Electronic Supporting Information

The Cu(I)-catalysed Huisgen 1,3-dipolar cycloaddition route to (bio-)organic functionalisation of polyoxovanadates

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1. Analytical methods and chemicals

All starting materials were from commercial sources and used as received. For reactions performed under dry nitrogen using standard Schlenk techniques, the solvents were dried over CaH_2 or molecular sieves (4 Å) and freshly distilled before use.

Elemental analysis was performed using a Vario EL elemental analyser.

^{1}H and ^{51}V NMR spectra were recorded at room temperature on a Bruker 400 spectrometer. Chemical shifts (δ) are given in ppm.

IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer by using KBr pellets ($m_{KBr} \approx 250$ mg) in the range $\nu = 4000–400$ cm^{-1}.

The ESI-MS spectra in positive ion modes were recorded on a 4000 QTRAP mass spectrometer system. The MALDI-TOF mass spectrum was recorded on a MALDI-LTQ-OrbitrapXL from Thermo with an error of < 10 ppm. *trans*-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix substance.

UV/Vis spectra were recorded on a Shimadzu UV-2600 spectrophotometer. The samples were dissolved in dry acetonitrile (**1** and **2a**-**2j**, 0.1 mM), dry dimethyl sulfoxide (TBA_2**2k**, 0.1 mM) or water (Na_2**2k**, 0.01 mM) and measured in quartz cuvettes ($d = 1$ cm).

TGA curves were obtained under nitrogen atmosphere and in air with a heating rate of 10 K min^{-1} using a Mettler Toledo TGA/SDTA 851e instrument.

CV measurements were performed with a BioLogic SP-50 potentiostat under inert conditions (argon) in a degassed and dry 0.1 M $TBAClO_4$-dichloromethane (DCM) solution at 25 °C. The used electrodes are $Ag/AgNO_3$ (reference electrode), glassy carbon (working electrode) and a Pt wire (counter electrode). The redox potentials were measured against the Fc/Fc^+ redox couple as an external standard.

Single-crystal X-ray diffraction data of compounds TBA_2**1** and TBA_2**2f** were collected on a Bruker D8 goniometer with APEX CCD detector and an Incoatec microsource with multilayer optics and Mo-Kα radiation ($\lambda = 0.71073$ Å) was used. The structures were solved by direct methods and refined with full-matrix least-squares on F^2. A summary of the crystal data and structure refinements is given in Table S1 in the Supporting Information. Details are described in the CIF files. CCDC 1558507 and 1558508 contain the supplementary crystallographic data for compounds TBA_2**1** and TBA_2**2f**, respectively.

2. Synthesis of compounds L_1, L_2, L_3 and TBA_2**1**

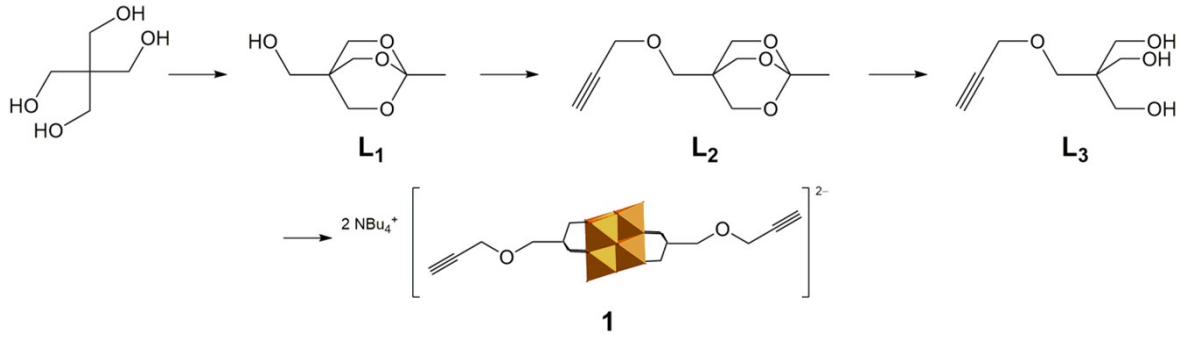


Figure S1: Synthetic steps employed in the preparation of compounds $\mathbf{L_3}$ and TBA_2**1**.

4-(Hydroxymethy1)- 1-met hyl-2,6,7-trioxabicycl0[2.2.2]oxetane (**L**$_1$)

Compound **L**$_1$ was prepared according to the literature procedure.[1] **^{1}H-NMR** (400 MHz, DMSO-d_6): δ = 3.85 (s, 6H), 3.21 (d, $^2J_{H,H}$ = 5.2 Hz, 2H), 1.28 (s, 3H) ppm.

1-Methyl-4-prop-2-ynyloxymethyl-2,6,7-trioxa-bicyclo[2.2.2]octane (**L**$_2$)

Compound **L**$_2$ was prepared according to the literature procedure.[2] **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 4.10 (d, J = 2.3 Hz, 2H), 4.01 (s, 6H), 3.29 (s, 2H), 2.45 (t, J = 2.5 Hz, 1H), 1.46 (s, 3H) ppm.

2,2-Bis-hydroxymethyl-3-prop-2-ynyloxy-propan-1-ol (**L**$_3$)

Compound **L**$_3$ was prepared according to the literature procedure.[2] **^{1}H-NMR** (400 MHz, DMSO-d_6): δ = 4.21 (t, J = 5.4 Hz, 3H), 4.08 (d, J = 2.3 Hz, 2H), 3.36 (m, 9H) ppm.

(nBu$_4$N)$_2$[V_6O_{13}{(OCH$_2$)$_3$CCH$_2$OCH$_2$C≡CH}$_2$] (TBA_2**1**)

Compound TBA_2**1** was prepared by stirring the decavanadate precursor (nBu$_4$N)$_3$[$H_3V_{10}O_{28}$] (2.50 g, 1.48 mmol, 1 eq.) and ligand **L**$_3$ (0.774 g, 4.44 mmol, 3 eq.) in 100 mL acetonitrile (MeCN) for 20 h at 80 °C. The solution was reduced under vacuum to *ca.* 20 mL and precipitated with diethyl ether (Et_2O, *ca.* 200 mL). The product was filtered off, dissolved in DCM and filtered via gravity filtration. The filtrate was purified by column chromatography (Silica, DCM to DCM:MeCN (*v*/*v* 3:1)). After solvent removal, the solid was washed twice with Et_2O and dried under vacuum. Re-crystallisation from MeCN/DMF/Et_2O (*v*/*v*/*v* 1:1:1) by Et_2O diffusion gives compound TBA_2**1** as red crystalline plates. Yield: 76 %.

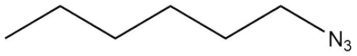
^{1}H-NMR (400 MHz, CD_3CN): δ = 5.03 (s, 12 H), 4.08 (d, J = 2.3 Hz, 4 H), 3.38 (s, 4 H), 3.25–3.09 (m, 16 H), 2.70 (t, J = 2.4 Hz, 2 H), 1.64 (p, J = 9.0 Hz, 16 H), 1.38 (h, J = 7.3 Hz, 16 H), 0.97 (t, J = 7.3 Hz, 24 H) ppm. **^{51}V-NMR** (105 MHz, CD_3CN): δ = –497.52 ppm. **Elemental analysis**, calcd (%) for $C_{48}H_{94}N_2O_{21}V_6 \cdot 2\ H_2O \cdot 0.6$ MeCN (M = 1401.58 g mol^{-1}): C, 42.16; H, 7.18; N, 2.60. Found: C, 42.19; H, 7.06; N, 2.58. **ESI-MS** (pos., MeCN): *m/z* = 1582.577 (1582.583, [M+TBA]$^+$), 1341.290 (1341.306, [M+H]$^+$). **FT-IR** (KBr, cm^{-1}): ν = 3442 (w), 3309 (w), 3236 (w), 2960 (m), 2872 (m), 2358 (w), 2110 (w), 1631 (w), 1480 (m), 1382 (w), 1134 (m), 1053 (vs), 951 (vs), 810 (s), 795 (s), 771 (s), 719 (vs), 622 (s), 581 (s). **UV/VIS** (MeCN): λ_{max} = 248 (sh), 355 (sh) nm.

3. Preparation of organoazides

General procedure for the synthesis of organoazides (**P_1**)

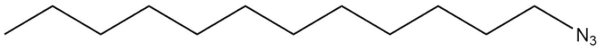
The brominated, chlorinated or mesylated educt (1.0 eq.) was stirred with sodium azide (2.5 eq.) and [18]-crown-6 (0.1 eq.) in dimethyl sulfoxide at room temperature overnight. The mixture was poured into water and extracted with diethyl ether or ethyl acetate three times. The combined organic layers were washed with water and brine. After the organic layer was dried over sodium sulfate, the solvent was removed under vacuum.

1-Azidohexene



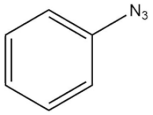
The compound was synthesised from 1-bromohexene following the procedure **P1**. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 1.65–1.56 (m, 2H), 1.46–1.23 (m, 8H), 0.94–0.87 (m, 3H) ppm.

1-Azidododecane



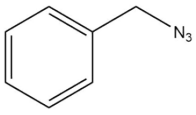
The compound was synthesised from 1-bromododecane following the procedure **P1**. **^{1}H-NMR** (400 MHz, DMSO-d_6): δ = 1.52 (p, J = 7.09 Hz, 2H), 1.38–1.18 (m, 20H), 0.86 (t, J = 6.7 Hz, 3H) ppm.

Azidobenzene



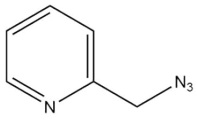
Azidobenzene was prepared according to the standard literature procedure.[3] Phenyl amine (5.60 g, 5.50 mL, 60 mmol) was dissolved in 60 mL aqueous HCl (15 %) under ice cooling. Sodium nitrite ($NaNO_2$, 5.00 g, 72 mmol) in 200 mL H_2O was added carefully and the mixture was stirred at 0 °C for 0.5 h. A solution of NaN_3 (7.82 g, 120 mmol) in 30 mL H_2O was added dropwise and the resulting mixture was stirred for an additional hour at 0 °C. The product was extracted twice with EtOAc and the combined organic layers were washed with water and brine and dried over Na_2SO_4. The product was obtained as a yellow-brown oil after removal of the solvent under reduced pressure. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.34–7.40 (m, 2 H), 7.13–7.19 (m, 1 H), 7.03–7.07 (m, 2 H) ppm.

(Azidomethyl)benzene



The compound was synthesised from (bromomethyl)benzene following the procedure **P_1**. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.39–7.19 (m, 5H), 4.28 (s, 2H) ppm.

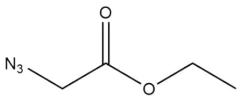
2-(Azidomethyl)pyridine



The compound was synthesised from 2-(pyridyl)methanol according to the literature procedure.[4] **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 8.56–8.62 (m, 1 H), 7.73

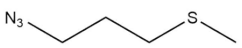
(td, J = 7.8, 1.8 Hz, 1 H), 7.48 (d, J = 7.8 Hz, 1 H), 7.25 (ddd, J = 7.7, 4.9, 1.0 Hz, 1 H), 4.69 (s, 2 H) ppm.

Ethyl 2-azidoacetate



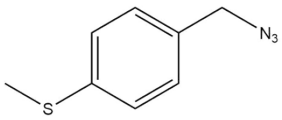
The compound was synthesised from ethyl 2-bromoacetate following the procedure **P1**. **^{1}H-NMR** (400 MHz, DMSO-d_6): δ = 4.17 (q, J = 7.2 Hz, 2H), 4.09 (s, 2H), 1.21 (t, J = 7.09 Hz, 3H) ppm.

(3-Azidopropyl)(methyl)sulfane



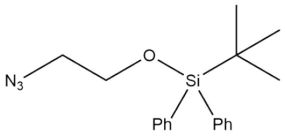
Step 1 ((3-bromopropyl)(methyl)sulfane): 3-(Methylthio)propanol (6.20 g, 6.02 mL, 58 mmol) was dissolved in dry diethyl ether (50 mL) under an inert atmosphere and the mixture was cooled down to 0 °C. After PBr_3 (6.32 g, 2.20 mL, 23 mmol) was slowly added over 30 min, the biphasic system was warmed up to room temperature and stirred overnight. After cooling the reaction mixture to 0 °C, 10 mL of water were slowly added. The organic phase was separated, washed with saturated $NaHCO_3$ and brine and the solvent was removed carefully. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 3.53 (t, J = 6.4 Hz, 2 H), 2.66 (t, J = 6.9 Hz, 2 H), 2.12 (s, 3H), 2.09–2.17 (pent, J = 7.0 Hz, 2 H) ppm.
Step 2: The final organoazide was prepared according to the procedure **P1**. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 3.37–3.50 (m, 2 H), 2.50–2.66 (m, 2 H), 2.11 (br. s., 3 H), 1.79–1.95 (m, 2 H) ppm.

(4-(Azidomethyl)phenyl)(methyl)sulfane



Step 1 (4-(methylthio)benzylalcohol): $NaBH_4$ (0.467 g, 12.3 mmol) was dissolved in MeOH (20 mL) and 4-(methylthio)benzaldehyde (4.70 g, 30.9 mmol) was added slowly. The mixture was stirred at room temperature for 12 h and 10 mL of water were added. The solvent was reduced under vacuum, poured into water and extracted twice with dichloromethane. The organic phases were combined, washed with brine and dried over $MgSO_4$. Further purification could be carried out using flash chromatography (DCM). Yield: 80 %. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.27–7.31 (m, 2 H), 7.24–7.27 (m, 2 H), 4.64 (d, J = 5.9 Hz, 2 H), 2.48–2.50 (m, 3 H) ppm.
Step 2 (4-(methylthio)benzylbromide): 4-(methylthio)benzylbromide was prepared according to the procedure described above for (3-bromopropyl)(methyl)sulfane. Yield: 98 %. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.30–7.34 (m, 2 H), 7.20–7.24 (m, 2 H), 4.49 (s, 2 H), 2.49 (s, 3 H) ppm.
Step 3: The final organoazide was prepared according to the procedure **P1**. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.37–7.18 (m, 4H), 4.31 (s, 2H), 2.51 (s, 3H) ppm.

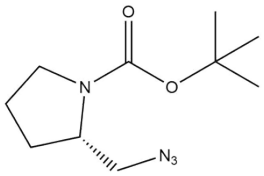
(2-Azidoethoxy)(*tert*-butyl)diphenylsilane



The compound was synthesised from (2-bromoethoxy)(*tert*-butyl)diphenylsilane via silylation of 2-bromoethanol,[5] followed by azidation according to the procedure **P1**. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ =

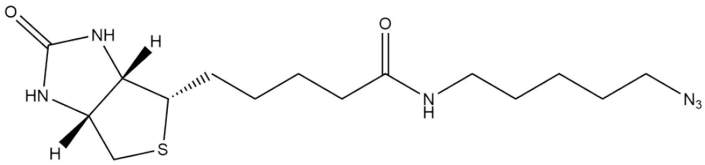
7.69–7.73 (m, 4 H), 7.39–7.47 (m, 6 H), 3.81–3.85 (m, 2 H), 3.29–3.34 (t, *J* = 5.1, 2 H), 1.10 (s, 9 H) ppm.

tert-Butyl (S)-2-(azidomethyl)pyrrolidine-1-carboxylate



The compound was synthesised from (*S*)-pyrrolidin-2-ylmethanol (*L*-prolinol) via the formation of a boc-protected amine and mesylation of the alcohol followed by azidation according to the literature procedure.[6] **^{1}H-NMR** (400 MHz, DMSO-d_6): δ = 4.03–3.77 (br s, 1H), 3.74–3.42 (br s, 1H), 3.43–3.30 (m, 3H), 2.04–1.76 (m, 4H), 1.48 (s, 9H) ppm.

N-(5-azidopentyl)-5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)pentanamide (biotin-(5-azido-pentyl)-amide)



Step 1 (5-azidopentyl-1-amine): The compound was synthesised from 1,5-dibromopentane via azidation and asymmetric reduction according to the literature procedures.[7] *Step 2:* The following amidation with biotin differs slightly from the reported one: Biotin (0.500 g, 2.0 mmol) and 1-hydroxybenzotriazole hydrate (1-HBT, 0.332 g, 2.5 mmol) were dissolved in dry DMF under a nitrogen atmosphere and the mixture was cooled down to 0 °C using an ice bath. *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDCI, 0.699 g, 4.5 mmol) was added dropwise. After stirring for 1 h at 0 °C and for 1 h at room temperature, a solution of 5-azidopentyl-1-amine (0.315 g, 2.5 mmol) and NEt_3 (0.85 mL, 6.1 mmol) in 2 mL of dry DMF was added. The resulting solution was stirred overnight. After solvent removal, washing with water and purification via column chromatography the product was obtained as a white solid. The acquired analytical data are consistent with the reported ones. **^{1}H-NMR** (400 MHz, DMSO-d_6): δ = 7.76 (t, *J* = 5.5 Hz, 1 H), 6.43 (s, 1 H), 6.36 (s, 1 H), 4.30 (dd, *J* = 7.4, 5.1 Hz, 1 H), 4.07–4.18 (m, 1 H), 3.31 (t, *J* = 6.9 Hz, 2 H), 3.06–3.13 (m, 1 H), 3.02 (q, *J* = 6.4 Hz, 2 H), 2.82 (dd, *J* = 12.4, 5.1 Hz, 1 H), 2.57 (d, *J* = 12.3 Hz, 1 H), 2.04 (t, *J* = 7.4 Hz, 2 H), 1.35–1.62 (m, 8 H), 1.25–1.34 (m, 4 H) ppm.

4. Preparation of compounds TBA_2**2a**–TBA_2**2k** and Na_2**2k**

General procedure. 10 mL of a catalyst stock solution (N_2) containing CuI (0.1 eq.) and diisopropylethylamine (DIPEA, 0.2 eq.) in MeCN were added to TBA_2**1** (100 mg, 1.0 eq.) and the corresponding organoazide (2.5 eq.) in a Schlenk flask under an inert (N_2) atmosphere. After the reaction solution was stirred for *ca.* 3h, the solvent was reduced to 2-3 mL under vacuum and the residue was diluted with dichloromethane and washed with a 0.25 % aqueous NH_4OH. The phases were separated and the organic one was filtered through a Celite pad. After solvent removal the residue was washed carefully three times with Et_2O and EtOAc by centrifugation. The product was dried under vacuum. Crystallisation of all compounds was performed by diffusion of Et_2O into a solution of DMF/MeCN/Et_2O (v/v/v 1:2:2). Single crystals suitable for X-ray diffraction analysis were obtained only in the case of compound TBA_2**2f**.

$(n\mathrm{Bu_4N})_2[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3(CH_2)_5CH_3\}_2]$ (TBA_2**2a**)

Yield: 97 %.

^{1}H-NMR (400 MHz, CD_3CN): δ = 7.74 (s, 2 H, C-*CH*=C), 4.99 (s, 12 H, -*CH_2*-O), 4.50 (s, 4 H, C=C-*CH_2*-O), 4.31 (t, *J* = 7.2 Hz, 4 H, N-*CH_2*-), 3.34 (s, 4 H, -O-*CH_2*-C), 3.08–3.24 (m, 16 H, $CH_3CH_2CH_2$-*CH_2*-N^+), 1.84 (p, *J* = 6.9 Hz, 4 H, NCH_2-*CH_2*-CH_2), 1.73–1.57 (m, 16 H, CH_3CH_2-*CH_2*-CH_2N^+), 1.37 (h, *J* = 7.2 Hz, 16 H, CH_3-*CH_2*-$CH_2CH_2N^+$), 1.22–1.32 (m, 12 H, -*CH_2*-), 0.97 (t, *J* = 7.3 Hz, 24 H, *CH_3*-$CH_2CH_2CH_2N^+$), 0.83–0.91 (m, 6 H, CH_2-*CH_3*) ppm. **^{51}V-NMR** (105 MHz, CD_3CN): δ = –497.08 ppm. **ESI-MS** (pos., MeCN): *m/z* = 1836.800 (1836.805, $[M+TBA]^+$), 1671.675 (1671.675, $[M+TBA-C_9H_{15}N_3]^+$), 1595.526 (1595.528, $[M+H]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3425 (w), 3122 (w), 2958 (s), 2931 (s), 2869 (s), 2674 (w), 1631 (w), 1548 (w), 1468 (s), 1380 (s), 1343 (m), 1304 (m), 1221 (m), 1190 (m), 1134 (vs), 1048 (vs), 994 (s), 951 (vs), 883 (m), 809 (vs), 795 (vs), 718 (vs), 581 (s), 511 (s), 461 (s), 418 (vs). **UV/Vis** (MeCN): λ_{max} = 244 (sh), 271 (sh), 356 (sh) nm.

$(n\mathrm{Bu_4N})_2[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3(CH_2)_{11}CH_3\}_2]$ (TBA_2**2b**)

Yield: 89 %.

^{1}H-NMR (400 MHz, CD_3CN): δ = 7.71 (s, 2 H, C-*CH*=C), 4.99 (s, 12 H, -*CH_2*-O), 4.49 (s, 4 H, C=C-*CH_2*-O), 4.30 (t, *J* = 7.2 Hz, 4 H), 3.34 (s, 4 H, -O-*CH_2*-C), 3.06–3.18 (m, 16 H, $CH_3CH_2CH_2$-*CH_2*-N^+), 1.75–1.90 (m, 4 H, -*CH_2*-), 1.62 (p, *J* = 8.3 Hz, 16 H, CH_3CH_2-*CH_2*-CH_2N^+), 1.34–1.45 (m, 16 H, CH_3-*CH_2*-$CH_2CH_2N^+$), 1.26–1.34 (m, 36 H, -*CH_2*-), 0.97 (t, *J* = 7.3 Hz, 24 H, *CH_3*-$CH_2CH_2CH_2N^+$), 0.92–0.84 (m, 6 H, CH_2-*CH_3*) ppm. **^{51}V-NMR** (105 MHz, CD_3CN): δ = –497.12 ppm. **ESI-MS** (pos., MeCN): *m/z* = 2004.987 (2004.939, $[M+TBA]^+$), 1785.691 (1785.698, $[M+Na]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3421 (m), 3118 (w), 2959 (vs), 2925(vs), 2852 (vs), 1628 (w), 1466 (m), 1382 (m), 1135 (vs), 1047 (vs), 951 (vs), 810 (s), 785 (s), 718 (vs), 581 (m). **UV/Vis** (MeCN): λ_{max} = 245 (sh), 271 (sh), 355 (sh) nm.

$(n\mathrm{Bu_4N})_2[\mathrm{V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3C_6H_5\}_2}]$ (TBA$_2$**2c**)

Yield: 65 %.

^{1}H-NMR (400 MHz, CD_3CN): δ = 8.28 (s, 2 H, C-*CH*=C), 7.86–7.80 (m, 4 H, -$C_{ar}H$), 7.62–7.56 (m, 4 H, -$C_{ar}H$), 7.53–7.47 (m, 2 H, -$C_{ar}H$), 5.06 (s, 12 H, -CH_2-O), 4.63 (s, 4 H, C=C-CH_2-O), 3.45 (s, 4 H, -O-CH_2-C), 3.11–3.18 (m, 16 H, $CH_3CH_2CH_2$-CH_2-N^+), 1.65 (p, J = 7.8 Hz, 16 H, CH_3CH_2-CH_2-CH_2N^+), 1.39 (h, J = 7.3 Hz, 16 H, CH_3-CH_2-$CH_2CH_2N^+$), 0.99 (t, J = 7.3 Hz, 24 H, CH_3-$CH_2CH_2CH_2N^+$) ppm. **^{51}V-NMR** (105 MHz, CD_3CN): δ = –497.30 ppm. **ESI-MS** (pos., MeCN): *m/z* = 1820.675 (1820.680, $[M+TBA]^+$), 1663.612 (1663.616, $[M+TBA-C_9H_7N_3]^+$). **FT-IR** (KBr, cm^{-1}): ν =3424 (w), 3124 (w), 3068 (w), 2959 (m), 2933 (m), 2817 (m), 1596 (w), 1545 (w), 1501 (m), 1468 (m), 1381 (m), 1349 (w), 1303 (w), 1232 (m), 1189 (m), 1134 (s), 1097 (m), 1049 (vs), 998 (m), 948 (vs), 881 (m), 808 (s), 763 (s), 718 (vs), 580 (s), 513 (m), 473 (m), 417 (vs). **UV/Vis** (MeCN): λ_{max} = 248, 345 (sh) nm.

$(n\mathrm{Bu_4N})_2[\mathrm{V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2C_6H_5\}_2}]$ (TBA$_2$**2d**)

Yield: 90 %.

^{1}H-NMR (400 MHz, CD_3CN): δ = 7.77 (s, 2 H, C-*CH*=C), 7.32–7.43 (m, 6 H, -$C_{ar}H$), 7.32–7.24 (m, 4 H, -$C_{ar}H$), 5.52 (s, 4H, N-CH_2-Ph), 4.97 (s, 12 H, -CH_2-O), 4.48 (s, 4 H, C=C-CH_2-O), 3.33 (s, 4 H, -O-CH_2-C), 3.20–3.05 (m, 16 H, $CH_3CH_2CH_2$-CH_2-N^+), 1.62 (p, J = 7.9 Hz, 16 H, CH_3CH_2-CH_2-CH_2N^+), 1.37 (h, J = 7.4 Hz, 16 H, CH_3-CH_2-$CH_2CH_2N^+$), 0.96 (t, J = 7.3 Hz, 24 H, CH_3-$CH_2CH_2CH_2N^+$) ppm. **^{51}V-NMR** (105 MHz, CD_3CN): δ = –497.26 ppm. **ESI-MS** (pos., MeCN): *m/z* = 1848.704 (1848.711, $[M+TBA]^+$), 1677.626 (1677.632, $[M+TBA-C_{10}H_9N_3]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3428 (w), 3112 (w), 2960 (m), 2872 (m), 1633 (w), 1468 (m), 1382 (w), 1134 (s), 1046 (s), 950 (vs), 795 (s), 720 (vs), 582 (s). **UV/Vis** (MeCN): λ_{max} = 250 (sh), 348 (sh) nm.

$(n\mathrm{Bu_4N})_2[\mathrm{V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2}$-*2*-$\mathrm{NC_5H_4\}_2}]$ (TBA$_2$**2e**)

Yield: 70 %.

^{1}H-NMR (400 MHz, CD_3CN): δ = 8.55 (d, J = 4.9 Hz, 2 H, N_{py}-$C_{ar}H$), 7.87 (s, 2 H, C-*CH*=C), 7.77 (td, J = 7.7, 1.8 Hz, 2 H, -$C_{ar}H$), 7.31 (ddd, J = 7.6, 4.8, 1.1 Hz, 2 H, -$C_{ar}H$), 7.20 (d, J = 7.8 Hz, 2 H, -$C_{ar}H$), 5.65 (s, 4 H, -CH_2-Py), 5.00 (s, 12 H, -CH_2-O), 4.54 (s, 4 H, C=C-CH_2-O), 3.37 (s, 4 H, -O-CH_2-C), 3.15 (t, J = 8.9 Hz, 16 H, $CH_3CH_2CH_2$-CH_2-N^+), 1.72–1.58 (m, 16 H, CH_3CH_2-CH_2-CH_2N^+), 1.39 (h, J = 7.3 Hz, 16 H, CH_3-CH_2-$CH_2CH_2N^+$), 0.99 (t, J = 7.3 Hz, 24 H, CH_3-$CH_2CH_2CH_2N^+$). **^{51}V-NMR** (105 MHz, CD_3CN): δ = –497.34 ppm. **ESI-MS** (pos., MeCN): *m/z* = 1850.698 (1850.701, $[M+TBA]^+$), 1678.624 (1678.627, $[M+TBA-C_9H_8N_4]^+$), 1609.422 (1609.424, $[M+H]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3430 (w), 3120 (w), 3069 (w), 2959 (s), 2934 (s), 2817 (s), 2098 (w), 1632 (w), 1591 (w), 1572 (w), 1476 (s), 1439 (m), 1381 (m), 1223 (m), 1190 (m), 1134 (s), 1096 (m), 1047 (vs), 987 (m), 949 (vs), 882 (m), 809 (vs), 795 (vs), 717 (vs), 581 (s), 510 (m), 460 (m), 418 (vs). **UV/Vis** (MeCN): λ_{max} = 247, 278 (sh), 347 (sh) nm.

$(n\mathrm{Bu_4N})_2[\mathrm{V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2CO_2CH_2CH_3\}_2}]$ ($\mathrm{TBA_2}$**2f**)

Yield: 68 %.

^{1}H-NMR (400 MHz, $\mathrm{CD_3CN}$): δ = 7.80 (s, 2 H, C-*CH*=C), 5.16 (s, 4 H, N-CH_2-CO_2), 4.99 (s, 12 H, -CH_2-O), 4.53 (s, 4 H, C=C-CH_2-O), 4.20 (q, J = 7.1 Hz, 4 H, O-CH_2-CH_3), 3.35 (s, 4 H, -O-CH_2-C), 3.20–3.06 (m, 16 H, $CH_3CH_2CH_2$-CH_2-N^+), 1.69–1.55 (m, 16 H, CH_3CH_2-CH_2-CH_2N^+), 1.37 (h, J = 7.3 Hz, 16 H, CH_3-CH_2-$CH_2CH_2N^+$), 1.24 (t, J = 7.2 Hz, 6 H, OCH_2-CH_3), 0.97 (t, J = 7.3 Hz, 24 H, CH_3-$CH_2CH_2CH_2N^+$) ppm. **^{51}V-NMR** (105 MHz, $\mathrm{CD_3CN}$): δ = –497.99 ppm. **ESI-MS** (pos., MeCN): *m/z* = 1840.676 (1840.691, $[M+TBA]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3425 (w), 3113 (w), 3072(w), 2960 (s), 2931(s), 2855 (s), 1738(s), 1628 (w), 1471 (m), 1384 (m), 1136 (s), 1046 (vs), 951 (vs), 810 (s), 785 (s), 719 (vs), 581 (s). **UV/Vis** (MeCN): λ_{max} = 246, 278 (sh), 351 (sh) nm.

$(n\mathrm{Bu_4N})_2[\mathrm{V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3(CH_2)_3SCH_3\}_2}]$ ($\mathrm{TBA_2}$**2g**)

Yield: 78 %.

^{1}H-NMR (400 MHz, $\mathrm{CD_3CN}$): δ = 7.75 (s, 2 H, C-*CH*=C), 4.99 (s, 12 H, -CH_2-O), 4.50 (s, 4 H, C=C-CH_2-O), 4.41 (t, J = 7.0 Hz, 4 H, N-CH_2-CH_2), 3.34 (s, 4 H, -O-CH_2-C), 3.15–3.11 (m, 16 H, $CH_3CH_2CH_2$-CH_2-N^+), 2.44 (t, J = 7.1 Hz, 4 H, S-CH_2-CH_2), 2.10–2.17 (m, 4 H, CH_2-CH_2-CH_2), 2.05 (s, 6 H, S-CH_3), 1.76–1.49 (m, 16 H, CH_3CH_2-CH_2-CH_2N^+), 1.37 (h, J = 7.3 Hz, 16 H, CH_3-CH_2-$CH_2CH_2N^+$), 0.97 (t, J = 7.3 Hz, 24 H, CH_3-$CH_2CH_2CH_2N^+$) ppm. **^{51}V-NMR** (105 MHz, $\mathrm{CD_3CN}$): δ = –497.44 ppm. **ESI-MS** (pos., MeCN): *m/z* = 1844.679 (1844.687, $[M+TBA]^+$), 1675.614 (1675.614, $[M+TBA-C_7H_{11}N_3S]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3426 (w), 3122 (w), 2959 (m), 2872 (m), 1630 (w), 1480 (m), 1382 (m), 1134 (m), 1049 (s), 951 (vs), 810 (s), 718 (s), 581 (m). **UV/Vis** (MeCN): λ_{max} = 248 (sh), 280 (sh), 344 (sh) nm.

$(n\mathrm{Bu_4N})_2[\mathrm{V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2}$-*4*-$\mathrm{(C_6H_4SCH_3\}_2}]$ ($\mathrm{TBA_2}$**2h**)

Yield: 87 %.

^{1}H-NMR (400 MHz, $\mathrm{CD_3CN}$): δ = 7.77 (s, 2 H, C-*CH*=C), 7.32–7.14 (m, 8 H, $C_{ar}H$), 5.47 (s, 4 H, N-CH_2-C_{ar}), 4.97 (s, 12 H, -CH_2-O), 4.48 (s, 4 H, C=C-CH_2-O), 3.32 (s, 4 H, -O-CH_2-C), 3.15–3.02 (m, 16 H, $CH_3CH_2CH_2$-CH_2-N^+), 2.48 (s, 6 H, S-CH_3), 1.70–1.50 (m, 16 H, CH_3CH_2-CH_2-CH_2N^+), 1.43–1.29 (m, 16 H, CH_3-CH_2-$CH_2CH_2N^+$), 0.97 ppm (t, J = 7.4 Hz, 24 H, CH_3-$CH_2CH_2CH_2N^+$). **^{51}V-NMR** (105 MHz, $\mathrm{CD_3CN}$): δ = –497.26 ppm. **ESI-MS** (pos., MeCN): *m/z* = 1940.678 (1940.678, $[M+TBA]^+$), 1723.612 (1723.619, $[M+TBA-C_{11}H_{11}N_3S]^+$), 1506.547 (1506.552, $[M+TBA-C_{22}H_{22}N_6S_2]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3425 (w), 3115 (w), 2959 (m), 2871 (m), 1601 (w), 1480 (m), 1381 (w), 1133 (m), 1047 (s), 950 (vs), 795 (s), 718 (vs), 581 (s). **UV/Vis** (MeCN): λ_{max} = 258, 350 (sh) nm.

$(n\mathrm{Bu_4N})_2[\mathrm{V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2CH_2SiPh_2Bu^t\}_2}]$ ($\mathrm{TBA_2}$**2i**)

Yield: 95 %.

^{1}H-NMR (400 MHz, $\mathrm{CD_3CN}$): δ = 7.77 (s, 2 H, C-*CH*=C), 7.53–7.48 (m, 8 H, Si-*Ph*), 7.48–7.42 (m, 4 H, Si-*Ph*), 7.42–7.35 (m, 8 H, Si-*Ph*), 4.99 (s, 12 H, -CH_2-O), 4.52 (s, 4 H, C=C-CH_2-O), 4.47 (t, J =

5.1 Hz, 4 H, -CH_2-*CH_2*-Si), 4.02–3.96 (m, 4 H, N-*CH_2*-CH_2Si), 3.34 (s, 4 H, -O-*CH_2*-C), 3.16–3.08 (m, 16 H, $CH_3CH_2CH_2$-*CH_2*-N^+), 1.68–1.56 (m, 16 H, CH_3CH_2-*CH_2*-CH_2N^+), 1.37 (h, *J* = 7.3 Hz, 16 H, CH_3-*CH_2*-$CH_2CH_2N^+$), 0.97 (t, *J* = 7.3 Hz, 24 H, *CH_3*-$CH_2CH_2CH_2N^+$), 0.94 (s, 18 H, SiC-(*CH_3*)$_3$) ppm. **^{51}V-NMR** (105 MHz, CD_3CN): δ = –496.97 ppm. **ESI-MS** (pos., MeCN): *m/z* = 2233.899 (2233.908, $[M+TBA]^+$), 1992.625 (1992.636, $[M+H_2O]^+$), 1869.723 (1869.723, $[M+TBA-C_{21}H_{25}N_3SiO]^+$), 1628.448 (1628.448, $[M+H^+-C_{21}H_{25}N_3SiO]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3430 (m), 3069 (w), 2959 (s), 2855 (s), 1732 (w), 1632 (w), 1472 (m), 1382 (m), 1134 (s), 1049 (vs), 950 (vs), 810 (vs), 718 (vs), 581 (s). **UV/Vis** (MeCN): λ_{max} = 219, 289 (sh), 352 (sh) nm.

(nBu$_4$N)$_2$[V_6O_{13}{$(OCH_2)_3CCH_2OCH_2CCHN_3CH_2$-*L*-$C_4H_7N$-$COOC(CH_3)_3$}$_2$] (TBA$_2$**2j**)

Yield: 82 %.

^{1}H-NMR (400 MHz, CD_3CN): δ = 7.66 (br. s, 2 H, C-*CH*=C), 4.98 (s, 12 H, -*CH_2*-O), 4.50 (s, 4 H, C=C-*CH_2*-O), 4.48–4.35 (m, 4 H, -*CH_2*-), 4.09 (s, 2 H, -*CH_2*-), 3.32 (br. s., 4 H, -O-*CH_2*-C), 3.28–3.18 (m, 4 H, -*CH_2*-), 3.18–3.06 (m, 16 H, $CH_3CH_2CH_2$-*CH_2*-N^+), 3.06–3.13 (m, 2 H, -*CH_2*-), 1.91–1.83 (m, 2H, -*CH_2*-), 1.78–1.70 (m, 4 H, -*CH_2*-), 1.70–1.56 (m, 16 H, CH_3CH_2-*CH_2*-CH_2N^+), 1.43 (br. s., 18 H, OC(-*CH_3*)$_3$), 1.43–1.34 (m, 16 H, CH_3-*CH_2*-$CH_2CH_2N^+$), 0.97 (t, *J* = 7.3 Hz, 24 H, *CH_3*-$CH_2CH_2CH_2N^+$) ppm. **^{51}V-NMR** (105 MHz, CD_3CN): δ = –497.34 ppm. **ESI-MS** (pos., MeCN): *m/z* = 2034.866 (2034.869, $[M+TBA]^+$), 1770.710 (1770.623, $[M+TBA-C_{13}H_{20}N_4O_2]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3441 (m), 3123 (w), 2961 (s), 2933 (s), 2872 (s), 1689 (s), 1479 (m), 1394 (s), 1366 (m), 1252 (w), 1222 (w), 1169 (m), 1133 (s), 1048 (s), 990 (w), 950 (vs), 882 (w), 808 (s), 796 (s), 718 (vs), 581 (m), 511 (w), 418 (s). **UV/Vis** (MeCN): λ_{max} = 249 (sh), 281 (sh), 350 (sh) nm.

(nBu$_4$N)$_2$[V_6O_{13}{$(OCH_2)_3CCH_2OCH_2CCHN_3(CH_2)_5NHCO(CH_2)_4C_5H_7N_2OS$}$_2$] (TBA$_2$**2k**)

Compound TBA$_2$**2k** was synthesised following the general procedure for the preparation of TBA$_2$**2a**–TBA$_2$**2j** via Cu(I)-catalysed Huisgen reactions; however, a different work-up method was used. TBA$_2$**2k** precipitated during the synthesis in acetonitrile and was simply filtered off, washed with a small amount of MeCN and Et_2O and dried under high vacuum.

Yield: 96 %.

^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.09 (s, 2 H, -*NH*-), 7.74 (t, *J* = 5.5 Hz, 2 H, C-*CH*=C), 7.06 (s, 4H, -*NH*-), 6.42 (s, 2 H, -*NH*-), 6.35 (s, 2 H, -*NH*-), 4.85 (s, 12 H, -*CH_2*-O), 4.47 (s, 4 H, C=C-*CH_2*-O), 4.29–4.35 (m, 6 H, -*CH_2*-), 4.11–4.16 (m, 2 H, -*CH_2*-), 3.29 (s, 4 H, -O-*CH_2*-C), 3.12–3.21 (m, 16 H, $CH_3CH_2CH_2$-*CH_2*-N^+), 2.99–3.12 (m, 6 H, -*CH_2*-), 2.83 (dd, *J* = 12.5, 5.0 Hz, 2 H, -*CH_2*-S), 2.57 (d, *J* = 12.5 Hz, 2 H, -*CH*-), 2.04 (t, *J* = 7.3 Hz, 4 H, OCH-*CH_2*-), 1.79 (m, 4 H, -*CH_2*-), 1.16–1.62 (m, 44 H, -*CH_2*-), 0.93 (t, *J* = 7.3 Hz, 24 H, *CH_3*-$CH_2CH_2CH_2N^+$) ppm. **^{51}V-NMR** (105 MHz, CD_3CN): δ = –495.02 ppm. **MALDI-TOF-MS** (pos., DCTB): *m/z* = 2291.95 (2291.95, $[M+TBA]^+$), 1927.78 (1927.79, $[M+TBA-(C_{16}H_{23}N_6O_2S)]^+$), 1898.75 (1898.75, $[M+TBA-(C_{18}H_{28}N_6O_2S)]^+$). **FT-IR** (KBr, cm^{-1}): ν = 3387 (vs), 2929 (s), 2856 (s), 1699 (s), 1643 (s), 1539 (m), 1458 (m), 1379 (m), 1331 (w), 1259 (w), 1190 (w), 1132 (m), 1043 (s), 951 (vs), 808 (s), 794 (s), 717 (vs), 581 (m), 511 (w), 419 (s). **UV/Vis** (DMSO): λ_{max} = 357 (sh) nm.

$Na_2[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3(CH_2)_5NHCO(CH_2)_4C_5H_7N_2OS\}_2]$ (Na_2**2k**)

Compound Na_2**2k** was prepared by suspending TBA_2**2k** in a 0.01 M pTSA-MeCN solution for 15 min. The obtained solid was filtered off and washed several times with MeCN and Et_2O. The residue was dissolved in a few milliliters of a 10 mM solution of Na_2CO_3 which was purified by water dialysis and dried in an exicator over $CaCl_2$ under vacuum for 4 days.

Yield: 95 %.

^{51}V-NMR (105 MHz, D_2O): δ = –507.57 ppm. **FT-IR** (KBr, cm^{-1}): ν = 3447 (vs), 2923 (m), 2856 (w), 2374 (w), 2343 (w), 1638 (s), 1461 (m), 1384 (m), 1132 (m), 1041 (m), 956 (s), 794 (m), 716 (s), 586 (s), 437 (vs). **UV/Vis** (H_2O): λ_{max} = 249 (sh), 360 (sh) nm.

5. X-ray crystallography for TBA_2**1** and TBA_2**2f**

Table S1: Crystal data and structure refinement details.

	TBA_2**1**	TBA_2**2f**
chemical formula	$C_{16}H_{22}O_{21}V_6 \cdot 2(C_{16}H_{36}N)$	$C_{24}H_{36}N_6O_{25}V_6 \cdot 2(C_{16}H_{36}N)$
formula weight	1340.89	1599.14
T / K	100(2)	100(2)
wavelength / Å	0.71073	0.71073
space group (No.)	$P2_1/c$ (14)	P-1 (2)
a / Å	17.244(2)	11.4733(17)
b / Å	22.208(3)	11.9543(17)
c / Å	15.317(2)	14.603(2)
α / deg	90	73.992(2)
β / deg	94.834(3)	71.464(2)
γ / deg	90	78.819(3)
V / Å^3	5844.9(13)	1812.9(5)
Z	4	1
D_{calcd} / g cm^{-3}	1.524	1.465
absorp. coeff. / mm^{-1}	0.995	0.821
R[a)]	0.051	0.056
wR_2[b)]	0.128	0.153

[a)] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b)] $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

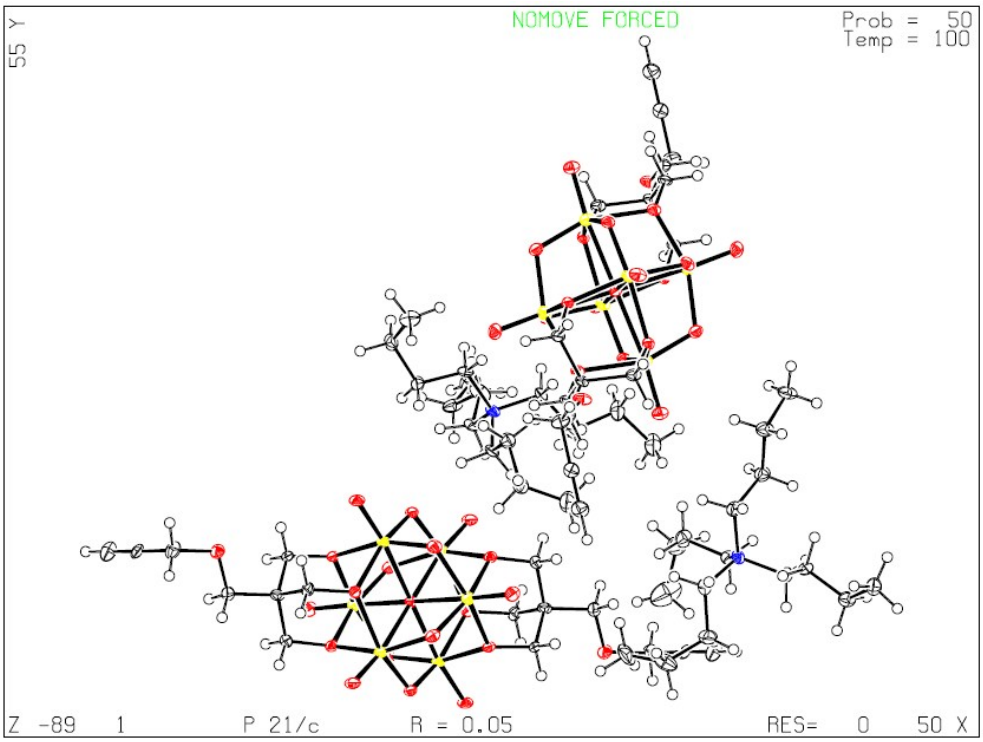


Figure S2: ORTEP plot of compound TBA_2**1** with thermal ellipsoids at the 50 % probability level. Colour code: V = yellow, O = red, N = blue, C = grey, H = white grey.

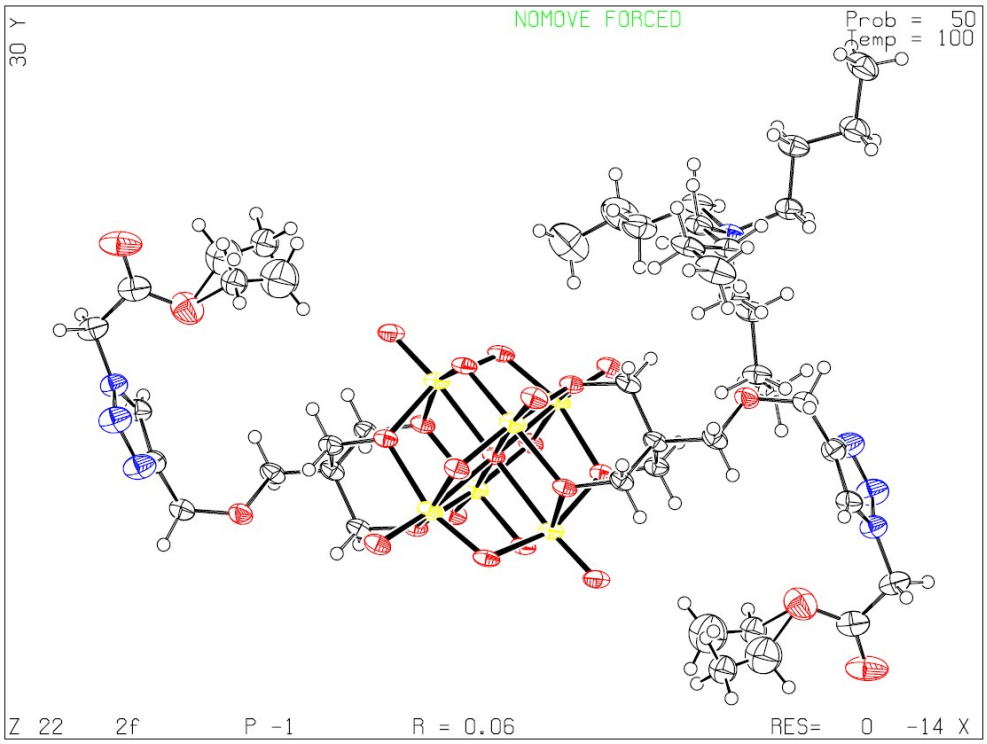


Figure S3: ORTEP plot of compound TBA_2**2f** with thermal ellipsoids at the 50 % probability level. Colour code: V = yellow, O = red, N = blue, C = grey, H = white grey.

6. IR spectra

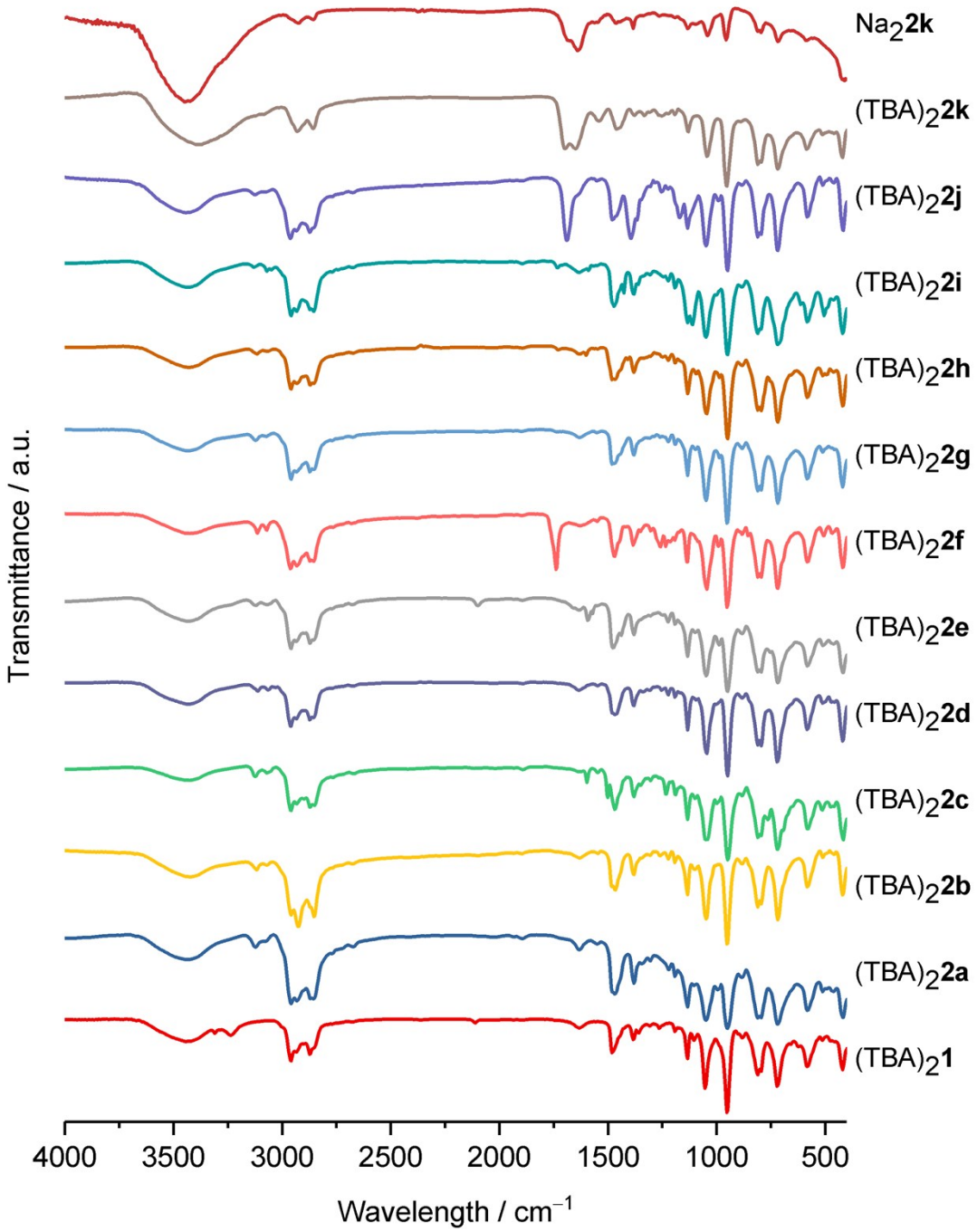
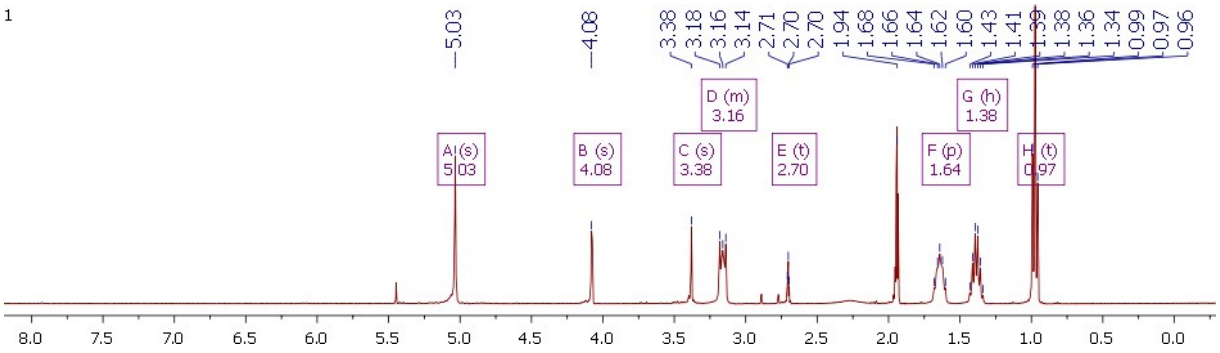
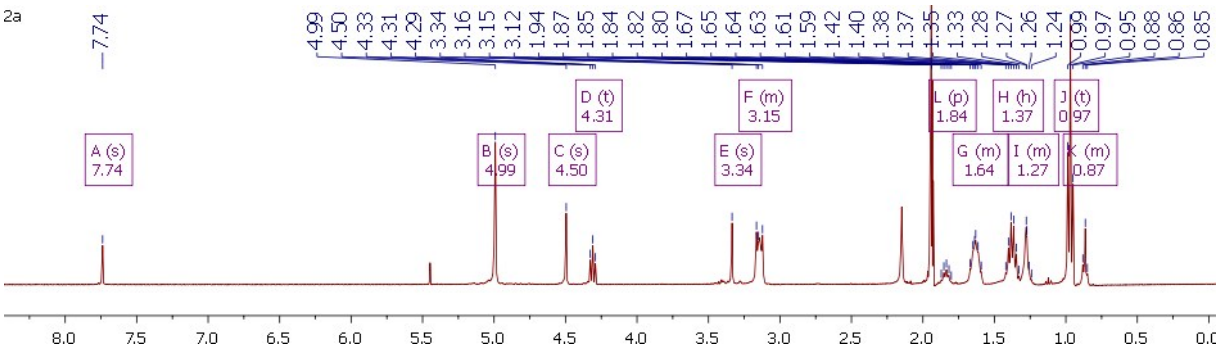
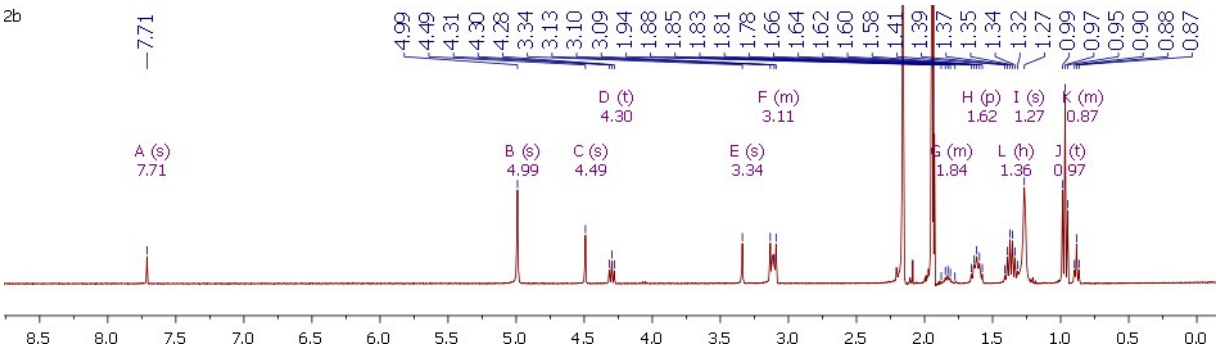


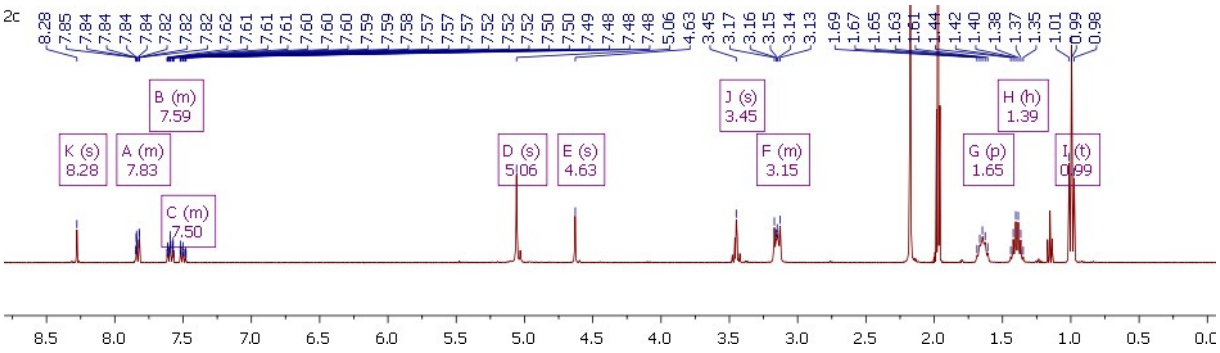
Figure S4: IR spectra of compounds TBA_2**1**, TBA_2**2a**–TBA_2**2k** and Na_2**2k** in the region ν = 4000–400 cm^{-1}.

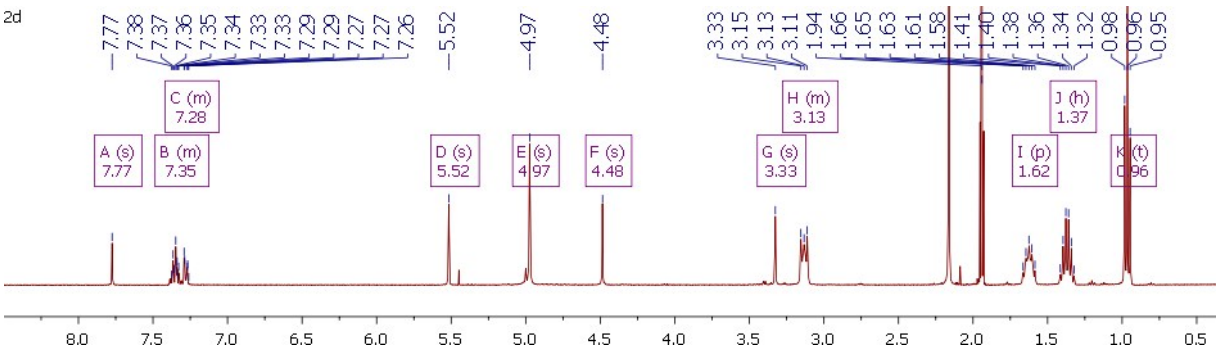
7. ^{1}H NMR spectra

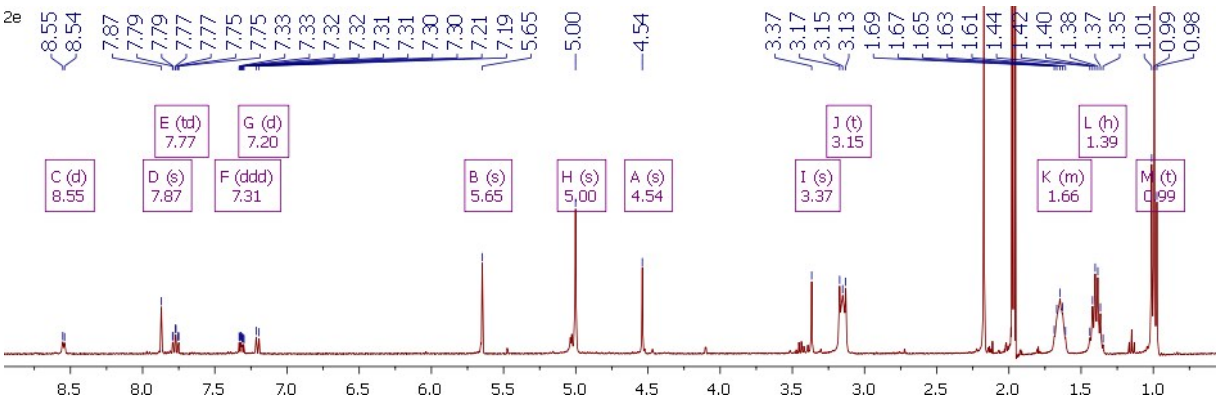


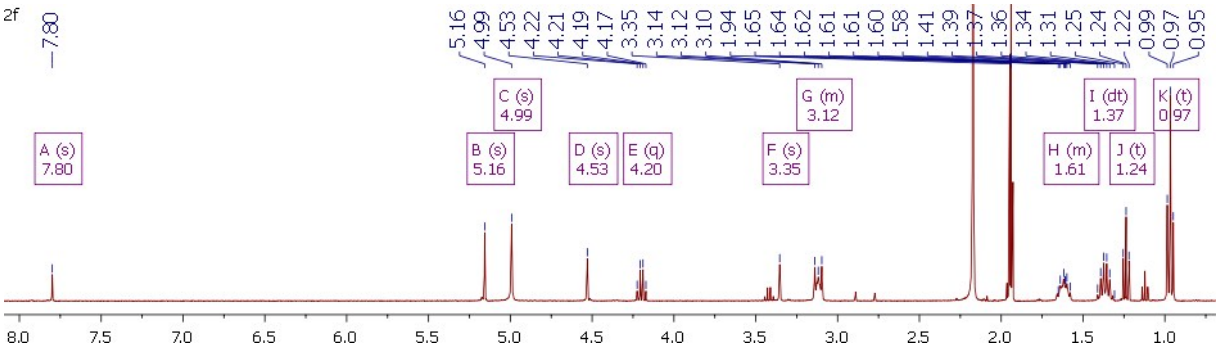


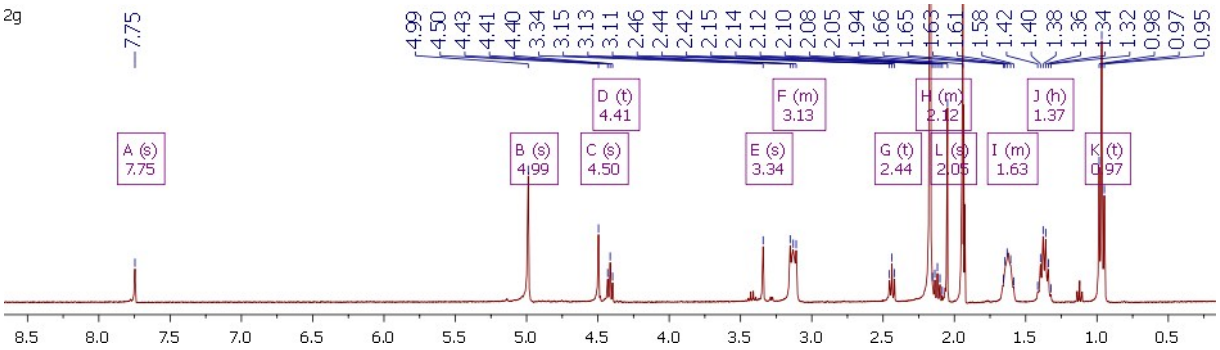





2d
A (s) 7.77
B (m) 7.35
C (m) 7.28
D (s) 5.52
E (s) 4.97
F (s) 4.48
G (s) 3.33
H (m) 3.13
I (p) 1.62
J (h) 1.37
K (t) 0.96


2e
C (d) 8.55
D (s) 7.87
E (td) 7.77
F (ddd) 7.31
G (d) 7.20
B (s) 5.65
H (s) 5.00
A (s) 4.54
I (s) 3.37
J (t) 3.15
K (m) 1.66
L (h) 1.39
M (t) 0.99


2f
A (s) 7.80
B (s) 5.16
C (s) 4.99
D (s) 4.53
E (q) 4.20
F (s) 3.35
G (m) 3.12
H (m) 1.61
I (dt) 1.37
J (t) 1.24
K (t) 0.97


2g
A (s) 7.75
B (s) 4.99
C (s) 4.50
D (t) 4.41
E (s) 3.34
F (m) 3.13
G (t) 2.44
H (m) 2.12
I (m) 1.63
J (h) 1.37
K (t) 0.97
L (s) 2.05

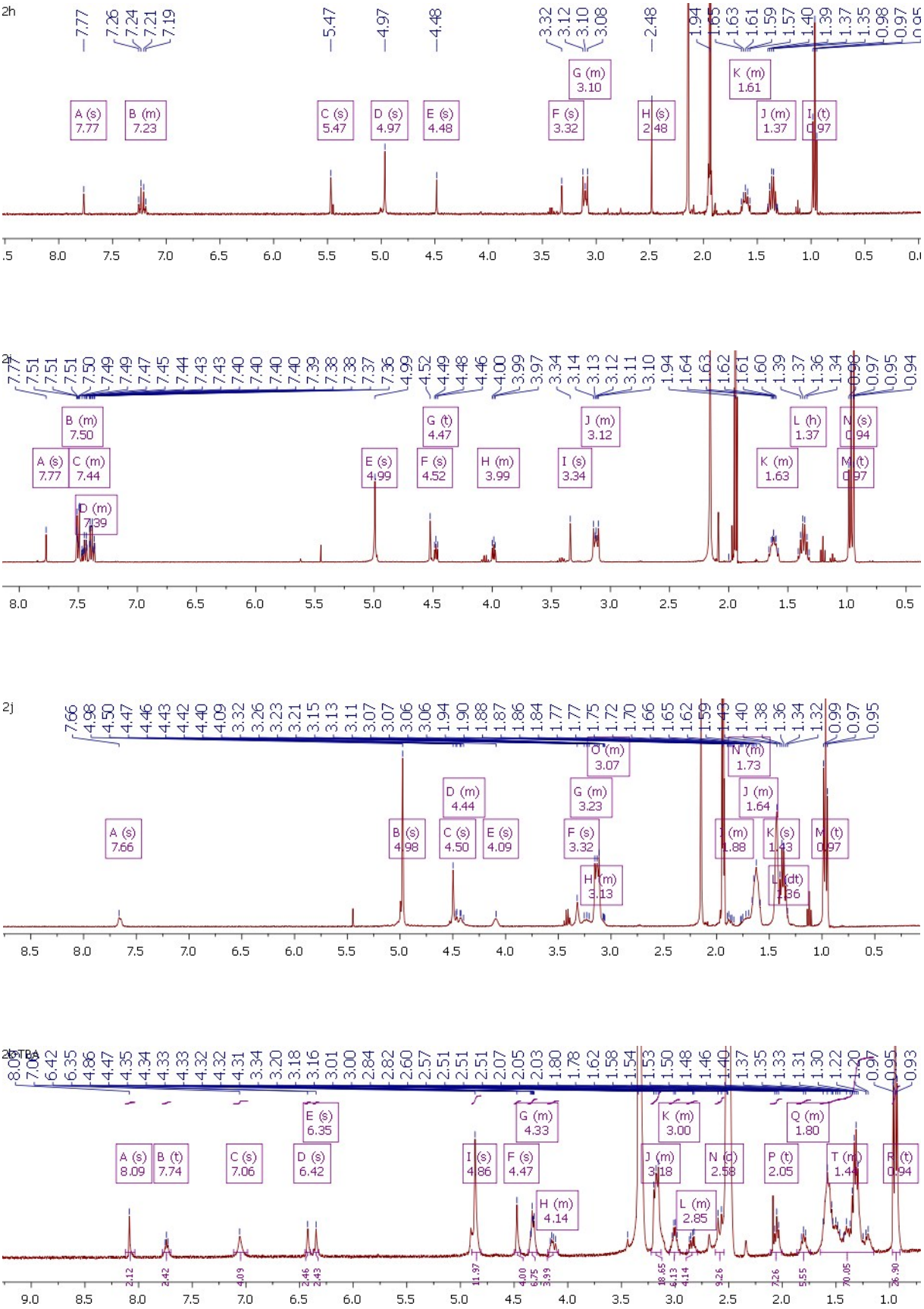


Figure S5: ^{1}H NMR spectra of compounds TBA_2**1** and TBA_2**2a**–TBA_2**2k**.

8. UV/Vis Spectra

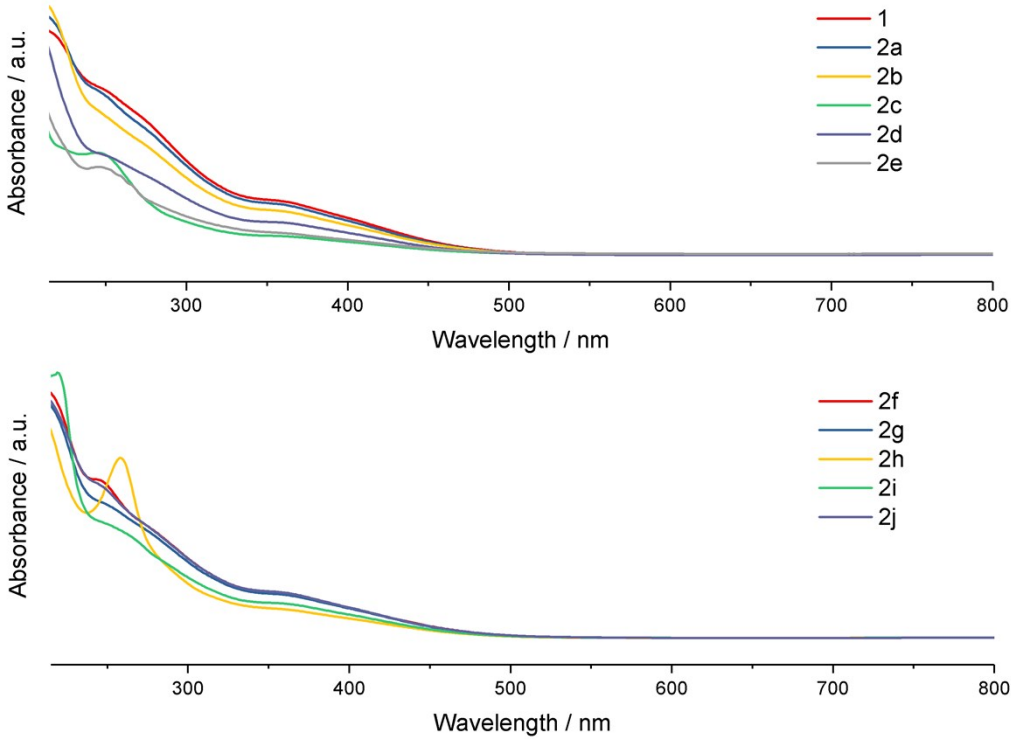


Figure S6: UV/Vis spectra of compounds TBA_2**1** and TBA_2**2a**–TBA_2**2j** in MeCN.

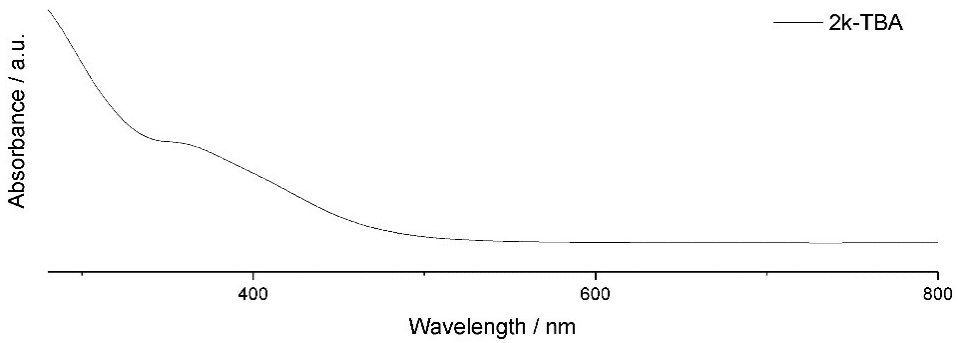


Figure S7: UV/Vis spectrum of compound TBA_2**2k** in DMSO.

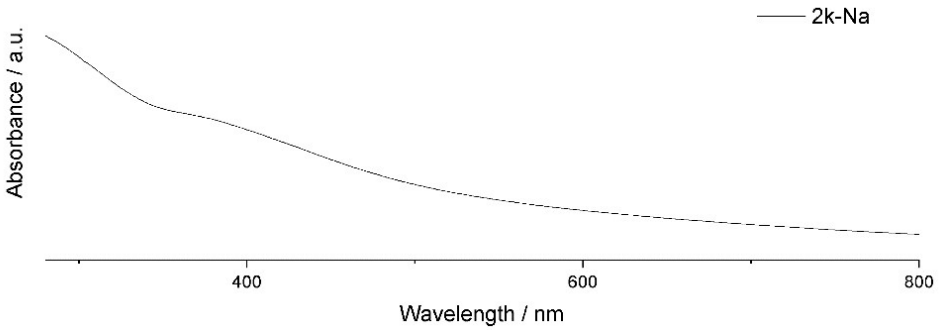


Figure S8: UV/Vis spectrum of compound Na_2**2k** in H_2O.

9. MALDI-TOF mass spectrum of TBA_2**2k**

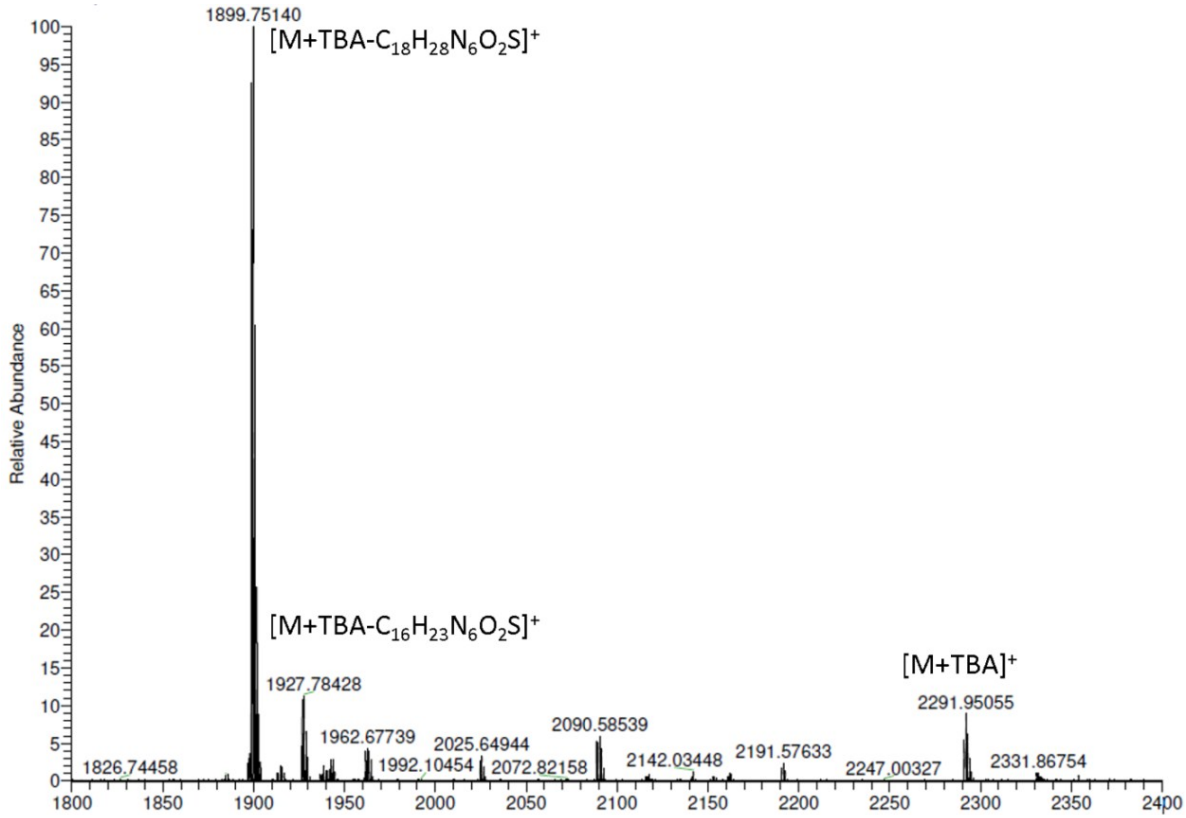


Figure S9: MALDI-TOF mass spectrum of compound TBA_2**2k** with main fragments assigned.

10. TGA thermograms of TBA_2**1**, TBA_2**2a** and TBA_2**2i**

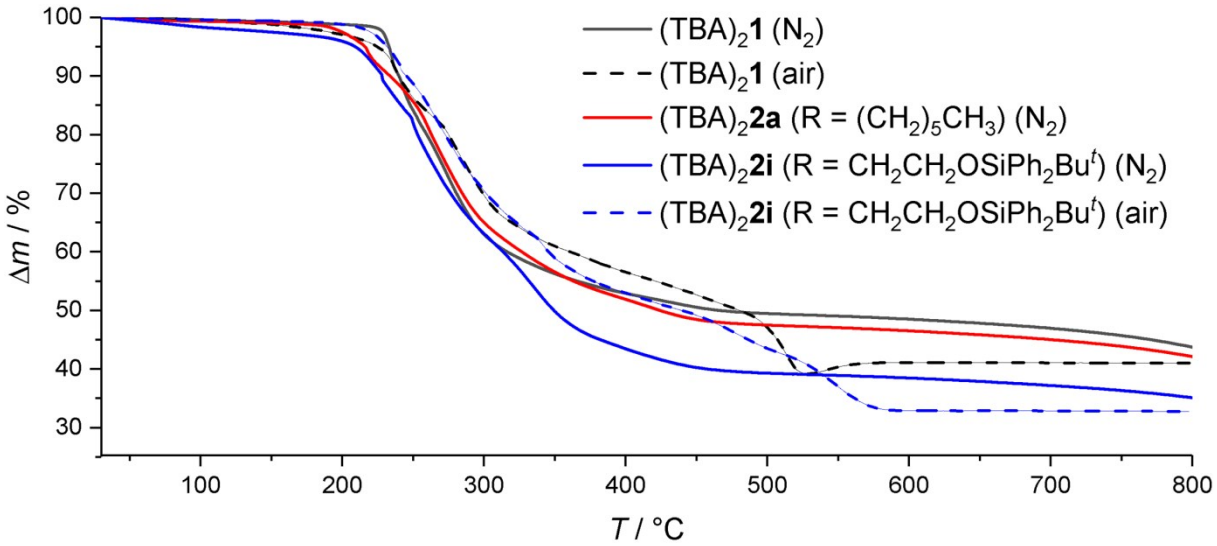


Figure S10: TGA curves obtained for exemplary studied compounds TBA_2**1**, TBA_2**2a** and TBA_2**2i**. The TGA curves reveal thermal stability of the chosen compounds up to *ca.* 190–220 °C against degradation under a N_2 atmosphere or in air.

11. Cyclic voltammogramms

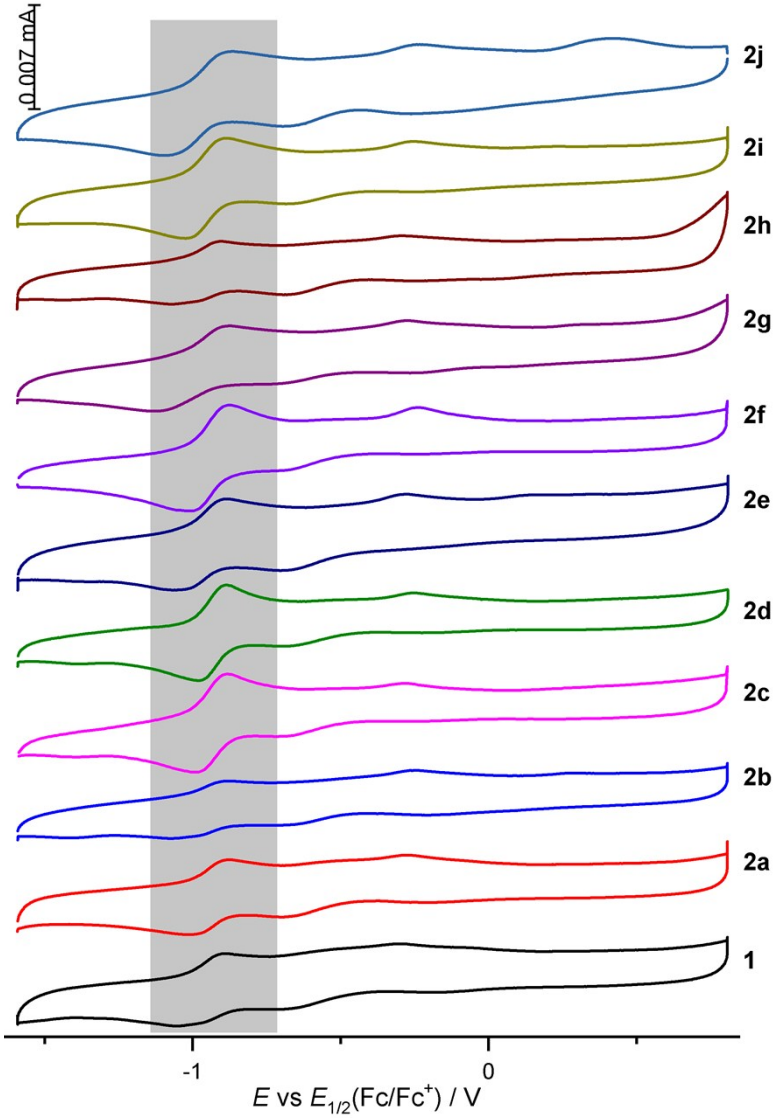


Figure S11: Cyclic voltammogramms of compounds TBA_2**1** and TBA_2**2a**–TBA_2**2j** in a 0.1 M $TBAClO_4$-DCM solution with scan rate of 100 $mV \cdot s^{-1}$ (range: –1.60–0.80 V), referenced to $E_{1/2}(Fc/Fc^+)$.

Table S2: Data from cyclic voltammogramms of compounds TBA_2**1** and TBA_2**2a**–TBA_2**2j**. For comparison, CV data of some reported Lindqvist-type hexavanadate structures are tabulated.

	R =	Solvent	*Ref.*	E_{ap} / V	E_{cp} / V	$\Delta E_{cp/ap}$ / V	ΔE_p / V	i_{cp} / i_{ap}
1	-	DCM	Fc/Fc^+	–0.88	–1.01	–0.95	0.13	0.9
2a	$-(CH_2)_5Me$	DCM	Fc/Fc^+	–0.86	–0.98	–0.92	0.12	1.0
2b	$-(CH_2)_{11}Me$	DCM	Fc/Fc^+	–0.87	–1.03	–0.95	0.16	0.9
2c	$-C_6H_5$	DCM	Fc/Fc^+	–0.86	–0.95	–0.91	0.09	0.8
2d	$-CH_2C_6H_5$	DCM	Fc/Fc^+	–0.86	–0.95	–0.91	0.08	0.9
2e	$-CH_2$-*2*-NC_5H_4	DCM	Fc/Fc^+	–0.87	–1.01	–0.94	0.14	0.8
2f	$-CH_2CO_2CH_2CH_3$	DCM	Fc/Fc^+	–0.86	–0.97	–0.92	0.11	1.0
2g	$-(CH_2)_3SCH_3$	DCM	Fc/Fc^+	–0.87	–1.06	–0.97	0.19	0.9
2h	$-CH_2$-*4*-$C_6H_4SCH_3$	DCM	Fc/Fc^+	–0.89	–1.04	–0.96	0.15	0.8
2i	$-CH_2CH_2SiPh_2Bu^t$	DCM	Fc/Fc^+	–0.87	–0.99	–0.93	0.12	0.9
2j	$-CH_2$-*L*-C_4H_7N-CO_2Bu^t	DCM	Fc/Fc^+	–0.86	–1.06	–0.96	0.20	1.0
Reported $\{V_6\}$ structures[8]								
$[V_6O_{13}\{(OCH_2)_3CNO_2\}_2]^{2-}$		MeCN	Fc/Fc^+	-	-	–0.67	0.062	1.0
$[V_6O_{13}\{(OCH_2)_3CCH_2OH\}_2]^{2-}$		MeCN	Fc/Fc^+	-	-	–0.76	0.060	1.0
$[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]^{2-}$		MeCN	Fc/Fc^+	-	-	–1.20	0.061	1.0
$[V_6O_{13}\{(OCH_2)_3CNMe_2\}_2]^{2-}$		MeCN	Fc/Fc^+	-	-	–1.18	0.077	1.2

12. Details of DFT calculations

Computational methods

DFT calculations were performed with the Amsterdam Density Functional program (ADF2016).[9] The all-electron basis set of triple-ζ quality for all atoms with one polarisation function (that is, TZP) was used.[10] Scalar relativistic effects were accounted for using the zeroth-order regular approximation (ZORA).[11] Solvent effects were modelled by using the COnductor-like Screening MOdel (COSMO) with the default parameters for water (ε = 78.39; solvent radius = 1.93 Å),[12] to enable better comparison with the calculated properties of other POMs. The change of the solvent to DCM did not impact the geometric and electronic properties of studied polyoxo(alkoxo)anions. Geometry optimisation of single conformational isomers was carried out using GGA Becke exchange[13] plus the Perdew 86 correlation[14] (BP) functional (i.e. at the BP86/ZORA-scalar/TZP/COSMO level of theory). Single-point calculations were conducted on the fully-optimised structures using the hybrid B3LYP functional[15] (i.e. at the B3LYP/ZORA-scalar/TZP/COSMO level of theory).

Geometric properties

Table S3: Comparison of characteristic bond lengths for polyoxo(alkoxo)anions **1** and **2f** determined crystallographically and at the BP86/ZORA-scalar/TZP/COSMO level of theory.

	1		**2f**	
Bond type	Experiment	Theory	Experiment	Theory
V–O_t	1.603–1.613	1.622	1.600–1.612	1.622
V–O_b	1.758–2.074	1.802–2.07	1.760–2.057	1.827–2.045
V–O_c	2.219–2.263	2.264–2.27	2.232–2.247	2.262–2.268
C–H	0.931–0.971	1.073–1.105	0.931–0.971	1.083–1.106
C–C	1.470–1.532	1.466–1.542	1.499–1.542	1.49–1.542
C–O	1.422–1.434	1.439–1.443	1.417–1.435	1.342–1.478
C≡C	1.18	1.212	NA	NA
C=O	NA	NA	1.211	1.222
N––N	NA	NA	1.314–1.357	1.316–1.361
C–N	NA	NA	1.347–1.36	1.355–1.45
C=C	NA	NA	1.337–1.362	1.384

Electronic properties

Table S4: Energies of frontier molecular orbitals (HOMO and LUMO) and the HOMO-LUMO energy gaps calculated for specified polyoxo(alkoxo)anions at the B3LYP/ZORA-scalar/TZP/COSMO level of theory.

Polyoxo(alkoxo)anions	E_{HOMO}	E_{LUMO}	$\Delta E_{HOMO-LUMO}$
1	–7.6	–4.1	3.5
2a	–7.4	–4	3.4
2b	–7.4	–4	3.4
2c	–7.1	–4.1	3
2d	–7.2	–4	3.2
2e	–7.4	–4.1	3.3
2f	–7.5	–4.1	3.4
2g	–6.4	–4.1	2.3
2h	–6.1	–4.1	2
2i	–7.1	–4	3
2j	–6.8	–4	2.7
2k	–6.7	–4.3	2.4

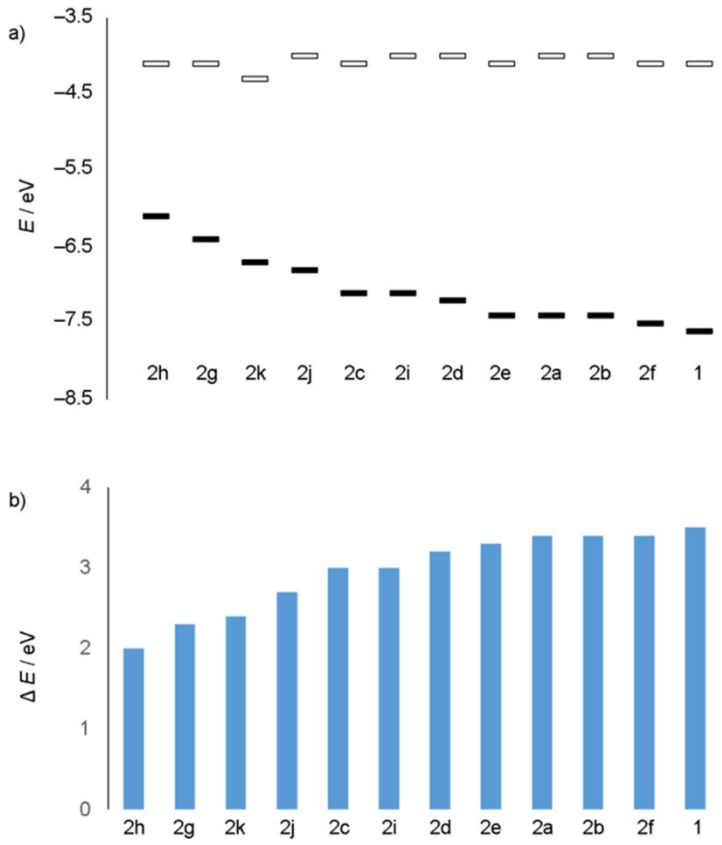


Figure S12: Graphical representation of the evolution of the HOMO-LUMO energy gaps for polyoxo(alkoxo)anions **1** and **2a-2k** calculated at the B3LYP/ZORA-scalar/TZP/COSMO level of theory.

Table S5: Contributions (in %) of the Kohn-Sham orbitals centred on vanadium, oxygen, carbon, nitrogen, hydrogen and sulfur to the HOMO and LUMO orbitals of specified polyoxo(alkoxo)anions. Calculations are performed at the B3LYP/ZORA-scalar/TZP/COSMO level of theory.

Polyoxo(alkoxo)anions		Contributions [%]					
		V	O	C	N	H	S
$[V_6O_{19}]^{8-}$	HOMO	0	100	NA	NA	NA	NA
	LUMO	72	27	NA	NA	NA	NA
	HOMO-LUMO	72	–73	NA	NA	NA	NA
1	HOMO	0	54	8	0	6	NA
	LUMO	81	5	0	0	0	NA
	HOMO-LUMO	81	–49	–8	0	–6	NA
2a	HOMO		16	41	22	5	NA
	LUMO	81	5	0	0	0	NA
	HOMO-LUMO	81	–11	–41	–22	–5	NA
2b	HOMO		6	49	28	1	NA
	LUMO	81	5	0	0	0	NA
	HOMO-LUMO	81	–1	–49	–28	–1	NA
2c	HOMO	0	0	81	0	1	NA
	LUMO	83	5	0	0	0	NA
	HOMO-LUMO	83	5	–81	0	–1	NA
2d	HOMO	0	0	84	5	0	NA
	LUMO	76	5	0	0	0	NA
	HOMO-LUMO	76	5	–84	–5	0	NA
2e	HOMO	0	0	0	0	0	NA
	LUMO	80	81	82	83	84	NA
	HOMO-LUMO	80	81	82	83	84	NA
2f	HOMO		54	10	3	16	NA
	LUMO	85	3	0	0	0	NA
	HOMO-LUMO	85	–51	–10	–3	–16	NA
2g	HOMO	0	0	0	0	10	87
	LUMO	81	5	0	0	0	0
	HOMO-LUMO	81	5	0	0	–10	–87
2h	HOMO	0	0	37	0	3	54
	LUMO	81	5	0	0	0	0
	HOMO-LUMO	81	5	–37	0	–3	–54
2i	HOMO	0	22	5	51	10	NA
	LUMO	81	5	0	0	0	NA
	HOMO-LUMO	81	–17	–5	–51	–10	NA
2j	HOMO	0	22	5	51	10	NA
	LUMO	81	5	0	0	0	NA
	HOMO-LUMO	81	–17	–5	–51	–10	NA
2k	HOMO			0	0	6	85
	LUMO	80	5	0	0	0	0
	HOMO-LUMO	80	5	0	0	–6	–85

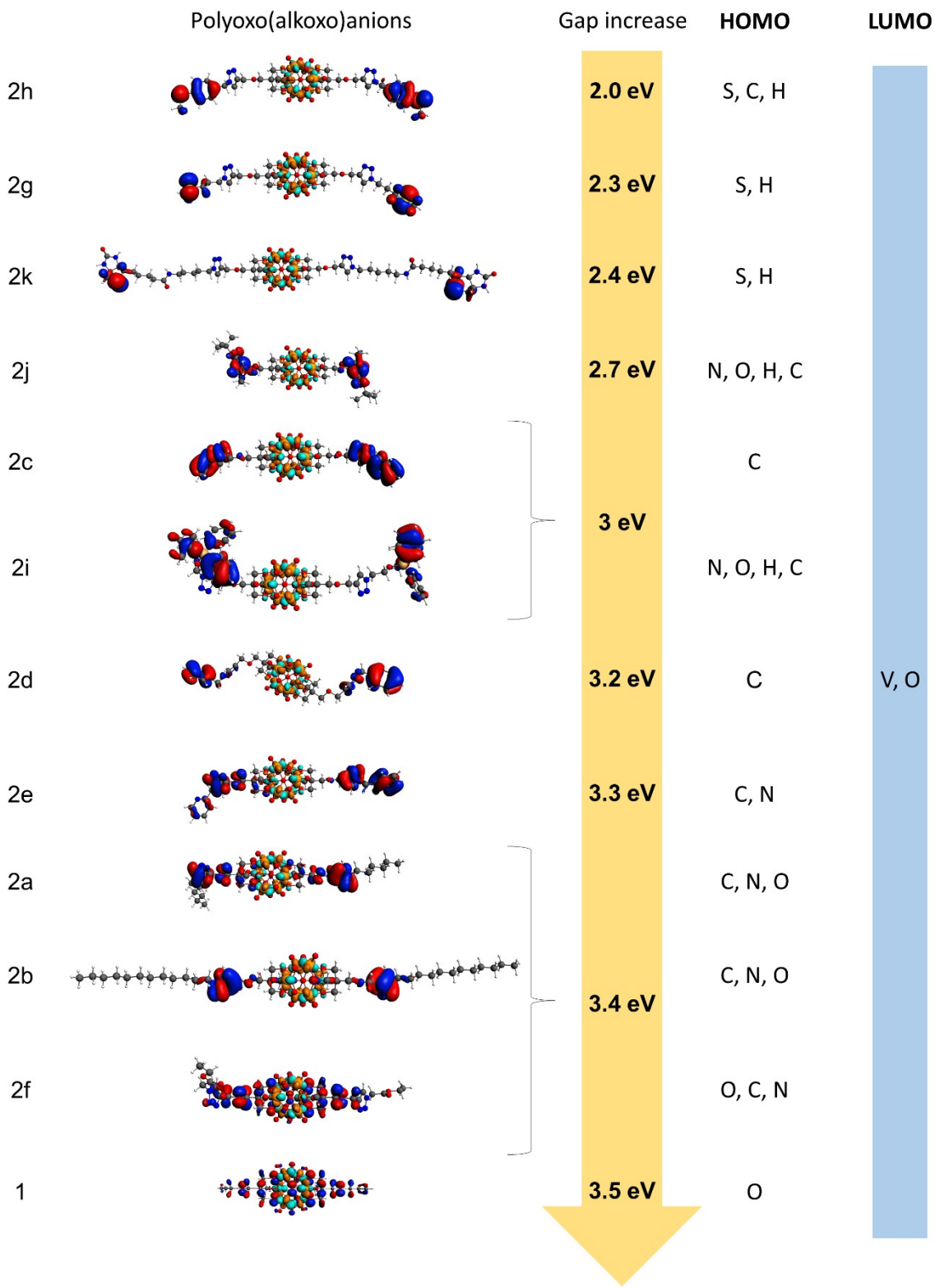


Figure S13: Depiction of HOMOs and LUMOs plotted over the optimised structures of polyoxo(alkoxo)anions **1** and **2a-2k**. The HOMO-LUMO energy gaps and the atomic composition of HOMOs and LUMOs, as calculated at the B3LYP/ZORA-scalar/TZP/COSMO level of theory, are shown. Colour code: highest occupied molecular orbitals = blue/red, lowest unoccupied molecular orbitals = orange/cyan.

Table S6: Cartesian coordinates (in Å) of the optimised structures of polyoxo(alkoxo)anions **1** and **2a-2k** computed at the BP86/ZORA-scalar/TZP/COSMO level of theory.

1 $[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCH\}_2]^{2-}$				**2a** $[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3(CH_2)_5CH_3\}_2]^{2-}$			
V	14.68591192	9.88803684	7.50835765	V	13.16951116	7.58805149	4.82971290
V	15.26899741	12.73188719	8.47243680	V	15.56445681	9.26897124	5.71454185
V	16.90545990	10.04217505	9.60991980	V	15.75436585	5.98270469	5.11910020
O	16.59862505	11.10400004	7.63125932	O	14.64827515	7.36772452	6.53394627
O	15.37249428	9.23489537	9.11066423	O	12.43854752	5.99650476	5.86966721
O	16.09526555	8.67305982	6.60573842	O	12.28624062	8.63189222	6.34237316
O	13.40802421	8.93293390	7.21603267	O	14.34995978	6.43172606	4.03710124
O	14.73166442	10.80916130	5.72142625	O	14.19904784	9.06735675	4.51042323
O	14.00714121	11.37944167	8.26031631	O	11.94212897	7.70738342	3.77619148
V	16.29179020	12.16582502	5.65259884	V	13.54324407	8.75438943	7.94831656
O	15.86988594	11.67894780	10.15021091	O	16.85703897	8.73879989	7.19939430
O	17.10198454	13.53494025	8.65678022	O	14.49649704	10.00346745	7.00579269
O	15.21936970	13.22797853	6.74049501	O	16.55983295	7.80291180	4.70103129
O	14.46092194	13.88788977	9.27402445	O	16.43304319	10.51386035	5.14296572
V	17.92825268	9.47611289	6.79008184	V	13.73256974	5.46704156	7.35196380
O	18.46558568	11.39883877	9.54109240	O	17.01171853	6.10425410	6.72522405
O	17.21157731	9.49470971	11.10599697	O	14.80165669	4.73239853	6.06233507
O	17.97788040	8.98002154	8.52202364	O	16.74328543	5.11265450	4.17216797
V	18.51133817	12.31996323	7.75416100	V	16.12736495	7.14804894	8.23867653
C	15.73556926	8.02677507	5.36735050	C	11.02229323	5.94376904	6.14311959
C	14.44890770	10.04024232	4.53324894	C	10.88186896	8.42544537	6.58720764
O	17.82475581	12.97310470	6.15185441	O	14.94713352	8.30432080	9.03173148
O	17.32736415	10.52905227	5.11230773	O	12.73771507	6.93443159	8.36743406
O	15.98567278	12.71329036	4.15652167	O	12.55439523	9.62506146	8.89482124
C	16.30256259	12.43101169	11.29900506	C	18.27350088	8.79279583	6.92808318
C	17.46168083	14.18122500	9.89516815	C	17.99340764	7.91075938	4.57354687
O	19.19010888	10.82855840	7.00220233	O	15.09747551	5.66865456	8.55761069
O	18.73632815	8.32011030	5.98849419	O	12.86419104	4.22228954	7.92467098
C	18.74834239	12.16775775	10.72926970	C	18.41619448	6.31188268	6.48110230
O	19.78922588	13.27506617	8.04648597	O	17.35459637	7.02819682	9.29233189
C	15.56789542	9.03254069	4.21407689	C	10.58394948	7.02182330	7.15013552
H	16.52970824	7.30476402	5.12053152	H	10.49167694	6.08664343	5.18887456
H	14.79478080	7.48488889	5.53610499	H	10.79412068	4.94412635	6.53807836
H	14.33460679	10.74788513	3.69750333	H	10.55047908	9.19426162	7.30205357
H	13.49809819	9.51319203	4.69246744	H	10.35115119	8.56891055	5.63331327
C	16.89468750	9.77698838	3.96351358	C	11.30423362	6.82791808	8.49630162
C	17.62935467	13.17545938	11.04844175	C	18.71326568	7.71633709	5.91984642
H	16.41907691	11.72771793	12.13789616	H	18.80325573	8.64900322	7.88272319
H	15.50758168	13.15244780	11.54250600	H	18.50149557	9.79280601	6.53475631
H	16.66754185	14.90323605	10.14198712	H	18.21940736	8.90555780	4.16619251
H	18.40246930	14.72311118	9.72641366	H	18.32555327	7.14198586	3.85838410
H	18.86264330	11.46011494	11.56501532	H	18.74864134	5.54323279	5.76641159
H	19.69915190	12.69480804	10.57005121	H	18.94611642	6.16882192	7.43546728
C	15.23415647	8.27880734	2.91842040	C	9.06437945	6.93743001	7.36430016
H	16.77817318	10.48028214	3.12462249	H	11.07721970	5.83356401	8.90366016
H	17.68966841	9.05555227	3.72001265	H	10.97304047	7.59709011	9.21154207
C	17.96309363	13.92919273	12.34409825	C	20.23280017	7.80467993	5.70647443
O	13.99121633	7.57108643	3.07308334	O	8.72668138	5.67593192	7.95659667
H	15.15058235	8.99240252	2.07853275	H	8.54428170	7.05448411	6.39501071
H	16.04627798	7.56842686	2.68290991	H	8.73524594	7.76227902	8.02411830
O	19.20603377	14.63691364	12.18943530	H	20.75479821	7.64097481	6.66800013
H	18.04666774	13.21559755	13.18398589	H	20.55850750	7.01121785	5.00764791
H	17.15097211	14.63957321	12.57960874	O	20.57221834	9.09353550	5.17780838
C	13.62189351	6.85549011	1.87860034	C	21.99812793	9.21134007	4.97302234
C	19.57535658	15.35250996	13.38391830	C	7.30142988	5.57186878	8.17149737
C	14.47320507	5.69022291	1.61922666	H	22.24263980	10.51076665	2.17772298
H	13.64009447	7.53252648	1.00675028	H	6.77448145	5.61256724	7.20243250
H	12.58421920	6.53184991	2.03283108	H	6.95523546	6.41818936	8.78849862
C	18.72404503	16.51777716	13.64329198	H	22.52509656	9.06054997	5.93096918
H	19.55715562	14.67547359	14.25576836	C	22.29869276	10.57061746	4.44080578
H	20.61303089	15.67615016	13.22968757	H	22.33796742	8.43645593	4.26532365
C	15.17831584	4.72500269	1.41761486	N	22.63566354	12.33873710	3.22000315
C	18.01893425	17.48299738	13.84490378	C	7.00560613	4.28254723	8.85788059
H	15.80053173	3.86924280	1.23688666	N	6.61913271	2.68552820	10.28223845
H	17.39671836	18.33875727	14.02563199	H	6.94152213	4.64333277	11.09079177

N	6.58399710	2.13887135	9.03976863
C	6.88003365	4.01249974	10.21142043
N	6.81652840	3.11071570	8.17551519
N	22.73642390	12.71792025	4.51846467
C	22.36637022	11.01488579	3.12907192
N	22.53072201	11.64264386	5.25960580
C	9.93685520	-1.03784572	16.03112020
C	8.62773180	-0.66025001	15.33045108
C	8.83963468	0.20538444	14.08249679
C	7.53256295	0.59396481	13.38132539
C	7.75530496	1.46401490	12.13896872
H	9.75253208	-1.65702208	16.92068479
H	10.48580889	-0.14081501	16.35598176
H	10.59712003	-1.60667365	15.35878710
H	7.97427122	-0.12156460	16.03722410
H	8.08390985	-1.57705861	15.04705028
H	9.48873168	-0.33448100	13.37124734
H	9.38695003	1.12160855	14.36489119
H	6.88414493	1.13325098	14.09285065
H	6.98576525	-0.32030279	13.09429845
H	8.37946754	0.92582180	11.40846156
C	6.43010634	1.85039439	11.47431935
H	5.88010536	0.96208091	11.14061491
H	5.78851817	2.40945467	12.16757648
H	8.30030507	2.37945118	12.41877985
C	29.09330473	12.53838194	0.73695687
C	27.65559813	12.03738279	0.90929857
C	26.68339725	13.13671699	1.35361690
C	25.24177120	12.64517933	1.53193071
C	24.28579605	13.75729935	1.97461415
H	29.76590887	11.72926939	0.41823679
H	29.48621258	12.94812783	1.67999147
H	29.14733137	13.33568580	-0.01998919
H	27.63733496	11.21821208	1.64785248
H	27.30082582	11.60267291	-0.04040996
H	26.69944763	13.95651098	0.61422536
H	27.03857301	13.57310466	2.30358938
H	25.22970288	11.82644380	2.27109982
H	24.88142379	12.21297310	0.58242617
H	24.28528084	14.56699742	1.22797718
C	22.82792459	13.31774722	2.13803221
H	22.44999548	12.84404316	1.22412305
H	22.18710729	14.17770252	2.36698117
H	24.63234948	14.20417925	2.91964865

2b

$[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3(CH_2)_{11}CH_3\}_2]^{2-}$

V	12.72685886	7.05722987	4.08925017
V	15.06440976	8.99383993	4.44630574
V	15.23634405	5.75242277	5.24751980
O	14.03318501	7.57169062	5.87056991
O	11.86828292	6.00995586	5.60752834
O	11.72407312	8.60700052	4.96222035
O	13.95002766	5.69959835	3.94837878
O	13.81524141	8.29834345	3.30019067
O	11.60746621	6.71965000	2.96511373
V	12.82769067	9.38852375	6.49188145
O	16.20284207	9.13274155	6.13180163
O	13.89469126	10.16769729	5.22061703
O	16.11713665	7.26015540	4.21003809
O	16.01039427	9.91684616	3.50562409
V	13.00247430	6.14706680	7.29498594
O	16.33714178	6.53447269	6.78120486
O	14.17150786	4.97358272	6.52105009
O	16.28921447	4.59026940	4.83242785
V	15.33849455	8.08569215	7.65163253
C	10.43171130	6.04305535	5.74010110
C	10.29803960	8.48997139	5.13573179
O	14.11529672	9.44277111	7.79161032
O	11.94847006	7.87903821	7.53286073
O	11.77485992	10.54997951	6.90903656
C	17.63972417	9.09416615	5.99778029

2c

$[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3C_6H_5\}_2]^{2-}$

V	12.92152547	6.98523073	4.33485040
V	15.22730580	8.97107528	4.62212083
V	15.49820805	5.72844315	5.39396529
O	14.27781464	7.51457500	6.07244805
O	12.13840537	5.90614381	5.87618560
O	11.91780789	8.50413863	5.25417238
O	14.16821887	5.65439332	4.14210448
O	13.95338476	8.25353457	3.51621977
O	11.77023338	6.62824034	3.24962232
V	13.05765395	9.30120476	6.74990330
O	16.41632424	9.12407874	6.26840895
O	14.05865112	10.11213719	5.44548324
O	16.30882464	7.26364723	4.33585103
O	16.11743838	9.92201206	3.65546628
V	13.32827846	6.05677843	7.52153049
O	16.63776398	6.52568636	6.89208450
O	14.49761138	4.91714231	6.69925080
O	16.56249914	4.59425536	4.93296987
V	15.63355902	8.04351425	7.81096376
C	10.70677512	5.90811257	6.06004719
C	10.50207480	8.35545999	5.47689332
O	14.38737474	9.37492367	8.00337165
O	12.24826092	7.76484027	7.81013875
O	11.99373584	10.43540628	7.21194379
C	17.84733123	9.12159529	6.08415100

C	17.55828528	7.33042910	4.18580630
O	14.25099952	6.84446009	8.44175056
O	12.05765544	5.22312307	8.23573935
C	17.76225542	6.64802023	6.60876094
O	16.45811684	8.42464291	8.77527794
C	9.92100876	7.42553745	6.18420607
H	9.99839883	5.78113149	4.76215372
H	10.14555502	5.28202325	6.47802074
H	9.91679363	9.47547752	5.44478791
H	9.86347238	8.22610271	4.15926826
C	10.50750236	7.80377618	7.55599865
C	18.14486851	7.70872711	5.55760490
H	18.07418358	9.35693033	6.97491542
H	17.92712688	9.85419012	5.25798513
H	17.84426274	8.07907081	3.43464943
H	17.93759193	6.34394552	3.87663115
H	18.14116122	5.66134555	6.30061293
H	18.19802704	6.91193080	7.58471836
C	8.38616893	7.39479856	6.27740771
H	10.22328887	7.05296088	8.30617783
H	10.12504649	8.78897356	7.86554550
C	19.67931523	7.71712168	5.47208050
O	7.98805738	6.35550624	7.18130871
H	7.95455266	7.20812641	5.27609572
H	8.01221723	8.37516872	6.62788324
H	20.10788526	7.98480907	6.45620987
H	20.03966128	6.70389072	5.21296504
O	20.10901511	8.65419700	4.47485578
C	21.54585729	8.61456873	4.31299881
C	6.54926695	6.25286021	7.27813222
N	22.28515138	10.12624197	1.11937233
H	6.11342445	6.17445996	6.26735242
H	6.13930905	7.15420735	7.76403642
H	22.03725951	8.92343139	5.25077868
C	22.33278936	10.84973052	3.22759742
H	21.86081997	7.58273992	4.08019719
N	21.91968095	9.11738687	1.88935099
C	6.21668158	5.02825917	8.06026913
N	5.84165098	3.52750977	9.58806071
H	6.10627025	5.54151420	10.26366568
N	5.84357745	2.89313604	8.38911708
C	6.06553373	4.85356545	9.42729382
N	6.07373450	3.80526496	7.46174676
H	1.13315942	-1.94965875	14.93064668
C	0.73032252	-0.06478930	13.94895596
C	2.19672022	0.32134544	13.72067475
C	2.40791051	1.26351707	12.52927761
C	3.88133710	1.61441997	12.28967601
C	4.09957239	2.49438635	11.05335274
C	5.58750967	2.77531048	10.82302621
H	0.13606755	0.84774392	14.13163201
H	0.32636713	-0.51417131	13.02468309
H	2.79090046	-0.59599698	13.56309788
H	2.59713910	0.79271961	14.63526345
C	21.93557243	9.52213292	3.19731793
N	22.53410519	11.18505031	1.93112572
H	22.47736585	11.55180184	4.04047811
H	1.83046096	2.19094144	12.68613835
H	1.99608348	0.79358147	11.61925005
H	4.45993214	0.68196501	12.17307721
H	4.28818997	2.12219542	13.18067310
H	3.56012736	3.44824724	11.16364879
H	3.69164590	1.99065997	10.16324926
H	6.01620961	3.36073078	11.64497952
H	6.15122633	1.83695928	10.74223252
C	-4.24257896	-4.27783767	18.04347581
C	-2.78098174	-3.86532124	17.83998270
C	-2.58799073	-2.86246502	16.69579129
C	-1.12802816	-2.44563327	16.48166641
C	-0.93305897	-1.44969717	15.33184556
C	0.52927132	-1.04311199	15.11277079
C	17.74611717	7.36864557	4.26200467
O	14.60250190	6.77520830	8.62922367
O	12.43874789	5.10576615	8.48857871
C	18.05325063	6.67464294	6.66993562
O	16.78507588	8.40154986	8.89588919
C	10.18445738	7.27710951	6.53112593
H	10.24447235	5.64315124	5.09637089
H	10.46354721	5.13634596	6.80259240
H	10.11117508	9.33064862	5.80603411
H	10.03840042	8.08800559	4.51496668
C	10.81127622	7.65883927	7.88400947
C	18.37140460	7.75250859	5.61515014
H	18.30960025	9.38753589	7.04769927
H	18.09139092	9.89274622	5.34079596
H	17.98746397	8.12858375	3.50632188
H	18.13746442	6.39327477	3.93292183
H	18.44431052	5.69946971	6.34100170
H	18.51661290	6.94169257	7.63225000
C	8.65522386	7.22126713	6.67672675
H	10.56953750	6.89714445	8.63801935
H	10.41943496	8.63363973	8.21421758
C	19.90100354	7.81174303	5.47648154
O	8.29888662	6.18687662	7.60411806
H	8.19204086	7.02106251	5.69236738
H	8.27974628	8.19889016	7.03319534
H	20.35387827	8.06882658	6.45231122
H	20.28949281	6.82037815	5.17647090
O	20.25861302	8.79576799	4.49585371
C	21.69371531	8.91253595	4.37444534
C	6.86896419	6.13186853	7.80228991
H	23.27944610	16.68609882	0.49589993
H	6.36021870	6.01396756	6.83008436
H	6.51874631	7.06938778	8.26580190
H	22.12653975	9.21289698	5.34341062
H	24.06820692	15.97156811	2.75279244
H	22.12604353	7.93827990	4.08847318
H	23.68421832	13.64401875	3.52976296
C	6.55039957	4.96542457	8.67379346
N	6.19442976	3.57775117	10.31169025
H	6.62090271	5.61631731	10.83507837
N	6.08933871	2.87248426	9.14473742
C	6.47611450	4.88205253	10.05229126
N	6.30832440	3.71718937	8.16067826
C	6.00935241	2.93732745	11.57550827
C	6.39927582	1.60179527	11.73113582
C	6.21481154	0.98016964	12.96791439
C	5.66004120	1.68710289	14.04080014
C	5.27934993	3.02289163	13.87228377
C	5.44432910	3.65378181	12.63684879
H	6.84925599	1.06602233	10.89660261
H	6.51848077	-0.05972967	13.09440861
H	5.52451012	1.19791466	15.00618094
H	4.83964204	3.57783120	14.70173834
H	5.12281758	4.68559602	12.49616915
C	22.00522054	9.92627442	3.32726278
N	22.39589305	11.73188752	2.17778295
H	22.13848490	11.96077479	4.29739255
N	22.36969385	10.68314975	1.30048462
C	22.17619709	11.29350004	3.44528264
N	22.13078712	9.59652369	2.00262627
C	22.63809331	13.06491106	1.72402230
C	22.18888548	13.45114280	0.45553590
C	22.42985218	14.75514185	0.01776705
C	23.10001948	15.66712926	0.84101016
C	23.53903912	15.26867417	2.10837166
C	23.31860400	13.96331377	2.55400398
H	21.64998533	12.74099497	-0.17000329
H	22.08046751	15.06101928	-0.96910932

H	0.92502305	-0.59284692	16.04012195				
H	-4.87163099	-3.40551861	18.27813543				
H	-4.34748399	-4.99692687	18.86862497				
H	-4.65172058	-4.74793351	17.13609180				
H	-2.17029235	-4.76235526	17.64084234				
H	-2.38837142	-3.42870037	18.77396223				
H	-3.19843501	-1.96382910	16.89498891				
H	-2.98260779	-3.29958659	15.76143168				
H	-0.51890273	-3.34626097	16.28780468				
H	-0.73495057	-2.00533832	17.41501889				
H	-1.53730081	-0.54606578	15.52626974				
H	-1.33047528	-1.88948604	14.40010197				
C	34.45090922	19.19916328	-3.37876068				
C	32.94170594	19.16950803	-3.11549515				
C	32.46828843	17.87161276	-2.44963916				
C	30.95903898	17.83077891	-2.18211699				
C	30.48656048	16.53274079	-1.51604998				
C	28.97653158	16.49066942	-1.25184093				
H	28.69515879	17.34684146	-0.61368797				
H	35.01871697	19.09586987	-2.44139745				
H	34.75908062	20.14160587	-3.85398249				
H	34.75360288	18.37520574	-4.04302201				
H	32.39961314	19.30648986	-4.06654893				
H	32.66269579	20.02539271	-2.47772784				
H	33.01081704	17.73452174	-1.49741127				
H	32.74816457	17.01455266	-3.08758292				
H	30.41775808	17.96783706	-3.13491035				
H	30.67991172	18.68851233	-1.54497287				
H	31.02635976	16.39635191	-0.56237084				
H	30.76742452	15.67516487	-2.15259048				
H	28.43735057	16.62894193	-2.20560007				
C	28.50369567	15.19063056	-0.58996497				
C	26.99231643	15.14589178	-0.33437574				
C	26.51861784	13.84024523	0.31537507				
C	25.00433487	13.79404504	0.55270572				
C	24.53517991	12.47601199	1.17921268				
C	23.01560406	12.45364029	1.37129642				
H	29.03883409	15.05341508	0.36613093				
H	28.78898480	14.33483160	-1.22684587				
H	26.45842044	15.28910336	-1.29021354				
H	26.70604799	15.99708807	0.30798100				
H	27.04303371	13.69847033	1.27621667				
H	26.81064004	12.98932037	-0.32426578				
H	24.48139736	13.94597220	-0.40697711				
H	24.70964079	14.63485249	1.20354519				
H	25.02716857	12.32489663	2.15300388				
H	24.82496591	11.63194705	0.53402762				
H	22.68867535	13.24880944	2.05238593				
H	22.49787658	12.59041268	0.41356259				
2d $[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2C_6H_5\}_2]^{2-}$				**2e** $[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2$-*2*-$NC_5H_4\}_2]^{2-}$			
V	12.87923911	7.02286528	4.10524670	V	12.83212845	6.80542495	4.02111132
V	15.06563475	9.08285050	4.67660421	V	15.00354910	8.91835511	4.42370447
V	15.52246046	5.78218223	5.00452320	V	15.43779466	5.68457876	5.16027937
O	14.19887901	7.38769150	5.90775084	O	14.08801289	7.38406952	5.81631055
O	12.15719314	5.68719548	5.51007920	O	12.05750654	5.65404896	5.51544222
O	11.78705136	8.32506349	5.18751380	O	11.70396180	8.24459957	4.92359569
O	14.19408442	5.74829333	3.78385251	O	14.16264680	5.55490128	3.85596983
O	13.85258283	8.38953912	3.44561464	O	13.81503293	8.14675857	3.26055287
O	11.75687508	6.71299813	2.97536448	O	11.74587634	6.39788195	2.88762358
V	12.87779485	8.99442394	6.81103344	V	12.73914227	9.08454799	6.47035235
O	16.23936086	9.08928992	6.30572770	O	16.11617648	9.11449557	6.11661443
O	13.81220372	10.02130321	5.57266021	O	13.73690831	9.97438357	5.21897801
O	16.24521700	7.46028580	4.17210249	O	16.19363663	7.28432334	4.15457810
O	15.89559681	10.18249286	3.82057162	O	15.86942861	9.93805954	3.50671056
V	13.33306849	5.69274689	7.13808717	V	13.17316308	5.84888483	7.20778660
O	16.61499110	6.45248616	6.62810087	O	16.47264715	6.52390946	6.71016962
O	14.58711797	4.75536046	6.24375454	O	14.43967941	4.79396950	6.41280130
O	16.65307038	4.76679075	4.43679207	O	16.58456624	4.62378757	4.72280014
V	15.52118537	7.75209244	7.71082222	V	15.34359622	7.96283218	7.61159420
C	10.72742047	5.58650939	5.68002344	C	10.62242339	5.56739175	5.64507369

C	10.38270856	8.06826131	5.37670539	C	10.29235009	8.00733463	5.08943966
O	14.20561768	9.02708677	8.03261419	O	14.01315816	9.21340759	7.77704357
O	12.15301457	7.31560087	7.64402891	O	11.98482719	7.48332752	7.47932377
O	11.74675133	10.00922578	7.37967173	O	11.59208933	10.14474602	6.90919132
C	17.66867218	9.19191138	6.13455591	C	17.55061638	9.20182702	5.98698635
C	17.67389377	7.65685873	4.12240385	C	17.62410046	7.47568963	4.13751736
O	14.54623690	6.38646222	8.36986146	O	14.36205246	6.62056676	8.37196668
O	12.50259562	4.59374091	7.99502826	O	12.30751574	4.82939179	8.12547901
C	18.01985608	6.71124568	6.43760200	C	17.88425330	6.76190225	6.54410038
O	16.64287771	8.06228535	8.84110209	O	16.42959650	8.37149408	8.74523345
C	10.12465480	6.86023063	6.29879971	C	10.00199330	6.89495518	6.11576369
H	10.28590928	5.40949782	4.68692490	H	10.21293804	5.29119604	4.66084495
H	10.52539183	4.72013717	6.32513156	H	10.39966947	4.76968891	6.36658477
H	9.93479655	8.97456904	5.81221142	H	9.83095801	8.95185477	5.41686081
H	9.93727167	7.88746440	4.38613653	H	9.88250196	7.72826546	4.10659248
C	10.72439035	7.12060656	7.69234566	C	10.55517472	7.29221182	7.49616227
C	18.27383780	7.91963790	5.51539739	C	18.17419321	7.87507214	5.51841530
H	18.11074909	9.36917656	7.12738171	H	17.95989191	9.47911362	6.97102284
H	17.86945990	10.05800407	5.48878537	H	17.77441680	9.99827674	5.26430006
H	17.86949108	8.51231097	3.46226568	H	17.84856201	8.26017453	3.40217893
H	18.12451523	6.75174752	3.68579248	H	18.08531326	6.53027513	3.81168642
H	18.46814265	5.80561800	6.00115136	H	18.34608861	5.81821773	6.21524852
H	18.46575110	6.89197468	7.42800373	H	18.29436064	7.03962992	7.52735164
C	8.60006653	6.70677076	6.41877950	C	8.47427757	6.74919582	6.20985567
H	10.52730921	6.26477470	8.35210602	H	10.32949926	6.50651564	8.23018517
H	10.27460023	8.02582556	8.12979865	H	10.09424853	8.23750365	7.82297297
C	19.79713836	8.08597963	5.38976202	C	19.70121162	8.03127415	5.43355560
O	8.28857867	5.62074252	7.30290077	O	8.14869728	5.68397749	7.11412051
H	8.16193357	6.52118930	5.42025218	H	8.05135548	6.54066657	5.20937194
H	8.16268530	7.64474968	6.80903883	H	8.03518511	7.69818942	6.57008296
H	20.23386668	8.29990977	6.38333852	H	20.10575743	8.29246468	6.42957915
H	20.24551357	7.14465120	5.02047560	H	20.15833309	7.07236208	5.12498808
O	20.08730246	9.15480221	4.47871150	O	20.02509710	9.05771852	4.48595401
C	21.51166750	9.32439233	4.30247788	C	21.45504874	9.22939528	4.36679696
C	6.85975364	5.49713451	7.48851153	C	6.73143927	5.64460298	7.39273182
N	21.98970464	11.08537264	1.18709600	N	22.01686466	11.10850564	1.33475970
H	6.37540984	5.26542874	6.52453987	H	6.16067709	5.50210114	6.45942882
H	6.45195205	6.45187038	7.86081107	H	6.42124761	6.60177479	7.84598849
H	21.97199879	9.64607452	5.25183560	H	21.87987628	9.52282858	5.34140427
C	21.87282392	11.71498584	3.32434566	C	21.89200321	11.64642820	3.49770845
H	21.96633137	8.36403286	4.00412844	H	21.92020572	8.27720182	4.05797044
N	21.82031744	9.99405528	1.91117549	N	21.81033844	9.99197596	2.00735649
C	6.59213289	4.40322466	8.46467381	C	6.45614607	4.50579254	8.31511275
N	6.28590207	3.17634329	10.23135769	N	6.29926810	3.13101452	9.99005040
H	6.60807830	5.26997941	10.55447489	H	7.15988976	5.05085245	10.39622687
N	6.21204703	2.35609329	9.15090182	N	5.78691895	2.50127529	8.90100093
C	6.51848108	4.45362541	9.84723549	C	6.72075170	4.37760329	9.66923346
N	6.40060690	3.10308593	8.07896804	N	5.88851054	3.33646987	7.88418655
C	22.22054813	13.50684431	1.54244420	C	22.31614680	13.49677343	1.80248786
H	21.93981255	14.17650151	2.36325210	H	21.99699198	14.15308009	2.62015568
C	21.74343768	10.33797777	3.23437780	C	21.72675502	10.27896885	3.34411389
N	22.02000556	12.13538788	2.04497733	N	22.06303816	12.11930031	2.24050712
H	21.86678245	12.39871206	4.16514330	H	21.89734458	12.29201022	4.36788381
H	21.51307304	13.65708089	0.71915149	H	21.68209738	13.69024391	0.93100189
C	6.11398417	2.64000301	11.59291852	C	6.35940683	2.44632325	11.28619950
H	7.01962503	2.87547369	12.16434546	H	7.41035501	2.35495006	11.58389654
H	6.05663931	1.55202156	11.47053264	H	5.96002888	1.44023762	11.10944042
C	4.88397409	3.18711235	12.28635293	C	5.55920510	3.15199339	12.36371904
C	5.01670568	4.08259111	13.35665360	C	6.17918686	3.57359039	13.54424887
C	3.88293156	4.58969992	14.00228914	C	5.40326775	4.18571933	14.53200128
C	2.60665468	4.20476118	13.58015995	C	4.03946249	4.36013016	14.29897784
C	2.46707433	3.30826469	12.51282161	C	3.50862353	3.91242390	13.08523547
C	3.59941589	2.80063072	11.87093674	N	4.24104738	3.31441702	12.12909438
H	6.01267417	4.38165735	13.69059349	H	7.24996514	3.42229414	13.68548275
H	3.99874291	5.28453515	14.83569942	H	5.85933255	4.52188626	15.46379182
H	1.72162676	4.59836221	14.08272640	H	3.39226249	4.83304486	15.03782151
H	1.47334226	2.99962510	12.18414923	H	2.44388386	4.03378259	12.87048021
H	3.48515987	2.09736269	11.04306611	H	25.83628304	14.64479667	-1.08330261
C	23.64090522	13.76331871	1.08221593	C	23.77639736	13.74072393	1.46893996
C	24.68202477	13.89737695	2.01432396	N	24.65603608	13.59770534	2.48084308
C	25.99043427	14.13414500	1.58420283	C	25.95489962	13.82256943	2.21274546

C	26.27080965	14.24583428	0.21654202	C	26.42878558	14.20157021	0.95330506
C	25.23717702	14.11961265	-0.71715026	C	25.50959425	14.35138333	-0.08505654
C	23.92822641	13.87812832	-0.28513256	C	24.15806493	14.11339005	0.17624123
H	24.46918733	13.82029323	3.08289468	H	23.40788041	14.21406700	-0.60876654
H	26.79188635	14.23876018	2.31737311	H	26.64769205	13.69821908	3.04885896
H	27.29195932	14.43448144	-0.11880653	H	27.49406509	14.37413629	0.79898081
H	25.44814299	14.20930248	-1.78408722				
H	23.12211257	13.78090293	-1.01527029				
2f				**2g**			
$[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2CO_2CH_2CH_3\}_2]^{2-}$				$[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3(CH_2)_3SCH_3\}_2]^{2-}$			
V	12.85515206	7.99847294	5.25644743	V	12.94754443	6.70635524	4.04003339
V	15.52871310	9.33050065	5.90847105	V	15.28130864	8.66013158	4.31975575
V	15.27396820	6.18927707	4.78907410	V	15.47637412	5.44013859	5.20011655
O	14.58737212	7.38890131	6.58731955	O	14.27275904	7.26889555	5.79149604
O	12.16637680	6.30914208	6.16355392	O	12.11001175	5.69176732	5.59833280
O	12.36712718	8.82958536	7.05467785	O	11.94946080	8.27026321	4.88411667
O	13.74859311	6.91018766	4.08335774	O	14.17355184	5.34588306	3.92305534
O	13.95587081	9.43180642	4.97250101	O	14.02235701	7.92535682	3.20503318
O	11.47646589	8.38115903	4.49277110	O	11.81600856	6.33218614	2.93993128
V	13.89815800	8.58622182	8.38370514	V	13.06841870	9.09682185	6.38185397
O	17.01005176	8.46633011	7.00981659	O	16.43499821	8.84577576	5.98573126
O	14.78954485	9.90941288	7.47634385	O	14.11414868	9.84653433	5.07293514
O	16.17129601	7.98875756	4.50537951	O	16.33938650	6.92303948	4.11373044
O	16.40163394	10.58950885	5.37485942	O	16.21209246	9.56118149	3.34334447
V	13.64543362	5.44428101	7.26561361	V	13.26412144	5.87509962	7.26298003
O	16.80214263	5.94490640	6.12156559	O	16.59303535	6.26628175	6.70076411
O	14.38452911	4.86633557	5.69755137	O	14.43173843	4.69019194	6.51037155
O	15.98150827	5.42321564	3.54658317	O	16.52937640	4.27153327	4.80397208
V	16.31742006	6.77767267	7.91937841	V	15.59603318	7.83087586	7.54440353
C	10.82427517	6.31089260	6.69516264	C	10.67502865	5.72481531	5.74952258
C	11.01586990	8.68383982	7.53373603	C	10.52626506	8.15308149	5.07815855
O	15.42497261	7.86702921	9.09082640	O	14.37089305	9.19197640	7.66078013
O	13.00532060	6.78504974	8.66758379	O	12.20832371	7.61342145	7.47046697
O	13.19026035	9.35065614	9.62704230	O	12.01546092	10.26543226	6.77854349
C	18.35183445	8.46206875	6.47760333	C	17.86964744	8.81174795	5.83578652
C	17.56120439	8.01146273	4.11773844	C	17.78002198	6.99967155	4.07149784
O	15.21842306	5.34350113	8.20240357	O	14.52264689	6.61149657	8.37901614
O	12.77455823	4.18387789	7.79840039	O	12.33478866	4.97409524	8.24052991
C	18.15245352	6.08728440	5.64377863	C	18.01562459	6.38325501	6.50861087
O	17.69659065	6.39557207	8.68293290	O	16.72788991	8.20550356	8.64429926
C	10.68616448	7.22963959	7.92214150	C	10.16590896	7.11774188	6.16110402
H	10.14791841	6.65123034	5.89554360	H	10.23016828	5.43460916	4.78481711
H	10.57099698	5.27766896	6.96889439	H	10.40110928	4.98311601	6.51200472
H	10.89843329	9.34289095	8.40773968	H	10.14537855	9.14534909	5.36479889
H	10.33899058	9.02242048	6.73430642	H	10.08030726	7.86095612	4.11491183
C	11.61558369	6.75884340	9.05498593	C	10.76815939	7.53596130	7.51431476
C	18.48817486	7.54034907	5.25255539	C	18.37902820	7.41843536	5.42593830
H	19.02808419	8.12232038	7.27754462	H	18.31421969	9.10210031	6.80060159
H	18.60610910	9.49536864	6.20343428	H	18.14526953	9.55270386	5.07295469
H	17.81135436	9.04163478	3.82983460	H	18.05301128	7.72856476	3.29622409
H	17.67662827	7.35281484	3.24270559	H	18.16102567	6.00692078	3.78516955
H	18.26957857	5.42736866	4.77031014	H	18.39719655	5.39089715	6.22279628
H	18.82870999	5.74816788	6.44364229	H	18.46047944	6.67563839	7.47235473
C	9.23135718	7.20790954	8.41856702	C	8.63305303	7.08937774	6.27389529
H	11.36584053	5.72770161	9.33919732	H	10.49513582	6.80612362	8.28853895
H	11.49884499	7.41598396	9.93100715	H	10.38709057	8.52860470	7.80116700
C	19.94421435	7.53902831	4.76187979	C	19.91223719	7.44506050	5.32651088
O	8.88283549	5.87295651	8.80847894	O	8.24568617	6.13118789	7.26768860
H	8.55469878	7.56048909	7.61758150	H	8.18989625	6.82187404	5.29621058
H	9.12100531	7.89437084	9.27896060	H	8.25986950	8.09392968	6.54850829
H	20.61158137	7.19702034	5.57508480	H	20.34167217	7.72903252	6.30556984
H	20.05013779	6.82941240	3.91990469	H	20.28947515	6.43633697	5.07365472
O	20.32239284	8.85568382	4.33669876	O	20.31782421	8.38683549	4.32369948
C	21.67418542	8.86027836	3.82448713	C	21.75789840	8.50428786	4.27658682
C	7.53999002	5.81222412	9.33675500	C	6.80871607	6.07266452	7.40923684
H	23.04421204	11.40064383	4.93471269	N	22.71198329	10.20668798	1.23768710
H	6.81872008	6.14096208	8.56887742	H	6.34933046	5.81294259	6.43986036
H	7.45033603	6.48358200	10.20719473	H	6.42345829	7.05754658	7.72246408
H	22.37892046	8.57404792	4.62288083	H	22.13320369	8.82463440	5.26321067
C	21.99701799	10.22148534	3.31158308	C	22.20621918	10.87767454	3.30398261
H	21.76107285	8.12540648	3.00566972	H	22.20778230	7.52584440	4.03559619

N	22.63068427	12.27755132	3.02411202
C	7.25119044	4.40471929	9.73340684
N	7.05159375	2.49207158	10.74048402
H	7.83356887	4.11397504	11.90097223
N	6.61701274	2.32262170	9.46234491
C	7.45670686	3.76830087	10.94569028
N	6.73656208	3.48593988	8.85603730
N	22.04690426	11.86880577	1.86483206
C	22.62395273	11.28204607	3.94317648
N	21.66055570	10.62320130	2.04448793
H	23.12937128	13.95890317	4.15385556
H	26.17005006	17.07767393	1.52696093
H	26.67556229	14.61520548	1.29479830
H	27.15181502	14.54949745	3.01497607
H	27.85596787	16.72675421	1.97340595
H	26.64893295	17.01342217	3.24877640
C	23.21000847	13.60331449	3.12001707
C	24.67914035	13.62535845	2.69363118
O	25.11912298	14.89265981	2.66353520
C	26.53430194	15.07856653	2.27872253
C	26.80790409	16.56520103	2.25913107
O	25.34494077	12.63568047	2.42817200
H	22.63275988	14.28143760	2.48176686
C	7.08714152	1.36897388	11.65625268
C	8.44931831	0.67196584	11.66105165
O	8.41228947	-0.38364806	12.48965433
C	9.66558680	-1.15923632	12.60340247
C	9.41184685	-2.29532427	13.56787438
O	9.41895690	1.02927959	11.00960292
H	6.85390231	1.71708169	12.66908796
H	6.31315172	0.65337841	11.35608644
H	9.13737329	-1.92033772	14.56264724
H	10.44807448	-0.47726362	12.95810113
H	9.92982243	-1.51468555	11.59992111
H	10.33236493	-2.88636450	13.66600224
H	8.61622191	-2.95798896	13.20263988

N	22.44604794	9.12594235	1.94843888
C	6.47182627	5.03373921	8.42343321
N	6.06073266	3.89422130	10.22787813
H	6.31856663	6.00705852	10.46194696
N	6.08376216	3.01749224	9.19193342
C	6.29369473	5.15527997	9.79235367
N	6.33613939	3.71076185	8.09686673
H	3.82148660	2.60819556	11.10615142
H	6.25721900	2.46394812	11.71225903
H	26.08775248	16.63868534	0.04456966
H	25.39788996	17.37371240	1.53610667
H	4.45579521	1.84423561	13.43001371
H	1.11130021	1.92370769	15.52970976
H	24.43144024	14.54095071	0.32748440
H	23.74787016	15.22975579	1.82571599
H	24.34207917	13.10182735	3.05396179
H	24.98323850	12.41516166	1.54750185
H	22.70796028	12.60298703	0.48682467
C	22.13124032	9.49580647	3.22866637
N	22.56050960	11.27697598	2.05960662
H	22.03753597	11.57682502	4.11491085
H	2.69904101	1.11831773	15.35560542
C	26.19165407	16.73336485	1.13240925
S	26.16333050	15.09090438	1.92724488
C	24.48937555	14.52349910	1.42526188
C	24.23905734	13.11300044	1.95857038
C	22.83290342	12.63358527	1.57563743
H	22.06289910	13.29392667	1.99292522
H	2.60665045	2.82690736	15.91493799
H	4.36973791	3.53416623	13.99795635
C	2.16264357	2.06999550	15.25684561
S	2.17114270	2.63818511	13.52267659
C	3.98005787	2.82050858	13.25781350
C	4.25033588	3.31102298	11.83549345
C	5.75911846	3.43308713	11.58641914
H	6.21965123	4.14854181	12.27758084
H	3.77316024	4.28923144	11.67569740
H	27.16749123	17.17420495	1.36627909

2h

$[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2$-*4*-$(C_6H_4SCH_3\}_2]^{2-}$

V	12.88118805	6.89901627	4.08928098
V	15.27496811	8.76349807	4.46438350
V	15.38878878	5.48848820	5.11945375
O	14.24612858	7.30412796	5.85478543
O	12.02922472	5.81851003	5.55024414
O	11.94616721	8.45666892	5.08015827
O	14.07769841	5.57739715	3.80559775
O	13.96629166	8.21759596	3.34974064
O	11.72532999	6.68029992	2.97258780
V	13.10405688	9.12012193	6.58901226
O	16.46195244	8.79049940	6.15948009
O	14.17808385	9.94285038	5.39330519
O	16.28135069	7.05367842	4.12034989
O	16.21923245	9.73564763	3.57245881
V	13.21790334	5.84293885	7.24497100
O	16.54540514	6.15162564	6.63139991
O	14.31474769	4.66507116	6.31628821
O	16.39671028	4.33456632	4.58619414
V	15.61087032	7.70880466	7.62099070
C	10.59794441	5.88193174	5.72509931
C	10.52345688	8.36646307	5.28317207
O	14.41442030	9.03050452	7.90451113
O	12.21312418	7.55345438	7.59126706
O	12.09606615	10.27390630	7.12293932
C	17.89311918	8.72599251	5.98509876
C	17.72349448	7.09027584	4.06379450
O	14.52589306	6.38973750	8.36054529
O	12.27338900	4.87074547	8.13649360
C	17.96842430	6.24150395	6.42913860
O	16.76654460	7.92859728	8.73774453

2i

$[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH_2CH_2SiPh_2Bu^t\}_2]^{2-}$

V	11.74608522	8.43817704	5.32965719
V	14.47138609	9.55235803	6.15341575
V	14.03216641	6.43173312	5.03969056
O	13.32791832	7.70323497	6.77806341
O	10.86099515	6.82056797	6.19189300
O	11.20447747	9.32364350	7.08737483
O	12.62688143	7.27452176	4.22372842
O	12.97813705	9.77752740	5.11870719
O	10.45929164	8.92582010	4.47143528
V	12.61985516	8.97344818	8.51481080
O	15.79374056	8.58052851	7.36556463
O	13.67733882	10.20534985	7.67038371
O	15.09587481	8.15222075	4.81000905
O	15.48039505	10.73129627	5.68090407
V	12.18194400	5.84798463	7.40259858
O	15.44226788	6.07655581	6.47246239
O	12.97658784	5.19763639	5.88597509
O	14.75834811	5.59975136	3.85126231
V	14.90541403	6.96591594	8.22947201
C	9.49015508	6.93729275	6.62868664
C	9.81576535	9.29289875	7.47347715
O	14.02550065	8.13013331	9.33378103
O	11.56352653	7.24819228	8.74632944
O	11.89346792	9.80360429	9.70464238
C	17.16424304	8.46002722	6.93019313
C	16.50693892	8.05667401	4.52123786
O	13.67518689	5.62462582	8.43979056
O	11.17567543	4.66795299	7.87549836
C	16.82993109	6.10324513	6.08828861
O	16.19175971	6.47726615	9.08871674

C	10.14035815	7.24643912	6.27056350
H	10.12939415	5.69332504	4.74647425
H	10.31307370	5.08229340	6.42221437
H	10.17523368	9.33929608	5.66350762
H	10.05925450	8.17707657	4.30306840
C	10.77179093	7.51638709	7.64797480
C	18.35227684	7.36134229	5.44211689
H	18.36106325	8.91512263	6.96387185
H	18.17992304	9.52395778	5.28657849
H	18.01205759	7.87889340	3.35540460
H	18.06652845	6.11623140	3.68160934
H	18.31595425	5.26901324	6.04757711
H	18.43270018	6.42978420	7.40941361
C	8.60894749	7.26671707	6.39830006
H	10.48245180	6.72743886	8.35602345
H	10.42848533	8.49031627	8.03045594
C	19.88445924	7.34628207	5.32339128
O	8.17860853	6.20561532	7.26195073
H	8.14786416	7.14979138	5.39945537
H	8.28443008	8.24244106	6.80610257
H	20.33466104	7.52438019	6.31794484
H	20.22264940	6.35266380	4.97378928
O	20.31161670	8.36024371	4.40351192
C	21.75397384	8.39481302	4.30762676
C	6.74655712	6.24678083	7.46014718
N	22.61772883	10.25620733	1.33681262
H	6.23230562	6.19460821	6.48523885
H	6.46842076	7.19603821	7.94851050
H	22.18567703	8.62316721	5.29668072
C	22.40700594	10.78150130	3.49278943
H	22.12913109	7.40808272	3.98572777
N	22.29003078	9.15022075	1.98040071
C	6.34025453	5.08425123	8.29933431
N	5.90283233	3.67855465	9.89914968
H	6.55104338	5.63285347	10.48613797
N	5.67327339	3.03929817	8.72369211
C	6.31339227	4.94975243	9.67898242
N	5.94342374	3.89326089	7.75250289
H	0.06548407	5.78507768	13.76115802
H	0.24789341	4.48222728	14.99837101
C	-0.30751539	4.81676460	14.11410238
C	29.04340410	15.18835510	4.02435392
H	28.62420587	14.87249311	4.98559647
H	26.46922010	15.01741751	3.98970543
H	4.58534680	4.66751402	13.09739221
H	2.24198032	4.93915490	13.78581087
H	24.10858247	14.47229519	3.56402187
H	28.53341225	16.08333858	3.64938946
H	30.11022512	15.40447954	4.14831687
C	22.15118096	9.43109111	3.31325872
N	22.68559014	11.25367332	2.25455880
H	22.40759235	11.41602866	4.37148193
H	-1.37023661	4.90834579	14.36720777
C	5.61728823	3.00170946	11.17882136
H	6.30019744	3.42448459	11.92359630
H	5.87923212	1.94780137	11.02917789
C	4.17497927	3.15403089	11.60923912
C	3.16297340	2.38401442	11.00963270
C	1.83257848	2.53195649	11.38935365
C	1.47561093	3.45801158	12.39133882
C	2.48266777	4.22189535	13.00253870
C	3.81566529	4.06636001	12.60805655
H	3.41914370	1.65875753	10.23483572
H	1.06162871	1.92449243	10.91175548
S	-0.25045901	3.57000567	12.79243829
C	23.07054930	12.61541408	1.84518527
H	22.41799099	13.31685451	2.37658997
H	22.83891552	12.67447731	0.77465282
C	24.52663206	12.92642484	2.11384934
C	25.54821892	12.23834192	1.43545187
C	26.88674720	12.53466862	1.67151089
C	9.34409261	7.87367800	7.84139892
H	8.90055444	7.32601652	5.78382075
H	9.13456248	5.93069030	6.88693029
H	9.69403493	9.96656038	8.33567639
H	9.22556175	9.67942230	6.62833188
C	10.15331316	7.33897078	9.03674193
C	17.30969243	7.52061813	5.71986873
H	17.75177723	8.07154959	7.77671959
H	17.52369181	9.46522385	6.67105070
H	16.86152074	9.05996471	4.24826538
H	16.62754816	7.38251543	3.65894680
H	16.95150690	5.42936281	5.22612480
H	17.41914588	5.71558333	6.93361167
C	7.86179923	7.96315897	8.24249728
H	9.80037553	6.33443551	9.30604720
H	10.03089718	8.01181760	9.89988465
C	18.79364059	7.40559975	5.33747857
O	7.39997223	6.65302306	8.59597397
H	7.26509795	8.36923884	7.40434332
H	7.74916424	8.64986469	9.10226080
H	19.36572774	6.99746965	6.19181916
H	18.90843716	6.70375421	4.49002078
O	19.30257197	8.69721467	4.97884130
C	20.71229872	8.63072769	4.66796476
C	6.06077737	6.67247393	9.13585569
H	21.79584302	11.08637608	6.19828336
H	5.34452429	7.02042692	8.37213574
H	6.01558947	7.36215612	9.99548782
H	21.26627789	8.24429588	5.54017561
C	21.19149962	9.99531678	4.30885206
H	20.87792394	7.94377604	3.82030103
N	21.90550545	12.04738642	4.28741368
C	5.72119682	5.28349247	9.55756250
N	5.55474534	3.36427844	10.56558827
H	6.51596634	4.94532727	11.64839971
N	4.97831908	3.23131117	9.34114636
C	6.02808792	4.62275730	10.73580219
N	5.07924547	4.39854119	8.73348118
N	21.63347397	11.70026663	3.00177609
C	21.64892497	11.01576062	5.12675394
N	21.19697978	10.45495391	3.01856177
H	10.72123678	4.48991917	15.68067235
H	12.18966025	3.11061706	14.20869524
H	11.27553378	1.15282459	13.02185061
C	9.70912174	-0.85963307	11.65706255
C	9.29072625	-1.04718418	10.32323825
C	10.13591417	-1.61891863	9.36530097
C	11.42601108	-2.02404931	9.72298816
C	11.86169610	-1.85780318	11.04234273
C	11.01300328	-1.28305131	11.99491805
H	8.28232170	-0.75258804	10.02596510
H	9.78507598	-1.75044366	8.33988051
H	12.08795626	-2.47050701	8.97872754
H	12.86494344	-2.17653338	11.33163344
C	7.86124661	-1.50224525	14.10536821
Si	8.50212208	-0.13493136	12.92438213
O	7.11860445	0.39924029	12.11759009
C	7.08614252	1.58107197	11.31530384
C	5.69256860	2.21063922	11.45267708
H	5.50989331	2.53787387	12.48284328
C	7.24965858	-2.64097368	13.25932971
C	6.78016311	-0.94777329	15.05631938
H	4.91935912	1.48861594	11.16862066
H	7.27007251	1.33210225	10.25777422
H	7.85480591	2.30409543	11.63711929
H	11.38127517	-1.17183629	13.01698537
C	9.03010938	-2.06216573	14.94283376
H	7.18375266	-0.18556986	15.73797404
H	6.38334361	-1.76726065	15.67972303
H	5.93642690	-0.50733810	14.50616869
H	9.80467508	-2.52470034	14.31402029

C	27.24332945	13.54036950	2.59456135
C	26.22846057	14.23419946	3.27197165
C	24.88600359	13.92148090	3.02973986
H	25.29437726	11.46091212	0.71148280
H	27.66598457	11.99084580	1.13407662
S	28.98079664	13.83878893	2.80768835

H	8.65518801	-2.84220130	15.62708857
H	9.50669105	-1.28409118	15.55791968
H	6.39773387	-2.28984719	12.65941837
H	6.88363229	-3.44157054	13.92458376
H	7.98733146	-3.08669454	12.57627862
C	9.26437075	1.35645736	13.81444322
C	8.45049532	2.16247769	14.64146421
C	8.96619846	3.27882506	15.30714667
C	10.31552355	3.62023304	15.16050142
C	11.13850582	2.84532629	14.33726034
C	10.61554356	1.73113517	13.67050245
H	7.39225427	1.92410828	14.76611083
H	8.31351819	3.88315759	15.93990746
C	25.81537701	17.16352895	5.03644727
Si	25.96426832	15.28765341	4.65796623
O	24.39179046	14.71380567	4.86342297
C	23.97489944	13.39435536	4.50591058
C	22.44483243	13.36836667	4.60299950
H	22.00606818	14.08268568	3.89724717
C	25.53331688	17.33203509	6.54738147
C	24.65102312	17.81254678	4.25681301
H	22.12054444	13.63090507	5.61627783
H	24.40728743	12.64483771	5.18992138
H	24.28660869	13.14262071	3.47943620
H	28.96437414	14.91677424	4.94177279
C	27.13864070	17.87913966	4.69273813
H	24.81010121	17.80513583	3.16984432
H	24.54881881	18.86795552	4.56251960
H	23.69692758	17.30818596	4.46243679
H	27.98944650	17.45929972	5.25045149
H	27.06516980	18.94654265	4.96212640
H	27.37550320	17.82253783	3.62051831
H	24.59910362	16.83437997	6.84606390
H	25.43095453	18.40476125	6.78427125
H	26.34702960	16.92846581	7.16617964
C	26.57727311	14.84204763	2.91779962
C	26.32994686	15.65232568	1.78914333
C	26.73982016	15.26645416	0.50855214
C	27.40446456	14.04957398	0.32168555
C	27.65598829	13.22404883	1.42234808
C	27.24827759	13.61892644	2.70150238
H	25.80950099	16.60445501	1.89958214
H	26.53878275	15.91721431	-0.34451400
H	27.72457513	13.74670930	-0.67692658
H	28.17254985	12.27196042	1.28642067
H	27.46199427	12.96073390	3.54633953
C	27.08608299	14.44099636	5.92722507
C	26.52926573	13.82668537	7.06770556
C	27.33903963	13.24727820	8.05121907
C	28.73161942	13.27867568	7.91844796
C	29.30729111	13.88672391	6.79690841
C	28.49180592	14.45710139	5.81316335
H	25.44434488	13.80359876	7.19332342
H	26.88298914	12.77380799	8.92295177
H	29.36619507	12.82998568	8.68494763
H	30.39310669	13.91363117	6.68651276

2j

$[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3CH2\text{-}L\text{-}C_4H_7N\text{-}COOC(CH_3)_3\}_2]^{2-}$

V	12.94754443	6.70635524	4.04003339
V	15.28130864	8.66013158	4.31975575
V	15.47637412	5.44013859	5.20011655
O	14.27275904	7.26889555	5.79149604
O	12.11001175	5.69176732	5.59833280
O	11.94946080	8.27026321	4.88411667
O	14.17355184	5.34588306	3.92305534
O	14.02235701	7.92535682	3.20503318
O	11.81600856	6.33218614	2.93993128
V	13.06841870	9.09682185	6.38185397
O	16.43499821	8.84577576	5.98573126

2k

$[V_6O_{13}\{(OCH_2)_3CCH_2OCH_2CCHN_3(CH_2)_5NHCO(CH_2)_4\text{-}C_5H_7N_2OS\}_2]^{2-}$

V	12.72685886	7.05722987	4.08925017
V	15.06440976	8.99383993	4.44630574
V	15.23634405	5.75242277	5.24751980
O	14.03318501	7.57169062	5.87056991
O	11.86828292	6.00995586	5.60752834
O	11.72407312	8.60700052	4.96222035
O	13.95002766	5.69959835	3.94837878
O	13.81524141	8.29834345	3.30019067
O	11.60746621	6.71965000	2.96511373
V	12.82769067	9.38852375	6.49188145
O	16.20284207	9.13274154	6.13180163

O	14.11414868	9.84653433	5.07293514	O	13.89469126	10.16769729	5.22061703
O	16.33938650	6.92303948	4.11373044	O	16.11713665	7.26015540	4.21003809
O	16.21209246	9.56118149	3.34334447	O	16.01039427	9.91684616	3.50562409
V	13.26412144	5.87509962	7.26298003	V	13.00247430	6.14706680	7.29498594
O	16.59303535	6.26628175	6.70076411	O	16.33714178	6.53447269	6.78120486
O	14.43173843	4.69019194	6.51037155	O	14.17150786	4.97358272	6.52105009
O	16.52937640	4.27153327	4.80397208	O	16.28921447	4.59026940	4.83242785
V	15.59603318	7.83087586	7.54440353	V	15.33849455	8.08569215	7.65163253
C	10.67502865	5.72481531	5.74952258	C	10.43171130	6.04305535	5.74010110
C	10.52626506	8.15308149	5.07815855	C	10.29803960	8.48997139	5.13573179
O	14.37089305	9.19197640	7.66078013	O	14.11529672	9.44277111	7.79161032
O	12.20832371	7.61342145	7.47046697	O	11.94847006	7.87903821	7.53286073
O	12.01546092	10.26543226	6.77854349	O	11.77485992	10.54997951	6.90903656
C	17.86964744	8.81174795	5.83578652	C	17.63972417	9.09416615	5.99778029
C	17.78002198	6.99967155	4.07149784	C	17.55828528	7.33042910	4.18580630
O	14.52264689	6.61149657	8.37901614	O	14.25099952	6.84446009	8.44175056
O	12.33478866	4.97409524	8.24052991	O	12.05765544	5.22312307	8.23573935
C	18.01562459	6.38325501	6.50861087	C	17.76225542	6.64802023	6.60876094
O	16.72788991	8.20550356	8.64429926	O	16.45811684	8.42464291	8.77527794
C	10.16590896	7.11774188	6.16110402	C	9.92100876	7.42553745	6.18420607
H	10.23016828	5.43460916	4.78481711	H	9.99839883	5.78113149	4.76215372
H	10.40110928	4.98311601	6.51200472	H	10.14555502	5.28202325	6.47802074
H	10.14537855	9.14534909	5.36479889	H	9.91679363	9.47547752	5.44478791
H	10.08030726	7.86095612	4.11491183	H	9.86347238	8.22610271	4.15926826
C	10.76815939	7.53596130	7.51431476	C	10.50750236	7.80377618	7.55599865
C	18.37902820	7.41843536	5.42593830	C	18.14486851	7.70872711	5.55760490
H	18.31421969	9.10210031	6.80060159	H	18.07418358	9.35693033	6.97491542
H	18.14678396	9.54997318	5.07092630	H	17.92712688	9.85419012	5.25798513
H	18.05358462	7.73098903	3.29870135	H	17.84426274	8.07907081	3.43464943
H	18.16102567	6.00692078	3.78516955	H	17.93759193	6.34394552	3.87663115
H	18.39719655	5.39089715	6.22279628	H	18.14116122	5.66134555	6.30061293
H	18.46047944	6.67563839	7.47235473	H	18.19802704	6.91193080	7.58471836
C	8.63305303	7.08937774	6.27389529	C	8.38616893	7.39479856	6.27740771
H	10.49513582	6.80612362	8.28853895	H	10.22328887	7.05296088	8.30617783
H	10.38709057	8.52860470	7.80116700	H	10.12504649	8.78897355	7.86554550
C	19.91223719	7.44506050	5.32651088	C	19.67931523	7.71712168	5.47208050
O	8.24568617	6.13118789	7.26768860	O	7.98805738	6.35550624	7.18130871
H	8.18989625	6.82187404	5.29621058	H	7.95455266	7.20812641	5.27609572
H	8.25986950	8.09392968	6.54850829	H	8.01221723	8.37516872	6.62788324
H	20.34167217	7.72903252	6.30556984	H	20.10788526	7.98480907	6.45620987
H	20.28947515	6.43633697	5.07365472	H	20.03966128	6.70389072	5.21296504
O	20.31782421	8.38683549	4.32369948	O	20.10901511	8.65419700	4.47485578
C	7.33764435	4.68901147	10.83247010	C	21.54585729	8.61456873	4.31299881
C	6.81811417	6.03784566	7.37546568	C	6.54926695	6.25286021	7.27813222
C	6.42775063	5.26019885	8.63179155	N	22.28515138	10.12624197	1.11937233
H	6.40398771	5.55194444	6.47638566	H	6.11342445	6.17445996	6.26735242
H	6.37713099	7.04930245	7.45384017	H	6.13930905	7.15420735	7.76403642
H	7.89196275	6.45839274	9.69785747	H	22.03725951	8.92343139	5.25077868
N	6.93440428	3.86179009	8.66707035	C	22.33278936	10.84973052	3.22759742
C	6.98574689	5.88401475	9.93360057	H	21.86081997	7.58273992	4.08019719
C	7.80881712	3.62931111	9.83109853	N	21.91968095	9.11738687	1.88935099
H	6.25636314	6.56535436	10.38889863	C	6.21668158	5.02825917	8.06026913
H	4.33789054	3.79979365	4.81922278	N	5.84165097	3.52750977	9.58806071
H	3.01227920	0.85865517	6.75417222	H	6.10627025	5.54151419	10.26366568
H	4.34290676	0.79718463	7.93861662	N	5.84357745	2.89313604	8.38911708
H	6.08814755	0.71737206	6.04243831	C	6.06553373	4.85356545	9.42729382
H	6.08842405	2.00283236	4.80125850	N	6.07373450	3.80526496	7.46174676
H	3.01811956	2.60621620	4.90364557	H	-1.74006485	0.63936788	15.83780222
H	3.13835936	3.88692274	6.13881275	N	0.79477664	0.02549338	13.97390113
O	6.67758387	1.62586383	8.20243150	C	2.19672022	0.32134544	13.72067475
H	8.86299747	3.78515116	9.55017845	C	2.40791051	1.26351707	12.52927761
C	6.36622078	2.81262757	8.00897733	C	3.88133710	1.61441997	12.28967601
O	5.43386437	3.24647661	7.11156873	C	4.09957239	2.49438635	11.05335274
C	4.58917975	2.27552035	6.35230659	C	5.58750967	2.77531048	10.82302621
H	5.32753791	5.23272887	8.64997314	C	26.99231643	15.14589178	-0.33437574
H	7.69028070	2.59819047	10.18032115	H	0.20100427	-0.19577312	13.17705723
C	5.45362217	1.38774852	5.45414965	H	2.79090046	-0.59599698	13.56309788
C	3.71776659	3.20391484	5.50295213	H	2.59713910	0.79271961	14.63526345
C	3.72892135	1.46591883	7.32483533	C	21.93557243	9.52213292	3.19731793
H	3.15882049	2.13581849	7.98309145	N	22.53410519	11.18505031	1.93112572
H	4.79588929	0.78153975	4.81552149	H	22.47736585	11.55180184	4.04047811

H	6.44458197	4.32527062	11.36204079
H	8.10567849	4.92805700	11.57854886
C	21.73335561	8.60018646	4.29629703
H	22.04326129	9.18595666	5.17771680
H	22.66653702	7.96533257	1.37205169
H	23.73218239	11.30193418	6.62640913
H	23.65545821	14.76866259	5.21139521
H	22.41077394	14.45583894	3.97097358
H	20.76363495	13.38543265	5.64885410
H	21.36599891	12.12942693	6.77014888
C	22.10198478	9.32938939	3.00116157
H	24.32494603	12.96741157	6.85430134
H	24.86600491	12.01836853	5.44743139
O	20.83313233	12.77239228	3.25541137
C	21.50692733	11.75025477	3.46739405
O	22.52077208	11.64816180	4.37748934
C	22.83057873	12.77849784	5.30337398
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H	20.38329660	11.51124859	1.15343524
C	21.63330474	13.04132493	6.21894247
C	24.01200738	12.22770359	6.10562589
C	23.25498050	14.01928738	4.51371103
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C	21.77843724	8.49731936	1.73423866
N	21.33387958	10.58293237	2.79438903
C	20.48028687	10.51483325	1.59801729
H	19.47457516	10.15089543	1.86503444
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H	21.00947893	7.75271425	1.98220702
H	22.27401293	7.63594314	4.31403970

H	1.83046096	2.19094143	12.68613835
H	1.99608348	0.79358147	11.61925005
H	4.45993214	0.68196501	12.17307721
H	4.28818997	2.12219542	13.18067310
H	3.56012735	3.44824724	11.16364879
H	3.69164590	1.99065997	10.16324926
H	6.01620961	3.36073078	11.64497952
H	6.15122633	1.83695928	10.74223252
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C	25.00433487	13.79404504	0.55270572
C	24.53517991	12.47601199	1.17921268
C	23.01560406	12.45364029	1.37129642
H	29.01867592	15.22911144	0.26853968
C	-5.40610821	-4.81991859	17.00230875
C	-5.02050923	-3.38429269	16.55065019
N	28.42923888	15.17926583	-0.55907564
H	26.45842044	15.28910336	-1.29021354
H	26.70604799	15.99708807	0.30798100
H	27.04303371	13.69847033	1.27621667
H	26.81064004	12.98932037	-0.32426578
H	24.48139736	13.94597220	-0.40697711
H	24.70964079	14.63485249	1.20354518
H	25.02716857	12.32489663	2.15300388
H	24.82496591	11.63194705	0.53402762
H	22.68867535	13.24880944	2.05238593
H	22.49787658	12.59041268	0.41356259
H	38.19722783	20.64644526	-2.42642983
C	36.48253719	19.07082299	-0.81156104
C	33.51756142	17.30738024	-2.79678314
C	32.75458217	16.20828698	-2.05015127
H	35.15099434	18.90241614	-3.95110253
C	31.26006163	16.14768562	-2.39153824
C	30.57563176	14.97290321	-1.66552131
C	29.05630721	15.00329170	-1.75034248
O	28.44296940	14.88628788	-2.83602276
H	37.41861325	18.49932585	-0.75039927
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H	33.52156211	17.08185086	-3.87644397
H	33.22472935	15.23344550	-2.26506613
S	35.04541613	17.96689061	-0.53788168
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H	32.85509020	16.36643346	-0.96207422
H	37.04642457	17.39422598	-4.50039172
H	33.00591765	18.27647356	-2.67347937
C	36.28316508	19.64966991	-2.22226534
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H	30.78218720	17.09521573	-2.09413880
H	35.57197902	20.48319195	-2.19576272
H	35.48342466	16.47958598	-2.42004012
C	38.02745924	18.98294823	-3.63806767
O	39.15081305	18.92612414	-4.17375996
N	37.52867343	20.03737707	-2.89411161
H	30.88960884	14.96516675	-0.61041706
C	35.77833275	18.50109916	-3.13993918
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H	36.47744386	19.84409527	-0.03503112
H	-7.82991419	-3.13398504	18.82361932
H	-8.36090245	-6.02822576	17.94221125
C	-7.26223984	-3.39902061	17.92484148
C	-3.51319732	-3.13492509	16.48450293
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H	-4.52872497	-5.31593423	17.44333202
C	-1.62594335	-1.53029284	15.84319998
C	-1.28699921	-0.15818251	15.22978443
C	0.20817614	0.11220439	15.19477141
O	0.85013849	0.38122571	16.23730634
H	-7.92050041	-3.34502549	17.04629535
N	-5.97161126	-5.63607674	15.91843825
H	-3.07742964	-3.89955773	15.81901550
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S	-5.86862229	-2.22402849	17.73843322

	H	-1.71688431	-0.08628404	14.21933356
	H	-3.56262911	-0.97014385	16.62367508
	H	-5.35087107	-6.10753728	15.26344599
	H	-3.07406517	-3.29817339	17.48291927
	C	-6.58403841	-4.77559031	18.02907445
	H	-1.18894682	-2.32589773	15.21837232
	H	-1.15894366	-1.61093991	16.83723060
	H	-6.21528147	-4.92210634	19.05120894
	H	-5.47022599	-3.20667785	15.56190685
	C	-7.09138636	-6.33534391	16.33581363
	O	-7.70290293	-7.19708880	15.67413009
	N	-7.40746532	-5.91009189	17.60762586

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