Supporting Information for:

Electrocatalytic nitrate reduction with Co-based catalysts: Comparison of DIM, TIM and cyclam ligands

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Experimental Section

General Considerations. All anaerobic manipulations, including non-aqueous electrochemical measurements, were performed under a nitrogen atmosphere in an MBraun Labmaster glovebox. Ultrapure deionized water was used for all aqueous experiments or measurements. All reagents were purchased from commercial venders and used as received. Ammonia was quantified according to literature protocols.[1] pH measurements were performed at 25.0 ºC on a Mettler Toledo pH meter. Solution pH was adjusted using 1 M HCl or conc. NaOH solution. The NaOH solutions were freshly prepared using ultrapure water to minimize carbonate formation.

Electrochemical Methods. Electrochemical measurements were recorded on a CHI 620E electrochemical analyser (CH Instruments). Cyclic voltammetry experiments were carried out in an argon purged, air-tight, single compartment cell while controlled-potential electrolysis (CPE) experiments were carried out in a two-compartment cell. Working electrode: glassy carbon electrode (3 mm diameter, CH Instruments) for cyclic voltammetry, carbon rod electrode (0.5 cm in diameter, 5 cm in length) for CPE. Auxiliary electrode: platinum wire (Alfa Aesar, 99.99%). Pseudo-reference electrode: Ag wire (Alfa Asear, 99.99%) for non-aqueous solution and Ag/AgCl (CH Instruments, 1.0 M KCl, −0.006 V *vs*. SCE) for aqueous solution. The final redox potentials measured under non-aqueous conditions were calculated by comparing the measured potentials with the $E_{1/2}$ of Fc/Fc^+ in the same solution. Non-aqueous potentials were then converted to SCE (Fc/Fc^+ = −0.38 V *vs*. SCE) for comparison to computational values. The reproducibility of all cyclic voltammetry experiments was verified by several repeated scans.

Synthesis of Compounds. $[Co(DIM)Br_2]^+$ (DIM = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene), $[Co(cyclam)Br_2]^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), and $[Co(TIM)Br_2]^+$ (TIM = 2,3,9,10-tetraazacyclotetradeca-1,3-diene) were prepared according to literature procedures.[2, 3]

Electrochemical Calculations. Faradaic efficiency: The amount of ammonia produced by CPE at −1.325 V *vs*. SCE was measured by the indophenol method.[1] Solution for CPE of $[Co(cyclam)Br_2]Br$: 0.5 mM $[Co(cyclam)Br_2]Br$, 0.1 M KBr pH 6.0, 10 mM $NaNO_3$ in H_2O (15 mL). Ammonia quantification shows 4.2 μM NH_3 produced over 2 hours CPE. According to equation 1, where n e^- is the number of electrons in the process (8 e^- from nitrate to ammonia),

$$FE = \frac{(ne^-)F(mol\ NH_3)}{Q} \times 100\% \qquad 1$$

mol NH_3 is the moles of ammonia produced in CPE, and Q is the charge consumption, the Faradaic efficiency can be calculated as:

$$FE = \frac{(8\ e^-)F(0.28\ \times 10^{-3}\ molNH_3)}{44.203\ C} \times 100\% = 7.2\% \qquad 2$$

Variable Temperature Electrochemical Measurements. The temperature of the cyclic voltammetry experiments was controlled using an IKA RCT Basic Magnetic Stirrer/Hot Plate equipped with an oil bath. The electrochemical cell was immersed in the oil bath, and the temperature of the solution was allowed to equilibrate for 30 minutes. All experiments were performed in 0.1 M KBr electrolyte with 0.5 mM [Co(DIM)Br_2] and 10 mM $NaNO_3$. All cyclic voltammograms were collected in the plateau region, where the catalytic current is independent of scan rate, with scan rate 400 mV/s. Equation 3 was used to calculate k_{cat} (the catalytic rate constant) at each temperature, where n = 8, F is the Faraday constant, A is the surface area of the electrode, C_p^0 is the concentration of the catalyst (in mol/cm^3), D is the diffusion coefficient, and C_A^0 is the concentration of the analyte (in mol/cm^3).[4]

$$i_c = nFAC_P^O\sqrt{Dk_{cat}C_A^O} \qquad 3$$

The values of k_{cat} at each temperature were used to generate an Eyring plot (Figure S15), wherein R is the gas constant, h is the Planck constant, and k_B is the Boltzmann constant. This data was fit using a linear regression, with slope = $-\Delta H^{\ddagger}$ and intercept = $\Delta S^{\ddagger}$. These values were used to calculate a $\Delta G^{\ddagger}$ value of 16.7 kcal/mol at 298 K.

Additional Electrochemical Data

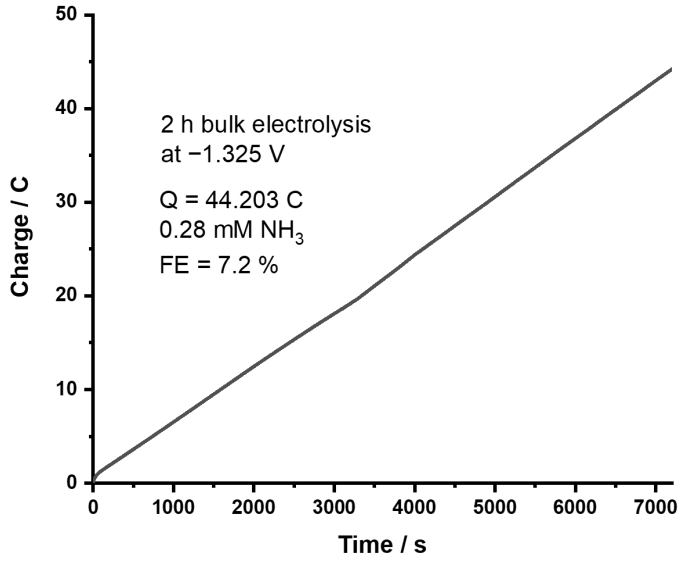

Figure S1. Bulk electrolysis of 0.5 mM $[Co(cyclam)Br_2]^+$ in 0.1 M KBr, pH 6.0 with 10 mM $NaNO_3$. Working electrode carbon rod, 2h at −1.325 V *vs*. SCE. Charge consumption = 44.203 C. Ammonia production from nitrate is confirmed at neutral pH despite background H^+ reduction.

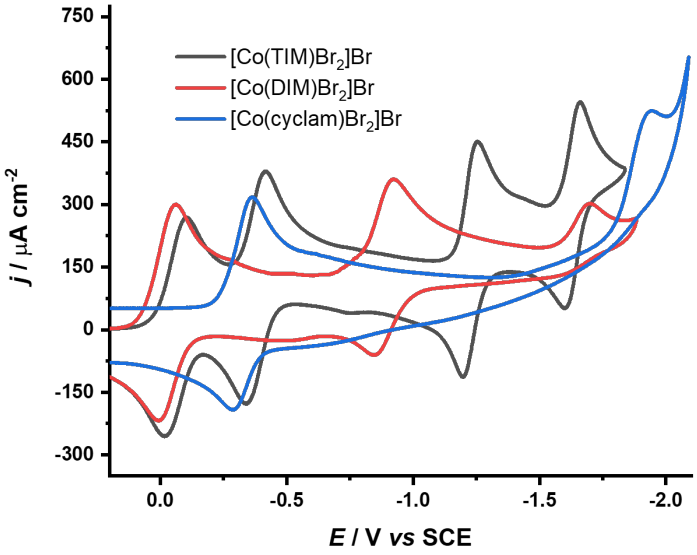

Figure S2. Cyclic voltammograms of 0.5 mM $[Co(TIM)Br_2]^+$ (black), $[Co(DIM)Br_2]^+$ (red), and $[Co(cyclam)Br_2]^+$ (blue) in 0.1 M $TBAPF_6$/ACN. Working electrode glassy carbon, scan rate 100 mV/s. Co(cyclam) has the most negative experimental $Co^{III/II}$ value.

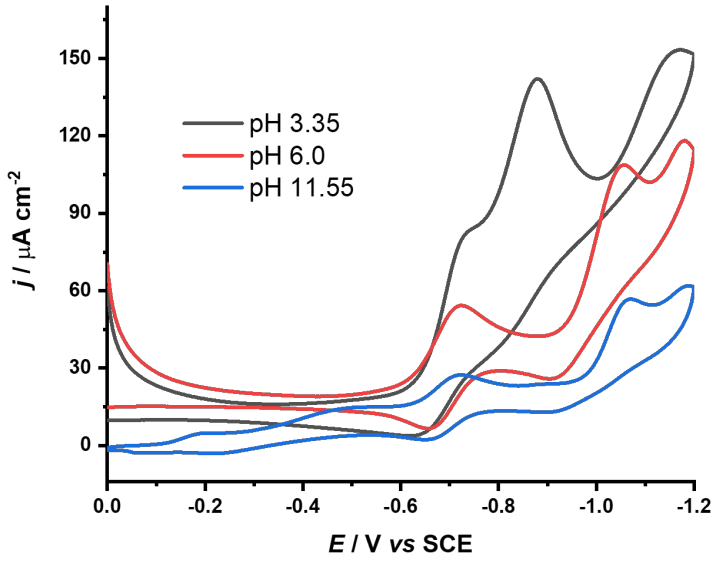

Figure S3. Cyclic voltammograms of 0.5 mM $[Co(TIM)Br_2]^+$ with 10 mM $NaNO_3$ in 0.1 M KBr, pH 3.35 (black), 6.0 (red) and 11.55 (blue). Working electrode glassy carbon, scan rate 5 mV/s. No catalytic activity is observed. Onset potential for 3rd reduction is pH dependent.

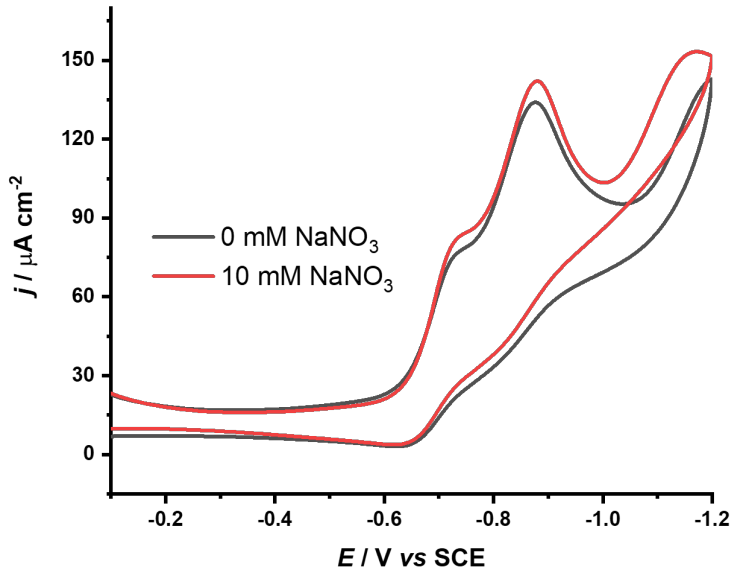

Figure S4. Cyclic voltammograms of 0.5 mM $[Co(TIM)Br_2]^+$ (black) with 10 mM $NaNO_3$ (red) in 0.1 M KBr, pH 3.35. Working electrode glassy carbon, scan rate 5 mV/s. No catalytic activity is observed.

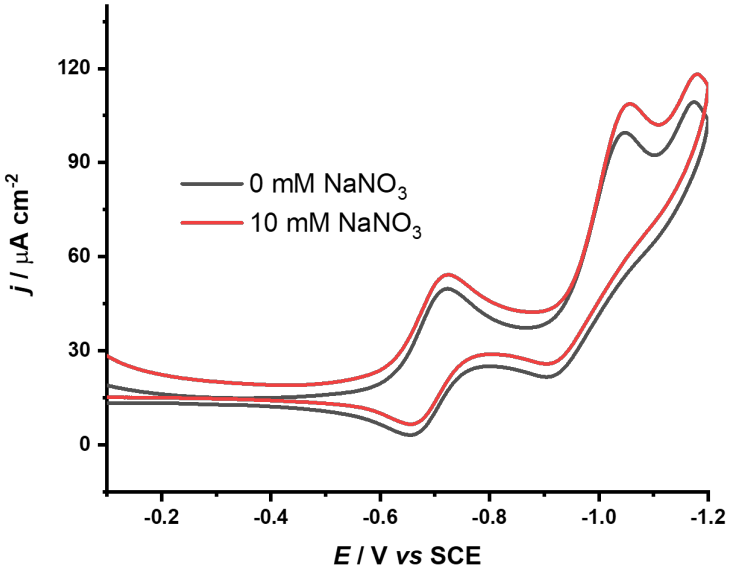

Figure S5. Cyclic voltammograms of 0.5 mM $[Co(TIM)Br_2]^+$ (black) with 10 mM $NaNO_3$ (red) in 0.1 M KBr, pH 6.0. Working electrode glassy carbon, scan rate 5 mV/s. No catalytic activity is observed.

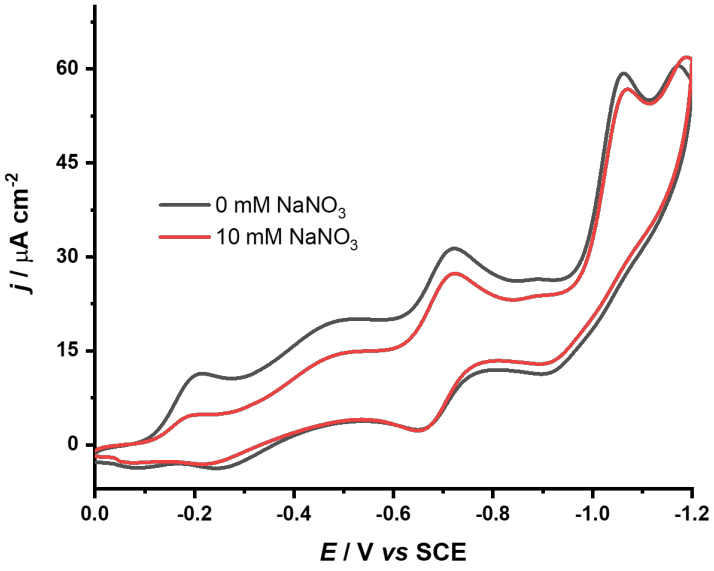

Figure S6. Cyclic voltammograms of 0.5 mM $[Co(TIM)Br_2]^+$ (black) with 10 mM $NaNO_3$ (red) in 0.1 M KBr, pH 11.55. Working electrode glassy carbon, scan rate 5 mV/s. No catalytic activity is observed.

UV-Vis spectra for $[Co(cyclam)Br_2]^+$

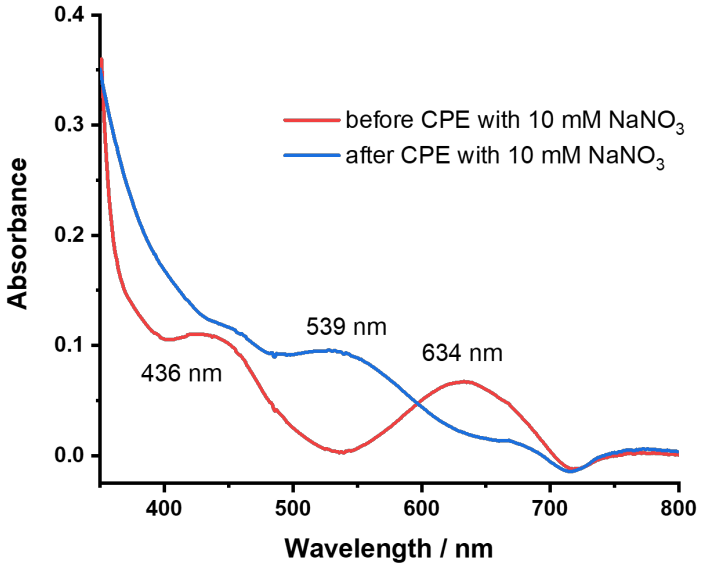

Figure S7. UV-vis spectra of 2 mM $[Co(cyclam)Br_2]^+$ in 0.1 M KBr (pH 6.0) with 10 mM $NaNO_3$ before (red) and after (blue) 1 h controlled potential electrolysis at −1.325 V *vs*. SCE.

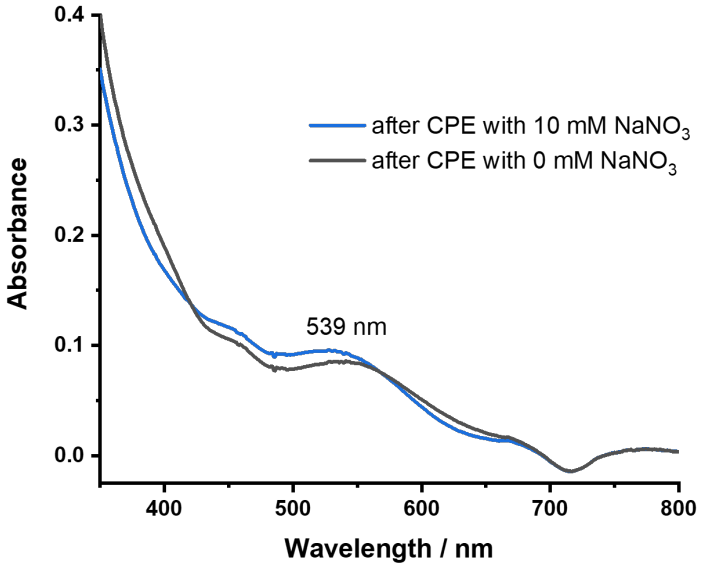

Figure S8. UV-vis spectra of 2 mM $[Co(cyclam)Br_2]^+$ in 0.1 M KBr (pH 6.0) with 10 mM $NaNO_3$ (blue) or without $NaNO_3$ (black) after 1 h controlled potential electrolysis at −1.325 V *vs*. SCE.

DFT Calculated Probable Reactions for $[Co(cyclam)Br_2]^+$ in pH 3.35 and pH 11.55

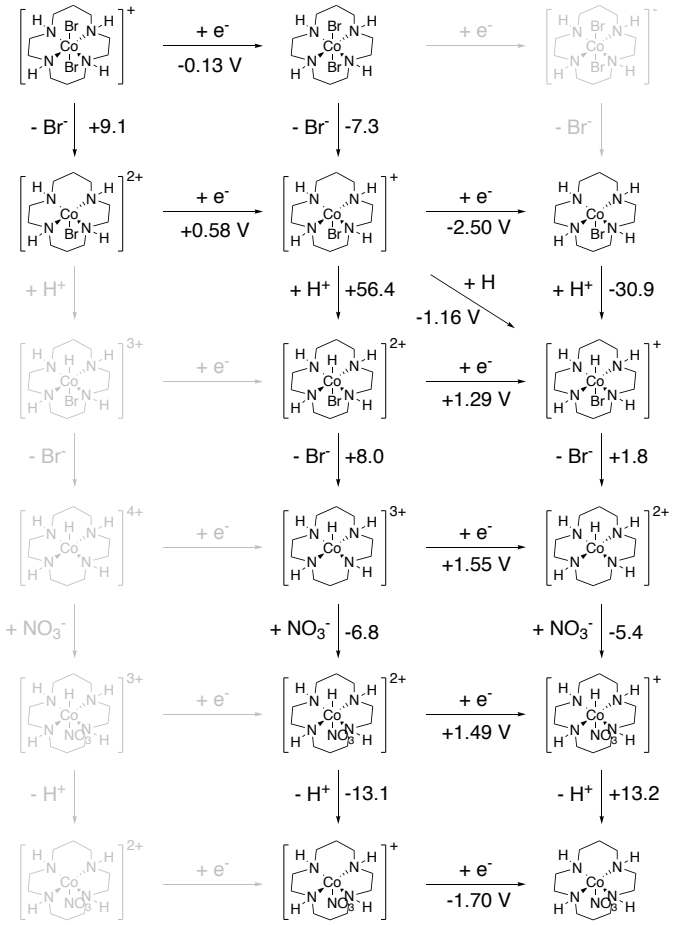

Figure S9. Mapped interactions between Co-cyclam complex and ligands in pH 3.35 solution. The horizontal pathways correspond to the free energy of the reaction (ΔG) in kcal/mol and the vertical pathways correspond to the one-electron reduction, with the potential reported in V *vs.* SCE.

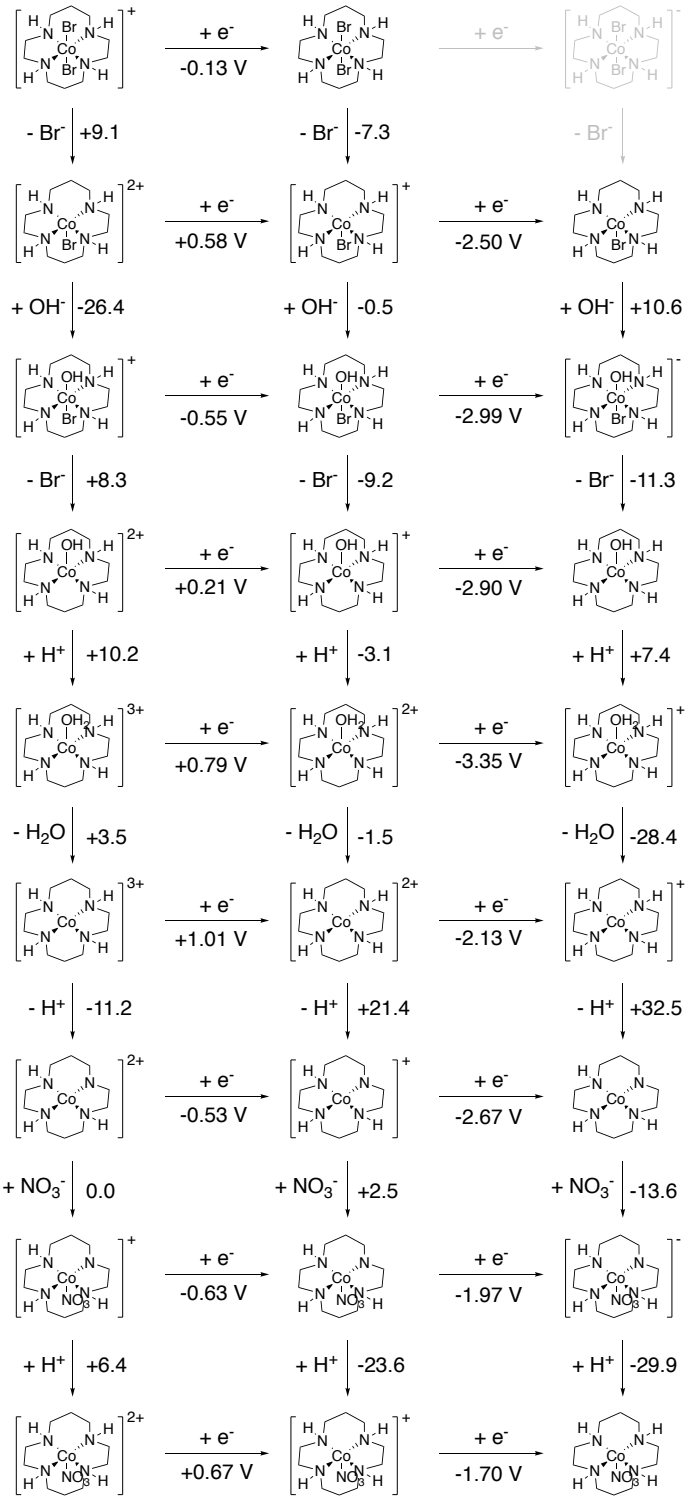

Figure S10. Mapped interactions between Co-cyclam complex and ligands in pH 11.55 solution. The horizontal pathways correspond to the free energy of the reaction (ΔG) in kcal/mol and the vertical pathways correspond to the one-electron reduction, with the potential reported in V *vs.* SCE.

Reduction Potentials in Aqueous Solution

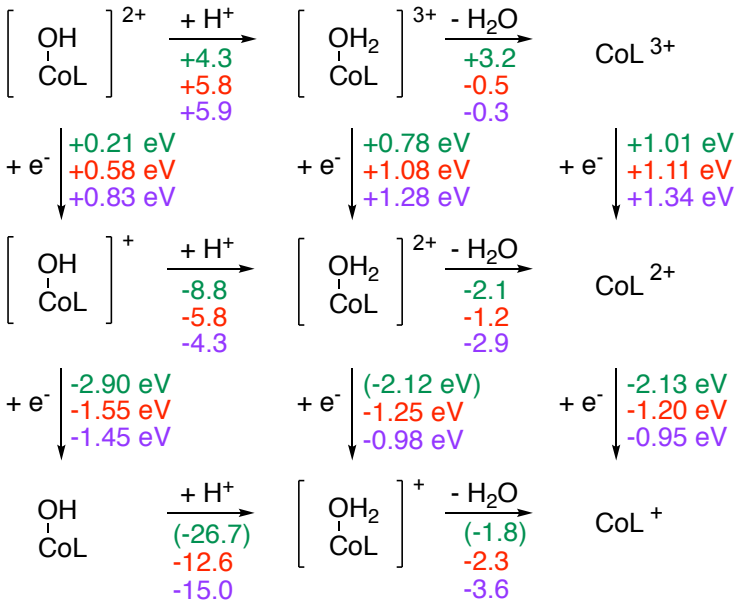

Figure S11. electron reduction scheme in water for Co-complexes generated by DFT calculations. The horizontal pathways correspond to the free energy of the reaction (ΔG) in kcal/mol and the vertical pathways correspond to the one-electron reduction, in which the potential is reported in V *vs.* SCE. Green values are for when L = cyclam, red values for L = DIM, and purple values for L = TIM. Water in the optimized structure of $[Co(cyclam)(H_2O)]^+$ is not bonded to Co.

Figure S11 shows possible catalyst regeneration pathways from the products of the hydroxyl transfer mechanism. While TIM complexes are most favorable for the reduction process, catalyst regeneration for all of the Co complexes are spontaneous.

Reaction Coordinate Diagrams

$[Co(cyclam)]^+$ has the lowest activation barrier for most of the investigated mechanisms except the bidentate mechanism because $[Co(cyclam)]^+$ is less stable than $[Co(DIM)]^+$ and $[Co(TIM)]^+$ due to the absence of a diimine group(s) to act as an electron reservoir. For the bidentate mechanism, the barrier is higher for $[Co(cyclam)]^+$ because the complex goes through a significant geometric distortion from trigonal prismatic (**BM3** in Figure S13) to an octahedral structure (**BM4** in Figure S13) while the DIM and TIM complexes are already octahedral at the point of **BM3**.

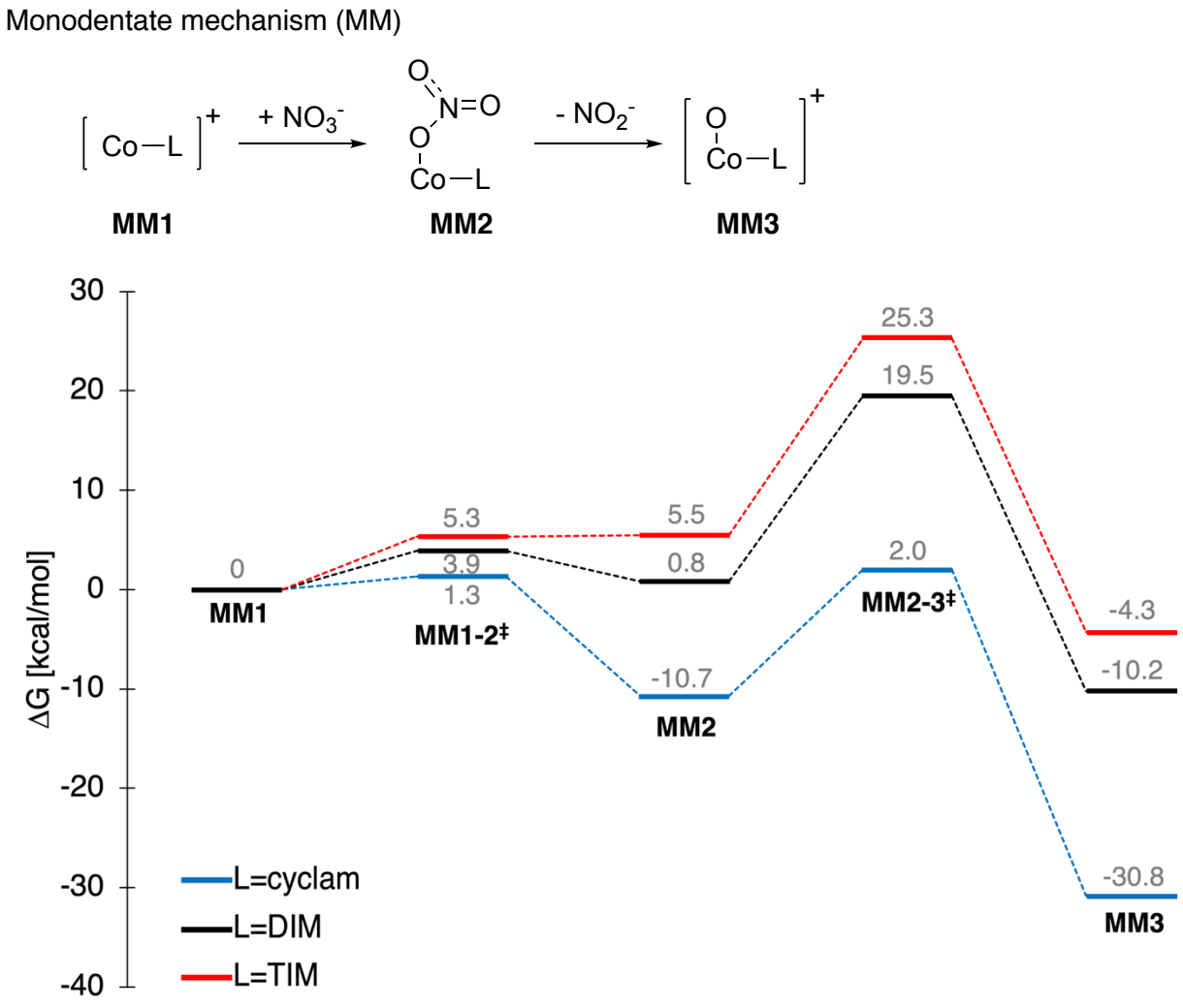

Figure S12. Reaction coordinate diagram for the monodentate mechanism of Co-catalysts.

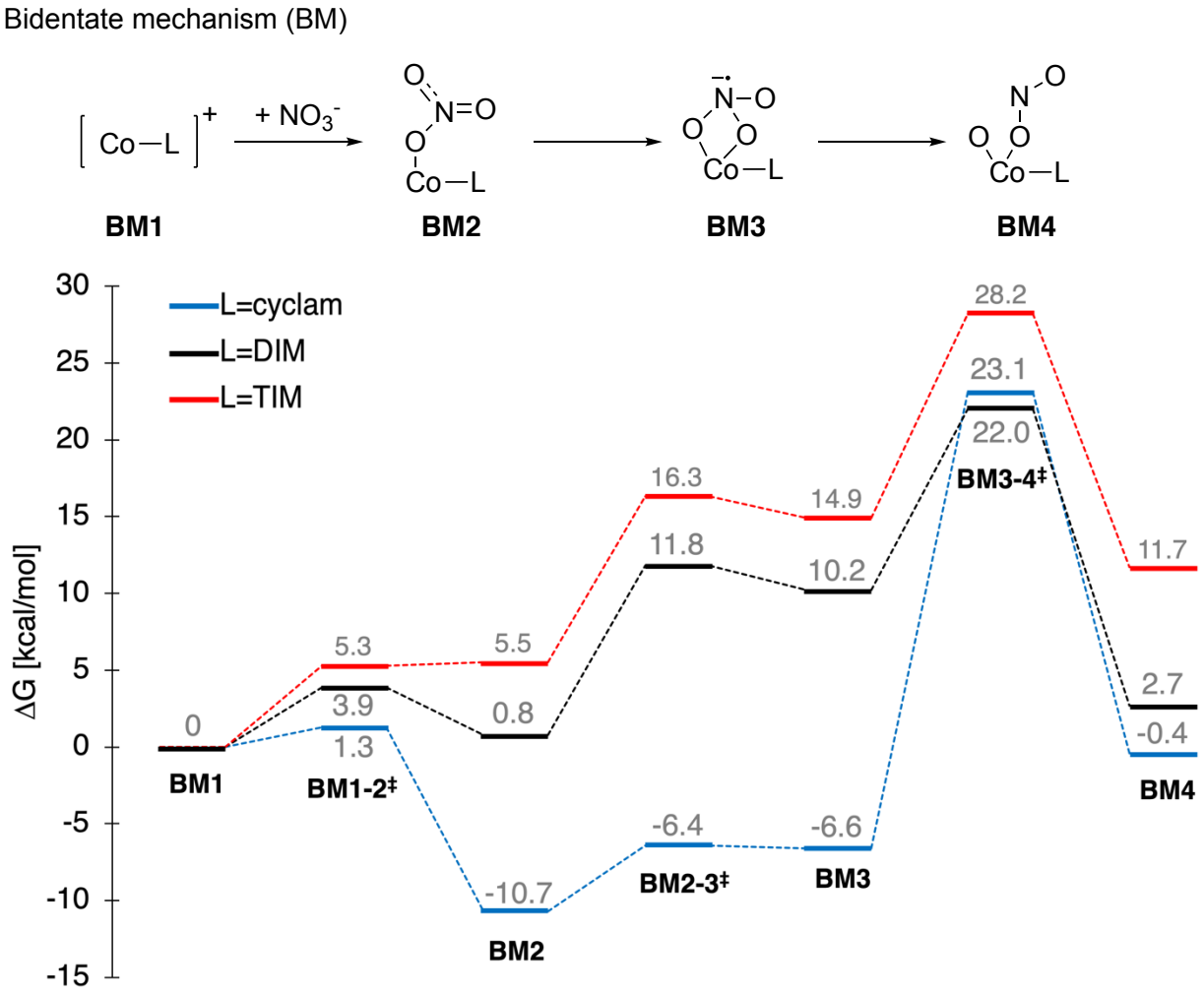

Figure S13. Reaction coordinate diagram for the bidentate mechanism for Co-catalysts.

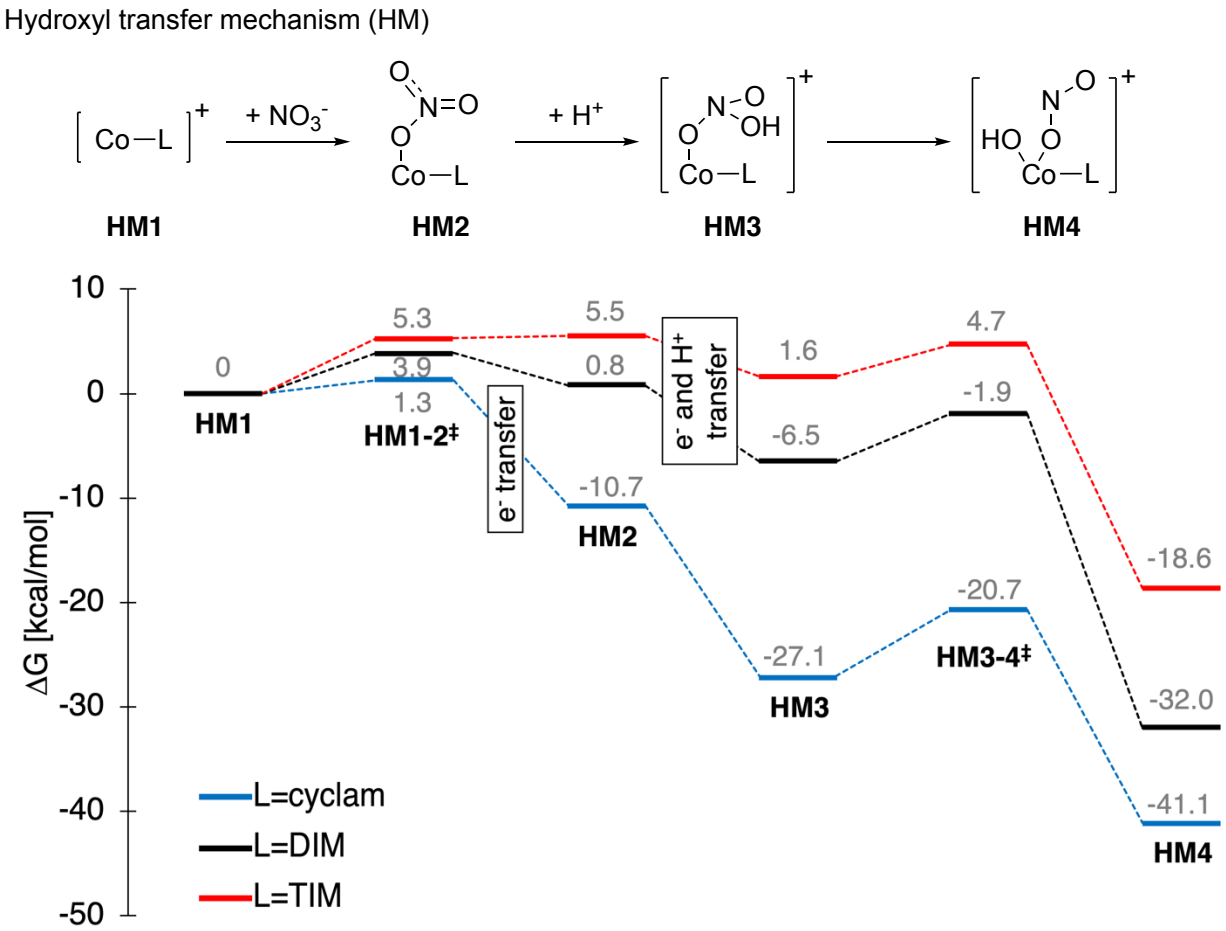

Figure S14. Reaction coordinate diagram for the hydroxyl transfer mechanism for Co-catalysts. The details on electron and proton transfer steps for DIM and TIM can be found Figure 11 and Figure 13. The electron transfer step for cyclam has not been shown since it is almost a barrierless process due to the instability of $[Co(cyclam)]^{+}$.

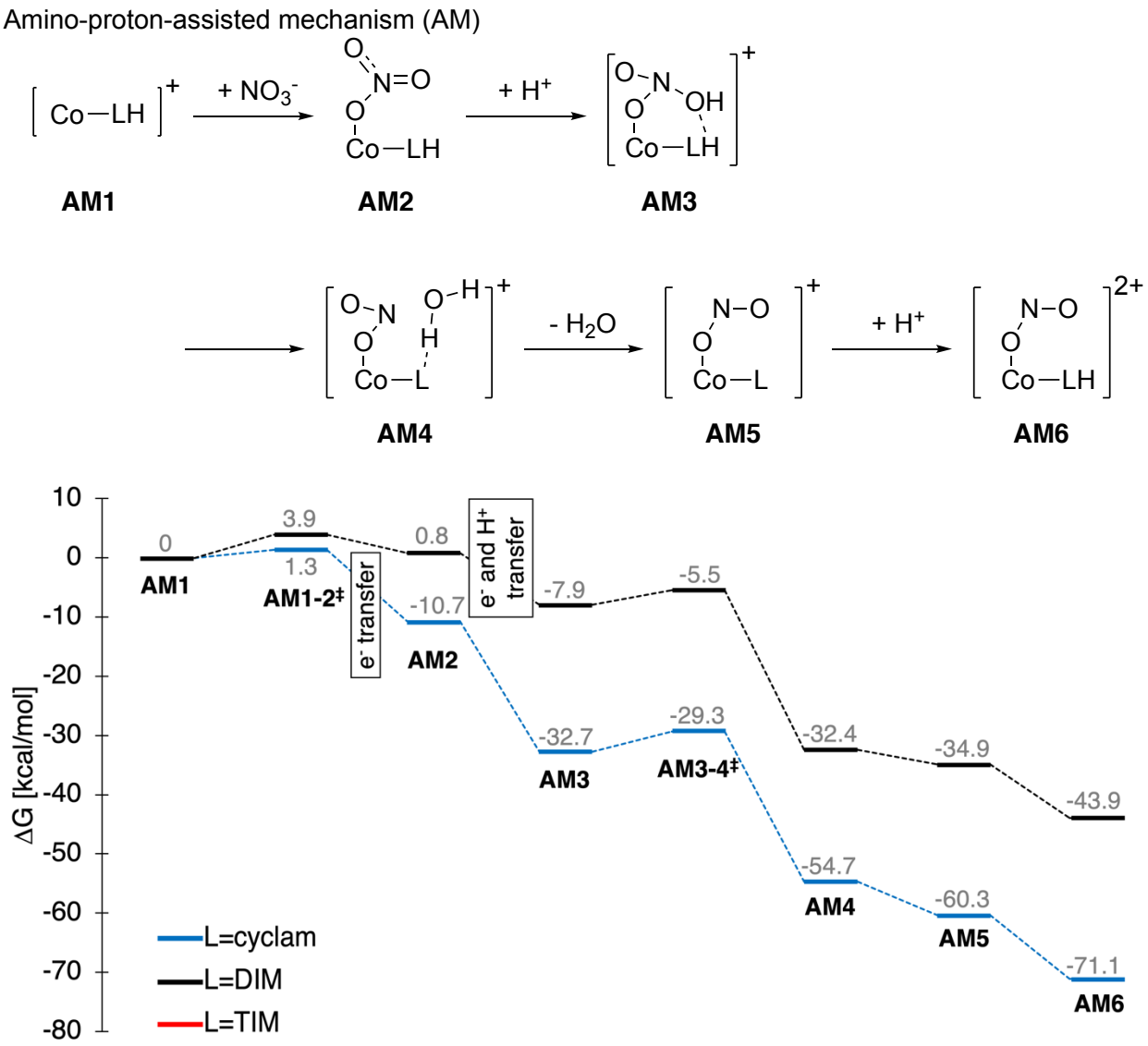

Figure S15. Reaction coordinate diagram for the amino-proton-assisted mechanism for Co-catalysts. The details on electron and proton transfer steps for DIM can be found Figure 11. The electron transfer step for cyclam has not been shown since it is almost a barrierless process due to the instability of $[Co(cyclam)]^{+}$.

Spin-State Energetics and DFT Functional Dependence

Three major criteria were used when the functional and the basis set were chosen: whether the optimized geometry matches the experimental data, whether the chosen method can reproduce reduction potentials of known Co complexes (tested with $[Co(sep)]^{3+}$, $[Co(phen)_3]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(tacn)_2]^{3+}$ and $[Co(DIM)Br_2]^{+}$), and whether the method properly describes redox non-innocence (i.e., orbital delocalization between the metal and the ligand).[5] However, these criteria do not guarantee that energy differences computed for cyclam and TIM complexes are also valid. Therefore, it was important to gauge how sensitive the spin-state energetics for these complexes were to variations in our chosen methodology. In order to investigate the dependence of spin-state energy differences, electronic energies were calculated with Hartree-Fock (HF) as well as several different DFT functionals, including PBE,[6, 7] M06,[8] M06-L[9] and BHandHLYP,[10] for a geometry that was previously optimized at the B3LYP+D2/6-31G* level of theory. Also, we have varied the HF exchange coefficient (C_1) from 0.0 to 1.0 in the B3LYP functional (Equation 1). Slater type hybrid functionals implemented in Gaussian 16 can be described as following generalized form:

$$C_1E_X^{HF} + C_2E_X^{Slater} + 0.72*\Delta E_x^{non\text{-}local} + E_C^{local} + 0.81*\Delta E_C^{non\text{-}local} \quad (1)$$

where E_X are exchange functionals and E_C are correlation functionals. For B3LYP, the C_1 parameter is 0.20 and the Slater exchange coefficient (C_2) is 0.80 as determined from:

$$C_1 + C_2 = 1 \quad (2)$$

GGA functionals (generalized gradient approximation; functionals with zero HF exchange) favored the low-spin states, while hybrid functionals favored the high-spin states, as expected.[11] This result shows that as the HF exchange parameter increases, the ligand field splitting of Co 3d orbitals becomes greater. In Figure S16, the slope of higher spin states energies *vs.* the singlet state energies with $[Co(TIM)]^{+}$ is noticeably steeper than those of $[Co(DIM)]^{+}$ and $[Co(cyclam)]^{+}$. Accordingly, $[Co(TIM)]^{+}$ is much more susceptible to the amount of exact exchange in the functional, so its results must be interpreted more cautiously, especially when there are not many reference values for calibrating the methodology. The B3LYP+D2 functional was chosen for this work because it reflected redox non-innocent character of DIM and TIM complexes and it was the same methodology used in the previous work on $[Co(DIM)]^{+}$ nitrate and nitrite reduction, which were used as a reference.[5, 12]

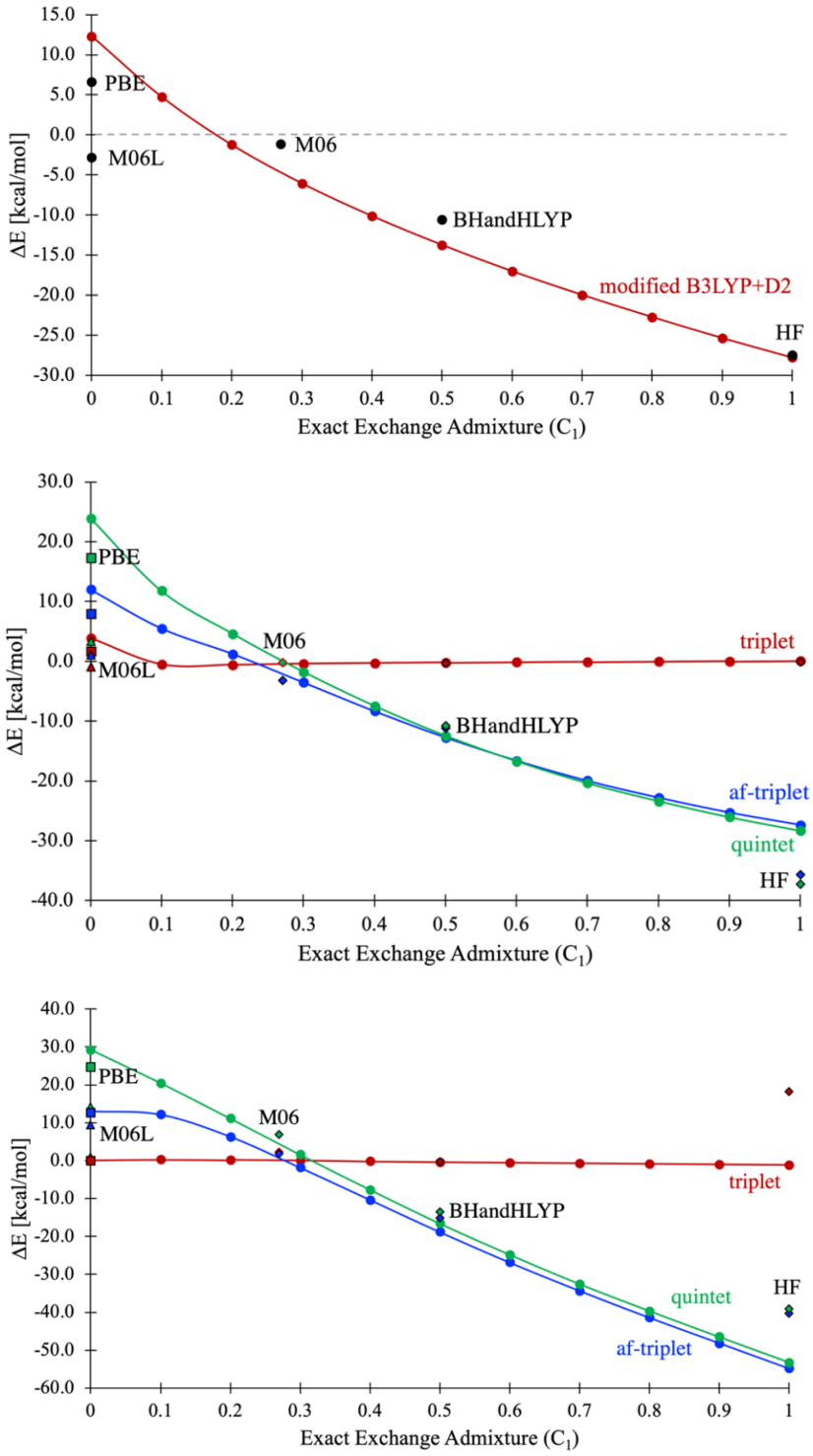

Figure S16. Exact exchange vs ΔE (= $E_{high\text{-}spin} - E_{singlet}$) for [Co(cyclam)]$^+$ (top), [Co(DIM)]$^+$ (center) and [Co(TIM)]$^+$ (bottom). $E_{singlet}$ for [Co(DIM)]$^+$ and [Co(TIM)]$^+$ are from AF-S. Modified B3LYP+D2 curves are shown for "triplet – singlet (red)," "AF-triplet – singlet (blue)," and "quintet – singlet (green)."

Eyring Plot for Co(DIM) Complex

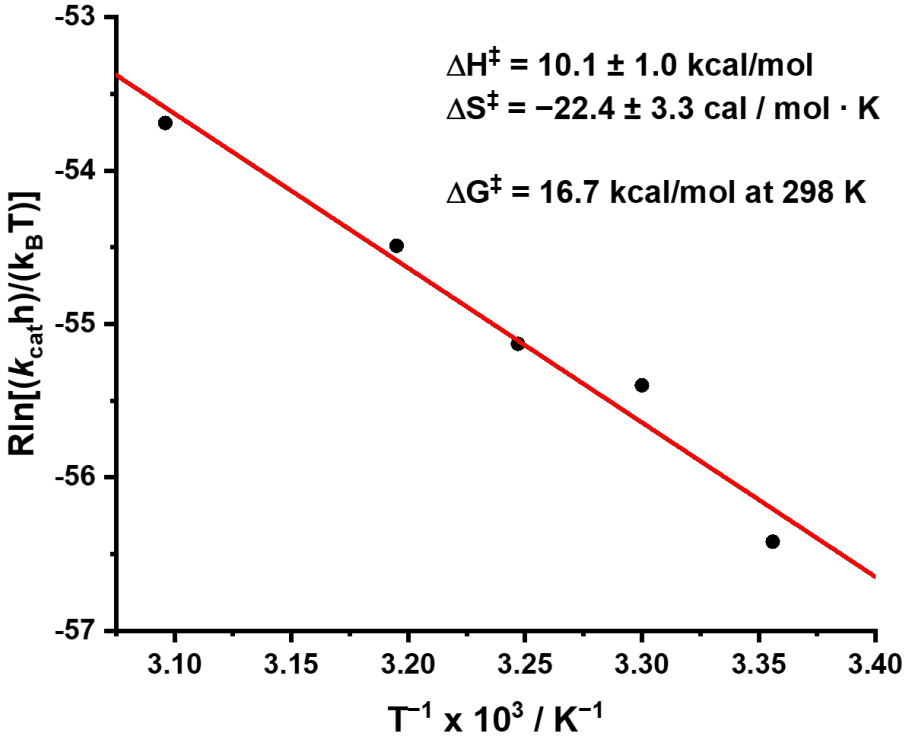

Figure S17. Plot of Rln[(k_{cat}h)/k_BT)] *vs.* T^{-1} and the best fit (red) from cyclic voltammetry data collected in 0.1 M KBr with 0.5 mM [Co(DIM)Br_2]Br and 10 mM $NaNO_3$. The plot fits to the equation: y = −10070x – 22.4, R^2 = 0.97.

Functional Dependence of Electronic Energy

Table S1. Electronic energy barrier (E_a in kcal/mol) between the lowest energy intermediate to N-O cleaving step (MM2-3‡ and HM3-4‡) for Monodentate and Proton-assisted Mechanisms (as suggested in Figure S10 and Figure S12) of $[Co(DIM)]^+$ and $[Co(TIM)]^+$ obtained from single point energy calculations on B3LYP+D2 optimized geometries. Note that the barrier energy is less consistent for the TIM complex.

	Monodentate Mechanism		**Hydroxyl Transfer Mechanism**	
Functional	DIM E_a	TIM E_a	DIM E_a	TIM E_a
B3LYP	20.6	26.9	5.2	2.3
PBE	25.8	35.5	8.2	18.3
M06	25.4	25.5	4.5	1.7
M06L	22.0	29.6	5.5	5.9
BHandHLYP	21.3	22.8	7.0	5.7

Table of Calculated DFT Data

Table S2. Electronic energies (E), zero-point energies (ZPE), entropic corrections to free energies (−TΔS), enthalpies (H), and Gibbs free energies (G) calculated with DFT. All optimizations were done with the SMD correction for solvent (water unless specified otherwise), hence E contains the solvation effects. The temperature (T) was set to 298.15 K, and the pressure to 1 atm. All values are reported in kcal/mol.

Compound	E	ZPE	-TΔS	H	G
Nitrate	-176051.61	8.75	-18.58	-176040.28	-176058.86
Water	-47986.87	13.14	-13.87	-47971.36	-47985.23
Hydroxide	-47677.25	5.18	-12.28	-47670.00	-47682.29
Bromide	-261741.10	0.00	-11.63	-261739.61	-261751.25
Nitric acid	-176320.51	16.27	-19.01	-176301.40	-176320.41
Nitrite	-128847.37	4.91	-17.30	-128840.03	-128857.33
$[Co(DIM)Br_2]^+$ (III) singlet	-1048410.28	234.91	-44.06	-1048161.88	-1048205.94
$[Co(DIM)Br_2]^+$ (III) triplet	-1048395.04	234.03	-46.09	-1048147.12	-1048193.20
$[Co(DIM)Br_2]^+$ (III) quintet	-1048380.03	232.46	-47.46	-1048133.24	-1048180.70
$[Co(DIM)Br_2]$ (II) doublet	-1048505.56	233.19	-47.29	-1048258.20	-1048305.48
$[Co(DIM)Br_2]$ (II) quartet	-1048502.50	231.30	-48.79	-1048256.60	-1048305.39
$[Co(DIM)Br]^{2+}$ (III) singlet	-786648.67	233.90	-41.32	-786402.38	-786443.69
$[Co(DIM)Br]^{2+}$ (III) triplet	-786649.18	233.60	-42.32	-786403.09	-786445.41
$[Co(DIM)Br]^{2+}$ (III) quintet	-786633.99	232.65	-43.48	-786388.57	-786432.05
$[Co(DIM)Br]^+$ (II) doublet	-786767.25	233.11	-42.52	-786521.54	-786564.06
$[Co(DIM)Br]^+$ (II) quartet	-786766.65	231.56	-44.64	-786521.96	-786566.59
[Co(DIM)Br] (I) AF-singlet	-786836.43	231.36	-42.49	-786592.32	-786634.81
[Co(DIM)Br] (I) triplet	-786835.66	231.24	-43.78	-786591.60	-786635.38
[Co(DIM)Br] (I) AF-triplet	-786838.40	230.21	-43.95	-786595.09	-786639.04
[Co(DIM)Br] (I) quintet	-786832.47	229.51	-45.20	-786589.60	-786634.80
$[Co(DIM)]^{3+}$ (III) singlet	-524879.88	233.00	-37.01	-524636.23	-524673.24
$[Co(DIM)]^{3+}$ (III) triplet	-524893.92	232.79	-38.94	-524649.94	-524688.88
$[Co(DIM)]^{2+}$ (II) doublet	-525024.36	232.57	-39.73	-524780.43	-524820.17
$[Co(DIM)]^{2+}$ (II) quartet	-525021.49	230.87	-40.73	-524778.80	-524819.52
$[Co(DIM)]^+$ (I) AF-singlet	-525098.87	230.91	-38.74	-524856.51	-524895.24
$[Co(DIM)]^+$ (I) triplet	-525099.46	231.15	-38.99	-524857.00	-524896.00
$[Co(DIM)]^+$ (I) AF-triplet	-525097.66	229.75	-40.48	-524856.13	-524896.61
$[Co(DIM)]^+$ (I) quintet	-525094.30	229.46	-40.30	-524853.09	-524893.39
$[Co(DIM)(NO_3)]^+$ (II) doublet	-701085.84	242.24	-47.72	-700829.28	-700877.00
$[Co(DIM)(NO_3)]^+$ (II) quartet	-701086.00	241.01	-47.60	-700830.44	-700878.03
$[Co(DIM)(NO_3)]$ (I) quintet	-701152.99	239.28	-47.75	-700899.05	-700946.80
$[Co(DIM)(NO_3)]$ (I) AF-singlet	-701157.83	240.99	-46.24	-700902.57	-700948.81

[Co(DIM)(NO_3)] (I) AF-triplet	-701158.16	239.49	-48.03	-700903.97	-700952.00
$[Co(cyclam)]^{3+}$ (III) singlet	-477059.63	228.56	-32.43	-476822.39	-476854.82
$[Co(cyclam)]^{3+}$ (III) triplet	-477073.54	228.08	-33.27	-476836.68	-476869.95
$[Co(cyclam)]^{2+}$ (II) doublet	-477200.61	228.81	-35.27	-476962.19	-476997.46
$[Co(cyclam)]^{2+}$ (II) quartet	-477196.23	227.03	-36.58	-476959.11	-476995.70
$[Co(cyclam)]^{+}$ (I) singlet	-477249.21	227.11	-35.02	-477012.29	-477047.30
$[Co(cyclam)]^{+}$ (I) triplet	-477250.43	225.31	-36.75	-477014.83	-477051.57
$[Co(cyclam)]^{+}$ (I) quintet	-477224.34	226.32	-37.11	-476987.76	-477024.87
[Co(cyclam)(NO_3)] (I) AF-singlet	-653326.82	236.96	-40.00	-653077.75	-653117.74
[Co(cyclam)(NO_3)] (I) triplet	-653322.97	236.85	-40.92	-653073.92	-653114.84
[Co(cyclam)(NO_3)] (I) AF-triplet	-653324.58	234.89	-42.33	-653076.91	-653119.25
[Co(cyclam)(NO_3)] (I) quintet	-653321.64	234.98	-42.69	-653073.88	-653116.57
$[Co(cyclam)(NO_3)]^{+}$ (II) doublet	-653263.15	238.90	-42.37	-653011.80	-653054.17
$[Co(cyclam)(NO_3)]^{+}$ (II) quartet	-653258.80	236.97	-43.85	-653008.90	-653052.75
$[Co(cyclam)(NO_3)]^{2+}$ (III) singlet	-653142.15	240.49	-39.50	-652889.86	-652929.37
$[Co(cyclam)(NO_3)]^{2+}$ (III) triplet	-653144.20	239.18	-41.70	-652892.77	-652934.47
$[Co(cyclam)(NO_3)(OH)]^{+}$ (III) singlet	-700867.03	249.91	-40.93	-700604.47	-700645.40
$[Co(cyclam)(NO_3)(OH)]^{+}$ (III) triplet	-700849.43	247.59	-43.74	-700588.39	-700632.13
$[Co(cyclam)(NO_3)(OH)]^{+}$ (III) quintet	-700838.78	246.59	-44.40	-700578.56	-700622.96
[Co(cyclam)(NO_3)(OH)] (II) doublet	-700950.94	246.25	-45.40	-700690.80	-700736.20
[Co(cyclam)(NO_3)(OH)] (II) quartet	-700955.40	244.81	-46.09	-700696.39	-700742.47
$[Co(cyclam)(NO_3)(OH)]^{-}$ (I) AF-singlet	-701004.70	243.87	-43.76	-700746.86	-700790.62
$[Co(cyclam)(NO_3)(OH)]^{-}$ (I) triplet	-701003.84	244.45	-43.85	-700745.62	-700789.47
$[Co(cyclam)(NO_3)(OH)]^{-}$ (I) AF-triplet	-701009.39	242.44	-45.05	-700752.78	-700797.83
$[Co(cyclam)(NO_3)(OH)]^{-}$ (I) quintet	-701007.90	242.38	-45.59	-700751.32	-700796.91
$[Co(cyclam)(NO_3)H]^{2+}$ (II) doublet	-653485.11	245.36	-40.98	-653227.62	-653268.60
$[Co(cyclam)(NO_3)H]^{2+}$ (II) quartet	-653532.07	247.05	-43.66	-653272.21	-653315.87
$[Co(cyclam)(NO_3)H]^{+}$ (I) singlet	-653624.87	245.82	-40.26	-653367.03	-653407.29
[Co(cyclam)(NO_3)H]+ (I) triplet	-653599.95	242.70	-42.48	-653344.50	-653386.98
$[Co(cyclam)(NO_3)H]^{+}$ (I) quintet	-653577.64	240.97	-43.74	-653323.66	-653367.40
$[Co(cyclam)(OH)]^{2+}$ (III) singlet	-524791.14	238.38	-36.37	-524542.29	-524578.66
$[Co(cyclam)(OH)]^{2+}$ (III) triplet	-524787.46	237.47	-37.94	-524539.15	-524577.09
$[Co(cyclam)(OH)]^{2+}$ (III) quintet	-524777.68	236.39	-38.70	-524530.21	-524568.91
$[Co(cyclam)(OH)]^{+}$ (II) doublet	-524889.73	236.29	-37.43	-524642.52	-524679.95
$[Co(cyclam)(OH)]^{+}$ (II) quartet	-524895.06	234.77	-38.87	-524648.97	-524687.83
[Co(cyclam)(OH)] (I) triplet	-524929.40	232.06	-39.83	-524685.47	-524725.30
[Co(cyclam)(OH)] (I) quintet	-524909.18	233.65	-39.59	-524664.01	-524703.60
$[Co(cyclam)(OH)_2]^{+}$ (III) singlet	-572506.99	246.82	-37.65	-572248.73	-572286.38
$[Co(cyclam)(OH)_2]^{+}$ (III) triplet	-572489.06	245.21	-38.84	-572232.13	-572270.96

$[Co(cyclam)(OH)_2]^+$ (III) quintet	-572477.60	243.55	-39.31	-572222.26	-572261.57
$[Co(cyclam)(OH)_2]$ (II) quartet	-572579.24	242.44	-40.20	-572324.43	-572364.64
$[Co(cyclam)(OH)_2]^-$ (I) singlet	-572579.87	241.69	-39.70	-572325.69	-572365.39
$[Co(cyclam)(OH)_2]^-$ (I) triplet	-572587.97	241.22	-40.79	-572334.09	-572374.88
$[Co(cyclam)(OH)_2]^-$ (I) quintet	-572590.04	241.71	-40.55	-572335.89	-572376.44
$[Co(cyclam)(NO_3)(H_2O)]^{2+}$ (III) singlet	-701152.02	259.01	-40.99	-700880.29	-700921.29
$[Co(cyclam)(NO_3)(H_2O)]^{2+}$ (III) triplet	-701085.18	256.57	-42.54	-700815.55	-700858.09
$[Co(cyclam)(NO_3)(H_2O)]^{2+}$ (III) quintet	-701073.57	254.42	-45.41	-700805.26	-700850.67
$[Co(cyclam)(NO_3)(H_2O)]^+$ (II) doublet	-701257.32	255.67	-44.65	-700987.75	-701032.40
$[Co(cyclam)(NO_3)(H_2O)]^+$ (II) quartet	-701254.60	254.24	-45.55	-700986.25	-701031.80
$[Co(cyclam)(NO_3)(H_2O)]$ (I) triplet	-701315.78	253.01	-44.29	-701048.92	-701093.21
$[Co(cyclam)(NO_3)(H_2O)]$ (I) quintet	-701314.30	251.58	-44.92	-701048.60	-701093.52
$[Co(cyclam)(H_2O)_2]^{3+}$ (III) singlet	-573080.00	266.68	-36.77	-572802.17	-572838.94
$[Co(cyclam)(H_2O)_2]^{3+}$ (III) triplet	-573072.15	264.56	-38.88	-572795.75	-572834.63
$[Co(cyclam)(H_2O)_2]^{3+}$ (III) quintet	-573046.55	263.37	-39.77	-572771.09	-572810.86
$[Co(cyclam)(H_2O)_2]^{2+}$ (II) doublet	-573189.25	261.04	-40.31	-572915.76	-572956.07
$[Co(cyclam)(H_2O)_2]^{2+}$ (II) quartet	-573187.57	259.01	-40.91	-572913.98	-572954.89
$[Co(cyclam)(H_2O)]^{3+}$ (III) singlet	-525069.08	247.85	-35.80	-524810.83	-524846.62
$[Co(cyclam)(H_2O)]^{3+}$ (III) triplet	-525074.33	246.57	-37.47	-524816.98	-524854.45
$[Co(cyclam)(H_2O)]^{3+}$ (III) quintet	-525051.86	244.86	-38.45	-524795.95	-524834.40
$[Co(cyclam)(H_2O)]^{2+}$ (II) doublet	-525195.50	245.74	-37.35	-524938.81	-524976.16
$[Co(cyclam)(H_2O)]^{2+}$ (II) quartet	-525193.57	244.01	-38.73	-524938.22	-524976.95
$[Co(cyclam)(H_2O)]^+$ (I) singlet	-525245.64	241.92	-38.74	-524992.16	-525030.90
$[Co(cyclam)(H_2O)]^+$ (I) quintet	-525215.16	239.73	-40.24	-524963.59	-525003.84
$[Co(cyclam)(HNO_3)]^+$ (I) AF-triplet	-653617.89	242.55	-43.47	-653362.06	-653405.53
$[Co(cyclam)(HNO_3)]^{2+}$ (II) doublet	-653530.55	246.48	-43.29	-653271.27	-653314.56
$[Co(cyclam)(HNO_3)]^{2+}$ (II) quartet	-653524.82	244.63	-44.27	-653266.99	-653311.26
$[Co(cyclam)(HNO_3)]^{3+}$ (III) singlet	-653337.53	244.63	-42.11	-653080.07	-653122.17
$[Co(cyclam)(HNO_3)]^{3+}$ (III) triplet	-653404.71	246.91	-42.11	-653145.30	-653187.41
$[Co(cyclam)(HNO_3)]^{3+}$ (III) quintet	-653378.77	245.44	-43.18	-653120.49	-653163.67
$[Co(cyclam)H]^{3+}$ (II) doublet	-477411.83	233.54	-36.40	-477168.38	-477204.79
$[Co(cyclam)H]^{2+}$ (I) singlet	-477555.00	235.02	-34.41	-477310.49	-477344.90
$[Co(cyclam)H]^{2+}$ (I) triplet	-477528.58	232.57	-35.74	-477286.13	-477321.87
$[Co(cyclam)H]^{2+}$ (I) quintet	-477519.42	231.00	-37.66	-477277.99	-477315.65
$[Co(cyclam)H]^+$ (0) doublet	-477628.96	231.66	-35.39	-477387.45	-477422.84
$[Co(cyclam)H]^+$ (0) quartet	-477632.27	229.77	-37.04	-477392.05	-477429.09
$[Co(deprotonated\text{-}cyclam)]^{2+}$ (III) singlet	-476789.55	219.70	-34.89	-476560.23	-476595.12
$[Co(deprotonated\text{-}cyclam)]^{2+}$ (III) triplet	-476791.94	219.88	-35.54	-476562.46	-476598.00
$[Co(deprotonated\text{-}cyclam)]^{2+}$ (III) quintet	-476783.52	217.88	-36.62	-476555.60	-476592.22

$[Co(deprotonated\text{-}cyclam)]^+$ (II) doublet	-476883.73	219.02	-34.96	-476655.16	-476690.12
$[Co(deprotonated\text{-}cyclam)]^+$ (II) quartet	-476879.99	217.28	-36.48	-476652.67	-476689.14
[Co(deprotonated-cyclam)] (I) singlet	-476920.08	216.99	-34.92	-476693.32	-476728.24
[Co(deprotonated-cyclam)] (I) triplet	-476921.50	215.27	-36.89	-476695.91	-476732.80
[Co(deprotonated-cyclam)] (I) quintet	-476893.07	216.07	-35.95	-476667.26	-476703.21
$[Co(deprotonated\text{-}cyclam)(NO_3)]^+$ (III) singlet	-652853.13	229.71	-41.74	-652611.00	-652652.75
$[Co(deprotonated\text{-}cyclam)(NO_3)]^+$ (III) triplet	-652854.92	230.01	-42.36	-652612.56	-652654.92
$[Co(deprotonated\text{-}cyclam)(NO_3)]^+$ (III) AF-triplet	-652849.86	228.87	-42.79	-652608.35	-652651.15
$[Co(deprotonated\text{-}cyclam)(NO_3)]^+$ (III) quintet	-652844.82	227.45	-43.89	-652604.39	-652648.27
$[Co(deprotonated\text{-}cyclam)(NO_3)]$ (II) doublet	-652943.77	228.89	-42.16	-652702.47	-652744.63
$[Co(deprotonated\text{-}cyclam)(NO_3)]$ (II) quartet	-652939.06	227.07	-43.57	-652699.14	-652742.71
$[Co(deprotonated\text{-}cyclam)(NO_3)]$ (I) AF-singlet	-652978.63	226.71	-42.45	-652739.17	-652781.62
$[Co(deprotonated\text{-}cyclam)(NO_3)]$ (I) triplet	-652998.88	224.98	-42.32	-652761.08	-652803.40
$[Co(deprotonated\text{-}cyclam)(NO_3)]$ (I) quintet	-652997.59	225.01	-43.04	-652759.72	-652802.76
$[Co(deprotonated\text{-}cyclam)(OH)]^+$ (III) singlet	-524485.03	228.30	-36.65	-524246.03	-524282.68
$[Co(deprotonated\text{-}cyclam)(OH)]^+$ (III) triplet	-524483.90	225.40	-38.18	-524247.46	-524285.64
$[Co(deprotonated\text{-}cyclam)(OH)]^+$ (III) quintet	-524483.49	226.00	-38.89	-524246.26	-524285.15
$[Co(deprotonated\text{-}cyclam)(OH)]^+$ (II) doublet	-524563.72	226.20	-37.34	-524326.63	-524363.97
$[Co(deprotonated\text{-}cyclam)(OH)]^+$ (II) quartet	-524571.37	224.54	-39.60	-524335.32	-524374.92
$[Co(deprotonated\text{-}cyclam)(OH)]^+$ (I) singlet	-524599.43	224.79	-37.47	-524363.59	-524401.06
$[Co(deprotonated\text{-}cyclam)(OH)]^+$ (I) triplet	-524592.99	222.18	-39.54	-524359.06	-524398.60
$[Co(deprotonated\text{-}cyclam)(OH)]^+$ (I) quintet	-524582.43	223.89	-39.57	-524347.02	-524386.59
$[Co(cyclam)(Br)(H)]^{2+}$ (II) doublet	-739171.15	236.08	-37.71	-738924.40	-738962.11
$[Co(cyclam)(Br)(H)]^{2+}$ (II) quartet	-739149.36	233.86	-39.95	-738904.23	-738944.19
$[Co(cyclam)(Br)(H)]^+$ (I) singlet	-739305.64	236.03	-37.00	-739059.02	-739096.02
$[Co(cyclam)(Br)(H)]^+$ (I) triplet	-739282.86	233.41	-38.88	-739038.28	-739077.16
$[Co(cyclam)(Br)(H)]^+$ (I) quintet	-739261.25	231.70	-39.79	-739018.16	-739057.95
$[Co(cyclam)(Br)(OH)]^+$ (III) singlet	-786549.33	239.66	-38.03	-786298.32	-786336.35
$[Co(cyclam)(Br)(OH)]^+$ (III) triplet	-786532.40	238.28	-40.11	-786282.27	-786322.38
$[Co(cyclam)(Br)(OH)]^+$ (III) quintet	-786520.19	236.99	-41.07	-786271.02	-786312.09
[Co(cyclam)(Br)(OH)] (II) doublet	-786629.39	236.52	-41.50	-786380.51	-786422.01
[Co(cyclam)(Br)(OH)] (II) quartet	-786633.28	235.18	-42.59	-786385.43	-786428.01
$[Co(cyclam)(Br)(OH)]^-$ (I) triplet	-786663.87	232.25	-45.20	-786418.18	-786463.37
$[Co(cyclam)(Br)(OH)]^-$ (I) quintet	-786647.64	233.73	-43.93	-786400.89	-786444.82
[Co(cyclam)(Br)] (I) singlet	-738985.31	227.24	-39.88	-738746.78	-738786.66
[Co(cyclam)(Br)] (I) triplet	-738986.36	225.43	-41.08	-738749.20	-738790.28
[Co(cyclam)(Br)] (I) quintet	-738958.61	226.85	-40.48	-738720.29	-738760.77
$[Co(cyclam)(Br)]^+$ (II) doublet	-738944.45	229.50	-38.11	-738704.16	-738742.28
$[Co(cyclam)(Br)]^+$ (II) quartet	-738942.87	227.64	-39.84	-738703.90	-738743.74

$[Co(cyclam)(Br)]^{2+}$ (III) singlet	-738828.80	230.85	-36.57	-738587.53	-738624.10
$[Co(cyclam)(Br)]^{2+}$ (III) triplet	-738829.17	230.11	-37.78	-738588.41	-738626.19
$[Co(cyclam)(Br)]^{2+}$ (III) quintet	-738810.35	228.79	-39.71	-738570.43	-738610.14
$[Co(cyclam)(Br)_2]$ (II) doublet	-1000685.29	229.69	-42.47	-1000443.31	-1000485.79
$[Co(cyclam)(Br)_2]$ (II) quartet	-1000682.59	228.21	-43.01	-1000441.81	-1000484.83
$[Co(cyclam)(Br)_2]^{+}$ (III) singlet	-1000589.06	231.82	-38.85	-1000345.77	-1000384.61
$[Co(cyclam)(Br)_2]^{+}$ (III) triplet	-1000576.76	230.59	-41.04	-1000334.23	-1000375.27
$[Co(cyclam)(Br)_2]^{+}$ (III) quintet	-1000559.37	229.53	-41.72	-1000317.64	-1000359.36
$[Co(TIM)]^{+}$ (I) AF-singlet	-572930.79	234.40	-42.93	-572683.25	-572726.19
$[Co(TIM)]^{+}$ (I) triplet	-572930.62	234.35	-43.65	-572683.14	-572726.79
$[Co(TIM)]^{+}$ (I) AF-triplet	-572924.52	233.87	-43.61	-572677.36	-572720.97
$[Co(TIM)]^{+}$ (I) quintet	-572919.69	232.70	-45.86	-572673.29	-572719.14
$[Co(TIM)]^{2+}$ (II) doublet	-572850.12	236.18	-43.98	-572600.75	-572644.72
$[Co(TIM)]^{2+}$ (II) quartet	-572845.40	234.97	-44.11	-572597.09	-572641.20
$[Co(TIM)]^{3+}$ (III) AF-singlet	-572700.89	236.63	-42.13	-572451.38	-572493.51
$[Co(TIM)]^{3+}$ (III) triplet	-572714.46	236.29	-42.87	-572465.23	-572508.10
$[Co(TIM)]^{3+}$ (III) quintet	-572695.38	233.92	-41.45	-572448.91	-572490.36
[Co(TIM)] (0) AF-doublet	-573001.17	233.50	-42.53	-572754.68	-572797.20
[Co(TIM)] (0) quartet	-572996.26	232.13	-42.95	-572751.18	-572794.13
$[Co(TIM)(NO_3)]$ (I) AF-singlet	-748988.23	244.04	-50.07	-748728.17	-748778.23
$[Co(TIM)(NO_3)]$ (I) triplet	-748984.38	243.10	-52.15	-748724.85	-748777.00
$[Co(TIM)(NO_3)]$ (I) quintet	-748978.38	243.16	-51.17	-748718.96	-748770.13
$[Co(TIM)(Br)_2]^{+}$ (III) singlet	-1096235.80	238.11	-50.08	-1095982.13	-1096032.21
$[Co(TIM)(Br)_2]^{+}$ (III) triplet	-1096217.64	237.15	-50.22	-1095965.09	-1096015.31
$[Co(TIM)(Br)_2]^{+}$ (III) quintet	-1096203.77	236.07	-52.11	-1095951.59	-1096003.69
$[Co(TIM)(Br)_2]$ (II) doublet	-1096327.57	236.53	-53.09	-1096074.82	-1096127.91
$[Co(TIM)(Br)_2]$ (II) quartet	-1096322.31	234.80	-53.75	-1096071.02	-1096124.77
$[Co(TIM)(Br)]^{2+}$ (III) singlet	-834472.67	237.44	-45.98	-834221.00	-834266.98
$[Co(TIM)(Br)]^{2+}$ (III) triplet	-834471.92	236.82	-47.64	-834220.64	-834268.29
$[Co(TIM)(Br)]^{+}$ (II) doublet	-834592.66	236.46	-47.64	-834341.64	-834389.29
$[Co(TIM)(Br)]^{+}$ (II) quartet	-834591.00	235.07	-49.60	-834340.99	-834390.59
[Co(TIM)(Br)] (I) singlet	-834666.82	234.59	-46.70	-834417.75	-834464.46
[Co(TIM)(Br)] (I) triplet	-834661.33	234.56	-48.43	-834412.14	-834460.57
[Co(TIM)(Br)] (I) quintet	-834658.51	233.43	-49.29	-834410.11	-834459.40
Fig.9 DIM D3-D4 TS quintet	-701152.77	239.12	-46.66	-700899.40	-700946.06
Fig.9 DIM D3-D4 TS AF-triplet	-701157.34	239.56	-46.09	-700903.61	-700949.70
Fig.S10 cyclam MM1-MM2 TS AF-singlet	-653308.72	236.56	-41.05	-653059.88	-653100.93
Fig.S10 cyclam MM1-MM2 TS triplet	-653312.18	234.95	-42.37	-653064.60	-653106.97
Fig.8 cyclam C2-C3 TS quartet	-653252.47	236.83	-42.82	-653003.13	-653045.95
Fig.11 TIM T3-T4 TS AF-singlet	-748988.73	244.10	-49.44	-748729.02	-748778.46
$[Co(DIM)(O)]^{+}$ quintet	-572311.01	233.09	-42.07	-572065.48	-572107.55

$[Co(DIM)(O)]^+$ triplet	-572298.43	233.73	-40.80	-572052.53	-572093.33
$[Co(DIM)(O)]^+$ AF-singlet	-572294.60	234.21	-39.59	-572048.40	-572087.99
$[Co(DIM)(O)]^+$ AF-triplet	-572295.63	233.73	-40.81	-572049.74	-572090.54
Fig.S10 DIM MM2-MM3 TS quintet	-701138.63	238.30	-47.61	-700885.70	-700933.31
Fig.S10 DIM MM2-MM3 TS triplet	-701136.63	238.33	-47.59	-700883.62	-700931.21
Fig.S10 DIM MM2-MM3 TS singlet	-701119.93	240.20	-43.10	-700866.13	-700909.23
Fig.S10 DIM MM2-MM3 TS AF-singlet	-701128.22	239.18	-45.50	-700874.79	-700920.29
Fig.S10 DIM MM2-MM3 TS AF-triplet	-701136.53	238.13	-47.76	-700883.57	-700931.33
Fig.S11 DIM BM2-BM3 TS quintet	-701142.93	237.72	-47.84	-700890.58	-700938.42
Fig.S11 DIM BM2-BM3 TS triplet	-701140.40	239.41	-45.53	-700886.99	-700932.51
Fig.S11 DIM BM2-BM3 TS AF-singlet	-701138.58	239.46	-44.73	-700885.16	-700929.89
Fig.S11 DIM BM2-BM3 TS AF-triplet	-701144.77	237.76	-48.63	-700892.36	-700940.99
$[Co(cyclam)(O)]^+$ quintet	-524486.00	229.16	-38.09	-524246.05	-524284.14
$[Co(cyclam)(O)]^+$ singlet	-524455.63	231.22	-35.89	-524214.14	-524250.03
$[Co(cyclam)(O)]^+$ AF-singlet	-524471.48	229.82	-36.11	-524231.26	-524267.37
$[Co(cyclam)(O)]^+$ triplet	-524467.66	229.40	-37.27	-524227.67	-524264.94
Fig.S10 cyclam MM2-MM3 TS quintet	-653310.85	234.58	-43.43	-653063.38	-653106.81
Fig.S10 cyclam MM2-MM3 TS triplet	-653311.02	234.64	-42.92	-653063.48	-653106.40
Fig.S10 cyclam MM2-MM3 TS AF-singlet	-653303.85	236.06	-40.51	-653055.50	-653096.01
Fig.S10 cyclam MM2-MM3 TS AF-triplet	-653304.72	235.74	-42.87	-653056.47	-653099.35
Fig.S10 cyclam MM2-MM3 TS singlet	-653282.96	236.20	-39.22	-653034.96	-653074.19
$[Co(TIM)(O)]^+$ quintet	-620137.51	236.88	-46.33	-619886.46	-619932.79
$[Co(TIM)(O)]^+$ triplet	-620119.98	237.20	-44.87	-619868.83	-619913.70
$[Co(TIM)(O)]^+$ AF-singlet	-620113.47	237.28	-44.23	-619862.27	-619906.50
$[Co(TIM)(O)]^+$ AF-triplet	-620119.04	236.04	-46.55	-619868.57	-619915.12
Fig.S10 TIM MM2-MM3 TS quintet	-748965.62	242.03	-51.48	-748707.25	-748758.73
Fig.S10 TIM MM2-MM3 TS triplet	-748953.10	243.25	-49.83	-748693.93	-748743.76
Fig.S10 TIM MM2-MM3 TS singlet	-748946.12	243.84	-48.13	-748686.72	-748734.85
Fig.S10 TIM MM2-MM3 TS AF-singlet	-748955.20	243.34	-48.90	-748695.98	-748744.88
Fig.S10 TIM MM2-MM3 TS AF-triplet	-748963.05	241.85	-51.57	-748704.75	-748756.32
Fig.S11 DIM BM3 quintet	-701148.33	239.43	-47.56	-700894.35	-700941.90
Fig.S11 DIM BM3 triplet	-701139.94	240.61	-45.14	-700885.31	-700930.45
Fig.S11 DIM BM3 singlet	-701133.68	241.47	-42.53	-700878.72	-700921.26
Fig.S11 DIM BM3 AF-singlet	-701139.36	240.64	-44.26	-700884.73	-700929.00
Fig.S11 DIM BM3 AF-triplet	-701150.50	239.71	-46.25	-700896.38	-700942.62
Fig.S11 DIM BM4 quintet	-701157.15	239.54	-47.38	-700902.78	-700950.16
Fig.S11 DIM BM4 triplet	-701147.25	239.97	-47.56	-700892.46	-700940.02
Fig.S11 DIM BM4 singlet	-701144.60	242.18	-43.70	-700888.59	-700932.29
Fig.S11 DIM BM4 AF-singlet	-701144.39	241.80	-43.97	-700888.61	-700932.58
Fig.S11 DIM BM4 AF-triplet	-701147.25	239.97	-47.55	-700892.46	-700940.01
Fig.S11 DIM BM3-BM4 TS quintet	-701136.82	238.42	-46.94	-700883.85	-700930.79

Fig.S11 DIM BM3-BM4 TS triplet	-701124.77	239.46	-45.33	-700871.19	-700916.52
Fig.S11 DIM BM3-BM4 TS singlet	-701113.08	241.02	-41.79	-700859.06	-700900.85
Fig.S11 DIM BM3-BM4 TS AF-singlet	-701124.61	239.27	-45.30	-700871.08	-700916.38
Fig.S11 DIM BM3-BM4 TS AF-triplet	-701135.74	238.33	-46.76	-700882.80	-700929.56
Fig.S11 cyclam BM3 quintet	-653320.53	235.38	-43.19	-653072.24	-653115.43
Fig.S11 cyclam BM3 triplet	-653321.89	235.56	-42.51	-653073.50	-653116.01
Fig.S11 cyclam BM3 AF-singlet	-653297.45	235.21	-42.60	-653049.22	-653091.82
Fig.S11 cyclam BM3 AF-triplet	-653321.88	235.56	-42.49	-653073.50	-653115.99
Fig.S11 cyclam BM4 triplet	-653313.12	236.22	-42.42	-653063.94	-653106.35
Fig.S11 cyclam BM4 AF-singlet	-653308.93	236.94	-40.29	-653059.61	-653099.90
Fig.S11 cyclam BM4 AF-triplet	-653312.96	234.25	-44.88	-653064.95	-653109.83
Fig.S11 cyclam BM2-BM3 TS quintet	-653319.77	234.79	-42.65	-653072.36	-653115.01
Fig.S11 cyclam BM2-BM3 TS triplet	-653320.55	234.99	-42.55	-653072.97	-653115.53
Fig.S11 cyclam BM2-BM3 TS AF-singlet	-653301.47	235.87	-41.29	-653053.20	-653094.49
Fig.S11 cyclam BM3-BM4 TS triplet	-653292.46	235.28	-41.62	-653044.67	-653086.29
Fig.S11 cyclam BM3-BM4 TS AF-singlet	-653295.05	237.17	-38.24	-653046.26	-653084.50
Fig.S11 cyclam BM3-BM4 TS AF-triplet	-653281.28	235.06	-41.47	-653033.70	-653075.17
Fig.S11 TIM BM3 quintet	-748975.51	243.17	-51.20	-748716.09	-748767.29
Fig.S11 TIM BM3 triplet	-748977.23	243.48	-50.46	-748717.65	-748768.11
Fig.S11 TIM BM3 AF-singlet	-748962.61	244.14	-48.55	-748702.73	-748751.28
Fig.S11 TIM BM3 AF-triplet	-748977.09	243.09	-51.34	-748717.71	-748769.06
Fig.S11 TIM BM4 quintet	-748980.36	242.91	-51.35	-748720.87	-748772.22
Fig.S11 TIM BM4 triplet	-748965.68	243.63	-52.27	-748705.49	-748757.76
Fig.S11 TIM BM4 singlet	-748963.25	245.35	-48.06	-748702.24	-748750.30
Fig.S11 TIM BM4 AF-singlet	-748961.98	244.89	-48.55	-748701.17	-748749.72
Fig.S11 TIM BM4 AF-triplet	-748968.42	243.20	-50.56	-748708.78	-748759.34
Fig.S11 TIM BM2-BM3 TS quintet	-748970.87	241.81	-50.69	-748712.99	-748763.68
Fig.S11 TIM BM2-BM3 TS triplet	-748975.34	242.31	-50.79	-748716.94	-748767.73
Fig.S11 TIM BM2-BM3 TS AF-singlet	-748960.76	242.79	-48.42	-748702.26	-748750.68
Fig.S11 TIM BM3-BM4 TS quintet	-748962.49	241.89	-52.10	-748704.16	-748756.26
Fig.S11 TIM BM3-BM4 TS triplet	-748962.09	241.90	-51.44	-748703.75	-748755.18
Fig.S11 TIM BM3-BM4 TS AF-singlet	-748951.84	243.17	-48.82	-748692.86	-748741.69
Fig.S11 TIM BM3-BM4 TS AF-triplet	-748962.09	241.90	-51.43	-748703.75	-748755.18
Fig.S12 DIM HM3 quintet	-701440.62	246.84	-48.15	-701178.77	-701226.92
Fig.S12 DIM HM3 triplet	-701440.06	248.01	-46.58	-701177.48	-701224.06
Fig.S12 DIM HM3 singlet	-701427.40	248.12	-44.27	-701165.13	-701209.39
Fig.S12 DIM HM3 AF-singlet	-701442.25	248.21	-45.57	-701179.58	-701225.15
Fig.S12 DIM HM3 AF-triplet	-701443.04	246.68	-48.19	-701181.29	-701229.48

Fig.S12 DIM HM4 quintet	-701456.45	246.78	-47.63	-701194.64	-701242.27
Fig.S12 DIM HM4 triplet	-701459.83	247.72	-47.00	-701197.23	-701244.22
Fig.S12 DIM HM4 singlet	-701475.39	249.94	-43.44	-701211.50	-701254.94
Fig.S12 DIM HM3-HM4 TS quintet	-701438.14	246.43	-47.30	-701177.10	-701224.40
Fig.S12 DIM HM3-HM4 TS triplet	-701430.28	247.48	-45.54	-701168.56	-701214.10
Fig.S12 DIM HM3-HM4 TS AF-singlet	-701430.04	247.44	-44.85	-701168.34	-701213.19
Fig.S12 DIM HM3-HM4 TS AF-triplet	-701439.16	246.36	-46.66	-701178.17	-701224.84
Fig.S12 cyclam HM3 quintet	-653615.36	242.83	-43.33	-653359.37	-653402.70
Fig.S12 cyclam HM3 triplet	-653618.61	244.37	-42.19	-653361.42	-653403.61
Fig.S12 cyclam HM3 AF-singlet	-653622.54	244.72	-40.87	-653365.22	-653406.09
Fig.S12 cyclam HM3 AF-triplet	-653618.33	242.81	-42.96	-653362.39	-653405.35
Fig.S12 cyclam HM4 quintet	-653626.13	243.09	-44.27	-653369.60	-653413.88
Fig.S12 cyclam HM4 triplet	-653629.84	244.26	-42.55	-653372.51	-653415.06
Fig.S12 cyclam HM4 singlet	-653638.64	246.29	-39.70	-653380.08	-653419.78
Fig.S12 cyclam HM4 AF-singlet	-653639.54	246.55	-39.19	-653380.89	-653420.08
Fig.S12 cyclam HM4 AF-triplet	-653623.70	243.34	-43.50	-653367.02	-653410.52
Fig.S12 cyclam HM3-HM4 TS quintet	-653612.10	242.83	-43.34	-653356.32	-653399.66
Fig.S12 cyclam HM3-HM4 TS AF-triplet	-653612.45	242.80	-42.99	-653356.69	-653399.68
Fig.S12 TIM HM3 quintet	-749265.49	250.71	-52.31	-748998.13	-749050.44
Fig.S12 TIM HM3 triplet	-749257.60	251.77	-49.54	-748989.75	-749039.29
Fig.S12 TIM HM3 singlet	-749250.95	251.77	-49.54	-748983.10	-749032.64
Fig.S12 TIM HM3 AF-singlet	-749267.74	251.84	-50.65	-748999.52	-749050.17
Fig.S12 TIM HM3 AF-triplet	-749266.85	250.62	-51.94	-748999.56	-749051.50
Fig.S12 TIM HM4 quintet	-749278.97	248.79	-54.71	-749012.47	-749067.18
Fig.S12 TIM HM4 triplet	-749280.45	250.89	-50.02	-749013.15	-749063.17
Fig.S12 TIM HM4 singlet	-749293.65	253.34	-48.04	-749024.56	-749072.60
Fig.S12 TIM HM4 AF-singlet	-749277.08	251.94	-48.40	-749009.01	-749057.41
Fig.S12 TIM HM4 AF-triplet	-749279.30	250.87	-50.87	-749011.86	-749062.73
Fig.S12 TIM HM3-HM4 TS septet	-749206.48	249.42	-50.33	-748941.01	-748991.34
Fig.S12 TIM HM3-HM4 TS quintet	-749264.69	250.20	-51.68	-748998.12	-749049.80
Fig.S12 TIM HM3-HM4 TS triplet	-749264.88	250.15	-50.86	-748998.45	-749049.30
Fig.S12 TIM HM3-HM4 TS AF-singlet	-749252.70	251.17	-48.87	-748985.62	-749034.49
Fig.S12 TIM HM3-HM4 TS AF-triplet	-749264.88	250.15	-50.86	-748998.45	-749049.30
Fig.S13 cyclam AM3 quintet	-653619.35	242.04	-43.90	-653363.85	-653407.75
Fig.S13 cyclam AM3 triplet	-653621.01	243.55	-43.05	-653364.30	-653407.36
Fig.S13 cyclam AM3 AF-singlet	-653622.55	244.73	-40.84	-653365.24	-653406.08
Fig.S13 cyclam AM3 AF-triplet	-653618.83	242.95	-43.06	-653362.76	-653405.82
Fig.S13 cyclam AM4 quintet	-653638.59	239.45	-46.79	-653384.70	-653431.50
Fig.S13 cyclam AM4 triplet	-653644.73	242.02	-44.09	-653389.05	-653433.13
Fig.S13 cyclam AM4 singlet	-653631.40	242.68	-42.07	-653375.66	-653417.73

Fig.S13 cyclam AM4 AF-singlet	-653641.66	241.96	-43.63	-653385.93	-653429.55
Fig.S13 cyclam AM4 AF-triplet	-653635.70	239.53	-46.28	-653381.79	-653428.06
Fig.S13 cyclam AM5 quintet	-605636.89	223.81	-42.21	-605400.57	-605442.78
Fig.S13 cyclam AM5 singlet	-605644.20	227.64	-38.93	-605405.05	-605443.99
Fig.S13 cyclam AM5 AF-singlet	-605650.28	226.15	-38.68	-605412.67	-605451.35
Fig.S13 cyclam AM5 triplet	-605652.75	226.34	-40.85	-605414.49	-605455.33
Fig.S13 cyclam AM6 quintet	-605925.92	234.61	-41.07	-605679.20	-605720.27
Fig.S13 cyclam AM6 triplet	-605944.11	235.83	-39.83	-605696.57	-605736.40
Fig.S13 cyclam AM6 singlet	-605945.48	236.83	-38.54	-605697.17	-605735.72
Fig.S13 cyclam AM6 AF-singlet	-605945.60	236.67	-38.66	-605697.41	-605736.07
Fig.S13 cyclam AM6 AF-triplet	-605941.81	235.72	-40.11	-605694.32	-605734.43
Fig.S13 cyclam AM3-AM4 TS quintet	-653602.27	237.91	-43.95	-653350.99	-653394.94
Fig.S13 cyclam AM3-AM4 TS triplet	-653613.51	239.10	-43.11	-653361.31	-653404.43
Fig.S13 cyclam AM3-AM4 TS AF-singlet	-653613.28	239.24	-42.90	-653360.92	-653403.82
Fig.S13 DIM AM3 AF-triplet	-701442.31	246.54	-48.58	-701180.64	-701229.22
Fig.S13 DIM AM3 AF-singlet	-701443.51	247.95	-46.63	-701180.90	-701227.54
Fig.S13 DIM AM3 quintet	-701440.30	246.71	-49.00	-701178.47	-701227.46
Fig.S13 DIM AM3-AM4 TS AF-singlet	-701435.50	243.22	-46.45	-701177.49	-701223.94
Fig.S13 DIM AM3-AM4 TS triplet	-701437.03	242.94	-47.71	-701179.12	-701226.83
Fig.S13 DIM AM3-AM4 TS AF-triplet	-701430.55	241.52	-48.00	-701173.78	-701221.77
Fig.S13 DIM AM4 triplet	-701467.11	245.95	-48.02	-701205.86	-701253.88
Fig.S13 DIM AM4 AF-triplet	-701464.41	244.02	-49.15	-701204.55	-701253.70
Fig.S13 DIM AM4 quintet	-701463.40	244.05	-49.87	-701203.47	-701253.34
Fig.S13 DIM AM5 AF-singlet	-653464.80	229.85	-43.89	-653221.29	-653265.18
Fig.S13 DIM AM5 triplet	-653468.74	230.39	-44.00	-653224.84	-653268.84
Fig.S13 DIM AM5 AF-triplet	-653472.45	228.37	-45.18	-653230.06	-653275.24
Fig.S13 DIM AM5 quintet	-653470.35	228.18	-46.14	-653228.00	-653274.14
Fig.S13 DIM AM6 singlet	-653764.56	240.32	-43.41	-653510.95	-653554.36
Fig.S13 DIM AM6 triplet	-653762.75	239.48	-44.03	-653509.75	-653553.78
Fig.S13 DIM AM6 AF-triplet	-653753.93	237.92	-47.10	-653501.65	-653548.75
Fig.S13 DIM AM6 quintet	-653753.67	238.16	-46.55	-653501.29	-653547.84

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