Supplementary Information

$[Ru^{IV}(F_{20}\text{-TPP})Cl_2]$ Efficiently Catalysed Inter- and Intra-Molecular Nitrene Insertion into sp^3 C-H Bonds of Hydrocarbons Using Phosphoryl Azides as Nitrene Source

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I. General Information

Unless otherwise stated, all reactions were performed under argon atmosphere. DPPA was purchased from Acros. $[Rh_2(esp)_2]$ was purchased from Sigma-Aldrich. Molecular sieves were dried at 400℃ for 3 h prior to use. All solvents and hydrocarbons were purified by distillation using standard methods. Metal porphyrin catalysts and other organic azides were synthesized according to previously reported methods. All ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV300, AV400 and AV500 NMR spectrometers with tetramethylsilane (TMS) as internal reference. ^{31}P NMR spectra were recorded on Bruker AV400 NMR spectrometer with 85% H_3PO_4 as external reference. Mass spectra were recorded on Finnigan MAT 95 mass spectrometer. ESI mass spectra were obtained on a Waters Micromess Q-Tof Premier quadrupole time-of-flight tandem mass spectrometer. ***Caution!*** Organic azides are potentially explosive and should be handled with great care.

II. Synthesis of Ruthenium(IV) Porphyrin Catalysts

Ruthenium(IV) porphyrin catalysts were synthesized according to the following references.

$[Ru^{IV}(TDCPP)Cl_2]$	J. -L. Zhang and C. -M. Che, *Chem. Eur. J.*, 2005, **11**, 3899.
$[Ru^{IV}(TPP)Cl_2]$	W.-H., Leung, T. S. M. Hun, H.-w. Hou, K.-Y. Wong, *J. Chem. Soc., Dalton Trans.* 1997, 237.
$[Ru^{IV}(F_{20}\text{-}TPP)Cl_2]$	C. Wang, K. V. Shalyaev, M. Bonchio, T. Carofiglio and J. T. Groves, *Inorg. Chem.*, 2006, **45**, 4769-4782.

Synthesis of $[Ru^{IV}(F_{20}\text{-}TPP)Cl_2]$

$$[Ru^{II}(F_{20}\text{-}TPP)(CO)] \xrightarrow[DCM]{m\text{-CPBA}} [Ru^{VI}(F_{20}\text{-}TPP)(O)_2] \xrightarrow[DCM]{HCl} [Ru^{IV}(F_{20}\text{-}TPP)Cl_2]$$

To a solution of $[Ru^{II}(F_{20}\text{-}TPP)(CO)]$ (66 mg, 0.06 mmol) in 20 mL of dichloromethane was added 202 mg of *m*-CPBA (77%, 0.9 mmol). The reaction mixture was stirred for 20 min until UV spectrum indicated complete consumption of $[Ru^{II}(F_{20}\text{-}TPP)(CO)]$. Then the reaction mixture was flushed through a short alumina column and concentrated by rotary

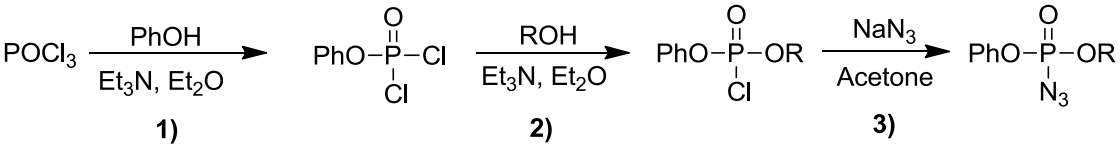
evaporator to give crude [$Ru^{VI}(F_{20}$-TPP)$(O)_2$] for the next step.

[$Ru^{VI}(F_{20}$-TPP)$(O)_2$] was dissolved in 100 mL of anhydrous dichloromethane. Anhydrous HCl was bubbled through the solution for 1 h. After 12 h, the solvent was removed. The obtained solid was washed with diethyl ether to give [$Ru^{IV}(F_{20}$-TPP)Cl_2] (21 mg) in total yield of 30% . ^{1}H NMR ($CDCl_3$, 400MHz): δ -51.1(br, 8H); ^{19}F NMR ($CDCl_3$, 376MHz): δ -129.7, -148.9, -158.9; UV-Vis (CH_2Cl_2) λ_{max}/nm (log ε): 406 (5.01), 507(3.91); LRMS(ESI) m/z Calcd. For $C_{44}H_8Cl_2F_{20}N_4Ru$ $[M]^+$ 1143.9, found 1144.0; $[M\text{-}Cl]^+$ 1108.9, found 1109.0; $[M\text{-}2Cl]^+$ 1073.9, found 1074.0.

III. Synthesis of Phosphoryl Azides

Bis(2,2,2-trichloroethyl) phosphorazidate was synthesized according to reported method. (W. Xiao, C.-Y. Zhou and C.-M. Che, *Chem. Commun.*, 2012, **48**, 5871-5873)

The general procedure for the synthesis of intramolecular substrates 4a, 4b, 4c and 4d



Step 1)

To a dry flask equipped with an argon inlet and an addition funnel was added phosphorus oxychloride (3.067 g, 20 mmol) and 60 mL of anhydrous diethyl ether under argon atmosphere. The solution was cooled down to -78^{o}C in an acetone-liquid nitrogen bath with stirring. A solution of phenol (1.882 g, 20 mmol) and triethylamine (2.226 g, 22 mmol) in 20 mL of diethyl ether was added dropwise within 1 hour. After the complete addition of phenol and triethylamine, the reaction mixture was slowly warmed up to room temperature and stirred for 12 hours. Subsequently, the reaction mixture was filtered to remove the white solid. The filtrate was concentrated by a rotary evaporator to give the light yellow liquid product in 95% yield. The product was directly used for the next step without further purification.

Step 2)

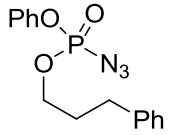
A dry flask equipped with an argon inlet and an addition funnel was charged with phenyl phosphorodichloridate (422 mg, 2 mmol) and 5 mL of anhydrous diethyl ether under argon

atmosphere. The solution was cooled down to -78°C in an acetone-liquid nitrogen bath with stirring. A solution of alcohol (2 mmol) and triethylamine (223 mg, 2.2 mmol) in 10 mL of diethyl ether was added dropwise within 0.5 hour. After the complete addition of alcohol and triethylamine, the reaction mixture was slowly warmed up to room temperature and stirred for 12 ~ 24 hours. When ^{31}P NMR indicated the complete consumption of phenyl phosphorodichloridate, the reaction mixture was filtered. The filtrate was concentrated by a rotary evaporator to give the corresponding product in high yield. The product was directly used for the next step without further purification.

Step 3)

The phosphorochloridate (3 mmol) was dissolved in 20 mL of acetone. Sodium azide (3.3 mmol) was added to the solution. The reaction mixture was stirred in darkness for several hours until the phosphorochloridate was completely consumed. The reaction mixture was filtered to remove the precipitated white solid. The filtrate was concentrated and purified by column chromatography (hexane : DCM = 3 : 1) to give the product.

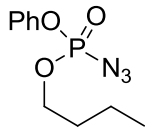
Phenyl (3-phenylpropyl) phosphorazidate 4a



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.40-7.15 (m, 10H), 4.24 (dd, 2H, *J* = 13.8, 6.4Hz), 2.73 (t, 2H, *J* = 7.6Hz), 2.09-2.02 (m, 2H); ^{13}C NMR ($CDCl_3$, 125MHz): δ 150.0(d, *J* = 7.5Hz), 140.5, 130.1, 128.7, 128.6, 126.3, 126.0, 120.3 (d, *J* = 4.7Hz), 68.8 (d, *J* = 6.8Hz), 31.7 (d, *J* = 6.9Hz), 31.5; ^{31}P NMR ($CDCl_3$,162MHz): δ -5.2.

HRMS(ESI) m/z Calcd for $C_{15}H_{17}N_3O_3P$ $[M+H]^+$ 318.1008, found 317.9998.

Butyl phenyl phosphorazidate 4b

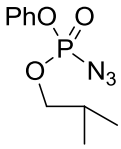


^{1}H NMR ($CDCl_3$, 500MHz): δ 7.38 (t, 2H, *J* = 7.8Hz), 7.26-7.22 (m, 3H), 4.27-4.22 (m, 2H), 1.76-1.69 (m, 2H), 1.44-1.40 (m, 2H), 0.94 (t, 3H, *J* = 7.4Hz); ^{13}C NMR ($CDCl_3$,125MHz): δ

150.0 (d, *J* = 7.6Hz), 130.0, 125.8, 120.2 (d, *J* = 4.8Hz), 69.4 (d, *J* = 6.9Hz), 32.1 (d, *J* = 6.8Hz), 18.6, 13.5; ^{31}P NMR ($CDCl_3$, 162MHz): δ -5.2.

HRMS(ESI) m/z Calcd for $C_{10}H_{15}N_3O_3P$ $[M+H]^+$ 256.0851, found 256.0869.

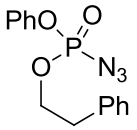
Isobutyl phenyl phosphorazidate 4c



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.37 (t, 2H, *J* = 7.7Hz), 7.26-7.21 (m, 3H), 4.00 (t, 2H, *J* = 6.8Hz), 2.07-1.97 (m, 1H), 0.97 (s, 3H), 0.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz): δ 150.1 (d, *J* = 7.4Hz), 130.0, 125.9, 120.3 (d , *J* = 4.7Hz), 75.4 (d, *J* = 7.2Hz), 29.1 (d , *J* = 7.1Hz), 18.6; ^{31}P NMR ($CDCl_3$, 162MHz): δ -5.3.

HRMS(ESI) m/z Calcd for $C_{10}H_{15}N_3O_3P$ $[M+H]^+$ 256.0851, found 256.0848.

Phenethyl phenyl phosphorazidate 4d



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.36-7.14 (m, 10H), 4.42 (dd, 2H, *J* = 14.7, 7.2Hz), 3.04 (t, *J* = 6.9Hz); ^{13}C NMR ($CDCl_3$, 100MHz): δ 149.9(d, *J* = 7.8Hz), 136.4, 130.0, 129.1, 128.7, 127.0, 125.9, 120.2 (d, *J* = 4.7Hz), 69.7 (d, *J* = 6.9Hz), 36.6 (d, *J* = 6.9Hz); ^{31}P NMR ($CDCl_3$, 162MHz): δ -5.4.

HRMS(ESI) m/z Calcd for $C_{14}H_{15}N_3O_3P$ $[M+H]^+$ 304.0851, found 304.0855.

IV. General Procedure for the Reactions in Table 1

To an oven-dried Schlenk flask with a rubber seal was added the corresponding nitrene source (0.1 mmol, 1 equiv.), Ru^{IV}(TDCPP)Cl_2 (2 mol %) and 50 mg of 4Å molecular sieve. The flask was evacuated and backfilled with argon three times. Then freshly distilled cyclohexane (2 mmol, 20 equiv.) and 1.5 mL of DCE were added via syringe. The mixture

was stirred at reflux for 12 h. Subsequently, the reaction mixture was allowed to cool down to room temperature and directly purified on a silica gel column with DCM/acetone (50:1, v/v) as eluent to give the pure product.

V. General Procedure for the Reactions in Table 2

An oven-dried Schlenk flask with a rubber seal was charged with bis(2,2,2-trichloroethyl) phosphorazidate (0.1 mmol, 1 equiv.), catalyst (2 mol %) and 50 mg of 4Å molecular sieve. The flask was evacuated and backfilled with argon three times. Then freshly distilled cyclohexane (2 mmol, 20 equiv.) and 1.5 mL of DCE were added via syringe. The mixture was stirred at reflux for 12h. Subsequently, the reaction mixture was allowed to cool down to room temperature and directly purified on a silica gel column with DCM/acetone (50:1, v/v) as eluent to give the pure product.

VI. General Procedure for the $[Ru^{IV}(F_{20}\text{-TPP})Cl_2]$-catalysed Intermolecular C-H Amination of Hydrocarbons with Phosphoryl Azide (Table 3)

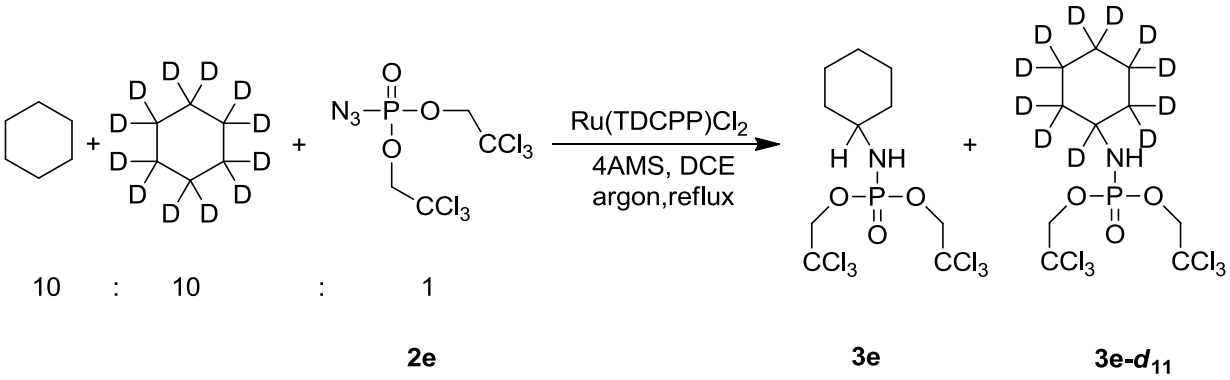
To an oven-dried Schlenk flask with a rubber seal was added bis(2,2,2-trichloroethyl) phosphorazidate (77 mg, 0.2 mmol), $[Ru^{IV}(F_{20}\text{-TPP})Cl_2]$ (4.2 mg, 2 mol %) and 100 mg of 4Å molecular sieve. The flask was evacuated and backfilled with argon three times. Then the substrate (4 mmol, 20 equiv.) and freshly distilled DCE (3 mL) were added via syringe. The mixture was stirred at reflux for 12h. Upon completion of the reaction, the reaction mixture was allowed to cool to room temperature and purified on a silica gel column with DCM/acetone (50:1, v/v) as eluent to give the pure product.

VII. General Procedure for the $[Ru^{IV}(F_{20}\text{-TPP})Cl_2]$-catalysed Intramolecular C-H Amination of Phosphorazidates (Scheme 1)

Phosphorazidate (0.2 mmol), $[Ru(F_{20}TPP)Cl_2]$ (0.2 mol %) and 100 mg of 4Å molecular

sieve were added into an oven-dried Schlenk flask which was subsequently evacuated and backfilled with argon three times. Then freshly distilled DCE (3 mL)was added via syringe into the flask. The reaction mixture was stirred at reflux for 12 h until the substrate was completely converted. Subsequently, the reaction mixture was filtered and concentrated by rotary evaporator to give corresponding product. Product **5a** and **5b** were purified on a short silica gel column with DCM as eluent.

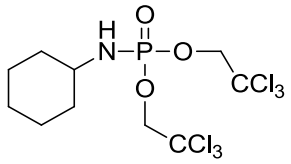
VIII. Procedure for the Study of Deuterium Kinetic Isotope Effects



To an oven-dried Schlenk flask was added 77 mg (1 equiv.) of **2e**, 4.2 mg (2 mol %) of [Ru^{IV}(TDCPP)Cl_2] and 100 mg of 4Å molecular sieve. The flask was sealed with a rubber septum, evacuated and backfilled with argon three times. Cyclohexane (2 mmol, 10 equiv.), cyclehexane-d_{12} (2 mmol, 10 equiv.) and 3 mL of freshly distilled DCE were added via syringe. The reaction mixture was stirred at reflux until azide **2e** was completely consumed. Then the reaction mixture was concentrated by rotary evaporator. The residue was purified by column chromatography (silica gel, hexane: EA = 3:1, v/v) to afford a mixture of **3e** and **3e-*d*$_{11}$** (N-D is liable to undergo H-D exchange). The value of k_H/k_D was determined according to the ^{1}H NMR spectrum of the product.

IX. Characterizations of Products

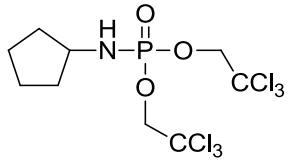
Bis(2,2,2-trichloroethyl) cyclohexylphosphoramidate 3e



^{1}H NMR ($CDCl_3$, 400MHz): δ 4.62-4.53 (m, 4H), 3.19-3.13 (m, 1H), 2.98 (t, 1H, *J* = 10.8Hz), 2.02-1.99 (m, 2H), 1.74-1.72 (m, 1H), 1.60-1.56 (m, 1H), 1.36-1.13 (m, 6H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 95.3, 95.2, 76.5, 76.4, 51.3, 35.6, 35.6, 25.3, 25.0; ^{31}P NMR ($CDCl_3$, 162MHz): δ 6.0.

HRMS(EI) m/z Calcd for $C_{10}H_{16}Cl_6NO_3P$ $[M]^+$ 440.8969, found 440.9071.

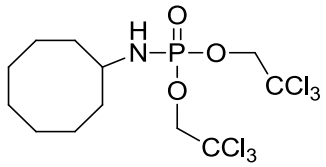
Bis(2,2,2-trichloroethyl) cyclopentylphosphoramidate 3f



^{1}H NMR ($CDCl_3$, 300MHz): δ 4.64-4.53 (m, 4H), 3.74-3.64 (m, 1H), 2.93 (t, 1H, *J* = 10.3Hz), 2.02-1.95 (m, 2H), 1.73-1.68 (m, 2H), 1.59-1.52 (m, 2H), 1.50-1.43 (m, 2H); ^{13}C NMR ($CDCl_3$, 75MHz): δ 95.3, 95.2, 76.5, 76.4, 53.9, 35.0, 34.9, 23.3; ^{31}P NMR ($CDCl_3$, 162MHz): δ 6.1.

HRMS(EI) m/z Calcd for $C_9H_{14}Cl_6NO_3P$ $[M]^+$ 426.8813, found 426.8814.

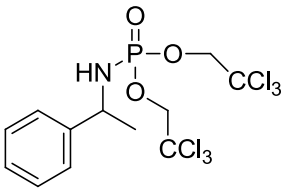
Bis(2,2,2-trichloroethyl) cyclooctylphosphoramidate 3g



^{1}H NMR ($CDCl_3$, 400MHz): δ 4.62-4.52 (m, 4H), 3.49-3.39 (m, 1H), 3.19 (t, 1H, *J* = 11.2Hz), 1.97-1.91 (m, 2H), 1.66-1.52 (m, 12H); ^{13}C NMR ($CDCl_3$, 75MHz): δ 95.3, 95.2, 76.4, 76.4, 52.3, 34.3, 34.3, 27.3, 25.4, 23.4; ^{31}P NMR ($CDCl_3$, 162MHz): δ 5.7.

HRMS(EI) m/z Calcd for $C_{12}H_{20}Cl_6NO_3P$ $[M]^+$ 468.9282, found 468.9281.

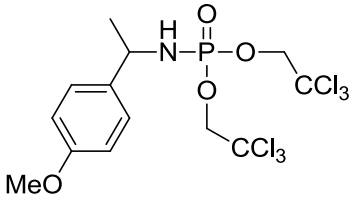
Bis(2,2,2-trichloroethyl) (1-phenylethyl)phosphoramidate 3h



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.35-7.34 (m,4H), 7.28-7.24 (m, 1H), 4.59-4.46 (m, 4H), 4.26-4.22 (dd, 1H, *J* = 11.0, 5.2Hz), 3.75 (t, 1H, *J* = 10.6Hz), 1.56 (d, 3H, *J* = 6.8Hz); ^{13}C NMR ($CDCl_3$, 100MHz): δ 144.2(d, *J* = 4.8Hz), 128.8, 127.6, 126.0, 95.2 (d, *J* = 12.0Hz), 95.0(d, *J* = 12.0Hz), 76.4 (d, *J* = 4.3Hz), 76.2 (d, *J* = 3.8Hz), 52.0, 24.9 (d, *J* = 6.6Hz); ^{31}P NMR ($CDCl_3$, 162MHz): δ 5.1.

HRMS(EI) m/z Calcd for $C_{12}H_{14}Cl_6NO_3P$ $[M]^+$ 462.8813, found 462.8809.

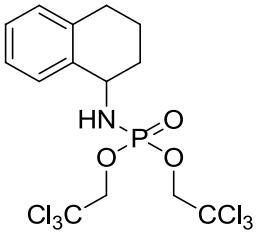
Bis(2,2,2-trichloroethyl) (1-(4-methoxyphenyl)ethyl)phosphoramidate 3i



^{1}H NMR ($CDCl_3$, 500MHz): δ 7.27 (d, 2H, *J* = 8.5Hz), 6.87 (d, 2H, *J* = 8.4Hz), 4.58-4.47 (m, 4H), 4.31 (dd, 1H, *J* = 11.0, 5.3Hz), 3.79 (s, 3H), 3.42 (t, 1H, *J* = 10.4Hz), 1.55 (d, 3H, *J* = 6.8Hz); ^{13}C NMR ($CDCl_3$, 125MHz): δ 159.1, 136.2 (d, *J* = 5.2Hz), 127.2, 114.2, 95.3, 95.2, 76.5 (d, *J* = 4.1Hz), 76.3 (d, *J* = 3.9Hz), 55.4, 51.4, 24.8 (d, *J* = 6.3Hz); ^{31}P NMR ($CDCl_3$, 162MHz): δ 5.5.

HRMS(ESI) m/z Calcd for $C_{13}H_{17}Cl_6NO_4P$ $[M+H]^+$ 493.8997, found 493.9019.

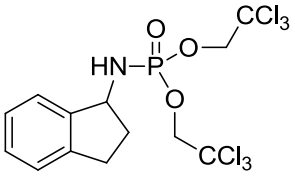
Bis(2,2,2-trichloroethyl) (1,2,3,4-tetrahydronaphthalen-1-yl)phosphoramidate 3j



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.54-7.52 (m, 1H), 7.25-7.17 (m, 2H), 7.09-7.07 (m, 1H), 4.69-4.61 (m, 4H), 4.54-4.52 (m, 1H), 3.29 (t, 1H, *J* = 11.2Hz), 2.81-2.74 (m, 2H), 2.15-2.12 (m, 1H), 1.92-1.82 (m, 3H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 137.2 (d, *J* = 2.7Hz), 137.1, 129.1, 128.7, 127.5, 126.3, 95.1, 95.0, 76.5, 76.4, 50.4, 32.4 (d, *J* = 1.4Hz), 29.0, 19.5; ^{31}P NMR ($CDCl_3$, 162MHz): δ 5.6.

HRMS(EI) m/z Calcd for $C_{14}H_{16}Cl_6NO_3P$ $[M]^+$ 488.8969, found 488.8960.

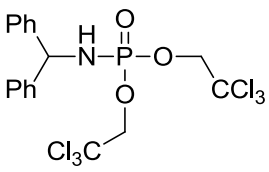
Bis(2,2,2-trichloroethyl) (2,3-dihydro-1H-inden-1-yl)phosphoramidate 3k



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.47-7.45 (m, 1H), 7.26-7.23 (m, 3H), 4.92-4.83 (m, 1H), 4.69-4.61 (m, 4H), 3.19 (t, 1H, *J* = 11.6Hz), 3.01-2.94 (m, 1H), 2.87-2.79 (m, 1H), 2.70-2.63 (m, 1H), 1.94-1.84 (m, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 143.5 (d, *J* = 7.9Hz), 142.9, 128.3, 127.0, 125.0, 124.1, 95.2, 95.1, 76.6, 76.6, 57.4, 36.5 (d, *J* = 3.3Hz), 30.0; ^{31}P NMR ($CDCl_3$, 162MHz): δ 5.9.

HRMS(EI) m/z Calcd for $C_{13}H_{14}Cl_6NO_3P$ $[M]^+$ 474.8813, found 474.8809.

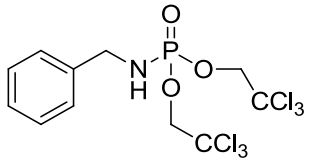
Bis(2,2,2-trichloroethyl) benzhydrylphosphoramidate 3l



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.35-7.25 (m, 10H), 5.61 (t, 1H, *J* = 9.8Hz), 4.53 (dd, 2H, *J* = 11.0, 6.5Hz), 4.32 (dd, 2H, *J* = 11.0, 5.3Hz), 4.15 (dd, 1H, *J* = 12.2, 9.9 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): δ 142.3, 142.2, 128.8, 127.8, 127.3, 95.1, 94.9, 76.3, 76.3, 59.6; ^{31}P NMR ($CDCl_3$, 162MHz): δ 4.6.

HRMS(ESI) m/z Calcd for $C_{17}H_{17}Cl_6NO_3P$ $[M+H]^+$ 525.9048, found 525.9195.

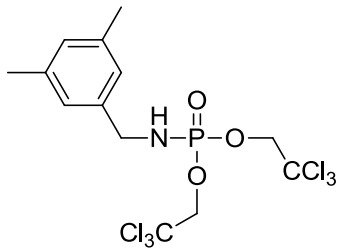
Bis(2,2,2-trichloroethyl) benzylphosphoramidate 3m



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.36-7.35 (m, 4H), 7.31-7.28 (m, 1H), 4.63-4.59 (m, 2H), 4.56-4.51 (m, 2H), 4.26 (d, 1H, *J* = 7.8Hz), 4.24 (d, 1H, *J* = 7Hz), 3.3 (m, 1H); ^{13}C NMR ($CDCl_3$, 75MHz): δ 138.7 (d, *J* = 6.2Hz), 128.9, 127.9, 127.6, 95.2, 95.0, 76.5, 76.5, 45.7; ^{31}P NMR ($CDCl_3$, 162MHz): δ 6.2.

HRMS(EI) m/z Calcd for $C_{11}H_{12}Cl_6NO_3P$ $[M]^+$ 448.8656, found 448.8654.

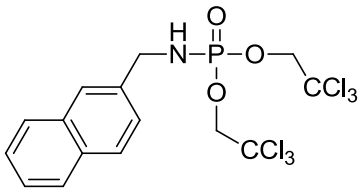
Bis(2,2,2-trichloroethyl) 3,5-dimethylbenzylphosphoramidate 3n



^{1}H NMR ($CDCl_3$, 400MHz): δ 6.97 (s, 2H), 6.92 (s, 1H), 4.62-4.58 (m, 2H), 4.55-4.51 (m, 2H), 4.17 (d, 1H, *J* = 6.8Hz), 4.14 (d, 1H, *J* = 6.8Hz), 3.40-3.33 (m, 1H), 2.30 (s, 6H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 138.6 (d, *J* = 5.9Hz), 138.5, 129.5, 125.4, 95.2, 95.1, 76.5, 76.4, 45.6, 21.3; ^{31}P NMR ($CDCl_3$, 162MHz): δ 6.4.

HRMS(ESI) m/z Calcd for $C_{13}H_{17}Cl_6NO_3P$ $[M+H]^+$ 477.9048, found 477.9086.

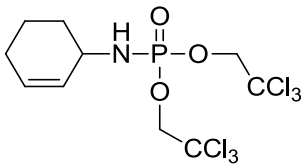
Bis(2,2,2-trichloroethyl) (naphthalen-2-ylmethyl)phosphoramidate 3o



^{1}H NMR ($CDCl_3$, 500MHz): δ 7.83-7.79 (m, 4H), 7.50-7.46 (m, 3H), 4.63-4.53 (m, 4H), 4.39 (dd, 2H, *J* = 11.2, 7.0Hz), 3.70-3.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 125MHz): δ 136.0 (d, *J* = 5.9Hz), 133.4, 132.9, 128.7, 127.9, 127.8, 126.5, 126.3, 126.2, 125.5, 95.2. 95.1. 76.6, 76.5. 45.8; ^{31}P NMR ($CDCl_3$, 162MHz): δ 6.0.

HRMS(ESI) m/z Calcd for $C_{15}H_{15}C_{l6}NO_3P$ $[M+H]^+$ 499.8891, found 499.8882.

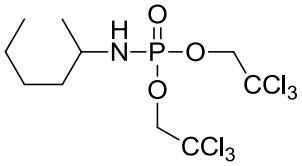
Bis(2,2,2-trichloroethyl) cyclohex-2-en-1-ylphosphoramidate 3p



^{1}H NMR ($CDCl_3$, 400MHz): δ 5.85-5.80 (m, 1H), 5.70-5.67 (m, 1H), 4.63-4.55 (m, 4H), 3.85 (br, 1H), 3.10 (t, 1H, *J* = 11.6Hz), 2.02-1.96 (m, 3H), 1.71-1.59 (m, 3H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 130.8, 129.1, 129.0, 95.3, 95.1, 76.5, 76.4, 47.6, 31.8 (d, *J* = 4.8Hz), 24.7, 19.7; ^{31}P NMR ($CDCl_3$, 162MHz): δ 5.9

HRMS(EI) m/z Calcd for $C_{10}H_{14}Cl_6NO_3P$ $[M]^+$ 438.8813, found 438.8801.

Bis(2,2,2-trichloroethyl) hexan-2-ylphosphoramidate 3q

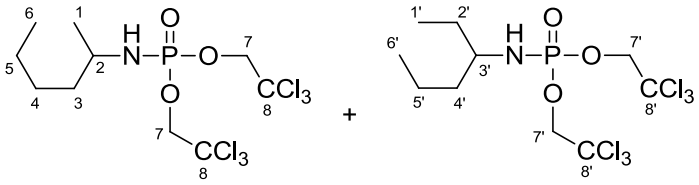


^{1}H NMR ($CDCl_3$, 500MHz): δ 4.63-4.53 (m, 4H), 3.40-3.30 (m, 1H), 2.92 (t, 1H, *J* = 11.0Hz), 1.54-1.41 (m, 2H), 1.41-1.28 (m, 4H), 1.23 (d, 3H, *J* = 6.5Hz), 0.90 (t, 3H, *J* = 6.9Hz); ^{13}C

NMR ($CDCl_3$, 125MHz): δ 95.3, 95.2, 76.5 (d, *J* = 4.1Hz), 76.4 (d, *J* = 4.3Hz), 48.7, 38.7 (d, *J* = 6.7Hz), 28.2, 23.3 (d, *J* = 3.9Hz), 22.6, 14.2; ^{31}P NMR ($CDCl_3$, 162MHz): δ 6.1.

HRMS(ESI) m/z Calcd for $C_{10}H_{19}C_{l6}NO_3P$ $[M+H]^+$ 443.9204, found 443.9131.

Bis(2,2,2-trichloroethyl) hexan-2-ylphosphoramidate 3q + Bis(2,2,2-trichloroethyl) hexan-3-ylphosphoramidate 3s

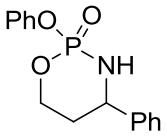


3q **3s**

^1H NMR ($CDCl_3$, 500MHz): δ 4.65-4.53 (m, C7–H + C7'–H), 3.40-3.32 (m, C2–H), 3.25-3.15 (m, C3'–H), 2.77-2.65 (m, NH, **3q + 3s)**, 1.60-1.56 (m, C2'–H), 1.53-1.41 (m, C3–H + C4'–H), 1.40-1.27 (m, C4–H + C5–H + C5'–H), 1.23 (d, *J* = 6.5Hz, C1-H), 0.97-0.88 (m, C6–H + C1'–H + C6'–H); ^{13}C NMR ($CDCl_3$, 125MHz): δ 95.3, 95.2, 76.5 (d, *J* = 4.1Hz), 76.4 (d, *J* = 4.4Hz), 54.0, 48.8, 38.7 (d, *J* = 6.7Hz), 38.5 (d, *J* = 5.4Hz), 29.3 (d, *J* = 4.9Hz), 28.3, 23.4 (d, *J* = 4.0Hz), 22.7, 19.0, 14.2, 10.0; ^{31}P NMR ($CDCl_3$, 162MHz): δ 6.4, 6.1.

HRMS(ESI) m/z Calcd for $C_{10}H_{19}Cl_6NO_3P$ $[M+H]^+$ 443.9204, found 443.9193.

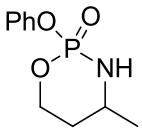
2-Phenoxy-4-phenyl-1,3,2-oxazaphosphinane 2-oxide 5a



^1H NMR ($CDCl_3$, 400MHz): δ 7.31-7.16 (m, 10H), 4.69 (m, 1H), 4.49-4.42 (m, 2H), 3.96 (m, 1H), 2.19(m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 151.3 (d, *J* = 7.2Hz), 142.8 (d, *J* = 3.9Hz), 129.7, 128.8, 127.9, 126.1, 124.6, 120.4 (d, *J* = 5.1Hz), 67.6 (d, *J* = 6.6Hz), 56.6, 33.3(d, *J* = 10.5Hz); ^{31}P NMR ($CDCl_3$,162MHz): δ -1.7.

HRMS(ESI) m/z Calcd for $C_{15}H_{17}NO_3P$ $[M+H]^+$ 290.0946, found 290.0949.

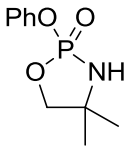
4-Methyl-2-phenoxy-1,3,2-oxazaphosphinane 2-oxide 5b



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.34-7.30 (t, 2H), 7.24 (t, 2H, *J* = 8.0Hz), 7.14 (t, 1H, *J* = 7.2Hz), 4.52-4.41 (m, 1H), 4.41-4.32 (m, 1H), 3.73-3.63 (m, 1H), 3.44 (br, 1H), 2.06-2.03 (m, 1H), 1.74-1.66 (m, 1H), 1.24 (d, 3H, *J* = 6.5Hz); ^{13}C NMR ($CDCl_3$, 100MHz): δ 151.3 (d, *J* = 7.4Hz), 129.7, 124.6, 120.4 (d, *J* = 4.9Hz), 67.1 (d, *J* = 6.9Hz), 48.1 (d, *J* = 2.3Hz), 31.8 (d, *J* = 9.3Hz), 23.3 (d, *J* = 2.0Hz); ^{31}P NMR ($CDCl_3$, 162MHz): δ -1.26.

HRMS(ESI) m/z Calcd for $C_{10}H_{15}NO_3P$ $[M+H]^+$ 228.0790, found 228.0812.

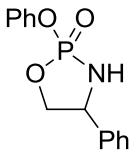
4,4-dimethyl-2-phenoxy-1,3,2-oxazaphospholidine 2-oxide 5c



^{1}H NMR ($CDCl_3$, 500MHz): δ 7.35-7.31 (t, 2H, *J* = 7.3Hz), 7.21-7.15 (m, 3H), 4.01 (dd, 1H, *J* = 14.5, 8.6Hz), 3.90 (d, 1H, *J* = 15.7Hz), 3.72 (t, 1H, *J* = 8.6Hz), 1.39 (s, 3H), 1.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz): δ 151.0 (d, *J* = 8.1Hz), 129.6, 125.1, 121.2 (d, *J* = 4.3Hz), 77.9 (d, *J* = 1.9Hz), 56.7 (d, *J* = 9.7Hz), 28.8 (d, *J* = 3.6Hz), 28.0 (d, *J* = 5.7Hz); ^{31}P NMR ($CDCl_3$, 162MHz): δ 19.6.

HRMS(ESI) m/z Calcd for $C_{10}H_{15}NO_3P$ $[M+H]^+$ 228.0790, found 228.0812.

2-phenoxy-4-phenyl-1,3,2-oxazaphospholidine 2-oxide 5d



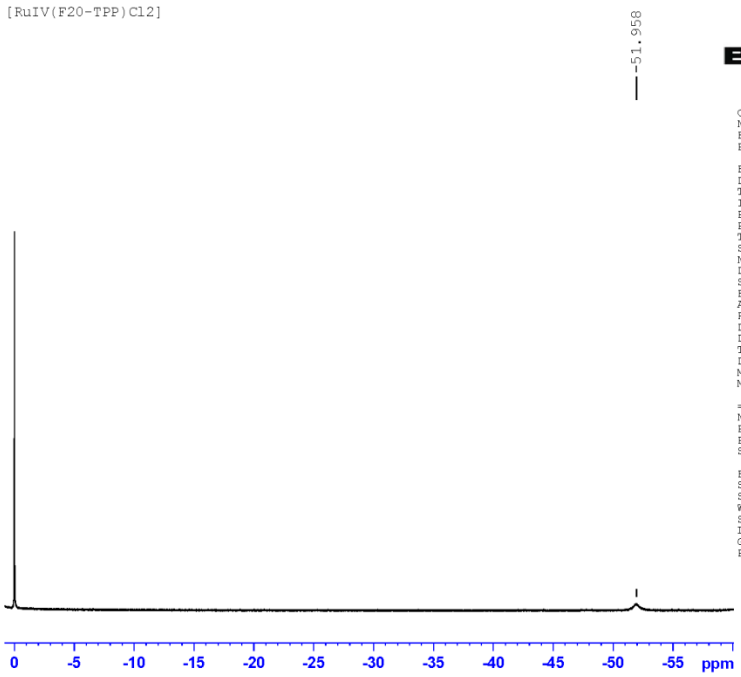
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.38-7.11 (m, 10H), 4.89 (t, 1H, *J* = 8.1Hz), 4.55-4.47 (m, 1H), 4.16 (d, *J* = 14.3Hz), 3.80 (td, 1H, *J* = 9.1, 2.1Hz); ^{13}C NMR ($CDCl_3$, 125MHz): δ 151.1 (d, *J*

= 8.3), 139.0 (d, *J* = 9.6Hz), 129.8, 128.9, 128.6, 126.4, 125.3, 121.2 (d, *J* = 4.2Hz), 73.0, 57.8 (d, *J* =11.0Hz); ^{31}P NMR ($CDCl_3$, 162MHz): δ 19.8.

HRMS(ESI) m/z Calcd for $C_{14}H_{15}NO_3P$ $[M+H]^+$ 276.0790, found 276.0774.

NMR Spectra

$[Ru^{IV}(F_{20}\text{-TPP})Cl_2]$

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EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
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Time                   12.13
INSTRUM                av400
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PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                      100
DS                        0
SWH               32051.281 Hz
FIDRES             0.978127 Hz
AQ                 0.5111808 sec
RG                     645.1
DW                    15.600 usec
DE                     6.00 usec
TE                    295.7 K
D1                1.00000000 sec
MCREST    0 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     32.00 usec
PL1                    -4.00 dB
SFO1             400.1219974 MHz

F2 - Processing parameters
SI                        32768
SF                400.1300078 MHz
WDW                          EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
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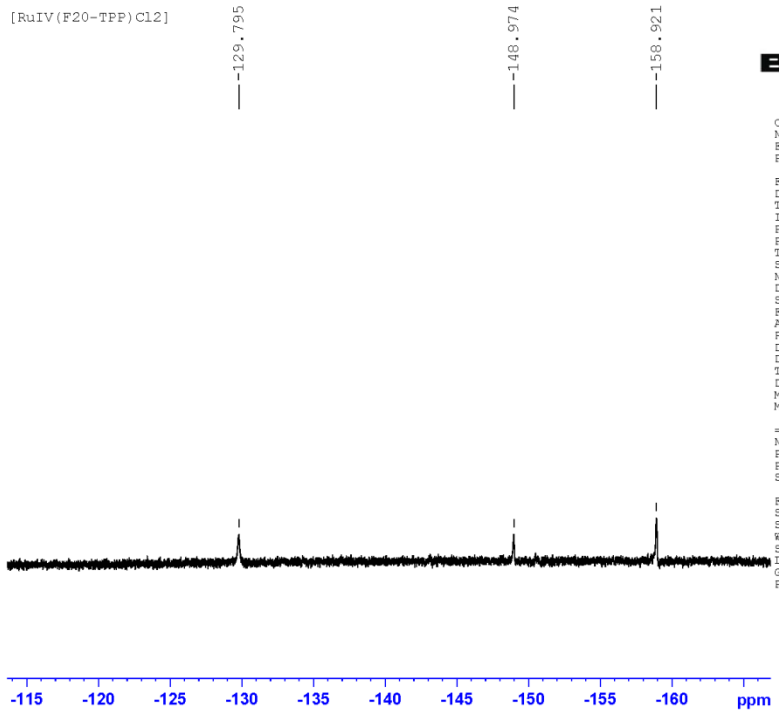


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Current Data Parameters
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EXPNO                     1
PROCNO                    2

F2 - Acquisition Parameters
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Time                   12.31
INSTRUM                av400
PROBHD   5 mm QNP 1H/13
PULPROG                zg
TD                    65536
SOLVENT               CDCl3
NS                      228
DS                        0
SWH               75187.969 Hz
FIDRES             1.147277 Hz
AQ                 0.4358144 sec
RG                    5160.6
DW                    6.650 usec
DE                    20.00 usec
TE                    298.0 K
D1                3.00000000 sec
MCREST    0 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     19F
P1                    14.30 usec
PL1                    -4.00 dB
SFO1             376.4533542 MHz

F2 - Processing parameters
SI                        65536
SF                376.4983550 MHz
WDW                          EM
SSB       0
LB                     2.00 Hz
GB        0
PC                     1.00
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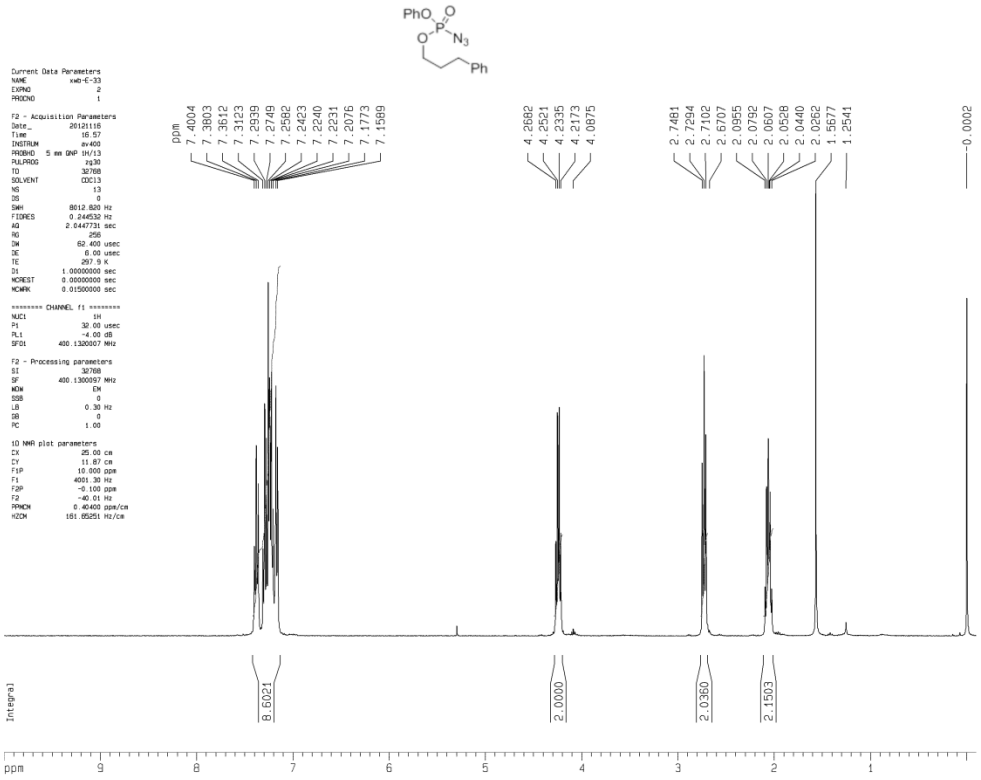
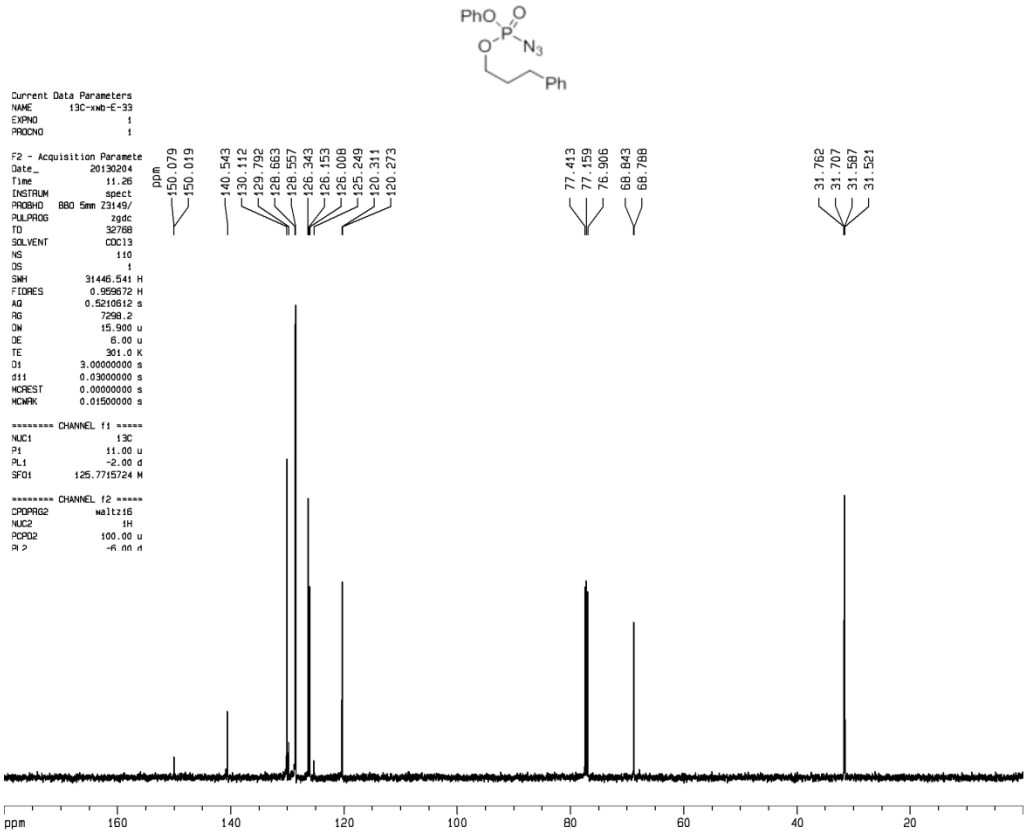
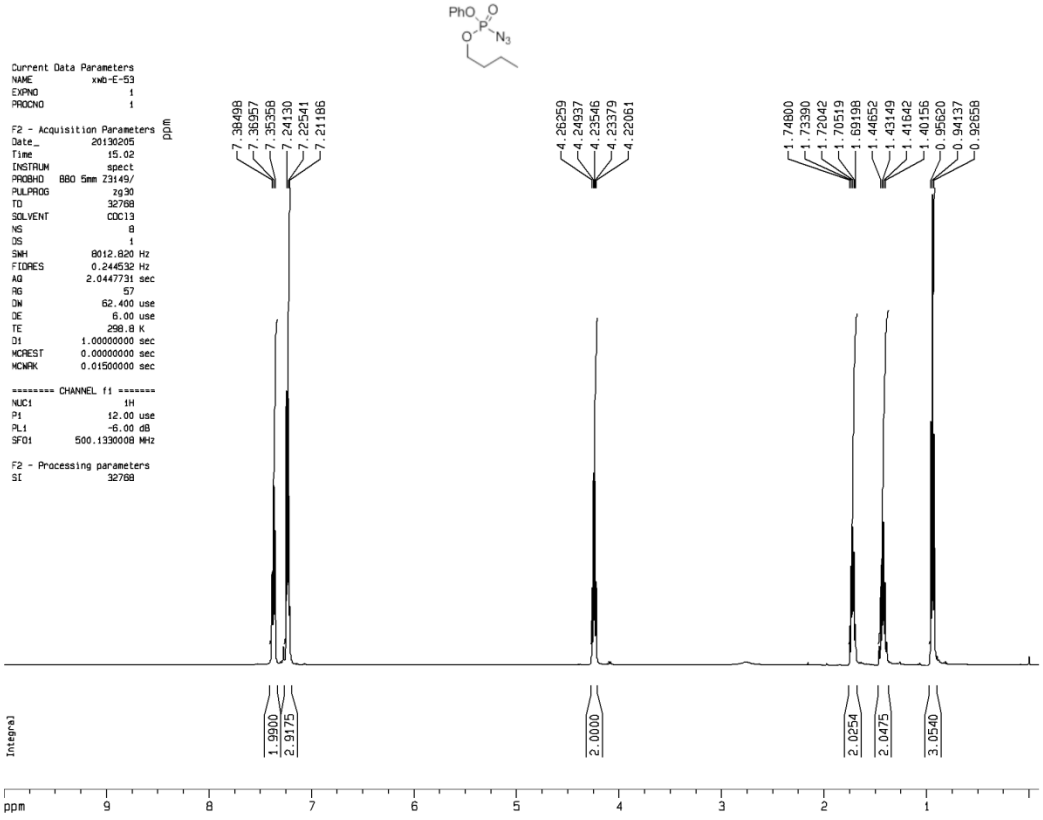
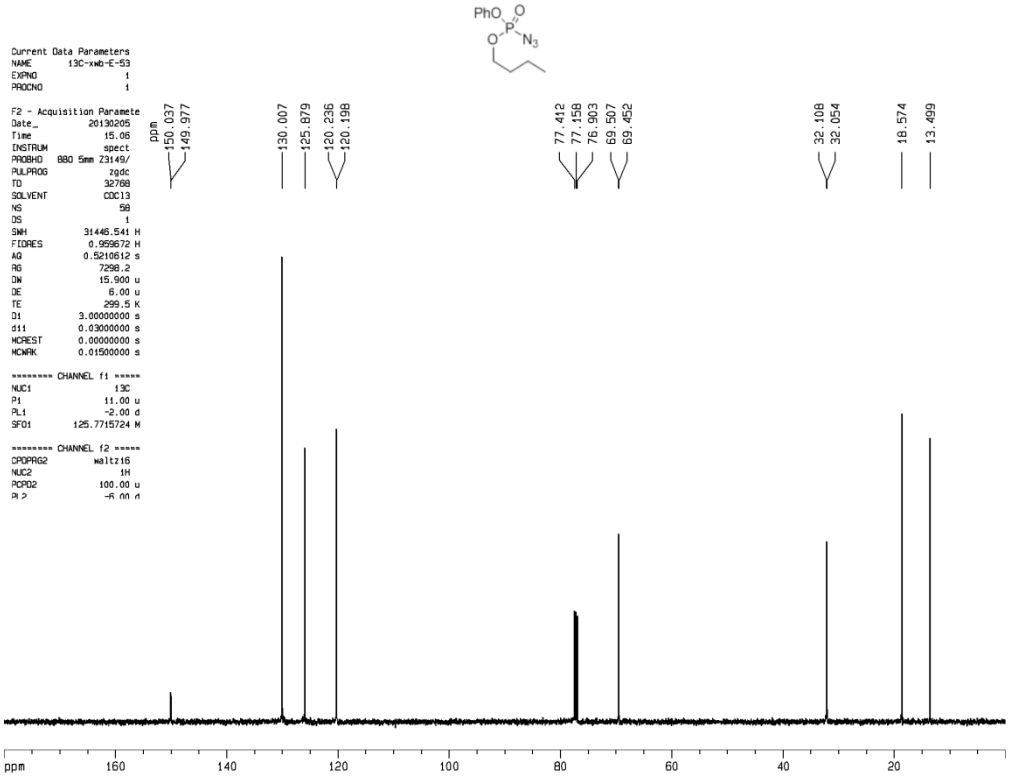
Phenyl (3-phenylpropyl) phosphorazidate 4a



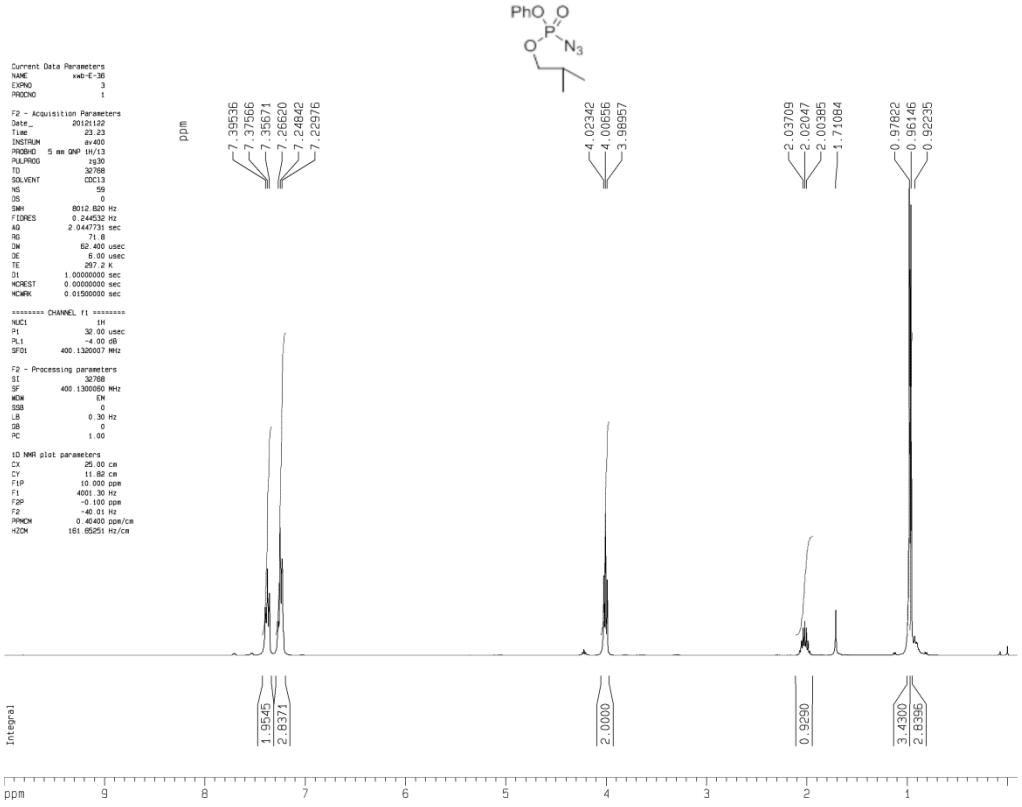


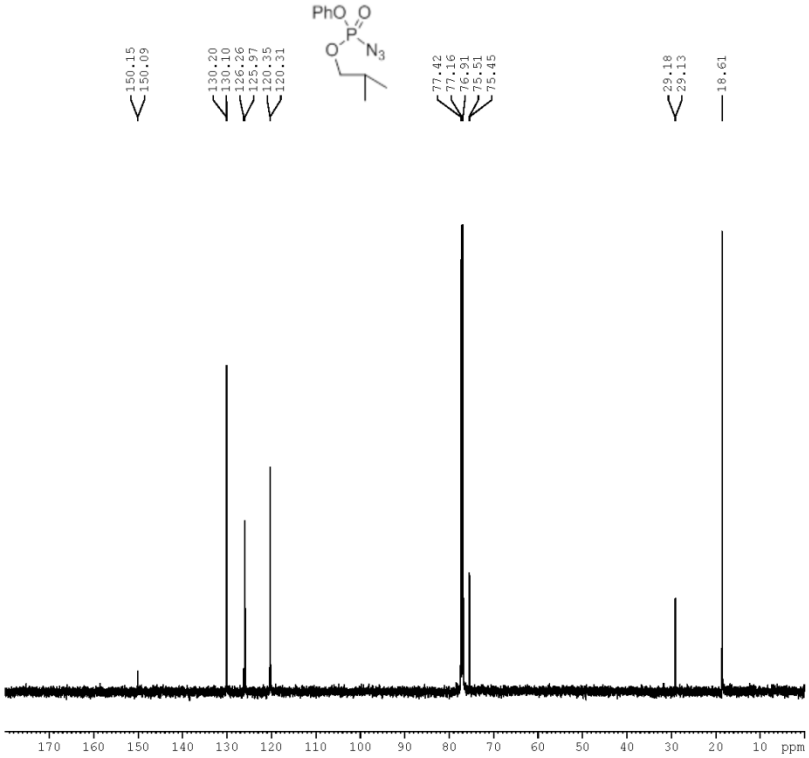
Butyl phenyl phosphorazidate 4b





Isobutyl phenyl phosphorazidate 4c





Current Data Parameters
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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time 23.56
INSTRUM spect
PROBHD BBO 5mm Z3149/
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 598
DS 1
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210112 sec
RG 7298.2
DW 15.900 usec
DE 6.00 usec
TE 300.4 K
D1 3.00000000 sec
d11 0.03000000 sec
TD0 1
SFO1 125.7715724 MHz
NUC1 13C
P1 11.00 usec
PLW1 -1.00000000 W
SFO2 500.1312000 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W

F2 - Processing parameters
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SF 125.7577716 MHz
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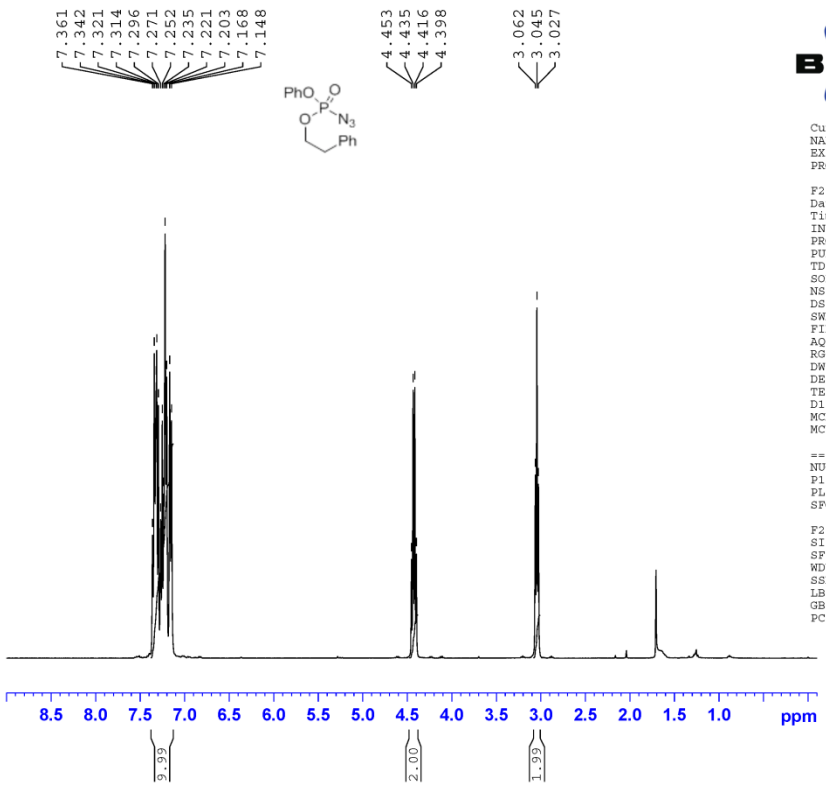
LB 1.20 Hz
GB 0
PC 1.00

Phenethyl phenyl phosphorazidate 4d



BRUKER

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Current Data Parameters
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EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
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Time                  16.18
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PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       29
DS                        0
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 2.0447233 sec
RG                     228.1
DW                    62.400 usec
DE                     6.00 usec
TE                    294.8 K
D1                 1.00000000 sec
MCREST     0 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                      9.80 usec
PL1                    -4.00 dB
SFO1            400.1324008 MHz

F2 - Processing parameters
SI                        32768
SF                400.1300113 MHz
WDW                          EM
SSB         0
LB                     0.30 Hz
GB          0
PC                     1.00
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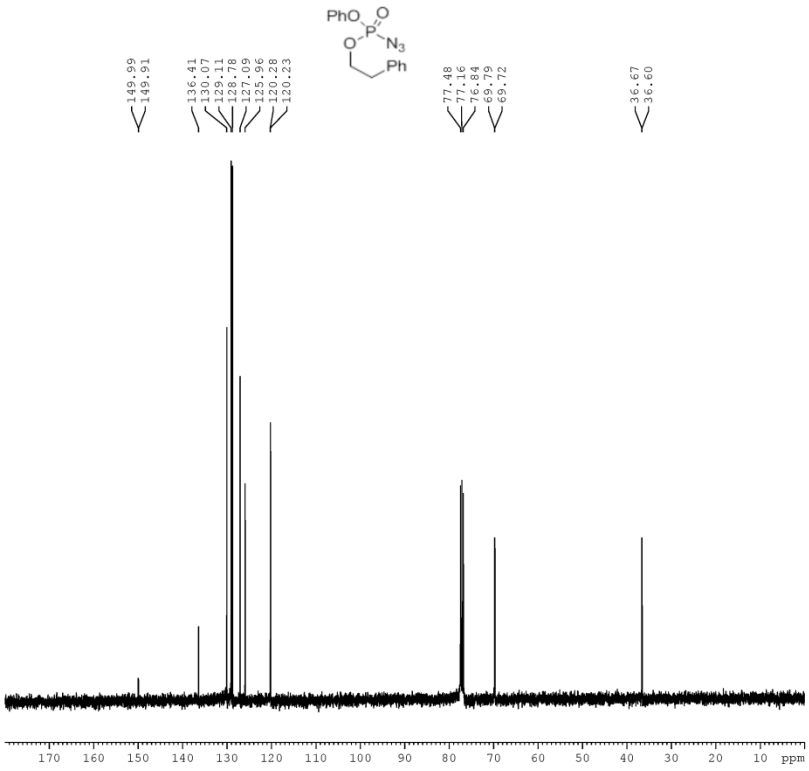

BRUKER

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Current Data Parameters
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EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
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Time                  16.21
INSTRUM                av400
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PULPROG                zgdc
TD                    32768
SOLVENT             Acetone
NS                      162
DS                        0
SWH               25125.629 Hz
FIDRES             0.766773 Hz
AQ                 0.6520832 sec
RG                     8192
DW                   19.900 usec
DE                     6.00 usec
TE                    294.8 K
D1                 2.50000000 sec
d11                0.03000000 sec
TD0                           1
SFO1            100.6238364 MHz
NUC1                        13C
P1                      9.10 usec
PLW1              -1.00000000 W
SFO2            400.1320007 MHz
NUC2                        1H
CPDPRG[2              waltz16
PCPD2                  80.00 usec
PLW2              -1.00000000 W
PLW12             -1.00000000 W

F2 - Processing parameters
SI                        32768
SF                100.6127603 MHz
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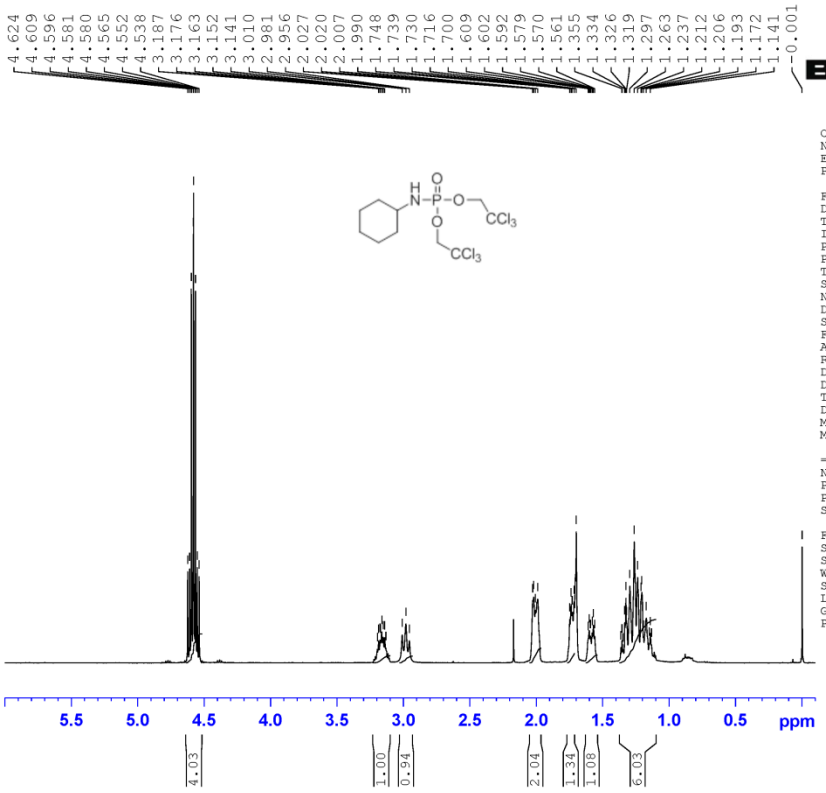
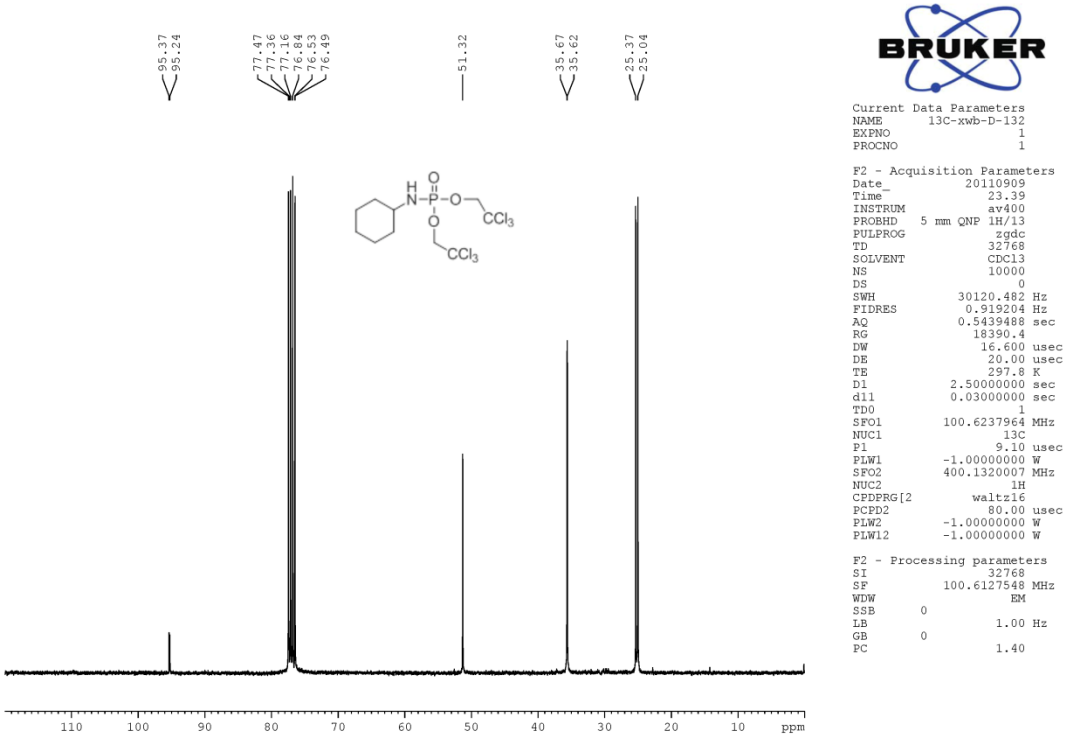
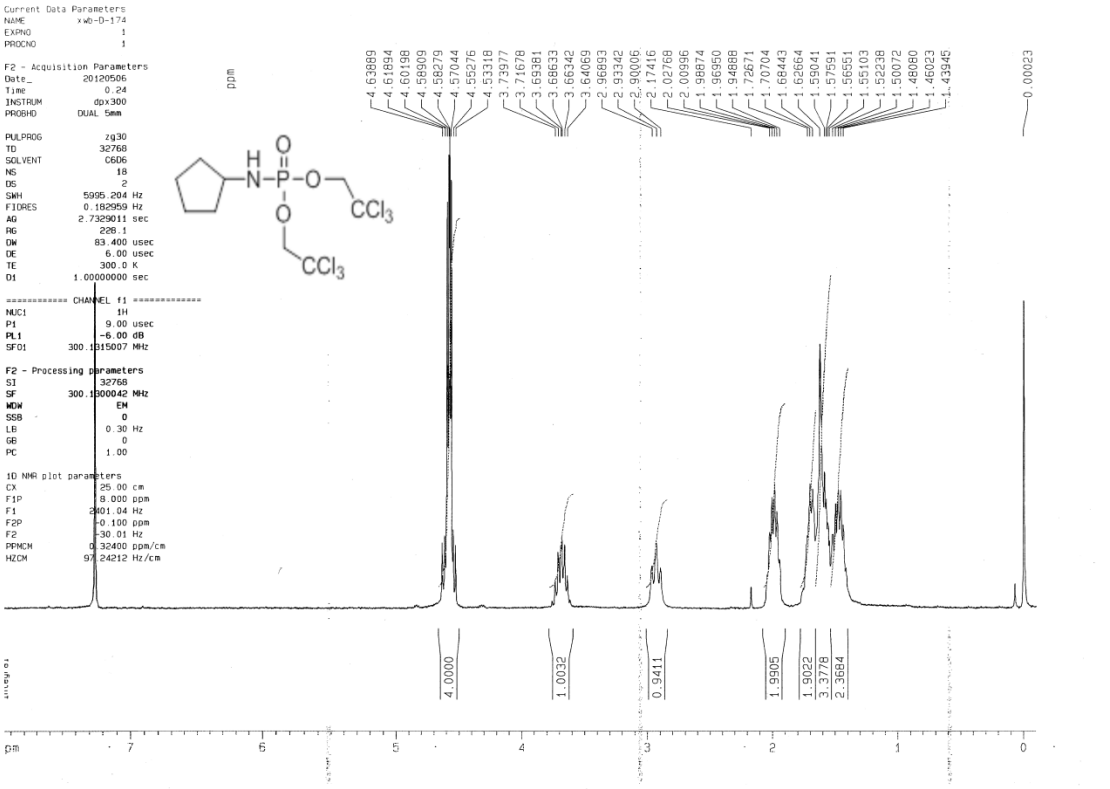
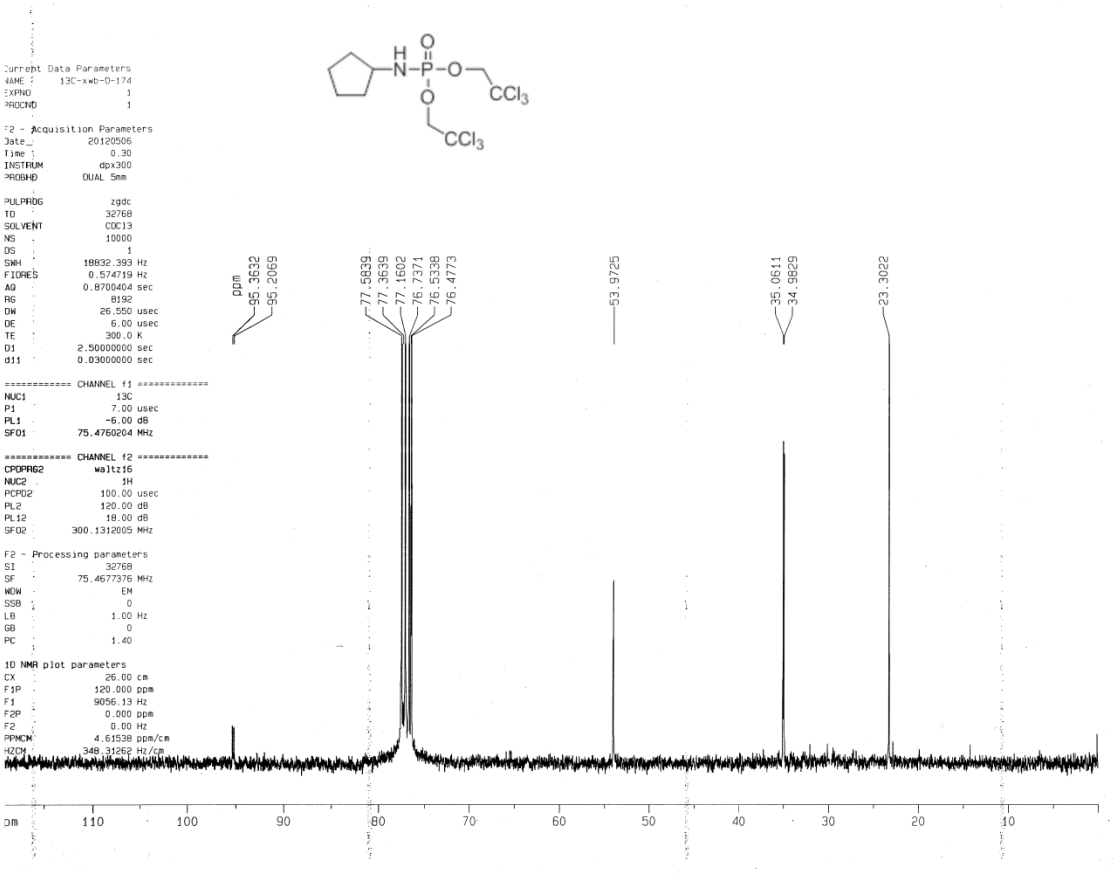
Bis(2,2,2-trichloroethyl) cyclohexylphosphoramidate 3e



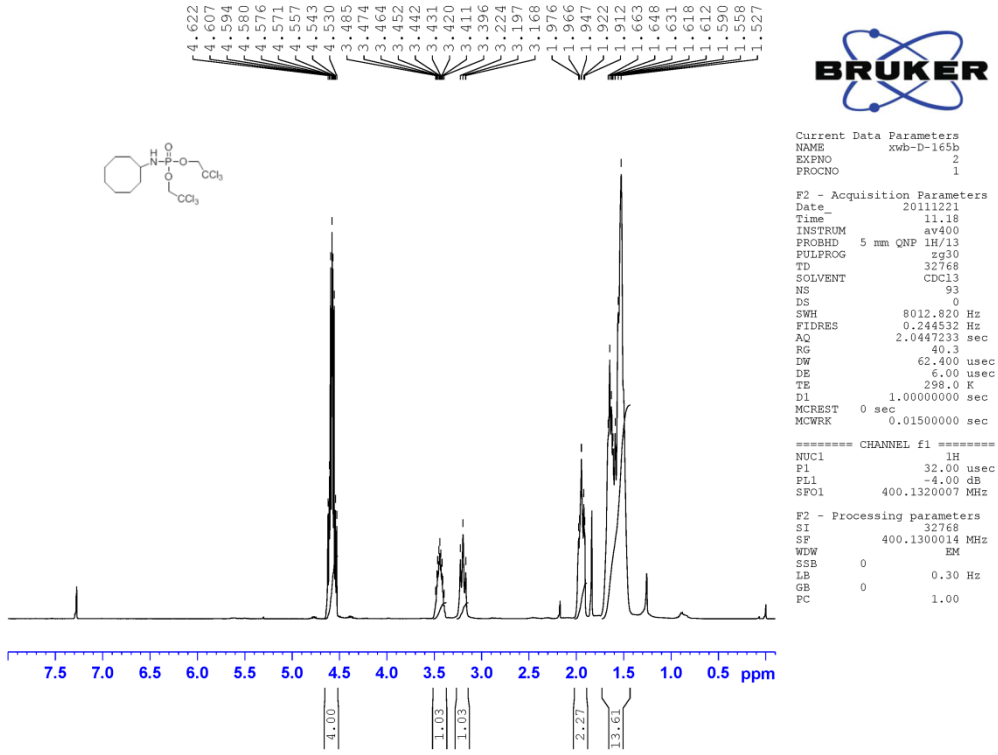


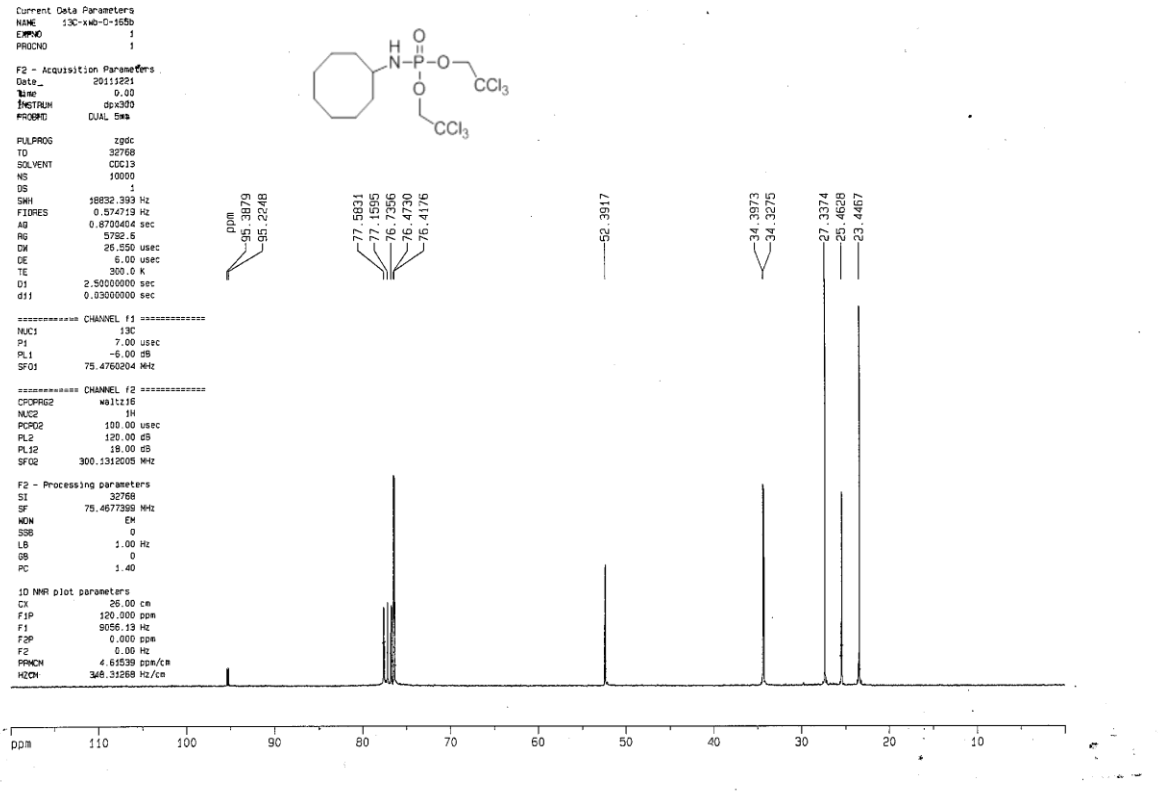
Bis(2,2,2-trichloroethyl) cyclopentylphosphoramidate 3f



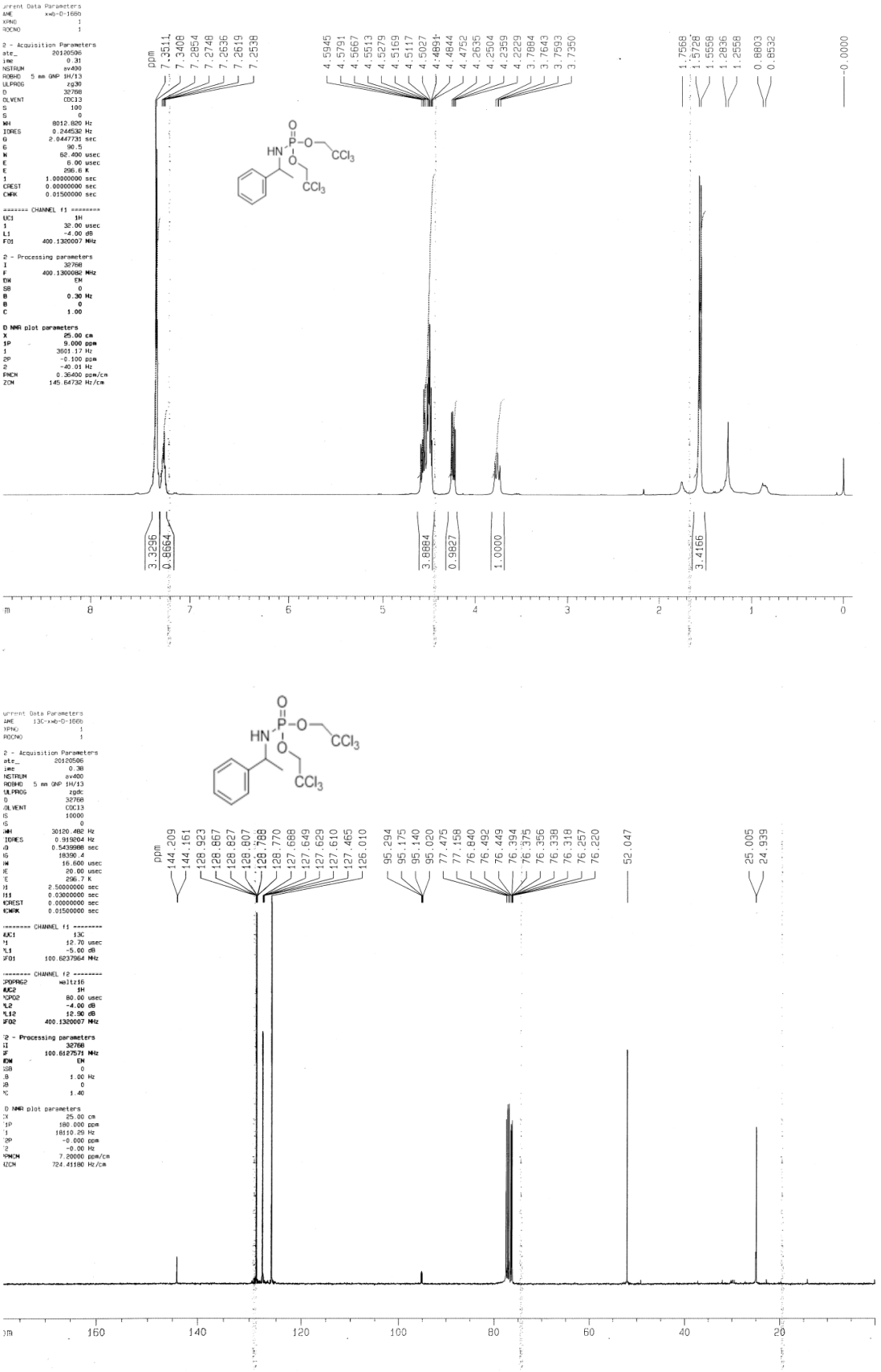


Bis(2,2,2-trichloroethyl) cyclooctylphosphoramidate 3g

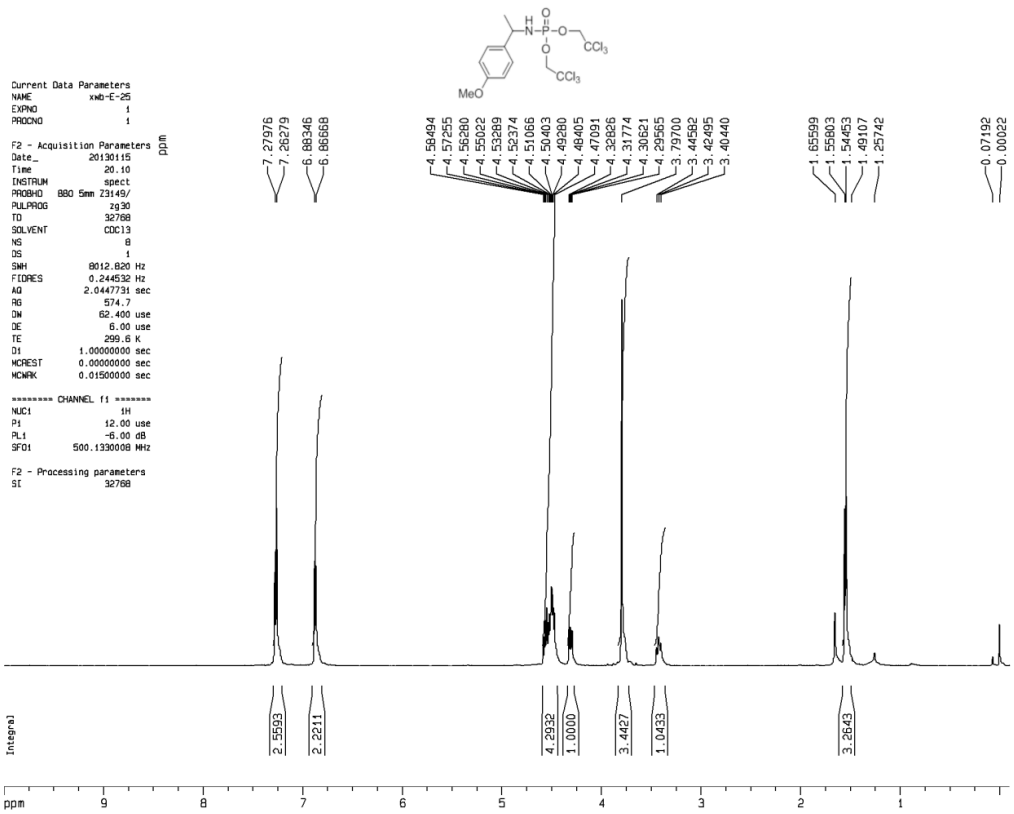


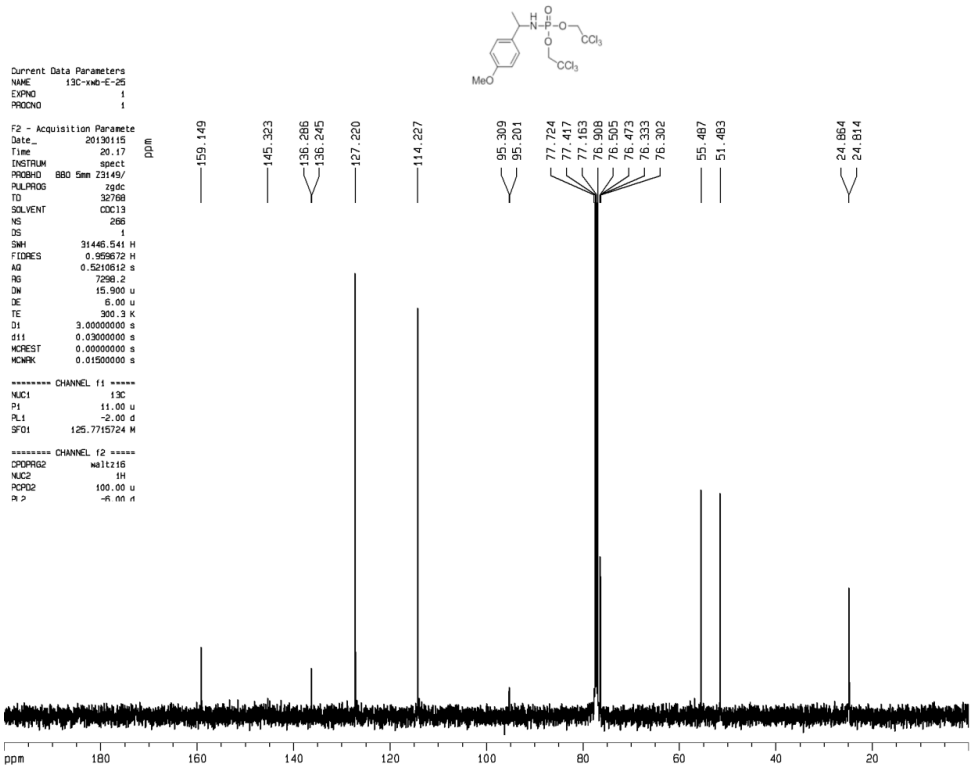


Bis(2,2,2-trichloroethyl) (1-phenylethyl)phosphoramidate 3h

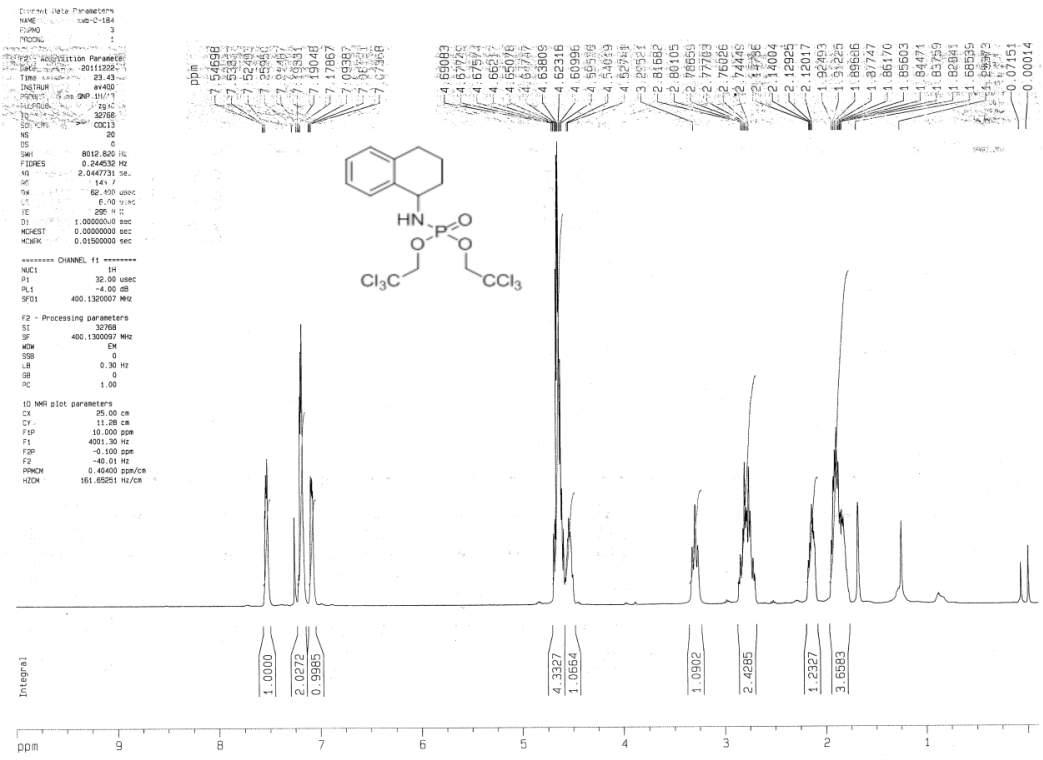


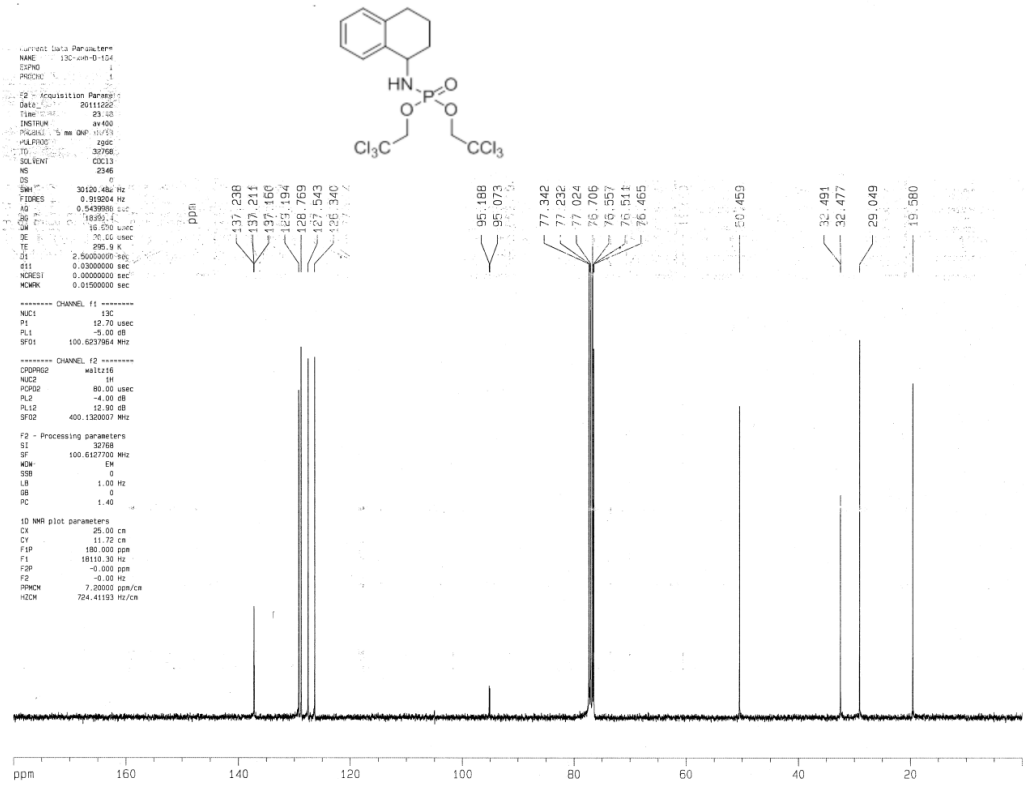
Bis(2,2,2-trichloroethyl) (1-(4-methoxyphenyl)ethyl)phosphoramidate 3i



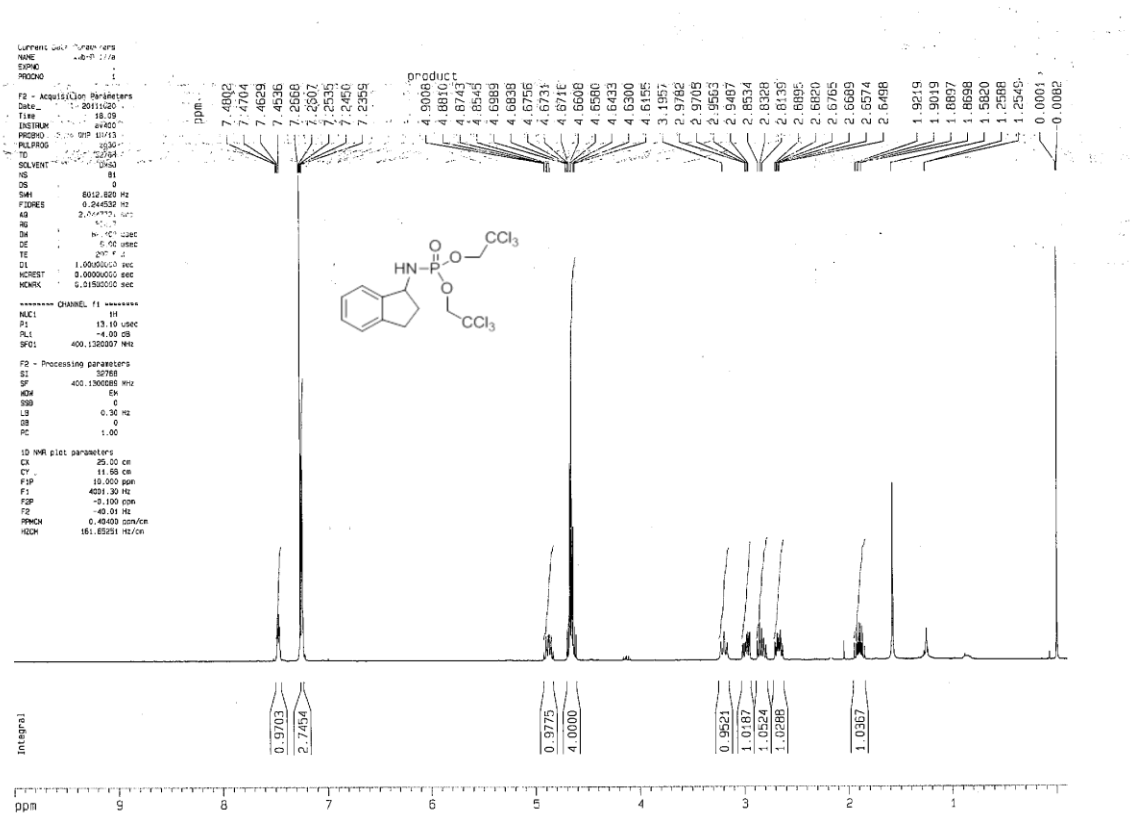


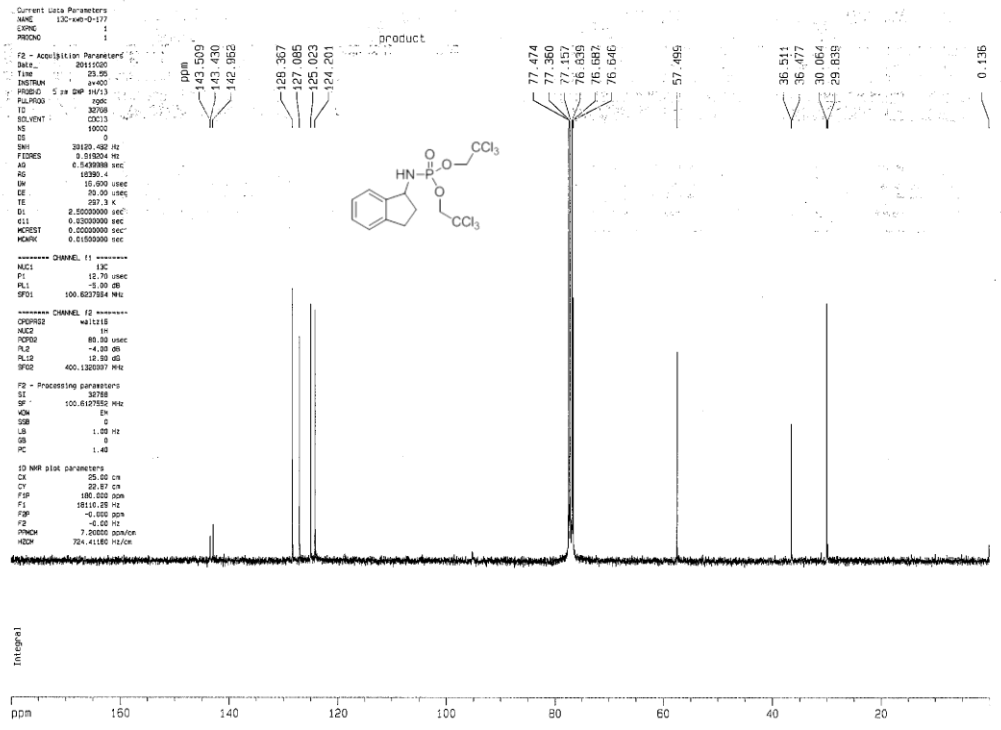
Bis(2,2,2-trichloroethyl) (1,2,3,4-tetrahydronaphthalen-1-yl)phosphoramidate 3j



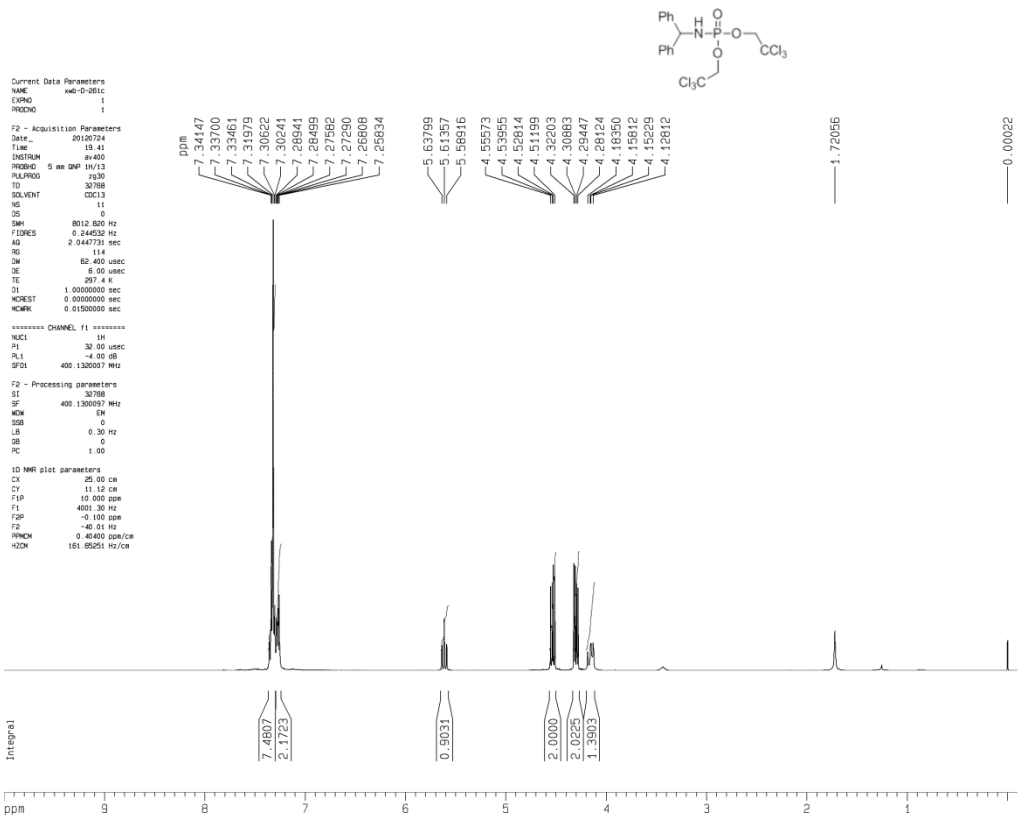


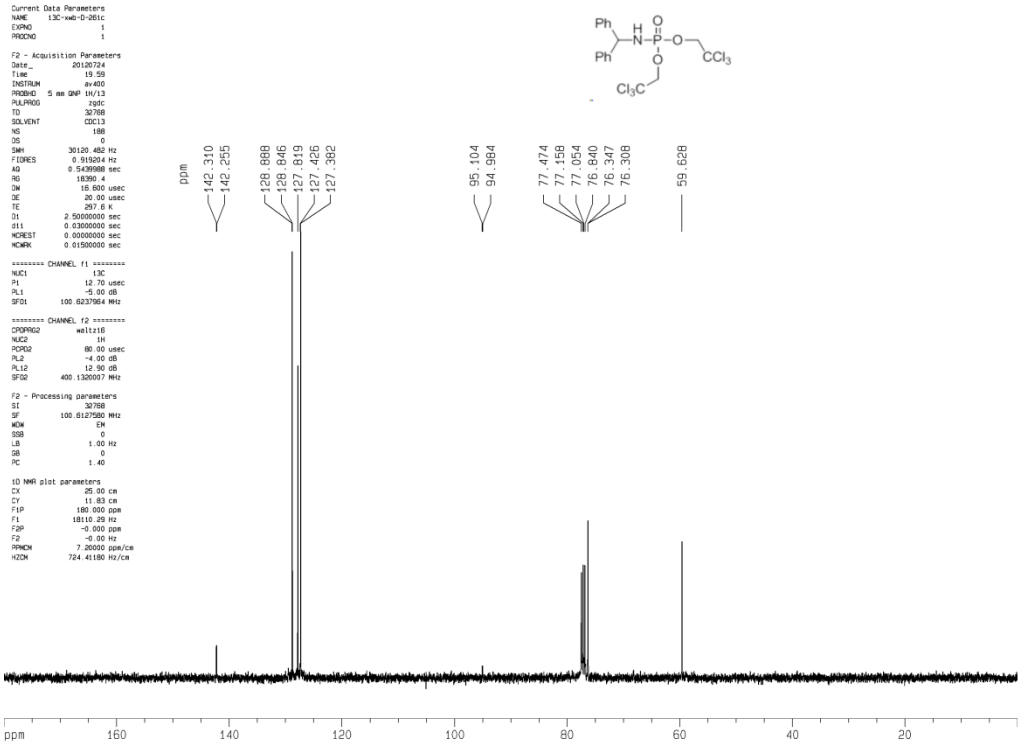
Bis(2,2,2-trichloroethyl) (2,3-dihydro-1H-inden-1-yl)phosphoramidate 3k



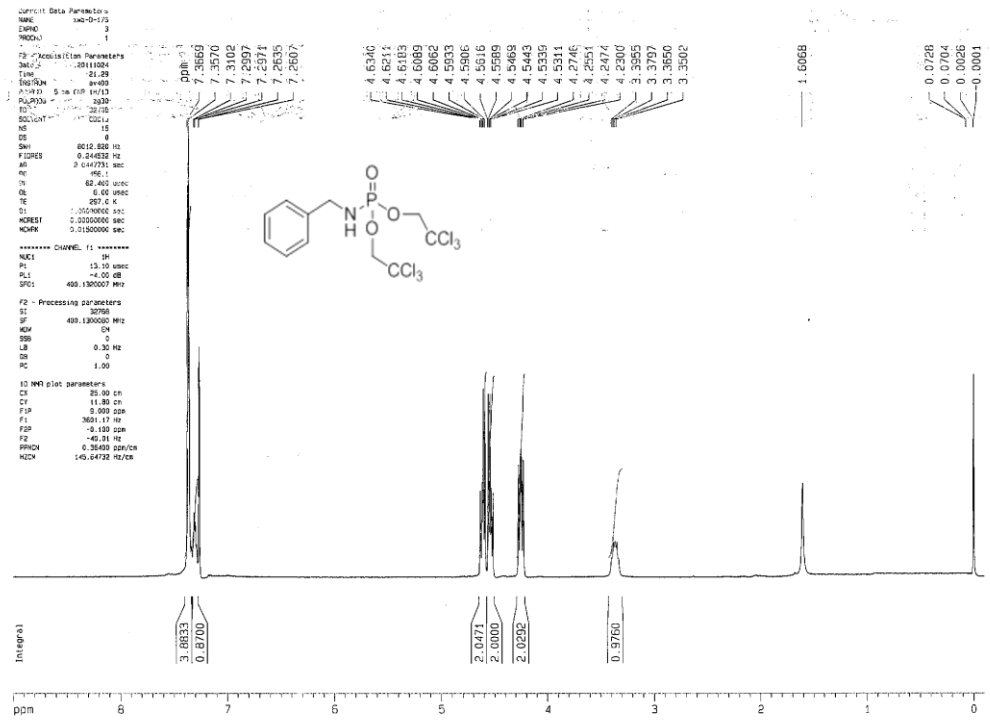


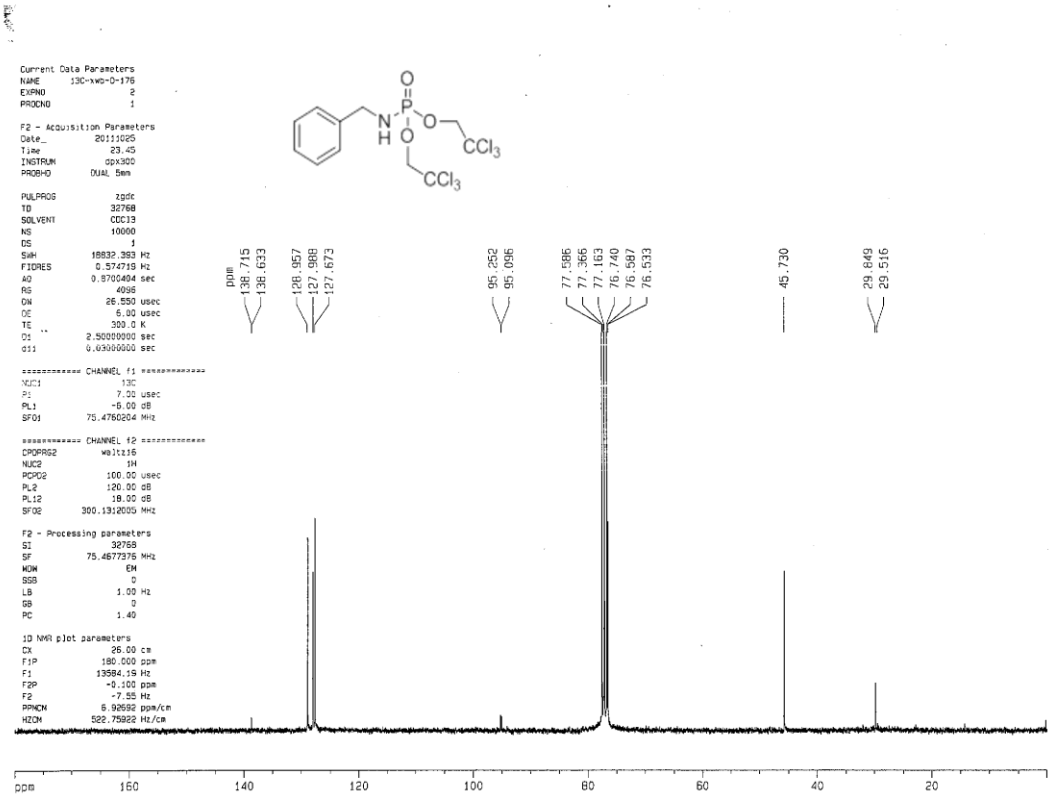
Bis(2,2,2-trichloroethyl) benzhydrylphosphoramidate 3l



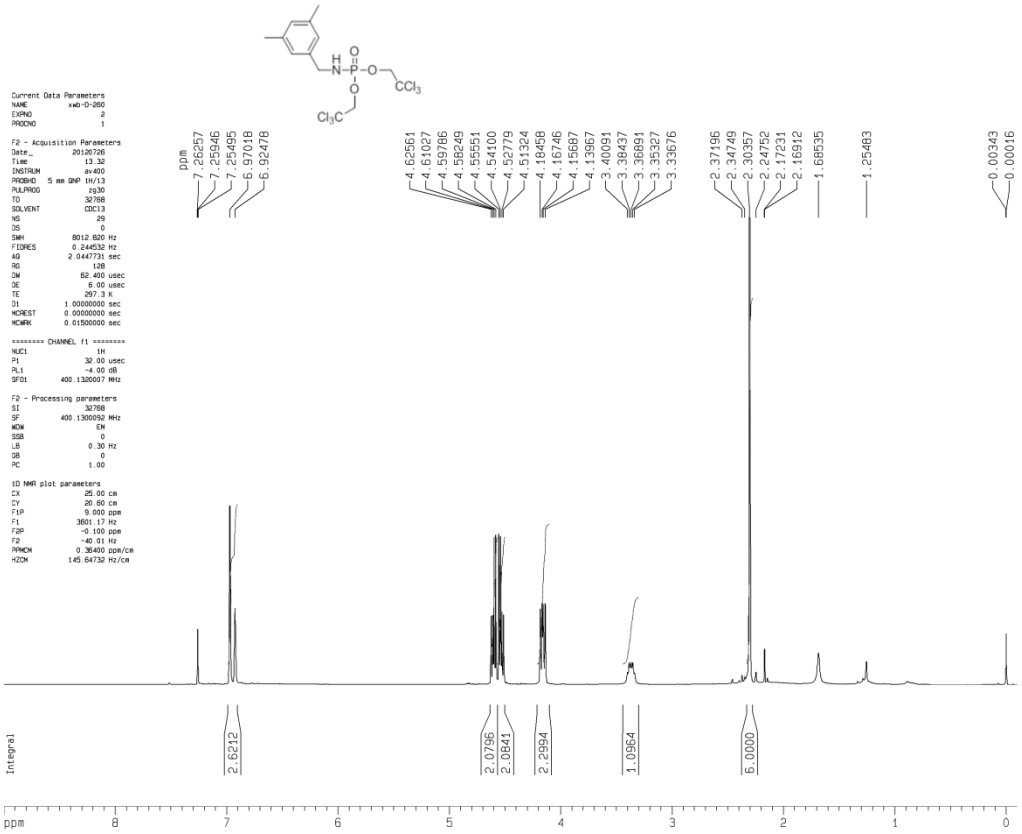


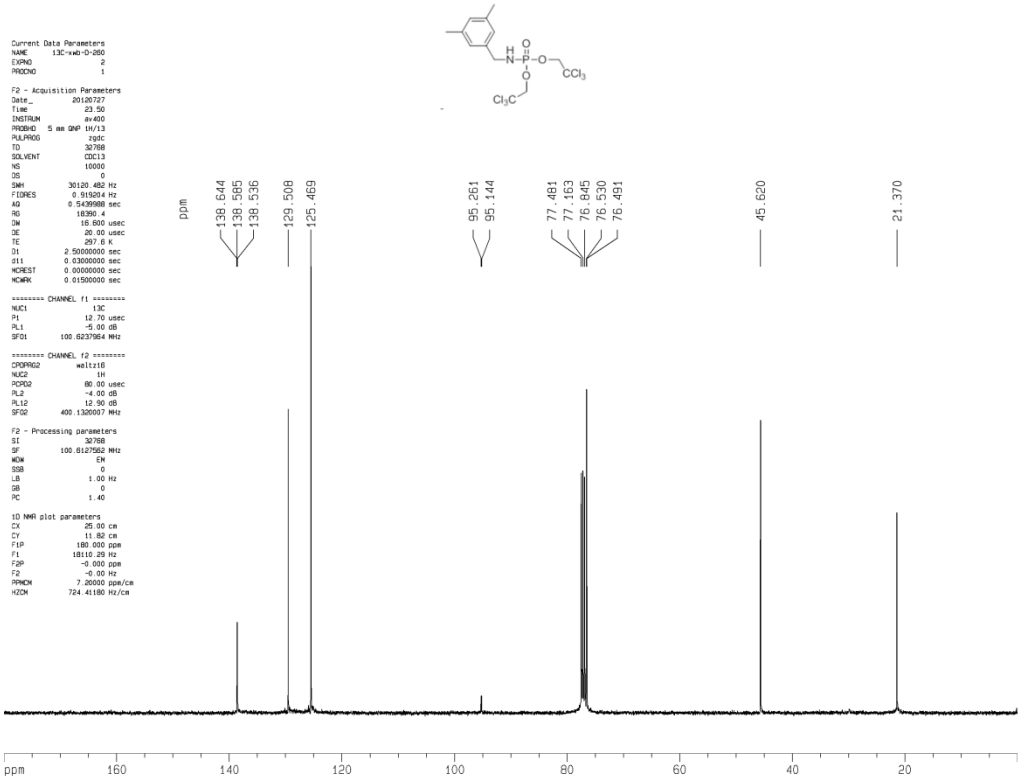
Bis(2,2,2-trichloroethyl) benzylphosphoramidate 3m



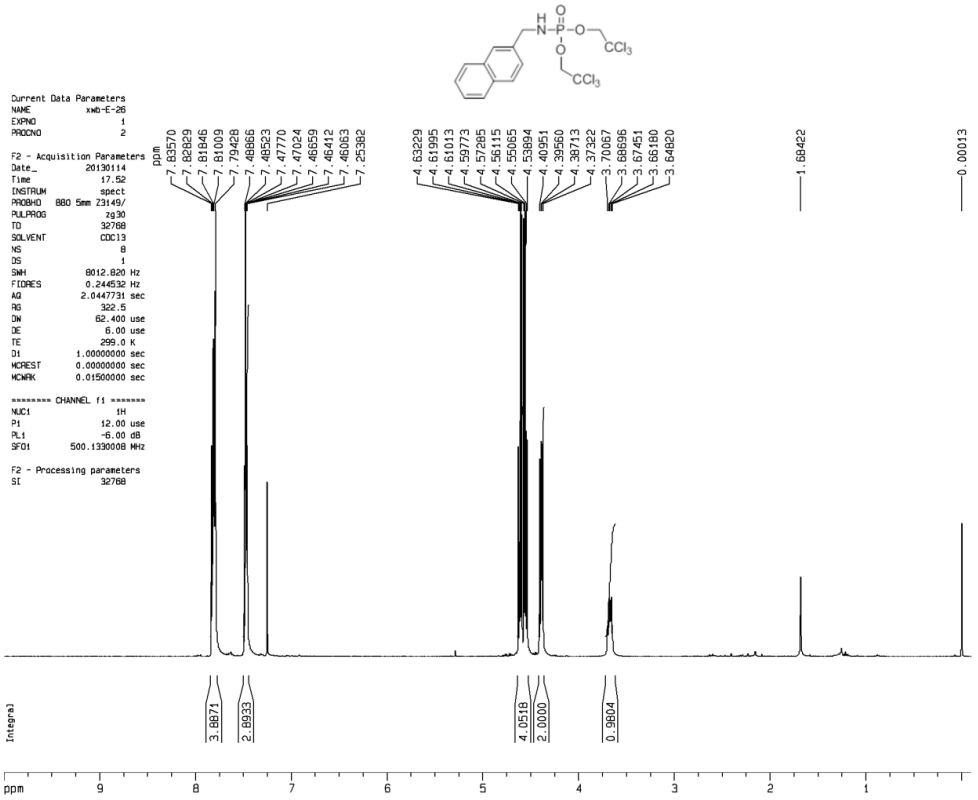


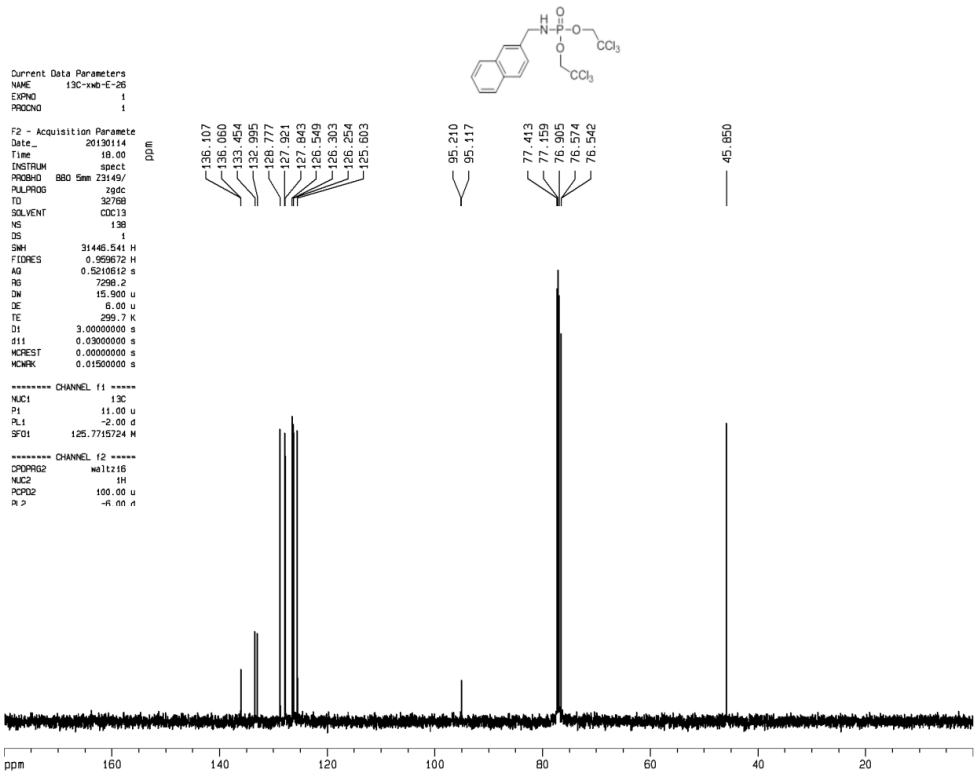
Bis(2,2,2-trichloroethyl) 3,5-dimethylbenzylphosphoramidate 3n



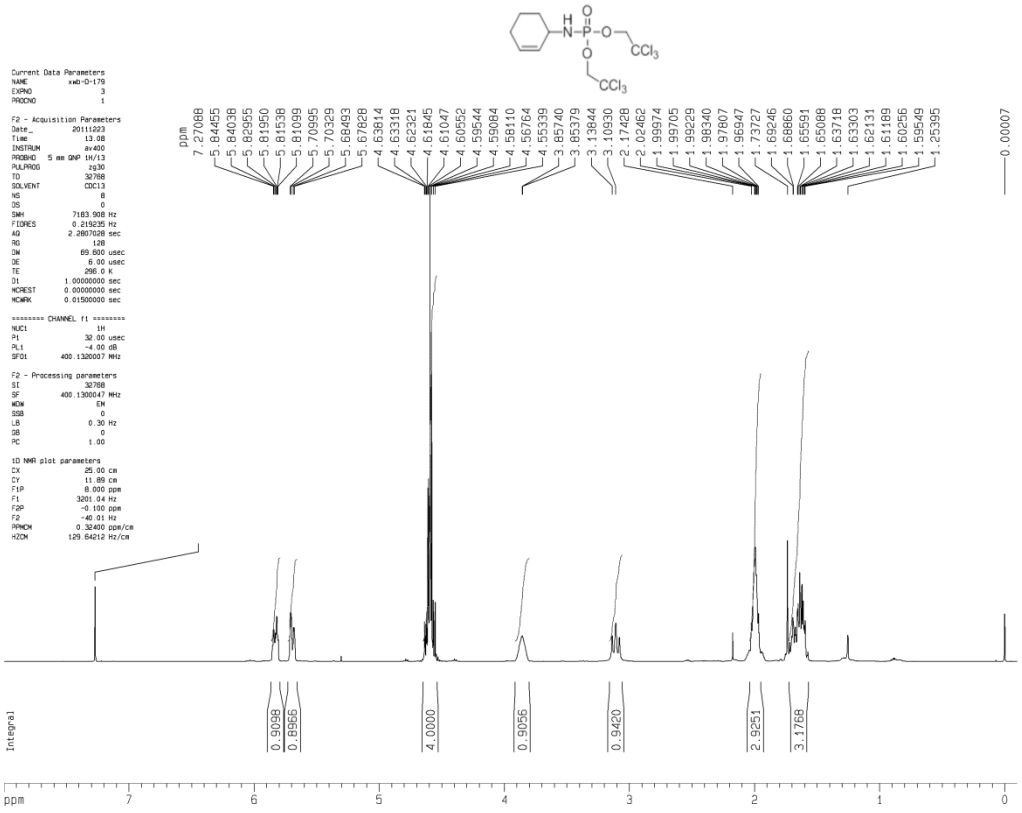


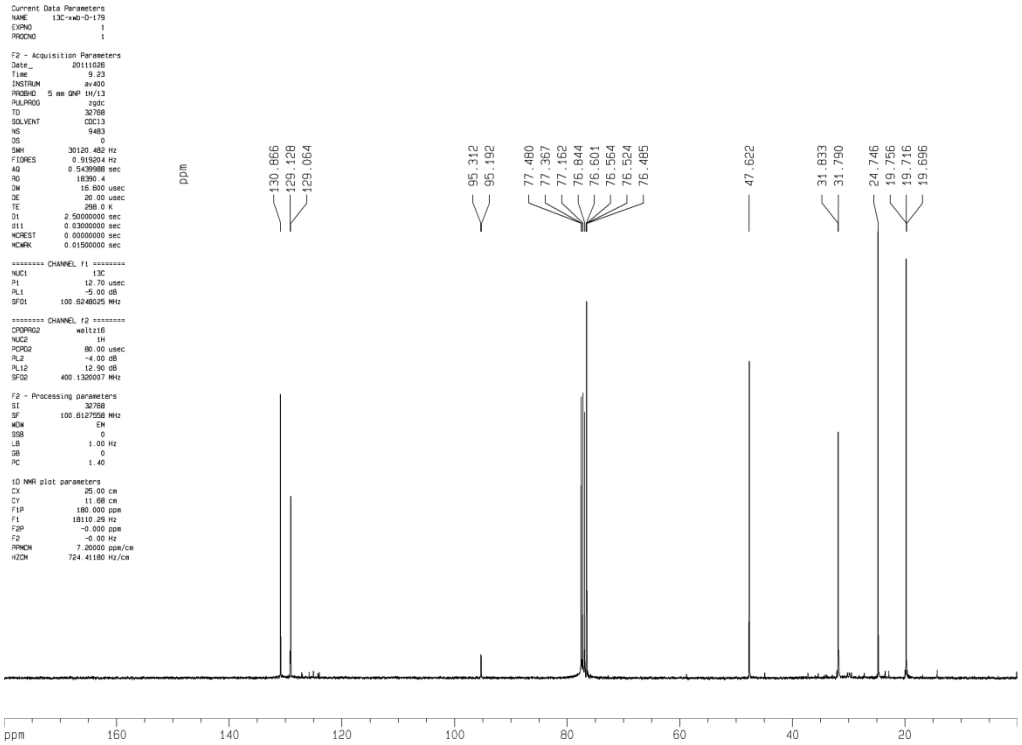
Bis(2,2,2-trichloroethyl) (naphthalen-2-ylmethyl)phosphoramidate 3o



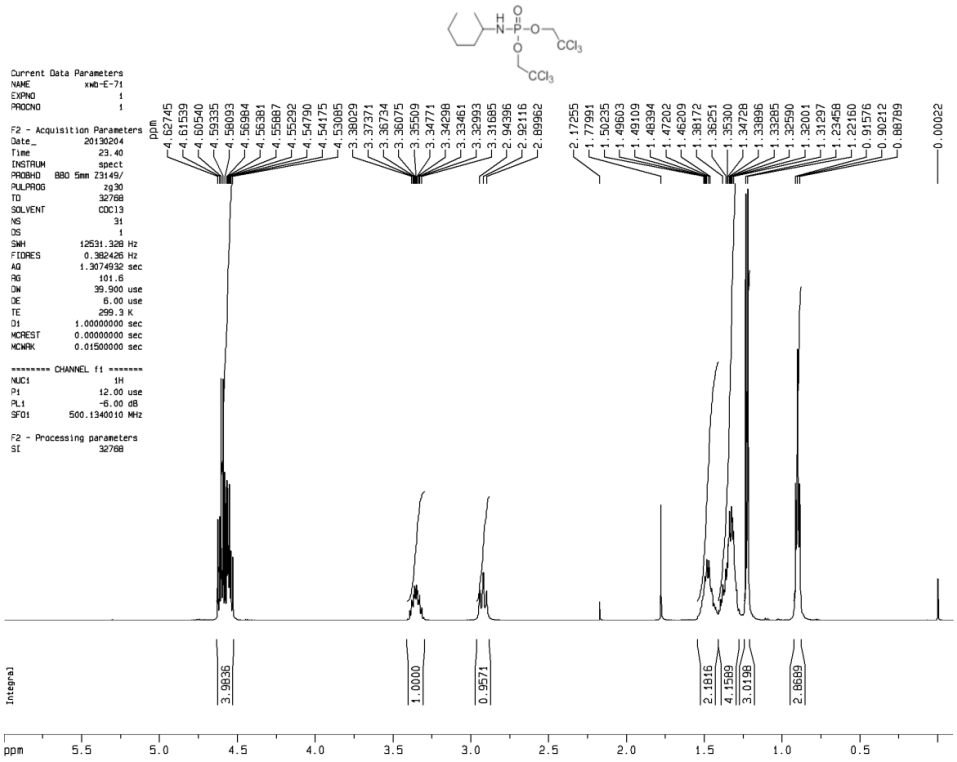


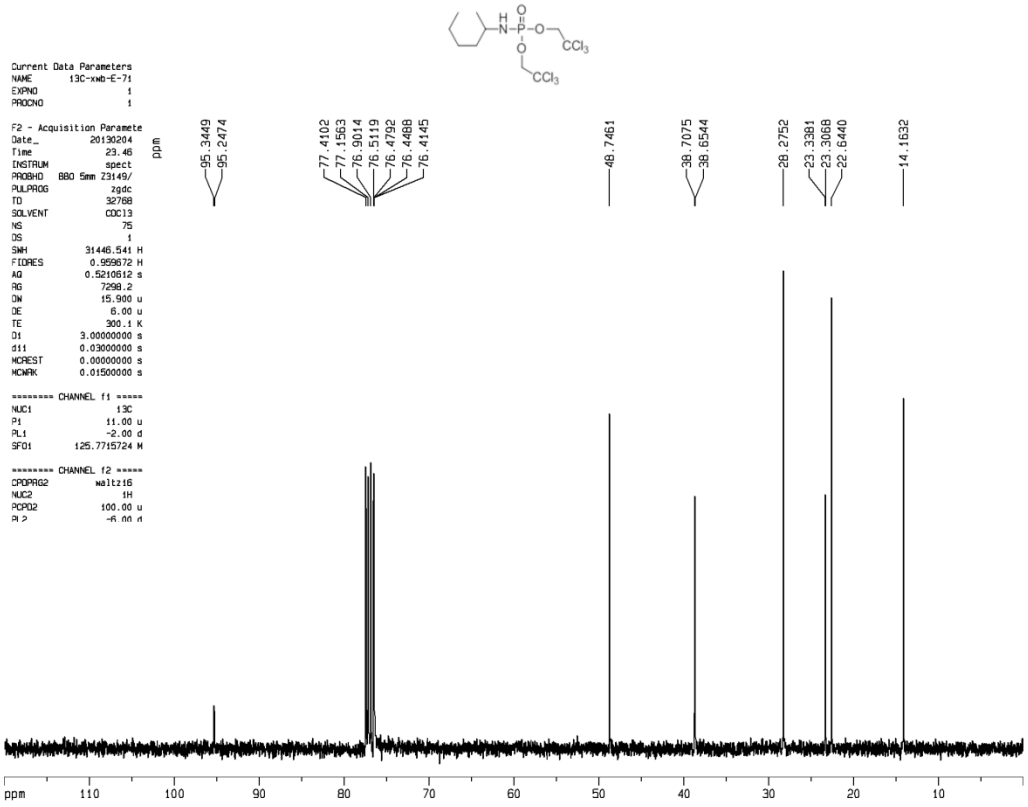
Bis(2,2,2-trichloroethyl) cyclohex-2-en-1-ylphosphoramidate 3p



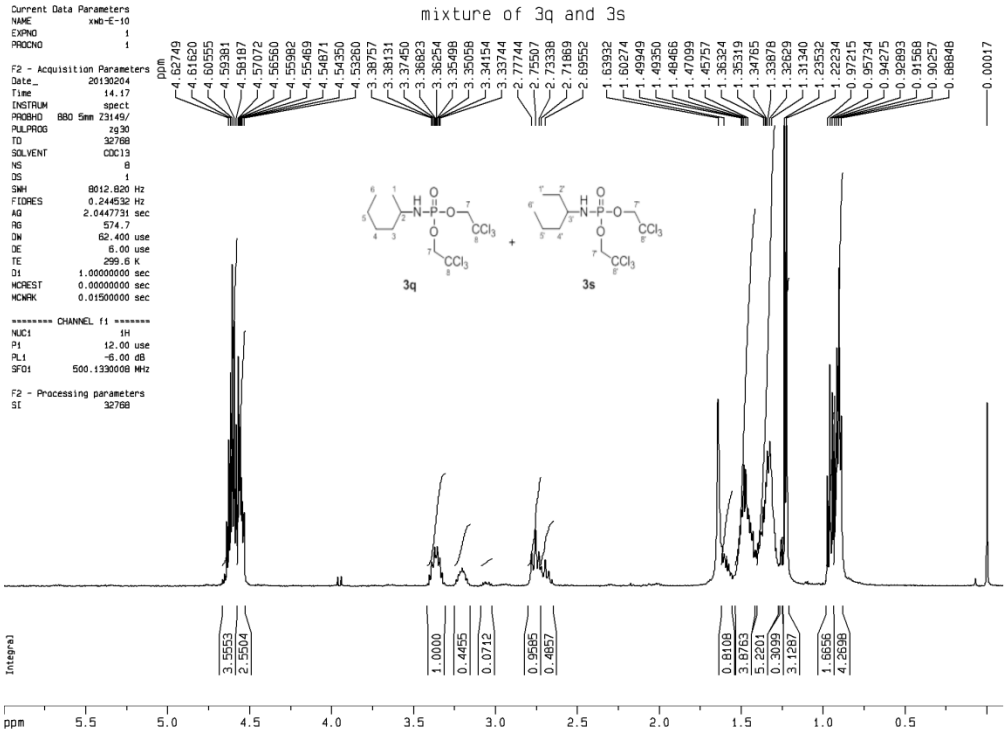


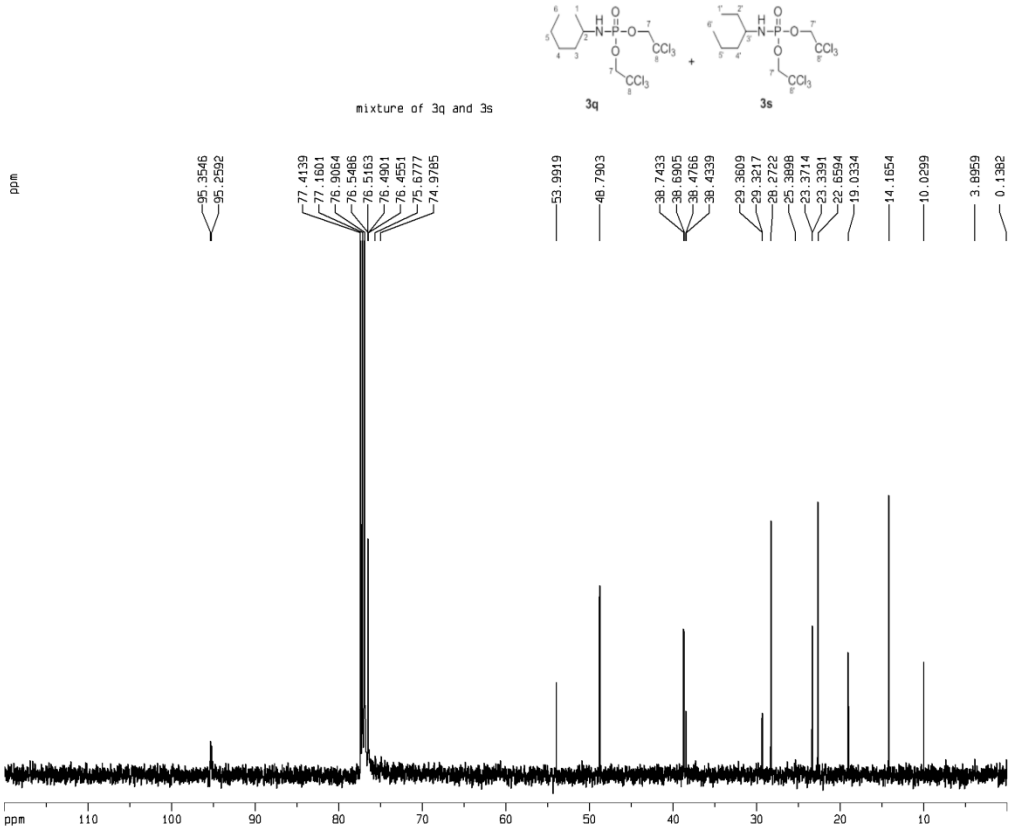
Bis(2,2,2-trichloroethyl) hexan-2-ylphosphoramidate 3q



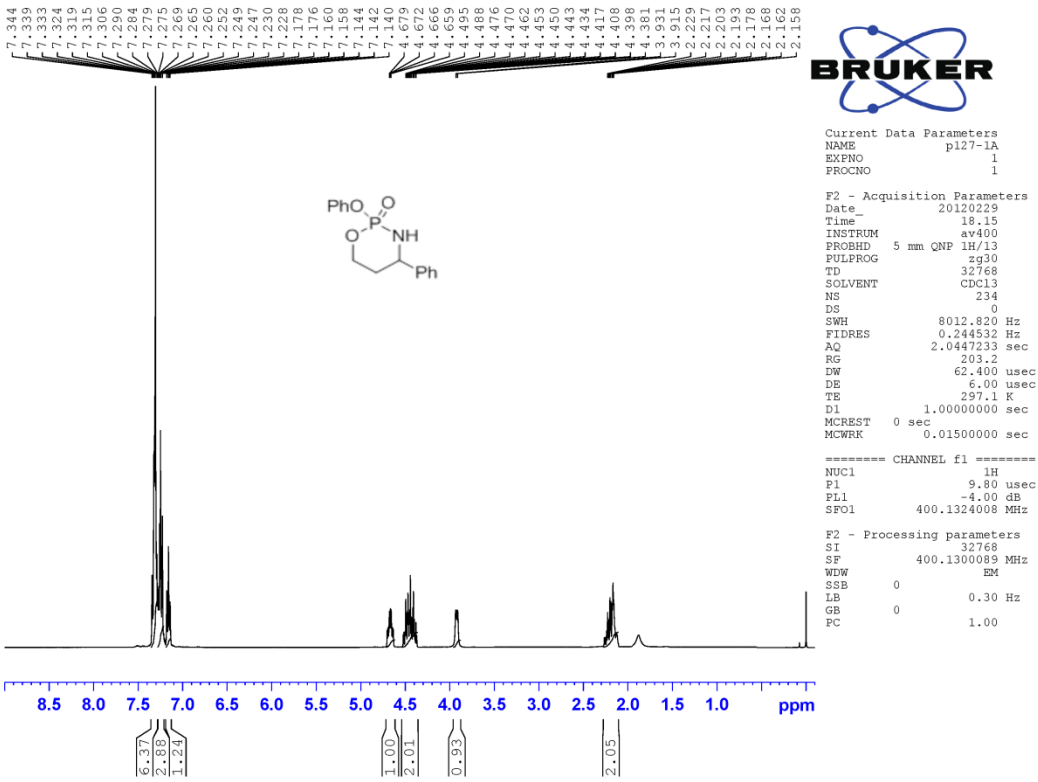


Mixture of 3q and 3s





2-Phenoxy-4-phenyl-1,3,2-oxazaphosphinane 2-oxide 5a



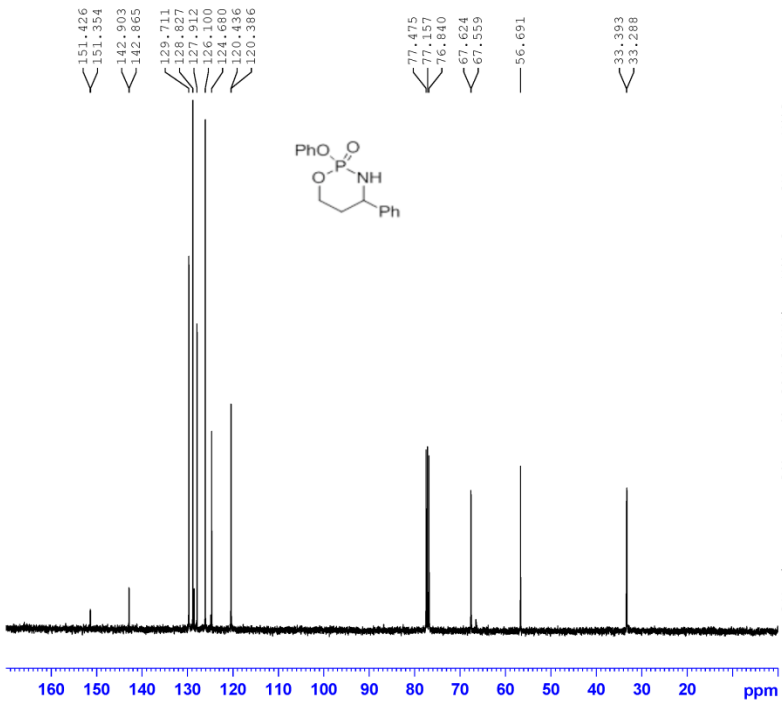
BRUKER

```
Current Data Parameters
NAME                  p127-1A
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20120229
Time                  18.15
INSTRUM               av400
PROBHD    5 mm QNP 1H/13
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                     234
DS                       0
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 2.0447233 sec
RG                    203.2
DW                   62.400 usec
DE                    6.00 usec
TE                   297.1 K
D1                1.00000000 sec
MCREST    0 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.80 usec
PL1                  -4.00 dB
SFO1           400.1324008 MHz

F2 - Processing parameters
SI                   32768
SF              400.1300089 MHz
WDW                     EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```



BRUKER

```
Current Data Parameters
NAME                  p127-1(C)
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_              20120424
Time                  12.50
INSTRUM               av400
PROBHD    5 mm QNP 1H/13
PULPROG               zgdc
TD                   32768
SOLVENT              CDCl3
NS                     280
DS                       0
SWH               25125.629 Hz
FIDRES                0.766773 Hz
AQ                 0.6520832 sec
RG                    9195.2
DW                   19.900 usec
DE                    6.00 usec
TE                   298.6 K
D1                2.50000000 sec
d11               0.03000000 sec
TD0                          1
SFO1           100.6238364 MHz
NUC1                      13C
P1                    9.10 usec
PLW1          -1.00000000 W
SFO2           400.1320007 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                80.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W

F2 - Processing parameters
SI                   32768
SF              100.6127607 MHz
WDW                     EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
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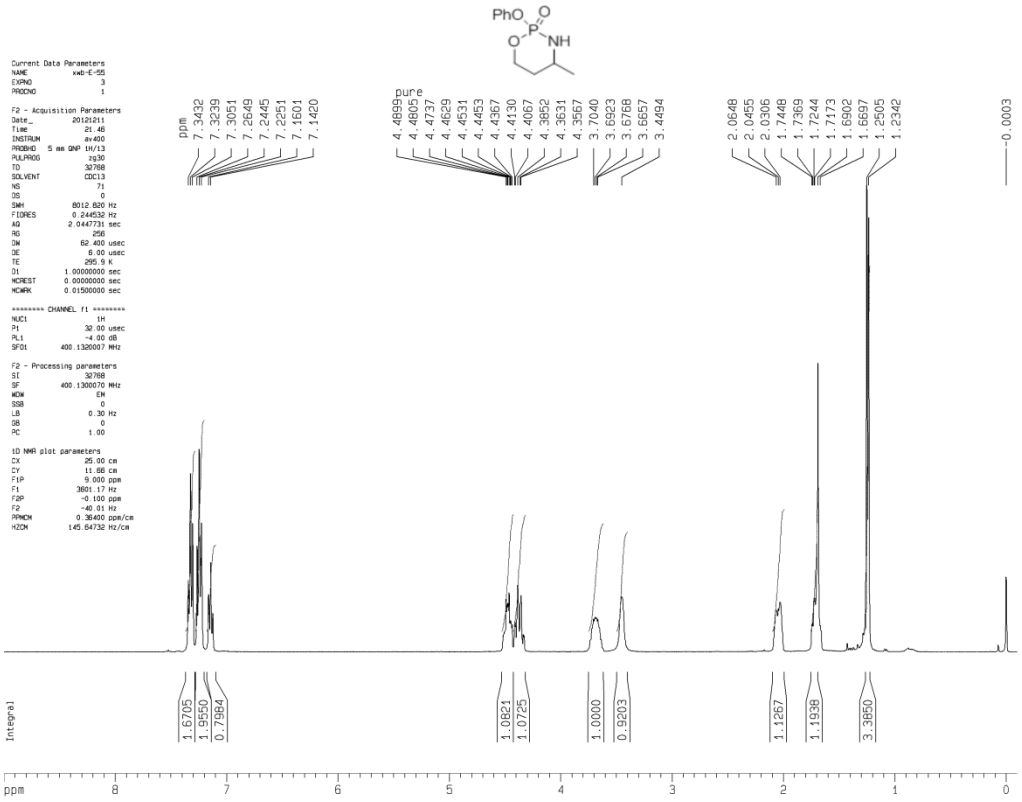
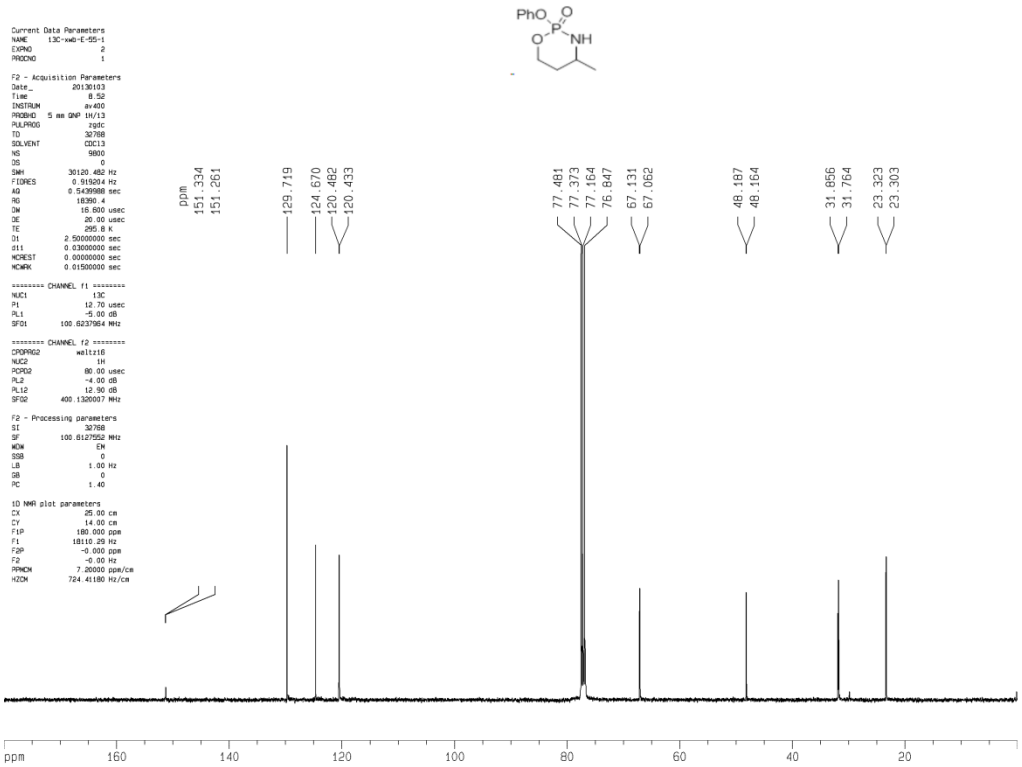
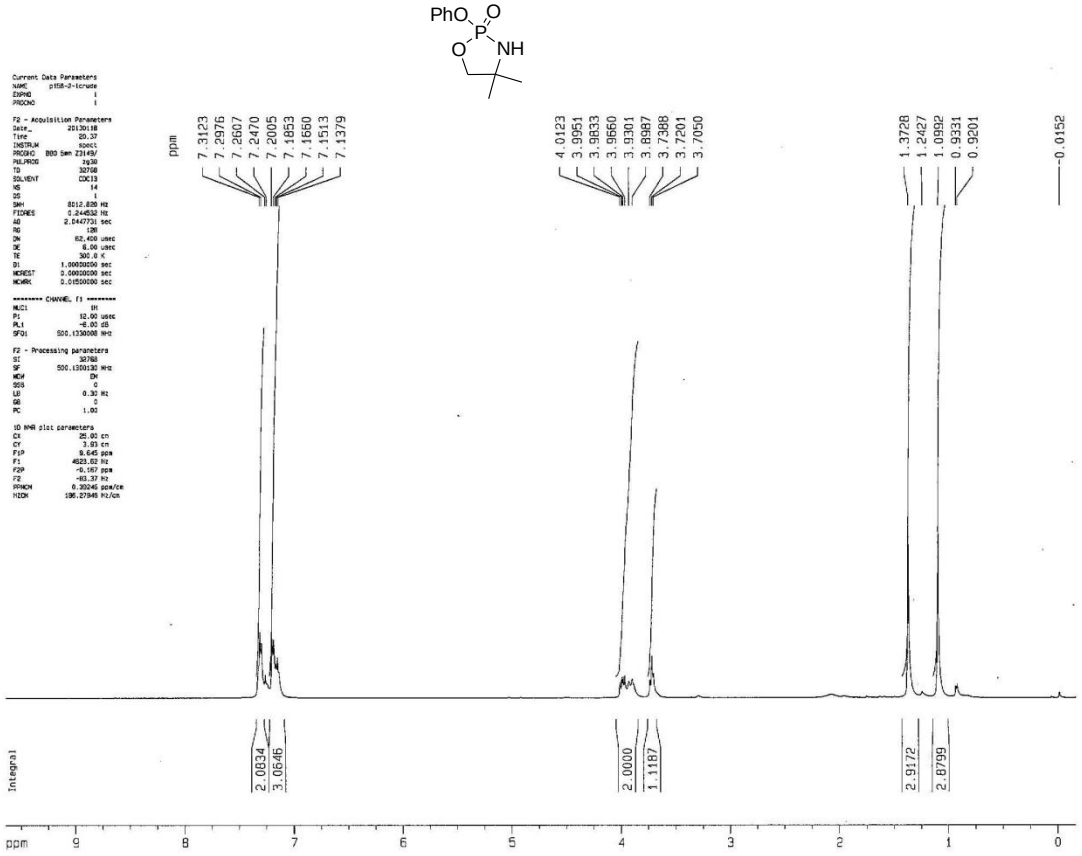
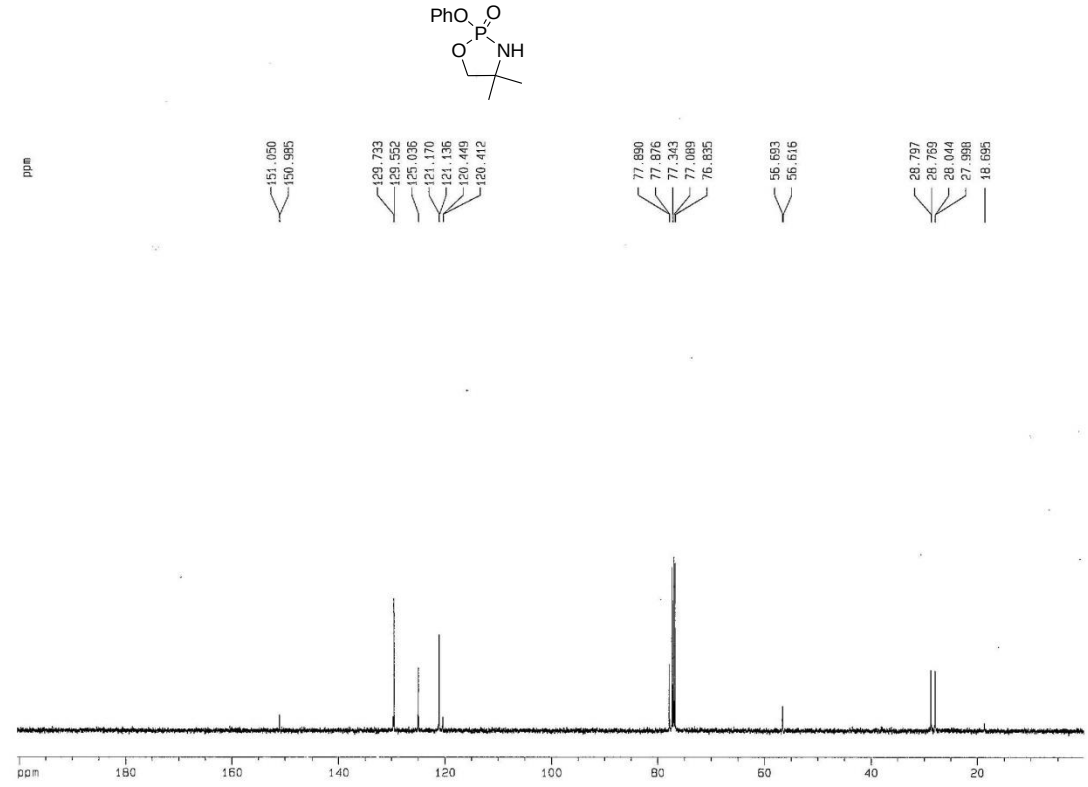
4-Methyl-2-phenoxy-1,3,2-oxazaphosphinane 2-oxide 5b



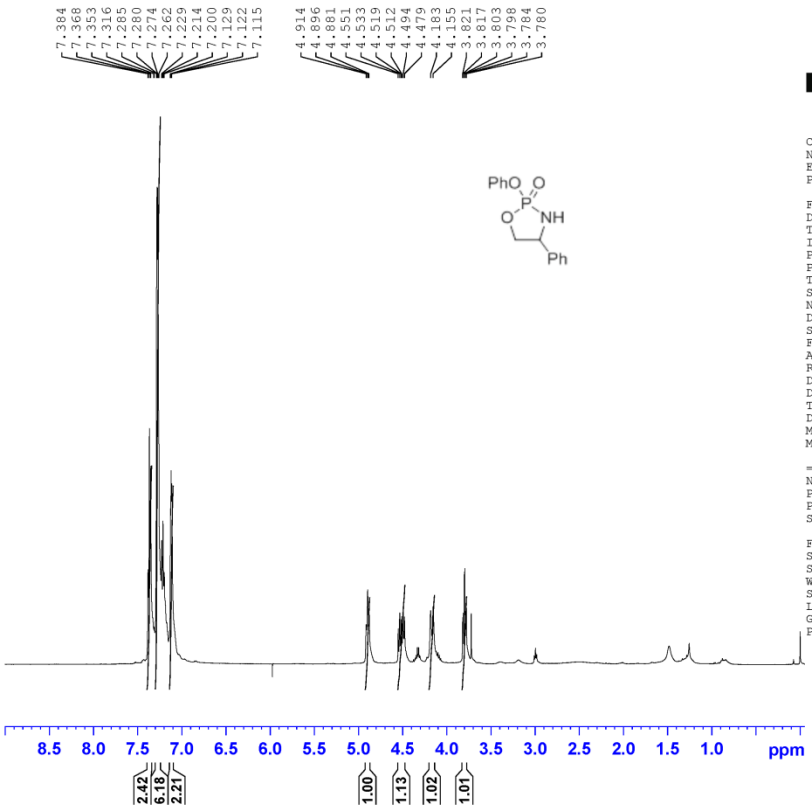


4,4-dimethyl-2-phenoxy-1,3,2-oxazaphospholidine 2-oxide 5c





2-phenoxy-4-phenyl-1,3,2-oxazaphospholidine 2-oxide 5d



BRUKER

```
Current Data Parameters
NAME        p157-4-3crude
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20130118
Time               15.32
INSTRUM            spect
PROBHD    BBO 5mm Z3149/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    18
DS                     1
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ             2.0447233 sec
RG                 322.5
DW                62.400 usec
DE                 6.00 usec
TE                299.5 K
D1             1.00000000 sec
MCREST    0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -6.00 dB
SFO1         500.1330008 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300125 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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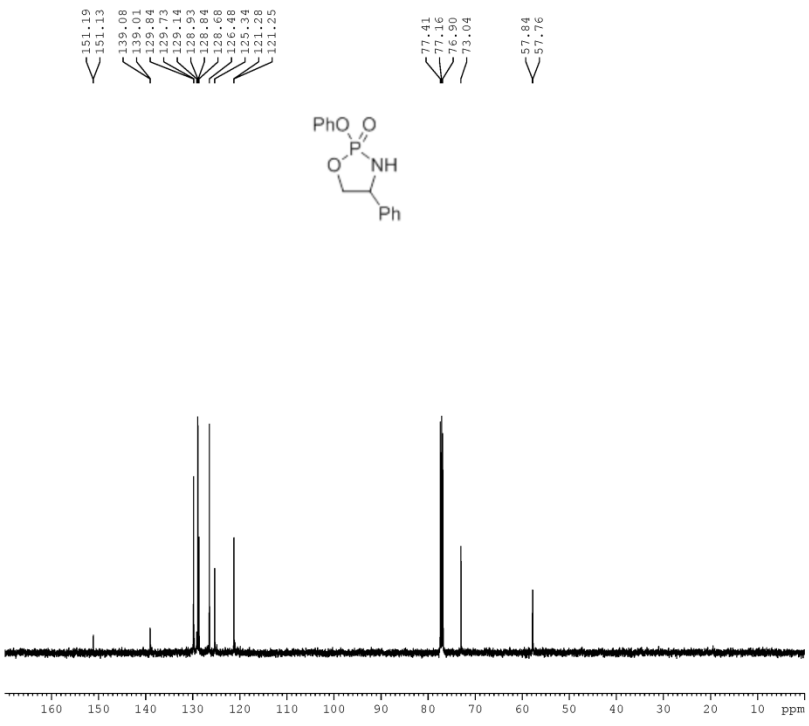

BRUKER

```
Current Data Parameters
NAME      p157-4-3crude(C)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20130118
Time               15.36
INSTRUM            spect
PROBHD    BBO 5mm Z3149/
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                    97
DS                     1
SWH            31446.541 Hz
FIDRES          0.959672 Hz
AQ             0.5210112 sec
RG                 7298.2
DW                15.900 usec
DE                 6.00 usec
TE                300.1 K
D1             3.00000000 sec
d11            0.03000000 sec
TD0                    1
SFO1         125.7715724 MHz
NUC1                  13C
P1                 11.00 usec
PLW1          -1.00000000 W
SFO2         500.1312000 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2             100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W

F2 - Processing parameters
SI                 32768
SF           125.7577792 MHz
WDW                   EM
SSB       0
LB                 1.20 Hz
GB        0
PC                 1.00
```

Study of Deuterium Kinetic Isotope Effects