checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

Bond precision: C-C = 0.0080 A Wavelength=1.54184

Cell: a=14.4683(14) b=10.6415(8) c=9.6020(8)
alpha=90 beta=98.111(8) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1463.6(2)	1463.6(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C15 H8 Br Mn N2 O3	C15 H8 Br Mn N2 O3
Sum formula	C15 H8 Br Mn N2 O3	C15 H8 Br Mn N2 O3
Mr	399.07	399.08
Dx,g cm-3	1.811	1.811
Z	4	4
Mu (mm-1)	10.662	10.662
F000	784.0	784.0
F000’	781.14	
h,k,lmax	18,13,12	18,13,11
Nref	3041	2981
Tmin,Tmax	0.206,0.556	0.447,0.911
Tmin’	0.106	

Correction method= # Reported T Limits: Tmin=0.447 Tmax=0.911
AbsCorr = GAUSSIAN

Data completeness= 0.980 Theta(max)= 75.811

R(reflections)= 0.0486(2125) wR2(reflections)= 0.1304(2981)

S = 1.031 Npar= 203

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT242_ALERT_2_C Low ’MainMol’ Ueq as Compared to Neighbors of C3 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.008 Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 5 Note
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 1 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 1 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br1A --Mn1 . 6.2 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br1B --Mn1 . 6.4 s.u.
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 5% Note
PLAT371_ALERT_2_G Long C(sp2)-C(sp1) Bond C11 - C14 . 1.44 Ang.
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 2 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 52 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 2 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
12 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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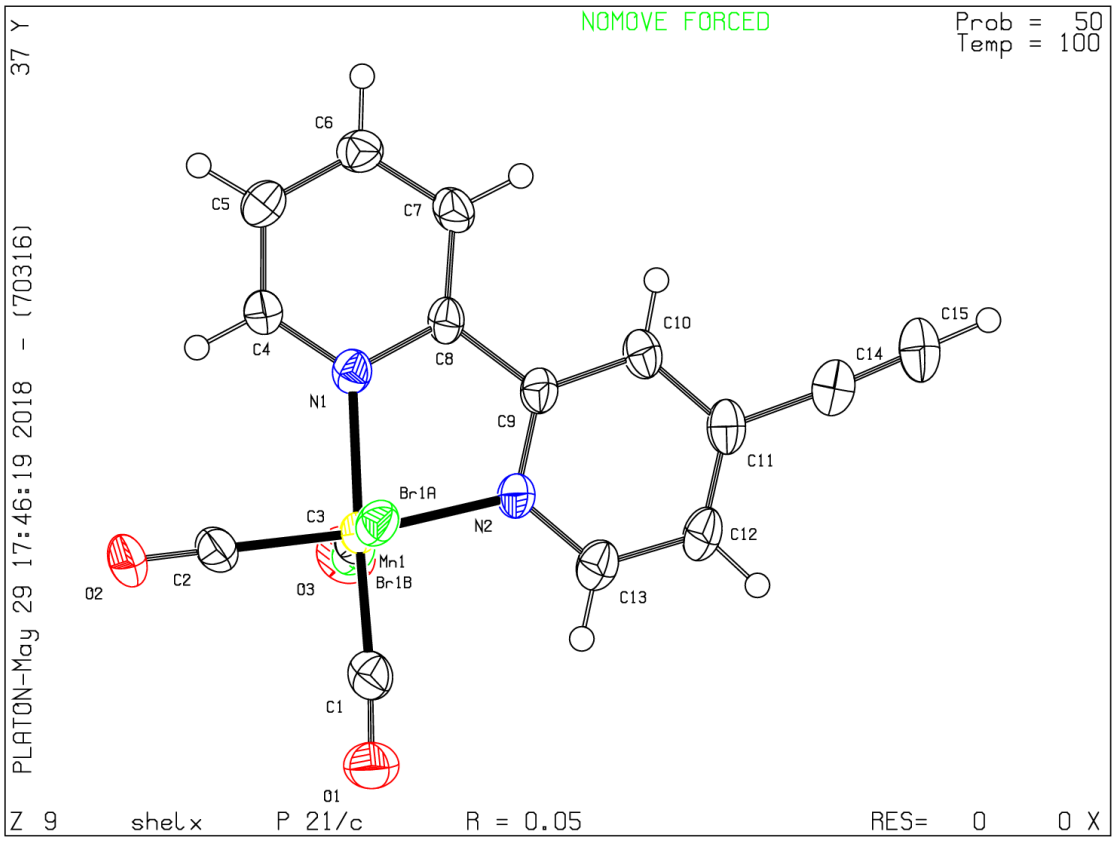
PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock shelx - ellipsoid plot



checkCIF/PLATON report

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

```
Bond precision:  C-C = 0.0069 A          Wavelength=1.54184

Cell:          a=7.3490(5)       b=9.1242(6)      c=12.5779(9)
               alpha=71.174(6)   beta=79.887(6)   gamma=81.860(6)
Temperature:   100 K
```

	Calculated	Reported
Volume	782.60(10)	782.60(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C17 H8 Br Mn N2 O3	C17 H8 Br Mn N2 O3
Sum formula	C17 H8 Br Mn N2 O3	C17 H8 Br Mn N2 O3
Mr	423.09	423.10
Dx,g cm-3	1.796	1.795
Z	2	2
Mu (mm-1)	10.016	10.016
F000	416.0	416.0
F000’	414.63	
h,k,lmax	9,11,15	8,11,15
Nref	3267	3124
Tmin,Tmax	0.134,0.748	0.172,1.000
Tmin’	0.037	

```
Correction method= # Reported T Limits: Tmin=0.172 Tmax=1.000
AbsCorr = GAUSSIAN

Data completeness= 0.956          Theta(max)= 75.681

R(reflections)= 0.0488( 2792)     wR2(reflections)= 0.1389( 3124)

S = 1.049                 Npar= 217
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00686 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          3 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          3 Note
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)       0.006 Degree
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          2 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for   C9       --C16       .       11.7 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1      --C1        .        6.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1      --C3        .       14.5 s.u.
PLAT371_ALERT_2_G Long   C(sp2)-C(sp1) Bond  C9       - C16      .       1.47 Ang.
PLAT794_ALERT_5_G Tentative Bond Valency for Mn1       (I)       .       0.84 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        114 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          2 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
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```

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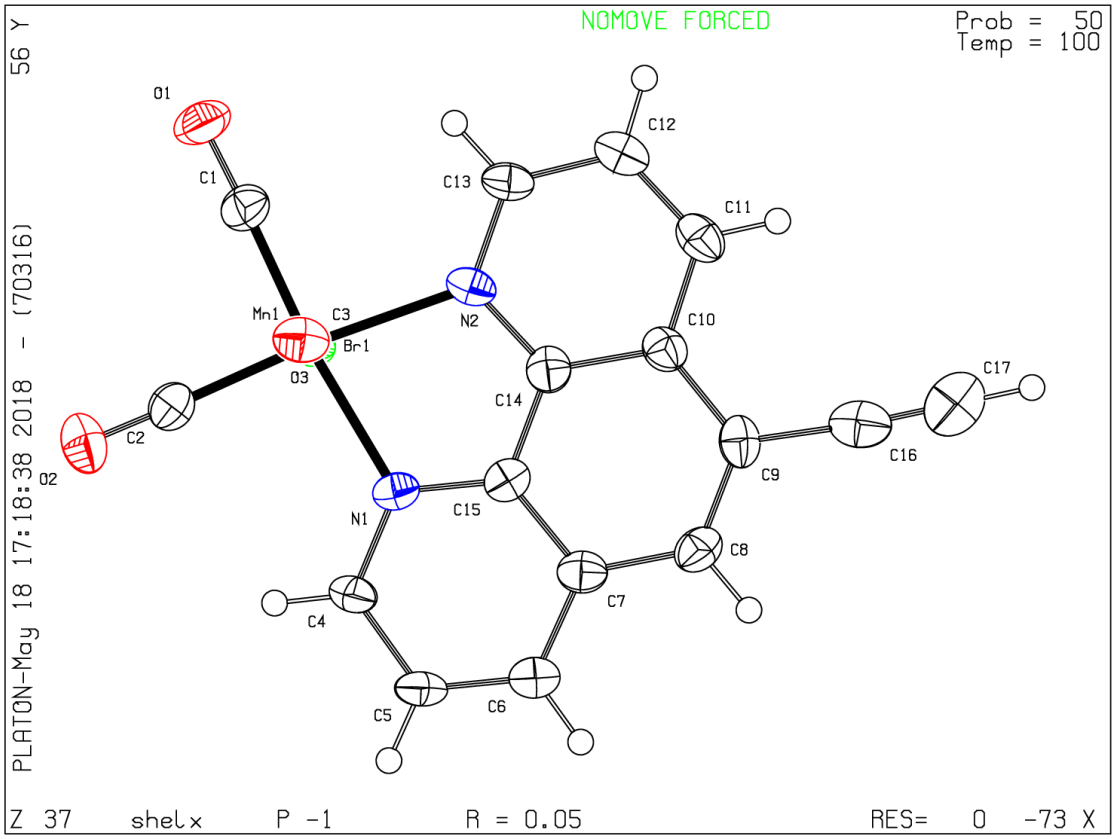
PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock shelx - ellipsoid plot



checkCIF/PLATON report

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

```
Bond precision:  C-C = 0.0052 A          Wavelength=1.54184

Cell:            a=12.4157(6)    b=10.8348(5)       c=12.8562(8)
                 alpha=90        beta=94.772(5)     gamma=90
Temperature:     100 K

                Calculated                Reported
Volume          1723.44(16)               1723.45(16)
Space group     P 21/c                    P 21/c
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C19 H12 Br Mn N2 O3       C19 H12 Br Mn N2 O3
Sum formula     C19 H12 Br Mn N2 O3       C19 H12 Br Mn N2 O3
Mr              451.15                    451.16
Dx,g cm-3       1.739                     1.739
Z               4                         4
Mu (mm-1)       9.138                     9.138
F000            896.0                     896.0
F000'           893.39
h,k,lmax        15,13,16                  15,13,16
Nref            3612                      3501
Tmin,Tmax       0.235,0.527               0.252,0.838
Tmin'           0.104

Correction method= # Reported T Limits: Tmin=0.252 Tmax=0.838
AbsCorr = GAUSSIAN

Data completeness= 0.969          Theta(max)= 76.195

R(reflections)= 0.0548( 3091)     wR2(reflections)= 0.1492( 3501)

S = 1.047                 Npar= 237
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         19 Report
PLAT971_ALERT_2_C Check Calcd Resid. Dens.  0.92A   From Br1             1.67 eA-3
PLAT971_ALERT_2_C Check Calcd Resid. Dens.  0.82A   From Br1             1.57 eA-3
```

Alert level G

```
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1      --C1        .        6.5 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1      --C3        .        6.7 s.u.
PLAT371_ALERT_2_G Long   C(sp2)-C(sp1) Bond  C9       - C16      .       1.45 Ang.
PLAT794_ALERT_5_G Tentative Bond Valency for Mn1       (I)       .       0.87 Info
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         93 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          9 Info
```

```
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   1 ALERT type 4 Improvement, methodology, query or suggestion
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```

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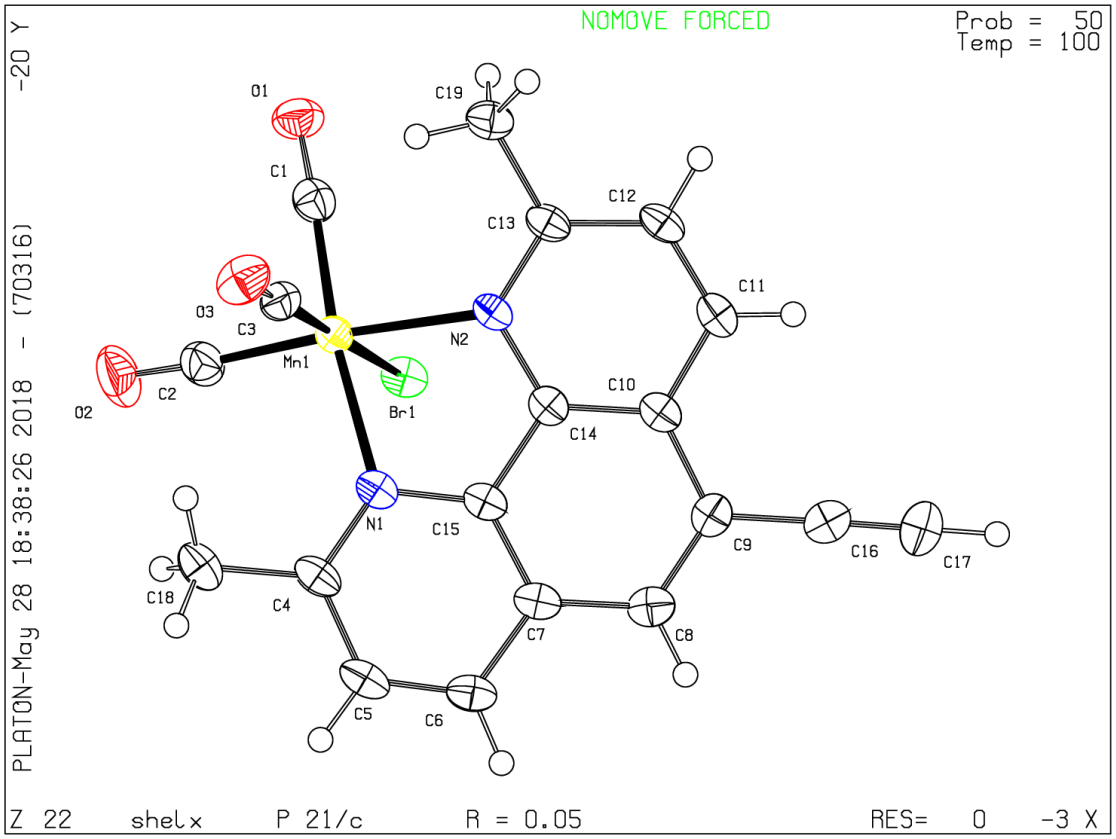
Datablock shelx - ellipsoid plot



checkCIF/PLATON report

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

```
Bond precision:  C-C = 0.0035 A          Wavelength=1.54184

Cell:          a=7.7032(3)       b=8.5452(4)      c=12.3936(5)
               alpha=81.123(4)   beta=84.120(3)   gamma=81.292(3)
Temperature:   100 K
```

	Calculated	Reported
Volume	794.13(6)	794.14(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C17 H12 Br Mn N2 O3	C17 H12 Br Mn N2 O3
Sum formula	C17 H12 Br Mn N2 O3	C17 H12 Br Mn N2 O3
Mr	427.13	427.14
Dx,g cm-3	1.786	1.786
Z	2	2
Mu (mm-1)	9.871	9.871
F000	424.0	424.0
F000’	422.63	
h,k,lmax	9,10,15	9,10,15
Nref	3302	3175
Tmin,Tmax	0.109,0.288	0.131,0.681
Tmin’	0.010	

```
Correction method= # Reported T Limits: Tmin=0.131 Tmax=0.681
AbsCorr = GAUSSIAN

Data completeness= 0.962          Theta(max)= 75.338

R(reflections)= 0.0298( 3116)     wR2(reflections)= 0.0775( 3175)

S = 1.089                 Npar= 229
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT430_ALERT_2_C Short Inter D...A Contact O2 ..O2 2.89 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 2 Report

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 3 Note
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 1 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br1A --Mn1 . 9.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1 --C1 . 6.7 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1 --C2 . 8.3 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1 --C3 . 7.0 s.u.
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 4% Note
PLAT371_ALERT_2_G Long C(sp2)-C(sp1) Bond C11 - C14 . 1.45 Ang.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 2 Check
C3 -BR1B -MN1 1.555 1.555 1.555 15.10 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 24 Check
BR1B -O3 -C3 1.555 1.555 1.555 20.80 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 33 Check
BR1B -C3 -O3 1.555 1.555 1.555 22.00 Deg.
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 125 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF .... 1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 8 Info

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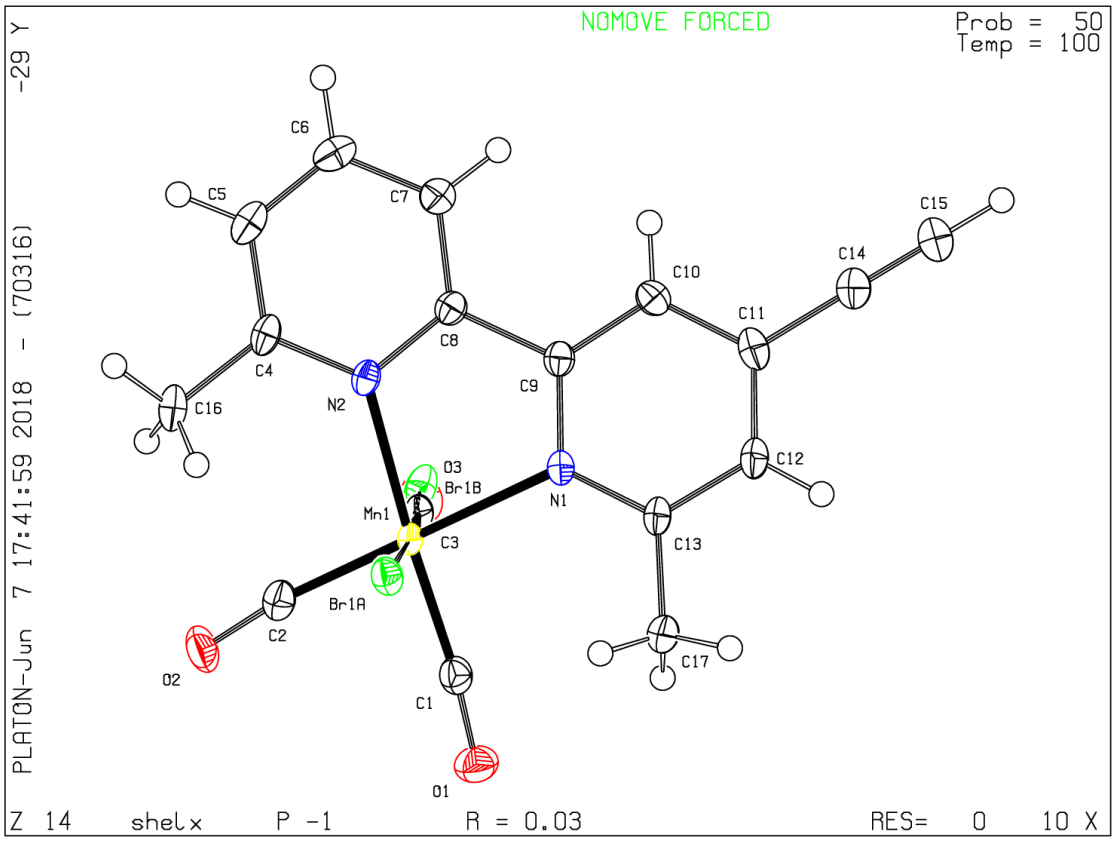
Datablock shelx - ellipsoid plot



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No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

```
Bond precision:  C-C = 0.0056 A          Wavelength=0.71073

Cell:            a=15.7084(3)     b=22.2447(5)     c=25.5612(6)
                 alpha=90         beta=90          gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	8931.8(3)	8931.8(3)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C74 H95 Co N15 O14 P, 8(H2O) [+ solvent]	C74 H95 Co N15 O14 P, 8(H2O)
Sum formula	C74 H111 Co N15 O22 P [+ solvent]	C74 H111 Co N15 O22 P
Mr	1652.68	1652.67
Dx,g cm-3	1.229	1.229
Z	4	4
Mu (mm-1)	0.284	0.284
F000	3512.0	3512.0
F000’	3515.40	
h,k,lmax	21,30,35	20,30,35
Nref	25241[13600]	22567
Tmin,Tmax	0.951,0.967	0.644,1.000
Tmin’	0.879	

```
Correction method= # Reported T Limits: Tmin=0.644 Tmax=1.000
AbsCorr = GAUSSIAN

Data completeness= 1.66/0.89      Theta(max)= 29.665

R(reflections)= 0.0504( 18663)    wR2(reflections)= 0.1282( 22567)

S = 1.025                 Npar= 1083
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

```
PLAT417_ALERT_2_B Short Inter D-H..H-D       H7B      ..H16B            1.99 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D       H11B     ..H20C            1.89 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D       H15B     ..H16B            1.99 Ang.
PLAT420_ALERT_2_B D-H Without Acceptor       O20      --H20C         Please Check
PLAT420_ALERT_2_B D-H Without Acceptor       O22      --H22A         Please Check
PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Theta(Min).       13 Note
```

Alert level C

```
PLAT213_ALERT_2_C Atom O2              has ADP max/min Ratio .....       3.3 prolat
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range       5.8 Ratio
PLAT220_ALERT_2_C Non-Solvent  Resd 1  N   Ueq(max)/Ueq(min) Range       4.3 Ratio
PLAT220_ALERT_2_C Non-Solvent  Resd 1  O   Ueq(max)/Ueq(min) Range       4.0 Ratio
PLAT222_ALERT_3_C Non-Solv.  Resd 1  H   Uiso(max)/Uiso(min) Range       6.3 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for   O3       --C28       .       7.0 s.u.
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C22 Check
PLAT355_ALERT_3_C Long   O-H (X0.82,N0.98A)  O16      - H16B     .      1.02 Ang.
PLAT417_ALERT_2_C Short Inter D-H..H-D       H19B     ..H21C            2.10 Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H36      ..O20             2.65 Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H26B     ..O6              2.65 Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H22B     ..O9              2.67 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         8 Report
PLAT915_ALERT_3_C No Flack x Check Done: Low Friedel Pair Coverage       85 %
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.        0 Info
```

Alert level G

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PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite       27 Note
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............       14 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records       14 Report
PLAT173_ALERT_4_G The CIF-Embedded .res File Contains DANG Records        8 Report
PLAT371_ALERT_2_G Long   C(sp2)-C(sp1) Bond  C55      - C56      .      1.44 Ang.
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O5          121.3 Degree
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O8          119.8 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O9          109.4 Degree
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure      ! Info
PLAT791_ALERT_4_G Model has Chirality at C2          (Chiral SPGR)        S Verify
PLAT791_ALERT_4_G Model has Chirality at C3          (Chiral SPGR)        S Verify
PLAT791_ALERT_4_G Model has Chirality at C4          (Chiral SPGR)        R Verify
PLAT791_ALERT_4_G Model has Chirality at C5          (Chiral SPGR)        R Verify
PLAT791_ALERT_4_G Model has Chirality at C6          (Chiral SPGR)        R Verify
PLAT791_ALERT_4_G Model has Chirality at C7          (Chiral SPGR)        R Verify
PLAT791_ALERT_4_G Model has Chirality at C11         (Chiral SPGR)        S Verify
PLAT791_ALERT_4_G Model has Chirality at C16         (Chiral SPGR)        S Verify
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PLAT791_ALERT_4_G Model has Chirality at C37         (Chiral SPGR)        R Verify
PLAT791_ALERT_4_G Model has Chirality at C38         (Chiral SPGR)        S Verify
PLAT791_ALERT_4_G Model has Chirality at C39         (Chiral SPGR)        R Verify
PLAT794_ALERT_5_G Tentative Bond Valency for Co1       (III)     .      3.62 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       31 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600      866 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....        1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...        7 Note
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  0 ALERT level A = Most likely a serious problem - resolve or explain
  6 ALERT level B = A potentially serious problem, consider carefully
 15 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 28 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 19 ALERT type 2 Indicator that the structure model may be wrong or deficient
  7 ALERT type 3 Indicator that the structure quality may be low
 21 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

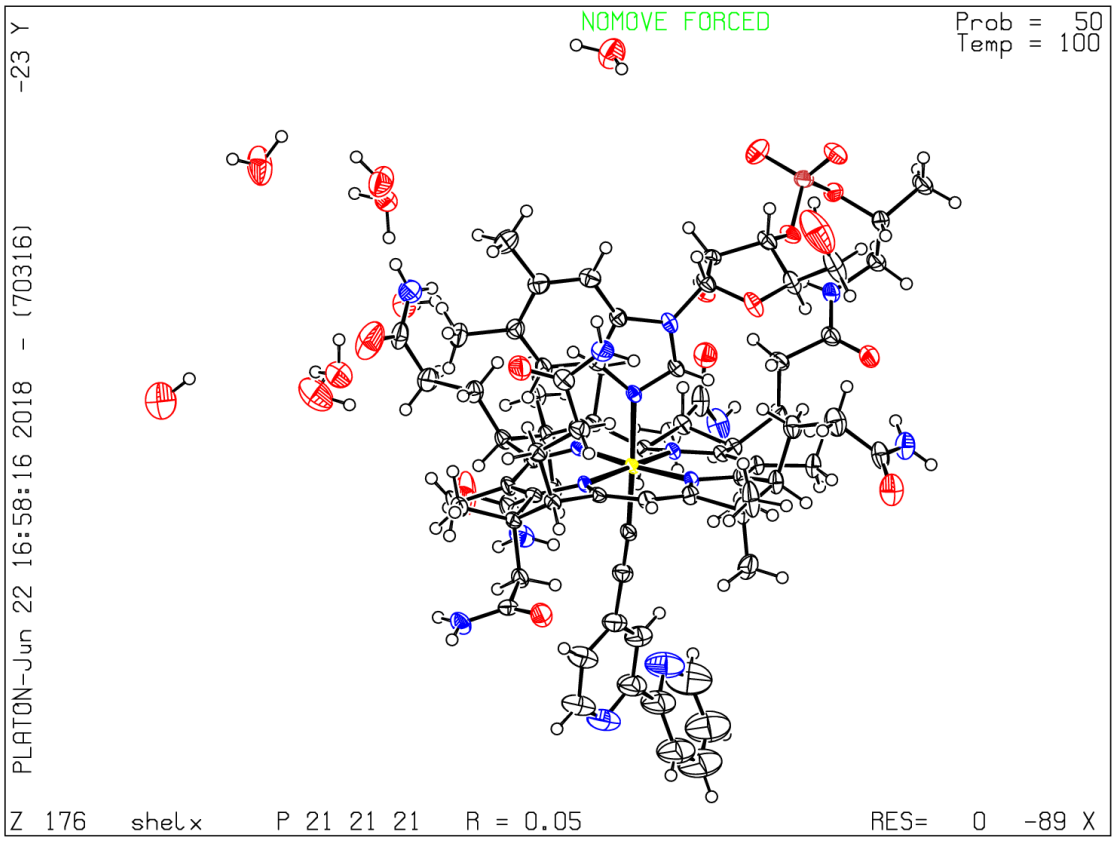
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock shelx - ellipsoid plot



SUPPORTING INFORMATION FOR

Cytotoxicity of Mn-based photoCORMs of ethynyl-α-diimine ligands against different cancer cell lines: The key role of CO-depleted metal fragments

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*To whom all the correspondence should be addressed.

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NMR Spectra

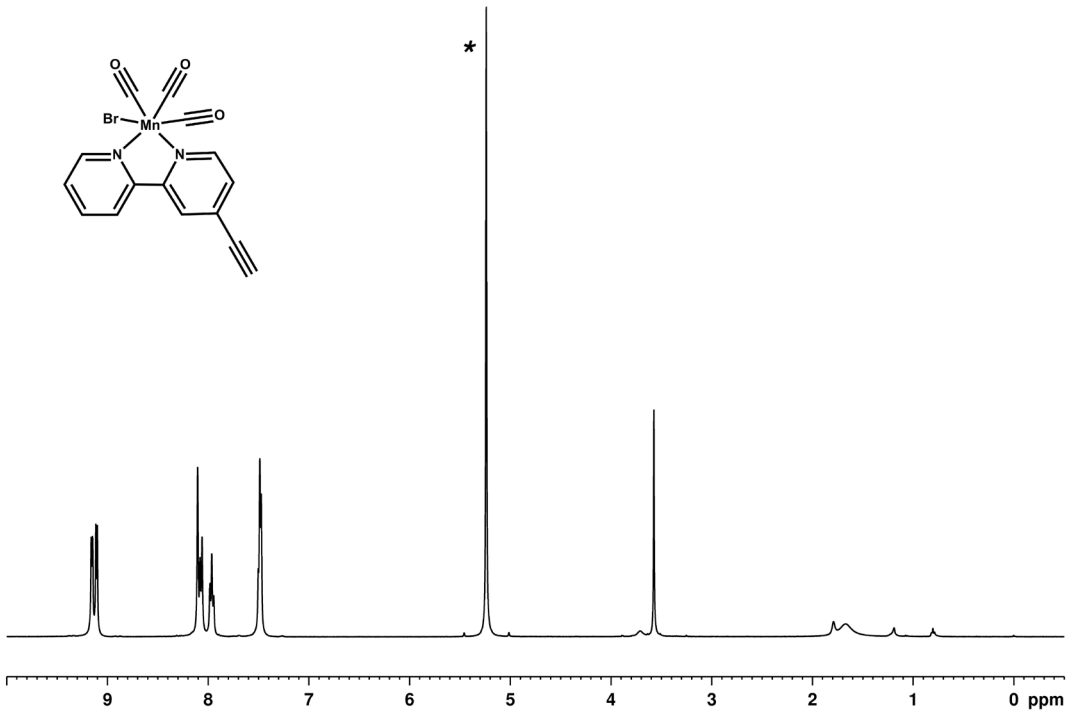


Figure S1. 500 MHz ^{1}H-NMR of compound Mn-**1** (in CD_2Cl_2, ✱= solvent residual peak)

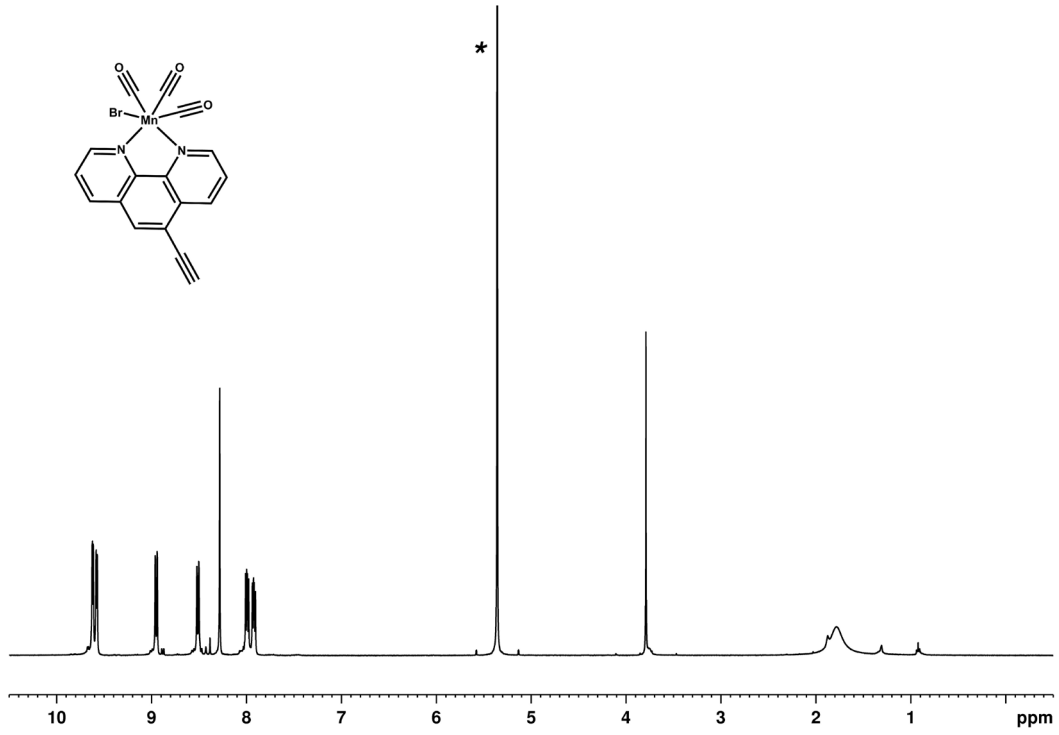


Figure S2. 500 MHz ^{1}H-NMR of compound Mn-**2** (in CD_2Cl_2, ✱= solvent residual peak)

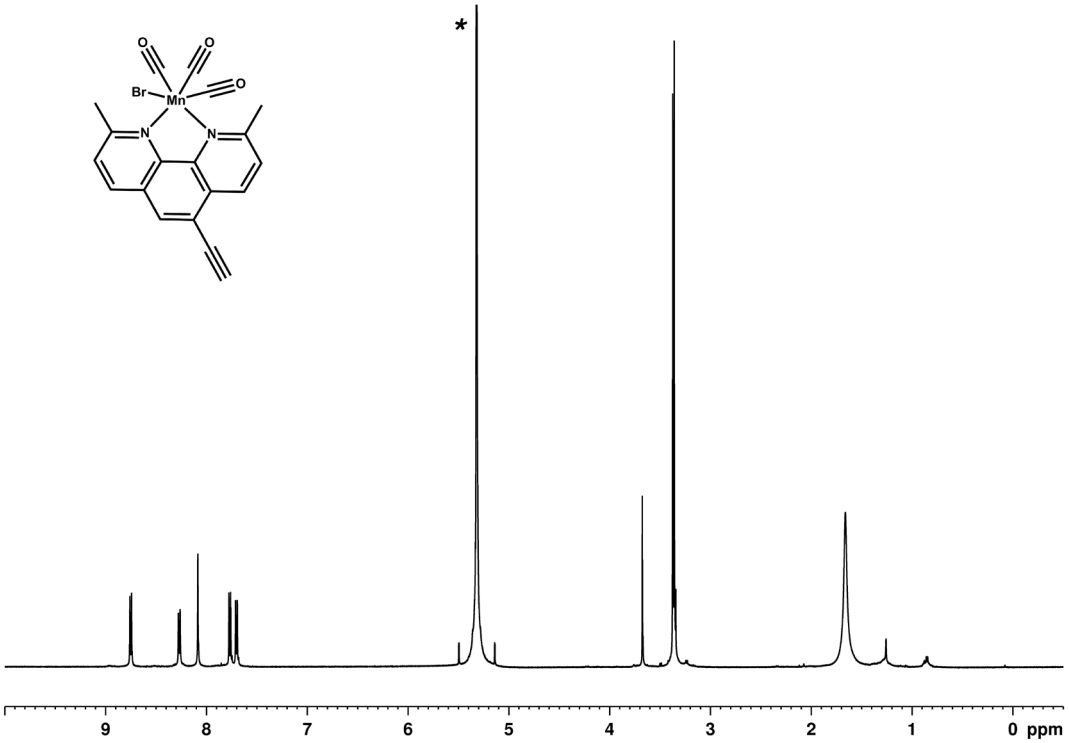


Figure S3. 500 MHz ^{1}H-NMR of compound Mn-**3** (in CD_2Cl_2, ✱= solvent residual peak)

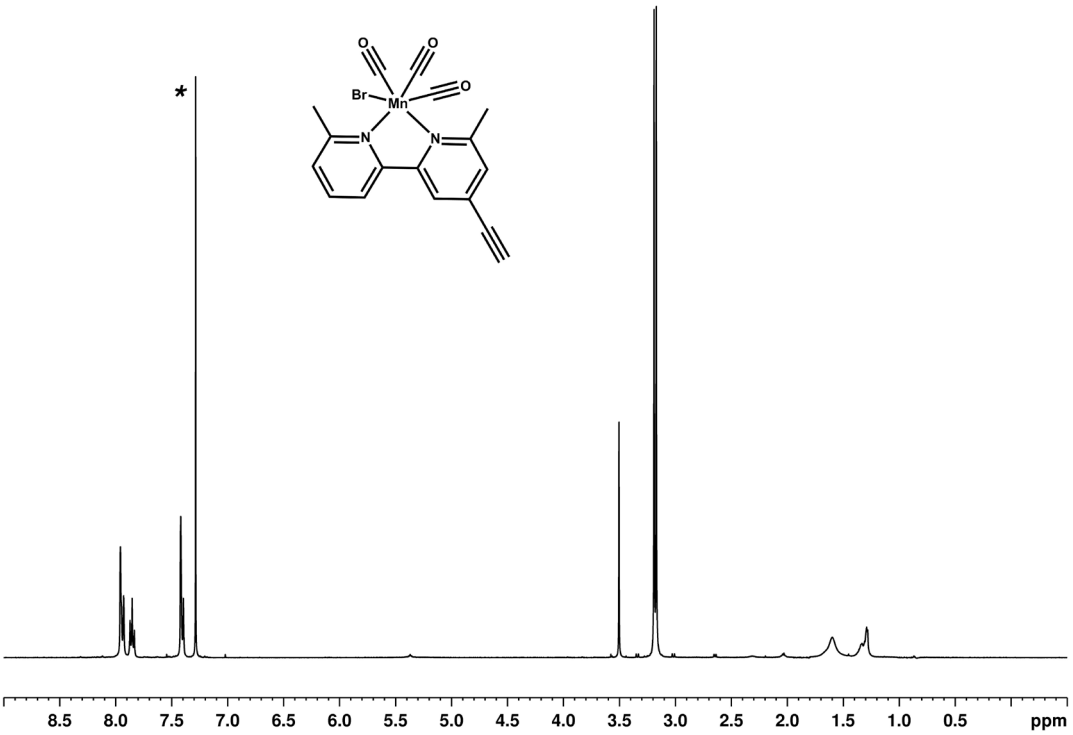


Figure S4. 500 MHz ^{1}H-NMR of compound Mn-**4** (in $CDCl_3$, ✱= solvent residual peak)

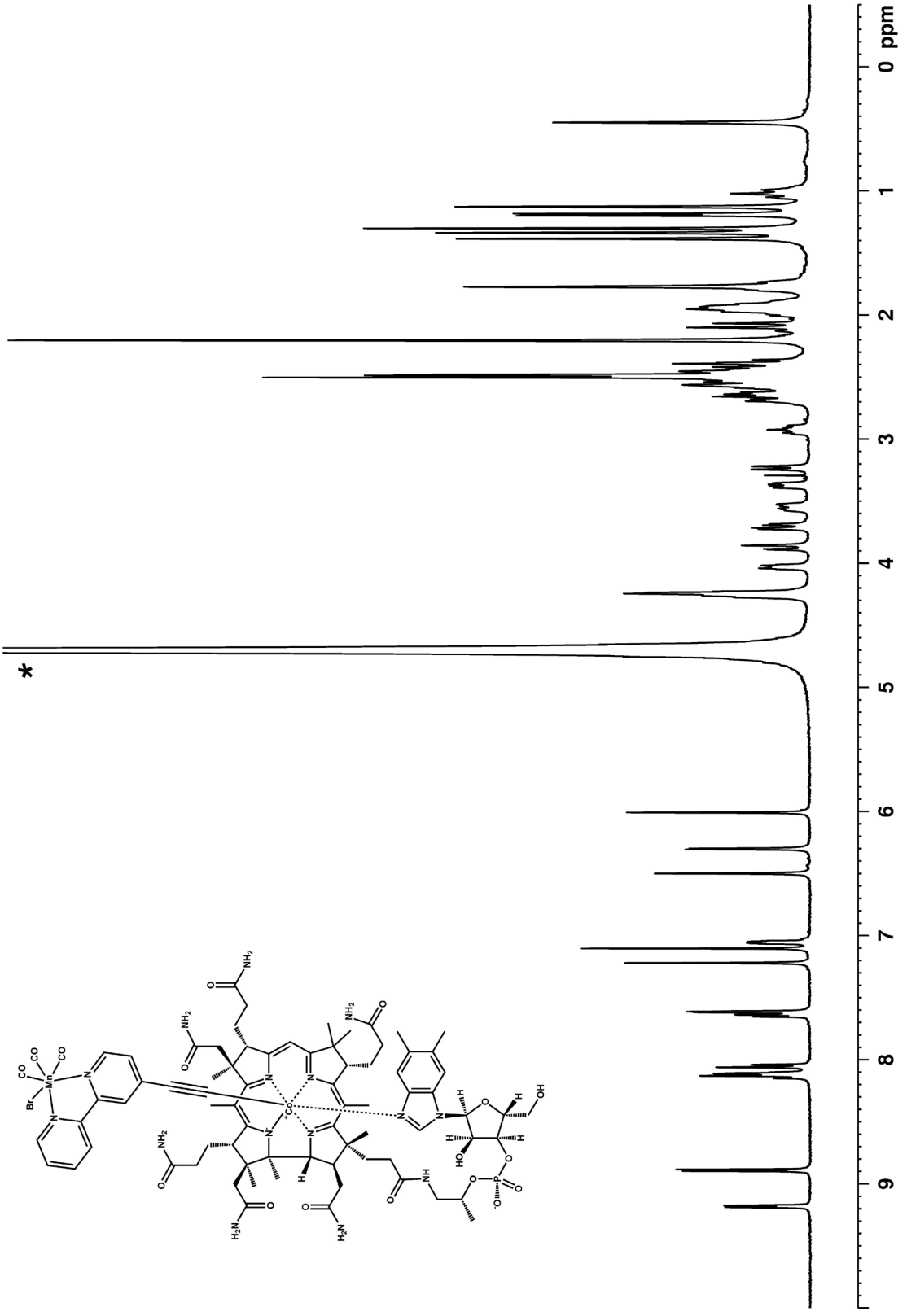


Figure S5. 500 MHz ^{1}H-NMR of compound B_{12}-Mn-**1** (in D_2O, ✱= solvent residual peak)

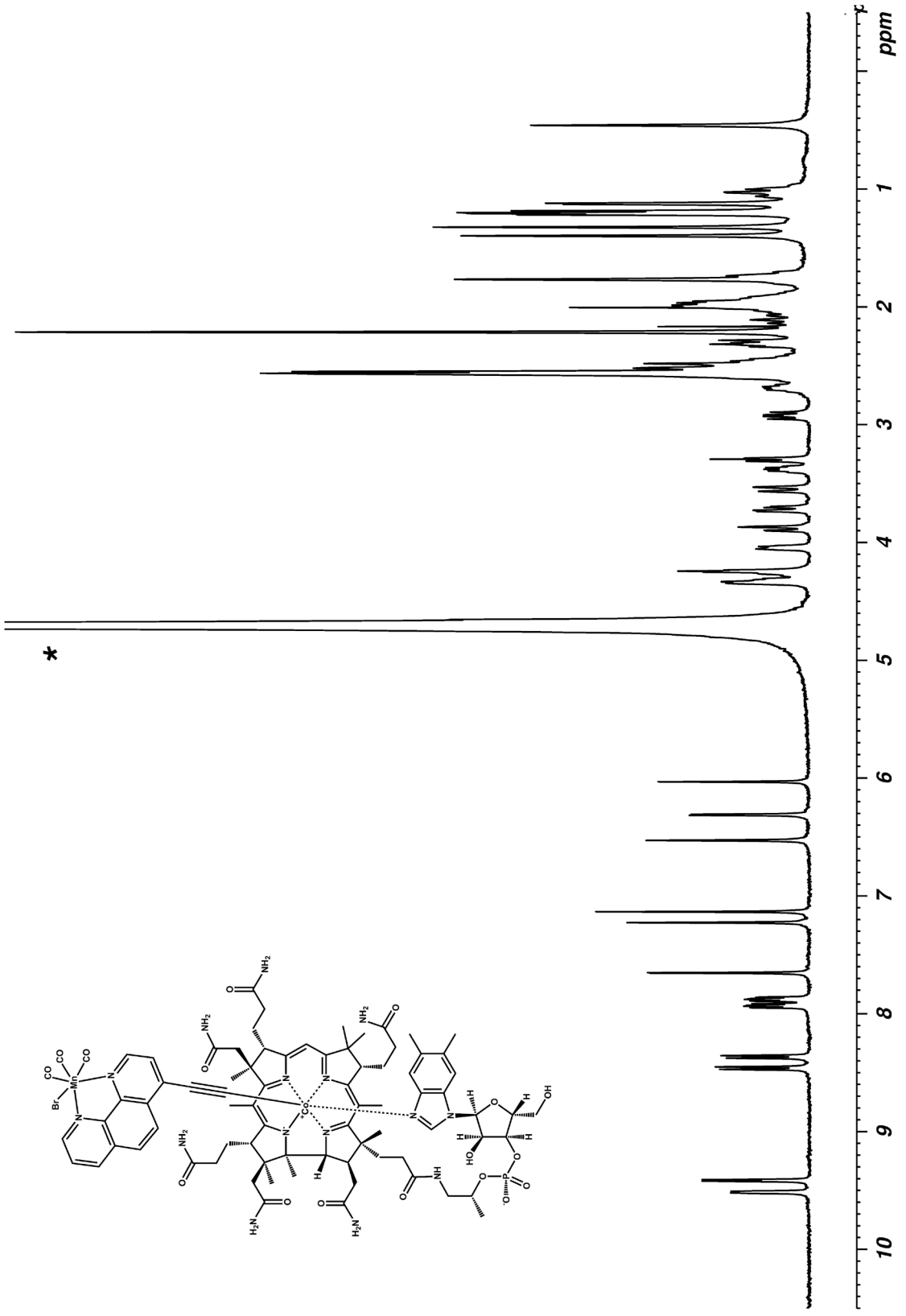


Figure S6. 500 MHz ^{1}H-NMR of compound B_{12}-Mn-**2** (in D_2O, ✱= solvent residual peak)

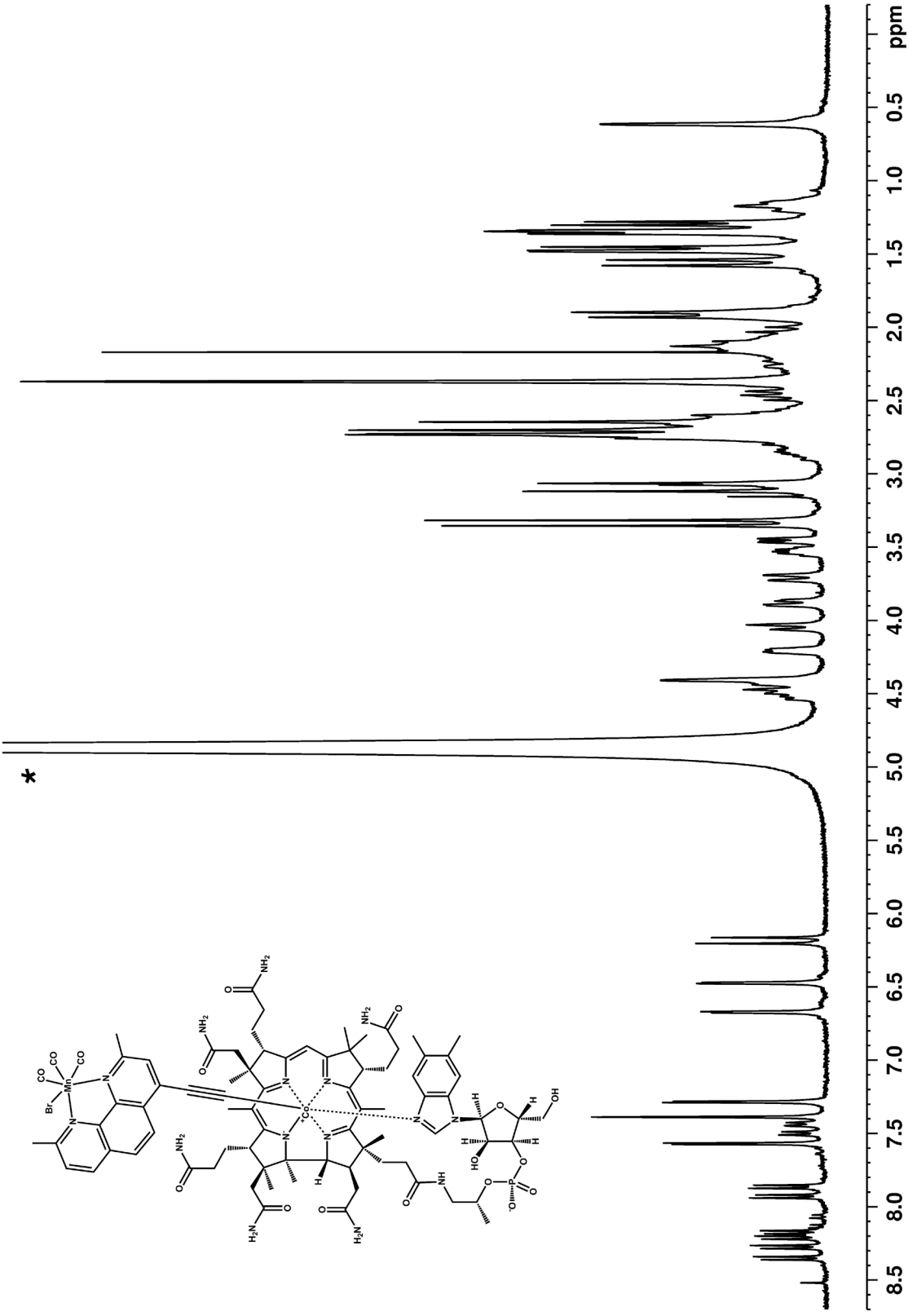


Figure S7. 500 MHz ^{1}H-NMR of compound B_{12}-Mn-**3** (in D_2O, ✱= solvent residual peak)

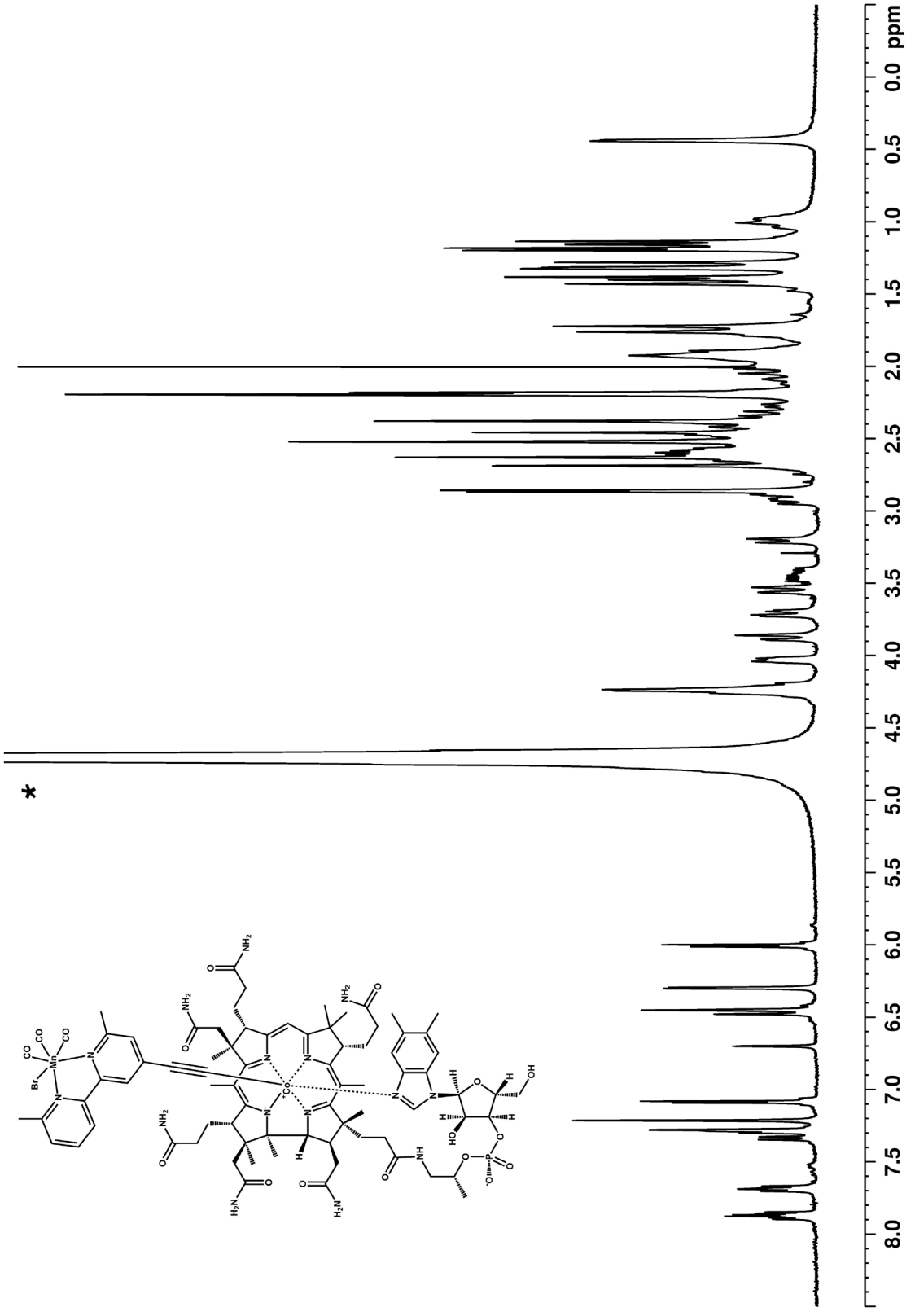


Figure S8. 500 MHz ^{1}H-NMR of compound B_{12}-Mn-**4** (in D_2O, ✱= solvent residual peak)

Equivalent of CO released

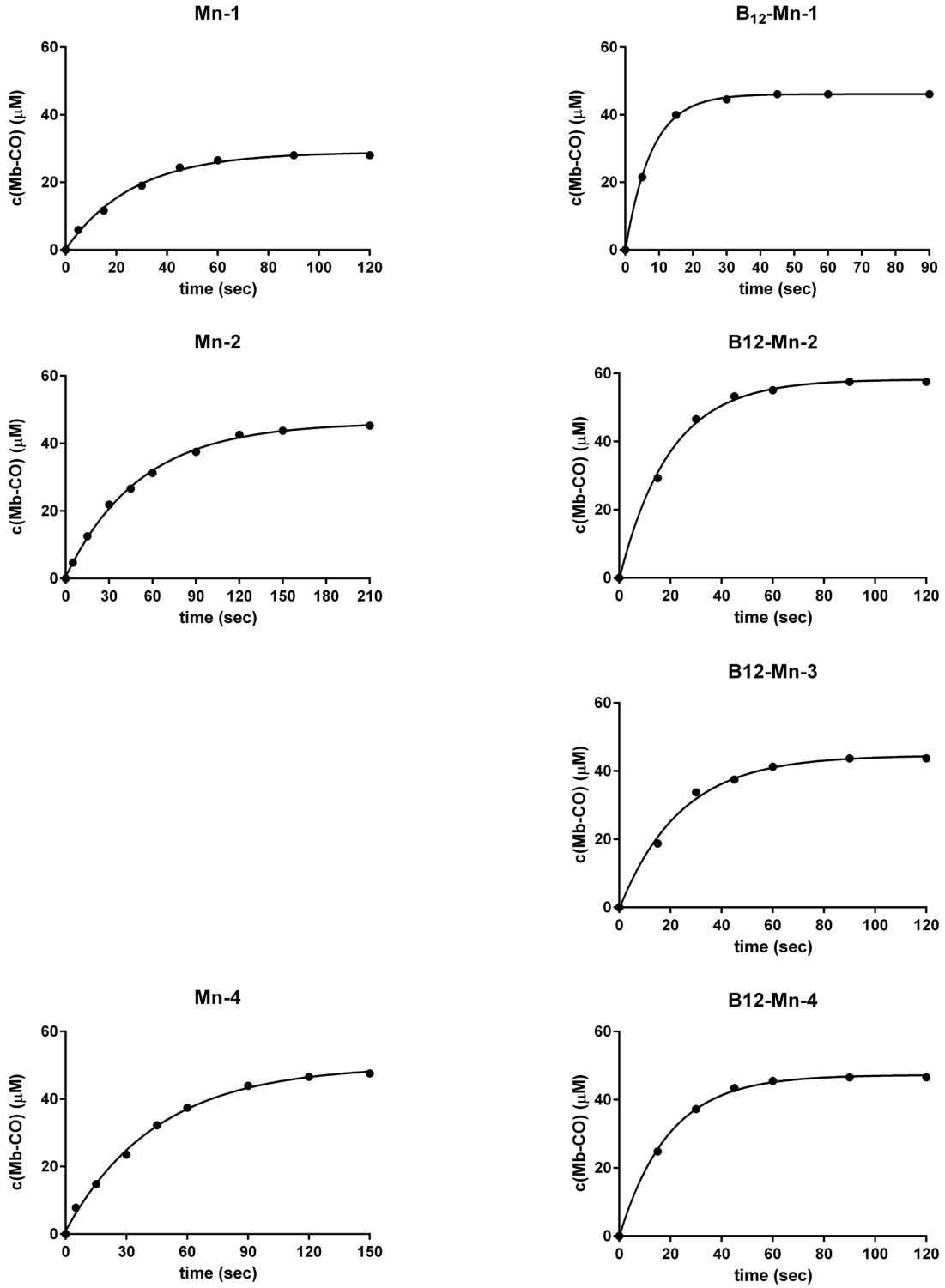


Figure S9. Amount of Mb-CO in µM formed with increasing irradiation time at 420 nm for solutions of compounds Mn-**1** to -**4** and B_{12}-Mn-**1** to -**4** (20 µM) in 0.1 M PBS at pH 7.4 in the presence of myoglobin (60 µM) and sodium dithionite (10 mM) under a dinitrogen atmosphere as determined from UV/vis spectroscopy. The complexes Mn-**1**, -**2** and -**4** were previously dissolved in DMSO (1% final concentration) while Mn-**3** could not be tested due to its poor solubility.

Half-life

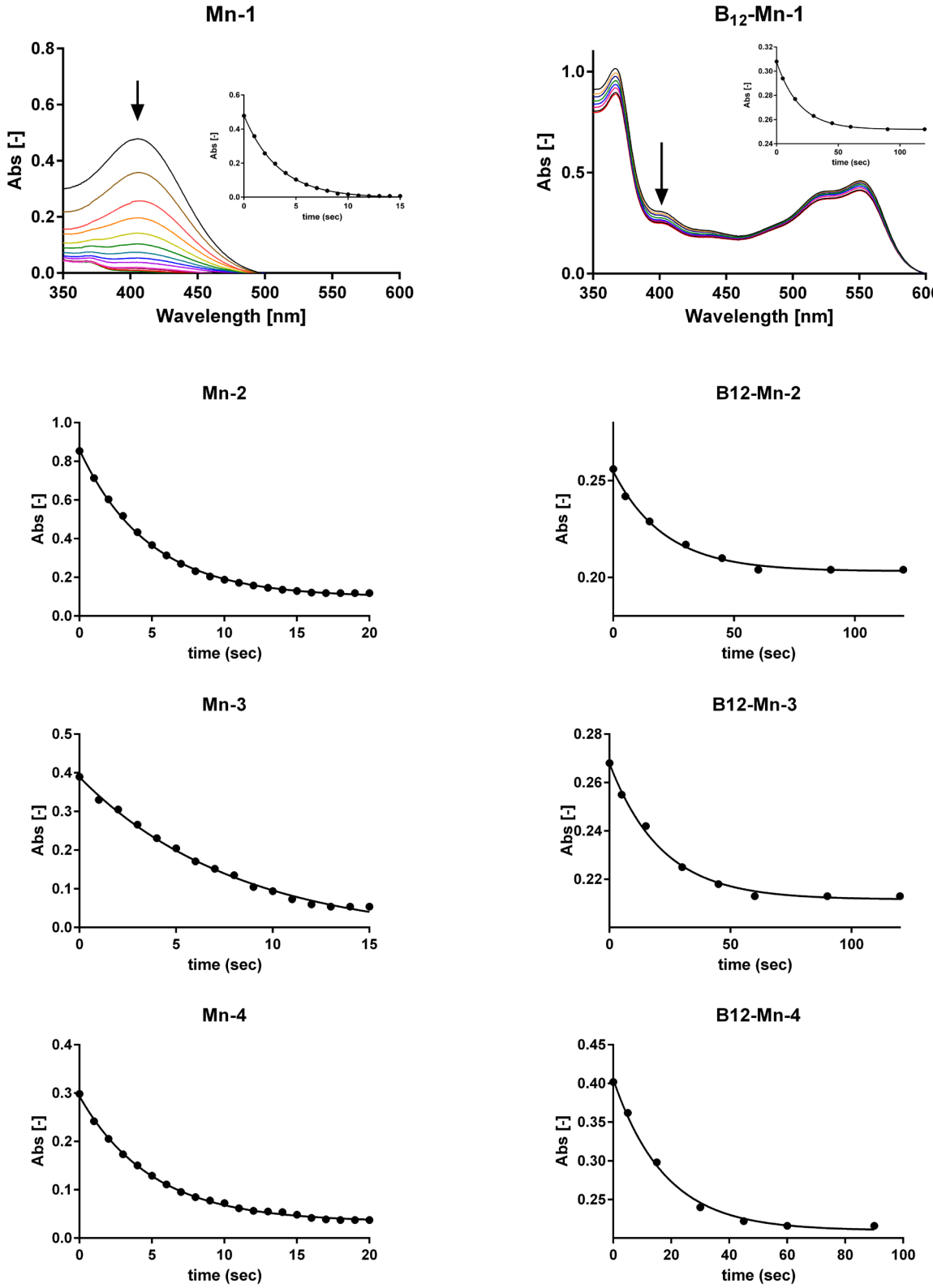


Figure S10. Monitoring of the spectral changes in the electronic absorption spectrum of compounds Mn-**1** to -**4** and B_{12}-Mn-**1** to -**4** in 0.1 M PBS upon irradiation with 420 nm light. The complexes Mn-**1**, -**2** and -**4** were previously dissolved in DMSO (1% final concentration) while Mn-**3** was tested in methanol.

UV-Vis spectra

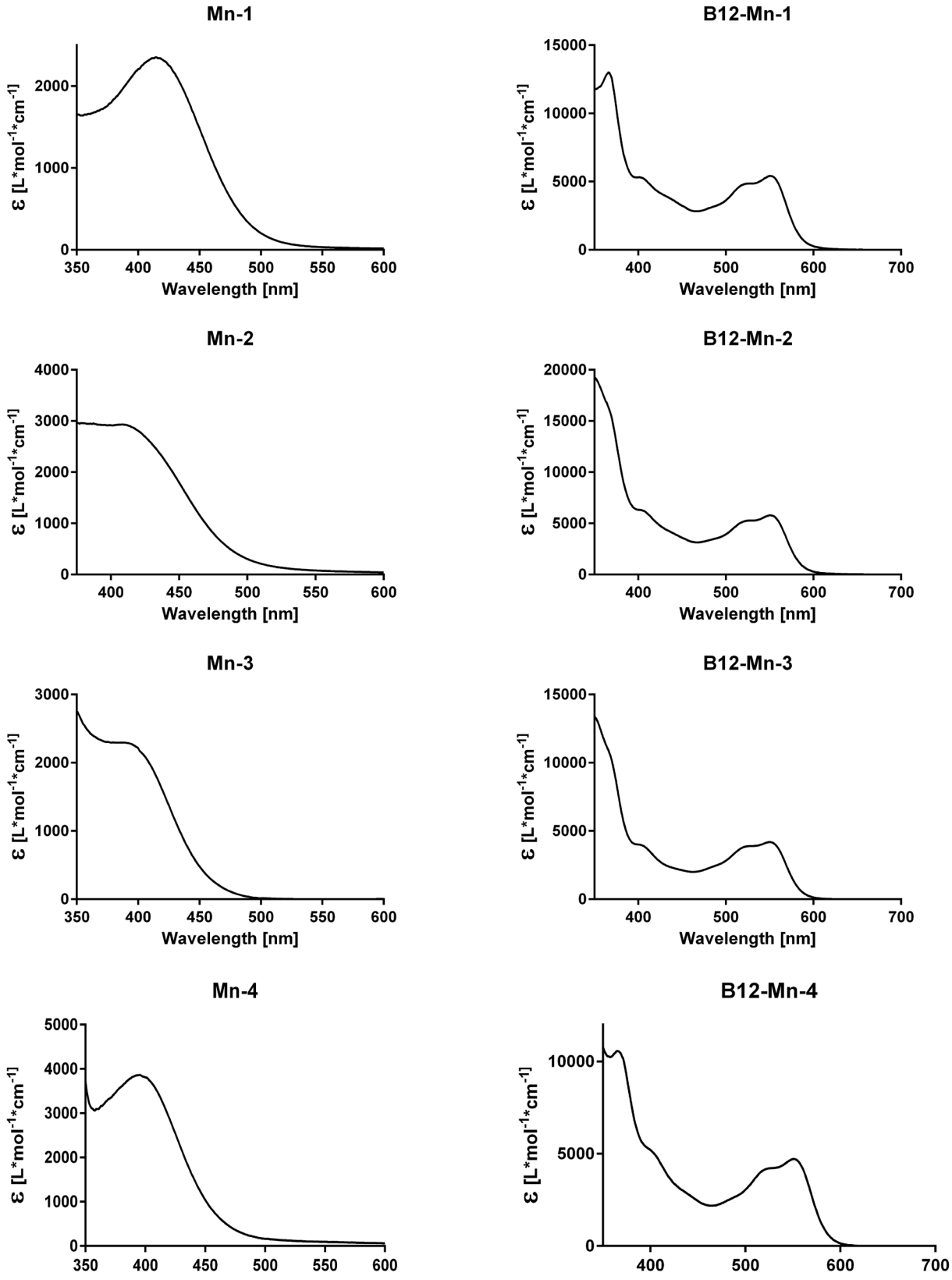


Figure S11. UV-Vis spectra of compounds Mn-1 to -4 (in methanol) and B12-Mn-**1** to -**4** (in 0.1M PBS)

Crystallographic details

Table S1: Crystal data and structure refinement for Mn-**1**

Empirical formula	$C_{15}H_8BrMnN_2O_3$
Formula weight	399.08
Temperature	100.00(10) K
Crystal system	monoclinic
Space group	*P*21/*c*
Unit cell dimensions	a = 7.3490(5) Å
	b = 9.1242(6) Å
	c = 12.5779(9) Å
Unit cell dimensions	α = 7.3490(5) Å
	β = 9.1242(6) Å
	γ = 12.5779(9) Å
Volume/Å^3	1463.6(2)
Z	4
Density (calculated)	1.811 Mg/m^3
Absorbtion coefficient	10.662 mm^{-1}
F(000)	784.0
Crystal size	0.190 × 0.141 × 0.055 mm^3
Radiation	Cu Kα (λ = 1.54184)
2*Θ* range for data collection/°	10.356 to 151.622
Index ranges	-16 ≤ h ≤ 18, -13 ≤ k ≤ 10, -11 ≤ l ≤ 11
Reflections collected	9952
Independent reflections	2981 [R_{int} = 0.0633, R_{sigma} = 0.0611]
Data/restraints/parameters	2981/2/203
Goodness-of-fit on F^2	1.031
Final *R* indexes [I > 2σ (I)]	R_1 = 0.0486, wR_2 = 0.1187
Final *R* indexes [all data]	R_1 = 0.0744, wR_2 = 0.1304
Largest diff. peak and hole	0.82/-0.95 e.Å^{-3}

Table S2: Crystal data and structure refinement for Mn-**2**.

Empirical formula	$C_{17}H_8BrMnN_2O_3$	
Formula weight	423.10	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 7.3490(5) Å	α= 71.174(6)°.
	b = 9.1242(6) Å	β= 79.887(6)°.
	c = 12.5779(9) Å	γ = 81.860(6)°.
Volume	782.60(10) $Å^3$	
Z	2	
Density (calculated)	1.795 Mg/m^3	
Absorption coefficient	10.016 mm^{-1}	
F(000)	416	
Crystal size	0.265 x 0.233 x 0.029 mm^3	
Radiation	Cu Kα (λ = 1.54184)	
ϑ range for data collection	3.749 to 75.681°.	
Index ranges	-8 ≤ h ≤ 5, -11 ≤ k ≤ 10, -15 ≤ l ≤ 14	
Reflections collected	5217	
Independent reflections	3124 [R_{int} = 0.0317]	
Completeness to ϑ = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.172	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3124 / 2 / 217	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2σ(I)]	R_1 = 0.0488, wR_2 = 0.1316	
R indices (all data)	R_1 = 0.0555, wR_2 = 0.1389	
Largest diff. peak and hole	1.126 and -0.734 $e.Å^{-3}$	

Table S3: Crystal data and structure refinement for Mn-**3**

Empirical formula	$C_{19}H_{12}BrMnN_2O_3$	
Formula weight	451.16	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 12.4157(6) Å	α= 90°.
	b = 10.8348(5) Å	β= 94.772(5)°.
	c = 12.8562(8) Å	γ = 90°.
Volume	1723.45(16) $Å^3$	
Z	4	
Density (calculated)	1.739 Mg/m^3	
Absorption coefficient	9.138 mm^{-1}	
F(000)	896	
Crystal size	0.203 x 0.199 x 0.070 mm3	
θ range for data collection	3.572 to 76.195°.	
Index ranges	-15 ≤ h ≤ 12, -10 ≤ k ≤ 13, -16 ≤ l ≤ 15	
Reflections collected	10459	
Independent reflections	3501 [Rint = 0.0535]	
Completeness to θ = 67.684°	99.4 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.838 and 0.252	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	3501 / 0 / 237	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2σ(I)]	R1 = 0.0548, wR2 = 0.1413	
R indices (all data)	R1 = 0.0603, wR2 = 0.1492	
Largest diff. peak and hole	1.542 and -0.844 e.Å-3	

Table S4: Crystal data and structure refinement for Mn-**4**.

Empirical formula	$C_{17}H_{12}BrMnN_2O_3$
Formula weight	427.14
Temperature	100.00(10) K
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 7.7032(3) Å
	b = 8.5452(4) Å
	c = 12.3936(5) Å
Unit cell dimensions	α = 81.123(4) Å
	β = 84.120(3) Å
	γ = 81.292(3) Å
Volume/Å^3	794.14(6)
Z	2
Density (calculated)	1.786 Mg/m^3
Absorbtion coefficient	9.871 mm^{-1}
F(000)	424.0
Crystal size	0.400 × 0.241 × 0.126 mm^3
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.242 to 150.676
Index ranges	-5 ≤ h ≤ 9, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected	5429
Independent reflections	3175 [R_{int} = 0.0198, R_{sigma} = 0.0248]
Data/restraints/parameters	3175/1/229
Goodness-of-fit on F^2	1.089
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0298, wR_2 = 0.0771
Final *R* indexes [all data]	R_1 = 0.0304, wR_2 = 0.0775
Largest diff. peak and hole	1.03/-0.54 e.Å^{-3}

Table S5: Crystal data and structure refinement for B_{12}-**bpy**.

Empirical formula	$C_{74}H_{111}CoN_{15}O_{22}P$	
Formula weight	1652.67	
Temperature	100.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 15.7084(3) Å	α= 90°.
	b = 22.2447(5) Å	β= 90°.
	c = 25.5612(6) Å	γ = 90°.
Volume	8931.8(3) $Å^3$	
Z	4	
Density (calculated)	1.229 Mg/m3	
Absorption coefficient	0.284 mm^{-1}	
F(000)	3512	
Crystal size	0.453 x 0.147 x 0.117 mm3	
θ range for data collection	2.560 to 29.665°.	
Index ranges	-20 ≤ h ≤ 19, -30 ≤ k ≤ 20, -34 ≤ l ≤ 35	
Reflections collected	78051	
Independent reflections	22567 [Rint = 0.0378]	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.644	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	22567 / 31 / 1083	
Goodness-of-fit on F2	1.025	
Final R indices [I>2σ(I)]	R1 = 0.0504, wR2 = 0.1196	
R indices (all data)	R1 = 0.0677, wR2 = 0.1282	
Absolute structure parameter	-0.009(4)	
Largest diff. peak and hole	0.623 and -0.420 e.Å-3	

Additional supporting images

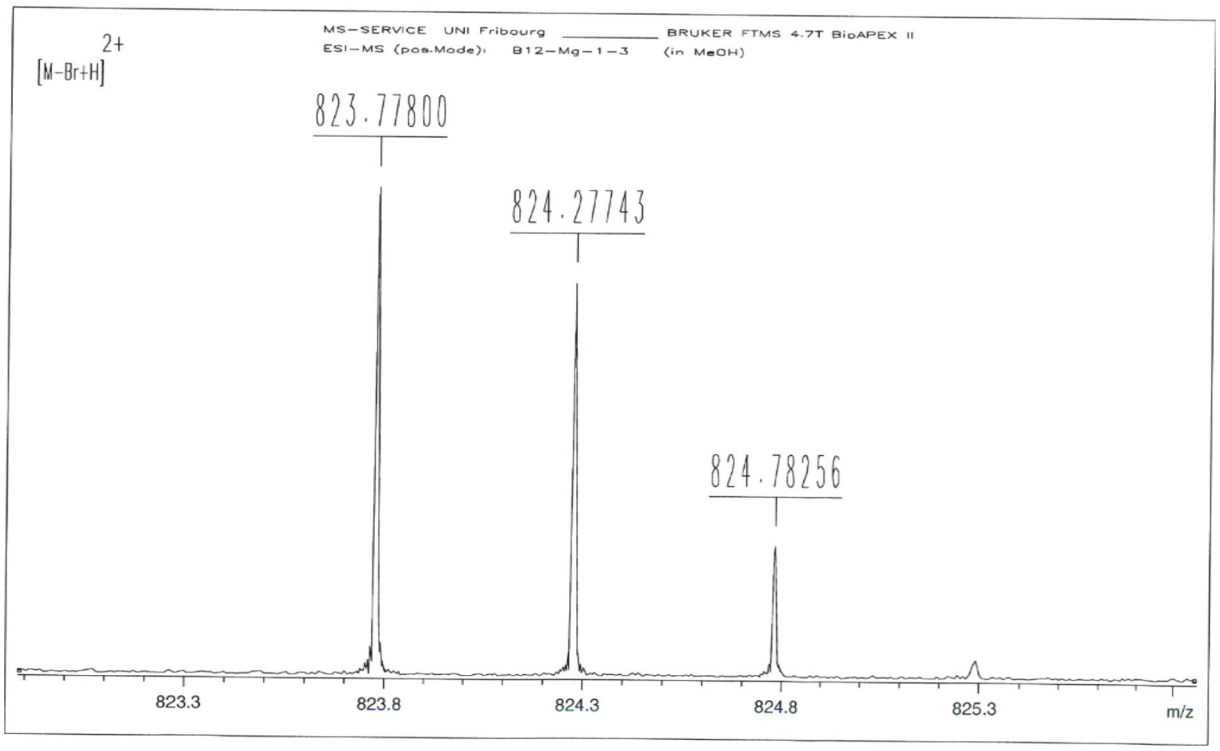


Figure S12: HR-ESI-MS spectrum (in MeOH) of compound B_{12}-Mn-**1**

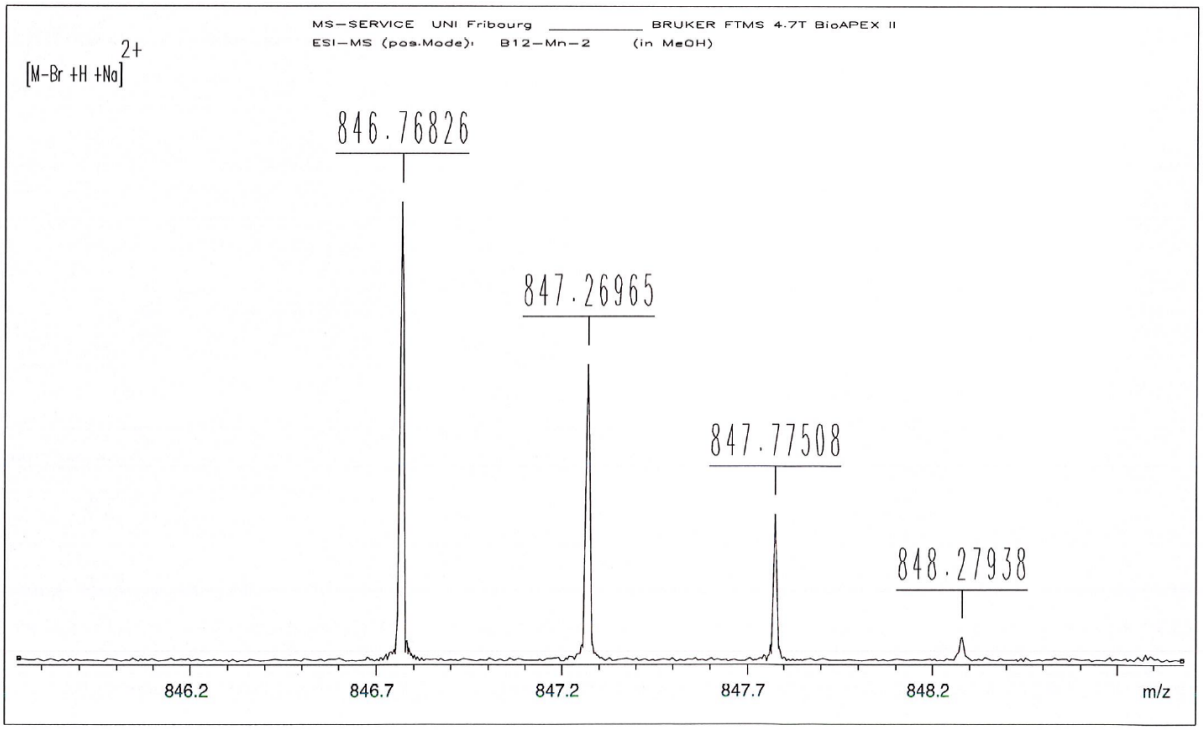


Figure S13: HR-ESI-MS spectrum (in MeOH) of compound B_{12}-Mn-**2**

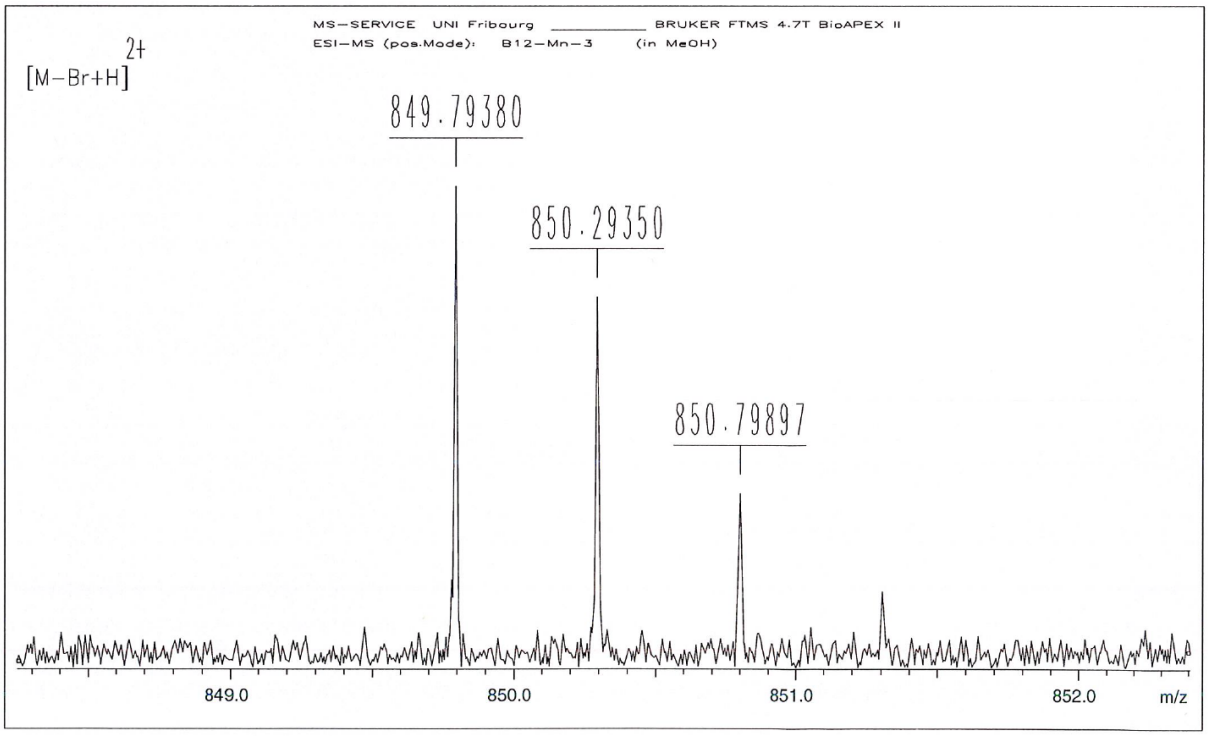


Figure S14: HR-ESI-MS spectrum (in MeOH) of compound B_{12}-Mn-**3**

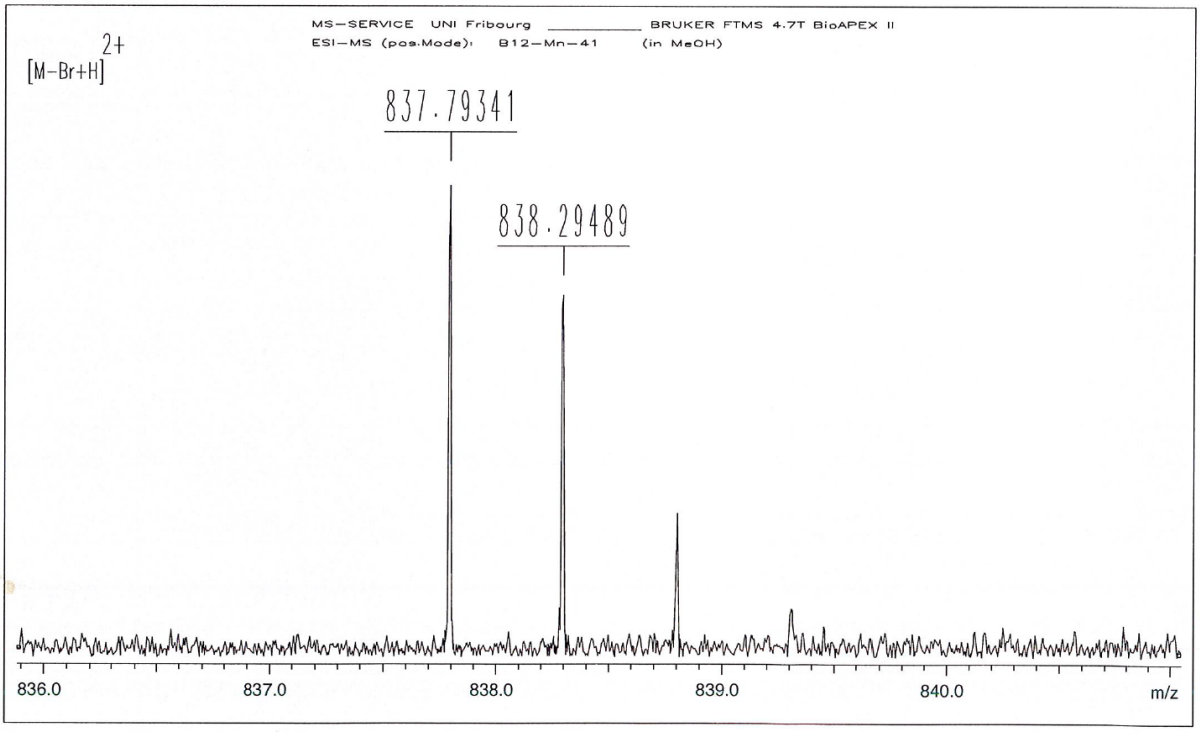


Figure S15: HR-ESI-MS spectrum (in MeOH) of compound B_{12}-Mn-**4**

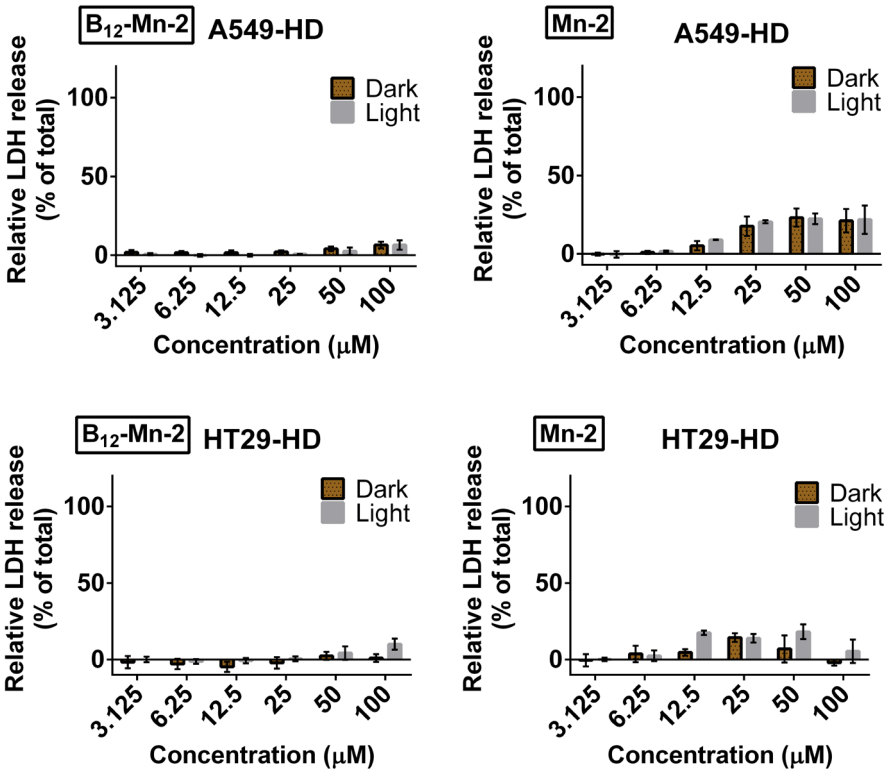


Figure S16: Graphs illustrating levels of LDH relative to the positive control (Triton X)

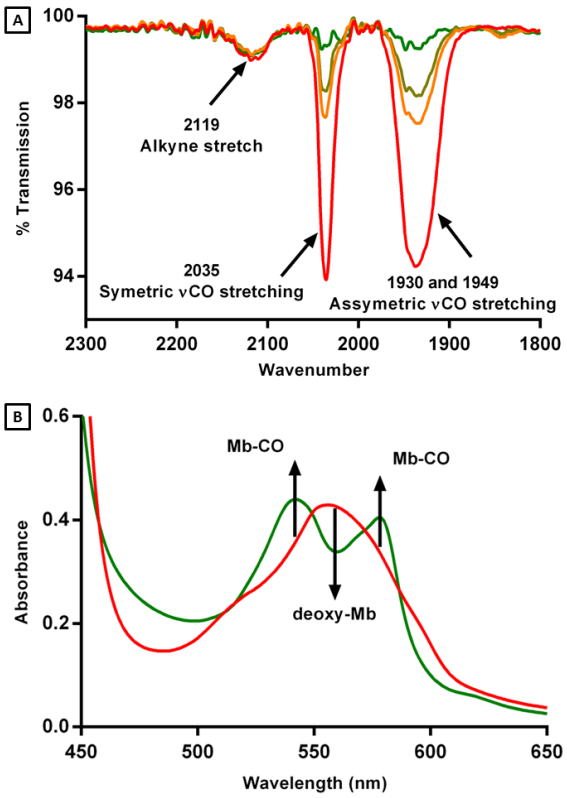
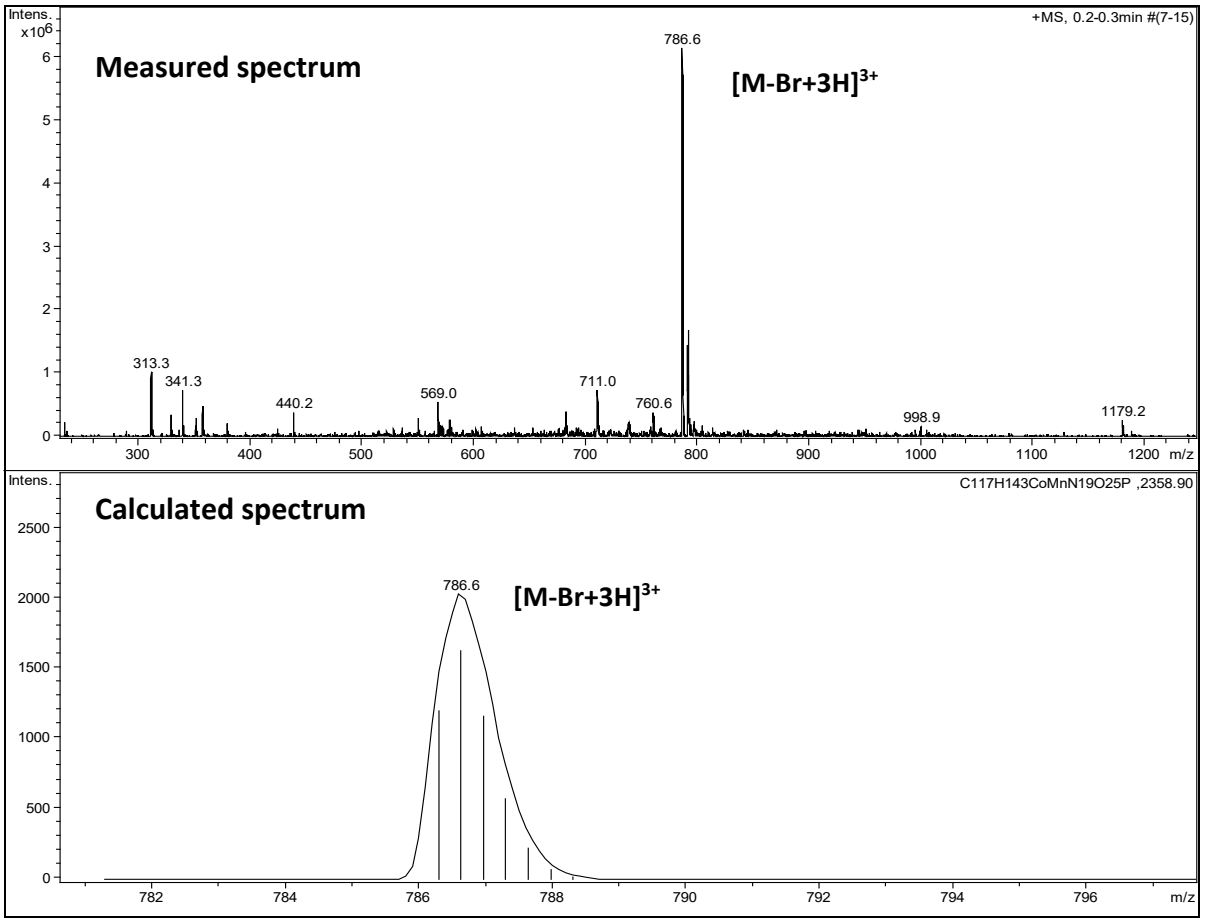


Figure S17: Typical CO releasing experiment. (A) IR spectrum of compound B_{12}-Mn-**4** in methanol following 20 seconds time lapses of irradiation (B) conversion of deoxy-Mb to Mb-CO by B_{12}-Mn-**4** under the myoglobin assay condition.



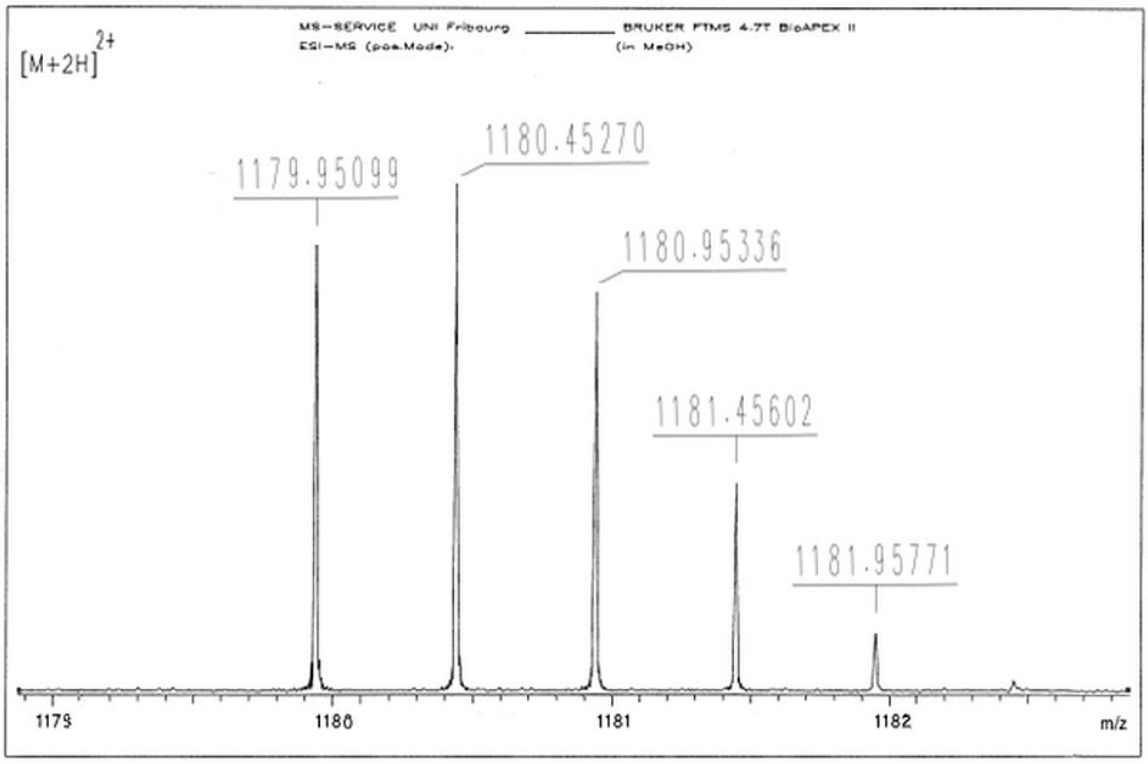


Figure S18: Mass spectrum (top) and HR-ESI-MS spectrum of compound B_{12}Mn-**2**-CBC

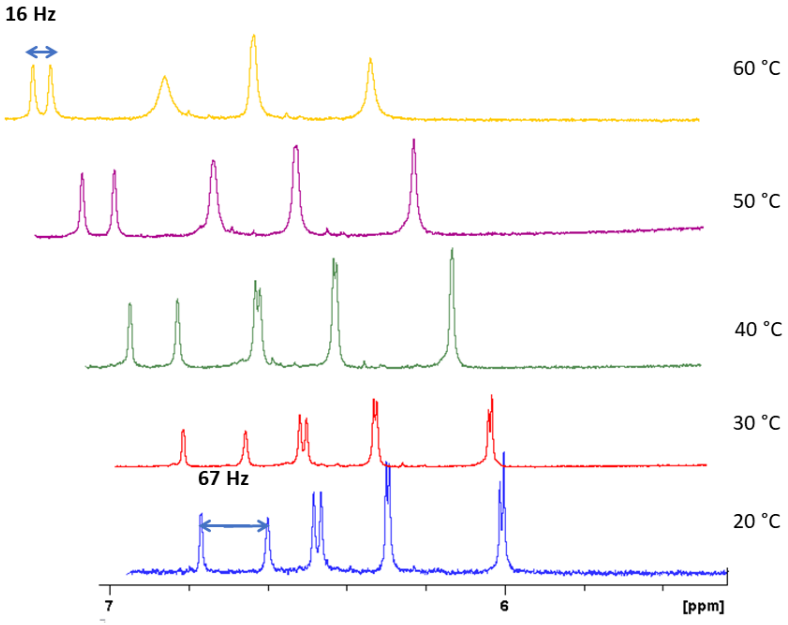


Figure S19: Temperature-dependent measurements of compound B_{12}-Mn-**4** showing the coalescence of split aromatic signals belonging to the same proton as evidence of the presence of two conformations at the upper ligand of the derivative.

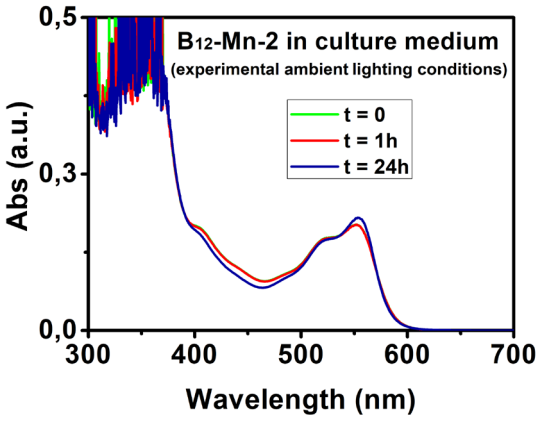


Figure S20: Spectral changes in the electronic absorption spectrum of B12-Mn-**2** incubated in cell culture medium and exposed to experimental ambient light conditions over the course of 24h.