Supporting Information

Gold-Catalyzed Alkenylation and Arylation of Phosphorothioates

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1. General information:

1.1. Practical considerations:

All reactions were carried out in oven-dried vials or reaction vessels with magnetic stirring under nitrogen atmosphere, unless otherwise mentioned. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. All the gold-catalyzed cross-coupling reactions were performed in 2.5 mL glass vials with a PTFE-lined cap, whereas all other reactions were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on 0.25 mm precoated silica gel plates (60 F254). After elution, plate was visualized under UV at 254 nm for UV active materials. Further visualization was achieved by staining in I_2 and $KMnO_4$ solution and charring on a hot plate. Solvents were removed *in vacuo* and heated in a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

1.2. Instrumentation:

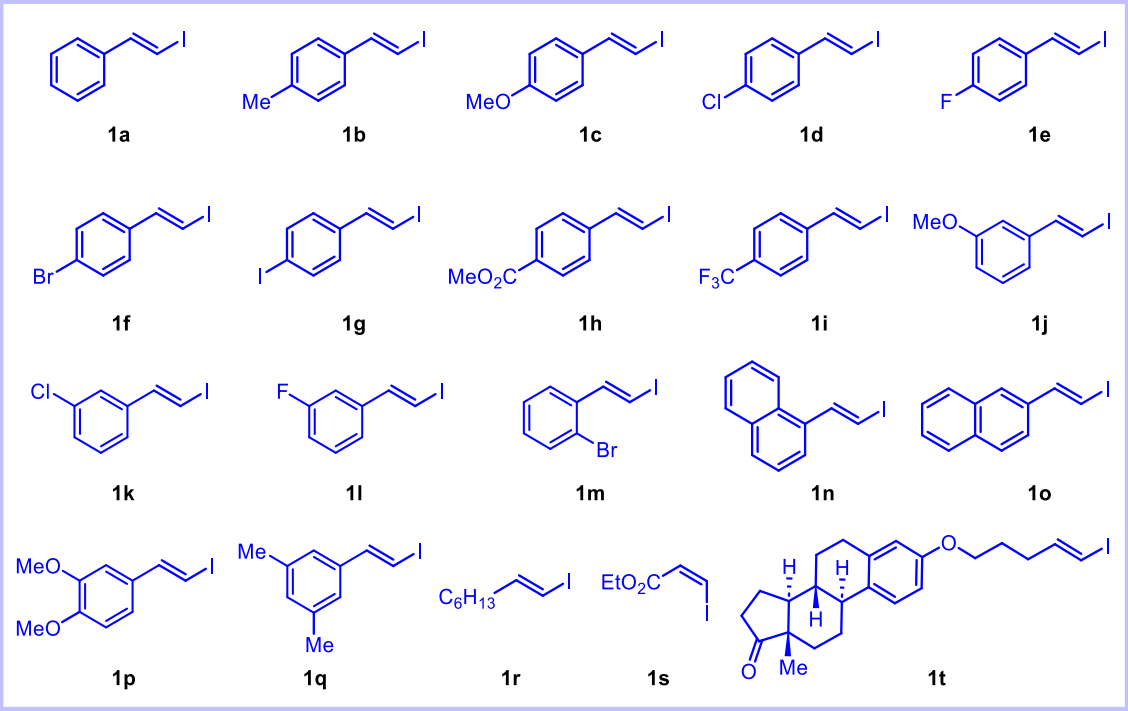
All ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded in Bruker AVANCE III 400, 500 and 700 MHz NMR spectrometers at 25 °C unless specified otherwise using TMS as an internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), br. s. (broad singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), t (triplet), q (quartet), m (multiplet) etc. HRMS (ESI) data were recorded on a Bruker Daltonics MicroTOF-Q-II spectrometer. Single crystal X-ray diffraction measurements were performed with Bruker D8 Venture Dual Source X-ray diffractometer and Bruker APEX-II CCD diffractometer.

1.3. Materials:

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF was distilled from Na/benzophenone under an atmosphere of N_2. DMSO, MeCN, DCM, 1,4-dioxane and acetone were dried using standard protocol under N_2. Gold, silver salts and deuterated solvents were purchased from Sigma-Aldrich and stored under nitrogen atmosphere.

2. Synthesis of starting materials

2.1. Synthesis of alkenyl iodides:

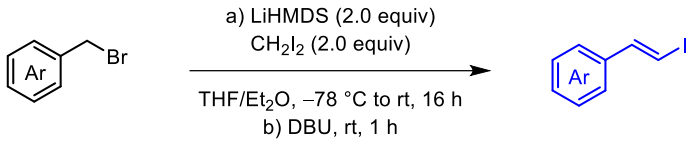


Alkenyl iodides	Sources
1a-1r	These compounds are known in the literature and synthesized by literature known procedures (General Method A, B or C)
1s[1] and **1t**[2]	These compounds are known in the literature and synthesized by literature known procedures

2.1.1. Synthesis of (*E*)-alkenyl iodides:

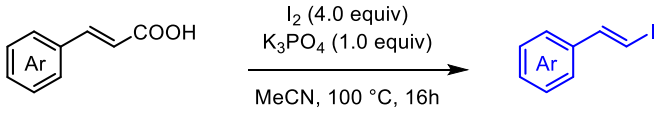
General Method A:

1) Paterson, I.; Paquet, T. *Org. Lett.* **2010**, *12*, 2158-2161.
2) Kumar, A.; Das, A.; Patil, N. T. *Org. Lett.* **2023**, *25*, 2934-2938.



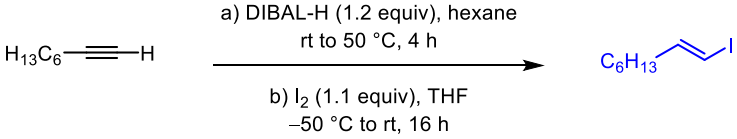
A two-neck round bottom flask was charged with a solution of freshly prepared LiHMDS (2.0 equiv) and the reaction mixture was cooled to –78 °C. At this temperature, a solution of CH_2I_2 (2.0 equiv) in THF (1 mL/mmol) was added dropwise and the reaction mixture was stirred for 20 minutes. Further, a solution of the corresponding benzyl bromide (1.0 equiv) in THF was added dropwise and the reaction mixture was stirred for 1 hour at –78 °C. Then, the solution was warmed to room temperature and was allowed to stir for 16 h. Next, DBU (2.0 equiv) was added to the reaction mixture followed by stirring for 1 h. Then the reaction mixture was filtered through a pad of celite, and the solvents were evaporated under reduced pressure. The crude product was purified by flash chromatography (hexane) to give the desired (*E*)-alkenyl iodides. Compounds 1a, 1d, 1f-1o and 1q were synthesized by following this route, and analytical data matched the literature.[3]

General Method B:



In a round bottom flask, the cinnamic acid derivative (1.0 equiv), iodine (4.0 equiv) and vacuum dried potassium phosphate (1.0 equiv) were mixed in acetonitrile (0.02 M). The reaction mixture was heated at 100 °C and was stirred for 16 hours maintaining dark conditions. After the completion of the reaction, sat. aq. $Na_2S_2O_3$ was added followed by the addition of sat. aq. Na_2CO_3. The organic portion was extracted with ethyl acetate, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The mixture was then purified by column chromatography over silica gel to afford desired (*E*)-alkenyl iodides. Compounds 1b, 1c, 1e and 1p were synthesized by following this route, and analytical data matched the literature.[4]

General Method C:

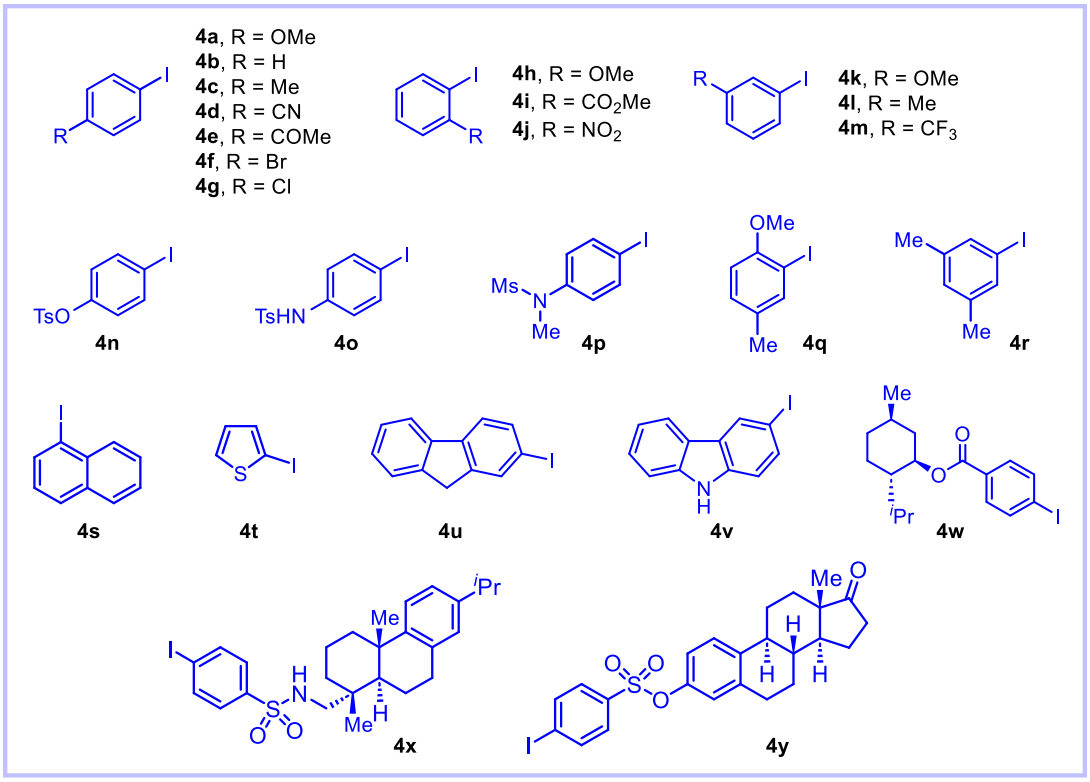


In a two-neck round bottom flask, the alkyne (5 mmol, 1 equiv) and dry hexane (5 mL) was taken under nitrogen atmosphere. To this solution, DIBAL-H (1 M solution in hexane, 6 mmol, 1.2 equiv) was added slowly, maintaining the temperature below 25 °C, and the reaction mixture was heated to 50 °C for 4 h. The reaction mixture was allowed to cool to room temperature and the hexane was removed under reduced pressure. Then, dry THF (5 mL) was added and the reaction mixture was cooled to −50 °C. A solution of iodine (5.5 mmol, 1.1 equiv) in THF (5 mL) was added at this temperature and the reaction mixture was stirred for

3) Bull, J. A.; Mousseau, J. J.; Charette, A. B. *Org. Lett.* **2008**, *10*, 5485–5488.
4) Cadge, J. A.; Sparkes, H. A.; Bower, J. F.; Russell, C. A. *Angew. Chem. Int. Ed.* **2020**, *59*, 6617–6621.

30 mins. Then, the solution was allowed to warm to room temperature and was stirred for 16 h. This was followed by the slow addition of cold 20% sulfuric acid (10 mL) to the reaction mixture and then the mixture was poured into ice-cold 20% sulfuric acid (10 mL) in a beaker. Further, the mixture was extracted with hexane (thrice), organic portions combined and washed with aq. 10% w/v $Na_2S_2O_3$ (30 mL), sat. aq. $NaHCO_3$ (30 mL) and brine (30 mL). After drying over Na_2SO_4, filtration, and evaporation in vacuo, the crude residue was purified by flash chromatography (hexane) to give desired (*E*)-alkenyl iodide. Compound 1r was synthesized by following this route, and analytical data matched the literature.[5]

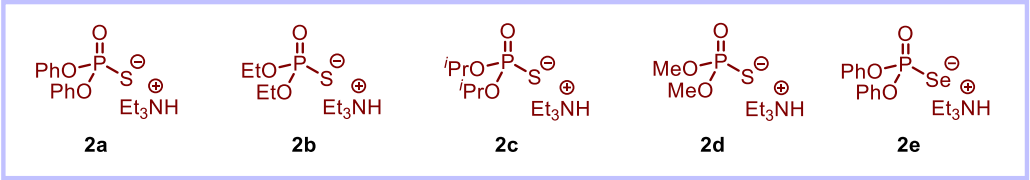
2.2. Synthesis of aryl iodides:



Iodo-arenes	Sources
4a-4m, **4q**, **4r**, **4t**, **4u** and **4v**	Commercially available
4n-4p, **4s**, **4w**,[6] **4x**[7] and **4y**[8]	These compounds are known in the literature and synthesized by literature known procedures

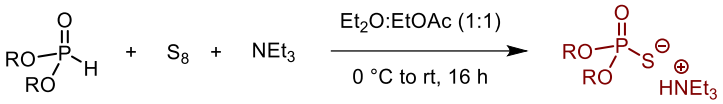
5) Trost, B. M.; Rudd, M. T. *Org. Lett.* **2003**, *5*, 4599–4602.
6) Yuan, F.; Hou, Z.-L.; Pramanick, P. K.; Yao, B. *Org. Lett.* **2019**, *21*, 9381–9385.
7) Akram, M. O.; Das, A.; Chakrabarty, I.; Patil, N. T. *Org. Lett.* **2019**, *21*, 8101–8105.
8) Xie, Q.; Li, L.; Zhu, Z.; Zhang, R.; Ni, C.; Hu, J. *Angew. Chem., Int. Ed.* **2018**, *57*, 13211–13215.

2.3. Synthesis of phosphorothioate/phosphoroselenoate salts:



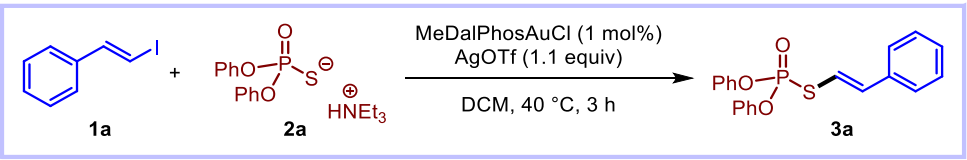
Phosphorothioates	Sources
2a-2e	These compounds are known in the literature and synthesized by literature known procedures

General Method:



A two-neck round bottom flask was charged with H-phosphonate diester (1.0 equiv) and sulphur (1.1 equiv). The flask was backfilled with nitrogen and sealed using a rubber septum. To the reaction mixture, a 1:1 mixture of ethyl acetate and diethyl ether was added via syringe, and the reaction mixture was cooled to 0 °C using an ice bath. Anhydrous triethylamine (3 equiv) was added drop-wise to the reaction mixture and upon completion of addition, the ice bath was removed followed by stirring at room temperature for 16 h. After complete conversion, the solvents were evaporated under reduced pressure and the product was purified by column chromatography (silica; dichloromethane:methanol:triethylamine/93:2:5). Compounds 2a-2d were synthesized by following this route, and analytical data matched the literature.[9]

3. Gold-catalyzed *S*-alkenylation of phosphorothioate salts:



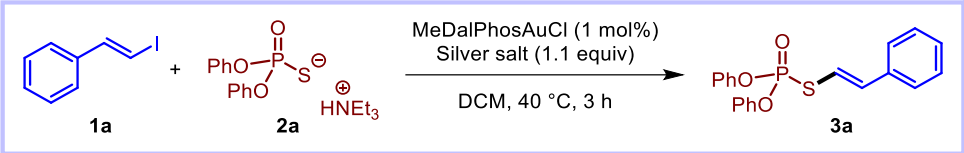
An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the (2-iodovinyl)benzene (*E:Z* = 97:3) (**1a**, 0.2 mmol, 1 equiv), *O*,*O*-diphenyl phosphorothioate (**2a**, 0.2 mmol, 1 equiv), MeDalPhosAuCl (0.002 mmol, 0.01 equiv) and dichloromethane (DCM) (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min, then AgOTf

9) Sarkar, S.; Kalek, M. *Org. Lett.* **2023**, *25*, 671–675.

(0.22 mmol, 1.1 equiv) was added and allowed to stir at 40 °C for 3 h. After completion of the reaction, it was diluted with DCM (5 mL), filtered through a short pad of celite, concentrated and subsequently purified by silica gel column chromatography to afford the desired cross-coupled product **3a** (*E:Z* = 97:3) in 28% yield. With this promising result, we initiated to optimize the reaction conditions in order to achieve maximum yield. The details of the optimization studies are given below.

3.1. Optimization of the reaction conditions:

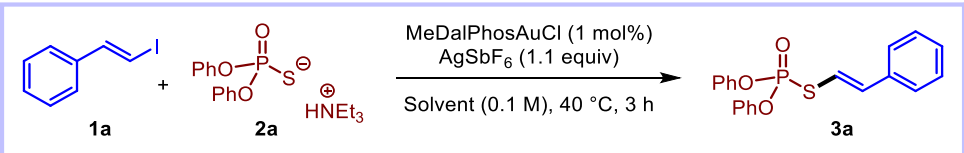
3.1.1. Screening of silver salts:[a]



Entry	Halide scavengers	Yields (%)[b]
1	$AgSbF_6$	66
2	$AgNTf_2$	trace
3	AgOTs	18
4	$AgBF_4$	61
5	AgOAc	NR
6[c]	$AgSbF_6$	trace

[a]**Reaction conditions**: 0.2 mmol **1a**, 0.2 mmol **2a**, 1 mol% MeDalPhosAuCl, 0.22 mmol AgX, DCM (0.1 M), 40 °C, 3 h. [b]Isolated yields. [c]0.01 mmol $AgSbF_6$ was used. NR = No reaction.

3.1.2. Screening of solvents:[a]

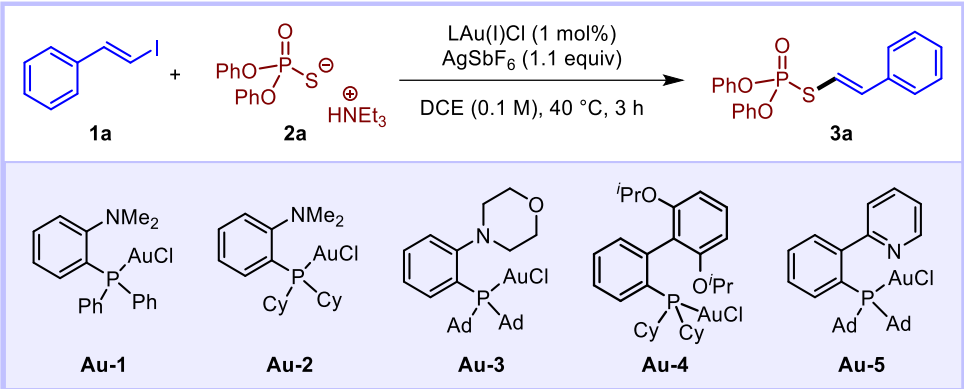


Entry	Solvent	Yields (%)[b]
1	*o*-DCB	83
2	DCE	98
3	MeCN	NR

4	MeOH	NR
5	$CHCl_3$	NR
6	1,4-dioxane	NR

[a]**Reaction conditions**: 0.2 mmol **1a**, 0.2 mmol **2a**, 1 mol% MeDalPhosAuCl, 0.22 mmol $AgSbF_6$, Solvent (0.1 M), 40 ºC, 3 h. [b]Isolated yields. NR = No reaction.

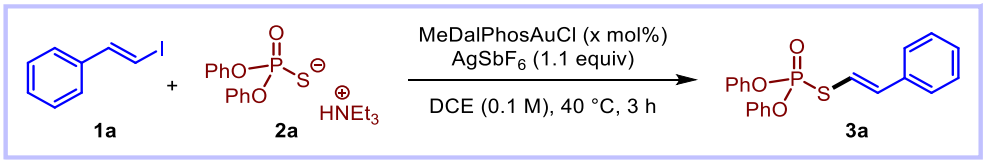
3.1.3. Screening of gold(I) catalysts:[a]



Entry	Au(I) catalyst	Yields (%)[b]
1	**Au-1**	NR
2	**Au-2**	NR
3	**Au-3** (MorDalPhosAuCl)	56
4	**Au-4**	NR
5	**Au-5**	NR

[a]**Reaction conditions**: 0.20 mmol **1a**, 0.20 mmol **2a**, 1 mol% LAuCl, 0.22 mmol $AgSbF_6$, DCE (0.1 M), 40 ºC, 3 h. [b]Isolated yields. NR = No reaction.

3.1.4. Effect of MeDalPhosAuCl loading:[a]

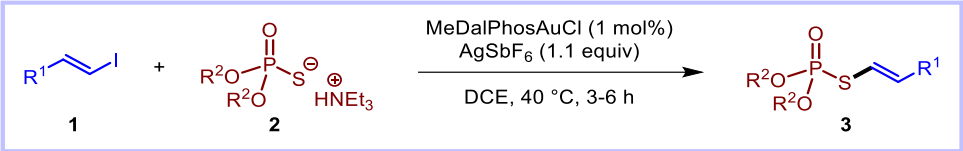


Entry	MeDalPhosAuCl loading (mol%)	Yields (%)[b]
1	0.1	13

2	1	98
3	5	99

[a]**Reaction conditions**: 0.20 mmol **1a**, 0.20 mmol **2a**, x mol% MeDalPhosAuCl, 0.22 mmol $AgSbF_6$, DCE (0.1 M), 40 ºC, 3 h. [b]Isolated yields.

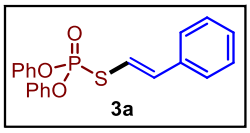
4. General procedure for gold-catalyzed *S*-alkenylation of phosphorothioate salts:



An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the vinyl iodide (**1**, 0.2 mmol, 1 equiv), phosphorothioate salt (**2**, 0.2 mmol, 1 equiv), MeDalPhosAuCl (0.002 mmol, 0.01 equiv) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then $AgSbF_6$ (0.22 mmol, 1.1 equiv) was added and allowed to stir at 40 °C for 3-6 h. After completion of the reaction, it was diluted with DCM (5 mL), filtered through a short pad of celite, concentrated and subsequently purified by silica gel column chromatography to afford the product **3**.

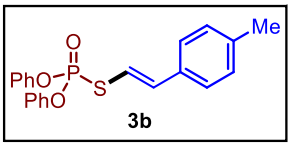
❖ Characterization data:

(*E*)-*O*,*O*-diphenyl *S*-styryl phosphorothioate (3a):



E:*Z* = 97:3, Colourless Liquid, 72 mg, 98% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.45 - 7.24 (m, 15 H), 6.89 - 6.82 (m, 1 H), 6.72 (d, *J* = 7.9 Hz, 1 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.3 (d, *J* = 8.17 Hz), 139.8 (d, *J* = 12.71 Hz), 135.7, 130.1, 129.0, 129.0, 126.7, 126.0, 120.9 (d, *J* = 4.54 Hz), 112.9 (d, *J* = 7.26 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.42. **HRMS (ESI)** calcd for $C_{20}H_{17}O_3PS$ (M + nH) 369.0709, found 369.0711.

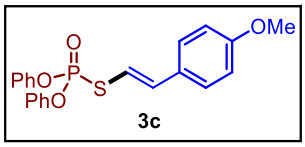
(*E*)-*S*-(4-methylstyryl) *O*,*O*-diphenyl phosphorothioate (3b):



3b

E:*Z* = 98:2, Yellow Liquid, 49.6 mg, 65% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.40 (t, *J* = 7.6 Hz, 4 H), 7.35 (d, *J* = 8.2 Hz, 4 H), 7.24 - 7.27 (m, 4 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 6.85 - 6.78 (m, 1 H), 6.62 (dd, *J* = 7.7, 15.3 Hz, 1 H), 2.38 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.2 (d, *J* = 8.2 Hz), 140.0 (d, *J* = 13.6 Hz), 138.9, 132.7, 129.9, 129.5, 126.5, 125.8, 120.8 (d, *J* = 4.5 Hz), 111.2 (d, *J* = 7.3 Hz), 21.3; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.59. **HRMS (ESI)** calcd for $C_{21}H_{19}O_3PS$ (M + nH) 383.0865, found 383.0855.

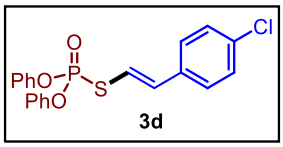
(*E*)-*S*-(4-methoxystyryl) *O*,*O*-diphenyl phosphorothioate (3c):



3c

E:*Z* = 93:7, Yellow Liquid, 50 mg, 63% yield, R_f = 0.60 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.38 (t, *J* = 7.9 Hz, 4 H), 7.33 (d, *J* = 7.6 Hz, 4 H), 7.28 - 7.21 (m, 4 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 6.77 (dd, *J* = 3.0, 15.2 Hz, 1 H), 6.47 (dd, *J* = 7.2, 15.3 Hz, 1 H), 3.82 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 160.4, 150.4 (d, *J* = 8.2 Hz), 140.4, 140.3, 130.1, 128.1, 126.0, 120.9 (d, *J* = 4.5 Hz), 114.4, 109.5 (d, *J* = 7.3 Hz), 55.5; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.72. **HRMS (ESI)** calcd for $C_{21}H_{19}O_4PS$ (M + nH) 399.0814, found 399.0809.

(*E*)-*S*-(4-chlorostyryl) *O*,*O*-diphenyl phosphorothioate (3d):

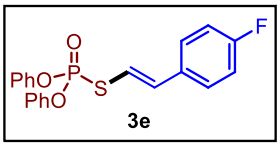


3d

Yellow Liquid, 66 mg, 82% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.44 - 7.38 (m, 4 H), 7.37 - 7.31 (m, 6 H), 7.30 - 7.24 (m, 4 H), 6.78 (dd, *J* = 2.6, 15.4 Hz, 1 H), 6.72 - 6.64 (m, 1 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.0 (d, *J* = 8.1 Hz), 137.7 (d, *J* = 13.2 Hz), 134.5, 133.9, 129.9 (d, *J* = 1.5 Hz), 129.0, 127.6, 125.9 (d, *J* = 1.5 Hz), 120.7 (d, *J* = 5.1 Hz), 113.8 (d, *J* = 6.6 Hz);

^{31}P NMR (202 MHz, CHLOROFORM-d) δ = 15.04. **HRMS (ESI)** calcd for $C_{20}H_{16}ClO_3PS$ (M + nH) 403.0319, found 403.0304.

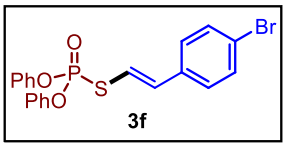
(*E*)-*S*-(4-fluorostyryl) *O*,*O*-diphenyl phosphorothioate (3e):



3e

E:*Z* = 91:9, Pale Yellow Liquid, 68.4 mg, 89% yield, R_f = 0.45 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.43 - 7.36 (m, 4 H), 7.36 - 7.31 (m, 4 H), 7.31 - 7.22 (m, 4 H), 7.04 (t, *J* = 8.6 Hz, 2 H), 6.79 (dd, *J* = 2.7, 15.3 Hz, 1 H), 6.59 (dd, *J* = 7.9, 15.4 Hz, 1 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 163.2 (d, *J* = 248 Hz), 150.3 (d, *J* = 8.2 Hz), 138.6 (d, *J* = 13.6 Hz), 131.9, 130.1, 128.4 (d, *J* = 8.2 Hz), 126.1, 120.9 (d, *J* = 4.5 Hz), 116.1 (d, *J* = 21.8 Hz), 112.7 (d, *J* = 7.3 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.28. **HRMS (ESI)** calcd for $C_{20}H_{16}FO_3PS$ (M + nH) 387.0615, found 387.0586.

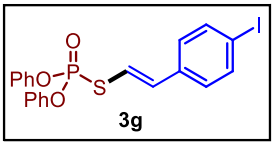
(*E*)-*S*-(4-bromostyryl) *O*,*O*-diphenyl phosphorothioate (3f):



3f

Yellow Liquid, 78 mg, 87% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.49 - 7.45 (m, 2 H), 7.44 - 7.36 (m, 4 H), 7.36 - 7.29 (m, 4 H), 7.29 - 7.22 (m, 2 H), 7.21 - 7.15 (m, 2 H), 6.81 - 6.63 (m, 2 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 149.8 (d, *J* = 8.2 Hz), 137.4 (d, *J* = 13.6 Hz), 134.0, 131.7, 129.6, 127.6, 125.6, 122.4, 120.4 (d, *J* = 4.5 Hz), 113.7 (d, *J* = 6.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 14.96. **HRMS (ESI)** calcd for $C_{20}H_{16}BrO_3PS$ (M + nH) 446.9814, found 446.9792.

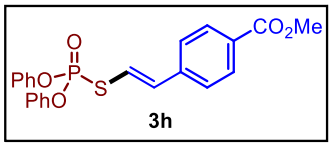
(*E*)-*S*-(4-iodostyryl) *O*,*O*-diphenyl phosphorothioate (3g):



3g

E:*Z* = 99:1, Yellow Liquid, 76 mg, 77% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.49 - 7.45 (m, 2 H), 7.44 - 7.36 (m, 4 H), 7.36 - 7.29 (m, 4 H), 7.29 - 7.22 (m, 2 H), 7.21 - 7.15 (m, 2 H), 6.81 - 6.63 (m, 2 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 149.8 (d, *J* = 8.2 Hz), 137.4 (d, *J* = 13.6 Hz), 134.0, 131.7, 129.6, 127.6, 125.6, 122.4, 120.4 (d, *J* = 4.5 Hz), 113.7 (d, *J* = 6.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 14.96. **HRMS (ESI)** calcd for $C_{20}H_{16}O_3PSI$ (M + nH) 494.9675, found 494.9681.

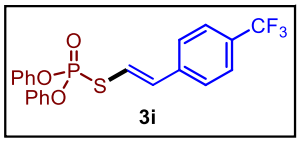
methyl (*E*)-4-(2-((diphenoxyphosphoryl)thio)vinyl)benzoate (3h):



3h

E:*Z* = 99:1, Colourless Liquid, 29 mg, 34% yield, R_f = 0.60 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 8.00 (d, *J* = 8.2 Hz, 2 H), 7.44 - 7.30 (m, 10 H), 7.26 (d, *J* = 7.5 Hz, 2 H), 6.88 - 6.79 (m, 2 H), 3.92 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 166.3, 149.7 (d, *J* = 8.2 Hz), 139.3, 136.8 (d, *J* = 13.6 Hz), 129.8, 129.7, 126.0, 125.7, 120.4 (d, *J* = 4.5 Hz), 116.3 (d, *J* = 6.4 Hz), 116.2, 51.9; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 14.77. **HRMS (ESI)** calcd for $C_{22}H_{19}O_5PS$ (M + nH) 427.0764, found 427.0745.

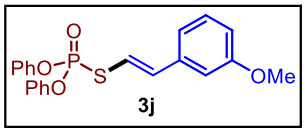
(*E*)-*O*,*O*-diphenyl *S*-(4-(trifluoromethyl)styryl) phosphorothioate (3i):



3i

Pale Yellow Liquid, 27 mg, 31% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.60 (d, *J* = 8.2 Hz, 2 H), 7.41 (t, *J* = 8.1 Hz, 6 H), 7.38 - 7.31 (m, 4 H), 7.28 (s, 2 H), 6.91 - 6.78 (m, 2 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.0, 149.9, 138.7, 136.7, 136.6, 130.4, 130.2, 129.9, 126.6, 126.0 (d, *J* = 1.8 Hz), 125.8 (m), 125.0, 122.8, 120.7 (d, *J* = 5.4 Hz), 116.7 (d, *J* = 6.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 14.72. **HRMS (ESI)** calcd for $C_{21}H_{16}F_3O_3PS$ (M + nH) 437.0583, found 437.0576.

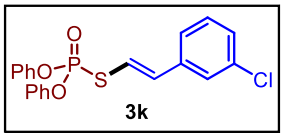
(*E*)-*S*-(3-methoxystyryl) *O*,*O*-diphenyl phosphorothioate (3j):



3j

E:*Z* = 94:6, Yellow Liquid, 56.4 mg, 71% yield, R_f = 0.50 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.42 - 7.36 (m, 4 H), 7.36 - 7.31 (m, 4 H), 7.27 - 7.23 (m, 3 H), 6.92 (d, *J* = 7.6 Hz, 1 H), 6.88 - 6.83 (m, 2 H), 6.78 (d, *J* = 2.7 Hz, 1 H), 6.69 (d, *J* = 7.9 Hz, 1 H), 3.82 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 159.8, 150.1 (d, *J* = 8.2 Hz), 139.3 (d, *J* = 13.6 Hz), 136.7, 129.9, 129.7, 125.8, 120.7 (d, *J* = 5.4 Hz), 119.1, 114.3, 113.1 (d, *J* = 7.3 Hz), 111.8, 55.3; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.33. **HRMS (ESI)** calcd for $C_{21}H_{19}O_4PS$ (M + nH) 399.0814, found 399.0827.

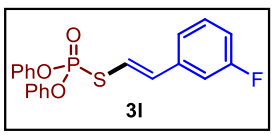
(*E*)-*S*-(3-chlorostyryl) *O*,*O*-diphenyl phosphorothioate (3k):



3k

Colourless Liquid, 38 mg, 48% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.44 - 7.39 (m, 4 H), 7.37 - 7.32 (m, 4 H), 7.32 - 7.25 (m, 5 H), 7.22 - 7.18 (m, 1 H), 6.79 - 6.69 (m, 2 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.0 (d, *J* = 8.2 Hz), 137.2 (d, *J* = 13.6 Hz), 137.1 134.7, 130.0, 129.9, 128.6, 126.3, 125.9, 124.6, 120.7 (d, *J* = 5.4 Hz), 115.1 (d, *J* = 7.3 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 14.88. **HRMS (ESI)** calcd for $C_{20}H_{16}ClO_3PS$ (M + nH) 403.0319, found 403.0315.

(*E*)-*S*-(3-fluorostyryl) *O*,*O*-diphenyl phosphorothioate (3l):

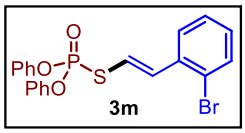


3l

E:*Z* = 98:2, Yellow Liquid, 60.8 mg, 79% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.44 - 7.38 (m, 4 H), 7.38 - 7.30 (m, 5 H), 7.30 - 7.26 (m, 2 H), 7.10 (d, *J* = 7.8 Hz, 1 H), 7.07 - 6.97 (m, 2 H), 6.83 - 6.68 (m, 2 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 163.0 (d, *J* = 247 Hz), 150.0 (d, *J* = 8.2 Hz), 137.6 (d, *J* = 6.4 Hz), 137.5 (d, *J* = 2.7 Hz), 130.3 (d, *J* = 9.1 Hz), 129.9, 125.9, 122.3, 120.7 (d, *J* = 5.4 Hz), 115.5 (d, *J* = 20.9 Hz), 114.9 (d, *J* = 6.4 Hz), 113.0 (d, *J* = 22.7 Hz); **^{31}P NMR**

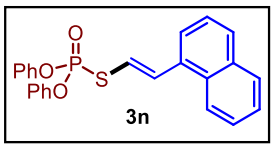
(202 MHz, CHLOROFORM-d) δ = 14.93. **HRMS (ESI)** calcd for $C_{20}H_{16}FO_3PS$ (M + nH) 387.0615, found 387.0621.

(*E*)-*S*-(2-bromostyryl) *O*,*O*-diphenyl phosphorothioate (3m):



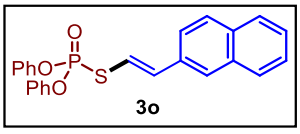
E:*Z* = 98:2, Pale Yellow Liquid, 74.8 mg, 84% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.58 (d, *J* = 8.1 Hz, 1 H), 7.46 (d, *J* = 7.8 Hz, 1 H), 7.41 (t, *J* = 7.9 Hz, 4 H), 7.36 (d, *J* = 8.2 Hz, 4 H), 7.33 - 7.25 (m, 3 H), 7.23 - 7.16 (m, 2 H), 6.73 (dd, *J* = 8.8, 15.3 Hz, 1 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.2 (d, *J* = 8.2 Hz), 137.4 (d, *J* = 13.6 Hz), 135.7, 133.3, 130.2, 130.1, 127.9, 127.4, 126.1, 123.5, 121.0 (d, *J* = 5.4 Hz), 116.9 (d, *J* = 6.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.07. **HRMS (ESI)** calcd for $C_{20}H_{16}BrO_3PS$ (M + nH) 446.9814, found 446.9805.

(*E*)-*S*-(2-(naphthalen-1-yl)vinyl) *O*,*O*-diphenyl phosphorothioate (3n):



E:*Z* = 98:2, Light Brown Liquid, 78 mg, 93% yield, R_f = 0.50 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.97 - 7.93 (m, 1 H), 7.89 - 7.83 (m, 2 H), 7.61 (dd, *J* = 2.4, 15.1 Hz, 1 H), 7.56 - 7.51 (m, 3 H), 7.48 - 7.44 (m, 1 H), 7.44 - 7.33 (m, 8 H), 7.29 - 7.23 (m, 2 H), 6.75 (dd, *J* = 8.1, 15.1 Hz, 1 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.3 (d, *J* = 8.2 Hz), 137.4 (d, *J* = 12.7 Hz), 133.8, 133.3, 130.9, 130.1, 129.4, 128.8, 126.7, 126.3, 126.1, 125.8, 124.6, 123.7, 120.9 (d, *J* = 5.4 Hz), 115.7 (d, *J* = 6.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.36. **HRMS (ESI)** calcd for $C_{24}H_{19}O_3PS$ (M + nH) 419.0865, found 419.0848.

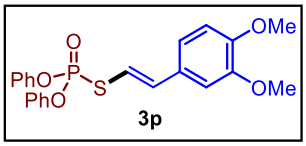
(*E*)-*S*-(2-(naphthalen-2-yl)vinyl) *O*,*O*-diphenyl phosphorothioate (3o):



Pale Yellow Solid, 72.7 mg, 87% yield, R_f = 0.50 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.87 - 7.80 (m, 3 H), 7.72 - 7.68 (m, 1 H), 7.56 - 7.50 (m, 3 H), 7.45 - 7.35 (m, 8 H), 7.31 - 7.26 (m, 2 H), 7.00 (dd, *J* = 2.9, 15.4 Hz, 1 H), 6.87

- 6.78 (m, 1 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.1 (d, *J* = 7.3 Hz), 139.5 (d, *J* = 13.6 Hz), 133.4 (d, *J* = 3.6 Hz), 132.9, 129.9, 128.6, 128.2, 127.8, 126.9, 126.6 (d, *J* = 7.3 Hz), 125.9, 123.1, 120.8 (d, *J* = 5.4 Hz), 113.0 (d, *J* = 7.3 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.36. **HRMS (ESI)** calcd for $C_{24}H_{19}O_3PS$ (M + nH) 419.0865, found 419.0858.

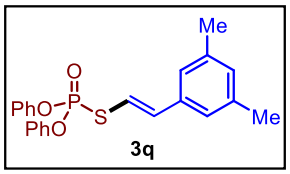
(*E*)-*S*-(3,4-dimethoxystyryl) *O*,*O*-diphenyl phosphorothioate (3p):



3p

E:*Z* = 99:1, Brown Liquid, 46 mg, 54% yield, R_f = 0.70 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.44 - 7.37 (m, 4 H), 7.37 - 7.31 (m, 4 H), 7.30 - 7.23 (m, 2 H), 6.89 - 6.82 (m, 3 H), 6.80 - 6.75 (m, 1 H), 6.53 - 6.45 (m, 1 H), 3.93 - 3.89 (m, 6 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.2 (d, *J* = 8.2 Hz), 149.8, 149.1, 140.2 (d, *J* = 12.7 Hz), 129.8, 128.5, 125.7, 120.7 (d, *J* = 4.5 Hz), 120.2, 111.0, 109.5 (d, *J* = 7.3 Hz), 108.7, 55.9; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.64. **HRMS (ESI)** calcd for $C_{22}H_{21}O_5PS$ (M + nH) 429.0920, found 429.0900.

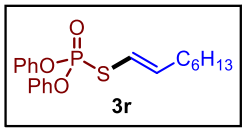
(*E*)-*S*-(3,5-dimethylstyryl) *O*,*O*-diphenyl phosphorothioate (3q):



3q

E:*Z* = 97:3, Colourless Liquid, 60.4 mg, 76% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.41 (t, *J* = 7.8 Hz, 4 H), 7.36 (d, *J* = 7.9 Hz, 4 H), 7.30 - 7.24 (m, 2 H), 6.97 (s, 3 H), 6.79 (d, *J* = 15.6 Hz, 1 H), 6.67 (dd, *J* = 7.8, 15.4 Hz, 1 H), 2.34 (s, 6 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.3 (d, *J* = 8.2 Hz), 140.1 (d, *J* = 13.6 Hz), 138.5, 135.6, 130.7, 130.1, 126.0, 124.6, 121.0 (d, *J* = 4.5 Hz), 112.3 (d, *J* = 7.3 Hz), 21.4; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.64. **HRMS (ESI)** calcd for $C_{22}H_{21}O_3PS$ (M + nH) 397.1022, found 397.1022.

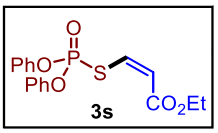
(*E*)-*S*-(oct-1-en-1-yl) *O*,*O*-diphenyl phosphorothioate (3r):



3r

Colourless Liquid, 56.5 mg, 75% yield, R_f = 0.30 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.40 - 7.35 (m, 4 H), 7.34 - 7.28 (m, 4 H), 7.26 - 7.21 (m, 2 H), 6.08 - 6.00 (m, 1 H), 5.99 - 5.91 (m, 1 H), 2.16 - 2.09 (m, 2 H), 1.40 - 1.34 (m, 2 H), 1.33 - 1.25 (m, 6 H), 0.92 - 0.87 (m, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 149.9, (d, *J* = 7.3 Hz), 144.1 (d, *J* = 11.8 Hz), 129.5, 125.4, 120.4 (d, *J* = 5.4 Hz), 111.1 (d, *J* = 7.3 Hz), 32.9, 31.3, 28.4, 28.2, 22.3, 13.8; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 16.51. **HRMS (ESI)** calcd for $C_{20}H_{25}O_3PS$ (M + nH) 377.1335, found 377.1340.

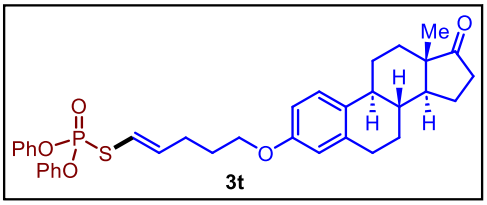
ethyl (*Z*)-3-((diphenoxyphosphoryl)thio)acrylate (3s):



3s

Pale Yellow Liquid, 66 mg, 91% yield, R_f = 0.35 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.41 - 7.35 (m, 5 H), 7.32 - 7.28 (m, 4 H), 7.28 - 7.23 (m, 2 H), 6.17 - 6.11 (m, 1 H), 4.25 - 4.19 (m, 2 H), 1.32 - 1.28 (m, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 165.9, 150.0 (d, *J* = 8.2 Hz), 137.2 (d, *J* = 2.7 Hz), 130.2, 126.2, 120.9 (d, *J* = 4.5 Hz), 119.6 (d, *J* = 8.2 Hz), 61.0, 14.4; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 16.99. **HRMS (ESI)** calcd for $C_{17}H_{17}O_5PS$ (M + nNa) 387.0427, found 387.0432.

***S*-((*E*)-5-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)pent-1-en-1-yl) *O*,*O*-diphenyl phosphorothioate (3t):**

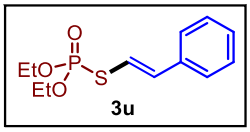


3t

Colourless Liquid, 94 mg, 78% yield, R_f = 0.75 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.37 (t, *J* = 7.8 Hz, 4 H), 7.29 (d, *J* = 8.1 Hz, 4 H), 7.26 - 7.18 (m, 3 H), 6.70 (d, *J* = 8.5 Hz, 1 H), 6.64 (s, 1 H), 6.13 - 6.00 (m, 2 H), 3.92 (t, *J* = 6.1 Hz, 2 H), 2.94 - 2.84 (m, 2 H), 2.51 (dd, *J* = 8.6, 19.0 Hz, 1 H), 2.40 (d, *J* = 9.8 Hz, 1 H), 2.36 - 2.30 (m, 2 H), 2.28 - 2.22 (m, 1 H), 2.19 - 2.11 (m, 1 H), 2.07 (dd, *J* = 5.2, 11.9 Hz, 1 H), 2.03 - 1.95 (m, 2 H), 1.88 - 1.82 (m, 2 H), 1.68 - 1.51 (m, 4 H), 1.50 - 1.38 (m, 2 H), 0.92 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 221.2, 157.1, 150.5 (d, *J* = 8.2 Hz), 143.1 (d, *J* = 12.7 Hz), 138.0, 132.4, 130.1, 126.6, 125.9, 121.0 (d, *J* = 5.4 Hz), 114.8, 112.9

(d, *J* = 7.3 Hz), 112.4, 66.8, 50.7, 48.3, 44.2, 38.6, 36.1, 31.9, 30.0, 29.9, 28.5 (d, *J* = 1.8 Hz), 26.8, 26.2, 21.9, 14.1; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 16.25. **HRMS (ESI)** calcd for $C_{35}H_{39}O_5PS$ (M + nNa) 625.2148, found 625.2122.

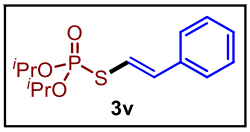
(*E*)-*O*,*O*-diethyl *S*-styryl phosphorothioate (3u):



3u

E:*Z* = 97:3, Pale Yellow Liquid, 53 mg, 97% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.38 - 7.22 (m, 5 H), 6.94 - 6.79 (m, 1 H), 6.66 (dd, *J* = 8.5, 15.6 Hz, 1 H), 4.31 - 4.18 (m, 4 H), 1.38 (t, *J* = 7.1 Hz, 6 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 137.3 (d, *J* = 12.7 Hz) 136.0, 129.0, 128.6, 126.5, 115.0 (d, *J* = 6.4 Hz), 64.3 (d, *J* = 6.4 Hz), 16.3 (d, *J* = 7.3 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 23.00. **HRMS (ESI)** calcd for $C_{12}H_{17}O_3PS$ (M + nH) 273.0709, found 273.0706.

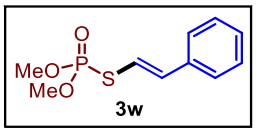
(*E*)-*O*,*O*-diisopropyl *S*-styryl phosphorothioate (3v):



3v

E:*Z* = 97:3, Light Brown Liquid, 54 mg, 90% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.38 - 7.23 (m, 5 H), 6.84 (d, *J* = 15.6 Hz, 1 H), 6.70 (dd, *J* = 8.9, 15.6 Hz, 1 H), 4.83 (td, *J* = 6.2, 8.9 Hz, 2 H), 1.43 - 1.35 (m, 12 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 136.5 (d, *J* = 11.8 Hz), 136.2, 128.9, 128.4, 126.4, 115.9 (d, *J* = 6.4 Hz), 73.4 (d, *J* = 6.4 Hz), 24.1 (d, *J* = 4.5 Hz), 23.8 (d, *J* = 5.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 20.36. **HRMS (ESI)** calcd for $C_{14}H_{21}O_3PS$ (M + nNa) 323.0841, found 323.0829.

(*E*)-*O*,*O*-dimethyl *S*-styryl phosphorothioate (3w):

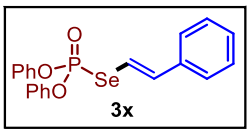


3w

E:*Z* = 97:3, Yellow Liquid, 30.4 mg, 62% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.39 - 7.26 (m, 5 H), 6.89 (d, *J* = 15.6 Hz, 1 H), 6.63 (dd, *J* = 8.4, 15.6 Hz, 1 H), 3.89 (s, 3 H), 3.87 - 3.84 (m, 3 H); **^{13}C NMR (126**

MHz, CHLOROFORM-d) δ = 137.9 (d, *J* = 12.9 Hz), 135.9, 129.0, 128.7, 126.6, 114.2 (d, *J* = 5.4 Hz), 54.4 (d, *J* = 5.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 26.51. **HRMS (ESI)** calcd for $C_{10}H_{13}O_3PS$ (M + nH) 245.0396, found 245.0385.

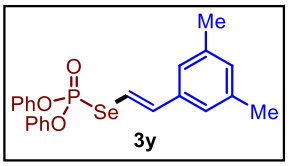
(*E*)-*O*,*O*-diphenyl *Se*-styryl phosphoroselenoate (3x):



3x

Yellow Liquid, 60 mg, 72% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.45 - 7.30 (m, 13 H), 7.30 - 7.24 (m, 2 H), 6.99 - 6.84 (m, 2 H); **^{13}C NMR (126 MHz, CHLOROFORM-d** δ = 150.3 (d, *J* = 8.2 Hz), 141.7 (d, *J* = 11.8 Hz), 136.2 (d, *J* = 1.8 Hz), 130.1, 129.0, 128.9, 126.7, 126.0, 121.1 (d, *J* = 5.4 Hz), 110.3 (d, *J* = 9.1 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 9.75. **HRMS (ESI)** calcd for $C_{20}H_{17}O_3PSe$ (M + nH) 417.0154, found 417.0176.

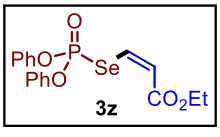
(*E*)-Se-(3,5-dimethylstyryl) *O*,*O*-diphenyl phosphoroselenoate (3y):



3y

Yellow Liquid, 55.5 mg, 63% yield, R_f = 0.35 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.45 - 7.38 (m, 4 H), 7.38 - 7.33 (m, 4 H), 7.30 - 7.25 (m, 2 H), 6.99 - 6.92 (m, 3 H), 6.91 - 6.83 (m, 2 H), 2.33 (s, 6 H); **^{13}C NMR (126 MHz, CHLOROFORM-d** δ = 150.1 (d, *J* = 8.1 Hz), 141.7 (d, *J* = 11.6 Hz), 138.2, 135.9, 130.4, 129.8, 129.5, 125.8, 124.3, 120.9 (d, *J* = 5.8 Hz), 115.3, 109.5 (d, *J* = 8.1 Hz), 21.2; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 10.00. **HRMS (ESI)** calcd for $C_{22}H_{21}O_3PSe$ (M + nH) 445.0467, found 445.0460.

ethyl (*Z*)-3-((diphenoxyphosphoryl)selanyl)acrylate (3z):

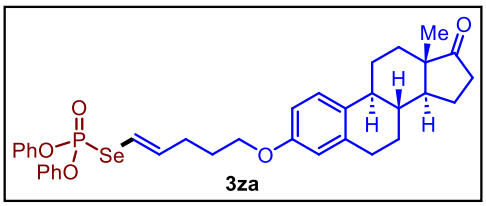


3z

Colourless Liquid, 46 mg, 60% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.88 (dd, *J* = 9.3, 16.3 Hz, 1 H), 7.39 (t, *J* = 7.8 Hz, 4 H), 7.31 (d, *J* = 8.4 Hz, 4 H), 7.28 - 7.23 (m, 2 H), 6.50 (d, *J* = 9.3 Hz, 1 H), 4.23 (q, *J* =

7.2 Hz, 2 H), 1.31 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d** δ = 166.6, 149.5 (d, *J* = 8.5 Hz), 138.1 (d, *J* = 3.6 Hz), 129.7, 125.6 (d, *J* = 1.8 Hz), 120.6 (d, *J* = 4.5 Hz), 120.5 (d, *J* = 5.4 Hz), 60.7, 13.9; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 12.77. **HRMS (ESI)** calcd for $C_{17}H_{17}O_5PSe$ (M + nH) 413.0052, found 413.0041.

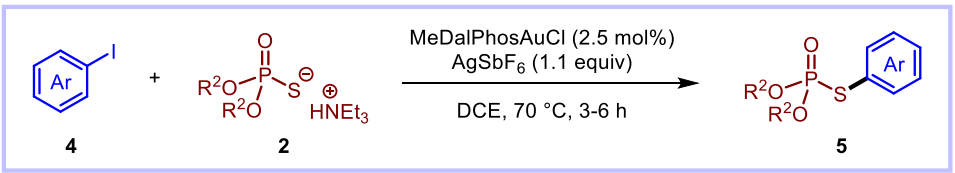
***Se*-((*E*)-5-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)pent-1-en-1-yl) *O*,*O*-diphenyl phosphoroselenoate (3za):**



3za

Pale Yellow Liquid, 99 mg, 76% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.37 (t, *J* = 7.7 Hz, 4 H), 7.30 (d, *J* = 7.9 Hz, 4 H), 7.27 - 7.17 (m, 3 H), 6.70 (dd, *J* = 2.4, 8.5 Hz, 1 H), 6.64 (br. s., 1 H), 6.27 - 6.12 (m, 2 H), 3.92 (t, *J* = 6.1 Hz, 2 H), 2.92 - 2.85 (m, 2 H), 2.54 - 2.48 (m, 1 H), 2.40 (d, *J* = 9.6 Hz, 1 H), 2.34 - 2.24 (m, 3 H), 2.20 - 2.06 (m, 2 H), 2.02 - 1.93 (m, 2 H), 1.85 (m, *J* = 6.7 Hz, 2 H), 1.70 - 1.55 (m, 4 H), 1.50 - 1.39 (m, 2 H), 0.92 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d** δ = 221.1, 157.1, 150.3 (d, *J* = 8.1 Hz), 144.6 (d, *J* = 11.6 Hz), 138.0, 132.3, 130.0, 126.6, 125.9, 121.0 (d, *J* = 4.6 Hz), 114.8, 112.3, 109.6 (d, *J* = 9.2 Hz), 66.8, 50.6, 48.2, 44.2, 38.6, 36.1, 31.8, 31.0, 29.9, 28.4, 26.8, 26.1, 21.8, 14.1; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 10.60. **HRMS (ESI)** calcd for $C_{35}H_{39}O_5PSe$ (M + nH) 651.1776, found 651.1763.

5. General procedure for gold-catalyzed *S*-arylation of phosphorothioate salts:



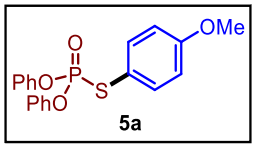
4 **2** **5**

An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the aryl iodide (**4**, 0.2 mmol, 1 equiv), phosphorothioate salt (**2**, 0.2 mmol, 1 equiv), MeDalPhosAuCl (0.005 mmol, 0.025 equiv) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then $AgSbF_6$ (0.22 mmol, 1.1 equiv) was added and allowed to stir at 70 °C for 3-6 h. After completion of the reaction, it was diluted

with DCM (5 mL), filtered through a short pad of celite, concentrated and subsequently purified by silica gel column chromatography to afford the product **5**.

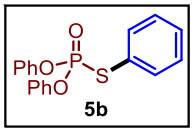
❖ Characterization data:

_S_-(4-methoxyphenyl) _O,O_-diphenyl phosphorothioate (5a):[10]



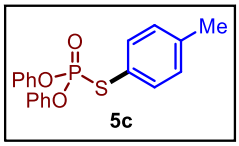
Colourless Liquid, 73.2 mg, 98% yield, R_f = 0.50 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.42 - 7.33 (m, 6 H), 7.26 - 7.17 (m, 6 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 3.82 (s, 3 H).

_O,O,S_-triphenyl phosphorothioate (5b):[10]



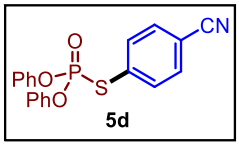
Colourless Liquid, 66 mg, 96% yield, R_f = 0.50 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.54 - 7.50 (m, 2 H), 7.42 - 7.33 (m, 7 H), 7.26 - 7.17 (m, 6 H).

_O,O_-diphenyl _S_-(p-tolyl) phosphorothioate (5c):[11]



Colourless Liquid, 46 mg, 65% yield, R_f = 0.50 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.41 - 7.33 (m, 6 H), 7.26 - 7.20 (m, 6 H), 7.18 - 7.13 (m, 2 H), 2.39 - 2.35 (m, 3 H).

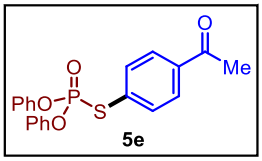
_S_-(4-cyanophenyl) _O,O_-diphenyl phosphorothioate (5d):



10) Sarkar, S.; Kalek, M. *Org. Lett.* **2023**, *25*, 671−675.
11) Chen, X.-Y.; Pu, M.; Cheng, H.-G.; Sperger, T.; Schoenebeck, F. *Angew. Chem. Int. Ed.* **2019**, *58*, 11395–11399.

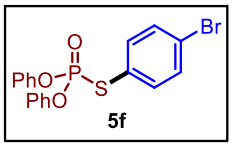
Colourless Liquid, 50 mg, 68% yield, R_f = 0.70 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.62 (s, 4 H), 7.42 - 7.36 (m, 4 H), 7.30 - 7.21 (m, 6 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.0 (d, *J* = 8.2 Hz), 135.2 (d, *J* = 5.4 Hz), 132.7(d, *J* = 1.8 Hz), 132.0 (d, *J* = 7.3 Hz), 130.0, 126.0, 120.4 (d, *J* = 4.5 Hz), 117.8 (d, *J* = 1.8 Hz), 113.2 (d, *J* = 2.8 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 12.61. **HRMS (ESI)** calcd for $C_{19}H_{14}NO_3PS$ (M + nH) 368.0505, found 368.0482.

***S*-(4-acetylphenyl) *O,O*-diphenyl phosphorothioate (5e):**



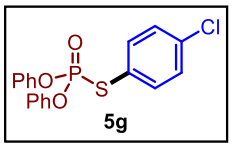
Colourless Liquid, 49 mg, 64% yield, R_f = 0.60 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.99 - 7.84 (m, 2 H), 7.70 - 7.57 (m, 2 H), 7.43 - 7.34 (m, 4 H), 7.31 - 7.20 (m, 6 H), 2.69 - 2.55 (m, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 197.4, 150.4 (d, *J* = 8.2 Hz), 137.7 (d, *J* = 3.6 Hz), 135.1 (d, *J* = 5.4 Hz), 131.6 (d, *J* = 7.3 Hz), 130.1, 129.3 (d, *J* = 1.8 Hz), 126.0, 120.7 (d, *J* = 4.5 Hz), 26.9; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 13.46. **HRMS (ESI)** calcd for $C_{20}H_{17}O_4PS$ (M + nH) 385.0658, found 385.0658.

***S*-(4-bromophenyl) *O,O*-diphenyl phosphorothioate (5f):**[10]



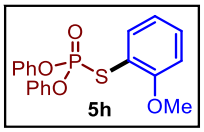
Colourless Liquid, 52 mg, 62% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.47 (d, *J* = 8.5 Hz, 2 H), 7.40 - 7.33 (m, 6 H), 7.26 - 7.18 (m, 6 H).

***S*-(4-chlorophenyl) *O,O*-diphenyl phosphorothioate (5g):**[11]



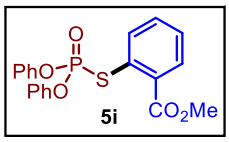
Pale Yellow Liquid, 54 mg, 72% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.44 - 7.40 (m, 2 H), 7.39 - 7.34 (m, 4 H), 7.33 - 7.29 (m, 2 H), 7.26 - 7.19 (m, 6 H).

***S*-(2-methoxyphenyl) *O*,*O*-diphenyl phosphorothioate (5h):**[11]



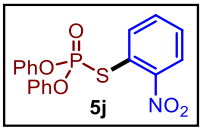
Colourless Liquid, 62.8 mg, 84% yield, R_f = 0.75 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.59 - 7.51 (m, 1 H), 7.42 - 7.33 (m, 5 H), 7.30 - 7.17 (m, 6 H), 6.94 (s, 1 H), 6.89 (d, *J* = 8.4 Hz, 1 H), 3.67 (s, 3 H).

methyl 2-((diphenoxyphosphoryl)thio)benzoate (5i):



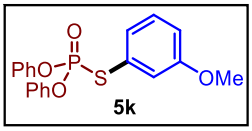
Pale Yellow Liquid, 72 mg, 90% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.89 (d, *J* = 7.8 Hz, 1 H), 7.85 (d, *J* = 7.6 Hz, 1 H), 7.50 - 7.46 (m, 1 H), 7.44 (d, *J* = 7.5 Hz, 1 H), 7.36 - 7.31 (m, 4 H), 7.24 - 7.17 (m, 6 H), 3.78 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 166.3 (d, *J* = 1.8 Hz), 150.0 (d, *J* = 8.2 Hz), 135.8 (d, *J* = 5.4 Hz), 134.5 (d, *J* = 6.4 Hz), 131.8 (d, *J* = 1.8 Hz), 130.8, 129.5, 128.6 (d, *J* = 1.8 Hz), 126.3 (d, *J* = 7.3 Hz), 125.3, 120.2 (d, *J* = 4.5 Hz), 52.1; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 14.56. **HRMS (ESI)** calcd for $C_{20}H_{17}O_5PS$ (M + nH) 401.0607, found 401.0590.

***S*-(2-nitrophenyl) *O*,*O*-diphenyl phosphorothioate (5j):**



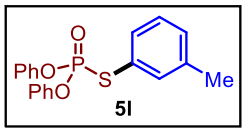
Yellow Liquid, 68 mg, 88% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 8.07 - 8.00 (m, 1 H), 7.92 (d, *J* = 8.1 Hz, 1 H), 7.60 - 7.55 (m, 1 H), 7.53 - 7.49 (m, 1 H), 7.39 - 7.32 (m, 4 H), 7.27 - 7.17 (m, 6 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 151.5, 150.0 (d, *J* = 9.1 Hz), 136.5 (d, *J* = 5.4 Hz), 133.0 (d, *J* = 1.8 Hz), 129.9, 129.7 (d, *J* = 2.7 Hz), 126.0, 125.5, 121.8 (d, *J* = 6.4 Hz), 120.4 (d, *J* = 5.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 12.70. **HRMS (ESI)** calcd for $C_{18}H_{14}NO_5PS$ (M + nH) 388.0403, found 388.0391.

***S*-(3-methoxyphenyl) *O*,*O*-diphenyl phosphorothioate (5k):**



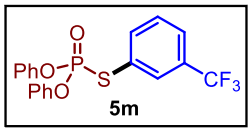
Pale Yellow Liquid, 60 mg, 81% yield, R_f = 0.75 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.40 - 7.35 (m, 4 H), 7.30 - 7.21 (m, 7 H), 7.13 (d, *J* = 7.6 Hz, 1 H), 7.07 - 7.03 (m, 1 H), 6.96 (d, *J* = 8.2 Hz, 1 H), 3.76 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 159.6 (d, *J* = 2.7 Hz), 150.1 (d, *J* = 8.2 Hz), 129.9 (d, *J* = 2.7 Hz), 129.5, 127.1 (d, *J* = 5.4 Hz), 125.5 (d, *J* = 7.3 Hz), 125.3, 120.2 (d, *J* = 5.4 Hz), 119.7 (d, *J* = 5.4 Hz), 115.8 (d, *J* = 3.6 Hz), 55.1; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 14.65. **HRMS (ESI)** calcd for $C_{19}H_{17}O_4PS$ (M + nH) 373.0658, found 373.0654.

***O,O*-diphenyl *S*-(m-tolyl) phosphorothioate (5l):**



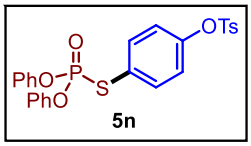
Colourless Liquid, 63.2 mg, 89% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.38 - 7.34 (m, 4 H), 7.32 (d, *J* = 7.5 Hz, 1 H), 7.26 - 7.19 (m, 8 H), 2.31 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.7 (d, *J* = 9.1 Hz), 139.6 (d, *J* = 2.7 Hz), 136.1 (d, *J* = 5.4 Hz), 132.5 (d, *J* = 5.4 Hz), 130.7 (d, *J* = 3.6 Hz), 130.0, 129.5 (d, *J* = 2.7 Hz), 125.7, 124.7 (d, *J* = 7.3 Hz), 120.7 (d, *J* = 4.5 Hz), 21.4; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.01. **HRMS (ESI)** calcd for $C_{19}H_{17}O_3PS$ (M + nH) 357.0709, found 357.0729.

***O,O*-diphenyl *S*-(3-(trifluoromethyl)phenyl) phosphorothioate (5m):**[10]



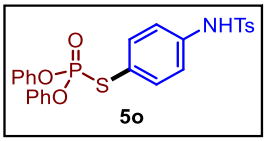
Colourless Liquid, 49.8 mg, 61% yield, R_f = 0.45 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.72 (d, *J* = 7.8 Hz, 1 H), 7.69 - 7.62 (m, 2 H), 7.50 - 7.45 (m, 1 H), 7.40 - 7.35 (m, 4 H), 7.27 - 7.19 (m, 6 H).

4-((diphenoxyphosphoryl)thio)phenyl 4-methylbenzenesulfonate (5n):



White Solid, 86.8 mg, 85% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.74 - 7.68 (m, *J* = 8.2 Hz, 2 H), 7.42 (dd, *J* = 2.1, 8.7 Hz, 2 H), 7.38 - 7.30 (m, 6 H), 7.26 - 7.21 (m, 2 H), 7.17 (d, *J* = 7.8 Hz, 4 H), 7.00 - 6.94 (m, *J* = 8.5 Hz, 2 H), 2.45 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.8 (d, *J* = 3.6 Hz), 150.5, 150.4, 146.0, 136.8 (d, *J* = 5.4 Hz), 132.3 , 130.1 (d, *J* = 1.8 Hz), 128.7, 126.0, 124.3 (d, *J* = 7.3 Hz), 123.7 (d, *J* = 1.8 Hz), 120.6 (d, *J* = 5.4 Hz), 22.0; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 13.81. **HRMS (ESI)** calcd for $C_{25}H_{21}O_6PS_2$ (M + nH) 513.0590, found 513.0569.

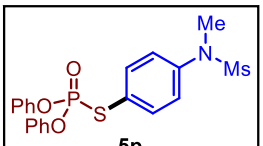
***S*-(4-((4-methylphenyl)sulfonamido)phenyl) *O*,*O*-diphenyl phosphorothioate (5o):**



5o

White Solid, 81 mg, 79% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.86 (s, 1 H), 7.69 - 7.63 (m, *J* = 8.2 Hz, 2 H), 7.35 - 7.30 (m, 4 H), 7.27 - 7.15 (m, 10 H), 6.99 - 6.94 (m, *J* = 8.5 Hz, 2 H), 2.35 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.2 (d, *J* = 8.2 Hz), 144.0, 138.8 (d, *J* = 3.6 Hz), 136.3 (d, *J* = 4.5 Hz), 136.1, 129.8, 129.6, 127.2, 125.7, 121.0 (d, *J* = 2.7 Hz), 120.5 (d, *J* = 5.4 Hz), 119.3 (d, *J* = 8.2 Hz), 21.5; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.23. **HRMS (ESI)** calcd for $C_{25}H_{22}NO_5PS_2$ (M + nH) 512.0750, found 512.0721.

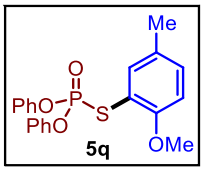
***S*-(4-(N-methylmethylsulfonamido)phenyl) *O*,*O*-diphenyl phosphorothioate (5p):**



5p

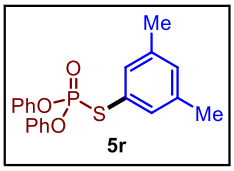
Colourless Liquid, 75.6 mg, 84% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.51 (d, *J* = 7.5 Hz, 2 H), 7.40 - 7.32 (m, 6 H), 7.26 - 7.18 (m, 6 H), 3.32 (s, 3 H), 2.84 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.5 (d, *J* = 8.2 Hz), 143.0 (d, *J* = 3.6 Hz), 136.4 (d, *J* = 5.4 Hz), 130.1, 126.5 (d, *J* = 1.8 Hz), 126.0, 123.8 (d, *J* = 7.3 Hz), 120.7 (d, *J* = 5.4 Hz), 37.9, 35.8; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 14.25. **HRMS (ESI)** calcd for $C_{20}H_{20}NO_5PS_2$ (M + nNa) 472.0413, found 472.0383.

***S*-(2-methoxy-5-methylphenyl) *O*,*O*-diphenyl phosphorothioate (5q):**



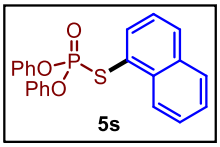
Pale Yellow Liquid, 54.8 mg, 71% yield, R_f = 0.70 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.40 - 7.34 (m, 4 H), 7.28 (m, 5 H), 7.24 - 7.20 (m, 2 H), 7.17 (d, *J* = 8.1 Hz, 1 H), 6.78 (d, *J* = 8.2 Hz, 1 H), 3.64 (s, 3 H), 2.25 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 157.5 (d, *J* = 5.4 Hz), 150.3(d, *J* = 8.2 Hz), 137.6 (d, *J* = 5.4 Hz), 131.8 (d, *J* = 3.6 Hz), 130.3 (d, *J* = 3.6 Hz), 129.3, 125.0, 120.2 (d, *J* = 5.4 Hz), 112.0 (d, *J* = 8.2 Hz), 111.1 (d, *J* = 3.6 Hz), 55.4, 19.9; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 14.86. **HRMS (ESI)** calcd for $C_{20}H_{19}O_4PS$ (M + nH) 387.0814, found 387.0804.

***S*-(3,5-dimethylphenyl) *O,O*-diphenyl phosphorothioate (5r):**[11]



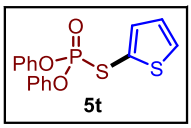
Pale Yellow Liquid, 71.6 mg, 97% yield, R_f = 0.45 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.39 - 7.34 (m, 4 H), 7.26 - 7.20 (m, 6 H), 7.07 (s, 2 H), 7.01 (s, 1 H), 2.27 (s, 6 H).

***S*-(naphthalen-1-yl) *O,O*-diphenyl phosphorothioate (5s):**[11]



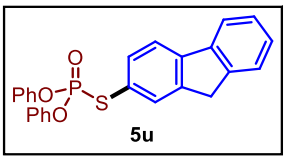
Colourless Liquid, 71.2 mg, 91% yield, R_f = 0.60 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 8.28 (d, *J* = 8.4 Hz, 1 H), 7.94 (d, *J* = 7.5 Hz, 1 H), 7.86 (t, *J* = 6.4 Hz, 2 H), 7.51 (d, *J* = 7.2 Hz, 1 H), 7.49 - 7.42 (m, 2 H), 7.33 - 7.25 (m, 4 H), 7.22 - 7.15 (m, 2 H), 7.13 (d, *J* = 7.8 Hz, 4 H).

***O,O*-diphenyl *S*-(thiophen-2-yl) phosphorothioate (5t):**



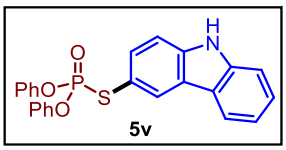
Yellow Liquid, 47.4 mg, 68% yield, R_f = 0.55 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.52 - 7.48 (m, 1 H), 7.43 - 7.36 (m, 4 H), 7.32 - 7.22 (m, 6 H), 7.22 - 7.17 (m, 1 H), 7.05 (dd, *J* = 3.8, 5.2 Hz, 1 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.2 (d, *J* = 8.2 Hz), 137.2 (d, *J* = 7.3 Hz), 131.9 (d, *J* = 4.5 Hz), 129.8, 127.9 (d, *J* = 3.6 Hz), 125.6, 121.1 (d, *J* = 10 Hz), 120.4 (d, *J* = 4.5 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 12.32. **HRMS (ESI)** calcd for $C_{16}H_{13}O_3PS_2$ (M + nH) 349.0116, found 349.0119.

***S*-(9H-fluoren-2-yl) *O*,*O*-diphenyl phosphorothioate (5u):**



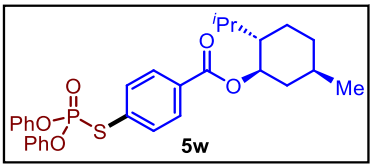
Colourless Liquid, 75.2 mg, 87% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.82 (d, *J* = 7.5 Hz, 1 H), 7.76 (d, *J* = 7.9 Hz, 1 H), 7.67 - 7.63 (m, 1 H), 7.60 - 7.56 (m, 1 H), 7.54 (s, 1 H), 7.43 (s, 1 H), 7.42 - 7.36 (m, 5 H), 7.30 - 7.21 (m, 6 H), 3.89 (s, 2 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.4 (d, *J* = 8.2 Hz), 144.3 (d, *J* = 2.7 Hz), 143.4, 143.3 (d, *J* = 3.6 Hz), 140.4, 134.0 (d, *J* = 5.4 Hz), 132.1 (d, *J* = 5.4 Hz), 129.7, 127.6, 127.0, 125.5, 125.1, 122.1 (d, *J* = 8.2 Hz), 120.5 (d, *J* = 2.7 Hz), 120.5 (d, *J* = 5.4 Hz), 120.4, 36.7; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 15.10. **HRMS (ESI)** calcd for $C_{25}H_{19}O_3PS$ (M + nH) 431.0865, found 431.0855.

***S*-(9H-carbazol-3-yl) *O*,*O*-diphenyl phosphorothioate (5v):**



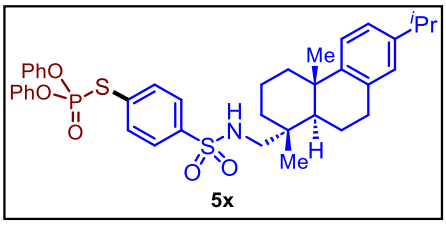
Light Pink Liquid, 85.2 mg, 99% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 8.98 (br. s., 1 H), 7.96 (br. s., 1 H), 7.79 (d, *J* = 7.6 Hz, 1 H), 7.43 - 7.36 (m, 5 H), 7.36 - 7.30 (m, 5 H), 7.30 - 7.24 (m, 3 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 6.94 (d, *J* = 8.4 Hz, 1 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 150.2 (d, *J* = 9.1 Hz), 139.9 (d, *J* = 1.8 Hz), 140.0, 132.1 (d, *J* = 4.5 Hz), 129.6, 127.8 (d, *J* = 5.4 Hz), 126.0, 125.3, 123.8 (d, *J* = 2.7 Hz), 121.8, 120.4 (d, *J* = 5.4 Hz), 119.8, 119.3, 111.6, 110.7; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 17.26. **HRMS (ESI)** calcd for $C_{24}H_{18}NO_3PS$ (M + nH) 432.0818, found 432.0813.

(1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl 4-((diphenoxyphosphoryl)thio)benzoate (5w):



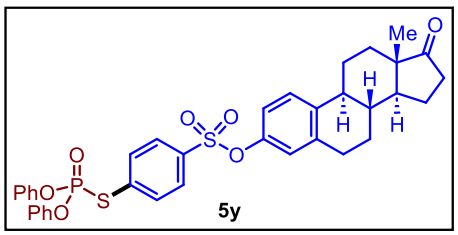
Colourless liquid, 82 mg, 78% yield, R_f = 0.40 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 8.00 (d, *J* = 8.2 Hz, 2 H), 7.58 (dd, *J* = 1.9, 8.5 Hz, 2 H), 7.41 - 7.33 (m, 4 H), 7.27 - 7.19 (m, 6 H), 4.95 (dt, *J* = 4.4, 10.9 Hz, 1 H), 2.13 (d, *J* = 11.7 Hz, 1 H), 1.94 (dt, *J* = 2.6, 6.9 Hz, 1 H), 1.75 (d, *J* = 11.6 Hz, 2 H), 1.60 - 1.52 (m, 2 H), 1.17 - 1.06 (m, 2 H), 0.94 (dd, *J* = 5.0, 6.7 Hz, 7 H), 0.81 (d, *J* = 7.0 Hz, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 165.4, 150.4 (d, *J* = 9.1 Hz), 134.9 (d, *J* = 5.4 Hz), 132.0 (d, *J* = 2.7 Hz), 131.0 (d, *J* = 8.2 Hz), 130.6 (d, *J* = 2.7 Hz), 130.1, 126.0, 120.7 (d, *J* = 5.4 Hz), 75.6, 47.5, 41.1, 34.5, 31.7, 26.7, 23.8, 22.2, 21.0, 16.7; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 13.63. **HRMS (ESI)** calcd for $C_{29}H_{33}O_5PS$ (M + nH) 525.1859, found 525.1832.

***S*-(4-(*N*-(((1*R*, 4*aS*, 10*aR*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)sulfamoyl)phenyl) *O*,*O*-diphenyl phosphorothioate (5x):**



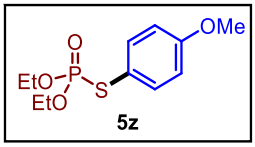
White Solid, 126 mg, 91% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.79 (d, *J* = 8.4 Hz, 2 H), 7.67 - 7.59 (m, 2 H), 7.43 - 7.34 (m, 4 H), 7.31 - 7.20 (m, 6 H), 7.15 (d, *J* = 8.1 Hz, 1 H), 7.00 (d, *J* = 7.9 Hz, 1 H), 6.89 (s, 1 H), 4.72 (t, *J* = 6.8 Hz, 1 H), 2.92 - 2.79 (m, 4 H), 2.70 (dd, *J* = 7.2, 12.7 Hz, 1 H), 2.27 (d, *J* = 13.0 Hz, 1 H), 1.76 - 1.63 (m, 5 H), 1.53 - 1.47 (m, 1 H), 1.39 - 1.32 (m, 2 H), 1.24 (d, *J* = 7.0 Hz, 6 H), 1.20 (s, 3 H), 0.91 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 149.8 (d, *J* = 8.2 Hz), 146.5, 145.4, 140.9 (d, *J* = 2.7 Hz), 134.9 (d, *J* = 6.4 Hz), 134.2, 130.8 (d, *J* = 8.2 Hz), 129.7, 127.4, 126.5, 125.6, 123.8, 123.6, 120.1 (d, *J* = 4.5 Hz), 53.6, 44.6, 37.9, 37.1, 36.7, 35.5, 33.1, 29.5, 24.9, 23.7 (d, *J* = 6.4 Hz), 18.4, 18.2, 18.1; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 13.02. **HRMS (ESI)** calcd for $C_{38}H_{44}NO_5PS_2$ (M + nNa) 712.2291, found 712.2274.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta-[a]phenanthren-3-yl 4-((diphenoxyphosphoryl)thio)benzenesulfonate (5y):



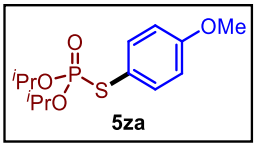
Colourless Liquid, 55.8 mg, 42% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 60/40); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.80 (d, *J* = 8.5 Hz, 2 H), 7.69 - 7.63 (m, 2 H), 7.40 - 7.33 (m, 4 H), 7.29 - 7.14 (m, 7 H), 6.80 - 6.74 (m, 1 H), 6.71 - 6.65 (m, 1 H), 2.83 (dd, *J* = 4.6, 9.2 Hz, 2 H), 2.49 (d, *J* = 8.9 Hz, 1 H), 2.32 (br. s., 1 H), 2.16 (d, *J* = 9.2 Hz, 1 H), 2.05 (br. s., 1 H), 2.00 - 1.93 (m, 2 H), 1.66 - 1.57 (m, 3 H), 1.52 - 1.44 (m, 3 H), 0.91 - 0.88 (m, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 220.3, 149.8 (d, *J* = 8.17 Hz), 147.0, 138.8, 138.4, 136.2 (d, *J* = 2.72 Hz), 134.7 (d, *J* = 5.45 Hz), 133.2 (d, *J* = 8.09 Hz), 129.7, 128.8, 126.4, 125.8, 122.0, 120.1 (d, *J* = 4.54 Hz), 118.8, 50.1, 47.6, 43.8, 37.5, 35.5, 31.2, 29.0, 25.8, 25.4, 21.3, 13.5; **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 12.42. **HRMS (ESI)** calcd for $C_{36}H_{35}O_7PS_2$ (M + nH) 675.1635, found 675.1608.

***O,O*-diethyl *S*-(4-methoxyphenyl) phosphorothioate (5z):**



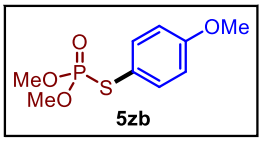
Yellow Liquid, 21 mg, 38% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.48 (d, *J* = 7.0 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 4.24 - 4.13 (m, 4 H), 3.81 (s, 3 H), 1.32 (t, *J* = 7.0 Hz, 6 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 160.5 (d, *J* = 2.7 Hz), 136.3 (d, *J* = 4.5 Hz), 116.6 (d, *J* = 7.3 Hz), 115.0 (d, *J* = 2.7 Hz), 63.9 (d, *J* = 6.4 Hz), 55.4, 16.0 (d, *J* = 7.3 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 23.60. **HRMS (ESI)** calcd for $C_{24}H_{18}NO_3PS$ (M + nH) 277.0658, found 277.0642.

***O,O*-diisopropyl *S*-(4-methoxyphenyl) phosphorothioate (5za):**



Brown Liquid, 44.4 mg, 73% yield, R_f = 0.80 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.50 (dd, *J* = 2.0, 8.9 Hz, 2 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 4.78 - 4.71 (m, 2 H), 3.80 (s, 3 H), 1.32 (d, *J* = 6.1 Hz, 6 H), 1.27 (d, *J* = 6.1 Hz, 6 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 160.5 (d, *J* = 2.7 Hz), 136.4 (d, *J* = 5.4 Hz), 117.5 (d, *J* = 7.3 Hz), 115.0 (d, *J* = 1.8 Hz), 73.4 (d, *J* = 6.4 Hz), 55.6, 24.1 (d, *J* = 4.5 Hz), 23.8 (d, *J* = 5.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 21.20. **HRMS (ESI)** calcd for $C_{13}H_{21}O_4PS$ (M + nNa) 327.0790, found 327.0763.

***S*-(4-methoxyphenyl) *O*,*O*-dimethyl phosphorothioate (5zb):**



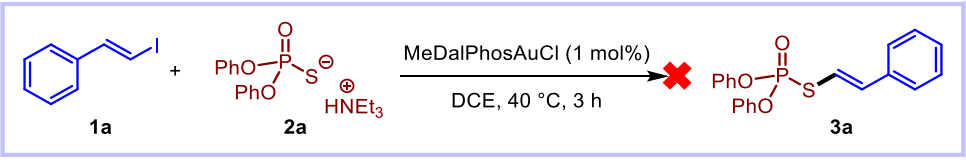
5zb

Yellow Liquid, 35 mg, 70% yield, R_f = 0.90 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.47 (dd, *J* = 2.1, 8.9 Hz, 2 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 3.81 (s, 3 H); **^{13}C NMR (126 MHz, CHLOROFORM-d)** δ = 160.8 (d, *J* = 2.7 Hz), 136.6 (d, *J* = 4.5 Hz), 116.3 (d, *J* = 8.2 Hz), 115.3 (d, *J* = 1.8 Hz), 55.6, 54.4 (d, *J* = 6.4 Hz); **^{31}P NMR (202 MHz, CHLOROFORM-d)** δ = 26.91. **HRMS (ESI)** calcd for $C_9H_{13}O_4PS$ (M + nNa) 271.0164, found 271.0160.

6. Mechanistic investigations

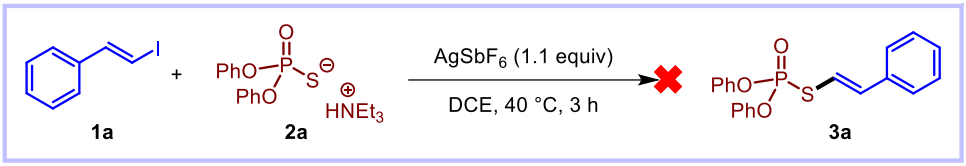
6.1. Control experiments:

A) For *S*-alkenylation of phosphorothioates



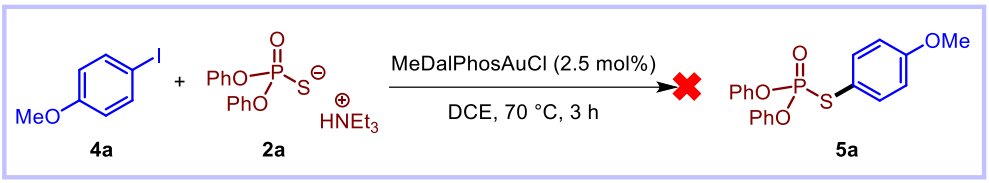
1a **2a** **3a**

An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with (2-iodovinyl)benzene (**1a**, 0.2 mmol, 1 equiv), *O*,*O*-diphenyl phosphorothioate (**2a**, 0.2 mmol, 1 equiv), MeDalPhosAuCl (0.002 mmol, 0.01 equiv) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at 40 °C for 3 h. In this case, no conversion was observed, which suggests the requirement of silver salt for the formation of the desired product.

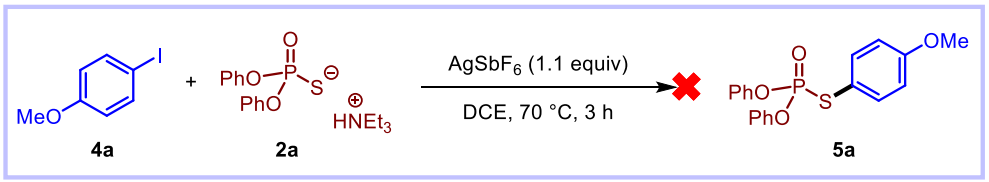


An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with (2-iodovinyl)benzene (**1a**, 0.2 mmol, 1 equiv), *O*,*O*-diphenyl phosphorothioate (**2a**, 0.2 mmol, 1 equiv), $AgSbF_6$ (0.22 mmol, 1.1 equiv) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at 40 °C for 3 h. In this case, no conversion was observed, which suggests the requirement of gold catalyst (MeDalPhosAuCl) for the formation of product.

B) For *S*-arylation of phosphorothioates



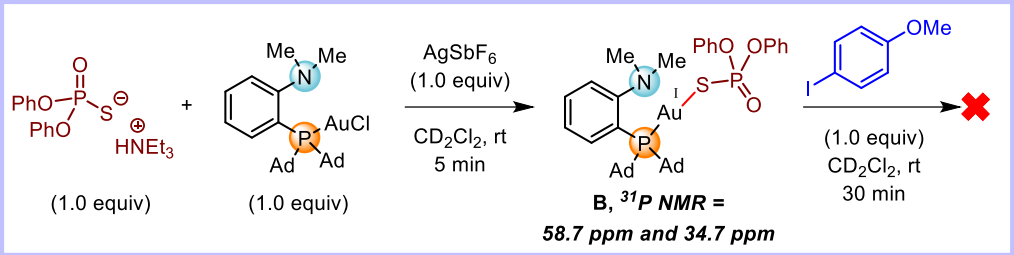
An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with 4-iodoanisole (**4a**, 0.2 mmol, 1 equiv), *O*,*O*-diphenyl phosphorothioate (**2a**, 0.2 mmol, 1 equiv), MeDalPhosAuCl (0.005 mmol, 0.025 equiv) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at 70 °C for 3 h. In this case, no conversion was observed, which suggests the requirement of silver salt for the formation of the desired product.



An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with 4-iodoanisole (**4a**, 0.2 mmol, 1 equiv), *O*,*O*-diphenyl phosphorothioate (**2a**, 0.2 mmol, 1 equiv), $AgSbF_6$ (0.22 mmol, 1.1 equiv) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at 70 °C for 3 h. In this case, no conversion was observed, which suggests the requirement of gold catalyst (MeDalPhosAuCl) for the formation of product.

6.2. NMR Studies:

A) ^{31}P NMR study for investigating catalytic activity of MeDalPhosAuSPO(OPh)$_2$



An oven-dried screw-cap reaction vial, equipped with a magnetic stir bar, was loaded with *O*,*O*-diphenyl phosphorothioate (0.03 mmol, 1.0 equiv), $AgSbF_6$ (0.03 mmol, 1.0 equiv) and CD_2Cl_2 (0.4 mL) and allowed to stir at room temperature. ^{31}P NMR analysis showed one peak at 34.5 ppm which resembles to the AgSPO(OPh)$_2$ complex **A**. In another vial, MeDalPhosAuCl (0.03 mmol, 1.0 equiv) was dissolved in CD_2Cl_2 (0.3 mL). The prepared solution was added to the vial at −78 °C by using a plastic syringe equipped with stainless steel needle. The reaction mixture was then allowed to stir at room temperature for 5 min and ^{31}P NMR was monitored by withdrawing an aliquot of 0.4 mL. Two peaks at 58.7 ppm and 34.7 ppm were observed which resemble to the MeDalPhosAuSPO(OPh)$_2$ complex **B**. The formation of both silver and gold complexes (**A** and **B** respectively) has been characterised by mass spectroscopic analysis as well. Next, 4-iodoanisole (0.03 mmol, 1.0 equiv) was dissolved in CD_2Cl_2 (0.3 mL) and was added to the vial by using a plastic syringe equipped with stainless steel needle. The reaction mixture was stirred for 30 minutes and ^{31}P NMR was monitored. No new peak corresponding to the oxidative addition of gold complex with 4-iodoanisole was observed. This clearly indicates that the MeDalPhosAuSPO(OPh)$_2$ complex **B** is catalytically inactive.

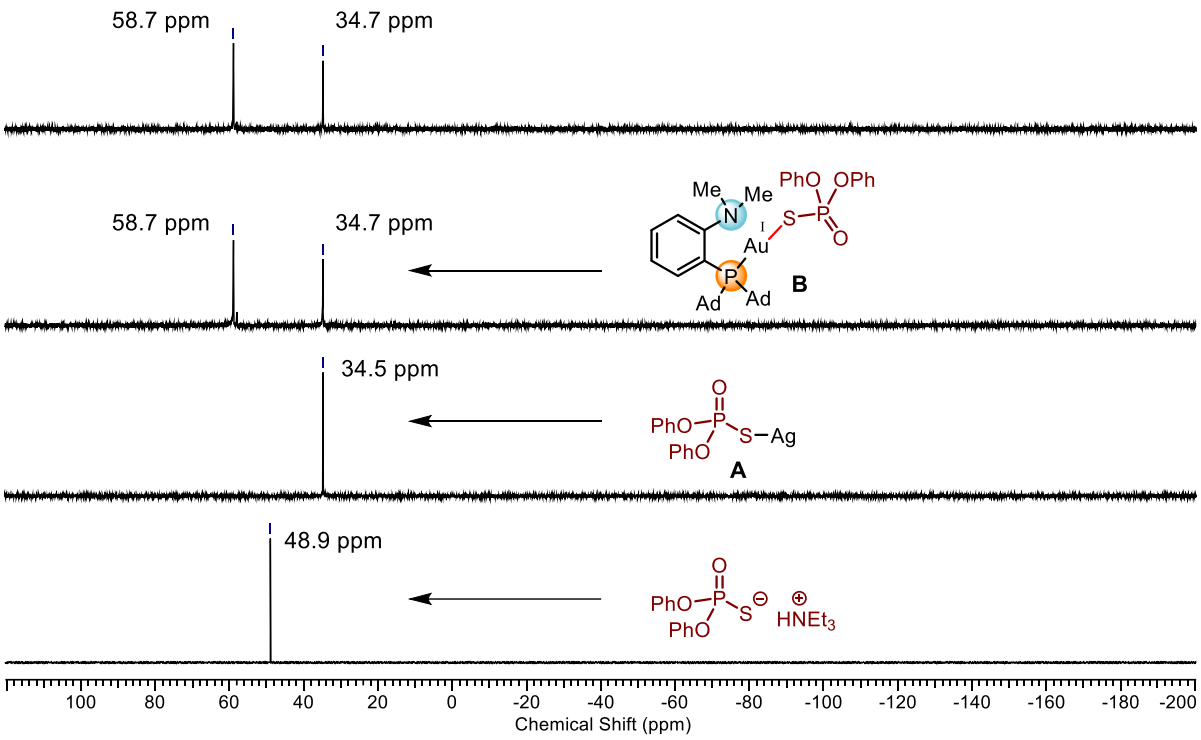
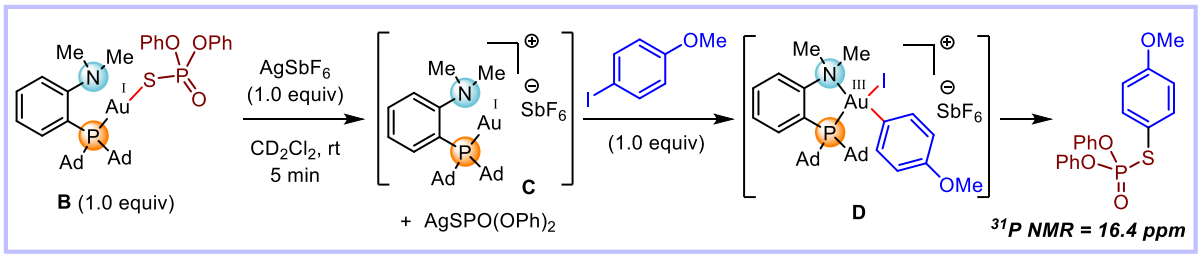


Figure 1: ^{31}P NMR spectrum for the investigation of catalytic activity of complex **B**

B) Activation of MeDalPhosAuSPO(OPh)$_2$ by AgSbF$_6$



An oven-dried screw-cap reaction vial, equipped with a magnetic stir bar, was loaded with MeDalPhosAuSPO(OPh)$_2$ complex (0.03 mmol, 1.0 equiv), $AgSbF_6$ (0.03 mmol, 1.0 equiv) and CD_2Cl_2 (0.3 mL) and allowed to stir at room temperature for 5 min. In another vial, 4-iodoanisole (**4a**, 0.03 mmol, 1.0 equiv) was dissolved in CD_2Cl_2 (0.3 mL). The prepared solution was added to the vial at −78 °C by using a plastic syringe equipped with stainless steel needle. The reaction mixture was then allowed to stir at room temperature for 15 min and ^{31}P NMR was monitored by withdrawing an aliquot of 0.4 mL. One peak at 16.4 ppm was observed which corresponds to the desired product **5a**. This indicates that $AgSbF_6$ is capable of generating cationic gold complex which would then undergo oxidative addition with aryl iodide and subsequent transmetalation to deliver the desired product. The detection of Au(III) intermediates **C** and **D** was not possible probably because of the rapid reaction kinetics.

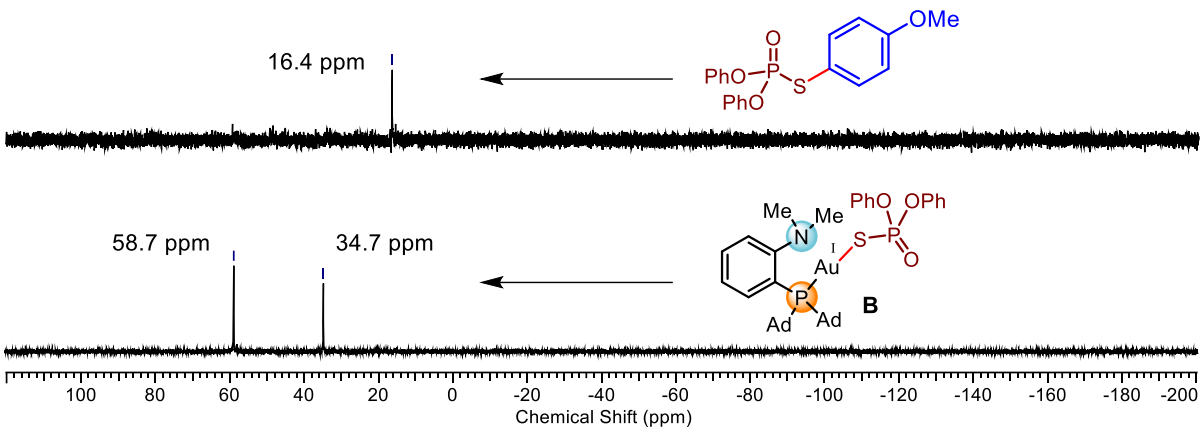
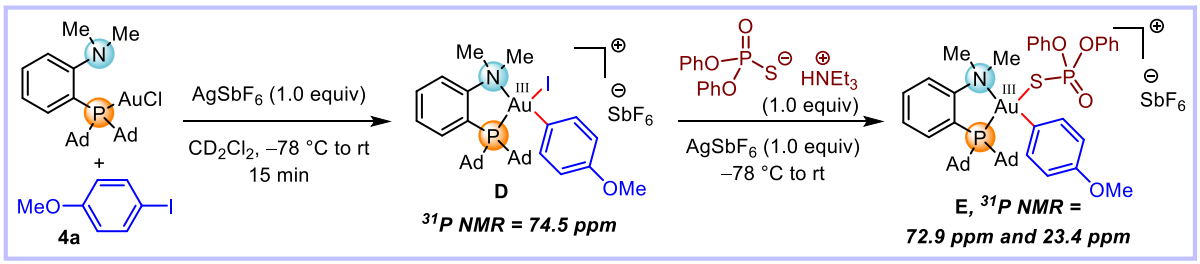


Figure 2: ^{31}P NMR spectrum for the activation of complex **B** by $AgSbF_6$

C) ^{31}P NMR studies to determine intermediates D and E:



An oven-dried screw-cap reaction vial, equipped with a magnetic stir bar, was loaded with $AgSbF_6$ (0.03 mmol, 1.0 equiv) and CD_2Cl_2 (0.3 mL) and allowed to stir at −78 °C. In another vial, MeDalPhosAuCl (0.03 mmol, 1 equiv) and 4-iodoanisole (**4a**, 0.033 mmol, 1.0 equiv) were dissolved in CD_2Cl_2 (0.3 mL). The prepared solution was added to the vial at −78 °C by using a plastic syringe equipped with stainless steel needle. The reaction mixture was then allowed to stir at room temperature for 15 min and ^{31}P NMR was monitored by withdrawing an aliquot of 0.4 mL. One peak appeared at 74.5 ppm which resembles the oxidative addition of aryl iodide with MeDalPhosAuCl (**intermediate D**) (Figure 1). After that, the reaction mixture was again kept at −78 °C and stirred for 2 min. In another vial, $AgSbF_6$ (0.03 mmol, 1.0 equiv) and *O,O*-diphenyl phosphorothioate (0.03 mmol, 1.0 equiv) were dissolved in CD_2Cl_2 (0.3 mL). The prepared solution was added to the reaction mixture and allowed to stir at room temperature. ^{31}P NMR was monitored by withdrawing an aliquot of 0.4 mL every time at different time intervals (Figure 2). After ~30 seconds, the oxidative addition peak of the gold complex at 74.5 ppm disappears completely and two new peaks (doublets with *J* value of 10 Hz) appeared at 72.9 ppm and 23.4 ppm which resembles with the Au(III) **intermediate E**. Next, after stirring for 5 mins, a peak at 16.4 ppm appears predominantly which resembles to

the corresponding product and the peaks corresponding to intermediate C disappears completely.

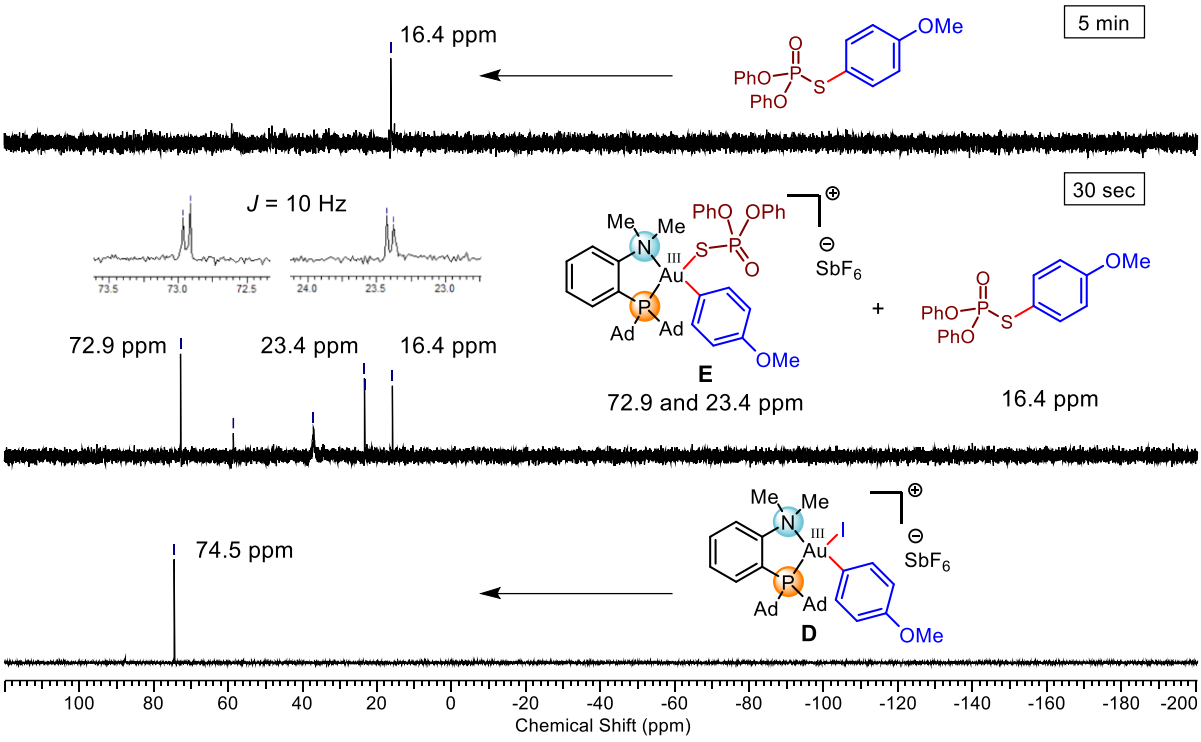
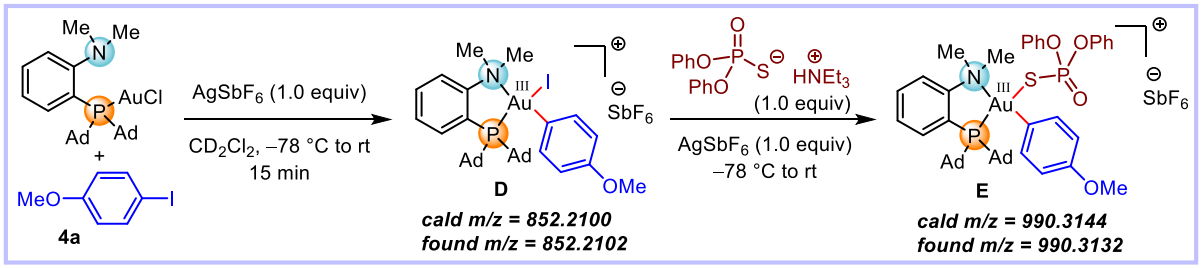


Figure 3: ^{31}P NMR spectrum for the identification of Au(III)-aryl intermediate **D** and **E**.

6.3. Mass spectrometry studies:

Detection of Au(III)-aryl intermediates D and E



An oven-dried screw-cap reaction vial, equipped with a magnetic stir bar, was loaded with $AgSbF_6$ (0.03 mmol, 1.0 equiv) and DCM (0.3 mL) and allowed to stir at −78 °C. In another vial, MeDalPhosAuCl (0.03 mmol, 1.0 equiv) and 4-iodoanisole (**1a**, 0.03 mmol, 1.0 equiv) were dissolved in DCM (0.3 mL). The prepared solution was added to the vial at −78 °C by using a plastic syringe equipped with stainless steel needle. The reaction mixture was then allowed to stir at room temperature for 15 minutes. An aliquot (40 µL) of the reaction mixture was taken and diluted in 1:10 ratio with acetonitrile for mass spectrometric analysis. The

desired peak at m/z 852.2102 corresponding to **intermediate D** was detected in ESI-HRMS (Figure 3). After that, $AgSbF_6$ (0.03 mmol, 1.0 equiv) and *O*,*O*-diphenyl phosphorothioate (0.03 mmol, 1.0 equiv) were added to the reaction mixture and allowed to stir at room temperature for 3 hours. An aliquot (40 μL) of the reaction mixture was taken and diluted in 1:10 ratio with acetonitrile for mass spectrometric analysis. The desired peak at m/z 990.3132 corresponds to **intermediate E** which was detected in ESI-HRMS (Figure 3).

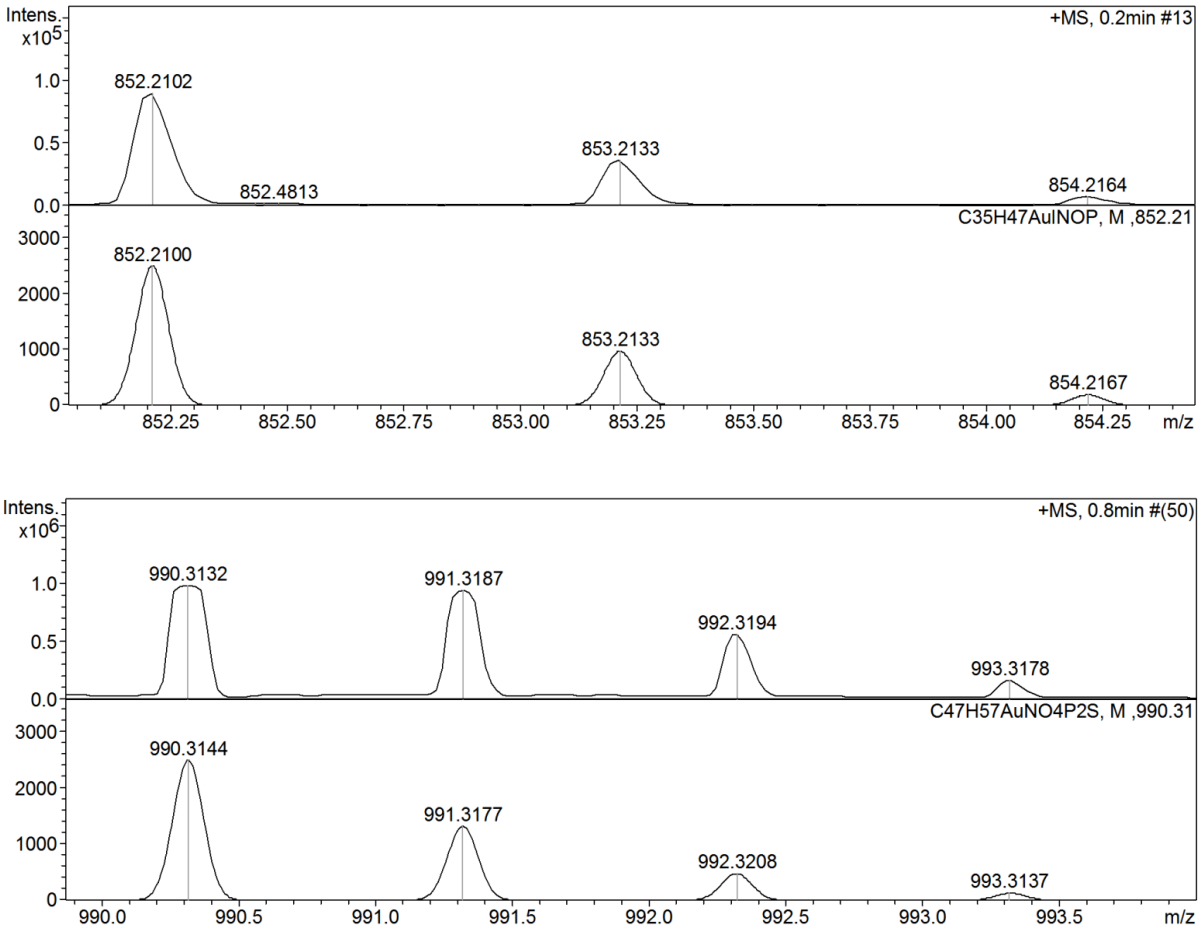
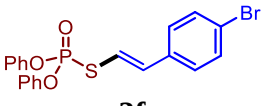
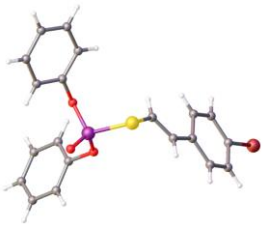
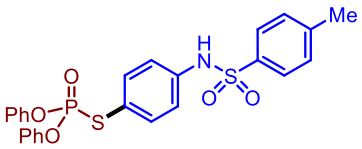
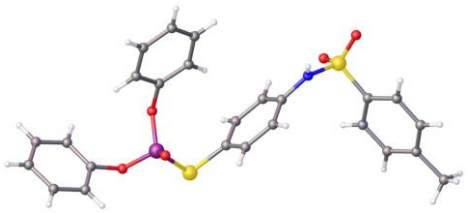


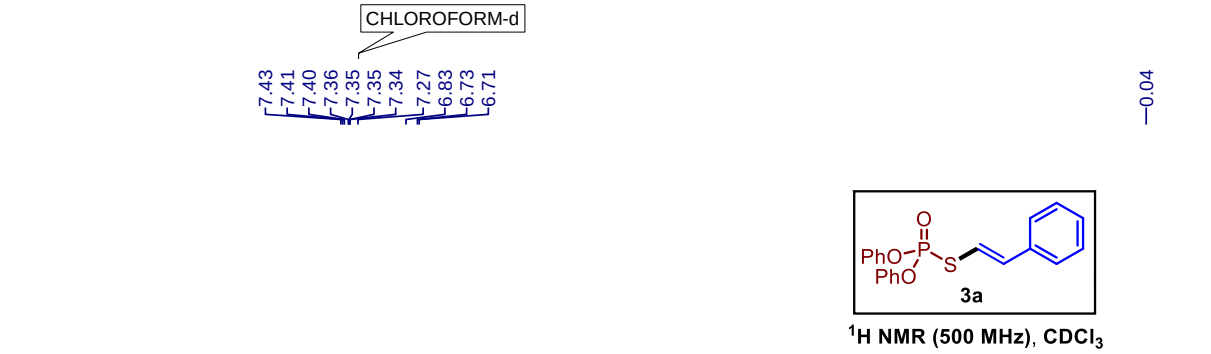
Figure 3: Identification of Au(III)-aryl intermediates **D** and **E** in ESI-HRMS.

7. X-ray crystallographic information

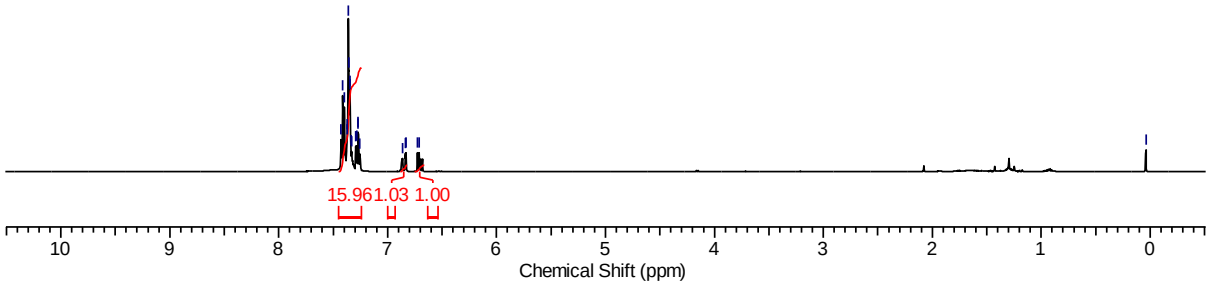
Sr. No.	Compound structure	ORTEP diagram
1	 **3f**	 **CCDC** = 2290839

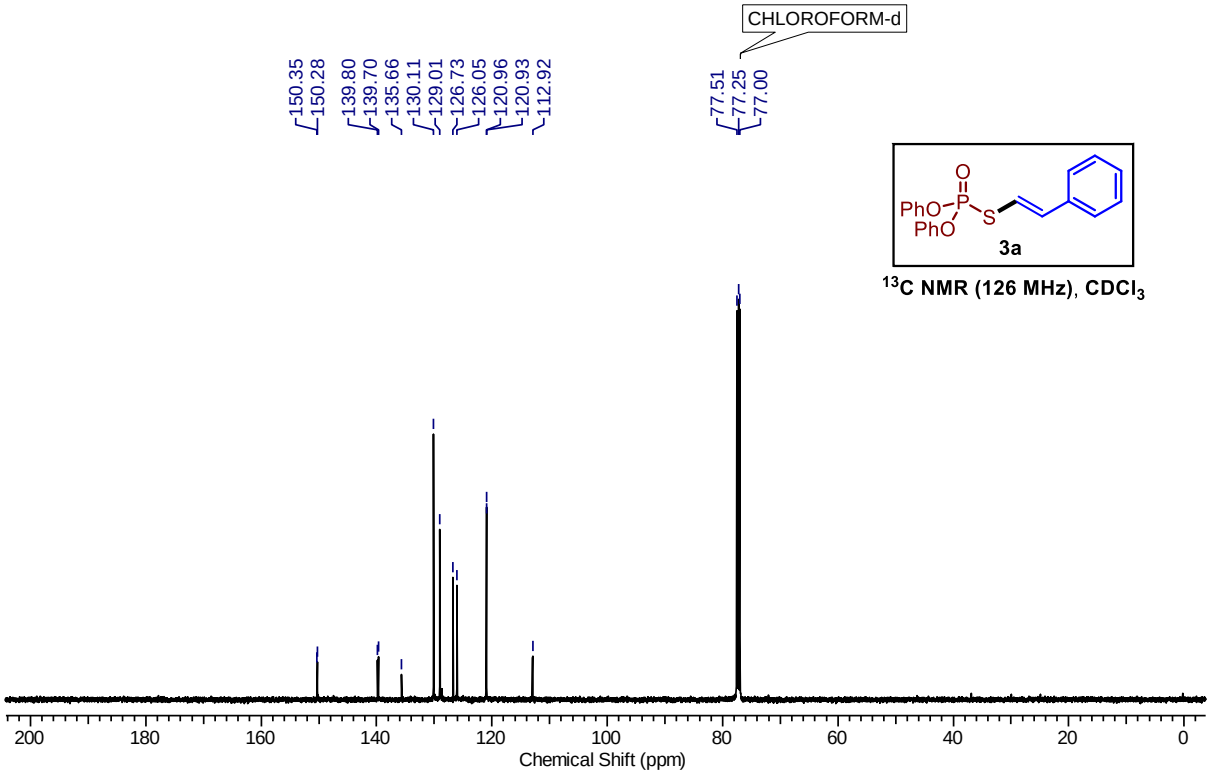
2	 **5o**	 **CCDC** = 2290838

8. NMR Spectra:

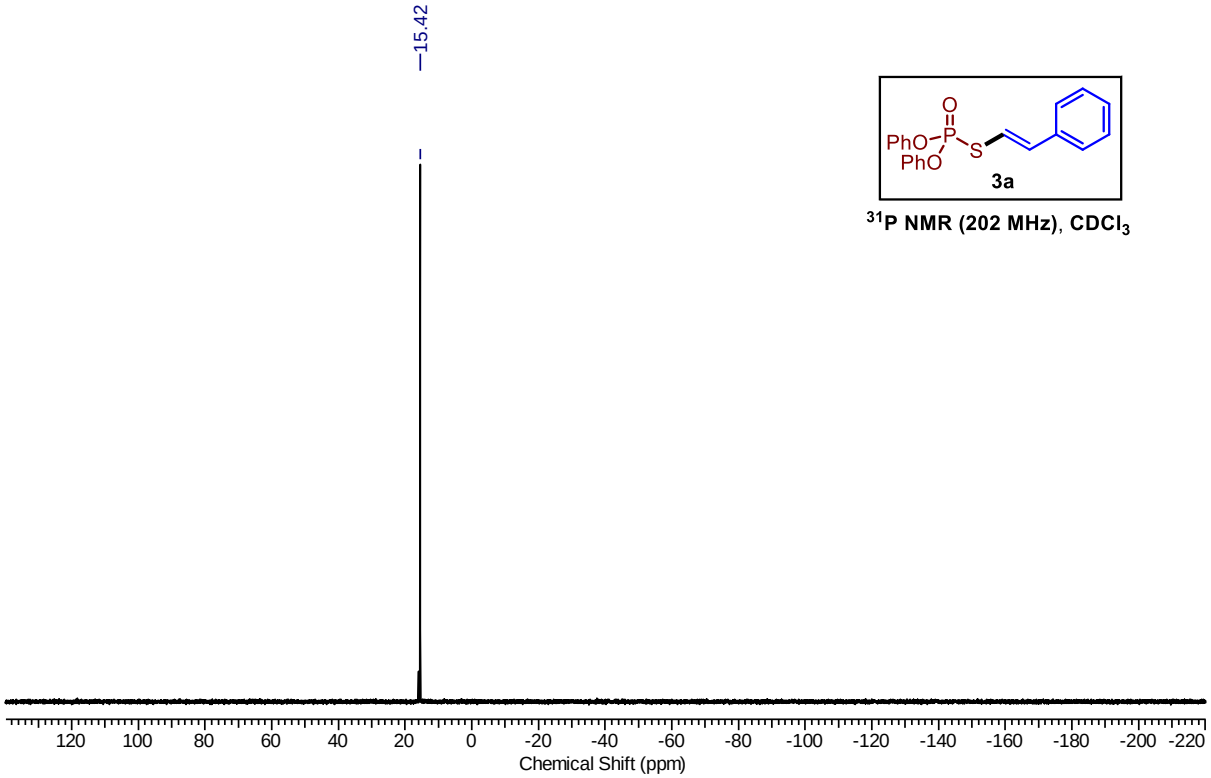


^{1}H NMR (500 MHz), $CDCl_3$

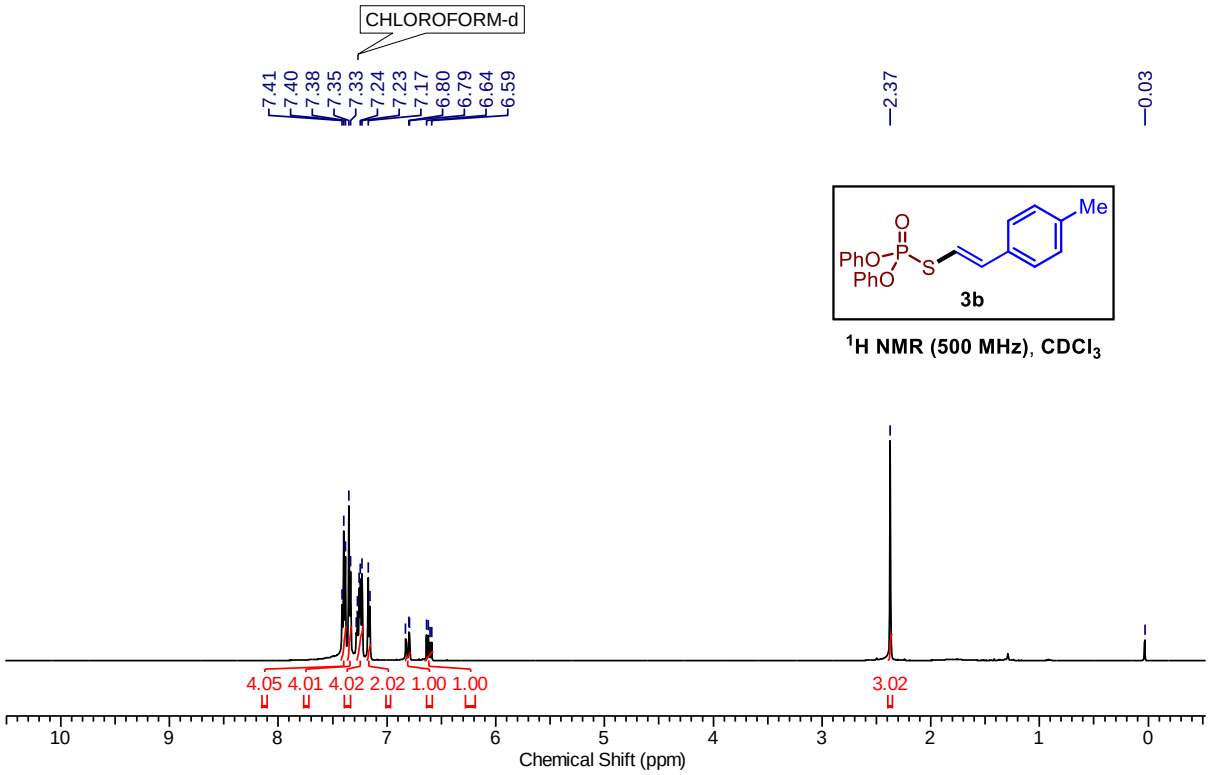




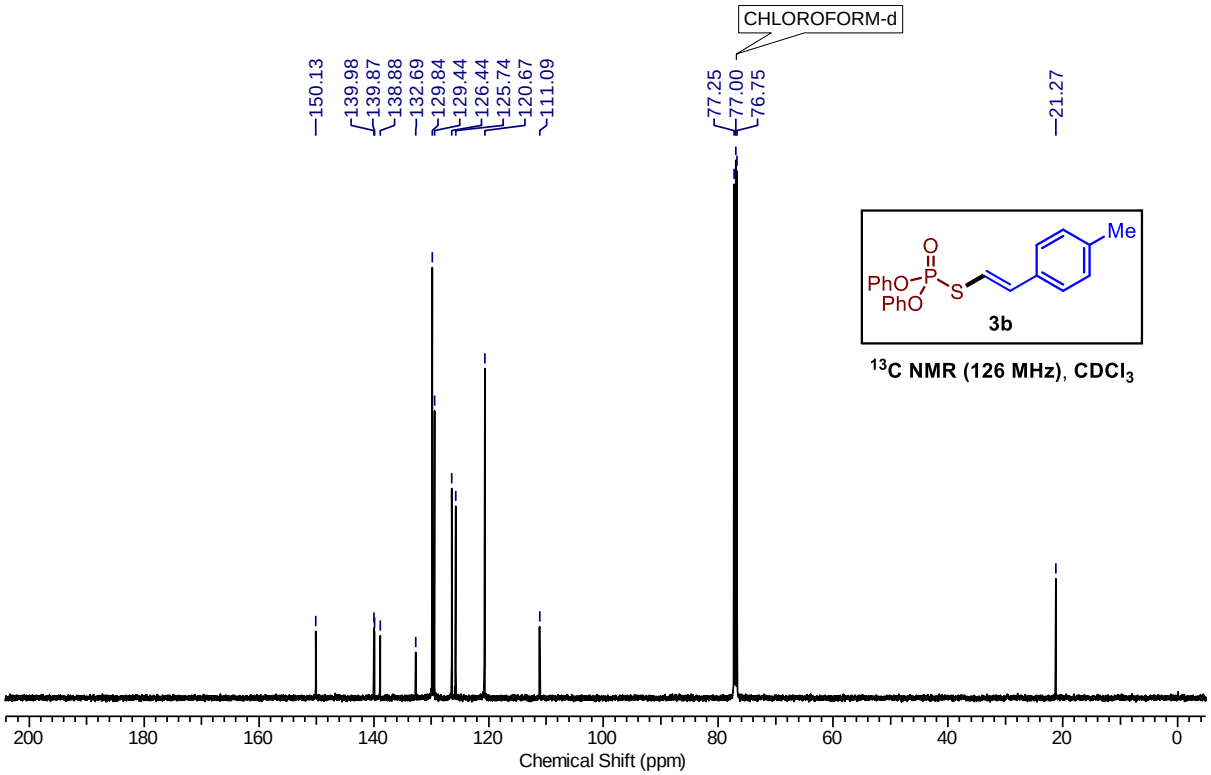
^{13}C NMR (126 MHz), $CDCl_3$



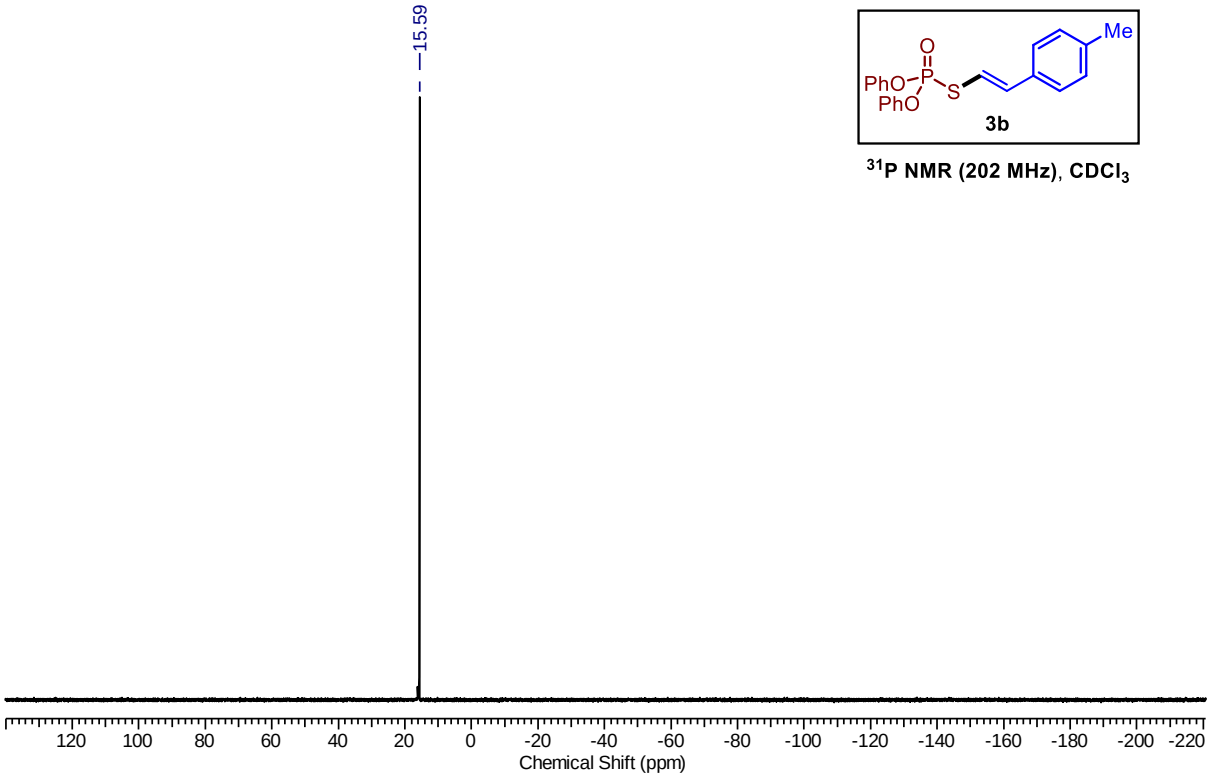
^{31}P NMR (202 MHz), $CDCl_3$



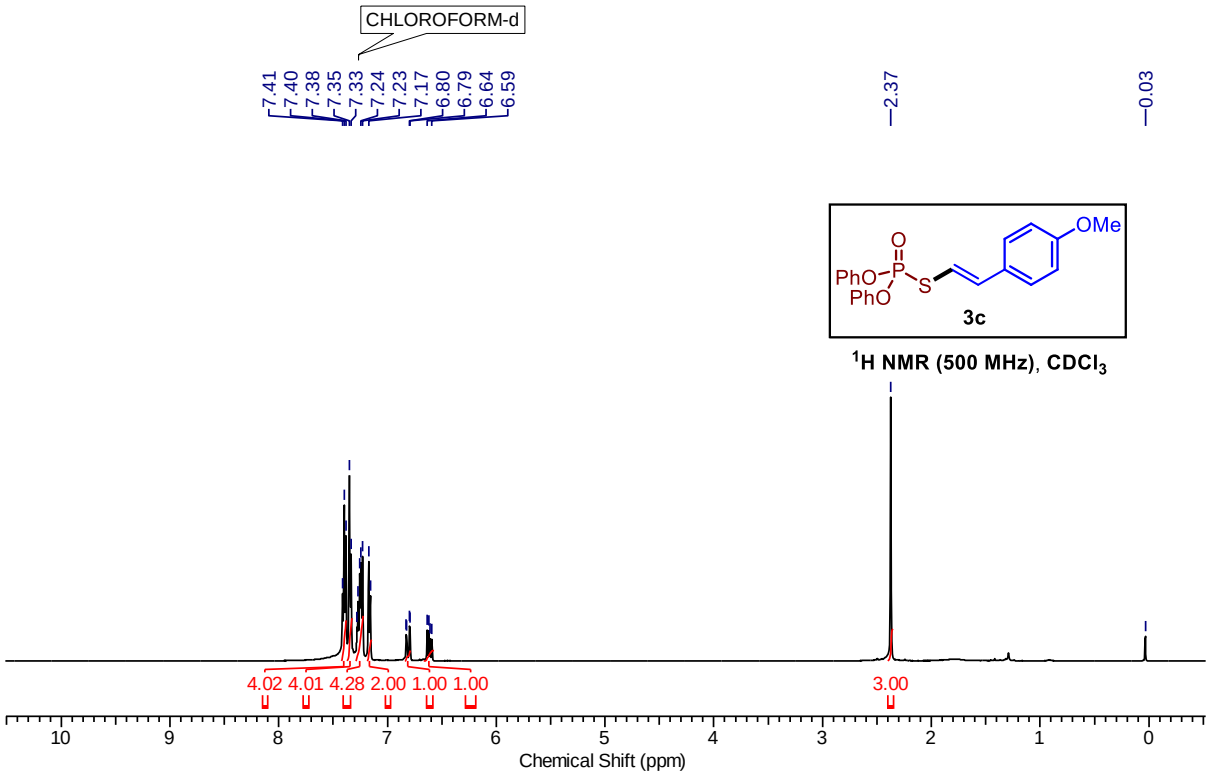
^{1}H NMR (500 MHz), $CDCl_3$



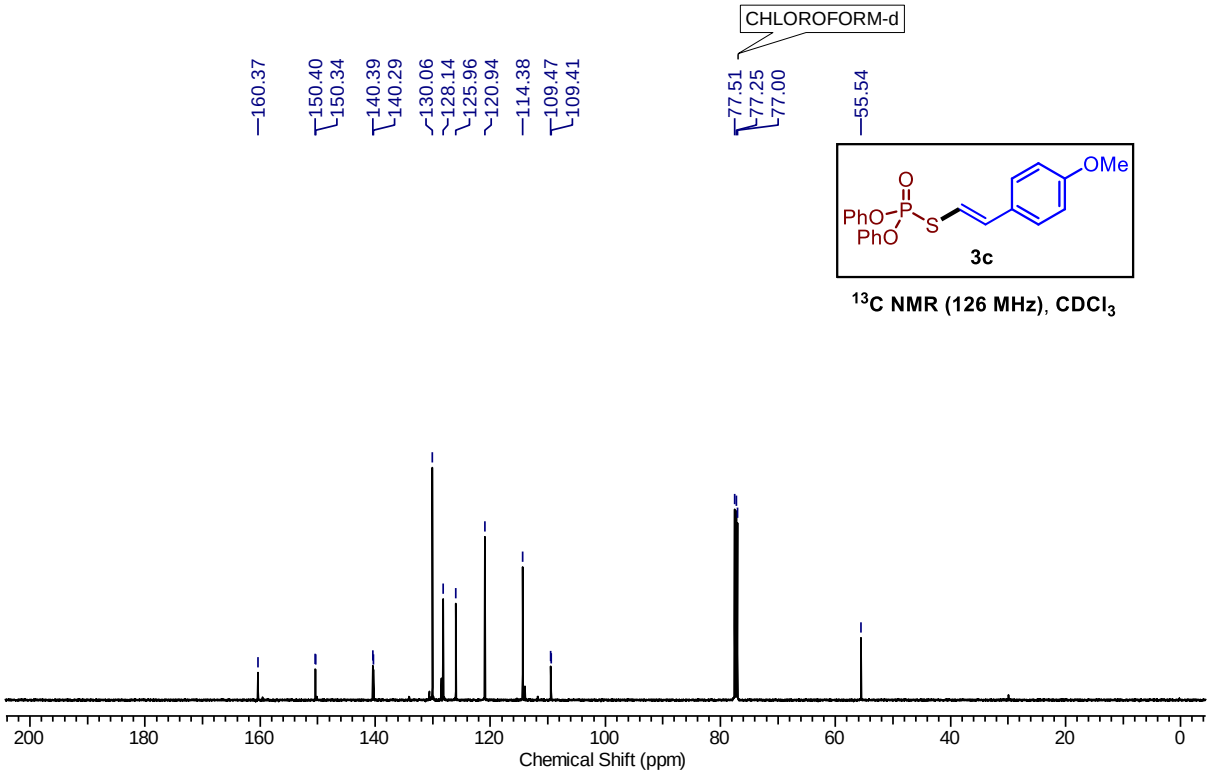
^{13}C NMR (126 MHz), $CDCl_3$



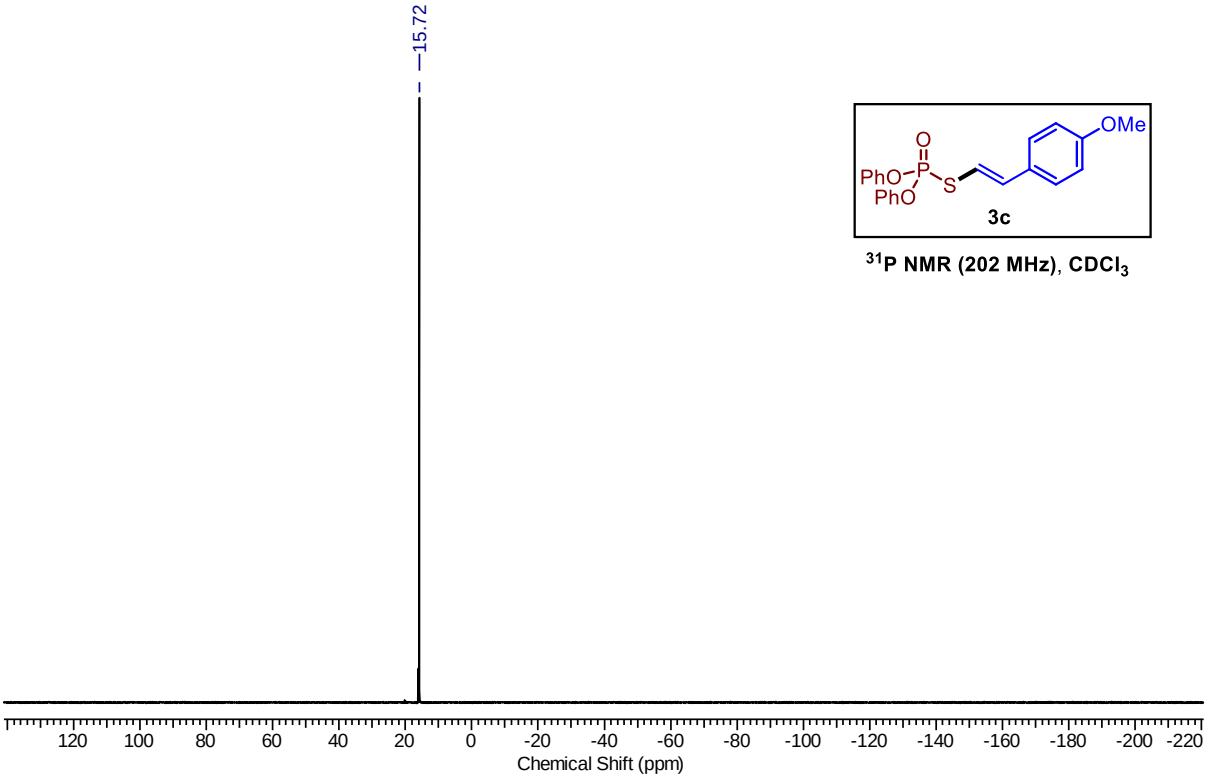
^{31}P NMR (202 MHz), $CDCl_3$



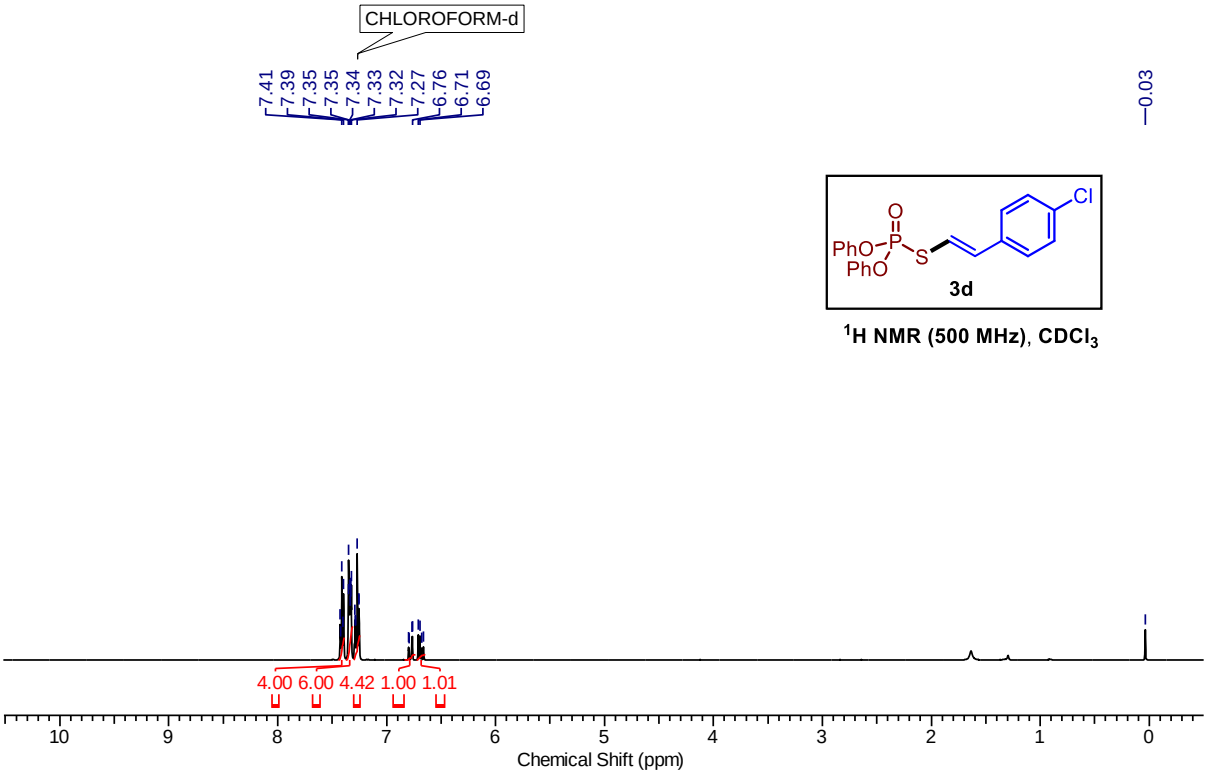
^{1}H NMR (500 MHz), $CDCl_3$



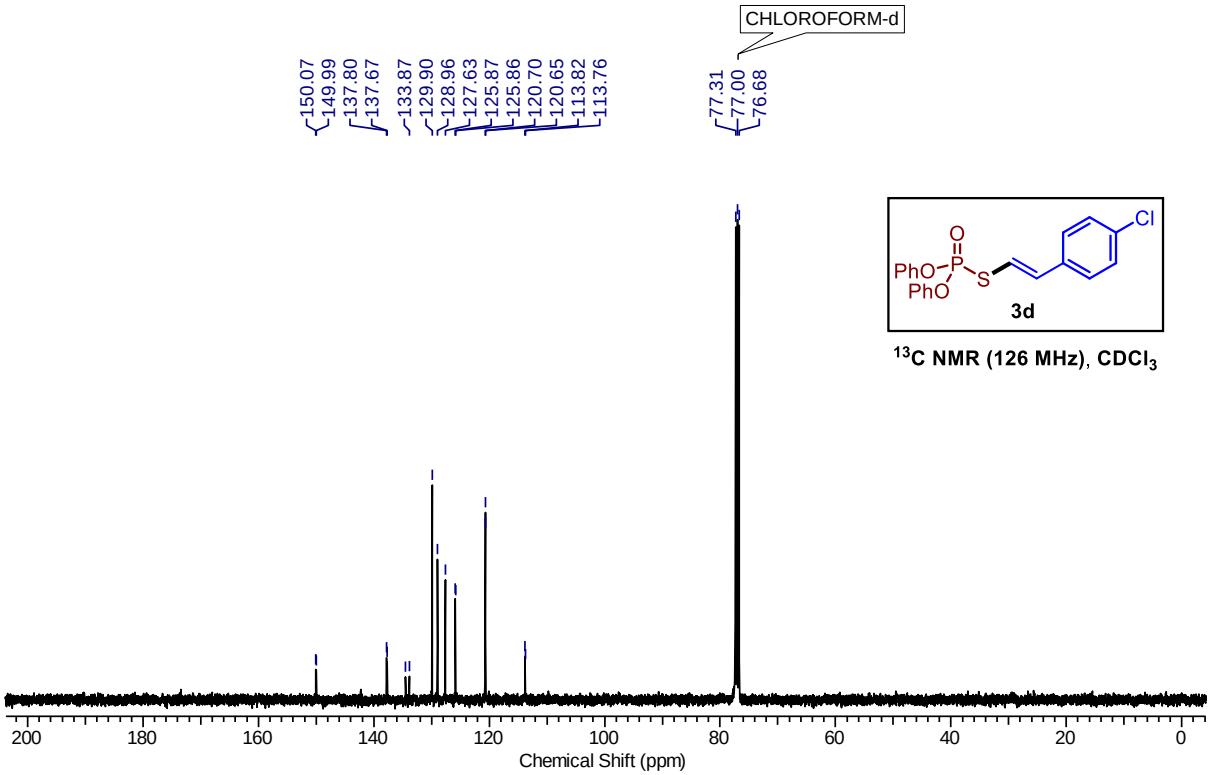
^{13}C NMR (126 MHz), $CDCl_3$



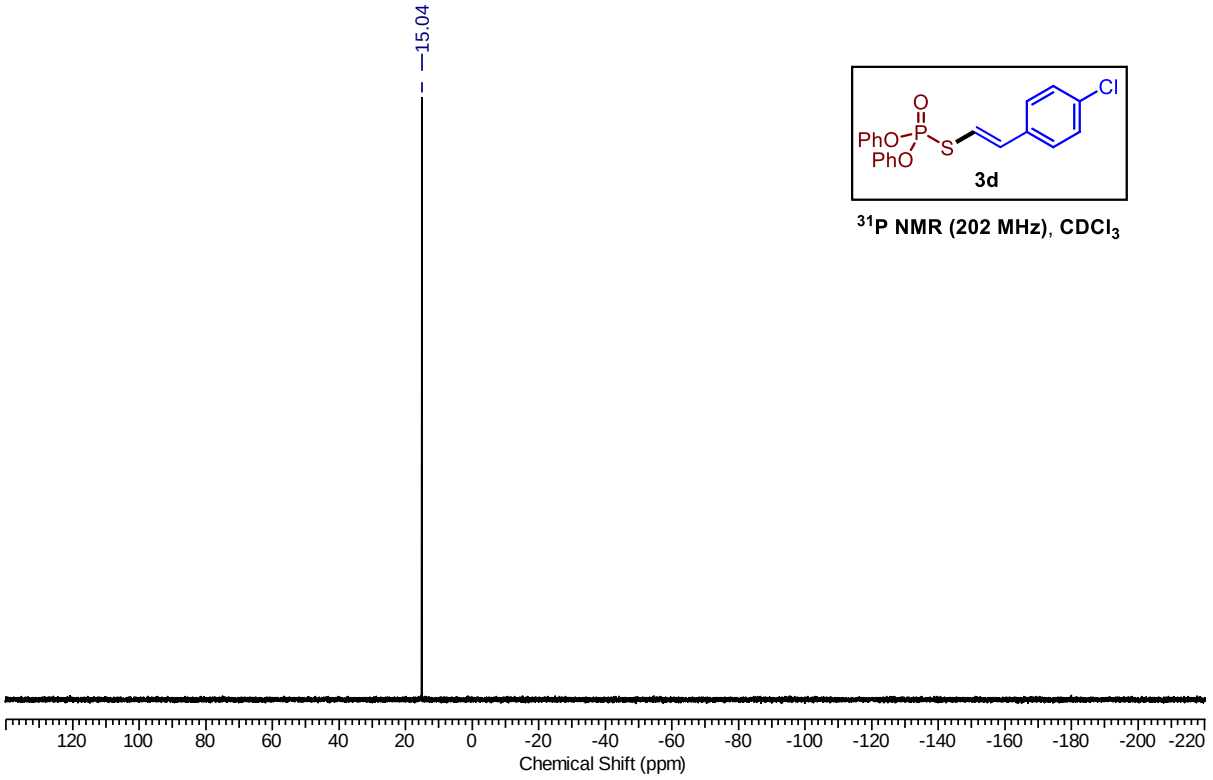
^{31}P NMR (202 MHz), $CDCl_3$



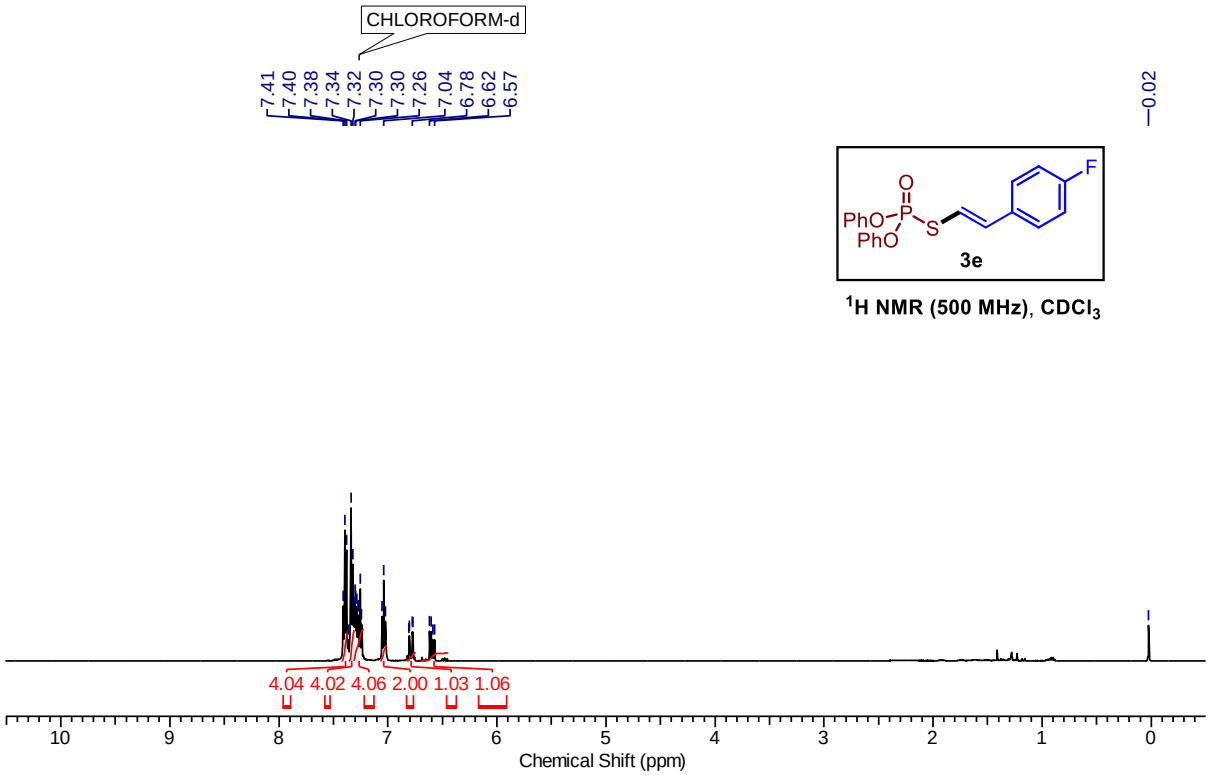
^{1}H NMR (500 MHz), $CDCl_3$



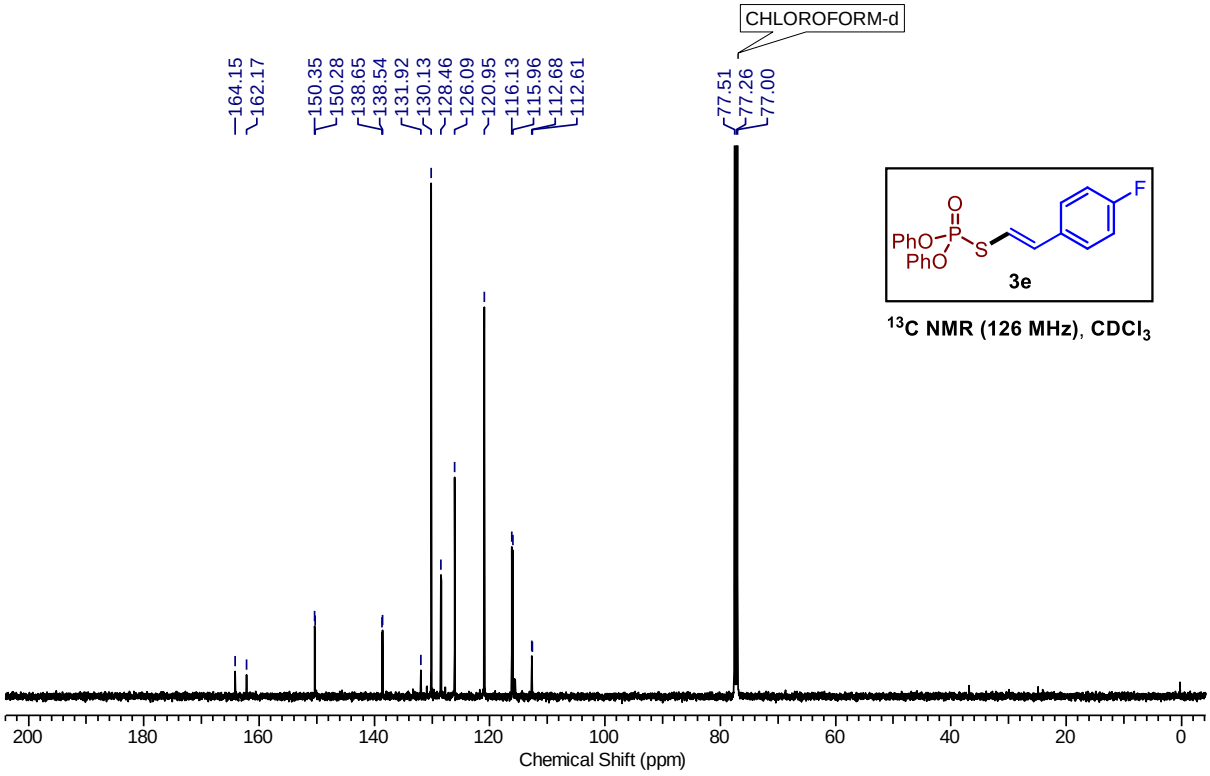
^{13}C NMR (126 MHz), $CDCl_3$



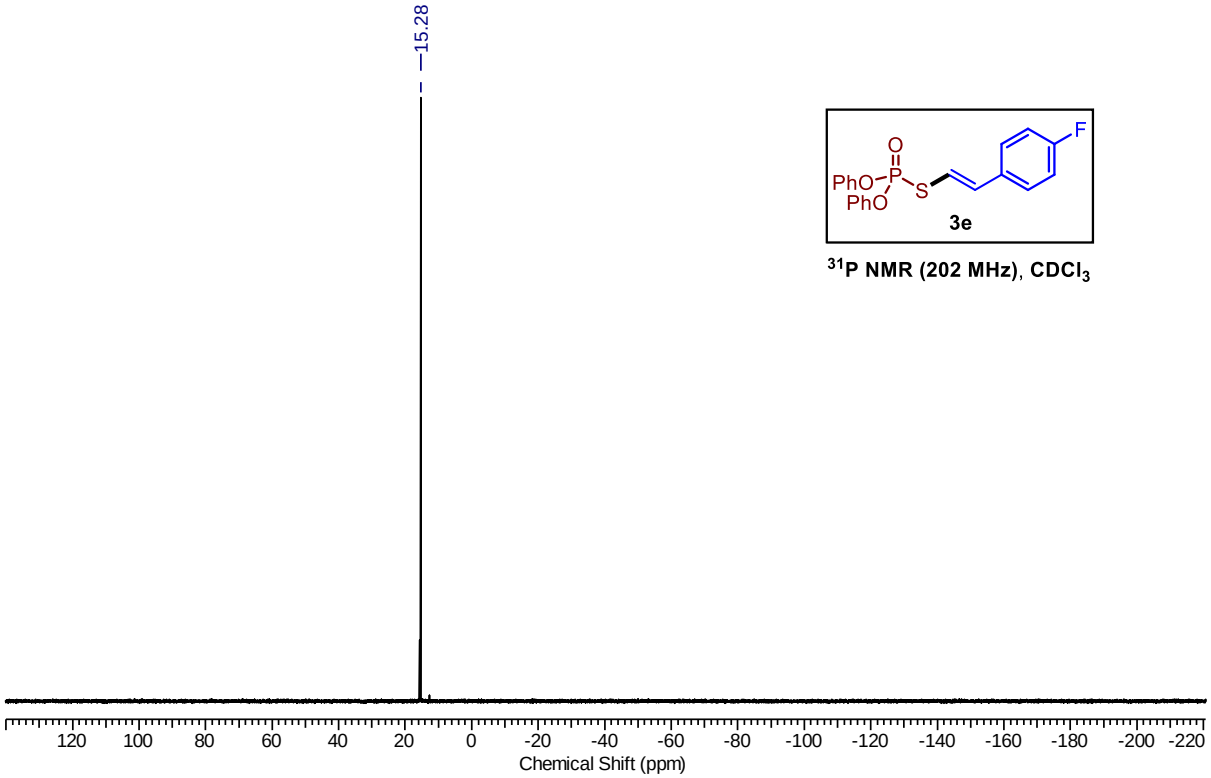
^{31}P NMR (202 MHz), $CDCl_3$



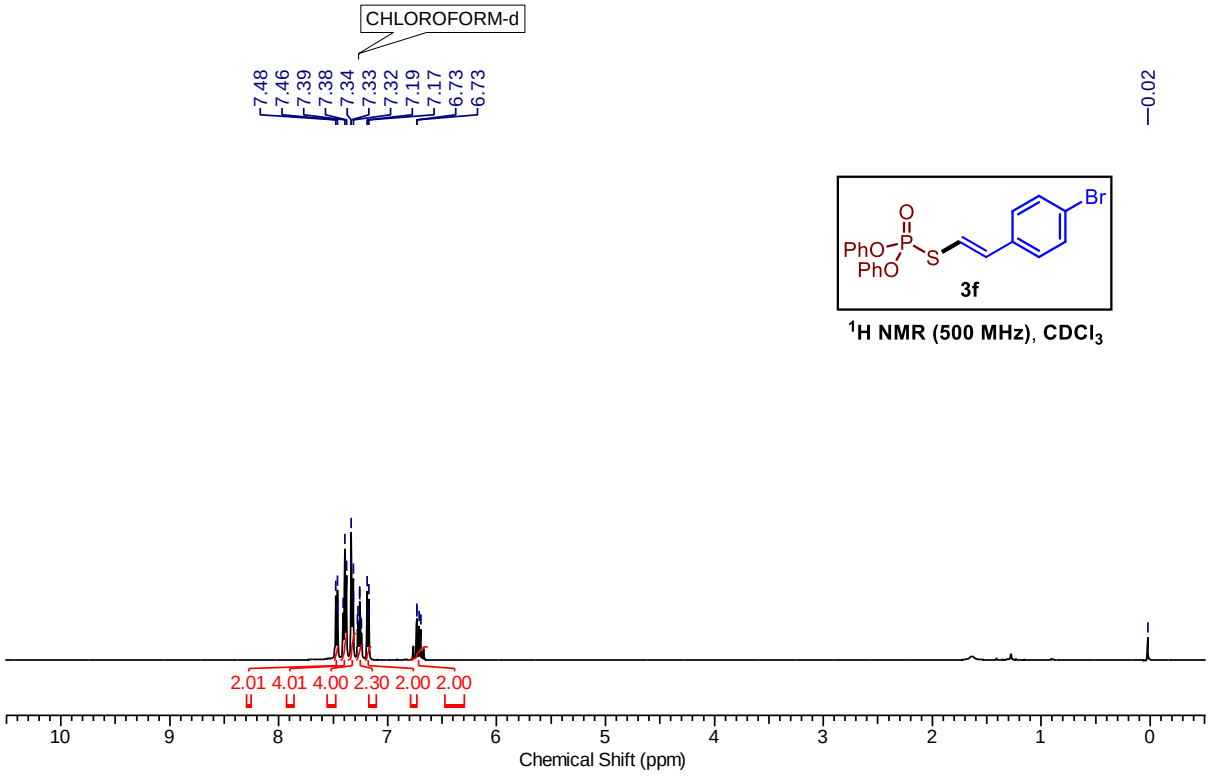
^{1}H NMR (500 MHz), $CDCl_3$



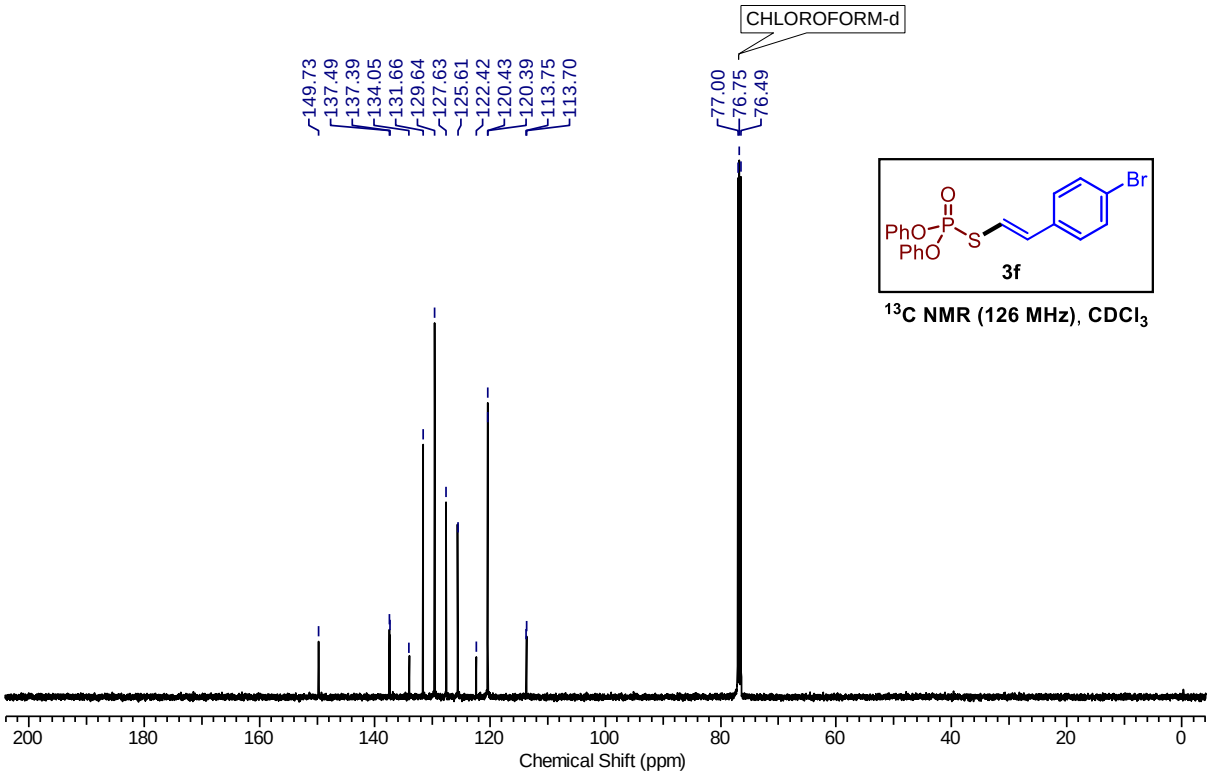
^{13}C NMR (126 MHz), $CDCl_3$



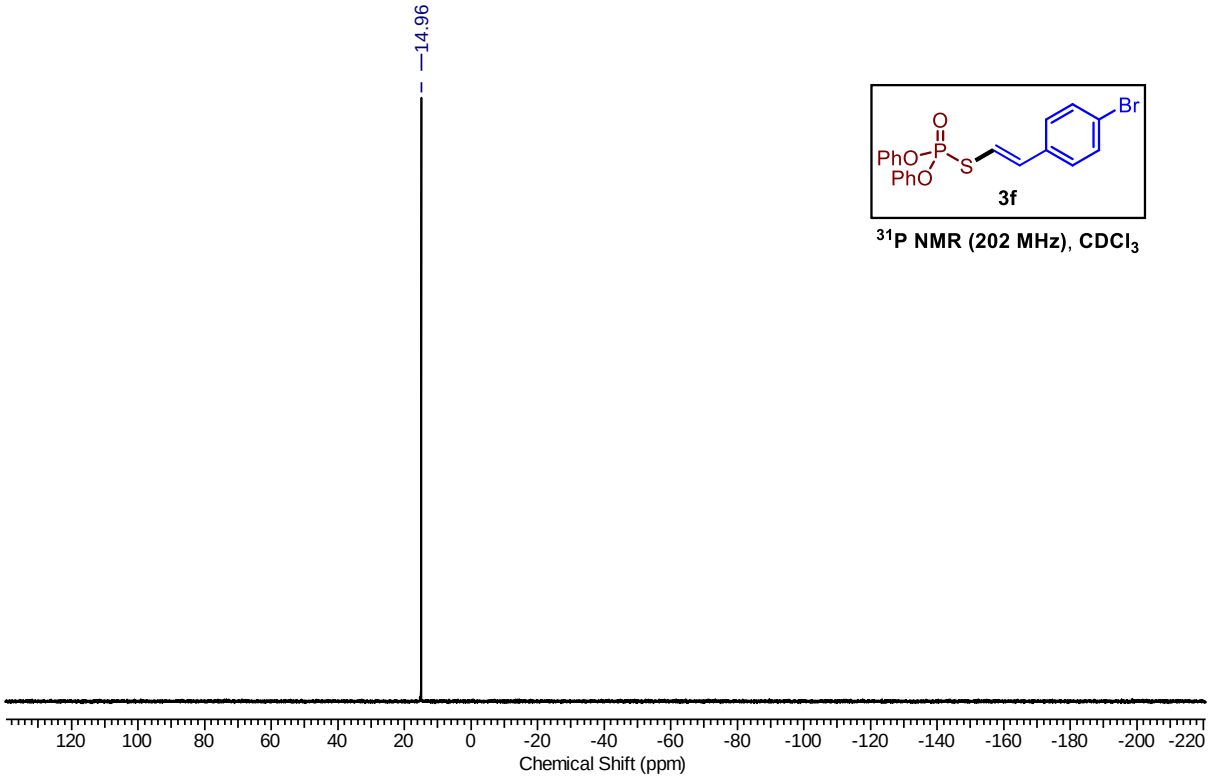
^{31}P NMR (202 MHz), $CDCl_3$



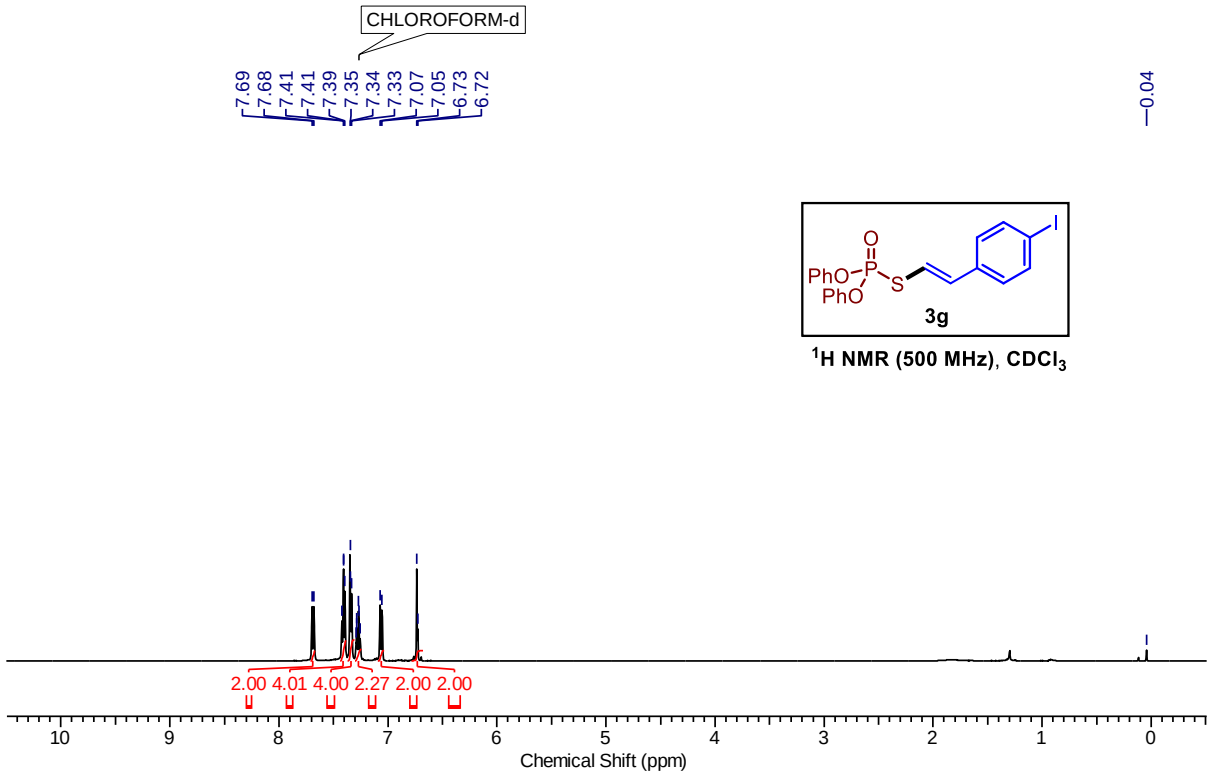
^{1}H NMR (500 MHz), $CDCl_3$



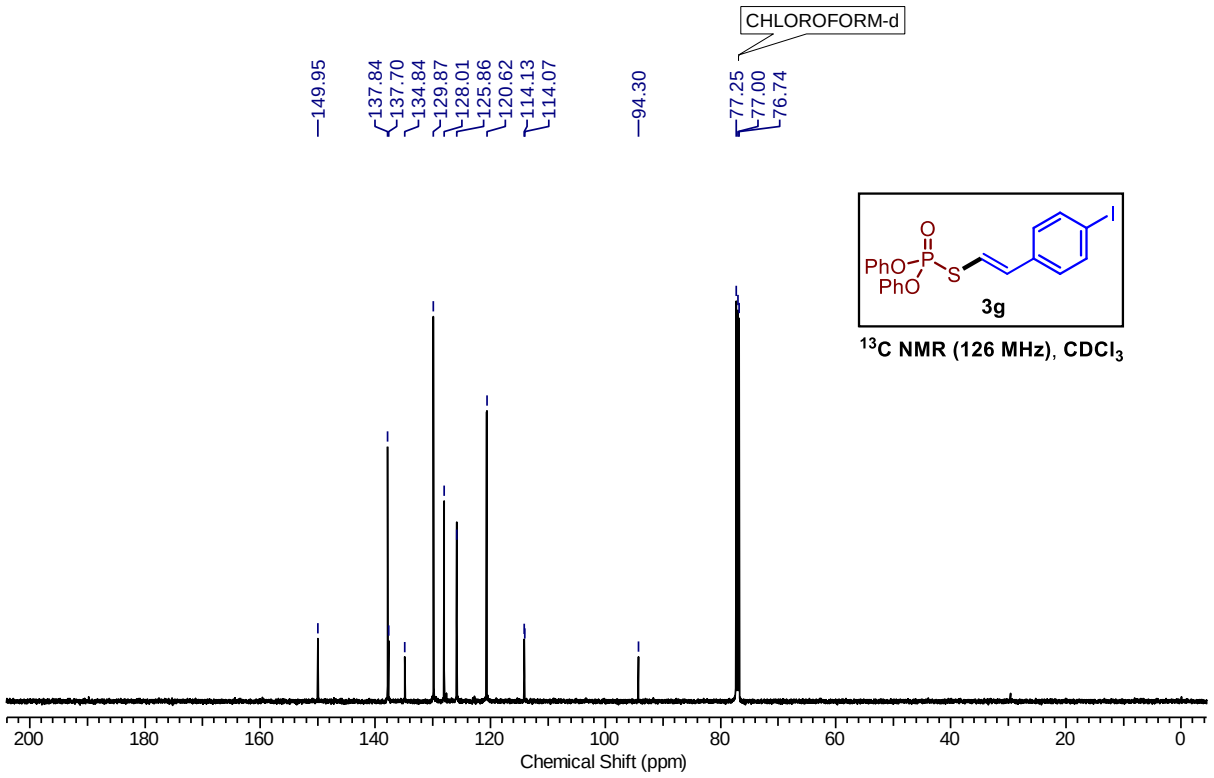
^{13}C NMR (126 MHz), $CDCl_3$



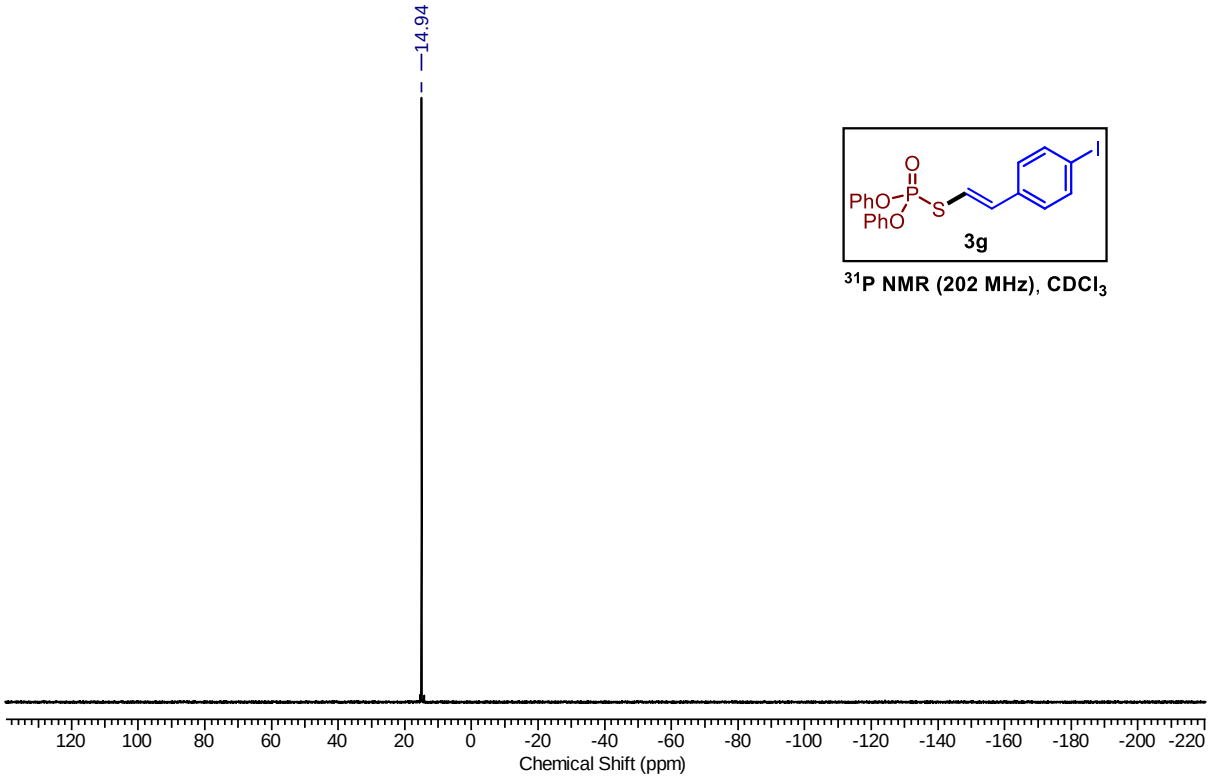
^{31}P NMR (202 MHz), $CDCl_3$



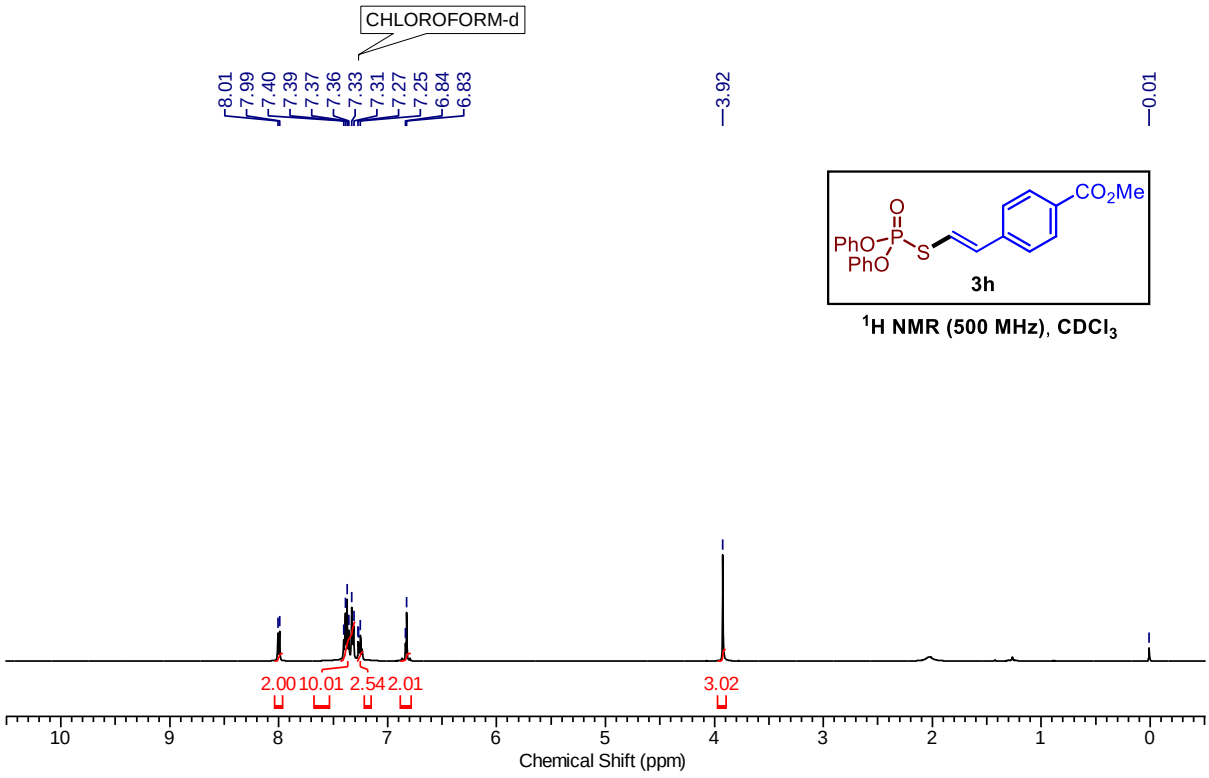
^{1}H NMR (500 MHz), $CDCl_3$



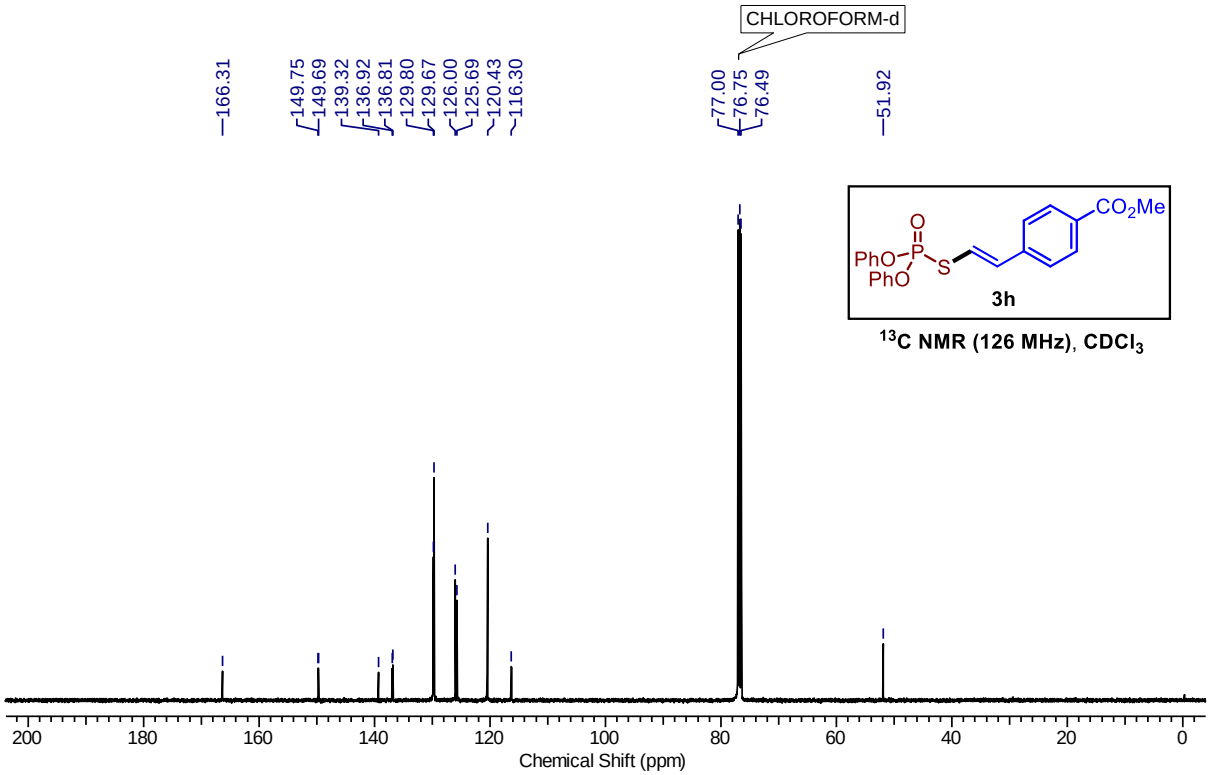
^{13}C NMR (126 MHz), $CDCl_3$



^{31}P NMR (202 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$



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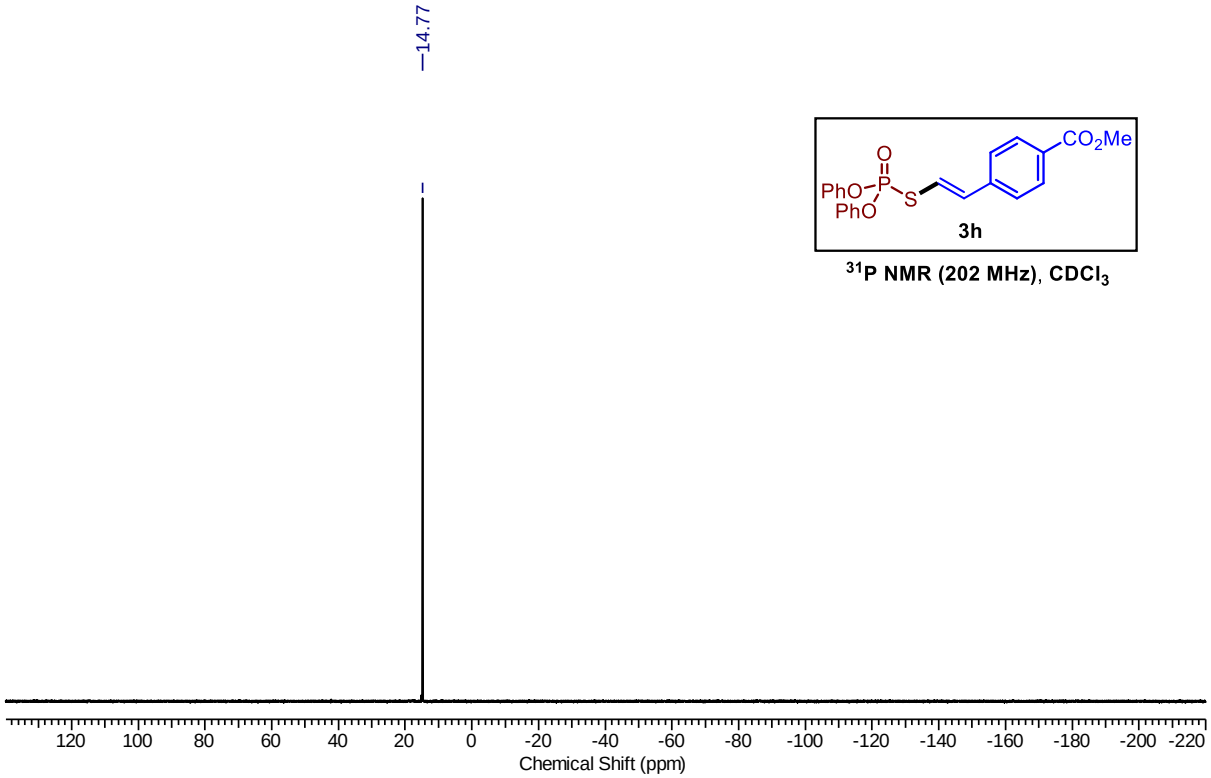
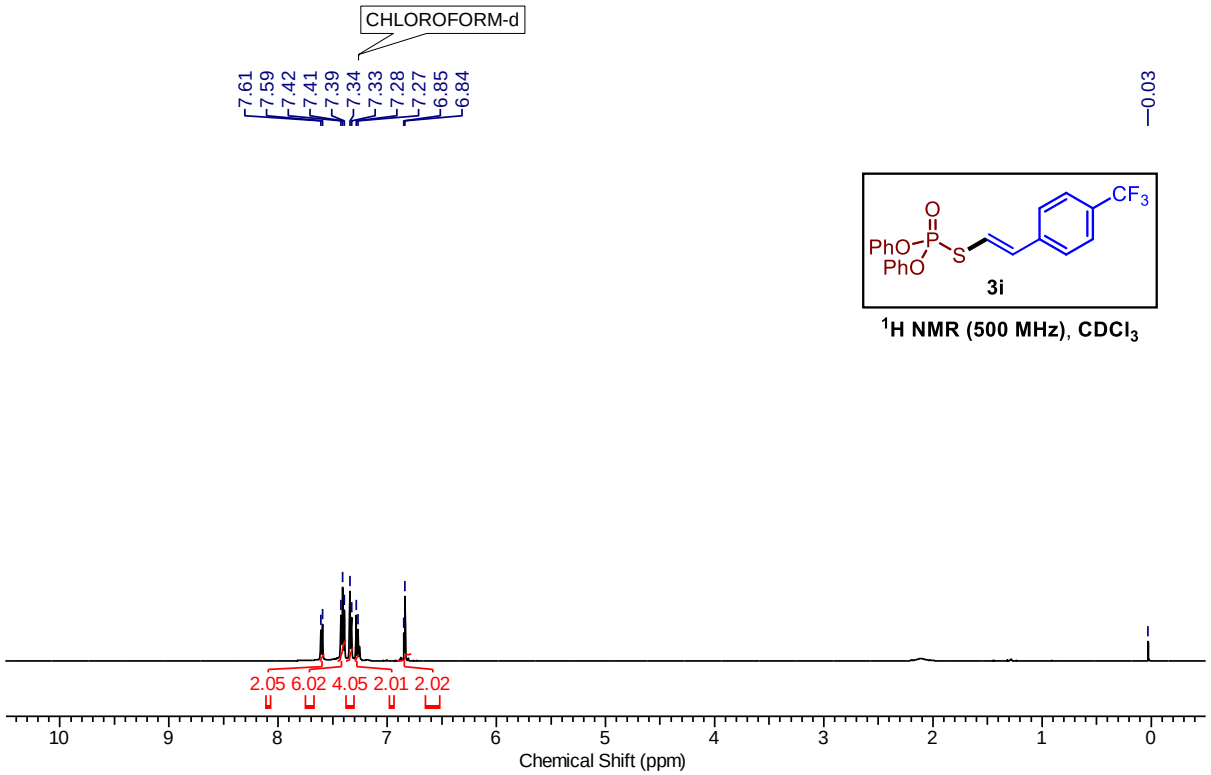


^{31}P NMR (202 MHz), $CDCl_3$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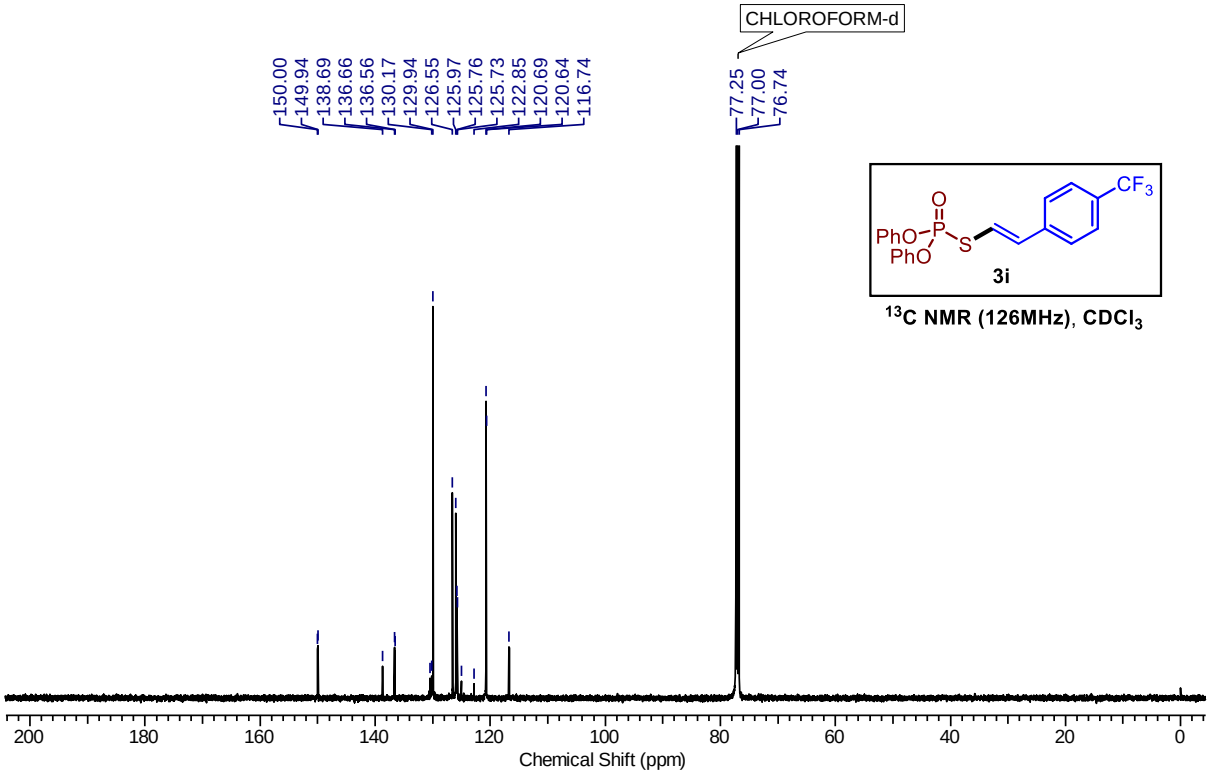
7.59
7.42
7.41
7.39
7.34
7.33
7.28
7.27
6.85
6.84
0.03
PhO
PhO
O
P
S
CF3
3i
1H NMR (500 MHz), CDCl3
2.05 6.02 4.05 2.01 2.02
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)


CHLOROFORM-d
150.00
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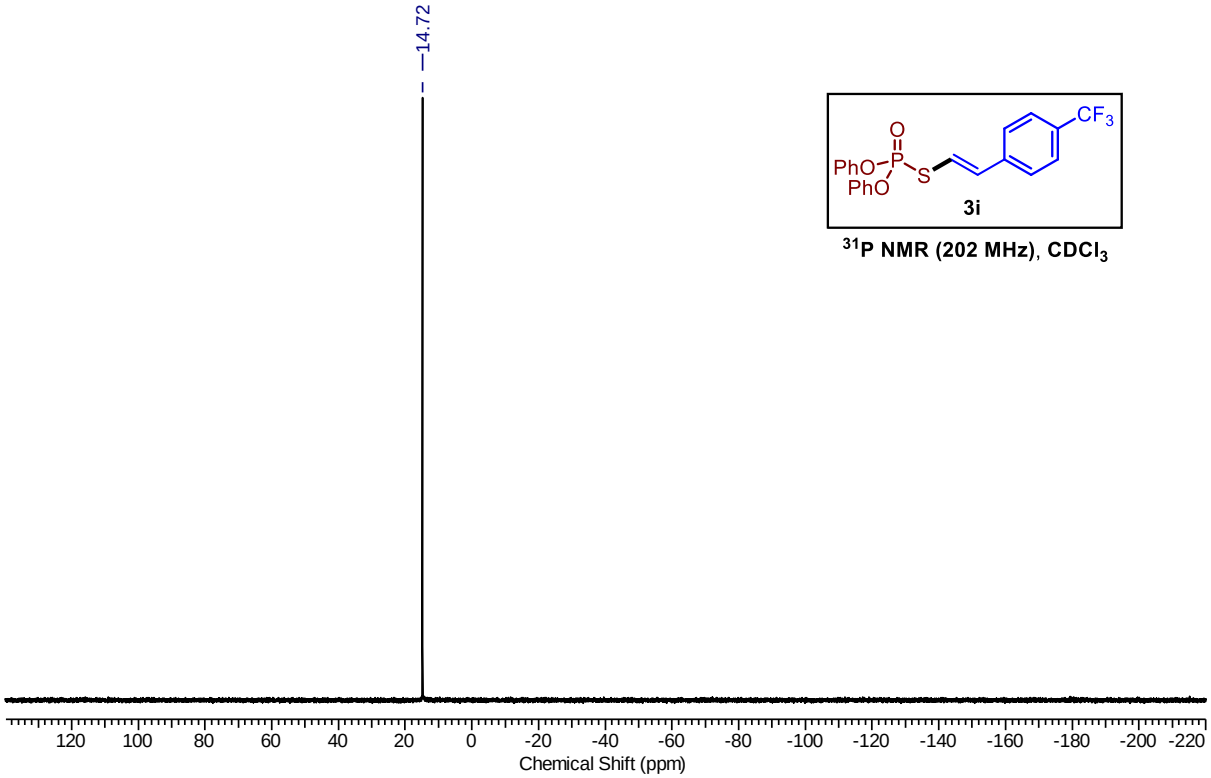
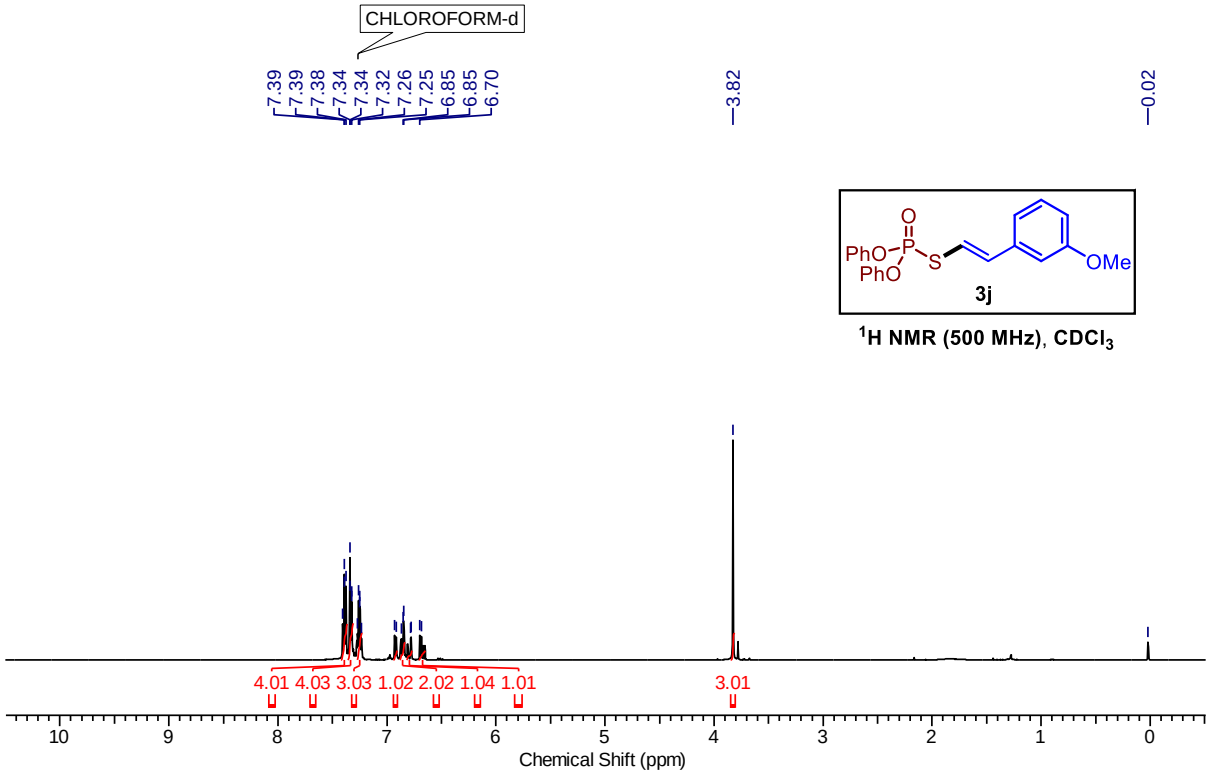
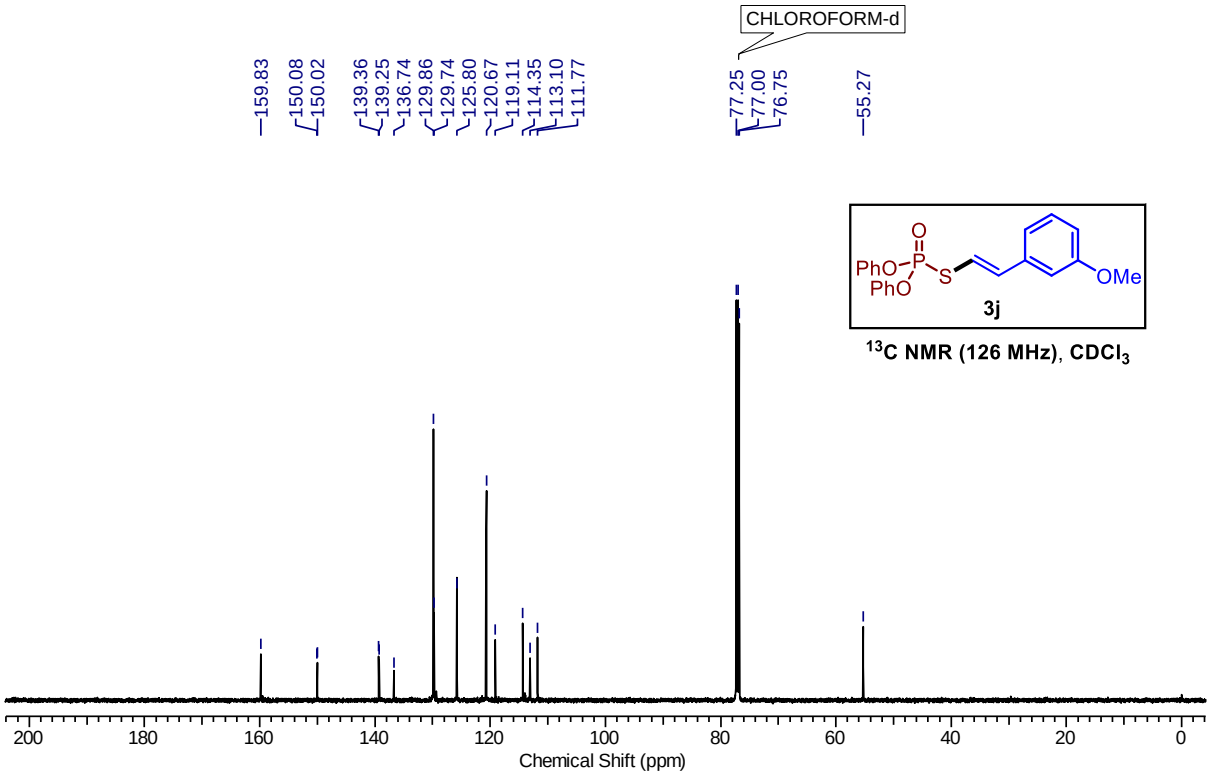
138.69
136.66
136.56
130.17
129.94
126.55
125.97
125.76
125.73
122.85
120.69
120.64
116.74
77.25
77.00
76.74
PhO
PhO
O
P
S
CF3
3i
13C NMR (126MHz), CDCl3
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)



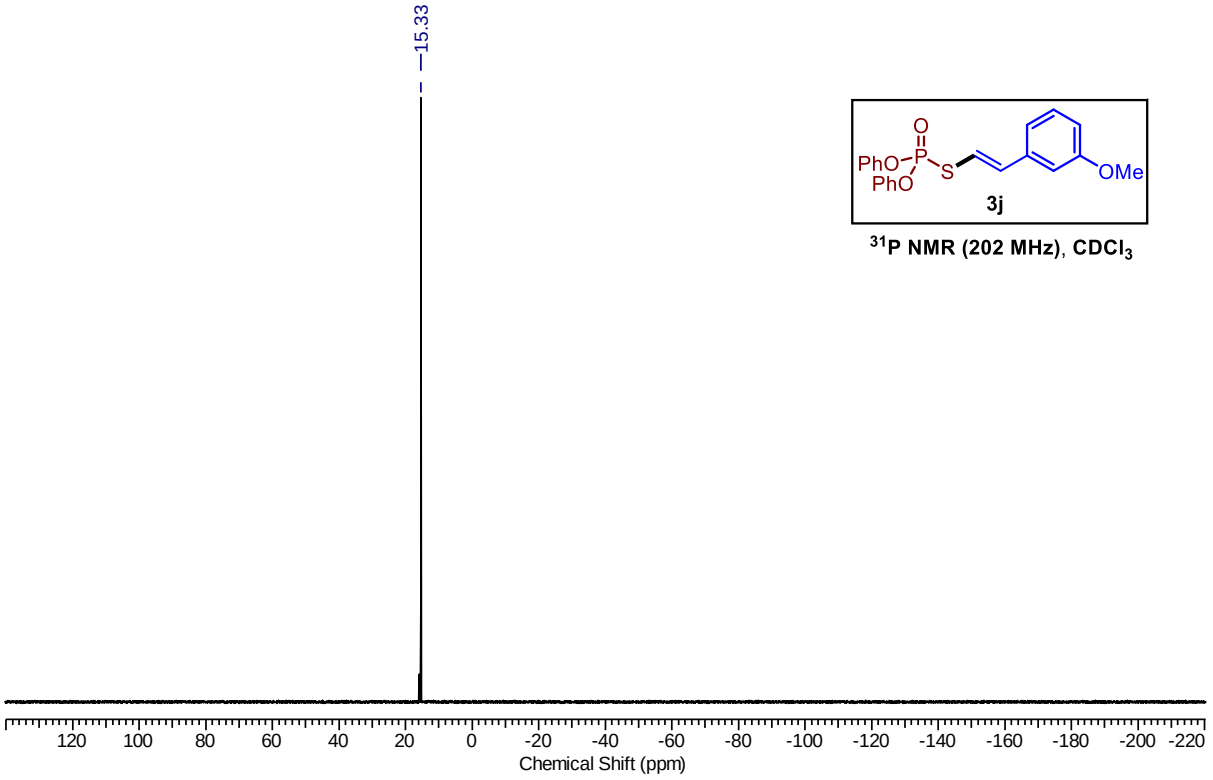
^{31}P NMR (202 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$

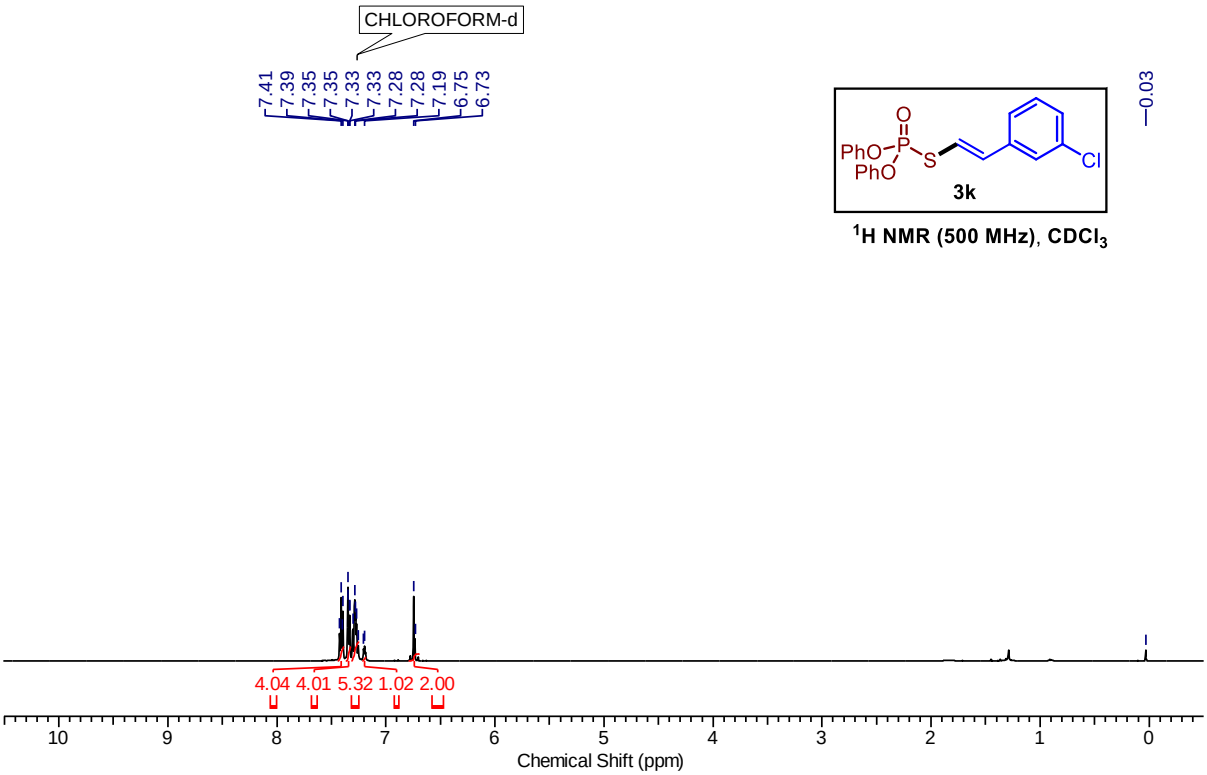


^{13}C NMR (126 MHz), $CDCl_3$

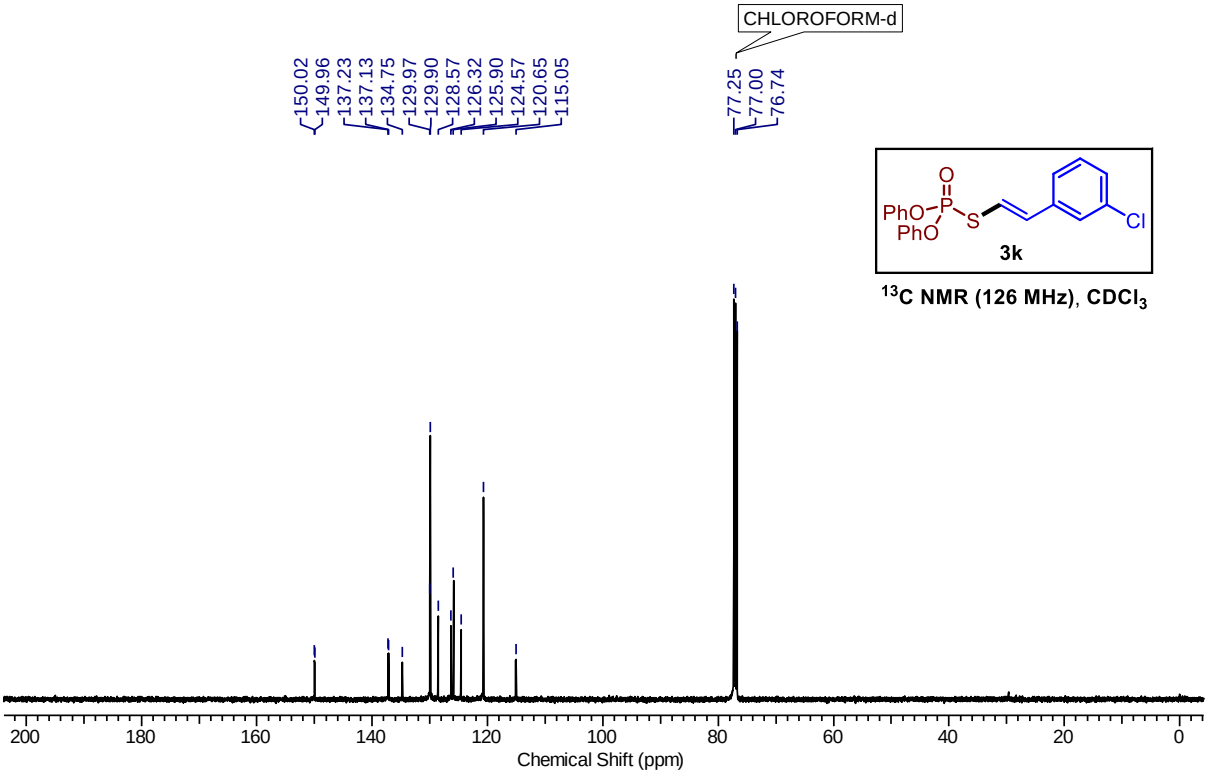


^{31}P NMR (202 MHz), $CDCl_3$

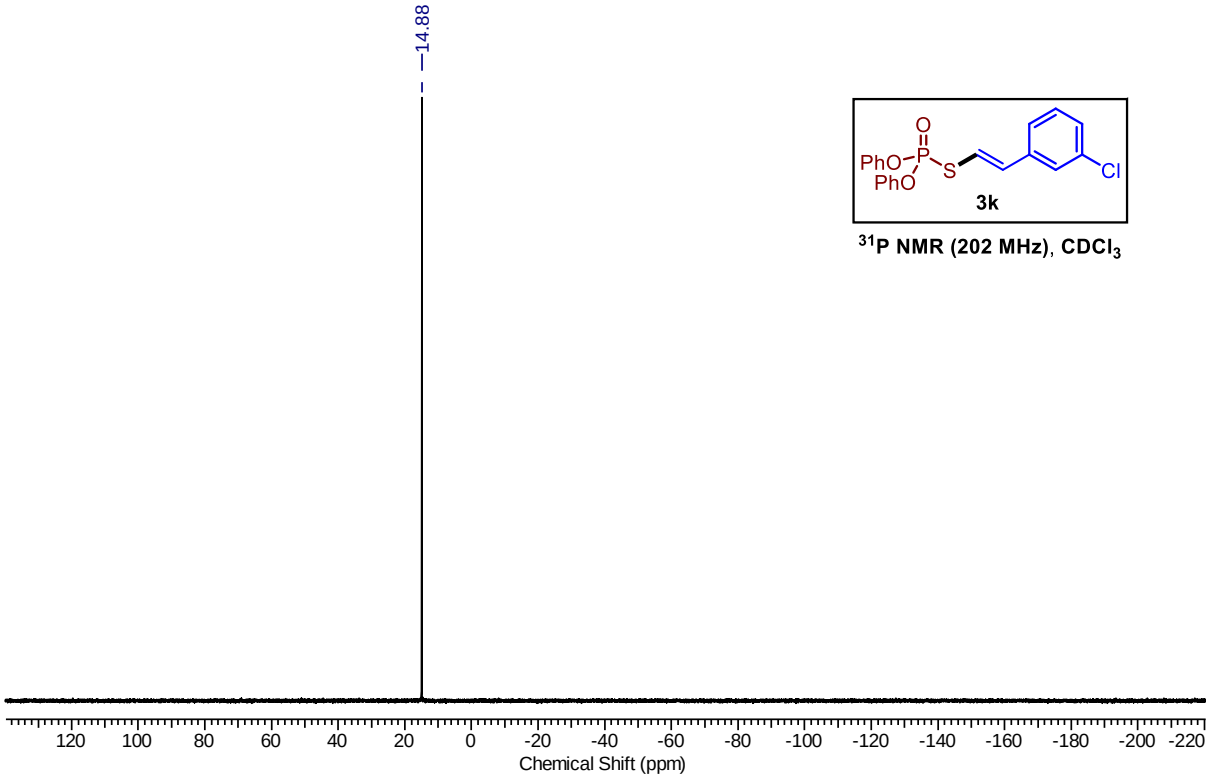
S



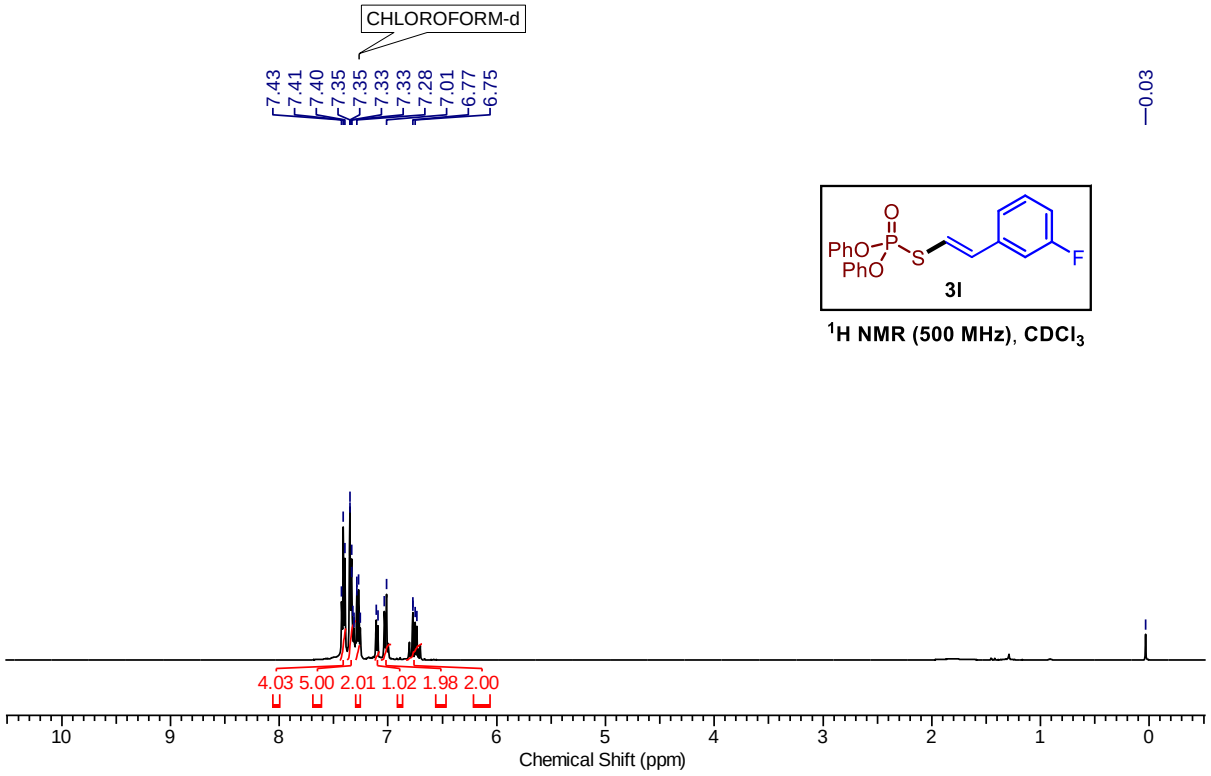
^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (126 MHz), $CDCl_3$



^{31}P NMR (202 MHz), $CDCl_3$



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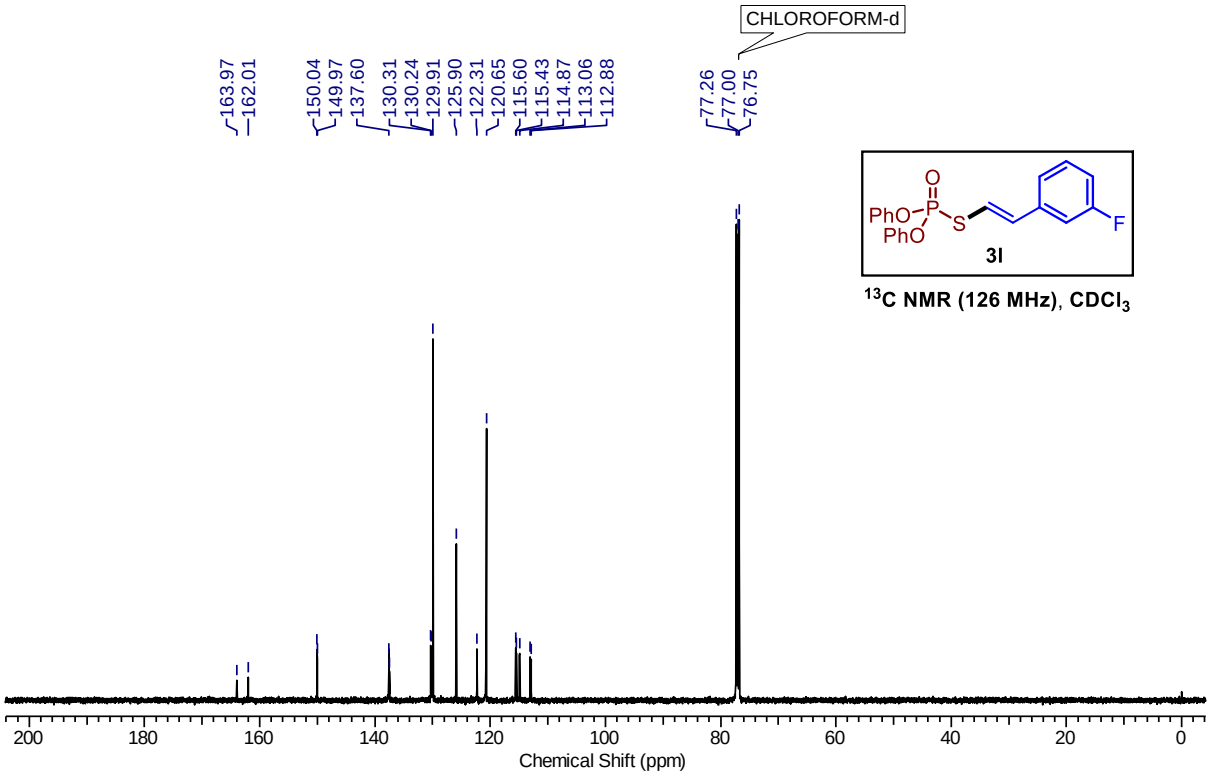
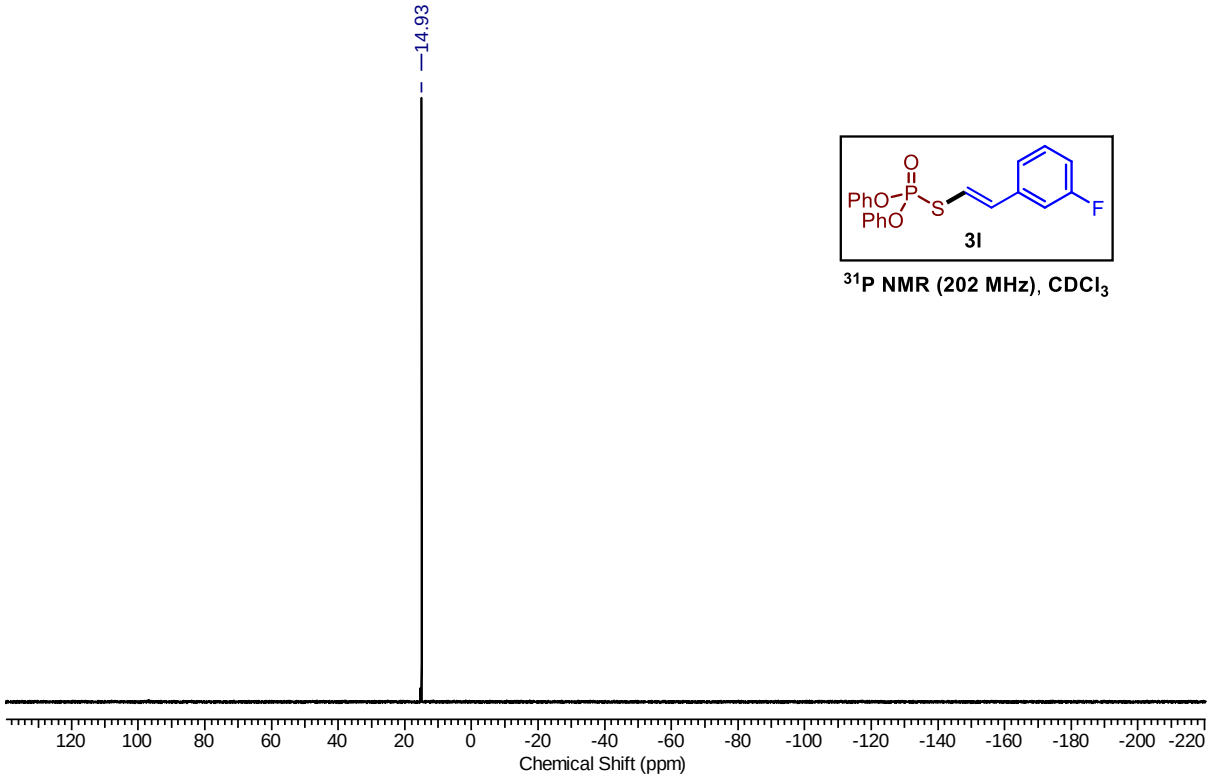


^{13}C NMR (126 MHz), $CDCl_3$



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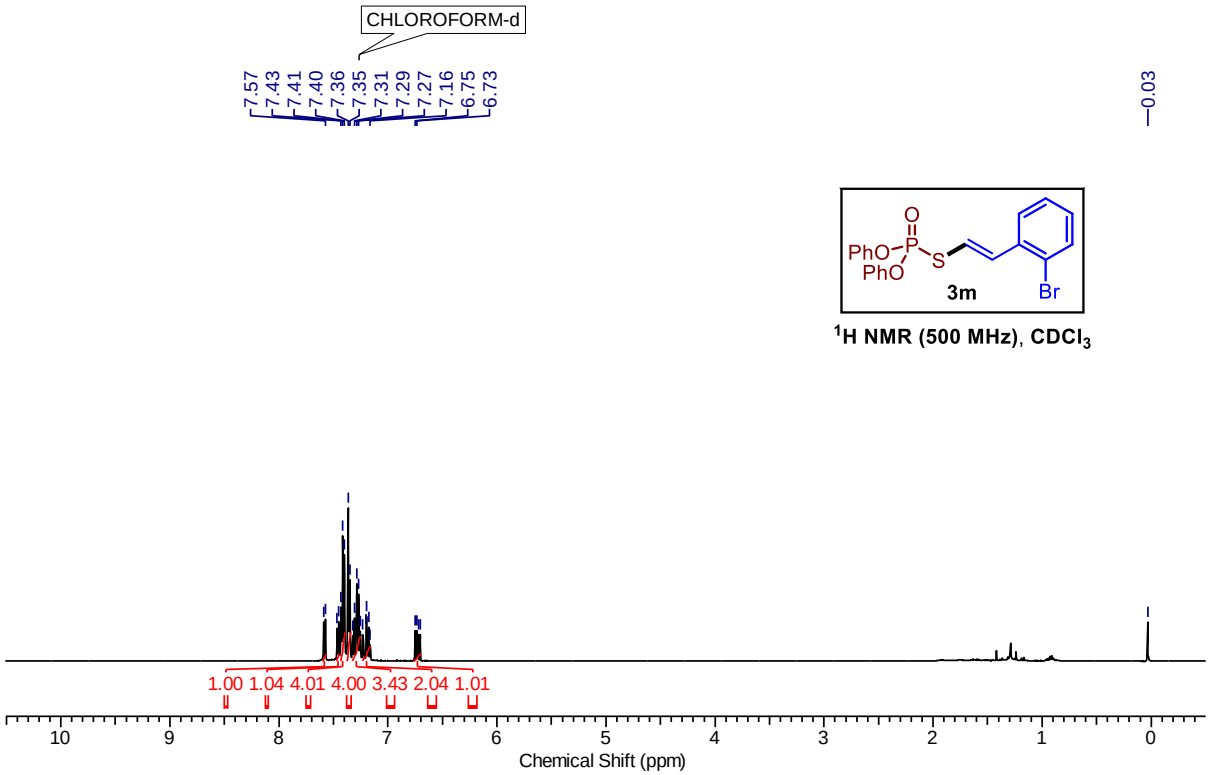
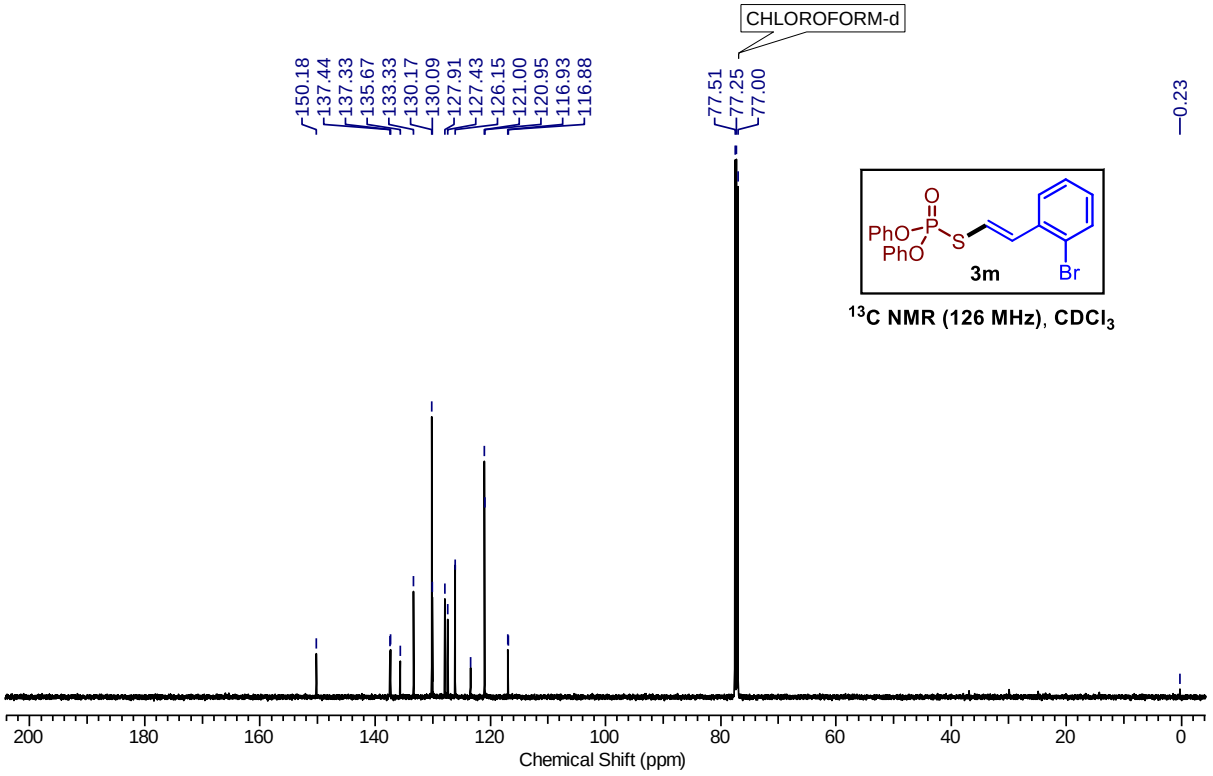
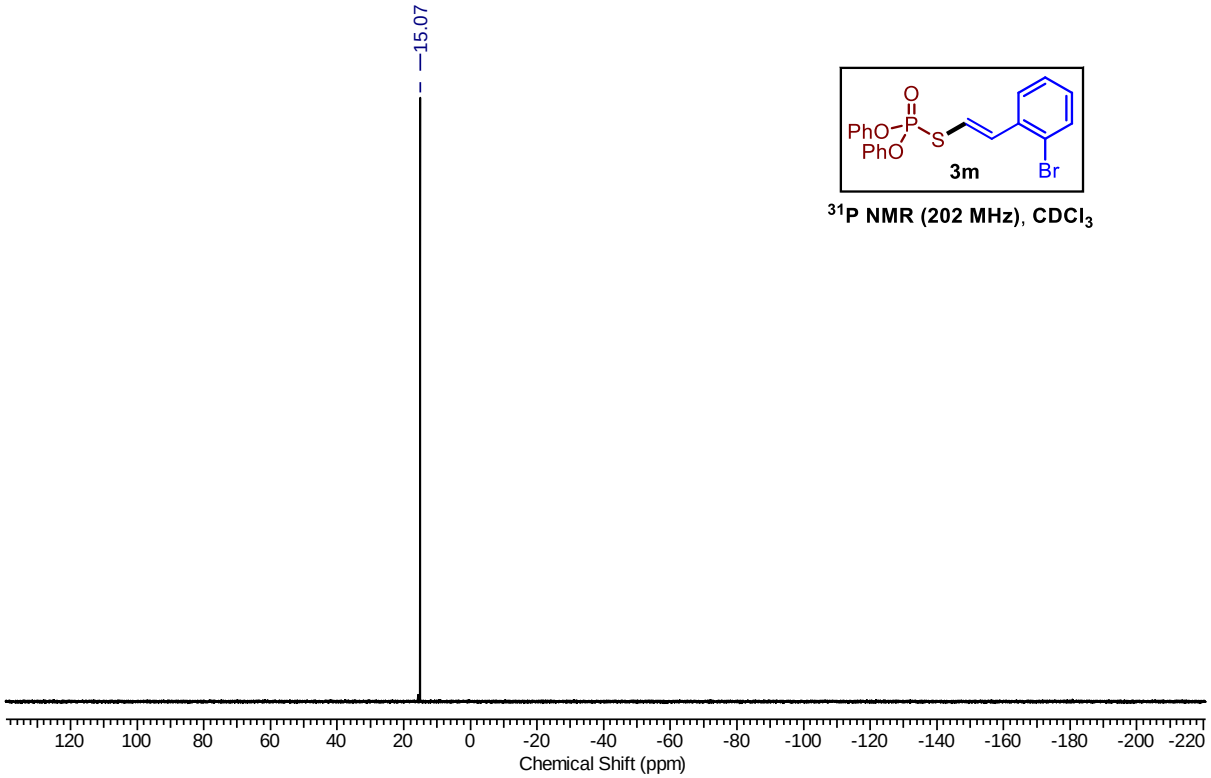
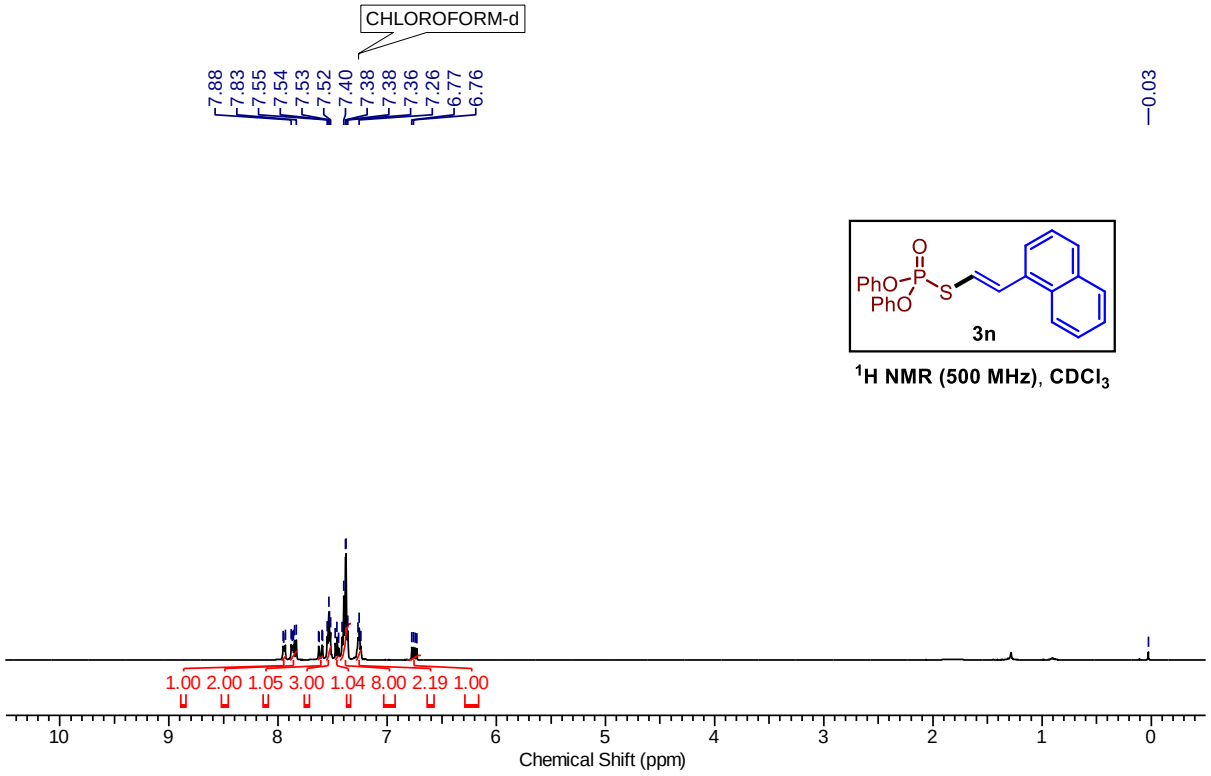

CHLOROFORM-d
7.57
7.43
7.41
7.40
7.36
7.35
7.31
7.29
7.27
7.16
6.75
6.73
0.03
PhO
PhO
O
P
S
3m
Br
1H NMR (500 MHz), CDCl3
1.00 1.04 4.01 4.00 3.43 2.04 1.01
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

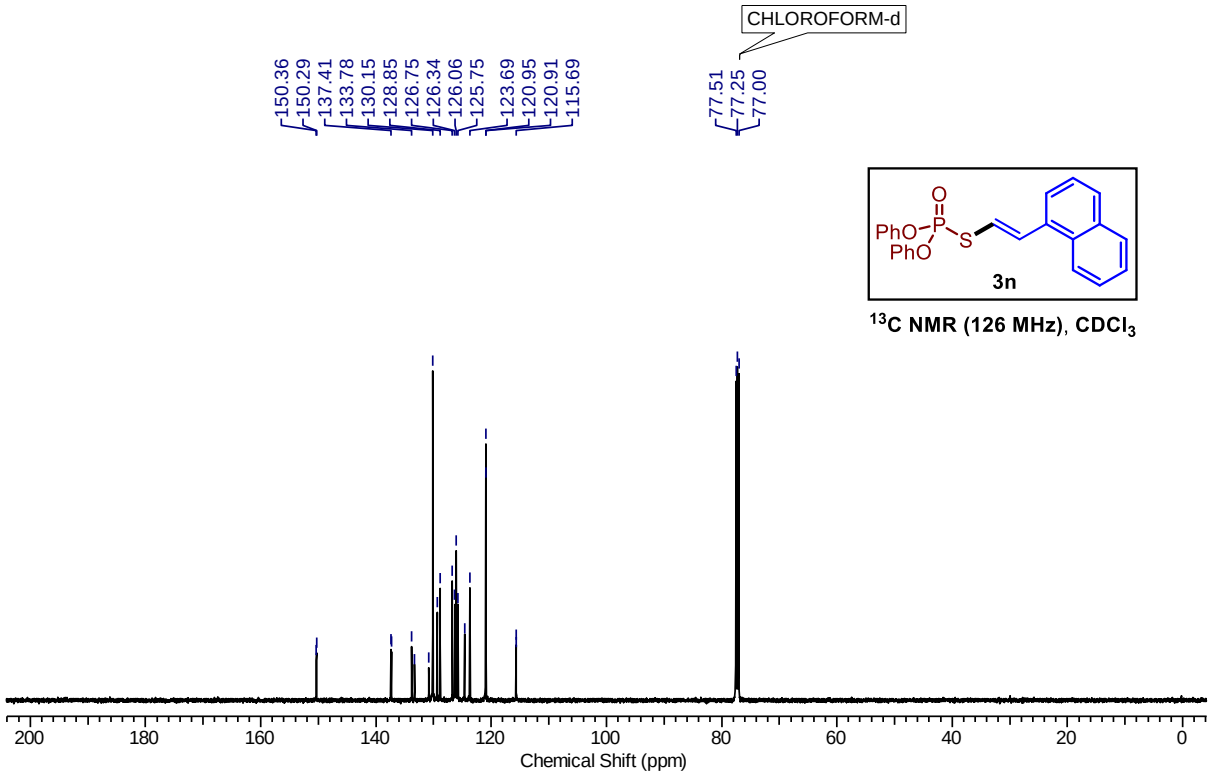

CHLOROFORM-d
150.18
137.44
137.33
135.67
133.33
130.17
130.09
127.91
127.43
126.15
121.00
120.95
116.93
116.88
77.51
77.25
77.00
0.23
PhO
PhO
O
P
S
3m
Br
13C NMR (126 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



^{31}P NMR (202 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$



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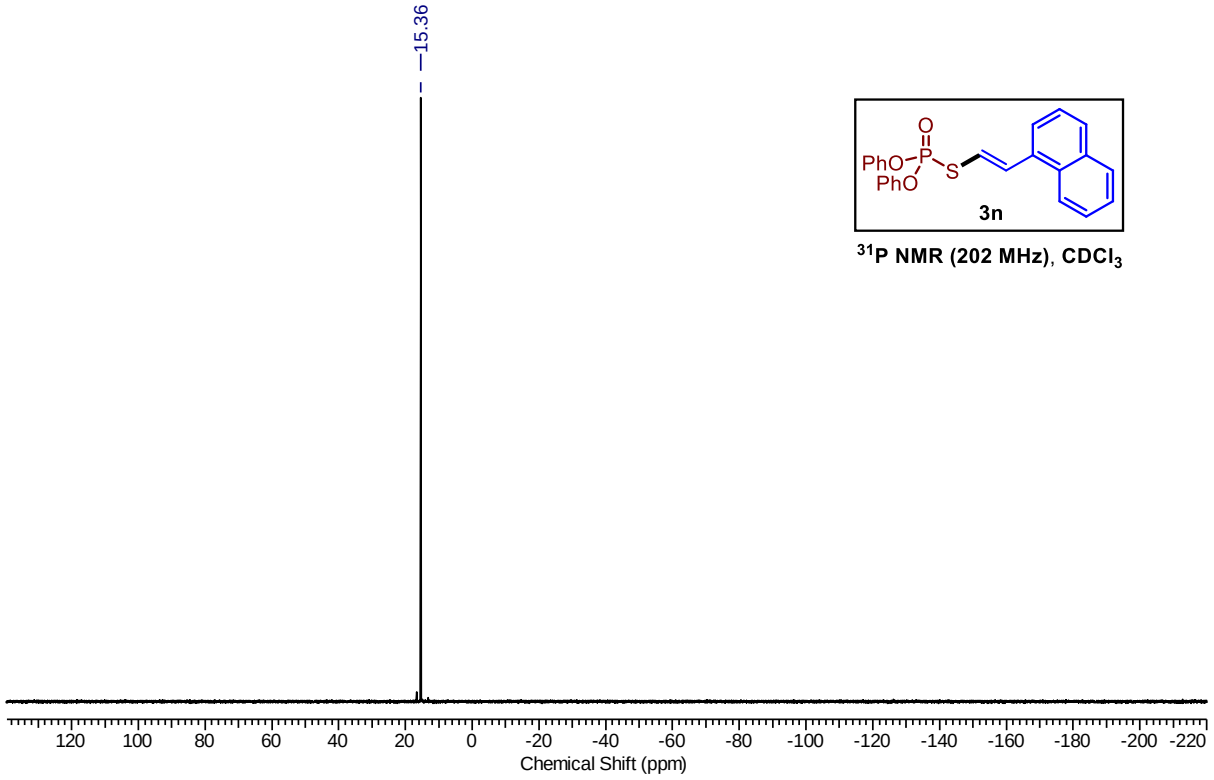

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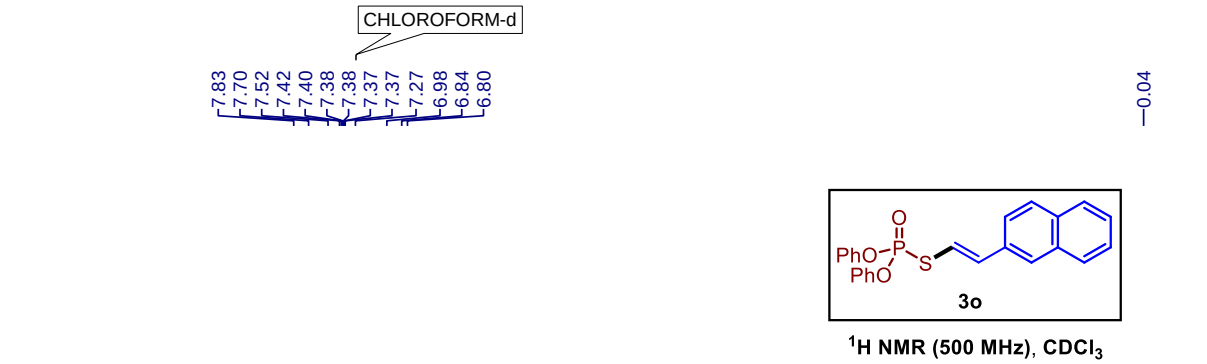
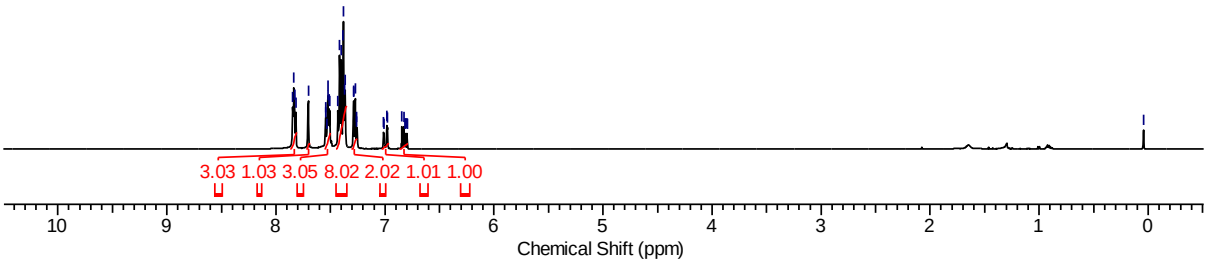
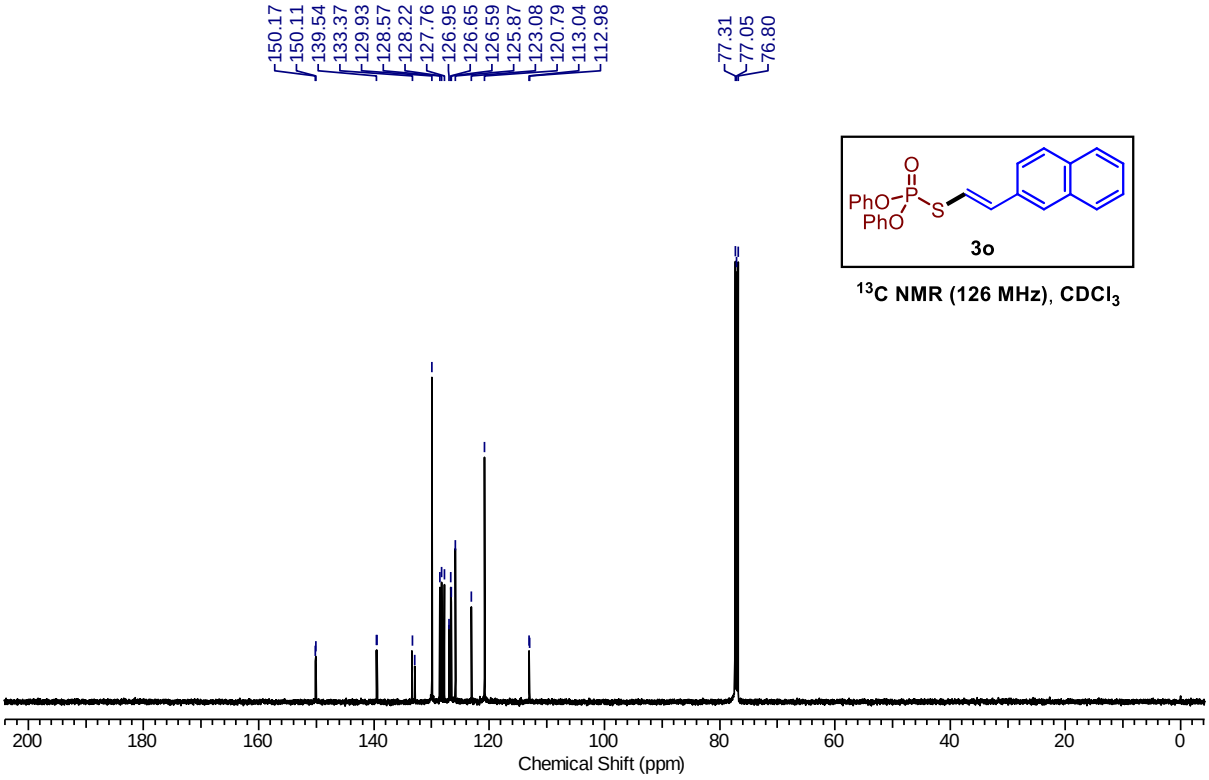


^{1}H NMR (500 MHz), $CDCl_3$





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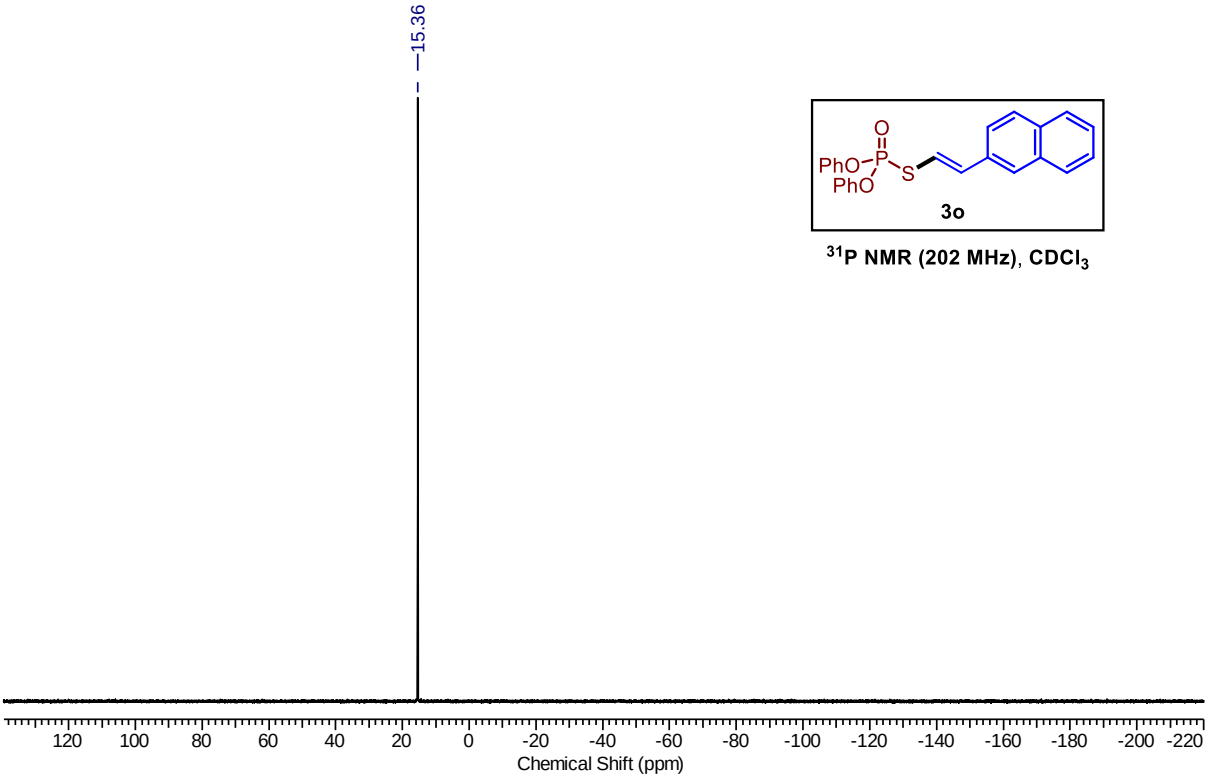
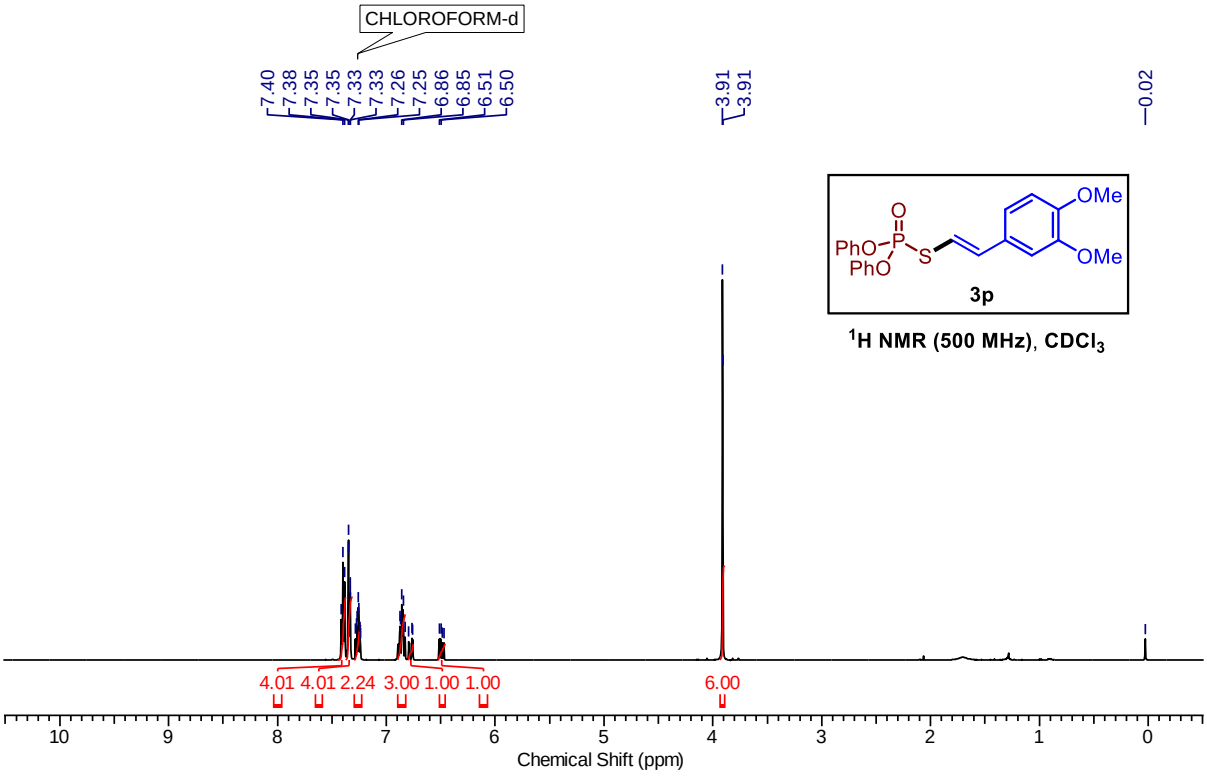
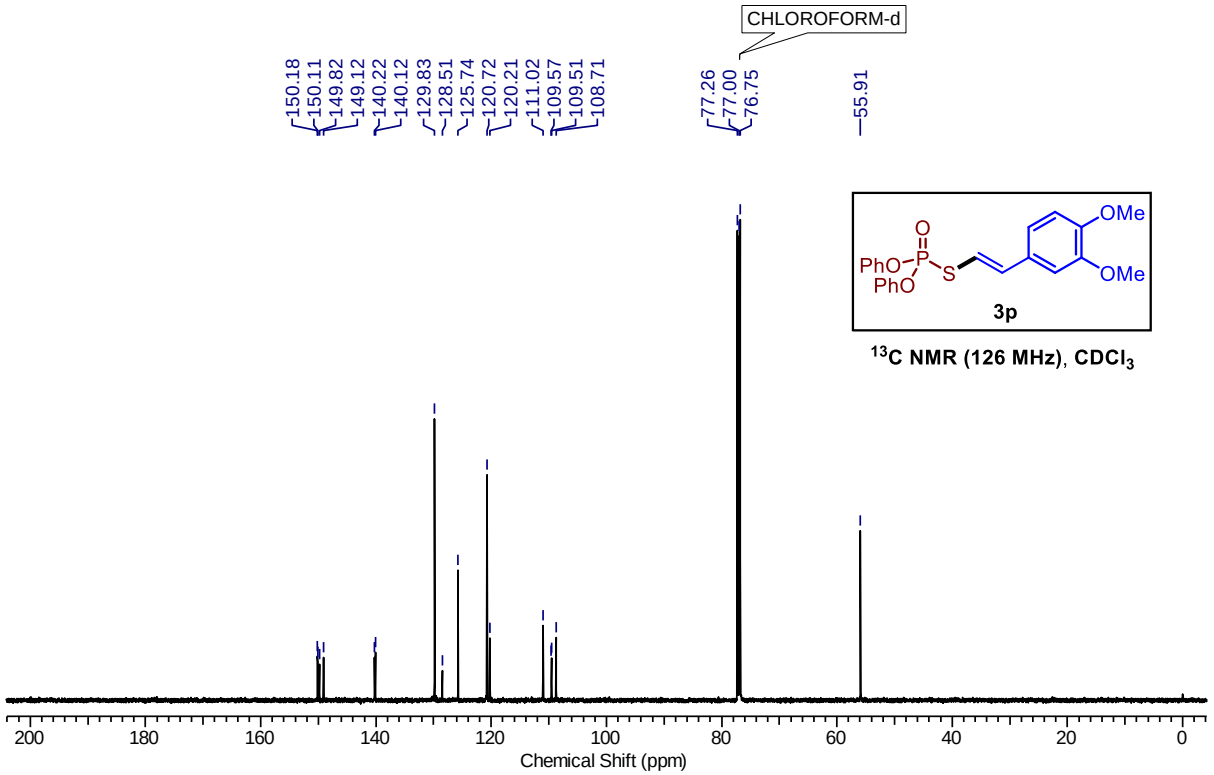


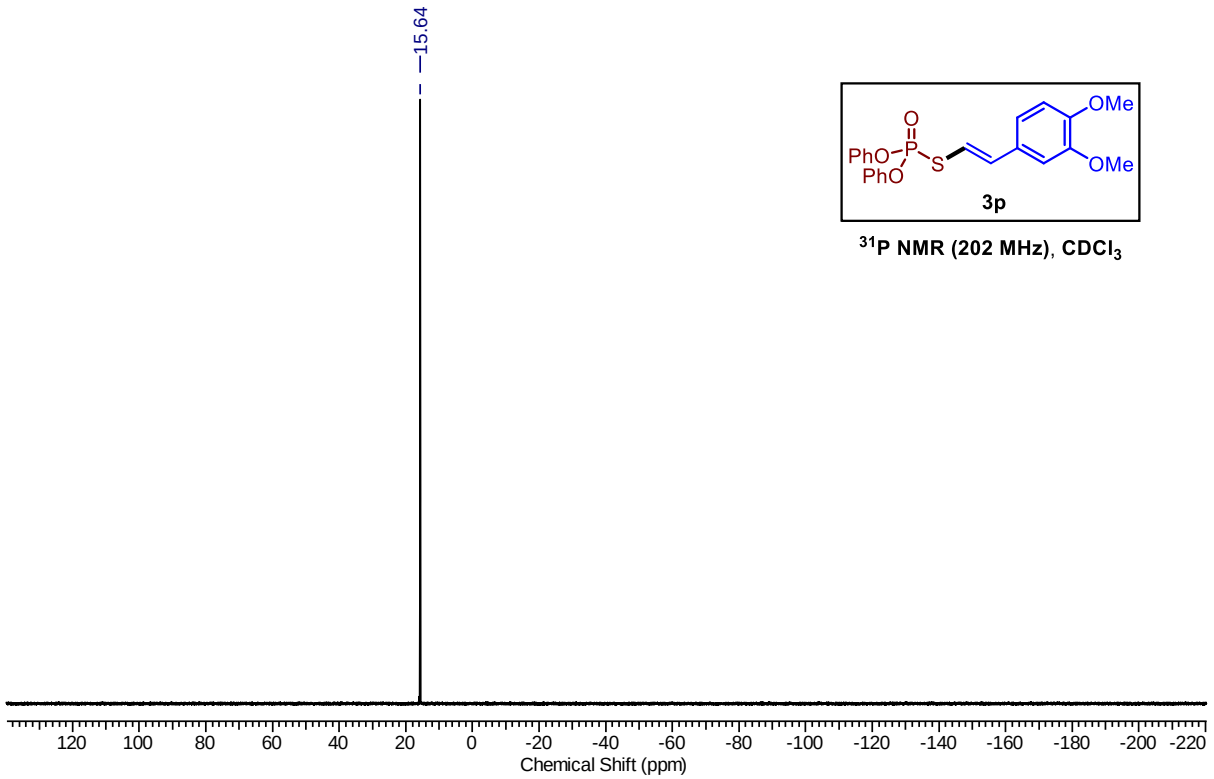
^{31}P NMR (202 MHz), $CDCl_3$



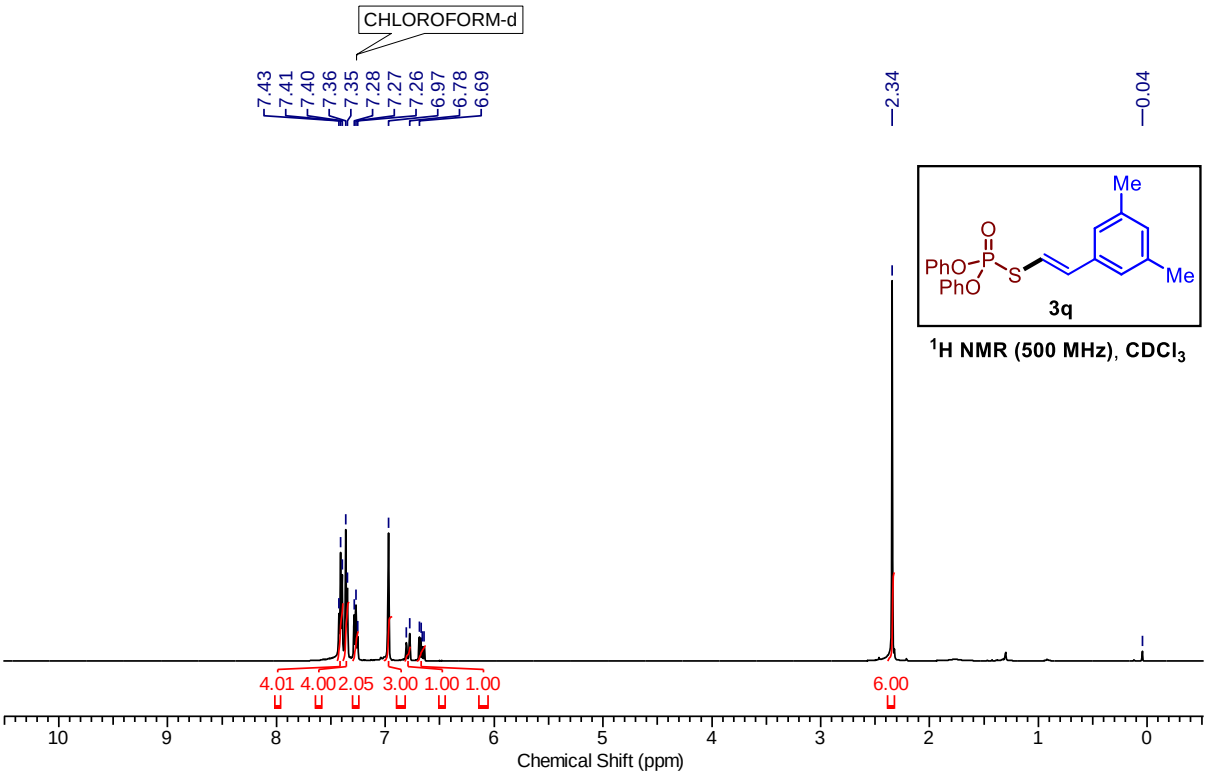
^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (126 MHz), $CDCl_3$



^{31}P NMR (202 MHz), $CDCl_3$



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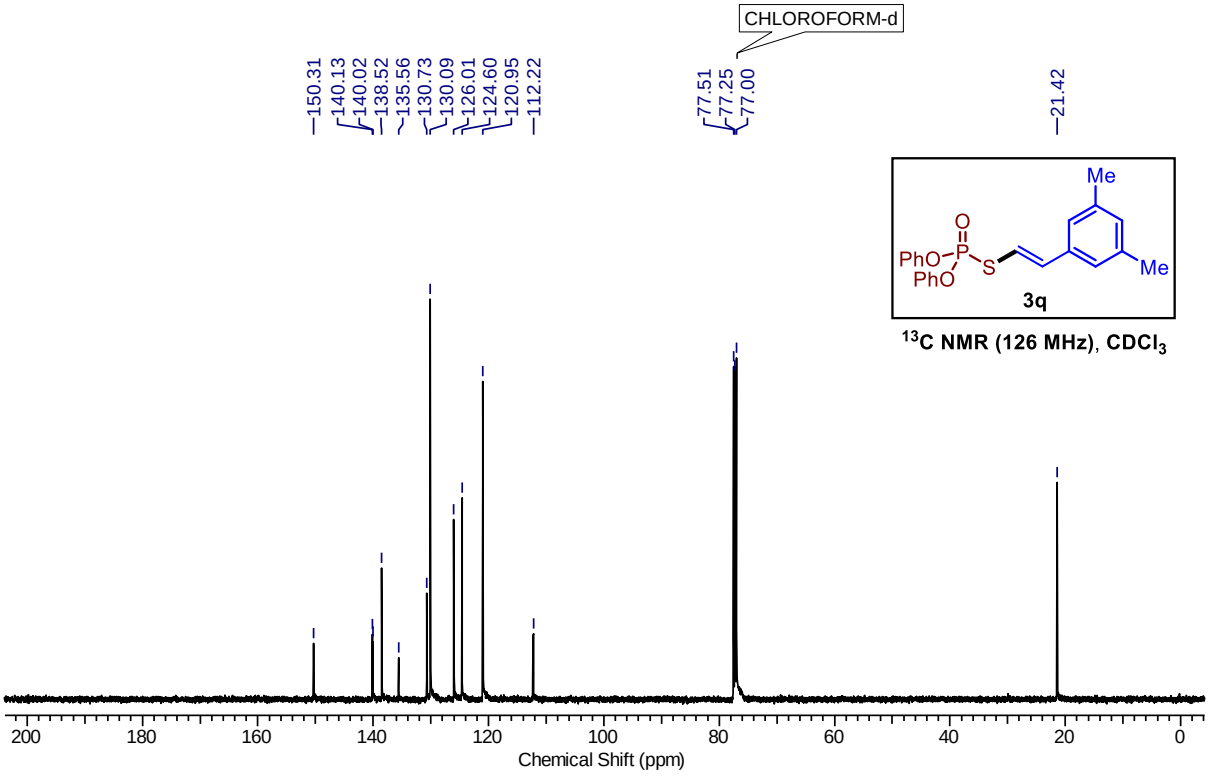
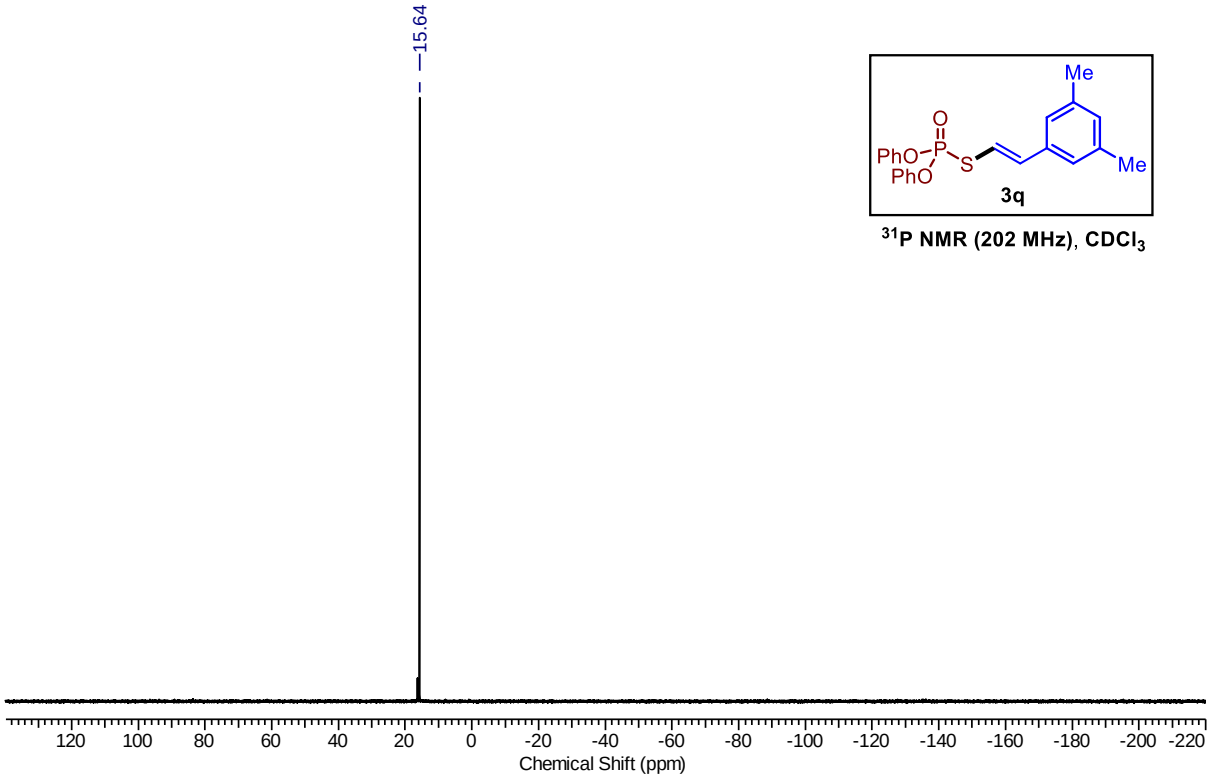
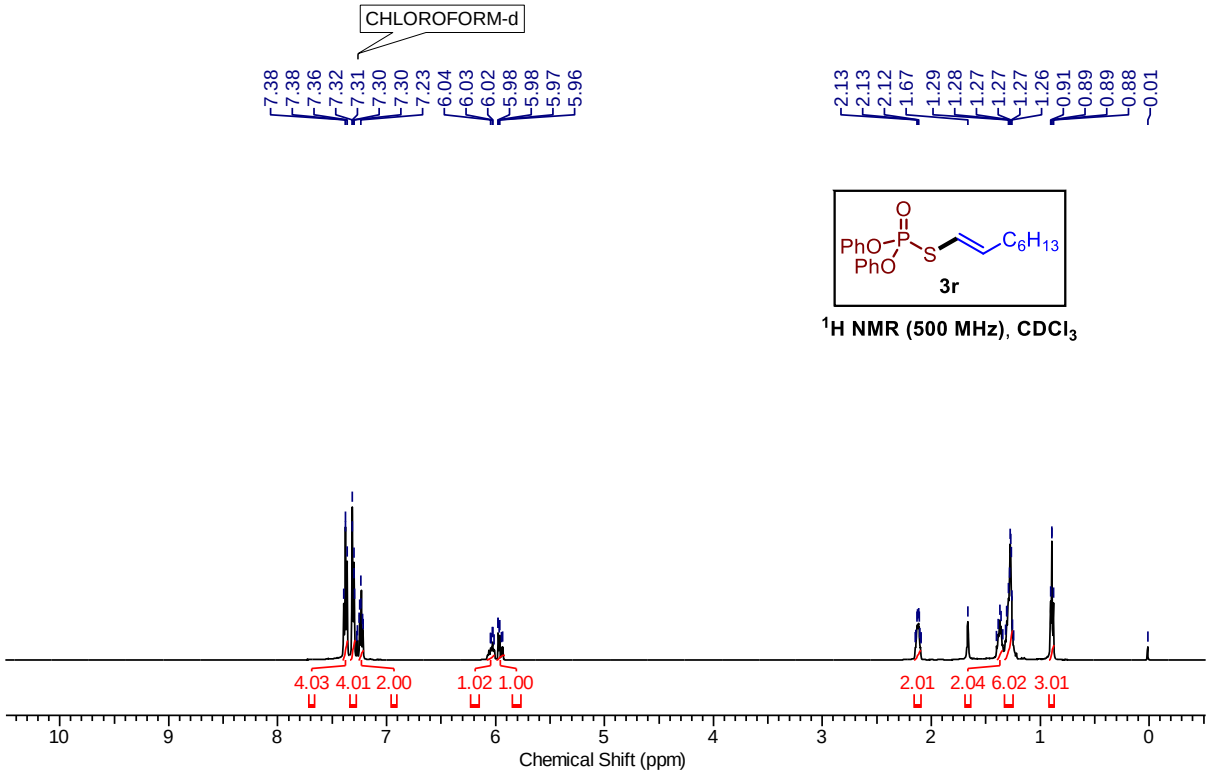


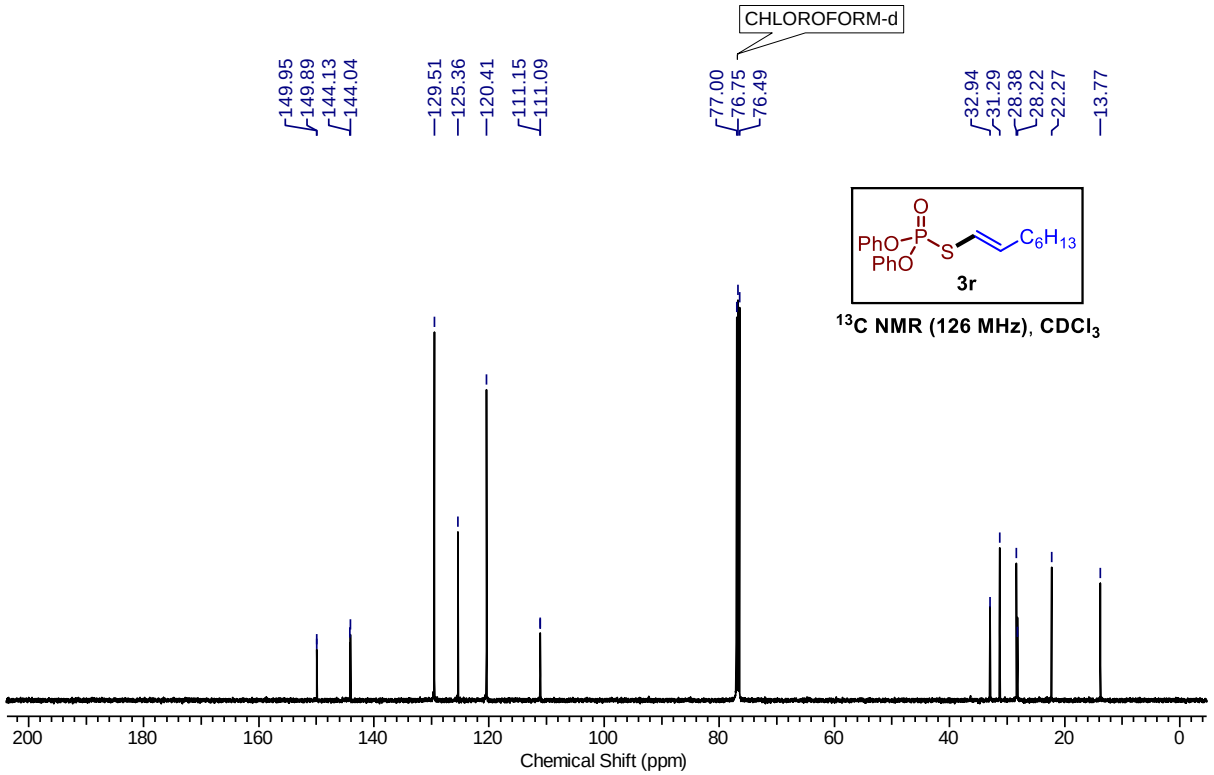
^{13}C NMR (126 MHz), $CDCl_3$



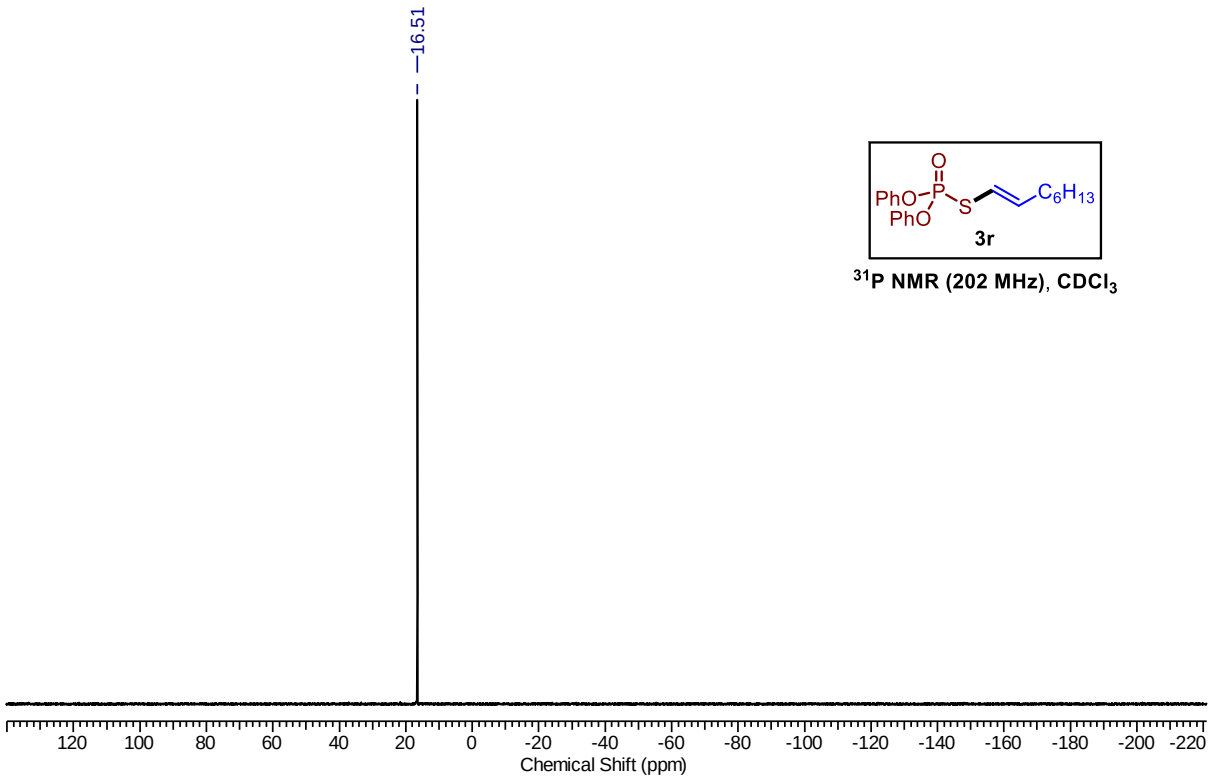
^{31}P NMR (202 MHz), $CDCl_3$



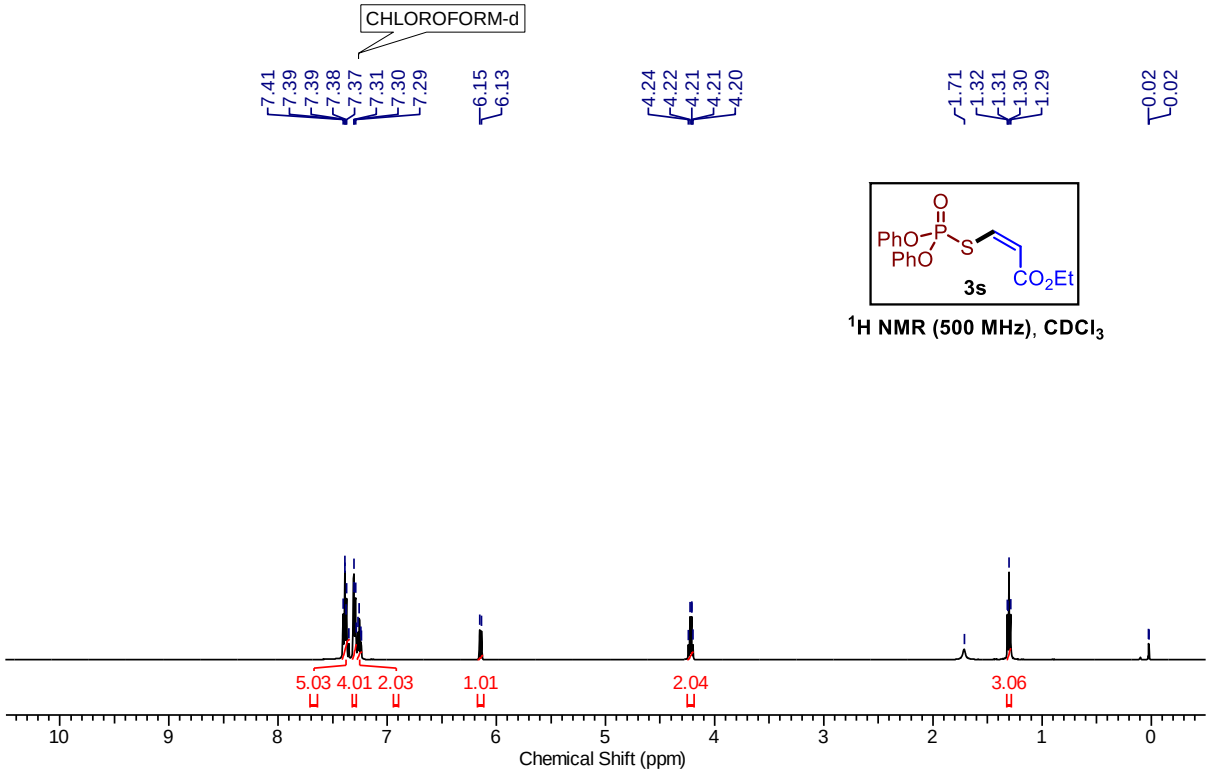
^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (126 MHz), $CDCl_3$



^{31}P NMR (202 MHz), $CDCl_3$


CHLOROFORM-d
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7.39
7.39
7.38
7.37
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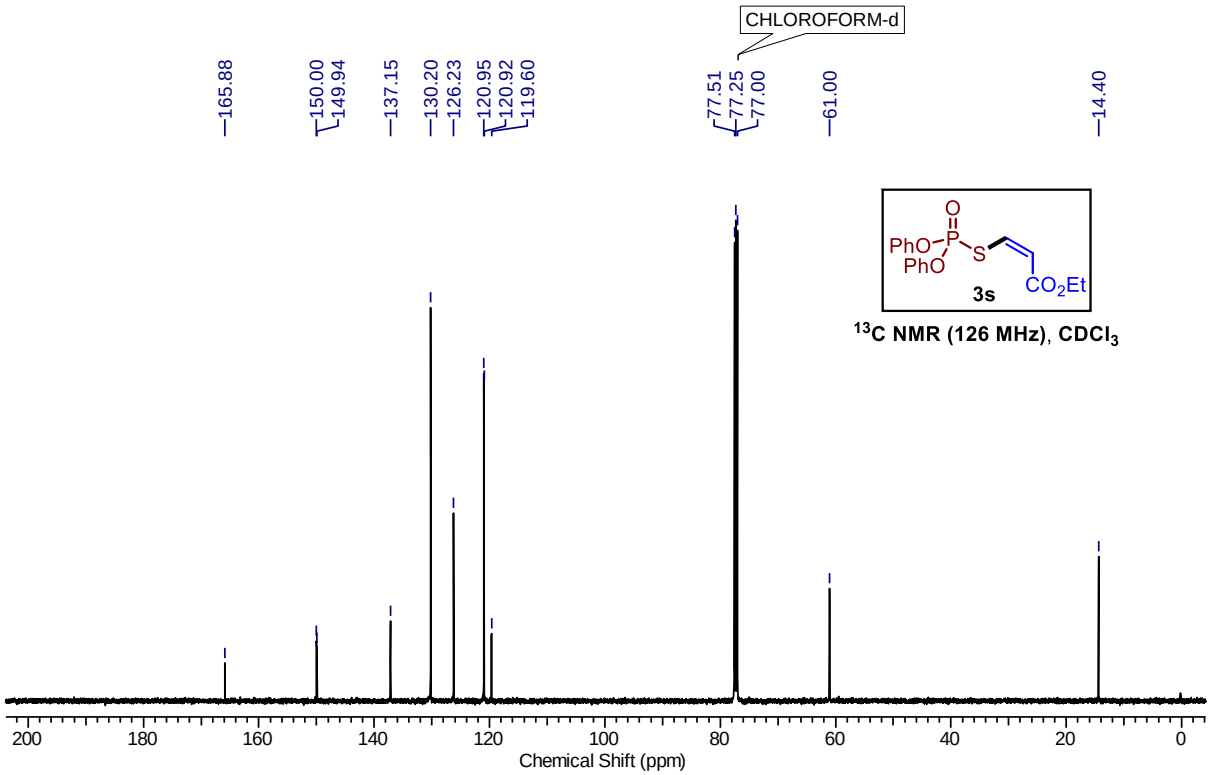
7.29
6.15
6.13
4.24
4.22
4.21
4.21
4.20
1.71
1.32
1.31
1.30
1.29
0.02
0.02
PhO
PhO
O
P
S
CO2Et
3s
1H NMR (500 MHz), CDCl3
5.03
4.01
2.03
1.01
2.04
3.06
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
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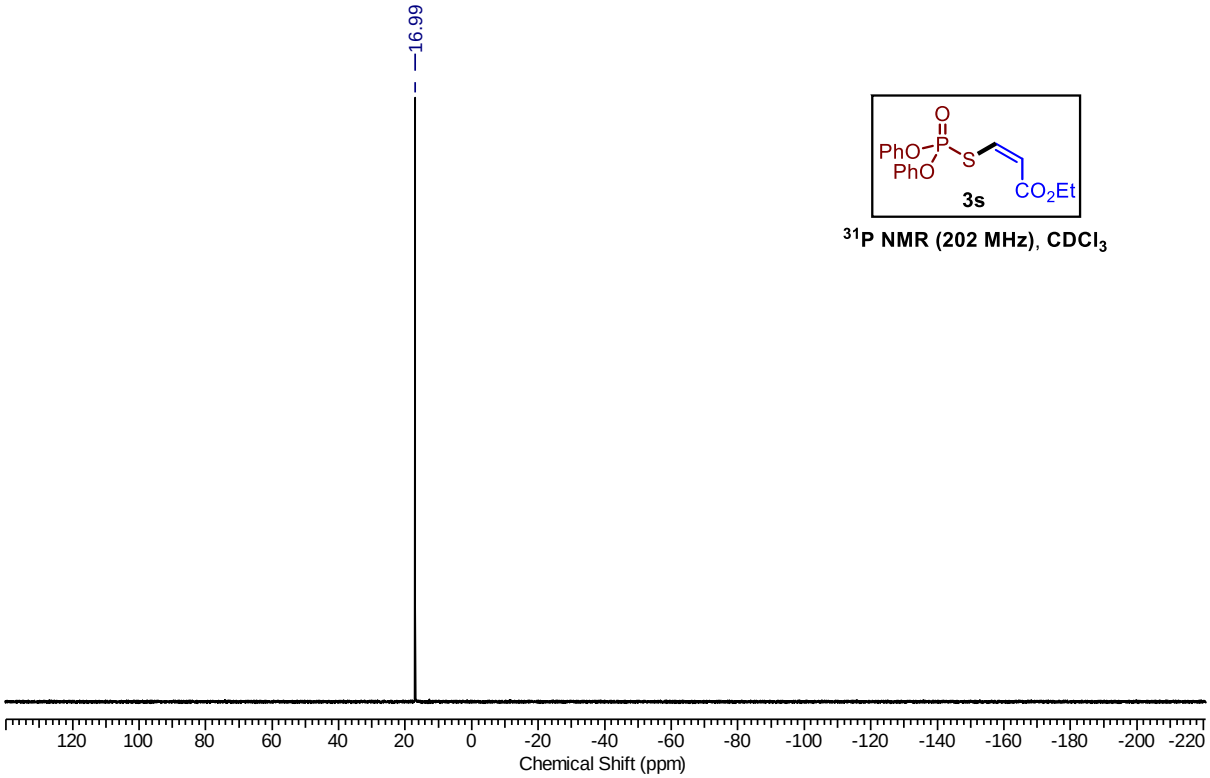
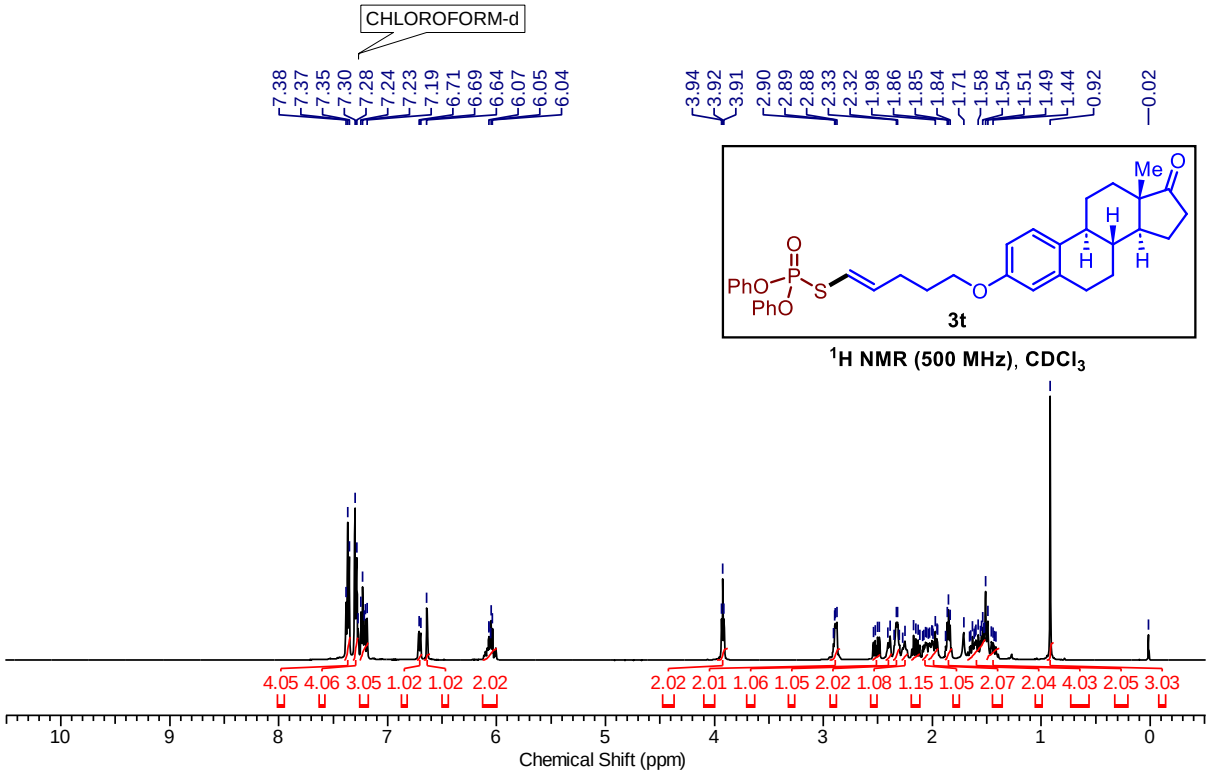
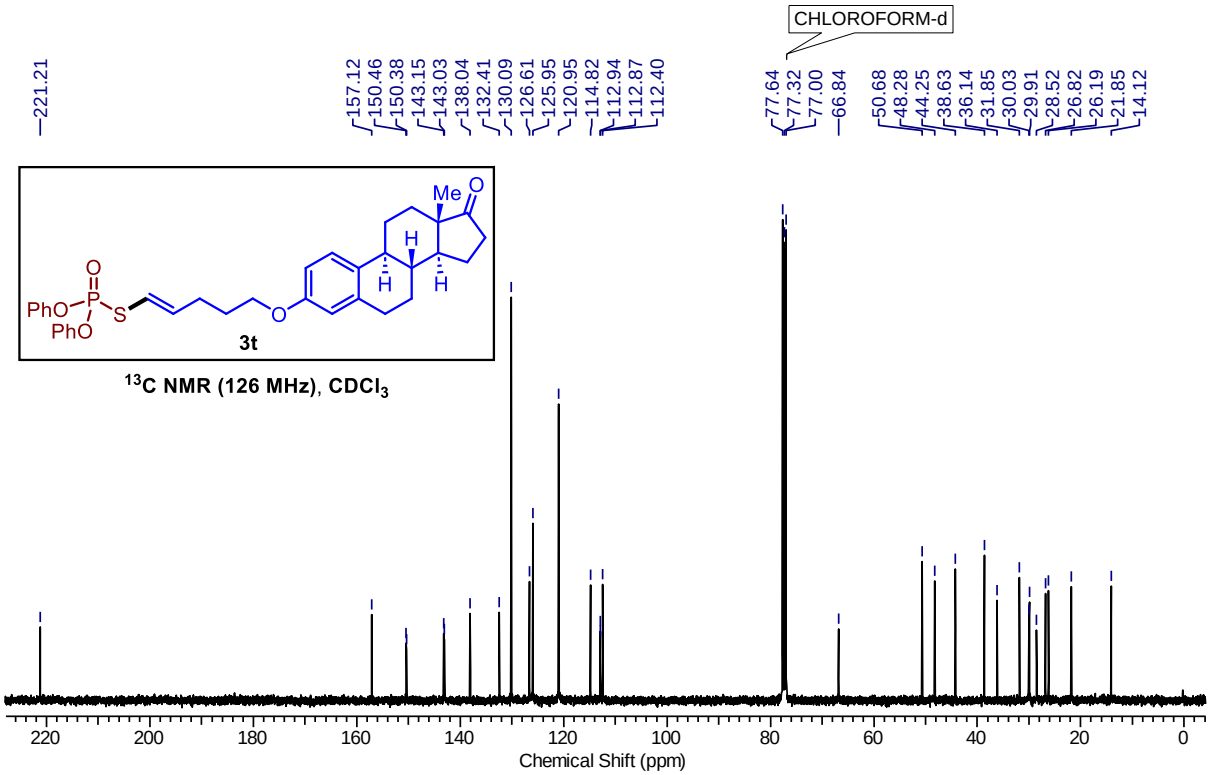
130.20
126.23
120.95
120.92
119.60
77.51
77.25
77.00
61.00
14.40
PhO
PhO
O
P
S
CO2Et
3s
13C NMR (126 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



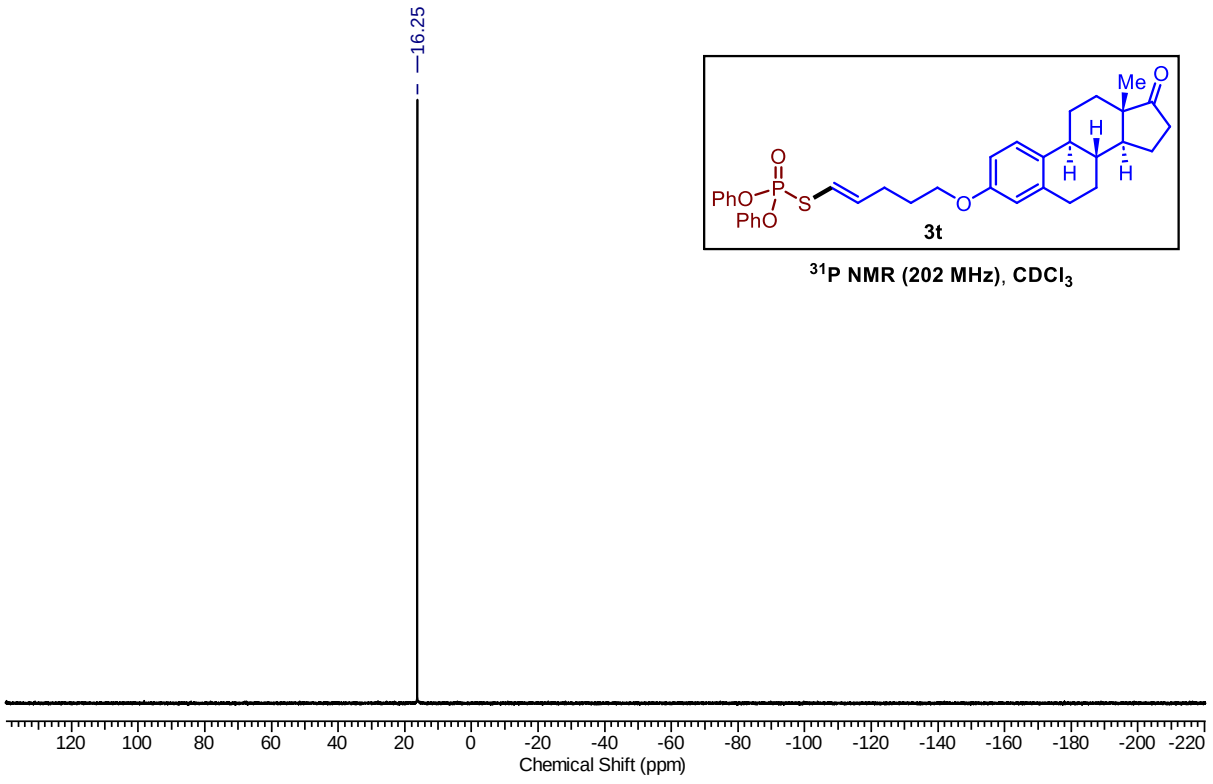
^{31}P NMR (202 MHz), $CDCl_3$



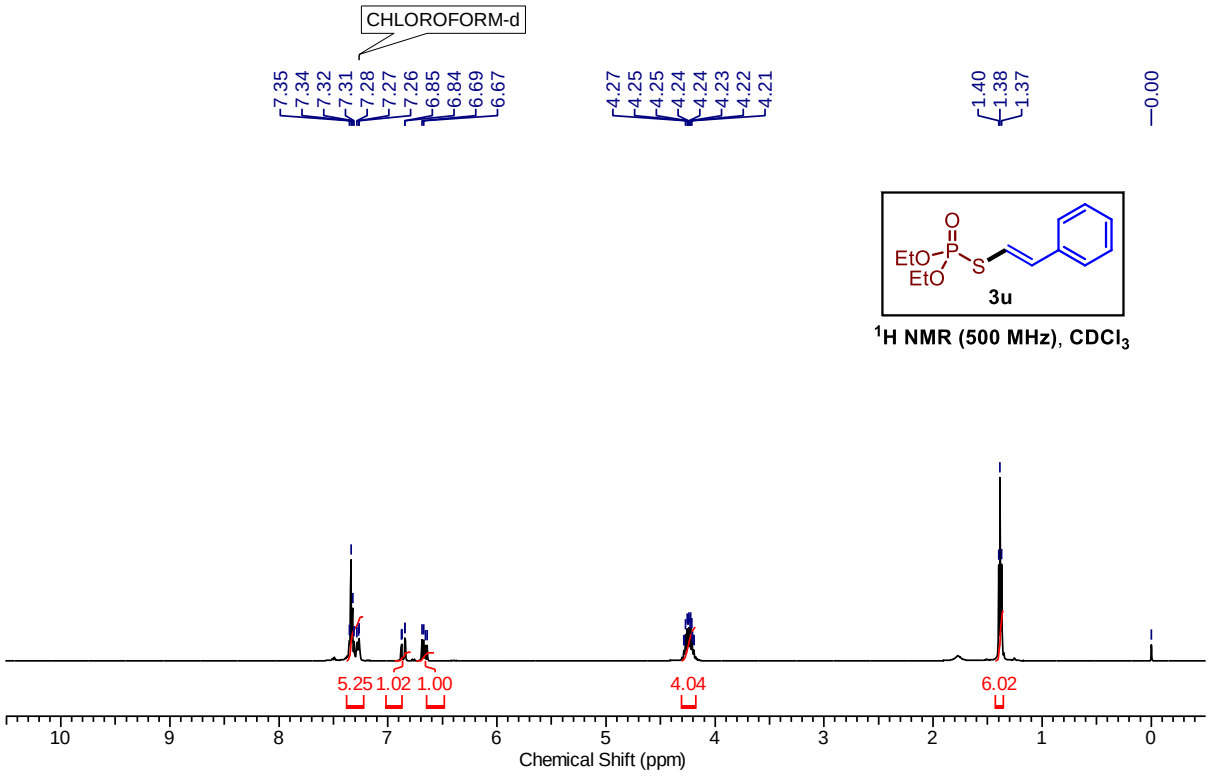
^{1}H NMR (500 MHz), $CDCl_3$



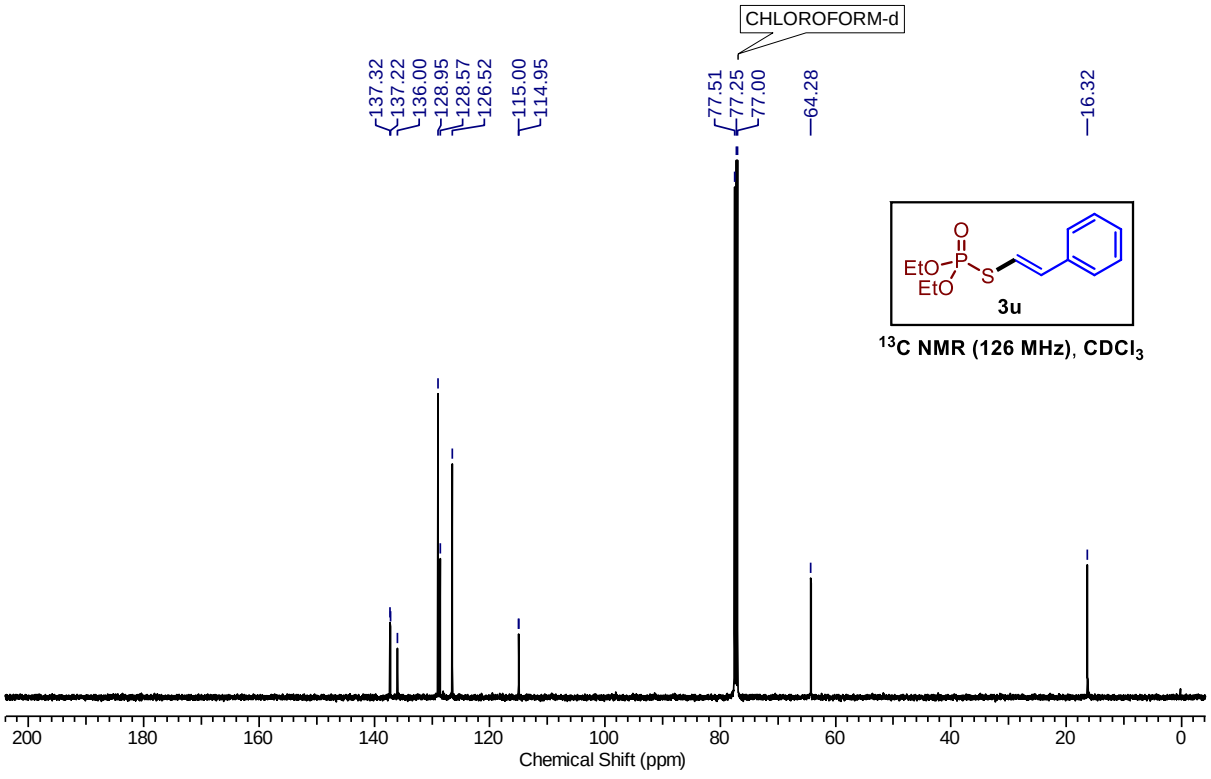
^{13}C NMR (126 MHz), $CDCl_3$



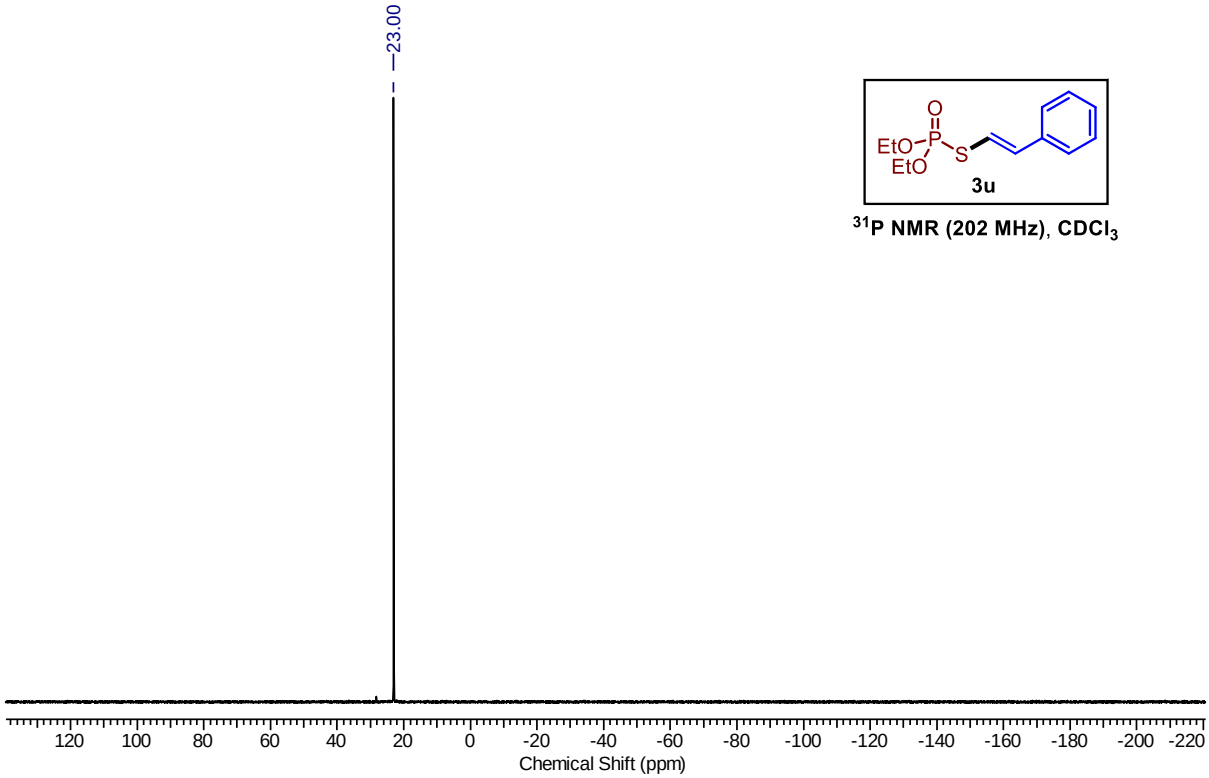
^{31}P NMR (202 MHz), $CDCl_3$



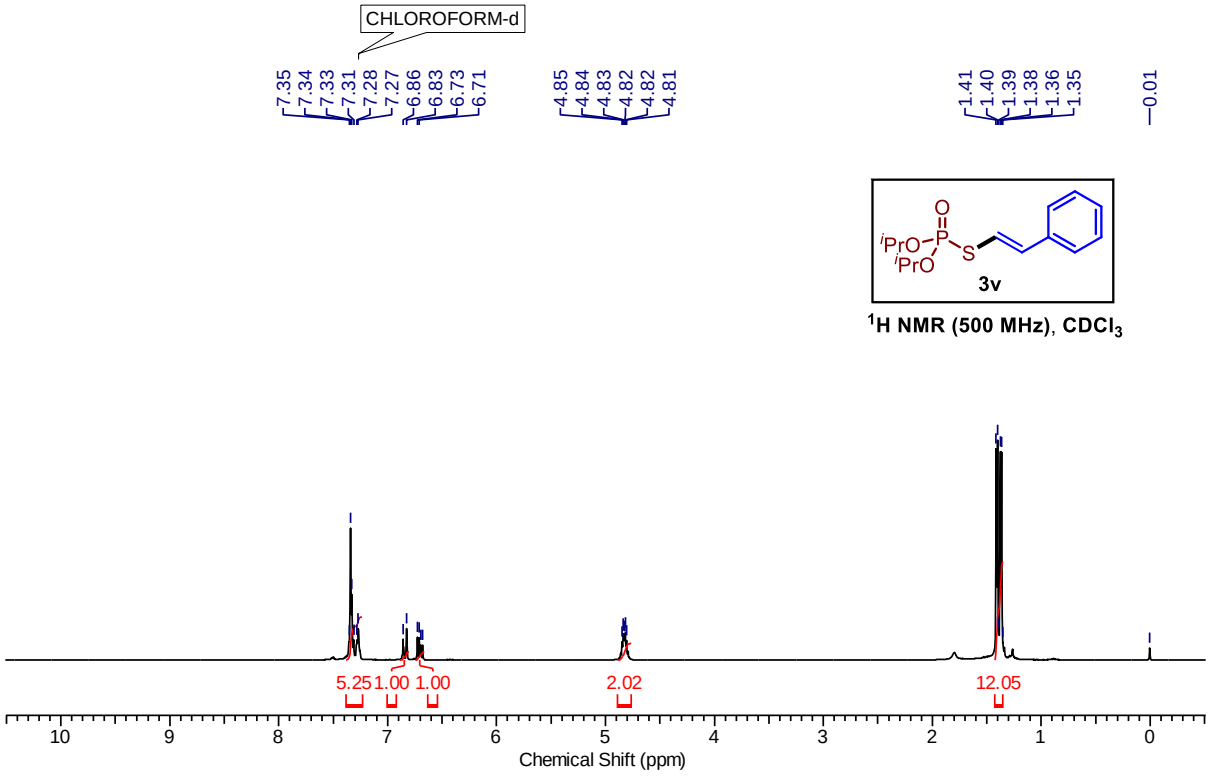
^{1}H NMR (500 MHz), $CDCl_3$



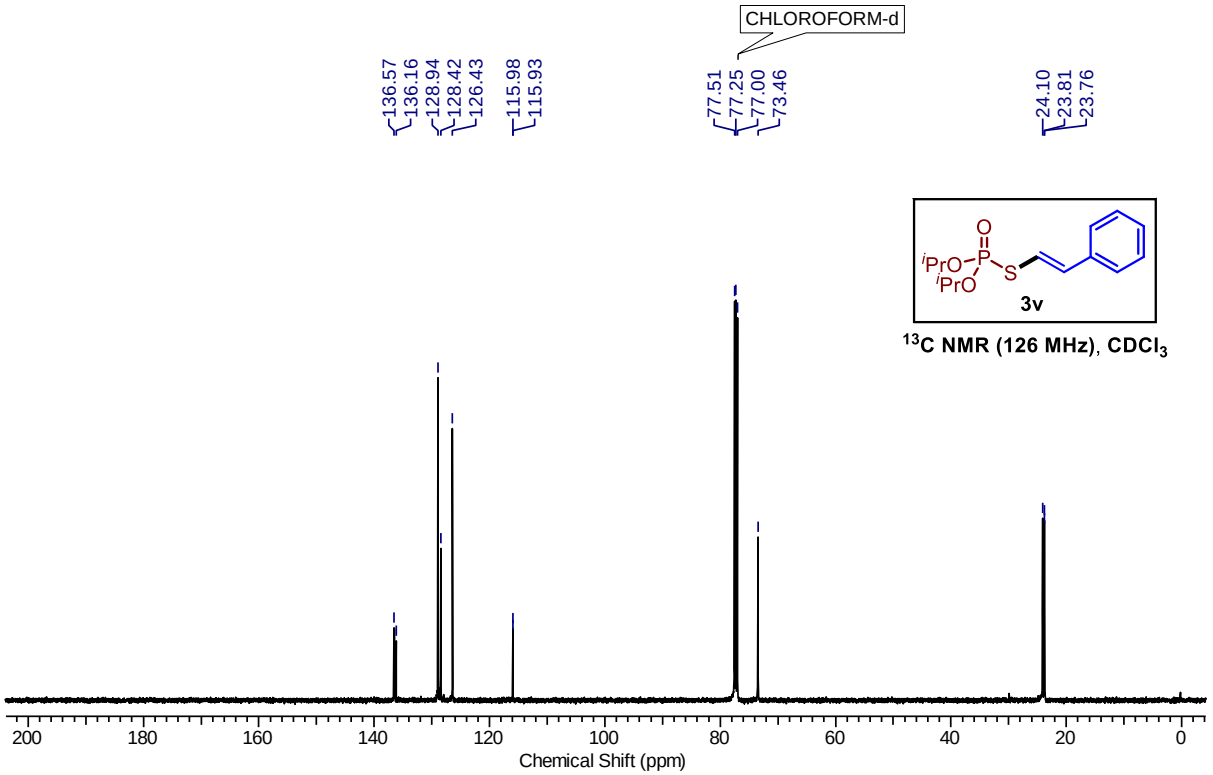
^{13}C NMR (126 MHz), $CDCl_3$



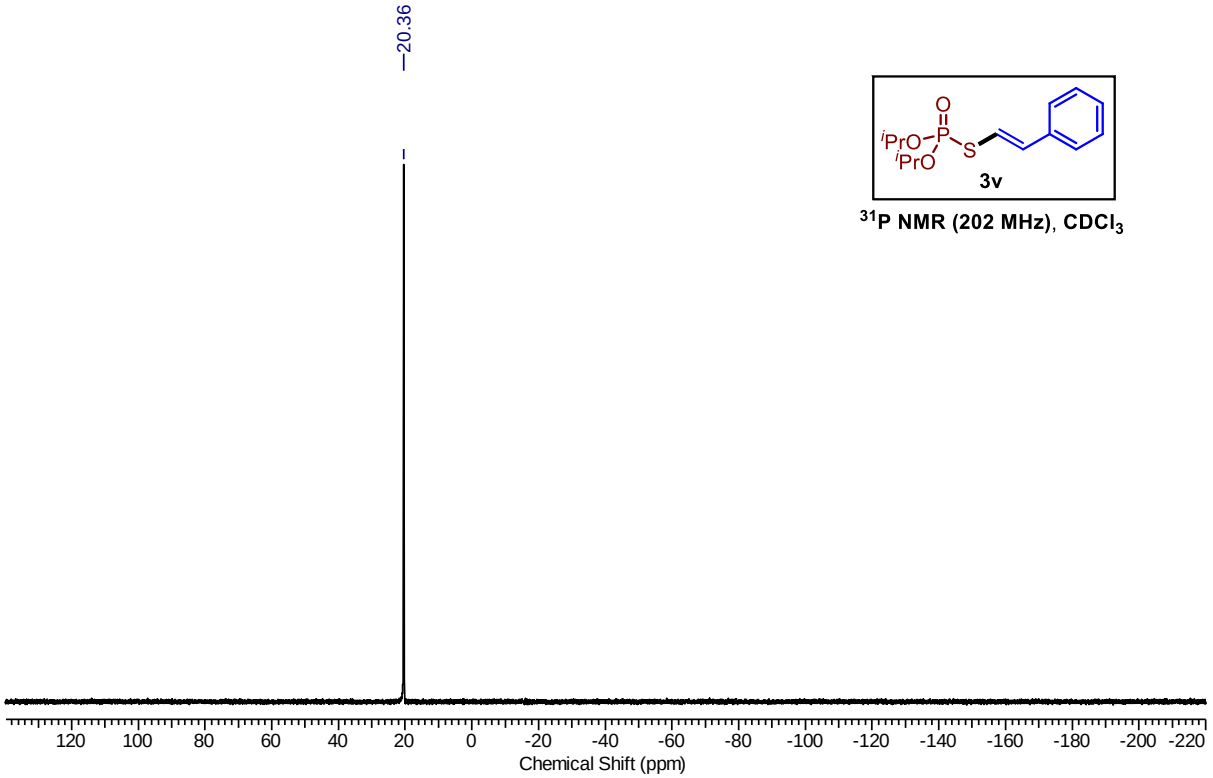
^{31}P NMR (202 MHz), $CDCl_3$



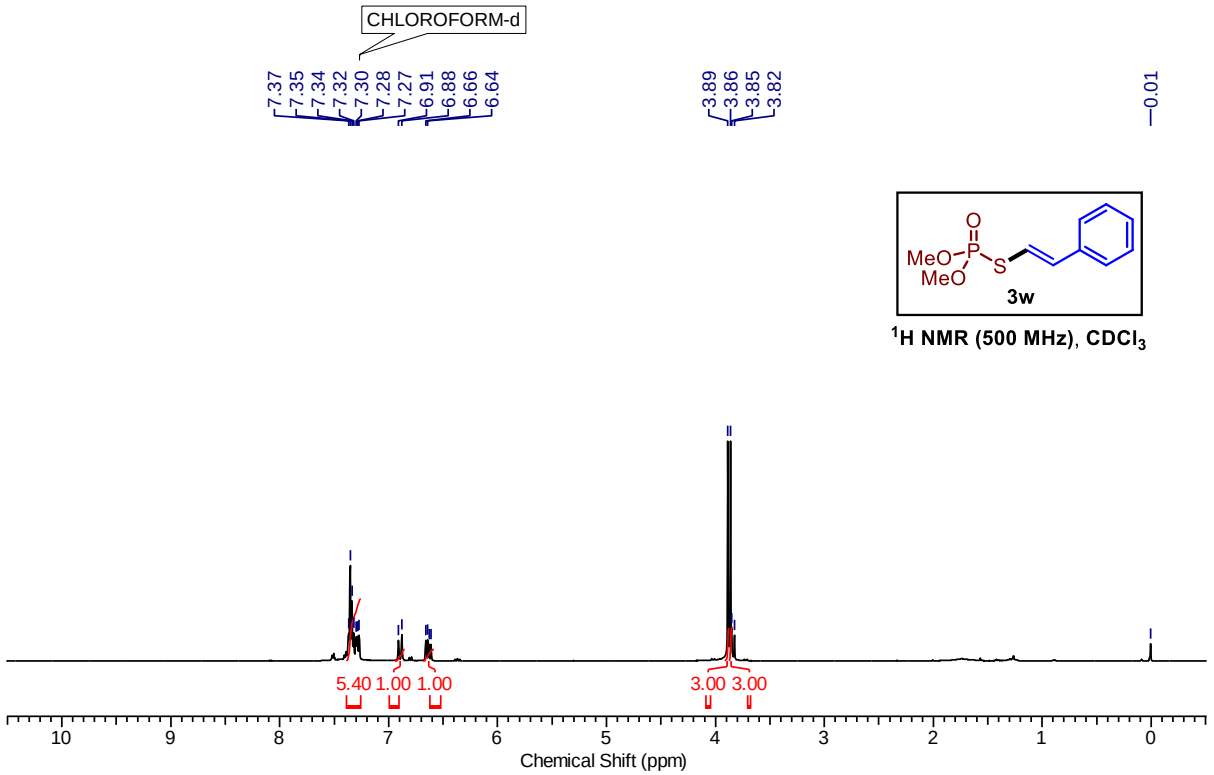
^{1}H NMR (500 MHz), $CDCl_3$



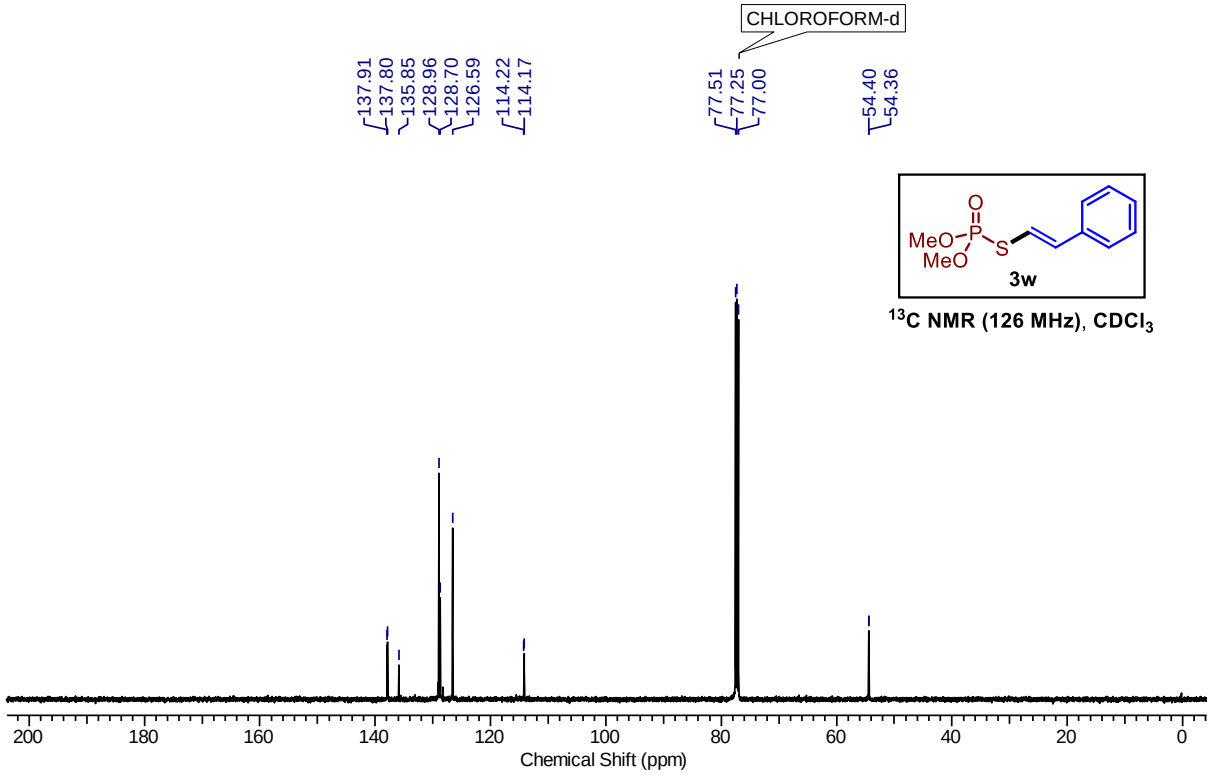
^{13}C NMR (126 MHz), $CDCl_3$



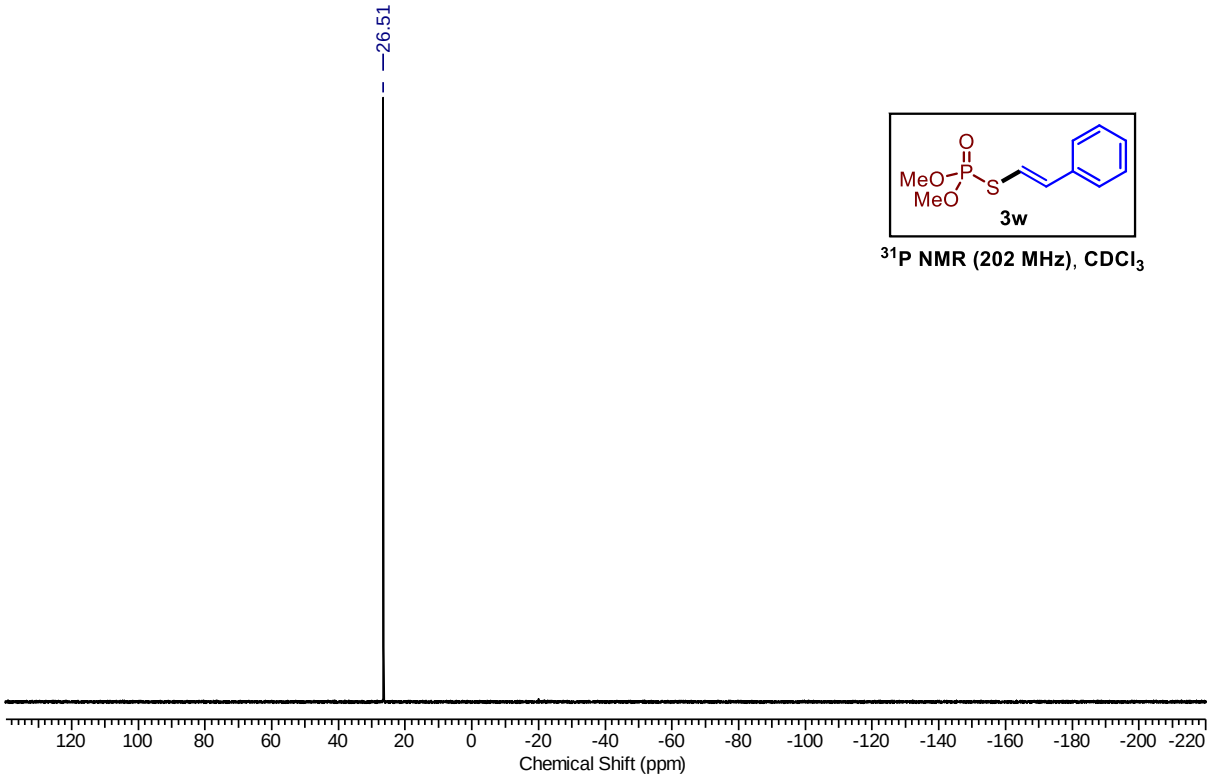
^{31}P NMR (202 MHz), $CDCl_3$



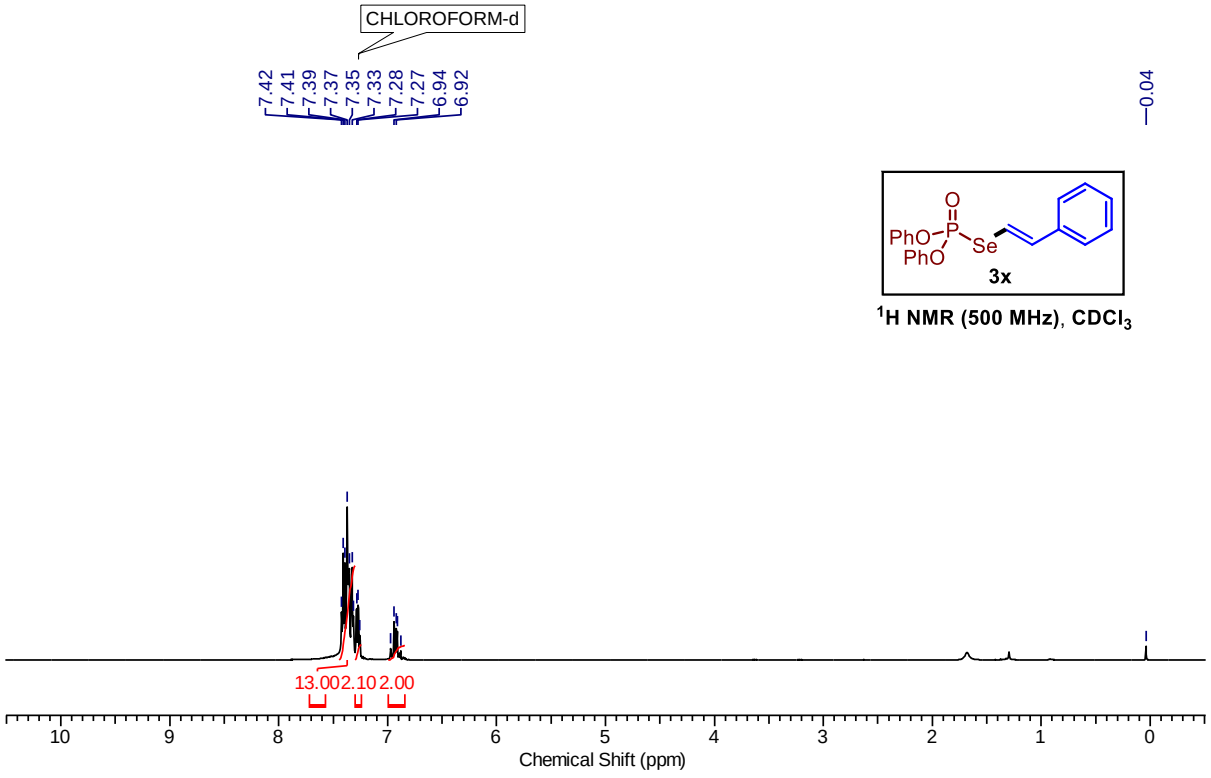
^{1}H NMR (500 MHz), $CDCl_3$



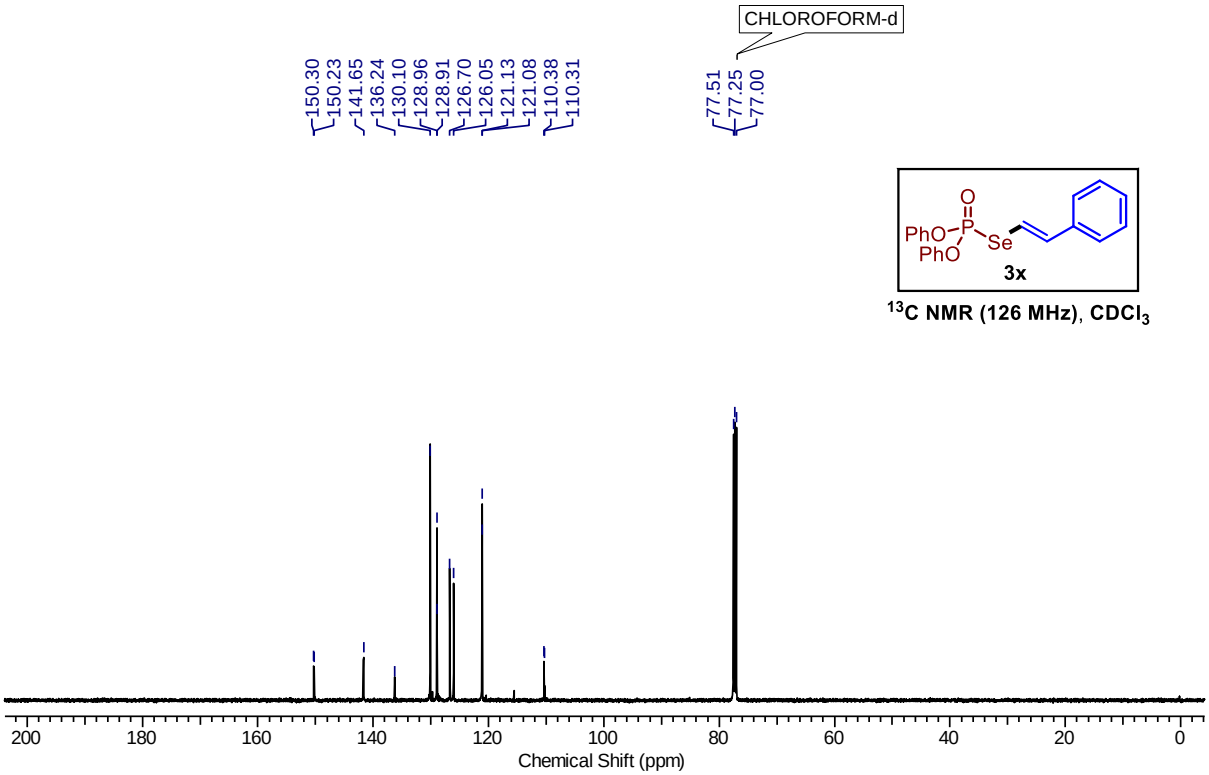
^{13}C NMR (126 MHz), $CDCl_3$



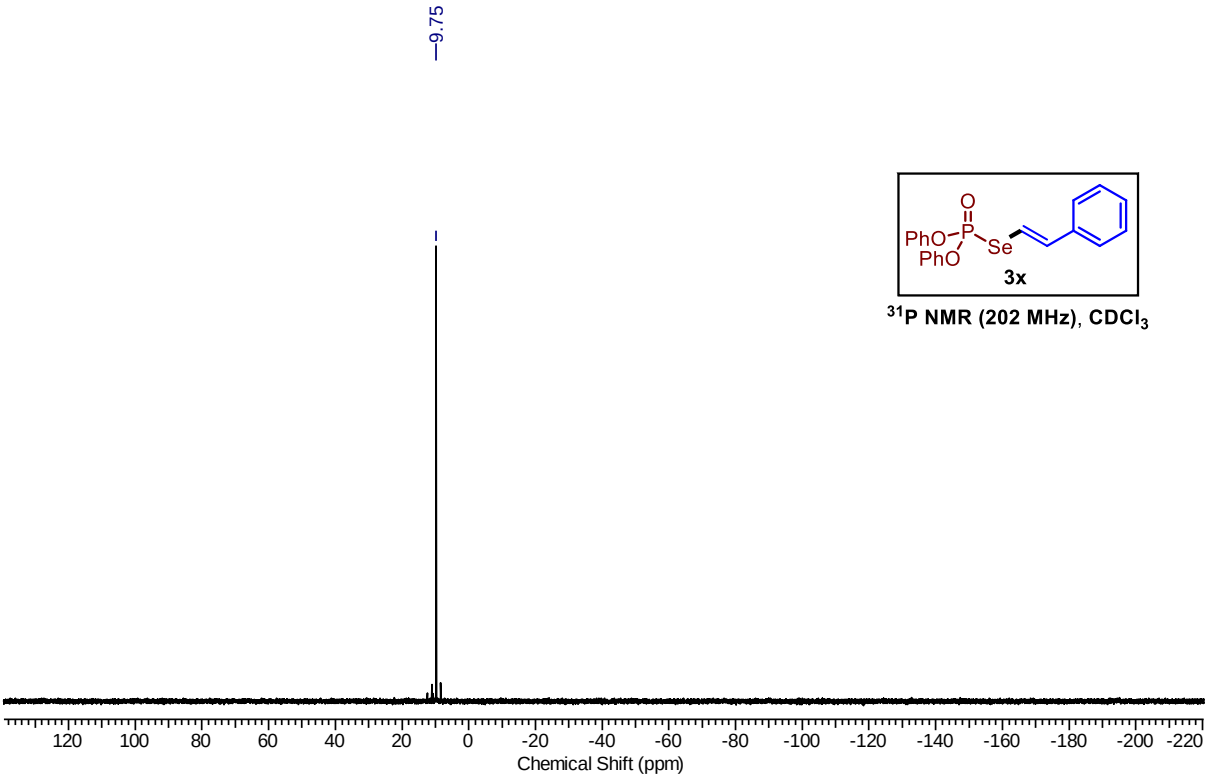
^{31}P NMR (202 MHz), $CDCl_3$



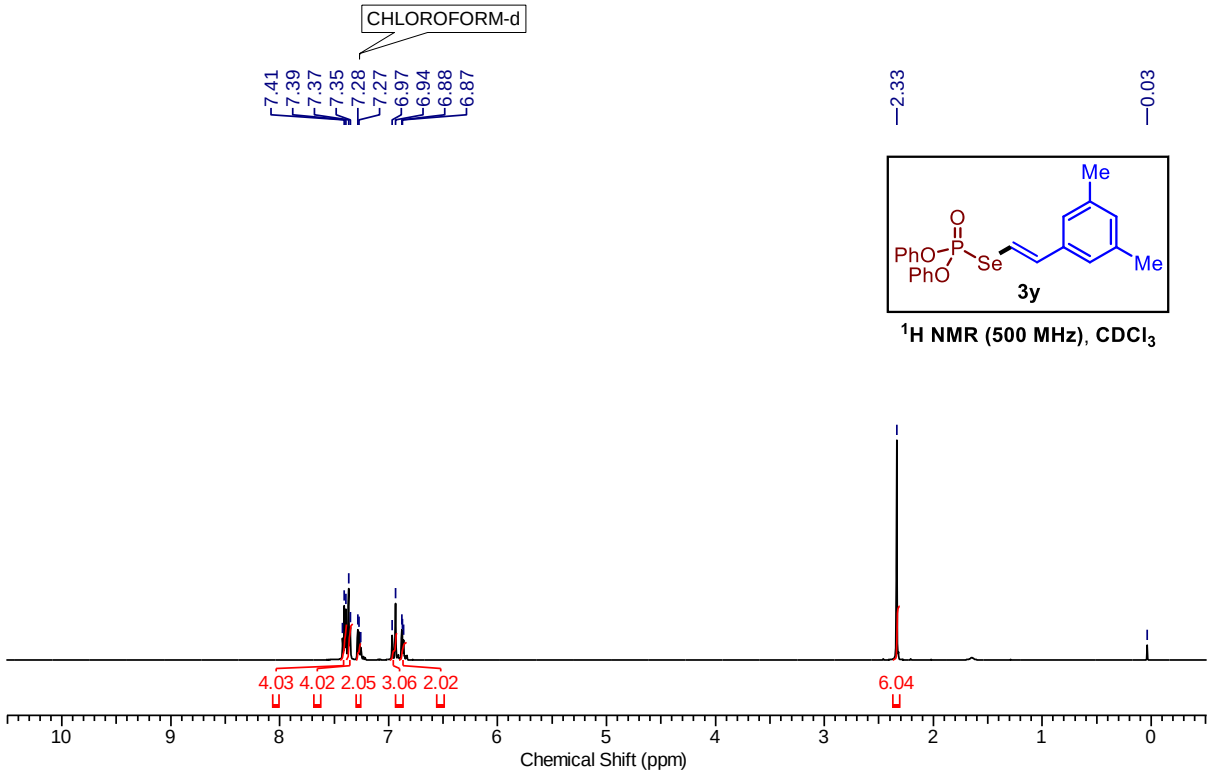
^{1}H NMR (500 MHz), $CDCl_3$



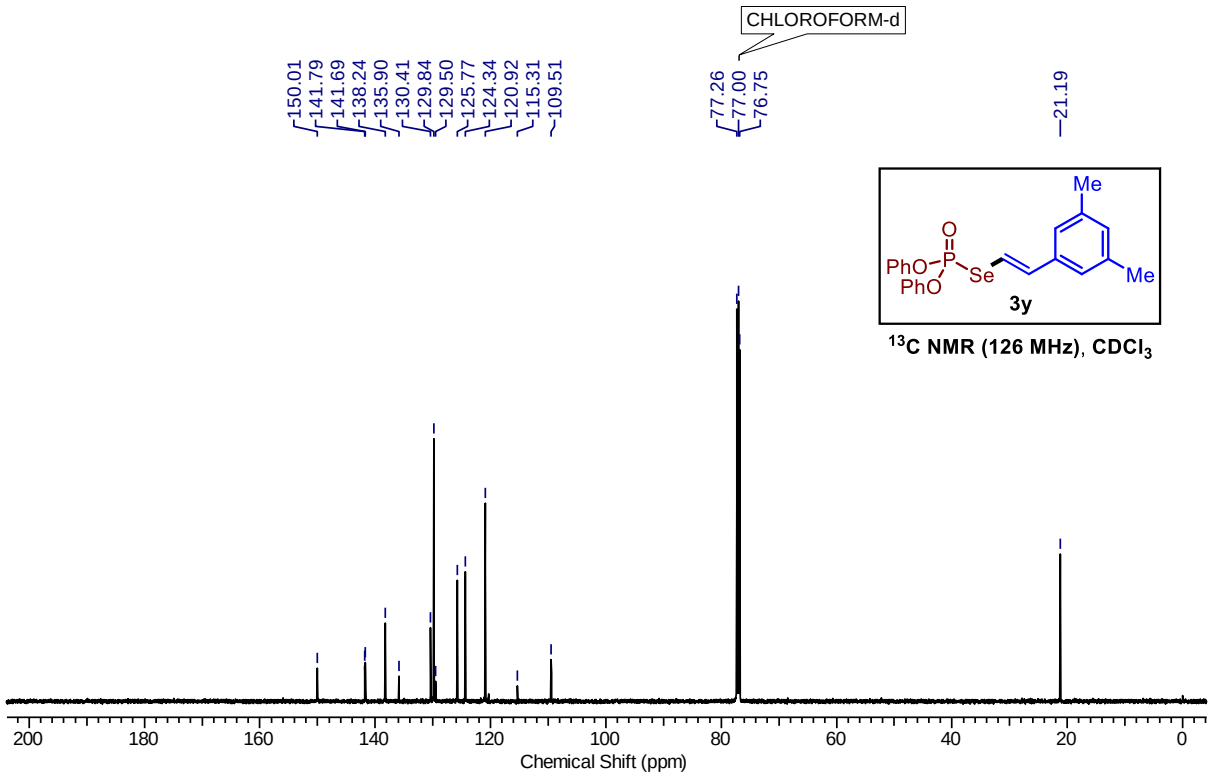
^{13}C NMR (126 MHz), $CDCl_3$



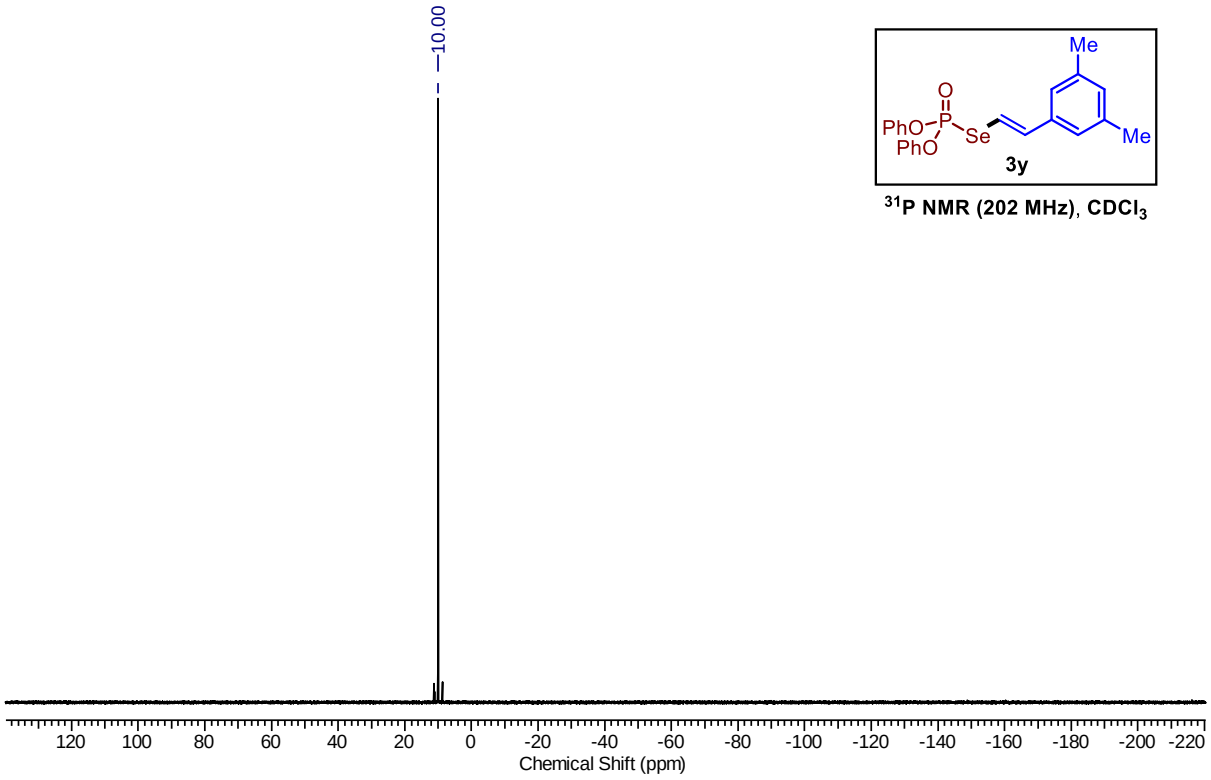
^{31}P NMR (202 MHz), $CDCl_3$



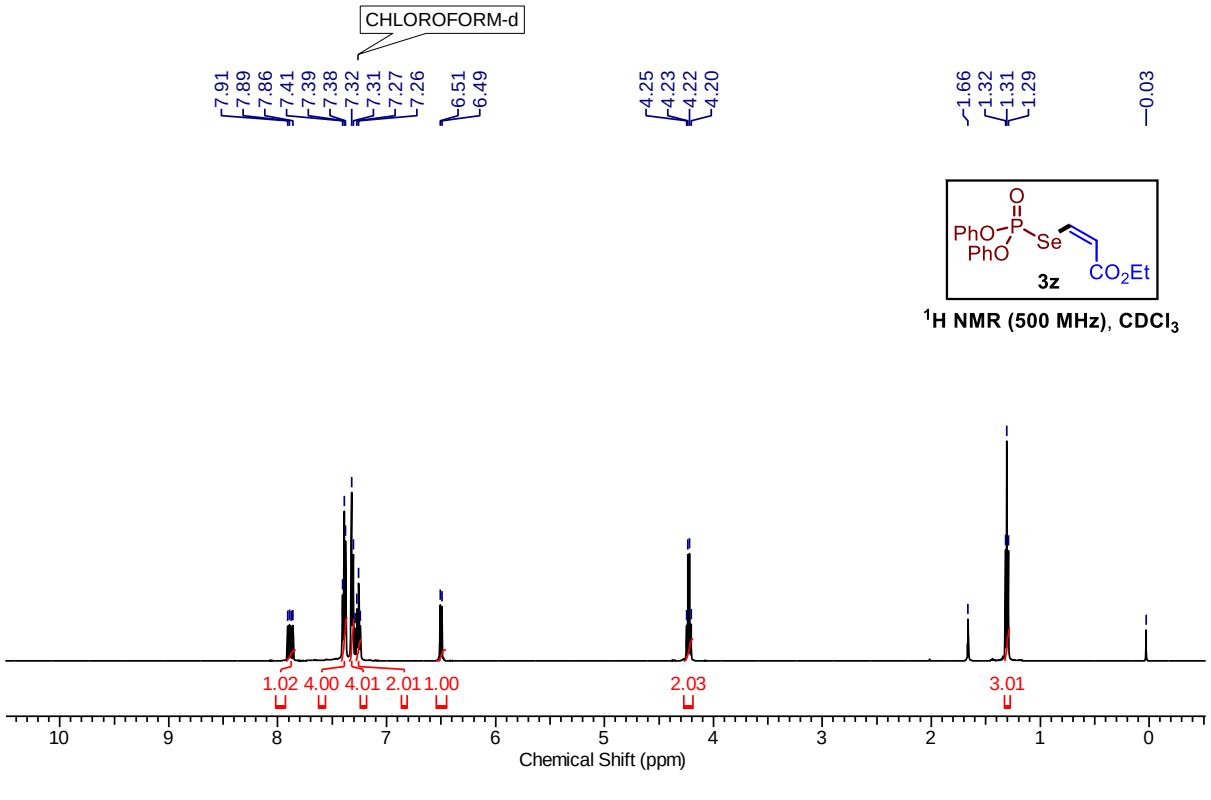
^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (126 MHz), $CDCl_3$



^{31}P NMR (202 MHz), $CDCl_3$



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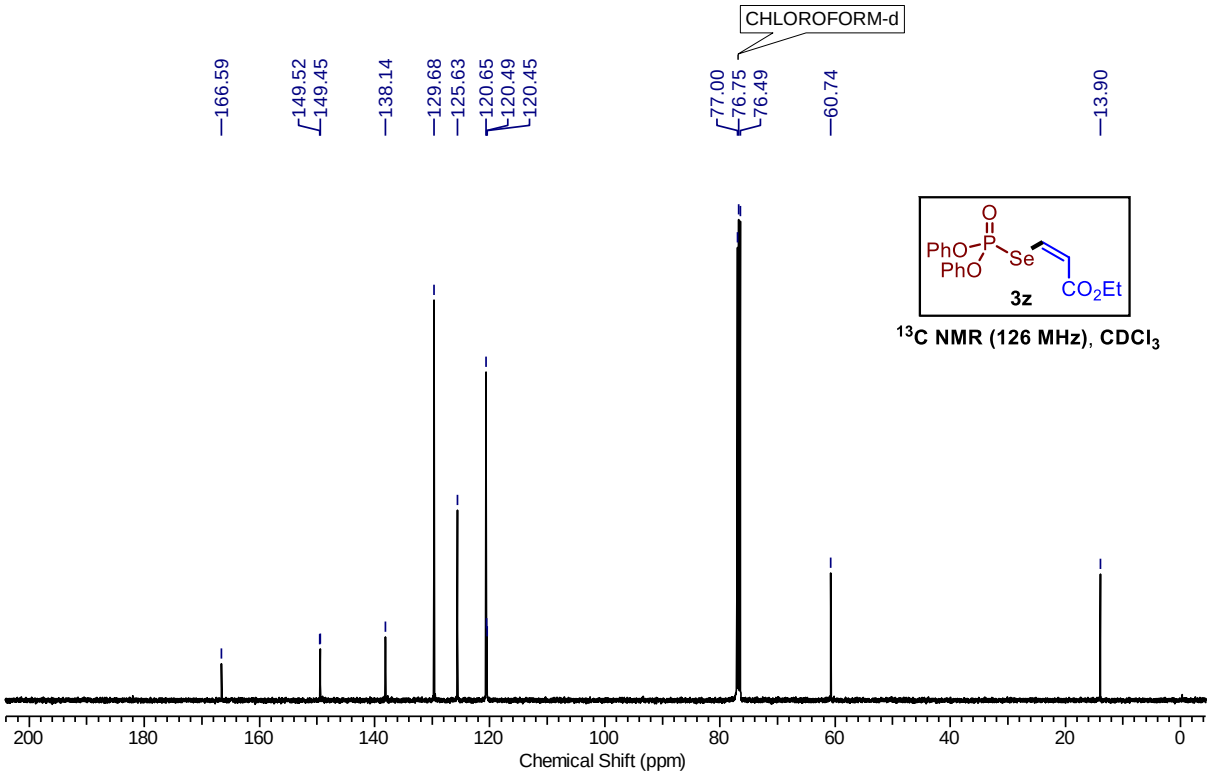
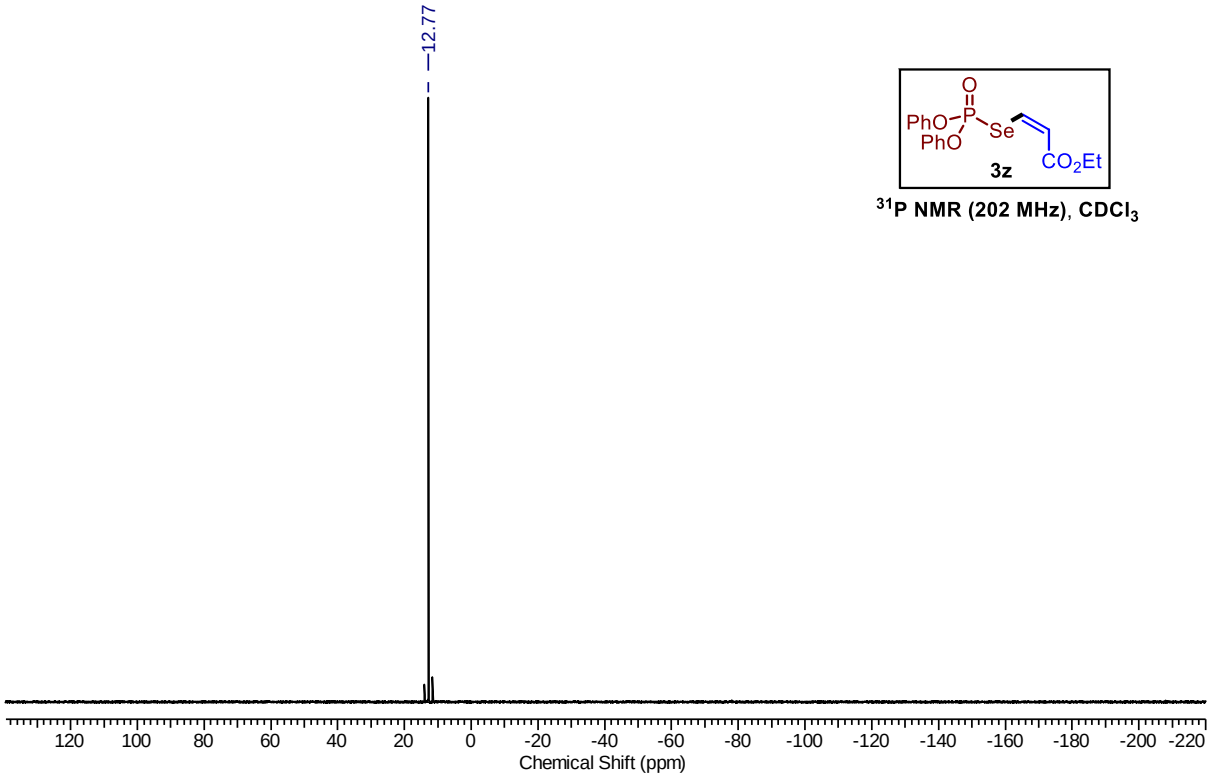
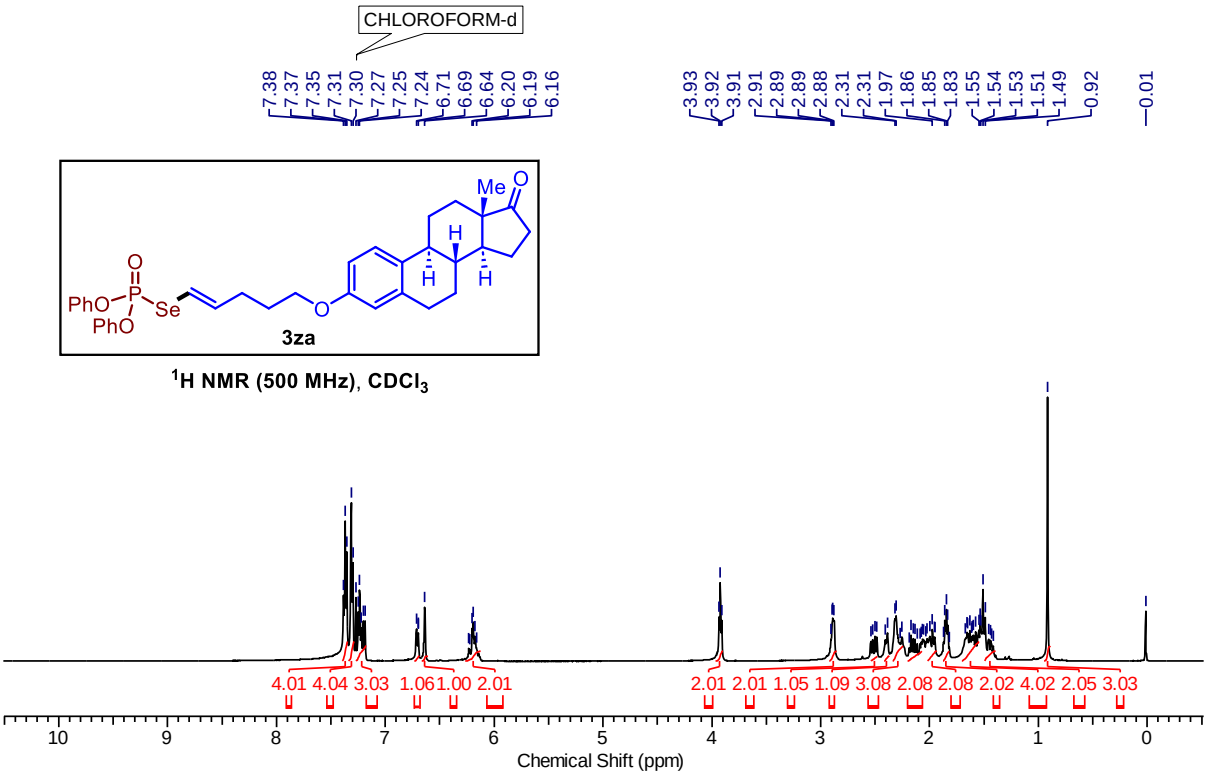


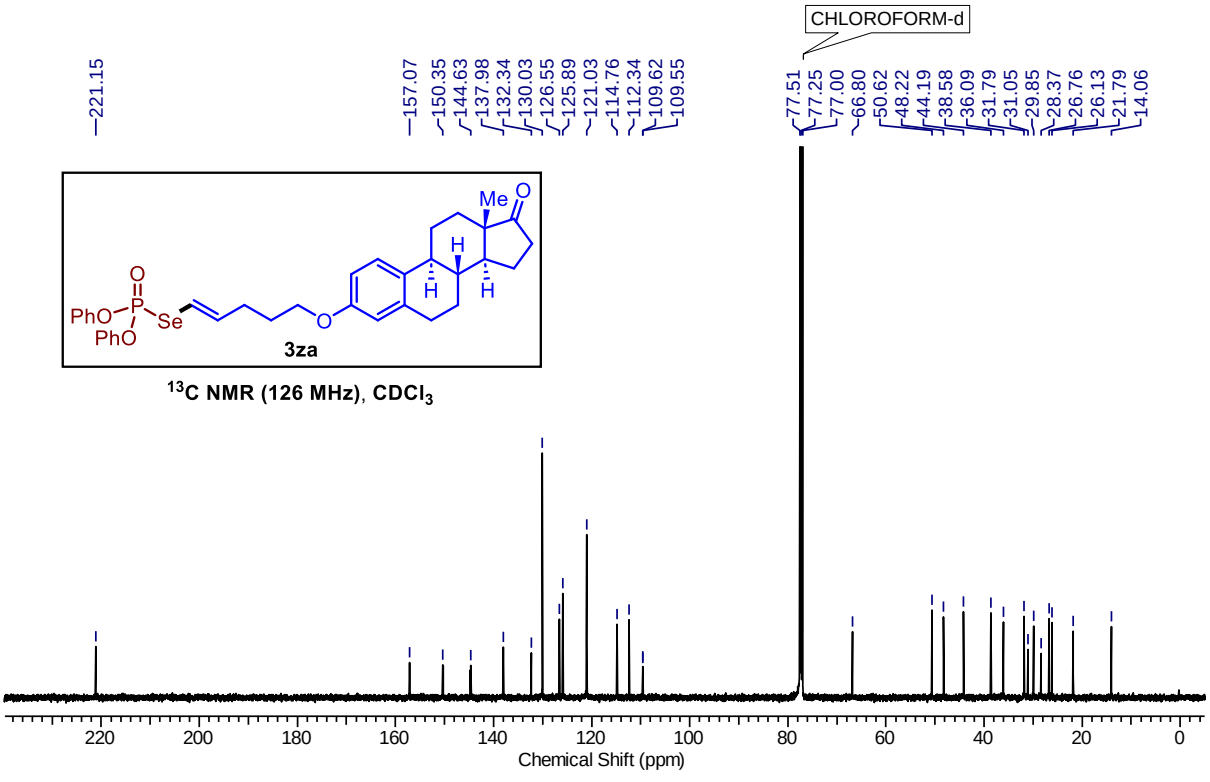
^{13}C NMR (126 MHz), $CDCl_3$



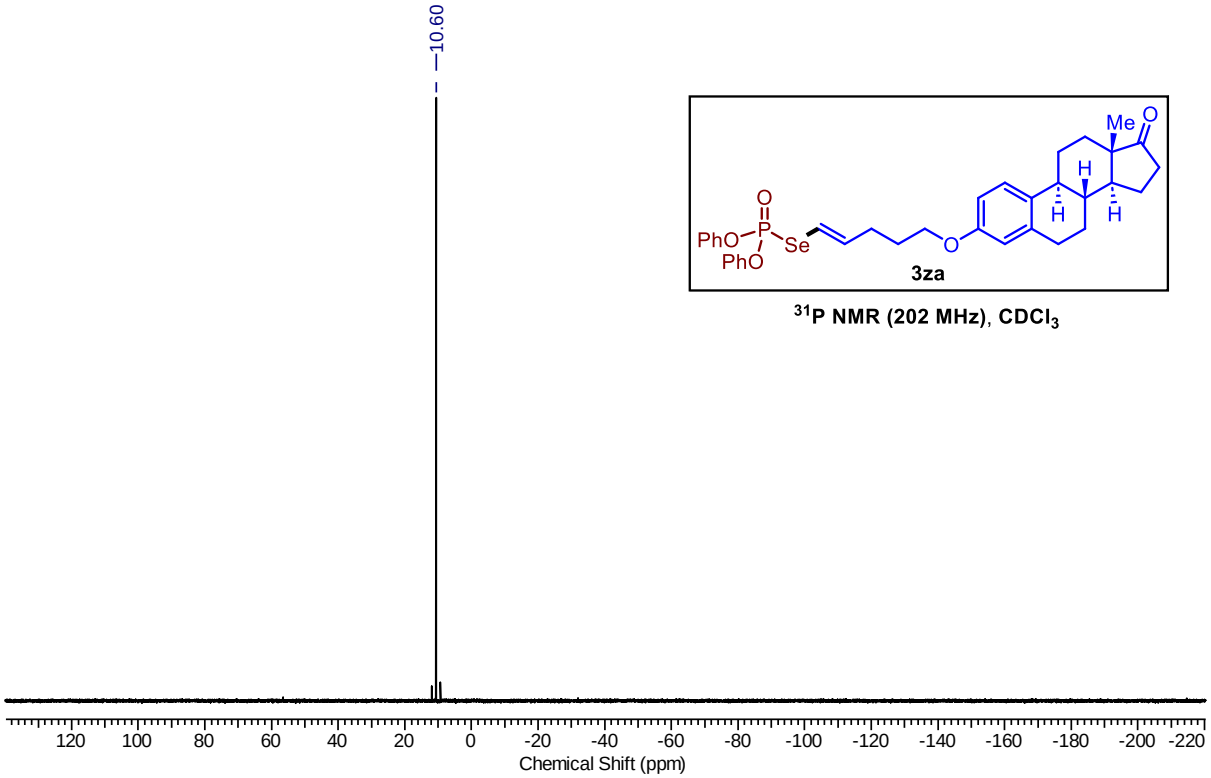
^{31}P NMR (202 MHz), $CDCl_3$



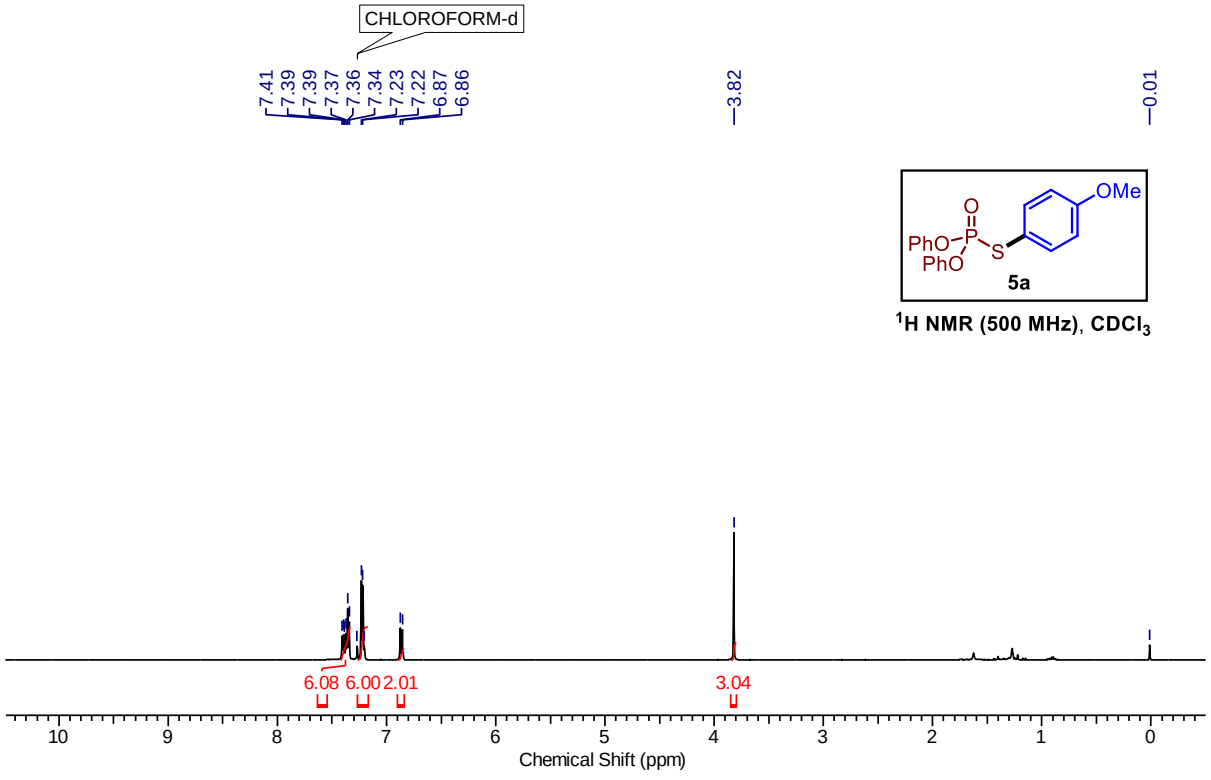
^{1}H NMR (500 MHz), $CDCl_3$



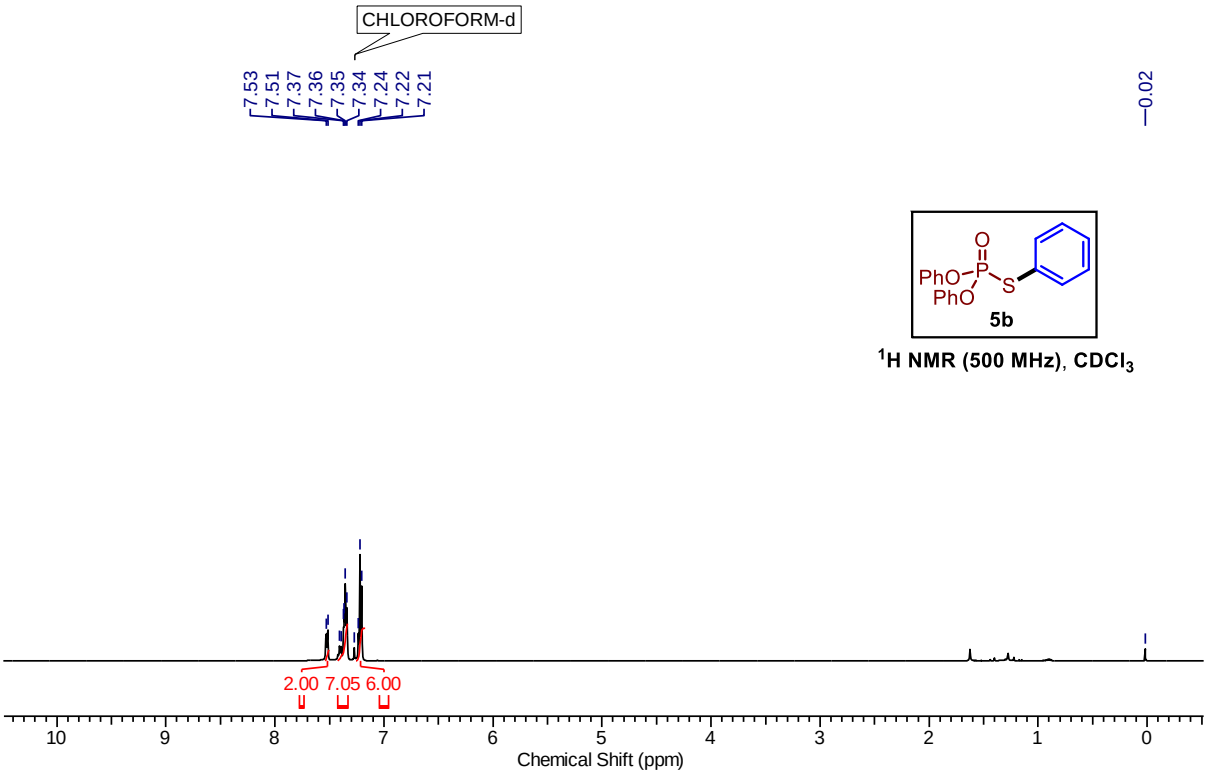
^{13}C NMR (126 MHz), $CDCl_3$



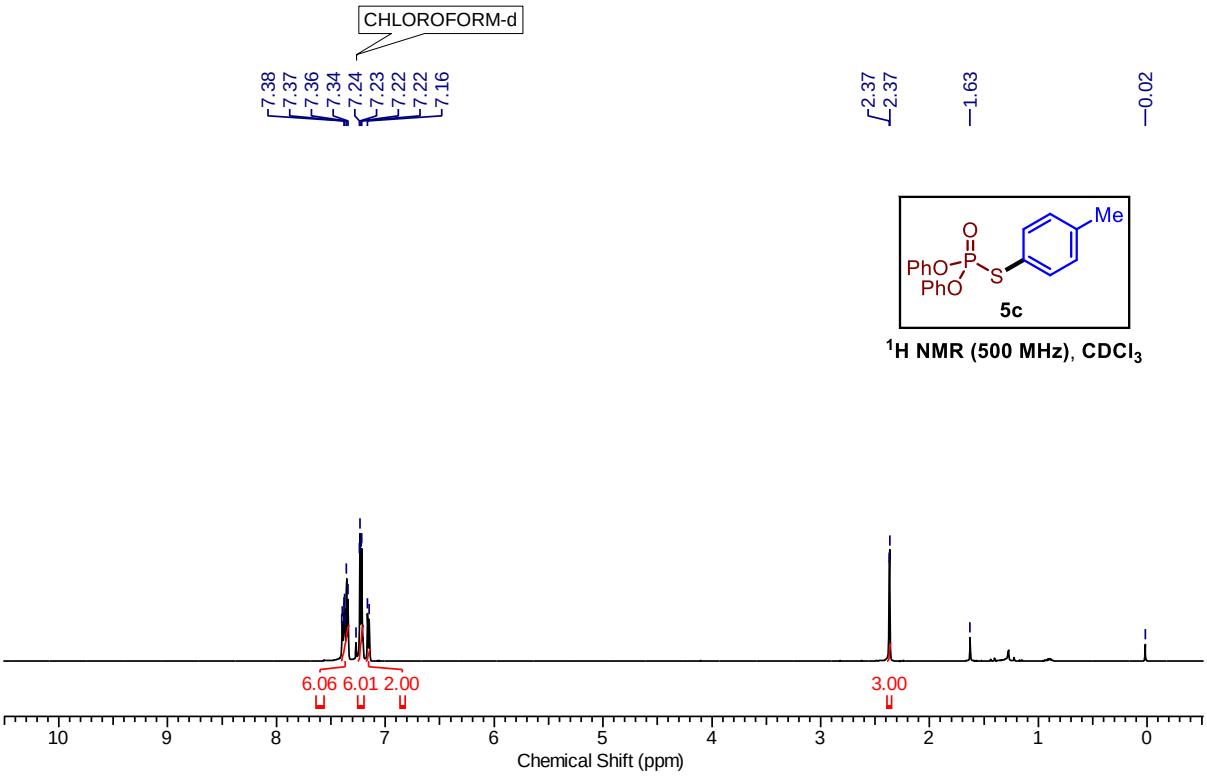
^{31}P NMR (202 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$



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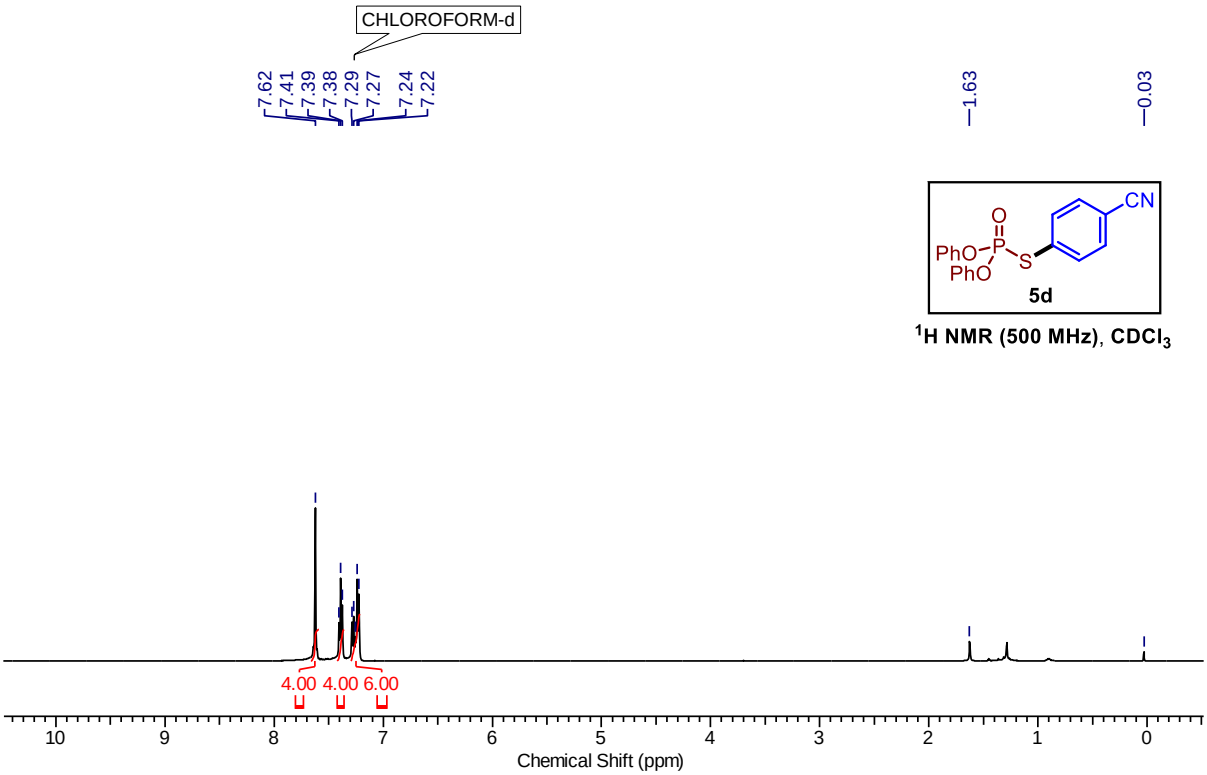
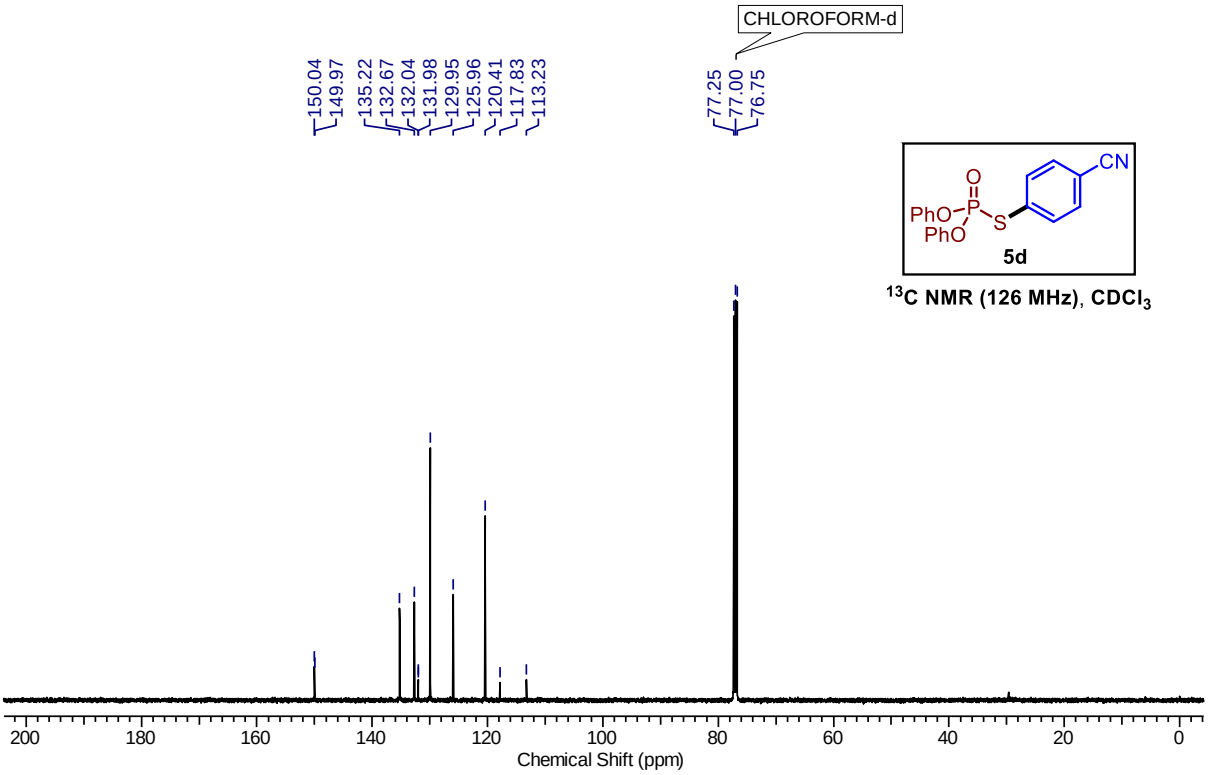
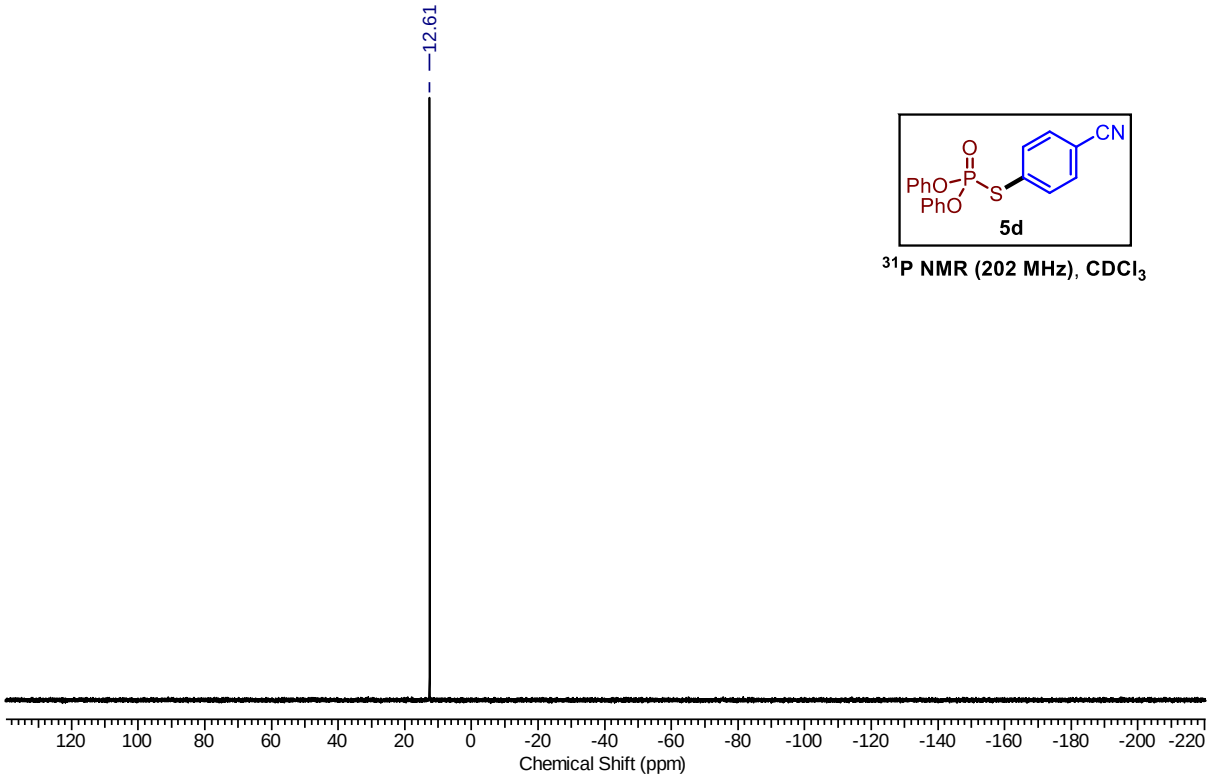


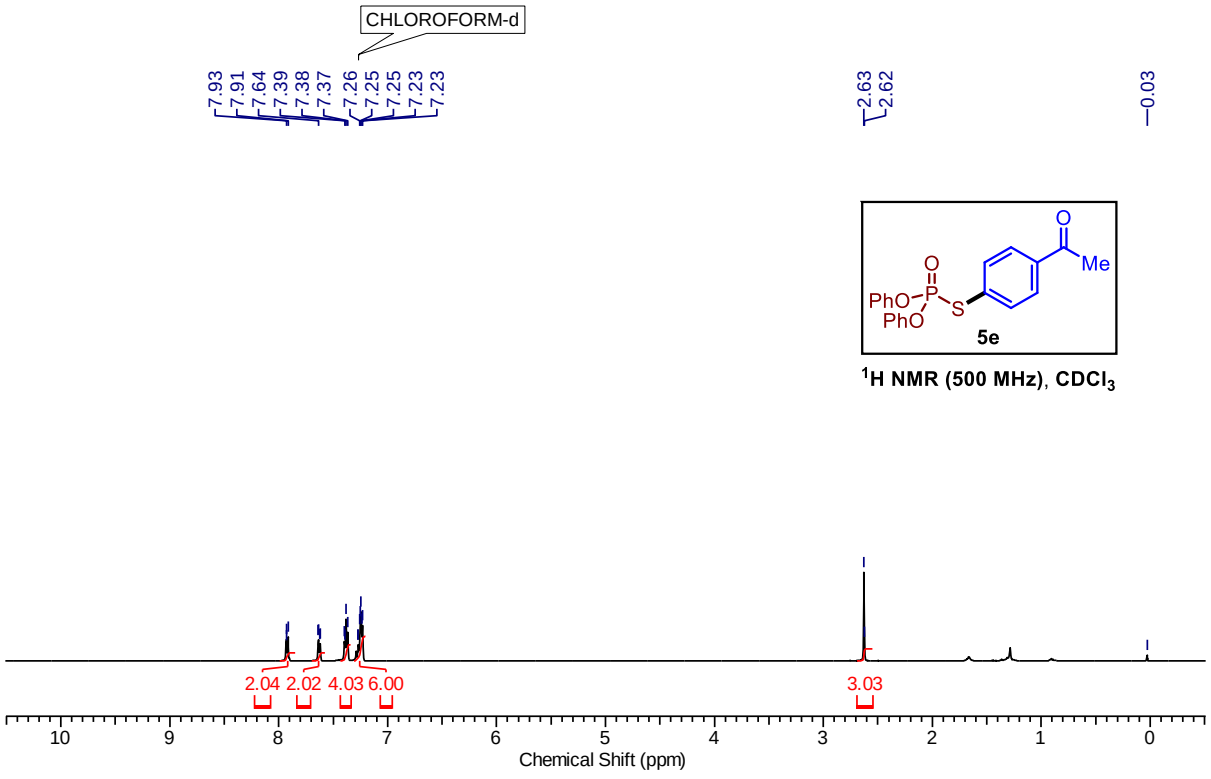
^{1}H NMR (500 MHz), $CDCl_3$



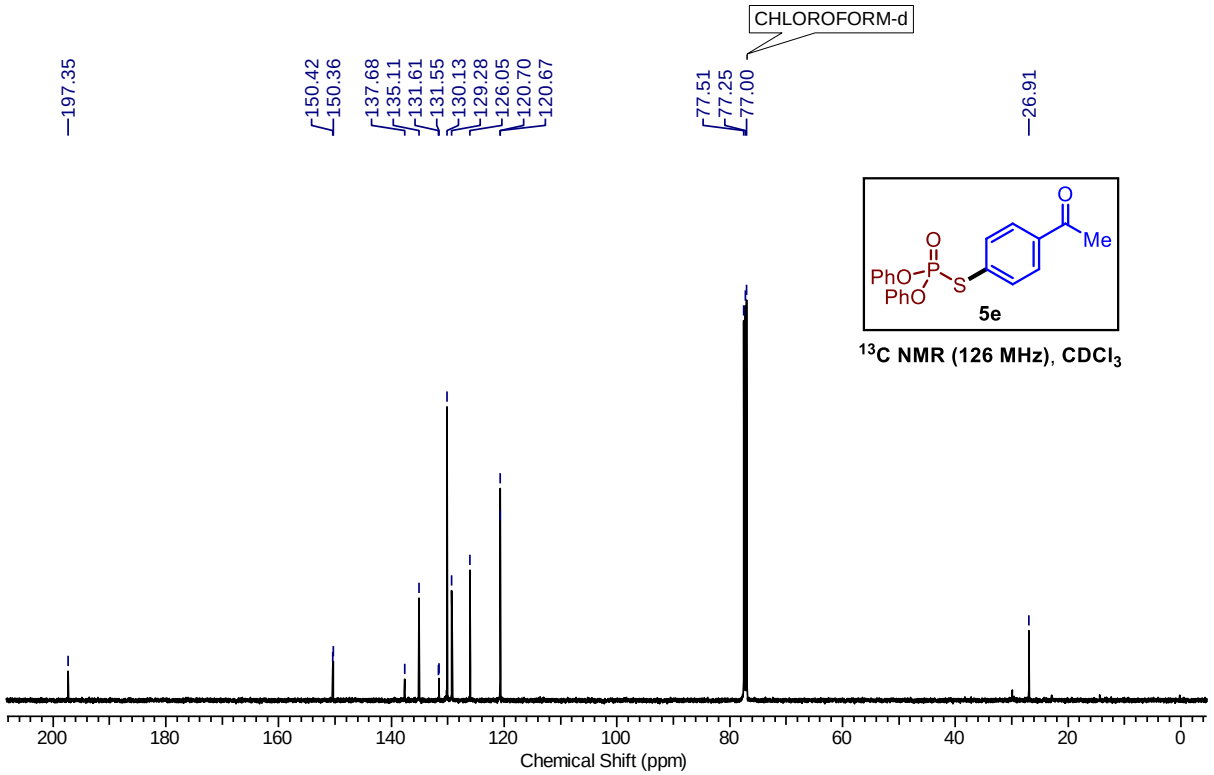
^{13}C NMR (126 MHz), $CDCl_3$



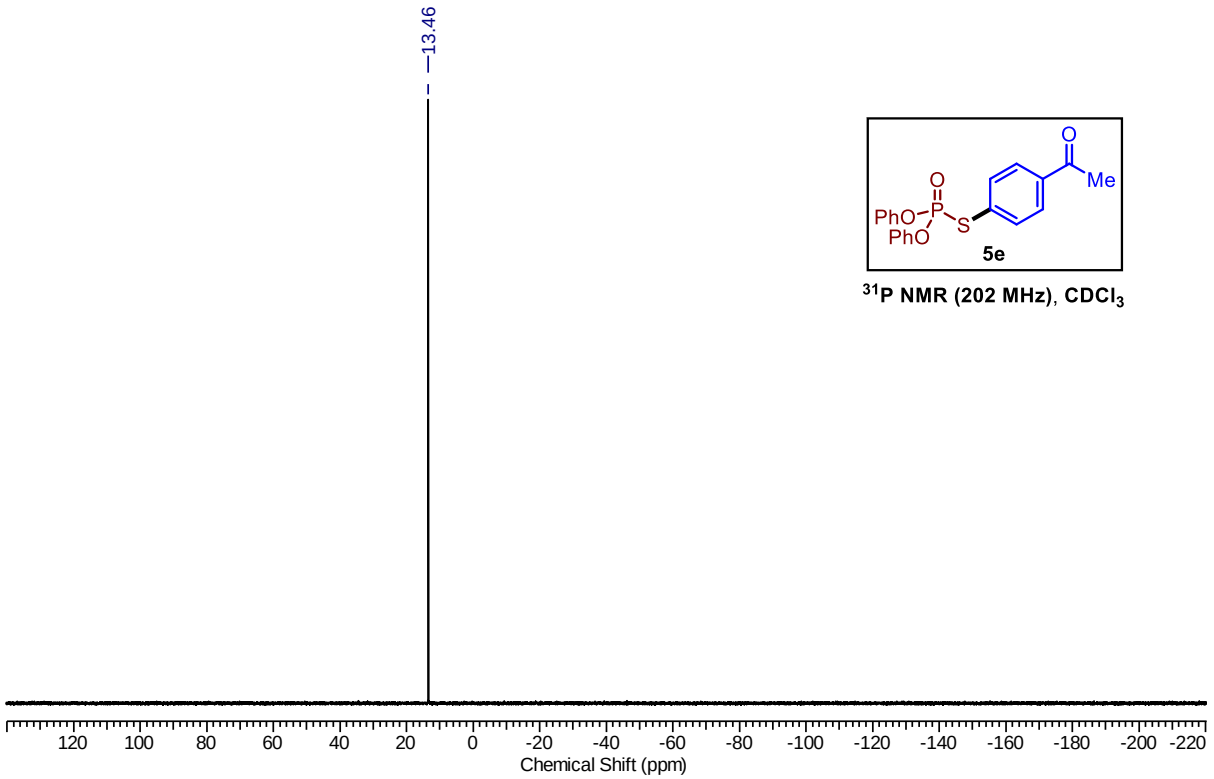
^{31}P NMR (202 MHz), $CDCl_3$



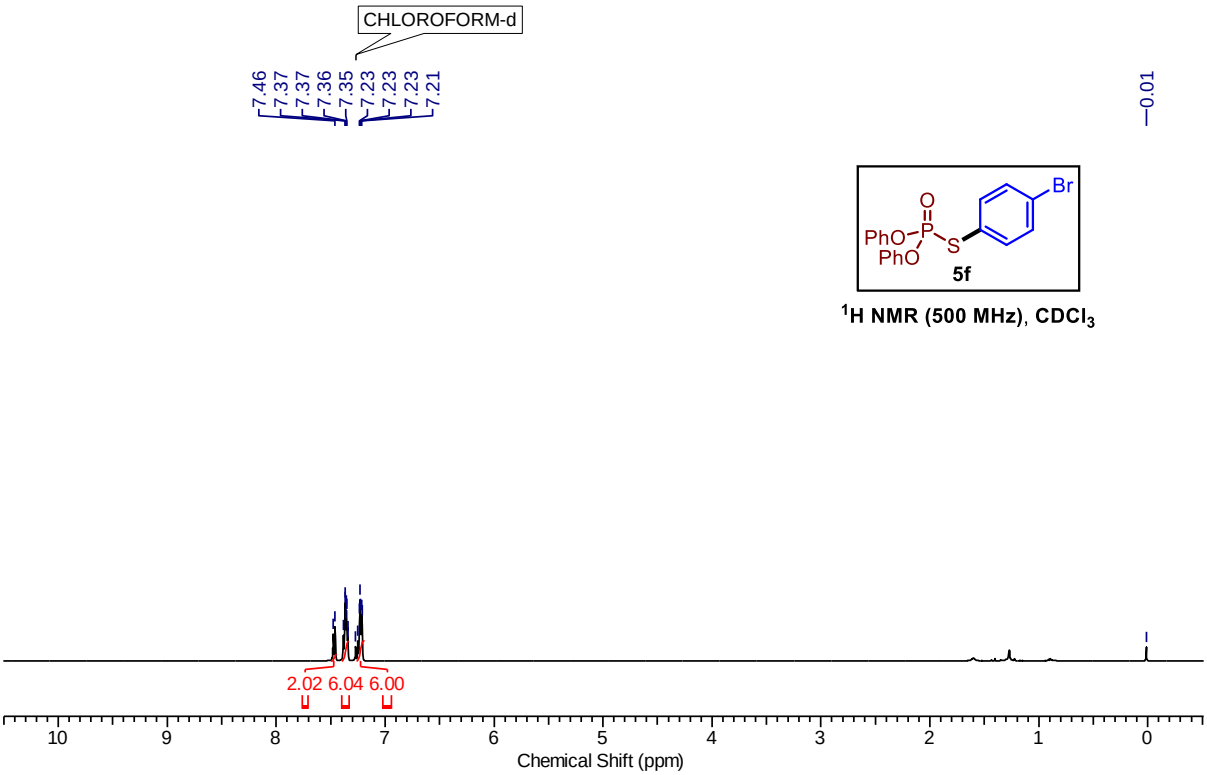
^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (126 MHz), $CDCl_3$



^{31}P NMR (202 MHz), $CDCl_3$



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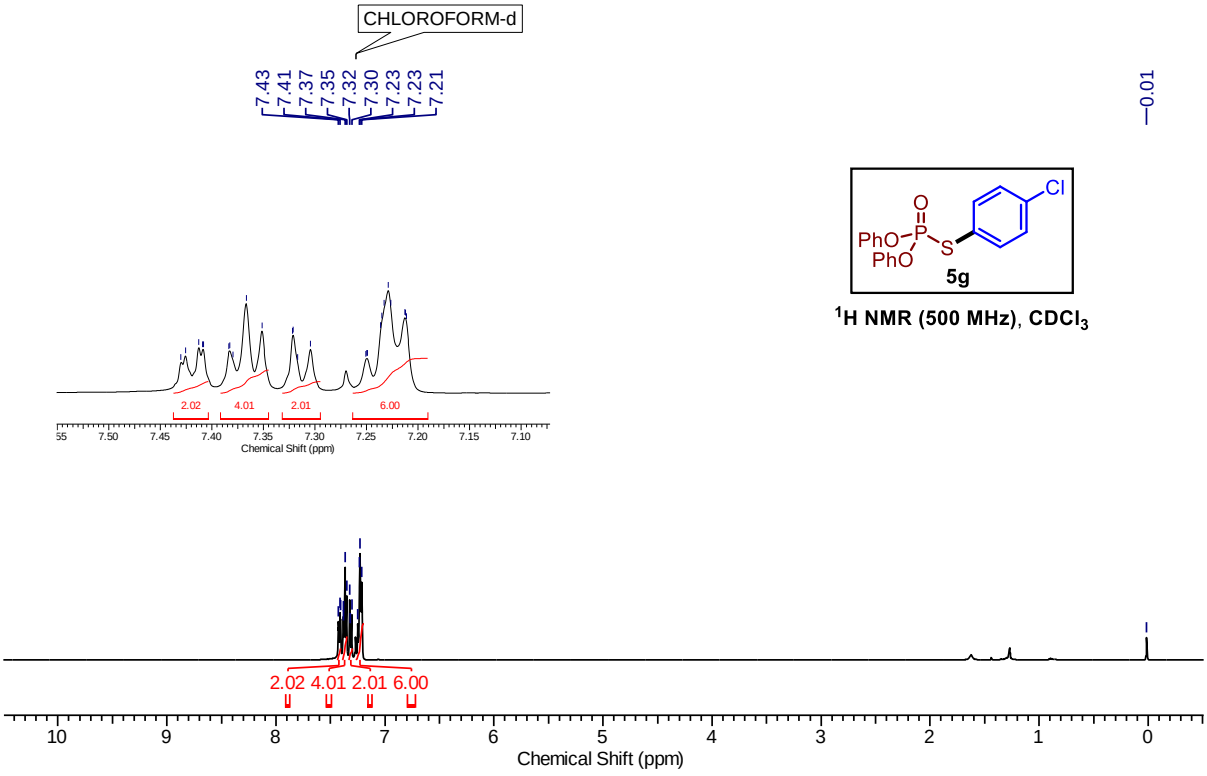

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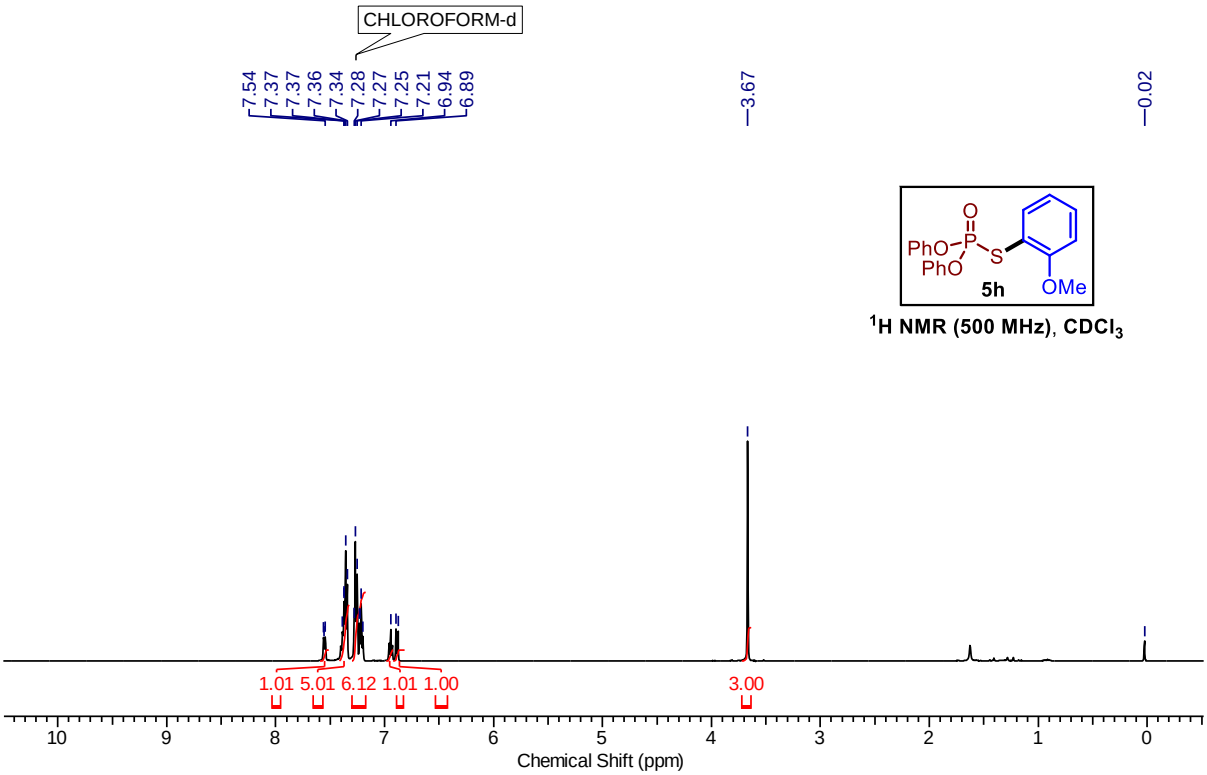

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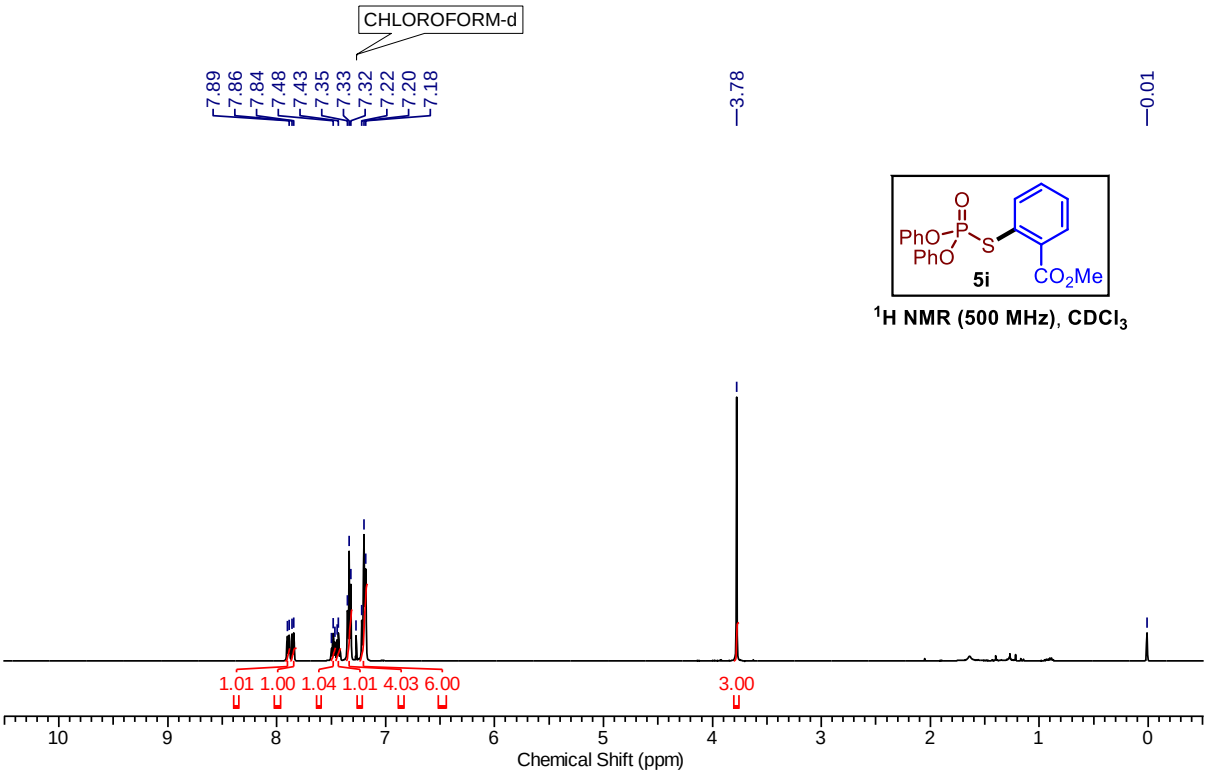

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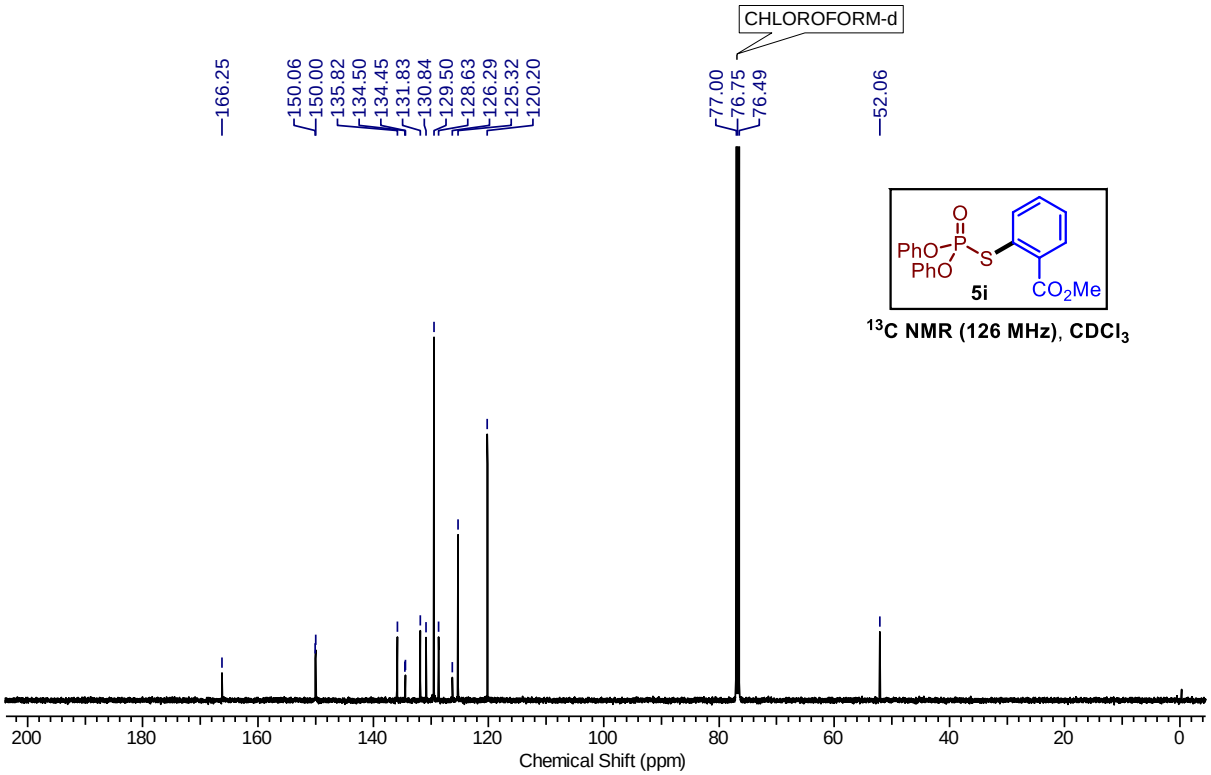
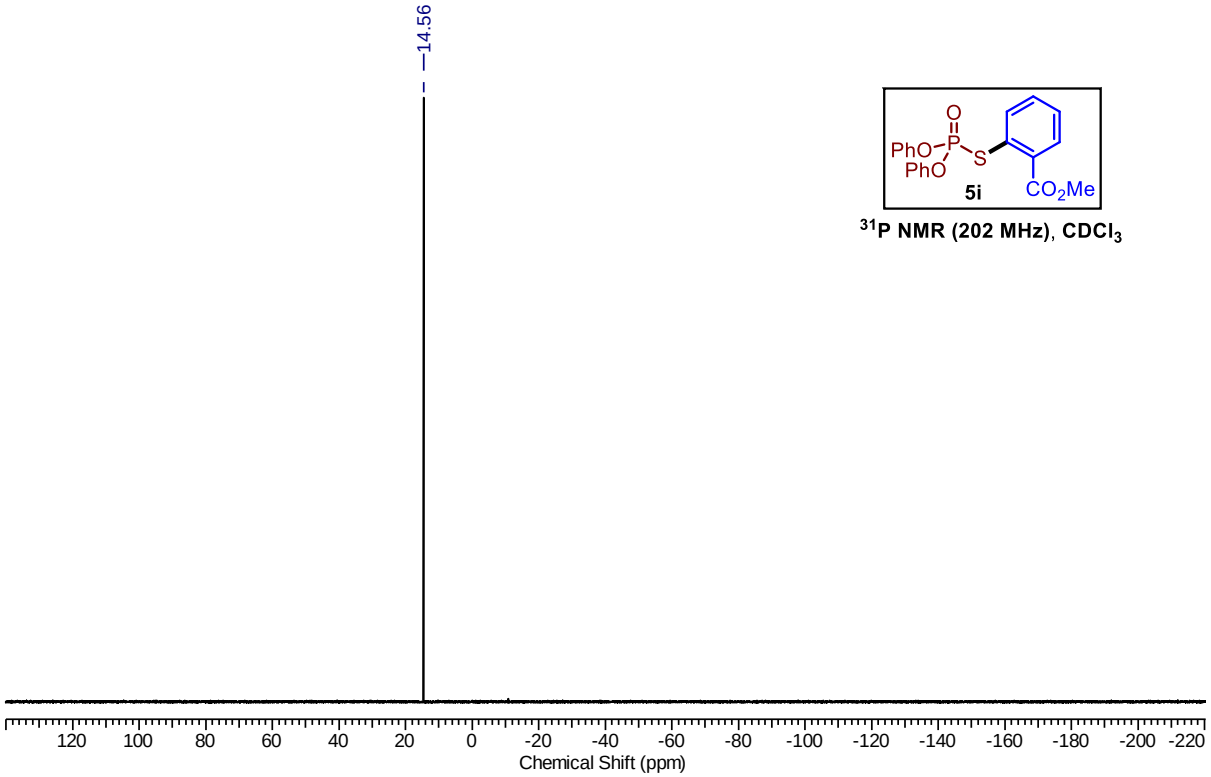
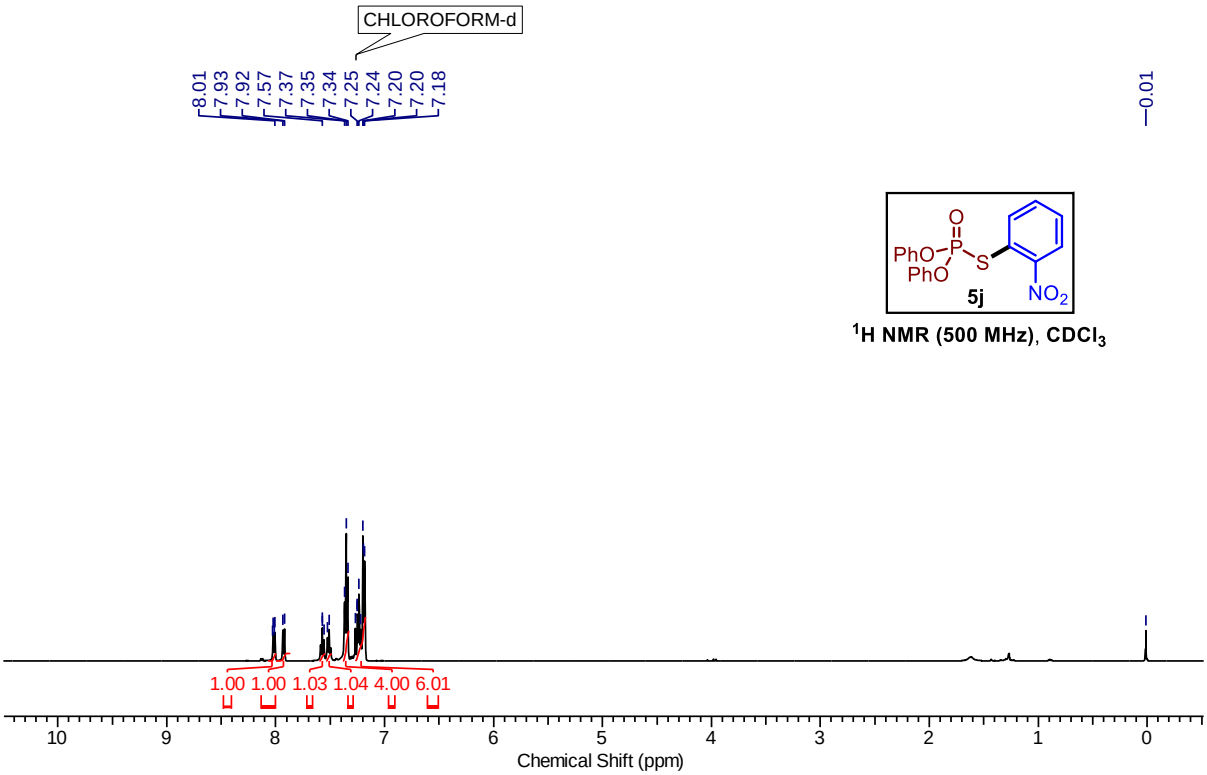


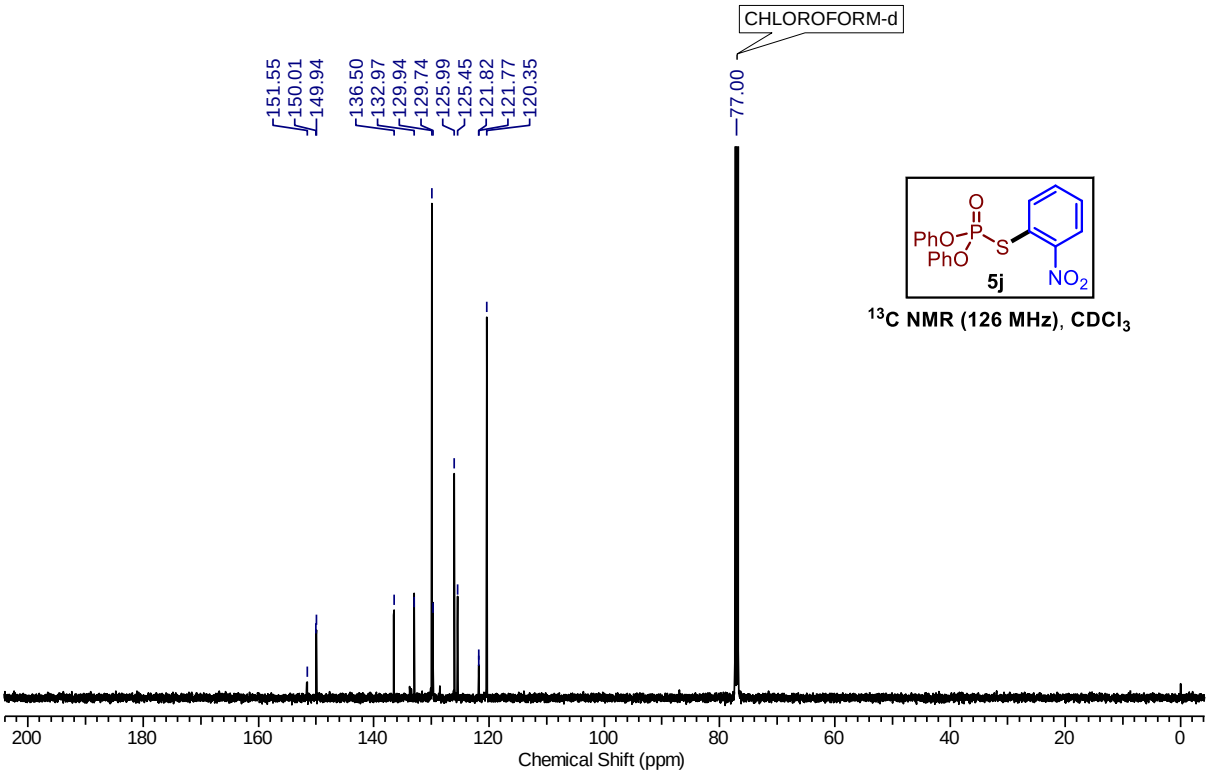
^{13}C NMR (126 MHz), $CDCl_3$



^{31}P NMR (202 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$



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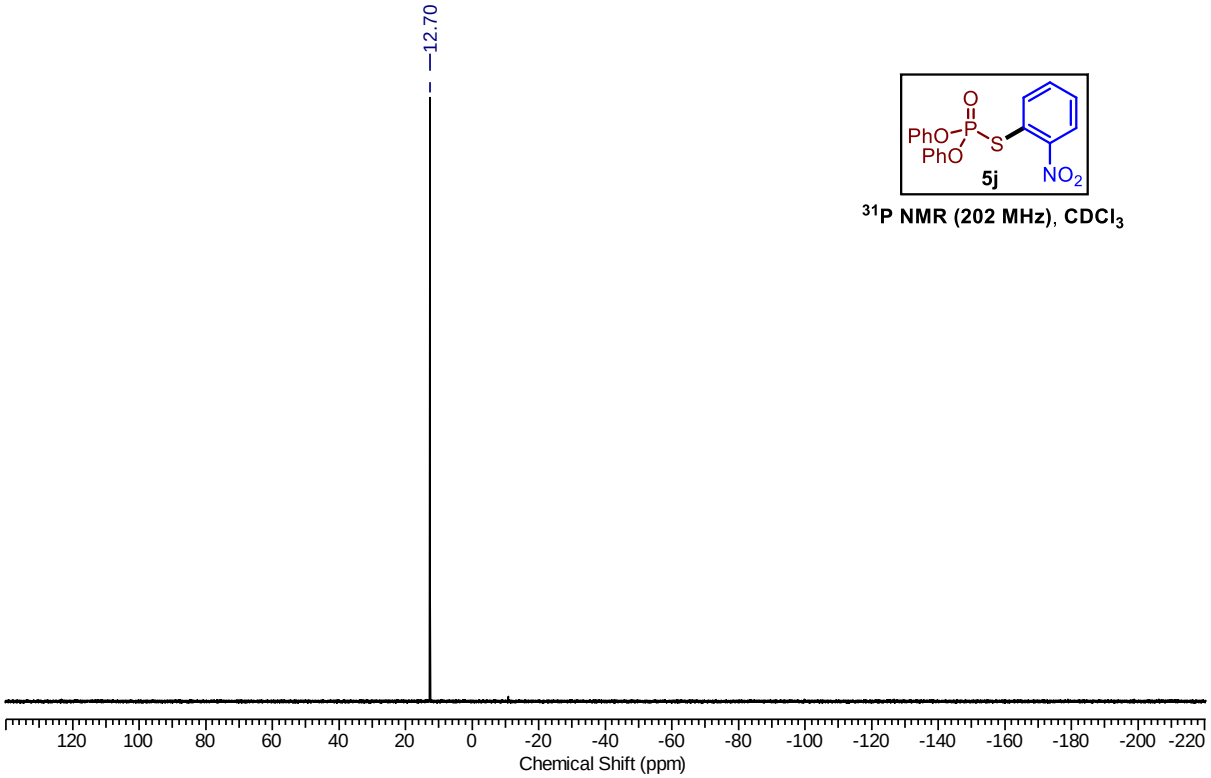

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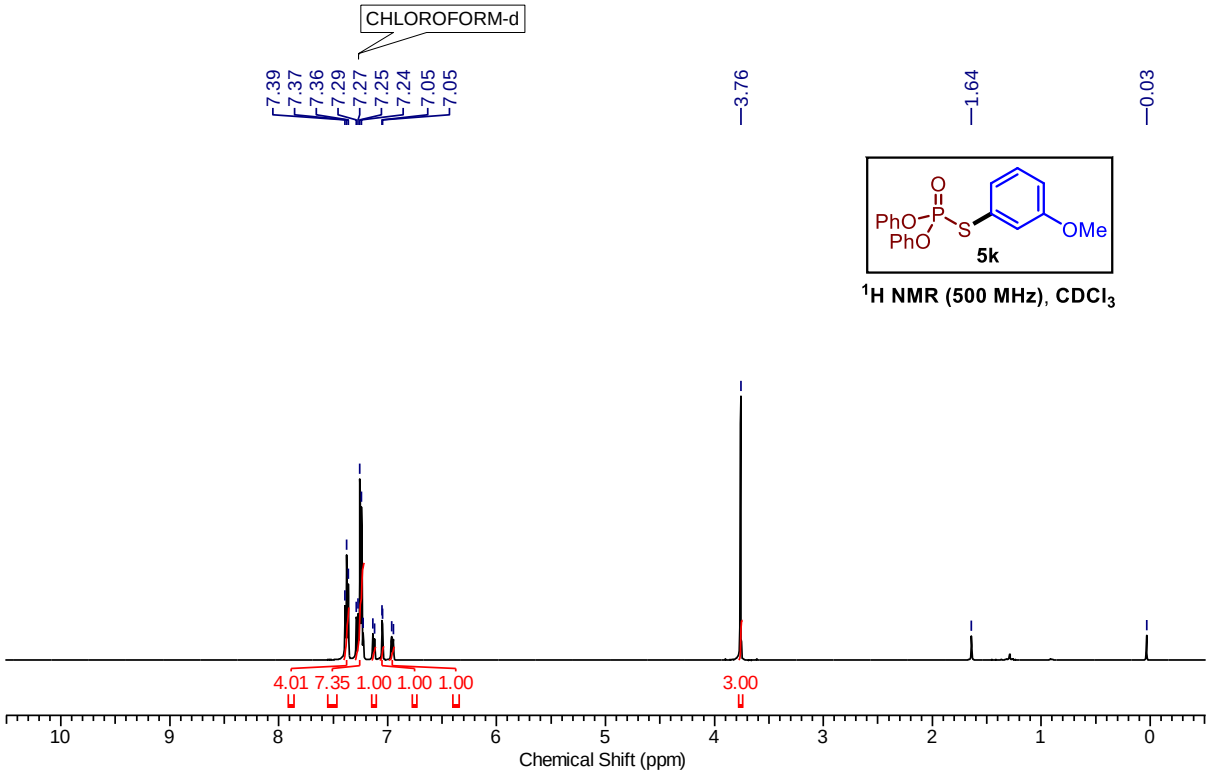

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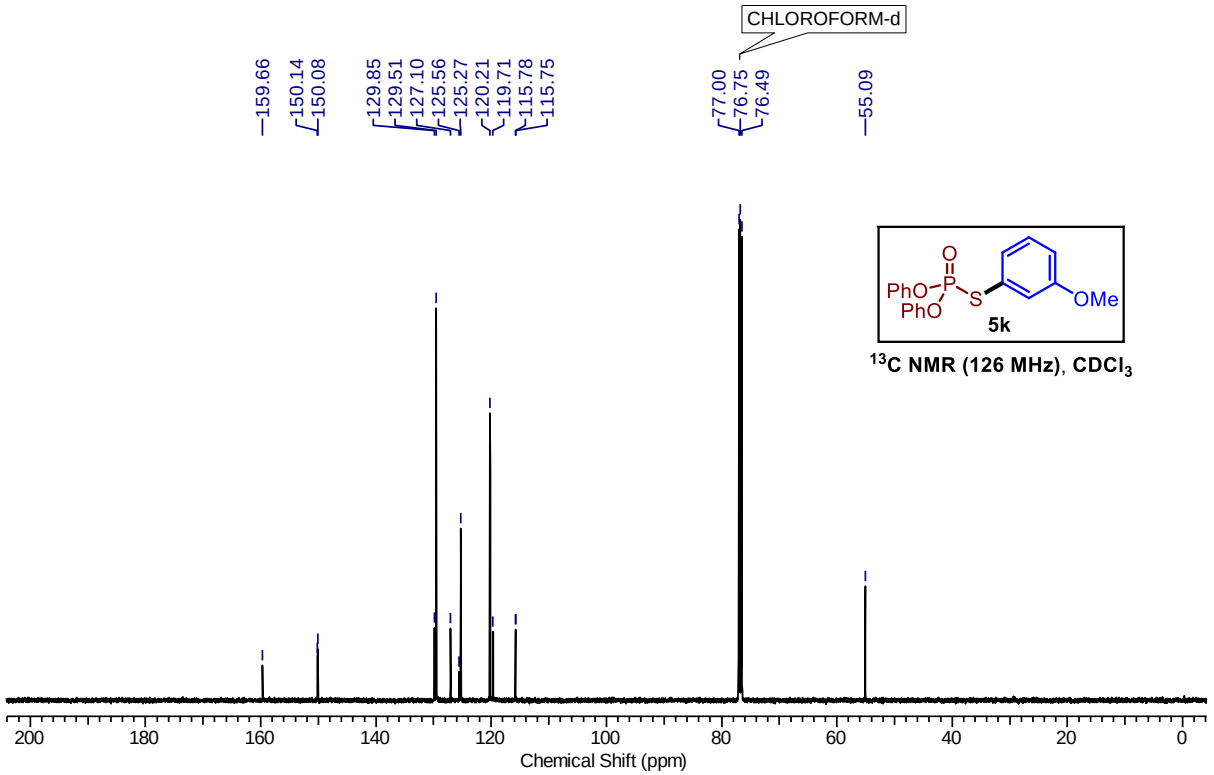

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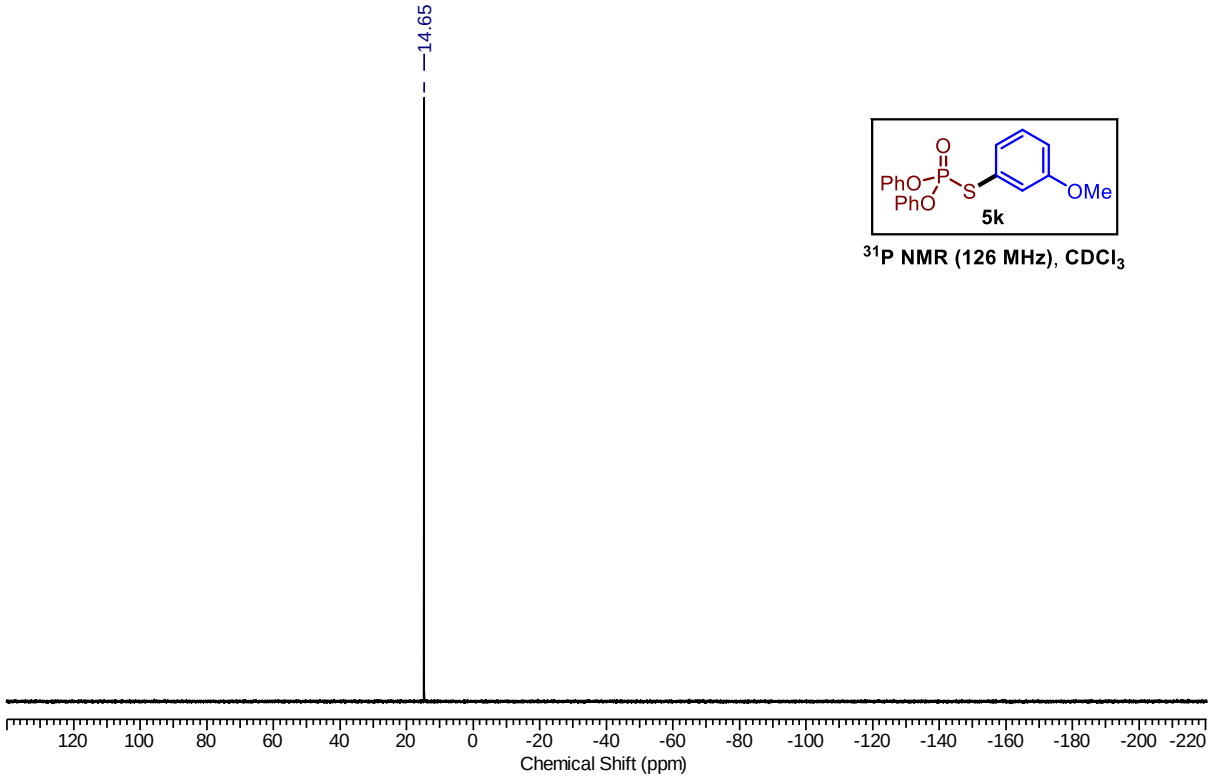

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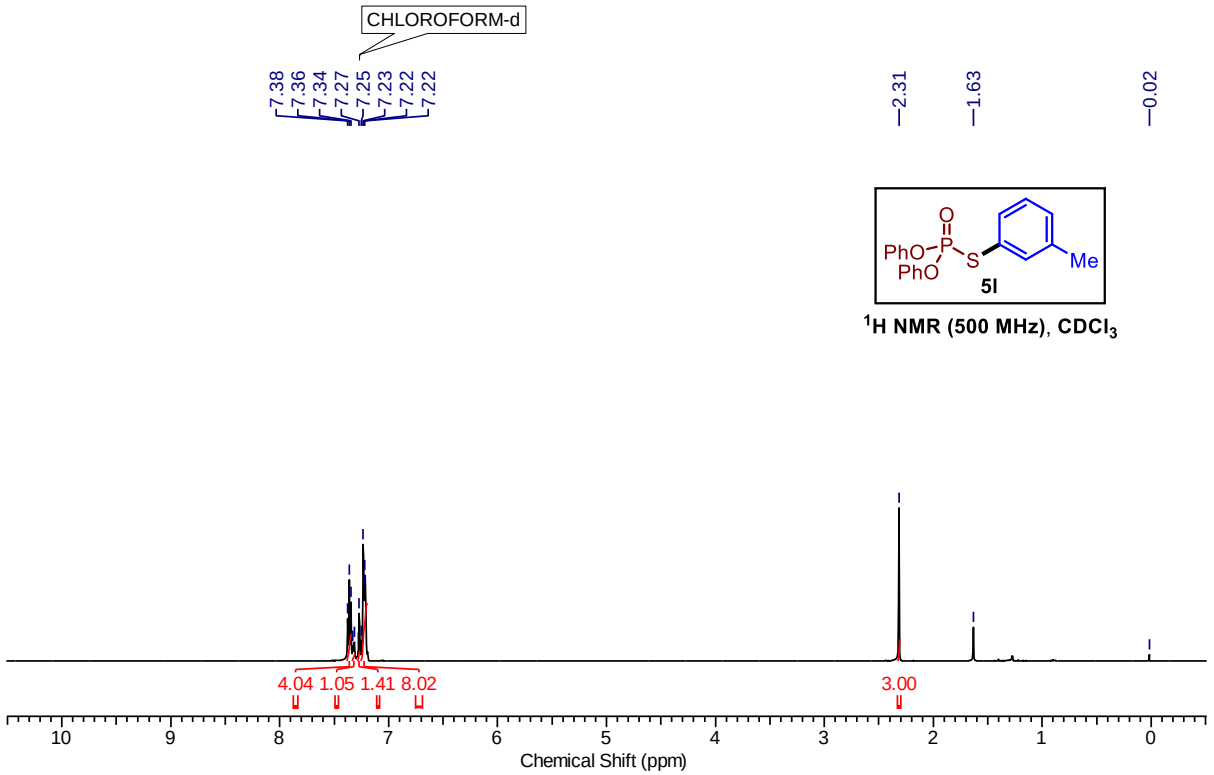

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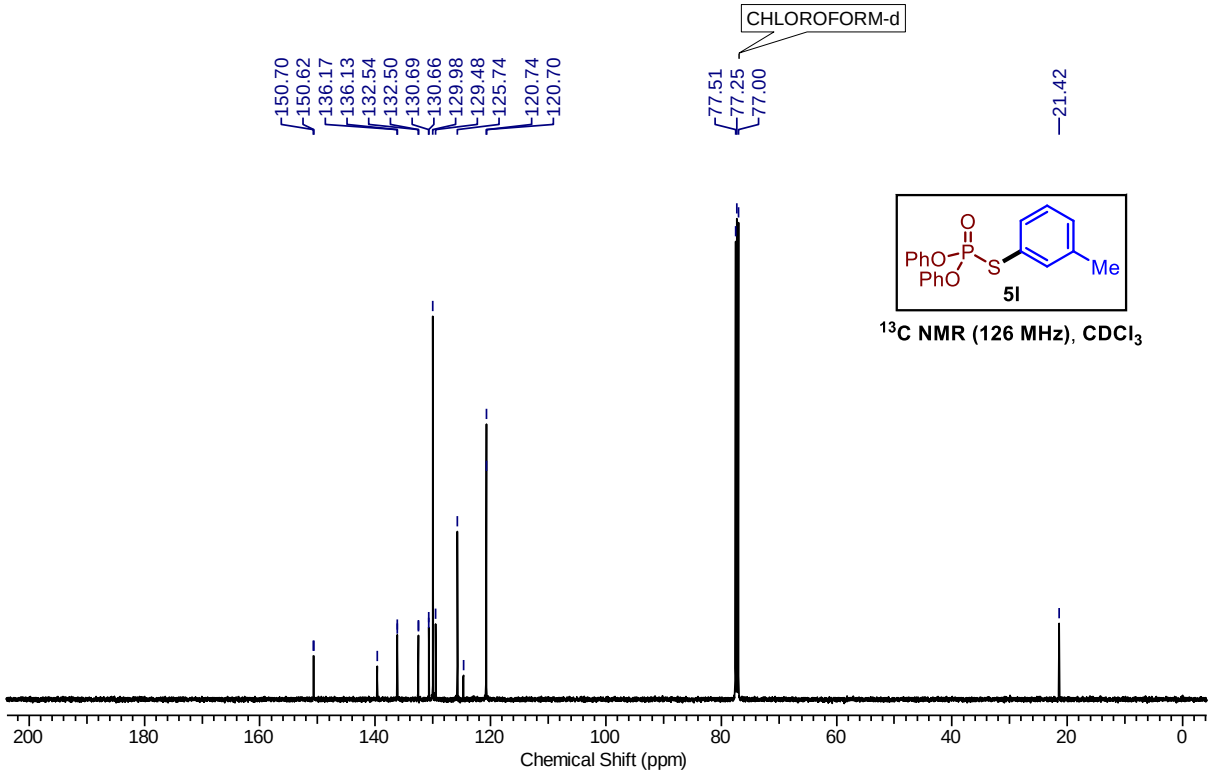

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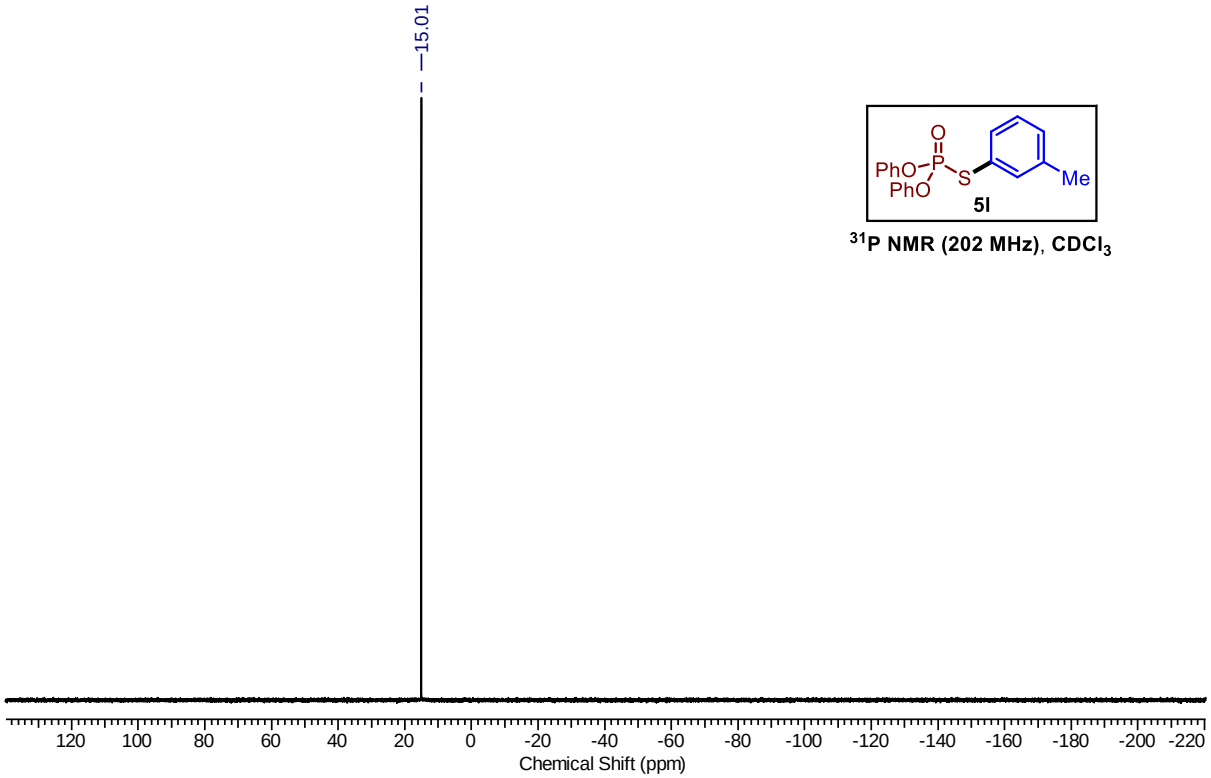

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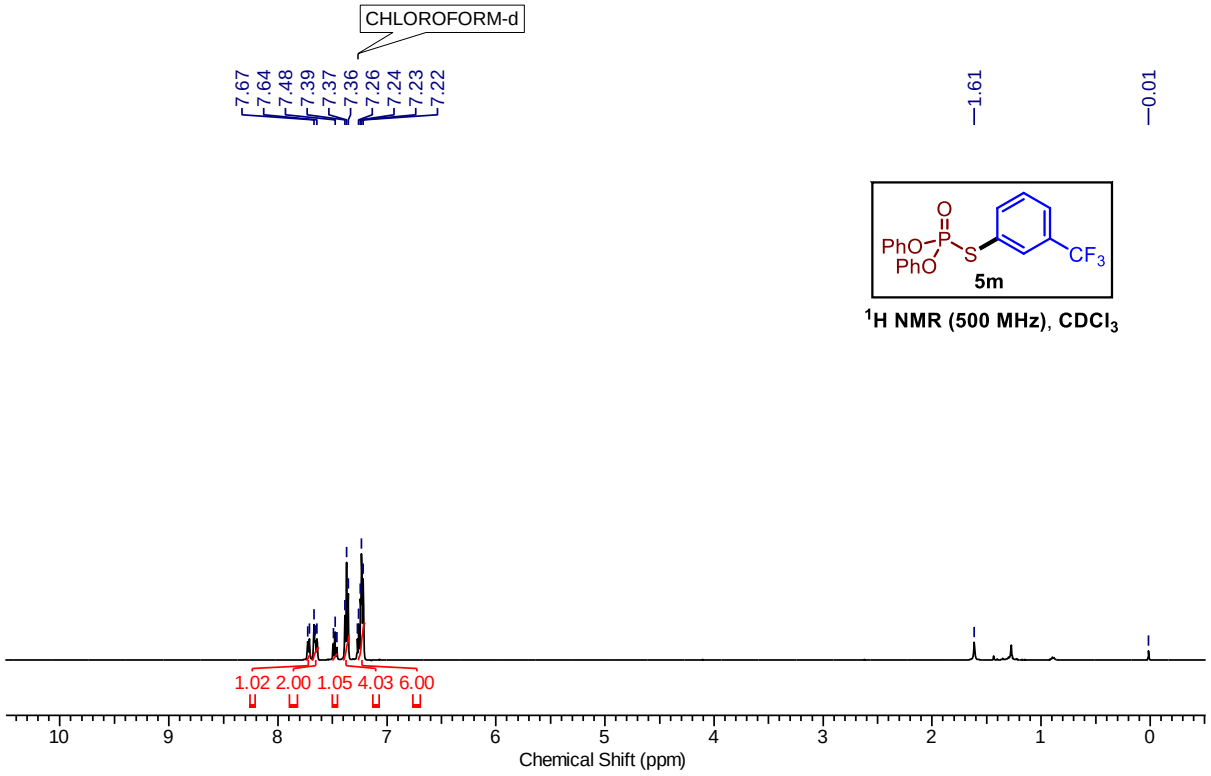
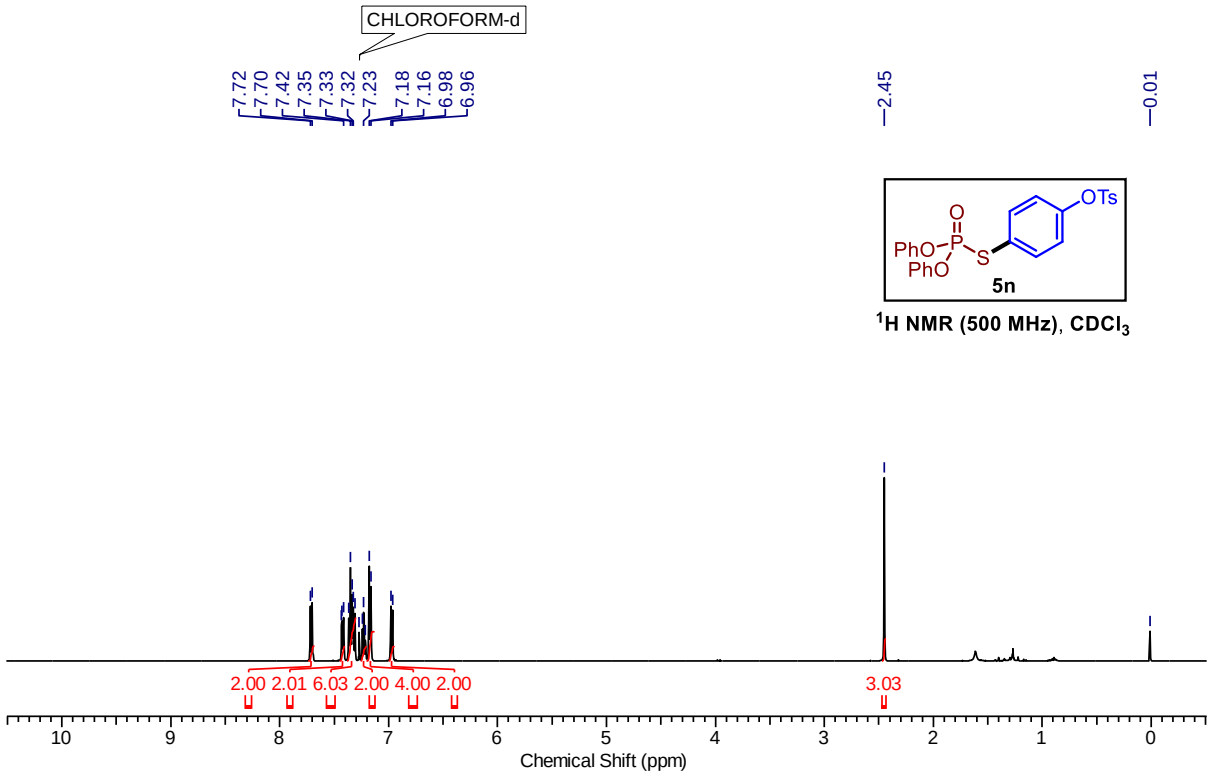


^{1}H NMR (500 MHz), $CDCl_3$



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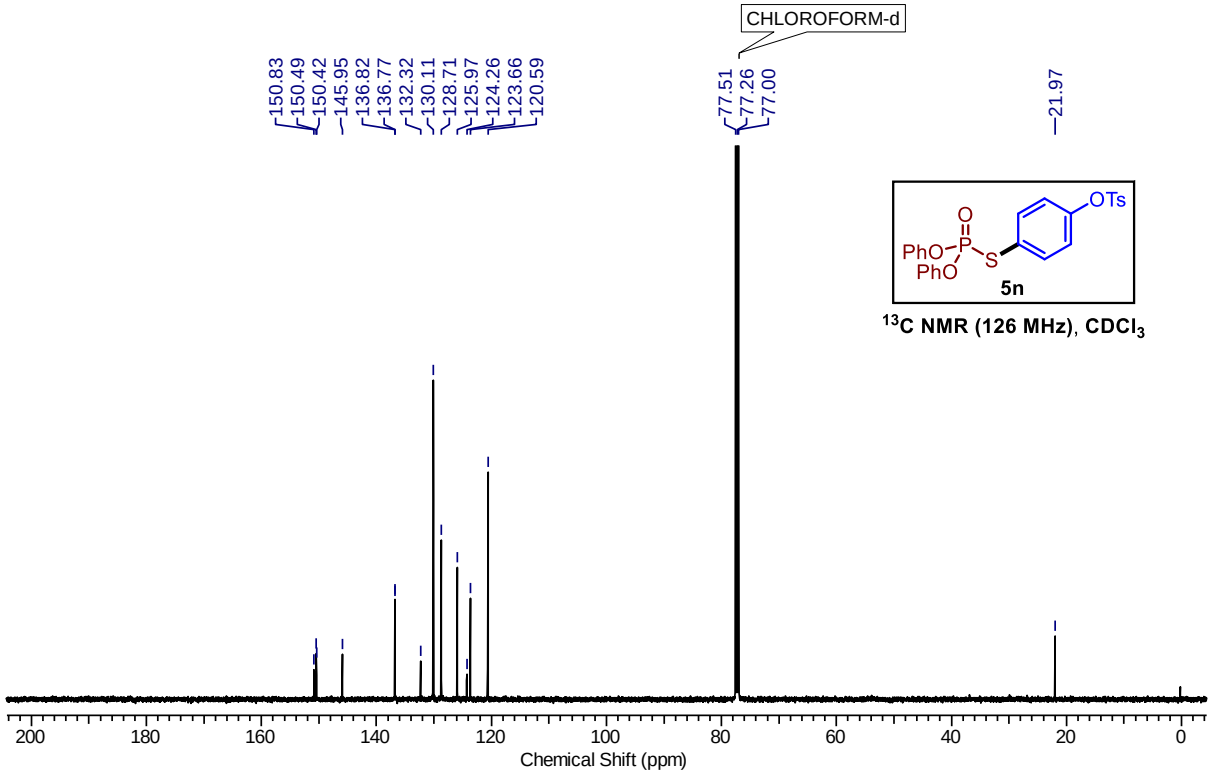

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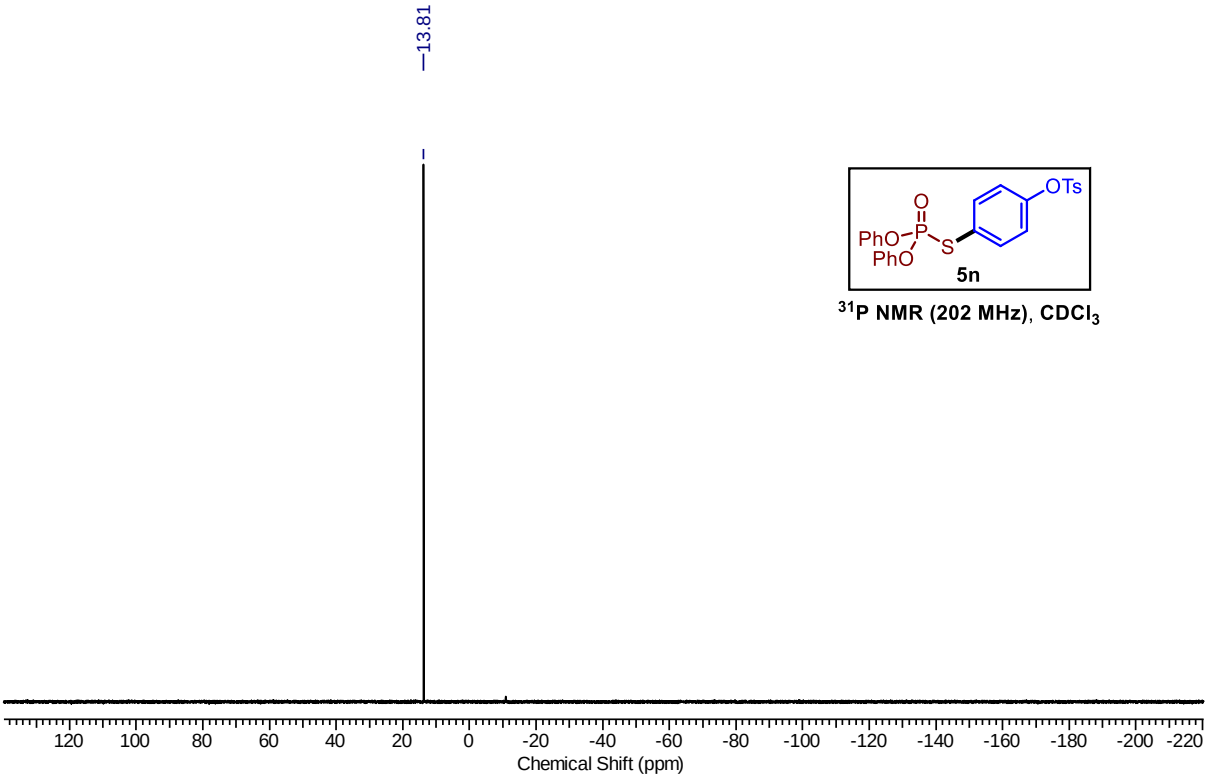
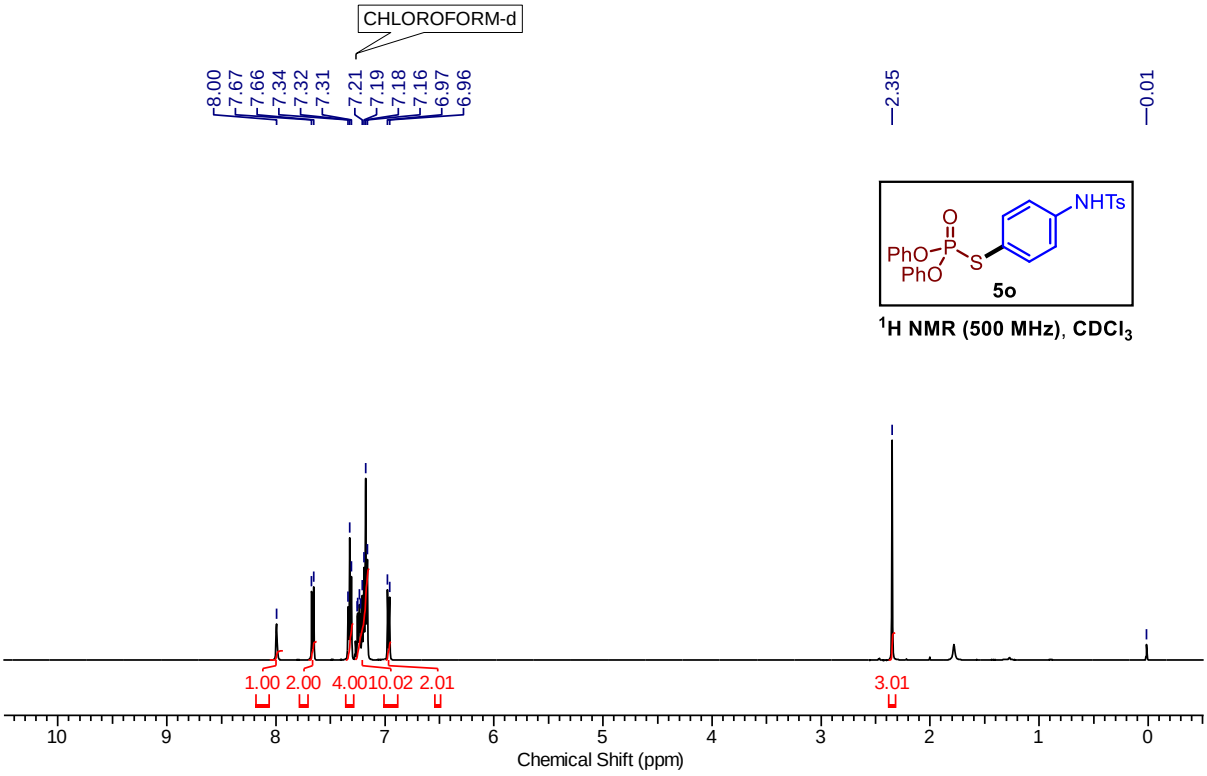
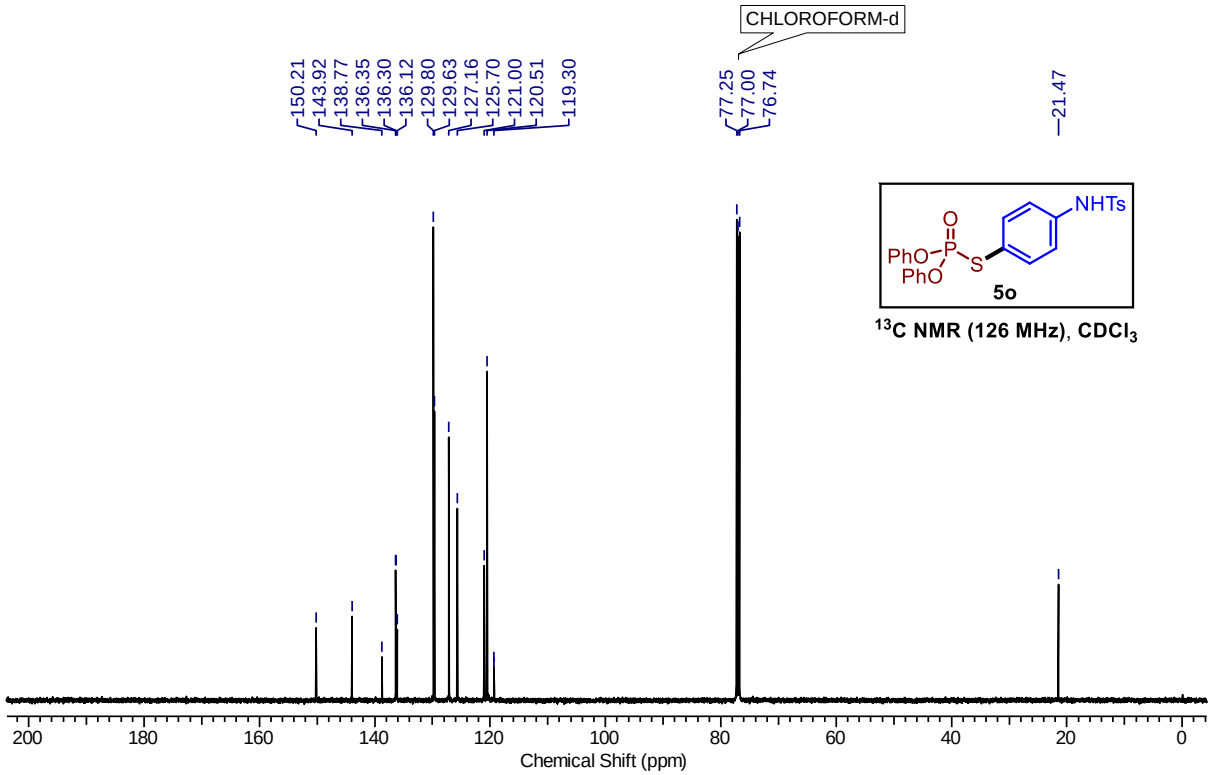


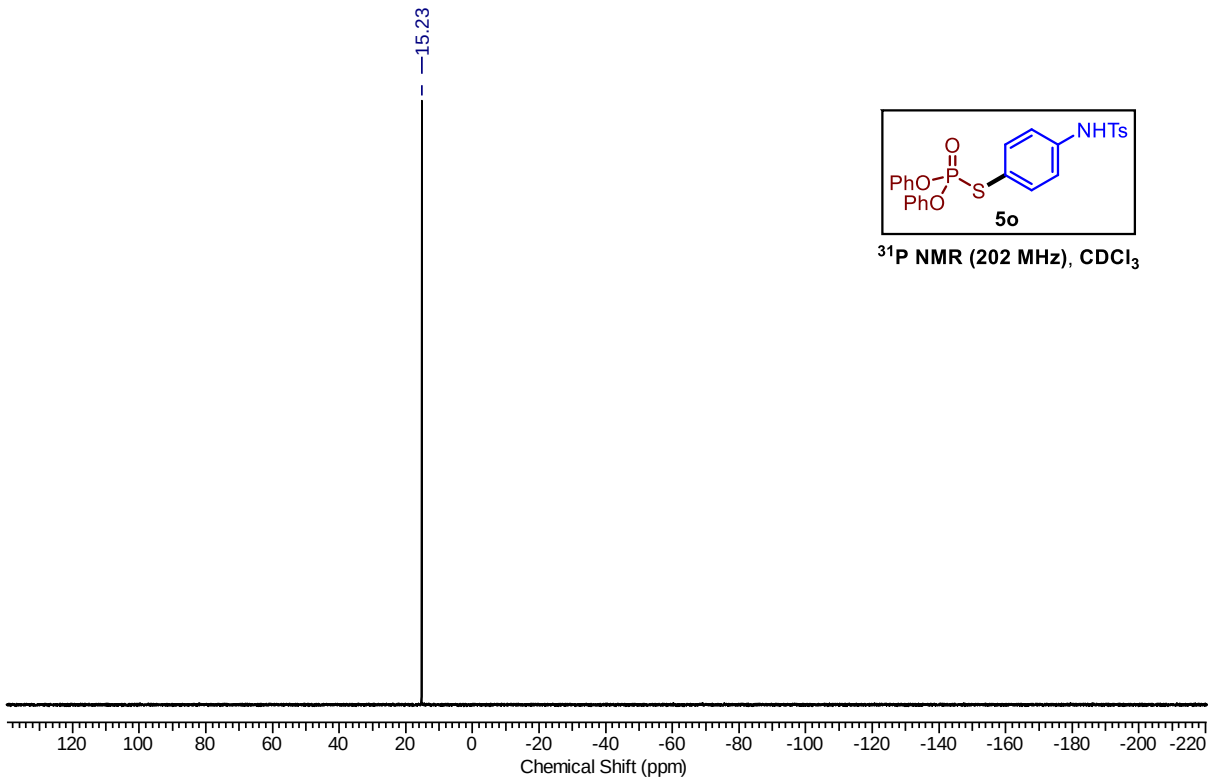
^{31}P NMR (202 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (126 MHz), $CDCl_3$



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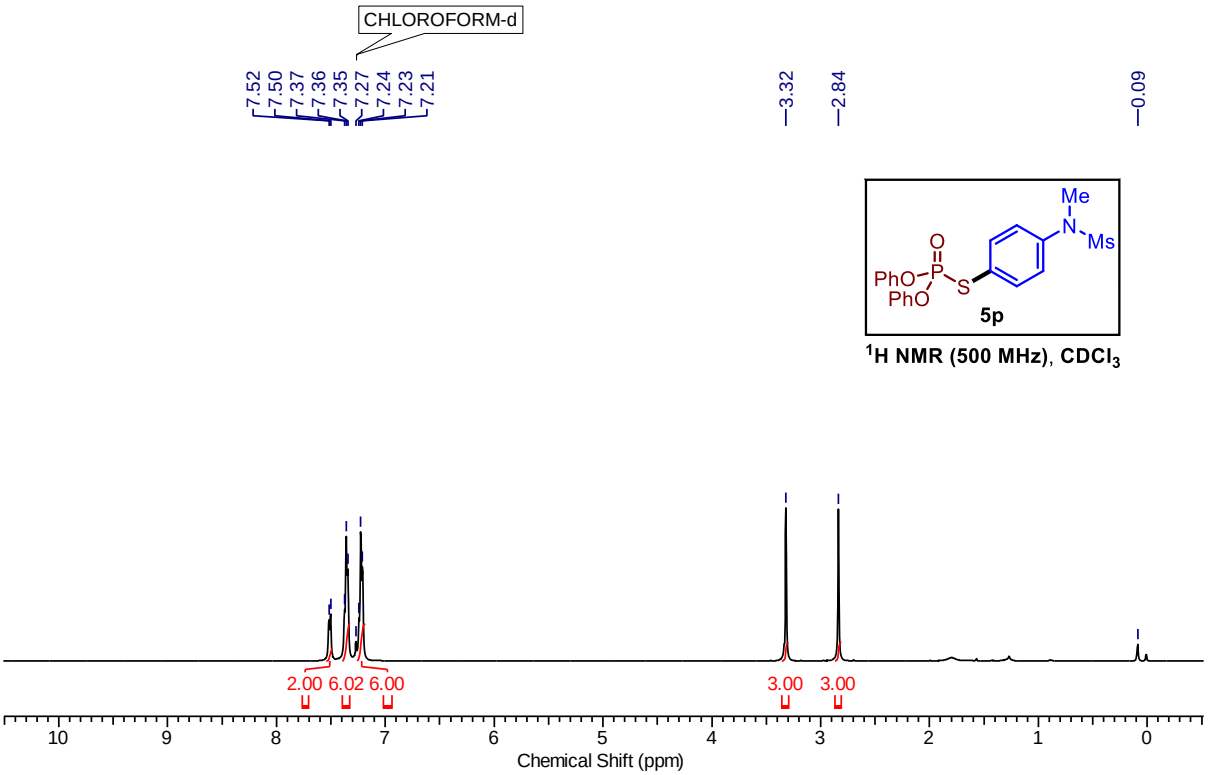
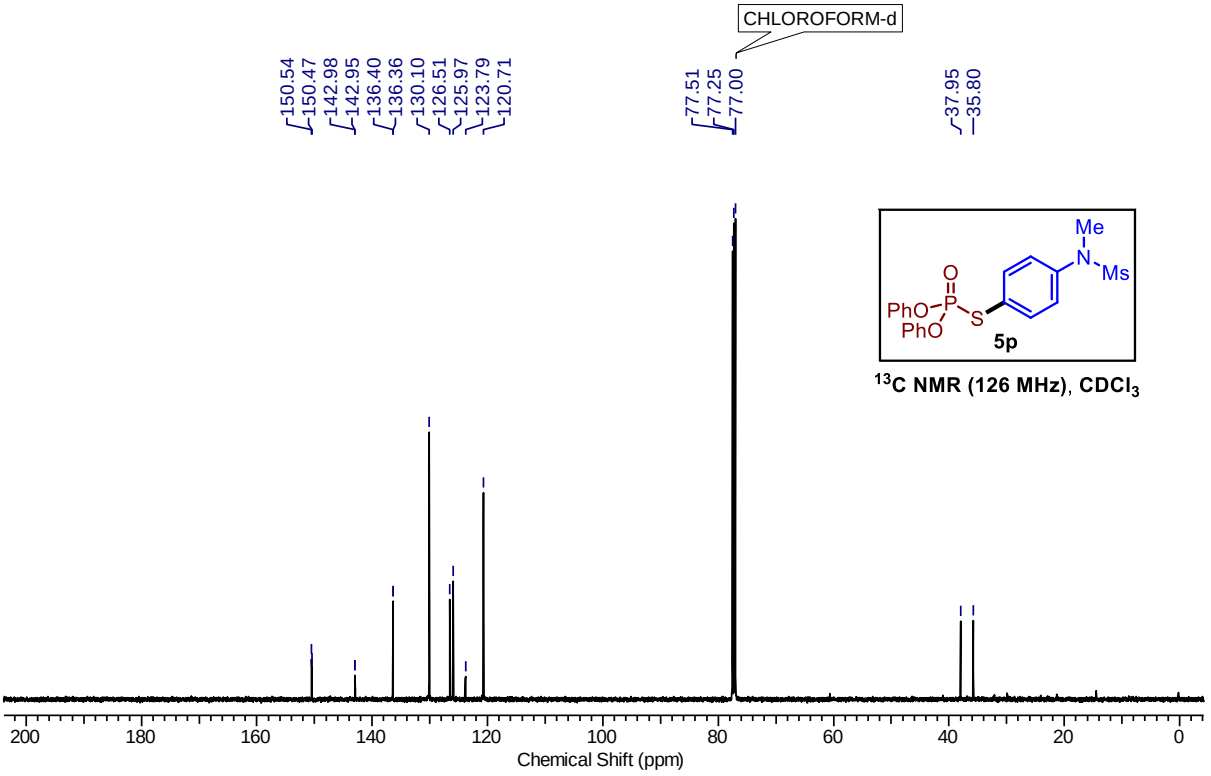
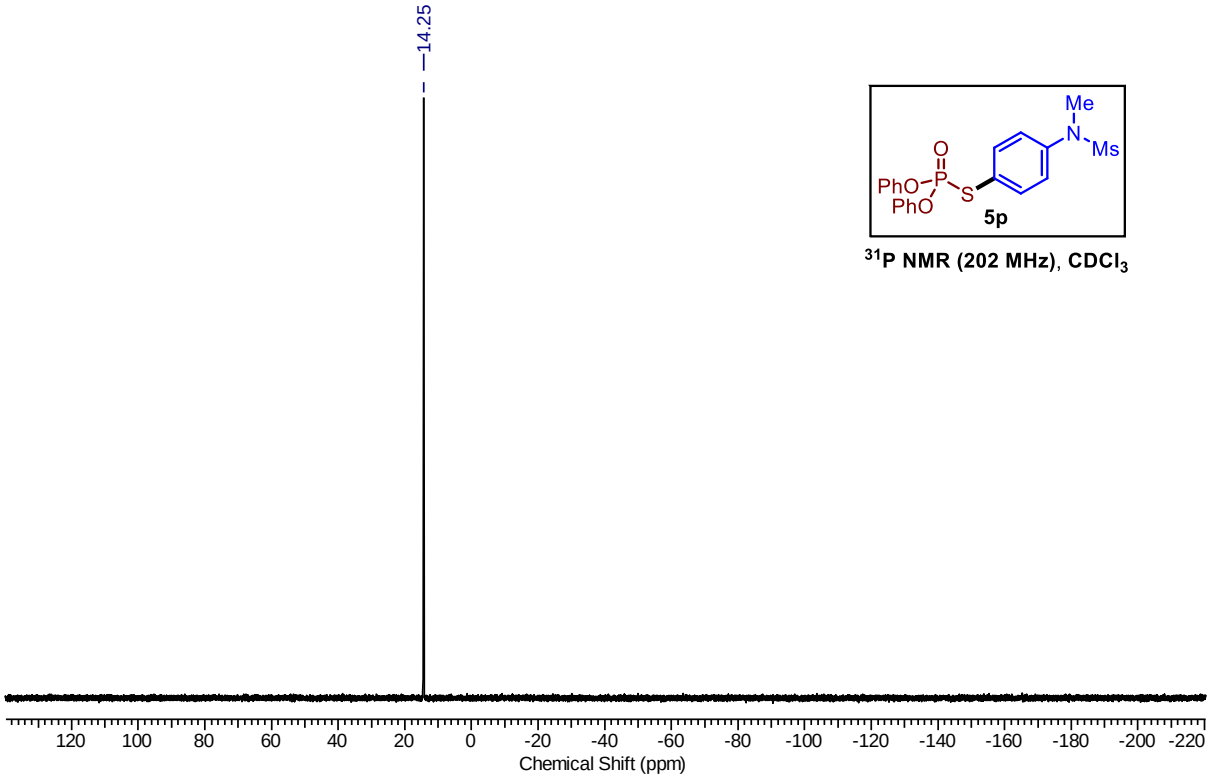


^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (126 MHz), $CDCl_3$



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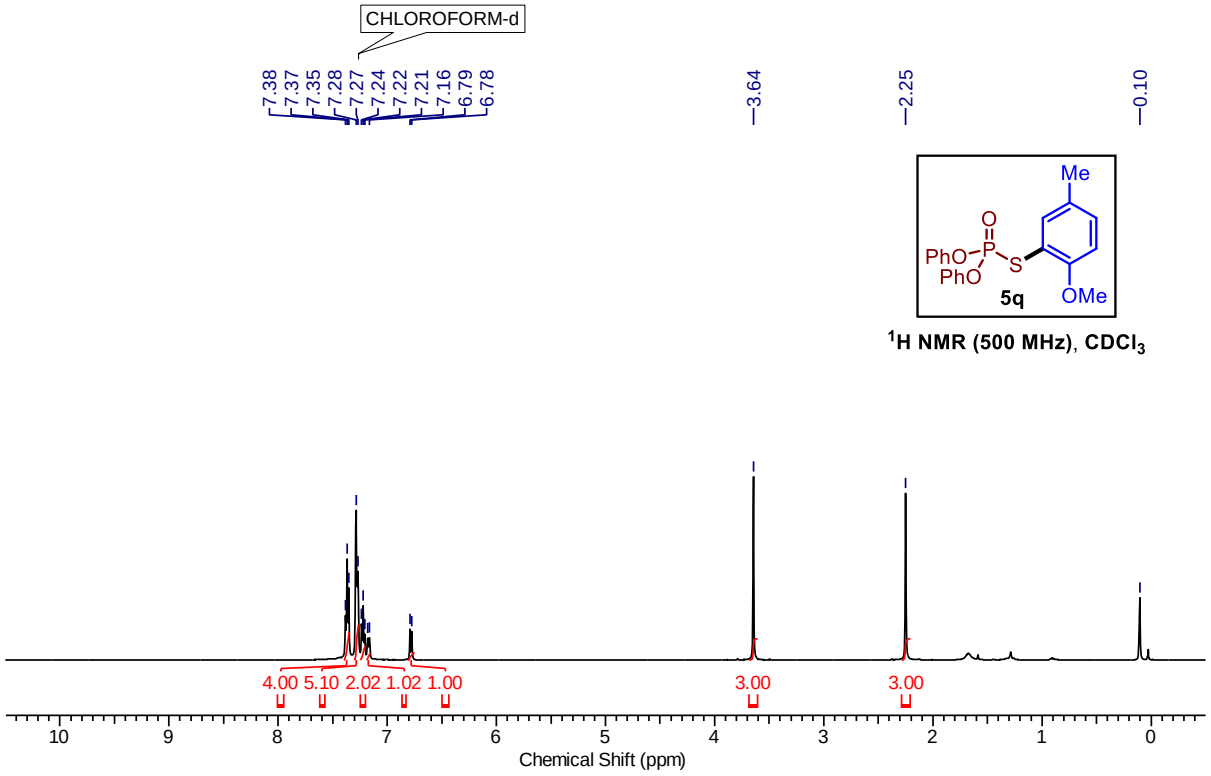

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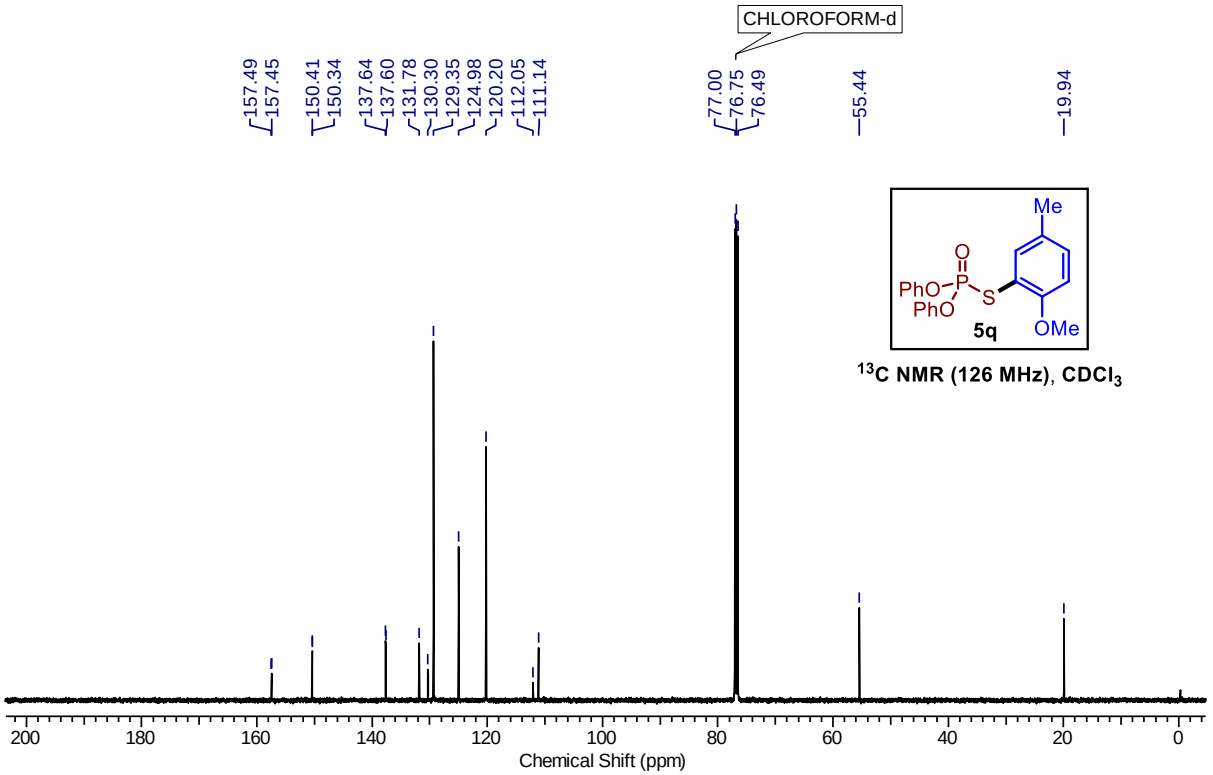
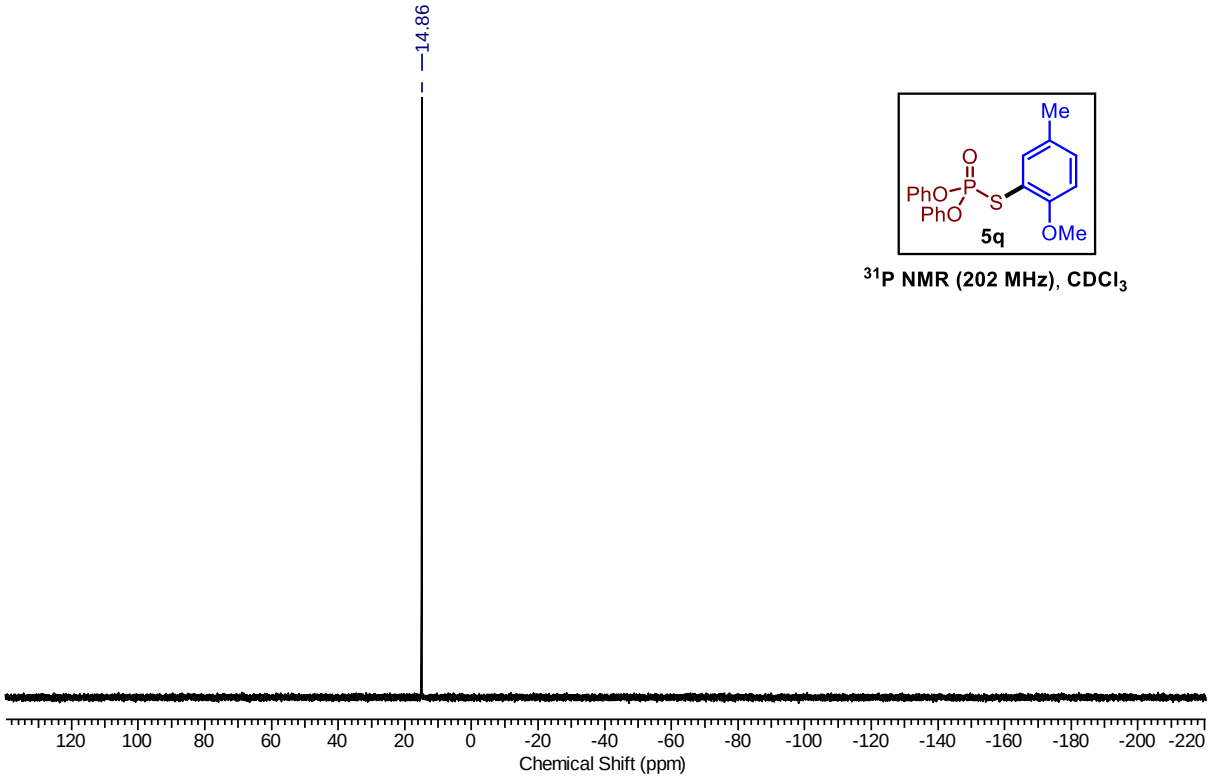
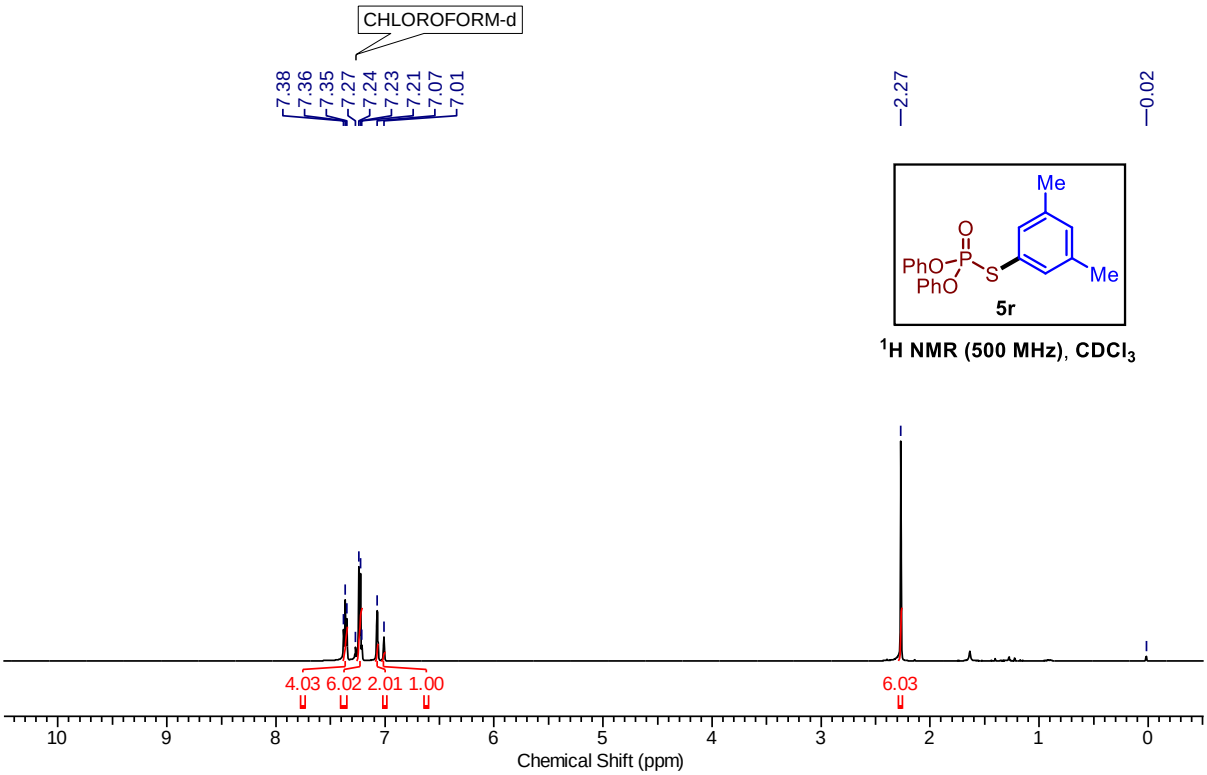


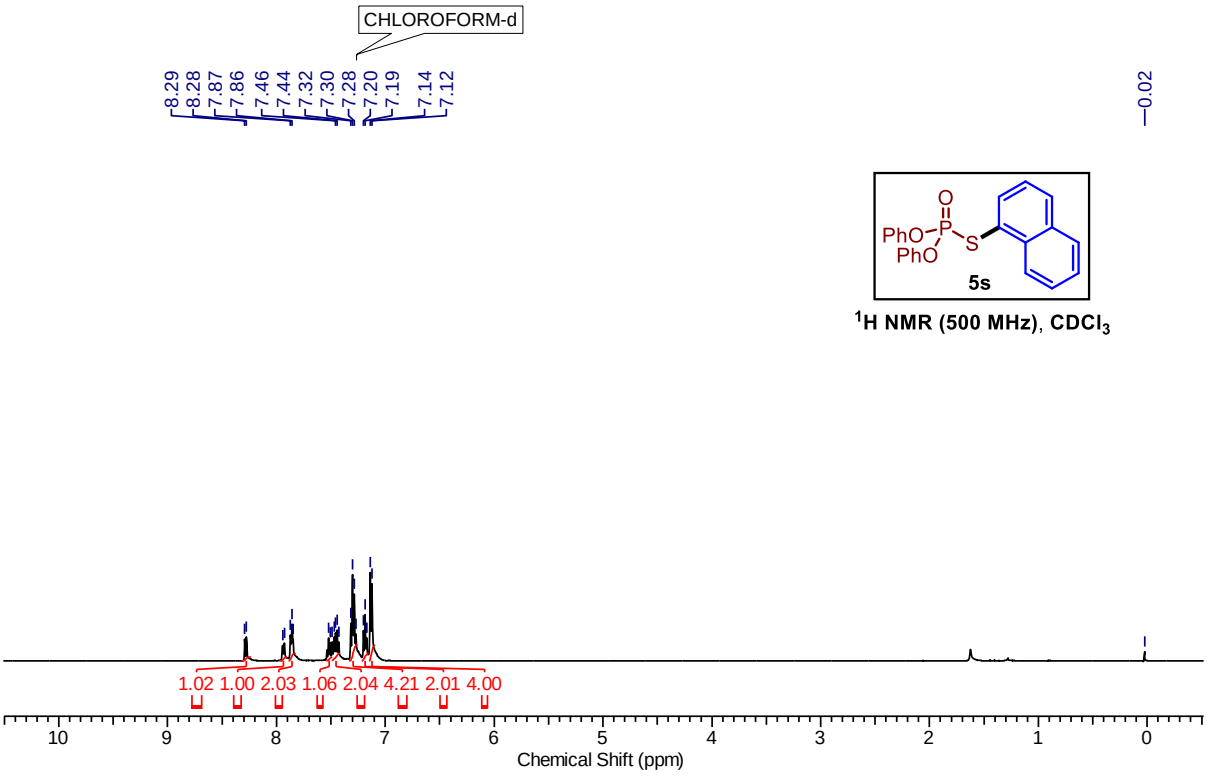
^{13}C NMR (126 MHz), $CDCl_3$



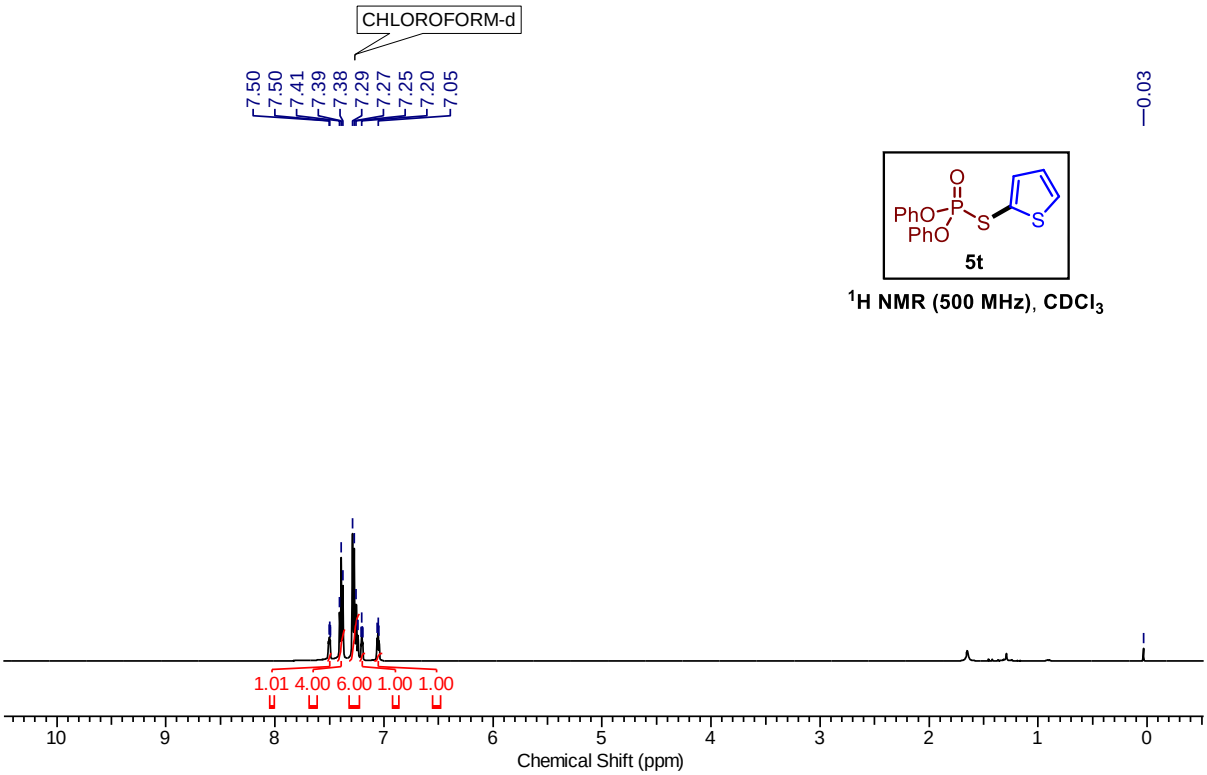
^{31}P NMR (202 MHz), $CDCl_3$

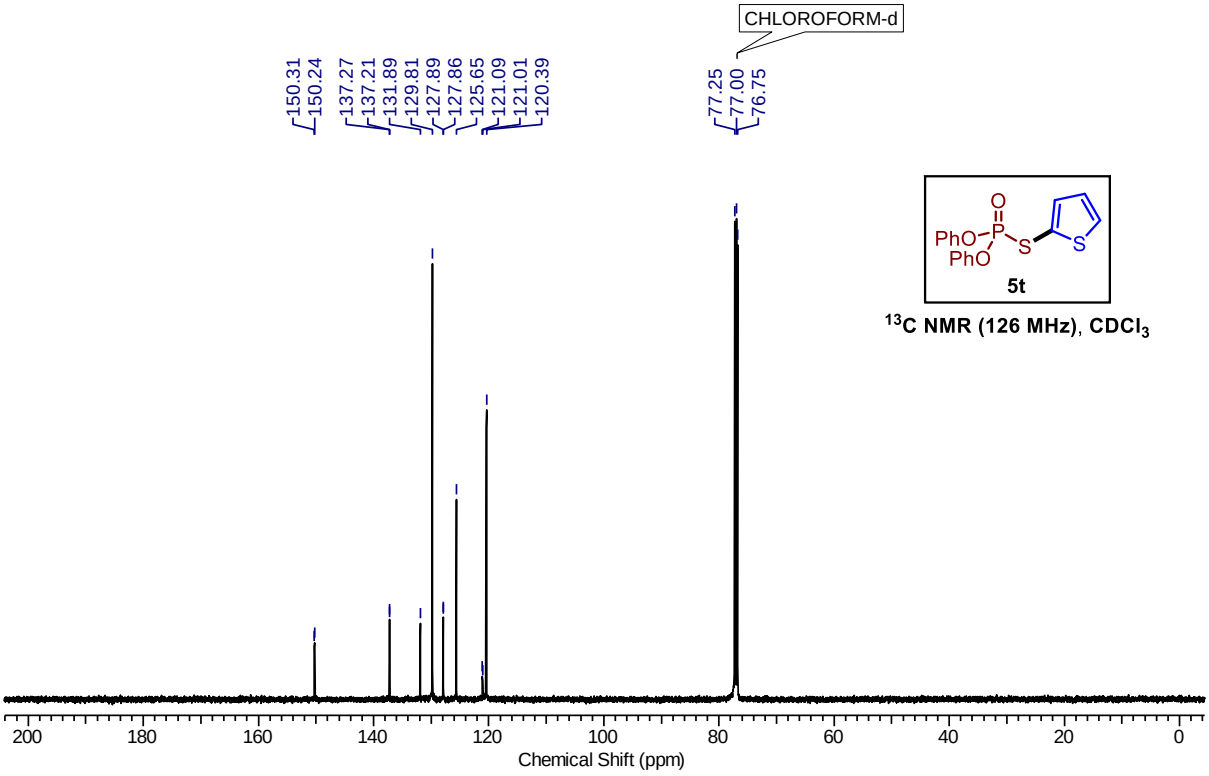


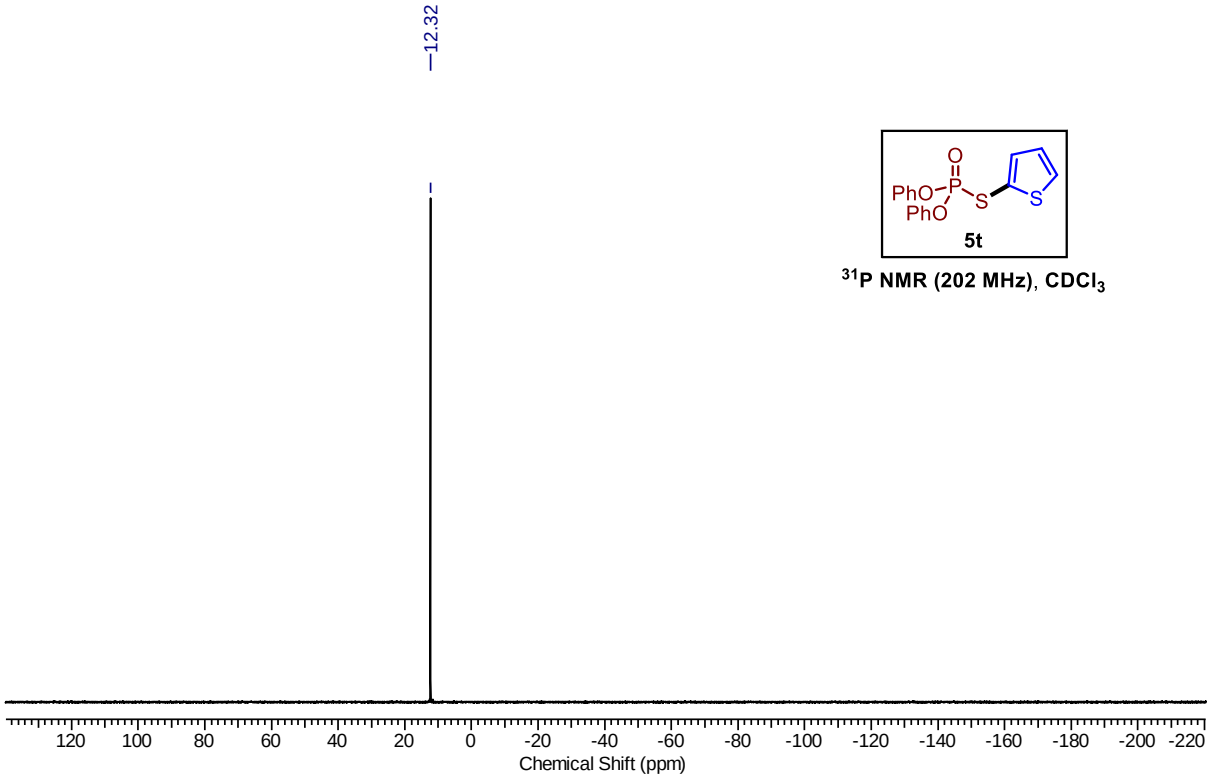
^{1}H NMR (500 MHz), $CDCl_3$

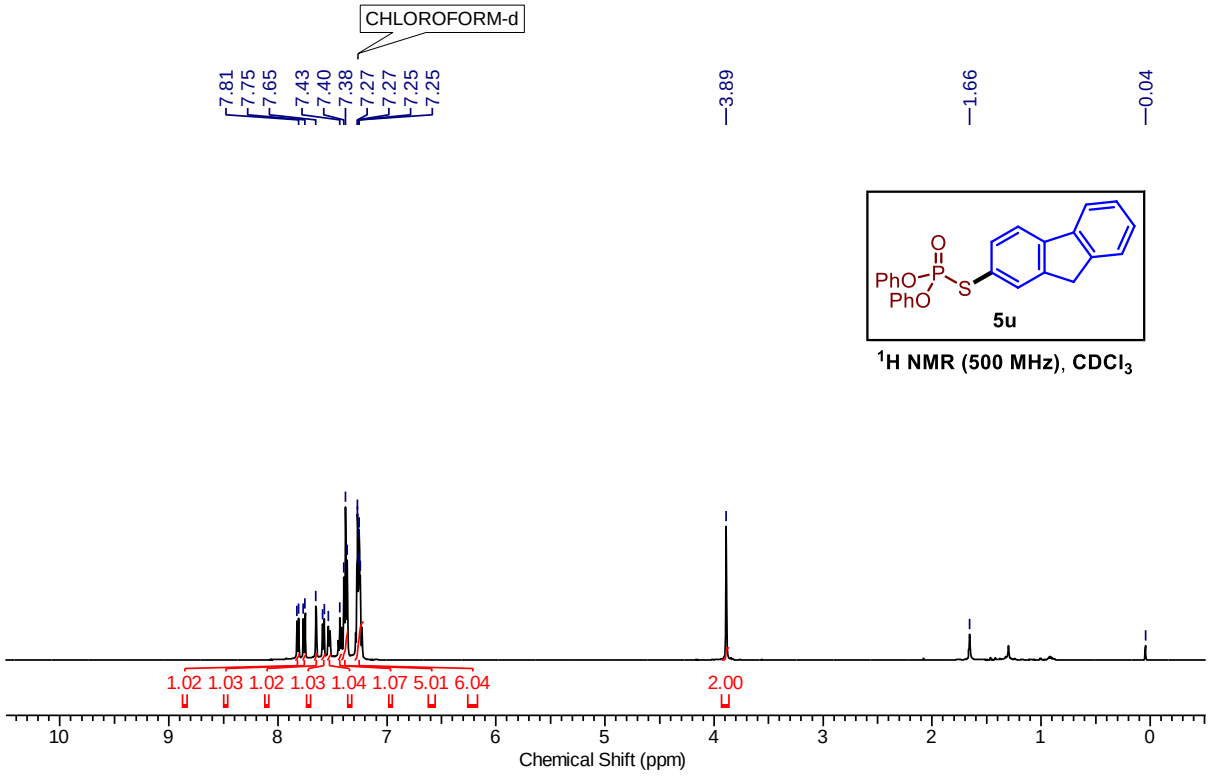


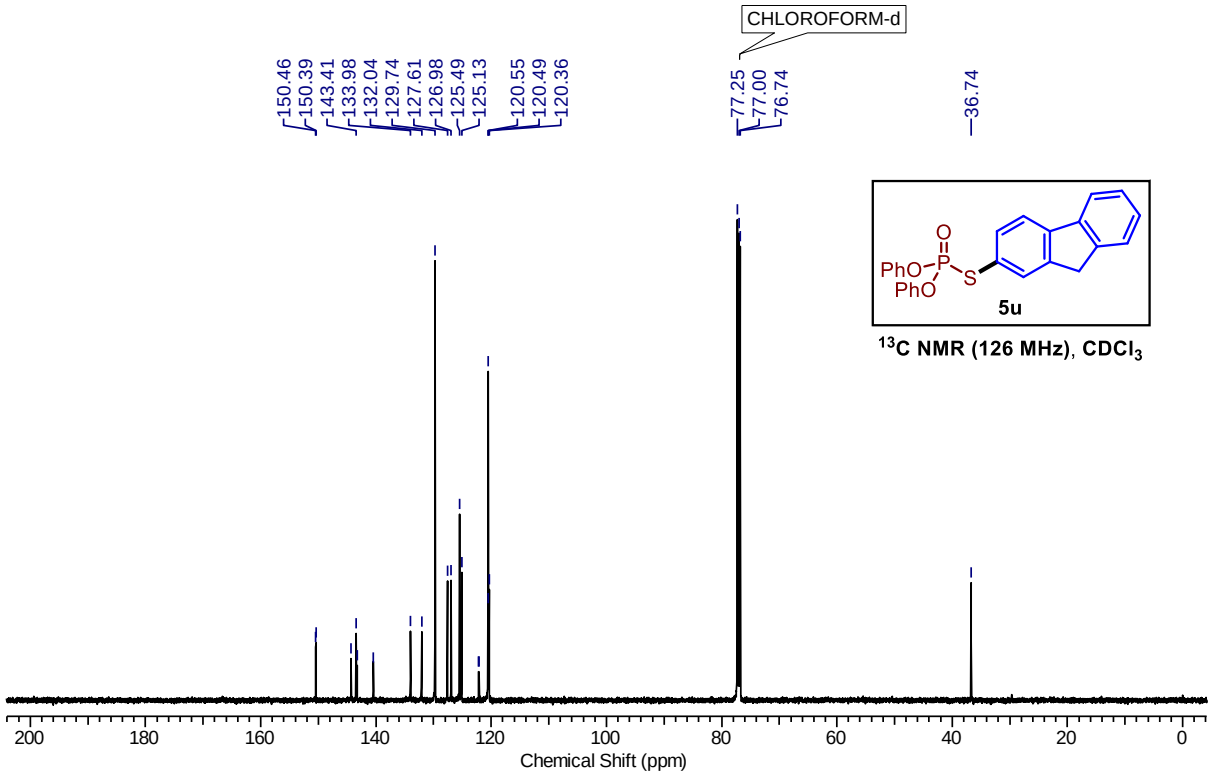
^{1}H NMR (500 MHz), $CDCl_3$


CHLOROFORM-d
7.50
7.50
7.41
7.39
7.38
7.29
7.27
7.25
7.20
7.05
0.03
PhO
PhO
O
P
S
S
5t
1H NMR (500 MHz), CDCl3
1.01 4.00 6.00 1.00 1.00
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

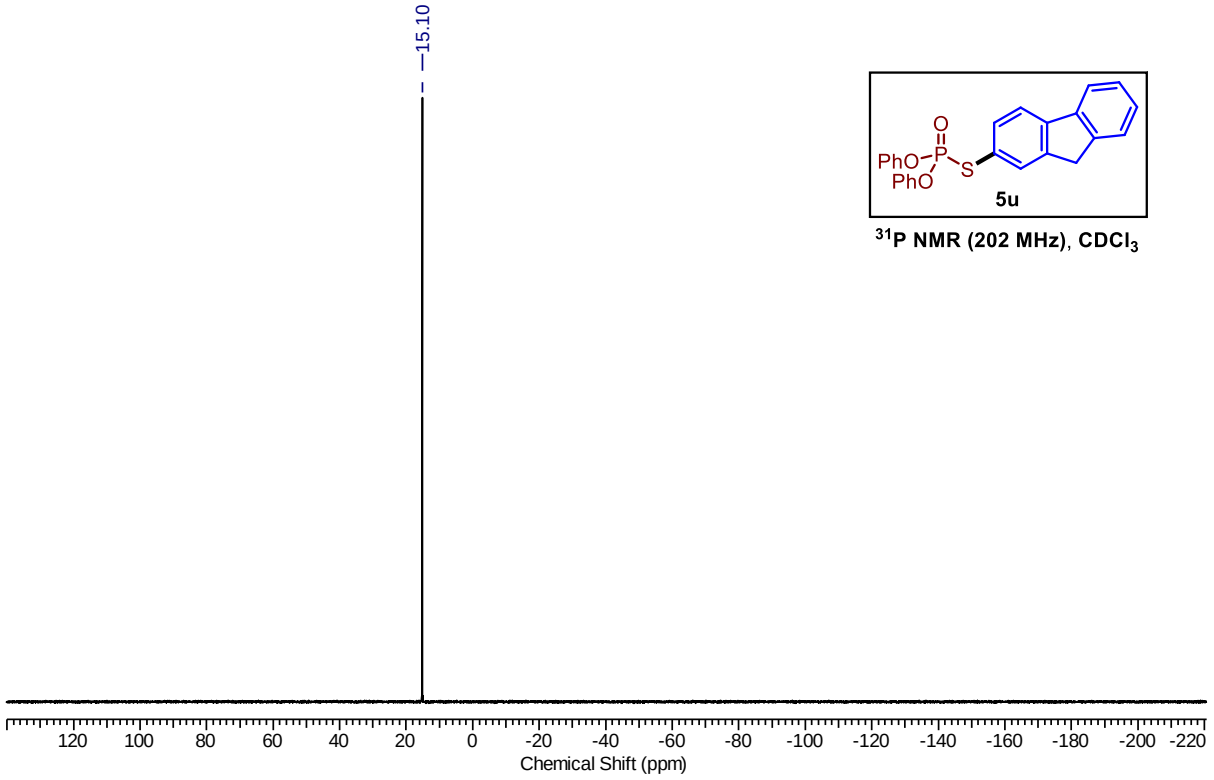

CHLOROFORM-d
150.31
150.24
137.27
137.21
131.89
129.81
127.89
127.86
125.65
121.09
121.01
120.39
77.25
77.00
76.75
PhO
PhO
O
P
S
S
5t
13C NMR (126 MHz), CDCl3
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)


12.32
PhO
PhO
O
P
S
S
5t
31P NMR (202 MHz), CDCl3
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220
Chemical Shift (ppm)

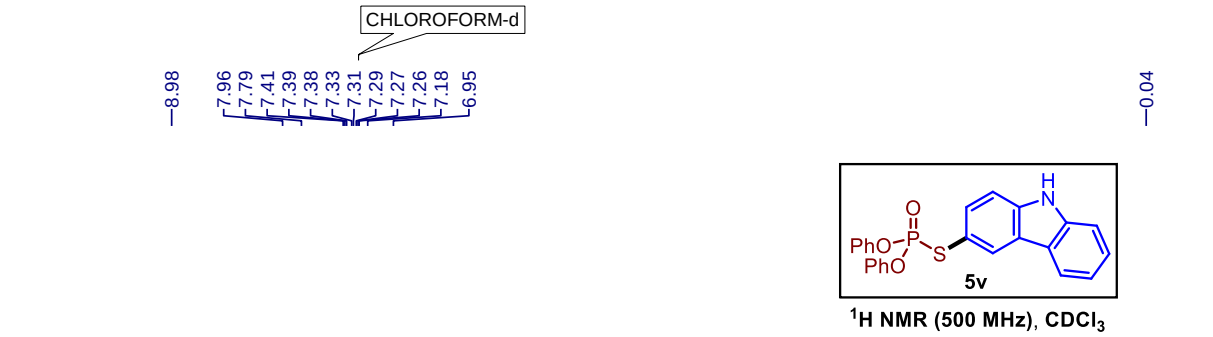

CHLOROFORM-d
7.81
7.75
7.65
7.43
7.40
7.38
7.27
7.27
7.25
7.25
3.89
1.66
0.04
PhO
PhO
O
P
S
5u
1H NMR (500 MHz), CDCl3
1.02 1.03 1.02 1.03 1.04 1.07 5.01 6.04
2.00
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)



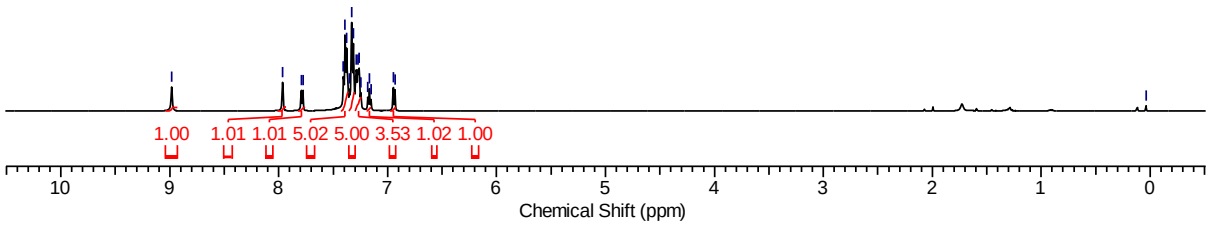
^{13}C NMR (126 MHz), $CDCl_3$

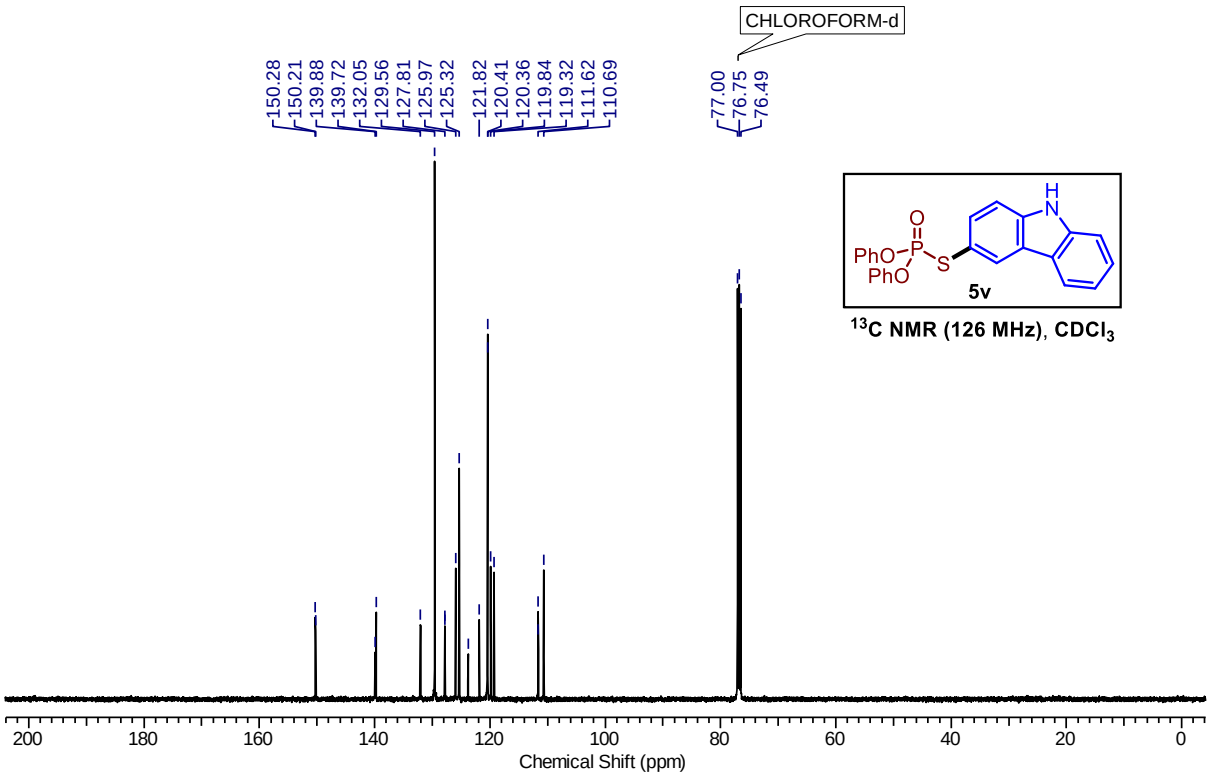


^{31}P NMR (202 MHz), $CDCl_3$

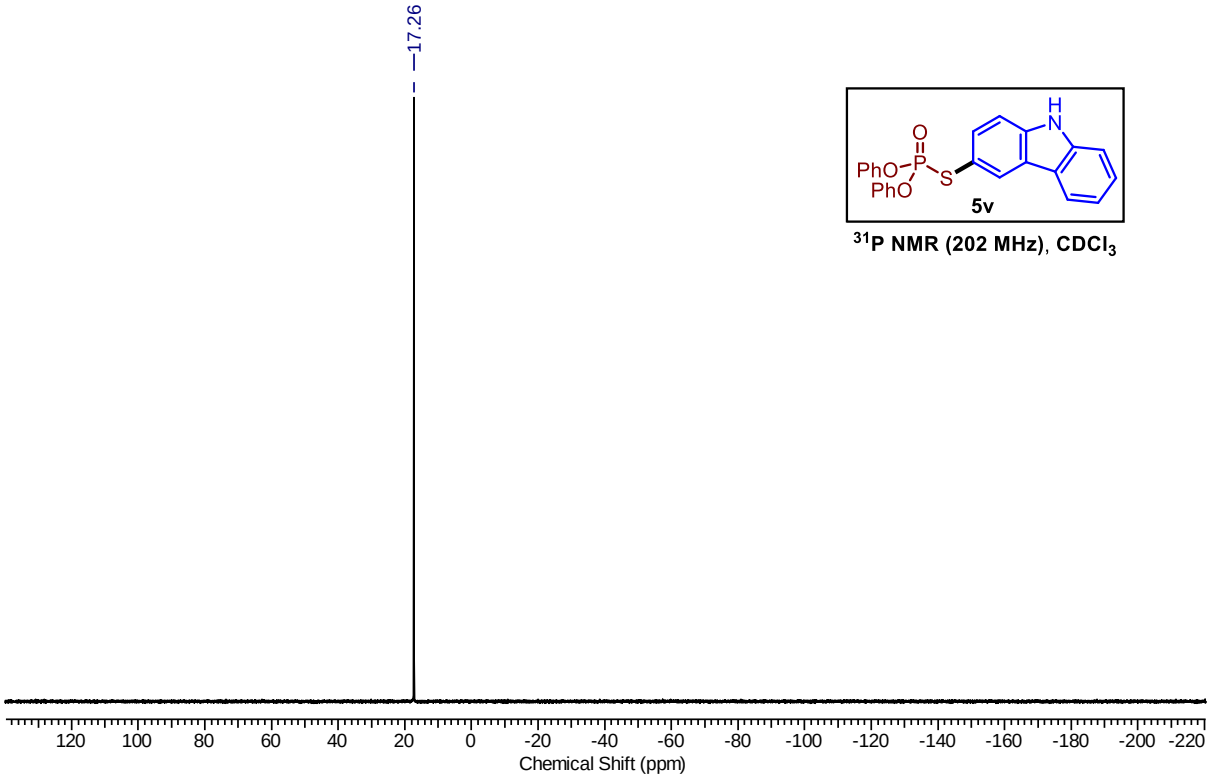


^{1}H NMR (500 MHz), $CDCl_3$

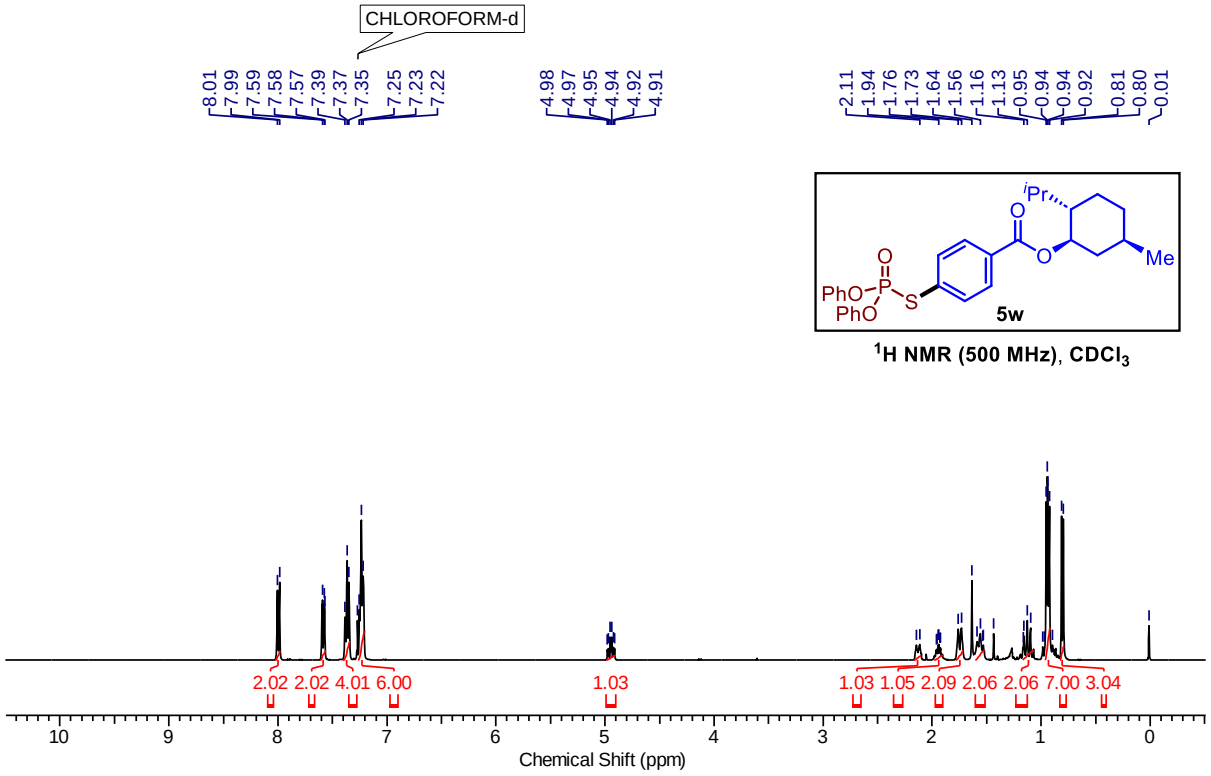




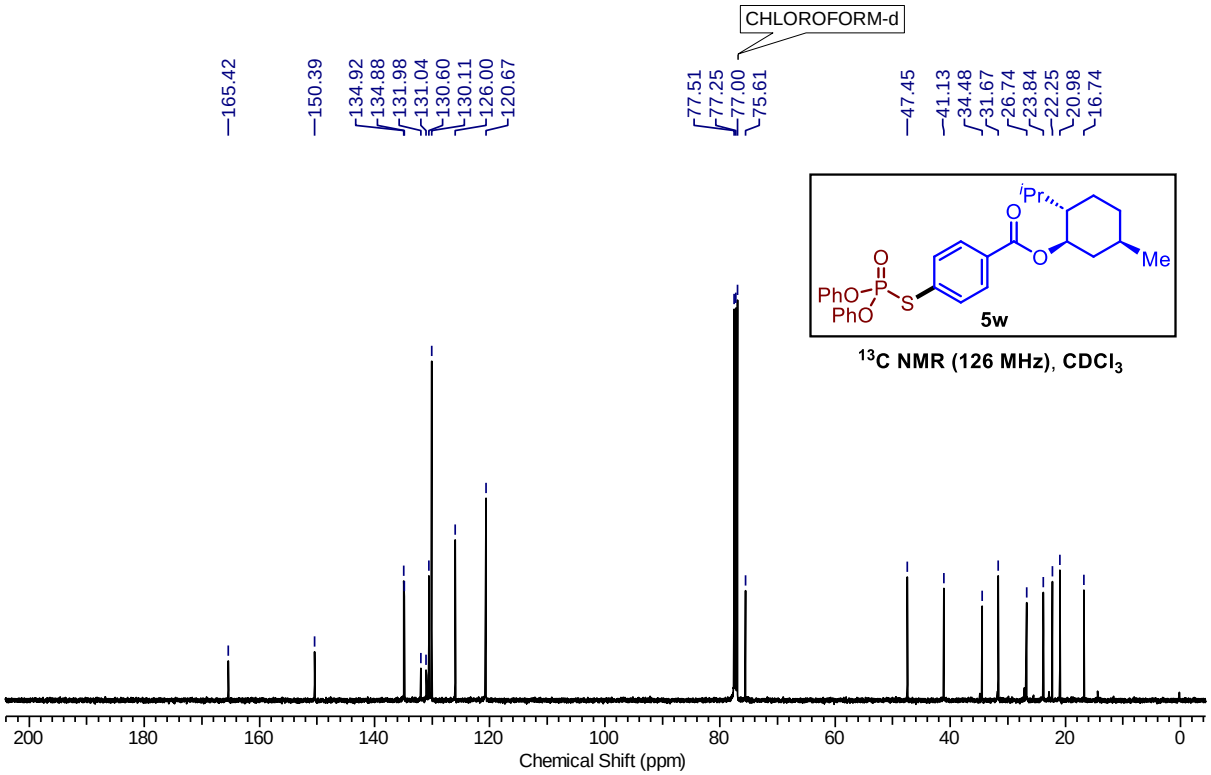
^{13}C NMR (126 MHz), $CDCl_3$



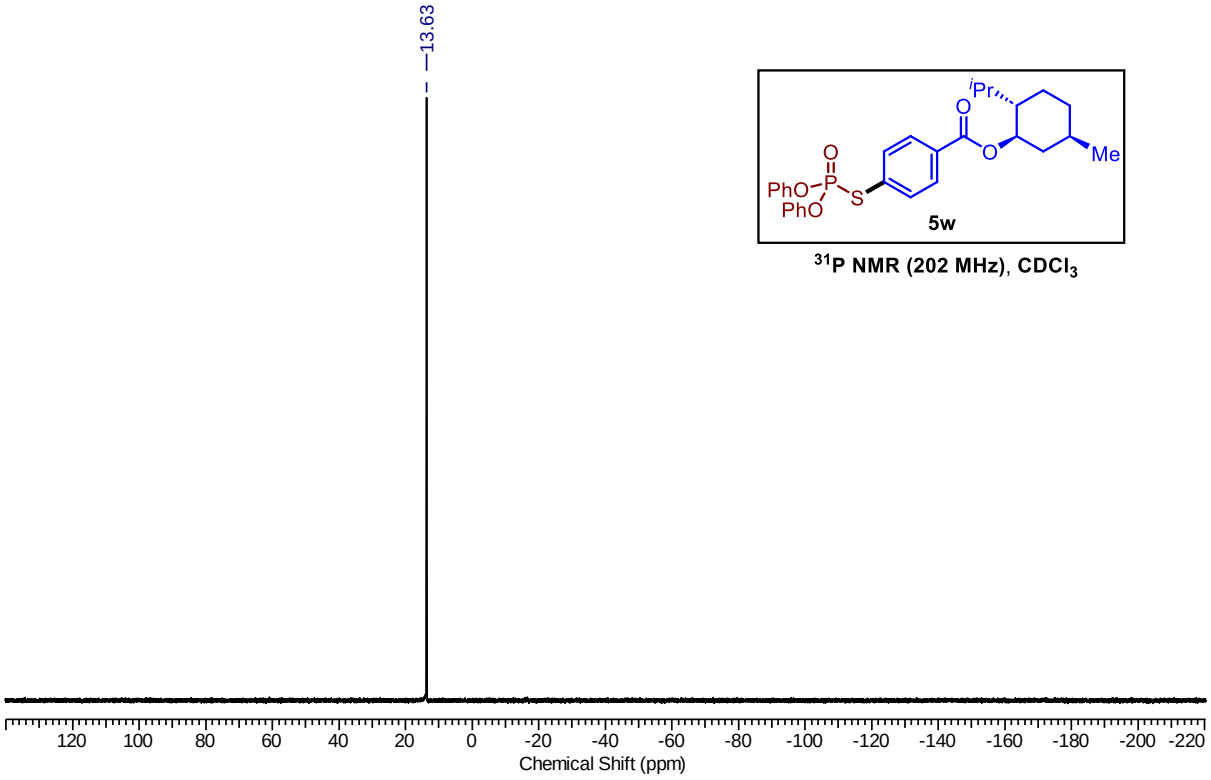
^{31}P NMR (202 MHz), $CDCl_3$



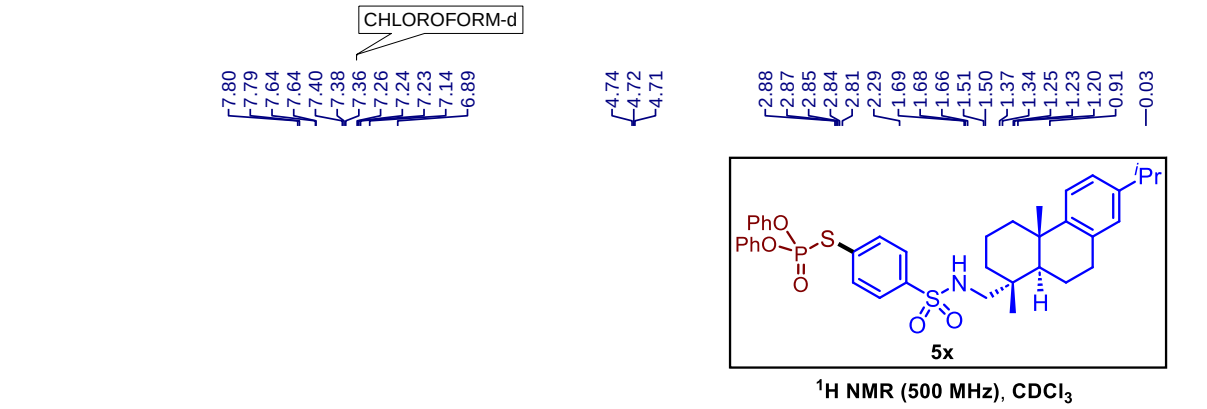
^{1}H NMR (500 MHz), $CDCl_3$



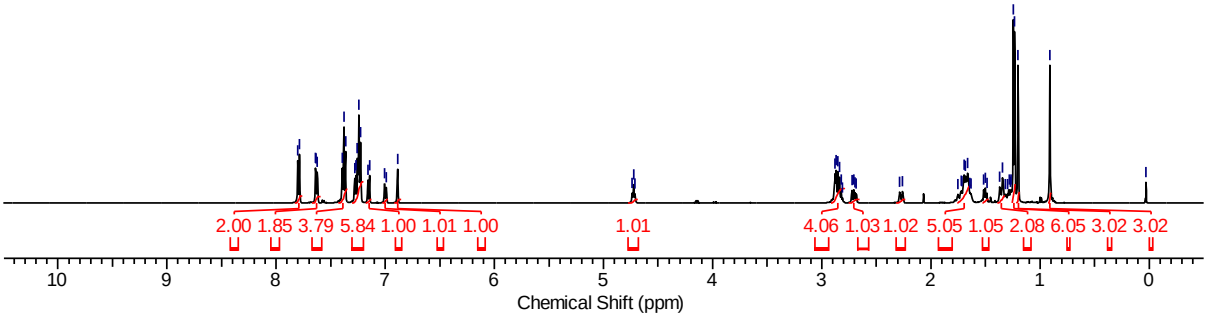
^{13}C NMR (126 MHz), $CDCl_3$

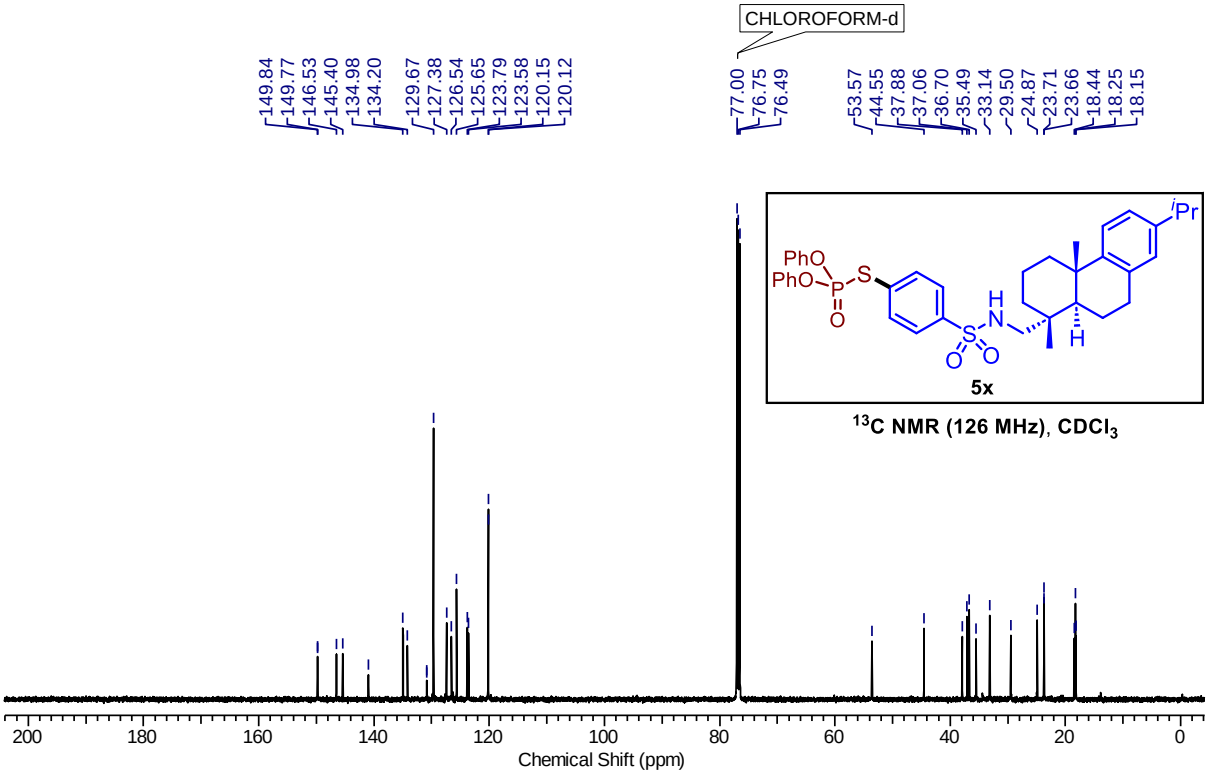


^{31}P NMR (202 MHz), $CDCl_3$

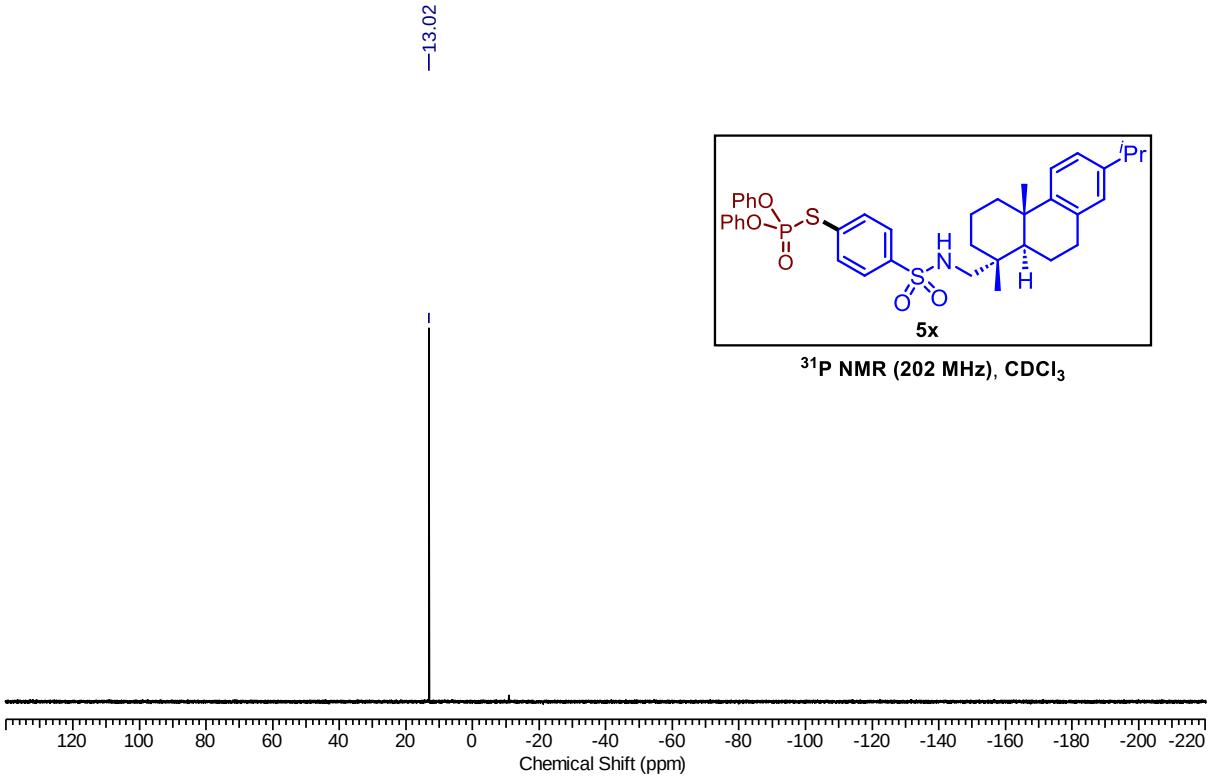


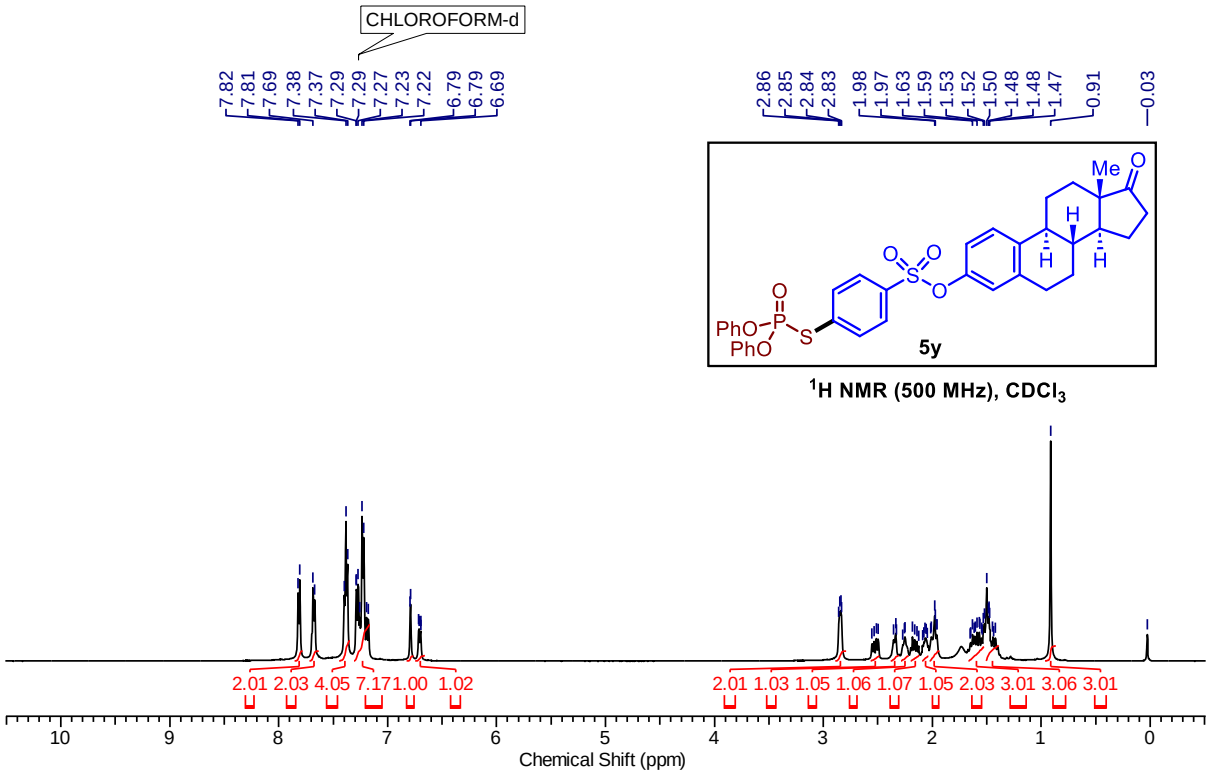
^{1}H NMR (500 MHz), $CDCl_3$

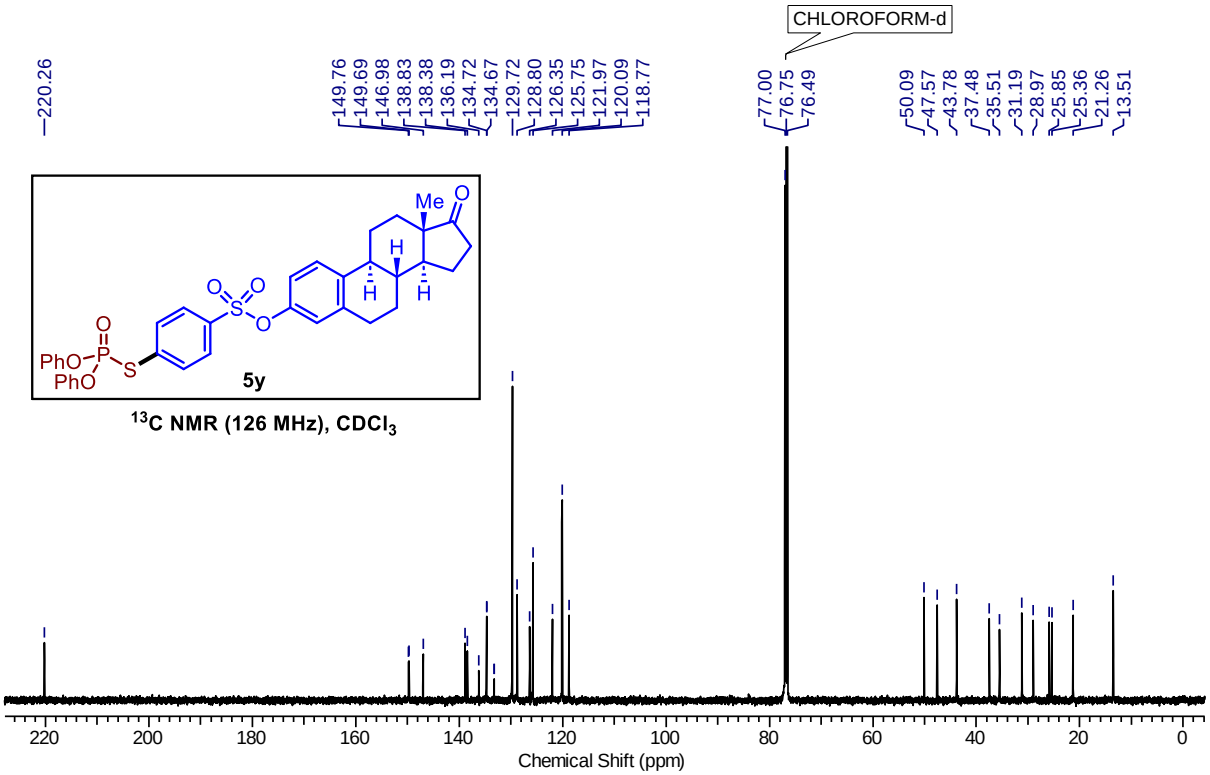




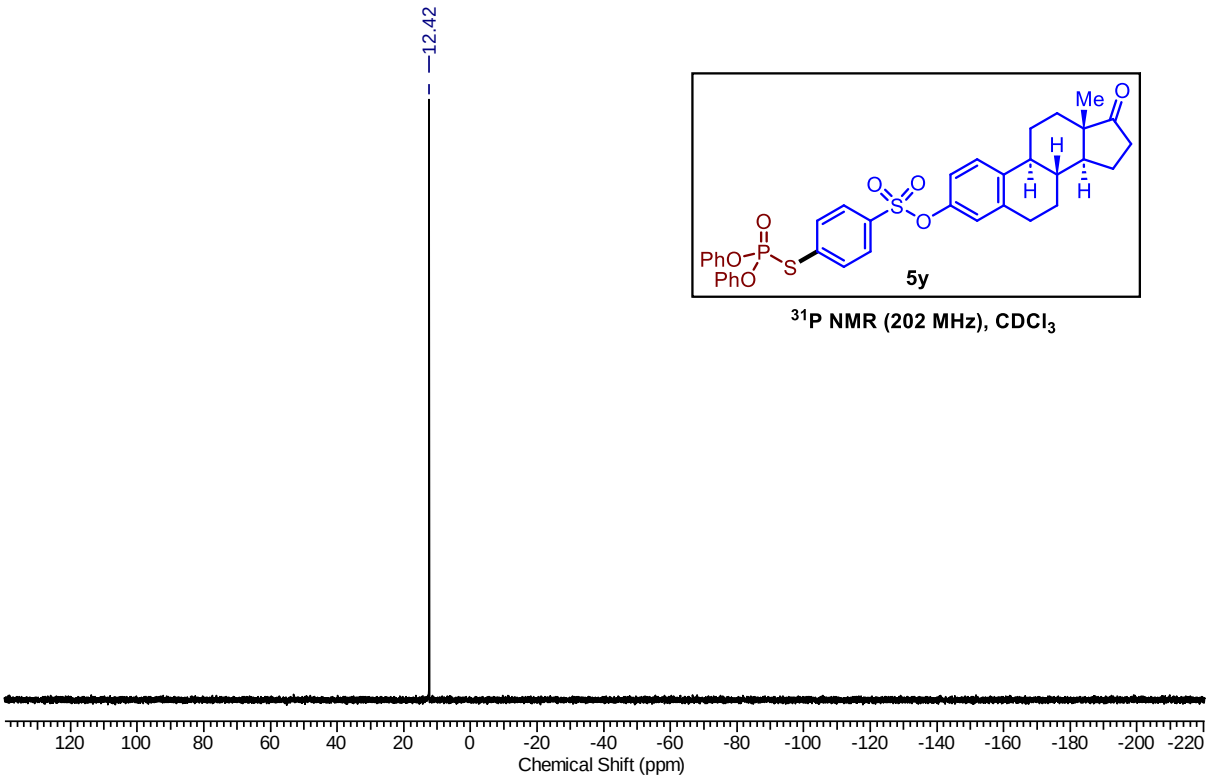
^{13}C NMR (126 MHz), $CDCl_3$


13.02
PhO
PhO
P
O
S
N
H
S
O
O
iPr
H
5x
31P NMR (202 MHz), CDCl3
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220
Chemical Shift (ppm)

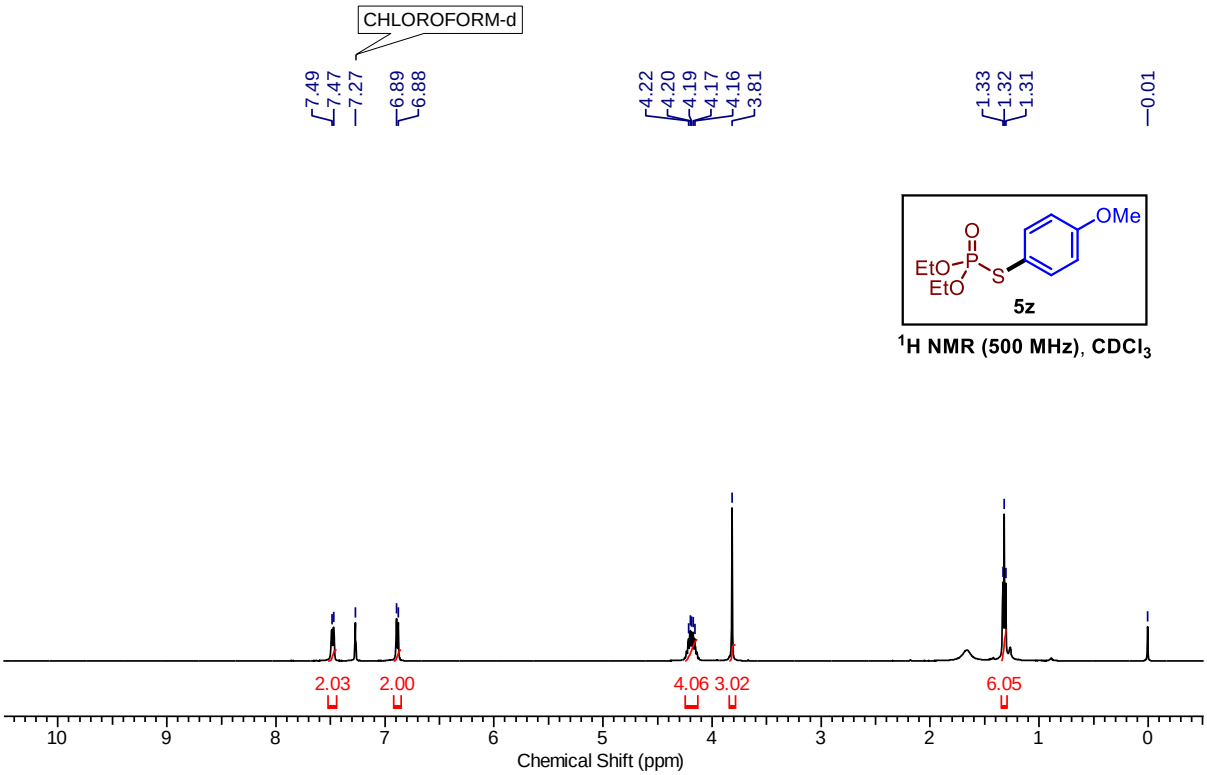

CHLOROFORM-d
7.82 7.81 7.69 7.38 7.37 7.29 7.29 7.27 7.23 7.22 6.79 6.79 6.69
2.86 2.85 2.84 2.83 1.98 1.97 1.63 1.59 1.53 1.52 1.50 1.48 1.48 1.47 0.91 0.03
Me
O
H
H
H
O
S
O
O
PhO
PhO
P
O
S
5y
1H NMR (500 MHz), CDCl3
2.01 2.03 4.05 7.17 1.00 1.02
2.01 1.03 1.05 1.06 1.07 1.05 2.03 3.01 3.06 3.01
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)



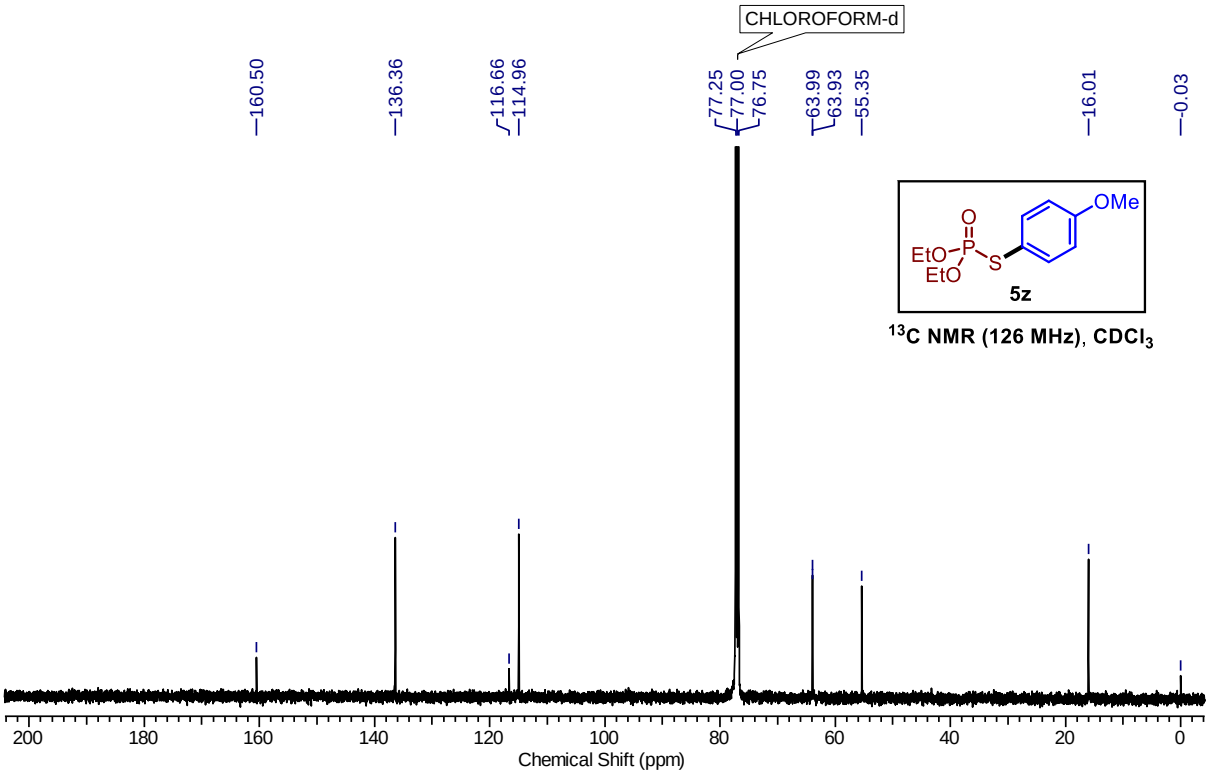
^{13}C NMR (126 MHz), $CDCl_3$



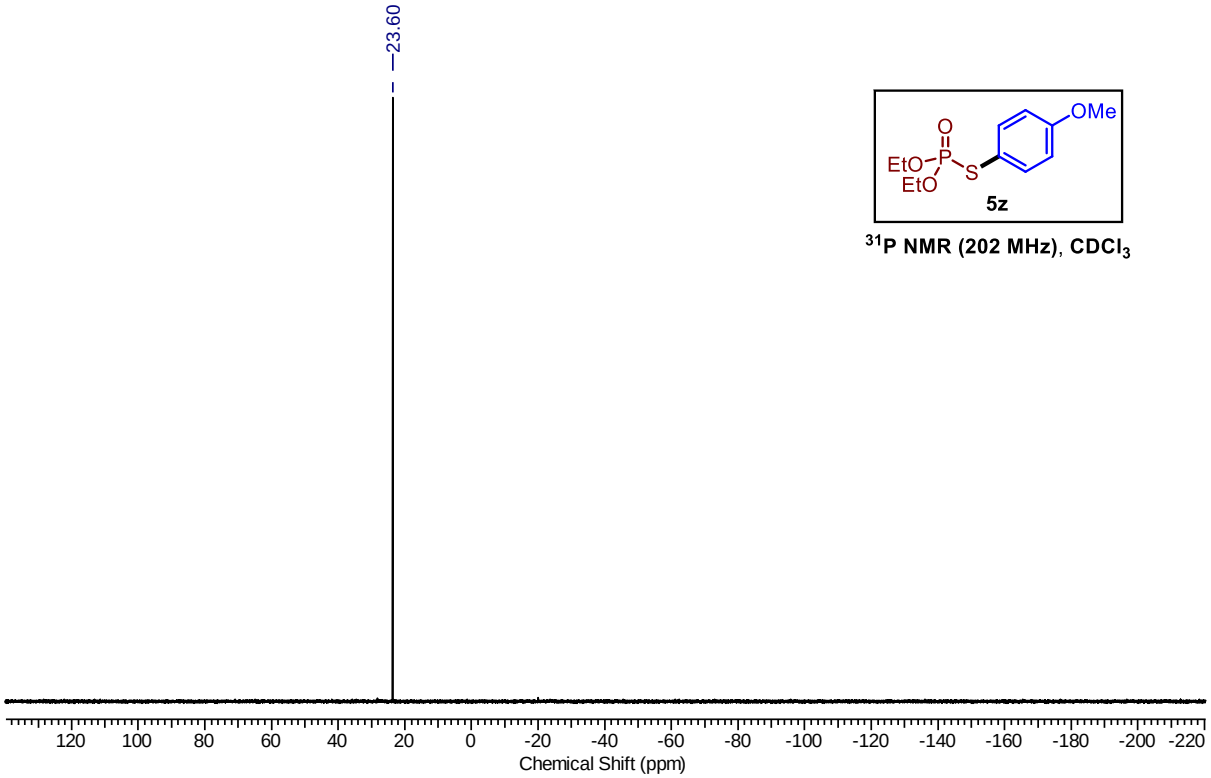
^{31}P NMR (202 MHz), $CDCl_3$



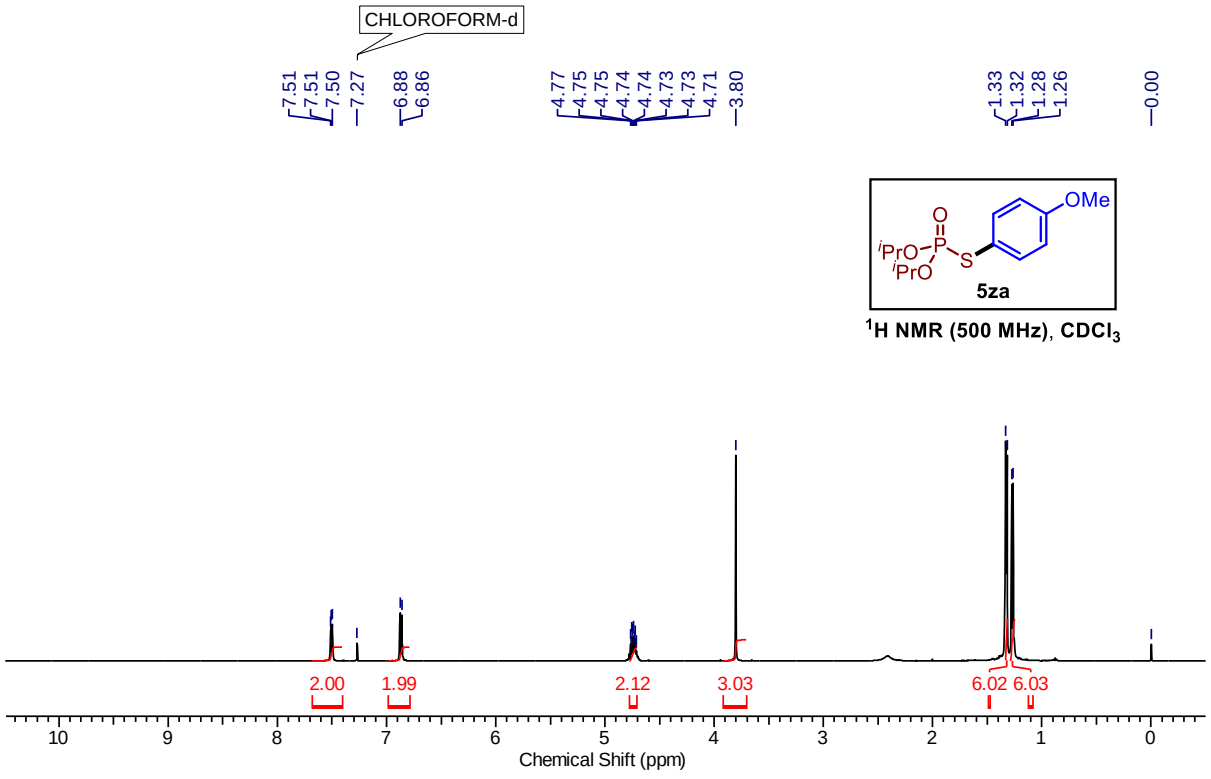
^{1}H NMR (500 MHz), $CDCl_3$



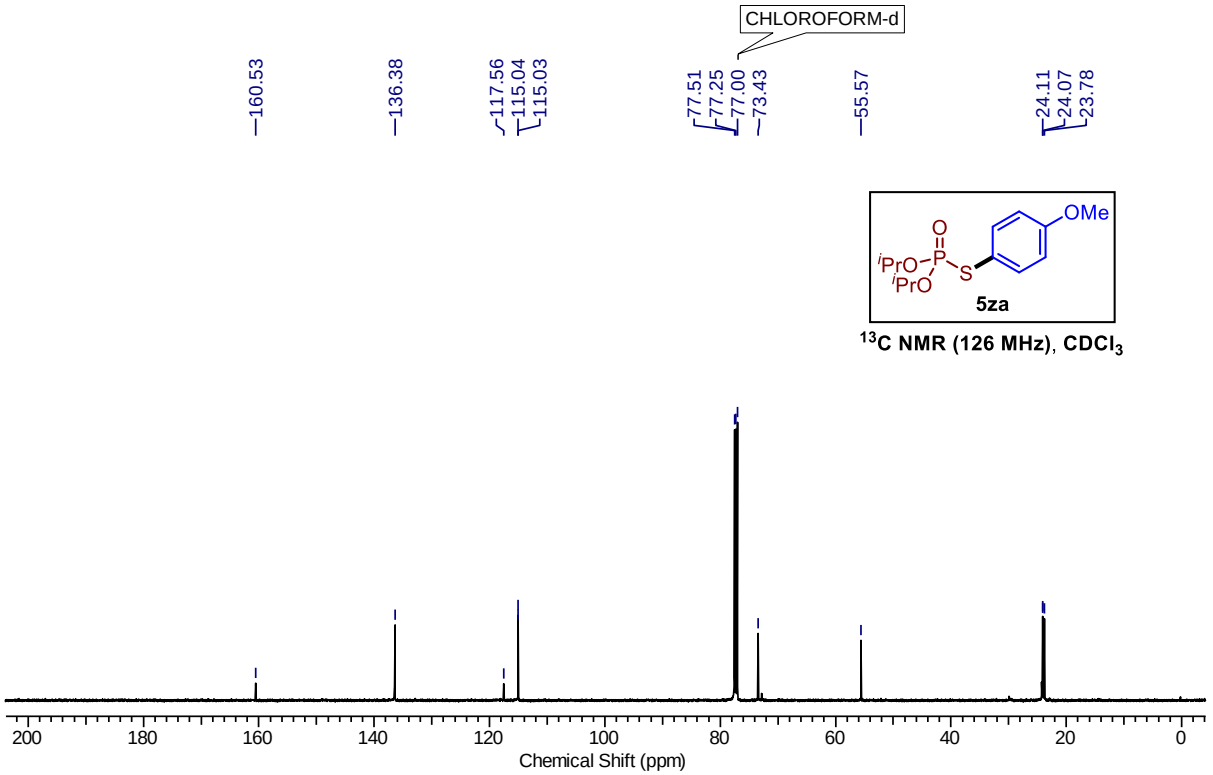
^{13}C NMR (126 MHz), $CDCl_3$

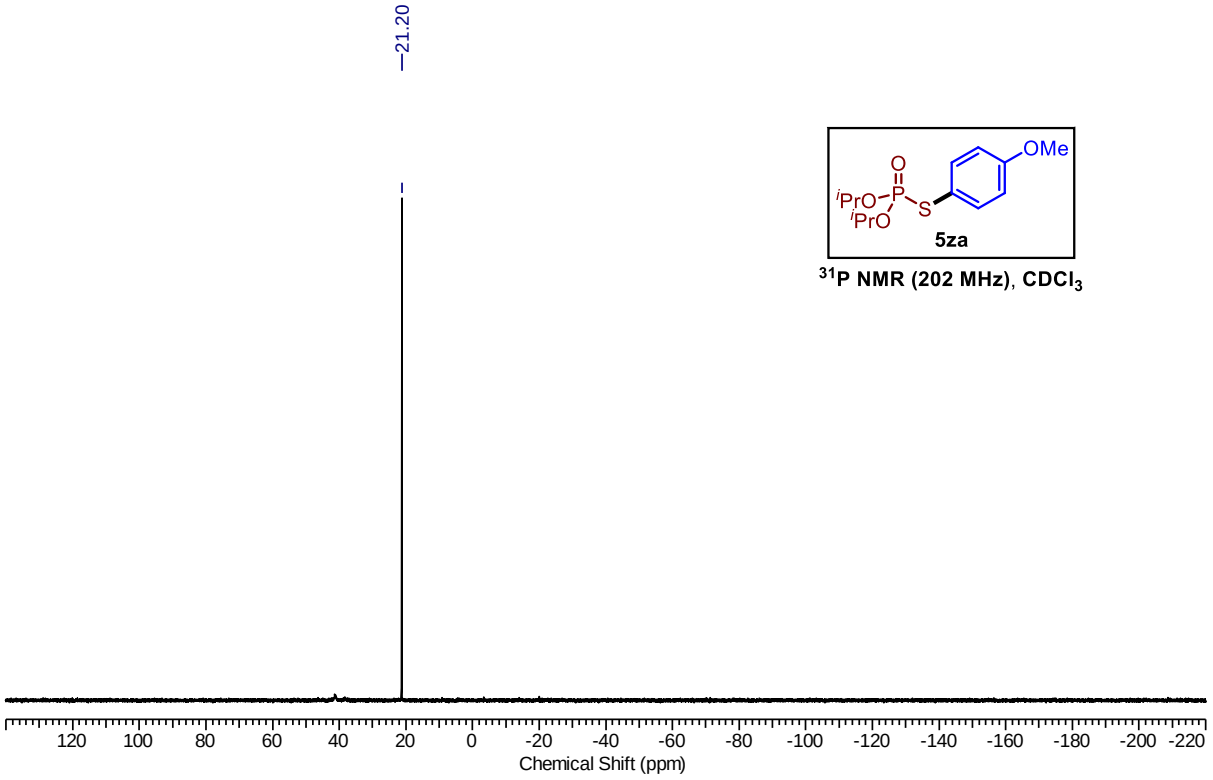


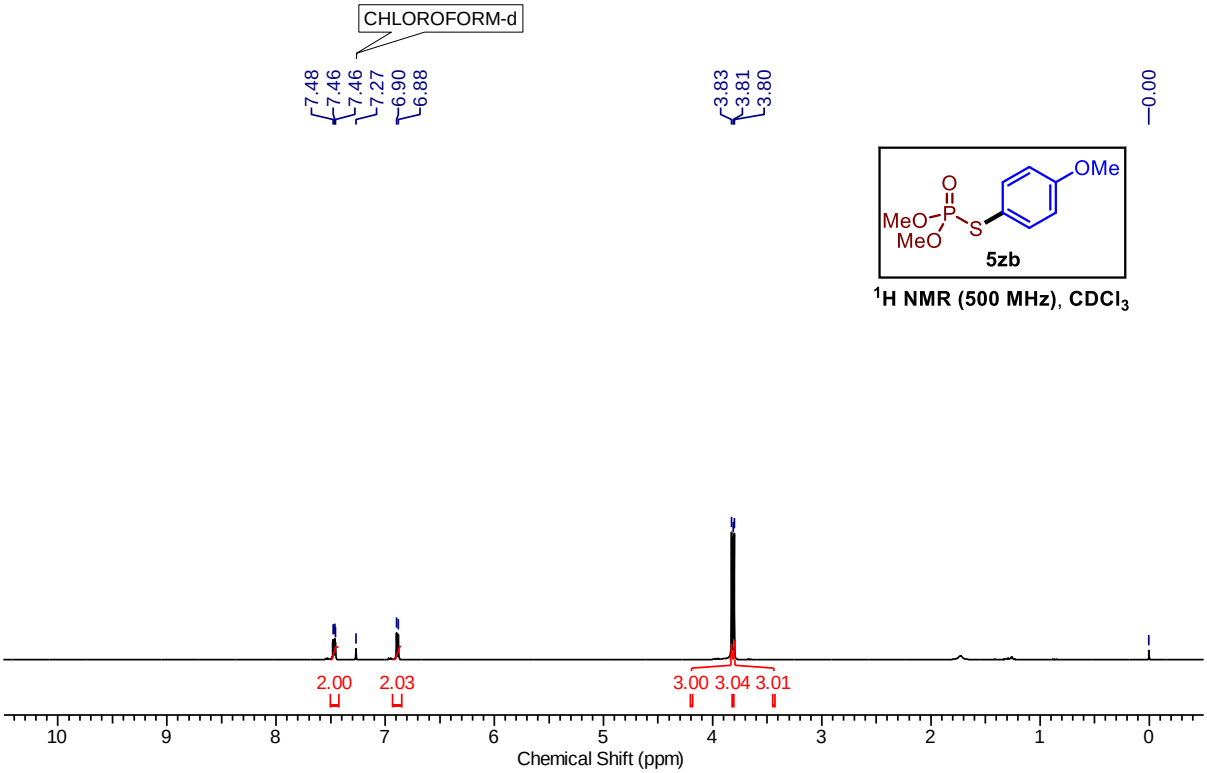
^{31}P NMR (202 MHz), $CDCl_3$



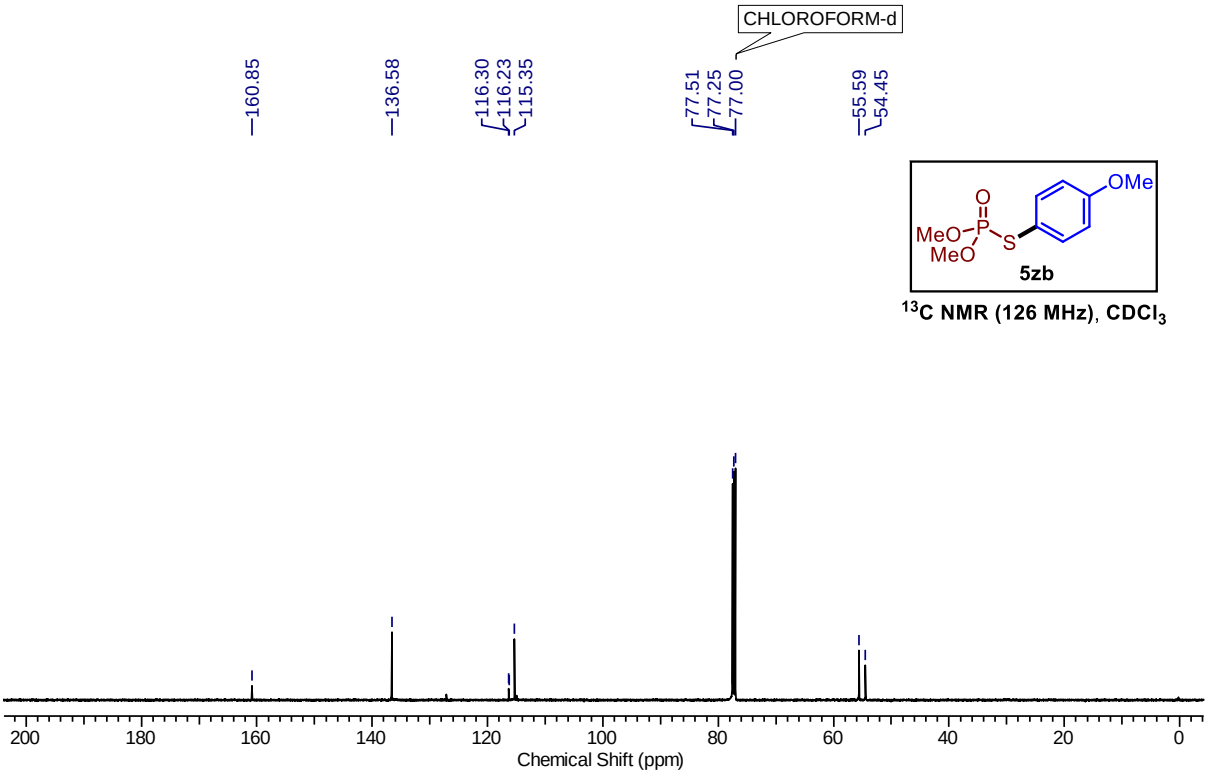
^{1}H NMR (500 MHz), $CDCl_3$


CHLOROFORM-d
160.53
136.38
117.56
115.04
115.03
77.51
77.25
77.00
73.43
55.57
24.11
24.07
23.78
OMe
O
P
S
iPrO
iPrO
5za
13C NMR (126 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

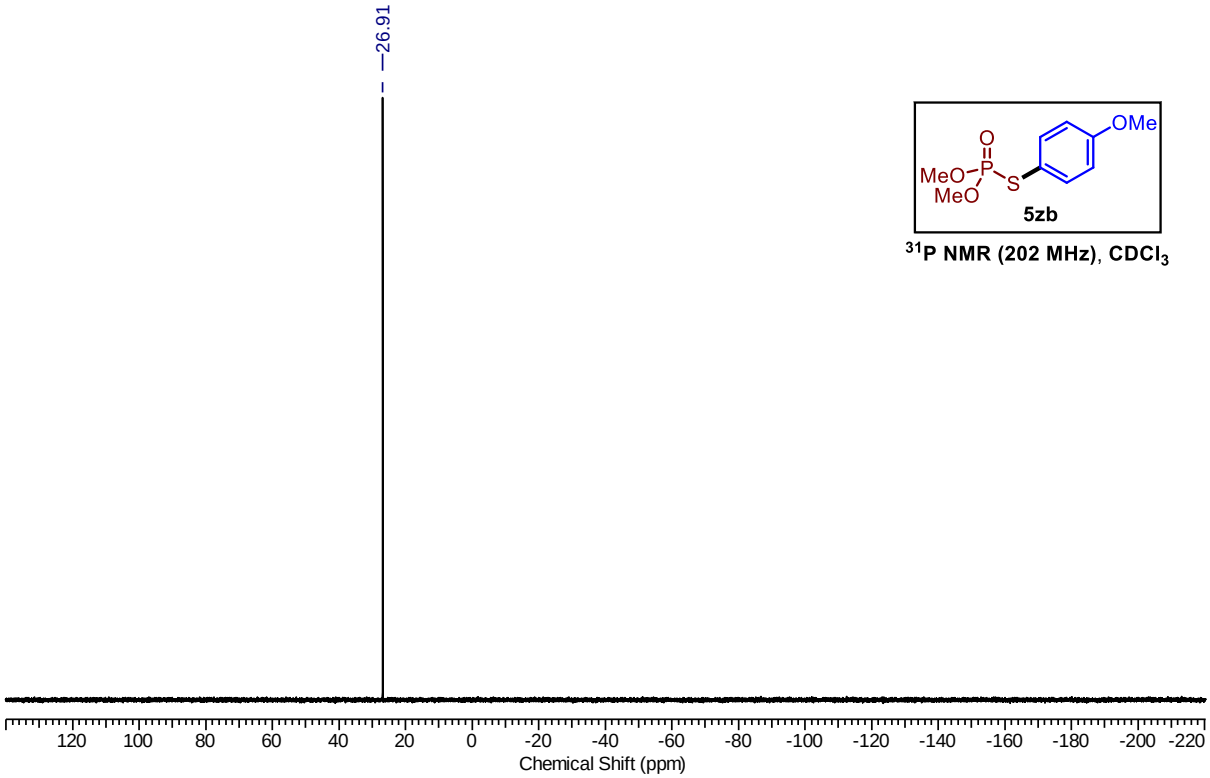

21.20
OMe
O
P
S
iPrO
iPrO
5za
31P NMR (202 MHz), CDCl3
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)



^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (126 MHz), $CDCl_3$



^{31}P NMR (202 MHz), $CDCl_3$
