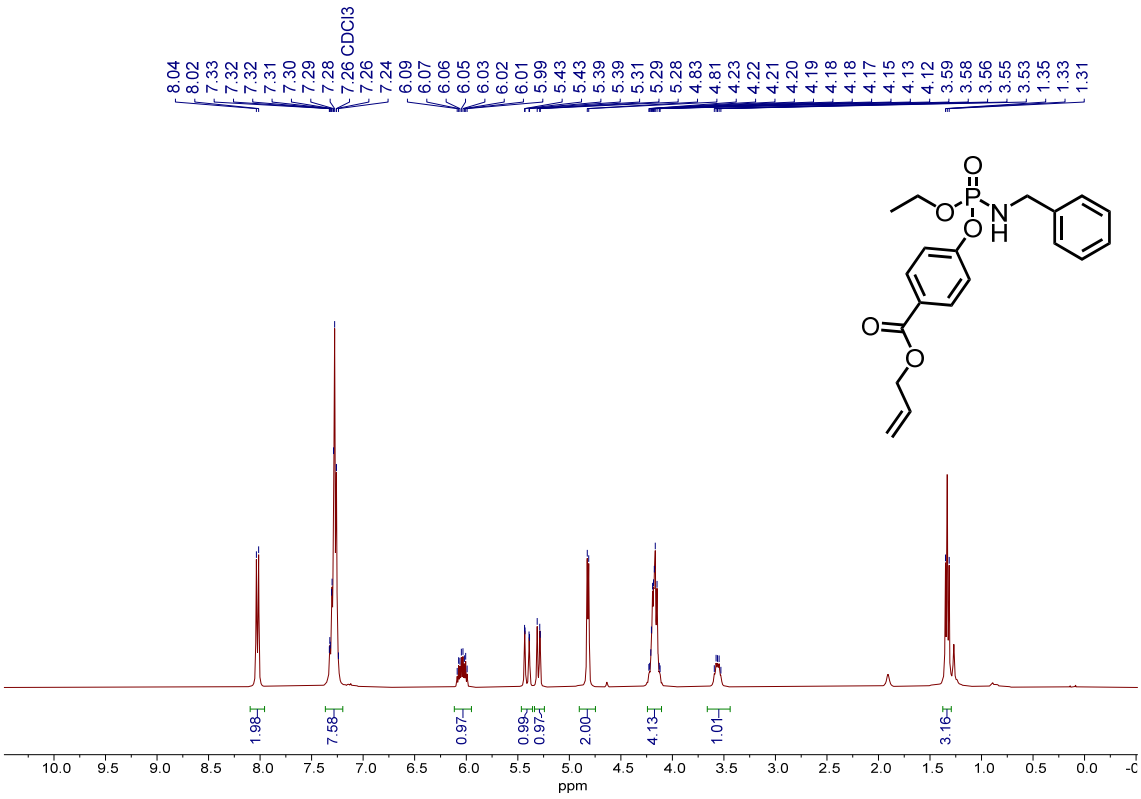
^{13}C NMR Spectrum for Compound **16h** (101 MHz, $CDCl_3$)



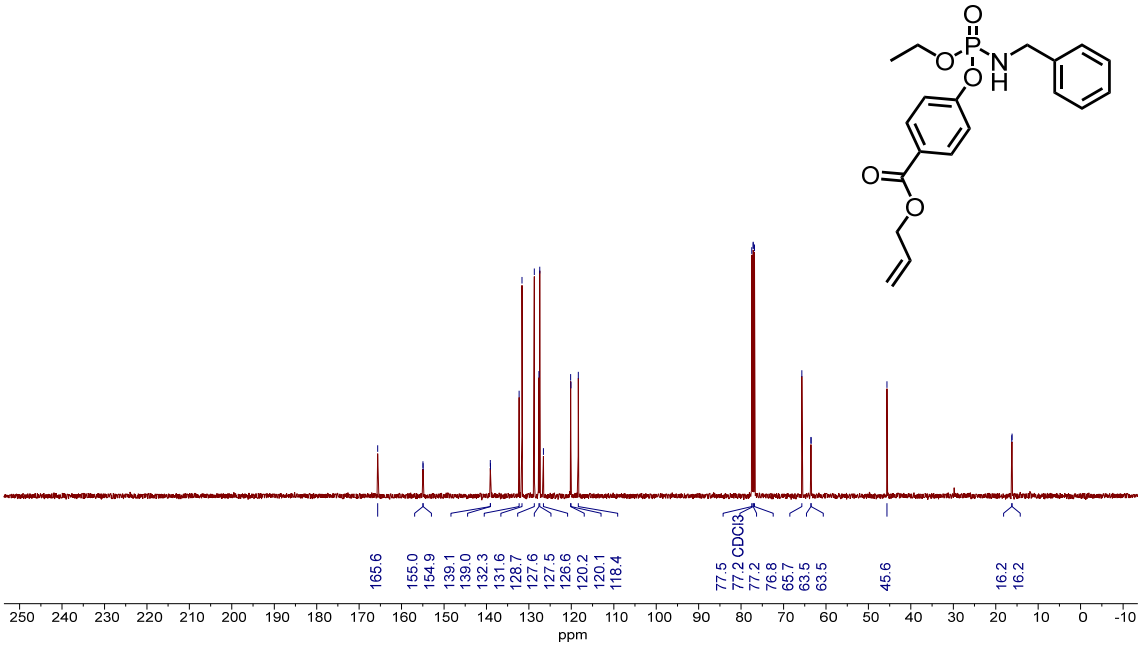
^{31}P NMR Spectrum for Compound **16h** (162 MHz, $CDCl_3$)



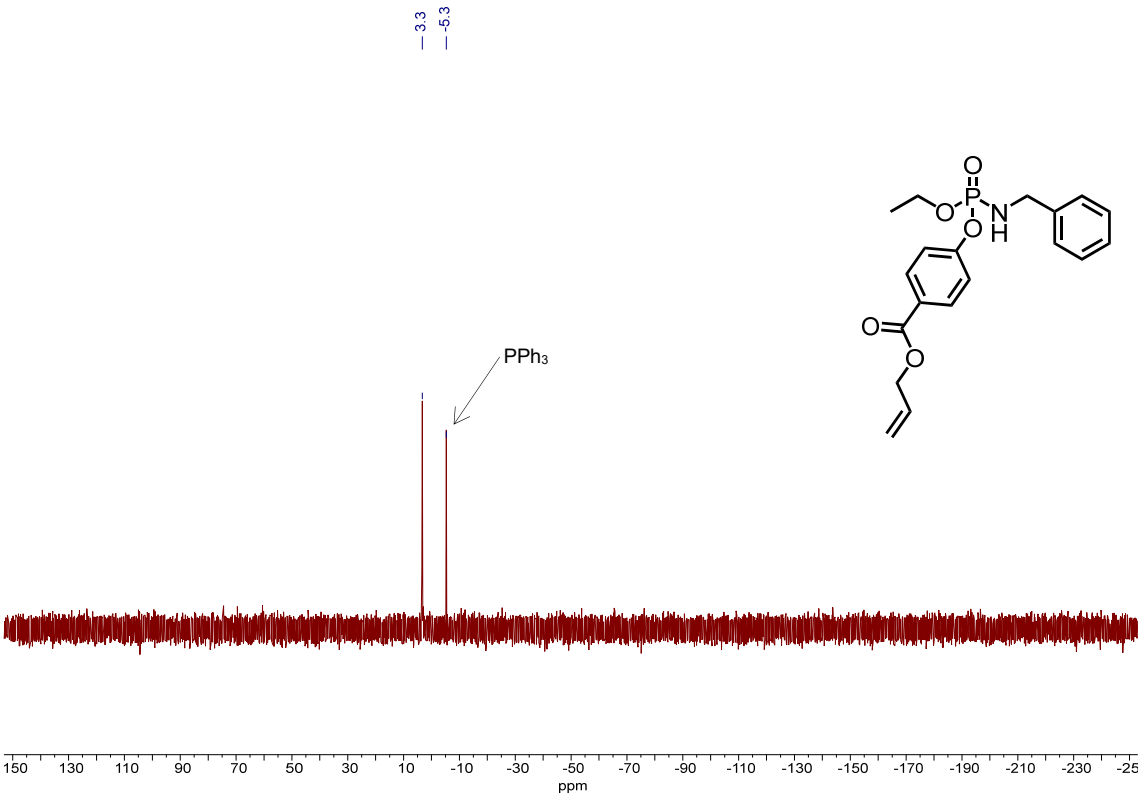
^{1}H NMR Spectrum for Compound **16i** (400 MHz, $CDCl_3$)



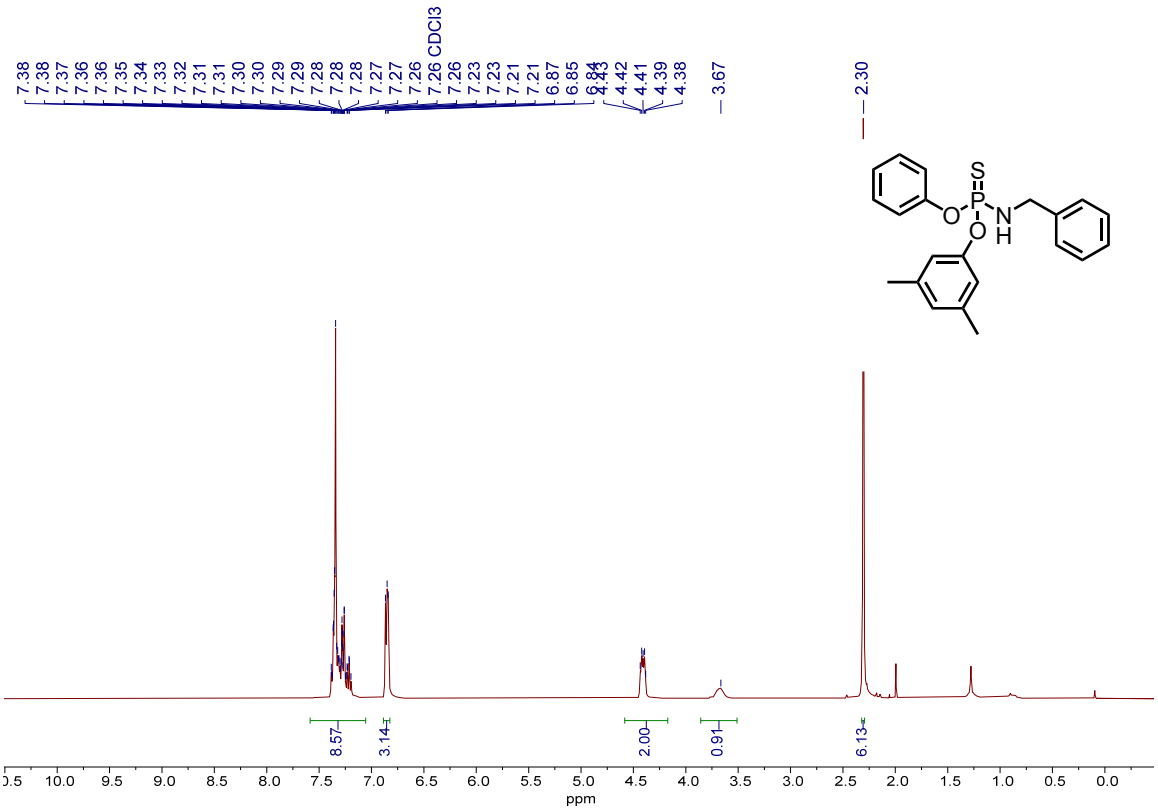
^{13}C NMR Spectrum for Compound **16i** (101 MHz, $CDCl_3$)



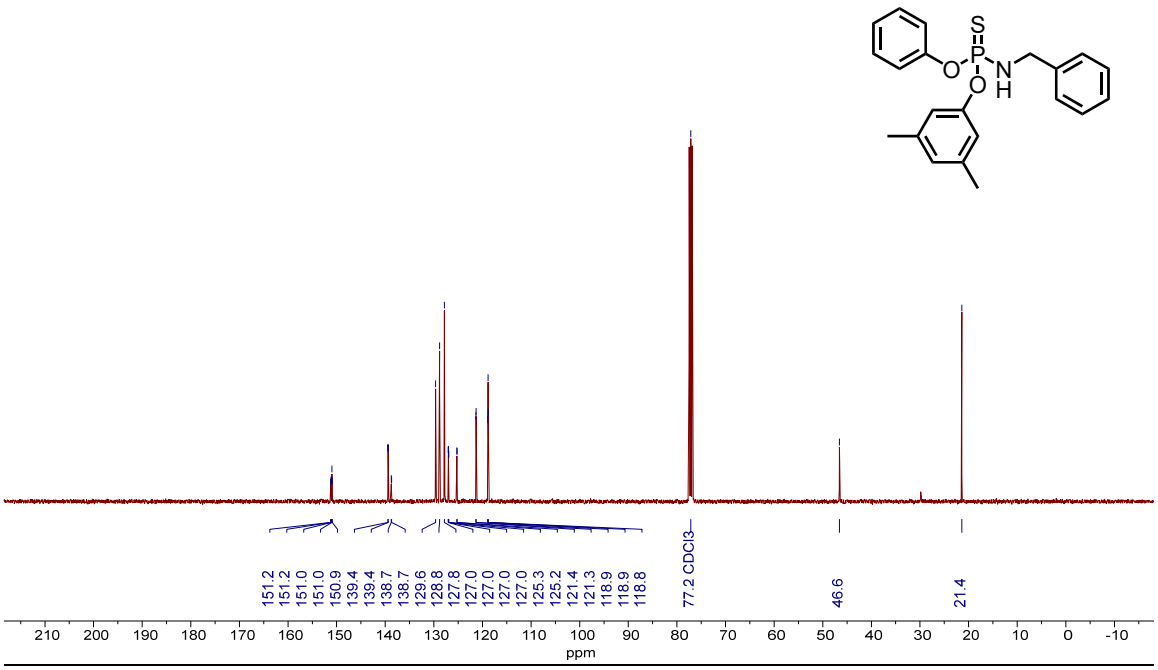
^{31}P NMR Spectrum for Compound **16i** (162 MHz, $CDCl_3$)



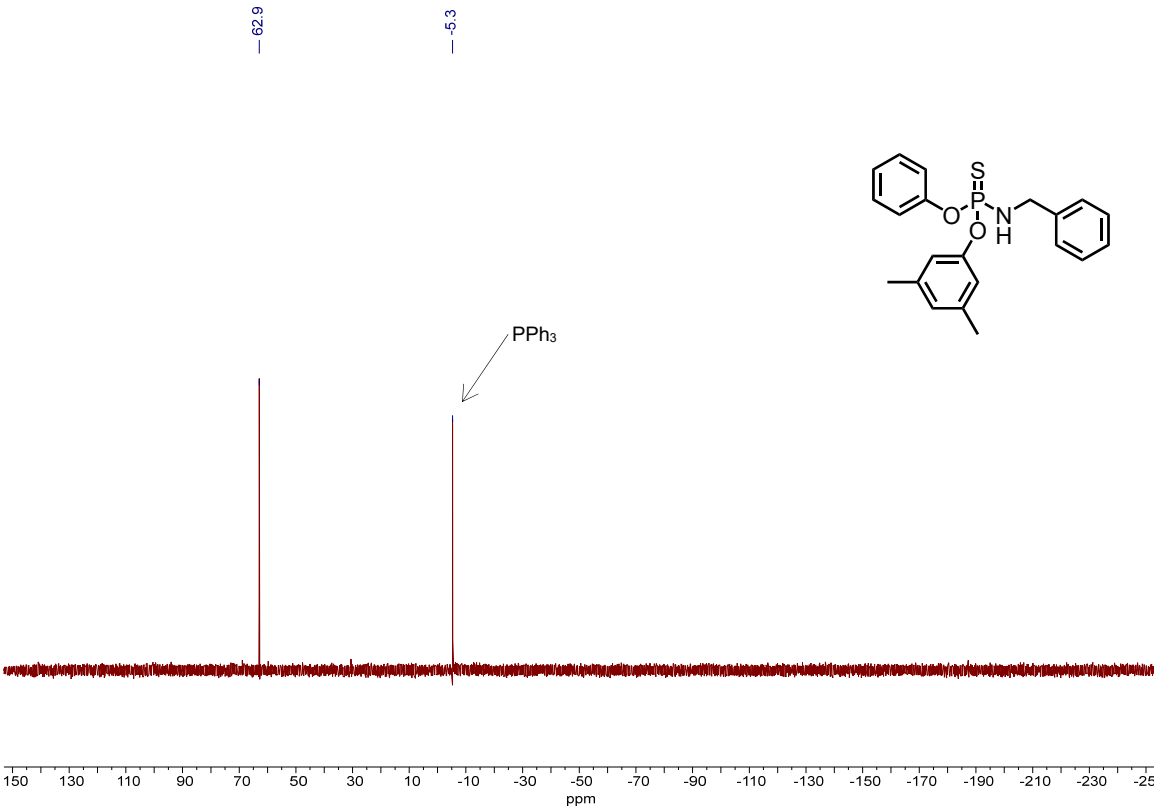
^{1}H NMR Spectrum for Compound **16j** (400 MHz, $CDCl_3$)



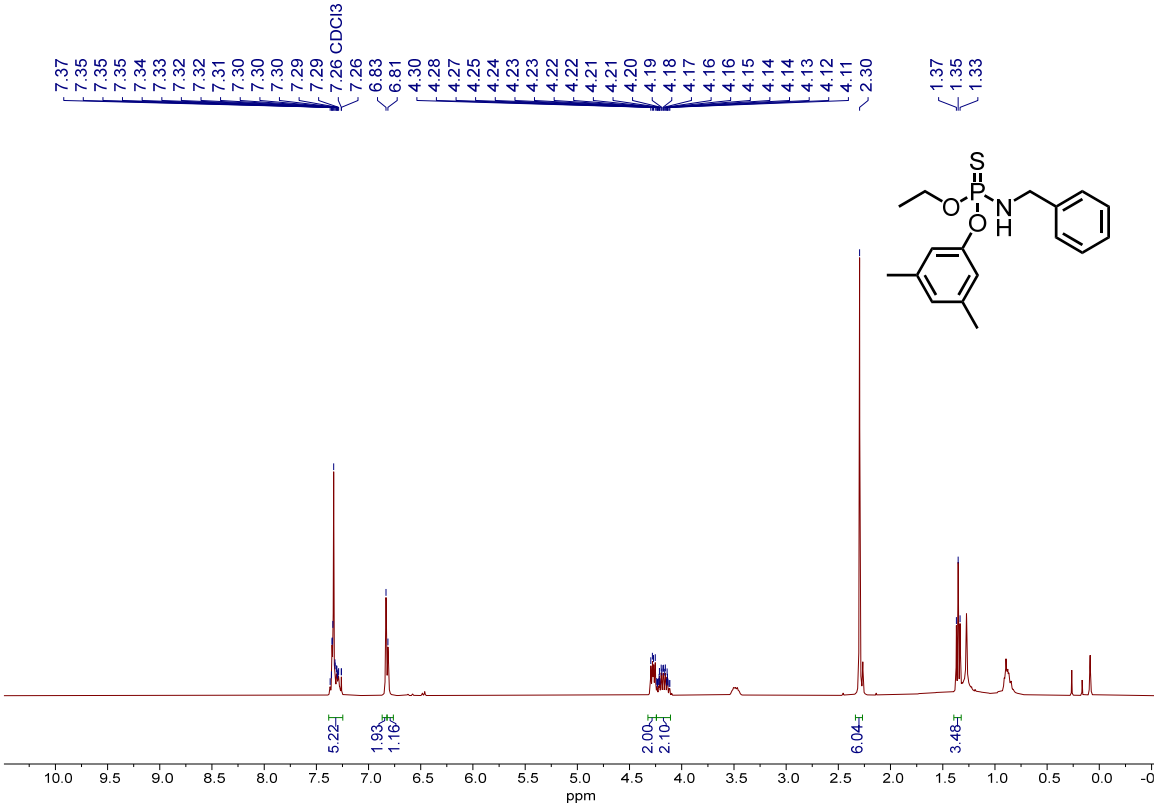
^{13}C NMR Spectrum for Compound **16j** (101 MHz, $CDCl_3$)



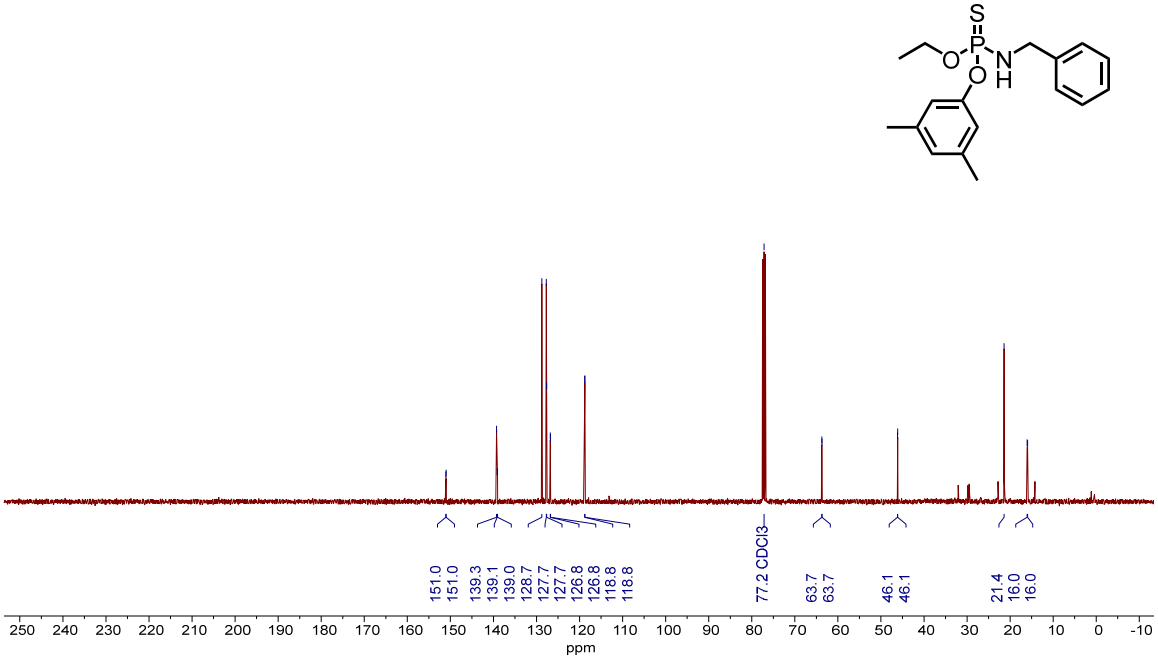
^{31}P NMR Spectrum for Compound **16j** (162 MHz, $CDCl_3$)



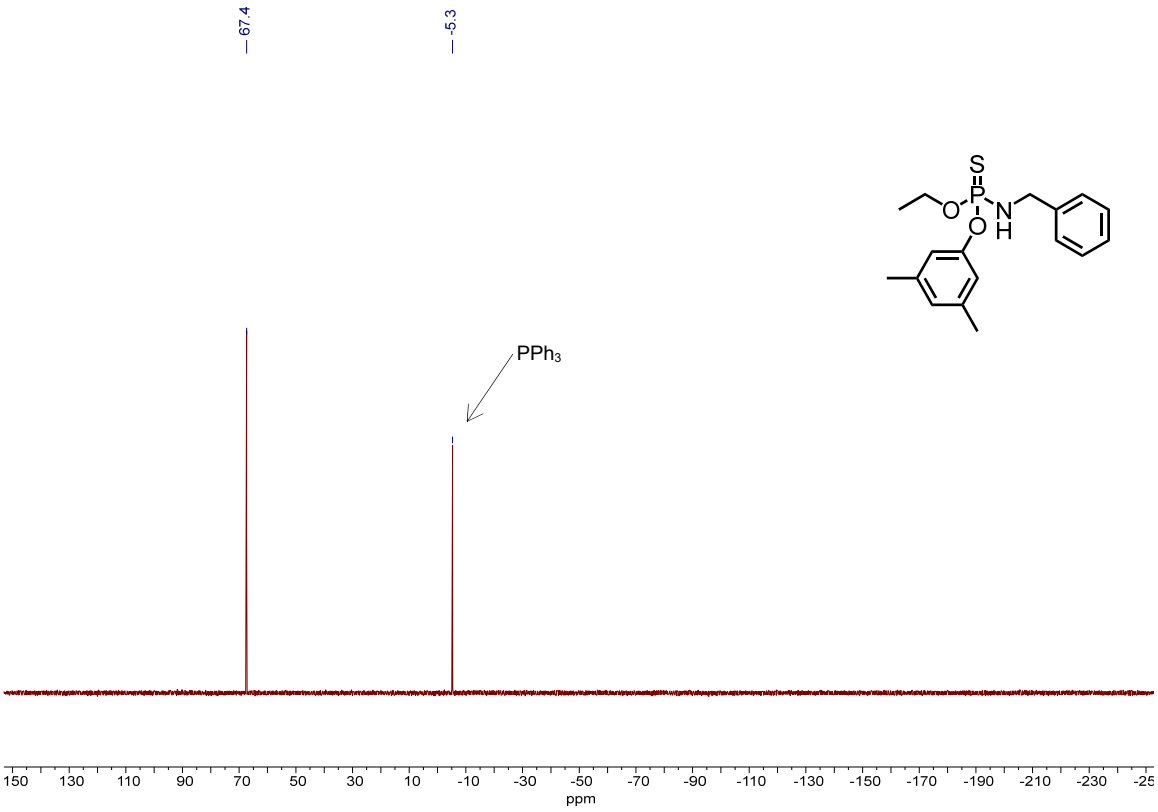
^{1}H NMR Spectrum for Compound **16k** (400 MHz, $CDCl_3$)



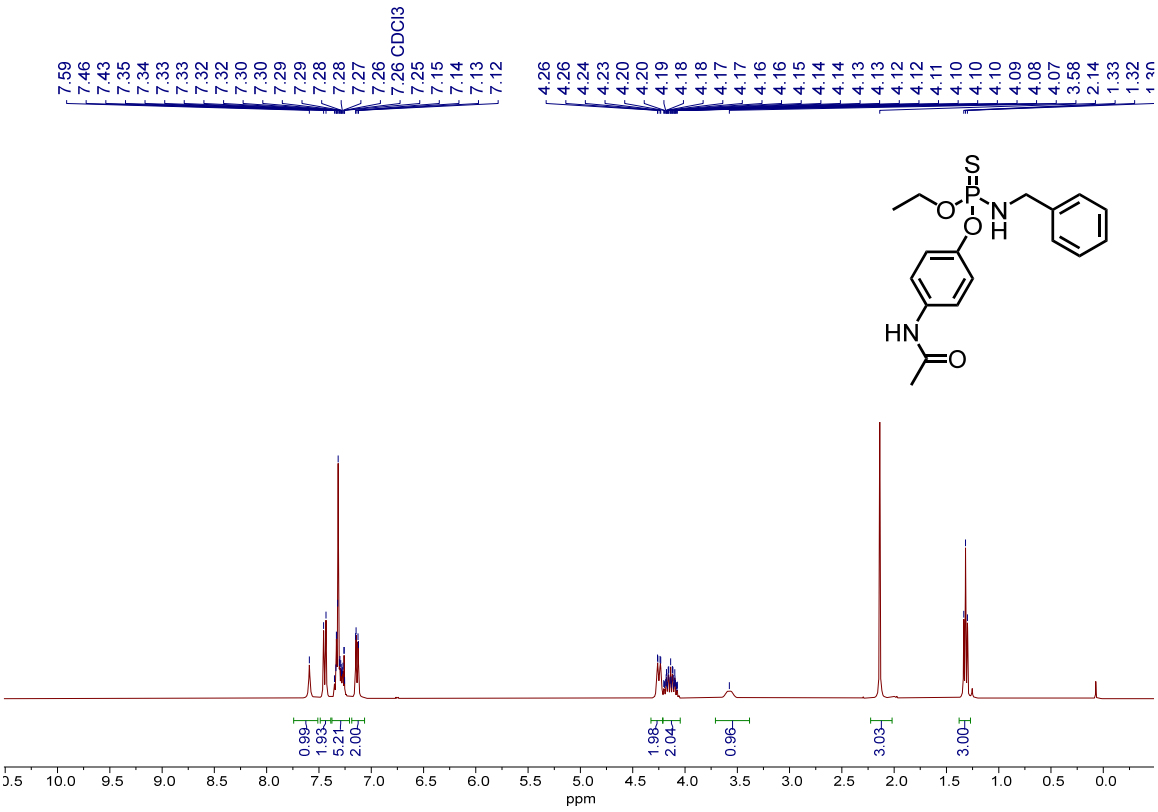
^{13}C NMR Spectrum for Compound **16k** (101 MHz, $CDCl_3$)



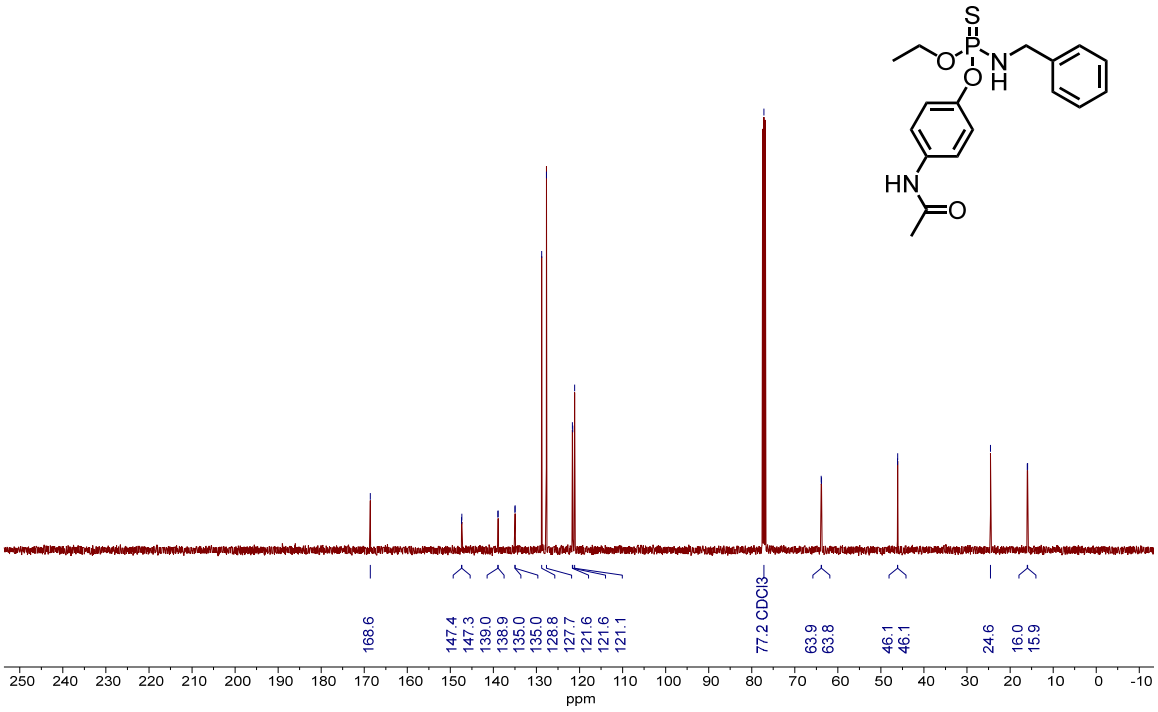
^{31}P NMR Spectrum for Compound **16k** (162 MHz, $CDCl_3$)



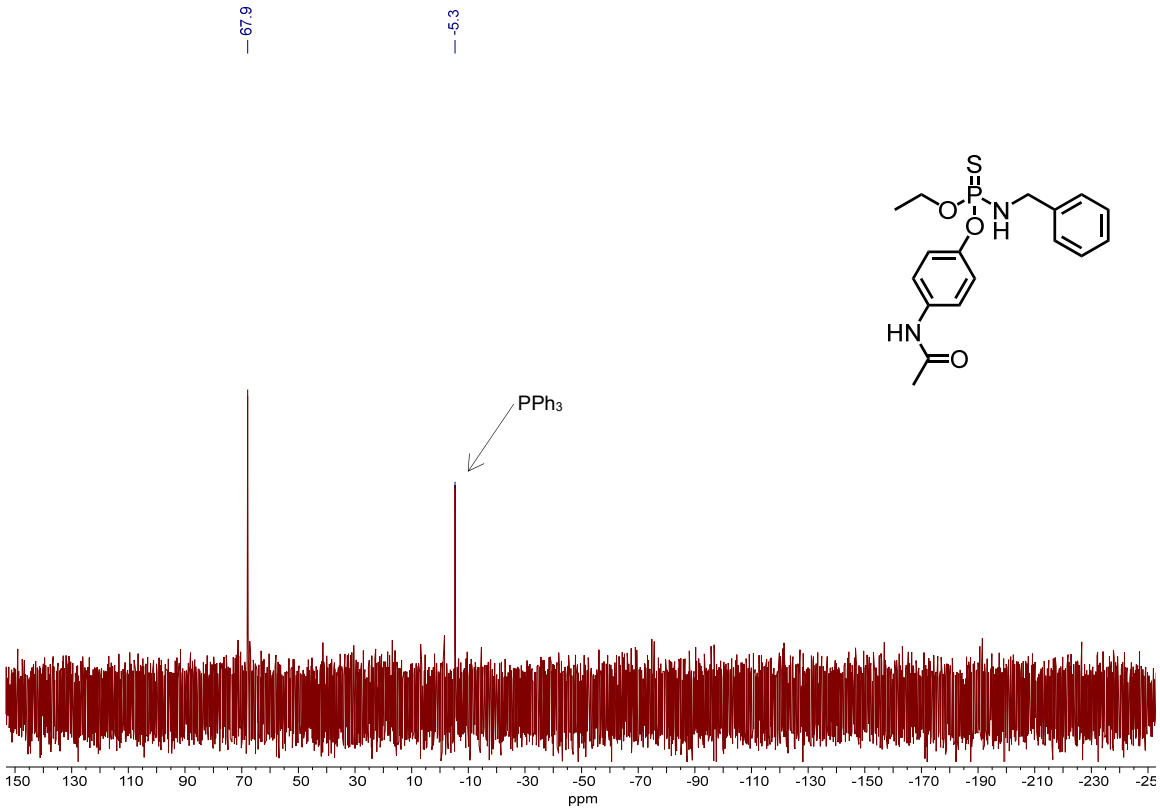
^{1}H NMR Spectrum for Compound **16l** (400 MHz, $CDCl_3$)



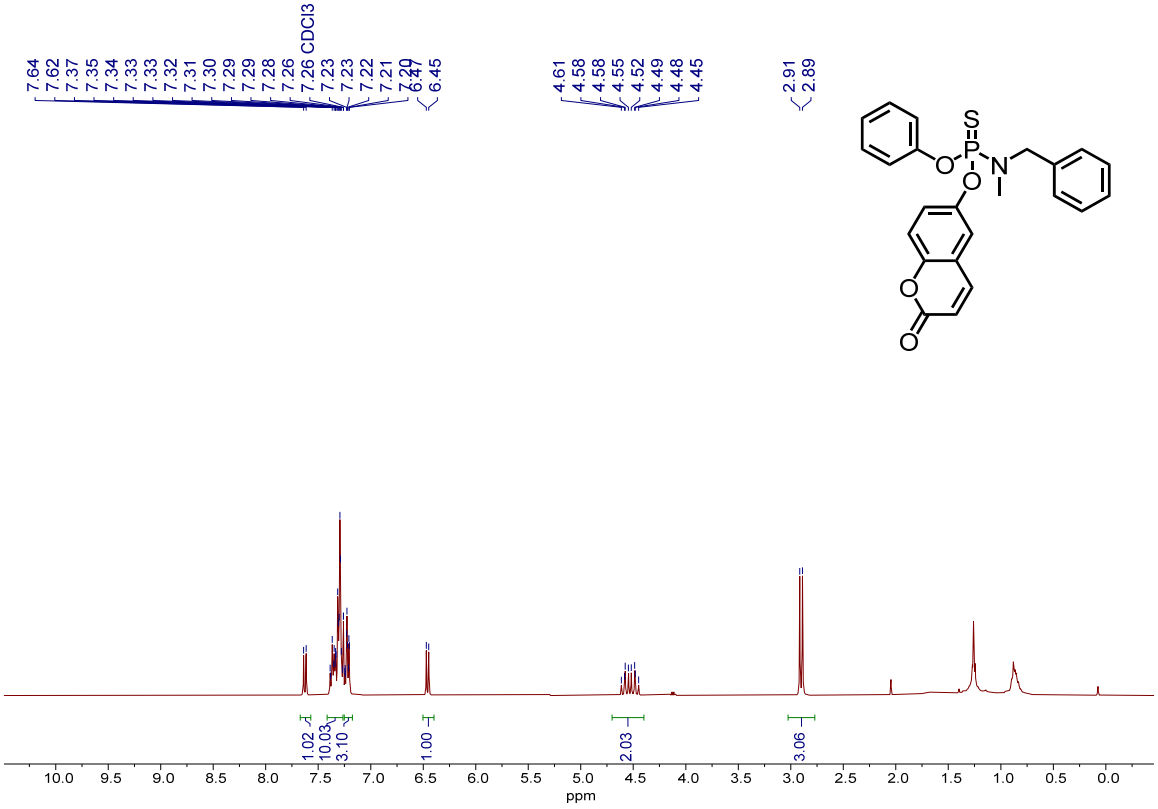
^{13}C NMR Spectrum for Compound **16l** (101 MHz, $CDCl_3$)



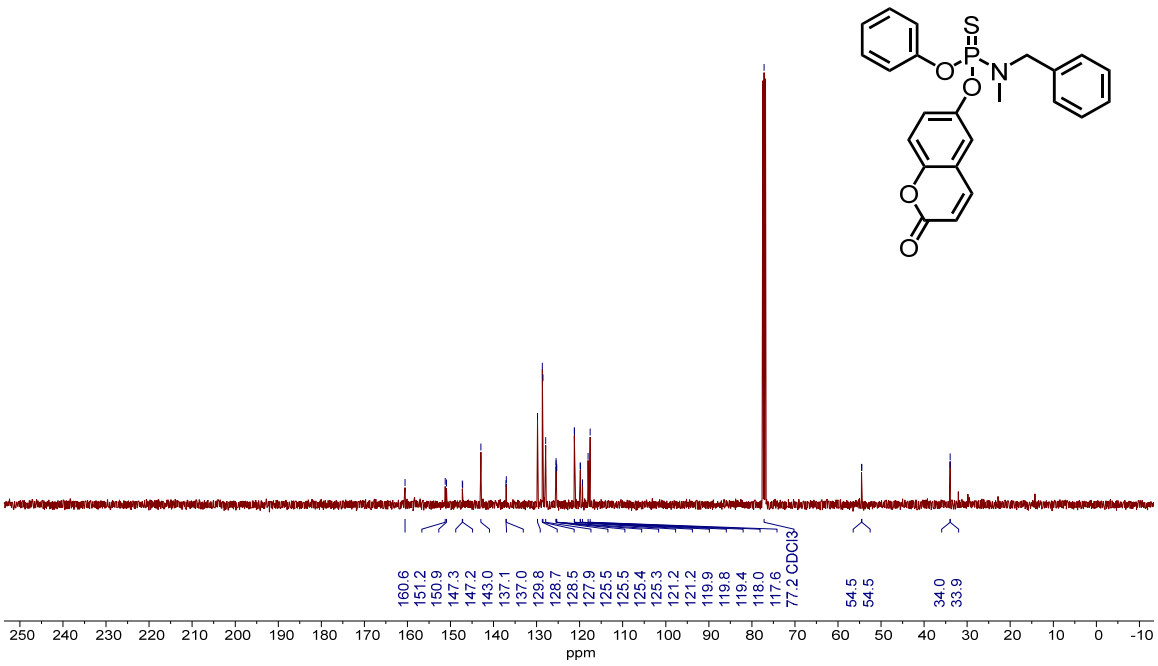
^{31}P NMR Spectrum for Compound **16l** (162 MHz, $CDCl_3$)



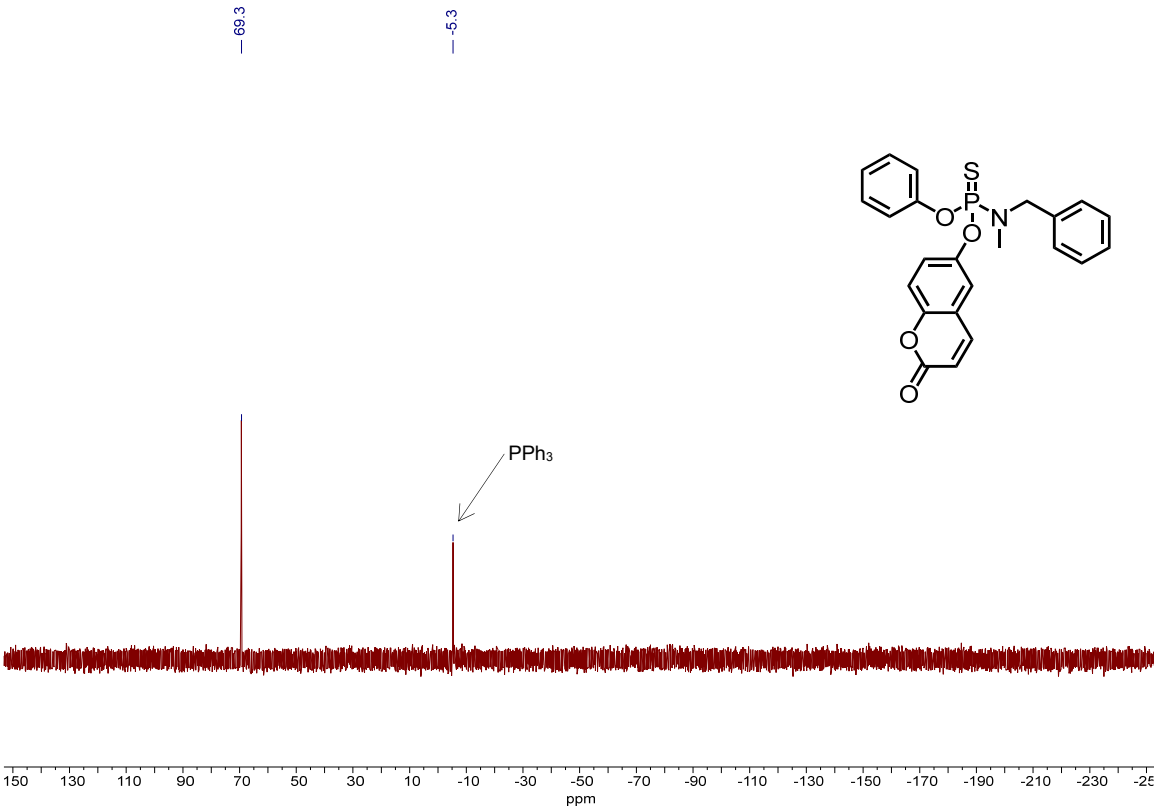
^{1}H NMR Spectrum for Compound **16m** (400 MHz, $CDCl_3$)



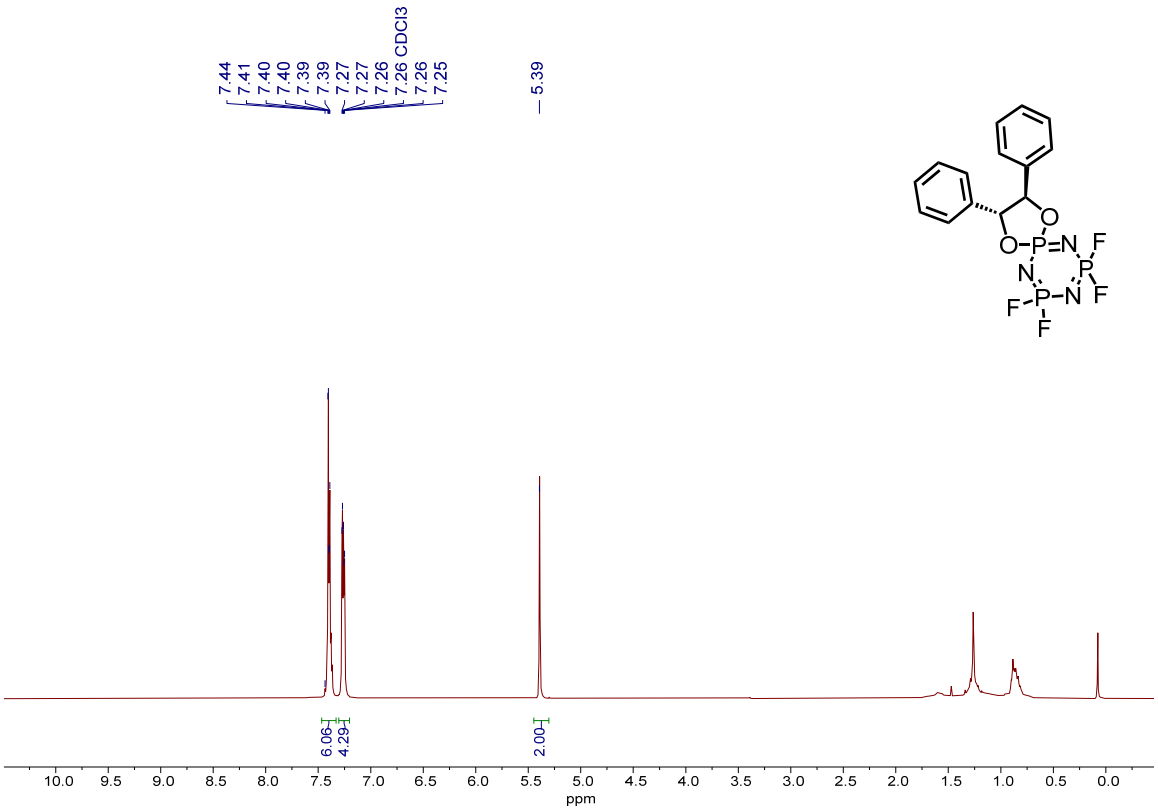
^{13}C NMR Spectrum for Compound **16m** (101 MHz, $CDCl_3$)



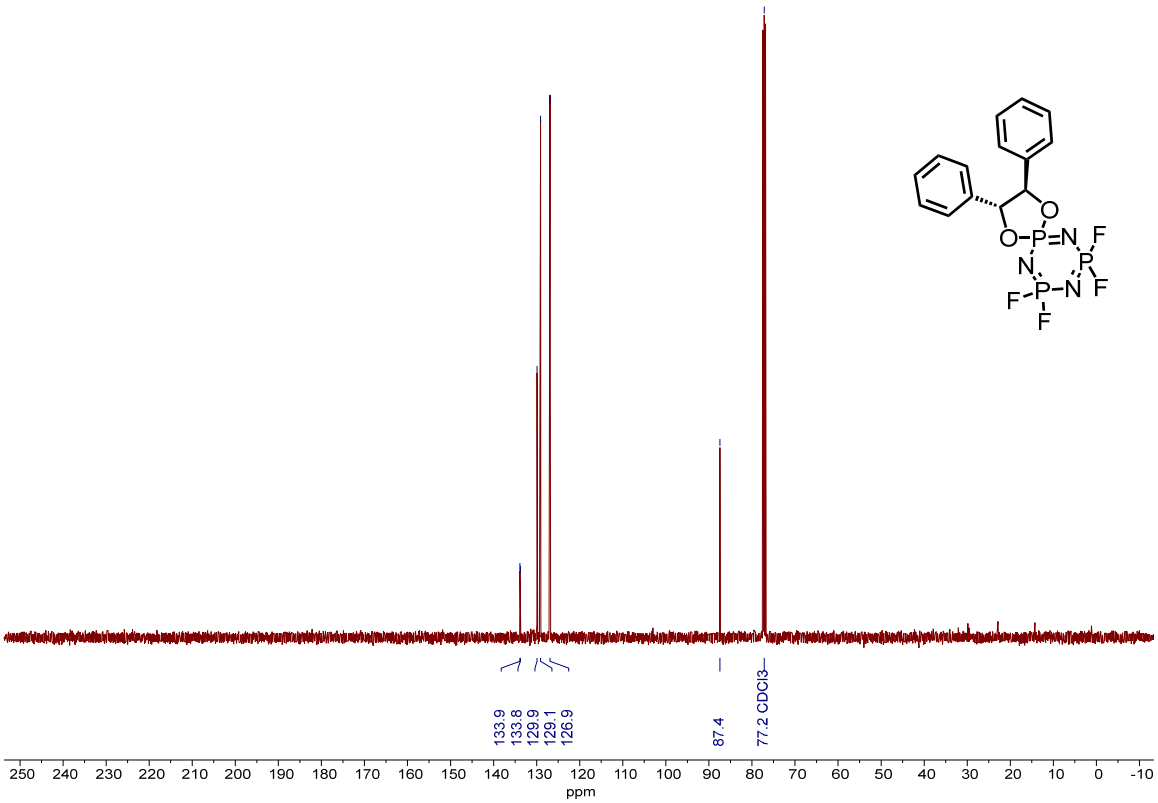
^{31}P NMR Spectrum for Compound **16m** (162 MHz, $CDCl_3$)



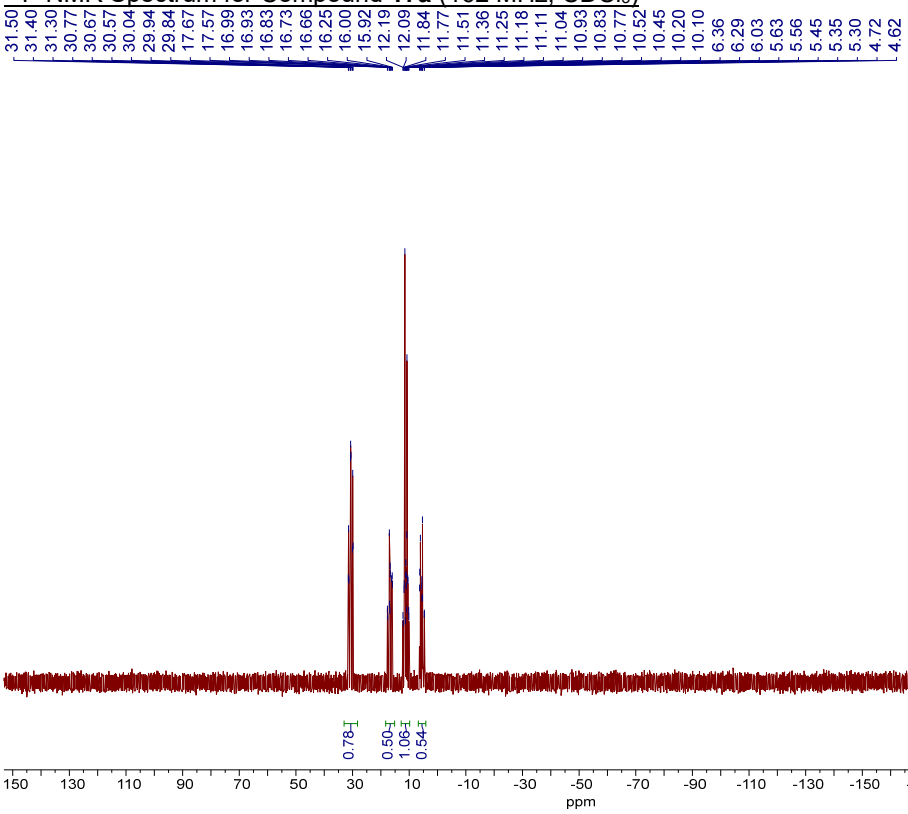
^{1}H NMR Spectrum for Compound **17a** (400 MHz, $CDCl_3$)

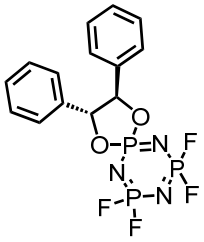


^{13}C NMR Spectrum for Compound **17a** (101 MHz, $CDCl_3$)

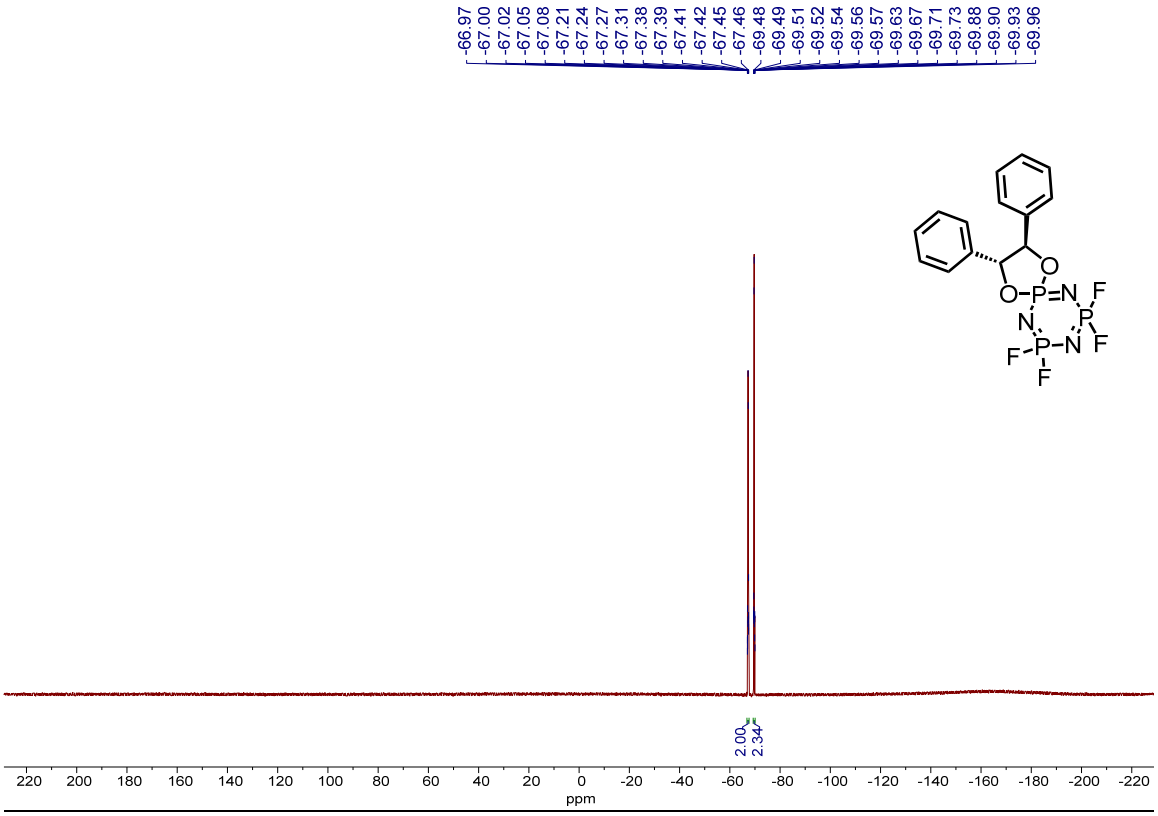


^{31}P NMR Spectrum for Compound **17a** (162 MHz, $CDCl_3$)

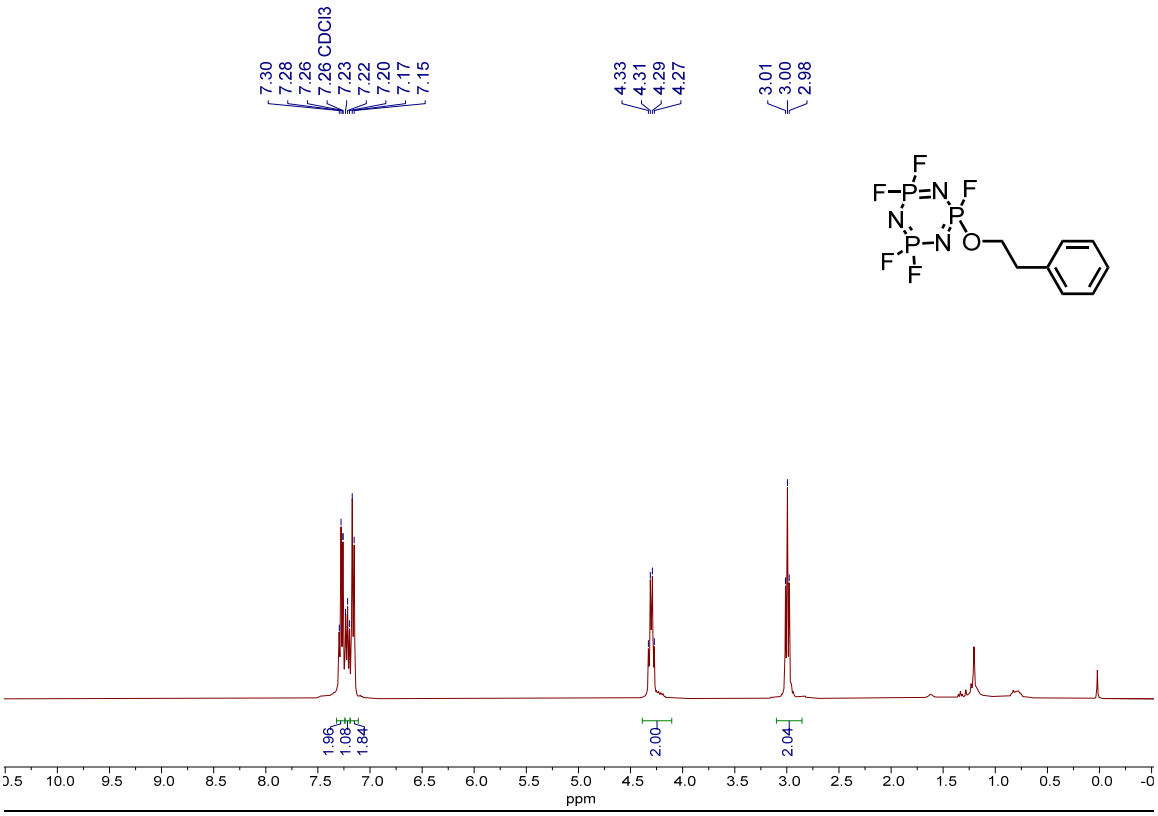




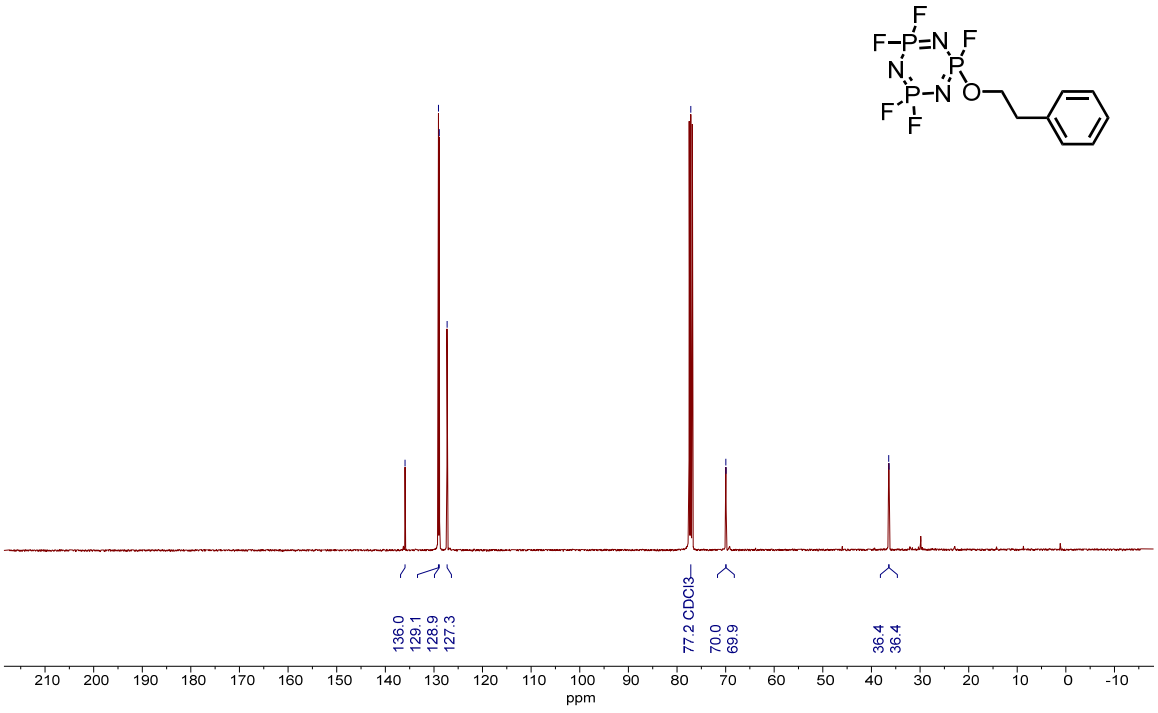
^{19}F NMR Spectrum for Compound **17a** (376 MHz, $CDCl_3$)



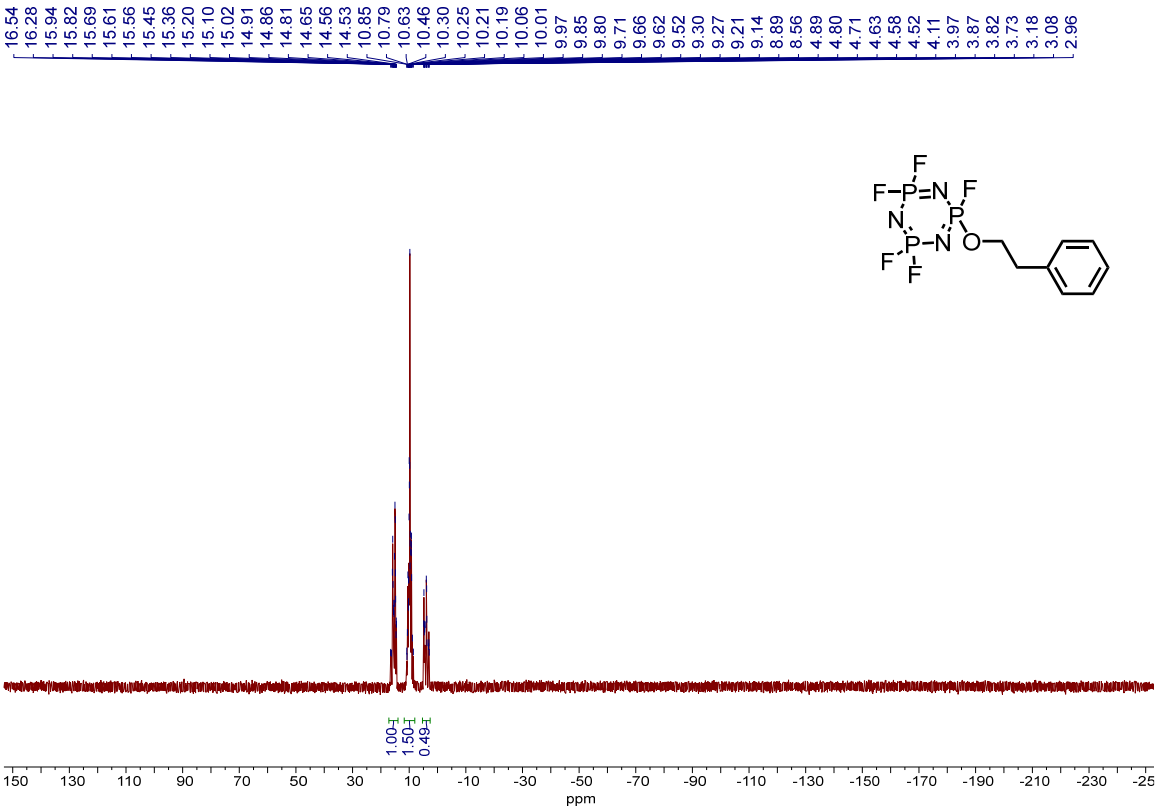
^{1}H NMR Spectrum for Compound **17b** (400 MHz, $CDCl_3$)



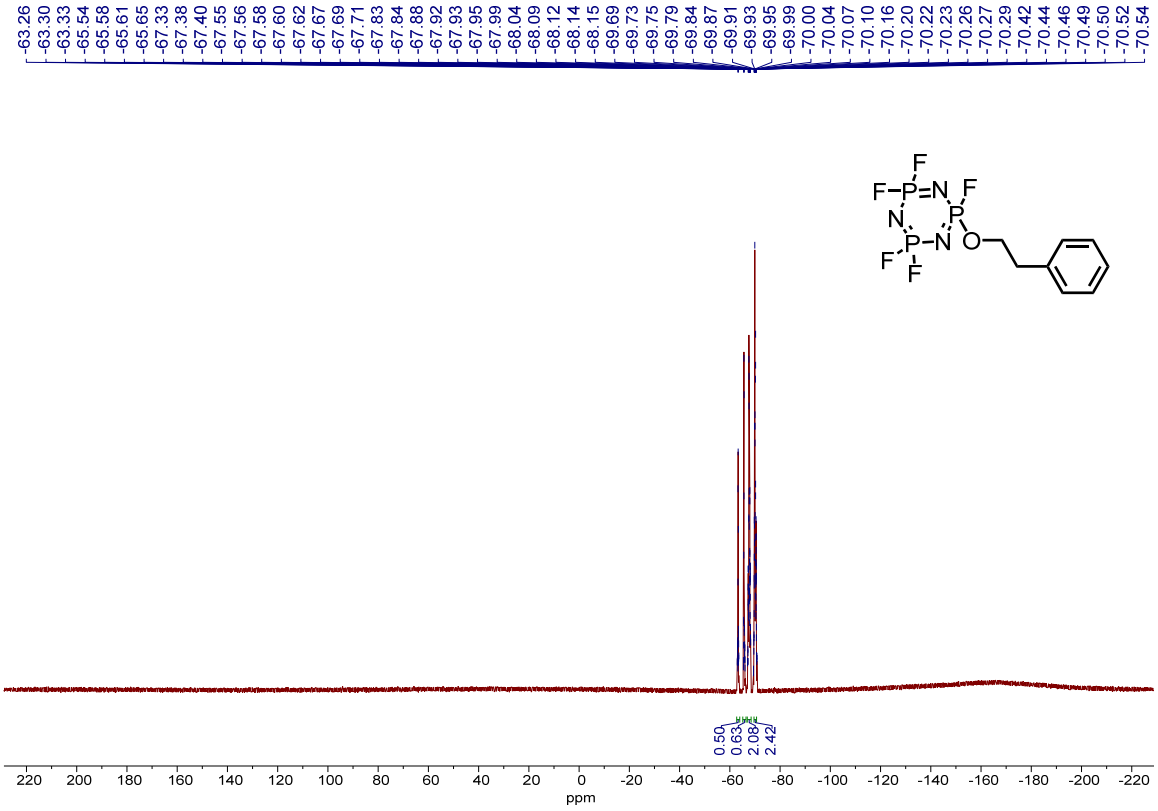
^{13}C NMR Spectrum for Compound **17b** (101 MHz, $CDCl_3$)



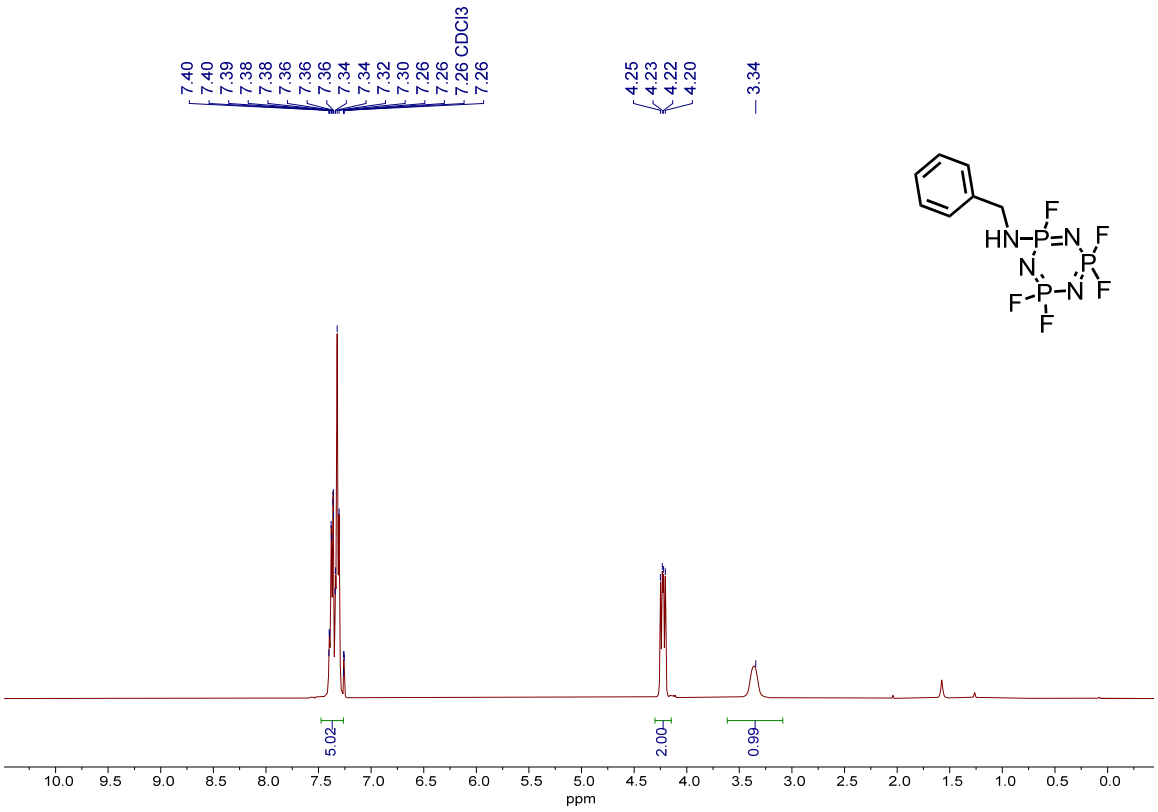
^{31}P NMR Spectrum for Compound **17b** (162 MHz, $CDCl_3$)



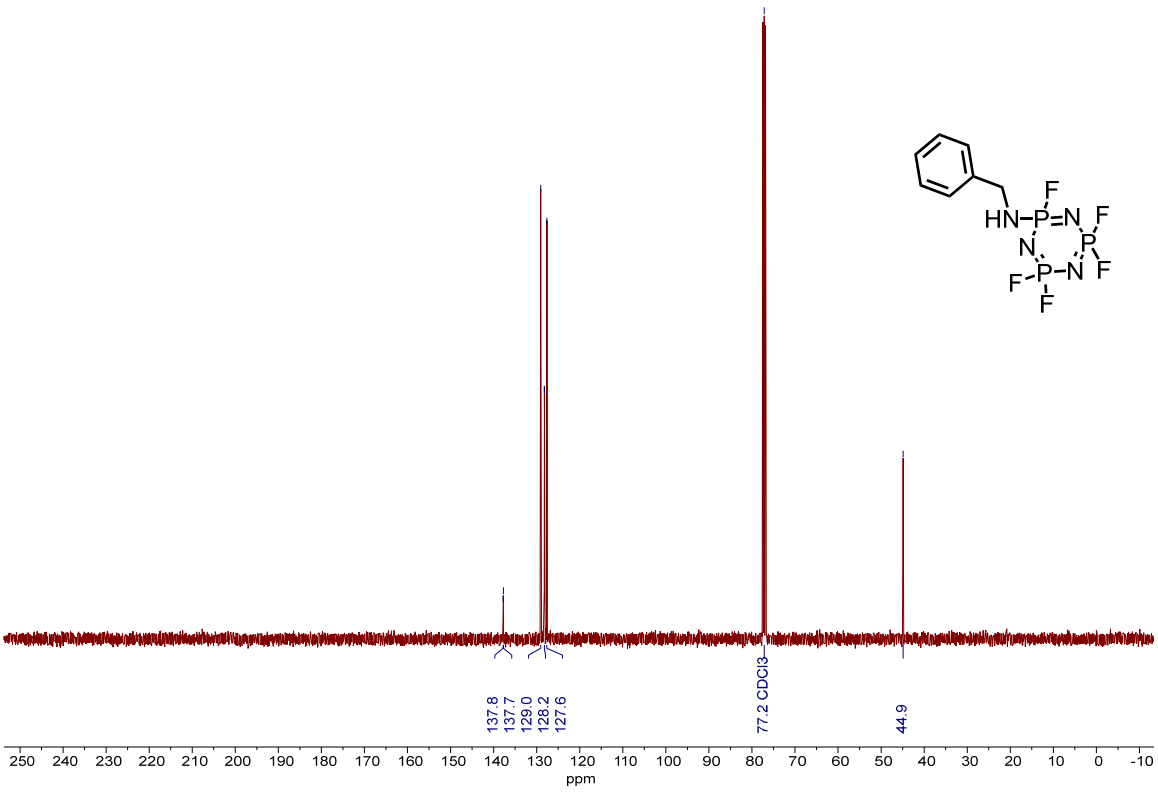
^{19}F NMR Spectrum for Compound **17b** (376 MHz, $CDCl_3$)



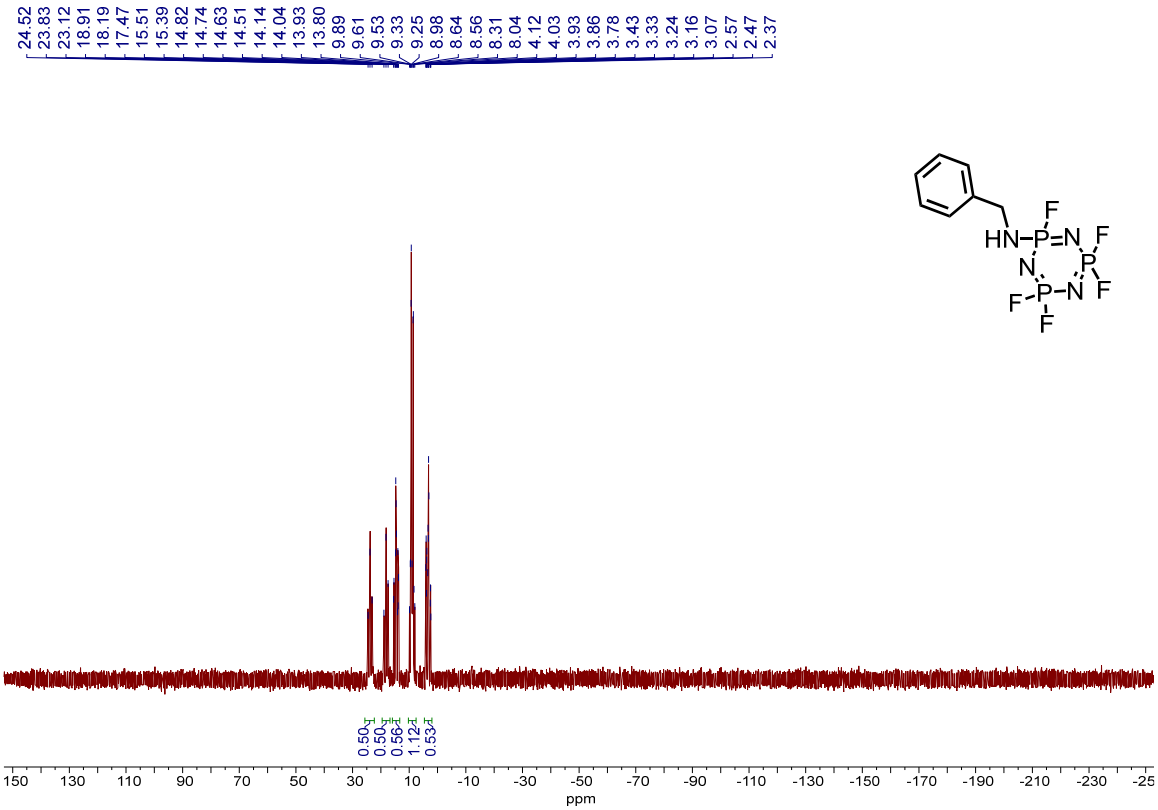
^{1}H NMR Spectrum for Compound **17c** (400 MHz, $CDCl_3$)



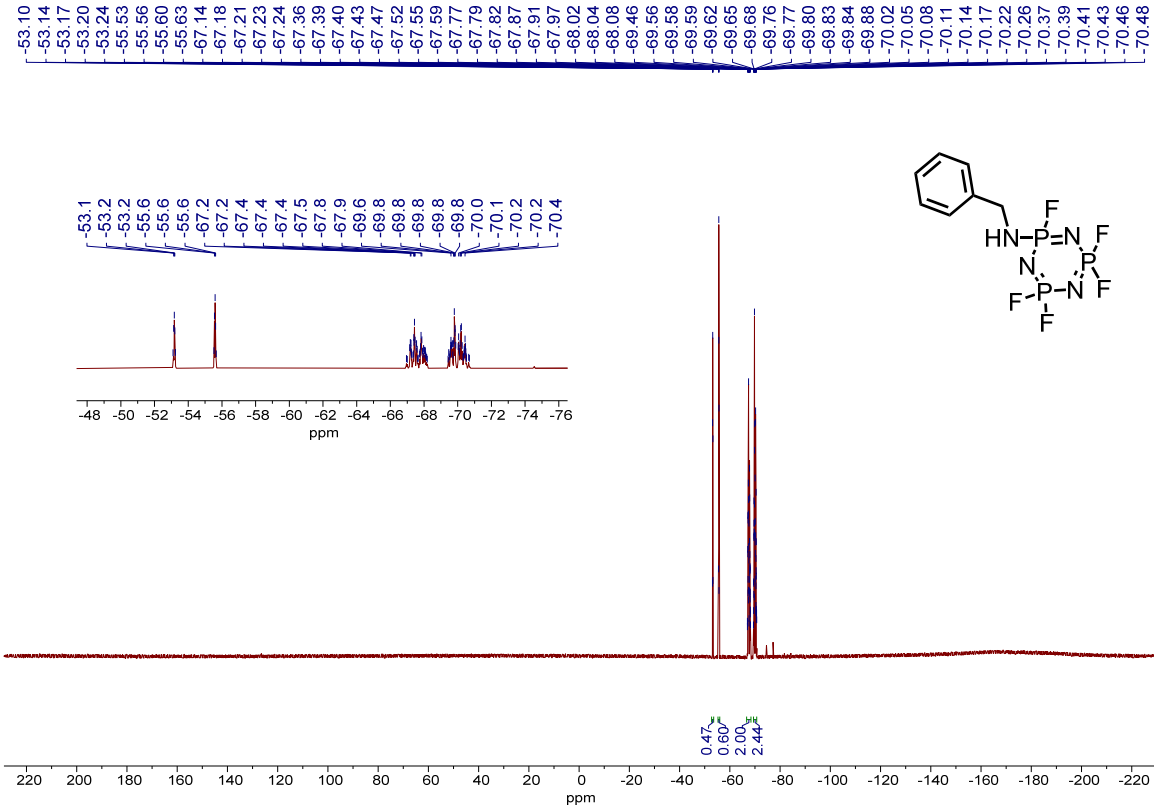
^{13}C NMR Spectrum for Compound **17c** (101 MHz, $CDCl_3$)



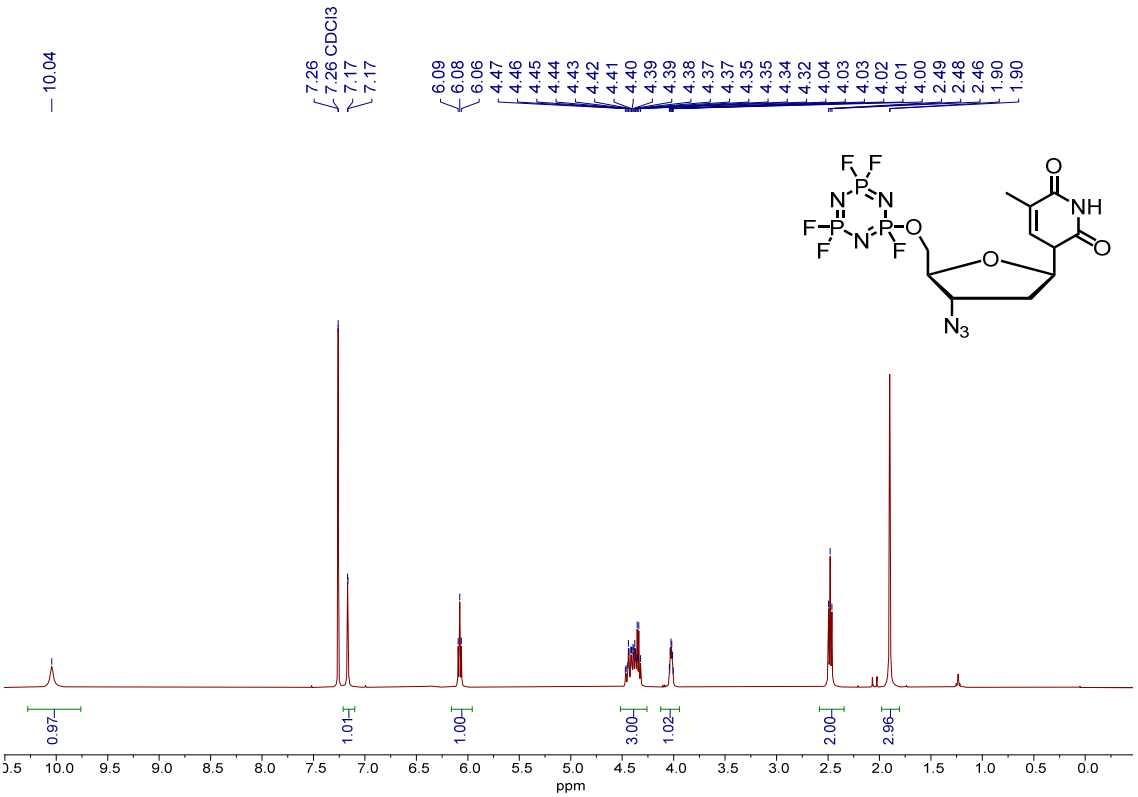
^{31}P NMR Spectrum for Compound **17c** (162 MHz, $CDCl_3$)



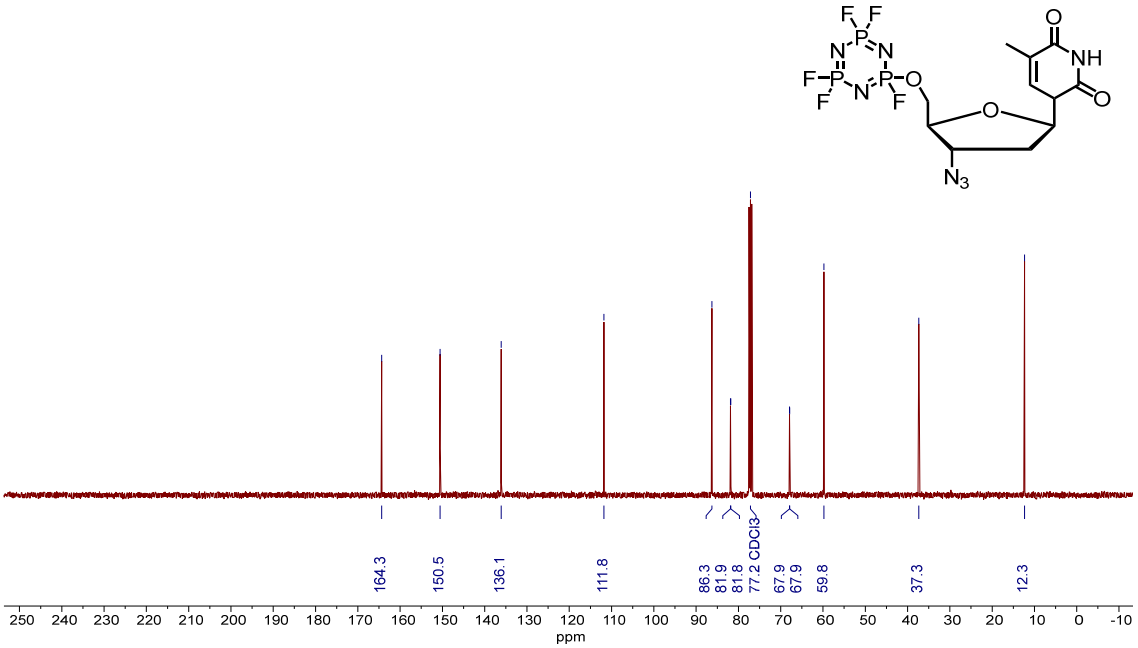
^{19}F NMR Spectrum for Compound **17c** (376 MHz, $CDCl_3$)



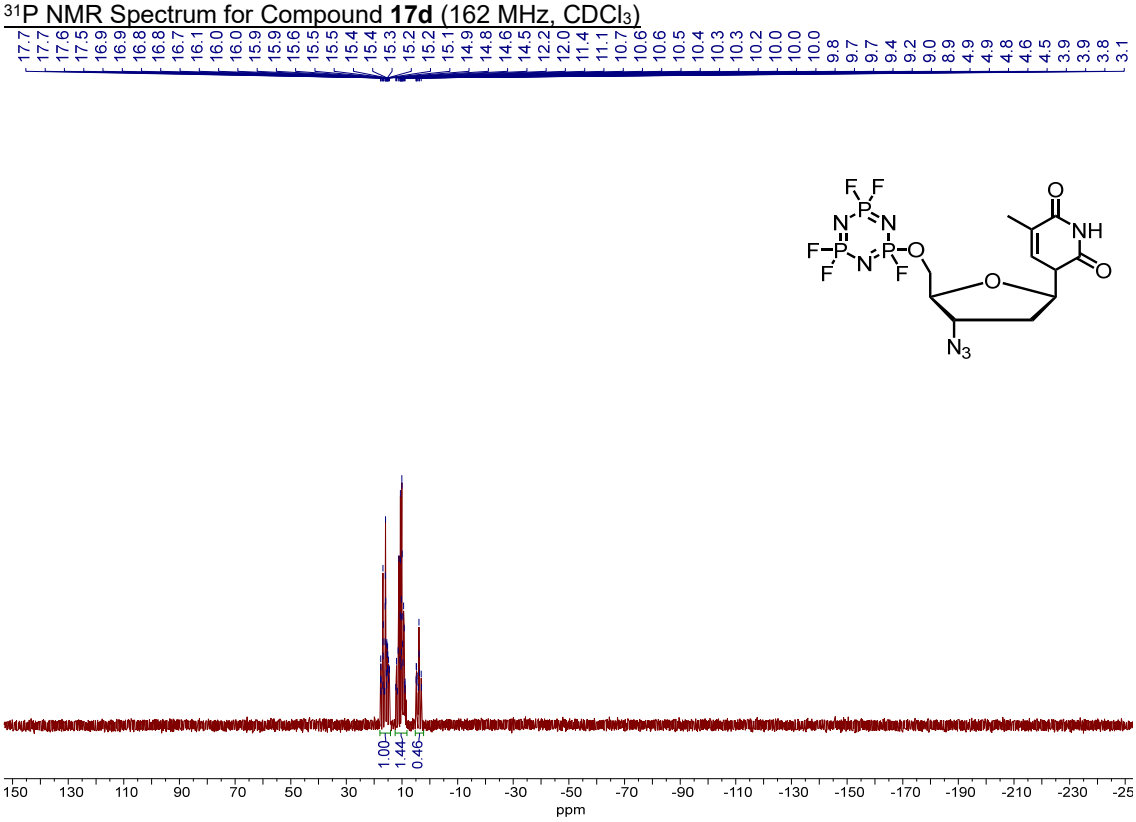
^{1}H NMR Spectrum for Compound **17d** (400 MHz, $CDCl_3$)



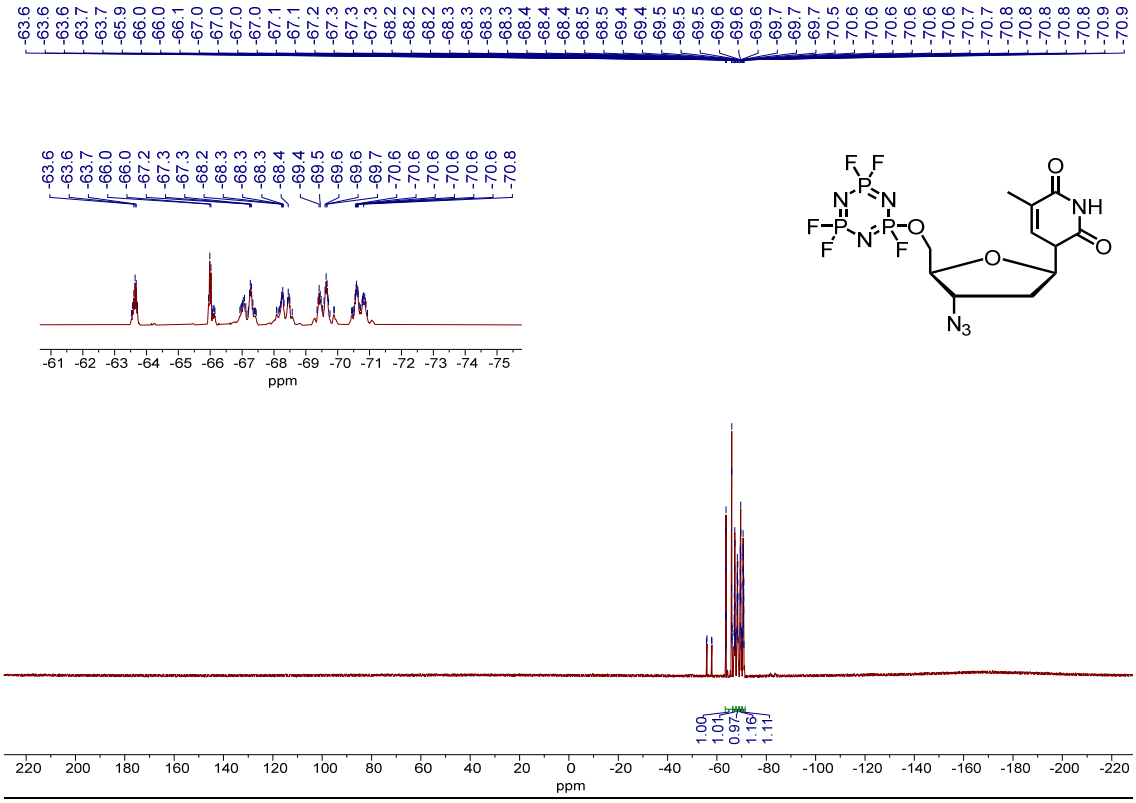
^{13}C NMR Spectrum for Compound **17d** (101 MHz, $CDCl_3$)



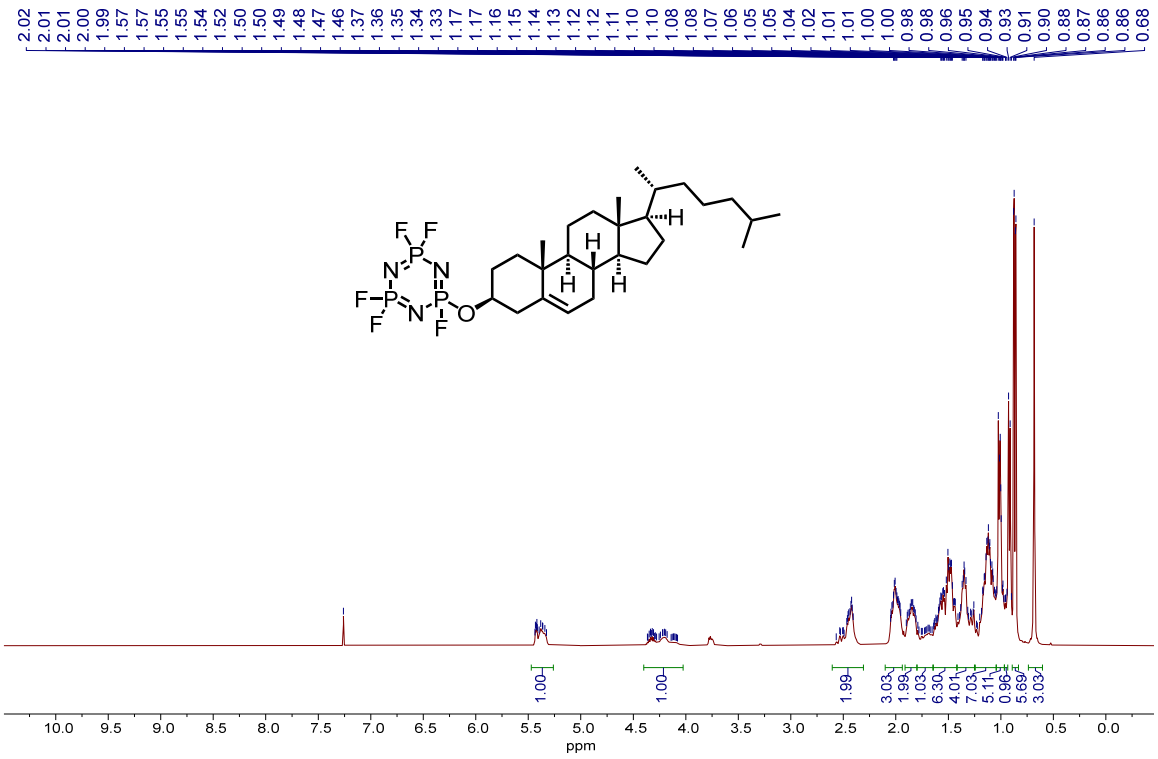
^{31}P NMR Spectrum for Compound **17d** (162 MHz, $CDCl_3$)



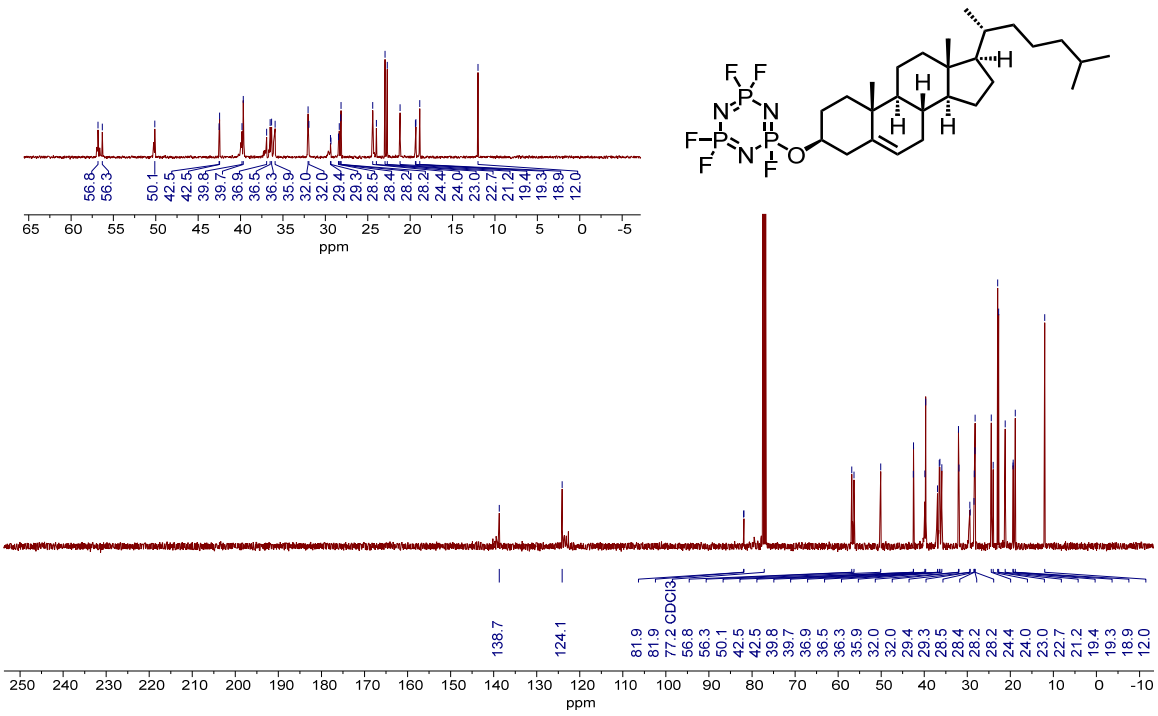
^{19}F NMR Spectrum for Compound **17d** (376 MHz, $CDCl_3$)



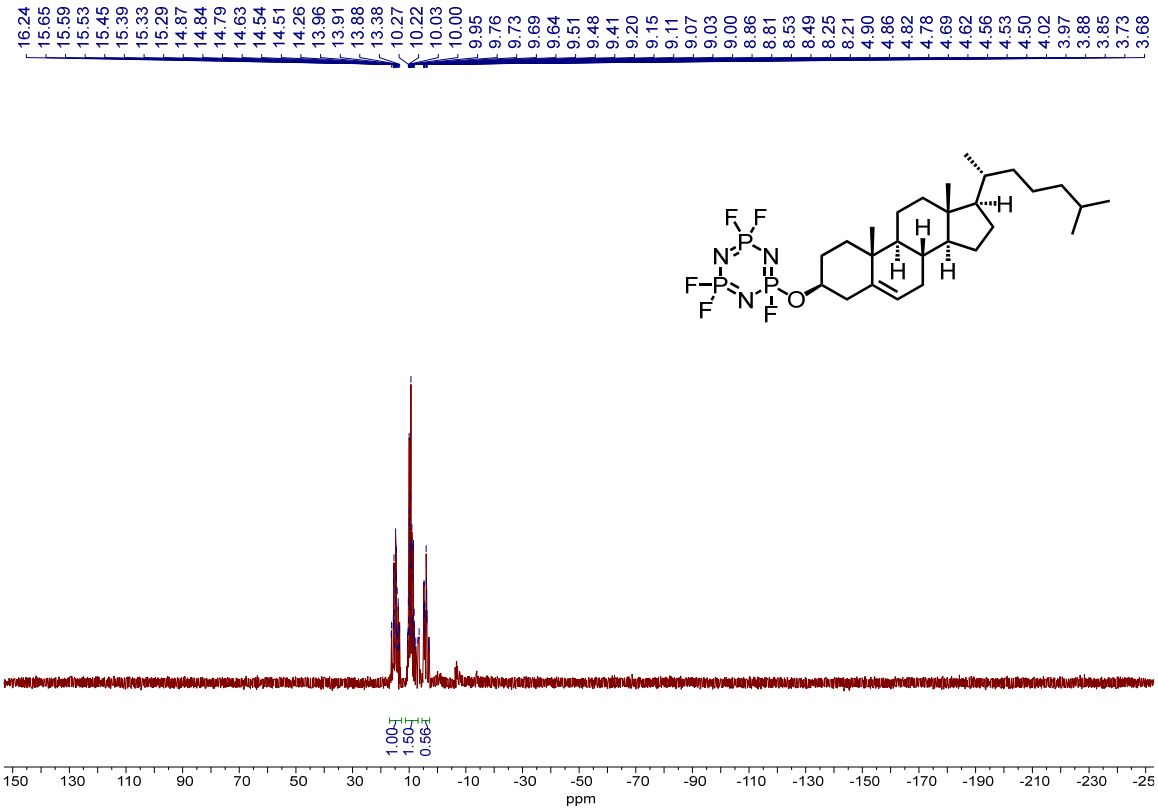
^{1}H NMR Spectrum for Compound **17e** (400 MHz, $CDCl_3$)



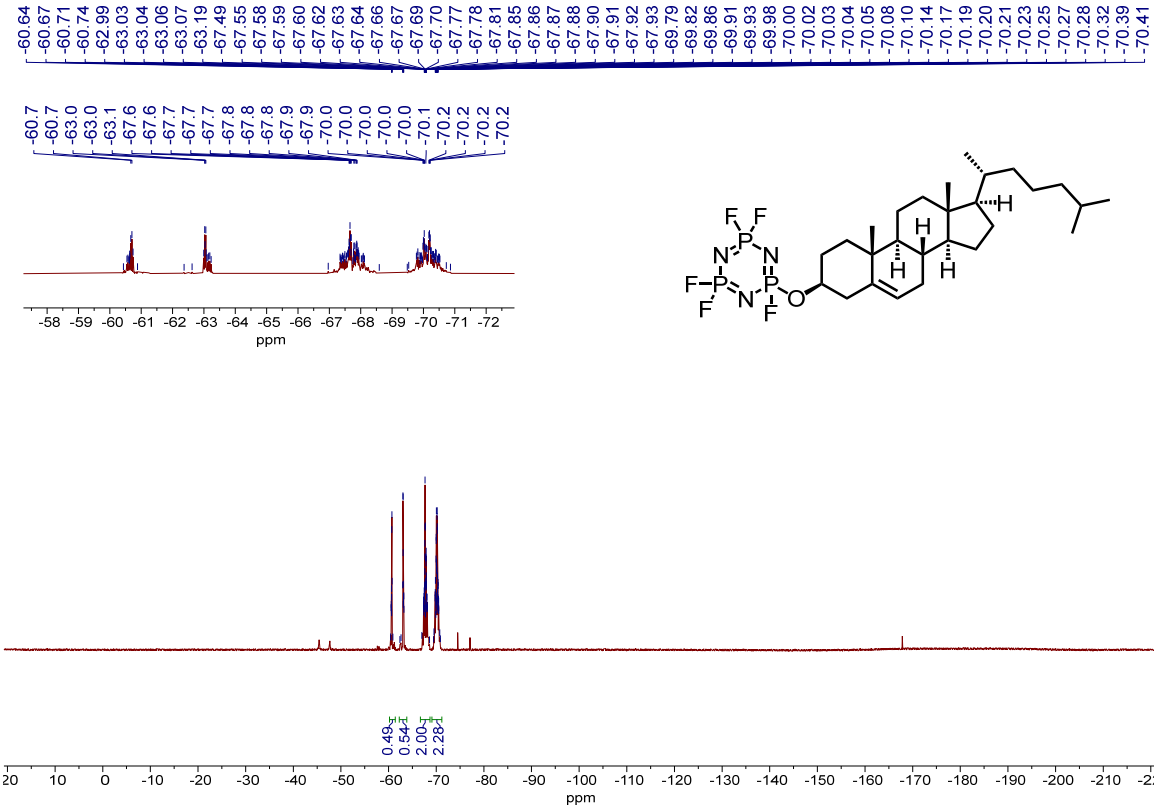
^{13}C NMR Spectrum for Compound **17e** (101 MHz, $CDCl_3$)



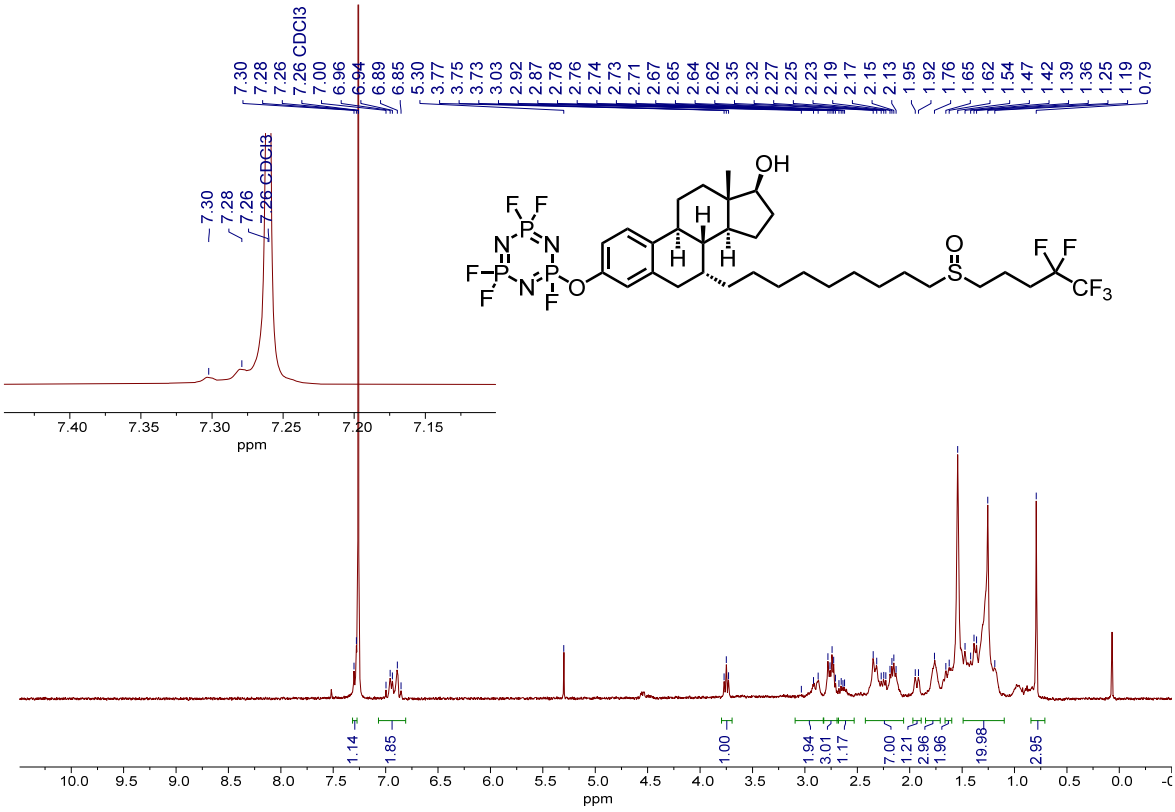
^{31}P NMR Spectrum for Compound **17e** (162 MHz, $CDCl_3$)



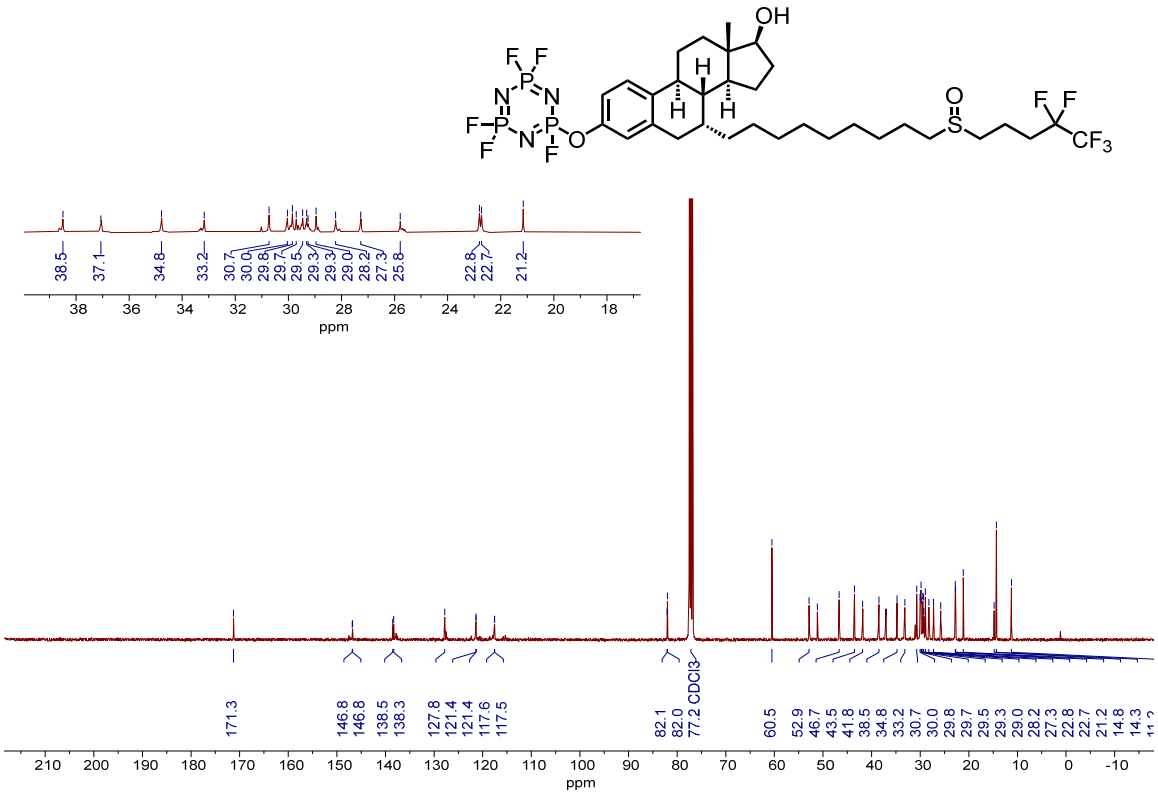
^{19}F NMR Spectrum for Compound **17e** (376 MHz, $CDCl_3$)



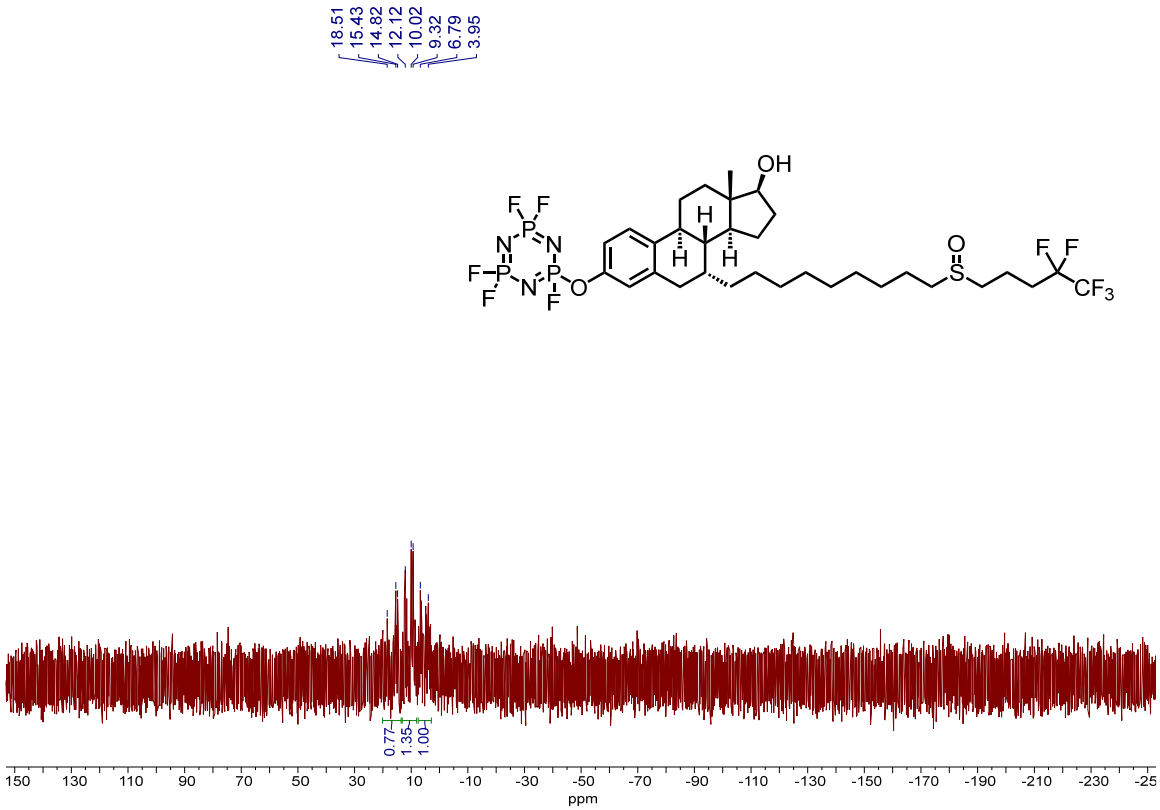
^{1}H NMR Spectrum for Compound **17f** (400 MHz, $CDCl_3$)



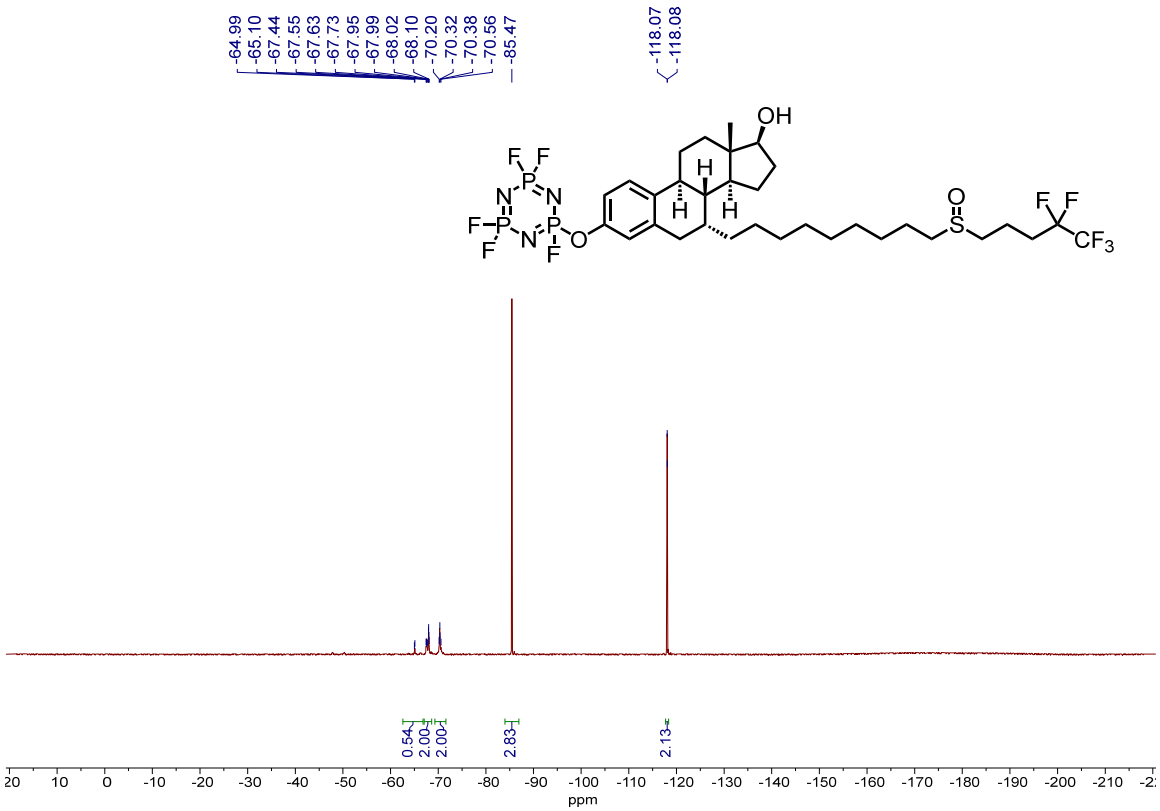
^{13}C NMR Spectrum for Compound **17f** (101 MHz, $CDCl_3$)



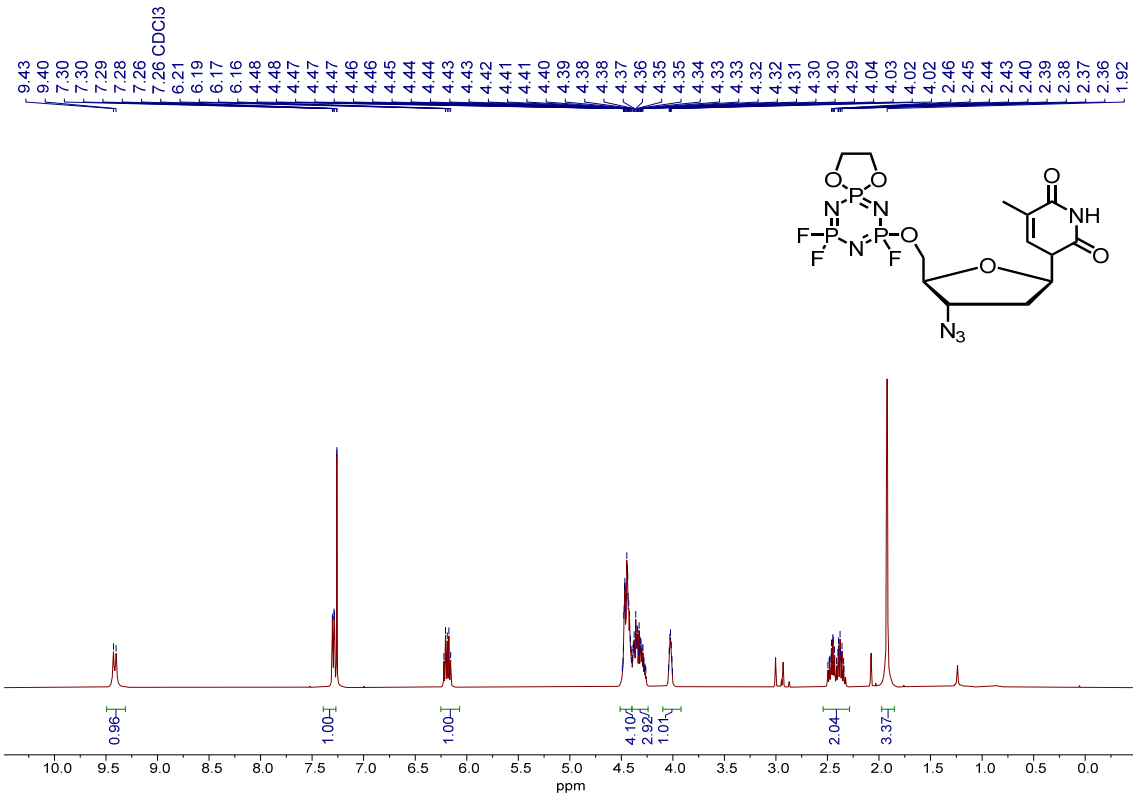
^{31}P NMR Spectrum for Compound **17f** (162 MHz, $CDCl_3$)



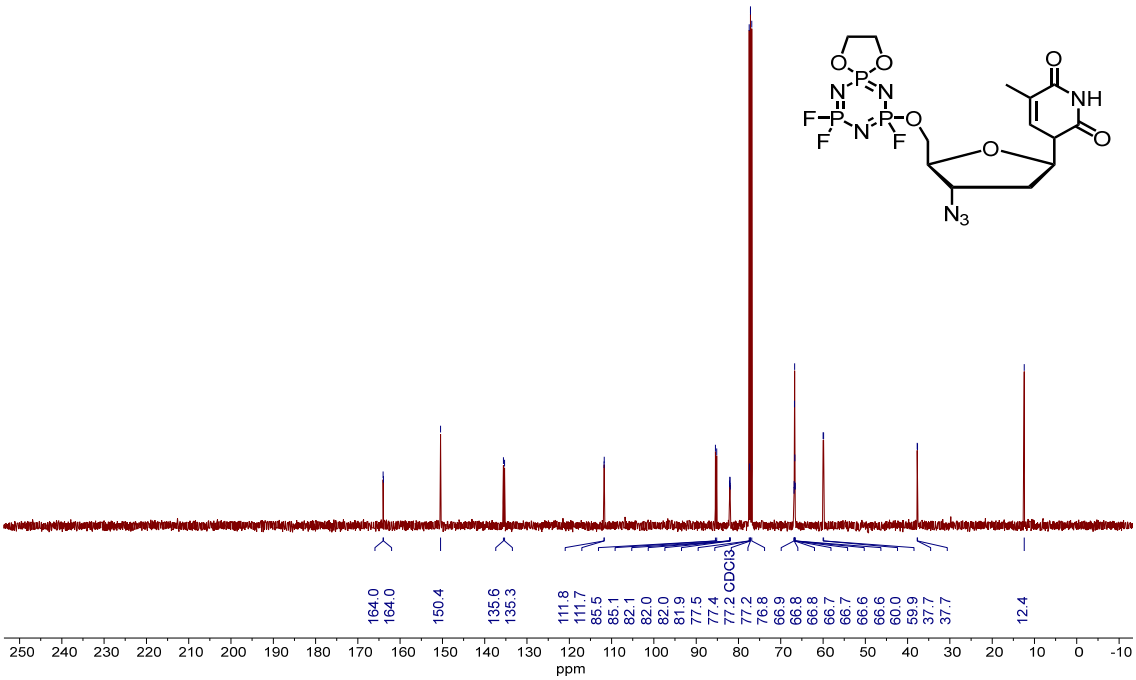
^{19}F NMR Spectrum for Compound **17f** (376 MHz, $CDCl_3$)



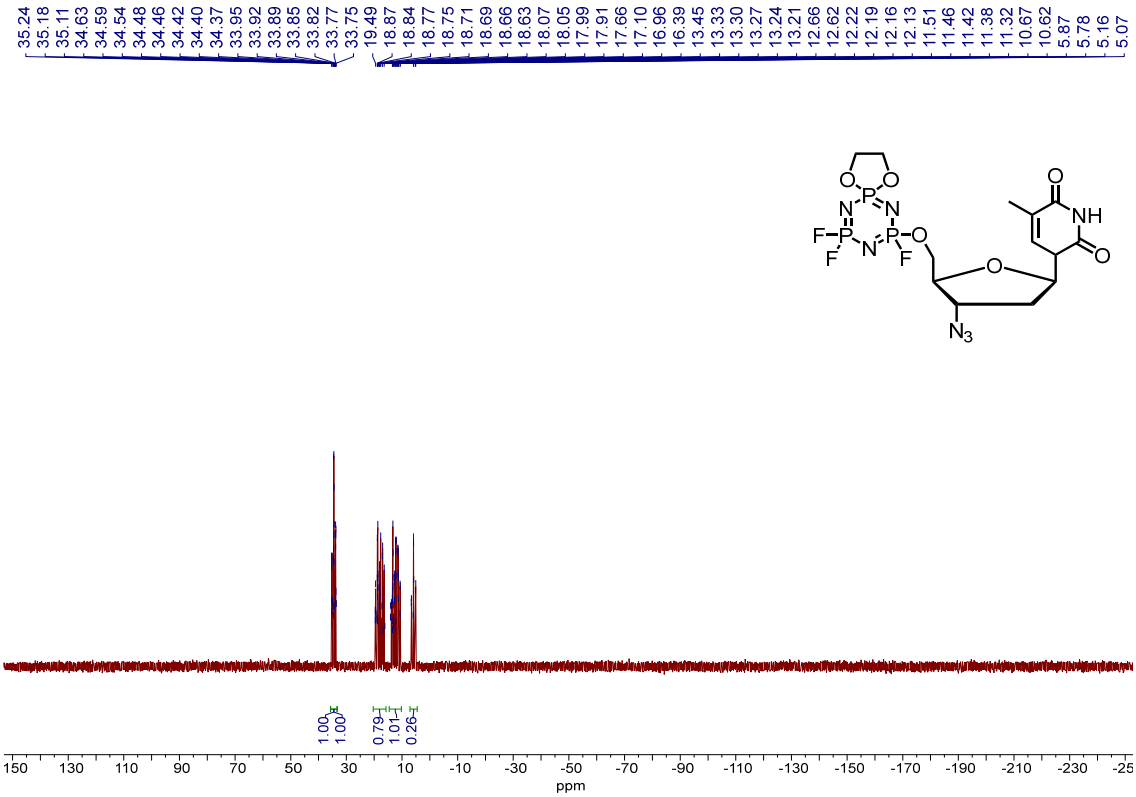
^{1}H NMR Spectrum for Compound **17g** (400 MHz, $CDCl_3$)



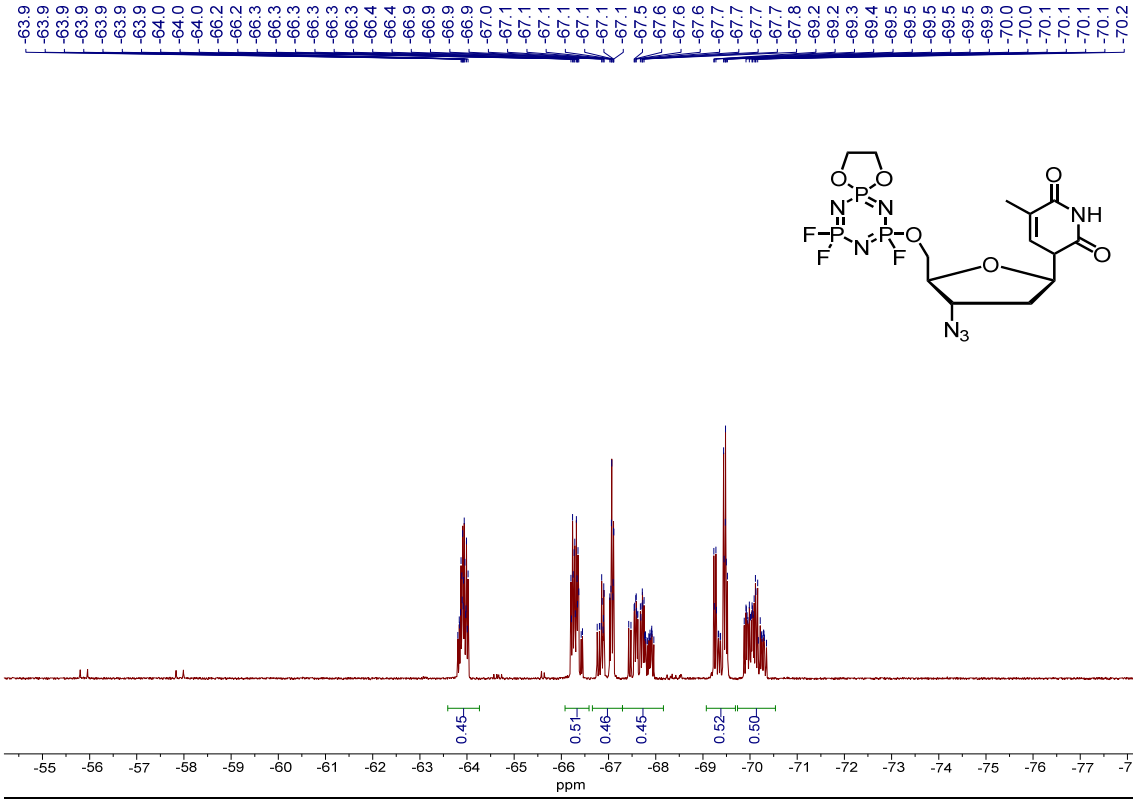
^{13}C NMR Spectrum for Compound **17g** (101 MHz, $CDCl_3$)



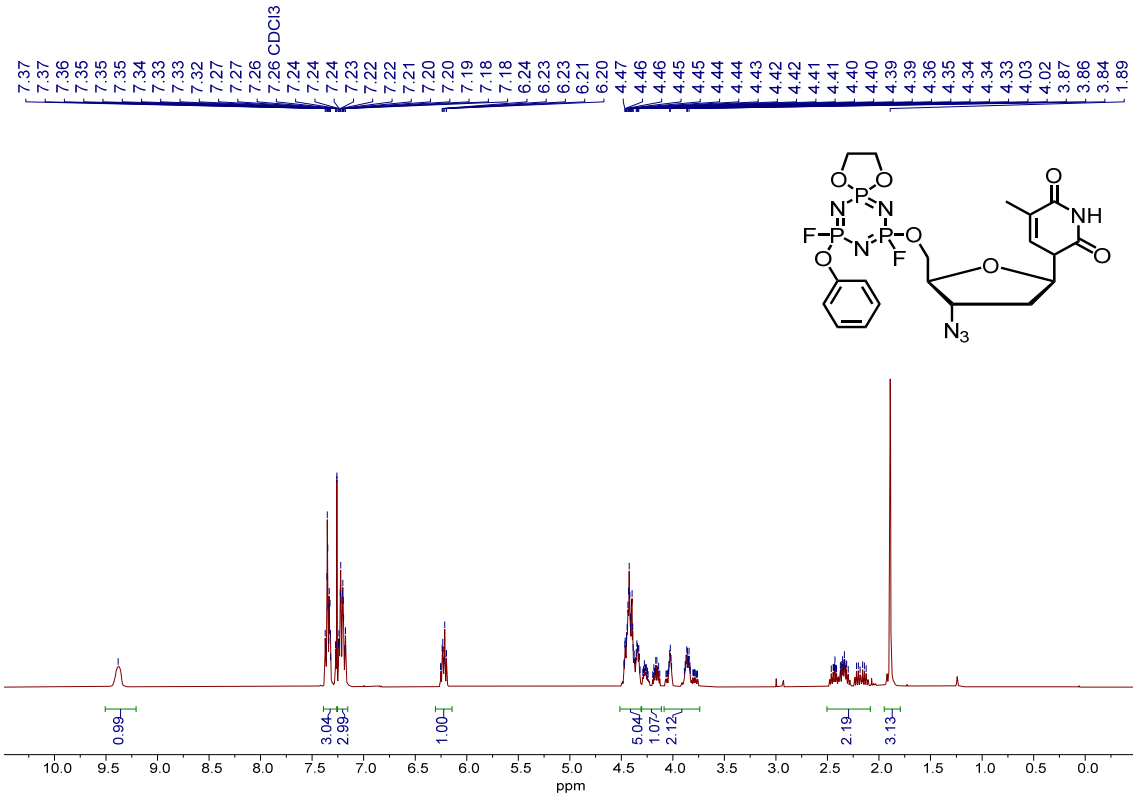
^{31}P NMR Spectrum for Compound **17g** (162 MHz, $CDCl_3$)



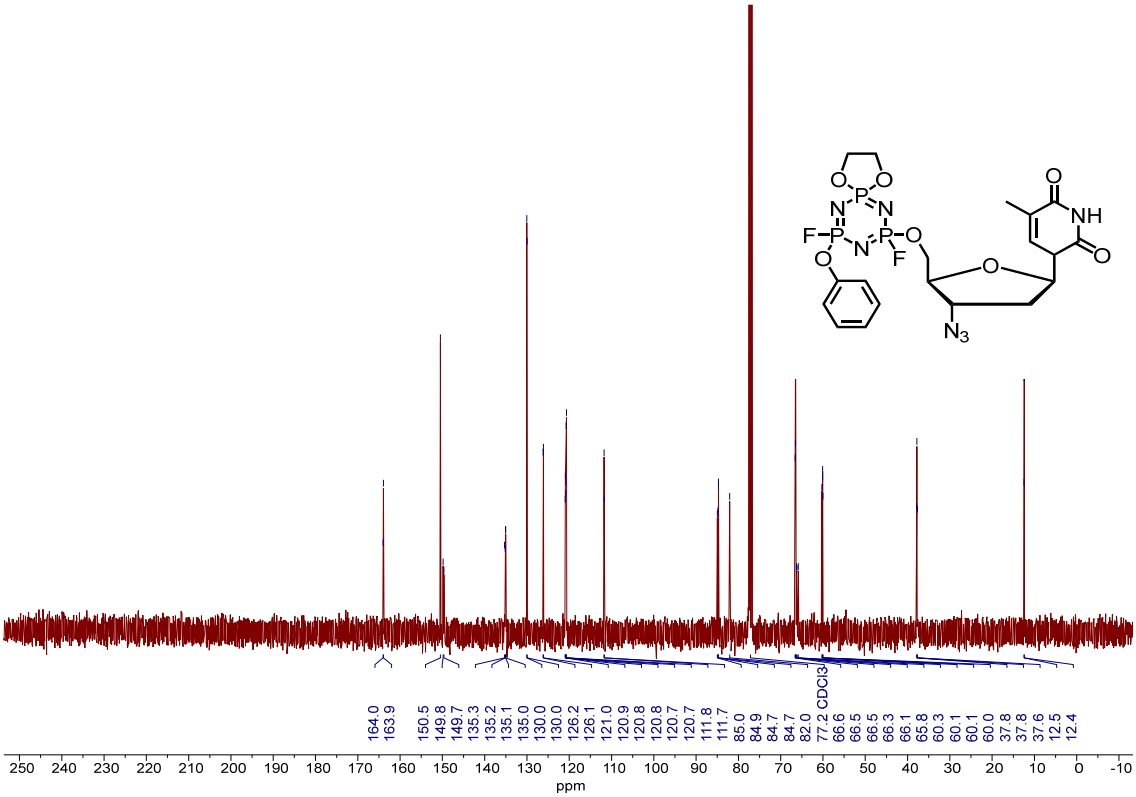
^{19}F NMR Spectrum for Compound **17g** (376 MHz, $CDCl_3$)



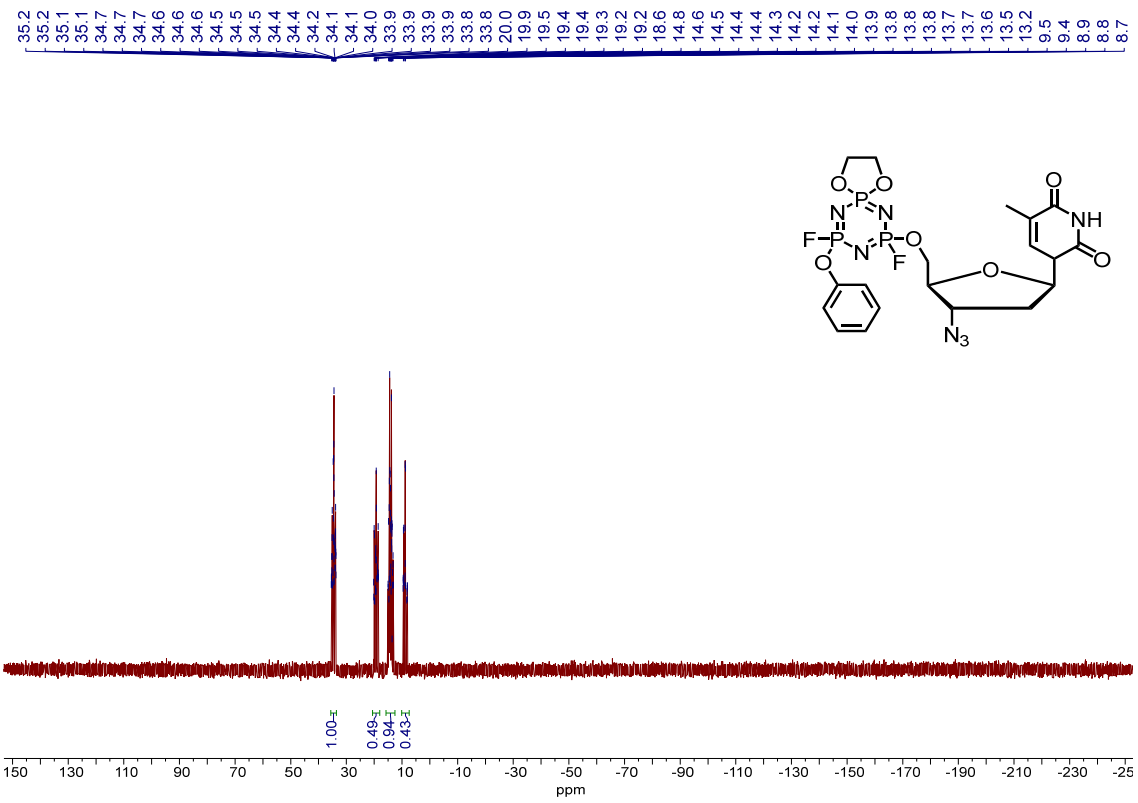
^{1}H NMR Spectrum for Compound **17h** (400 MHz, $CDCl_3$)



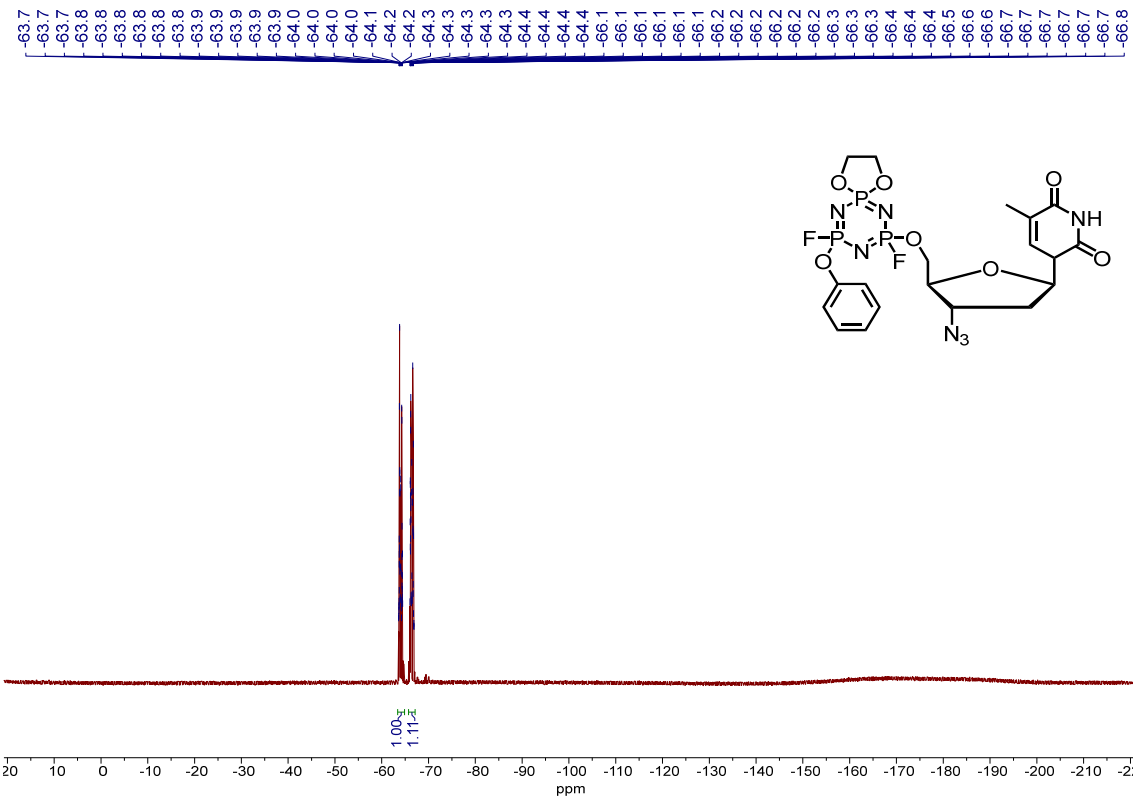
^{13}C NMR Spectrum for Compound **17h** (101 MHz, $CDCl_3$)



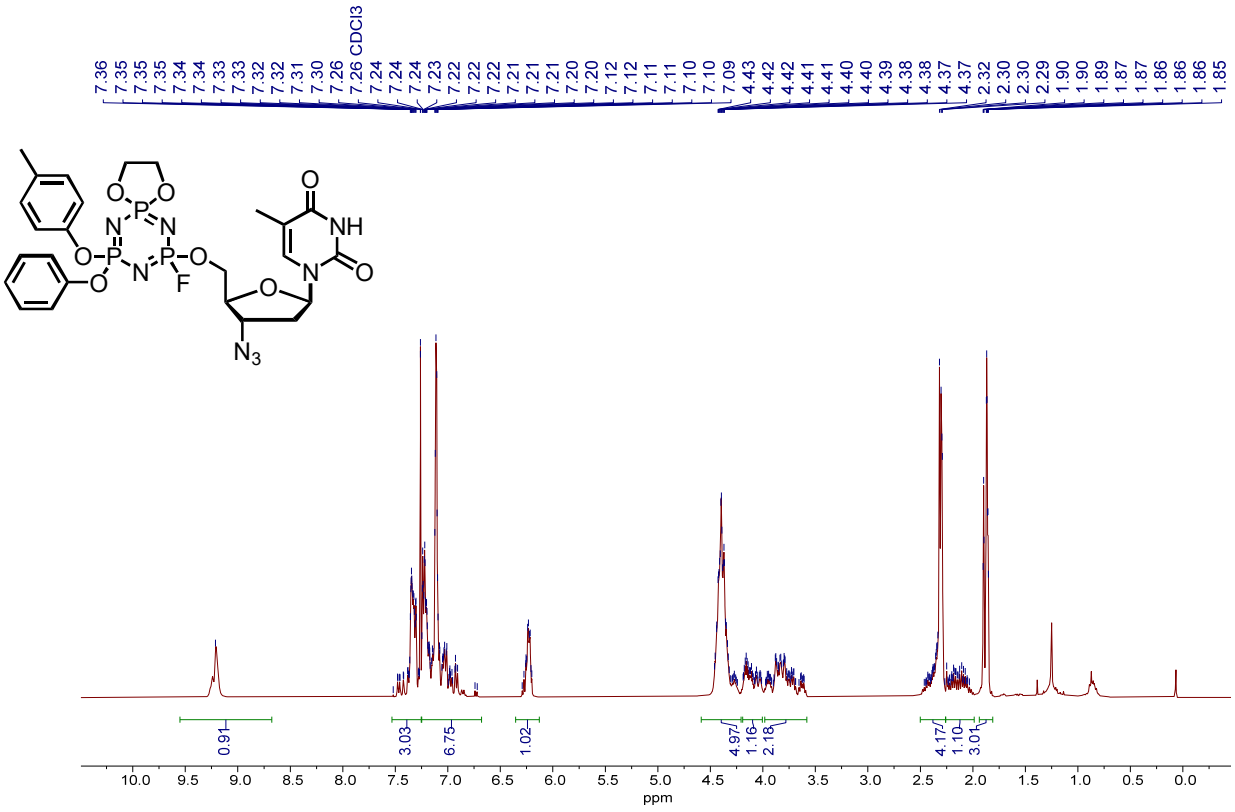
^{31}P NMR Spectrum for Compound **17h** (162 MHz, $CDCl_3$)



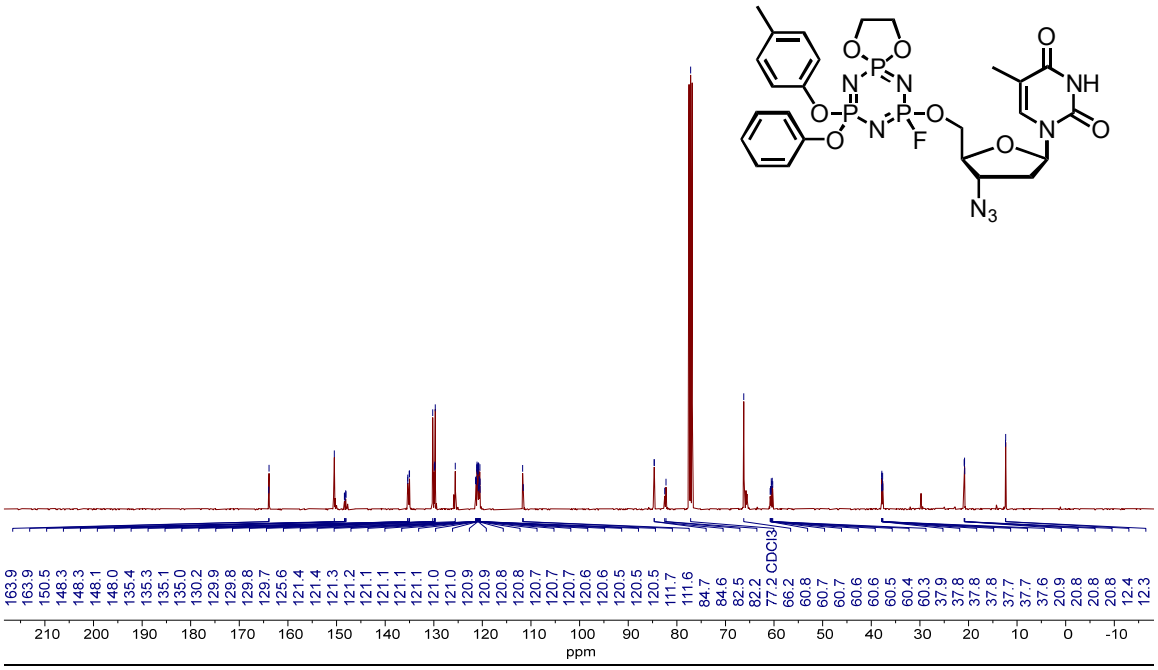
^{19}F NMR Spectrum for Compound **17h** (376 MHz, $CDCl_3$)



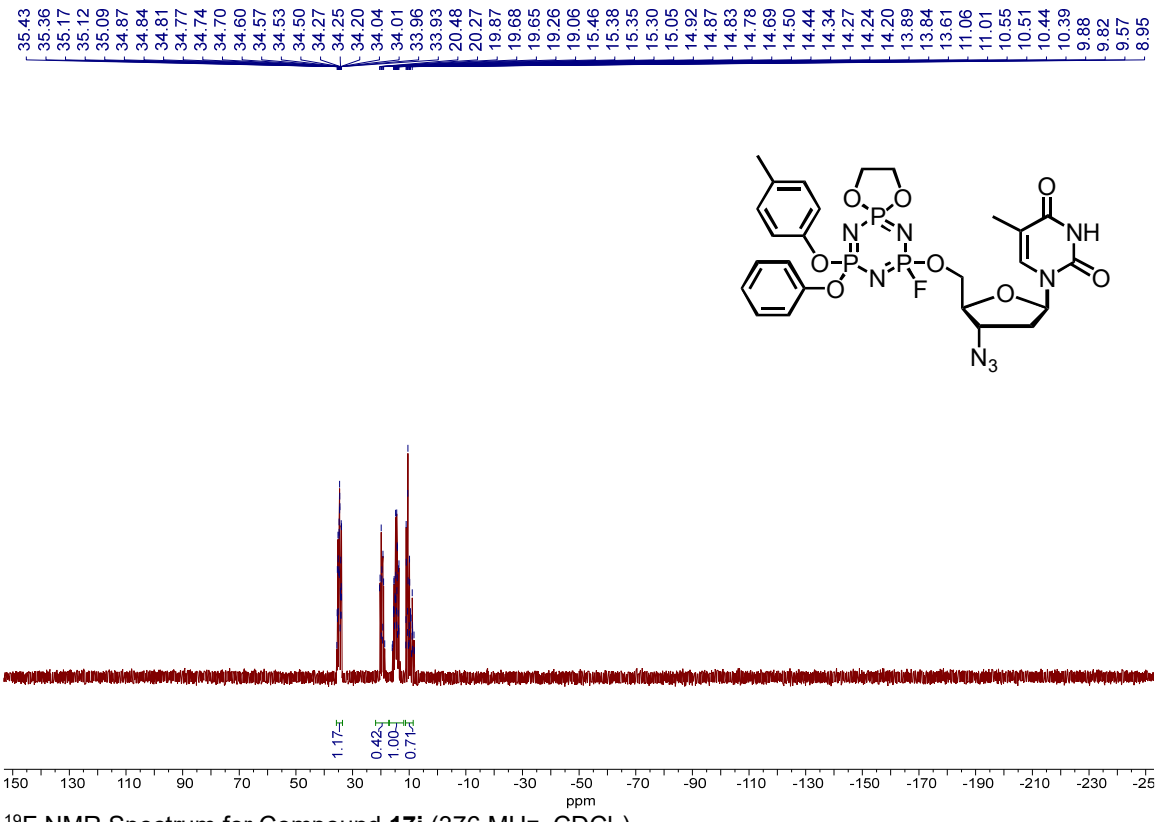
^{1}H NMR Spectrum for Compound **17i** (400 MHz, $CDCl_3$)



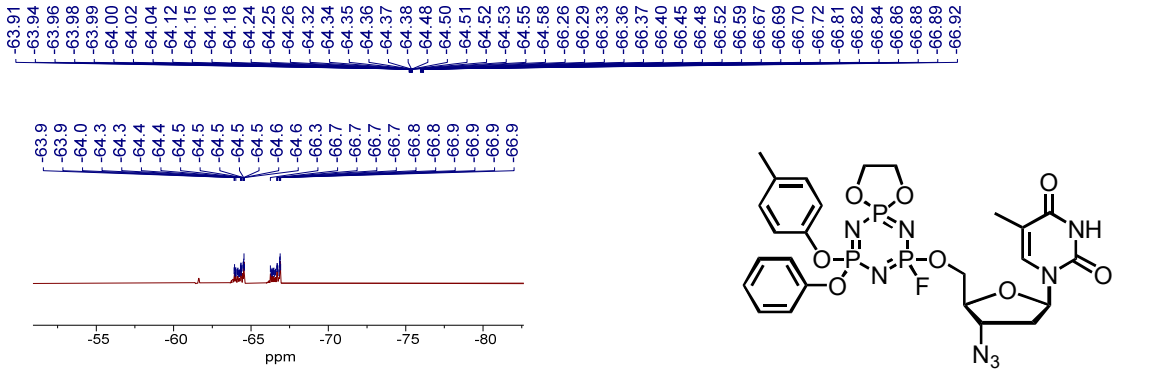
^{13}C NMR Spectrum for Compound **17i** (101 MHz, $CDCl_3$)



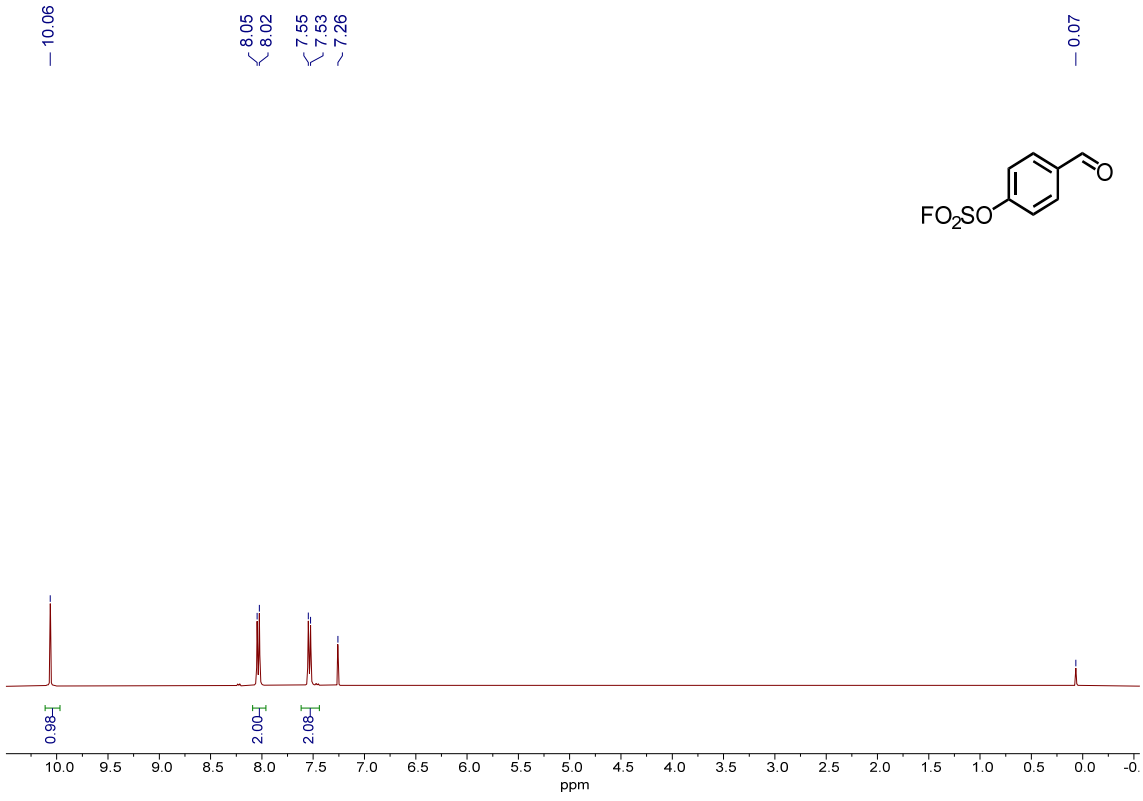
^{31}P NMR Spectrum for Compound **17i** (162 MHz, $CDCl_3$)



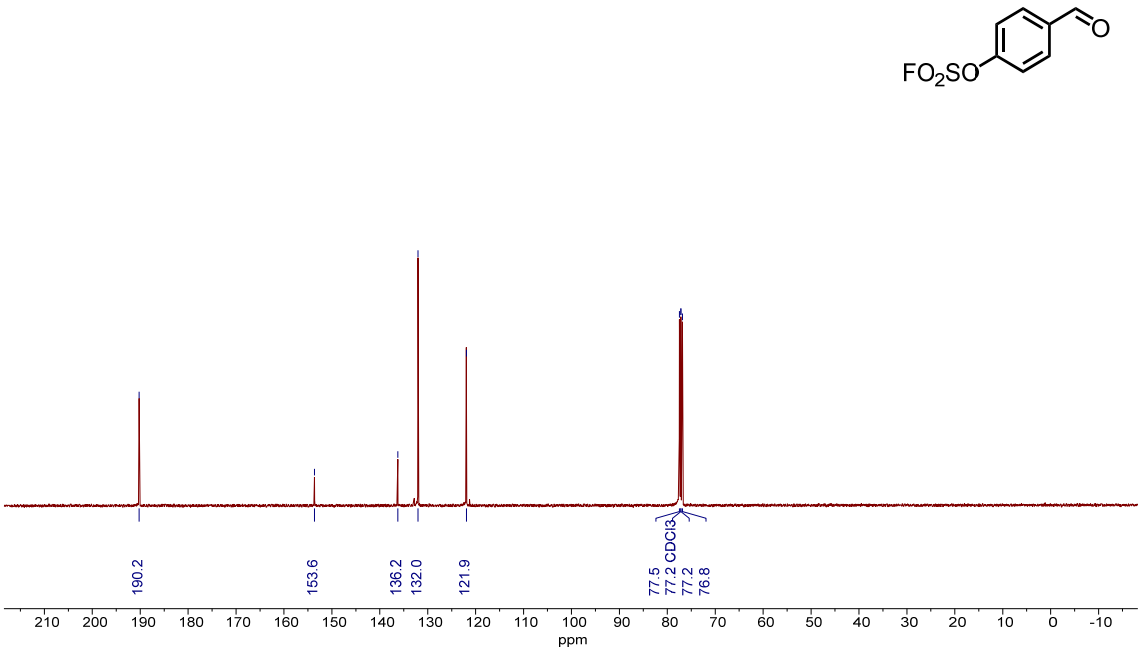
^{19}F NMR Spectrum for Compound **17i** (376 MHz, $CDCl_3$)



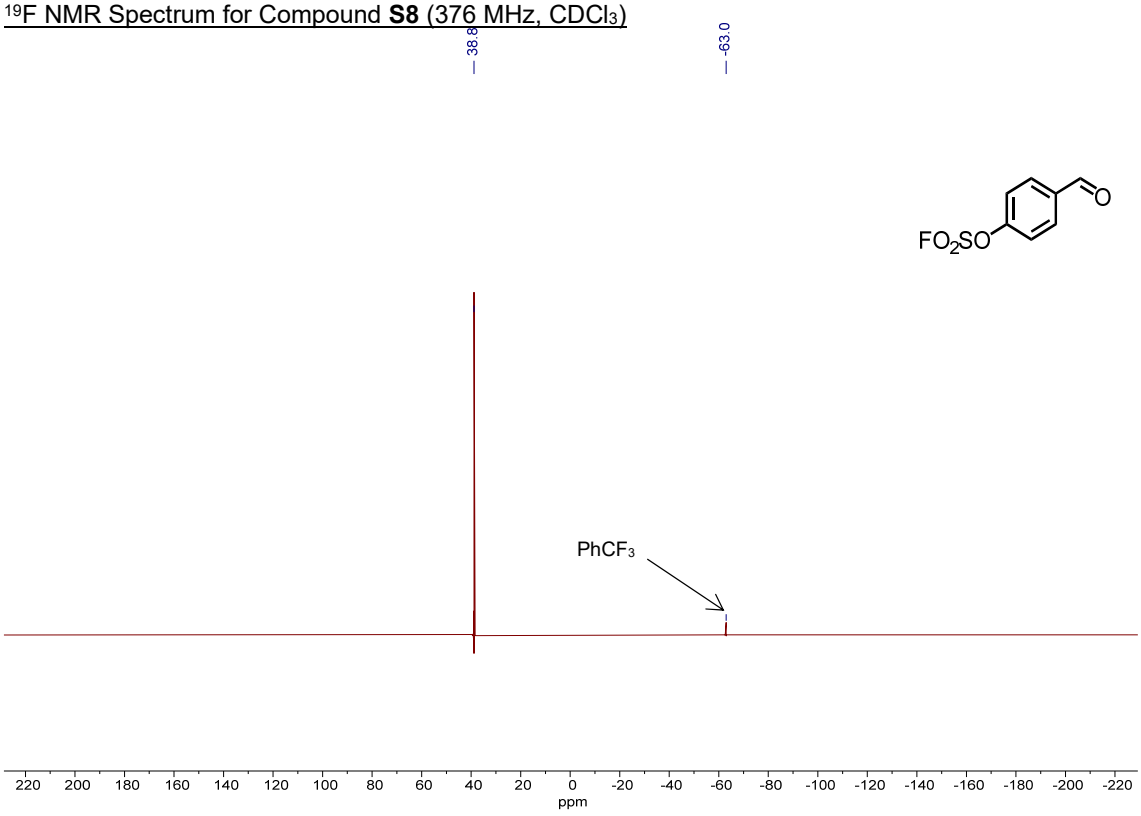
[1]H NMR Spectrum for Compound **S8** (400 MHz, $CDCl_3$)



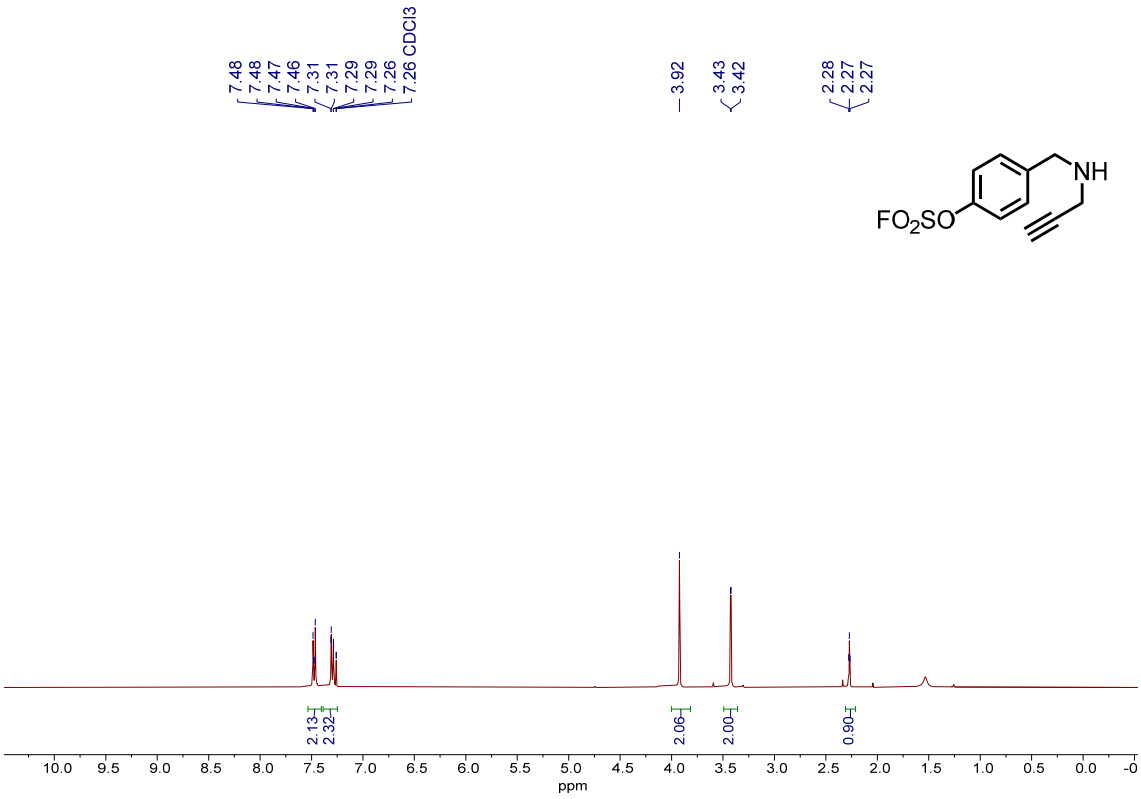
^{13}C NMR Spectrum for Compound **S8** (101 MHz, $CDCl_3$)



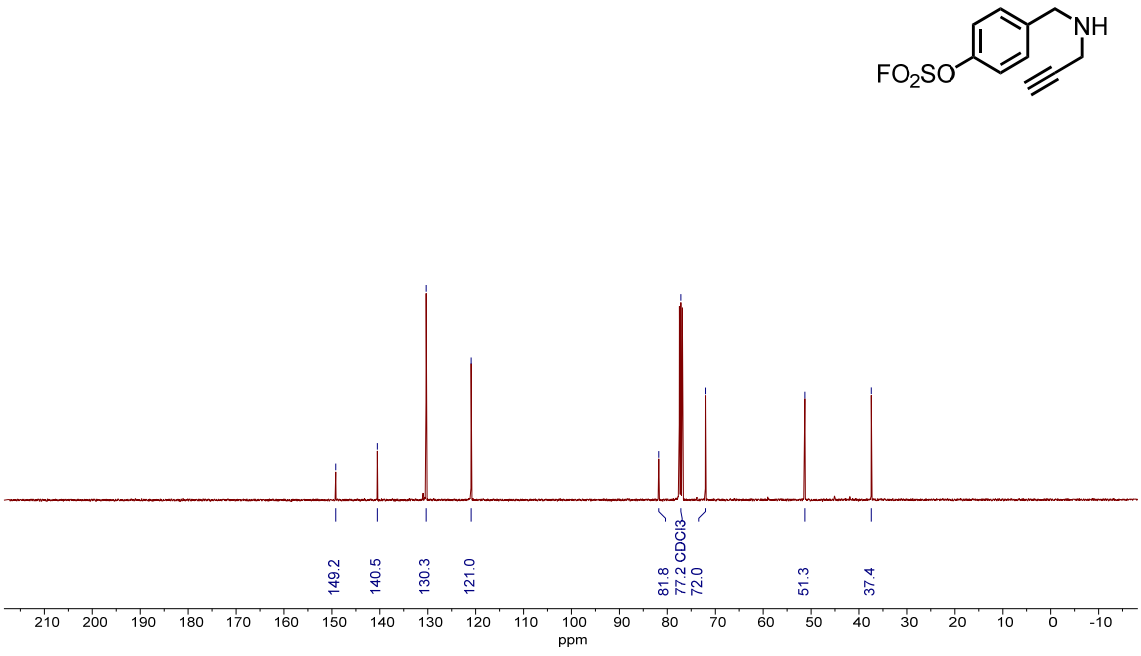
^{19}F NMR Spectrum for Compound **S8** (376 MHz, $CDCl_3$)



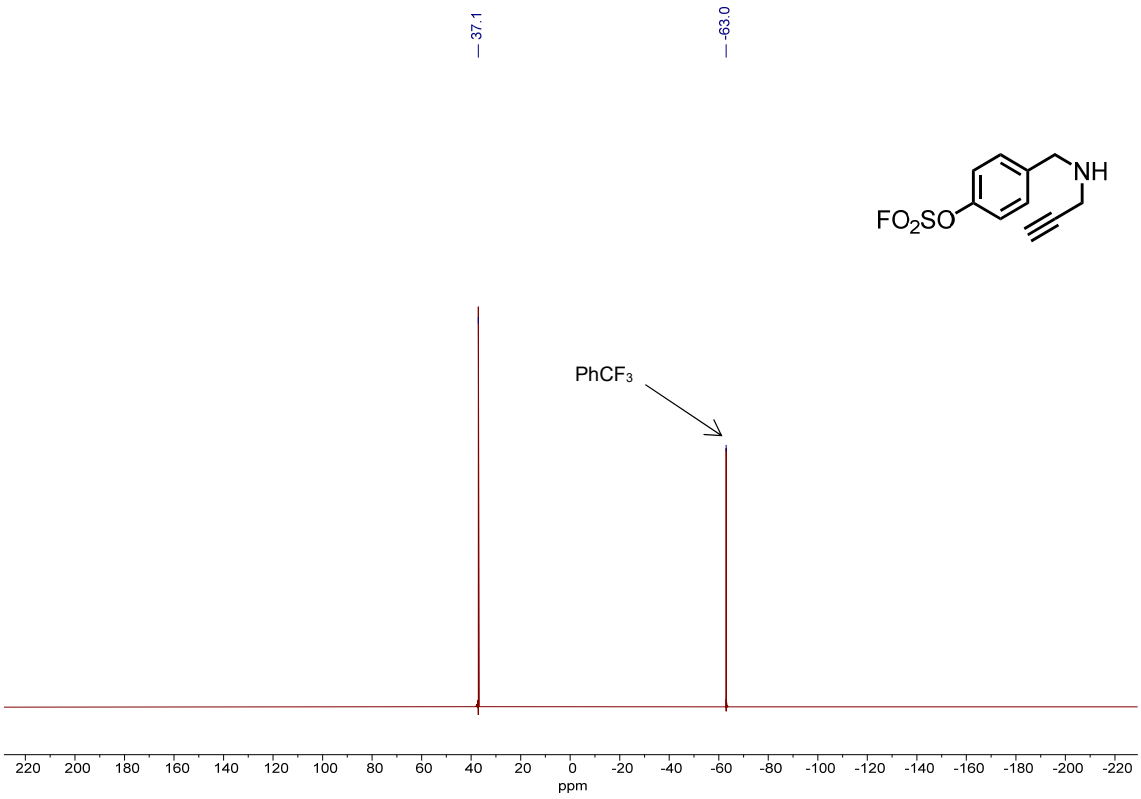
[1]H NMR Spectrum for Compound **S9** (400 MHz, $CDCl_3$)



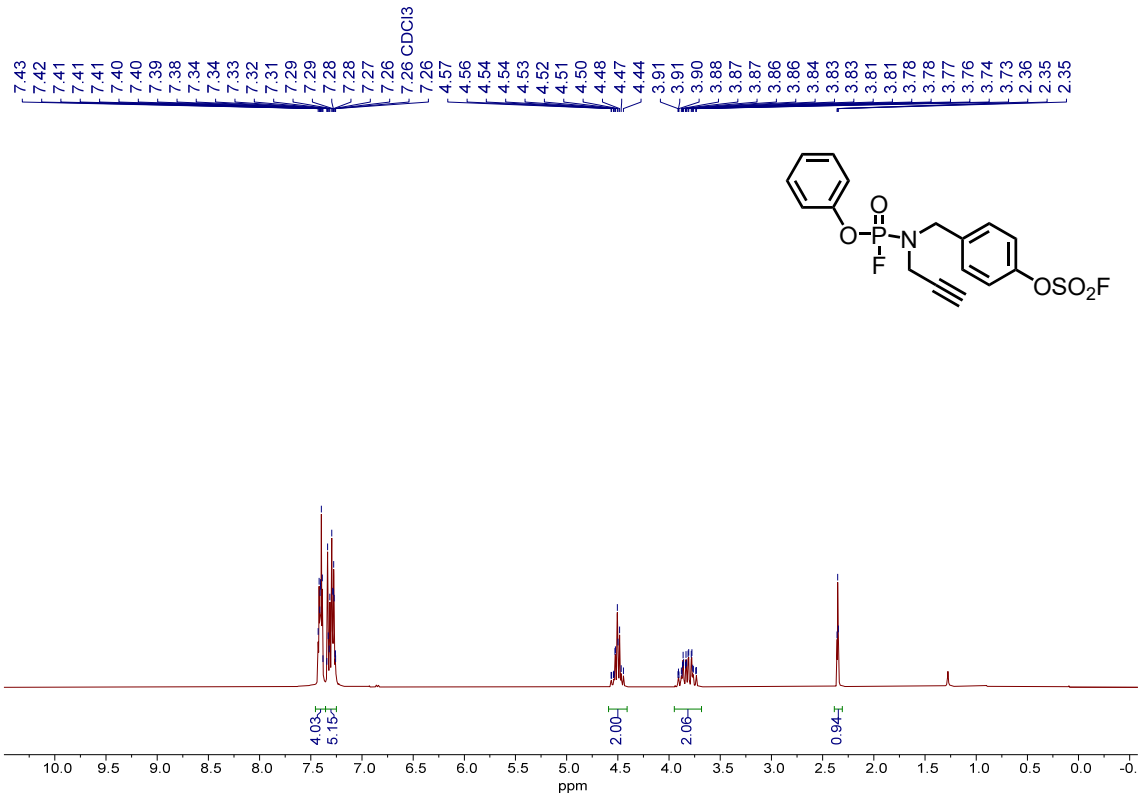
[13]C NMR Spectrum for Compound **S9** (101 MHz, $CDCl_3$)



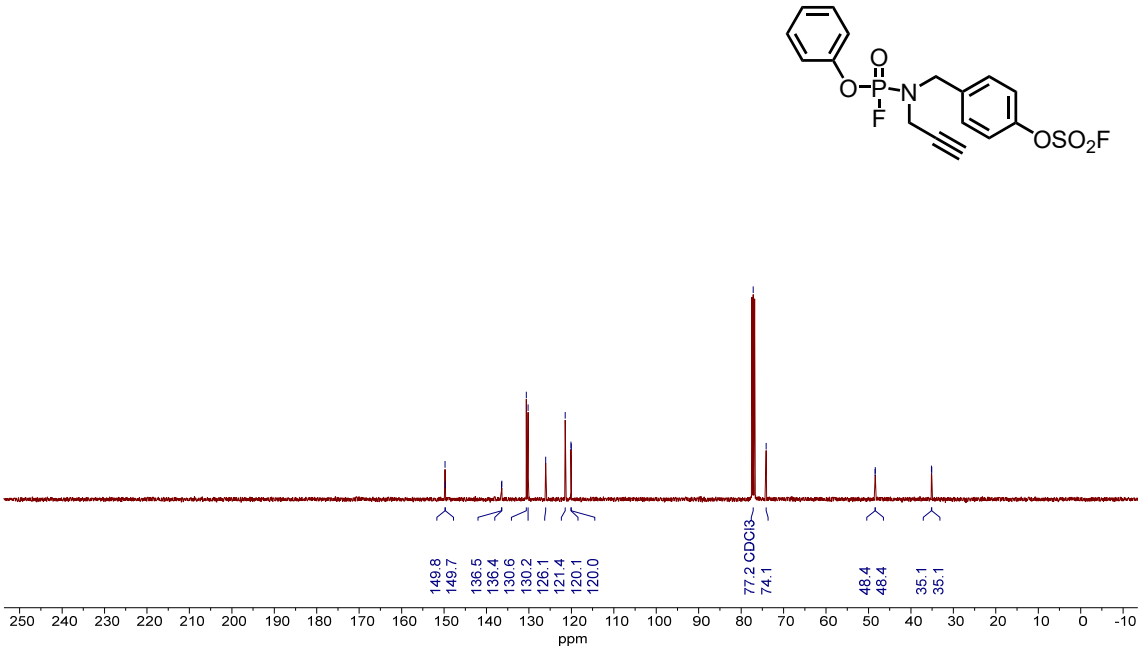
^{19}F NMR Spectrum for Compound **S9**(376 MHz, $CDCl_3$)



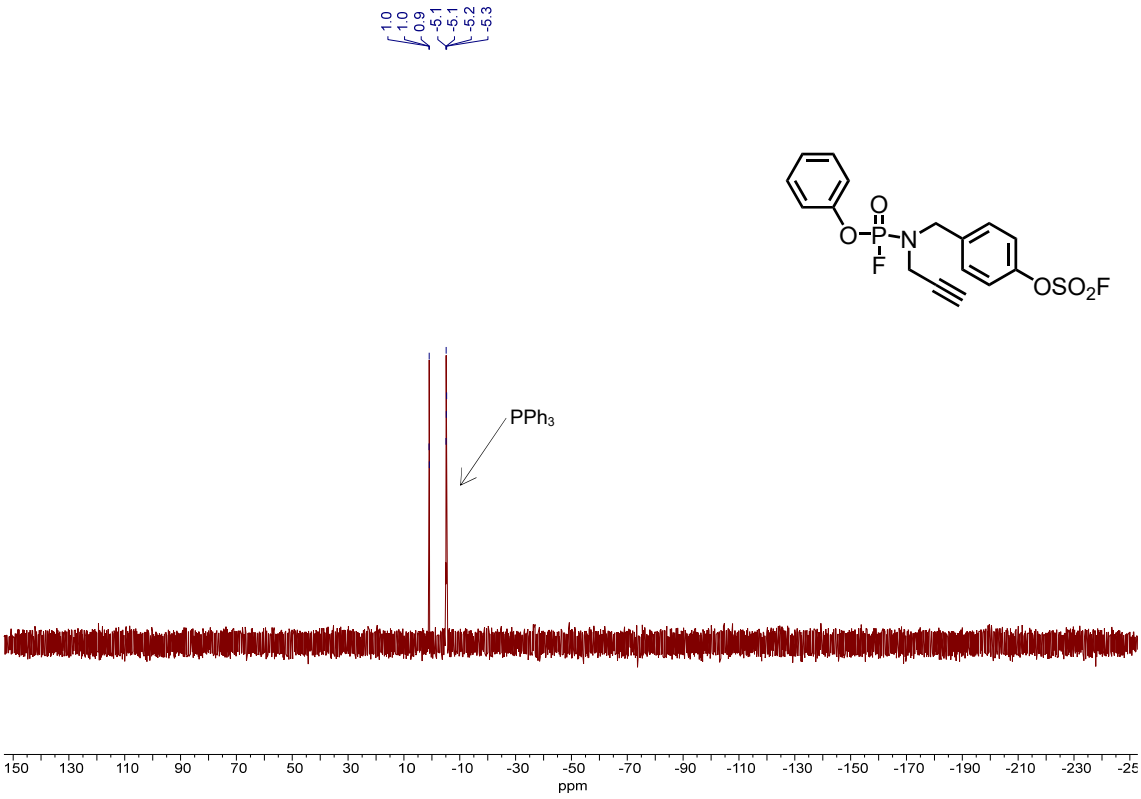
^{1}H NMR Spectrum for Compound **18** (400 MHz, $CDCl_3$)



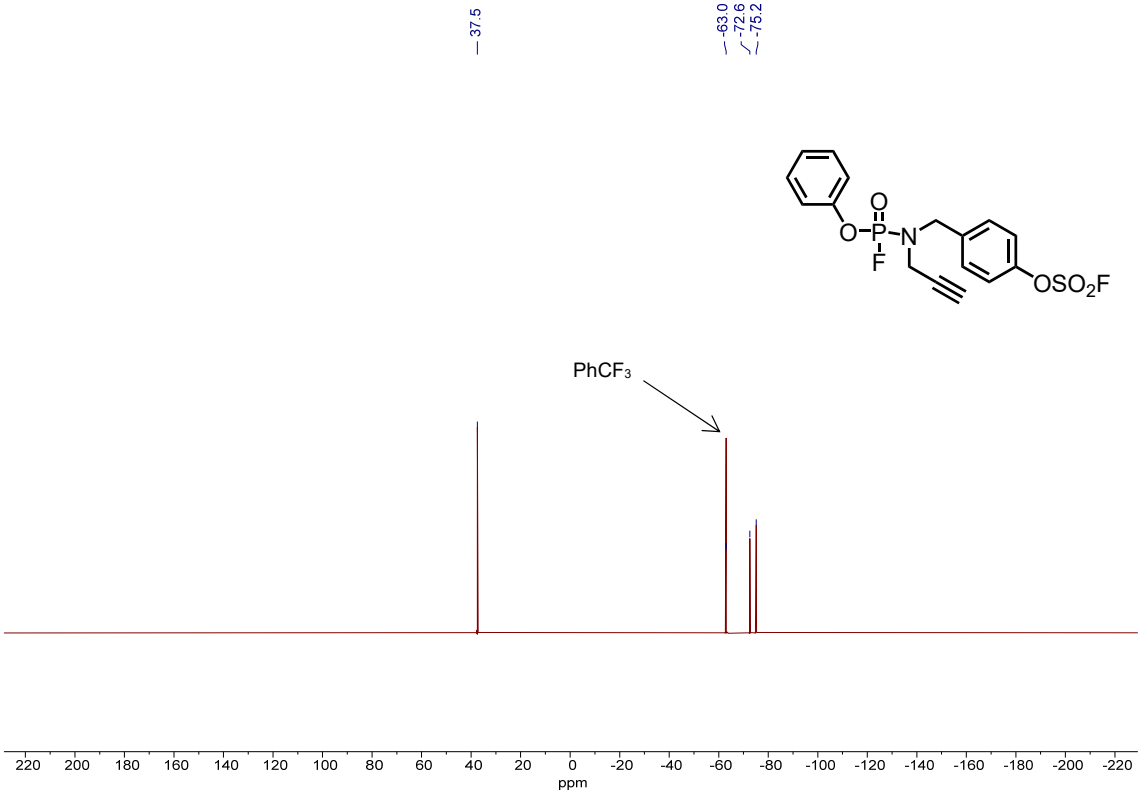
^{13}C NMR Spectrum for Compound **18** (101 MHz, $CDCl_3$)



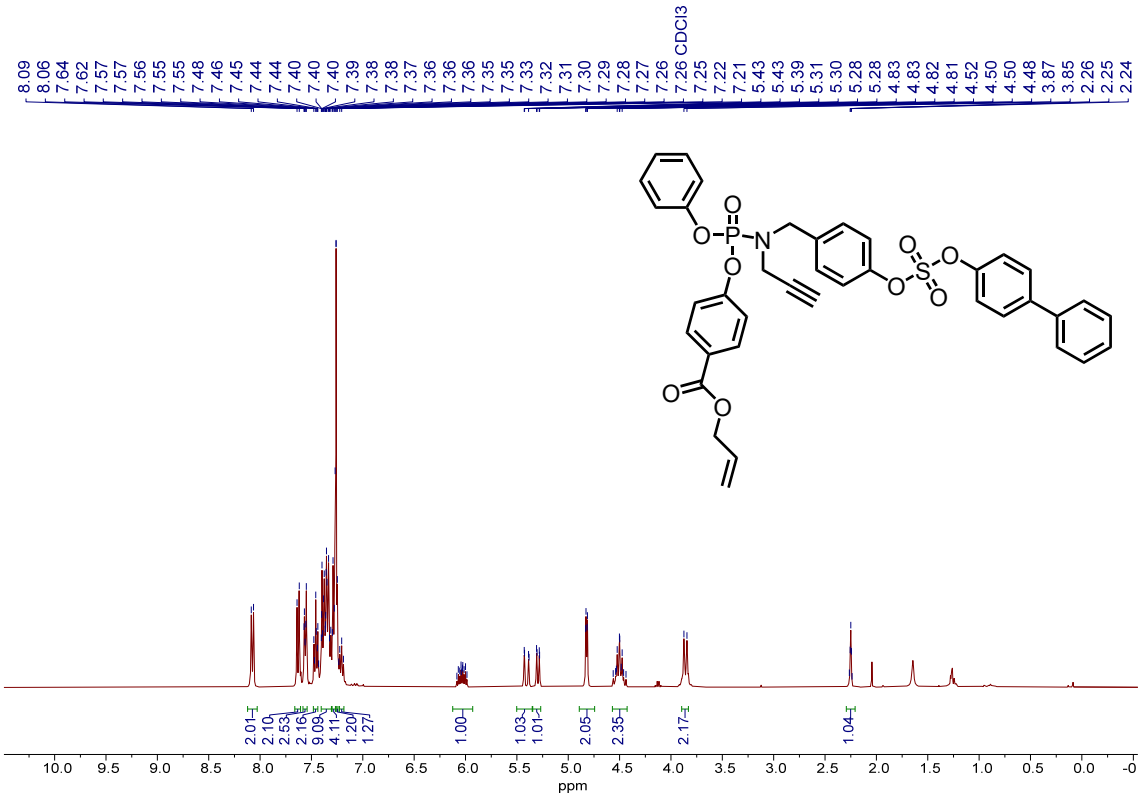
^{31}P NMR Spectrum for Compound **18** (162 MHz, $CDCl_3$)



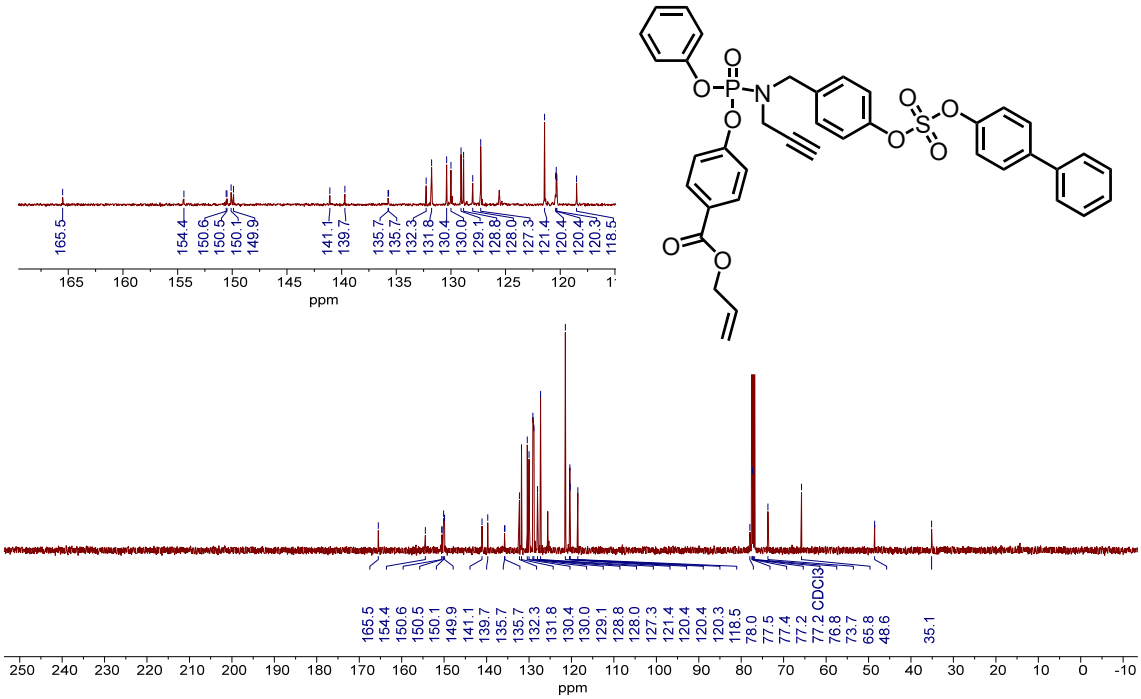
^{19}F NMR Spectrum for Compound **18** (376 MHz, $CDCl_3$)



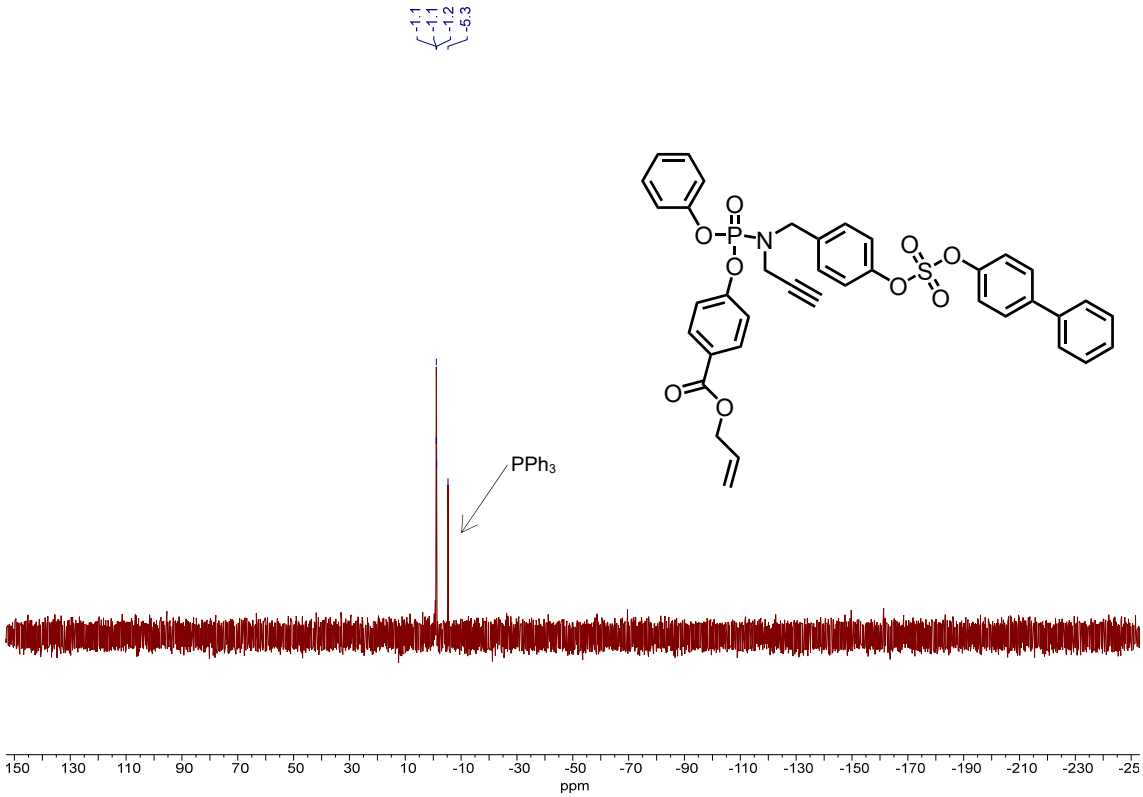
^{1}H NMR Spectrum for Compound **20** (400 MHz, $CDCl_3$)



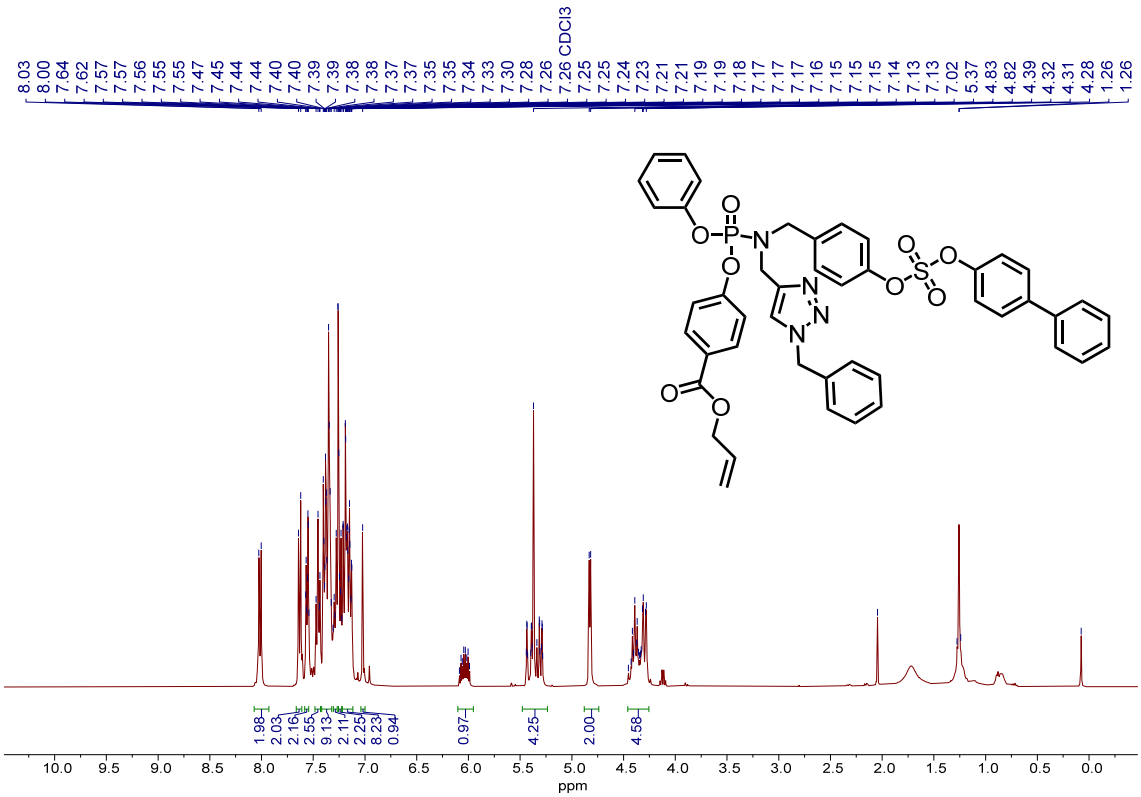
^{13}C NMR Spectrum for Compound **20** (101 MHz, $CDCl_3$)



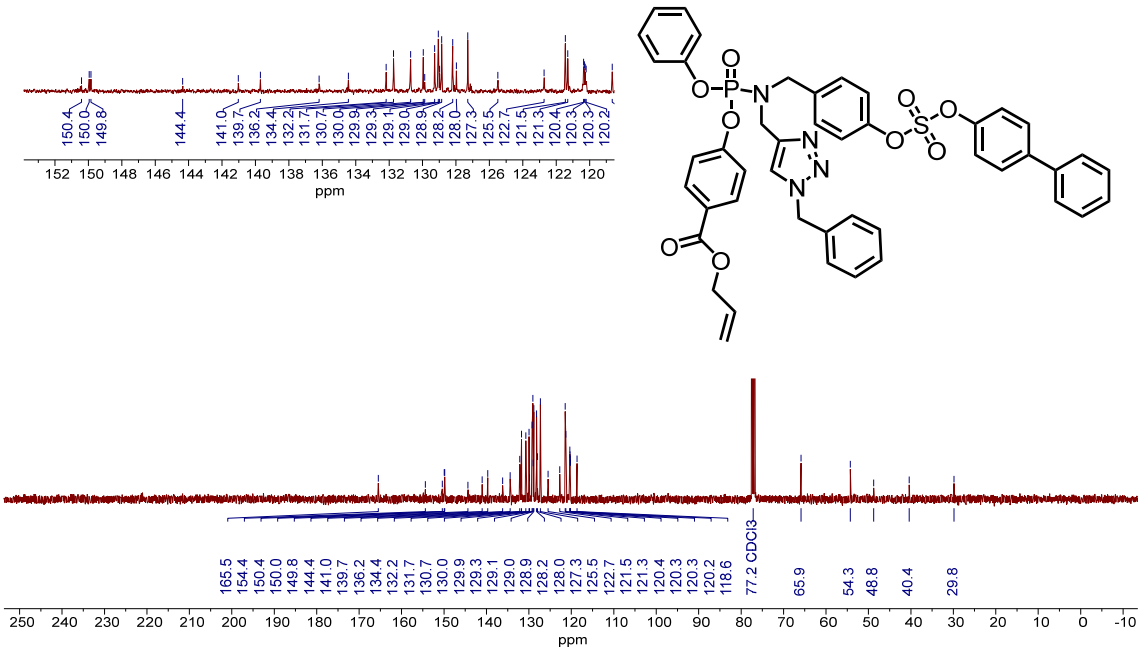
^{31}P NMR Spectrum for Compound **20** (162 MHz, $CDCl_3$)



^{1}H NMR Spectrum for Compound **21** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum for Compound **21** (101 MHz, $CDCl_3$)



^{31}P NMR Spectrum for Compound **21** (162 MHz, $CDCl_3$)