

Supporting Information

Facile biomimetic catalytic activity through hydrogen atom abstraction by the secondary coordination sphere in manganese(III) complexes

Narayan Ch. Jana^a, Paula Brandão,^b Antonio Frontera,^c and Anangamohan Panja^{*a,d}

^a *Department of Chemistry, Panskura Banamali College, Panskura RS, WB 721152, India*

^b *Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal*

^c *Departament de Química, Universitat de les Illes Balears, Crta de Valldemossa, km 7.5, 07122 Palma de Mallorca (Balears), Spain*

^d *Department of Chemistry, Gokhale Memorial Girls' College, 1/1 Harish Mukherjee Road, Kolkata-700020, India.*

* Corresponding author e-mail: ampanja@yahoo.co.in

Table S1. Selected bond angles for complexes **1–4**. Highlighted data are indicating lowest and highest values of bond angles

		1		2	
		MnA	MnB		
O1A MnA O1A	180.00(4)	O1B MnB O1B	180.00(8)	O1 Mn O1	180.00(4)
O1A MnA N1A	88.85(6)	O1B MnB N1B	88.64(6)	O1 Mn N1	88.86(5)
O1A MnA N1A	91.15(6)	O1B MnB N1B	91.36(6)	O1 Mn N1	91.14(5)
O1A MnA N1A	91.15(6)	O1B MnB N1B	91.36(6)	O1 Mn N1	91.14(5)
O1A MnA N1A	88.85(6)	O1B MnB N1B	88.63(6)	O1 Mn N1	88.86(5)
N1A MnA N1A	180.00(6)	N1B MnB N1B	180.0 (2)	N1 Mn N1	180.00(5)
O1A MnA N2A	89.12(6)	O1B MnB N2B	92.71(6)	O1 Mn N2	88.79(5)
O1A MnA N2A	90.88(6)	O1B MnB N2B	87.29(6)	O1 Mn N2	91.22(5)
N1A MnA N2A	81.11(6)	N1B MnB N2B	98.17(6)	N1 Mn N2	81.29(5)
N1A MnA N2A	98.90(6)	N1B MnB N2B	81.83(6)	N1 Mn N2	98.71(5)
O1A MnA N2A	90.86(6)	O1B MnB N2B	87.29(6)	O1 Mn N2	91.21(5)
O1A MnA N2A	89.12(6)	O1B MnB N2B	92.71(6)	O1 Mn N2	88.78(5)
N1A MnA N2A	98.89(6)	N1B MnB N2B	81.83(6)	N1 Mn N2	98.71(5)
N1A MnA N2A	81.11(6)	N1B MnB N2B	98.17(6)	N1 Mn N2	81.29(5)
N2A MnA N2A	180.0 (2)	N2B MnB N2B	180.00(8)	N2 Mn N2	180.0(3)
		3		4	
		MnA	MnB		
O1 Mn O1	180.0 (3)	O2A MnA O1A	177.43(13)	O2B MnB O1B	178.54(14)
O1 Mn N1	88.99(4)	O2A MnA N1A	90.23(14)	O2B MnB N4B	88.08(14)
O1 Mn N1	91.01(4)	O1A MnA N1A	89.12(14)	O1B MnB N4B	93.24(14)
O1 Mn N1	91.01(4)	O2A MnA N4A	88.50(14)	O2B MnB N1B	91.05(14)
O1 Mn N1	88.99(4)	O1A MnA N4A	92.25(14)	O1B MnB N1B	87.65(14)
N1 Mn N1	180.0 (3)	N1A MnA N4A	177.35(14)	N4B MnB N1B	178.60(14)
O1 Mn N2	90.65(4)	O2A MnA N5A	87.07(13)	O2B MnB N2B	92.04(13)
O1 Mn N2	89.35(4)	O1A MnA N5A	90.59(13)	O1B MnB N2B	88.41(13)
N1 Mn N2	100.05(4)	N1A MnA N5A	99.65(14)	N4B MnB N2B	97.67(14)
N1 Mn N2	79.95(4)	N4A MnA N5A	82.61(14)	N1B MnB N2B	81.26(14)
O1 Mn N2	89.35(4)	O2A MnA N2A	93.22(13)	O2B MnB N5B	89.72(14)
O1 Mn N2	90.65(4)	O1A MnA N2A	89.14(13)	O1B MnB N5B	89.86(13)
N1 Mn N2	79.95(4)	N1A MnA N2A	81.39(15)	N4B MnB N5B	81.11(5)
N1 Mn N2	100.05(4)	N4A MnA N2A	96.35(14)	N1B MnB N5B	99.98(14)
N2 Mn N2	180.0 (3)	N5A MnA N2A	178.92(14)	N2B MnB N5B	177.82(12)

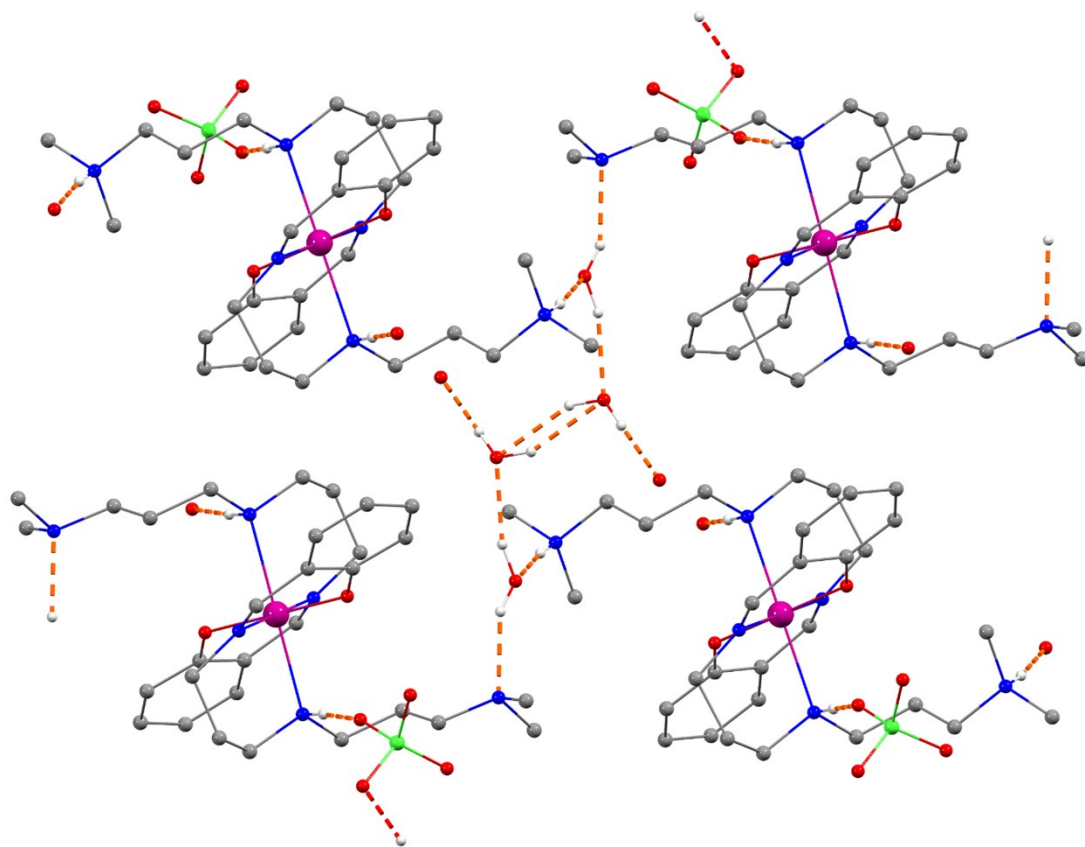


Fig. S1. Crystal packing of complex **1** showing hydrogen bonding interactions.

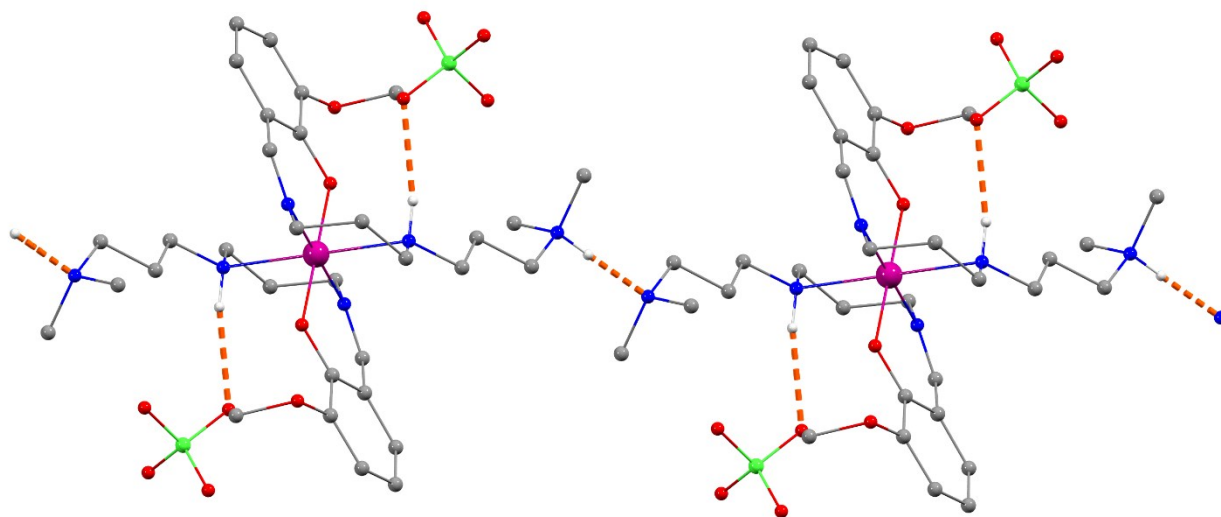


Fig. S2. Hydrogen bonded supramolecular chain structure of **2**.

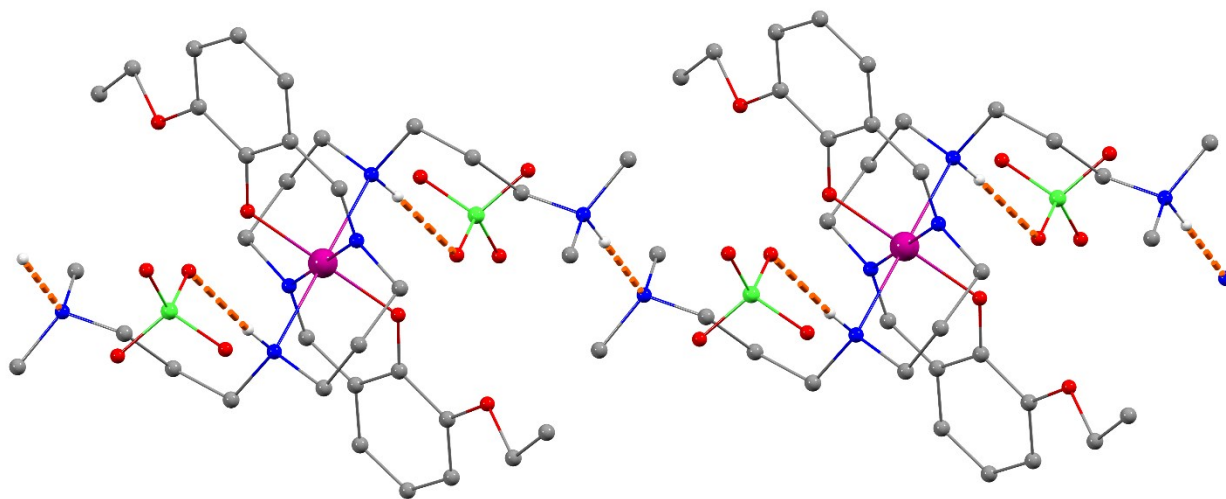


Fig. S3. Hydrogen bonded supramolecular chain structure of **3**.

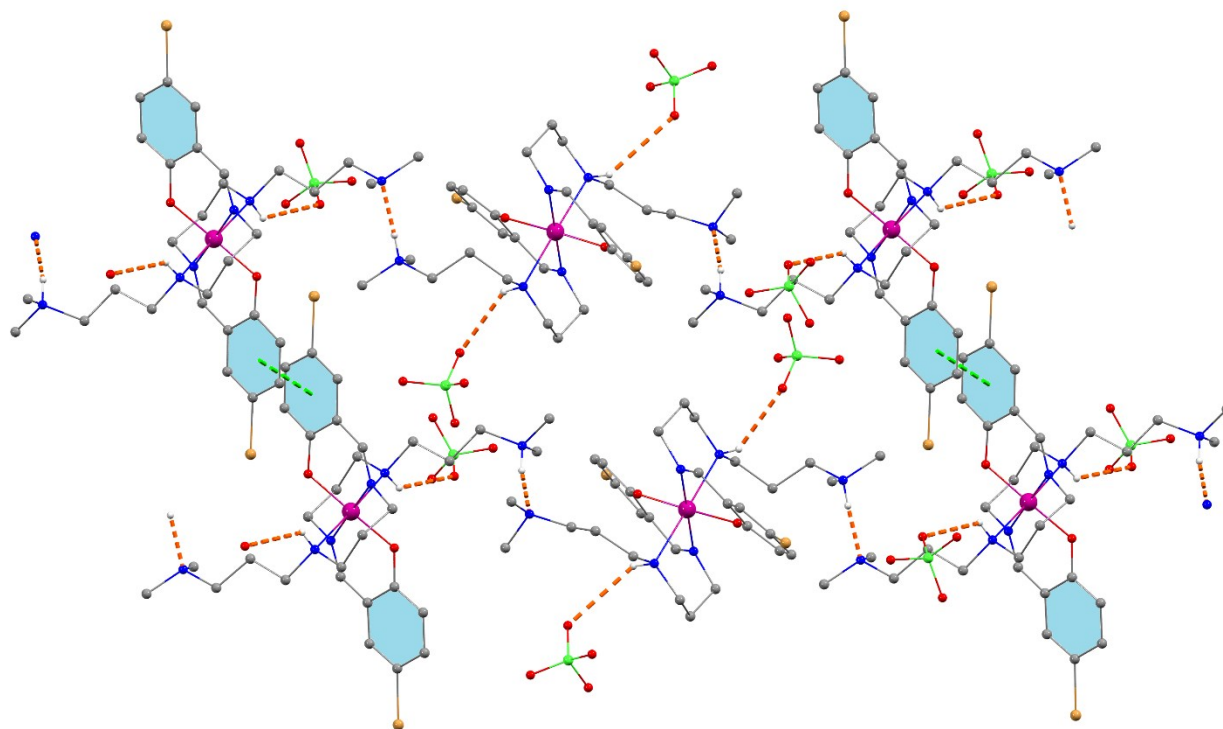


Fig. S4. The solid-state packing of complex **4** showing hydrogen bonding and $\pi \cdots \pi$ stacking interactions.

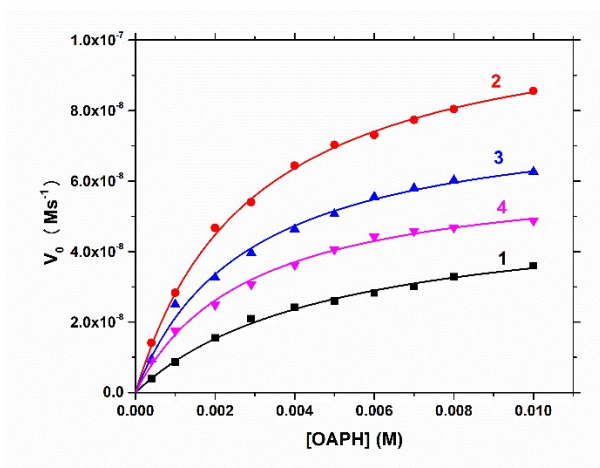


Fig S5: Michaelis–Menten plot (left) and double reciprocal Lineweaver–Burk plot (right) for the oxidation of OAPH in dioxygen-saturated methanol catalysed by complexes **1–4** at room temperature. Symbols and solid lines represent the experimental and simulated profiles, respectively

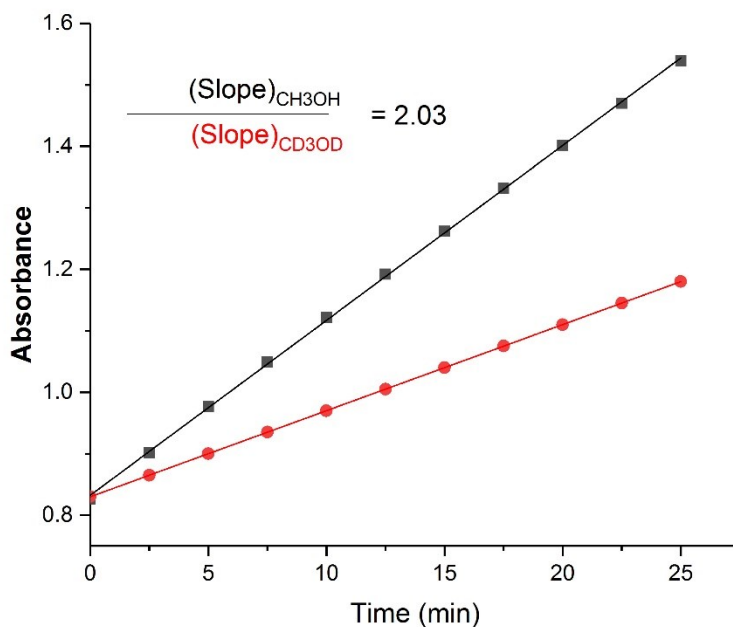


Fig. S6. KIE studies in methanol and methanol- d_6 showing the oxidation of 3,5-DTBC (at $\lambda_{\max} = 400$ nm). Typical conditions: $[3,5\text{-DTBC}] = 1 \times 10^{-2}$ M and $[\text{complex } 2] = 5 \times 10^{-5}$ M.

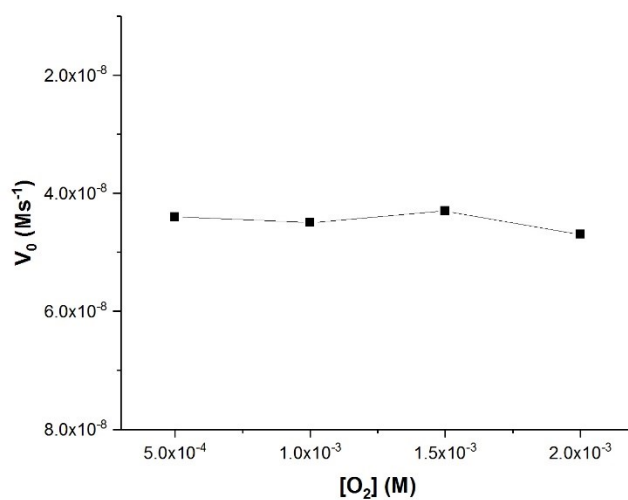


Fig. S7. Plot of initial rate vs [O₂] for the oxidation of 3,5-DTBC (1×10^{-2} M) catalysed by complex **2** (5×10^{-5} M) in air-saturated methanol at room temperature.

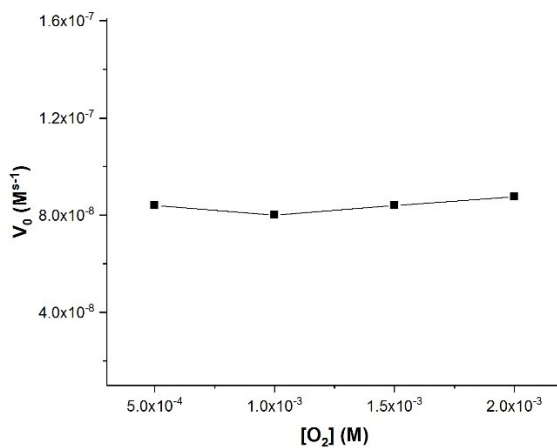
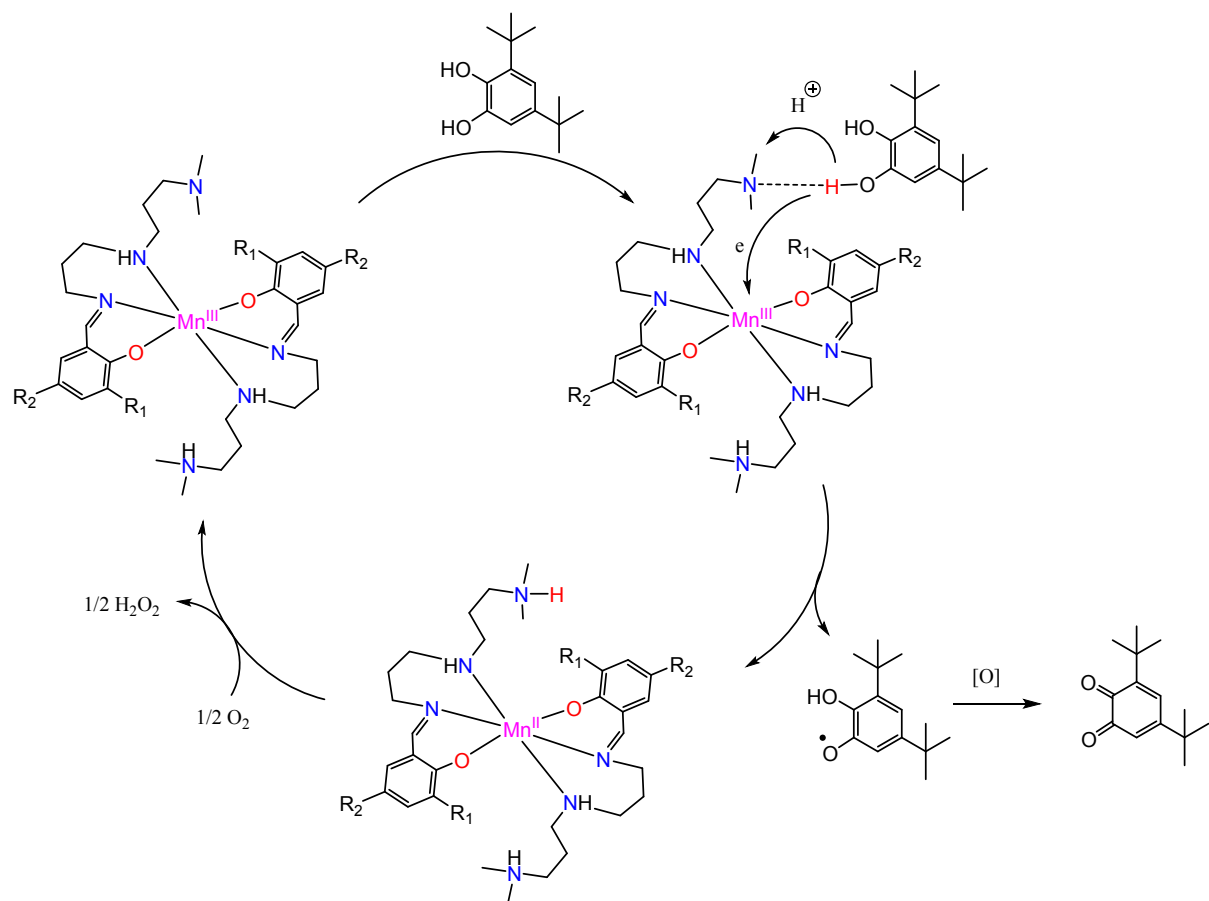


Fig. S8. Plot of initial rate vs [O₂] for the oxidation of OAPH (1×10^{-2} M) catalysed by complex **2** (1×10^{-5} M) in air-saturated methanol at room temperature.



Scheme S1. Possible catalytic cycle for the manganese(III) complexes catalysed oxidation of 3,5-DTBC

Cartesian coordinates of compounds 1-4

1

O	0.37559	-1.71321	-0.68793
N	-1.673	0.04169	-1.0058
N	-1.12329	-0.93487	1.43843
N	0.32174	-5.15712	1.82861
C	0.05975	-2.16224	-1.86788
C	-1.06414	-1.68748	-2.60378
C	-1.38528	-2.25012	-3.85946
H	-2.26601	-1.88022	-4.39257
C	-0.6048	-3.24364	-4.41467
H	-0.85135	-3.66705	-5.38944
C	0.51063	-3.70806	-3.69633
H	1.13511	-4.49754	-4.12277
C	0.83587	-3.18926	-2.45459
H	1.69721	-3.56189	-1.89788
C	-1.92623	-0.69877	-2.03359
H	-2.90604	-0.56879	-2.52026
C	-2.77432	0.80585	-0.44227
H	-3.55701	0.95328	-1.20387
H	-2.39861	1.7855	-0.12462
C	-3.33641	0.05276	0.75205
H	-4.17863	0.61977	1.17835
H	-3.75202	-0.91092	0.40655
C	-2.3318	-0.19342	1.86033
H	-2.00931	0.75112	2.3185
H	-2.82972	-0.77402	2.65478
C	-0.43457	-1.49785	2.62534
H	-1.20948	-1.75803	3.36812
H	0.16529	-0.70202	3.08238
C	0.39341	-2.73186	2.32853
H	1.01582	-2.95545	3.20884
H	1.07184	-2.52484	1.4932
C	-0.45655	-3.96122	2.02701
H	-1.12901	-4.13407	2.88414
H	-1.12565	-3.76214	1.1496
C	-0.45945	-6.36061	1.98825
H	-1.25721	-6.47298	1.21931
H	-0.93869	-6.37666	2.97895
H	0.19346	-7.24377	1.92077
C	1.06839	-5.16256	0.59574
H	1.70048	-6.06166	0.54464
H	1.73525	-4.28969	0.53639
H	0.41692	-5.14992	-0.3077
H	-1.42277	-1.73471	0.87365
O	-0.37559	1.71321	0.68793
N	1.673	-0.04169	1.0058
N	1.12329	0.93487	-1.43843
N	-0.32174	5.15712	-1.82861
C	-0.05975	2.16224	1.86788
C	1.06414	1.68748	2.60378
C	1.38528	2.25012	3.85946
H	2.26601	1.88022	4.39257
C	0.6048	3.24364	4.41467
H	0.85135	3.66705	5.38944

C	-0.51063	3.70806	3.69633
H	-1.13511	4.49754	4.12277
C	-0.83587	3.18926	2.45459
H	-1.69721	3.56189	1.89788
C	1.92623	0.69877	2.03359
H	2.90604	0.56879	2.52026
C	2.77432	-0.80585	0.44227
H	3.55701	-0.95328	1.20387
H	2.39861	-1.7855	0.12462
C	3.33641	-0.05276	-0.75205
H	4.17863	-0.61977	-1.17835
H	3.75202	0.91092	-0.40655
C	2.3318	0.19342	-1.86033
H	2.00931	-0.75112	-2.3185
H	2.82972	0.77402	-2.65478
C	0.43457	1.49785	-2.62534
H	1.20948	1.75803	-3.36812
H	-0.16529	0.70202	-3.08238
C	-0.39341	2.73186	-2.32853
H	-1.01582	2.95545	-3.20884
H	-1.07184	2.52484	-1.4932
C	0.45655	3.96122	-2.02701
H	1.12901	4.13407	-2.88414
H	1.12565	3.76214	-1.1496
C	0.45945	6.36061	-1.98825
H	1.25721	6.47298	-1.21931
H	0.93869	6.37666	-2.97895
H	-0.19346	7.24377	-1.92077
C	-1.06839	5.16256	-0.59574
H	-1.70048	6.06166	-0.54464
H	-1.73525	4.28969	-0.53639
H	-0.41692	5.14992	0.3077
H	1.42277	1.73471	-0.87365
Mn	0.00000	0.00000	0.00000
2			
O	-0.32187	0.06936	-1.86152
O	-1.16432	1.29249	-4.01473
N	-0.78588	-1.78771	0.07924
N	1.7681	-0.96987	-0.20939
N	2.73006	-0.62185	-4.37664
C	-1.30576	-0.47519	-2.48673
C	-1.94527	-1.67192	-2.06017
C	-2.95618	-2.26719	-2.84165
H	-3.41329	-3.20049	-2.50322
C	-3.37087	-1.67062	-4.01551
H	-4.15708	-2.12589	-4.62012
C	-2.7845	-0.46503	-4.43985
H	-3.13361	-0.00299	-5.36393
C	-1.77972	0.13769	-3.69683
C	-1.55396	1.99197	-5.18081
H	-2.63582	2.21628	-5.13571
H	-1.38254	1.35796	-6.0705
C	-1.51679	-2.30778	-0.84348
H	-1.8683	-3.34113	-0.69441
C	-0.33005	-2.67364	1.13892
H	-1.00974	-3.53868	1.21557
H	-0.32887	-2.13021	2.09138

C	1.07845	-3.14088	0.81795
H	1.06162	-3.69928	-0.13349
H	1.41154	-3.84031	1.60098
C	2.09535	-2.01687	0.71695
H	2.29089	-1.60548	1.73237
H	3.06161	-2.45964	0.41466
C	2.91999	-0.23542	-0.60519
H	3.82055	-0.86182	-0.4652
H	3.09313	0.63083	0.07585
C	2.89241	0.27263	-2.03917
H	3.8561	0.76021	-2.26155
H	2.09943	1.01907	-2.17635
C	2.6293	-0.90747	-2.98325
H	3.32293	-1.73138	-2.74828
H	1.60929	-1.26437	-2.72912
C	4.00293	-0.79128	-5.01729
H	3.87152	-0.84517	-6.10959
H	4.47721	-1.72706	-4.68631
H	4.71239	0.04056	-4.81349
C	1.90071	0.42482	-4.89724
H	2.35497	1.43428	-4.78801
H	0.93676	0.4434	-4.37222
H	1.71628	0.26746	-5.973
O	0.32187	-0.06936	1.86152
O	1.16432	-1.29249	4.01473
N	0.78588	1.78771	-0.07924
N	-1.7681	0.96987	0.20939
N	-2.73006	0.62185	4.37664
C	1.30576	0.47519	2.48673
C	1.94527	1.67192	2.06017
C	2.95618	2.26719	2.84165
H	3.41329	3.20049	2.50322
C	3.37087	1.67062	4.01551
H	4.15708	2.12589	4.62012
C	2.7845	0.46503	4.43985
H	3.13361	0.00299	5.36393
C	1.77972	-0.13769	3.69683
C	1.55396	-1.99197	5.18081
H	2.63582	-2.21628	5.13571
H	1.38254	-1.35796	6.0705
C	1.51679	2.30778	0.84348
H	1.8683	3.34113	0.69441
C	0.33005	2.67364	-1.13892
H	1.00974	3.53868	-1.21557
H	0.32887	2.13021	-2.09138
C	-1.07845	3.14088	-0.81795
H	-1.06162	3.69928	0.13349
H	-1.41154	3.84031	-1.60098
C	-2.09535	2.01687	-0.71695
H	-2.29089	1.60548	-1.73237
H	-3.06161	2.45964	-0.41466
C	-2.91999	0.23542	0.60519
H	-3.82055	0.86182	0.4652
H	-3.09313	-0.63083	-0.07585
C	-2.89241	-0.27263	2.03917
H	-3.8561	-0.76021	2.26155
H	-2.09943	-1.01907	2.17635

C	-2.6293	0.90747	2.98325
H	-3.32293	1.73138	2.74828
H	-1.60929	1.26437	2.72912
C	-4.00293	0.79128	5.01729
H	-3.87152	0.84517	6.10959
H	-4.47721	1.72706	4.68631
H	-4.71239	-0.04056	4.81349
C	-1.90071	-0.42482	4.89724
H	-2.35497	-1.43428	4.78801
H	-0.93676	-0.44340	4.37222
H	-1.71628	-0.26746	5.97300
Mn	0.00000	0.00000	0.00000
H	0.97963	-2.89322	5.23354
H	-0.97963	2.89322	-5.23354

3

O	-0.37442	-0.17322	-1.84485
O	-1.20092	0.78775	-4.13297
N	-0.89935	-1.69911	0.35212
N	1.69283	-1.1108	-0.1056
N	2.5454	-1.4257	-4.29921
C	-1.4111	-0.73097	-2.36413
C	-2.11464	-1.80746	-1.75644
C	-3.1865	-2.43558	-2.42246
H	-3.69347	-3.2772	-1.94372
C	-3.59725	-1.98416	-3.66073
H	-4.43025	-2.46462	-4.17669
C	-2.94606	-0.89489	-4.26637
H	-3.29251	-0.54544	-5.23957
C	-1.88102	-0.26445	-3.63933
C	-1.57966	1.34013	-5.37887
H	-2.64242	1.64355	-5.34335
H	-1.47826	0.57588	-6.17167
C	-0.69089	2.5272	-5.65222
H	-0.80487	3.28739	-4.86527
H	-0.95528	2.98616	-6.61539
H	0.36587	2.22548	-5.69134
C	-1.69139	-2.29256	-0.47045
H	-2.10555	-3.26721	-0.16693
C	-0.47023	-2.45533	1.51813
H	-1.20283	-3.25115	1.73281
H	-0.4035	-1.78365	2.38235
C	0.89367	-3.06055	1.23758
H	0.81038	-3.74577	0.37685
H	1.20407	-3.6633	2.10569
C	1.97892	-2.036	0.95438
H	2.23273	-1.49934	1.89572
H	2.90396	-2.58355	0.69826
C	2.8778	-0.52216	-0.62738
H	3.73896	-1.18368	-0.41811
H	3.12889	0.41774	-0.08176
C	2.83918	-0.22209	-2.11857
H	3.82556	0.16053	-2.42927
H	2.09333	0.55084	-2.34461
C	2.46945	-1.50295	-2.87741
H	3.11415	-2.33156	-2.54136
H	1.43651	-1.74809	-2.55287

C	3.78373	-1.77276	-4.93594
H	3.61509	-1.97182	-6.00609
H	4.20527	-2.6829	-4.48413
H	4.55257	-0.97199	-4.86902
C	1.77115	-0.40819	-4.94697
H	2.29425	0.57236	-4.99368
H	0.82736	-0.24805	-4.40958
H	1.54332	-0.70336	-5.98476
O	0.37442	0.17322	1.84485
O	1.20092	-0.78775	4.13297
N	0.89935	1.69911	-0.35212
N	-1.69283	1.1108	0.1056
N	-2.5454	1.4257	4.29921
C	1.4111	0.73097	2.36413
C	2.11464	1.80746	1.75644
C	3.1865	2.43558	2.42246
H	3.69347	3.2772	1.94372
C	3.59725	1.98416	3.66073
H	4.43025	2.46462	4.17669
C	2.94606	0.89489	4.26637
H	3.29251	0.54544	5.23957
C	1.88102	0.26445	3.63933
C	1.57966	-1.34013	5.37887
H	2.64242	-1.64355	5.34335
H	1.47826	-0.57588	6.17167
C	0.69089	-2.5272	5.65222
H	0.80487	-3.28739	4.86527
H	0.95528	-2.98616	6.61539
H	-0.36587	-2.22548	5.69134
C	1.69139	2.29256	0.47045
H	2.10555	3.26721	0.16693
C	0.47023	2.45533	-1.51813
H	1.20283	3.25115	-1.73281
H	0.4035	1.78365	-2.38235
C	-0.89367	3.06055	-1.23758
H	-0.81038	3.74577	-0.37685
H	-1.20407	3.6633	-2.10569
C	-1.97892	2.036	-0.95438
H	-2.23273	1.49934	-1.89572
H	-2.90396	2.58355	-0.69826
C	-2.8778	0.52216	0.62738
H	-3.73896	1.18368	0.41811
H	-3.12889	-0.41774	0.08176
C	-2.83918	0.22209	2.11857
H	-3.82556	-0.16053	2.42927
H	-2.09333	-0.55084	2.34461
C	-2.46945	1.50295	2.87741
H	-3.11415	2.33156	2.54136
H	-1.43651	1.74809	2.55287
C	-3.78373	1.77276	4.93594
H	-3.61509	1.97182	6.00609
H	-4.20527	2.6829	4.48413
H	-4.55257	0.97199	4.86902
C	-1.77115	0.40819	4.94697
H	-2.29425	-0.57236	4.99368
H	-0.82736	0.24805	4.40958
H	-1.54332	0.70336	5.98476

Mn	0.00000	0.00000	0.00000
4			
O	0.37431	-1.71428	-0.68667
N	-1.67346	0.04126	-1.00597
N	-1.12273	-0.93473	1.43989
N	0.32049	-5.1558	1.82406
C	0.05901	-2.16015	-1.86692
C	-1.06105	-1.6841	-2.60487
C	-1.38408	-2.23685	-3.86326
H	-2.25968	-1.86953	-4.40414
C	-0.59814	-3.22989	-4.41347
C	0.51605	-3.7063	-3.69875
H	1.13419	-4.49528	-4.13279
C	0.83252	-3.18832	-2.45634
H	1.69247	-3.56783	-1.90241
C	-1.92699	-0.69636	-2.03469
H	-2.9069	-0.56805	-2.52105
C	-2.77514	0.80535	-0.44177
H	-3.55787	0.95273	-1.20314
H	-2.39908	1.78505	-0.12498
C	-3.33642	0.05144	0.7524
H	-4.1793	0.61789	1.17805
H	-3.75163	-0.91227	0.40675
C	-2.33237	-0.19434	1.86114
H	-2.01106	0.74993	2.32057
H	-2.83041	-0.7755	2.65495
C	-0.43473	-1.49817	2.62765
H	-1.21048	-1.75805	3.36945
H	0.16466	-0.70288	3.08616
C	0.39293	-2.73253	2.33165
H	1.01274	-2.95727	3.21343
H	1.07437	-2.52601	1.49857
C	-0.45757	-3.96097	2.02716
H	-1.12895	-4.13616	2.88456
H	-1.12826	-3.75921	1.1513
C	-0.45793	-6.36093	1.98763
H	-1.25918	-6.47453	1.22274
H	-0.93184	-6.37781	2.9808
H	0.19631	-7.24275	1.91689
C	1.06184	-5.15979	0.58835
H	1.6943	-6.05834	0.53358
H	1.72807	-4.28642	0.52701
H	0.4062	-5.14761	-0.31232
H	-1.422	-1.73561	0.87628
O	-0.37431	1.71428	0.68667
N	1.67346	-0.04126	1.00597
N	1.12273	0.93473	-1.43989
N	-0.32049	5.1558	-1.82406
C	-0.05901	2.16015	1.86692
C	1.06105	1.6841	2.60487
C	1.38408	2.23685	3.86326
H	2.25968	1.86953	4.40414
C	0.59814	3.22989	4.41347
C	-0.51605	3.7063	3.69875
H	-1.13419	4.49528	4.13279
C	-0.83252	3.18832	2.45634
H	-1.69247	3.56783	1.90241

C	1.92699	0.69636	2.03469
H	2.9069	0.56805	2.52105
C	2.77514	-0.80535	0.44177
H	3.55787	-0.95273	1.20314
H	2.39908	-1.78505	0.12498
C	3.33642	-0.05144	-0.7524
H	4.1793	-0.61789	-1.17805
H	3.75163	0.91227	-0.40675
C	2.33237	0.19434	-1.86114
H	2.01106	-0.74993	-2.32057
H	2.83041	0.7755	-2.65495
C	0.43473	1.49817	-2.62765
H	1.21048	1.75805	-3.36945
H	-0.16466	0.70288	-3.08616
C	-0.39293	2.73253	-2.33165
H	-1.01274	2.95727	-3.21343
H	-1.07437	2.52601	-1.49857
C	0.45757	3.96097	-2.02716
H	1.12895	4.13616	-2.88456
H	1.12826	3.75921	-1.1513
C	0.45793	6.36093	-1.98763
H	1.25918	6.47453	-1.22274
H	0.93184	6.37781	-2.9808
H	-0.19631	7.24275	-1.91689
C	-1.06184	5.15979	-0.58835
H	-1.6943	6.05834	-0.53358
H	-1.72807	4.28642	-0.52701
H	-0.4062	5.14761	0.31232
H	1.422	1.73561	-0.87628
Br	1.01069	3.95326	6.10012
Br	-1.01069	-3.95326	-6.10012
Mn	0.00000	0.00000	0.00000