Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

A mild post-functionalization method for the vanadium substituted Wells-Dawson polyoxometalate, $P_2W_{15}V_3$

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General remarks

Reagents and solvents were purchased from commercial sources and used without further purification and were used as such. The precursor $TBA_5H[P_2W_{15}V_3O_{62}]$ POM was synthesized and characterized following published procedures ($K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$[1] → $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$[2] → $K_8H[P_2W_{15}V_3O_{62}]\cdot 9H_2O$[3] → $TBA_5H_4[P_2W_{15}V_3O_{62}]$[3] . All reactions were performed under an argon atmosphere with magnetic stirring and in the dark to prevent photoreduction of the V^{5+} containing POM to mixed valence V^{5+}/V^{4+} POMs. In the case of the CuAAC reactions the solvents were purged with argon for a short time.

Techniques

NMR spectroscopy

^1H, ^1H-decoupled ^{13}C, ^{31}P and ^{51}V NMR spectra were recorded on a bruker AvanceII 300 (300/75 Mhz), 400 (400/100 Mhz) and 600 (600/150 Mhz) spectrometer. 2D ^1H-^{13}C HSQC measurements were performed on a bruker Avance 400 (400-75) spectrometer. All measurements were performed at room temperature and in CD_3CN, as mentioned in the description of every compound. TMS (δ = 0.00 ppm) [^1H] or the deuterated solvent peaks of CD_3CN (δ = 1.32 or 118.26 ppm) [^{13}C] were used as an internal reference. 25% H_3PO_4 [^{31}P] and $NaVO_3$ (1M in H_2O at pH 12) [^{51}V] were used as an external reference. NMR spectra for all compounds can be found in figures S1-24.

IR spectroscopy

FT-IR spectra were recorded in solid state on a Bruker Vertex 70 spectrometer. Spectra were atmosphere corrected when measured.

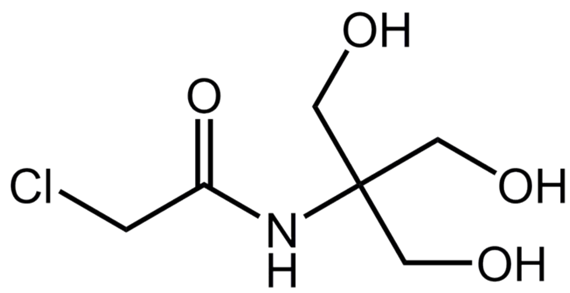
Mass spectroscopy

Electrospray ionization mass spectra were obtained in negative ion mode on a quadrupole/time-of-flight mass spectrometer (Q-TOF-2, Micromass, Manchester UK) equipped with a standard ionization source. The instruments was tuned to a resolution of over 8000 (full peak width at half maximum). The samples were dissolved in acetontrile prior to injection.

Synthetic procedures and characterization

Synthesis of the azide-functionalized $P_2W_{15}V_3$ POM

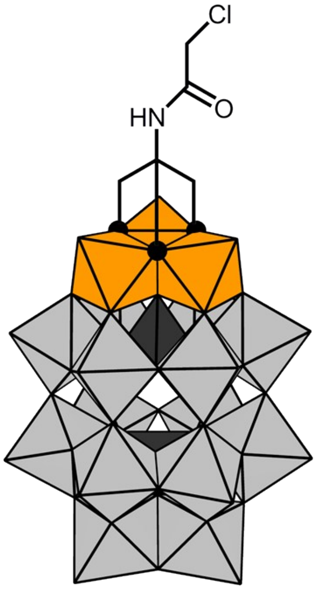
Compound 1: Chloride-functionalized tris ligand, $C_6H_{12}NO_4Cl$



To an ice-cooled solution of 12.84 ml of ethyl chloroacetate (0.120 mmol, 1.2 eq.) in 7.5 ml of methanol was added 12.10 g of tris(hydroxymethyl)aminomethane (0.100 mmol, 1 eq.) in small portions together with an additional 25 ml of methanol. The ice bath was removed and the suspension was stirred for 2 days, during which the solid tris(hydroxymethyl)aminomethane slowly disappeared. The solution was partially evaporated and the remaining solution was placed in the fridge for 30 min, after which the obtained crystals were collected on a glass-filter. The product was recrystallized by redissolving in hot methanol and placing the solution in the fridge overnight. Large off-white crystals formed overnight which were collected on a glass-filter. Yield: 7.85 g (40 %). ^{1}H NMR (400 MHz, D_2O): δ = 4.20 ppm (s, 2H, CO-C**H_2**-Cl), 3.84 ppm (s, 6H, O-C**H_2**-C). ^{13}C NMR (100 MHz, D_2O): δ = 170.99 ppm (NH-**C**O), 63.65 ppm (CH_2-**C**-NH), 61.60 ppm (O-**C**H_2-C), 44.27 ppm (CO-**C**H_2-Cl). ESI-MS $C_4H_{11}NO_3Cl$: 220 [M+Na^+]. Elemental analysis (%) for $C_6H_{12}NO_4Cl$ (197.6 g mol^{-1}): calcd. C 36.47, H 6.12, N 7.09; found: C 36.26, H 4.92, N 6.93.

NMR-spectra of compound **1** can be found in the supporting information of previously published work by our research group.[4]

Compound 2: Chloride-functionalized POM, $(C_{16}H_{36}N)_6$-$[P_2W_{15}V_3O_{59}(OCH_2)_3C_3H_3NOCl]$



1 equivalent of TBA_5H_4-$P_2W_{15}V_3O_{62}$ (2.08 g, 0.40 mmol) and 1.3 equivalents of compound **1** (0,103 g, 0.52 mmol) were dissolved in 65 ml of dry acetonitrile. The orange clear solution was stirred and refluxed for 3 days in the dark and under an argon atmosphere, after which a bright yellow-orange solution was obtained. After cooling down, the solution was evaporated under vacuo to a volume of approximately 10 ml, which was then added to a 10-fold excess of diethylether. The yellow precipitate which formed was collected through centrifugation and redissolved in 10 ml of fresh acetonitrile. Subsequently, the solution was passed through a tetrabutylammonium loaded amberlyst-15 resin to remove any formed dimethylammonium counterions resulting from the hydrolysis of residual DMF in the starting material. The solution was subsequently added to a large excess of diethylether to precipitate a yellow solid, which was collected through centrifugation (4000 rpm, 5 min). Finally, the solid was washed twice more with diethylether and the pure product was air-dried for several days.

Yield: 1.87 g (84%). ^{1}H NMR (600 MHz, CD_3CN): δ = 6.53 ppm (s, 1H, C-N**H**-CO), 5.68 ppm (s, 6H, O-C$\mathbf{H_2}$-C), 3.97 ppm (s, 2H, CO-C$\mathbf{H_2}$-Cl), 3.19 ppm (m, 48H, $\mathbf{H_{TBA}}$), 1.66 ppm (m, 48H, $\mathbf{H_{TBA}}$), 1.44 ppm (m, 48H, $\mathbf{H_{TBA}}$), 1.00 ppm (t, 72H, $\mathbf{H_{TBA}}$). ^{13}C NMR (100 MHz, CD_3CN): δ = 167.37 ppm (NH-**C**O-CH_2), 86.85 ppm (O-**C**H_2-C), 59.27 ppm ($\mathbf{C_{TBA}}$), 55.34 ppm (CH_2-**C**-NH), 44.10 ppm (CO-**C**H_2-Cl), 24.43 ppm ($\mathbf{C_{TBA}}$), 20.39 ppm ($\mathbf{C_{TBA}}$), 13.97 ppm ($\mathbf{C_{TBA}}$). ^{31}P NMR (162 MHz, CD_3CN): δ = -6.64 ppm (**P**W_6V_3), -12.68 ppm (**P**W_9). ^{51}V NMR (105 MHz, CD_3CN): δ = -544.76 ppm ($\mathbf{V_3}$). IR (cm^{-1}): $\tilde{\nu}$ = 3477 (w), 2962 (m), 2873 (m), [**CO**NH-stretch], 1484 (m), 1084 (s), 947 (s), 901 (s), 798 (vs), 721 (vs), 526 (s), 478 (m).

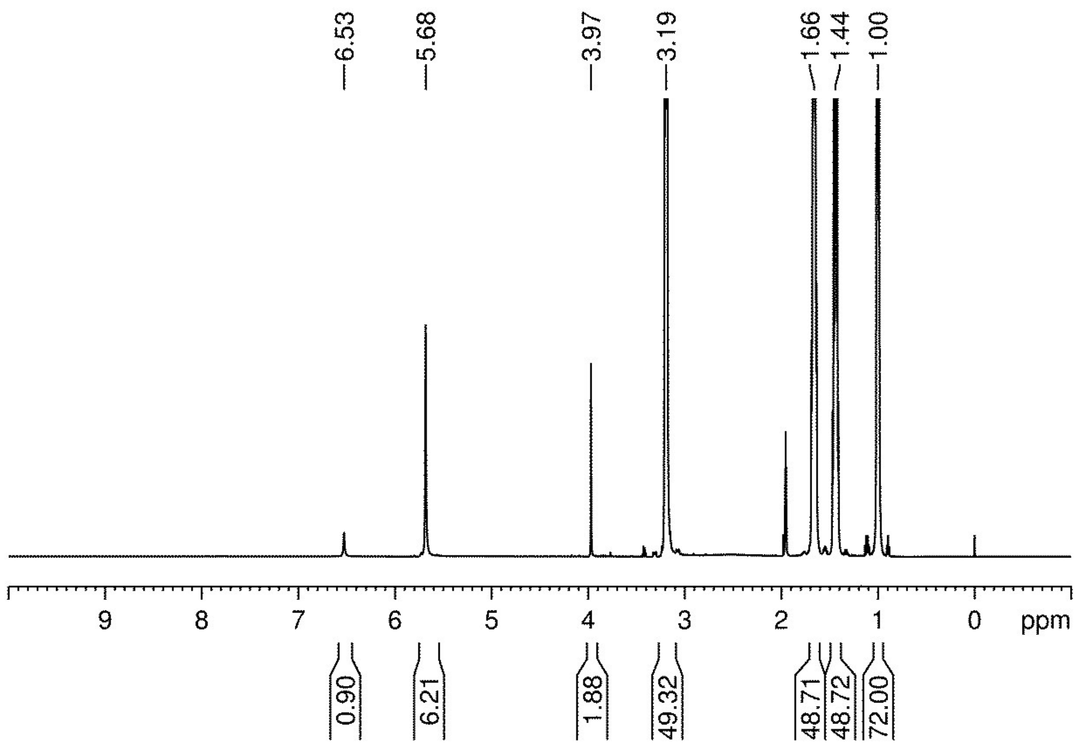


Figure S1: ^{1}H NMR spectrum of compound **2** in CD_3CN at 600 MHz

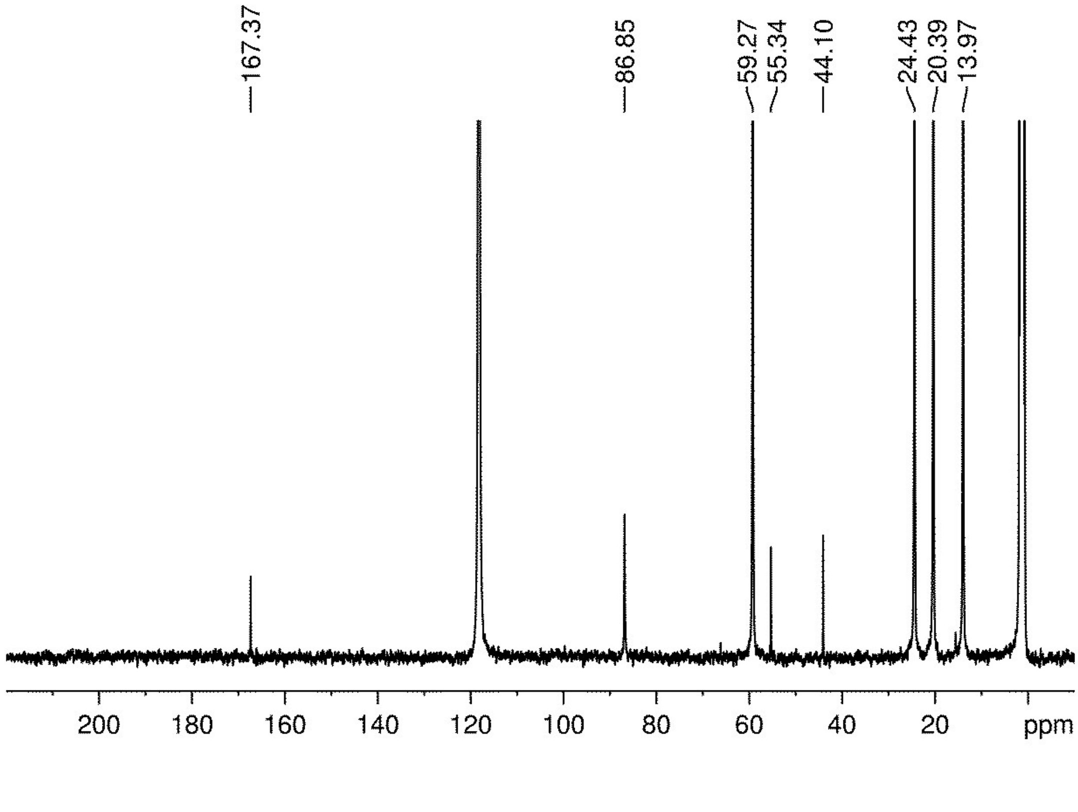


Figure S2: ^{13}C NMR spectrum of compound **2** in CD_3CN at 100 MHz

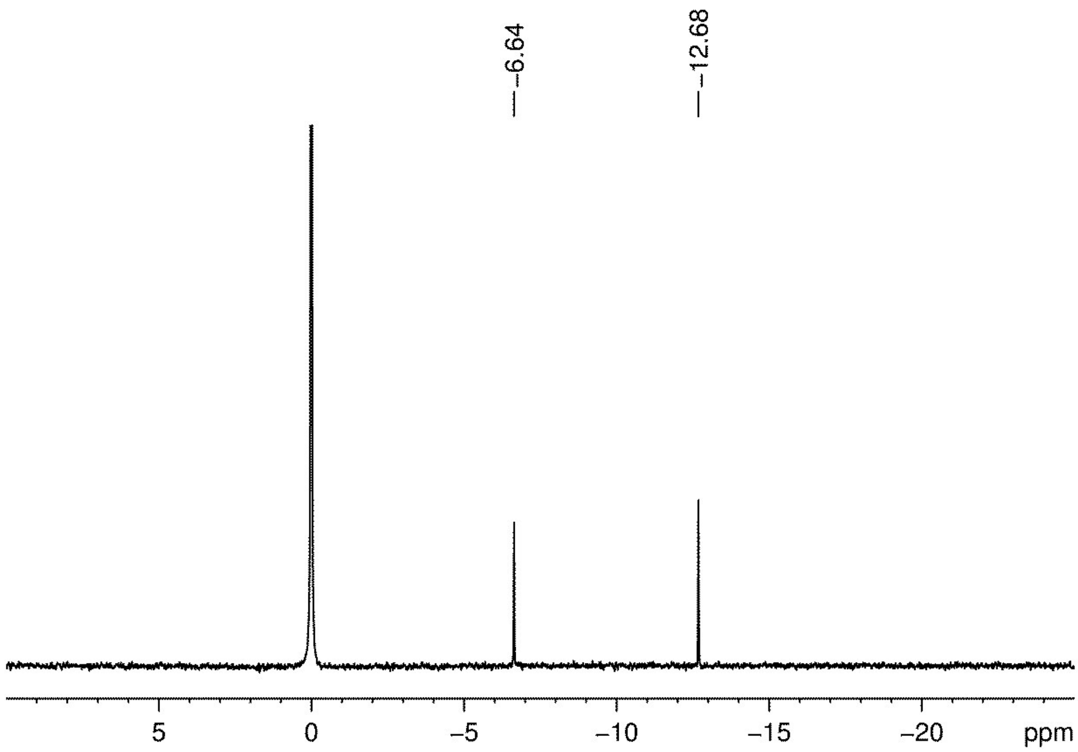


Figure S3: ^{31}P NMR spectrum of compound **2** in CD_3CN at 162 MHz

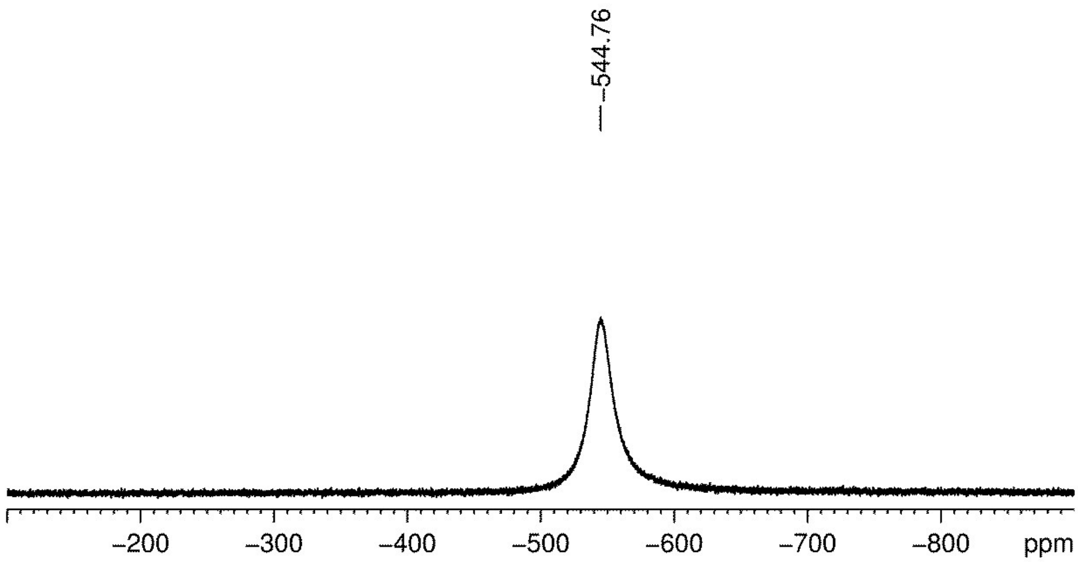
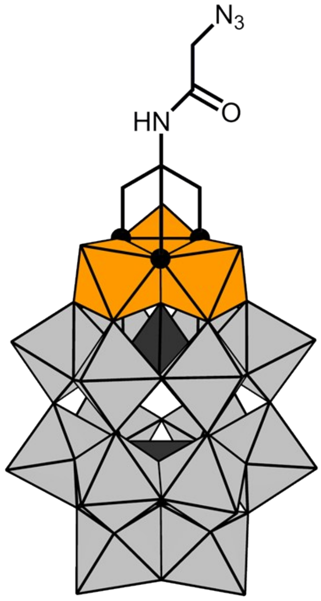


Figure S4: ^{51}V NMR spectrum of compound **2** in CD_3CN at 105 MHz

Compound 3: Azide-functionalized POM, $(C_{16}H_{36}N)_6$-$[P_2W_{15}V_3O_{59}(OCH_2)_3C_3H_3N_4O]$



To a solution containing 1 equivalent of compound **2** (1.08 g, 0.19 mmol) in 50 ml of dry DMF was added 4 equivalents of NaN_3 (0.05 g, 0.76 mmol). The yellow suspension was stirred and heated to 55 °C for two days in the dark and under an argon atmosphere. Subsequently, the suspension was concentrated in vacuo to almost dry and 10 ml of fresh acetonitrile was added. The resulting suspension was then centrifuged (5000 rpm, 10 min) to discard residual NaN3 and the formed NaCl and the remaining supernatans was added to a large excess of diethylether to precipitate a yellow solid, which was collected through centrifugation (4000 rpm, 5 min). The solid was washed twice more with diethylether and the pure product dried at air for several days.

Yield: 0.87 g (82%). ^{1}H NMR (400 MHz, CD_3CN): δ = 6.29 ppm (s, 1H, C-N**H**-CO), 5.66 ppm (s, 6H, O-C$\mathbf{H_2}$-C), 3.74 ppm (s, 2H, CO-C$\mathbf{H_2}$-N_3), 3.17 ppm (m, 48H, $\mathbf{H_{TBA}}$), 1.65 ppm (m, 48H $\mathbf{H_{TBA}}$), 1.42 ppm (m, 48H, $\mathbf{H_{TBA}}$), 0.99 ppm (t, 72H, $\mathbf{H_{TBA}}$). ^{13}C NMR (100 MHz, CD_3CN): δ = 168.72 ppm (NH-**C**O-CH_2), 86.85 ppm (O-**C**H_2-C), 59.26 ppm ($\mathbf{C_{TBA}}$), 55.49 ppm (CH_2-**C**-NH), 52.39 ppm (CO-**C**H_2-N_3), 24.44 ppm ($\mathbf{C_{TBA}}$), 20.39 ppm ($\mathbf{C_{TBA}}$), 13.97 ppm ($\mathbf{C_{TBA}}$). ^{31}P NMR (162 MHz, CD_3CN): δ = -6.65 ppm (**P**W_6V_3), -12.73 ppm (**P**W_9). ^{51}V NMR (105 MHz, CD_3CN): δ = -541.39 ppm ($\mathbf{V_3}$). IR (cm^{-1}): $\tilde{\nu}$ = 3480 (w), 3275 (w), 2961 (m), 2872 (m), 2105 (m) [$\mathbf{N_3}$-stretch], 1690 (w) [**CO**NH-stretch], 1482 (m), 1379 (w), 1083 (s), 946 (s), 901 (s), 794 (vs), 718 (vs), 525 (s), 476 (m).

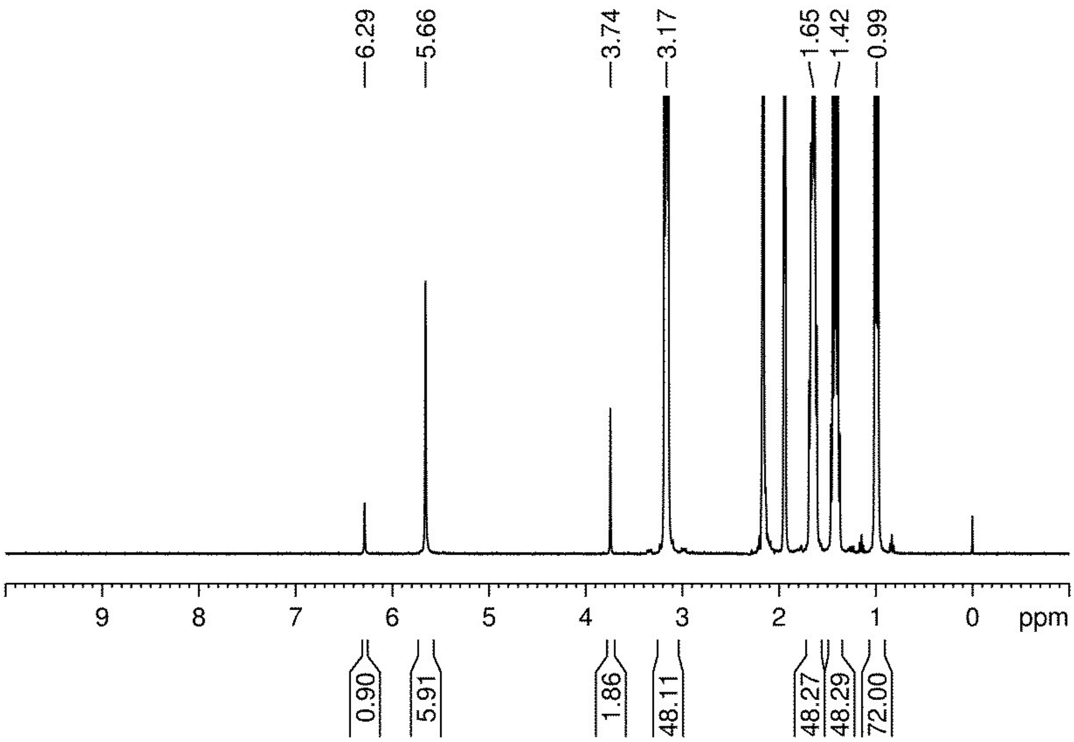


Figure S5: ^{1}H NMR spectrum of compound **3** in CD_3CN at 400 MHz

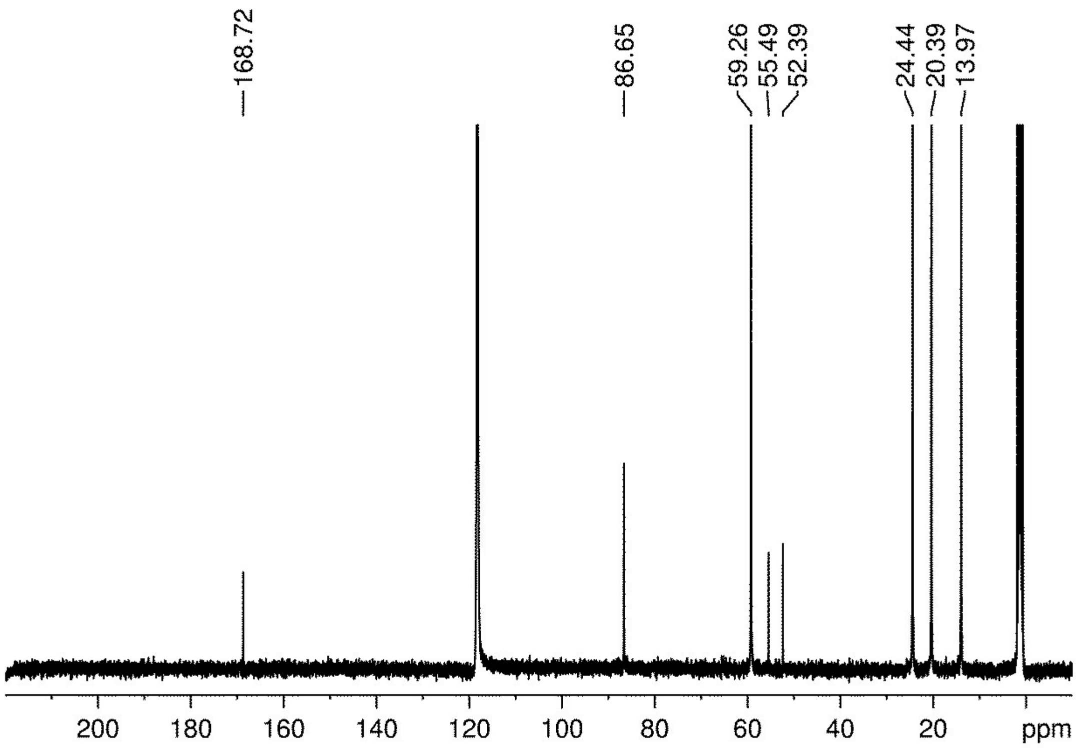


Figure S6: ^{13}C NMR spectrum of compound **3** in CD_3CN at 100 MHz

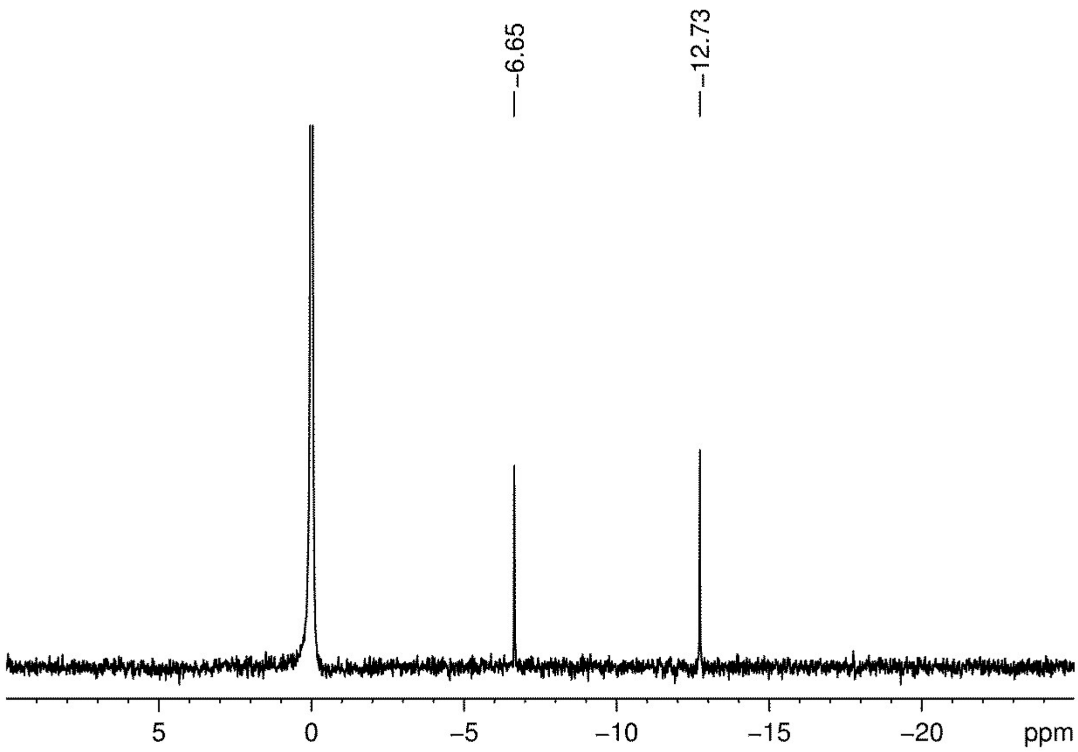


Figure S7: ^{31}P NMR spectrum of compound **3** in CD_3CN at 162 MHz

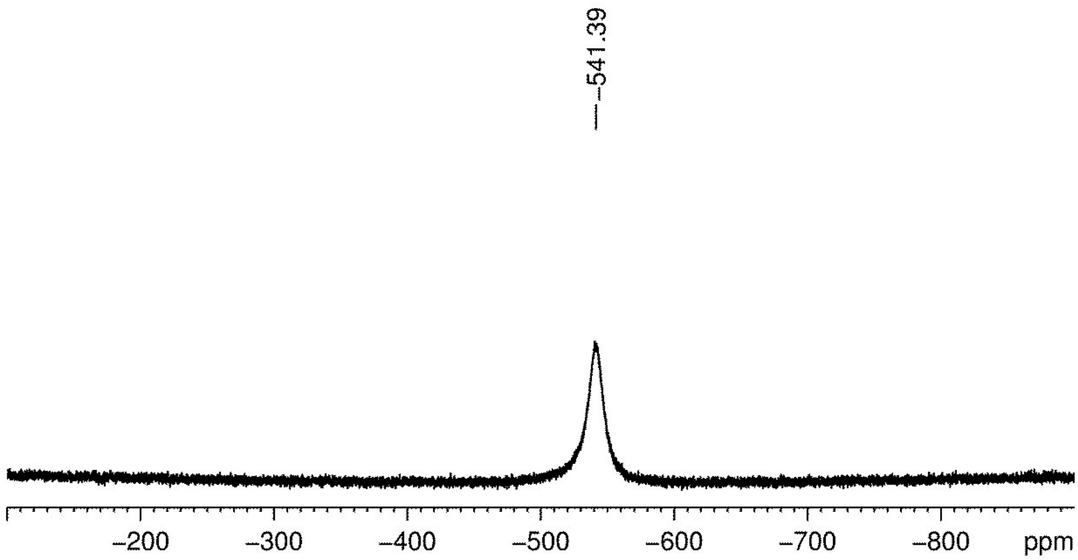


Figure S8: ^{51}V NMR spectrum of compound **3** in CD_3CN at 105 MHz

Copper catalyzed azide-alkyne cycloaddition (CuAAC) coupling method

To a solution of 1 equivalent of compound **3** (85.1 g, 0.015 mmol) and 2 equivalents of alkyne-substrate in 2 ml of dry acetonitrile, 0.5 equivalents of $Cu(I)(CH_3CN)_4PF_6$ were added (from a stock-solution). While stirring, 0.5 equivalents of DIPEA were added to the homogeneous solution. The reaction mixture was kept at 70 °C under argon and in the dark during the course of the reaction. The progress of the reaction was monitored by taking samples from the reaction mixture and recovering the POM by precipitation in diethylether, after which an IR absorbance spectrum was taken. The disappearance of the absorption peak at 2105 cm^{-1} assigned to the azide functionality was a clear indication for the course of the cycloaddition reaction. When the reaction was complete, the solution was cooled down and passed through a TBA^+-loaded cation-exchange resin. The resin was filtered off and the clear solution was added dropwise to an excess of diethylether. The precipitate was collected through centrifugation (4000 rpm, 5 min) and subsequently the remaining solid was washed with water and diethylether (2x) and dried at air for several days to afford a pure yellow solid.

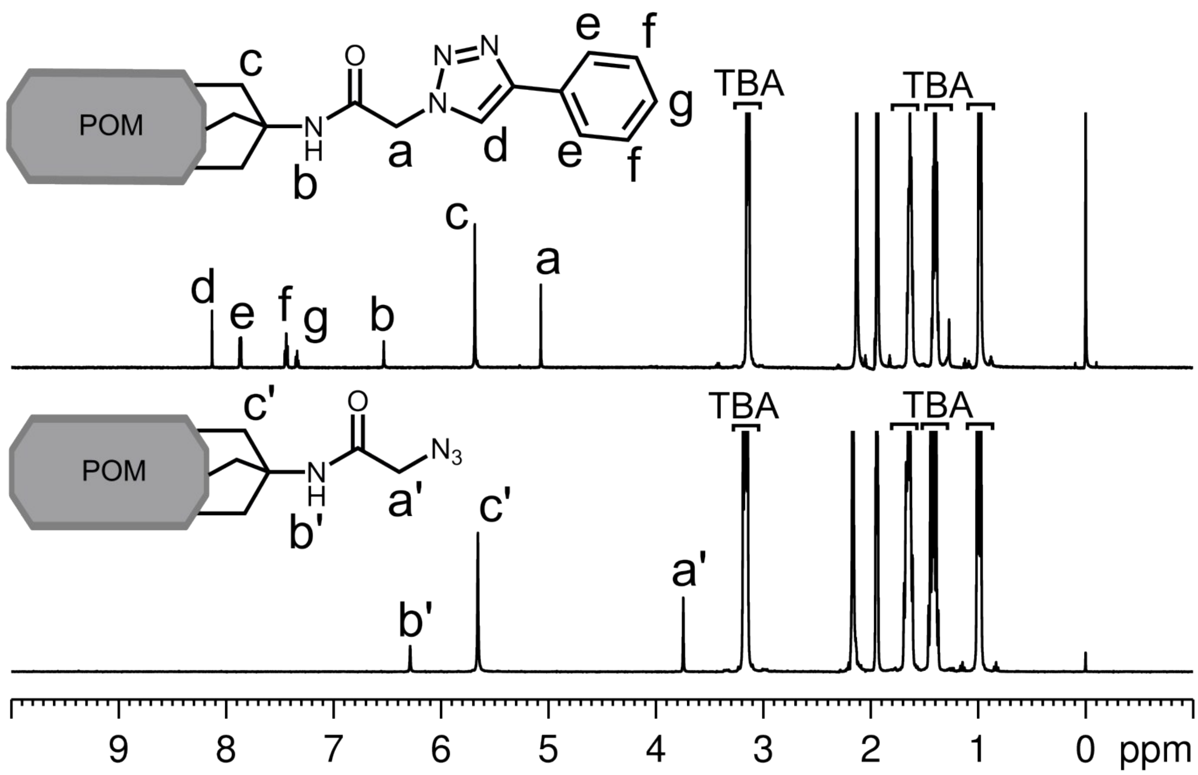
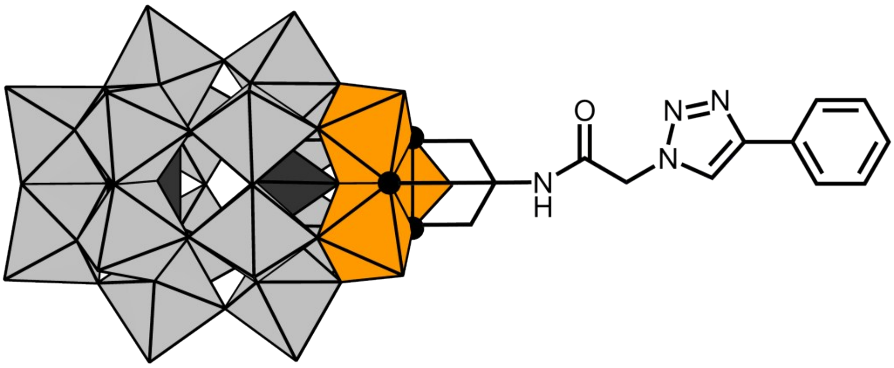


Figure S9: ^1H NMR spectra of compound **3** (bottom) and the CuAAC-coupled product **4a** (top).

Experimental details of compounds 4a-4e

Compound 4a: $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_{11}H_9N_4O]$



Yield: 80 mg (94%). ^{1}H NMR (600 MHz, CD_3CN): δ = 8.13 ppm (s, 1H, N-C**H**=C), 7.87 ppm (d, 2H, C**H**$_{\mathbf{arom, ortho}}$), 7.44 ppm (m, 2H, **CH**$_{\mathbf{arom, meta}}$), 7.34 ppm (t, 1H, **CH**$_{\mathbf{arom, para}}$), 6.53 ppm (s, 1H, C-N**H**-CO), 5.69 ppm (s, 6H, O-C**H**$_\mathbf{2}$-C), 5.07 ppm (s, 2H, CO-C**H**$_\mathbf{2}$-N), 3.14 ppm (m, 48H, **H**$_{\mathbf{TBA}}$), 1.64 ppm (m, 48H, **H**$_{\mathbf{TBA}}$), 1.40 ppm (m, 48H, **H**$_{\mathbf{TBA}}$), 0.98 ppm (t, 72H, **H**$_{\mathbf{TBA}}$). ^{31}P NMR (243 MHz, CD_3CN): δ = -6.74 ppm (**P**W_6V_3), -12.82 ppm (**P**W_9). ^{51}V NMR (157 MHz, CD_3CN): δ = -543.03 ppm (**V**$_3$). IR (cm^{-1}): $\tilde{\nu}$ = 3485 (w), 3241 (w), 2961 (m), 2873 (m), 1699 (w) [**CO**NH-stretch], 1483 (m), 1379 (w), 1084 (s), 947 (s), 903 (s), 804 (vs), 725 (vs), 526 (s), 477 (m). Elemental analysis (%) for $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_{11}H_9N_4O]$ (5674.41 g mol^{-1}): calcd: C 23.28, H 4.10, N 2.47; found: C 22.14, H 3.92, N 2.34. ESI-MS (CH_3CN, negative mode): 1568.81 ([POM+TBA$_2$+H]$^{3-}$), 1649.24 ([POM+TBA$_3$]$^{3-}$)

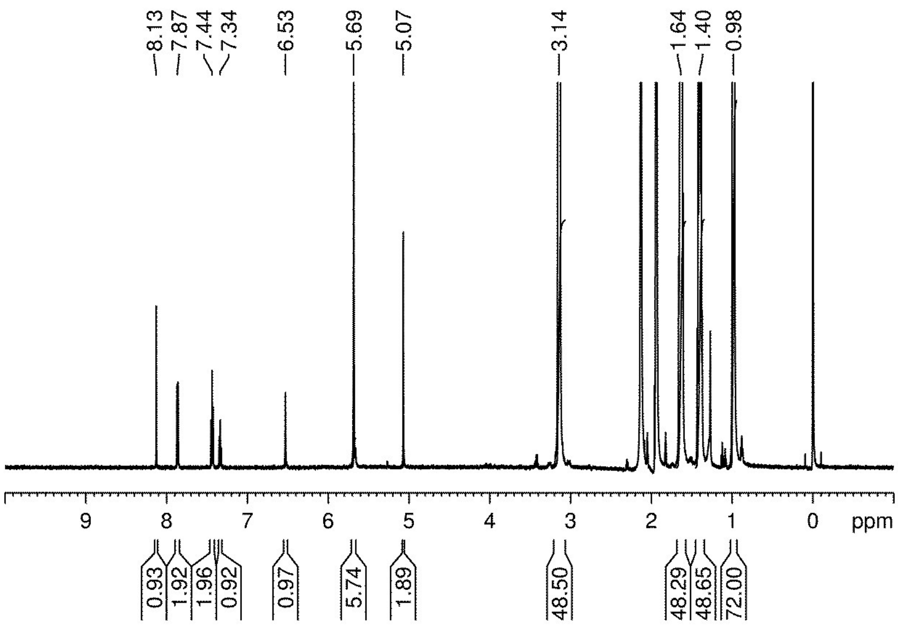


Figure S10: ^{1}H NMR spectrum of compound **4a** in CD_3CN at 600 MHz.

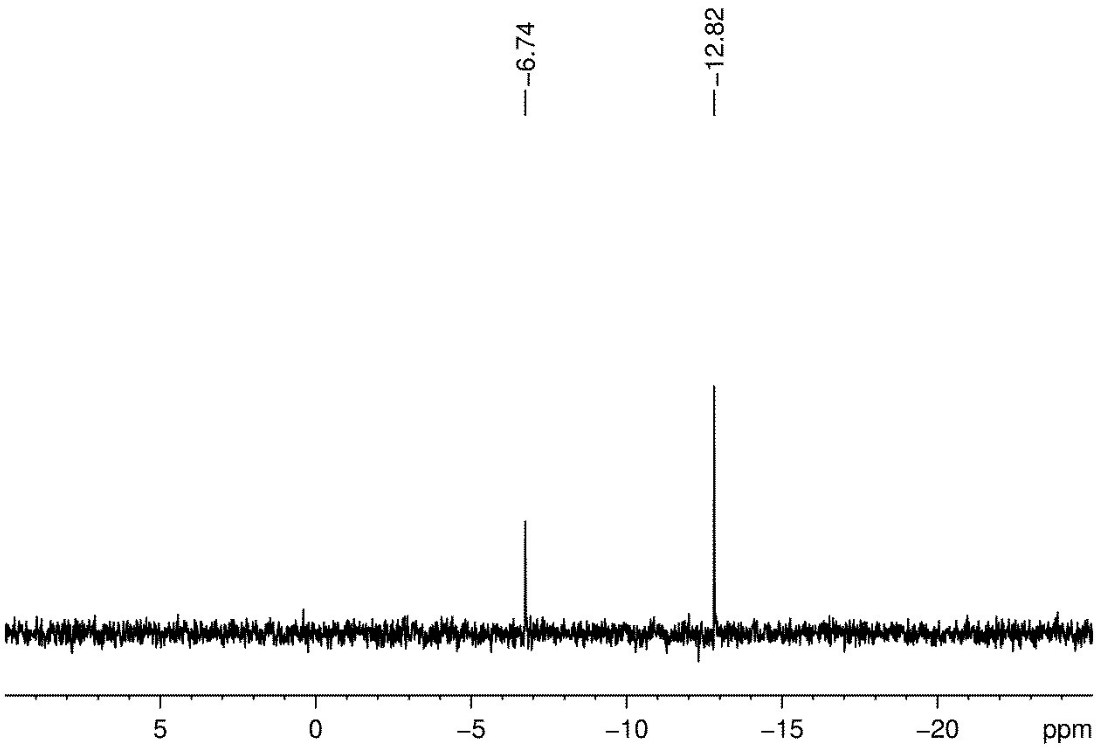


Figure S11: ^{31}P NMR spectrum of compound **4a** in CD_3CN at 243 MHz.

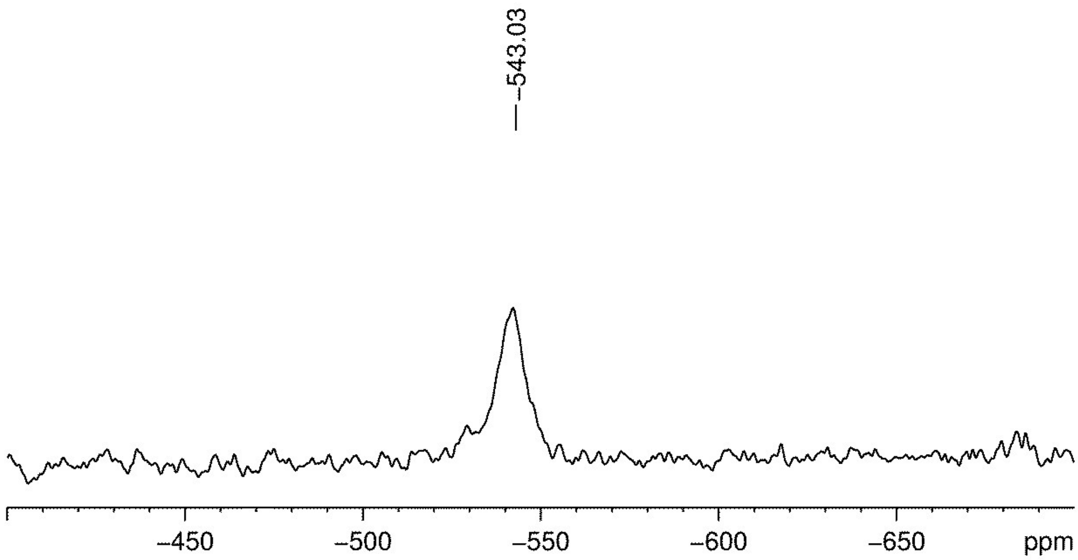
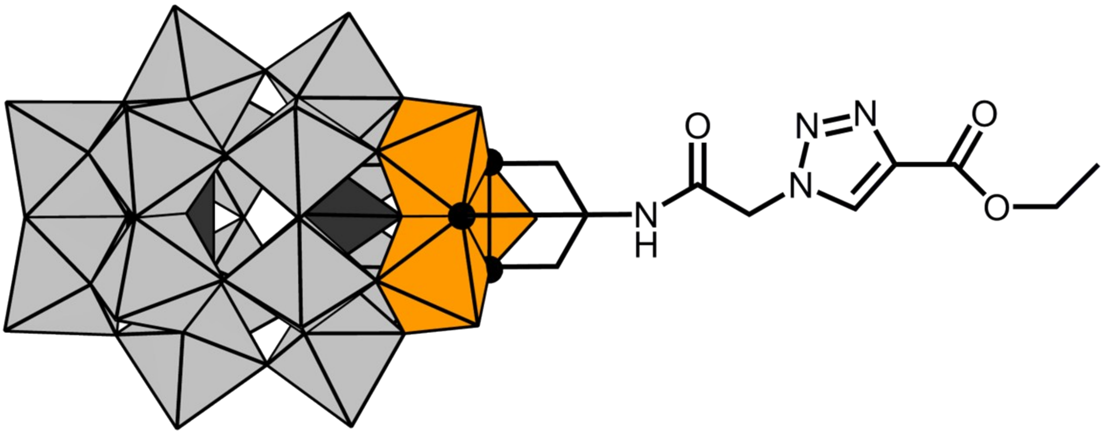


Figure S12: ^{51}V NMR spectrum of compound **4a** in CD_3CN at 157 MHz.

Compound 4b: $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_8H_9N_4O_3]$



Yield: 78 mg (92%). ^{1}H NMR (600 MHz, CD_3CN): δ = 8.27 ppm (s, 1H, N-C**H**=C), 6.55 ppm (s, 1H, C-N**H**-CO), 5.67 ppm (s, 6H, O-C**H₂**-C), 5.10 ppm (s, 2H, CO-C**H₂**-N), 4.33 ppm (q, 2H, O-C**H₂**-CH_3), 3.17 ppm (m, 48H, $\mathbf{H_{TBA}}$), 1.65 ppm (m, 48H, $\mathbf{H_{TBA}}$), 1.42 ppm (m, 48H, $\mathbf{H_{TBA}}$), 1.34 ppm (t, 3H, CH_2-C**H₃**), 0.99 ppm (t, 72H, $\mathbf{H_{TBA}}$). ^{31}P NMR (243 MHz, CD_3CN): δ = -6.74 ppm (**P**W_6V_3), -12.82 ppm (**P**W_9). ^{51}V NMR (157 MHz, CD_3CN): δ = -541.73 ppm ($\mathbf{V_3}$). IR (cm^{-1}): $\tilde{\nu}$ = 3494 (w), 3233 (w), 2961 (m), 2873 (m), 1726 (w) [**CO**O-stretch], 1701 (w) [**CO**NH-stretch], 1483 (m), 1379 (w), 1234 (w), 1084 (s), 947 (s), 902 (s), 803 (vs), 724 (vs), 526 (s), 477 (m). Elemental analysis (%) for $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_8H_9N_4O_3]$ (5670.4 g mol^{-1}): calcd: C 22.66, H 4.11, N 2.47; found: C 21.48, H 3.90, N 2.27. ESI-MS (CH_3CN, negative mode): 1566.47 ($[POM+TBA_2+H]^{3-}$), 1647.56 ($[POM+TBA_3]^{3-}$)

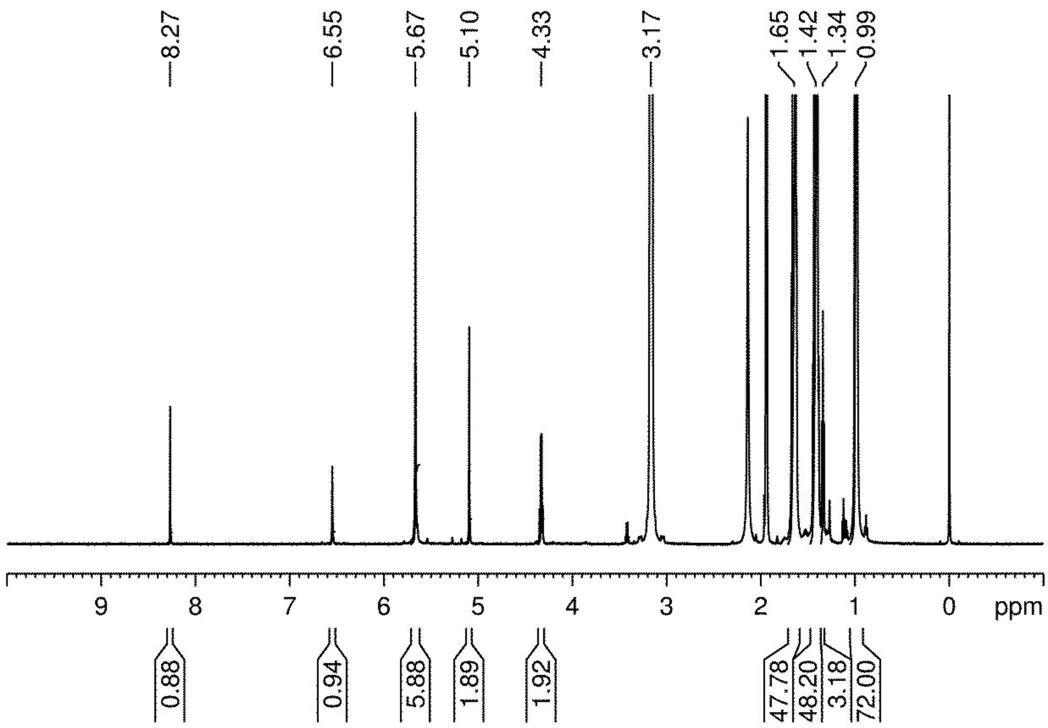


Figure S13: ^{1}H NMR spectrum of compound **4b** in CD_3CN at 600 MHz.

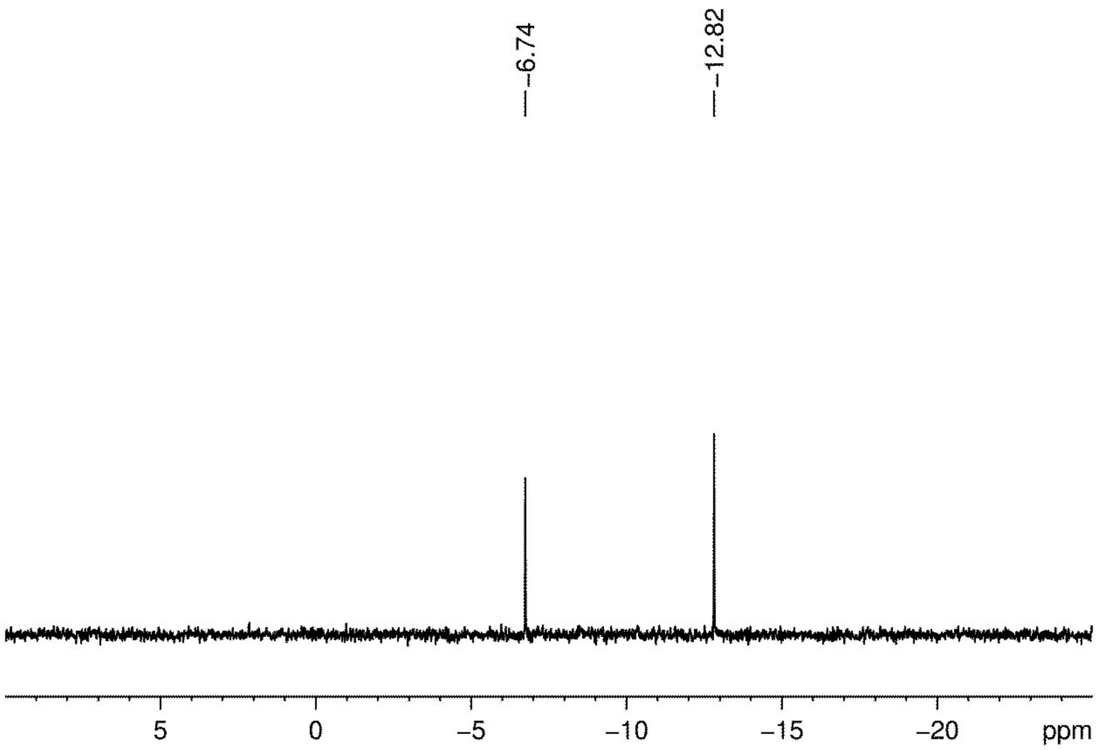


Figure S14: ^{31}P NMR spectrum of compound **4b** in CD_3CN at 243 MHz.

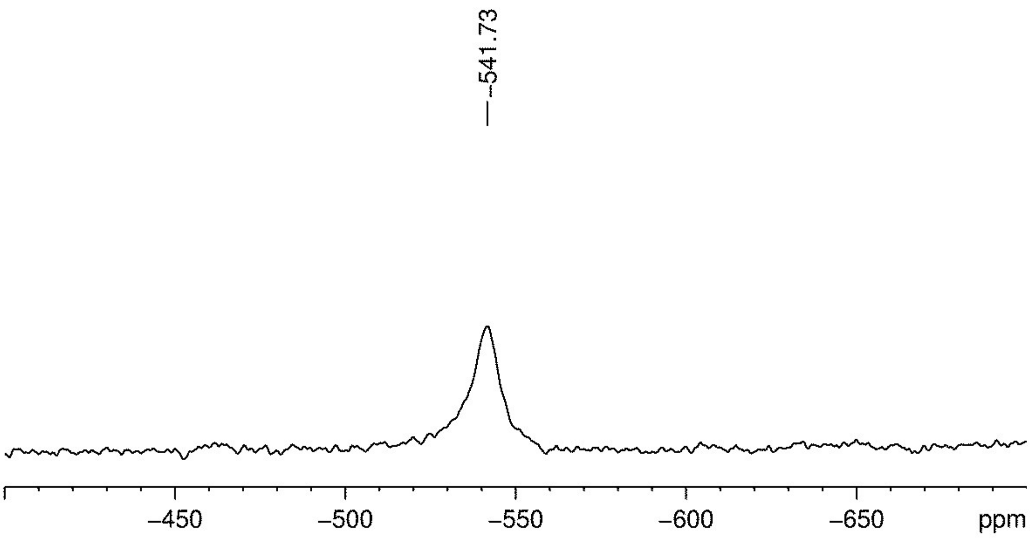
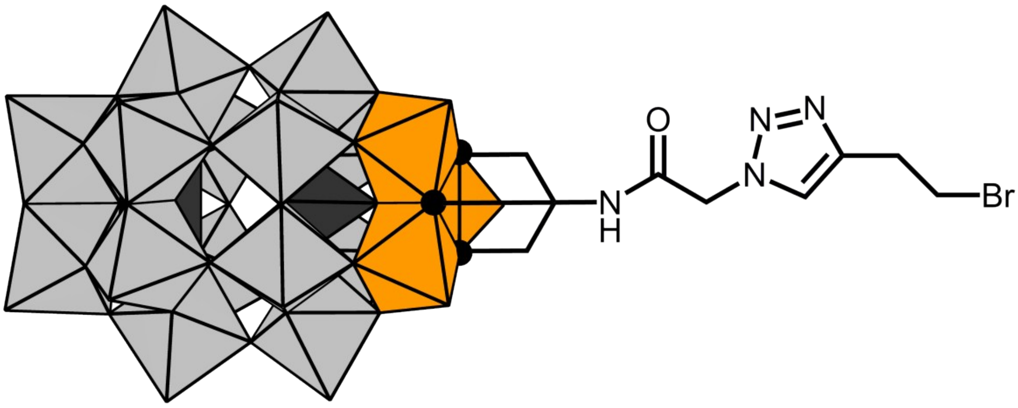


Figure S15: ^{51}V NMR spectrum of compound **4b** in CD_3CN at 157 MHz.

Compound 4c: $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_7H_8N_4OBr]$



Yield: 79 mg (92%). ^{1}H NMR (600 MHz, CD_3CN): δ = 7.69 ppm (s, 1H, N-C**H**=C), 6.46 ppm (s, 1H, C-N**H**-CO), 5.66 ppm (s, 6H, O-C**H₂**-C), 5.00 ppm (s, 2H, CO-C**H₂**-N), 3.70 ppm (t, 2H, CH_2-C**H₂**-Br), 3.25 ppm (t, 2H, C-C**H₂**-CH_2), 3.15 ppm (m, 48H, $\mathbf{H_{TBA}}$), 1.64 ppm (m, 48H, $\mathbf{H_{TBA}}$), 1.40 ppm (m, 48H, $\mathbf{H_{TBA}}$), 0.99 ppm (t, 72H, $\mathbf{H_{TBA}}$). ^{31}P NMR (243 MHz, CD_3CN): δ = -6.75 ppm ($\mathbf{P}W_6V_3$), -12.82 ppm ($\mathbf{P}W_9$). ^{51}V NMR (157 MHz, CD_3CN): δ = -542.14 ppm ($\mathbf{V_3}$). IR (cm^{-1}): $\tilde{\nu}$ = 3478 (w), 3262 (w), 2961 (m), 2873 (m), 1700 (w) [**CO**NH-stretch], 1483 (m), 1379 (w), 1083 (s), 947 (s), 902 (s), 794 (vs), 722 (vs), 526 (s), 477 (m). Elemental analysis (%) for $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_7H_8N_4OBr]$ (5705.3 g mol^{-1}): calcd: C 22.31, H 4.06, N 2.45; found: C 21.05, H 3.83, N 2.27. ESI-MS (CH_3CN, negative mode): 1579.45 ($[POM+TBA_2+H]^{3-}$), 1659.21 ($[POM+TBA_3]^{3-}$)

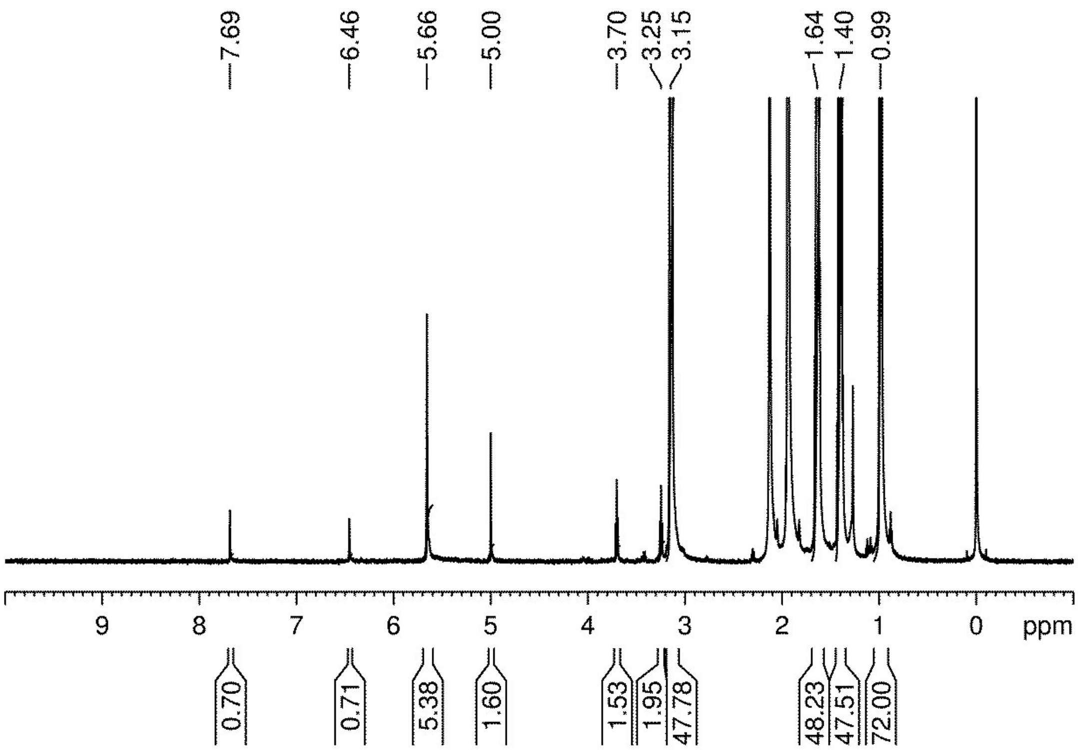


Figure S16: ^{1}H NMR spectrum of compound **4c** in CD_3CN at 600 MHz.

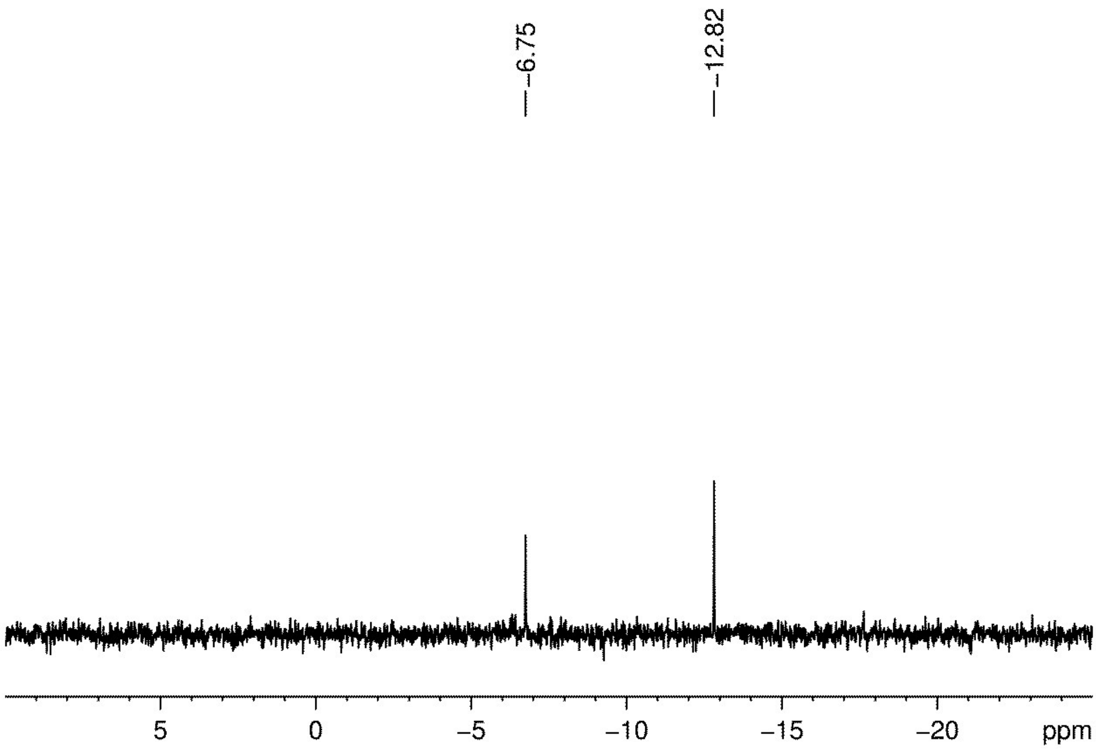


Figure S17: ^{31}P NMR spectrum of compound **4c** in CD_3CN at 243 MHz.

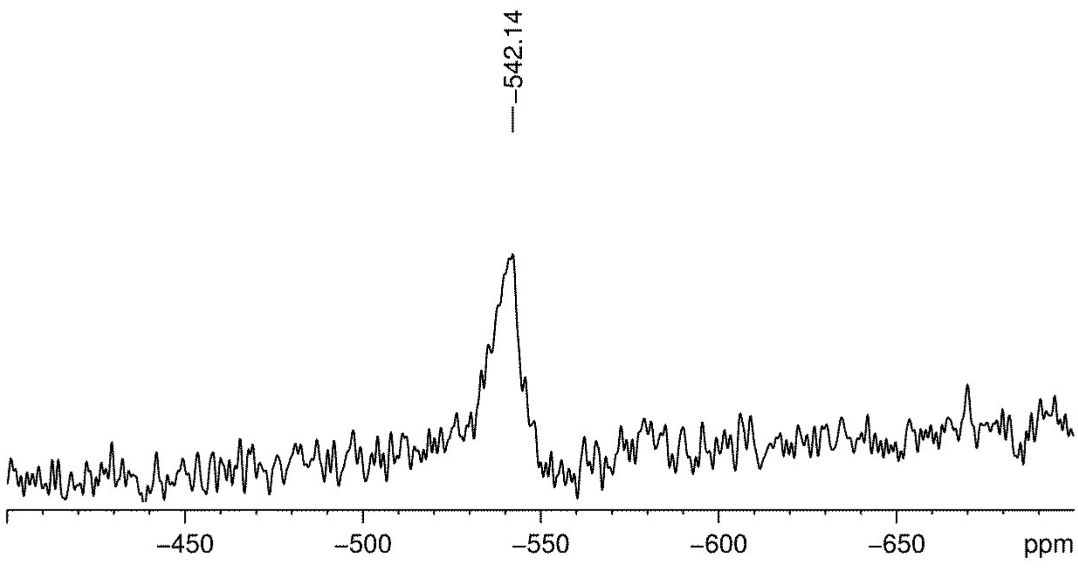
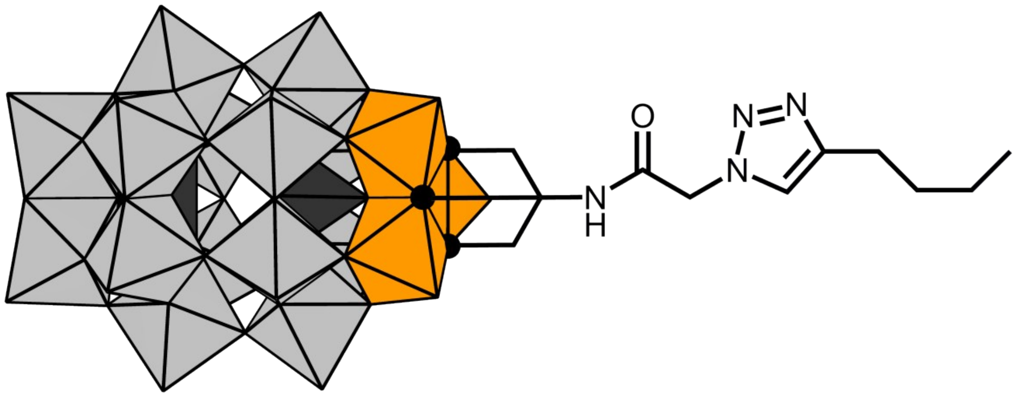


Figure S18: ^{51}V NMR spectrum of compound **4c** in CD_3CN at 157 MHz.

Compound 4d: $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_9H_{13}N_4O]$



Yield: 76 mg (90%). ^{1}H NMR (600 MHz, CD_3CN): δ = 7.54 ppm (s, 1H, N-C**H**=C), 6.45 ppm (s, 1H, C-N**H**-CO), 5.66 ppm (s, 6H, O-C**H$_2$**-C), 4.96 ppm (s, 2H, CO-C**H$_2$**-N), 3.16 ppm (m, 48H, **H$_{TBA}$**), 2.67 ppm (t, 2H, C-C**H$_2$**-CH$_2$) 1.65 ppm (m, 50H, **H$_{TBA}$** + CH$_2$-C**H$_2$**-CH$_2$), 1.42 + 1.37 ppm (m, 50H, **H$_{TBA}$** + CH$_2$-C**H$_2$**-CH$_3$), 0.98 ppm (t, 72H, **H$_{TBA}$**), 0.93 ppm (t, 3H, CH$_2$-C**H$_3$**). ^{31}P NMR (243 MHz, CD_3CN): δ = -6.74 ppm (**P**W$_6$V$_3$), -12.82 ppm (**P**W$_9$). ^{51}V NMR (157 MHz, CD_3CN): δ = -541.90 ppm (**V$_3$**). IR (cm^{-1}): $\tilde{\nu}$ = 3478 (w), 3242 (w), 2961 (m), 2872 (m), 1699 (w) [**CO**NH-stretch], 1483 (m), 1379 (w), 1084 (s), 947 (s), 902 (s), 806 (vs), 726 (vs), 527 (s), 478 (m). Elemental analysis (%) for $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_9H_{13}N_4O]$ (5654.4 g mol^{-1}): calcd: C 22.94, H 4.19, N 2.48; found: C 21.72, H 3.97, N 2.29. ESI-MS (CH_3CN, negative mode): 1562.49 ([POM+TBA$_2$+H]$^{3-}$), 1642.24 ([POM+TBA$_3$]$^{3-}$)

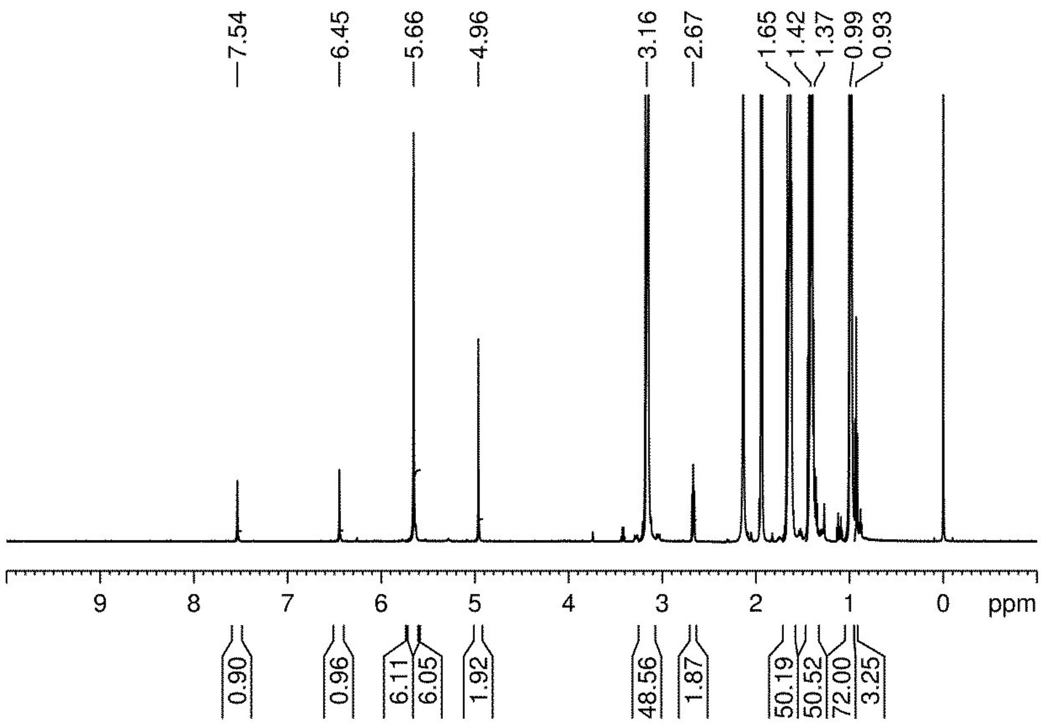


Figure S19: ^{1}H NMR spectrum of compound **4d** in CD_3CN at 600 MHz.

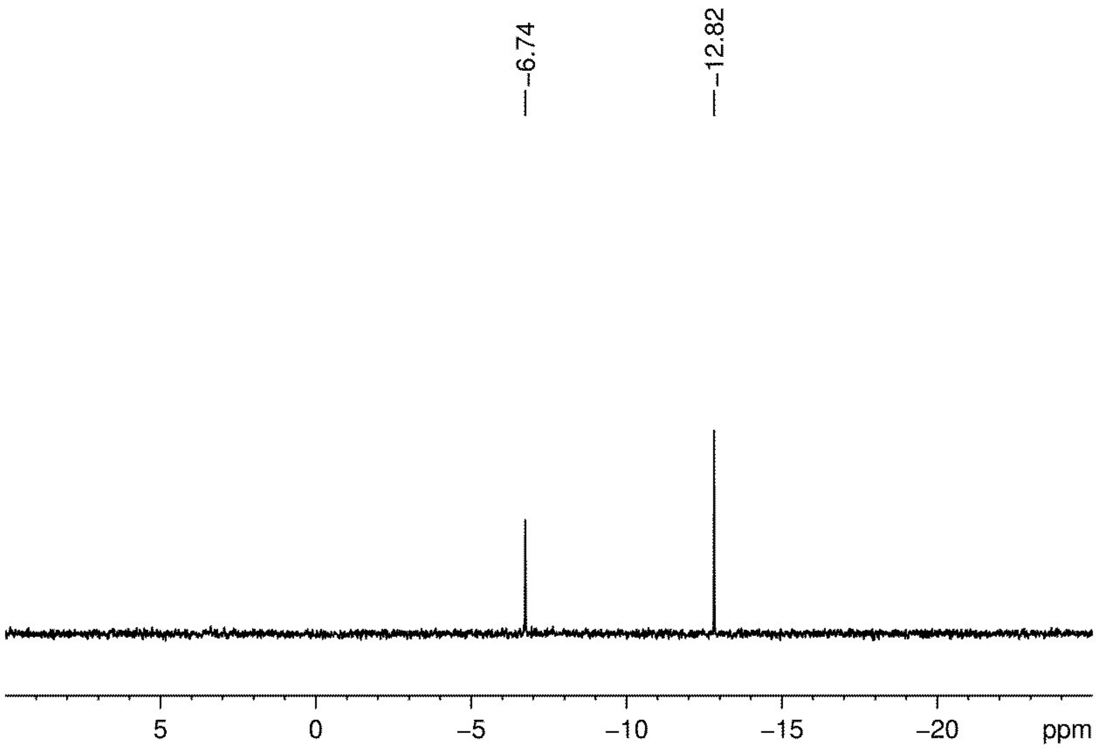


Figure S20: ^{31}P NMR spectrum of compound **4d** in CD_3CN at 243 MHz.

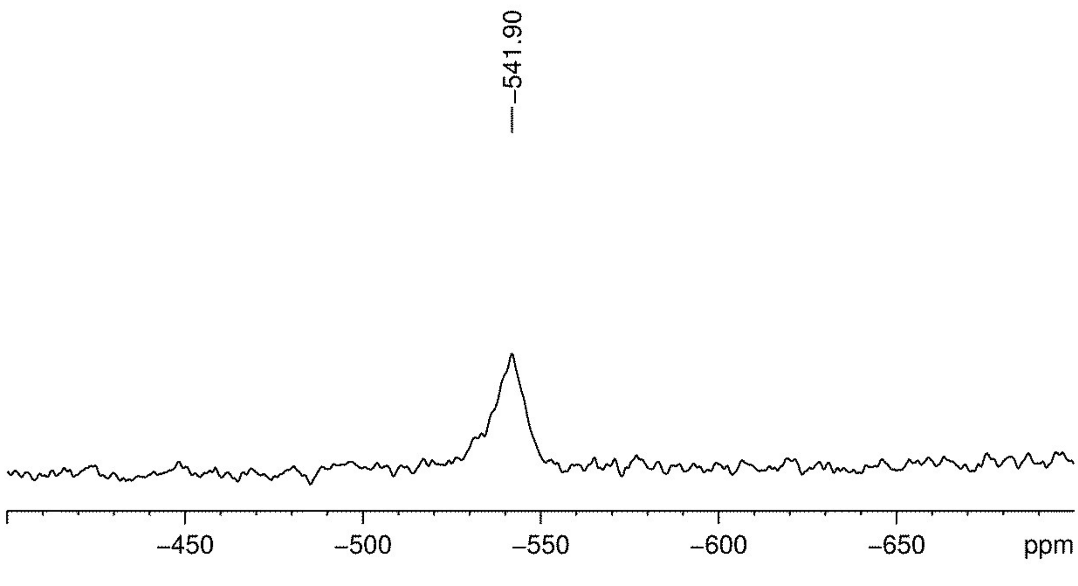
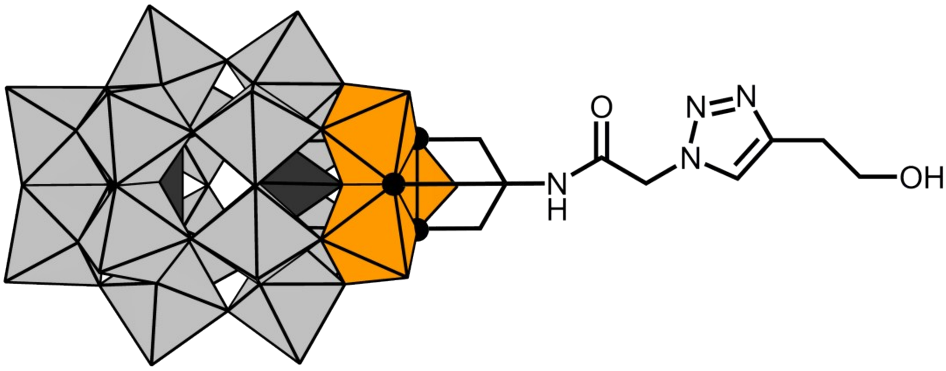


Figure S21: ^{51}V NMR spectrum of compound **4d** in CD_3CN at 157 MHz.

Compound 4e: $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_7H_9N_4O_2]$



Yield: 77 mg (91%). ^{1}H NMR (600 MHz, CD_3CN): δ = 7.63 ppm (s, 1H, N-C**H**=C), 6.45 ppm (s, 1H, C-N**H**-CO), 5.66 ppm (s, 6H, O-C**H₂**-C), 4.99 ppm (s, 2H, CO-C**H₂**-N), 3.76 ppm (br, 2H, CH_2-C**H₂**-OH), 3.16 ppm (m, 48H, **H_{TBA}**), 2.91 ppm (br, 1H, CH_2-O**H**), 2.85 ppm (br, 2H, C-C**H₂**-CH_2), 1.64 ppm (m, 48H, **H_{TBA}**), 1.41 ppm (m, 48H, **H_{TBA}**), 0.99 ppm (t, 72H, **H_{TBA}**). ^{31}P NMR (243 MHz, CD_3CN): δ = -6.75 ppm (**P**W_6V_3), -12.82 ppm (**P**W_9). ^{51}V NMR (157 MHz, CD_3CN): δ = -541.37 ppm (**V_3**). IR (cm^{-1}): $\tilde{\nu}$ = 3477 (w), 3247 (w), 2960 (m), 2872 (m), 1698 (w) [**CO**NH-stretch], 1483 (m), 1379 (w), 1084 (s), 946 (s), 903 (s), 794 (vs), 718 (vs), 526 (s), 477 (m). Elemental analysis (%) for $(C_{16}H_{36}N)_6[P_2W_{15}V_3O_{59}(OCH_2)_3C_7H_9N_4O_2]$ (5642.4 g mol^{-1}): calcd: C 22.56, H 4.13, N 2.48; found: C 19.44, H 3.65, N 2.29. ESI-MS (CH_3CN, negative mode): 1477.05 ($[POM+TBA+H_2]$)$^{3-}$, 1557.81 ($[POM+TBA_2+H]^{3-}$), 1639.57 ($[POM+TBA_3]^{3-}$)

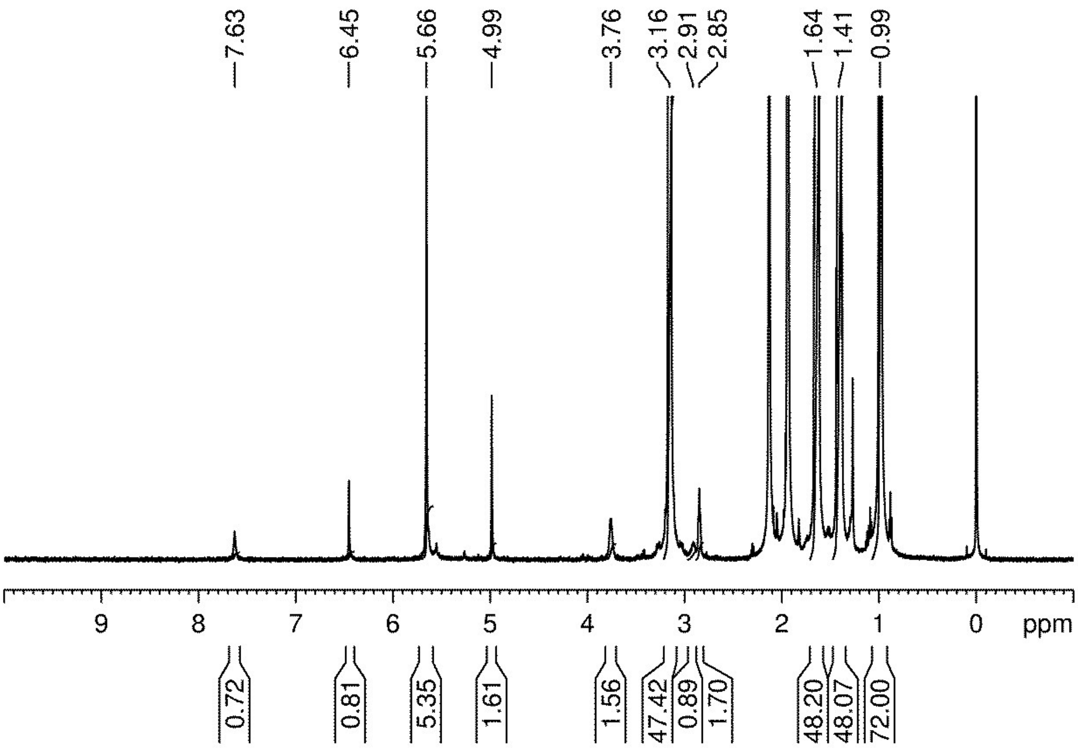


Figure S22: ^{1}H NMR spectrum of compound **4e** in CD_3CN at 600 MHz.

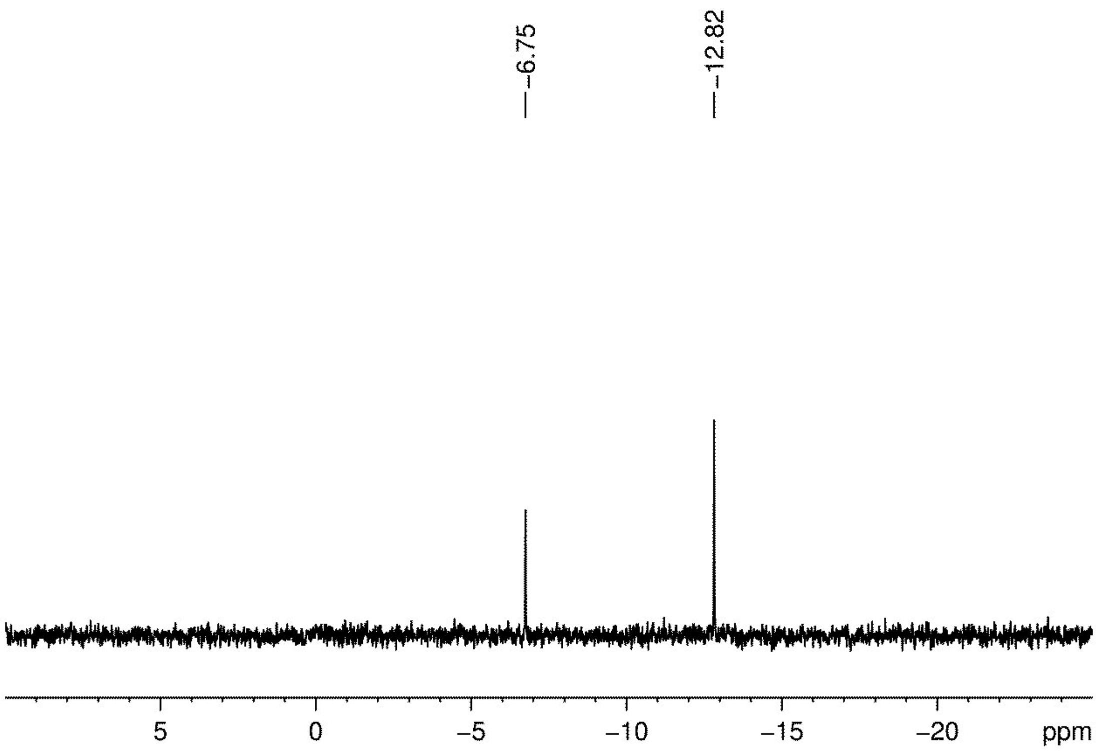


Figure S23: ^{31}P NMR spectrum of compound **4e** in CD_3CN at 243 MHz.

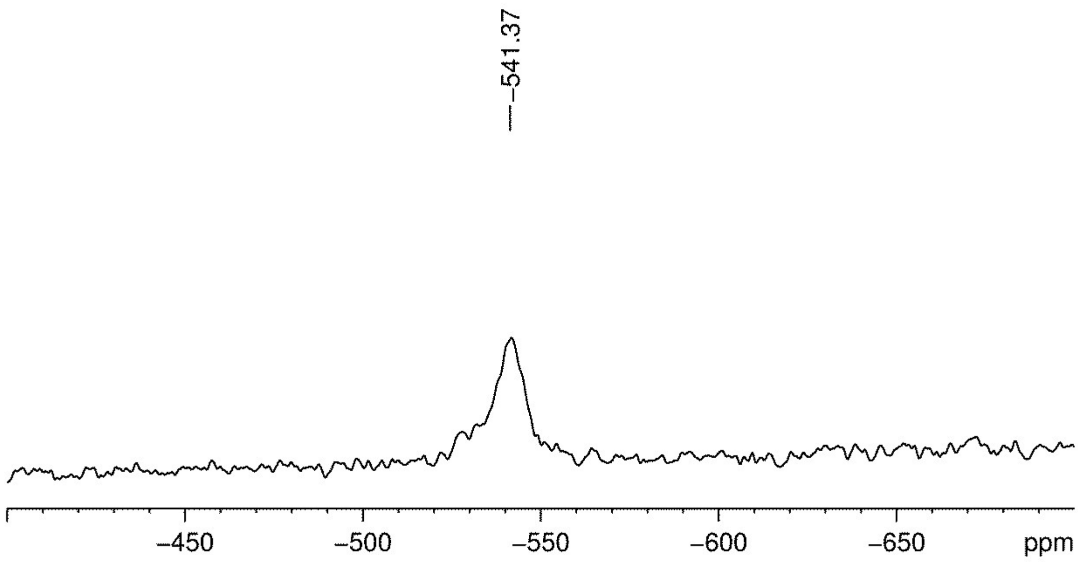
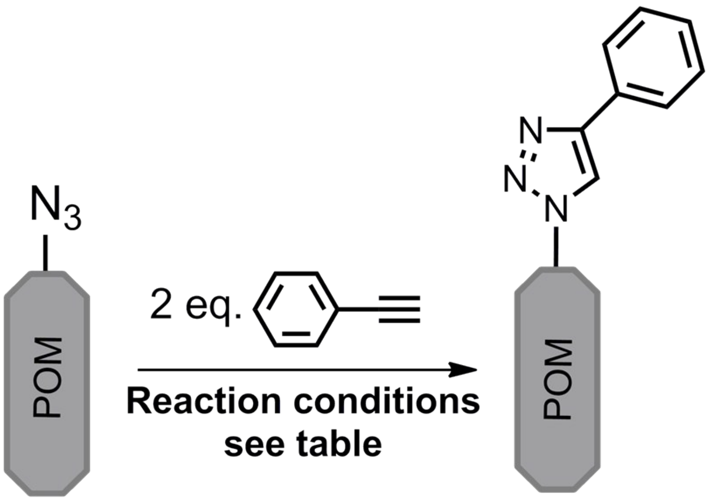


Figure S24: ^{51}V NMR spectrum of compound **4e** in CD_3CN at 157 MHz.

Tables

Table S1: Coupling of phenylacetylene to compound **3** using different reaction conditions in a CuAAC coupling reaction.



Compound 3

Compound 4a

Cu-source	Cu eq.	DIPEA eq.	t (h)	Result
$Cu(I)Br(PPh_3)_3$	0.5	0.5	2	Impure
$Cu(I)Br(PPh_3)_3$	0.5	-	2	Impure
$Cu(I)(CH_3CN)_4PF_6$	1	1	0.5	Pure
$Cu(I)(CH_3CN)_4PF_6$	0.5	0.5	1	Pure
$Cu(I)(CH_3CN)_4PF_6$	0.2	0.2	4	Pure
$Cu(I)(CH_3CN)_4PF_6$	0.5	-	-	No reaction

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3. R. G. Finke, B. Rapko, R. J. Saxton and P. J. Domaille, *J. Am. Chem. Soc.*, 1986, **108**, 2947-2960.
4. S. Vanhaecht, J. Jacobs, L. Van Meervelt and T. N. Parac-Vogt, *Dalton Trans*, 2015, **44**, 19059-19062.