Supporting Information for

Manganese Catalyzed Partial Oxidation of Light Alkanes

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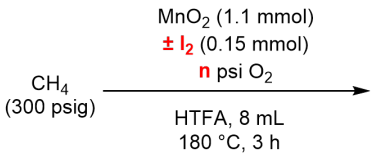
Supplementary Figures



Conditions	MeTFA (mmol)
50 psig O_2	0.61 ± 0.06
I_2 + 50 psig O_2	0.54 ± 0.04
100 psig O_2	0.55 ± 0.11
I_2 + 100 psig O_2	0.57 ± 0.08

Figure S1. Effect of addition of O_2 on the activity of MnO_2 for methane oxidation to MeTFA, in the presence or absence of I_2. Deviations calculated from three experiments.

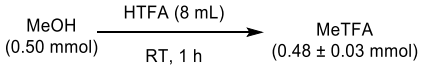


Figure S2. Solvolysis of MeOH to MeTFA in HTFA at 180°C. Deviation calculated from three experiments.

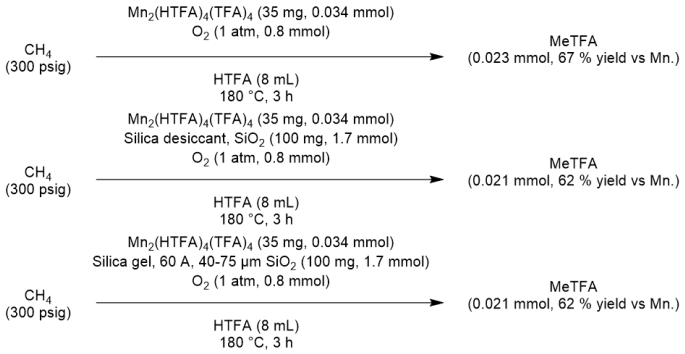


Figure S3. Effect of SiO_2 desiccant on the activity of $Mn_2(HTFA)_4(TFA)_4$ for methane oxidation to MeTFA.

Field Code Changed

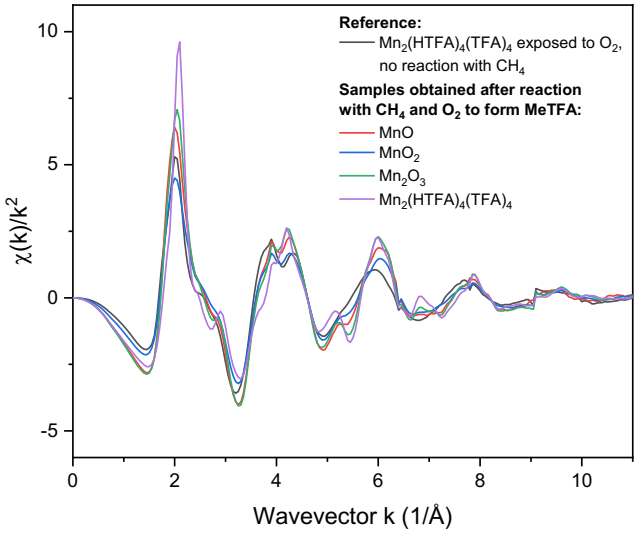


Figure S4. EXAFS k-space (k^2 weighed) of samples reacted only with O_2 and reacted with O_2 and CH_4.

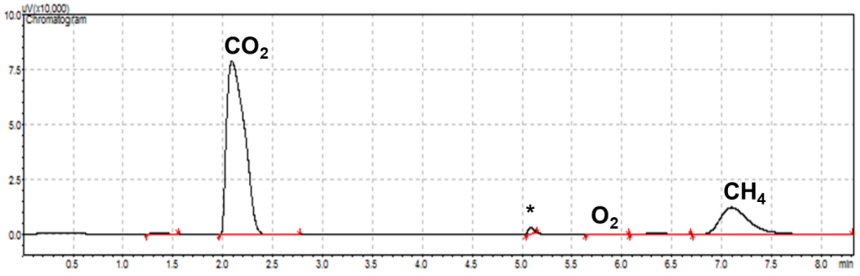


Figure S5. Typical GC-TCD spectrum for the headspace of the oxidation of methane with $Mn_2(HTFA)_4(TFA)_4$. No ethylene or ethane are observed. * The signal at 5.0 min is due to a brief change in column pressure from the position switching of a two-way valve and does not represent a change in gas composition, but rather in gas flow after a brief over-pressurization of the column.

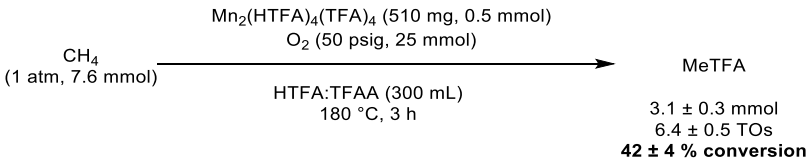


Figure S6. Scaled-up reaction in a 300 mL reactor, using $Mn_2(HTFA)_4(TFA)_4$ (510 mg, 0.5 mmol) for the conversion of methane to MeTFA in the presence of O_2. Conditions: CH_4 (1 atm), HTFA:TFAA 4:1 vol. ratio (300 mL), 180 °C, 3 h. Deviation is calculated based on three independent experiments.

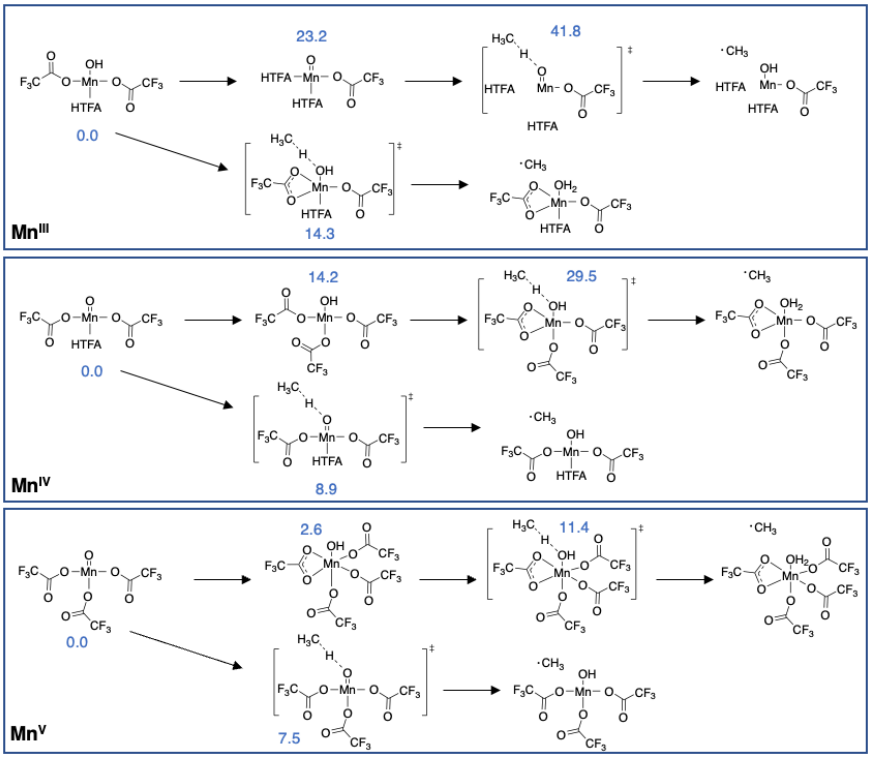


Figure S7. Relative DFT-calculated free energies at 473 K for Mn^{III} (top), Mn^{IV} (middle), and Mn^{V} (bottom) species. Values are reported in kcal/mol. The ground state Mn species for each oxidation state were normalized to 0.0 kcal/mol to illustrate the variation in HAT barrier with varying Mn oxidation. We note that the Mn^{IV} and Mn^{V} states are significantly higher in energy than the Mn^{III} due to the additional oxidation required.

Starting with Mn^{III}, we calculated the relative energies of $Mn^{III}(O)(TFA)(HTFA)_2$, $Mn^{III}(OH)(TFA)_2(HTFA)$, and $Mn^{III}(OO)(TFA)_2(HTFA)$ for which OO is a peroxo ligand. The peroxo ligand was calculated to be unstable; upon geometry optimization, the peroxo complex $Mn^{III}(OO)(TFA)_2(HTFA)$ dissociated O_2. Thus, only Mn^{III}–OH and Mn^{III}=O remained as likely candidates for the active Mn species to break methane C–H bonds. The conversion of the hydroxo complex $Mn^{III}(OH)(TFA)_2(HTFA)$ to the oxo complex $Mn^{III}(O)(TFA)(HTFA)_2$ requires H atom

transfer from the hydroxo ligand to a TFA ligand. Setting the $Mn^{III}(OH)(TFA)_2(HTFA)$ species to 0.0 kcal/mol, DFT predicts the $Mn^{III}(O)(TFA)(HTFA)_2$ complex to be 23.2 kcal/mol higher in free energy, indicating that Mn^{III} prefers bearing hydroxo/TFA ligand combination over an oxo/HTFA configuration. We calculated the HAT barriers from CH_4 to the hydroxo and oxo ligands of these two species. Relative to the $Mn^{III}(OH)(TFA)_2(HTFA)$ ground state, HAT from methane to generate the methyl radical and $Mn^{II}(OH_2)(TFA)_2(HTFA)$ requires a free energy barrier of 14.3 kcal/mol at 473 K. The HAT transition state from CH_4 to the oxo ligand $Mn^{III}(O)(TFA)(HTFA)_2$ lies 41.8 kcal/mol above the ground state, or 18.6 kcal/mol above the Mn^{III}=O species. We find that for Mn^{III} the hydroxo ligand provides a more facile route for methane HAT compared to the oxo.

In analogous calculations for Mn^{IV}, we find that the peroxo ligand is likely to undergo rapid dissociation from the Mn center to form molecular O_2, indicating that Mn^{IV}-OO would not be a stable intermediate. In contrast to Mn^{III}, DFT predicts Mn^{IV} to favor an oxo ligand over a hydroxo ligand. Specifically, DFT predicts $Mn^{IV}(O)(TFA)_2(HTFA)$ to be 14.2 kcal/mol lower than $Mn^{IV}(OH)(TFA)_3$. Moreover, DFT predicts that HAT from CH_4 to the oxo ligand of $Mn^{IV}(O)(TFA)_2(HTFA)$ requires a barrier of 8.9 kcal/mol, while HAT from CH_4 to the hydroxo ligand of $Mn^{IV}(OH)(TFA)_3$ requires a barrier of 29.5 kcal/mol (or 15.3 kcal/mol relative to the Mn^{III}-OH species).

Finally, an identical analysis was made for Mn^{V}. Again, the peroxo ligand was unstable, leaving Mn^{V}-OH and Mn^{V}=O as potential species. DFT predicts the $Mn^{V}(O)(TFA)_3$ species to be 2.6 kcal/mol more stable than $Mn^{V}(OH)(TFA)_4$. Homolytic breaking of the CH_4 C–H bond by $Mn^{V}(O)(TFA)_3$ would require a free energy barrier of 7.5 kcal/mol while the same reaction using $Mn^{V}(OH)(TFA)_4$ would require a barrier of 11.4 kcal/mol (or 8.8 kcal/mol relative to the Mn^{V}-OH state). While Mn^{IV} and Mn^{V} states provide lower free energy barriers for HAT from CH_4, they are highly unlikely to form under our reaction conditions and are intrinsically higher in energy than the Mn^{II} and Mn^{III} states, suggesting that the solution likely consists primarily of Mn^{II}, Mn^{III}. Hence, herein, we focus on the mechanism for partial oxidation of methane to MeTFA by a Mn^{III} active center. As we have calculated the Mn^{III}-OH species to be lower in free energy and to require a lower HAT barrier than the Mn^{III}=O species, we investigate the mechanism using $Mn^{III}(OH)(TFA)_2(HTFA)$ as the active catalyst (**Error! Reference source not found.**).

Table S1. XAFS Refinement of Mn–O first shell.

Parameter	**Value**	**Error**
S_0(Fixed)	0.93	
ΔE_0	3.7	0.8
CN_O	7.0	0.16
ΔR-O	2.179	0.013
σ^2 -O	0.007	0.007
CN_C_{2nd}	2.8	0.4
ΔR-C_{2nd}	3.523	0.006
σ^2 -C_{2nd}	0.005	0.001
CN_C_{3rd}	3.2	0.3
ΔR-C_{3rd}	4.135	0.013
σ^2 -C_{3rd}	0.008	0.0009

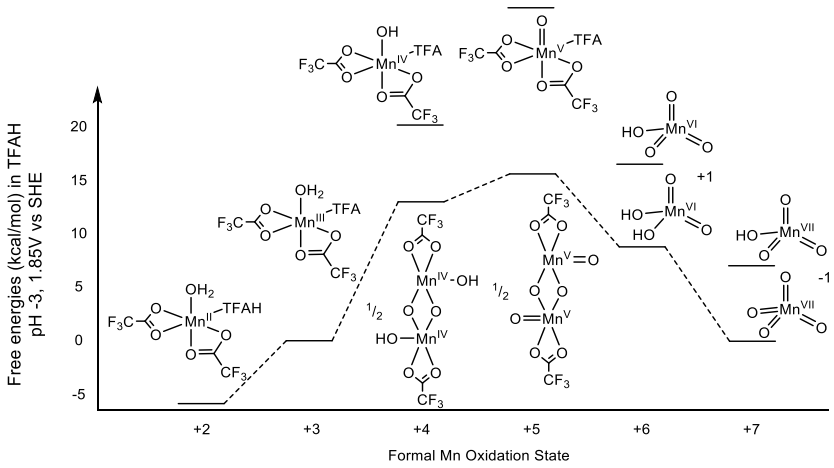


Figure S8. DFT free energies for the different oxidation states of Mn when exposed to the HTFA solvent and O_2. Even at conditions that theoretically favor higher oxidation states, the Mn(IV) monomer remains > 25 kcal/mol above the Mn(II) monomer. Energies were calculated with the B3LYP-D3 functional.

Figure S9. DFT free energy barrier for the methyl radical to combine with a free TFA anion to generate a MeTFA radical anion.

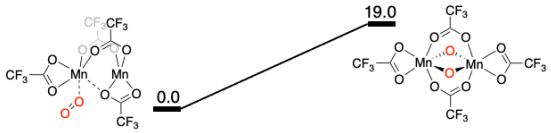


Figure S10. DFT free energies at 473 K for oxidation of $Mn_2(TFA)_4$ to $Mn_2(O)_2(TFA)_4$ via O_2. Energies are in kcal/mol.

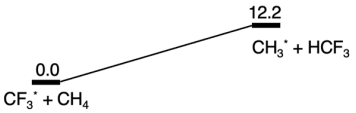


Figure S11. DFT free energies at 473 K for the reaction of the CF_3 radical with methane to generate fluoroform (HCF_3) and the methyl radical (radicals are denoted by $^{\bullet}$).

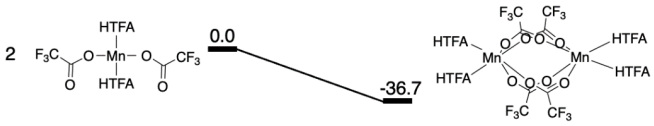


Figure S12. DFT free energy at 473 K for the dimerization of two $Mn^{II}(TFA)_2(HTFA)_2$ to $[Mn^{II}(TFA)_2(HTFA)_2]_2$.

DFT Structures

CH_4+Mn(III)(OH)$(TFA)_2$(HTFA)

Mn2	4.7538578764	7.9906184663	9.7593508777
F15	3.7109539784	5.3512242358	5.7999838269
F16	5.3978444500	4.4663440195	6.8168019458
F17	3.3929787505	4.1275438005	7.5506273971
O35	4.8990944241	6.0912022912	9.0121576849
C50	4.3087561953	6.2735898063	7.9022256992
C51	4.2033001461	5.0321197915	6.9903222700
O73	3.8181864294	7.3456606693	7.5456960894
O27	3.9840095001	9.7688306157	9.1926064524
O29	5.6210109014	10.6691266035	7.9298592117
C44	4.5195187437	10.6695296823	8.4370611390
C45	3.5946968629	11.8959409565	8.2333004827
F55	3.6862767395	12.7016176840	9.2961430146
F56	3.9293966816	12.5819798304	7.1519817622
F57	2.3149306166	11.5153480293	8.1189669336
O41	1.5034023999	8.8333434759	9.0085738017
H42	2.2961068874	9.4416531488	9.0623434394
C46	1.7641366772	7.7297760979	9.6036432878
C47	0.6497494799	6.6658685475	9.5369306815
F46	-0.4649749045	7.1418529761	9.0111047405
F47	1.0977171663	5.6622493580	8.7836273251
F48	0.4013703943	6.2016757964	10.7550675434
O43	2.8023237870	7.4194463376	10.1797460467
O24	6.3709660313	8.3602536385	9.1885687872
H25	6.4202660082	9.1392894574	8.5891970272
C27	3.0970147217	9.9593864308	5.3579161739
H28	2.6906154432	9.5365589540	6.2786398722
H29	2.9516930208	9.2422766462	4.5496815457
H30	2.5830426916	10.8911577693	5.1215555556
H31	4.1641579034	10.1512837244	5.4789066605

HAT-Mn(III)(OH)$(TFA)_2$(HTFA)

Mn2	4.6860500128	7.7727676915	9.7160671740
F15	3.9512421628	5.1083219518	5.6957620054

F16	6.0538916428	5.0543208027	6.1888686697
F17	4.6746527257	3.7244900742	7.1844245752
O35	5.0564593401	5.7354208694	8.9361641286
C50	4.6283585747	6.0304740613	7.7912556489
C51	4.8154005138	4.9578928426	6.6966912118
O73	4.1254932127	7.1192249573	7.4808825996
O27	3.8899689644	9.6490748989	9.1224448038
O29	5.6911127822	10.8110965647	8.4477351717
C44	4.4929199705	10.6469085885	8.5992997602
C45	3.5389128236	11.7399440773	8.0552074576
F55	4.0944057190	12.9443696191	8.1069425746
F56	3.2403286475	11.4716404080	6.7789210185
F57	2.3910746827	11.7735635886	8.7419401028
O41	1.3813497093	9.0750322525	9.4690120043
H42	2.2920753391	9.4848760569	9.3196287117
C46	1.5061863341	7.8281566982	9.7741202065
C47	0.1383228661	7.1396639482	9.9739417333
F46	-0.6707888097	7.3990639266	8.9521447848
F47	0.2893579452	5.8306059120	10.0858061229
F48	-0.4321053311	7.6041024939	11.0875899888
O43	2.5395723796	7.1995236725	9.9186182763
O24	6.4864424603	8.2344976237	8.9156754358
H25	6.6490424941	9.1601610996	8.6212092083
C27	8.4335895713	6.9113429635	7.8515861159
H28	8.1926940117	5.8705638967	8.0573209579
H29	8.4227779156	7.1519122066	6.7914594972
H30	7.5192494679	7.5163989480	8.3335507929
H31	9.3279430067	7.2554198187	8.3647695290

CH_4+Mn(III)(O)$(TFA)_2(HTFA)_2$

Mn2	4.7785207917	7.9272293835	9.5439950046
F15	5.6758736822	2.6769862229	9.9039863009
F16	7.1131778111	4.0436733489	10.7652371651
F17	5.5149669807	3.2432830002	11.9824588108
O35	5.4184742422	5.9577341789	10.1387194771
C50	4.9370285241	4.8660472490	10.3747124755
C51	5.8445705402	3.6771395345	10.7663830903
O73	3.6870775166	4.5263187113	10.3478412798
O27	3.7861371016	9.6239960989	9.0457931056
O29	5.2865016973	11.3122596767	9.0764624225
C44	4.2349002211	10.8123855826	8.7739677697
C45	3.2002348552	11.6204867447	7.9540183558
F55	2.0239026144	11.6481967662	8.6022511884
F56	3.5932822344	12.8654440546	7.7401695370
F57	2.9870255191	11.0316127621	6.7710059170
O41	1.4356624598	8.7324861801	9.1402221558
H42	2.3257928625	9.2525787949	9.0593430902
C46	1.6756542527	7.5277992407	9.4807529472
C47	0.4090010590	6.6583110122	9.6173039383

F46	-0.3681404481	7.1393950689	10.5799473876
F47	-0.2695107386	6.6592526364	8.4769313967
F48	0.7501769539	5.4105341545	9.9194779904
O43	2.7800432467	7.0277239031	9.6956988703
O24	6.3038841257	8.4231991474	9.2082282653
H25	3.1191547481	5.3008051732	10.1093074608
C27	10.2569766308	8.1503762143	9.2049608309
H28	9.1756116778	8.2370339127	9.3184987779
H29	10.4967505087	7.9889885926	8.1536938116
H30	10.7328519676	9.0699721227	9.5490043812
H31	10.6210398290	7.3088455599	9.7945713105

HAT- $Mn(III)(O)(TFA)_2(HTFA)_2$

Mn2	6.7390555369	9.1891849454	8.6529668096
F15	5.7892152576	3.7245921215	11.2064232826
F16	6.6920702811	5.4238957368	12.1842381083
F17	4.7468811420	4.7258326493	12.8117431045
O35	4.8752695464	7.0734635272	10.9951974399
C50	4.8447559234	5.8938554814	10.7801646948
C51	5.5409709595	4.9127491990	11.7502120476
O73	4.2153650296	5.2565399785	9.8288966351
O27	3.0162440723	9.7387714682	7.5701323351
O29	4.8025782353	9.9751794575	8.9296870285
C44	3.5958022603	10.0722843014	8.6106349568
C45	2.6705059872	10.7765607096	9.6435390771
F55	1.5508434507	10.0609098935	9.8302205415
F56	3.2376449506	10.9699482057	10.8309991519
F57	2.2990881110	11.9758566839	9.1658973972
O41	0.9034587814	8.1019798804	7.6559843329
H42	1.5667771476	8.8459824928	7.5400658340
C46	1.4645857434	7.1205291313	8.2982635119
C47	0.4802283825	5.9553720542	8.5484529504
F46	-0.4831404381	6.3455432763	9.3859914648
F47	-0.0915488446	5.5532471870	7.4147647265
F48	1.1203030349	4.9267139975	9.0909011332
O43	2.6028592573	7.0726610014	8.6986434708
O24	6.5080825434	7.3661211312	8.3726207525
H25	3.6831088706	5.8895188917	9.2794727740
C27	7.3407186683	5.0101306364	8.5532707906
H28	6.8895072556	6.2131768153	8.4647440666
H29	6.4641767431	4.3716698812	8.4603189429
H30	8.0420062340	4.8962103062	7.7298969388
H31	7.8173759204	4.9496512056	9.5300076409

CH_4+$Mn(IV)(O)(TFA)_2(HTFA)$

Mn2	5.1990502412	7.8571185882	7.9321410698
F15	2.4720277291	3.8762848653	6.4622119005

F16	4.4448881793	3.4001325809	7.2010487677
F17	2.8544803412	3.8645702018	8.5892067718
O35	4.9083818180	5.9468702383	7.7742000490
C50	3.7168350222	5.6721978009	7.3771186717
C51	3.3752806435	4.1653752721	7.3916328825
O73	2.8607055897	6.4814721247	7.0728659563
O27	3.1093863380	9.8124506499	7.6757784039
O29	5.1736513753	9.7181008709	8.5146867792
C44	4.0701755911	10.3036604432	8.2523631187
C45	3.9585229204	11.7394216148	8.8101612491
F55	3.4299123483	11.6608506633	10.0390130513
F56	5.1406192030	12.3382647456	8.8966124603
F57	3.1564711904	12.4813660410	8.0564467947
O41	1.5740028680	8.1396953705	9.1086921898
H42	1.9173359952	8.6087563583	8.3055565889
C46	2.5229485957	7.6180124177	9.8015552769
C47	2.0347333334	6.9120058379	11.0867691873
F46	0.7244545891	7.0000563551	11.2399343771
F47	2.3785812676	5.6276196386	11.0181753085
F48	2.6355938563	7.4550654161	12.1406802486
O43	3.7219152559	7.6117646268	9.5685827831
O24	5.4574792734	8.1596186688	6.3695800819
C27	5.0495817605	11.3742345456	5.3475018245
H28	4.2673652853	12.1245123119	5.4700569408
H29	5.5931237800	11.5631216676	4.4215131594
H30	5.7481646126	11.4284068256	6.1854999301
H31	4.5968767176	10.3829576428	5.3049022472

HAT- $Mn(IV)(O)(TFA)_2(HTFA)$

Mn2	5.0608473656	7.8938848579	8.1453424661
F15	2.1588854489	3.9700700467	6.7667692952
F16	4.2307909636	3.8095498350	6.1736861635
F17	3.6696736518	3.5109296076	8.2404742929
O35	4.8242283736	6.0014415946	7.7658918216
C50	3.6181778630	5.7274814259	7.4185173704
C51	3.4058214605	4.2219330379	7.1410172284
O73	2.6991535419	6.5201550019	7.3181955050
O27	2.8874168086	10.0140887276	8.0497062726
O29	5.0474487664	9.8331174233	8.6020379091
C44	3.9844343805	10.4757965107	8.3673828749
C45	4.0846123769	12.0108382398	8.5431529519
F55	3.6360755843	12.3407803576	9.7615055931
F56	5.3335316069	12.4501498728	8.4311248164
F57	3.3309691950	12.6388536649	7.6447669965
O41	1.6206635923	8.2569806214	9.4849445819
H42	1.9931921137	8.9014467713	8.8026065111
C46	2.5412701548	7.5441966280	10.0115898745
C47	2.0356546774	6.5017167215	11.0319463658
F46	0.7615384919	6.6693160312	11.3407396081

F47	2.1932410842	5.2940277108	10.4830269398
F48	2.7658655146	6.5596584696	12.1385010573
O43	3.7455432634	7.5583708271	9.7807550251
O24	5.3292313756	8.3183622288	6.5030923429
C27	5.6182313642	6.5226811510	4.7759678426
H28	4.6152043293	6.3917902485	4.3761429772
H29	6.3022907181	7.0447335493	4.1110956103
H30	5.4596736657	7.3863054491	5.6877686760
H31	6.0374867186	5.6545328650	5.2746442531

CH_4+Mn(IV)(OH)$(TFA)_3$

Mn2	5.0899876976	8.8098294090	9.2839515237
F15	4.0924404327	6.6751470061	5.0494686010
F16	5.7966675080	5.6648665918	5.9154849375
F17	3.8061043554	5.2384028159	6.6331394399
O35	5.7677006468	7.4425437959	7.9064210356
C50	4.6881403371	7.3111737996	7.2576748530
C51	4.6145402279	6.2051538477	6.1825415093
O73	3.6659044046	7.9669001971	7.4799435135
O27	3.2778729906	9.6382637484	9.7282021821
O29	2.9934014433	11.0021915519	7.9850592919
C44	2.5611257646	10.3673125753	8.9164075617
C45	1.0432375470	10.4086008467	9.2259106557
F55	0.4290834454	9.3991509471	8.6062714231
F56	0.8006983205	10.3201375560	10.5299518206
F57	0.5266268182	11.5457257533	8.7745238470
O41	2.0856456332	7.8992504491	10.1784403348
H42	4.9660830635	10.6987949930	7.9024433676
C46	3.0066773711	7.0575746650	10.2823302651
C47	2.5174891395	5.6025289416	10.5776111657
F46	1.2056489624	5.5397381559	10.7166956429
F47	2.8927070238	4.8363918676	9.5608938227
F48	3.1026711470	5.1675769100	11.6847504221
O43	4.2325137276	7.1905712310	10.1623839583
O24	5.6667593380	10.1788953755	8.3468220214
C27	7.2180392155	7.3550595953	3.4135619513
H28	7.9587012874	6.5548815493	3.3994303809
H29	7.4556002785	8.0847691723	2.6388935571
H30	6.2300578464	6.9353670359	3.2279661584
H31	7.2275251670	7.8418707964	4.3890885015

HAT- Mn(IV)(OH)$(TFA)_3$

Mn2	3.9687328743	8.3822643419	8.1168079105
F15	6.0528101566	5.7027160480	4.7887475193
F16	7.7004603567	6.4912755998	5.9399956967
F17	6.6317772154	4.7488308128	6.6377698660
O35	5.9252112544	7.2023762259	7.9526043283

C50	5.5375693757	6.8343947749	6.8274420429
C51	6.4913727122	5.9275033429	6.0226283508
O73	4.4351352696	7.1556544153	6.3289059508
O27	2.6270034126	9.4742218887	9.2524602615
O29	3.0985748505	11.6203860271	8.9295015341
C44	2.4839330581	10.7350154772	9.4851719176
C45	1.4239919072	11.0756480314	10.5611181398
F55	0.2409385945	10.5524450959	10.2391871849
F56	1.7909741493	10.5874866666	11.7474289692
F57	1.2848582917	12.3902537951	10.6756237712
O41	1.5619485085	8.0561412914	10.4947916804
H42	4.7156834643	10.8896235142	7.7040940467
C46	2.0998138228	6.9872856690	10.0813573643
C47	1.5008371351	5.7045223229	10.7483944172
F46	0.6321683193	5.9918343943	11.7054210766
F47	0.8909564523	4.9861176791	9.8113381371
F48	2.4904424050	4.9846886260	11.2598452604
O43	2.9918363141	6.8130146555	9.2543918577
O24	5.0523626725	9.9845050774	7.5325268340
C27	7.5042057444	10.4459098495	6.8712688306
H28	8.0144343861	9.5104039257	7.0950851337
H29	7.4946839460	10.6952223772	5.8125168965
H30	6.3574902261	10.2135642389	7.1556623875
H31	7.8119340275	11.2695339976	7.5113266631

CH_4+Mn(V)(O)$(TFA)_3$

Mn2	4.4073584675	7.6968929508	8.6988438212
F15	3.2916132060	5.0407014059	5.1734875936
F16	4.5311406303	3.7389366522	6.3772451519
F17	2.4657564536	4.0781705512	6.9254336645
O35	5.0346199898	5.8814588503	7.9017252111
C50	3.9532492341	5.8456855941	7.2710803275
C51	3.5581821277	4.6336090475	6.4101070404
O73	3.1580649527	6.8191087350	7.3518762316
O27	3.5861399134	9.3865322802	8.3968147129
O29	5.5271456357	10.4607015731	8.7019027672
C44	4.3387606512	10.4213694394	8.4206363222
C45	3.6138919564	11.7197305724	7.9690214010
F55	2.4262835080	11.8105242315	8.5452877204
F56	4.3313134970	12.7910584182	8.2618863286
F57	3.4486275309	11.6510359465	6.6485757400
O41	1.3171133958	7.8196806483	9.6215877433
C46	2.0539215719	7.0226348090	10.1229284761
C47	1.5468397671	5.8855547949	11.0413766453
F46	1.7707244255	4.7154354523	10.4356190146
F47	2.1937712751	5.8852925891	12.2059152974
F48	0.2498541557	6.0089147319	11.2710258952
O43	3.3576487732	6.9131759355	9.9772169828
O23	5.8317298157	8.3467494996	8.8370295154

C27	5.4773242528	8.6409828716	5.6584005905
H28	5.6638171566	8.7386494365	4.5894382324
H29	4.4029800201	8.7298110008	5.8359070558
H30	5.8446977608	7.6686282906	5.9924044281
H31	6.0151608296	9.4250495189	6.1923679210

HAT- $Mn(V)(O)(TFA)_3$

Mn2	5.1933723908	7.4694272774	8.8746114512
F15	3.3032741173	4.8159451818	5.3555961611
F16	4.5164418665	3.4867389944	6.5492419145
F17	2.5316379848	4.0287443893	7.2126600901
O35	5.1025882416	5.5055054941	8.2046977931
C50	4.1729771735	5.7007609535	7.3697627141
C51	3.6333179323	4.4786400727	6.5999193588
O73	3.6479001561	6.8019514842	7.1698634666
O27	4.1421082804	9.1632988954	8.7373874263
O29	5.3541108099	10.9200804486	8.0997637741
C44	4.3089677634	10.4136381118	8.4180362501
C45	3.0043442549	11.2471493727	8.4687964782
F55	2.5198379833	11.2847853607	9.7114651572
F56	3.2435739561	12.4914812937	8.0765886471
F57	2.0794359950	10.7202426756	7.6672671985
O41	2.1709723743	8.5661507067	9.3804610625
C46	2.4862339080	7.4776979906	9.9177368999
C47	1.2708591667	6.6921244486	10.5132712158
F46	1.1492506326	5.5571670689	9.8353311016
F47	1.5218887410	6.4096656901	11.7838778104
F48	0.1443996917	7.3772145850	10.4293747621
O43	3.5864049674	6.9209353829	10.0273272886
O23	6.4294902778	7.8378341497	7.7412920127
C27	5.6262634441	8.9072384265	5.5956822260
H28	5.9666026860	9.9391490291	5.5876631278
H29	4.5487336112	8.7814106277	5.6584351532
H30	6.1050826642	8.2624356186	4.8624574726
H31	6.0519454276	8.4610963724	6.6726445936

CH_4+$Mn(V)(OH)(TFA)_4$

Mn2	4.4956594498	8.2290905469	9.0904691286
F15	4.8703685380	6.0752184536	5.0019618966
F16	6.7295330406	5.7126617371	6.0422073815
F17	4.9781601761	4.5440824827	6.5206873834
O35	5.7289725894	6.8753086733	8.2843664081
C50	5.0009695911	6.7700468203	7.2543892527
C51	5.4094136314	5.7554097569	6.1697821689
O73	3.9620441196	7.4471427983	7.1399623942
O27	2.9894791695	9.3095443694	9.5791245766
O29	3.4798907787	11.4106196019	8.9944149337

C44	2.7389165582	10.5836120199	9.4653307272
C45	1.3472111978	10.9629156791	10.0250009682
F55	0.3946705218	10.2689212265	9.4027625812
F56	1.2873122888	10.6807422397	11.3271630166
F57	1.1166828383	12.2552575173	9.8558896708
O41	6.4680144396	10.3697893809	10.1044832733
H42	5.1238734515	10.4581254831	8.2787685108
C46	6.2282517033	9.4811738054	10.9395529984
C47	6.9873369189	9.5853223919	12.2956304008
F46	8.0484357053	10.3717903907	12.2013434299
F47	6.1595860442	10.0828492998	13.2134386726
F48	7.3763672017	8.3801113848	12.6900490699
O43	5.4369579570	8.5155506240	10.8403597342
O24	5.5696592385	9.5824365251	8.3423883547
C27	6.6089476929	8.8741633359	5.1034772394
H28	7.0448201451	8.1261570752	4.4413636257
H29	6.9762885156	9.8634648775	4.8293711906
H30	5.5218522108	8.8552871071	5.0113515323
H31	6.8928906754	8.6657338153	6.1357794131
O30	1.6050464587	7.8985137630	10.6003698280
C31	2.3145503660	6.8722778401	10.4234471440
C32	1.6290555257	5.5879460614	11.0395622175
F33	0.3869020841	5.4933250490	10.5979848007
F34	2.3159715416	4.5240024151	10.6873439878
F35	1.6193417963	5.7000216285	12.3581160942
O36	3.4101337812	6.7390493155	9.8755564178

HAT-Mn(V)(OH)$(TFA)_4$

Mn2	4.5689321914	8.4926336049	9.0931556435
F15	4.7845684276	5.8844431677	5.2796858199
F16	6.6894292063	5.6135276211	6.2696048953
F17	4.9123132741	4.6646206907	7.0625904810
O35	5.8290780757	7.1527639143	8.3640285462
C50	5.0872988371	6.9629973634	7.3549072798
C51	5.3829087971	5.7548036302	6.4542551856
O73	4.0924093537	7.6856659253	7.1561213776
O27	2.9649489407	9.4332645537	9.4705771809
O29	3.1508113673	11.4246648547	8.4795876829
C44	2.5717958819	10.6436614236	9.1921923490
C45	1.2358883010	10.9980824157	9.8844000283
F55	0.2614622505	10.2210788783	9.4101462748
F56	1.3346203868	10.7951725545	11.1964864987
F57	0.9218584452	12.2637288629	9.6626911174
O41	7.5127278231	9.0555099887	10.2391718285
H42	4.9565408370	10.6151191233	7.8088849816
C46	6.5968957434	9.0055143301	11.0246589229
C47	6.8089976499	9.2938908377	12.5279544434
F46	8.0668382472	9.6239922451	12.7942351678
F47	6.0149878167	10.2989336781	12.9137782627

F48	6.4924471843	8.2179681615	13.2560100442
O43	5.3532301969	8.7272399346	10.8042642419
O24	5.4545757391	10.0113394229	8.4106818120
C27	7.7000354799	9.5014791642	6.9277509283
H28	8.0696109288	8.5387608240	7.2750524970
H29	8.4047904993	10.3095237330	7.1241752675
H30	7.3691556793	9.4839072907	5.8907154159
H31	6.7909951468	9.7416190809	7.5838179769
O30	1.6670617855	7.9724306507	10.5146060532
C31	2.4226943988	6.9940664185	10.3021982178
C32	1.8075218571	5.6336069765	10.8185994269
F33	0.5004422621	5.6170819937	10.6324001898
F34	2.3688038991	4.6402843603	10.1619075825
F35	2.0731417067	5.5225396859	12.1105011472
O36	3.5417233148	6.9292875588	9.7835816143

$Mn(H_2O)(TFA)_2(HTFA)$

Mn2	7.0753843877	8.1271002274	6.5485185153
F15	8.1533948542	11.2930664651	9.7715392290
F16	7.5707017736	9.9063910828	11.3225310745
F17	9.6458773960	10.1025049051	10.7805577337
O35	8.4640482323	7.8190840824	9.7220107606
C50	8.2257637669	8.9454202332	9.2674626661
C51	8.4029395977	10.0958094965	10.2907061083
O73	7.8502340115	9.2775643658	8.1191491984
O41	7.7858198201	5.4329982935	9.1752198800
H42	8.0427270665	6.4175006012	9.3222585492
C46	7.3954315938	5.1921657089	7.9805845852
C47	7.0071477508	3.7179629091	7.7228320876
F46	7.6999058217	3.2542420898	6.6830776596
F47	7.2421372618	2.9390204729	8.7698731765
F48	5.7110599457	3.6536225376	7.4210584975
O43	7.2972559687	5.9695648421	7.0451764658
O24	5.9608931713	-13.6281008062	14.6760832274
H31	6.5477072036	-14.0926990867	15.2852584115
H32	5.2673063670	-14.2597630983	14.4495876295
F20	2.0714450704	6.1360121310	5.5481208560
F21	3.4587494833	6.6463935673	3.9768310289
F22	3.9657272660	5.1064067951	5.4059596791
O23	5.2385191888	7.5737990047	5.8343272000
C24	4.0447392592	7.3389933380	6.1884485360
C25	3.3625284653	6.2962067884	5.2662803011
O26	3.3977776203	7.7876187672	7.1238195030
O27	3.9817849547	7.8454258907	10.1506043386
H28	4.1615808239	6.9399616978	10.4676311955
C29	4.8131037322	8.2143990774	9.2126701101
C30	4.5958110649	9.6988310533	8.8452809239
F31	3.3263166524	10.0649252301	8.8937325848
F32	5.2836730762	10.4406126659	9.7264637303

F33	5.0813765074	9.9616220430	7.6350354899
O34	5.7251581750	7.5745180961	8.7464662366

TS-CH3+Mn(OH)$(TFA)_2$(HTFA)

Mn2	4.8281251918	6.3188453457	8.3165537127
F15	6.4115939471	7.1438739845	3.2181615243
F16	5.2228372816	8.6651722757	4.1874415654
F17	7.3787386456	8.7434548076	4.3061970541
O35	5.3130314776	7.1272664472	6.3044258546
C50	6.2900121053	7.0872036933	5.5768242447
C51	6.3218344976	7.9344797024	4.2872125922
O73	7.3633850040	6.3999530581	5.7487751826
O27	6.0101489034	10.3376875003	9.9125921275
O29	5.7021928106	8.2993024604	9.1513618942
C44	6.1625820808	9.4610658817	9.0633242436
C45	6.9770320996	9.7757158582	7.7901559067
F55	6.1457146515	9.9660528478	6.7572696139
F56	7.7271379806	10.8585429537	7.9277021581
F57	7.7719486762	8.7439734865	7.4838468954
O41	9.1495317678	5.9300737450	8.6284012772
C46	7.9821213686	6.0073017796	8.9616071076
C47	7.7179939758	6.3665642875	10.4461509881
F46	8.4761515068	5.6308621002	11.2579038759
F47	8.0280472247	7.6554980263	10.6669239824
F48	6.4413332639	6.1898711770	10.8044871288
O43	6.9473205207	5.8565593285	8.2277251475
O24	3.5343759587	6.3540710618	9.7517619003
C27	4.9374014121	8.8287713453	11.2092204237
H28	4.3777488568	7.9575686296	10.8739343269
H29	5.8851813294	8.6944923381	11.7173299572
H30	4.4024184286	9.7530113499	11.3871715518
H31	2.5954000696	6.1998014136	9.5942831294
H32	7.3344967054	5.9743270355	6.6750158906

Mn(II)(OH)(TFA)(HTFA)(MeTFA)

Mn2	5.1236120837	6.7285449451	8.1306479704
F15	7.1429684708	6.8319566130	3.1755280909
F16	6.7408359865	8.7600808929	4.0779173508
F17	8.7236866050	7.9017816451	4.1912811327
O35	6.0755550111	7.3067164165	6.1685276872
C50	7.0353870082	6.9235197377	5.5321578527
C51	7.4181652897	7.6297485376	4.2116935985
O73	7.8338134381	5.9530871041	5.8271589314
O27	5.9558495437	10.1581073368	10.2306431966
O29	6.5048559330	8.5195148067	8.7825320603
C44	5.9615581411	9.5627640568	9.0770197840
C45	5.2905806771	10.4626418964	8.0191233009

F55	4.9912631141	9.7787664560	6.9259960133
F56	4.1974539580	11.0564411222	8.4791432440
F57	6.1658428466	11.4218181409	7.6759853117
O41	8.6406258787	4.3724857590	9.0177121470
C46	7.7478895438	5.1852497035	9.1476868810
C47	7.5795108141	5.8447272034	10.5380179981
F46	7.9125885925	5.0184229051	11.5236962089
F47	8.3726455799	6.9219368569	10.6204832419
F48	6.3152125052	6.2509165351	10.7495444169
O43	6.9543729392	5.6331270935	8.2472524767
O24	3.9014174215	7.9528676181	9.0087408935
C27	6.6261642152	9.5053388198	11.3306033436
H28	6.1780747462	8.5293606742	11.4880875107
H29	7.6875047648	9.4102824970	11.1020133786
H30	6.4677209613	10.1478913685	12.1901111736
H31	2.9457045076	7.8450670839	9.0573137713
H32	7.5668213529	5.5815218835	6.7310218308

$Mn(II)(OH)(TFA)(HTFA)_2$

Mn2	5.3068666158	8.2270005810	5.5274061403
F15	2.7763427411	4.0611972378	7.6529427348
F16	4.8921026946	4.3649026756	7.9575655251
F17	3.4762965162	5.1089193360	9.4080380003
O35	4.4650768175	6.5432904575	6.5231374126
C50	3.5519629694	6.2802024282	7.3398075818
C51	3.6930988229	4.9304480534	8.0968898528
O73	2.5338958128	6.9184781546	7.6196281162
O27	5.9579183631	10.4901264221	8.1936237457
O29	4.4377709380	9.7689987763	6.6978421204
C44	4.8362475010	10.4372531376	7.6935452697
C45	3.7237039752	11.2776191252	8.3704789892
F55	3.0129468564	11.9696021909	7.4740166484
F56	2.8734013688	10.4614285867	9.0169638283
F57	4.2123919158	12.1367632817	9.2603070776
O41	2.4513535908	7.7633081063	10.1331003644
H42	2.3100324146	7.4064498904	9.2083761133
C46	3.7077671916	8.0570005516	10.3069993375
C47	3.9805527403	8.7471834743	11.6619018003
F46	2.9019678311	8.8385493997	12.4316525680
F47	4.9201524894	8.0719230977	12.3281841181
F48	4.4403645144	9.9792282920	11.4357989529
O43	4.6323337180	7.8675143738	9.5535256865
O24	6.6782006913	8.0569925088	7.3213811203
C27	6.8995340375	5.7352312944	10.6149761980
H28	6.1105929269	5.5576122608	9.9014903130
H29	7.7134401175	5.0324531745	10.7066066186
H30	6.8473100285	6.5997481251	11.2579871800
H31	6.3177931763	7.4422444560	7.9798521486
H32	6.6830298308	8.9378762642	7.7598891588

HTFA+Mn(II)$(TFA)_2(HTFA)_2$

Mn2	5.0821387887	8.3092342754	7.3217948260
F15	5.3731246631	3.1947882308	7.5251204690
F16	6.6799611430	3.5765406107	9.2036801012
F17	4.5784830676	4.0641163304	9.3382705814
O35	7.0889456714	5.6730178534	7.5860387371
C50	5.9482971912	5.4565498955	7.9491392934
C51	5.6380555868	4.0491265112	8.5207811237
O73	4.9414679882	6.2478392626	7.9291009511
O27	8.6329090368	8.6382739969	7.0522376068
O29	6.7035128565	8.1552236839	6.0022978298
C44	7.9389769097	8.1495727576	6.1369894921
C45	8.7529564994	7.4499143124	5.0214834011
F55	9.3818415908	6.3830200802	5.5221320368
F56	7.9844696461	7.0458126732	4.0157123171
F57	9.6814805043	8.2776622544	4.5330753465
O41	3.5223906376	6.6418154816	10.0834452941
H42	3.8732904113	6.2949842405	9.2094468206
C46	3.6899569352	7.9184473550	10.1624811118
C47	3.4524963680	8.4506725678	11.5889055132
F46	2.3922573543	7.8774353792	12.1484741266
F47	4.5303935390	8.1620230069	12.3232254887
F48	3.2814038698	9.7634991957	11.5784134627
O43	4.0421653105	8.6825071735	9.2844796078
O24	8.8829743431	7.3189893245	9.3788350130
O25	6.7102420681	7.9387933198	9.3335962500
C26	7.6541951796	7.3339655205	9.7932930700
C27	7.4285047920	6.4654832481	11.0496243551
F28	7.4402451240	7.2368906812	12.1358710765
F29	6.2253631134	5.8936108337	10.9561623618
F30	8.3420500913	5.5157668756	11.1845242113
H31	8.9709135305	7.8090153757	8.5162457101
O32	7.9887253210	10.4981610454	8.8441817194
O33	5.9252574653	10.3032844527	7.9777363511
C34	6.7074484884	10.6439137151	8.8450477261
C35	6.1919934965	11.2658230275	10.1609295744
F36	6.9926264287	12.2317288810	10.5957670427
F37	4.9700926746	11.7513287463	10.0032513805
F38	6.1556906416	10.2979291378	11.0835826571
H39	8.2823847996	9.9290342546	8.0660266532

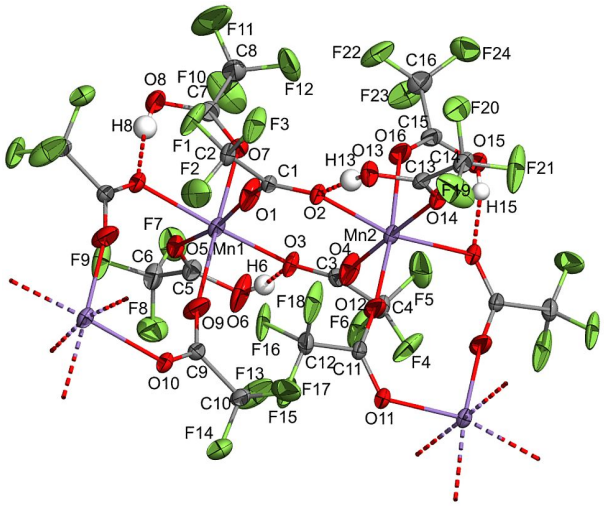


Figure S13. Solid state structure of $Mn_2(HTFA)_4(TFA)_4$. Thermal ellipsoids are shown at 50% probability. Only the major orientation of the disordered CF_3 groups is shown. While only 8 TFA or HTFA units are bound to one of the two Mn atoms in the crystal unit of formula $Mn_2(HTFA)_4(TFA)_4$, we have chosen to shown 10 TFA ligands along with two Mn atoms that do not belong to the crystal unit to help the reader understand the close coordinating environment of each Mn atom.

Table S2. Crystallographic data for $Mn_2(HTFA)_4(TFA)_4$

	$Mn_2(HTFA)_4(TFA)_4$
CCDC number	2131612
Formula	$C_{16}H_4F_{24}Mn_2O_{16}$
FW (g/mol)	1018.64
Temp (K)	100(2)
λ (Å)	0.71073
Size (mm)	0.090 x 0.188 x 0.213
Crystal habit	colorless plate
Crystal system	triclinic
Space group	P -1
a (Å)	10.3615(15)
b(Å)	13.550(2)
c (Å)	13.954(2)
α (°)	105.108(4)

β (°)	111.269(4)
γ (°)	107.177(4)
Volume ($Å^3$)	1588.5(4)
Z	2
Density (g/cm^3)	2.130
μ (mm^{-1})	1.005
F(000)	989
θ range (°)	1.72 to 26.45
Index ranges	$-12 \leq h \leq 12$ $-16 \leq k \leq 16$ $-17 \leq l \leq 17$
Reflns collected	34969
Independent reflns	6519 [$R_{int} = 0.0965$]
Data / restraints /parameters	6519 / 53 / 581
GOF on F^2	1.009
R_1 ($I>2\sigma(I)$)	0.0490
wR_2 (all data)	0.1354