

Supporting Information for

17 e⁻ Rhenium Dicarbonyl CO-Releasing Molecules on a Cobalamin Scaffold for Biological Application

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Figure S5. Theoretical UV-Vis absorption spectra (in H₂O) of the *cis-trans*-[Re^{II}(CO)₂Br₂(H₂O)(N≡C-H)] and *cis*-[Re^{II}(CO)₂(H₂O)₃(N≡C-H)]²⁺ species.

Figure S6. HPLC trace recorded ca. 30 min after dissolution of B₁₂-ReCORM-2 in water. Species number assignments are as shown in Scheme 2. The identity of the species was derived from HPLC-MS analysis.

Figure S7. HPLC trace of B₁₂-ReCORM-4.

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Figure S9. Left: liquid IR spectrum of ReCORM-1 in phosphate buffer (0.1M, pH = 7.4) 2 and 30 min after dissolution. Right: MS spectra (negative mode) of a H₂O:CH₃OH (3:1) solution of ReCORM-1 after dissolution (top) and after 12h (bottom) (S_a = H₂O, S_b = CH₃OH). Methanol is present as a required volatile solvent for the ionization of the sample.

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Figure S13. Effect of CORMs' supplementation on the oxygen levels in the cell-free culture medium. Top: original recording of the changes in O₂ concentrations (in blue) and oxygen flux (in red) over time of experiment. Addition of ReCORM-1 at concentrations 7.5-75 µM had no effect on the basal

O₂ flux (M(0)) during the time on 30 min, but resulted in acute dose-dependent changes in O₂ levels (blue line) and in O₂ flux levels (M7.5)-M(75). New steady state O₂ levels were reached with 1-2 min after ReCORM-1 administration. Bottom: Acute changes in O₂ flux as a function of ReCORM-1 concentration.

Figure S14. Oxygen consumption by NRCs exposed to various concentrations of CORMs concentration. Changes in oxygen concentrations in the cell culture medium were measured during the 40 min of incubation of NRCs in Oxygraph-2k. Oxygen consumption by cells was assessed as “basal” steady state O₂ flux recorded ~4-5 min after the CORM administration (see the example in Fig S14A) which was sensitive to the inhibitors of mitochondrial complexes I-III (rotenone, antimycin A and KCN). Responses of the cells to addition of DMSO alone (in control) or the aliquots of 100 mM stock solutions of CORMs in DMSO were recorded as a function of CORMs concentration.

Figure S15. ¹H-NMR spectrum (500 MHz, D₂O, 300 K) of **3**.

Table S1. Crystallographic data for compounds **3** and **5**.

Table S2. Cartesian coordinates of DFT optimized molecules.

Figure S16. Two-layer ONIOM(B3LYP/LanL2DZ:UFF) optimized B₁₂-ReCORM-2 and B₁₂-ReCORM-4. The different layers are represented with balls and sticks (high) and wireframe (low).

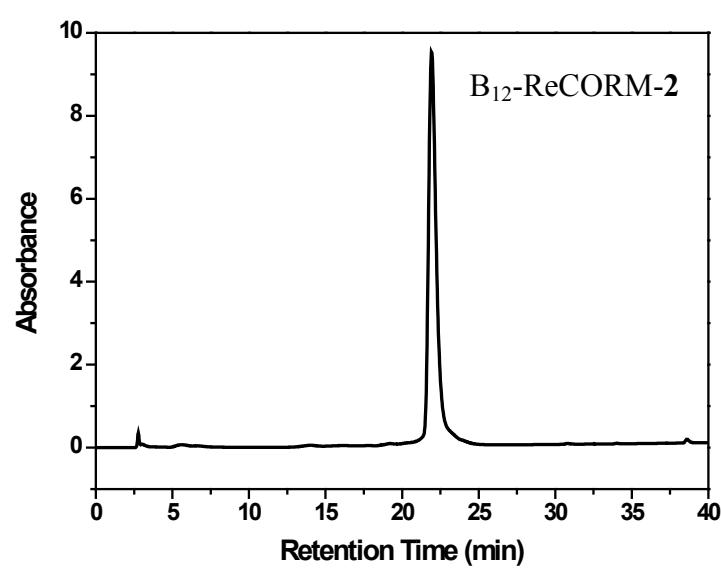


Figure S1. HPLC trace of B₁₂-ReCORM-2.

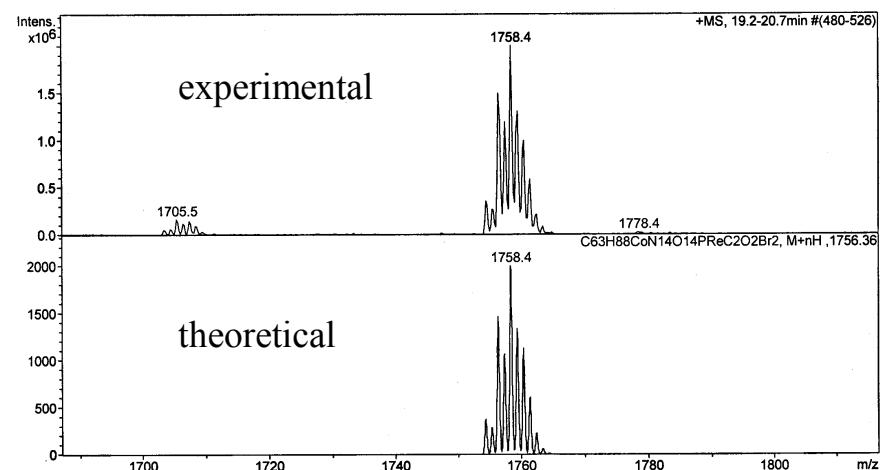


Figure S2. MS spectrum of B₁₂-ReCORM-2.

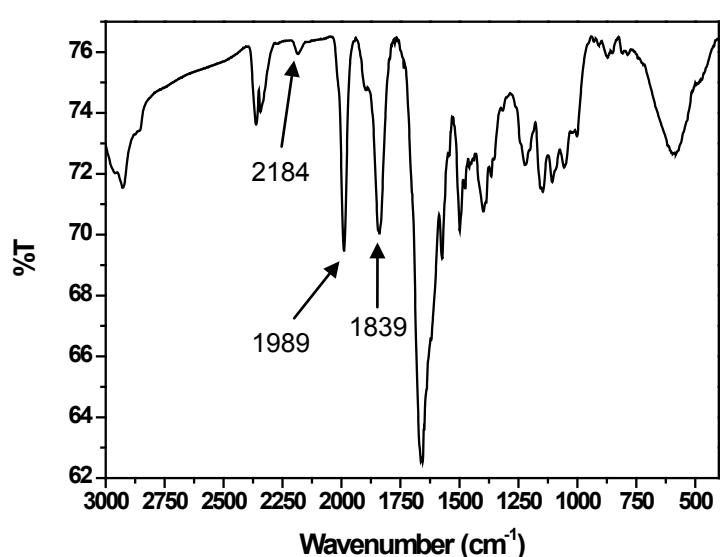


Figure S3. IR spectrum of B₁₂-ReCORM-2.

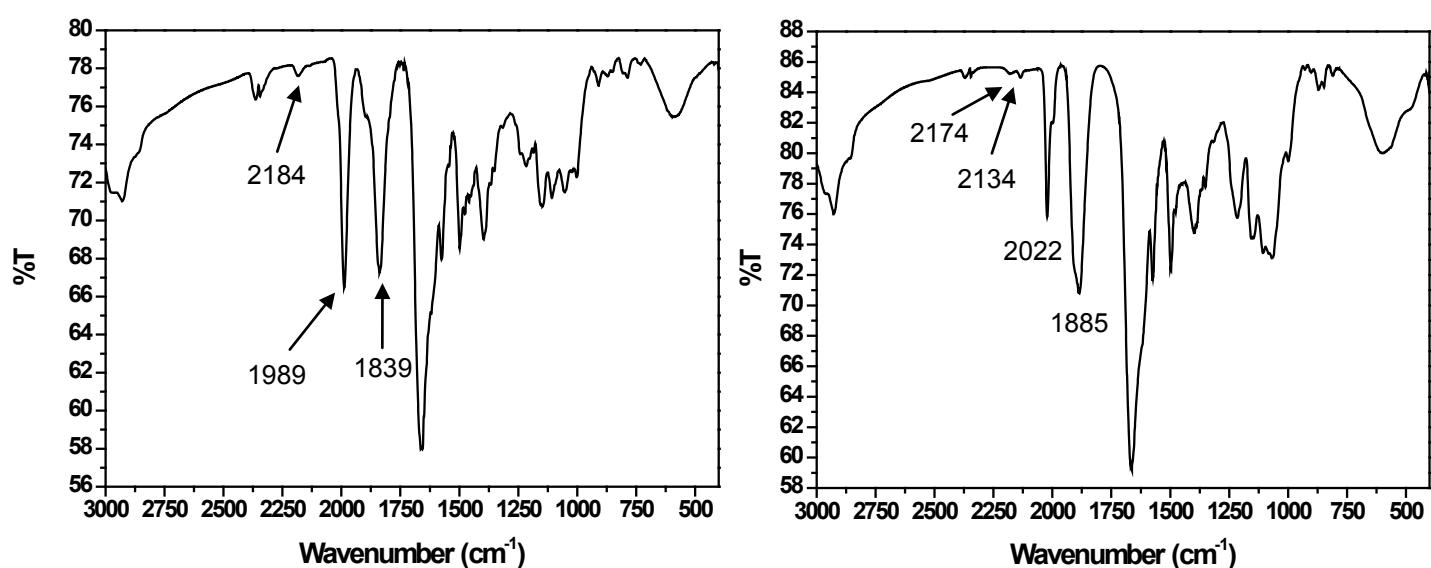


Figure S4. IR spectrum of B₁₂-ReCORM-4 (left) and of the product collected after prolonged reaction time (right).

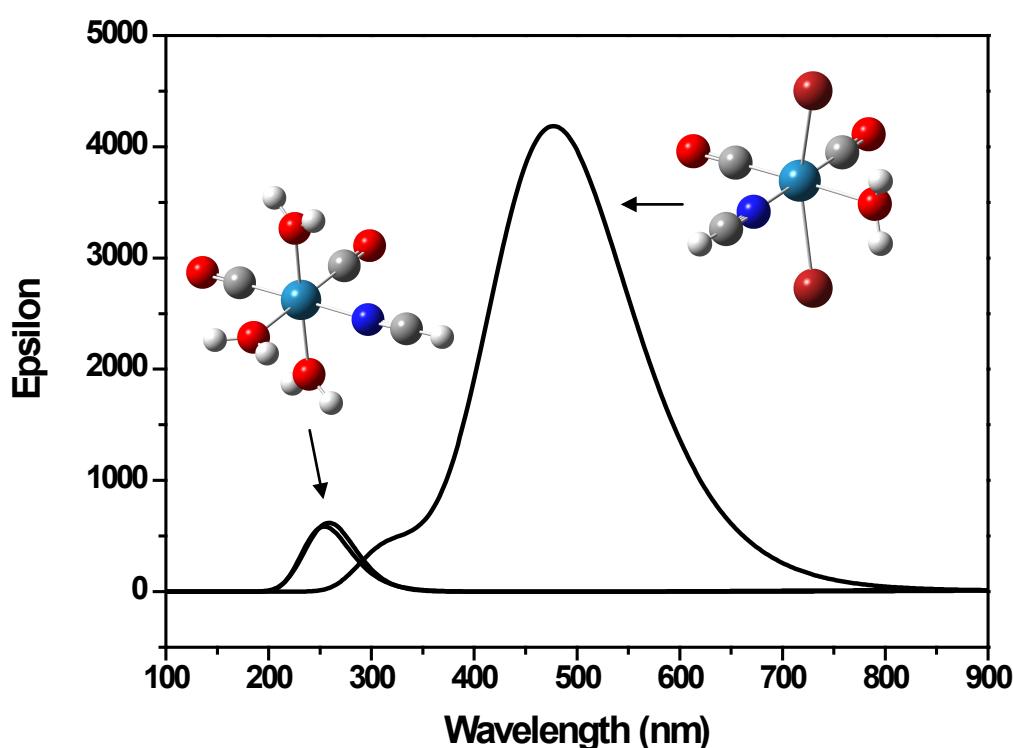


Figure S5. Theoretical UV-Vis absorption spectra (in H₂O) of the *cis-trans*-[Re^{II}(CO)₂Br₂(H₂O)(N≡C-H)] and *cis*-[Re^{II}(CO)₂(H₂O)₃(N≡C-H)]²⁺ species.

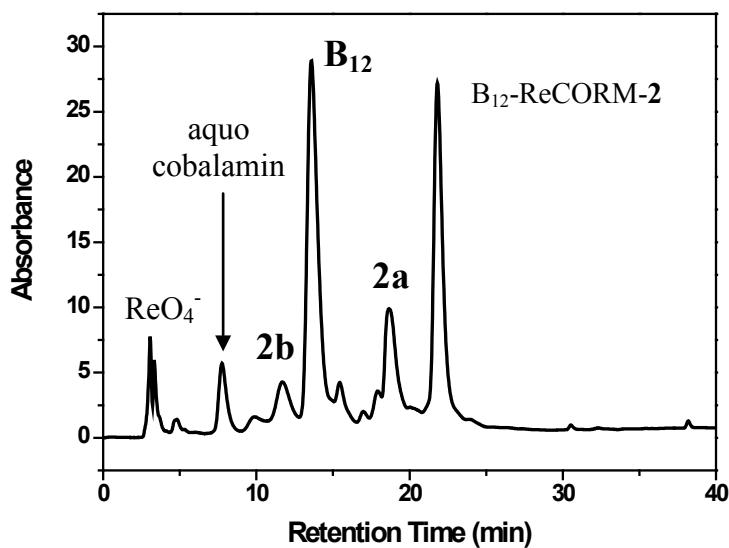


Figure S6. HPLC trace recorded ca. 30 min after dissolution of B₁₂-ReCORM-2 in water. Species number assignments are as shown in Scheme 2. The identity of the species was derived from HPLC-MS analysis.

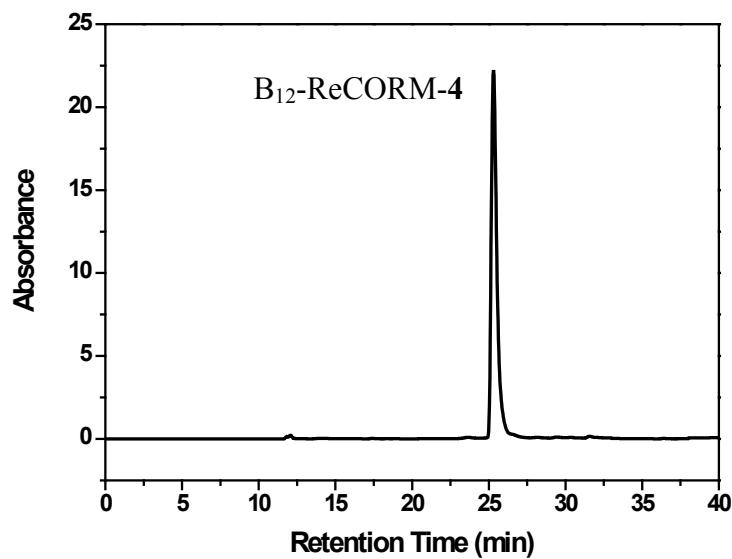


Figure S7. HPLC trace of $B_{12}\text{-ReCORM-4}$.

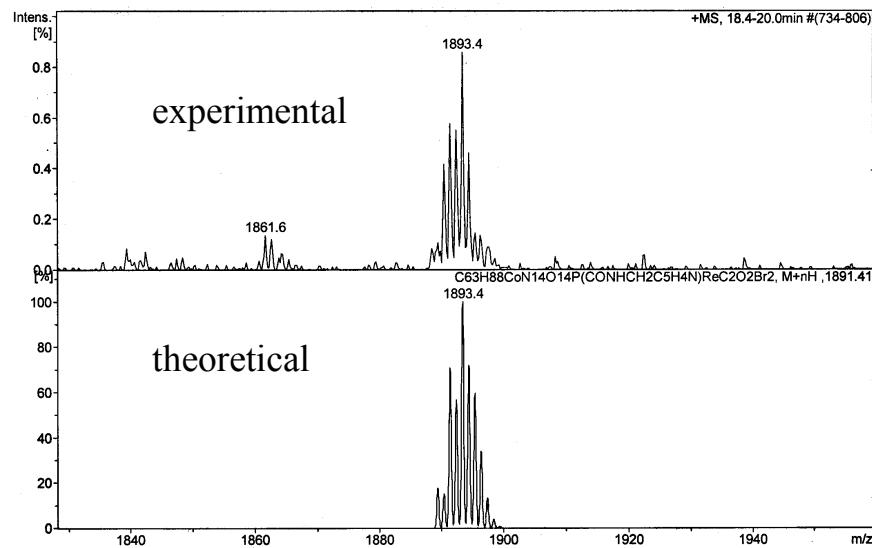


Figure S8. MS spectrum of $B_{12}\text{-ReCORM-4}$.

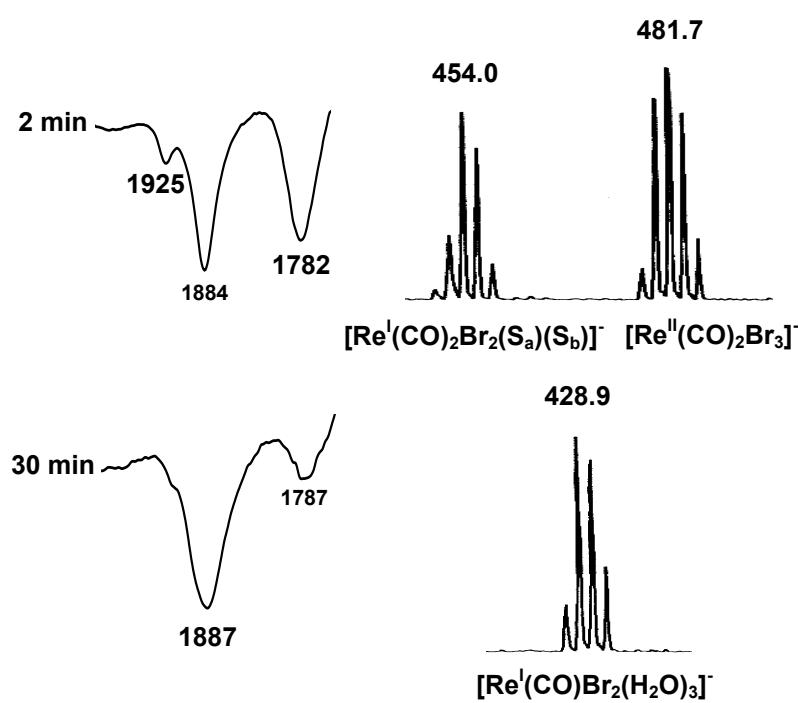


Figure S9. Left: liquid IR spectrum of ReCORM-1 in phosphate buffer (0.1M, pH = 7.4) 2 and 30 min after dissolution. Right: MS spectra (negative mode) of a H₂O:CH₃OH (3:1) solution of ReCORM-1 after dissolution (top) and after 12h (bottom) (S_a = H₂O, S_b = CH₃OH). Methanol is present as a required volatile solvent for the ionization of the sample.

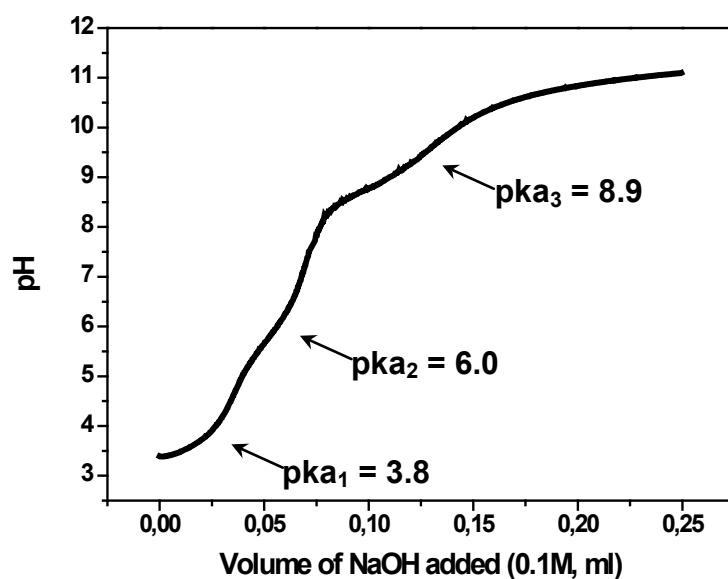


Figure S10. Titration curve of an aqueous solution of ReCORM-1 (0.1M KNO₃, 25 °C, completed within 15 min).

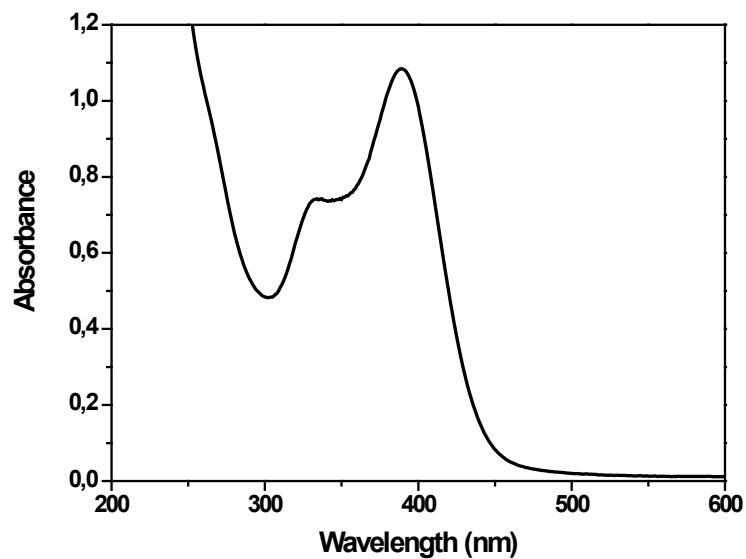


Figure S11. UV-Vis absorption spectrum of ReCORM-1 soon after dissolution in water.

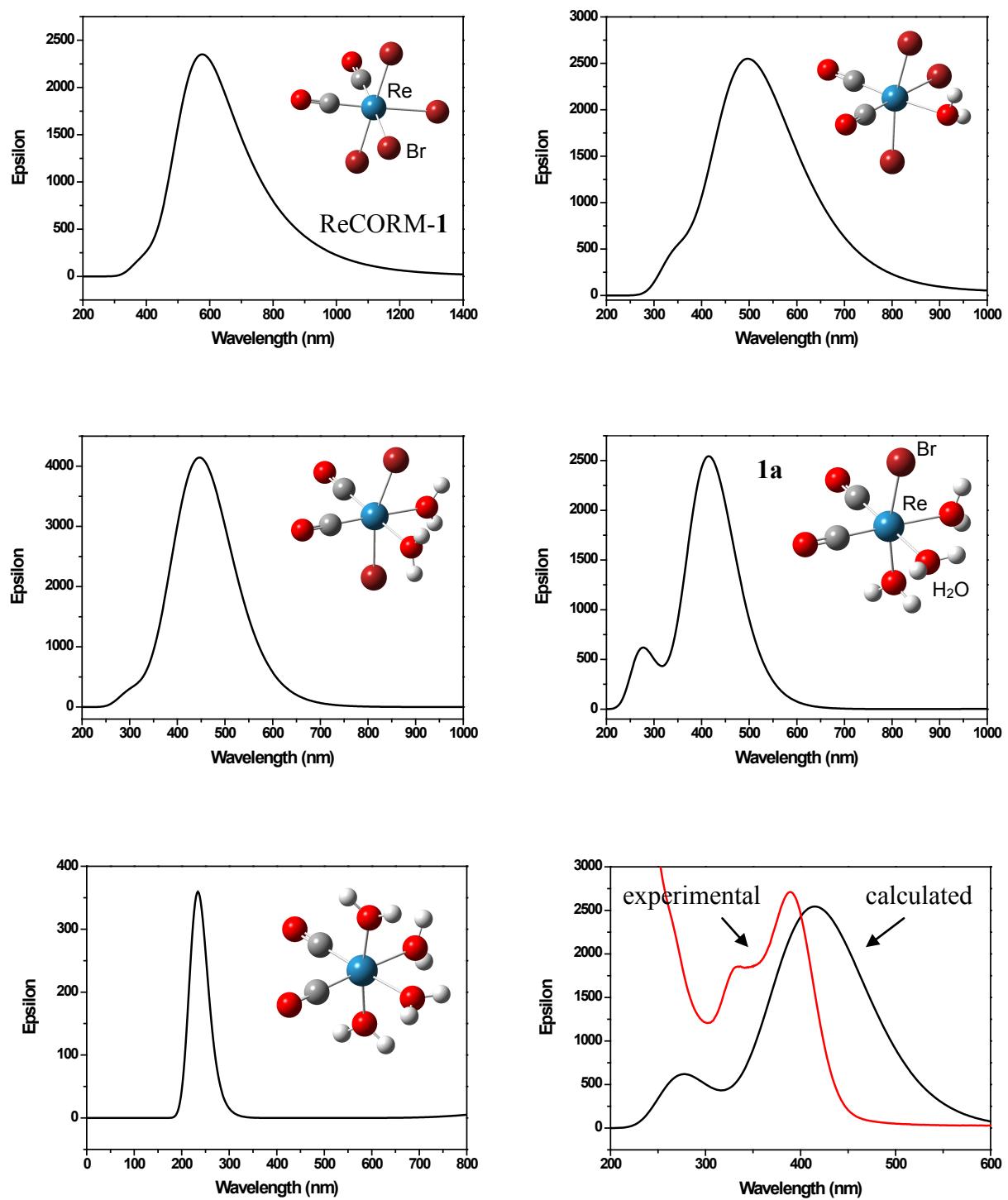


Figure S12. Calculated UV-Vis absorption spectra (in H₂O) of the progressive aquation of ReCORM-1. Bottom-left spectrum shows a superimposition of the experimental spectrum of ReCORM-1 soon after dissolution in water and the theoretical spectrum of *cis*-[Re^{II}(CO)₂Br(H₂O)₃]⁺ (**1a** in Scheme 3).

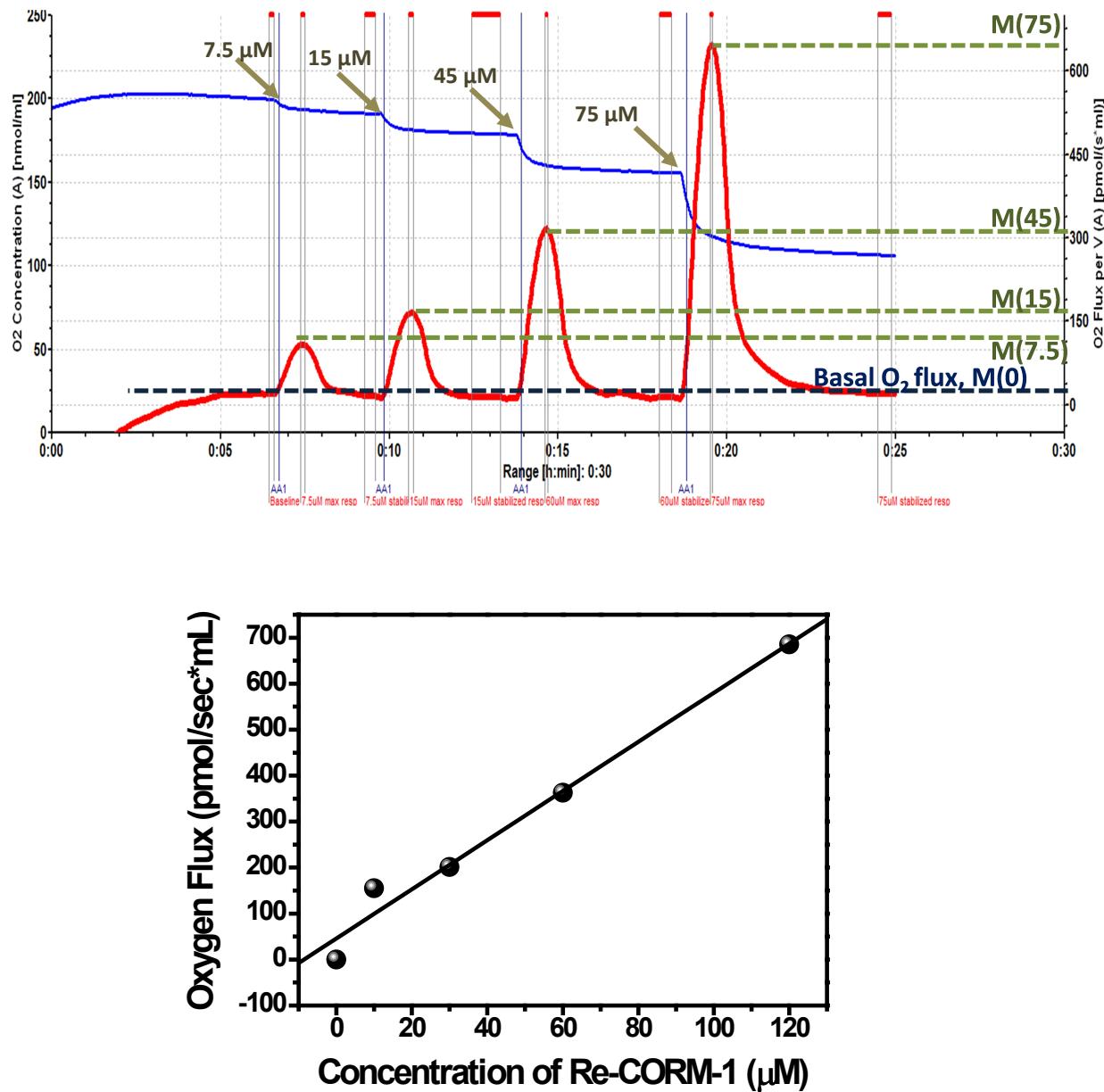


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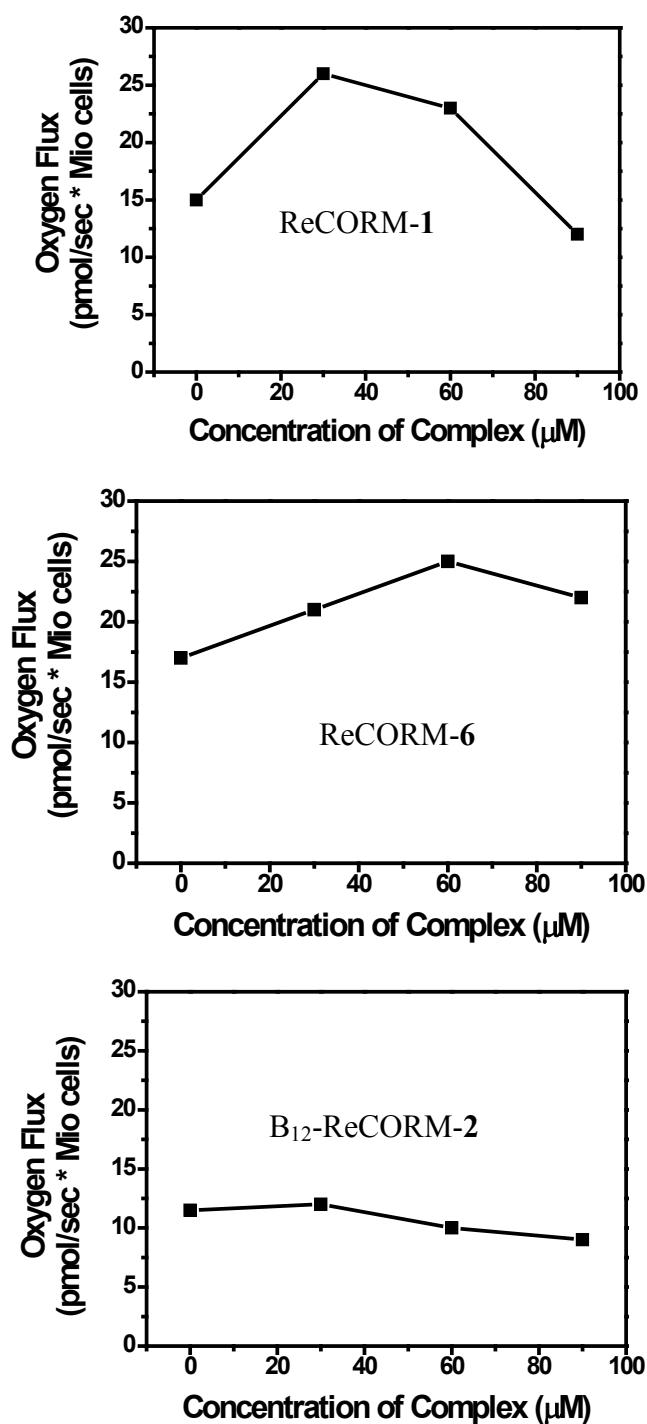


Figure S14. Oxygen consumption by NRCs exposed to various concentrations of CORMs concentration. Changes in oxygen concentrations in the cell culture medium were measured during the 40 min of incubation of NRCs in Oxygraph-2k. Oxygen consumption by cells was assessed as “basal” steady state O_2 flux recorded ~4–5 min after the CORM administration (see the example in Fig S14A) which was sensitive to the inhibitors of mitochondrial complexes I-III (rotenone, antimycin A and KCN). Responses of the cells to addition of DMSO alone (in control) or the aliquots of 100 mM stock solutions of CORMs in DMSO were recorded as a function of CORMs concentration.

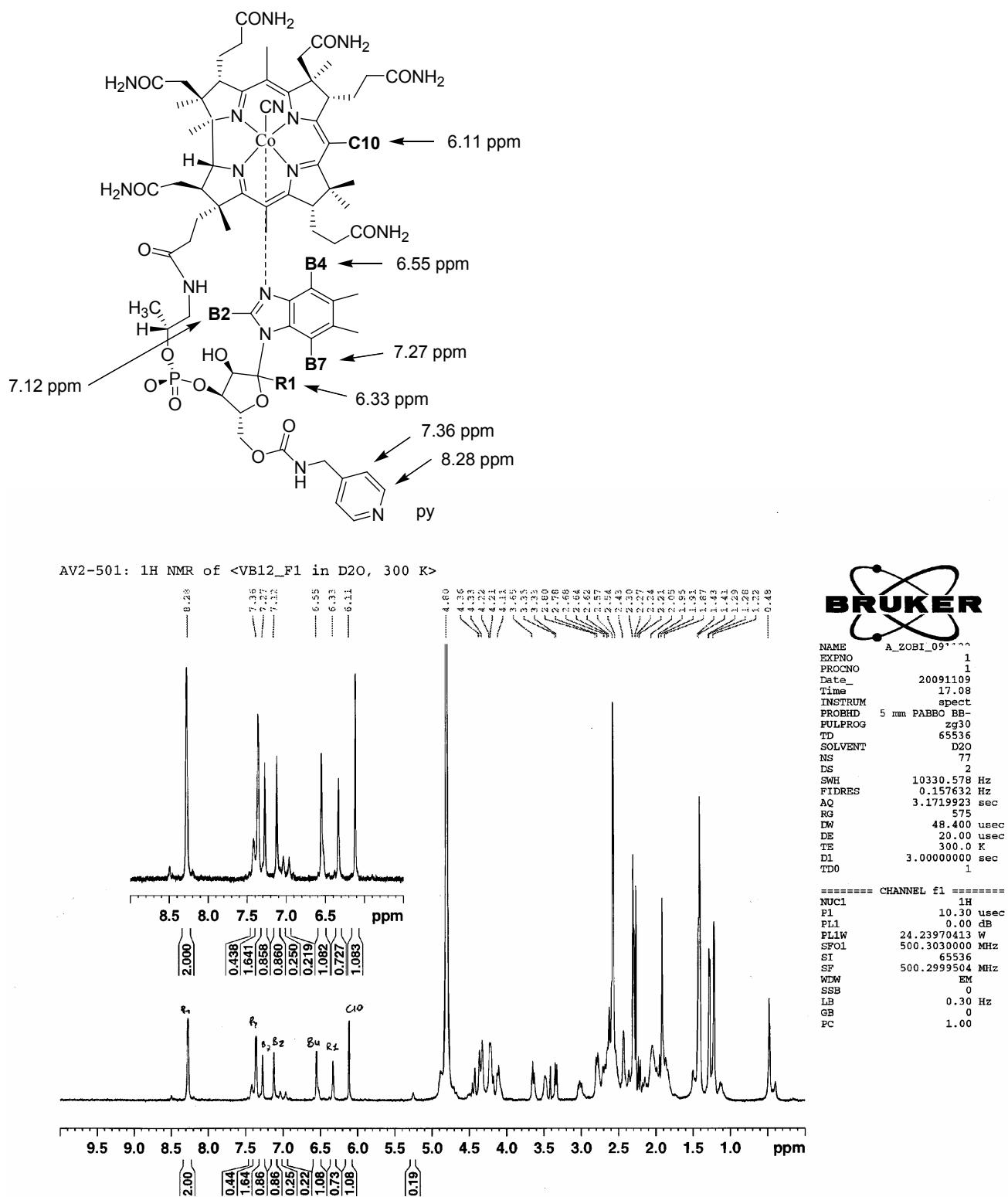


Figure S15. ¹H-NMR spectrum (500 MHz, D₂O, 300 K) of **3**.

Table S1. Crystallographic data for compounds **3** and **5**.

| | 3 | 5 |
|---|--|---|
| empirical formula | $2(\text{C}_{70}\text{H}_{94}\text{CoN}_{16}\text{O}_{15}\text{P}) \cdot 5(\text{C}_3\text{H}_6\text{O}) \cdot 16(\text{H}_2\text{O})$ | $\frac{0.53(\text{C}_{63}\text{H}_{86}\text{CoN}_{14}\text{O}_{14}\text{P})}{\cdot 0.47(\text{C}_{66}\text{H}_{88}\text{CoBrN}_{14}\text{O}_{18}\text{PRe})} \cdot \underline{\text{C}_3\text{H}_6\text{O}} \cdot \underline{6.53(\text{H}_2\text{O})}$ |
| formula weight (g·mol ⁻¹) | 3525.43 | 1700.37 |
| temperature (K) | 183(2) | 183(2) |
| wavelength (Å) | 0.71073 | 0.71073 |
| crystal system, space group | orthorhombic, $P\ 2_12_12_1$ | orthorhombic, $P\ 2_12_12_1$ |
| <i>a</i> (Å) | 15.5066(4) | 15.8806(2) |
| <i>b</i> (Å) | 22.9558(7) | 21.8255(3) |
| <i>c</i> (Å) | 25.1741(7) | 26.2738(4) |
| α (deg) | 90 | 90 |
| β (deg) | 90 | 90 |
| γ (deg) | 90 | 90 |
| volume (Å ³) | 8961.1(4) | 9106.6(2) |
| <i>Z</i> , density (calcd) (Mg·m ⁻³) | 2, 1.307 | 4, 1.240 |
| abs coefficient (mm ⁻¹) | 0.291 | 1.096 |
| <i>F</i> (000) | 3728 | 3559.4 |
| crystal size (mm ³) | 0.49 x 0.07 x 0.03 | 0.48 x 0.20 x 0.06 |
| θ range (deg) | 2.58 to 25.68 | 2.57 to 27.10 |
| reflections collected | 71958 | 79318 |
| reflections unique | 16995 / $R_{\text{int}} = 0.1164$ | 20093 / $R_{\text{int}} = 0.0603$ |
| completeness to θ (%) | 99.8 | 99.9 |
| absorption correction | analytical | analytical |
| max/min transmission | 0.988 and 0.895 | 0.884 and 0.530 |
| data / restraints / parameters | 8376 / 117 / 1123 | 13534 / 113 / 1076 |
| goodness-of-fit on F^2 | 0.898 | 1.063 |
| final R_I and wR_2 indices [$I > 2\sigma(I)$] | 0.0722, 0.1465 | 0.0656, 0.1816 |
| R_I and wR_2 indices (all data) | 0.1487, 0.1655 | 0.0932, 0.1884 |
| absolute structure parameter | 0.03(2) | 0.039(7) |
| largest diff. peak and hole (e·Å ⁻³) | 0.786, -0.495 | 1.140, -0.560 |

The unweighted *R*-factor is $R_I = \sum(Fo - Fc)/\sum Fo$; $I > 2\sigma(I)$ and the weighted *R*-factor is $wR_2 = \{\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2\}^{1/2}$

Table S2. Cartesian coordinates of DFT optimized molecules.

Cartesian coordinates of $[\text{Re}^{\text{II}}(\text{CO})_2(\text{H}_2\text{O})_4]^{2+}$

| | | | |
|----|-------------|-------------|-------------|
| Re | 0.10811700 | -0.00458200 | 0.00318700 |
| C | -1.28960900 | 1.32298300 | -0.01831200 |
| C | -1.35378300 | -1.29154100 | 0.01441500 |
| H | 2.71849900 | -1.15904800 | 0.04172600 |
| H | -0.46665400 | 0.29830900 | 2.70185500 |
| H | 2.13273400 | 1.82510000 | -0.86668000 |
| O | 0.26437300 | 0.03956400 | 2.10138900 |
| O | 1.82019300 | 1.40141400 | -0.03930100 |
| O | 1.77975400 | -1.44079900 | 0.02840900 |
| O | -2.23991300 | -2.05247300 | 0.01205800 |
| O | -2.13242700 | 2.13597000 | -0.02832100 |
| H | 0.99150800 | -0.50374900 | -2.57354300 |
| O | 0.26677000 | -0.04567900 | -2.09700000 |
| H | 1.69838900 | -2.41689400 | 0.04329500 |
| H | 1.00792800 | -0.36605100 | 2.59610200 |
| H | 2.05563100 | 1.96123200 | 0.73101600 |
| H | -0.45647100 | 0.21213600 | -2.70726000 |

Cartesian coordinates of $[\text{Re}^{\text{II}}(\text{CO})_2\text{Br}(\text{H}_2\text{O})_3]^+$

| | | | |
|----|-------------|-------------|-------------|
| Re | 0.37993100 | -0.11548600 | 0.01081900 |
| C | 0.58895300 | 1.28821100 | 1.29377800 |
| C | 0.71060600 | 1.26365500 | -1.26868900 |
| H | -0.19089800 | -2.63088000 | -1.04362200 |
| H | 0.51416800 | -2.16451500 | 2.05808800 |
| O | -0.08857100 | -1.82424100 | 1.36734500 |
| O | 0.25492400 | -1.82793100 | -1.38356400 |
| O | 0.90490700 | 2.11851400 | -2.05677900 |
| O | 0.71761600 | 2.15430800 | 2.08219100 |
| H | 2.64889200 | -1.67169600 | -0.32096700 |
| O | 2.40775900 | -0.83906000 | 0.13261200 |
| H | 0.09642800 | -1.70752100 | -2.34088400 |
| H | -1.02781700 | -1.85347900 | 1.65320400 |
| H | 3.18151800 | -0.27432900 | 0.32076000 |
| Br | -2.14535800 | 0.15428400 | -0.06922900 |

Cartesian coordinates of $[\text{Re}^{\text{II}}(\text{CO})_2\text{Br}_2(\text{H}_2\text{O})_2]$

| | | | |
|----|-------------|-------------|-------------|
| Re | 0.00015000 | 0.04469300 | -0.00091300 |
| C | -0.00044200 | 1.45039100 | 1.27641700 |
| C | 0.00024500 | 1.45524700 | -1.27300800 |
| Br | -2.57211600 | -0.34575000 | 0.00033100 |
| Br | 2.57225000 | -0.34565100 | 0.00057700 |
| O | 0.00029800 | 2.34165600 | -2.06078900 |
| O | -0.00129800 | 2.33294700 | 2.06860200 |
| O | 0.00005100 | -1.63422000 | 1.42850800 |
| H | -0.82543800 | -1.96887700 | 1.82501700 |
| H | 0.82580900 | -1.96930000 | 1.82416200 |
| H | 0.82464200 | -1.97302400 | -1.82282400 |
| O | -0.00066000 | -1.62801500 | -1.43515100 |
| H | -0.82691000 | -1.97453300 | -1.81952000 |

Cartesian coordinates of [Re^{II}(CO)₂Br₃(H₂O)]⁻

| | | | |
|----|-------------|-------------|-------------|
| Re | -0.01194800 | -0.24451600 | 0.05232300 |
| C | 0.00796500 | -2.15145400 | -0.14846600 |
| C | -0.08500700 | -0.55018500 | 1.90312000 |
| Br | -2.59872300 | -0.33432200 | -0.38651700 |
| Br | -0.03358600 | 2.44169900 | 0.21950200 |
| Br | 2.63403200 | -0.31162700 | -0.28115700 |
| O | -0.12620300 | -0.73516600 | 3.08298300 |
| O | 0.01825400 | -3.33742200 | -0.23730900 |
| O | 0.15587000 | 0.33603800 | -2.13085500 |
| H | -0.20907300 | 1.25002600 | -2.16921600 |
| H | 1.12374500 | 0.33964500 | -2.31544600 |

Cartesian coordinates of [Re^{II}(CO)₂Br₄]²⁻

| | | | |
|----|-------------|-------------|-------------|
| Re | 0.00000000 | 0.00000000 | 0.33761800 |
| C | 0.00000000 | 1.28941400 | 1.72049300 |
| C | 0.00000000 | -1.28941400 | 1.72049300 |
| Br | 2.69052600 | 0.00000000 | 0.31932600 |
| Br | 0.00000000 | -1.97098400 | -1.57803500 |
| Br | 0.00000000 | 1.97098400 | -1.57803500 |
| Br | -2.69052600 | 0.00000000 | 0.31932600 |
| O | 0.00000000 | -2.06884400 | 2.63389600 |
| O | 0.00000000 | 2.06884400 | 2.63389600 |

Cartesian coordinates of B12-ReCORM-4

| | | | |
|---|-------------|-------------|-------------|
| H | -1.29382800 | -2.22505300 | -3.78675700 |
| C | -0.14250300 | -0.39865600 | -4.23516400 |
| C | -1.21009800 | -1.20818500 | -3.39604200 |
| H | 1.06350200 | 2.14504000 | -4.38029700 |
| C | -0.55593800 | -1.18159500 | -1.96979400 |
| C | 0.44408200 | 0.50902100 | -3.15064300 |
| C | -0.88441000 | -2.02676500 | -0.90526900 |
| C | 1.11395200 | 1.71375600 | -3.38784800 |
| H | -2.08214300 | -4.16381800 | 1.24962400 |
| N | 0.31325900 | -0.08184300 | -1.92192000 |
| O | -4.68513900 | -3.44660700 | 1.29109700 |
| H | 2.95926300 | 3.57150900 | -4.02158100 |
| C | 2.68206400 | -0.66965000 | -0.78259500 |
| C | -0.25637500 | -1.90562500 | 0.41654100 |
| C | -1.72305100 | -3.43685600 | 2.00223100 |
| C | 1.98462300 | 2.35652000 | -2.51091000 |
| C | -0.30602400 | -2.92640900 | 1.62658800 |
| H | -6.85883200 | 0.88284000 | -1.19665100 |
| H | -1.67047300 | -4.03906200 | 2.92938100 |
| C | 2.82986500 | 3.54595500 | -2.93507000 |
| H | -6.31727000 | -4.36932900 | 3.05434100 |
| C | -4.15833000 | -2.93763400 | 2.31852600 |
| N | 0.57102800 | -0.90737000 | 0.70808400 |

| | | | |
|----|-------------|-------------|-------------|
| Co | 1.31955900 | 0.53061200 | -0.35233500 |
| H | -2.77417300 | -1.60453500 | 1.38219600 |
| H | -8.77227100 | -3.84631600 | 2.75372800 |
| N | 2.33538400 | 1.92973900 | -1.26839800 |
| C | 4.18316600 | 3.21127400 | -2.14500500 |
| H | 2.21881600 | -1.64739900 | 1.74839700 |
| C | -2.78314600 | -2.33608500 | 2.21503500 |
| H | -4.24265700 | -0.34173100 | -0.12429300 |
| C | -6.10293300 | 0.06646600 | -1.13538600 |
| H | -1.81029400 | 0.50351200 | -0.43969700 |
| H | -5.69163600 | -0.13113100 | -2.14822200 |
| C | -6.19540700 | -3.43547500 | 3.64703100 |
| C | 3.59790600 | 2.43861200 | -0.90238900 |
| C | 0.33875500 | -2.05343400 | 2.80164300 |
| C | 1.30415700 | -1.10853600 | 2.02012400 |
| O | -4.25510800 | 1.58396200 | -0.82081100 |
| C | -4.95158800 | 0.51140600 | -0.23200600 |
| C | -1.49090400 | 1.48490600 | -0.12973800 |
| C | -8.63925500 | -2.92553200 | 3.36126000 |
| H | -6.36806500 | -3.69787200 | 4.71430300 |
| H | -2.56640100 | -1.77437800 | 3.14518900 |
| N | -0.21860800 | 1.85177900 | 0.01310300 |
| H | -9.37465600 | -2.16987100 | 3.01226200 |
| H | -0.43544900 | -1.42982500 | 3.26019400 |
| N | 2.21598000 | 0.99095400 | 1.28219600 |
| H | -8.84901200 | -3.16101600 | 4.42697400 |
| C | 4.13843100 | 2.23018800 | 0.36209300 |
| N | -2.35951500 | 2.50465100 | 0.20406400 |
| C | 1.70797200 | 0.33018500 | 2.54911000 |
| C | -3.79889900 | 2.41202600 | 0.23073900 |
| C | 3.34510900 | 1.65585400 | 1.43406100 |
| C | -5.44045200 | 0.96384300 | 1.13787700 |
| C | -0.23767900 | 3.19093900 | 0.47633100 |
| H | -4.23130000 | 3.42308100 | 0.06442900 |
| O | -5.57539100 | -0.09410100 | 1.94705000 |
| O | -7.07957700 | -1.28936700 | 3.96440300 |
| C | 2.98965000 | 0.52811700 | 3.56536200 |
| O | -8.18124600 | 0.32964900 | 2.20635600 |
| C | -1.58889300 | 3.61197800 | 0.61003500 |
| H | 1.83522400 | 3.76875000 | 0.72214700 |
| H | -6.36379600 | 1.57953500 | 0.99441300 |
| C | -4.31861700 | 1.87429300 | 1.57127000 |
| H | 4.81152200 | 1.71008600 | 3.04146000 |
| C | 0.80207100 | 4.07532500 | 0.81632100 |
| C | 3.72968700 | 1.79317000 | 2.92074400 |
| P | -6.90976800 | 0.11239200 | 2.99916200 |
| C | -1.92150400 | 4.89519400 | 1.07640500 |
| H | -4.69339900 | 2.69609700 | 2.21955200 |
| H | -2.95435800 | 5.21527900 | 1.18303700 |
| C | 0.48980600 | 5.36528200 | 1.26936500 |
| H | 2.58866000 | 5.89815500 | 1.36686300 |

| | | | |
|---|-------------|-------------|------------|
| C | -0.88003600 | 5.77816000 | 1.40314200 |
| O | -6.67131800 | 1.30280500 | 3.90040900 |
| H | 1.51603100 | 7.27574200 | 1.07720300 |
| C | 1.61283400 | 6.32537100 | 1.61894000 |
| H | -2.29288800 | 7.32371600 | 1.97149900 |
| C | -1.21086200 | 7.17636700 | 1.88942900 |
| H | 1.62004900 | 6.56887700 | 2.69091100 |
| H | -0.82079300 | 7.94113100 | 1.20336700 |
| H | -0.76839500 | 7.37761700 | 2.87433300 |
| N | -4.83199100 | -2.92151200 | 3.49958100 |
| H | -4.39982300 | -2.45986100 | 4.33191200 |
| C | -7.21815700 | -2.38144700 | 3.19803000 |
| H | -7.05593300 | -2.22578900 | 2.10289200 |
| O | -3.32923500 | 1.15750500 | 2.25889200 |
| C | 0.58020000 | -4.13147500 | 1.26080200 |
| H | 0.59498700 | -4.87717400 | 2.08134900 |
| H | 0.21570800 | -4.65624400 | 0.35929200 |
| H | 1.62169800 | -3.81417800 | 1.05194900 |
| C | 1.03000100 | -2.82361300 | 3.93526300 |
| H | 1.49005700 | -2.10210400 | 4.62895400 |
| H | 1.84718900 | -3.46229200 | 3.54111900 |
| O | -0.85510000 | -3.05570500 | 5.38730400 |
| C | 0.07660900 | -3.63278500 | 4.76472700 |
| N | 0.25738100 | -5.04096900 | 4.91548500 |
| H | 1.05373200 | -5.53301900 | 4.45345200 |
| H | -0.40378700 | -5.59510000 | 5.50357100 |
| C | 0.43295000 | 1.05165200 | 3.02897900 |
| H | -0.42669000 | 0.84942600 | 2.36239600 |
| H | 0.12844500 | 0.69939800 | 4.03503500 |
| H | 0.56435600 | 2.14637300 | 3.05899000 |
| C | 2.58773700 | 0.73106800 | 5.03672400 |
| H | 3.47678300 | 0.87640800 | 5.68027900 |
| H | 1.94414900 | 1.62133800 | 5.17622900 |
| H | 2.03459400 | -0.14289900 | 5.42483200 |
| C | 3.96038300 | -0.68439600 | 3.45304500 |
| H | 3.45363600 | -1.62083500 | 3.73654500 |
| H | 4.27598600 | -0.80959900 | 2.39379400 |
| C | 5.20719400 | -0.58500200 | 4.29624600 |
| O | 6.29063500 | -0.21956600 | 3.76629500 |
| H | 6.10737600 | -1.12250200 | 6.17625400 |
| H | 4.36160300 | -1.53343000 | 6.04057300 |
| N | 5.22498000 | -1.12529400 | 5.61822600 |
| C | 3.35707300 | 3.21157300 | 3.40788600 |
| H | 3.53675500 | 3.93323000 | 2.58066100 |
| H | 2.28544100 | 3.28869800 | 3.65716100 |
| C | 4.20549000 | 3.69058600 | 4.59591600 |
| H | 4.03706200 | 3.05950100 | 5.48881700 |
| H | 5.28353200 | 3.62819900 | 4.32913800 |
| C | 3.86434400 | 5.10879800 | 4.94863700 |
| O | 4.72352800 | 6.01731100 | 4.79458600 |
| H | 2.33899200 | 6.42487000 | 5.70625900 |

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|---|-------------|-------------|-------------|
| H | 1.86601600 | 4.69042000 | 5.64516400 |
| N | 2.57728700 | 5.43531300 | 5.47371400 |
| C | 5.60473300 | 2.44793100 | 0.64333200 |
| H | 6.21556000 | 2.48942900 | -0.27003700 |
| H | 5.74576000 | 3.37610300 | 1.23536000 |
| H | 6.02181400 | 1.58234000 | 1.19824600 |
| C | 4.97695900 | 4.47155100 | -1.76741900 |
| H | 6.01798200 | 4.25220900 | -1.46792500 |
| H | 5.04867100 | 5.15431500 | -2.63975700 |
| H | 4.48355900 | 5.01386200 | -0.93298600 |
| C | 5.05361300 | 2.23141800 | -2.97145100 |
| H | 4.46984300 | 1.30967800 | -3.19166600 |
| H | 5.93389900 | 1.89305000 | -2.38942100 |
| C | 5.54006700 | 2.80773600 | -4.27473400 |
| H | 7.09668700 | 3.93807100 | -5.23808900 |
| H | 7.30886600 | 3.74296000 | -3.46444800 |
| N | 6.74303300 | 3.57524600 | -4.32521400 |
| O | 4.96277300 | 2.49178500 | -5.34940600 |
| C | 2.16424200 | 4.87414700 | -2.52300600 |
| H | 2.08261800 | 4.93279600 | -1.41909800 |
| H | 2.80690500 | 5.71522400 | -2.85998700 |
| C | 0.77133600 | 5.06759900 | -3.14200200 |
| H | 0.84169300 | 5.02697300 | -4.25027700 |
| H | 0.09346200 | 4.25476000 | -2.80647900 |
| C | 0.18806800 | 6.39045600 | -2.73729900 |
| H | -1.41847000 | 7.37228100 | -1.69448600 |
| O | 0.75964300 | 7.45921400 | -3.08219200 |
| H | -1.54456200 | 5.57998400 | -1.73821400 |
| N | -1.02685400 | 6.45061000 | -1.98980700 |
| C | 0.96742000 | -1.35264500 | -4.70563600 |
| H | 0.56776100 | -2.07875500 | -5.44607100 |
| H | 1.79627100 | -0.78478100 | -5.18176900 |
| H | 1.39432500 | -1.92873900 | -3.85564800 |
| C | -0.67786600 | 0.35223200 | -5.45769300 |
| H | -1.13861400 | -0.35911900 | -6.17324400 |
| H | -1.41645700 | 1.12810800 | -5.17008200 |
| H | 0.14524100 | 0.85667500 | -6.00632600 |
| C | -1.88925000 | -3.13520100 | -1.14288200 |
| H | -1.45588600 | -4.12312200 | -0.91370500 |
| H | -2.80020500 | -2.95188400 | -0.54482900 |
| H | -2.24062000 | -3.22643400 | -2.17973200 |
| C | -2.61923300 | -0.57313300 | -3.29354100 |
| H | -3.09318200 | -0.86091600 | -2.33135100 |
| H | -2.53619600 | 0.53371500 | -3.25404800 |
| C | -3.59227200 | -0.97423700 | -4.41802500 |
| H | -4.53885700 | -0.40769500 | -4.29174900 |
| H | -3.19125900 | -0.68891600 | -5.40751300 |
| C | -3.91679600 | -2.44086700 | -4.40652200 |
| O | -3.56437900 | -3.16511500 | -5.37529500 |
| H | -4.90969200 | -4.02889500 | -3.34669600 |
| N | -4.67641500 | -3.01134200 | -3.34044800 |

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|----|--------------|-------------|-------------|
| H | -4.98012000 | -2.43174200 | -2.52836600 |
| N | 3.52996100 | -1.46858900 | -0.95355100 |
| Re | 4.96333400 | -2.99897200 | -0.98952700 |
| Br | 3.10026800 | -4.48997000 | -2.24355200 |
| Br | 6.82980100 | -1.07113300 | -0.64476800 |
| C | 4.56070600 | -3.40456200 | 0.77710900 |
| O | 4.24207000 | -3.61740400 | 1.92720500 |
| C | 6.25434400 | -4.39514200 | -1.00577900 |
| O | 7.06544200 | -5.27649900 | -1.00909300 |
| H | 6.22391500 | -1.97398000 | -3.22304500 |
| H | 5.10048300 | -3.06345200 | -3.76987200 |
| O | 5.33323200 | -2.36887700 | -3.12164900 |
| O | -6.68150700 | -1.12979700 | -0.59789100 |
| C | -7.71679400 | -1.61912600 | -1.16182500 |
| O | -8.22779600 | -2.65208400 | -0.65329900 |
| N | -8.33427700 | -1.03295600 | -2.32911400 |
| C | -9.73302900 | -1.27573500 | -2.67852800 |
| C | -10.51150700 | 0.00539100 | -2.56285500 |
| C | -10.64591700 | 0.63464700 | -1.31612300 |
| C | -11.10980500 | 0.58756000 | -3.69018700 |
| C | -11.36723800 | 1.82692200 | -1.22123300 |
| H | -10.19467800 | 0.20700100 | -0.42896000 |
| C | -11.82330600 | 1.78076000 | -3.55045300 |
| H | -11.02393000 | 0.12667300 | -4.66628500 |
| N | -11.93567000 | 2.36998300 | -2.33035300 |
| H | -11.47508100 | 2.32081200 | -0.26480300 |
| H | -12.28762900 | 2.23901900 | -4.41342300 |
| H | -10.19373500 | -2.03337400 | -2.00929100 |
| H | -9.77767500 | -1.67920000 | -3.71315700 |
| H | -7.79942500 | -0.40269300 | -2.96667900 |

Cartesian coordinates of B12-ReCORM-2

| | | | |
|---|-------------|-------------|-------------|
| H | -1.26607600 | -2.17603600 | -4.37477500 |
| C | -0.00239700 | -0.38309700 | -4.55806100 |
| C | -1.23071000 | -1.17032600 | -3.95006400 |
| H | 1.31755100 | 2.09809800 | -4.43439700 |
| C | -0.86482100 | -1.17663000 | -2.42475100 |
| C | 0.39252700 | 0.49436700 | -3.36608000 |
| C | -1.42826000 | -2.01310900 | -1.45536400 |
| C | 1.14109900 | 1.67237900 | -3.45404600 |
| H | -3.16145300 | -4.06857100 | 0.39294500 |
| N | 0.00207900 | -0.09895100 | -2.19466900 |
| O | -5.69517000 | -3.26403500 | -0.21100600 |
| H | 3.17301400 | 3.43163400 | -3.67745800 |
| C | 2.03728000 | -0.73321800 | -0.53297800 |
| C | -1.12056000 | -1.87935400 | -0.02632700 |
| C | -2.97226300 | -3.32472800 | 1.18994400 |
| C | 1.83142100 | 2.28787600 | -2.41175600 |
| C | -1.49038400 | -2.86407500 | 1.15783000 |
| H | -7.21470300 | 1.39637600 | -3.06625600 |

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|----|--------------|-------------|-------------|
| H | -3.16677400 | -3.89391400 | 2.11907700 |
| C | 2.80511900 | 3.43147300 | -2.64664000 |
| H | -7.65747500 | -4.18562300 | 1.19805400 |
| C | -5.39475800 | -2.75632000 | 0.90431700 |
| N | -0.36219100 | -0.89019600 | 0.43543400 |
| Co | 0.64573600 | 0.50755800 | -0.44537900 |
| H | -3.78911200 | -1.49691400 | 0.26957500 |
| H | -9.91766300 | -3.70868100 | 0.22745200 |
| N | 1.88116400 | 1.86546200 | -1.12113600 |
| C | 3.93274900 | 3.05122800 | -1.57379800 |
| H | 0.96776400 | -1.64545100 | 1.85171200 |
| C | -4.01555900 | -2.19082600 | 1.10437500 |
| H | -5.12489000 | -0.29517800 | -1.53504200 |
| C | -6.65570300 | 0.45833400 | -2.86200800 |
| H | -2.39032400 | 0.52509100 | -1.21156900 |
| H | -6.11746300 | 0.16780700 | -3.78765300 |
| C | -7.67146300 | -3.23204900 | 1.77112900 |
| C | 3.05054300 | 2.33168800 | -0.48536700 |
| C | -1.11983400 | -1.97334900 | 2.43476900 |
| C | 0.03274700 | -1.07523800 | 1.88771600 |
| O | -4.68197500 | 1.61655200 | -2.12230100 |
| C | -5.64892200 | 0.66870100 | -1.72803300 |
| C | -2.12336800 | 1.51104800 | -0.86848100 |
| C | -9.97638100 | -2.80068700 | 0.86510900 |
| O | -7.55631200 | -0.55452100 | -2.52733000 |
| H | -8.07600900 | -3.46248100 | 2.78123300 |
| H | -4.00651700 | -1.59313500 | 2.03724300 |
| N | -0.90549200 | 1.86405200 | -0.46172700 |
| H | -10.62816100 | -2.05843700 | 0.35682400 |
| H | -1.96249500 | -1.31913000 | 2.68040500 |
| N | 1.15271100 | 0.98156600 | 1.34465200 |
| H | -10.43659700 | -3.06997400 | 1.84016600 |
| C | 3.28063000 | 2.13137000 | 0.87097100 |
| N | -3.02380800 | 2.55133900 | -0.75678300 |
| C | 0.34510700 | 0.36595200 | 2.47135100 |
| C | -4.43925100 | 2.46934400 | -1.02168800 |
| C | 2.23908400 | 1.61516900 | 1.74143500 |
| C | -6.31594100 | 1.15939000 | -0.44768700 |
| C | -0.99901600 | 3.21411800 | -0.04342900 |
| H | -4.81690200 | 3.47913600 | -1.29599000 |
| O | -6.71978000 | 0.09508000 | 0.33338100 |
| O | -8.70298000 | -1.06324500 | 1.84083200 |
| C | 1.36201200 | 0.55890100 | 3.75452400 |
| O | -8.54744600 | 1.51272500 | 1.55240100 |
| C | -2.33869900 | 3.65778400 | -0.21574200 |
| H | 0.97948800 | 3.75862400 | 0.64588200 |
| H | -7.18038300 | 1.82004600 | -0.68897200 |
| C | -5.22182000 | 1.97065800 | 0.19447000 |
| H | 3.29348400 | 1.67876300 | 3.64468400 |
| C | -0.04088200 | 4.08791000 | 0.50106200 |
| C | 2.27253000 | 1.78506500 | 3.27279400 |

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|---|-------------|-------------|------------|
| P | -7.69726100 | 0.26932900 | 1.68387800 |
| C | -2.73858800 | 4.95644200 | 0.14268700 |
| H | -5.63511800 | 2.81468800 | 0.78848000 |
| H | -3.76299700 | 5.29557300 | 0.01528000 |
| C | -0.41837000 | 5.39203200 | 0.85231300 |
| H | 1.61371600 | 5.88231600 | 1.42488500 |
| C | -1.77575300 | 5.82927300 | 0.67442000 |
| O | -6.83088400 | 0.38841300 | 2.91641500 |
| H | 0.68314100 | 7.26959500 | 0.84075900 |
| C | 0.61973300 | 6.34089600 | 1.42390900 |
| H | -3.24645100 | 7.41019700 | 0.88776700 |
| C | -2.17719800 | 7.24210400 | 1.05388400 |
| H | 0.38206600 | 6.62902500 | 2.45766900 |
| H | -1.62611000 | 7.98749200 | 0.46374500 |
| H | -1.96407000 | 7.45272200 | 2.11057400 |
| N | -6.30763700 | -2.71961200 | 1.91116500 |
| H | -6.04889200 | -2.28192500 | 2.82427400 |
| C | -8.58385000 | -2.20737100 | 1.07437400 |
| H | -8.17612200 | -1.96515500 | 0.06829800 |
| O | -4.42656900 | 1.16551100 | 1.02034500 |
| C | -0.58127700 | -4.10203100 | 1.04684700 |
| H | -0.79000100 | -4.82201000 | 1.86388800 |
| H | -0.73187000 | -4.64602100 | 0.09736300 |
| H | 0.48946800 | -3.81788100 | 1.09069500 |
| C | -0.74349800 | -2.72618800 | 3.71829100 |
| H | -0.44321100 | -1.99493200 | 4.48587200 |
| H | 0.12654200 | -3.39316900 | 3.54680700 |
| O | -2.92898700 | -2.87786800 | 4.67577900 |
| C | -1.89023000 | -3.49145400 | 4.31082600 |
| N | -1.78822000 | -4.89789300 | 4.53443900 |
| H | -0.91650000 | -5.41863100 | 4.29208600 |
| H | -2.58602500 | -5.42141100 | 4.95805900 |
| C | -0.98475400 | 1.12882400 | 2.63048500 |
| H | -1.67386000 | 0.92854900 | 1.78901000 |
| H | -1.52230300 | 0.80893200 | 3.54574200 |
| H | -0.83290900 | 2.22066000 | 2.66883600 |
| C | 0.63670800 | 0.81485900 | 5.08728900 |
| H | 1.35668200 | 0.95621000 | 5.91637700 |
| H | 0.00666600 | 1.72491900 | 5.05357300 |
| H | -0.01791500 | -0.03375300 | 5.35573400 |
| C | 2.29096600 | -0.68208300 | 3.89811800 |
| H | 1.69991300 | -1.59509000 | 4.07654500 |
| H | 2.83979000 | -0.84587400 | 2.94468000 |
| C | 3.31048800 | -0.59213300 | 5.00621400 |
| O | 4.49848100 | -0.27006100 | 4.73568500 |
| H | 3.73155000 | -1.09908200 | 7.05545300 |
| H | 2.05273700 | -1.46773600 | 6.52566500 |
| N | 3.00339100 | -1.09493500 | 6.30726600 |
| C | 1.84104500 | 3.22614200 | 3.62571900 |
| H | 2.23115500 | 3.91817700 | 2.84683300 |
| H | 0.74370600 | 3.33693500 | 3.61526400 |

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|---|-------------|-------------|-------------|
| C | 2.40349800 | 3.71935900 | 4.96773400 |
| H | 2.01554000 | 3.11695200 | 5.81060400 |
| H | 3.51188400 | 3.62628600 | 4.96020300 |
| C | 2.02868400 | 5.15373400 | 5.20030300 |
| O | 2.92455100 | 6.03908700 | 5.22986600 |
| H | 0.40575100 | 6.52237300 | 5.55487100 |
| H | -0.08717500 | 4.79743400 | 5.42315200 |
| N | 0.66442200 | 5.52197500 | 5.40532900 |
| C | 4.65368900 | 2.29469400 | 1.47413300 |
| H | 5.45598100 | 2.27239300 | 0.72169400 |
| H | 4.70443700 | 3.23850900 | 2.05600700 |
| H | 4.88873300 | 1.43428400 | 2.13418000 |
| C | 4.68561500 | 4.28034900 | -1.04189000 |
| H | 5.62141600 | 4.01748100 | -0.51548700 |
| H | 4.98324000 | 4.94050500 | -1.88327200 |
| H | 4.04755000 | 4.86281600 | -0.34374000 |
| C | 4.91475500 | 2.01528600 | -2.17627500 |
| H | 4.35033700 | 1.11382600 | -2.50449800 |
| H | 5.63094900 | 1.65509900 | -1.41085700 |
| C | 5.69867700 | 2.53756900 | -3.35103300 |
| H | 7.47498500 | 3.58173500 | -3.96979200 |
| H | 7.28582100 | 3.42748000 | -2.18955200 |
| N | 6.91502000 | 3.25793100 | -3.15024300 |
| O | 5.35713600 | 2.21492400 | -4.52032500 |
| C | 2.12957200 | 4.79564700 | -2.40220300 |
| H | 1.80867300 | 4.87762600 | -1.34422300 |
| H | 2.87058100 | 5.60064700 | -2.59430100 |
| C | 0.91917800 | 5.04076200 | -3.31628000 |
| H | 1.23159900 | 4.97966500 | -4.38092600 |
| H | 0.14662800 | 4.26414800 | -3.13539100 |
| C | 0.32260400 | 6.39410600 | -3.05866100 |
| H | -1.42935400 | 7.46162600 | -2.40783900 |
| O | 1.00576000 | 7.43120500 | -3.27221600 |
| H | -1.62429700 | 5.67592400 | -2.46633500 |
| N | -1.02453100 | 6.51917300 | -2.60261400 |
| C | 1.14976900 | -1.36375300 | -4.82835700 |
| H | 0.87778200 | -2.06771300 | -5.64426100 |
| H | 2.06878800 | -0.81498800 | -5.12904200 |
| H | 1.39206100 | -1.96321900 | -3.92351300 |
| C | -0.27880900 | 0.39814700 | -5.84662300 |
| H | -0.62400700 | -0.28873500 | -6.64590900 |
| H | -1.03135500 | 1.19727900 | -5.68924200 |
| H | 0.64727800 | 0.87860000 | -6.22668100 |
| C | -2.36036900 | -3.11916300 | -1.90707400 |
| H | -2.01413200 | -4.10379200 | -1.55221600 |
| H | -3.38857500 | -2.91190800 | -1.55895500 |
| H | -2.44197500 | -3.24092700 | -2.99591700 |
| C | -2.61521600 | -0.49370800 | -4.10545300 |
| H | -3.26174700 | -0.74918100 | -3.23909400 |
| H | -2.50888000 | 0.61081200 | -4.06591300 |
| C | -3.38162400 | -0.89219600 | -5.37892000 |

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|----|-------------|-------------|-------------|
| H | -4.29298200 | -0.26290400 | -5.46037400 |
| H | -2.77654800 | -0.69022200 | -6.28210700 |
| C | -3.80439700 | -2.33349900 | -5.36301900 |
| O | -3.32974300 | -3.13282800 | -6.21334000 |
| H | -5.06664000 | -3.80008000 | -4.42103000 |
| N | -4.77679000 | -2.79715300 | -4.42538800 |
| H | -5.19402400 | -2.15042400 | -3.72084500 |
| N | 2.87326900 | -1.56130700 | -0.48974300 |
| Re | 4.21425400 | -3.14154200 | -0.16723600 |
| Br | 2.59089600 | -4.61914900 | -1.73215400 |
| Br | 6.04709800 | -1.27018800 | 0.50812900 |
| C | 3.42874300 | -3.46490000 | 1.48361700 |
| O | 2.86213900 | -3.62642200 | 2.54309300 |
| C | 5.41659400 | -4.58381700 | 0.13459000 |
| O | 6.17041800 | -5.49369300 | 0.33070800 |
| H | 5.95278800 | -2.24820900 | -2.12493800 |
| H | 4.91495200 | -3.31432500 | -2.85642600 |
| O | 5.04447300 | -2.60832700 | -2.19190600 |

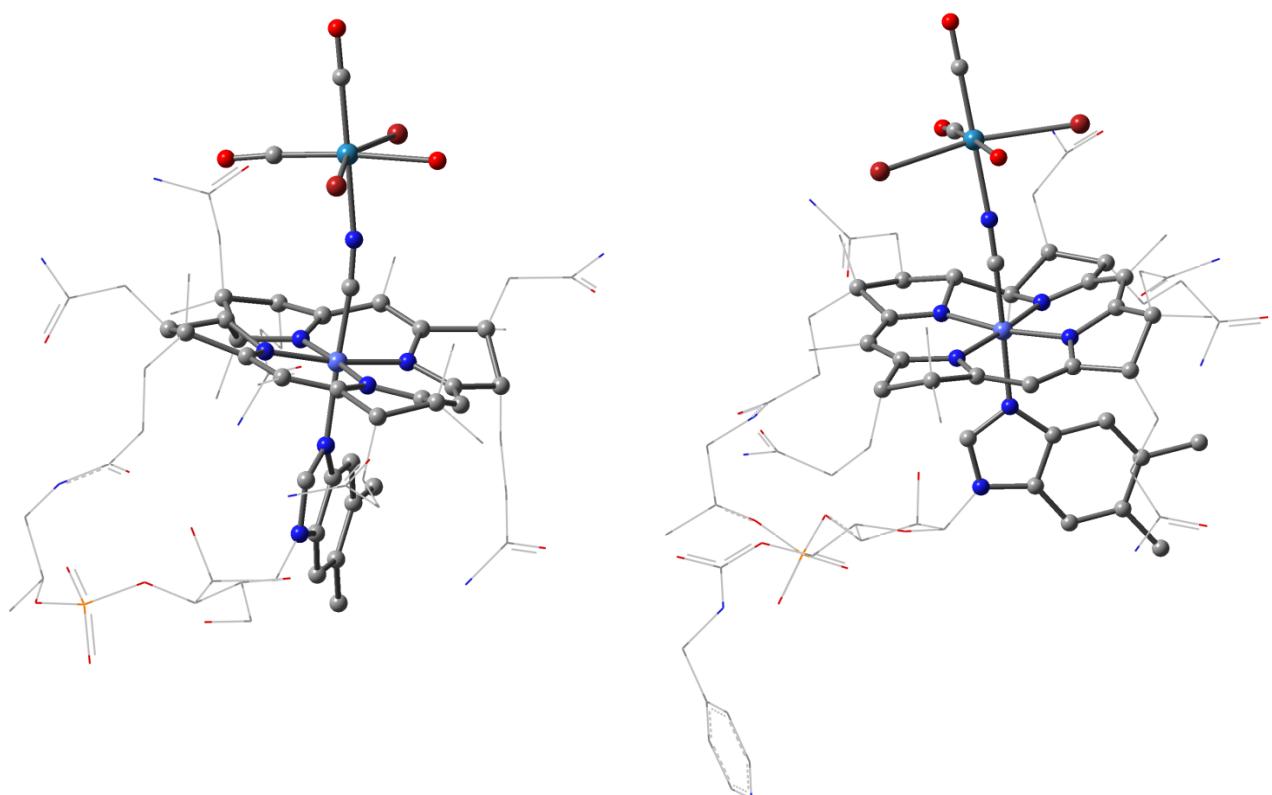


Figure S16. Two-layer ONIOM(B3LYP/LanL2DZ:UFF) optimized **B₁₂-ReCORM-2** and **B₁₂-ReCORM-4**. The different layers are represented with balls and sticks (high) and wireframe (low).