Electronic Supporting Information

A Biotin-Conjugated photo-activated CO-Releasing Molecule (BiotinCORM): Efficient CO-release from an avidin-BiotinCORM protein adduct

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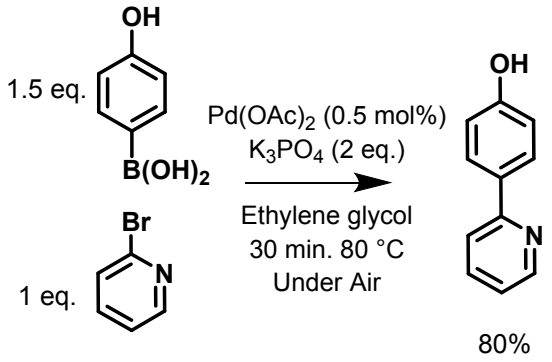
ESI 1 Synthesis of phenylpyridine ligands

Synthesis of 2(4-hydroxy-phenyl)pyridine (6)

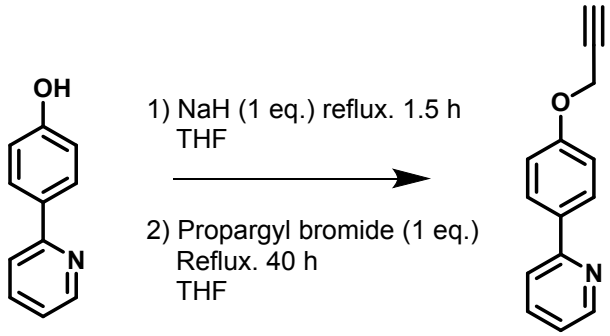


This compound was synthesised using a modified literature procedure.[1]

To a 250 ml round bottomed flask equipped with a magnetic stirrer was added $Pd(OAc)_2$ (0.005 eq., 50 µMol, 11.2 mg), 4-hydroxybenzeneboronic acid (1.5 eq., 15 mmol, 2.06 g), potassium tri-phosphate (2 eq., 20 mmol, 4.24 g), 2-bromopyridine (1 eq., 10 mmol, 950 µl/1.58 g), and ethylene glycol (60 ml). The reaction was heated to 80 °C for 30 minutes and was allowed to cool to room temperature. Water (75 ml) and saturated brine (75 ml) were added and the aqueous layer was extracted with dichloromethane (4 × 100 ml). The organic layers were combined and dried with $MgSO_4$ and filtered. Solvent was removed under reduced pressure to yield the crude product. The crude product was purified by silica gel column chromatography (40:60 v/v PET ether/ethyl acetate followed by 50:50 v/v petroleum ether/ethyl acetate). The solvent was removed to isolate the title compound as a white solid (1.37 g, 80% yield).

M.P. (DSC): 164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, J = 5.0, 1.8, 1.0 Hz, 1H), 7.79–7.71 (m, 3H), 7.65 (d, J = 8.0 Hz, 1H), 7.21 (dd, J = 7.4, 4.9 Hz, 1H), 6.80 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 157.9, 149.2, 137.7, 130.8, 128.9, 121.9, 121.1, 116.2; Elemental Analysis (CHN) C: 76.85% H: 5.31% N: 8.04% (calc.: C: 76.17% H: 5.30% N: 8.18%); ESI-MS m/z = 172.0755 $[M+H]^+$ (calc. for $C_{11}H_{10}NO$= 172.0762); IR (KBr disc): 3367–2120, 1603, 1560, 1523, 1470, 1425, 1381, 1273, 1245, 1183, 1153, 1097, 998, 966, 839, 778, 744, 714, 646, 623, 580, 552, 492, 473 cm^{-1}.

Synthesis of 2-[4-(prop-2-ynyloxy)phenyl]pyridine (7)



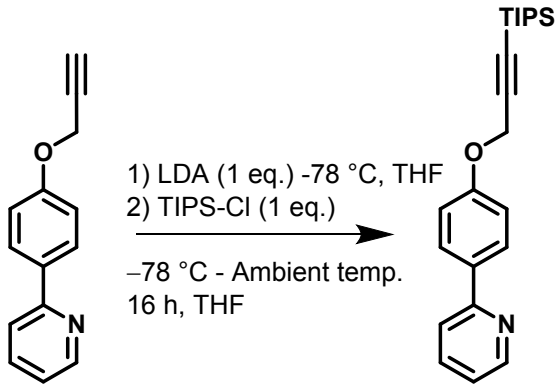
75%

This compound was prepared using a modified literature procedure.[2]

To a suspension of sodium hydride (1 eq., 7 mmol, 178 mg) in dry THF (40 ml), was added a solution of 2-(4-hydroxyphenyl)pyridine (1 eq., 7 mmol, 1.21 g) in dry THF (40 ml) in a Schlenk tube *via* cannula transfer over 10 min. The resulting solution was refluxed for 1.5 h. The solution was allowed to cool and propargyl bromide (1 eq., 7 mmol, 833 mg) was then added. The solution was refluxed for a further 40 h. The reaction mixture was then allowed to cool to room temperature, and water (40 ml) was added. The aqueous phase was then extracted with CH_2Cl_2 (3 × 50 ml). The organic layers were combined, then washed with saturated sodium carbonate (2 × 50 ml), water (2 × 50 ml), were then dried with $MgSO_4$ and filtered. The solvent was evaporated to yield the crude product. The crude was dissolved in dichloromethane and was loaded on to silica. The crude mixture was purified by silica gel column chromatography using 30:70 (*v/v)* Et_2O:petroleum ether increasing to 40:60. Removal of solvent yielded pure product as an off-white solid (1.10 g, 75% yield).

M.P. (DSC): 81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.8 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.72 (apr. td, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.17 (ddd, *J* = 7.2, 4.8, 1.4 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.75 (d, *J* = 2.5 Hz, 2H), 2.54 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 157.3 ,149.9, 137.0, 133.3, 128.5, 121.9, 120.2, 115.4, 78.7, 76.0, 56.2; ESI-MS: *m/z* = 210.0920 $[M+H]^+$ (calc. for $C_{14}H_{12}NO$ = 210.0193); Elemental Analysis (CHN) C: 80.02% H: 5.26% N: 6.58% (calc.: C: 80.36% H: 5.30% N: 6.69%); IR (THF):3232, 2128, 2118, 1608, 1588, 1564, 1514, 1467, 1436, 1377, 1307, 1275, 1242, 1223, 1176, 1154, 1112 cm^{-1}.

Synthesis of 2-[4-(3-triisopropylsilyl-prop-2-ynyloxy)phenyl]pyridine (8)



76%

This compound was synthesised using a modified literature procedure.[3]

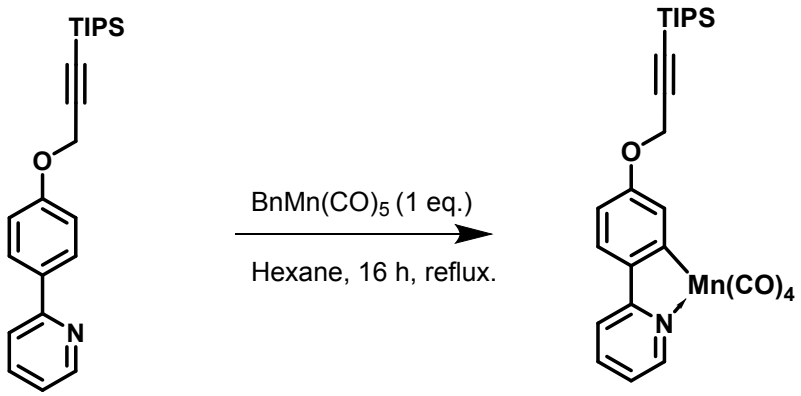
This compound was synthesised using a modified literature procedure.[3]

2-[4-(prop-2-ynyloxy)phenyl]pyridine (1 eq., 1 mmol, 209 mg) was dissolved in dry THF (10 ml). The mixture was cooled to −78 °C and LDA (1 eq., 1 mmol) was added over five mins *via* syringe. The reaction mixture was allowed to warm to 0 °C for five mins. The mixture was cooled back to −78 °C and TIPS chloride (1 eq., 1 mmol, 192 mg/214 µl) was added. The mixture was allowed to warm to ambient temperature and was stirred overnight. Saturated $NH_4Cl_{(aq)}$(10 ml) was added and the mixture was extracted with Et_2O (2 × 20 ml). The organic layer was then washed with water (10 ml) and saturated brine (10 ml) and was dried with $MgSO_4$ and filtered. Removal of solvent under reduced pressure yielded crude product. The crude product was loaded on to silica using dichloromethane which was subsequently evaporated under reduced pressure. The product was purified by silica gel column chromatography. The column was started using petroleum ether to remove apolar impurities. The product was eluted with 8% Et_2O: petroleum ether (*v/v*). Removal of solvent under reduced pressure yielded the product as a clear orange oil (279 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (ddd, J = 4.8, 1.6, 1.0 Hz, 1H), 7.94 (d, J = 8.8 Hz, 2H), 7.78–7.59 (m, 2H), 7.16 (ddd, J = 7.0, 4.8, 1.4 Hz, 1H), 7.10 (d, J = 8.8 Hz, 2H), 4.78 (s, 2H), 1.04 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 157.3, 149.8, 137.0, 132.8, 128.3, 121.8, 120.2, 115.6, 102.1, 89.7, 57.1, 18.8, 11.4; ESI-MS: *m/z* = 366.2238 $[M+H]^+$ (calc. for $C_{23}H_{32}SiNO$ = 366.2248)

ESI 2 Synthesis of manganese(I) complexes

Synthesis of tetracarbonyl 2-[4-(3-triisopropylsilyl-prop-2-ynyloxy)phenyl]κ,C^2-pyridine-κ,N) manganese(I)(9)

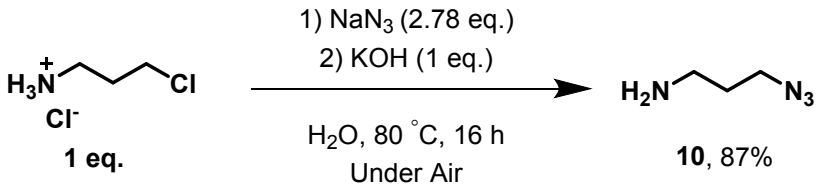


9, 97%

2-[4-(3-triisopropylsilyl-prop-2-ynyloxy)phenyl]pyridine (1 eq., 2.285 mmol, 833 mg) and $BnMn(CO)_5$ (1 eq., 2.285 mmol, 654 mg) were dried under vacuum in a Schlenk tube for 15 minutes. Hexane (30 ml) was then added via cannula transfer from an ampoule. The reaction mixture was refluxed with stirring for 16 h. The solution was allowed to cool to room temperature and was filtered through a pipette packed with Celite™. The solvent was removed under reduced pressure to yield the product as an off-yellow solid (1.17 g, 97% yield). The compound did not require further purification after the reaction but if it was required this could be done using silica gel column chromatography.

M.P. (DSC): 95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dt, *J* = 5.5, 1.3 Hz, 1H), 7.77–7.72 (m, 2H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.60 (d, *J* = 2.5 Hz, 1H), 7.03 (td, *J* = 5.5, 3.1 Hz, 1H), 6.79 (dd, *J* = 8.6, 2.5 Hz, 1H), 4.84 (s, 2H), 1.05 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 166.4, 159.3, 154.0, 139.9, 137.9, 126.3, 125.4, 121.6, 119.0, 112.0, 102.3, 89.3, 56.8, 18.9, 11.4; ESI-MS: *m/z* = 532.1345 $[MH]^+$ (calc. for $C_{27}H_{31}MnNO_5Si$ = 532.1347); Elemental Analysis (CHN) C: 60.58% H: 5.77% N: 2.56% (calc.: C: 61.01% H: 5.69% N: 2.64%); IR (Solution: THF): 2073, 1989, 1973, 1931, 1604, 1580, 1553, 1468, 1431, 1317, 1281, 1211, 1198, 1165 cm^{-1}.

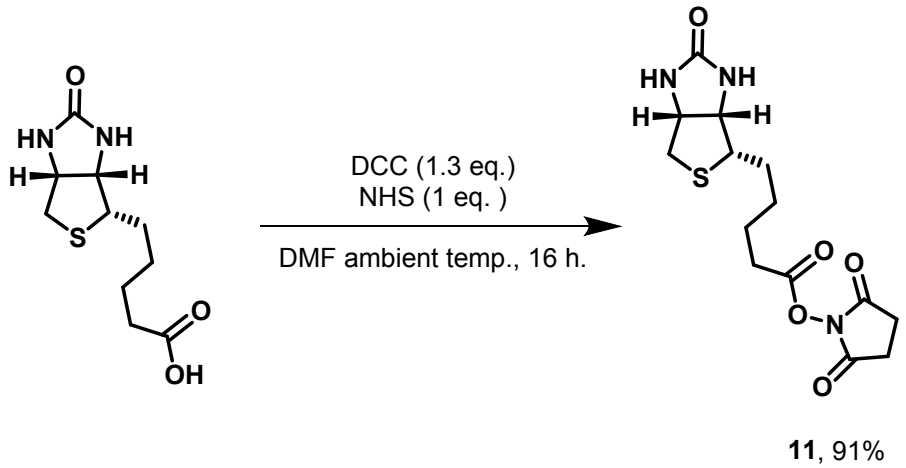
Synthesis of 3-azido-1-propylamine (10)[4, 5]



To a stirred solution of 3-chloropropylamine hydrochloride (1 eq., 4.31 mmol, 560 mg), dissolved in water (5 ml) was added NaN_3 (2.78 eq., 12.0 mmol, 840 mg), and the mixture heated to 80 °C. After 16 h, KOH pellets (1 eq.) were added to basify the solution, followed by extraction with diethyl ether (3 × 5 ml). The organic phase was dried with $MgSO_4$ and filtered. Removal of solvent under reduced pressure gave pure product as a colourless oil (312 mg, 72% yield). Note: This molecule is volatile, so low pressure and temperature on a rotator evaporator is essential.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (td, *J* = 6.8, 2.0 Hz, 1H), 2.76 (td, *J* = 6.8, 2.0 Hz, 1H), 1.68 (qnd, *J* = 6.8, 2.0 Hz, 1H), 1.39 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 49.4, 39.5, 32.6; ESI-MS: *m/z* = 101.0822 $[M+H]^+$ (Calc. for $N_4C_3H_9$ = 101.0822).

Synthesis of Biotin-NHS (11)[6]



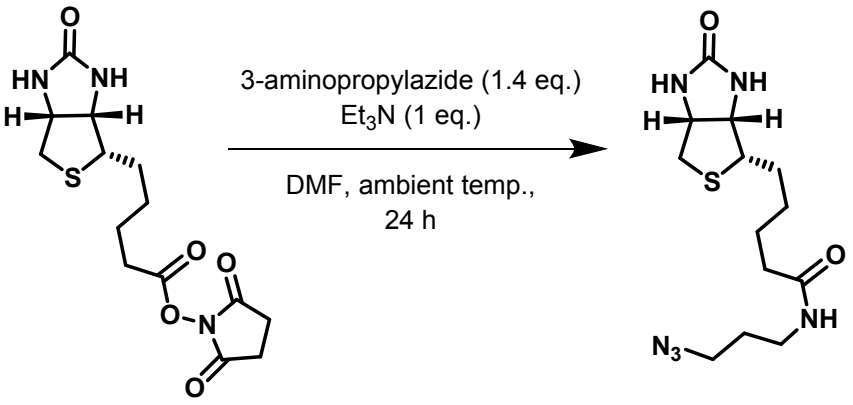
11, 91%

d-Biotin (1 eq., 2.05 mmol, 0.5 g) and *N*-hydroxysuccinimide (1 eq., 2.05 mmol, 236 mg) were dissolved in hot DMF (15 ml) in a 50 ml round-bottom flask with stirring. *N,N*-dicyclohexylcarbodiimide (1.3 eq., 2.66 mmol, 0.55 g) was added, and the solution was stirred overnight at ambient temperature (20 °C), during which time a white precipitate formed. The reaction mixture was filtered, and the filtrate was evaporated and triturated with ether. The white precipitate obtained by trituration with Et_2O was filtered and washed with Et_2O to give a white powder. (627 mg, 91% Yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.40 (s, 1H), 6.34 (s, 1H), 4.26 (dd, J = 7.5, 5.2 Hz, 1H), 4.10 (ddd, J = 7.5, 4.4, 1.7 Hz, 1H), 3.11–3.02 (m, 1H), 2.83–2.72 (m, 5H), 2.63 (t, J = 7.5 Hz, 2H), 2.54 (d, J = 12.4 Hz, 1H), 1.73–1.29 (m, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.8, 169.0, 163.0, 61.0, 59.2, 55.3, 33.4, 30.0, 27.8, 27.6, 25.5, 24.3. ESI-MS: m/z = 342.1122 $[M+H]^+$ (Calc. for $C_{14}H_{20}N_3O_5S$ = 342.1118); Note: There are some small unknown impurities in this material. These do not affect the

next step in any significant fashion. Pure material has been obtained in subsequent steps by using this material.

Synthesis of a biotin-azide-conjugate (12)



12, 76%

This experimental procedure is based on a modified literature procedure.[6]

Et_3N (1 eq., 0.879 mmol, 187 µL) was added to a solution of 3-aminopropylazide (1.4 eq., 1.23 mmol, 123.2 mg) in DMF (13 ml), followed by the addition of biotin-NHS (1 eq., 70 mg, 0.20 mmol) in DMF (9 ml). The resulting solution was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography (acetone/MeOH, 10:1) to give the desired biotin-azide-conjugate (220 mg, 0.674 mmol, 76 %) as an off white solid.

^{1}H NMR (400 MHz, MeOD-d_4) δ 4.49 (dd, J = 7.9, 4.5 Hz, 1H), 4.30 (dd, J = 7.9, 4.5 Hz, 1H), 3.36 (t, J = 6.9 Hz, 2H), 3.25 (t, J = 6.9 Hz, 2H), 3.23–3.18 (m, 1H), 2.93 (dd, J = 12.8, 5.0 Hz, 1H), 2.71 (d, J = 12.8 Hz, 1H), 2.21 (t, J = 7.5 Hz, 2H), 1.92–1.54 (m, 6H), 1.51–1.37 (m, 2H); ^{13}C NMR (101 MHz, MeOD-d_4) δ 176.2 ,166.1, 63.4, 61.6, 57.1, 50.2, 41.0, 37.7, 36.8, 29.80, 29.74, 29.5, 26.9; ESI-MS: m/z = 349.1411 $[M+Na]^+$ (Calc. for $SO_2N_6C_{13}H_{22}Na$ = 349.1417).

ESI 3 ^{1}H and ^{13}C NMR spectra of novel compounds

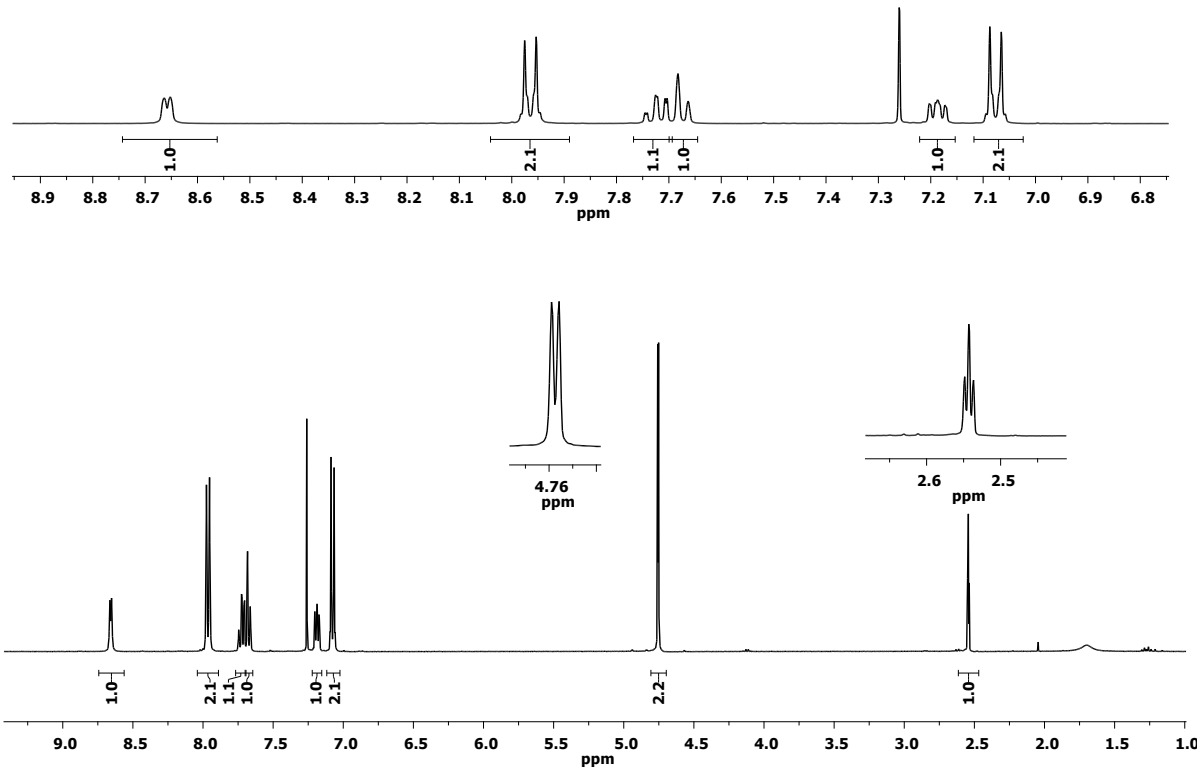


Figure S1: 400 MHz ^{1}H NMR spectrum of 2-[4-(prop-2-ynyloxy)phenyl]pyridine (7) in $CDCl_3$ at 300 K.

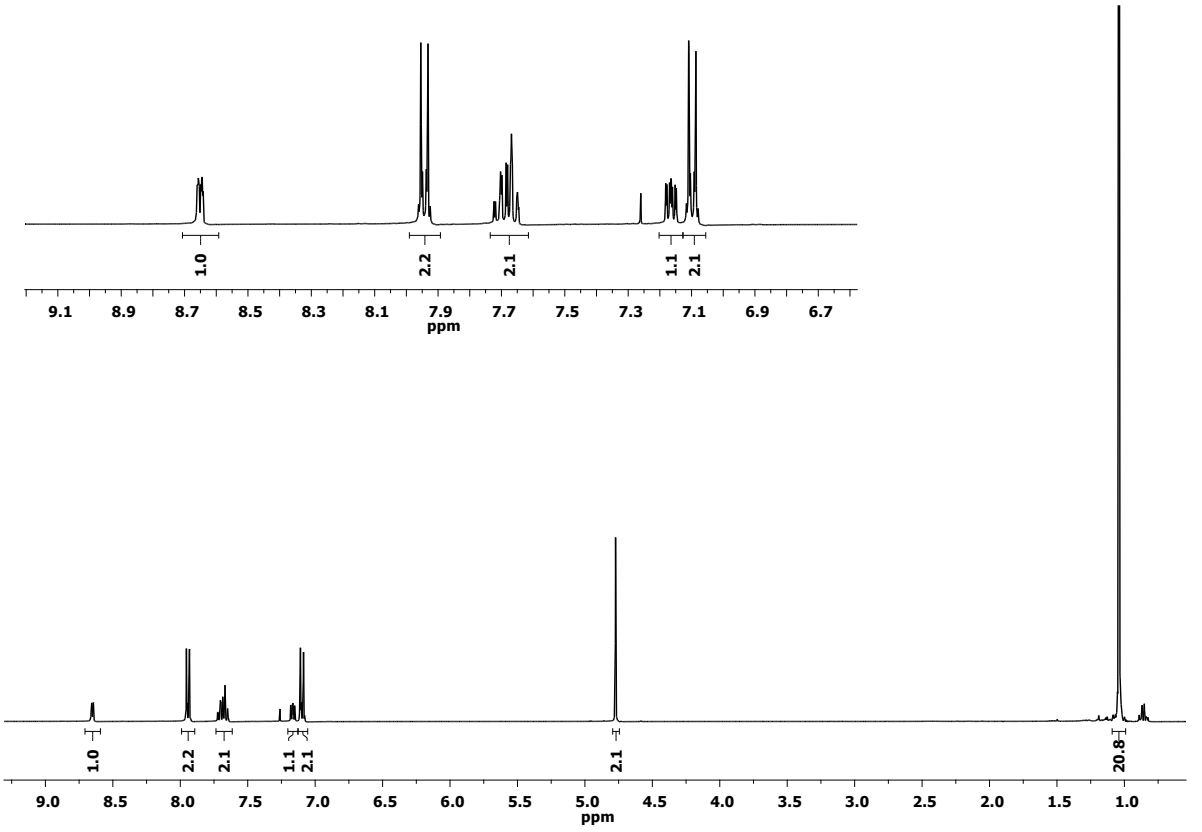


Figure S2: 400 MHz ^{1}H NMR spectrum of 2-[4-(3-triisopropylsilyl-prop-2-ynyloxy)phenyl]pyridine (8) in $CDCl_3$ at 300 K.

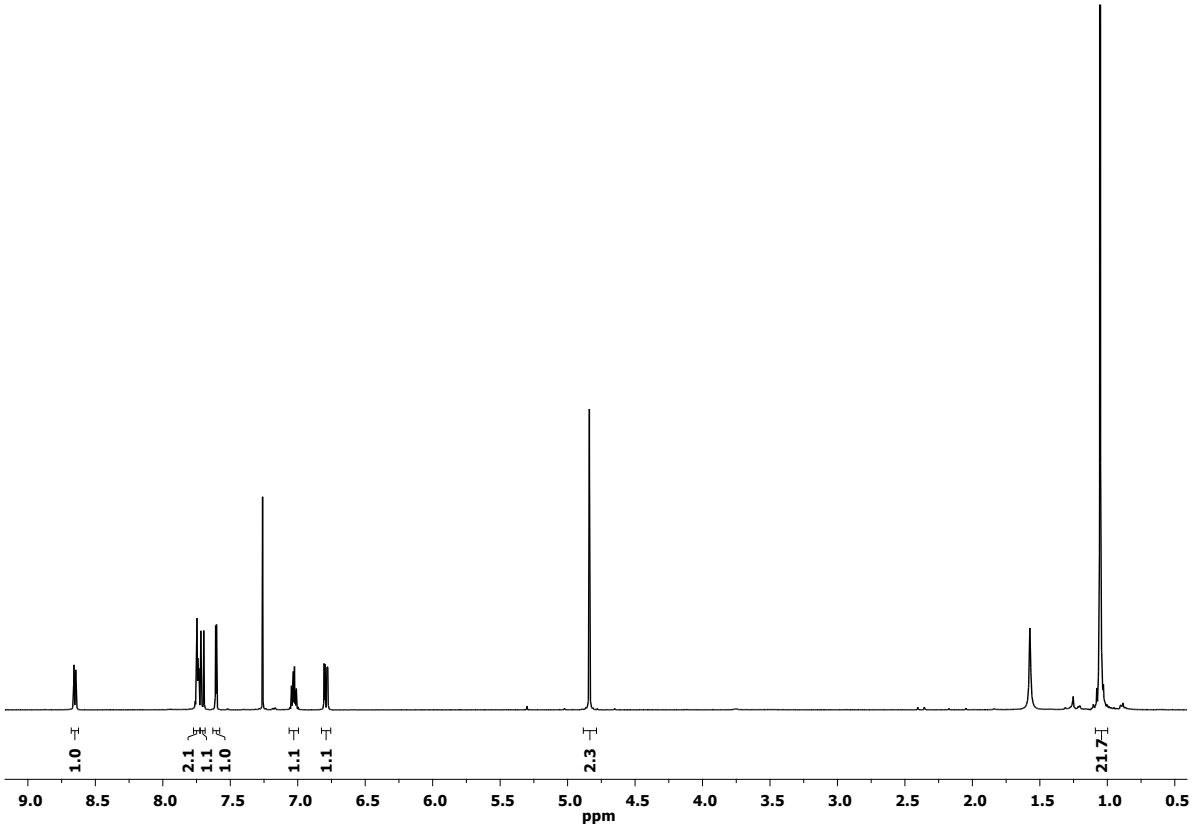


Figure S3: 400 MHz [1]H NMR spectrum of tetracarbonyl 2-[4-(3-triisopropylsilyl-prop-2-ynyloxy)phenyl]κ,C2-pyridine-κ,N) manganese(I) (9) in $CDCl_3$ at 300 K.

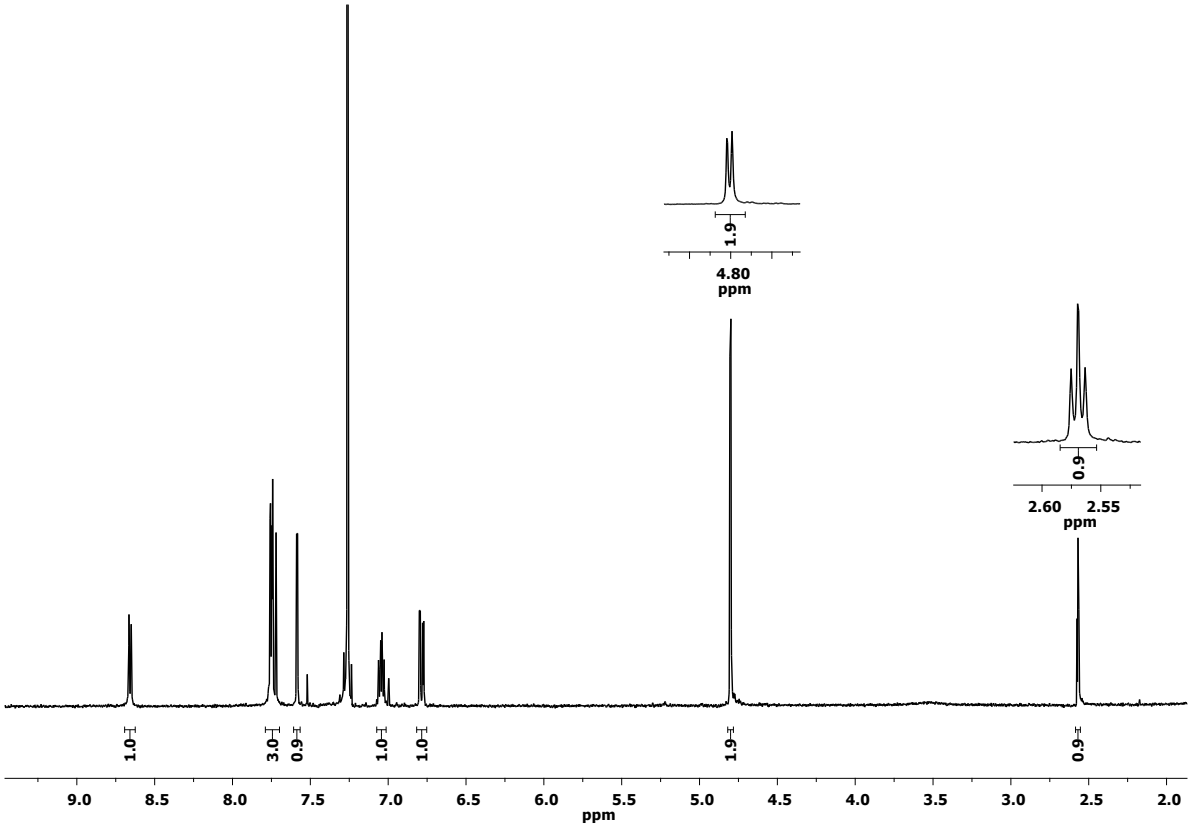


Figure S4: 400 MHz [1]H NMR spectrum of 2-[4-(prop-2-ynyloxy)phenyl] κ,C2-pyridine-κ,N) manganese(I) (2) in $CDCl_3$ at 300 K.

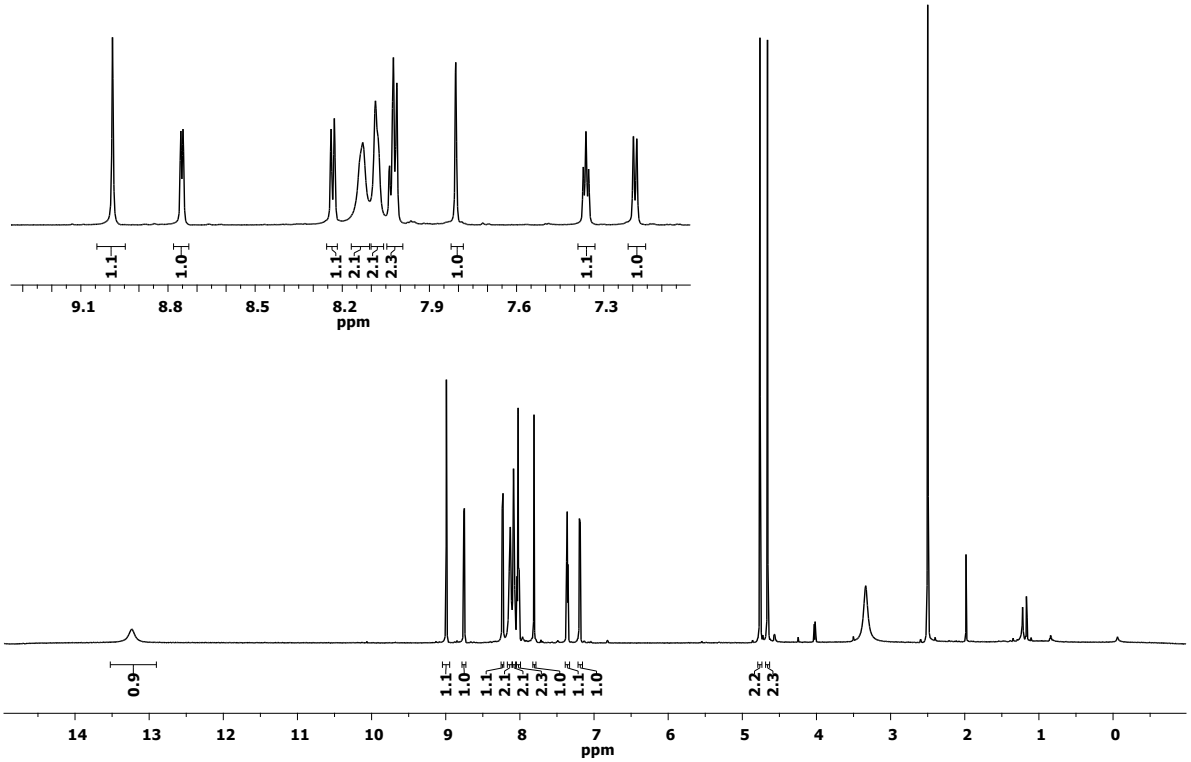


*Figure S5: 700 MHz [1]H NMR spectrum of tetracarbonyl (2-[4-(([1-(4-carboxy-phenyl)-1H-1,2,3-triazol-4-yl]methoxy)methyl)phenyl κ,C2]pyridine κ,N) manganese(I) (**4**) in DMSO-d_6 at 300 K.*

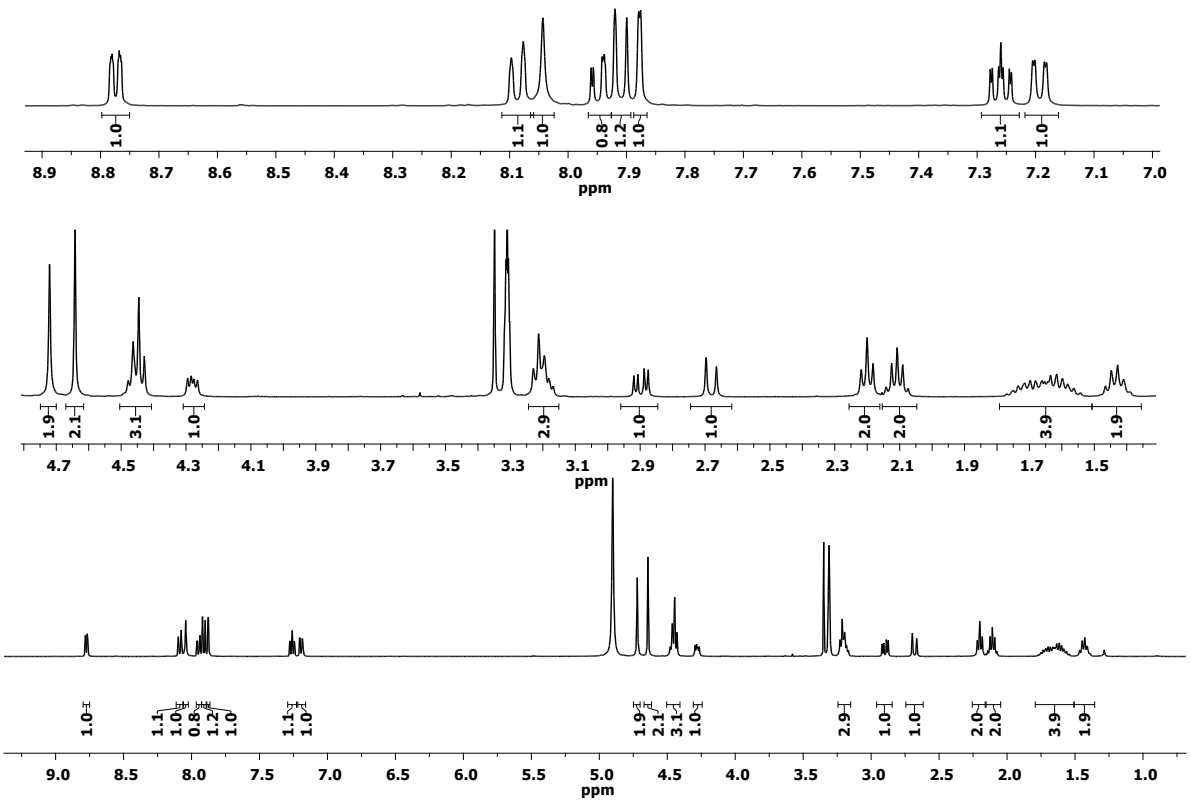


*Figure S6: 400 MHz [1]H NMR spectrum of CO-RM **5** in MeOD-d_4 at 300K. Spectrum is expanded above for clarity.*

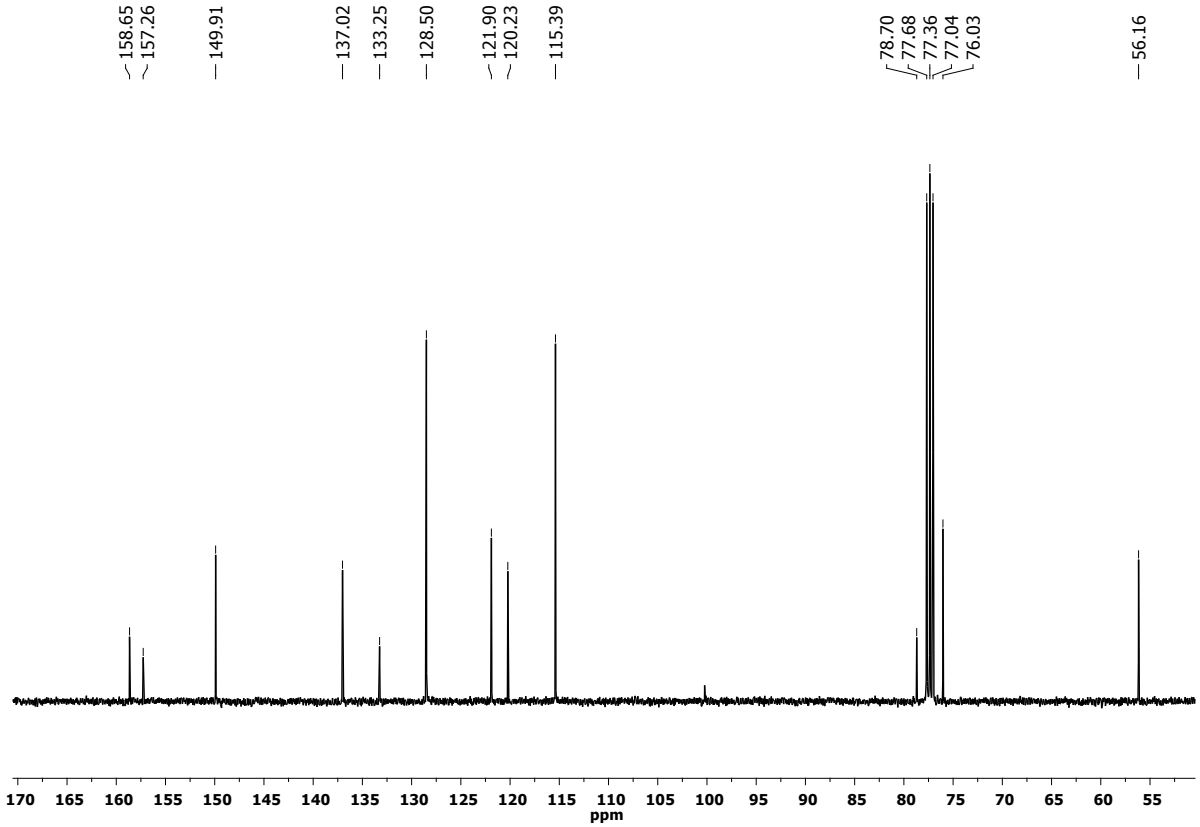


Figure S7: 100 MHz ^{13}C NMR spectrum of 2-[4-(prop-2-ynyloxy)phenyl]pyridine (7) in $CDCl_3$ at 300 K

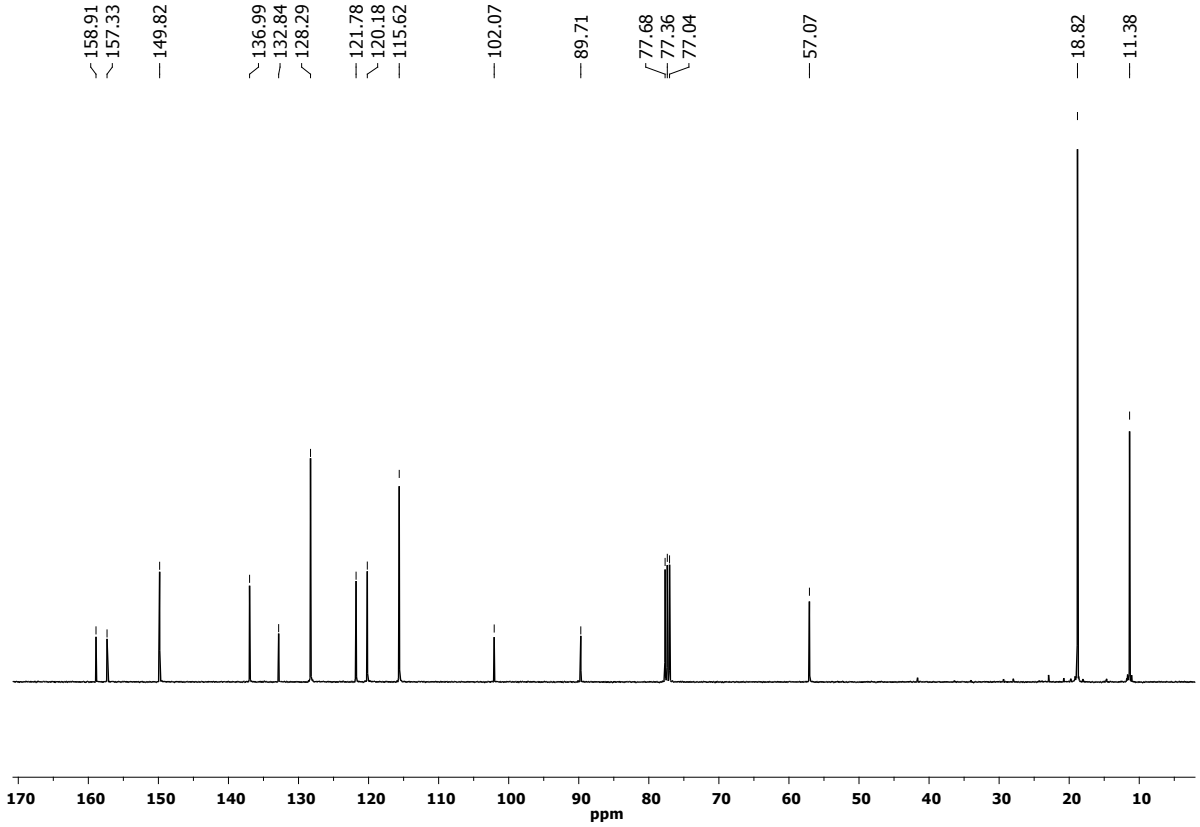


Figure S8: 100 MHz ^{13}C NMR spectrum of 2-[4-(3-triisopropylsilyl-prop-2-ynyloxy)phenyl]pyridine (8) in $CDCl_3$ at 300 K.

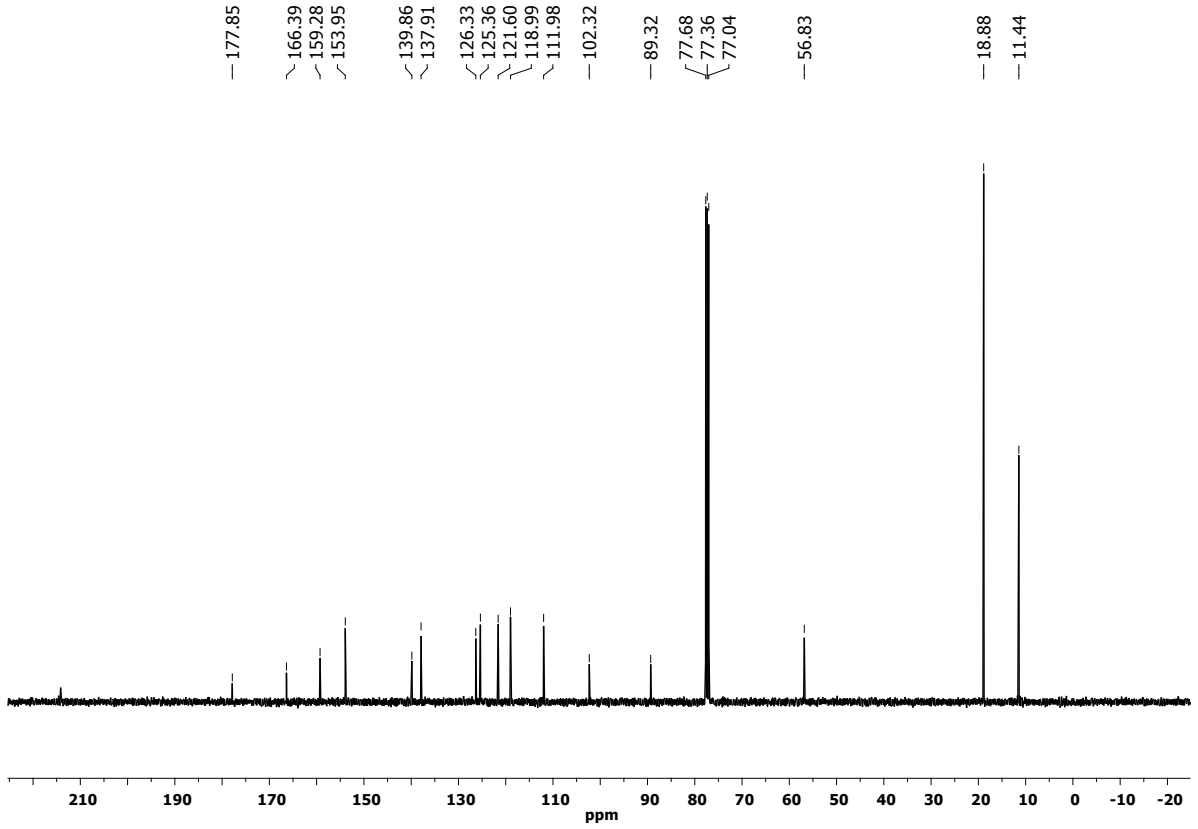


Figure S9: 100 MHz ^{13}C NMR spectrum of tetracarbonyl 2-[4-(3-triisopropylsilyl-prop-2-ynyloxy)phenyl]κ,C2-pyridine-κ,N) manganese(I) (9) in $CDCl_3$ at 300 K.

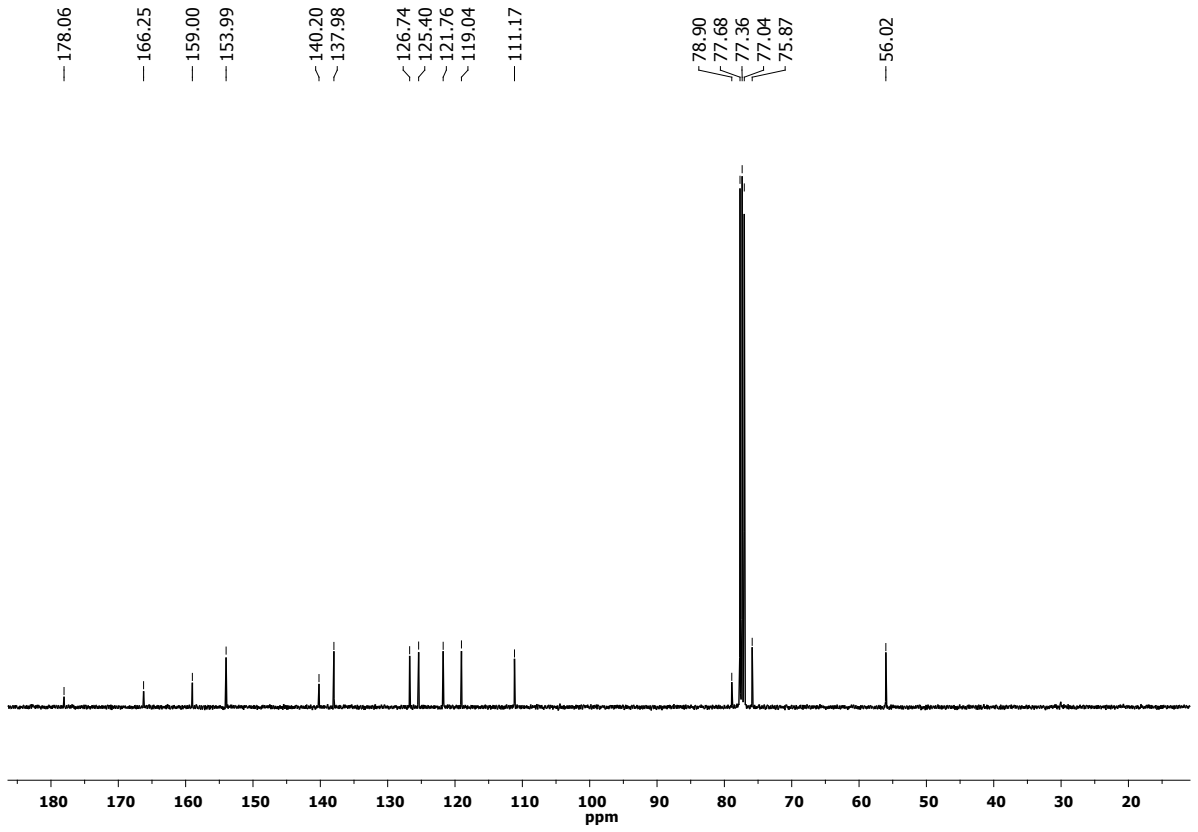


Figure S10: 100 MHz ^{13}C NMR spectrum of tetracarbonyl 2-[4-(prop-2-ynyloxy)phenyl] κ,C2-pyridine-κ,N) manganese(I) (2) in $CDCl_3$ at 300 K.

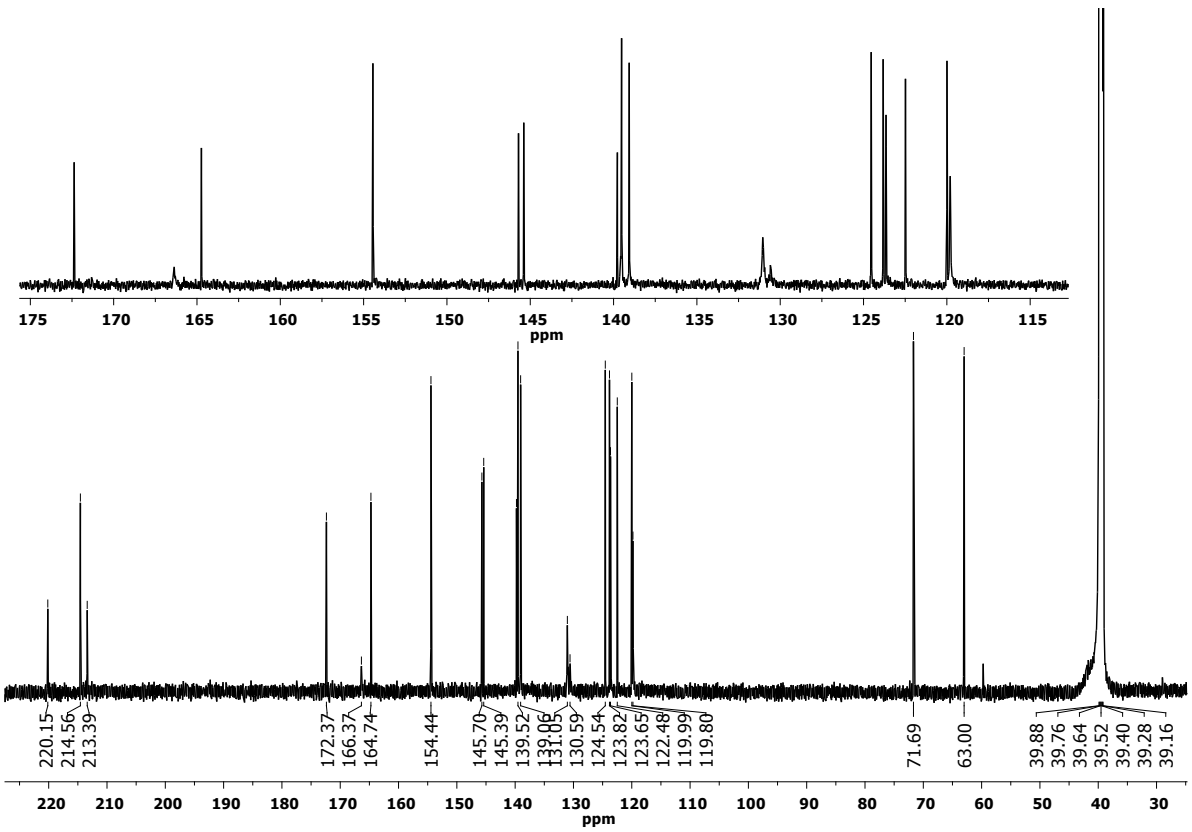


Figure S11: 121 MHz ^{13}C NMR spectrum of tetracarbonyl (2-[4-(([1-(4-carboxy-phenyl)-1H-1,2,3-triazol-4-yl]methoxy)methyl)phenyl κ,C2]pyridine κ,N) manganese(I) (4) in DMSO-d_6 at 298 K.

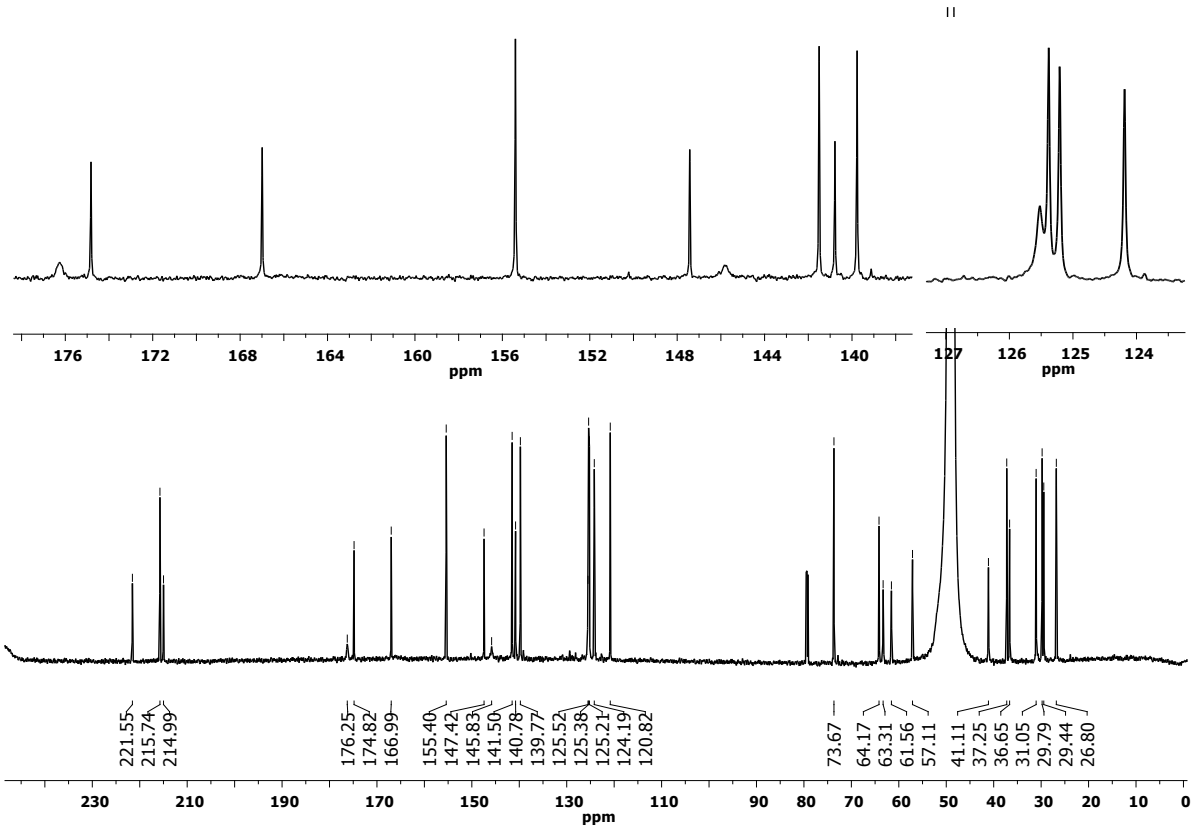


Figure S12: 121 MHz ^{13}C NMR spectrum of BB-CO-RM (5) in MeOD-d_4 at 298 K.

ESI 4 Isothermal Titration Calorimetry details

Titration of BB-CO-RM(or d-biotin) solution in to an avidin solution at 25°C was carried out using a G.E Microcal VP-ITC system. The data was collected and analysed using the manufacturers software. 280 µl of a 20 µM BB-CO-RM solution was added over 18 injections (15 µl), 240 seconds apart to a 2 µM solution of avidin monomer (0.5 µM tetramer). Both protein and CO-RM were in a 0.5% DMSO/ 50 mM phosphate buffer solution pH 7.49. The mixing paddle was rotating at a 308 rpm (recommended machine speed)

The ITC has a cell volume of 1.4 ml and a total injection volume of 280 µl. Using the concentrations above, the end point CO-RM/binding site ratio was 2:1.

A DMSO control was also carried out which added over 28 injections (10 µl) to check there were not any large energy changes due to pipette errors between the ligand and protein solutions. The energy signature is very similar to the residual energy seen at the end of the real titrations. The residual energy at the end of experiments is subtracted from each peak area.

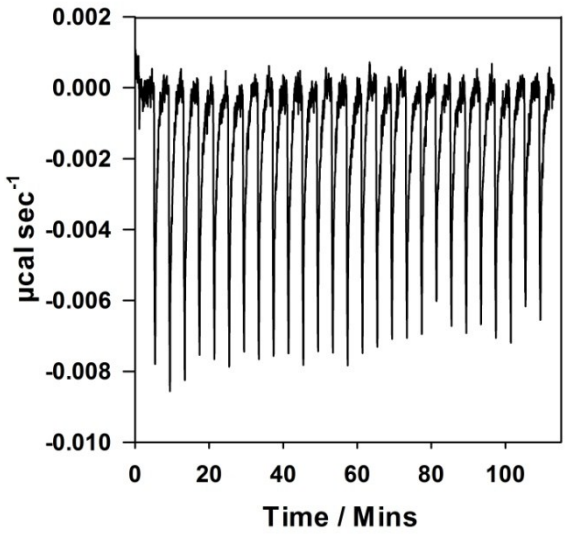


Figure S13: ITC experiment DMSO control buffer experiment, no protein or ligand in each solution. Data shows no significant energy release in the control experiment.

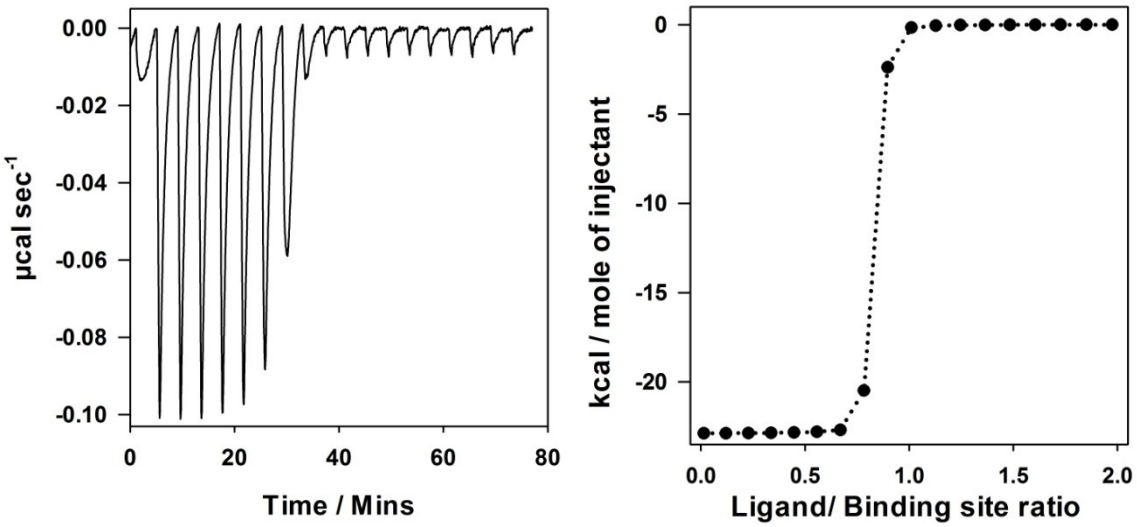


Figure S14 - ITC titration curves for the addition of biotin into avidin in PBS buffer pH 7.49. End of the titration results in a 2:1 ligand/protein binding site ratio.

ESI 5 HABA/Avidin Assay Details

A HABA/avidin reagent kit (H2153) was used to determine the concentration of biotinylated CO-RM within an already known concentration of biotinylated CO-RM. The kit was used as the manufacturer directed. A 30 µM solution of free biotin and **5** and **4** (as a control) was accurately prepared (with 0.5% DMSO for solubility reasons). A 0.5% DMSO control was also prepared.

ESI 6 Additional Myoglobin assay information

Myoglobin assays were performed as previously reported in the literature.[7, 8]

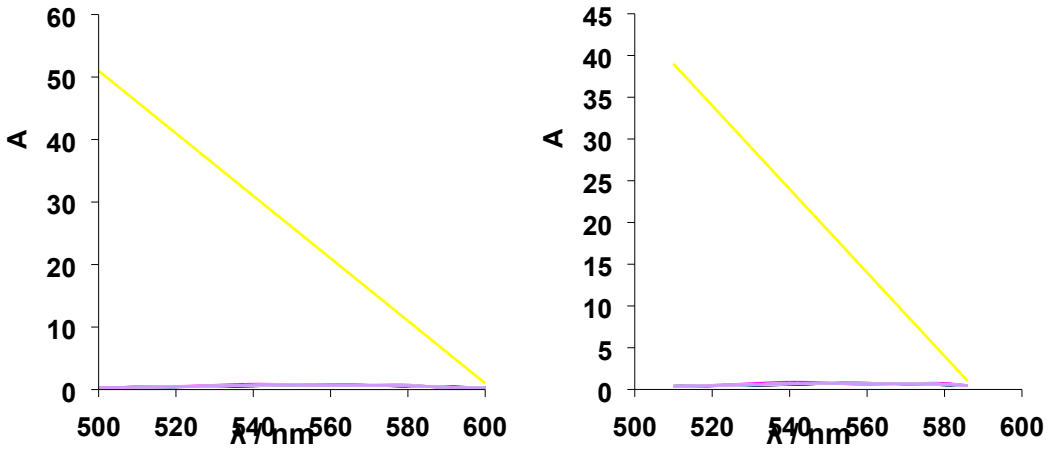


*Figure S15: 50 µM myoglobin assay data for **5** at 10 µM with 20 µM avidin monomer. Left: Raw data without correction. Right: Four point corrected data [7]for the same experiment. This data highlights that the presence of avidin and **5** do not interfere with the overall absorption spectrum, demonstrating clear conversion from deoxy-Mb to carboxy-Mb.*

ESI 7 Computational results (using DFT/TD-DFT methods)

The structure of BiotinCORM **5** was optimised at the PBE0/DGDZVP/def2tzv level of theory, with DMSO as the implicit solvent (using CPCM, Gaussian 09 RevD.01). TD-DFT calculations were then performed on the optimised structure of **5** at two different levels of theory using Gaussian 16 Rev. A.03 Win64. Firstly, TD-DFT calculations run at the rPBE0/dgdzvp/def2tzv level (for 50 states, using CPCM) did not predict a low-energy HOMO-LUMO transition which appears to be present on examination of the experimental spectrum. Hence the model at the rCAM-B3LYP/dgdzvp/def2tzv level (for 50 states) with CPCM solvation in DMSO is believed to better represent the experimental situation.

Results from calculations at the PBE0/dgdzvp/def2tzv level with cpcm solvation in DMSO (Optimisation/Frequency calculation)

Table S1 Frontier Orbital Energies (ground state)

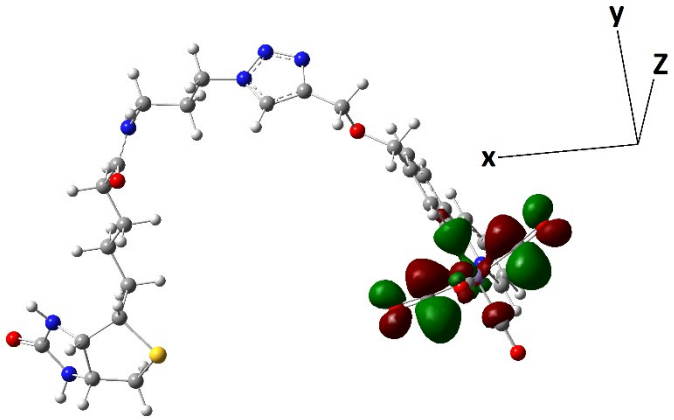
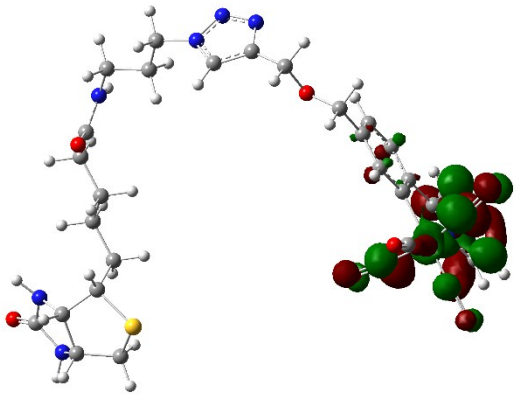
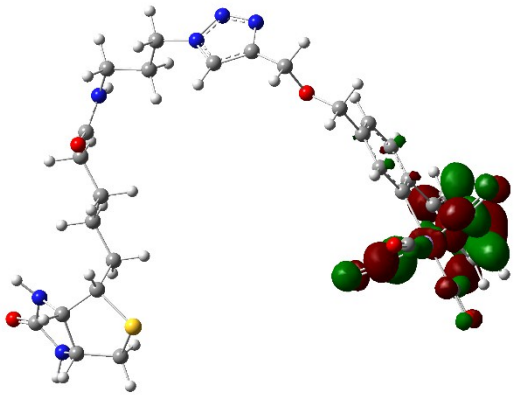
Orbital	Designation	Energy / Hartree	Energy / eV
190	LUMO+3	-0.05304	-1.443
189	LUMO+2	-0.06565	-1.786
188	LUMO+1	-0.07828	-2.130
187	LUMO	-0.08412	-2.289
186	HOMO	-0.19521	-5.312
185	HOMO-1	-0.20268	-5.515
184	HOMO-2	-0.20926	-5.694
183	HOMO-3	-0.21020	-5.720

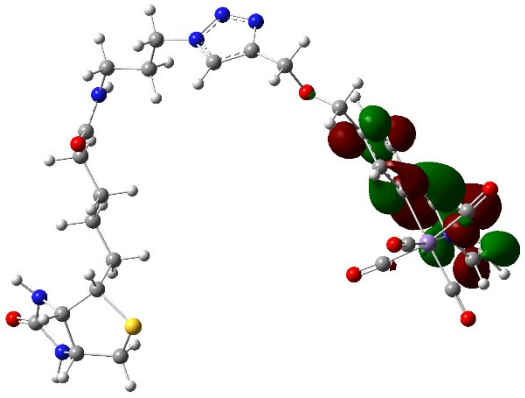
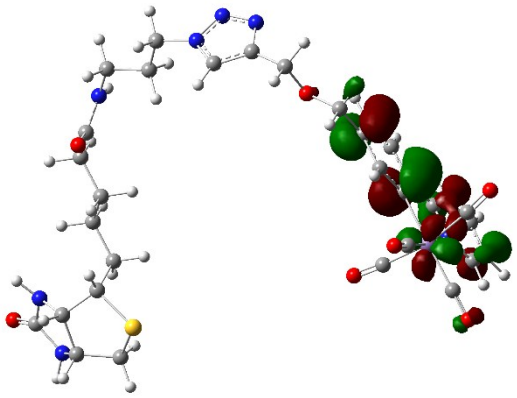
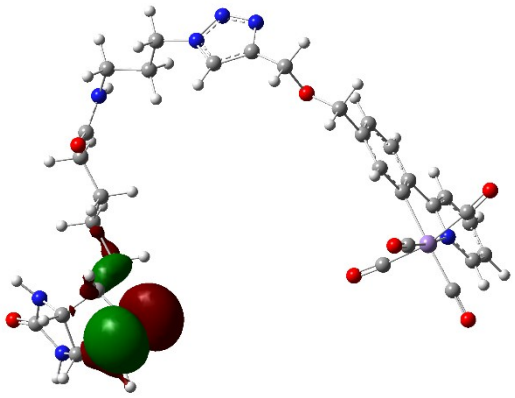
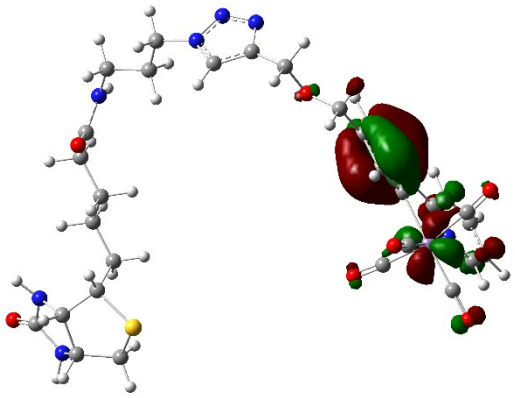
Results from calculations at the CAM-B3LYP/dgdzvp/def2tzv level with cpcm solvation in DMSO (TD-DFT Calculations)

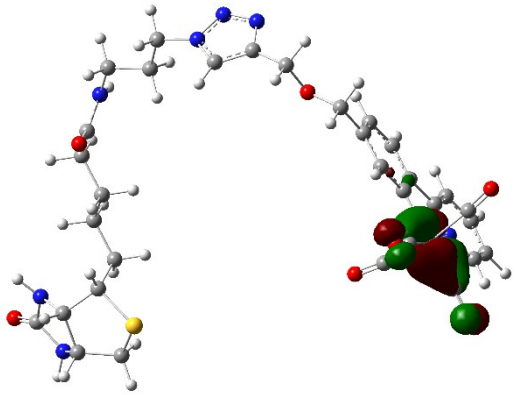
Table S2 Calculated Excitation Energies and Transitions (details of the first 5 excited states shown)

Excited State	Energy / nm	Oscillator Strength	From	To
1	344.51	0.0089	183	188
			183	189
			183	196
			183	200
			183	201
			183	203
			183	204
2	329.91	0.0074	178	188
			178	189
			182	188
			182	189
			182	203
			182	204
			183	193
			184	188
			184	189
			186	188
			186	189
3	318.89	0.0075	178	188
			178	189
			182	188
			182	189
			182	194
			182	200
			182	201
			182	203
			182	204
			182	206
			184	188
			184	189
			186	188
			186	189
4	305.49	0.2775	186	187
5	279.53	0.0023	182	190
			182	194
			182	206
			183	193
			183	195

Table S3 Diagrams of the frontier orbitals at the 0.04 iso value level. Manganese shown in purple, carbon grey, hydrogen white, nitrogen blue and oxygen red.

Orbital	Designation	
190	LUMO+3	
189	LUMO+2	
188	LUMO+1	

187	LUMO	
186	HOMO	
185	HOMO-1	
184	HOMO-2	

183	HOMO-3	

Collated energies

[**5**]

```
Zero-point correction=                           0.618398
Thermal correction to Energy=                    0.666980
Thermal correction to Enthalpy=                  0.667924
Thermal correction to Gibbs Free Energy=         0.523136
Sum of electronic and zero-point Energies=          -3696.819254
Sum of electronic and thermal Energies=             -3696.770672
Sum of electronic and thermal Enthalpies=           -3696.769728
Sum of electronic and thermal Free Energies=        -3696.914516

xyz coordinates
82

Mn                     6.00281  -1.96755   0.85801
 C                     4.21739  -2.47481   0.97079
 C                     5.94454  -1.36858   2.56969
 C                     6.70422  -3.58343   1.39928
 C                     7.61272  -1.07701   0.59769
 O                     8.57543  -0.44589   0.43684
 O                     7.1464   -4.59982   1.76841
 O                     5.89953  -0.96859   3.66702
 O                     3.0825   -2.71621   1.0307
 C                     5.21455  -0.22514   0.05977
 C                     4.96463  -0.29026  -1.33602
 C                     4.87142   0.96017   0.73093
 C                     4.35873   0.7933   -2.00723
 C                     4.27136   2.04521   0.06873
 H                     5.05192   1.04854   1.80769
 C                     4.01687   1.9519   -1.31222
 H                     4.15331   0.74647  -3.08029
 H                     3.54381   2.78915  -1.83137
 C                     6.4355   -3.60307  -1.73179
 C                     5.38238  -1.51995  -2.01338
 C                     6.36006  -3.88661  -3.09375
 H                     6.89266  -4.31635  -1.04362
 C                     5.30561  -1.74286  -3.40124
 C                     5.7751   -2.9369   -3.94272
 H                     6.75303  -4.83302  -3.47109
 H                     4.86473  -0.98785  -4.05416
 H                     5.70182  -3.12006  -5.01796
 N                     5.95537  -2.4582   -1.19027
 C                     3.9755    3.32016   0.81885
 H                     3.92055   3.13102   1.90769
 H                     4.77872   4.06544   0.64318
 O                     2.71877   3.87231   0.35135
 C                     2.44298   5.16067   0.97122
 H                     2.40338   5.05027   2.07049
 H                     3.25832   5.864     0.71854
 C                     1.13353   5.67118   0.46689
 C                    -0.12931   5.59062   1.03377
 H                    -0.48816   5.17446   1.97148
 N                     1.0111    6.31052  -0.74704
 N                    -0.24795   6.62672  -0.94844
 N                    -0.95711   6.19276   0.13507
 C                    -2.41475   6.37395   0.20184
 H                    -2.67523   6.57684   1.25218
```

H	-2.64097	7.27571	-0.38622
C	-3.17954	5.15753	-0.33963
H	-2.86594	4.96347	-1.37965
H	-2.93081	4.26403	0.25682
C	-4.69828	5.39746	-0.2863
H	-5.02459	5.5553	0.7539
H	-4.96778	6.29172	-0.87227
N	-5.4701	4.26556	-0.80771
H	-5.53007	4.15525	-1.82003
C	-5.9073	3.2368	-0.01425
O	-5.74487	3.23565	1.22675
C	-6.63994	2.11086	-0.728
H	-7.6962	2.15905	-0.40575
H	-6.63334	2.26025	-1.82244
C	-6.06562	0.72333	-0.38041
H	-6.04867	0.62305	0.71835
H	-5.01422	0.66953	-0.7193
C	-6.87782	-0.4089	-1.02937
H	-7.92993	-0.34211	-0.70009
H	-6.89428	-0.25697	-2.12448
C	-6.32624	-1.82527	-0.7541
H	-6.80158	-2.54141	-1.44717
H	-5.24412	-1.83954	-0.9706
C	-6.53214	-2.32629	0.6916
C	-7.90139	-3.00614	1.00087
H	-6.36794	-1.50279	1.40548
C	-7.79786	-4.56308	0.80984
H	-8.16452	-2.78206	2.04701
C	-6.3612	-4.95173	0.42606
H	-8.07612	-5.07372	1.74683
H	-6.06413	-5.93158	0.82972
H	-6.23329	-4.95816	-0.66743
N	-9.00995	-2.63681	0.10829
N	-8.78819	-4.84339	-0.24391
C	-9.62422	-3.75004	-0.45332
O	-10.70439	-3.75815	-1.06806
H	-9.23101	-5.76203	-0.28739
H	-9.61313	-1.84638	0.33622
S	-5.29278	-3.64087	1.17343

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