Cymantrene–triazole "Click" Products: Structural Characterization and Electrochemical Properties

David P. Day,[a] Thomas Dann,[a] David. L. Hughes,[a] Vasily. S. Oganesyan,[a] Dietmar Steverding,[b]

Gregory G. Wildgoose[a]*

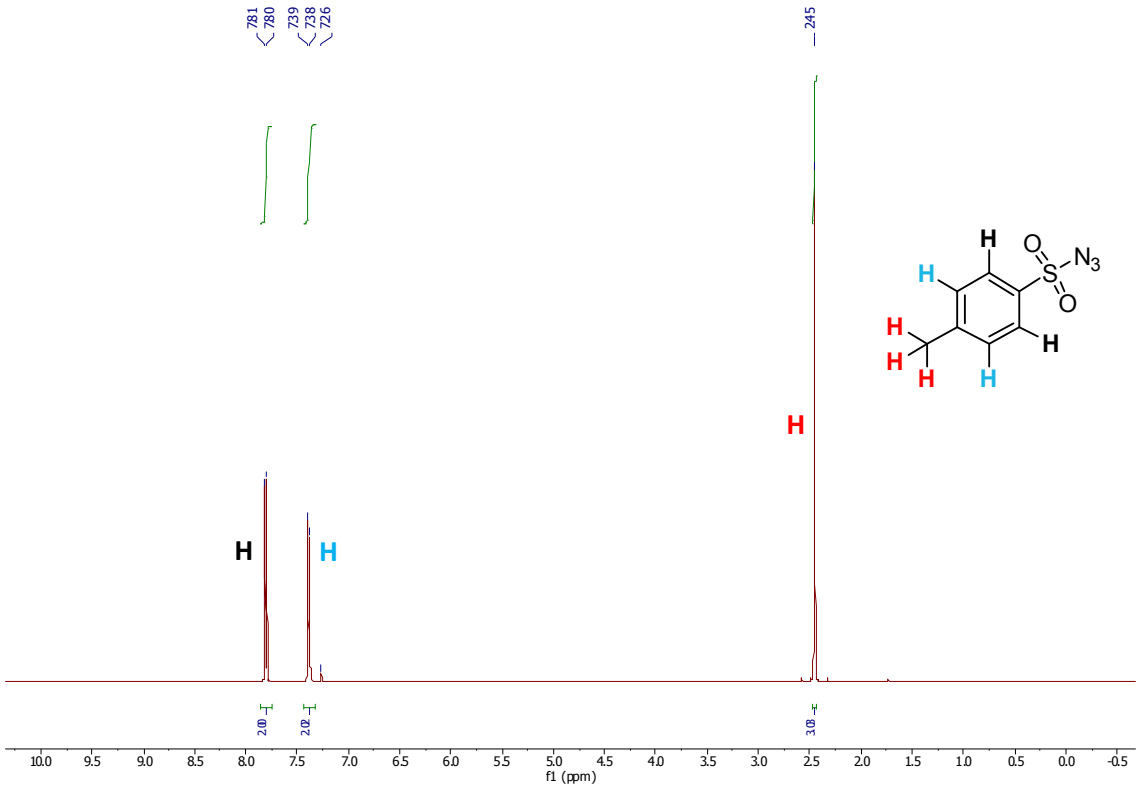
[a] Energy & Materials Laboratory, School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, United Kingdom

[b] BioMedical Research Centre, Norwich Medical School, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, United Kingdom

Contents:

S1. NMR characterization data

Figure S1: ^{1}H-NMR (top) and ^{13}C–NMR (bottom) of *p*-tosylazide



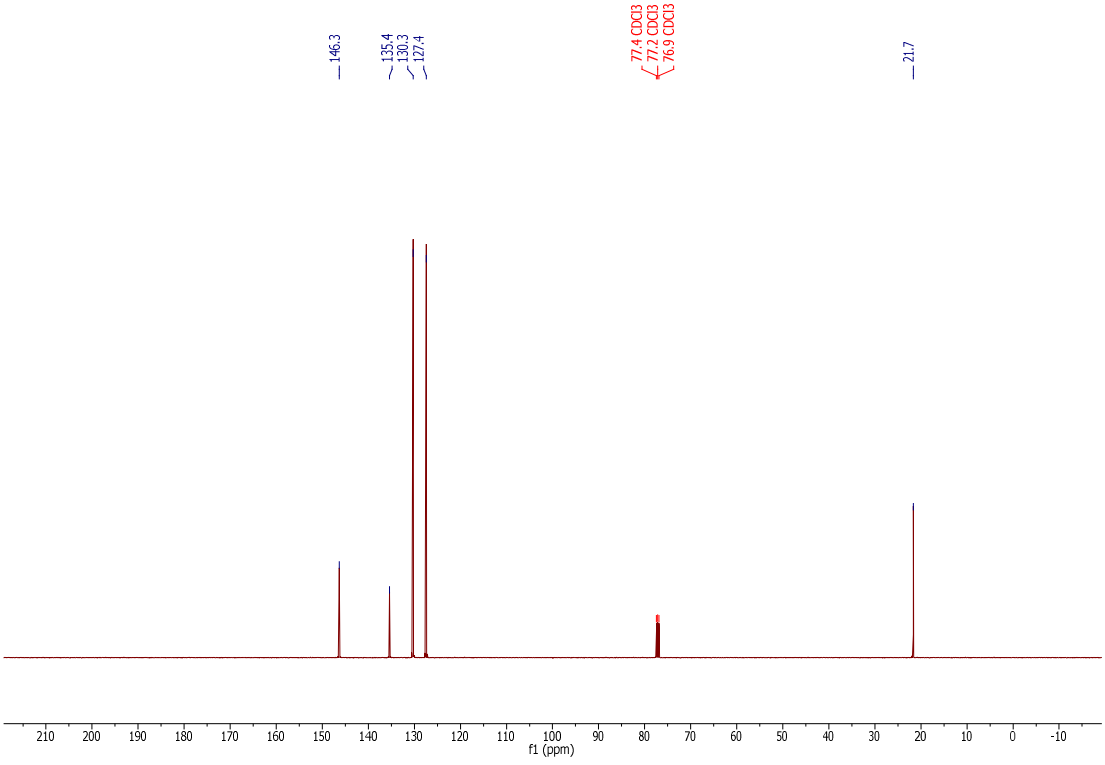


Figure S2: ^{1}H-NMR (top) and ^{13}C–NMR (bottom) of **2**.

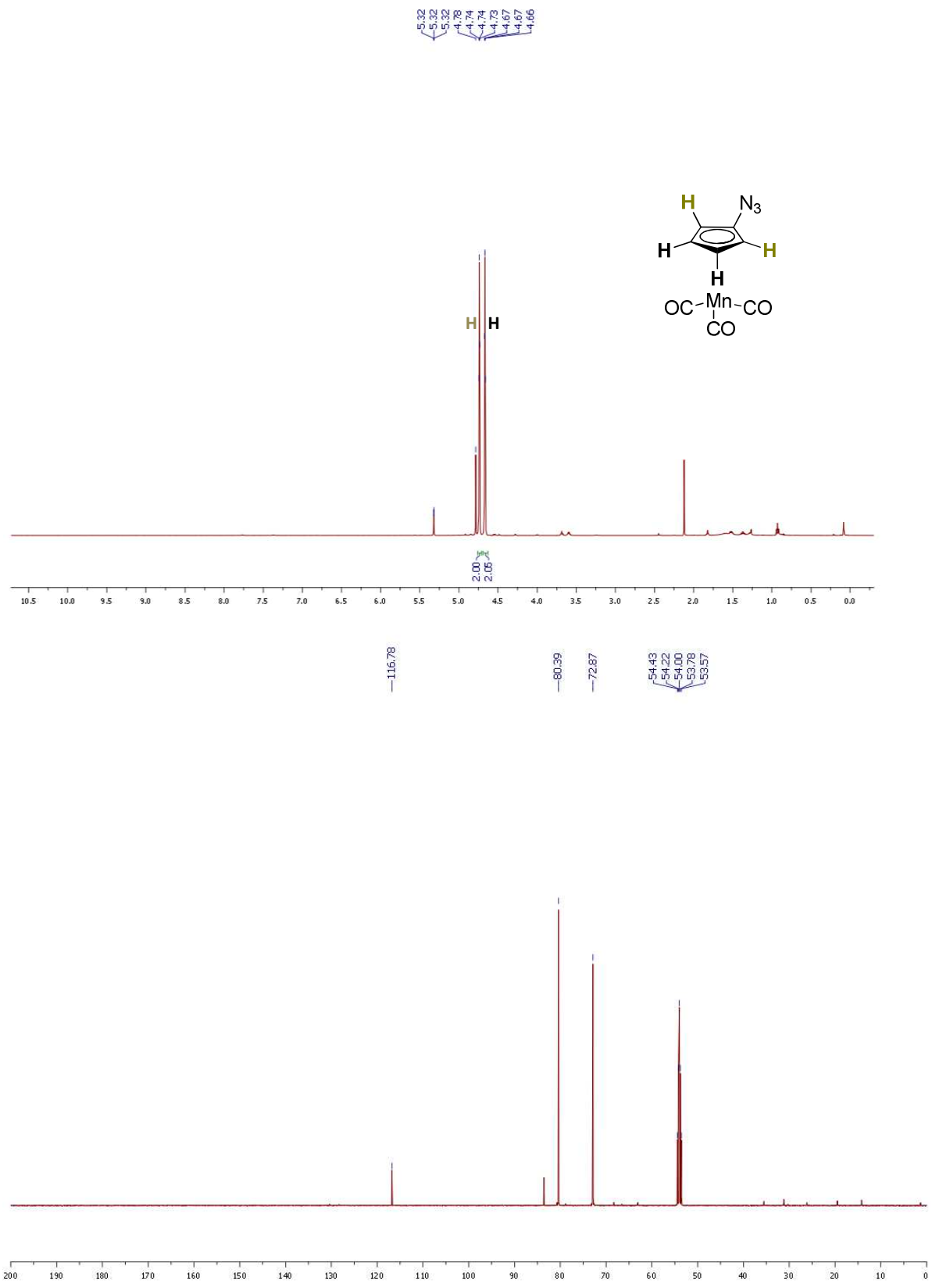


Figure S3: ^{1}H-NMR (top) and ^{13}C–NMR (bottom) of **3**.

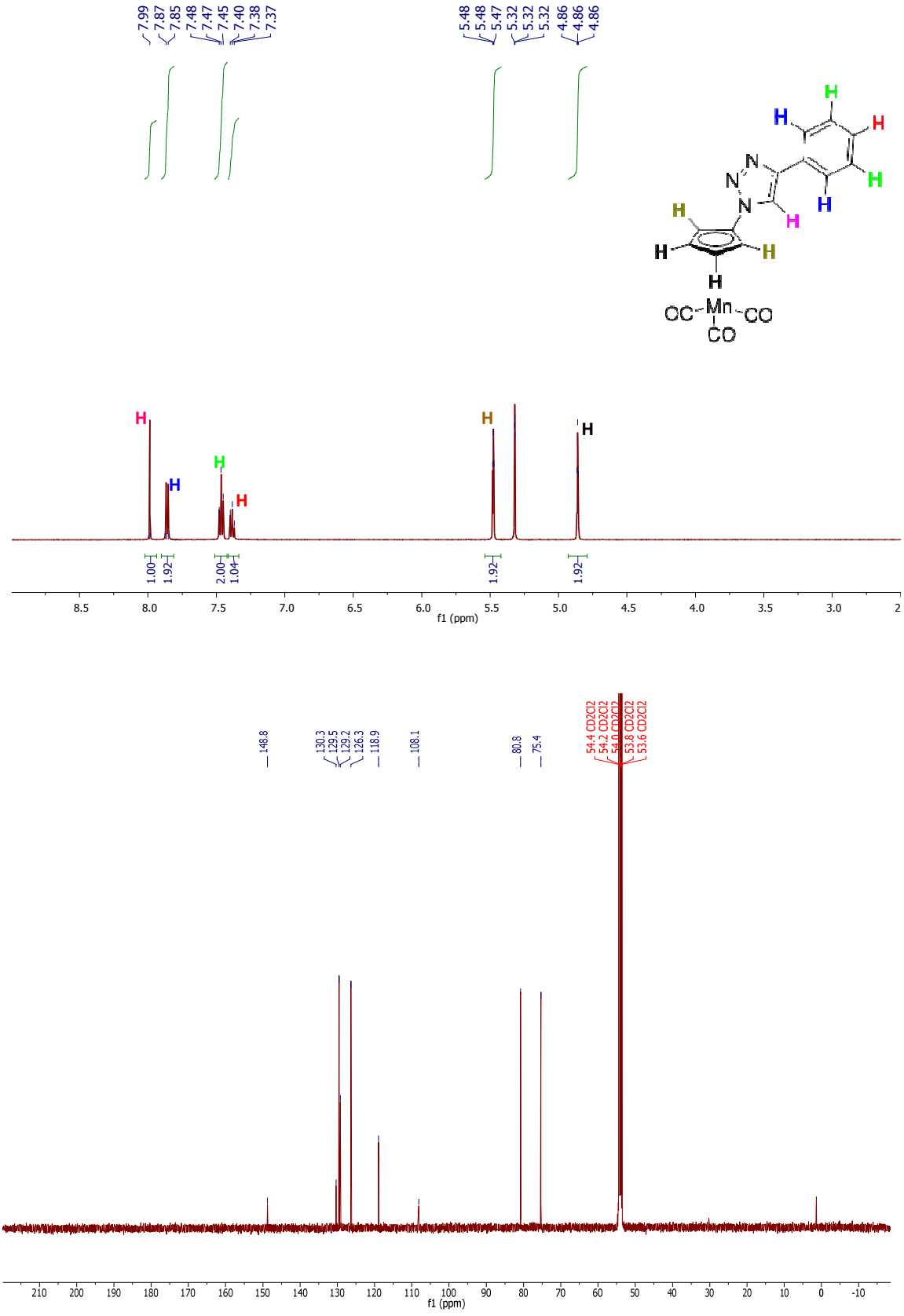


Figure S4: ^{1}H-NMR (top) and ^{13}C–NMR (bottom) of **4**.

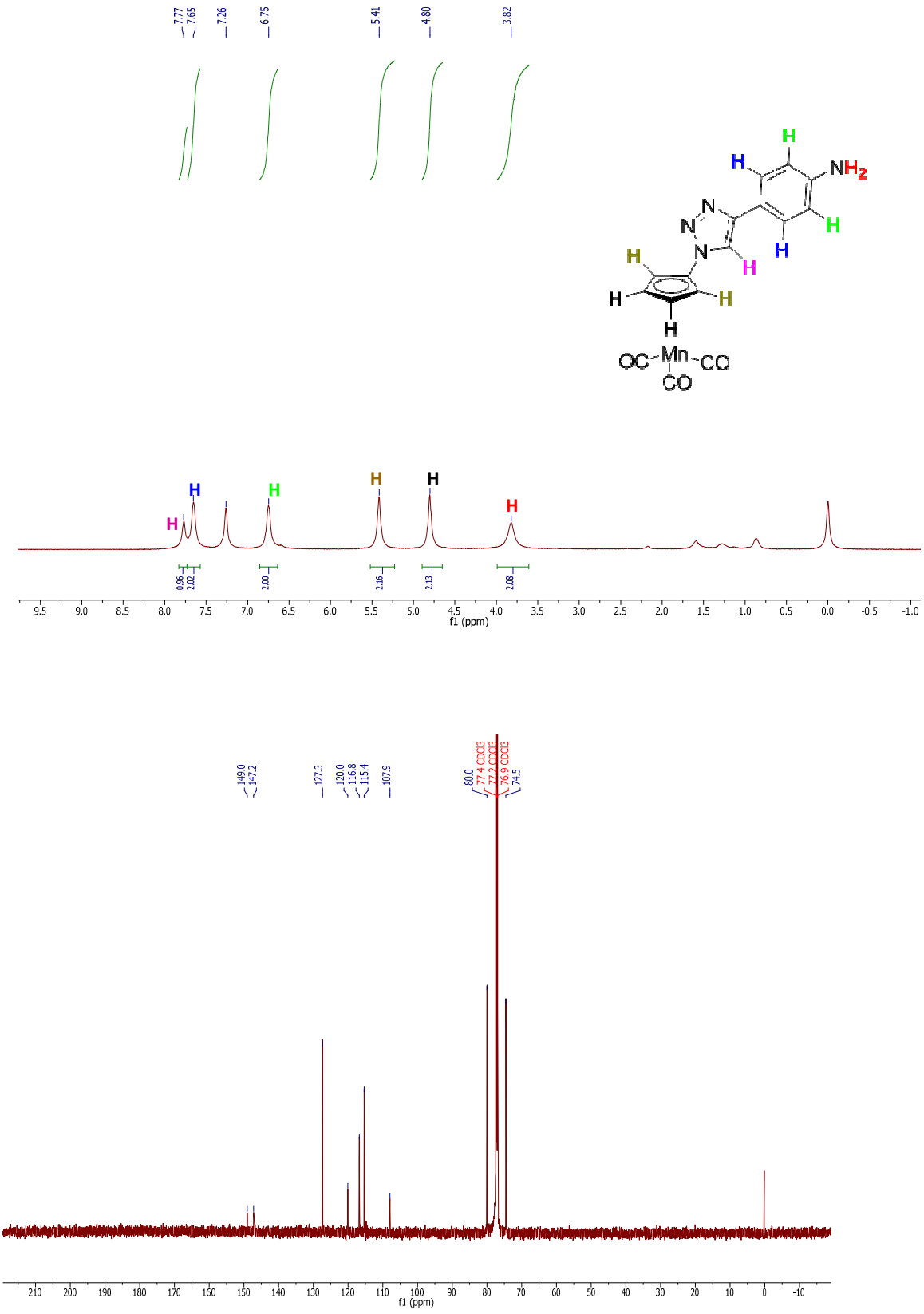
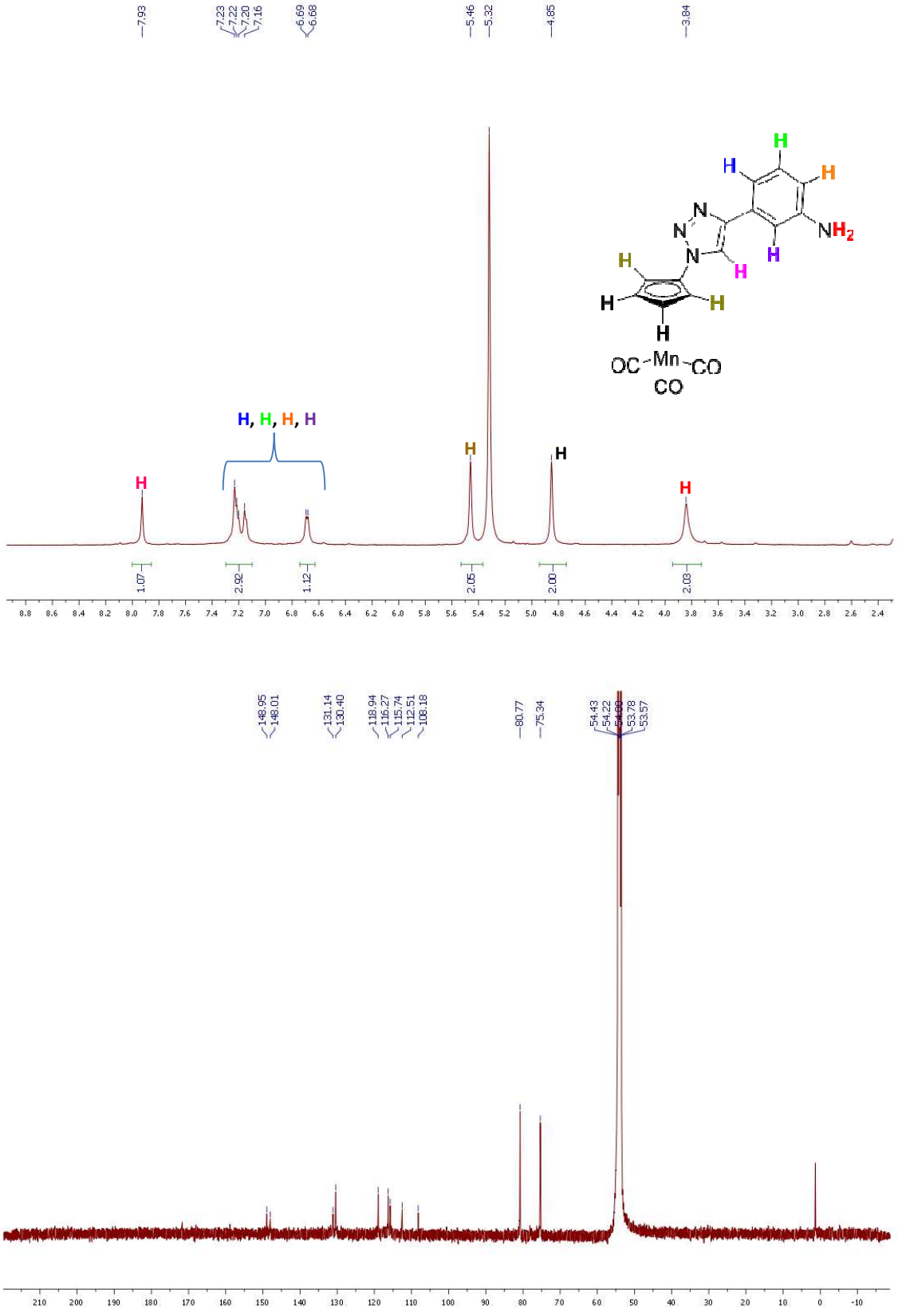
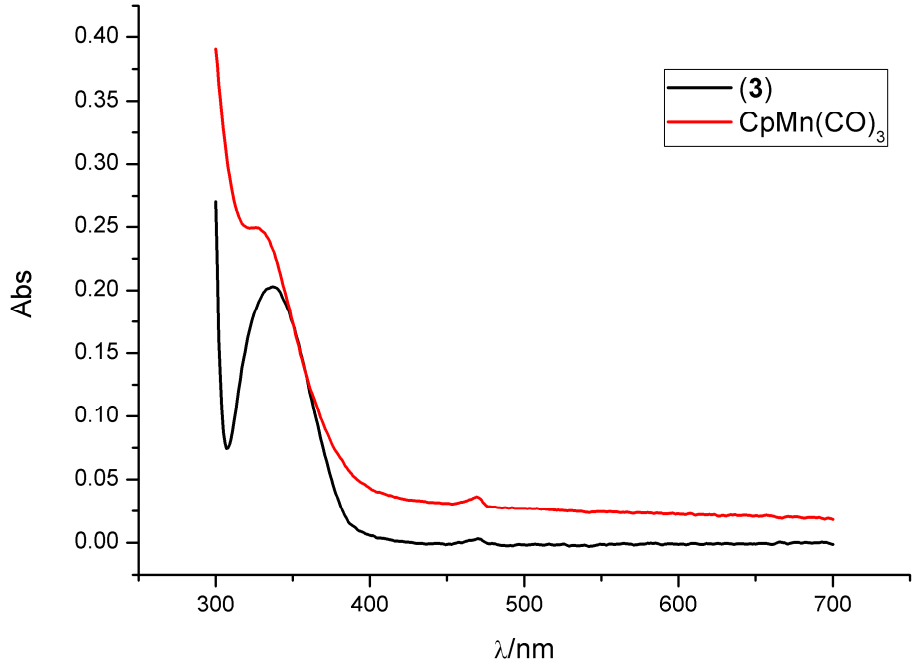


Figure S5: ^{1}H-NMR (top) and ^{13}C–NMR (bottom) of **5**.

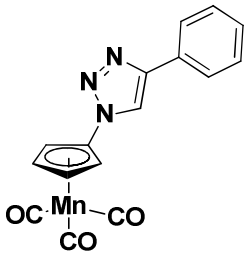


S2. UV-vis spectroscopy

Figure S6. UV-vis spectrum of $CpMn(CO)_3$ (red line), and (η^5-[4-phenyltriazol-1-yl]cyclopentadienyl tricarbonyl manganese (I) **3** (black line). Both spectra were recorded at room temperature in dichloromethane (concentration ca. 1 x 10^{-4} mol L^{-1}).



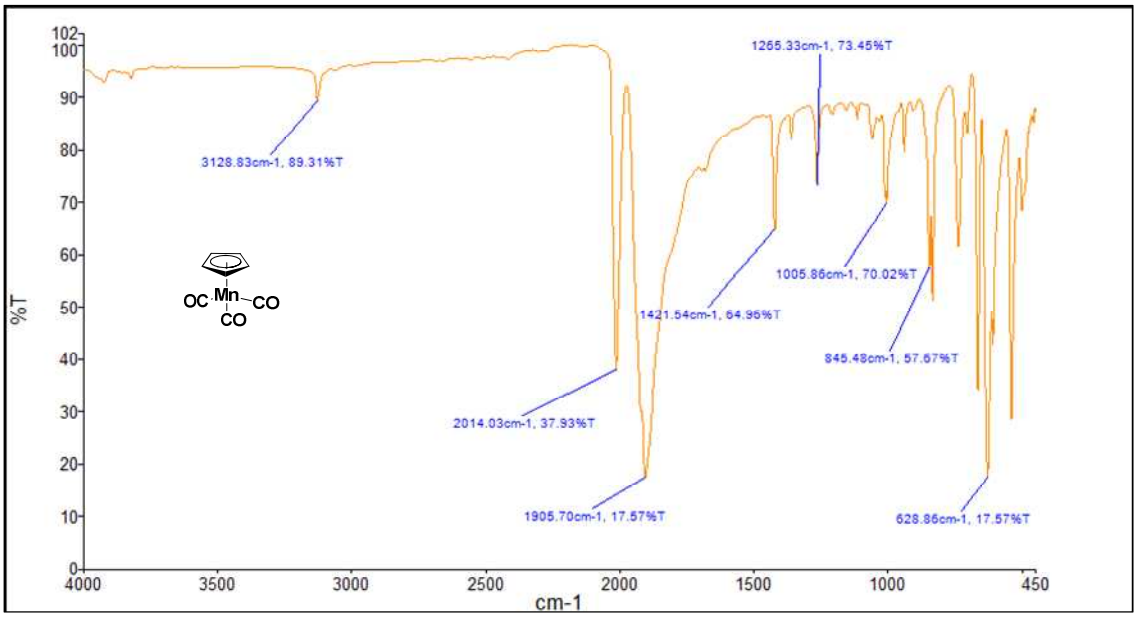
3 =



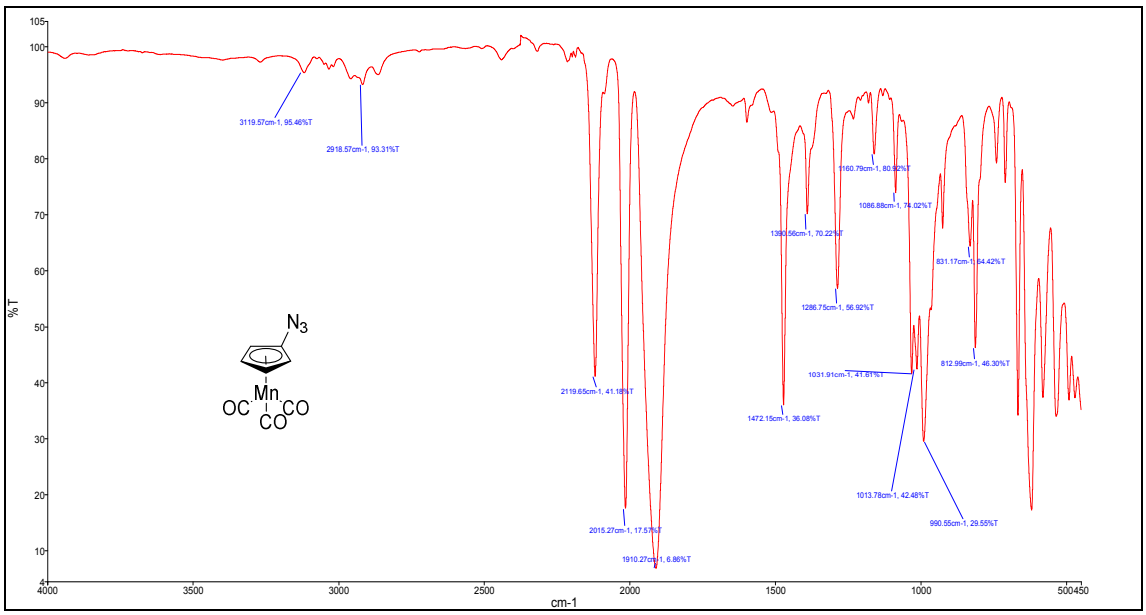
S3. Infra-red spectroscopy

Figure S7. Infra-red spectrum of (a) Cymantrene, **1**; (b) Cymantrene azide, **2**; (c) Complex **3**; (d) Complex **4**; and (e) Complex **5**. All spectra were recorded at room temperature, and were collected neat (as solids/liquids) utilizing the ATR unit of the spectrometer.

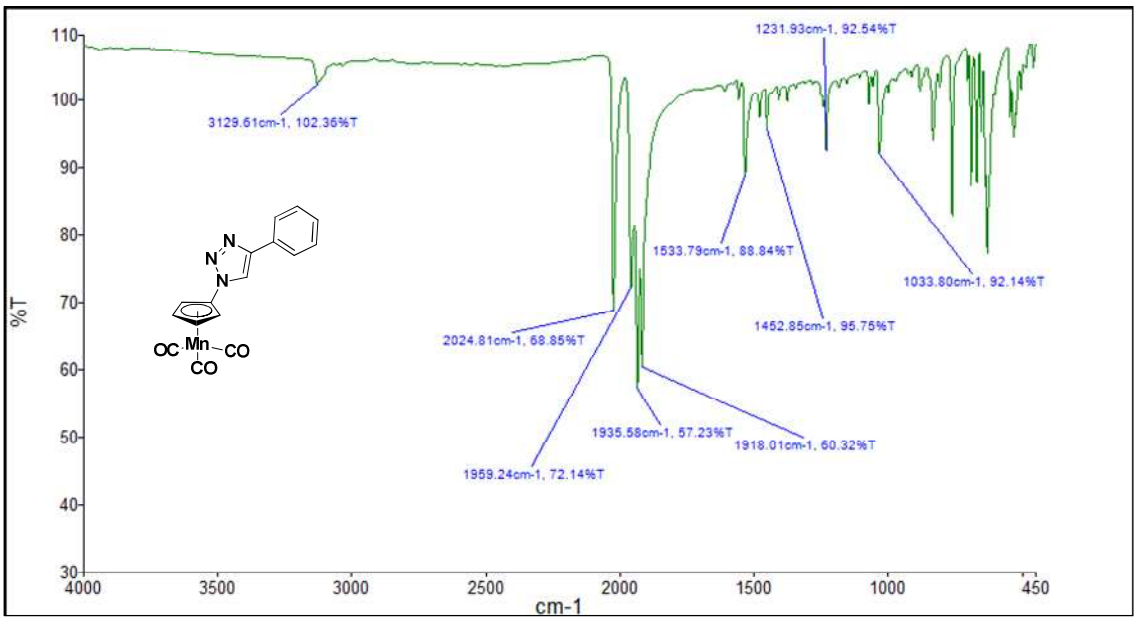
(a)



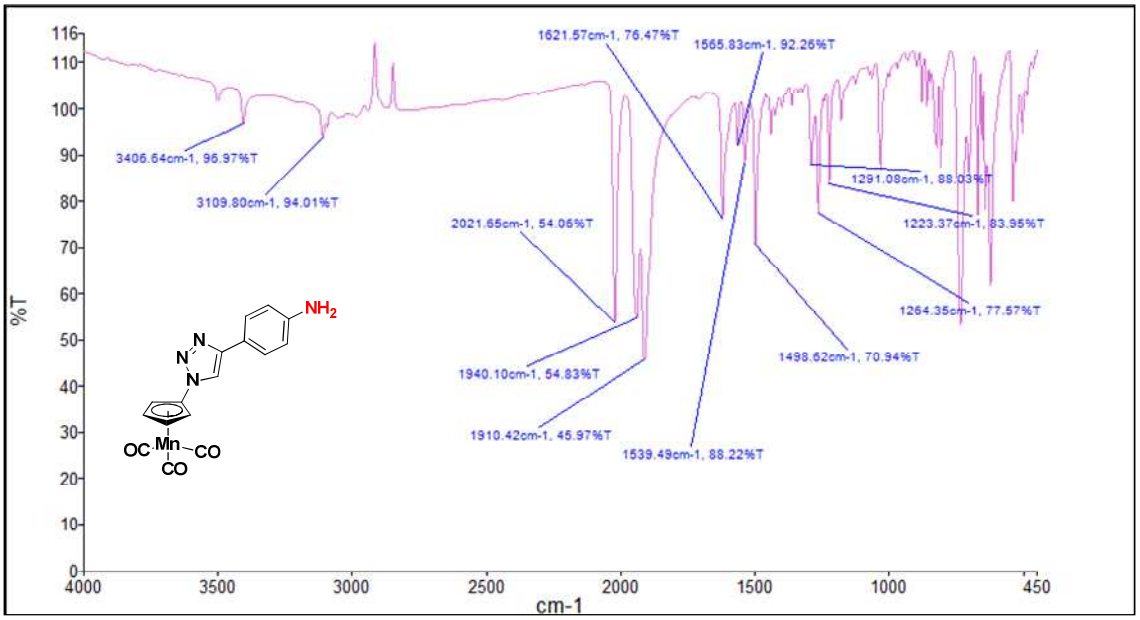
(b)



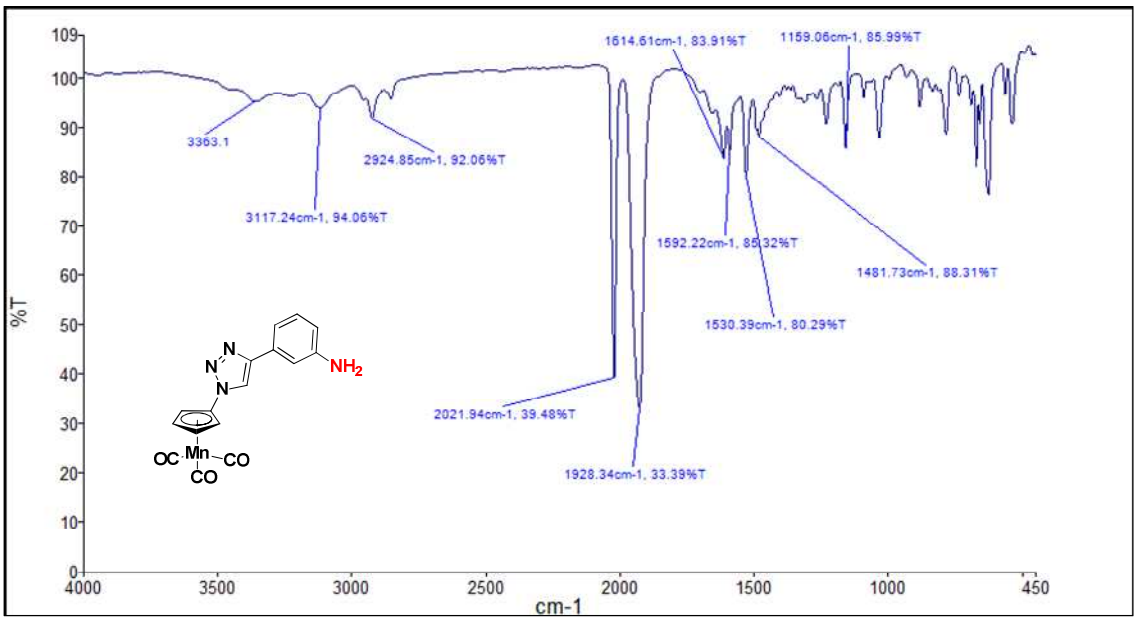
(c)


3129.61cm-1, 102.36%T
1231.93cm-1, 92.54%T
1533.79cm-1, 88.84%T
1033.80cm-1, 92.14%T
1452.85cm-1, 95.75%T
2024.81cm-1, 68.85%T
1935.58cm-1, 57.23%T
1918.01cm-1, 60.32%T
1959.24cm-1, 72.14%T
%T
cm-1

(d)


1621.57cm-1, 76.47%T
1565.83cm-1, 92.26%T
3406.64cm-1, 95.97%T
3109.80cm-1, 94.01%T
1291.08cm-1, 88.03%T
1223.37cm-1, 83.95%T
2021.65cm-1, 54.06%T
1264.35cm-1, 77.57%T
1498.62cm-1, 70.94%T
1940.10cm-1, 54.83%T
1910.42cm-1, 45.97%T
1539.49cm-1, 88.22%T
NH2
%T
cm-1

(e)


3363.1
3117.24cm-1, 94.06%T
2924.85cm-1, 92.06%T
2021.94cm-1, 39.48%T
1928.34cm-1, 33.39%T
1614.61cm-1, 83.91%T
1592.22cm-1, 85.32%T
1530.39cm-1, 80.29%T
1481.73cm-1, 88.31%T
1159.06cm-1, 85.99%T
%T
cm-1
NH2
OC
Mn
CO

S4. Cyclic Voltammetry of compounds 3-5 and associated digital simulations

Figure S8. Cyclic voltammogram recorded for 2 mM (η^5-[4-phenyltriazol-1-yl]cyclopentadienyl tricarbonyl manganese (I) **3** in CH_2Cl_2 at a scan rate of 100 mV s^{-1}. (ii) Oxidation between +1 → +2 V, (Where bold line = 1st scan, dotted line = 5th scan, dashed line = 10th scan).

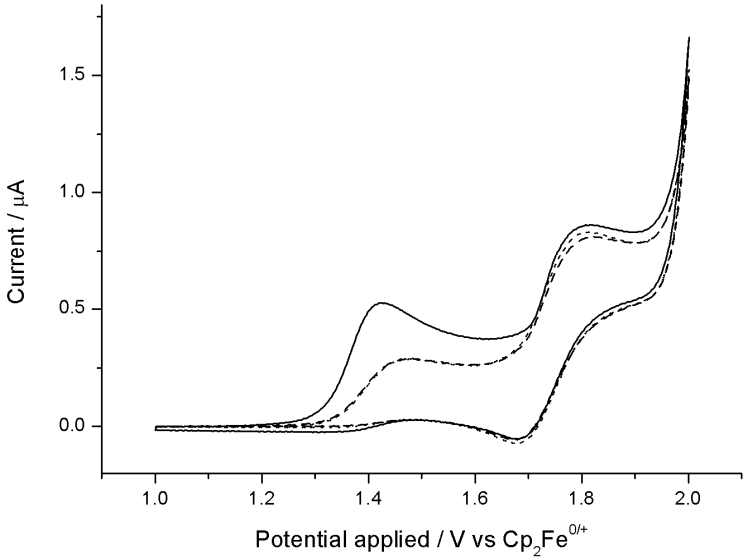


Figure S9. A comparison of experimental (solid line) vs. simulated data (open circles) for **3** (2mM, in CH_2Cl_2) at a scan rate of $1Vs^{-1}$. Note no attempt to model the triazloe/triazolium redox process has been made due to complex adsorption processes.

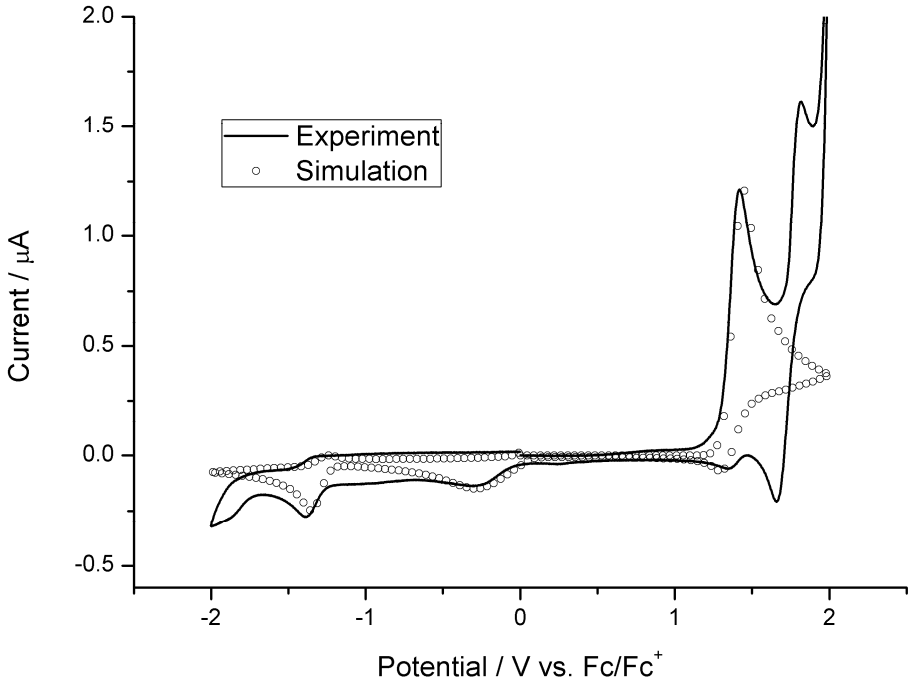
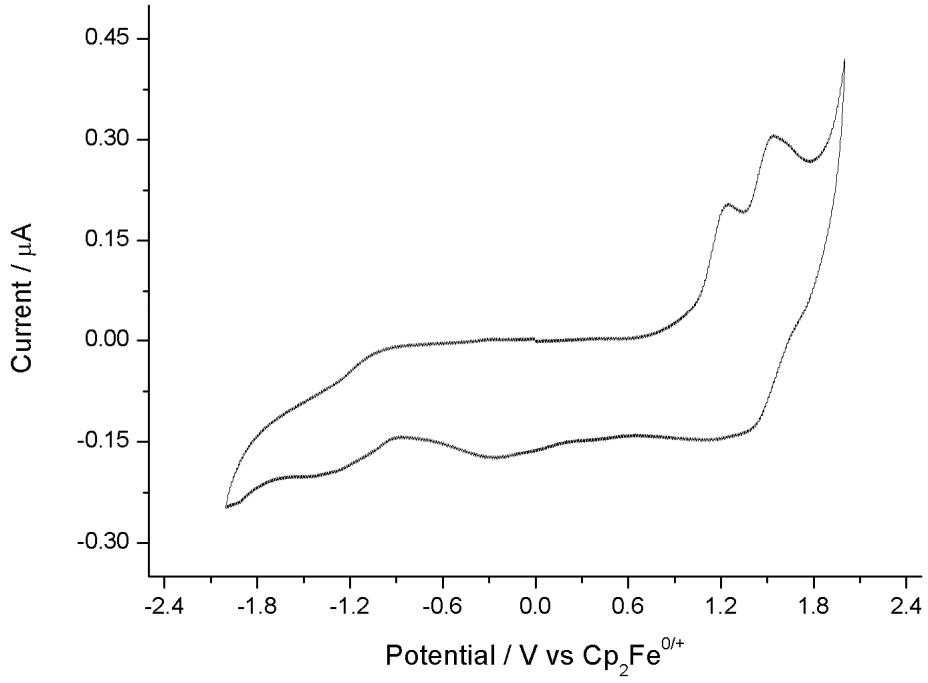


Figure S10. The CV recorded for **5** (2mM, in CH_2Cl_2) at a scan rate of $0.1Vs^{-1}$.



S5. Crystallographic details

Crystal structure analysis of (η^5-[4-phenyltriazol-1-yl]cyclopentadienyl tricarbonyl manganese(I) 3

Crystal data and structure refinement for [(η^5-[4-phenyltriazol-1-yl]cyclopentadienyl tricarbonyl manganese(I) (3)].

Identification code	davidd1
Elemental formula	C16 H10 Mn N3 O3
Formula weight	347.21
Crystal system, space group	Orthorhombic, $P2_1cn$ (equiv. to no. 33)
Unit cell dimensions	a = 33.3395(13) Å α = 90 ° b = 5.9474(2) Å β = 90 ° c = 14.4477(5) Å γ = 90 °
Volume	2864.74(18) $Å^3$
Z, Calculated density	8, 1.610 Mg/m^3
F(000)	1408
Absorption coefficient	0.940 mm^{-1}
Temperature	140(1) K
Wavelength	0.71073 Å
Crystal colour, shape	colourless plate
Crystal size	0.35 x 0.28 x 0.02 mm
Crystal mounting:	on a glass fibre, in oil, fixed in cold N_2 stream
On the diffractometer:	
Theta range for data collection	3.36 to 30.00 °
Limiting indices	-46<=h<=46, -8<=k<=8, -20<=l<=20
Completeness to theta = 30.00	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.702
Reflections collected (not including absences)	51567
No. of unique reflections	8347 [R(int) for equivalents = 0.084]
No. of 'observed' reflections ($I > 2\sigma_I$)	7612
Structure determined by:	direct methods, in SHELXS
Refinement:	Full-matrix least-squares on F^2, in SHELXL

Data / restraints / parameters	8347 / 1 / 423
Goodness-of-fit on F^2	1.160
Final R indices ('observed' data)	R_1 = 0.071, wR_2 = 0.158
Final R indices (all data)	R_1 = 0.077, wR_2 = 0.161
Reflections weighted: $w = [\sigma^2(Fo^2)+(0.0489P)^2+7.397P]^{-1}$ where $P=(Fo^2+2Fc^2)/3$	
Absolute structure parameter	0.59(3)
Largest diff. peak and hole	0.71 and -0.93 e.Å^{-3}
Location of largest difference peak	near Mn(2)

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^4). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor. E.s.ds are in parentheses.

	x	y	z	U(eq)	S.o.f.#
Mn(1)	4058.6(2)	4790.4(11)	502.7(5)	208.1(14)	
N(1)	3117.4(13)	5577(6)	852(3)	225(8)	
N(2)	3068.2(15)	7830(7)	940(3)	272(9)	
N(3)	2707.6(14)	8309(7)	610(3)	247(8)	
C(4)	2529.1(15)	6348(7)	302(3)	209(9)	
C(5)	2796.7(15)	4610(7)	458(3)	192(9)	
C(11)	3480.1(15)	4627(7)	1172(3)	218(9)	
C(12)	3756.8(16)	5757(9)	1758(3)	248(10)	
C(13)	4062.0(21)	4199(9)	1969(3)	349(11)	
C(14)	3983.4(18)	2200(9)	1501(4)	338(12)	
C(15)	3613.1(19)	2447(8)	992(4)	272(11)	
C(41)	2125.7(15)	6377(7)	-119(3)	200(8)	
C(42)	1979.1(15)	4520(8)	-591(3)	233(9)	
C(43)	1599.8(18)	4571(9)	-984(4)	306(11)	
C(44)	1365.9(17)	6507(9)	-912(4)	300(11)	
C(45)	1509.1(17)	8353(9)	-453(4)	300(11)	
C(46)	1892.2(16)	8292(8)	-44(3)	250(10)	
C(101)	3856.0(17)	6419(11)	-425(4)	359(12)	
O(101)	3723.1(16)	7473(10)	-1012(4)	565(16)	
C(102)	4289.7(19)	2916(9)	-318(4)	298(11)	
O(102)	4440.3(16)	1716(8)	-824(3)	486(12)	
C(103)	4485.4(16)	6640(8)	582(4)	271(10)	
O(103)	4754.4(14)	7851(7)	642(4)	409(10)	
Mn(2)	406.4(2)	5516.8(11)	1939.0(5)	224.3(15)	
N(6)	1340.6(13)	4592(7)	1548(3)	248(8)	
N(7)	1389.0(15)	2368(7)	1438(3)	284(10)	
N(8)	1742.2(15)	1851(7)	1775(3)	303(10)	
C(9)	1922.1(15)	3742(8)	2099(3)	220(9)	
C(1)	1672.(16)	5526(8)	1958(4)	257(11)	
C(61)	981.9(16)	5633(8)	1248(3)	243(9)	
C(62)	696.8(18)	4553(10)	666(4)	320(11)	
C(63)	394.5(21)	6174(10)	485(3)	361(12)	
C(64)	485.6(18)	8161(10)	960(4)	348(13)	
C(65)	850.7(17)	7832(8)	1449(4)	270(11)	
C(91)	2322.7(16)	3646(8)	2505(3)	230(9)	
C(92)	2483.3(16)	5507(8)	2968(3)	263(10)	
C(93)	2863.0(17)	5387(8)	3371(4)	274(10)	
C(94)	3085.9(18)	3444(10)	3306(4)	318(11)	
C(95)	2932.7(17)	1591(9)	2831(4)	326(12)	
C(96)	2549.5(18)	1720(8)	2438(4)	280(10)	
C(601)	600.9(15)	3714(10)	2831(4)	306(11)	
O(601)	730.5(17)	2587(10)	3397(4)	593(16)	
C(602)	189.8(19)	7389(10)	2773(4)	338(12)	
O(602)	66.7(17)	8585(10)	3307(4)	595(15)	
C(603)	-56.4(18)	3971(10)	1889(4)	328(11)	
O(603)	-348.4(15)	3008(9)	1855(4)	521(13)	
Mn(1A)	4046(10)	462(36)	352(16)	247(46)*	0.03
Mn(2A)	423(11)	9658(41)	1809(18)	284(50)*	0.03

- site occupancy, if different from 1.
* - U(iso) ($Å^2$ x 10^4)

Table S2. Molecular dimensions. Bond lengths are in Ångstroms, angles in degrees. E.s.ds are in parentheses.

(a) About the manganese atom

Mn(1)-C(101)	1.786(6)	Mn(2)-C(601)	1.797(5)
Mn(1)-C(102)	1.801(6)	Mn(2)-C(602)	1.792(6)
Mn(1)-C(103)	1.802(5)	Mn(2)-C(603)	1.798(6)
Mn(1)-C(11)	2.159(5)	Mn(2)-C(61)	2.164(5)
Mn(1)-C(12)	2.152(5)	Mn(2)-C(62)	2.156(6)
Mn(1)-C(13)	2.148(5)	Mn(2)-C(63)	2.136(5)
Mn(1)-C(14)	2.125(6)	Mn(2)-C(64)	2.131(5)
Mn(1)-C(15)	2.156(5)	Mn(2)-C(65)	2.143(5)
C(101)-Mn(1)-C(102)	90.2(3)	C(602)-Mn(2)-C(601)	92.0(3)
C(101)-Mn(1)-C(103)	90.9(2)	C(602)-Mn(2)-C(603)	89.9(3)
C(102)-Mn(1)-C(103)	94.7(3)	C(601)-Mn(2)-C(603)	91.9(2)
C(101)-Mn(1)-C(14)	149.1(2)	C(602)-Mn(2)-C(64)	92.1(3)
C(102)-Mn(1)-C(14)	92.8(2)	C(601)-Mn(2)-C(64)	150.6(2)
C(103)-Mn(1)-C(14)	119.5(2)	C(603)-Mn(2)-C(64)	117.2(2)
C(101)-Mn(1)-C(13)	146.2(3)	C(602)-Mn(2)-C(63)	122.6(3)
C(102)-Mn(1)-C(13)	123.1(3)	C(601)-Mn(2)-C(63)	145.2(3)
C(103)-Mn(1)-C(13)	91.9(2)	C(603)-Mn(2)-C(63)	92.2(3)
C(14)-Mn(1)-C(13)	38.0(2)	C(64)-Mn(2)-C(63)	38.3(2)
C(101)-Mn(1)-C(12)	108.1(2)	C(602)-Mn(2)-C(65)	95.8(2)
C(102)-Mn(1)-C(12)	157.0(2)	C(601)-Mn(2)-C(65)	111.8(2)
C(103)-Mn(1)-C(12)	98.8(2)	C(603)-Mn(2)-C(65)	155.3(2)
C(14)-Mn(1)-C(12)	64.3(2)	C(64)-Mn(2)-C(65)	38.8(2)
C(13)-Mn(1)-C(12)	38.3(2)	C(63)-Mn(2)-C(65)	64.6(2)
C(101)-Mn(1)-C(15)	109.7(2)	C(602)-Mn(2)-C(62)	156.8(3)
C(102)-Mn(1)-C(15)	96.4(2)	C(601)-Mn(2)-C(62)	106.9(2)
C(103)-Mn(1)-C(15)	156.6(2)	C(603)-Mn(2)-C(62)	102.4(2)
C(14)-Mn(1)-C(15)	39.4(2)	C(64)-Mn(2)-C(62)	64.8(2)
C(13)-Mn(1)-C(15)	64.8(2)	C(63)-Mn(2)-C(62)	38.6(2)
C(12)-Mn(1)-C(15)	64.79(19)	C(65)-Mn(2)-C(62)	65.1(2)
C(101)-Mn(1)-C(11)	91.3(2)	C(602)-Mn(2)-C(61)	130.4(2)
C(102)-Mn(1)-C(11)	130.5(2)	C(601)-Mn(2)-C(61)	91.7(2)
C(103)-Mn(1)-C(11)	134.8(2)	C(603)-Mn(2)-C(61)	139.4(2)
C(14)-Mn(1)-C(11)	63.8(2)	C(64)-Mn(2)-C(61)	63.9(2)
C(13)-Mn(1)-C(11)	63.6(2)	C(63)-Mn(2)-C(61)	63.7(2)
C(12)-Mn(1)-C(11)	38.50(18)	C(65)-Mn(2)-C(61)	38.19(19)
C(15)-Mn(1)-C(11)	37.71(18)	C(62)-Mn(2)-C(61)	38.44(19)

(b) In the cp ligand

N(1)-C(5)	1.341(6)	C(41)-C(42)	1.388(6)
N(1)-N(2)	1.356(6)	C(42)-C(43)	1.386(8)
N(1)-C(11)	1.413(7)	N(6)-N(7)	1.342(5)
N(2)-N(3)	1.325(7)	N(6)-C(10)	1.371(6)
N(3)-C(4)	1.383(6)	N(6)-C(61)	1.415(7)
C(4)-C(5)	1.384(7)	N(7)-N(8)	1.310(7)
C(4)-C(41)	1.476(7)	N(8)-C(9)	1.358(6)
C(11)-C(15)	1.395(7)	C(9)-C(10)	1.365(7)
C(11)-C(12)	1.421(7)	C(9)-C(91)	1.460(7)
C(12)-C(13)	1.409(8)	C(61)-C(65)	1.409(7)
C(13)-C(14)	1.393(8)	C(61)-C(62)	1.422(7)
C(14)-C(15)	1.444(9)	C(62)-C(63)	1.418(9)
C(41)-C(46)	1.384(6)	C(63)-C(64)	1.400(8)

C(64)-C(65)	1.421(8)	C(44)-C(45)	1.368(8)
C(91)-C(96)	1.376(7)	C(45)-C(46)	1.408(8)
C(91)-C(92)	1.399(7)	C(93)-C(94)	1.377(8)
C(92)-C(93)	1.395(8)	C(94)-C(95)	1.395(8)
C(43)-C(44)	1.395(8)	C(95)-C(96)	1.400(8)

C(5)-N(1)-N(2)	111.6(4)	N(7)-N(6)-C(10)	110.7(4)
C(5)-N(1)-C(11)	130.5(4)	N(7)-N(6)-C(61)	119.8(4)
N(2)-N(1)-C(11)	117.9(4)	C(10)-N(6)-C(61)	129.5(4)
N(3)-N(2)-N(1)	106.8(4)	N(8)-N(7)-N(6)	107.2(4)
N(2)-N(3)-C(4)	109.0(4)	N(7)-N(8)-C(9)	109.3(4)
N(3)-C(4)-C(5)	107.5(4)	N(8)-C(9)-C(10)	108.8(5)
N(3)-C(4)-C(41)	121.0(4)	N(8)-C(9)-C(91)	120.7(4)
C(5)-C(4)-C(41)	131.6(4)	C(10)-C(9)-C(91)	130.4(4)
N(1)-C(5)-C(4)	105.2(4)	C(9)-C(10)-N(6)	104.0(4)
C(15)-C(11)-N(1)	125.7(5)	C(65)-C(61)-N(6)	127.2(5)
C(15)-C(11)-C(12)	110.1(5)	C(65)-C(61)-C(62)	109.5(5)
N(1)-C(11)-C(12)	124.2(4)	N(6)-C(61)-C(62)	123.3(5)
C(15)-C(11)-Mn(1)	71.0(3)	C(65)-C(61)-Mn(2)	70.1(3)
N(1)-C(11)-Mn(1)	126.9(3)	N(6)-C(61)-Mn(2)	126.4(3)
C(12)-C(11)-Mn(1)	70.5(3)	C(62)-C(61)-Mn(2)	70.5(3)
C(13)-C(12)-C(11)	106.7(5)	C(63)-C(62)-C(61)	106.1(5)
C(13)-C(12)-Mn(1)	70.7(3)	C(63)-C(62)-Mn(2)	69.9(3)
C(11)-C(12)-Mn(1)	71.0(3)	C(61)-C(62)-Mn(2)	71.1(3)
C(14)-C(13)-C(12)	108.7(5)	C(64)-C(63)-C(62)	109.2(5)
C(14)-C(13)-Mn(1)	70.1(3)	C(64)-C(63)-Mn(2)	70.6(3)
C(12)-C(13)-Mn(1)	71.0(3)	C(62)-C(63)-Mn(2)	71.5(3)
C(13)-C(14)-C(15)	108.7(5)	C(63)-C(64)-C(65)	108.2(5)
C(13)-C(14)-Mn(1)	71.9(3)	C(63)-C(64)-Mn(2)	71.1(3)
C(15)-C(14)-Mn(1)	71.4(3)	C(65)-C(64)-Mn(2)	71.0(3)
C(11)-C(15)-C(14)	105.8(5)	C(61)-C(65)-C(64)	106.9(5)
C(11)-C(15)-Mn(1)	71.3(3)	C(61)-C(65)-Mn(2)	71.7(3)
C(14)-C(15)-Mn(1)	69.1(3)	C(64)-C(65)-Mn(2)	70.1(3)
C(46)-C(41)-C(42)	119.7(5)	C(96)-C(91)-C(92)	118.8(5)
C(46)-C(41)-C(4)	119.3(4)	C(96)-C(91)-C(9)	120.4(4)
C(42)-C(41)-C(4)	120.9(4)	C(92)-C(91)-C(9)	120.8(4)
C(43)-C(42)-C(41)	120.4(5)	C(93)-C(92)-C(91)	120.4(5)
C(42)-C(43)-C(44)	119.8(5)	C(94)-C(93)-C(92)	120.2(5)
C(45)-C(44)-C(43)	120.2(5)	C(93)-C(94)-C(95)	119.9(6)
C(44)-C(45)-C(46)	120.0(5)	C(94)-C(95)-C(96)	119.3(5)
C(41)-C(46)-C(45)	119.9(5)	C(91)-C(96)-C(95)	121.2(5)

(c) In the carbonyl ligands

C(101)-O(101)	1.144(7)	C(601)-O(601)	1.142(7)
C(102)-O(102)	1.138(7)	C(602)-O(602)	1.128(7)
C(103)-O(103)	1.154(7)	C(603)-O(603)	1.130(7)

O(101)-C(101)-Mn(1)	179.2(6)	O(601)-C(601)-Mn(2)	178.8(5)
O(102)-C(102)-Mn(1)	178.7(6)	O(602)-C(602)-Mn(2)	177.6(6)
O(103)-C(103)-Mn(1)	178.7(5)	O(603)-C(603)-Mn(2)	179.6(6)

Table S3. Anisotropic displacement parameters ($Å^2$ x 10^4) for the expression:

$$\exp\{-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})\}$$

E.s.ds are in parentheses.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn(1)	231(3)	225(3)	168(3)	23(2)	23(3)	-28(3)
N(1)	290(20)	168(18)	213(19)	-42(14)	81(16)	-76(14)
N(2)	340(20)	194(19)	280(20)	-71(16)	62(18)	-27(16)
N(3)	310(20)	189(18)	240(20)	-19(15)	69(17)	-24(15)
C(4)	310(20)	140(18)	170(20)	-46(15)	119(17)	-67(16)
C(5)	290(20)	190(20)	98(19)	-38(15)	69(15)	-107(16)
C(11)	280(20)	190(20)	190(20)	-23(16)	96(17)	-67(16)
C(12)	330(30)	280(20)	141(19)	-10(18)	39(18)	-70(18)
C(13)	440(30)	360(30)	250(20)	61(19)	10(30)	-70(30)
C(14)	370(30)	280(20)	360(30)	40(20)	50(20)	-50(20)
C(15)	410(30)	160(20)	250(20)	52(17)	50(20)	-65(19)
C(41)	330(20)	162(19)	112(18)	-17(15)	91(17)	-26(17)
C(42)	340(20)	190(20)	170(20)	-39(16)	92(18)	-34(17)
C(43)	380(30)	270(30)	260(30)	-30(20)	60(20)	-70(20)
C(44)	310(30)	360(30)	220(20)	40(20)	31(19)	10(20)
C(45)	370(30)	220(20)	310(30)	10(20)	90(20)	20(20)
C(46)	350(30)	170(20)	230(20)	-46(17)	85(18)	0(18)
C(101)	270(30)	450(30)	350(30)	110(30)	70(20)	-10(20)
O(101)	340(30)	860(40)	500(30)	380(30)	-30(20)	90(20)
C(102)	400(30)	260(20)	240(30)	-40(20)	60(20)	-30(20)
O(102)	630(30)	370(20)	450(30)	-90(20)	170(20)	-10(20)
C(103)	270(20)	260(20)	280(20)	22(19)	-6(19)	13(19)
O(103)	370(20)	320(20)	530(30)	60(20)	20(20)	-104(17)
Mn(2)	244(3)	251(3)	179(3)	5(3)	16(3)	-36(3)
N(6)	270(20)	191(18)	280(20)	-79(16)	79(16)	-64(15)
N(7)	350(30)	149(18)	350(20)	-72(16)	88(19)	-43(16)
N(8)	420(30)	195(19)	290(20)	-104(17)	74(19)	-57(17)
C(9)	300(20)	190(20)	170(20)	-30(16)	83(17)	-62(17)
C(10)	260(20)	160(20)	350(30)	-55(19)	83(19)	-97(17)
C(61)	310(20)	230(20)	190(20)	-7(17)	64(18)	-96(17)
C(62)	380(30)	360(30)	220(20)	-40(20)	70(20)	-110(20)
C(63)	390(30)	510(30)	180(20)	90(20)	30(20)	-70(30)
C(64)	390(30)	320(30)	330(30)	160(20)	20(20)	-30(20)
C(65)	270(30)	230(20)	310(30)	37(19)	50(20)	-47(18)
C(91)	360(20)	200(20)	133(19)	-26(16)	83(17)	-63(18)
C(92)	380(30)	190(20)	220(20)	17(18)	70(20)	2(18)
C(93)	370(30)	230(20)	220(20)	18(18)	80(20)	-80(19)
C(94)	360(30)	340(30)	250(20)	-10(20)	90(20)	40(20)
C(95)	400(30)	280(30)	290(30)	70(20)	170(20)	70(20)
C(96)	430(30)	200(20)	220(20)	7(18)	100(20)	-50(20)
C(601)	210(20)	380(30)	330(30)	80(20)	70(20)	24(19)
O(601)	440(30)	730(40)	610(30)	440(30)	30(20)	130(20)
C(602)	310(30)	370(30)	330(30)	-20(20)	-30(20)	-10(20)
O(602)	590(30)	710(40)	480(30)	-250(30)	80(20)	200(30)
C(603)	360(30)	390(30)	230(20)	90(20)	30(20)	-50(20)
O(603)	410(30)	660(30)	490(30)	170(20)	-100(20)	-250(20)

Table S4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3). All hydrogen atoms were included in idealised positions with U(iso)'s set at 1.2*U(eq) of the parent carbon atoms.

	x	y	z	U(iso)
H(5)	2762	3095	319	23
H(12)	3740	7236	1963	30
H(13)	4280	4462	2357	42
H(14)	4143	918	1514	41
H(15)	3489	1374	622	33
H(42)	2136	3234	-645	28
H(43)	1502	3318	-1295	37
H(44)	1112	6544	-1176	36
H(45)	1354	9647	-413	36
H(46)	1988	9537	277	30
H(10)	1716	7027	2107	31
H(62)	707	3083	447	38
H(63)	171	5951	111	43
H(64)	333	9471	957	42
H(65)	979	8870	1829	32
H(92)	2336	6832	3007	32
H(93)	2966	6624	3685	33
H(94)	3338	3367	3578	38
H(95)	3084	283	2776	39
H(96)	2446	481	2126	34

Table S5. Torsion angles, in degrees. E.s.ds are in parentheses.

C(5)-N(1)-N(2)-N(3)	0.9(5)	C(103)-Mn(1)-C(13)-C(14)	-139.2(4)
C(11)-N(1)-N(2)-N(3)	-179.0(4)	C(12)-Mn(1)-C(13)-C(14)	119.0(5)
N(1)-N(2)-N(3)-C(4)	-0.6(5)	C(15)-Mn(1)-C(13)-C(14)	38.4(4)
N(2)-N(3)-C(4)-C(5)	0.1(5)	C(11)-Mn(1)-C(13)-C(14)	80.4(4)
N(2)-N(3)-C(4)-C(41)	-179.0(4)	C(101)-Mn(1)-C(13)-C(12)	7.4(6)
N(2)-N(1)-C(5)-C(4)	-0.8(5)	C(102)-Mn(1)-C(13)-C(12)	-161.4(3)
C(11)-N(1)-C(5)-C(4)	179.1(4)	C(103)-Mn(1)-C(13)-C(12)	101.8(3)
N(3)-C(4)-C(5)-N(1)	0.4(5)	C(14)-Mn(1)-C(13)-C(12)	-119.0(5)
C(41)-C(4)-C(5)-N(1)	179.4(4)	C(15)-Mn(1)-C(13)-C(12)	-80.6(4)
C(5)-N(1)-C(11)-C(15)	12.2(8)	C(11)-Mn(1)-C(13)-C(12)	-38.5(3)
N(2)-N(1)-C(11)-C(15)	-167.8(5)	C(12)-C(13)-C(14)-C(15)	-1.5(6)
C(5)-N(1)-C(11)-C(12)	-165.3(5)	Mn(1)-C(13)-C(14)-C(15)	-62.3(4)
N(2)-N(1)-C(11)-C(12)	14.6(6)	C(12)-C(13)-C(14)-Mn(1)	60.9(4)
C(5)-N(1)-C(11)-Mn(1)	104.4(5)	C(101)-Mn(1)-C(14)-C(13)	-119.4(6)
N(2)-N(1)-C(11)-Mn(1)	-75.6(5)	C(102)-Mn(1)-C(14)-C(13)	145.6(4)
C(101)-Mn(1)-C(11)-C(15)	121.4(4)	C(103)-Mn(1)-C(14)-C(13)	48.6(5)
C(102)-Mn(1)-C(11)-C(15)	30.0(5)	C(12)-Mn(1)-C(14)-C(13)	-37.0(4)
C(103)-Mn(1)-C(11)-C(15)	-146.1(4)	C(15)-Mn(1)-C(14)-C(13)	-117.8(5)
C(14)-Mn(1)-C(11)-C(15)	-39.5(3)	C(11)-Mn(1)-C(14)-C(13)	-80.0(4)
C(13)-Mn(1)-C(11)-C(15)	-82.2(3)	C(101)-Mn(1)-C(14)-C(15)	-1.6(6)
C(12)-Mn(1)-C(11)-C(15)	-120.5(5)	C(102)-Mn(1)-C(14)-C(15)	-96.6(4)
C(101)-Mn(1)-C(11)-N(1)	0.5(4)	C(103)-Mn(1)-C(14)-C(15)	166.4(3)
C(102)-Mn(1)-C(11)-N(1)	-90.8(5)	C(13)-Mn(1)-C(14)-C(15)	117.8(5)
C(103)-Mn(1)-C(11)-N(1)	93.0(5)	C(12)-Mn(1)-C(14)-C(15)	80.8(3)
C(14)-Mn(1)-C(11)-N(1)	-160.4(5)	C(11)-Mn(1)-C(14)-C(15)	37.8(3)
C(13)-Mn(1)-C(11)-N(1)	156.9(4)	N(1)-C(11)-C(15)-C(14)	-176.8(4)
C(12)-Mn(1)-C(11)-N(1)	118.6(5)	C(12)-C(11)-C(15)-C(14)	1.0(5)
C(15)-Mn(1)-C(11)-N(1)	-120.9(5)	Mn(1)-C(11)-C(15)-C(14)	60.9(4)
C(101)-Mn(1)-C(11)-C(12)	-118.1(3)	N(1)-C(11)-C(15)-Mn(1)	122.3(5)
C(102)-Mn(1)-C(11)-C(12)	150.5(4)	C(12)-C(11)-C(15)-Mn(1)	-59.9(3)
C(103)-Mn(1)-C(11)-C(12)	-25.6(4)	C(13)-C(14)-C(15)-C(11)	0.3(6)
C(14)-Mn(1)-C(11)-C(12)	80.9(3)	Mn(1)-C(14)-C(15)-C(11)	-62.3(3)
C(13)-Mn(1)-C(11)-C(12)	38.3(3)	C(13)-C(14)-C(15)-Mn(1)	62.6(4)
C(15)-Mn(1)-C(11)-C(12)	120.5(5)	C(101)-Mn(1)-C(15)-C(11)	-65.0(4)
C(15)-C(11)-C(12)-C(13)	-1.9(5)	C(102)-Mn(1)-C(15)-C(11)	-157.5(4)
N(1)-C(11)-C(12)-C(13)	176.0(4)	C(103)-Mn(1)-C(15)-C(11)	84.9(6)
Mn(1)-C(11)-C(12)-C(13)	-62.1(3)	C(14)-Mn(1)-C(15)-C(11)	115.9(4)
C(15)-C(11)-C(12)-Mn(1)	60.2(3)	C(13)-Mn(1)-C(15)-C(11)	78.8(3)
N(1)-C(11)-C(12)-Mn(1)	-122.0(4)	C(12)-Mn(1)-C(15)-C(11)	36.4(3)
C(101)-Mn(1)-C(12)-C(13)	-175.7(4)	C(101)-Mn(1)-C(15)-C(14)	179.1(3)
C(102)-Mn(1)-C(12)-C(13)	43.2(8)	C(102)-Mn(1)-C(15)-C(14)	86.6(4)
C(103)-Mn(1)-C(12)-C(13)	-81.9(3)	C(103)-Mn(1)-C(15)-C(14)	-31.0(7)
C(14)-Mn(1)-C(12)-C(13)	36.7(3)	C(13)-Mn(1)-C(15)-C(14)	-37.0(3)
C(15)-Mn(1)-C(12)-C(13)	80.6(4)	C(12)-Mn(1)-C(15)-C(14)	-79.5(3)
C(11)-Mn(1)-C(12)-C(13)	116.2(4)	C(11)-Mn(1)-C(15)-C(14)	-115.9(4)
C(101)-Mn(1)-C(12)-C(11)	68.1(4)	N(3)-C(4)-C(41)-C(46)	-12.5(6)
C(102)-Mn(1)-C(12)-C(11)	-73.0(7)	C(5)-C(4)-C(41)-C(46)	168.6(5)
C(103)-Mn(1)-C(12)-C(11)	161.9(3)	N(3)-C(4)-C(41)-C(42)	167.0(4)
C(14)-Mn(1)-C(12)-C(11)	-79.5(3)	C(5)-C(4)-C(41)-C(42)	-11.8(7)
C(13)-Mn(1)-C(12)-C(11)	-116.2(4)	C(46)-C(41)-C(42)-C(43)	-0.3(7)
C(15)-Mn(1)-C(12)-C(11)	-35.6(3)	C(4)-C(41)-C(42)-C(43)	-179.9(4)
C(11)-C(12)-C(13)-C(14)	2.0(6)	C(41)-C(42)-C(43)-C(44)	0.6(8)
Mn(1)-C(12)-C(13)-C(14)	-60.3(4)	C(42)-C(43)-C(44)-C(45)	-0.1(8)
C(11)-C(12)-C(13)-Mn(1)	62.3(3)	C(43)-C(44)-C(45)-C(46)	-0.8(8)
C(101)-Mn(1)-C(13)-C(14)	126.4(5)	C(42)-C(41)-C(46)-C(45)	-0.5(7)
C(102)-Mn(1)-C(13)-C(14)	-42.4(5)	C(4)-C(41)-C(46)-C(45)	179.1(4)

C(44)-C(45)-C(46)-C(41)	1.1(7)
C(102)-Mn(1)-C(101)-O(101)	162(100)
C(103)-Mn(1)-C(101)-O(101)	-103(53)
C(14)-Mn(1)-C(101)-O(101)	67(53)
C(13)-Mn(1)-C(101)-O(101)	-8(53)
C(12)-Mn(1)-C(101)-O(101)	-3(53)
C(15)-Mn(1)-C(101)-O(101)	66(53)
C(11)-Mn(1)-C(101)-O(101)	32(53)
C(101)-Mn(1)-C(102)-O(102)	163(100)
C(103)-Mn(1)-C(102)-O(102)	73(29)
C(14)-Mn(1)-C(102)-O(102)	-47(29)
C(13)-Mn(1)-C(102)-O(102)	-23(29)
C(12)-Mn(1)-C(102)-O(102)	-53(30)
C(15)-Mn(1)-C(102)-O(102)	-87(29)
C(11)-Mn(1)-C(102)-O(102)	-105(29)
C(101)-Mn(1)-C(103)-O(103)	81(25)
C(102)-Mn(1)-C(103)-O(103)	171(100)
C(14)-Mn(1)-C(103)-O(103)	-93(25)
C(13)-Mn(1)-C(103)-O(103)	-65(25)
C(12)-Mn(1)-C(103)-O(103)	-27(25)
C(15)-Mn(1)-C(103)-O(103)	-71(25)
C(11)-Mn(1)-C(103)-O(103)	-11(25)
C(10)-N(6)-N(7)-N(8)	0.5(6)
C(61)-N(6)-N(7)-N(8)	-179.8(4)
N(6)-N(7)-N(8)-C(9)	-0.2(6)
N(7)-N(8)-C(9)-C(10)	-0.2(6)
N(7)-N(8)-C(9)-C(91)	-179.4(4)
N(8)-C(9)-C(10)-N(6)	0.4(5)
C(91)-C(9)-C(10)-N(6)	179.6(5)
N(7)-N(6)-C(10)-C(9)	-0.6(5)
C(61)-N(6)-C(10)-C(9)	179.8(5)
N(7)-N(6)-C(61)-C(65)	168.0(5)
C(10)-N(6)-C(61)-C(65)	-12.4(8)
N(7)-N(6)-C(61)-C(62)	-12.9(7)
C(10)-N(6)-C(61)-C(62)	166.7(5)
N(7)-N(6)-C(61)-Mn(2)	76.3(6)
C(10)-N(6)-C(61)-Mn(2)	-104.0(5)
C(602)-Mn(2)-C(61)-C(65)	-30.1(5)
C(601)-Mn(2)-C(61)-C(65)	-124.2(4)
C(603)-Mn(2)-C(61)-C(65)	140.9(4)
C(64)-Mn(2)-C(61)-C(65)	38.7(3)
C(63)-Mn(2)-C(61)-C(65)	81.6(4)
C(62)-Mn(2)-C(61)-C(65)	120.3(5)
C(602)-Mn(2)-C(61)-N(6)	92.0(5)
C(601)-Mn(2)-C(61)-N(6)	-2.0(4)
C(603)-Mn(2)-C(61)-N(6)	-97.0(5)
C(64)-Mn(2)-C(61)-N(6)	160.8(5)
C(63)-Mn(2)-C(61)-N(6)	-156.3(5)
C(65)-Mn(2)-C(61)-N(6)	122.2(5)
C(62)-Mn(2)-C(61)-N(6)	-117.5(5)
C(602)-Mn(2)-C(61)-C(62)	-150.4(4)
C(601)-Mn(2)-C(61)-C(62)	115.5(4)
C(603)-Mn(2)-C(61)-C(62)	20.6(5)
C(64)-Mn(2)-C(61)-C(62)	-81.6(4)
C(63)-Mn(2)-C(61)-C(62)	-38.7(3)
C(65)-Mn(2)-C(61)-C(62)	-120.3(5)
C(65)-C(61)-C(62)-C(63)	2.2(6)
N(6)-C(61)-C(62)-C(63)	-177.0(4)
Mn(2)-C(61)-C(62)-C(63)	61.6(4)
C(65)-C(61)-C(62)-Mn(2)	-59.4(4)
N(6)-C(61)-C(62)-Mn(2)	121.4(4)
C(602)-Mn(2)-C(62)-C(63)	-43.1(8)
C(601)-Mn(2)-C(62)-C(63)	173.6(4)
C(603)-Mn(2)-C(62)-C(63)	77.7(4)
C(64)-Mn(2)-C(62)-C(63)	-36.8(4)
C(65)-Mn(2)-C(62)-C(63)	-79.8(4)
C(61)-Mn(2)-C(62)-C(63)	-115.9(5)
C(602)-Mn(2)-C(62)-C(61)	72.8(7)
C(601)-Mn(2)-C(62)-C(61)	-70.6(4)
C(603)-Mn(2)-C(62)-C(61)	-166.5(3)
C(64)-Mn(2)-C(62)-C(61)	79.1(3)
C(63)-Mn(2)-C(62)-C(61)	115.9(5)
C(65)-Mn(2)-C(62)-C(61)	36.1(3)
C(61)-C(62)-C(63)-C(64)	-1.5(6)
Mn(2)-C(62)-C(63)-C(64)	60.8(4)
C(61)-C(62)-C(63)-Mn(2)	-62.3(4)
C(602)-Mn(2)-C(63)-C(64)	42.3(5)
C(601)-Mn(2)-C(63)-C(64)	-129.9(5)
C(603)-Mn(2)-C(63)-C(64)	133.6(4)
C(65)-Mn(2)-C(63)-C(64)	-37.9(4)
C(62)-Mn(2)-C(63)-C(64)	-119.1(5)
C(61)-Mn(2)-C(63)-C(64)	-80.5(4)
C(602)-Mn(2)-C(63)-C(62)	161.4(4)
C(601)-Mn(2)-C(63)-C(62)	-10.8(6)
C(603)-Mn(2)-C(63)-C(62)	-107.3(4)
C(64)-Mn(2)-C(63)-C(62)	119.1(5)
C(65)-Mn(2)-C(63)-C(62)	81.2(4)
C(61)-Mn(2)-C(63)-C(62)	38.6(3)
C(62)-C(63)-C(64)-C(65)	0.3(6)
Mn(2)-C(63)-C(64)-C(65)	61.6(4)
C(62)-C(63)-C(64)-Mn(2)	-61.4(4)
C(602)-Mn(2)-C(64)-C(63)	-145.5(4)
C(601)-Mn(2)-C(64)-C(63)	116.7(6)
C(603)-Mn(2)-C(64)-C(63)	-54.4(5)
C(65)-Mn(2)-C(64)-C(63)	117.9(5)
C(62)-Mn(2)-C(64)-C(63)	37.0(4)
C(61)-Mn(2)-C(64)-C(63)	79.9(4)
C(602)-Mn(2)-C(64)-C(65)	96.6(4)
C(601)-Mn(2)-C(64)-C(65)	-1.2(7)
C(603)-Mn(2)-C(64)-C(65)	-172.3(3)
C(63)-Mn(2)-C(64)-C(65)	-117.9(5)
C(62)-Mn(2)-C(64)-C(65)	-80.9(4)
C(61)-Mn(2)-C(64)-C(65)	-38.0(3)
N(6)-C(61)-C(65)-C(64)	177.2(5)
C(62)-C(61)-C(65)-C(64)	-2.0(6)
Mn(2)-C(61)-C(65)-C(64)	-61.7(4)
N(6)-C(61)-C(65)-Mn(2)	-121.2(5)
C(62)-C(61)-C(65)-Mn(2)	59.7(4)
C(63)-C(64)-C(65)-C(61)	1.1(6)
Mn(2)-C(64)-C(65)-C(61)	62.7(3)
C(63)-C(64)-C(65)-Mn(2)	-61.7(4)
C(602)-Mn(2)-C(65)-C(61)	157.4(4)
C(601)-Mn(2)-C(65)-C(61)	62.9(4)
C(603)-Mn(2)-C(65)-C(61)	-99.9(6)
C(64)-Mn(2)-C(65)-C(61)	-116.5(5)
C(63)-Mn(2)-C(65)-C(61)	-79.1(4)
C(62)-Mn(2)-C(65)-C(61)	-36.3(3)
C(602)-Mn(2)-C(65)-C(64)	-86.2(4)
C(601)-Mn(2)-C(65)-C(64)	179.4(4)
C(603)-Mn(2)-C(65)-C(64)	16.5(7)

C(63)-Mn(2)-C(65)-C(64)	37.3(4)	C(63)-Mn(2)-C(601)-O(601)	76(30)
C(62)-Mn(2)-C(65)-C(64)	80.2(4)	C(65)-Mn(2)-C(601)-O(601)	0(30)
C(61)-Mn(2)-C(65)-C(64)	116.5(5)	C(62)-Mn(2)-C(601)-O(601)	69(30)
N(8)-C(9)-C(91)-C(96)	10.1(7)	C(61)-Mn(2)-C(601)-O(601)	33(30)
C(10)-C(9)-C(91)-C(96)	-169.0(5)	C(601)-Mn(2)-C(602)-O(602)	65(15)
N(8)-C(9)-C(91)-C(92)	-170.0(5)	C(603)-Mn(2)-C(602)-O(602)	157(15)
C(10)-C(9)-C(91)-C(92)	10.9(8)	C(64)-Mn(2)-C(602)-O(602)	-86(15)
C(96)-C(91)-C(92)-C(93)	-1.5(7)	C(63)-Mn(2)-C(602)-O(602)	-111(15)
C(9)-C(91)-C(92)-C(93)	178.7(4)	C(65)-Mn(2)-C(602)-O(602)	-47(15)
C(91)-C(92)-C(93)-C(94)	1.0(7)	C(62)-Mn(2)-C(602)-O(602)	-80(15)
C(92)-C(93)-C(94)-C(95)	0.3(8)	C(61)-Mn(2)-C(602)-O(602)	-29(15)
C(93)-C(94)-C(95)-C(96)	-1.0(8)	C(602)-Mn(2)-C(603)-O(603)	80(100)
C(92)-C(91)-C(96)-C(95)	0.7(7)	C(601)-Mn(2)-C(603)-O(603)	172(100)
C(9)-C(91)-C(96)-C(95)	-179.4(4)	C(64)-Mn(2)-C(603)-O(603)	-12(100)
C(94)-C(95)-C(96)-C(91)	0.5(7)	C(63)-Mn(2)-C(603)-O(603)	-43(100)
C(602)-Mn(2)-C(601)-O(601)	-97(30)	C(65)-Mn(2)-C(603)-O(603)	-24(100)
C(603)-Mn(2)-C(601)-O(601)	173(100)	C(62)-Mn(2)-C(603)-O(603)	-80(100)
C(64)-Mn(2)-C(601)-O(601)	1(30)	C(61)-Mn(2)-C(603)-O(603)	-93(100)

Crystal structure analysis of (η^5-[4-phenyltriazol-1-yl]cyclopentadienyl tricarbonyl manganese(I) 3

Crystal data: $C_{16}H_{10}MnN_3O_3$, M = 347.21. Orthorhombic, space group $P2_1cn$ (equiv. to no. 33), a = 33.3395(13), b = 5.9474(2), c = 14.4477(5) Å, V = 2864.74(18) $Å^3$. Z = 8, Dc = 1.610 g cm^{-3}, F(000) = 1408, T = 140(1) K, μ(Mo-Kα) = 9.4 cm^{-1}, λ(Mo-Kα) = 0.71069 Å.

Crystals are clear, elongated,colourless plates. From a sample under oil, one, c*a* 0.35 x 0.28 x 0.02 mm, was mounted on a glass fibre and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans. Total no. of reflections recorded, to θ_{max} = 30°, was 51567 of which 8347 were unique (Rint = 0.084); 7612 were 'observed' with $I > 2\sigma_I$.

Data were processed using the CrysAlisPro-CCD and -RED (1) programs. The structure was determined by the direct methods routines in the SHELXS program (2A) and refined by full-matrix least-squares methods, on F^2's, in SHELXL (2B). The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms. Two persistent difference peaks [at *ca* y+0.5 from Mn(1) and Mn(2)] were thought to be Mn atoms of disordered molecules and were included with s.o.fs of 0.03 in the final refinement cycles. At the conclusion of the refinement, wR_2 = 0.161 and R_1 = 0.077 (2B) for all 8347 reflections weighted $w = [\sigma^2(F_o^2) + (0.0489P)^2 + 7.40.P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the 'observed' data only, R_1 = 0.071.

In the final difference map, the highest peaks (to *ca* 0.7 $eÅ^{-3}$) were near Mn(2).

Scattering factors for neutral atoms were taken from reference (3). Computer programs used in this analysis have been noted above, and were run through WinGX (4) on a Dell Precision 370 PC at the University of East Anglia.

Notes on the structure

There are two independent molecules in the crystal, and these lie adjacent, about 3.4 Å apart and related by a pseudo-centre of symmetry.

The manganese atoms are coordinated by three carbonyl groups and the Cp group of the triazole ligand, in a three-legged stool arrangement. The three rings of each triazole ligand are approximately coplanar, with angles of 14.0(3)° between the normals to the Cp and N_3C_2 rings and 12.2(2)° between the normals to the N_3C_2 and phenyl rings in the first ligand and, correspondingly, 12.9(3)° and 10.6(3)° in the second molecule.

The triazole ligands of the molecules of Mn(1) and Mn(2) overlap with N(6) above the centre of the phenyl ring of C(41-46) and N(1) below the ring of C(91-96). The overlaps of the next ligands are more offset, with H(5^1)

tilted towards C(94), at a distance of 3.24 Å, and H(42[1]) and H(43[1])directed towards C(91) and C(9) at 2.96 and 2.98 Å, respectively; the symmetry operation here, superscript 1, is *x, ½-y, z+½*. The alignment of these ligands can be seen in the packing diagram, Figure 2.

Crystal structure analysis of (η^5-[4-(3-aminophenyl)triazol-1-yl]cyclopentadienyl tricarbonyl manganese(I) 5:

Crystal data and structure refinement for [(η^5-[4-(3-aminophenyl)triazol-1-yl]cyclopentadienyl tricarbonyl manganese (I) 5]

Identification code	davidd2
Elemental formula	C16 H11 Mn N4 O3
Formula weight	362.23
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.8394(3) Å α = 106.742(5) ° b = 9.7556(5) Å β = 94.508(4) ° c = 13.9033(8) Å γ = 102.614(4) °
Volume	731.61(7) Å^3
Z, Calculated density	2, 1.644 Mg/m^3
F(000)	368
Absorption coefficient	0.926 mm^{-1}
Temperature	140(1) K
Wavelength	0.71073 Å
Crystal colour, shape	colourless shard
Crystal size	0.42 x 0.11 x 0.045 mm
Crystal mounting:	on a glass fibre, in oil, fixed in cold N_2 stream
On the diffractometer:	
Theta range for data collection	3.10 to 27.50 °
Limiting indices	-7<=h<=7, -12<=k<=12, -18<=l<=18
Completeness to theta = 27.50	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.964
Reflections collected (not including absenses)	11972
No. of unique reflections	3366 [R(int) for equivalents = 0.040]
No. of 'observed' reflections (I > 2σ_I)	2913
Structure determined by:	direct methods, in SHELXS
Refinement:	Full-matrix least-squares on F^2, in SHELXL

Data / restraints / parameters	3366 / 0 / 225
Goodness-of-fit on F^2	1.173
Final R indices ('observed' data)	R_1 = 0.048, wR_2 = 0.117
Final R indices (all data)	R_1 = 0.058, wR_2 = 0.121
Reflections weighted: $w = [\sigma^2(Fo^2)+(0.0353P)^2+1.311P]^{-1}$ where $P=(Fo^2+2Fc^2)/3$	
Largest diff. peak and hole	0.59 and -0.29 e.Å^{-3}
Location of largest difference peak	near C(33)

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^4). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor. E.s.ds are in parentheses.

	x	y	z	U(eq)
Mn	2325.1(8)	2952.7(5)	1008.4(4)	214.5(14)
C(11)	2445(5)	3453(3)	2631(2)	225(6)
C(12)	3256(6)	2169(3)	2248(2)	249(6)
C(13)	1341(6)	1100(3)	1547(2)	268(7)
C(14)	-592(6)	1748(4)	1498(3)	30(7)
C(15)	82(5)	3218(4)	2170(2)	264(7)
N(1)	3751(4)	4768(3)	3388.6(19)	224(5)
N(2)	6153(5)	5172(3)	3535(2)	297(6)
N(3)	6811(5)	6436(3)	4271(2)	287(6)
C(4)	4845(5)	6850(3)	4608(2)	222(6)
C(5)	2873(5)	5782(3)	4042(2)	223(6)
C(41)	4953(5)	8217(3)	5431(2)	216(6)
C(42)	7039(5)	9346(3)	5752(2)	224(6)
C(43)	7140(6)	10649(3)	6541(2)	252(6)
N(43)	9222(6)	11767(3)	6874(3)	351(7)
C(44)	5127(6)	10779(3)	6999(2)	267(7)
C(45)	3068(6)	9661(4)	6678(2)	265(7)
C(46)	2944(6)	8368(4)	5896(2)	244(6)
C(6)	4438(6)	4684(4)	1180(2)	292(7)
O(6)	5795(5)	5793(3)	1308(2)	448(7)
C(7)	451(6)	3217(4)	19(3)	307(7)
O(7)	-758(5)	3360(3)	-619(2)	434(7)
C(8)	3848(6)	1961(3)	95(2)	266(6)
O(8)	4824(5)	1294(3)	-482.7(19)	381(6)

Table S7. Molecular dimensions. Bond lengths are in Ångstroms, angles in degrees. E.s.ds are in parentheses.

Mn-C(11)	2.158(3)	Mn-C(15)	2.152(3)
Mn-C(12)	2.155(3)	Mn-C(6)	1.801(3)
Mn-C(13)	2.133(3)	Mn-C(7)	1.802(3)
Mn-C(14)	2.125(3)	Mn-C(8)	1.784(3)
C(12)-Mn-C(11)	38.21(11)	C(15)-Mn-C(13)	64.93(12)
C(13)-Mn-C(11)	63.95(12)	C(6)-Mn-C(13)	146.03(14)
C(14)-Mn-C(11)	64.03(12)	C(7)-Mn-C(13)	121.99(14)
C(15)-Mn-C(11)	38.36(11)	C(8)-Mn-C(13)	90.67(13)
C(6)-Mn-C(11)	90.87(13)	C(14)-Mn-C(15)	38.69(12)
C(7)-Mn-C(11)	134.26(14)	C(6)-Mn-C(14)	148.52(14)
C(8)-Mn-C(11)	134.45(13)	C(7)-Mn-C(14)	93.05(15)
C(13)-Mn-C(12)	38.73(12)	C(8)-Mn-C(14)	118.87(14)
C(14)-Mn-C(12)	64.99(13)	C(6)-Mn-C(15)	109.85(14)
C(15)-Mn-C(12)	65.00(12)	C(7)-Mn-C(15)	99.01(14)
C(6)-Mn-C(12)	107.51(14)	C(8)-Mn-C(15)	155.38(13)
C(7)-Mn-C(12)	158.01(14)	C(6)-Mn-C(7)	91.80(15)
C(8)-Mn-C(12)	98.46(13)	C(8)-Mn-C(6)	92.10(15)
C(14)-Mn-C(13)	38.81(13)	C(8)-Mn-C(7)	91.06(15)
C(11)-C(12)	1.411(4)	C(4)-C(41)	1.471(4)
C(11)-N(1)	1.416(4)	C(41)-C(42)	1.393(4)
C(11)-C(15)	1.416(4)	C(41)-C(46)	1.399(4)
C(12)-C(13)	1.422(5)	C(42)-C(43)	1.405(4)
C(13)-C(14)	1.415(5)	C(43)-N(43)	1.387(4)
C(14)-C(15)	1.417(5)	C(43)-C(44)	1.393(4)
N(1)-N(2)	1.353(4)	N(43)-H(43A)	0.74(4)
N(1)-C(5)	1.358(4)	N(43)-H(43B)	0.87(5)
N(2)-N(3)	1.311(4)	C(44)-C(45)	1.377(5)
N(3)-C(4)	1.371(4)	C(45)-C(46)	1.392(4)
C(4)-C(5)	1.375(4)		
C(12)-C(11)-N(1)	125.5(3)	C(5)-N(1)-C(11)	127.3(3)
C(12)-C(11)-C(15)	109.9(3)	N(3)-N(2)-N(1)	106.9(2)
N(1)-C(11)-C(15)	124.6(3)	N(2)-N(3)-C(4)	109.7(3)
C(12)-C(11)-Mn	70.79(17)	N(3)-C(4)-C(5)	107.8(3)
N(1)-C(11)-Mn	126.9(2)	N(3)-C(4)-C(41)	123.7(3)
C(15)-C(11)-Mn	70.58(18)	C(5)-C(4)-C(41)	128.5(3)
C(11)-C(12)-C(13)	106.6(3)	N(1)-C(5)-C(4)	104.8(3)
C(11)-C(12)-Mn	71.00(18)	C(42)-C(41)-C(46)	120.2(3)
C(13)-C(12)-Mn	69.80(18)	C(42)-C(41)-C(4)	120.5(3)
C(14)-C(13)-C(12)	108.3(3)	C(46)-C(41)-C(4)	119.3(3)
C(14)-C(13)-Mn	70.29(18)	C(41)-C(42)-C(43)	120.4(3)
C(12)-C(13)-Mn	71.47(17)	N(43)-C(43)-C(44)	120.6(3)
C(13)-C(14)-C(15)	108.6(3)	N(43)-C(43)-C(42)	120.7(3)
C(13)-C(14)-Mn	70.90(18)	C(44)-C(43)-C(42)	118.7(3)
C(15)-C(14)-Mn	71.67(18)	C(43)-N(43)-H(43A)	120(3)
C(11)-C(15)-C(14)	106.6(3)	C(43)-N(43)-H(43B)	119(3)
C(11)-C(15)-Mn	71.05(18)	H(43A)-N(43)-H(43B)	115(4)
C(14)-C(15)-Mn	69.64(18)	C(45)-C(44)-C(43)	120.7(3)
N(2)-N(1)-C(5)	110.9(2)	C(44)-C(45)-C(46)	121.1(3)
N(2)-N(1)-C(11)	121.8(2)	C(45)-C(46)-C(41)	118.8(3)
C(6)-O(6)	1.150(4)	C(8)-O(8)	1.152(4)
C(7)-O(7)	1.149(4)	O(6)-C(6)-Mn	178.8(3)

O(7)-C(7)-Mn	178.8(3)	O(8)-C(8)-Mn	178.3(3)

Table S8. Anisotropic displacement parameters ($Å^2$ x 10^4) for the expression:

$$\exp\{-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})\}$$

E.s.ds are in parentheses.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	213(2)	209(2)	211(2)	57(2)	26(2)	47(2)
C(11)	211(14)	230(14)	233(15)	65(12)	59(12)	54(12)
C(12)	276(15)	264(15)	238(15)	91(13)	67(12)	110(13)
C(13)	346(17)	210(15)	253(16)	87(13)	74(13)	49(13)
C(14)	251(16)	278(16)	314(17)	64(14)	38(13)	-7(13)
C(15)	219(15)	277(16)	294(16)	74(13)	65(12)	71(12)
N(1)	200(12)	266(13)	187(12)	31(10)	38(10)	70(10)
N(2)	206(13)	343(15)	279(14)	-7(12)	28(11)	86(11)
N(3)	223(13)	311(14)	257(14)	-24(11)	18(11)	82(11)
C(4)	226(14)	262(15)	188(14)	64(12)	46(11)	88(12)
C(5)	217(14)	260(15)	207(15)	60(12)	51(11)	101(12)
C(41)	249(14)	259(15)	157(13)	66(12)	21(11)	97(12)
C(42)	219(14)	278(15)	204(14)	79(12)	43(11)	110(12)
C(43)	281(15)	256(15)	236(15)	93(13)	21(12)	86(12)
N(43)	310(16)	285(16)	362(17)	-26(14)	59(14)	46(13)
C(44)	381(18)	243(15)	212(15)	53(12)	67(13)	167(13)
C(45)	285(16)	333(17)	251(16)	121(14)	101(13)	171(14)
C(46)	248(15)	299(16)	207(14)	88(13)	50(12)	98(12)
C(6)	336(17)	279(16)	234(16)	65(13)	40(13)	43(14)
O(6)	517(16)	318(14)	402(15)	97(12)	78(13)	-97(12)
C(7)	292(17)	291(17)	320(18)	84(14)	12(14)	67(13)
O(7)	395(14)	492(16)	421(15)	201(13)	-74(12)	94(12)
C(8)	263(15)	253(15)	259(16)	81(13)	15(13)	27(13)
O(8)	394(14)	366(14)	349(14)	35(11)	140(11)	100(11)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3). The amino hydrogen atoms were located in a difference map and were refined freely. The remaining hydrogen atoms were included in idealised positions with U(iso)'s set at 1.2*U(eq) of the parent carbon atoms.

	x	y	z	U(iso)
H(12)	4752	2046	2421	30
H(13)	1356	140	1183	32
H(14)	-2061	1286	1093	36
H(15)	-846	3895	2285	32
H(5)	1289	5759	4096	27
H(42)	8372	9237	5443	27
H(44)	5173	11630	7527	32
H(45)	1738	9773	6989	32

H(46)	1548	7616	5686	29
H(43A)	10070(70)	11880(40)	6520(30)	21(10)
H(43B)	9240(80)	12560(50)	7370(40)	47(12)

Table S10. Torsion angles, in degrees. E.s.ds are in parentheses.

C(8)-Mn-C(11)-C(12)	-24.1(3)	Mn-C(13)-C(14)-C(15)	-62.1(2)
C(6)-Mn-C(11)-C(12)	-117.9(2)	C(12)-C(13)-C(14)-M)	61.7(2)
C(7)-Mn-C(11)-C(12)	148.8(2)	C(8)-Mn-C(14)-C(13)	48.4(2)
C(14)-Mn-C(11)-C(12)	81.9(2)	C(6)-Mn-C(14)-C(13)	-120.2(3)
C(13)-Mn-C(11)-C(12)	38.47(18)	C(7)-Mn-C(14)-C(13)	141.3(2)
C(15)-Mn-C(11)-C(12)	120.3(3)	C(15)-Mn-C(14)-C(13)	-118.1(3)
C(8)-Mn-C(11)-N(1)	96.4(3)	C(12)-Mn-C(14)-C(13)	-37.49(19)
C(6)-Mn-C(11)-N(1)	2.6(3)	C(11)-Mn-C(14)-C(13)	-80.0(2)
C(7)-Mn-C(11)-N(1)	-90.7(3)	C(8)-Mn-C(14)-C(15)	166.5(2)
C(14)-Mn-C(11)-N(1)	-157.7(3)	C(6)-Mn-C(14)-C(15)	-2.2(4)
C(13)-Mn-C(11)-N(1)	158.9(3)	C(7)-Mn-C(14)-C(15)	-100.6(2)
C(15)-Mn-C(11)-N(1)	-119.2(3)	C(13)-Mn-C(14)-C(15)	118.1(3)
C(12)-Mn-C(11)-N(1)	120.5(3)	C(12)-Mn-C(14)-C(15)	80.6(2)
C(8)-Mn-C(11)-C(15)	-144.3(2)	C(11)-Mn-C(14)-C(15)	38.09(19)
C(6)-Mn-C(11)-C(15)	121.9(2)	C(12)-C(11)-C(15)-C(14)	0.8(4)
C(7)-Mn-C(11)-C(15)	28.5(3)	N(1)-C(11)-C(15)-C(14)	-177.1(3)
C(14)-Mn-C(11)-C(15)	-38.41(19)	Mn-C(11)-C(15)-C(14)	60.9(2)
C(13)-Mn-C(11)-C(15)	-81.8(2)	C(12)-C(11)-C(15)-M)	-60.1(2)
C(12)-Mn-C(11)-C(15)	-120.3(3)	N(1)-C(11)-C(15)-M)	122.0(3)
N(1)-C(11)-C(12)-C(13)	176.8(3)	C(13)-C(14)-C(15)-C(11)	-0.2(4)
C(15)-C(11)-C(12)-C(13)	-1.1(4)	Mn-C(14)-C(15)-C(11)	-61.9(2)
Mn-C(11)-C(12)-C(13)	-61.0(2)	C(13)-C(14)-C(15)-M)	61.6(2)
N(1)-C(11)-C(12)-M)	-122.2(3)	C(8)-Mn-C(15)-C(11)	87.2(4)
C(15)-C(11)-C(12)-M)	60.0(2)	C(6)-Mn-C(15)-C(11)	-64.5(2)
C(8)-Mn-C(12)-C(11)	162.89(19)	C(7)-Mn-C(15)-C(11)	-159.8(2)
C(6)-Mn-C(12)-C(11)	68.0(2)	C(14)-Mn-C(15)-C(11)	116.7(3)
C(7)-Mn-C(12)-C(11)	-82.4(4)	C(13)-Mn-C(15)-C(11)	79.0(2)
C(14)-Mn-C(12)-C(11)	-79.13(19)	C(12)-Mn-C(15)-C(11)	36.11(18)
C(13)-Mn-C(12)-C(11)	-116.7(3)	C(8)-Mn-C(15)-C(14)	-29.4(4)
C(15)-Mn-C(12)-C(11)	-36.26(18)	C(6)-Mn-C(15)-C(14)	178.8(2)
C(8)-Mn-C(12)-C(13)	-80.4(2)	C(7)-Mn-C(15)-C(14)	83.6(2)
C(6)-Mn-C(12)-C(13)	-175.3(2)	C(13)-Mn-C(15)-C(14)	-37.6(2)
C(7)-Mn-C(12)-C(13)	34.3(4)	C(12)-Mn-C(15)-C(14)	-80.6(2)
C(14)-Mn-C(12)-C(13)	37.57(19)	C(11)-Mn-C(15)-C(14)	-116.7(3)
C(15)-Mn-C(12)-C(13)	80.4(2)	C(12)-C(11)-N(1)-N(2)	27.5(5)
C(11)-Mn-C(12)-C(13)	116.7(3)	C(15)-C(11)-N(1)-N(2)	-155.0(3)
C(11)-C(12)-C(13)-C(14)	0.9(4)	Mn-C(11)-N(1)-N(2)	-64.2(4)
Mn-C(12)-C(13)-C(14)	-61.0(2)	C(12)-C(11)-N(1)-C(5)	-153.4(3)
C(11)-C(12)-C(13)-M)	61.8(2)	C(15)-C(11)-N(1)-C(5)	24.2(5)
C(8)-Mn-C(13)-C(14)	-139.1(2)	Mn-C(11)-N(1)-C(5)	114.9(3)
C(6)-Mn-C(13)-C(14)	126.2(3)	C(5)-N(1)-N(2)-N(3)	-0.3(4)
C(7)-Mn-C(13)-C(14)	-47.4(2)	C(11)-N(1)-N(2)-N(3)	179.0(3)
C(15)-Mn-C(13)-C(14)	37.51(19)	N(1)-N(2)-N(3)-C(4)	0.3(4)
C(12)-Mn-C(13)-C(14)	118.2(3)	N(2)-N(3)-C(4)-C(5)	-0.2(4)
C(11)-Mn-C(13)-C(14)	80.2(2)	N(2)-N(3)-C(4)-C(41)	-180.0(3)
C(8)-Mn-C(13)-C(12)	102.8(2)	N(2)-N(1)-C(5)-C(4)	0.1(3)
C(6)-Mn-C(13)-C(12)	8.0(3)	C(11)-N(1)-C(5)-C(4)	-179.1(3)
C(7)-Mn-C(13)-C(12)	-165.58(19)	N(3)-C(4)-C(5)-N(1)	0.1(3)
C(14)-Mn-C(13)-C(12)	-118.2(3)	C(41)-C(4)-C(5)-N(1)	179.8(3)
C(15)-Mn-C(13)-C(12)	-80.65(19)	N(3)-C(4)-C(41)-C(42)	15.6(5)
C(11)-Mn-C(13)-C(12)	-37.95(17)	C(5)-C(4)-C(41)-C(42)	-164.1(3)
C(12)-C(13)-C(14)-C(15)	-0.4(4)	N(3)-C(4)-C(41)-C(46)	-163.8(3)

C(5)-C(4)-C(41)-C(46)	16.5(5)	C(12)-Mn-C(6)-O(6)	-23(15)
C(46)-C(41)-C(42)-C(43)	-0.4(4)	C(11)-Mn-C(6)-O(6)	12(15)
C(4)-C(41)-C(42)-C(43)	-179.8(3)	C(8)-Mn-C(7)-O(7)	62(15)
C(41)-C(42)-C(43)-N(43)	179.1(3)	C(6)-Mn-C(7)-O(7)	154(15)
C(41)-C(42)-C(43)-C(44)	0.7(4)	C(14)-Mn-C(7)-O(7)	-57(15)
N(43)-C(43)-C(44)-C(45)	-179.1(3)	C(13)-Mn-C(7)-O(7)	-29(15)
C(42)-C(43)-C(44)-C(45)	-0.7(5)	C(15)-Mn-C(7)-O(7)	-95(15)
C(43)-C(44)-C(45)-C(46)	0.6(5)	C(12)-Mn-C(7)-O(7)	-54(16)
C(44)-C(45)-C(46)-C(41)	-0.3(5)	C(11)-Mn-C(7)-O(7)	-113(15)
C(42)-C(41)-C(46)-C(45)	0.2(4)	C(6)-Mn-C(8)-O(8)	136(11)
C(4)-C(41)-C(46)-C(45)	179.6(3)	C(7)-Mn-C(8)-O(8)	-132(11)
C(8)-Mn-C(6)-O(6)	-122(15)	C(14)-Mn-C(8)-O(8)	-38(11)
C(7)-Mn-C(6)-O(6)	146(15)	C(13)-Mn-C(8)-O(8)	-10(11)
C(14)-Mn-C(6)-O(6)	48(15)	C(15)-Mn-C(8)-O(8)	-17(11)
C(13)-Mn-C(6)-O(6)	-28(15)	C(12)-Mn-C(8)-O(8)	28(11)
C(15)-Mn-C(6)-O(6)	46(15)	C(11)-Mn-C(8)-O(8)	43(11)

Crystal structure analysis of [(η^5-[4-(3-aminophenyl)triazol-1-yl]cyclopentadienyl tricarbonyl manganese (I) 5]

Crystal data: $C_{16}H_{11}MnN_4O_3$, M = 362.23. Triclinic, space group P-1 (no. 2), a = 5.8394(3), b = 9.7556(5), c = 13.9033(8) Å, α = 106.742(5), β = 94.508(4), γ = 102.614(4) °, V = 731.61(7) $Å^3$. Z = 2, Dc = 1.644 g cm^{-3}, F(000) = 368, T = 140(1) K, μ(Mo-Kα) = 9.3 cm^{-1}, λ(Mo-Kα) = 0.71069 Å.

Crystals are clear, colourless shards. From a sample under oil, one, *ca* 0.045 x 0.11 x 0.42 mm, was mounted on a glass fibre and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans. Total no. of reflections recorded, to θ_{max} = 27.5°, was 11972 of which 3366 were unique (Rint = 0.040); 2913 were 'observed' with $I > 2\sigma_I$.

Data were processed using the CrysAlisPro-CCD and -RED (1) programs. The structure was determined by the direct methods routines in the SHELXS program (2A) and refined by full-matrix least-squares methods, on F^2's, in SHELXL (2B). The non-hydrogen atoms were refined with anisotropic thermal parameters. The amino hydrogen atoms were located in a difference map and were refined freely. The remaining hydrogen atoms were included in idealised positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms. At the conclusion of the refinement, wR_2 = 0.121 and R_1 = 0.058 (2B) for all 3366 reflections weighted $w = [\sigma^2(F_o^2) + (0.0353P)^2 + 1.311P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the 'observed' data only, R_1 = 0.048.

In the final difference map, the highest peak (*ca* 0.6 $eÅ^{-3}$) was near C(33).

Scattering factors for neutral atoms were taken from reference (3). Computer programs used in this analysis have been noted above, and were run through WinGX (4) on a Dell Optiplex GX620 PC at the University of East Anglia.

Notes on the structure

The manganese atom lies 1.774(2) Å from the mean-plane of the Cp ring atoms (Figure 3), and the three carbonyl ligands are arranged in an almost rectangular pattern on the opposite side of the metal; the mean C_{CO}–Mn–C_{CO} angle is 91.7°.

The three rings form a progression in orientation (Figure 3); by rotation about the C(11)–N(1) bond, the normals to the Cp and triazole rings are 26.0(2)° apart and the corresponding rotation about the C(4)–C(41) bond is 16.2(2)° in the same direction.

There are no close contacts of the amino group, and nothing close enough to be considered for hydrogen bonding.

There are π…π interactions between offset overlapping of phenyl rings *ca* 3.45 Å apart, around centres of symmetry. The parallel alignment of pairs of triazole rings are further apart, at *ca* 3.63 Å. The closest intermolecular contact is of a triazole C(12)–H(12) group pointing to the edge of a phenyl ring with H(12)…C(46') 2.78 Å.

Crystallography References

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S6. DFT calculations

DFT computational details.

All calculations were performed using the Gaussian 09[1] computational package. Geometry optimisation and frequency calculations have been carried out using the three-parameter exchange functional of Becke[2] (B3) and the correlation functional of Lee, Yang, and Parr (LYP), B3LYP[3] In each case an all electron 6-311+G(d,p)[4] basis set has been implemented. Structures were geometry optimised in the gas phase with the default convergence criteria and confirmed as minima through frequency calculations. Zero-point energies and thermodynamic properties were calculated at 298.15 K/1atm. All geometries were optimised in both gas phase and implicit solvent. Solvation was accounted using the integral equation formalism polarisible continuum model (IEFPCM) in dichloromethane (ε = 8.93), in combination with the united atom topological model for radii setting (RADII=UAHF).

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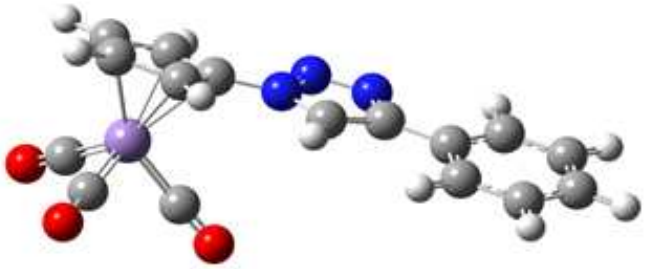
2. Becke, A.D., J. Chem. Phys., 98, 5648–5652 (1993)
3. Lee, C., Yang, W., Parr, R.G., Phys. Rev. B: Condens. Matter 37, 785–789 (1988)
4. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.,* 72, 650–654, (1980).

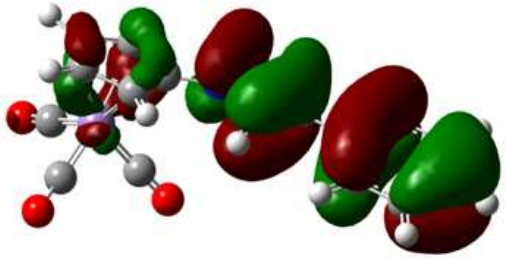
Figure S11

A) Neutral compound **3** in the gas phase

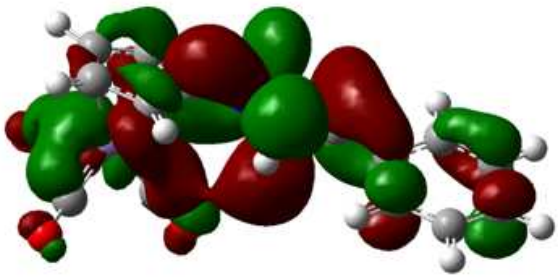
Optimised structure of **3**



HOMO:

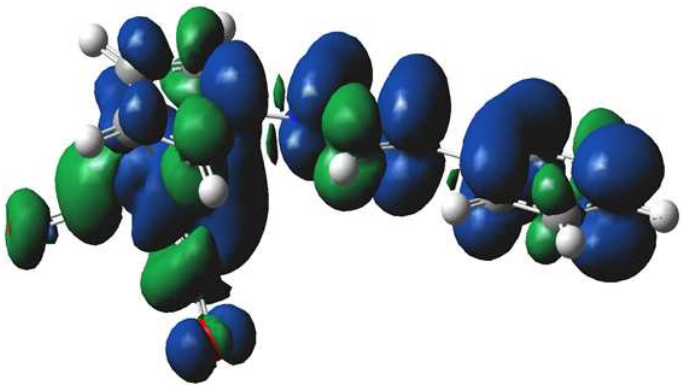


LUMO:



B) Cationic compound **3**$^{+\bullet}$ in the gas phase. S=1/2

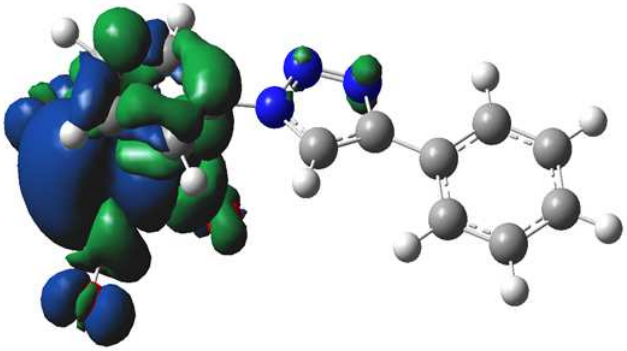
Spin density:



(Spin density on Mn corresponds to 64% in the gas phase)

C) Cationic compound **3**$^{+\bullet}$ in dichloromethane. S=1/2

Spin density



(In the solvent spin density on Mn corresponds to 97% in the solvent)

Figure S12. Predicted IR spectra for neutral **3** (top) and cationic $\mathbf{3}^{+\bullet}$ (bottom) in dichloromethane