Supporting Information

Visible-Light-Driven Organophotocatalyzed *mono*-, *di*- and *tri*-C(sp^3)–H Alkylation of Phosphoramides

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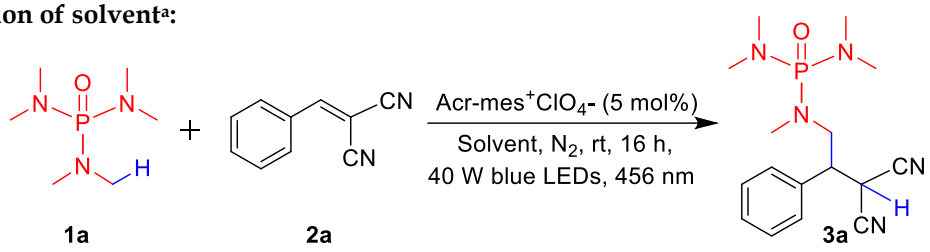
1. Optimization of reaction conditions:

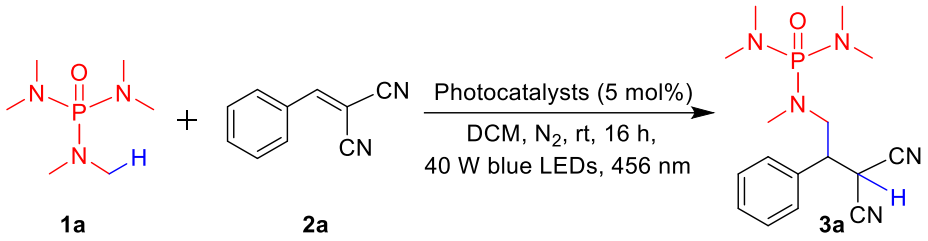
Table S1. Optimization of solvent[a]:



Entry	Solvent	Yield[b] (%)
1	Acetone	56
2	DMSO	35
3	THF	62
4	CH_3CN	84
5	$CHCl_3$	93
6	**DCM**	**95**
7	DCE	92
8	DMF	76
9	Benzene	41
10	NMP	18
11	Chlorobenzene	78
12	EtOAc	52
13	DME	47
14	Dioxane	50

[a]Reaction condition: **1a** (1.0 mmol), **2a** (0.2 mmol), Acr-mes$^+$ClO$_4^-$ (5 mol%), solvent (1.0 mL), irradiation with 456 nm, 40 W Blue LED, rt, 16 h, [b]^{1}H NMR Yield using tetrachloroethane as internal standard.

Table S2. Optimization of photocatalysts[a]:

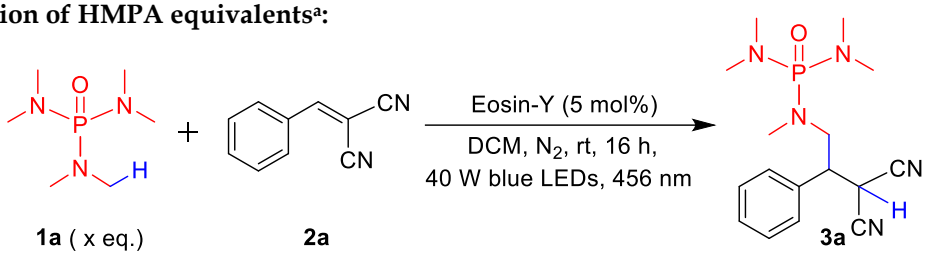


1a **2a** **3a**

Entry	Photocatalysts	Yield[b] (%)
1	Acr-mes$^+$$ClO_4^-$	97
2	$Ru(bpy)_3Cl_2$	0
3[c]	*fac*-$Ir(ppy)_3$	0
4	$Ru(phen)_3Cl_2$	0
5	$Ru(bpm)_3PF_6$	0
6	$Ru(bpz)_3PF_6$	0
7[c]	$Ir[(dFCF_3)ppy]_2(dtbbpy)BF_4^-$	14
8[c]	$Ir(ppy)_2(dtbbpy)BF_4^-$	0
9[c]	$Ir(ppy)_2$(4-Me-bpy)BF_4-	0
10	Eosin-B	0
11	Eosin-Y	99
12	Na_2Eosin-Y	89
12	Rhodhamine B	0
13	Rose Bengal	0
14	Erythrosine B	0
15	T(*p*-F)PPT	36
16	T(*p*-CH_3)PPT	66
17	T(*p*-Cl)PPT	63

[a]Reaction condition: **1a** (1.0 mmol), **2a** (0.2 mmol), photocatalysts (5 mol%), DCM (1.0 mL), irradiation with 456 nm, 40 W Blue LED, rt, 16 h, [b]^{1}H NMR Yield using tetrachloroethane as internal standard. [c]2 mol% of photocatalysts was used.

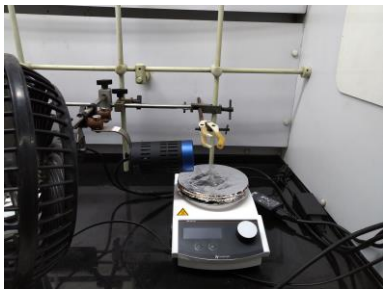
Table S3. Optimization of HMPA equivalents[a]:

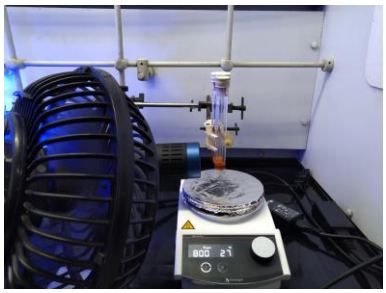


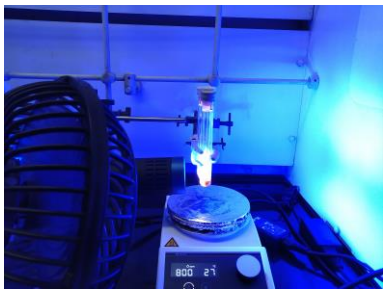
Entry	1a (eq.)	Yield[b] (%)
1	1	52
2	2	72
3	3	81
4	4	89
5	5	99

[a]Reaction condition: **1a** (x eq.), **2a** (0.2 mmol), Eosin-Y (5 mol%), DCM (1.0 mL), irradiation with 456 nm, 40 W Blue LED, rt, 16 h, [b]^{1}H NMR Yield using tetrachloroethane as internal standard.

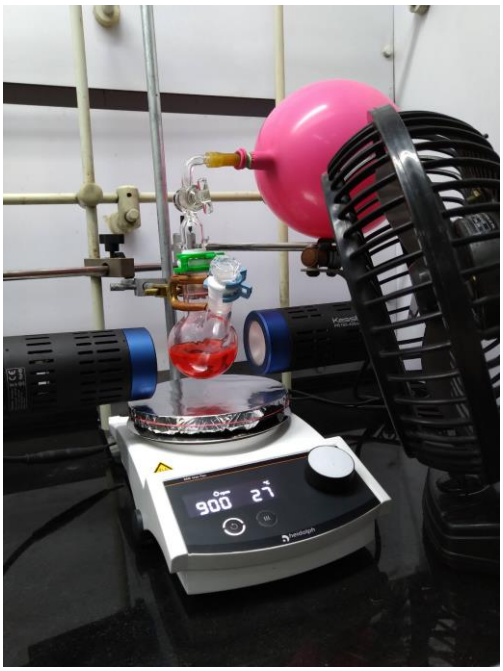
2.1. Reaction setup for synthesis of 3, 4, 5 and 6:

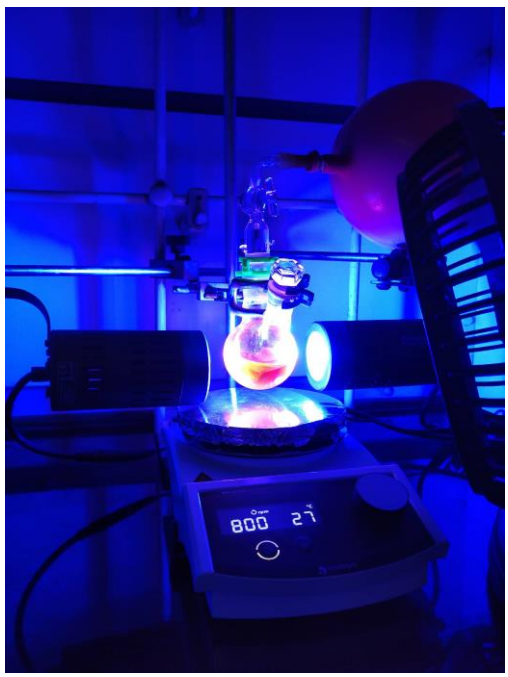






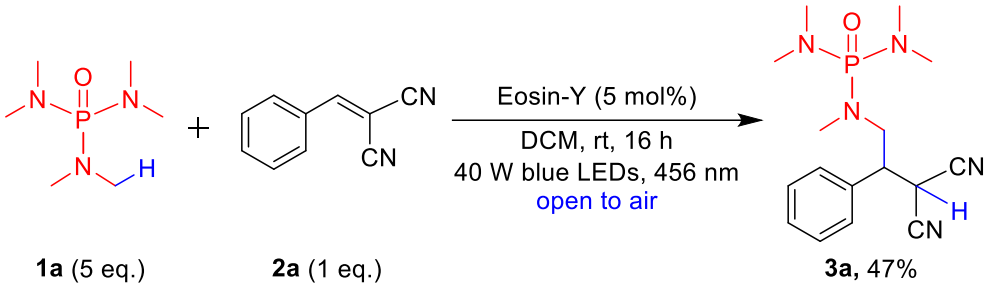
2.2. Reaction setup for gram scale synthesis of 3a:



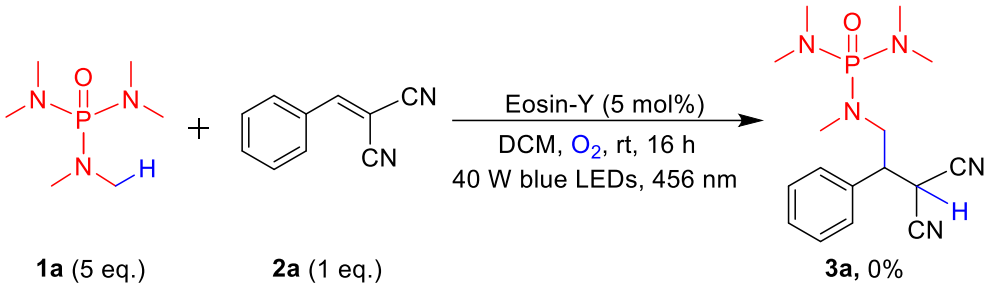


3. Mechanistic investigation:

3.1. Effect of air and O_2:



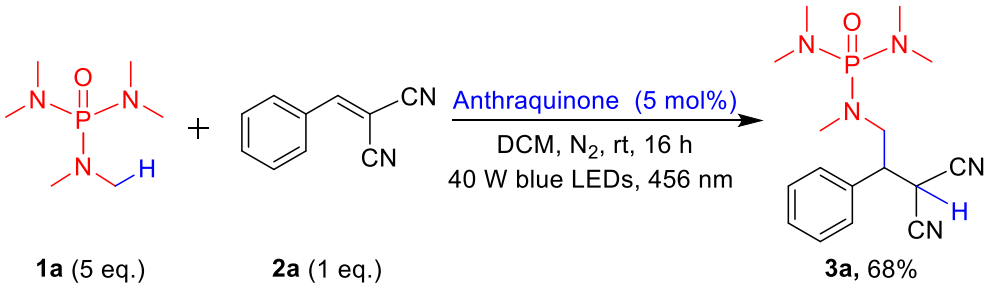
To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar, 0.2 mmol of **2** (1 eq.), 1 mmol of **1** (5 eq.), and 0.01 mmol of Eosin-Y (5 mol%) was added. Then, 1 mL of dry DCM was added and the reaction tube was placed ~2.5 away cm from a Kessil 40 W 456 nm LED setup and ~30 cm from a cooling fan to maintain room temperature. The reaction was kept open to air. After 16 h of the reaction 10 mL of water was added and extracted with DCM (3 x 20 mL). The combined organic layer was dried over Na_2SO_4 and solvent was evaporated under reduced pressure. ^{1}H NMR showed a decreased yield of 47% using tetrachloroethane as a standard.



To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar, 0.2 mmol of **2** (1 eq.), 1 mmol of **1** (5 eq.), and 0.01 mmol of Eosin-Y (5 mol%) was added. The reaction tube was vacuumed and backfilled with oxygen (3 times) and sealed with a septum. Then, 1 mL of dry DCM was added through the septum by a syringe and placed ~2.5 away cm from a Kessil 40 W 456 nm LED setup and ~30 cm away from a cooling fan to maintain room temperature. After 16 h of the reaction, 10 mL of water was added and extracted with DCM (3 x 20 mL). The combined organic layer was dried over Na_2SO_4 and solvent was evaporated under reduced pressure. ^{1}H NMR was recorded from the crude which indicated the failure of the reaction.

The above results suggest that oxygen can quench the reaction. Hence, the active catalysts for this reaction is triplet state of Eosin-Y.

3.2. Experiment with Anthraquinone photocatalyst:

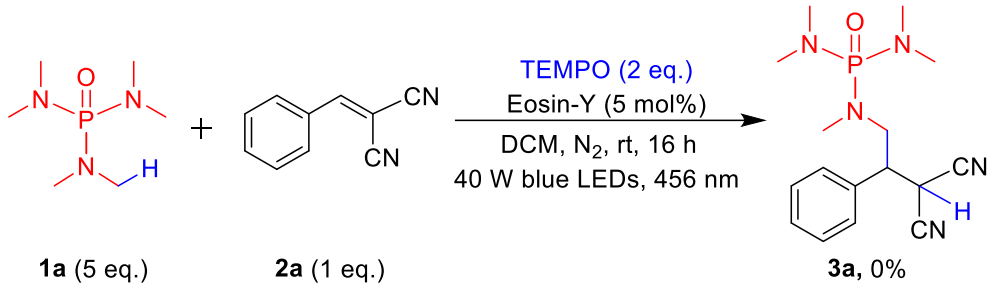


To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar, 0.2 mmol of **2** (1 eq.), 1 mmol of **1** (5 eq.), and 0.01 mmol of anthraquinone (5 mol%) was added. The reaction tube was vacuumed and backfilled with nitrogen (3 times) and secured with a septum. Then, 1 mL of dry DCM was added using a syringe and the reaction tube was placed ~3 cm away from a Kessil 40 W 456 nm LED setup and ~30 cm away from a cooling fan to maintain room temperature. After 16 h of the reaction, 10 mL of water was added and extracted with DCM (3 x 20 mL). The combined organic layer

was dried over Na_2SO_4 and solvent was evaporated under reduced pressure. ^1H NMR yield of the reaction was 68% based on tetrachloroethane as an internal standard.

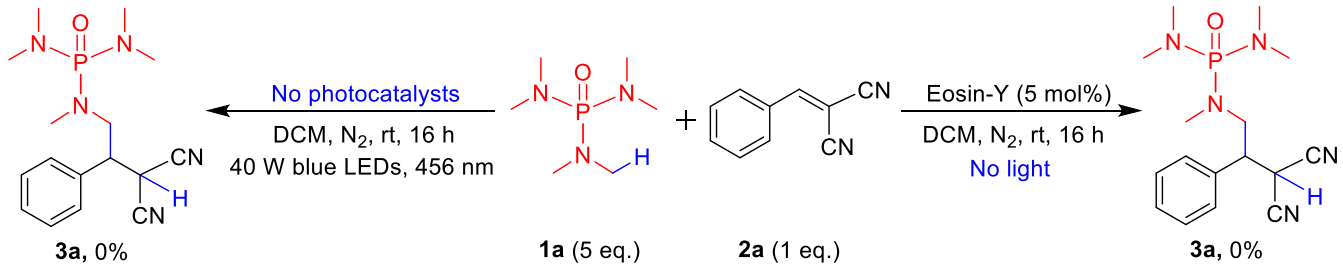
Anthraquinone is a well-known direct HAT photocatalyst. Therefore, the above result suggests that our reaction proceeds through direct HAT mechanism.

3.3. Radical trapping experiment with TEMPO:



To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar, 0.2 mmol of **2** (1 eq.), 1 mmol of **1** (5 eq.), 0.01 mmol of Eosin-Y (5 mol%) and 0.4 mmol of TEMPO (2 eq.) was added. The reaction tube was vacuumed and backfilled with nitrogen (3 times) and sealed with a septum. Then, 1 mL of dry DCM was added using a syringe and placed ~3 cm away from a Kessil 40 W 456 nm LED setup and ~30 cm away from a cooling fan to maintain temperature. After 16 h of the reaction 10 mL of water was added and extracted with DCM (3 x 20 mL). The combined organic layer was dried over Na_2SO_4 and solvent was evaporated under reduced pressure. ^1H and ^{31}P NMR was recorded from the crude which indicated the complete failure of the reaction. Thus, it indicates that our reaction is proceeds through radical mechanism.

3.4. Reaction without photocatalyts or without light:



When our standard reaction was performed in the absence of any photocatalyst or light irradiation source, no trace of desired product was found, which indicates the absolute necessity of photocatalyst and/or light.

4. UV-Vis Absorption of Eosin-Y:

To measure the UV-Vis absorption of the different forms of Eosin-Y, 10 mM of commercially available Eosin-Y, 1 mM of Na_2Eosin-Y, 10 mM of TFA and 1 M of HMPA solution in acetonitrile were prepared and used as stock solution and all other solutions with different concentration was prepared by dilution. (1 mM Eosin-Y + 1 mM TFA) solution in acetonitrile was considered as neutral Eosin-Y and (50 µM Eosin-Y + 50 µM NaOH aq.) solution in acetonitrile was considered as NaEosin-Y.

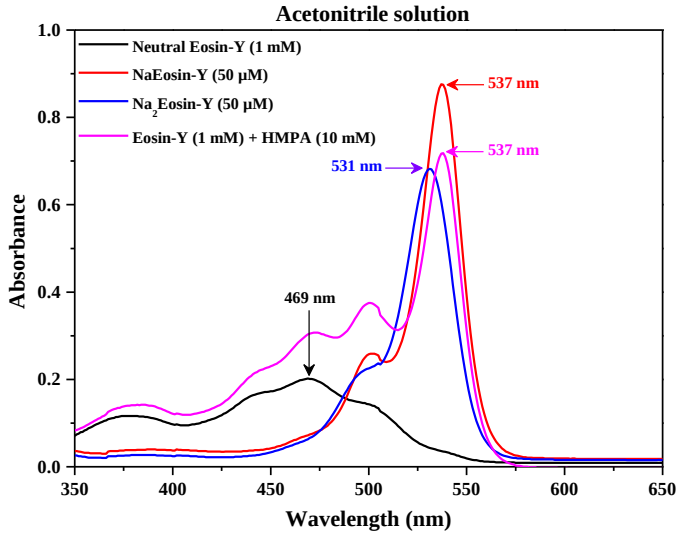


Figure S1. UV-Vis spectrum of different forms of Eosin Y in acetonitrile solution.

Acetonitrile solution: Neutral Eosin-Y (1 mM) (black line); NaEosin-Y (50 µM) (red line); Na_2Eosin-Y (50 µM) (blue line); Eosin-Y (1 mM) + HMPA (10 mM) (pink line).

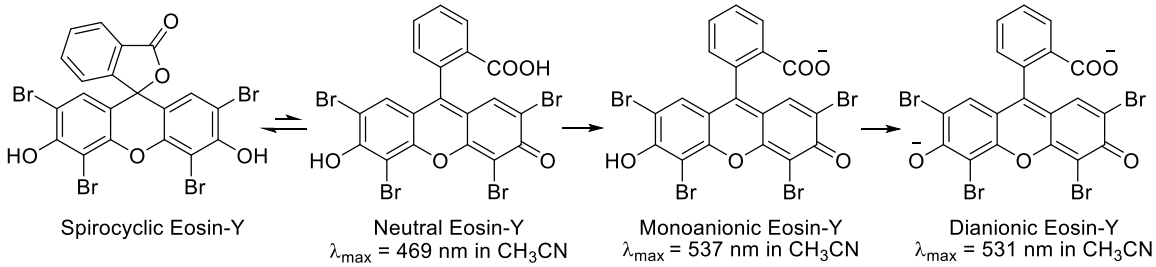


Figure S2. λ_{max} of different forms of Eosin-Y in acetonitrile

We have measured the UV-vis absorption of different forms of Eosin-Y in acetonitrile as depicted in Figure S1. The neutral Eosin-Y has an absorption maximum at 469 nm. The monoanionic Eosin-Y (NaEosin-Y) and dianionic Eosin-Y have absorption maximum at 537 nm and 531 nm respectively. Again, when we measured the absorption maximum of neutral Eosin-Y after addition of HMPA (neutral Eosin-Y + HMPA), we observed an absorption maximum at 537 nm, similar to monoanionic Eosin-Y. Based on UV-Vis studies, we conclude that the active catalyst for our reaction system is the monoanionic form of Eosin-Y.

5. Luminescence quenching studies on different forms of Eosin-Y with substrate 2a and HMPA:

To perform luminescence quenching studies on different forms of Eosin-Y, 10 mM of commercially available Eosin-Y, 1 mM of Na_2Eosin-Y, 10 mM of TFA, 1 M of HMPA, and 1 M of substrate **2a** solution in acetonitrile were prepared as stock solution and all other solutions with different concentration was prepared by dilution. (1 mM Eosin-Y + 1 mM TFA) solution in acetonitrile was considered as neutral Eosin-Y and (50 µM Eosin-Y + 50 µM NaOH aq.) solution in acetonitrile was considered as NaEosin-Y.

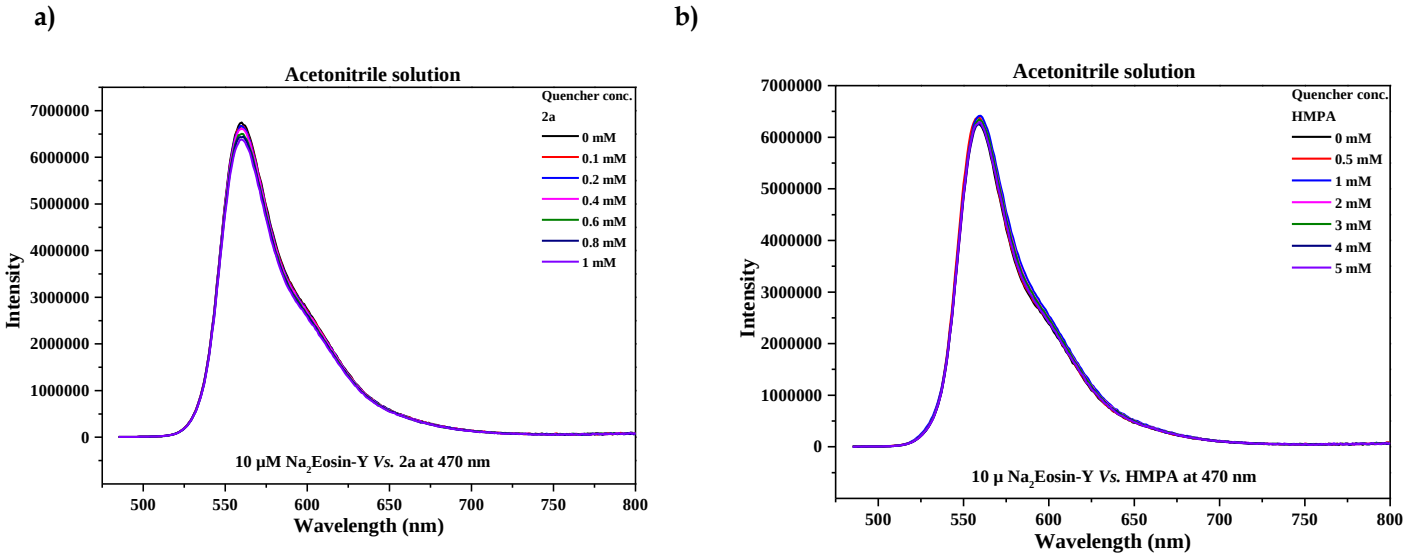


Figure S3. Luminescence quenching spectra of Na_2Eosin-Y *Vs.* **2a** and **HMPA** at λ_{ex} 470 nm

In acetonitrile solution: a) 10 µM Na_2Eosin-Y *Vs.* **2a** at 470 nm; b) 10 µM Na_2Eosin-Y *Vs.* **HMPA** at 470 nm.

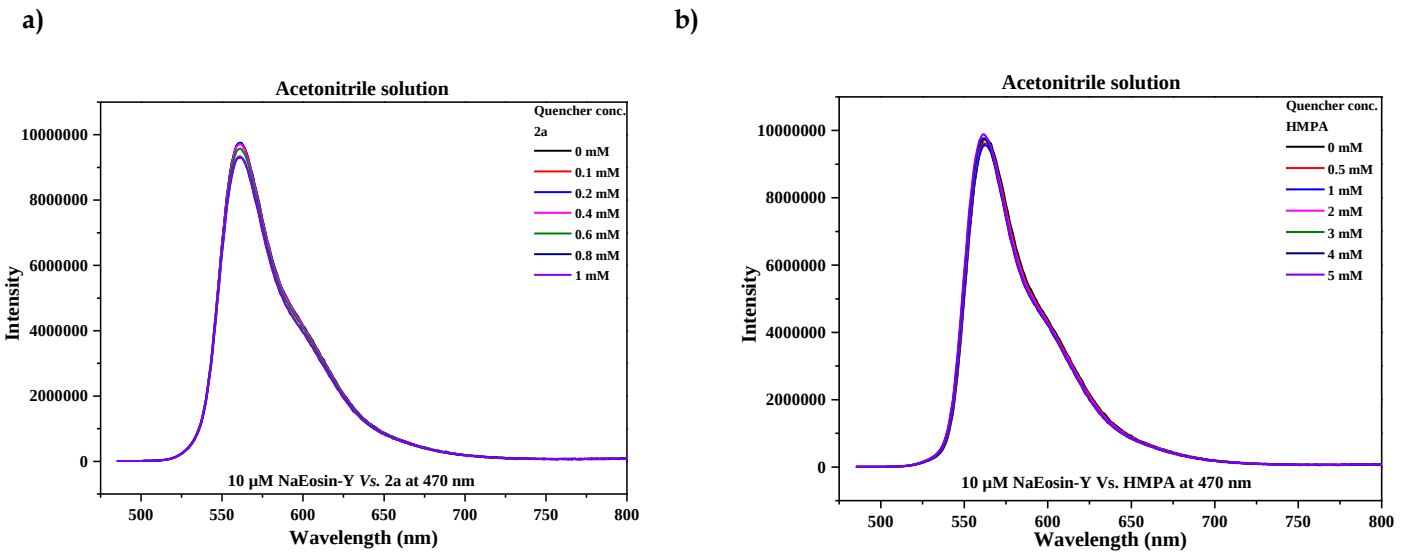


Figure S4. Luminescence quenching spectra of NaEosin-Y *Vs.* **2a** and **HMPA** at λ_{ex} 470 nm.

In acetonitrile solution: a) 10 µM NaEosin-Y *Vs.* **2a** at 470 nm; b) 10 µM NaEosin-Y *Vs.* **HMPA** at 470 nm.

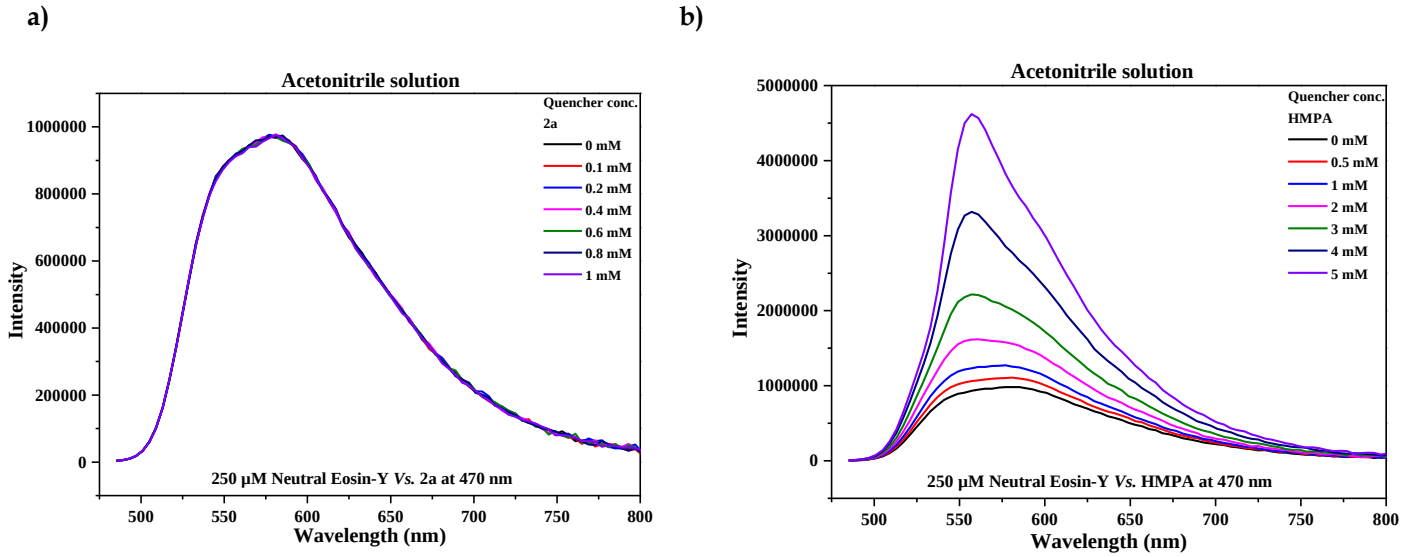


Figure S5. Luminescence quenching spectra of Eosin-Y *Vs*. **2a** and **HMPA** at λ_{ex} 470 nm.

In acetonitrile solution: a) 250 µM Eosin-Y *Vs*. **2a** at 470 nm; b) 250 µM Eosin-Y *Vs*. **HMPA** at 470 nm.

Although our active catalyst is the monoanionic form of Eosin-Y, we have performed luminescence quenching experiments on all three forms of Eosin-Y. There was no quenching of observed for dianionic Eosin-Y (Na_2Eosin-Y) and monoanionic Eosin-Y (NaEosin-Y) neither with Michael acceptor nor with HMPA. In the case of neutral Eosin-Y also, no quenching was observed with respect to Michael acceptor. However, an increase in emission value was observed in the case of neutral Eosin-Y with increasing concentration of HMPA. This increase in emission again suggests that the active form of the catalyst is the monoanionic form of Eosin-Y. As there was no quenching was observed for monoanionic and dianionic Eosin-Y with respect to HMPA, we believe that our reaction follows a direct hydrogen atom transfer (HAT) mechanism.

6. Luminescence quenching studies of Acr-mes$^+$ClO$_4^-$ with substrate 2a and HMPA:

To perform luminescence quenching studies of Acr-mes$^+$ClO$_4^-$, 10 mM of commercially available Acr-mes$^+$ClO$_4^-$, 1 M of HMPA, and 1 M of substrate **2a** solution in acetonitrile was prepared as a stock solution and all other solutions with different concentration were prepared by dilution.

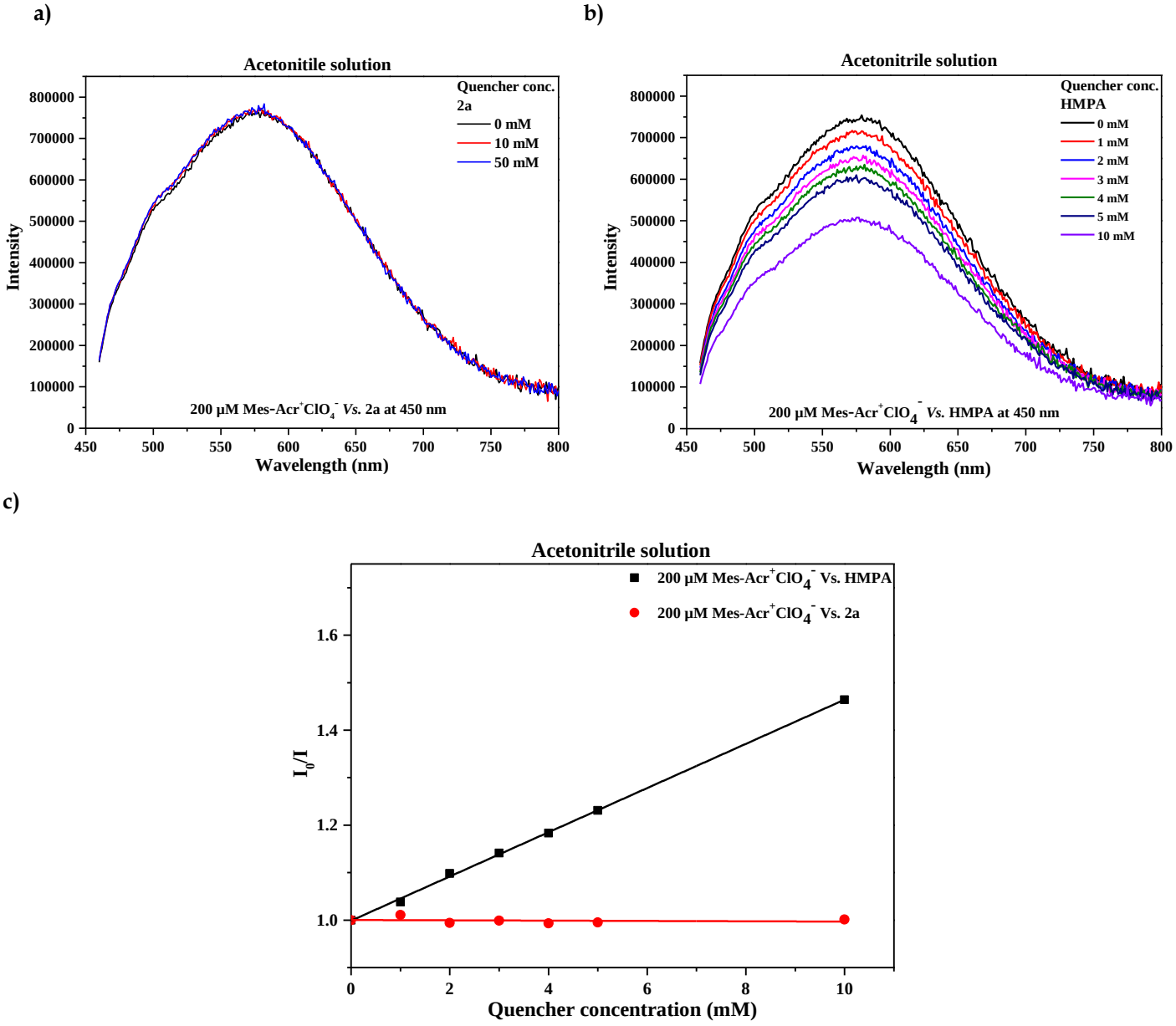
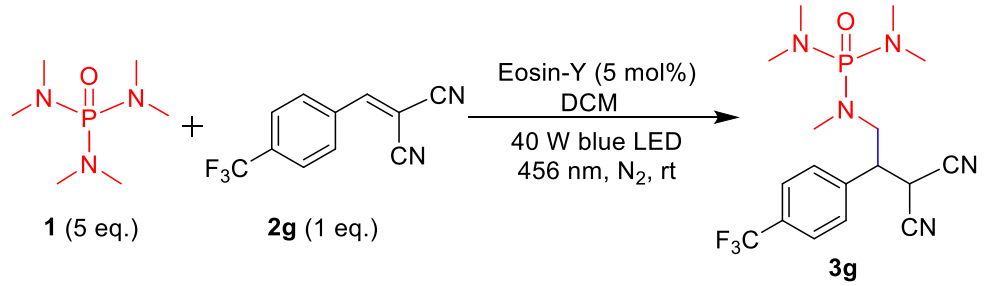


Figure S6. Luminescence quenching spectra of Acr-mes$^+$ClO$_4^-$ at λ_{ex} 450 nm.

In acetonitrile solution: a) 200 µM Acr-mes$^+$ClO$_4^-$ *Vs.* **2a** at 450 nm; b) 200 µM Acr-mes$^+$ClO$_4^-$*Vs.* HMPA at 450 nm; c) Stern-Volmer plot of luminescence quenching of 200 µM Acr-mes$^+$ClO$_4^-$*Vs.* **2a** and HMPA.

In the case of acridinium photocatalyst, as expected, no quenching was observed with respect to Michael acceptor shown in Figure S6a. However, quenching of the acridinium photocatalyst was observed with respect to HMPA, as shown in Figure S6b, as well as in Stern-Volmer plot Figure S6c. Therefore, we can conclude that in the case of acridinium photocatalyst, the reaction follows a single electron transfer (SET) pathway mechanism.

7. Light on/off experiment over time:



To an oven-dried 25 mL two-neck round bottom flask equipped with a magnetic stirring bar, 2.25 mmol of **2g** (1 eq.), 11.25 mmol of **1** (5 eq.) and 0.1125 mmol of Eosin-Y (5 mol%) were added. One neck of the flask was sealed with a septum and an adapter with a stopcock was attached to the other. The flask was vacuumed, backfilled with nitrogen (5 times) and a nitrogen balloon was connected to the adapter. Then, 10 mL of dry DCM and 2.25 mmol of benzotrifluoride (1 eq.) (was used as an internal standard for ^{19}F NMR) were added using a syringe and the flask was placed ~3 cm away from one Kessil 40 W 456 nm LED setup and ~30 cm away from a cooling fan to maintain room temperature. The light on/off experiment was performed by altering light-dark conditions (light : dark; 2 : 2 h) for up to 30 h. At the end of each light/dark session, the reaction progress was monitored by measuring the yield based on ^{19}F NMR using benzotrifluoride as an internal standard. The results in Figure S7 show the essential role of light, as the reaction progressed in the presence of light and stopped in the dark. From the experiment, we also speculate that our reaction does not proceed through a chain propagation mechanism.

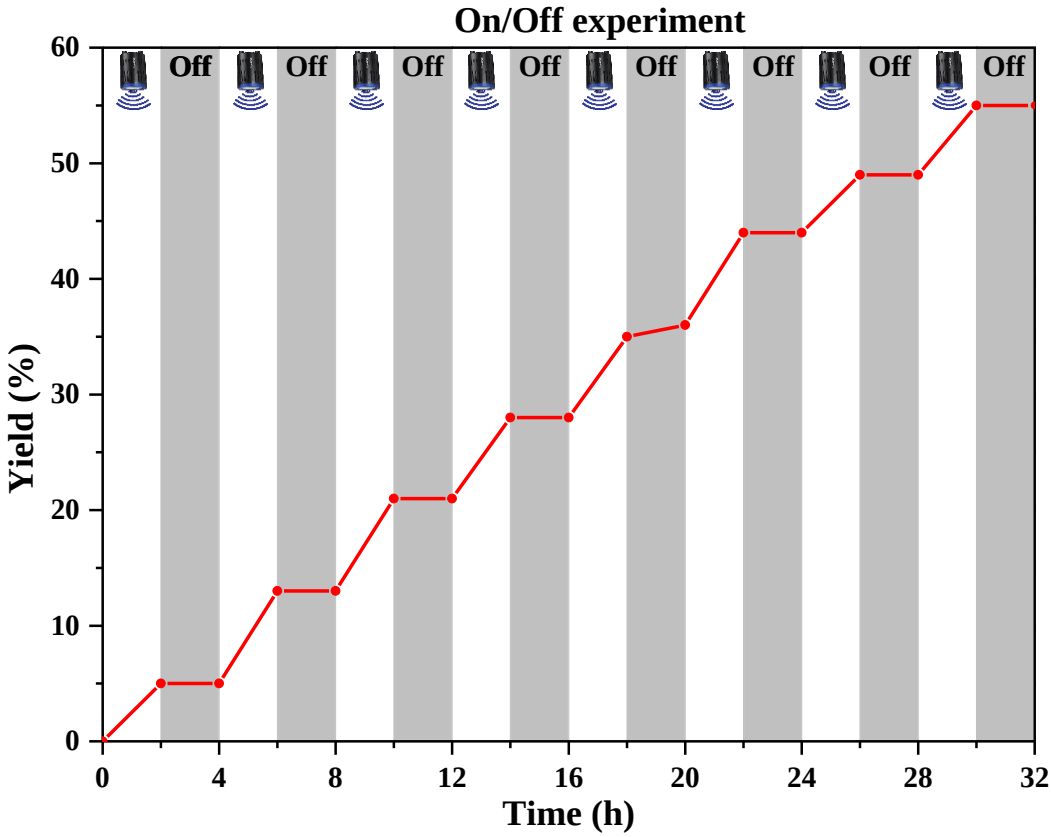
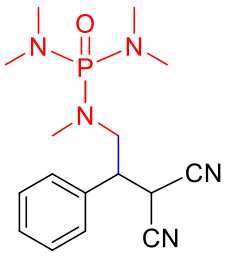


Figure S7. Light On/Off experiment

8. X-ray crystallographic data:

8.1. X-ray crystallographic data of 3a with 50% ellipsoid contour probability:



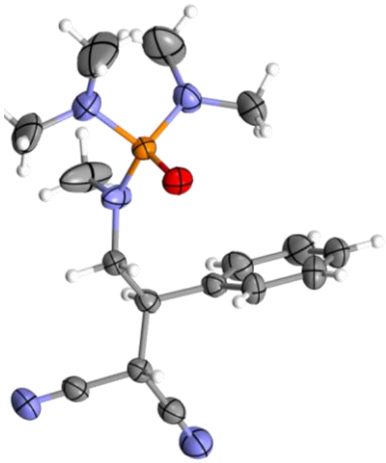
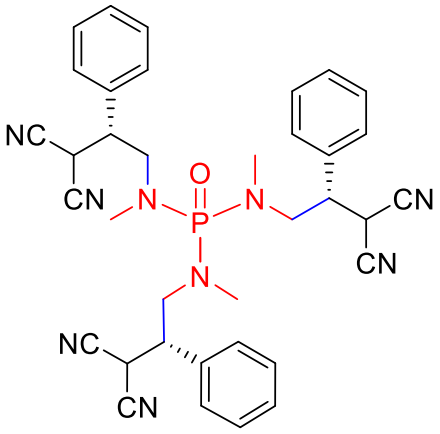


Table S4 Crystal data and structure refinement for Compound 3a:

Identification code	Compound **3a**
Empirical formula	$C_{16}H_{24}N_5OP$
CCDC Number	2003244
Formula weight	333.37
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.6517(2)
b/Å	11.4441(2)
c/Å	16.4948(3)
α/°	90.00
β/°	100.088(2)
γ/°	90.00
Volume/Å³	1979.62(6)
Z	4
ρ_{calc}g/cm³	1.119
μ/mm⁻¹	1.314
F(000)	712.0
Crystal size/mm³	0.3 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.2 to 132.22
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -18 ≤ l ≤ 19
Reflections collected	15379
Independent reflections	3438 [R_{int} = 0.0544, R_{sigma} = 0.0368]
Data/restraints/parameters	3438/0/217
Goodness-of-fit on F²	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0658, wR_2 = 0.1804
Final R indexes [all data]	R_1 = 0.0779, wR_2 = 0.1889
Largest diff. peak/hole / e Å⁻³	0.37/-0.30

8.2. X-ray crystallographic data of compound major isomer (±)-6a' with 50% ellipsoid contour probability:



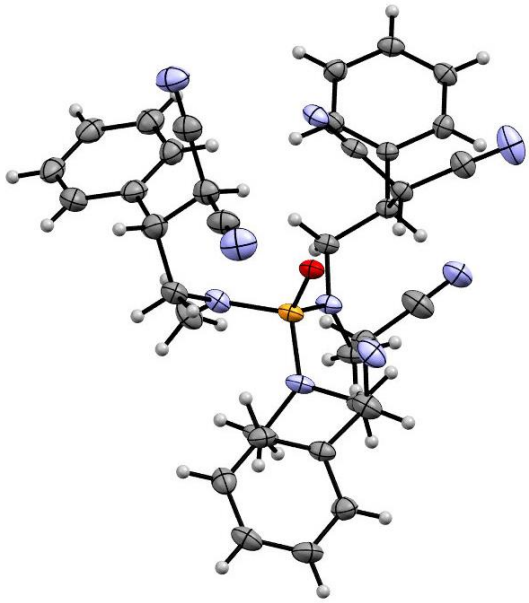
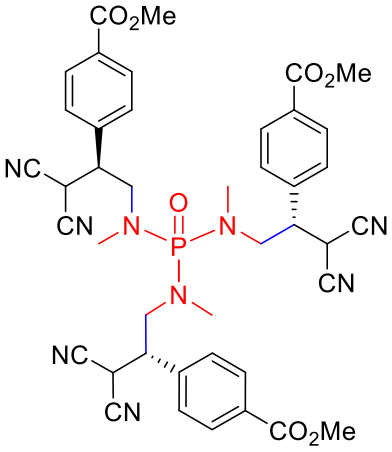


Table S5 Crystal data and structure refinement for Compound (±)-6a':

Identification code	major isomer (±)-**6a'**
Empirical formula	$C_{36}H_{36}N_9OP$
CCDC Number	2003245
Formula weight	641.71
Temperature/K	100.00(10)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	10.13530(10)
b/Å	16.17310(10)
c/Å	21.1190(2)
α/°	90
β/°	90
γ/°	90
Volume/Å³	3461.81(5)
Z	4
ρ_{calc}g/cm³	1.231
μ/mm⁻¹	1.040
F(000)	1352.0
Crystal size/mm³	0.4 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.884 to 132.254
Index ranges	-11 ≤ h ≤ 12, -19 ≤ k ≤ 19, -25 ≤ l ≤ 19
Reflections collected	17178
Independent reflections	5766 [R_{int} = 0.0210, R_{sigma} = 0.0200]
Data/restraints/parameters	5766/0/427
Goodness-of-fit on F²	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0938
Final R indexes [all data]	R_1 = 0.0365, wR_2 = 0.0942
Largest diff. peak/hole / e Å⁻³	0.60/-0.20
Flack parameter	0.013(7)

8.3. X-ray crystallographic data of compound (±)-6e'' with 50% ellipsoid contour probability:



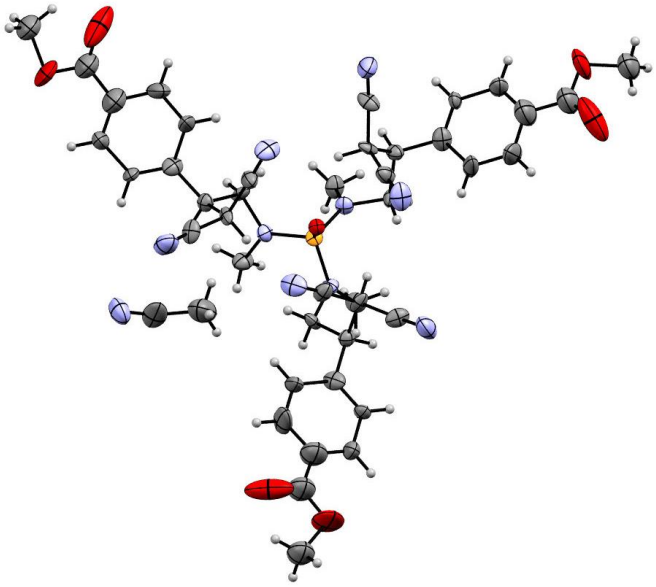
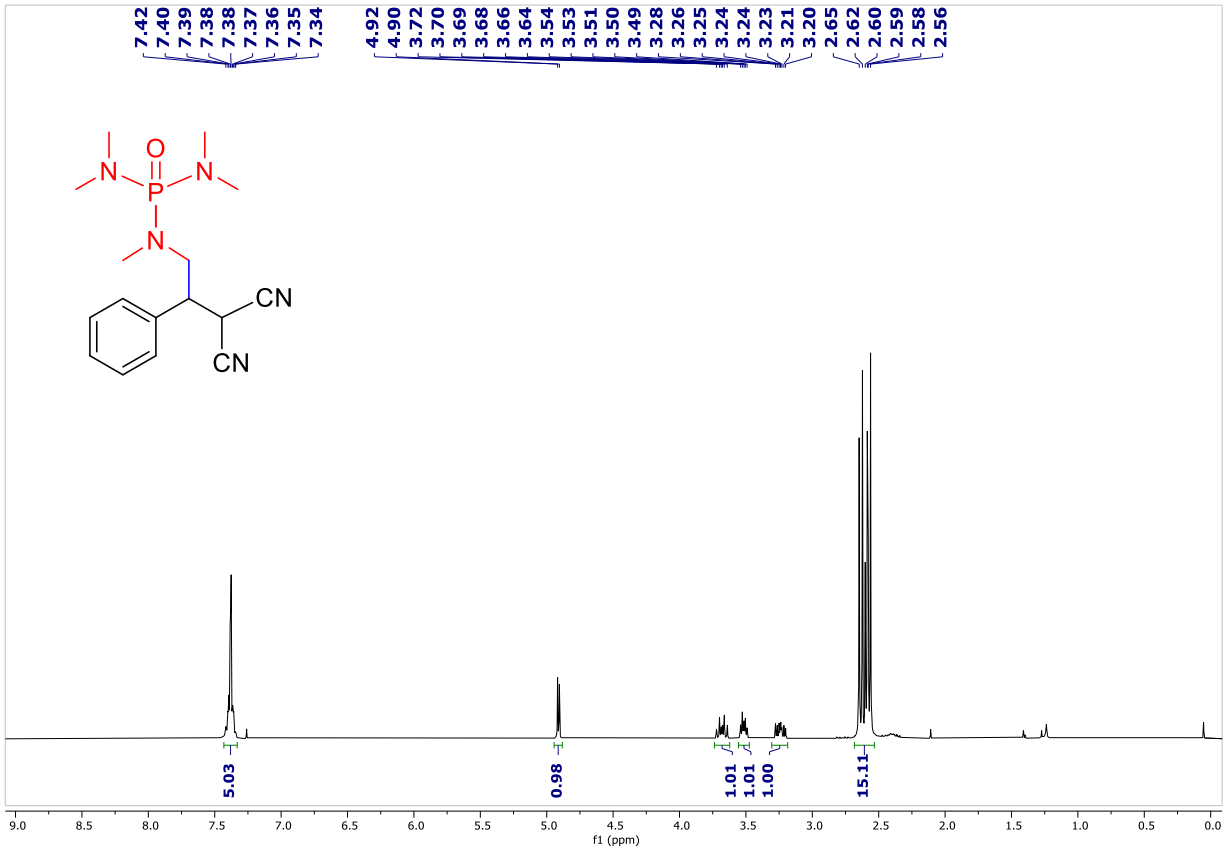


Table S6 Crystal data and structure refinement for compound (±)-6e'':

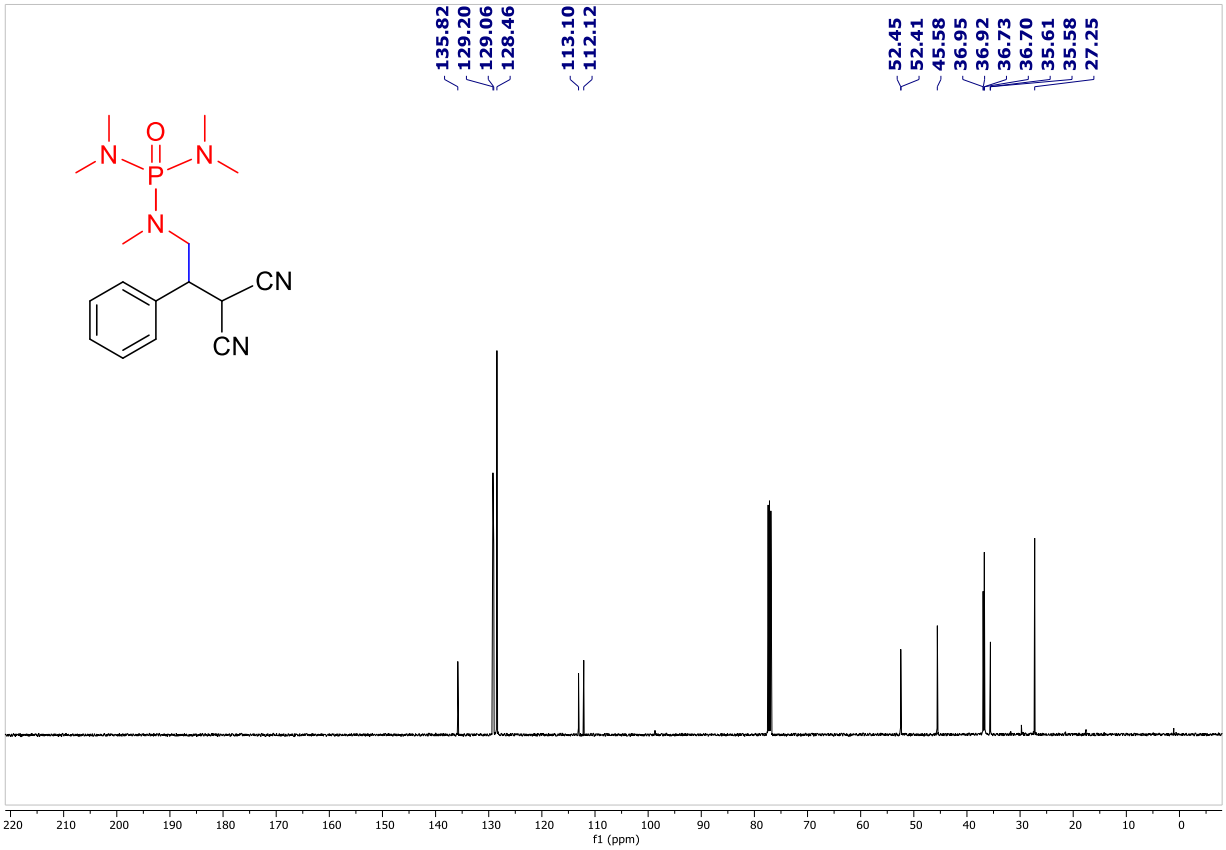
Identification code	minor isomer (±)-**6e''**
Empirical formula	$C_{44}H_{45}N_{10}O_7P$
CCDC Number	2003294
Formula weight	856.88
Temperature/K	100.00(10)
Crystal system	Trigonal
Space group	P31c
a/Å	18.6068(8)
b/Å	18.6068(8)
c/Å	8.2273(3)
α/°	90
β/°	90
γ/°	120
Volume/Å³	2466.8(2)
Z	1.99998
ρ_{calc}g/cm³	1.154
μ/mm⁻¹	0.950
F(000)	900.0
Crystal size/mm³	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.506 to 132.074
Index ranges	-22 ≤ h ≤ 21, -21 ≤ k ≤ 21, -7 ≤ l ≤ 9
Reflections collected	17046
Independent reflections	2688 [R_{int} = 0.0480, R_{sigma} = 0.0296]
Data/restraints/parameters	2688/1/198
Goodness-of-fit on F²	2.352
Final R indexes [I>=2σ (I)]	R_1 = 0.1711, wR_2 = 0.4437
Final R indexes [all data]	R_1 = 0.1716, wR_2 = 0.4451
Largest diff. peak/hole / e Å⁻³	1.14/-1.48
Flack parameter	0.24(5)

9. NMR spectra of the products:

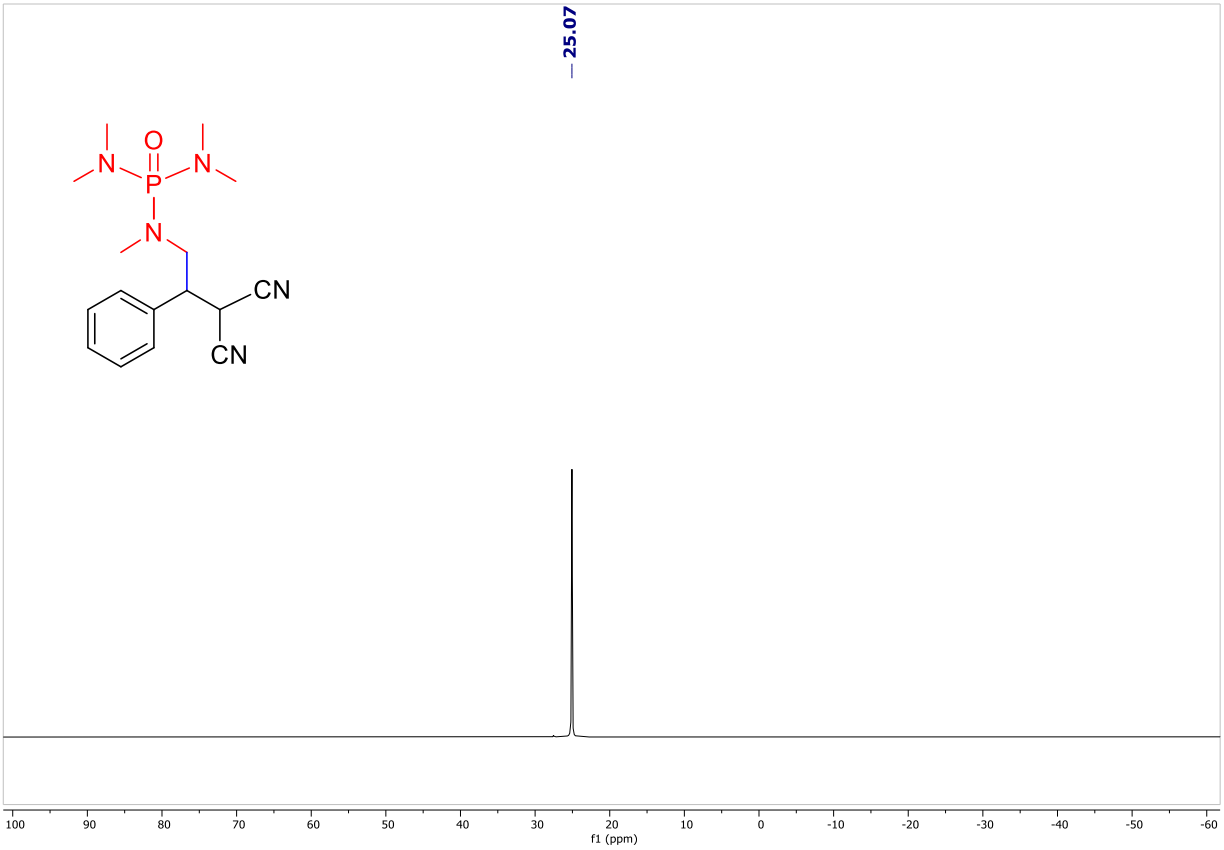
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**



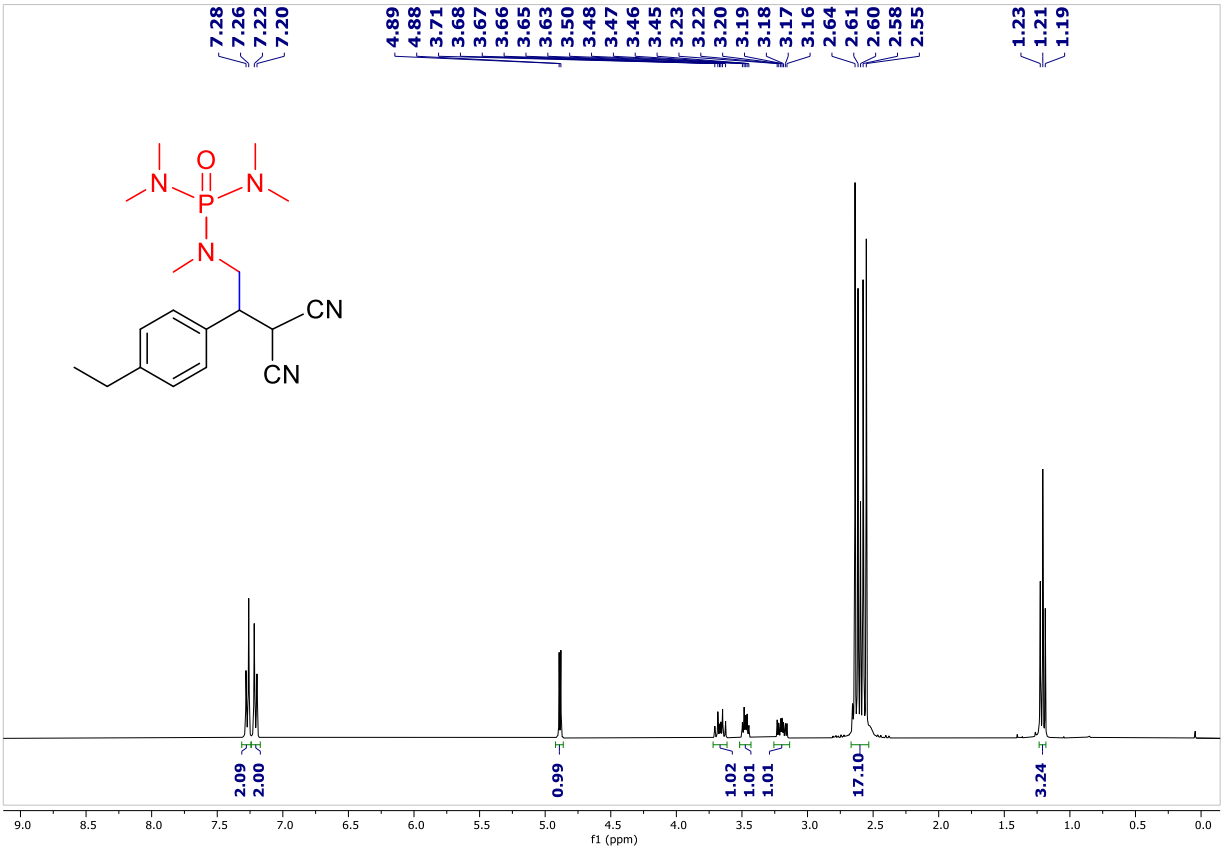
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3a**



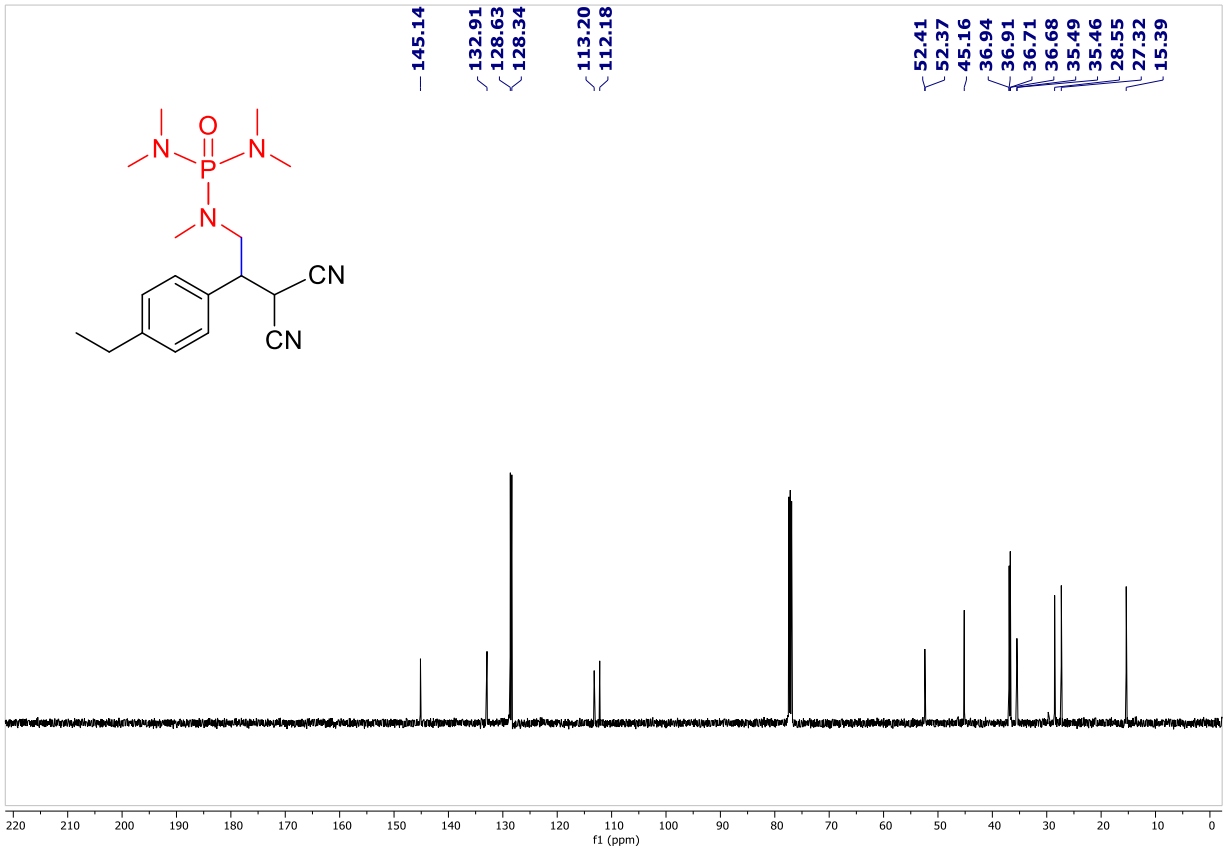
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3a**



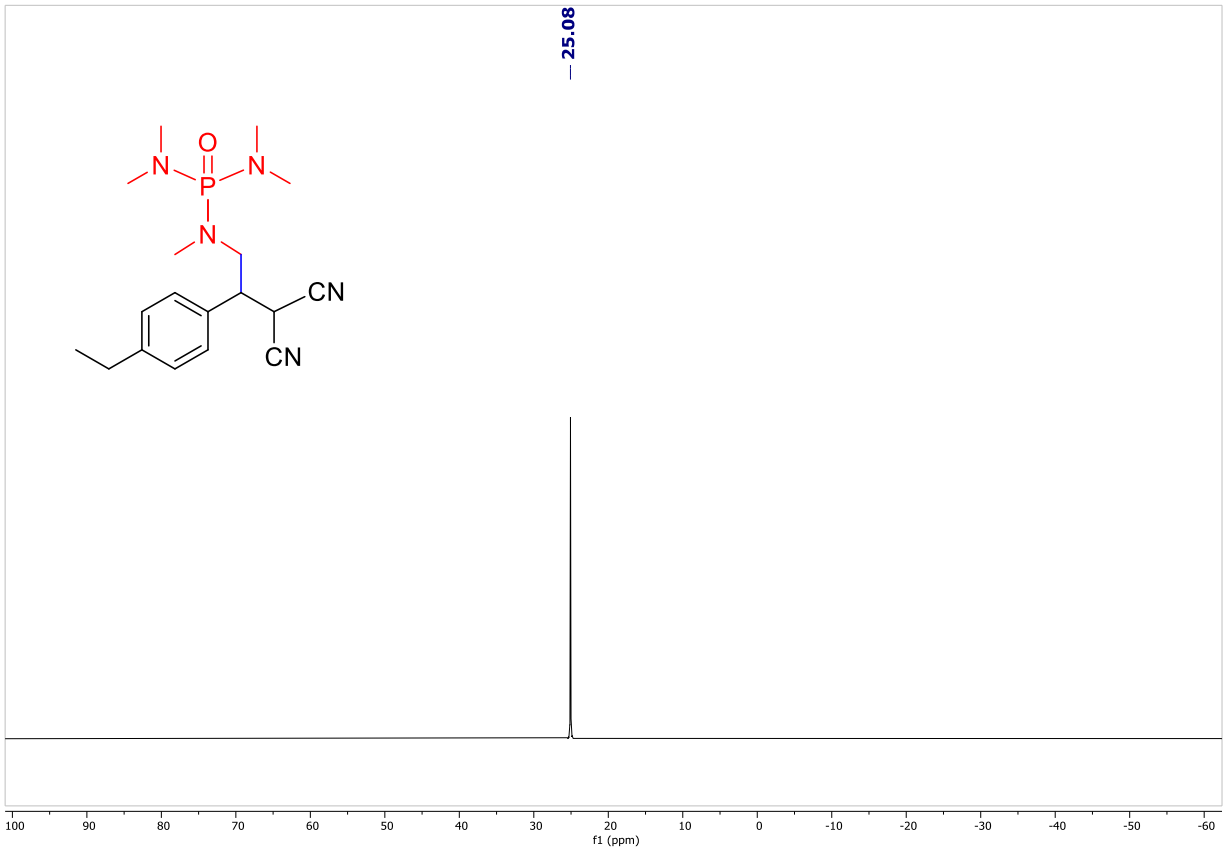
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**



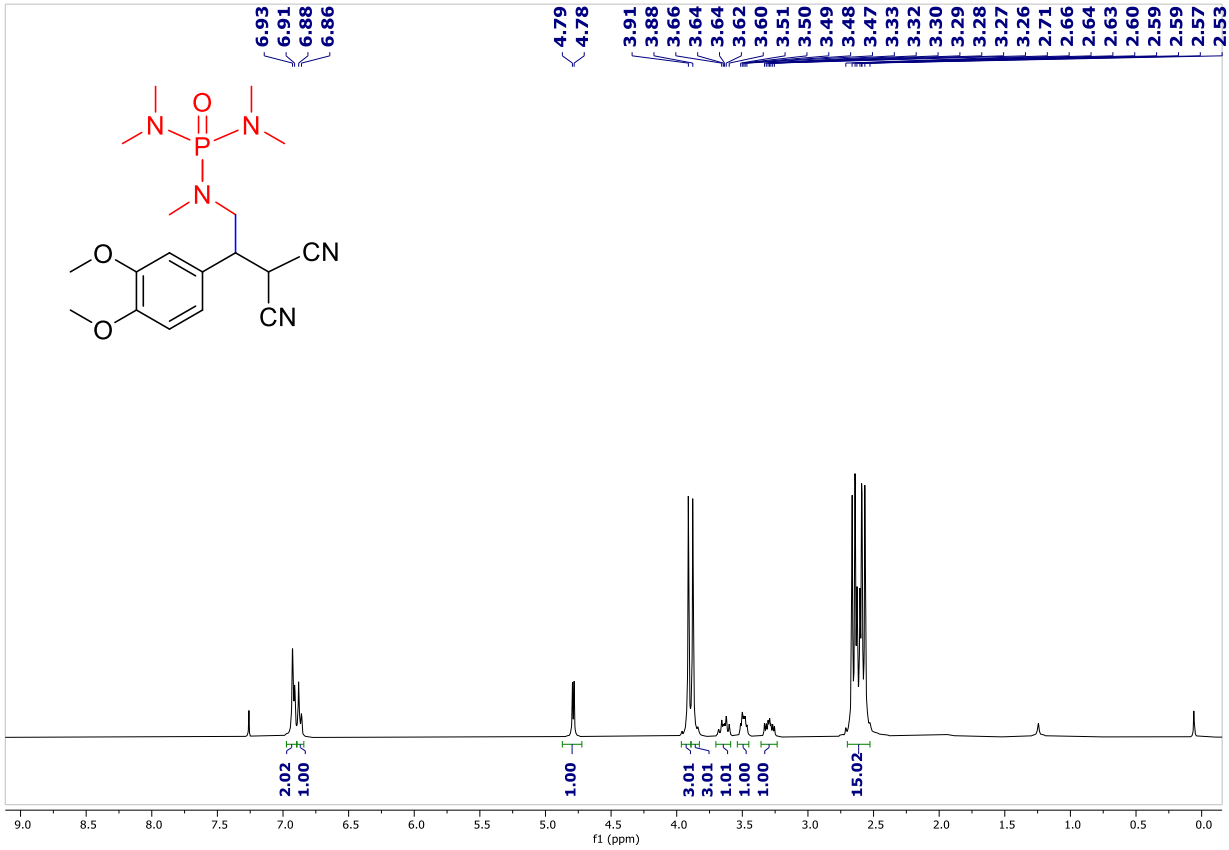
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3b**



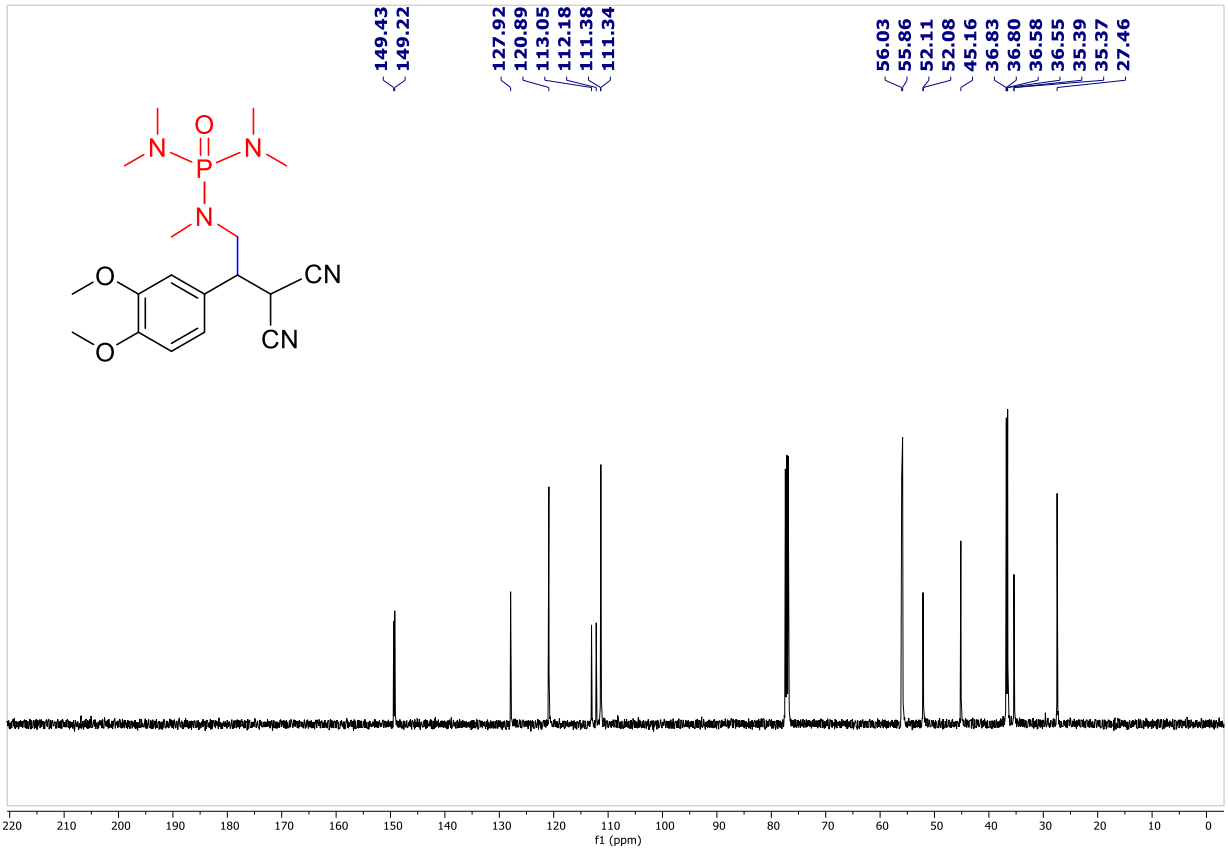
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3b**



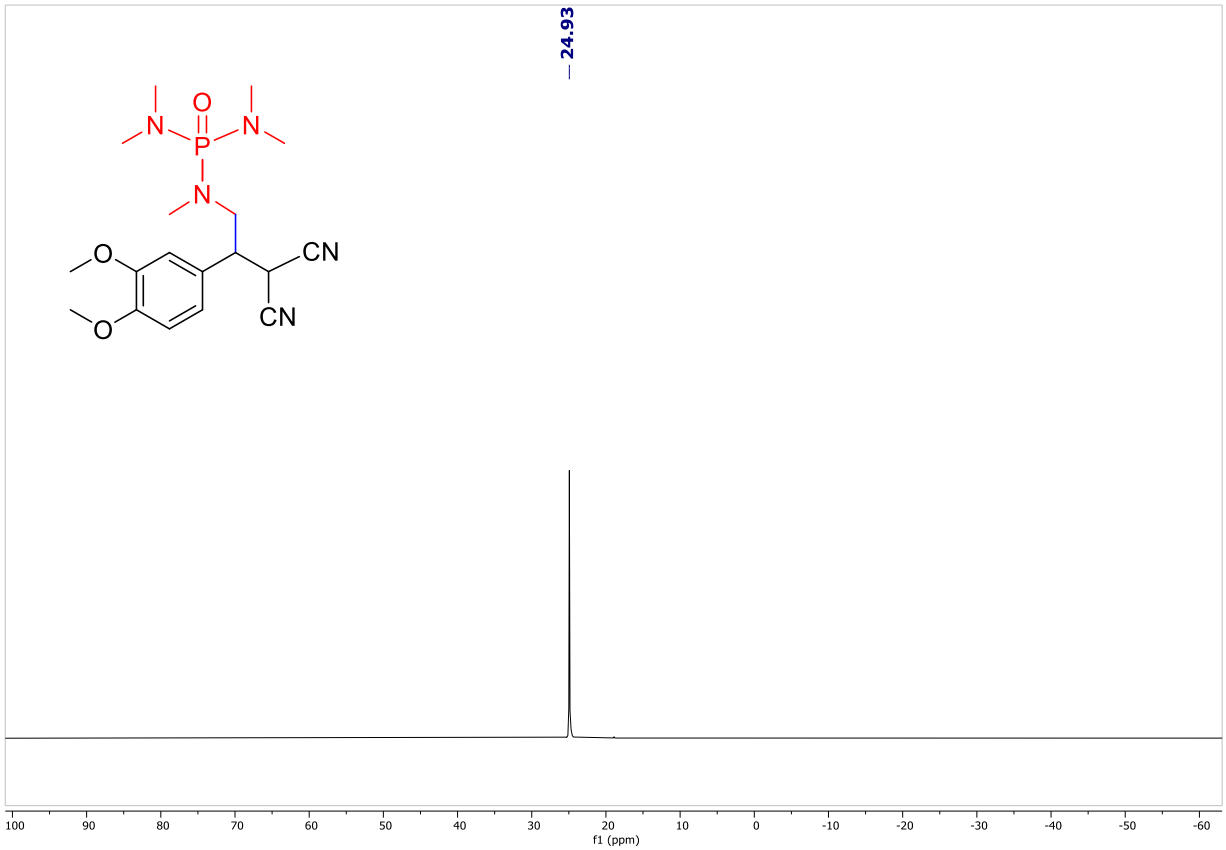
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**



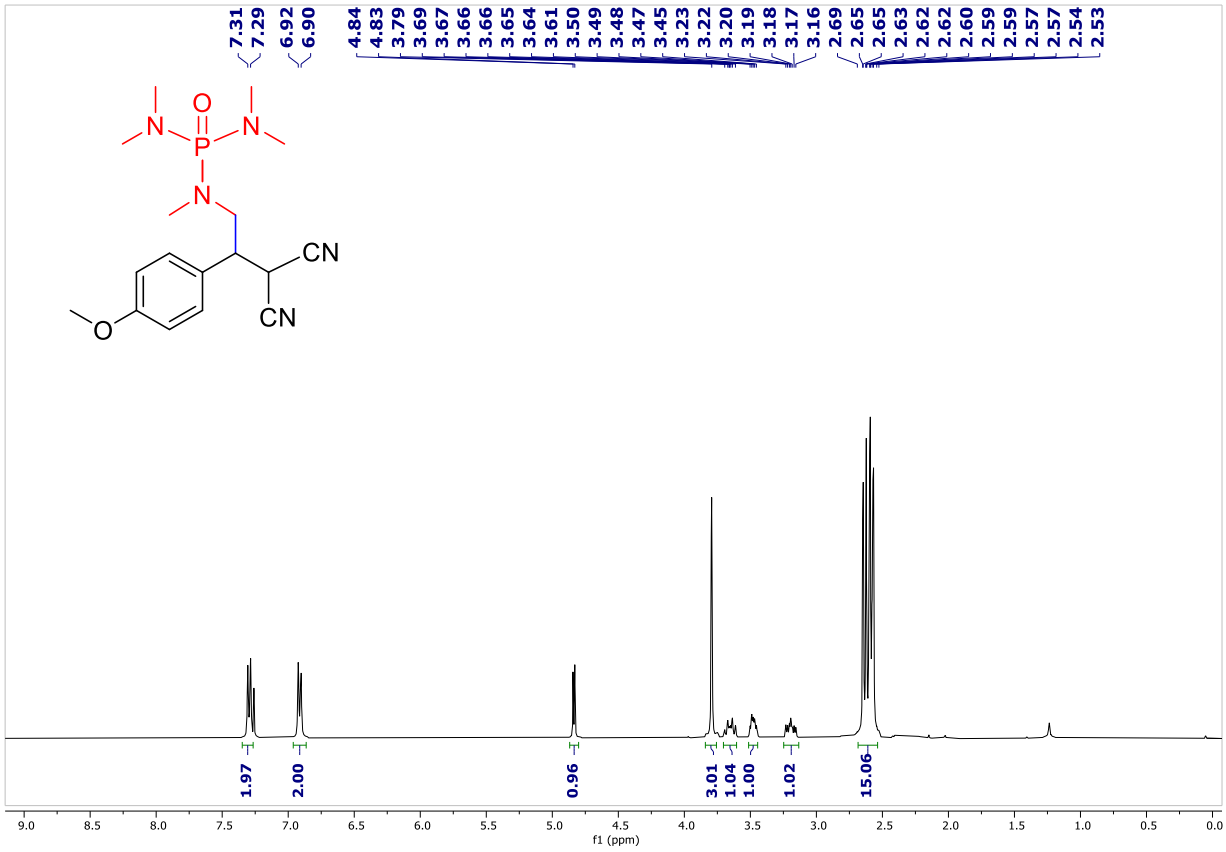
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3c**



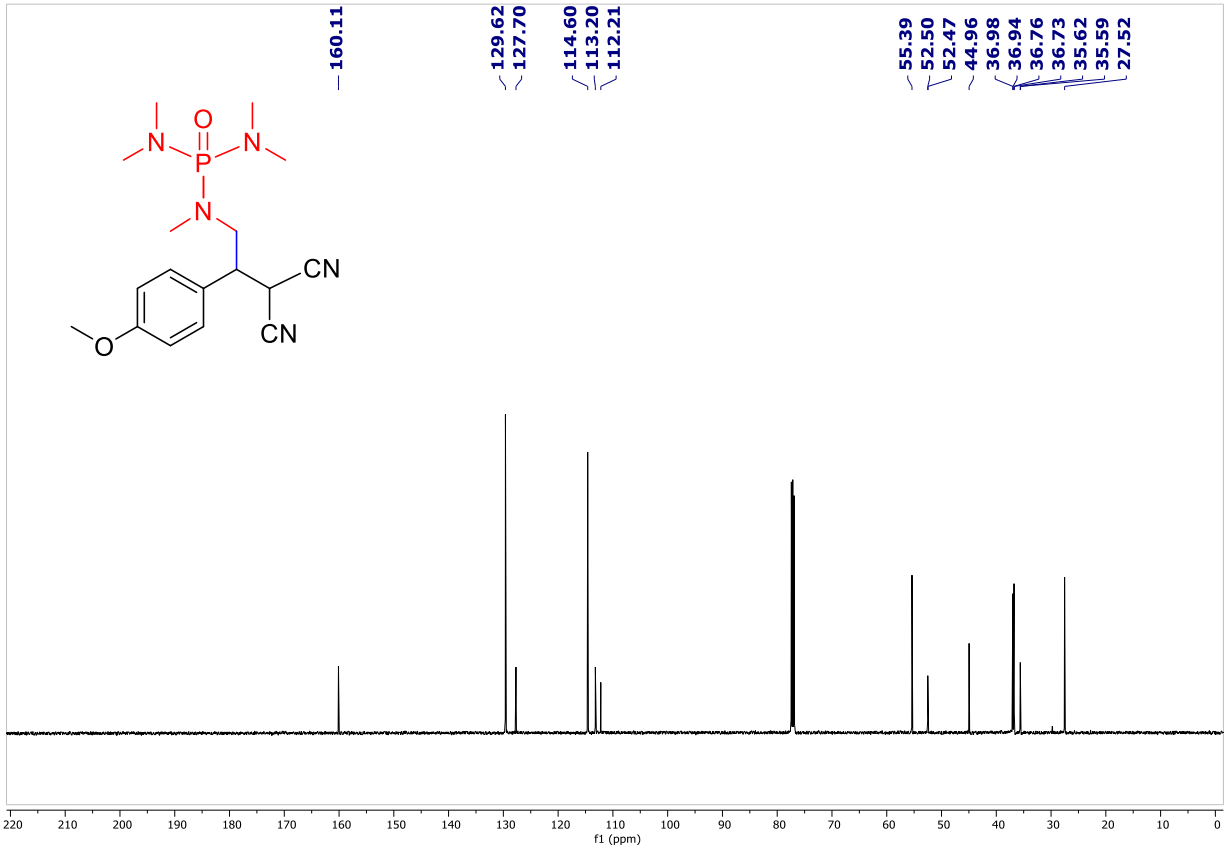
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3c**



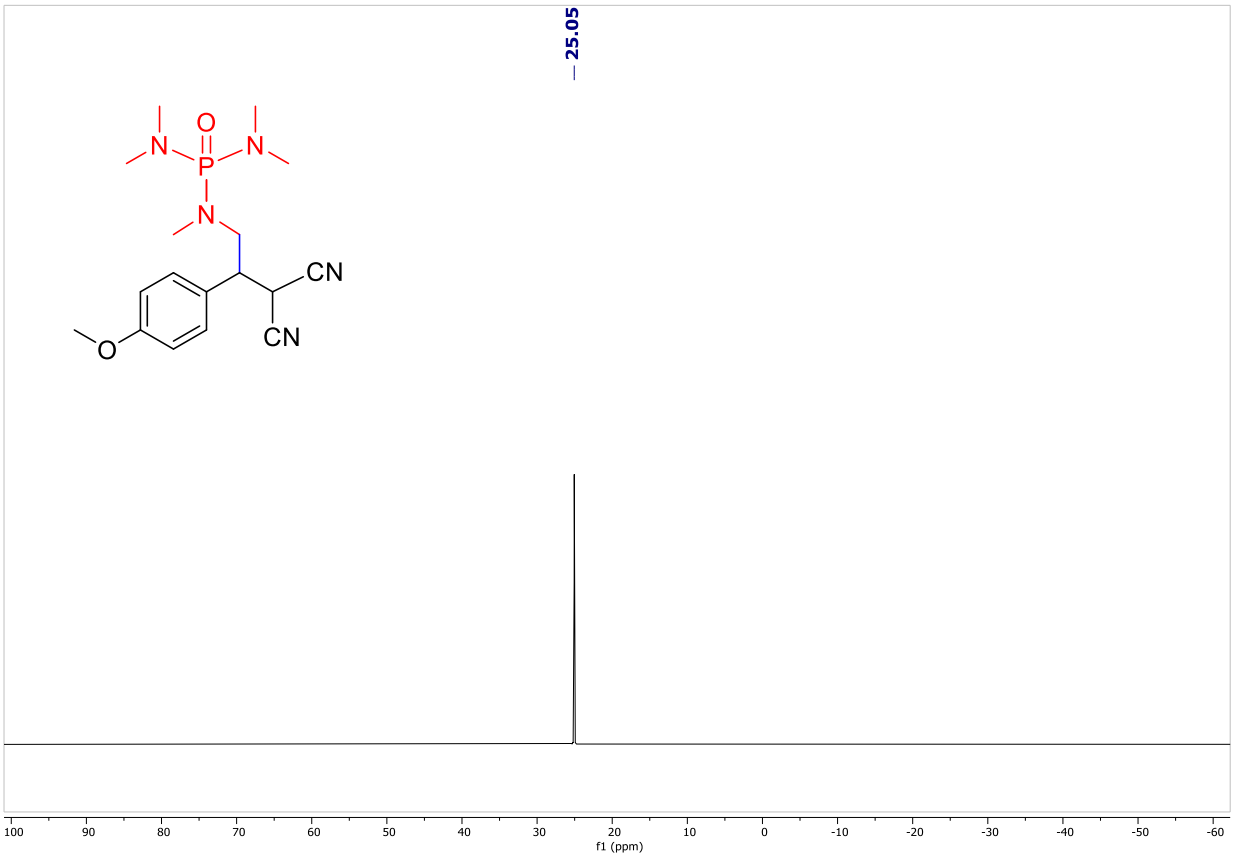
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**



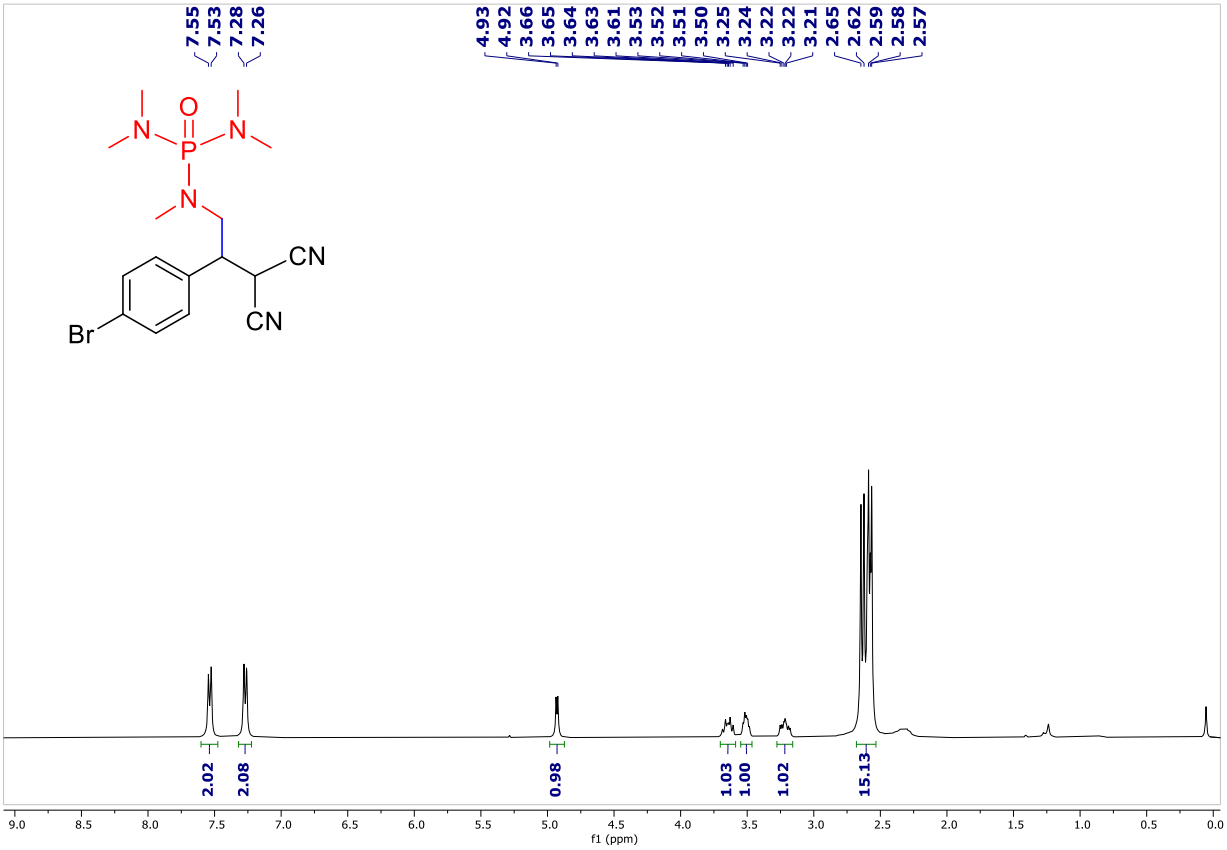
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3d**



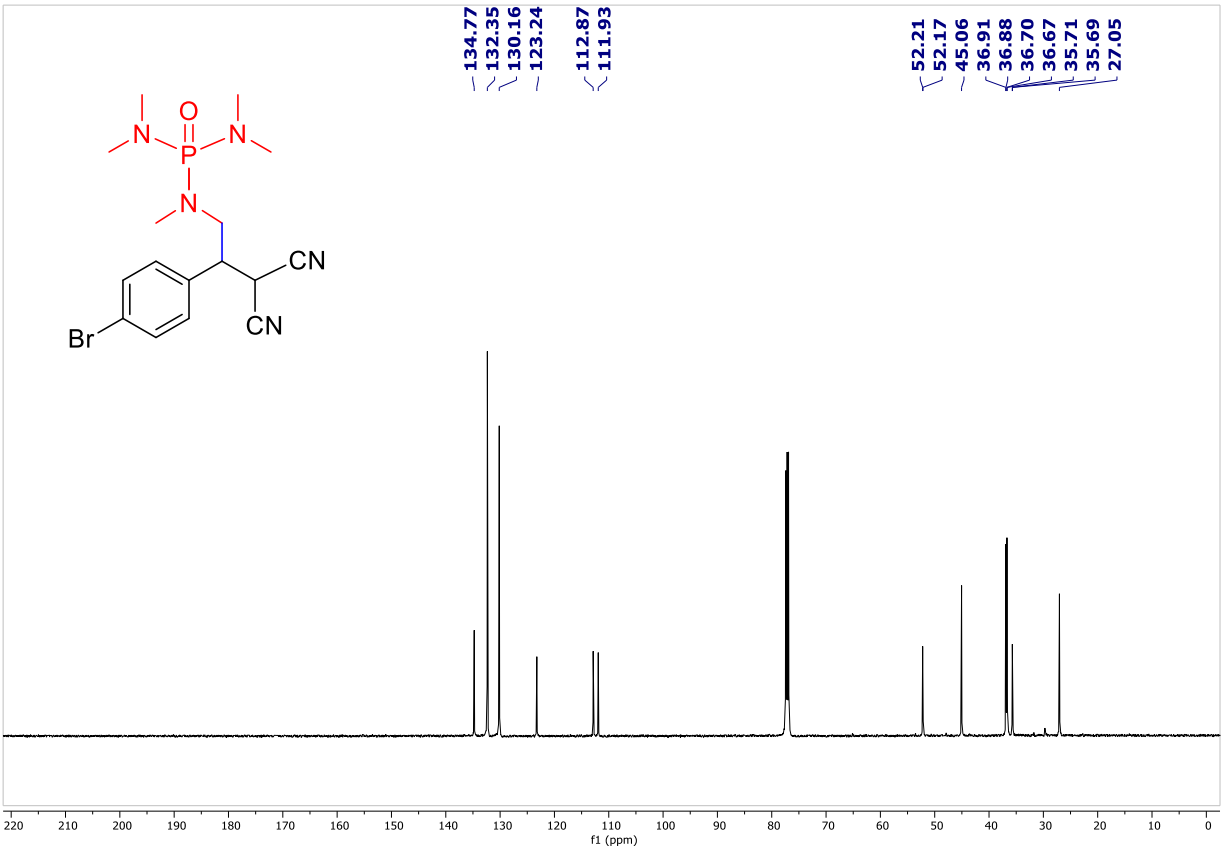
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3d**



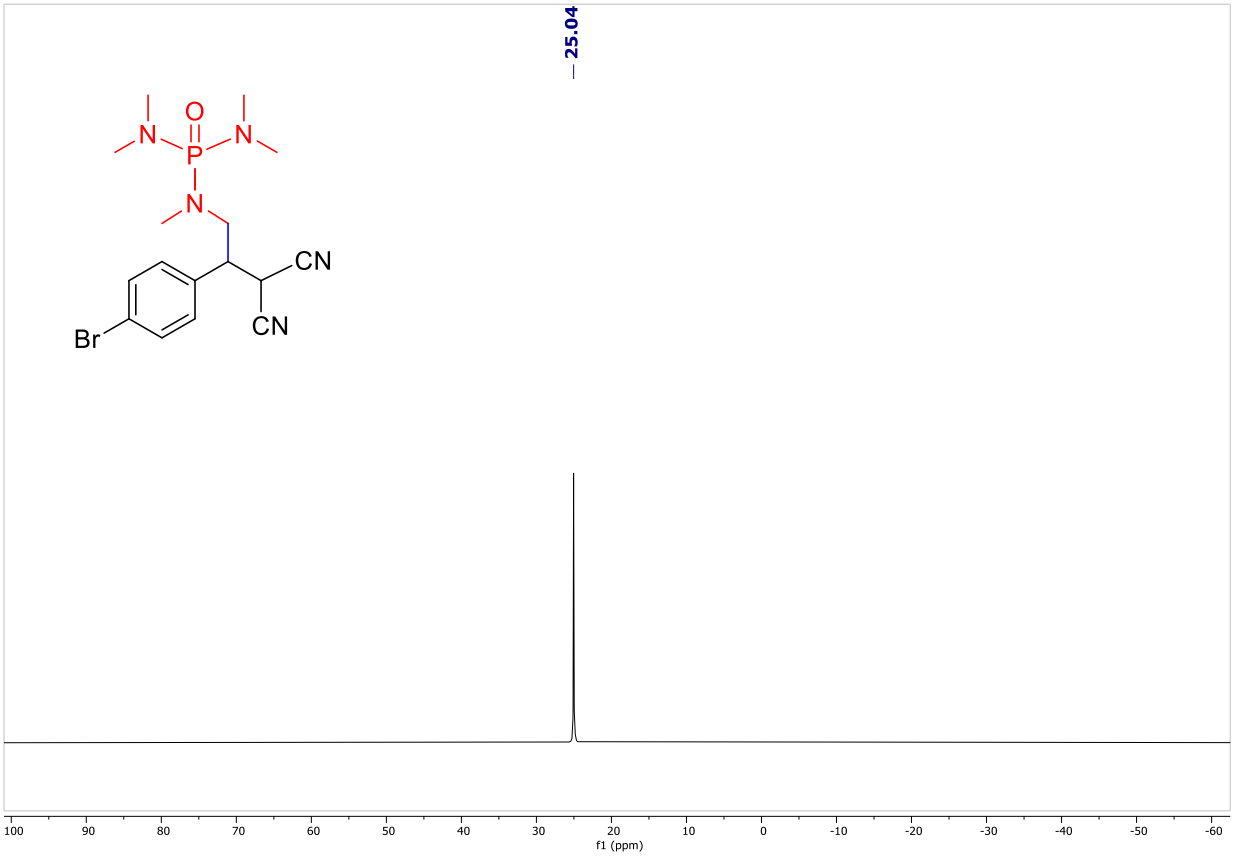
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**



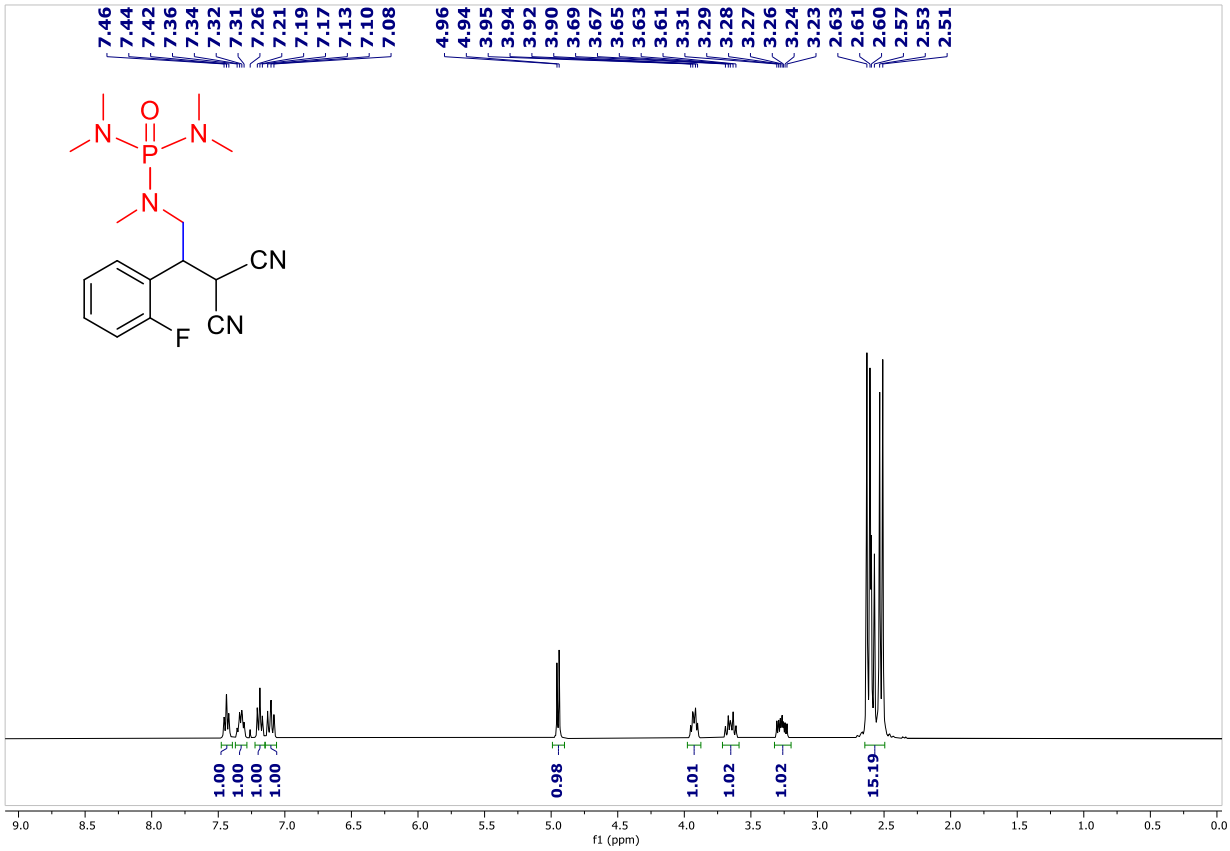
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3e**



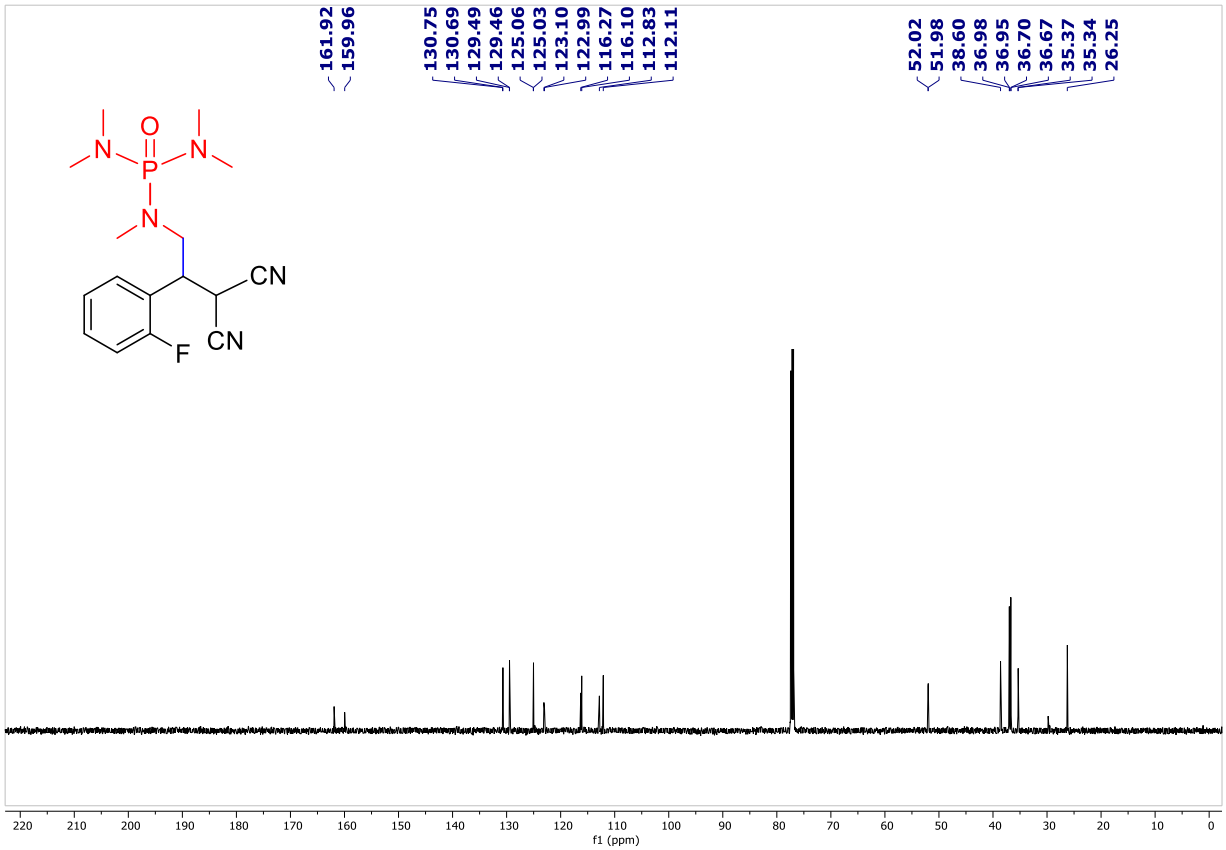
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3e**



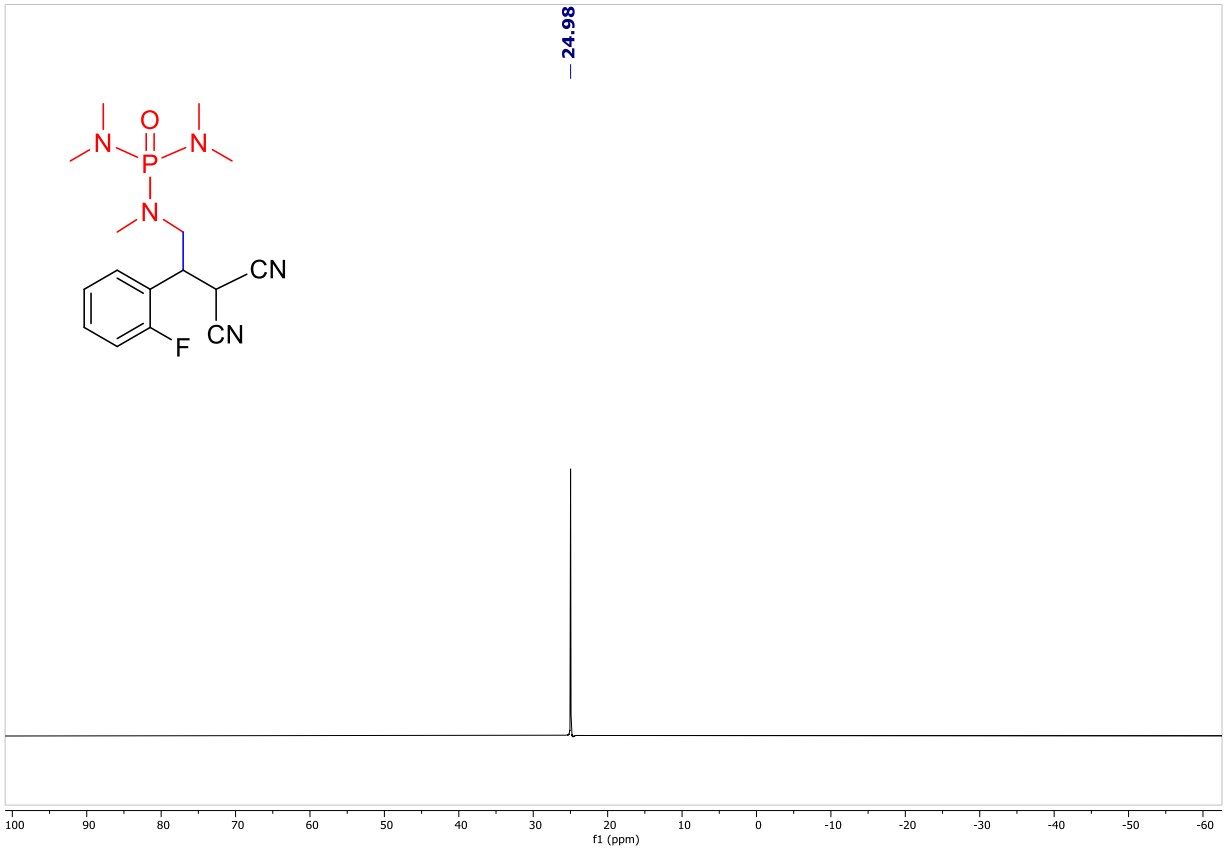
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**



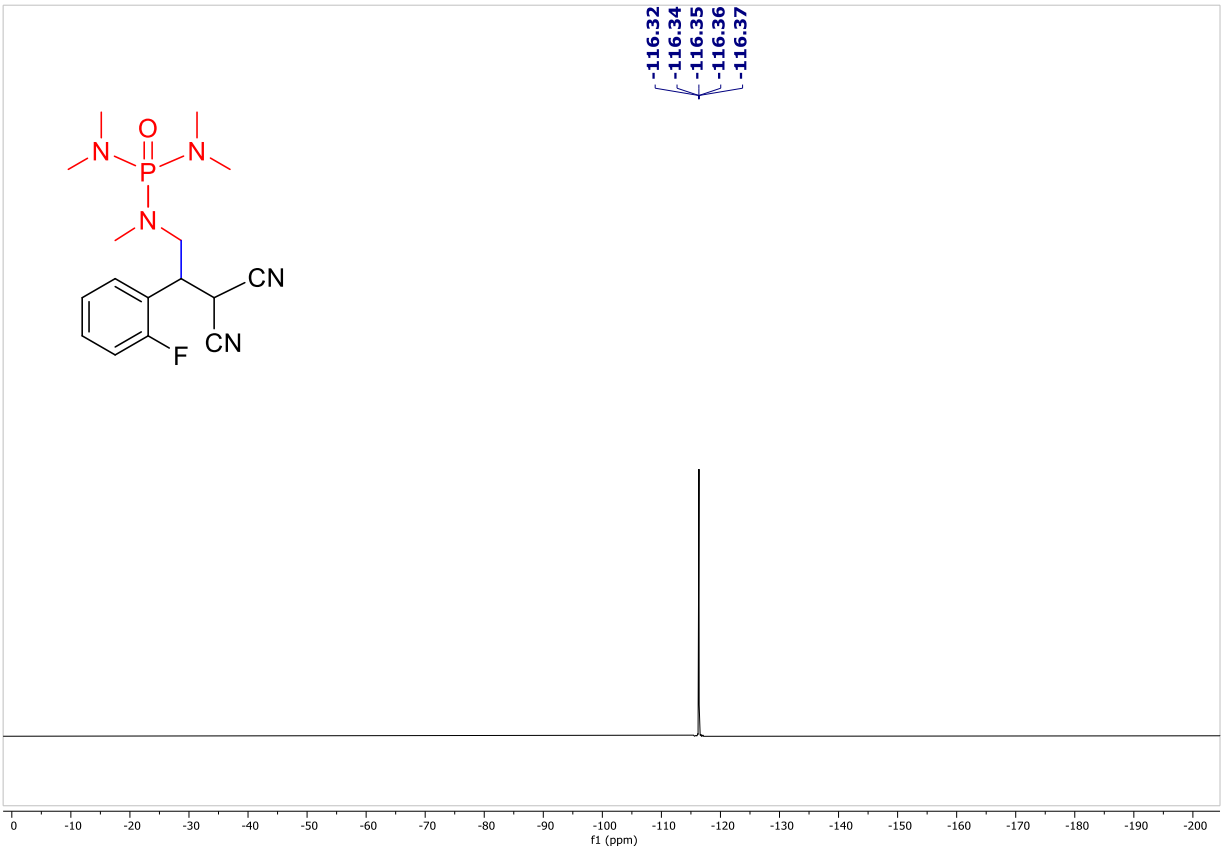
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3f**



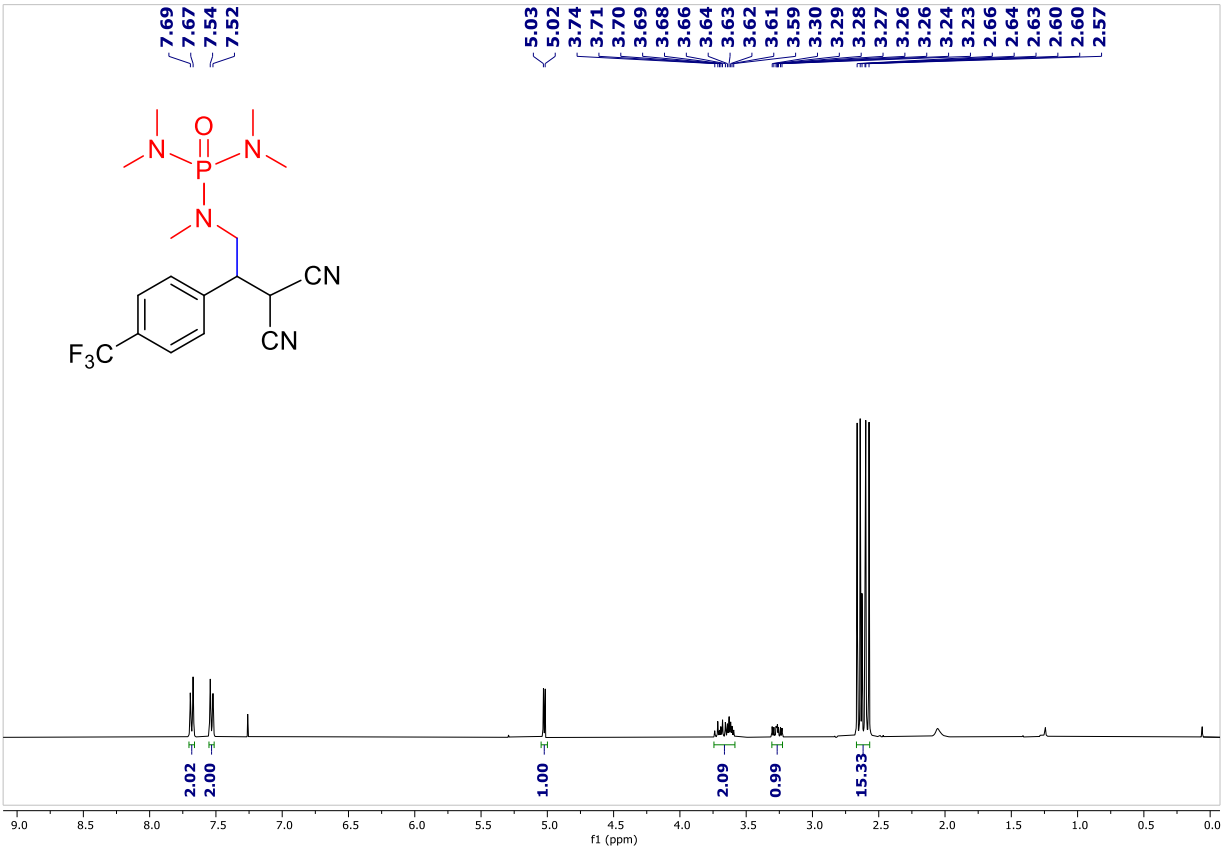
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3f**



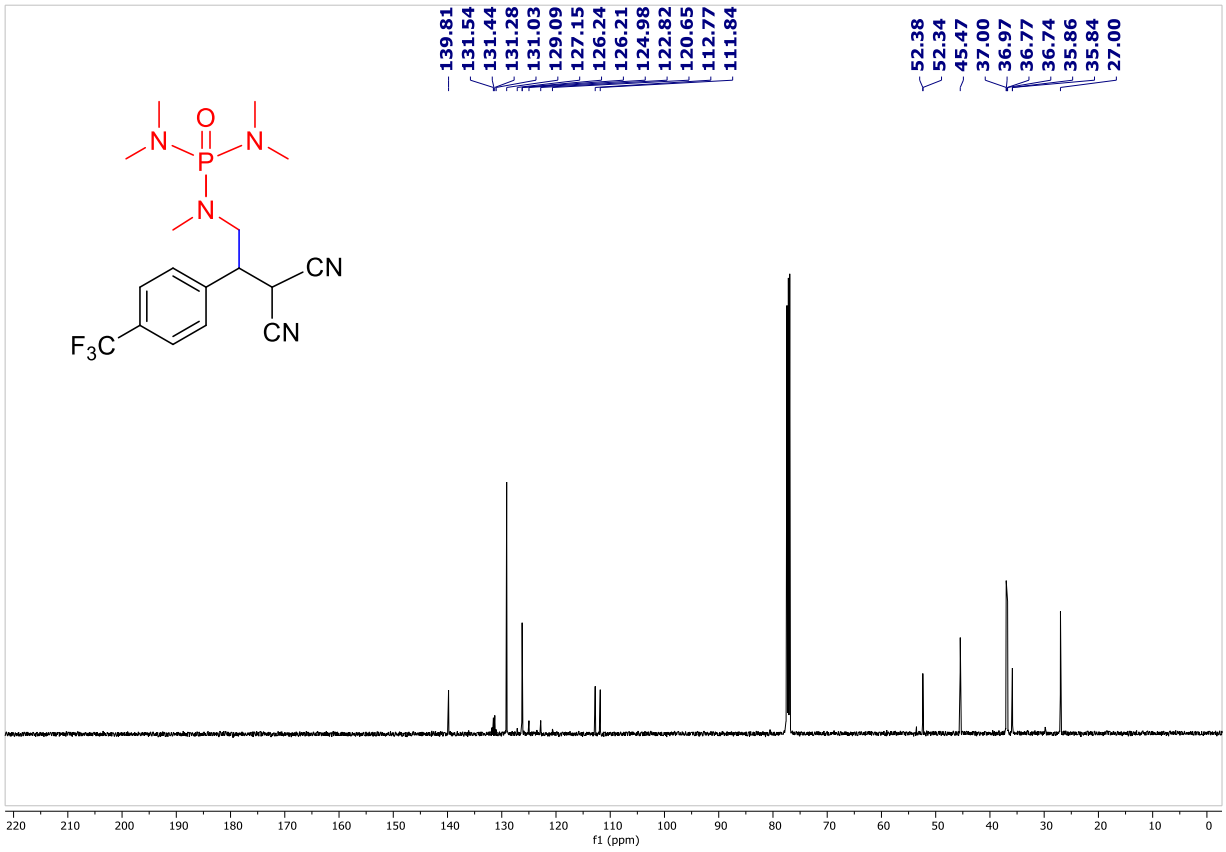
^{19}F NMR (471 MHz, $CDCl_3$) of compound **3f**



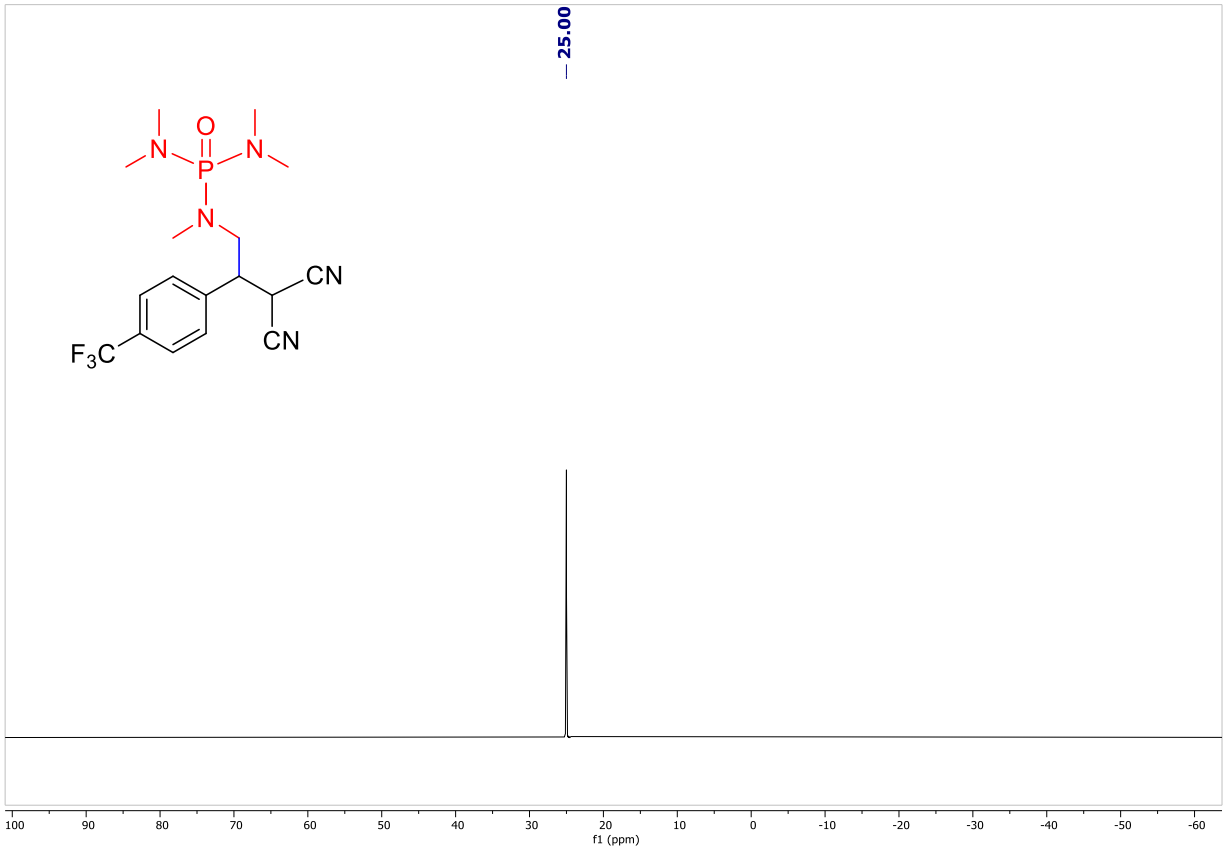
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**



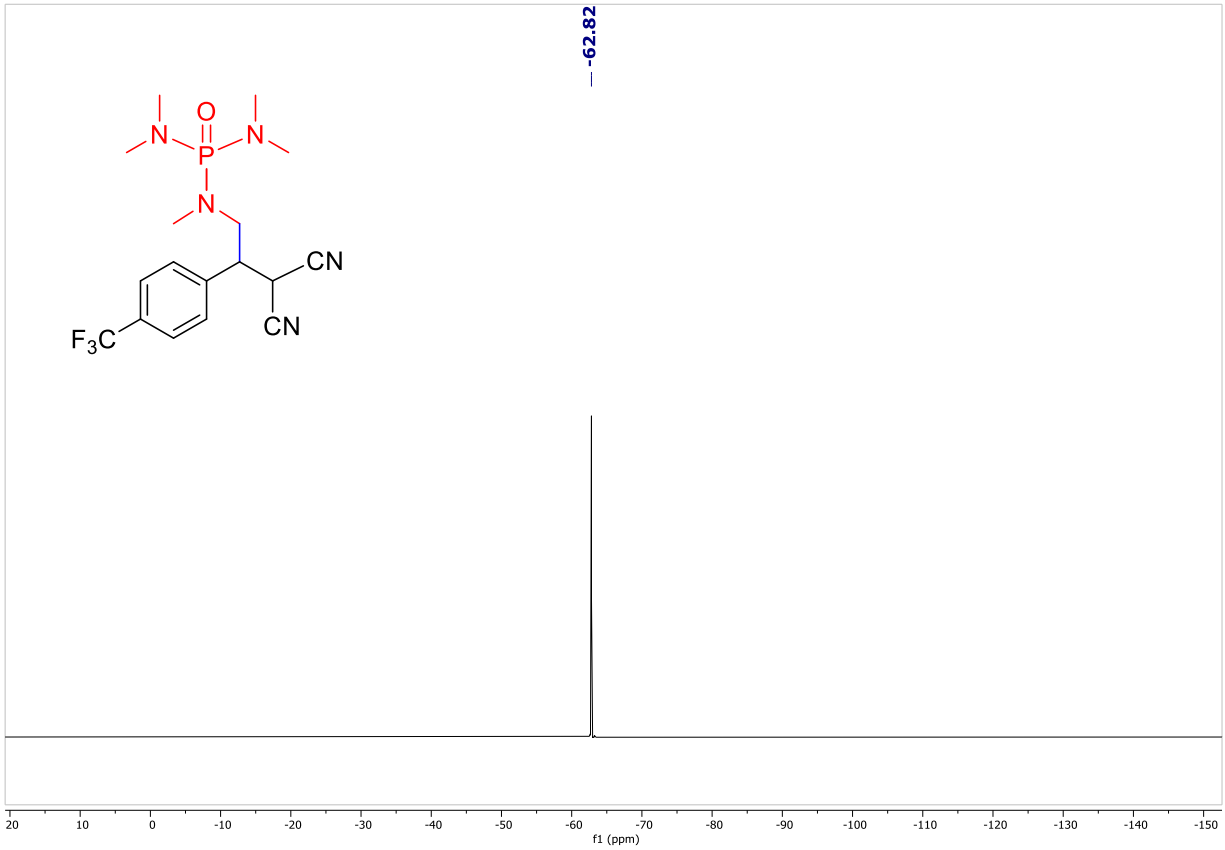
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3g**



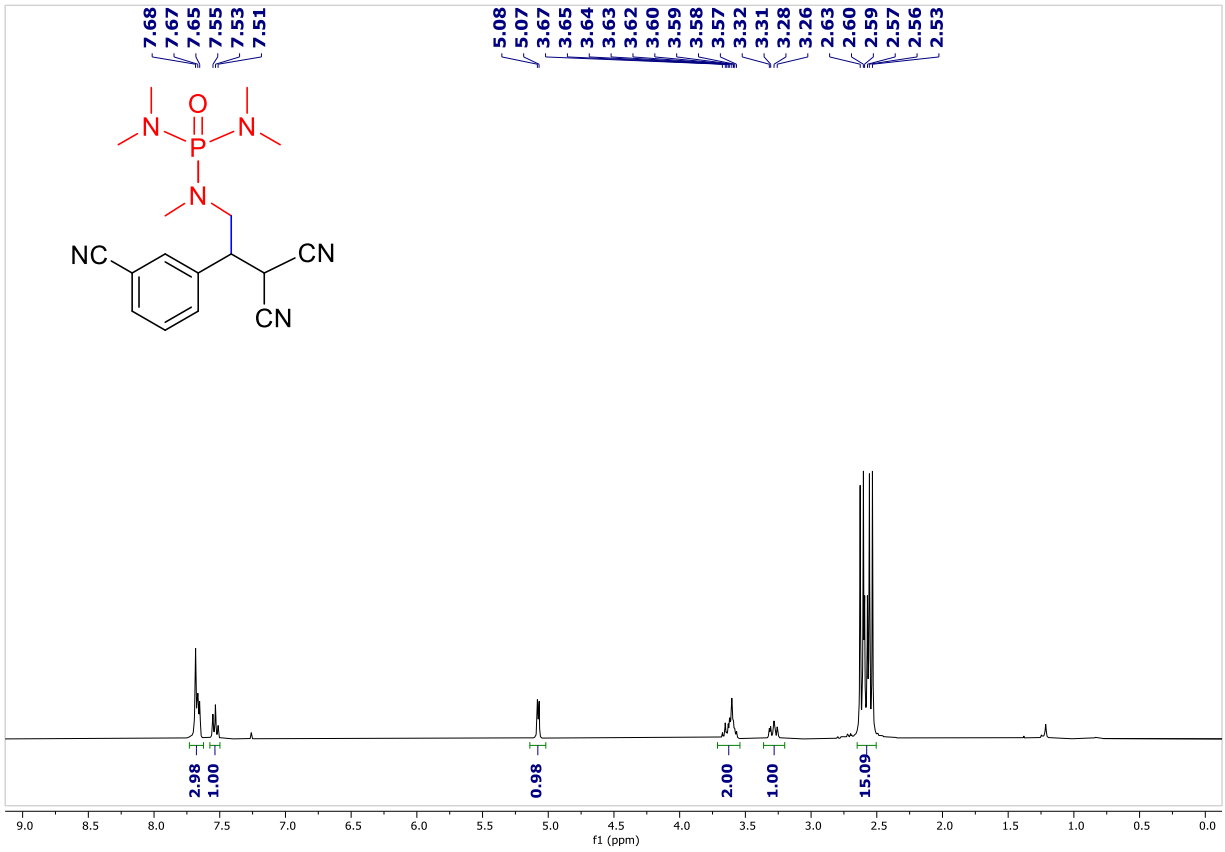
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3g**



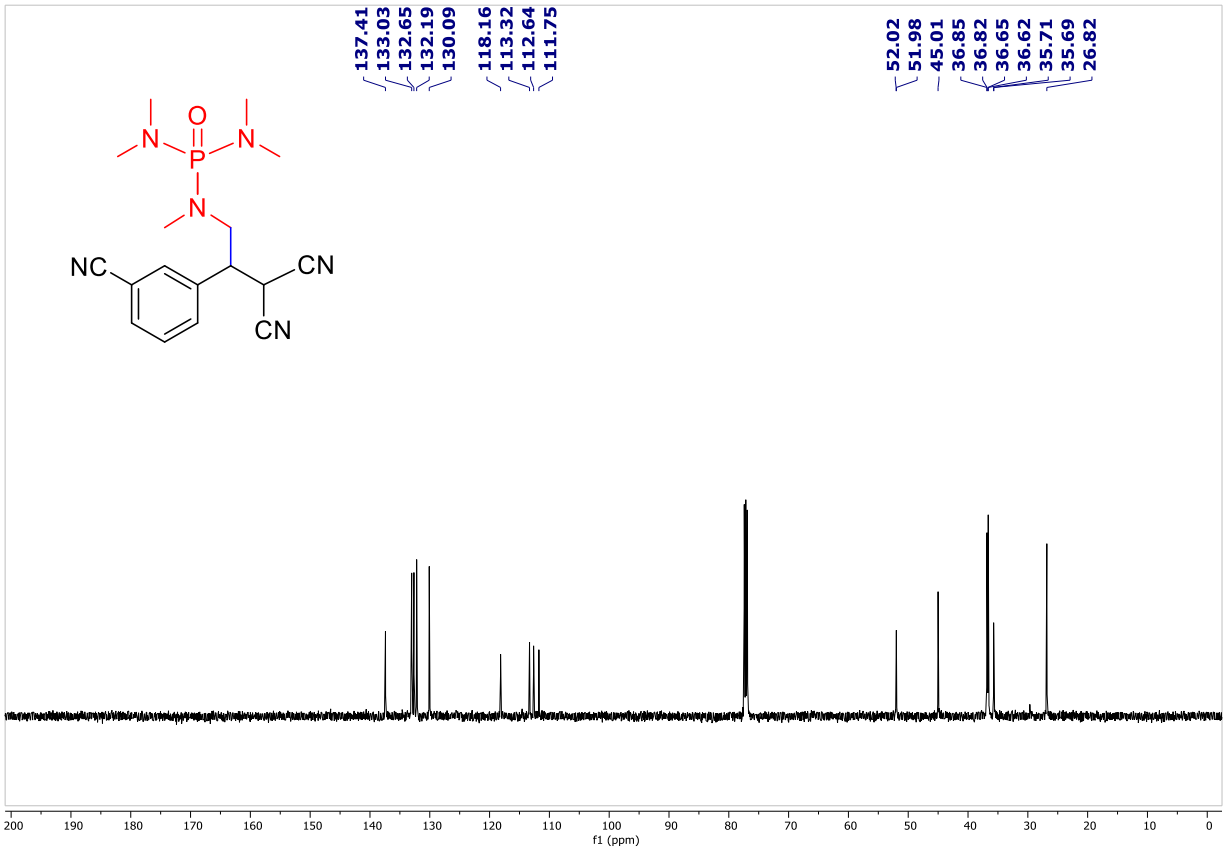
^{19}F NMR (471 MHz, $CDCl_3$) of compound **3g**



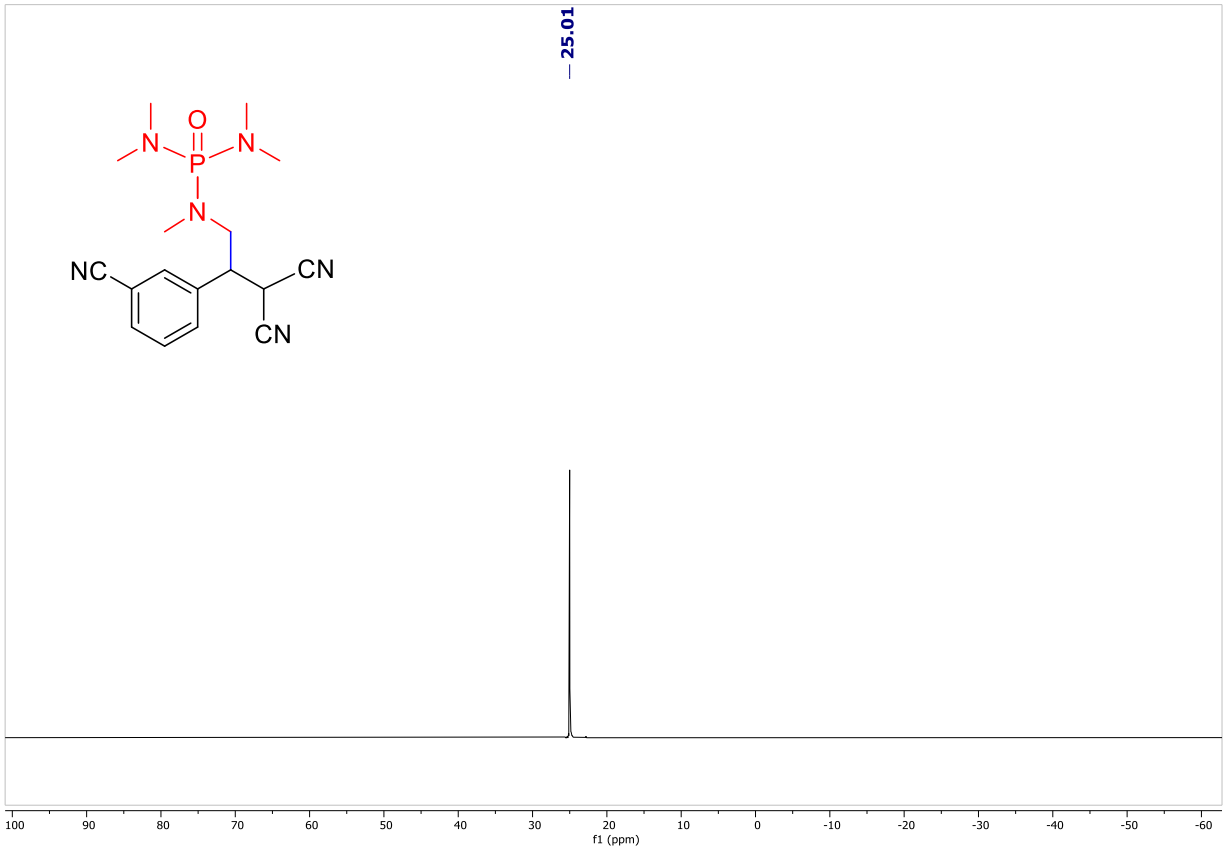
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**



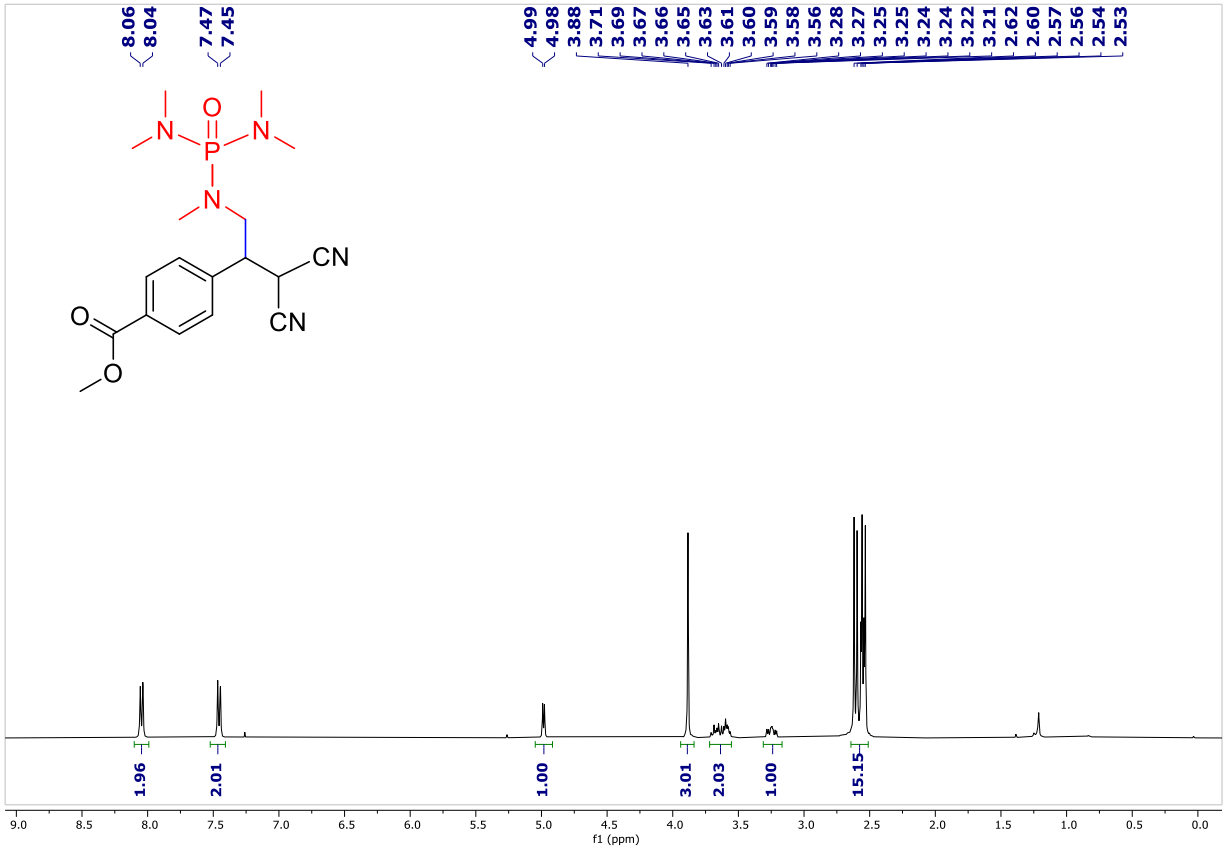
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3h**



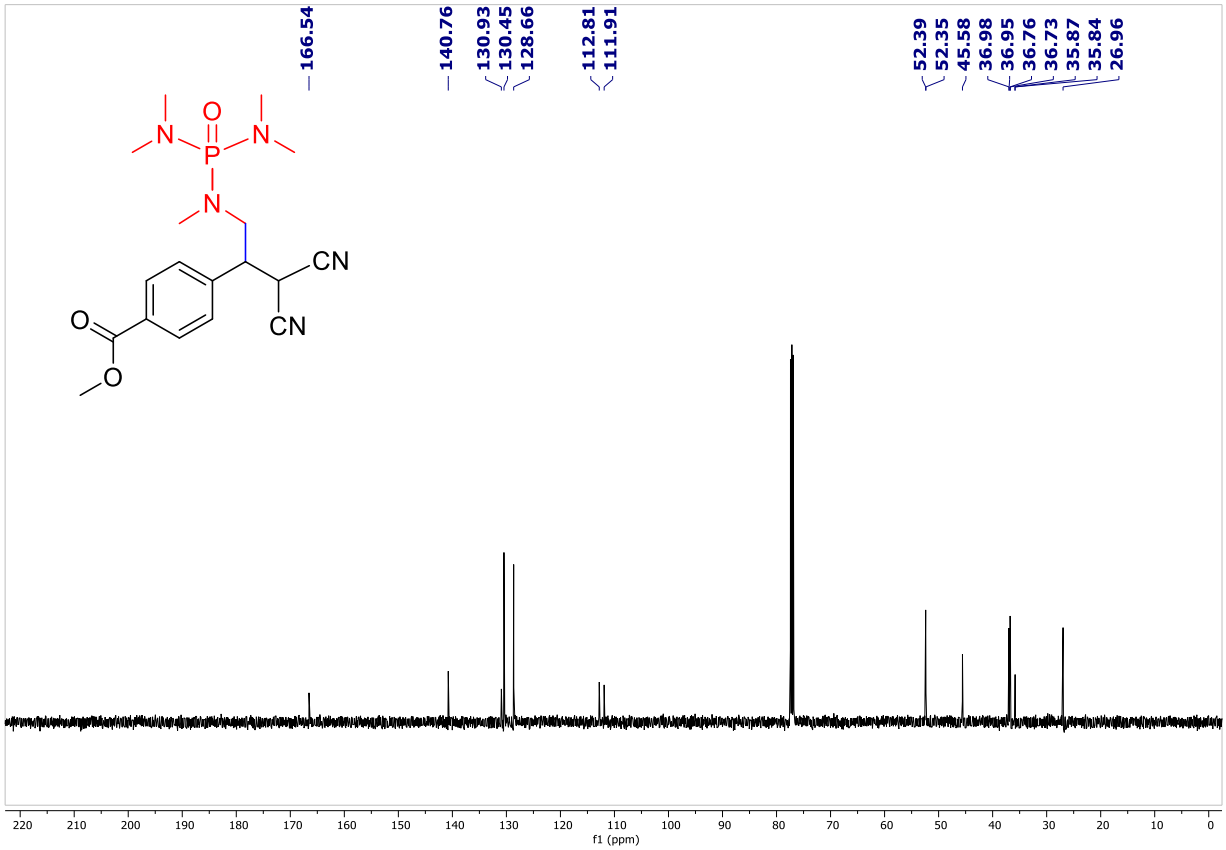
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3h**



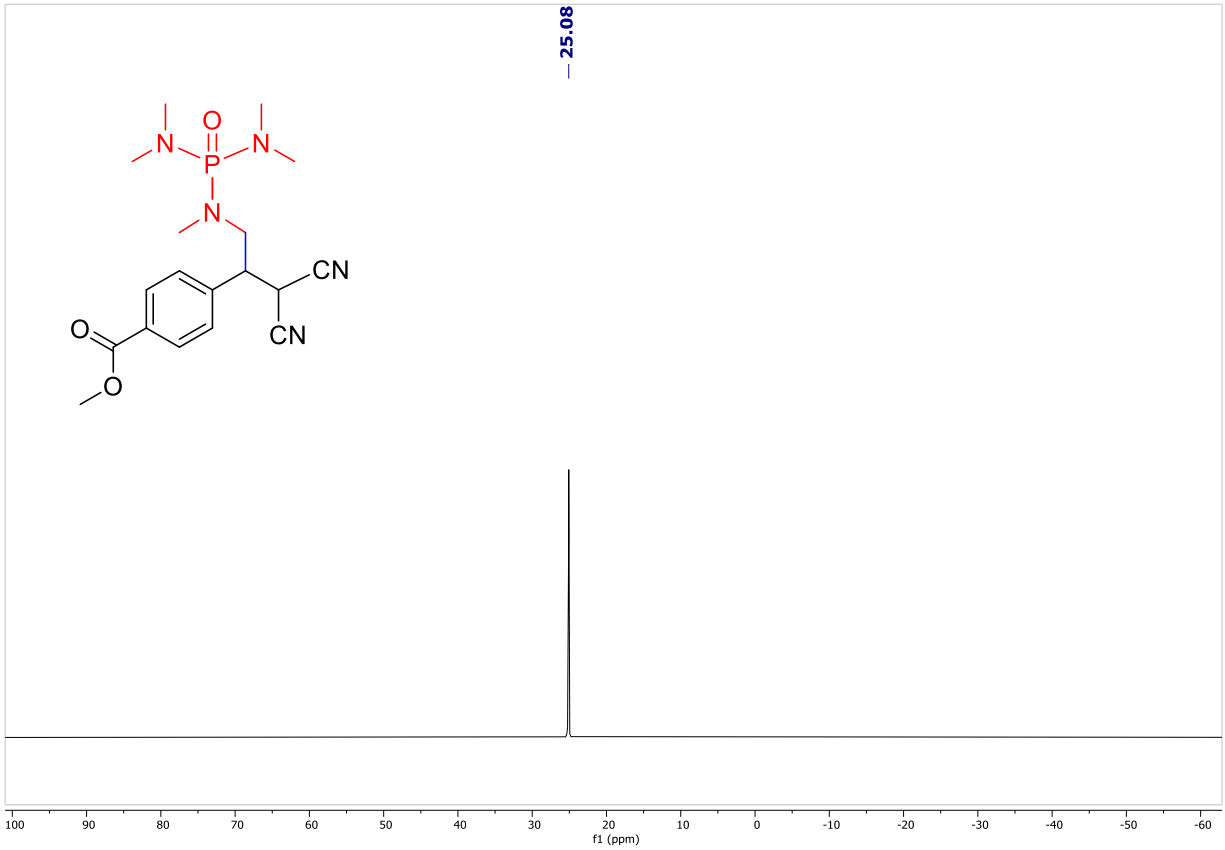
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**



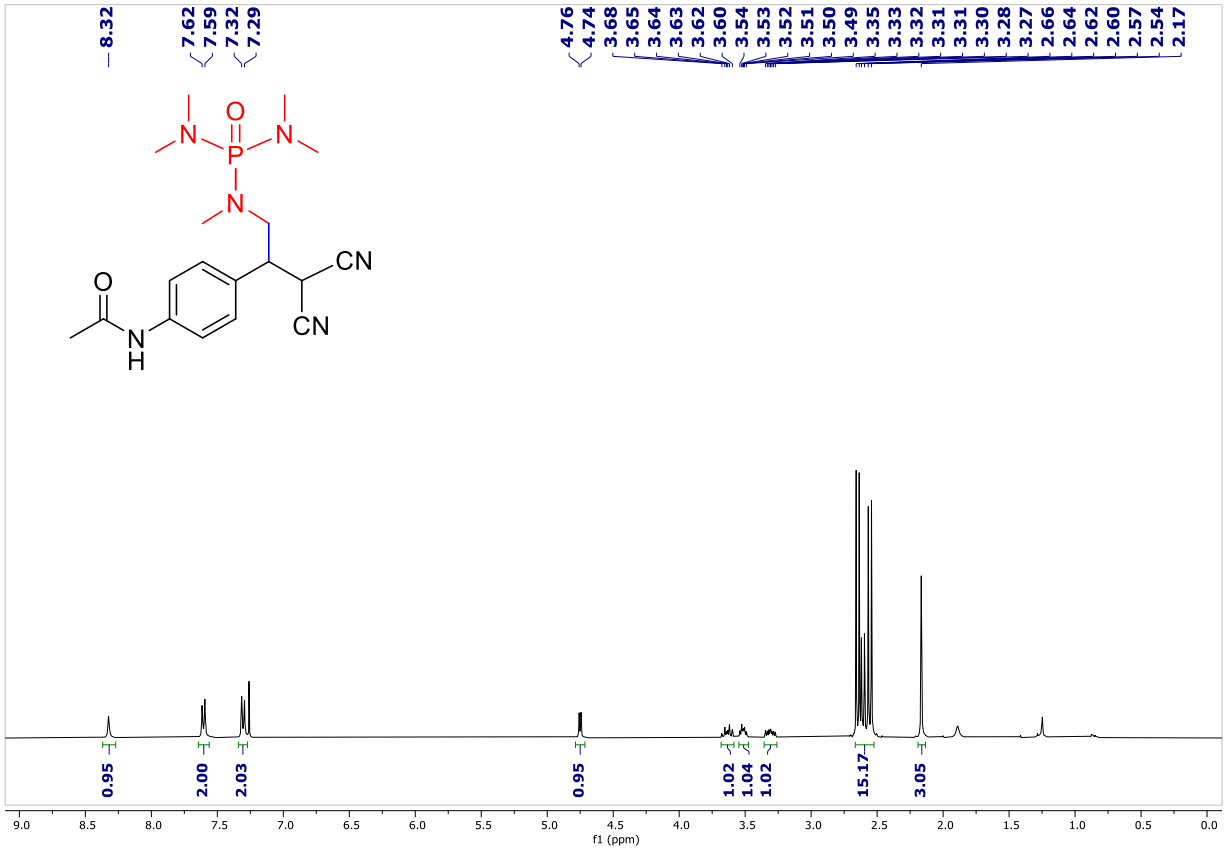
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3i**



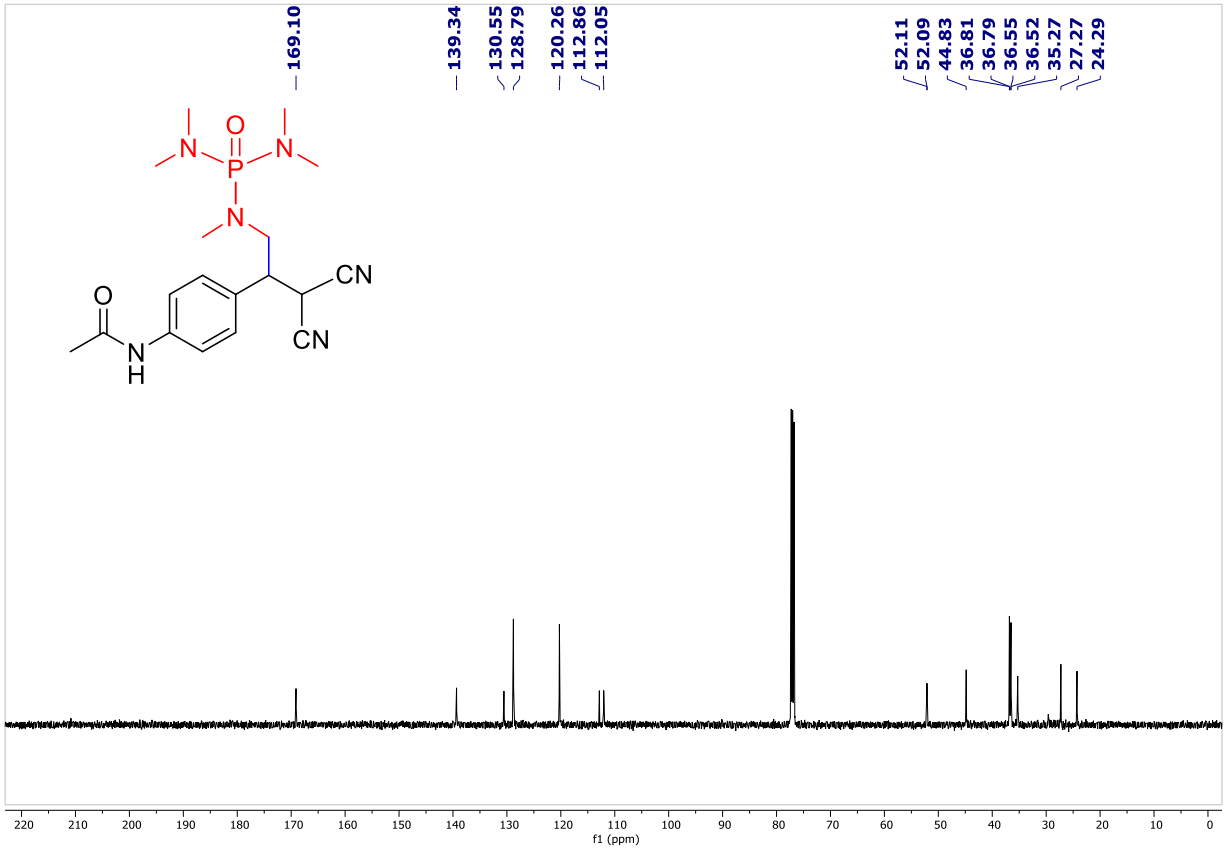
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3i**



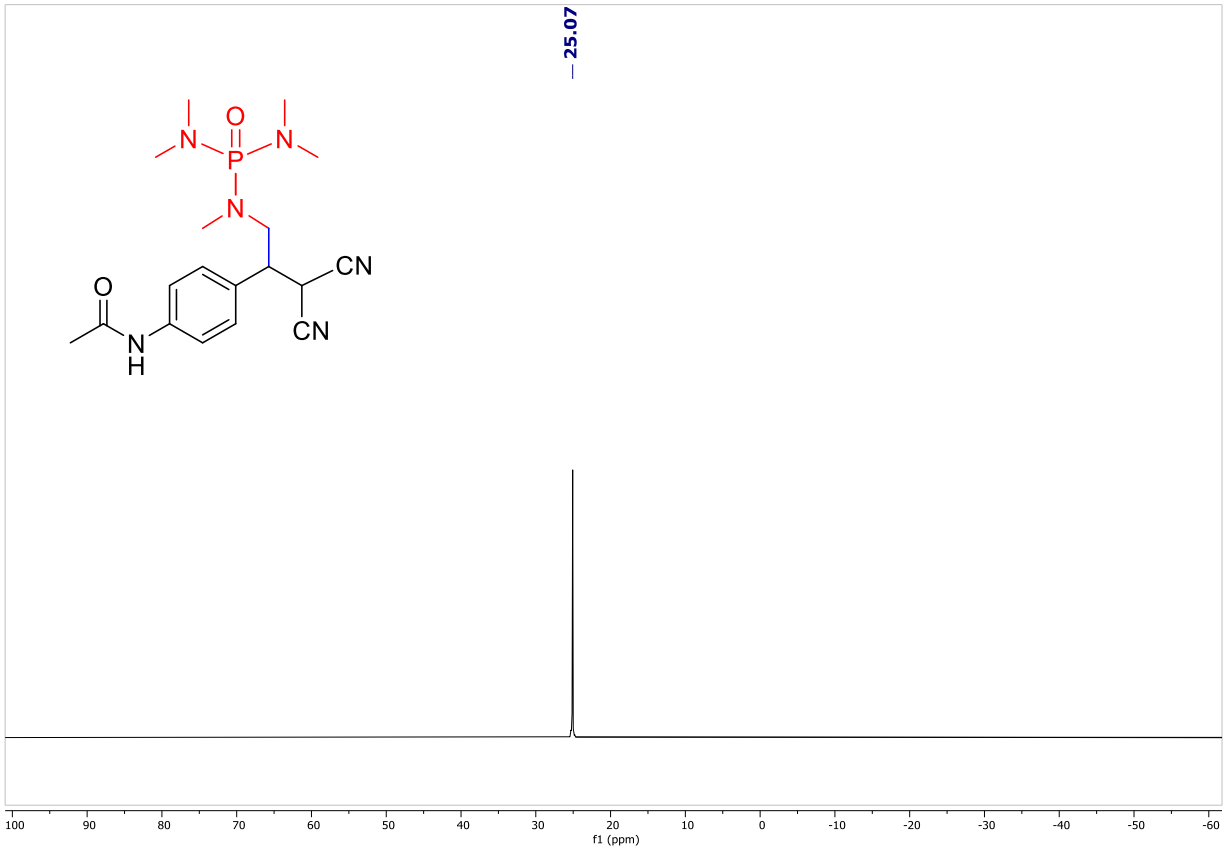
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**



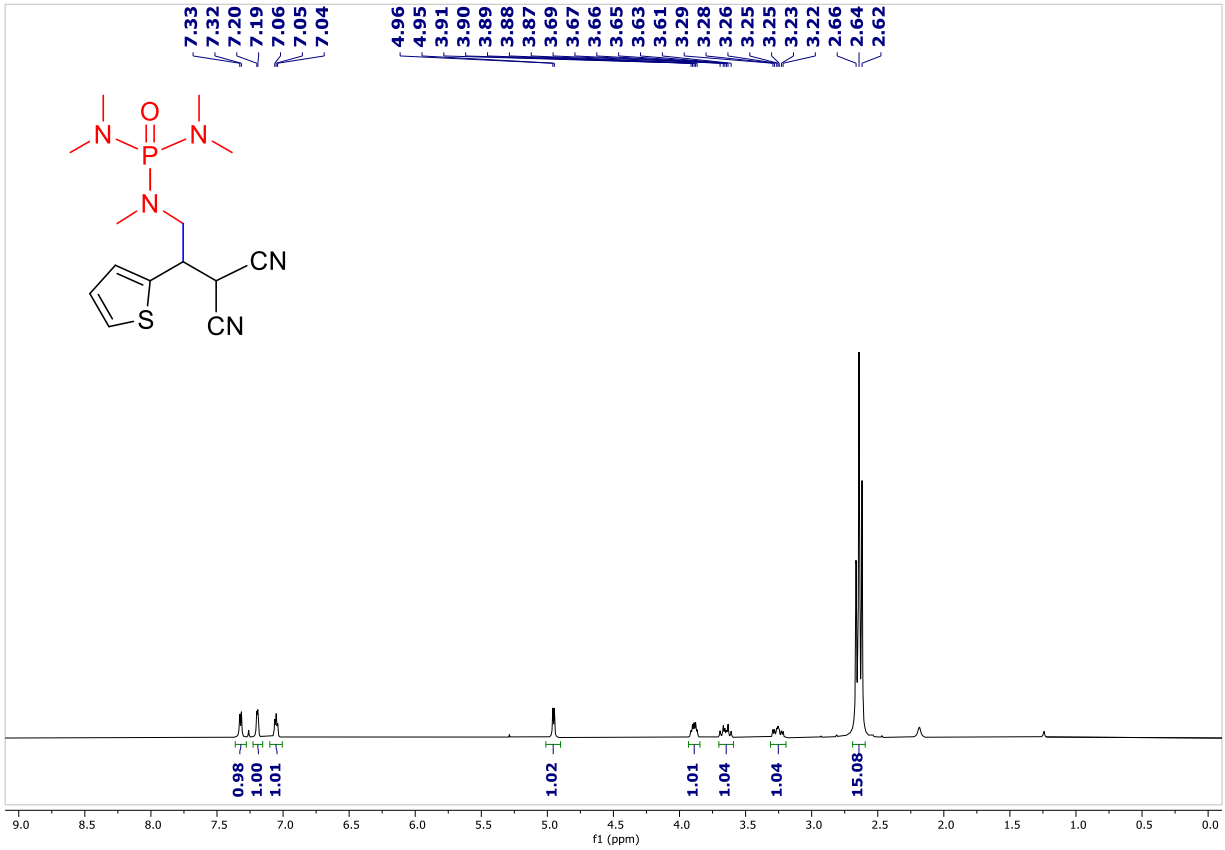
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3j**



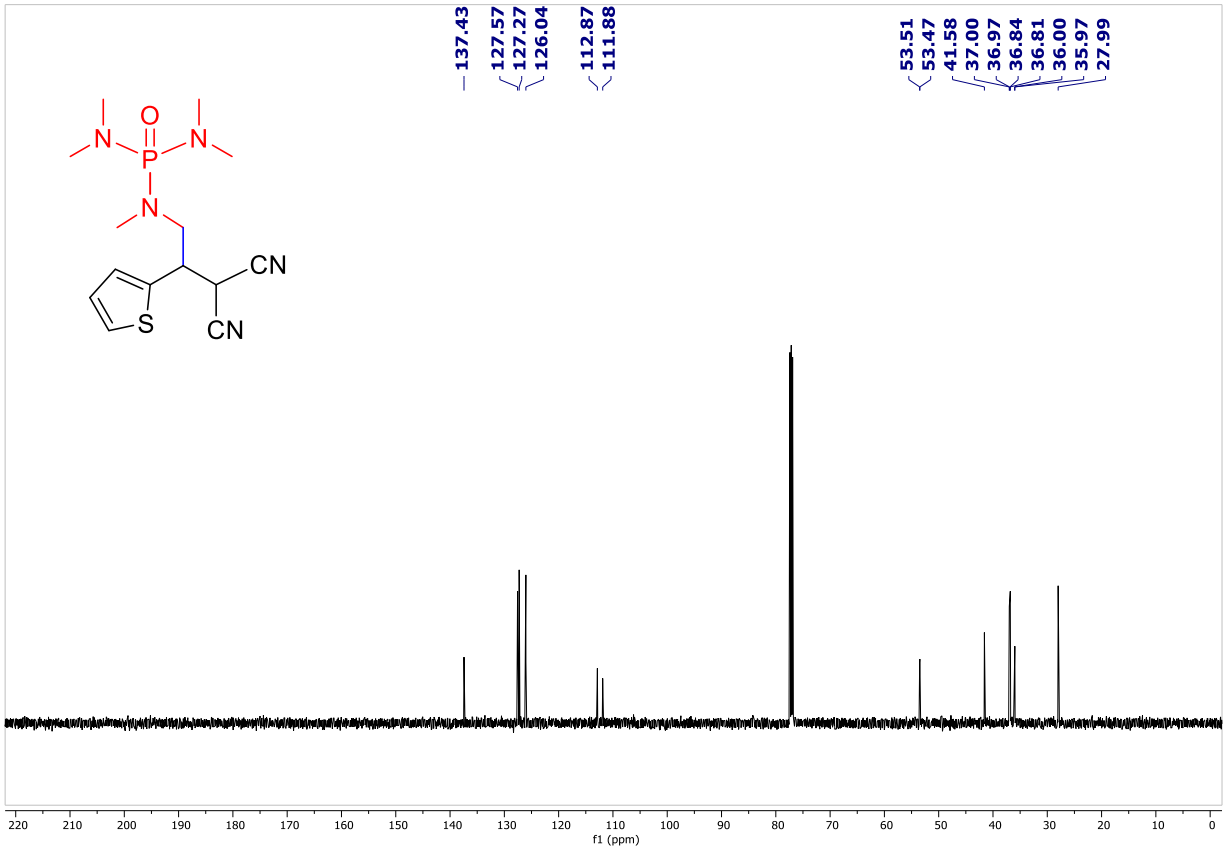
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3j**



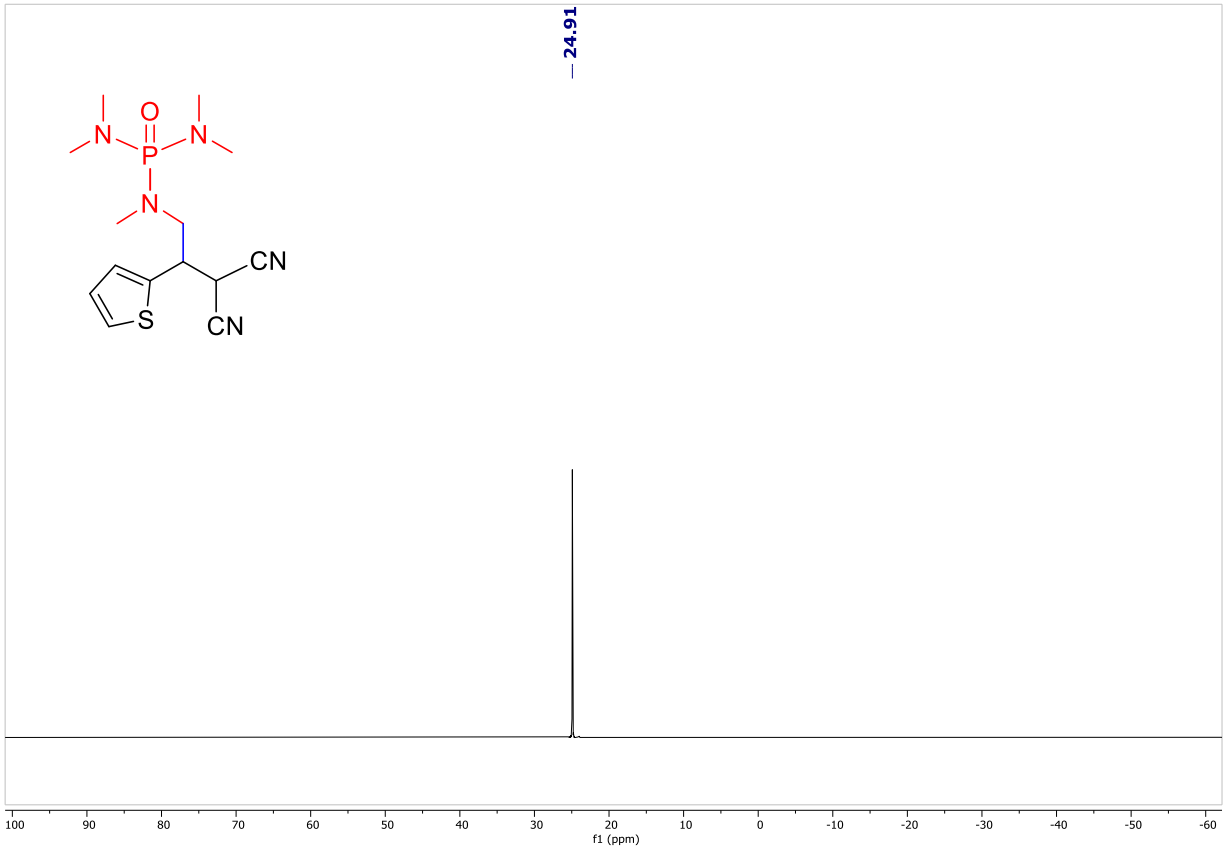
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**



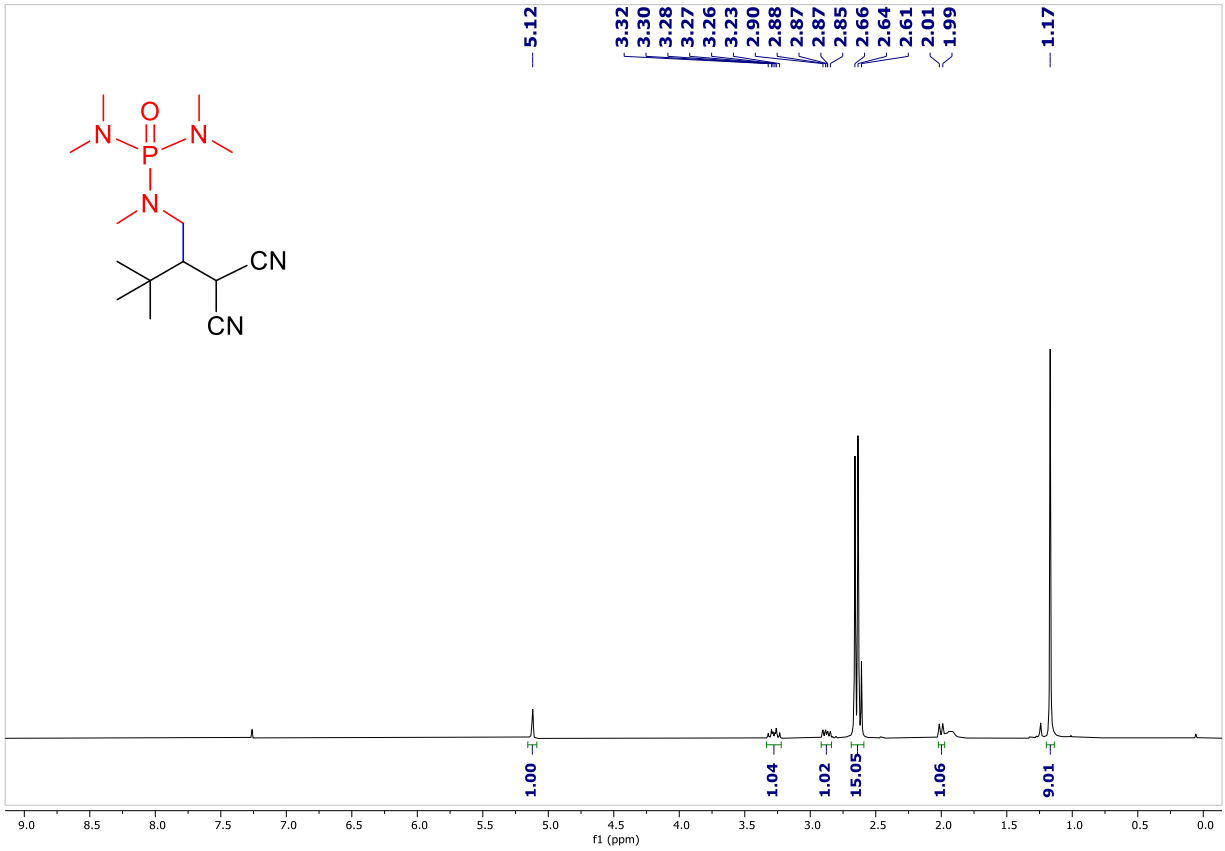
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3k**



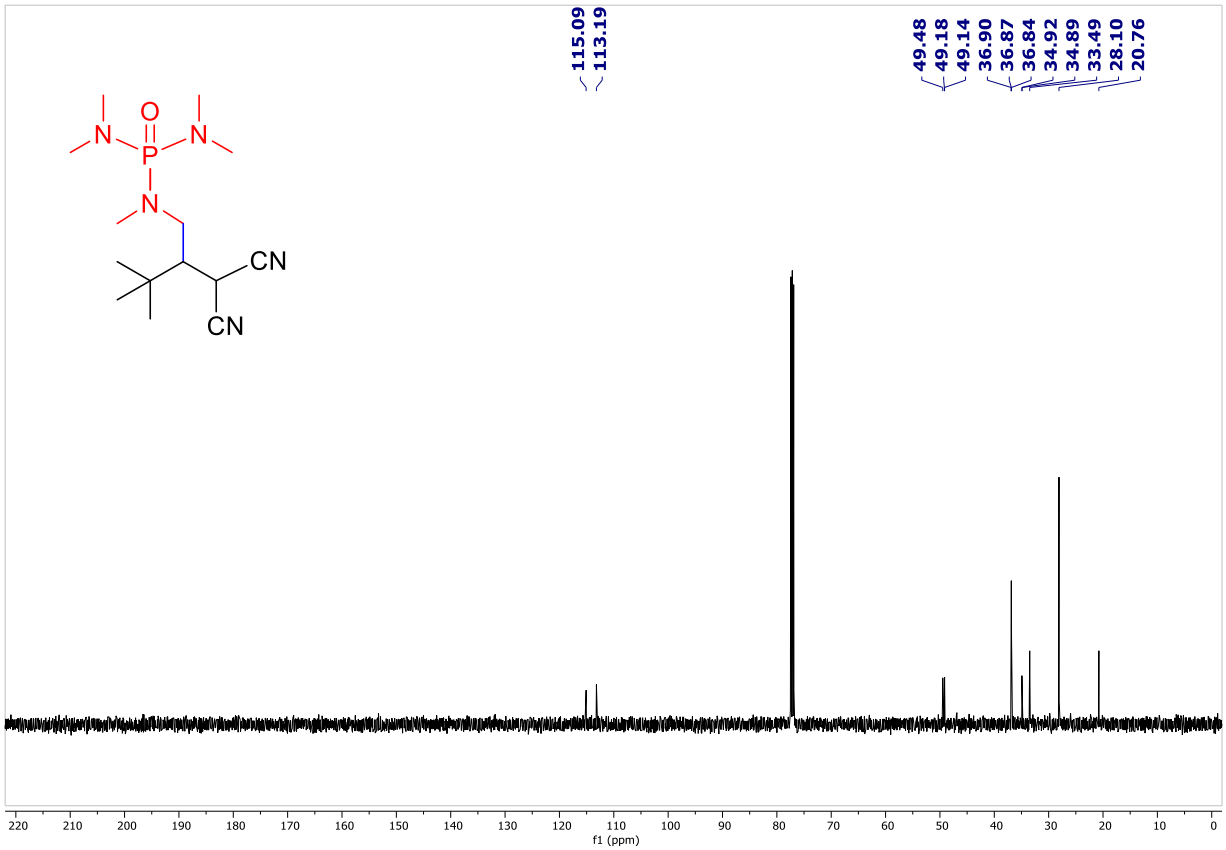
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3k**



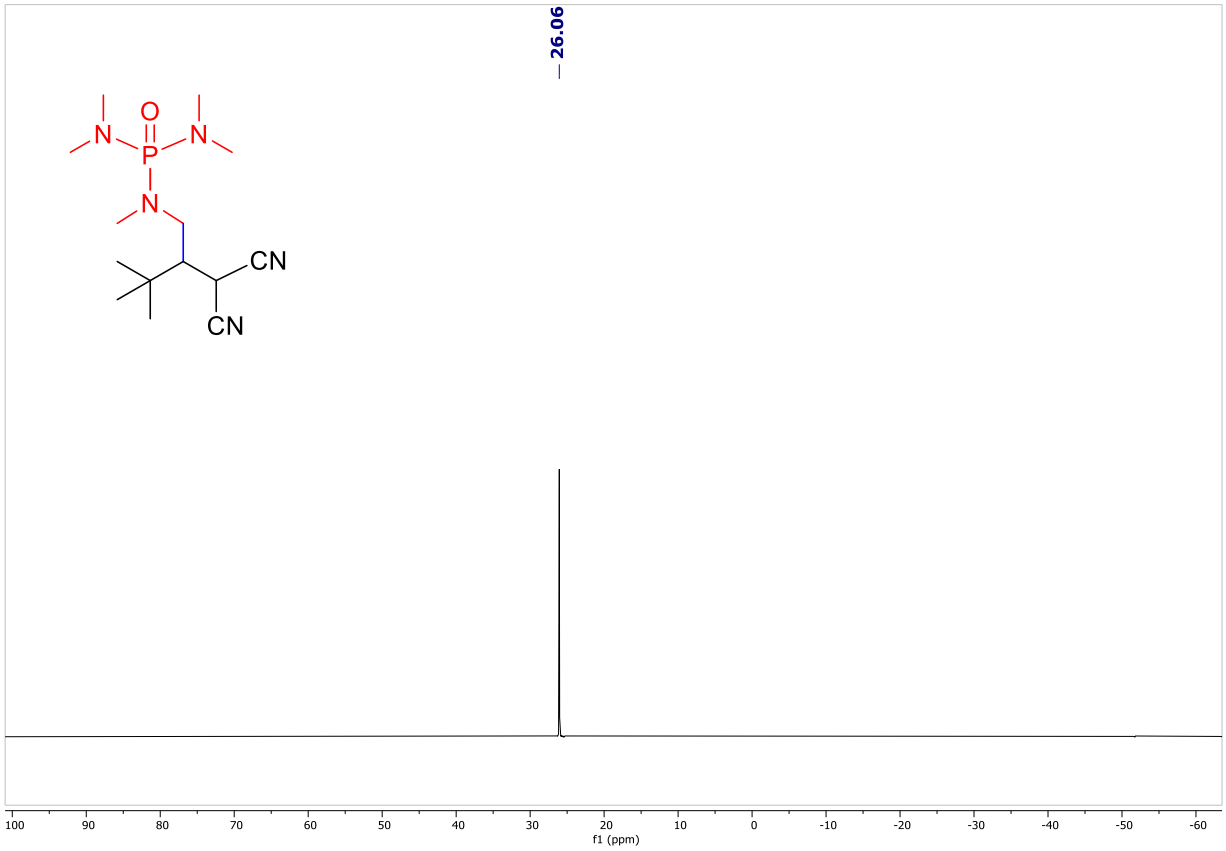
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**



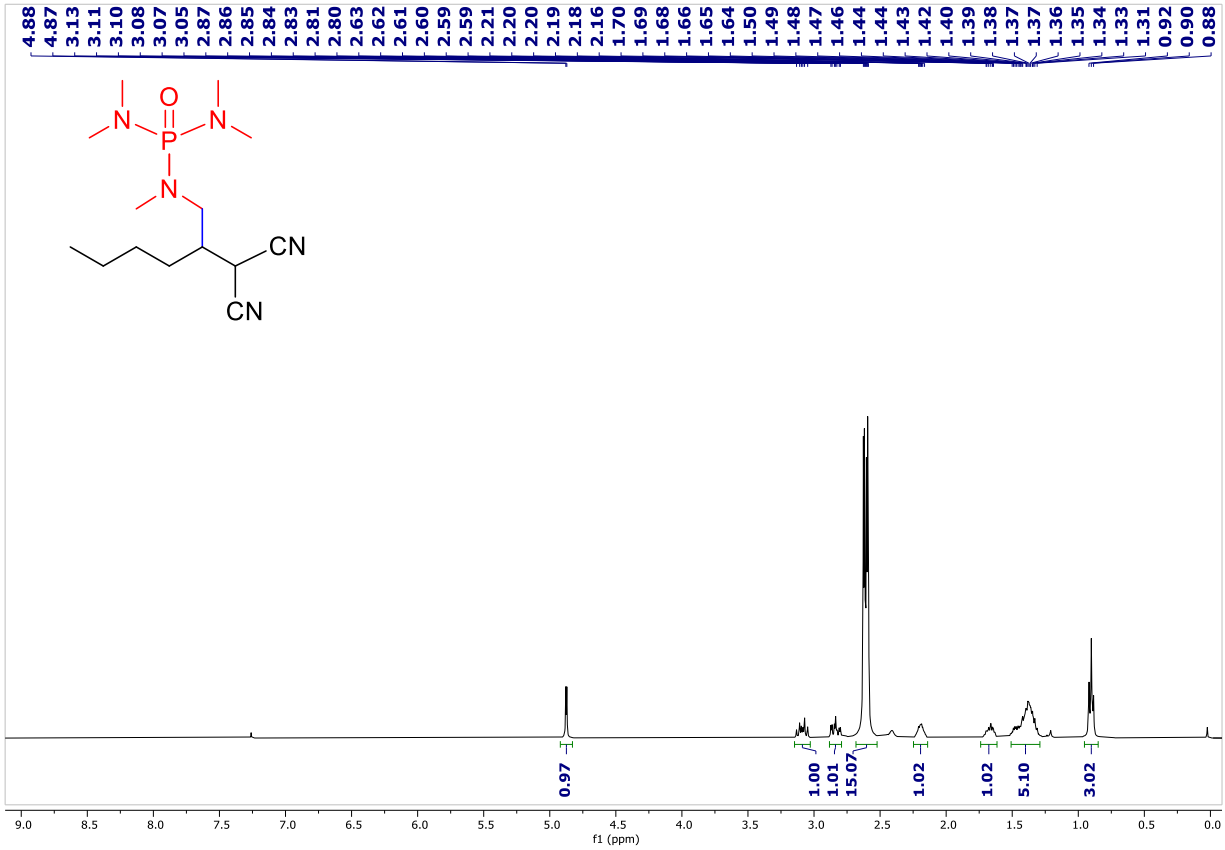
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **31**



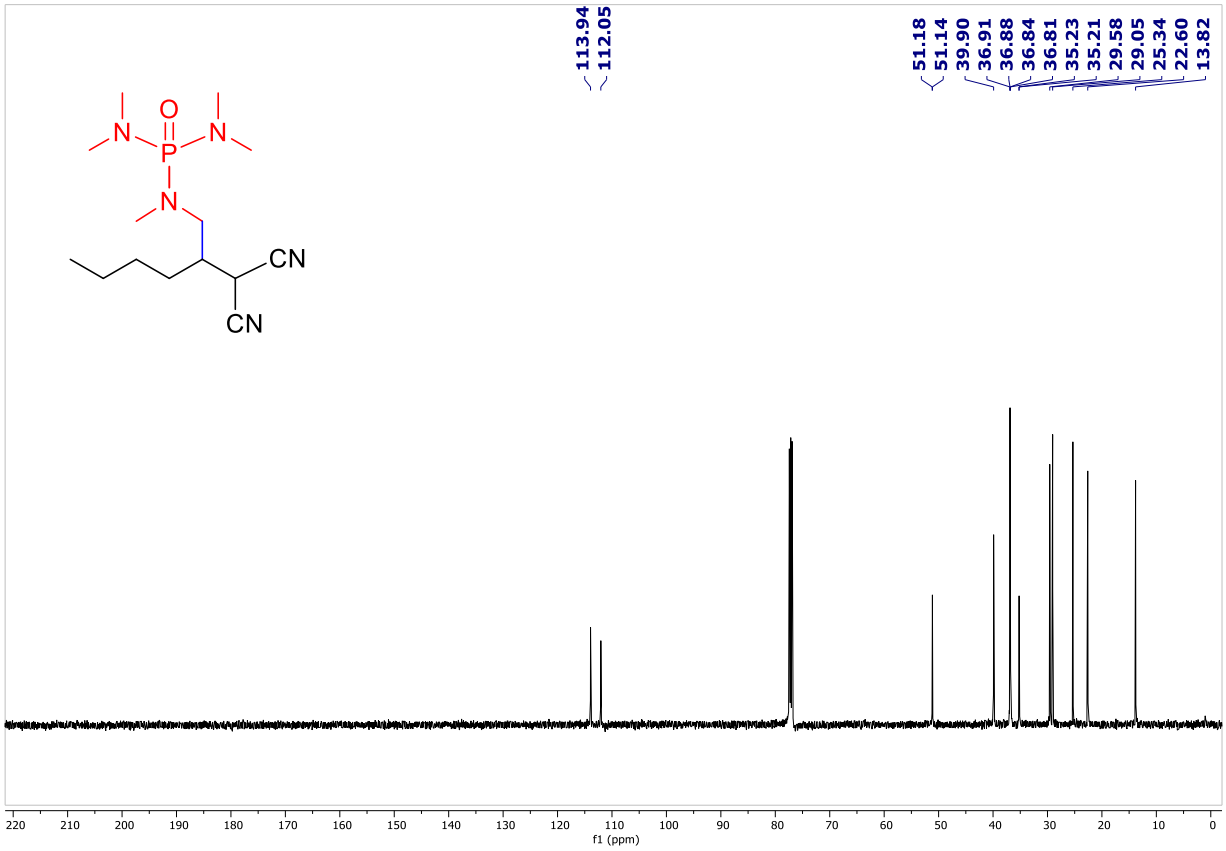
^{31}P NMR (203 MHz, $CDCl_3$) of compound **31**



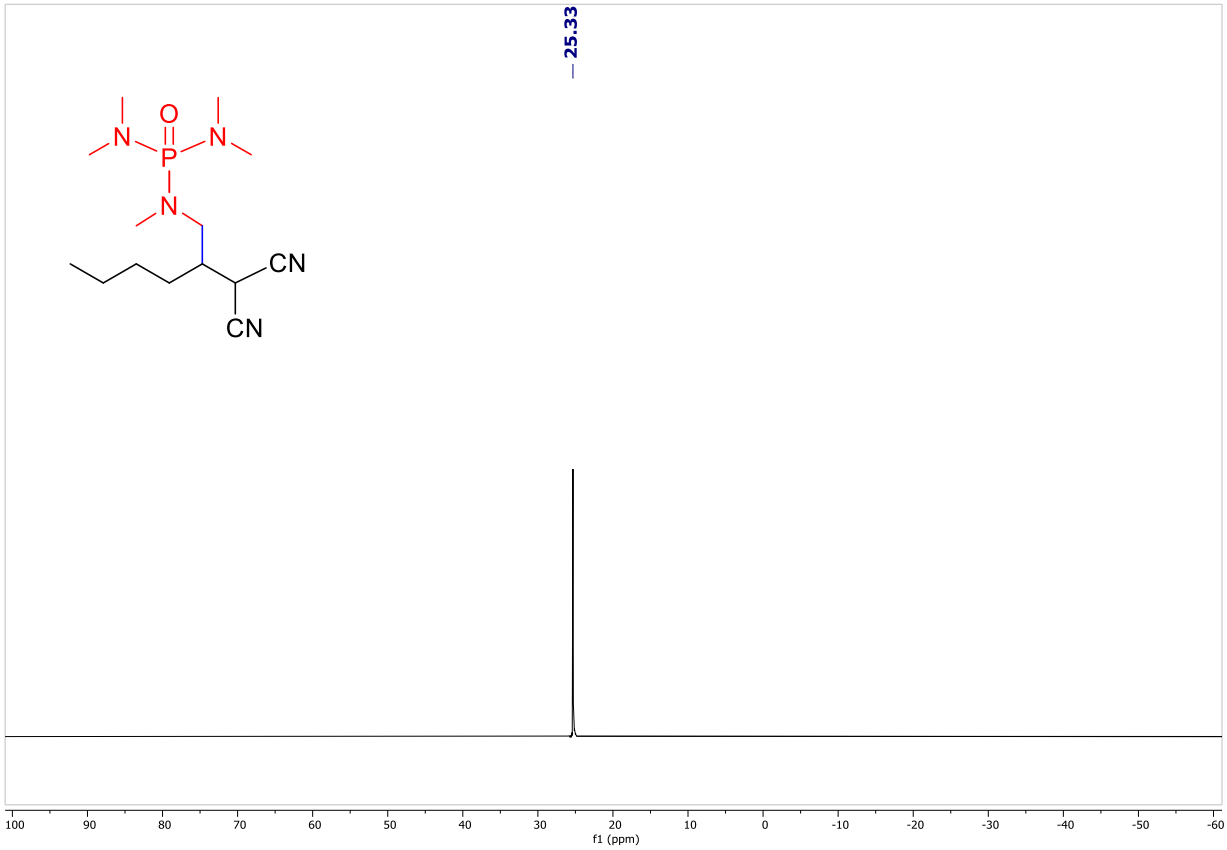
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**



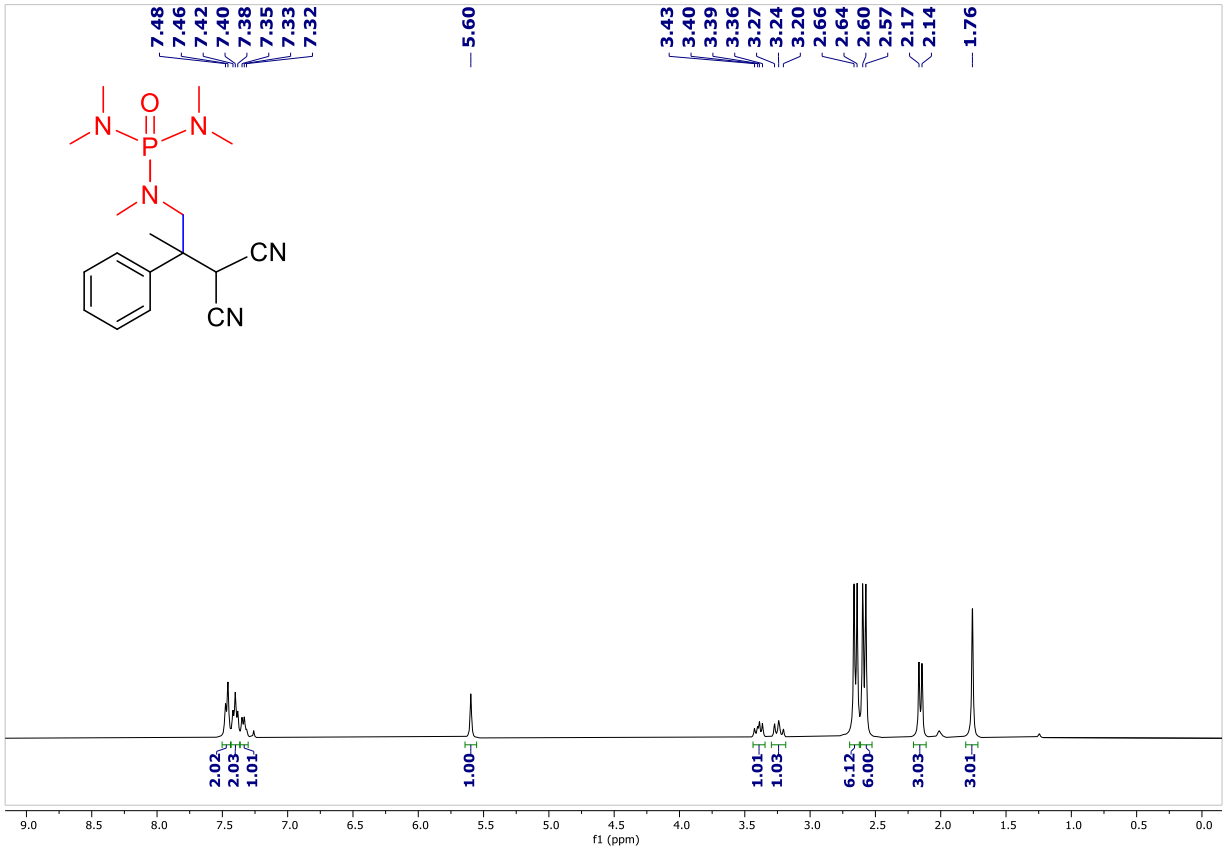
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3m**



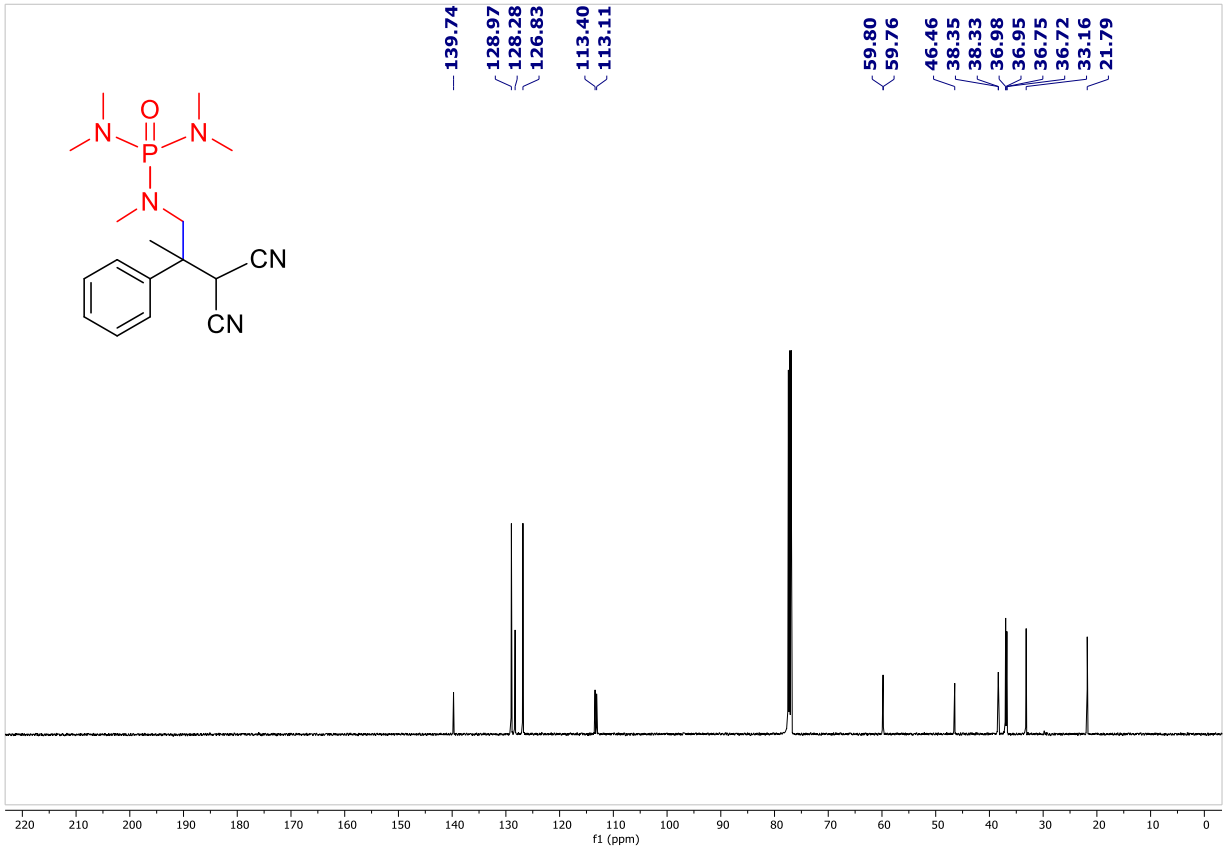
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3m**



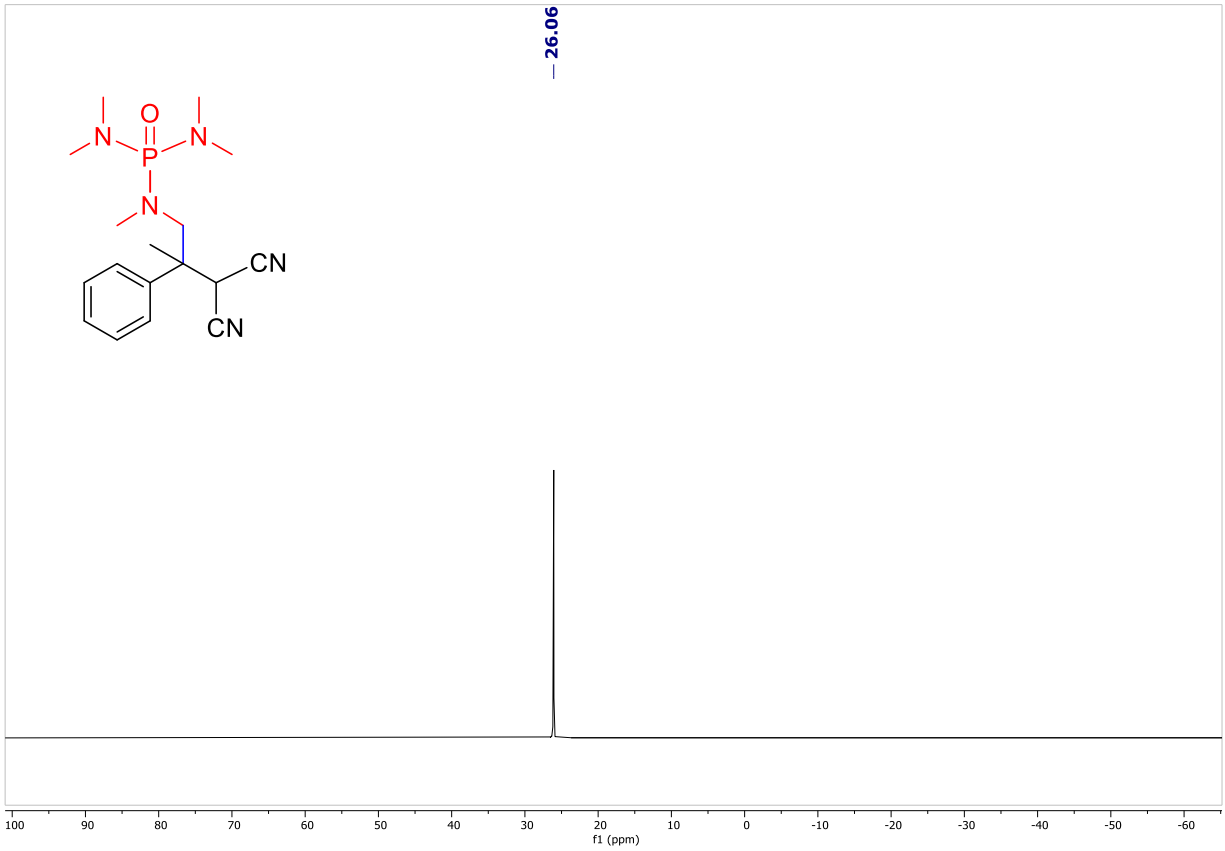
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**



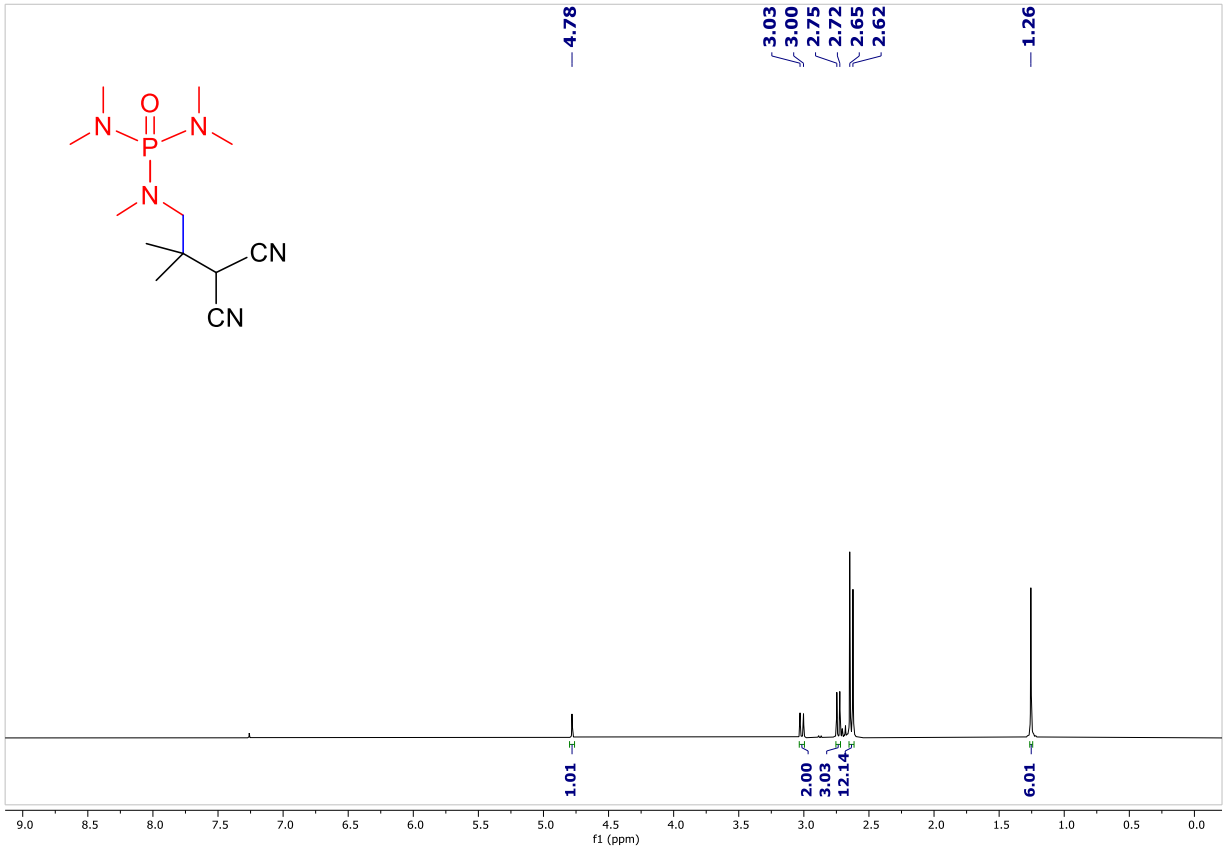
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3n**



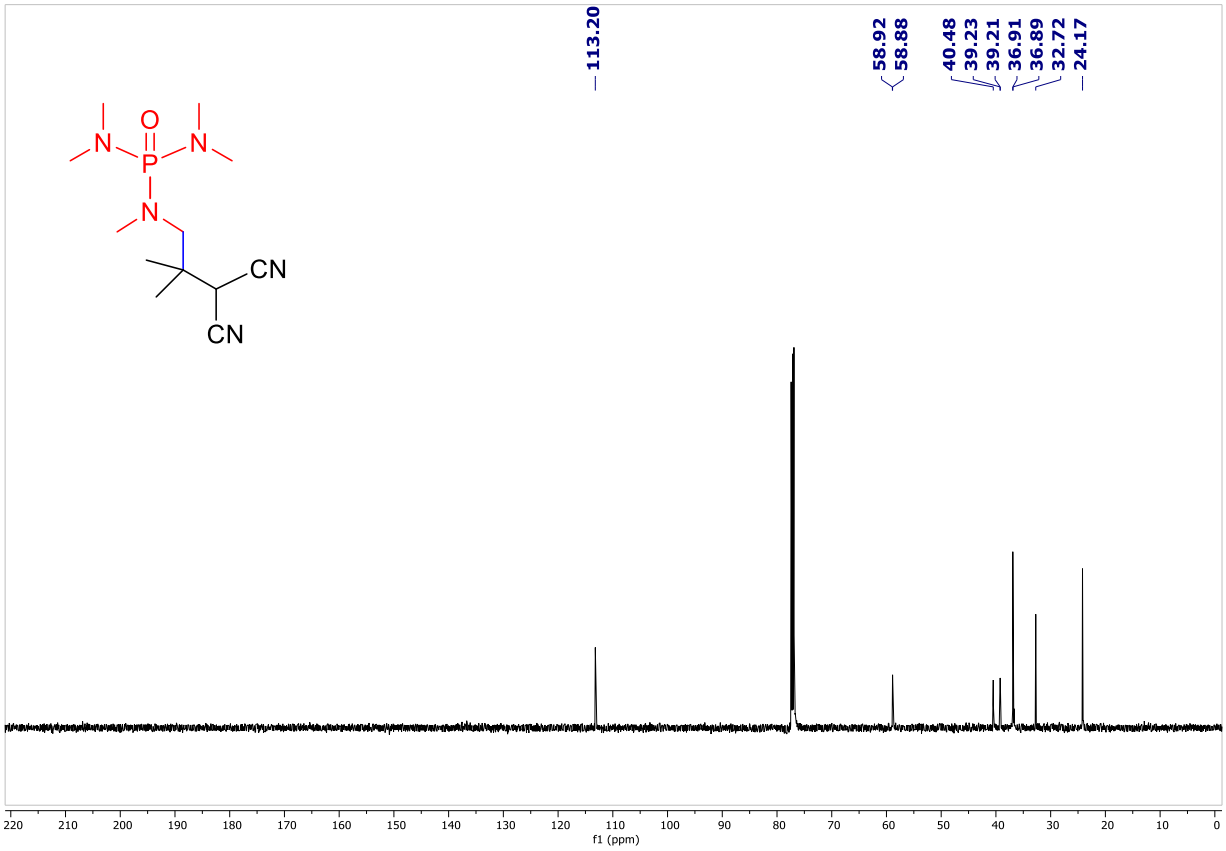
^{31}P NMR (203 MHz, $CDCl_3$) of compound 3**n**



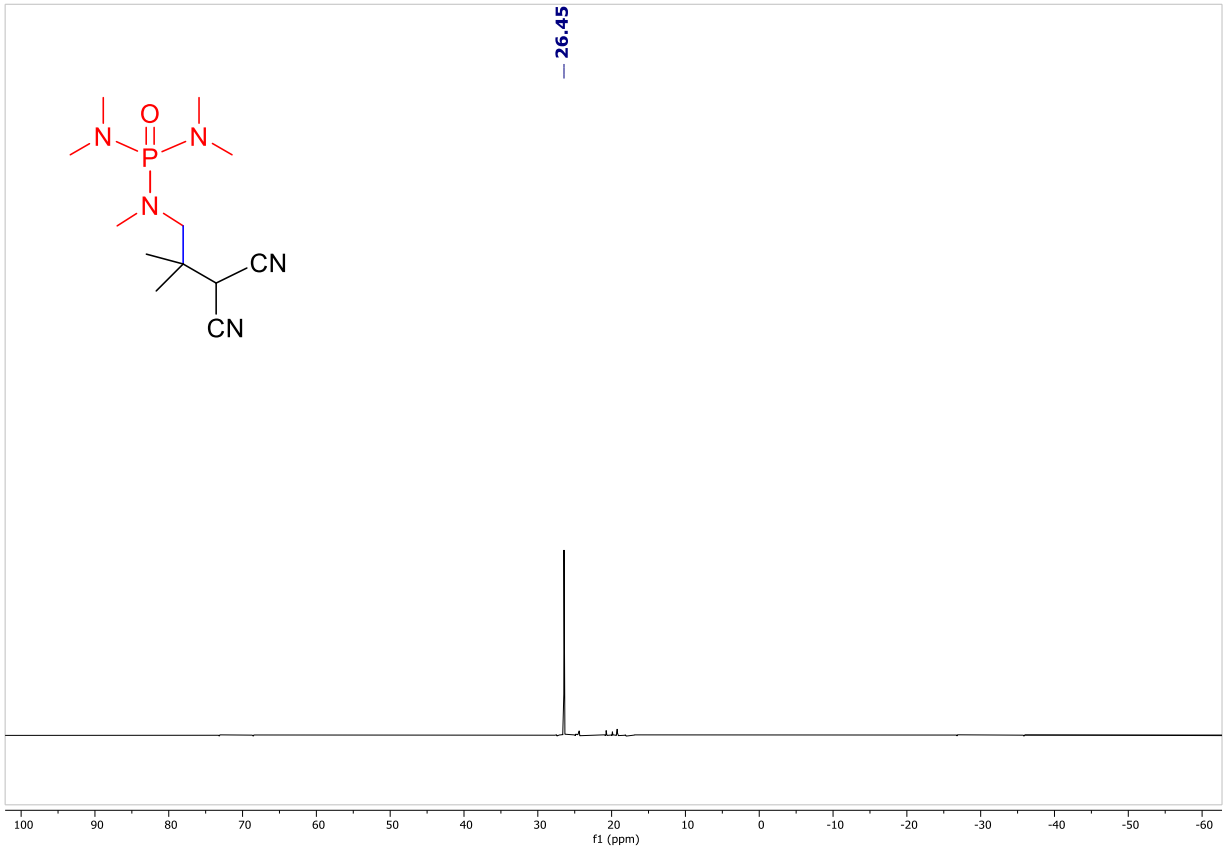
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**



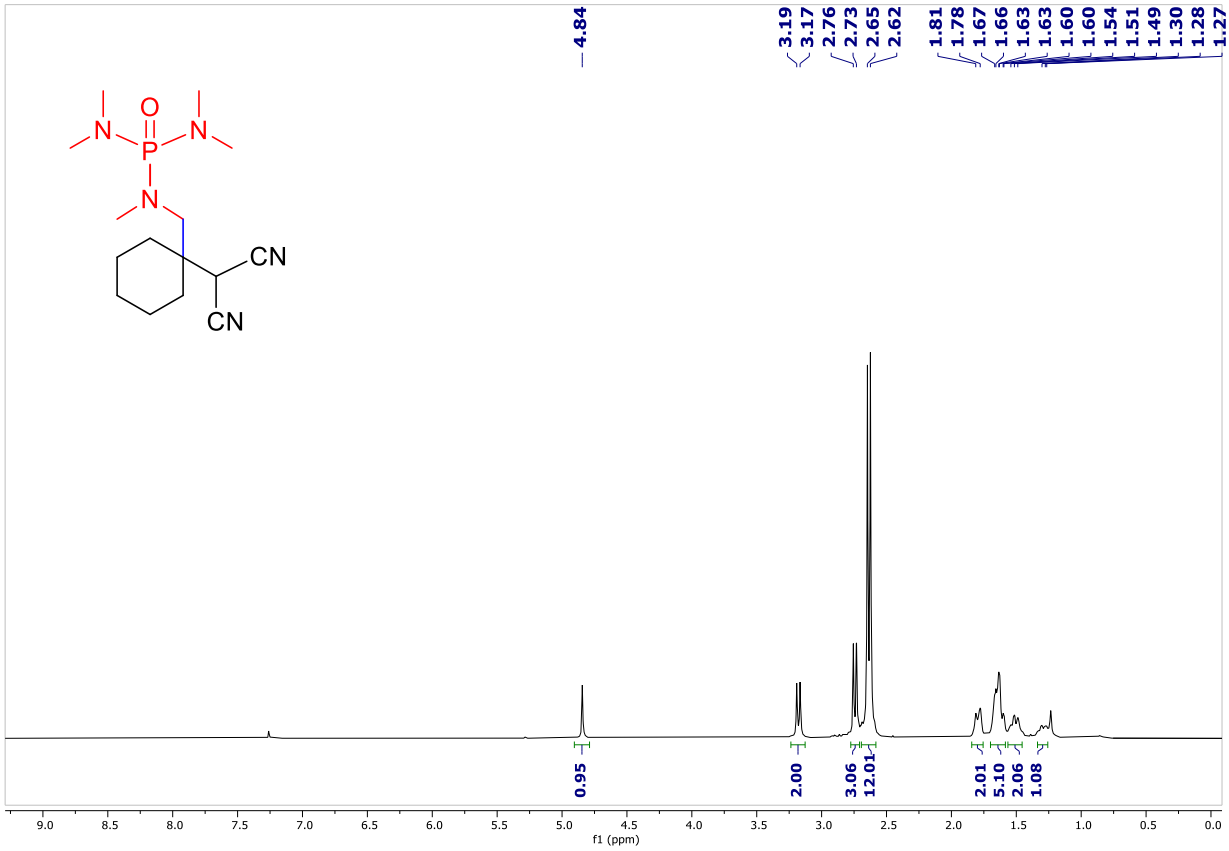
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3o**



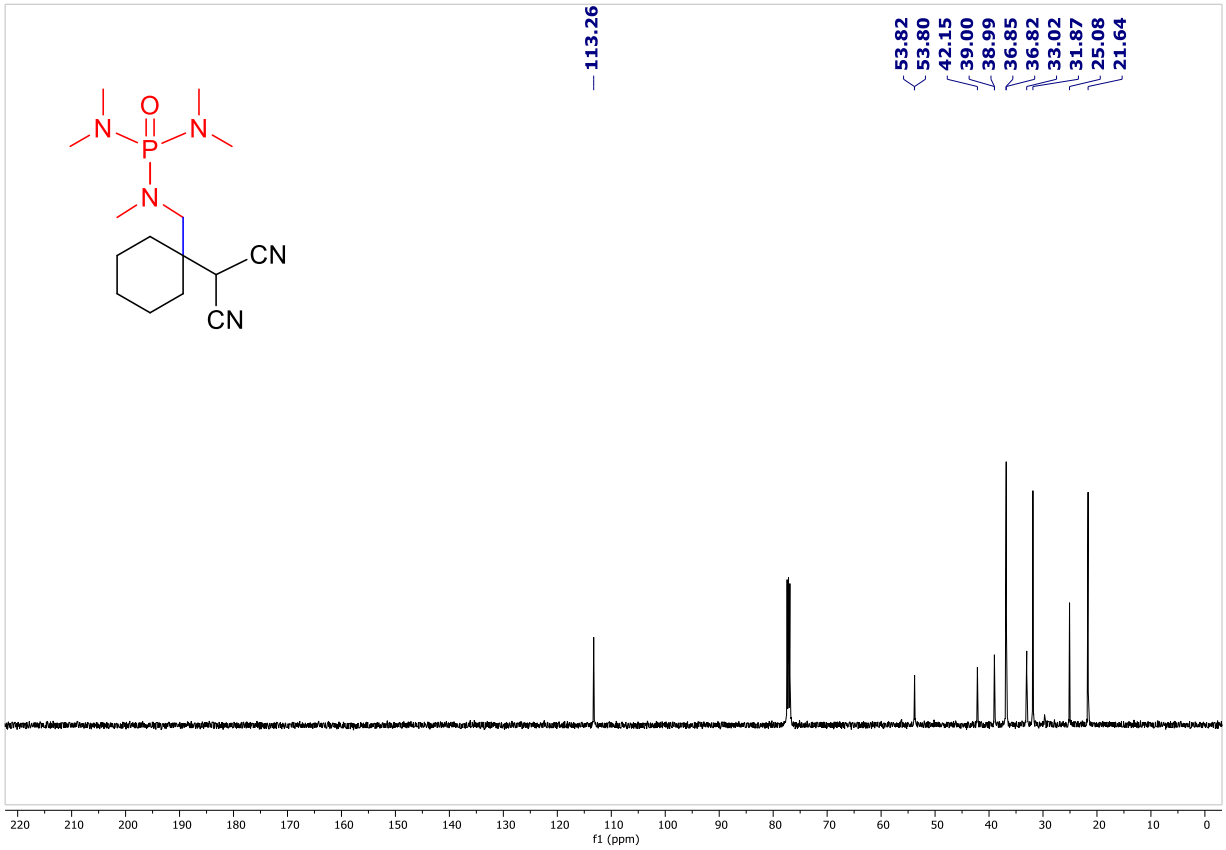
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3o**



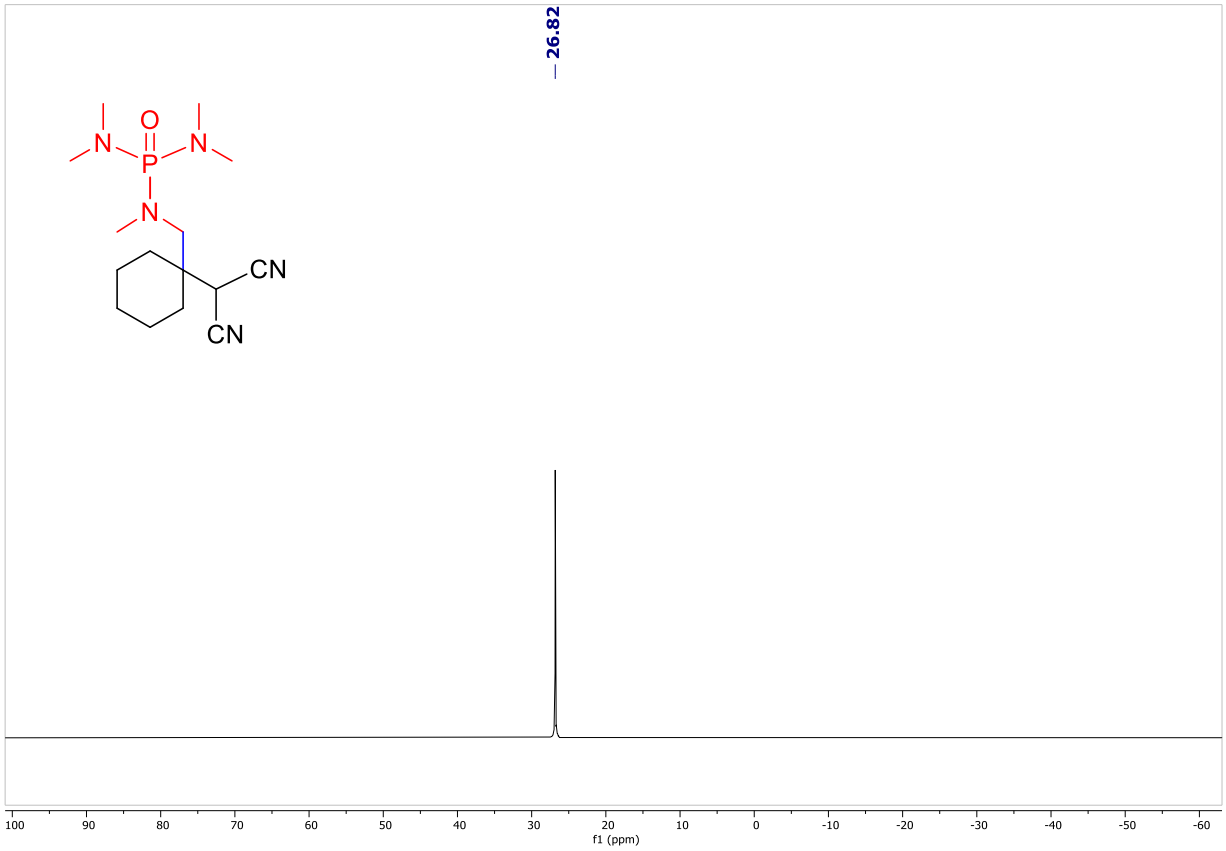
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**



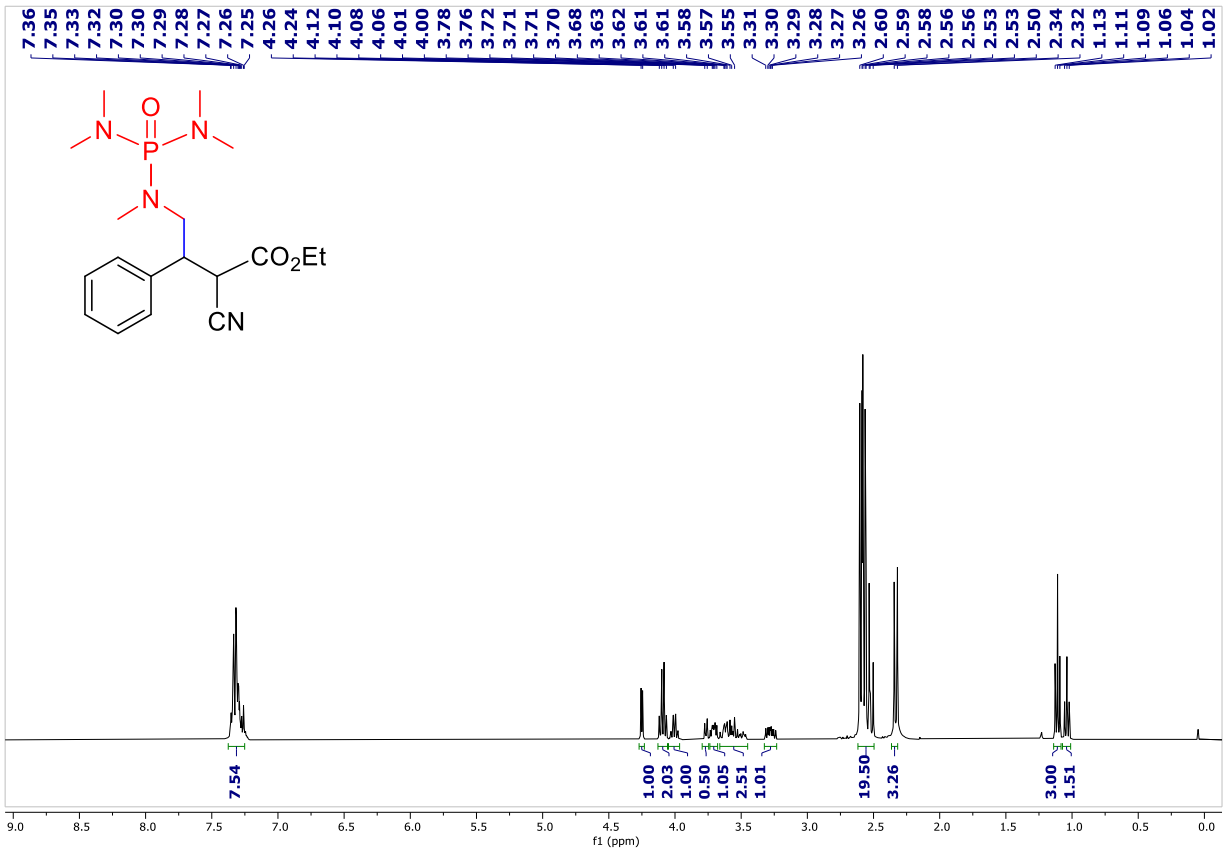
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3p**



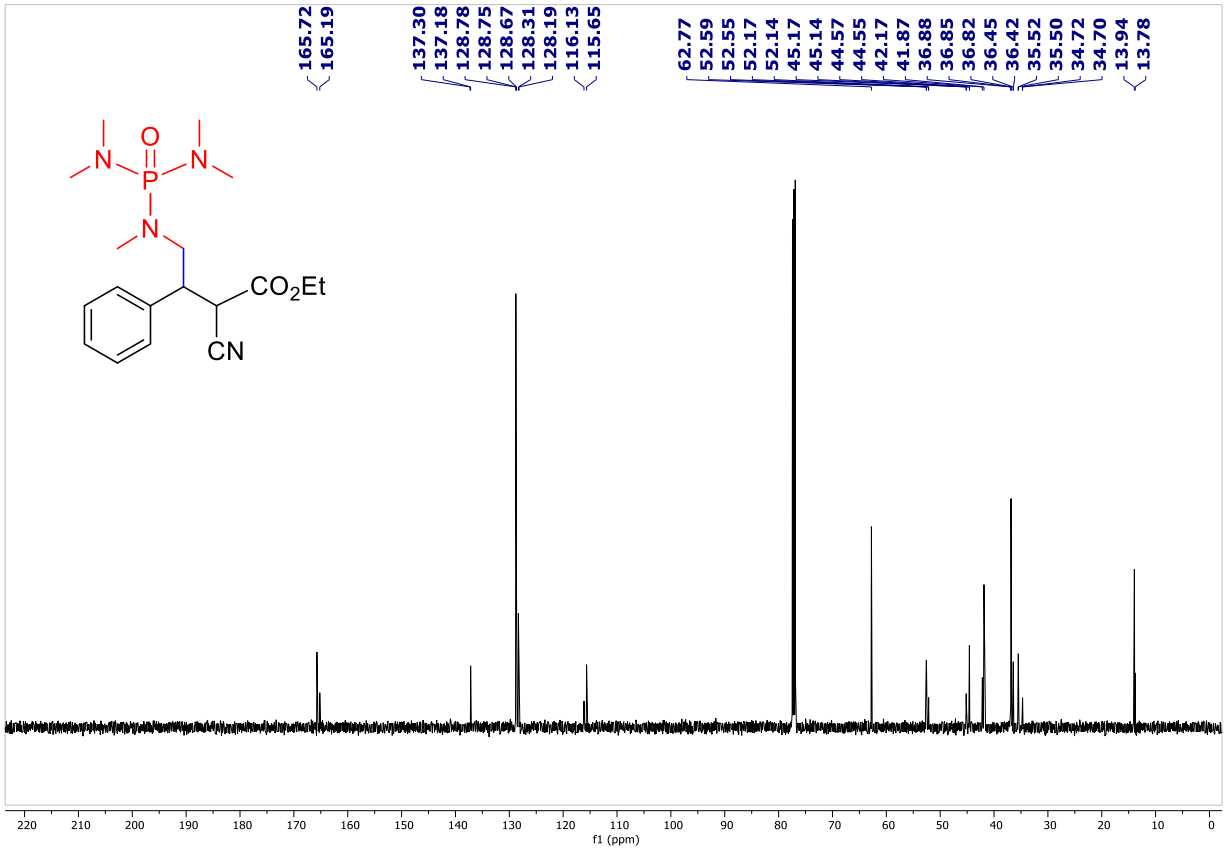
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3p**



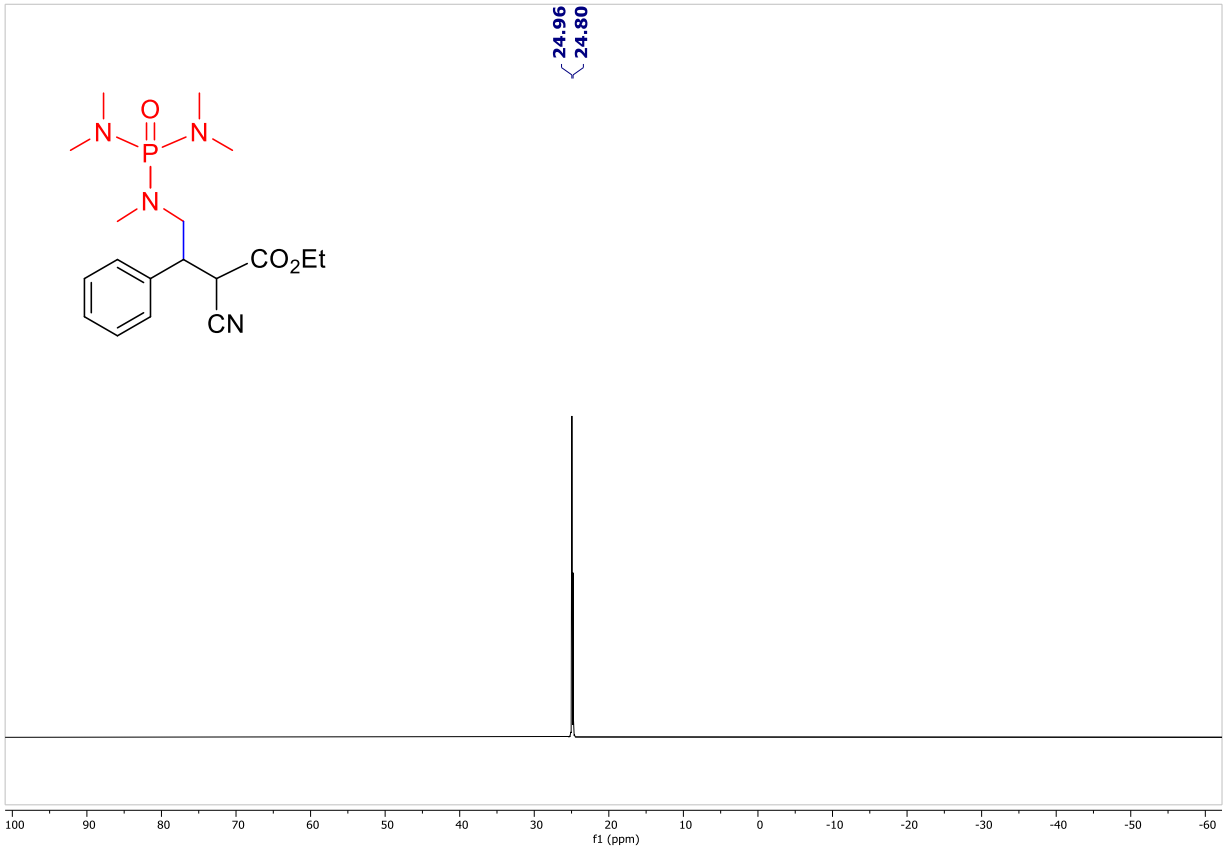
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q**



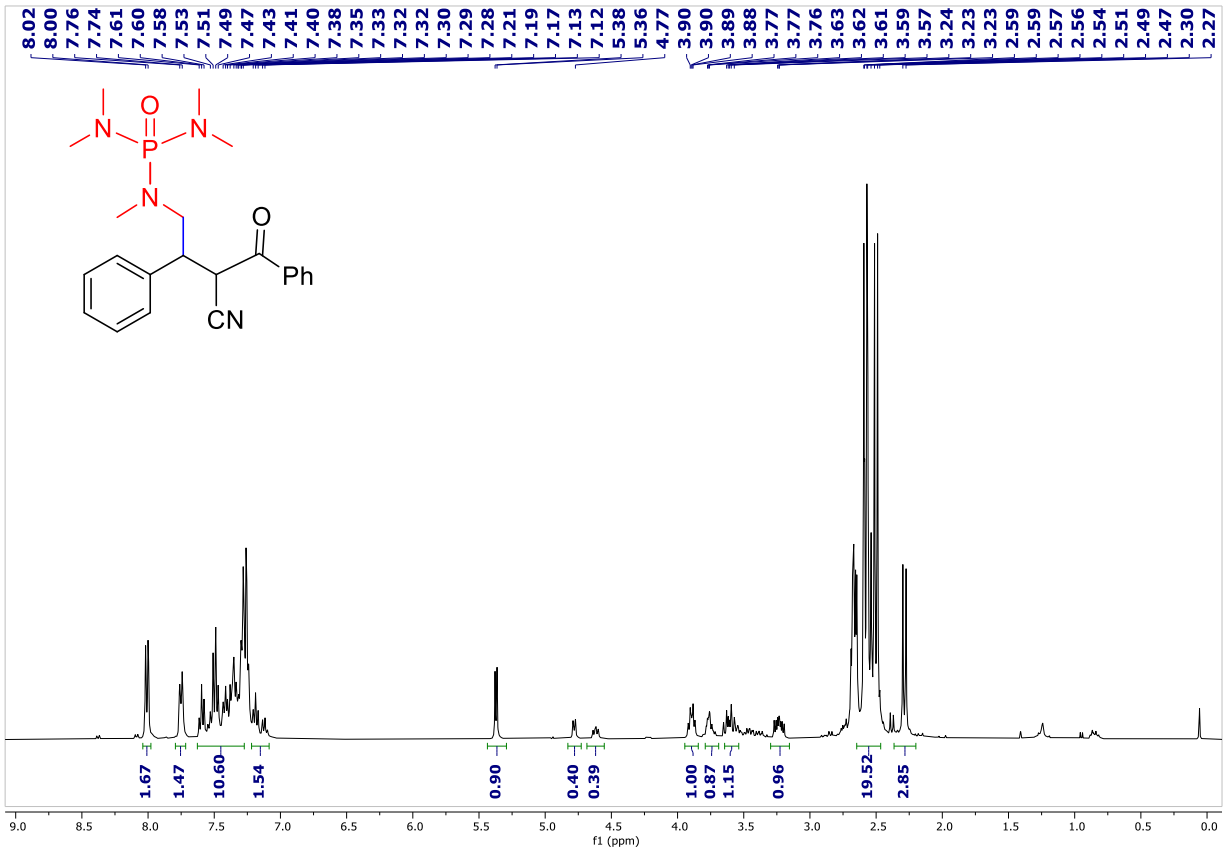
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3q**



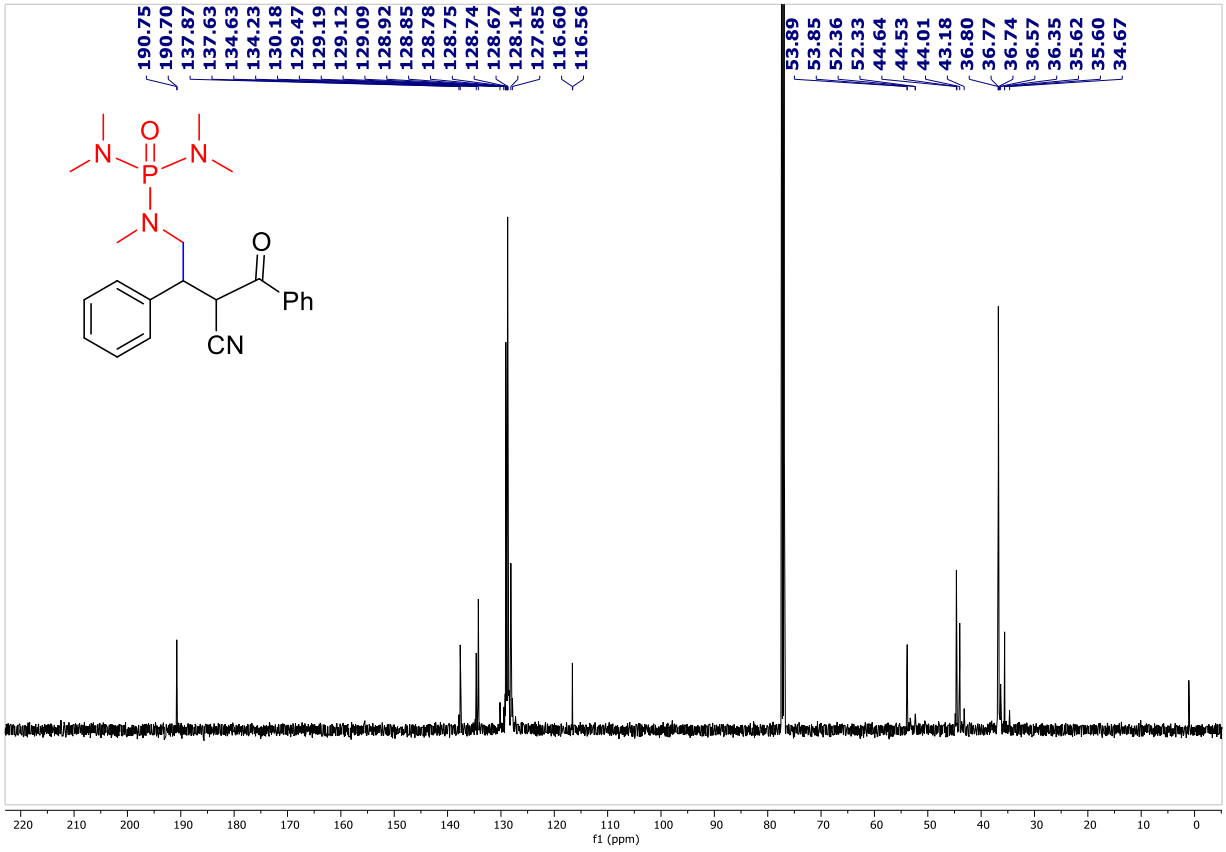
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3q**



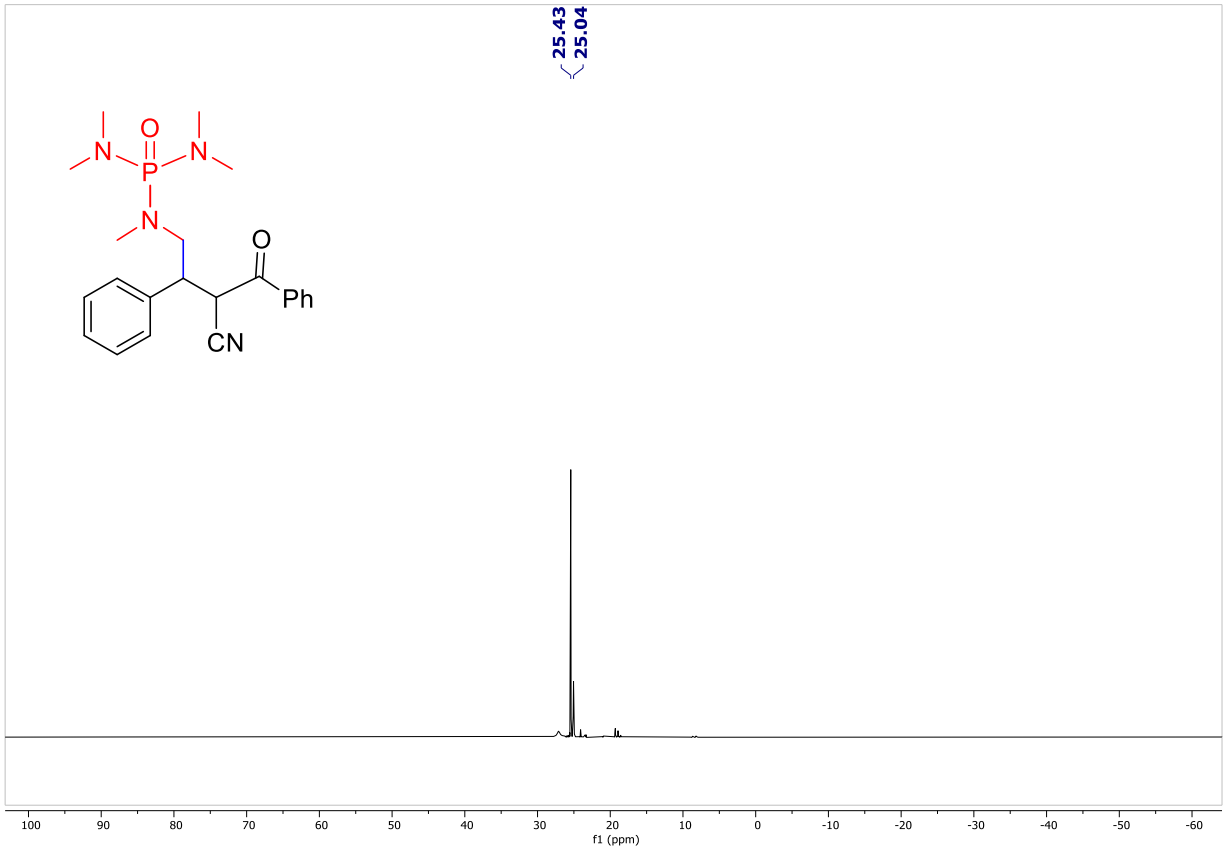
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r**



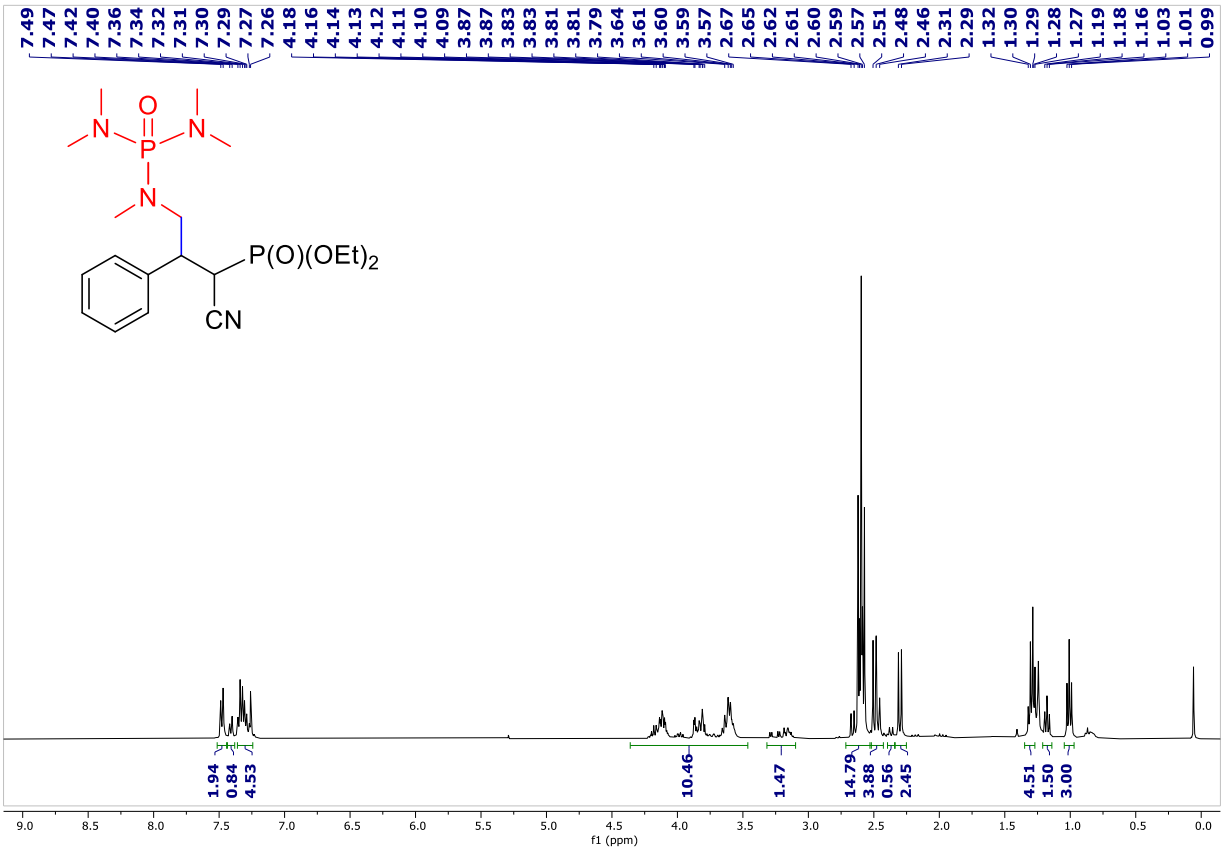
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3r**



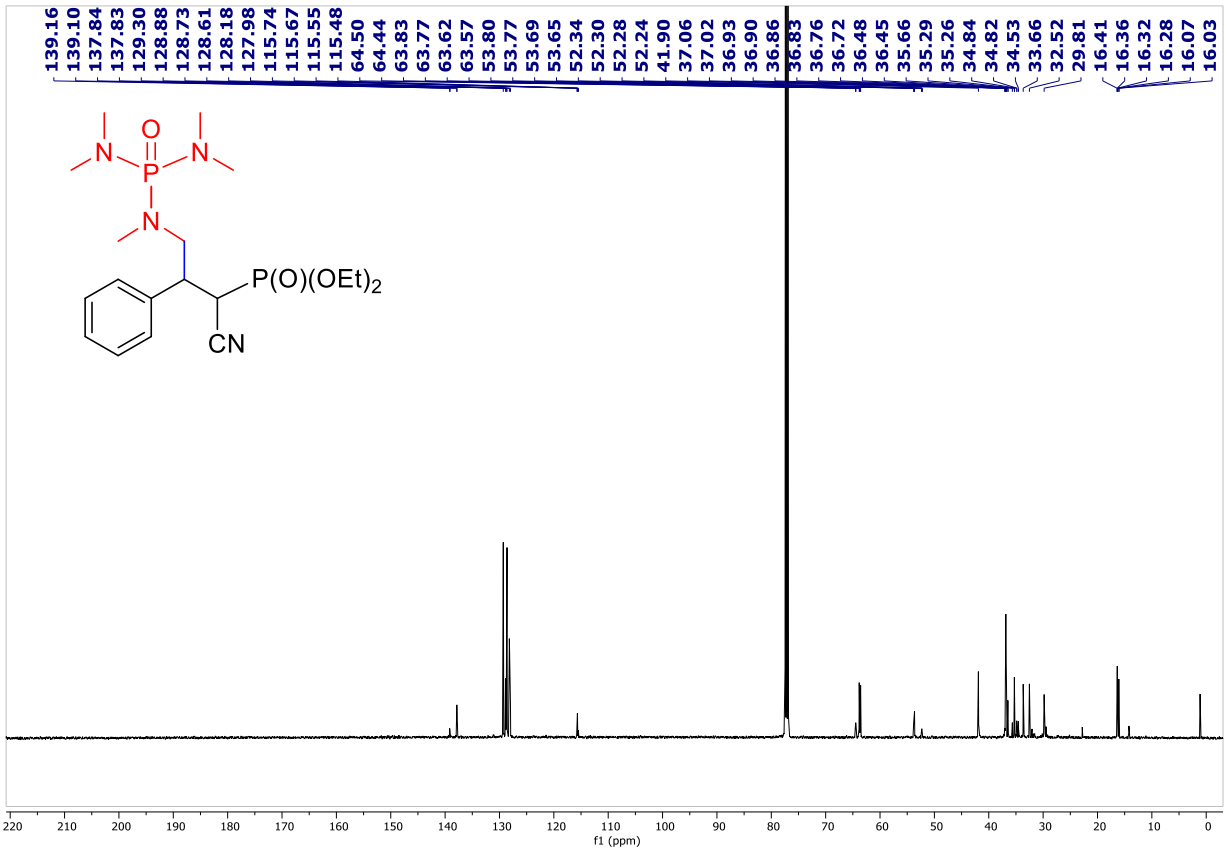
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3r**



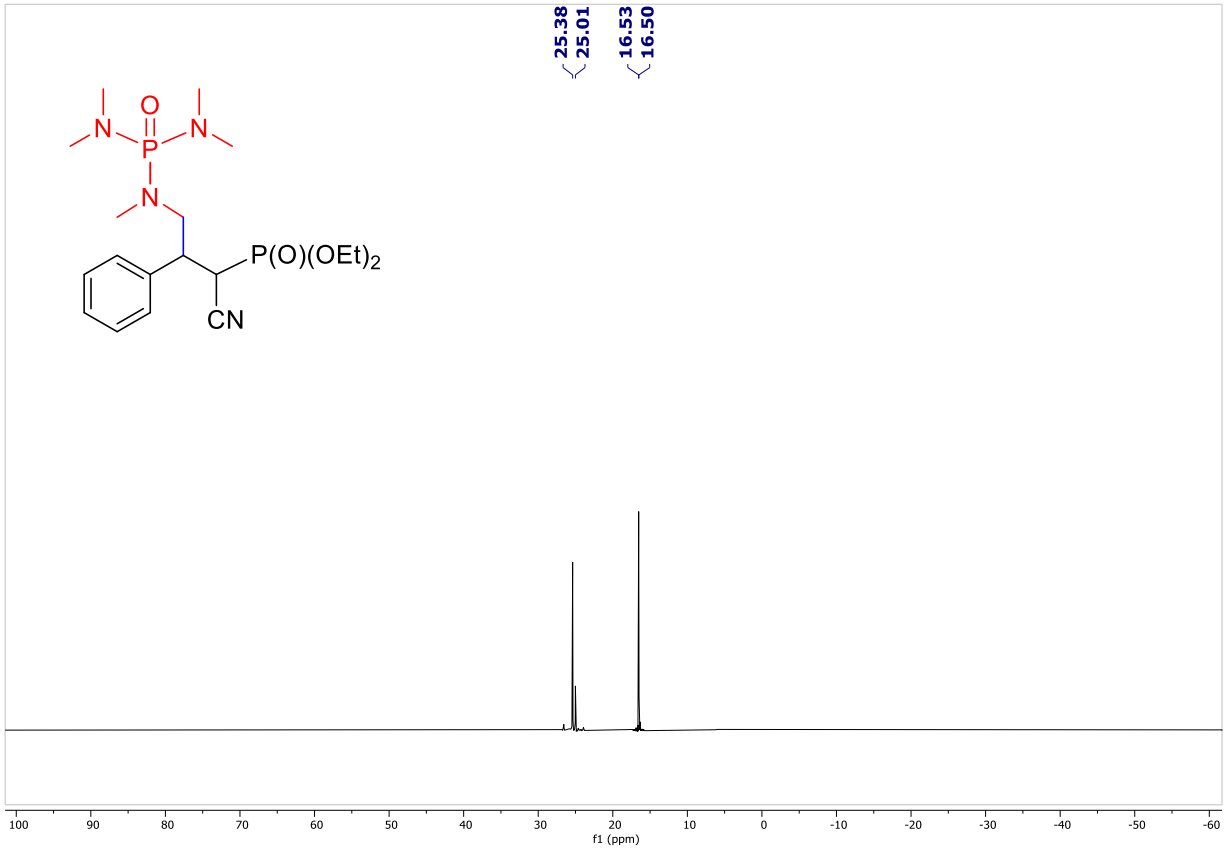
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s**



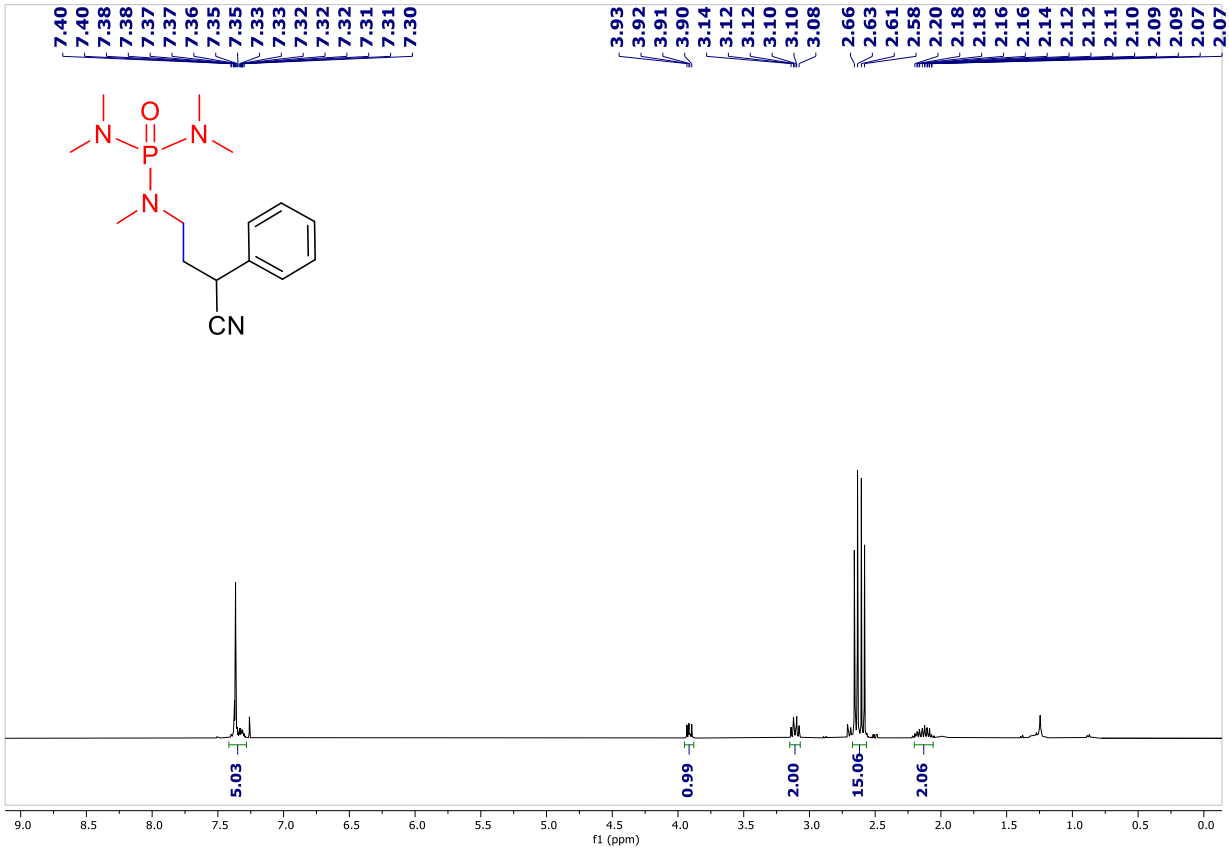
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3s**



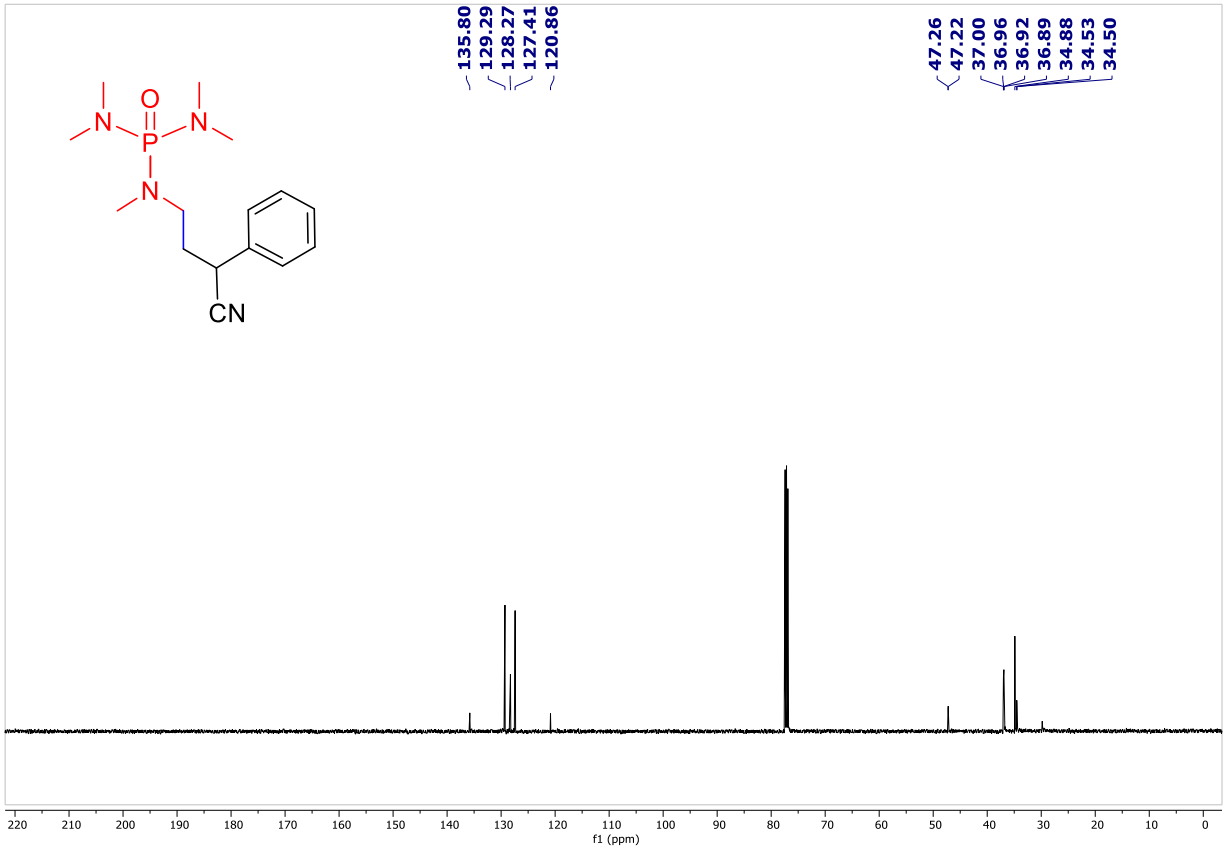
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3s**



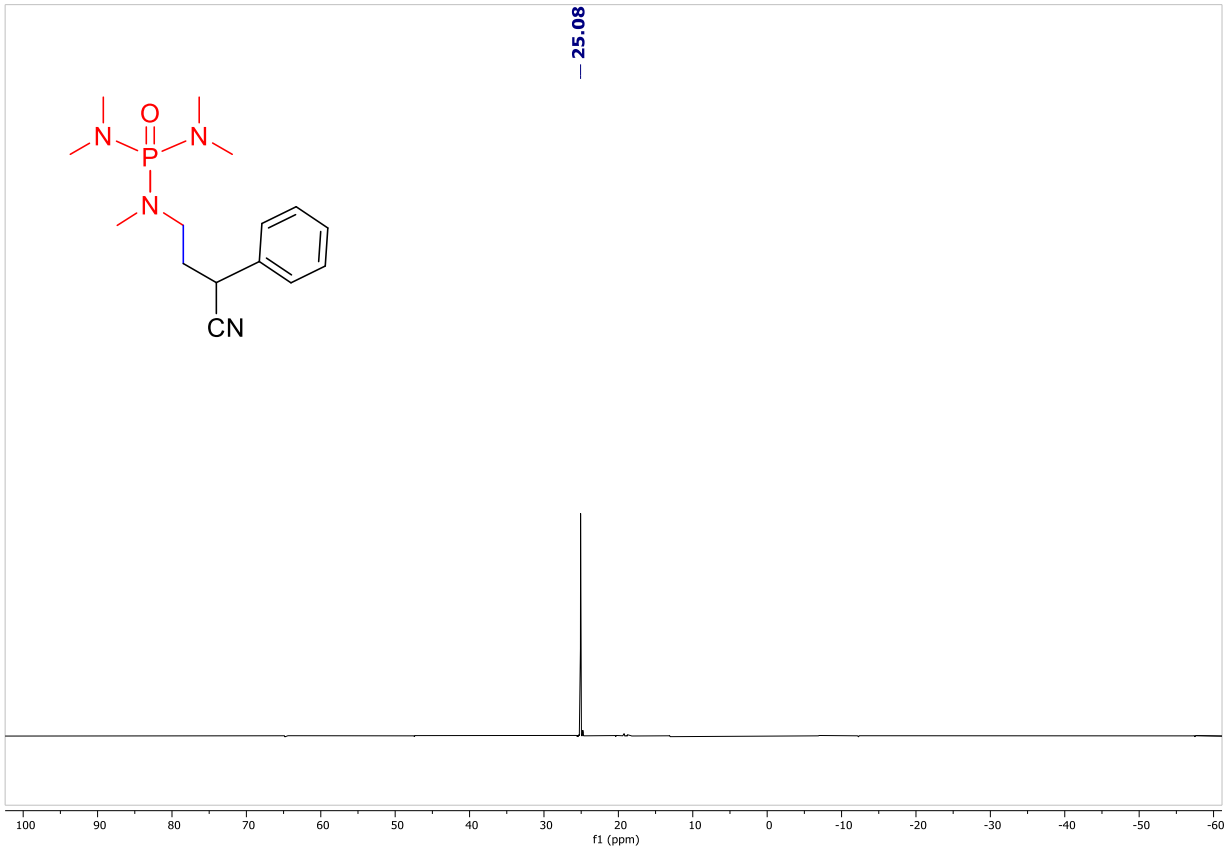
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t**



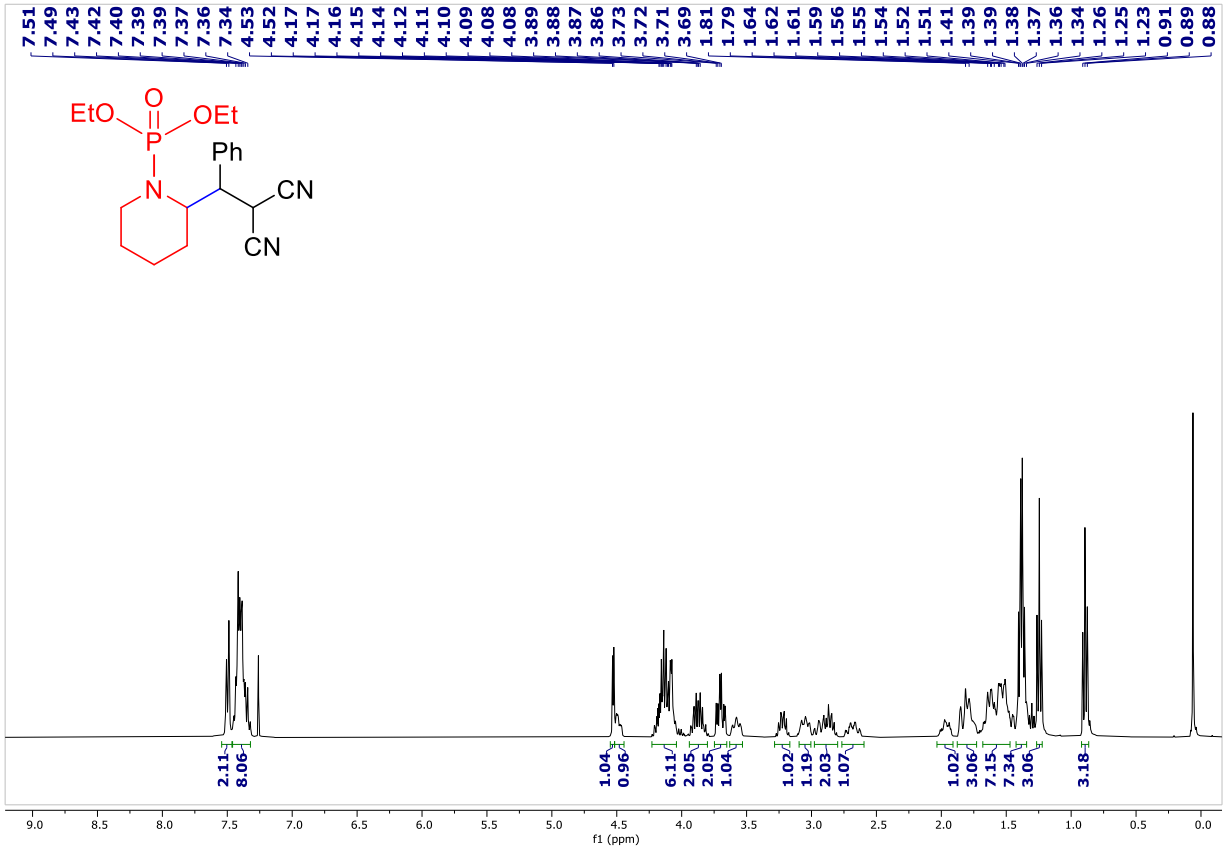
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3t**



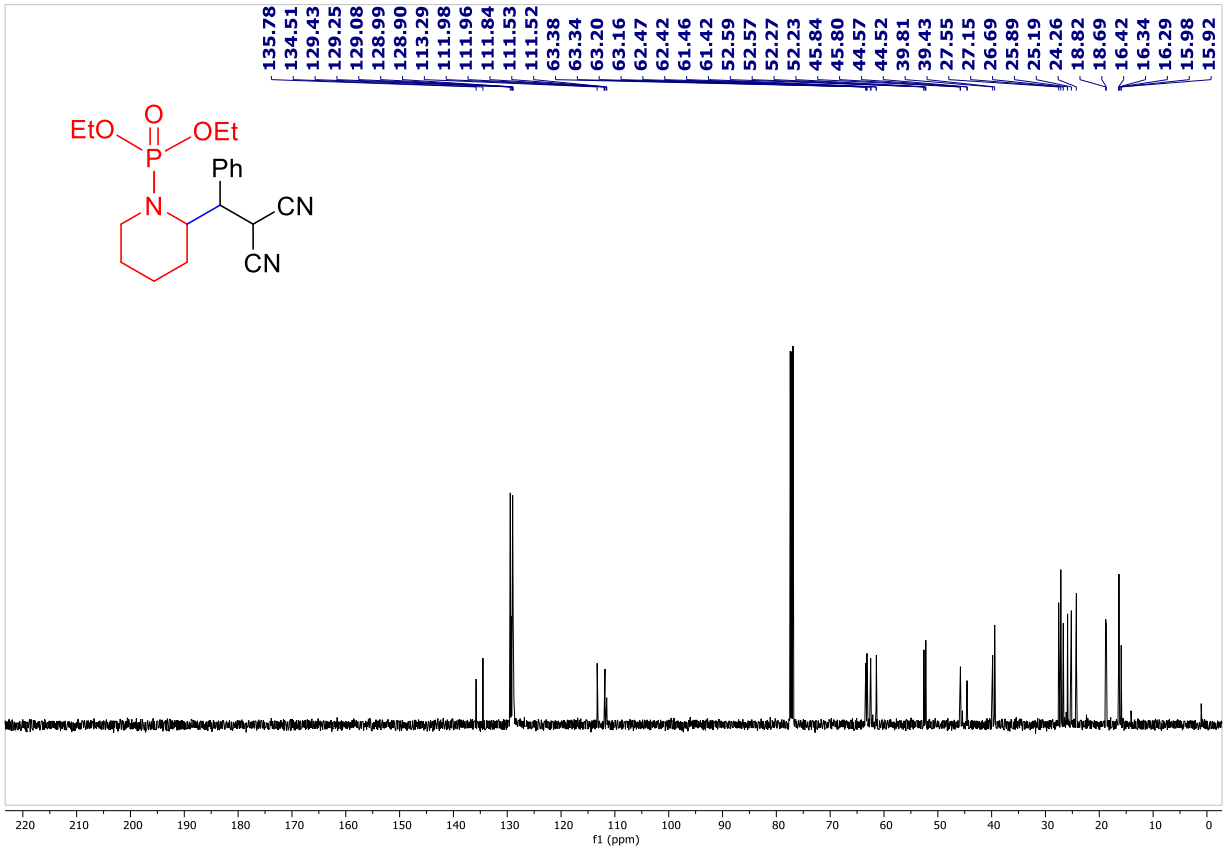
^{31}P NMR (203 MHz, $CDCl_3$) of compound **3t**



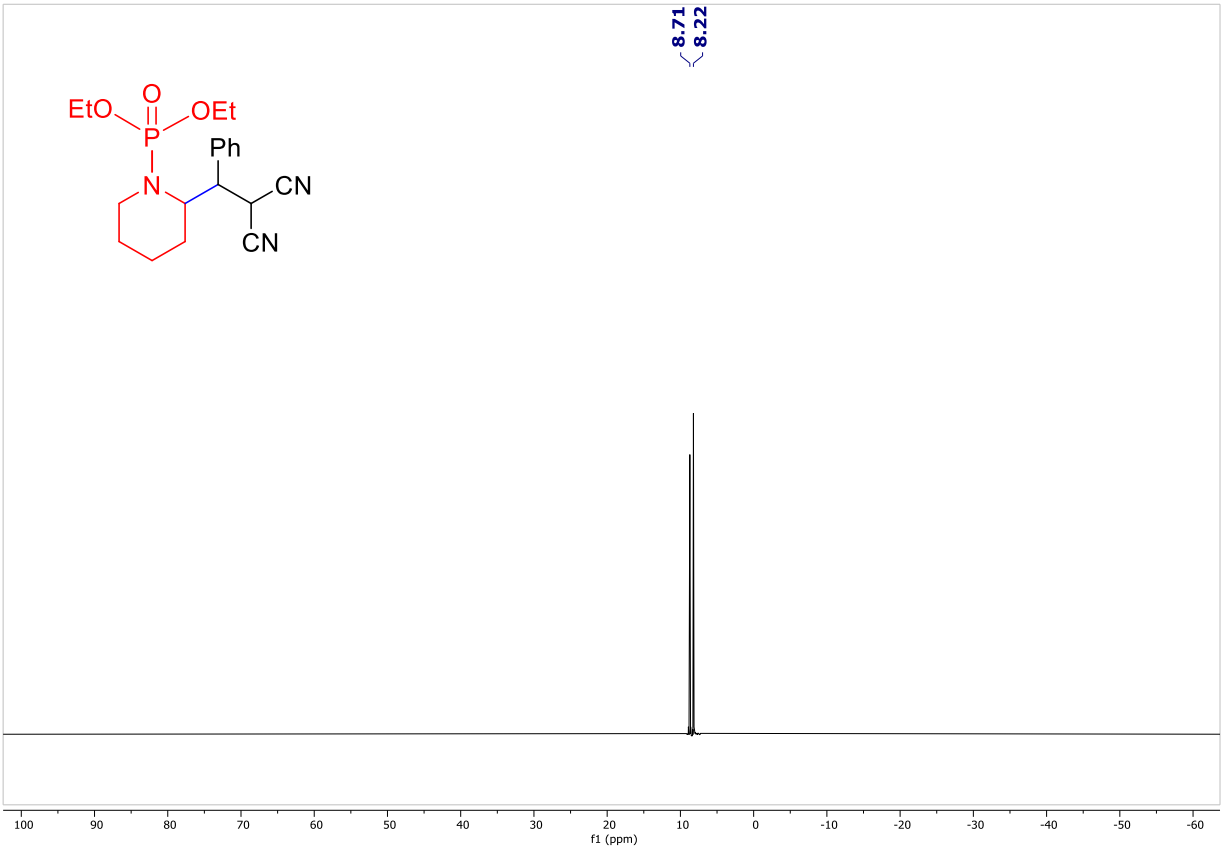
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a**



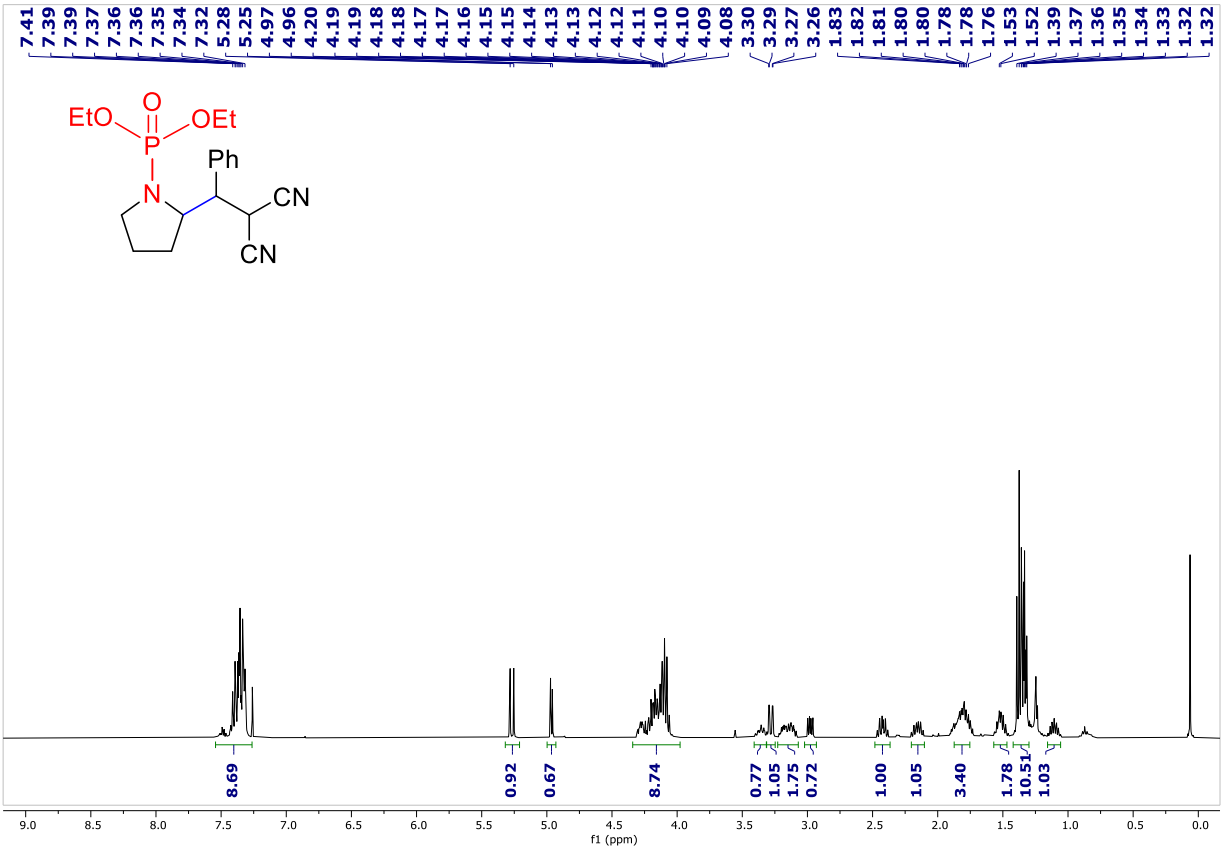
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4a**



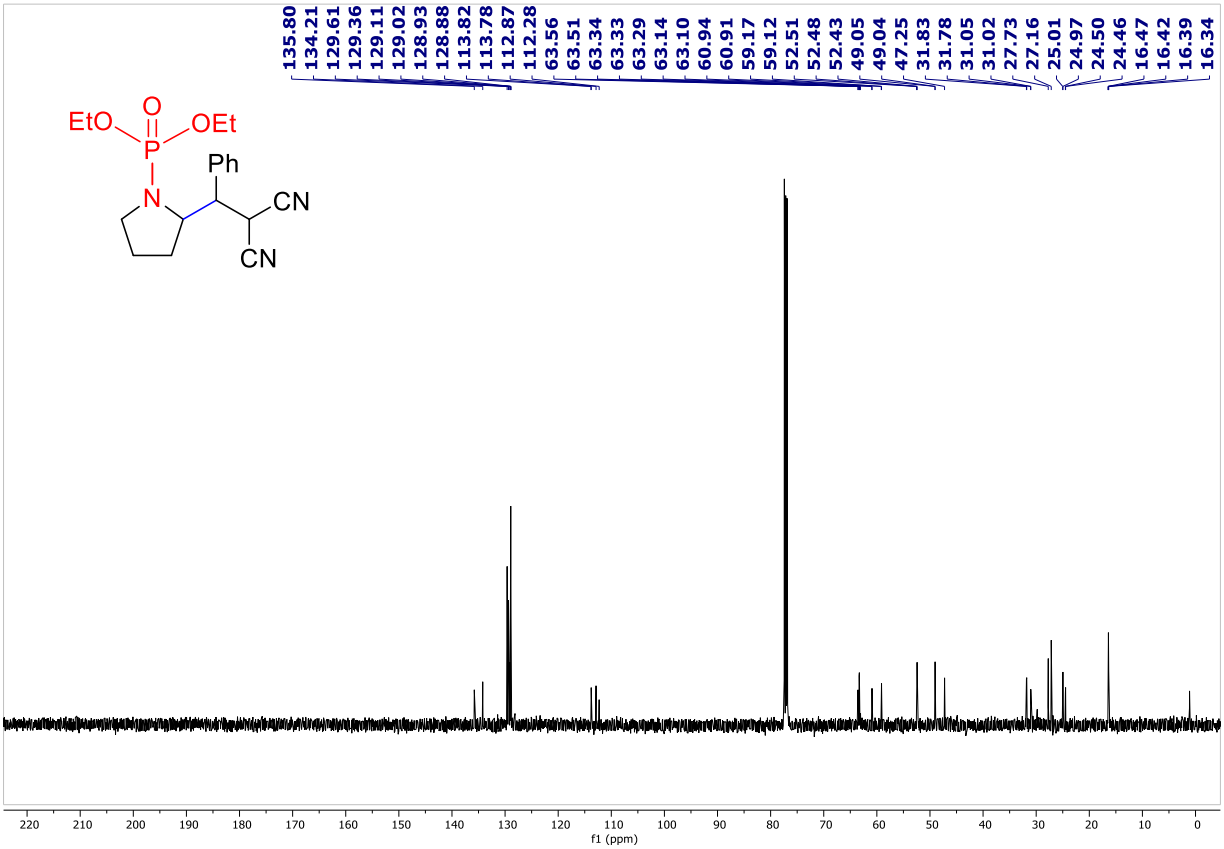
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4a**



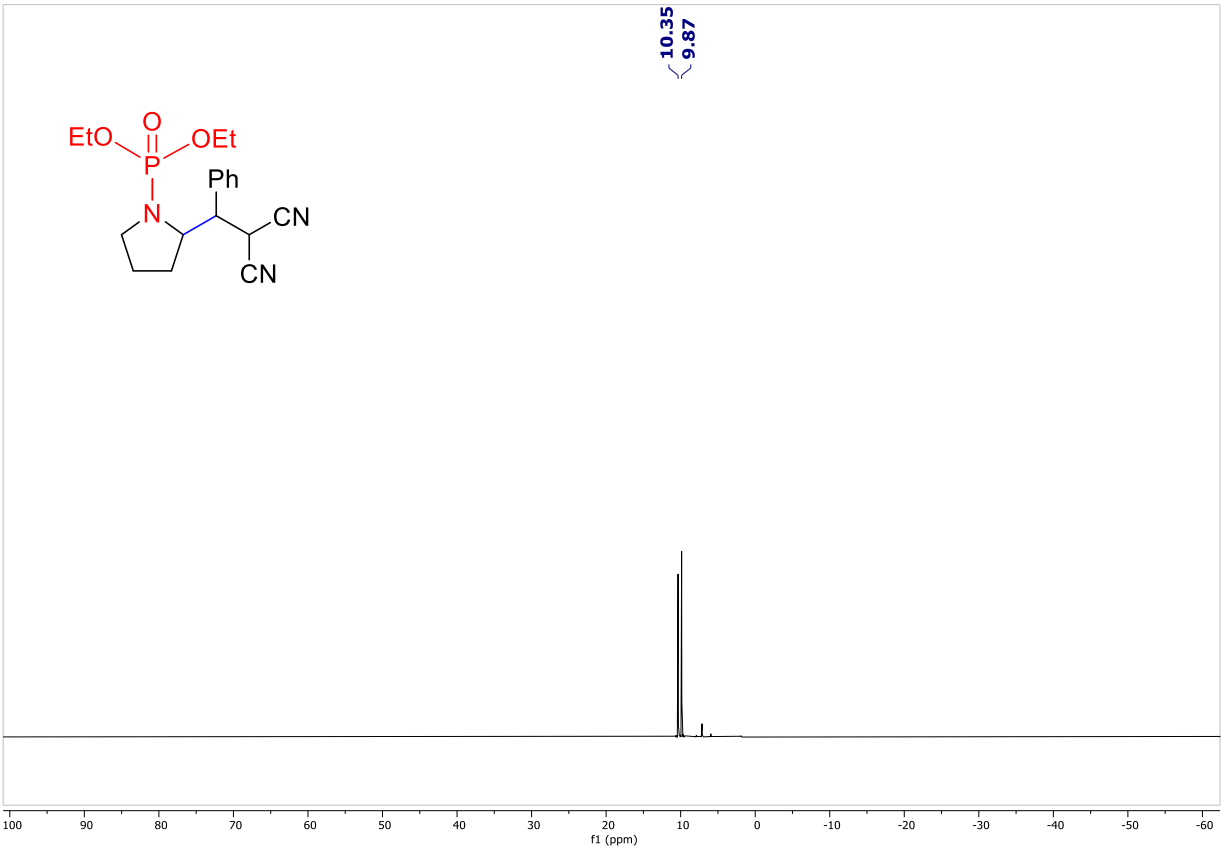
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b**



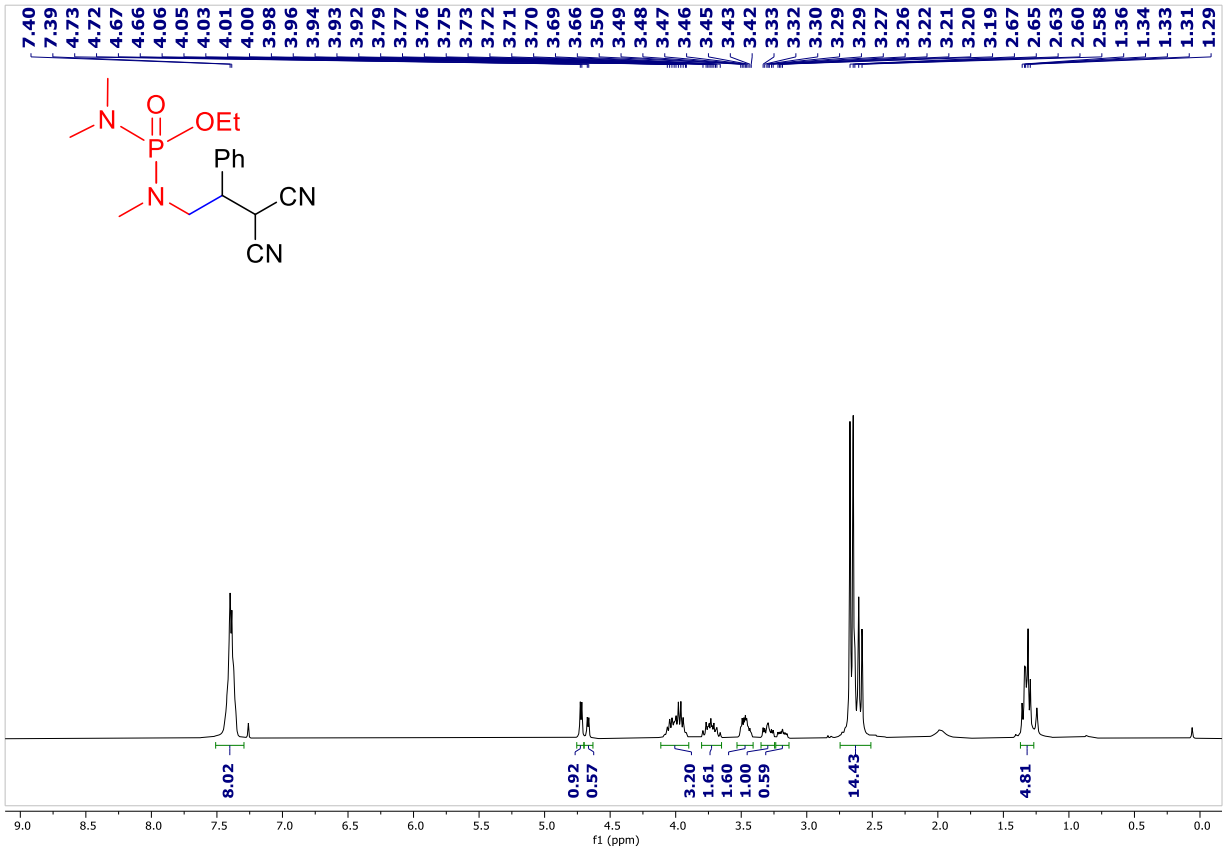
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **4b**



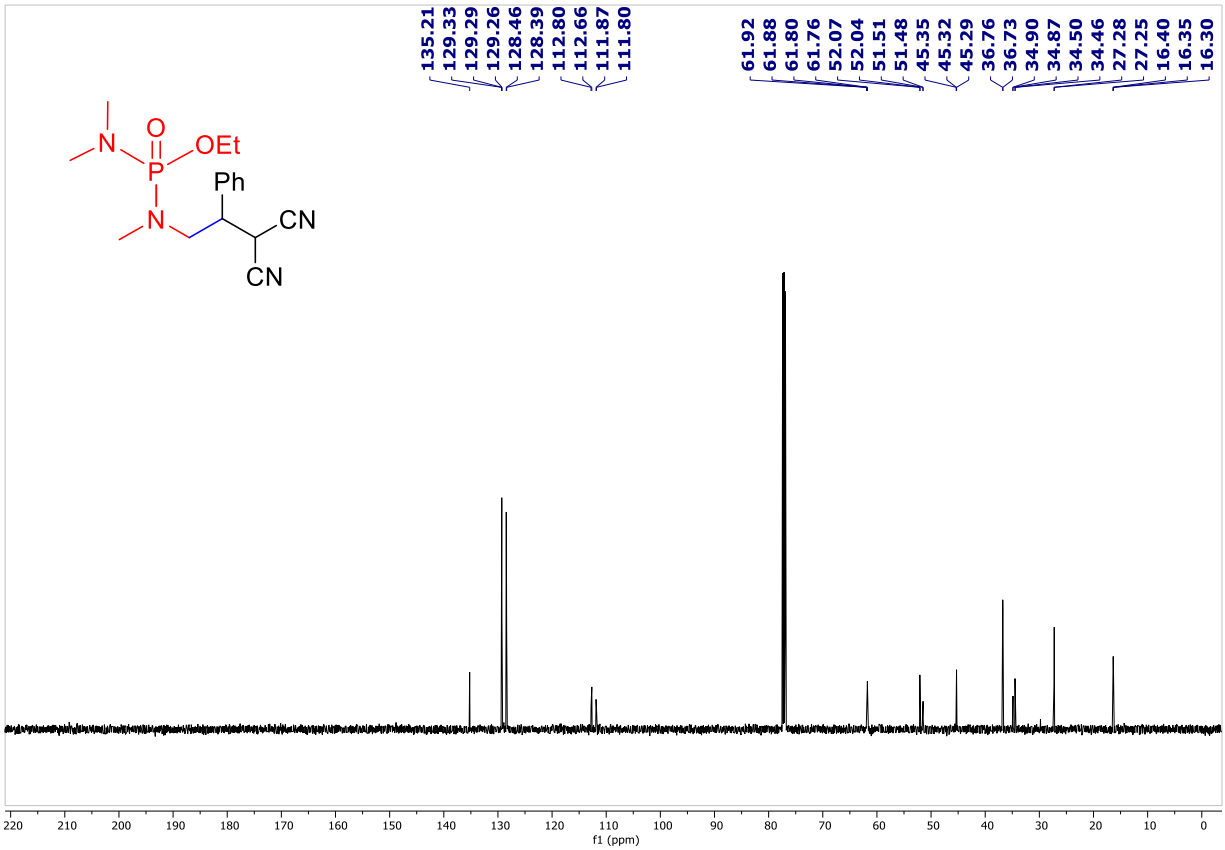
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4b**



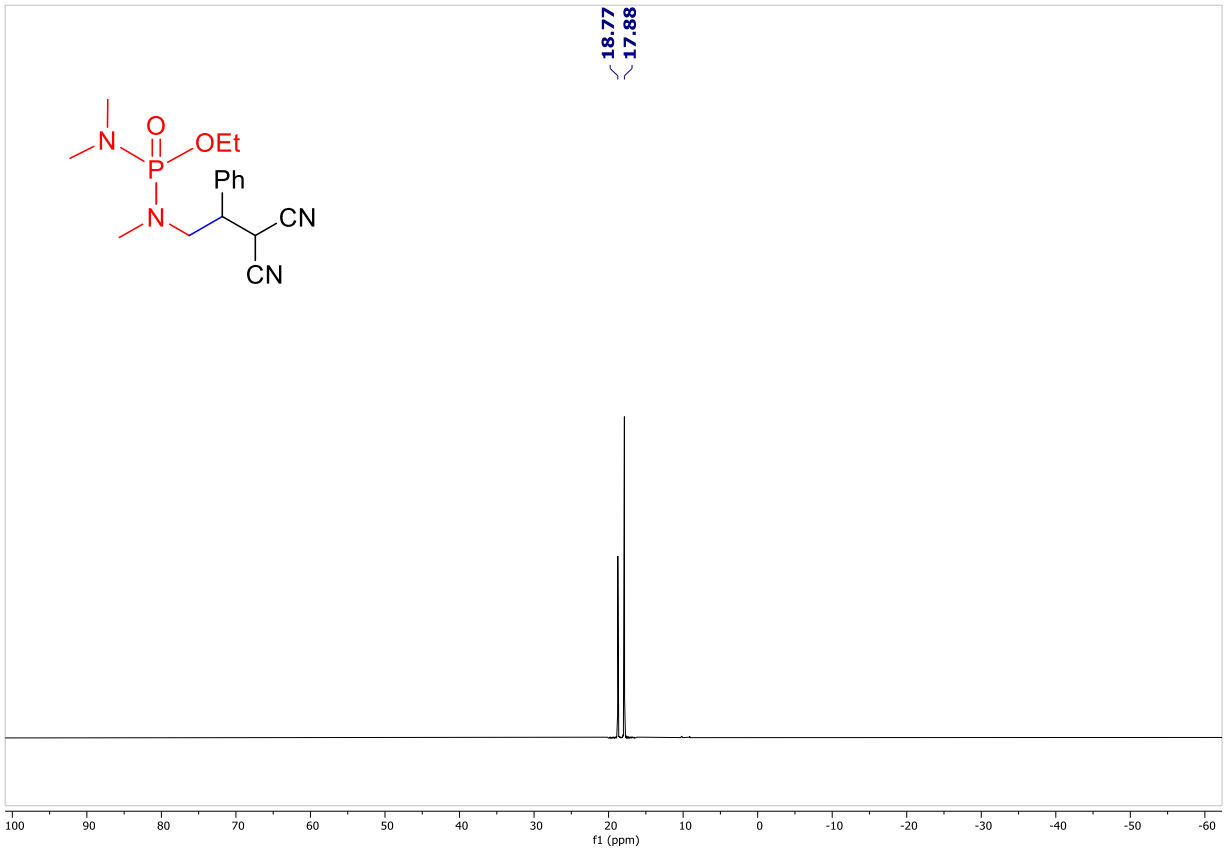
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c**



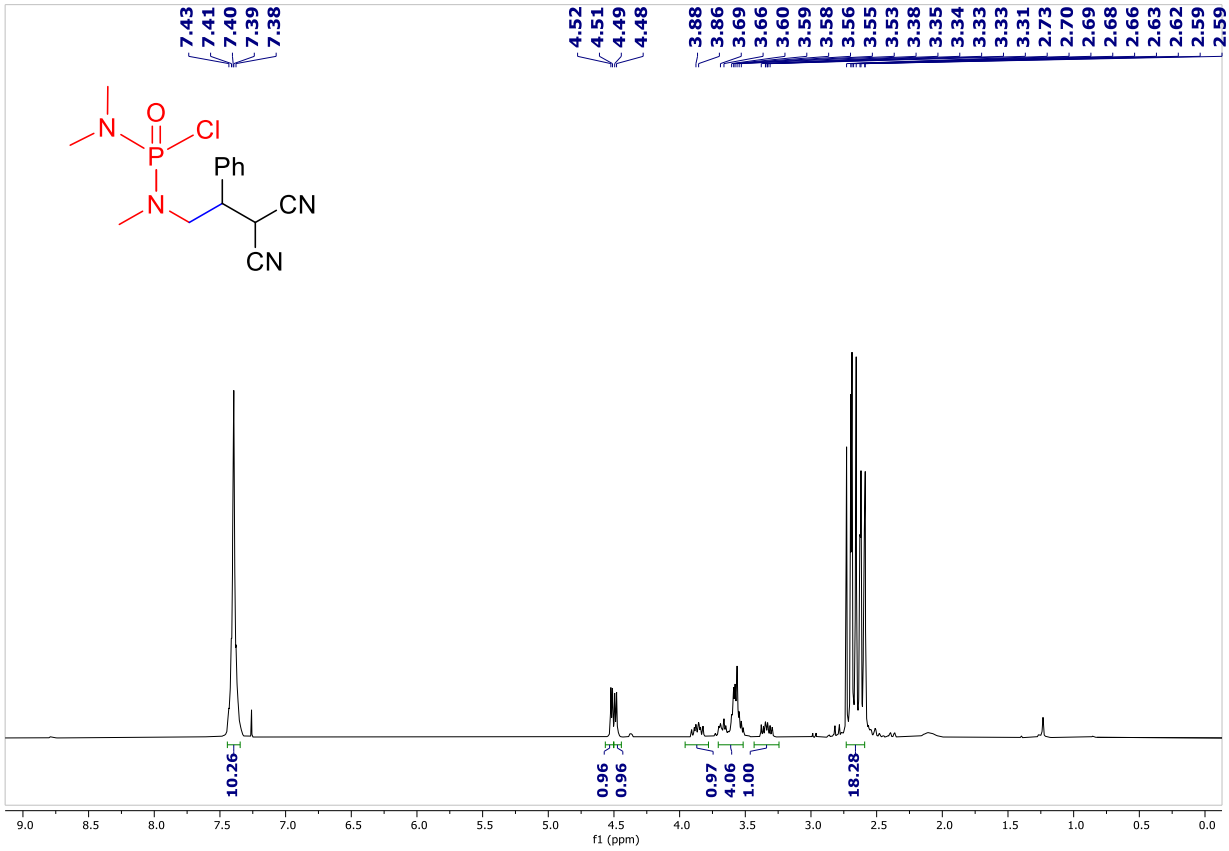
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4c**



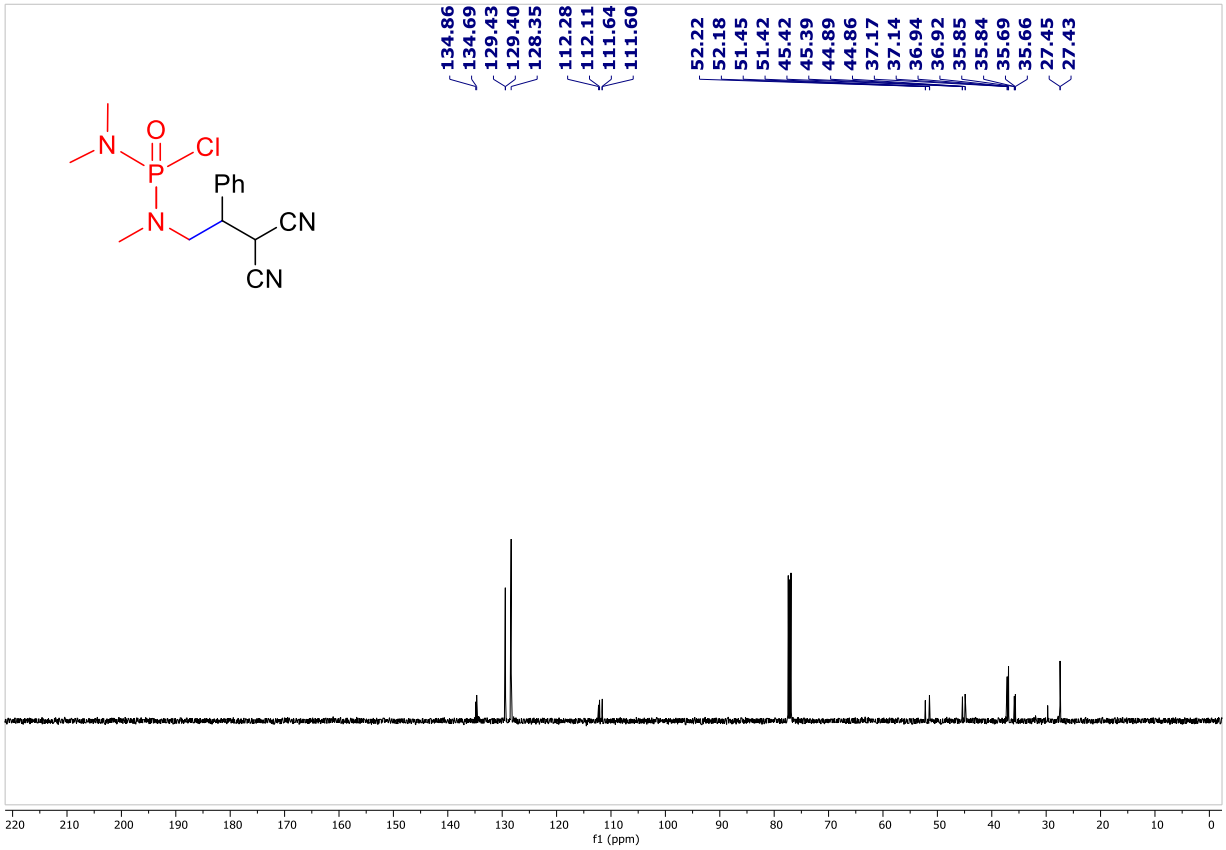
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4c**



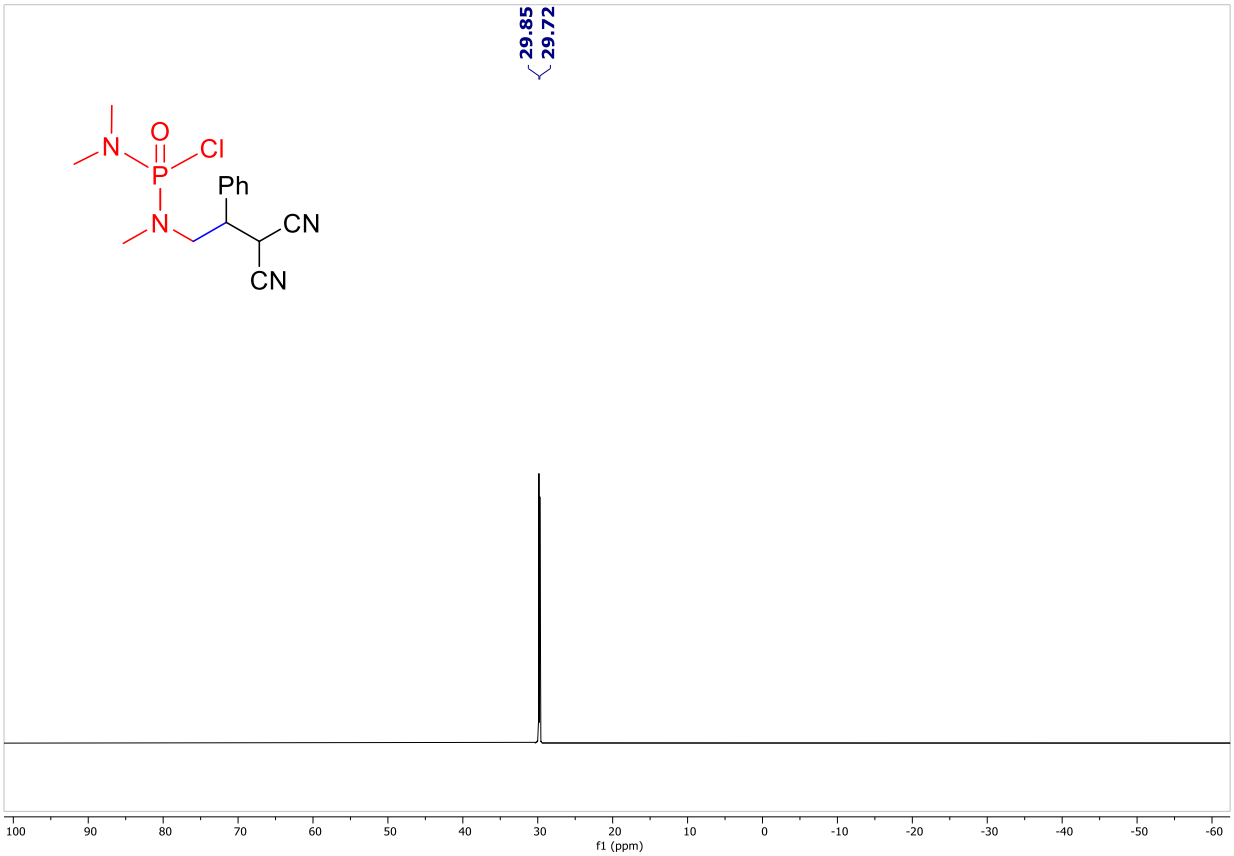
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d**



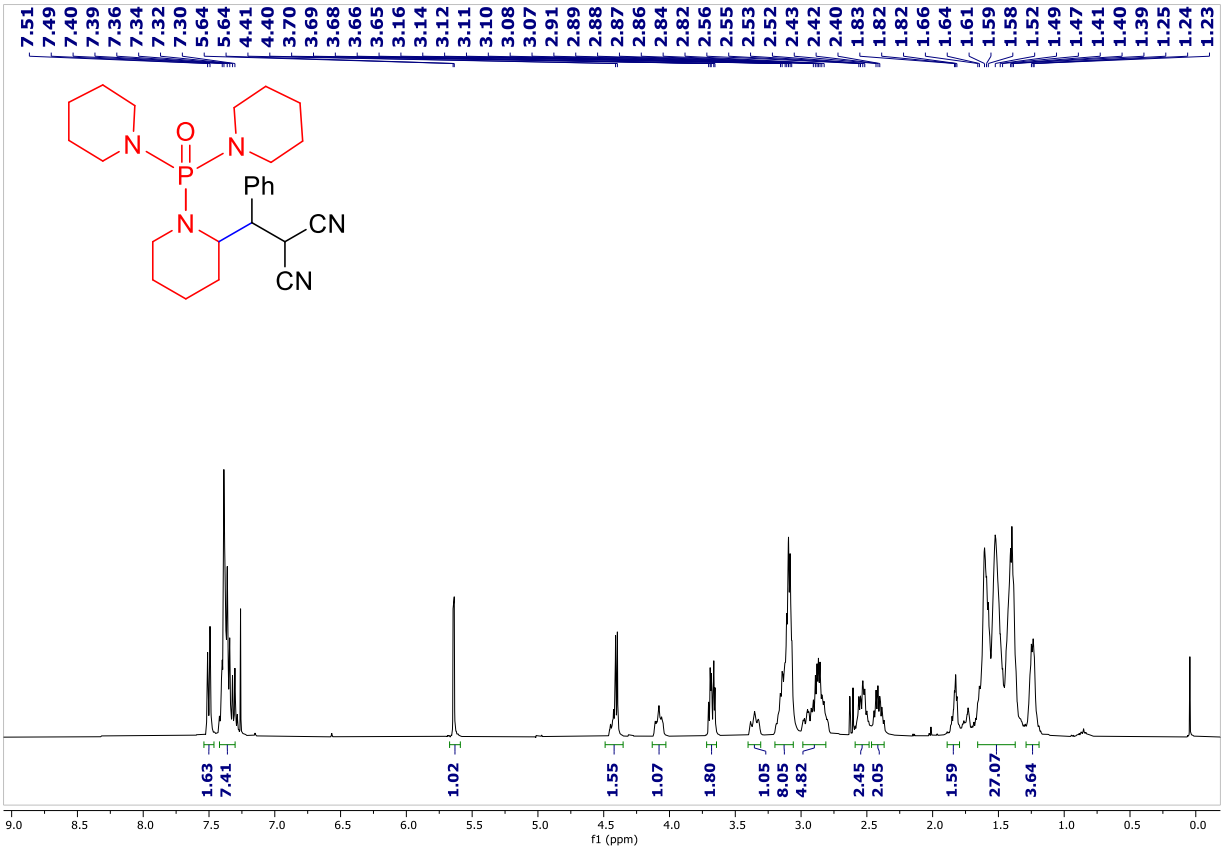
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **4d**



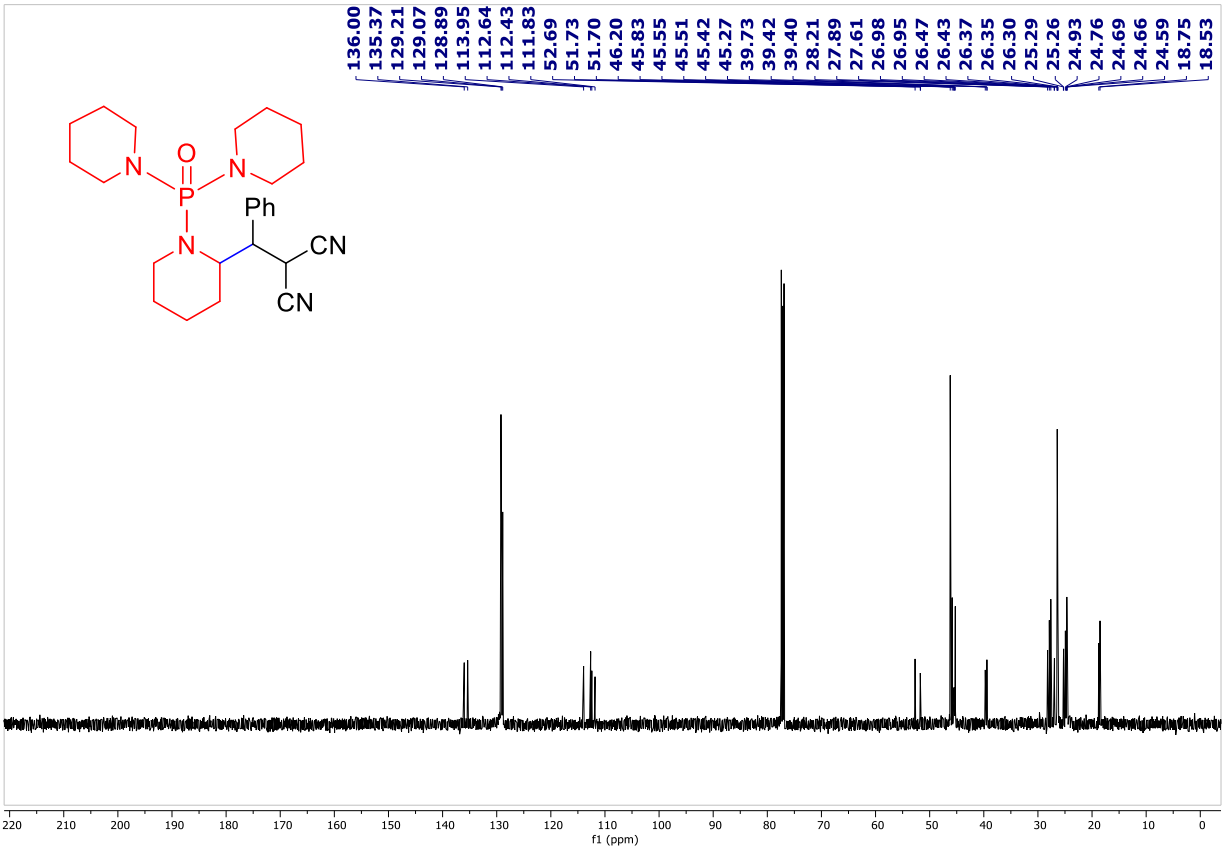
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4d**



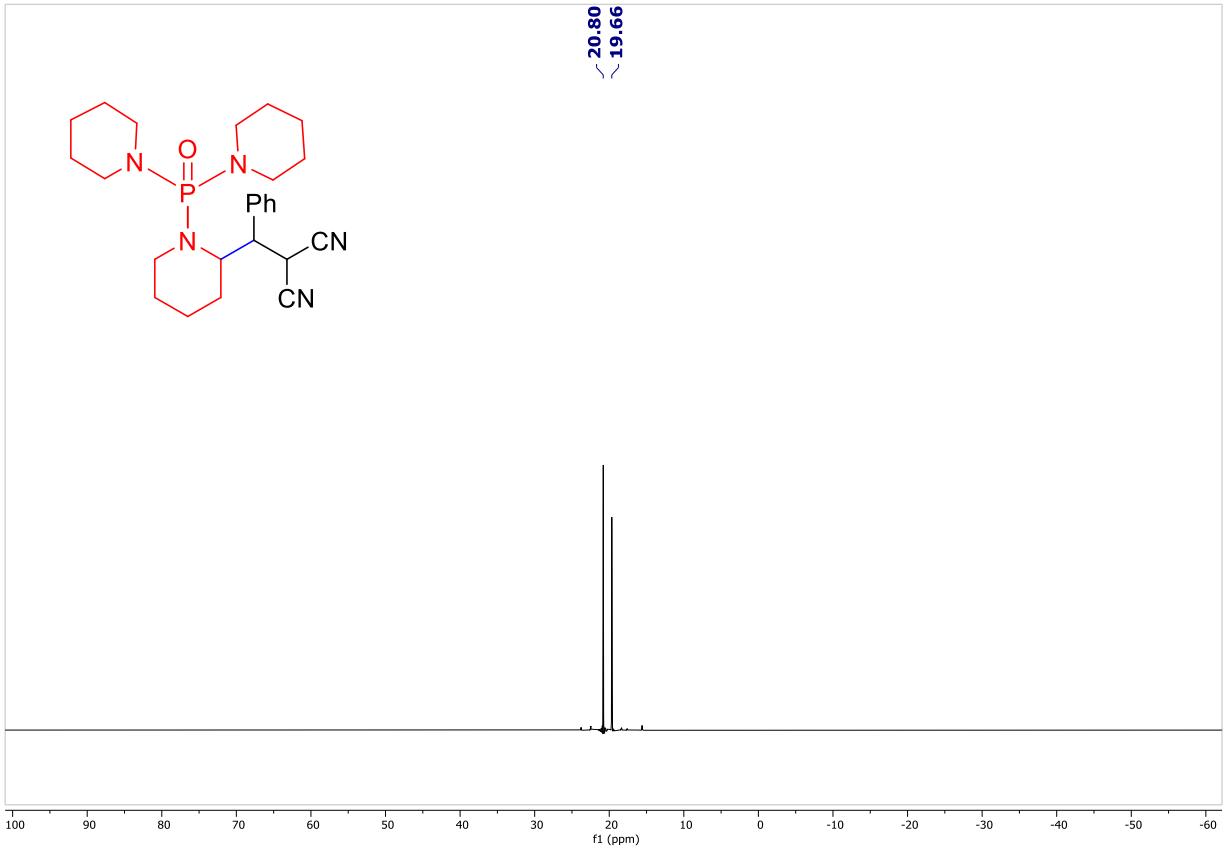
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4e**



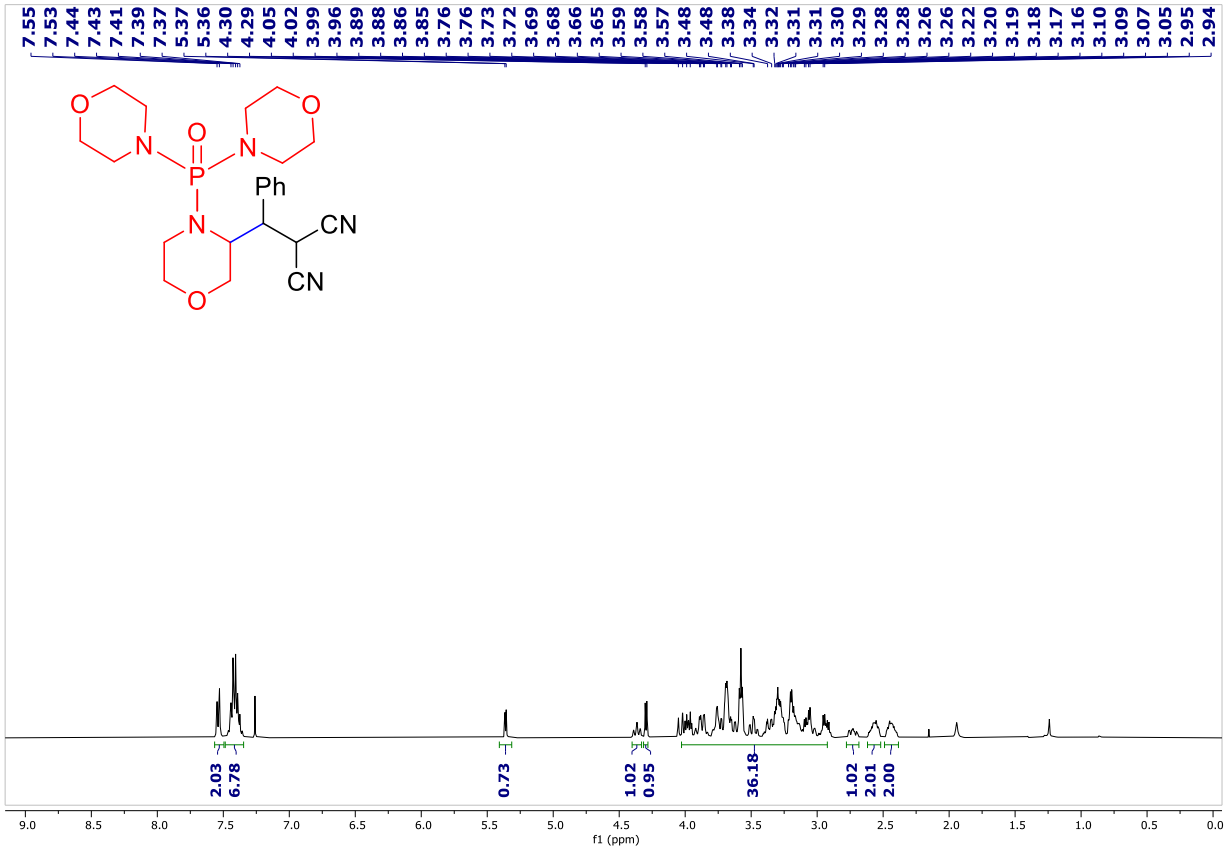
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **4e**



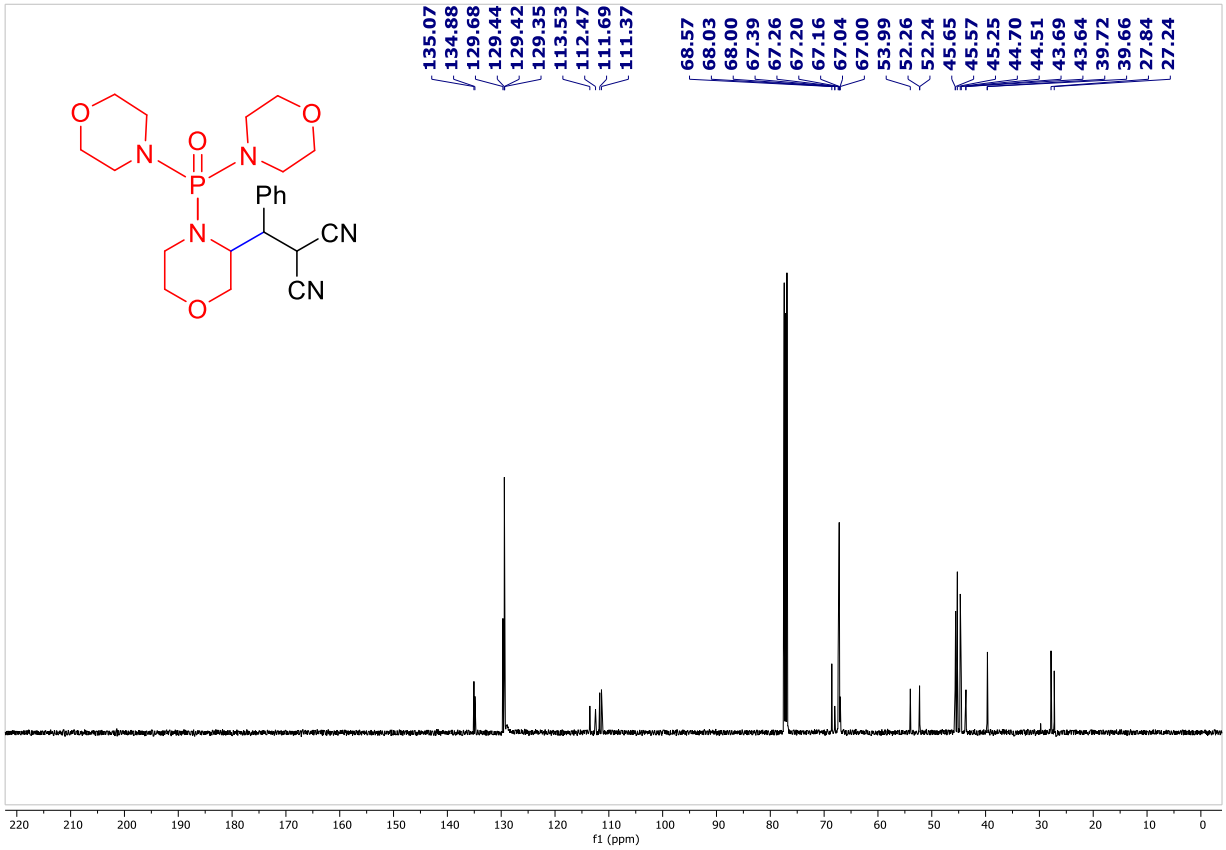
^{31P} NMR (203 MHz, $CDCl_3$) of compound **4e**



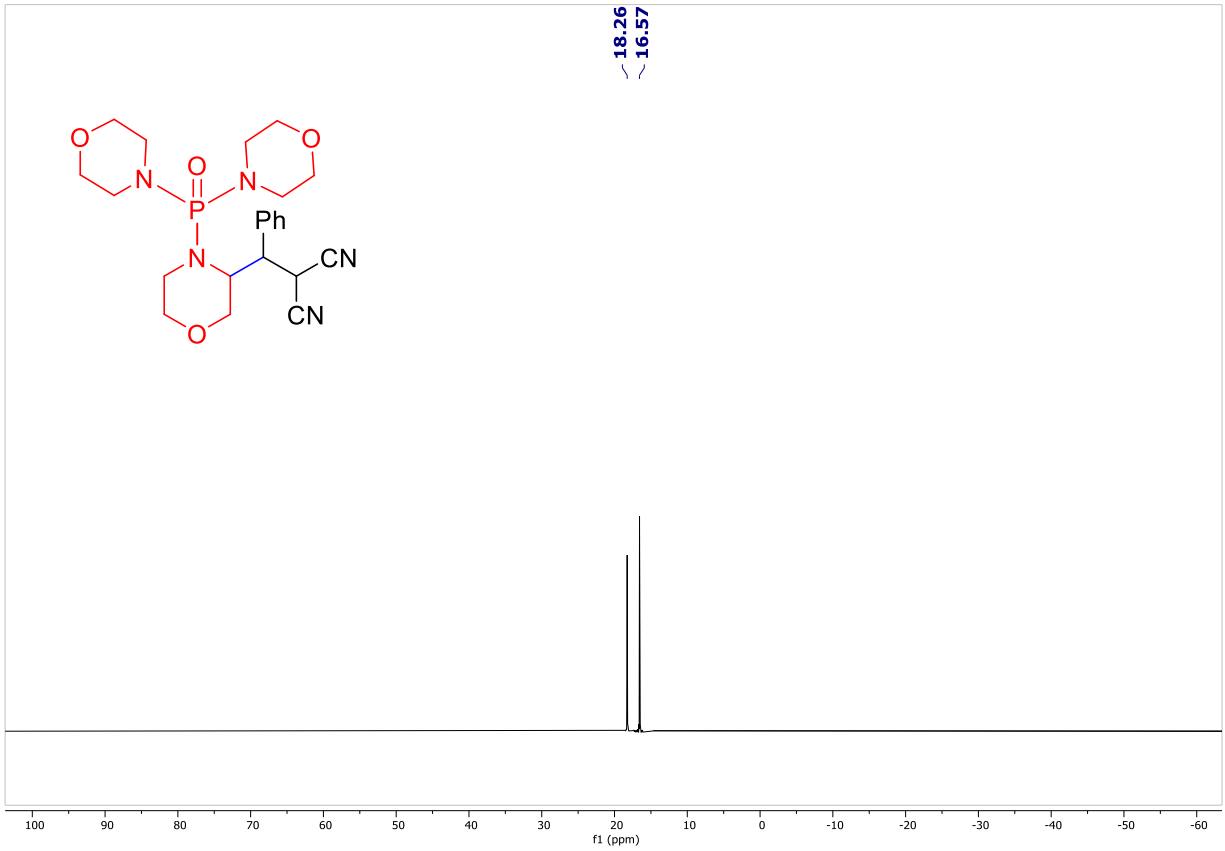
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4f**



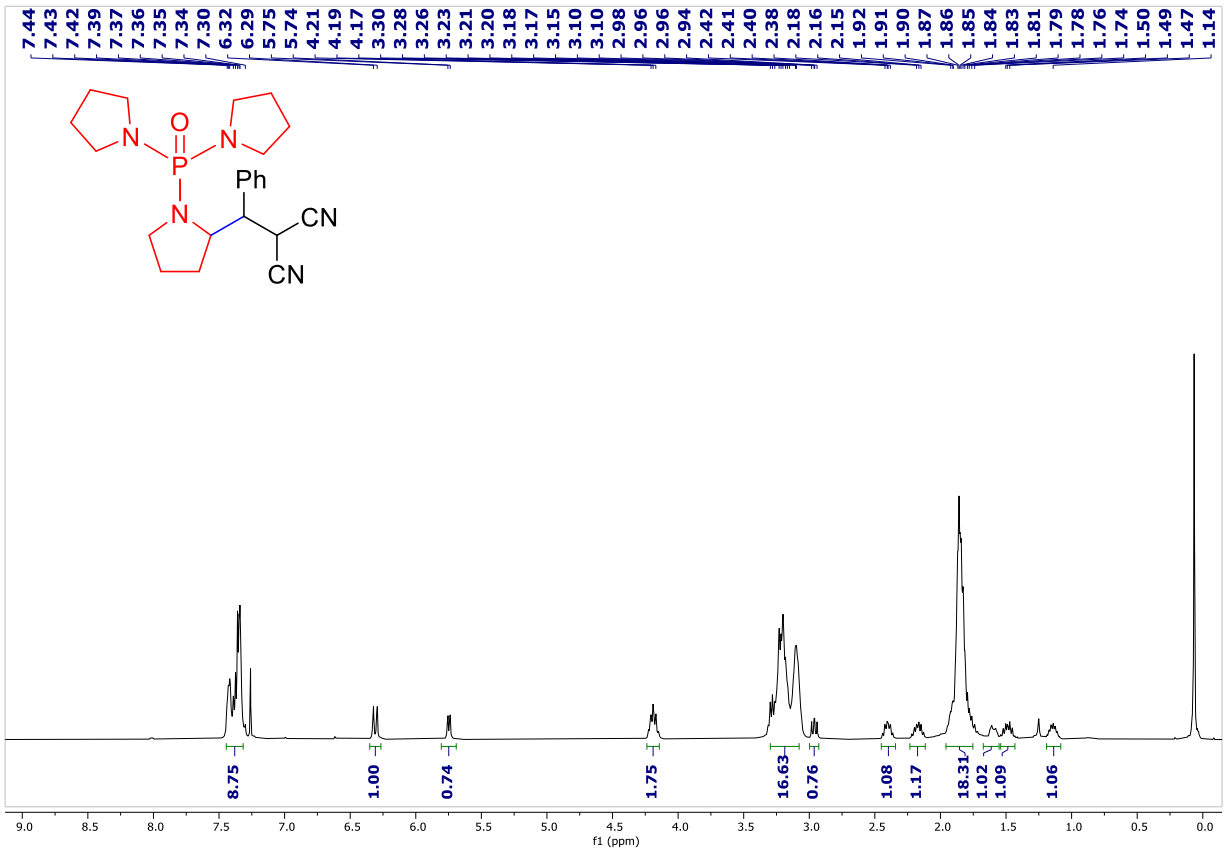
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **4f**



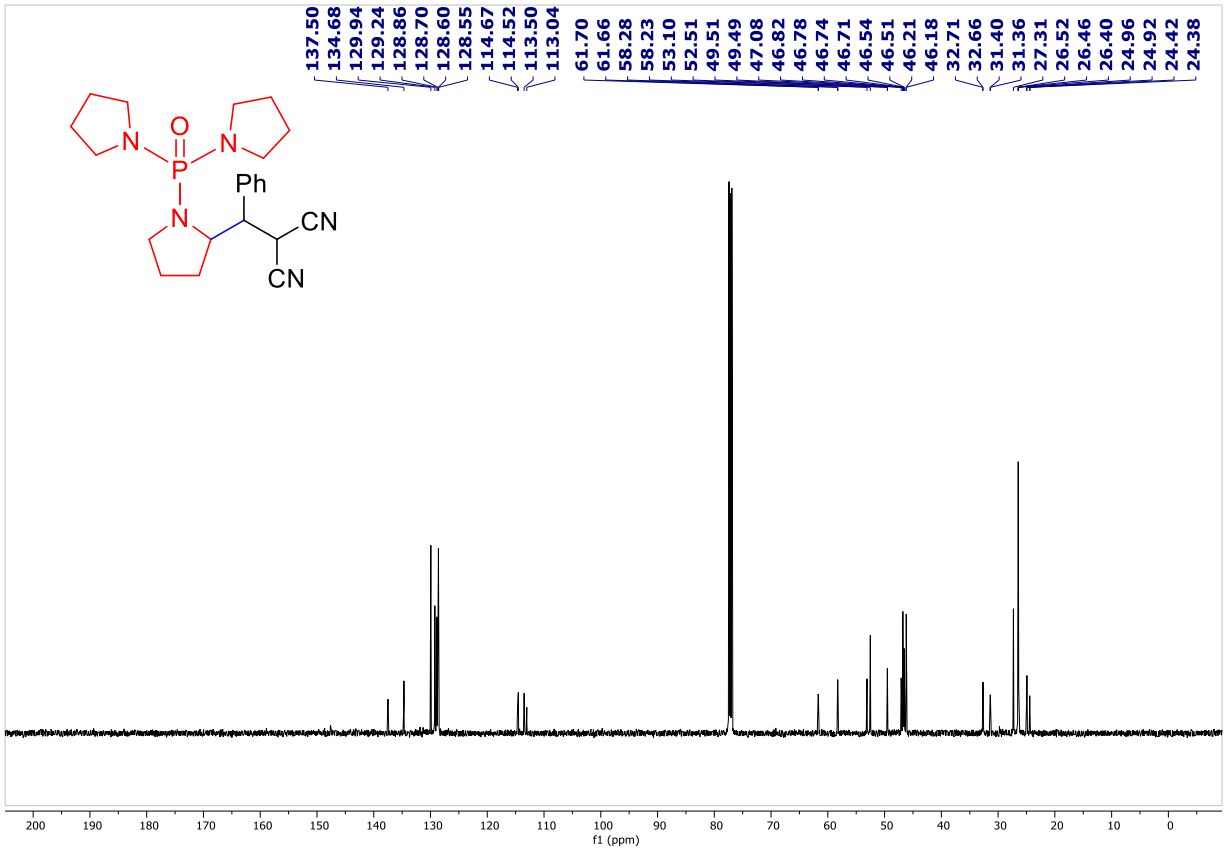
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4f**



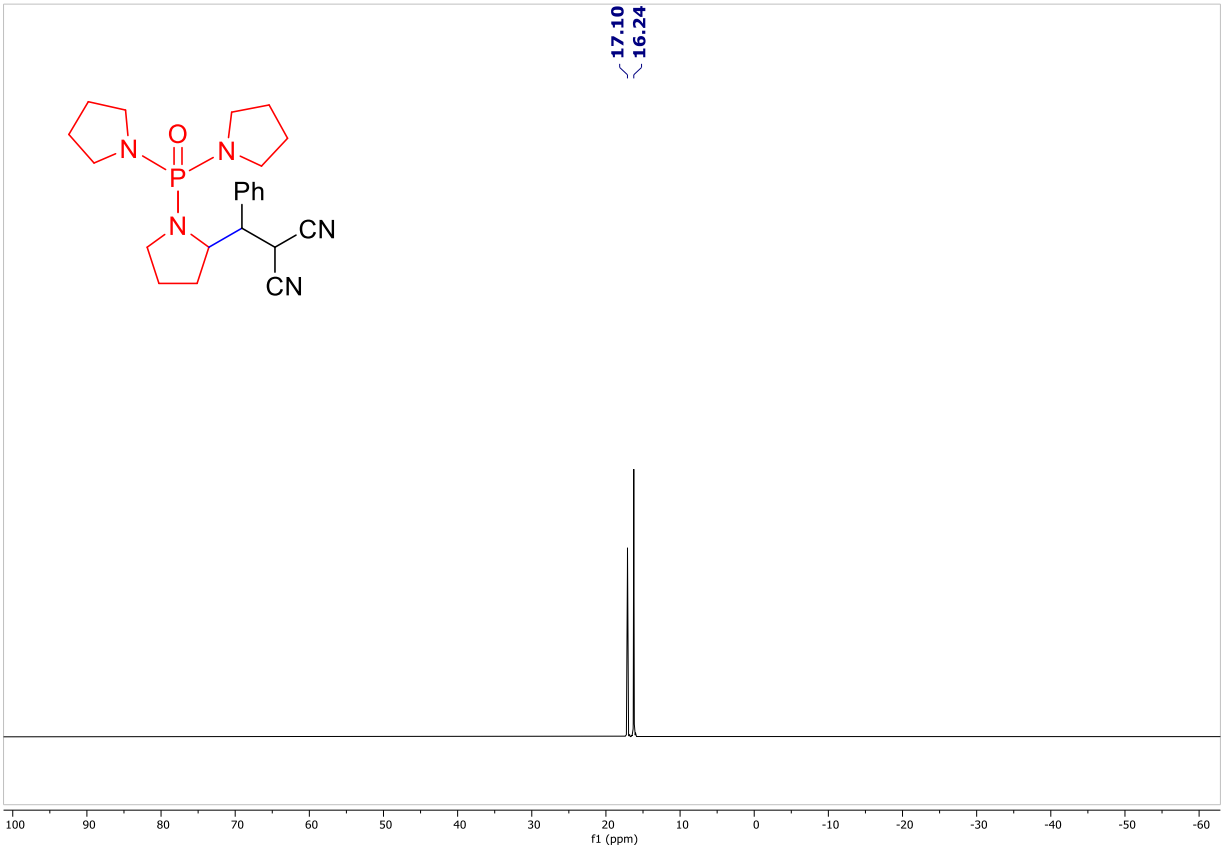
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4g**



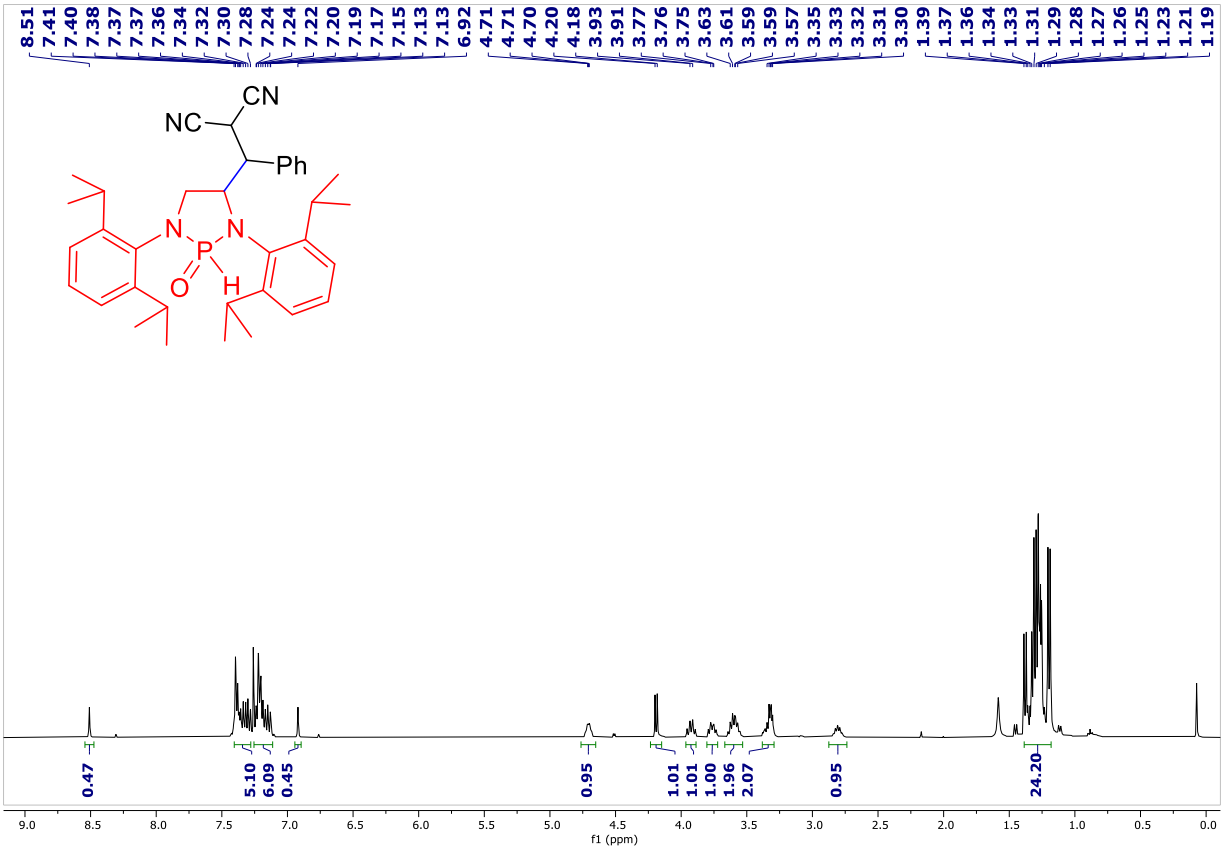
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4g**



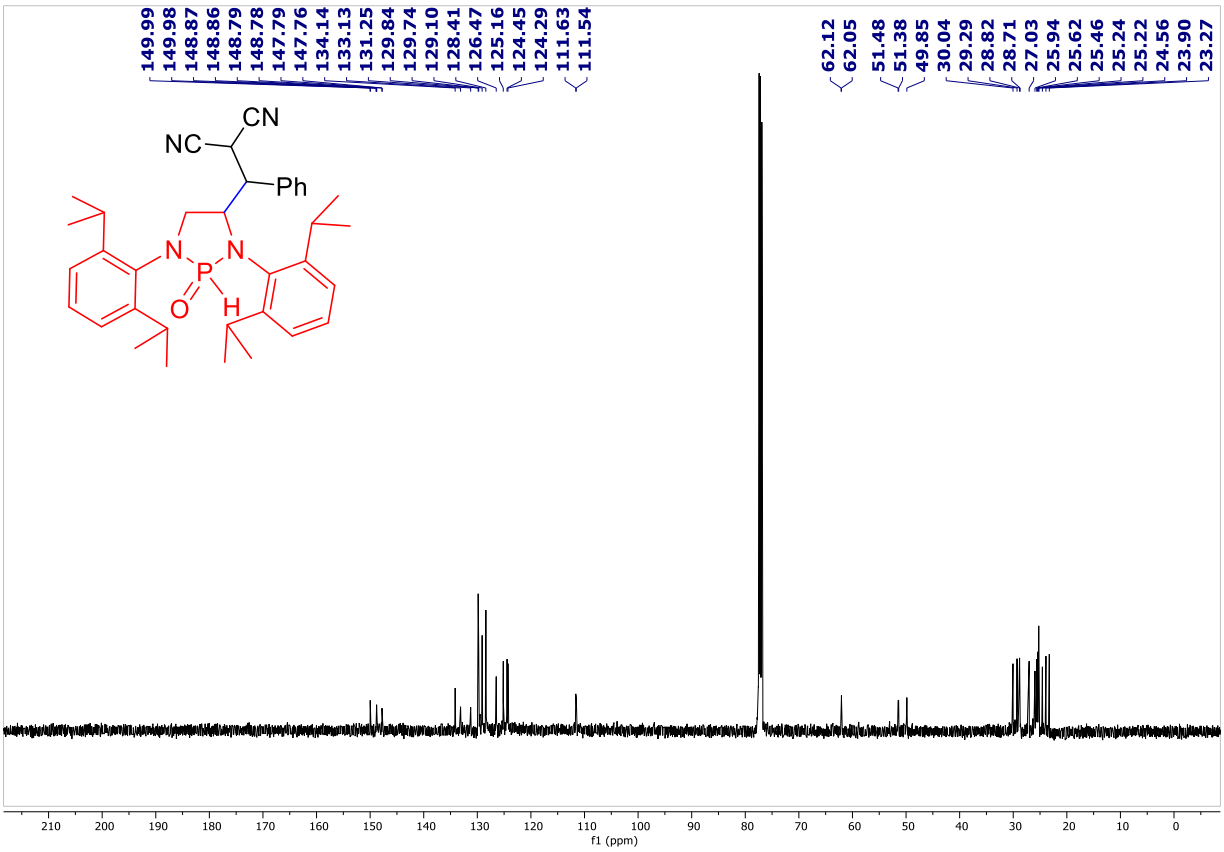
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4g**



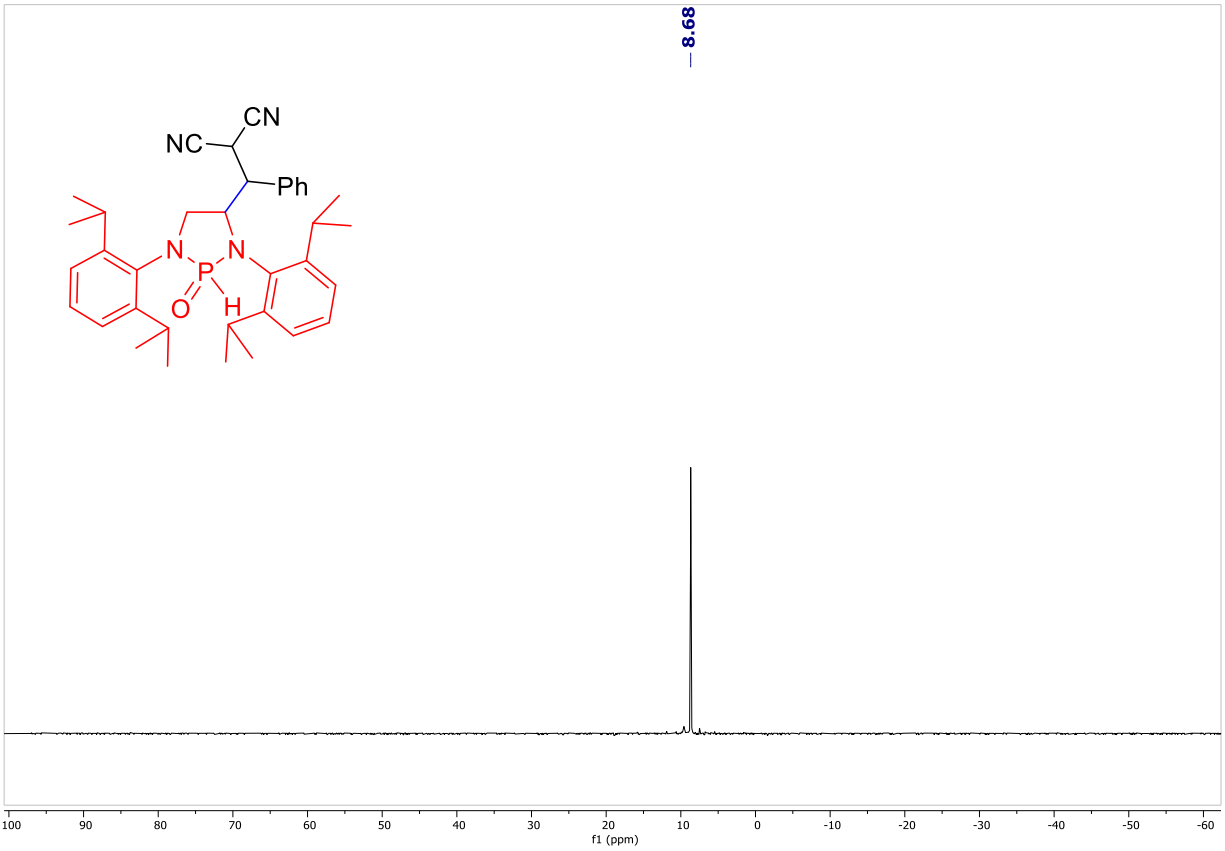
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4h**



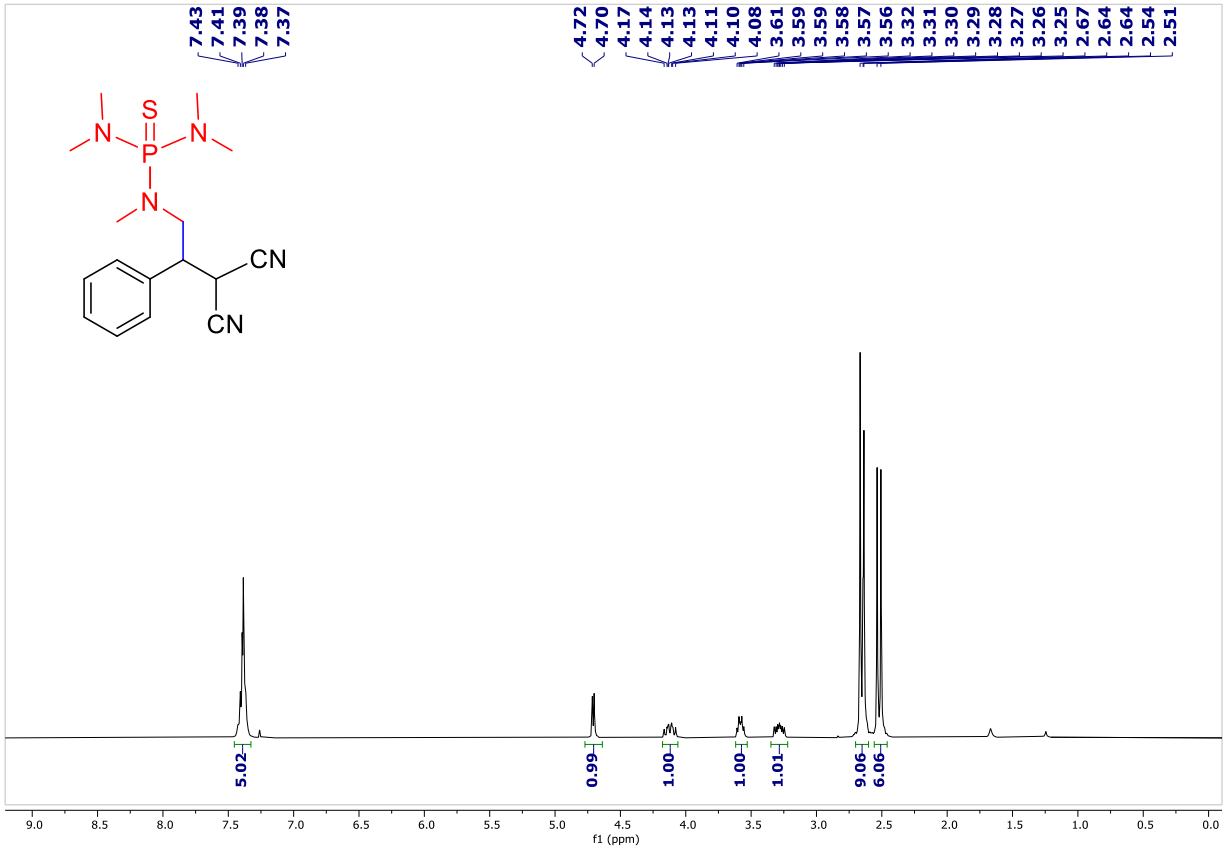
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **4h**



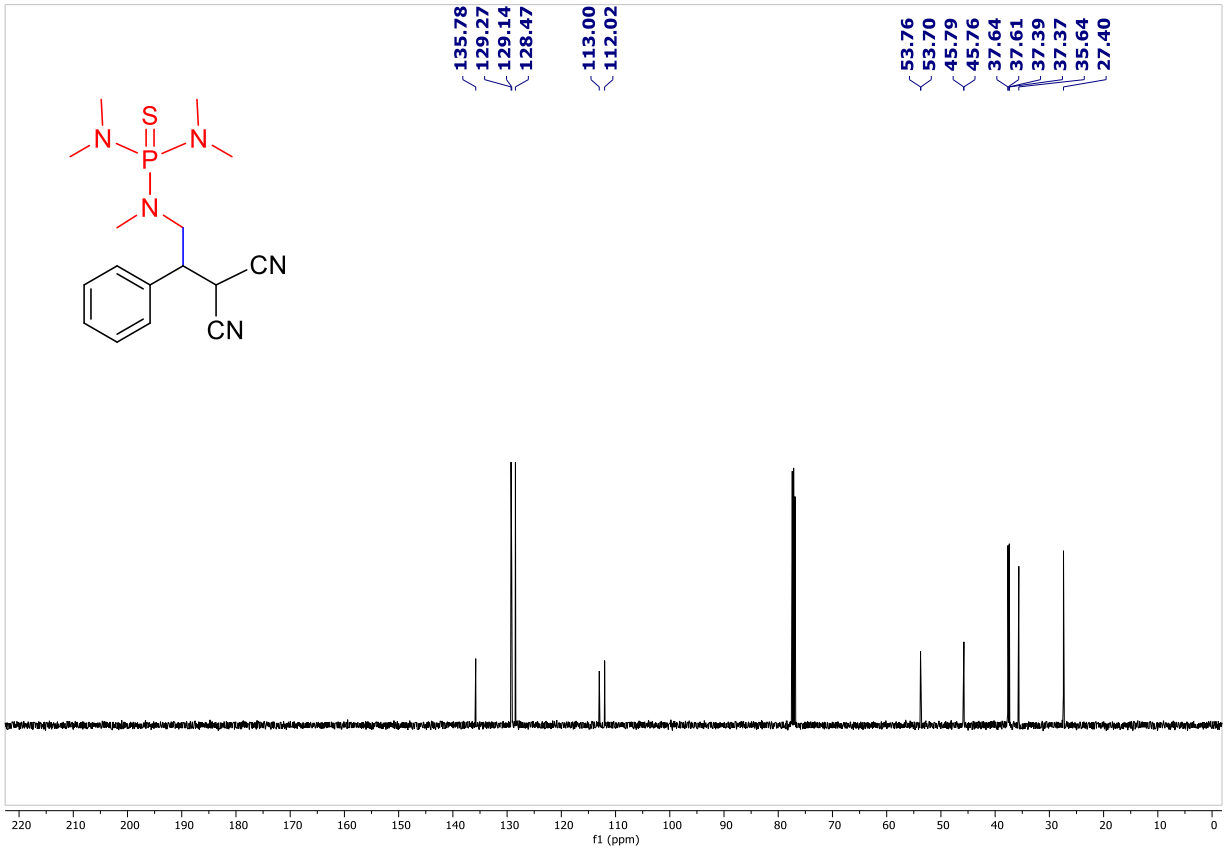
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4h**



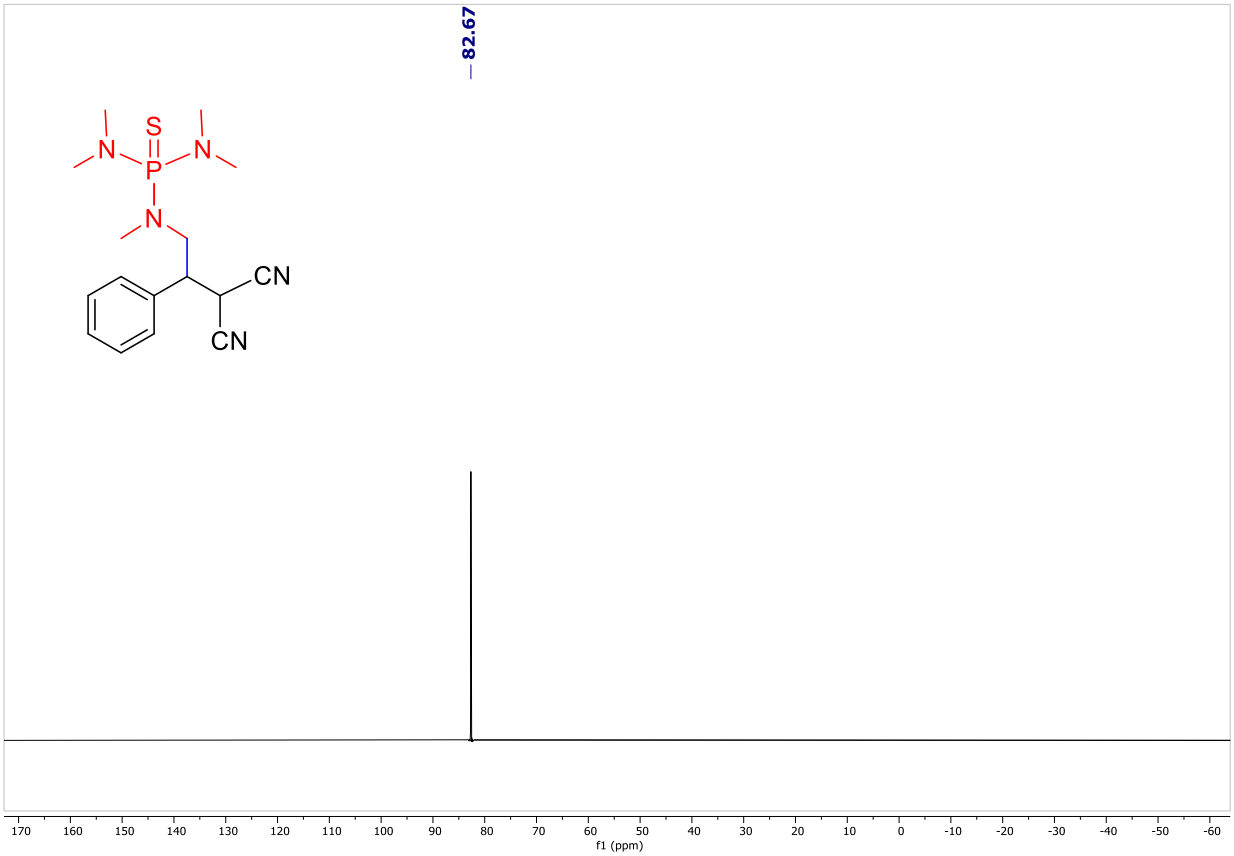
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4i**



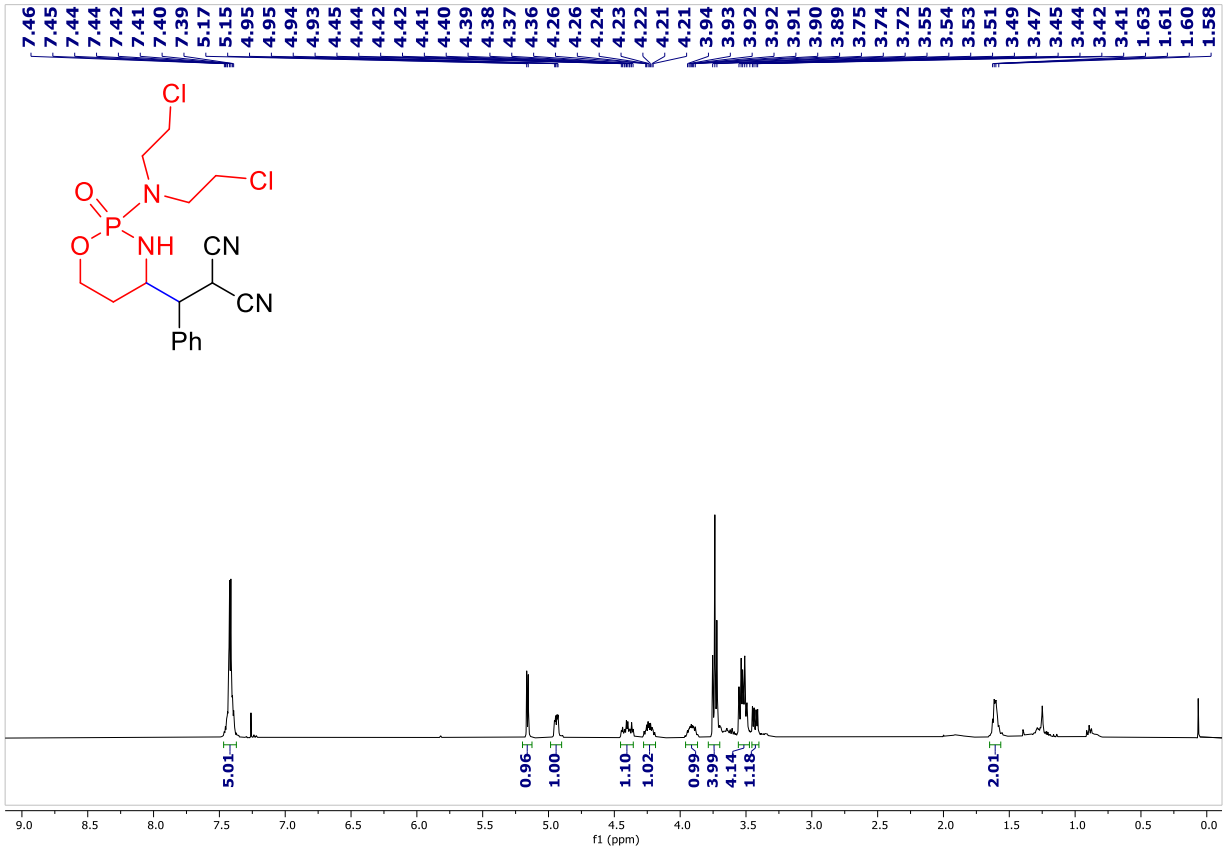
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4i**



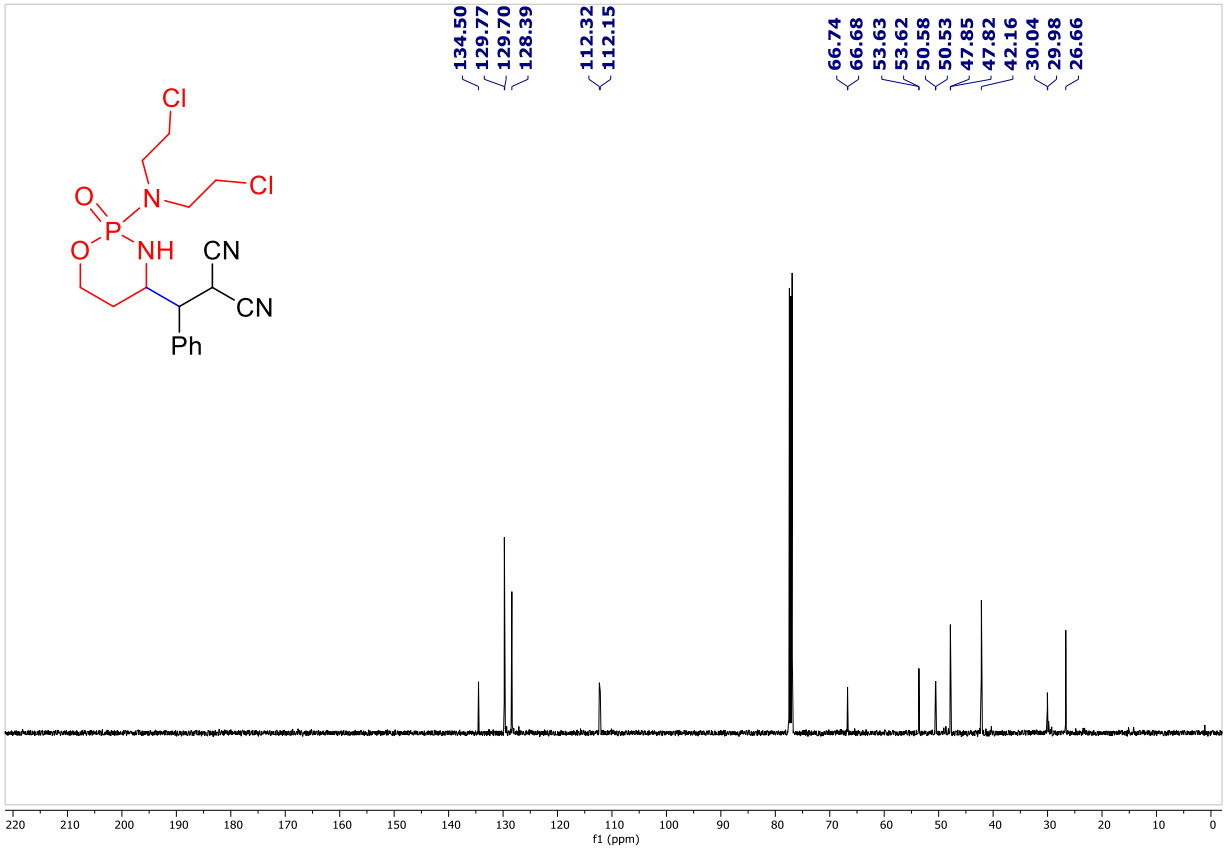
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4i**



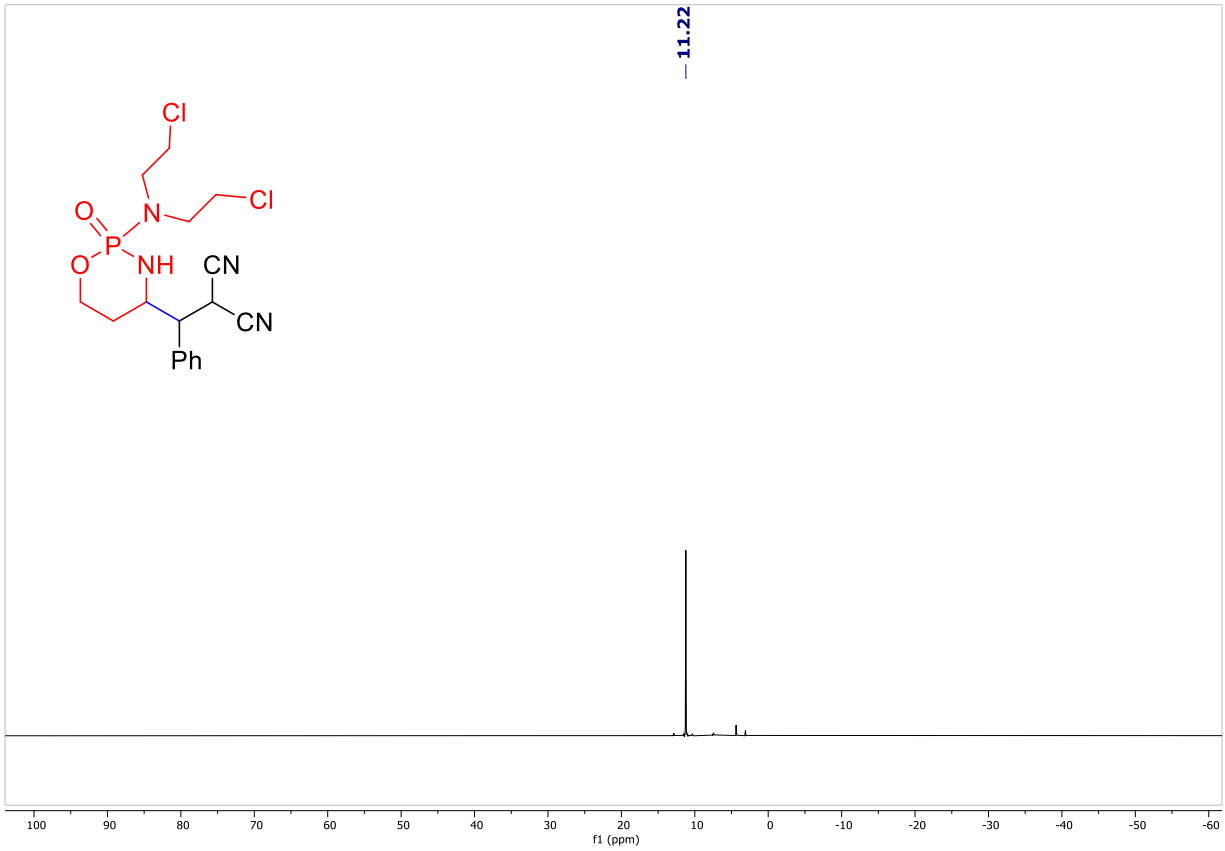
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4j'**



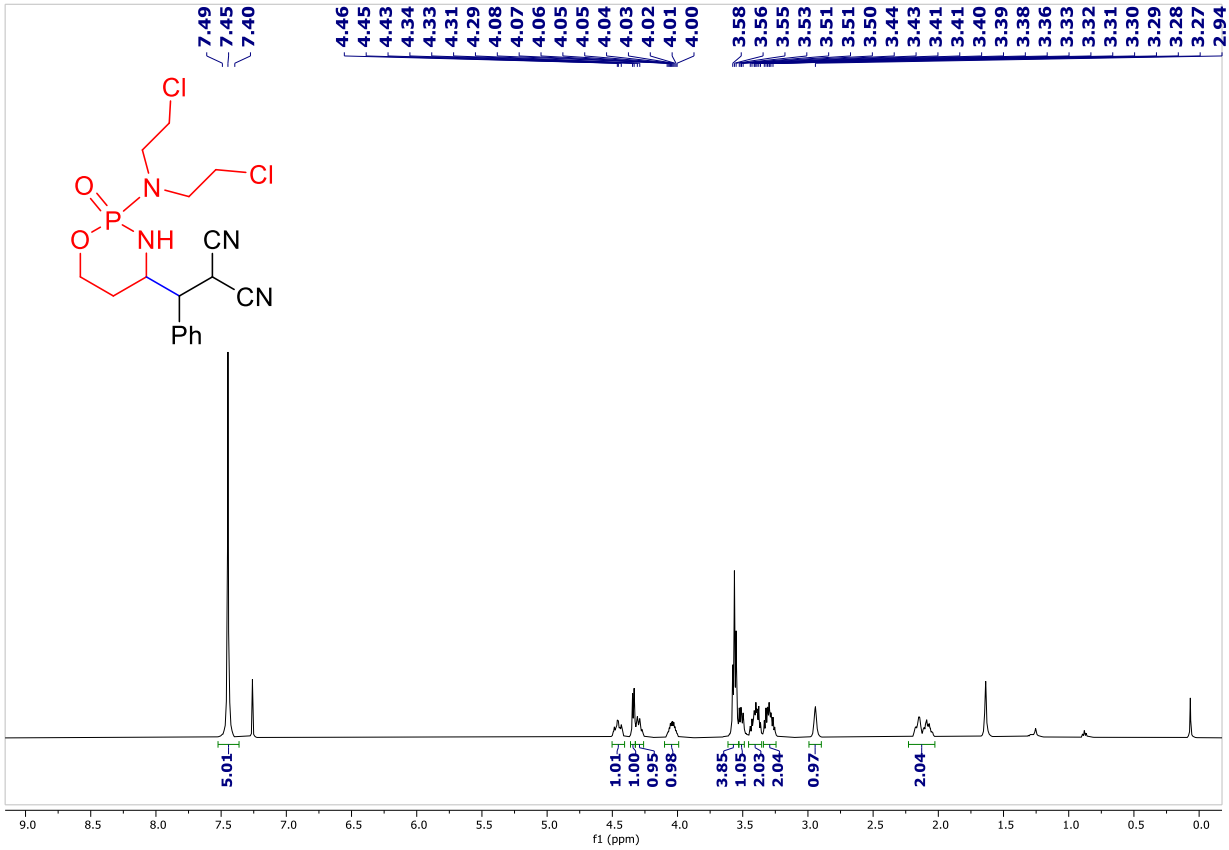
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **4j'**



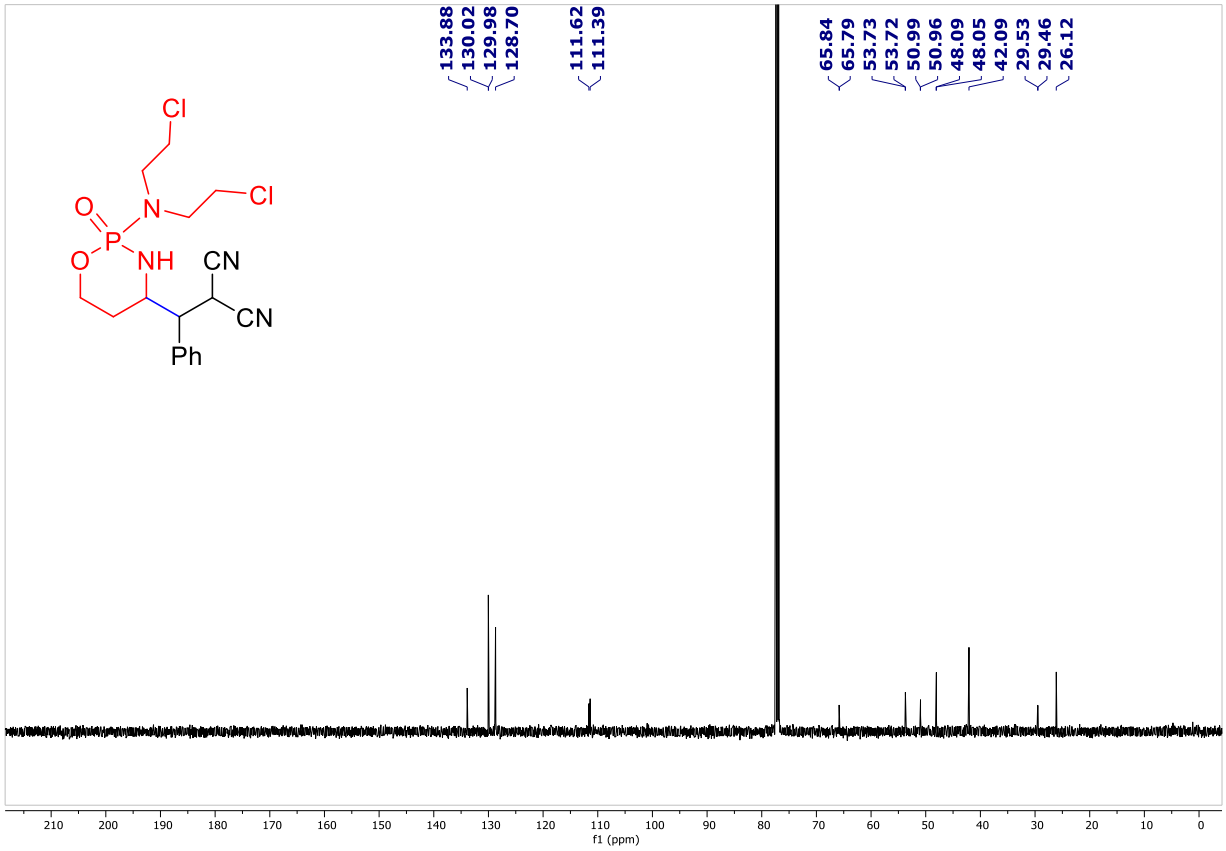
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4j'**



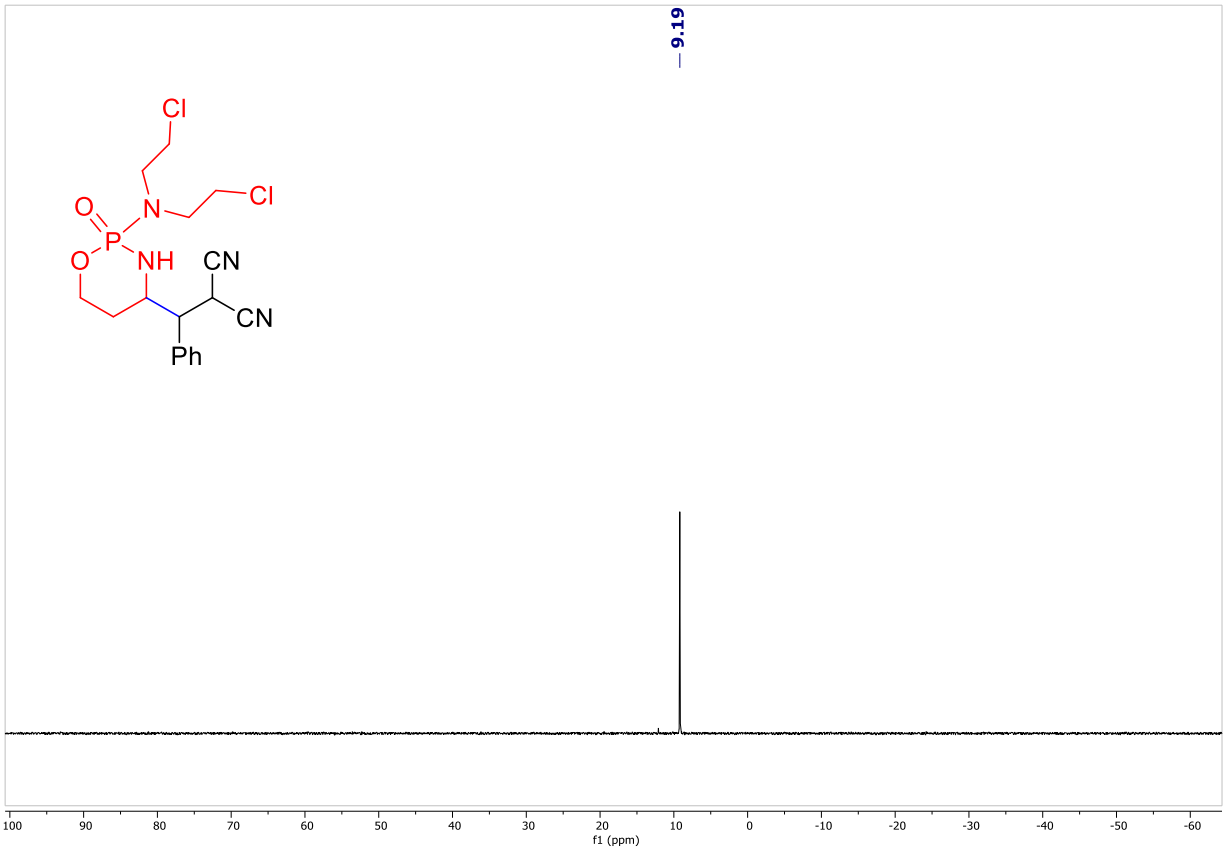
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4j"**



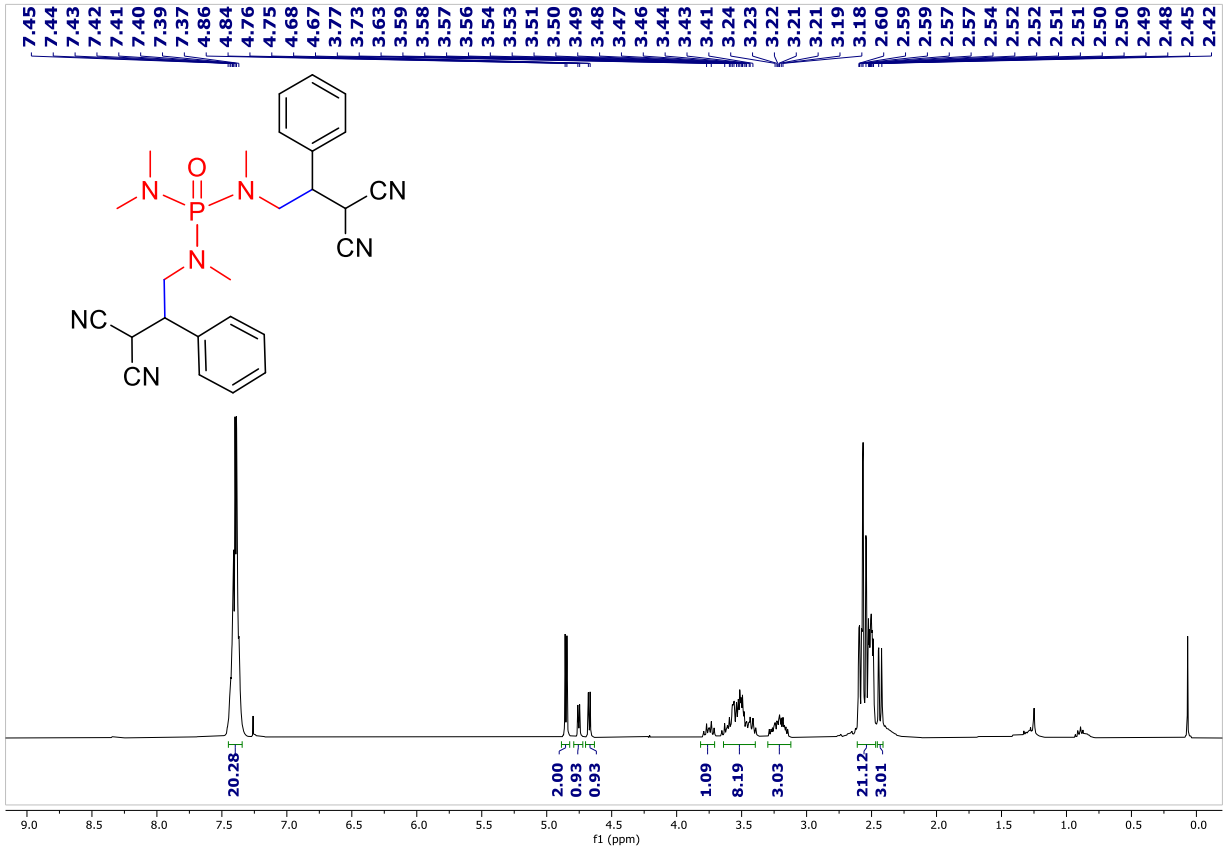
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4j"**



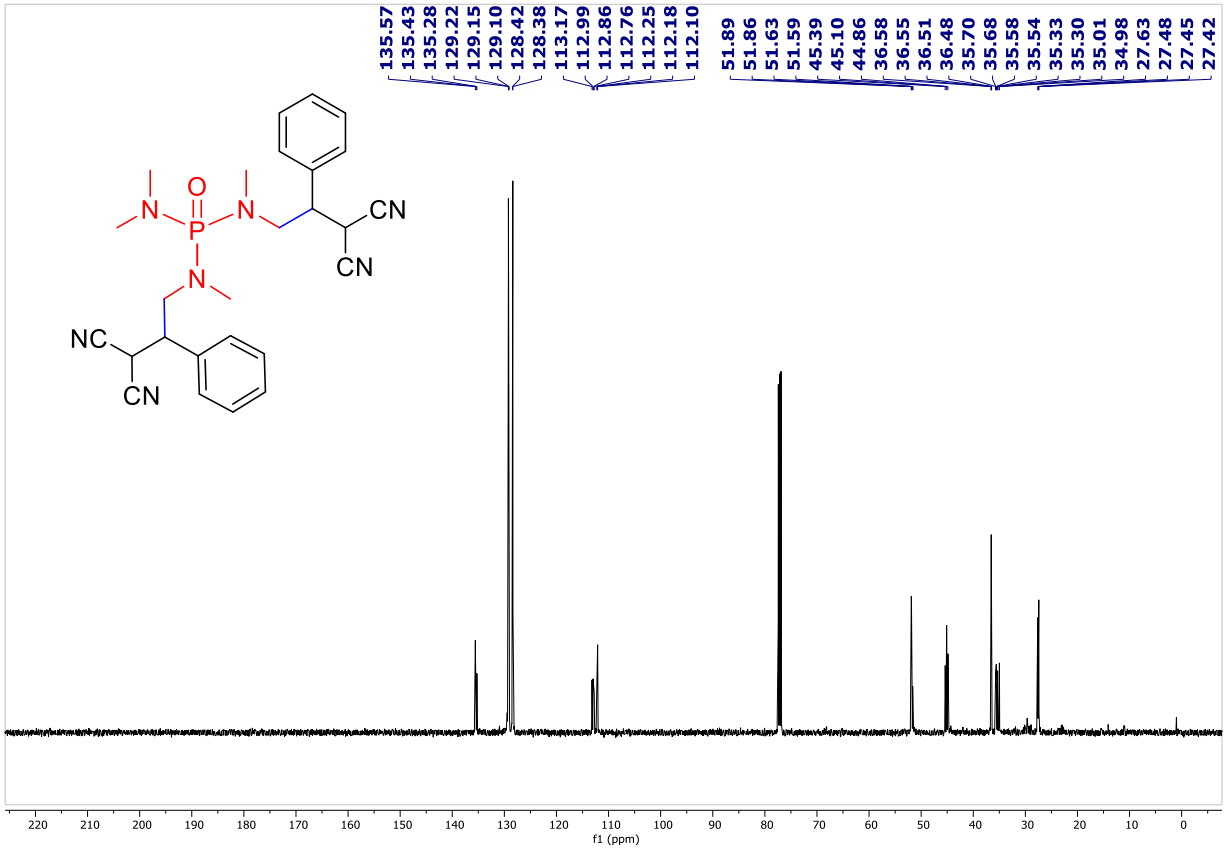
^{31}P NMR (203 MHz, $CDCl_3$) of compound **4j"**



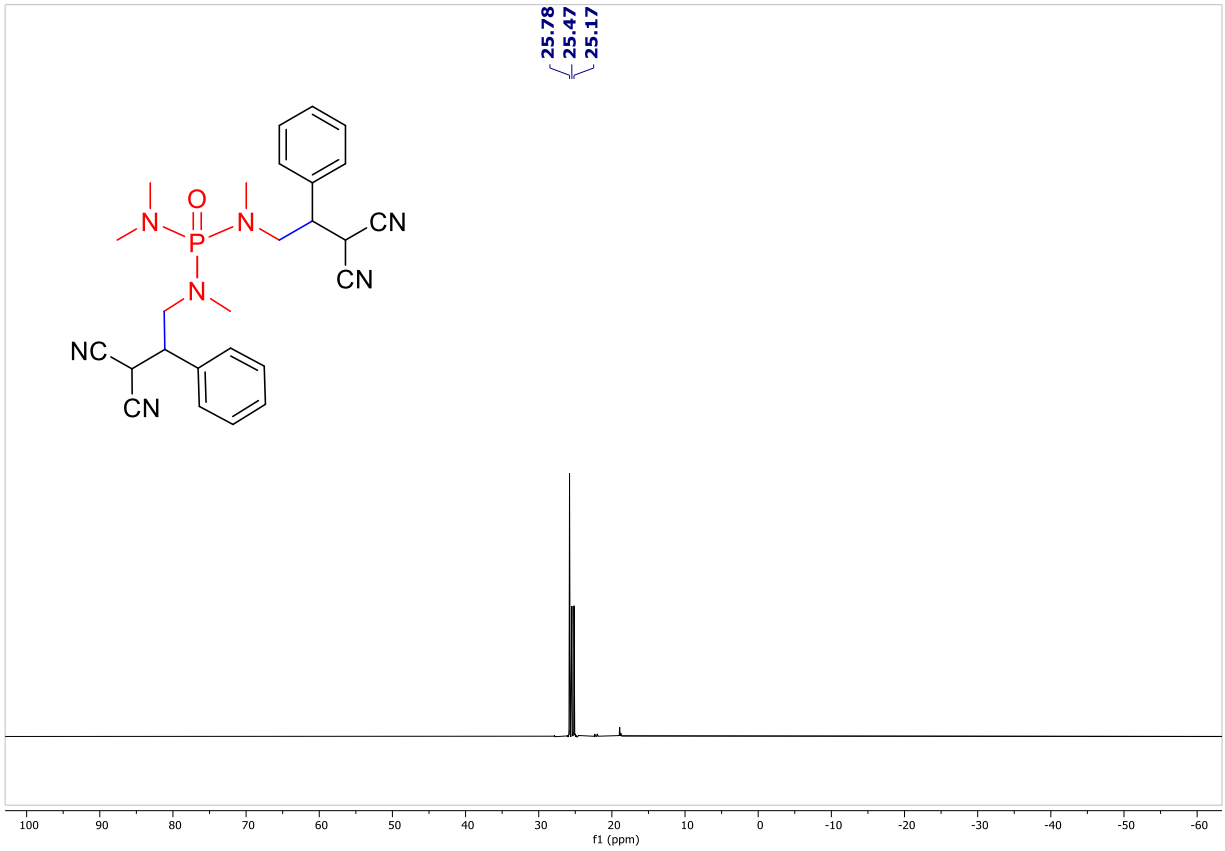
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5a**



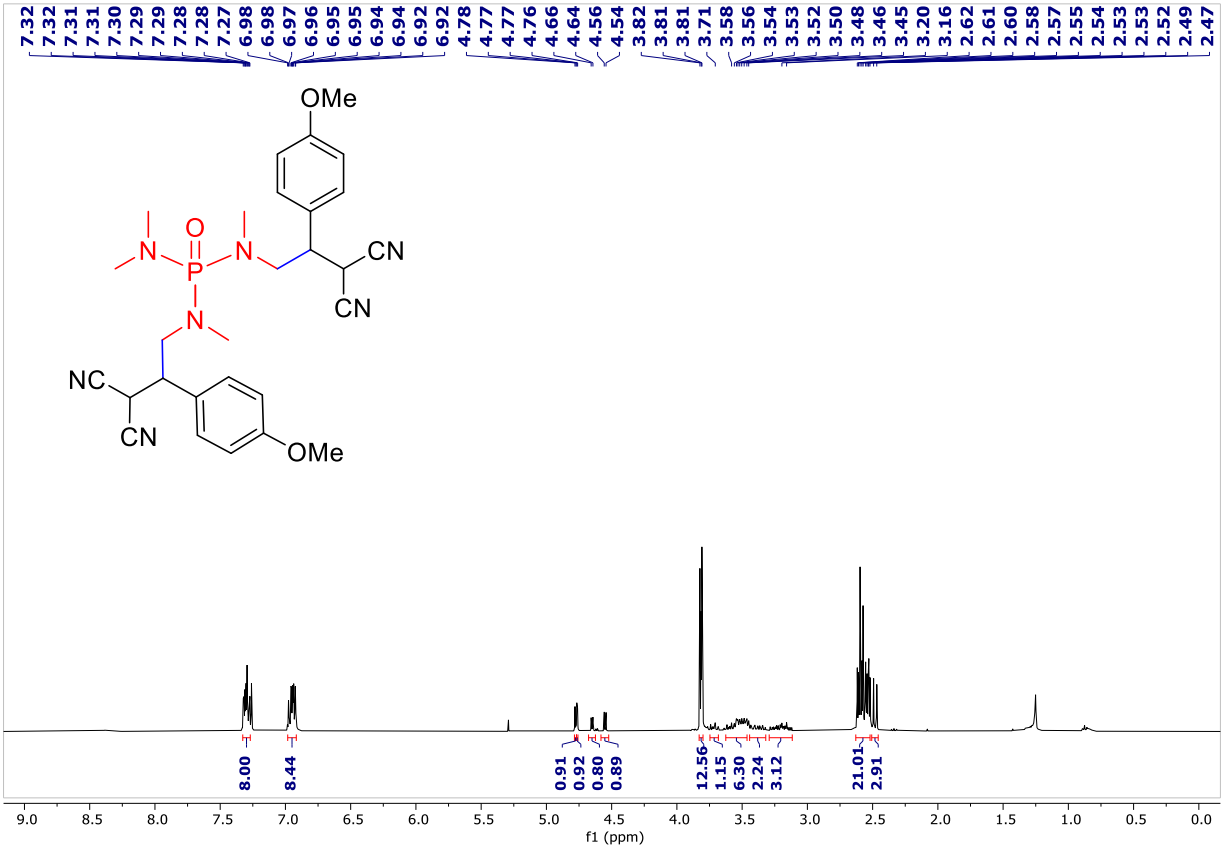
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **5a**



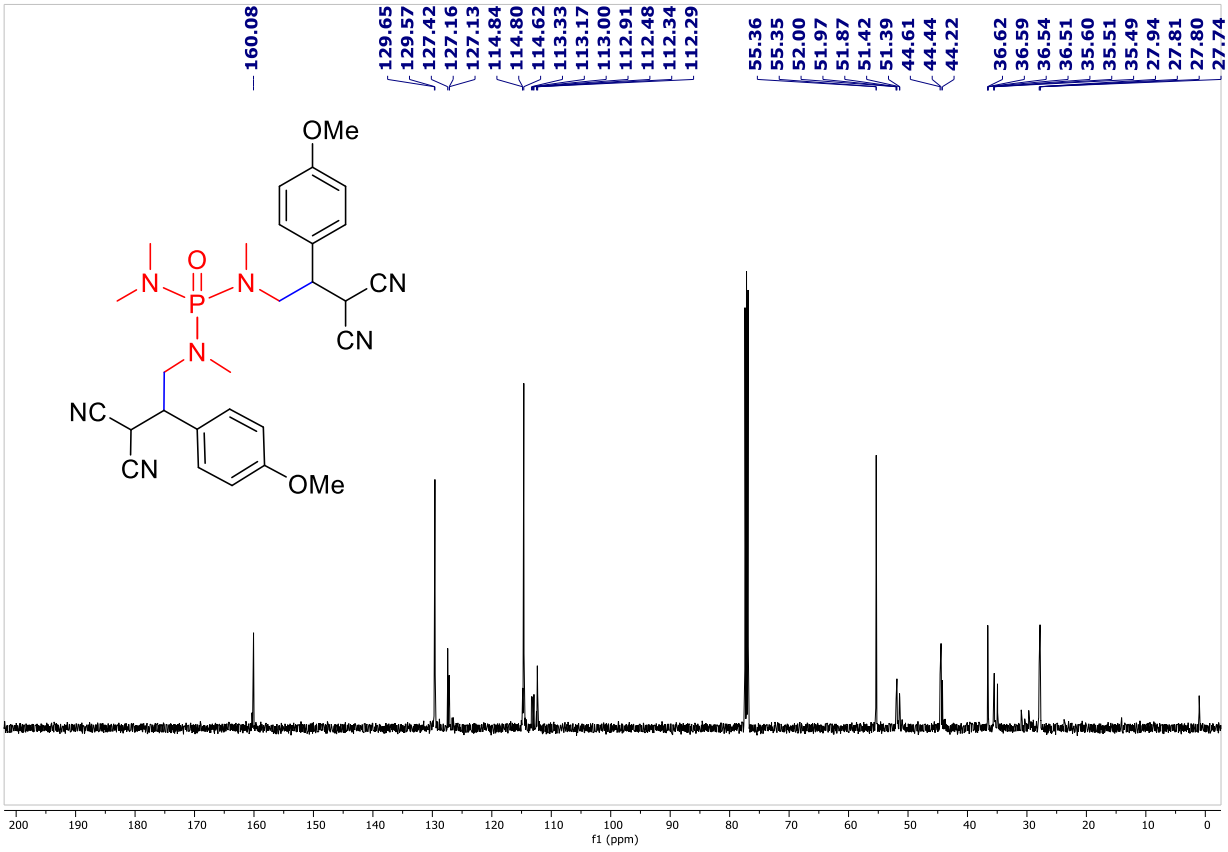
^{31}P NMR (203 MHz, $CDCl_3$) of compound **5a**



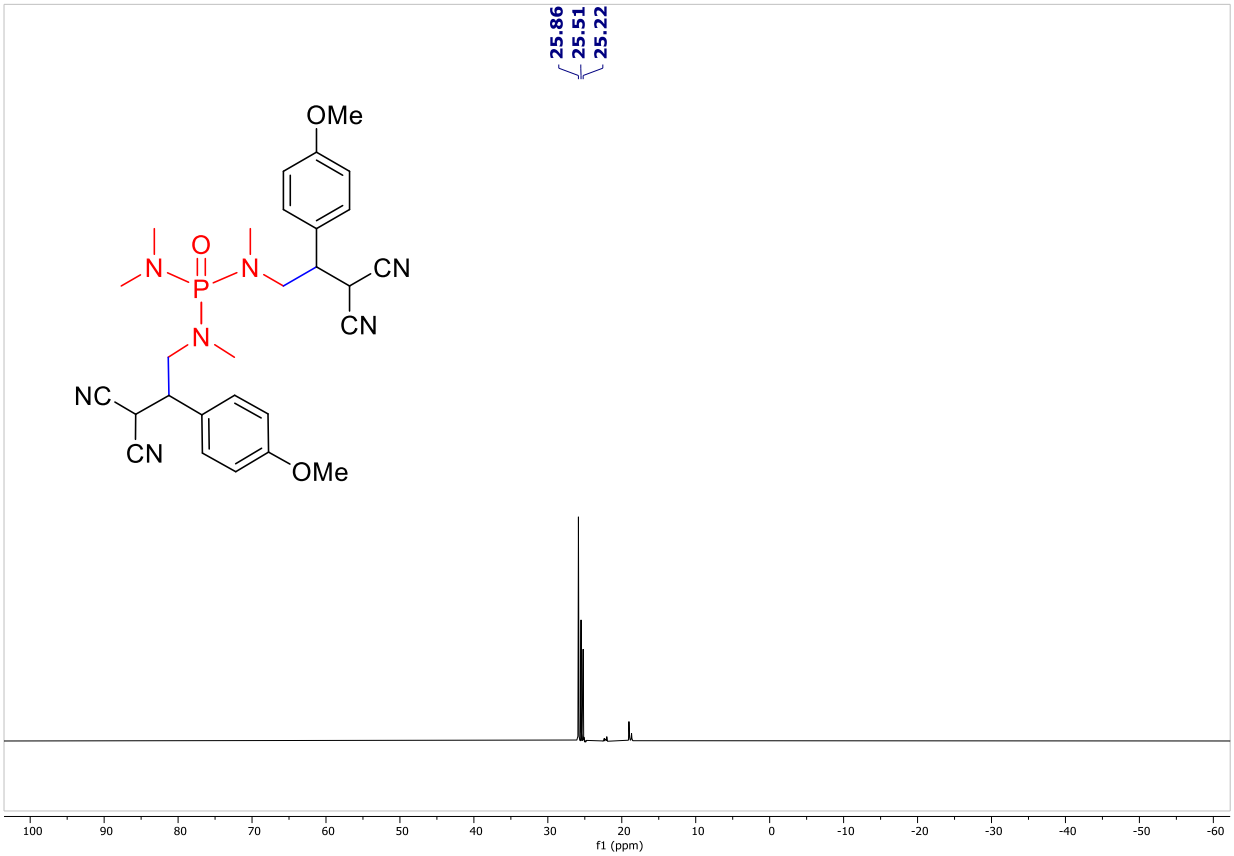
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5b**



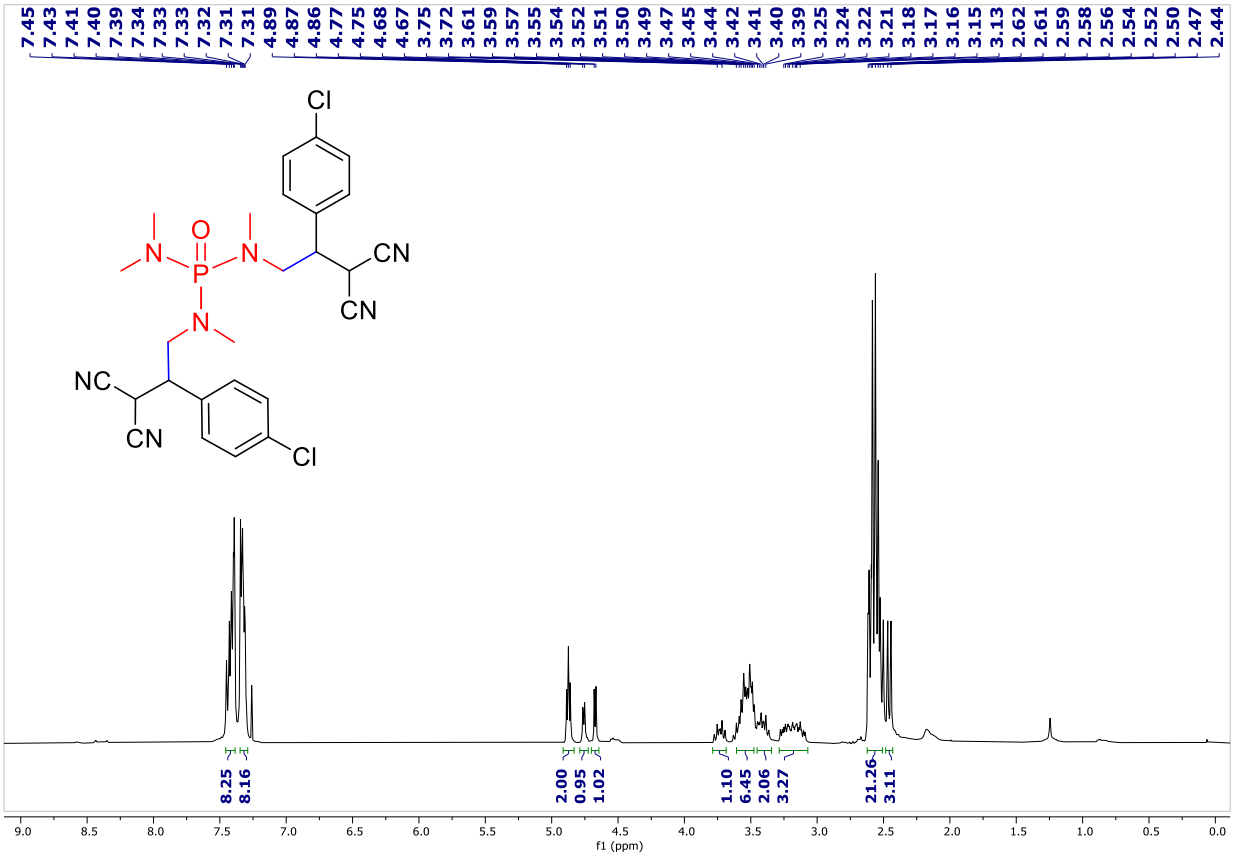
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **5b**



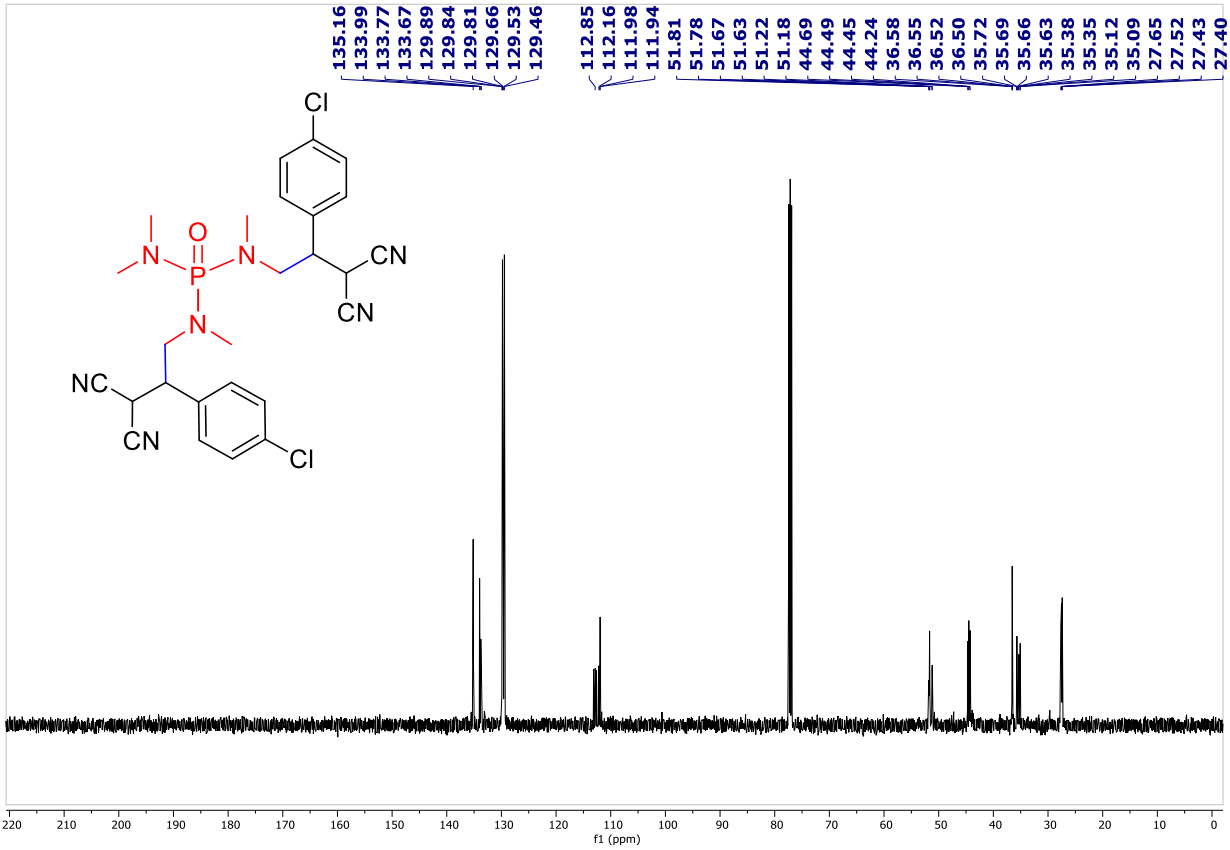
^{31}P NMR (203 MHz, $CDCl_3$) of compound **5b**



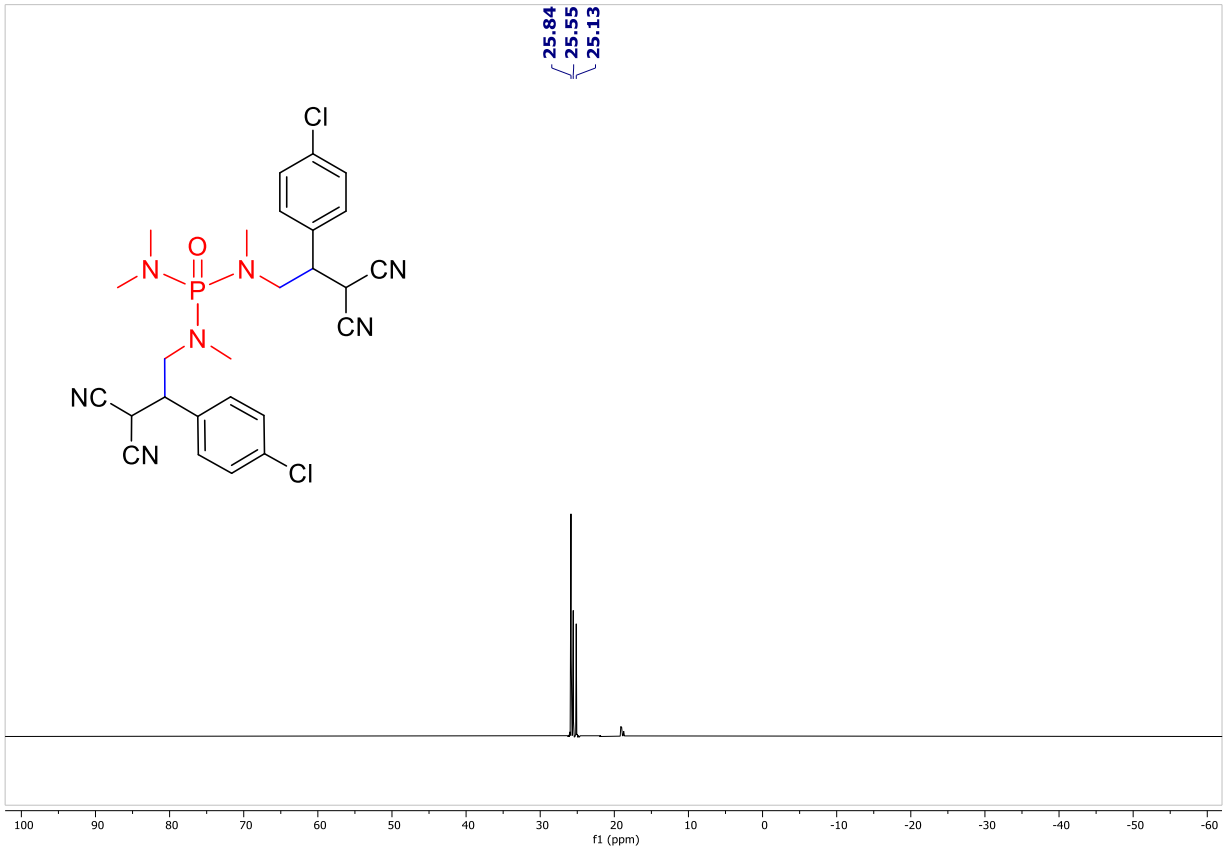
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5c**



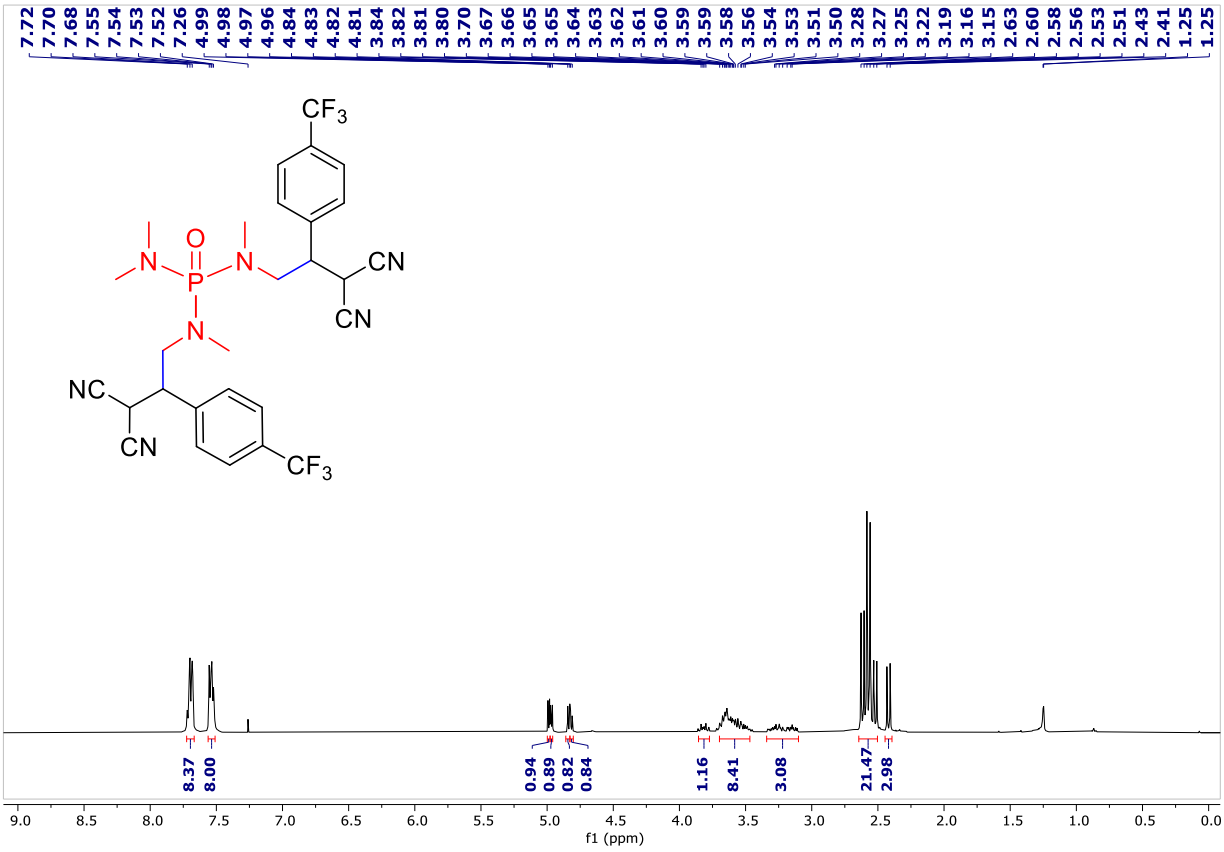
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **5c**



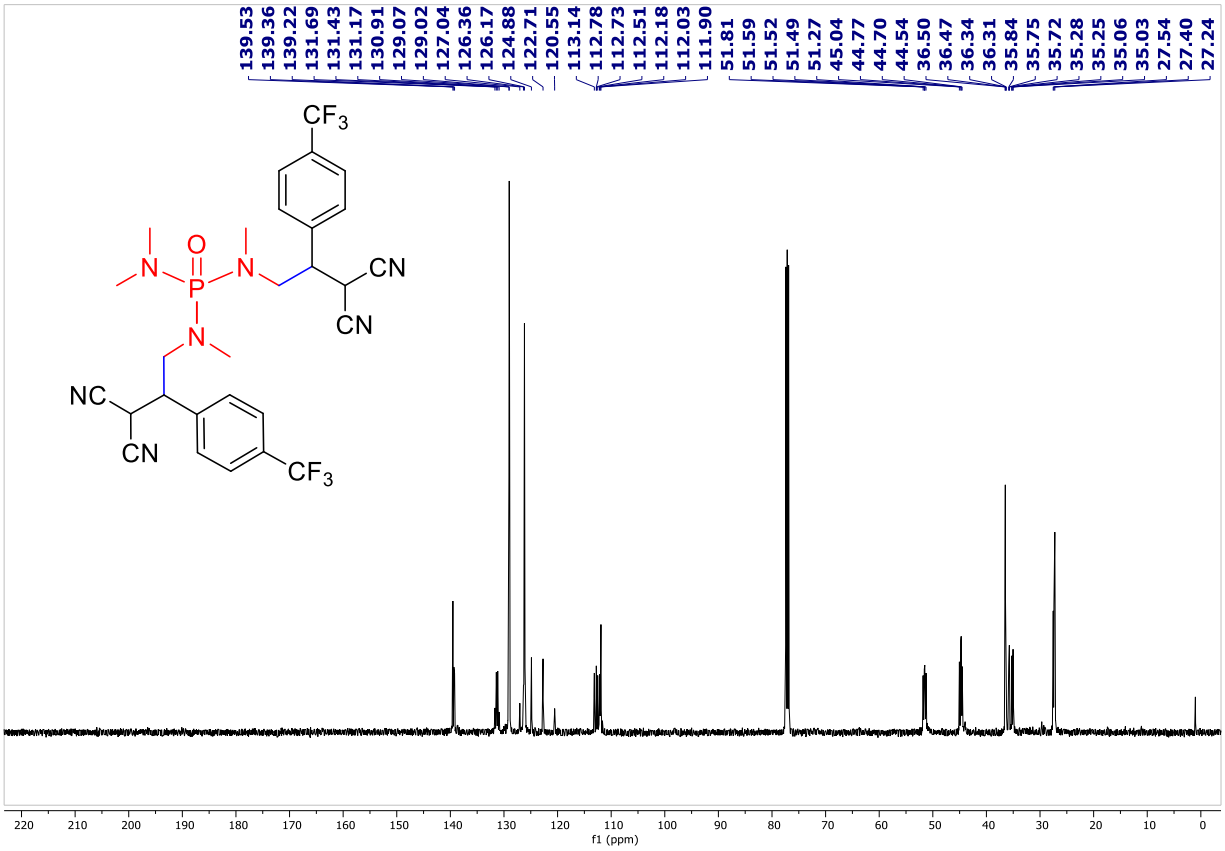
^{31}P NMR (203 MHz, $CDCl_3$) of compound **5c**



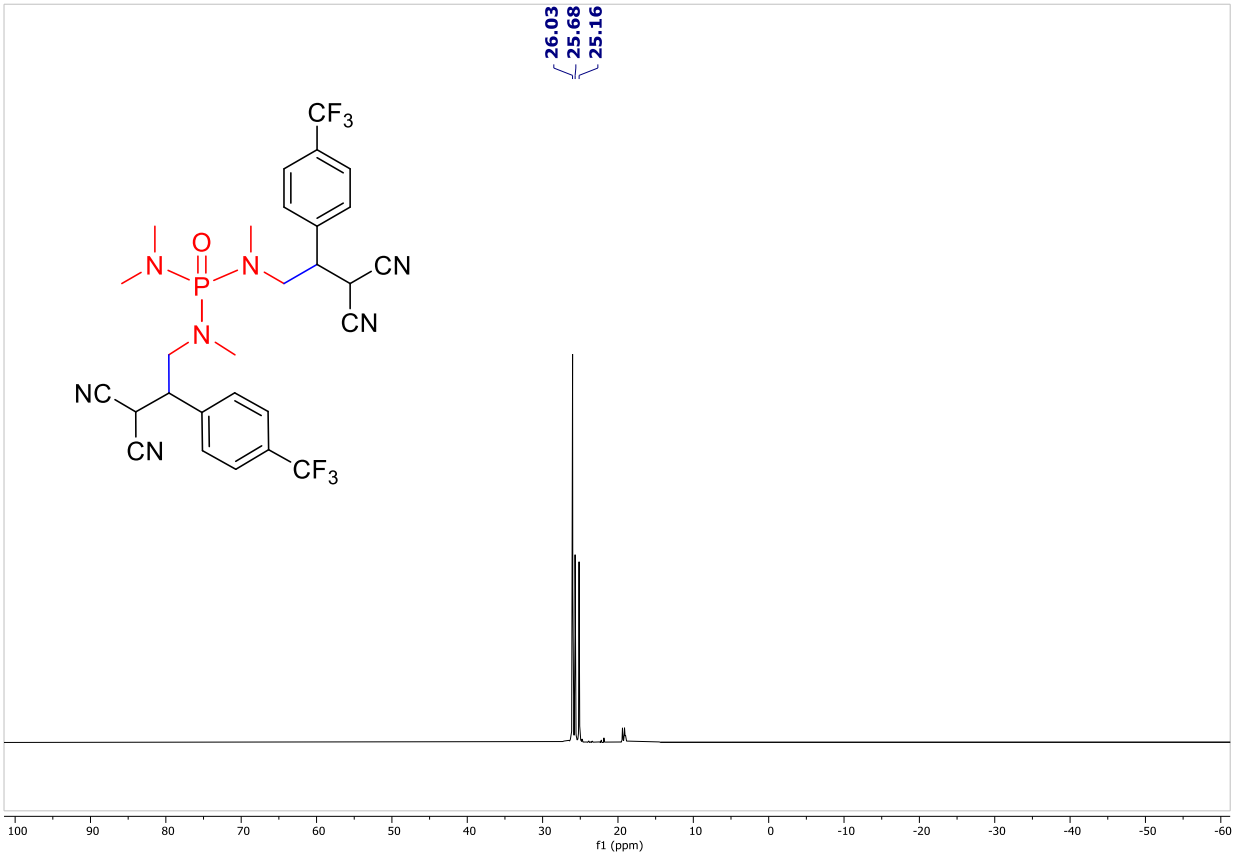
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5d**



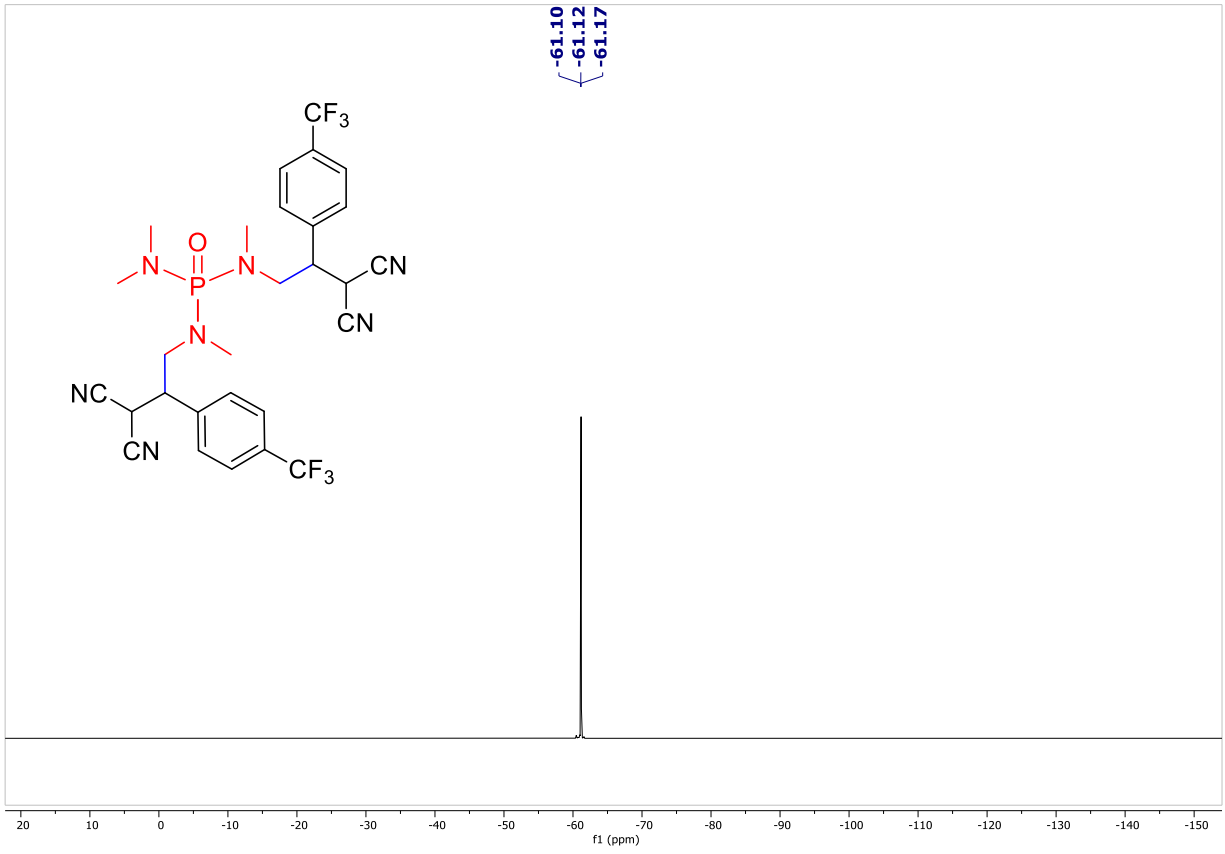
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **5d**



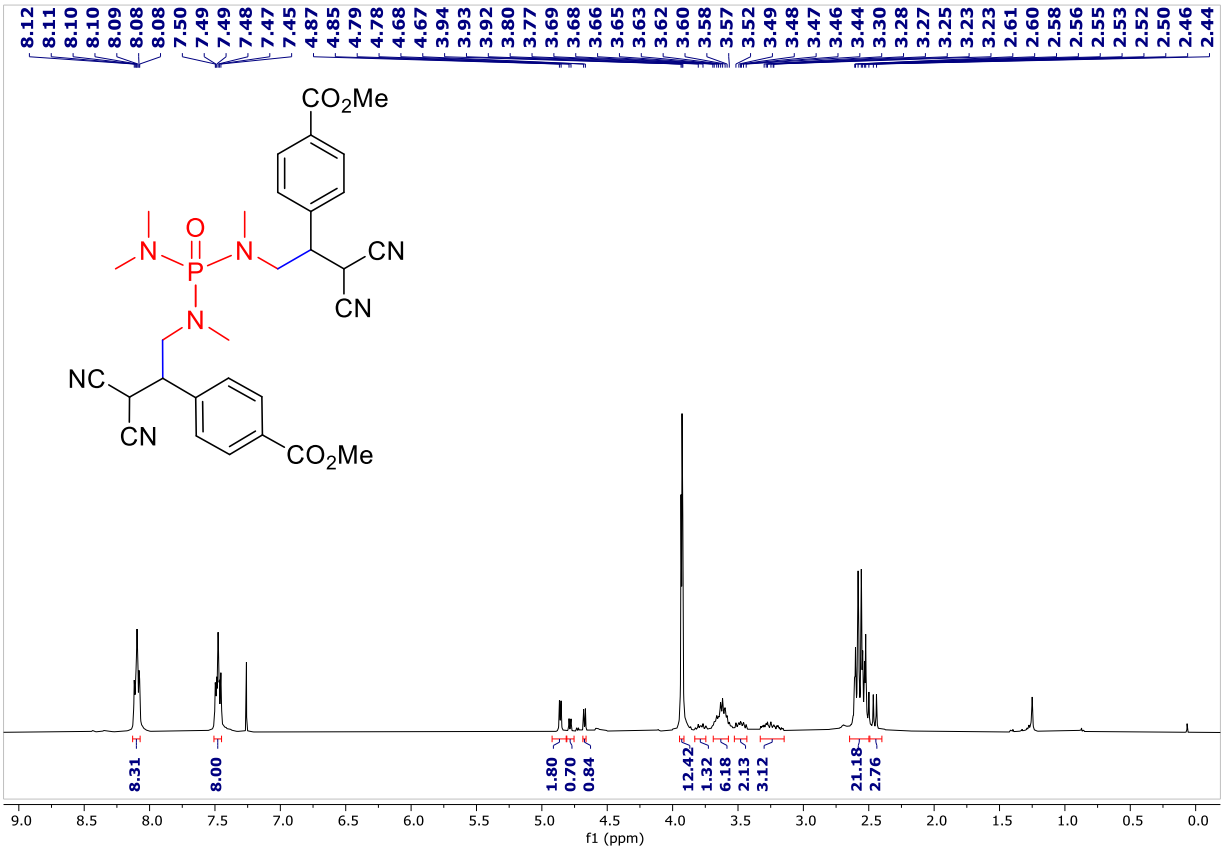
^{31}P NMR (203 MHz, $CDCl_3$) of compound **5d**



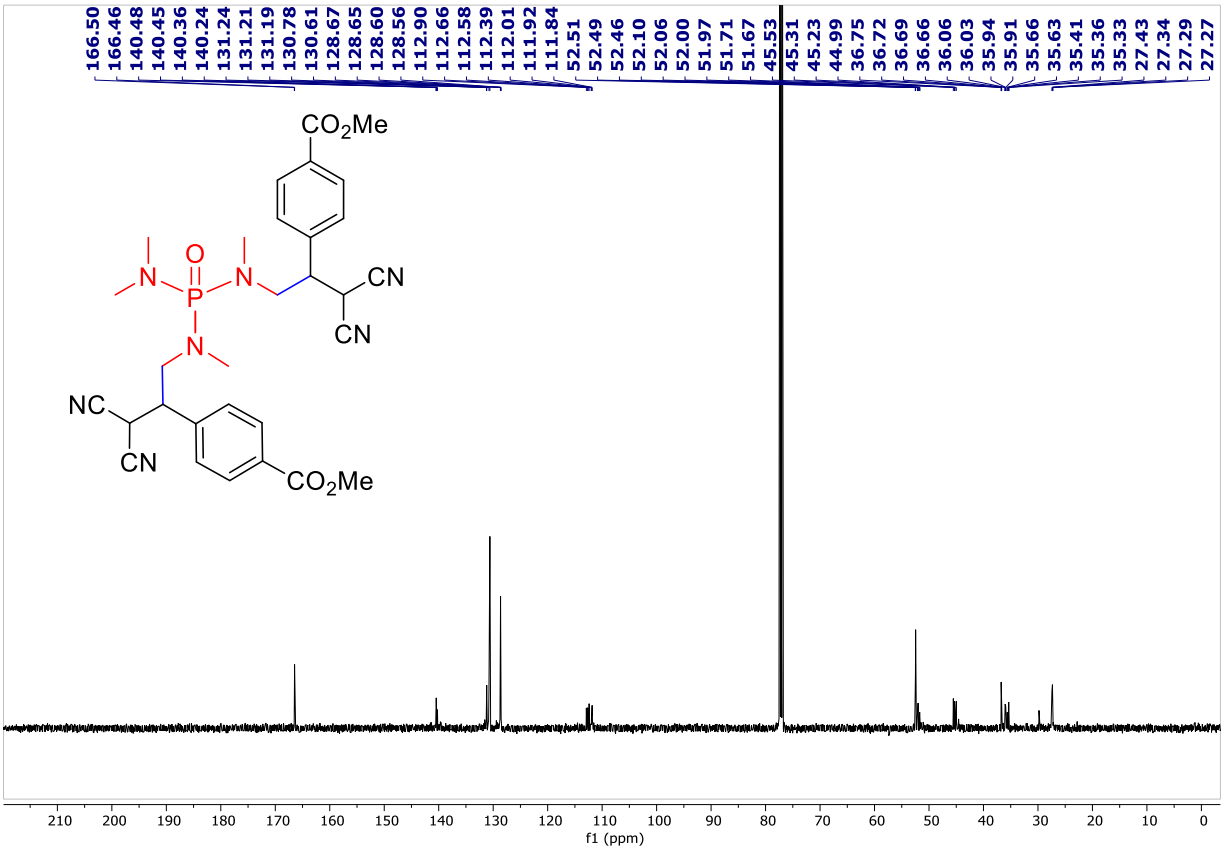
^{19}F NMR (471 MHz, $CDCl_3$) of compound **5d**



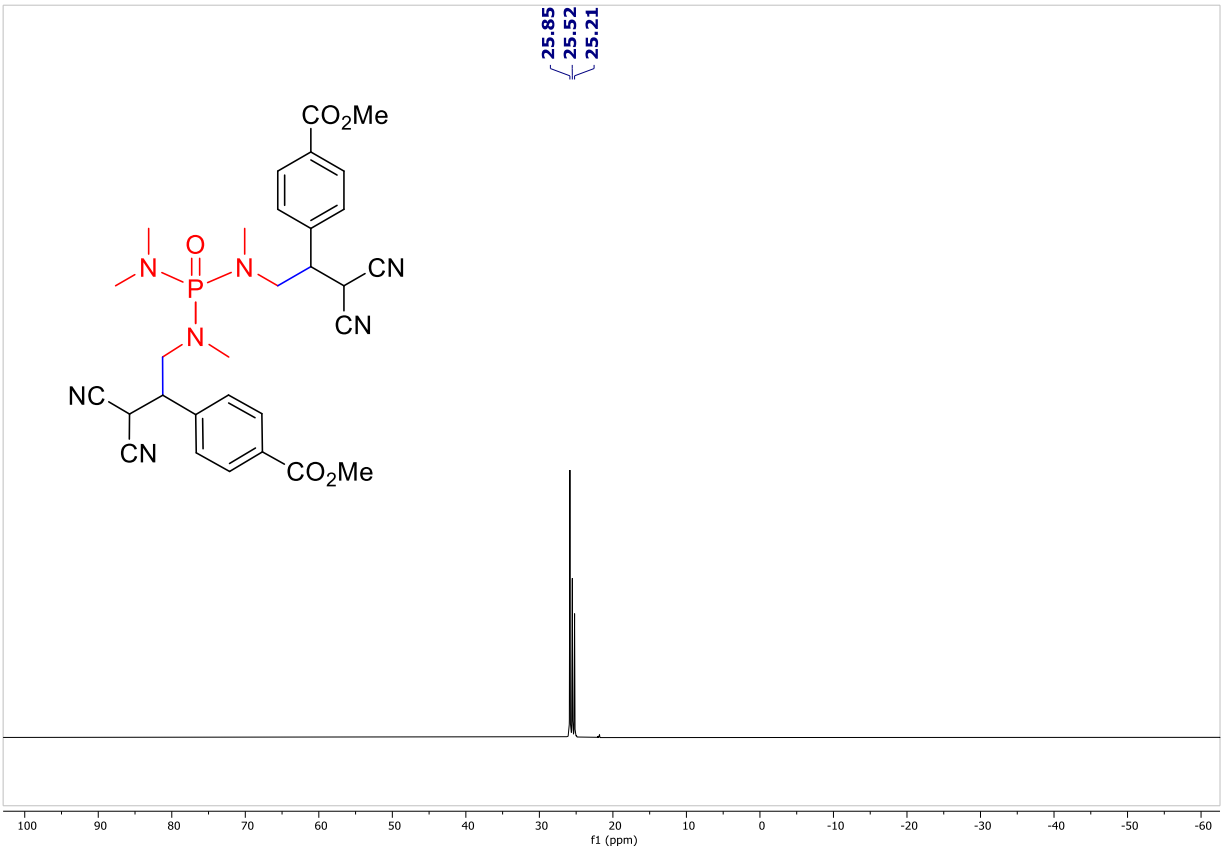
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5e**



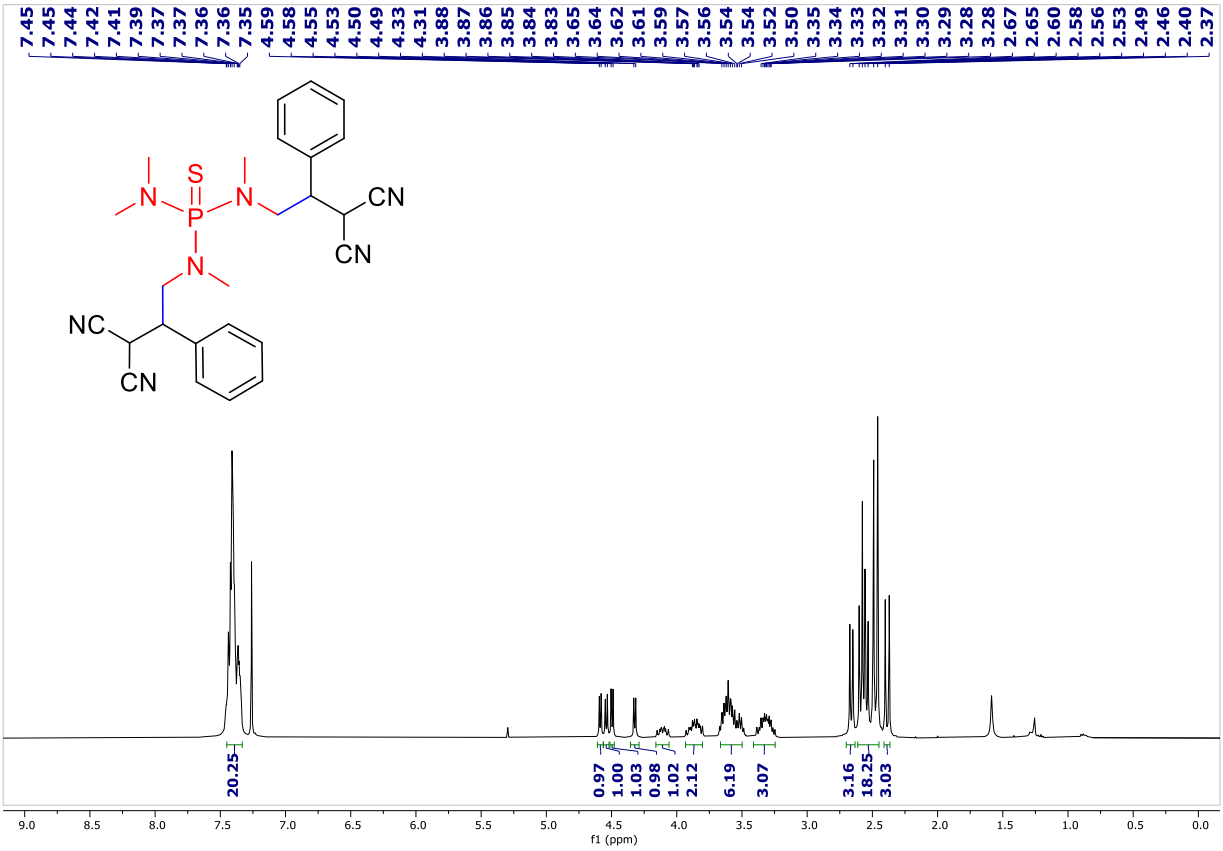
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **5e**



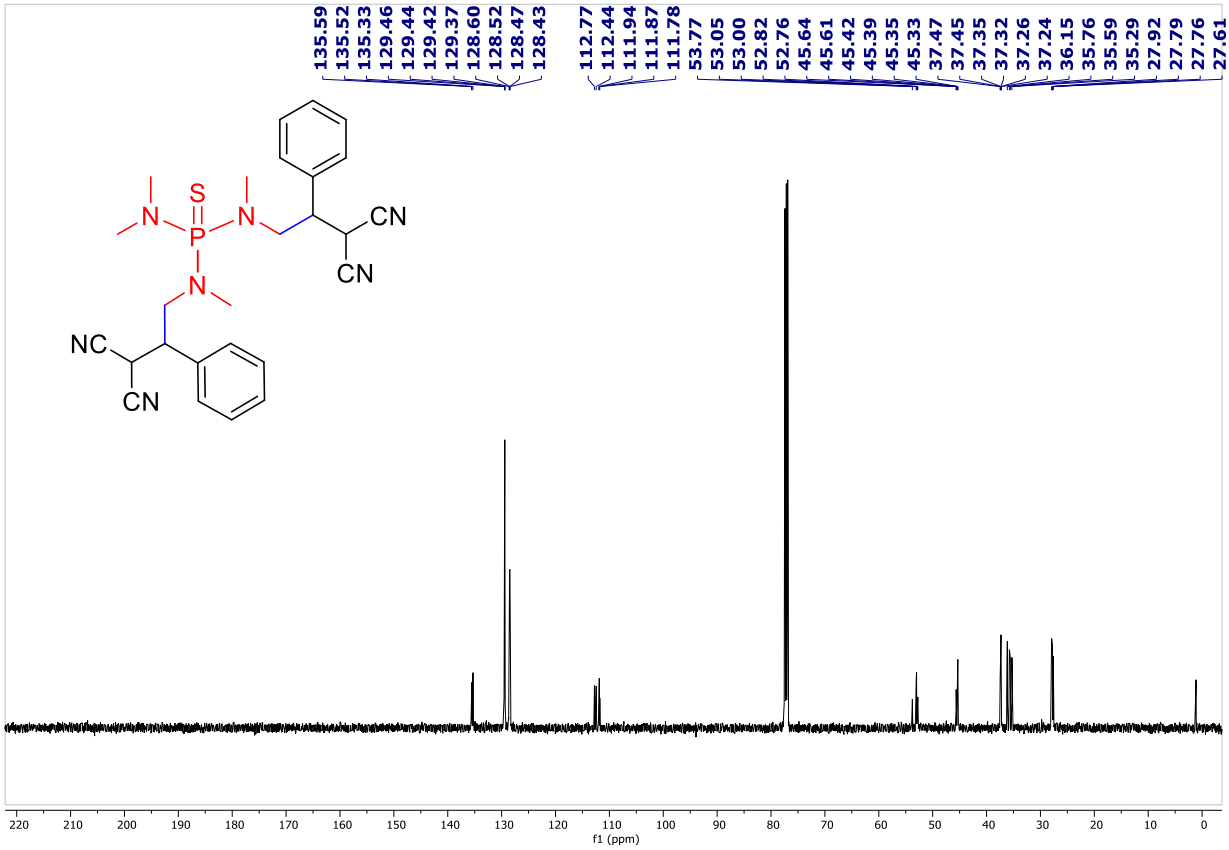
^{31}P NMR (203 MHz, $CDCl_3$) of compound **5e**



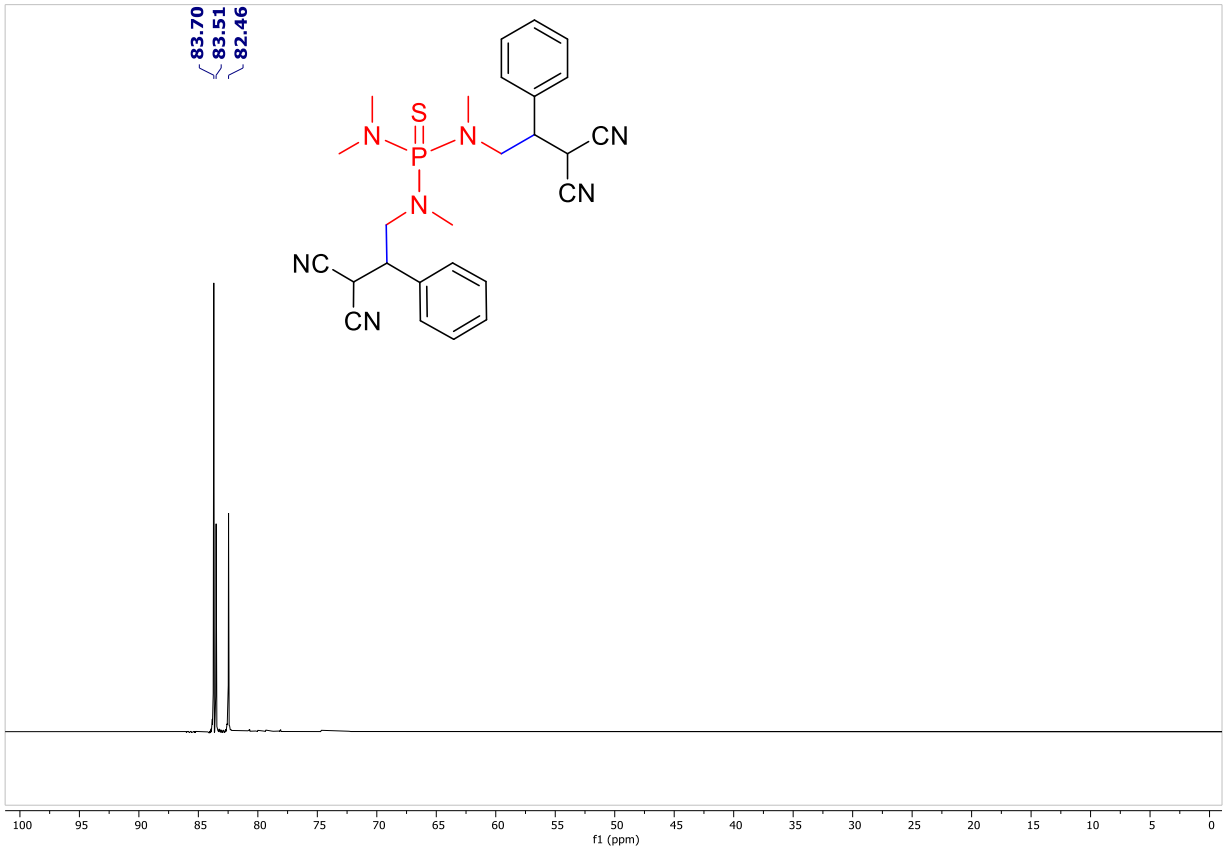
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5f**



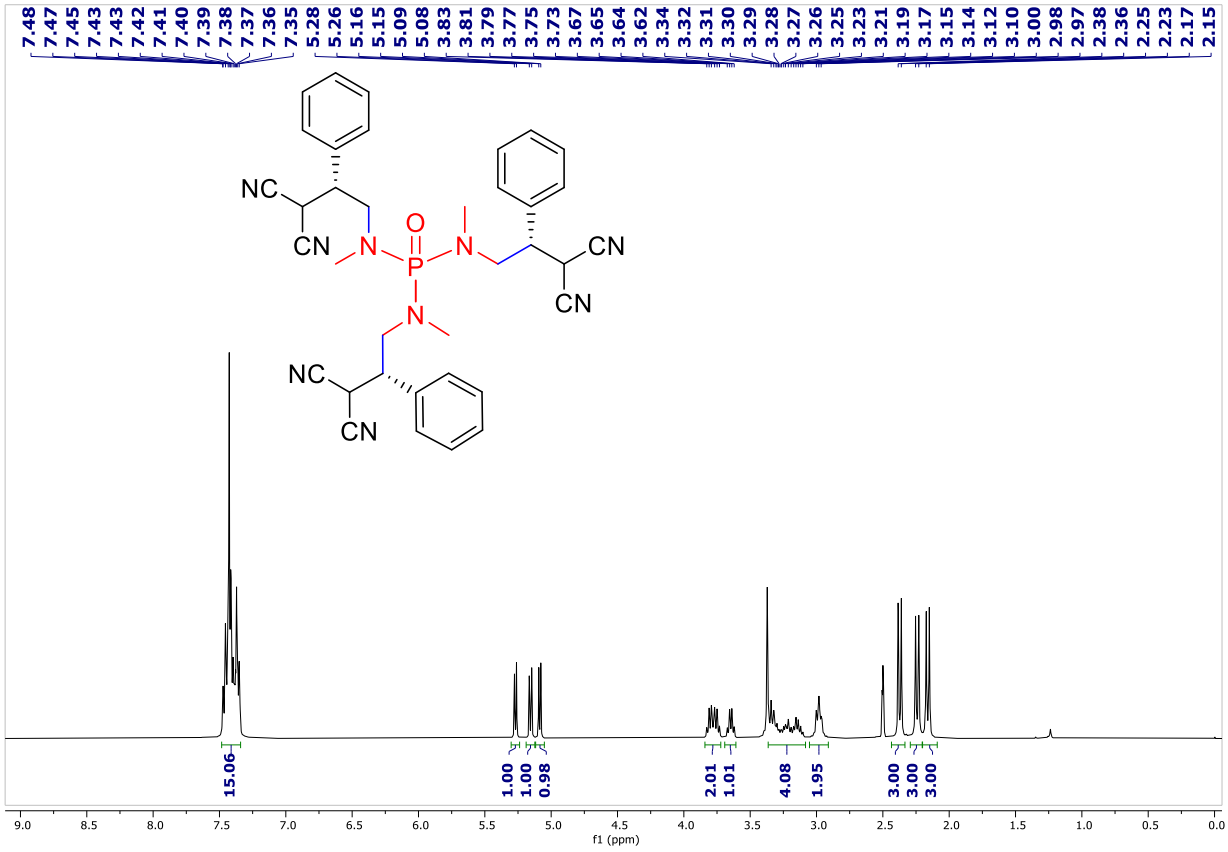
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **5f**



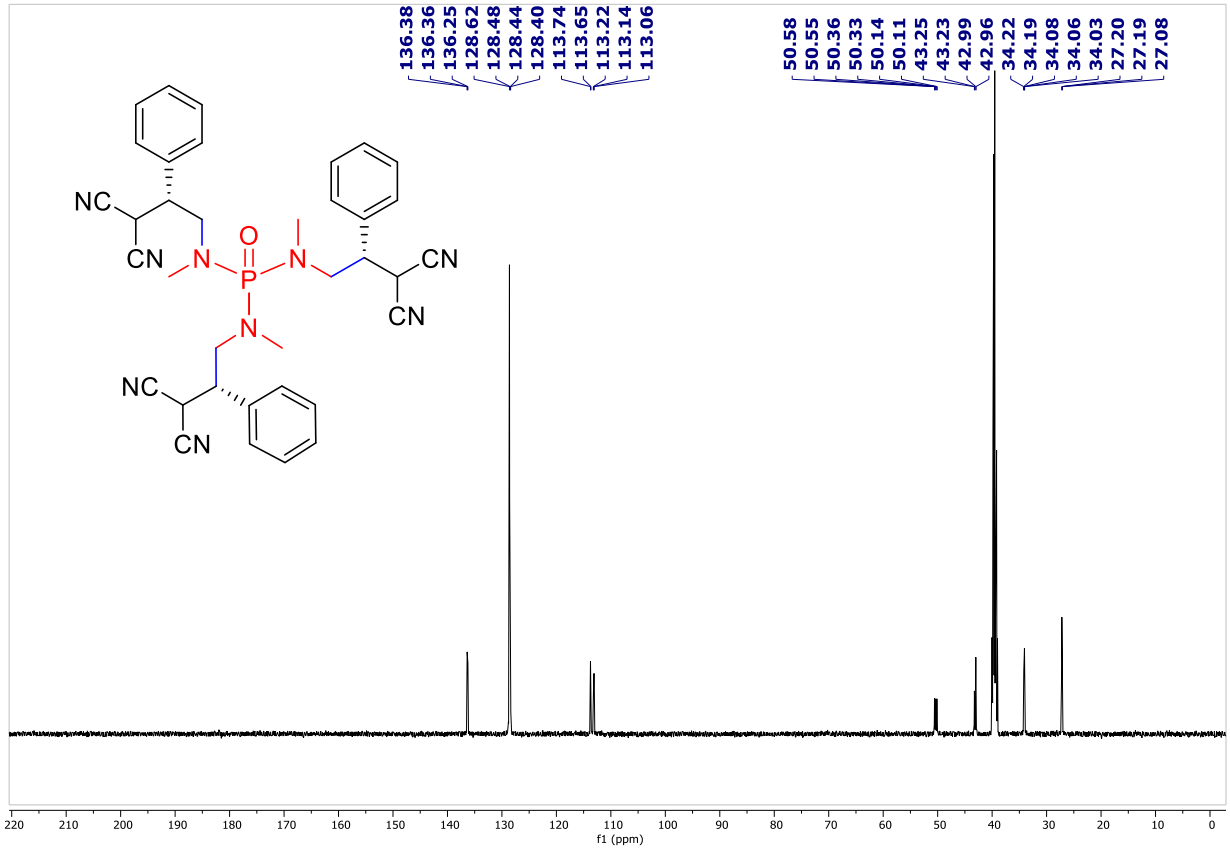
^{31}P NMR (203 MHz, $CDCl_3$) of compound **5f**



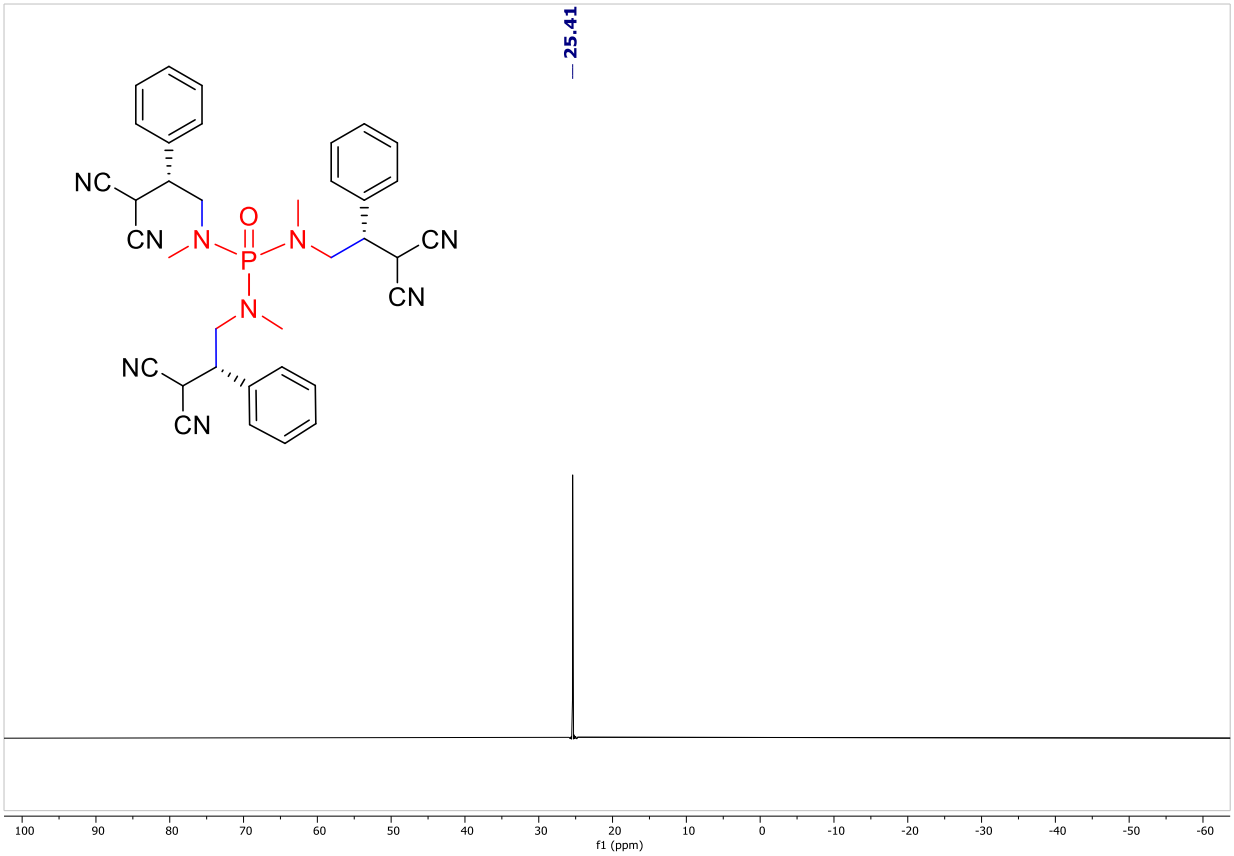
^{1}H NMR (400 MHz, DMSO-d_6) of compound major (±)-**6a'**



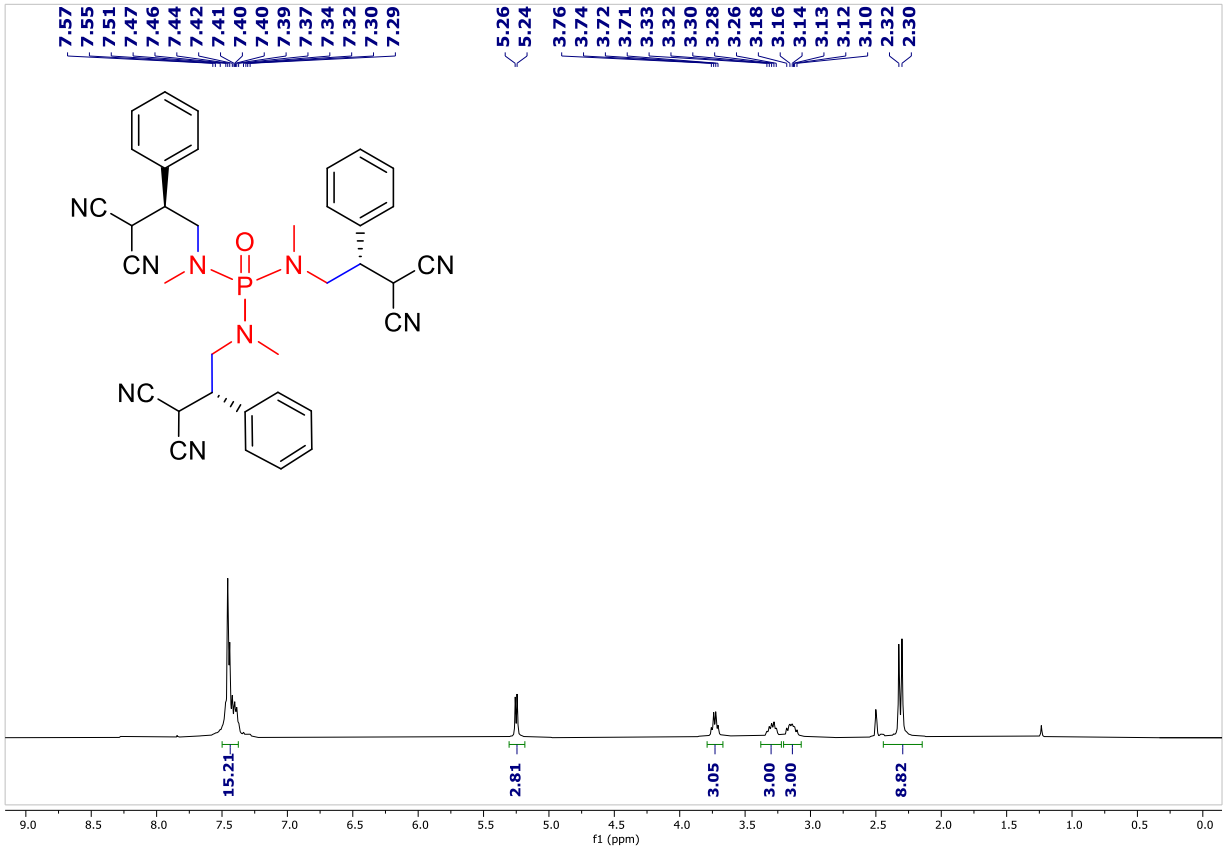
^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) of compound major (±)-**6a'**



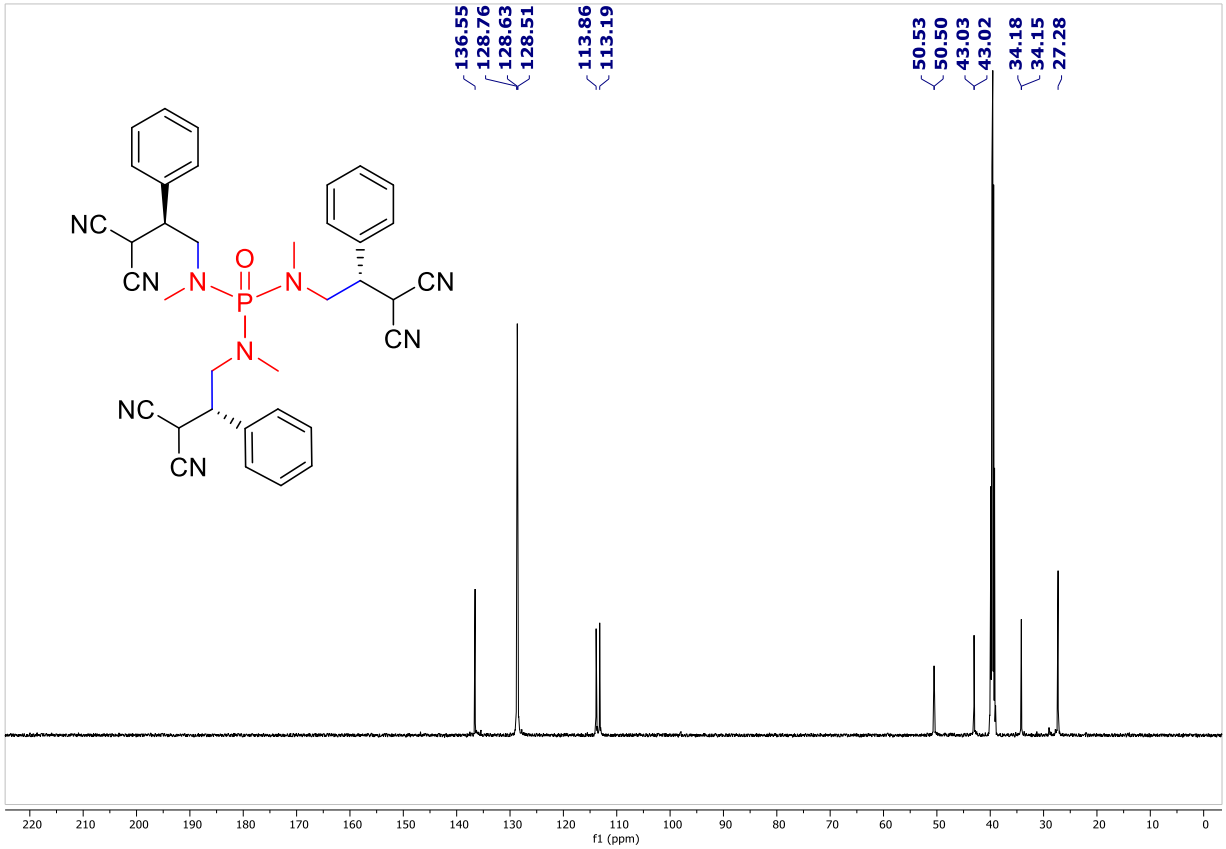
^{31}P NMR (203 MHz, DMSO-d_6) of compound major (±)-**6a'**



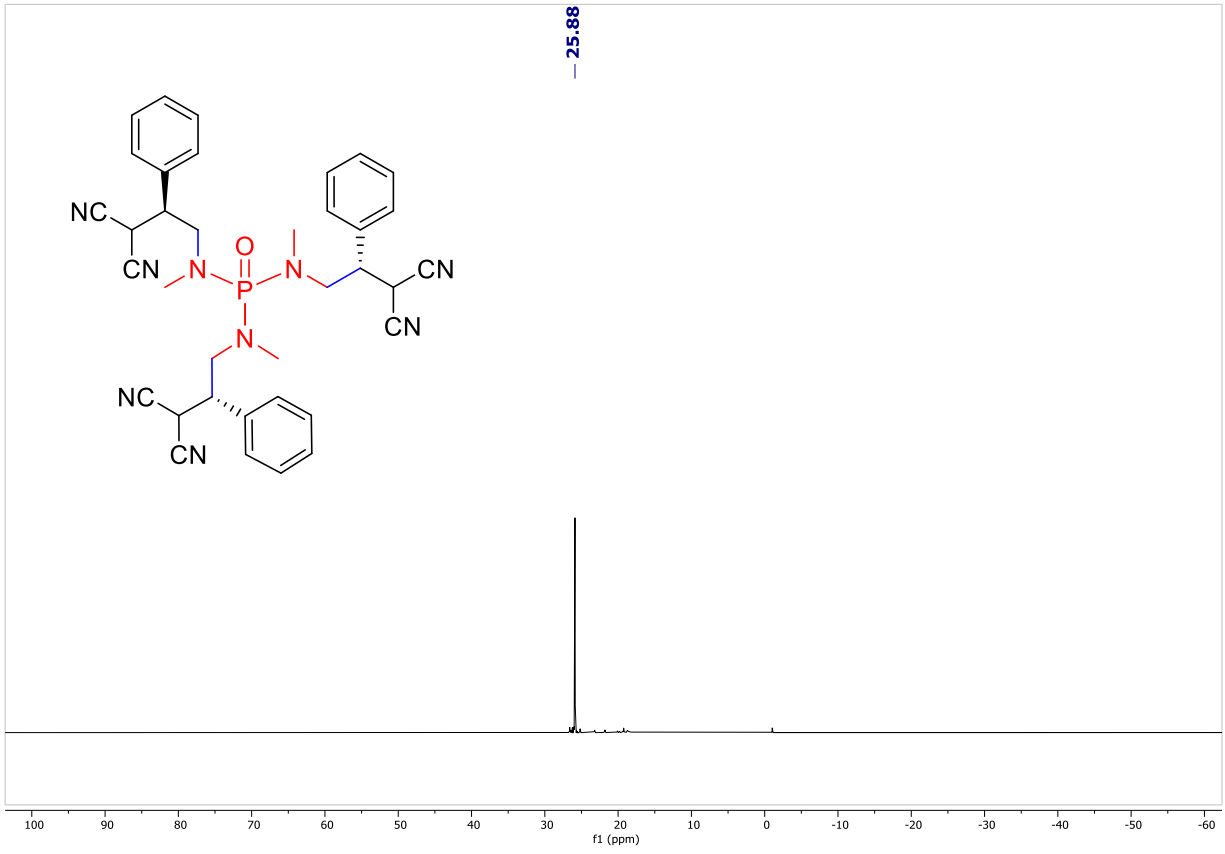
^{1}H NMR (400 MHz, DMSO-d_6) of compound minor (±)-**6a''**



$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) of compound minor (±)-**6a''**



^{31}P NMR (203 MHz, DMSO-d_6) of compound minor (±)-**6a''**



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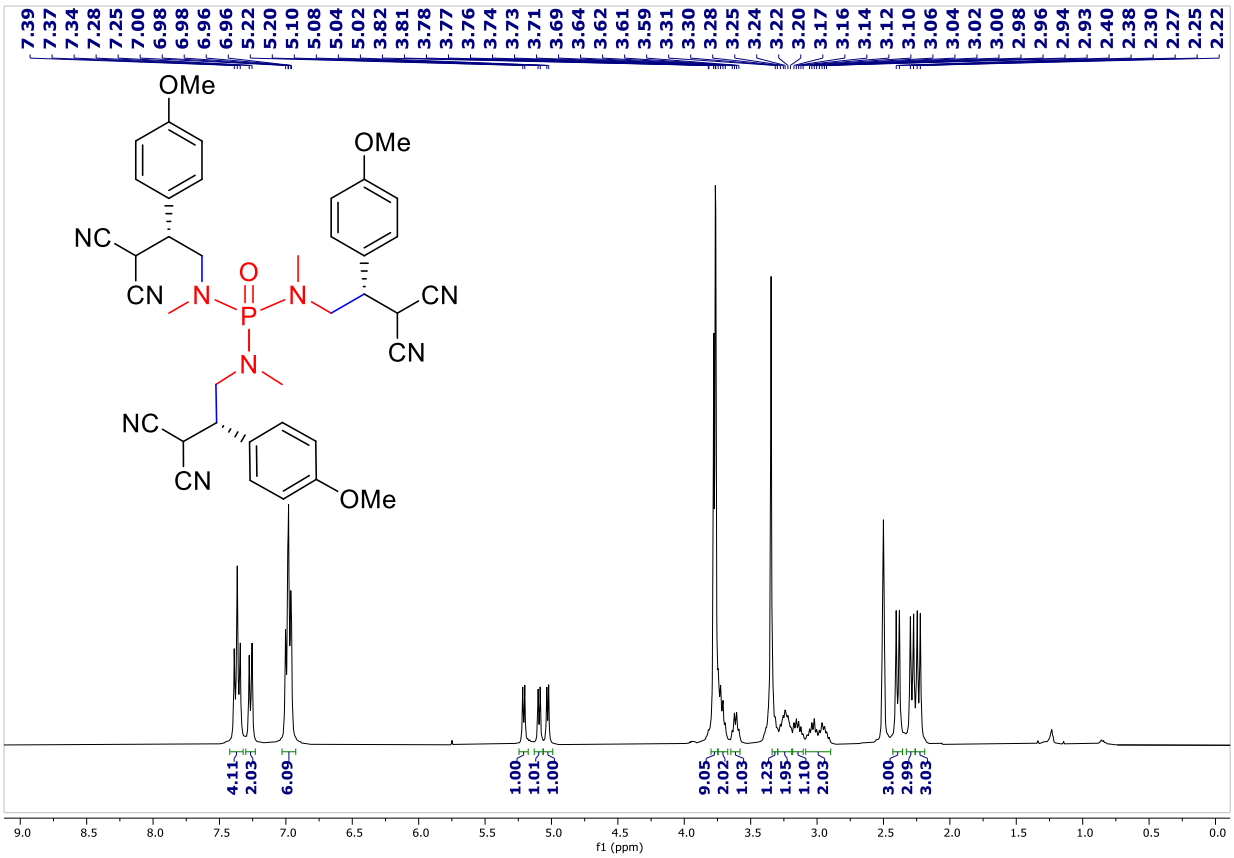

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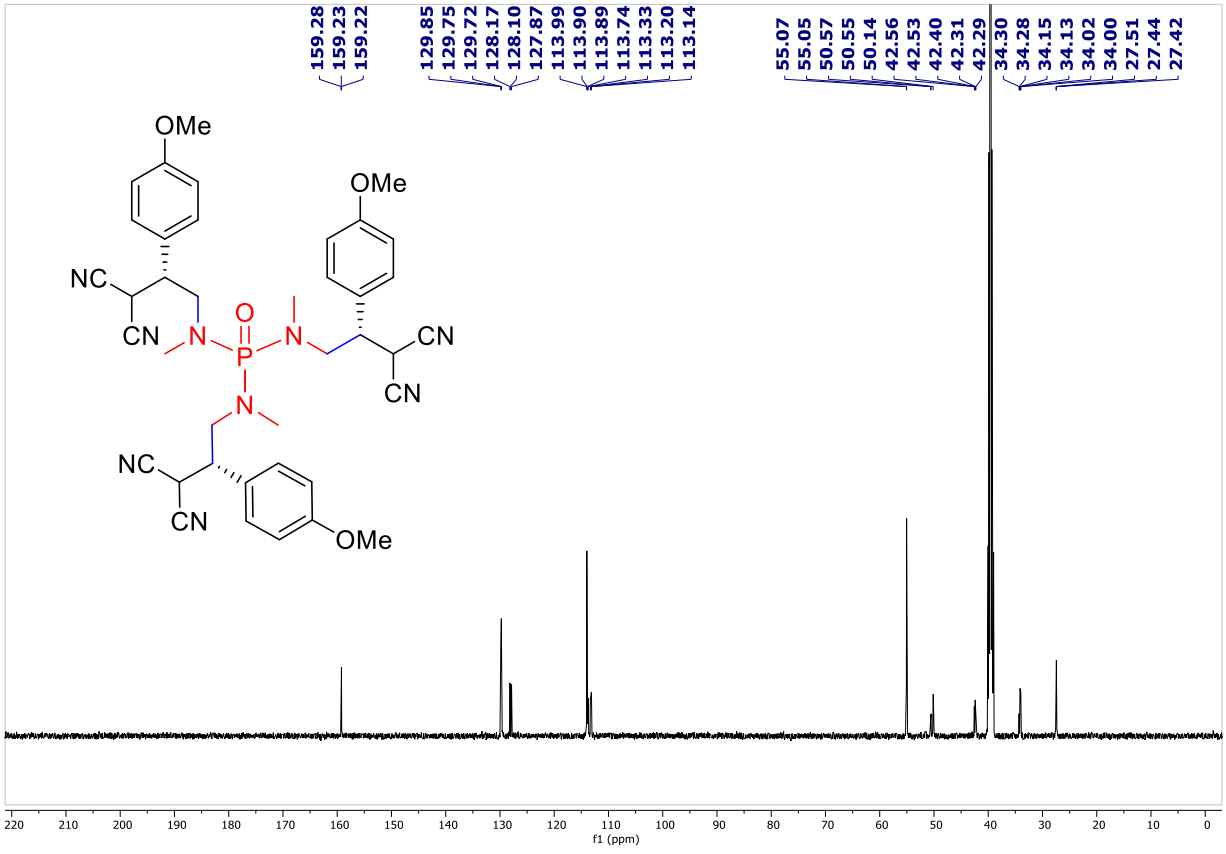
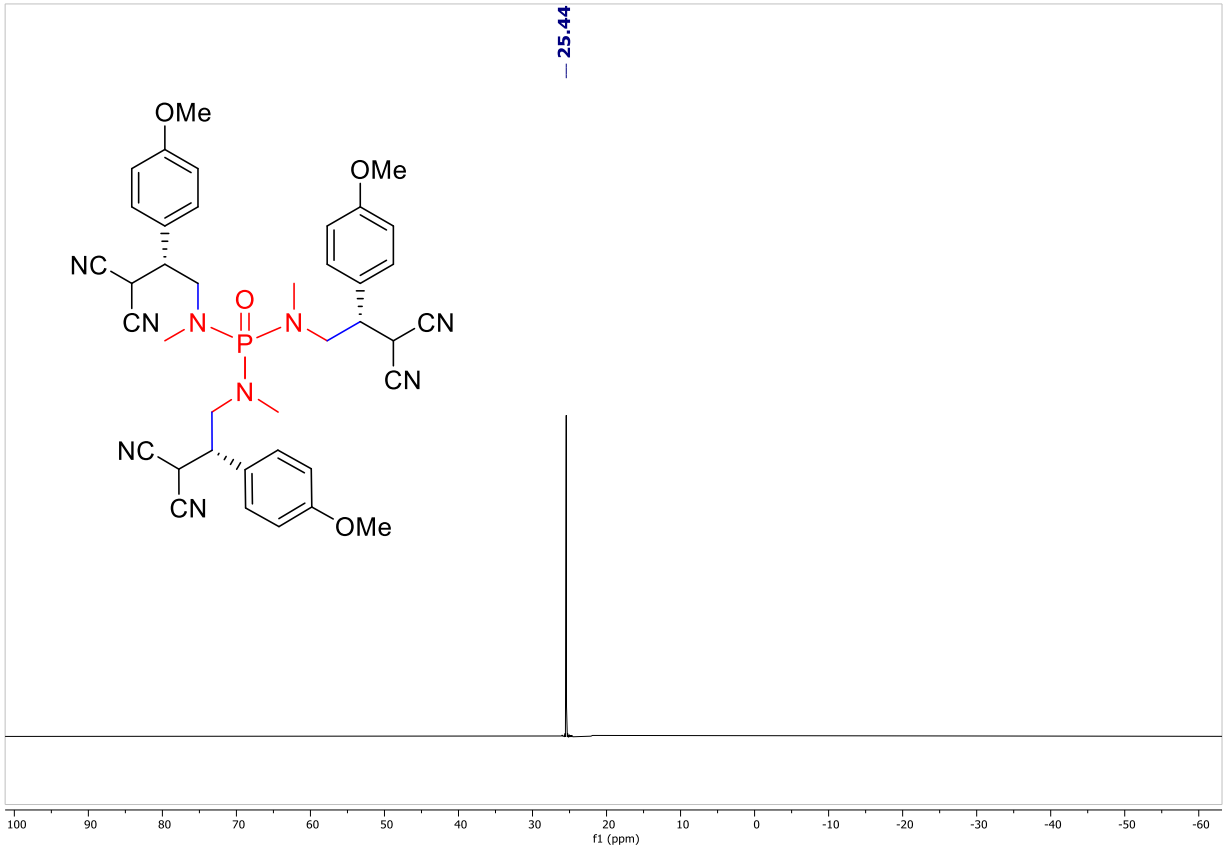
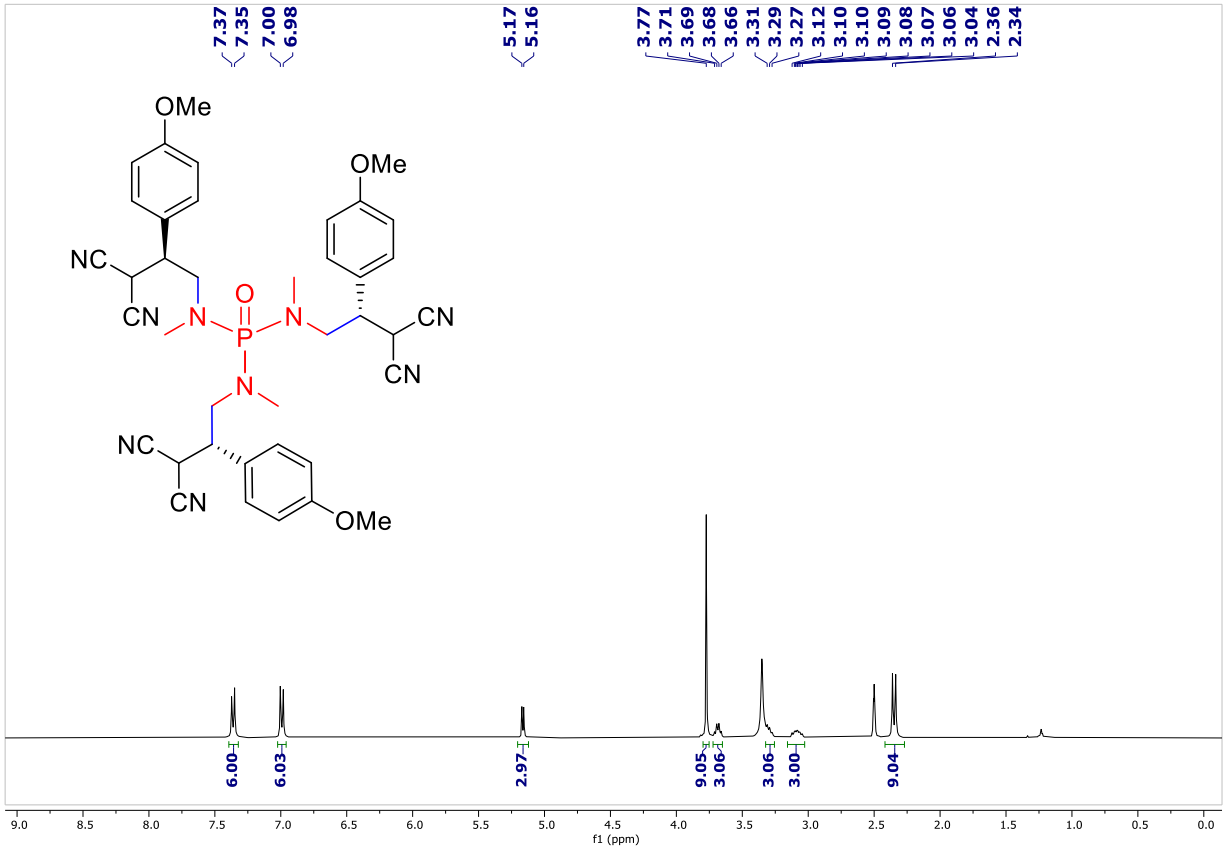


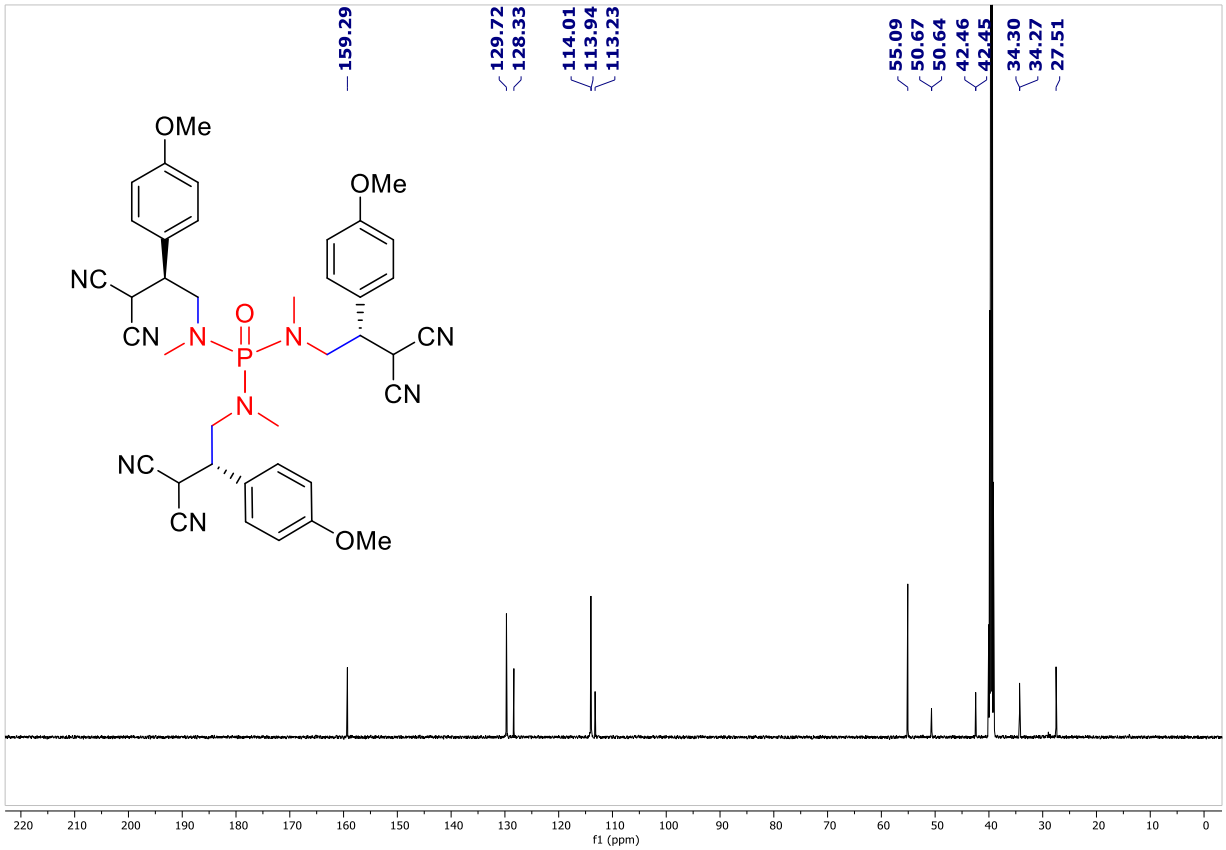
^{31}P NMR (203 MHz, DMSO-d_6) of compound major (±)-**6b'**



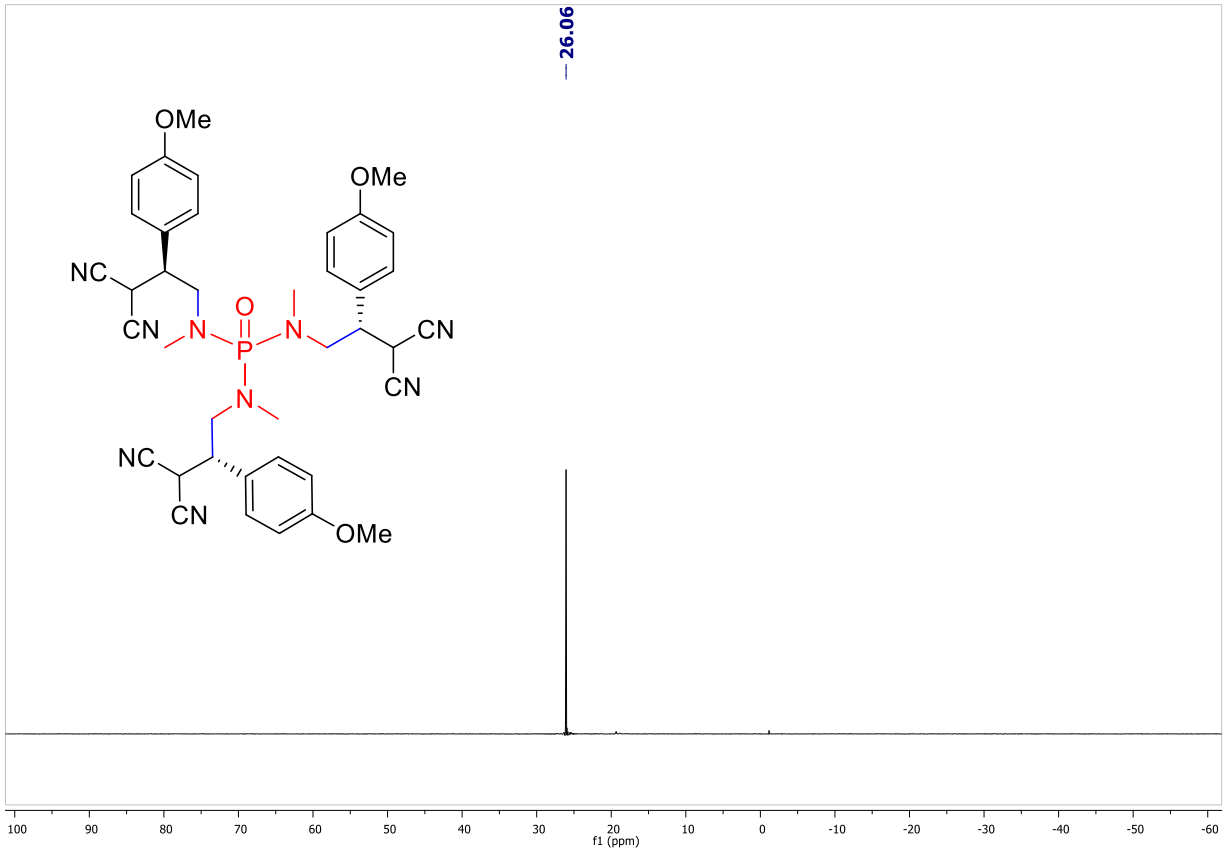
^{1}H NMR (400 MHz, DMSO-d_6) of compound minor (±)-**6b''**



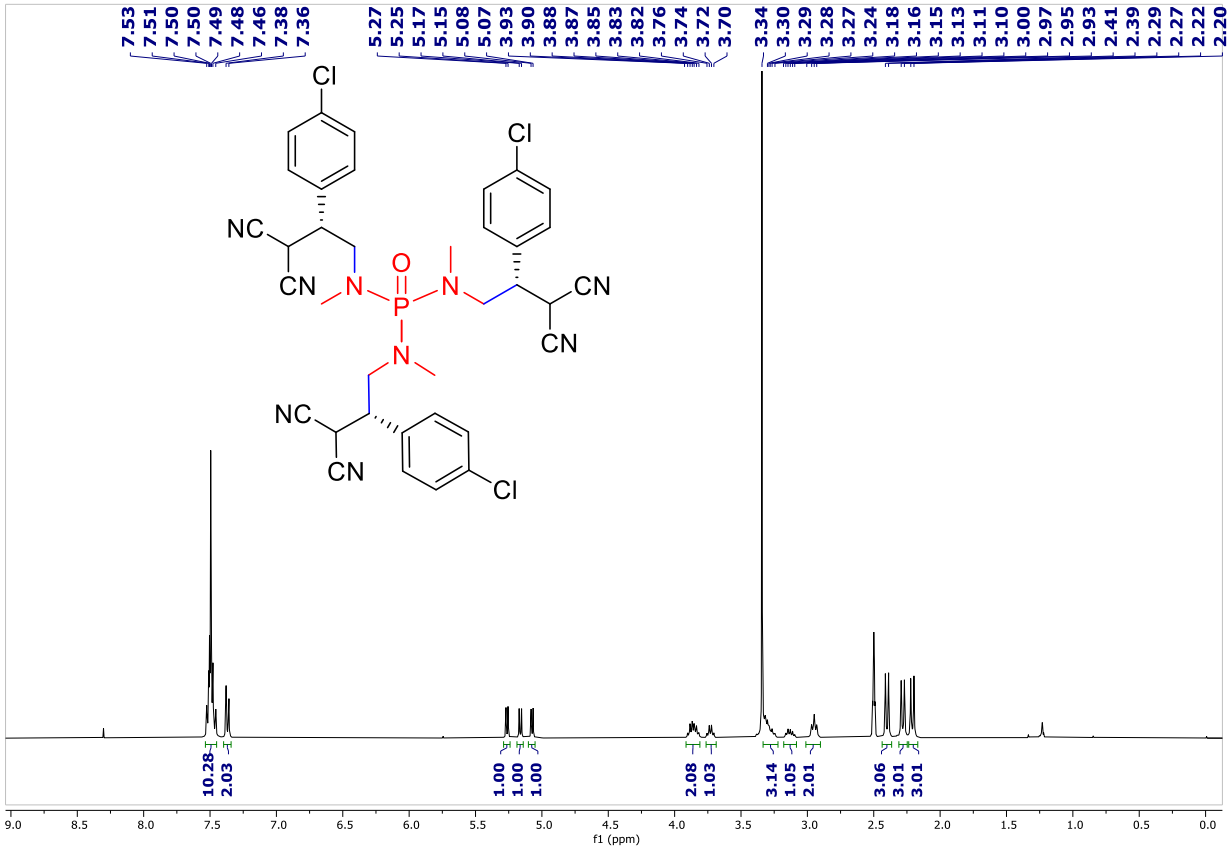
$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) of compound minor (±)-**6b"**



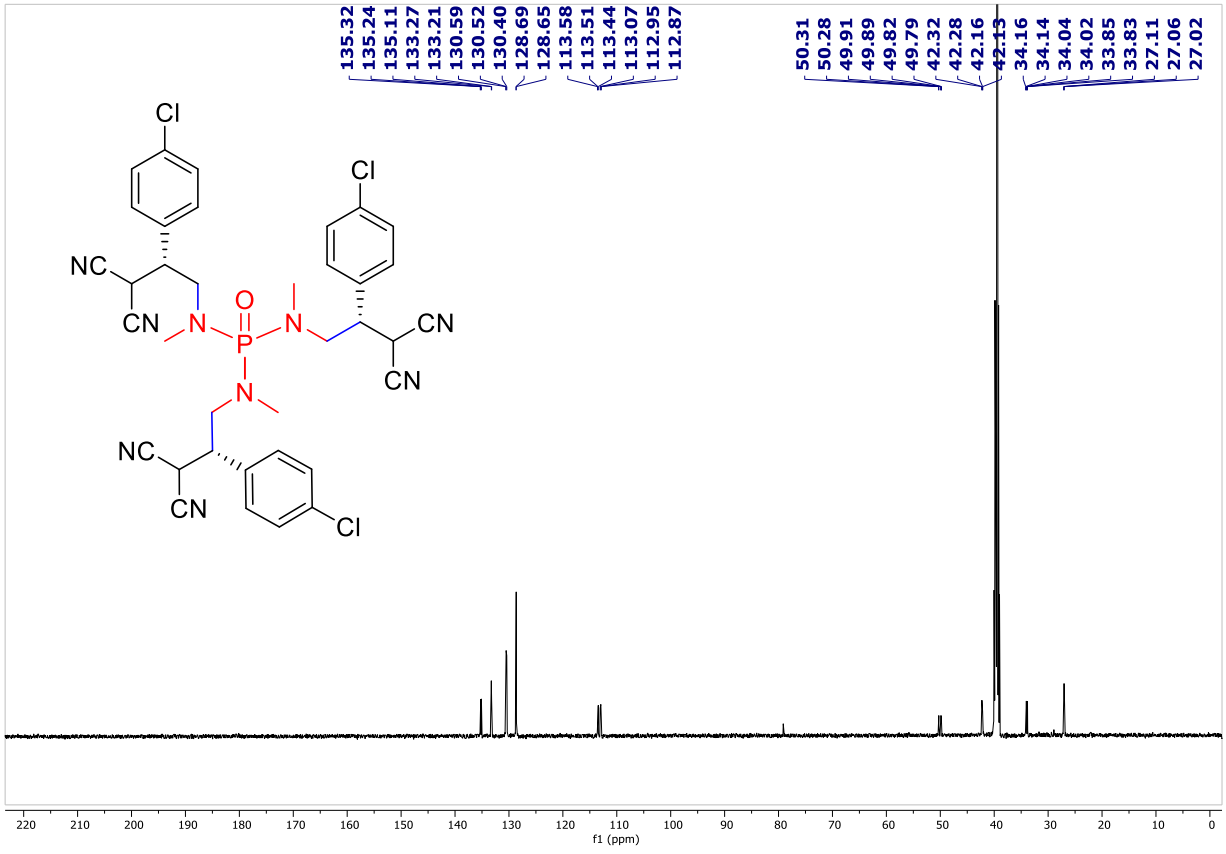
^{31}P NMR (203 MHz, DMSO-d_6) of compound minor (±)-**6b"**



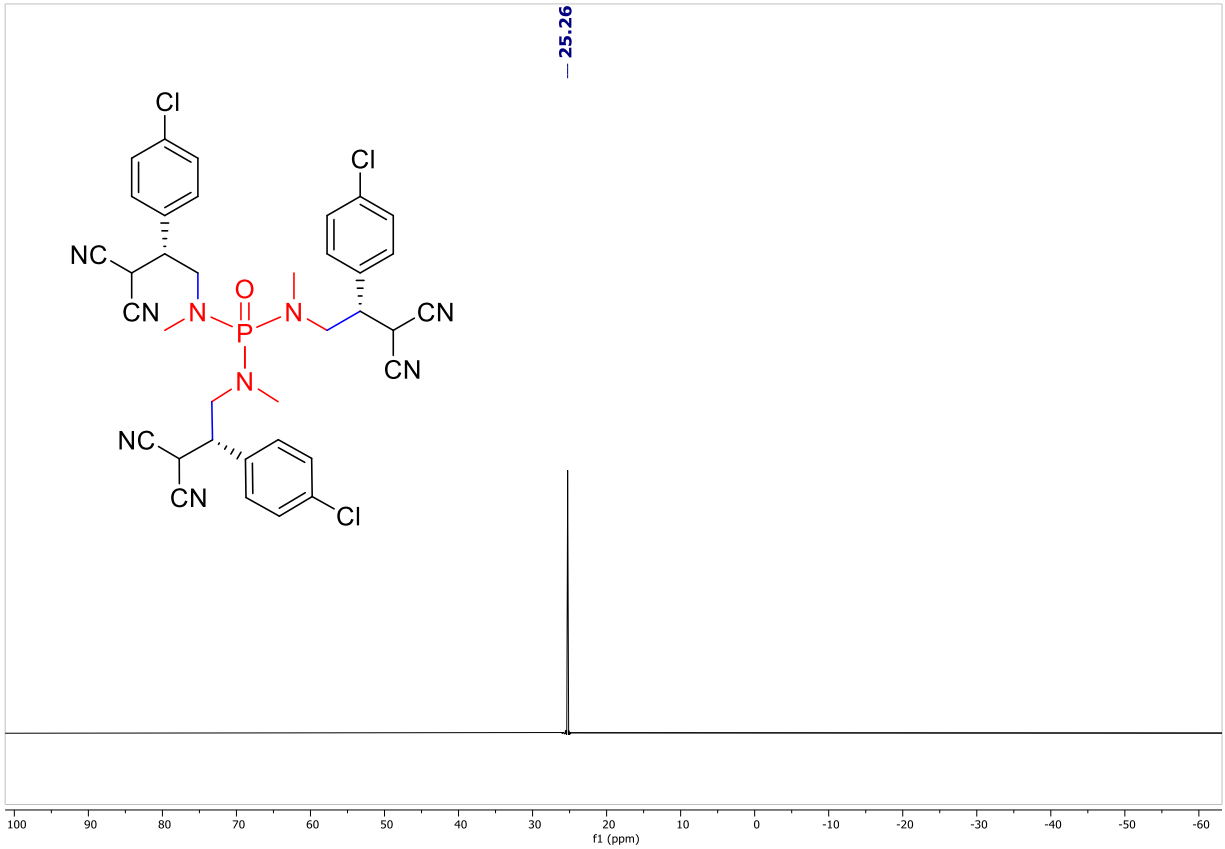
^{1}H NMR (400 MHz, DMSO-d_6) of compound major (±)-**6c'**



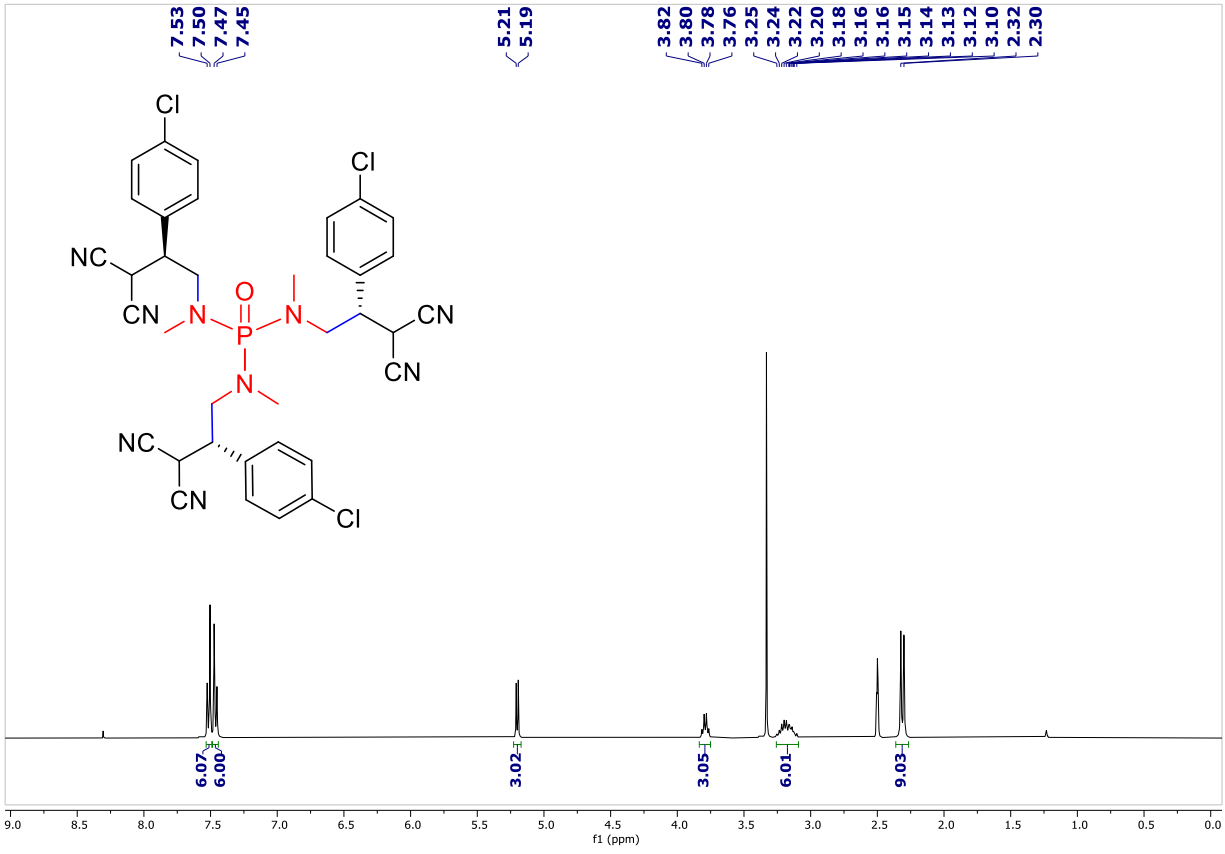
^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) of compound major (±)-**6c'**



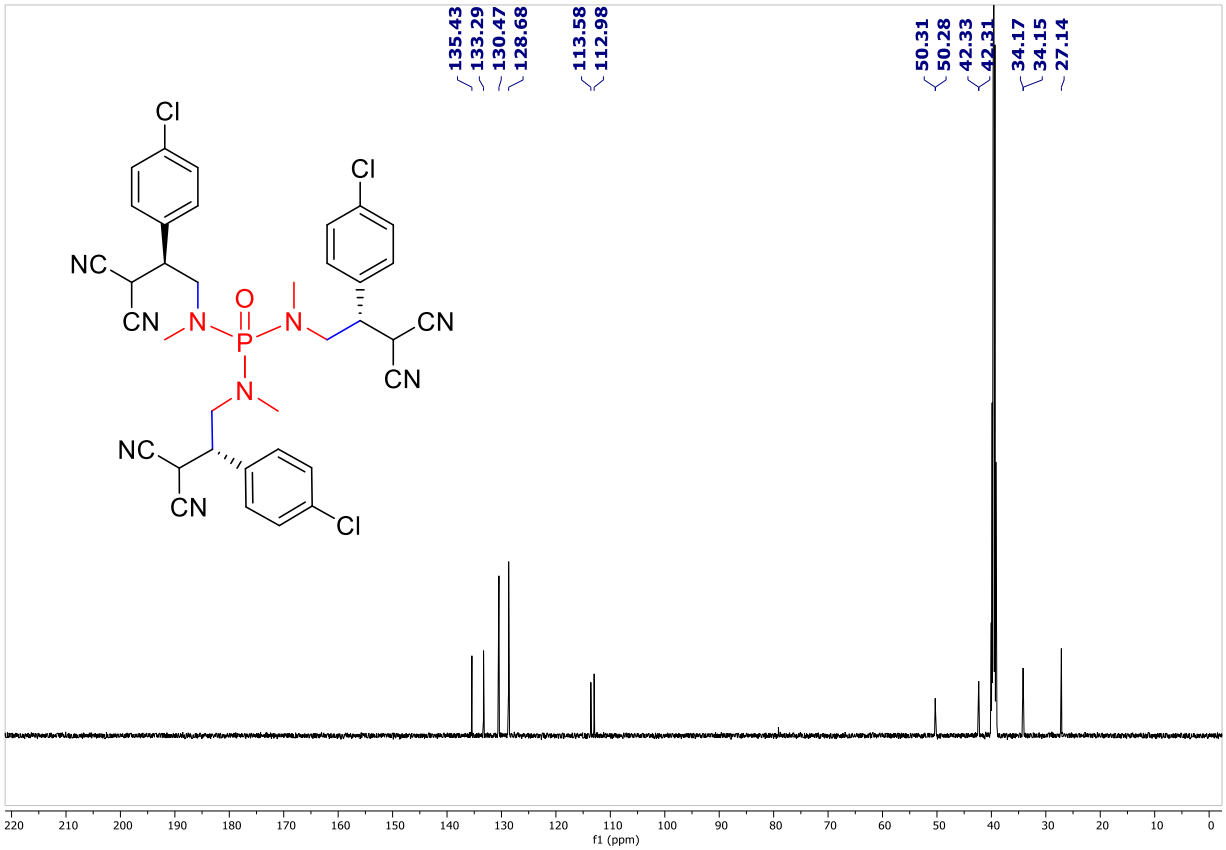
^{31}P NMR (203 MHz, DMSO-d_6) of compound major (±)-**6c'**



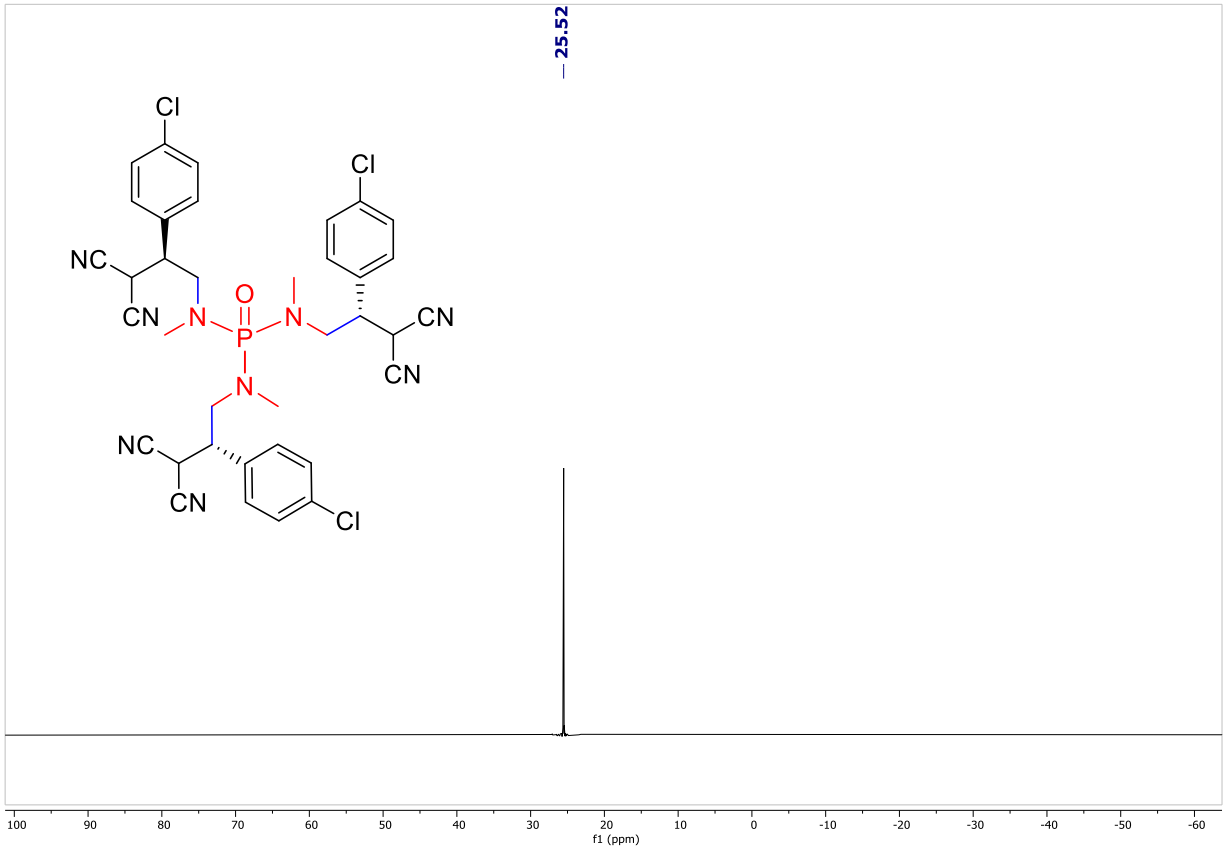
^{1}H NMR (400 MHz, DMSO-d_6) of compound minor (±)-**6c''**



$^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) of compound minor (±)-**6c''**



^{31}P NMR (203 MHz, DMSO-d_6) of compound minor (±)-**6c''**



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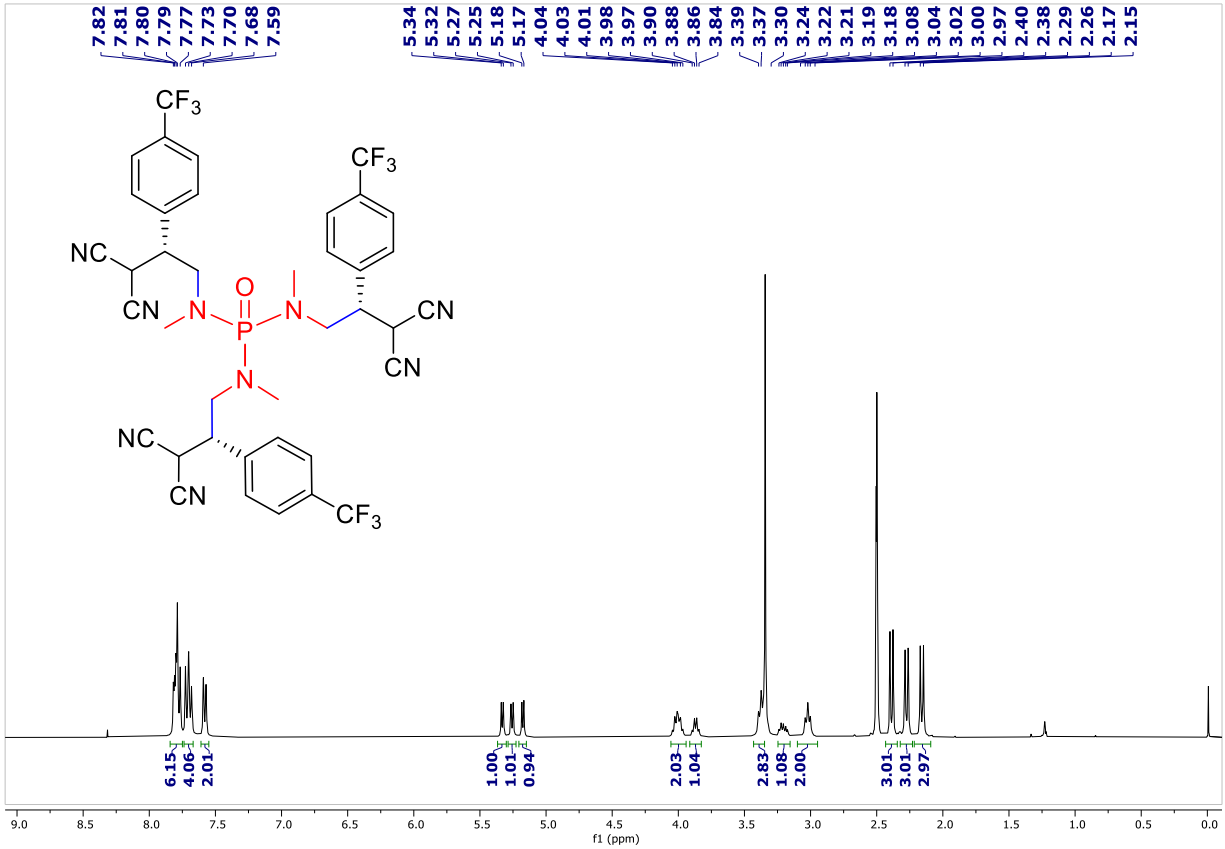
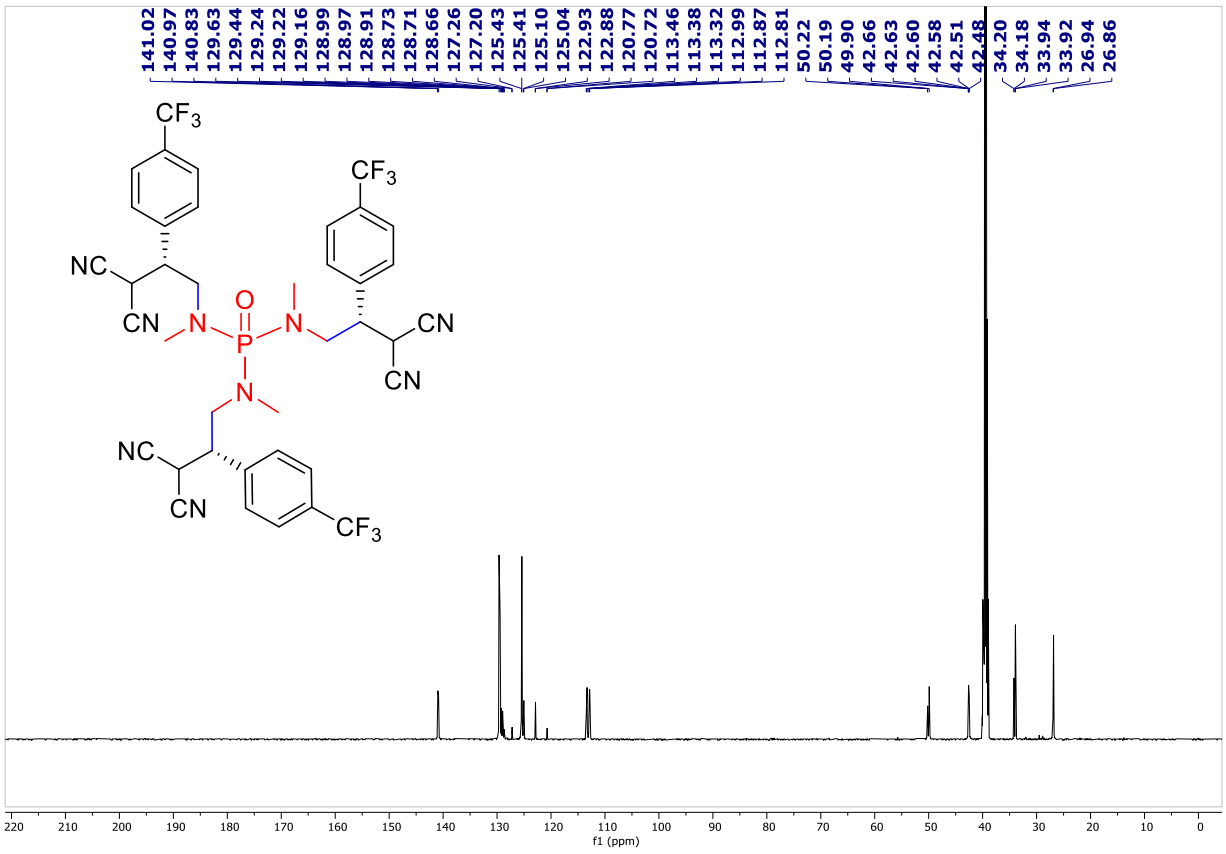
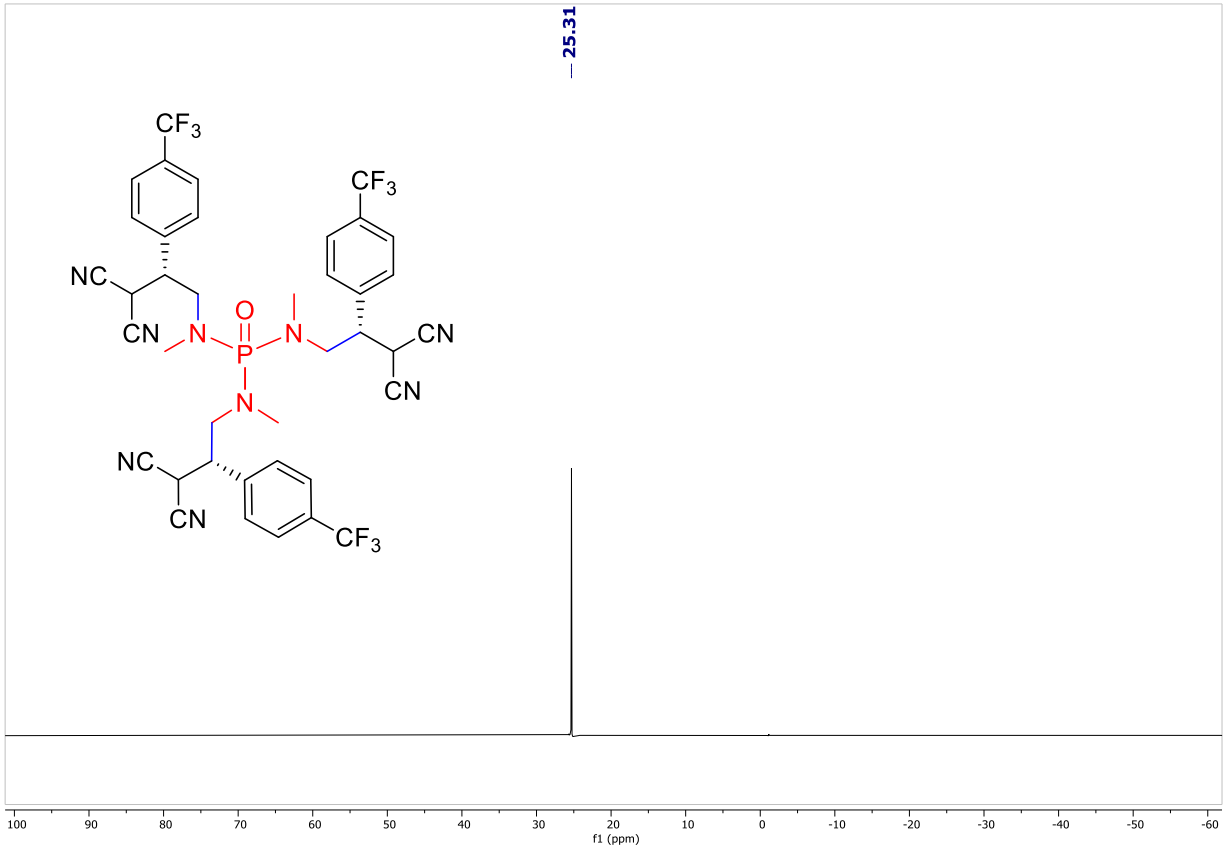


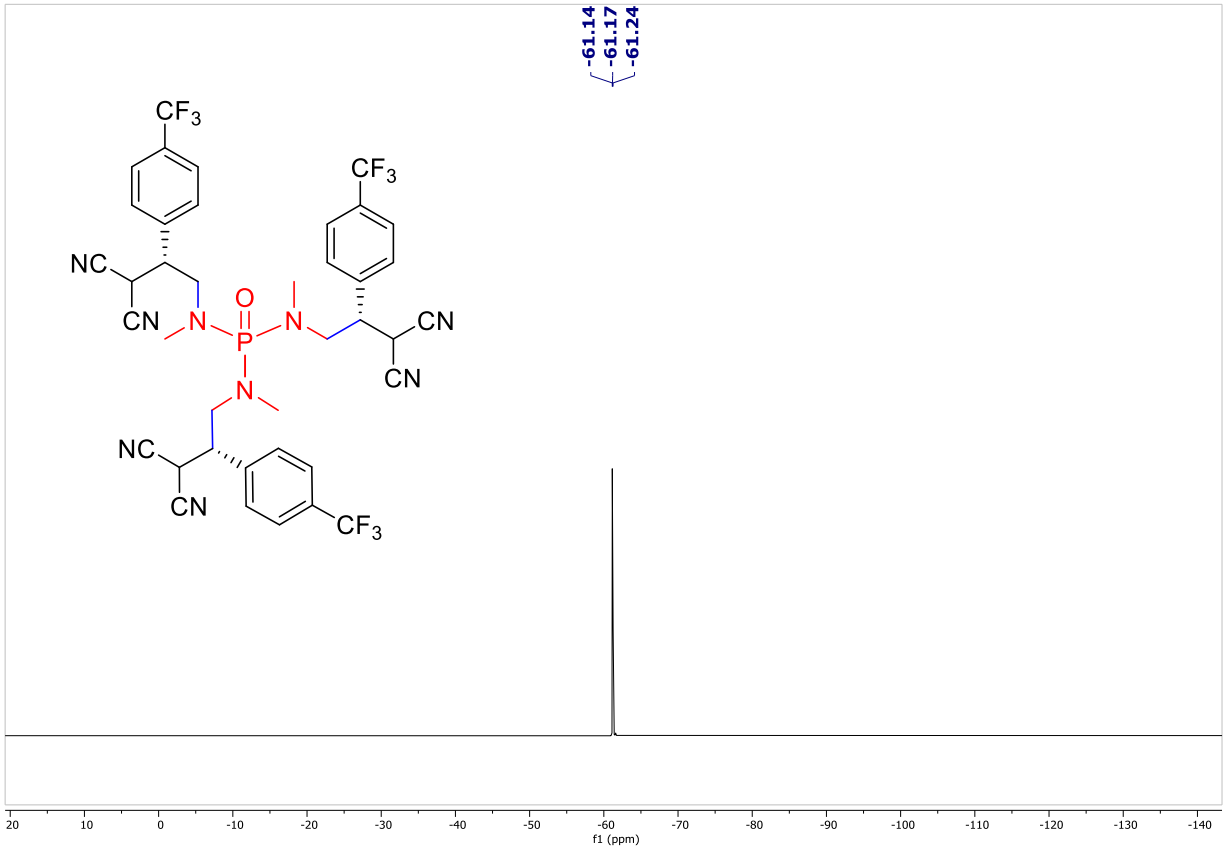
^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) of compound major (±)-**6d'**



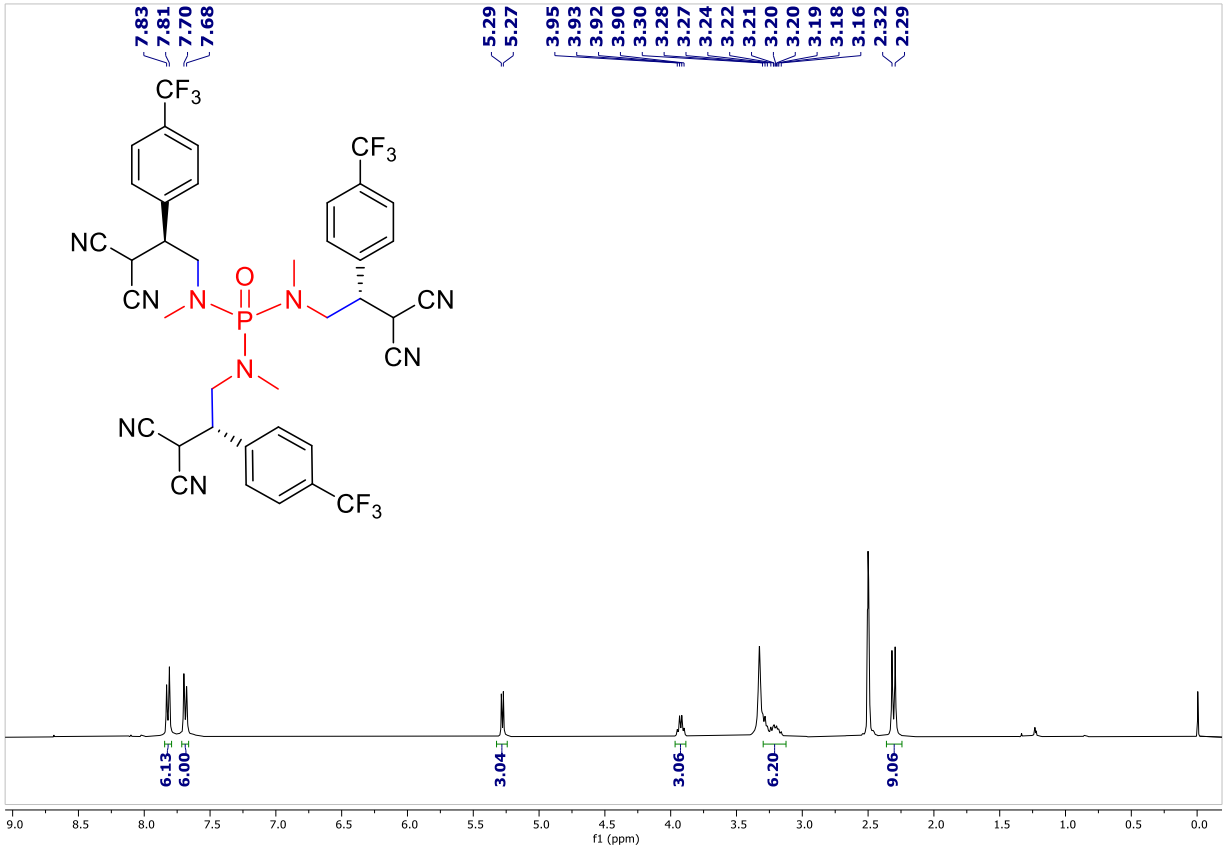
^{31}P NMR (203 MHz, DMSO-d_6) of compound major (±)-**6d'**



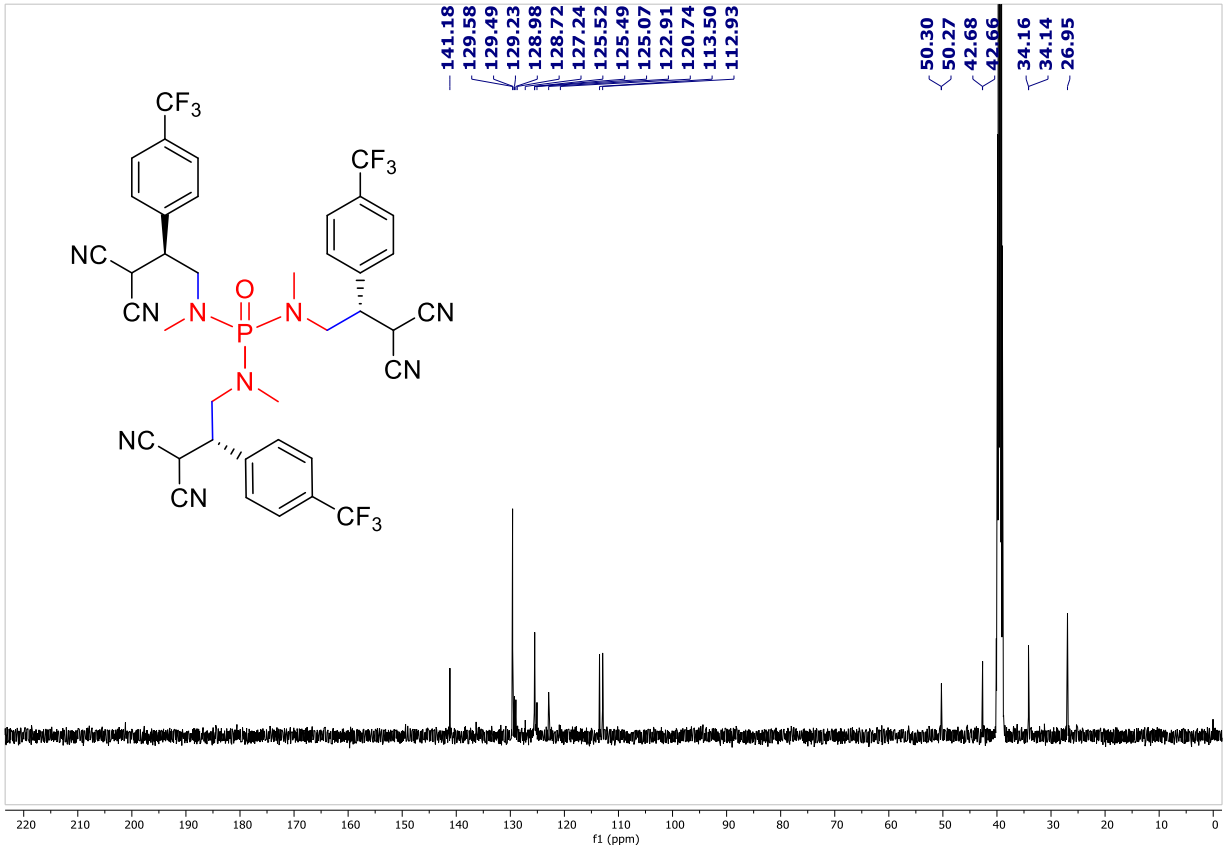
^{19}F NMR (471 MHz, DMSO-d_6) of compound major (±)-**6d'**



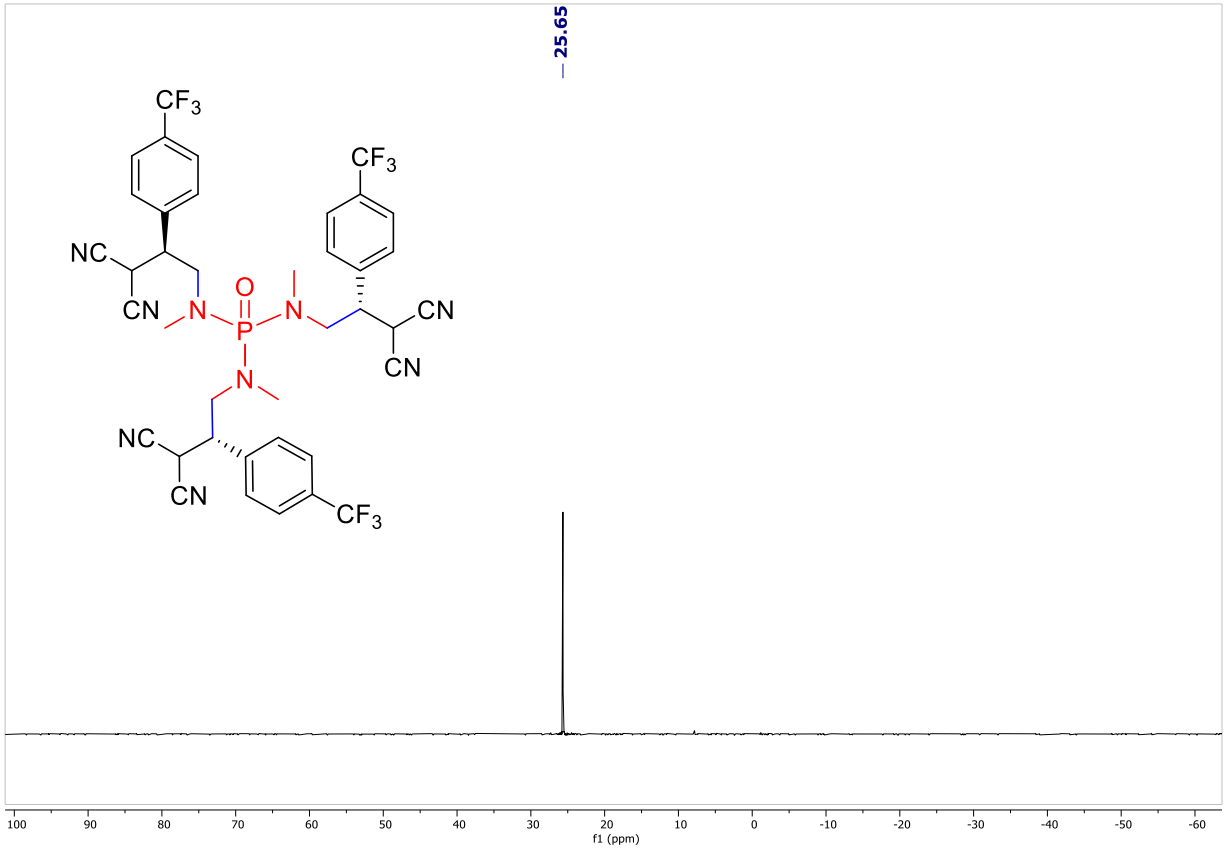
^{1}H NMR (400 MHz, DMSO-d_6) of compound minor (±)-**6d"**



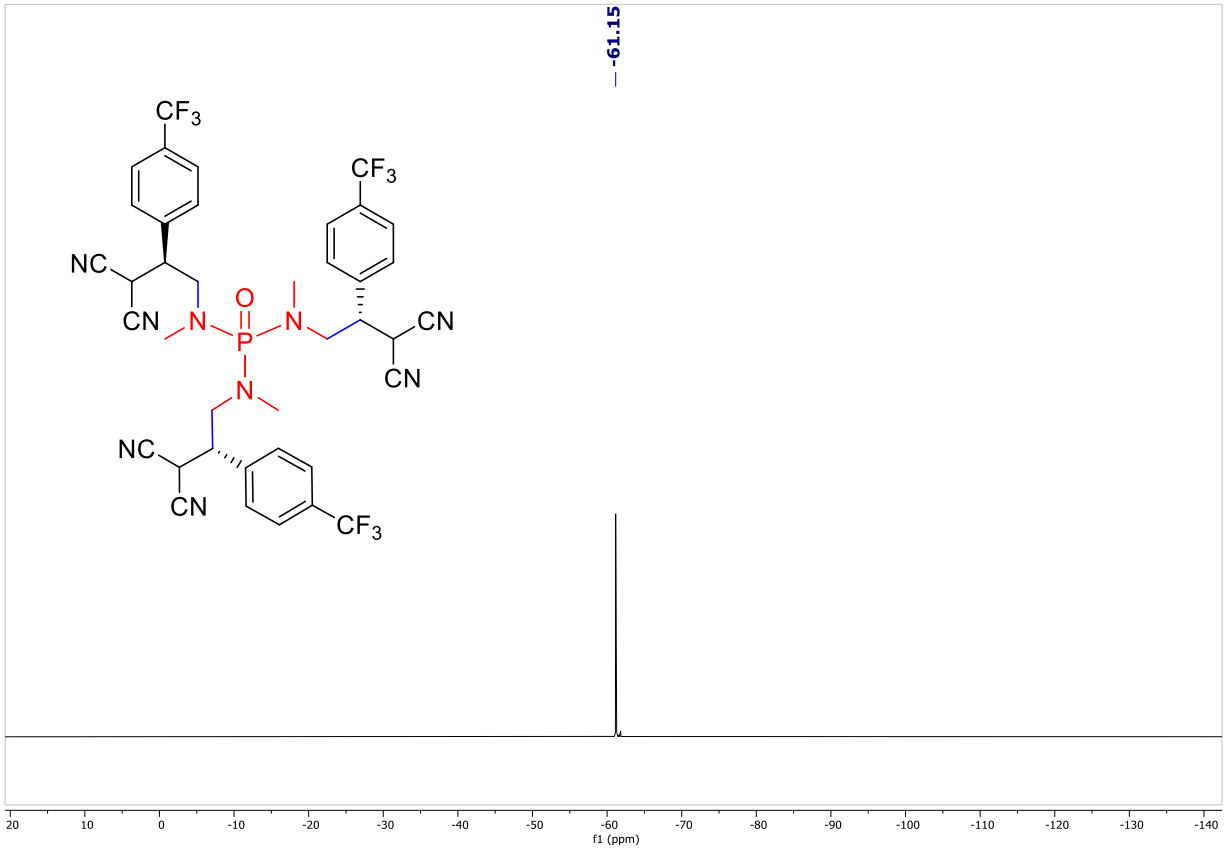
^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) of compound minor (±)-**6d"**



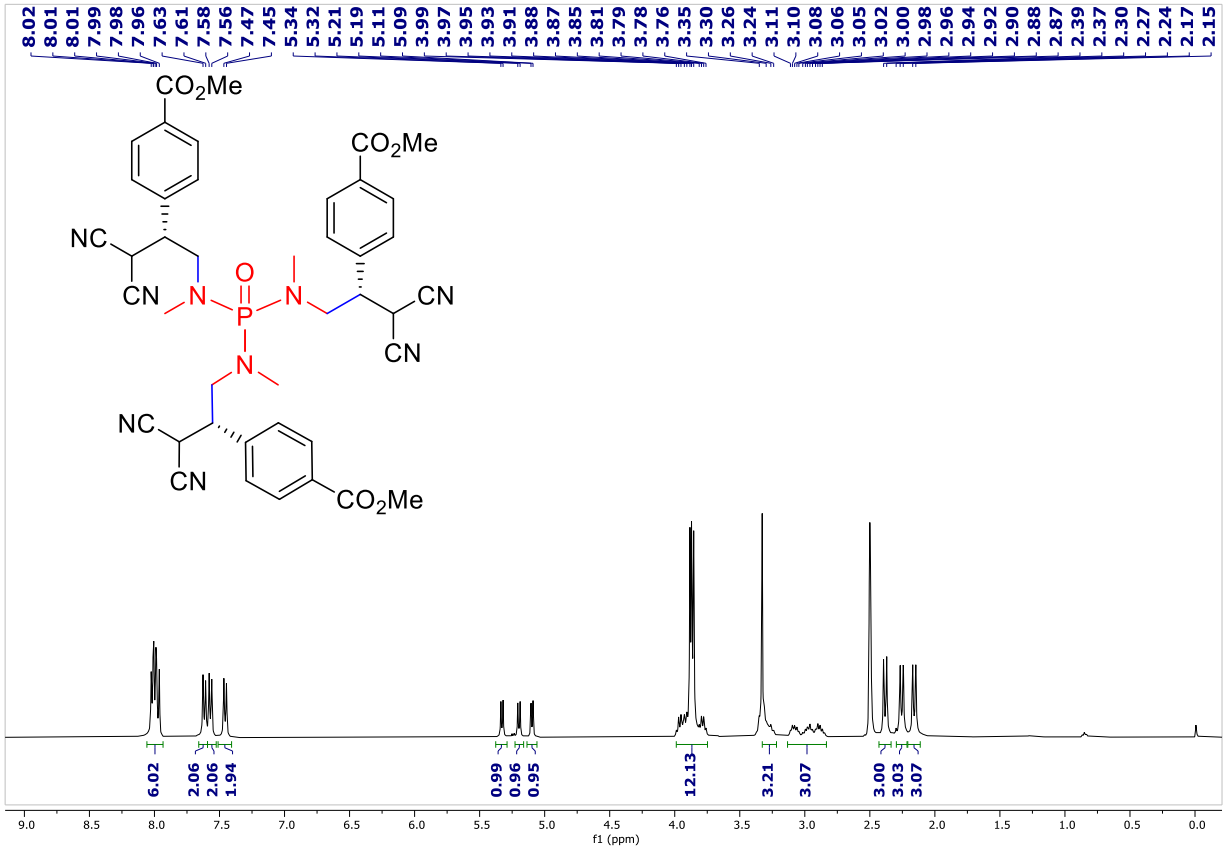
^{31}P NMR (203 MHz, DMSO-d_6) of compound minor (±)-**6d"**



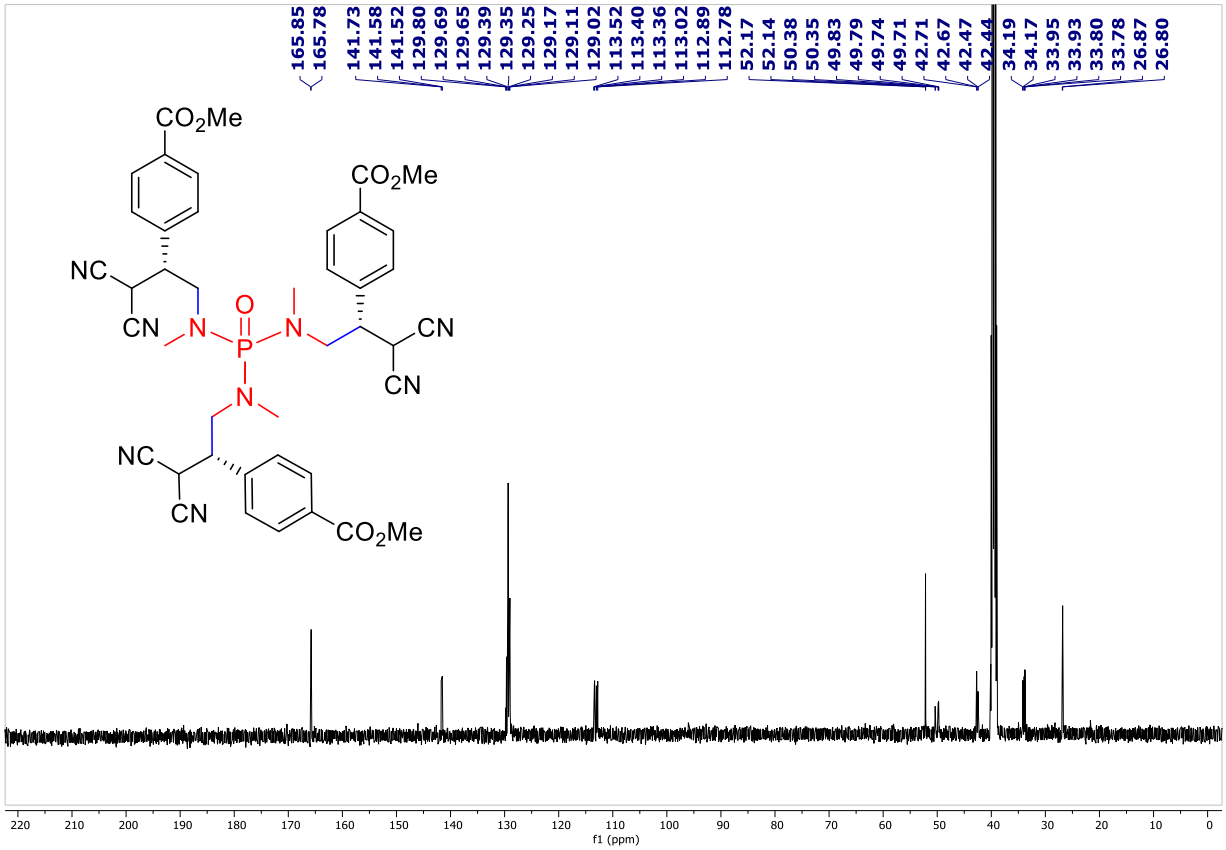
^{19}F NMR (471 MHz, DMSO-d_6) of compound minor (±)-**6d"**



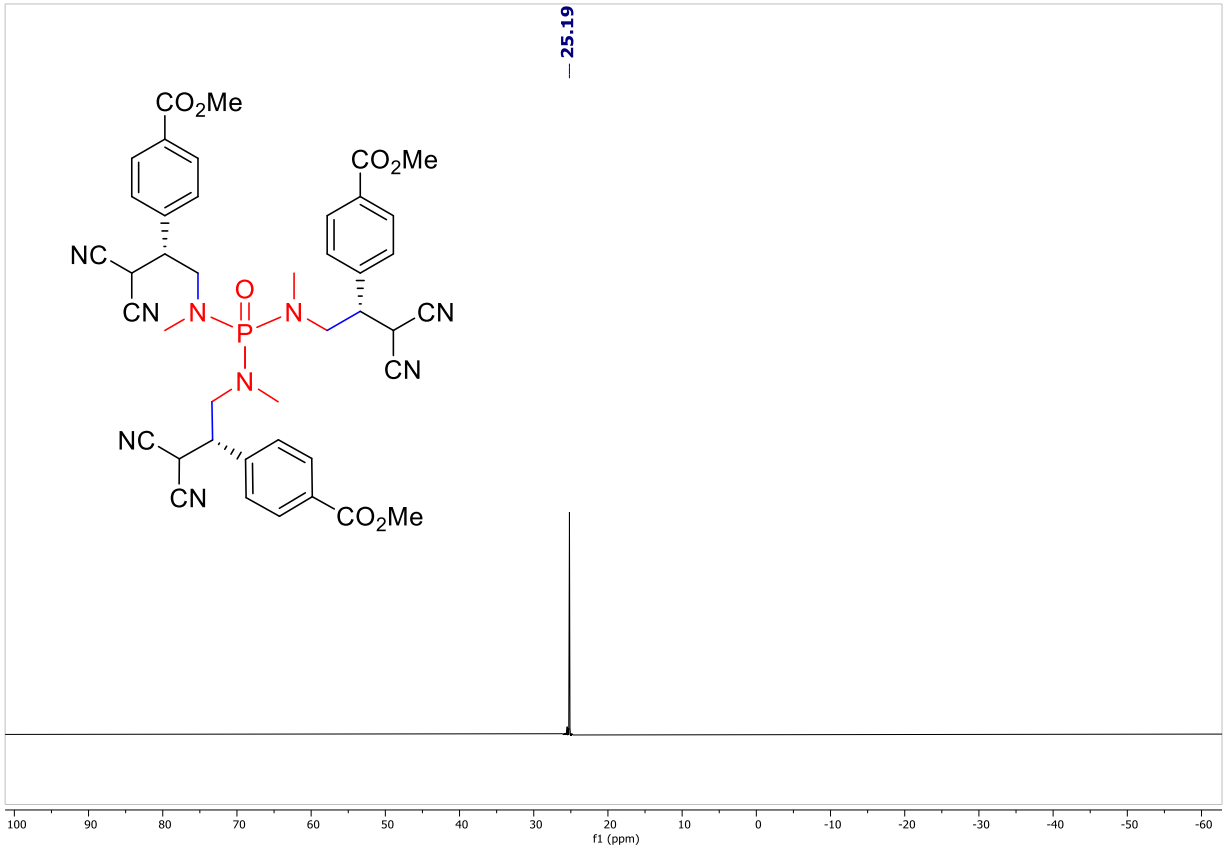
^{1}H NMR (400 MHz, DMSO-d_6) of compound major (±)-**6e'**



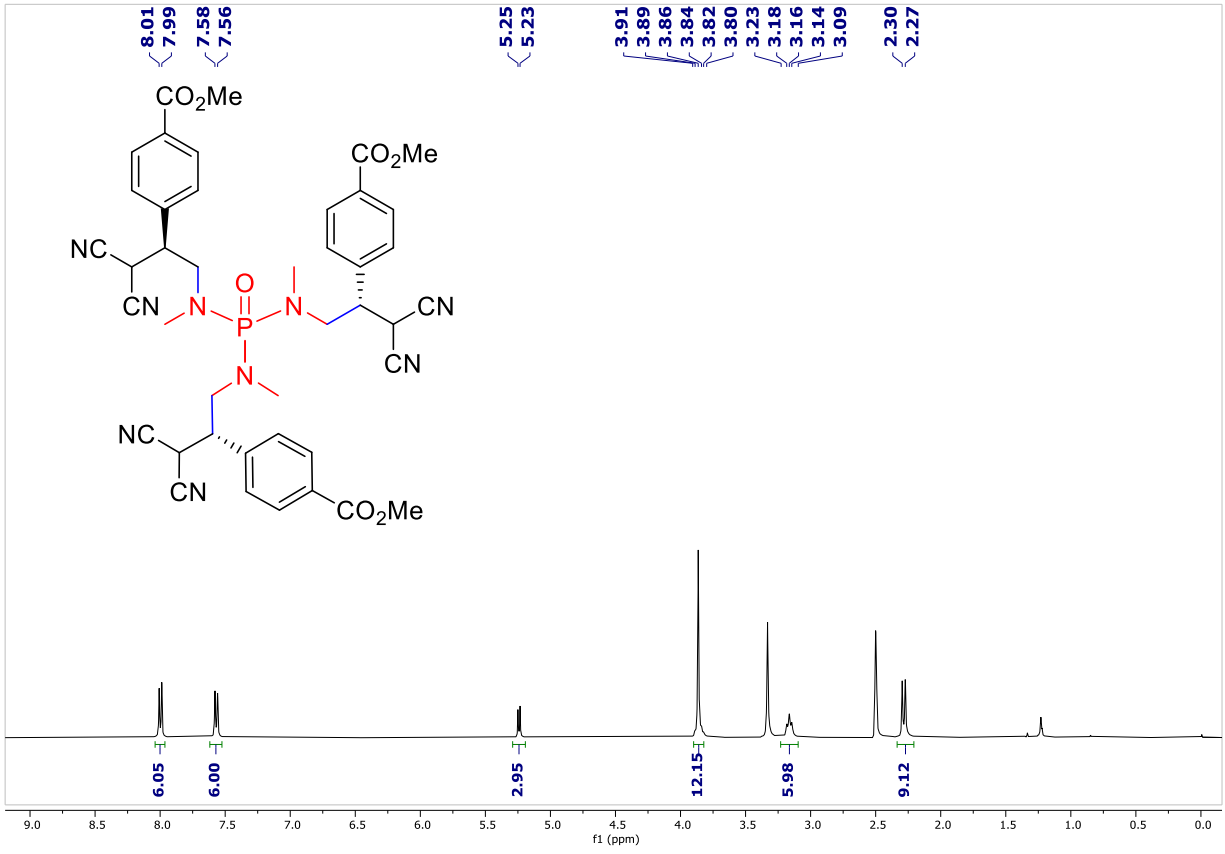
^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) of compound major (±)-**6e'**



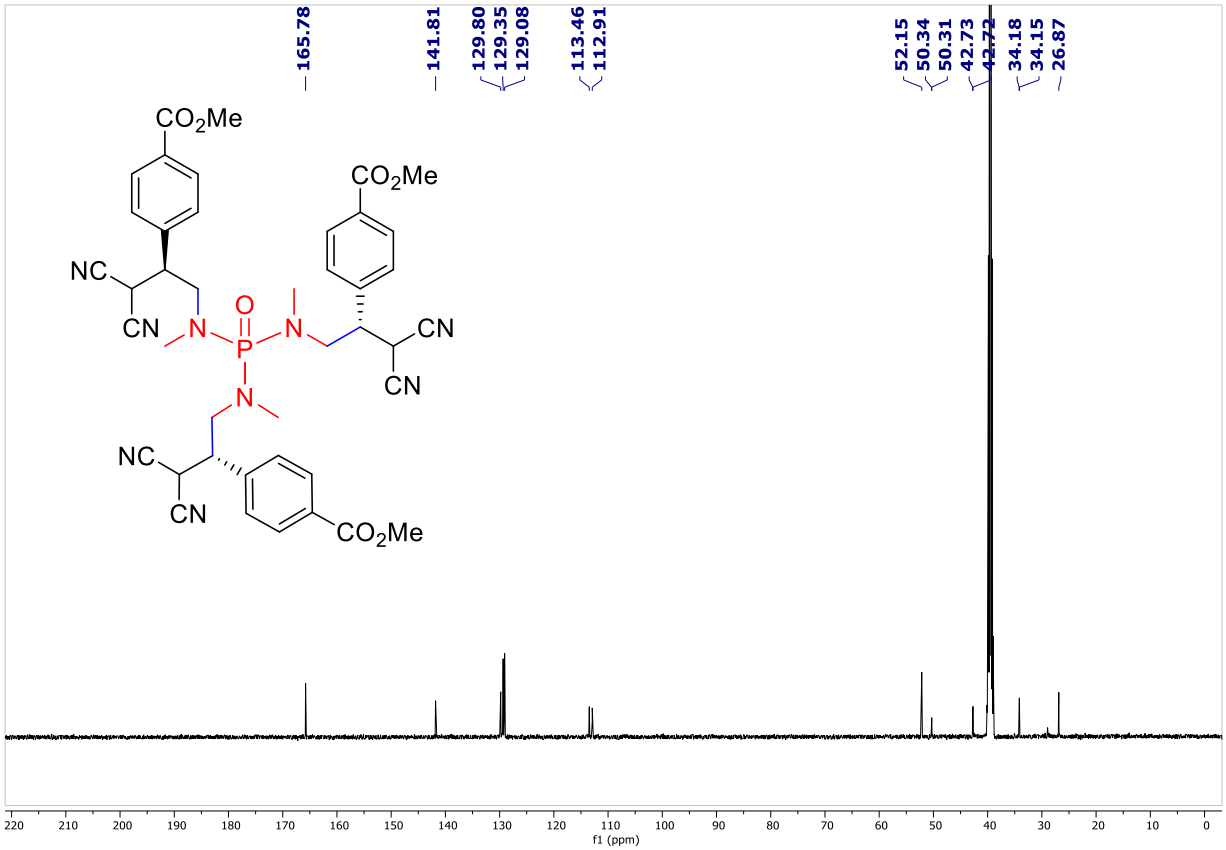
^{31}P NMR (203 MHz, DMSO-d_6) of compound major (±)-**6e'**



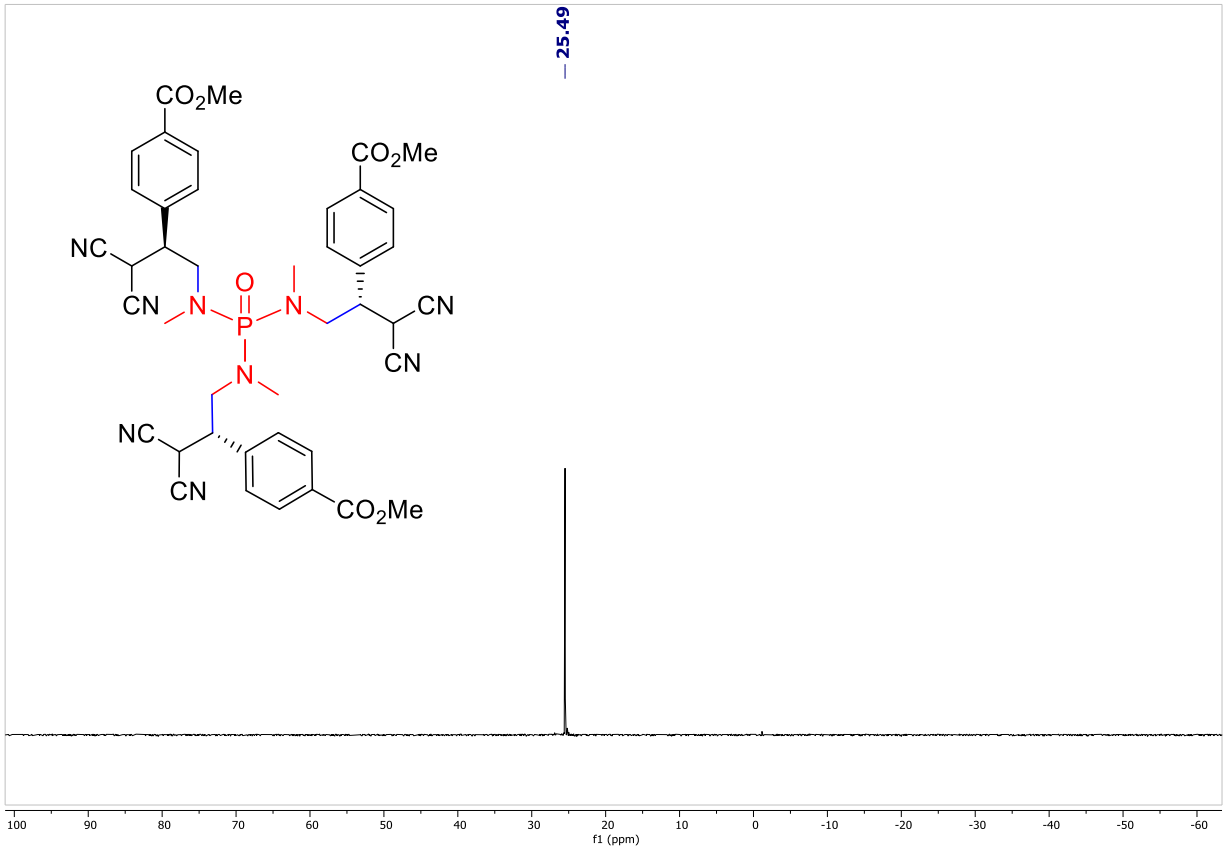
^{1}H NMR (400 MHz, DMSO-d_6) of compound minor (±)-**6e''**



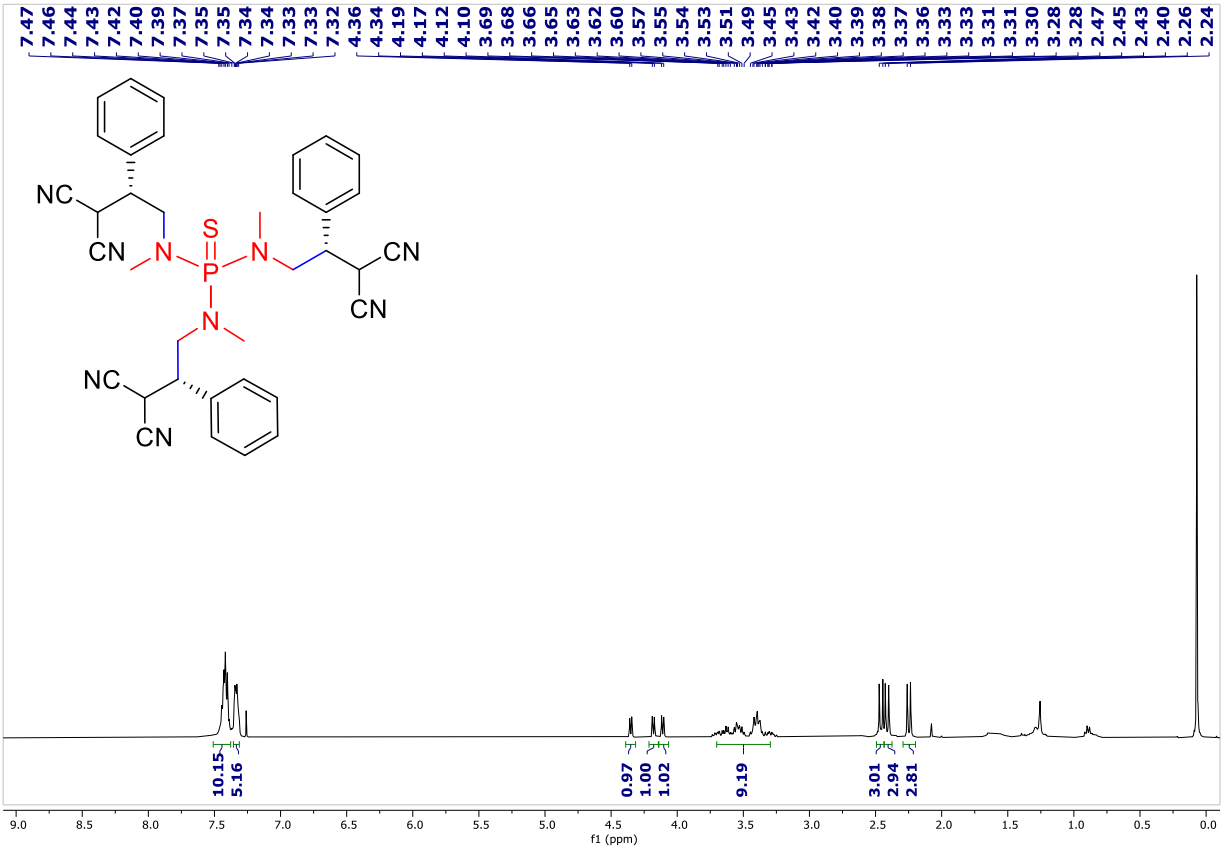
$^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) of compound minor (±)-**6e''**



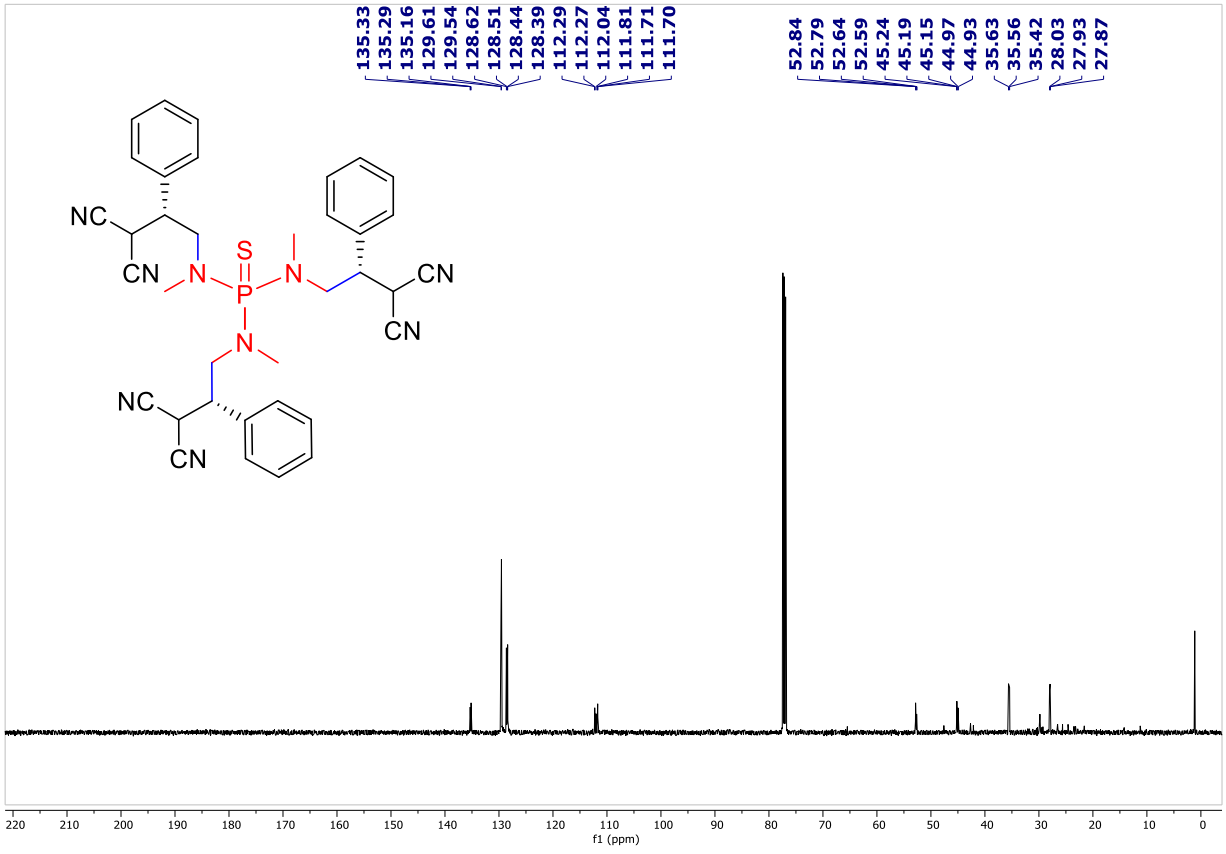
^{31}P NMR (203 MHz, DMSO-d_6) of compound minor (±)-**6e''**



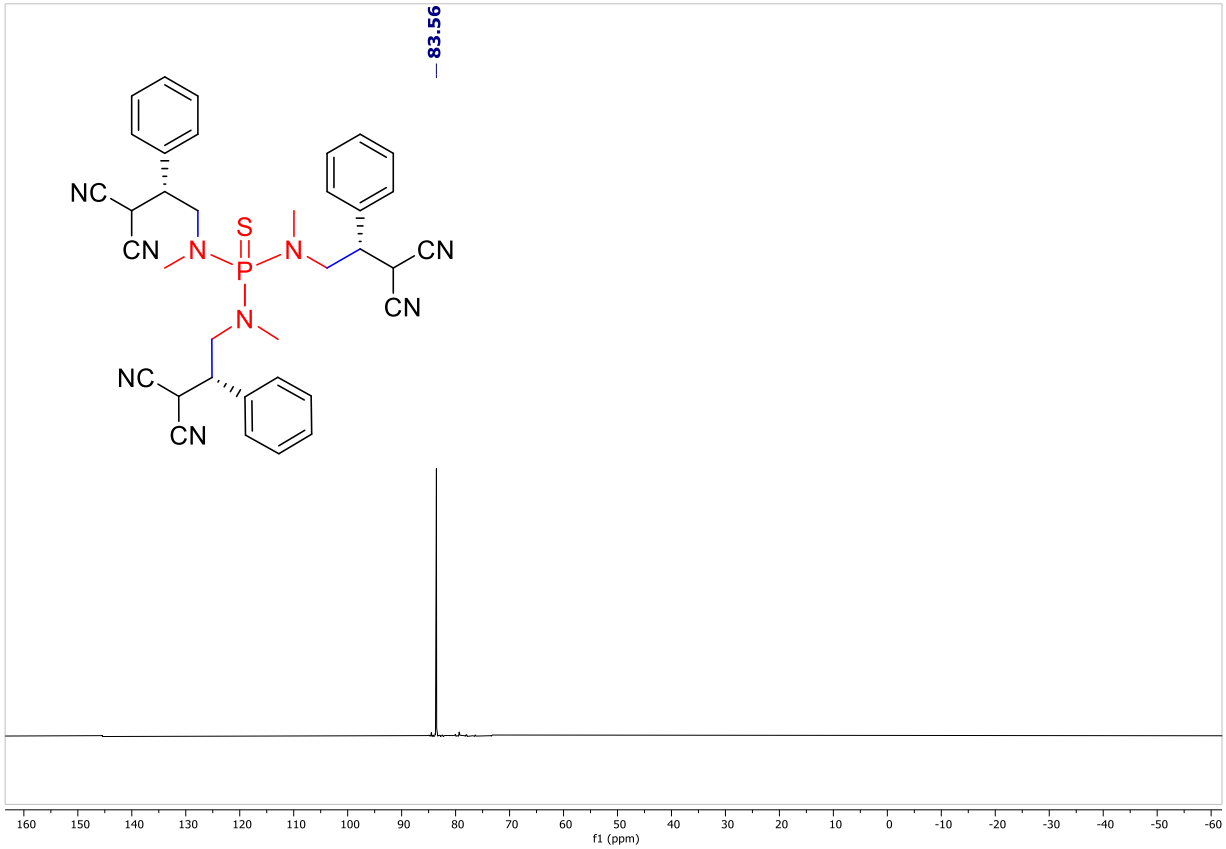
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6f**



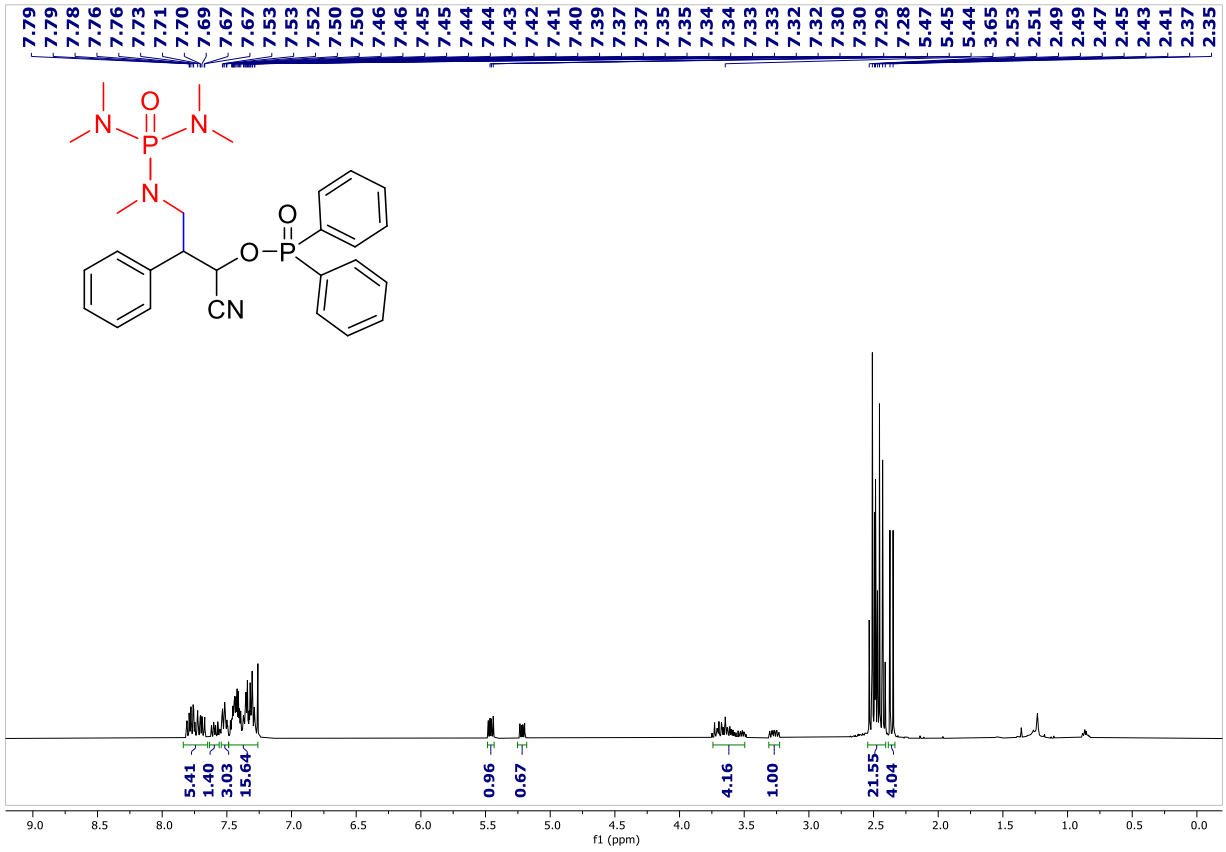
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound (±)-**6f**



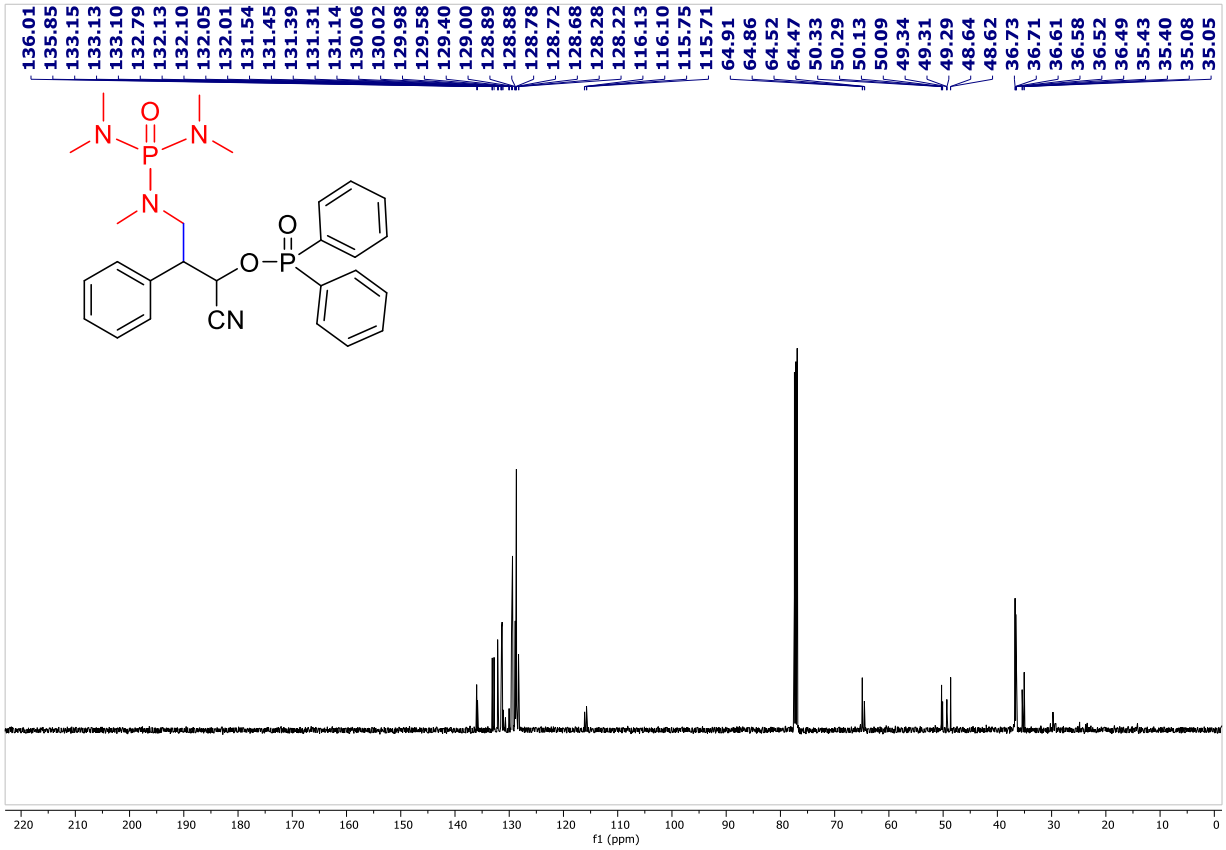
^{31}P NMR (203 MHz, $CDCl_3$) of compound (±)-**6f**



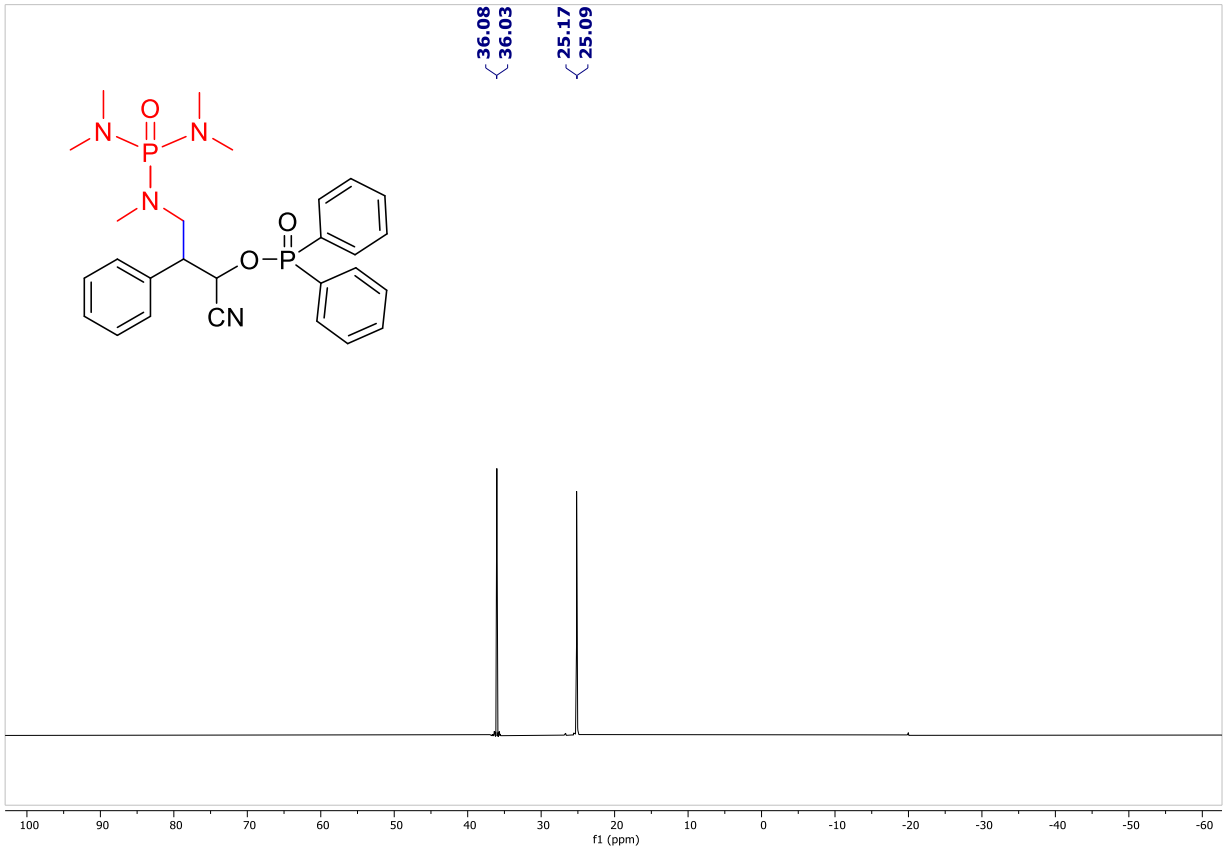
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**



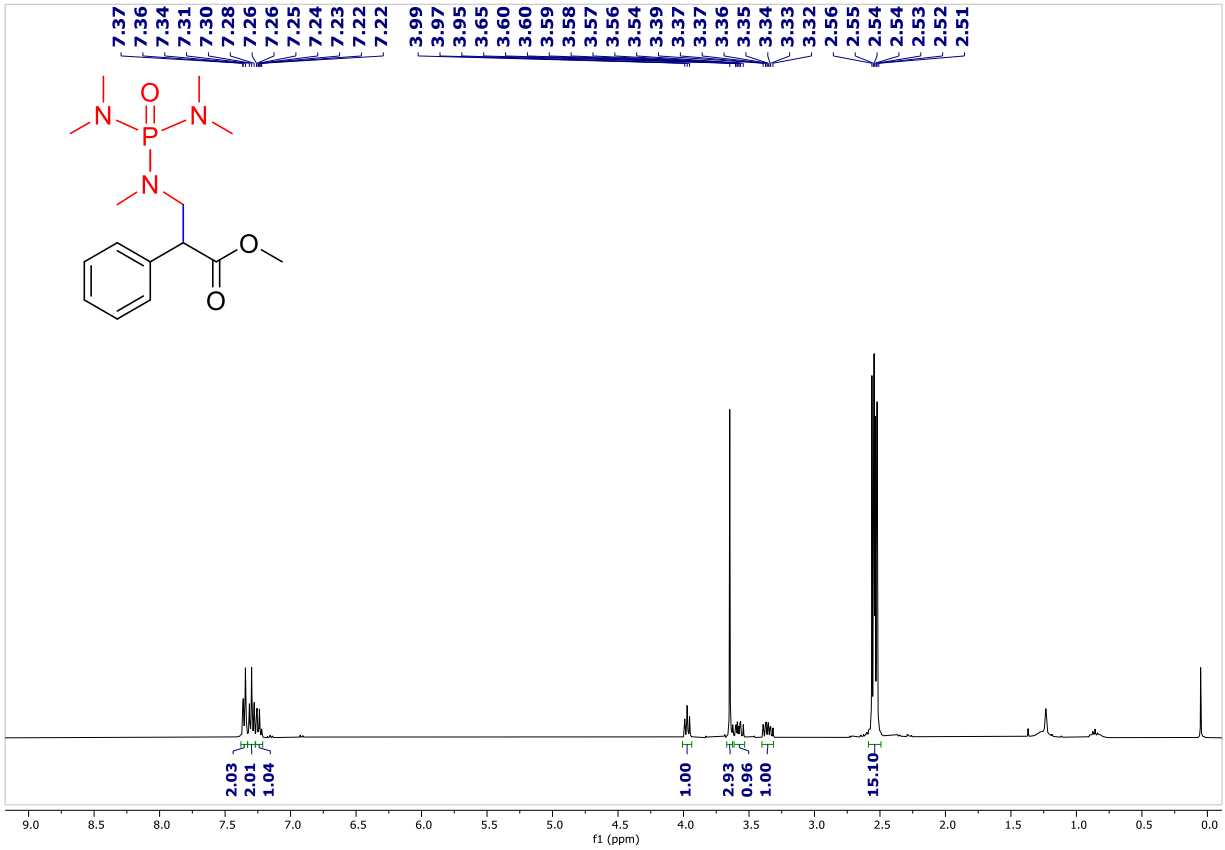
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **7**



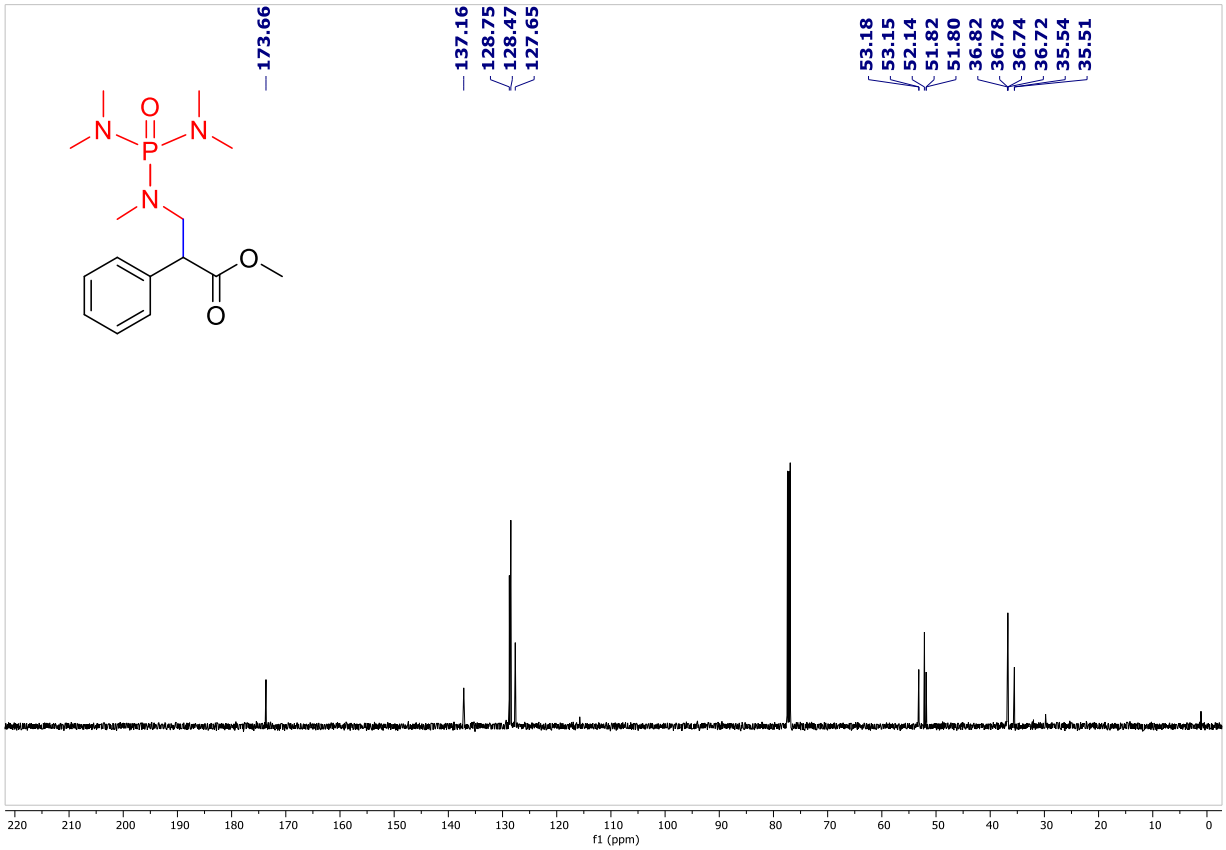
^{31}P NMR (203 MHz, $CDCl_3$) of compound **7**



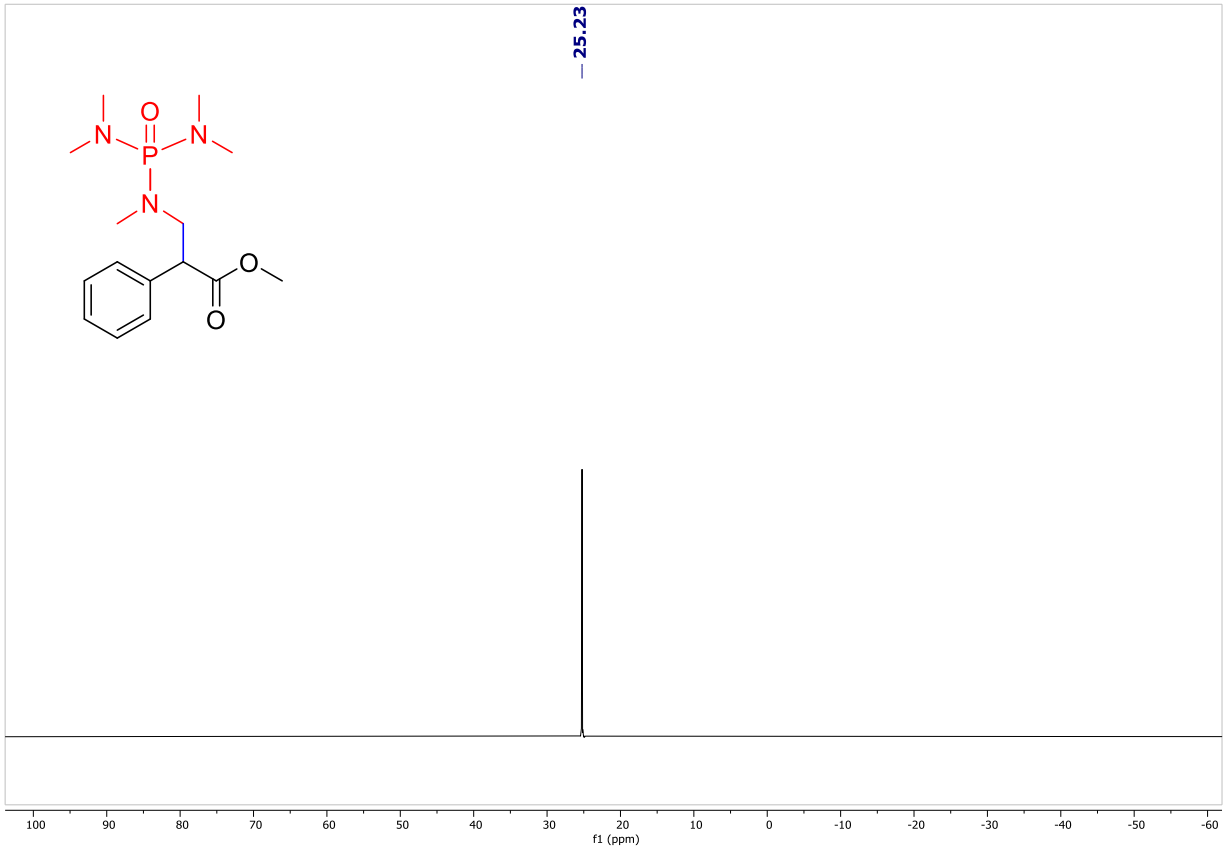
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8**



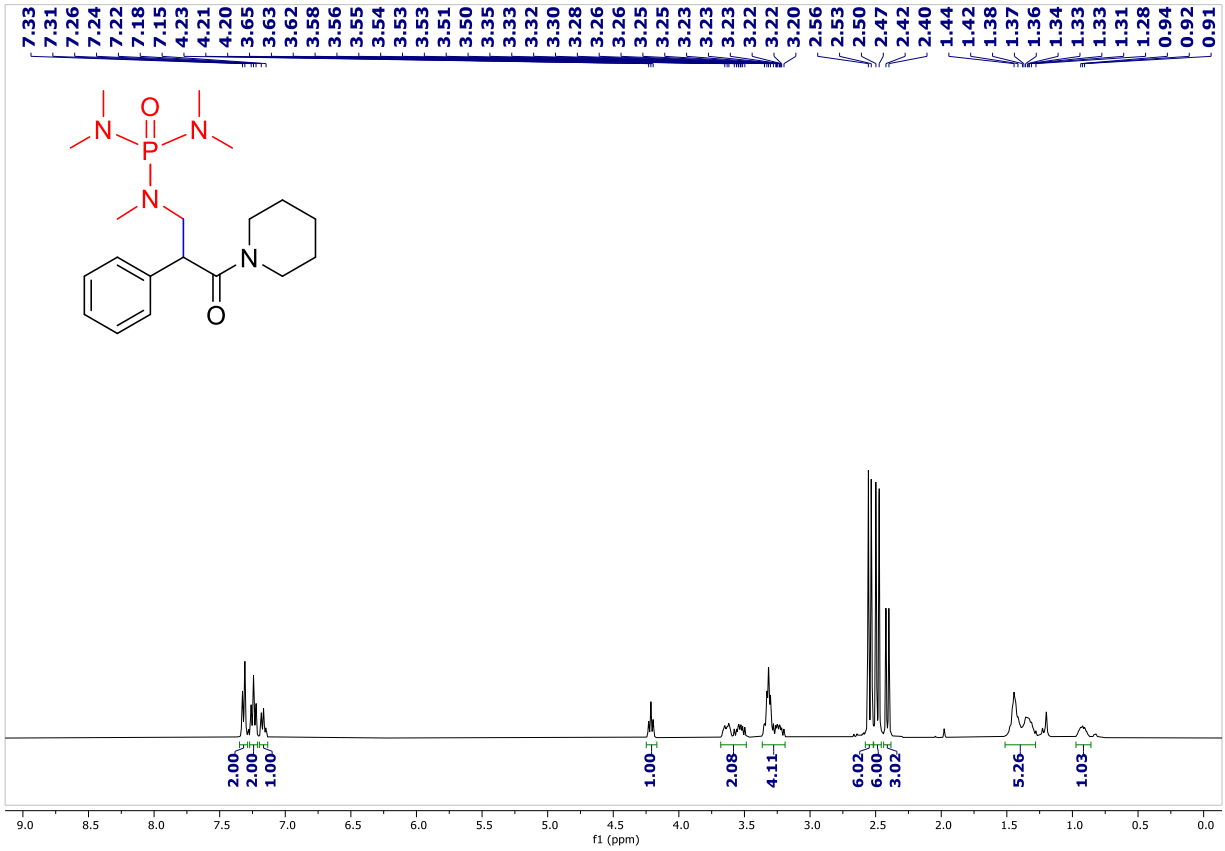
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **8**



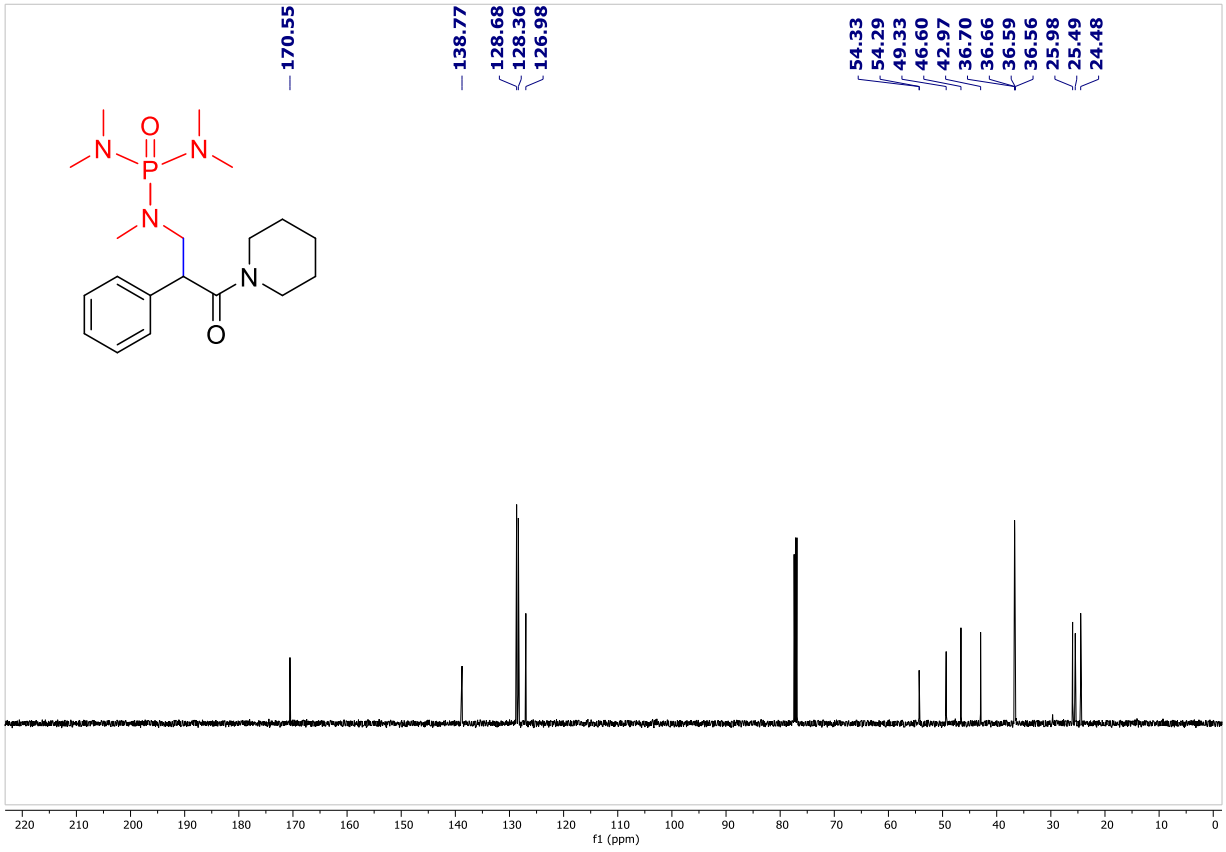
^{31}P NMR (203 MHz, $CDCl_3$) of compound **8**



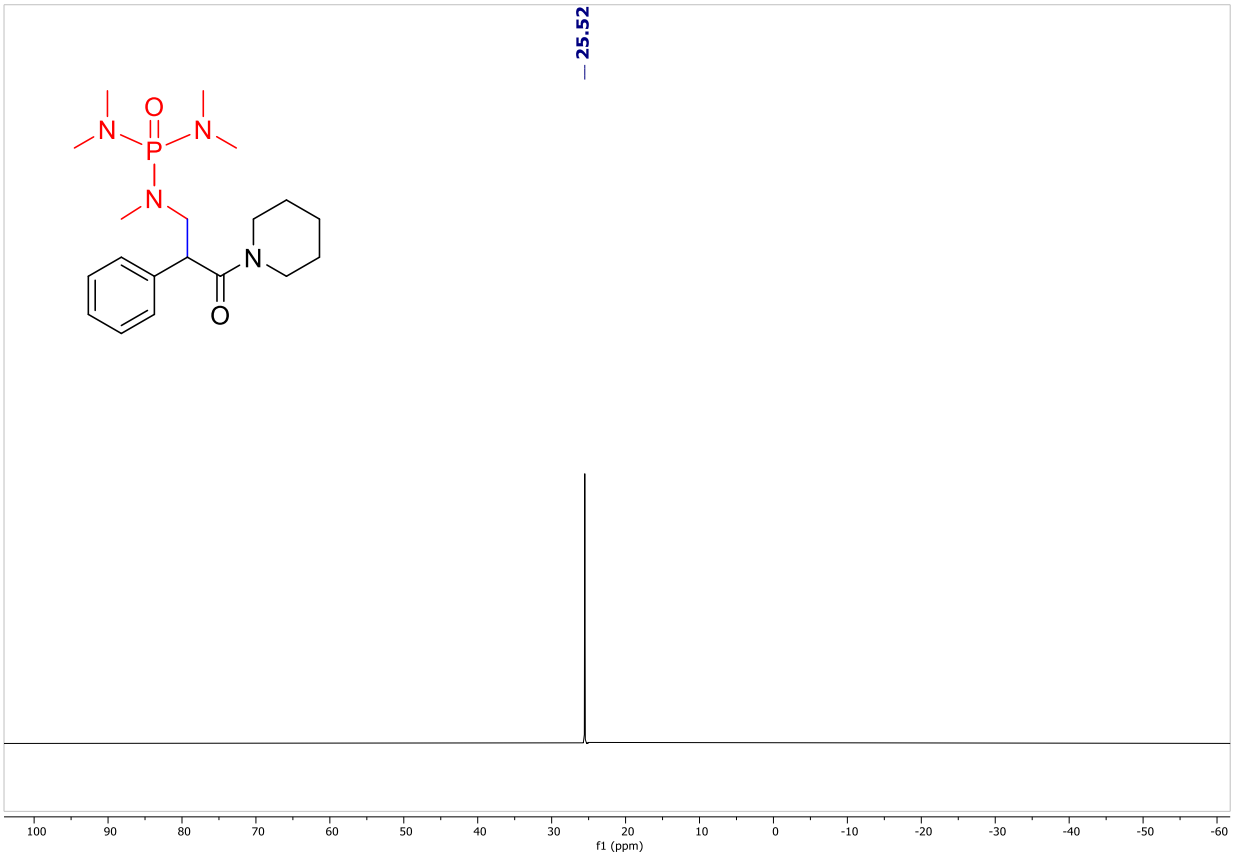
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**



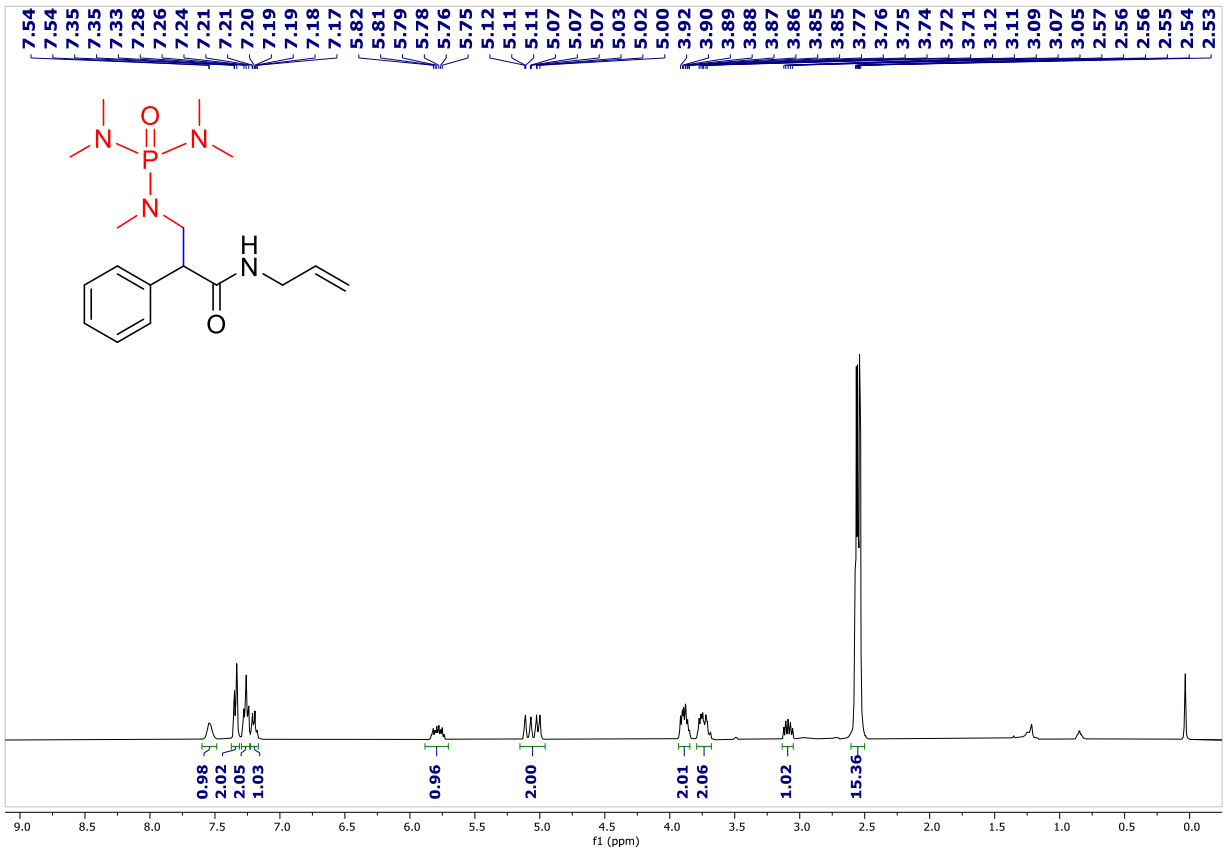
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **9**



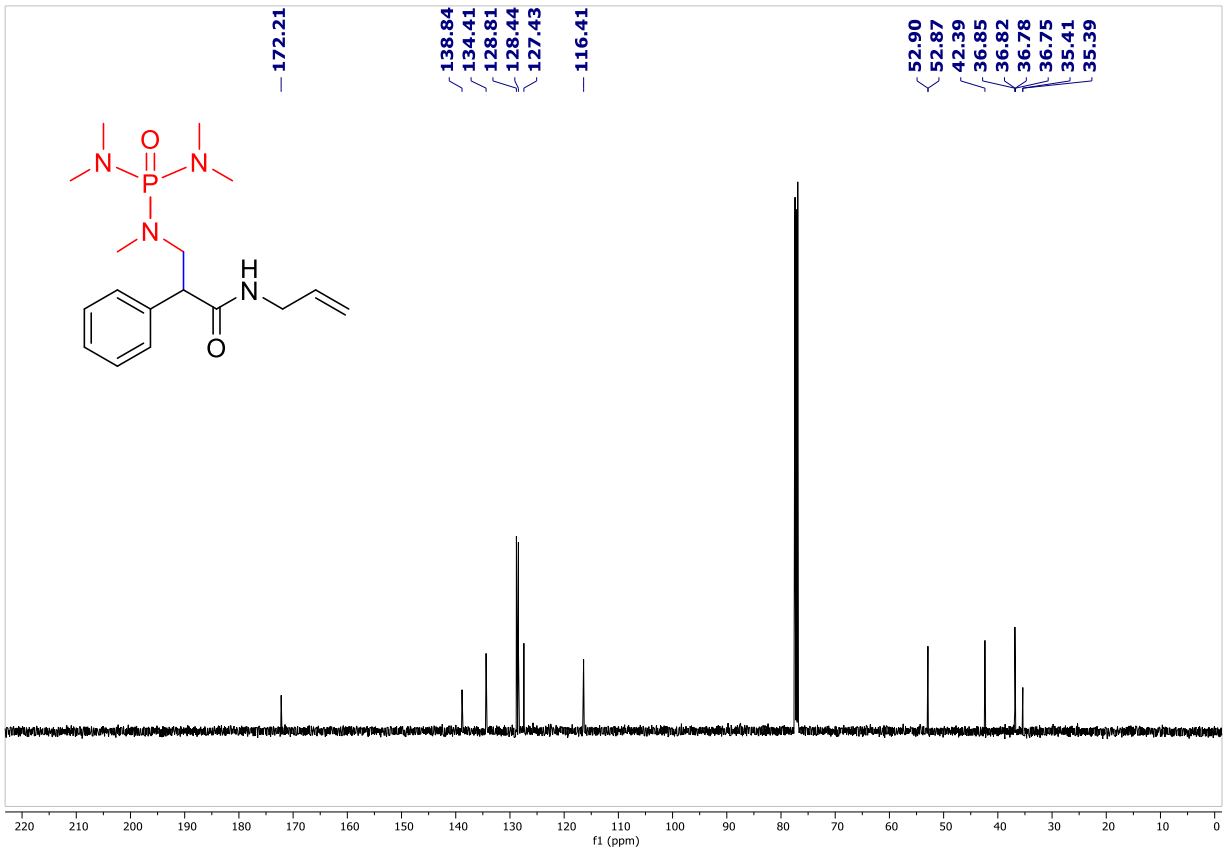
^{31}P NMR (203 MHz, $CDCl_3$) of compound **9**



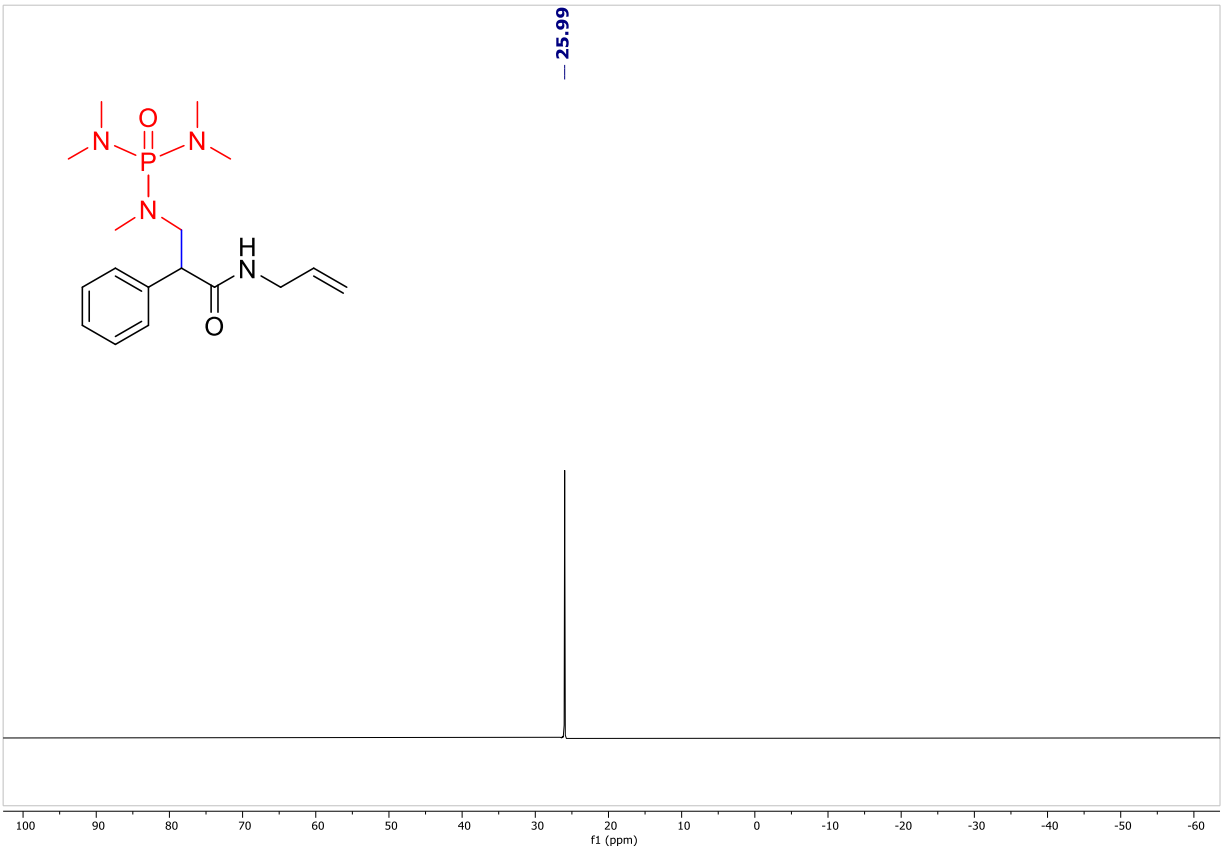
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10**



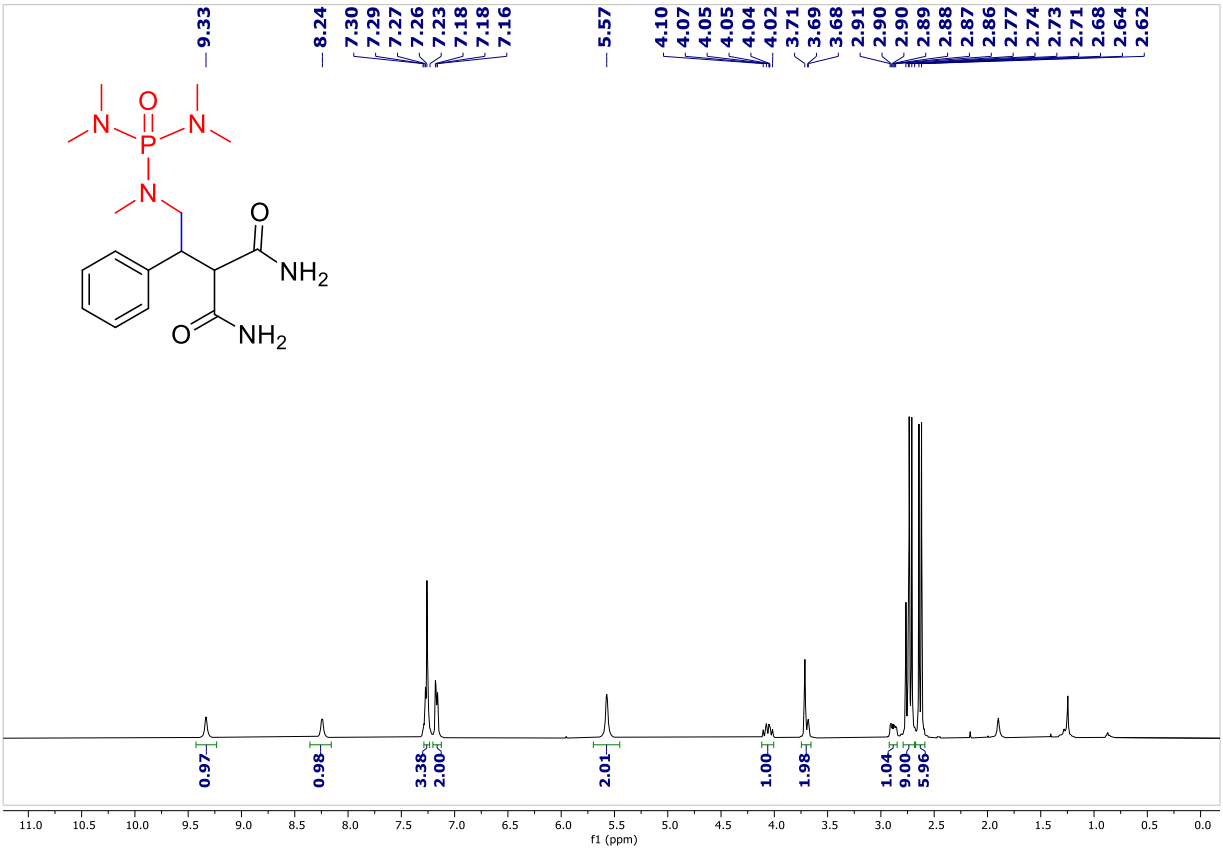
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **10**



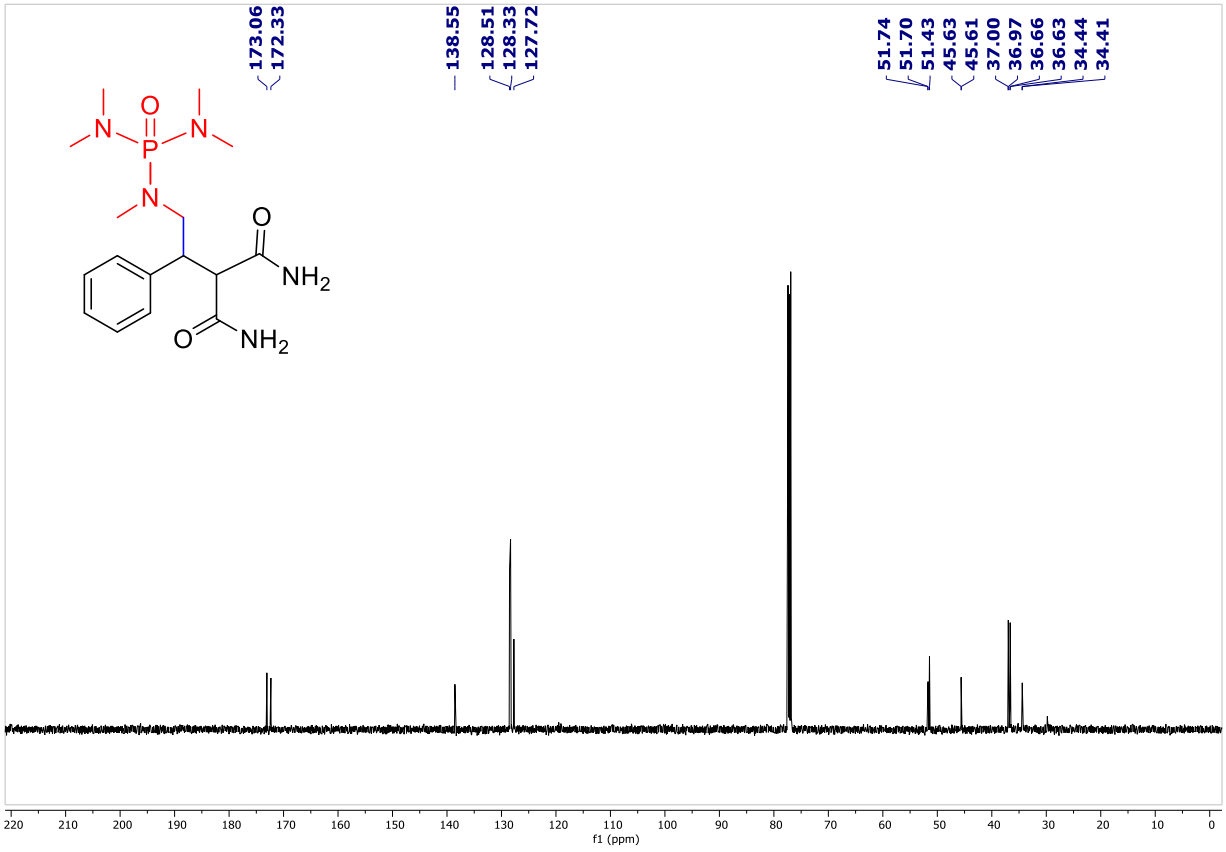
^{31}P NMR (203 MHz, $CDCl_3$) of compound **10**



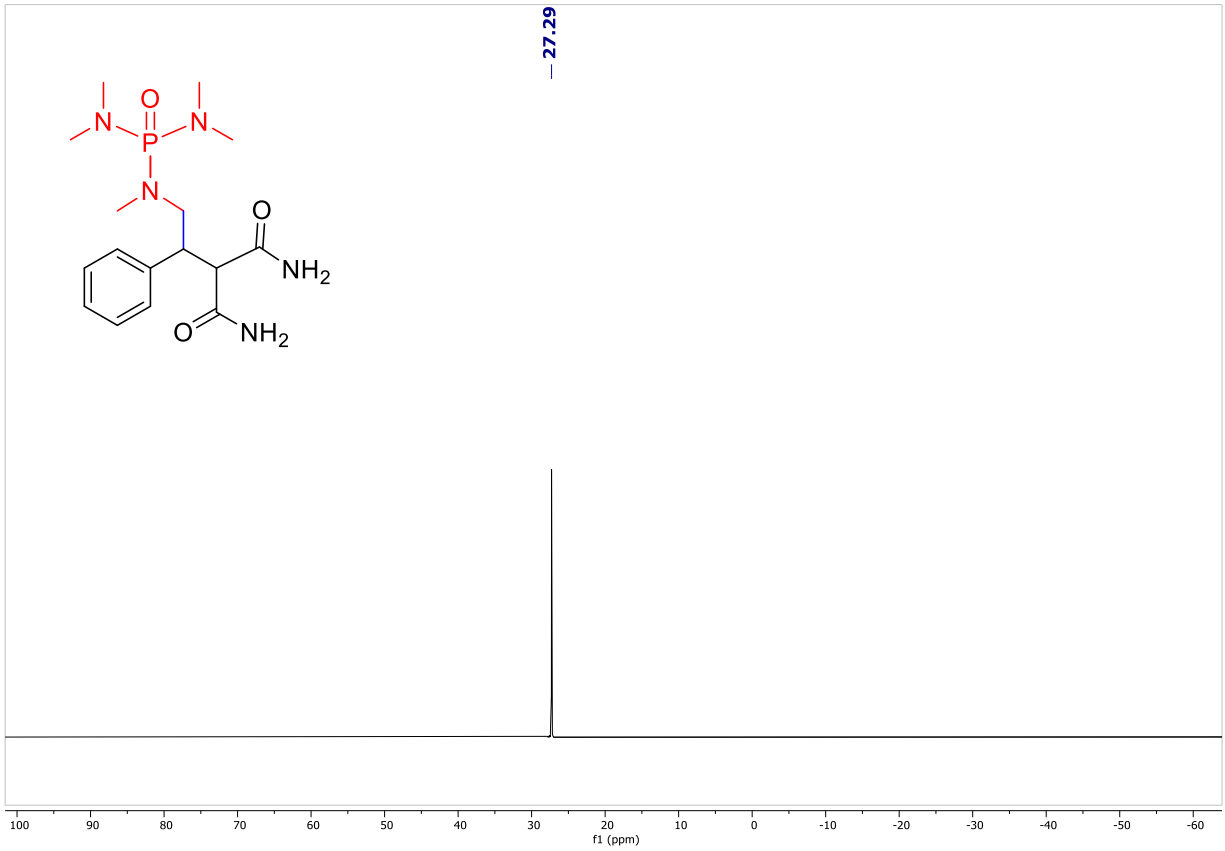
^{1}H NMR (400 MHz, $CDCl_3$) of compound **11**



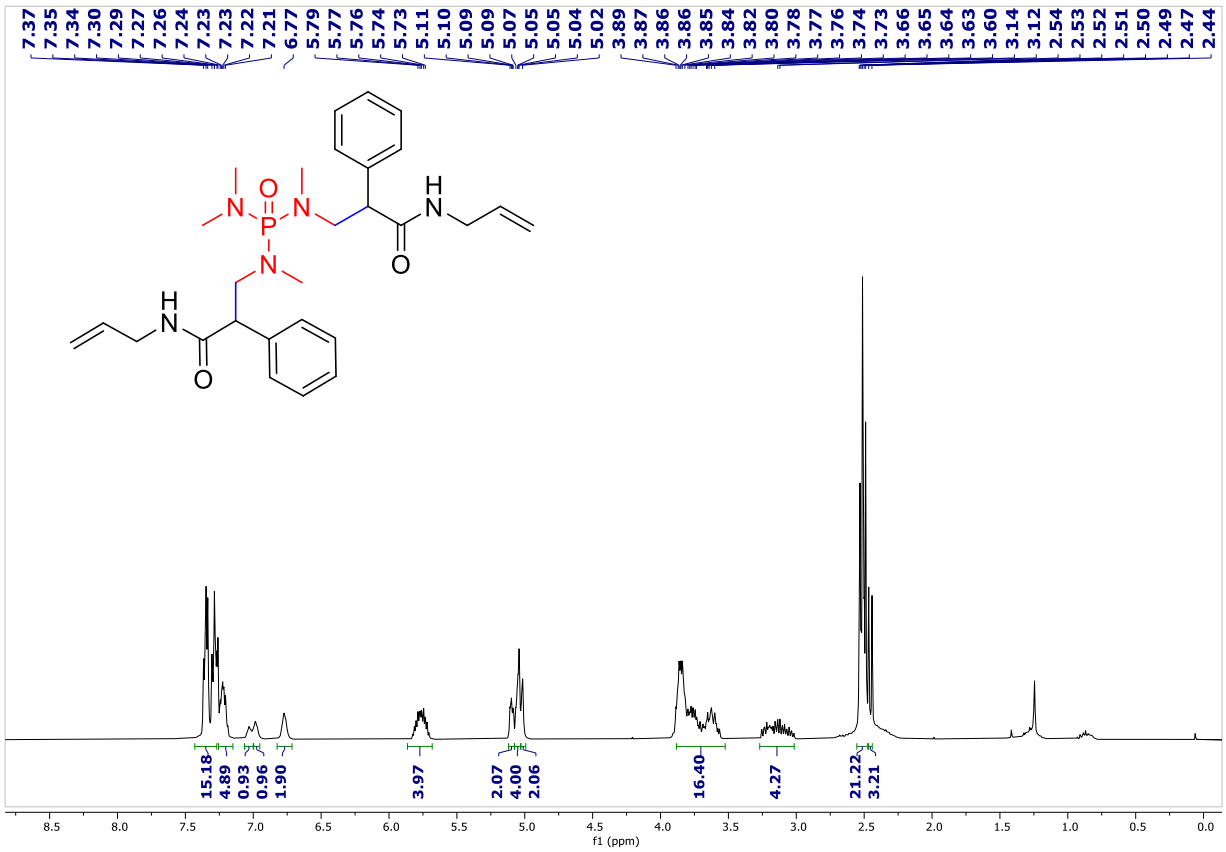
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **11**



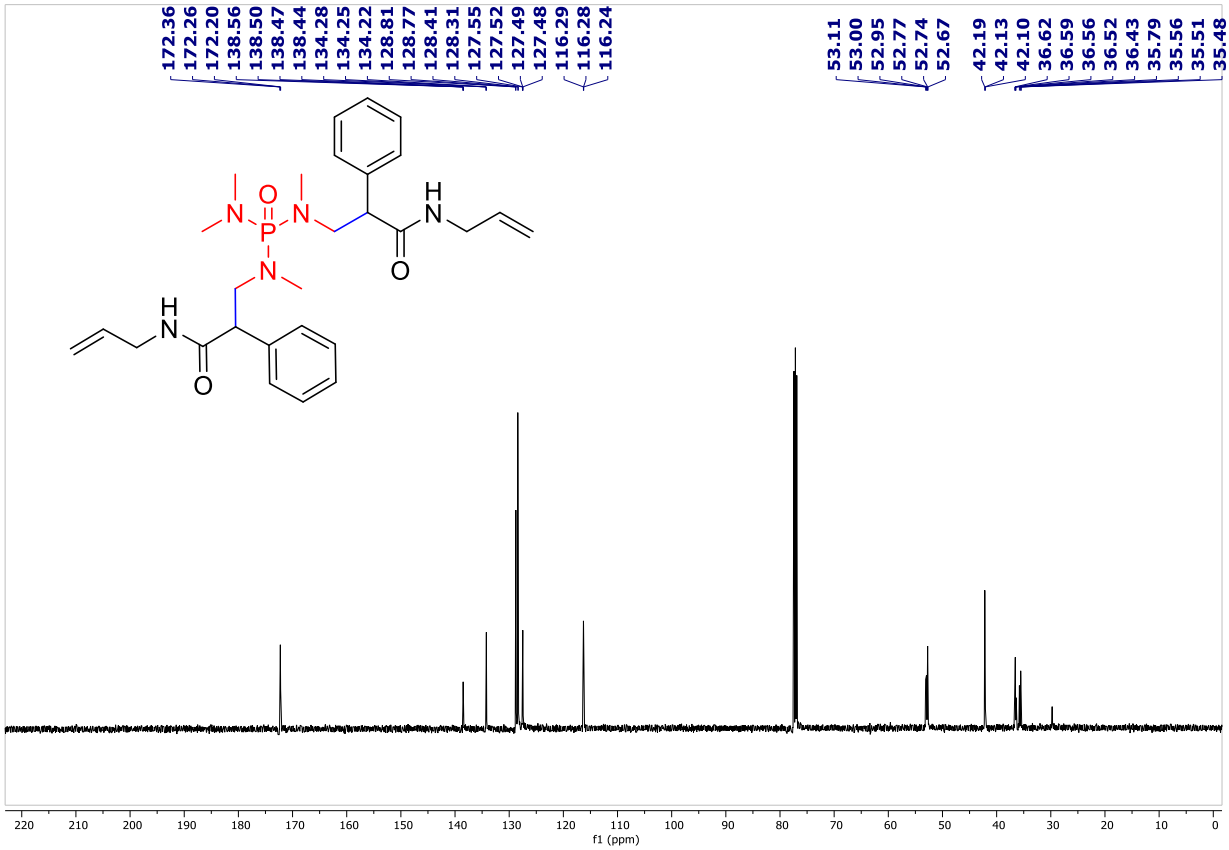
^{31}P NMR (203 MHz, $CDCl_3$) of compound **11**



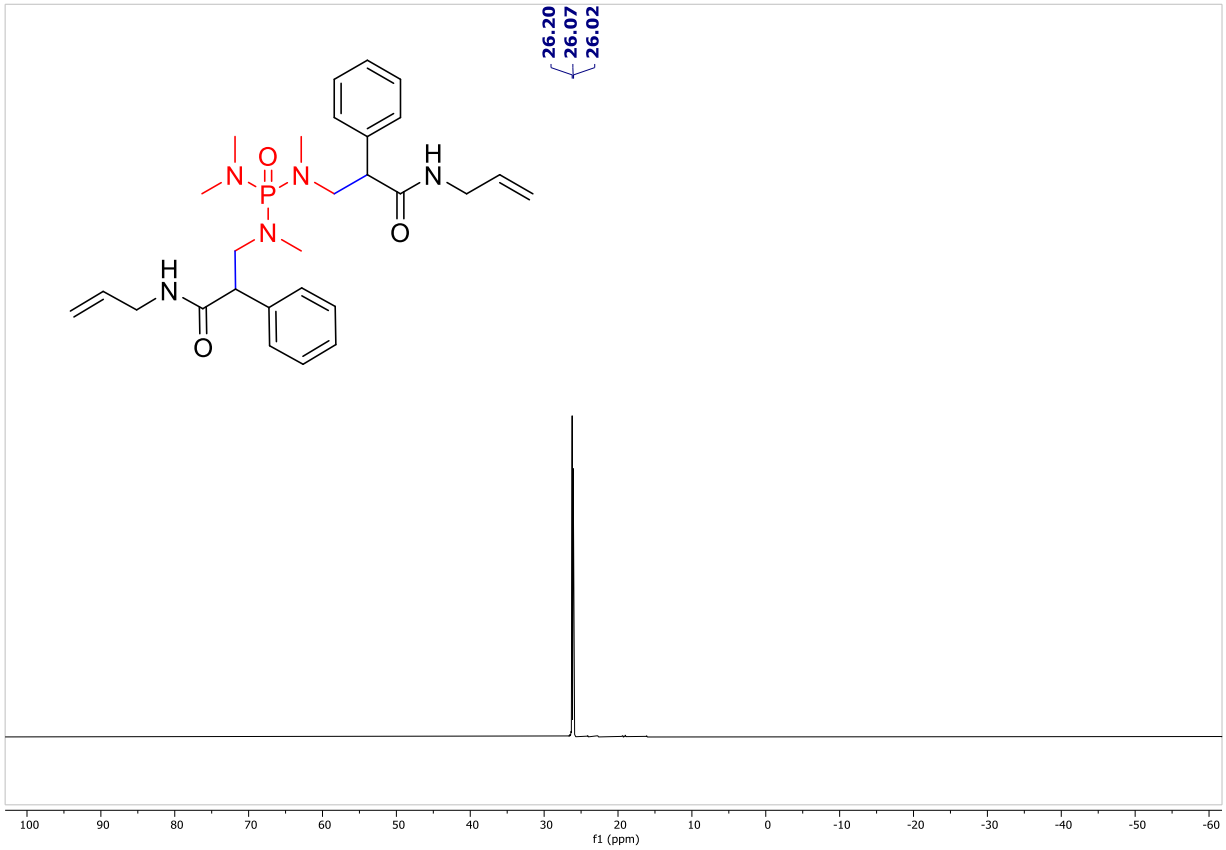
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12**



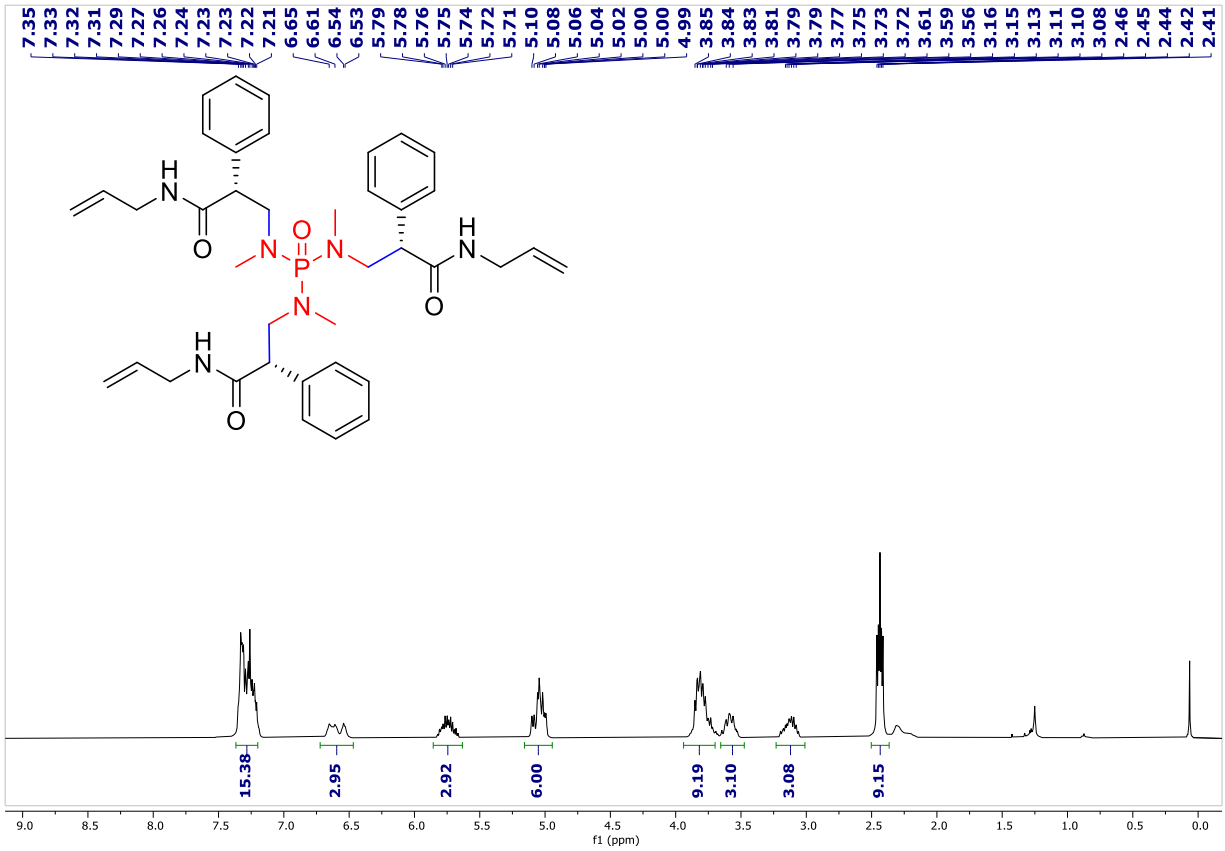
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **12**



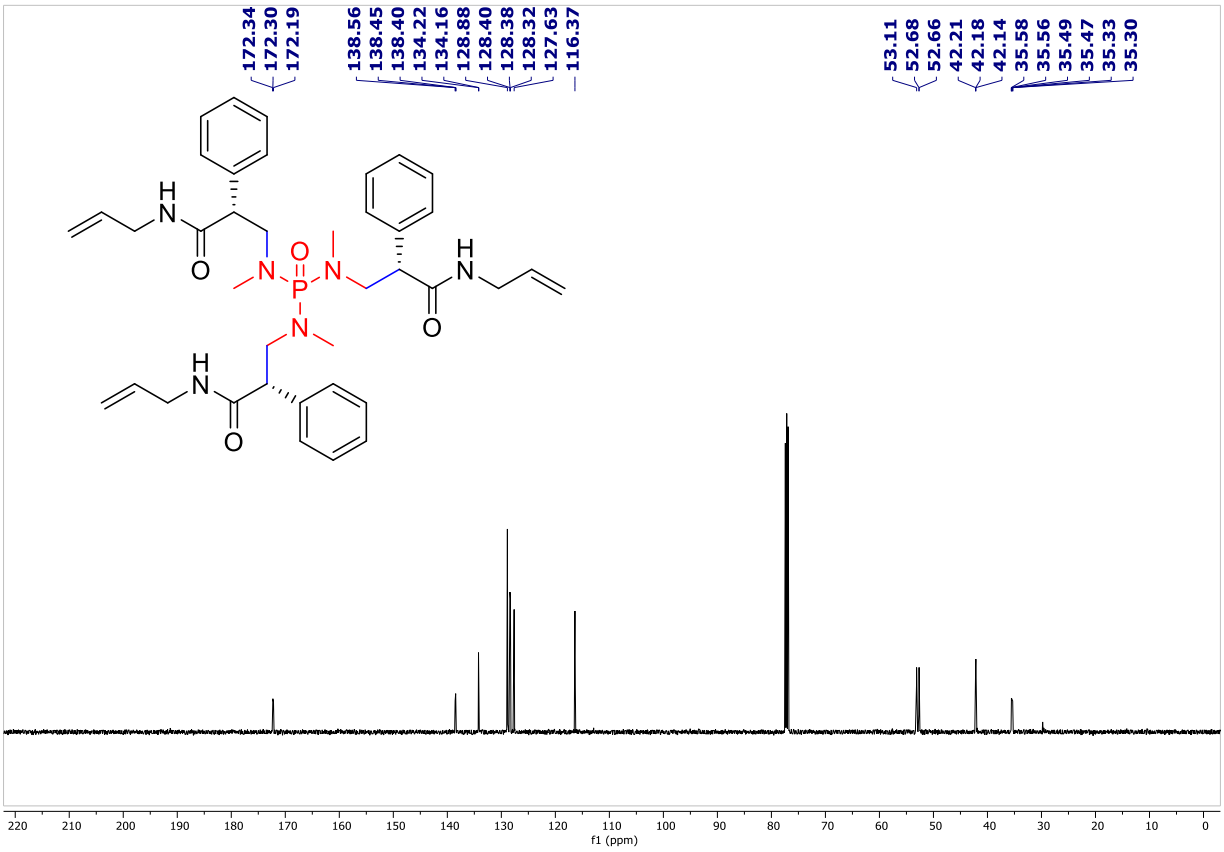
^{31}P NMR (203 MHz, $CDCl_3$) of compound **12**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **(±)-13**



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **(±)-13**



^{31}P NMR (203 MHz, $CDCl_3$) of compound **(±)-13**