Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A PhotoCORM Nanocarrier for CO Release Using NIR Light

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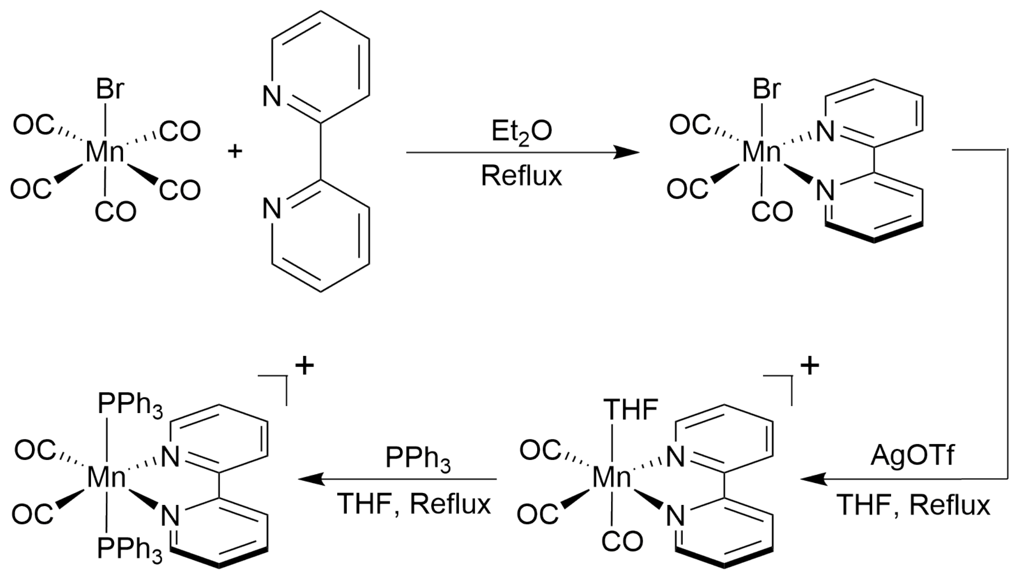
Contents

Experimental Details

Instrumentation: Optical absorption spectra were recorded using a Shimadzu dual beam UV-2401 PC spectrometer and a StellarNet BLACK-Comet SR spectrometer with 1.0 cm path length quartz cells. Infrared spectra of solutions were recorded using a Mattson Research Series FTIR spectrometer. CO generation was measured using an Agilent 6890 gas chromatograph with a thermal conductivity detector (GC-TCD).

Synthesis of *dicarbonyl(bipyridine)bis(triphenylphosphine)manganese(I) trifluoromethyl-sulfonate*: [Mn(bpy)(CO)$_2$(PPh$_3$)$_2$](CF$_3$SO$_3$) (2): Organometallic syntheses were done under an argon atmosphere using standard Schlenk line and glovebox techniques. All organic solvents were freshly distilled, and other reagents were used without further purification, unless otherwise noted. This compound was prepared by a modified literature procedure[1-3] shown in Scheme S-1.



Scheme S-1. Synthetic sequence for the preparation of $Mn(bpy)(CO)_2(PPh_3)_2^+$

In a typical preparation, manganese pentacarbonyl bromide (0.275 g, 1.0 mmol) was refluxed with 2,2' bipyridine (0.172 g, 1.1 mmol) in diethyl ether (50 mL) for 4 h. Upon cooling the reaction solution to -40°C, an orange solid, Mn(bpy)(CO)$_3$Br, precipitated and was collected. To 50 mL dry THF, Mn(bpy)(CO)$_3$Br (0.188 g, 0.5 mmol) and Ag(CF$_3$SO$_3$) (0.141 g, 0.55 mmol) were added, and this mixture was allowed to reflux for 6 h to give a solution of Mn(bpy)(CO)$_3$(THF)$^+$ and insoluble AgCl (removed by filtering through a fine porosity sintered glass frit). To the resulting solution, triphenylphosphine (1.310 g, 5.0 mmol) was added and the mixture was refluxed for 18 h. The remaining THF was removed *in vacuo*, to give dark orange, air-stable [Mn(bpy)(CO)$_2$(PPh$_3$)](CF$_3$SO$_3$) (**2**) with a 70% yield. This salt was then purified by flash chromatography over silica gel. Crystals (yellow plates) suitable for X-ray structural determination were grown from acetonitrile/hexane solution at -20°C. In dichloromethane **2** shows two ν(CO) bands at 1940 and 1871 cm^{-1} in the IR spectrum and a MLCT band at λ_{max} 400 nm (ϵ = 5400 M^{-1}cm^{-1}). These spectral data agree well with the reported literature values for the closely related phenanthroline analog.[4]

Syntheses of UCNPs: The NaGdF$_4$:Tm,Yb@NaGdF$_4$ upconverting nanoparticles were synthesized by thermal decomposition of rare-earth oleates according to literature procedures[6]

These were composed of $NaGdF_4$ cores doped with Yb^{3+} (20%) as the light harvesting ion and Tm^{3+} (0.1%) as the emitting ion with a thin $NaGdF_4$ shell to reduce environmental quenching. A TEM image of these particles is shown in Figure S-1. The UCNP@PL-PEG conjugates were prepare as described in the text using DSPE-PEG(2000) carboxylic acid (1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-N-[carboxy(polyethylene glycol)-2000), (mol. wt. 2849.50) purchased from Avanti Polar Lipids. This is designated as PL-PEG in the text.

Photochemical procedures: Continuous visible photolysis was performed using a 470 nm Luxeon Rebel Light Emitting Diode mounted on an optical train. This light was first passed through a pinhole to reduce the light intensity, then a series of lenses to collimate the light, and finally a shutter to control the irradiation time. Photon flux was determined by measuring the light intensity at the point of irradiation, and calculating the flux using equation S-1. Quantum yields were determined by plotting the incremental quantum yields for the decrease of the band at 400 nm versus the elapsed irradiation time over the initial 10% of the reaction. A linear fit of this data provided an equation with a y-intercept equal to the overall quantum yield, ϕ_{rxn}.[5]

Equation S-1:

$$I_o = \frac{P \cdot \lambda}{h \cdot c \cdot N_A}$$

I_o = photon flux (Einsteins/second), P = power, λ = wavelength of light, h = Planck's constant, c = speed of light, N_A = Avogadro's constant.

The NIR photoexcitation source was a 976 nm Sheaupac fiber coupled laser module with diode laser controller (LDX 3500B - 200 mA to 6 A) and laser diode temperature controller (LDT 5545B) from ILX Lightwave.

Inductively coupled plasma /optical emission spectroscopy (ICP-OES) experiments to determine photoCORM incorporation and leaching. The standard solutions were prepared by dissolving a known amount of manganese (II) chloride tetrahydrate $[MnCl_2(H_2O)_4]$ (crystallized from water) in 18.2 MΩ deionized water with 5% HNO_3. Serial dilutions were made using volumetric glassware and acidified 18.2 MΩ deionized water. The unknown samples were prepared by digesting a known amount of sample in aqua regia (3:1 $HCl:HNO_3$) for 24 hours. After digestion, the unknown samples were diluted with volumetric glassware using 18.2 MΩ deionized water. All measurements were obtained with a Thermo iCAP 6300 ICP equipped with a 6000 K argon plasma. Reference emission lines were monitored at 257.610 nm, 259.373 nm, 260.569 nm, 279.482 nm, 293.930 nm, 294.920 nm, and 403.076 nm. Each measurement is the average of three replicates. (The MRL Shared Experimental Facilities are supported by the MRSEC Program of the NSF under Award No. DMR 1121053)

Dynamic Light Scattering (DLS) experiments: These were carried out on a Malvern Zetasizer Nano-ZS at the California NanoScience Institute. Samples were prepared from phosphate-buffered saline (PBS) stock solutions (pH 7.4) of UCNPs@PL-PEG infused with photoCORMs by dilution with PBS solution and filtered with a 0.2 μm nylon syringe filter into a disposable polystyrene cuvette. The diameters of the particles were determined based on the fitting by population. The refractive index of materials and solvent are 1.5 and 1.33 respectively. All measurements were preformed under air atmosphere at 25 °C.

Detecting photoreleased CO upon NIR irradiation: Photochemical release of CO was demonstrated using the myoglobin assay[7] and by GC-TCD analysis. For the former method, a quartz cuvette containing 65 µM equine myoglobin, excess sodium dithionite, and 0.5 mg/mL nanocarriers in pH 7.4 phosphate buffered saline was irradiated. Periodically during the irradiation, the UV-visible spectra of the myoglobin Q-band region were recorded. The characteristic spectral changes corresponding to the formation of carboxymyoglobin were observed (see Figure S-5).

Photochemical release of CO from the photoCORM-loaded UCNP@PL-PEG nanocarriers was also confirmed by headspace analysis using GC-TCD. A 500 µL suspension of the nanocarriers in pH 7.4 phosphate buffered saline (2 mg/mL based on the mass of UCNPs) was placed in a 2-mL screw-cap vial with a septum. This solution was irradiated with a 980 nm continuous wave laser operating at 2.0 watts for 5 minutes. A 500 µL aliquot of the headspace was injected into the GC inlet operating in splitless mode and separated on a carbonPLOT column. Carbon monoxide was identified based on the retention time as calibrated using standard gas mixtures (see Figure S-6).

References:

(1) Pierri, A. E.; Pallaoro, A.; Wu, G.; Ford, P. C. *J. Am. Chem. Soc.* **2012**, *134*, 18197.
(2) Hori, H; Johnson, F. P. A.; Koike, K.; Ishitani, O.; Ibusuki, T.J. *Photochem. Photobiol. A* **1996**, 96, 171-174.
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(4) Usón, R.; Riera, V.; Gimeno, J.; Laguna, M. *Transition Met. Chem.* **1977**, *2*, 123.
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Supporting Figures

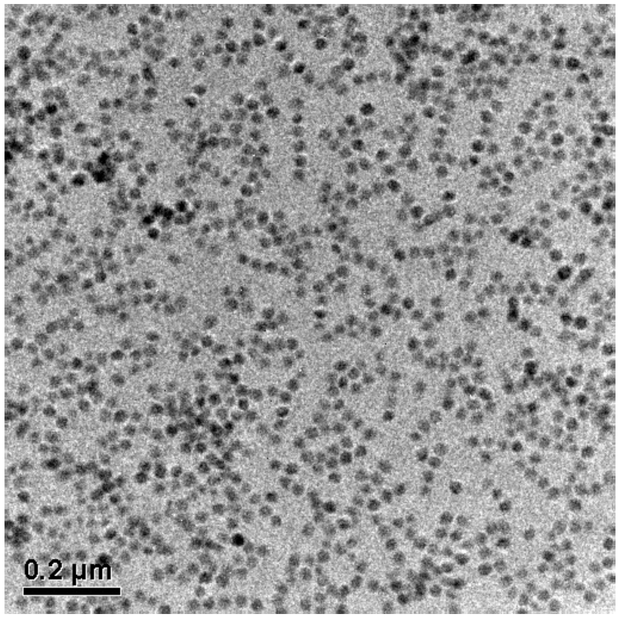

Figure S-1: TEM image of $NaGdF_4$:Tm,Yb@$NaGdF_4$ UCNPs

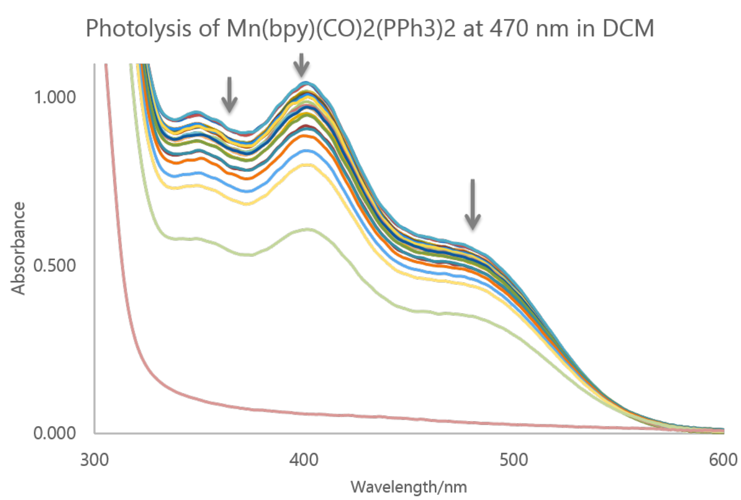

Figure S-2: Spectral changes of an aerated DCM solution of **2** in the UV-visible region upon irradiation with 470 nm light.

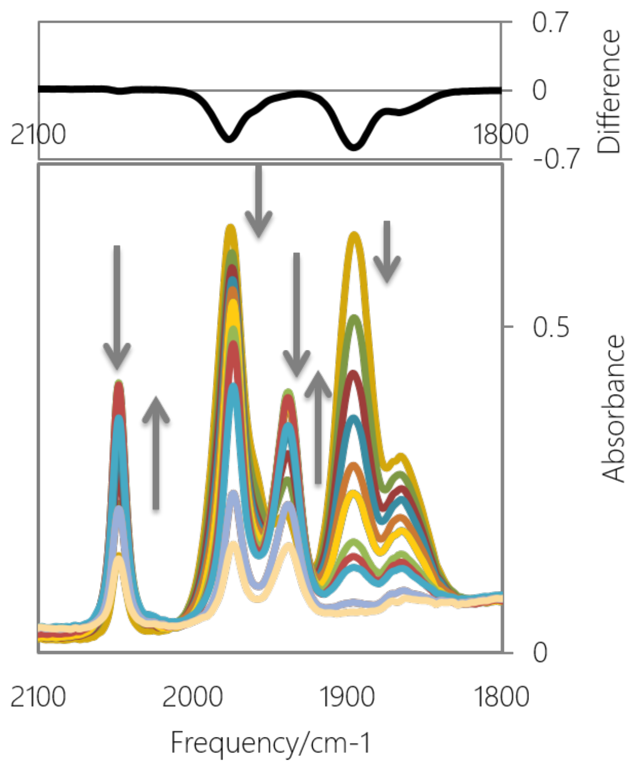

Figure S-3: Spectral changes of an aerated DCM solution of **2** in the ν_{CO} region upon irradiation with 470 nm light.

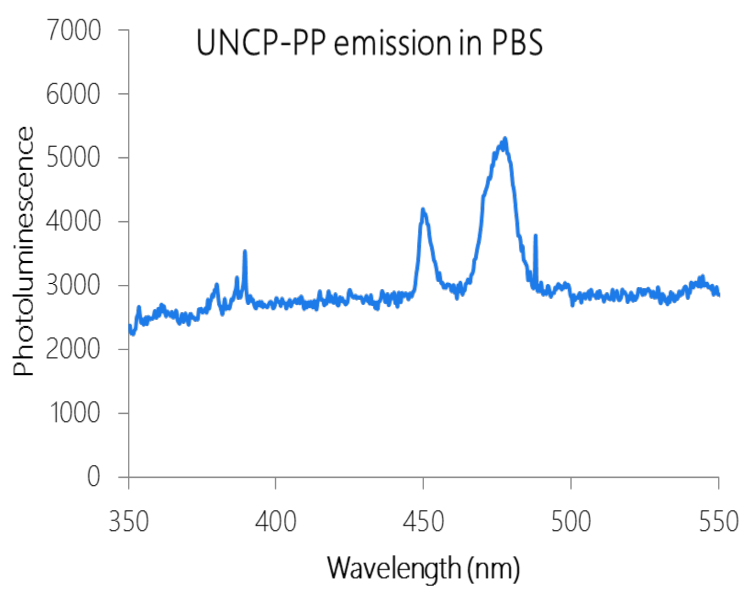

Figure S-4. Visible range spectrum of the upconversion emission from a dilute solution of UCNP@PL-PEG nanocarriers in pH 7.4 PBS upon irradiation with 980 nm light at 1.0 W. This shows the characteristic emission peaks at 450 and 475 nm associated with Tm-doped UCNPs.

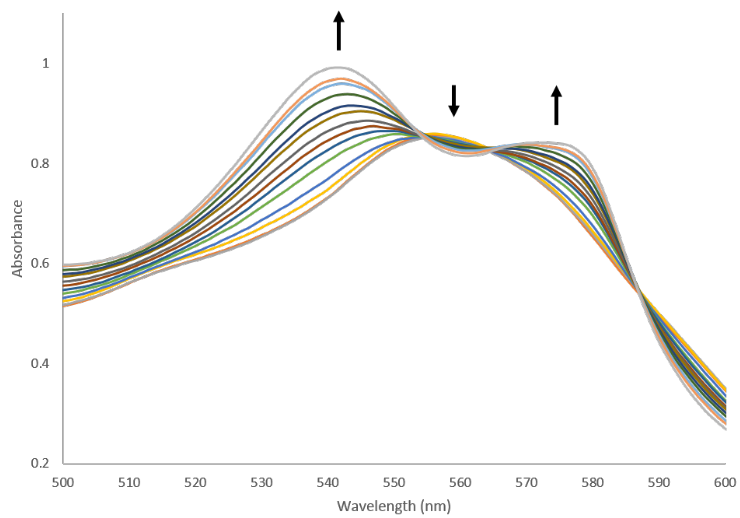

Figure S-5: UV-visible spectral changes corresponding to the formation of carboxymyoglobin upon 980 nm photolysis of a pH 7.4 phosphate buffered saline solution containing myoglobin, excess dithionite and the photoCORM loaded UCNP@PL-PEG nanocarriers.

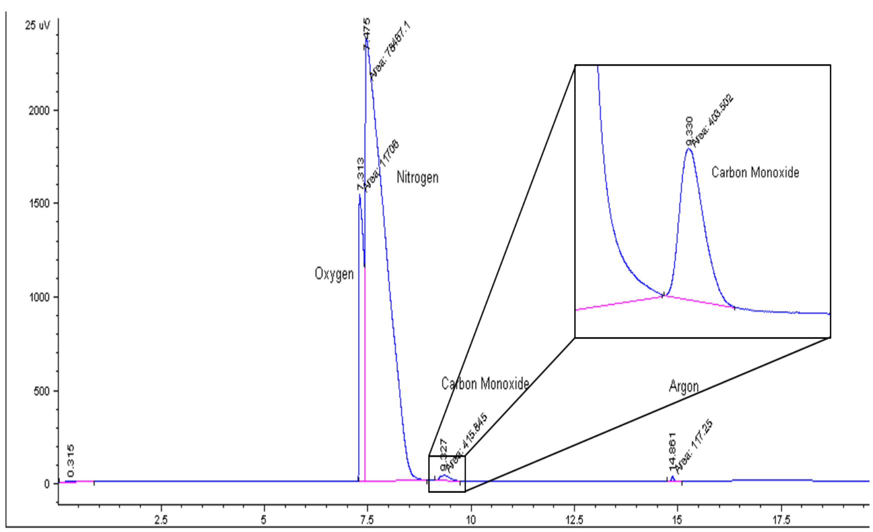

Figure S-6: GC trace showing the production of CO in the headspace of a vial containing an aqueous suspension of the photoCORM loaded UCNP@PL-PEG nanocarriers when irradiated with 980 nm light.

X-ray Crystallography

The solid state crystal structure of [Mn(bpy)$(CO)_2(PPh_3)_2$]OTf (**2**) was determined by X-ray diffraction on a Kappa Apex II single-crystal diffractometer.

Table S-1. Crystal data and structure refinement for [Mn(bpy)$(CO)_2(PPh_3)_2$]OTf .

Empirical formula	C111 H110 F6 Mn2 N5 O10 P4 S2	
Formula weight	2085.91	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.451(2) Å	a= 90°.
	b = 27.816(4) Å	b= 105.155(4)°.
	c = 14.753(2) Å	g = 90°.
Volume	4932.0(13) $Å^3$	
Z	2	
Density (calculated)	1.405 Mg/m^3	
Absorption coefficient	0.439 mm^{-1}	
F(000)	2174	
Crystal size	0.250 x 0.100 x 0.050 mm^3	
Theta range for data collection	1.464 to 28.493°.	
Index ranges	-16<=h<=16, -34<=k<=37, -14<=l<=19	
Reflections collected	36069	
Independent reflections	12413 [R(int) = 0.0433]	
Completeness to theta =	25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6376	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12413 / 27 / 644	
Goodness-of-fit on F2	1.164	
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1165	
R indices (all data)	R1 = 0.0817, wR2 = 0.1254	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.909 and -0.802 e.$Å^{-3}$	

Table S-2 (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5894(2)	2544(1)	1461(2)	13(1)
C(2)	5728(2)	2534(1)	3173(2)	12(1)
C(3)	5848(2)	3517(1)	538(2)	14(1)
C(4)	5826(2)	3912(1)	-33(2)	18(1)
C(5)	5731(2)	4366(1)	326(2)	21(1)
C(6)	5668(2)	4411(1)	1247(2)	19(1)
C(7)	5689(2)	3997(1)	1782(2)	14(1)
C(8)	5638(2)	3998(1)	2770(2)	15(1)
C(9)	5585(3)	4414(1)	3274(2)	27(1)
C(10)	5572(3)	4379(1)	4207(2)	37(1)
C(11)	5617(3)	3929(1)	4613(2)	26(1)
C(12)	5656(2)	3528(1)	4069(2)	16(1)
C(13)	2976(2)	3209(1)	2447(2)	14(1)
C(14)	3259(2)	3079(1)	3395(2)	15(1)
C(15)	2616(2)	3225(1)	3984(2)	18(1)
C(16)	1673(2)	3501(1)	3632(2)	20(1)
C(17)	1371(2)	3627(1)	2688(2)	20(1)
C(18)	2018(2)	3482(1)	2099(2)	18(1)
C(19)	3161(2)	2367(1)	1467(2)	14(1)
C(20)	3730(2)	1933(1)	1652(2)	16(1)
C(21)	3158(3)	1498(1)	1493(2)	21(1)
C(22)	2007(2)	1493(1)	1150(2)	22(1)
C(23)	1431(2)	1924(1)	952(2)	23(1)
C(24)	1998(2)	2357(1)	1108(2)	19(1)
C(25)	3385(2)	3270(1)	597(2)	14(1)
C(26)	3209(2)	3768(1)	541(2)	18(1)
C(27)	2988(2)	4000(1)	-323(2)	22(1)
C(28)	2970(2)	3742(1)	-1132(2)	25(1)
C(29)	3160(2)	3250(1)	-1082(2)	22(1)
C(30)	3369(2)	3017(1)	-219(2)	17(1)
C(31)	8244(2)	3329(1)	3964(2)	13(1)

C(32)	8010(2)	3107(1)	4744(2)	17(1)
C(33)	8301(2)	3325(1)	5620(2)	20(1)
C(34)	8834(2)	3767(1)	5735(2)	21(1)
C(35)	9103(3)	3983(1)	4981(2)	23(1)
C(36)	8815(2)	3766(1)	4102(2)	18(1)
C(37)	8491(2)	2458(1)	3077(2)	13(1)
C(38)	8009(2)	2002(1)	2953(2)	15(1)
C(39)	8680(2)	1593(1)	3118(2)	18(1)
C(40)	9824(2)	1635(1)	3407(2)	22(1)
C(41)	10312(2)	2088(1)	3550(2)	24(1)
C(42)	9650(2)	2496(1)	3393(2)	20(1)
C(43)	8319(2)	3308(1)	1977(2)	14(1)
C(44)	8727(2)	3022(1)	1362(2)	17(1)
C(45)	9068(2)	3230(1)	626(2)	22(1)
C(46)	9019(2)	3724(1)	502(2)	24(1)
C(47)	8614(2)	4012(1)	1103(2)	20(1)
C(48)	8255(2)	3805(1)	1832(2)	17(1)
C(49)	1984(5)	4656(3)	4417(6)	37(2)
C(50)	3109(5)	4572(2)	4403(5)	37(2)
C(51)	1607(13)	4730(6)	4517(7)	84(6)
C(52)	2148(9)	4864(5)	5534(6)	99(4)
C(53)	1389(6)	4730(3)	6081(4)	41(2)
C(54)	1843(7)	4862(3)	7102(4)	36(2)
C(55)	914(11)	4711(6)	7508(6)	103(5)
C(56)	1094(5)	4797(2)	8464(4)	31(2)
C(57)	537(10)	4783(5)	9964(7)	95(4)
C(58)	79(9)	4792(4)	8939(7)	89(4)
C(59)	1060(13)	4814(5)	8522(9)	390(30)
C(60)	552(9)	4728(6)	7543(8)	99(5)
C(61)	1193(10)	4909(8)	6930(9)	195(10)
C(62)	2379(6)	4842(2)	7187(5)	29(1)
C(63)	3037(3)	5314(1)	2102(3)	37(1)
F(1)	2601(2)	5452(1)	1216(2)	57(1)
F(2)	3212(2)	4838(1)	2098(2)	55(1)
F(3)	2267(2)	5388(1)	2565(2)	59(1)
Mn(1)	5769(1)	2985(1)	2313(1)	10(1)

N(1)	5782(2)	3551(1)	1435(1)	12(1)
N(2)	5664(2)	3553(1)	3157(1)	13(1)
N(3)	1060(5)	4718(2)	4423(6)	49(2)
O(1)	5984(2)	2268(1)	897(1)	19(1)
O(2)	5703(2)	2249(1)	3739(1)	19(1)
O(3)	5033(2)	5489(1)	2069(2)	33(1)
O(4)	3968(2)	6138(1)	2522(2)	35(1)
O(5)	4626(2)	5467(1)	3584(2)	36(1)
P(1)	3838(1)	2959(1)	1725(1)	12(1)
P(2)	7698(1)	3019(1)	2836(1)	11(1)
S(1)	4312(1)	5643(1)	2634(1)	23(1)

Table S-3 Bond lengths [A] and angles [deg] for **2**.

C(1)-O(1)	1.160(3)
C(1)-Mn(1)	1.792(3)
C(2)-O(2)	1.157(3)
C(2)-Mn(1)	1.794(3)
C(3)-N(1)	1.351(3)
C(3)-C(4)	1.379(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.386(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.388(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.393(4)
C(6)-H(6)	0.9500
C(7)-N(1)	1.361(3)
C(7)-C(8)	1.475(3)
C(8)-N(2)	1.360(3)
C(8)-C(9)	1.385(4)
C(9)-C(10)	1.383(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.383(4)
C(10)-H(10)	0.9500
C(11)-C(12)	1.384(4)
C(11)-H(11)	0.9500
C(12)-N(2)	1.351(3)
C(12)-H(12)	0.9500
C(13)-C(18)	1.394(4)
C(13)-C(14)	1.397(3)
C(13)-P(1)	1.836(3)
C(14)-C(15)	1.387(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.386(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.389(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.390(4)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(20)	1.390(4)
C(19)-C(24)	1.406(4)
C(19)-P(1)	1.843(3)
C(20)-C(21)	1.394(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.389(4)

C(21)-H(21)	0.9500
C(22)-C(23)	1.388(4)
C(22)-H(22)	0.9500
C(23)-C(24)	1.384(4)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(25)-C(30)	1.391(4)
C(25)-C(26)	1.399(4)
C(25)-P(1)	1.829(3)
C(26)-C(27)	1.391(4)
C(26)-H(26)	0.9500
C(27)-C(28)	1.389(4)
C(27)-H(27)	0.9500
C(28)-C(29)	1.386(4)
C(28)-H(28)	0.9500
C(29)-C(30)	1.391(4)
C(29)-H(29)	0.9500
C(30)-H(30)	0.9500
C(31)-C(36)	1.395(4)
C(31)-C(32)	1.402(4)
C(31)-P(2)	1.839(3)
C(32)-C(33)	1.388(4)
C(32)-H(32)	0.9500
C(33)-C(34)	1.386(4)
C(33)-H(33)	0.9500
C(34)-C(35)	1.382(4)
C(34)-H(34)	0.9500
C(35)-C(36)	1.391(4)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
C(37)-C(38)	1.393(4)
C(37)-C(42)	1.400(4)
C(37)-P(2)	1.831(3)
C(38)-C(39)	1.395(4)
C(38)-H(38)	0.9500
C(39)-C(40)	1.381(4)
C(39)-H(39)	0.9500
C(40)-C(41)	1.390(4)
C(40)-H(40)	0.9500
C(41)-C(42)	1.386(4)
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
C(43)-C(48)	1.397(4)
C(43)-C(44)	1.399(4)
C(43)-P(2)	1.833(3)
C(44)-C(45)	1.391(4)

C(44)-H(44)	0.9500
C(45)-C(46)	1.386(4)
C(45)-H(45)	0.9500
C(46)-C(47)	1.384(4)
C(46)-H(46)	0.9500
C(47)-C(48)	1.393(4)
C(47)-H(47)	0.9500
C(48)-H(48)	0.9500
C(49)-N(3)	1.165(7)
C(49)-C(50)	1.425(7)
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
C(51)-C(52)	1.522(9)
C(52)-C(53)	1.442(8)
C(53)-C(54)	1.510(7)
C(54)-C(55)	1.495(9)
C(55)-C(59)	1.487(16)
C(57)-C(58)	1.471(8)
C(57)-C(57)#1	1.83(2)
C(58)-C(59)	1.506(10)
C(59)-C(60)	1.437(9)
C(60)-C(61)	1.445(9)
C(61)-C(62)	1.436(9)
C(63)-F(3)	1.330(4)
C(63)-F(1)	1.335(4)
C(63)-F(2)	1.341(4)
C(63)-S(1)	1.823(4)
Mn(1)-N(2)	2.037(2)
Mn(1)-N(1)	2.041(2)
Mn(1)-P(2)	2.3256(8)
Mn(1)-P(1)	2.3337(8)
O(3)-S(1)	1.441(2)
O(4)-S(1)	1.440(2)
O(5)-S(1)	1.438(2)
O(1)-C(1)-Mn(1)	178.3(2)
O(2)-C(2)-Mn(1)	178.8(2)
N(1)-C(3)-C(4)	123.1(2)
N(1)-C(3)-H(3)	118.5
C(4)-C(3)-H(3)	118.5
C(3)-C(4)-C(5)	118.9(2)
C(3)-C(4)-H(4)	120.5
C(5)-C(4)-H(4)	120.5
C(4)-C(5)-C(6)	119.3(3)
C(4)-C(5)-H(5)	120.4

C(6)-C(5)-H(5)	120.4
C(5)-C(6)-C(7)	118.9(3)
C(5)-C(6)-H(6)	120.6
C(7)-C(6)-H(6)	120.6
N(1)-C(7)-C(6)	122.1(2)
N(1)-C(7)-C(8)	113.8(2)
C(6)-C(7)-C(8)	124.0(2)
N(2)-C(8)-C(9)	122.2(2)
N(2)-C(8)-C(7)	114.3(2)
C(9)-C(8)-C(7)	123.6(2)
C(10)-C(9)-C(8)	119.5(3)
C(10)-C(9)-H(9)	120.3
C(8)-C(9)-H(9)	120.3
C(9)-C(10)-C(11)	118.9(3)
C(9)-C(10)-H(10)	120.5
C(11)-C(10)-H(10)	120.5
C(10)-C(11)-C(12)	118.9(3)
C(10)-C(11)-H(11)	120.6
C(12)-C(11)-H(11)	120.6
N(2)-C(12)-C(11)	123.1(3)
N(2)-C(12)-H(12)	118.5
C(11)-C(12)-H(12)	118.5
C(18)-C(13)-C(14)	118.5(2)
C(18)-C(13)-P(1)	124.5(2)
C(14)-C(13)-P(1)	116.70(19)
C(15)-C(14)-C(13)	121.0(2)
C(15)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(16)-C(15)-C(14)	119.9(2)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
C(15)-C(16)-C(17)	119.8(2)
C(15)-C(16)-H(16)	120.1
C(17)-C(16)-H(16)	120.1
C(16)-C(17)-C(18)	120.3(3)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
C(17)-C(18)-C(13)	120.5(3)
C(17)-C(18)-H(18)	119.8
C(13)-C(18)-H(18)	119.8
C(20)-C(19)-C(24)	118.5(2)
C(20)-C(19)-P(1)	123.6(2)
C(24)-C(19)-P(1)	117.8(2)
C(19)-C(20)-C(21)	120.7(3)
C(19)-C(20)-H(20)	119.7
C(21)-C(20)-H(20)	119.7

C(22)-C(21)-C(20)	120.1(3)
C(22)-C(21)-H(21)	119.9
C(20)-C(21)-H(21)	119.9
C(23)-C(22)-C(21)	119.7(3)
C(23)-C(22)-H(22)	120.1
C(21)-C(22)-H(22)	120.1
C(24)-C(23)-C(22)	120.2(3)
C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.9
C(23)-C(24)-C(19)	120.7(3)
C(23)-C(24)-H(24)	119.7
C(19)-C(24)-H(24)	119.7
C(30)-C(25)-C(26)	118.9(2)
C(30)-C(25)-P(1)	118.6(2)
C(26)-C(25)-P(1)	121.9(2)
C(27)-C(26)-C(25)	120.3(3)
C(27)-C(26)-H(26)	119.9
C(25)-C(26)-H(26)	119.9
C(28)-C(27)-C(26)	120.2(3)
C(28)-C(27)-H(27)	119.9
C(26)-C(27)-H(27)	119.9
C(29)-C(28)-C(27)	119.9(3)
C(29)-C(28)-H(28)	120.0
C(27)-C(28)-H(28)	120.0
C(28)-C(29)-C(30)	119.8(3)
C(28)-C(29)-H(29)	120.1
C(30)-C(29)-H(29)	120.1
C(25)-C(30)-C(29)	120.9(3)
C(25)-C(30)-H(30)	119.6
C(29)-C(30)-H(30)	119.6
C(36)-C(31)-C(32)	118.2(2)
C(36)-C(31)-P(2)	126.4(2)
C(32)-C(31)-P(2)	115.34(19)
C(33)-C(32)-C(31)	120.8(3)
C(33)-C(32)-H(32)	119.6
C(31)-C(32)-H(32)	119.6
C(34)-C(33)-C(32)	120.1(3)
C(34)-C(33)-H(33)	119.9
C(32)-C(33)-H(33)	119.9
C(35)-C(34)-C(33)	119.8(3)
C(35)-C(34)-H(34)	120.1
C(33)-C(34)-H(34)	120.1
C(34)-C(35)-C(36)	120.2(3)
C(34)-C(35)-H(35)	119.9
C(36)-C(35)-H(35)	119.9
C(35)-C(36)-C(31)	120.8(3)

C(35)-C(36)-H(36)	119.6
C(31)-C(36)-H(36)	119.6
C(38)-C(37)-C(42)	118.9(2)
C(38)-C(37)-P(2)	123.9(2)
C(42)-C(37)-P(2)	117.1(2)
C(37)-C(38)-C(39)	120.1(2)
C(37)-C(38)-H(38)	119.9
C(39)-C(38)-H(38)	119.9
C(40)-C(39)-C(38)	120.4(3)
C(40)-C(39)-H(39)	119.8
C(38)-C(39)-H(39)	119.8
C(39)-C(40)-C(41)	120.0(3)
C(39)-C(40)-H(40)	120.0
C(41)-C(40)-H(40)	120.0
C(42)-C(41)-C(40)	119.9(3)
C(42)-C(41)-H(41)	120.0
C(40)-C(41)-H(41)	120.0
C(41)-C(42)-C(37)	120.6(3)
C(41)-C(42)-H(42)	119.7
C(37)-C(42)-H(42)	119.7
C(48)-C(43)-C(44)	118.6(2)
C(48)-C(43)-P(2)	121.5(2)
C(44)-C(43)-P(2)	119.3(2)
C(45)-C(44)-C(43)	120.4(3)
C(45)-C(44)-H(44)	119.8
C(43)-C(44)-H(44)	119.8
C(46)-C(45)-C(44)	120.2(3)
C(46)-C(45)-H(45)	119.9
C(44)-C(45)-H(45)	119.9
C(47)-C(46)-C(45)	120.0(3)
C(47)-C(46)-H(46)	120.0
C(45)-C(46)-H(46)	120.0
C(46)-C(47)-C(48)	119.9(3)
C(46)-C(47)-H(47)	120.0
C(48)-C(47)-H(47)	120.0
C(47)-C(48)-C(43)	120.7(3)
C(47)-C(48)-H(48)	119.6
C(43)-C(48)-H(48)	119.6
N(3)-C(49)-C(50)	179.1(9)
C(49)-C(50)-H(50A)	109.5
C(49)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(49)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
C(53)-C(52)-C(51)	107.6(8)

C(52)-C(53)-C(54)	111.5(6)
C(55)-C(54)-C(53)	101.8(6)
C(59)-C(55)-C(54)	116.4(10)
C(58)-C(57)-C(57)#1	87.4(9)
C(57)-C(58)-C(59)	106.5(8)
C(60)-C(59)-C(55)	18.4(7)
C(60)-C(59)-C(58)	102.3(9)
C(55)-C(59)-C(58)	120.3(11)
C(59)-C(60)-C(61)	113.6(8)
C(62)-C(61)-C(60)	119.2(9)
F(3)-C(63)-F(1)	107.2(3)
F(3)-C(63)-F(2)	107.3(3)
F(1)-C(63)-F(2)	107.7(3)
F(3)-C(63)-S(1)	111.3(3)
F(1)-C(63)-S(1)	111.3(2)
F(2)-C(63)-S(1)	111.9(3)
C(1)-Mn(1)-C(2)	92.36(11)
C(1)-Mn(1)-N(2)	172.28(10)
C(2)-Mn(1)-N(2)	95.28(10)
C(1)-Mn(1)-N(1)	93.78(10)
C(2)-Mn(1)-N(1)	173.83(10)
N(2)-Mn(1)-N(1)	78.59(8)
C(1)-Mn(1)-P(2)	89.34(8)
C(2)-Mn(1)-P(2)	90.64(8)
N(2)-Mn(1)-P(2)	89.50(6)
N(1)-Mn(1)-P(2)	90.02(6)
C(1)-Mn(1)-P(1)	89.31(8)
C(2)-Mn(1)-P(1)	91.38(8)
N(2)-Mn(1)-P(1)	91.58(6)
N(1)-Mn(1)-P(1)	88.10(6)
P(2)-Mn(1)-P(1)	177.62(3)
C(3)-N(1)-C(7)	117.7(2)
C(3)-N(1)-Mn(1)	125.55(17)
C(7)-N(1)-Mn(1)	116.69(16)
C(12)-N(2)-C(8)	117.5(2)
C(12)-N(2)-Mn(1)	125.90(18)
C(8)-N(2)-Mn(1)	116.61(16)
C(25)-P(1)-C(13)	105.05(12)
C(25)-P(1)-C(19)	102.73(12)
C(13)-P(1)-C(19)	98.82(11)
C(25)-P(1)-Mn(1)	111.46(8)
C(13)-P(1)-Mn(1)	118.28(9)
C(19)-P(1)-Mn(1)	118.43(9)
C(37)-P(2)-C(43)	101.83(12)
C(37)-P(2)-C(31)	99.91(11)
C(43)-P(2)-C(31)	107.27(12)

C(37)-P(2)-Mn(1)	119.16(9)
C(43)-P(2)-Mn(1)	111.93(9)
C(31)-P(2)-Mn(1)	115.11(8)
O(5)-S(1)-O(4)	115.76(14)
O(5)-S(1)-O(3)	114.23(14)
O(4)-S(1)-O(3)	115.46(14)
O(5)-S(1)-C(63)	103.49(16)
O(4)-S(1)-C(63)	103.40(16)
O(3)-S(1)-C(63)	101.85(16)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2

Table S-4

(Å^{2}x 10^3) for 2. The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	11(1)	16(1)	12(1)	3(1)	1(1)	0(1)
C(2)	12(1)	14(1)	11(1)	-4(1)	3(1)	1(1)
C(3)	13(1)	17(1)	12(1)	0(1)	3(1)	1(1)
C(4)	19(1)	24(1)	13(1)	4(1)	5(1)	2(1)
C(5)	22(1)	19(1)	20(1)	9(1)	4(1)	2(1)
C(6)	21(1)	15(1)	19(1)	2(1)	3(1)	3(1)
C(7)	14(1)	14(1)	13(1)	0(1)	2(1)	2(1)
C(8)	18(1)	15(1)	13(1)	0(1)	2(1)	4(1)
C(9)	48(2)	13(1)	21(1)	1(1)	9(1)	6(1)
C(10)	73(3)	18(2)	21(2)	-5(1)	14(2)	8(2)
C(11)	45(2)	22(2)	14(1)	-3(1)	9(1)	6(1)
C(12)	19(1)	18(1)	12(1)	0(1)	4(1)	2(1)
C(13)	12(1)	16(1)	13(1)	-1(1)	4(1)	-1(1)
C(14)	11(1)	20(1)	14(1)	0(1)	4(1)	2(1)
C(15)	21(1)	21(1)	13(1)	1(1)	7(1)	2(1)
C(16)	18(1)	24(2)	21(1)	-3(1)	12(1)	-1(1)
C(17)	14(1)	26(2)	21(1)	2(1)	6(1)	6(1)
C(18)	16(1)	24(1)	16(1)	2(1)	4(1)	3(1)
C(19)	16(1)	17(1)	11(1)	-2(1)	7(1)	-3(1)
C(20)	18(1)	20(1)	11(1)	0(1)	4(1)	-1(1)
C(21)	31(2)	17(1)	16(1)	-1(1)	6(1)	-3(1)
C(22)	28(2)	22(2)	16(1)	-2(1)	7(1)	-9(1)
C(23)	18(1)	29(2)	22(1)	-1(1)	6(1)	-5(1)
C(24)	16(1)	21(1)	18(1)	0(1)	5(1)	-1(1)
C(25)	11(1)	18(1)	11(1)	1(1)	1(1)	0(1)
C(26)	15(1)	21(1)	17(1)	2(1)	5(1)	4(1)
C(27)	19(1)	23(2)	24(1)	8(1)	5(1)	6(1)
C(28)	23(2)	34(2)	16(1)	9(1)	4(1)	1(1)

C(29)	21(1)	32(2)	12(1)	-1(1)	5(1)	-4(1)
C(30)	15(1)	22(1)	14(1)	-1(1)	4(1)	-2(1)
C(31)	13(1)	15(1)	11(1)	-1(1)	2(1)	2(1)
C(32)	16(1)	20(1)	14(1)	0(1)	2(1)	-3(1)
C(33)	20(1)	28(2)	11(1)	1(1)	3(1)	1(1)
C(34)	24(1)	24(2)	14(1)	-7(1)	2(1)	1(1)
C(35)	28(2)	19(1)	21(1)	-4(1)	3(1)	-6(1)
C(36)	21(1)	17(1)	16(1)	-1(1)	4(1)	-3(1)
C(37)	15(1)	13(1)	10(1)	1(1)	4(1)	3(1)
C(38)	19(1)	17(1)	10(1)	-1(1)	4(1)	1(1)
C(39)	29(2)	13(1)	14(1)	1(1)	6(1)	4(1)
C(40)	28(2)	22(2)	20(1)	4(1)	10(1)	13(1)
C(41)	18(1)	29(2)	24(1)	2(1)	4(1)	6(1)
C(42)	16(1)	20(1)	22(1)	1(1)	6(1)	0(1)
C(43)	11(1)	19(1)	12(1)	1(1)	1(1)	-3(1)
C(44)	21(1)	15(1)	16(1)	0(1)	6(1)	-3(1)
C(45)	27(2)	28(2)	14(1)	-3(1)	10(1)	-4(1)
C(46)	26(2)	31(2)	16(1)	4(1)	7(1)	-6(1)
C(47)	22(1)	18(1)	18(1)	6(1)	2(1)	-4(1)
C(48)	14(1)	17(1)	17(1)	1(1)	2(1)	-1(1)
C(49)	43(5)	26(4)	48(5)	1(3)	22(4)	-9(3)
C(50)	34(4)	34(4)	38(4)	7(3)	0(3)	-17(3)
C(63)	43(2)	25(2)	41(2)	7(2)	9(2)	-1(2)
F(1)	54(2)	58(2)	44(1)	11(1)	-11(1)	-5(1)
F(2)	63(2)	23(1)	69(2)	-2(1)	2(1)	-6(1)
F(3)	49(1)	48(1)	89(2)	18(1)	32(1)	-2(1)
Mn(1)	11(1)	10(1)	8(1)	0(1)	3(1)	1(1)
N(1)	11(1)	13(1)	10(1)	0(1)	2(1)	1(1)
N(2)	13(1)	15(1)	11(1)	-1(1)	2(1)	1(1)
N(3)	45(5)	30(4)	77(5)	-2(3)	29(4)	6(3)
O(1)	25(1)	20(1)	15(1)	-4(1)	7(1)	2(1)
O(2)	22(1)	20(1)	15(1)	5(1)	6(1)	1(1)
O(3)	48(2)	27(1)	29(1)	6(1)	19(1)	11(1)
O(4)	41(1)	15(1)	49(2)	3(1)	13(1)	7(1)
O(5)	60(2)	27(1)	18(1)	-2(1)	9(1)	12(1)
P(1)	11(1)	14(1)	9(1)	0(1)	3(1)	1(1)

P(2)	12(1)	11(1)	9(1)	0(1)	3(1)	0(1)
S(1)	35(1)	14(1)	21(1)	1(1)	9(1)	4(1)

Table S-5

Displacement parameters ($Å^2$x 10 ^{3}) for **2**.

	x	y	z	U(eq)
H(3)	5913	3207	287	17
H(4)	5874	3873	-661	22
H(5)	5710	4643	-55	25
H(6)	5612	4720	1508	22
H(9)	5557	4719	2982	33
H(10)	5533	4661	4562	44
H(11)	5620	3896	5255	32
H(12)	5678	3219	4351	20
H(14)	3902	2888	3639	18
H(15)	2823	3135	4628	21
H(16)	1234	3603	4034	24
H(17)	719	3813	2443	24
H(18)	1806	3570	1454	22
H(20)	4516	1934	1890	20
H(21)	3556	1203	1620	26
H(22)	1617	1196	1050	26
H(23)	646	1921	709	28
H(24)	1597	2650	970	22
H(26)	3240	3947	1095	21
H(27)	2849	4336	-359	27
H(28)	2827	3902	-1720	29
H(29)	3148	3073	-1635	26
H(30)	3502	2681	-187	20
H(32)	7647	2803	4671	20
H(33)	8136	3170	6142	24
H(34)	9013	3920	6331	25
H(35)	9487	4282	5064	27
H(36)	9010	3916	3589	22
H(38)	7223	1970	2755	18

H(39)	8347	1283	3032	22
H(40)	10276	1356	3509	27
H(41)	11099	2118	3754	29
H(42)	9986	2805	3501	23
H(44)	8771	2683	1447	20
H(45)	9335	3033	207	26
H(46)	9264	3865	5	29
H(47)	8581	4351	1018	24
H(48)	7964	4003	2235	20
H(50A)	3401	4857	4159	55
H(50B)	3140	4295	3999	55
H(50C)	3558	4505	5043	55

Table S-6

N(1)-C(3)-C(4)-C(5)	0.0(4)
C(3)-C(4)-C(5)-C(6)	0.4(4)
C(4)-C(5)-C(6)-C(7)	-0.7(4)
C(5)-C(6)-C(7)-N(1)	0.8(4)
C(5)-C(6)-C(7)-C(8)	179.4(3)
N(1)-C(7)-C(8)-N(2)	-1.6(3)
C(6)-C(7)-C(8)-N(2)	179.7(2)
N(1)-C(7)-C(8)-C(9)	177.5(3)
C(6)-C(7)-C(8)-C(9)	-1.2(4)
N(2)-C(8)-C(9)-C(10)	0.9(5)
C(7)-C(8)-C(9)-C(10)	-178.2(3)
C(8)-C(9)-C(10)-C(11)	0.2(6)
C(9)-C(10)-C(11)-C(12)	-1.0(5)
C(10)-C(11)-C(12)-N(2)	0.7(5)
C(18)-C(13)-C(14)-C(15)	-1.2(4)
P(1)-C(13)-C(14)-C(15)	-175.8(2)
C(13)-C(14)-C(15)-C(16)	0.5(4)
C(14)-C(15)-C(16)-C(17)	0.5(4)
C(15)-C(16)-C(17)-C(18)	-0.8(4)
C(16)-C(17)-C(18)-C(13)	0.0(4)
C(14)-C(13)-C(18)-C(17)	0.9(4)
P(1)-C(13)-C(18)-C(17)	175.1(2)
C(24)-C(19)-C(20)-C(21)	-0.6(4)
P(1)-C(19)-C(20)-C(21)	176.1(2)
C(19)-C(20)-C(21)-C(22)	-0.3(4)
C(20)-C(21)-C(22)-C(23)	1.0(4)
C(21)-C(22)-C(23)-C(24)	-0.9(4)
C(22)-C(23)-C(24)-C(19)	0.0(4)
C(20)-C(19)-C(24)-C(23)	0.7(4)
P(1)-C(19)-C(24)-C(23)	-176.2(2)
C(30)-C(25)-C(26)-C(27)	1.9(4)
P(1)-C(25)-C(26)-C(27)	172.7(2)
C(25)-C(26)-C(27)-C(28)	-1.7(4)
C(26)-C(27)-C(28)-C(29)	0.7(4)

C(27)-C(28)-C(29)-C(30)	0.0(4)
C(26)-C(25)-C(30)-C(29)	-1.2(4)
P(1)-C(25)-C(30)-C(29)	-172.3(2)
C(28)-C(29)-C(30)-C(25)	0.3(4)
C(36)-C(31)-C(32)-C(33)	2.4(4)
P(2)-C(31)-C(32)-C(33)	-175.0(2)
C(31)-C(32)-C(33)-C(34)	-0.2(4)
C(32)-C(33)-C(34)-C(35)	-1.9(4)
C(33)-C(34)-C(35)-C(36)	1.7(4)
C(34)-C(35)-C(36)-C(31)	0.5(4)
C(32)-C(31)-C(36)-C(35)	-2.6(4)
P(2)-C(31)-C(36)-C(35)	174.5(2)
C(42)-C(37)-C(38)-C(39)	-1.7(4)
P(2)-C(37)-C(38)-C(39)	177.51(19)
C(37)-C(38)-C(39)-C(40)	0.1(4)
C(38)-C(39)-C(40)-C(41)	1.1(4)
C(39)-C(40)-C(41)-C(42)	-0.6(4)
C(40)-C(41)-C(42)-C(37)	-1.0(4)
C(38)-C(37)-C(42)-C(41)	2.2(4)
P(2)-C(37)-C(42)-C(41)	-177.1(2)
C(48)-C(43)-C(44)-C(45)	0.5(4)
P(2)-C(43)-C(44)-C(45)	171.6(2)
C(43)-C(44)-C(45)-C(46)	0.8(4)
C(44)-C(45)-C(46)-C(47)	-1.0(4)
C(45)-C(46)-C(47)-C(48)	0.0(4)
C(46)-C(47)-C(48)-C(43)	1.2(4)
C(44)-C(43)-C(48)-C(47)	-1.5(4)
P(2)-C(43)-C(48)-C(47)	-172.4(2)
C(51)-C(52)-C(53)-C(54)	-178.4(8)
C(52)-C(53)-C(54)-C(55)	177.8(10)
C(53)-C(54)-C(55)-C(59)	-177.0(13)
C(57)#1-C(57)-C(58)-C(59)	136.5(10)
C(54)-C(55)-C(59)-C(60)	153(5)
C(54)-C(55)-C(59)-C(58)	164.6(12)
C(57)-C(58)-C(59)-C(60)	169.2(10)
C(57)-C(58)-C(59)-C(55)	165.3(13)

C(55)-C(59)-C(60)-C(61)	-34(3)
C(58)-C(59)-C(60)-C(61)	157.1(13)
C(59)-C(60)-C(61)-C(62)	42(2)
C(4)-C(3)-N(1)-C(7)	0.0(4)
C(4)-C(3)-N(1)-Mn(1)	178.31(19)
C(6)-C(7)-N(1)-C(3)	-0.4(4)
C(8)-C(7)-N(1)-C(3)	-179.2(2)
C(6)-C(7)-N(1)-Mn(1)	-178.9(2)
C(8)-C(7)-N(1)-Mn(1)	2.4(3)
C(11)-C(12)-N(2)-C(8)	0.4(4)
C(11)-C(12)-N(2)-Mn(1)	178.0(2)
C(9)-C(8)-N(2)-C(12)	-1.2(4)
C(7)-C(8)-N(2)-C(12)	178.0(2)
C(9)-C(8)-N(2)-Mn(1)	-179.0(2)
C(7)-C(8)-N(2)-Mn(1)	0.1(3)
C(30)-C(25)-P(1)-C(13)	-144.7(2)
C(26)-C(25)-P(1)-C(13)	44.5(2)
C(30)-C(25)-P(1)-C(19)	-41.8(2)
C(26)-C(25)-P(1)-C(19)	147.4(2)
C(30)-C(25)-P(1)-Mn(1)	86.0(2)
C(26)-C(25)-P(1)-Mn(1)	-84.8(2)
C(18)-C(13)-P(1)-C(25)	14.3(3)
C(14)-C(13)-P(1)-C(25)	-171.5(2)
C(18)-C(13)-P(1)-C(19)	-91.6(2)
C(14)-C(13)-P(1)-C(19)	82.7(2)
C(18)-C(13)-P(1)-Mn(1)	139.3(2)
C(14)-C(13)-P(1)-Mn(1)	-46.4(2)
C(20)-C(19)-P(1)-C(25)	127.0(2)
C(24)-C(19)-P(1)-C(25)	-56.3(2)
C(20)-C(19)-P(1)-C(13)	-125.3(2)
C(24)-C(19)-P(1)-C(13)	51.4(2)
C(20)-C(19)-P(1)-Mn(1)	3.7(2)
C(24)-C(19)-P(1)-Mn(1)	-179.60(17)
C(38)-C(37)-P(2)-C(43)	-122.7(2)
C(42)-C(37)-P(2)-C(43)	56.5(2)
C(38)-C(37)-P(2)-C(31)	127.2(2)

C(42)-C(37)-P(2)-C(31)	-53.6(2)
C(38)-C(37)-P(2)-Mn(1)	0.9(2)
C(42)-C(37)-P(2)-Mn(1)	-179.83(17)
C(48)-C(43)-P(2)-C(37)	-157.6(2)
C(44)-C(43)-P(2)-C(37)	31.4(2)
C(48)-C(43)-P(2)-C(31)	-53.2(2)
C(44)-C(43)-P(2)-C(31)	135.9(2)
C(48)-C(43)-P(2)-Mn(1)	74.0(2)
C(44)-C(43)-P(2)-Mn(1)	-96.9(2)
C(36)-C(31)-P(2)-C(37)	118.9(2)
C(32)-C(31)-P(2)-C(37)	-63.9(2)
C(36)-C(31)-P(2)-C(43)	13.1(3)
C(32)-C(31)-P(2)-C(43)	-169.7(2)
C(36)-C(31)-P(2)-Mn(1)	-112.2(2)
C(32)-C(31)-P(2)-Mn(1)	65.0(2)
F(3)-C(63)-S(1)-O(5)	57.8(3)
F(1)-C(63)-S(1)-O(5)	177.3(2)
F(2)-C(63)-S(1)-O(5)	-62.2(3)
F(3)-C(63)-S(1)-O(4)	-63.3(3)
F(1)-C(63)-S(1)-O(4)	56.2(3)
F(2)-C(63)-S(1)-O(4)	176.7(3)