

## Supporting Information

# New Spectroelectrochemical Insights in Mn and Re bipyridine Complexes as Catalysts for the Electrochemical Reduction of CO<sub>2</sub>

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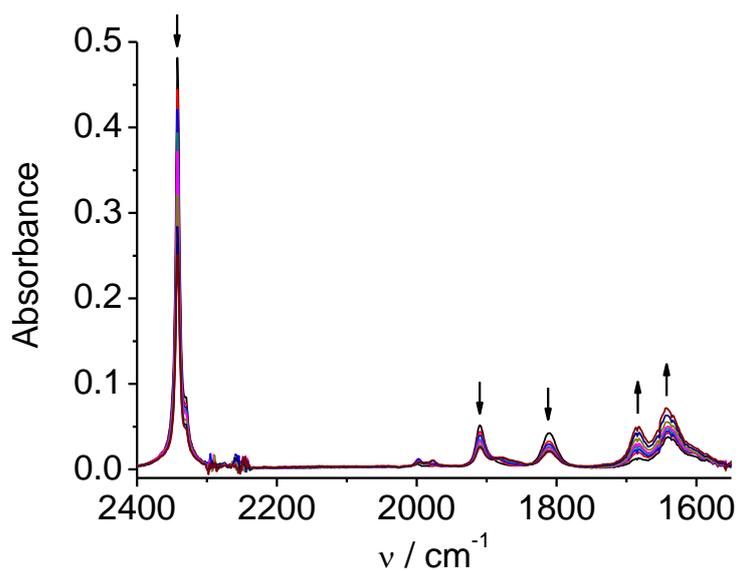
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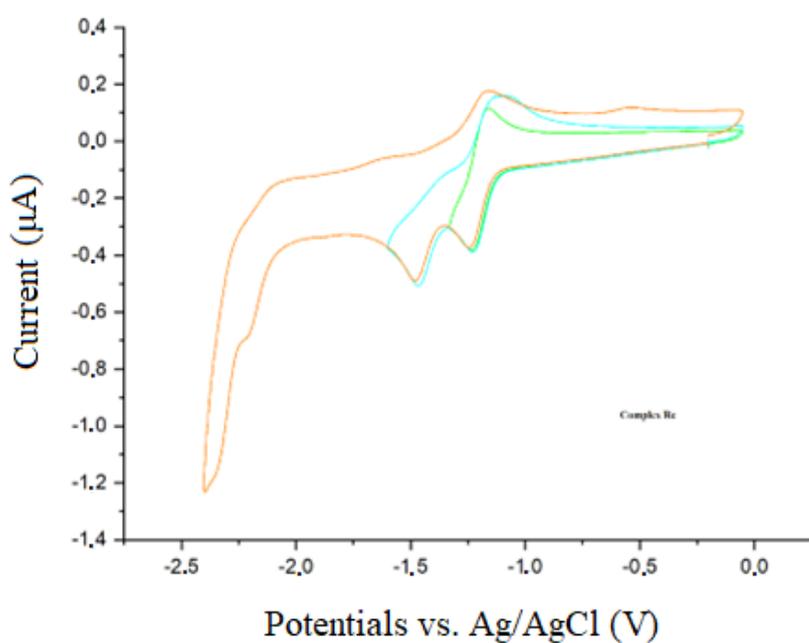
\* Correspondence: carlo.nervi@unito.it

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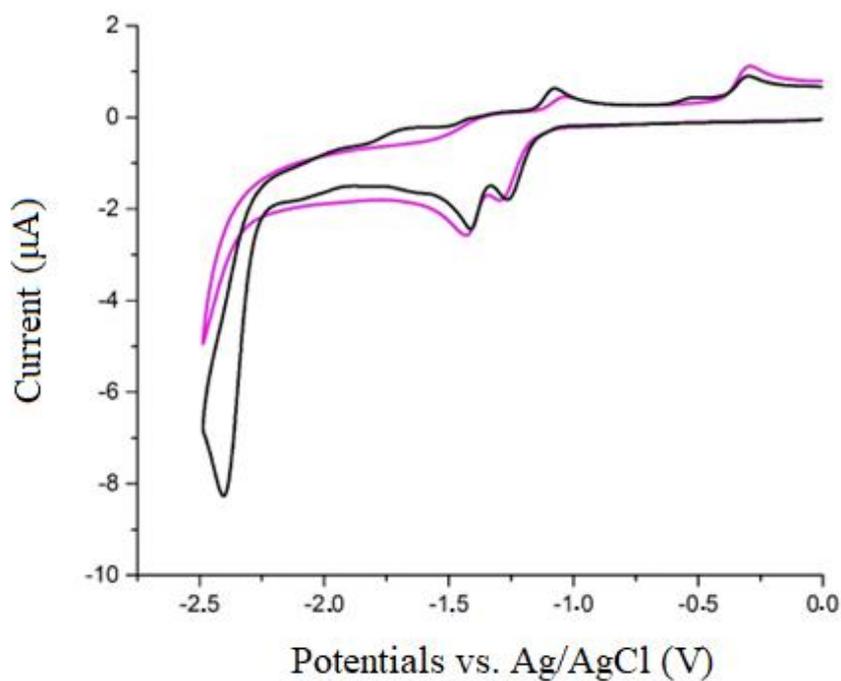
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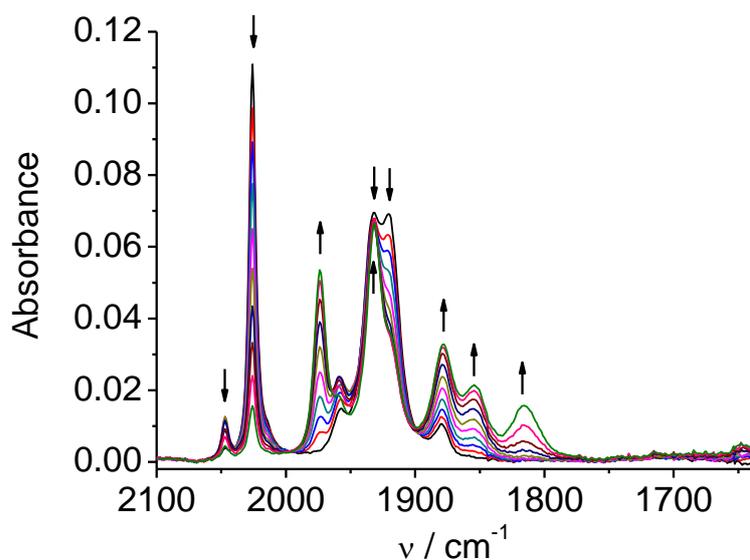
**Figure S1** Spectroelectrochemistry of **1** in MeCN / 0.1 TBAPF<sub>6</sub> under CO<sub>2</sub>: reduction behind the second reduction peak (-2.1 V vs. Fc/Fc<sup>+</sup>). Noise between  $\approx 2250$  and  $2300$  cm<sup>-1</sup> is due to solvent absorptions and subsequent background subtraction.



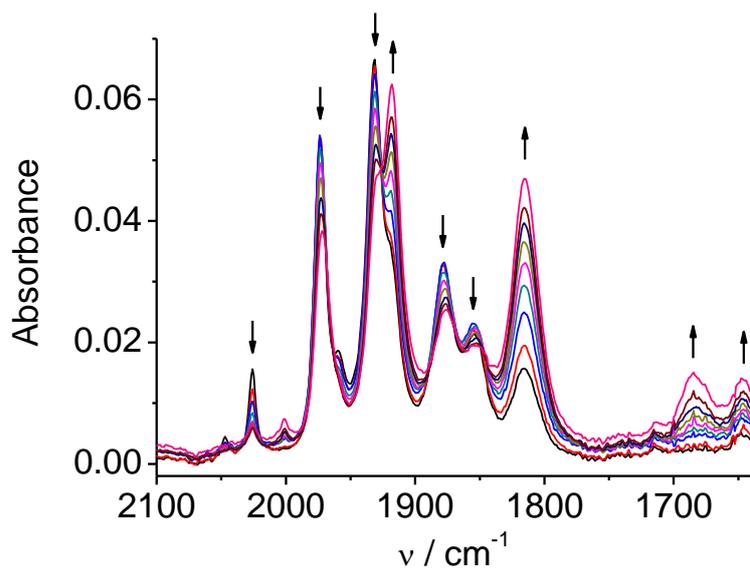
**Figure S2** Cyclic Voltammetry of **2** in MeCN / 0.1 M TBAPF<sub>6</sub> under Ar.



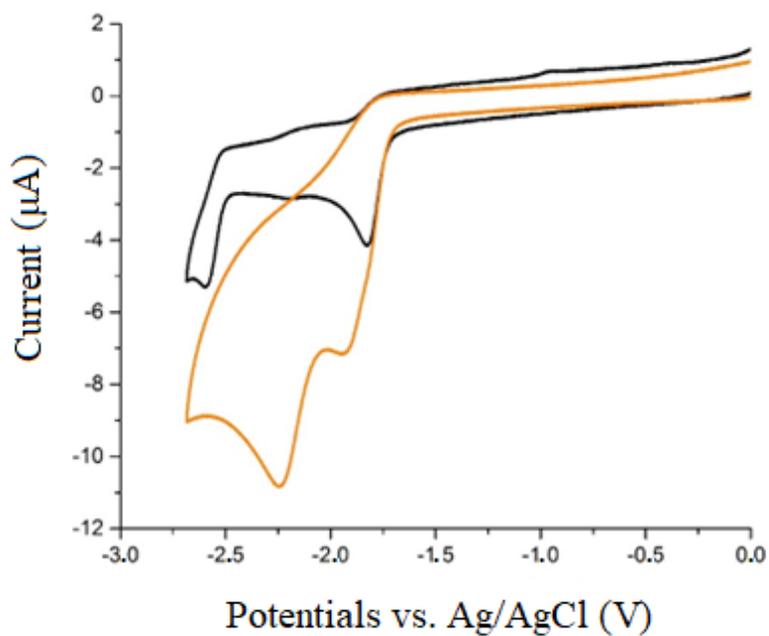
**Figure S3** Cyclic Voltammetry of **3** in MeCN / 0.1 M TBAPF<sub>6</sub> under Ar (violet line) and under CO<sub>2</sub> (black line).



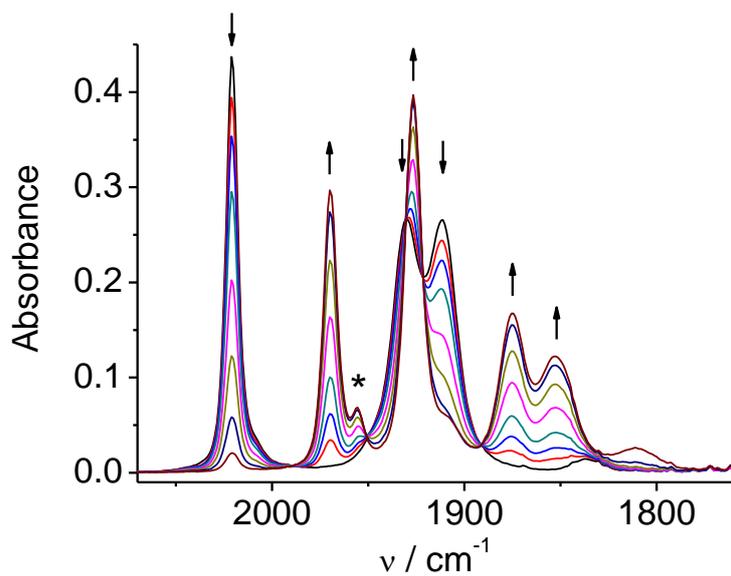
**Figure S4** Spectroelectrochemistry of **3** in MeCN / 0.1 M TBAPF<sub>6</sub> under CO<sub>2</sub>: reduction at the first reduction peak (last spectra show a partial formation of the 2e reduction product)



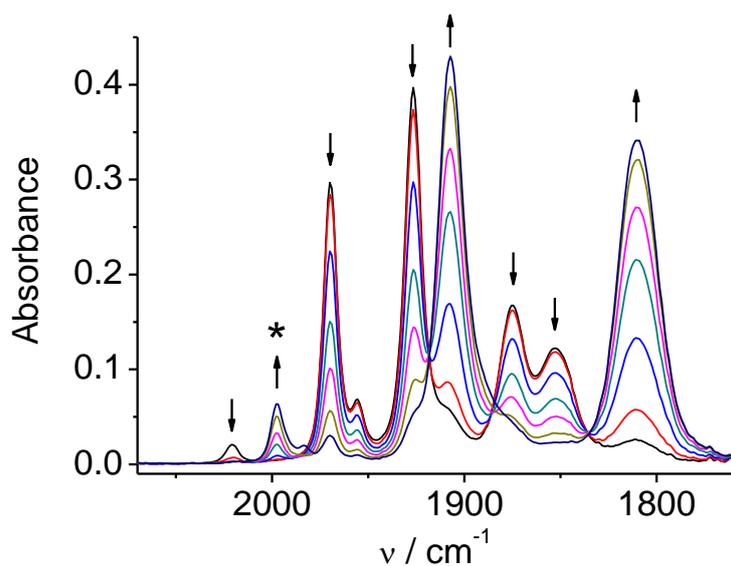
**Figure S5** Spectroelectrochemistry of **3** in MeCN / 0.1 M TBAPF<sub>6</sub> under CO<sub>2</sub>: reduction at the second reduction peak (and still finishing first reduction in the beginning)



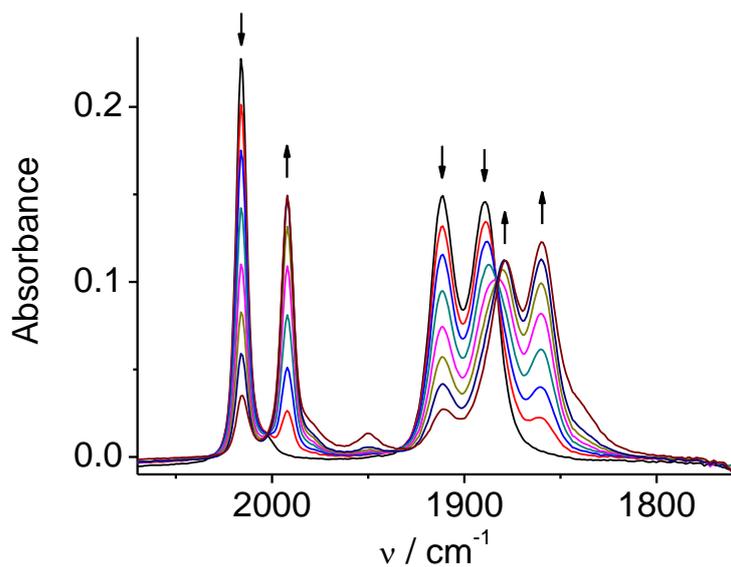
**Figure S6** Cyclic Voltammetry of **4** in MeCN / 0.1 M TBAPF<sub>6</sub> under Ar (black line) and under CO<sub>2</sub> (orange line).



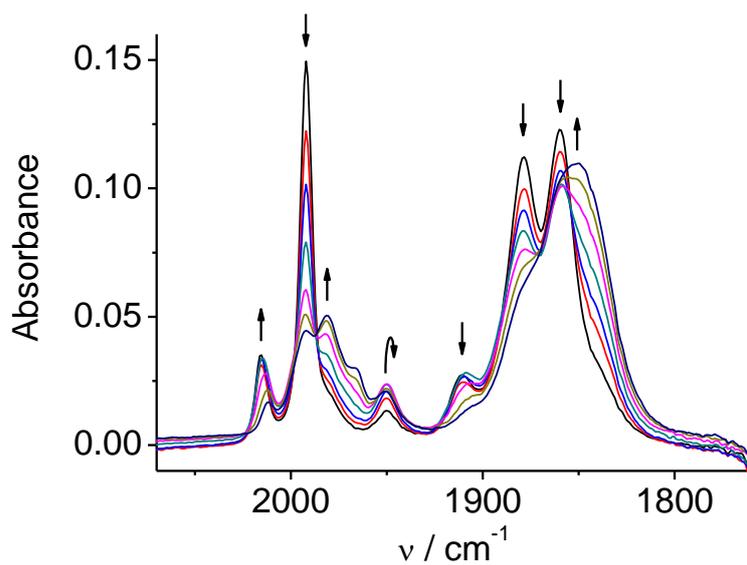
**Figure S7** Spectroelectrochemistry of **1** in DMA / 0.1 M TBAPF<sub>6</sub>: reduction at the first reduction peak (\* = unidentified side-product)



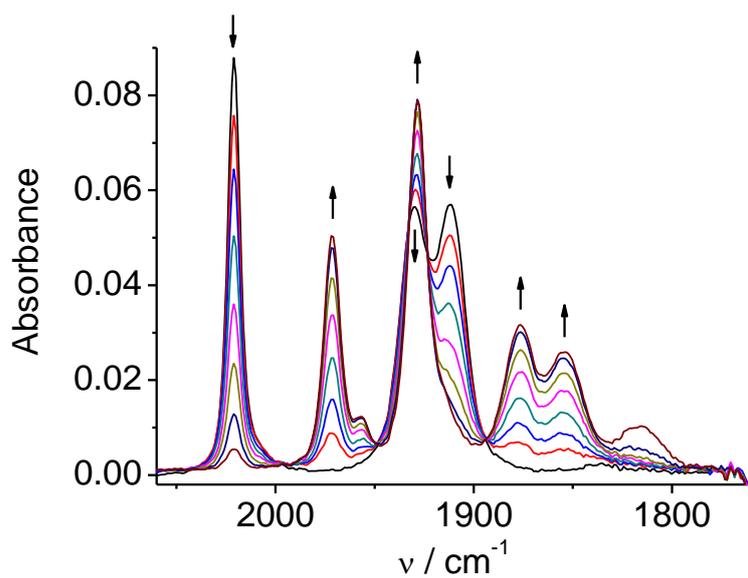
**Figure S8** Spectroelectrochemistry of **1** in DMA / 0.1 M TBAPF<sub>6</sub>: reduction at the second reduction peak (\* = unidentified side-product)



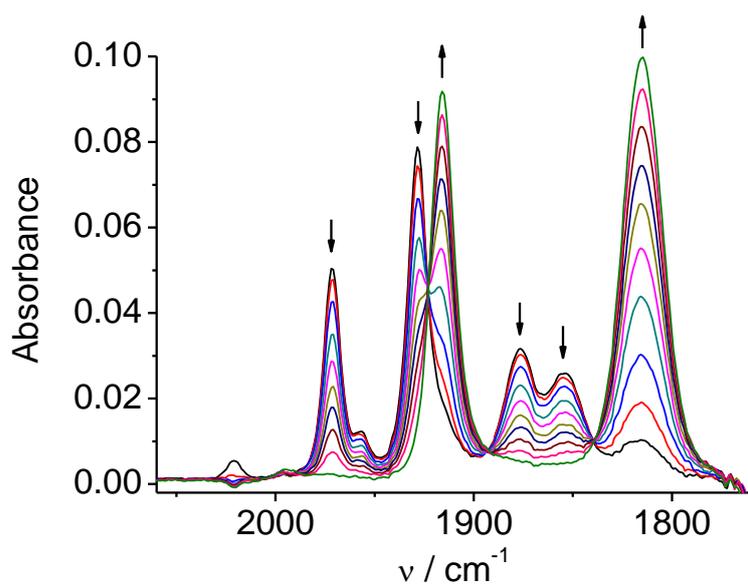
**Figure S9** Spectroelectrochemistry of **2** in DMA / 0.1 M TBAPF<sub>6</sub>: reduction at the first reduction peak



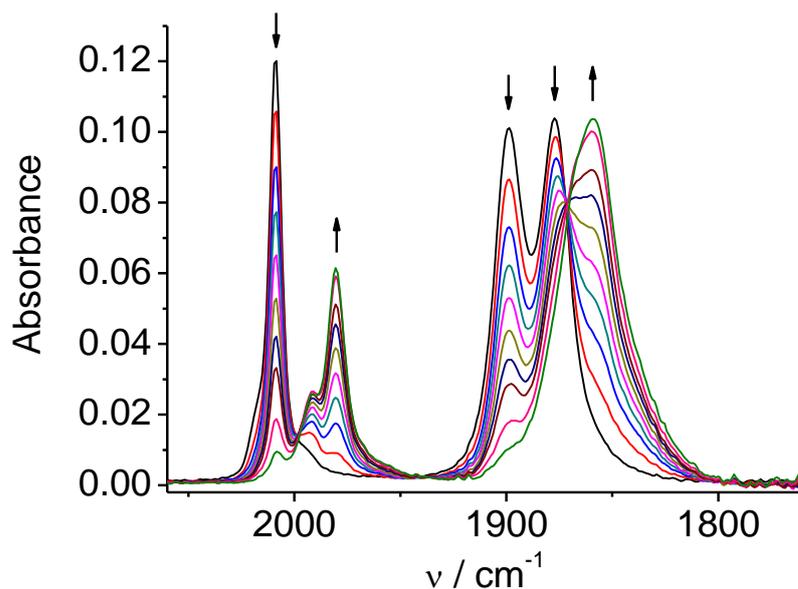
**Figure S10** Spectroelectrochemistry of **2** in DMA / 0.1 M TBAPF<sub>6</sub>: reduction at the second reduction peak



**Figure S11** Spectroelectrochemistry of **3** in DMA / 0.1 M TBAPF<sub>6</sub>: reduction at the first reduction peak



**Figure S12** Spectroelectrochemistry of **3** in DMA / 0.1 M TBAPF<sub>6</sub>: reduction at the second reduction peak



**Figure S13** Spectroelectrochemistry of **4** in DMA / 0.1 M TBAPF<sub>6</sub>: reduction at the two-electron reduction peak

**DFT optimized geometry of 1.**

```

C 1.89971300 -1.62870300 0.27796700
C 2.54764100 -0.38073500 0.17760600
C 1.70578700 0.74766600 0.17726600
C 0.32213200 0.60931100 0.26423600
C 0.51709300 -1.69238400 0.36490200
C -0.60768000 1.75420100 0.27591900
C -0.19744200 3.09006400 0.19764400
C -1.15362700 4.10219100 0.22122600
H -0.84941900 5.14855100 0.16090600
C -2.50066800 3.75268300 0.32403100
C -2.83663300 2.40358600 0.39594400
H 2.46217100 -2.56153200 0.26586800
H 0.01965200 -2.65966600 0.43416100
H -3.28758600 4.50721200 0.34786500
H -3.87946200 2.09710200 0.47368500
N -0.27063900 -0.60541900 0.35448500
N -1.91809500 1.42623000 0.37032100
C -2.49831800 -2.40331400 0.26947000
O -2.60688100 -3.54484300 0.17007300
C -4.13347900 -0.40873400 0.28502200
O -5.27548400 -0.29486200 0.19579200
C -2.34825200 -0.62933400 2.20569800
O -2.35325700 -0.64417900 3.35753700
H 0.85953000 3.33858100 0.11832800
H 2.13788900 1.74434300 0.13164500
C 4.00926100 -0.25928400 0.08104100
C 4.62029100 0.88539000 -0.47445000
C 4.86463500 -1.28503000 0.53729900
C 5.99873100 1.00311300 -0.57345900
H 4.00431600 1.69541100 -0.86933600
C 6.24491500 -1.17706800 0.45381600
H 4.44365600 -2.18274600 0.99357200
C 6.85023100 -0.02662700 -0.10635700
H 6.43701800 1.89699100 -1.02369800
H 6.87713800 -1.98472600 0.83039200
N 8.20879400 0.10023800 -0.16261600
H 8.78709500 -0.71865700 -0.02148900

```

H 8.61261900 0.82824600 -0.73866900  
Br -2.24296200 -0.50069000 -2.20080500  
Mn -2.32809500 -0.59772700 0.40293900

### DFT optimized geometry of 1.

C 1.90859000 -1.62242900 0.32384700  
C 2.55830200 -0.35380800 0.17982300  
C 1.73071000 0.76192400 0.15629000  
C 0.32386200 0.64929700 0.25557600  
C 0.53401800 -1.67643100 0.42164400  
C -0.57940900 1.75862800 0.25431300  
C -0.19306500 3.12083200 0.14177700  
C -1.14246300 4.11958200 0.16267500  
H -0.84540800 5.16682500 0.07416800  
C -2.50963300 3.76427500 0.30295600  
C -2.83040300 2.42315900 0.41053500  
H 2.47464800 -2.55321000 0.32537900  
H 0.03737300 -2.64314500 0.52348100  
H -3.29889900 4.51654100 0.32438500  
H -3.87247000 2.11747600 0.51924500  
N -0.27205700 -0.59451100 0.38480400  
N -1.91883900 1.42899200 0.38346400  
C -2.46988200 -2.37507300 0.39035200  
O -2.57923700 -3.52163100 0.30405200  
C -4.10444500 -0.38070700 0.38672200  
O -5.25039700 -0.26547500 0.29889700  
C -2.31365100 -0.57840300 2.29627100  
O -2.29418900 -0.56232100 3.45249900  
H 0.86278300 3.37161200 0.03716200  
H 2.16750900 1.75709200 0.08483300  
C 4.02565600 -0.24531400 0.07217200  
C 4.64717500 0.86039500 -0.54614900  
C 4.87832800 -1.24746400 0.57989700  
C 6.02944400 0.96730900 -0.64510300  
H 4.03311500 1.64852300 -0.98689800  
C 6.26366100 -1.15106500 0.48968200  
H 4.45096100 -2.11869100 1.08000200  
C 6.87498200 -0.03781000 -0.12511300  
H 6.47237700 1.83460100 -1.14196100  
H 6.89081000 -1.94437000 0.90517300  
N 8.24863300 0.08815500 -0.17585900  
H 8.79086400 -0.76354100 -0.08167400  
H 8.62467100 0.72689600 -0.86785700  
Mn -2.30459900 -0.57286700 0.51809700  
Br -2.35364600 -0.59998200 -2.38249500

### DFT optimized geometry of 2.

C 2.19969000 -1.60750000 0.01526500  
C 2.88960700 -0.37713400 0.03821300  
C 2.08296500 0.77717700 0.08227800  
C 0.69363900 0.68596300 0.09445800  
C 0.81515100 -1.63096000 0.03414900  
C -0.18870800 1.87109700 0.14939500  
C 0.28925000 3.18602500 0.18013000  
C -0.61301500 4.24502000 0.24045800  
H -0.25047100 5.27402300 0.26449300  
C -1.98048800 3.96751000 0.26961100  
C -2.39095100 2.63931200 0.23368600  
H 2.73229200 -2.55593300 -0.04035300  
H 0.27804700 -2.57905900 0.00890000  
H -2.72562200 4.76207700 0.31731600  
H -3.44895400 2.37867600 0.25069100  
N 0.06296000 -0.51631500 0.07128500  
N -1.52122100 1.61640800 0.17498400  
Re -2.12968500 -0.49409800 0.02269400  
C -2.39665400 -2.39128900 -0.22686000  
O -2.50867700 -3.53335900 -0.38733400  
C -4.03541600 -0.19995400 -0.11513000  
O -5.16892300 0.02397100 -0.20496200  
C -2.27098800 -0.69645900 1.92429500  
O -2.34812000 -0.81260600 3.07719100  
Cl -1.78983000 -0.10735700 -2.45577600  
H 1.35895600 3.38442600 0.15572700  
H 2.54999800 1.75723200 0.13131000  
C 4.35529500 -0.29744900 0.01993500

C 5.02765500 0.87461600 -0.39073700  
C 5.15710100 -1.39214100 0.41083000  
C 6.41133700 0.95416400 -0.41337100  
H 4.45764300 1.74067400 -0.73159000  
C 6.54165000 -1.32429100 0.40291500  
H 4.68863200 -2.31543500 0.75562600  
C 7.20815300 -0.14512100 -0.01055500  
H 6.89804100 1.87191600 -0.75170900  
H 7.13030900 -2.18620100 0.72574100  
N 8.56834900 -0.06046500 0.00720800  
H 9.12107800 -0.90040000 0.12223400  
H 9.02706200 0.71743800 -0.44954700

## DFT optimized geometry of 2:

C 2.19905900 -1.61199700 -0.00904100  
C 2.88562000 -0.35336900 0.02591600  
C 2.09258100 0.78434700 0.07952500  
C 0.67636600 0.71458800 0.08815300  
C 0.82095200 -1.63146200 0.00413900  
C -0.18127700 1.85715200 0.14727800  
C 0.27456600 3.20498700 0.19553400  
C -0.62235900 4.24767700 0.25566800  
H -0.26557300 5.27935000 0.29199800  
C -2.01496800 3.96399200 0.26938200  
C -2.40995000 2.64042800 0.21935400  
H 2.74125000 -2.55401200 -0.07961200  
H 0.28596100 -2.58252800 -0.03249300  
H -2.76291900 4.75599600 0.31556300  
H -3.46948400 2.37756500 0.22557200  
N 0.04918500 -0.52460000 0.04941900  
N -1.54777200 1.60354900 0.15828600  
Re -2.12428300 -0.49446900 0.03491900  
C -2.37652100 -2.39585400 -0.20787000  
O -2.48164000 -3.54380400 -0.36231200  
C -4.03063200 -0.19754800 -0.09887800  
O -5.16854000 0.02733200 -0.18570900  
C -2.25690300 -0.68825500 1.92562300  
O -2.32840500 -0.79887800 3.08360300  
Cl -1.83361200 -0.14437100 -2.50810100  
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C 4.35929400 -0.28025100 0.01205000  
C 5.04371800 0.86210200 -0.45438500  
C 5.15463400 -1.35461000 0.46144500  
C 6.43158400 0.93567200 -0.46356200  
H 4.47655200 1.70870300 -0.84689500  
C 6.54485200 -1.29241900 0.46057000  
H 4.67625200 -2.25809600 0.84436600  
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H 6.92508500 1.83405800 -0.84385500  
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H 9.02849000 0.64078900 -0.55958900