

**Supplementary Information for “Steric Control of Dioxygen
Activation Pathways for Mn^{II} Complexes Supported by
Pentadentate, Amide-containing Ligands”**

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Figure S1. Overlay of electronic absorption spectra obtained during O₂-titration experiments for [Mn^{II}(dpaq)]⁺.

Figure S2. Comparison of the time courses of the reactions of [Mn^{II}(dpaq)](OTf) with excess O₂ in MeCN and *d*₃-MeCN.

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Figure S6. ¹H-NMR analysis of the oxidation of 9,10-dihydroanthracene in the presence of [Mn^{II}(dpaq^{2Me})]⁺ and [Mn^{III}(OH)(dpaq^{2Me})]⁺.

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Table S7. Coordinates for the DFT optimized structure of [Mn^{II}(MeCN)(dpaq^H)]⁺.

Table S8. Coordinates for the DFT optimized structure of [Mn^{II}(MeCN)(dpaq^{2Me})]⁺.

Table S9. Coordinates for the DFT optimized structure of [Mn^{III}Mn^{III}(μ-O)(dpaq)₂]²⁺ without solvent.

Table S10. Coordinates for the DFT optimized structure of [Mn^{III}Mn^{III}(μ-O)(dpaq^{2Me})₂]²⁺.

Table S11. Coordinates for the DFT optimized structure of MeCN.

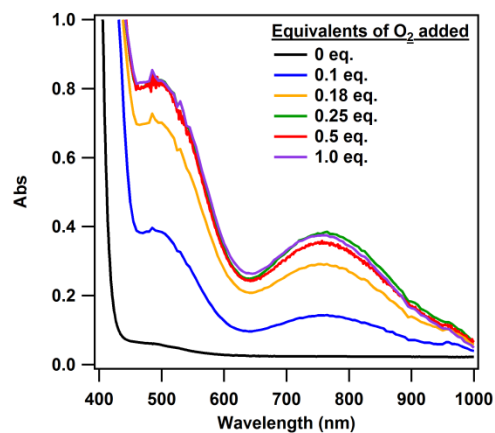


Figure S1. Overlay of electronic absorption spectra obtained during O_2 -titration experiments for $[\text{Mn}^{\text{II}}(\text{dpaq})]^+$ (6 mM in MeCN, 20°C).

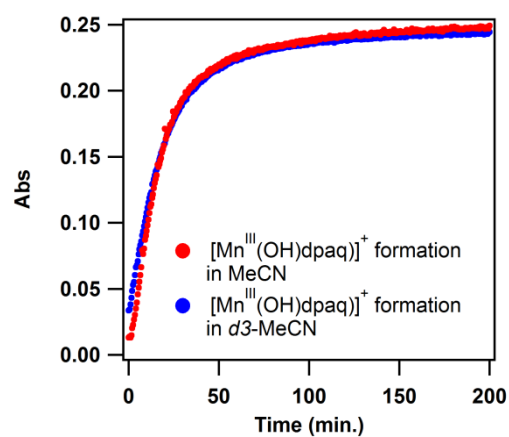


Figure S2. Time course of the reaction of a 6 mM solution of $[\text{Mn}^{\text{II}}(\text{dpaq})]^+$ with excess O_2 in non-deuterated MeCN (red trace) or in d_3 -MeCN (blue trace) at 25°C, monitored at 750 nm).

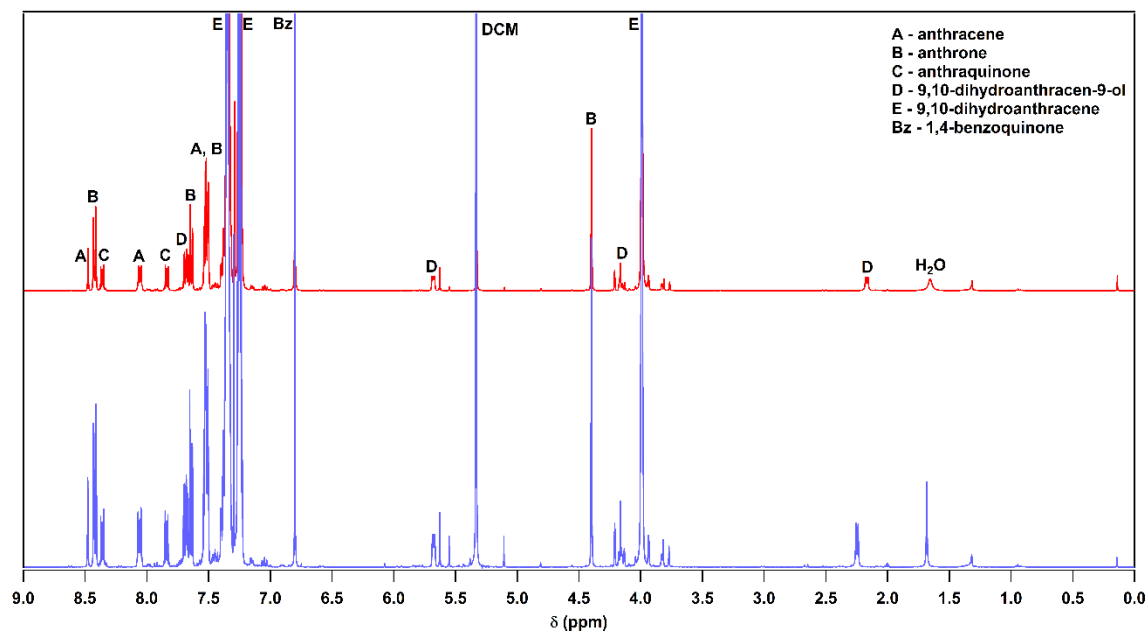


Figure S3. ^1H -NMR analysis of the oxidation of 9,10-dihydroanthracene in the presence of $[\text{Mn}^{\text{II}}(\text{dpaq})]^+$ (top) or $[\text{Mn}^{\text{III}}(\text{OH})(\text{dpaq})]^+$ (bottom) and excess O_2 in d_3 -MeCN (6 mM) at 25°C . Quantification of products was obtained by using 1,4-benzoquinone (10 molar equivalent relative to starting Mn^{II} complex) as an internal concentration reference.

Table S1. Experimental yield of DHA oxidation products during oxygenation experiments.

Complex	Anthracene yield ^a	Anthrone yield ^a	Anthraquinone yield ^a	9,10- dihydroanthran- 9-ol yield ^a	Total DHA converted ^a
<i>O₂ present</i>					
$[\text{Mn}^{\text{II}}(\text{dpaq})]^+$	3.0	12.9	2.0	7.9	25.8
$[\text{Mn}^{\text{II}}(\text{dpaq}^{2\text{Me}})]^+$	3.0	11.5	1.5	7.5	23.5
$[\text{Mn}^{\text{III}}(\text{OH})(\text{dpaq})]^+$	3.1	15.0	2.4	9.4	29.9
$[\text{Mn}^{\text{III}}(\text{OH})(\text{dpaq}^{2\text{Me}})]^+$	4.0	15.7	2.6	11.5	33.8

^a Molar equivalents relative to starting Mn concentration.

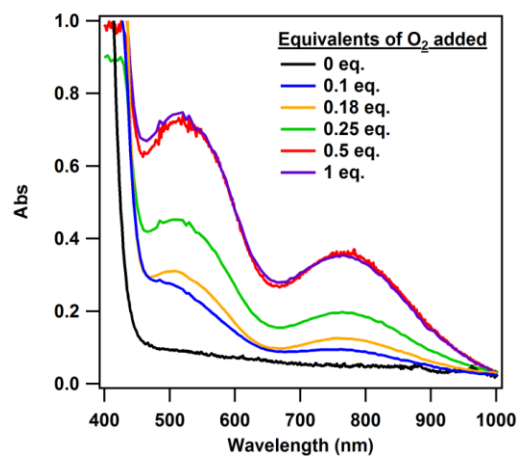


Figure S4. Overlay of electronic absorption spectra obtained during O_2 -titration experiments for $[\text{Mn}^{\text{II}}(\text{dpaq}^{2\text{Me}})]^+$ (6 mM in MeCN, 20 °C).

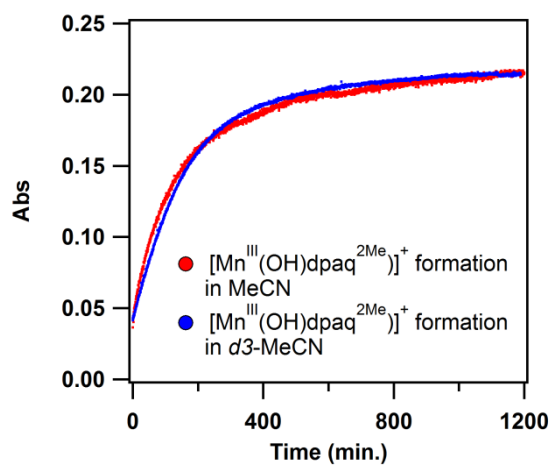


Figure S5. Time course of the reaction of a 6 mM solution of $[\text{Mn}^{\text{II}}(\text{dpaq}^{2\text{Me}})]^+$ with excess O_2 in non-deuterated MeCN (red trace) or in d_3 -MeCN (blue trace) at 25 °C, monitored at 750 nm).

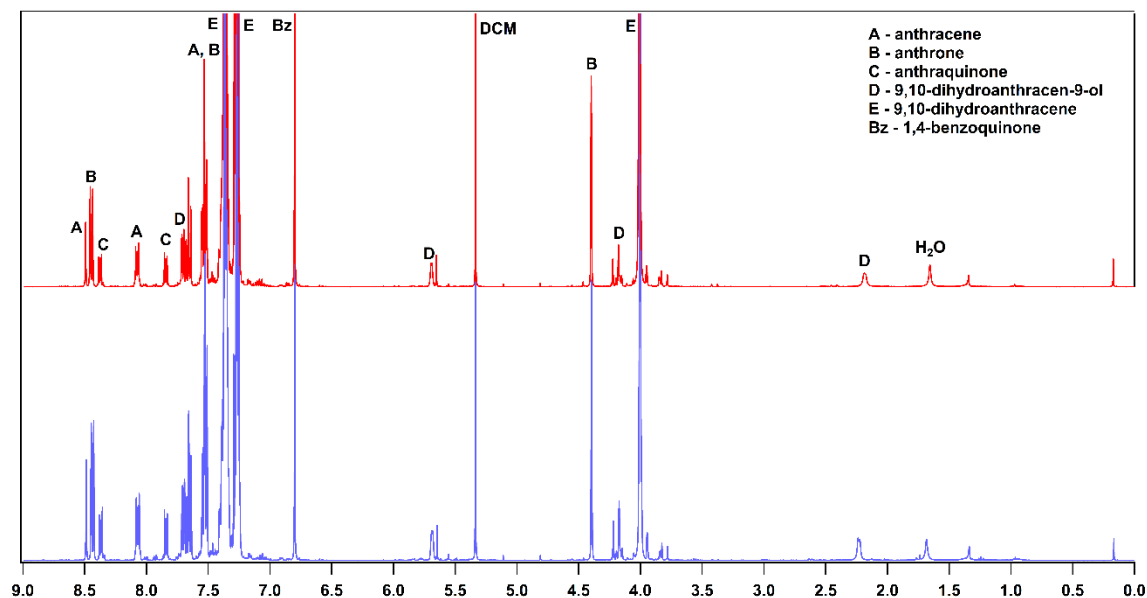


Figure S6. ^1H -NMR spectra after the treatment of $[\text{Mn}^{\text{II}}(\text{dpaq}^{2\text{Me}})]^+$ (top) or $[\text{Mn}^{\text{III}}(\text{OH})(\text{dpaq}^{2\text{Me}})]^+$ (bottom) with 9,10-dihydroanthracene in the presence of and excess O_2 in d_3 -MeCN (6 mM) at 25°C . Quantification of products was obtained by using 1,4-benzoquinone (10 molar equivalent relative to starting Mn^{II} complex) as an internal concentration reference.

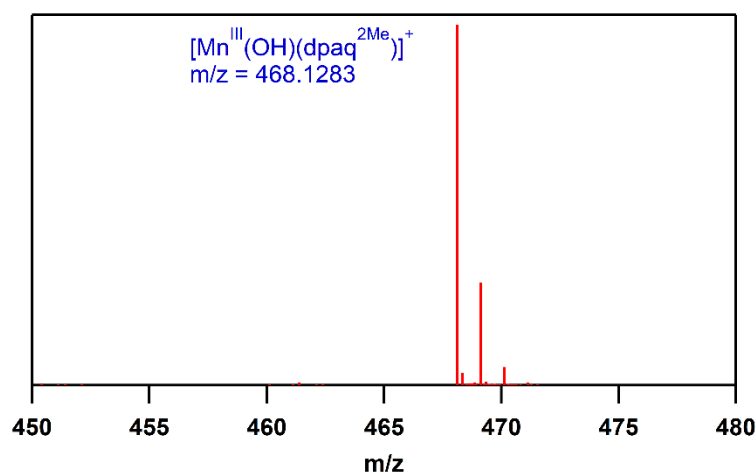


Figure S7. ESI-MS data for $[\text{Mn}^{\text{III}}(\text{OH})(\text{dpaq}^{2\text{Me}})]^+$ from the reaction of $[\text{Mn}^{\text{II}}(\text{dpaq}^{2\text{Me}})](\text{OTf})$ with 1 equivalent of O_2 in the presence of 100 equivalents of DHA in deuterated MeCN.

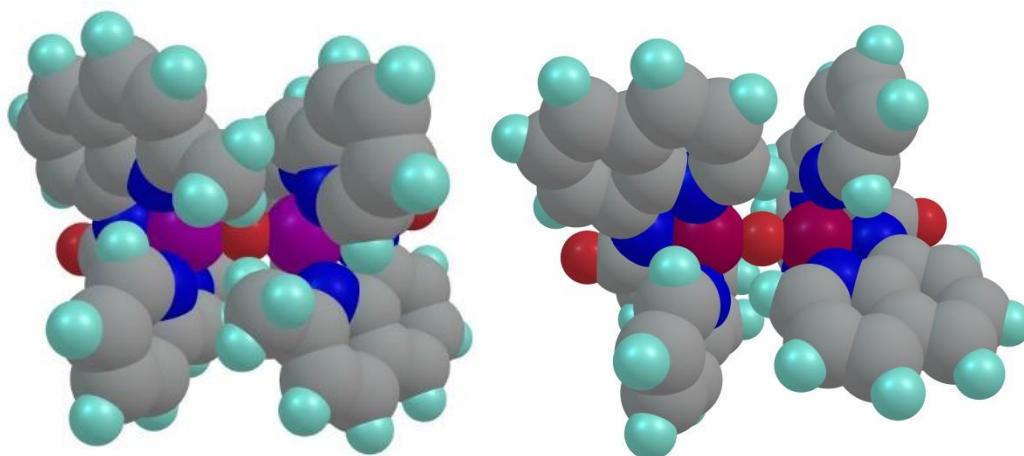


Figure S8. Space-filling model of the DFT-optimized structure of $[\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}(\mu\text{-O})(\text{dpaq}^{2\text{Me}})_2]^{2+}$ (left) and $[\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}(\mu\text{-O})(\text{dpaq})_2]^{2+}$ (right)

Table S2. Key Structural Parameters of DFT Optimized Structures

Distances (Å) and Angles	$[\text{Mn}^{\text{III}}_2(\mu\text{-O})(\text{dpaq}^{\text{H}})_2]^{2+}$	$[\text{Mn}^{\text{III}}_2(\mu\text{-O})(\text{dpaq}^{2\text{Me}})_2]^{2+}$	$[\text{Mn}^{\text{IV}}(\text{O})(\text{dpaq})]^+$	$[\text{Mn}^{\text{IV}}(\text{O})(\text{dpaq}^{2\text{Me}})]^+$
Mn1-O	1.810	1.820	1.703	1.700
Mn2-O	1.810	1.820	-	-
Avg. Mn1-N _{eq}	2.243	2.245	2.038	2.052
Avg. Mn2-N _{eq}	2.244	2.244	-	-
Mn1-N _{ax}	1.981	1.996	2.026	2.022
Mn2-N _{ax}	1.981	1.996	-	-
Mn-O-Mn angle	179.162	166.839	-	-
Mn...Mn	3.621	3.642	-	-
N _{ax} -Mn-O angle	-	-	177.998	175.760

Table S3. DFT calculated reactant and product energies in kcal/mol

	dpaq	dpaq ^{2Me}
	Reactants	Reactants
Mn ^{II} -Solvento	-1581885.78	-1606547.81
Mn ^{IV} -oxo	-1545761.88	-1570421.75
Sum	-3127647.66	-3176969.56
	Products	Products
dimer	-3044370.94	-3093676.66
MeCN	-83296.06	-83296.06
Sum	-3127667.00	-3176972.72
Reaction Energy ^a	-19.34	-3.16
ΔE ^b =16.19		

^a Sum of products minus sum of reactants. ^b Difference in reaction energy for dpaq and dpaq^{2Me}

Table S4. Coordinates for the DFT optimized structure of $[\text{Mn}^{\text{IV}}(\text{O})(\text{dpqH})]^+$ with solvent

	x	y	z
Mn	1.35960602444327	7.48008394022854	9.79189567038362
O	2.45299584501639	3.49984874151863	10.10052148313744
O	0.69481746497581	8.93712581571868	9.21201250022972
N	2.14953262244612	8.21092424323418	11.47987184366914
N	2.17498337124972	5.78216689015642	10.53793287524939
N	0.76495667155053	6.25249568822792	8.24714442421568
N	3.00373804729808	7.66538119463027	8.59233459592081
N	-0.43869418762729	6.87016264171167	10.54762617891158
C	2.08169182009934	9.48682814770678	11.87961723805709
C	2.67057388260580	9.91693090201453	13.08944724975437
H	2.58956345234131	10.97430841598043	13.37748175564091
C	3.33987081201544	8.99633112380197	13.89086754437795
H	3.80608888384730	9.31155744867512	14.83702332674183
C	3.42747870139403	7.63147893108975	13.49040608553752
C	4.08830973151599	6.61261997373232	14.23839724577320
H	4.57089398498258	6.87322690623160	15.19200431041552
C	4.11129310416077	5.30881323987993	13.75017986732790
H	4.62114945142620	4.52254593161208	14.32803393966980
C	3.49465502467219	4.95177867891269	12.52139810737618
H	3.52924361163971	3.91624623781637	12.16193681910899
C	2.83298508353772	5.92382085200596	11.75247525219414
C	2.80502871220517	7.27156162773321	12.25051220960579
C	2.03277882802998	4.64138168512908	9.82511532862664
C	1.24300442635816	4.84063528595568	8.51890514932724
H	0.36907045643246	4.16041750204446	8.53867020808299
H	1.88040525268130	4.50615547014840	7.67708182025315
C	1.38482729278229	6.82731852222884	7.01379065336416
H	1.32540141097442	6.11529322752527	6.16650621528601
H	0.80698037006034	7.73462144088626	6.74552242336714
C	2.79852254717268	7.23756566931738	7.31847585461423
C	3.83283642732853	7.24781122325641	6.37408316682162
H	3.64073399261634	6.88264197261824	5.35521763309042
C	5.09610656724044	7.72895439328092	6.75116532279439
H	5.92201571674711	7.74870301996023	6.02501863939676
C	5.28888313024951	8.17706009450693	8.06676950231426
H	6.25965522021462	8.56207691383038	8.40878232917649
C	4.21629145637943	8.12227008552621	8.96400725053125
H	4.32500416398624	8.45312008367183	10.00478551678914

C	-0.72724873921349	6.34356093377131	8.21239875204585
H	-1.16267828117274	5.54749569571530	7.57588327967609
H	-0.98747224204911	7.32487704888043	7.76716988909871
C	-1.25522853319758	6.30499899991054	9.61932596132270
C	-2.50823989433139	5.78897100518533	9.97330137782058
H	-3.14112880095656	5.32540759575300	9.20336862568135
C	-2.93031207709954	5.87816040292406	11.30877457527190
H	-3.91154298080022	5.48167904375369	11.60849860489364
C	-2.07999343085854	6.47318280472827	12.25305949017359
H	-2.36573195177149	6.56481399381473	13.31021747061609
C	-0.83380941551249	6.95248634814917	11.83379870401427
H	-0.13283342764298	7.41526245567816	12.54023366804574
H	1.54206380774010	10.16872177860842	11.20731992398699

Table S5. Coordinates for the DFT optimized structure of $[\text{Mn}^{\text{IV}}(\text{O})(\text{dpaq}^{\text{H}})]^+$ without solvent

	x	y	z
Mn	1.36323446000081	7.47734730924183	9.79760056465443
O	2.45310385976281	3.50017550291913	10.09769823211329
O	0.69084632315536	8.91193510704997	9.19450209419889
N	2.14590033619393	8.21118384029271	11.47387564813758
N	2.17544102977526	5.78409534460570	10.53888460344250
N	0.76166428947809	6.24946735069923	8.24122868743711
N	3.00953783447942	7.66367240032470	8.59712560003299
N	-0.43773509695351	6.86787149455633	10.55423194301635
C	2.07160194250952	9.49085007990144	11.86531476511030
C	2.65967765501655	9.92349377531957	13.07504224079187
H	2.57797385084107	10.98125522371400	13.36285020251947
C	3.33121084279799	9.00511414722234	13.87995842034949
H	3.79497360794265	9.32702343603508	14.82566627044902
C	3.42538144251703	7.63838247295800	13.48815692500852
C	4.08680593935144	6.62024645577211	14.23488273227553
H	4.57051249102686	6.87711814595772	15.18889683757070
C	4.11071446014827	5.31569765677931	13.74551451211317
H	4.62254133746128	4.53201796740978	14.32487504462258
C	3.49593693811084	4.95333531740907	12.51869969923450
H	3.52823756977285	3.91848693731149	12.15418927140500
C	2.83233848559073	5.92554426600418	11.74933173346765
C	2.80324482469046	7.27391348311566	12.24702781733782
C	2.03813607161800	4.63020577802081	9.82941183733326
C	1.23854464080133	4.83648287733828	8.51601623375684

H	0.36530287369426	4.15508753597262	8.54401072908258
H	1.87595459524406	4.49544335296407	7.67634318144907
C	1.38318033236631	6.84387181538851	7.02060834525208
H	1.31566525293715	6.15521025637574	6.15203756460353
H	0.81775360575503	7.76970968151933	6.78666565761089
C	2.80438168590401	7.23821187394760	7.32365533475416
C	3.83828637528639	7.24161619770914	6.37859393075574
H	3.64713598155099	6.87995790187257	5.35771293067799
C	5.10526800225658	7.71532941263555	6.75371324938921
H	5.93141041829729	7.73058958681314	6.02748017296482
C	5.29893882650776	8.16200836785686	8.06890436083896
H	6.27284905779154	8.54116967735543	8.40927238593612
C	4.22476299133407	8.11243366886039	8.96538810534368
H	4.33159262451520	8.43965252782012	10.00772923814172
C	-0.72702831053248	6.36467418047992	8.21689005113173
H	-1.18561329262319	5.59124739519928	7.56515136035946
H	-0.96721918051516	7.36704614229343	7.80569232324671
C	-1.25514272830626	6.30696763054590	9.62569153886383
C	-2.50640699403156	5.78440550792533	9.97678750119812
H	-3.14264745114960	5.32455021076577	9.20656383654530
C	-2.92922156372192	5.86320651653570	11.31301137489629
H	-3.90936544053689	5.46263203455302	11.61137920518875
C	-2.07891033943668	6.45463881438776	12.25849202554263
H	-2.36569254419283	6.53825478641725	13.31626564354706
C	-0.83410344459081	6.93921061646654	11.83936642345362
H	-0.12965366117652	7.39837179949510	12.54500852663248
H	1.52782059946825	10.16146840726344	11.18297094599652

Table S6. Coordinates for the DFT Optimized structure of $[\text{Mn}^{\text{IV}}(\text{O})(\text{dpaq}^{2\text{Me}})]^+$

	x	y	z
Mn	1.35075884184000	7.50073691723344	9.77913780069959
O	2.45982923706545	3.52134289315172	10.12071885444901
O	0.62752767808231	8.85447895584507	9.04812902721307
N	2.14604568207191	8.27439670928205	11.49690210797527
N	2.16633632615091	5.80956592069346	10.53082011290192
N	0.76771515230972	6.23763699244807	8.24414829917053
N	3.00319718999940	7.67151574735641	8.58851967203666
N	-0.44231937422540	6.88120691824123	10.54144025848612
C	2.09918032119982	9.55421455836617	11.93859357778854
C	2.72315466425880	9.90837366282197	13.16929193672684

H	2.66599299690289	10.95592535939471	13.49590589197163
C	3.38423585755696	8.96451472044050	13.93597746463652
H	3.86409981143734	9.24788512847671	14.88538651641763
C	3.44485713626903	7.61469833931305	13.49374003314734
C	4.10379147724401	6.58197818024319	14.22267814236553
H	4.59302342744361	6.83148145571103	15.17599492203838
C	4.11645260717934	5.28612148100245	13.71879956626019
H	4.62363253379503	4.48471211905656	14.27775513208844
C	3.48575486396349	4.96717558908228	12.49029175053834
H	3.50299360490205	3.94134561385741	12.10410784976885
C	2.82594920800849	5.95911366804567	11.74251920886720
C	2.80367756721748	7.30416791815347	12.24990060404526
C	2.03277312957670	4.65887606446189	9.83279765428678
C	1.24271117408024	4.83246422435724	8.52704558500526
H	0.36973876377998	4.15136405581445	8.56012430051346
H	1.87842698348603	4.48518574730595	7.68904614144559
C	1.39321026962823	6.80646972198135	7.01189912427630
H	1.33991813611287	6.08971218782040	6.16834285233956
H	0.81616627693129	7.71263975017515	6.73948184103688
C	2.80490014833688	7.22261815660630	7.32063574060766
C	3.84576462831644	7.21721813561642	6.38330290693980
H	3.66095554526914	6.83492010125063	5.36936278125552
C	5.10677523337136	7.70488461685703	6.76017160691152
H	5.93700762116332	7.71287837160432	6.03872644107158
C	5.29182540066363	8.17394893347219	8.06949196178005
H	6.26057688012881	8.56437217254658	8.41112601137897
C	4.21355945636811	8.13256196670827	8.96090978070379
H	4.31513364664417	8.47726864040293	9.99803600929761
C	-0.72344021217695	6.33075711583206	8.20857348882627
H	-1.15982201356906	5.53117202476680	7.57712647618815
H	-0.98054810571572	7.31142434187848	7.76074887230300
C	-1.25209705215461	6.30110892575174	9.61607876400456
C	-2.50011823513434	5.77550197970388	9.97398600495958
H	-3.12819545314850	5.29881618710873	9.20808147362514
C	-2.92455359511011	5.87151836449235	11.30841845885807
H	-3.90238444475770	5.46823744378182	11.61020733294704
C	-2.08052884302635	6.48089998814319	12.24908784290465
H	-2.36786690851211	6.57752108992205	13.30537411870709
C	-0.83801744323475	6.96753366677807	11.82684055862470
H	-0.13936579193747	7.43907709894824	12.52994403338518

C	1.39662574332789	10.62035197239316	11.15310345211349
H	0.32579753152024	10.37436602030179	11.01736673674714
H	1.81575868315049	10.70462076078285	10.13237243592674
H	1.4858222252211	11.59215410204698	11.67082122521181

Table S7. Coordinates for the DFT optimized structure of $[\text{Mn}^{\text{II}}(\text{MeCN})(\text{dpaq}^{\text{H}})]^{+}$

	x	y	z
Mn	-0.33849605898677	0.03722807106679	0.07907911104541
O	0.82225296854107	-1.13720317593218	-3.86247144108616
N	-0.88595607919012	2.11556370654106	-0.49839208881899
N	-0.04115113628409	0.08955830189518	-2.05344538079484
N	0.38126642915475	-2.16076421946078	-0.34874880562973
N	-2.20018050333562	-1.21934110396389	0.09877979350398
N	1.90252280995689	0.11432826574724	0.36498261623393
C	-1.32272973598155	3.07441833950778	0.31944148895090
H	-1.44928338172810	2.79559933875317	1.37702801654170
C	-1.61352202979245	4.38807361276028	-0.12145067436057
H	-1.97291300701777	5.13695487376529	0.59877964291616
C	-1.43331768080533	4.69643524380499	-1.46312689470074
H	-1.64677984665347	5.70743673968216	-1.84438911325713
C	-0.96599113556437	3.69760055609556	-2.36687787325033
C	-0.75619992719646	3.94271984034244	-3.75574618467644
H	-0.95931437151366	4.94486865871094	-4.16306910164241
C	-0.29916906962903	2.90948665482635	-4.56559269908536
H	-0.13432130703488	3.08985935801509	-5.63977505840339
C	-0.03537834914529	1.61454086082700	-4.04835946246047
H	0.32421937800170	0.81886217037547	-4.71056692393474
C	-0.22830903908287	1.31502107982549	-2.68549189925221
C	-0.70021969928880	2.38788328768963	-1.83085953259089
C	0.43237694642670	-1.01504295653973	-2.67421490596283
C	0.39874357338582	-2.30615369166059	-1.82980548919449
H	1.24342475289657	-2.95227831479256	-2.15030501726356
H	-0.52798929430204	-2.83206865180293	-2.14122135082288
C	-0.61249906823594	-3.05922380043680	0.28385874234529
H	-0.42029115763246	-3.06011015328749	1.37757641427739
H	-0.51153540775874	-4.11190857082818	-0.06058606341915
C	-2.02571114284092	-2.56193490972016	0.05688771101573
C	-3.10778564636685	-3.43709143573451	-0.13199032973661
H	-2.93224237233242	-4.52214330186947	-0.17449285038245
C	-4.40077005772032	-2.90689335384046	-0.26347998706365

H	-5.26289379370695	-3.57435544578609	-0.41226316049003
C	-4.57332259803322	-1.51455306593778	-0.21023377034891
H	-5.56610368867921	-1.05316432801844	-0.31089339771584
C	-3.44115612612061	-0.70906399349437	-0.03312632173427
H	-3.52504279686810	0.38807657012683	0.00514677555672
C	1.72767049685831	-2.31183376447009	0.24815525596571
H	1.59379793325377	-2.52830821238223	1.32875402667465
H	2.27782440562569	-3.17458882423220	-0.18732305984444
C	2.55826555404676	-1.04917161908605	0.14235530158941
C	3.94299023497780	-1.08054382504543	-0.08988228233768
H	4.44454142090366	-2.04108952848476	-0.27939900029507
C	4.66609560440597	0.12277824873353	-0.07126788030478
H	5.75168935541915	0.12221414325184	-0.25140282432528
C	3.98108855044632	1.32303172306317	0.17579887478893
H	4.50452444064660	2.28947715483654	0.20287430449909
C	2.59604402686434	1.26982993004883	0.38126323367322
H	2.01427946790052	2.18609883196353	0.56672429707316
N	-0.61379221097172	0.42554304336266	2.24898883297601
C	-0.68929033640019	0.36292018629494	3.40804105952331
C	-0.78365331247664	0.28391759171637	4.85198740296615
H	0.22446636709431	0.38914377044687	5.29939619835432
H	-1.21254903702979	-0.69459811025842	5.14580912217281
H	-1.43673051146896	1.09550638963451	5.22956547811428

Table S8. Coordinates for the DFT optimized structure of $[\text{Mn}^{\text{II}}(\text{MeCN})(\text{dpaq}^{2\text{Me}})]^+$

	x	y	z
Mn	2.03214048487284	7.52888100568184	8.04260400550537
O	3.39537306054175	3.49425775142484	7.58185626966659
N	1.86250203550998	7.44185250452337	10.25698477551090
N	2.72838154593486	5.54771857618240	8.51450196039318
N	2.59340633369576	6.68526984802529	5.91765745758345
N	4.09326053350021	8.35664916568074	7.57955600758314
N	0.11300449777126	6.53628076610507	7.29161260582880
C	1.45632050697555	8.42657919119589	11.07614185524069
C	1.32870891065733	8.21515127288267	12.47807952998602
H	0.99549949026394	9.04619405970467	13.11607362699233
C	1.62317250415488	6.97442553363140	13.01757133263405
H	1.52742321092982	6.79388213778439	14.09980735316647
C	2.06012475785502	5.91637898999083	12.17117258408143
C	2.38340827210581	4.61966425828266	12.66767889201735

H	2.29048994897632	4.41938153323735	13.74602442786779
C	2.80871108222652	3.63955728389222	11.77994398762042
H	3.06098064676455	2.63370466970967	12.15157845442637
C	2.93007684857730	3.90277847930394	10.39208117031815
H	3.26937260073618	3.11649770962678	9.70838930261298
C	2.62587926536868	5.16725695017065	9.84866134529234
C	2.17335861652499	6.19863501912441	10.76447669417321
C	3.10278403557796	4.71594720214891	7.51781549475652
C	3.26691215743161	5.37817357001992	6.13470141986846
H	2.95468046995624	4.64306408311588	5.36267959741874
H	4.36040043990306	5.51457582897166	6.00069333506165
C	3.49791150494934	7.68580107777089	5.30805166669884
H	4.00436473277572	7.29845798337159	4.39660886345407
H	2.88002646104646	8.55074201331776	4.98795110166046
C	4.52448213343719	8.18300979525751	6.30700130647468
C	5.84188734627163	8.49302890931165	5.93008924897918
H	6.16596884411782	8.32860727070886	4.89178815081647
C	6.72567453739172	9.00841524401059	6.89097073088513
H	7.76171206627149	9.25825018037118	6.61677374635328
C	6.26909823046388	9.18858016433176	8.20618577821369
H	6.92542736811407	9.58363123165636	8.99478537771222
C	4.94489864909865	8.84177676047877	8.50458002707968
H	4.54717631458188	8.95291851905697	9.52527397197525
C	1.32290462779959	6.54913466647869	5.17199588178241
H	1.43973042260045	5.90874964106563	4.26983668195189
H	1.03348665382078	7.55932683690293	4.81411896198372
C	0.19168757182443	6.03004116211114	6.03815554179881
C	-0.76705501289705	5.12715560223753	5.54890925097766
H	-0.66975822724864	4.72447653862925	4.52977523304838
C	-1.84039618482354	4.75525516783266	6.37411779858155
H	-2.60278354090743	4.04941513615034	6.01123484765281
C	-1.91953056251891	5.29297170902714	7.66823851589613
H	-2.74070038386900	5.03164399475028	8.35109631547374
C	-0.91360117508724	6.17554229689976	8.08533796229623
H	-0.92718145133035	6.61243229287700	9.09610912826555
C	1.12422139788337	9.76733506837197	10.47843714629208
H	0.19903974408758	9.70762705661586	9.86857377106189
H	1.93424168838820	10.12335325350378	9.81141266126475
H	0.96237755620728	10.52492440537651	11.26702541655469
N	1.19034680584344	9.42066310114413	7.19734855053111

C	0.73549911735771	10.37692978339727	6.71755339402424
C	0.16814748627770	11.57034060844608	6.12256301226186
H	-0.30906762867439	12.18945434251179	6.90778879726885
H	-0.59367502311986	11.28706294016809	5.36955724022475
H	0.96710604325255	12.15918716579876	5.63010596217147

Table S9. Coordinates for the DFT optimized structure of $[\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}(\mu\text{-O})(\text{dpaq})_2]^{2+}$ without solvent

	x	y	z
Mn	-0.13148684918908	-0.22576284511502	-3.65847403991850
O	-0.07813021789512	-0.11524302638309	-1.85228020834012
O	-0.11401442971771	-1.66691587720587	-7.52293931269269
N	-0.03770749531744	1.79110004651017	-4.08025057955805
N	-0.10751194841451	-0.29104415962284	-5.63837280673350
N	-0.38527758936530	-2.42877917481379	-3.93242459553467
N	-2.43747260251530	-0.59794758233814	-3.87090888421612
N	2.02903196177366	-1.07633813184544	-3.86782026489422
C	-0.05767003352930	2.79884581742232	-3.20126161294948
C	0.02098344160954	4.15061548066175	-3.60519982726819
C	0.13024464222658	4.45389363510562	-4.95951912751634
C	0.14912321433683	3.40696589012271	-5.92299691482346
C	0.24760329226970	3.60684119323188	-7.33037927383139
C	0.23970509634733	2.50322330538867	-8.17626672121796
C	0.13092546391941	1.17319873532347	-7.68813682550828
C	0.03171066218793	0.93328561412061	-6.30702869721831
C	0.05206683887913	2.06146832657661	-5.42826128100472
C	-0.19158112985150	-1.49306386573714	-6.30750428102796
C	4.36084828387405	-2.44791009043603	-4.57865410316408
C	4.30749382836427	-1.04743332146182	-4.65293062380490
C	-0.45146781735824	-2.70586611313748	-5.40370568447723
C	-1.64884752606072	-2.79286543987553	-3.23984778331952
C	-2.77235022021503	-1.89860257025348	-3.72192836385621
C	-4.06424073175988	-2.36813074031843	-4.00665605421140
C	-5.03206493325702	-1.45738432556473	-4.46224353380184
C	-4.67251730064733	-0.11055064642303	-4.62753046018148
C	-3.35876231192481	0.27359202324965	-4.32139840217396
C	0.79377219023557	-3.07947309324611	-3.31078537394707
C	2.07019028173400	-2.42610711455606	-3.79960605102210
C	3.22151655793927	-3.14927157206973	-4.14963464860494
C	3.11458414824888	-0.40373369865149	-4.29272730452449

Mn	-0.00112237479213	-0.01662548148757	-0.04632227633213
O	1.34050176591279	-0.08235436270352	3.85314479339896
N	-2.02138090611598	0.17242194671229	0.32411749283066
N	0.01756769326288	0.02679958739458	1.93415082532184
N	2.20697326693965	-0.06754090116381	0.27632014558558
N	0.69010227989295	2.22216670865471	0.10503686030601
N	0.52600837982787	-2.26826199374023	0.25723778724048
C	-2.99898972899184	0.28341694219080	-0.58186386372838
C	-4.35728543268282	0.40362522235595	-0.21141298284446
C	-4.70053052792082	0.40052445227837	1.13773229367747
C	-3.68601479276907	0.28752757531499	2.12898080256160
C	-3.92707844857164	0.28153658984679	3.53335974435067
C	-2.85074011009768	0.17899096027396	4.40772505978463
C	-1.50844203711325	0.08390140418373	3.95144862084826
C	-1.22809094898242	0.08714752121624	2.57437563897645
C	-2.32965001200049	0.18079248627136	1.66701206345169
C	1.20498069558930	-0.03169166828834	2.63142513859209
C	1.53620391000517	-4.74139546640684	1.08518990742313
C	0.15608096534748	-4.48869461550990	1.11776206875848
C	2.46107271345157	0.01398063307087	1.75098482948211
C	2.75936589865288	1.10567122400480	-0.45046645364817
C	2.02795128566433	2.36163409571273	-0.02384002516414
C	2.67378665274264	3.58122591361079	0.23324814367505
C	1.90418646279207	4.68406426938915	0.63963333075613
C	0.51684994525555	4.52714829328981	0.78526533923330
C	-0.04728933466592	3.27312539770321	0.50881557348790
C	2.69545434245900	-1.34984670082348	-0.28736869473802
C	1.85750462455732	-2.50163067807073	0.22839963962780
C	2.40190282855494	-3.72933486454117	0.63742707983637
C	-0.30353341786353	-3.23142147769610	0.69907127221610
H	-0.13382335104801	2.50869635525630	-2.14529093405882
H	-0.00321982986639	4.94331856249657	-2.84434681082789
H	0.19771368900894	5.49993800107810	-5.29717746236149
H	0.32573940964442	4.62904684732458	-7.72921958904284
H	0.31528026591807	2.65261012403860	-9.26408306174855
H	0.11941210827235	0.32624215963865	-8.38331437248915
H	5.27326772451224	-2.99106442612023	-4.86756164296082
H	5.16982723007412	-0.45968365512199	-4.99960039326652
H	0.26627115221438	-3.50252570701325	-5.68390168427921
H	-1.45621828675484	-3.09123937218861	-5.66979431413741

H	-1.48606939610930	-2.63388996577198	-2.15350543060886
H	-1.90395918015023	-3.86424657729619	-3.39524375934229
H	-4.30624889954275	-3.43489395222571	-3.88602466280223
H	-6.05003579280941	-1.80033229680217	-4.70135727435838
H	-5.39250864255550	0.63232134083282	-5.00050495783374
H	-3.02611284390311	1.31615223639483	-4.44362687329046
H	0.70366494569236	-2.94075581474063	-2.21441785315725
H	0.80818368269753	-4.17248899876580	-3.51587683705662
H	3.22170393814210	-4.24862264276520	-4.09958479752517
H	3.01736350005308	0.69159504101936	-4.35746367891791
H	-2.67963115352267	0.26983211794903	-1.63210180039787
H	-5.12369967937858	0.49639026014596	-0.99361979192944
H	-5.75297116825207	0.48884534261247	1.44971354421599
H	-4.95863436588385	0.36020649517925	3.90722104484888
H	-3.03180584815514	0.17382615936456	5.49333889768831
H	-0.68268062935497	0.01095912530787	4.66807188261056
H	1.93766277102843	-5.70971151882467	1.42013454935556
H	-0.55580119543141	-5.24620976053366	1.47643161517153
H	3.13711646600774	-0.80172805441244	2.07630824679111
H	2.98554013200542	0.96025641556097	1.99225056754795
H	2.59423390356361	0.92890534131213	-1.53366406976861
H	3.85373575160371	1.21044093167881	-0.28187357312654
H	3.76633182893741	3.66336207237189	0.12995772131713
H	2.38606439197512	5.64934804529704	0.85658027412802
H	-0.12093437728784	5.35786528873235	1.12068075022172
H	-1.12899968956032	3.09804774560658	0.61780744191856
H	2.59107392023073	-1.28420655943953	-1.38906257438389
H	3.77109096536524	-1.51056452740382	-0.05501083524774
H	3.49094561174120	-3.88659289132361	0.61803178968730
H	-1.37520846439050	-2.97839698015079	0.72845919579306

Table S10. Coordinates for the DFT optimized structure of $[\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}(\mu\text{-O})(\text{dpaq}^{2\text{Me}})_2]^{2+}$

	x	y	z
Mn	0.41220044617117	-0.21033826752801	-0.52857578097427
O	-0.32315569244777	-1.88360843001615	3.16192357515265
O	0.59535249213018	-0.12742348770207	-2.34992393297917
N	0.12414787005791	1.84628934512569	0.02285524177574
N	-0.03311395316932	-0.39264296480955	1.39013245773001
N	1.00266536135105	-2.36315016106261	-0.20535216437697
N	2.67295921248367	-0.23476185380100	0.08247600821595

N	-1.57909976908622	-1.41336377696375	-0.61250161500806
C	0.43170061217907	2.99044503661501	-0.61889618353735
C	-0.12633860134375	4.23222099234374	-0.20075301685909
C	-0.96509552573823	4.29371578726929	0.90118363497439
C	-1.22177217944568	3.11719536626675	1.65751045767708
C	-1.99193462644451	3.09426683213226	2.85547192993562
C	-2.11549304584694	1.90482704916719	3.56322561821172
C	-1.48698887816352	0.70871263756493	3.13044517191714
C	-0.73736433839772	0.68719307625557	1.94044667899001
C	-0.62661197605917	1.89899078198423	1.18485550310627
C	0.09314283279988	-1.60401570970005	2.03828753131089
C	0.90736623161291	-2.64219745022386	1.25832417340515
C	2.39044831147245	-2.49940098183003	-0.70883175324264
C	3.25894329735073	-1.44433507366812	-0.05680692030574
C	4.56613665893593	-1.69227467527351	0.39055286684373
C	5.28499426814235	-0.64906209246379	0.99797869474960
C	4.66392984678149	0.59969183906701	1.15345203930019
C	3.35098040525921	0.75709947206067	0.68570446579637
C	0.03966831745421	-3.17651240142219	-0.97915570695624
C	-1.37772408546448	-2.74936198536760	-0.66503579121215
C	-2.41499206968420	-3.66393801324053	-0.42315100815293
C	-3.69583921890930	-3.17837370384429	-0.11487586287454
C	-3.89304460507213	-1.79098853794932	-0.04457800968040
C	-2.80187639499189	-0.94667413935219	-0.29455553981977
C	1.44931508799789	2.95690566210804	-1.72071731141213
H	0.13340012047866	5.14233575201868	-0.76060039623023
H	-1.40505609416178	5.25156088252951	1.22020753080368
H	-2.46044804829552	4.02279838522279	3.21411952989371
H	-2.69643476502975	1.88212265919961	4.49766323995956
H	-1.56116719504275	-0.20425085396424	3.73136373808317
H	0.47826655605647	-3.64646390770167	1.44887510411204
H	1.92359593927265	-2.64484637089728	1.70052221431459
H	2.79833393698891	-3.51725566737954	-0.52073821601864
H	2.36380114817372	-2.34142054400737	-1.80743218718032
H	5.00959398936072	-2.69323911871863	0.27809924725483
H	6.30953072805952	-0.81658588366144	1.36310108580810
H	5.17954591735645	1.43811030847945	1.64368647468538
H	2.81328198741684	1.70934450319933	0.80870165079924
H	0.17315293825341	-4.26287081591576	-0.78088329645334
H	0.24336759727247	-2.99332558898551	-2.05150187195882

H	-2.21484420368618	-4.74521409249144	-0.45896301245278
H	-4.52244108429031	-3.87509204769886	0.09036706827355
H	-4.87136016398549	-1.36343011273923	0.21868694481892
H	-2.90654199508281	0.14723575847484	-0.22111269247966
H	1.42907586095625	1.99005061529800	-2.25392514456088
H	2.46501418986181	3.08402303439304	-1.28718170250940
H	1.30236833071672	3.78852625882513	-2.43467842692735
Mn	0.45924922935298	-0.30296933104086	-4.16919188345232
O	-1.36852735052183	-0.72863671416523	-7.83699944661900
N	2.42125916086650	-0.96822819331279	-4.74625586644550
N	0.17151113408842	-0.71410403387622	-6.08359840780160
N	-1.55532473458487	0.67012184934048	-4.46930830861251
N	0.83992540169697	1.91738976351947	-4.79495660049768
N	-1.07691503406382	-2.03604115264659	-4.05198549781565
C	3.61016943460729	-0.87880448833034	-4.11863656274197
C	4.72251823887217	-1.65588172416831	-4.55100522480965
C	4.61433086684864	-2.49070175968461	-5.65227662641611
C	3.40092958870005	-2.52614086450456	-6.39285868487548
C	3.22094041063176	-3.28051895973027	-7.58748038286194
C	2.01933391713767	-3.18497717015734	-8.27873309666603
C	0.96478586973848	-2.34735464343832	-7.83239057867678
C	1.09740681216010	-1.60417136268764	-6.64551767680312
C	2.31942916414163	-1.71629512359753	-5.90662572355097
C	-1.00472908096248	-0.37015748952545	-6.71749848679955
C	-1.87080809064565	0.61721395600121	-5.92747335129036
C	-1.42853897747420	2.06256965286111	-3.97748728263929
C	-0.23905322823427	2.71724183676910	-4.64785573903534
C	-0.24657559017978	4.04515034673386	-5.10287534817475
C	0.90456620467618	4.55573115463599	-5.72594837924865
C	2.01586208384411	3.71427221820195	-5.88819123524272
C	1.93355356865286	2.39753765062777	-5.41207553006941
C	-2.51487827751376	-0.12513690738144	-3.67340355435355
C	-2.35433397595479	-1.59831489794004	-3.98033633976333
C	-3.44333658160341	-2.45733889833997	-4.19665288911167
C	-3.19959918799965	-3.80659074512291	-4.49936450942030
C	-1.87119262859469	-4.24932233775370	-4.58911641549163
C	-0.84128395421956	-3.32487019319580	-4.36388165852784
C	3.77660401466436	0.12397868523739	-3.01529364261456
H	5.67171737089594	-1.56926531811700	-4.00259887128965
H	5.47037642759443	-3.09975610188011	-5.98247191806187

H	4.04271419328572	-3.91209263177391	-7.95640333595834
H	1.87734643945463	-3.75343427714408	-9.21033171757066
H	0.04527999856983	-2.25498029900233	-8.42067562634075
H	-2.93767107317339	0.36905583796944	-6.09886270747758
H	-1.70432682221134	1.61591612515034	-6.37836939660610
H	-2.35606114082127	2.64928724205724	-4.15955468646104
H	-1.26568887473273	2.01536038765541	-2.88032307776799
H	-1.14726365187892	4.66630966603608	-4.98394742711627
H	0.92478714858826	5.59139090752576	-6.09750651002447
H	2.92976366082017	4.06368517465343	-6.39001831912768
H	2.76914255859467	1.69287352458106	-5.53936990983899
H	-3.56309833107658	0.19980111624847	-3.85498403283980
H	-2.27770934294876	0.04848259485880	-2.60636873728008
H	-4.47073279029809	-2.06693306351887	-4.14585803579894
H	-4.03617293531185	-4.49684593803003	-4.68512837635548
H	-1.62994975383557	-5.29031259134370	-4.84863915366367
H	0.21506984627266	-3.62345856845025	-4.45278270950643
H	2.82663622343862	0.28217211643753	-2.47458624827439
H	4.08793174684138	1.09956069079823	-3.44772776964405
H	4.57158666824356	-0.17826720626212	-2.30847353530974

Table S11. Coordinates for the DFT optimized structure of MeCN

	x	y	z
N	-0.09694215968529	-0.19742181423489	-3.76390254275031
C	-0.14531143047964	-0.08882550572601	-2.60478394823602
H	-1.20494662505969	0.41521774069234	-0.85226823220838
H	-0.02442748243863	-0.93693554233534	-0.67768496790188
H	0.56435043108885	0.76257317111549	-0.81069460546224
C	-0.20595573342560	0.04539195048840	-1.15669670344116