

Development of sterically hindered siloxide functionalized polyoxotungstates for the complexation of 5d-metals

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1. NMR spectra

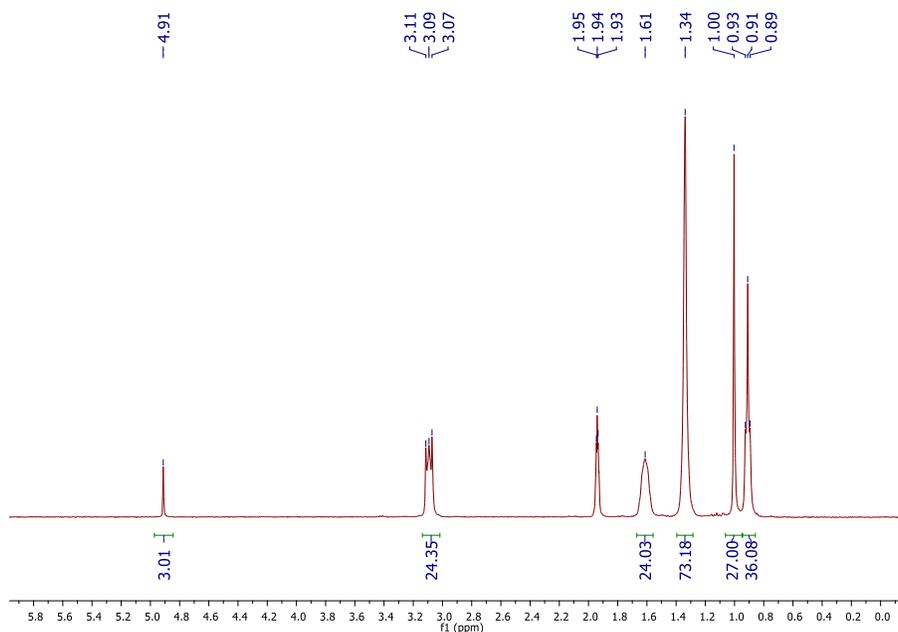


Figure S1 ¹H NMR spectra of compound 1 in CD₃CN

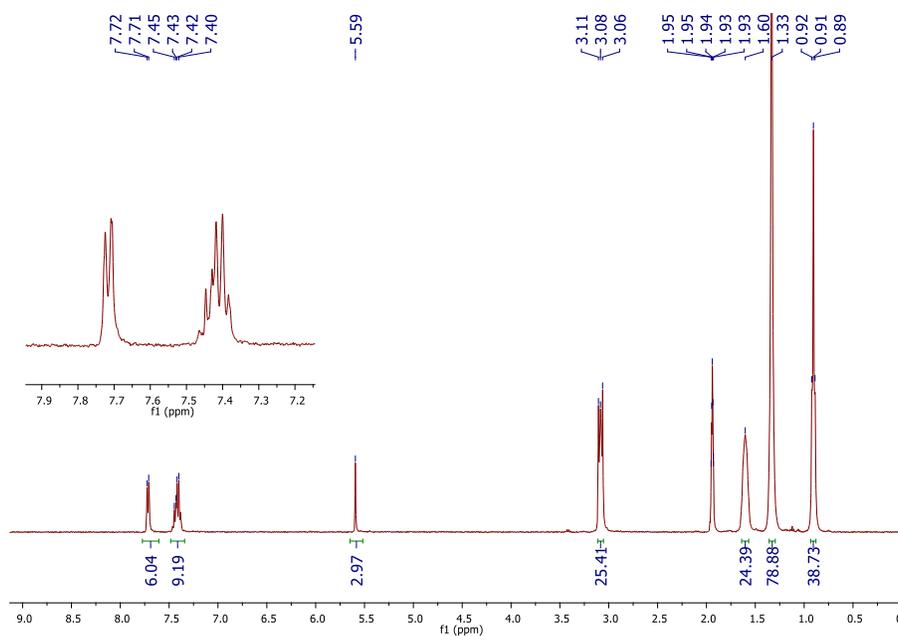


Figure S2 ¹H NMR spectra of compound 2 in CD₃CN

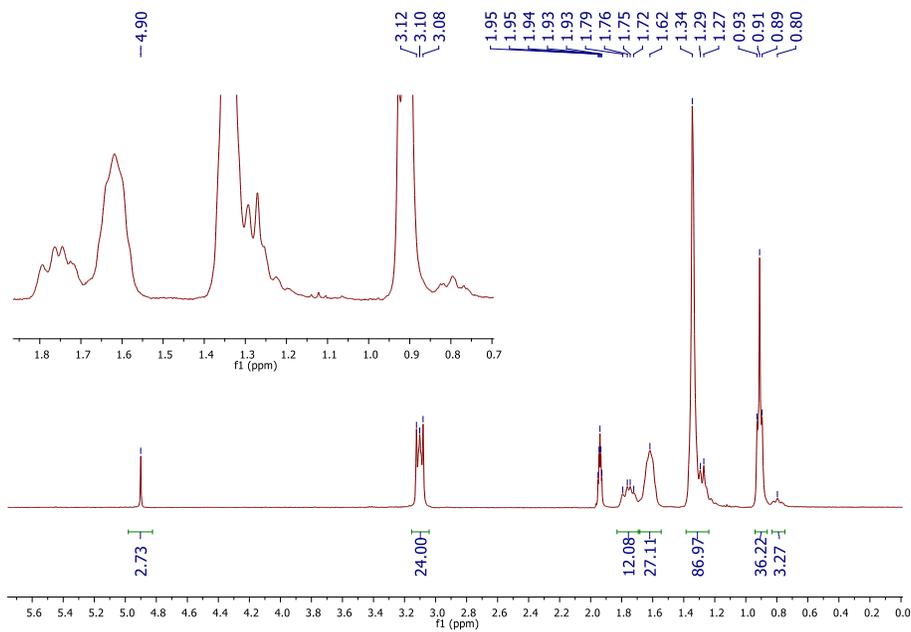


Figure S3 ^1H NMR spectra of compound **3** in CD_3CN

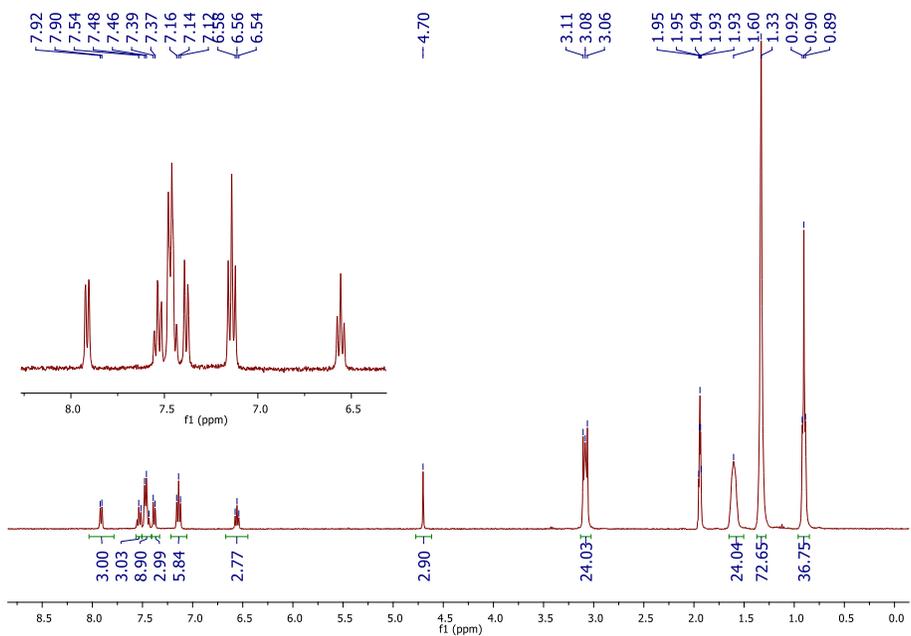


Figure S4 ^1H NMR spectra of compound **4** in CD_3CN

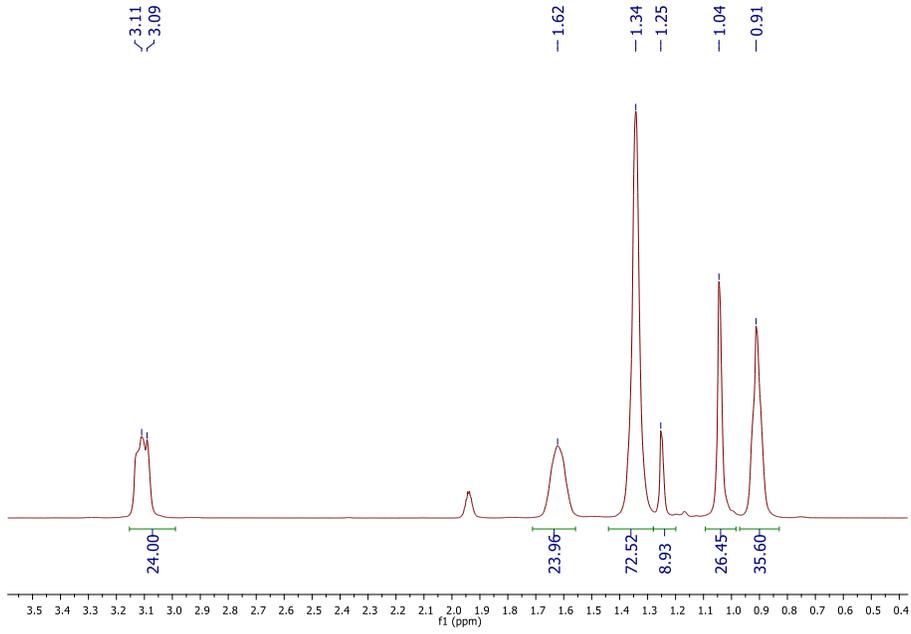


Figure S5 ^1H NMR spectra of compound **5** in CD_3CN

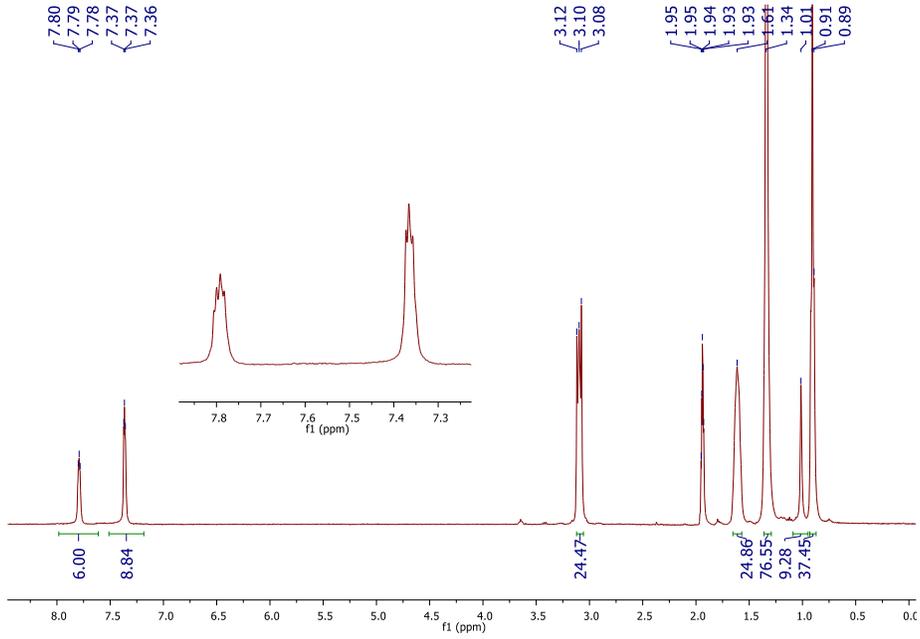


Figure S6 ^1H NMR spectra of compound **6** in CD_3CN

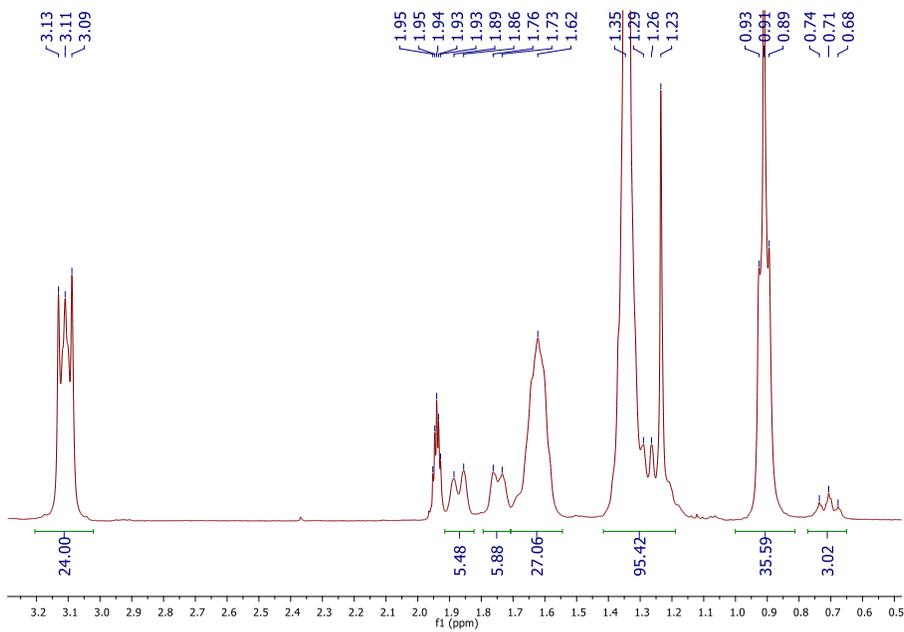


Figure S7 ^1H NMR spectra of compound **7** in CD_3CN

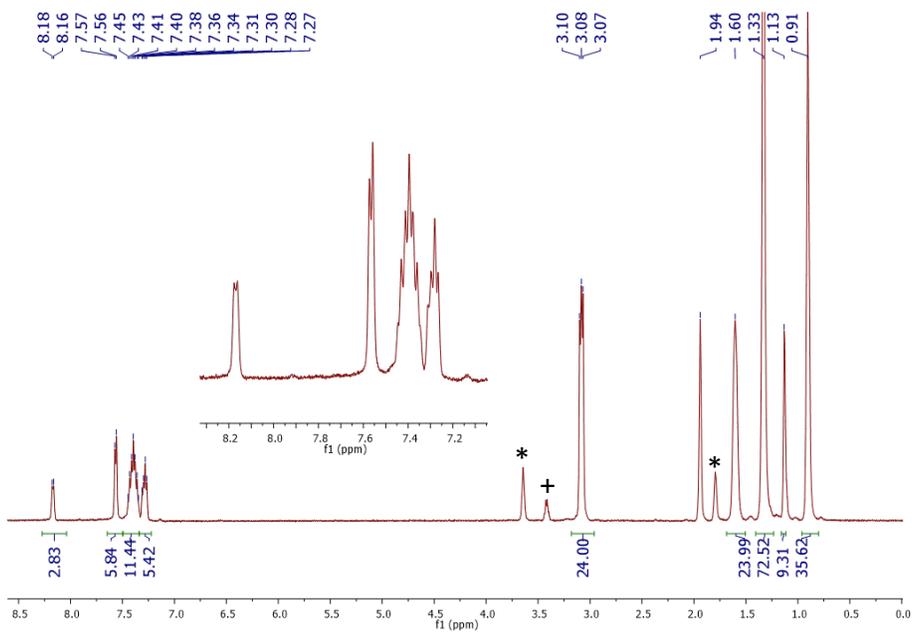


Figure S8 ^1H NMR spectra of compound **8** in CD_3CN (residual solvents from incomplete drying: * THF, + t BuOH)

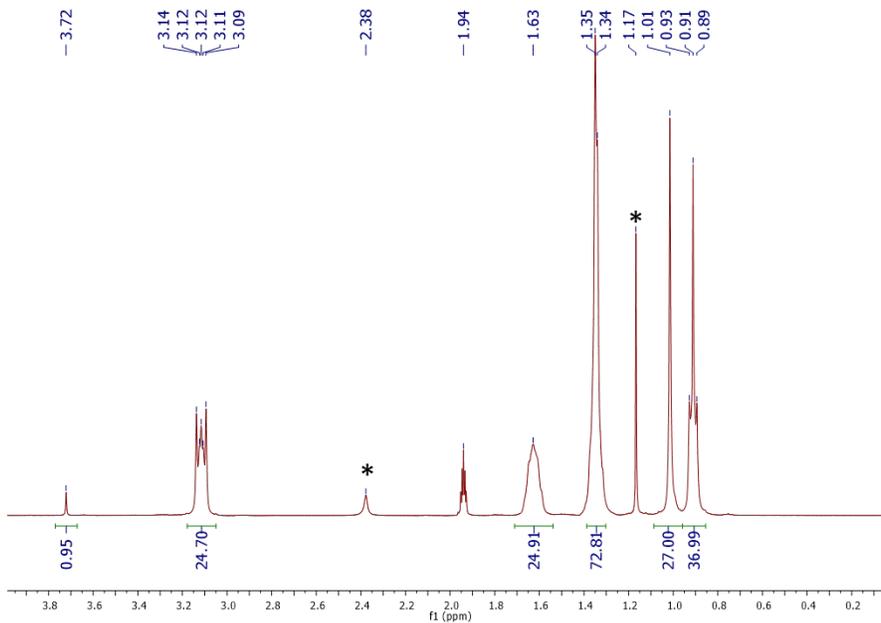


Figure S9 ^1H NMR spectra of the hydrolyzed form of compound **5** in CD_3CN (* signals from free $^t\text{BuOH}$)

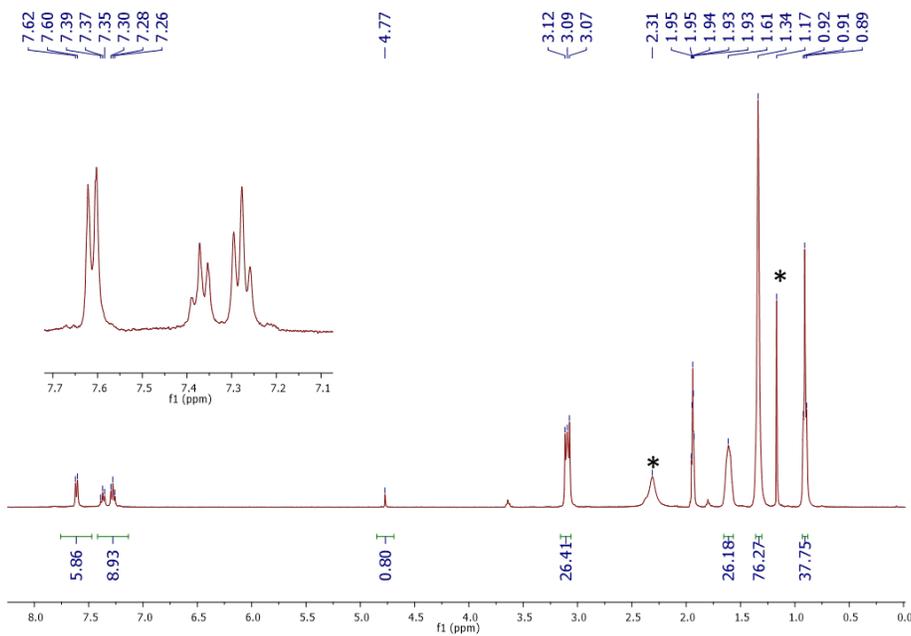


Figure S10 ^1H NMR spectra of the hydrolyzed form of compound **6** in CD_3CN (* signals from free $^t\text{BuOH}$)

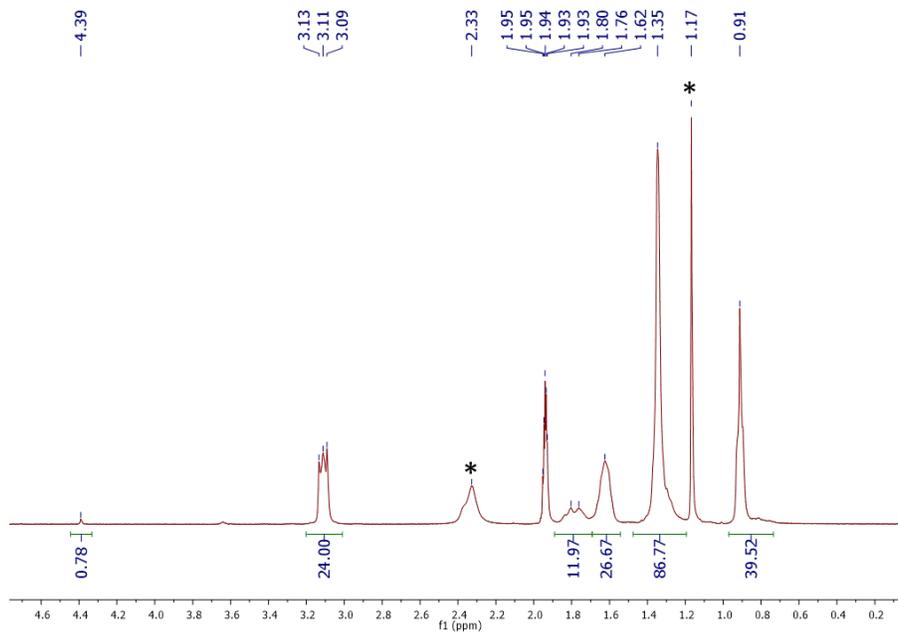


Figure S11 ^1H NMR spectra of the hydrolyzed form of compound **7** in CD_3CN (* signals from free $^t\text{BuOH}$)

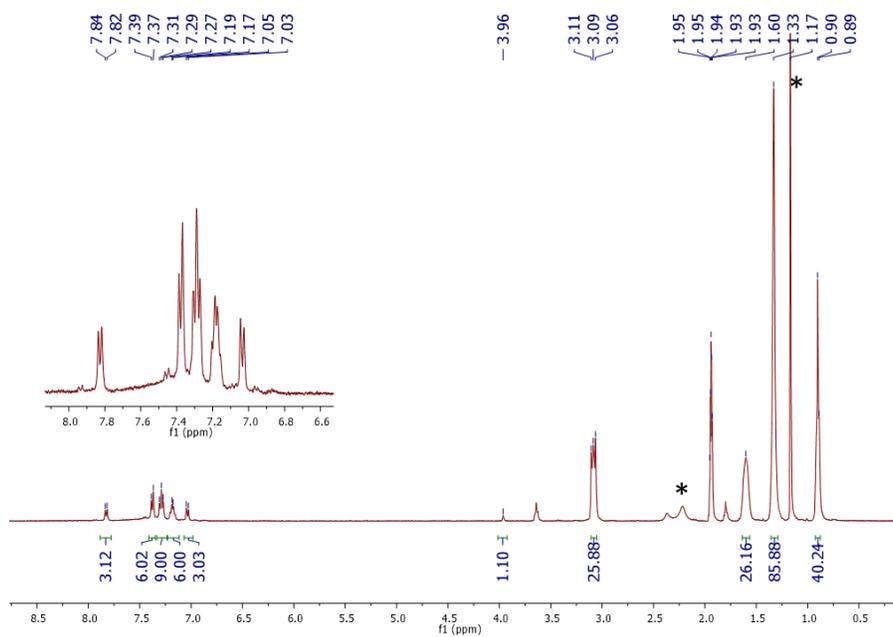


Figure S12 ^1H NMR spectra of the hydrolyzed form of compound **8** in CD_3CN (* signals from free $^t\text{BuOH}$)

2. Crystallographic study

Structure of compound 4: Crystals suitable for X-ray diffraction analysis were obtained by layering a concentrated solution of **4** in acetonitrile with methanol. A crystal (0.143 x 0.123 x 0.099 mm³) was placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections.¹ A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source with frame times of 1.73 and 6.93 seconds and a detector distance of 31.2 mm. Series of frames were collected in 0.50° steps in w at different $2q$, k , and f settings. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids of 151374 strong reflections from the actual data collection after integration.¹ See Table 1 for additional crystal and refinement information.

The structure was solved using SHELXT² and refined using SHELXL.³ The space group $Pca2_1$ was determined based on systematic absences and intensity statistics. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The O-H hydrogen atoms were unable to be found from the difference Fourier map. Additionally, the hydrogen bonding scenario is likely bi-directionally disordered (i.e., clockwise or counter-clockwise). As such, the O-H hydrogen atoms were placed in two positions on each oxygen atom and given occupancies of 0.5. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

All tetrahexylammonium cations are disordered to some degree. The ones containing N1, N3, N4, N5, and N6 appear to be disordered with one another in three dimensions. After multiple failed attempts to produce reasonable disorder models, the atoms of the cations were each placed in the major positions from the difference Fourier map and their positional and anisotropic displacement parameters were heavily restrained. Analogous bond lengths and angles among the tetrahexylammonium cations were restrained to be similar and restrained toward ideal values. Anisotropic displacement parameters for proximal atoms were restrained to be similar and restrained toward the expected thermal motion relative to bond direction. For the majority of the atoms in the cations, their anisotropic displacement parameters were restrained toward an isotropic model. Additionally, an “anti-bumping” restraint was applied to keep the atoms at distances beyond the sums of their individual van der Waals radii (except in the cases of hydrogen bonding).

There are four major voids per unit cell each containing 111 electrons in 328 Å³, for a total of 444 electrons in 1312 Å³ per unit cell. Because the voids are likely composed of alternate positions of disorder of the cations (see below), which are potentially disordered with cocrystallized solvent, they were not given atomic assignments nor were they treated with SQUEEZE.⁵ The void space accounts for 4.8 % of the cell volume and 3.1 % of the electron density. The final full matrix least squares refinement converged to $R1 = 0.0536$ (F^2 , $I > 2s(I)$) and $wR2 = 0.1402$ (F^2 , all data).

The structure is the one suggested. The asymmetric unit contains six tetrahexylammonium cations and two trianionic W₉ clusters in general positions. Part or all of two of the six biphenyl groups were modeled as disordered over two positions each: C43-C48, 0.64:0.36 and C61-C72, 0.71:0.29.

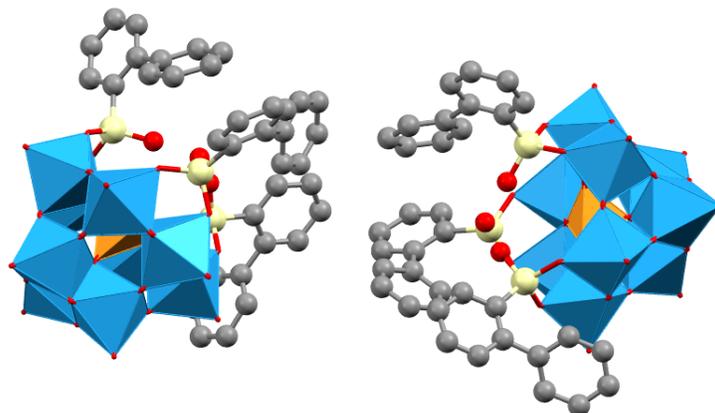


Figure S13 Combined ball-stick and polyhedral representation of both independent clusters in the asymmetric unit of ligand **4**. Counter-cations and hydrogen atoms were omitted for clarity.

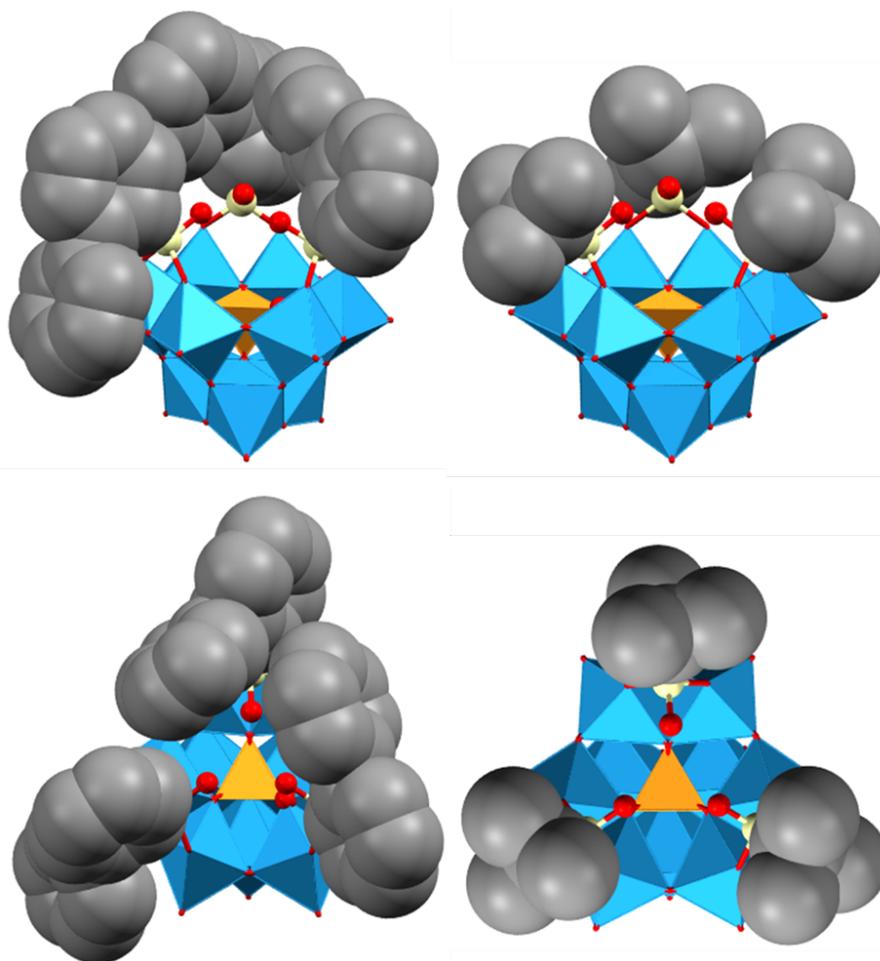


Figure S14 Comparison of the steric hindrance around the coordination pocket in **4** (left) and **1** (right) using combined spacefill and polyhedral representation in both cases. Counter-cations and hydrogen atoms were omitted for clarity.

Table S1. Crystal data and structure refinement for ligand 4.

Empirical formula	C108 H186 N3 O37 P Si3 W9	
Formula weight	3888.48	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	orthorhombic	
Space group	<i>Pca</i> 2 ₁	
Unit cell dimensions	<i>a</i> = 30.2815(2) Å	$\alpha = 90^\circ$
	<i>b</i> = 31.4764(2) Å	$\beta = 90^\circ$
	<i>c</i> = 28.51028(19) Å	$\gamma = 90^\circ$
Volume	27174.7(4) Å ³	
<i>Z</i>	8	
Density (calculated)	1.901 Mg/m ³	
Absorption coefficient	14.604 mm ⁻¹	
<i>F</i> (000)	14992	
Crystal color, morphology	colourless, block	
Crystal size	0.143 x 0.123 x 0.099 mm ³	
Theta range for data collection	2.550 to 89.915°	
Index ranges	-39 ≤ <i>h</i> ≤ 39, -38 ≤ <i>k</i> ≤ 34, -36 ≤ <i>l</i> ≤ 36	
Reflections collected	504469	
Independent reflections	57366 [<i>R</i> (int) = 0.0996]	
Observed reflections	51756	
Completeness to theta = 74.504°	99.1%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00000 and 0.72451	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	57366 / 2656 / 3009	
Goodness-of-fit on <i>F</i> ²	1.037	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0536, <i>wR</i> 2 = 0.1356	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0592, <i>wR</i> 2 = 0.1402	
Absolute structure parameter	0.028(12)	
Largest diff. peak and hole	1.015 and -1.919 e.Å ⁻³	

THF adduct of compound 6: Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to a concentrated solution of **6** in THF- d^8 . A crystal (0.078 x 0.076 x 0.046 mm³) was placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLab Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections.¹ A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source with frame times of 1.29 and 5.17 seconds and a detector distance of 31.2 mm. Series of frames were collected in 0.50° steps in ω at different 2θ , κ , and ϕ settings. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids of 50074 strong reflections from the actual data collection after integration.¹

The structure was solved using ShelXT² and refined using ShelXL.³ The space group $P2_1/c$ was determined based on systematic absences. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0487$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.1389$ (F^2 , all data). Structure manipulation and figure generation were performed using Olex2.⁴ Unless noted otherwise all structural diagrams containing anisotropic displacement ellipsoids are drawn at the 50 % probability level.

The asymmetric unit contains three tetrahexylammonium cations, one trianionic hafnium-capped nonatungsten cluster, and a cocrystallized deuterated THF solvent molecule of partial occupancy (0.85), all in general positions. One methylene linkage of one THF ligand is modeled as disordered over two positions (0.61:0.39) and hexyl chains C49-C54 and C97-C102 are modeled as disordered over two positions each (0.69:0.31 and 0.75:0.25, respectively).

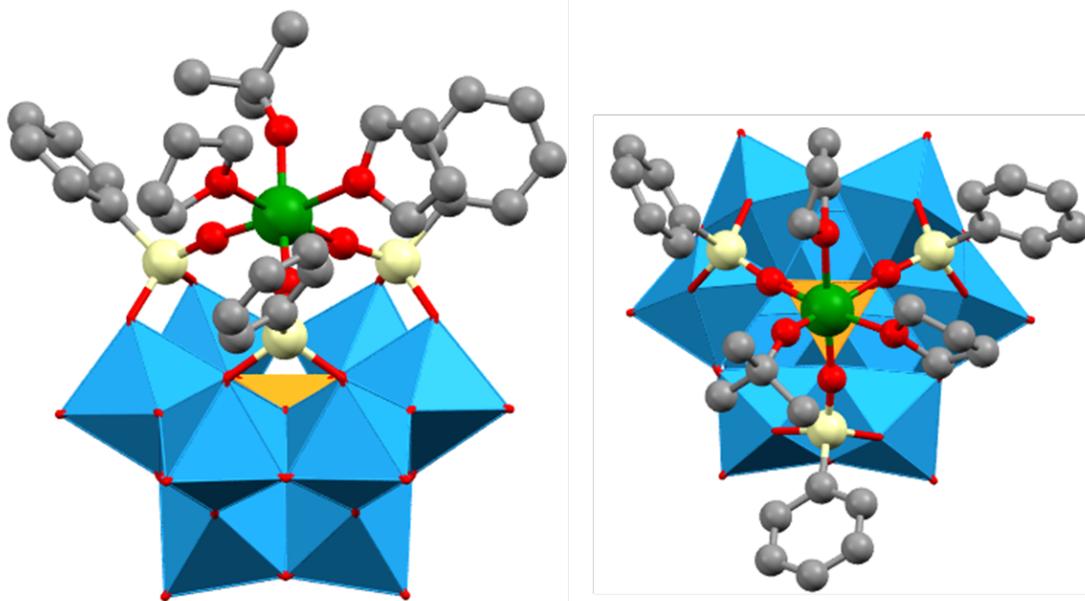


Figure S15 Combined ball-stick and polyhedral representation of both complex **6** as its THF adduct. Counter-cations, cocrystallized solvent molecule and hydrogen atoms were omitted for clarity.

Table S2. Crystal data and structure refinement for the THF adduct of compound 6.

Empirical formula	C105.39 H180 D22.77 Hf N3 O40.85 P Si3 W9	
Formula weight	4136.93	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 23.6019(2)$ Å	$\alpha = 90^\circ$
	$b = 19.8230(2)$ Å	$\beta = 95.8670(10)^\circ$
	$c = 29.5100(2)$ Å	$\gamma = 90^\circ$
Volume	13734.2(2) Å ³	
Z	4	
Density (calculated)	2.001 Mg/m ³	
Absorption coefficient	15.815 mm ⁻¹	
$F(000)$	7911	
Crystal color, morphology	colourless, block	
Crystal size	0.078 x 0.076 x 0.046 mm ³	
Theta range for data collection	2.690 to 77.924°	
Index ranges	$-29 \leq h \leq 29$, $-19 \leq k \leq 24$, $-37 \leq l \leq 35$	
Reflections collected	142062	
Independent reflections	28793 [$R(\text{int}) = 0.0625$]	
Observed reflections	24803	
Completeness to theta = 74.504°	99.7%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00000 and 0.37677	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	28793 / 373 / 1566	
Goodness-of-fit on F^2	1.075	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0487$, $wR2 = 0.1339$	
R indices (all data)	$R1 = 0.0558$, $wR2 = 0.1389$	
Largest diff. peak and hole	2.105 and -2.694 e.Å ⁻³	

Hydrolyzed form of compound 5: Crystals suitable for X-ray diffraction formed upon exposure to ambient air of a diethyl ether – THF concentrated solution of **5**. We were however unable to collect a complete dataset, but the partial set of reflections allowed us to obtain a preliminary structure (Figure S). This structure points to the formation of a dimeric product where two hafnium-capped organosilyl-derivatized polyoxotungstate are bridged by two hydroxo groups (attributed as hydroxo as opposed to oxo based on charge balance). Electron densities located around the Hf centers were attributed as oxygen atoms and could indicate the presence of coordinated water molecule(s) resulting in hexa- or heptacoordinated metal centers.

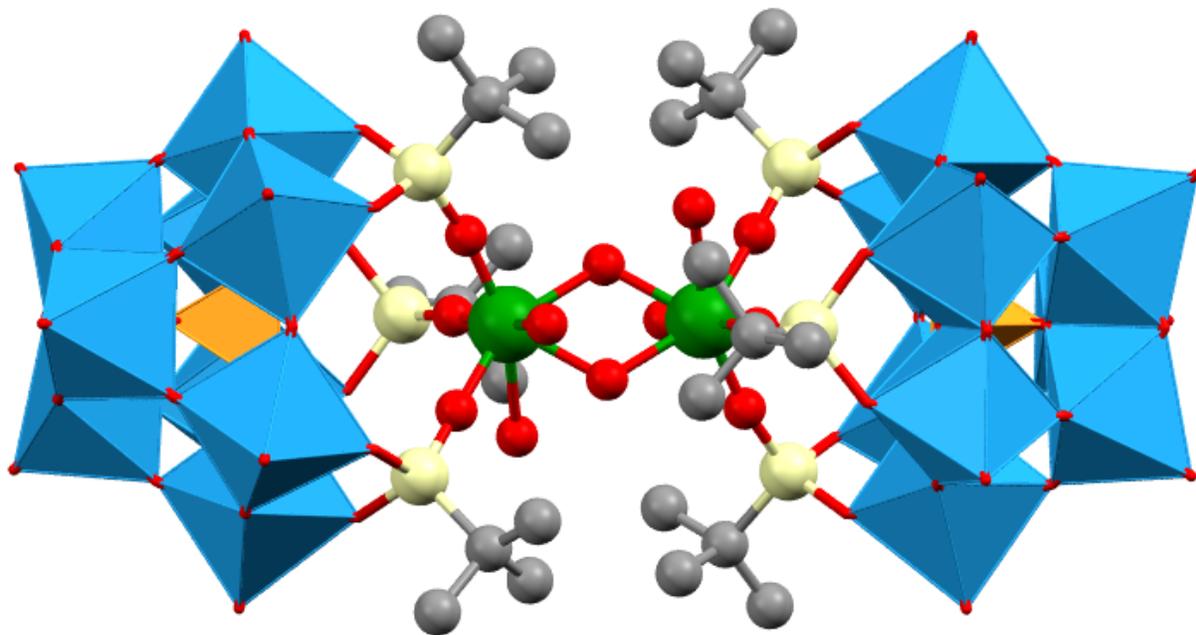


Figure S16 Combined ball-stick and polyhedral representation of the preliminary structure of the hydrolyzed form of complex 5. Counter-cations and hydrogen atoms were omitted for clarity.

Hydrolyzed form of compound 7: Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of “wet” diethyl ether to a concentrated solution of compound 7 hydrolyzed in “wet” THF (wet meaning that no particular attention was taken to removed water from the solvents obtained from the manufacturer). A crystal (0.253 x 0.186 x 0.12 mm³) was placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections.¹ A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source with frame times of 0.35 and 1.39 seconds and a detector distance of 31.2 mm. Series of frames were collected in 0.50° steps in ω at different 2θ , k , and f settings. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids of 56089 strong reflections from the actual data collection after integration.¹

The structure was solved using SHELXT² and refined using SHELXL.³ The space group $P2_1/c$ was determined based on systematic absences. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0645$ (F^2 , $I > 2s(I)$) and $wR2 = 0.1882$ (F^2 , all data). Structure manipulation and figure generation were performed using Olex2.⁴ Unless noted otherwise all structural diagrams containing anisotropic displacement ellipsoids are drawn at the 50 % probability level.

The asymmetric unit contains one-half of a $W_{18}Hf_2$ cluster next to a crystallographic inversion center, three tetrahexylammonium cations, two co-crystallized water solvent molecules and 1.7 co-crystallized THF solvent molecules in general positions. One cyclohexyl group is modeled as disordered over three positions (0.49:0.36:0.15). Co-crystallized THF solvent molecule O42/C98-102 was refined as partially occupied (0.70). One solvent pocket was modeled as a co-crystallized water molecule disordered over three positions (0.37:0.35:0.28). The cations containing atoms N2 and N3 are badly disordered, but each is modeled in a single approximate position to support the charge balance. It is likely that these cations are disordered over multiple positions and with the adjacent solvent molecules. An anti-bumping restraint was applied to keep the atoms at distances beyond the sums of their individual van der Waals radii (except in the cases of hydrogen bonding).

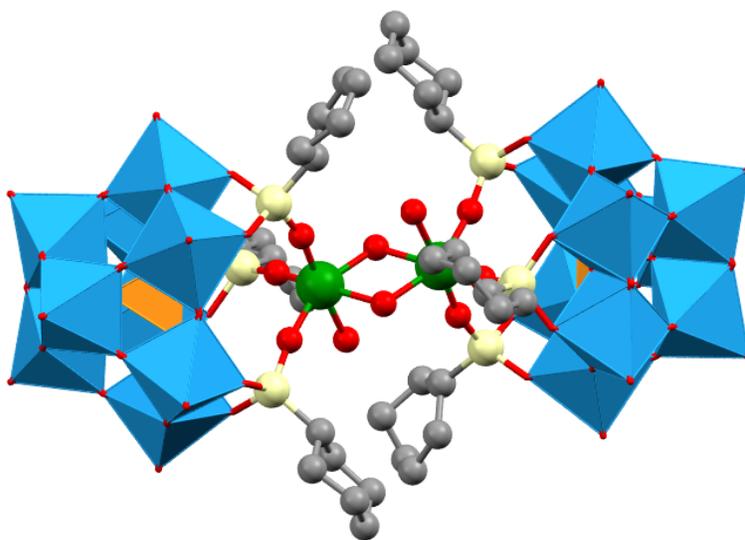


Figure S17 Combined ball-stick and polyhedral representation of the hydrolyzed form of complex 7. Counter-cations, co-crystallized solvent molecules and hydrogen atoms were omitted for clarity.

Table S3. Crystal data and structure refinement for the hydrolyzed form of compound 7.

Empirical formula	C193.59 H419.17 Hf2 N6 O85.39 P2 Si6 W18	
Formula weight	8094.59	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 25.2799(3)$ Å	$\alpha = 90^\circ$
	$b = 25.7240(3)$ Å	$\beta = 99.6830(10)^\circ$
	$c = 21.8787(3)$ Å	$\gamma = 90^\circ$
Volume	14025.0(3) Å ³	
Z	2	
Density (calculated)	1.917 Mg/m ³	
Absorption coefficient	15.482 mm ⁻¹	
$F(000)$	7792	
Crystal color, morphology	colourless, block	
Crystal size	0.253 x 0.186 x 0.12 mm ³	
Theta range for data collection	2.674 to 77.827°	
Index ranges	$-29 \leq h \leq 32$, $-24 \leq k \leq 32$, $-27 \leq l \leq 26$	
Reflections collected	175802	
Independent reflections	29494 [$R(\text{int}) = 0.0839$]	
Observed reflections	25500	
Completeness to theta = 74.504°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00000 and 0.26782	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	29494 / 1307 / 1559	
Goodness-of-fit on F^2	1.041	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0645$, $wR2 = 0.1808$	
R indices (all data)	$R1 = 0.0718$, $wR2 = 0.1882$	
Largest diff. peak and hole	2.082 and -1.853 e.Å ⁻³	

- ¹ *CrysAlisPro*, version 171.40.71a; Rigaku Corporation: Oxford, UK, 2020.
- ² Sheldrick, G. M. *SHELXT*, version 2018/2; *Acta. Crystallogr.* **2015**, *A71*, 3-8.
- ³ Sheldrick, G. M. *SHELXL*, version 2018/3; *Acta. Crystallogr.* **2015**, *C71*, 3-8.
- ⁴ Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Olex2*, version 1.2-ac3; *J. Appl. Cryst.* **2009**, *42*, 339-341.
- ⁵ Spek, A. L. *PLATON*, version 250420; *Acta. Crystallogr.* **2015**, *C71*, 9-18.

3. Electrochemical study

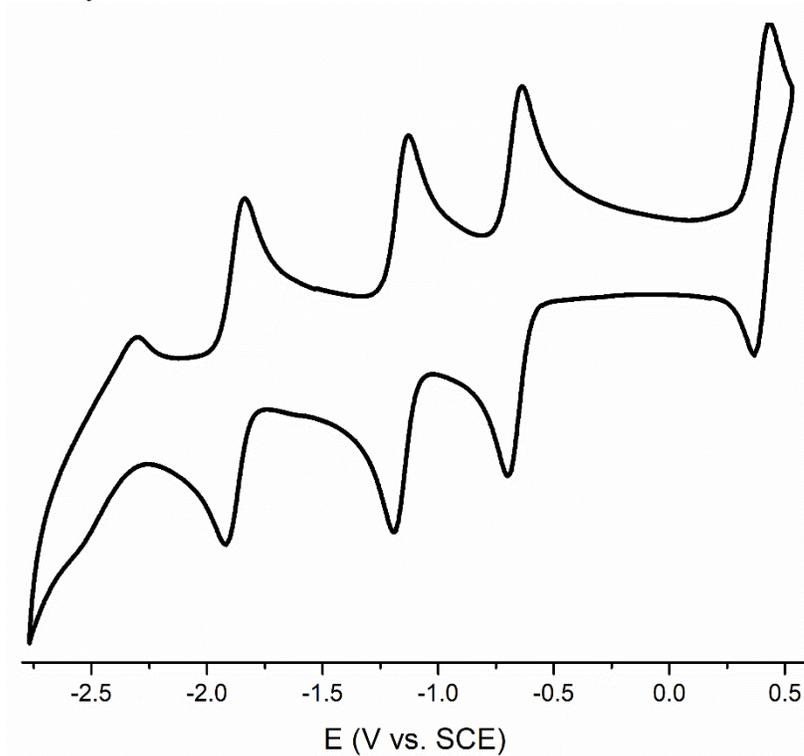


Figure S18. Cyclic voltammogram for compound 1 in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

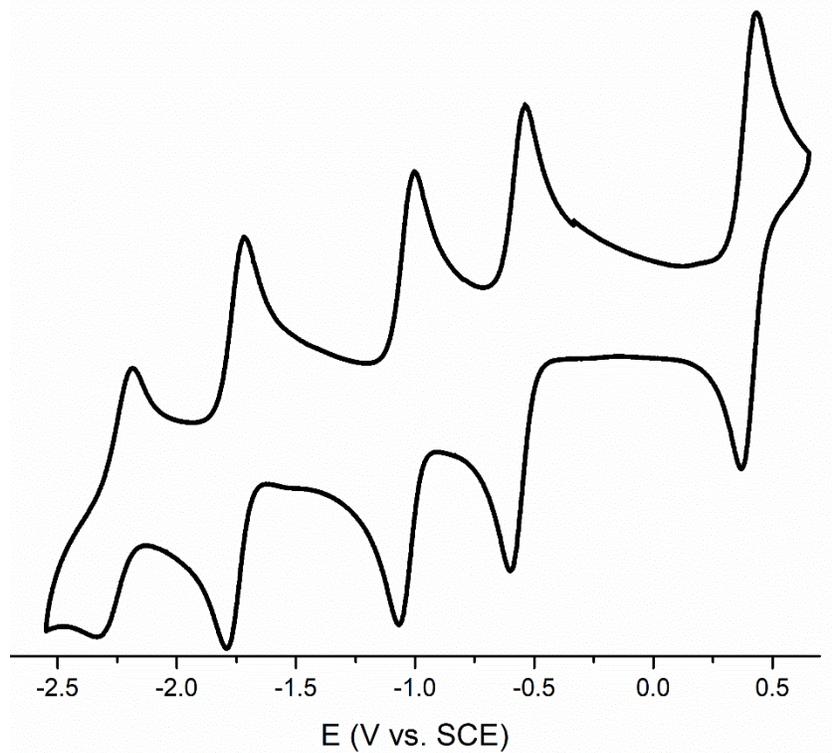


Figure S19. Cyclic voltammogram for compound 2 in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

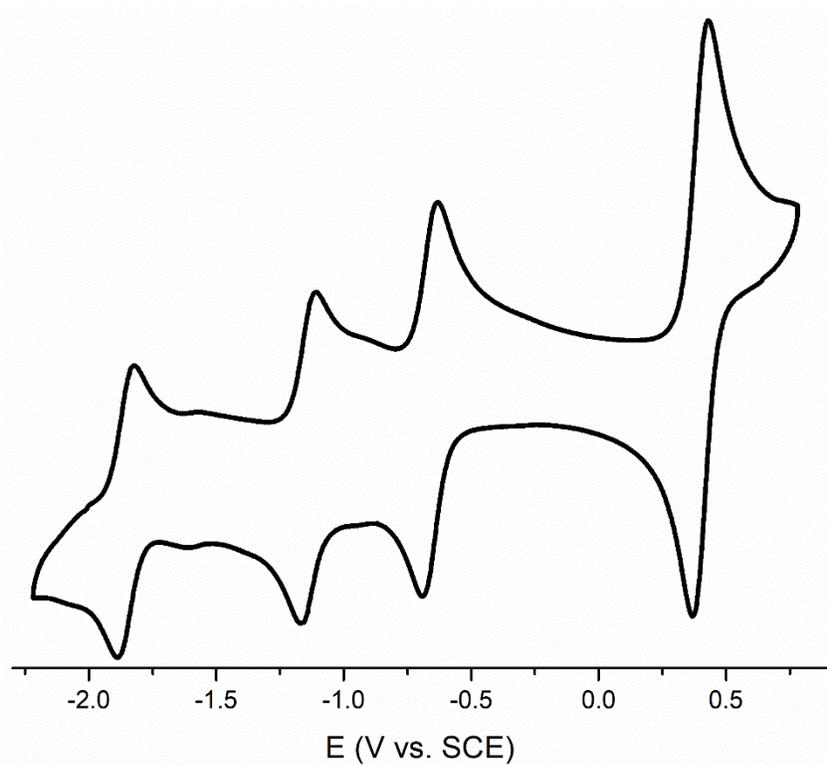


Figure S20. Cyclic voltammogram for compound 3 in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

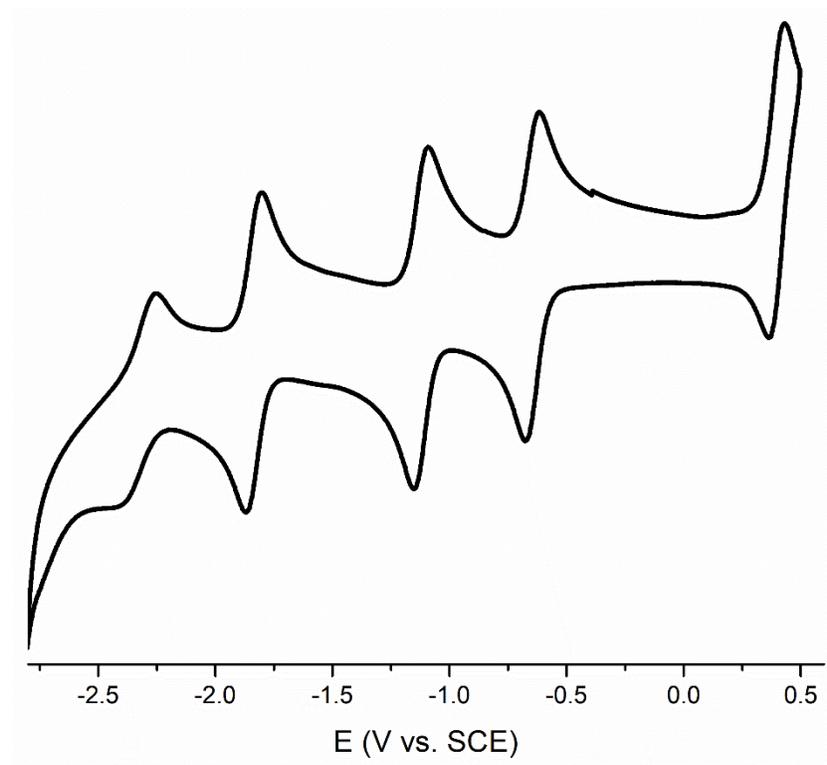


Figure S21. Cyclic voltammogram for compound 4 in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

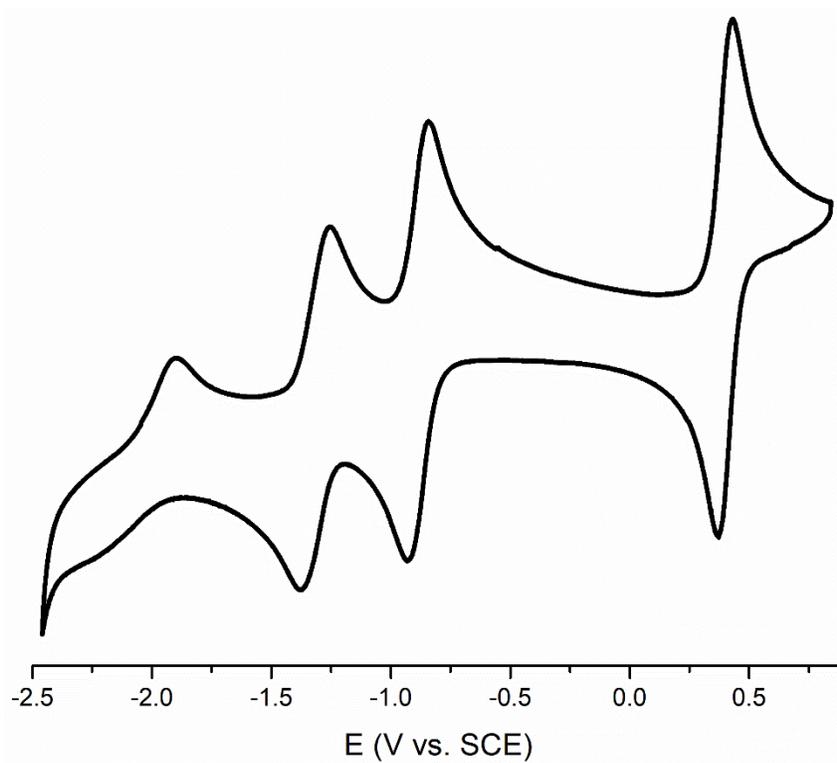


Figure S22. Cyclic voltammogram for compound 5 in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

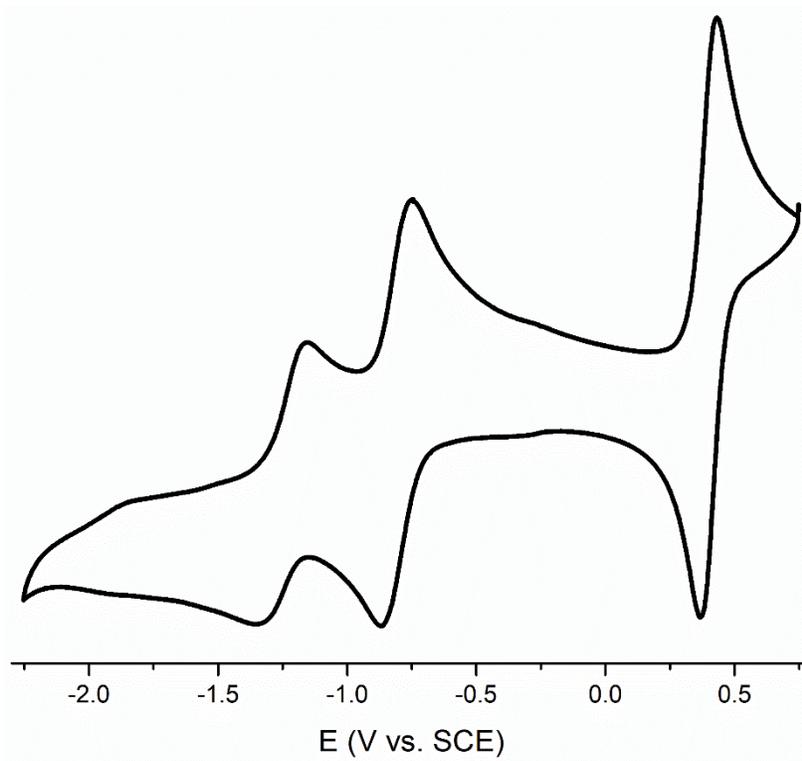


Figure S23. Cyclic voltammogram for compound 6 in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

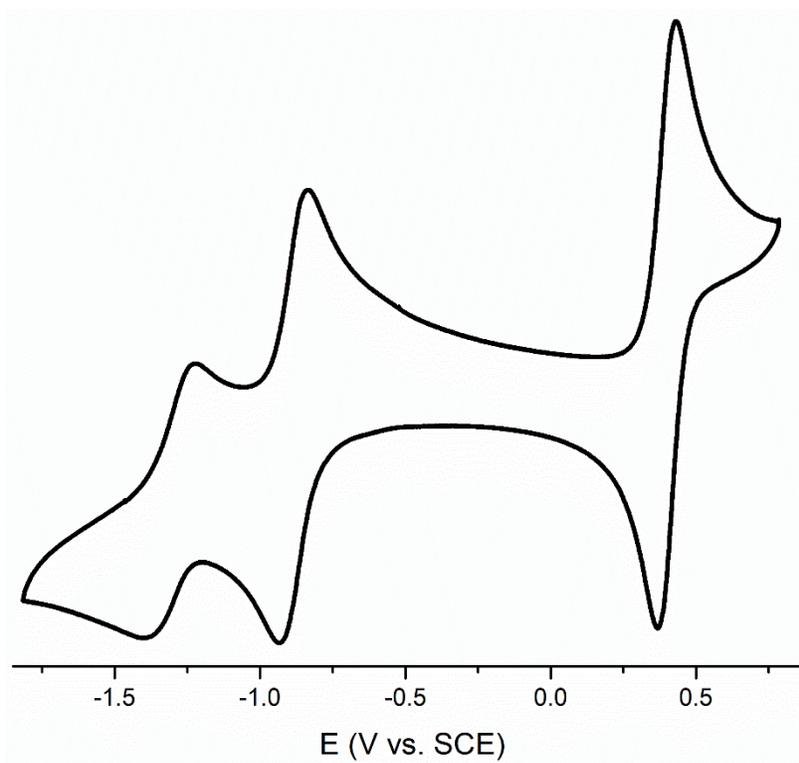


Figure S24. Cyclic voltammogram for compound **7** in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

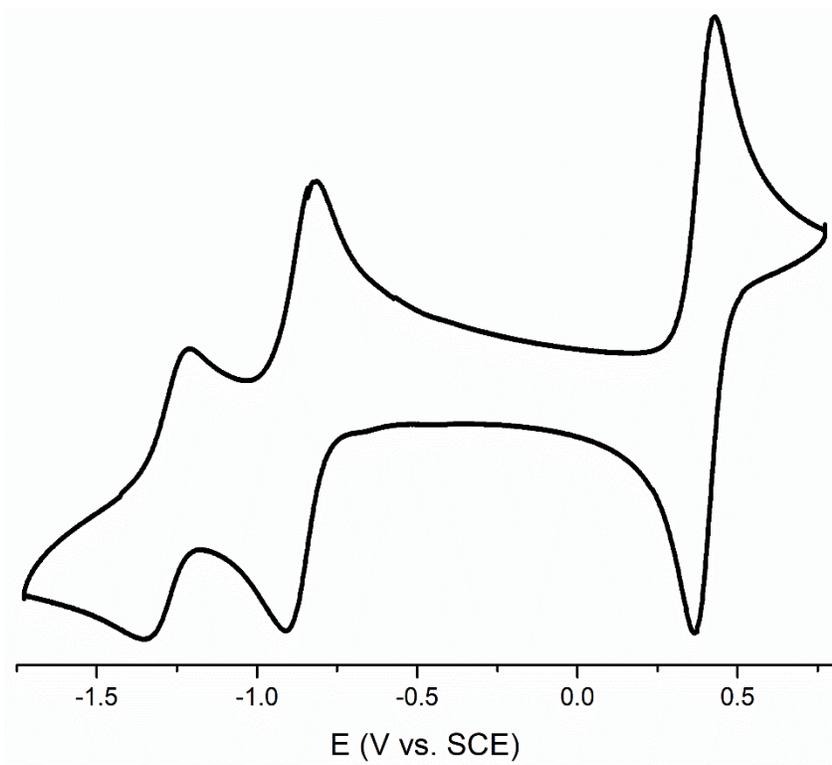


Figure S25. Cyclic voltammogram for compound **8** in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

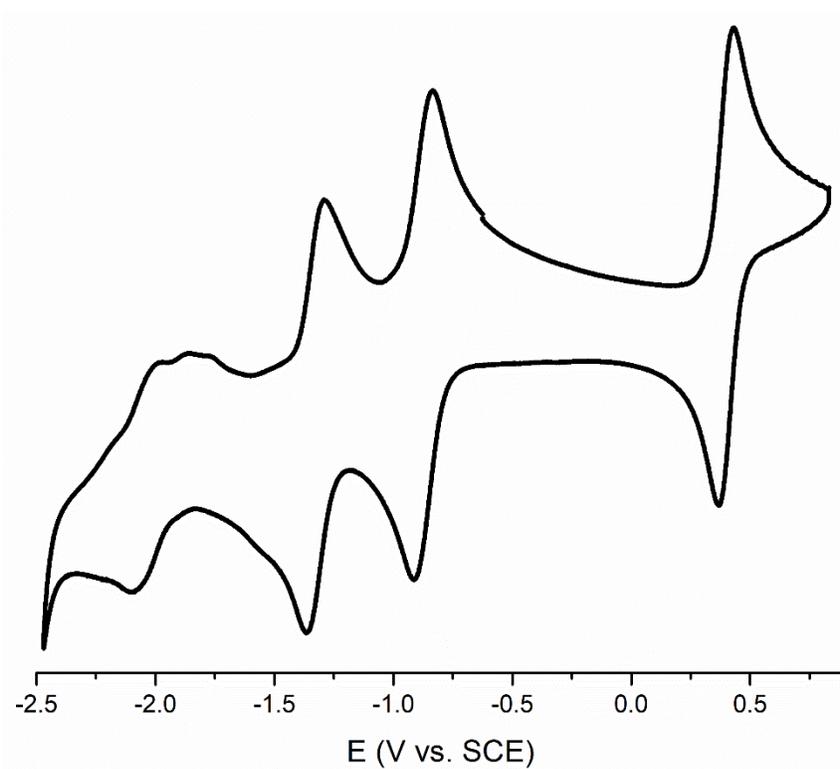


Figure S26. Cyclic voltammogram for the hydrolyzed form of compound **5** in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

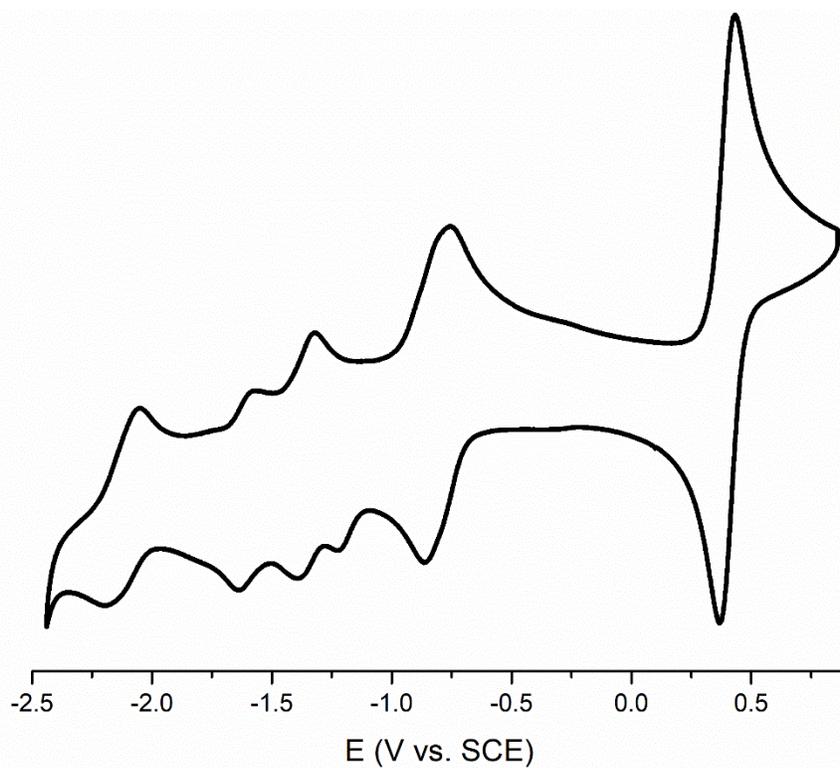


Figure S27. Cyclic voltammogram for the hydrolyzed form of compound **6** in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

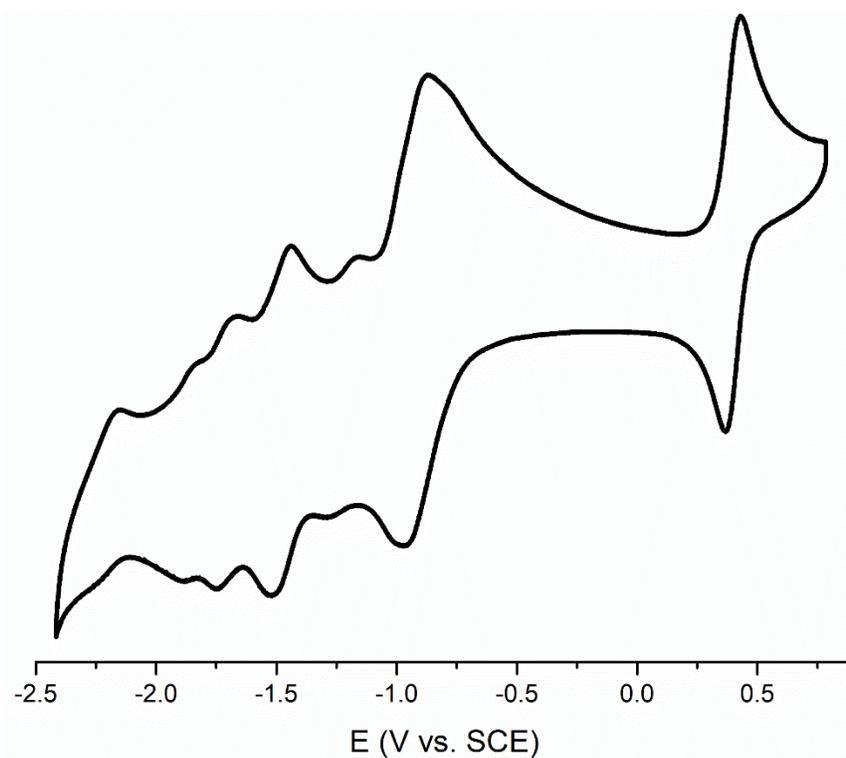


Figure S28. Cyclic voltammogram for the hydrolyzed form of compound **7** in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard

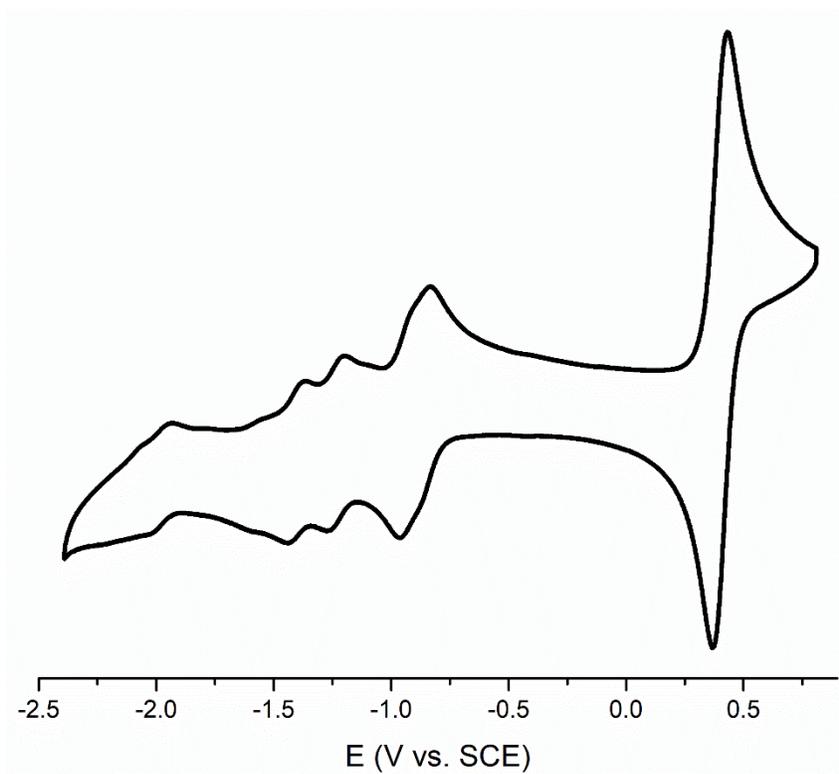


Figure S29. Cyclic voltammogram for the hydrolyzed form of compound **8** in MeCN with TBAPF₆ 0.1 M as electrolyte and Fc⁺/Fc as internal standard