Selective separations of Am(III)/Eu(III) Using Heterocyclic Bistriazinyl Phosphonate Grafted Zirconia and Titania Solid Phase Extractants

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Caution! The Am-241 and Eu-152 solutions used in this study were highly radioactive. All handling and performance were carried out in a dedicated radiological facility using well-established radiological safety protocols.

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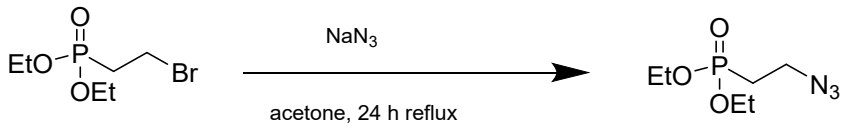
Chapter I: Ligand synthesis

Synthesis of diethyl-2-azidoethylphosphonate

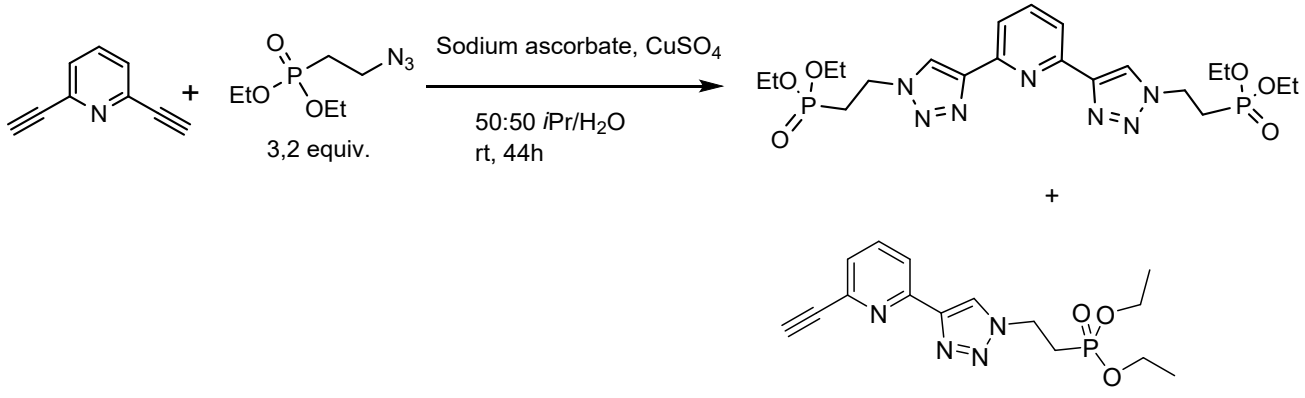


Diethyl-2-azidoethylphosphonate was synthesized according to the synthesis described by *Ma et al.*[1] Diethyl(2-bromoethyl)phosphonate (6.000 g 24.48 mmol) and sodium azide (2.240 g, 36.90 mmol) were dissolved in 45 mL of anhydrous acetone and the solution was refluxed under argon for 24 h. After the reaction, the mixture was filtered over a pad of celite and the solvent was removed under reduced pressure. The remaining oil was diluted with water and extracted with Et_2O three times. Combined organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The product was obtained as clear, slightly yellow oil (4,500 g, 21,70 mmol, 89% yield) and that was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, *J* = 7.1 Hz, 6H), 1.99–2.12 (m, 2H), 3.49–3.60 (m, 2H), 4.03–4.21 (m, 4H).[2]

^{13}C NMR (101 MHz, $CDCl_3$): δ 16.6 (d, *J* = 6.1 Hz, 2 C), 26.2 (d, *J* = 140.8 Hz), 45.6 (d, *J* = 2.1 Hz), 62.1 (d, *J* = 6.4 Hz, 2 C).[2]

Synthesis of 2,6-bis(1,2,3-triazol-1-diethylethanephosphonate)pyridine (PyTri) and formation of ethynylpyridine-1,2,3-triazol-1-diethylethanephosphonate (EPTEP) as byproduct



2,6-bis(1,2,3-triazol-1-diethylethanephosphonate)pyridine (PyTri ligand) was synthetized following the literature protocols,[3,4] including slight modifications. Crude diethyl-2-azidoethylphosphonate (2,000 g, 9.66 mmol, 3,2 equiv.) and 2,6-diethynylpyridine (0.395 g, 3.10 mmol) were added to a solution of 2-propanol and H_2O (11:11 mL solution), followed by an addition of sodium ascorbate (0.125 g, 0.65 mmol, 0.2 equiv.) and $CuSO_4 \cdot 5\ H_2O$ (17 mg, 0.063 mmol, 0.02 equiv.) to the reaction mixture. The obtained brown solution was then stirred for 48 h at rt. Thereafter, the organic solvent was removed under reduced pressure, and the residual mixture was transferred to an extraction funnel and diluted with 10 mL water. Consequently, the aqueous solution was extracted with DCM (3x 30 mL). The organic phases were finally combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. As a result, ethynylpyridine-1,2,3-triazol-1-diethylethanephosphonate was formed together with 2,6-bis(1,2,3-triazol-1-diethylethanephosphonate)pyridine and the crude products were purified and isolated via gradient column chromatography (starting from 99:1 DCM:MeOH up to 90:10 DCM:MeOH). Both products were obtained as a brown viscous oil. The click reaction favoured the formation of Ethynylpyridine-1,2,3-triazol-1-diethylethanephosphonate in the prevalent conditions.

2,6-bis(1,2,3-triazol-1-diethylethanephosphonate)pyridine (550 mg, 1.02 mmol, 33 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (t, *J* = 7.1 Hz, 12H), 2.43–2.56 (m, 4H), 4.06–4.17 (m, 8H), 4.64–4.77 (m, 4H), 7.82–7.90 (m, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 8.24 (s, 2H).[3]

^{13}C NMR (101 MHz, $CDCl_3$): δ 16.5 (d, *J* = 6.1 Hz), 27.5 (d, *J* = 141.3 Hz), 44.9, 62.4 (d, *J* = 6.5 Hz), 119.4, 122.7, 137.9, 148.6, 150.0.[3]

^{31}P NMR (162 MHz, D_2O): δ 25.2.[3]

HRMS (ESI-TOF) m/z: [PyTRI+Na]+ calculated for $C_{21}H_{33}N_7O_6P_2Na$ 564.1860; Found 564.1853; Error 1.2 ppm

Ethynylpyridine-1,2,3-triazol-1-diethylethanephosphonate (580 mg, 1.69 mmol, 56 % yield).

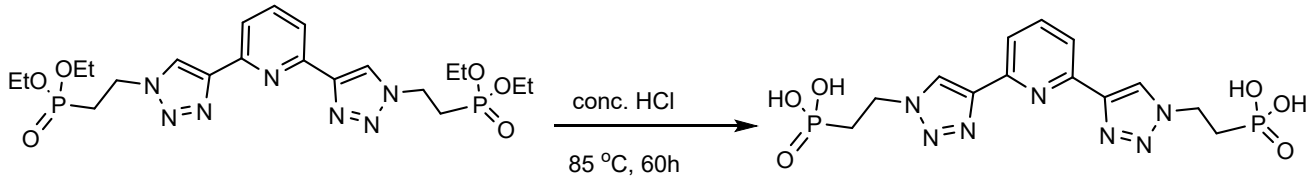
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (t, *J* = 7.1 Hz, 6H), 2.40–2.53 (m, 2H), 3.17 (s, 1H), 4.05–4.20 (m, 4zH), 4.62–4.73 (m, 2H), 7.42 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.71-7.82 (m, 1H), 8.16 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.27 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$):z δ 16.5 (d, *J* = 6.1 Hz), 27.5 (d, *J* = 141.4 Hz), 45.0, 62.4 (d, *J* = 6.5 Hz), 77.2, 82.9, 120.2, 123.1, 126.8, 137.2, 142.1, 148.0, 150.8.

^{31}P NMR (162 MHz, D_2O): δ 25.1.

HRMS (ESI-TOF) m/z: [EPTEP-H+Na]+ calculated for $C_{15}H_{19}N_4O_3P_1Na$ 357.1087; Found 357.1085; Error 0.55 ppm

Synthesis of 2,6-bis(1,2,3-triazol-1-ethanephosphonate)pyridine (hydrolysed PyTri)



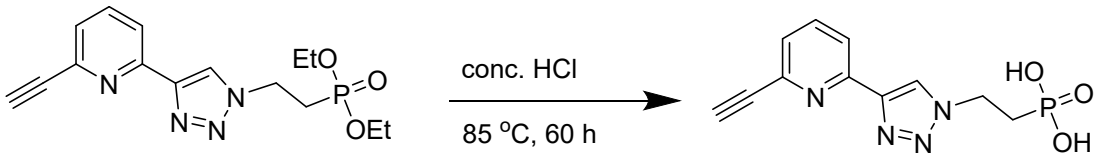
2,6-bis(1,2,3-triazol-1-diethylethanephosphonate)pyridine was hydrolyzed by diluting 210 mg (0.39 mmol) of the product in 3 mL of conc. HCl (37%) and refluxing the resulting solution at 85 °C with vigorous stirring for 60 h. The resulting mixture was kept under reduced pressure for 24 h to yield the product (hydrolyzed PyTri) as sticky brown semisolid (139 mg, 0.32 mmol, 83 % yield).

^{1}H NMR (400 MHz, D_2O): δ 2.39–2.52 (m, 4H), 4.67–4.77 (m, 4H), 7.99 (d, *J* = 8.0 Hz, 2H), 8.26–8.34 (m, 1H), 8.70 (s, 2H).[3]

^{13}C NMR (101 MHz, D_2O): δ 26.9, 28.2, 45.6 (2 C), 122.7, 126.5, 140.5, 144.1, 145.3.[3]

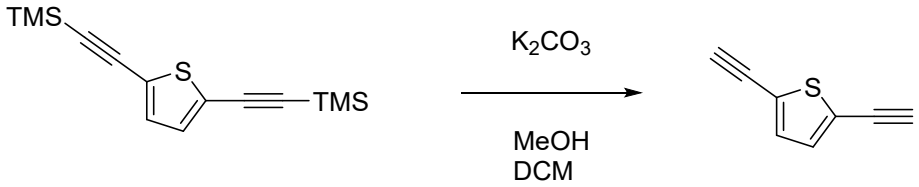
^{31}P NMR (162 MHz, D_2O): δ 23.1.[3]

Synthesis of ethynylpyridine-1,2,3-triazol-1-ethanephosphonate (hydrolysed EPTEP)



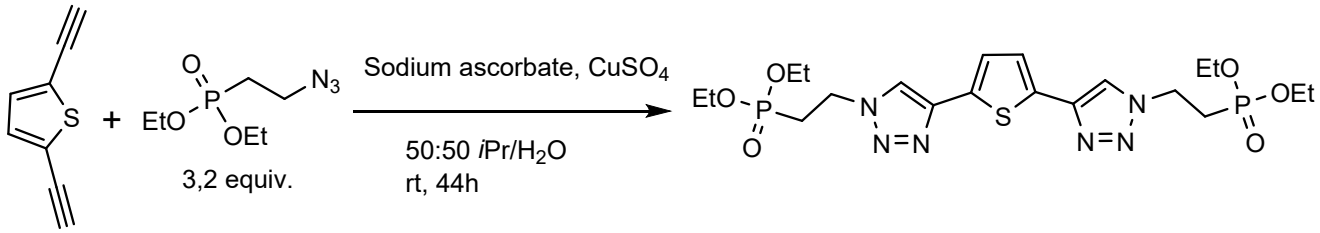
Hydrolysis of ethynylpyridine-1,2,3-triazol-1-diethylethanephosphonate (100 mg, 0.30 mmol) was carried out by dilution in 3 mL of conc. HCl (37%) and refluxing the solution at 85 °C with vigorous stirring for 60 h. The solvent was removed under vacuum to afford ethynylpyridine-1,2,3-triazol-1-ethanephosphonate as light opaque brown solid (65 mg, 23 mmol, 78 % crude yield). The obtained product was used as such and dissolved in 1 M HCl prior to functionalization of zirconia.

Synthesis of 2,5-diethynyltiophene



2,5-diethyltiophene was synthetized according to the synthesis pathway described by *Roy et al.*[5] 2,5-Bis[ethynyl(trimethylsilyl)]thiophene (500 mg, 1.81 mmol) and potassium carbonate (410 mg, 2.98 mmol) were put in a mixture of DCM (7.5 mL) and MeOH (5 mL) and the reaction was stirred at room temperature for 2 h. After, reaction mixture was poured into water and solution was extracted with DCM three times. The combined organic phases were washed with brine solution and dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, crude product (220mg, 1.66 mmol, 92% yield) was obtained, and it was used later without further purification.

Synthesis of 2,5-bis(1,2,3-triazol-1-diethylethanephosphonate)tiophene



2,5-bis(1,2,3-triazol-1-diethylethanephosphonate)tiophene was synthetized according to the modified synthesis adopted from *Brunet et al.*[3] Crude 2,5-diethynylthiophene (200 mg, 1.51 mmol) and crude diethyl-2-azidophosphonate (1.000 g, 4.83 mmol 3.2 equiv.) were dissolved in a mixture of 2-propanol and H_2O (9:9 mL solution) and sodium ascorbate (90 mg, 0.47 mmol) and $CuSO_4.5H_2O$ (15 mg) were added. The resulting light brown solution was stirred at room temperature for 48 h. After the organic solvent was removed under reduced pressure, the mixture was transferred to an extraction funnel, diluted with 5 ml of water and extracted with DCM (3 x 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The resulting crude product was purified via gradient column

chromatography (starting from 99:1 DCM:MeOH up to 90:10:1 DCM:MeOH:Et_3N) to afford the product (610 mg, 1.12 mmol, 74% yield, around 90-95% purity) as off-white solid.

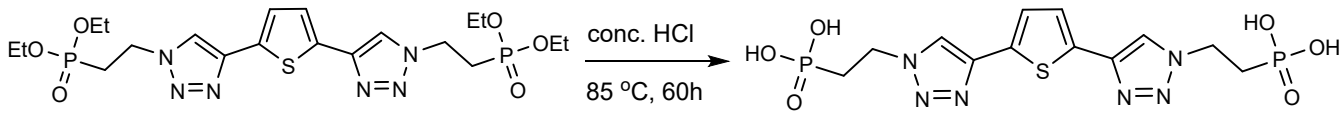
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (t, *J* = 7.1 Hz, 12H), 2.44–2.52 (m, 4H), 4.08–4.17 (m, 8H), 4.66–4.73 (m, 4H), 7.38 (s, 2H), 7.81 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 16.5 (d, *J* = 6.0 Hz), 27.4 (d, *J* = 141.5 Hz), 44.9 (d, *J* = 2.3 Hz), 62.3 (d, *J* = 6.5 Hz), 119.9, 124.9, 132.4, 142.7.

^{31}P NMR (162 MHz, D_2O): δ 25.3

HRMS (ESI-TOF) m/z: [BTEPT+Na]+ calculated for $C_{20}H_{32}N_6O_6P_2S_1Na$ 569.1471; Found 569.1474; Error 0.44 ppm

Synthesis of 2,5-bis(1,2,3-triazol-1-ethanephosphonate)tiophene (BTEPT)



Hydrolysis of 2,5-Bis(1,2,3-triazol-1-diethylethanephosphonate)tiophene (250 mg, 0.46 mmol) was carried out in 4 mL of conc. HCl (37%) and refluxing the resulting solution at 85 °C with vigorous stirring for 60 h. The aqueous HCl was removed under vacuum to afford 2,6-bis(1,2,3-triazol-1-ethanephosphonate)tiophene as brown solid (173 mg, 0.40 mmol, 87 % crude yield). The obtained product was used as such and dissolved in 1 M HCl prior to functionalization of zirconia.

Thin layer chromatography

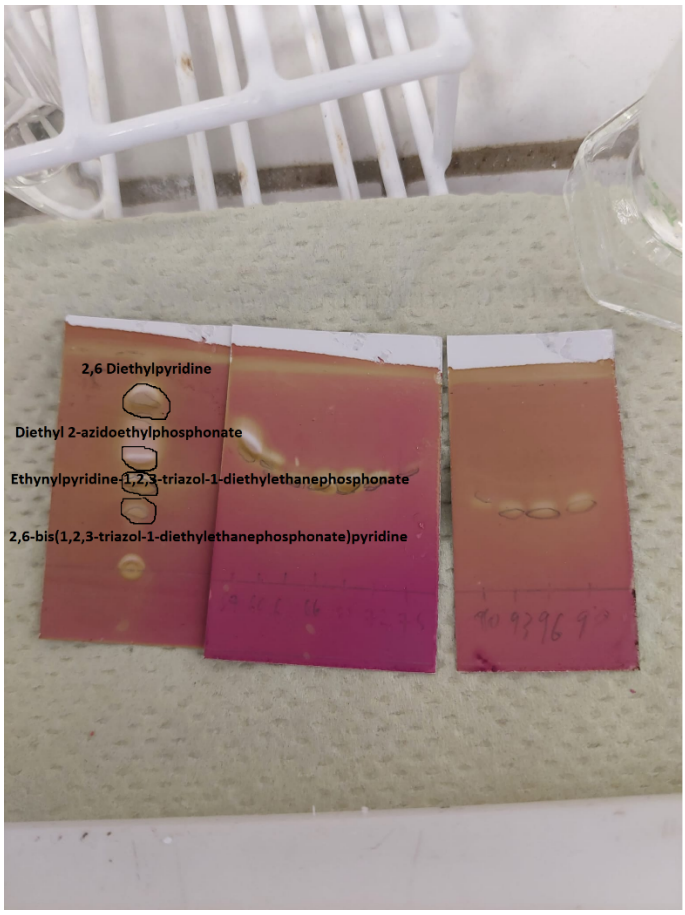


Figure S1. Thin layer chromatography of the PyTri and ETPTEP ligand purification.

Chapter II: Hybrid material synthesis

Titanium dioxide synthesis

Porous titanium dioxide was prepared according to the literature with modifications.[6] Around 200 mL of 1-propanol (Fischer Scientific 99.94 %, total amount 243 mL, 3.25 mol) was heated and stearic acid (Sigma Aldrich, 97.0%, 44.51 g, 0.156 mol) was gradually added. Titanium isopropoxide:stearic acid:1-propanol molar ratio in the synthesis was 1:2.5:52. Titanium isopropoxide (>97.0%, 17.92 g, 0.063 mol) was mixed with

43 mL 1-propanol and transferred to a 100 mL separation funnel. This mixture was added dropwise to propanol-stearic acid solution and heating was stopped prior to addition. Vigorous stirring was maintained. After addition of all titaniumisopropoxide solution, stirring was stopped and the final mixture was left standing uncovered to a fumehood at room temperature overnight. The resulting mixture was a white viscous gel, and it was transferred to a ceramic crucible for drying at 50 °C for 24 h. Heating was continued at 170 °C for 1 h and then at 450 °C for 4h. Finally the crude white product was grinded to a fine powder via mortar and pestle and sieved to a size of 74-149 um.

ZrPyTri synthesis

ZrO_2 was purchased from Saint-Gobain NorPro. Reagents were used as supplied without further purification. 2,6-bis(1,2,3-triazol-1-ethanephosphonate)pyridine (37.9 mg, 0,089 mmol) (PyTri) was diluted in 9 mL 1 M HCl for **ZrPyTri1** after which the resulting solution was quenched with zirconiumdioxide (300 mg, 2.44 mmol) in a 15 mL centrifuge tube. For **ZrPyTri2,** PyTri ligand (20.0 mg, 0.047 mmol) was diluted in 10 mL 1 M HCl and the solution was quenched with zirconium dioxide (300 mg, 2.44 mmol). The resulting suspension was rocked bottom-to-top to detach all the solid, and the mixture was equilibrated in rotary mixer for 24 h at room temperature. The solution was centrifuged using a Thermo Fischer Scientific Heareus Megafuge 1.0R with 2773 rcf for 10 minutes and the supernatant was decanted away. The remaining solid material was washed with 10 mL H_2O and vigorously shaken five times. The solution was centrifuged after each cycle and the water decanted away. Finally, the solid was transferred to a crucible and dried in oven at 70 °C for 24h. The resulting opaque brown solid was ground to a fine powder in a mortar and pestle.

TiPyTri synthesis

2,6-bis(1,2,3-triazol-1-ethanephosphonate)pyridine (41.1 mg, 0,100 mmol) (PyTri) was diluted in 9 mL 1 M HCl after which the resulting solution was quenched with titanium dioxide (200 mg, 2.50 mmol) in a 15 mL centrifuge tube. The resulting suspension was rocked bottom-to-top to detach all the solid, and the mixture was equilibrated in rotary mixer for 24 h at room temperature. The solution was centrifuged using a Thermo Fischer Scientific Heareus Megafuge 1.0R with 2773 rcf for 10 minutes and the supernatant was decanted away. The remaining solid material was washed with 10 mL H_2O and vigorously shaken five times. The solution was centrifuged after each cycle and the water decanted away. Finally, the solid was transferred to

a crucible and dried in oven at 70 °C for 24h. The resulting off- white solid was ground to a fine powder in a mortar and pestle.

ZrEPTEP synthesis

1-Triazolyl ethylene phosphonic acid pyridine (31.2 mg, 0.112 mmol) (EPTEP) was diluted in 10 mL 1 M HCl after which the resulting solution was quenched with zirconium dioxide (300 mg, 2.44 mmol) in a 15 mL centrifuge tube. The resulting suspension was rocked bottom-to-top to detach all the solid, and the mixture was equilibrated in rotary mixer for 24 h at room temperature. The solution was centrifuged using a Thermo Fischer Scientific Heareus Megafuge 1.0R with 2773 rcf for 10 minutes and the supernatant was decanted away. The remaining solid material was washed with 10 mL H_2O and vigorously shaken five times. The solution was centrifuged after each cycle and the water decanted away. Finally, the solid was transferred to a crucible and dried in oven at 70 °C for 24h. The resulting opaque brown solid was ground to a fine powder in a mortar and pestle.

ZrBTEPT synthesis

2,4-bis(1,2,3-triazol-1-ethanephosphonate)tiophene (48.1 mg, 0.109 mmol) (BTEPT) was diluted in 10 mL 1 M HCl after which the resulting solution was quenched with zirconium dioxide (300 mg, 2.44 mmol) in a 15 mL centrifuge tube. The resulting suspension was rocked bottom-to-top to detach all the solid, and the mixture was then equilibrated in a rotary mixer for 24 h at room temperature. The solution was centrifuged using a Thermo Fischer Scientific Heareus Megafuge 1.0R with 2773 rcf for 10 minutes and the supernatant was decanted away. The remaining solid material was washed with 10 mL H_2O and vigorously shaken five times. The solution was centrifuged after each cycle and the water decanted away. Finally, the solid was transferred to a crucible and dried in oven at 70 °C for 24h. The resulting opaque brown solid was ground to a fine powder in a mortar and pestle.

Chapter III: Characterisation

Infrared spectroscopy

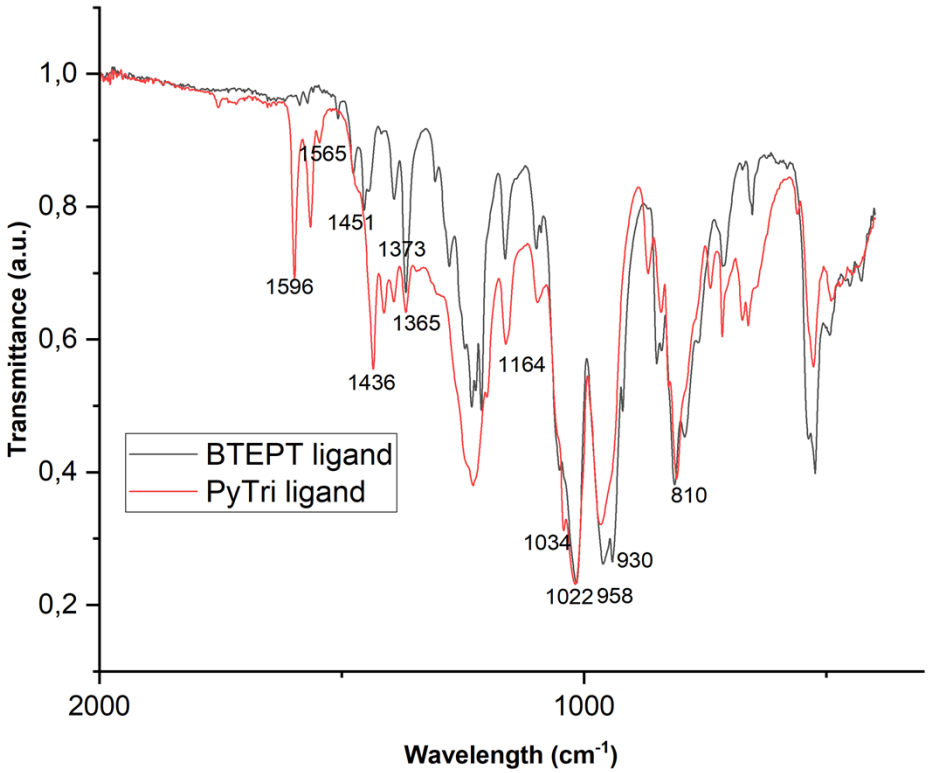


Figure S2. FTIR-ATR spectra of PyTri and BTEPT phosphonate ligands. (PyTri represents the pyridyl-based phosphonate ligand)

The PyTri ligand spectrum showed strongest absorbance at 958-1034 cm^{-1}, similarly BTEPT ligand had corresponding absorbance from 930 to 1022 cm^{-1} originating from ν_s(P–O) vibrations. The coordination to metal centers accomplishes absorbance band shifts higher in wavenumber, hence the P-O stretch region can be detected lower in wavenumber for bare ligands. For both ligands, sharp bands were detected at 810 cm^{-1}

and around 1565-1596 cm^{-1} which can be attributed to CH deformation of a heterocycle ring. The stretches of P=O bond with H-bonding can be found at around 1164 cm^{-1}. Sharp CH_2 twists at 1365-1373 cm^{-1} could be found as well as P-CH_2 stretches at 1436-1451.[7]

Solid-state NMR

The deconvolusion of the peaks were obtained by peak fitting iteration algorithms assuming a Gaussian distribution using the Origin(Pro), Version 2022 (OriginLab Corporation, Northampton, MA, USA).

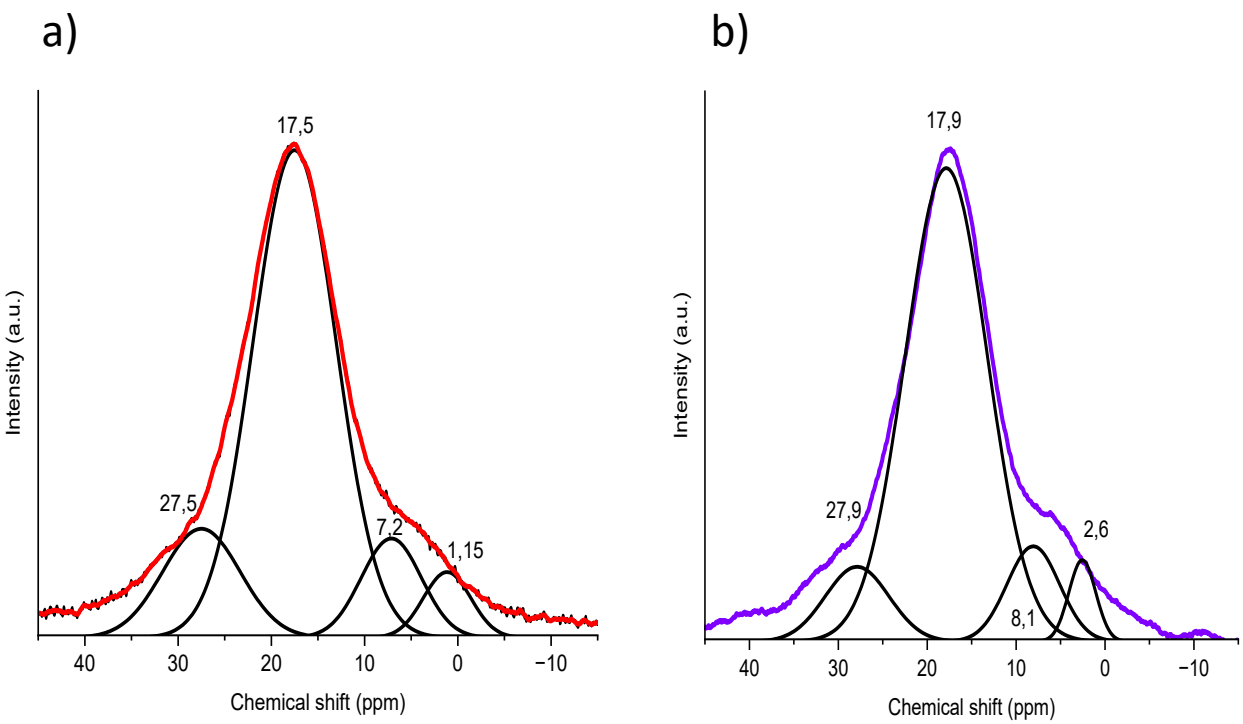
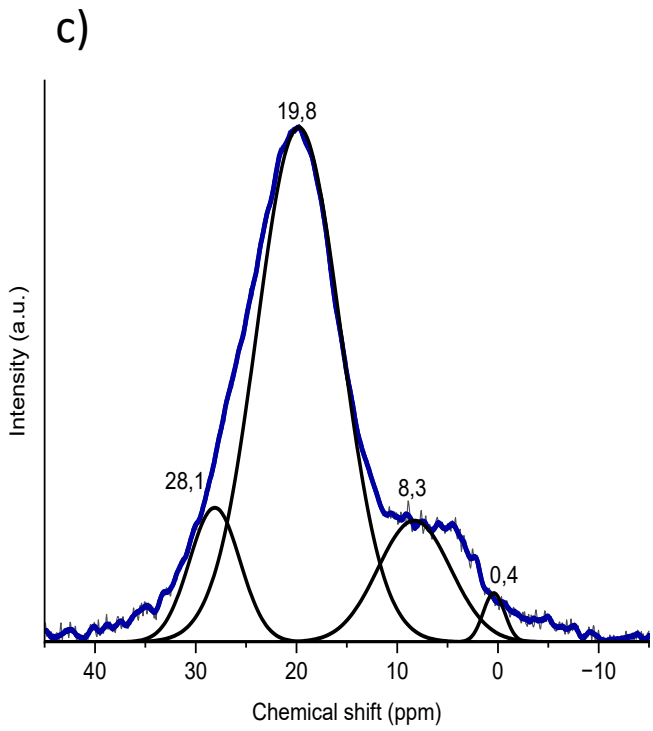
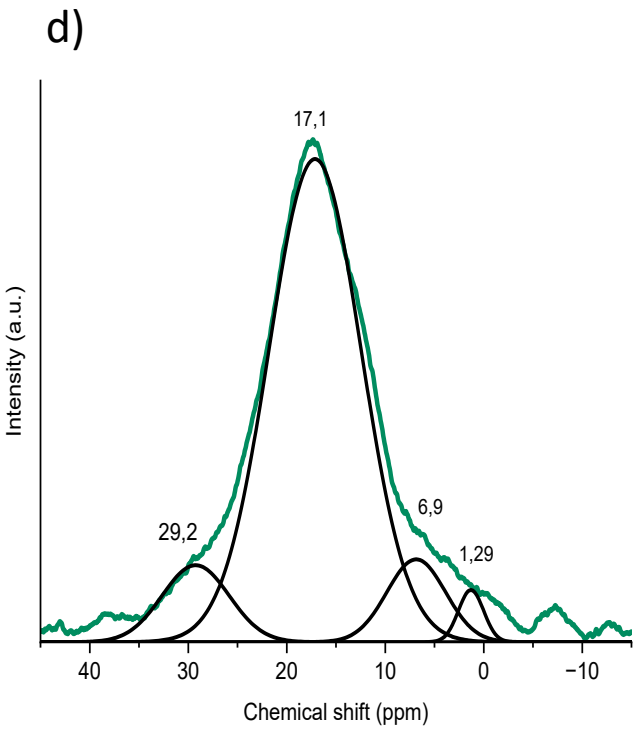
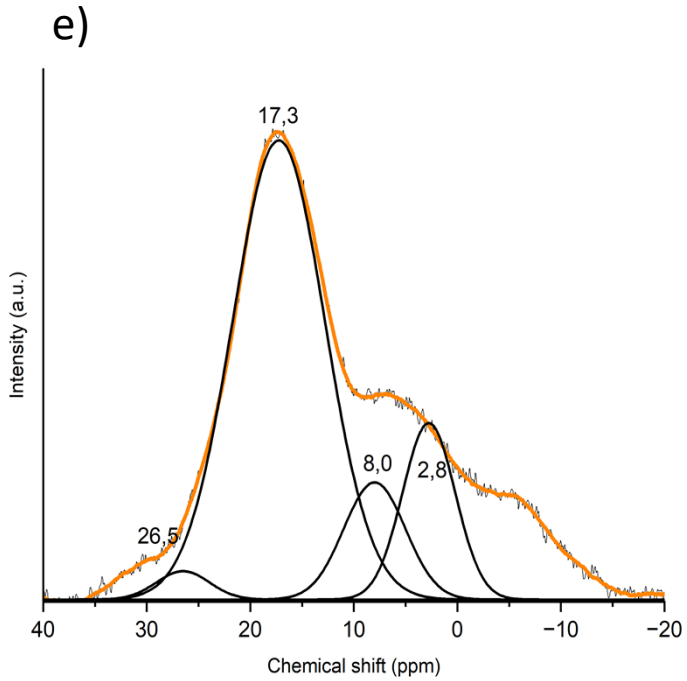


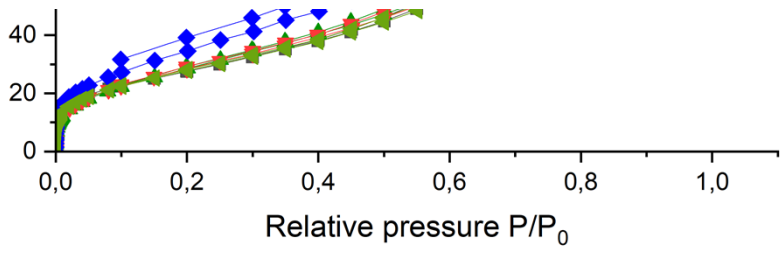
Figure S3. 31P MAS-NMR spectra of a) ZrPyTri2, (b) ZrPyTri1, (c) TiPyTri (d), ZrTEPAP and (e) and ZrBTEPT.

Figure S3. (Continued.)









Nitrogen porosimetry

Figure S4. Nitrogen adsorption-desorption isotherms of the bare zirconia, and all functionalized zirconia hybrids.

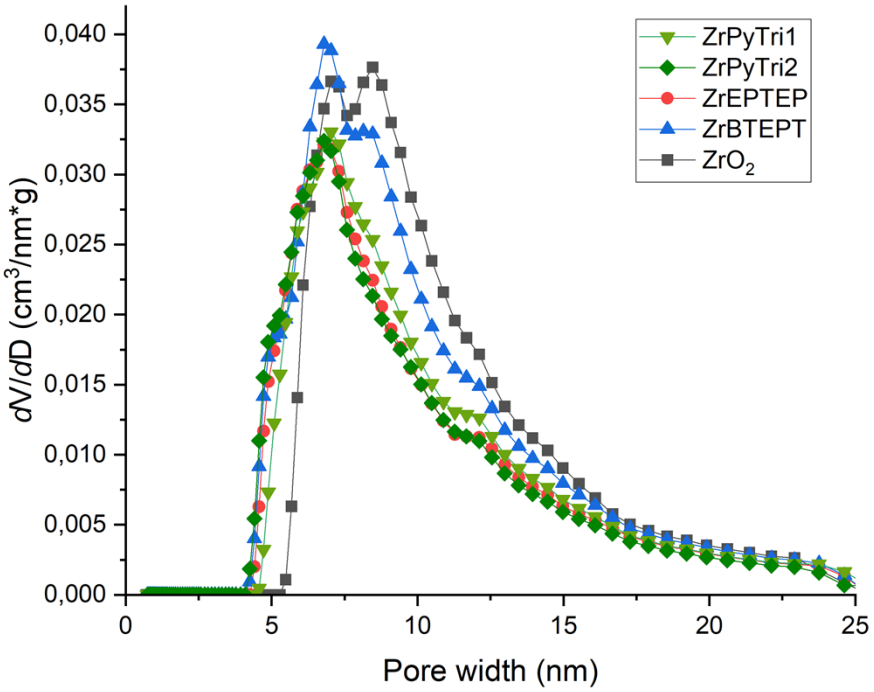


Figure S5. Pore size distributions of the bare zirconium dioxide and all functionalized hybrid materials. The values were calculated using the DFT.

X-Ray diffraction

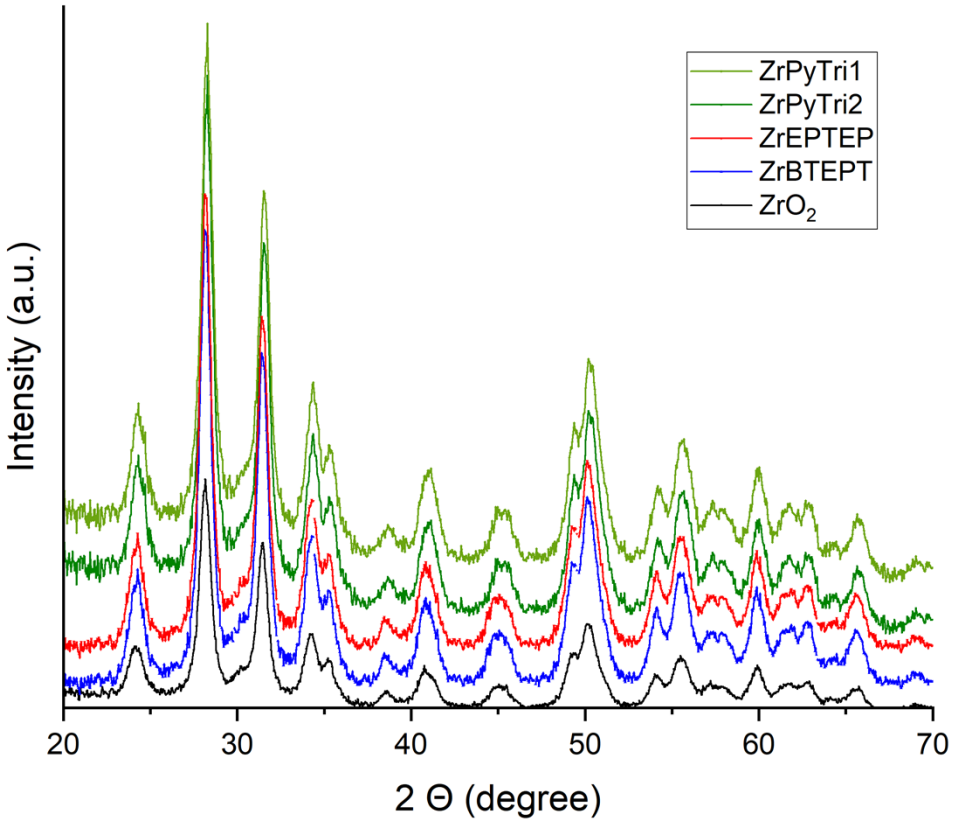


Figure S6. XRD patterns of the bare zirconium dioxide and all the functionalized zirconia hybrid materials.

Figure S6 illustrates that the bare zirconia and all the grafted zirconia hybrids show similar monoclinic structure with no difference in the patterns. Therefore, the crystalline structure of the material remains invariant despite the hybridization. Corresponding effect can be seen within the bare titania and the PyTri grafted titania since both materials show similar diffractograms indicating mostly anatase structure. Crystal sizes were calculated for ZrPyTri2 14.9±1.0 nm and TiPyTri 14.0±3. The determination of mean crystal sizes was done using the XRD data and by the Rietveld refinement with a MAUD software.[8]

Scanning electron microscopy

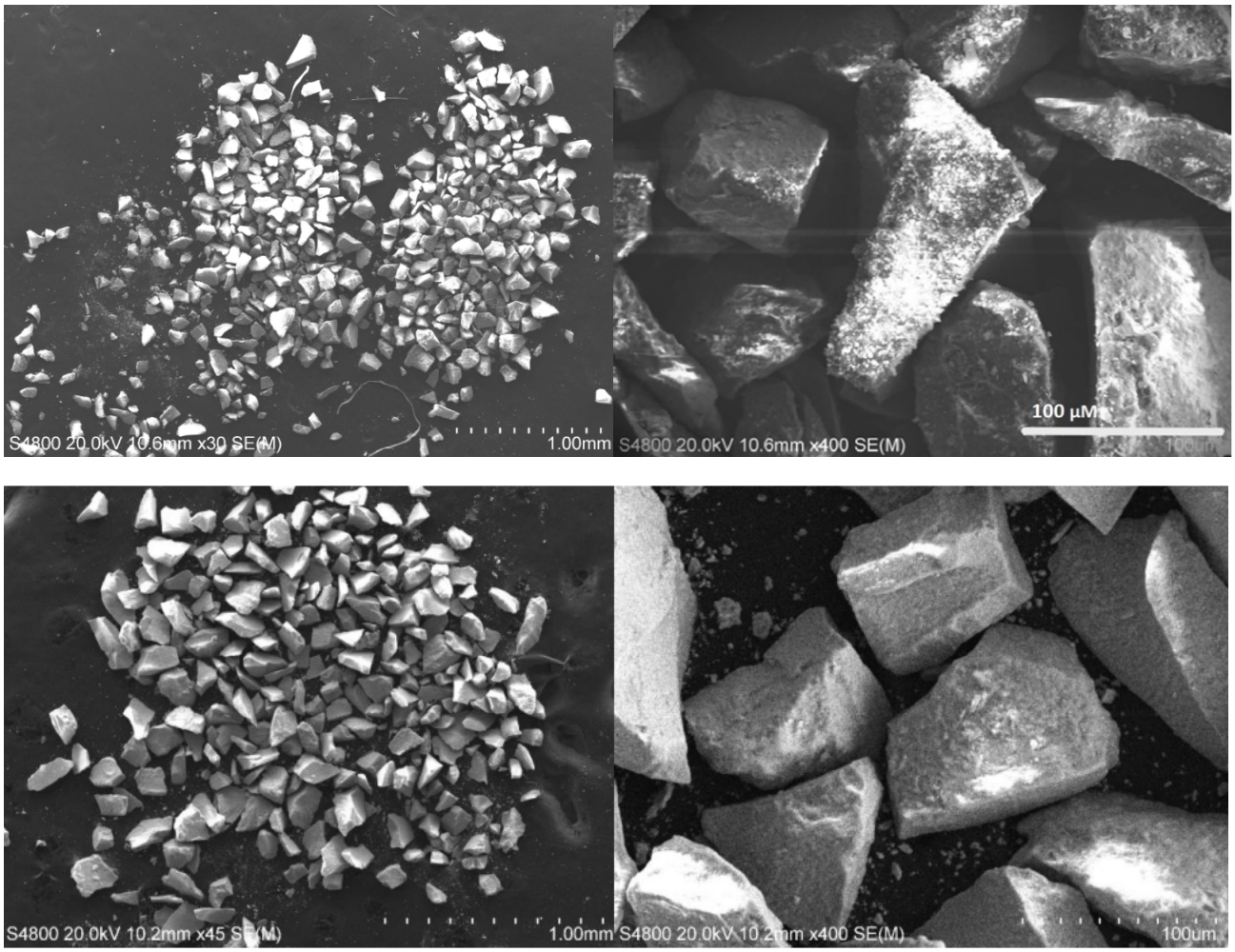


Figure S7. The SEM images of ZrPyTri (above) and bare zirconia (below)[9] at 1,0 mm and 100 µm.

NMR spectra

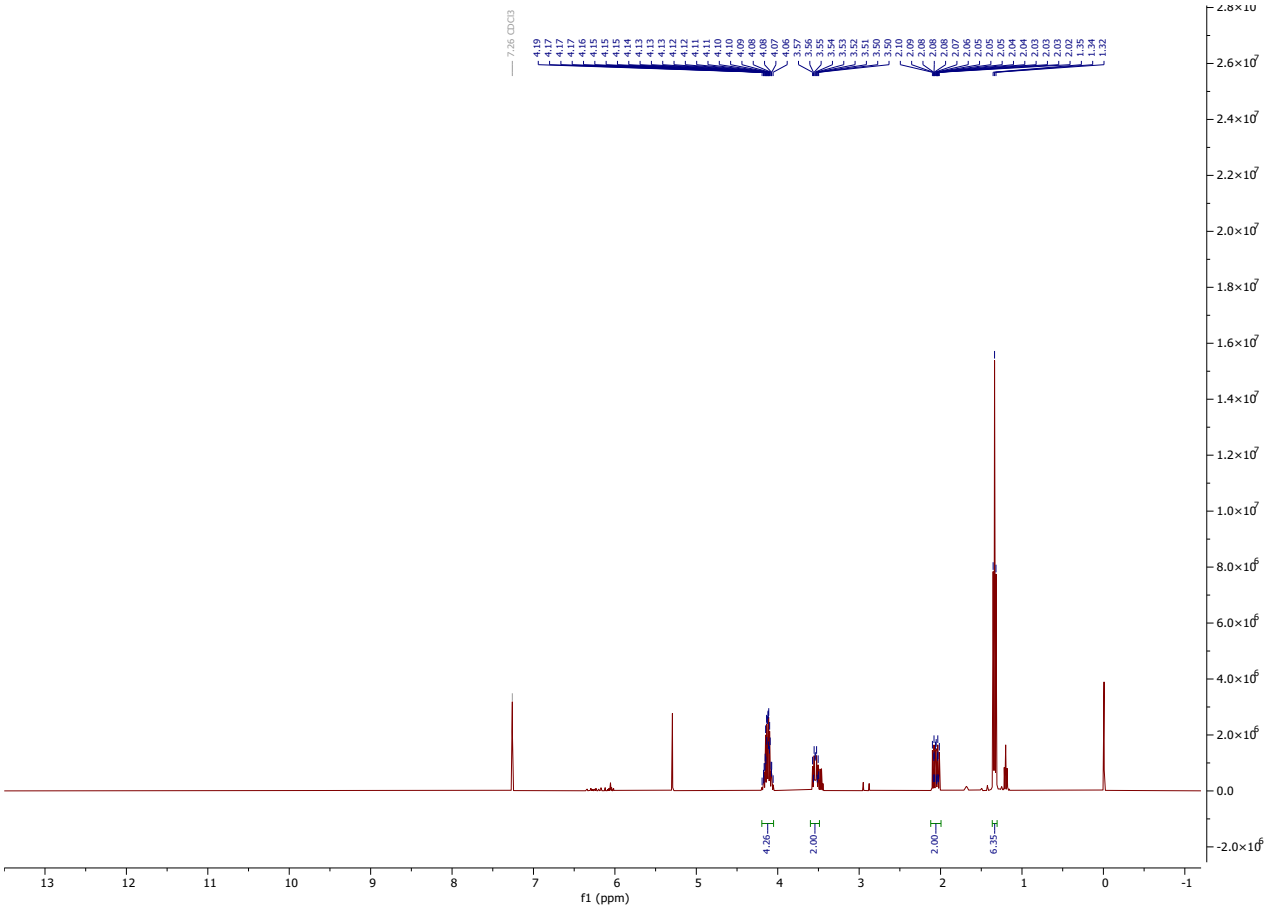


Figure S8: ^{1}H NMR spectrum of diethyl-2-azidoethylphosphonate.

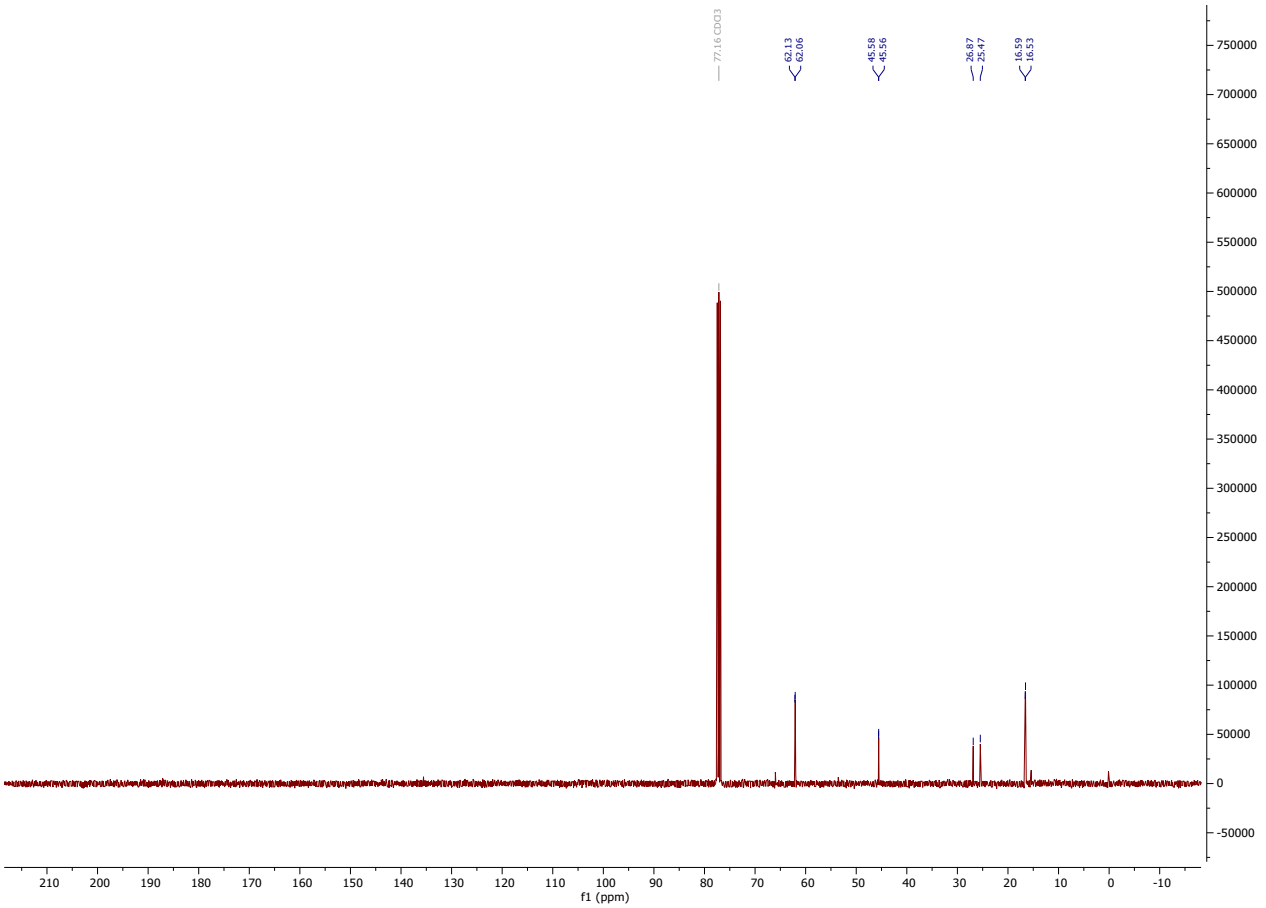


Figure S9: ^{13}C NMR spectrum of diethyl-2-azidoethylphosphonate.

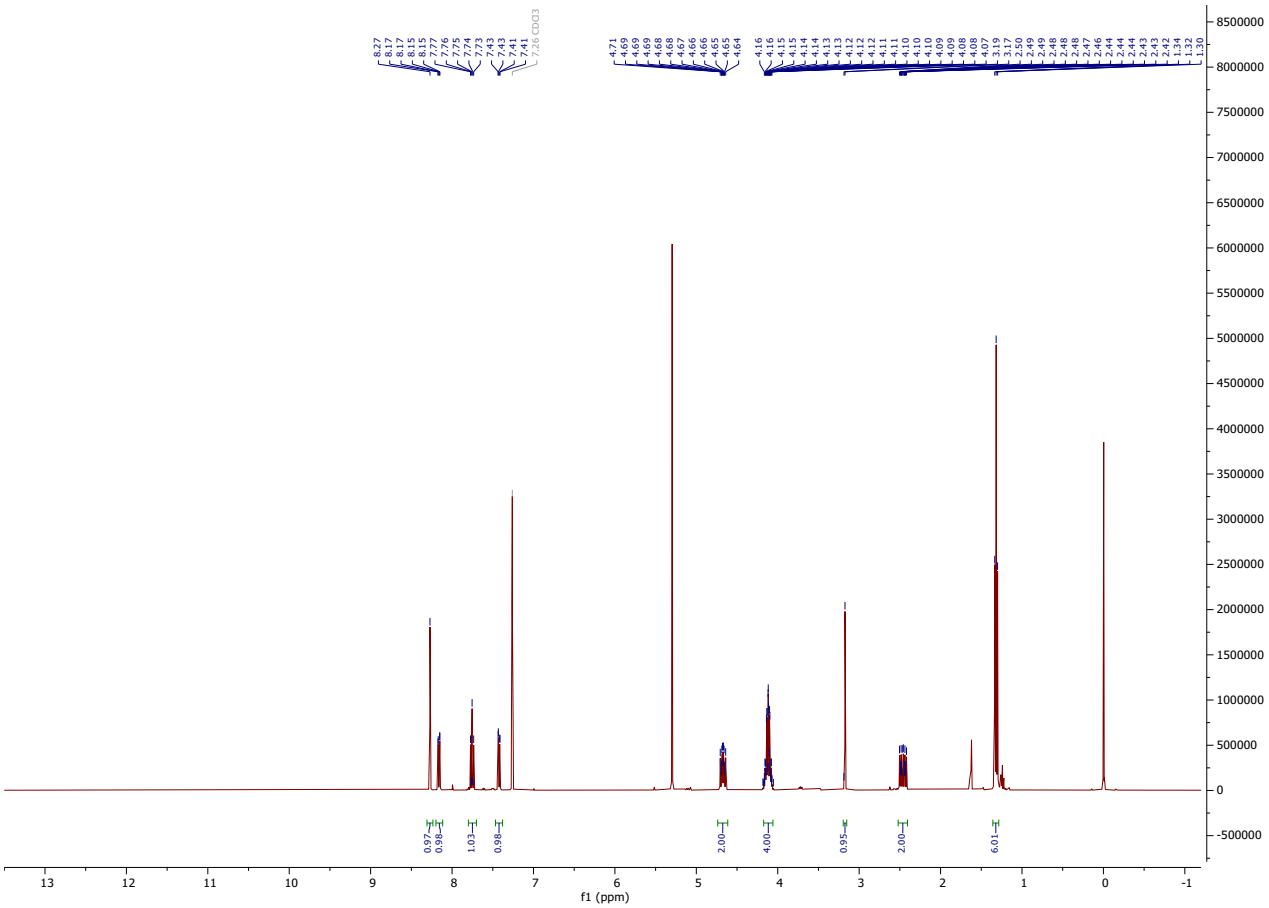


Figure S10: ^{1}H NMR spectrum of ethynylpyridine-1,2,3-triazol-1-diethylethanephosphonate.

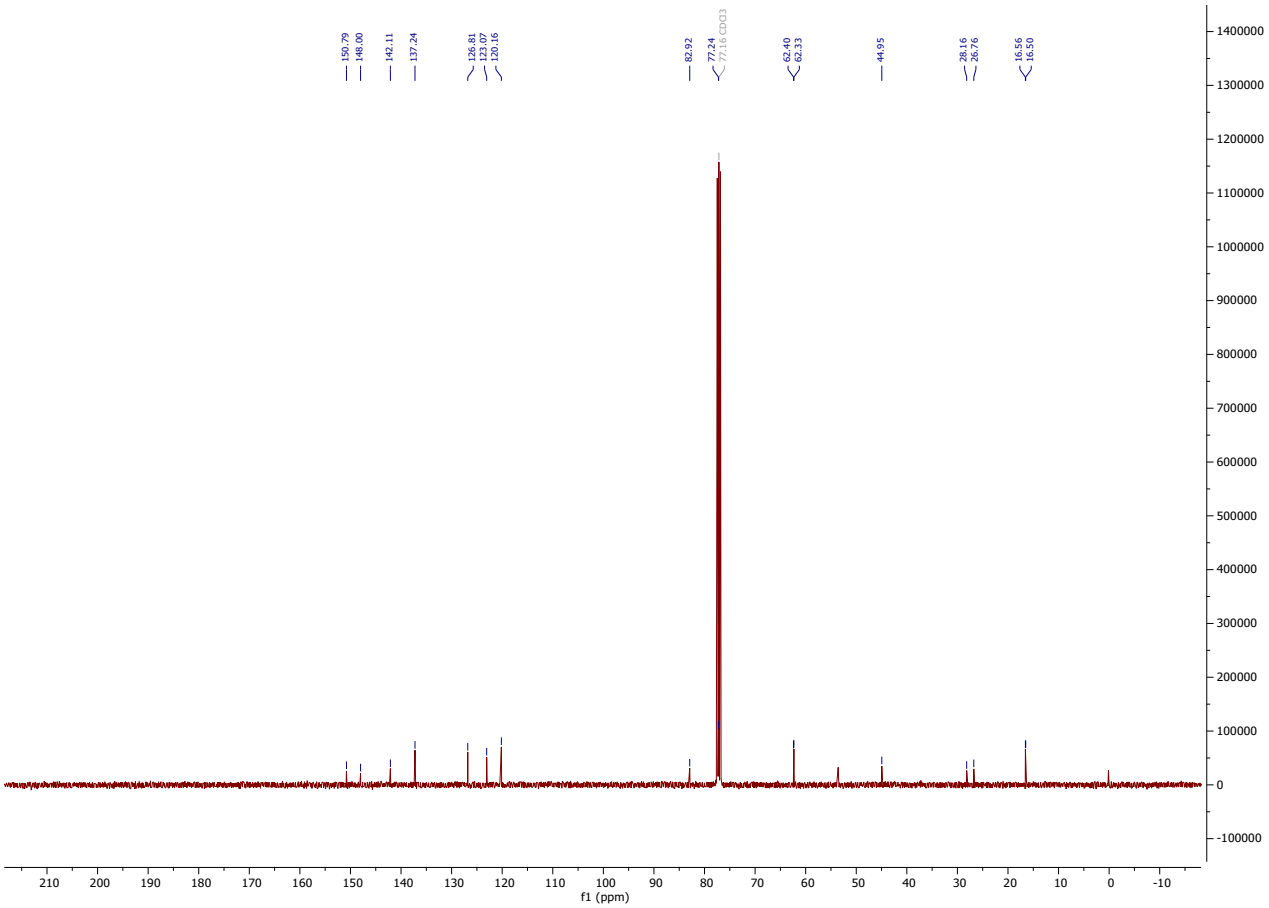


Figure S11: ^{13}C NMR spectrum of ethynylpyridine-1,2,3-triazol-1-diethylethanephosphonate.

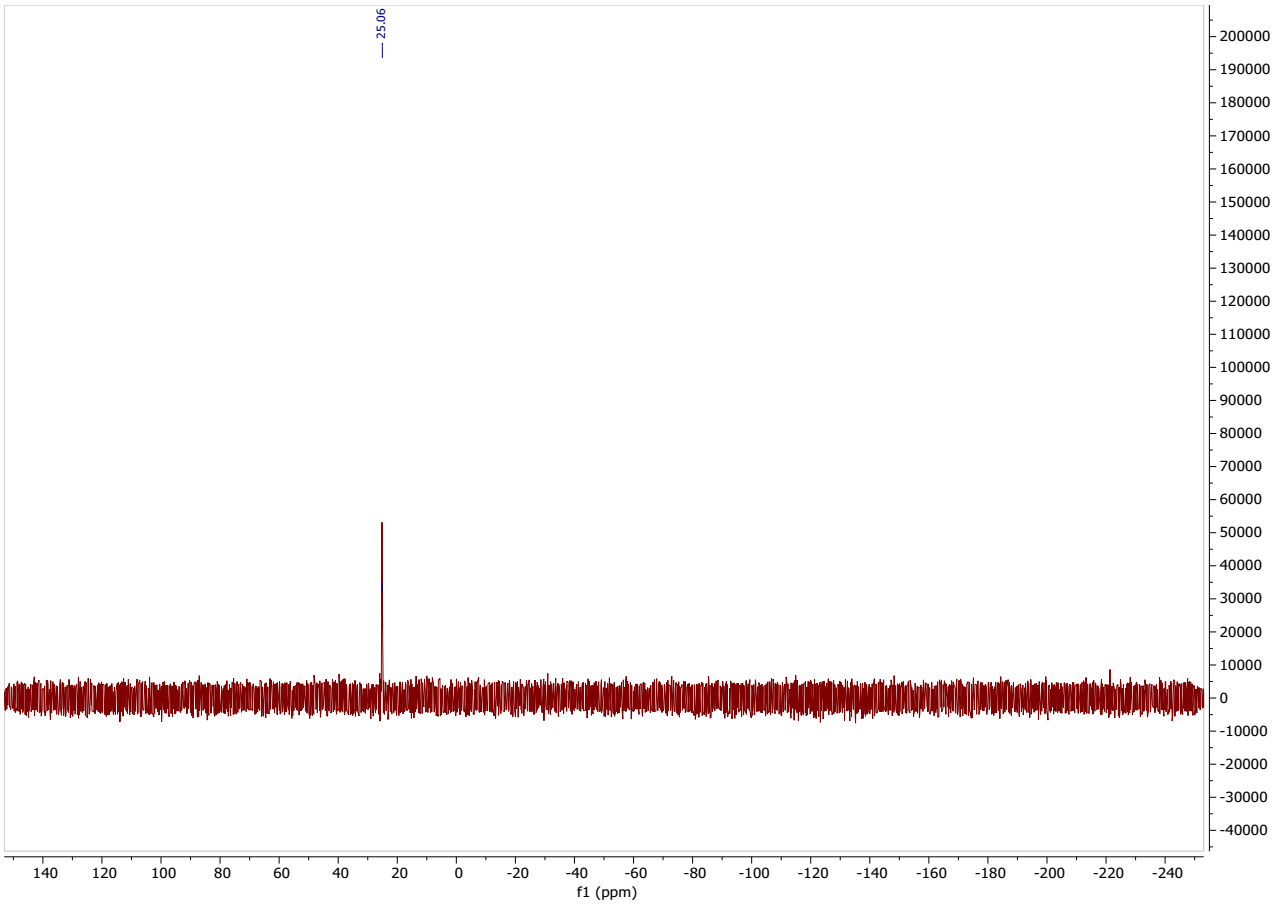


Figure S12: ^{31}P NMR spectrum of ethynylpyridine-1,2,3-triazol-1-diethylethanephosphonate.

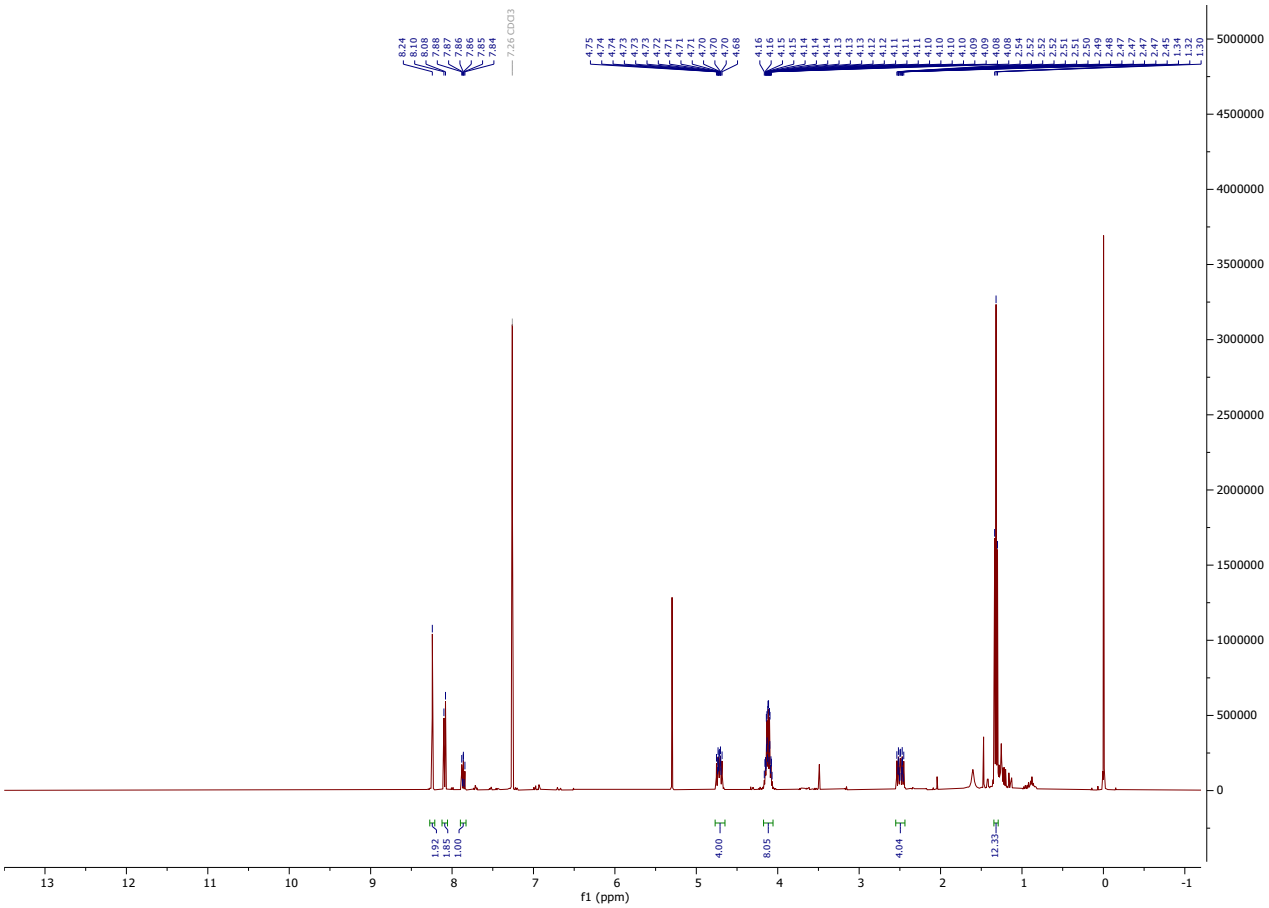


Figure S13: ^{1}H NMR spectrum of 2,6-bis(1,2,3-triazol-1-diethylethanephosphonate)pyridine.

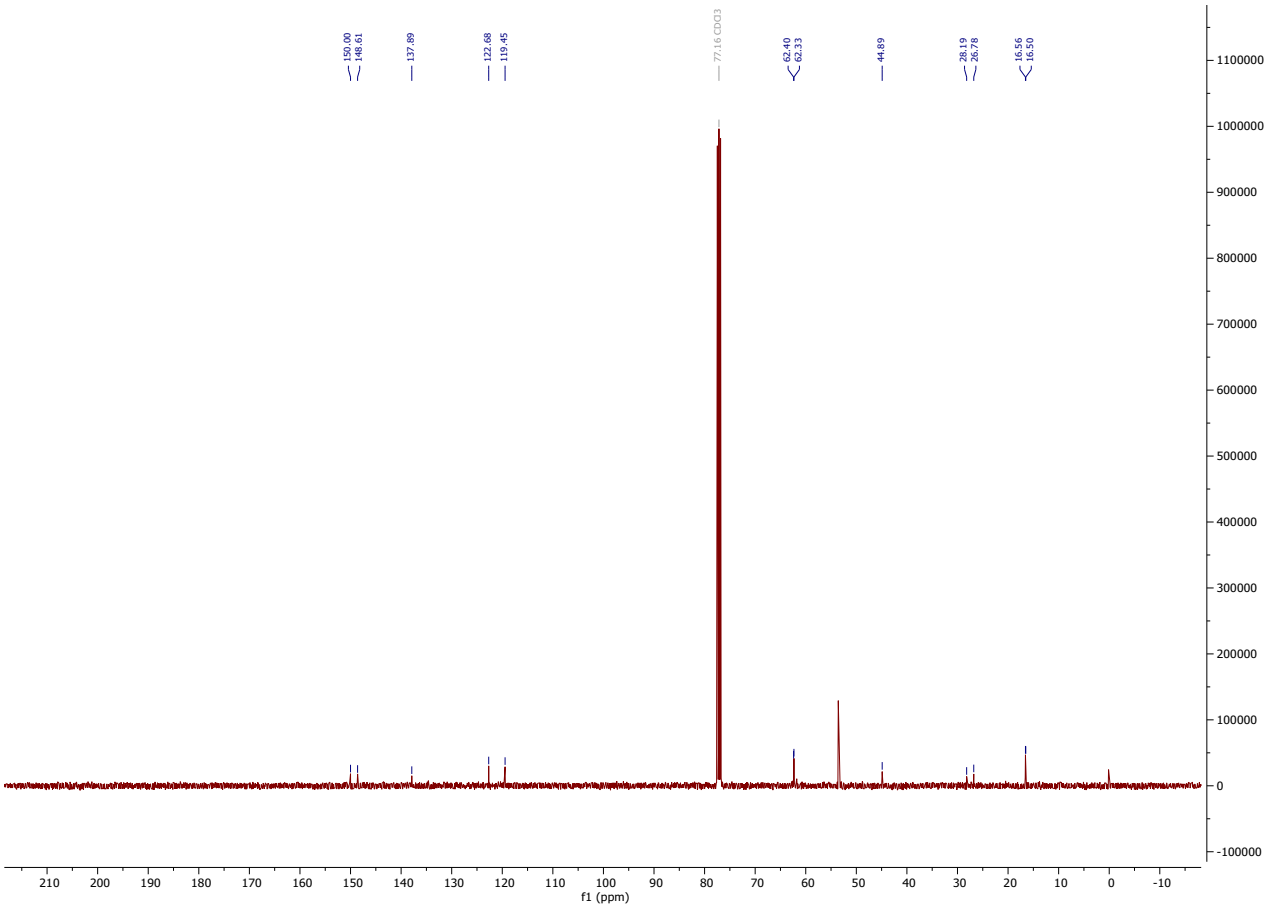


Figure S14: ^{13}C NMR spectrum of 2,6-bis(1,2,3-triazol-1-diethylethanephosphonate)pyridine.

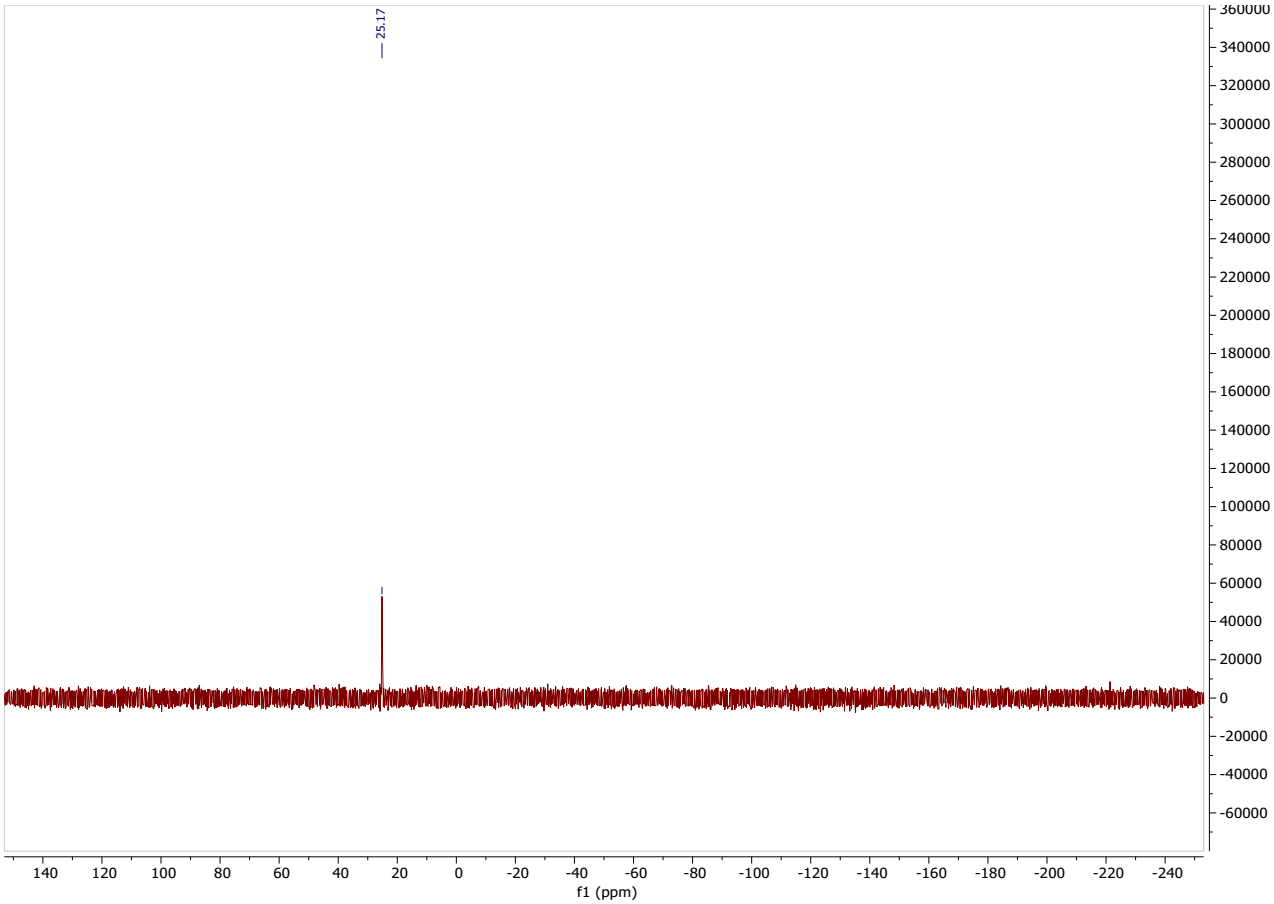


Figure S15: ^{31}P NMR spectrum of 2,6-bis(1,2,3-triazol-1-diethylethanephosphonate)pyridine.

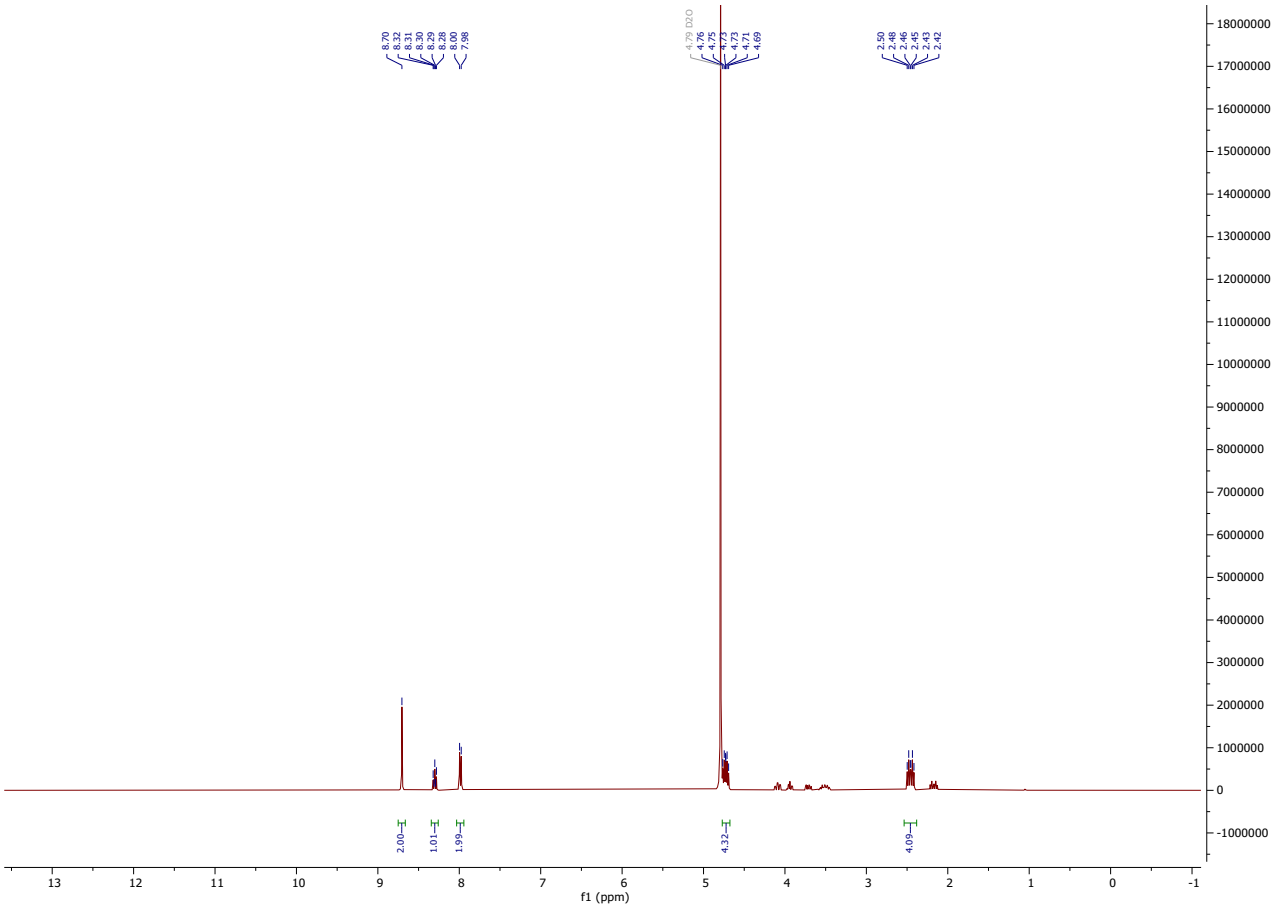


Figure S16: ^{1}H NMR spectrum of 2,6-bis(1,2,3-triazol-1-ethanephosphonate)pyridine.

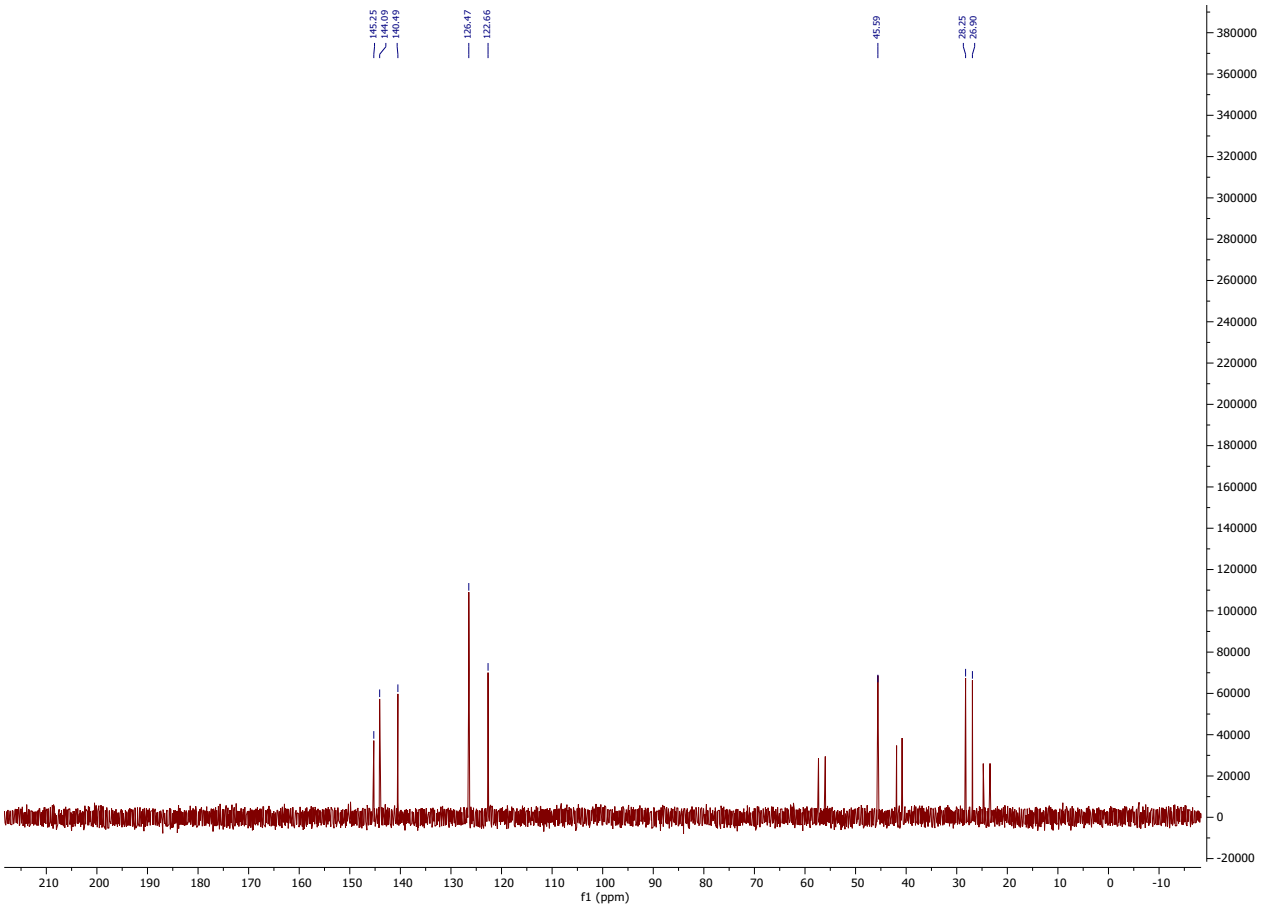


Figure S17: ^{13}C NMR spectrum of 2,6-bis(1,2,3-triazol-1-ethanephosphonate)pyridine.

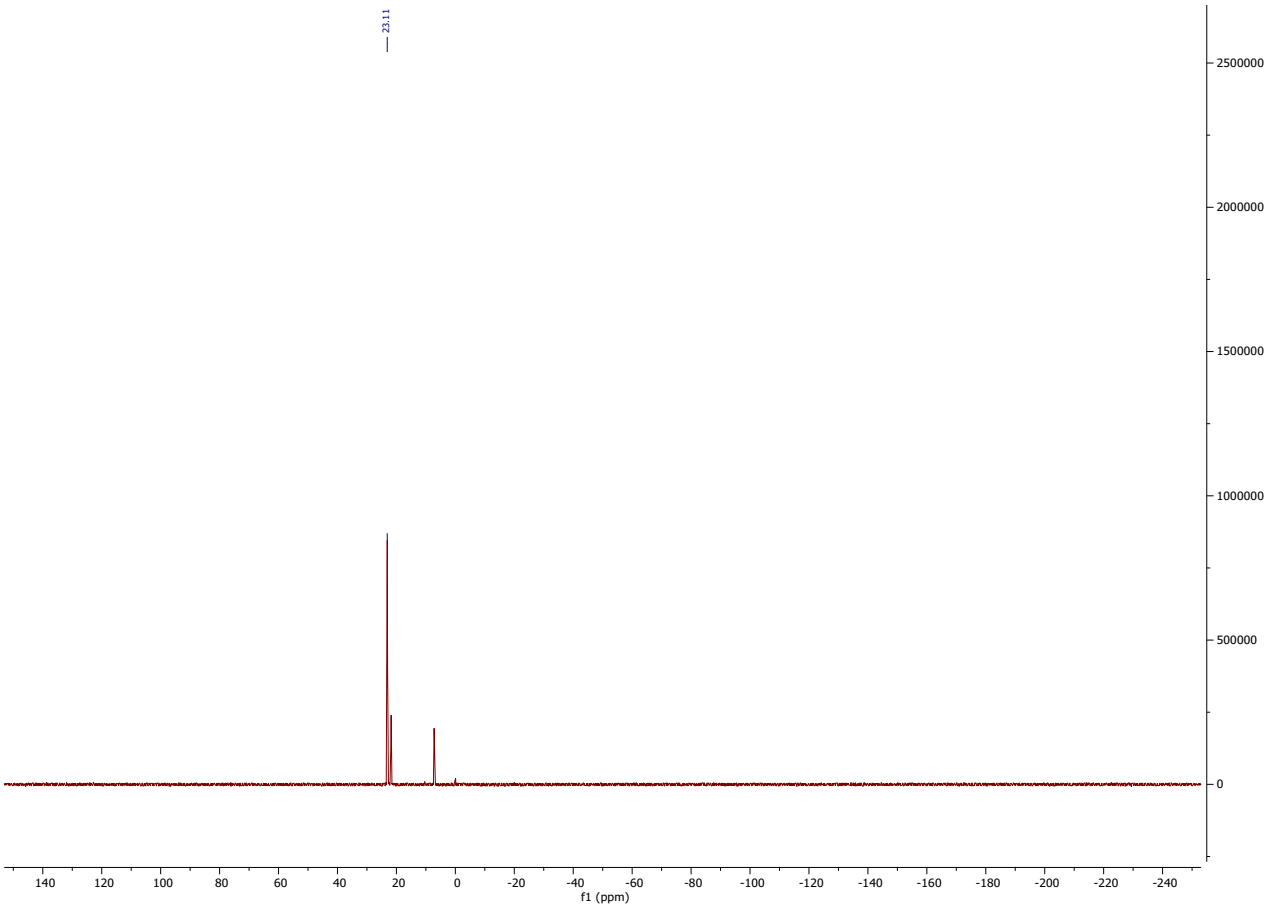


Figure S18: ^{31}P NMR spectrum of 2,6-bis(1,2,3-triazol-1-ethanephosphonate)pyridine.

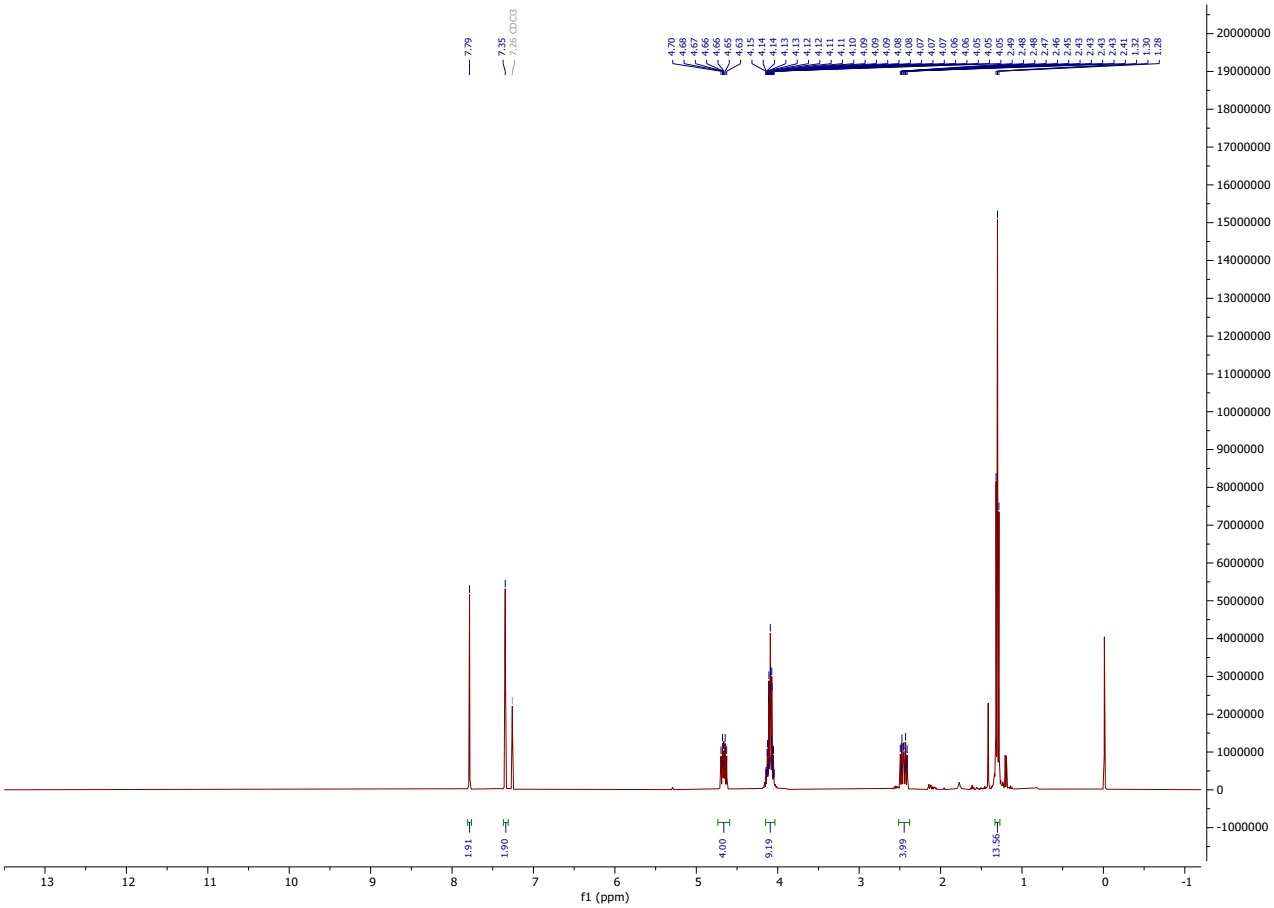


Figure S19: ^{1}H NMR spectrum of 2,5-bis(1,2,3-triazol-1-diethylethanephosphonate)tiophene.

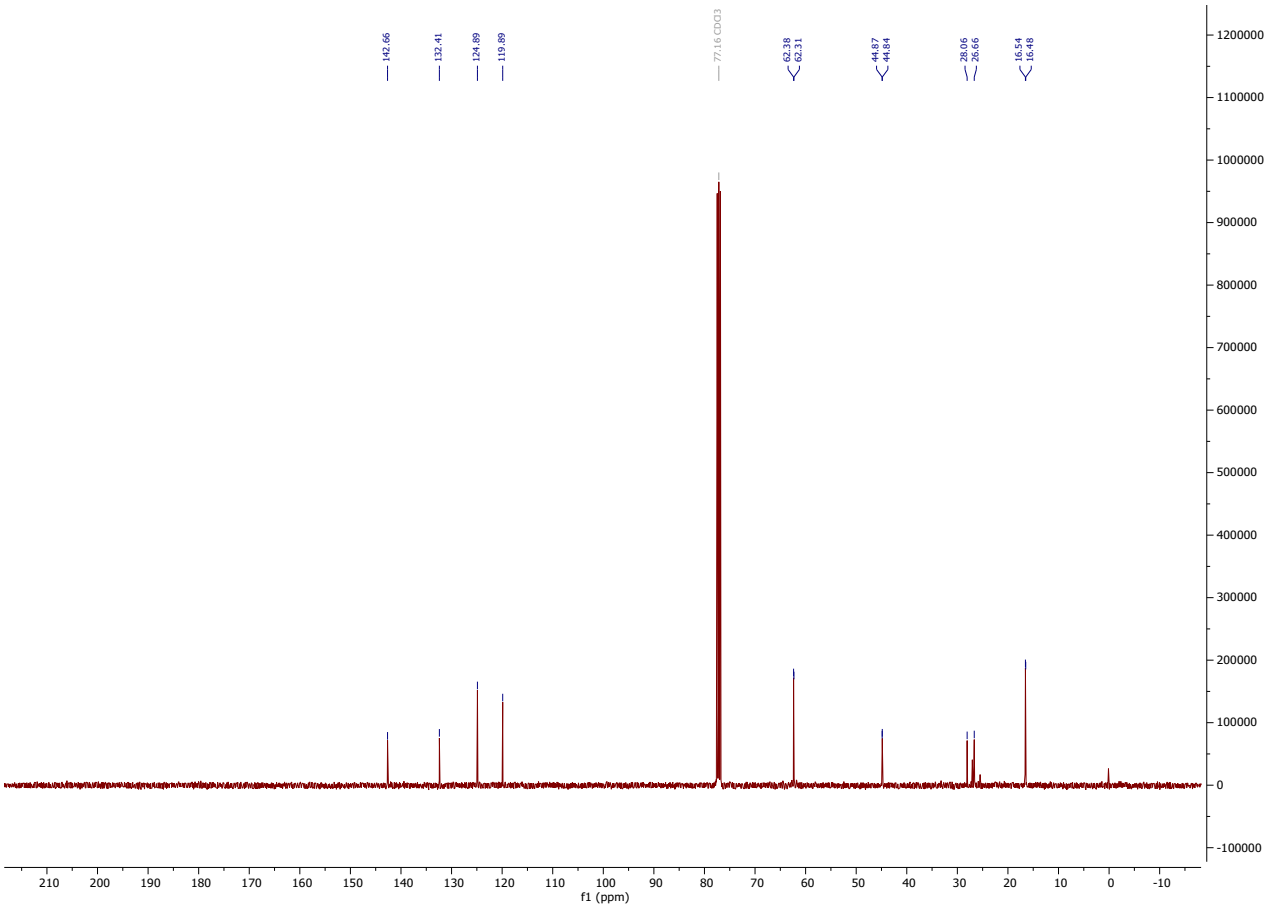


Figure S20: ^{13}C NMR spectrum of 2,5-bis(1,2,3-triazol-1-diethylethanephosphonate)tiophene.

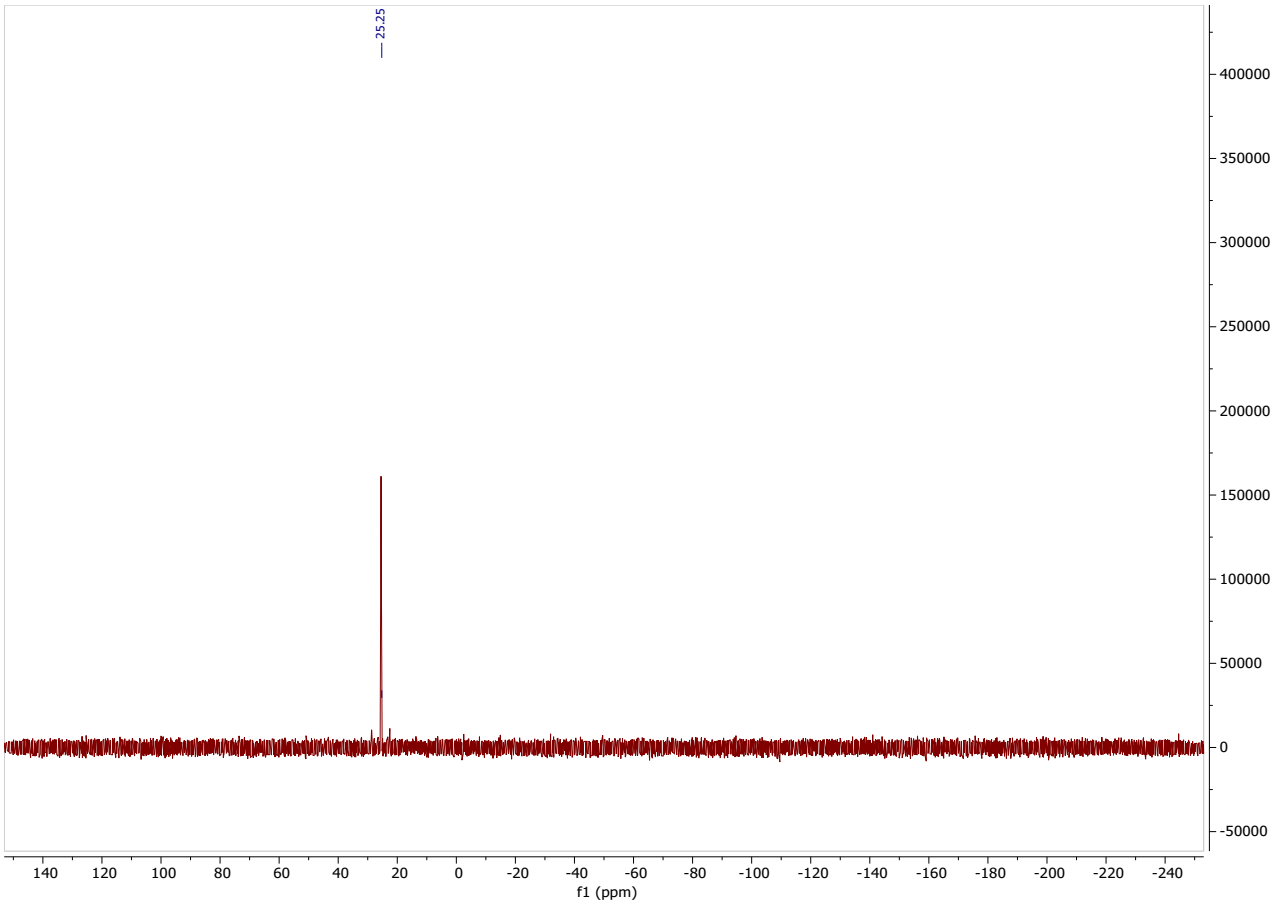


Figure S21: ^{31}P NMR spectrum of 2,5-bis(1,2,3-triazol-1-diethylethanephosphonate)tiophene.

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