Supplementary Material

One-pot multiphosphinylation & -phosphonylation of pyridine and related heterocycles towards the synthesis of piperidinylphosphonates and -phosphine oxides

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Table of Contents

Experimental Procedures

Commercially available starting materials, reagents and solvents were purchased from common chemical suppliers and used without further purification. Dry solvents were obtained via the MBraun SPS-800 solvent purification system. Under pressure of N_2 gas the solvents flow through two filter/dry columns. The columns are made of stainless steel (1.4301/ US304) with an internal volume of 4.8 L. The molecular sieves, as packing material, varies in accordance to the desired solvent.

Infrared spectroscopy (IR)

IR spectra with a S/N-ratio of 30,000:1 were obtained from samples in neat form with a Quest ATR (Attenuated Total Reflectance) accessory with diamond crystal puck using a Shimadzu IRAFFINITY-1S Fourier Transform Infrared Spectrophotometer (FTIR).

Liquid chromatography – mass spectrometry (LC-MS)

LC-MS analyses were conducted with an Agilent 1200 Series High performance liquid chromatograph equipped with a Supelco Ascentic Express C18 column (3 cm x 4.6 mm, 2.7 µm fused-core particles, 90 Å), Phenomenex Guard column (SecurityGuard Standard). The mobile phase was a mixture of acetonitrile (ACN), methanol and/or water, depending on the selected program. The HPLC was coupled to an UV-DAD (Ultra-Violet Diode Array Detector) and an Agilent 1100 Series MS with Electrospray Ionisation (ESI, 4000 V) with a single quadrupole detector.

Nuclear magnetic resonance spectrometry (NMR)

^{1}H, ^{13}C, ^{31}P and 2D NMR spectra, were recorded at 400, 100.6 or 161.9 MHz respectively, on a Bruker Avance III, equipped with ^{1}H/BB z-gradient probe (BBO, 5 mm). Before analysis, samples were dissolved in deuterated solvents ($CDCl_3$) and tetramethylsilane (TMS) was added as internal chemical shift standard. All spectra were processed using TOPSPIN 4.0.8. The chemical shift as δ-value was reported in ppm.

Thin layer chromatography (TLC)

TLC was used to determine a suitable mobile phase for the automated flash chromatography via determination of the Rf-value. Compound mixtures were spotted on silica plates (Merck Silicagel 60 F254, precoated, thickness 0.25 mm). Detection of the compounds was done using a UV detector.

Normal phase automated flash chromatography

Automatic flash chromatography was performed on a Büchi Reveleris X2 flash chromatography system. Reusable columns (SiO_2, particle size of 0.040-0.063 mm) were used for the purification of the crude products. The effluent was analysed by an Evaporative Light Scattering Detector (ELSD) and three ultraviolet detectors of which the wavelengths were adjusted depending on the mixture to be purified.

Reverse phase automated flash chromatography

Automatic flash chromatography was performed on a Grace Reveleris X1 flash chromatography system, equipped with an adjustable UV detector (2 distinct wavelengths). Reusable columns (C18, particle size of 0.040 mm, irregular shape) were used to purify the products.

High Resolution Mass Spectrometry (HRMS)

HRMS analysis was conducted on an Agilent 1100 high-performance liquid chromatograph (HPLC) coupled to an Agilent 6220A TOF MS (Time of Flight Mass Spectrometer) equipped with an ESI/APCI (Electrospray Ionisation/ Atmospheric Pressure Chemical Ionization) multimode ionisation source.

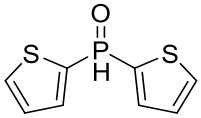
Thermogravimetric analysis (TGA)

In TGA, a sample is heated in a controlled atmosphere (air, N_2, argon etc.) while recording the weight and rate of weight change as a function of increasing temperature and time or isothermally as a function of time. A Q5000 TGA from TA Instruments was used with platinum pans (100 µl, TA Instruments). The mass calibration of the TGA was performed using a set of mass calibration standards purchased from Ohaus. For this work, the standard mass calibrant of 5 mg was used. Temperature calibration was performed according to the procedures recommended by the manufacturer, which are based on ASTM standard E1582-93, using the Curie temperature (T_c) of paramagnetic materials.[1] A 4-point calibration was performed using Alumel® foil (T_c = 152.6 ± 1.0 °C), nickel foil (T_c = 358.2 ± 1.1 °C), $Ni._{83}Co._{17}$ alloy foil (T_c = 554.4 ± 2.2 °C) and $Ni._{63}Co._{37}$ alloy foil (T_c = 746.4 ± 1.6 °C). The nickel and nickel-cobalt foils were obtained from the US National Metallurgical Laboratories at Ames, Iowa through ICTAC , while the Alumel® was obtained from Hoskins Manufacturing at Hamburg, Michigan through ICTAC. The same calibration set for temperature and mass was used for all TGA measurements.[2] The TGA pans (100 µL platinum pans, TA Instruments) were cleaned using a Bunsen burner, where the temperature can reach 1200-1400 °C. Any char left in the crucible was carefully cleaned with a glass fibre brush. The empty crucible was then loaded into the TGA Q5000 autosampler and tared. After taring, the sample to be tested was loaded into the pans, the TGA experiment was set up according to the temperature programme and measurements were carried out. TGA measurements were done at a heating rate of 60 $K.min^{-1}$, heating from 50 °C to 650 °C under Air and also in inert conditions of N_2. Measurements were repeated 3 times for each sample.

Pyrolysis combustion flow calorimetry (PCFC)

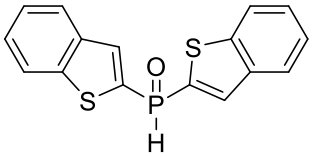
The PCFC used in this work, also called micro Calorimeter, is procured from Fire Testing Technology Ltd. (FTT). The operating parameters and procedures of PCFC are performed according to the ASTM D7309-21b "**A Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry**" (American Society for Testing and Materials).[3] In each PCFC measurement, each sample was between 5-7 mg and was subjected to a heating rate of 1 $K.s^{-1}$ (60 $K.min^{-1}$) in the pyrolysis zone under inert conditions of N_2. The sample was heated from 120 °C to 750 °C in this zone and the gases released during the pyrolysis are passed to the oven for combustion. In the combustor, the temperature is at 900 °C and it has the gaseous mixture of 80/20 N2/O2 where total combustion of the pyrolysis products takes place. Measurements were repeated at least 2 times for each material. PCFC calculated the heat release rate (HRR) using the oxygen consumed according to Huggett's relation, i.e., 1 kg of O_2 consumed corresponds to 13.1 MJ of heat released.[4] The curve of the heat release rate (HRR, in $W.g^{-1}$) versus temperature obtained for a material in PCFC provides several parameters such as: (pHRR, in $W.g^{-1}$) which is the maximum rate at which heat is generated by the burning of the released combustible gases, the temperature at the maximum heat release rate (T_p) and finally the most important parameter, the total heat release (THR, in $kJ.g^{-1}$), which is the integral of the HRR over the entire temperature range. The latter parameter should be low for a better flame behaviour.[5] The graphs of the PCFC measurements can be found lower in this document.

Di(thiophen-2-yl)phosphine oxide (89%)



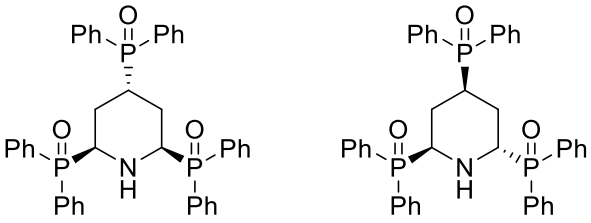
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.44 (d, J_{H-H} = 515.2 Hz, 1H, P-*H*), 7.76 (txd, J_{H-H} = 4.5 Hz, 0.9 Hz, 2H, S-C*H*), 7.63 (dxdxd, J_{H-H} = 9.0 Hz, 3.6 Hz, 0.9 Hz, 2H, Cq-C*H*), 7.18-7.22 (m, 2H, S-CH-C*H*)
^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: -1.31
Spectral data is in accordance with literature.[6]

bis(benzo[b]thiophen-2-yl)phosphine oxide (77%)



^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.60 (d, J_{P-H} = 518.3 Hz, 1H, P-*H*), 7.99 (d, J_{H-H} = 10.3 Hz, 2H, P-Cq-C*H*), 7.84-7.92 (m, 4H, C*H*$_{arom}$), 7.40-7.49 (m, 4H, C*H*$_{arom}$)
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 143.7 (d, J_{C-P} = 6.6 Hz, 1C, *Cq*), 139.0 (d, J_{C-P} = 15.4 Hz, 1C, *Cq*), 133.8 (d, J_{C-P} = 11.3 Hz, 1C, P-Cq-*C*H), 132.1 (d, J_{C-P} = 112.8 Hz, 1C, P-*Cq*), 126.9 (1C, *C*H$_{arom}$), 125.4 (1C, *C*H$_{arom}$), 125.3 (1C, *C*H$_{arom}$), 122.7 (d, J_{C-P} = 1.3 Hz, 1C, *C*H$_{arom}$)
^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 1.21

3a (82%)

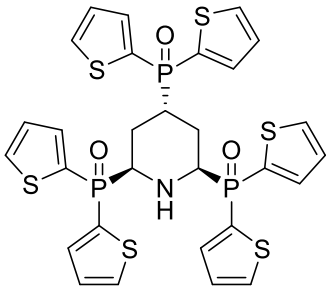


Major Minor

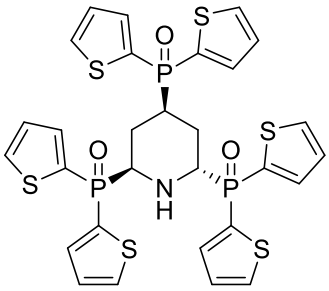
73:27

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.13-7.81 (m, 60H, *Phenyl*$_{major\&minor}$), 4.46-4.65 (m, 3H, 2xP-C*H*$_{major}$-NH & P-C*H*$_{minor}$-NH), 3.87 (d, J_{H-H} = 5.7 Hz, 1H, P-C*H*$_{minor}$-NH), 3.54-3.66 (m, 1H, P-C*H*$_{minor}$-CH_2), 2.70 (br s, 1H, P-C*H*$_{major}$-CH_2), 1.76-2.16 (m, 7H, 2x C*H*$_{2,\ major}$ & C*H*$_{2,minor}$ & C*H*$_{2,minor}$), 1.56 (~t, J_{H-H} = 11.5 Hz, 1H, N*H*$_{major}$), 1.41-1.50 (m, 1H, C*H*$_{2,minor}$)
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 128.0-129.1 & 130.0-134.2 (m, 72C, *Phenyl*$_{major\&minor}$), 52.6 (dxd, J_{C-P} = 83.8, 12.9 Hz, 2C, 2xP-*C*H$_{major}$-NH), 49.6-52.0 (m, 2C, 2xP-*C*H$_{minor}$-NH); 31.7 (d, J_{C-P} = 66.7 Hz, 1C, P-*C*H$_{minor}$), 30.9 (d, J_{C-P} = 70.5 Hz, 1C, P-*C*H$_{major}$), 24.1 (2C, 2x*C*H$_{2,major}$), 23.2 (d, J_{C-P} = 13.3 Hz, 1C, 2x *C*H$_{2,minor}$)
^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 37.26 (1P, *P*-CH-CH_2-CH-NH$_{major}$), 35.48 (1P, *P*-CH-CH_2-CH-NH$_{minor}$), 33.54 (d, J_{P-P} = 5.8 Hz, 1P, *P*-CH-NH$_{minor}$), 32.18 (d, J_{P-P} = 5.8 Hz, 1P, *P*-CH-NH$_{minor}$), 30.84 (2P, *P*-CH-NH$_{major}$)
FT-IR (cm^{-1}): 1435, 1194, 1182, 1119, 723, 692, 556
m/z (ESI, 70 eV): 686.2 ($[M+H]^+$, 100%) **Calc. Mass $C_{41}H_{38}NO_3P_3^+$:** 685.2065 m/z

3b (75%)



Major



Minor

56:44

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.05-7.19 & 7.42-7.73 (m, 36H, *Thioph$_{major\&minor}$*), 4.29-4.41 (m, 3H, 2xP-C*H$_{major}$*-NH & P-C*H$_{minor}$*-NH), 3.61 (d, J_{H-H} = 4.8 Hz, 1H, P-C*H$_{minor}$*-NH), 3.35-3.48 (m, 1H, P-C*H$_{minor}$*-CH_2), 2.50 (br s, 1H, P-C*H$_{major}$*-CH_2), 1.87-2.30 (m, 7H, 2x C*H$_{2,\ major}$* & C*H$_{2,minor}$* & C*H$_{2,minor}$*), 1.74-1.87 (m, 1H, C*H$_{2,minor}$*), 1.60 (m, 1H, N*H$_{major}$*)

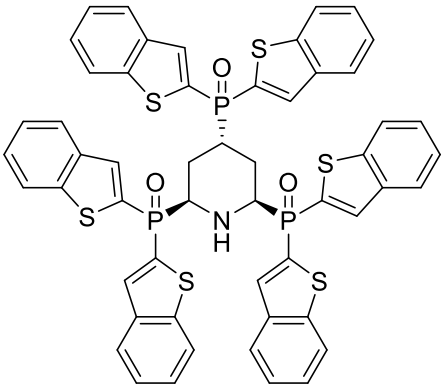
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 127.9-128.8 & 129.6-134.4 & 135.5-137.5 (m, 48C, *Thioph$_{major\&minor}$*), 55.0 (dxd, J_{C-P} = 93.6, 14.4 Hz, 2C, 2xP-*C*H$_{major}$-NH), 53.2-55.3 (m, 2C, 2xP-*C*H$_{minor}$-NH); 35.1-36.3 (m, 2C, P-*C*H$_{minor}$ & P-*C*H$_{major}$), 24.3 (2C, 2x*C*H$_{2,major}$), 23.4 (d, J_{C-P} = 16.7 Hz, 2C, 2x *C*H$_{2,minor}$)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 29.36 (1P, *P*-CH-CH_2-CH-NH_{major}), 26.92 (1P, *P*-CH-CH_2-CH-NH_{minor}), 25.50 (d, J_{P-P} = 5.9 Hz, 1P, *P*-CH-NH_{minor}), 23.09 (d, J_{P-P} = 5.9 Hz, 1P, *P*-CH-NH_{minor}), 22.43 (2P, *P*-CH-NH_{major})

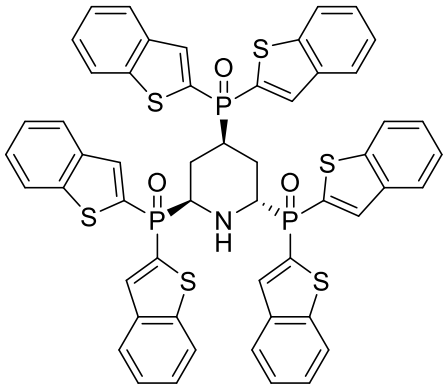
FT-IR (cm^{-1}): 1404, 1217, 1184, 1094, 1006, 712, 521

m/z (ESI, 70 eV): 722.0 ($[M+H]^+$, 100%) **Calc. Mass $C_{29}H_{26}NO_3P_3S_6^+$:** 720.9450 m/z

3c (42%)



Major



Minor

53:47

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.22-8.05 (m, 60H, C*H$_{major\&minor}$*), 4.61-4.74 (m, 3H, 2xP-C*H$_{major}$*-NH & P-C*H$_{minor}$*-NH), 3.82 (d, J_{H-H} = 5.1 Hz, 1H, P-C*H$_{minor}$*-NH), 3.69-3.80 (m, 1H, P-C*H$_{minor}$*-CH_2), 2.50 (br s, 1H, P-C*H$_{major}$*-CH_2), 2.68 (br s, 1H, C*H$_{2,minor}$*), 1.99-2.54 (m, 8H, 2x C*H$_{2,\ major}$* & 2x C*H$_{2,minor}$*)

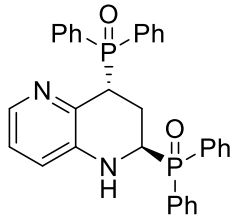
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 121.9-122.9 & 124.5-125.7 & 126.1-127.0 & 129.6-136.0 & 138.4-139.6 & 143.1-144.3 (m, 96C, *C*H$_{major\&minor}$), 55.2 (dxd, J_{C-P} = 92.8, 14.0 Hz, 2C, 2xP-*C*H$_{major}$-NH), 53.2-54.5 (m, 2C, 2xP-*C*H$_{minor}$-NH); 35.7 (d, J_{C-P} = 92.7 Hz, 1C, P-*C*H$_{minor}$), 35.3 (d, J_{C-P} = 77.8 Hz, 1C, P-*C*H$_{major}$), 24.6 (2C, 2x*C*H$_{2,major}$), 23.5 (2C, 2x *C*H$_{2,minor}$)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 30.41 (1P, *P*-CH-CH_2-CH-NH_{major}), 28.03 (1P, *P*-CH-CH_2-CH-NH_{minor}), 26.24 (1P, *P*-CH-NH_{minor}), 24.49 (d, J_{P-P} = 5.5 Hz, 1P, *P*-CH-NH_{minor}), 23.27 (2P, *P*-CH-NH_{major})

FT-IR (cm^{-1}): 1494, 1246, 1180, 1155, 999, 743, 604, 559

m/z (ESI, 70 eV): 708.1 ([M-$C_{16}H_{14}OPS_2$+H]$^+$, 100%) **Calc. Mass $C_{53}H_{38}NO_3P_3S_6^+$:** 1021.0389 m/z (fragment to 707.0400)

3d (99%)



100:0

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.27-7.34 & 7.36-7.66 & 7.69-7.79 & 7.90-8.04 (m, 21H, *Phenyl* & N-C*H*), 6.82 (dxdxd, J_{H-H} = 8.2 Hz, 4.6 Hz, 1.7 Hz, 1H, N-CH-C*H*), 6.72 (dxd, J_{H-H} = 8.2 Hz, 1.2 Hz, 1H, NH-Cq-C*H*), 5.14 (d, J_{H-H} = 12.2 Hz, 1H, NH-C*H*-P), 4.15 (~d, J_{H-H} = 3.0 Hz, 1H, N*H*), 4.06-4.14 (m, 1H, P-C*H*-CH_2-CH-NH), 2.48-2.59 (m, 1H, CH_2), 2.04-2.25 (m, 1H, CH_2)

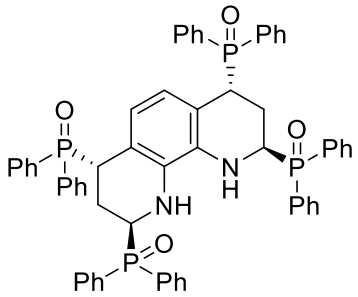
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 140.5 (dxd, J_{C-P} = 8.8 Hz, 3.6 Hz, 1C, N-*Cq*), 138.5 (d, J_{C-P} = 2.1 Hz, 1C, N-*C*H), 135.8 (d, J_{C-P} = 5.7 Hz, 1C, NH-*Cq*), 127.6-132.7 (m, 24C, *Phenyl*), 122.8 (d, J_{C-P} = 2.4 Hz, 1C, N-CH-*C*H), 122.0 (1C, NH-Cq-*C*H); 47.3 (d, J_{C-P} = 80.0 Hz, 1C, P-*C*H-NH), 40.8 (dxd, J_{C-P} = 65.7 Hz, 11.8 Hz, 1C, P-*C*H-Cq), 22.2 (1C, *C*H_2)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 33.34 (s, 1P), 30.78 (s, 1P)

FT-IR (cm^{-1}): 1433, 1182, 1171, 1117, 1098, 748, 723, 694

m/z (ESI, 70 eV): 535.2 ([M+H]$^+$, 100%) **Calc. Mass $C_{32}H_{28}N_2O_2P_2^+$:** 534.1626 m/z

3e (66%)



100:0

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.27-7.86 (m, 40H, *Phenyl*), 5.27 (s, 1H, NH-Cq-Cq-C*H*), 5.25 (s, 1H, NH-Cq-Cq-C*H*), 4.99 (dxt, J_{H-H} = 12.6 Hz, 2.5 Hz, 1H, P-C*H*-NH), 4.82-4.91 (m, 1H, P-C*H*-NH), 3.57-3.70 (m, 2H, 2x P-C*H*-Cq), 3.43-3.53 (m, 2H, 2x N*H*), 1.94-2.42 (m, 4H, 2x CH_2)

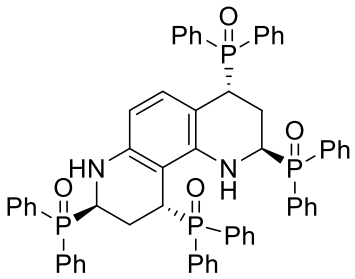
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 128.1-134.7 (m, 50C, *Phenyl* & 2x NH-*Cq*), 120.1 (1C, NH-Cq-Cq-*C*H), 119.8 (1C, NH-Cq-Cq-*C*H), 114.6 (2C, 2x NH-Cq-*Cq*), 47.7 (d, J_{C-P} = 83.5 Hz, 1C, P-*C*H-NH), 47.0 (d, J_{C-P} = 81.7 Hz, 1C, P-*C*H-NH), 37.0- 38.6 (m, 2C, 2x P-*C*H-Cq), 22.1 (1C, *C*H_2), 21.9 (1C, *C*H_2)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 32.07 (s, 1P), 31.73 (s, 1P), 31.09 (s, 1P), 30.35 (s, 1P)

FT-IR (cm^{-1}): 1435, 1173, 1117, 1098, 721, 692

m/z (ESI, 70 eV): 989.3 ([M+H]$^+$, 100%) **Calc. Mass $C_{60}H_{52}N_2O_4P_4^+$:** 988.2878 m/z

3f (93%)



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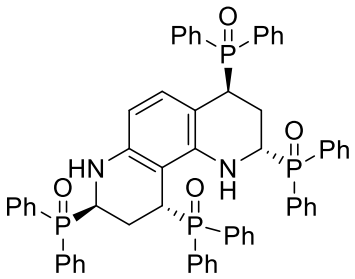


Minor

79:21

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.15-7.91 (m, 80H, *Phenyl*$_{major\ \&\ minor}$), 5.90 (d, $J_{H\text{-}H}$ = 8.4 Hz, 1H, NH-Cq-Cq-C*H*$_{major}$), 5.76 (d, $J_{H\text{-}H}$ = 8.4 Hz, 1H, NH-Cq-Cq-C*H*$_{minor}$), 5.68 (d, $J_{H\text{-}H}$ = 8.4 Hz, 1H, NH-Cq-C*H*$_{minor}$), 5.57 (d, $J_{H\text{-}H}$ = 8.4 Hz, 1H, NH-Cq-C*H*$_{major}$), 5.11-5.22 (m, 1H, P-C*H*-NH$_{minor}$), 5.00 (br s, 1H, N*H*$_{major}$), 4.64-4.79 (m, 2H, P-C*H*-NH$_{major}$, P-C*H*-NH$_{minor}$), 4.24 (dxd, $J_{H\text{-}H}$ = 12.9 Hz, 3.5 Hz, 1H, P-C*H*-NH$_{major}$), 3.92 (br s, 1H, N*H*$_{minor}$), 3.74 (d, $J_{H\text{-}H}$ = 4.5 Hz, 1H, P-C*H*-Cq$_{major}$), 3.53-3.65 (m, 5H, P-C*H*-Cq$_{major}$ & N*H*$_{major}$ & N*H*$_{minor}$ & 2x P-C*H*-Cq$_{minor}$), 1.38-2.44 (m, 8H, 2x C*H*$_{2,major}$ & 2x C*H*$_{2,minor}$)

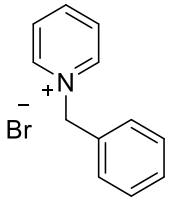
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: (**only major product sufficiently visible**) 144.7 (1C, NH-*Cq*), 142.8 (1C, NH-*Cq*), 127.3-132.9 (m, 49C, *Phenyl* & NH-Cq-Cq-*C*H), 105.6 (1C, NH-Cq-*C*H), 105.2 (d, $J_{C\text{-}P}$ = 4.8 Hz, 1C, NH-Cq-*Cq*-CH), 102.6 (dxd, $J_{C\text{-}P}$ = 5.1 Hz, 1.7 Hz, 1C, NH-Cq-*Cq*-Cq), 47.9 (d, $J_{C\text{-}P}$ = 85.1 Hz, 1C, P-*C*H-NH), 47.6 (d, $J_{C\text{-}P}$ = 80.3 Hz, 1C, P-*C*H-NH), 37.9 (dxd, $J_{C\text{-}P}$ = 68.9 Hz, 12.0 Hz, 1C, P-*C*H-Cq), 35.7 (dxd, $J_{C\text{-}P}$ = 69.7 Hz, 12.7 Hz, 1C, P-*C*H-Cq), 21.8 (1C, *C*H$_2$), 21.7 (1C, *C*H$_2$)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 34.78 (s, 1P, minor), 33.84 (s, 1P, major), 33.19 (s, 1P, minor), 31.83 (s, 1P, major), 31.49 (s, 1P, major), 31.22 (s, 1P, minor), 31.09 (s, 1P, minor), 30.05 (s, 1P, major)

FT-IR (cm^{-1}): 1435, 1175, 1153, 1117, 1099, 721, 691

m/z (ESI, 70 eV): 989.3 ($[M+H]^+$, 100%) **Calc. Mass $C_{60}H_{52}N_2O_4P_4^+$:** 988.2878 m/z

4a, 1-Benzylpyridinium bromide (95%)

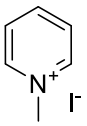


^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 9.71 (d, $J_{H\text{-}H}$ = 5.5 Hz, 2H, *Pyr*$_{ortho}$), 8.48 (txt, $J_{H\text{-}H}$ = 7.8 Hz, 1.2 Hz, 1H, *Pyr*$_{para}$), 8.05 (~t, $J_{H\text{-}H}$ = 7.2 Hz, 2H, *Pyr*$_{meta}$), 7.70-7.77 (m, 2H, *Phenyl*$_{ortho}$), 7.32-7.39 (m, 3H, *Phenyl*$_{meta,para}$), 6.36 (s, 2H, C*H*$_2$)

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 145.3 (1C, *Pyr*$_{para}$), 145.1 (2C, *Pyr*$_{ortho}$), 133.0 (1C, *Cq*), 130.0 (1C, *Phenyl*$_{para}$), 129.6 (4C, *Phenyl*$_{ortho,\ meta}$), 128.3 (2C, *Pyr*$_{meta}$), 63.9 (1C, *C*H$_2$)

Spectral data is in accordance with literature.[7]

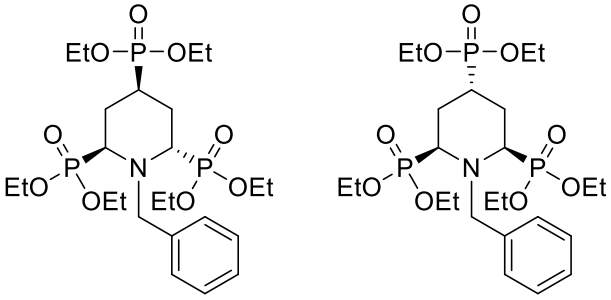
4b, 1-Methylpyridinium iodide (92%)



^{1}H NMR (400 MHz, DMSO-d_8, 298 K) δ: 8.99 (d, $J_{H\text{-}H}$ = 5.9 Hz, 2H, N-C*H*); 8.58 (t, $J_{H\text{-}H}$ = 7.5 Hz, 1H, N-CH-CH-C*H*); 8.14 (t, $J_{H\text{-}H}$ = 8.1 Hz, 2H, N-CH-C*H*); 4.36 (s, 3H, C*H*$_3$).

Spectral data is in accordance with literature.[8]

5a (81%)



Major Minor

97:3

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.36-7.43 (m, 2H, *Phenyl*), 7.21-7.34 (m, 3H, *Phenyl*), 4.35-4.50 (m, 2H, N-C*H*$_2$ & P-C*H*-N), 3.89-4.27 (m, 12H, O-C*H*$_2$-CH_3), 3.83 (d, J_{H-H} = 13.7 Hz, 1H, N-C*H*$_2$), 3.04-3.18 (m, 1H, P-C*H*-N), 2.56-2.74 (m, 1H, P-C*H*-CH_2), 1.83-2.29 (m, 4H, 2x P-CH-C*H*$_2$), 1.18-1.40 (m, 18H, CH_2-C*H*$_3$)

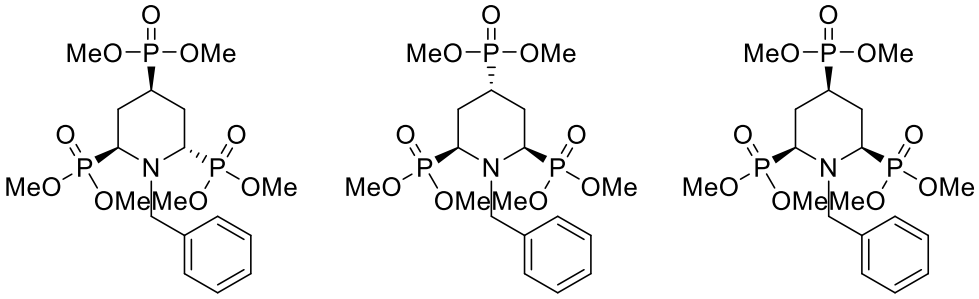
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 138.6 (1C, *Cq*), 129.2 (2C, *Phenyl*), 128.2 (2C, *Phenyl*), 127.3 (1C, *Phenyl$_{para}$*), 62.9 (d, J_{C-P} = 6.8 Hz, 1C, O-CH_2-CH_3), 62.3 (d, J_{C-P} = 6.9 Hz, 1C, O-CH_2-CH_3), 61.7-61.9 (m, 3C, 3x O-CH_2-CH_3), 61.4 (d, J_{C-P} = 7.0 Hz, 1C, O-CH_2-CH_3), 54.3 (dxd, J_{C-P} = 159.7 Hz, 15.3 Hz, 1C, P-CH-N), 53.2 (1C, N-CH_2), 51.5 (dxt, J_{C-P} = 161.9 Hz, 14.6 Hz, 1C, P-CH-N), 30.91 (dxd, J_{C-P} = 132.9 Hz, 14.2 Hz, 1C, P-CH-CH_2), 19.2 (1C, P-CH-CH_2), 16.9 (1C, P-CH-CH_2), 16.2-16.7 (m, 6C, 6x CH_2-CH_3)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 29.58 (d, J_{P-P} = 17.4 Hz, 1P), 25.25 (d, J_{P-P} = 16.5 Hz, 1P), 24.31 (s, 1P)

FT-IR (cm^{-1}): 1234, 1045, 1016, 947

m/z (ESI, 70 eV): 584.2 ($[M+H]^+$, 100%) **Calc. Mass $C_{24}H_{44}NO_9P_3^+$:** 583.2229 m/z

5b (58%)



Major Minor Minor'

88:6:6

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.23-7.43 (m, 5H, *Phenyl*), 4.32-4.48 (m, 2H, P-C*H*-N & N-C*H*$_2$), 3.72-3.88 (m, 13H, 4x O-C*H*$_3$ & N-C*H*$_2$), 3.67 (d, J_{H-H} = 10.5 Hz, 3H, O-C*H*$_3$), 3.59 (d, J_{H-H} = 10.8 Hz, 3H, O-C*H*$_3$), 3.07-3.24 (m, 1H, P-C*H*-N), 2.59-2.77 (m, 1H, P-C*H*), 1.80-2.32 (m, 4H, 2x P-CH-C*H*$_2$)

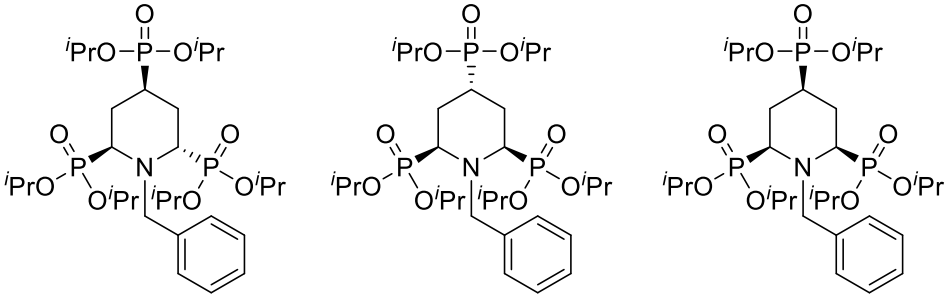
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 138.3 (1C, *Cq*), 129.1 (2C, *Phenyl*), 128.3 (2C, *Phenyl*), 127.5 (1C, *Phenyl$_{para}$*), 51.6-54.9 (m, 8C, 6x O-CH_3 & N-CH_2 & P-CH-N), 51.0 (dxt, J_{C-P} = 161.5 Hz, 14.8 Hz, 1C, P-CH-N), 30.4 (dxd, J_{C-P} = 147.2 Hz, 14.3 Hz, 1C, P-CH-CH_2), 19.3 (1C, P-CH-CH_2), 16.9 (1C, P-CH-CH_2)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 35.00 (s, 1P, minor), 33.06 (s, 1P, minor'), 31.77 (d, J_{P-P} = 17.5 Hz, 1P, major), 27.61 (d, J_{P-P} = 16.9 Hz, 1P, major), 27.06 (s, 2P, minor), 26.61 (s, 1P, major), 25.32 (s, 1P, minor')

FT-IR (cm^{-1}): 1238, 1180, 1020, 824, 723

m/z (ESI, 70 eV): 500.1 ($[M+H]^+$, 100%) **Calc. Mass $C_{18}H_{32}NO_9P_3^+$:** 499.1290 m/z

5c (63%)



Major Minor Minor'

90:7:3 (after chromatography) / 80:6:14 (before)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.39-7.49 (m, 2H, *Phenyl*), 7.18-7.33 (m, 3H, *Phenyl*), 4.56-4.82 (m, 6H, 6x C*H*-CH_3), 4.29-4.45 (m, 2H, P-C*H*-N & N-C*H*$_2$), 3.86 (d, J_{H-H} = 13.8 Hz, 1H, N-C*H*$_2$), 2.97-3.11 (m, 1H, P-C*H*-N), 2.52-2.70 (m, 1H, P-C*H*), 1.84-2.23 (m, 4H, 2x P-CH-C*H*$_2$), 1.20-1.39 (m, 36H, 12x C*H*$_3$)

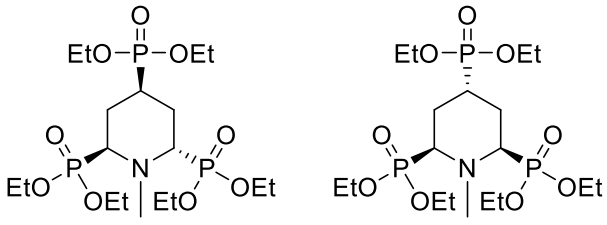
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 138.8 (1C, *Phenyl*$_{Cq}$), 129.3 (1C, *Phenyl*), 128.1 (1C, *Phenyl*), 127.1 (1C, *Phenyl*), 69.8-71.29 (m, 6C, 6x *C*H-CH_3), 55.2 (dxd, J_{C-P} = 161.2 Hz, 15.2 Hz, 1C, P-*C*H-N), 53.1 (1C, N-*C*H_2), 52.3 (dxt, J_{C-P} = 163.2 Hz, 14.6 Hz, 1C, P-*C*H-N), 31.4 (dxd, J_{C-P} = 148.1 Hz, 13.9 Hz, 1C, P-*C*H-CH_2), 23.9-24.4 (m, 12C, 12x *C*H_3), 19.3 (1C, P-CH-*C*H_2), 17.2 (1C, P-CH-*C*H_2)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 31.26 (s, 1P, minor), 29.91 (s, 1P, minor'), 27.94 (d, J_{P-P} = 16.0 Hz, 1P, major), 25.66 (s, 1P, minor'), 24.65 (s, 1P, minor'), 23.45 (d, J_{P-P} = 16.8 Hz, 1P, major), 23.19 (s, 1P, major), 23.10 (s, 2P, minor)

FT-IR (cm^{-1}): 1180, 1171, 1117, 1099, 997, 982

m/z (ESI, 70 eV): 668.3 ($[M+H]^+$, 100%) **Calc. Mass $C_{30}H_{56}NO_9P_3^+$:** 667.3168 m/z

5d (38%)



Major Minor

76:23

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 3.95-4.29 (m, 13H, P-C*H*-N$_{,major}$ & O-C*H*$_2$-$CH_{3,major\&minor}$), 3.34-3.45 (m, 1H, P-C*H*-N$_{,minor}$), 3.11-3.24 (1H, P-C*H*-N$_{,major}$), 2.70 (s, 3H, N-C*H*$_{3,major}$), 2.42-2.58 (m, 1H, P-C*H*$_{,major}$), 2.15 (s, 3H, N-C*H*$_{3,minor}$), 1.84-2.14 (m, 4H, 2x C*H*$_2$, major), 1.20-1.42 (m, 18H, O-CH_2-C*H*$_{3,major\&minor}$)

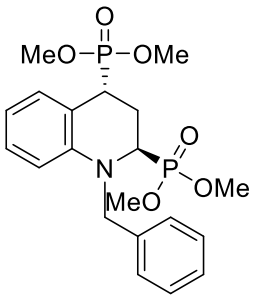
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 61.0-63.4 (m, 6C, O-*C*H_2-$CH_{3,major\&minor}$), 58.4 (dxt, J_{C-P} = 152.6 Hz, 14.9 Hz, 1C, P-*C*H-N$_{,major}$), 53.9 (dxd, J_{C-P} = 159.8 Hz, 15.8 Hz, 1C, P-*C*H-N$_{,major}$), 40.9 (s, 1C, N-*C*$H_{3,major}$), 30.9 (s, 1C, N-*C*$H_{3,minor}$), 30.5 (dxd, J_{C-P} = 148.7 Hz, 15.6 Hz, 1C, P-*C*H-CH_2), 20.0 (d, J_{C-P} = 4.1 Hz, 1C, P-CH-*C*$H_{2,major}$), 19.6 (s, 1C, P-CH-*C*$H_{2,major}$), 18.98 (s, 2C, 2x P-CH-*C*$H_{2,minor}$), 16.0-16.6 (m, 6C, O-CH_2-*C*$H_{3,major\&minor}$)

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 32.13 (s, 1P, minor), 29.56 (d, J_{P-P} = 14.0 Hz, 1P, major), 24.89 (d, J_{P-P} = 14.3 Hz, 1P, major), 24.20 (s, 2P, minor), 24.08 (s, 1P, major)

FT-IR (cm^{-1}): 1243, 1053, 1023, 966

m/z (ESI, 70 eV): 508.2 ($[M+H]^+$, 100%) **Calc. Mass $C_{18}H_{40}NO_9P_3^+$:** 507.1916 m/z

5f (65%)



100:0

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.65 (d, J_{H-H} = 7.7 Hz, 1H, N-Cq-Cq-C*H*), 7.20-7.34 (m, 5H, *Phenyl*), 7.04 (~t, J_{H-H} = 7.7 Hz, 1H, N-Cq-CH-C*H*), 6.72 (t, J_{H-H} = 7.4 Hz, 1H, N-Cq-CH-CH-C*H*), 6.67 (d, J_{H-H} = 8.4 Hz, 1H, N-Cq-C*H*), 4.80 (d, J_{H-H} = 16.4 Hz, 1H, N-CH_2), 4.53 (d, J_{H-H} = 16.5 Hz, 1H, N-CH_2), 3.82-3.89 (m, 1H, P-C*H*-N), 3.75 (d, J_{H-H} = 10.7 Hz, 3H, O-CH_3), 3.63-3.77 (m, 1H, P-C*H*-Cq), 3.63 (d, J_{H-H} = 10.5 Hz, 3H, O-CH_3), 3.57 (d, J_{H-H} = 10.6 Hz, 3H, O-CH_3), 3.44 (d, J_{H-H} = 10.5 Hz, 3H, O-CH_3), 2.40-2.66 (m, 2H, P-CH-CH_2)

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 144.4 (d, J_{C-P} = 8.0 Hz, 1C, N-*Cq*), 137.9 (1C, *Cq*-CH_2), 129.6 (d, J_{C-P} = 5.0 Hz, 1C, N-Cq-Cq-*C*H), 128.6 (2C, *Phenyl*), 128.2 (d, J_{C-P} = 2.0 Hz, 1C, N-Cq-CH-*C*H), 127.1 (1C, *Phenyl*$_{para}$), 127.0 (2C, *Phenyl*), 117.8 (1C, N-Cq-CH-CH-*C*H), 117.0 (d, J_{C-P} = 6.0 Hz, 1C, N-Cq-*Cq*), 113.7 (1C, N-Cq-*C*H), 55.3 (1C, N-*C*H_2), 53.9 (dxd, J_{C-P} = 151.8 Hz, 10.4 Hz, 1C, P-*C*H-N), 53.5 (d, J_{C-P} = 6.7 Hz, 1C, O-*C*H_3), 52.7 (d, J_{C-P} = 6.8 Hz, 1C, O-*C*H_3), 52.7 (d, J_{C-P} = 6.7 Hz, 1C, O-*C*H_3), 52.2 (d, J_{C-P} = 7.5 Hz, 1C, O-*C*H_3), 32.7 (dxd, J_{C-P} = 142.2 Hz, 3.7 Hz, 1C, P-*C*H-Cq), 25.4 (d, J_{C-P} = 3.5 Hz, 1C, P-CH-*C*H_2)

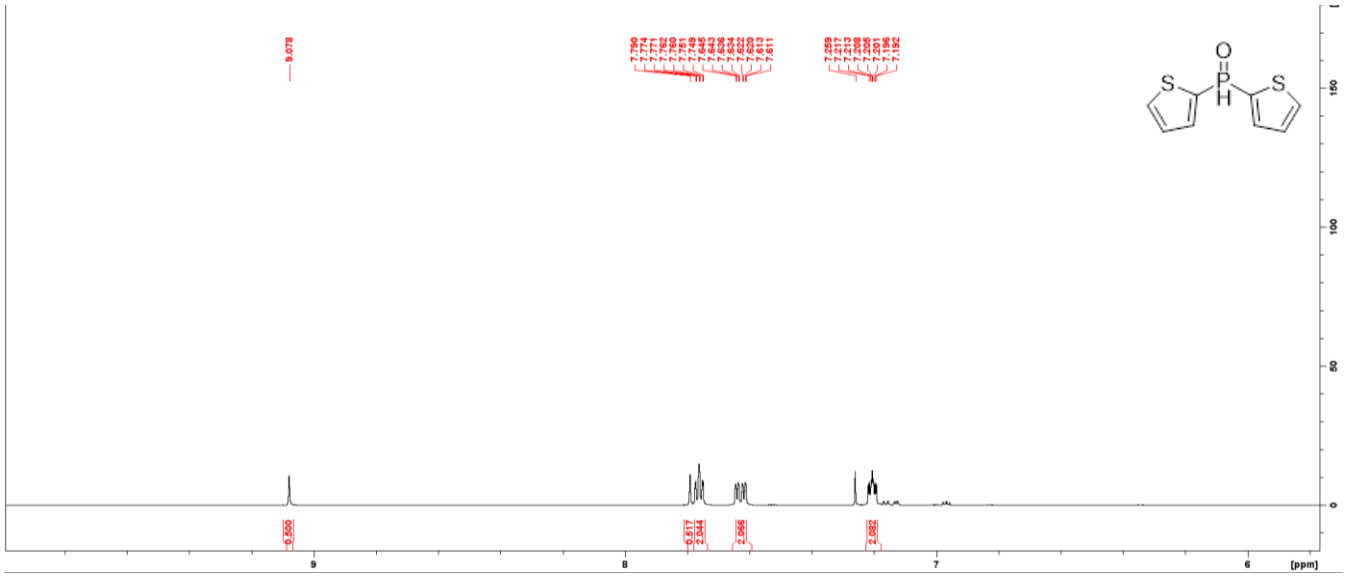
^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 30.80 (s, 1P), 26.85 (s, 1P)

FT-IR (cm^{-1}): 1497, 1217, 1180, 1024, 824, 797

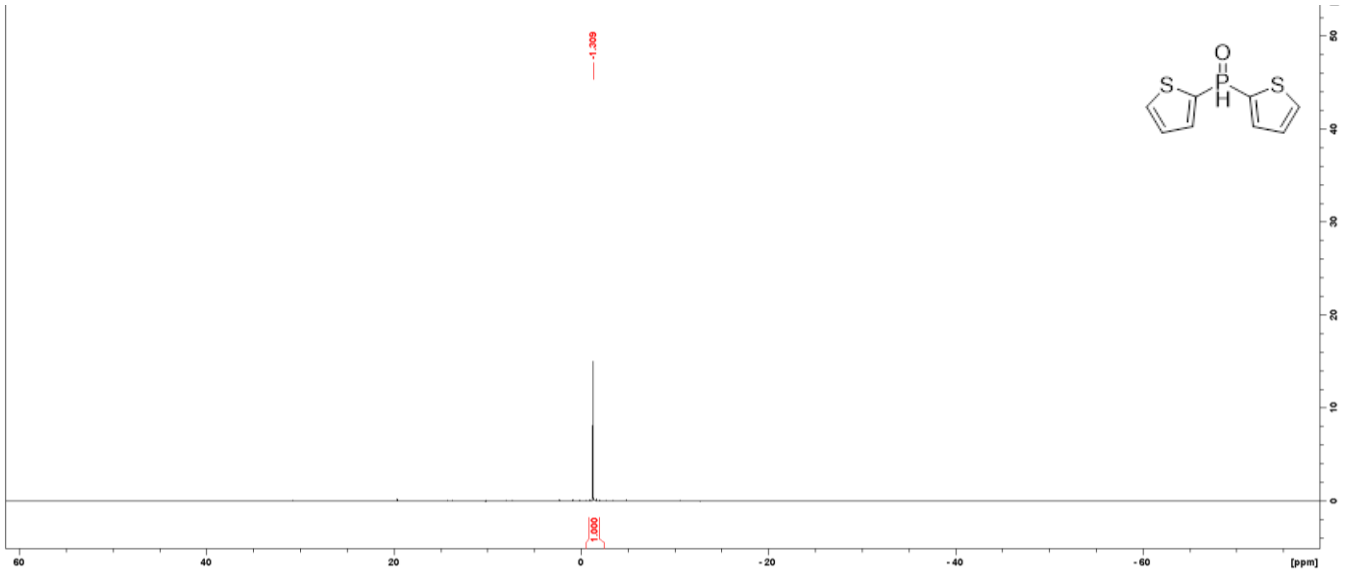
m/z (ESI, 70 eV): 440.1 ($[M+H]^+$, 100%) **Calc. Mass $C_{20}H_{27}NO_6P_2^+$:** 439.1314 m/z

NMR spectra

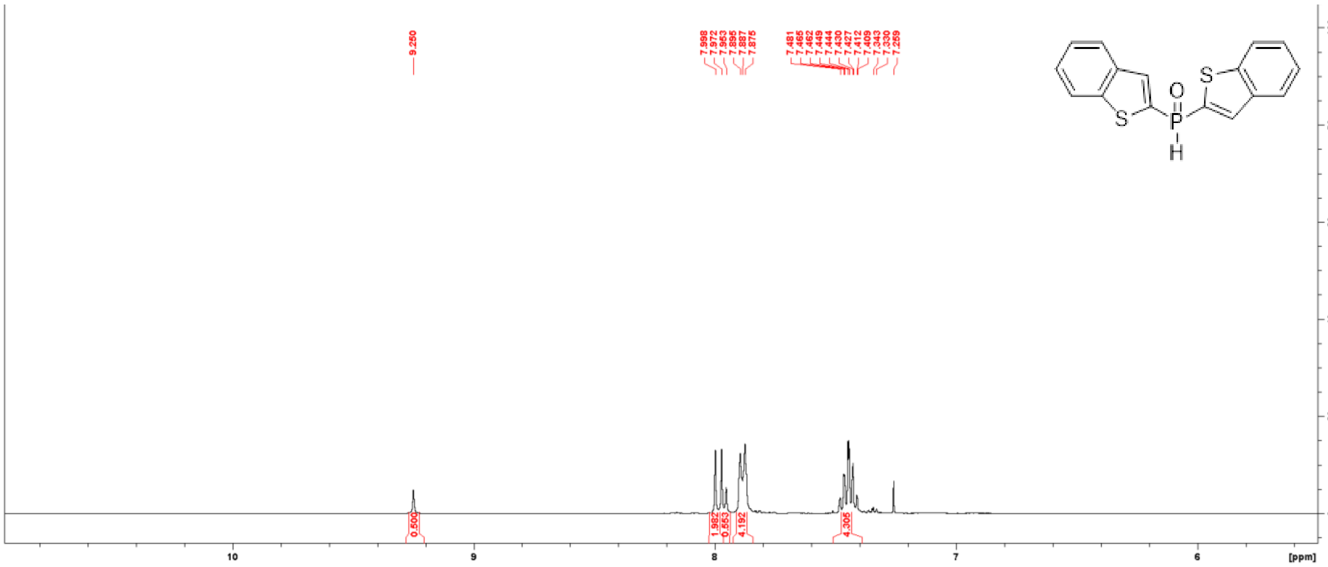
^{1}H



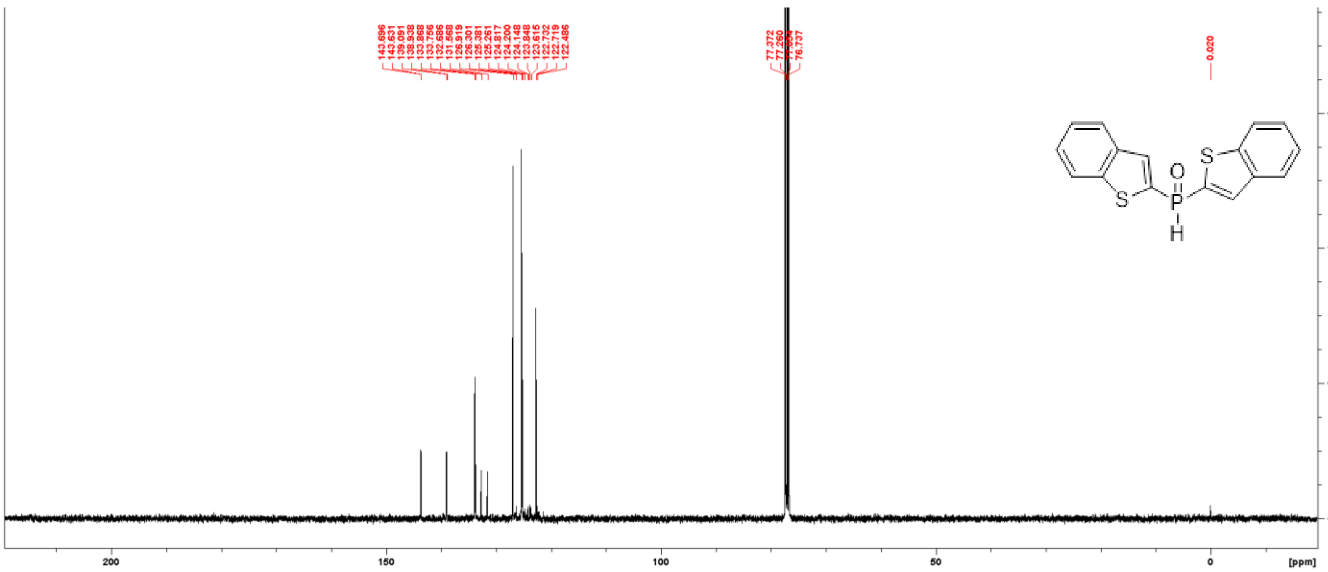
^{31}P



^{1}H



^{13}C



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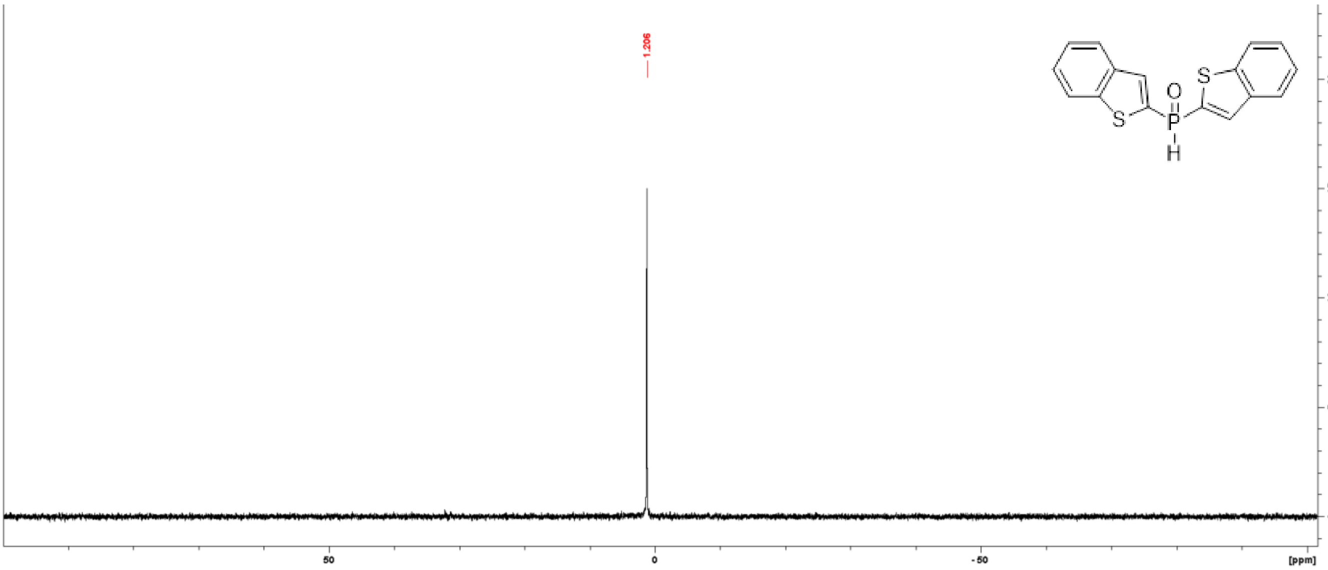

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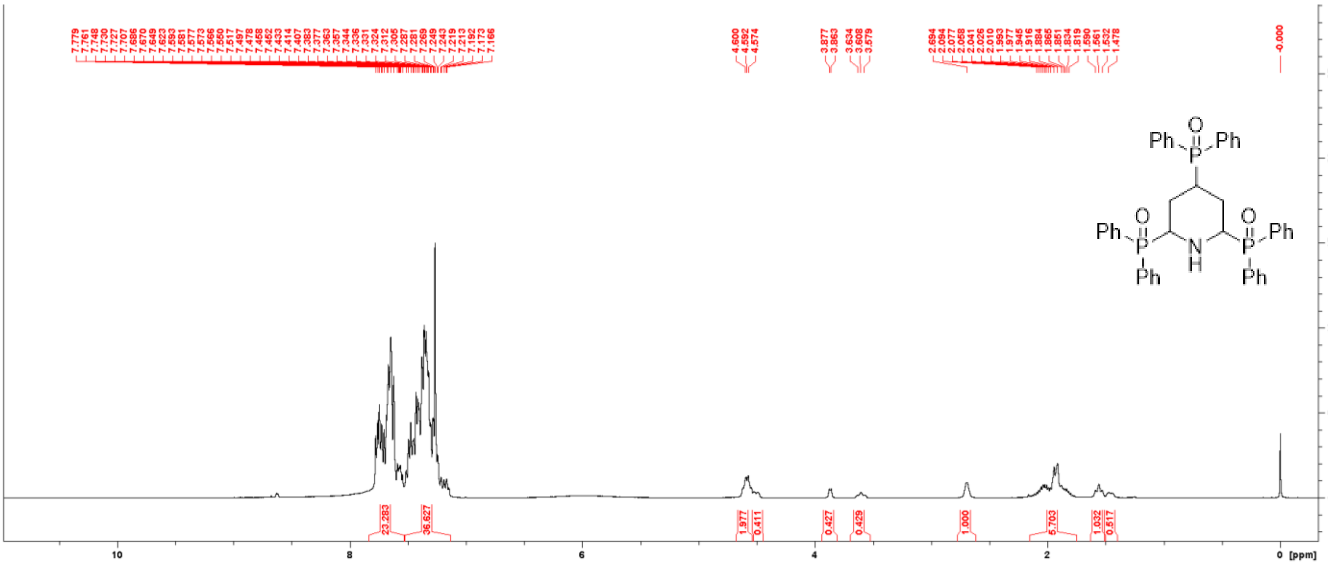

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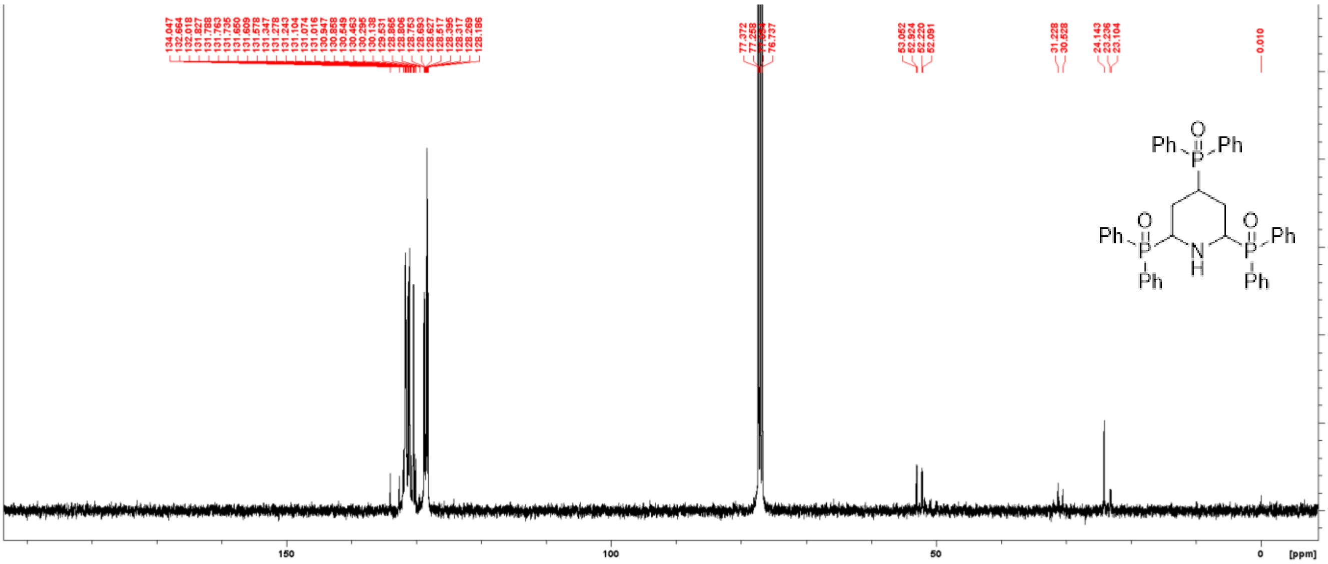

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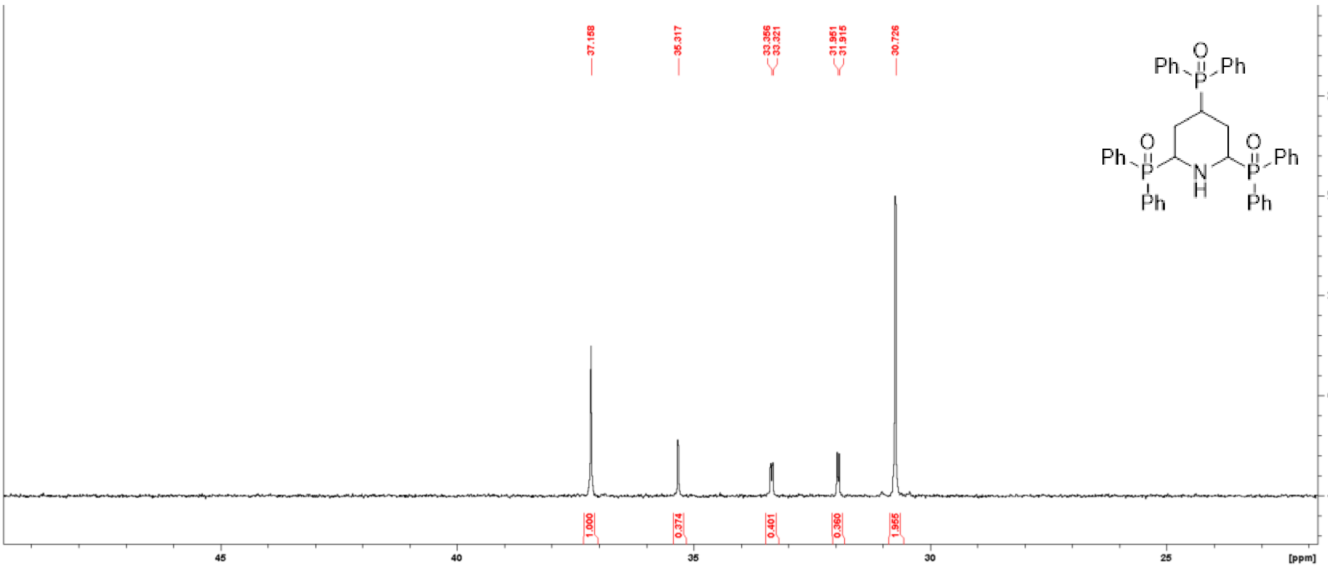
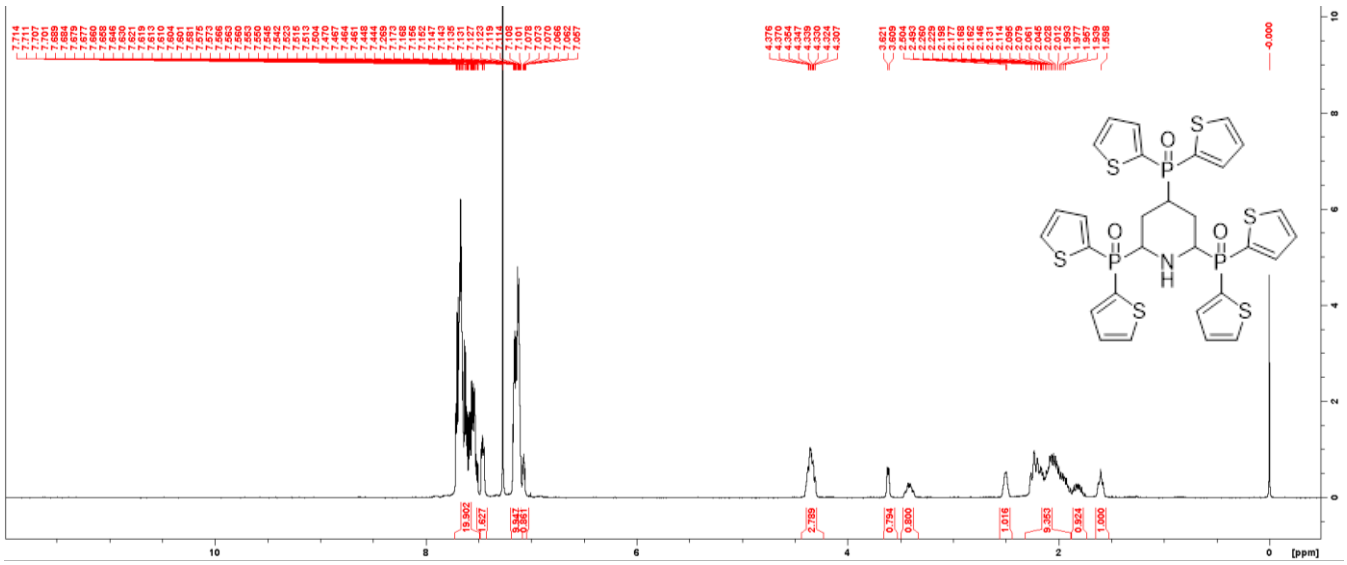
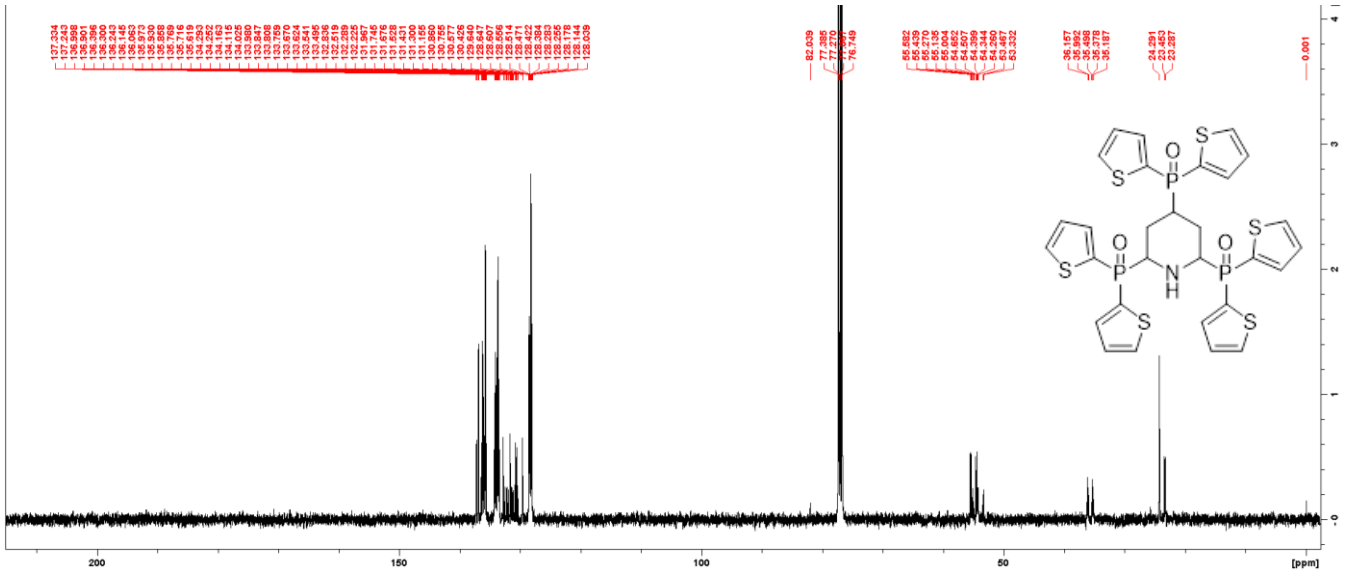


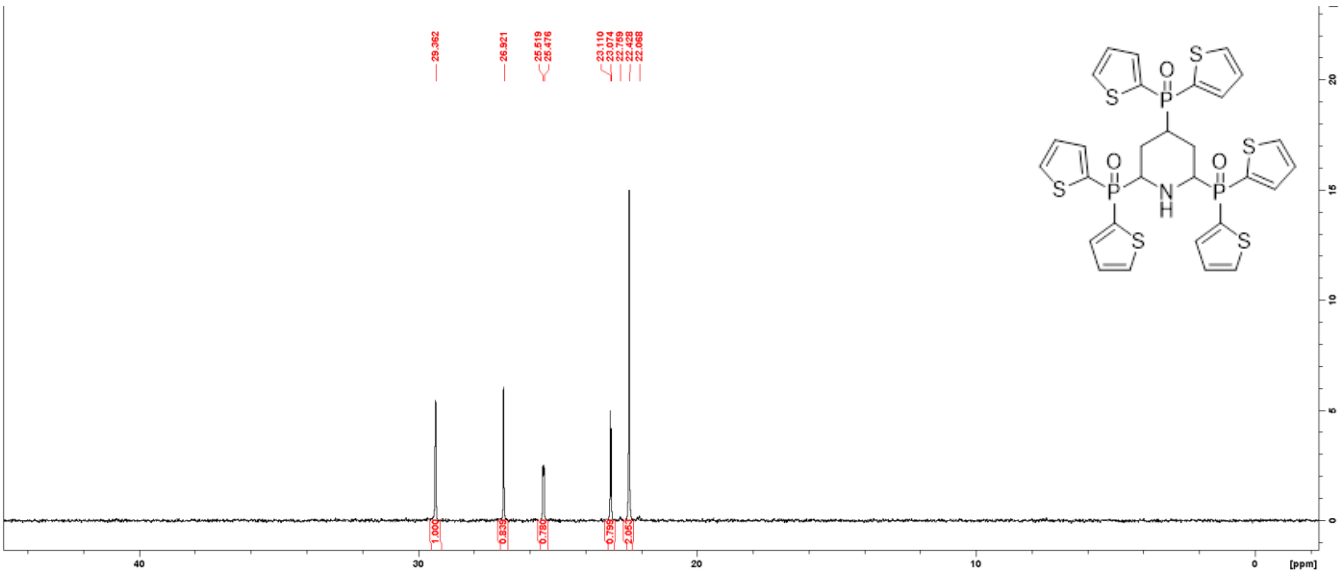
^{1}H



^{13}C



^{31}P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30
20
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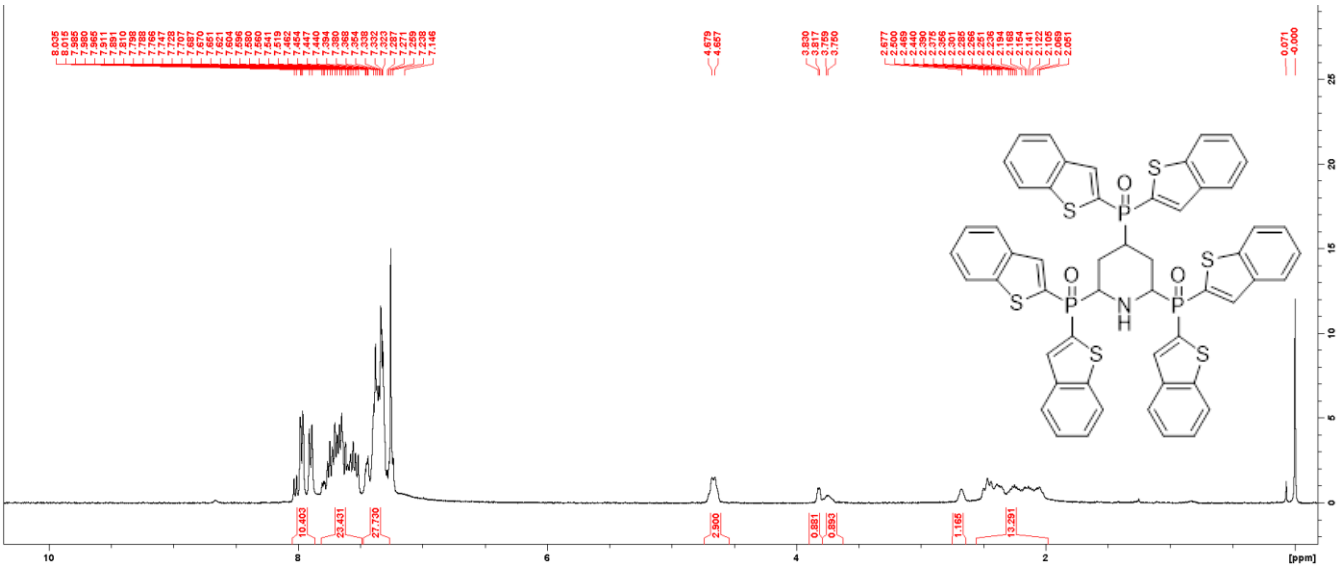
0
[ppm]

^{1}H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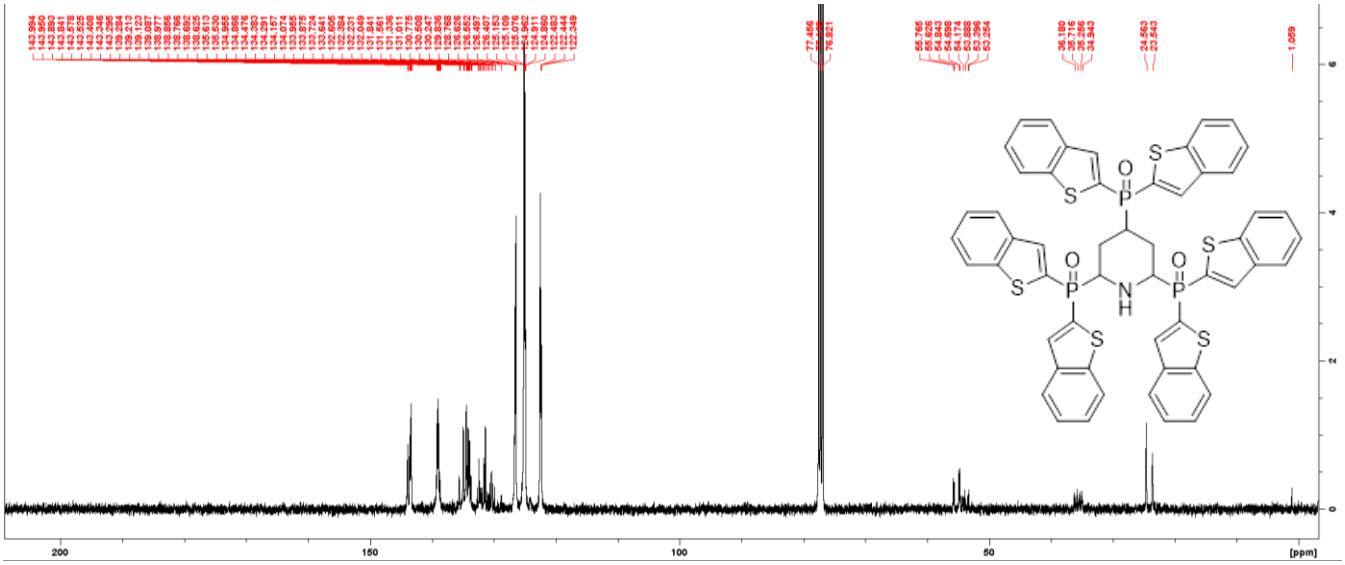
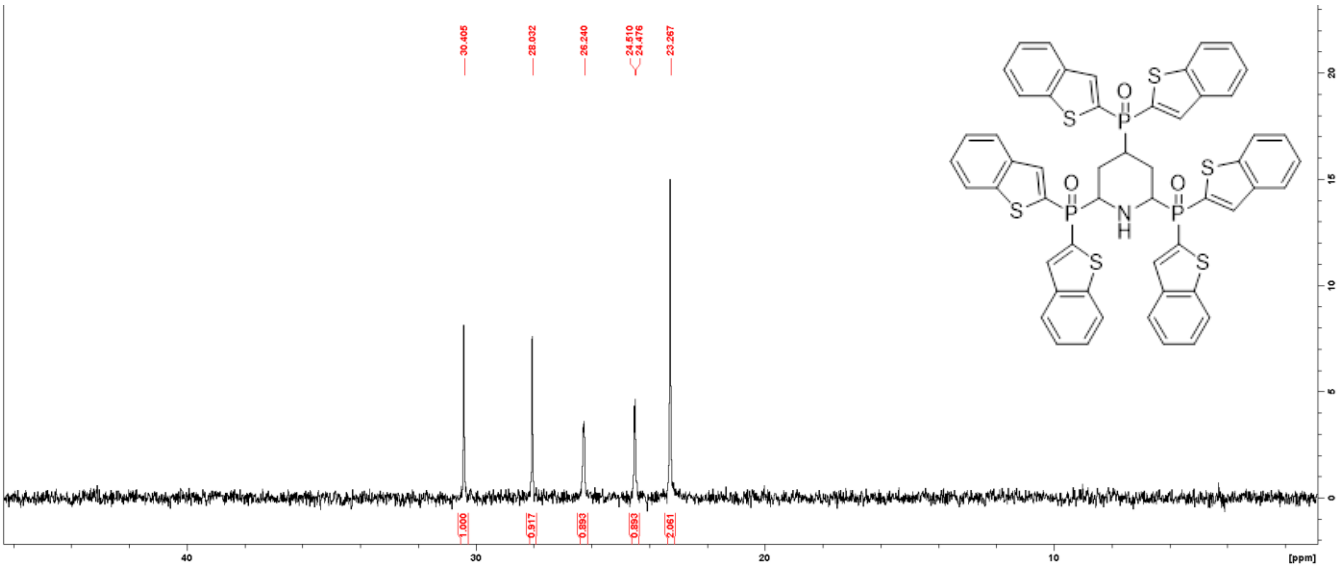
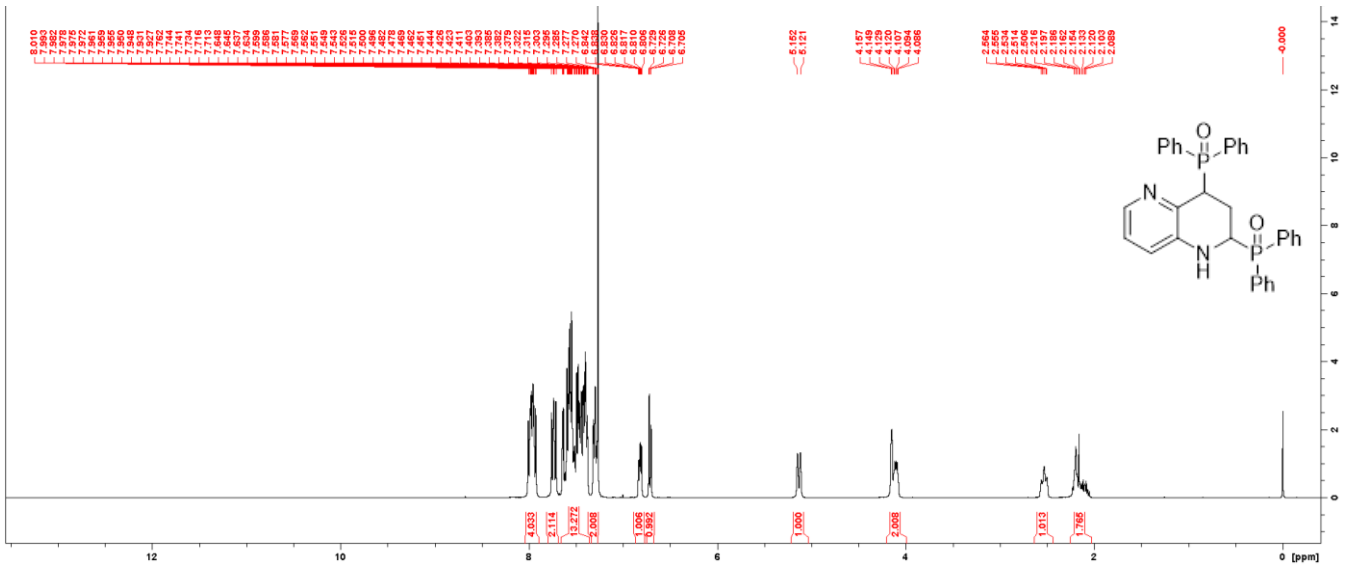
^{13}C



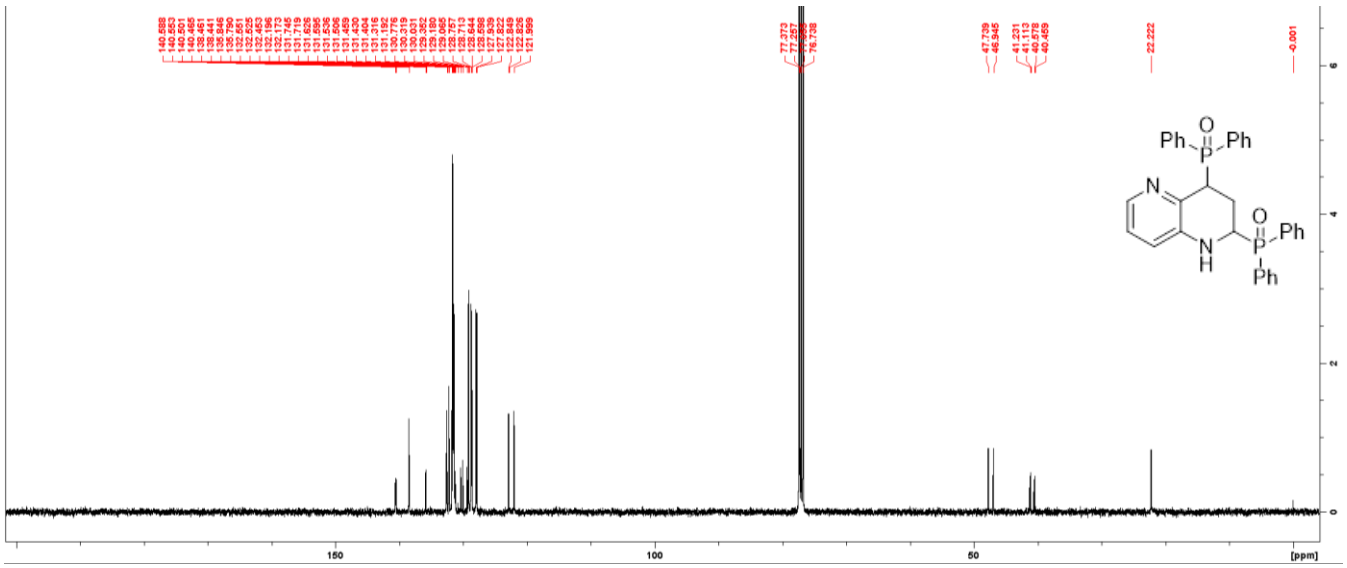
^{31}P



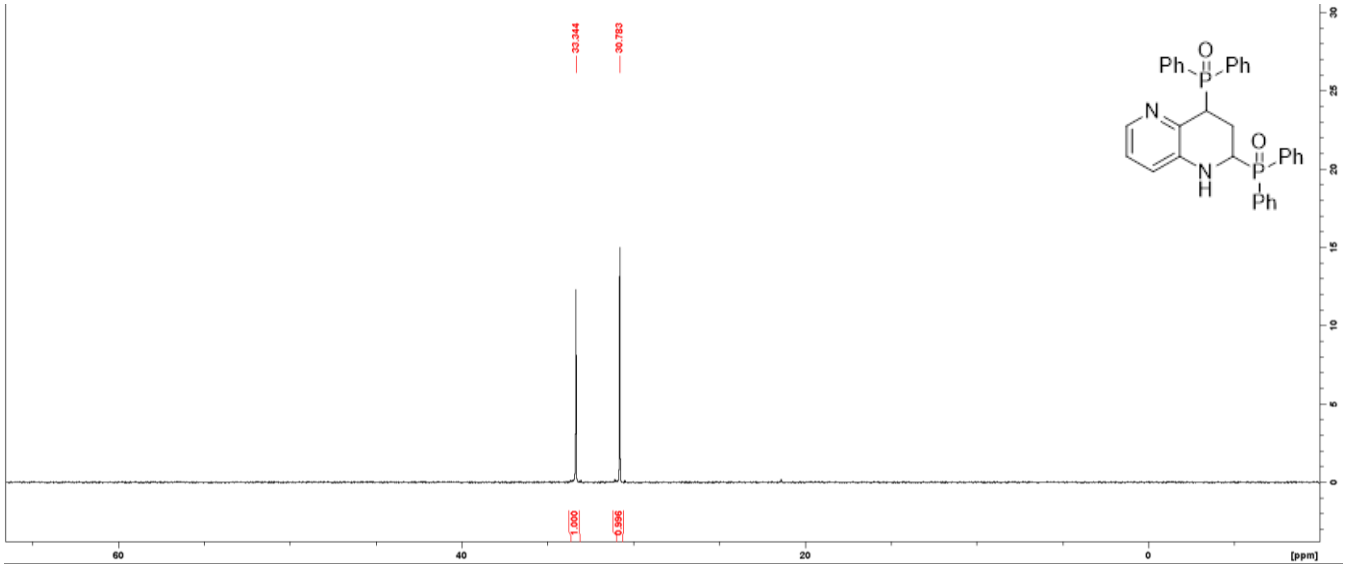
^{1}H



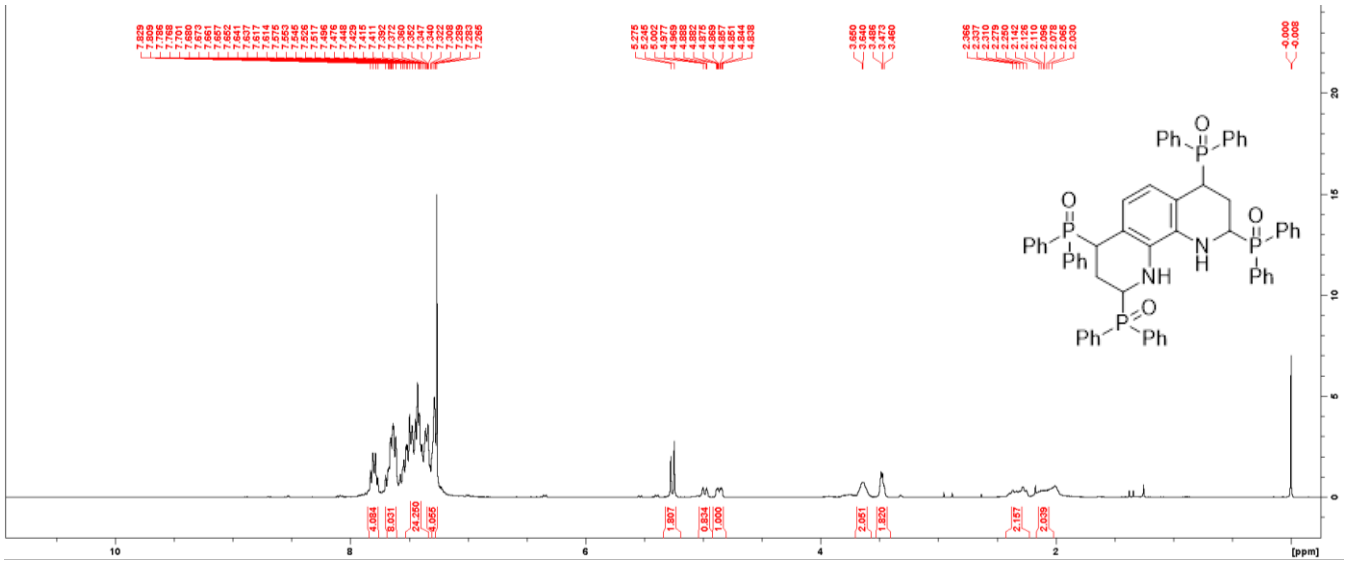
^{13}C



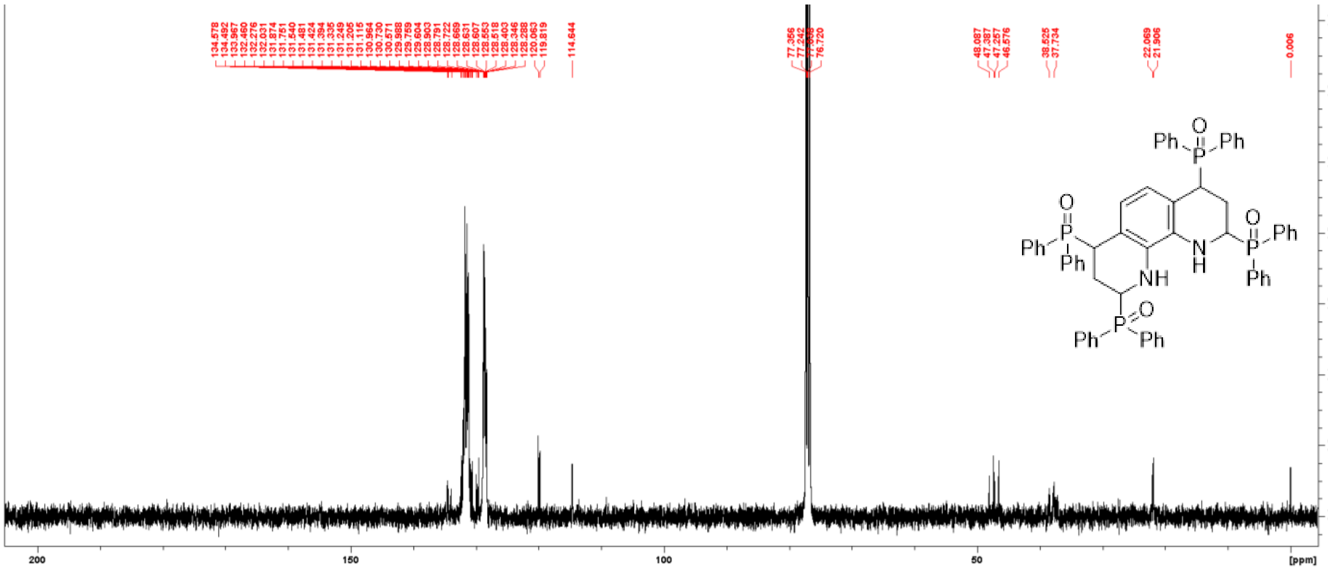
^{31}P


33.344
30.783
1.000
0.996
60
40
20
0
[ppm]

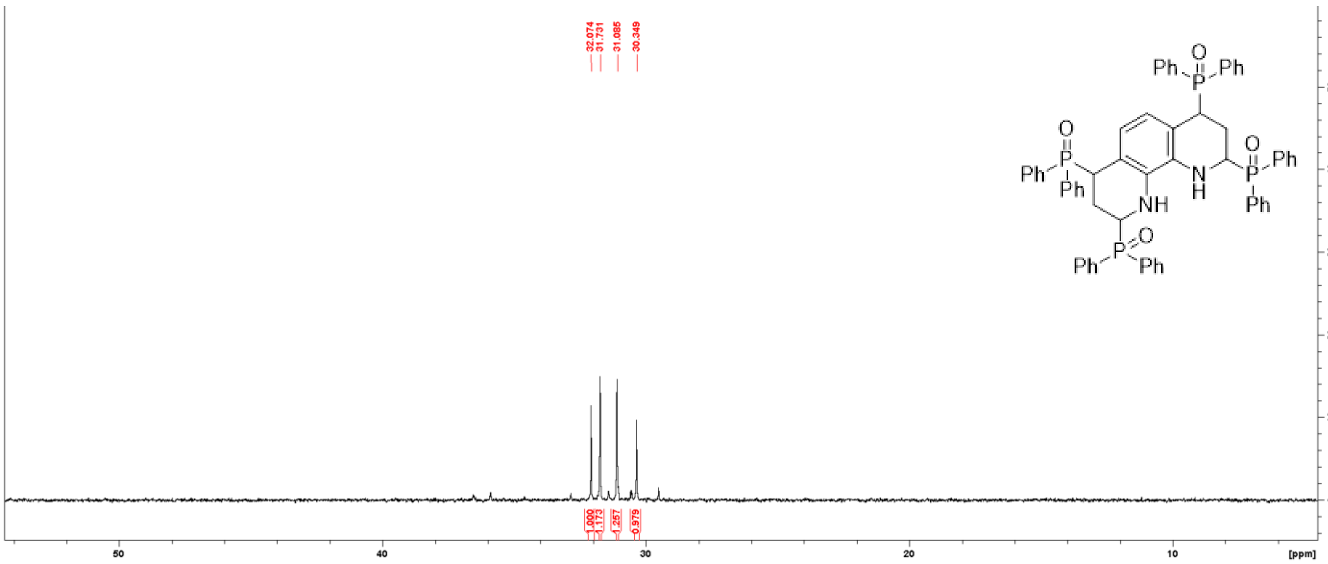
^{1}H


4.084
8.031
24.259
6.095
1.897
0.834
1.000
2.051
1.820
2.157
2.039
10
8
6
4
2
[ppm]

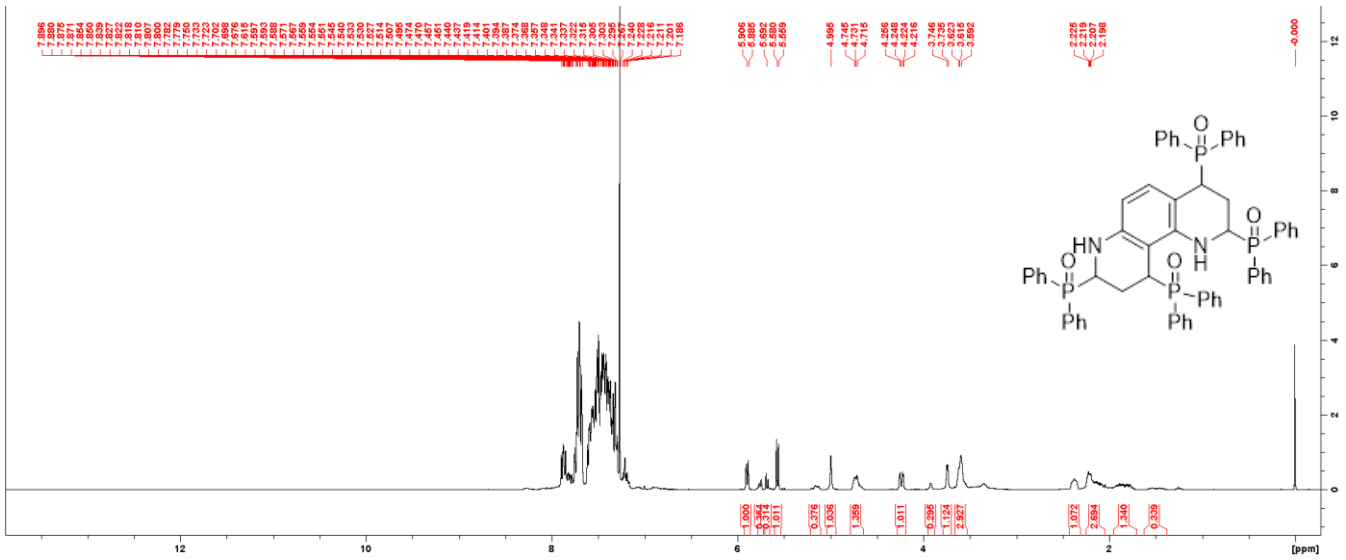
^{13}C


Ph
P
O
Ph
Ph
P
O
Ph
NH
N
H
P
O
Ph
Ph
P
O
Ph
Ph
[ppm]

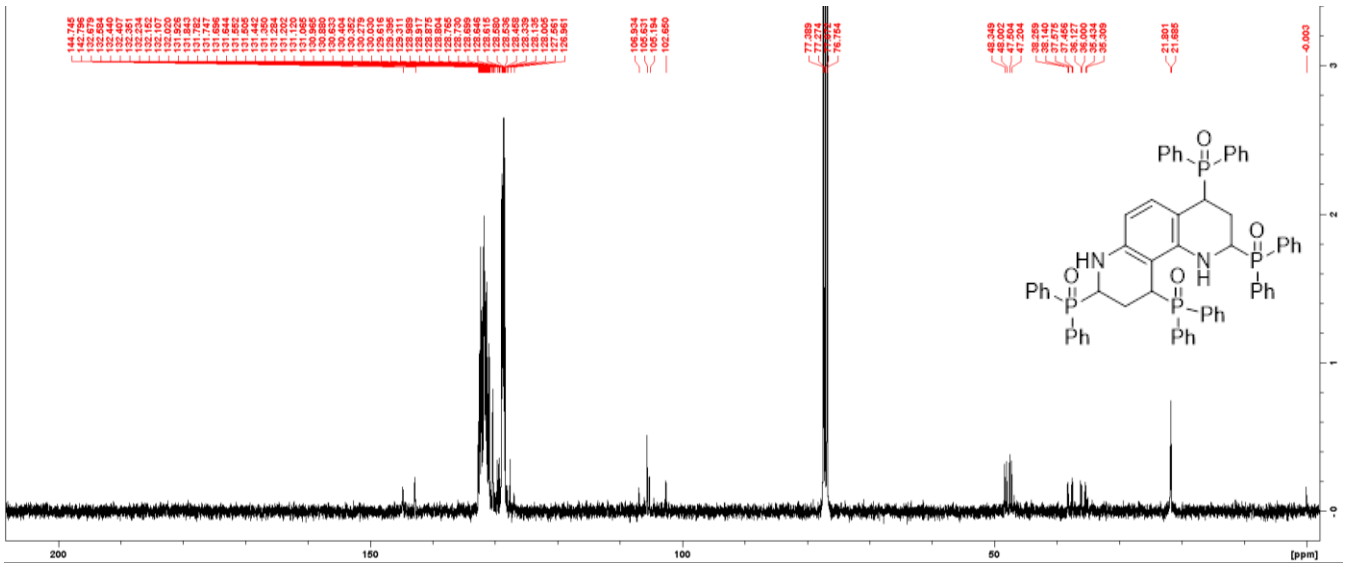
^{31}P


32.074
31.731
31.085
30.349
Ph
P
O
Ph
NH
N
H
[ppm]

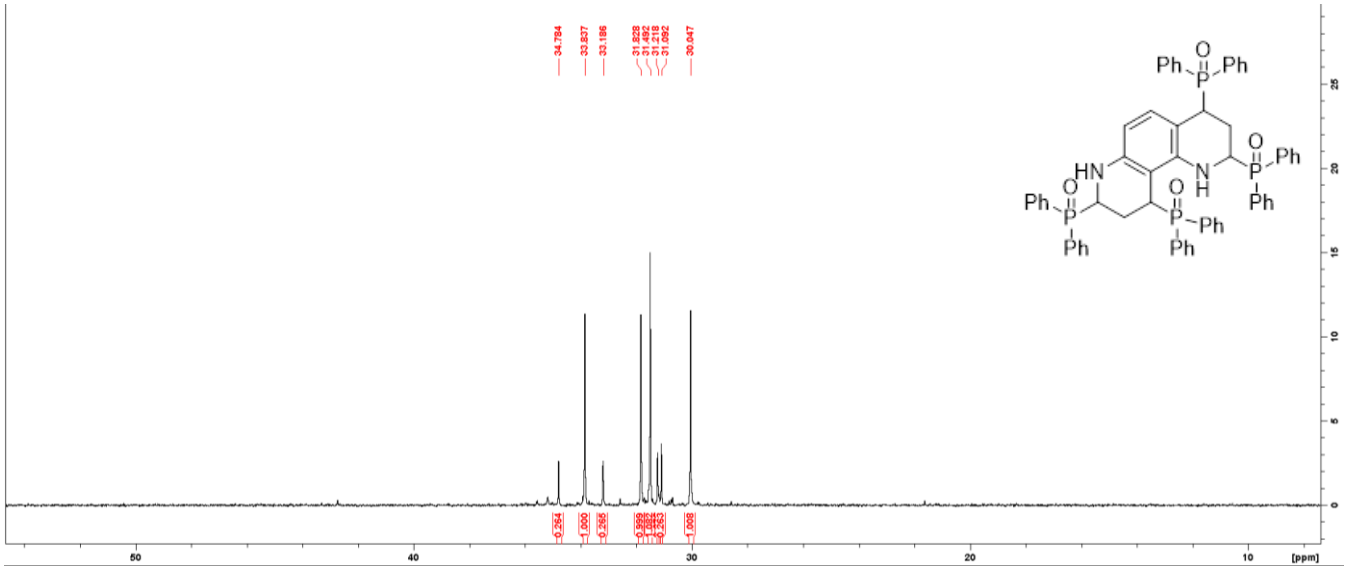
^{1}H



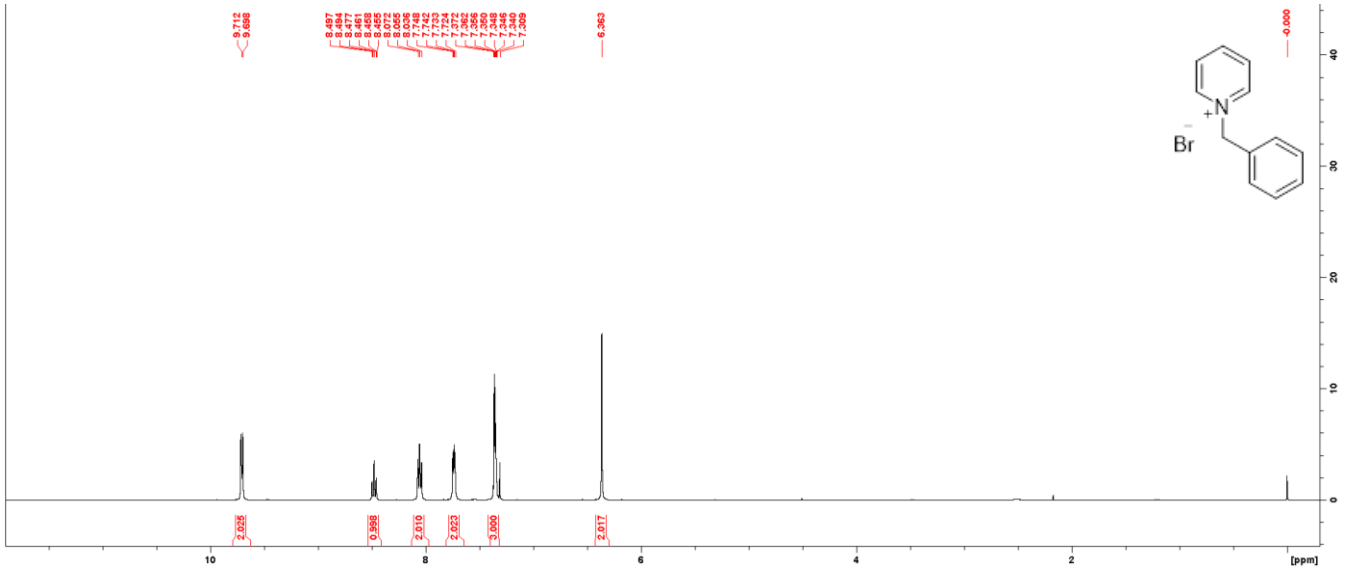
^{13}C



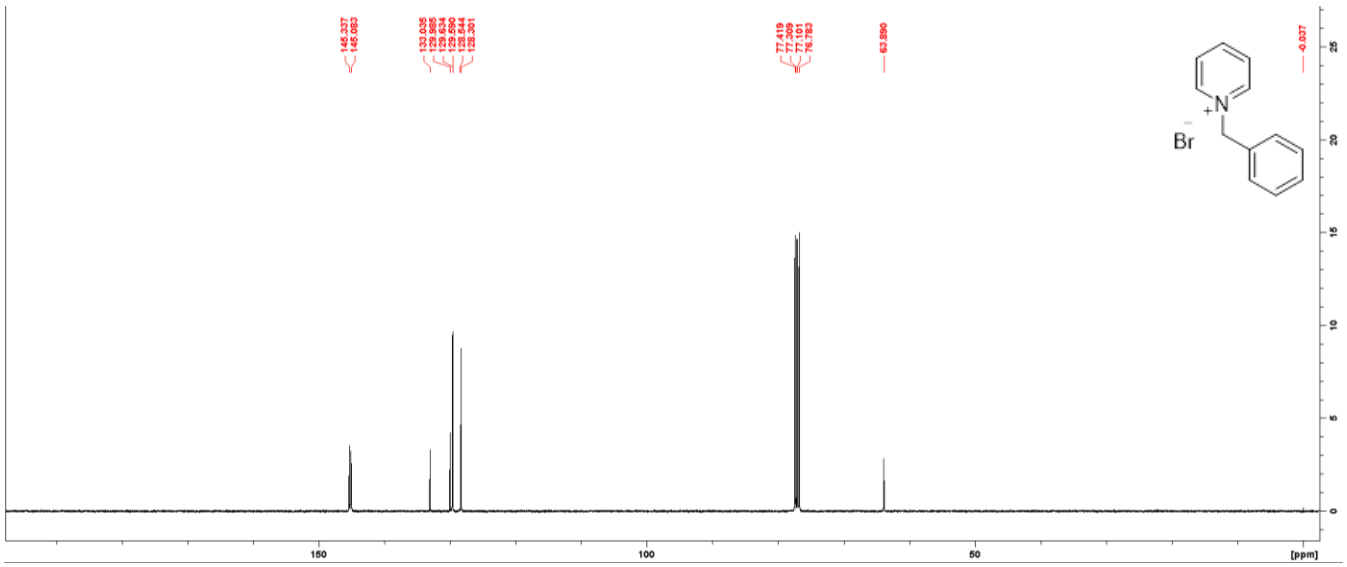
^{31}P


34.784
33.837
33.186
31.828
31.492
31.218
31.092
30.047
Ph
O
P
Ph
HN
N
H
50
40
30
20
10
[ppm]

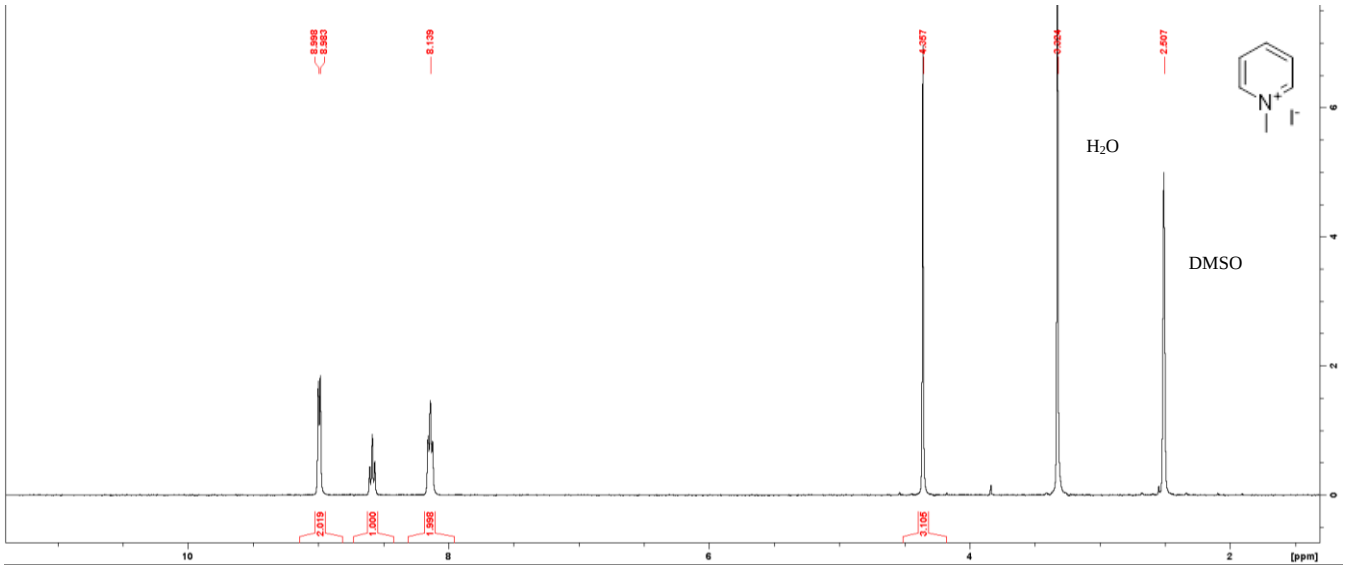
^{1}H


9.712
9.698
8.487
8.484
8.477
8.461
8.458
8.455
8.072
8.055
8.036
7.748
7.747
7.743
7.724
7.722
7.382
7.366
7.349
7.348
7.346
7.340
7.339
6.363
0.000
Br
N
10
8
6
4
2
[ppm]

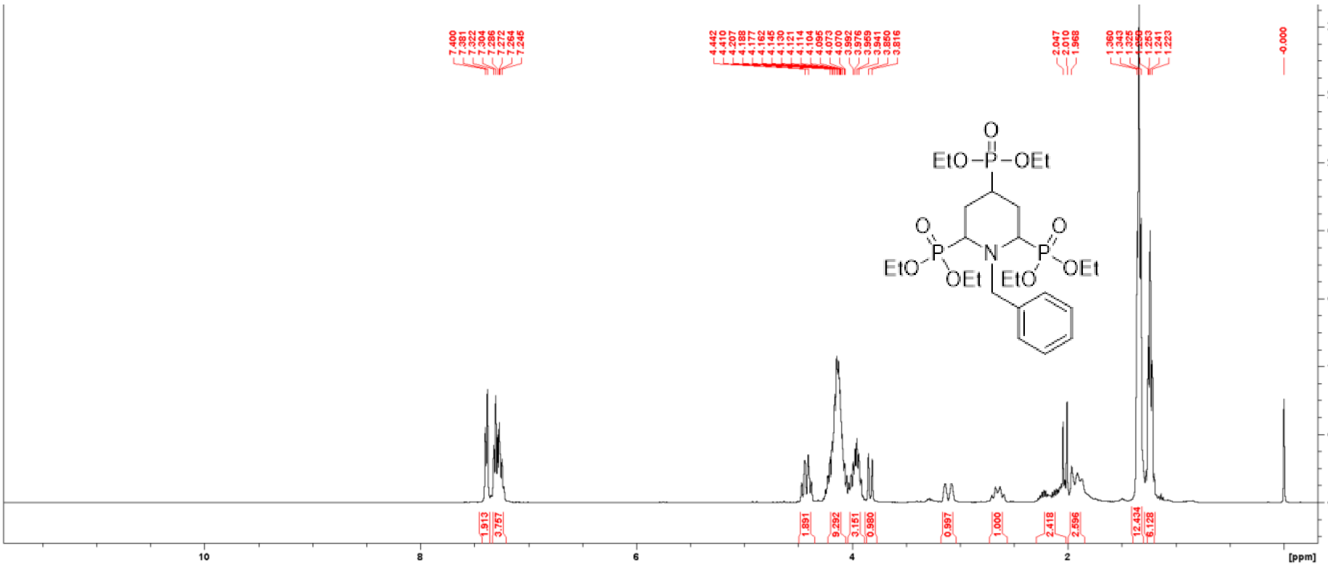
^{13}C


145.327
145.063
133.035
129.985
129.634
129.290
128.544
128.301
77.419
77.099
77.101
76.783
63.890
-0.037
Br
150
100
50
[ppm]

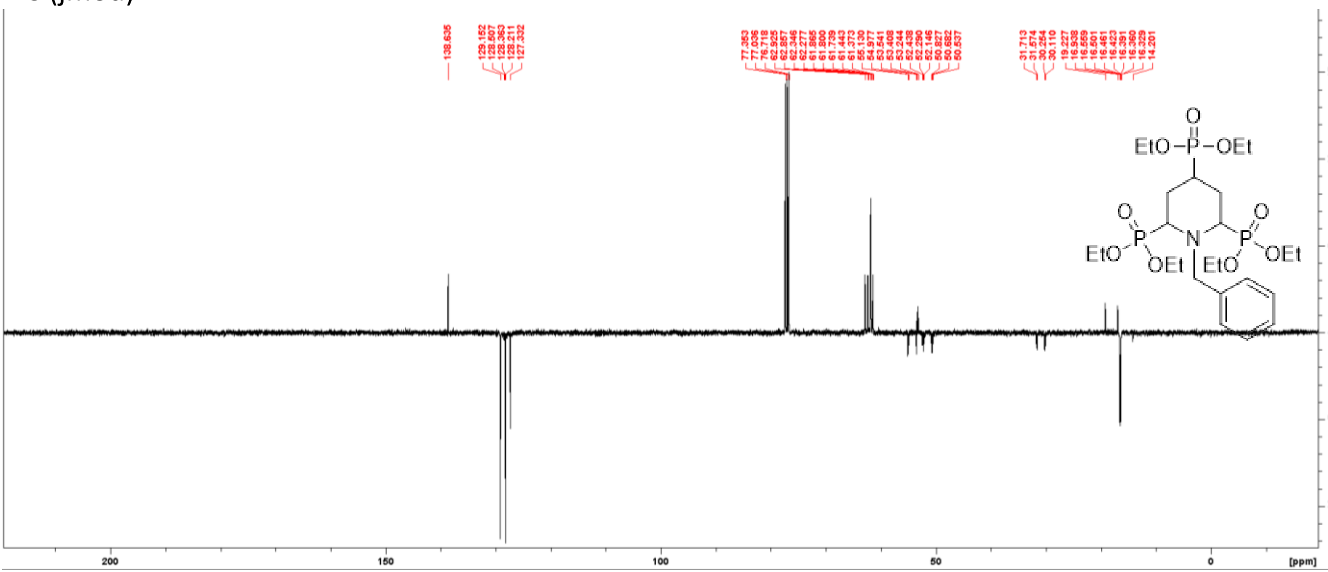
^{1}H


8.998
8.983
8.139
4.357
3.324
2.507
H2O
DMSO
2.019
1.000
1.998
3.105
10
8
6
4
2
[ppm]

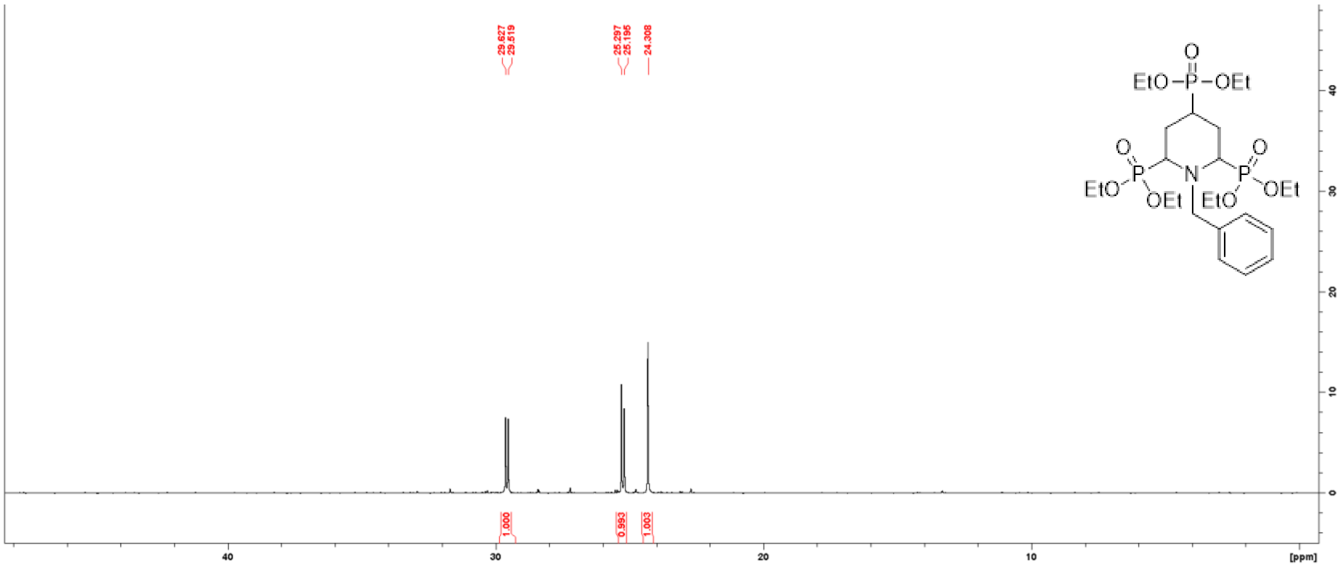
^1H



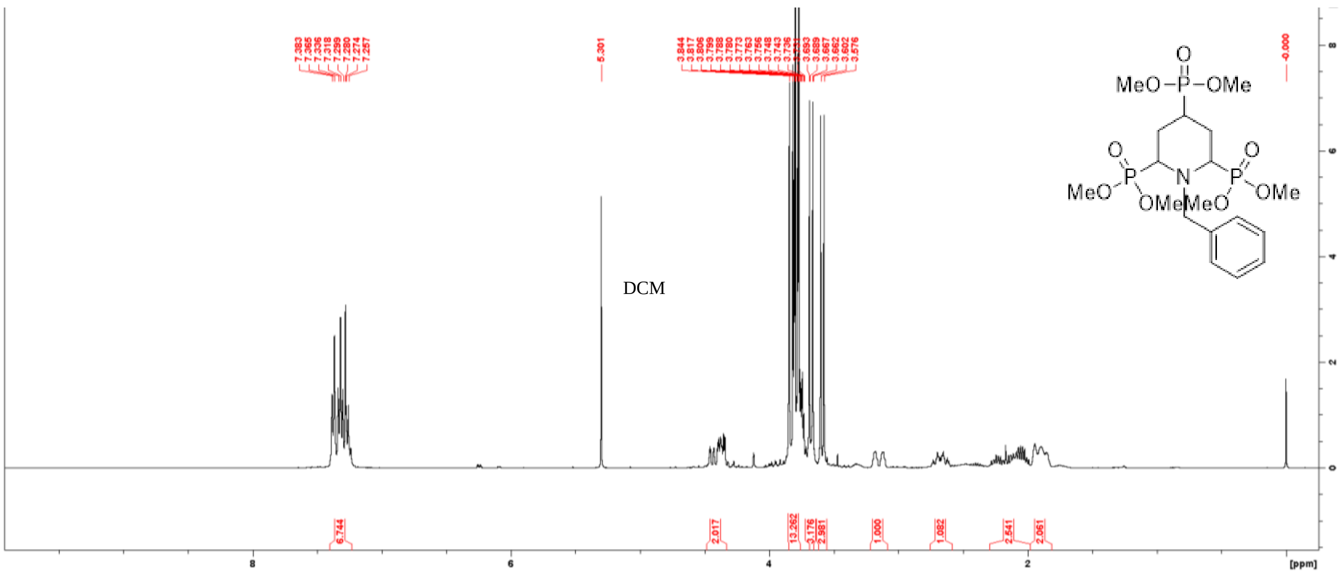
^{13}C (jmod)



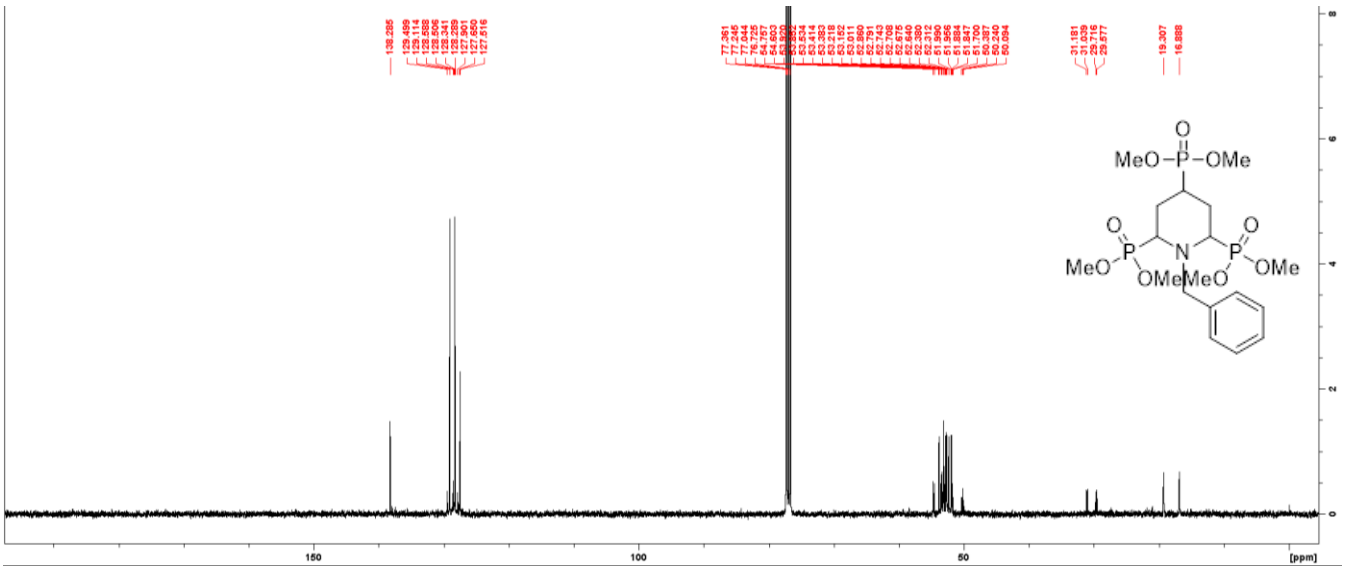
^{31}P



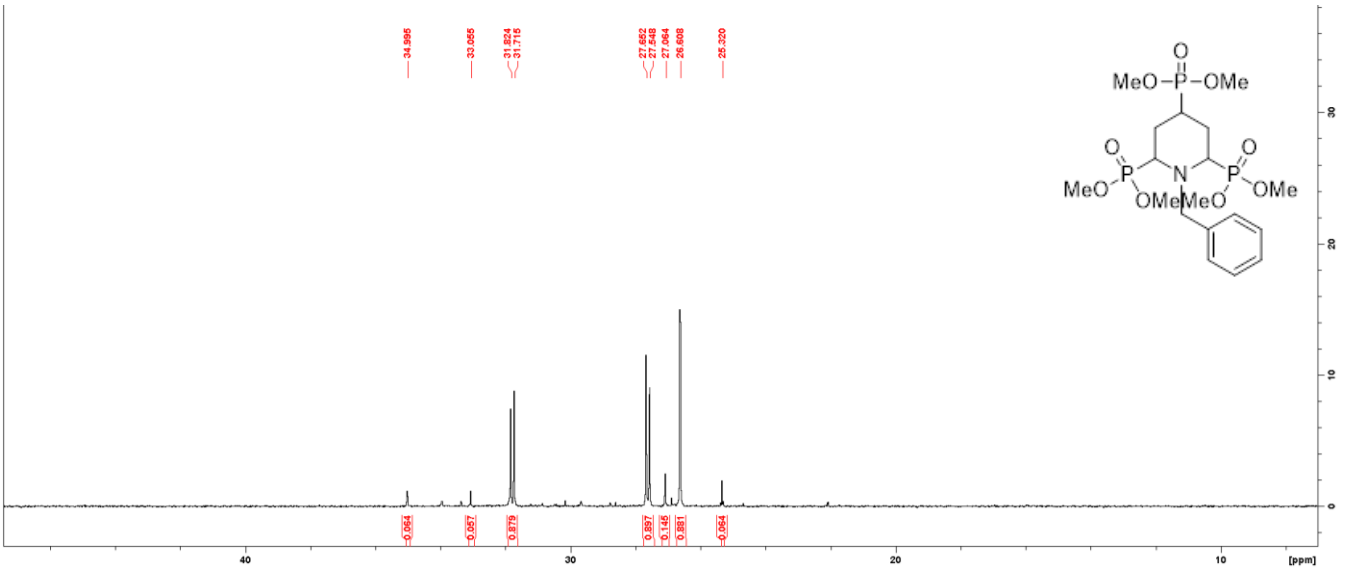
^{1}H



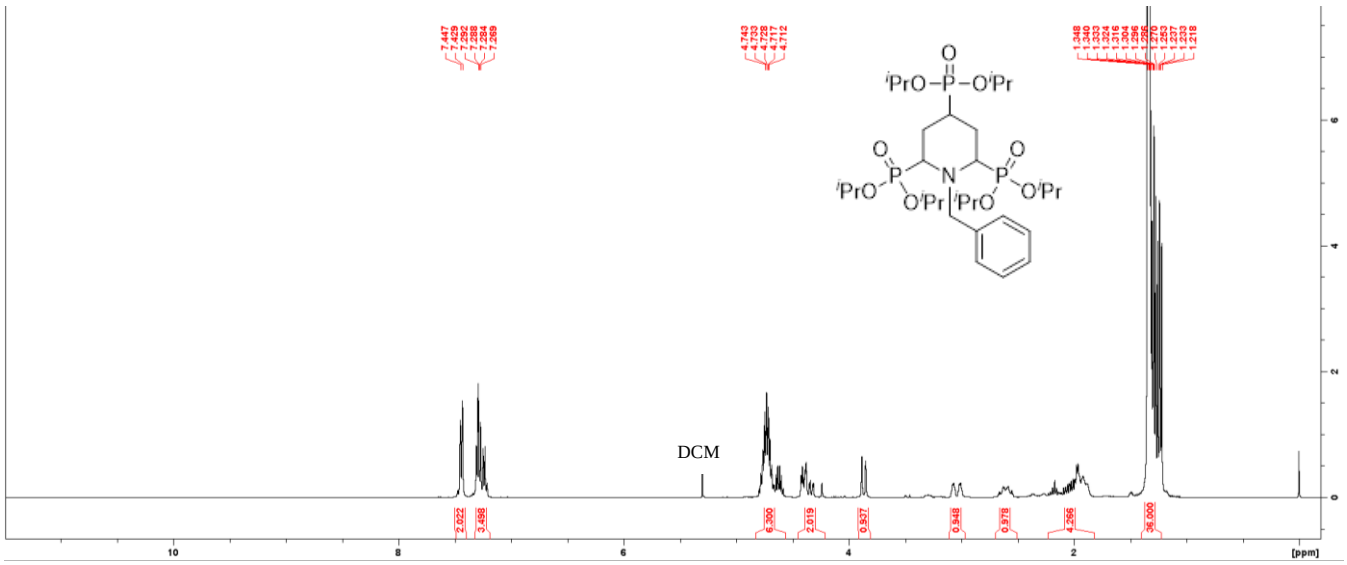
^{13}C



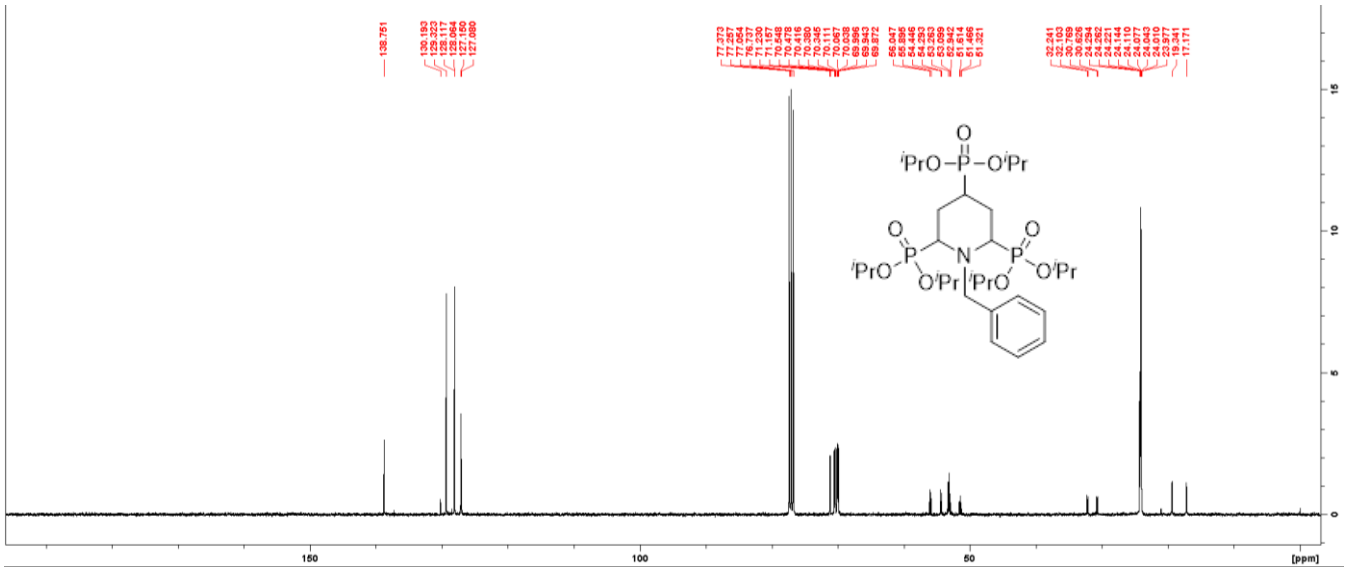
^{31}P



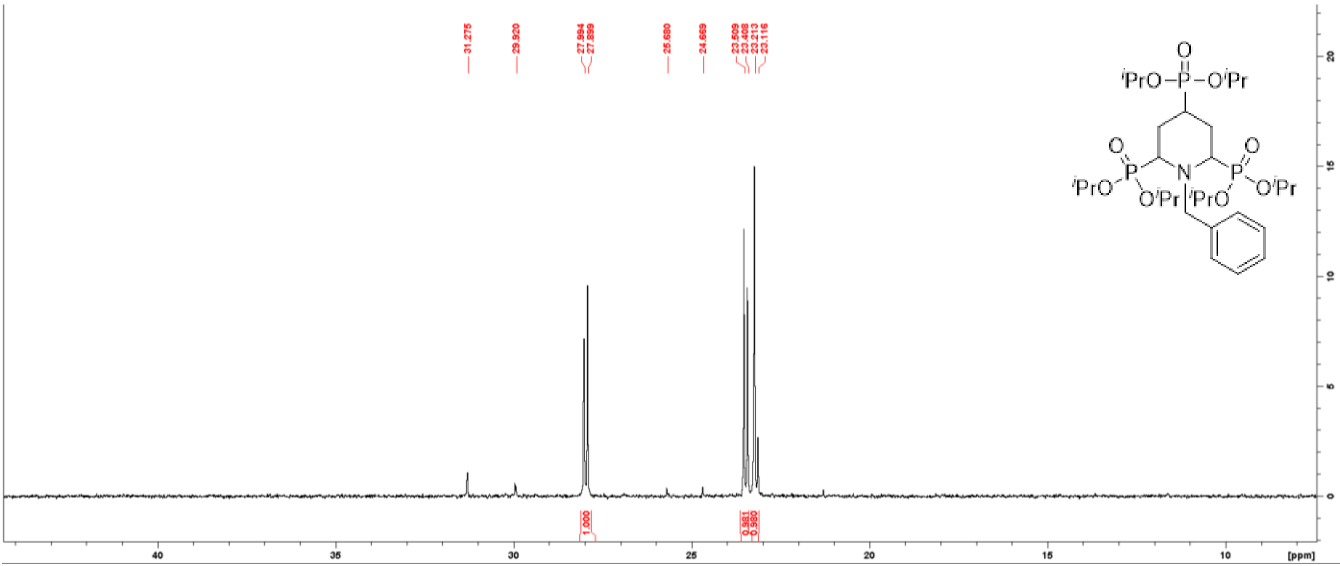
^{1}H



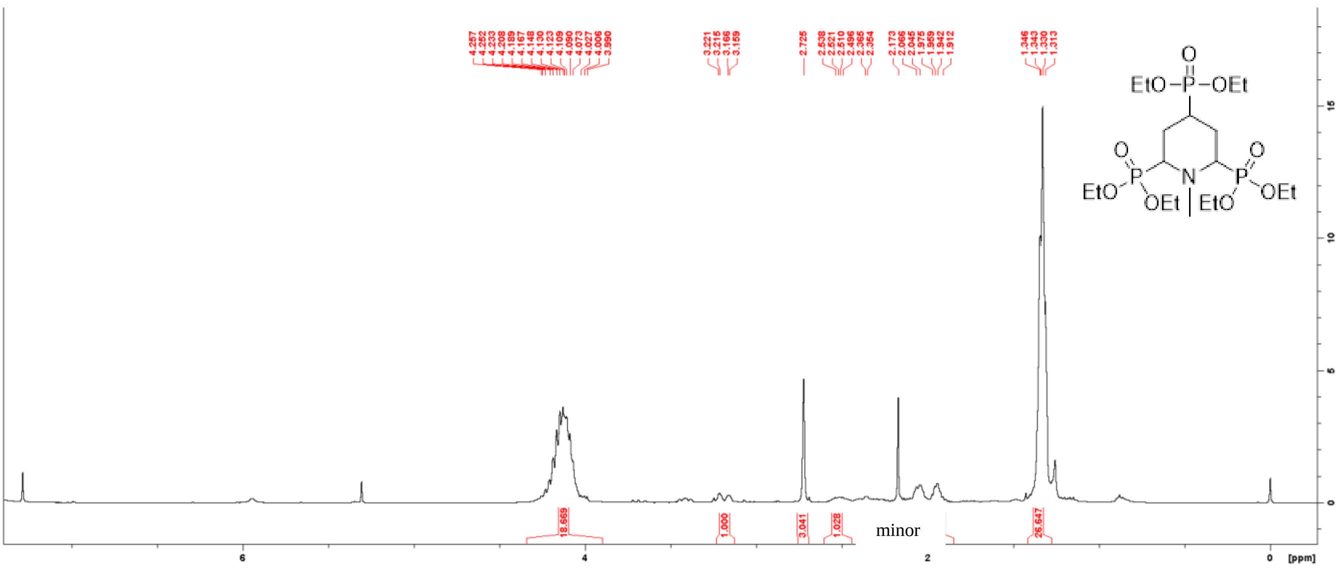
^{13}C



^{31}P

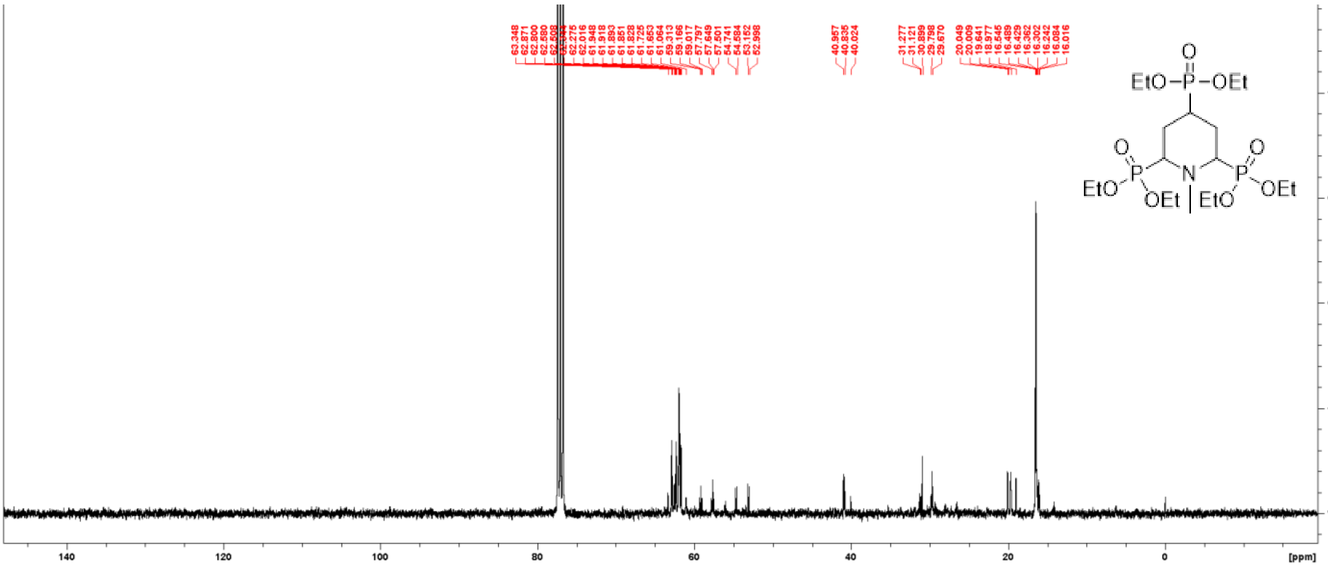

31.275
29.920
27.994
27.899
25.680
24.669
23.509
23.408
23.213
23.116
1.000
0.981
0.980
40
35
30
25
20
15
10
[ppm]

^{1}H

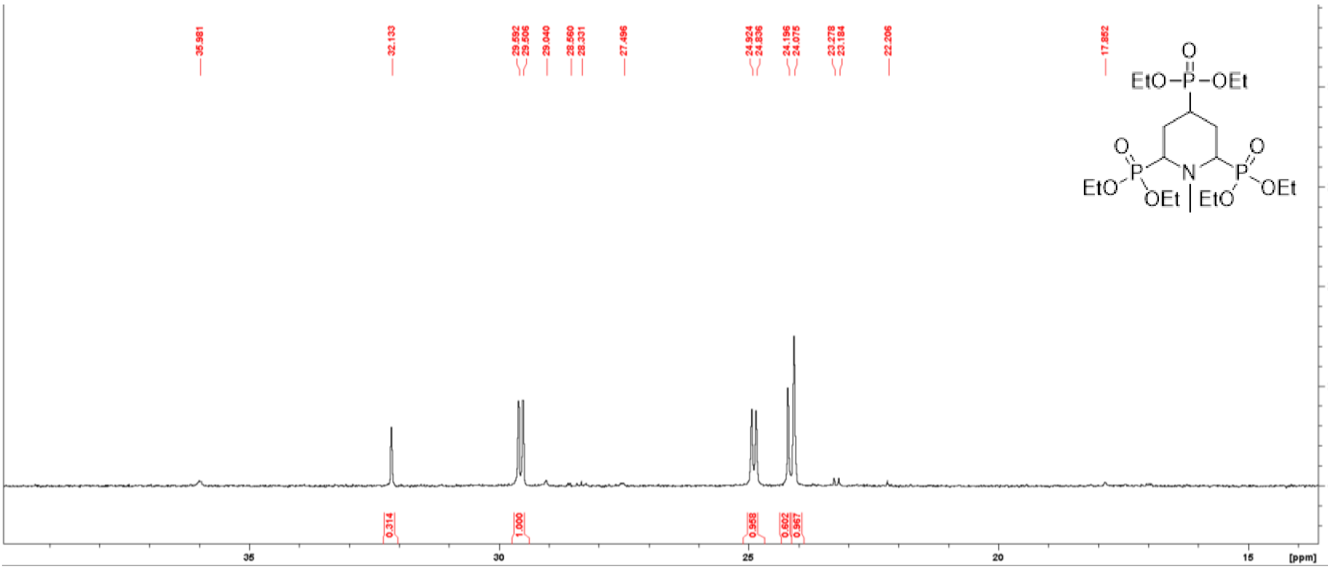

2.726
18.669
1.000
3.041
1.028
minor
25.647
6
4
2
0
[ppm]

DCM

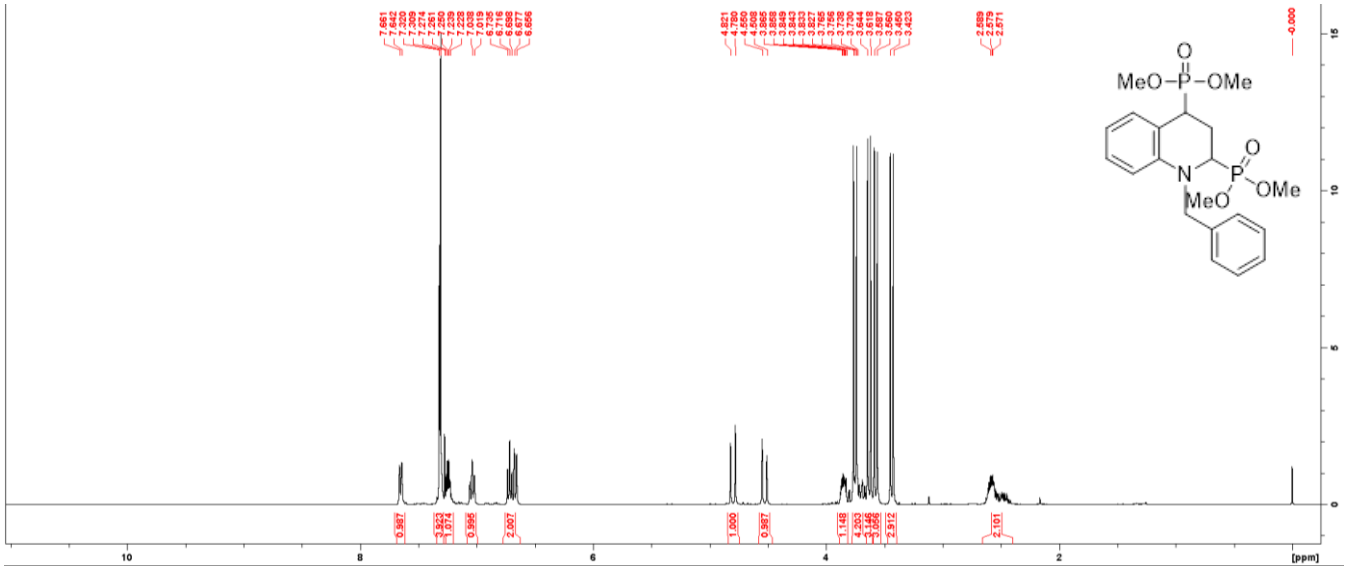
^{13}C



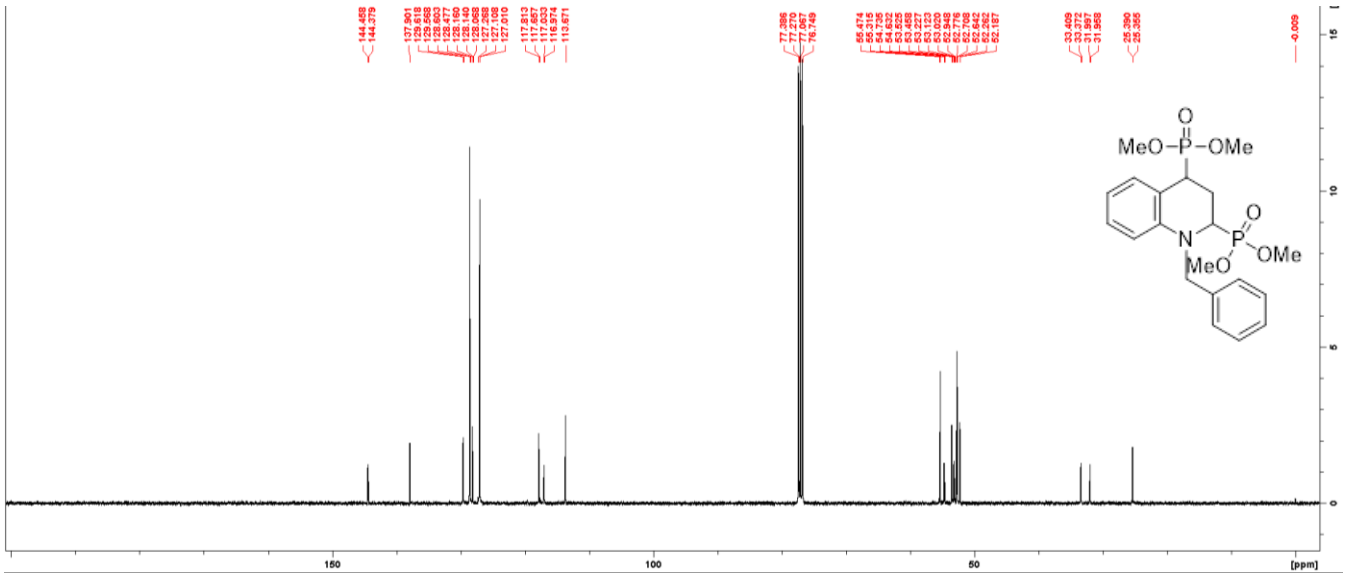
^{31}P



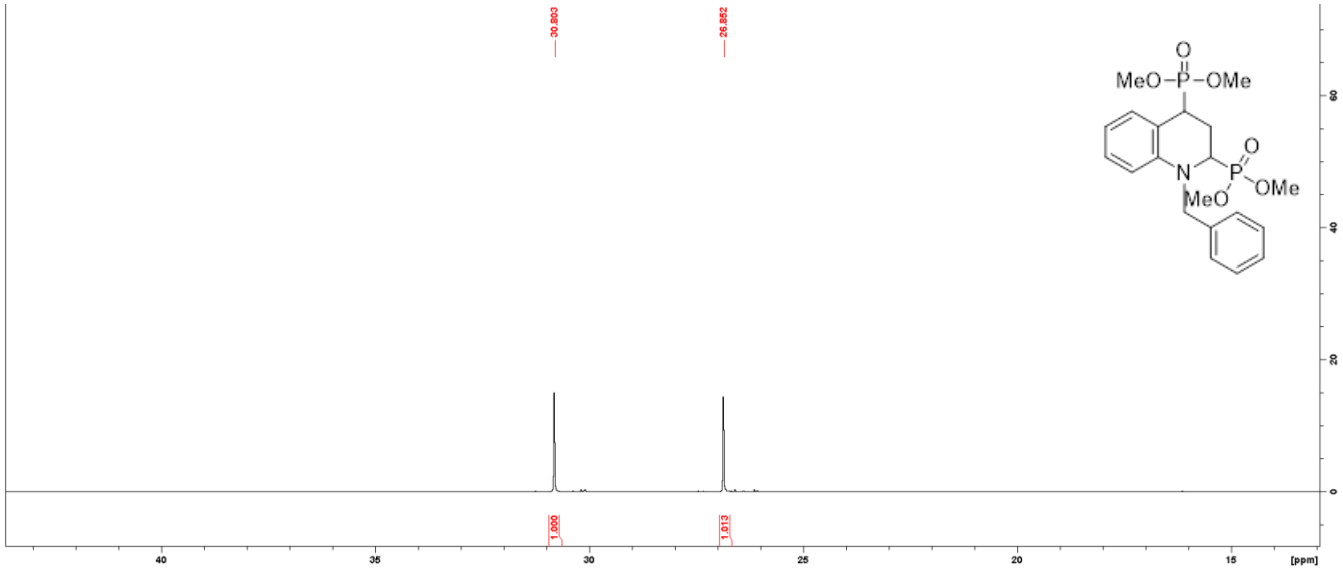
^{1}H



^{13}C

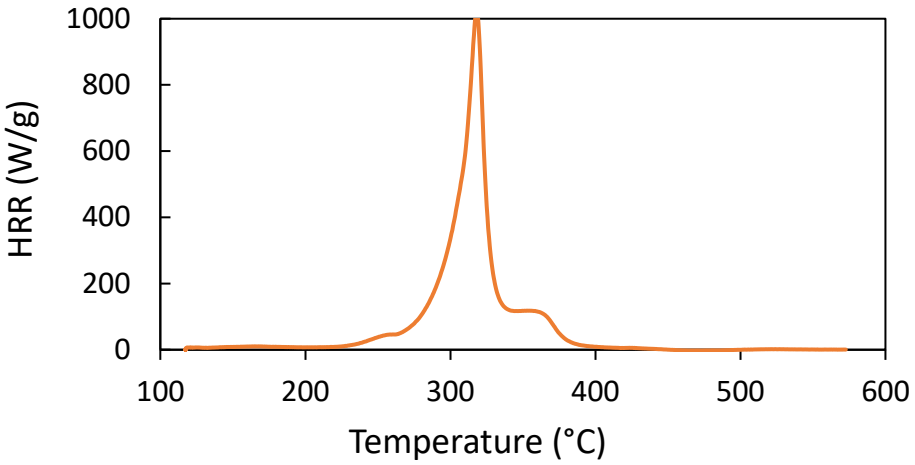


^{31}P

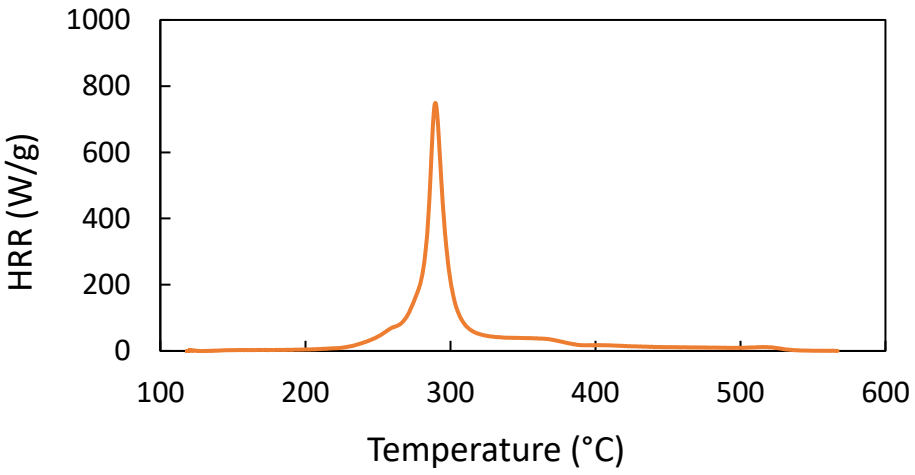


PCFC measurements

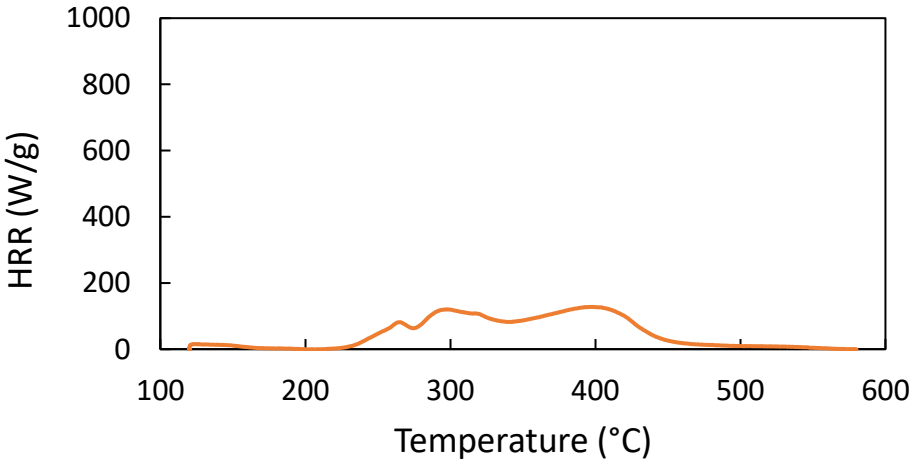
3a

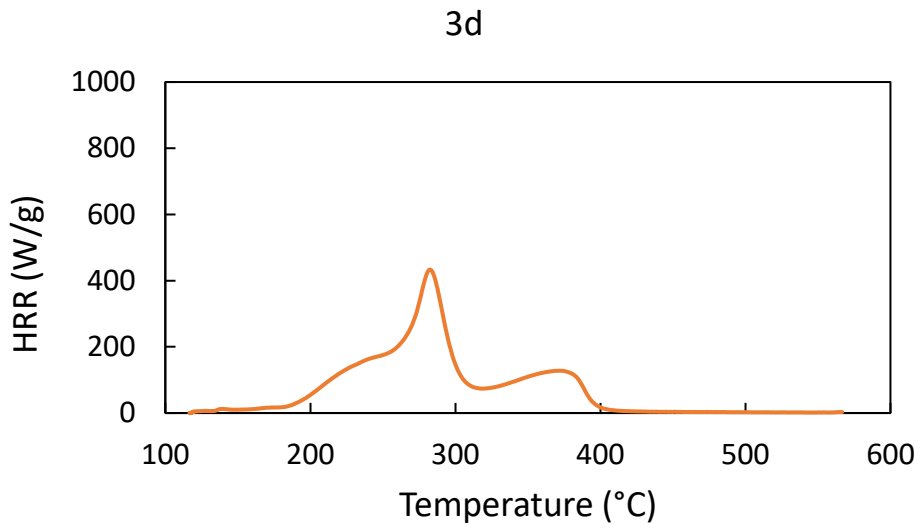


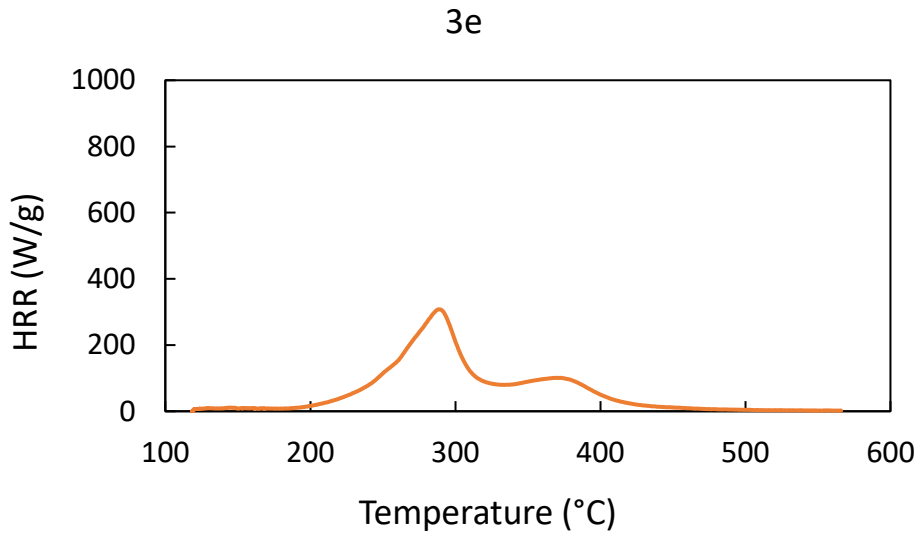
3b

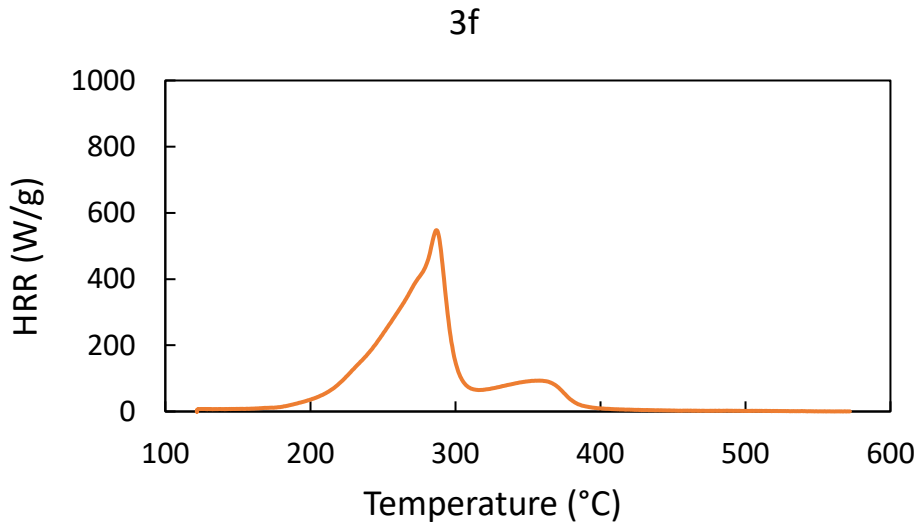


3c




3d
1000
800
600
400
200
0
HRR (W/g)
100
200
300
400
500
600
Temperature (°C)


3e
1000
800
600
400
200
0
HRR (W/g)
100
200
300
400
500
600
Temperature (°C)


3f
1000
800
600
400
200
0
HRR (W/g)
100
200
300
400
500
600
Temperature (°C)

References

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