

A Pentametallic Co₅L₄ Architecture Constructed From *Bis*-substituted Phosphate-based Ligands

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Experimental Details

General Considerations

All reagents were used as received without further purification from commercial sources. The ^1H and ^{31}P NMR spectroscopy were conducted on an Agilent 400 NMR spectrometer operating at 400 MHz for ^1H and 162 MHz for ^{31}P . Chemical shifts are described in parts per million (ppm) on the δ scale. High resolution mass spectra were recorded with a Bruker maXis 3G UHR-TOF mass spectrometer by the Departmental Service at the University of Canterbury. Microanalytical data was collected by the Departmental Service at the University of Otago.

X-ray Crystallography

Crystallographic data for all compounds was collected at the Australian Synchrotron MX1 Beamline with silicon double crystal-monochromatised Mo K α ($\lambda = 0.7108 \text{ \AA}$) radiation and ADSC Quantum 210r detector, with data reduction performed using Bluice and XDS.^{1,2} All structures were solved using direct methods with SHELXT and refined on F^2 using all data by full matrix least-squares procedures with SHELXL within OLEX2.³⁻⁵ Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms.

Experimental Details

Synthesis of *tris*(3-nitrophenyl)phosphate. Compound was prepared as previously reported in good yield.⁶ ^1H NMR (400 MHz, CDCl_3): 7.65 (dd, $J_{\text{HH}} = 15.6 \text{ Hz}$, $J_{\text{HH}} = 8.4 \text{ Hz}$, 3H), 7.68 (d, $J_{\text{HH}} = 8.4 \text{ Hz}$, 3H), 8.15 (s, 3H), 8.19 (d, $J_{\text{HH}} = 7.6 \text{ Hz}$, 3H); ^{31}P NMR (162 MHz, CDCl_3): -18.4 (s). Acc. Mass: Found: $m/z = 462.0351$. Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_4\text{P}$ 462.0333 $[\text{M} + \text{H}]^+$.

Synthesis of *bis*(3-aminophenyl)phosphoric acid. *Tris*(3-nitrophenyl)phosphate (1.60 g, 3.5 mmol) was suspended in dry MeOH (100 mL), then Pd/C catalyst (0.16 g, 10% by weight of precursor) was added and the system immediately purged with vacuum and flushed with H_2 gas, which was repeated three times to ensure removal of air. The grey suspension was stirred under H_2 gas for 90 hours to give a black suspension that was filtered through celite to collect the Pd/C catalyst and other insoluble impurities. All volatiles were removed from the pale-yellow filtrate under reduced pressure to leave a crystalline orange/brown residue. Sonicated in Et_2O (200 mL) for 30 minutes, then the filtrate decanted off and the precipitate was dried under reduced pressure to give a khaki powder. Yield = 0.107 g (2.88 mmol, 82%). ^1H NMR (400 MHz, CD_3OD): 6.35 (s.br, 2H), 6.49 (s.br, 2H), 6.51 (s.br, 2H), 6.88 (s.br, 2H), NH_2 groups not observed in CD_3OD due to H/D exchange; ^{31}P NMR (162 MHz, CD_3OD): -10.5 (s). Acc. Mass: Found: $m/z = 281.0793$. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_4\text{P}$ 281.0686 $[\text{M} + \text{H}]^+$. Acc. Mass: Found: $m/z = 561.1470$. Calcd for $\text{C}_{24}\text{H}_{27}\text{N}_4\text{O}_8\text{P}_2$ 561.1299 $[2\text{M} + \text{H}]^+$. Crystal data: $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_4\text{P}$, $M_r = 280.21$, $T = 100(2) \text{ K}$, triclinic, space group $P-1$ (No. 2), $a = 6.9800(14) \text{ \AA}$, $b = 9.0400(18) \text{ \AA}$, $c = 10.340(2) \text{ \AA}$, $\alpha = 83.62(3)^\circ$, $\beta = 81.85(3)^\circ$, $\gamma = 77.85(3)^\circ$, $V = 629.2(2) \text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 1.479 \text{ Mg m}^{-3}$, $\mu(\text{synchrotron}) = 0.23 \text{ mm}^{-1}$, colourless plate, $0.01 \times 0.05 \times 0.05 \text{ mm}$, 11100 measured reflections with $2\theta_{\text{max}} = 52.8^\circ$, 2560 independent reflections, 2560 absorption-corrected data used in F^2 refinement, 192 parameters, no restraints, $R_1 = 0.040$, $wR_2 = 0.107$ for 2265 reflections with $I > 2\sigma(I)$, CCDC 1569646.

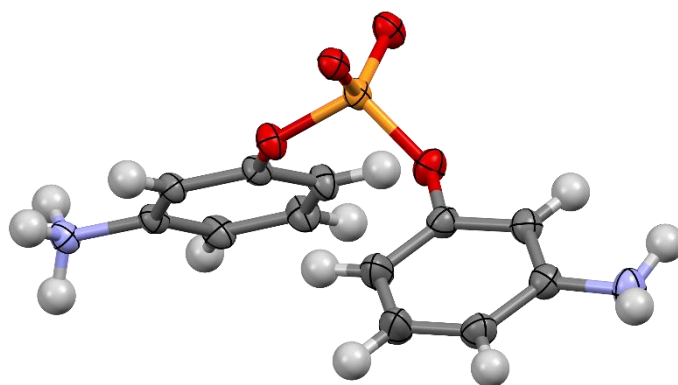


Figure S1: The solid-state structure of bis(3-aminophenyl)phosphoric acid in a zwitterionic form (thermal ellipsoids at 50% probability).

Synthesis of $[\text{Co}_5\text{L}_4(\text{MeCN})_4][\text{BF}_4]_6$. Bis(4-aminophenyl)phosphoric acid (44.8 mg, 0.16 mmol) and $\text{Co}(\text{BF}_4)_2 \cdot 6(\text{H}_2\text{O})$ (68.1 mg, 0.20 mmol) were suspended in acetonitrile (40 mL), followed by addition of 2-pyridinecarboxaldehyde (30.4 μL , 0.32 mmol) to immediately give an orange solution. The reaction was stirred for 2 hours, filtered through a grade 3 or 4 sinter and the filtrate subsequently vapour diffused with an excess of benzene as the anti-solvent to yield X-ray diffraction quality crystals after several days. Yield = 21.3 mg (0.0076 mmol, 19%). Anal. Found: C, 42.30; H, 3.24; N, 7.88%. Calcd for $[\text{C}_{96}\text{H}_{72}\text{Co}_5\text{N}_{16}\text{O}_{16}\text{P}_4][\text{BF}_4]_6 \cdot 4(\text{H}_2\text{O})$: C, 42.44; H, 2.97%; N, 8.25% (*N.B. satisfactory elemental analysis could not be obtained from the isolated crystalline material. Subsequent drying under reduced pressure removed all volatile solvates, though opportunistic water (acquired during transport of the samples) was detected during analysis as a consequence*).

Crystal data: $[\text{C}_{104}\text{H}_{84}\text{Co}_5\text{N}_{20}\text{O}_{16}\text{P}_4][\text{BF}_4]_6 \cdot 7(\text{C}_6\text{H}_6) \cdot 4(\text{C}_2\text{H}_3\text{N})$, $M_r = 3520.27$, $T = 100(2)$ K, monoclinic, space group $I2$, $a = 20.379(4)$ Å, $b = 20.997(4)$ Å, $c = 20.579(4)$ Å, $\beta = 92.08(3)^\circ$, $V = 8800(3)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.329$ Mg m⁻³, $\mu(\text{synchrotron}) = 0.59$ mm⁻¹, yellow plate, 0.01 x 0.10 x 0.20 mm, 34571 measured reflections with $2\theta_{\text{max}} = 54.2^\circ$, 19143 independent reflections, 19143 absorption-corrected data used in F^2 refinement, 1074 parameters, 186 restraints, $R_1 = 0.061$, $wR_2 = 0.165$ for 17926 reflections with $I > 2\sigma(I)$, CCDC 1569647.

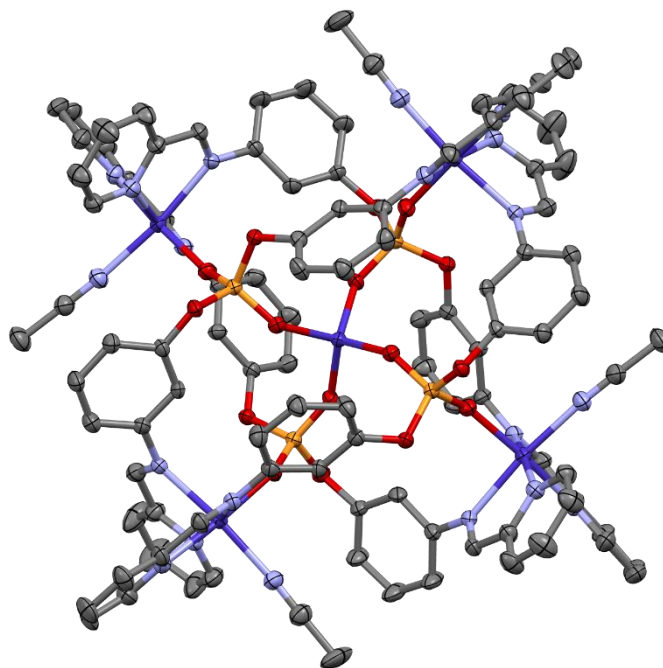


Figure S2: The solid-state structure of $[\text{Co}_5\text{L}_4(\text{MeCN})_4]^{6+}$ from $[\text{Co}_5\text{L}_4(\text{MeCN})_4][\text{BF}_4]_6 \cdot 7(\text{C}_6\text{H}_6) \cdot 4(\text{C}_2\text{H}_3\text{N})$ (hydrogen atoms, anions, and solvates omitted for clarity; thermal ellipsoids at 50% probability).

Side-product. A trace amount of a monometallic coordination complex was observed as a side-product by SCXRD when crystallising $[\text{Co}_5\text{L}_4(\text{MeCN})_4][\text{BF}_4]_6$ (*vide supra*). Crystal data: $[\text{C}_{24}\text{H}_{16}\text{CoN}_6\text{O}_4][\text{BF}_4] \cdot 2(\text{C}_2\text{H}_3\text{N})$, $M_r = 680.27$, $T = 100(2)$ K, monoclinic, space group $P2_1/c$, $a = 12.803(3)$ Å, $b = 16.333(3)$ Å, $c = 14.884(3)$ Å, $\beta = 112.62(3)^\circ$, $V = 2873.1(12)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.573$ Mg m⁻³, $\mu(\text{synchrotron}) = 0.68$ mm⁻¹, orange plate, 0.01 x 0.10 x 0.20 mm, 23903 measured reflections with $2\theta_{\text{max}} = 56.6^\circ$, 7032 independent reflections, 7032 absorption-corrected data used in F^2 refinement, 417 parameters, no restraints, $R_1 = 0.055$, $wR_2 = 0.154$ for 5225 reflections with $I > 2\sigma(I)$, CCDC 1569648.

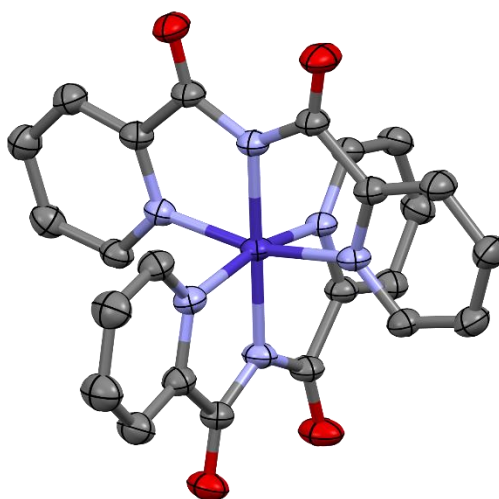


Figure S3: The solid-state structure of $[\text{C}_{24}\text{H}_{16}\text{CoN}_6\text{O}_4]^+$ from $[\text{C}_{24}\text{H}_{16}\text{CoN}_6\text{O}_4][\text{BF}_4] \cdot 2(\text{C}_2\text{H}_3\text{N})$ (hydrogen atoms, anion, and solvates omitted for clarity; thermal ellipsoids at 50% probability).

NMR Spectroscopy

Figure S4: The ^1H NMR spectrum for tris(3-nitrophenyl)phosphate in CDCl_3 .

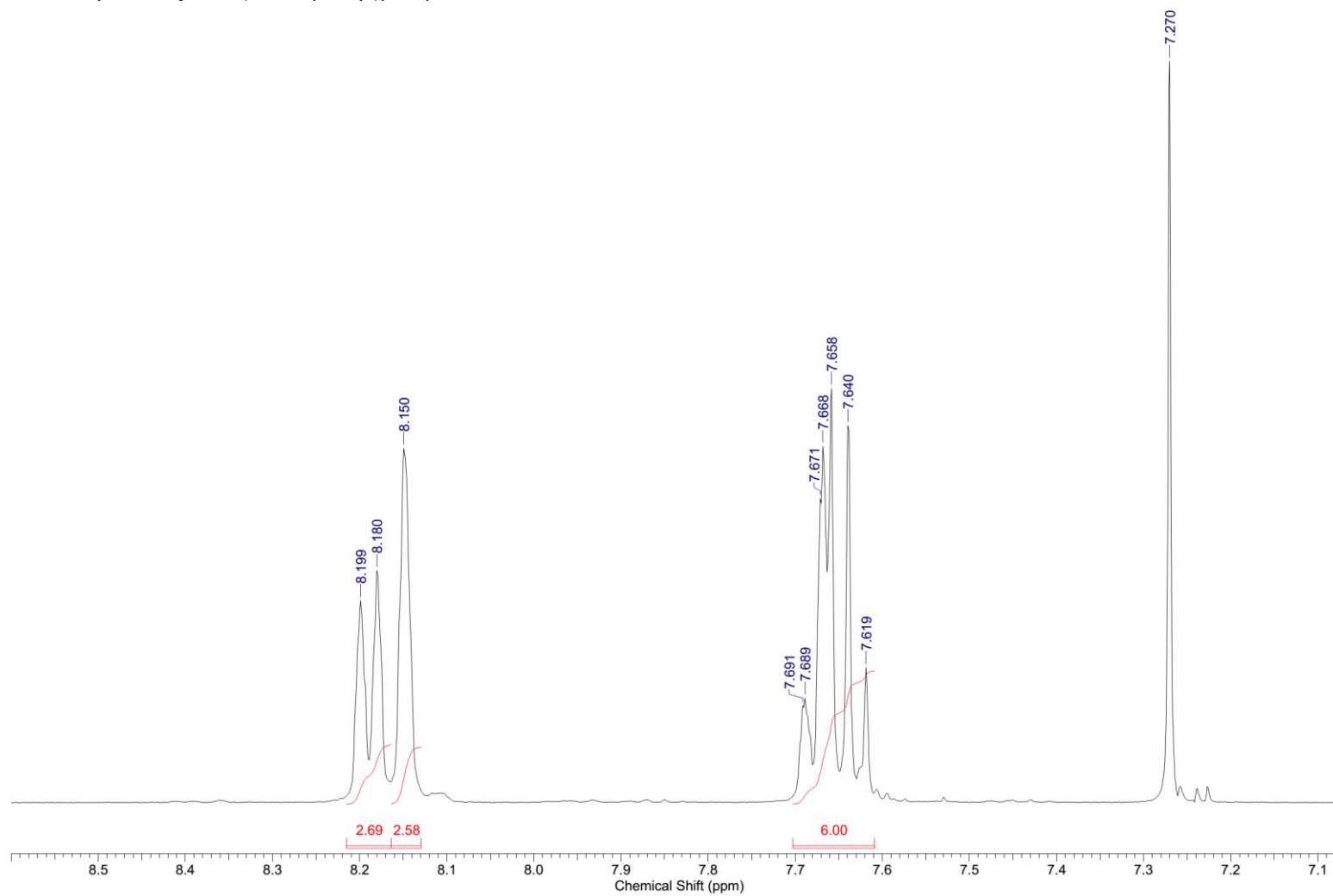


Figure S5: The ^{31}P NMR spectrum for tris(3-nitrophenyl)phosphate in CDCl_3 .

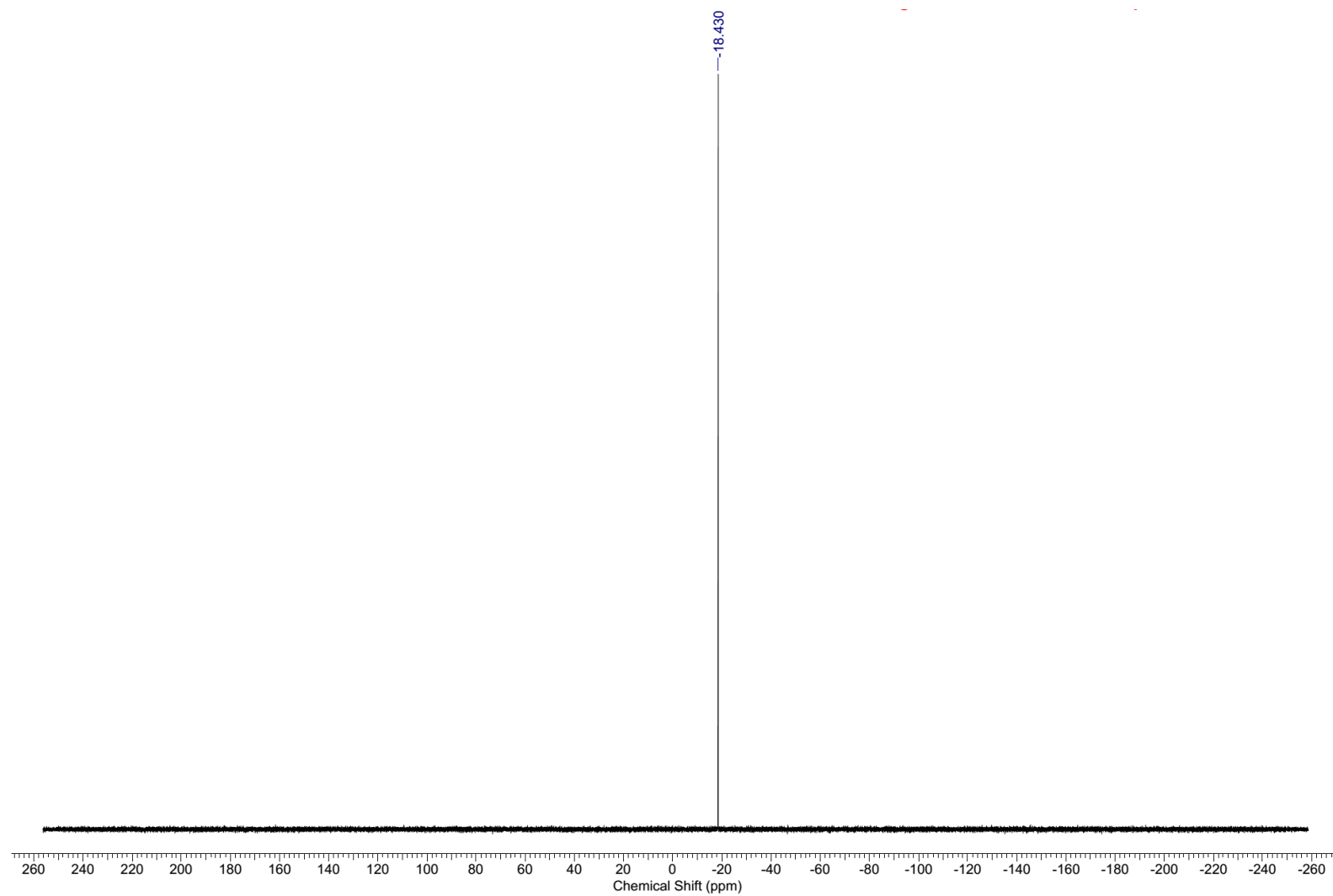


Figure S6: The ^1H NMR spectrum for bis(3-aminophenyl)phosphoric acid in CD_3OD .

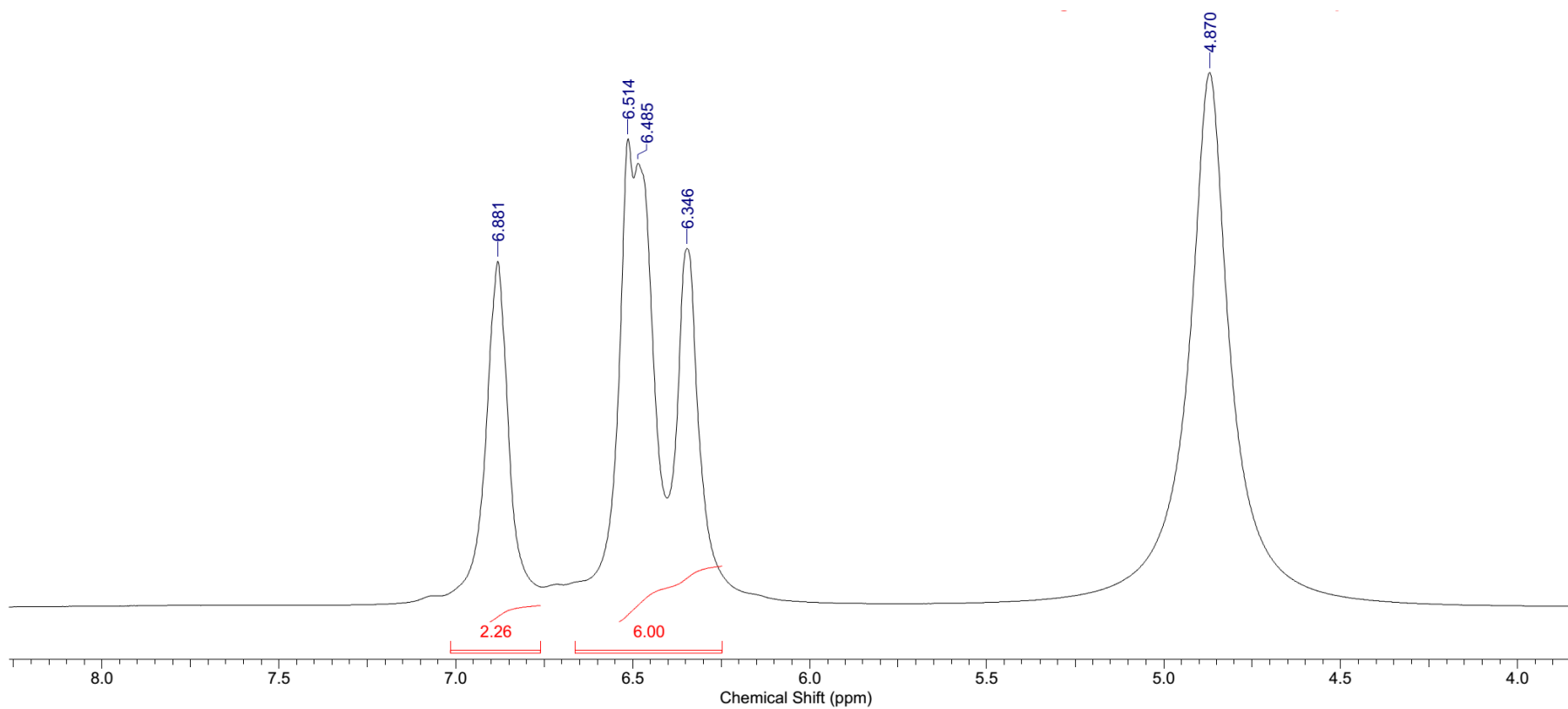
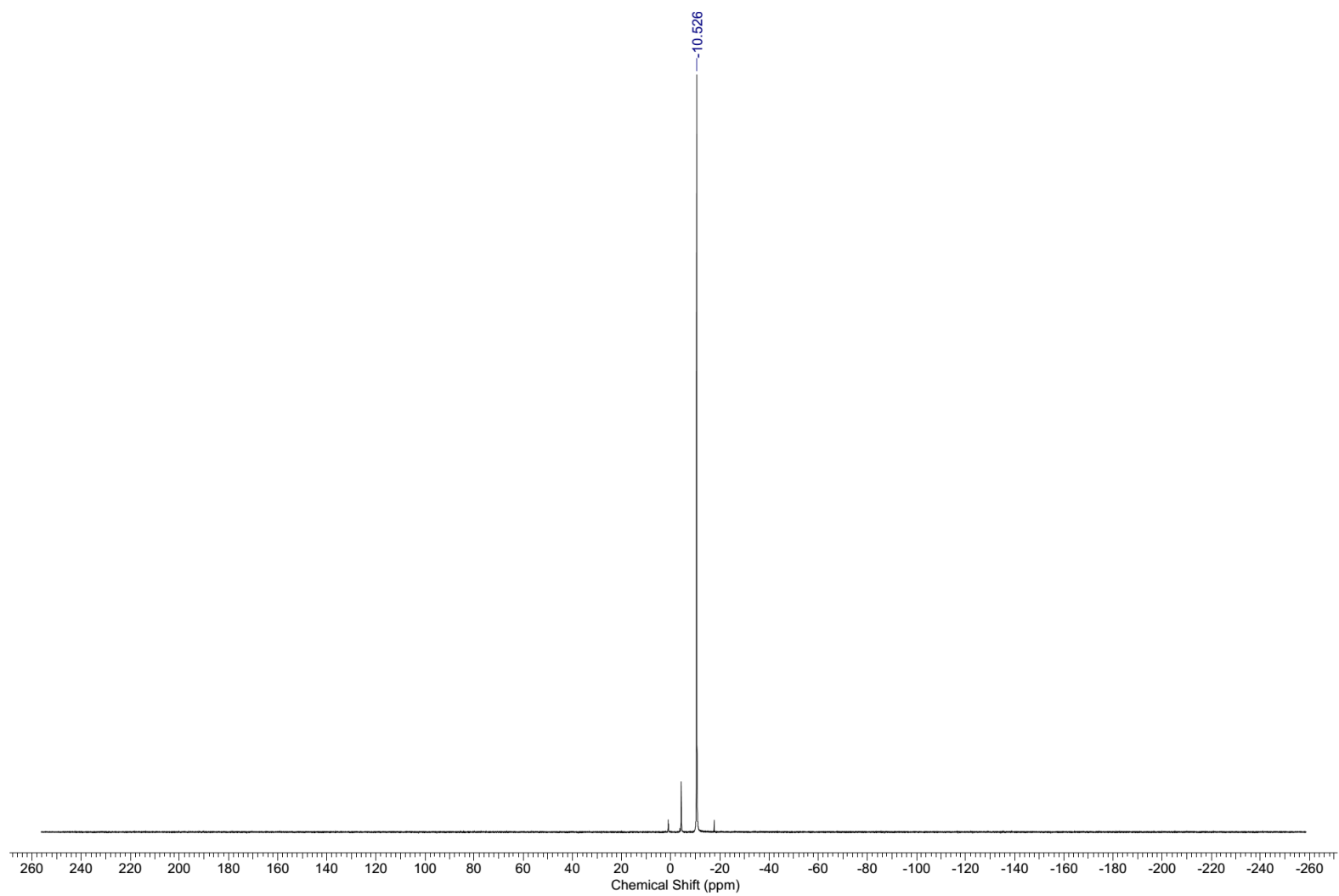


Figure S7: The ^{31}P NMR spectrum for bis(3-aminophenyl)phosphoric acid in CD_3OD .



High Resolution Mass Spectroscopy

tris(3-nitrophenyl)phosphate

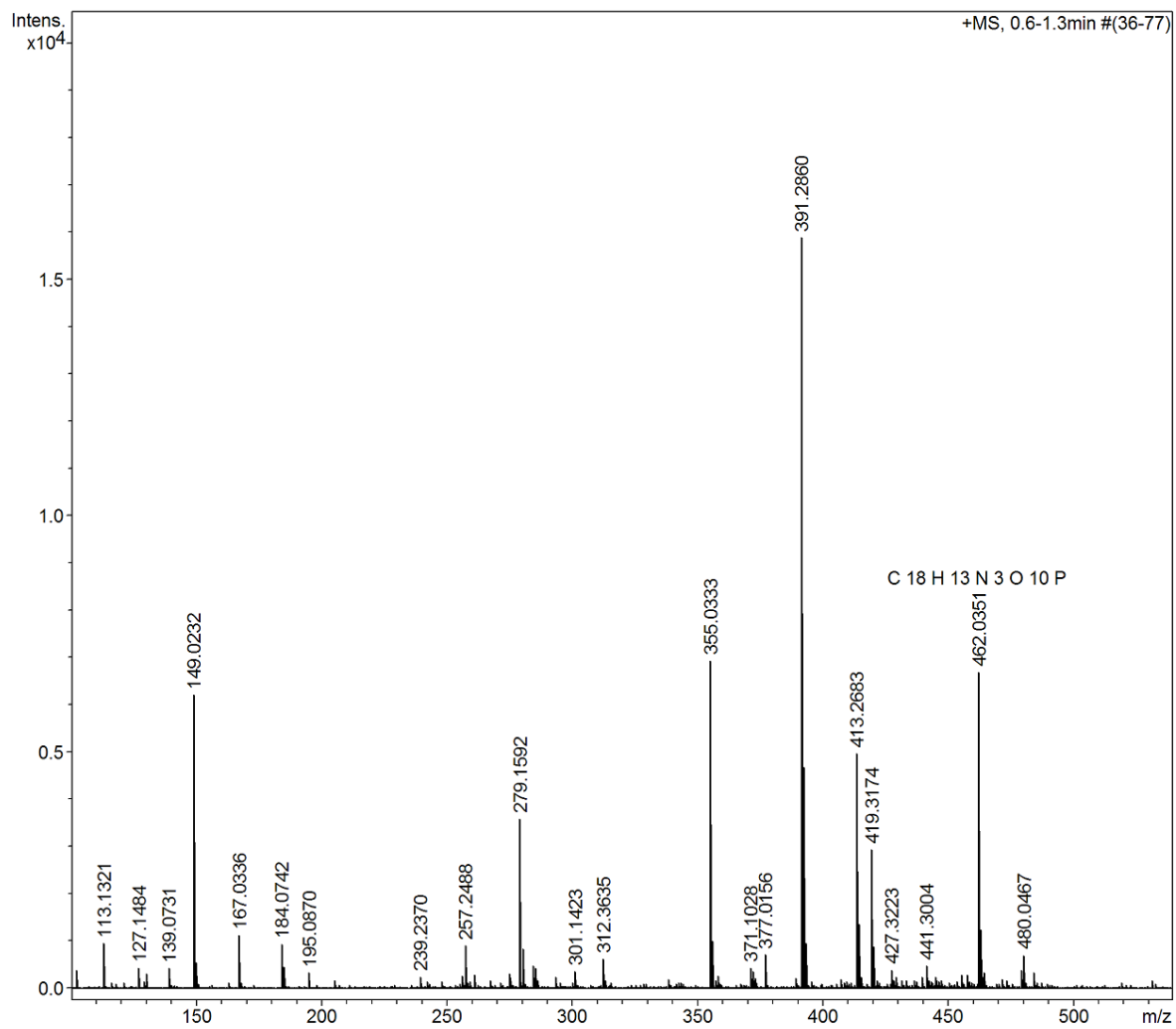


Figure S8: The experimental mass spectrum from a methanol diluted CHCl₃ solution of C₁₈H₁₃N₃O₁₀P.

bis(3-aminophenyl)phosphoric acid

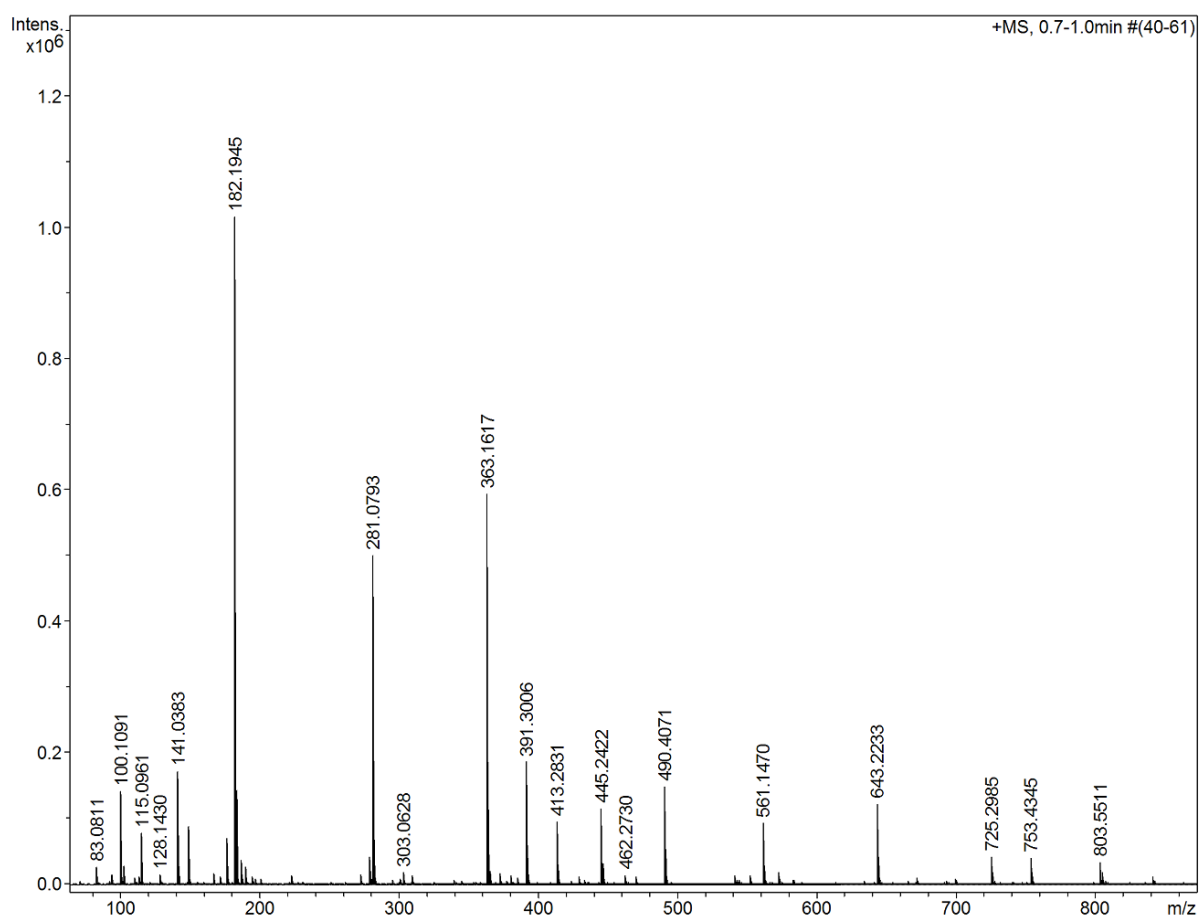


Figure S9: The experimental mass spectrum from a methanol solution of C₁₂H₁₃N₂O₄P.

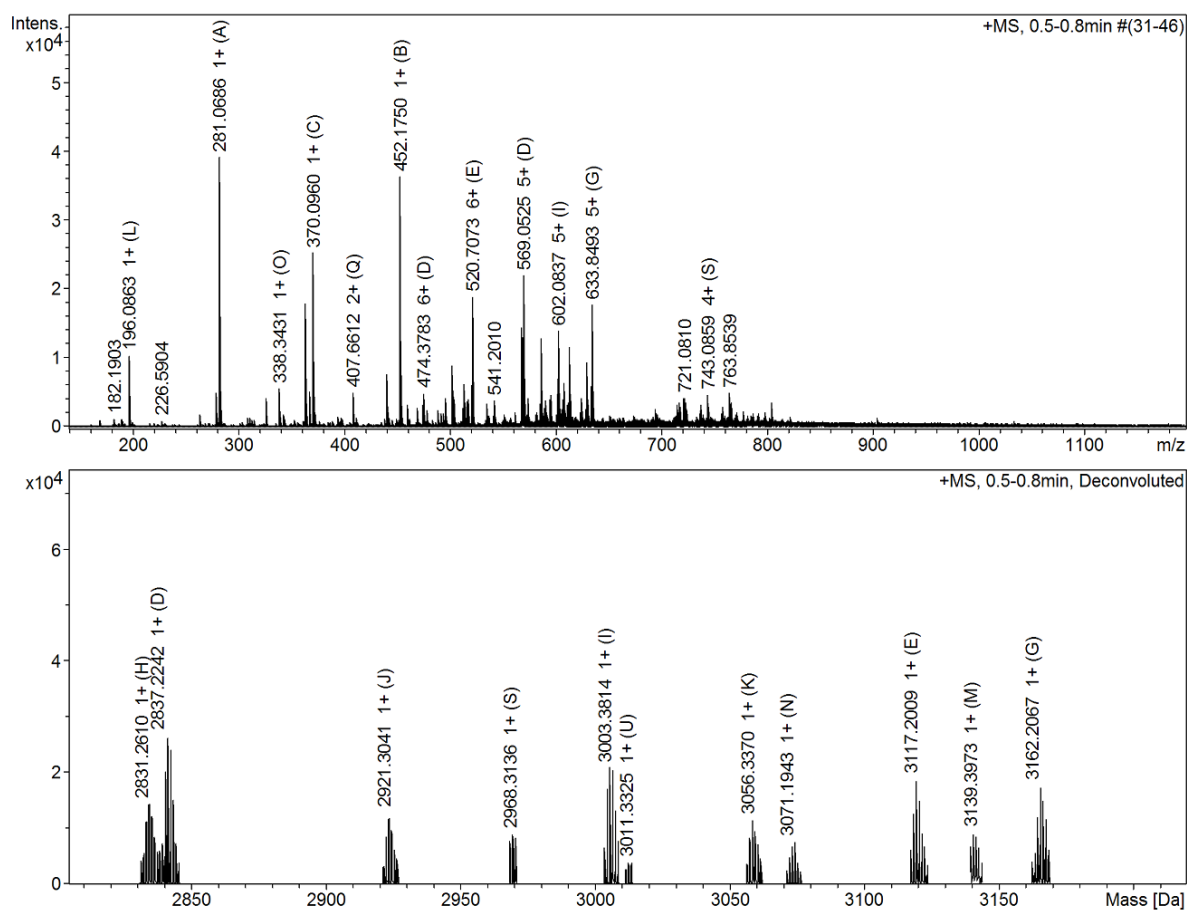


Figure S10: The experimental mass spectrum from an acetonitrile solution of C₁₀₄H₈₄B₆Co₅F₂₄N₂₀O₁₆P₄.

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