# Electronic Supplementary Information
# for
# A cobalt-substituted Keggin-type polyoxometalate for catalysis of oxidative aromatic cracking reactions in water

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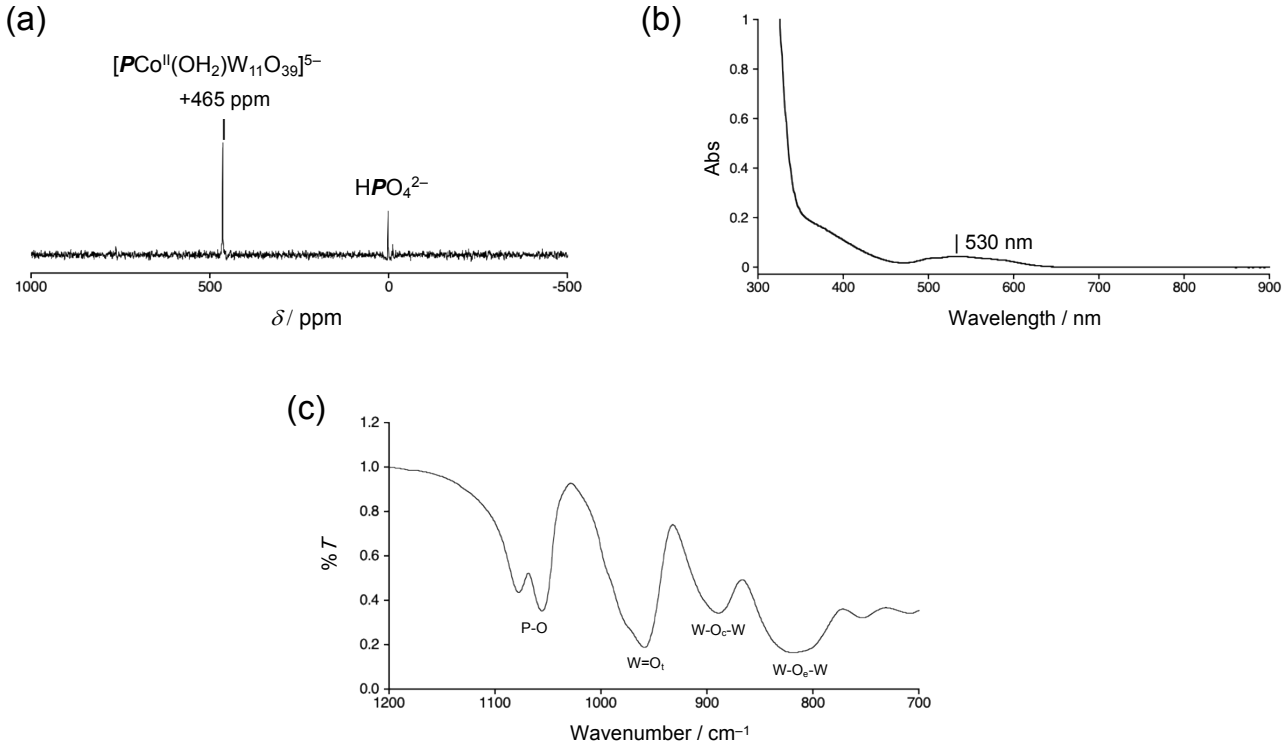



**Fig. S1** Characterizations of $K_5[PCo^{II}(OH_2)W_{11}O_{39}]$ by (a) Paramagnetic $^{31}P$ NMR spectrum in $D_2O$ using $Na_2HPO_4$ as an internal standard, (b) UV-vis spectrum in water and (c) FT-IR spectrum in a KBr pellet.

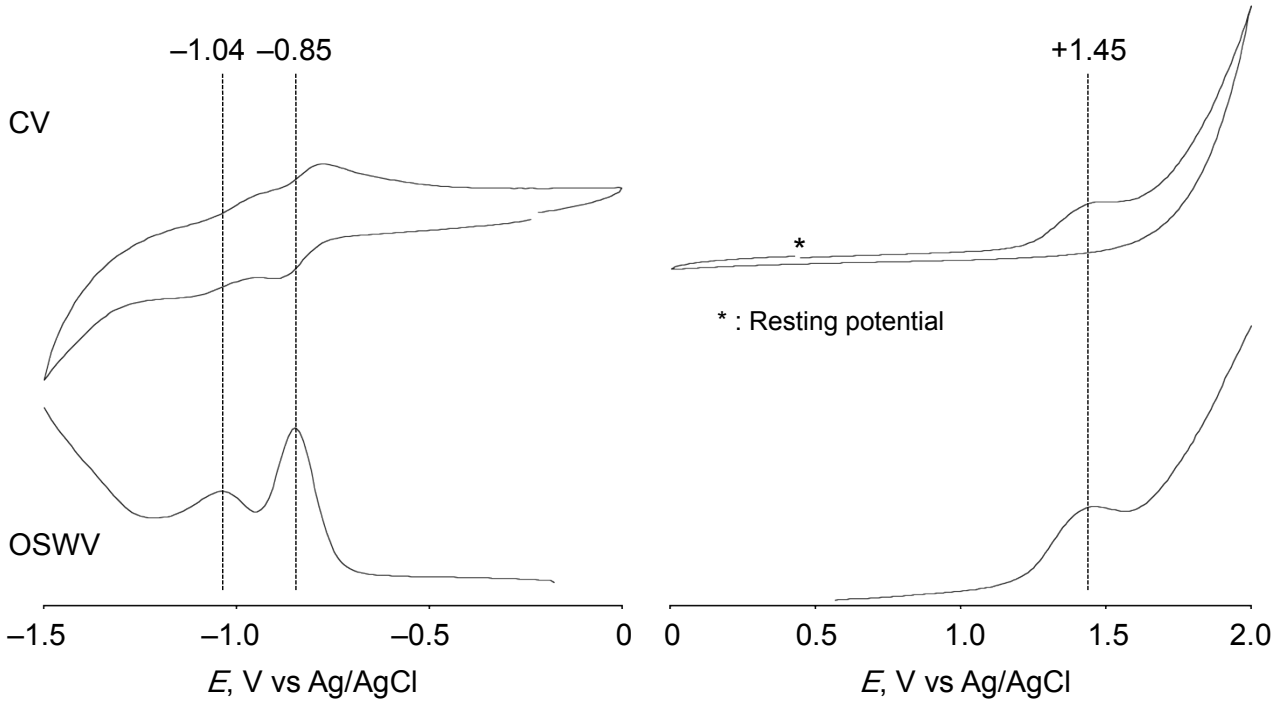



**Fig. S2** Electrochemical measurements of **Co-POM** in water. Solvent: water (pH 6.0), electrolyte: 50 mM $Na_2SO_4$, temp.: 25 ºC, working electrode: Glassy carbon, counter electrode: Pt disk, reference electrode: Ag/AgCl, scan rate: 100 mV/s. CV: Cyclic voltammograms, OSWV: Osteryoung square-wave voltammograms.

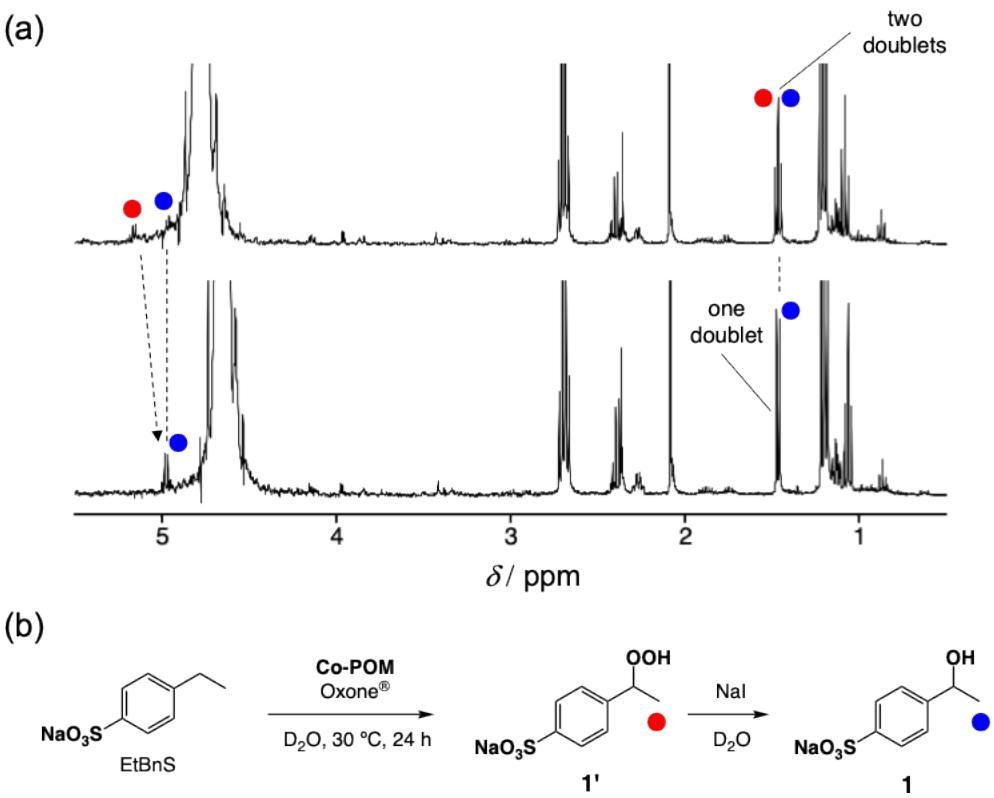
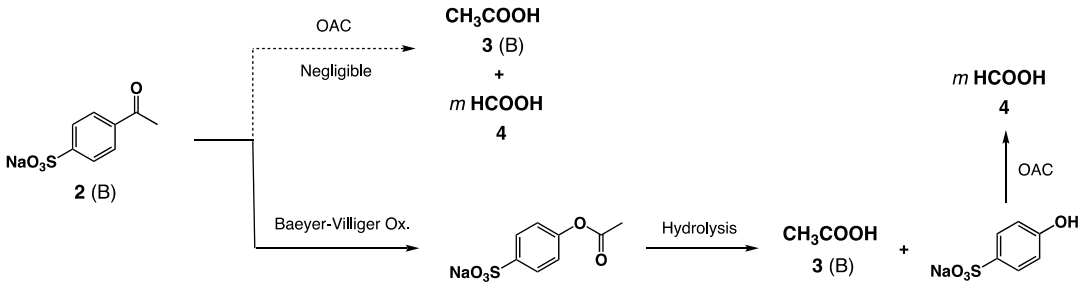



**Fig. S3** (a) $^{1}$H NMR spectra of the reaction mixture in the catalytic OAC reaction of EtBnS by **Co-POM** (top) before and (bottom) after addition of excess NaI. (b) Schematic representation for peroxidation of EtBnS to afford **1'** and subsequent reduction of **1'** into **1** by NaI. The concentration of **1** has been unified with that of **1'**.



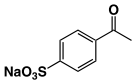
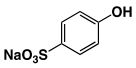

| Substrate | Yield, % | |
|---|---|---|
| | Acetic acid (**3**) | Formic acid (**4**) |
|  | 3.1 | 0.7 |
|  | n. d. | 9.6 |

**Fig. S4.** Overoxidation pathway of sodium 4-acetylbenzenesulfonate (**2)** to afford acetic acid through Baeyer-Villiger oxidation of **2** and the yields of acetic and formic acid in the catalytic oxidation of **2** and sodium 4-hydroxybenzenesulfonate in $D_2O$. Reaction conditions: [**Co-POM**]: 0.20 mM, [$NaHCO_3$]: 1.0 M, [Oxone®]: 0.30 M, [Subst.]: 0.10 M, temp.: 30 ºC, reaction time: 24 h.

Comment: Acetic acid obtained from oxidative cracking of **2** in this work can be negligible because the electrophilic attack of the $Co^{III}$-oxyl species to the aromatic ring of **2** having electron-withdrawing groups (sulfonate and acetyl) is unfavorable in the reaction conditions as suggested by the Hammett plots in Fig. 4d.

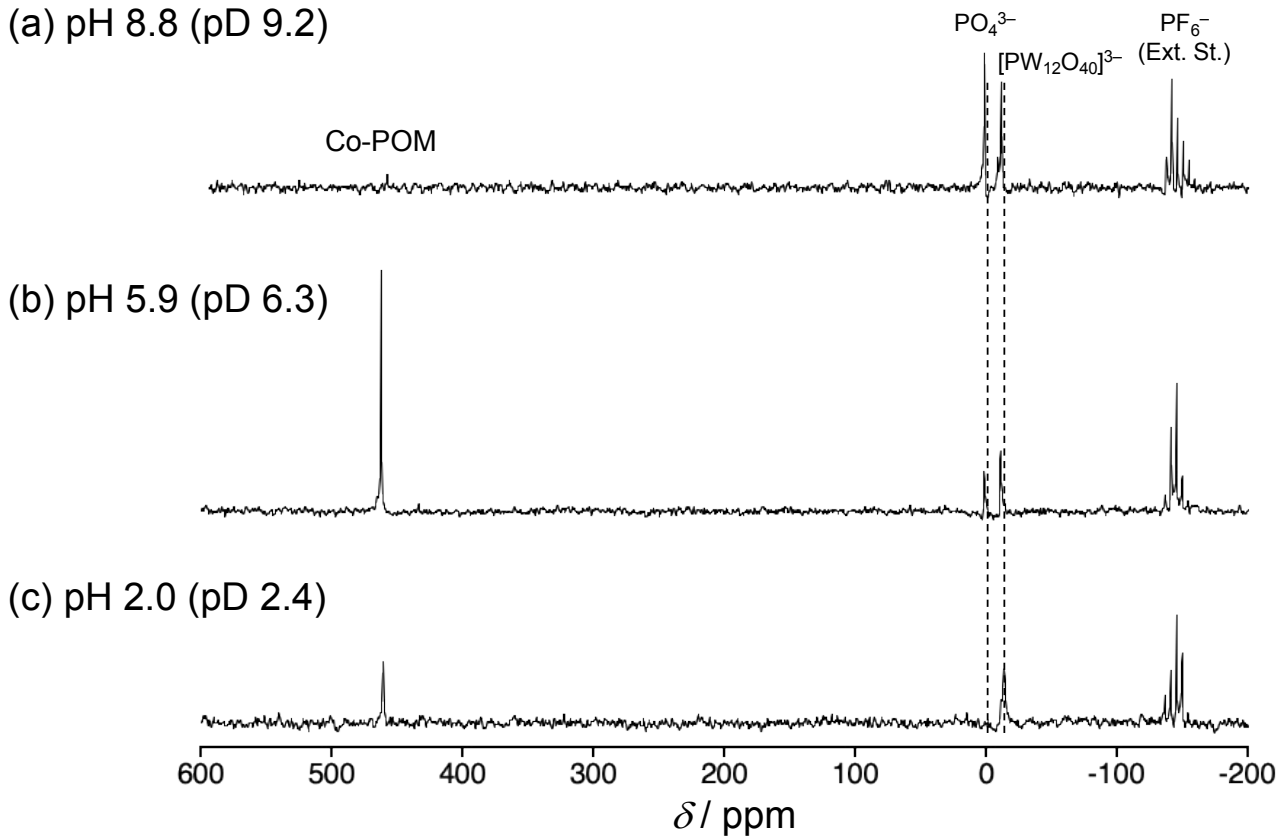



**Fig. S5** $^{31}$P NMR spectra of **Co-POM** (10 mM) in different pH (pD = 0.4 + pH reading) of $D_2O$. (a) pH 8.8, (b) pH 5.9, (c) pH 2.0. $KPF_6$ in $D_2O$ was used as an external standard.

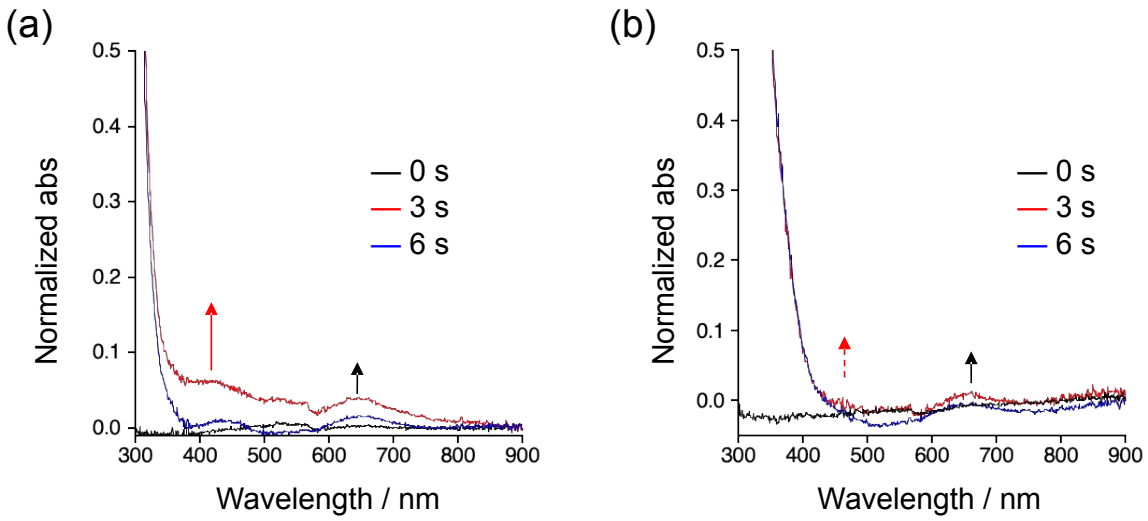



**Fig. S6** Normalized UV-vis absorption spectra of the initial reaction mixture (a) in the absence and (b) presence of EtBnS in water. Conditions: [**Co-POM**]: 0.20 mM, [$NaHCO_3$]: 1.0 M, [Oxone®]: 0.30 M, [EtBnS]: 0.10 M, temp.: 30 ºC.

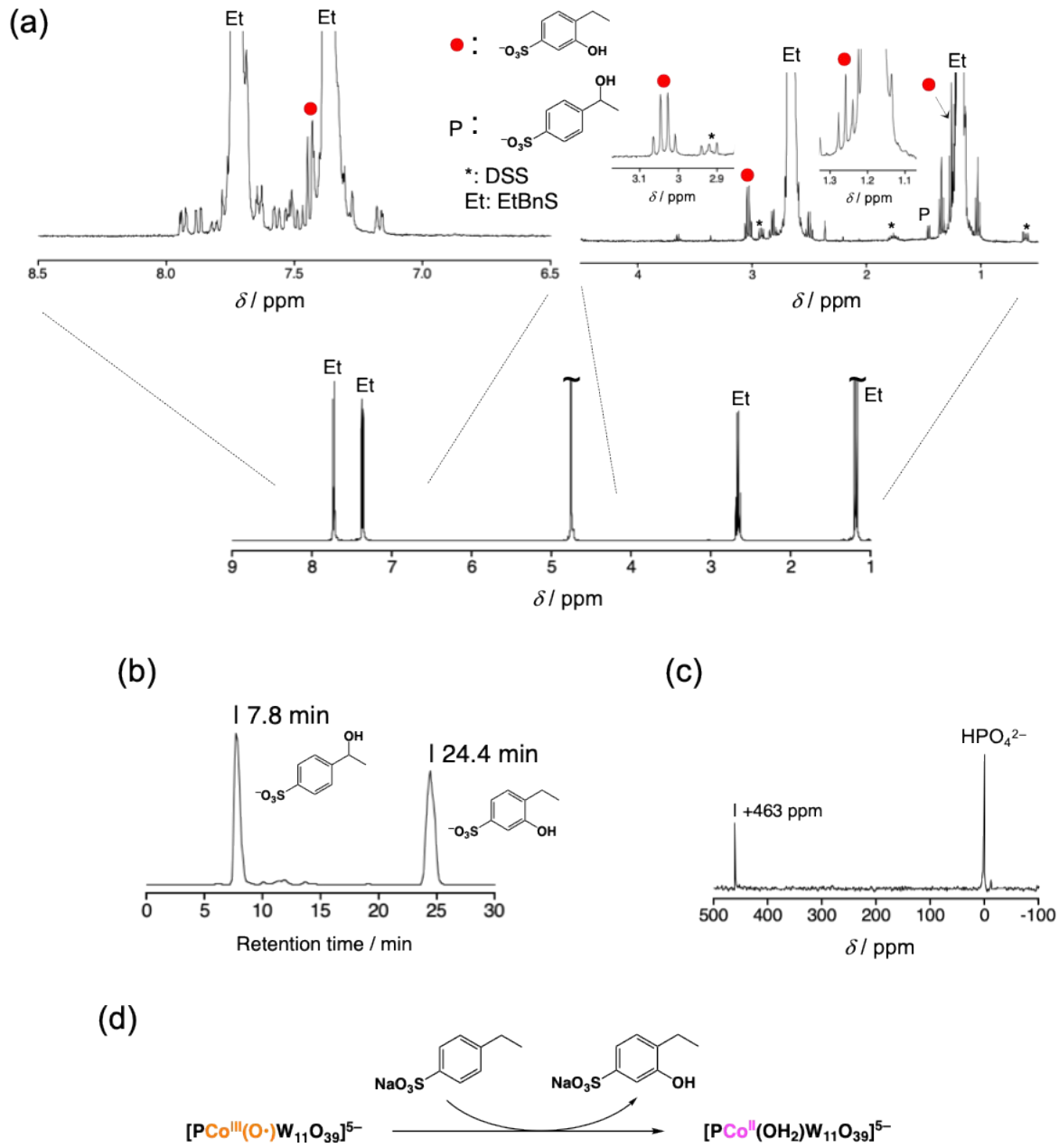



**Fig. S7** (a) $^{1}$H NMR spectrum of $D_2O$ solution containing hydroxylated EtBnS obtained from the sub-stoichiometric oxidation of EtBnS by **Co-POM**. The sample of hydroxylated EtBnS was prepared as follows: Aqueous solution of $HSO_5^-$ was titrated into the aqueous solution containing **Co-POM** (1.0 mM), $NaHCO_3$ (20 mM). After addition of 14 mol equiv of $HSO_5^-$, 10 mol equiv of EtBnS was immediately added to the solution. The water was removed from the reaction mixture under vacuum and 1.0 mL of $D_2O$ was added to the residue to replace the water. (b) LC-MS (MC at $m/z$ = 200.9) chart of the reaction mixture (50 μL) diluted with 950 μL of water (eluent: water with 0.1% formic acid). (c) Paramagnetic $^{31}$P NMR spectrum of the reaction mixture in $D_2O$ using $Na_2HPO_4$ as an internal standard. The $^{31}$P NMR signal with the chemical shift of +463 ppm indicates the recovery of **Co-POM**. (d) Schematic representation of the sub-stoichiometric oxidation of EtBnS by the orange-brown species.

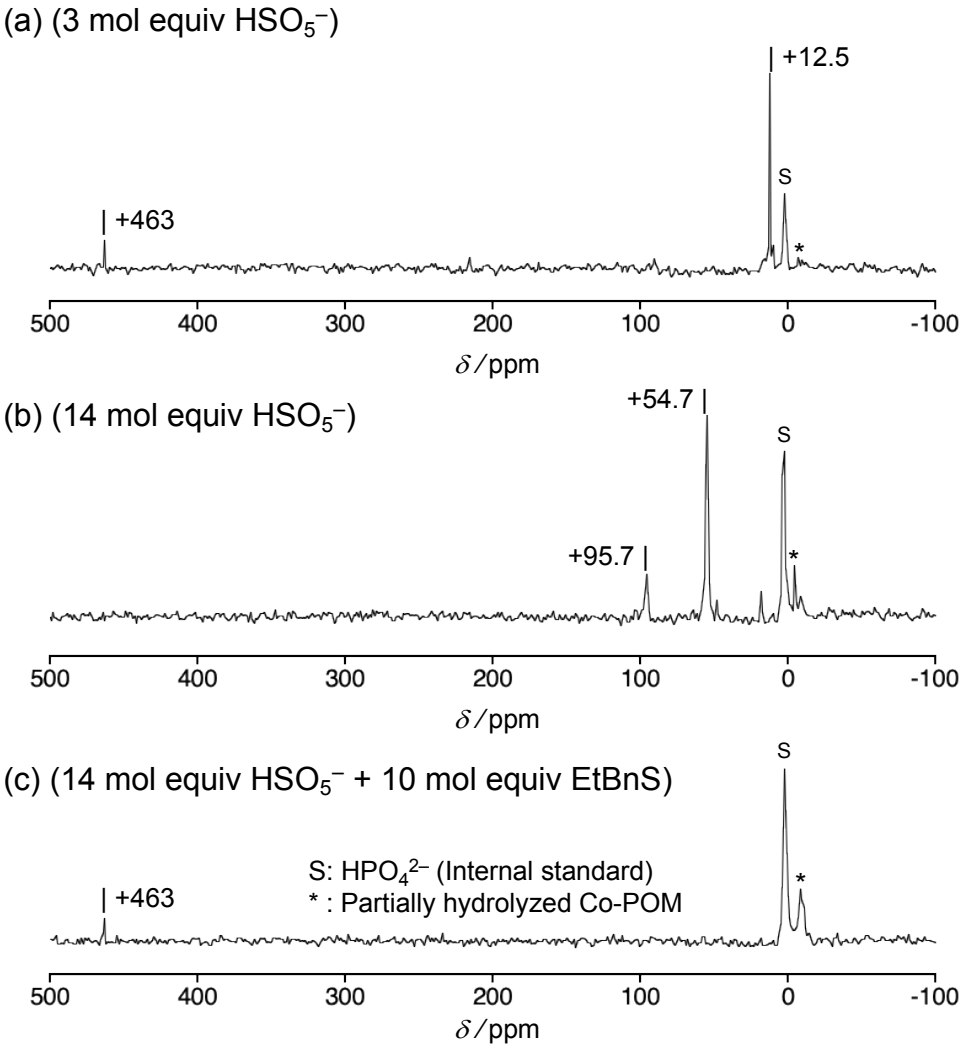



**Fig. S8** $^{31}P$ NMR spectra for **Co-POM** (10 mM) in $D_2O$ upon addition of (a) 3 mol equiv. of $HSO_5^-$ and (b) 14 mol equiv of $HSO_5^-$ in the presence of $NaHCO_3$ (20 mM) and $Na_2SO_4$ (50 mM). (c) $^{31}P$ NMR spectrum of the solution (b) with addition of 10 mol equiv of EtBnS.

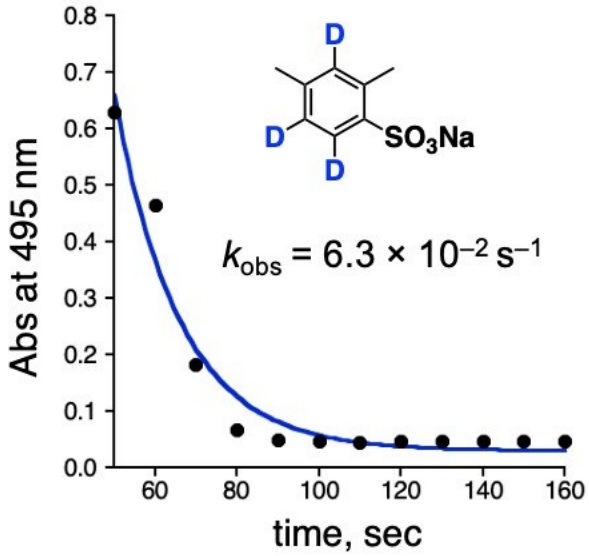



**Fig. S9** Time profiles of absorption decay of **Co-POM** in the presence of Oxone® monitored at 495 nm in sub-stoichiometric oxidation of *m*XyS-$d_3$. [**Co-POM**]: 1.0 mM, [Oxone®]: 7.0 mM ([$HSO_5^-$] = 14 mM), [*m*XyS] = [*m*XyS-$d_3$]: 10 mM, [$NaHCO_3$]: 10 mM, Temp.: 25 ºC

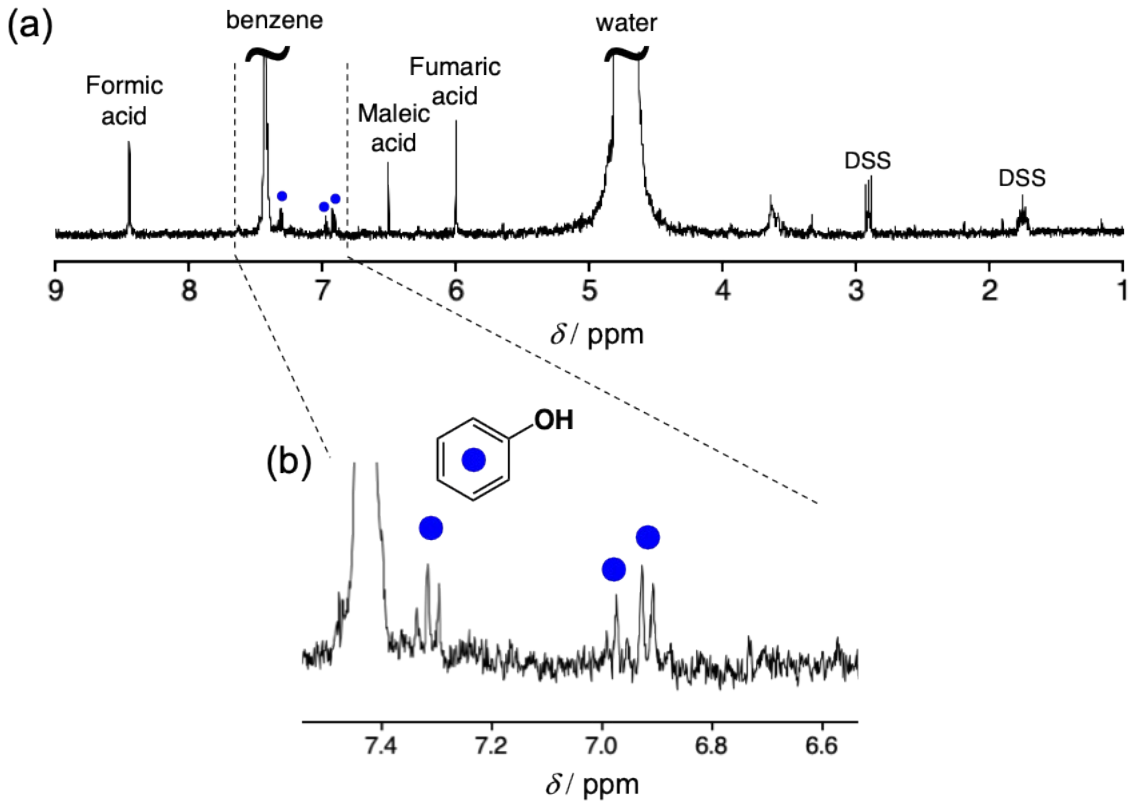



**Fig. S10** (a) $^{1}$H NMR spectrum of the reaction mixture in the catalytic OAC reaction of benzene by **Co-POM** in $D_2O$. [**Co-POM**]: 0.20 mM, [Oxone®]: 0.30 M, [$NaHCO_3$]: 1.0 M, temp.: 30 ºC, reaction time: 24 h. (b) Expanded region of the $^{1}$H NMR spectrum from 6.5 to 7.6 ppm.

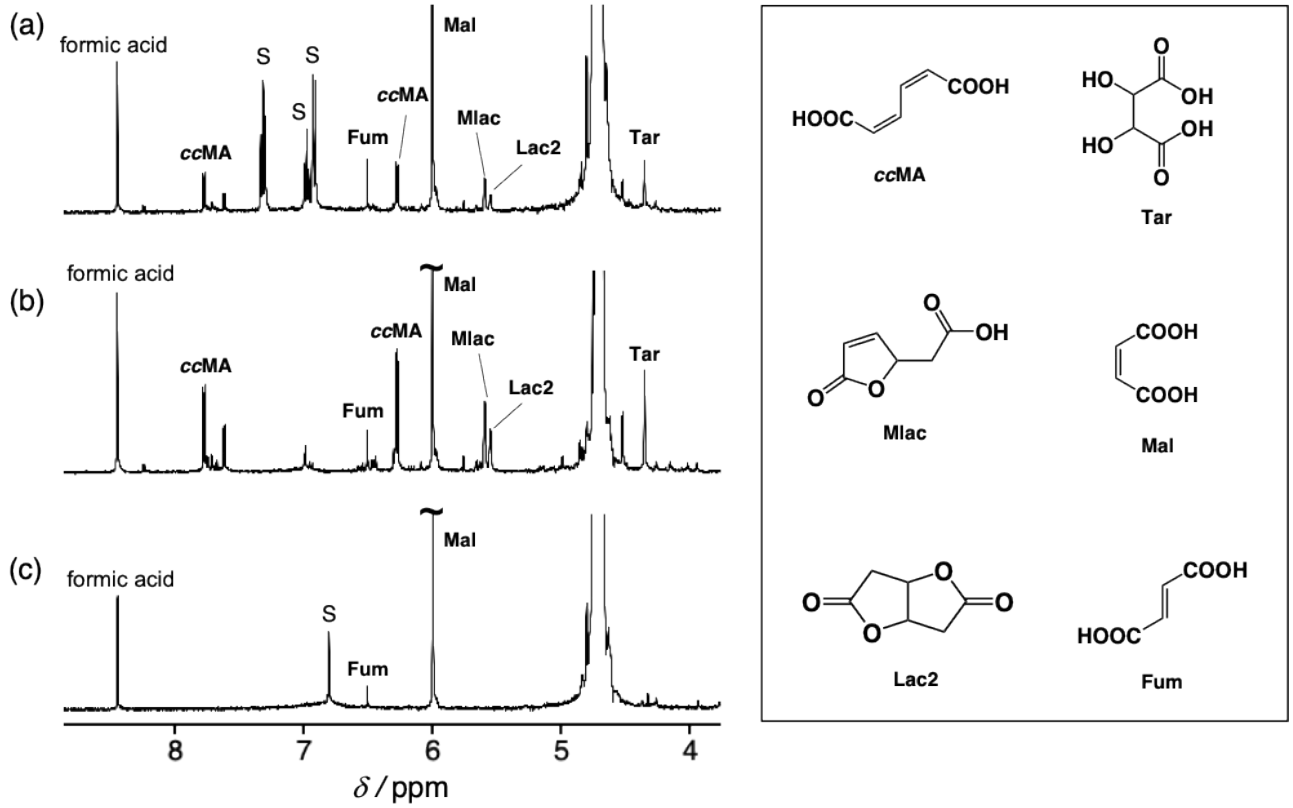



**Fig. S11** $^{1}$H NMR spectra of the reaction mixture obtained from the catalytic OAC reactions by **Co-POM** using (a) phenol, (b) catechol and (c) hydroquinone as substrates in $D_2O$. Conditions: [**Co-POM**]: 0.20 mM, [$NaHCO_3$]: 1.0 M, [Oxone®]: 0.30 M, [Subst.]: 0.10 M, temp.: 30 ºC, reaction time: 24 h.

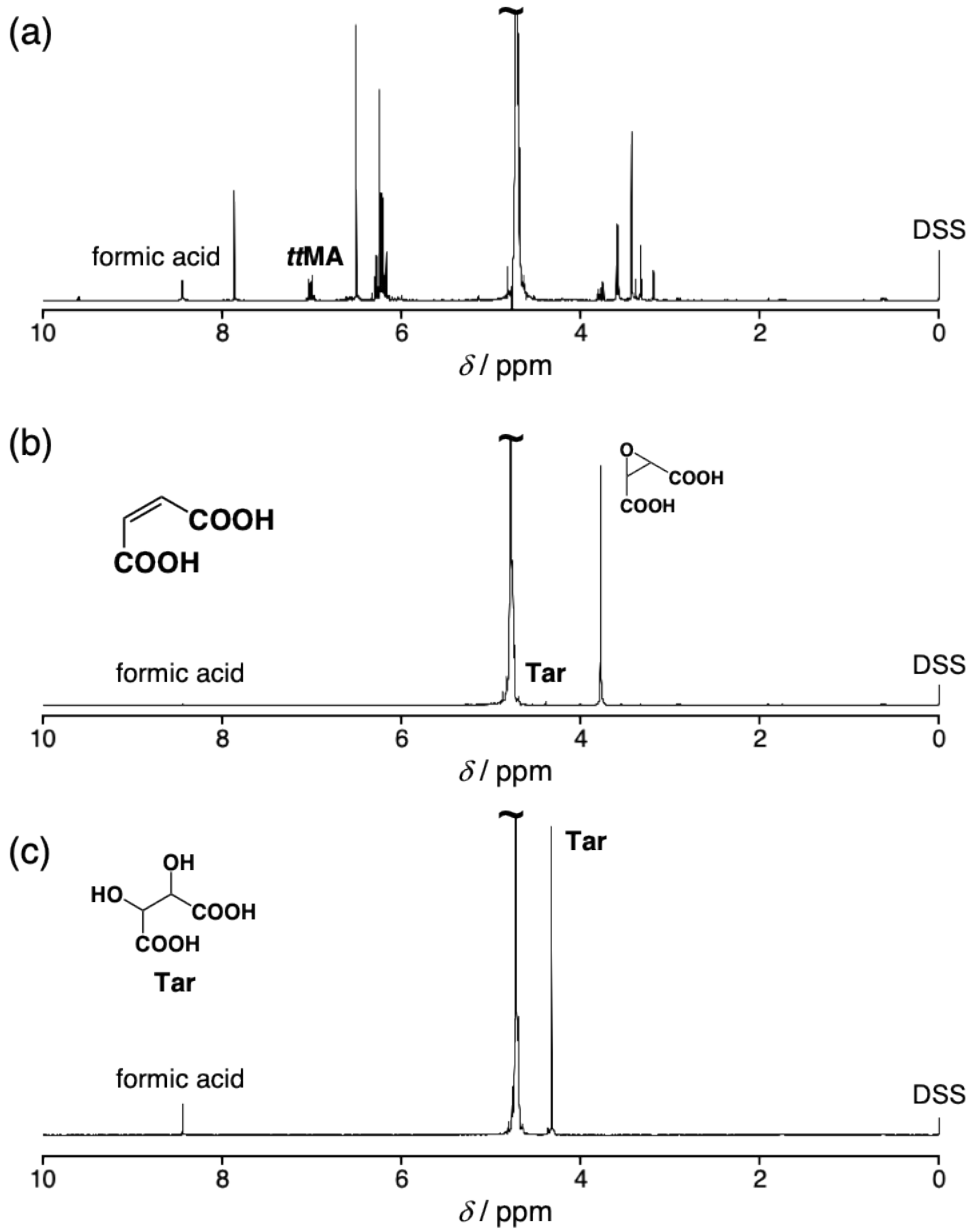



**Fig. S12** $^{1}$H NMR spectra of reaction mixtures obtained from the catalytic OAC reactions by **Co-POM** using (a) *trans*,*trans*-muconic acid (***tt*MA**), (b) maleic acid and (c) tartaric acid (**Tar**) as a substrate in $D_2O$. Conditions: [**Co-POM**]: 0.20 mM, [$NaHCO_3$]: 1.0 M, [Oxone®]: 0.30 M, [Subst.]: 0.10 M, temp.: 30 ºC, reaction time: 24 h.

**Table S1.** TONs of the product obtained from the catalytic OAC reactions of EtBnS. [a]

| Entry | Catalyst | TON [b] (Yield, % [c]) | | | | |
|---|---|---|---|---|---|---|
| | | **1** | **2** | **3** | **4** | **5** |
| 1 | **Co-POM** | 16 (3.1) | 11 (2.2) | 2 (0.4) | 10 (2.0) | 31 (6.1) |
| 2 | **Co-POM** [d] | 39 (7.8) | 63 (12.6) | 11 (2.1) | 18 (3.5) | 20 (4.0) |
| 3 | – | – (0.9) | – (1.6) | n.d. | – (0.4) | – (0.3) |
| 4 | $Co^{II}(ClO_4)_2$ | 36 (7.1) | 42 (8.3) | 1 (0.2) | 1 (0.2) | 4 (0.9) |
| 5 | $H_3[PW_{12}O_{40}]$ | 6 (1.1) | 6 (1.1) | n. d. | 2 (0.3) | 2 (0.4) |
| 6 | $Co^{II}(ClO_4)_2$ + $H_3[PW_{12}O_{40}]$ | 24 (4.8) | 33 (6.6) | 1 (0.2) | 5 (1.0) | 7 (1.4) |
| 7 | $Co^{II}Cl_2$ + $Na_2WO_4$ + $Na_2HPO_4$ | 25 (5.0) | 34 (6.7) | 1 (0.2) | 5 (0.9) | 8 (1.5) |
| 8 [e] | Ru(II)-NHC [f] | 5 (1.0) | 67 (14) | 1 (0.1) | 11 (2.3) | 6 (1.3) |

[a] Conditions: [Catalyst] = 0.20 mM, [$NaHCO_3$] = 1.0 M, [EtBnS] = 0.10 M, [Oxone®] = 0.30 M, Temp. = 30 ℃, Solvent: $D_2O$, reaction time: 24 h. [b] TON = [product]/[catalyst]. [c] Yield = ([product]/[EtBnS]) × 100. [d] No additive. [e] [Ru(II)-NHC] = 0.20 mM, [$(NH_4)_2Ce^{IV}(NO_3)_6$] = 0.10 M, [EtBnS] = 0.10 M, Temp.: 30 ℃, Solvent: $D_2O$, reaction time: 24 h. [f] Ru(II)-NHC catalyst was synthesized according to the previous literature (ref 11 in the manuscript).

**Table S2.** Summary for total energies of optimized structures of $[PCo(O)W_{11}O_{39}]^{5-}$ under three spin states.

| Spin state | Total energy (atomic unit) | $<S^2>$ | $\Delta E$ (kcal/mol) |
|---|---|---|---|
| Doublet state | –5481.498232 | 0.7951 | 6.303 |
| Quartet state | –5481.503239 | 3.7796 | 3.161 |
| Sextet state | –5481.508277 | 8.7735 | 0.000 |

**Table S3.** Cartesian coordinates of $[PCo(O)W_{11}O_{39}]^{5-}$ in the $S = 1/2$ (doublet) state at the UB3LYP/LanL2TZ (W), 6-31G* (Co), 6-31+G* (O, P) level of theory.

| Atom | x / Å | y / Å | z / Å |
|---|---|---|---|
| Co | -0.17355023 | -0.11538287 | -3.40615965 |
| O | 0.07818771 | 0.04283796 | -5.14532147 |
| O | 4.56248987 | -0.06161278 | 2.59836804 |
| O | 3.95387816 | 0.04740113 | -0.14965653 |
| O | 2.54391416 | 1.64667779 | 1.50210509 |
| O | 1.71052979 | -0.43587847 | 2.79285521 |
| O | 3.10429525 | -2.07013914 | 1.21224763 |
| O | 1.44240451 | -0.58160429 | -0.15492406 |
| O | 2.72748074 | -4.56699715 | -0.10945948 |
| O | 3.10902764 | -2.09984460 | -1.43251678 |
| O | 0.65124918 | -3.10676921 | 1.21697744 |
| O | 0.60983905 | -3.14592904 | -1.38288521 |
| O | 0.21976722 | 0.14677769 | 5.16042296 |
| O | -0.48739312 | -1.88455969 | 3.29731329 |
| O | -1.92069006 | 0.33027745 | 3.29567433 |
| O | 0.30073371 | 1.74220544 | 2.78959514 |
| O | -0.75222199 | -0.48773929 | 1.11259022 |
| O | 1.81300488 | 4.18924038 | 2.59152727 |
| O | -0.61552228 | 3.68096419 | 1.20484661 |
| O | 1.66269552 | 3.58464438 | -0.15636395 |
| O | 0.05968524 | 1.55167160 | -0.15818442 |
| O | 4.45081739 | -0.11979975 | -3.01145426 |
| O | 1.67719850 | -0.47443770 | -3.06448400 |
| O | 2.55890982 | 1.65419498 | -1.76081932 |
| O | -1.61654130 | -4.36383564 | 2.42233090 |
| O | -1.60448958 | -3.01627128 | -0.07616805 |
| O | -2.79902238 | -1.80962978 | 2.02238260 |
| O | 1.71570045 | 4.10290525 | -3.01551709 |
| O | 0.25948102 | 1.71638277 | -3.07428439 |
| O | -0.64120693 | 3.68884324 | -1.44078981 |
| O | -1.66467419 | -4.39379030 | -2.65025437 |
| O | -0.60198785 | -1.97635488 | -3.51791970 |
| O | -2.88747546 | -1.86917265 | -2.10214318 |
| O | -0.74835398 | -0.48684102 | -1.43524791 |
| O | -4.64546911 | 0.31633143 | 2.42042240 |
| O | -2.56724632 | 1.86940337 | 1.21597977 |
| O | -3.40982257 | -0.22696782 | -0.07592630 |
| O | -3.04660000 | 4.36075954 | -0.11523197 |
| O | -2.62498042 | 1.84541798 | -1.38380944 |
| O | -2.05130025 | 0.26152259 | -3.51422250 |
| O | -4.69429494 | 0.27900800 | -2.65303868 |
| P | 0.00147790 | -0.00088364 | -0.15459402 |
| W | 3.19496221 | -0.16977902 | 1.54840698 |
| W | 1.15419375 | 2.98378906 | 1.54418832 |
| W | 3.06975351 | -0.19798518 | -1.96922892 |
| W | -1.17987559 | -2.83816830 | 1.73870005 |
| W | 1.07851520 | 2.87596698 | -1.97271706 |
| W | -1.21201882 | -2.84005620 | -2.04131983 |
| W | -3.07479116 | 0.08877903 | 1.73703164 |
| W | -3.09064871 | 0.05783445 | -2.04437033 |
| W | -1.89007313 | 3.07900687 | -0.13381425 |
| W | 2.03573406 | -2.98526441 | -0.12971178 |
| W | -0.03117611 | -0.01744945 | 3.45917229 |

**Table S4.** Cartesian coordinates of $[PCo(O)W_{11}O_{39}]^{5-}$ in the $S = 3/2$ (quartet) state at the UB3LYP/LanL2TZ (W), 6-31G* (Co), 6-31+G* (O, P) level of theory.

| Atom | x / Å | y / Å | z / Å |
|---|---|---|---|
| Co | -0.17099450 | -0.11642308 | -3.52139733 |
| O | 0.03000961 | 0.01783794 | -5.09780616 |
| O | 4.55780047 | -0.06988925 | 2.63643203 |
| O | 3.97516803 | 0.05419111 | -0.11335354 |
| O | 2.54543373 | 1.64631497 | 1.51371203 |
| O | 1.70930291 | -0.43040195 | 2.80606938 |
| O | 3.09648420 | -2.06548068 | 1.22676113 |
| O | 1.44974902 | -0.58320442 | -0.17874470 |
| O | 2.72094155 | -4.55641375 | -0.11787401 |
| O | 3.15240219 | -2.09676941 | -1.41071696 |
| O | 0.65021820 | -3.09745548 | 1.20392505 |
| O | 0.60977684 | -3.12682949 | -1.39754255 |
| O | 0.21501536 | 0.14559706 | 5.17508148 |
| O | -0.47793126 | -1.87693714 | 3.28961427 |
| O | -1.90861373 | 0.33144011 | 3.29229674 |
| O | 0.30113142 | 1.74388386 | 2.79852933 |
| O | -0.76235967 | -0.49685307 | 1.05675258 |
| O | 1.80665565 | 4.18865395 | 2.60352053 |
| O | -0.61079920 | 3.66894571 | 1.19901174 |
| O | 1.67186935 | 3.58315887 | -0.14689983 |
| O | 0.06643883 | 1.54790891 | -0.18332375 |
| O | 4.53375083 | -0.09785992 | -2.96800278 |
| O | 1.77741818 | -0.51219356 | -3.06732344 |
| O | 2.58479429 | 1.65857013 | -1.76795738 |
| O | -1.60731341 | -4.35787447 | 2.41795690 |
| O | -1.61029676 | -3.00939201 | -0.07984204 |
| O | -2.79289624 | -1.80629650 | 2.03111350 |
| O | 1.74221343 | 4.11670317 | -2.99522275 |
| O | 0.27097584 | 1.74056904 | -3.07247078 |
| O | -0.63284960 | 3.68593015 | -1.44358890 |
| O | -1.69155751 | -4.41349817 | -2.60952879 |
| O | -0.62981361 | -2.03974861 | -3.55666890 |
| O | -2.89480363 | -1.86344605 | -2.10465000 |
| O | -0.72332043 | -0.47293828 | -1.51079147 |
| O | -4.64082690 | 0.32442984 | 2.43500001 |
| O | -2.56176498 | 1.86831847 | 1.21628146 |
| O | -3.42569516 | -0.23481984 | -0.06019315 |
| O | -3.03669108 | 4.35766735 | -0.12223549 |
| O | -2.64994936 | 1.83914985 | -1.38059598 |
| O | -2.20896028 | 0.30041496 | -3.54721758 |
| O | -4.79457295 | 0.25210601 | -2.57425855 |
| P | 0.00674292 | -0.00528325 | -0.19927878 |
| W | 3.19998979 | -0.17382826 | 1.57288353 |
| W | 1.15448138 | 2.97974437 | 1.55581701 |
| W | 3.12952294 | -0.18631012 | -1.95386048 |
| W | -1.17649694 | -2.83095237 | 1.73199605 |
| W | 1.10291252 | 2.88317946 | -1.96030503 |
| W | -1.22543741 | -2.84682197 | -2.04444712 |
| W | -3.07662499 | 0.09209116 | 1.73648478 |
| W | -3.15631419 | 0.05728662 | -2.04803211 |
| W | -1.88739197 | 3.06948477 | -0.14573815 |
| W | 2.03865323 | -2.97042147 | -0.14123138 |
| W | -0.03107697 | -0.01553528 | 3.47245987 |

**Table S5.** Cartesian coordinates of $[PCo(O)W_{11}O_{39}]^{5-}$ in the $S$ = 5/2 (sextet) state at the UB3LYP/LanL2TZ (W), 6-31G* (Co), 6-31+G* (O, P) level of theory.

| Atom | x / Å | y / Å | z / Å |
|---|---|---|---|
| Co | -0.13441920 | -0.09204102 | -3.72001540 |
| O | 0.05384915 | 0.04034213 | -5.42498630 |
| O | 4.56260913 | -0.06008099 | 2.61030958 |
| O | 3.94740223 | 0.05075150 | -0.13555962 |
| O | 2.54821657 | 1.64961773 | 1.51850106 |
| O | 1.71266550 | -0.43401355 | 2.80727104 |
| O | 3.10355767 | -2.06686656 | 1.21870726 |
| O | 1.42742680 | -0.58417995 | -0.15363236 |
| O | 2.72310981 | -4.55500915 | -0.10070500 |
| O | 3.10636853 | -2.09144362 | -1.43189171 |
| O | 0.64849583 | -3.10599162 | 1.22607319 |
| O | 0.60876461 | -3.13403669 | -1.37571733 |
| O | 0.21848822 | 0.14438504 | 5.17065334 |
| O | -0.48503204 | -1.89175972 | 3.32269002 |
| O | -1.92318363 | 0.33493249 | 3.31723959 |
| O | 0.30001204 | 1.74401290 | 2.80062005 |
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| O | 1.80853459 | 4.18834065 | 2.60511782 |
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| O | 0.04154387 | 1.54183673 | -0.14736731 |
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| O | 1.73692197 | -0.48137812 | -3.12837042 |
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| O | -3.04082071 | 4.35314429 | -0.10939318 |
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| P | -0.02419050 | -0.01623607 | -0.14096738 |
| W | 3.19286151 | -0.16435395 | 1.56228338 |
| W | 1.15076454 | 2.97792140 | 1.56251923 |
| W | 3.08636127 | -0.20292105 | -1.96850842 |
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| W | -0.03623256 | -0.02488089 | 3.46994374 |