Supporting Information for Synthesis of α,δ-Disubstituted Tetraphosphates and Terminally-Functionalized Nucleoside Pentaphosphates

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1 General Considerations

All chemical syntheses were performed in a Vacuum Atmospheres model MO-40M glovebox under an inert atmosphere of purified nitrogen unless otherwise stated. All solvents used in the glovebox were obtained anhydrous and oxygen-free by bubble degassing with argon and purification through columns of alumina and Q5 by the method of Grubbs.[4] HPLC grade water was purchased from Sigma Aldrich and used as received. $[PPN]_2[P_4O_{11}]$,[5] methylenetriphenylphosphorane,[6] and $[TBA][HPO_3Ph]$[7] were synthesized according to the literature procedures. The tetrabutylammonium salts of 5'-AMP, 5'-UMP, 5'-dAMP were synthesized according to literature procedures,[8] and were stored as DMF stock solutions (0.10 g/mL) over 4 Å molecular sieves for at least 24 hours prior to use. $MgCl_2$ was dried under vacuum at 110 °C for 12 hours prior to use and stored in the glovebox. All other reagents were purchased and used as received. Deuterated solvents were purchased from Cambridge Isotope Labs and used as received. NMR spectra were obtained at ambient temperature (ca. 25 °C) on a Bruker Avance 400 instrument. ^{1}H and ^{13}C NMR spectra were referenced internally to residual solvent signals. ^{31}P NMR spectra were referenced internally to the PPN signal. Electrospray ionization mass spectra (ESI-MS(−)) were acquired on a Micromass Q-TOF ESI spectrometer. Samples were prepared in acetonitrile at an approximate concentration of 20 ng/μL, and a source temperature of 80 °C and desolvation gas temperature of 300 °C were used. Elemental analyses were performed by Midwest Microlab. RP-HPLC was performed with Waters 515 HPLC pumps coupled to a Waters 2487 UV absorbance detector and a Macherey-Nagel VP 250/21 Nucleosil 100-5 C18 column. RP-HPLC purifications were carried out with a gradient method from 100% A, 0% B to 50% A, 50% B (A = 95% water, 5% acetonitrile, 50 mM triethylammonium acetate; B = 5% water, 95% acetonitrile, 50 mM triethylammonium acetate) with a 12 mL/min flow rate. AX-HPLC was performed on the same system but with a 250 x 4.6 mm Hamilton PRP-X100 anion exchange column. An AX-HPLC gradient method from 100% A, 0% B to 0% A, 100% B (A = 100% water; B = 1M aqueous ammonium bicarbonate) with a 2 mL/min flow rate was used. The HPLC purifications were monitored by absorbance at 320 nm for 4-methylumbelliferone derived linear phosphates, 260 nm for the ϵ-fluorophore labelled nucleosides as well as the 3',4'-didehydronucleoside. Several compounds were found to contain some residual diethyl ether by NMR. In all cases, ^{1}H NMR integration suggests less than one equivalent of residual diethyl ether, corresponding to less than 2% of the mass of the isolated compounds, and the reported yields were not adjusted to reflect this trace solvent impurity.

2 Synthesis of $[PPN]_2[1]$

2.1 Synthesis of $Na_4P_4O_{12}\cdot 10\,H_2O$[1]

This synthesis is adapted from Hossner.[1] To 100 mL deionized water in an erlenmeyer flask was added 72 g sodium bicarbonate. The flask was placed in a water ice bath and the suspension stirred for 30 minutes. Over the course of two hours, 64 g of powdered phosphorus pentoxide intermixed with powdered dry ice was sprinkled into the stirring bicarbonate solution in small portions. Alkaline pH and a reaction temperature of less than 5 °C were

maintained by the addition of more dry ice or sodium bicarbonate as necessary. The reaction vessel was then removed from the ice bath and stirred at room temperature for one hour. The resulting viscous solution was filtered through a Büchner funnel, yielding a clear solution. The resulting solution was dried on a rotary evaporator at 60 °C until solid precipitate began to form. The flask was then removed from the rotary evaporator and allowed to cool to room temperature, resulting in the precipitation of the product as colorless crystals. The crystals were then isolated by filtration and rinsed with a small amount of cold water followed by ethanol. The crystalline product is then dried under vacuum on a Schlenk line at 70 °C for several hours (23 g, 39 mmol, 17% yield). $^{31}P\{^{1}H\}$ NMR (CD_3CN, 122 MHz, ppm): δ −23.2 (s).

2.2 Synthesis of $[PPN]_4[P_4O_{12}]\cdot 5\,H_2O$[2]

To a solution containing [PPN]Cl (4.58 g, 8.0 mmol) in deionized water (200 mL) was added a solution of $Na_4P_4O_{12}\cdot 10\,H_2O$ (1.30 g, 2.2 mmol) in deionized water (100 mL) at 60 °C. A white precipitate formed immediately, and this suspension was stirred at 60 °C for 40 min. Then the mixture was cooled to room temperature and filtered. The white precipitate was dried in vacuo at 80 °C for 14 h to give $[PPN]_4[P_4O_{12}]\cdot 5\,H_2O$ as a white hygroscopic powder (4.74 g, 19 mmol, 84%). IR (KBr, cm^1): 1285 (s), 1266 (s), 1184(w), 1115 (s), 996 (m). ^{31}P NMR ($CDCl_3$, 18 °C): δ 21.1 (s, PPN+), −25.0 (s, P_4O_{12}). Anal. Calc'd for $C_{144}H_{130}N_4O_{17}P_{12}$: C, 67.55; H, 5.12; N, 2.19. Found: C, 67.72; H, 5.33; N, 1.83.

2.3 Synthesis of $[PPN]_2[P_4O_{12}H_2]$[3]

Under open air conditions in a fume hood, $[PPN]_4[P_4O_{12}]\cdot 5\,H_2O$ (4.227 g, 1.670 mmol, 1.0 equiv.) was suspended in acetone (40 mL). To this stirring suspension was added dropwise a solution of $(CF_3CO)_2O$ (240 μL, 1.700 mmol, 1.02 equiv.) in acetone (10 mL). After addition of ca. 50% of the $(CF_3CO)_2O$ solution, white solid began to precipitate out of the reaction mixture. After complete addition of the $(CF_3CO)_2O$ solution, the suspension was allowed to stir for a total of 40 minutes to allow complete precipitation of $[PPN]_2[P_4O_{12}H_2]$. The solids were then collected by filtration on a medium porosity fritted funnel, washed with acetone (10 mL), and dried in vacuo affording the product as a white solid (Yield: 2.194 g, 1.572 mmol, 94%). ESI-MS(−)(CH3CN, m/z): 318.8122 ($[P_4O_{12}H_2]^{2-} + H^+$), 158.8814 ($[P_4O_{12}H_2]^{2-}$). IR (ATR, cm^{-1}): 1270 (s, P–O), 1022 (s, P-O), 996 (s, P-O). ^1H NMR (CD_3CN, 300 MHz, ppm) δ: 14.03 (br, 2 H, OH), 7.51-7.69 (m, 60 H, Ph). ^{31}P NMR (CD_3CN, 122 MHz, ppm) δ: 22.10 (s, 4 P, [PPN]+), −25.60 (s, 4 P). ^{13}C NMR (CD_3CN, 75 MHz, ppm) δ: 133.62 (s), 132.26 (m), 129.39 (m), 127.78 (s), 126.69 (s). Anal. Calc'd for $C_{72}H_{62}N_2O_{12}P_8$ (1395.08): C, 61.99; H, 4.48; N, 2.01; Found: C, 61.95; H, 4.64; N, 2.04

2.4 Synthesis of $[PPN]_2[P_4O_{11}]$,[3] $[PPN]_2$[1]

In a glove box, $[PPN]_2[P_4O_{12}H_2]$ (320.2 mg, 0.230 mmol, 1 equiv.) and DCC (47.6 mg, 0.231 mmol, 1.01 equiv.) were mixed in dry acetonitrile (5 mL) affording a white suspension due to the production of the byproduct dicyclohexylurea (DCU), which is insoluble in acetonitrile. Note that this reaction must be performed in rigorously anhydrous solvents due to the water

sensitivity of the product. The reaction mixture was allowed to stir at room temperature for 30 minutes. The mixture then was filtered through a glass microfiber filter and the volatile materials were removed in vacuo from the filtrate to give a white solid, which was then washed with THF (3 × 3 mL), diethyl ether (3 × 3 mL), and dried in vacuo to give $[PPN]_2[P_4O_{11}]$ as white powder (Yield: 258.6 mg, 0.188 mmol, 82%). ESI-MS (−)(CH_3CN, m/z): 300.8838 (100%, $[P_4O_{11}]^{2-} + H^+$). IR (ATR, cm^{-1}): 1262 (s, P=O), 995 (s, P-O). ^{1}H NMR (CD_3CN, 300 MHz, ppm) δ: 7.48-7.71 (m, 60 H, Ph). ^{31}P NMR (CD_3CN, 161.9 MHz, ppm) δ: 21.96 (s), −24.40 (t), −32.51 (t). ^{13}C NMR (CD_3CN, 100 MHz, ppm) δ: 133.61 (s), 132.26 (m), 129.38 (m), 127.78 (s), 126.71 (s). Anal. Calc'd for $C_{72}H_{60}N_2O_{11}P_8$ (1377.07): C, 62.80; H, 4.39; N, 2.03; Found: C, 62.56; H, 4.56; N, 2.03.

3 Synthesis of Substituted Metaphosphates ($[P_4O_{11}Nuc^1]^{3-}$)

3.1 $[PPN]_2[Et_3NH]$[2]

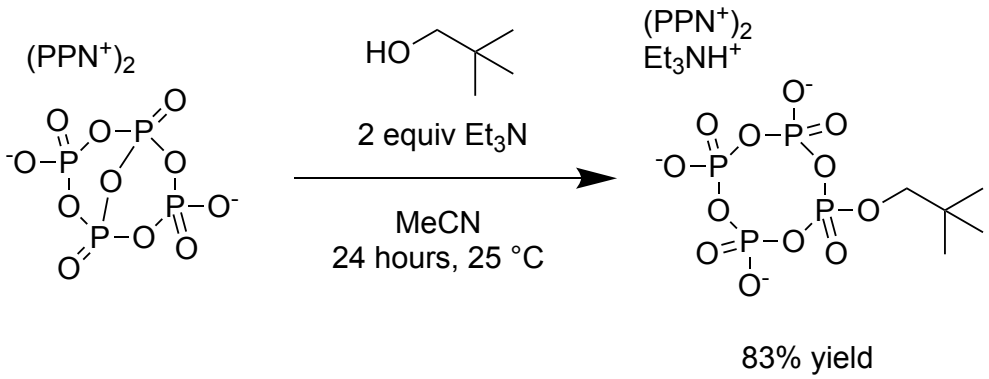

Figure S1: Synthesis of $[PPN]_2[Et_3NH][P_4O_{11}-ONp]$.

In the glovebox, a stock solution was made of neopentanol in acetonitrile at a concentration of 0.10 g/mL and stored over activated 4Å molecular sieves for at least 24 hours. Then, $[PPN]_2[P_4O_{11}]$ (0.32 g, 0.23 mmol) was dissolved in 3 mL of acetonitrile. To this solution was added triethylamine (0.065 mL, 0.46 mmol) followed by the acetonitrile stock solution of neopentanol (0.20 mL, 0.23 mmol). The resulting mixture was stirred at room temperature for 24 hours. Diethyl ether (10 mL) was then added to this mixture, giving a cloudy solution. After several hours, the mixture separated into an oil at the bottom of the vessel and a supernatant solution. The supernatant was decanted off, and the oil was dried under vacuum for several hours, giving the product as a colorless solid (0.30 g, 0.19 mmol, 83% yield).

Elem. Anal. Found(Calc'd) for $C_{83}H_{87}N_3O_{12}P_8$: C 62.53 (63.63), H 5.66 (5.60), N 2.49 (2.68)

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 11.32 (br, 1H), 7.68 to 7.48 (m, 60H), 3.79 (d, 2H, $J_{PH} = 4.9Hz$), 3.09 (q, 6H), 1.21 (t, 9H), 0.90 (s, 9H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 134.6, 133.28 to 133.10 (m), 130.43 to 130.24 (m), 128.7 (d), 127.6 (d), 77.0 (d), 45.9, 32.5 (d), 26.4, 8.8.

$^{31}P\{^{1}H\}$ NMR (acetonitrile-d_3, 162.0 MHz): δ 23.0, −22.6 to −23.5 (m).

ESI-MS(−) of $[PPN]_2[Et_3NH][P_4O_{11}{-}ONp]$ (CH_3CN) found 388.86 m/z for $[P_4O_{11}{-}ONpH_2]^-$ (388.94 calc'd for $C_5H_{13}O_{12}P_4$)

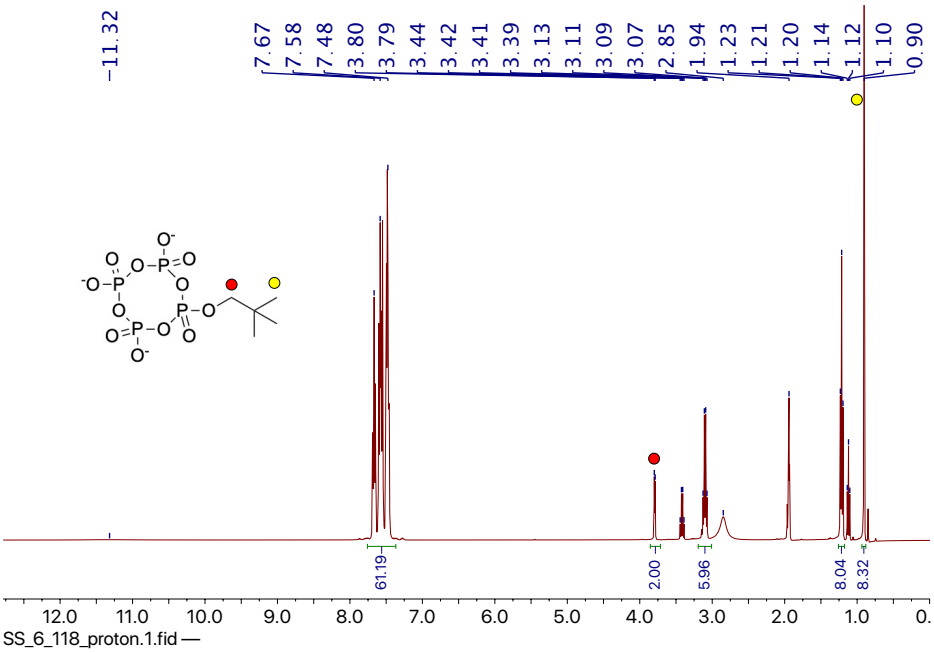

Figure S2: ^{1}H NMR spectrum of $[PPN]_2[Et_3NH][P_4O_{11}{-}ONp]$ (acetonitrile-d_3, 400 MHz) with residual diethyl ether (3.42 and 1.12 ppm).

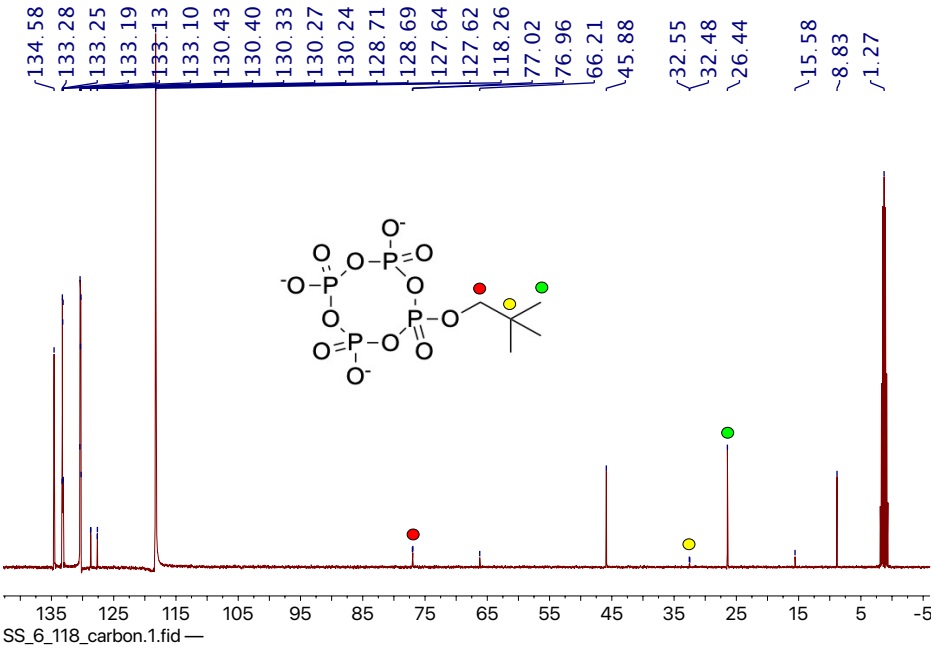

Figure S3: $^{13}C\{^1H\}$ NMR spectrum of $[PPN]_2[Et_3NH][P_4O_{11}{-}ONp]$ (acetonitrile-d_3, 100.6 MHz) with residual diethyl ether (66.2 and 15.6 ppm).

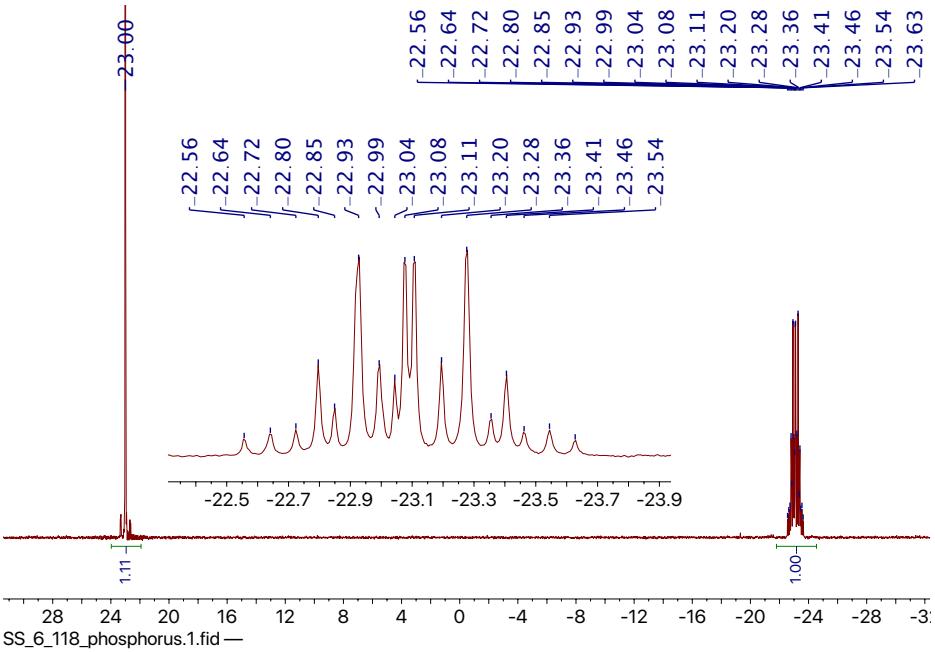

Figure S4: $^{31}P\{^1H\}$ NMR spectrum of $[PPN]_2[Et_3NH][P_4O_{11}{-}ONp]$ (acetonitrile-d_3, 162.0 MHz).

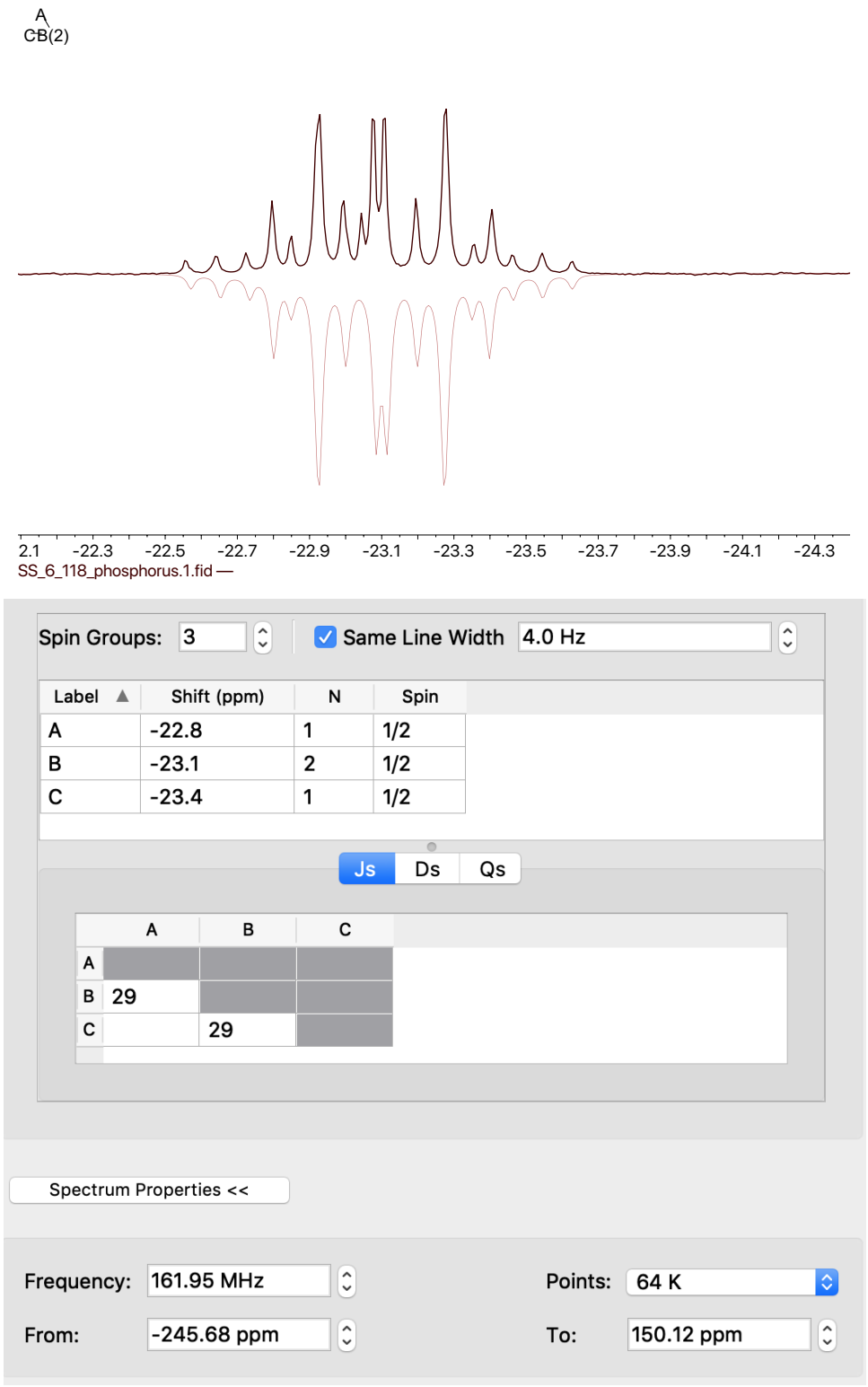

Figure S5: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[Et_3NH][P_4O_{11}{-}ONp]$ (acetonitrile-d_3, 162.0 MHz, black) and simulated spectrum using MestreNova (red) with simulation parameters (bottom).

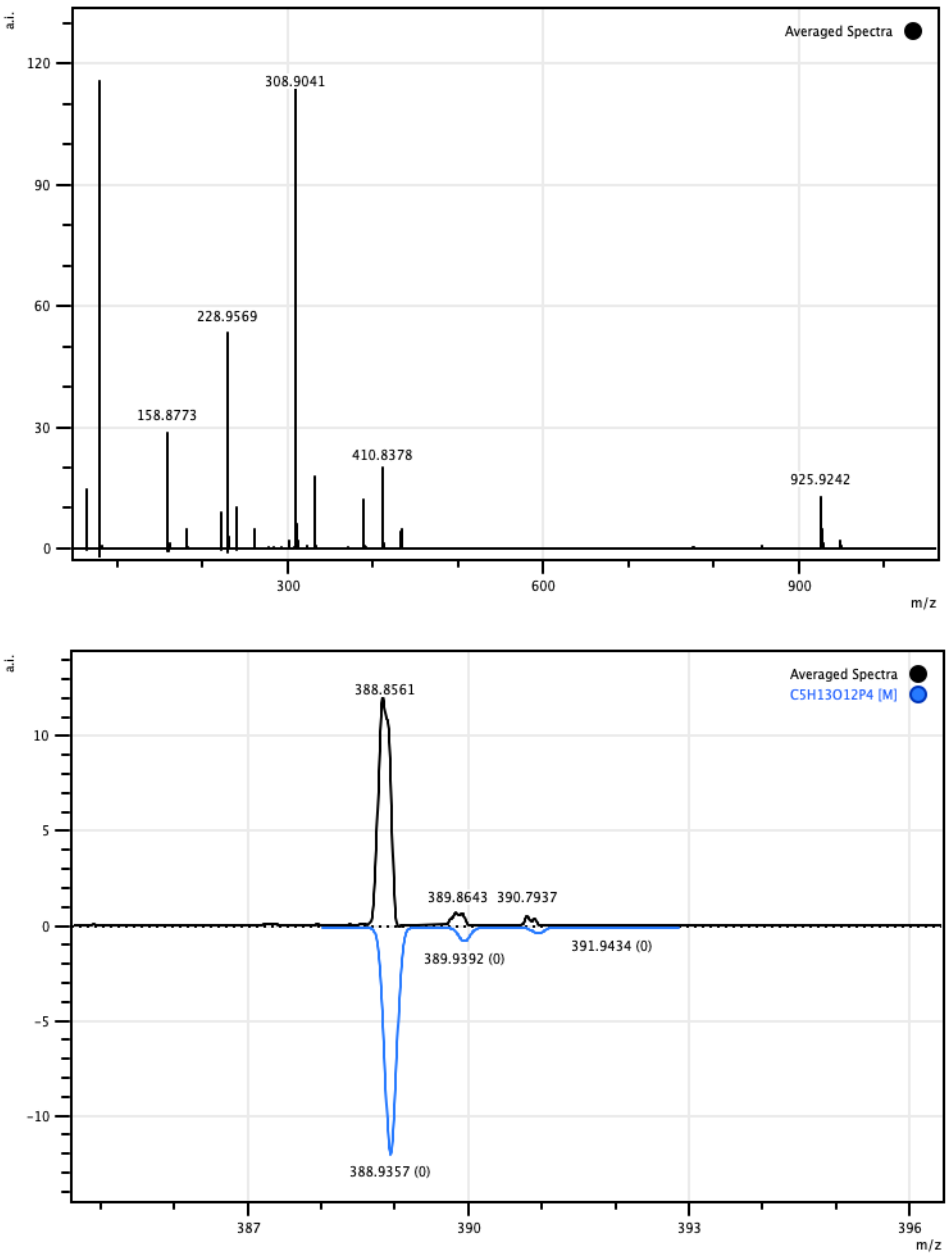

Figure S6: ESI-MS(−) of $[PPN]_2[Et_3NH][P_4O_{11}{-}ONp]$ (CH_3CN) with zoomed in portion showing the molecular ion ($[P_4O_{11}{-}ONpH_2]^-$, top) and calculated isotope pattern ($C_5H_{13}O_{12}P_4^-$, bottom).

3.2 $[PPN]_2[Et_3NH][3]$

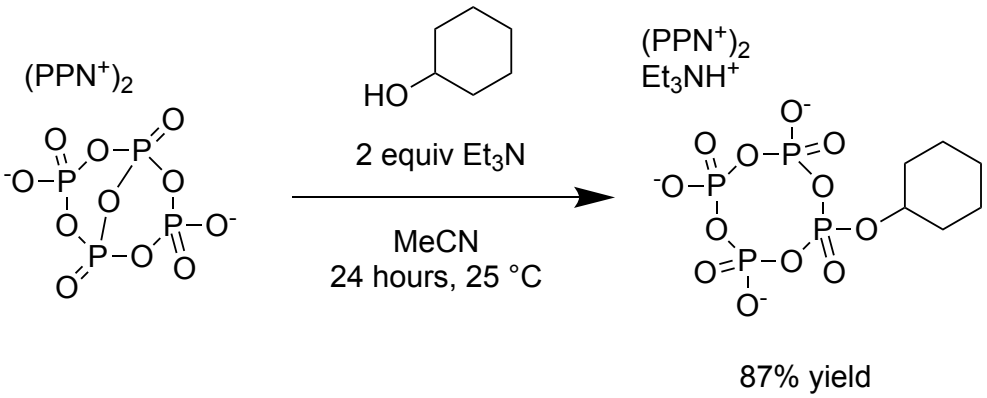

Figure S7: Synthesis of $[PPN]_2[Et_3NH][P_4O_{11}{-}OCy]$.

In the glovebox, a stock solution was made of cyclohexanol in acetonitrile at a concentration of 0.10 g/mL and stored over activated 4Å molecular sieves for at least 24 hours. Then, $[PPN]_2[P_4O_{11}]$ (0.071 g, 0.051 mmol) was dissolved in 2 mL of acetonitrile. To this solution was added triethylamine (0.014 mL, 0.10 mmol) followed by the acetonitrile stock solution of cyclohexanol (0.051 mL, 0.051 mmol). The resulting mixture was stirred at room temperature for 24 hours. Diethyl ether (10 mL) was then added to this mixture, giving a cloudy solution. After several hours, the mixture separated into an oil at the bottom of the vessel and a supernatant solution. The supernatant was decanted off, and the oil was dried under vacuum for several hours, giving the product as a colorless solid (0.070 g, 0.044 mmol, 87% yield).

Elem. Anal. Found(Calc'd) for $C_{84}H_{87}O_{12}N_3P_8$: C 62.21 (63.66), H 5.74 (5.56), N 2.58 (2.66)

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 11.19 (b, 1H), 7.69 to 7.46 (m, 60H), 4.46 (m, 1H), 3.10 (q, 6H), 1.67 (m, 4H), 1.46 (m, 4H), 1.31 (m, 2H), 1.22 (t, 9H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 134.7, 133.27 to 133.09 (m), 130.43 to 130.23 (m), 128.7 (d), 127.6 (d), 77.3 (d), 46.0, 33.9 (d), 26.0, 23.9, 8.3.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 23.0, -22.6 to -23.5 (m), -24.5 (m).

ESI-MS($-$) of $[PPN]_2[Et_3NH][P_4O_{11}{-}OCy]$ (CH_3CN, found 938.18 m/z) for $[P_4O_{11}{-}ONpH][PPN]^-$ (938.11 calc'd for $C_{42}H_{42}NO_{12}P_6$)

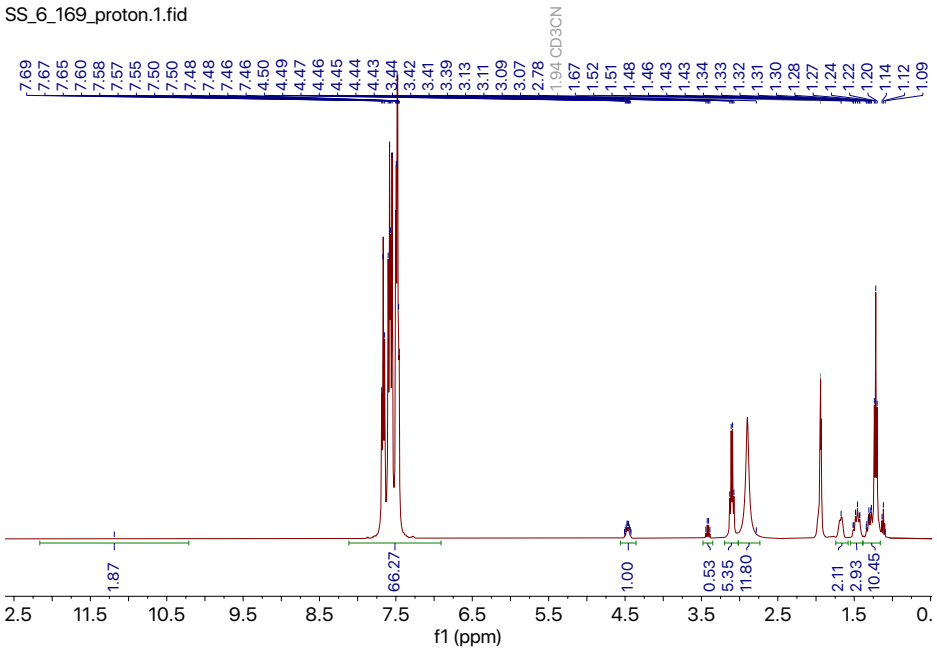

Figure S8: ^{1}H NMR spectrum of $[PPN]_2[Et_3NH][P_4O_{11}{-}OCy]$ (acetonitrile-d_3, 400 MHz).

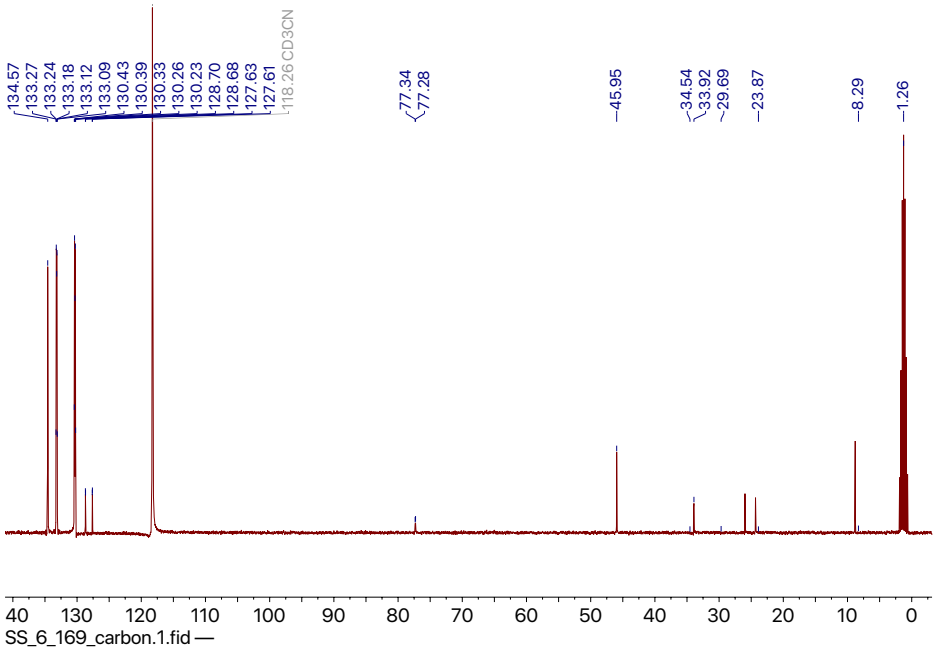

Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum of $[PPN]_2[Et_3NH][P_4O_{11}{-}OCy]$ (acetonitrile-d_3, 100.6 MHz).

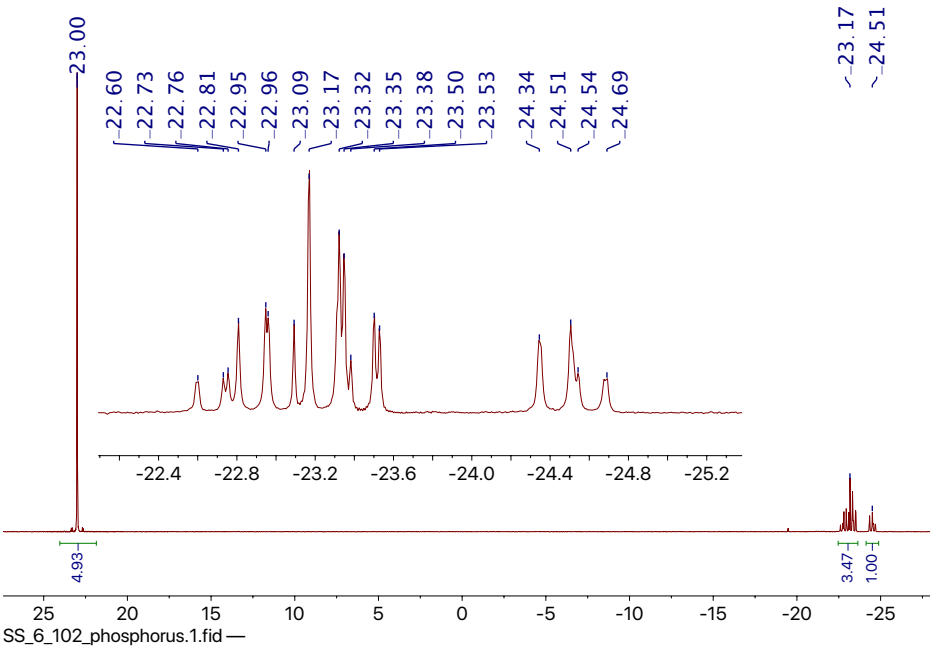

Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[Et_3NH][P_4O_{11}{-}OCy]$ (acetonitrile-d_3, 162.0 MHz).

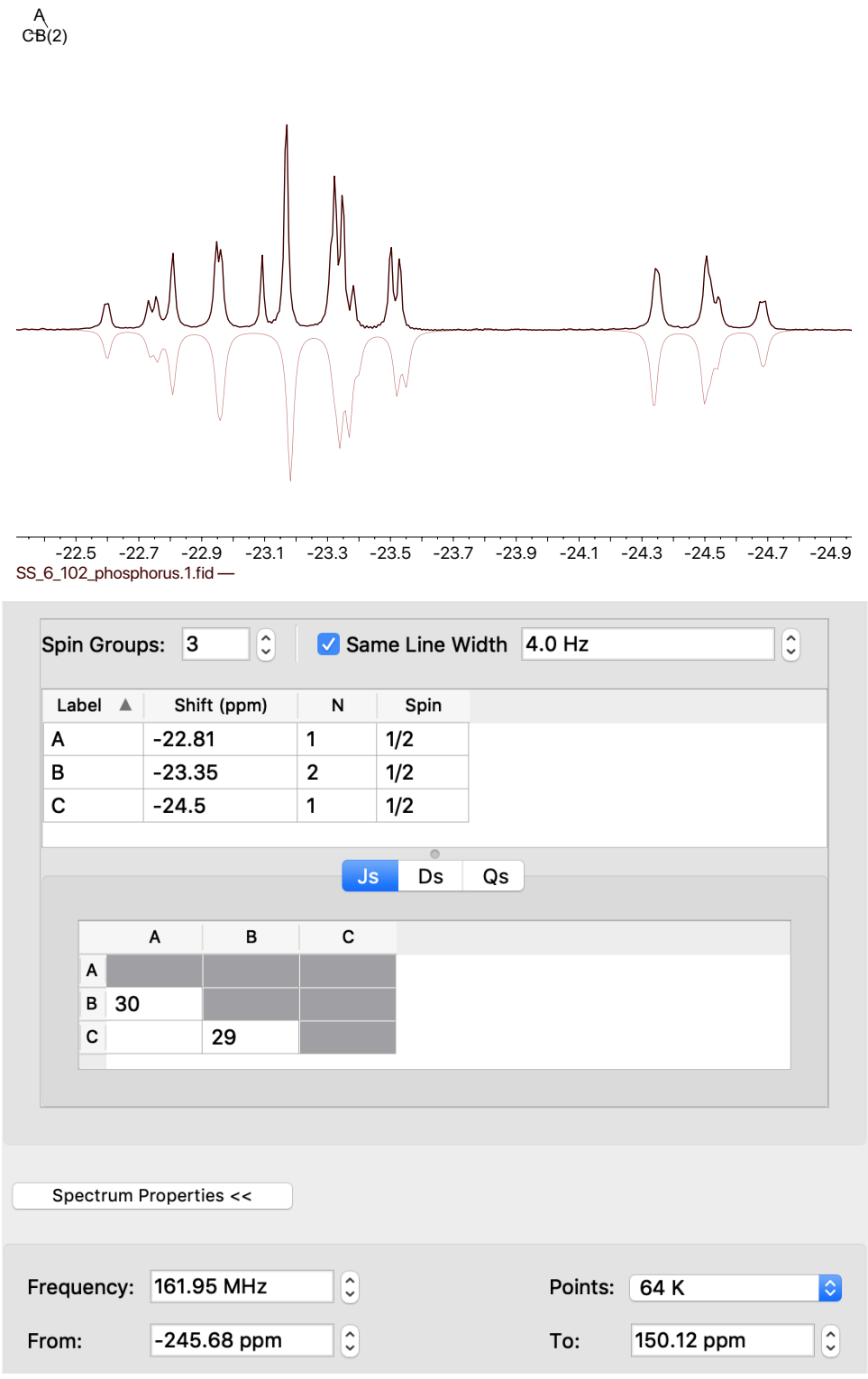

Figure S11: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[Et_3NH][P_4O_{11}{-}OCy]$ (acetonitrile-d_3, 162.0 MHz, black) and simulated spectrum using MestreNova (red) with simulation parameters (bottom).

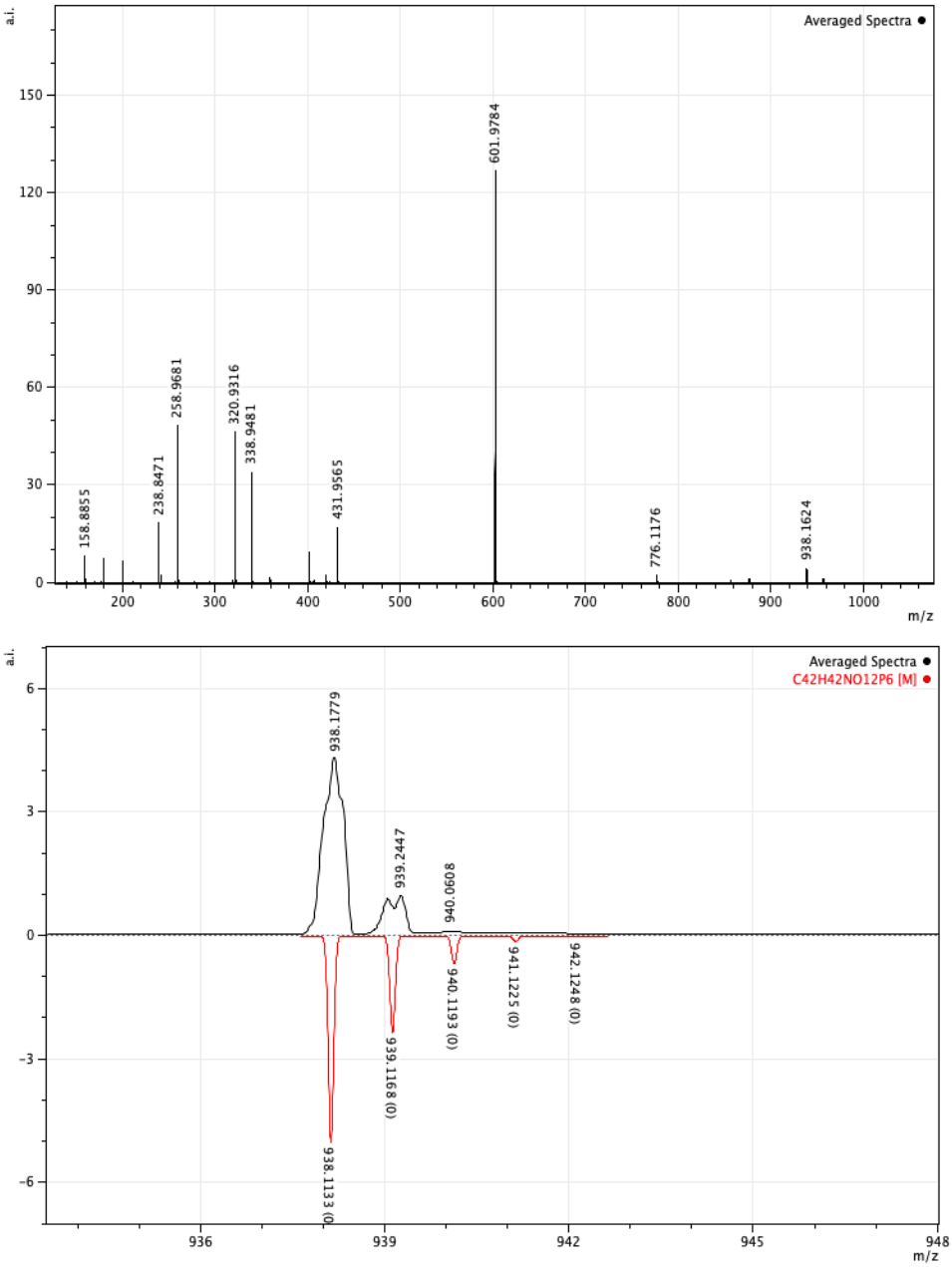

Figure S12: ESI-MS(−) of $[PPN]_2[Et_3NH][P_4O_{11}{-}OCy]$ (CH_3CN) with zoomed in portion showing the molecular ion ($[P_4O_{11}{-}OCyH][PPN]^-$, top) and calculated isotope pattern ($C_{42}H_{42}NO_{12}P_6$, bottom).

3.3 $[PPN]_2[Et_3NH][4]$

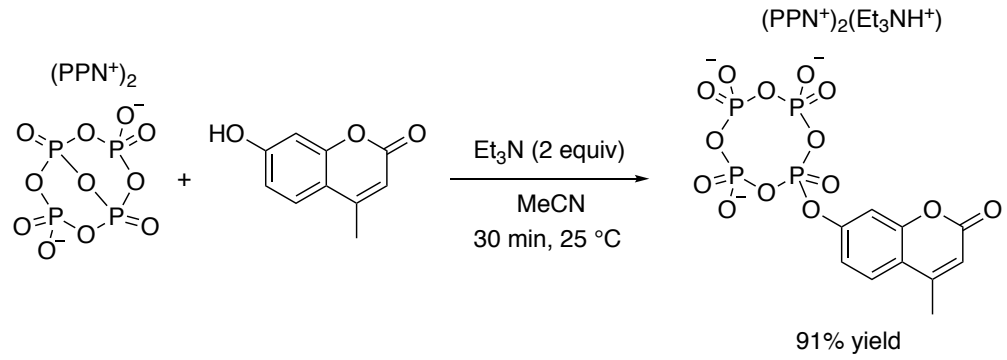

Figure S13: Synthesis of $[PPN]_2[Et_3NH][4\text{-methyl-2-oxo-2}H\text{-chromen-7-yl-}P_4O_{11}]$.

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.050 g, 0.036 mmol) was dissolved in acetonitrile (0.5 mL), and triethylamine (0.01 mL, 0.073 mmol) was added. 4-methylumbelliferone (0.0058 g, 0.036 mmol) was then added, and the resulting mixture was stirred for 30 minutes. Diethyl ether (5 mL) was added, resulting in a cloudy solution. After vigorous stirring and letting the solution stand for several hours at room temperature, the mixture separated into a colorless solution and a colorless oil at the bottom of the reaction vial. The supernatant was decanted off, and the oil was dried under vacuum for 5 hours, giving the product as a hygroscopic white solid (0.055 g, 0.033 mmol, 91%).

Elem. Anal. Found(Calc'd) for $C_{88}H_{83}N_3O_{14}P_8$: C 63.81 (63.87), H 5.35 (5.06), N 2.54 (2.55)

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 11.51 (br, 1H), 7.84 to 7.52 (m, 63H), 6.28 (s, 1H), 3.25 (q, 6H), 2.49 (s, 3H), 1.21 (t, 9H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 161.2, 155.1, 155.0, 153.8, 134.5, 133.1 (m), 130.3 (m), 128.6 (d), 127.5 (d), 126.9, 118.4 (d, J = 4.8 Hz), 114.0, 110.0 (d, J = 5.6 Hz), 45.9, 18.7, 15.8.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 23.0, −22.6 to −22.8 (m), −27.8 to −28.1 (m).

ESI-MS(−) of $[C_{10}H_7O_{14}P_4]H_2^-$ (CH_3CN, m/z) 476.87 (calc'd 476.89)

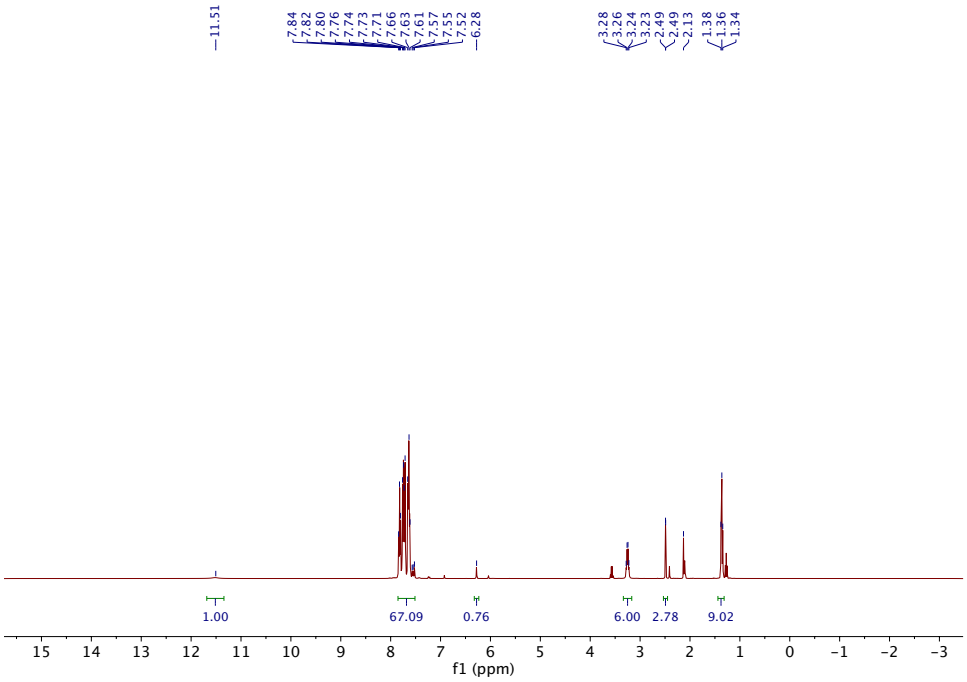

Figure S14: ^{1}H NMR spectrum of $[PPN]_2[Et_3NH][4\text{-methyl-2-oxo-2}H\text{-chromen-7-yl-}P_4O_{11}]$ (acetonitrile-d_3, 400 MHz).

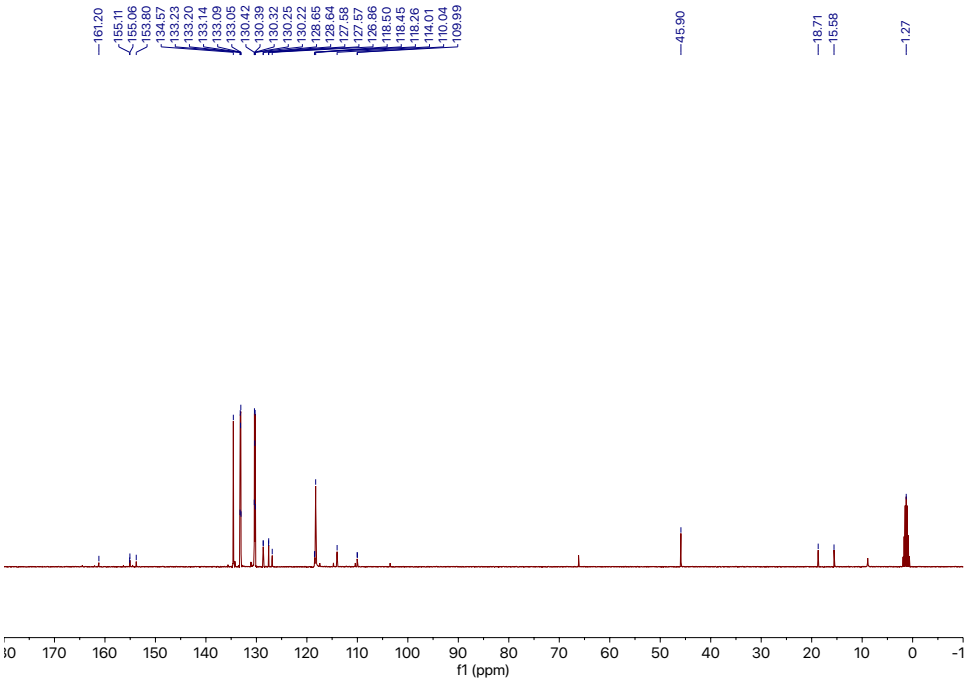

Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of $[PPN]_2[Et_3NH][4\text{-methyl-2-oxo-2}H\text{-chromen-7-yl-}P_4O_{11}]$ (acetonitrile-d_3, 100.6 MHz).

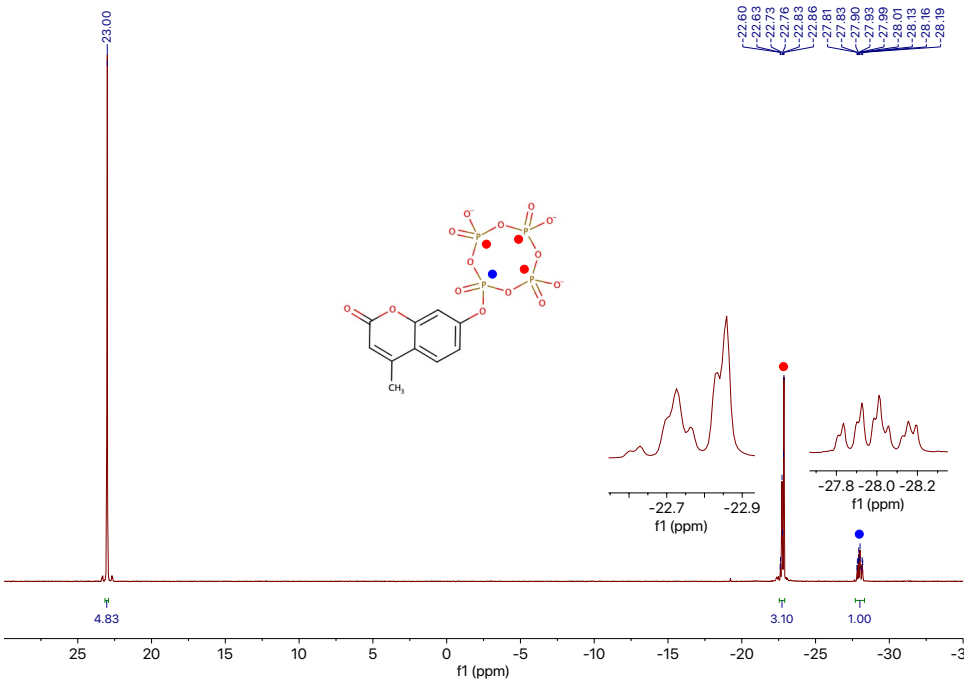

Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[Et_3NH][4\text{-methyl-2-oxo-2}H\text{-chromen-7-yl-}P_4O_{11}]$ (acetonitrile-d_3, 162.0 MHz).

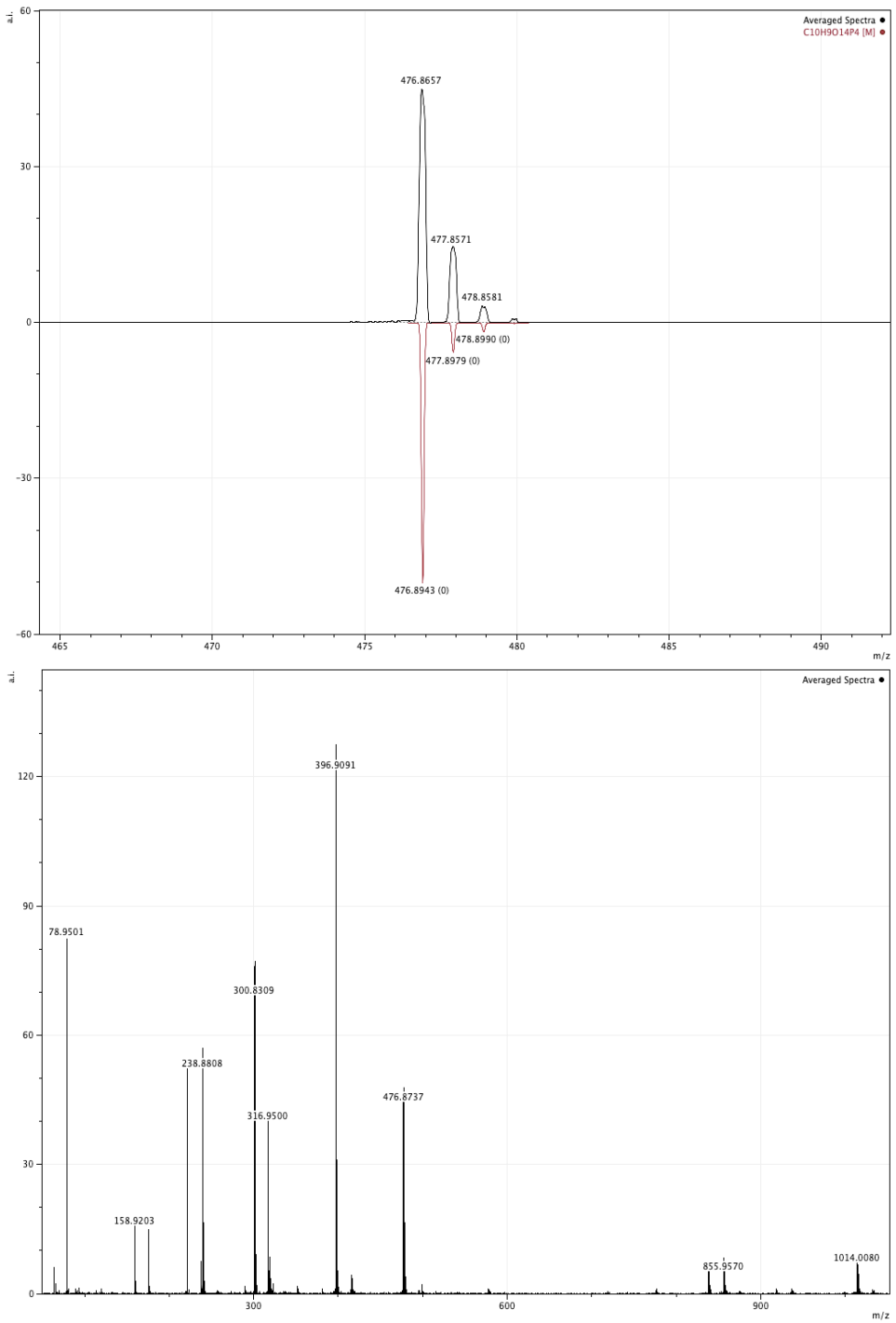

Figure S17: ESI-MS(−) of $[PPN]_2[Et_3NH][C_{10}H_7O_{14}P_4]$ (CH_3CN) with zoomed in portion of the molecular ion ($[C_{10}H_7O_{14}P_4]H_2^-$, top), and calculated isotope pattern ($C_{10}H_9O_{14}P_4$, bottom).

3.4 $[PPN]_2[C_3H_6N][5]$

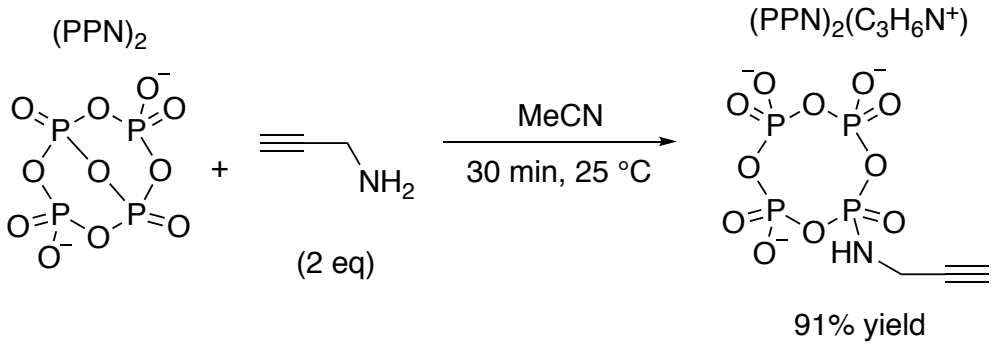

Figure S18: Synthesis of $[PPN]_2[C_3H_6N]$[propargylamino$-P_4O_{11}$].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.06 g, 0.044 mmol) was dissolved in acetonitrile (1 mL). To this solution was added propargylamine (6 μL, 0.087 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Diethyl ether (5 mL) was then added to this mixture, giving a cloudy solution. The mixture was stirred vigorously, resulting in the formation of a colorless solution, and a light yellow oil on the bottom of the vial. The supernatant was decanted off, and the oil was dried under vacuum for several hours, giving the product as a light yellow solid (0.0590 g, 0.040 mmol, 91% yield).

Elem. Anal. Found(Calc'd) for $C_{78}H_{70}N_4O_{11}P_8$: C 64.30 (62.98), H 5.34 (4.75), N 4.03 (3.77)

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 8.73 (b, 1H), 7.85-7.62 (m, 60H), 4.90 (s, 1H), 3.77 (d, J = 2.6 Hz, 2H), 3.74 (d, J = 2.6 Hz, 2H), 2.75 (t, J = 2.4 Hz, 1H), 2.56 (t, J = 2.5 Hz, 1H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 134.6, 133.22 to 133.04 (m), 130.42 to 130.22 (m), 128.6 (d), 127.6 (d), 83.6 (d), 78.6, 75.3, 71.6, 31.0, 29.1.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 23.0, -11.0 to -11.4 (m), -22.6 to -23.3 (m).

ESI-MS($-$) of $[C_3H_4NO_{11}P_4]H_2^-$ (CH_3CN, m/z) 355.90 (calc'd 355.89)

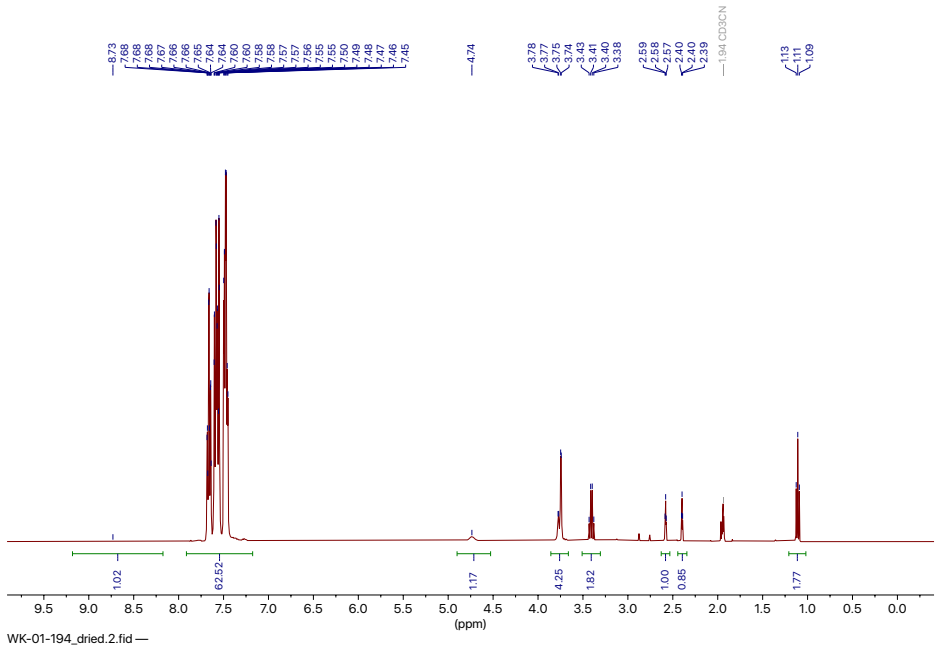

Figure S19: ^{1}H NMR spectrum of $[PPN]_2[C_3H_6N][propargylamino{-}P_4O_{11}]$ (acetonitrile-d_3, 400 MHz), with residual diethyl ether (3.40 and 1.11 ppm).

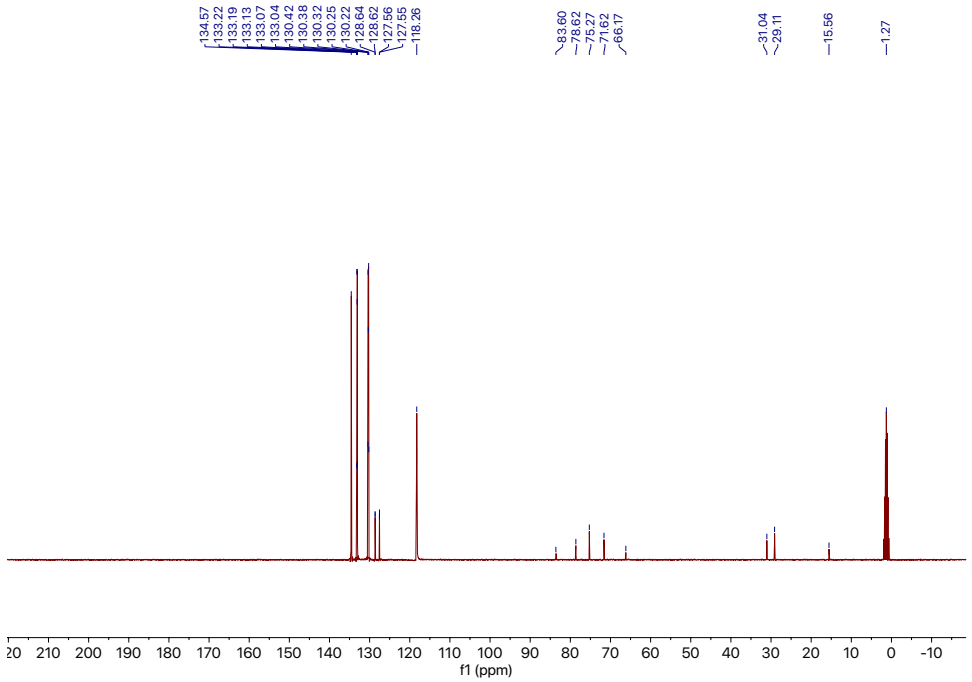

Figure S20: ^{13}C NMR spectrum of $[PPN]_2[C_3H_6N][propargylamino{-}P_4O_{11}]$ with residual diethyl ether (66.2 and 15.6 ppm) (acetonitrile-d_3, 100.6 MHz).

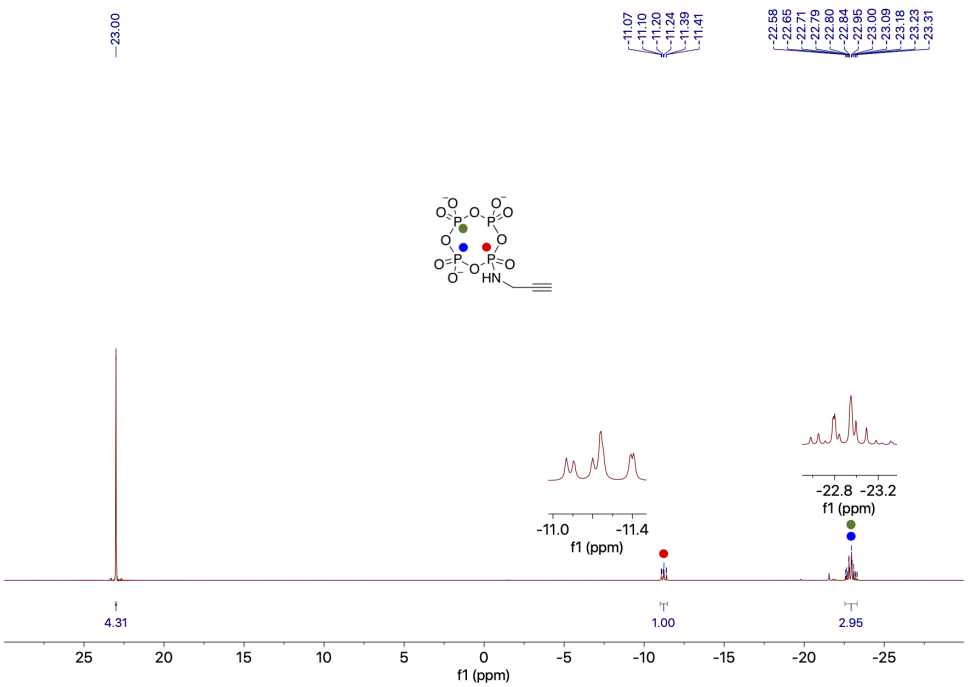

Figure S21: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[C_3H_6N][propargylamino{-}P_4O_{11}]$ (acetonitrile-d_3, 162.0 MHz).

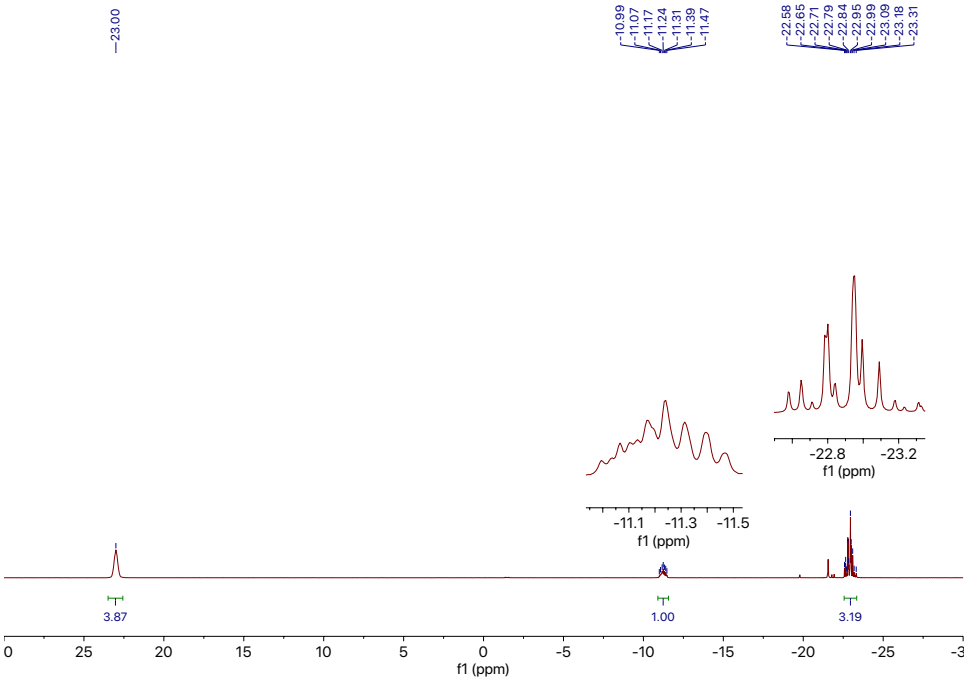

Figure S22: ^{31}P NMR spectrum of $[PPN]_2[C_3H_6N][propargylamino{-}P_4O_{11}]$ (acetonitrile-d_3, 162.0 MHz).

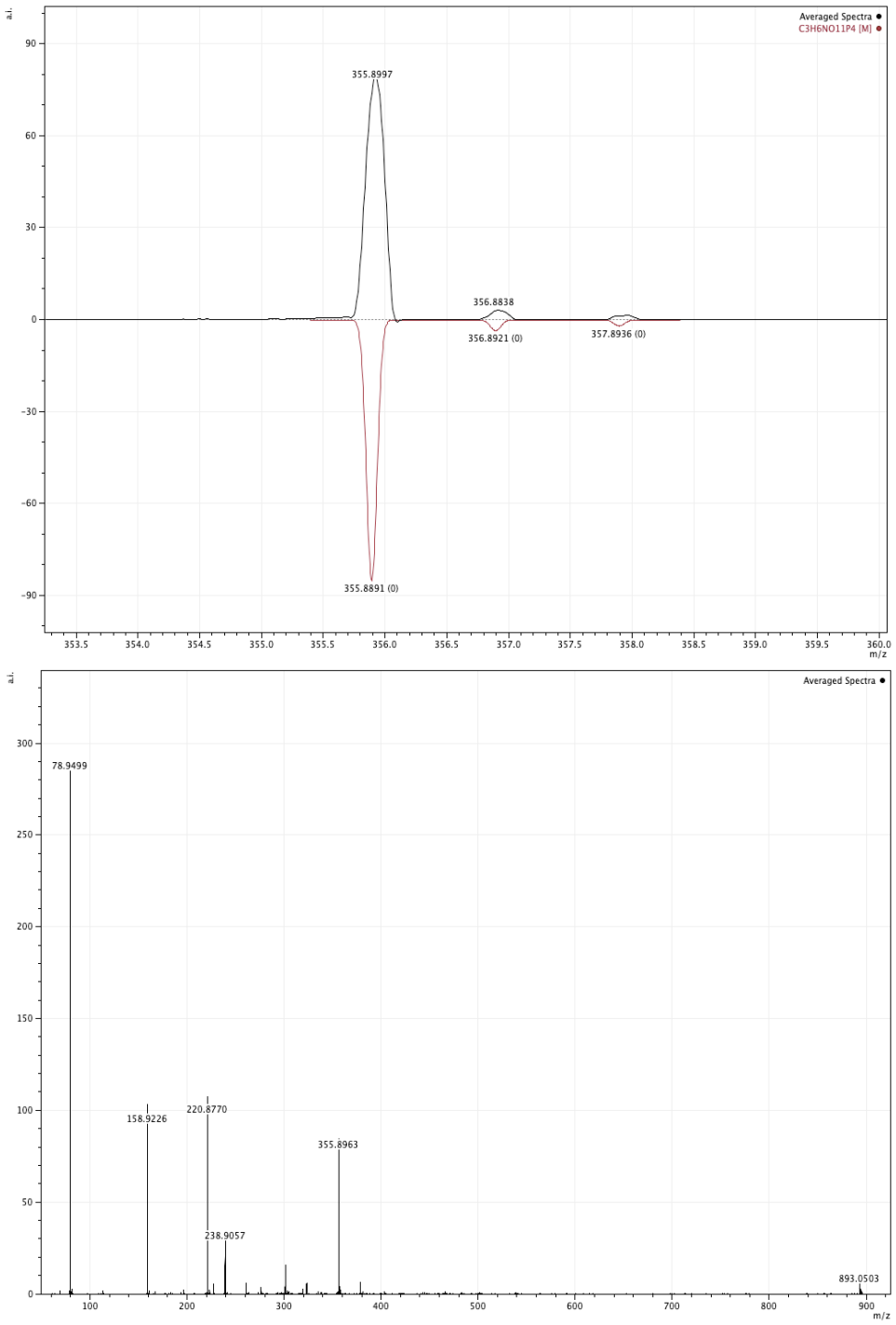

Figure S23: ESI-MS(−) of $[PPN]_2[C_3H_6N][C_3H_4NO_{11}P_4]$ (CH_3CN) with zoomed in portion of the molecular ion ($[C_3H_4NO_{11}P_4]H_2^-$, top), and calculated isotope pattern ($C_3H_6NO_{11}P_4$, bottom).

3.5 $[PPN]_2[H_2NEt_2][6]$

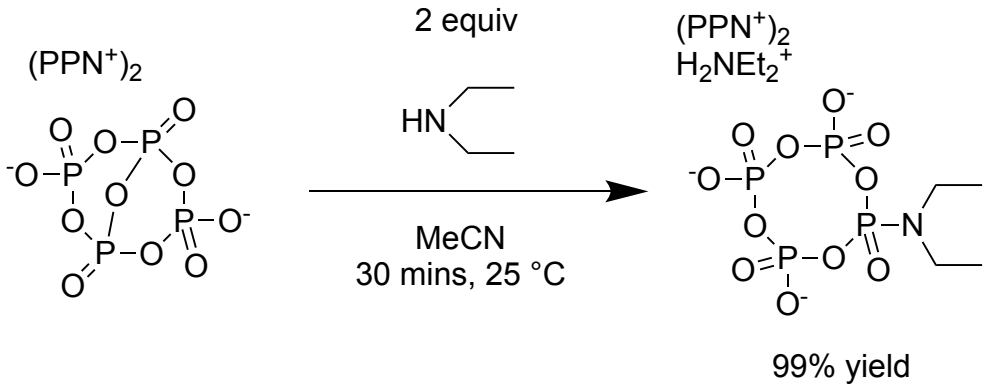

Figure S24: Synthesis of $[PPN]_2[H_2NEt_2][P_4O_{11}{-}NEt_2]$.

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.14 g, 0.11 mmol) was dissolved in 2 mL of acetonitrile. To this solution was added diethylamine (0.0153 g, 0.21 mmol). The resulting mixture was stirred at room temperature for 30 min. Diethyl ether (10 mL) was then added to this mixture, giving a cloudy solution. After several hours, the product crystallized on the bottom of the vial. The supernatant was decanted off, and the crystals were dried under vacuum for several hours, giving the product as a colorless solid (0.17 g, 0.11 mmol, 99% yield).

Elem. Anal. Found(Calc'd) for $C_{80}H_{82}N_4O_{11}P_8$: C 62.77 (63.08), H 5.48 (5.43), N 3.68 (3.68) .

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 9.80 (b, 2H), 7.68 to 7.46 (m, 60H), 3.12 (dq, 4H), 2.94 (q, 4H), 1.19 (t, 6H), 1.04 (t, 6H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 133.7, 132.26 to 133.07 (m), 130.43 to 130.23 (m), 127.8 (d), 126.7 (d), 40.4 (d), 39.6, 14.2 (d), 11.7.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 23.0, -12.6 to -13.0 (m), -22.9 to -23.1 (m).

ESI-MS($-$) of $[PPN]_2[H_2NEt_2][P_4O_{11}{-}NEt_2]$ in CH_3CN/H_2O, found 374.03 m/z (calc'd 373.94 m/z) for $C_4H_{12}NO_{11}P_4$

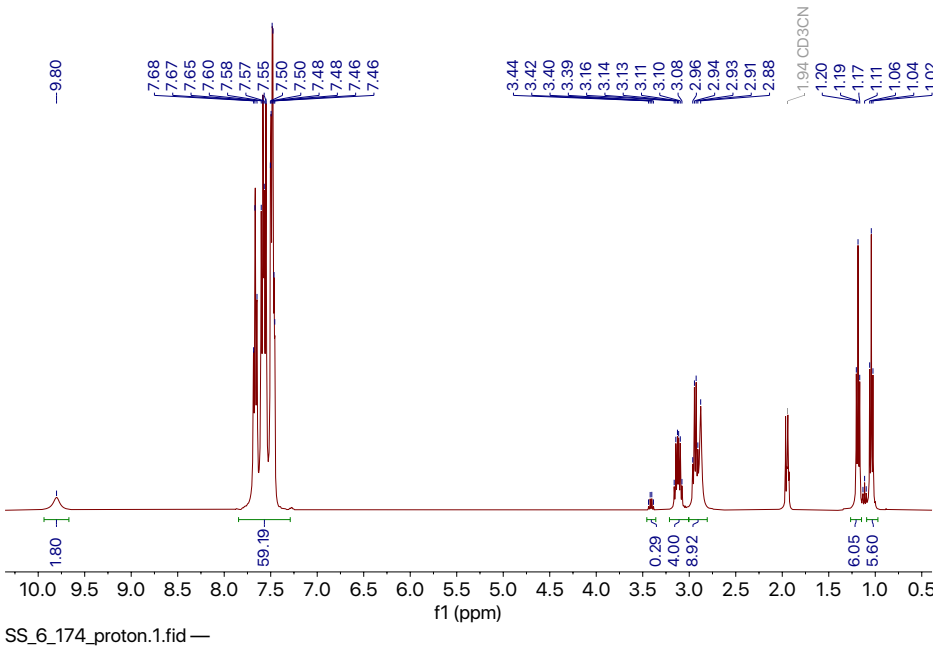

Figure S25: ^{1}H NMR spectrum of $[PPN]_2[H_2NEt_2][P_4O_{11}{-}NEt_2]$ (acetonitrile-d_3, 400 MHz).

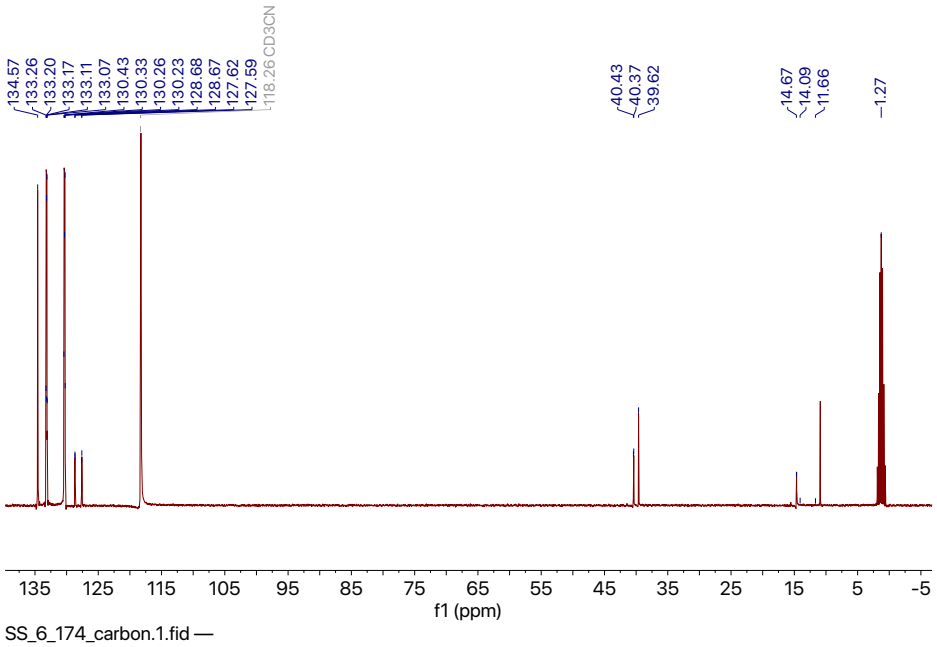

Figure S26: ^{13}C{^{1}H} NMR spectrum of $[PPN]_2[H_2NEt_2][P_4O_{11}{-}NEt_2]$ (acetonitrile-d_3, 100.6 MHz).

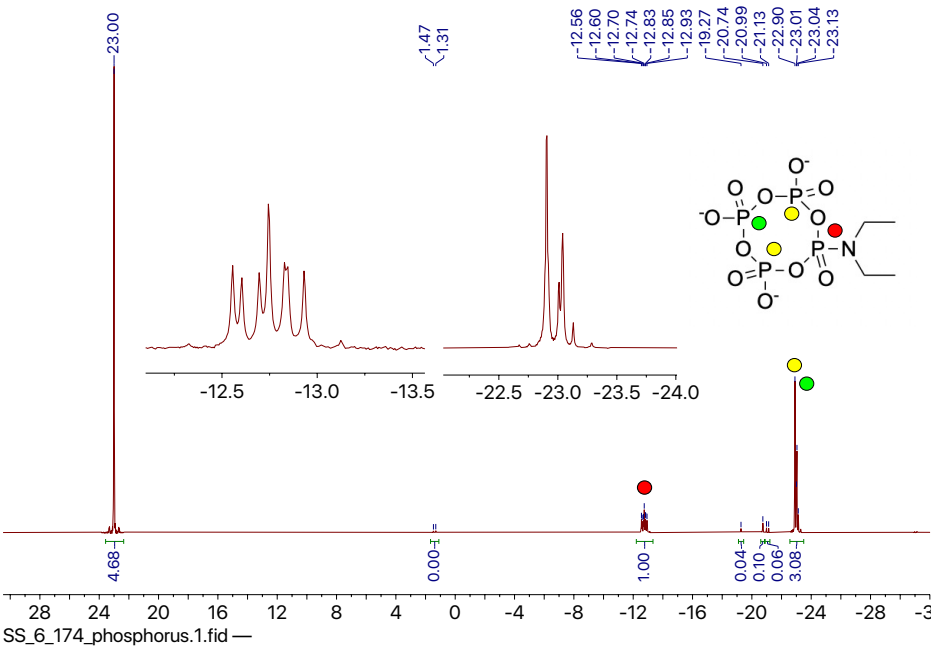

Figure S27: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[H_2NEt_2][P_4O_{11}{-}NEt_2]$ (acetonitrile-d_3, 162.0 MHz).

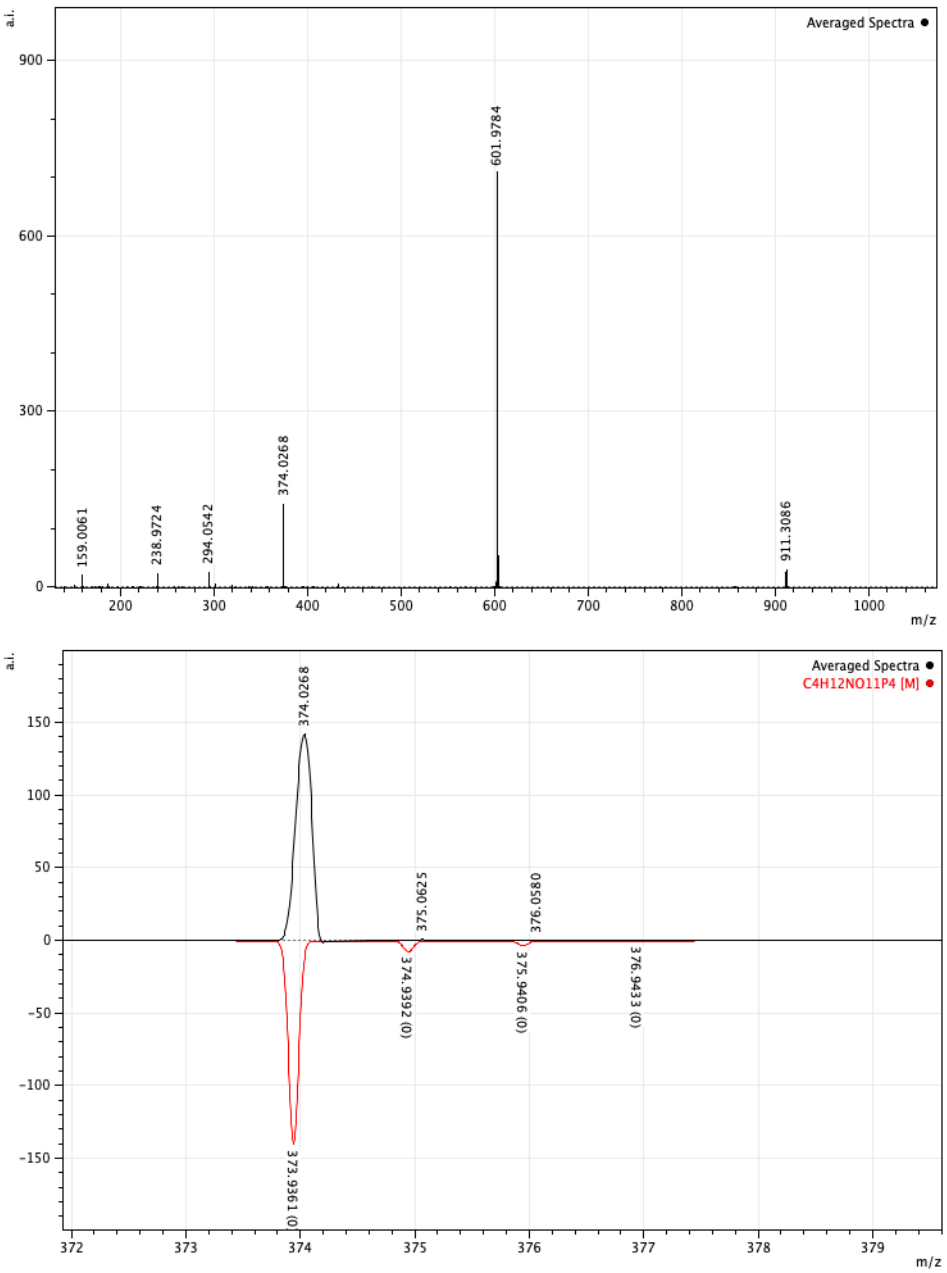

Figure S28: ESI-MS(−) of $[PPN]_2[H_2NEt_2][P_4O_{11}{-}NEt_2]$ (CH_3CN) with zoomed in portion showing the molecular ion ($[P_4O_{11}{-}NEt_2H_2]^-$, top) and calculated isotope pattern ($C_4H_{12}NO_{11}P_4$, bottom).

3.6 $[PPN]_2[C_4H_{10}NO][7]$

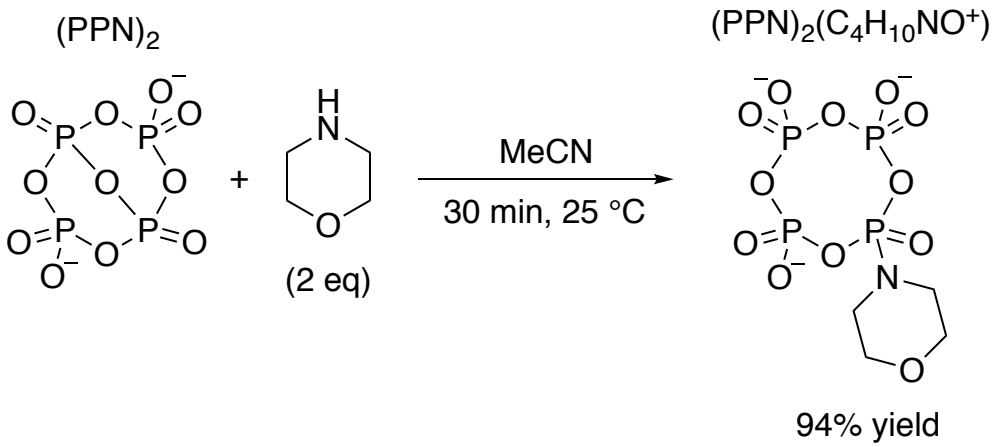

Figure S29: Synthesis of $[PPN]_2[C_4H_{10}NO]$[morpholino$-P_4O_{11}$].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.06 g, 0.044 mmol) was dissolved in acetonitrile (1 mL). To this solution was added morpholine (8 μL, 0.087 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Diethyl ether (5 mL) was then added to this mixture, giving a cloudy solution. The mixture was stirred vigorously, resulting in the formation of a colorless solution, and a colorless oil on the bottom of the vial. The supernatant was decanted off, and the oil was dried under vacuum for several hours, giving the product as a white solid (0.0633 g, 0.041 mmol, 94% yield).

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 10.33 (br, 2H), 7.71 to 7.45 (m, 60H), 3.75 to 3.71 (m, 4H), 3.52 to 3.50 (m, 4H), 3.19 to 3.15 (m, 4H), 3.09 to 3.07 (m, 4H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 134.6, 133.24 to 133.05 (m), 130.42 to 130.22 (m), 128.7 (d), 127.6 (d), 67.5 (d), 65.1, 45.2, 43.6.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 23.0, -14.5 to -14.9 (m), -22.1 to -23.0 (m).

ESI-MS($-$) of $[C_4H_8NO_{12}P_4]H_2^-$ (CH_3CN, m/z) 387.90 (calc'd 387.92)

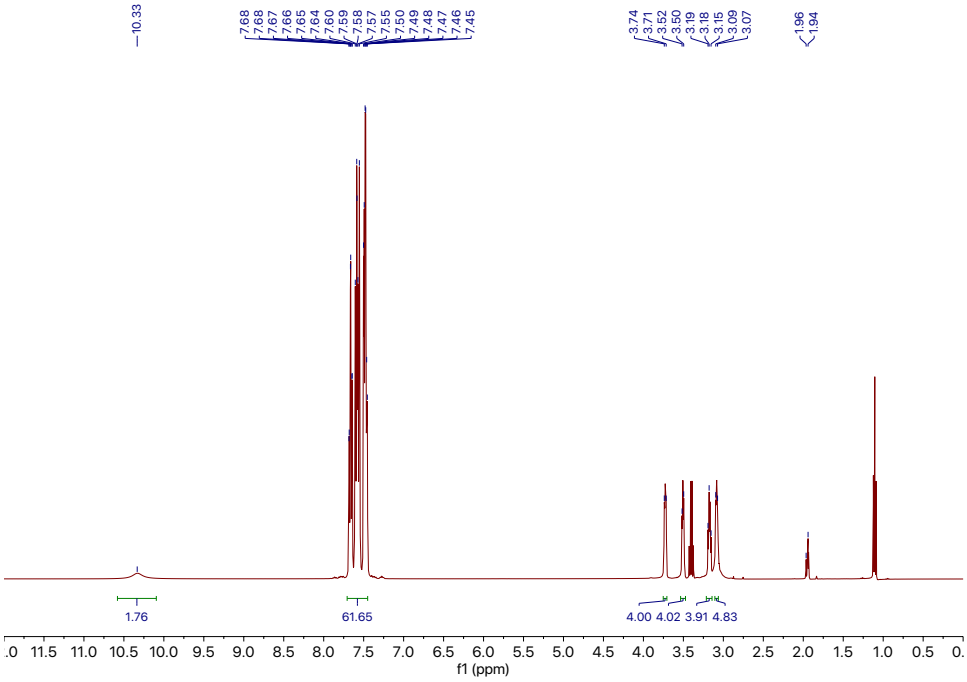

Figure S30: ^{1}H NMR spectrum of $[PPN]_2[C_4H_{10}NO][morpholino{-}P_4O_{11}]$ with residual diethyl ether (3.42 and 1.12 ppm) (acetonitrile-d_3, 400 MHz).

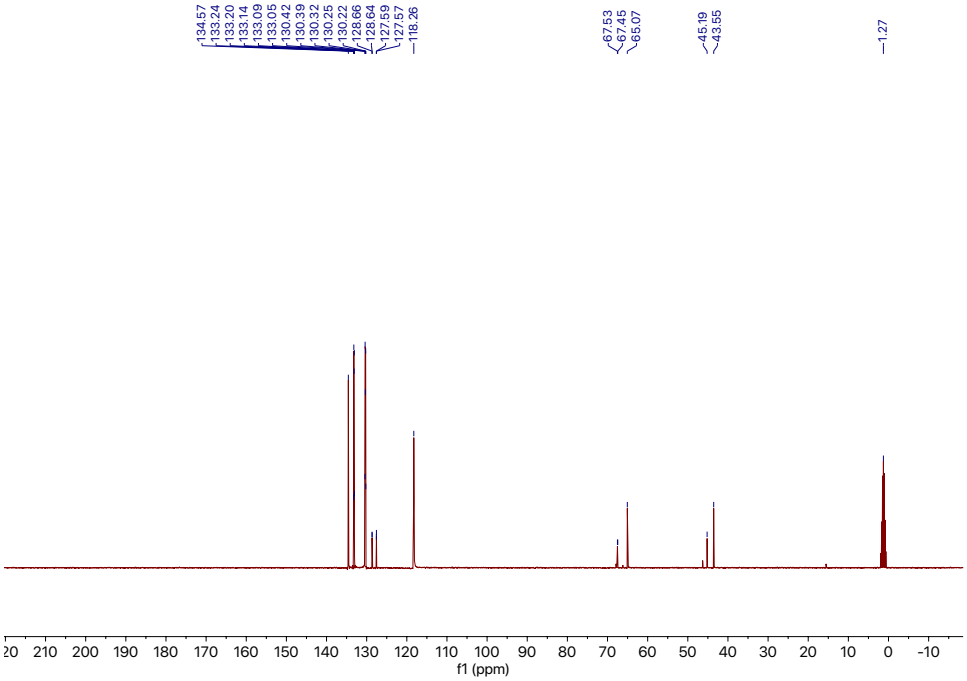

Figure S31: ^{13}C NMR spectrum of $[PPN]_2[C_4H_{10}NO][morpholino{-}P_4O_{11}]$ (acetonitrile-d_3, 100.6 MHz).

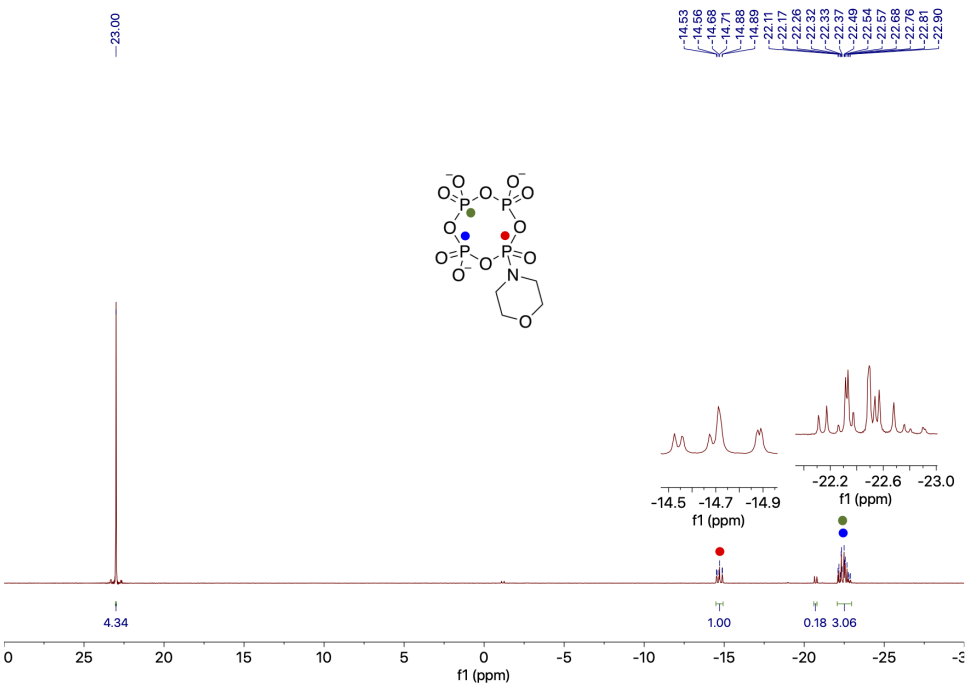

Figure S32: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[C_4H_{10}NO][morpholino{-}P_4O_{11}]$ (acetonitrile-d_3, 162.0 MHz).

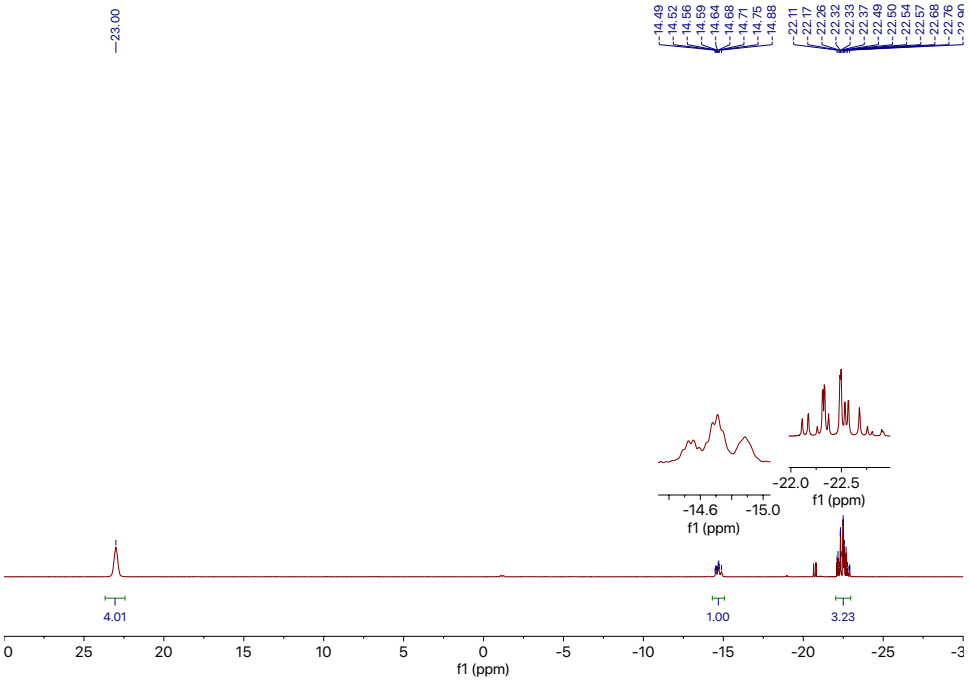

Figure S33: ^{31}P NMR spectrum of $[PPN]_2[C_4H_{10}NO][morpholino{-}P_4O_{11}]$ (acetonitrile-d_3, 162.0 MHz).

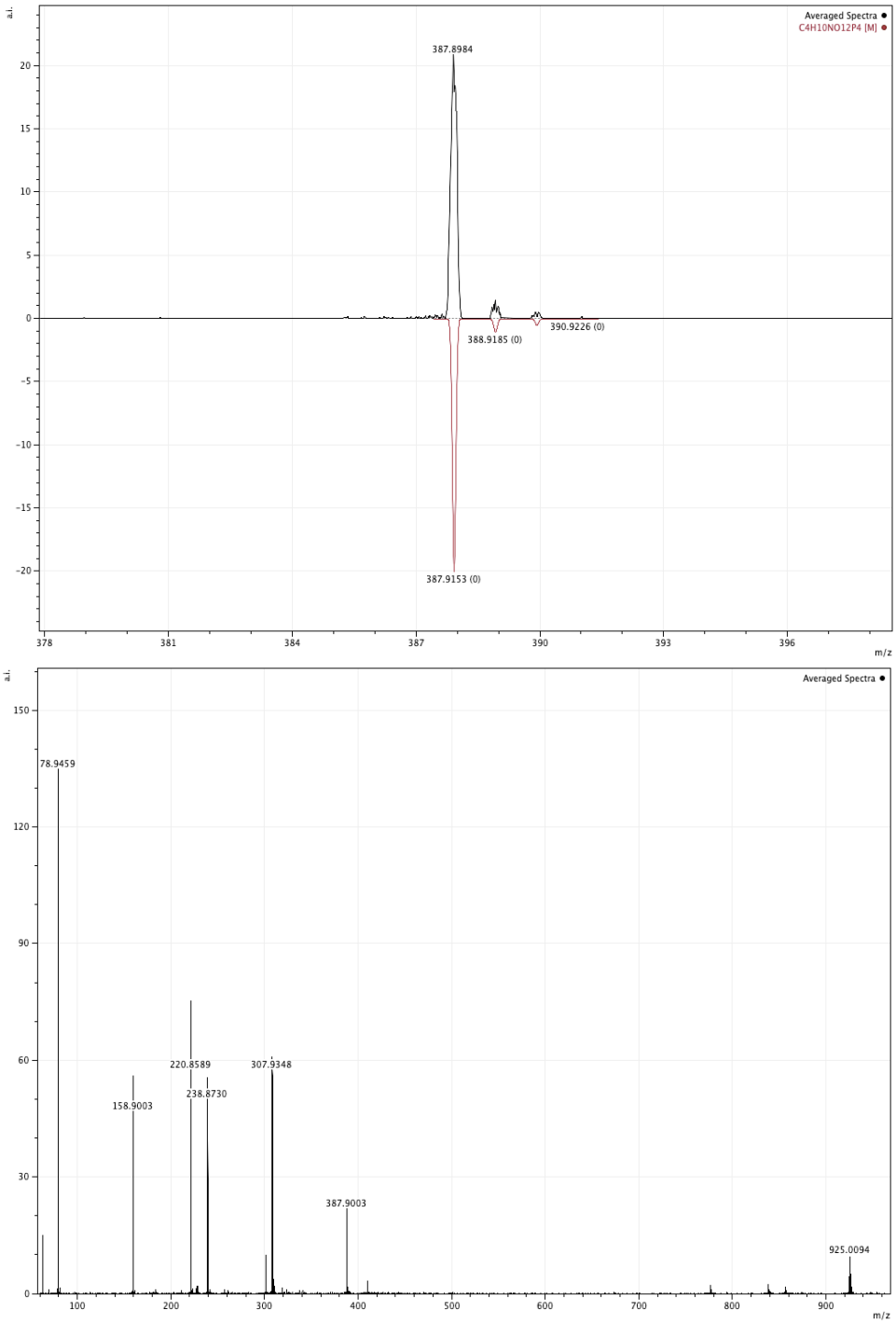

Figure S34: ESI-MS(−) of $[PPN]_2[C_4H_{10}NO][C_4H_8NO_{12}P_4]$ (CH_3CN) with zoomed in portion of the molecular ion ($[C_4H_8NO_{12}P_4]H_2^-$, top), and calculated isotope pattern ($C_4H_{10}NO_{12}P_4$, bottom).

3.7 [PPN]$_2$[8]

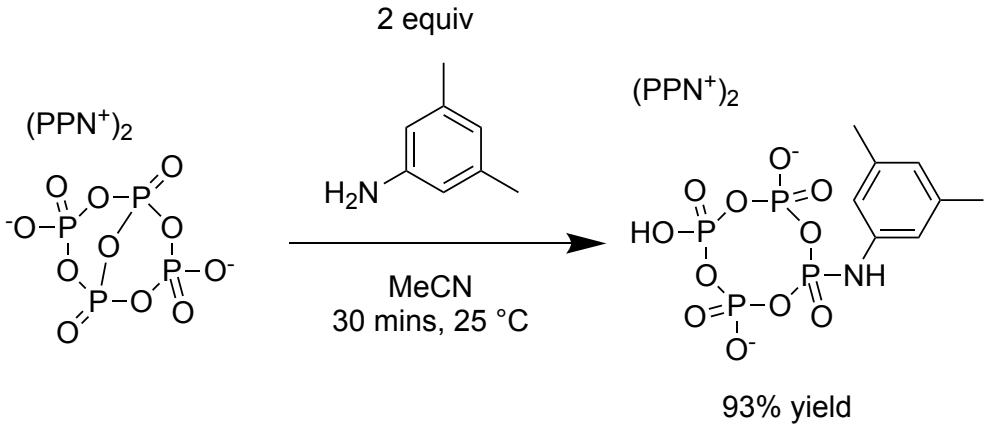

Figure S35: Synthesis of [PPN]$_2$[P_4O_{11}H−HNArMe_2].

In the glovebox, [PPN]$_2$[P_4O_{11}] (0.33 g, 0.24 mmol) was dissolved in acetonitrile (2 mL). To this solution was added 3,5-dimethylaniline (0.058 g, 0.48 mmol). The resulting mixture was stirred at room temperature for 30 min. Diethyl ether (10 mL) was then added to this mixture, giving a cloudy solution. After several hours, the product crystallized on the bottom of the vial. The supernatant was decanted off, and the crystals were dried under vacuum for several hours, giving the product as a colorless solid (0.33 g, 0.12 mmol, 93% yield).

Note: Two equivalents of 3,5-dimethylaniline were utilized in this reaction, but no ammonium counterion was formed by scavenging the acidic proton. Therefore, 3,5-dimethylaniline is too weak of a base to deprotonate the phosphoric acid functionality.

Elem. Anal. Found(Calc'd) for $C_{80}H_{71}N_3O_{11}P_8$: C 62.81 (64.13), H 5.04 (4.78), N 3.00 (2.80)

^{1}H NMR (acetonitrile-d_3, 400 MHz) δ 7.68 to 7.45 (m, 60H), 6.71 (s, 2H), 6.55 (s, 1H), 2.18 (s, 6H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz) δ 141.0, 140.0, 134.6, 133.22 to 133.05 (m), 130.38 to 130.25 (m), 128.7, 127.6, 123.3, 116.8 (d), 21.3.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz) δ 23.0, −20.4 (t), −22.2 (t), −23.6 (dd).

ESI-MS(−) of [PPN]$_2$[P_4O_{11}H−HNPhMe_2] in CH_3CN/H_2O, found 421.92 m/z (calc'd 421.94 m/z) for $C_8H_{12}NO_{11}P_4$

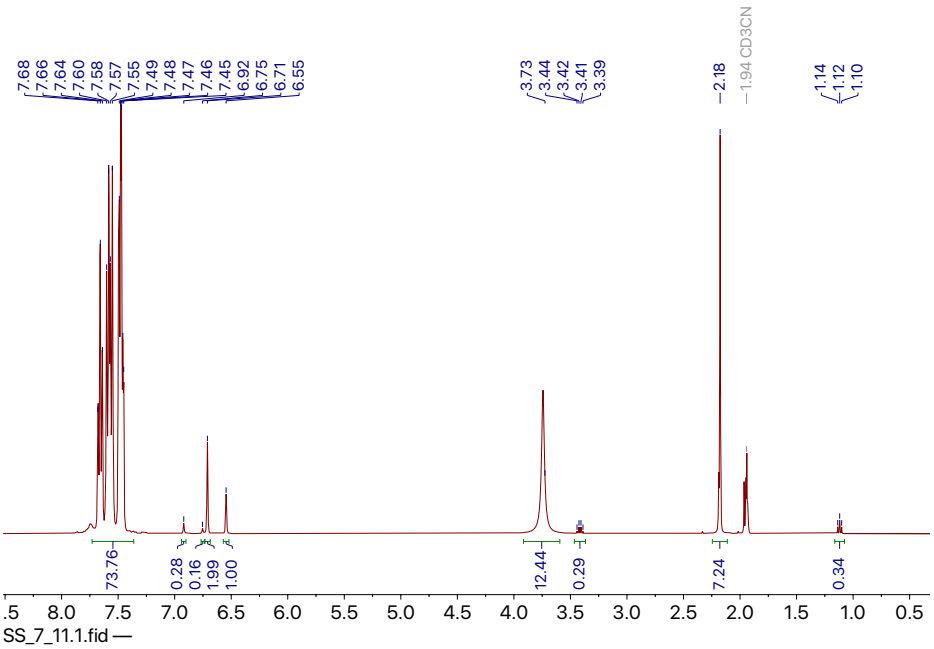

Figure S36: ^{1}H NMR spectrum of $[PPN]_2[P_4O_{11}H{-}HNArMe_2]$ (acetonitrile-d_3, 400 MHz).

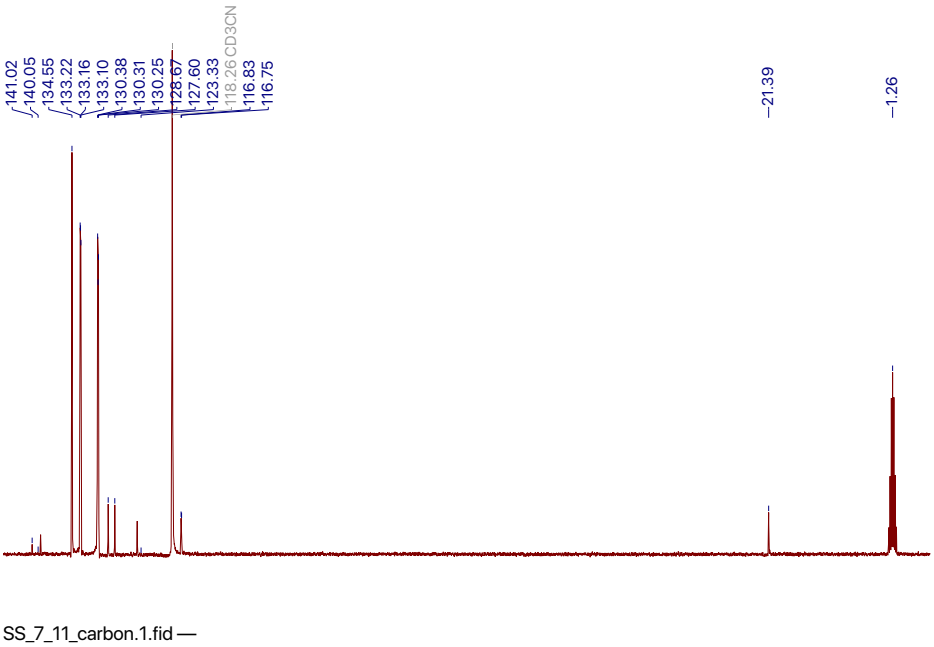

Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of $[PPN]_2[P_4O_{11}H{-}HNArMe_2]$ (acetonitrile-d_3, 100.6 MHz).

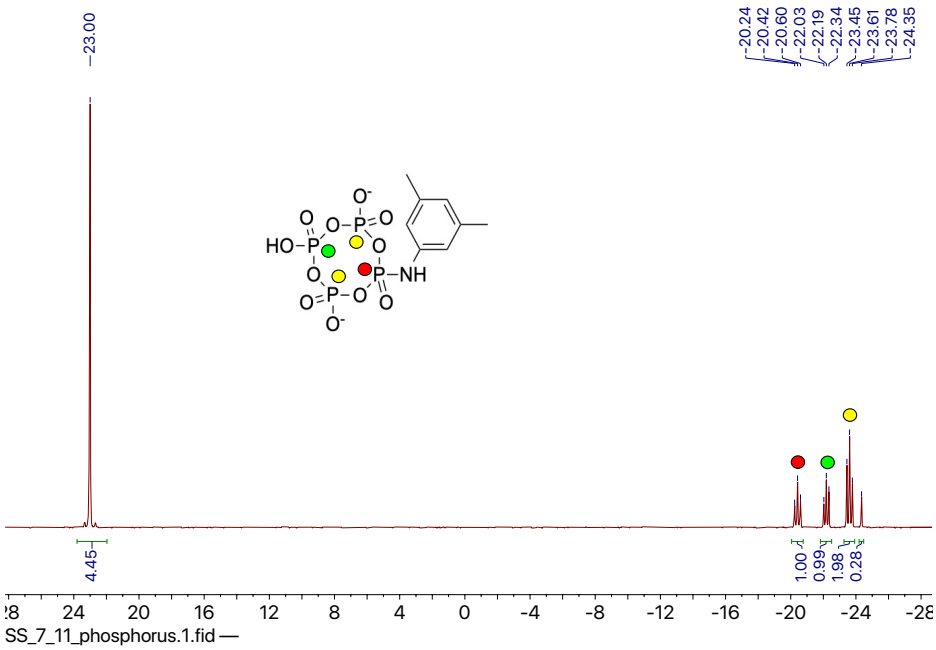

Figure S38: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[P_4O_{11}H{-}HNArMe_2]$ (acetonitrile-d_3, 162.0 MHz).

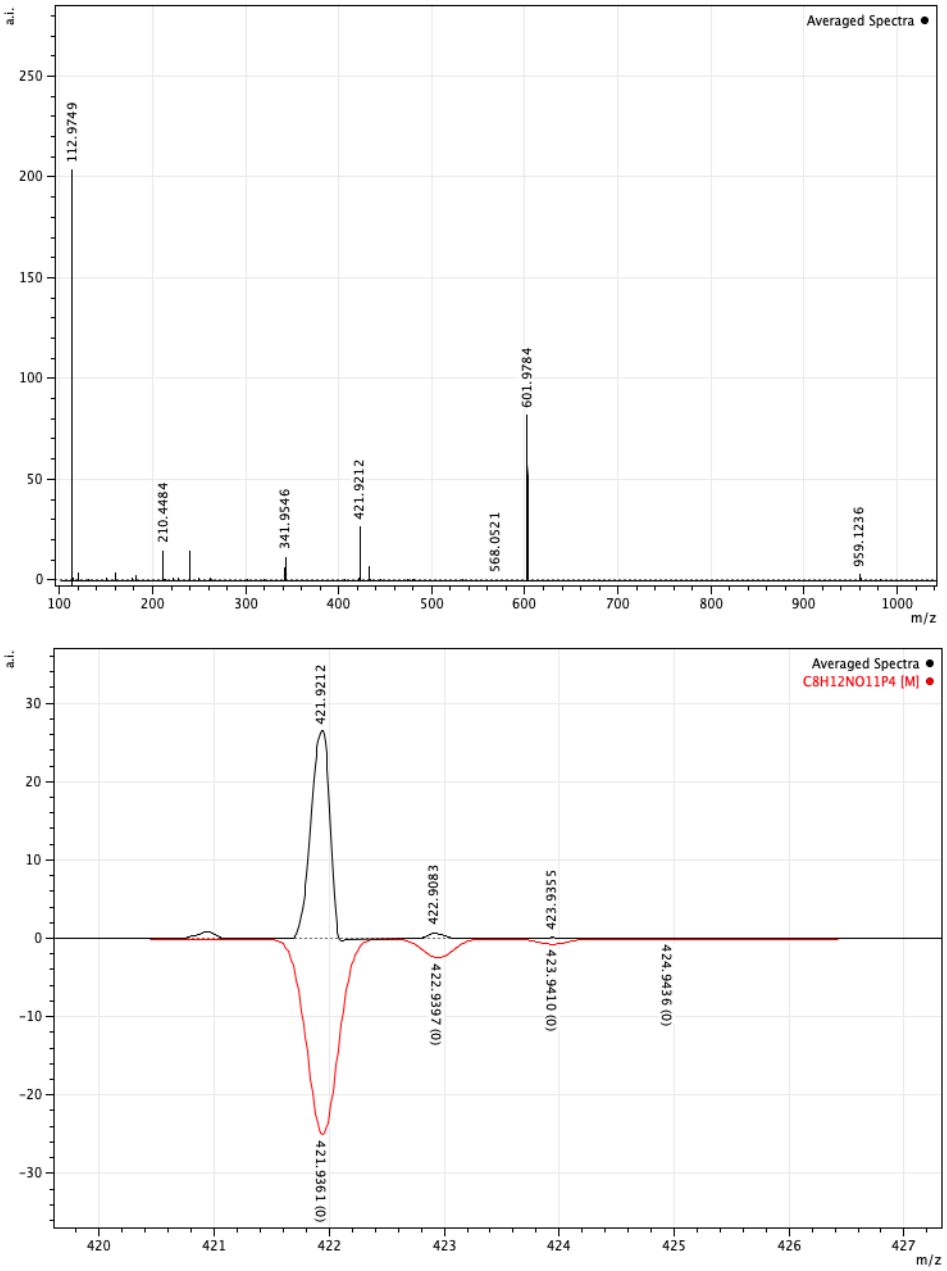

Figure S39: ESI-MS(−) of $[PPN]_2[P_4O_{11}H{-}HNArMe_2]$ (CH_3CN) with zoomed in portion showing the molecular ion ($[P_4O_{11}{-}NHArMe_2H_2]^-$, top) and calculated isotope pattern ($C_8H_{12}NO_{11}P_4$, bottom).

3.8 $[PPN]_2[H_3NiPr][9]$

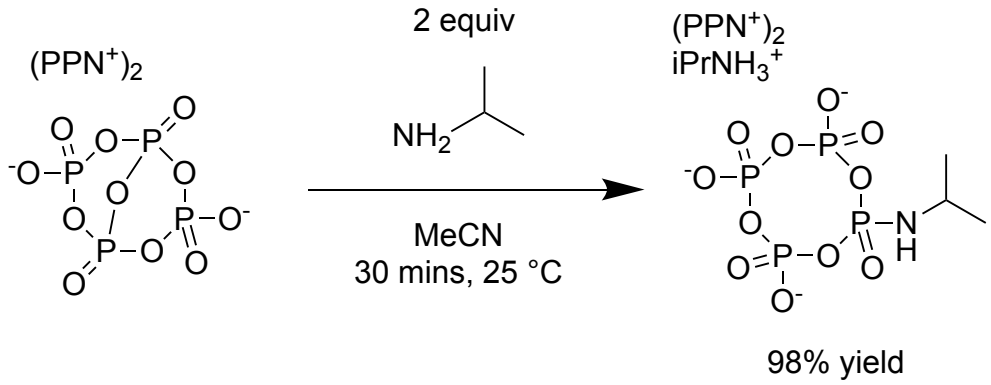

Figure S40: Synthesis of $[PPN]_2[H_3NiPr][P_4O_{11}{-}NH^iPr]$.

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.21 g, 0.15 mmol) was dissolved in acetonitrile (2 mL). To this solution was added isopropylamine (0.018 g, 0.31 mmol). The resulting mixture was stirred at room temperature for 30 min. Diethyl ether (10 mL) was then added to this mixture, giving a cloudy solution. After several hours, the product crystallized on the bottom of the vial. The supernatant was decanted off, and the crystals were dried under vacuum for several hours, giving the product as a colorless solid (0.22 g, 0.15 mmol, 98% yield).

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 8.21 (b, 3H), 7.67 to 7.48 (m, 60H), 4.11 (b, 1H), 3.47 to 3.37 (m, 1H), 3.35 to 3.30 (m, 1H), 1.22 (d, 6H), 1.11 (d, 6H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 134.6, 132.36 to 132.17 (m), 129.52 to 129.32 (m), 128.7 (d), 127.6 (d), 43.2 (d), 42.4, 24.7 (d), 20.4.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 23.0, -11.3 (t), -22.59 to -22.97 (m), -23.38 to -23.77 (m).

ESI-MS($-$) of $[PPN]_2[P_4O_{11}H{-}NHiPr]$ in CH_3CN/H_2O, found 359.88 m/z (calc'd 359.92 m/z) for $C_3H_{10}NO_{11}P_4$

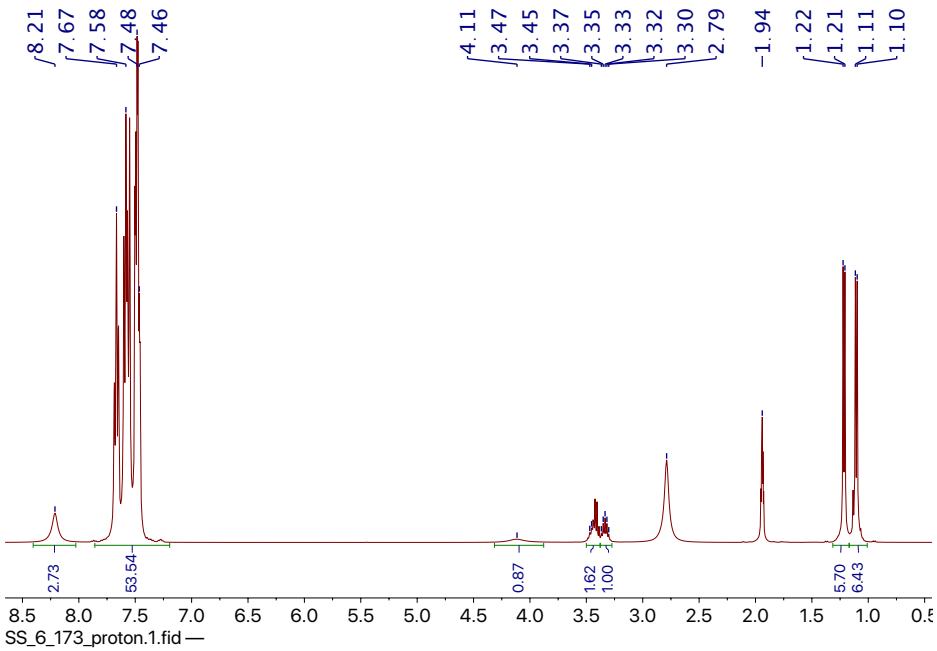

Figure S41: ^{1}H NMR spectrum of $[PPN]_2[H_3NiPr][P_4O_{11}{-}NH^{i}Pr]$ (acetonitrile-d_3, 400 MHz).

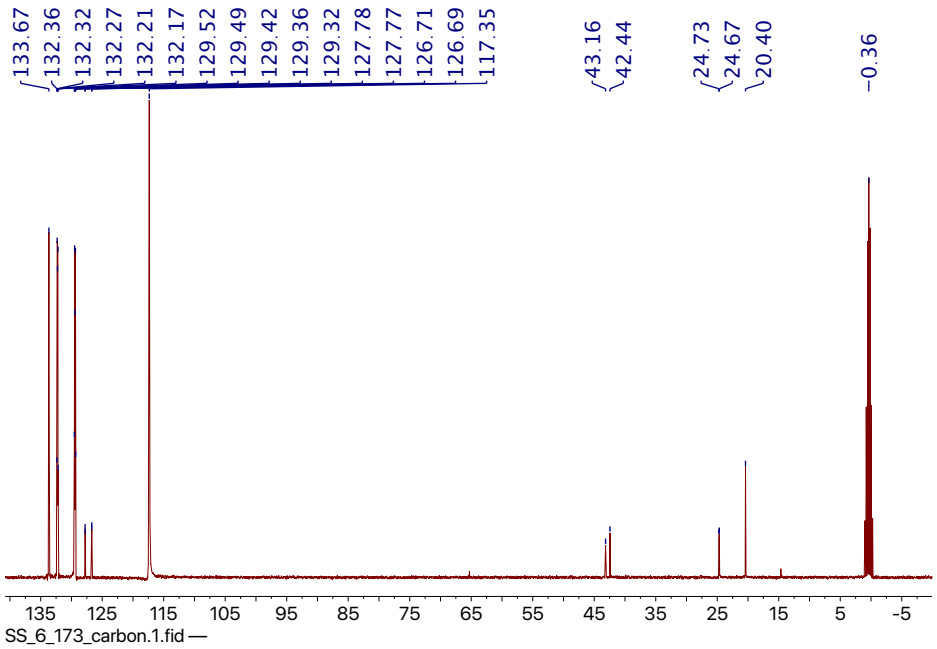

Figure S42: $^{13}C\{^{1}H\}$ NMR spectrum of $[PPN]_2[H_3NiPr][P_4O_{11}{-}NH^{i}Pr]$ (acetonitrile-d_3, 100.6 MHz).

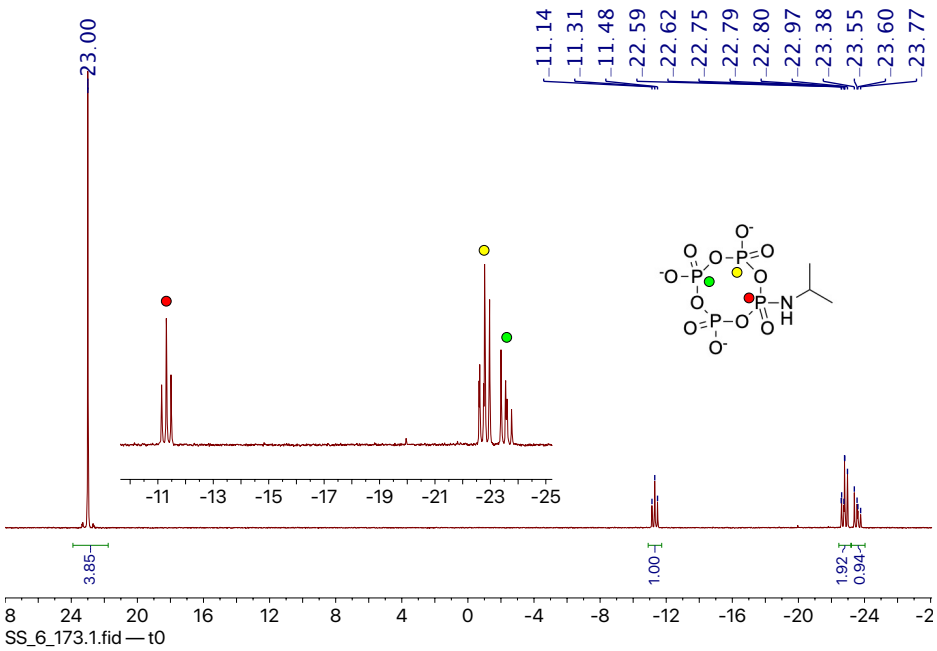

Figure S43: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[H_3NiPr][P_4O_{11}{-}NH^{i}Pr]$ (acetonitrile-d_3, 162.0 MHz).

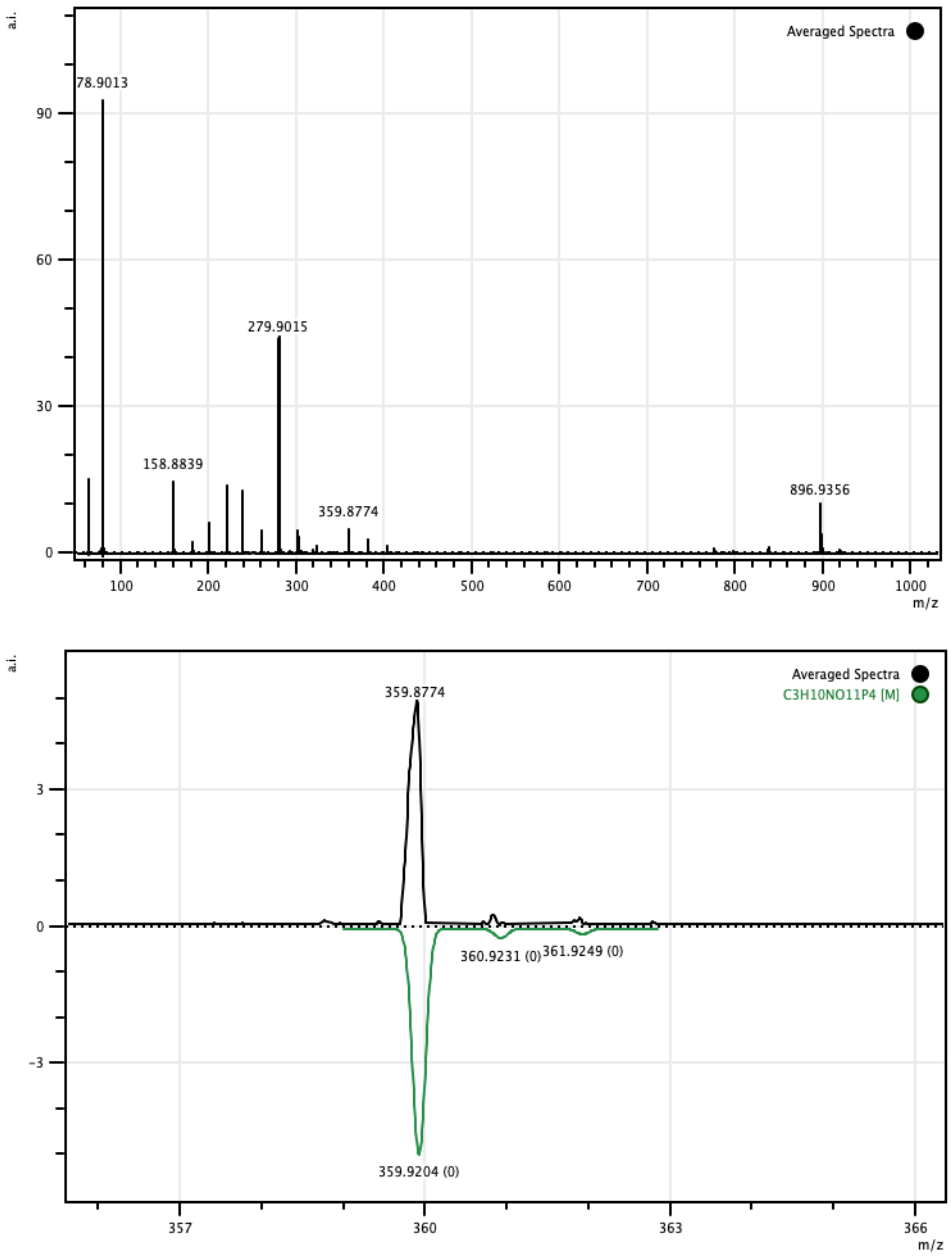

Figure S44: ESI-MS(−) of $[PPN]_2[H_3NiPr][P_4O_{11}{-}NH^{i}Pr]$ (CH_3CN) with zoomed in portion showing the molecular ion ($[P_4O_{11}H_2{-}NHiPr]^-$, top) and calculated isotope pattern ($C_3H_{10}NO_{11}P_4$, bottom).

3.9 [PPN]$_2$[TBA][10]

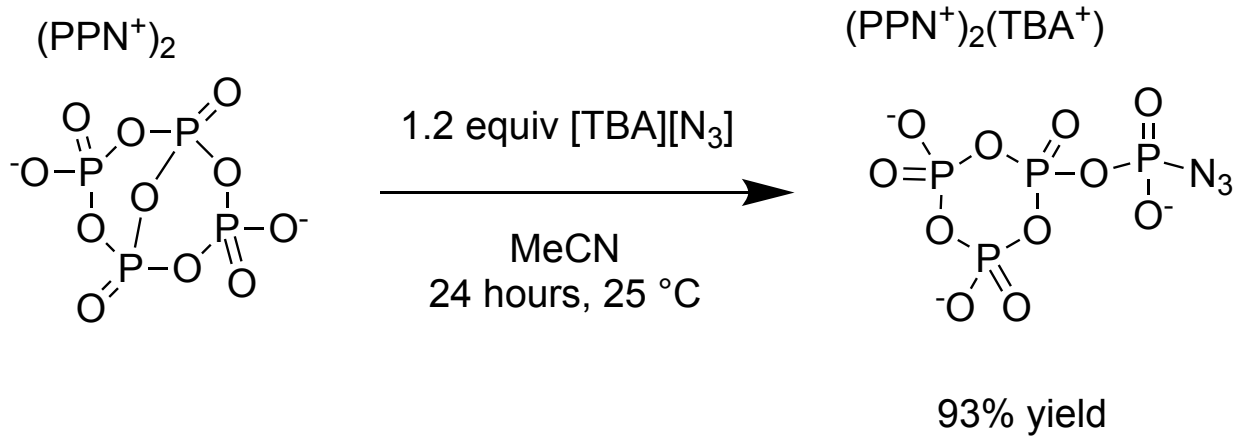

Figure S45: Synthesis of [PPN]$_2$[TBA][**10**].

In the glovebox, [PPN]$_2$[P_4O_{11}] (0.14 g, 0.10 mmol) was dissolved in acetonitrile (1 mL), to which tetrabutylammonium azide (0.035 g, 0.12 mmol) in acetonitrile (1 mL) was added. The reaction mixture was stirred for 24 hours at ambient temperature. To this mixture was added 10 mL of diethyl ether, resulting in a cloudy suspension, which settled after 4 hours into an oil and supernatant solution. The supernatant solution was decanted off, and the remaining oil dried under vacuum at room temperature to give the product as a colorless solid (0.16 g, 0.094 mmol, 94% yield).

Elem. Anal. Found(Calc'd) for $C_{88}H_{96}N_6O_{11}P_8$: C 63.80 (63.61), H 6.01 (5.82), N 4.97 (5.06)

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 7.91 to 7.12 (m, 60H), 3.27 to 2.99 (m, 8H), 1.63 (p, J = 7.8 Hz, 8H), 1.37 (h, J = 7.4 Hz, 8H), 0.97 (t, J = 7.3 Hz, 12H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 134.58 (d, J = 1.7 Hz), 134.01 to 132.52 (m), 131.31 to 129.44 (m), 128.68 (d, J = 1.8 Hz), 127.61 (d, J = 2.1 Hz), 63.77 to 54.42 (m), 24.33, 20.29, 13.82.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 23.00, −14.42 (d, J = 20.1 Hz), −20.93 (d, J = 23.1 Hz), −30.66 (q, J = 22.6 Hz).

ESI-MS(−) of [PPN]$_2$[TBA][**10**] in CH_3CN, found 585.34 m/z (calc'd 585.14 m/z) for $C_{16}H_{37}N_4O_{11}P_4$.

IR (ATR, cm^{-1}): 2117 (m, $-N_3$).

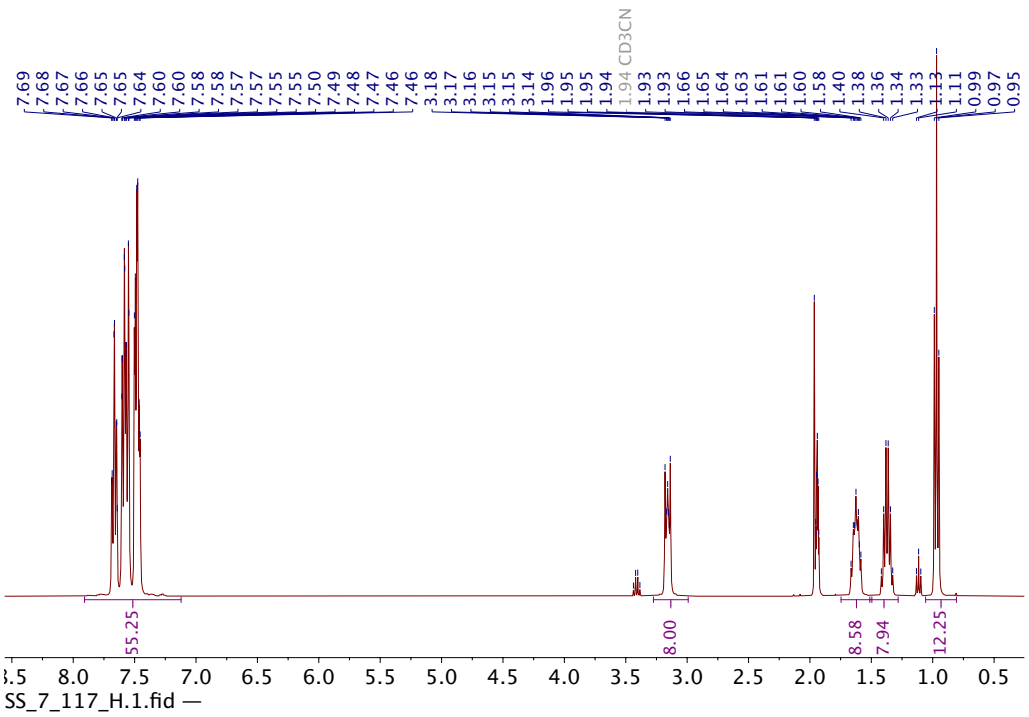

Figure S46: ^{1}H NMR spectrum of [PPN]$_2$[TBA][**10**] (acetonitrile-d_3, 400 MHz) with residual diethyl ether (3.42 and 1.12 ppm).

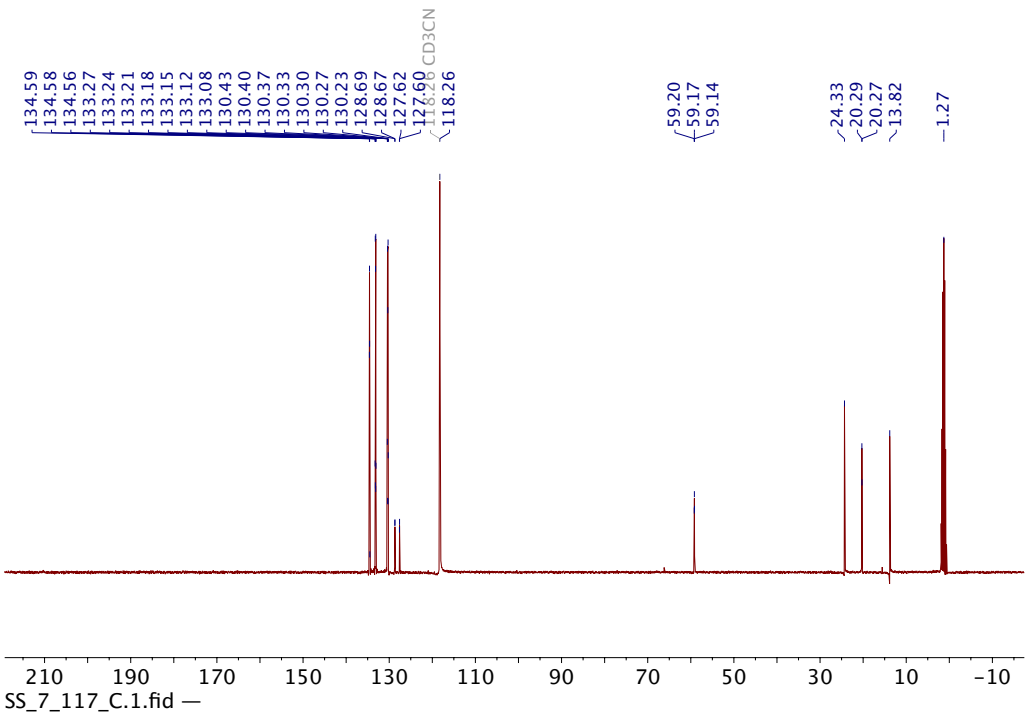

Figure S47: $^{13}C\{^{1}H\}$ NMR spectrum of $[PPN]_2[TBA][\mathbf{10}]$ (acetonitrile-d_3, 101 MHz).

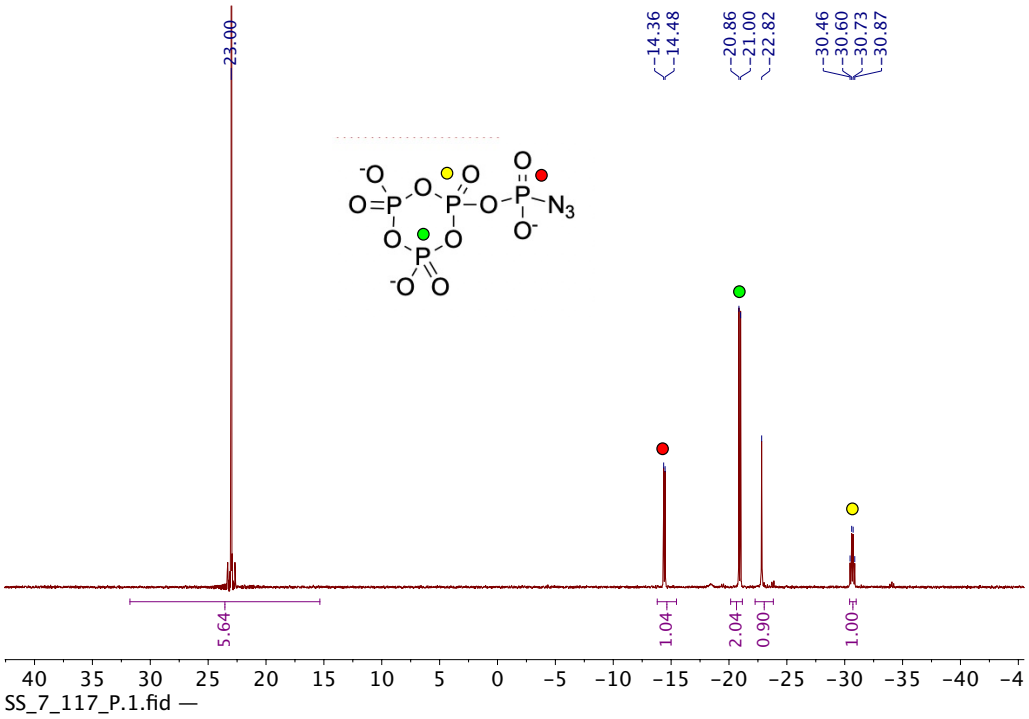

Figure S48: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[TBA][\mathbf{10}]$ (acetonitrile-d_3, 162 MHz). The singlet at −22.8 ppm corresponds to tetrametaphosphate as an impurity.

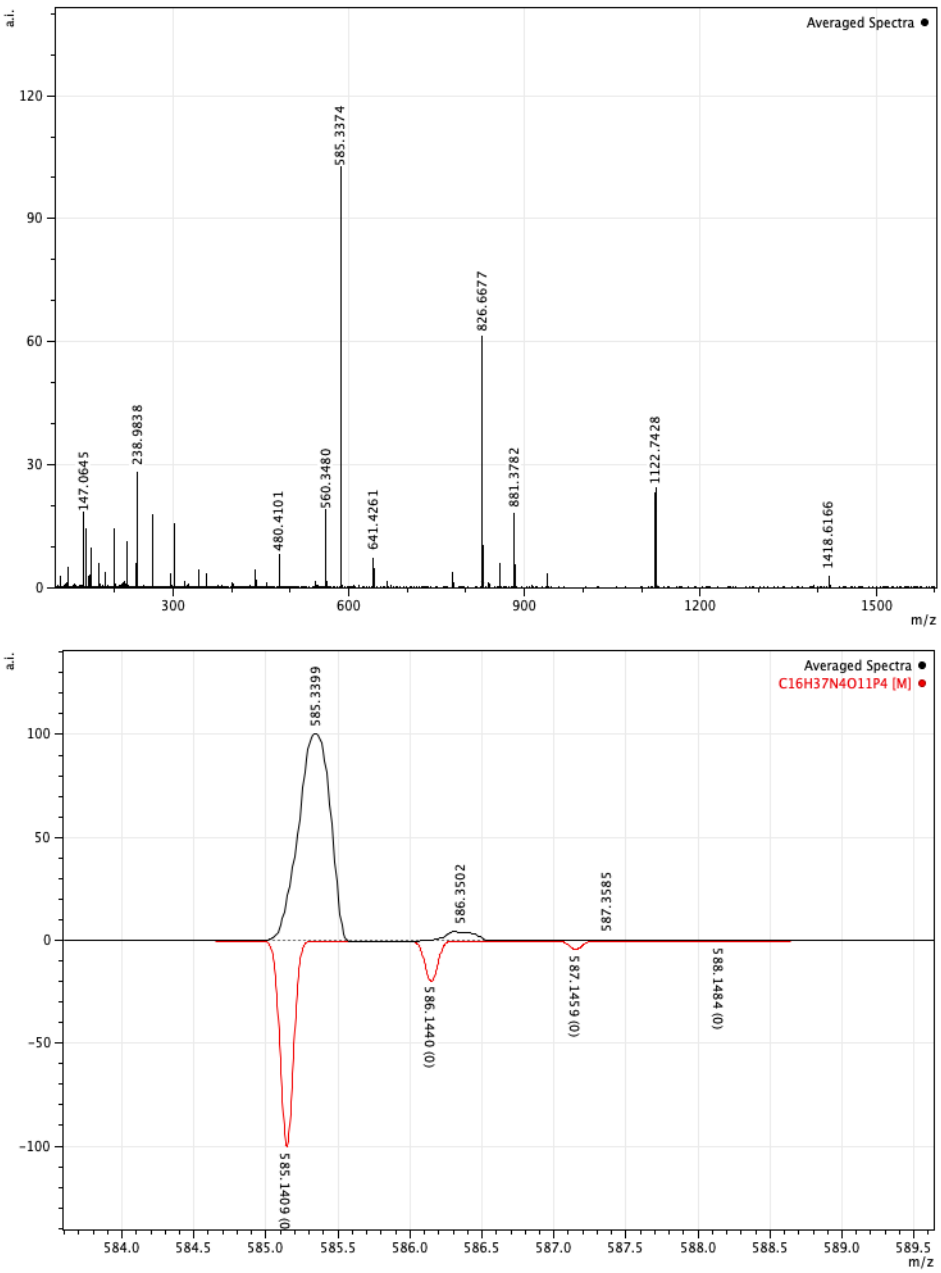

Figure S49: ESI-MS(−) of $[PPN]_2[TBA][\mathbf{10}]$ (CH_3CN) with zoomed in portion showing the molecular ion ($[P_4O_{11}{-}N_3H][TBA]^-$, top) and calculated isotope pattern ($C_{16}H_{37}N_4O_{11}P_4$, bottom).

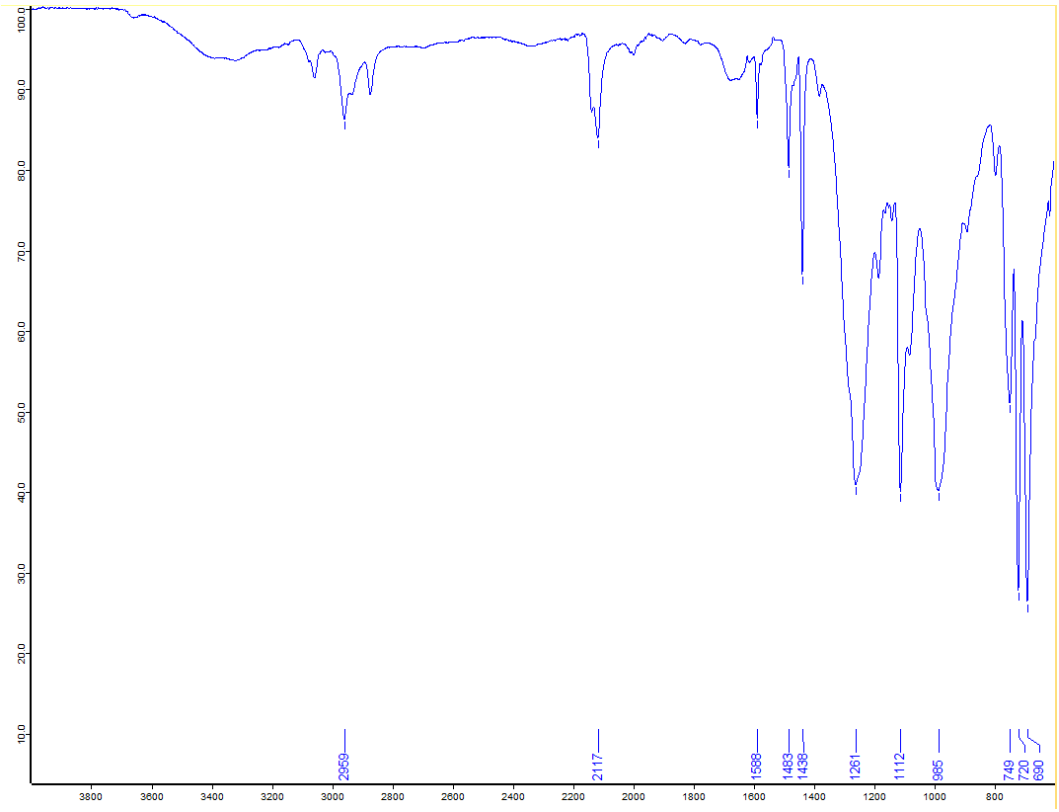

Figure S50: ATR-IR spectrum of solid $[PPN]_2[TBA]$[**10**].

3.10 $[PPN]_2[H_2NEt_2]$[11]

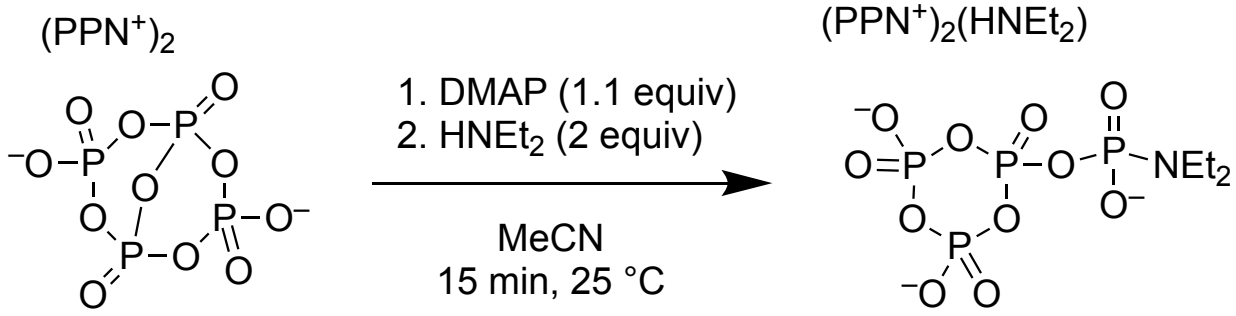

Figure S51: Synthesis of $[PPN]_2[H_2NEt_2]$[**11**].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.064 g, 0.047 mmol) was dissolved in acetonitrile (1 mL), to which DMAP (0.0063 g, 0.051 mmol) in acetonitrile (1 mL) was added. The reaction mixture was stirred for 15 minutes at ambient temperature. To this mixture was then added diethylamine (0.01 mL, 0.094 mmol) and the resulting mixture stirred for 5 minutes. To this mixture was then added 10 mL of diethyl ether, resulting in a cloudy suspension, which settled after 4 hours into an oil and a supernatant solution. The supernatant solution was

decanted off, and the remaining oil dried under vacuum at room temperature to give the product as a colorless solid (0.066 g, 0.043 mmol, 92% yield).

Elem. Anal. Found(Calc'd) for $C_{76}H_{71}N_3O_{11}P_8$: C 61.87 (62.95), H 5.49 (4.94), N 3.56 (2.90)

^{1}H NMR (D_2O, 400 MHz): δ 10.05 (b, 2H), 7.69 to 7.46 (m, 60H), 3.07 (dq, 4H), 2.85 (q, 4H), 1.22 (t, 6H), 1.02 (t, 6H).

^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 134.58 (t, J = 1.5 Hz), 133.95 âĂŞ 132.43 (m), 131.36 âĂŞ 129.84 (m), 128.70 (d, J = 2.0 Hz), 127.63 (d, J = 1.8 Hz), 41.48 (d, J = 4.1 Hz), 40.84, 15.25 (d, J = 3.1 Hz), 11.06.

^{31}P{^{1}H} NMR (D_2O, 162.0 MHz): δ 23.00 (s), 1.43 (d, J = 25.2 Hz), −20.90 (d, J = 23.5 Hz), −31.00 (q, J = 24.0 Hz).

ESI-MS(−) of $[PPN]_2[H_2NEt_2]$[**11**] in CH_3CN, found 911.21 m/z (calc'd 911.11 m/z) for $[PPN][11]^-$ ($C_{40}H_{41}N_2O_{11}P_6$)

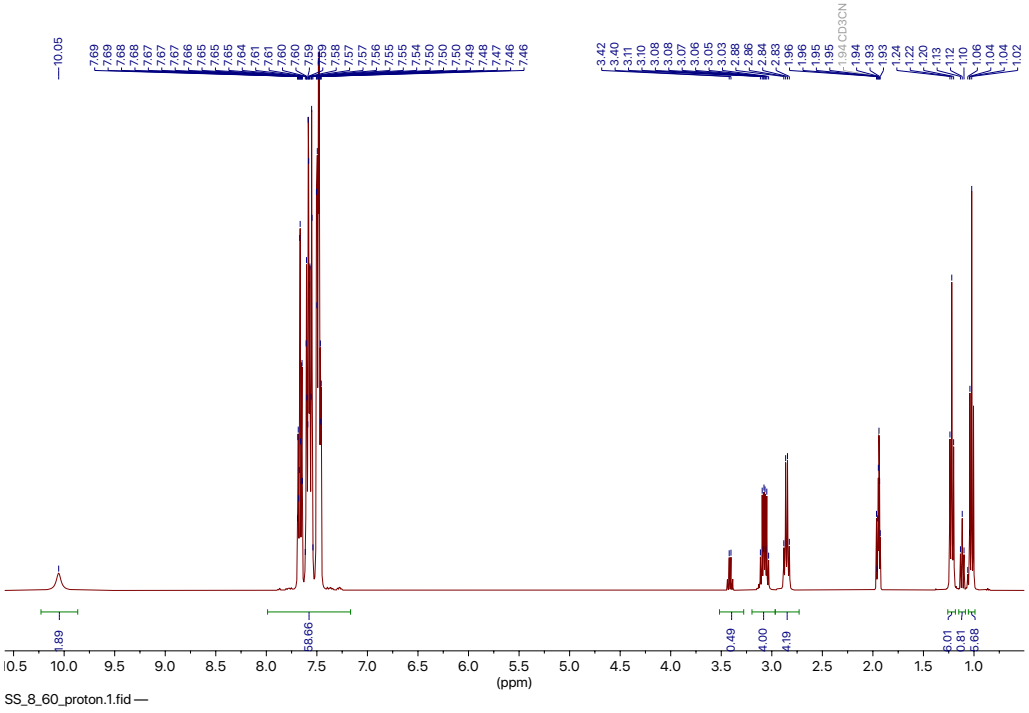

Figure S52: ^{1}H NMR spectrum of $[PPN]_2[H_2NEt_2]$[**11**] (acetonitrile-d_3, 400 MHz).

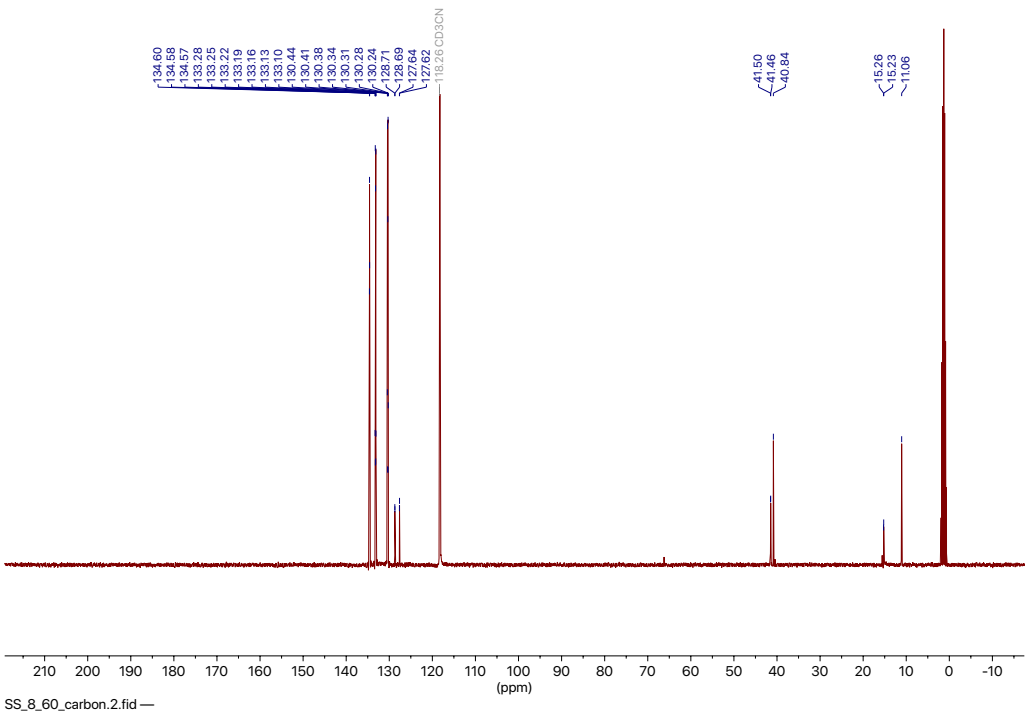

Figure S53: $^{13}C\{^{1}H\}$ NMR spectrum of $[PPN]_2[H_2NEt_2]$[**11**] (acetonitrile-d_3, 101 MHz).

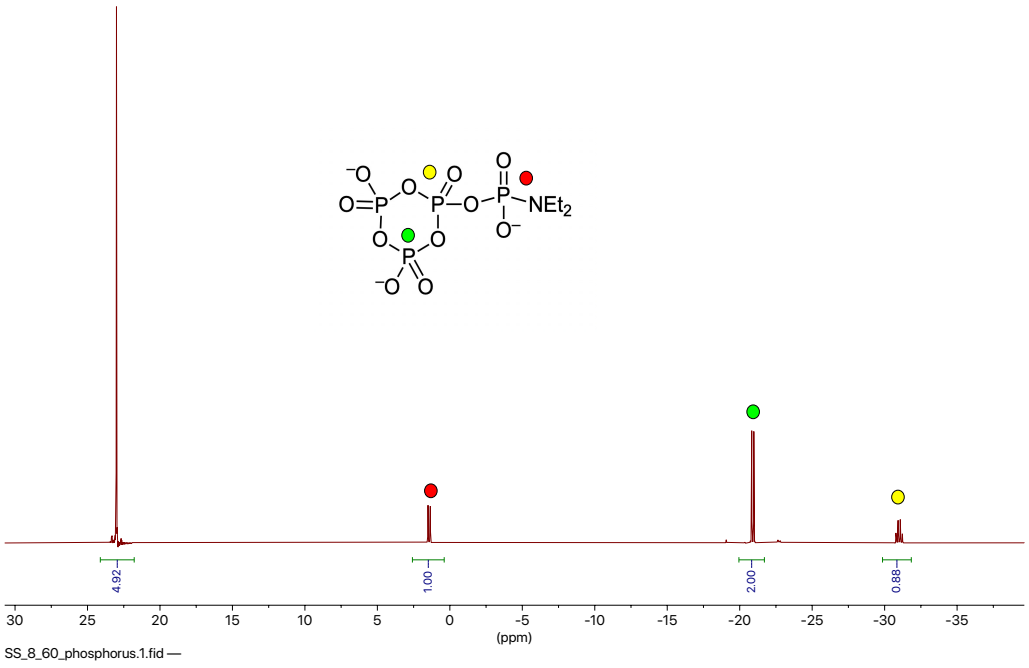

Figure S54: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[H_2NEt_2]$[**11**] (acetonitrile-d_3, 162 MHz).

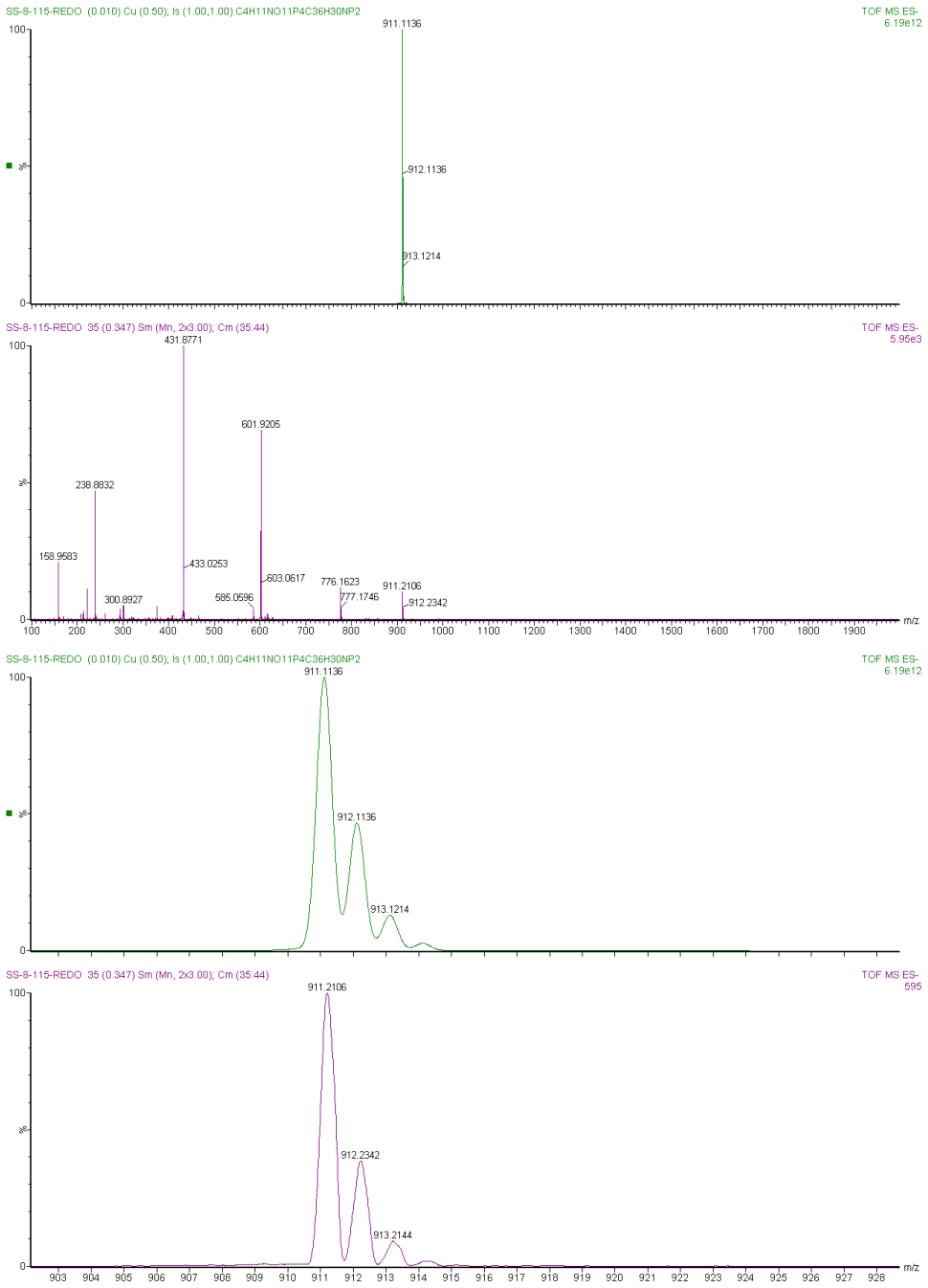

Figure S55: ESI-MS(−) of $[PPN]_2[H_2NEt_2]$[**11**] in CH_3CN, with zoomed in portion showing the molecular ion ($[PPN][11]^-$, $C_{40}H_{41}N_2O_{11}P_6$).

3.11 [PPN]$_3$[12a]

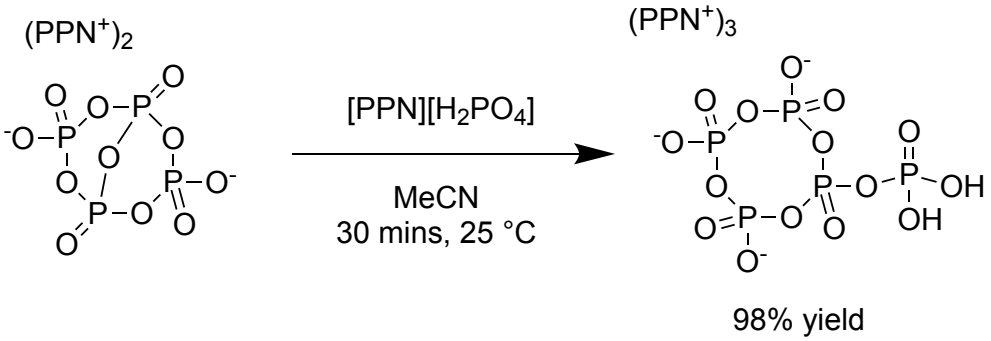

Figure S56: Synthesis of [PPN]$_3$[H_2PO_4−P_4O_{11}].

In the glovebox, [PPN]$_2$[P_4O_{11}] (0.15 g, 0.11 mmol) was dissolved in acetonitrile (2 mL). To this solution was added [PPN][H_2PO_4] (0.071 g, 0.11 mmol). The resulting mixture was stirred at room temperature for 30 min. Diethyl ether (10 mL) was then added to this mixture, giving a cloudy solution. After several hours, the product formed an oil on the bottom of the vial. The supernatant was decanted off, and the oil was dried under vacuum for several hours, giving the product as a colorless solid (0.22 g, 0.11 mmol, 98% yield).

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 7.68 to 7.46 (m, 90H), 6.10 (br, 2H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 133.7, 132.28 to 133.09 (m), 130.43 to 130.23 (m), 127.8 (d), 126.7 (d).

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 23.0, −12.8 (d, J_{PP} = 33.9 Hz), −26.1 (dd, J_{PP} = 32.4, 33.1 Hz), −27.5 (t, J_{PP} = 32.4 Hz), −42.5 (dt, J_{PP} = 33.1, 33.9 Hz).

ESI-MS(−) of [PPN]$_3$[H_2PO_4−P_4O_{11}] (CH_3CN, found 935.96 m/z for [PPN][H_2PO_4−$P_4O_{11}H$]$^-$) (calc'd 936.00 for $C_{36}H_{33}NO_{15}P_7$)

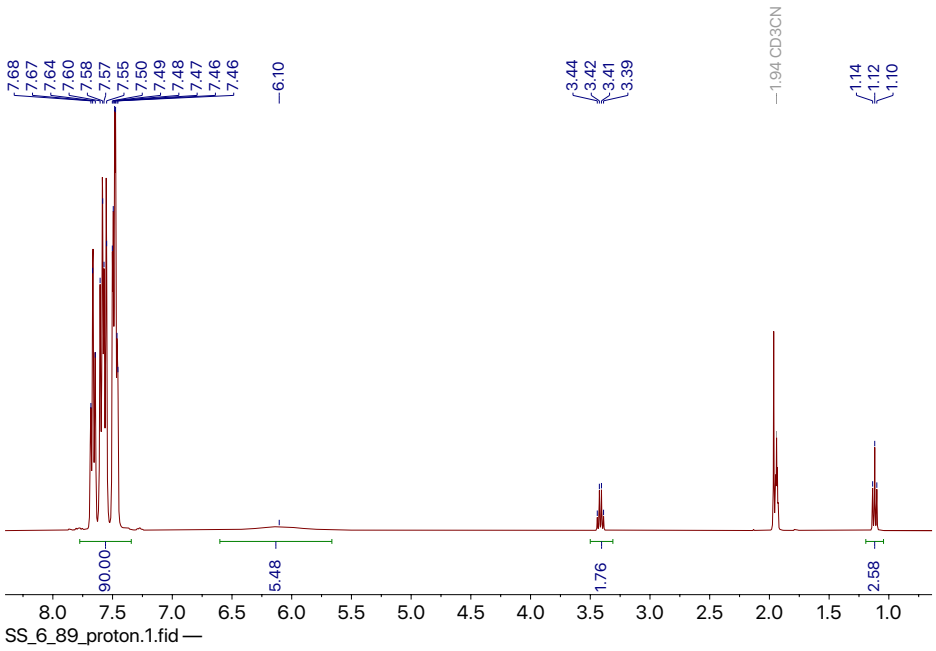

Figure S57: ^{1}H NMR spectrum of $[PPN]_3[H_2PO_4{-}P_4O_{11}]$ (acetonitrile-d_3, 400 MHz) with residual diethyl ether (3.42 and 1.12 ppm).

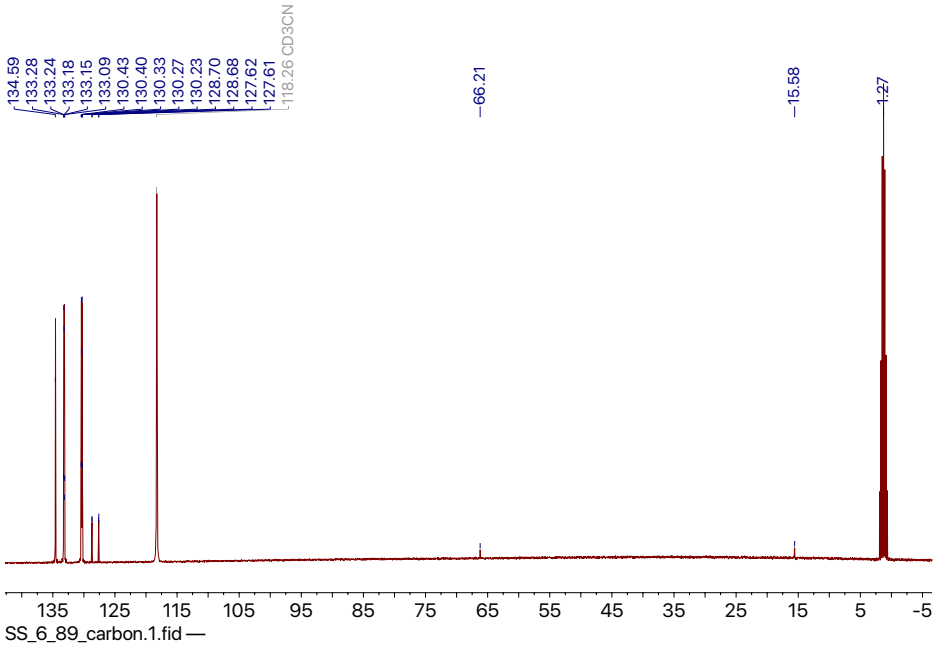

Figure S58: ^{13}C{^{1}H} NMR spectrum of $[PPN]_3[H_2PO_4{-}P_4O_{11}]$ (acetonitrile-d_3, 100.6 MHz) with residual diethyl ether (66.2 and 15.6 ppm).

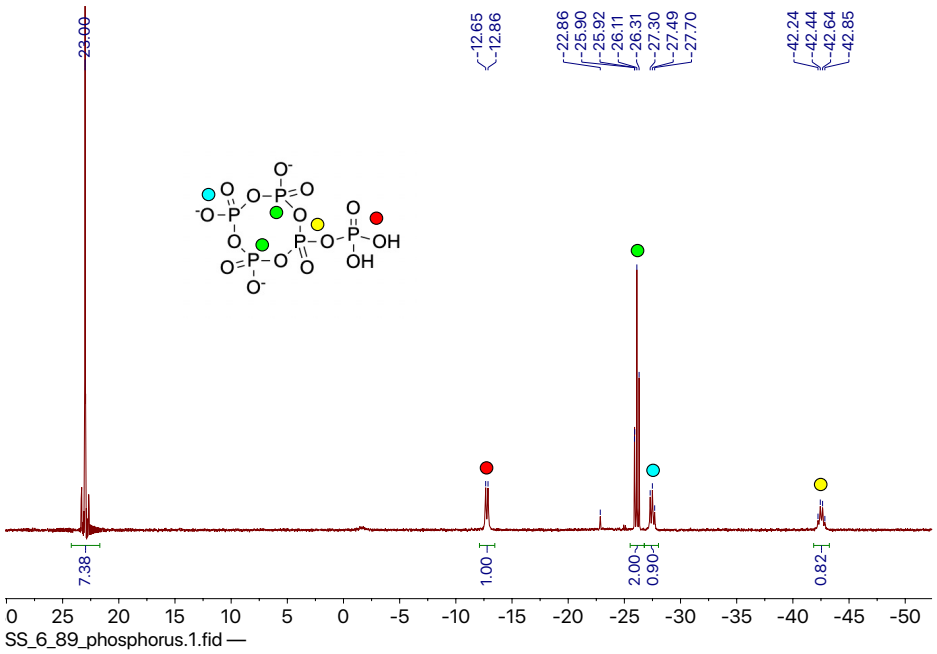

Figure S59: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_3[H_2PO_4{-}P_4O_{11}]$ (acetonitrile-d_3, 162.0 MHz).

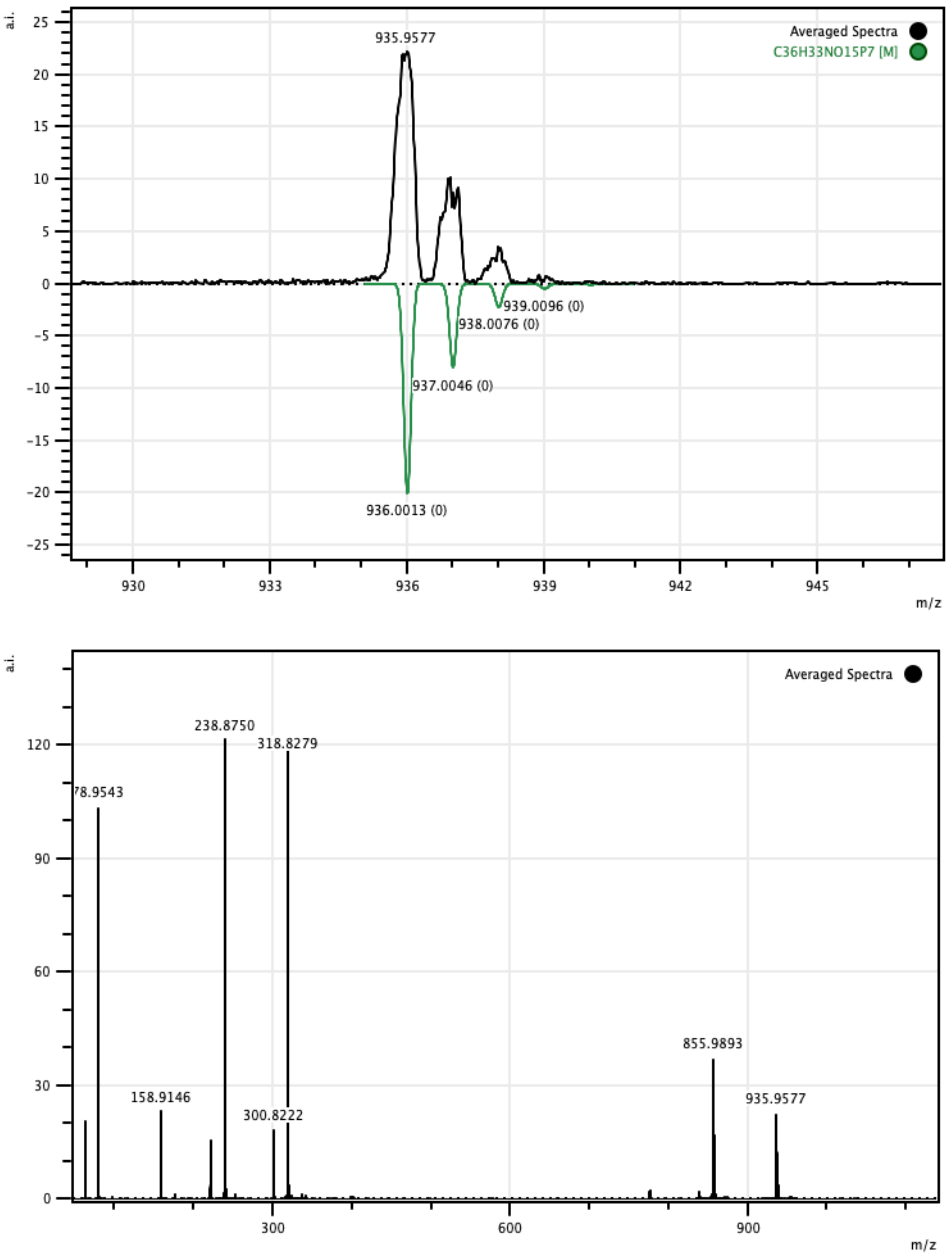

Figure S60: ESI-MS(−) of $[PPN]_3[H_2PO_4{-}P_4O_{11}]$ (CH_3CN) with zoomed in portion showing the molecular ion ($[PPN][H_2PO_4{-}P_4O_{11}H]^-$, top) and calculated isotope pattern ($C_{36}H_{33}NO_{15}P_7$, bottom).

3.12 $[PPN]_2[TBA][12b]$

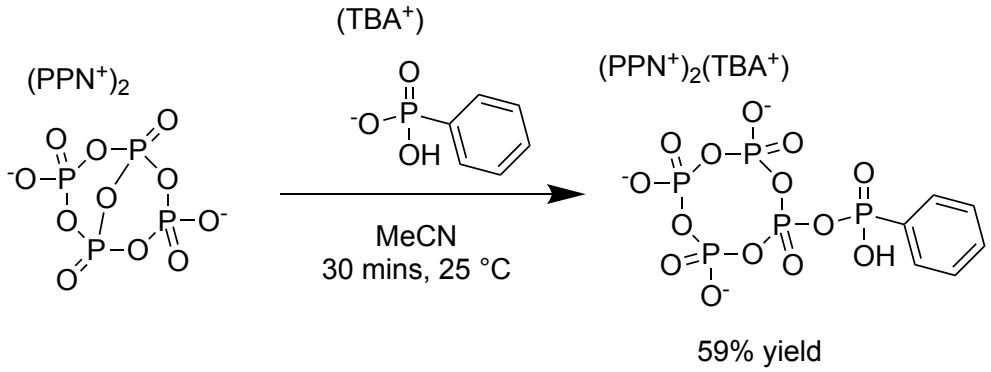

Figure S61: Synthesis of $[PPN]_2[TBA][\mathbf{12b}]$.

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.13 g, 0.096 mmol) was dissolved in acetonitrile (2 mL). To this solution was added $[TBA][HPO_3Ph]$[7] (0.038 g, 0.096 mmol). The resulting mixture was stirred at room temperature for 30 min. Diethyl ether (10 mL) was then added to this mixture, giving a cloudy solution. After several hours, the product formed an oil on the bottom of the vial. The supernatant was decanted off, and the oil was dried under vacuum for several hours, giving the product as a colorless solid (0.10 g, 0.057 mmol, 59% yield). $^{31}P\{^1H\}$ NMR of the isolated product revealed tetrametaphosphate as an impurity (14% of total phosphate NMR integration), giving a corrected yield of 51%.

Elem. Anal. Found(Calc'd) for $C_{94}H_{102}N_3O_{14}P_6$: C 62.60 (63.55), H 5.57 (5.79), N 1.97 (2.37)

^1H NMR (acetonitrile-d_3, 400 MHz): δ 13.72 (s, 1H), 7.99 to 7.84 (m, 2H), 7.74 to 7.41 (m, 60H), 7.37 to 7.25 (m, 3H), 3.26 to 3.04 (m, 8H), 1.73 to 1.52 (m, 8H), 1.37 (h, J = 7.3 Hz, 8H), 0.96 (t, J = 7.3 Hz, 12H).

$^{13}C\{^1H\}$ NMR (acetonitrile-d_3, 100.6 MHz): δ 134.58 (t, J = 1.5 Hz), 133.92 to 132.85 (m), 132.64 (d, J = 9.7 Hz), 130.71, 130.55 to 130.10 (m), 128.67 (d, J = 1.9 Hz), 128.29 (d, J = 14.3 Hz), 127.60 (d, J = 1.9 Hz), 59.13, 24.34, 20.28, 13.84.

$^{31}P\{^1H\}$ NMR (acetonitrile-d_3, 162.0 MHz): δ 23.00, 2.92 (d, J = 35.0 Hz), −24.43 (d, J = 31.3 Hz), −37.21 (d, J = 34.2 Hz).

ESI-MS(−) of $[PPN]_2[TBA][\mathbf{12b}]$ (CH_3CN, found 700.37 m/z for $[TBA][P_4O_{11}H{-}HPO_3Ph]^-$) (calc'd 700.14 for $C_{22}H_{43}NO_{14}P_5$)

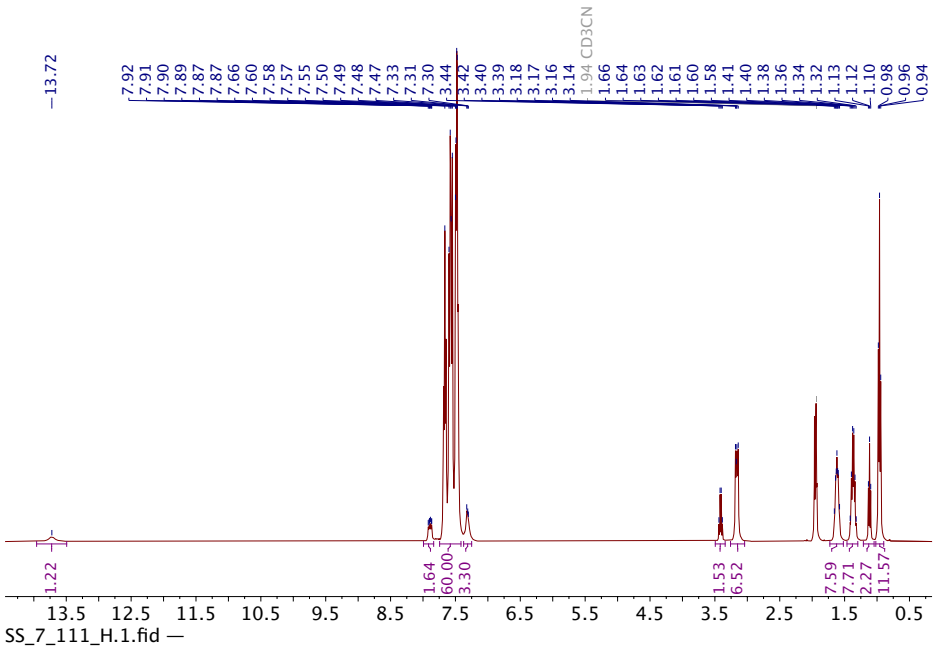

Figure S62: ^{1}H NMR spectrum of [PPN]$_2$[TBA][**12b**] (acetonitrile-d_3, 400 MHz) with residual diethyl ether (3.42 and 1.12 ppm).

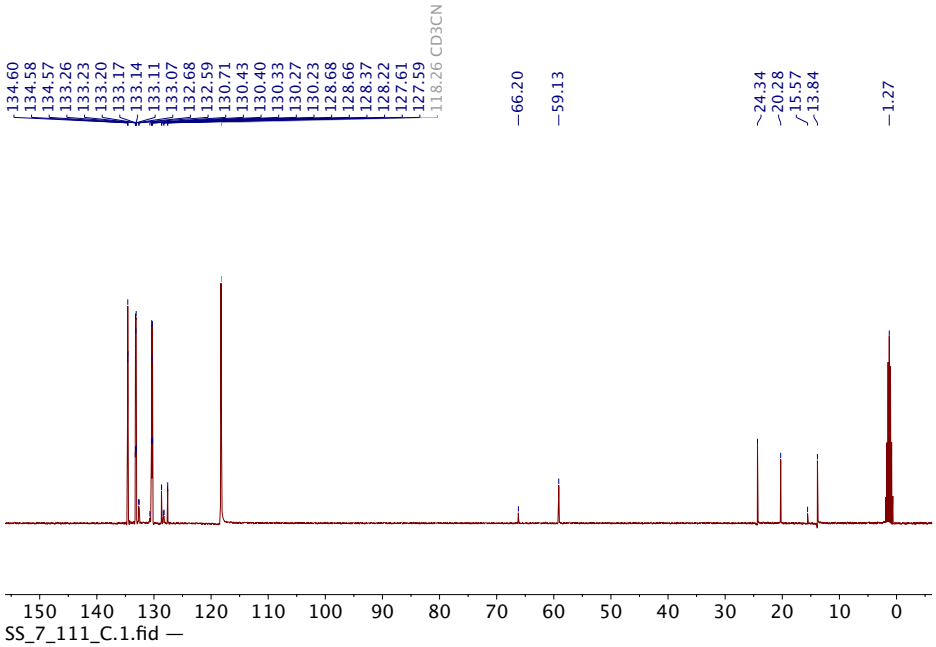

Figure S63: ^{13}C{^{1}H} NMR spectrum of [PPN]$_2$[TBA][**12b**] (acetonitrile-d_3, 100.6 MHz) with residual diethyl ether (66.2 and 15.6 ppm).

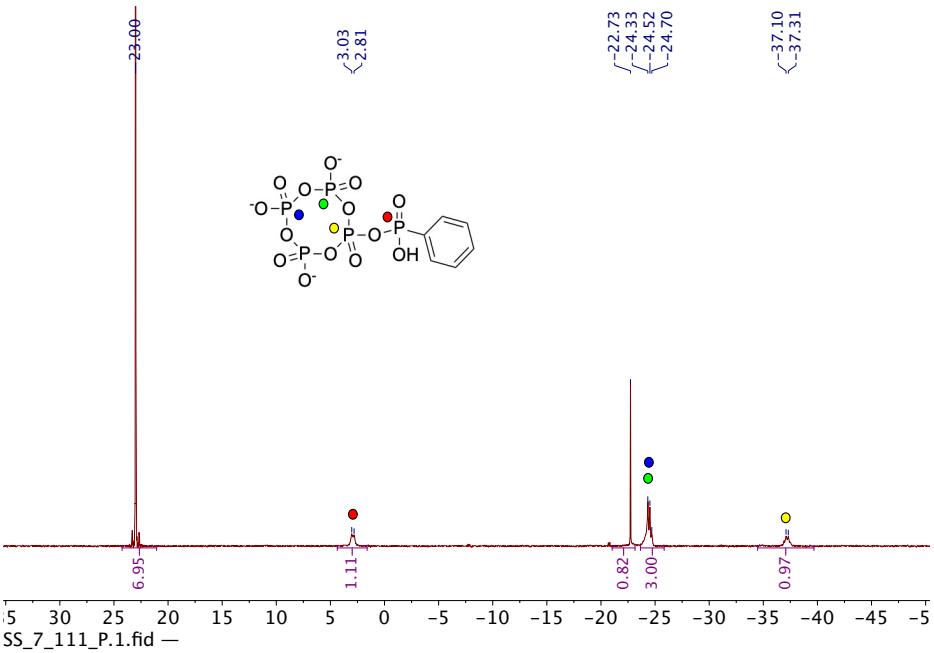

Figure S64: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[TBA]$[**12b**] (acetonitrile-d_3, 162.0 MHz) with tetrametaphosphate as an impurity (−22.7 ppm).

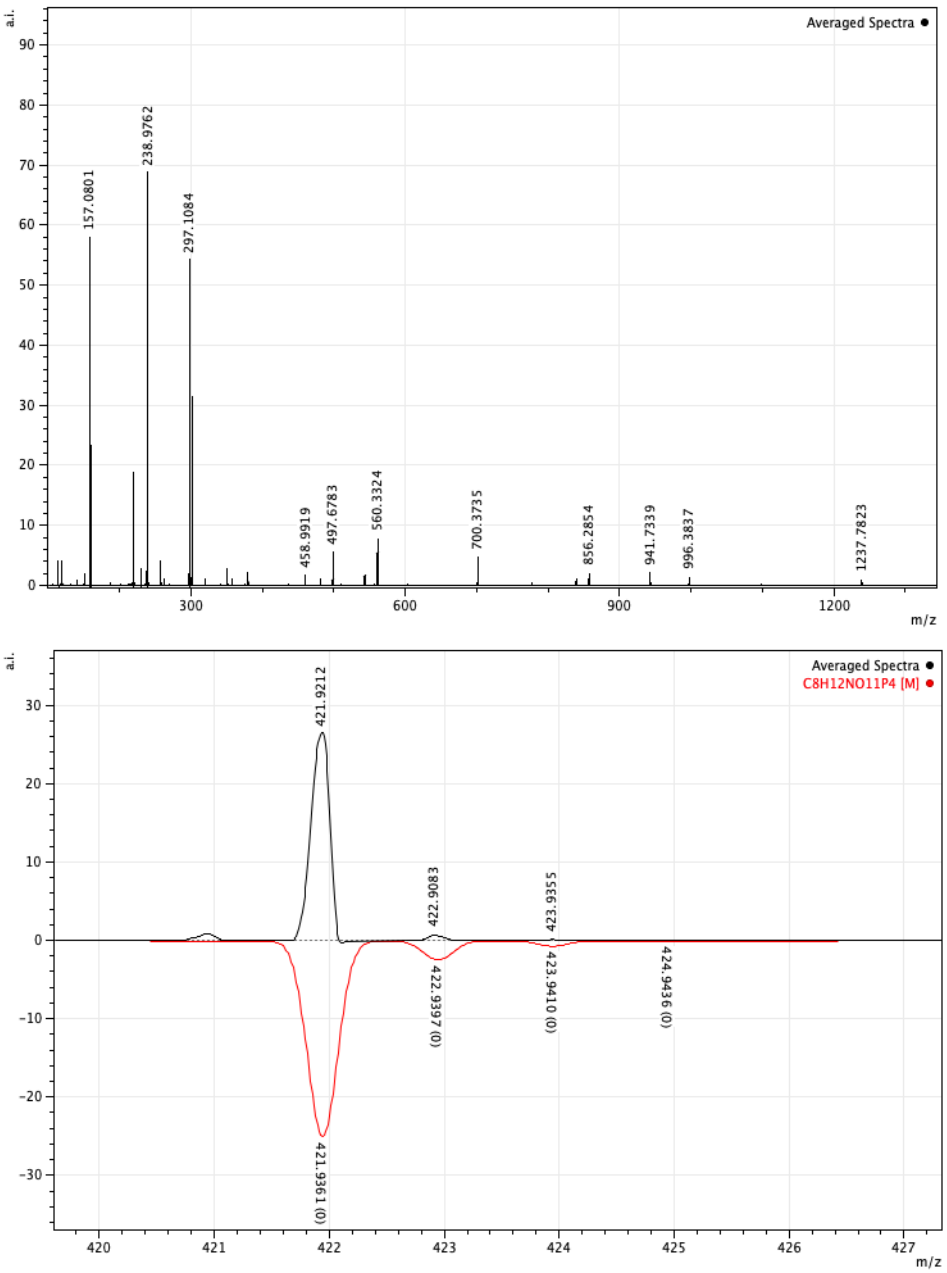

Figure S65: ESI-MS(−) of $[PPN]_2[TBA]$[**12b**] (CH_3CN) with zoomed in portion showing the molecular ion ($[TBA][P_4O_{11}H{-}HPO_3Ph]^-$, top) and calculated isotope pattern ($C_{22}H_{43}NO_{14}P_5$, bottom).

3.13 $[PPN]_2[HNEt_3][13]$

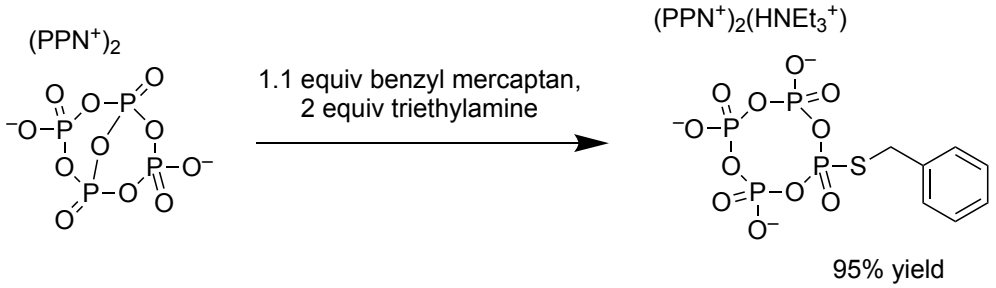

Figure S66: Synthesis of $[PPN]_2[HNEt_3]$[**13**].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.10 g, 0.072 mmol) was dissolved in acetonitrile (2 mL). To this solution was added benzyl mercaptan (0.010 mL, 0.080 mmol). The resulting mixture was stirred at room temperature for 30 min. Diethyl ether (10 mL) was then added to this mixture, giving a cloudy solution. After several hours, the product formed an oil on the bottom of the vial. The supernatant was decanted off, and the oil was dried under vacuum for several hours, giving the product as a colorless solid (0.11 g, 0.068 mmol, 95% yield).

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 11.18 (s, 1H), 7.72 to 7.44 (m, 60H), 7.41 (dd, J = 7.4, 1.7 Hz, 2H), 7.27 (t, J = 7.4 Hz, 2H), 7.20 (d, J = 7.3 Hz, 1H), 4.27 (d, J = 11.5 Hz, 2H), 3.09 (q, J = 7.3 Hz, 6H), 1.21 (t, J = 7.3 Hz, 9H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 133.66, 132.62 to 131.64 (m), 129.69 to 129.21 (m), 129.15, 128.46, 127.77 (d, J = 2.0 Hz), 127.01, 126.70 (d, J = 2.0 Hz), 45.08, 34.13 (d, J = 3.9 Hz), 14.66.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): 23.00, 1.28 to 0.47 (m), −21.81 to −24.56 (m).

ESI-MS(−) of $[PPN]_2[HNEt_3]$[**13**] (CH_3CN, found 424.86 m/z for $[_{13}]H_2^-$) (calc'd 424.88 for $C_7H_9O_{11}P_4S$)

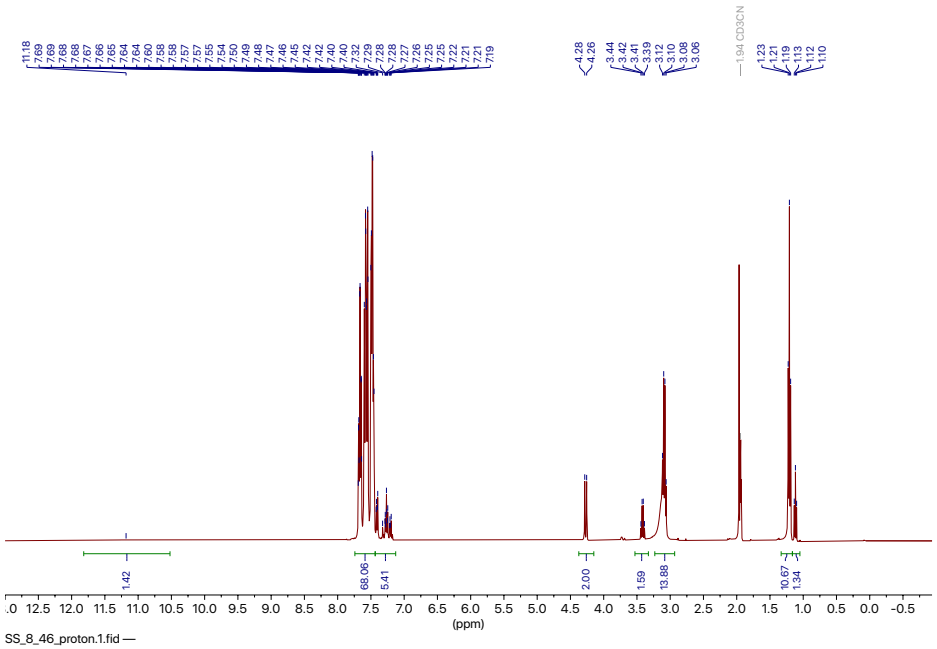

Figure S67: ^{1}H NMR spectrum of $[PPN]_2[HNEt_3]$[**13**] (acetonitrile-d_3, 400 MHz).

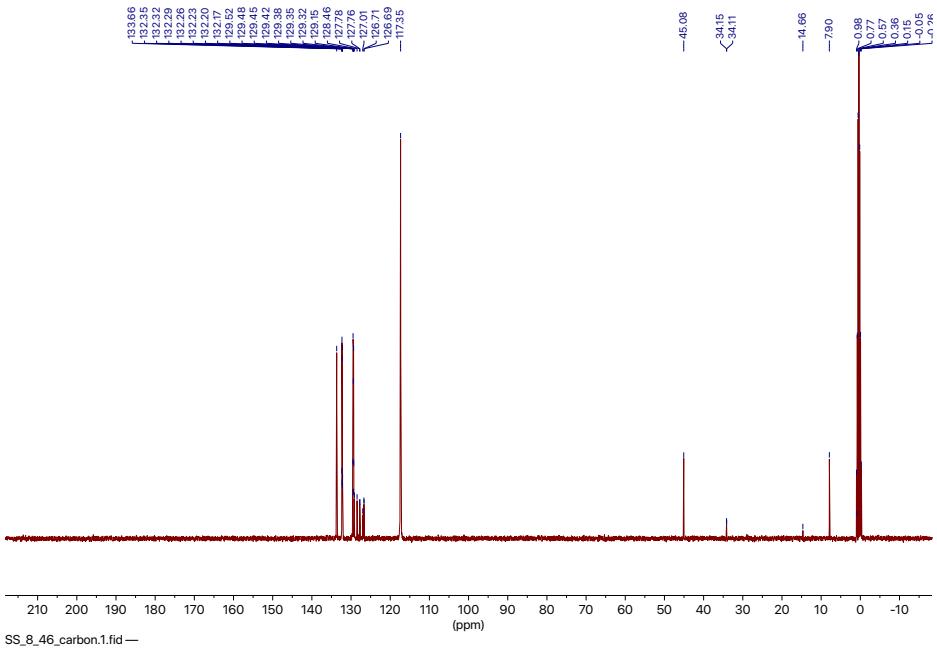

Figure S68: ^{13}C{^{1}H} NMR spectrum of $[PPN]_2[TBA]$[**13**] (acetonitrile-d_3, 100.6 MHz).

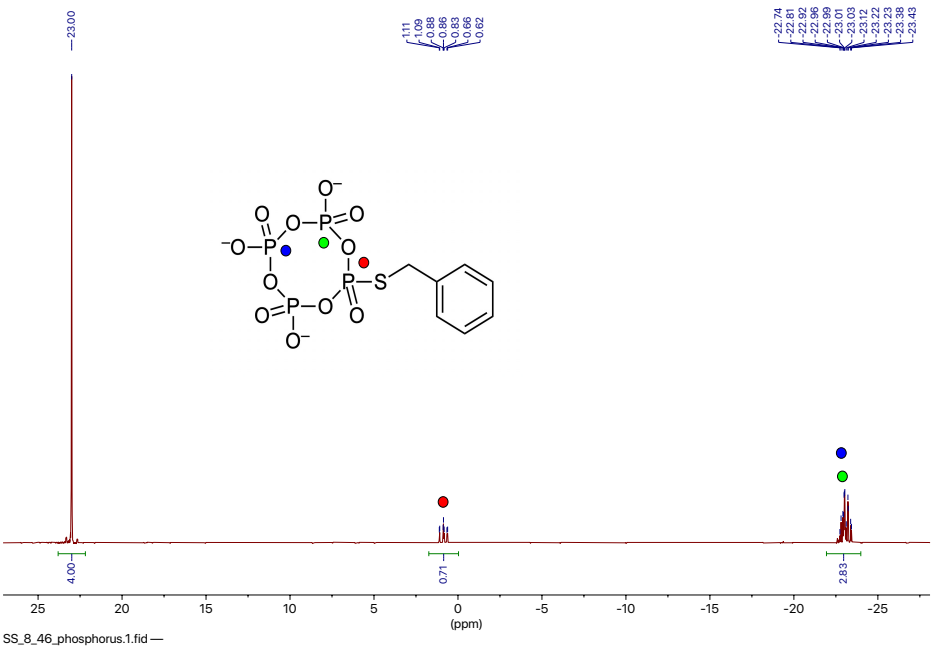

Figure S69: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[HNEt_3]$[**13**] (acetonitrile-d_3, 162.0 MHz).

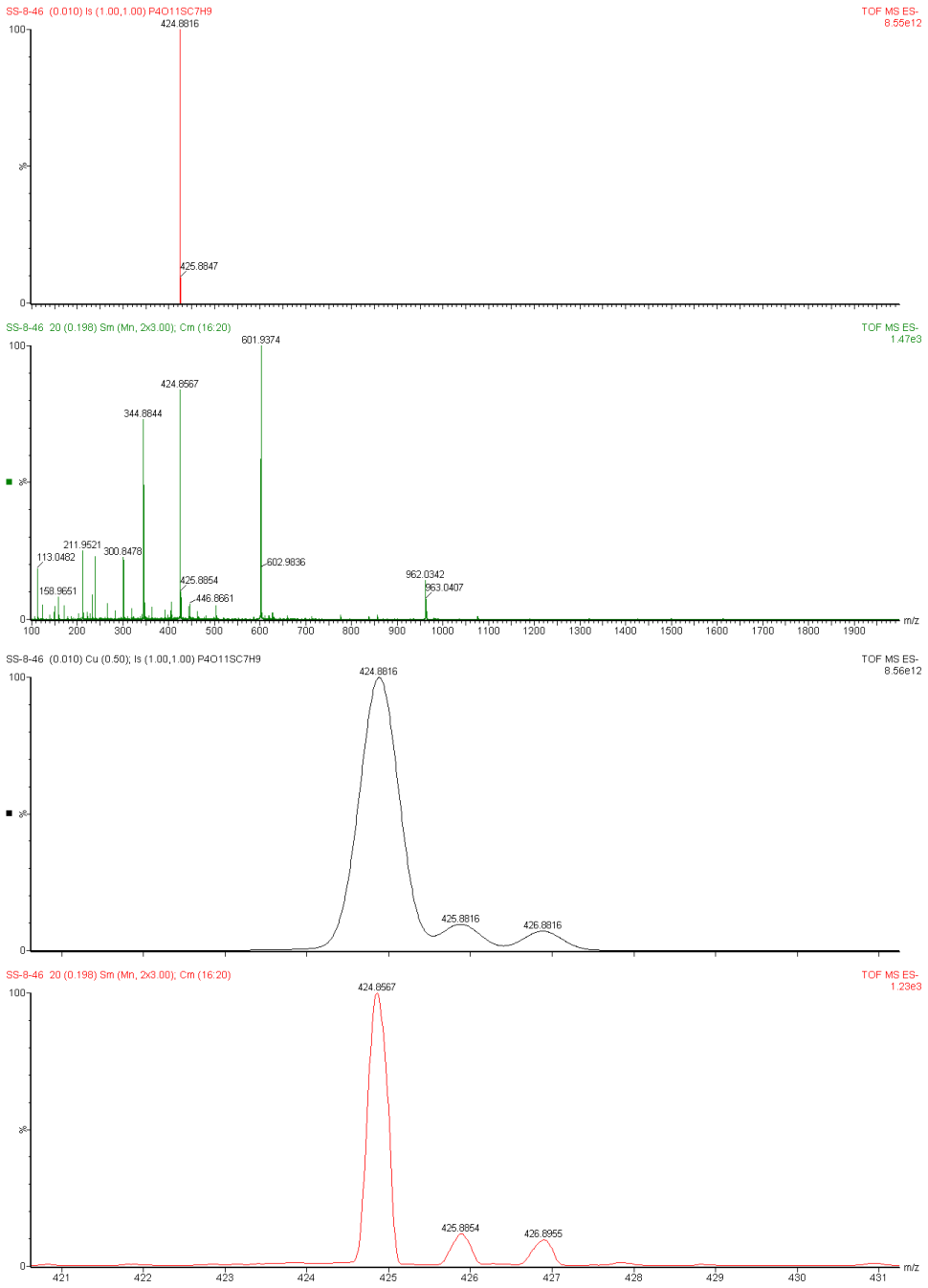

Figure S70: ESI-MS(−) of $[PPN]_2[HNEt_3]$[**13**] (CH_3CN) with zoomed in portion showing the molecular ion ($[13]H_2^-$, top) and calculated isotope pattern ($C_7H_9O_{11}P_4S$, bottom).

3.14 $[PPN]_2[HNEt_3][14]$

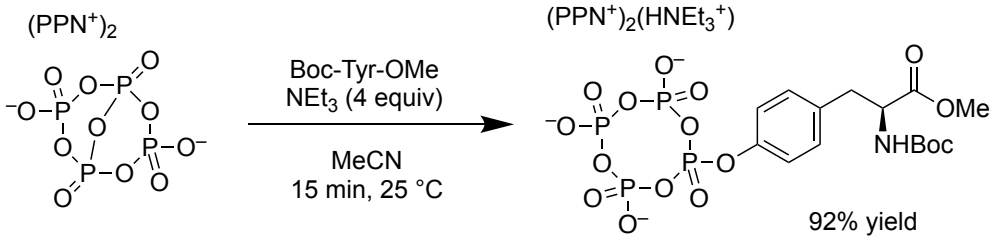

Figure S71: Synthesis of $[PPN]_2[HNEt_3][\mathbf{14}]$.

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.11 g, 0.078 mmol) was dissolved in acetonitrile (2 mL). To this solution was added triethylamine (0.04 mL, 0.31 mmol) followed by a 0.10 g/mL acetonitrile solution of Boc-Tyr-OMe that had been stored over 4Å sieves for 24 hours (0.22 mL, 0.078 mmol). The resulting mixture was stirred at room temperature for 15 min. Volatiles were removed under reduced pressure and the resulting oil was dried under vacuum for several hours, giving the product as a colorless solid (0.13 g, 0.067 mmol, 92% yield).

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 11.38 (s, 1H), 7.91 to 7.37 (m, 60H), 7.26 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 5.58 (d, J = 8.2 Hz, 1H), 4.32 (q, J = 7.7 Hz, 1H), 3.63 (s, 3H), 3.10 (q, J = 7.2 Hz, 6H) 3.02 (dd, J = 14.0, 5.5 Hz, 2H), 2.88 (dd, J = 13.9, 8.4 Hz, 2H), 1.35 (s, 9H), 1.20 (t, J = 7.2 Hz, 9H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 173.31, 151.18 (d, J = 5.5 Hz), 134.57 (t, J = 1.5 Hz), 133.82 to 132.65 (m), 131.04, 130.72 to 129.90 (m), 128.66 (d, J = 2.0 Hz), 127.59 (d, J = 2.0 Hz), 121.81 (d, J = 4.9 Hz), 79.90, 55.88, 52.62, 45.89, 37.37, 28.46, 8.79.

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 21.53, −23.74 to −25.72 (m), −28.96 (m).

ESI-MS(−) of $[PPN]_2[HNEt_3][\mathbf{14}]$ (CH_3CN, found 596.04 m/z for $[\mathbf{14}]H_2^-$) (calc'd 595.99 for $C_{15}H_{22}NO_{16}P_4$)

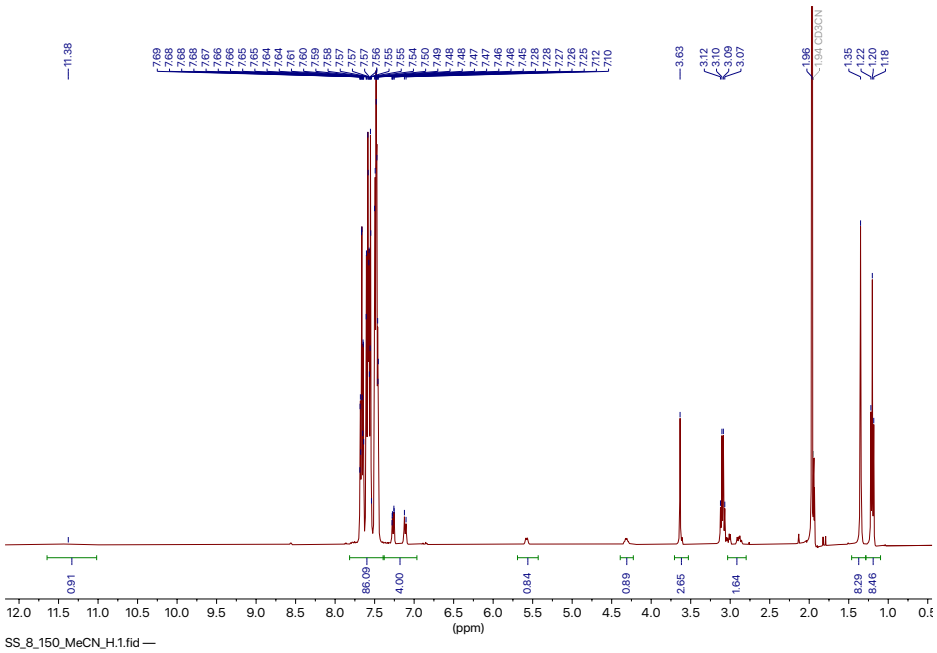

Figure S72: ^{1}H NMR spectrum of $[PPN]_2[HNEt_3]$[**14**] (acetonitrile-d_3, 400 MHz).

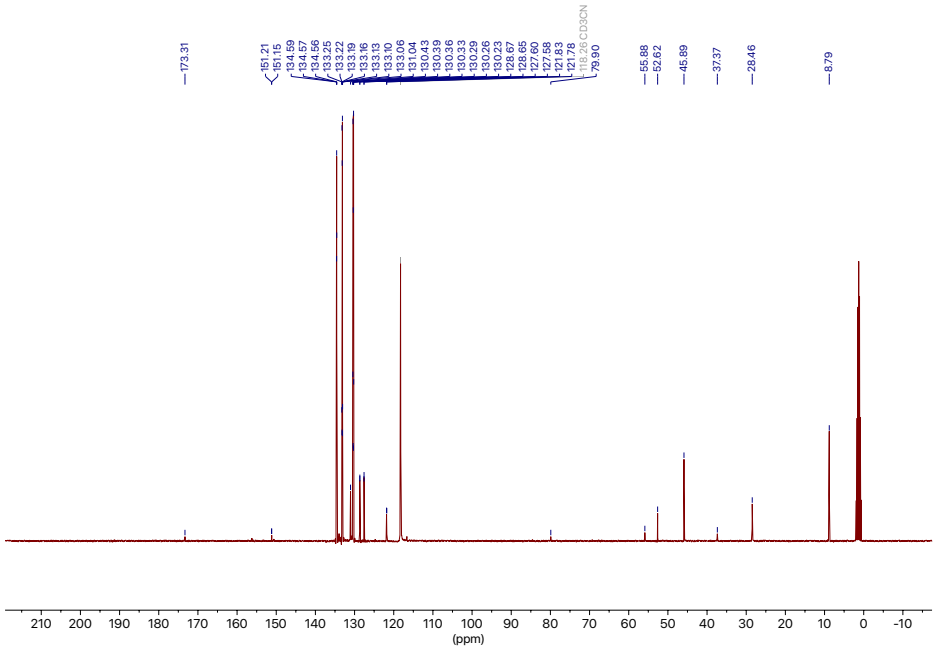

Figure S73: ^{13}C{^{1}H} NMR spectrum of $[PPN]_2[HNEt_3]$[**14**] (acetonitrile-d_3, 100.6 MHz).

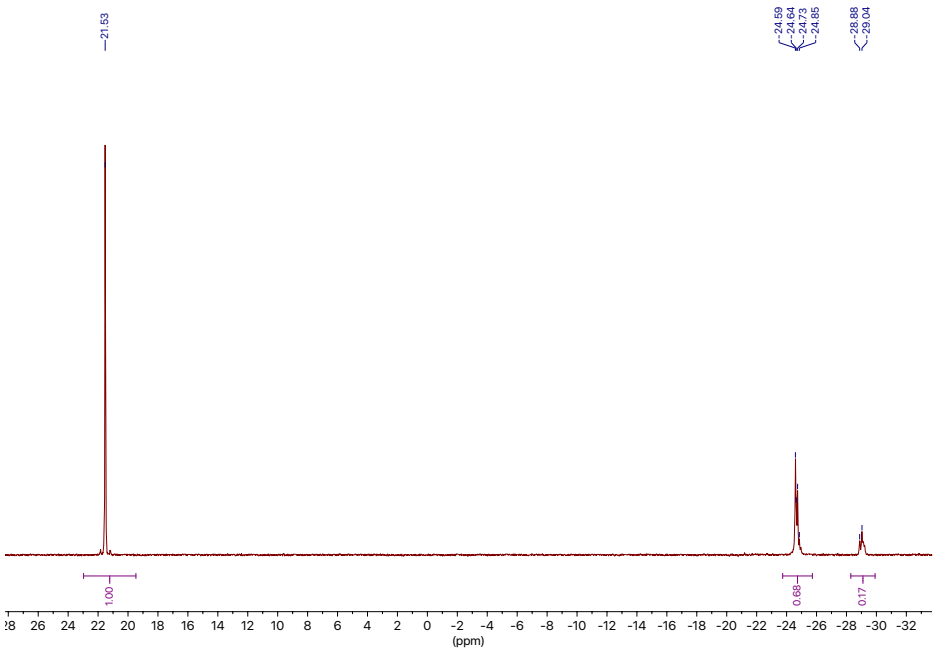

Figure S74: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[HNEt_3]$[**14**] (acetonitrile-d_3, 162.0 MHz).

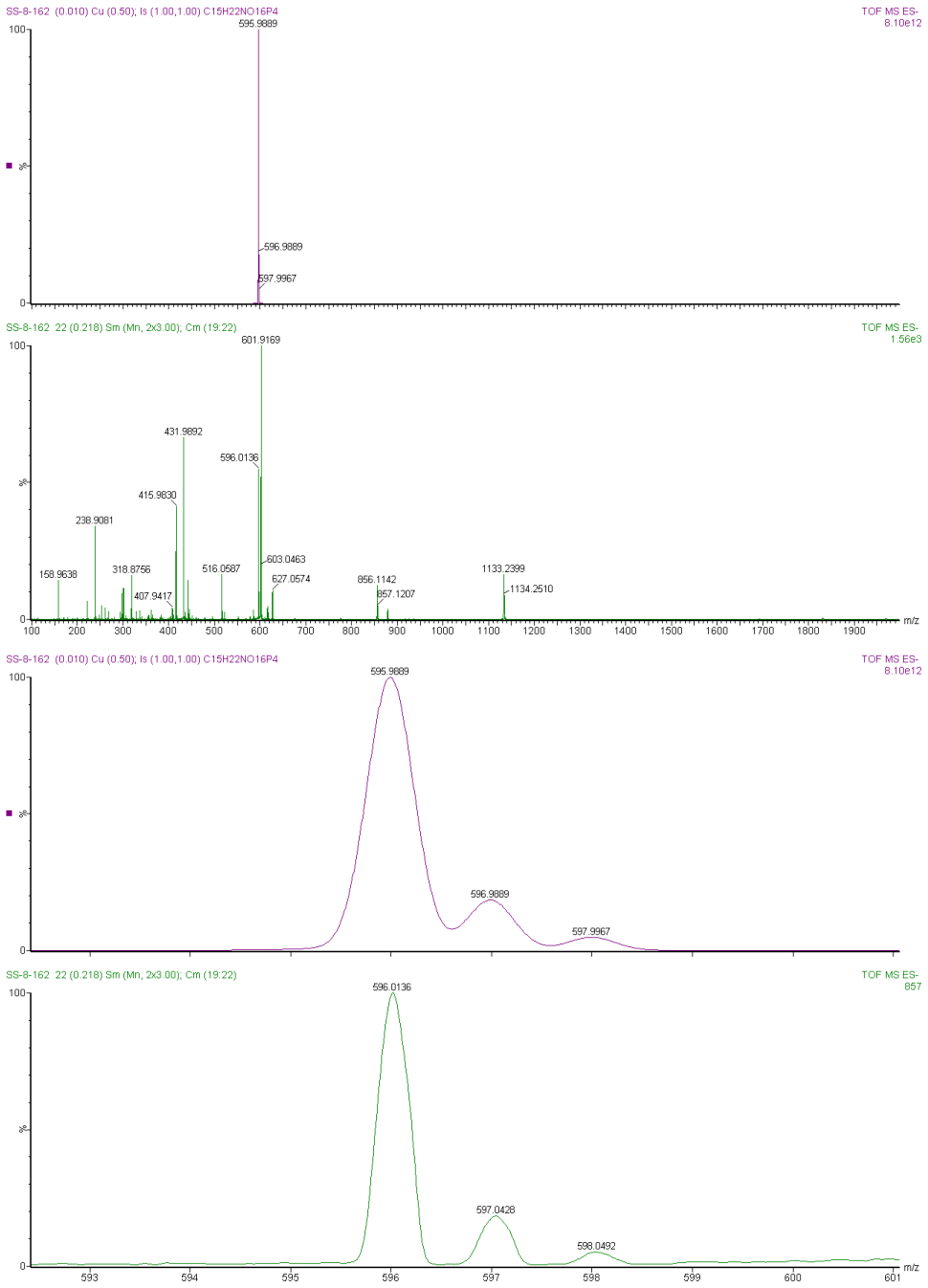

Figure S75: ESI-MS(−) of $[PPN]_2[HNEt_3]$[**14**] (CH_3CN) with zoomed in portion showing the molecular ion ($[14]H_2^-$) and calculated isotope pattern ($C_{15}H_{22}NO_{16}P_4$).

3.15 $[PPN]_2[MePPh_3][15]$

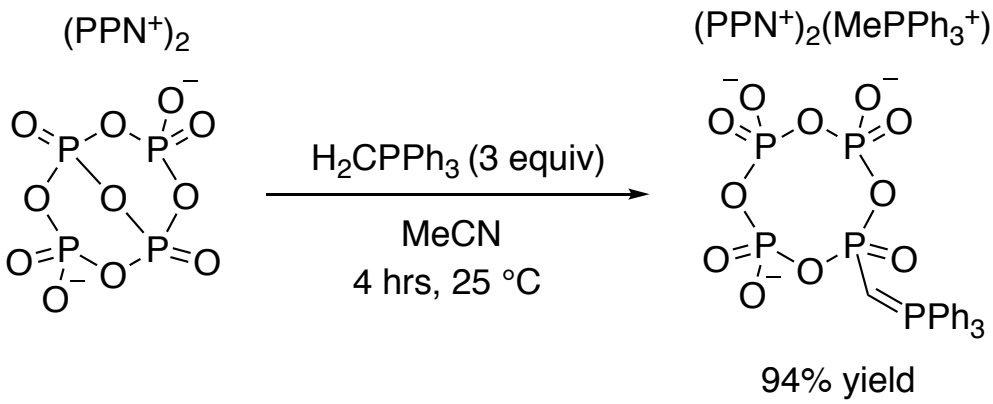

Figure S76: Synthesis of $[PPN]_2[MePPh_3][P_4O_{11}CHPPh_3]$.

In a glovebox, $[PPN]_2[P_4O_{11}]$ (1.00 g, 0.73 mmol) was dissolved in dry acetonitrile (2 mL), to which a solution of methylenetriphenylphosphorane (0.61 g, 2.20 mmol) in dry acetonitrile (13 mL) was added. The reaction was stirred for 4 hours, during which no color change was observed. The solution was then filtered through Celite® to remove any insoluble material. The mixture was concentrated under vacuum to a volume of 5 mL and diethyl ether (15 mL) was added, resulting in a cloudy white suspension. Upon vigorous stirring, the suspension settled into a dark yellow oil and a yellow solution. The solution was decanted away, and the oil was dried under vacuum for 30 minutes to give a foamy yellow solid. Diethyl ether (5 mL) was added and the mixture was vigorously stirred to give a suspension. The solution was decanted off and the powder was washed with diethyl ether (3×15 mL) until the ether layer was colorless. The solid product was dried under vacuum for 5 hours to give the product as a pale yellow powder (1.33 g, 0.69 mmol, 94%).

Elem. Anal. Found(Calc'd) for $C_{110}H_{94}N_2O_{11}P_{10}$: C 66.70 (68.45), H 5.14 (4.92), N 1.44 (1.45).

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 8.03 to 7.51 (m, 90H), 3.46 (d, $J_{PH} = 13.6$ Hz, 3H), 1.95 (dd, $J_{PH} = 9.1, 3.1$ Hz, 1H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 135.3 (d), 134.6, 134.5, 134.0 (d), 133.20 to 133.05 (m), 132.0 (d), 131.0 (d), 130.20 to 130.15 (m), 129.2 (d), 128.6 (d), 127.5 (d), 121.9, 121.0, 9.2 (d, $J_{CP} = 56.0$ Hz).

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 24.5, 23.0, 21.7 (d, $J_{PP} = 49.4$ Hz), 11.3 to 10.48 (m), −21.88 to −22.58 (m).

ESI-MS(−) of $[P_4O_{11}CHPPh_3]H_2^-$ (CH_3CN, m/z) 577.11 (calc'd 576.95)

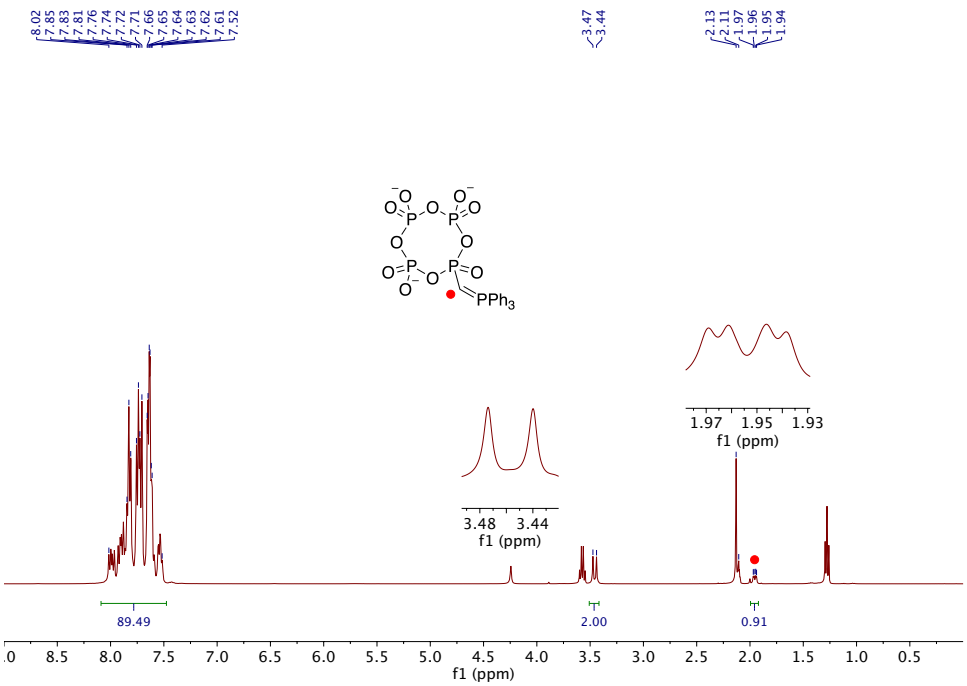

Figure S77: ^{1}H NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}CHPPh_3]$ (acetonitrile-d_3, 400 MHz), with residual diethyl ether (3.47 and 1.15 ppm). The doublet at 3.46 ppm corresponds to the methyl group of the methyltriphenylphosphonium counterion.

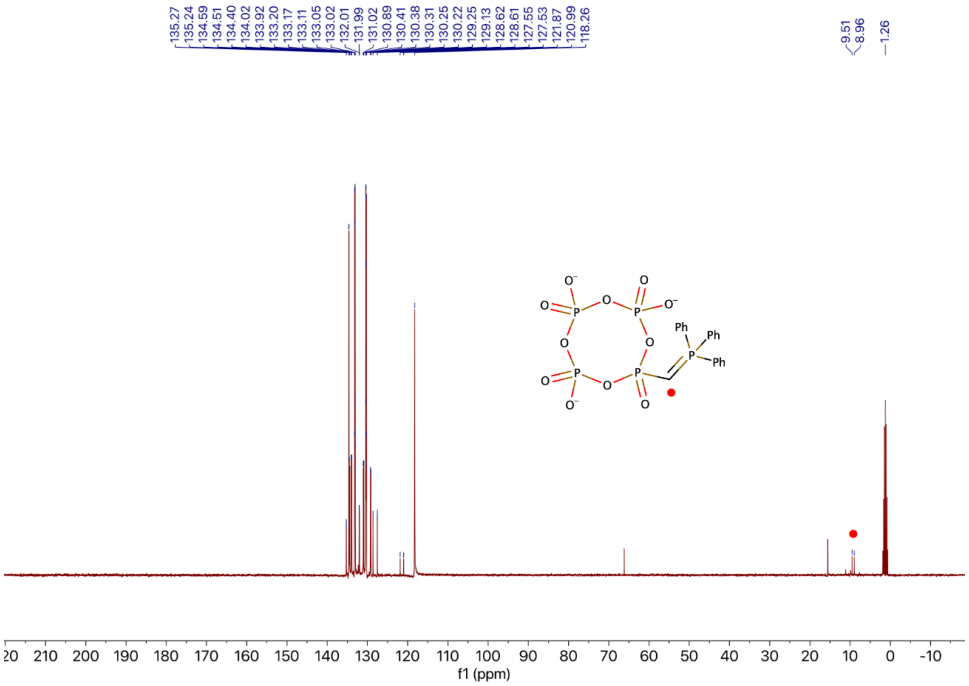

Figure S78: ^{13}C{^{1}H} NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}CHPPh_3]$ (acetonitrile-d_3, 100.6 MHz) with residual diethyl ether (66.9 and 15.5 ppm).

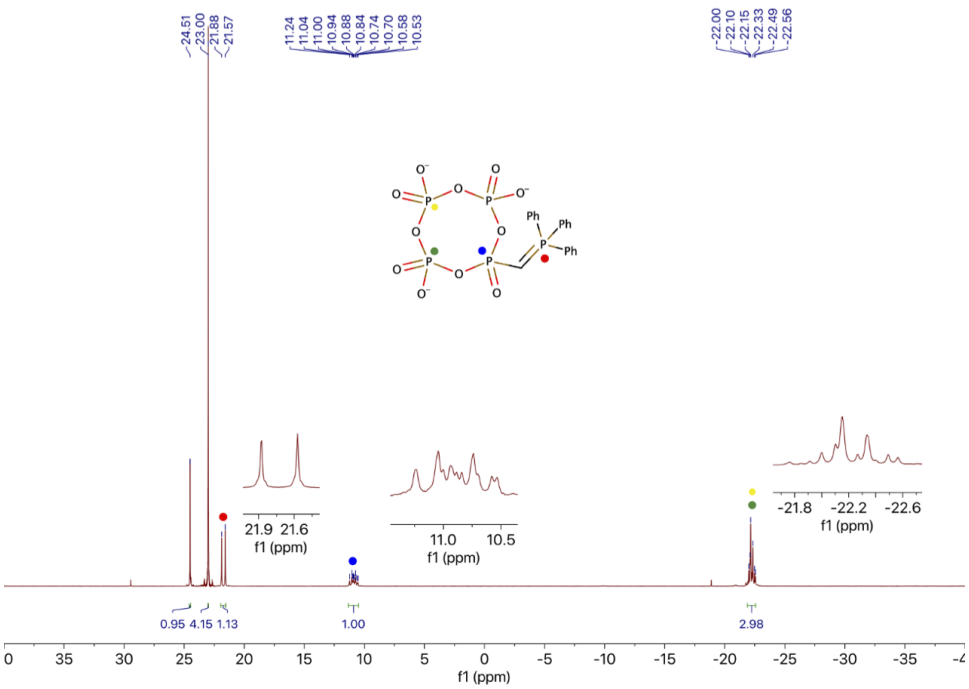

Figure S79: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}CHPPh_3]$ (acetonitrile-d_3, 162.0 MHz).

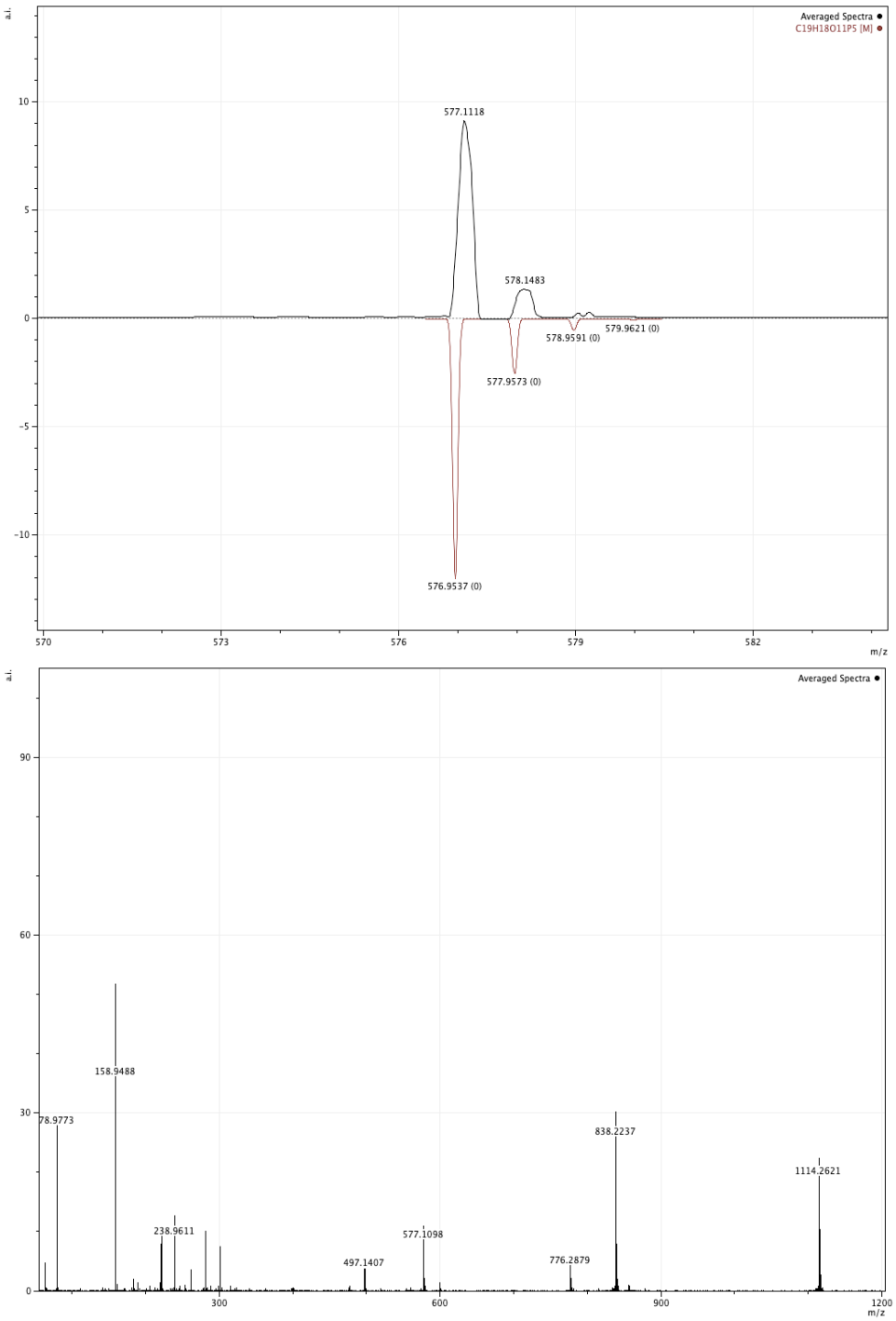

Figure S80: ESI-MS(−) of $[PPN]_2[MePPh_3][P_4O_{11}CHPPh_3]$ (CH_3CN) with zoomed in portion of the molecular ion ($[P_4O_{11}CHPPh_3]H_2^-$, top), and calculated isotope pattern ($C_{19}H_{18}O_{11}P_5$, bottom).

4 Synthesis of Linear Phosphates ($[Nuc^1(PO_3)_3PO_2Nuc^2]^{4-}$)

4.1 Ring Opening with Hydroxide/Water

4.1.1 $[Et_3NH]_4$[16]

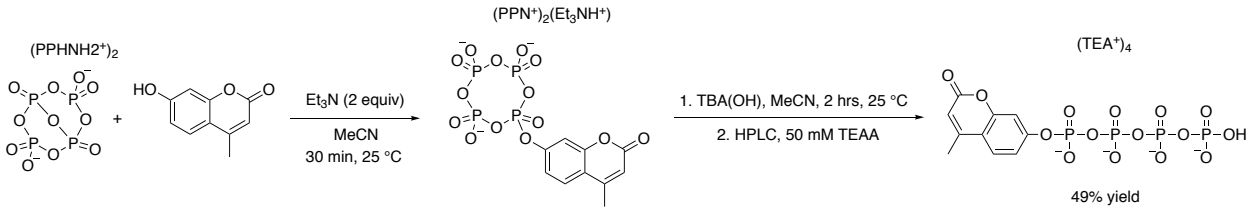

Figure S81: Synthesis of $[Et_3NH]_4$[4-methyl-2-oxo-2*H*-chromen-7-yl-$P_4O_{12}H$].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.070 g, 0.051 mmol) was dissolved in dry acetonitrile (0.5 mL), and triethylamine (0.014 mL, 0.10 mmol, 2 equiv) was added. 4-methylumbelliferone (0.0090 g, 0.051 mmol) was then added, and the resulting mixture was stirred for 30 minutes. This solution was brought out of the glovebox, and immediately a solution of 40 wt% aqueous tetrabutylammonium hydroxide (0.20 g, 0.305 mmol, 6 equiv) in acetonitrile (1 mL) was added. The resulting mixture was stirred for 2 hours in the fumehood, during which the mixture turned from a light green to a light purple color. Volatiles were removed under vacuum, and deionized water (2 mL) was added, resulting in a cloudy solution. This aqueous mixture was then filtered through an Acrodisc 0.2 μm wwPTFE syringe filter and was purified by HPLC according to the procedures outlined in the General Considerations section above. The fractions containing the desired product were pooled in a flask, and volatiles were removed under vacuum at 60 °C. The resulting residue was repeatedly dissolved in water and evaporated under vacuum at 60 °C to remove excess triethylammonium acetate buffer. The product was isolated as a white solid (0.0224 g, 0.025 mmol, 49% yield).

^{1}H NMR (D_2O, 400 MHz): δ 7.81 (d, $J = 8.8$ Hz, 1H), 7.35 (dd, $J = 8.7, 2.3$ Hz, 1H), 7.30 (d, $J = 2.2$ Hz, 1H), 6.32 (d, $J = 1.4$ Hz, 1H), 3.19 (q, $J = 7.3$ Hz, 24H), 2.08 (s, 3H), 1.27 (t, $J = 7.3$ Hz, 36H).

^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 164.6, 156.3, 154.8 (d), 153.5, 126.6, 117.8 (d, $J = 4.5$ Hz), 116.6, 111.9, 108.5 (d, $J = 5.0$ Hz), 46.6, 18.0, 8.2.

^{31}P{^{1}H} NMR (D_2O, 162.0 MHz): δ -10.9 (d, $J_{PP} = 18.4$ Hz), -17.0 (d, $J_{PP} = 18.0$ Hz), -23.5 (m).

ESI-MS($-$) of $[C_{10}H_8O_{15}P_4]H_3^-$ (CH_3CN/H_2O, m/z) 495.15 (calc'd 494.90)

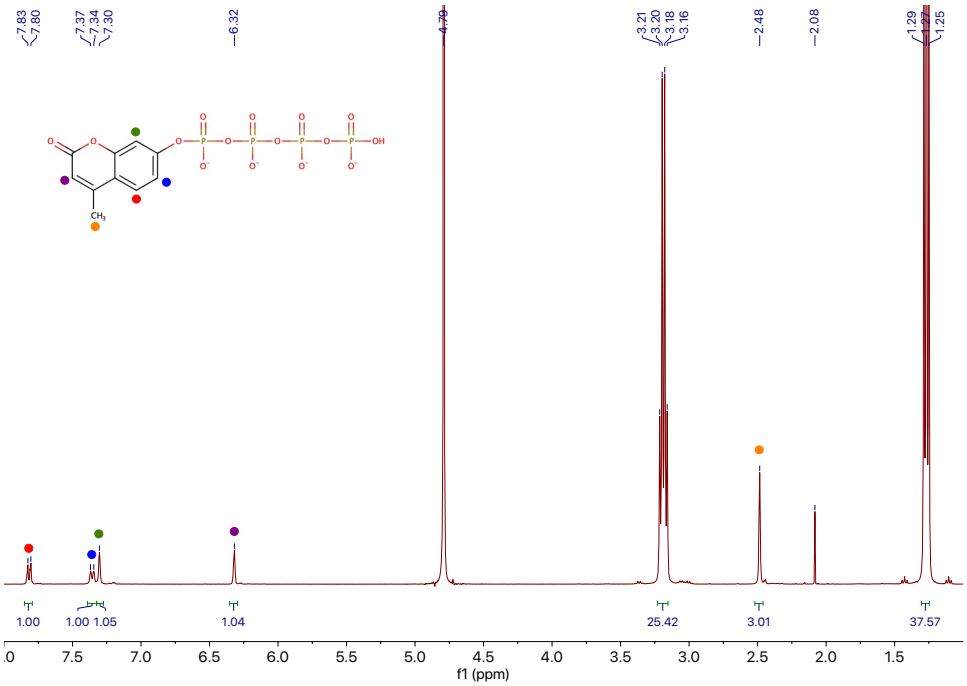

Figure S82: ^{1}H NMR spectrum of $[Et_3NH]_4$[4-methyl-2-oxo-2*H*-chromen-7-yl-$P_4O_{12}H$] (D_2O, 400 MHz).

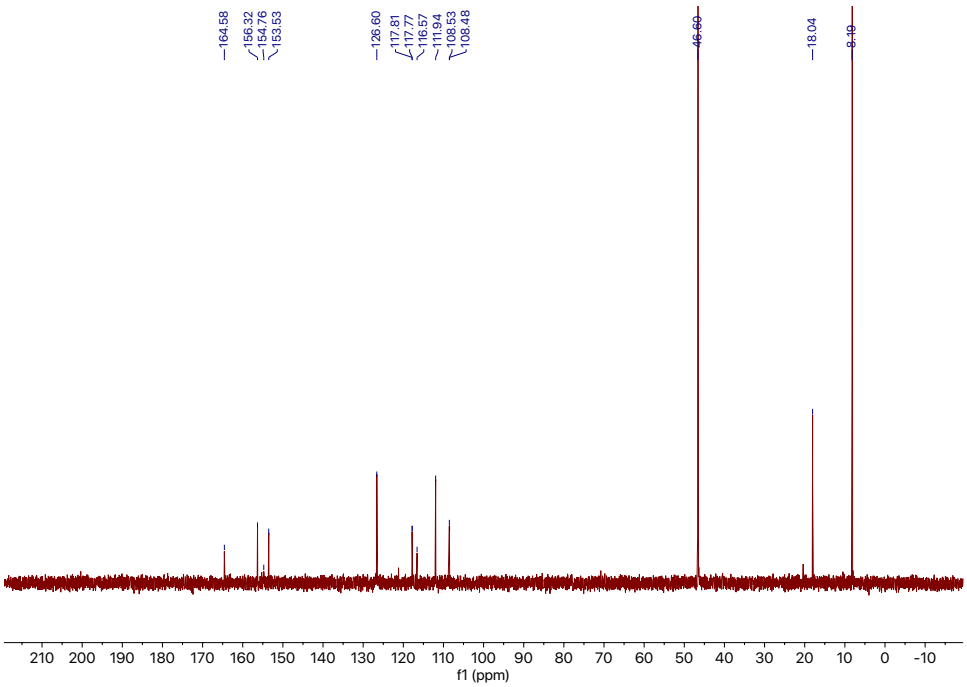

Figure S83: ^{13}C{^{1}H} NMR spectrum of $[Et_3NH]_4$[4-methyl-2-oxo-2*H*-chromen-7-yl-$P_4O_{12}H$] (D_2O, 100.6 MHz).

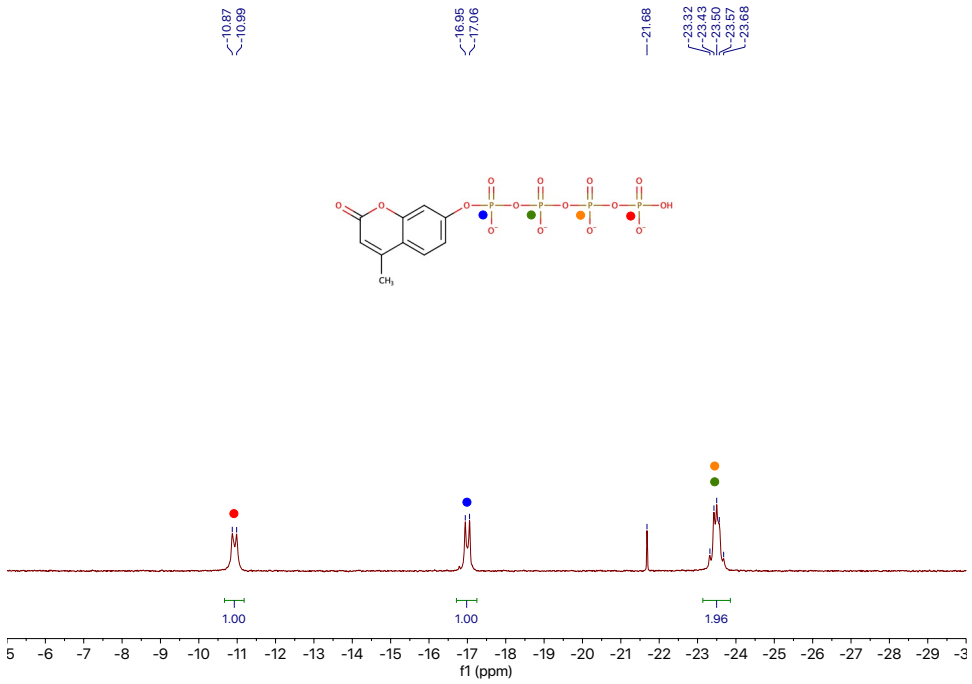

Figure S84: $^{31}P\{^{1}H\}$ NMR spectrum of $[Et_3NH]_4$[4-methyl-2-oxo-2*H*-chromen-7-yl-$P_4O_{12}H$] with residual tetrametaphosphate (−21.7 ppm) as a trace impurity (D_2O, 162.0 MHz).

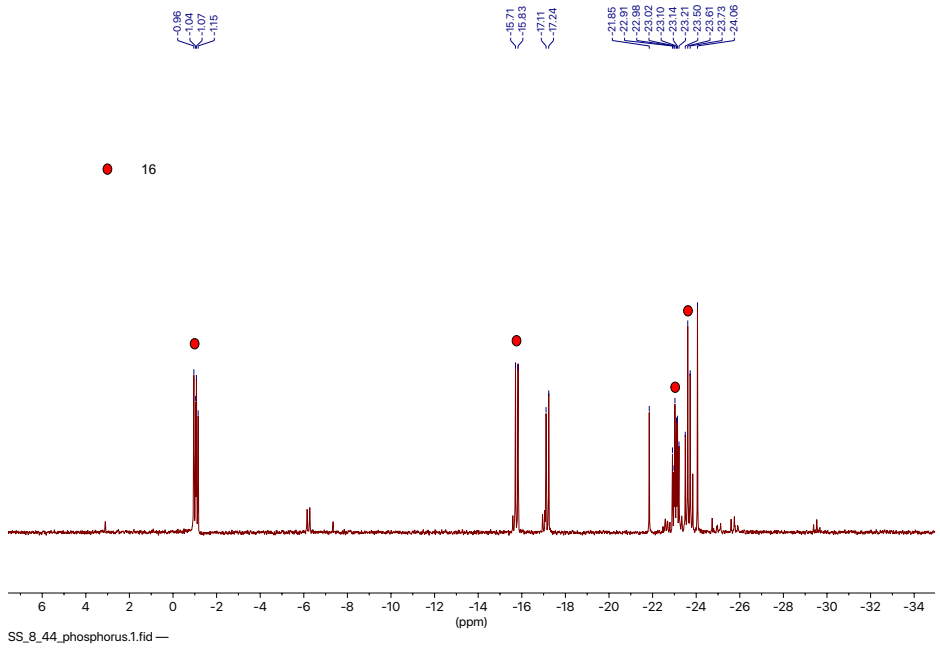

Figure S85: $^{31}P\{^{1}H\}$ NMR spectrum of crude 16 before HPLC purification, demonstrating the variety of side products that form (D_2O, 162.0 MHz).

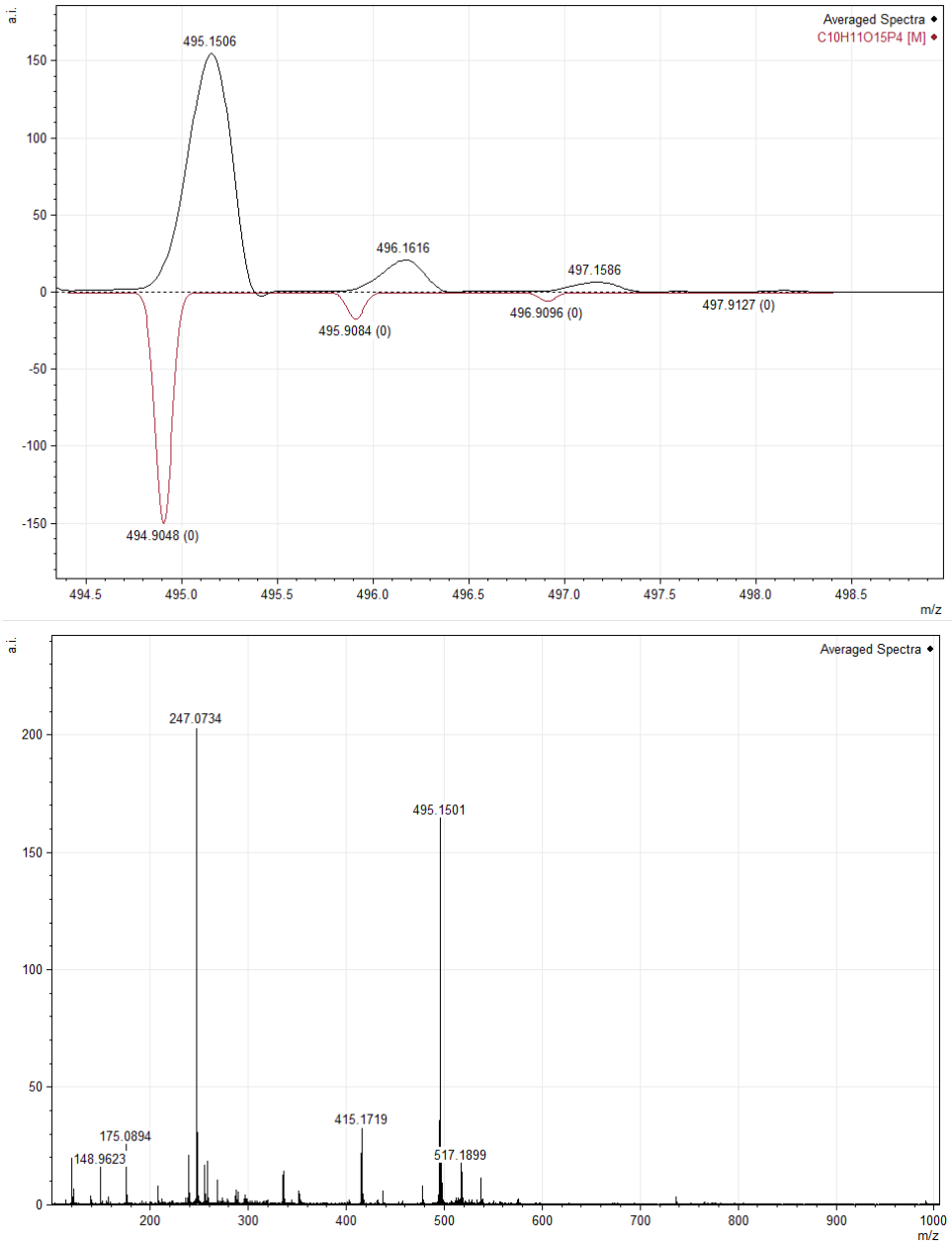

Figure S86: ESI-MS(−) of $[Et_3NH]_4[C_{10}H_8O_{15}P_4]$ (CH_3CN/H_2O) with zoomed in portion of the molecular ion ($[C_{10}H_8O_{15}P_4]H_3^-$, top), and calculated isotope pattern ($C_{10}H_{11}O_{15}P_4$, bottom). The mass at 517.19 corresponds to $[C_{10}H_8O_{15}P_4]NaH_2^-$.

4.1.2 [TBA]$_5$[17]

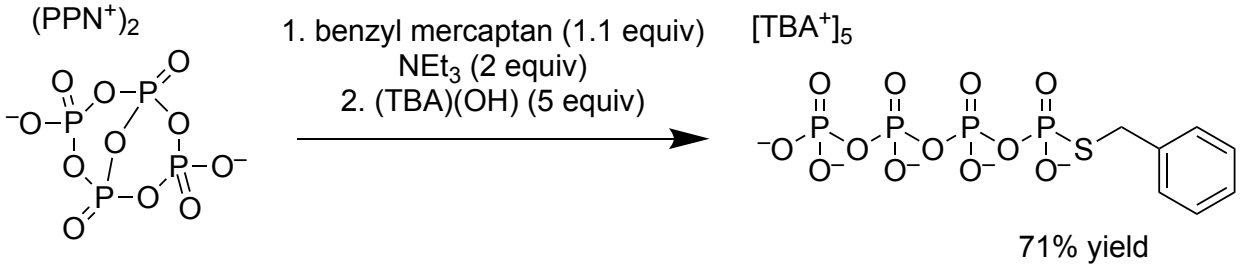

Figure S87: Synthesis of [TBA]$_5$[**17**].

In the glovebox, [PPN]$_2$[P_4O_{11}] (0.094 g, 0.068 mmol) was dissolved in acetonitrile (2 mL), and triethylamine (0.019 mL, 0.14 mmol) was added. Benzyl mercaptan (0.0088 mL, 0.0575 mmol) was then added, and the resulting mixture was stirred for 15 minutes. This solution was brought out of the glovebox, and immediately a solution of 40 wt% aqueous tetrabutylammonium hydroxide (0.22 g, 0.34 mmol) in acetonitrile (1 mL) was added. The resulting mixture was stirred for 30 min in the fumehood. Volatiles were removed under vacuum, and deionized water (2 mL) was added, resulting in a cloudy solution. This aqueous mixture was then filtered through an Acrodisc 0.2 μm wwPTFE syringe filter. This aqueous solution was then rinsed with DCM (3 x 3 mL) and the organic layers discarded. Volatiles were then removed from the aqueous fraction under reduced pressure at 40 °C, yielding the product as a colorless solid (0.079 g, 0.048 mmol, 71% yield).

^{1}H NMR (D_2O, 400 MHz): δ 7.50 (d, J = 7.3 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 4.16 (d, J = 9.3 Hz, 2H), 3.60 to 2.53 (m, 40H), 1.63 (dd, J = 10.6, 6.1 Hz, 40H), 1.35 (q, J = 7.4 Hz, 40H), 0.94 (t, J = 7.4 Hz, 60H).

^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 138.60 (d, J = 9.2 Hz), 129.15, 128.81, 127.29, 62.26 to 53.42 (m), 34.52 (d, J = 3.6 Hz), 23.09, 20.60 to 18.42 (m), 12.84.

^{31}P{^{1}H} NMR (D_2O, 162.0 MHz): δ 7.32 (d, J = 25.9 Hz), −6.52 (d, J = 20.3 Hz), −22.73 (dd, J = 20.4, 17.8 Hz), −23.76 (dd, J = 25.5, 17.7 Hz).

ESI-MS(−) of [TBA]$_5$[**17**] (CH_3CN/H_2O, m/z) found 684.16 ([**17**][TBA]H_3^-) (calc'd 684.17)

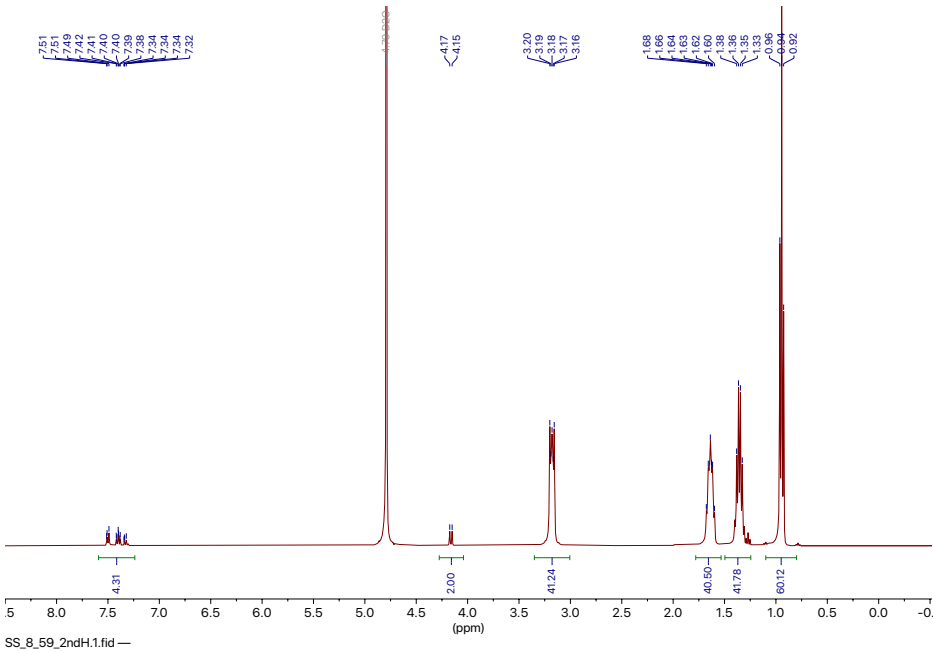

Figure S88: ^{1}H NMR spectrum of [TBA]$_5$[**17**] (D_2O, 400 MHz).

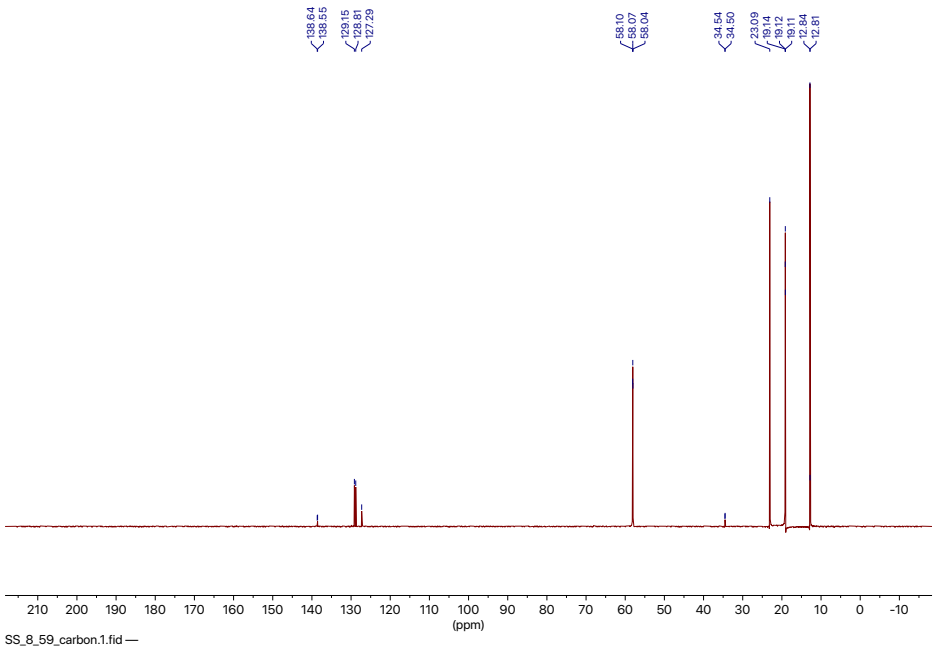

Figure S89: ^{13}C{^{1}H} NMR spectrum of [TBA]$_5$[**17**] (D_2O, 100.6 MHz).

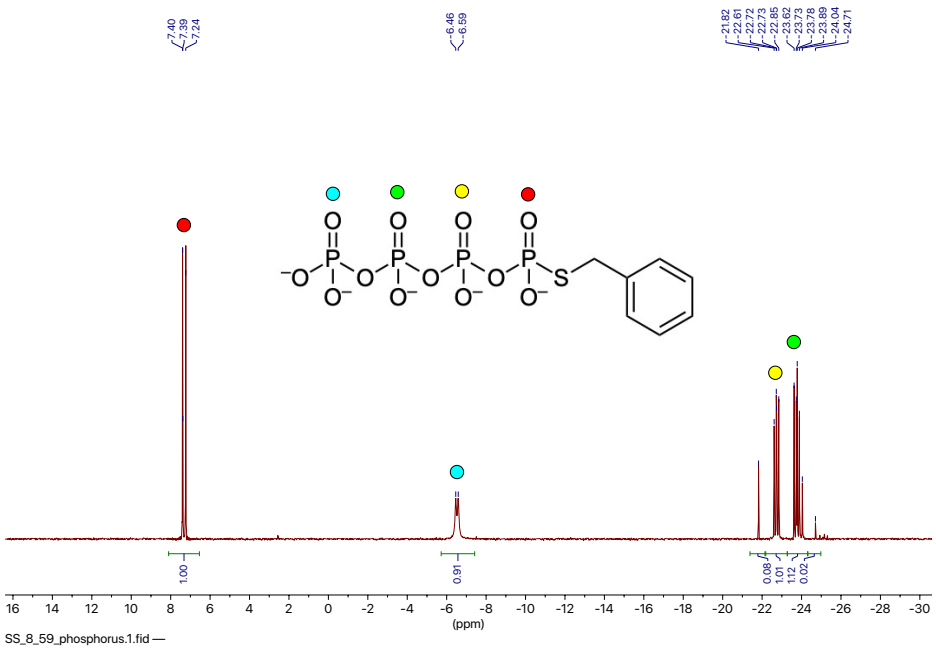

Figure S90: $^{31}P\{^{1}H\}$ NMR spectrum of $[TBA]_5$[**17**] (D_2O, 162.0 MHz).

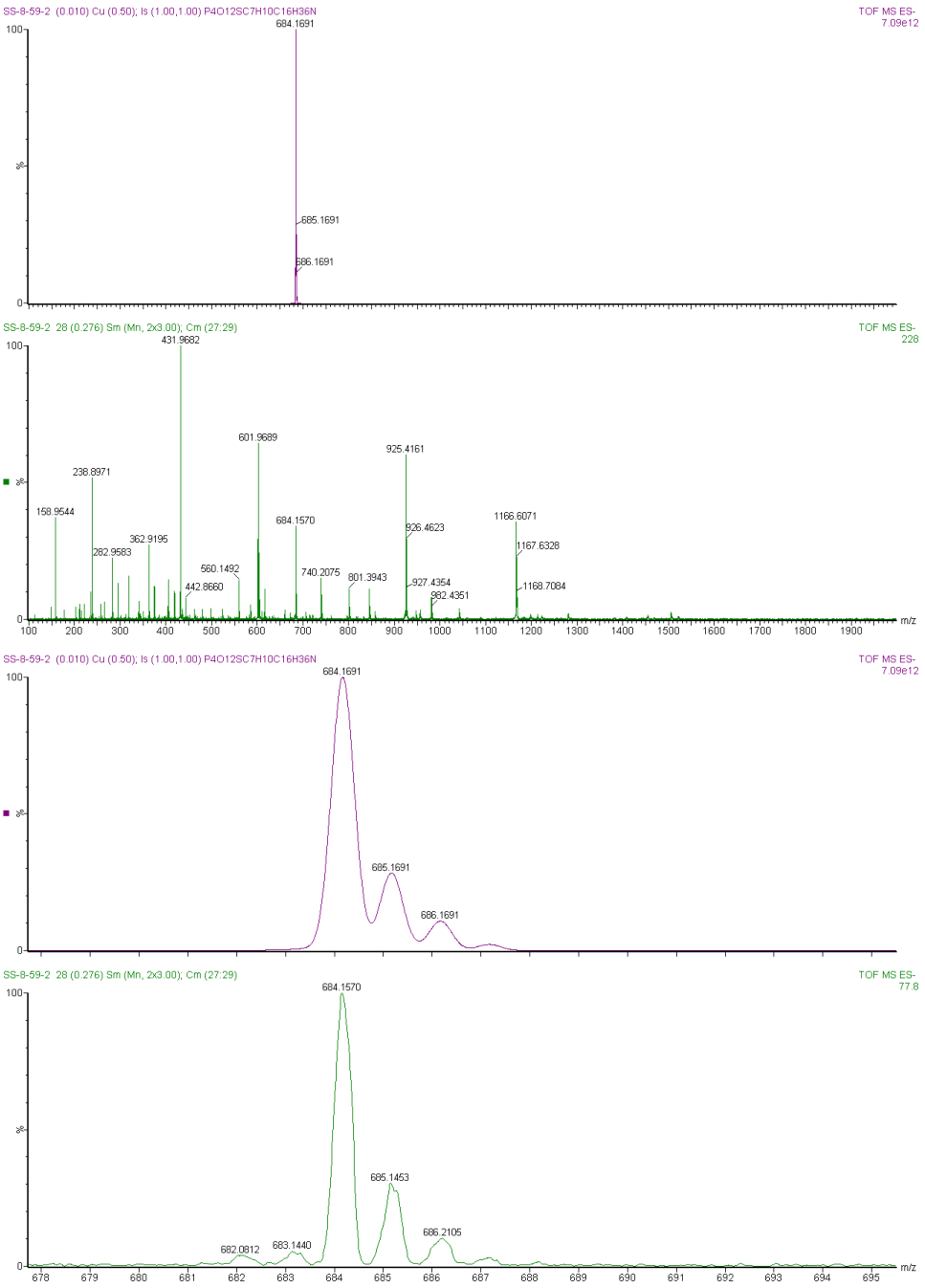

Figure S91: ESI-MS(−) of $[TBA]_5$[**17**] (CH_3CN/H_2O) with zoomed in portion of the molecular ion ([17][TBA]H_3^-), and calculated isotope pattern ($C_{23}H_{46}NO_{12}P_4S$).

4.1.3 $[NH_4]_6$[18]

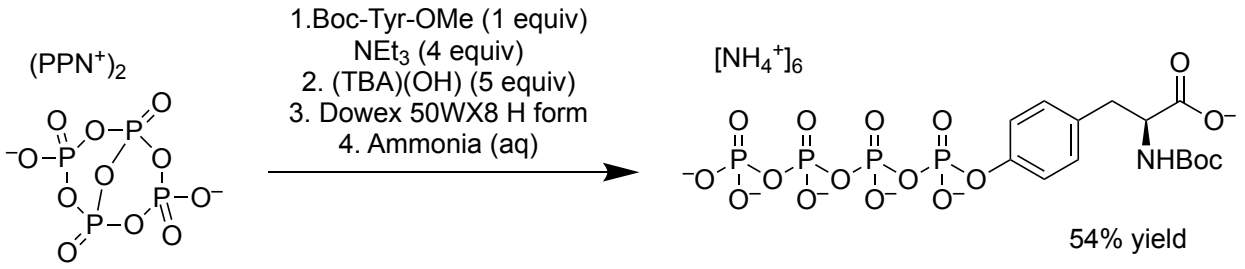

Figure S92: Synthesis of $[NH_4]_6$[**18**].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.044 g, 0.032 mmol) was dissolved in acetonitrile (2 mL), and triethylamine (0.018 mL, 0.13 mmol) was added. A 0.10 g/mL acetonitrile solution of Boc-Tyr-OMe that had been stored over 4Å sieves for 24 hours (0.089 mL, 0.032 mmol) was then added, and the resulting mixture was stirred for 15 minutes. This solution was brought out of the glovebox, and immediately a solution of 40 wt% aqueous tetrabutylammonium hydroxide (0.10 g, 0.16 mmol) in acetonitrile (1 mL) was added. The resulting mixture was stirred for 24 hours in the fumehood. Volatiles were removed under vacuum, and deionized water (2 mL) was added, resulting in a cloudy solution. This aqueous mixture was then filtered through an Acrodisc 0.2 μm wwPTFE syringe filter. This aqueous solution was then acidified with Dowex 50WX8 H form resin (0.5 mL). After stirring for 5 minutes, the mixture was filtered to remove the resin. The resulting acidic aqueous solution was rinsed with DCM (3 x 3 mL) and the organic layers discarded. The remaining aqueous solution was basified by addition of aqueous ammonia (0.5 mL). Volatiles were then removed from the aqueous solution under reduced pressure at 40 °C, yielding the product as a colorless solid (0.013 g, 0.019 mmol, 59% yield). $^{31}P\{^1H\}$ NMR found several unfunctionalized metaphosphates as impurities (8.3% of total $^{31}P\{^1H\}$ NMR integration), giving a corrected yield of 54%.

^1H NMR (D_2O, 400 MHz): δ 7.26 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 4.16 (dd, J = 8.9, 4.9 Hz, 1H), 3.13 (dd, J = 14.1, 4.9 Hz, 2H), 2.91 to 2.82 (m, 2H), 1.37 (s, 9H).

$^{13}C\{^1H\}$ NMR (D_2O, 100.6 MHz): δ 179.08, 150.31, 130.33, 120.53 (d, J = 4.5 Hz), 80.91, 57.28, 37.28, 27.62.

$^{31}P\{^1H\}$ NMR (D_2O, 162.0 MHz): δ −6.15 (d, J = 19.6 Hz), −15.69 (d, J = 18.0 Hz), −22.50 (dd, J = 20.0, 17.2 Hz), −23.18 (t, J = 17.7 Hz).

ESI-MS(−) of $[NH_4]_6$[18] (CH_3CN/H_2O, m/z) found 599.99 ([18]H_5^-) (calc'd 599.98)

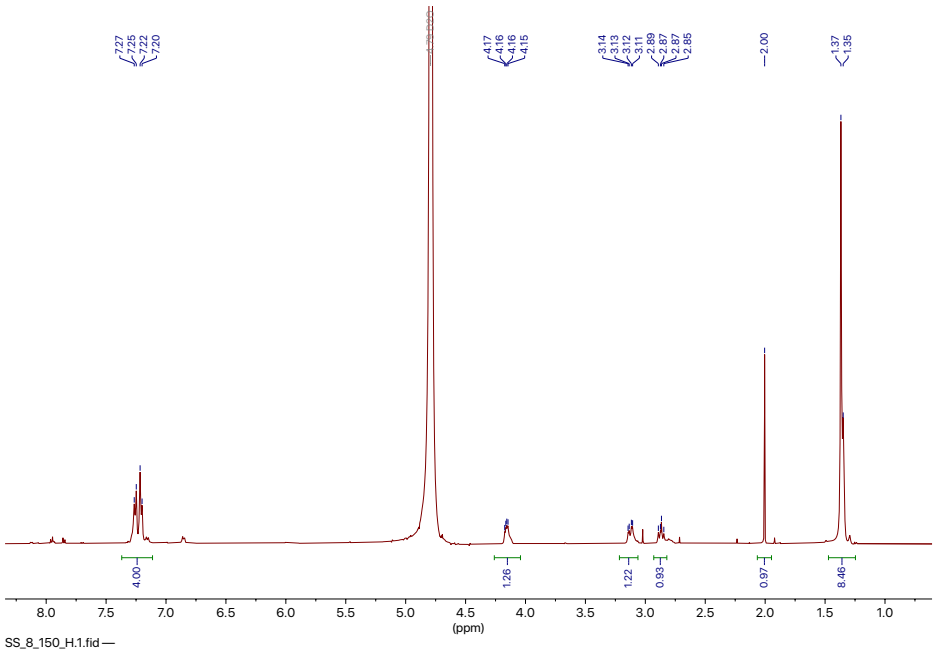

Figure S93: ^{1}H NMR spectrum of $[NH_4]_6$[**18**] (D_2O, 400 MHz).

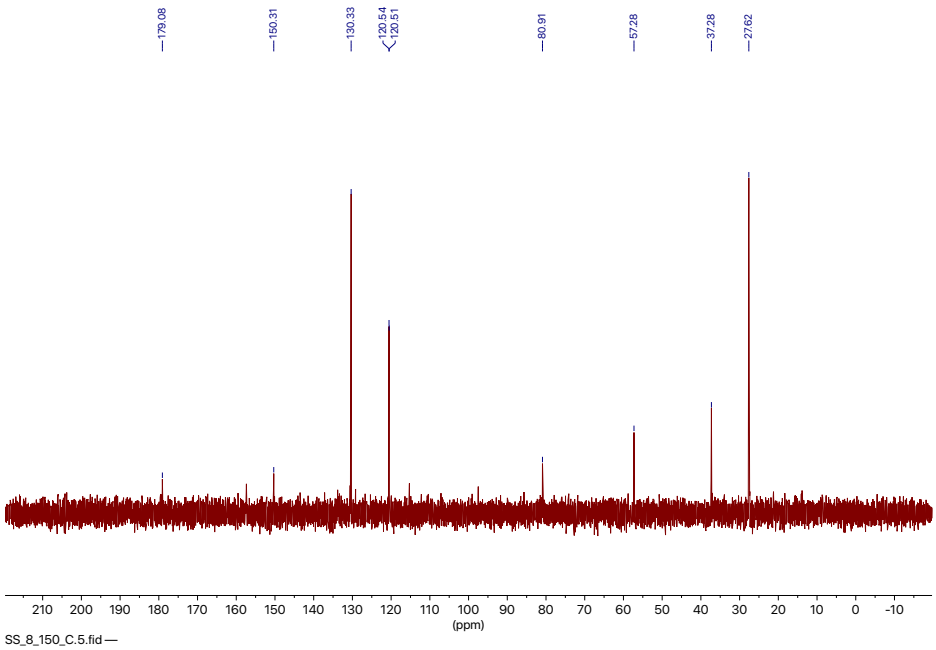

Figure S94: ^{13}C{^{1}H} NMR spectrum of $[NH_4]_6$[**18**] (D_2O, 100.6 MHz).

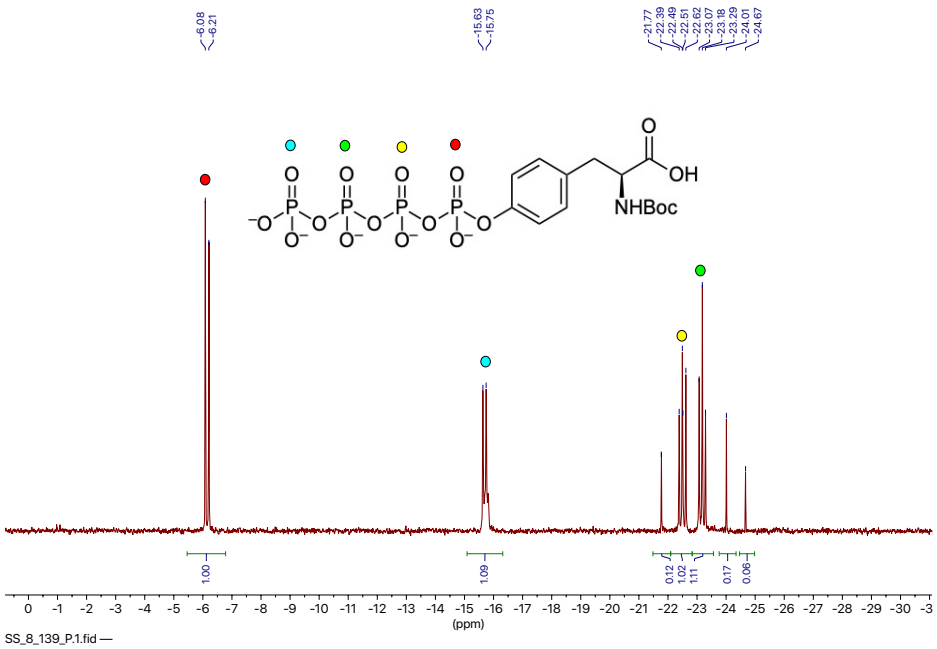

Figure S95: $^{31}P\{^{1}H\}$ NMR spectrum of $[NH_4]_6$[**18**] with residual metaphosphate impurities (−21.77, −24.01, and −24.67) (D_2O, 162.0 MHz).

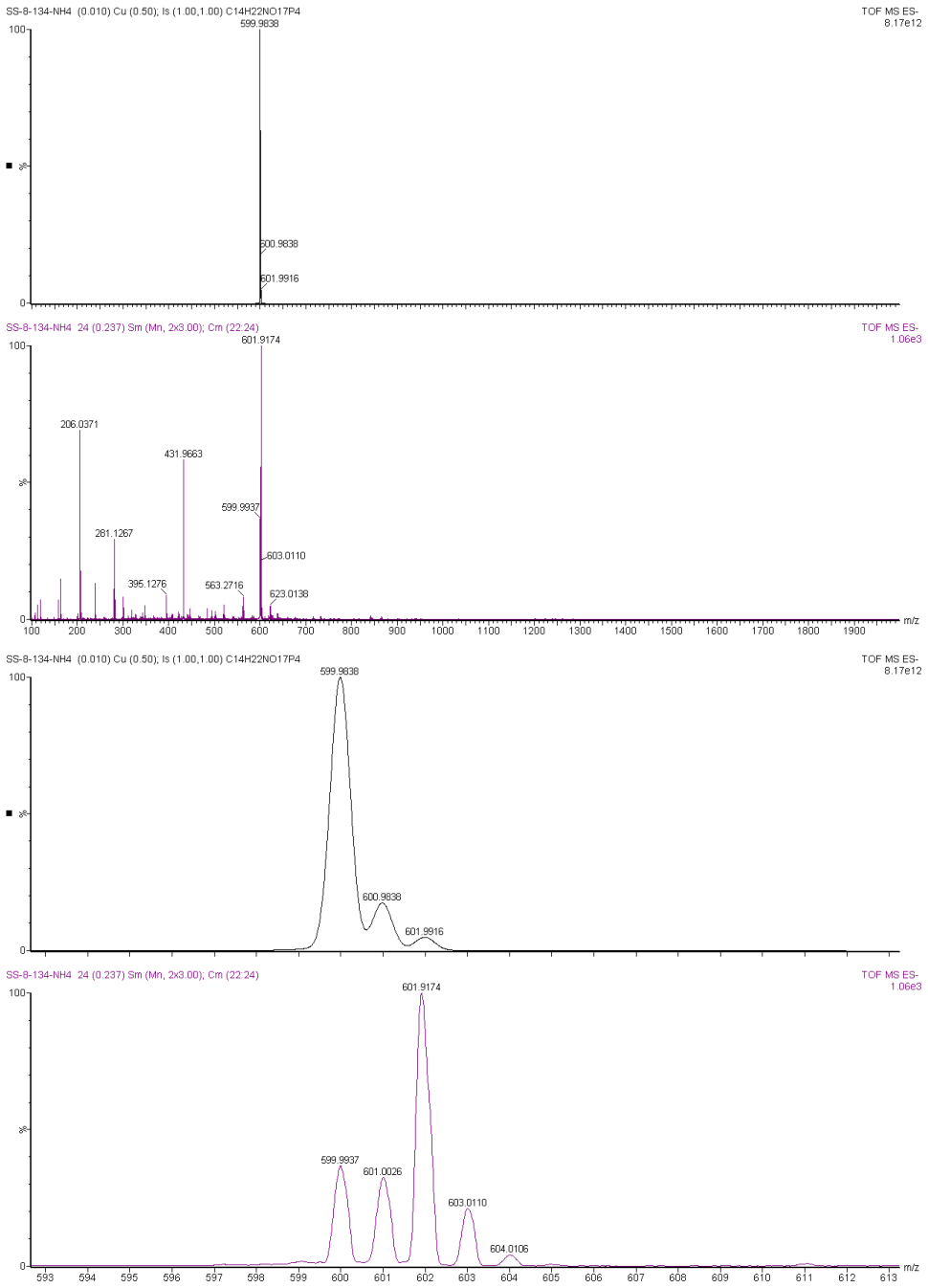

Figure S96: ESI-MS(−) of $[NH_4]_6$[**18**] (CH_3CN/H_2O) with zoomed in portion of the molecular ion ($[18]H_5^-$), and calculated isotope pattern ($C_{14}H_{22}NO_{17}P_4$). The peak at 601.92 corresponds to the internal reference compound used as a lock mass.

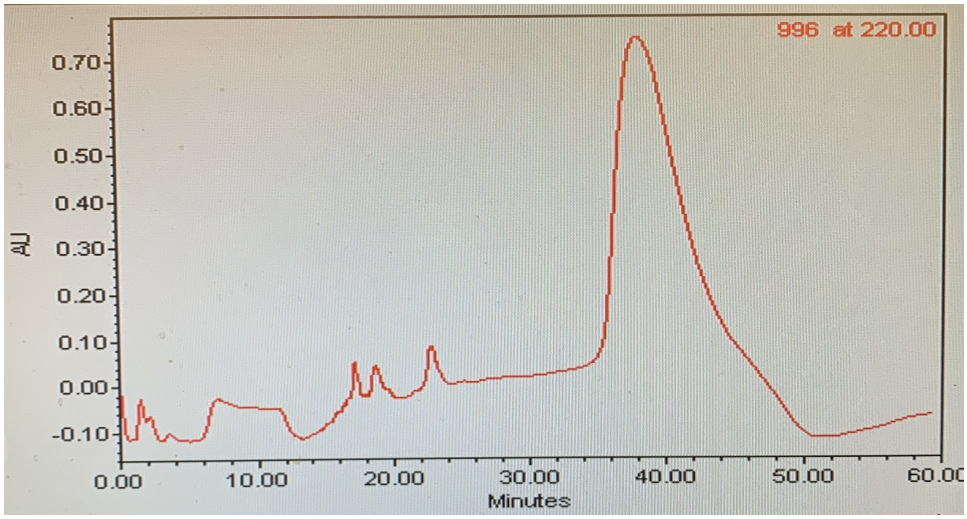

Figure S97: Analytical AX-HPLC trace of $[NH_4]_6$[**18**] with a gradient method from deionized water to 1M aqueous LiCl monitored by absorbance at 220 nm. The low absorbance peaks towards the beginning of the run are assigned as ghost peaks resulting from the strong absorbance of most organic compounds at 220 nm.

4.1.4 [TBA][Na]$_2$[19]

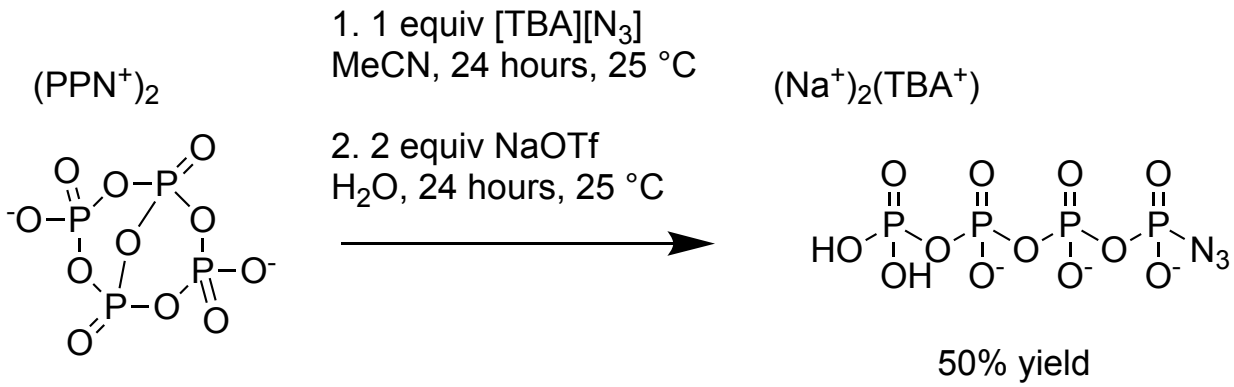

Figure S98: Synthesis of [TBA][Na]$_2$[**19**].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.14 g, 0.10 mmol) was dissolved in acetonitrile (1 mL). To this solution was added a solution of tetrabutylammonium azide (0.028 g, 0.10 mmol) in acetonitrile (1 mL). The resulting mixture was stirred for 24 hours and then removed from the glovebox. A solution of sodium triflate (0.034 g, 0.20 mmol) in acetonitrile (1 mL) was then added and the resulting cloudy mixture stirred for 15 minutes. Volatile materials were then evaporated under reduced pressure on a Schlenk line at room temperature giving an oily residues. This solid was then suspended in water (3 mL). This mixture was then extracted with DCM (3 × 3 mL). The resulting aqueous layer was then filtered through an Acrodisc 0.2 μm wwPTFE syringe filter. This aqueous solution was then lyophilized, giving the product as a white solid (0.048 g, 0.075 mmol, 75% yield). $^{31}P\{^1H\}$ NMR revealed significant residual

phosphate impurities (33% of total $^{31}P\{^{1}H\}$ NMR integration). We were unable to purify this compound by HPLC due to the lack of any UV absorbing moiety. Therefore a corrected yield for this compound is 50%.

^{1}H NMR (D_2O, 400 MHz): δ 3.67 to 2.94 (m, 8H), 1.63 (td, J = 11.4, 9.8, 5.8 Hz, 8H), 1.35 (h, J = 7.4 Hz, 8H), 0.94 (t, J = 7.4 Hz, 12H).

$^{13}C\{^{1}H\}$ NMR (D_2O, 100.6 MHz): δ 64.62 to 55.58 (m), 23.09, 20.51 to 17.66 (m), 12.79.

$^{31}P\{^{1}H\}$ NMR (D_2O, 162.0 MHz): δ −11.41 (d, J = 18.1 Hz), −13.28 (d, J = 20.2 Hz), −23.19 to −23.60 (m), −23.73 to −24.12 (m).

ESI-MS(−) of [TBA][Na]$_2$[**21**] in CH_3CN, found 603.38 m/z (calc'd 603.15 m/z) for $C_{16}H_{39}N_4O_{12}P_4$.

IR (ATR, cm^{-1}): 2169 (m, $-N_3$).

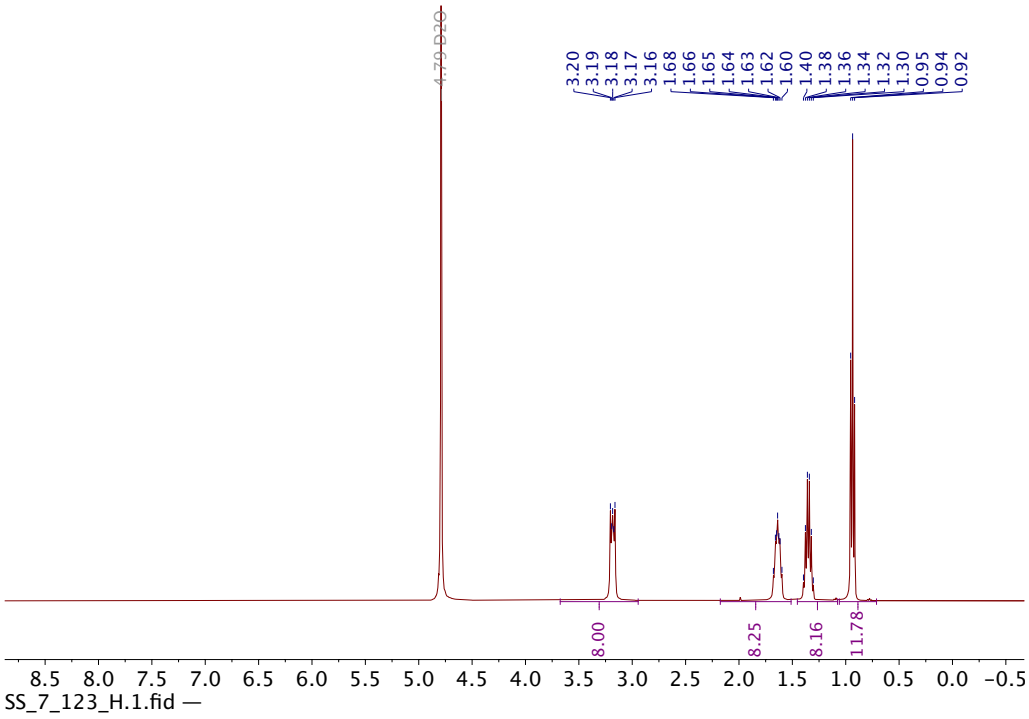

Figure S99: ^{1}H NMR spectrum of [TBA][Na]$_2$[**19**] (D_2O, 400 MHz).

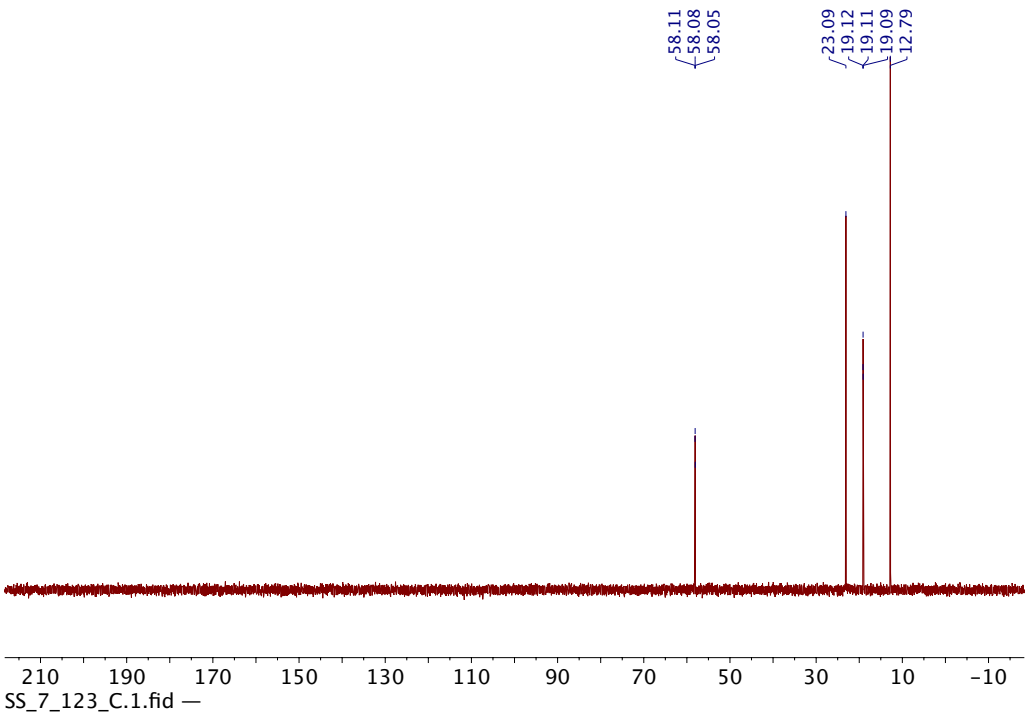

Figure S100: $^{13}C\{^{1}H\}$ NMR spectrum of [TBA][Na]$_2$[**19**] (D_2O, 101 MHz).

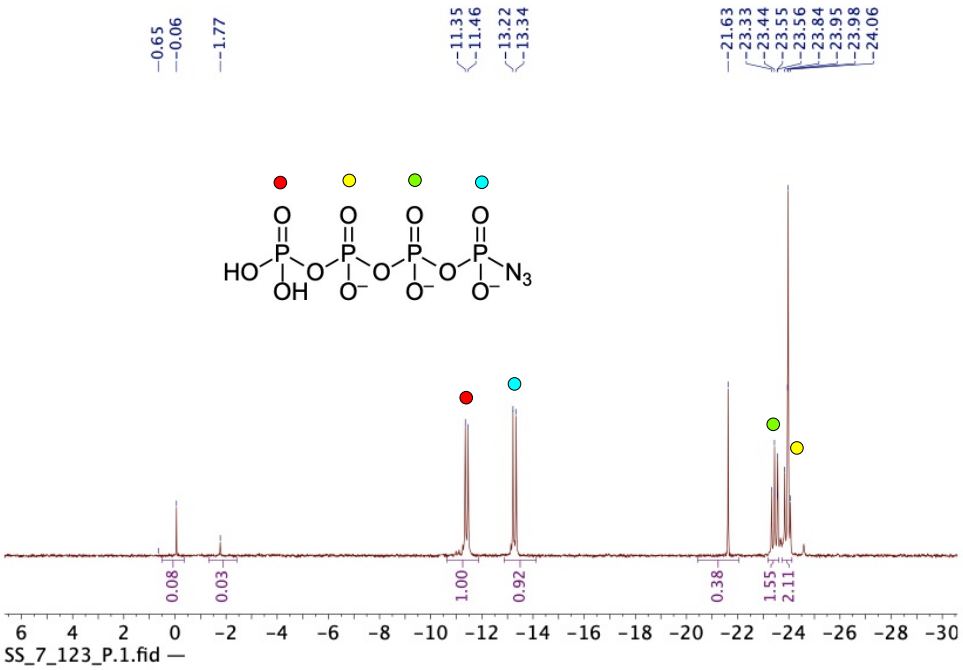

Figure S101: $^{31}P\{^{1}H\}$ NMR spectrum of [TBA][Na]$_2$[**19**] (D_2O, 162 MHz). The singlets in the NMR spectrum correspond to inorganic phosphate impurities: orthophosphate (−0.1 ppm), trimetaphosphate (−21.6 ppm), and tetrametaphosphate (−24.0 ppm).

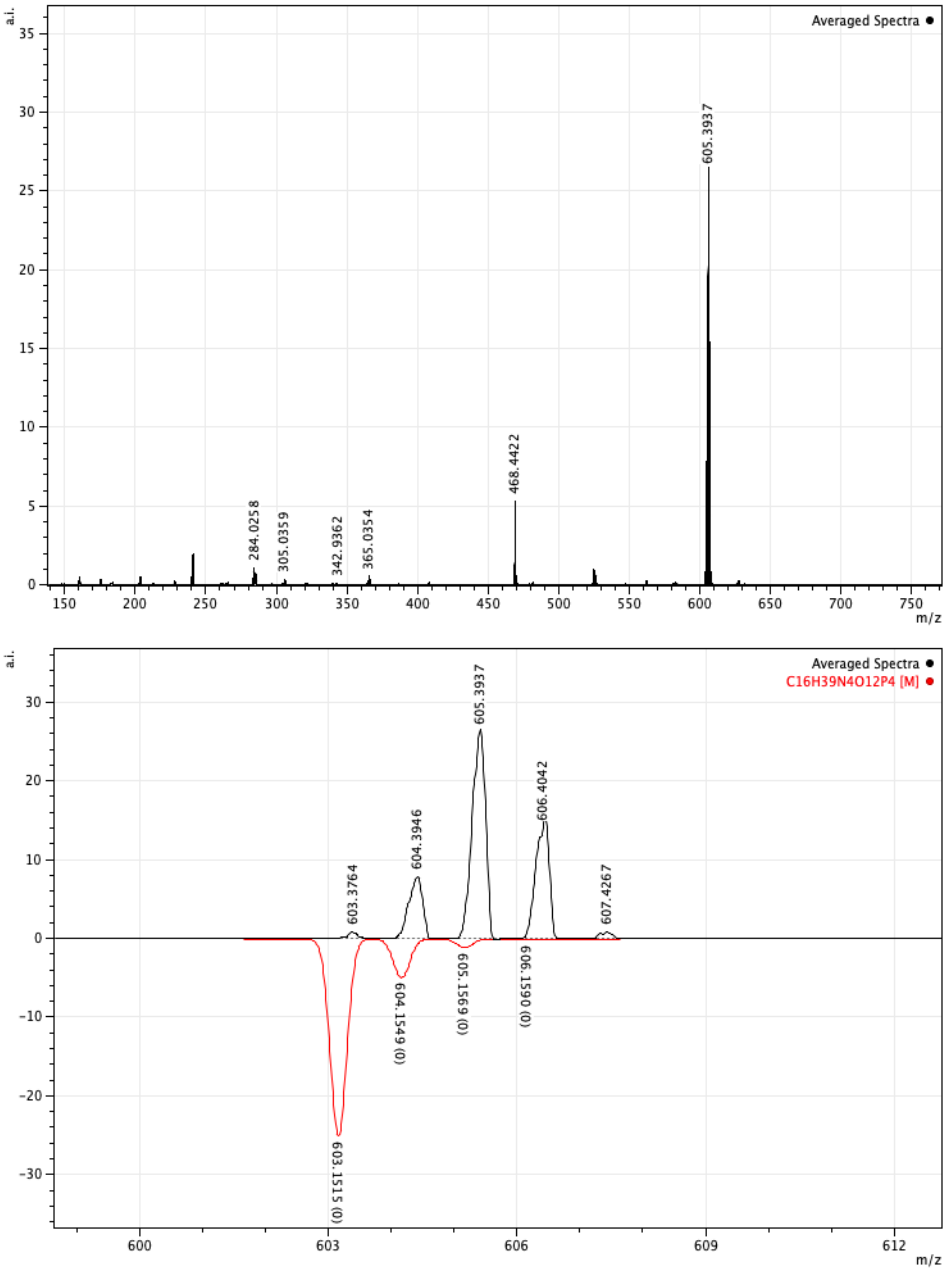

Figure S102: ESI-MS(−) of [TBA][Na]$_2$[**19**] (CH_3CN) with zoomed in portion showing the molecular ion ([P_4O_{12}−N_3H_3][TBA]$^-$, top) and calculated isotope pattern ($C_{16}H_{39}N_4O_{12}P_4$, bottom). The difference between calculated and experimental isotope patterns is due to the MS sample being prepared in deuterium oxide, thereby enriching the sample in deuterium.

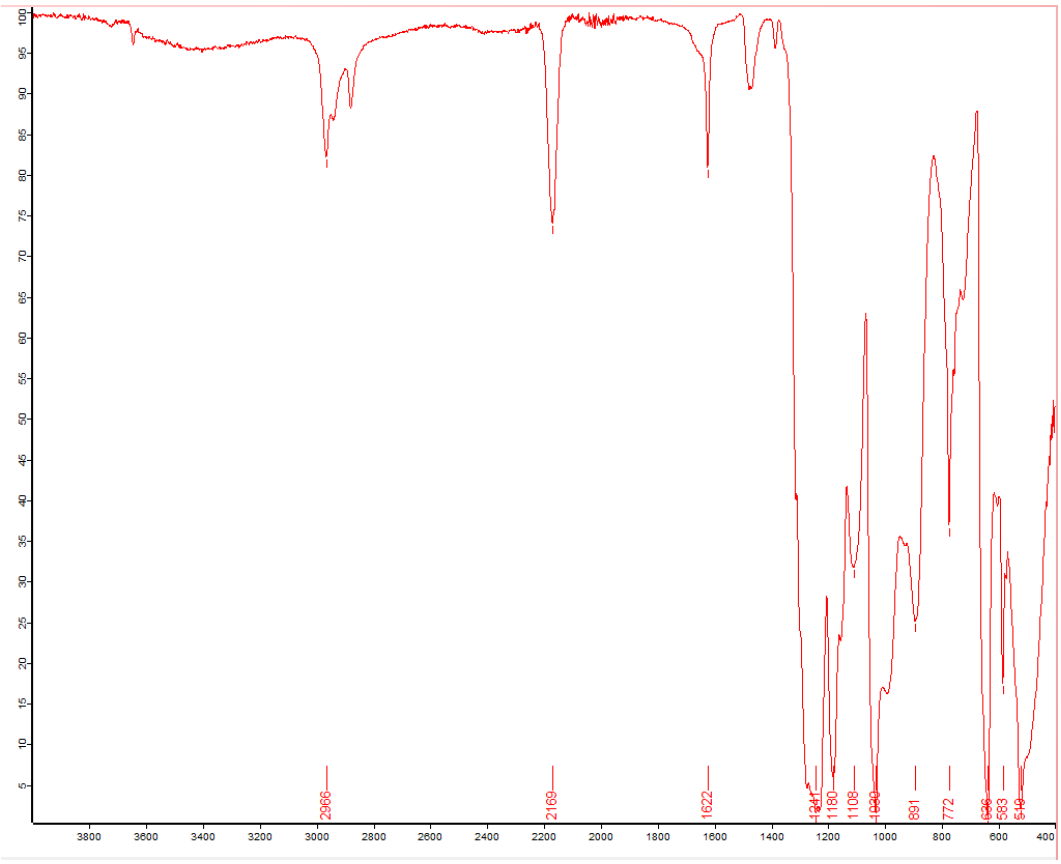

Figure S103: ATR-IR spectrum of solid [TBA][Na]$_2$[**19**].

4.2 Ring Opening with an Amine

4.2.1 [Et$_3$NH]$_4$[20]

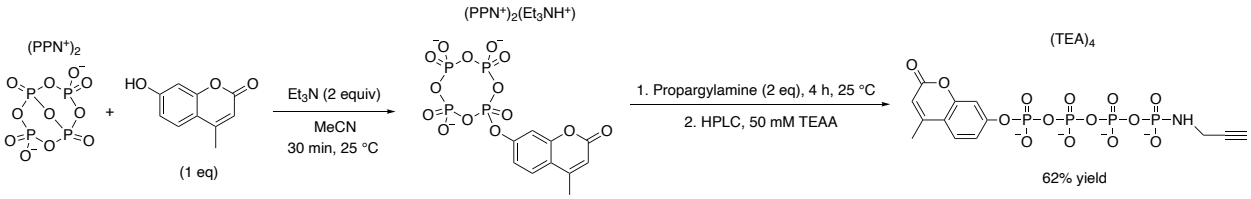

Figure S104: Synthesis of [Et$_3$NH]$_4$[4-methyl-2-oxo-2*H*-chromen-7-yl-P$_4$O$_{12}$−propargylamine].

In the glovebox, [PPN]$_2$[P$_4$O$_{11}$] (0.070 g, 0.051 mmol) was dissolved in acetonitrile (0.5 mL), and triethylamine (0.014 mL, 0.10 mmol, 2 equiv) was added. 4-methylumbelliferone (0.0090 g, 0.051 mmol) was then added, and the resulting mixture was stirred for 30 minutes. Propargylamine (6 μL, 0.102 mmol, 2 equiv) was then added, and the mixture was stirred for 4 hours. The reaction vial was transferred into the fumehood, where a solution of NaOTf (0.035 g, 0.203 mmol, 4 equiv) in MeCN (1 mL) was added. Volatiles were evaporated

under vacuum at room temperature, and the resulting solids were suspended in deionized water (5 mL). The mixture was filtered through an Acrodisc 0.2 μm wwPTFE syringe filter, and purified by HPLC according to the procedures outlined in the General Considerations section above. The fractions containing the product were pooled together, and repeatedly lyophilized to remove excess triethylammonium acetate buffer. The product was obtained as a white solid (0.0297 g). The resulting material was found to contain one equivalent of residual triethylammonium acetate HPLC buffer by NMR. Correcting for this impurity gives 0.027 mmol of product (53% yield). In the proton NMR, no resonance could be assigned as the acetylenic CH. However, we are confident in our assignment due to the presence of the resonance for the corresponding methylene of the propargylamino group and the mass spectrum. We hypothesize that at basic pH this resonance is broadened due to proton exchange with the deuterium oxide solvent.

^{1}H NMR (D_2O, 400 MHz): δ 7.83 (d, $J = 8.8$ Hz, 1H), 7.37 (d, $J = 8.7$ Hz, 1H), 7.32 (s, 1H), 6.32 (s, 1H), 3.56 (dd, $J = 9.6, 2.2$ Hz, 2H), 3.18 (q, $J = 7.1$ Hz, 24H), 2.50 (t, $J = 2.3$ Hz, 1H), 2.49 (s, 3H), 1.27 (t, $J = 7.3$ Hz, 36H).

^{13}C$\{^{1}$H$\}$ NMR (D_2O, 100.6 MHz): δ 164.6, 156.4, 155.0 (d, $J = 7.3$ Hz), 153.6, 126.6, 117.8 (d, $J = 4.7$ Hz), 116.5, 111.9, 108.5 (d, $J = 4.8$ Hz), 83.1 (d, $J = 11.7$ Hz), 71.2, 46.6, 31.0, 18.1, 8.2.

^{31}P$\{^{1}$H$\}$ NMR (D_2O, 162.0 MHz): δ -2.9 (d, $J_{PP} = 19.9$ Hz), -17.1 (d, $J_{PP} = 18.2$ Hz), -23.2 (t, $J_{PP} = 18.0$ Hz), -23.7 (t, $J_{PP} = 17.3$ Hz).

^{31}P NMR (D_2O, 162.0 MHz): δ -2.9 (dt, $J = 19.6, 7.6$ Hz), -17.1 (d, $J_{PP} = 18.1$ Hz), -23.2 (t, $J_{PP} = 18.0$ Hz), -23.7 (t, $J_{PP} = 17.3$ Hz).

ESI-MS($-$) of $[C_{13}H_{11}NO_{14}P_4]H_3^-$ (CH_3CN/H_2O, m/z) 531.67 (calc'd 531.94)

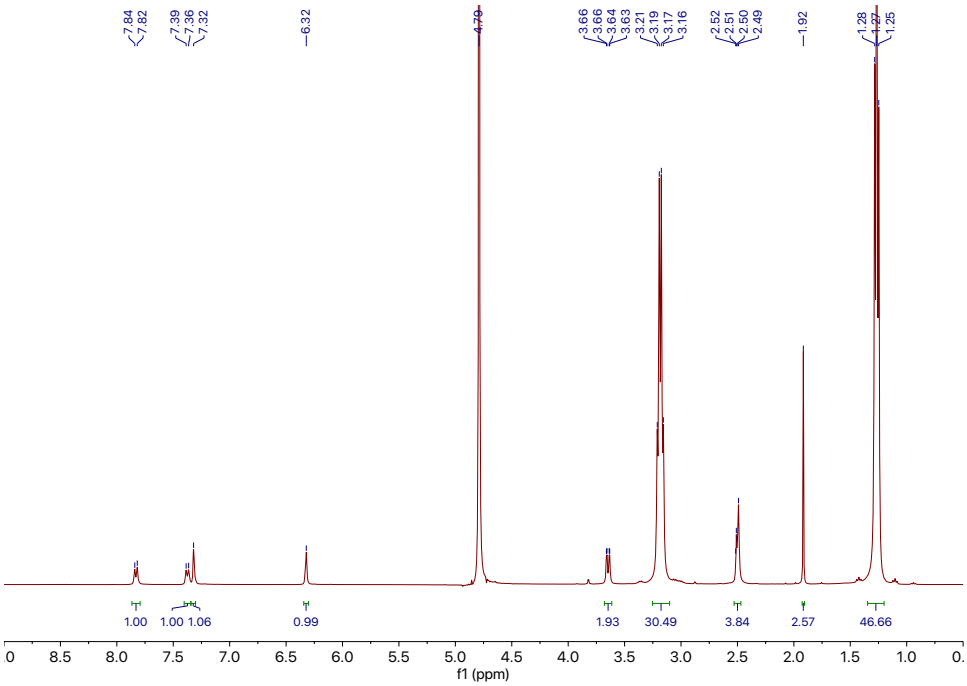

Figure S105: ^{1}H NMR spectrum of $[Et_3NH]_4$[4-methyl-2-oxo-2*H*-chromen-7-yl-P_4O_{12}−amine] (D_2O, 400 MHz) with approximately one equivalent of residual triethylammonium acetate buffer (3.19, 1.92, and 1.27 ppm).

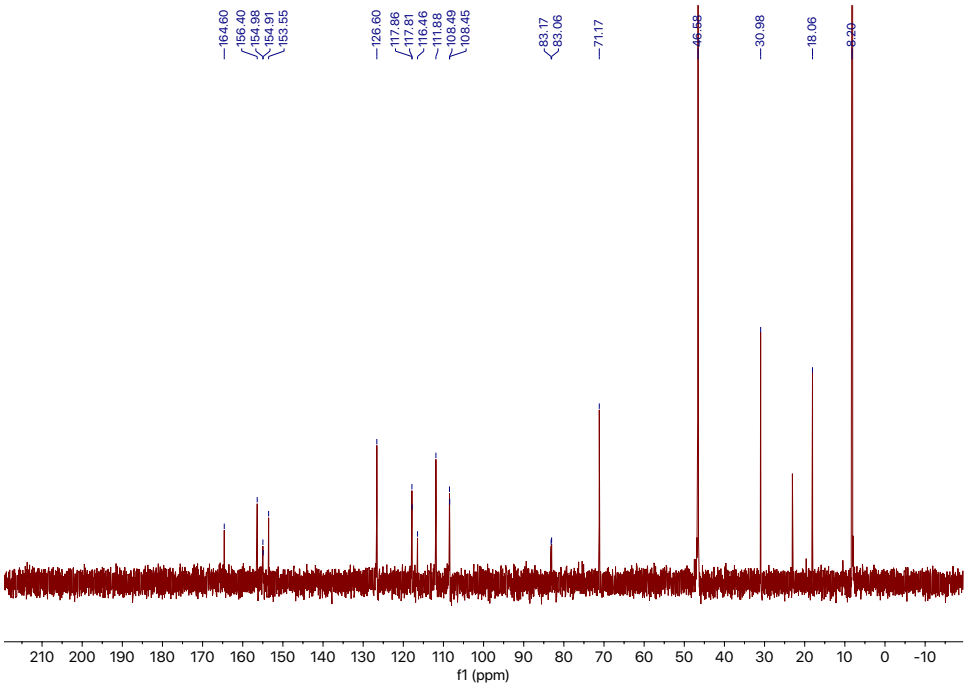

Figure S106: $^{13}C\{^{1}H\}$ NMR spectrum of $[Et_3NH]_4$[4-methyl-2-oxo-2*H*-chromen-7-yl-P_4O_{12}−amine] (D_2O, 100.6 MHz) with residual triethylammonium acetate buffer (164.6, 46.6, 20.6, and 8.2 ppm).

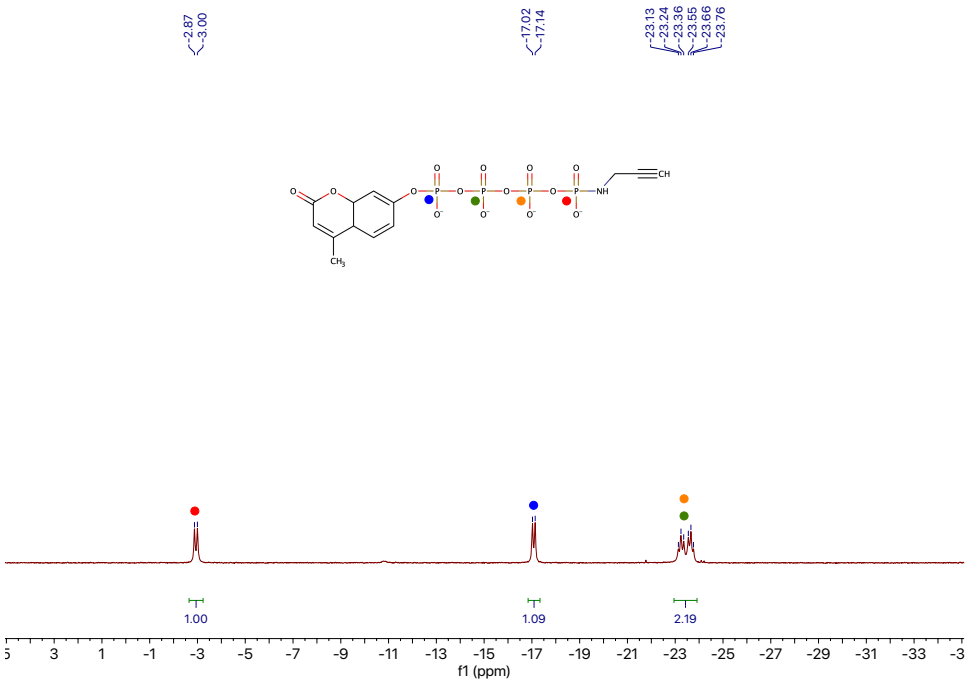

Figure S107: $^{31}P\{^{1}H\}$ NMR spectrum of $[Et_3NH]_4$[4-methyl-2-oxo-2*H*-chromen-7-yl-P_4O_{12}−amine] (D_2O, 162.0 MHz).

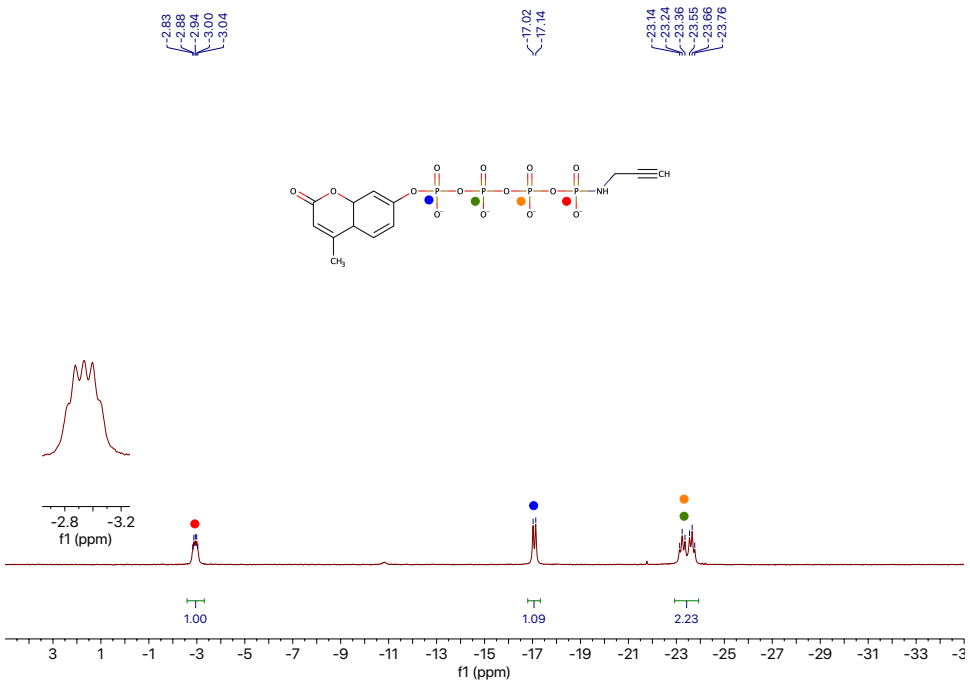

Figure S108: ^{31}P NMR spectrum of $[Et_3NH]_4$[4-methyl-2-oxo-2*H*-chromen-7-yl-P_4O_{12}−amine], with inset zoomed in on phosphoramidate phosphorus resonance (D_2O, 162.0 MHz).

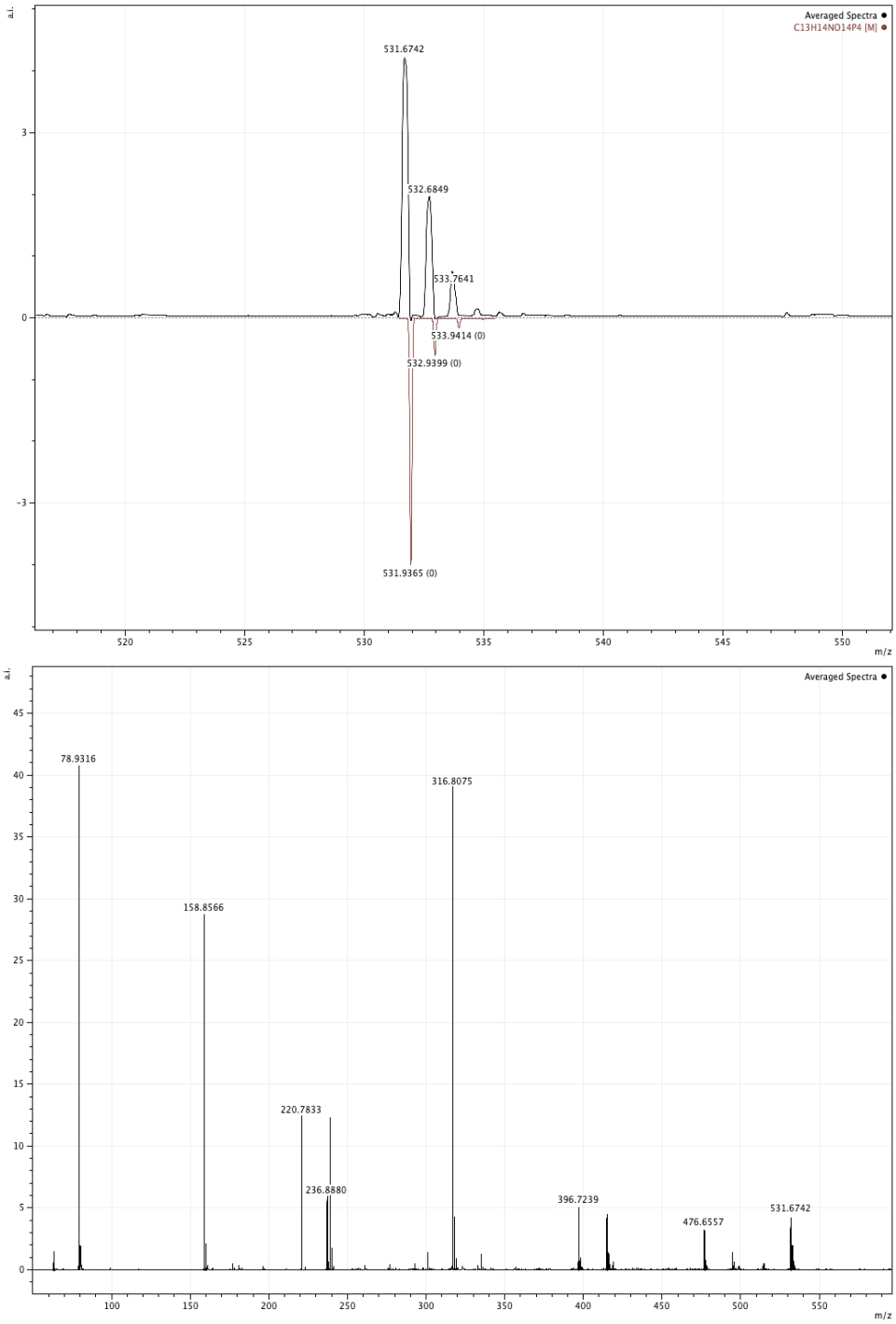

Figure S109: ESI-MS(−) of $[Et_3NH]_4[C_{13}H_{11}NO_{14}P_4]$ (CH_3CN/H_2O) with zoomed in portion of the molecular ion ($[C_{13}H_{11}NO_{14}P_4]H_3^-$, top), and calculated isotope pattern ($C_{13}H_{14}NO_{14}P_4$, bottom).

4.2.2 $[PPN]_2[EthanolamineH]_2$[21]

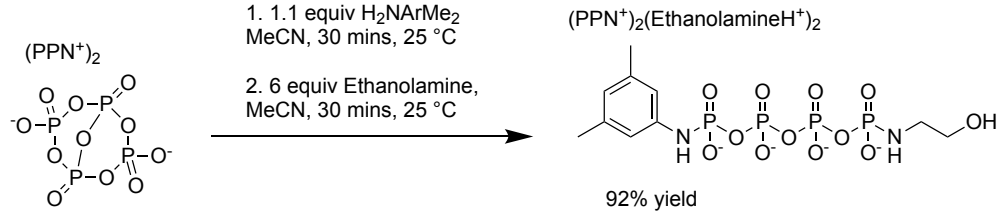

Figure S110: Synthesis of $[PPN]_2[EthanolamineH]_2$[**21**].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.012 g, 0.090 mmol) was dissolved in acetonitrile (2 mL). To this solution was added 3,5-dimethylaniline (0.012 mL, 0.098 mmol). The resulting mixture was stirred at room temperature for 30 min. The reaction mixture was then removed from the glovebox, and ethanolamine (0.033 mL, 0.54 mmol) was added. The resulting solution was stirred for 30 minutes. Diethyl ether (10 mL) was then added to this mixture, giving a cloudy solution. After several hours, the product crystallized on the bottom of the vial. The supernatant was decanted off, and the crystals were dried under vacuum for several hours, giving the product as a colorless solid (0.14 g, 0.082 mmol, 92% yield).

Treatment of an acetonitrile solution of $[PPN]_2[EthanolamineH]_2$[**21**] with an acetonitrile solution of sodium triflate immediately gives a cloudy precipitate. Evaporating volatiles under reduced pressure yielded a solid which was then suspended in water. Filtering through a syringe filter yielded a clear aqueous solution. $^{31}P\{^1H\}$ NMR of this solution revealed a mixture of phosphates consisting primarily of an orthophosphate derivative and a triphosphate derivative. Therefore, **21** hydrolyzes much more rapidly than similar compounds, such as **25**.

^1H NMR (acetonitrile-d_3, 400 MHz): δ 7.91 to 7.33 (m, 60H), 6.77 (s, 2H), 6.31 (s, 1H), 5.14 (br, 1H), 3.58 (br, 4H), 3.50 to 3.37 (m, 2H), 2.90 (dt, J = 14.5, 4.9 Hz, 2H), 2.84 (br, 4H).

$^{13}C\{^1H\}$ NMR (acetonitrile-d_3, 100.6 MHz): δ 145.46, 138.59, 134.60, 133.96 to 132.72 (m), 131.63 to 129.91 (m), 128.70 (d, J = 2.0 Hz), 127.62 (d, J = 1.9 Hz), 120.97, 115.84 (d, J = 7.0 Hz), 63.56, 60.78, 46.13, 43.60, 21.64.

$^{31}P\{^1H\}$ NMR (acetonitrile-d_3, 162.0 MHz): δ 23.00, 0.58 (d, J = 20.0 Hz), −8.63 (d, J = 19.2 Hz), −18.84 to −19.52 (m).

ESI-MS(−) of $[PPN]_2[EthanolamineH]_2$[**21**] in CH_3CN, found 483.03 m/z (calc'd 482.99 m/z) for $C_{10}H_{19}N_2O_{12}P_4$)

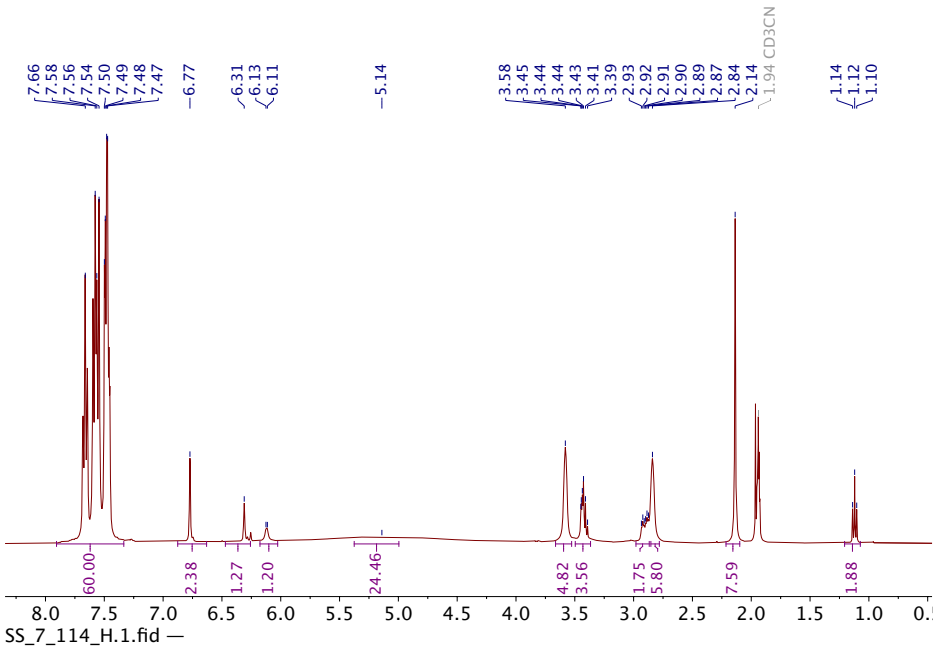

Figure S111: ^{1}H NMR spectrum of [PPN]$_2$[EthanolamineH]$_2$[**21**] (acetonitrile-d_3, 400 MHz).

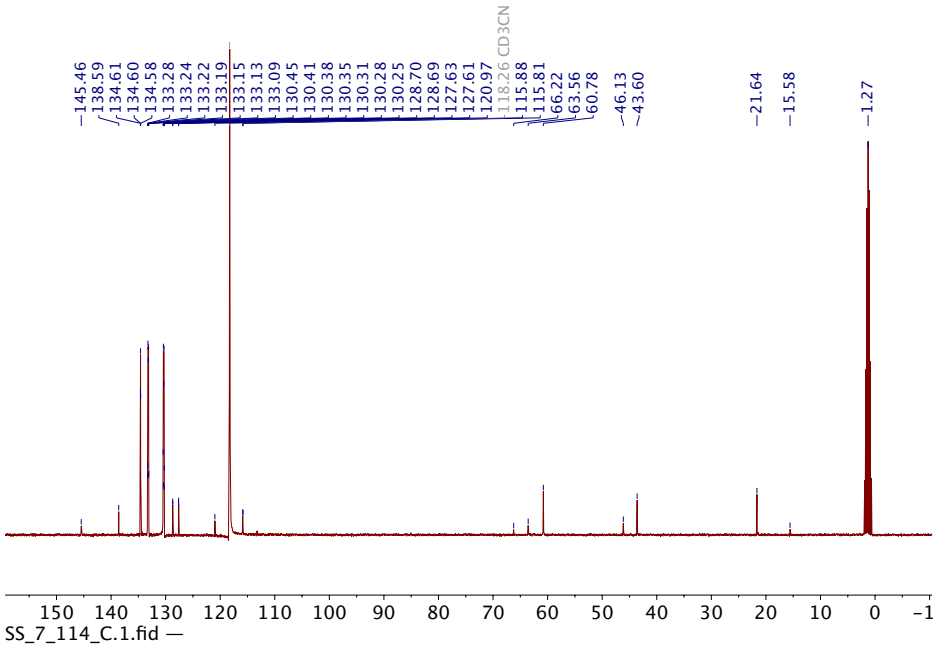

Figure S112: ^{13}C{^{1}H} NMR spectrum of [PPN]$_2$[EthanolamineH]$_2$[**21**] (acetonitrile-d_3, 100.6 MHz).

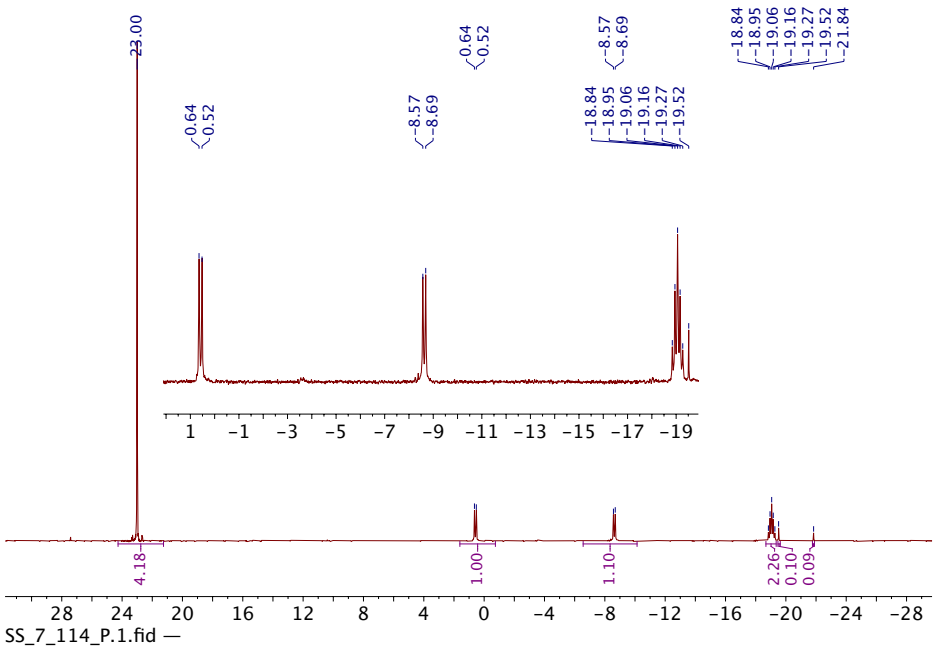

Figure S113: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[EthanolamineH]_2$[**21**] (acetonitrile-d_3, 162.0 MHz) with residual trimetaphosphate (−19.5 ppm) and tetrametaphosphate (−21.8 ppm) as trace impurities.

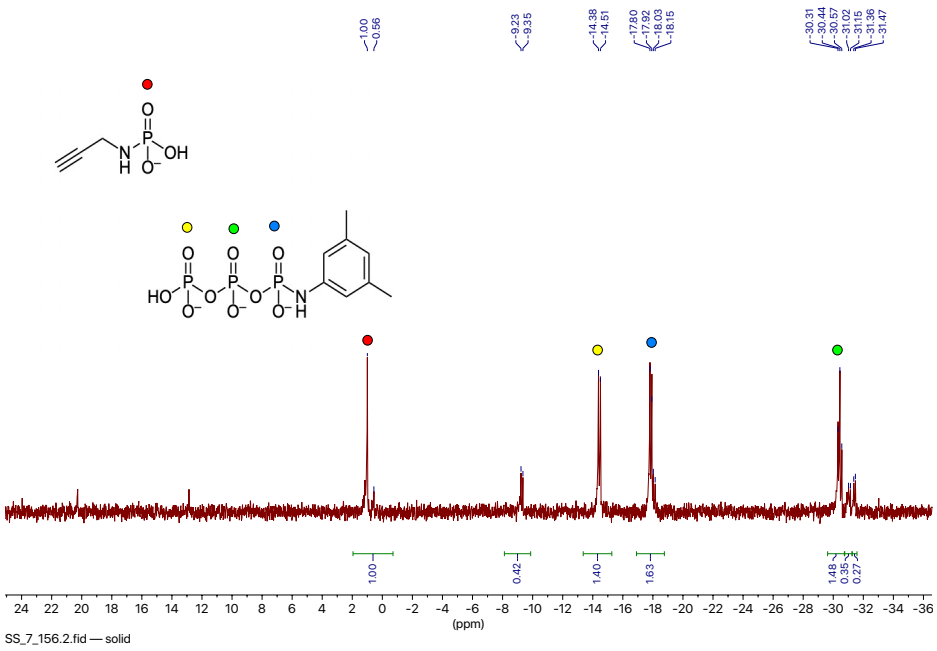

Figure S114: $^{31}P\{^{1}H\}$ NMR spectrum of $[Na]_4$[**21**], formed by precipitation with sodium triflate, in water. This shows a mixture of phosphate consisting primarily of an orthophosphate derivative (1.00 ppm) and a triphosphate derivative (−14.4, −17.9, and −30.4 ppm) with proposed structures for the major decomposition products.

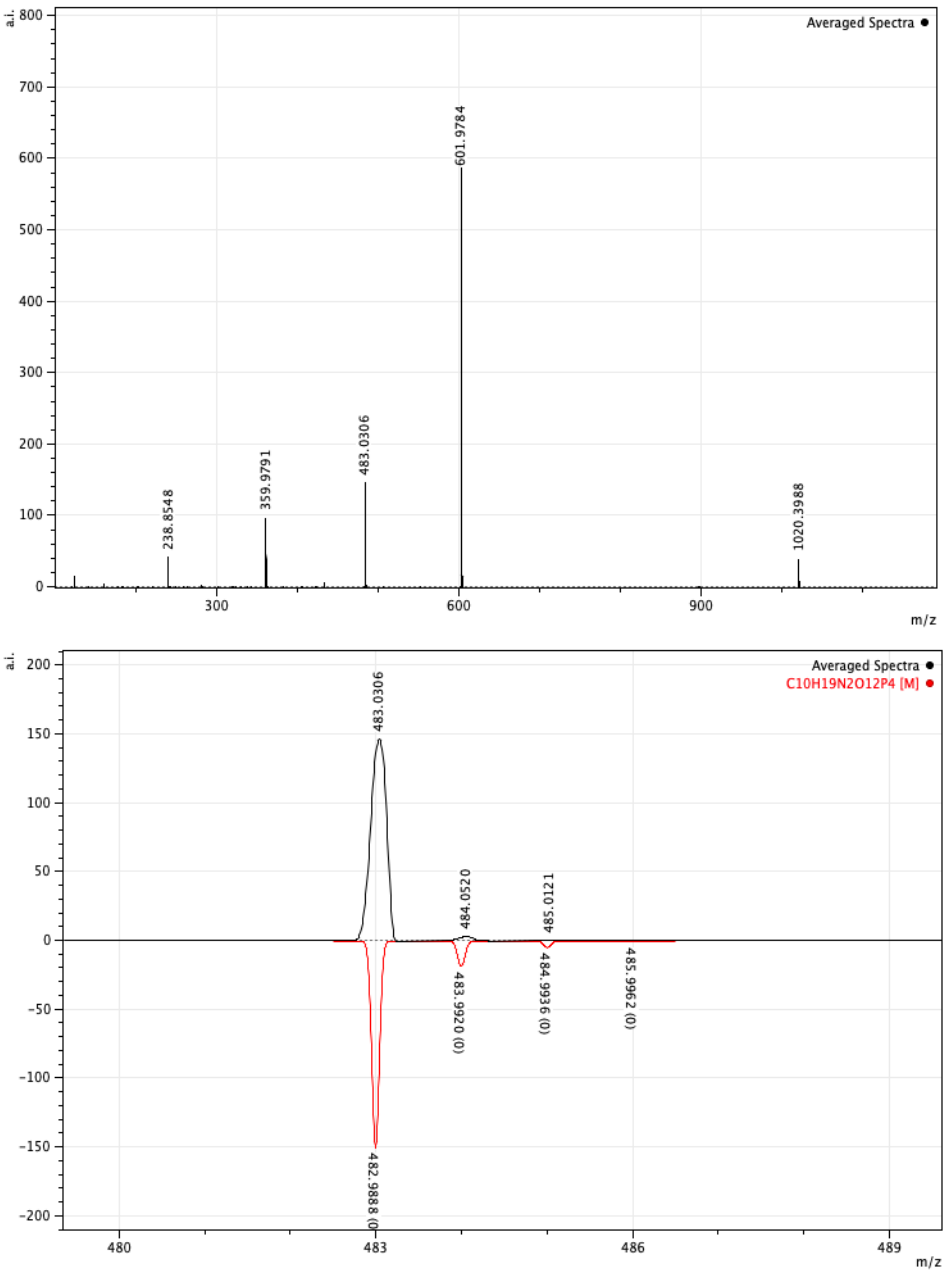

Figure S115: ESI-MS(−) of $[PPN]_2[EthanolamineH]_2$[**21**] (CH_3CN) with zoomed in portion showing the molecular ion ([ethanolamine$-P_4O_{11}-NHArMe_2]H_3^-$, top) and calculated isotope pattern ($C_{10}H_{19}N_2O_{12}P_4$, bottom).

4.2.3 $[NH_4]_4$[22]

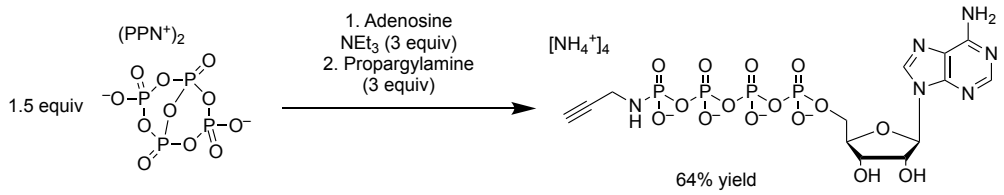

Figure S116: Synthesis of $[NH_4]_4$[**22**].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.048 g, 0.035 mmol) was dissolved in DMF (1 mL). To this solution was added triethylamine (0.01 mL, 0.069 mmol) followed by a solution of adenosine in DMF at a concentration of 0.013 g/mL that had been stored over 4Å sieves for 24 hours (0.48 mL, 0.023 mmol). The resulting mixture was stirred at room temperature for 48 hours. Propargylamine (0.0044 mL, 0.069 mmol) was then added, and the resulting solution was stirred for 24 hours. The mixture was then removed from the glovebox, and volatiles were removed under reduced pressure. The resulting solid was suspended in water and filtered through an Acrodisc 0.2 μm wwPTFE syringe filter. This solution was then purified by AX-HPLC as described in the General Considerations. The fractions containing the desired product were pooled and repeatedly lyophilized until no excess buffer remained, yielding the product as a white powder (0.016 g, 0.022 mmol, 64% yield).

^{1}H NMR (D_2O, 400 MHz): δ 8.48 (s, 1H), 8.21 (s, 1H), 6.12 (d, J = 5.7 Hz, 1H), 4.58 to 4.49 (m, 1H), 4.47 to 4.37 (m, 1H), 4.27 (dd, J = 5.3, 2.8 Hz, 1H), 3.67 (d, J = 11.5 Hz, 2H).

^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 159.08, 155.52, 152.81, 149.00, 139.79, 86.86, 83.69 (d, J = 8.7 Hz), 74.26, 70.29, 65.43, 30.62.

^{31}P{^{1}H} NMR (D_2O, 162.0 MHz): δ −2.26 (d, J = 18.9 Hz), −11.61 (d, J = 15.8 Hz), −21.40, −21.98.

ESI-MS(−) of $[NH_4]_4$[22] in CH_3CN, found 623.02 m/z (calc'd 622.99 m/z) for ($C_{13}H_{19}N_6O_{15}P_4$)

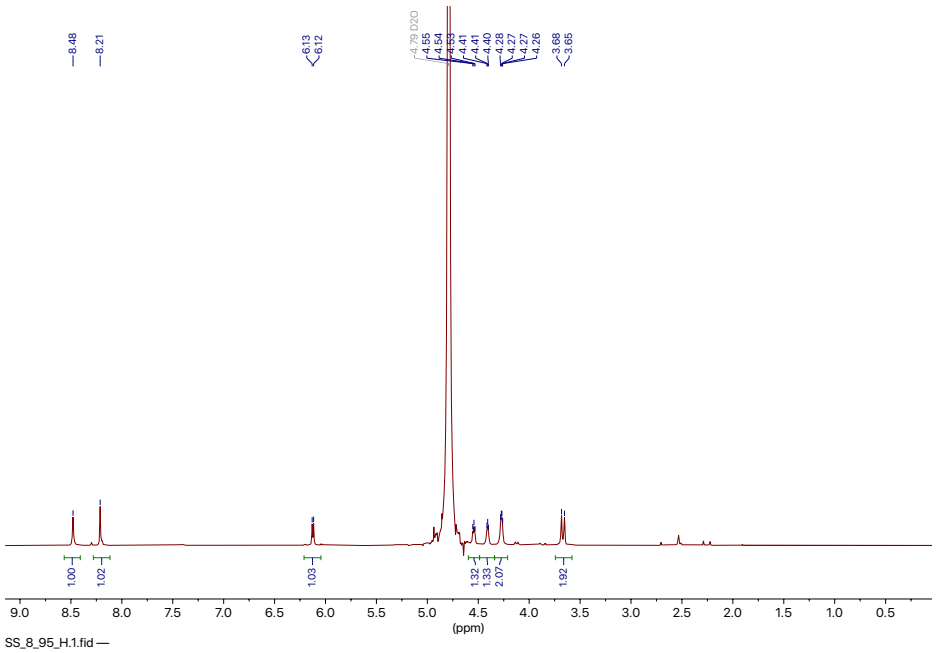

Figure S117: ^{1}H NMR spectrum of $[NH_4]_4$[**22**] (D_2O, 400 MHz).

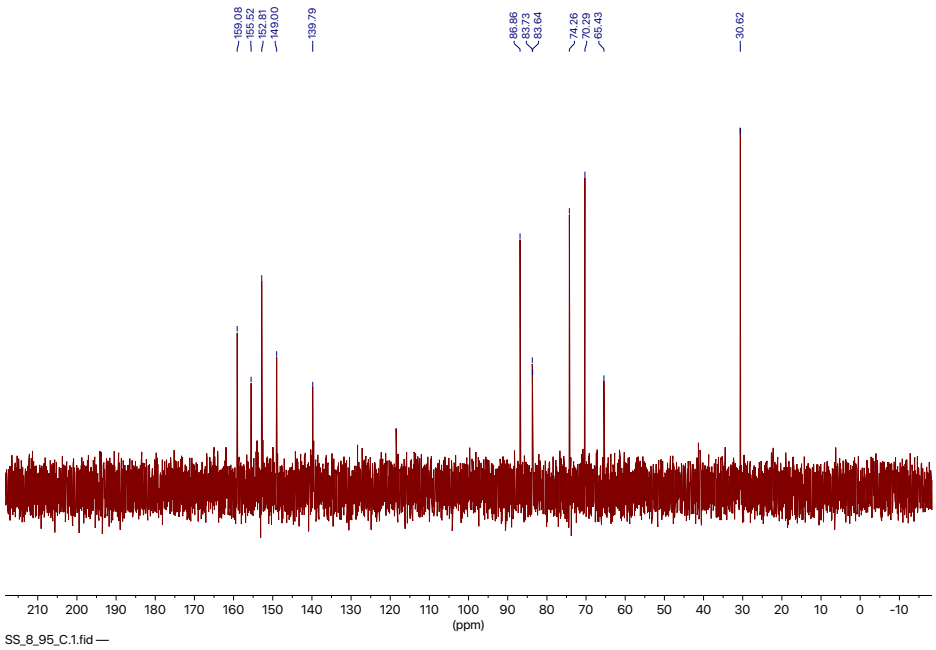

Figure S118: ^{13}C{^{1}H} NMR spectrum of $[NH_4]_4$[**22**] (D_2O, 100.6 MHz).

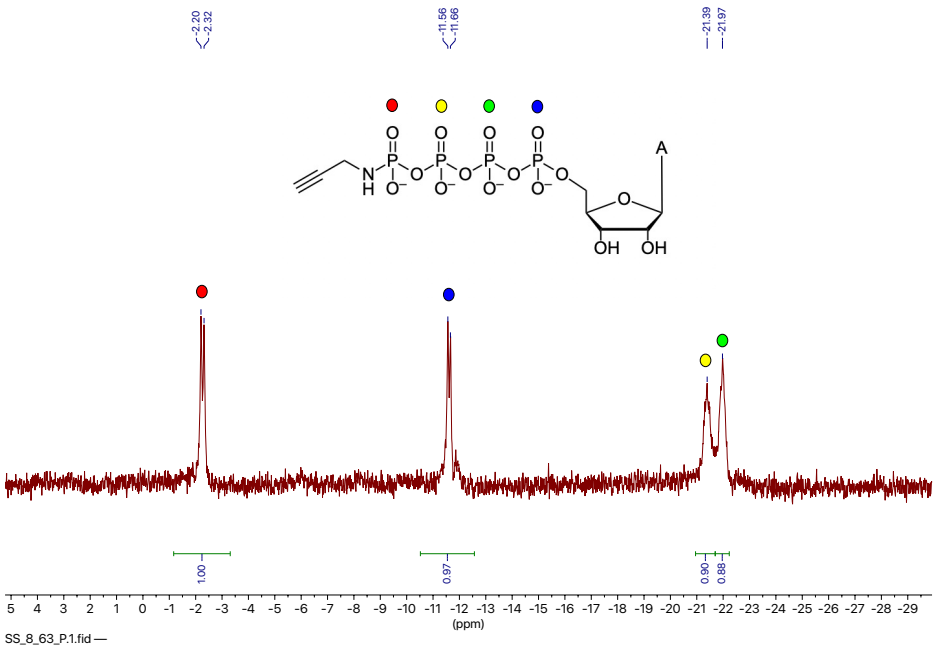

Figure S119: $^{31}P\{^{1}H\}$ NMR spectrum of $[NH_4]_4$[**22**] (D_2O, 162.0 MHz).

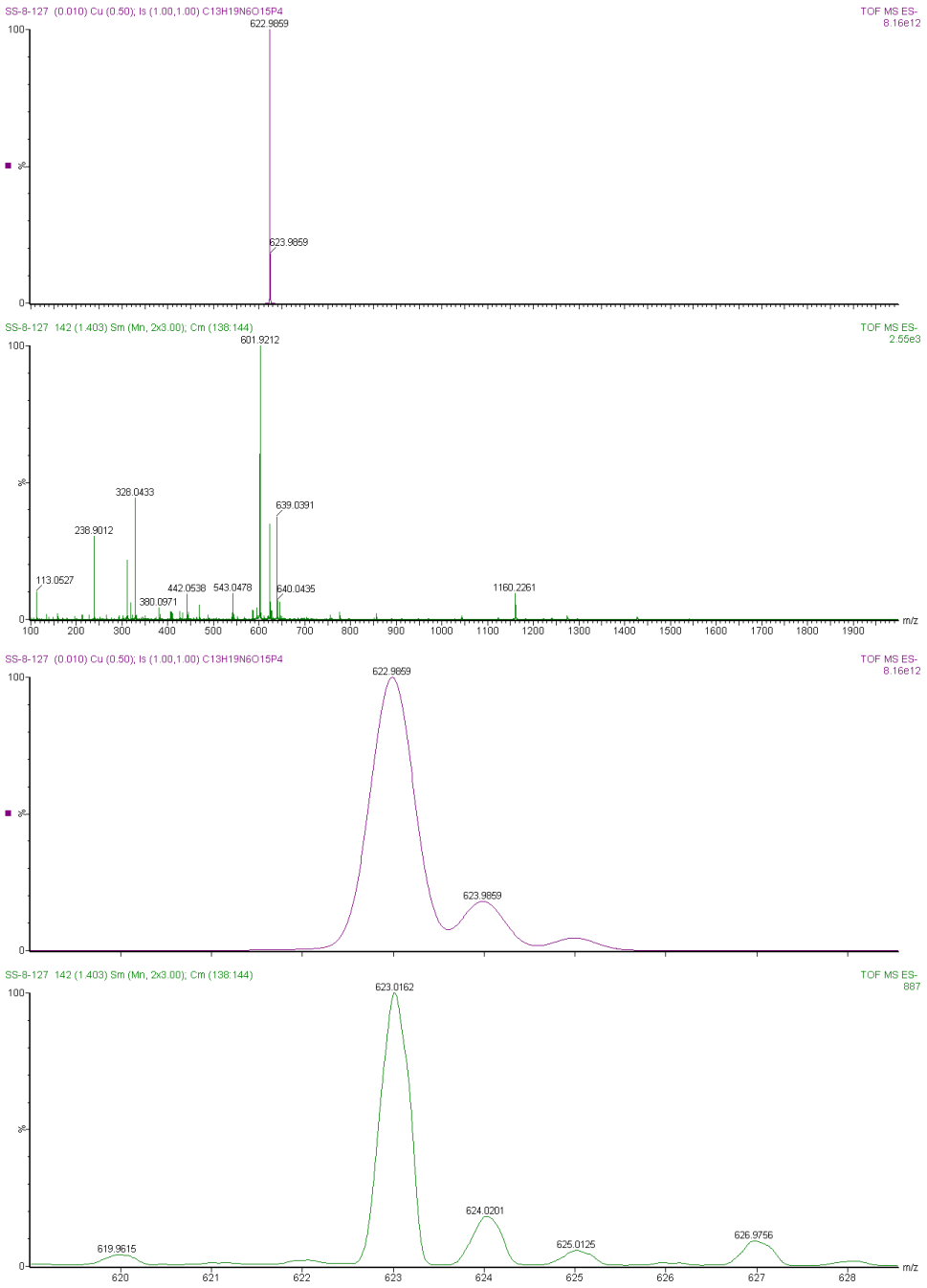

Figure S120: ESI-MS(−) of $[NH_4]_4$[**22**] (CH_3CN/H_2O) with zoomed in portion of the molecular ion ($[22]H_3^-$), and calculated isotope pattern ($C_{13}H_{19}N_6O_{15}P_4$).

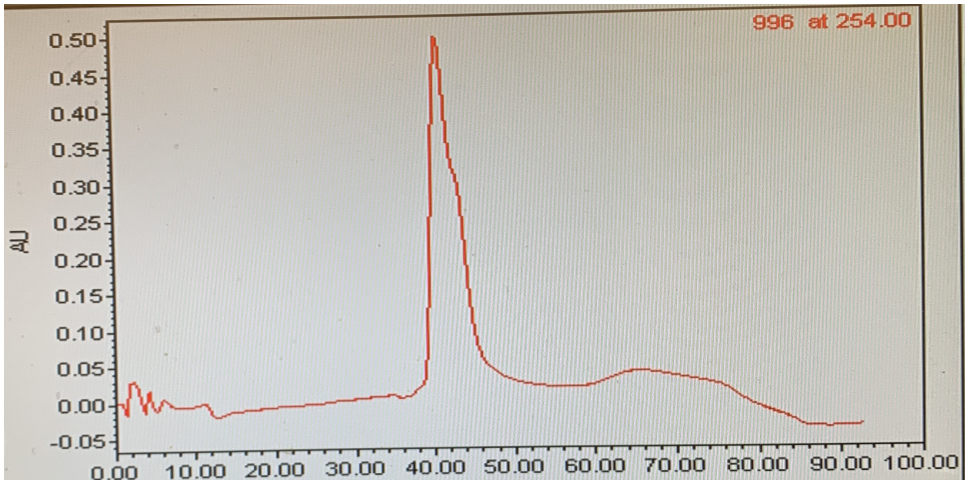

Figure S121: Analytical AX-HPLC trace of $[NH_4]_4$[**22**].

4.3 Ring Opening with a Phosphate

4.3.1 $[Et_3NH]_5$[23]

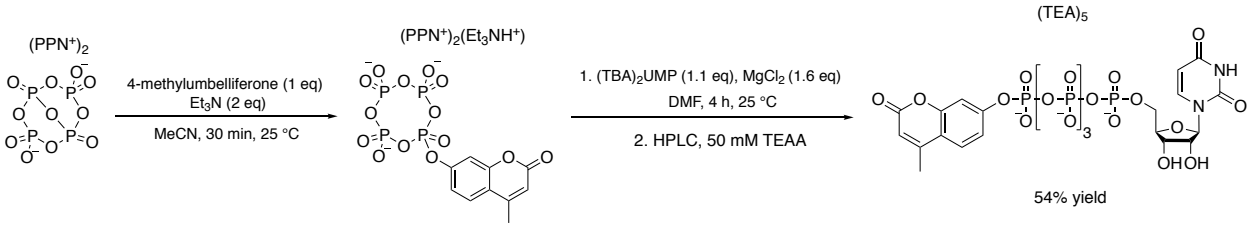

Figure S122: Synthesis of $[Et_3NH]_5[\epsilon-(4\text{-methyl-2-oxo-2}H\text{-chromen-7-yl})\text{uridinepentaphosphate}]$.

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.070 g, 0.051 mmol) was dissolved in acetonitrile (0.50 mL), to which triethylamine (14 μL, 0.10 mmol, 2 equiv) was added. 4-methylumbelliferone (0.0090 g, 0.051 mmol) was then added, and this mixture was stirred at room temperature for 30 minutes. In a separate vial, anhydrous $MgCl_2$ (0.0077 g, 0.081 mmol, 1.6 equiv) was dissolved in anhydrous DMF (1 mL), and the stock solution of $(TBA)_2$UMP in anhydrous DMF (0.10 g/mL) was added (0.44 mL, 0.056 mmol, 1.1 equiv). To this mixture, the solution of fluorophore tetrametaphosphate was added dropwise, and the reaction was stirred at room temperature for 4 hours. After this time, the reaction mixture was taken into the fumehood, to which an acetonitrile (2 mL) solution of NaOTf (0.044 g, 0.10 mmol, 5 equiv) was added and stirred for 5 minutes. Volatiles were evaporated under vacuum at 50 °C, and the solids were suspended in deionized water (5 mL). The mixture was filtered through an Acrodisc 0.2 μm wwPTFE syringe filter, and purified by HPLC according to the procedures outlined in the General Considerations section above. The fractions containing the desired product were pooled and repeatedly lyophilized until the ^{1}H NMR spectrum indicated that there

was none of the triethylammonium acetate buffer remaining. The product was obtained as a white powder (0.036 g, 0.027 mmol, 54% yield).

^{1}H NMR (D_2O, 400 MHz): δ 7.86 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.36 (dd, J = 8.8, 1.9 Hz, 1H), 7.28 (d, J = 2.0 Hz, 1H), 6.31 (s, 1H), 5.92 (d, J = 5.4 Hz, 1H), 5.89 (d, J = 8.1 Hz, 1H), 4.39 to 4.38 (m, 1H), 4.34 (t, J = 5.3 Hz, 1H), 4.23 to 4.22 (m, 3H), 3.19 (q, J = 7.3 Hz, 30H), 2.48 (s, 3H), 1.27 (t, J = 7.3 Hz, 45H).

^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 166.0, 164.5, 156.3, 154.8 (d, J = 6.3 Hz), 153.5, 151.7, 141.6, 126.6, 117.8 (d, J = 4.6 Hz), 116.5, 111.9, 108.5 (d, J = 5.4 Hz), 102.7, 87.9, 83.4 (d, J = 9.5 Hz), 73.6, 69.8, 65.2 (d, J = 5.6 Hz), 46.6, 18.1, 8.2.

^{31}P{^{1}H} NMR (D_2O, 162.0 MHz): δ −11.6 (d, J = 17.2 Hz), −17.0 (d, J = 16.8 Hz), −22.3 to −23.4 (m).

ESI-MS(−) of $[Et_3NH]_5[C_{19}H_{18}N_2O_{23}P_5]$ in CH_3CN/H_2O, found 801.49 m/z (calc'd 800.93 m/z) for $C_{19}H_{22}N_2O_{23}P_5^-$

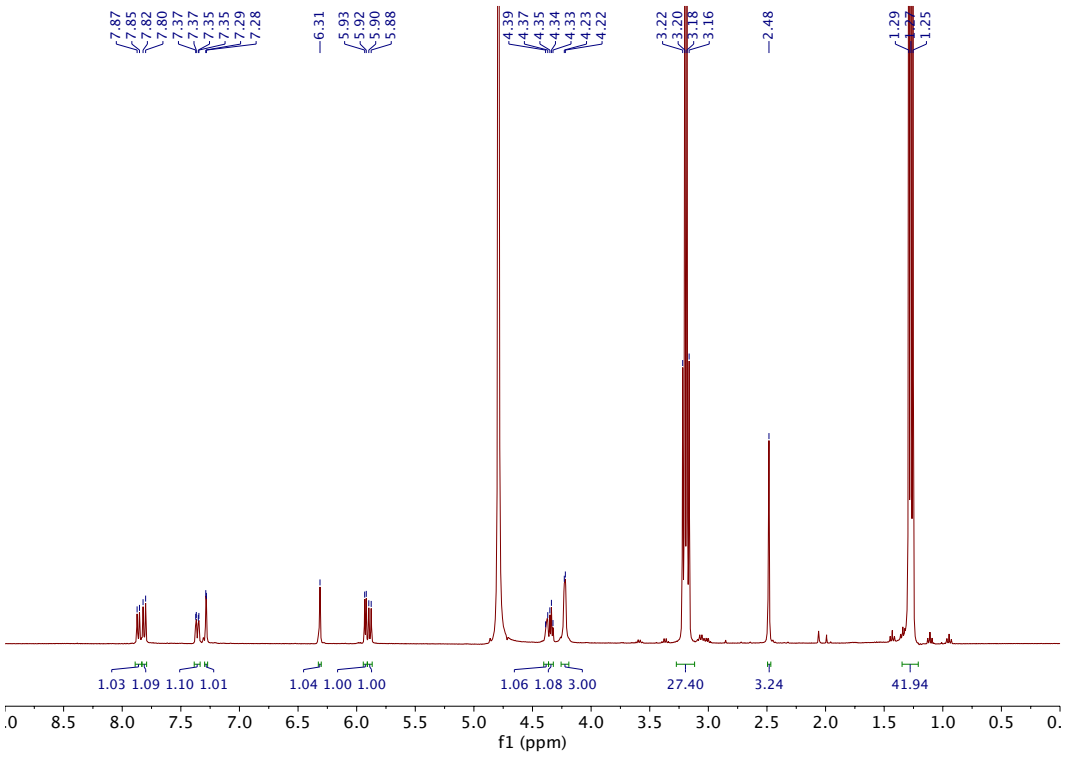

Figure S123: ^{1}H NMR spectrum of $[Et_3NH]_5$[**23**] (D_2O, 400 MHz).

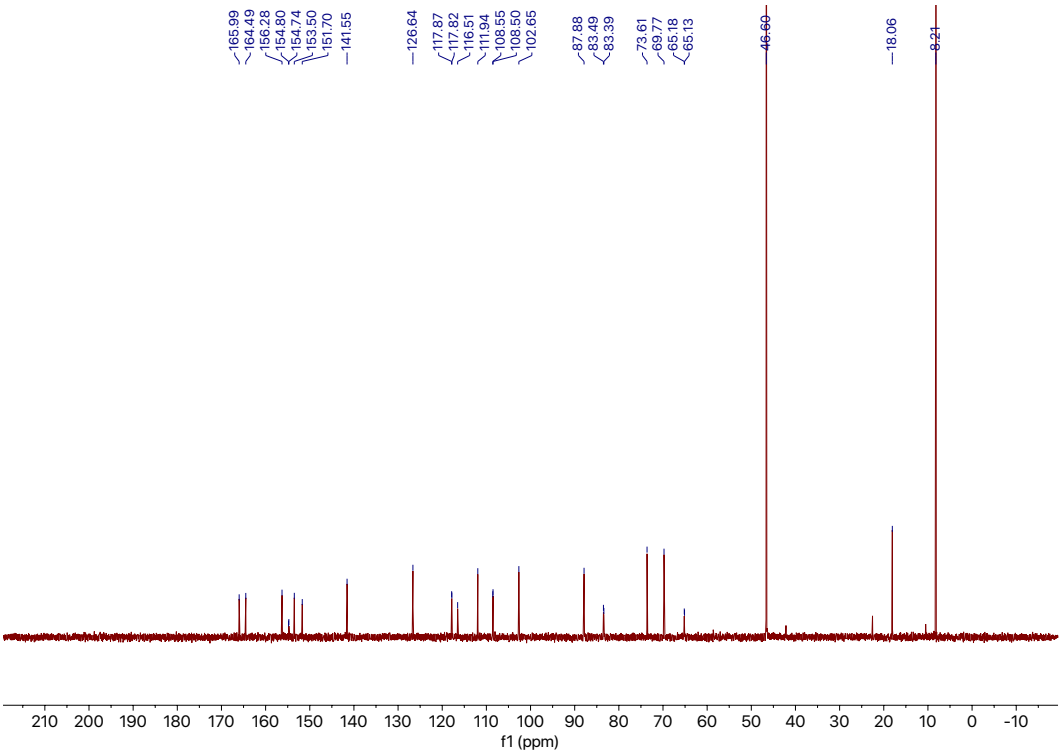

Figure S124: $^{13}C\{^{1}H\}$ NMR spectrum of $[Et_3NH]_5$[**23**] (D_2O, 101 MHz).

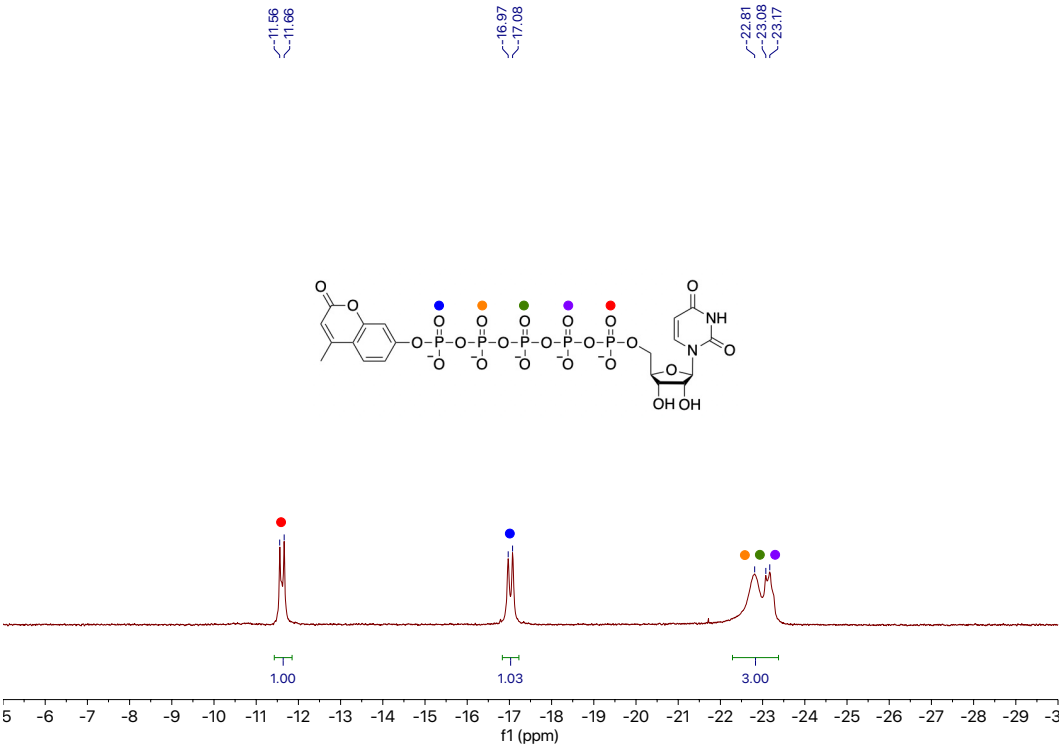

Figure S125: $^{31}P\{^{1}H\}$ NMR spectrum of $[Et_3NH]_5$[**23**] (D_2O, 162 MHz).

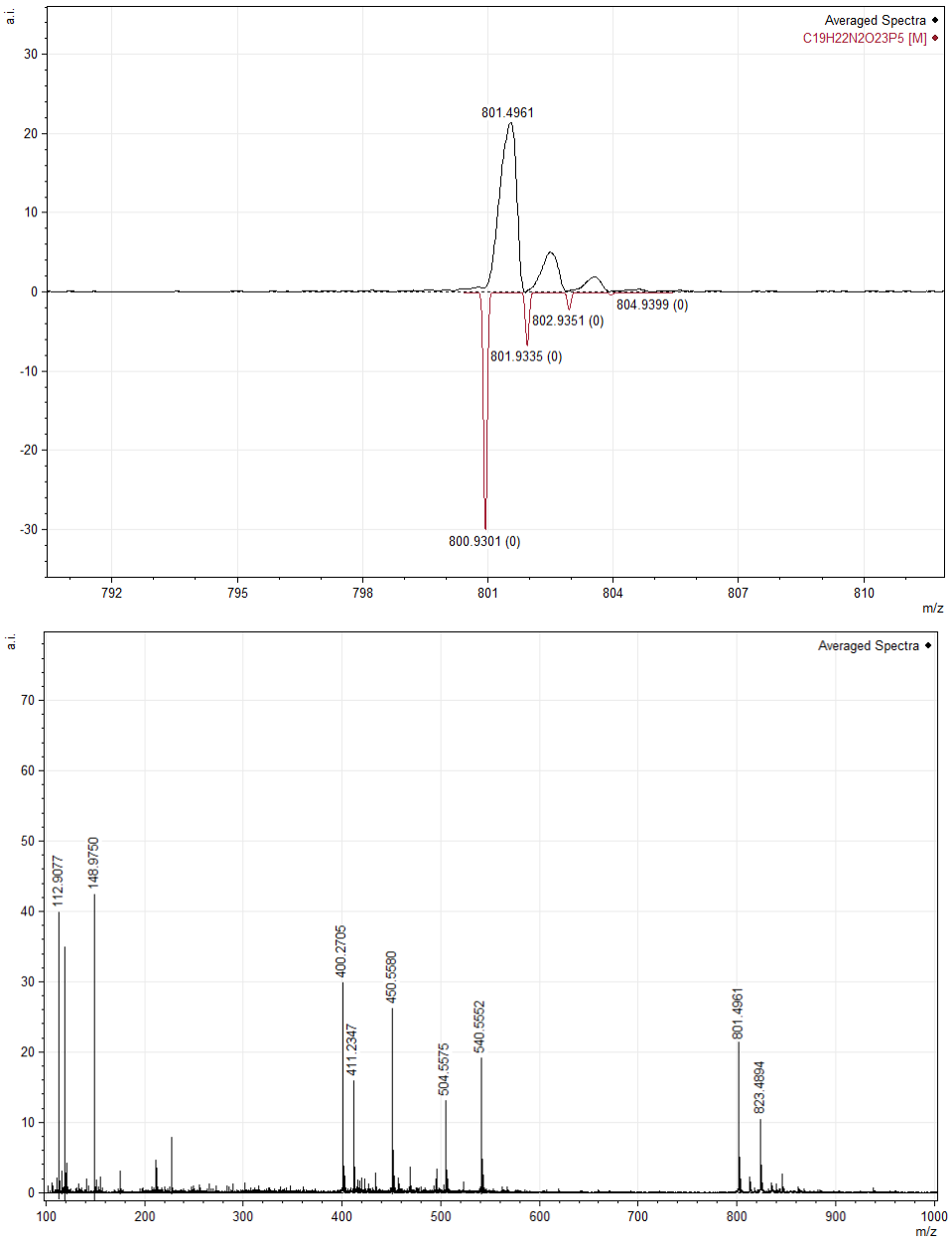

Figure S126: ESI-MS(−) of $[Et_3NH]_5[C_{19}H_{18}N_2O_{23}P_5]$ (CH_3CN/H_2O) with zoomed in portion of the molecular ion ($[C_{19}H_{18}N_2O_{23}P_5]H_4^-$, top), and calculated isotope pattern ($C_{19}H_{22}N_2O_{23}P_5$, bottom). The mass at 823.49 corresponds to $[C_{19}H_{18}N_2O_{23}P_5]NaH_3^-$.

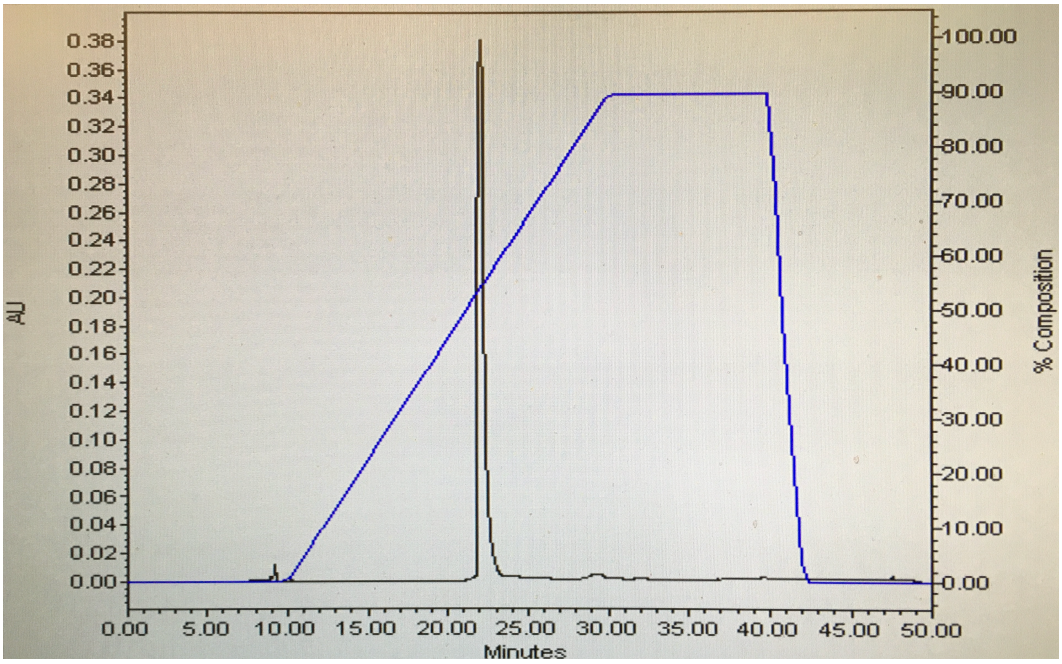

Figure S127: HPLC trace of purified $[Et_3NH]_5[\epsilon-$(4-methyl-2-oxo-2H-chromen-7-yl)uridinepentaphosphate].

4.3.2 $[Et_3NH]_5$[24]

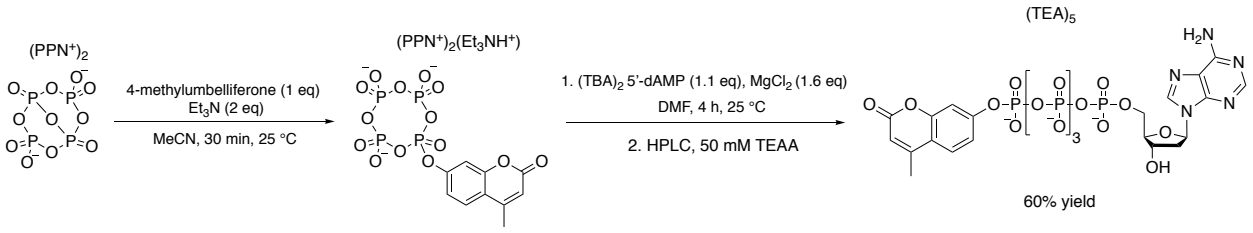

Figure S128: Synthesis of $[Et_3NH]_5[\epsilon-$(4-methyl-2-oxo-2H-chromen-7-yl)deoxyadenosinepentaphosphate].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.07 g, 0.051 mmol) was dissolved in acetonitrile (0.5 mL), to which triethylamine (14 μL, 0.10 mmol, 2 equiv) was added. 4-methylumbelliferone (0.0090 g, 0.051 mmol) was then added, and this mixture was stirred at room temperature for 30 minutes. In a separate vial, anhydrous $MgCl_2$ (0.0077 g, 0.081 mmol, 1.6 equiv) was dissolved in anhydrous DMF (1 mL), and the stock solution of $(TBA)_2$dAMP in anhydrous DMF (0.10 g/mL) was added (0.46 mL, 0.056 mmol, 1.1 equiv). To this mixture, the solution of fluorophore tetrametaphosphate was added dropwise, and the reaction was stirred at room temperature for 4 hours. After this time, the reaction mixture was taken into the fumehood, to which an acetonitrile (2 mL) solution of NaOTf (0.044 g, 0.10 mmol, 5 equiv) was added and stirred for 5 minutes. Volatiles were evaporated under vacuum at 50 °C, and the solids were suspended in deionized water (5 mL). The mixture was filtered through an Acrodisc

0.2 μm wwPTFE syringe filter, and purified by HPLC according to the procedures outlined in the General Considerations section above. The fractions containing the desired product were pooled and repeatedly lyophilized until the ^{1}H NMR spectrum indicated that there was none of the triethylammonium acetate buffer remaining. The product was obtained as a white powder. (0.0402 g, 0.031 mmol, 60% yield).

^{1}H NMR (D_2O, 400 MHz): δ 8.43 (s, 1H), 8.07 (s, 1H), 7.55 (d, $J = 8.8$ Hz, 1H), 7.21 (dd, $J = 8.7, 1.8$ Hz, 1H), 7.08 (s, 1H), 6.32 (t, $J = 6.8$ Hz, 1H), 6.08 (s, 1H), 4.26 (s, 1H), 4.23 to 4.11 (m, 4H), 3.18 (q, $J = 7.3$ Hz, 30H), 2.84 to 2.75 (m, 1H), 2.61 to 2.55 (m, 1H), 2.30 (s, 3H), 1.26 (t, $J = 7.3$ Hz, 45H).

^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 163.9, 155.7, 154.4 (d, $J = 6.4$ Hz), 154.0, 153.0, 151.2, 147.9, 140.5, 126.2, 117.5 (d, $J = 4.1$ Hz), 115.8, 111.6, 108.6, 108.1, 108.0, 85.8 (d, $J = 9.5$ Hz), 83.7, 71.4, 65.6 (d, $J = 6.1$ Hz), 46.6, 39.3, 18.0, 8.2.

^{31}P{^{1}H} NMR (D_2O, 162.0 MHz): δ −11.7 (d, $J = 16.5$ Hz), −17.2 (d, $J = 16.6$ Hz), −22.11 to 23.01 (m).

ESI-MS(−) of $[Et_3NH]_5[C_{20}H_{19}N_5O_{20}P_5]$ in CH_3CN/H_2O, found 808.56 m/z (calc'd 807.96 m/z) for $C_{20}H_{23}N_5O_{20}P_5^-$

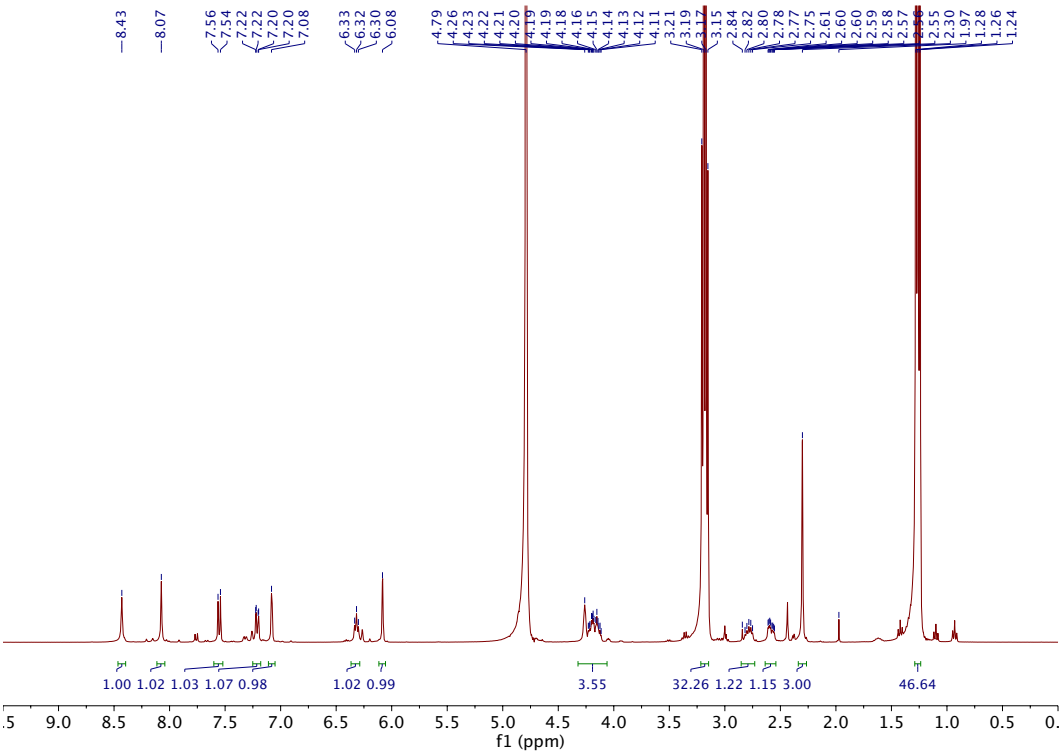

Figure S129: ^{1}H NMR spectrum of $[Et_3NH]_5$[**24**] (D_2O, 400 MHz).

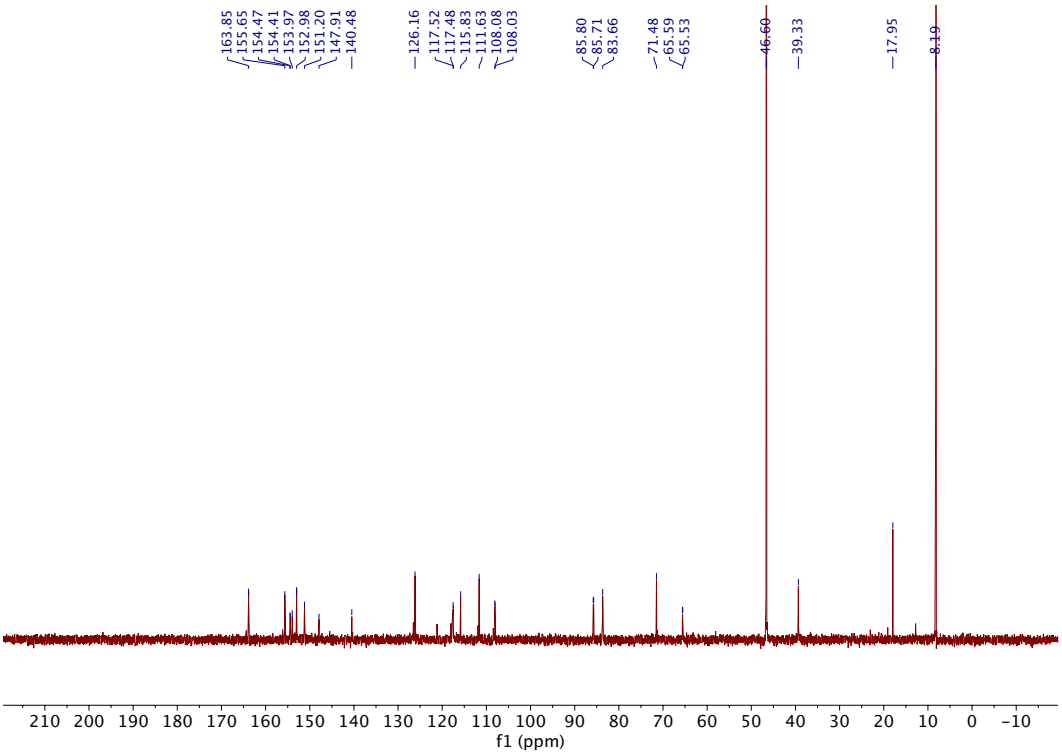

Figure S130: $^{13}C\{^{1}H\}$ NMR spectrum of $[Et_3NH]_5$[**24**] (D_2O, 101 MHz).

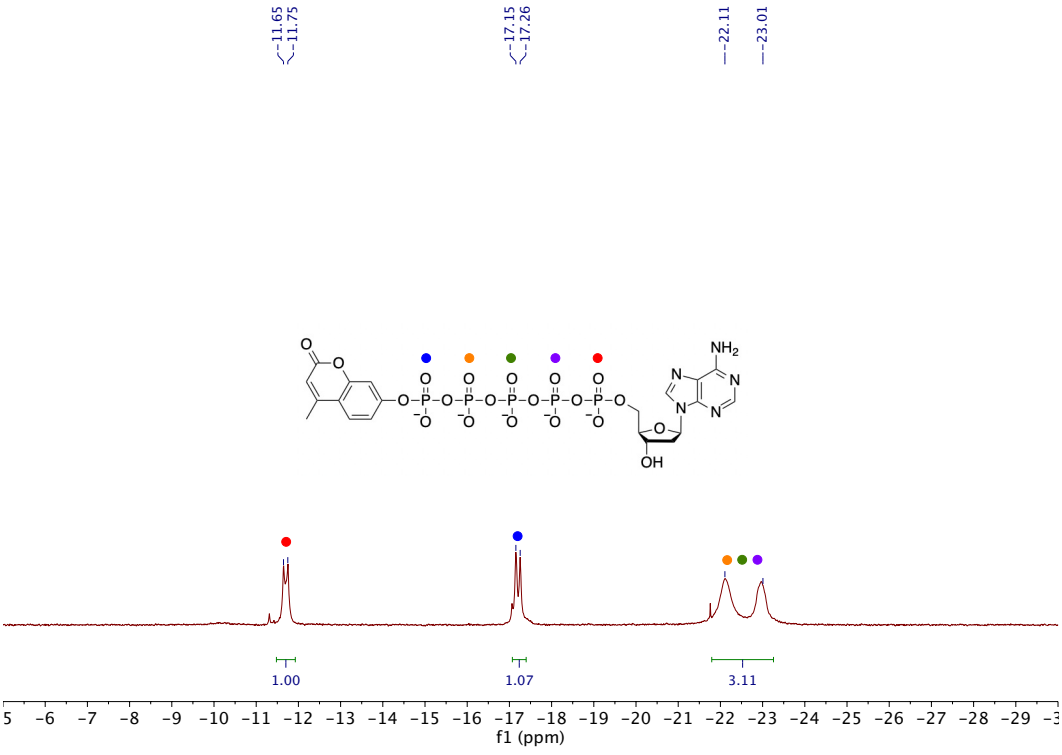

Figure S131: $^{31}P\{^{1}H\}$ NMR spectrum of $[Et_3NH]_5$[**24**] (D_2O, 162 MHz).

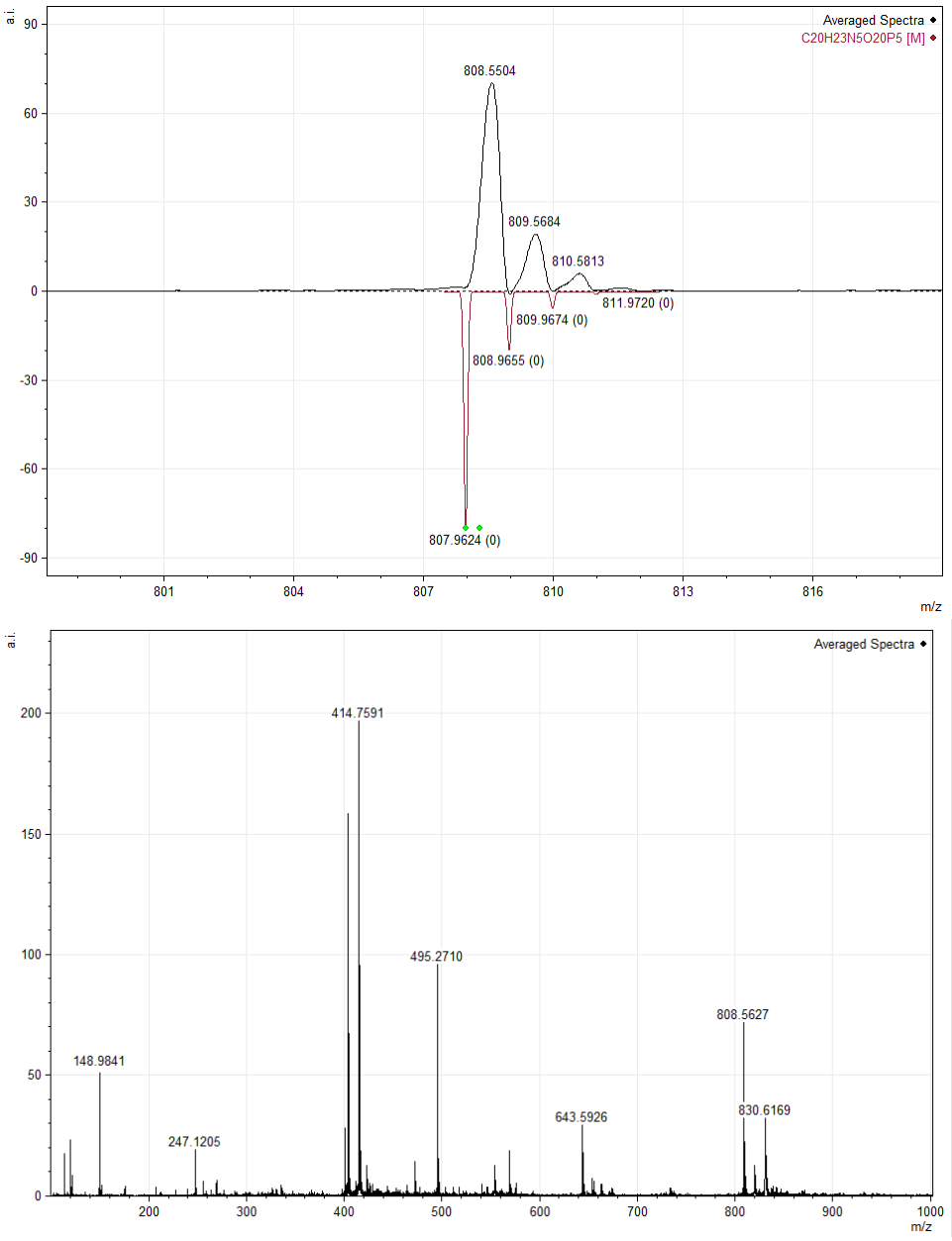

Figure S132: ESI-MS(−) of $[Et_3NH]_5[C_{20}H_{19}N_5O_{20}P_5]$ (CH_3CN/H_2O) with zoomed in portion of the molecular ion ($[C_{20}H_{19}N_5O_{20}P_5]H_4^-$, top), and calculated isotope pattern ($C_{20}H_{23}N_5O_{20}P_5$, bottom). The mass at 830.62 corresponds to $[C_{20}H_{19}N_5O_{20}P_5]NaH_3^-$.

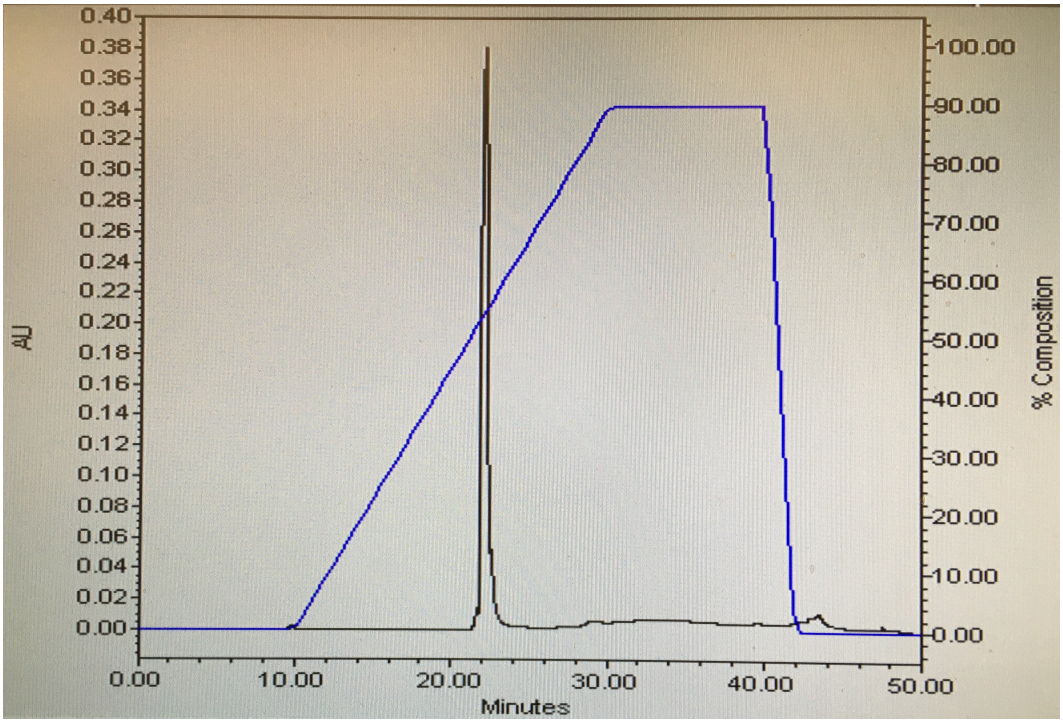

Figure S133: HPLC trace of purified $[Et_3NH]_5[\epsilon-(4\text{-methyl-2-oxo-2}H\text{-chromen-7-yl})\text{deoxyadenosinepentaphosphate}]$.

4.3.3 $[NH_4]_5$[25]

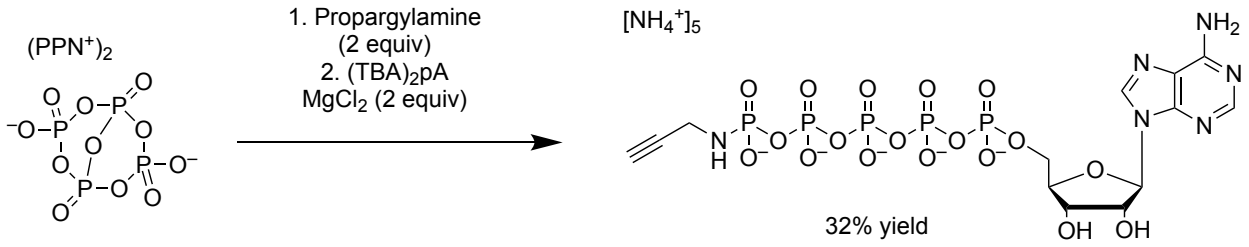

Figure S134: Synthesis of $[NH_4]_5$[**25**].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.046 g, 0.034 mmol) was dissolved in DMF (1 mL). Propargylamine (0.0037 g, 0.068 mmol) was then added, and this mixture was stirred at room temperature for 15 minutes. To this mixture was then added anhydrous $MgCl_2$ (0.0065 g, 0.068 mmol) and the 0.10 g/mL stock solution of $(TBA)_2$pA in anhydrous DMF (0.28 mL, 0.034 mmol). The reaction was stirred for 24 hours and then taken into the fumehood. Volatiles were evaporated under vacuum at 50 °C, and the solids were suspended in deionized water (3 mL). The mixture was filtered through an Acrodisc 0.2 μm wwPTFE syringe filter, and purified by AX-HPLC according to the procedures outlined in the General Considerations section above. The fractions containing the desired product were pooled and

repeatedly lyophilized until there was no remaining buffer, yielding the product as a white powder. (0.0086 g, 0.011 mmol, 32% yield).

^{1}H NMR (D_2O, 400 MHz): δ 8.28 (s, 1H), 8.05 (s, 1H), 5.93 (d, J = 5.7 Hz, 1H), 4.33 (t, J = 4.5 Hz, 1H), 4.20 (t, J = 3.3 Hz, 1H), 4.05 (t, J = 4.3 Hz, 2H), 3.48 (dd, J = 11.7, 2.4 Hz, 2H).

^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 155.63, 152.88, 149.11, 139.88, 120.86, 118.58, 86.80, 83.82 (d, J = 9.0 Hz), 74.26, 70.37, 65.40, 30.68, 12.78.

^{31}P{^{1}H} NMR (D_2O, 162.0 MHz): δ −2.41 (d, J = 19.1 Hz), −11.73 (d, J = 17.5 Hz), −21.88 to −22.97 (m).

We were unable to identify the molecular ion in the ESI-MS(−) of $[NH_4]_5$[**25**].

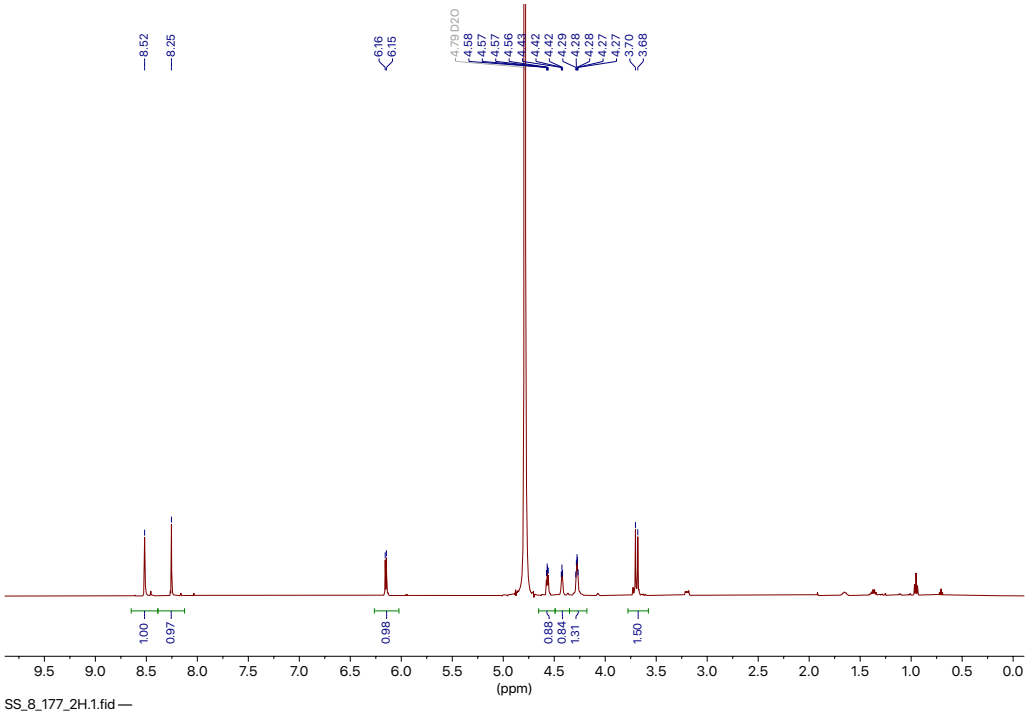

Figure S135: ^{1}H NMR spectrum of $[NH_4]_5$[**25**] (D_2O, 400 MHz).

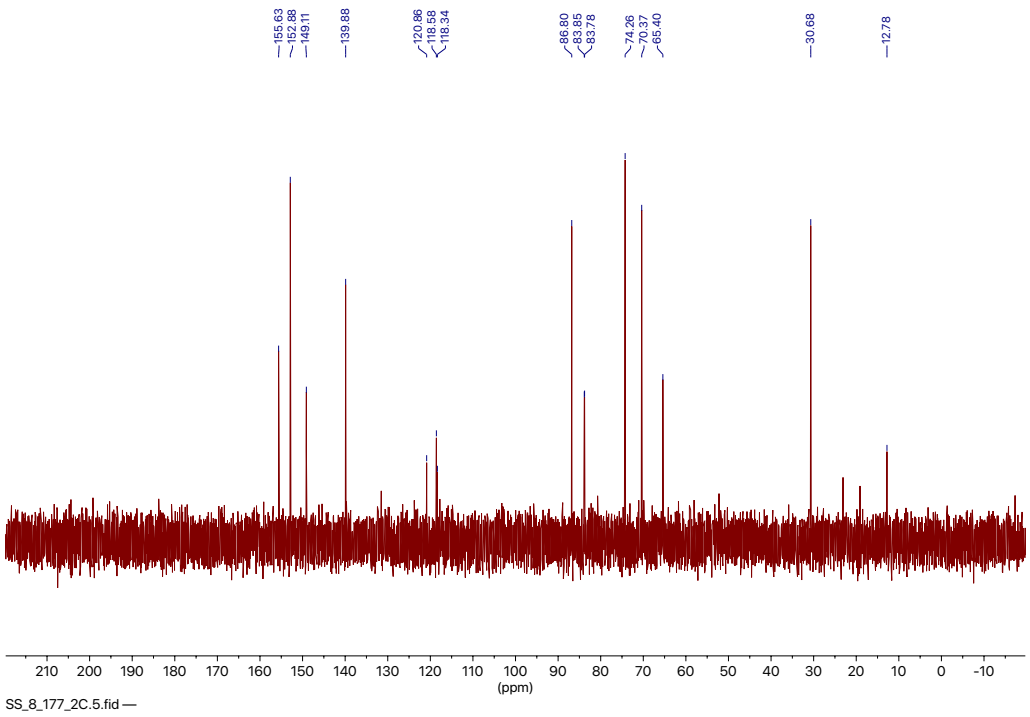

Figure S136: $^{13}C\{^{1}H\}$ NMR spectrum of $[Et_3NH]_5$[**25**] (D_2O, 101 MHz).

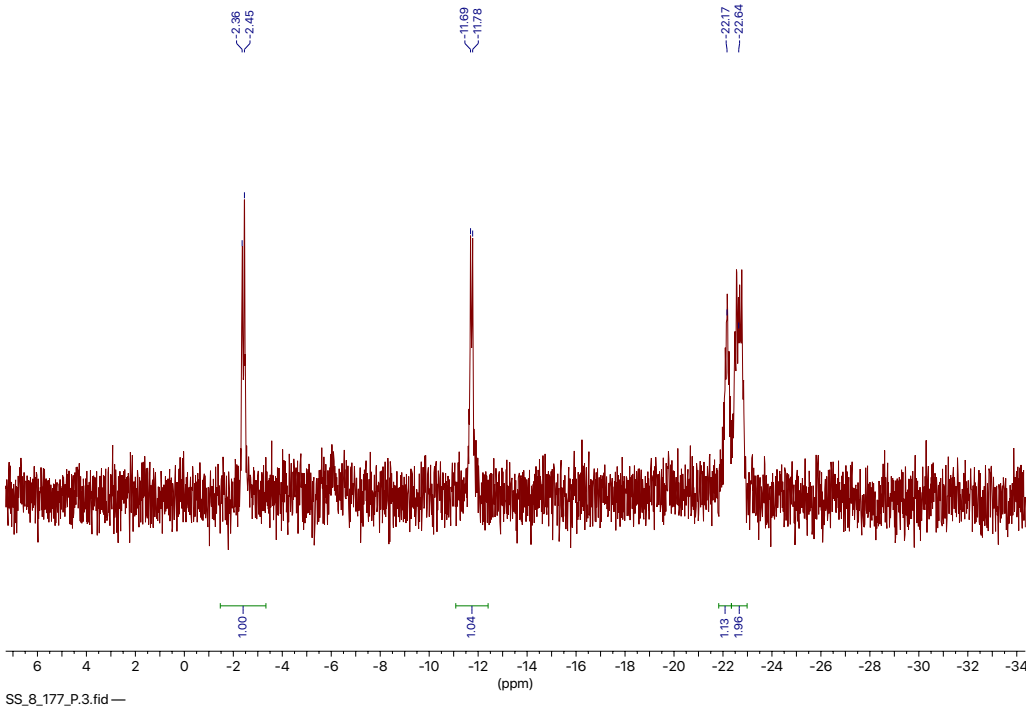

Figure S137: $^{31}P\{^{1}H\}$ NMR spectrum of $[NH_4]_5$[**25**] (D_2O, 162 MHz).

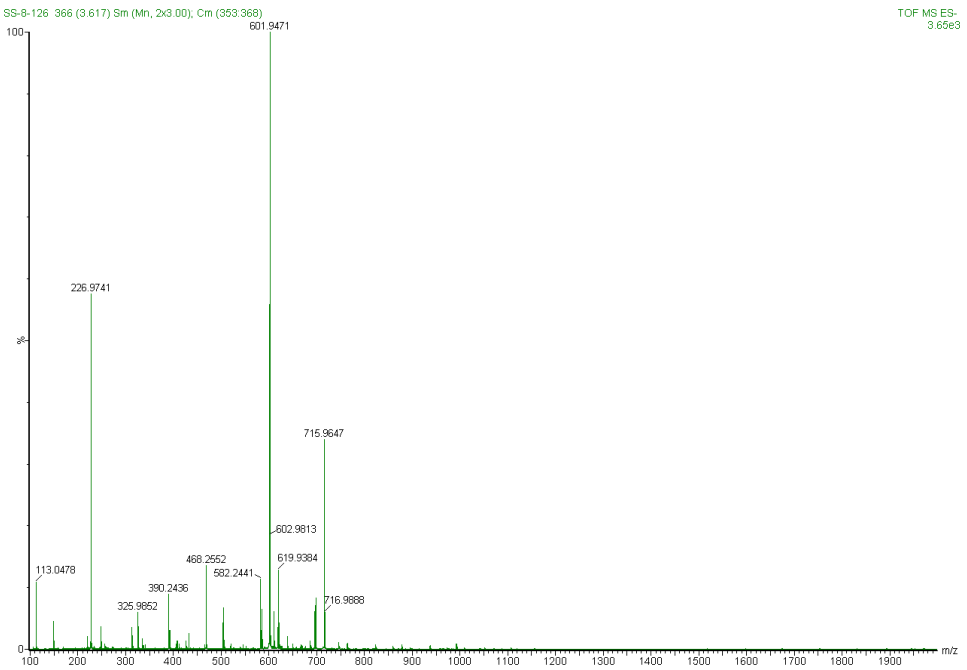

Figure S138: ESI-MS(−) of $[NH_4]_5$[**25**] (CH_3CN).

4.4 Ring Opening with a Phenoxide

4.4.1 $[Et_3NH]_4$[26]

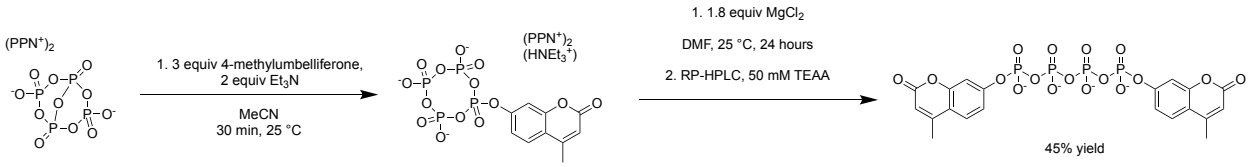

Figure S139: Synthesis of $[Et_3NH]_4[\alpha,\delta-bis-$(4-methyl-2-oxo-2$H$-chromen-7-yl)-tetraphosphate].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.097 g, 0.071 mmol) was dissolved in acetonitrile (1 mL), to which triethylamine (49 μL, 0.35 mmol) was added. 4-methylumbelliferone (0.038 g, 0.21 mmol) was then added, and this mixture was stirred at room temperature for 30 minutes. In a separate vial, anhydrous $MgCl_2$ (0.012 g, 0.13 mmol, 1.8 equiv) was dissolved in anhydrous DMF (1 mL). The two solutions were mixed together and the resulting mixture stirred for 24 hours. After this time, the reaction mixture was taken into the fumehood, to which an acetonitrile (2 mL) solution of NaOTf (0.024 g, 0.14 mmol) was added and stirred for 5 minutes. Volatiles were evaporated under vacuum at 50 °C, and the solids were suspended in deionized water (2.5 mL). The mixture was filtered through an Acrodisc 0.2 μm wwPTFE syringe filter, and purified by HPLC according to the procedures outlined in the General Considerations section above. The fractions containing the desired product were pooled and

repeatedly lyophilized until the ^{1}H NMR spectrum indicated that there was none of the triethylammonium acetate buffer remaining. The product was obtained as a white powder. (0.034 g, 0.032 mmol, 45% yield).

^{1}H NMR (D_2O, 400 MHz): δ 7.48 (d, J = 8.8 Hz, 2H), 7.14 (dd, J = 8.8, 2.3 Hz, 2H), 6.88 (d, J = 2.3 Hz, 2H), 6.13 (d, J = 1.4 Hz, 2H), 3.20 (q, J = 7.3 Hz, 24H), 2.33 (s, J = 1.2 Hz, 6H), 1.28 (t, J = 7.3 Hz, 36H).

^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 164.05, 156.09, 154.61 (d, J = 6.9 Hz), 152.82, 126.20, 117.50 (d, J = 4.7 Hz), 115.66, 111.47, 107.98 (d, J = 6.1 Hz), 46.61, 23.23, 17.88, 8.19.

^{31}P{^{1}H} NMR (D_2O, 162.0 MHz): δ −15.50 to −18.96 (m), −20.69 to −24.01 (m).

ESI-MS(−) of $[Et_3NH]_4$[α,δ−bis−(4-methyl-2-oxo-2*H*-chromen-7-yl)-tetraphosphate] in CH_3CN/H_2O, found 652.96 *m/z* (calc'd 652.94 *m/z*) for $C_{20}H_{17}O_{17}P_4$

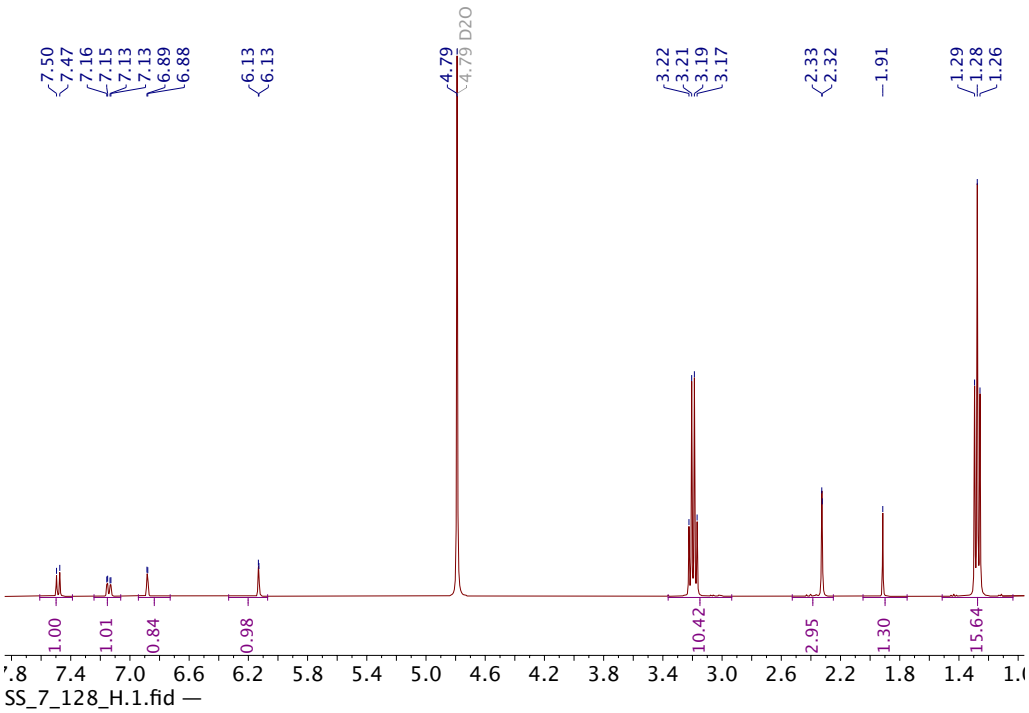

Figure S140: ^{1}H NMR spectrum of $[Et_3NH]_4$[**26**] (D_2O, 400 MHz).

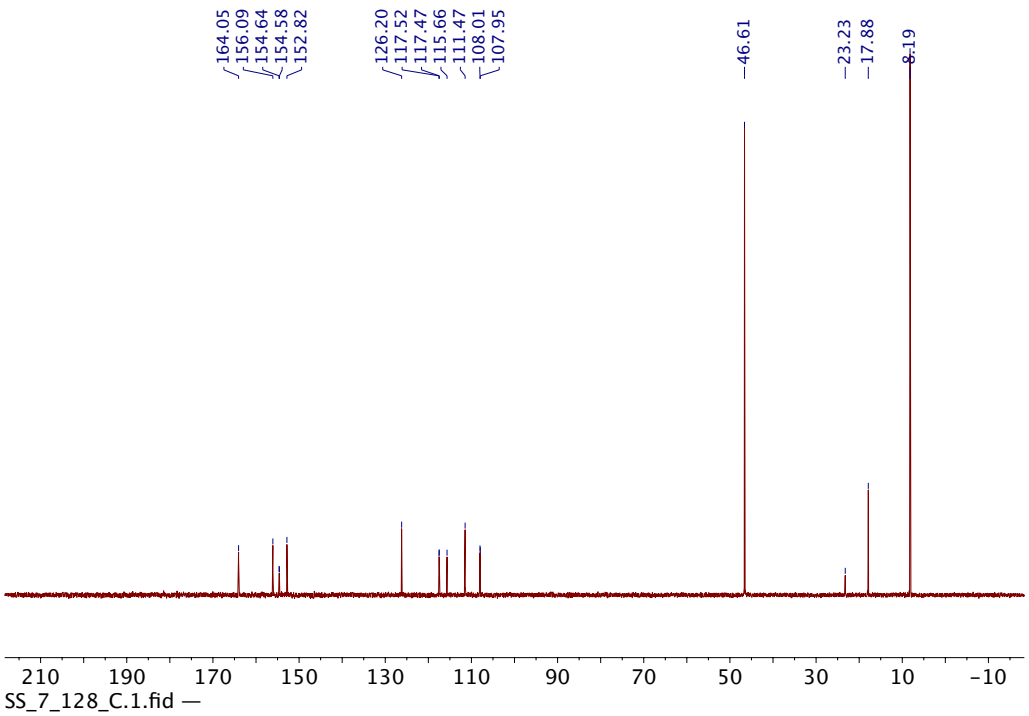

Figure S141: $^{13}C\{^{1}H\}$ NMR spectrum of $[Et_3NH]_4$[**26**] (D_2O, 101 MHz).

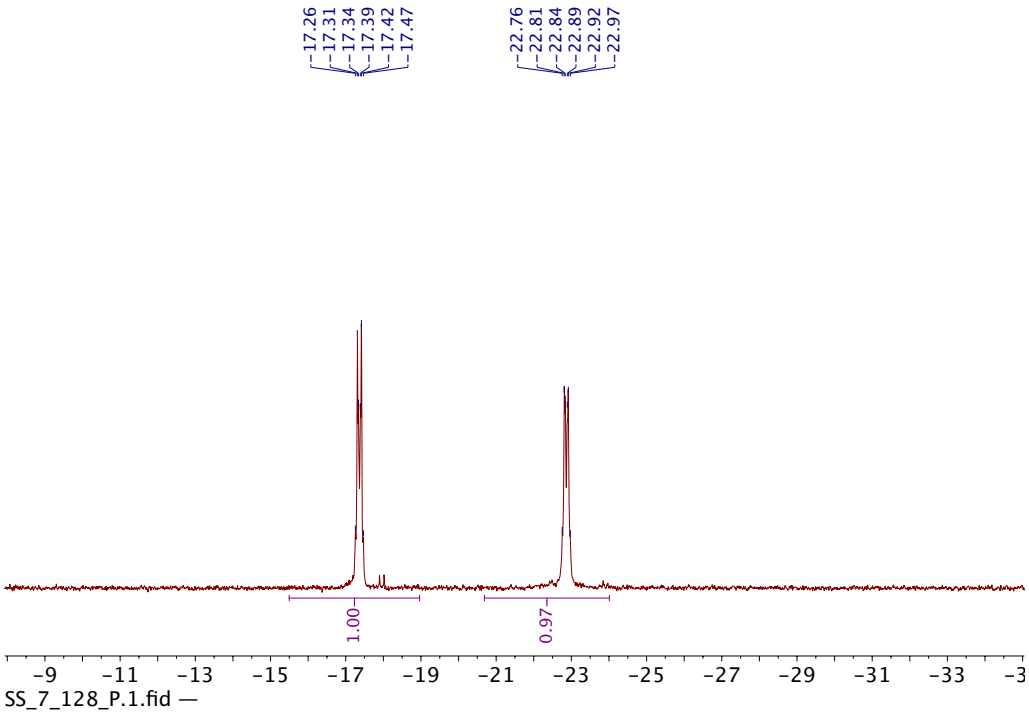

Figure S142: $^{31}P\{^{1}H\}$ NMR spectrum of $[Et_3NH]_4$[**26**] (D_2O, 162 MHz).

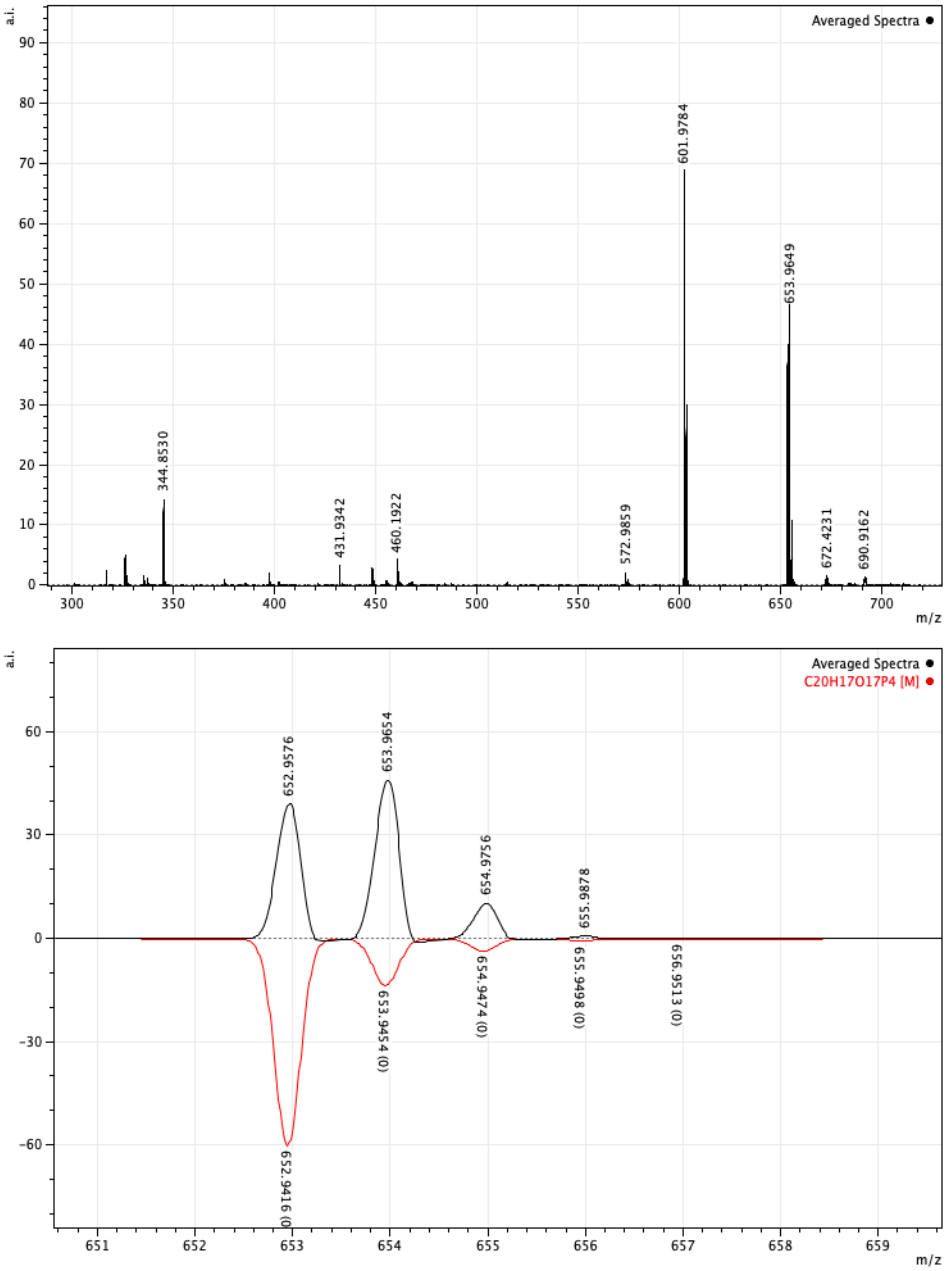

Figure S143: ESI-MS(−) of $[Et_3NH]_4$[**26**] (CH_3CN) with zoomed in portion showing the molecular ion ($[26]H_3^-$, top) and calculated isotope pattern ($C_{20}H_{17}O_{17}P_4$, bottom). The difference between calculated and actual isotope pattern is due the MS sample being prepared in deuterium oxide, thereby enriching the sample in deuterium.

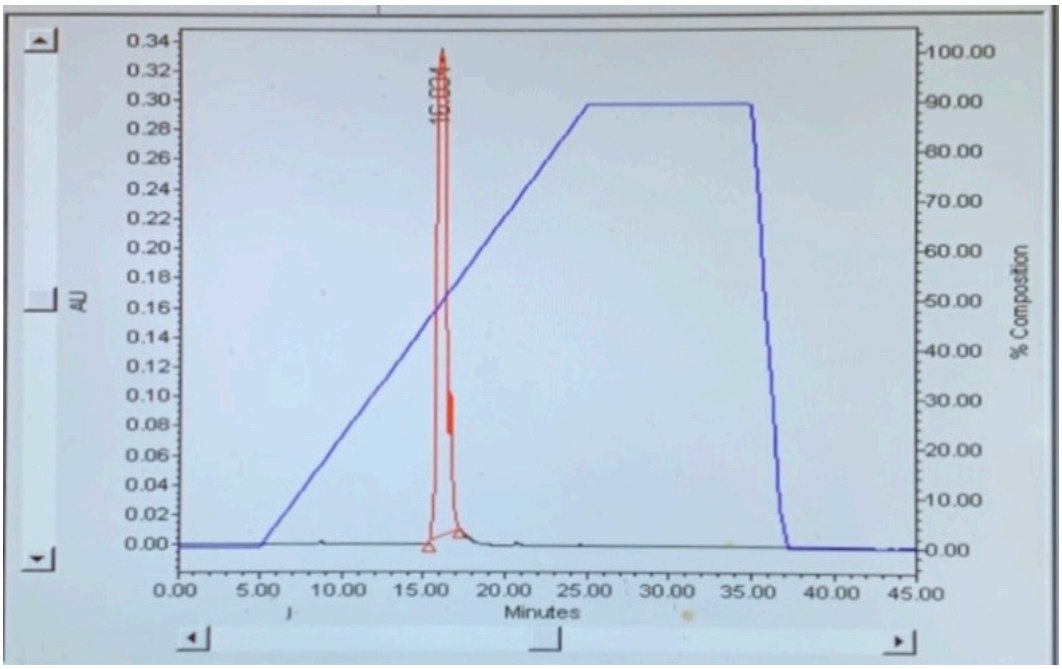

Figure S144: HPLC trace of purified $[Et_3NH]_4$[**26**].

4.5 Ring Opening with Fluoride

4.5.1 $[Na]_4$[27]

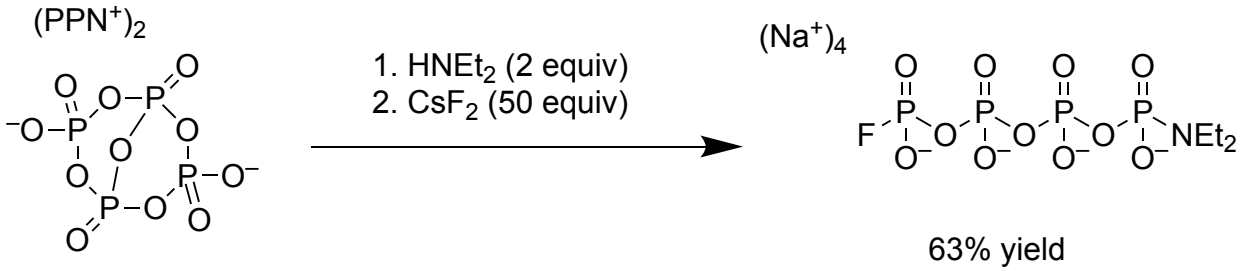

Figure S145: Synthesis of $[Na]_4$[**27**].

In the glovebox, $[PPN]_2[P_4O_{11}]$ (0.13 g, 0.097 mmol) was dissolved in DMF (2 mL), to which diethylamine (0.014 g, 0.19 mmol) was added. This mixture was stirred at room temperature for 15 minutes and then removed from the glovebox. To this solution was added solid cesium fluoride (0.74 g, 4.9 mmol) followed immediately by 2 mL of water. The resulting homogenous solution was stirred for 24 hours at room temperature. To this solution was then added 2 mL of a 0.5 M solution of sodium perchlorate in acetone, resulting in precipitation of a white solid. This mixture was centrifuged and the resulting pellet rinsed with acetone. The remaining solids were dissolved in 4 mL of deionized water, and this solution was cooled to 0 °C in an ice bath. This mixture was then filtered through an Acrodisc 0.2 μm wwPTFE

syringe filter to remove insoluble cesium perchlorate. To the resulting aqueous solution was added sodium triflate (0.050 g) and volatiles were removed under vacuum at 40 °C. The resulting white powder was rinsed with acetonitrile to remove residual diethylammonium and cesium triflate. Drying the remaining solids under vacuum gave the product as a white powder (0.0328 g, 0.068 mmol, 70% yield). $^{31}P\{^{1}H\}$ NMR of this compound revealed tri- and tetrametaphosphate as impurities (11% of total $^{31}P\{^{1}H\}$ NMR integration) resulting in a corrected yield of 63%.

^{1}H NMR (D_2O, 400 MHz): δ 3.04 (dq, J = 11.4, 7.1 Hz, 1H), 1.07 (t, J = 7.1 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (D_2O, 100.6 MHz): δ 40.30 (d, J = 3.5 Hz), 13.65 (d, J = 3.7 Hz).

$^{31}P\{^{1}H\}$ NMR (D_2O, 162.0 MHz): δ −0.04 (d, J = 23.3 Hz), −17.80 (dd, J = 924.2, 15.5 Hz), −22.13 to −22.99 (m).

^{19}F NMR (D_2O, 377 MHz): δ −71.30 (d, J = 924.0 Hz).

No signal was observed under ESI-MS(−) conditions for this compound. Inorganic salts soluble only in water are sometimes difficult to observe by ESI-MS.

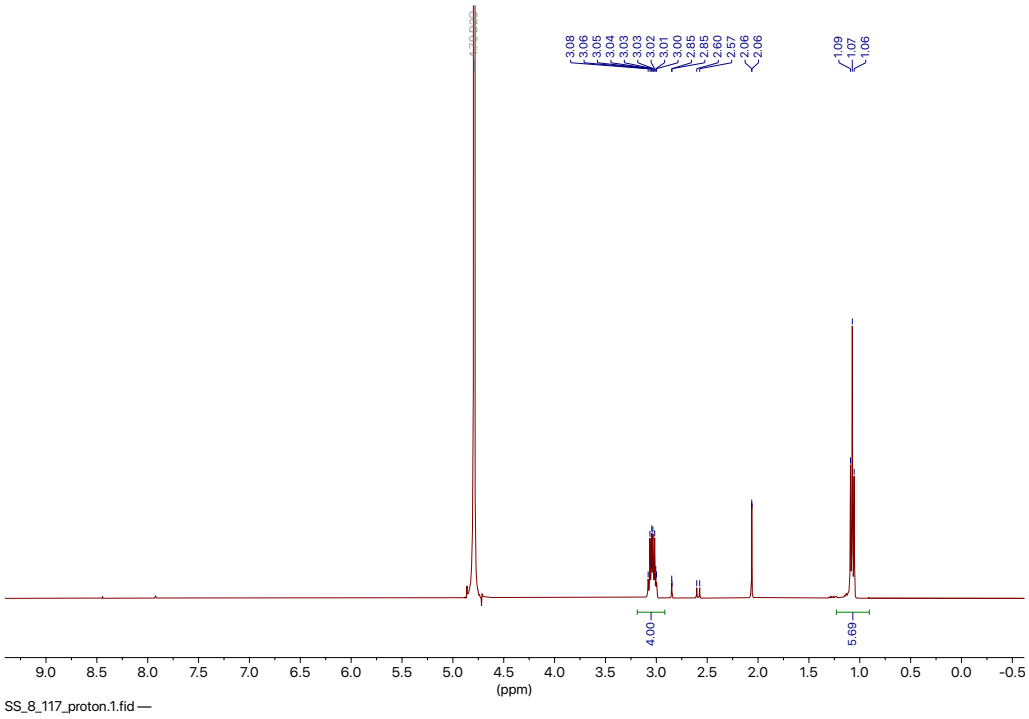

Figure S146: ^{1}H NMR spectrum of $[Na]_4$[**27**] (D_2O, 400 MHz).

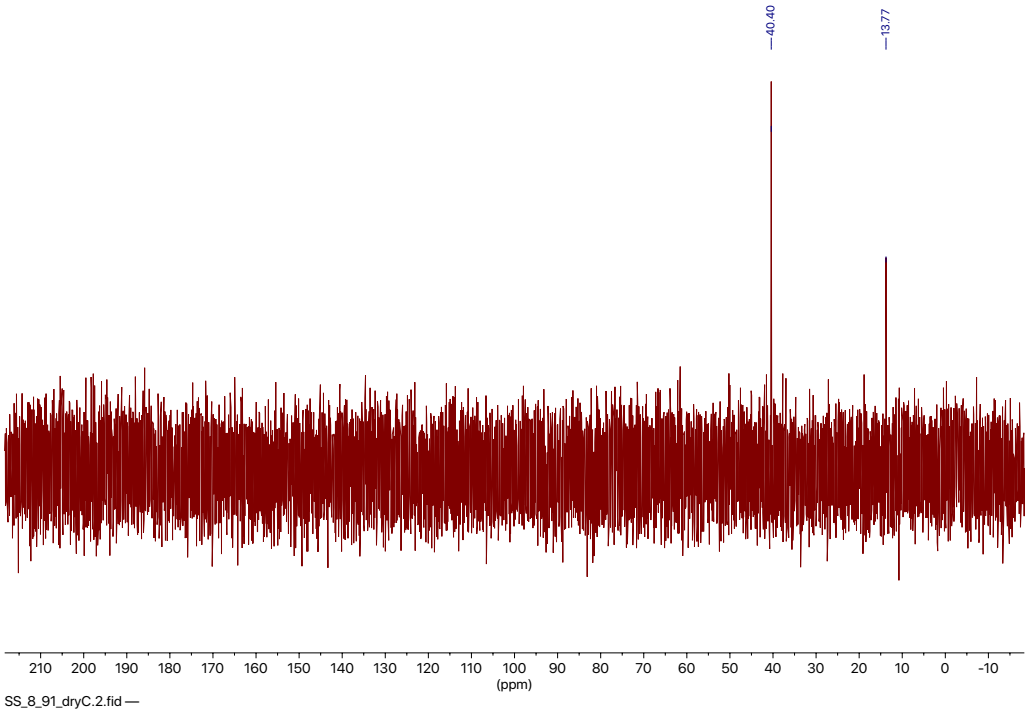

Figure S147: $^{13}C\{^{1}H\}$ NMR spectrum of $[Na]_4$[**27**] (D_2O, 101 MHz).

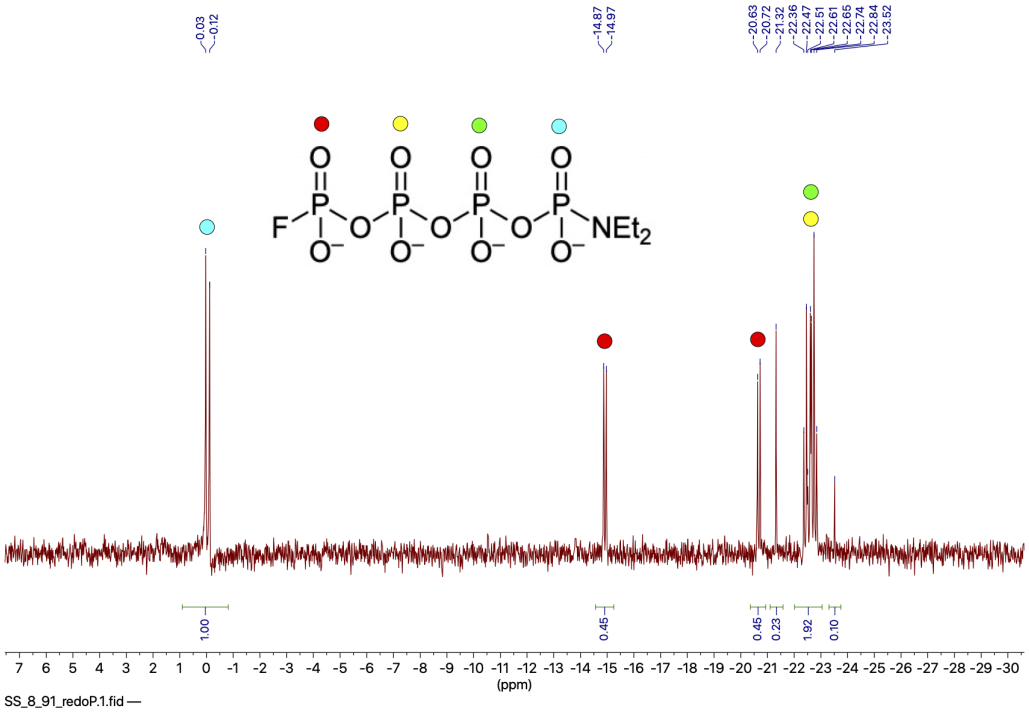

Figure S148: $^{31}P\{^{1}H\}$ NMR spectrum of $[Na]_4$[**27**] (D_2O, 162 MHz).

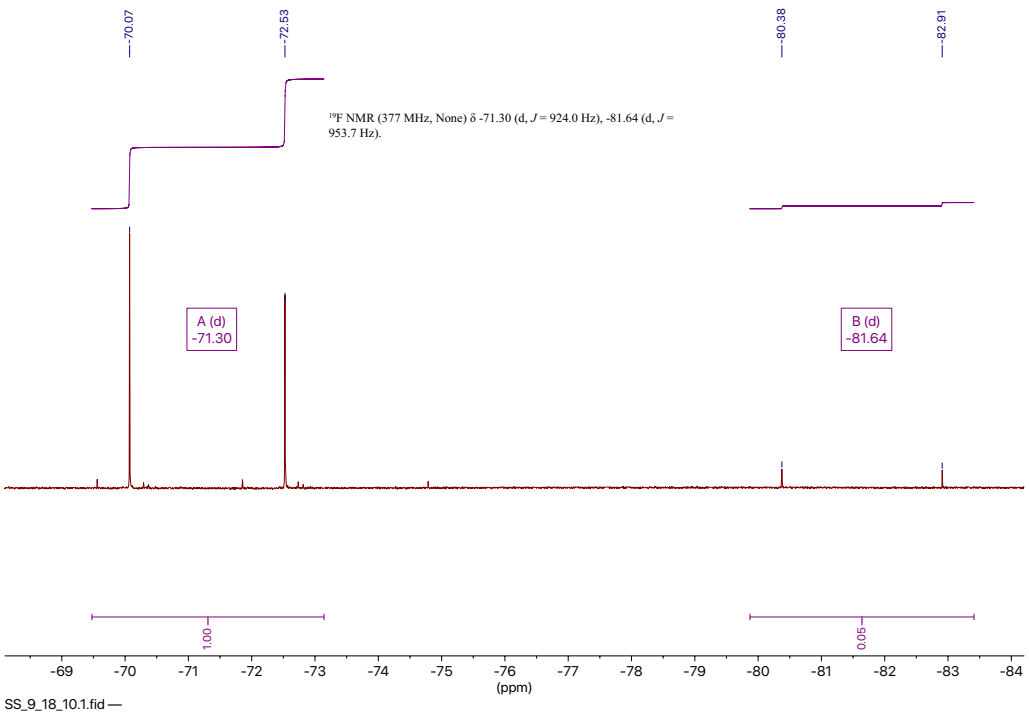

Figure S149: ^{19}F NMR spectrum of $[Na]_4$[**27**] (D_2O, 377 MHz). The doublet at −81.64 ppm corresponds to an unidentified fluorophosphate impurity.

5 Reactivity of 15

5.1 $[PPN]_2[MePPh_3]$[28]

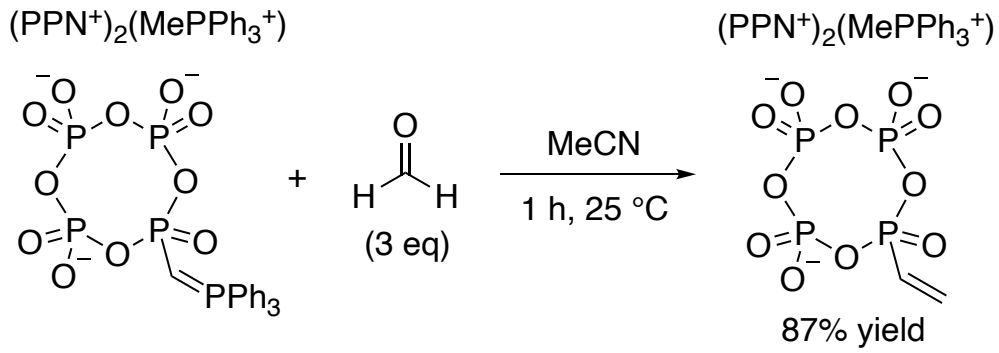

Figure S150: Synthesis of $[PPN]_2[MePPh_3][P_4O_{11}C_2H_3]$.

In a glovebox, $[PPN]_2[MePPh_3][P_4O_{11}CH_2PPh_3]$ (0.1 g, 0.052 mmol) was dissolved in dry acetonitrile (1 mL), to which solid paraformaldehyde (0.047 g, 0.16 mmol) was added. The reaction was stirred for 1 hour, after which the solution was then filtered through Celite®

to remove any insoluble material. Diethyl ether (5 mL) was added, resulting in a cloudy white suspension. After several hours, the suspension settled into a colorless solution and a colorless oil. The solution was decanted away, and the oil was dried under vacuum for 30 minutes to give a foamy solid. The powder was washed with diethyl ether (3 × 2 mL), and was dried under vacuum to give the product as a highly hygroscopic white powder (0.0757 g, 0.045 mmol, 87%).

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 7.92 to 7.45 (m, 75H), 6.55 (ddd, J_{PH} = 21.0, J_{HH} = 19.0, 12.6 Hz, 1H), 6.27 (ddd, J_{PH} = 26.9, J_{HH} = 18.9, 2.6 Hz, 1H), 6.03 (ddd, J_{PH} = 53.7, J_{HH} = 12.6, 2.6 Hz, 1H), 3.04 (d, J_{HH} = 13.8 Hz, 3H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 135.6 (d), 134.9 (d), 134.6, 134.3 (d), 133.20 to 133.10 (m), 131.1 (d), 130.7 (d), 130.2 to 130.1 (m), 128.1 (dd), 120.9 (dd), 9.1 (d, J_{CP} = 57.0 Hz).

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 24.2, 23.0 (s), −4.25 to −4.65 (m), −22.51 to −22.77 (m).

ESI-MS(−) of $[PPN]_2[MePPh_3][P_4O_{11}C_2H_3]$ (CH_3CN), found 866.39 m/z for $[PPN][P_4O_{11}C_2H_4]^-$) (calc'd 866.06 for $C_{38}H_{34}NO_{11}P_6$)

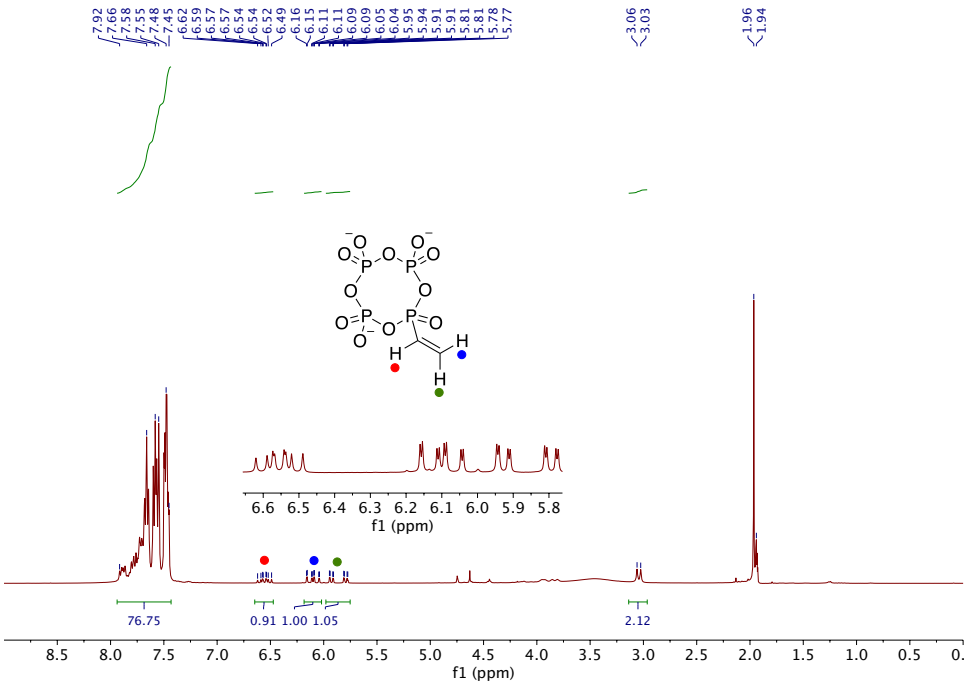

Figure S151: ^{1}H NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}C_2H_3]$ (acetonitrile-d_3, 400 MHz).

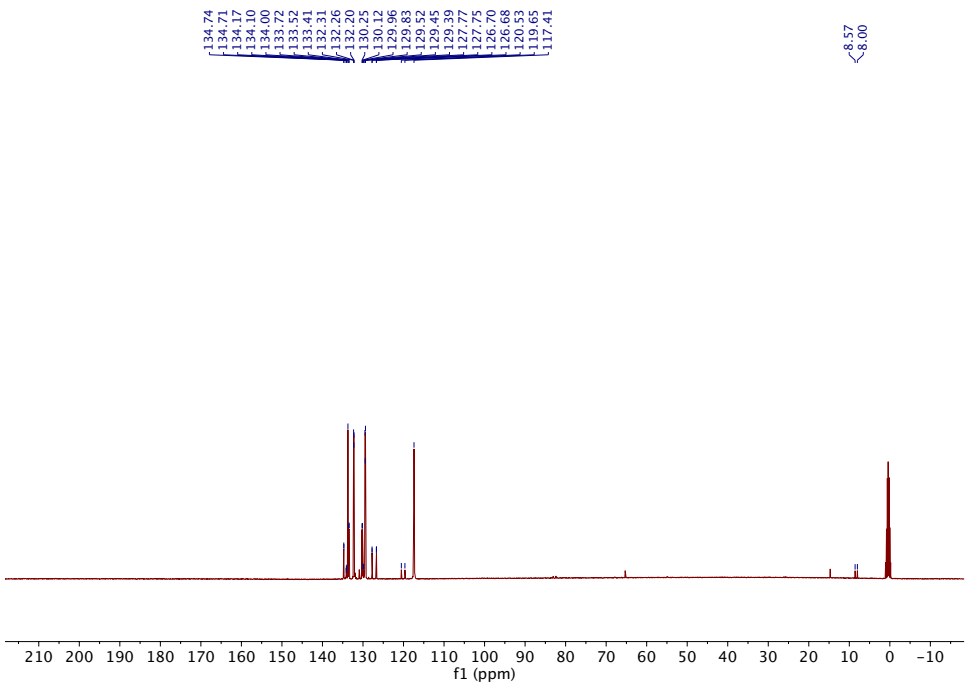

Figure S152: $^{13}C\{^{1}H\}$ NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}C_2H_3]$ (acetonitrile-d_3, 100.6 MHz).

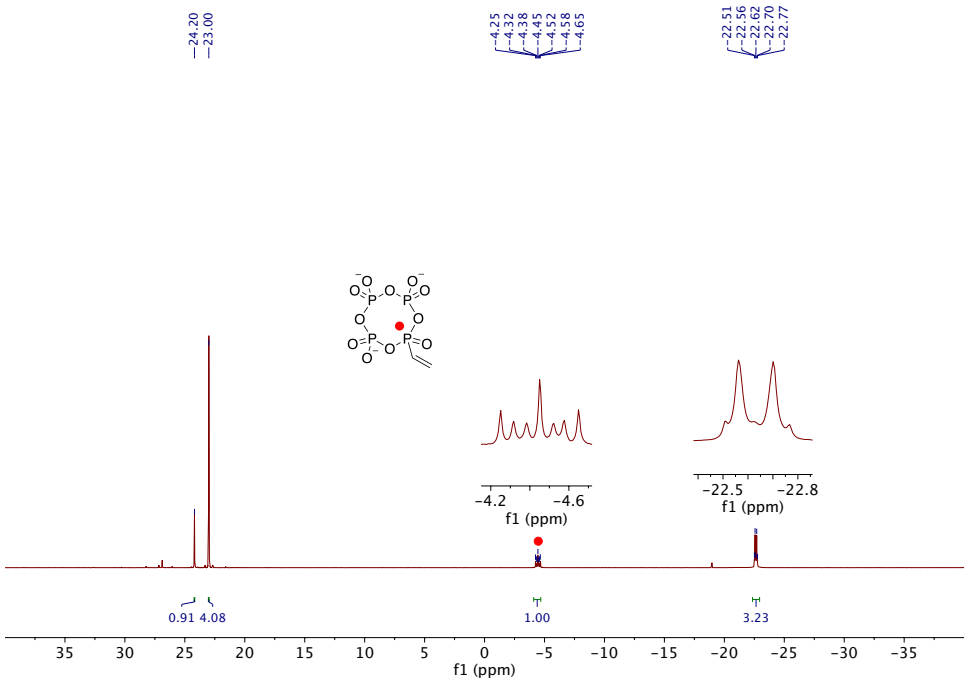

Figure S153: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}C_2H_3]$ (acetonitrile-d_3, 162.0 MHz).

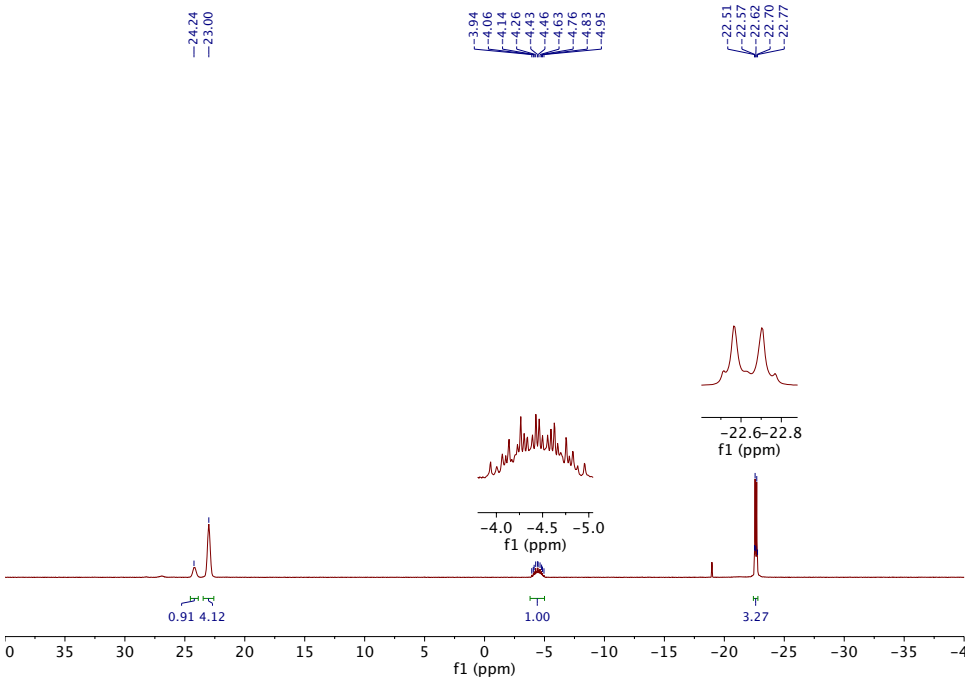

Figure S154: ^{31}P NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}C_2H_3]$ (acetonitrile-d_3, 162.0 MHz).

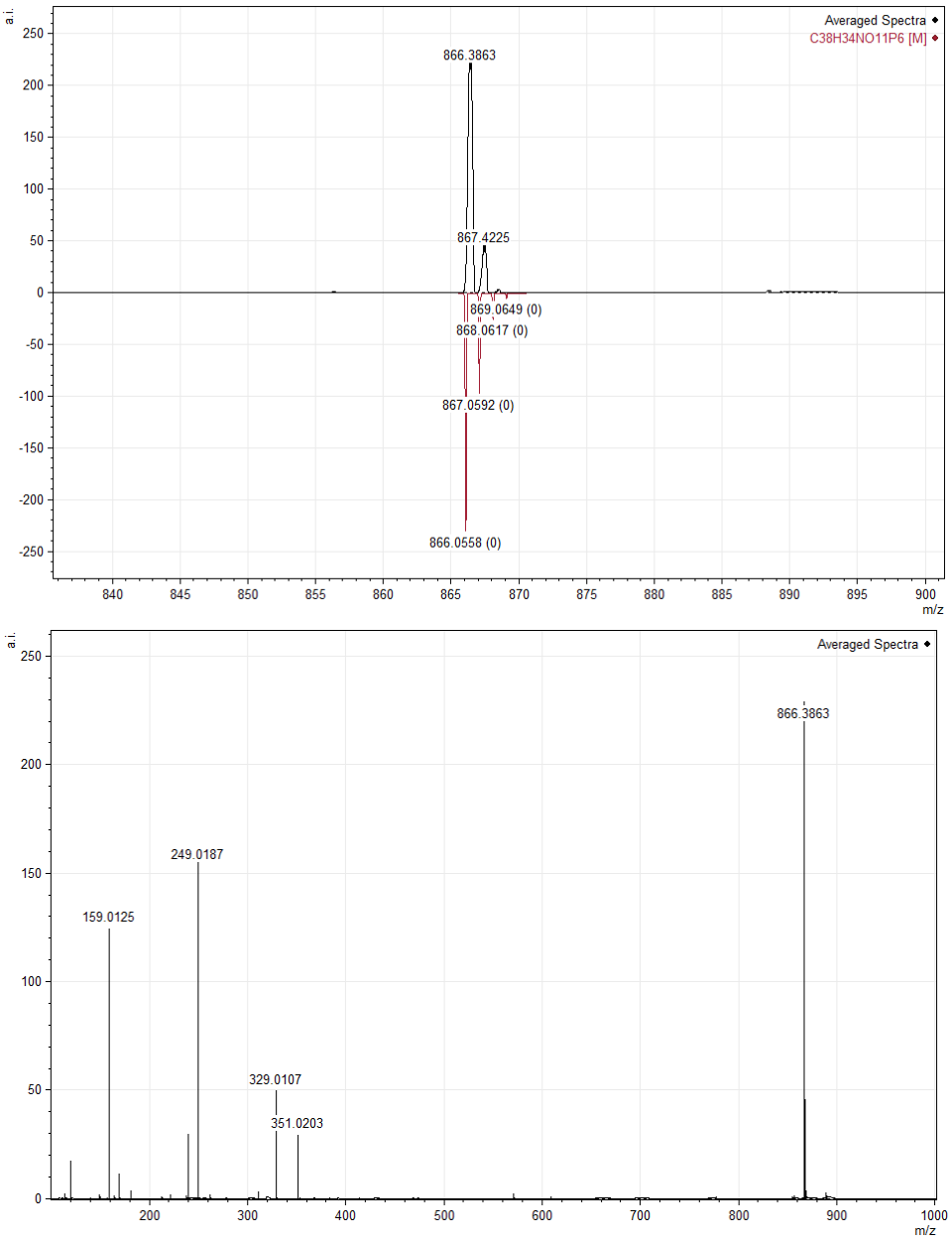

Figure S155: ESI-MS(−) of $[PPN]_2[MePPh_3][P_4O_{11}C_2H_3]$ (CH_3CN) with zoomed in portion of the molecular ion ($[PPN][P_4O_{11}C_2H_3]H^-$, top), and calculated isotope pattern ($C_{38}H_{34}NO_{11}P_6$, bottom).

5.2 $[PPN]_2[MePPh_3]$[29]

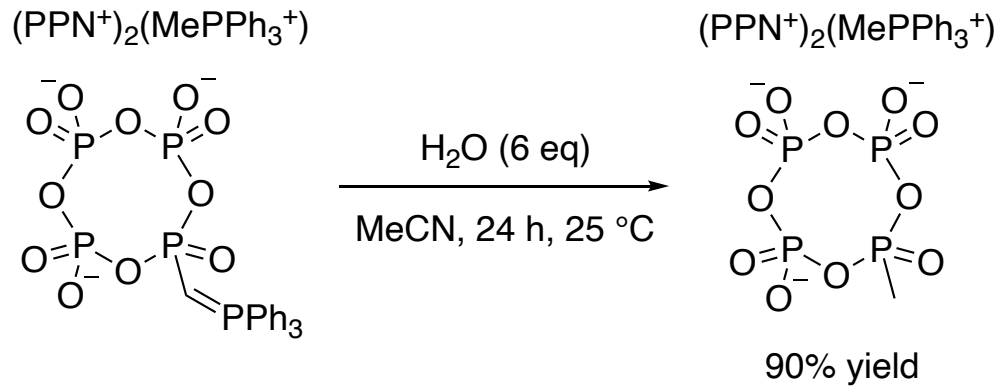

Figure S156: Synthesis of $[PPN]_2[MePPh_3][P_4O_{11}CH_3]$.

In a glovebox, $[PPN]_2[MePPh_3][P_4O_{11}CH_2PPh_3]$ (0.1 g, 0.052 mmol) was dissolved in dry acetonitrile (1 mL), after which it was taken out of the glovebox into the fumehood. Deionized water (6 μL, 0.31 mmol) was added, and the reaction was stirred for 24 hours. Diethyl ether (5 mL) was added, resulting in a cloudy white suspension. After several hours, the suspension settled into a colorless solution and a colorless oil. The solution was decanted away, and the oil was dried under vacuum for 30 minutes to give a foamy solid. The powder was washed with diethyl ether (3 × 2 mL), and was dried under vacuum at 50 °C to give the product as a highly hygroscopic, white powder (0.0779 g, 0.047 mmol, 90%).

^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 7.86 to 7.44 (m, 75H), 3.23 (d, J_{PH} = 13.7 Hz, 3H), 1.55 (d, J_{PH} = 19.0 Hz, 3H).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 100.6 MHz): δ 135.4 (d), 134.6, 134.4 (d), 133.20 to 133.15 (m), 131.1 (d), 130.20 to 130.15 (m), 128.1 (dd), 121.2 (dd), 13.9 (d, J_{CP} = 143.1 Hz), 9.2 (d, J_{CP} = 56.4 Hz).

^{31}P{^{1}H} NMR (acetonitrile-d_3, 162.0 MHz): δ 24.4, 23.0, 8.2 to 7.8 (m), −22.31 to −22.46 (m).

ESI-MS(−) of $[PPN]_2[MePPh_3][P_4O_{11}CH_3]$ (CH_3CN, found 854.38 m/z for $[PPN][P_4O_{11}CH_4]^-$) (calc'd 854.06 for $C_{37}H_{34}NO_{11}P_6$)

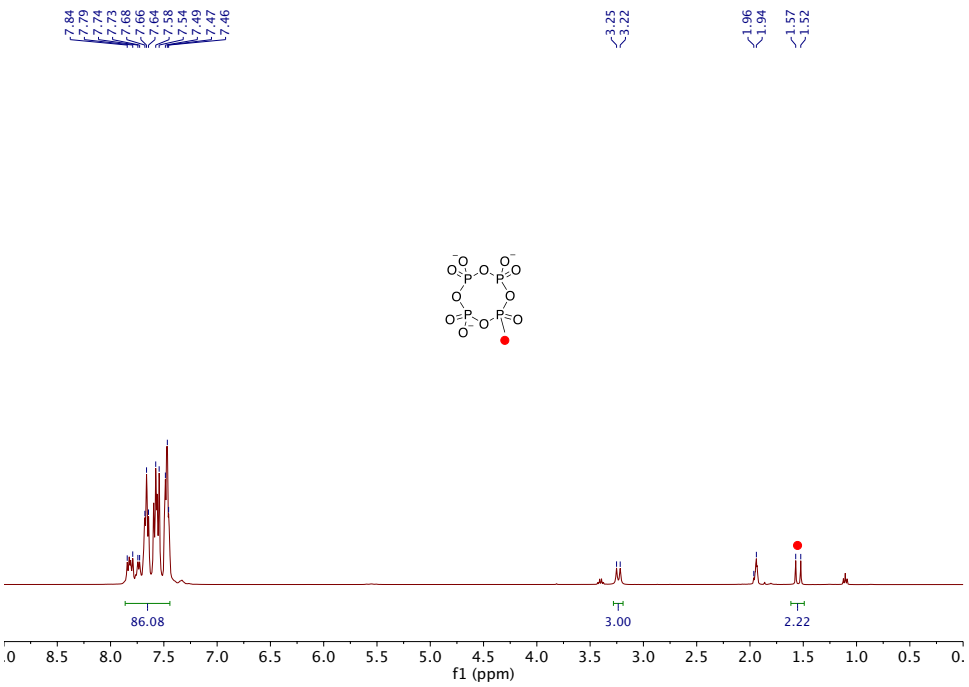

Figure S157: ^{1}H NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}CH_3]$ (acetonitrile-d_3, 400 MHz), with residual diethyl ether signals (3.42 and 1.12 ppm).

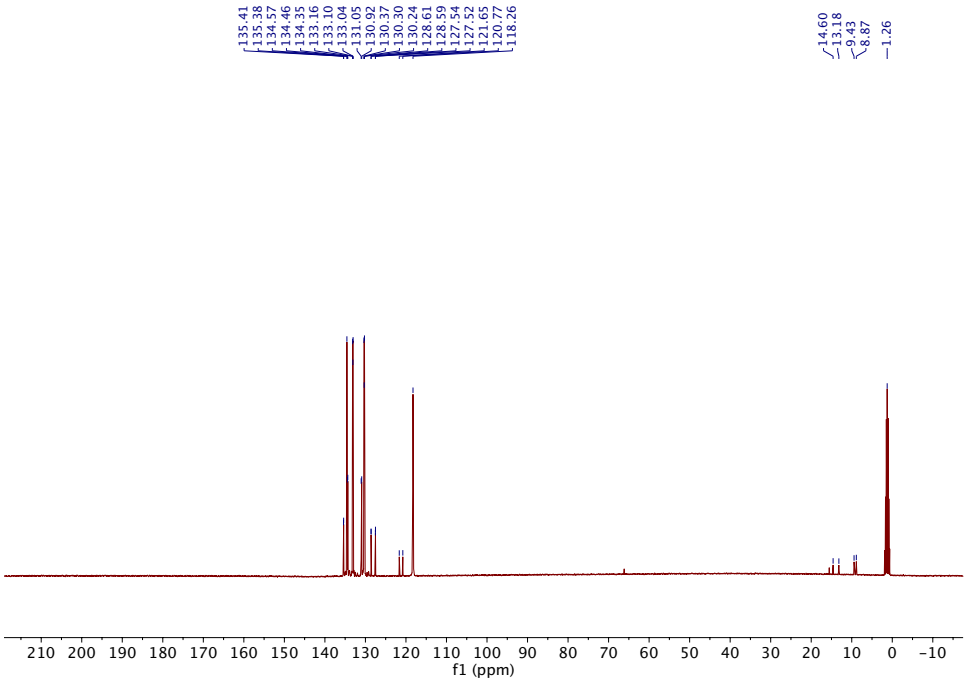

Figure S158: ^{13}C{^{1}H} NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}CH_3]$ (acetonitrile-d_3, 100.6 MHz).

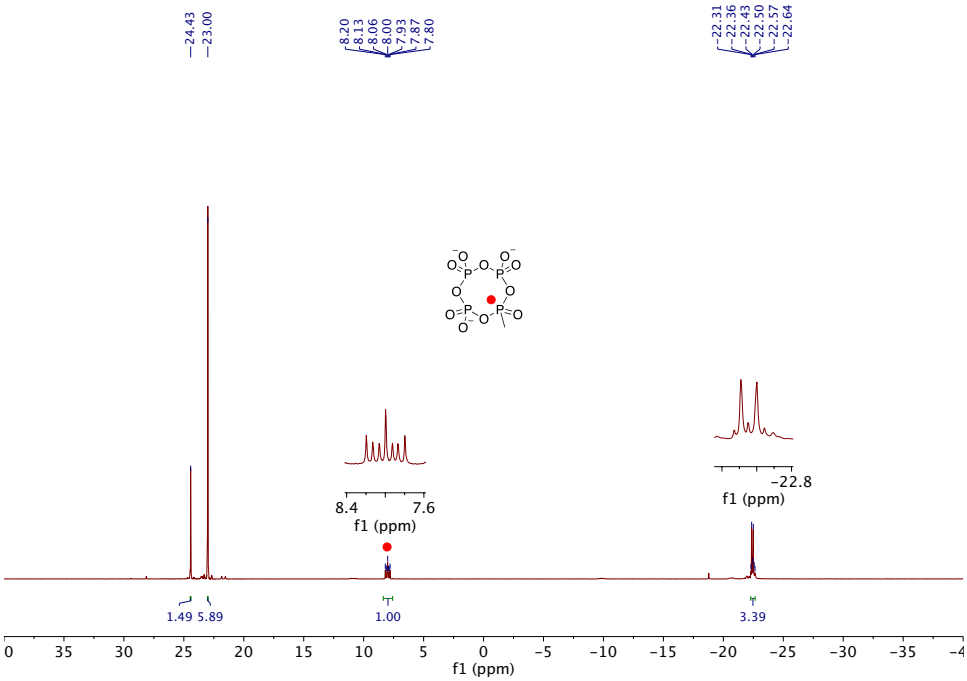

Figure S159: $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}CH_3]$ (acetonitrile-d_3, 162.0 MHz).

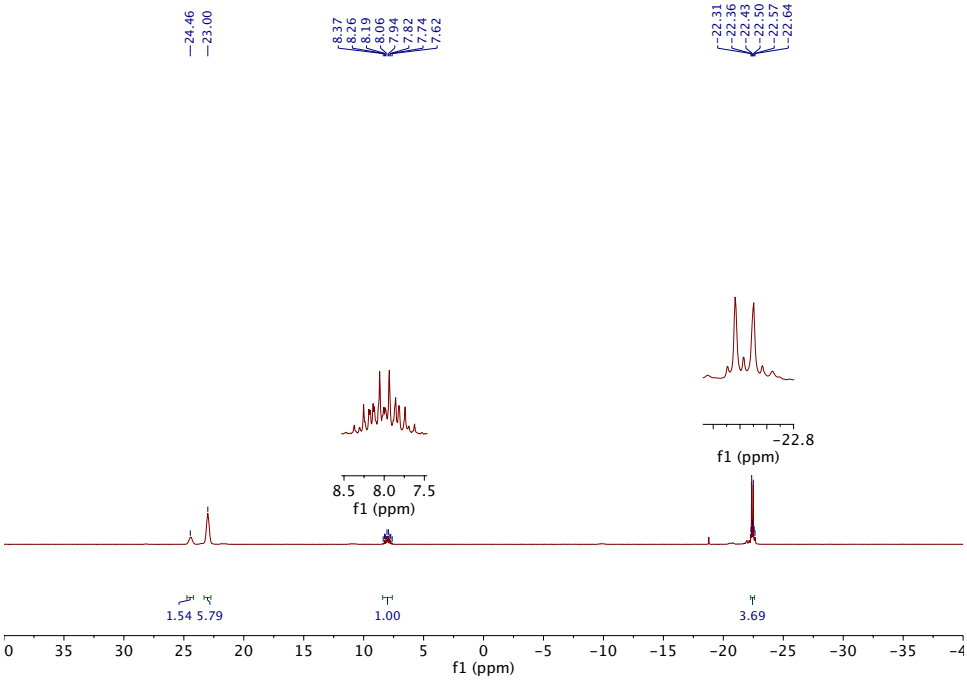

Figure S160: ^{31}P NMR spectrum of $[PPN]_2[MePPh_3][P_4O_{11}CH_3]$ (acetonitrile-d_3, 162.0 MHz).

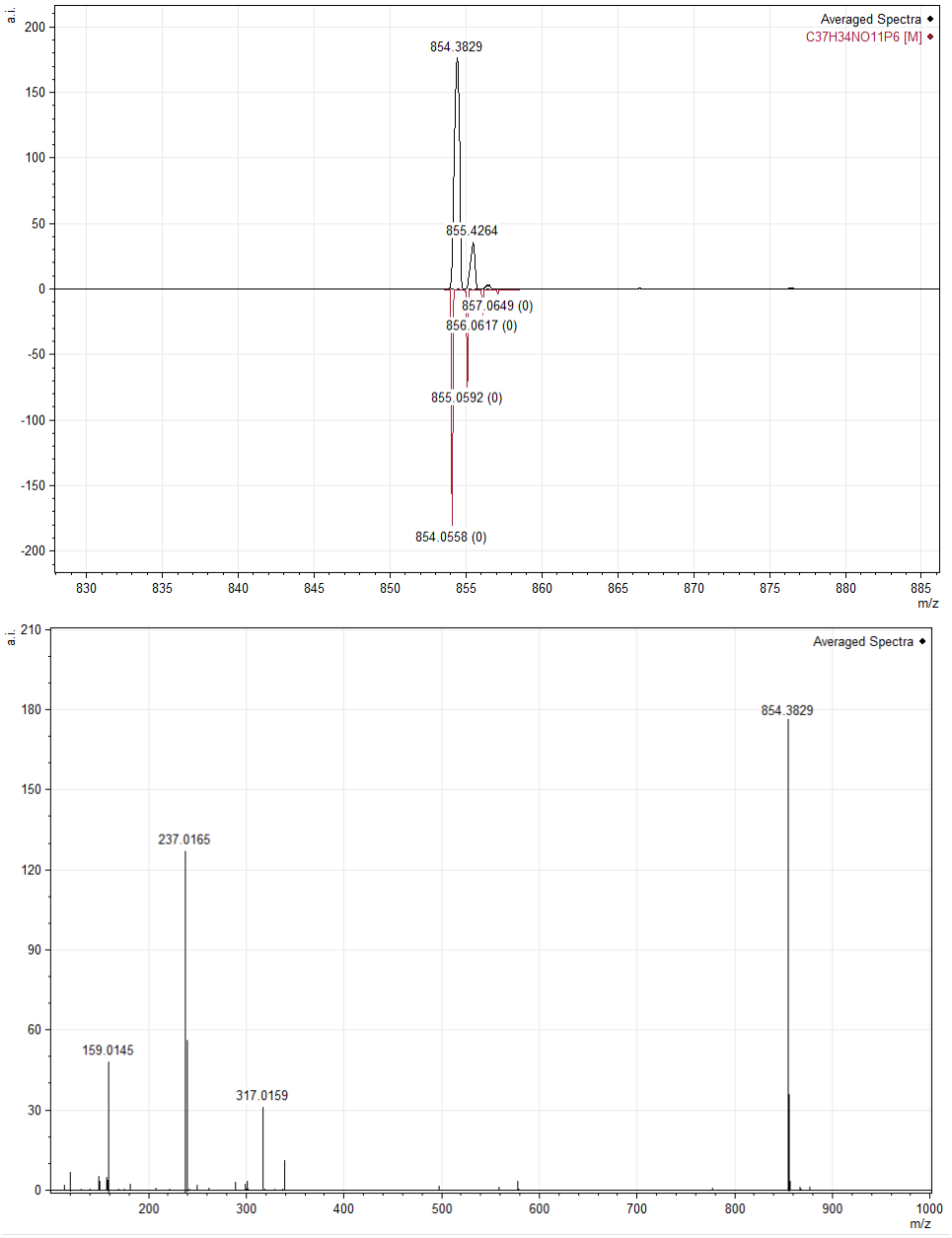

Figure S161: ESI-MS(−) of $[PPN]_2[MePPh_3][P_4O_{11}CH_3]$ (CH_3CN) with zoomed in portion of the molecular ion ($[PPN][P_4O_{11}CH_3]H^-$, top), and calculated isotope pattern ($C_{37}H_{34}NO_{11}P_6$, bottom).

5.3 $[Et_3NH]_4$[30]

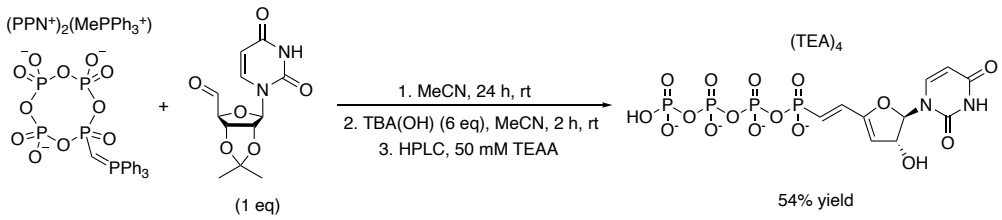

Figure S162: Synthesis of $[Et_3NH]_4$[**30**].

2',3'-O-isopropylidene-5'-deoxy-5'-uridylaldehyde was synthesized according to a literature procedure.[9] In a glovebox, $[PPN]_2[MePPh_3][P_4O_{11}CH_2PPh_3]$ (0.068 g, 0.035 mmol), 2',3'-O-isopropylidene-5'-deoxy-5'-uridylaldehyde (0.01 g, 0.035 mmol, 1 equiv) were each dissolved in dry acetonitrile (0.5 mL), then combined. The mixture was stirred overnight at room temperature, after which it was brought out of the glovebox, and a solution of 40 wt% aqueous tetrabutylammonium hydroxide (0.137 g, 0.211 mmol, 6 equiv) in acetonitrile (1 mL) was immediately added. The resulting mixture was stirred for 2 hours in the fumehood. Volatiles were removed under vacuum at room temperature, after which deionized water (3 mL) was added, resulting in a cloudy solution. This mixture was extracted with DCM (3 × 3 mL), and filtered through Celite®. It was then purified by HPLC according to the procedures outlined in the General Considerations section above. The fractions containing the desired product were pooled in a flask, and volatiles were removed under vacuum at 60 °C. The resulting residue was repeatedly dissolved in water and evaporated under vacuum at 60 °C to remove excess triethylammonium acetate buffer. The product was isolated as a light brown solid (0.0190 g, 0.019 mmol, 54%).

^{1}H NMR (D_2O, 400 MHz): δ 7.43 (d, J = 8.1 Hz, 1H), 6.89 (dd, J = 21.8, 17.4 Hz, 1H), 6.45 (t, J = 17.6 Hz, 1H), 6.31 (d, J_{HH} = 2.0 Hz, 1H), 5.85 (d, J = 8.0 Hz, 1H), 5.68 (d, J_{HH} = 2.8 Hz, 1H), 5.04 (m, 1H), 3.20 (q, 24H), 1.29 (t, 36H).

^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 166.2, 156.8 (d, J_{CP} = 24.2 Hz), 151.2, 141.6, 130.2 (d, J_{CP} = 6.8 Hz), 125.6 (d, J_{CP} = 184.1 Hz), 106.39, 102.41, 92.77, 78.60, 46.6, 8.2.

^{31}P{^{1}H} NMR (D_2O, 202.6 MHz): δ 3.7 (d, J = 20.9 Hz), −10.8 (d, J = 17.9 Hz), −22.97 to −23.35 (m).

ESI-MS(−) of $[Et_3NH]_4[C_{10}H_{10}N_2O_{16}P_4]$ in CH_3CN/H_2O, 541.14 m/z (calc'd 540.92 m/z) for $C_{10}H_{13}N_2O_{16}P_4^-$

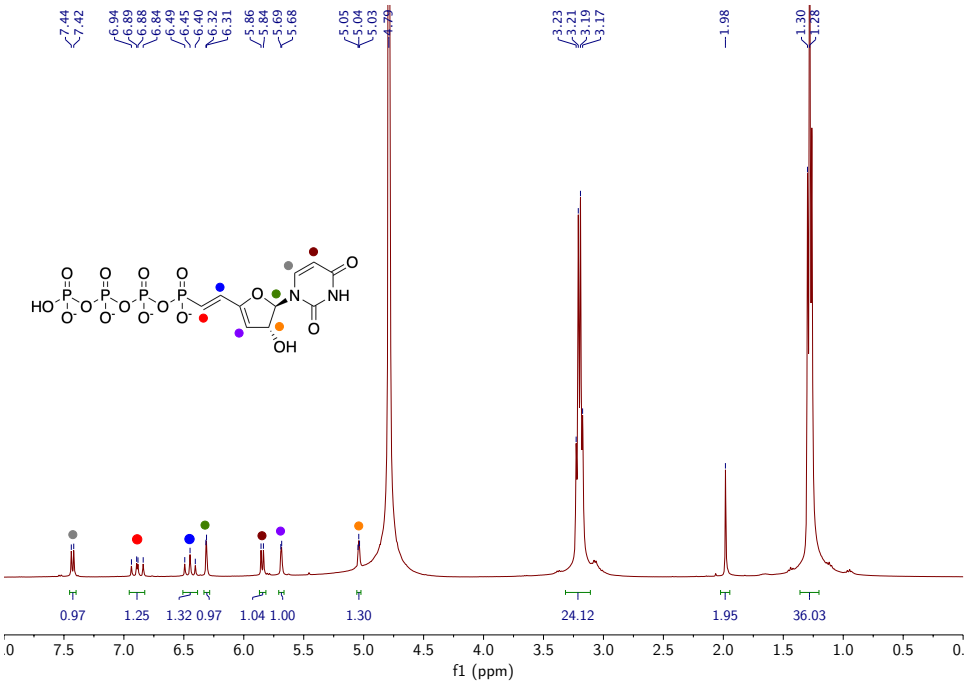

Figure S163: ^{1}H NMR spectrum of $[Et_3NH]_4$[**30**] (D_2O, 400 MHz).

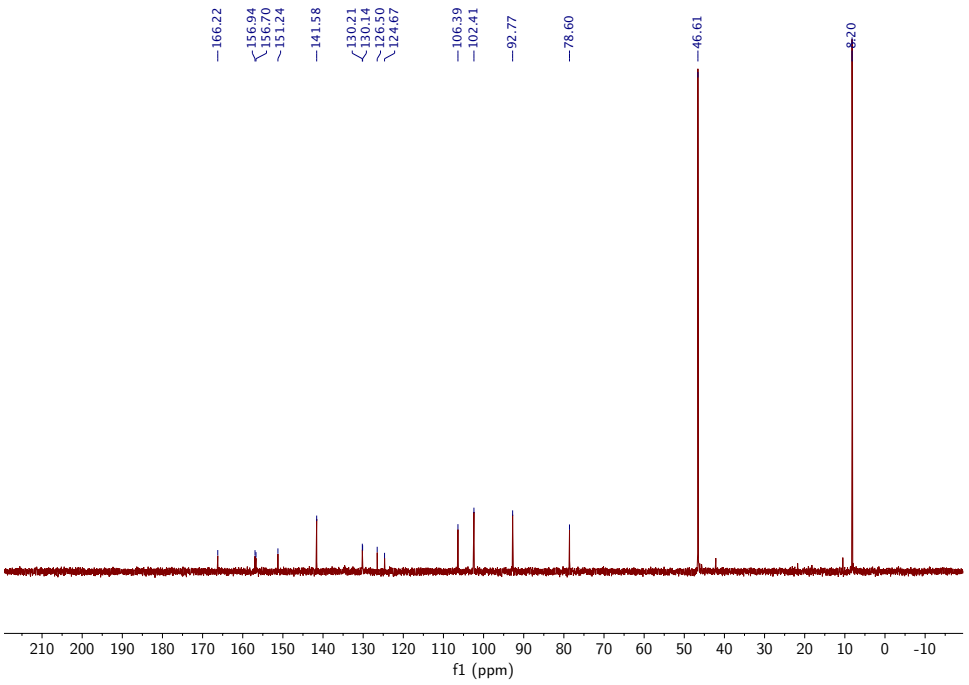

Figure S164: ^{13}C{^{1}H} NMR spectrum of $[Et_3NH]_4$[**30**] (D_2O, 100.6 MHz).

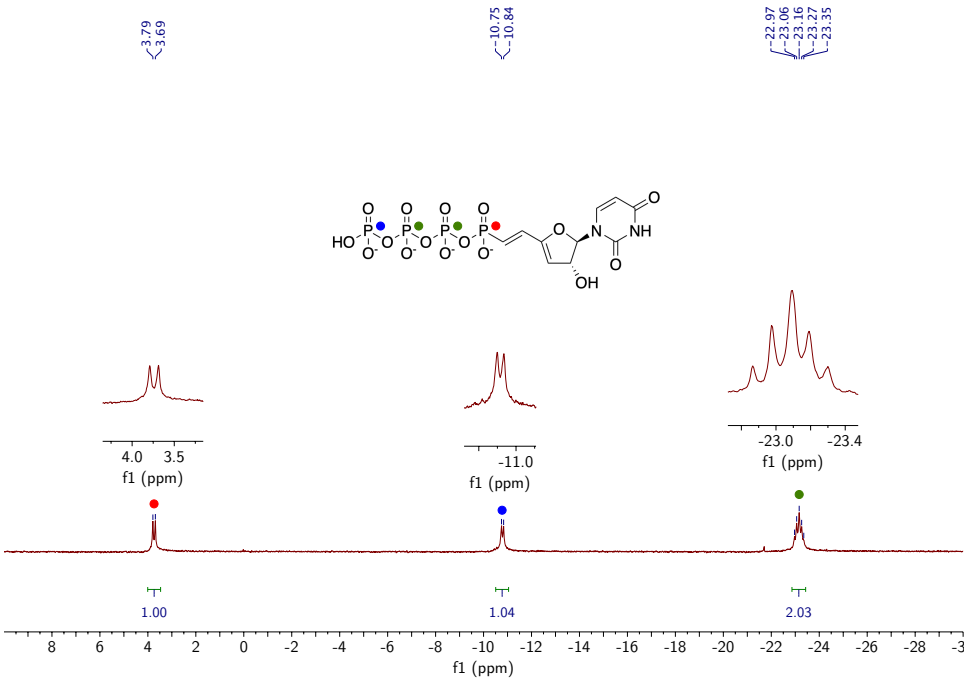

Figure S165: $^{31}P\{^{1}H\}$ NMR spectrum of $[Et_3NH]_4$[**30**] (D_2O, 202.6 MHz).

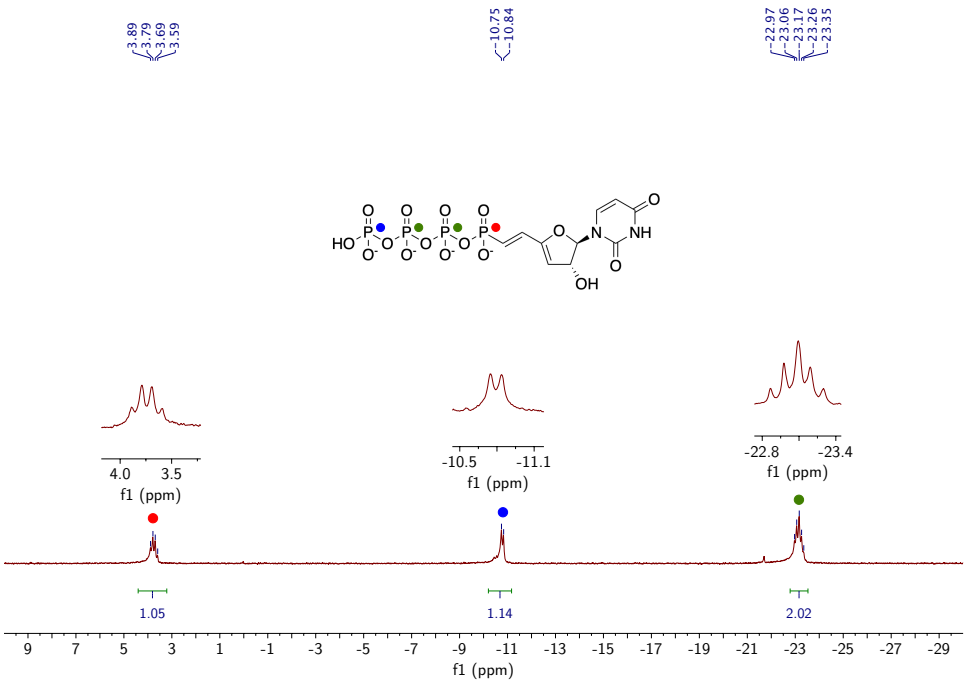

Figure S166: ^{31}P NMR spectrum of $[Et_3NH]_4$[**30**] (D_2O, 202.6 MHz).

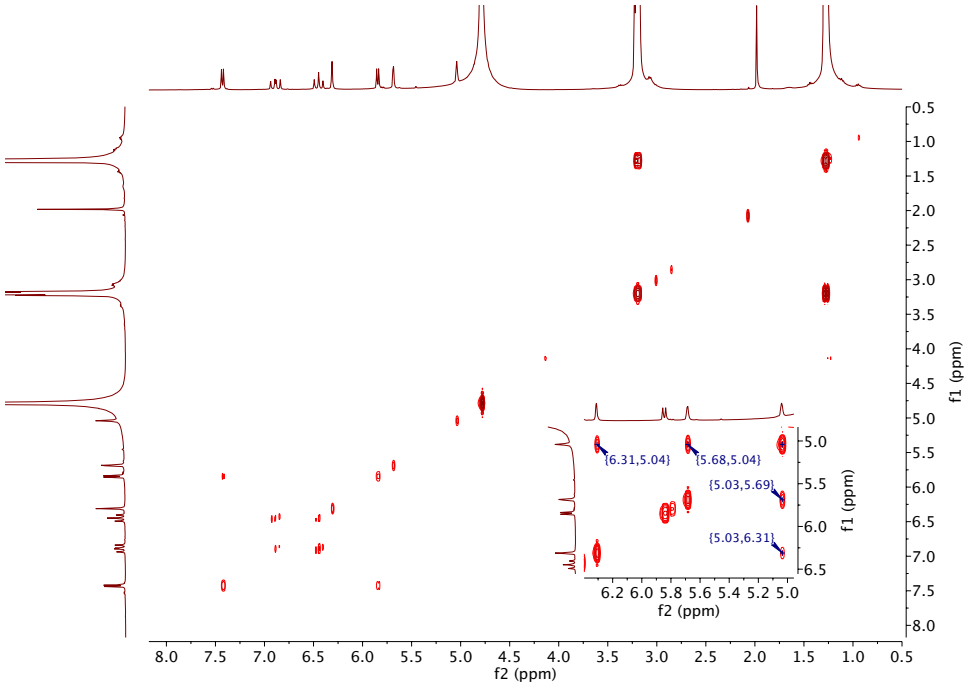

Figure S167: ^{1}H-^{1}H-COSY 2D NMR spectrum (D_2O, 500 MHz) of $[Et_3NH]_4$[**30**]. Inset shows coupling between proton resonance of $H_{2'}$ at 5.04 ppm and those of $H_{3'}$ and $H_{1'}$ at 5.68 and 6.31 ppm, respectively.

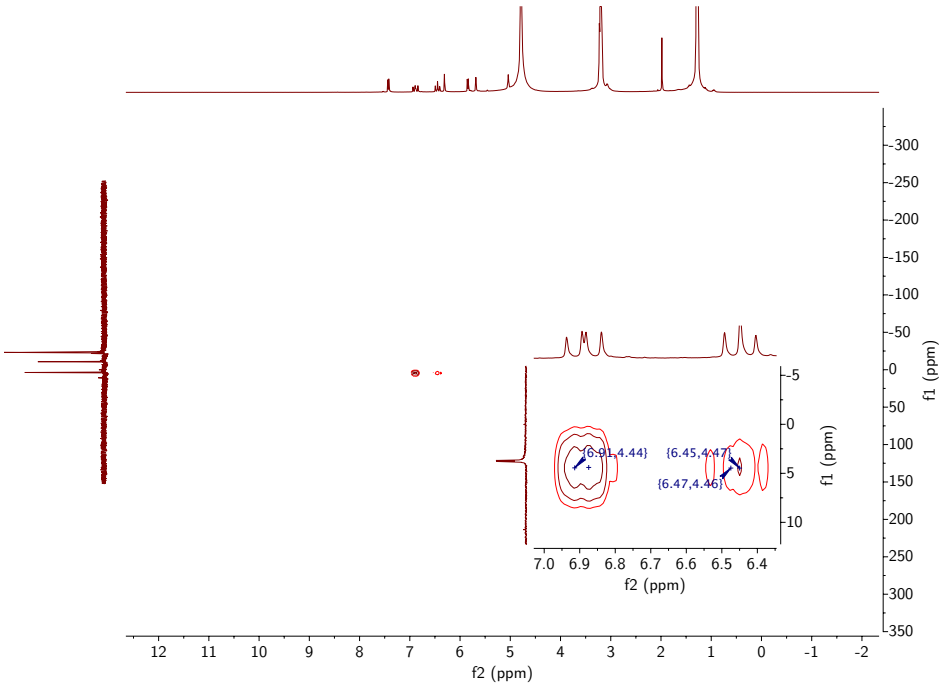

Figure S168: ^{1}H-^{31}P-HMBC 2D NMR spectrum (D_2O, 500 MHz and 202.6 MHz) of $[Et_3NH]_4$[**30**]. Inset shows coupling between phosphorus resonance at 3.74 ppm and alkene proton resonances at 6.89 and 6.45 ppm.

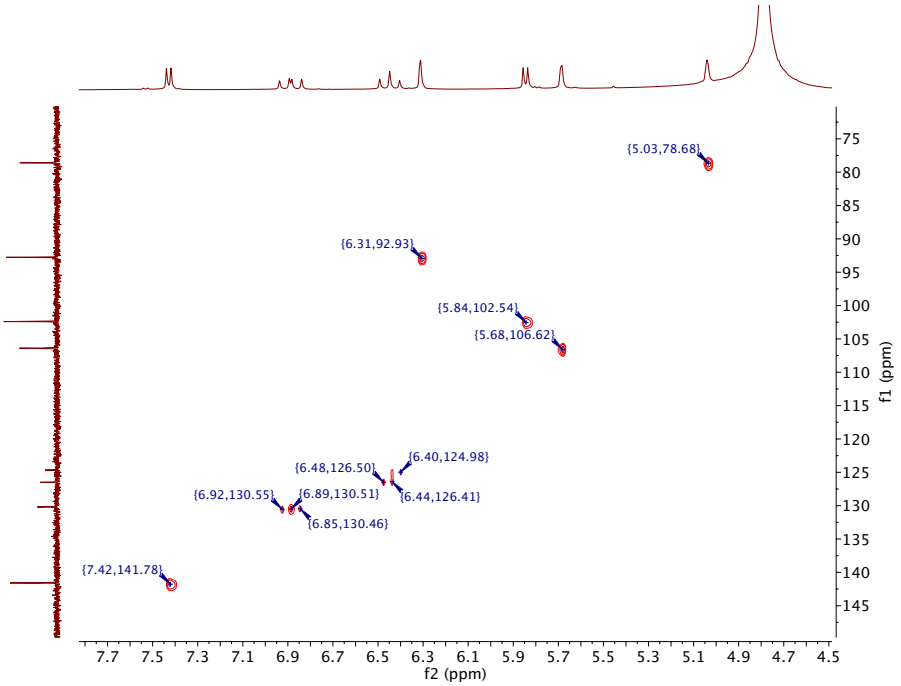

Figure S169: ^{1}H-^{13}C-HSQC 2D NMR spectrum (D_2O, 400 MHz and 100.6 MHz) of $[Et_3NH]_4$[**30**].

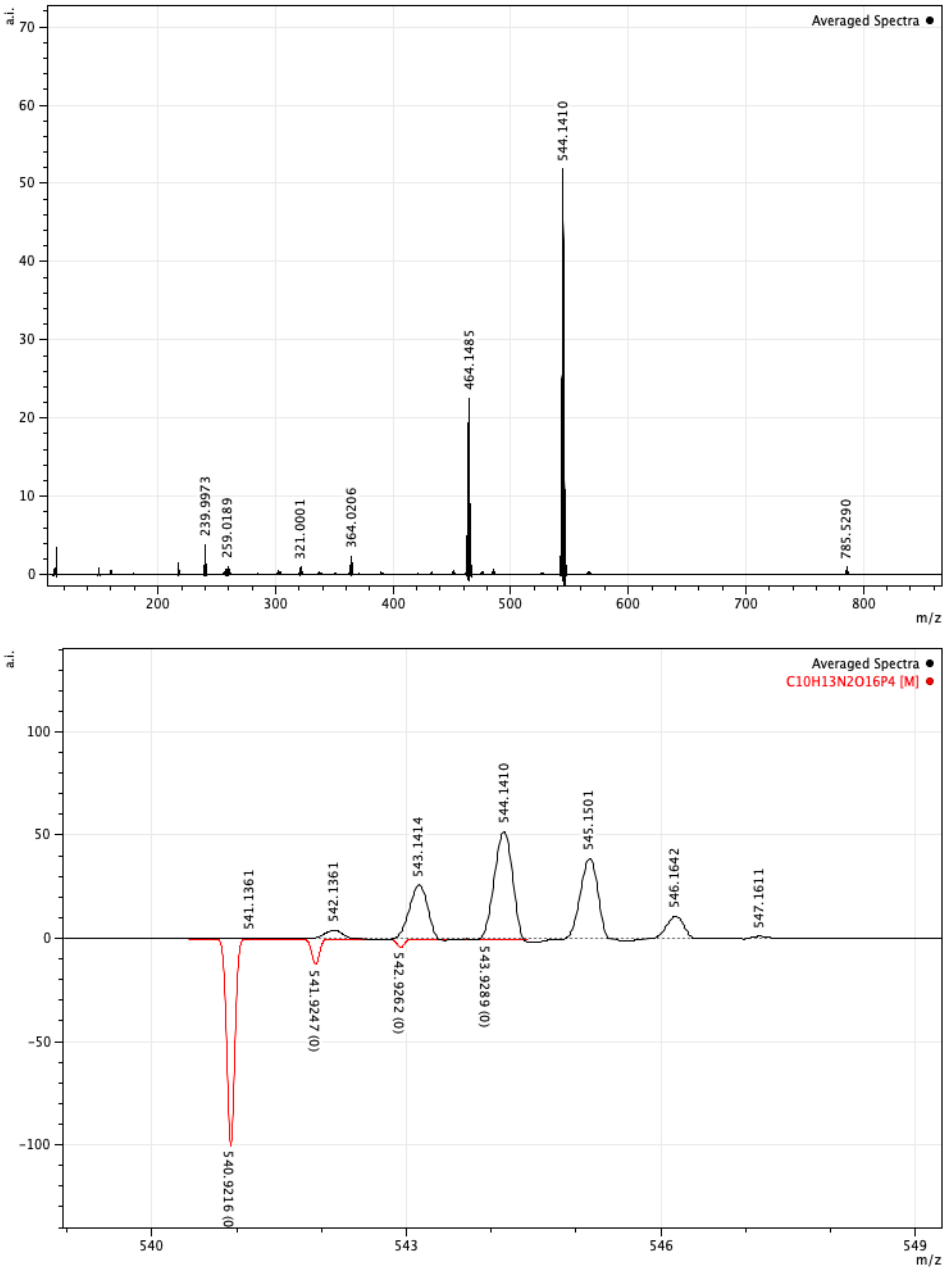

Figure S170: ESI-MS(−) of $[Et_3NH]_4[C_{10}H_{10}N_2O_{16}P_4]$ (CH_3CN/H_2O) with zoomed in portion of the molecular ion ($[C_{10}H_{10}N_2O_{16}P_4]H_3^-$, top), and calculated isotope pattern ($C_{10}H_{13}N_2O_{16}P_4$, bottom). The difference between calculated and experimental isotope patterns is due to the MS sample being prepared in deuterium oxide, causing enrichment in deuterium.

6 Equilibria

6.1 Treatment of $[PPN]_2[1]$ with [TBA][OAc]

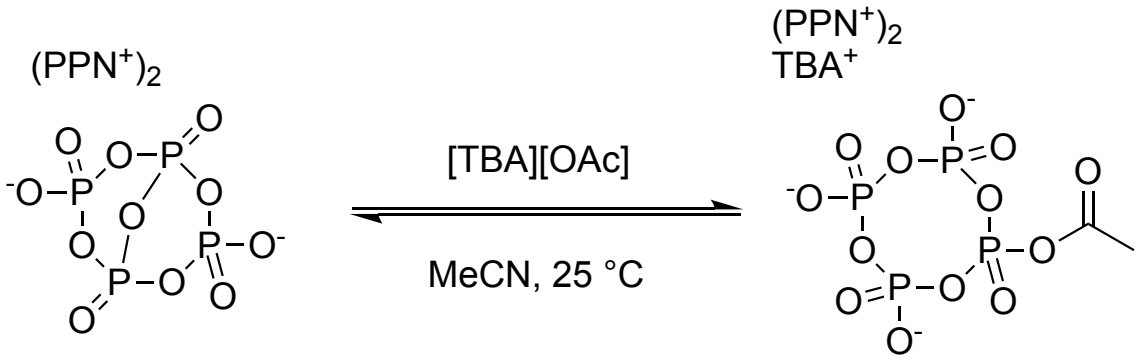

Figure S171: Treatment of $[PPN]_2[\mathbf{1}]$ with [TBA][OAc].

In the glovebox, [TBA][OAc] was recrystallized from cold THF. A stock solution of [TBA][OAc] in acetonitrile at a concentration of 0.1 g/mL was then prepared and dried over activated 4Å molecular sieves overnight. $[PPN]_2[P_4O_{11}]$ (0.23 g, 0.16 mmol) was dissolved in MeCN (2 mL). To this solution was added the stock solution of [TBA][OAc] (0.50 ml, 0.16 mmol). The resulting mixture as stirred for one hour and analyzed by NMR. Precipitation of this material by the addition of diethyl ether (10 mL) resulted in a cloudy suspension which settled into an oil after several hours. Decanting off the supernatant solution, rinsing the oil with diethyl ether, and drying under vacuum resulted a solid material. In contrast to the crude NMR spectra, this solid was found to be a mixture of the starting $[PPN]_2[P_4O_{11}]$ and desired $[PPN]_2[TBA][P_4O_{11}{-}OAc]$.

$^{31}P\{^1H\}$ NMR (acetonitrile, 162.0 MHz): δ 23.0, −22.4 to −23.4 (m), −31.1 (t).

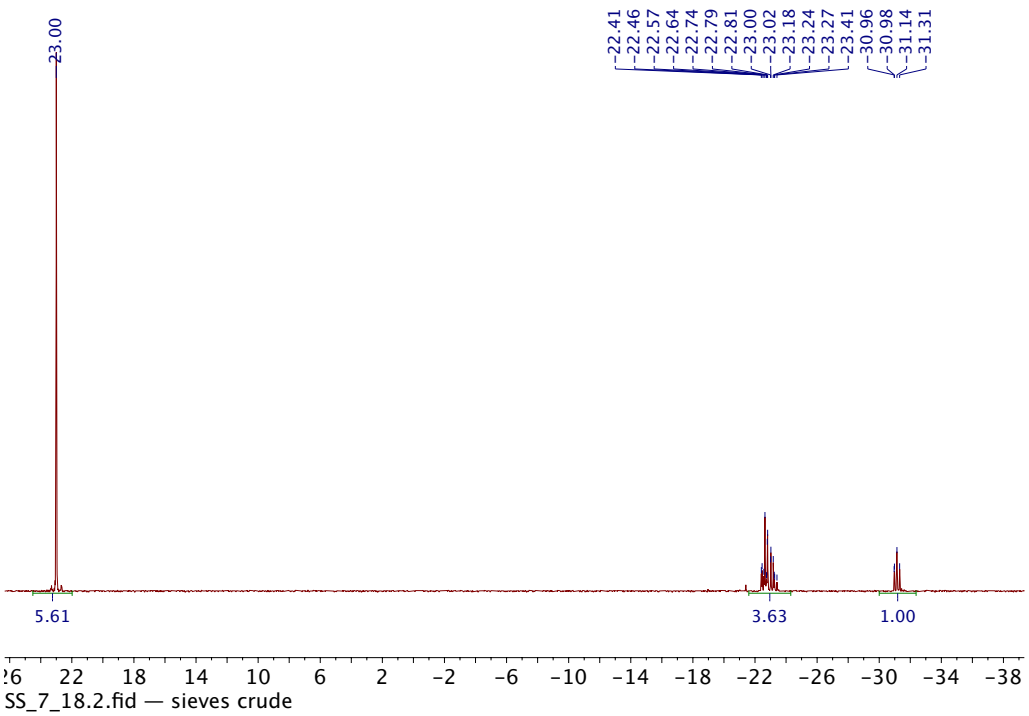

Figure S172: $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture of $[PPN]_2[TBA][P_4O_{11}{-}OAc]$ (acetonitrile, 162 MHz).

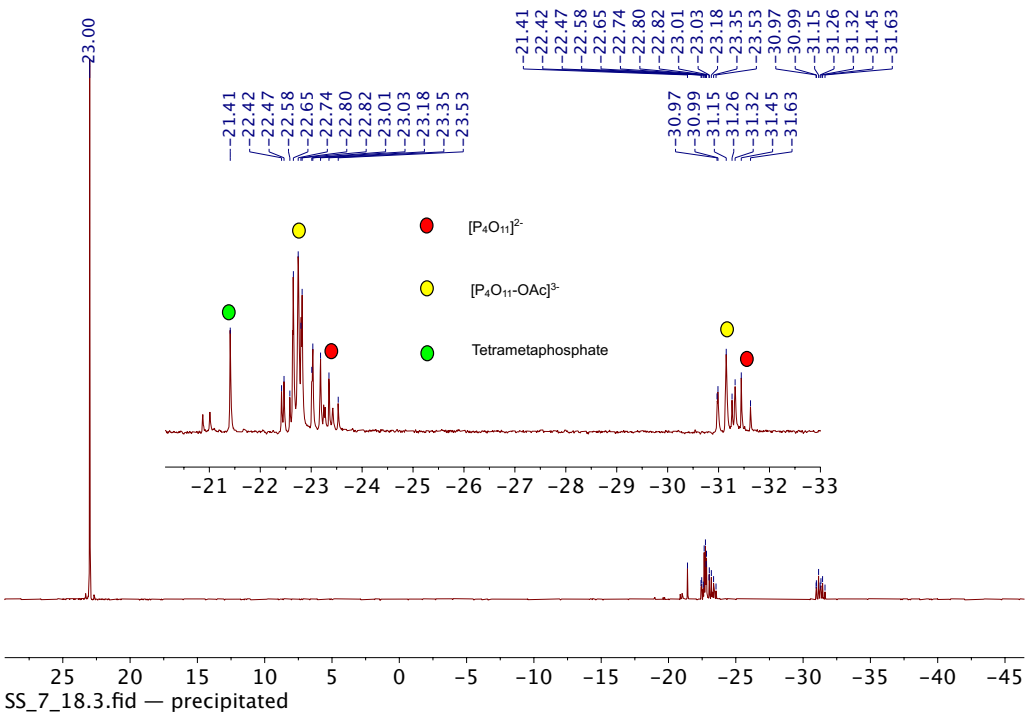

Figure S173: $^{31}P\{^{1}H\}$ NMR spectrum of the solid material obtained after precipitating the crude mixture of $[PPN]_2[TBA][P_4O_{11}{-}OAc]$ with diethyl ether showing a mixture of starting material and product (acetonitrile, 162 MHz).

6.2 Treatment of $[PPN]_2[1]$ with $[TBA][HSO_4]$

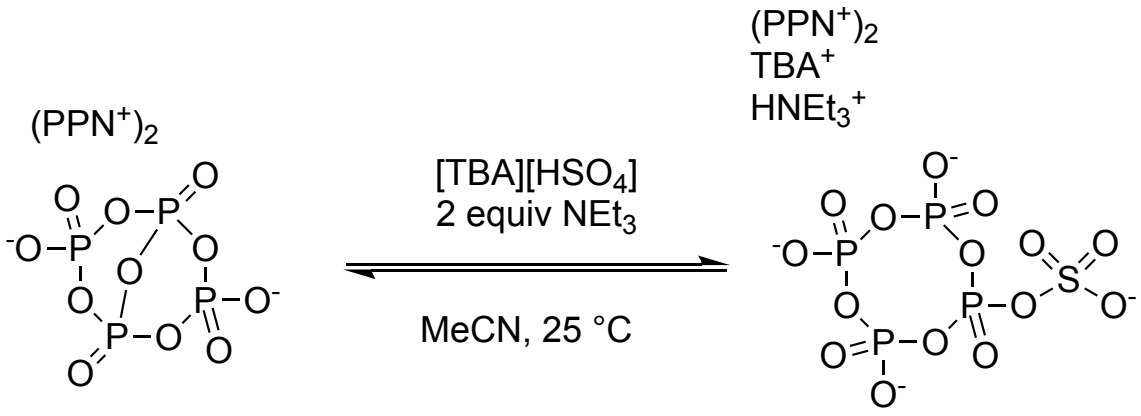

Figure S174: Treatment of $[PPN]_2[\mathbf{1}]$ with $[TBA][HSO_4]$.

In the glovebox, a stock solution of [TBA][OAc] in acetonitrile at a concentration of 0.1 g/mL was then prepared and dried over activated 4Å molecular sieves overnight. $[PPN]_2[P_4O_{11}]$ (0.042 g, 0.031 mmol) was dissolved in MeCN (2 mL). To this solution was added the stock

solution of [TBA][OAc] (0.1 ml, 0.031 mmol). To this solution was added triethylamine (0.01 mL, 0.062 mmol). The resulting mixture as stirred for one hour and analyzed by NMR. Precipitation of this material by the addition of diethyl ether (10 mL) resulted in a cloudy suspension which settled into an oil after several hours. Decanting off the supernatant solution, rinsing the oil with diethyl ether, and drying under vacuum resulted in solid material. In contrast to he composition indicated by NMR spectra of the crude reaction mixture, this solid was found to be mostly tetrametaphosphate.

$^{31}P\{^{1}H\}$ NMR (acetonitrile, 162.0 MHz): δ 23.0, −22.4 to −23.6 (m), −34.6 (t).

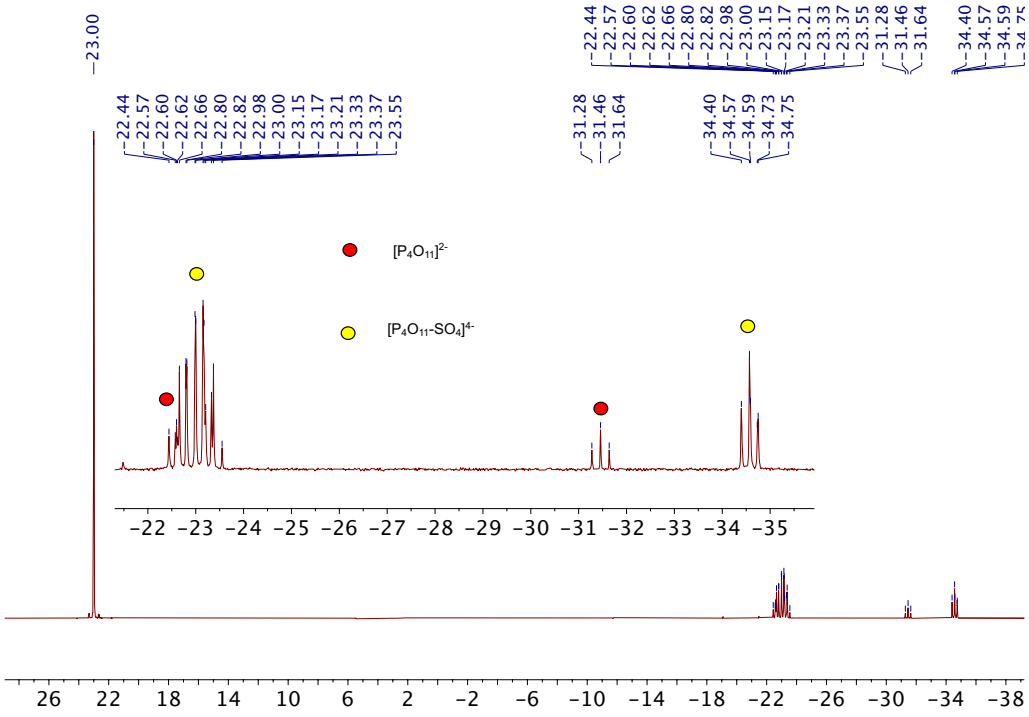

Figure S175: $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture of $[PPN]_2[TBA][HNEt_3][P_4O_{11}{-}SO_4]$ (acetonitrile, 162 MHz).

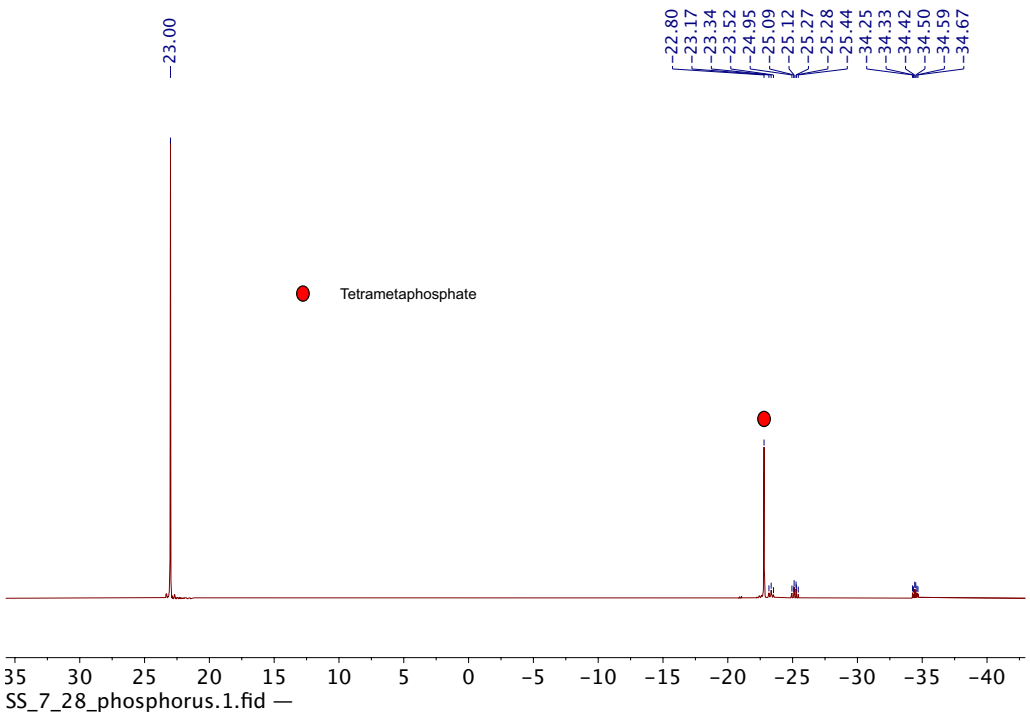

Figure S176: $^{31}P\{^{1}H\}$ NMR spectrum of the solid material obtained after precipitating the crude mixture of $[PPN]_2[TBA][HNEt_3][P_4O_{11}{-}SO_4]$ with diethyl ether showing primarily tetrametaphosphate (acetonitrile, 162 MHz).

7 Computational Details

7.1 General Considerations

Geometries were optimized and frequency calculations performed at the B3LYP-D3BJ/ma-def2-TZVP(-f) level of theory[10–12] in Orca 4.2 with a CPCM acetonitrile solvation model.[13] Thermochemistry data is calculated at 298.15 K.

7.2 Calculated Reaction Coordinate

	10	TS1	1 + azide	TS2	iso-10	TS3
ΔG (kcal/mol)	−2.0	26.5	0.0	21.8	2.4	31.1
ΔH (kcal/mol)	−11.2	16.5	0.0	11.2	−7.2	22.0
$T\Delta S$ (kcal/mol)	−9.2	−10.0	0.0	−10.6	−9.5	−9.1

Table S1: Calculated energies for the reaction of **1** and azide ion. **TS3** corresponds to a direct conversion from **10** to **iso-10**

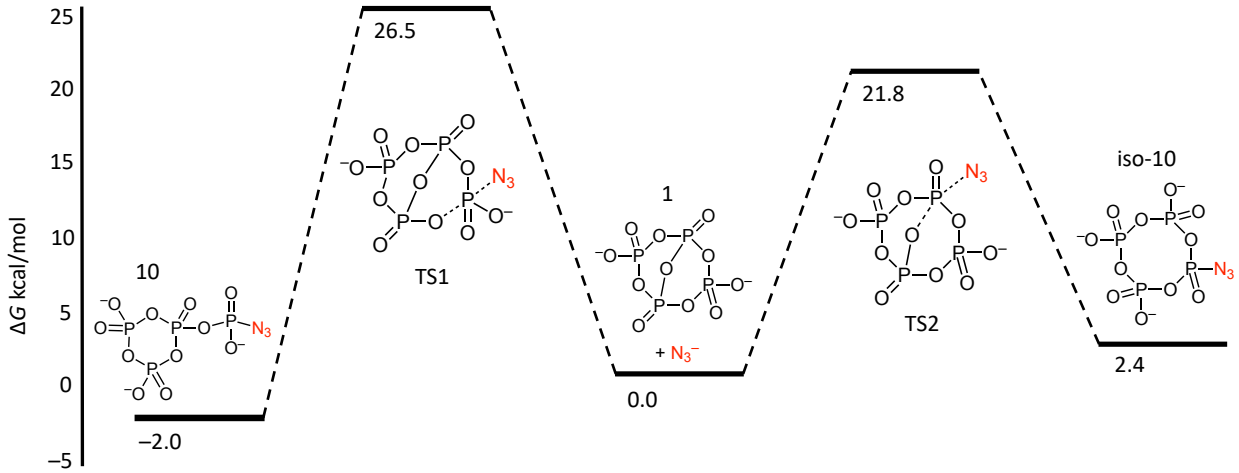

Figure S177: Calculated reaction coordinate for treatment of **1** with azide ion.

7.3 XYZ Coordinates of Azide

N	0.00000000659267	-0.00000001398801	0.00000002867476
N	-0.00000000329633	0.00000000699400	1.17589352798337
N	-0.00000000329633	0.00000000699400	-1.17589355665813

7.4 XYZ Coordinates of 1

P	0.01690779200397	-0.02055719258928	-0.00355990816158
O	1.37406548778301	-0.14762309262020	0.51719406544003
O	-0.74500885290629	1.31643639586718	0.35213834441839
P	-1.39758304884212	2.42947611966504	-0.71459600039596
O	-0.28599374338180	3.11905879218087	-1.40502742030772
O	-2.49524706556054	3.10991291678578	-0.00379868710828
O	-2.10339106961578	1.36340952260783	-1.79533684981646
P	-1.48041141884715	0.03273244412722	-2.37492884504484
O	-0.04936034254213	-0.06114493346372	-1.62160250798210
O	-1.36851981804166	-0.04882958297281	-3.82758192257551
O	-2.30470329939743	-1.14836650517723	-1.73074940865330
P	-2.50349633985026	-1.50832857779345	-0.10527989977382
O	-2.68144920846345	-2.97105448539584	-0.02506339958277
O	-3.41331529939561	-0.51025264687998	0.49042321909983
O	-0.94415477294274	-1.19567817434142	0.42595722044409

7.5 XYZ Coordinates of iso-10

P	0.03169075556545	-0.03667152566337	0.04097096084834
N	0.06869682356083	0.03828618122840	1.73236340284912
N	1.13526696709540	0.05864163556072	2.34209043614038
N	2.04798436641456	0.05525232647700	2.99143249041585
O	-1.14547721631474	-0.80238445092469	-0.39140871748448
O	1.45464119712076	-0.60926206019697	-0.30218396235578
P	2.26900907360965	-0.80497583759720	-1.75997168323376
O	1.32919469171454	-1.39269851259415	-2.74376720669864
O	3.53751520131805	-1.47475952184659	-1.37082087851916
O	2.63663702819324	0.73373473578416	-2.08404628888270
P	1.92434460902513	1.96936018476326	-2.88989025782814
O	0.64966119258780	1.54700077767261	-3.52407532696101
O	3.00089251323682	2.63613809556005	-3.67655681285670
O	1.60032393610110	2.98212645819201	-1.64091570289664
P	0.95425706042857	2.75952615059653	-0.17814848825895
O	0.04937862815200	3.90719890943288	0.09399843266424
O	1.99032622160659	2.32571309304990	0.79497468363049
O	-0.04398604941576	1.44861236050543	-0.48719508057243

7.6 XYZ Coordinates of 10

P	-0.04380053042987	0.00488901703953	0.03376327412086
N	0.04786667834695	0.02837320313682	1.77074264405412
N	1.14707180293014	0.01085656319957	2.30558505034301
N	2.11519544417277	-0.01755088637153	2.87919886241617
O	-1.36027374091447	-0.59299606925898	-0.29377398542036
O	1.24999103324793	-0.46408704734776	-0.52619485519443
P	1.14272318873849	3.00514706908952	-3.15436822145238
O	0.12319975934443	2.00793184462157	-3.55846999221983
O	2.35325125522485	3.28438000052026	-3.96714217042548
O	0.45603703341602	4.44637483913332	-2.80466893791310
P	-0.62242937169815	4.79895575598024	-1.63381211567758
O	-1.91434469673427	4.10670376643692	-1.86118408604995
O	-0.54016657527026	6.26055946829923	-1.38579289585739
O	0.13612641242634	4.07707789610485	-0.32476725503938
P	0.93732200414223	2.71814494161349	-0.25349819853110
O	1.84129612931957	2.63735716719795	0.90183941153616
O	1.70592423668084	2.60532180895060	-1.63057870070144
O	-0.21591606294356	1.62776266165437	-0.26898782798791

7.7 XYZ Coordinates of TS1

P	-0.68147151805570	-1.41674211021899	0.90917117159134
N	-0.75008318413738	-1.12796923132264	3.16138375797379
N	0.32551022736256	-1.00599153786507	3.64967100379573
N	1.37820823578993	-0.89476567152106	4.12173823743433
O	-2.12742439138514	-1.71293409492249	0.92631404608601
O	0.50670666102618	-2.28995924136809	1.03213460125895
P	0.49559431751328	-0.70615942186565	-1.89927289048277
O	-0.61914292684297	-1.34373196067969	-1.08312837586410
O	1.30056454118147	-1.51170917190430	-2.83006118875642
O	-0.08926455712339	0.59078434509468	-2.64957467508946
P	-0.84160734205942	1.89800301489921	-1.97389393894369
O	-2.20471703463049	1.53105412594852	-1.53164363045073
O	-0.55564654361277	3.05429717265151	-2.85503326531822
O	0.11613513654832	2.11402077274190	-0.61250444355760
P	0.82950722110127	1.01860125993634	0.27640292402800
O	1.80274901383263	1.58297299181295	1.21035869005944
O	1.47581024951776	0.01245373930635	-0.78576019942359
O	-0.36142810602614	0.20777501927652	0.93369817565900

7.8 XYZ Coordinates of TS2

P	1.32165252167759	-0.35218623386746	0.16229939208744
N	1.50269362769185	-0.48899026706375	2.43131391817377
N	0.67604746431838	0.05141587108104	3.09195653125062
N	-0.11673886521716	0.58387656234676	3.74647002102597
O	2.78366570786745	-0.51583489658385	0.12188440294523
O	0.57722402216691	1.00121872906089	0.54381336541815
P	-0.11994072634583	2.17421330408329	-0.40104297015466
O	0.94028514859569	2.86201743500606	-1.17830485066875
O	-1.08869524764886	2.89299771871247	0.45360007467073
O	-1.01073014875145	1.21475241151729	-1.42798081483347
P	-0.43336642843119	-0.08875873812157	-2.13961140540747
O	1.01164440727729	-0.24278014792445	-1.53423765083068
O	-0.49744878518914	-0.05548877974370	-3.60462205832254
O	-1.26817750936233	-1.29444201347458	-1.53253282003829
P	-1.21652232024945	-1.84999884306124	0.04171947254479
O	-1.42812884924998	-3.31460307329267	-0.02774937062048
O	-2.02451394815237	-0.94249558576014	0.88366799238201
O	0.39104992900260	-1.63491345291440	0.36935677037762

8 X-ray Diffraction Studies

8.1 General Considerations

Crystals were mounted in hydrocarbon oil on a nylon fiber. Low-temperature (100 K) data were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo κ_α radiation ($\lambda = 0.71073$ Å) with ω- and ϕ- scans. A semi-empirical absorption correction was applied to the diffraction data using SADABS.[14] All structures were solved by intrinsic phasing using SHELXT[15] and refined against F^2 on all data by full-matrix least squares with SHELXL-2015[16] using established methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). Descriptions of the individual refinements follow below and details of the data quality and a summary of the residual values of the refinements for all structures are given. Further details can be found in the form of .cif files available from the CCDC.

8.2 X-Ray Diffraction Study of [PPN][H_3NiPr][9]

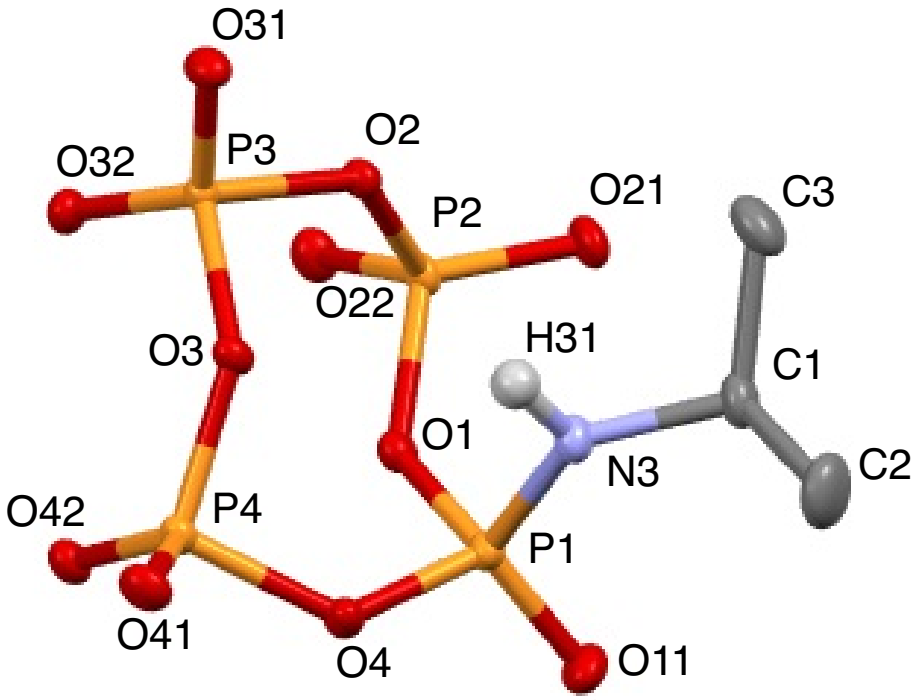

Figure S178: Single crystal X-ray Structure of [PPN][H_3NiPr][**9**] with thermal ellipsoids set at 50% and the PPN and isopropylammonium counterions and most hydrogen atoms omitted for clarity.

Colorless diffraction quality crystals of [PPN][H_3NiPr][**9**] were grown by vapor diffusion of diethyl ether into an acetonitrile solution of [PPN][H_3NiPr][9]. No disorder was modeled and the ammonium NH hydrogens were located in the difference electron density map.

Table S2: Crystallographic Table for [PPN][H_3NiPr][**9**].

Identification code	**9**	
CCDC Code	CCDC 1991326	
Empirical formula	C78 H78 N4 O11 P8	
Formula weight	1495.20	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 16.3718(13) Å	α= 80.413(2)°
	b = 16.3947(13) Å	β= 63.417(2)°
	c = 16.8901(14) Å	γ = 61.422(2)°
Volume	3553.8(5) Å^3	
Z	2	
Density (calculated)	1.397 Mg/m^3	
Absorption coefficient	0.262 mm^{-1}	
$F(000)$	1564.0	
Crystal size	0.300 × 0.200 × 0.160 mm^3	
Theta range for data collection	1.351° to 29.188°	
Index ranges	-22<=h<=22, -22<=k<=22, -23<=l<=23	
Reflections collected	170934	
Independent reflections	16754 [R(int) = 0.0319]	
Completeness to theta = 29.188°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16754 / 1 / 926	
Goodness-of-fit on F2	1.032	
Final R indices [I>2σ(I)]	R_1 = 0.0319, wR_2 = 0.0859	
R indices (all data)	R_1 = 0.0319, wR_2 = 0.0859	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.418 and -0.436 eÅ^{-3}	

References

[1] Hossner, L. R.; Trostle, C. L.; Shahandeh, H. Preparation and analysis of cyclotri-and cyclotetraphosphate and their hydrolysis products in soil. *J. Agri. Food Chem.* **2003**, *51*, 6274–6279.

[2] Kamimura, S.; Kuwata, S.; Iwasaki, M.; Ishii, Y. *Inorg. Chem.* **2004**, *43*, 399–401.

[3] Jiang, Y.; Chakarawet, K.; Kohout, A. L.; Nava, M.; Marino, N.; Cummins, C. C. *J. Am. Chem. Soc.* **2014**, *136*, 11894–11897.

[4] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and convenient procedure for solvent purification. *Organometallics* **1996**, *15*, 1518–1520.

[5] Jiang, Y.; Chakarawet, K.; Kohout, A. L.; Nava, M.; Marino, N.; Cummins, C. C. Dihydrogen tetrametaphosphate, $[P_4O_{12}H_2]^{2-}$: Synthesis, solubilization in organic media, preparation of its anhydride $[P_4O_{11}]^{2-}$ and acidic methyl ester, and conversion to tetrametaphosphate metal complexes via protonolysis. *J. Am. Chem. Soc.* **2014**, *136*, 11894–11897, PMID: 25102033.

[6] Transue, W. J.; Yang, J.; Nava, M.; Sergeyev, I. V.; Barnum, T. J.; McCarthy, M. C.; Cummins, C. C. Synthetic and spectroscopic investigations enabled by modular synthesis of molecular phosphaalkyne precursors. *J. Am. Chem. Soc.* **2018**, *140*, 17985–17991.

[7] Nakamura, T.; Yonemura, S.; Nabeshima, T. Synthesis of per (5-N-carboxamide-5-dehydroxylmethyl)-β-cyclodextrins and their selective recognition ability utilizing multiple hydrogen bonds. *Chem. Comm.* **2019**, *55*, 3872–3875.

[8] Mohamady, S.; Taylor, S. D. Synthesis of nucleoside 5'-tetraphosphates containing terminal fluorescent labels via activated cyclic trimetaphosphate. *J. Org. Chem.* **2014**, *79*, 2308–2313.

[9] Michailidou, F.; Chung, C.-W.; Brown, M. J.; Bent, A. F.; Naismith, J. H.; Leavens, W. J.; Lynn, S. M.; Sharma, S. V.; Goss, R. J. Pac13 is a Small, Monomeric Dehydratase that Mediates the Formation of the 3'-Deoxy Nucleoside of Pacidamycins. *Angew. Chem. Int. Ed.* **2017**, *56*, 12492–12497.

[10] Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785.

[11] Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[12] Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[13] Neese, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci* **2012**, *2*, 73–78.

[14] Sheldrick, G. M. SADABS. 1996.

[15] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.

[16] Sheldrick, G. M.; Schneider, T. R. *[16] SHELXL: High-resolution refinement*; 1997; pp 319–343.