SUPPORTING INFORMATION FOR

Unraveling the Catalytic Mechanisms of H_2 Production with Thiosemicarbazone Nickel Complexes

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DFT calculations

All theoretical calculations were performed exactly as in our previous publication. All calculations were performed with ORCA 4.2.1,[1,2] using BP86 as our functional, with def2-TZVP basis set.[3-6] Solvation in DMF was modelled using the CPCM implicit solvation model.[7] Single-point Broken-Symmetry DFT calculations were performed to evaluate all possible spin configurations using the "FlipSpin" feature of ORCA.[8,9] All chemical structure images were generated using Chemcraft.[10]

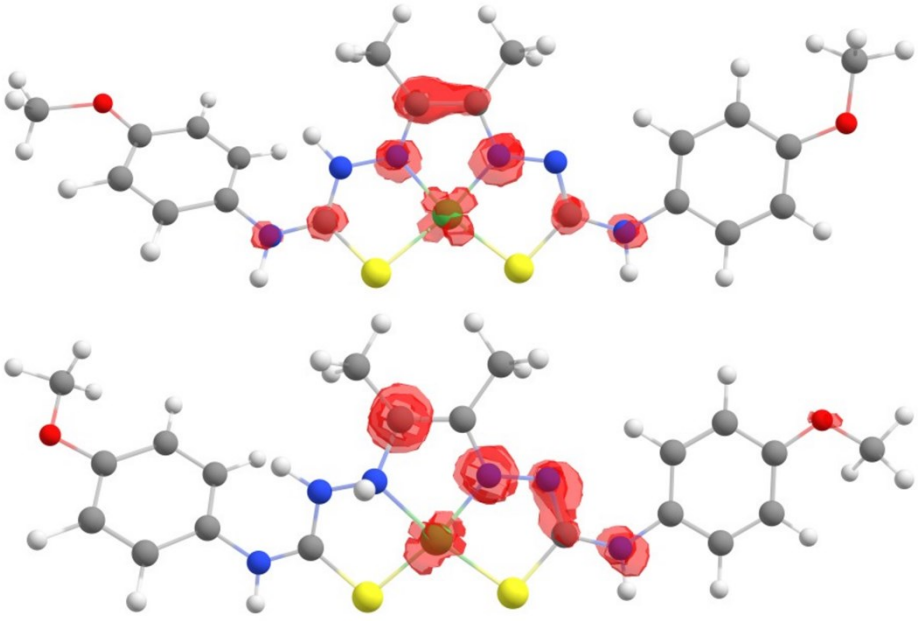

Figure S1. Spin densities for the one-electron reduced **$NiOCH_3$** for the first (top) and second (bottom) protonation in the two-proton mechanism.

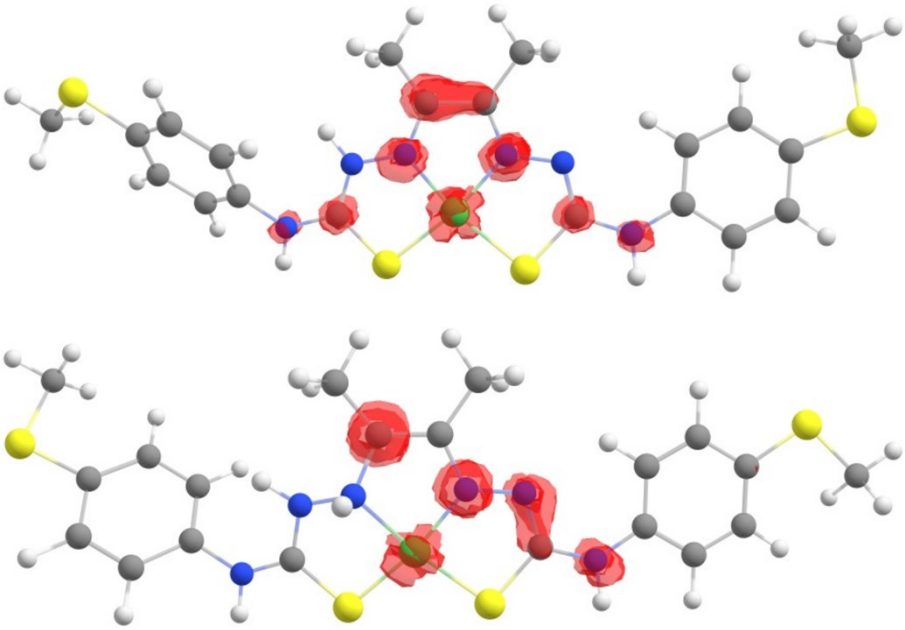

Figure S2. Spin densities for the one-electron reduced **NiSCH$_3$** for the first (top) and second (bottom) protonation.

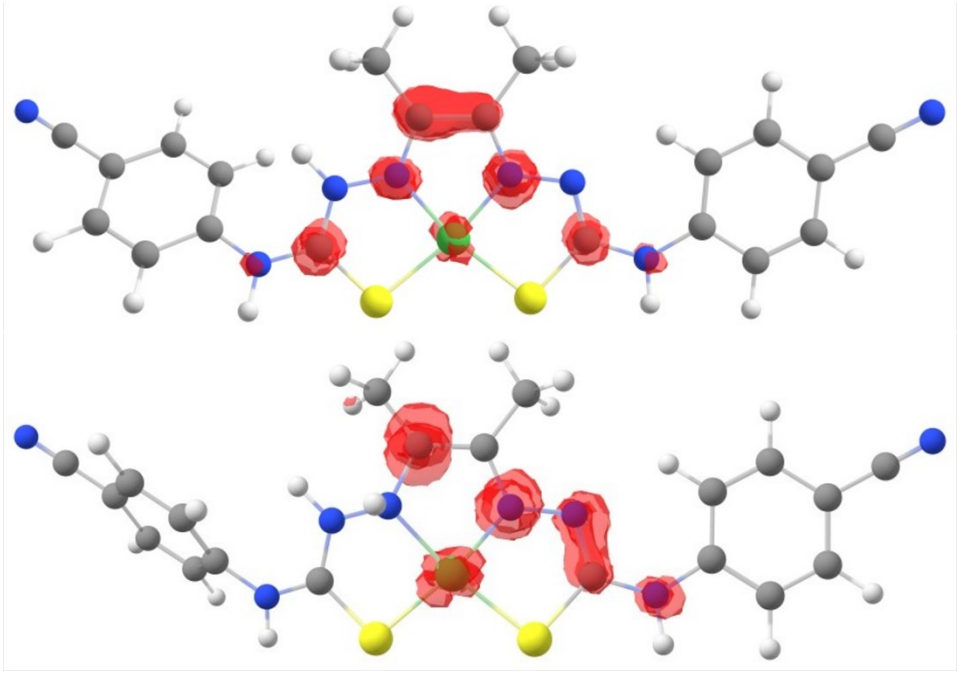

Figure S3. Spin densities for the one-electron reduced **NiCN** for the first reduction for the first (top) and second (bottom) protonation.

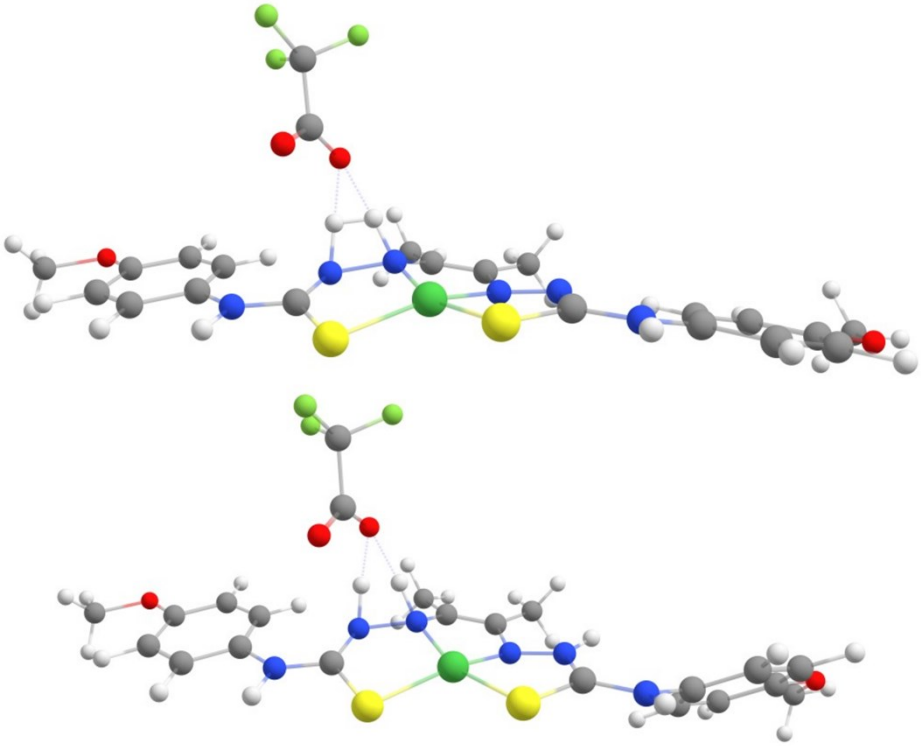

Figure S4. Representation of highest energy configuration in the potential energy surface of H-H distance scan for **$NiOCH_3$** for the two- (top) and three- (bottom) proton mechanisms.

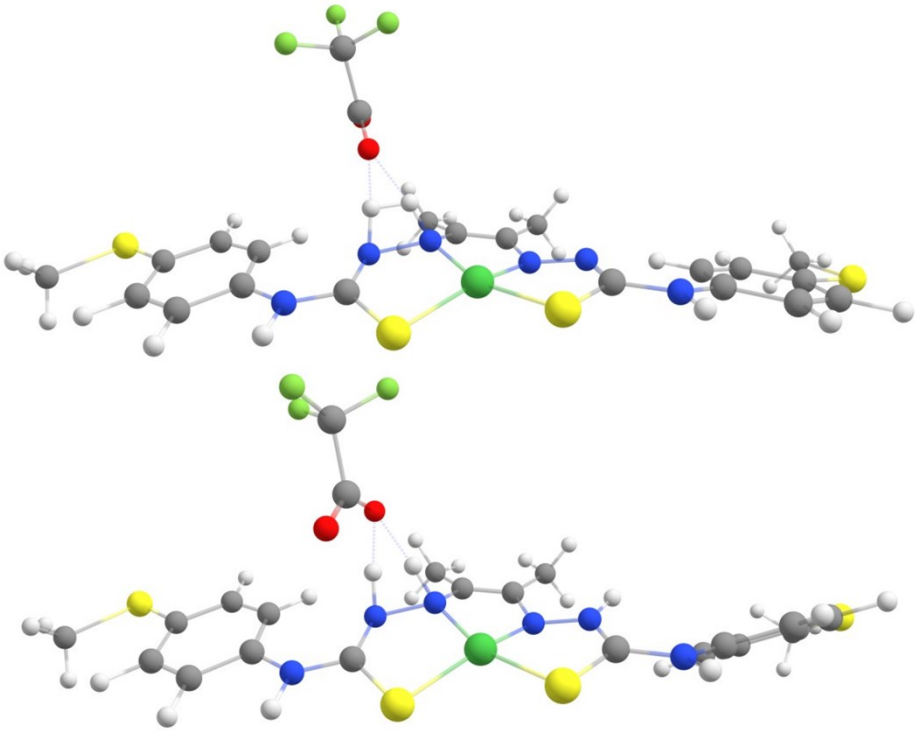

Figure S5. Representation of highest energy configuration in the potential energy surface of H-H distance scan for **$NiSCH_3$** for the two- (top) and three- (bottom) proton mechanisms.

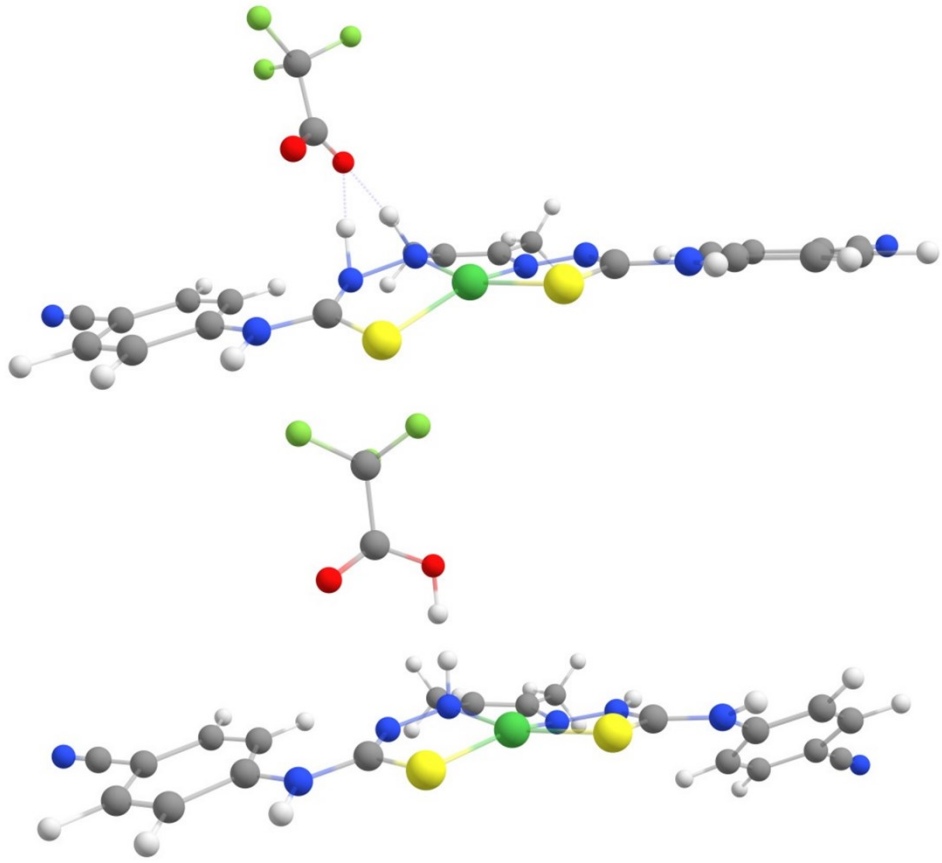

Figure S6. Representation of highest energy configuration in the potential energy surface of H-H distance scan for **NiCN** for the two- (top) and three- (bottom) proton mechanisms.

Table S1. PES scan for the distance between the two protons forming H_2 for the two-proton mechanism in **$NiOCH_3$**, in the presence of **TFA^-.**

H-H (Å)	E (Hartree)
0.75	-4087.83753728
0.80	-4087.83624443
0.85	-4087.83268344
0.90	-4087.82701003
0.95	-4087.72734559
1.00	-4087.73591171
1.05	-4087.74530472
1.10	-4087.75377425
1.15	-4087.76150638
1.20	-4087.76844687
1.25	-4087.77474948
1.30	-4087.78038249
1.35	-4087.78543603
1.40	-4087.78996483
1.45	-4087.79396574
1.50	-4087.79749039
1.55	-4087.80136115
1.60	-4087.80519918
1.65	-4087.80862434
1.70	-4087.81165992
1.75	-4087.81436238
1.80	-4087.81668842
1.85	-4087.81869727
1.90	-4087.82041406
1.95	-4087.82180825
2.00	-4087.82287038
2.05	-4087.82364181
2.10	-4087.82407527
2.15	-4087.82425747
2.20	-4087.82418560
2.25	-4087.82388469
2.30	-4087.82332388
2.35	-4087.82256230

Table S2. PES scan for the distance between the two protons forming H_2 for the two-proton mechanism in **$NiSCH_3$**, in the presence of **TFA^-.**

H-H (Å)	E (Hartree)
0.75	-4733.84265352
0.80	-4733.84159026
0.85	-4733.83798945
0.90	-4733.83265900
0.95	-4733.73162567
1.00	-4733.74192942
1.05	-4733.75122779
1.10	-4733.75974983
1.15	-4733.76744458
1.20	-4733.77437765
1.25	-4733.78066151
1.30	-4733.78408439
1.35	-4733.78968321
1.40	-4733.79457897
1.45	-4733.79919179
1.50	-4733.80420104
1.55	-4733.80824250
1.60	-4733.81145749
1.65	-4733.81487125
1.70	-4733.81800498
1.75	-4733.82067999
1.80	-4733.82303368
1.85	-4733.82503226
1.90	-4733.82669621
1.95	-4733.82807548
2.00	-4733.82912040
2.05	-4733.82985964
2.10	-4733.83032120
2.15	-4733.83049462
2.20	-4733.83038326
2.25	-4733.83006523
2.30	-4733.82943614
2.35	-4733.82859187

Table S3. PES scan for the distance between the two protons forming H_2 for the two-proton mechanism in **NiCN**, in the presence of **TFA^-.**

H-H (Å)	E (Hartree)
0.75	-4043.26370697
0.80	-4043.26221335
0.85	-4043.25877678
0.90	-4043.25294367
0.95	-4043.19338674
1.00	-4043.16926112
1.05	-4043.17856874
1.10	-4043.18695943
1.15	-4043.19460019
1.20	-4043.20146027
1.25	-4043.20768003
1.30	-4043.21323353
1.35	-4043.21606925
1.40	-4043.22096496
1.45	-4043.22563701
1.50	-4043.23008936
1.55	-4043.23428106
1.60	-4043.23812796
1.65	-4043.24160657
1.70	-4043.24468604
1.75	-4043.24738246
1.80	-4043.24970983
1.85	-4043.25172043
1.90	-4043.25337782
1.95	-4043.25469316
2.00	-4043.25573122
2.05	-4043.25643116
2.10	-4043.25685680
2.15	-4043.25697712
2.20	-4043.25673850
2.25	-4043.25631583
2.30	-4043.25578886
2.35	-4043.25489679

Table S4. PES scan for the distance between the two protons forming H_2 for the three-proton mechanism in **NiOCH$_3$**, in the presence of **TFA$^-$.**

H-H (Å)	E (Hartree)
0.75	-4088.27415006
0.80	-4088.27280243
0.85	-4088.27032577
0.90	-4088.26477662
0.95	-4088.21500051
1.00	-4088.19219190
1.05	-4088.20166144
1.10	-4088.21012290
1.15	-4088.21786042
1.20	-4088.22441340
1.25	-4088.23067030
1.30	-4088.23628797
1.35	-4088.24132027
1.40	-4088.24408295
1.45	-4088.24882872
1.50	-4088.25329681
1.55	-4088.25762289
1.60	-4088.26156171
1.65	-4088.26514224
1.70	-4088.26822037
1.75	-4088.27100017
1.80	-4088.27340206
1.85	-4088.27552227
1.90	-4088.27720712
1.95	-4088.27856674
2.00	-4088.27964558
2.05	-4088.28040926
2.10	-4088.28089166
2.15	-4088.28104205
2.20	-4088.28096406
2.25	-4088.28063788
2.30	-4088.28013211
2.35	-4088.27945572

Table S5. PES scan for the distance between the two protons forming H_2 for the three-proton mechanism in **NiSCH$_3$**, in the presence of **TFA$^-$.**

H-H (Å)	E (Hartree)
0.75	-4734.27983707
0.80	-4734.27849036
0.85	-4734.27323503
0.90	-4734.21347003
0.95	-4734.21987548
1.00	-4734.19728504
1.05	-4734.20625212
1.10	-4734.21473349
1.15	-4734.22242789
1.20	-4734.22931317
1.25	-4734.23553743
1.30	-4734.24112773
1.35	-4734.24614967
1.40	-4734.24893134
1.45	-4734.25369744
1.50	-4734.25821784
1.55	-4734.26250983
1.60	-4734.26644245
1.65	-4734.26998347
1.70	-4734.27307139
1.75	-4734.27586989
1.80	-4734.27823095
1.85	-4734.28028216
1.90	-4734.28199178
1.95	-4734.28337107
2.00	-4734.28441893
2.05	-4734.28517535
2.10	-4734.28561584
2.15	-4734.28579351
2.20	-4734.28567094
2.25	-4734.28532437
2.30	-4734.28471785
2.35	-4734.28401656

Table S6. PES scan for the distance between the two protons forming H_2 for the three-proton mechanism in **NiCN**, in the presence of **TFA^-.**

H-H (Å)	E (Hartree)
0.75	-4043.69234846
0.80	-4043.69100020
0.85	-4043.62809346
0.90	-4043.63604264
0.95	-4043.64251239
1.00	-4043.64802989
1.05	-4043.65270292
1.10	-4043.63488683
1.15	-4043.64247453
1.20	-4043.64930557
1.25	-4043.65546823
1.30	-4043.66064677
1.35	-4043.66349549
1.40	-4043.66842586
1.45	-4043.67326303
1.50	-4043.67789097
1.55	-4043.68210140
1.60	-4043.68607491
1.65	-4043.68962798
1.70	-4043.69280791
1.75	-4043.69560031
1.80	-4043.69800793
1.85	-4043.70000124
1.90	-4043.70169845
1.95	-4043.70304958
2.00	-4043.70406362
2.05	-4043.70480878
2.10	-4043.70512689
2.15	-4043.70523236
2.20	-4043.70500574
2.25	-4043.70452533
2.30	-4043.70373137
2.35	-4043.70282241

Table S7. Cartesian coordinates of **$NiOCH_3$** in neutral form, in the presence of **TFAH (Q=0, S=0).**

C	-2.81974764629026	18.13382992858585	4.57820916482388
C	-2.22683840500557	19.22857621857752	3.93269034412357
C	-3.01317121838559	20.02065661943799	3.06958310236088
C	-4.35193553501637	19.72696386461631	2.85918758239227
C	-4.94672715639518	18.62858885735412	3.50779000623494
C	-4.17058174104543	17.83701457924068	4.36647380187445
N	-0.87785406360788	19.61229855491939	4.08000987862985
C	0.14285315919956	19.07509625044369	4.79067913950391
N	-0.02551379033505	17.98890507286720	5.53292903814803
N	1.13276030527446	17.63010269805829	6.14164658371460
C	1.17470138556822	16.55279452828891	6.91184847443183
C	-0.02321674489514	15.69778947673901	7.15486273995877
O	-6.27064947410909	18.41760367945607	3.23938419028987
C	-6.91336042457949	17.30641876957118	3.88650750913173
Ni	2.74502653961234	18.55230741216226	5.97534162963616
S	1.70371569186447	19.92002723022091	4.65392325442753
N	3.37771459241335	17.23629101348325	7.13918522246937
C	2.49621234917378	16.30700329747215	7.47420792238761
C	2.81306141969044	15.11481353263131	8.31393582740513
N	4.66446304771023	17.20998007800661	7.61856276888515
C	5.41433134778528	18.16369185122963	7.05809641817608
S	4.75798493254806	19.35089328459083	5.93201417445498
N	6.72992169835745	18.27710972572532	7.34612668195427
C	7.61752265753991	17.39629451865127	8.01109541007009
C	8.80794185895894	17.94286186693897	8.51162366316981
C	9.76210487350675	17.13841825221503	9.13594668904308
C	9.53004811786500	15.76032072898347	9.26798761475636
C	8.34211979624021	15.20914312939506	8.75536490656010
C	7.39569801023696	16.01279105894566	8.13096708984487
O	10.39052576777113	14.88364459232861	9.86599562063483
C	11.61312865666698	15.41250149497986	10.40753488771587
H	-0.62132329907102	20.44428377297987	3.55018450654034
H	7.15956910895755	19.13533032501997	7.00308541500469
H	10.67503314497024	17.59547181011076	9.51379120840339
H	-2.56101846152609	20.87431893483272	2.56039848738847
H	-4.95539477455764	20.34216501958575	2.19041887251007
H	-4.60378071542380	16.98128177794626	4.88178537744975
H	8.99261044128571	19.01425152906454	8.41088809259845
H	-2.22563204725806	17.51446515725159	5.24530960637246
H	-0.86942175532629	16.31606363847773	7.48815210520423
H	0.17831049315454	14.93362843999018	7.91245559067161
H	-0.33900320942940	15.19800871423814	6.22540256031734
H	6.49063750076142	15.56357191349036	7.72737935954633
H	2.28571270146460	14.23040021503931	7.93320134857684
H	2.49210372781542	15.26604806349151	9.35696045762158
H	3.88962541317893	14.91299418158995	8.31275304867495
H	8.17412142669850	14.13519542805705	8.84792673262284
H	-7.95088592998874	17.32134503370057	3.53688469127419
H	-6.88863063486374	17.41864419251223	4.98126379266200
H	-6.43939782658899	16.35466595065854	3.60138694933624
H	12.22771703294365	15.87353830158635	9.61934452823899
H	12.14242993817778	14.55388829573875	10.83334312865696
H	11.40762941478772	16.15114117173072	11.19723800656611
H	4.81246783228955	17.00816048257231	9.14991130186692
O	4.83701176482683	16.83602548890941	10.20519685983905
C	4.90585572804732	17.95236815237016	10.89326518802378
O	4.96458824135658	19.09707614725097	10.48354518306951
C	4.90080652902078	17.64348580040773	12.42572823981097
F	5.00127631907243	18.77541071095855	13.14949257631378
F	3.75206817240414	17.01585596988023	12.78965228398542
F	5.93769771450166	16.83583221444155	12.76687116364283

Table S8. Cartesian coordinates of **$NiOCH_3$(H)** after first PCET step in the presence of **TFA^- (Q=-1, S=1/2)**.

C	7.33447942191252	16.01776424794305	8.18188808875188
C	7.59317380765219	17.39689161282822	8.08904700870143
C	8.79413667472449	17.89757151935662	8.61199416330489
C	9.72320075134802	17.05216041428993	9.22310298457251
C	9.45306896730094	15.67942033668105	9.32506476967195
C	8.25385250305447	15.17398889413825	8.79476989925152
N	6.73514934104701	18.30658276319107	7.42835558385546
C	5.41934849543353	18.20799710370590	7.09541307162506
S	4.80340830985390	19.23228347318471	5.82984473781766
Ni	2.71557717576503	18.64897288156498	6.03737663638675
N	3.25886612229691	17.45571484465288	7.35480127780525
N	4.59246039376099	17.36343562149992	7.73168866326865
O	10.28688322804378	14.76391738904181	9.91301427543608
C	11.51613248417402	15.25099133381846	10.47344879192259
N	1.10210718876272	17.72476261742253	6.19298399212628
C	1.10004548190083	16.69955402594725	7.07915583150399
C	2.37651537694290	16.47145794185325	7.66346862285299
C	2.75858481245310	15.28276550114170	8.48674991157714
N	-0.06426007807035	18.10651537383363	5.59514085595023
C	0.10075624315638	19.17056645143872	4.83607147070836
S	1.65268738423796	20.03597966317103	4.73406363584758
N	-0.91706998664240	19.69002612907885	4.07502624128448
C	-2.23633517188106	19.25805755067707	3.86876694306032
C	-2.80584005103404	18.12325704897263	4.46898418670916
C	-4.13542994470783	17.76899260020078	4.20195369421799
C	-4.91738325256045	18.54055801537323	3.33353088199477
C	-4.35070122481504	19.67887472232419	2.73083125683761
C	-3.03449167936627	20.03008600684663	2.99470990590122
O	-6.22562472319929	18.27489647008057	3.01115544599428
C	-6.83136151766722	17.12022760613723	3.61068390567583
C	-0.15068151164781	15.93344380825174	7.37440792432810
O	4.93684257029814	16.82594761030158	10.34080641309207
C	5.13189670920091	17.82498793248715	11.09579119647110
C	5.25916971944588	17.41375822579640	12.61039231919658
F	6.27732868418374	16.52592469128219	12.80938575173653
O	5.22610589228830	19.03431698133525	10.82771912147269
F	5.49279102761831	18.46799775010633	13.43443987739185
F	4.11666387109076	16.81059983002722	13.05878587846901
H	-0.66164275806020	20.53427267505804	3.56810645353931
H	7.19278134264524	19.13068353217232	7.04292203691364
H	10.64588871375911	17.47606118936953	9.61611247252673
H	-2.60798735909445	20.91633377519337	2.51882759779826
H	-4.95797402799185	20.28144713690875	2.05339324990002
H	-4.54548197501700	16.88290963186259	4.68478403262026
H	9.00913042887592	18.96564222224055	8.53773139590079
H	-2.20494749923800	17.52051116169874	5.14605734653667
H	-0.91693291029505	16.58918663219090	7.81821053380714
H	0.04195680074019	15.11230488465880	8.07390058930010
H	-0.58803858947631	15.51575938422981	6.45425572796026
H	6.42095163482773	15.59676529712361	7.76505356446743
H	3.64078033522881	14.78493516801325	8.05105360085535
H	1.94333279167797	14.55254891770800	8.52645840785393
H	3.02892432521506	15.56140242980796	9.51666028321540
H	8.05322910915801	14.10375780581676	8.86561855947316
H	-7.85749118789444	17.09066791105981	3.22877725608885
H	-6.84774319279161	17.20468982739257	4.70870889257206
H	-6.30256226906575	16.19829903035079	3.32166444004780
H	12.15144052416951	15.70945753440834	9.69958616007856
H	12.02009943685594	14.37272331896216	10.89062566559847
H	11.32441036375649	15.98282867174793	11.27355085778053
H	4.78850746565873	17.10087887204086	8.76326265839347

Table S9. Cartesian coordinates of **$NiOCH_3(H)$** after the first PCET and a second reduction, in the presence of **TFA^- (Q=-2, S=0)**.

C	-2.59793498508368	18.00452485996371	4.20827153809940
C	-1.74527166955506	18.56086176097362	3.23599348669207
C	-2.30376647645677	18.89904930086397	1.97906226632719
C	-3.65001841963657	18.69303728174060	1.71058350215253
C	-4.49638108947357	18.13899043285924	2.68884353123161
C	-3.95901460113507	17.79856356645484	3.93481455871389
N	-0.38401220407008	18.79943193616785	3.42360327558377
C	0.43935848835341	18.59641492654056	4.52848868020216
N	0.01949792361970	18.01080201892032	5.62160693045284
N	0.94602166317593	18.07240334892770	6.64422532429266
C	0.78005986771302	17.21351998492891	7.71494835338002
C	-0.50778435483102	16.46469966236352	7.89303070479889
O	-5.81642847495249	17.97289660997833	2.32550218995569
C	-6.69798412957847	17.41013057272736	3.30503225289791
Ni	2.70253228559135	18.68780985898926	6.40331641352962
S	2.10912046523679	19.18369419323348	4.35687345484259
N	3.02920227791144	17.67241080678932	7.95719597571860
C	1.89379862077417	17.13013166987147	8.55104427845129
C	1.92164197594096	16.58703463527696	9.94653221498532
N	4.14493524891684	17.95333249115724	8.69940334189383
C	5.05211079065495	18.79026673045850	8.17057016956455
S	4.62128668224234	19.66662194024772	6.74486024485480
N	6.32973155098909	18.82997234837682	8.74550426938450
C	7.31890679452644	17.85356390393382	8.50120060244410
C	8.62647552239334	18.06772983098319	8.96508331805862
C	9.63489227862030	17.12001615311194	8.76093306166310
C	9.34532711639648	15.92424822843041	8.08833852635929
C	8.04120679994423	15.70484540575639	7.61839089584947
C	7.04143114443631	16.65495018321667	7.81763694739218
O	10.26034974551666	14.92250356513792	7.84089914810695
C	11.59794970566455	15.12591652883799	8.31296855580259
H	0.10123527449180	19.19487524140983	2.62311057691769
H	6.70258391109314	19.76912865266447	8.86702944590933
H	10.63740356381205	17.32684137804559	9.13368496294462
H	-1.66227911817752	19.33138907104489	1.20701026594668
H	-4.06488125622081	18.96014999406966	0.73679236562818
H	-4.58606839215665	17.36557399830724	4.71366779416989
H	8.86254505064771	18.99290309968957	9.49637728275600
H	-2.18405556856784	17.73279929464562	5.17726160411193
H	-1.37708768422816	17.14107901944026	7.86340513432768
H	-0.52295052047603	15.92227752414618	8.84662131561486
H	-0.65968948957176	15.72973668619667	7.08508291062230
H	6.03844814816299	16.46489459102354	7.43442004286341
H	2.65979669643089	15.77890963843704	10.07543125741204
H	0.93753789287496	16.19605664020277	10.23201307095405
H	2.19327415379618	17.36873678089078	10.67879123317533
H	7.81858876979413	14.77782017677817	7.08635537737386
H	-7.68296572307329	17.36012116305610	2.82783472702955
H	-6.75561394532681	18.04564368674575	4.20346609194450
H	-6.37764091268888	16.39671164213229	3.59616661436864
H	12.05663072373966	16.01261127351525	7.84635151249686
H	12.15699173865135	14.22934659856439	8.02312587104428
H	11.62280692089169	15.23726273648203	9.40902018181067
H	4.38066086912636	17.42232093966524	9.58652176312063
O	5.02547087577853	16.51703883547919	10.92526235767133
C	5.07316165568342	17.08125482600350	12.05053651313828
O	4.65424705361690	18.19523916043223	12.42381054898831
C	5.81121272656687	16.21210332666889	13.13943621027069
F	5.69936912041647	16.71064113678828	14.40087210688667
F	5.33782092335511	14.93108466972105	13.18560555061681
F	7.15122999771200	16.12472248053379	12.87310529620288

Table S10. Cartesian coordinates of **$NiOCH_3(H)$** after the first PCET step, in the presence of **TFAH (Q=0, S=1/2)**. Structure preceding the second protonation and reduction of the complex in the two-proton mechanism.

C	7.12759655555565	16.13208556561478	7.92447335327420
C	7.29794270234892	17.52044721309349	7.78305894579340
C	8.30924431582373	18.16546980393635	8.50554629272546
C	9.13614168954034	17.44869926167302	9.37221951745981
C	8.94756241951627	16.06605571436411	9.53168358368321
C	7.93893178523447	15.41647026290499	8.79825672102345
N	6.51740018208666	18.29490238426908	6.88008871106833
C	5.19724702996112	18.20884103143332	6.61560642795865
S	4.49476312818031	19.24653588967185	5.41956888067216
Ni	2.42561161027368	18.67092377366917	5.76067984537322
N	3.00841888768295	17.53929182919910	7.16569715035196
N	4.41884659971696	17.32684905348639	7.27490196117049
O	9.69069023666578	15.27517991030494	10.35906421039642
C	10.73712504504492	15.90150060323895	11.12205773883475
N	0.86183049908648	17.68656679038205	5.89961152732178
C	0.93789369940012	16.57091634072517	6.68906656501317
C	2.20619354145096	16.38437721055747	7.24602001638045
C	2.71270939927484	15.15372760585313	7.91690675911013
N	-0.31265066879421	18.01037234922780	5.32288286690846
C	-0.20948379789039	19.11119174774154	4.58587094583856
S	1.29051057716614	20.04178989784772	4.49432987126972
N	-1.26439342958504	19.58252419774867	3.85941889003690
C	-2.57156795137652	19.09647674135744	3.67852400264312
C	-3.09451310740524	17.95531978788047	4.30646210373393
C	-4.41366077026244	17.55438601523716	4.06248465659275
C	-5.23053806512168	18.28623734477146	3.18998427515753
C	-4.70860989972159	19.43109434642968	2.55946942653058
C	-3.40170479294083	19.82781687965829	2.80058204106787
O	-6.53017141888340	17.97381947936169	2.89060839599778
C	-7.09513075781280	16.81167310298617	3.51820361058300
C	-0.25598719585180	15.69145218886697	6.88539857359416
O	2.49553496949102	18.98060675501194	9.28088691683347
C	3.24255802430709	18.54270253770695	10.26223673353391
C	2.93551044206204	19.31313401741500	11.58493370238505
F	1.65261150783975	19.09910274572661	11.97520577914601
O	4.08411387530928	17.65551753695124	10.23587757610796
F	3.74665418572253	18.91161069896034	12.58235215406852
F	3.10145944362791	20.64958251970825	11.42108157800987
H	-1.06058064749341	20.43794540533549	3.34620804324356
H	6.99401515505373	19.06710773478927	6.41630505264341
H	9.91397645340879	17.97732838319994	9.92037375949022
H	-3.00769926303187	20.71735909979540	2.30392759906729
H	-5.34310086172615	20.00115168140729	1.87923226595276
H	-4.78962342346184	16.66465403786729	4.56536275341726
H	8.45274059372982	19.24117259787500	8.38986038848102
H	-2.46880943241896	17.38189781616744	4.98591863792244
H	-1.07102298373808	16.24933395468480	7.37152390868863
H	-0.01168115950360	14.82584770039981	7.51063813617947
H	-0.64360480343603	15.33421532300681	5.91977593218083
H	6.38497743319396	15.59989730622060	7.32997067770398
H	1.94354873337209	14.37530194491901	7.94894236081605
H	3.04357425309950	15.35418772550009	8.94885539706785
H	3.58048758741789	14.74697667742415	7.37113284518406
H	7.81154265930380	14.33901307318557	8.90991735197935
H	-8.12379089851197	16.74627366884897	3.14838010034361
H	-7.10121208624012	16.91668350655302	4.61421473307556
H	-6.54220871004081	15.90170805727267	3.23816381013065
H	11.48895307043695	16.35803700634310	10.46050588134566
H	11.19743767229046	15.09719550638684	11.70494090756354
H	10.32734021022679	16.66462704608412	11.80088092625968
H	2.67899074027644	18.40982449195865	8.37349371915360
H	4.71978921106864	17.03134811980139	8.21505550445948

Table S11. Cartesian coordinates of **$NiOCH_3(H_2)$**, after first PCET step, followed by a proton transfer, in the presence of **TFA^- (Q=0, S=1/2)**. Structure preceding the second reduction.

C	7.12759655555565	16.13208556561478	7.92447335327420
C	7.29794270234892	17.52044721309349	7.78305894579340
C	8.30924431582373	18.16546980393635	8.50554629272546
C	9.13614168954034	17.44869926167302	9.37221951745981
C	8.94756241951627	16.06605571436411	9.53168358368321
C	7.93893178523447	15.41647026290499	8.79825672102345
N	6.51740018208666	18.29490238426908	6.88008871106833
C	5.19724702996112	18.20884103143332	6.61560642795865
S	4.49476312818031	19.24653588967185	5.41956888067216
Ni	2.42561161027368	18.67092377366917	5.76067984537322
N	3.00841888768295	17.53929182919910	7.16569715035196
N	4.41884659971696	17.32684905348639	7.27490196117049
O	9.69069023666578	15.27517991030494	10.35906421039642
C	10.73712504504492	15.90150060323895	11.12205773883475
N	0.86183049908648	17.68656679038205	5.89961152732178
C	0.93789369940012	16.57091634072517	6.68906656501317
C	2.20619354145096	16.38437721055747	7.24602001638045
C	2.71270939927484	15.15372760585313	7.91690675911013
N	-0.31265066879421	18.01037234922780	5.32288286690846
C	-0.20948379789039	19.11119174774154	4.58587094583856
S	1.29051057716614	20.04178989784772	4.49432987126972
N	-1.26439342958504	19.58252419774867	3.85941889003690
C	-2.57156795137652	19.09647674135744	3.67852400264312
C	-3.09451310740524	17.95531978788047	4.30646210373393
C	-4.41366077026244	17.55438601523716	4.06248465659275
C	-5.23053806512168	18.28623734477146	3.18998427515753
C	-4.70860989972159	19.43109434642968	2.55946942653058
C	-3.40170479294083	19.82781687965829	2.80058204106787
O	-6.53017141888340	17.97381947936169	2.89060839599778
C	-7.09513075781280	16.81167310298617	3.51820361058300
C	-0.25598719585180	15.69145218886697	6.88539857359416
O	2.49553496949102	18.98060675501194	9.28088691683347
C	3.24255802430709	18.54270253770695	10.26223673353391
C	2.93551044206204	19.31313401741500	11.58493370238505
F	1.65261150783975	19.09910274572661	11.97520577914601
O	4.08411387530928	17.65551753695124	10.23587757610796
F	3.74665418572253	18.91161069896034	12.58235215406852
F	3.10145944362791	20.64958251970825	11.42108157800987
H	-1.06058064749341	20.43794540533549	3.34620804324356
H	6.99401515505373	19.06710773478927	6.41630505264341
H	9.91397645340879	17.97732838319994	9.92037375949022
H	-3.00769926303187	20.71735909979540	2.30392759906729
H	-5.34310086172615	20.00115168140729	1.87923226595276
H	-4.78962342346184	16.66465403786729	4.56536275341726
H	8.45274059372982	19.24117259787500	8.38986038848102
H	-2.46880943241896	17.38189781616744	4.98591863792244
H	-1.07102298373808	16.24933395468480	7.37152390868863
H	-0.01168115950360	14.82584770039981	7.51063813617947
H	-0.64360480343603	15.33421532300681	5.91977593218083
H	6.38497743319396	15.59989730622060	7.32997067770398
H	1.94354873337209	14.37530194491901	7.94894236081605
H	3.04357425309950	15.35418772550009	8.94885539706785
H	3.58048758741789	14.74697667742415	7.37113284518406
H	7.81154265930380	14.33901307318557	8.90991735197935
H	-8.12379089851197	16.74627366884897	3.14838010034361
H	-7.10121208624012	16.91668350655302	4.61421473307556
H	-6.54220871004081	15.90170805727267	3.23816381013065
H	11.48895307043695	16.35803700634310	10.46050588134566
H	11.19743767229046	15.09719550638684	11.70494090756354
H	10.32734021022679	16.66462704608412	11.80088092625968
H	2.67899074027644	18.40982449195865	8.37349371915360
H	4.71978921106864	17.03134811980139	8.21505550445948

Table S12. Cartesian coordinates of **$NiOCH_3(H_2)$** after two proton and electron transfers, in the presence of **TFA^- (Q=-1, S=0)**.

C	6.89210553463122	16.16521724136168	8.11054769724384
C	7.18829674720027	17.51058734272707	7.82861629083551
C	8.38066769095617	18.06229272748583	8.31609959429548
C	9.26566438273316	17.30031315096888	9.08193354949472
C	8.95716807118018	15.96345780811644	9.37729014866017
C	7.76543985656271	15.40616267629506	8.88188858098852
N	6.37118496820491	18.33143541178405	7.00772189735005
C	5.03668799693761	18.30598299554915	6.78431112414726
S	4.37232894089059	19.31414215924084	5.55635019777001
Ni	2.28183278054262	18.78304766996256	5.86660749963453
N	2.82363230917382	17.74900875864517	7.39898156806318
N	4.24716159921740	17.49144201336312	7.53322008484782
O	9.74568700956717	15.13211961079343	10.12402189566237
C	10.97437681929402	15.66790644076113	10.64298341498303
N	0.76078844608828	17.71637435666431	5.90622907112033
C	0.78076678923294	16.72013920903206	6.87126833526292
C	1.95821372423703	16.58190971151675	7.56515887696763
C	2.40200896298194	15.47209701319436	8.46029800103480
N	-0.46077553429790	18.10879427897144	5.41115351912004
C	-0.37345374927829	19.19704466504655	4.68809765239950
S	1.13440478560376	20.13847267647312	4.60600665418369
N	-1.43427003241418	19.69470597814933	3.94824053018486
C	-2.66728077409131	19.12317145205767	3.61705548982825
C	-3.10271740176879	17.86227785404463	4.06046386549029
C	-4.35723444122491	17.36400958340440	3.67794607463413
C	-5.20049359712648	18.11468711678890	2.85122844312656
C	-4.77173109134722	19.37895704359090	2.40698964557917
C	-3.53001024116037	19.87251969119440	2.78314046258933
O	-6.44724813708721	17.71347839127863	2.42597361858574
C	-6.90760671637030	16.42875430889239	2.86568132601611
C	-0.43019228843458	15.85219994813358	7.05485996357907
O	2.71706432425230	19.25171662349620	9.77397551104434
C	3.56151326997813	18.71186838908743	10.53438486216347
C	3.54157428487654	19.27534354912371	12.00036518371551
F	2.31333861901409	19.11298054296608	12.57223873907307
O	4.40132038532437	17.80836370845902	10.29695965595140
F	4.44205866310963	18.68077965681081	12.82219602386631
F	3.81323215281233	20.61298274618749	12.01411579680379
H	-1.26067286773324	20.61022526517486	3.54295937932378
H	6.86021873787602	19.06635804929463	6.49888929002935
H	10.18395866975414	17.76004275775387	9.44323452903909
H	-3.21171713728237	20.85550043356996	2.42733214251225
H	-5.42644547150874	19.96727203056890	1.76155698572648
H	-4.66034024759556	16.38271426617358	4.04147583849952
H	8.62361215062296	19.10287148151465	8.09253688984744
H	-2.45616657415869	17.27654526748179	4.71047566520866
H	-1.27005096705169	16.43873850086643	7.45695427888041
H	-0.22610743312411	15.02539872772609	7.74485858598872
H	-0.76347170822513	15.43774123595523	6.09213406532646
H	5.99000408024018	15.70079119374961	7.71518475307435
H	1.64336992233475	14.68123031364343	8.49652282861243
H	2.59371833891003	15.80678685487704	9.49368881390153
H	3.33670430761813	15.00926594208985	8.09697175962096
H	7.53772183634781	14.36192464321396	9.10077621395527
H	-7.90252285223091	16.30131828471816	2.42518487405969
H	-6.98197625980045	16.38616033605837	3.96409267788730
H	-6.24208311140315	15.62443105557682	2.51351535857881
H	11.64089734877989	15.99002138009026	9.82814176619099
H	11.44149736846341	14.84873118905287	11.19955222447858
H	10.78219985689314	16.51414464642705	11.32026968939393
H	2.62485365232275	18.43061978593443	8.18829070847381
H	4.49802824994923	17.41876185686946	8.55568483509340

Table S13. Cartesian coordinates of **$NiSCH_3$** in neutral form, in the presence of **TFAH (Q=0, S=0)**.

C	-2.80236028304196	18.22406552858294	4.50589043971357
C	-2.19105053432786	19.32240063625257	3.88102081601626
C	-2.96239792876947	20.13694359728964	3.02565219303648
C	-4.30375347422416	19.86232549081962	2.80356510187307
C	-4.92405400206896	18.76087035123028	3.42953512783517
C	-4.15396218517558	17.95127156390043	4.27882358568698
N	-0.84096905767950	19.68584534042157	4.04224111105714
C	0.16701326378535	19.12983355071426	4.75981451996791
N	-0.02378771260791	18.04331613310363	5.49498373940898
N	1.12369719860572	17.66543946971100	6.11278963794790
C	1.14248531767289	16.58578237152204	6.88037538204089
C	-0.06955009536729	15.74730271620294	7.10998640853633
S	-6.63756071458947	18.50350544861545	3.07747261601358
C	-7.07077901073035	17.03159967121111	4.04300546185219
Ni	2.74987419633683	18.56576095117688	5.96412265156626
S	1.73933946482342	19.95400486340881	4.64002458441981
N	3.35281352686096	17.23697764666355	7.12926845811537
C	2.45525179397991	16.31987908092944	7.45491025228988
C	2.74604531361130	15.12161586969964	8.29501155149004
N	4.63510694594634	17.19051917800405	7.61909351537961
C	5.40218718076369	18.13521621602074	7.06904639147839
S	4.77384284508870	19.33727098562898	5.94352048636326
N	6.71841055045639	18.22993509233882	7.36967412484632
C	7.59194580839809	17.33185958679897	8.02351911646727
C	8.80602744739428	17.85223225990294	8.49940460936351
C	9.74527007977198	17.02714861494743	9.11508379507814
C	9.49000144594093	15.65395397644769	9.26775816342501
C	8.27526528266180	15.13501551131074	8.77727153558894
C	7.33700470287973	15.95628667850696	8.16164465912234
S	10.59635431494229	14.50949189530625	10.03643811375965
C	12.02310349074485	15.52390065581878	10.50576647848320
H	-0.56801658716144	20.51839760701477	3.52134326917829
H	7.16025232166808	19.08683221065296	7.03855199121754
H	10.67411471459662	17.46799633754429	9.47420400272746
H	-2.49736692658377	20.99295153414468	2.53205832667423
H	-4.87851485779014	20.50825966685896	2.13705030871602
H	-4.59776605039100	17.09150336472662	4.77925935339312
H	9.01683833541447	18.91737435625183	8.38632049546032
H	-2.22116366853097	17.58634024576356	5.16718611658519
H	-0.90452078215135	16.37359071529871	7.45702212830950
H	0.12040700951117	14.96573756951575	7.85270355742692
H	-0.39564122519836	15.27126215435997	6.17175424298017
H	6.41475042219824	15.52530345345358	7.77790058651099
H	2.22606611522521	14.24159768884889	7.89414938298513
H	2.39752819501422	15.26747878402484	9.32981173060251
H	3.82146183717900	14.91548846852875	8.32115576905137
H	8.06233868590105	14.06841867732367	8.87236823236965
H	-8.13415847536043	16.85823675381925	3.83594121317553
H	-6.93568737316886	17.20640000271869	5.11774357678910
H	-6.49223210243108	16.15766504254247	3.71880942762851
H	12.49991823641628	15.97240493207512	9.62530867055757
H	12.72434615431351	14.82641410149303	10.98020925653479
H	11.74037368899265	16.29910099553992	11.22864306130443
H	4.76508042892072	16.99389825633142	9.16269250247780
O	4.77382952363075	16.82989486301745	10.21611344394320
C	4.85013052844514	17.95147959709327	10.89655716582532
O	4.93248851369127	19.09107228040077	10.47795274773431
C	4.82850892759093	17.65354934898534	12.43087353676108
F	4.87362322885792	18.79423507866182	13.14669911378772
F	3.70259419812874	16.98273364821243	12.78494392798478
F	5.89462581098835	16.89246033230882	12.79088623308403

Table S14. Cartesian coordinates of **$NiSCH_3(H)$** after first PCET step in the presence of **TFA^- (Q=-1, S=1/2)**.

C	7.31377125828588	16.04517254757237	8.12207584850498
C	7.55497835052511	17.41944768984500	7.96689305986918
C	8.73031550850606	17.97859304853040	8.48743338128257
C	9.65323103464587	17.18504373428527	9.16635934484473
C	9.41496152505189	15.81063357922025	9.33521530384031
C	8.23450015188618	15.25619377858660	8.80039519214497
N	6.70373648897436	18.27598180859970	7.22241861597066
C	5.39764617830190	18.18506350925021	6.91619572406816
S	4.80074523261137	19.17423822251401	5.61233027643343
Ni	2.74215258159528	18.52855533368742	5.77501790806886
N	3.27301256968432	17.38152114565011	7.14637687664443
N	4.57431663030655	17.36181263779192	7.60274044341174
S	10.50554911006784	14.70353729222546	10.17341291900612
C	11.88967984641186	15.75364801285331	10.69033179705942
N	1.06881720484975	17.76253691548486	6.07157677359049
C	1.03205268159294	16.83109585437756	7.01343405716109
C	2.33175350596543	16.59283367896051	7.63377179918028
C	2.52940262408345	15.55265341689090	8.67995187117902
N	-0.05729498030061	18.09635893393819	5.40011313940900
C	0.18875934840208	19.03434920937122	4.49345775895699
S	1.80538041033197	19.73050630894301	4.23908523310712
N	-0.79143942020281	19.52368372342585	3.69802749515585
C	-2.16357235904345	19.22432566207936	3.60199644397078
C	-2.82819357295812	18.26361123657981	4.38023358873593
C	-4.19639286287948	18.04434072589180	4.20301693926115
C	-4.93013794146106	18.77272127206687	3.25298398508372
C	-4.25563434176334	19.73625039387878	2.47390408337432
C	-2.89749856347596	19.95701233166810	2.64584716750928
S	-6.65959254110895	18.57357877433040	2.95247464806151
C	-7.16310334181721	17.27634643938044	4.11379319714302
C	-0.22278654530182	16.11431907335103	7.37886758229687
O	4.92302210954175	17.43463302605266	10.16054676368867
C	5.12177257497977	16.46757848032416	10.96288731441561
C	5.37324366622526	16.89856934940864	12.45346463387935
F	5.45708245582839	18.24058956996143	12.63699909856563
O	5.13130966437012	15.24535528242745	10.75817084054003
F	4.36316188625155	16.44985124361374	13.25639164505301
F	6.52983184970603	16.35908582141055	12.93177819312463
H	-0.47736022961410	20.24425502762049	3.04865389288853
H	7.17653385987213	19.06225002574828	6.77597236640519
H	10.55588217612620	17.65006935297793	9.55963840175127
H	-2.38969592744558	20.70596294366928	2.03421959408379
H	-4.80150088940352	20.31603868262921	1.72720986760611
H	-4.68279799721035	17.29133962762655	4.82194722187302
H	8.92612478075044	19.04474146989650	8.35726506771893
H	-2.27623116857600	17.69062696321129	5.12103142023164
H	-1.00663268178223	16.83547914466057	7.65478793643567
H	-0.06150051969606	15.42867092497359	8.21668474629998
H	-0.60395810058753	15.54088328416977	6.51958434674049
H	6.42140538705417	15.58411434508290	7.70213489611703
H	2.08073829721652	14.60506750430629	8.34787573745443
H	2.01607808564007	15.84415728375949	9.61001723050181
H	3.58461268112464	15.38129330086955	8.91796642806973
H	8.03713295133064	14.18844879496722	8.91030625299722
H	-8.23804149114934	17.14154215884689	3.94138345295563
H	-7.00013893842446	17.58716186729755	5.15318822371006
H	-6.64277141174603	16.33302929110362	3.90669996948279
H	12.39965706690571	16.19481399639859	9.82492265665584
H	12.57974828698621	15.07797467852839	11.21059498871510
H	11.55850768247800	16.53609931019391	11.38425562379493
H	4.74777212148036	17.22127695703269	8.69920173391780

Table S15. Cartesian coordinates of **$NiSCH_3(H)$** after the first PCET and a second reduction, in the presence of **TFA^- (Q=-2, S=0)**.

C	-2.57949035966970	18.06309224649468	4.11721206388382
C	-1.70498517074234	18.59817423162153	3.14918450570795
C	-2.24689796773636	18.94737859519537	1.88753634909937
C	-3.59574643696003	18.77371619171538	1.61130881703345
C	-4.47054666781552	18.24105209960268	2.58213033049256
C	-3.93951797511016	17.89189453283509	3.83093455535509
N	-0.34438240911445	18.80430396775457	3.34717685669941
C	0.46716182721677	18.58668446169685	4.46003114102811
N	0.03091469430615	17.99622515598876	5.54387381081457
N	0.94652161548497	18.04047809392882	6.57443651692728
C	0.76262498090438	17.17810510568471	7.63934613422387
C	-0.53157308327735	16.43642774027714	7.79884579834599
S	-6.17705777907132	18.05926491187073	2.11658174422061
C	-6.96475293290512	17.39764148429111	3.60927962107217
Ni	2.70767824789798	18.65121591262085	6.35919756744662
S	2.14194565404633	19.16167227179659	4.30945862422592
N	3.00942040630856	17.63009806542900	7.91304163403139
C	1.86587359719888	17.08469356044898	8.48766097005138
C	1.87830036107143	16.52317596963032	9.87588978849739
N	4.11772347136073	17.89993563143452	8.66749592680804
C	5.03314372254986	18.73751416975089	8.15434247188075
S	4.62553799820722	19.62097011306901	6.72645886138672
N	6.30376420756014	18.77120681790369	8.74723473319669
C	7.29700849176571	17.80698118435227	8.51256420684919
C	8.59759845365170	18.02163664818893	9.00236008696672
C	9.60846175832011	17.07946273186548	8.80453248205314
C	9.34689038692341	15.88672589829903	8.11143926865780
C	8.04686887125899	15.67301936096333	7.61744711571936
C	7.03768233444079	16.61399191009325	7.81071693111177
S	10.54941848862242	14.61160910918777	7.80687419960961
C	12.07253566356673	15.26651956382767	8.54077140910338
H	0.15483381675182	19.19641944580234	2.55321137660863
H	6.66222374018024	19.70458140632837	8.93677216686632
H	10.60223261234479	17.28880205651379	9.19993449436696
H	-1.59015595244929	19.36334271506473	1.11933808727347
H	-3.97864791895039	19.05649440007595	0.62796348133845
H	-4.58032473155373	17.47505899879525	4.60828978486750
H	8.82098046987675	18.94198354229215	9.54743367076390
H	-2.18022223422838	17.78219062820003	5.08982269397888
H	-1.39628020118638	17.11796916682859	7.75925800242479
H	-0.56219821088649	15.89240632610990	8.75107549007329
H	-0.67662108268299	15.70384838974683	6.98749222431280
H	6.04251653806888	16.42358359510646	7.40770389536829
H	2.60629286715776	15.70456661979870	9.99783968244290
H	0.88820876816564	16.13941553357902	10.14990899119818
H	2.15460444523840	17.29150083093108	10.62012997415119
H	7.81868281796706	14.75747997414003	7.06647744332646
H	-8.02493183071636	17.28426245332940	3.35060625299806
H	-6.87159038352746	18.09448315922182	4.45208527725833
H	-6.55293713970222	16.41668451097852	3.87883877236159
H	12.37912843089894	16.20290851637281	8.05731696100660
H	12.83472586350203	14.49935636002291	8.35552543520761
H	11.96560177793734	15.41315632358496	9.62313907896121
H	4.33872187967790	17.37109916777176	9.56046604698572
O	4.96428872714448	16.48808712024373	10.91728488524147
C	4.97468416893720	17.07352559126074	12.03279787257532
O	4.52916455677442	18.18806383708502	12.37302548799168
C	5.69718012871745	16.23742996335565	13.15703059017851
F	5.53954340986581	16.75503569675955	14.40549342251853
F	5.24767312264592	14.94837392619917	13.21189753220576
F	7.04552109376997	16.17267100668159	12.92940440264744

Table S16. Cartesian coordinates of **$NiSCH_3(H)$** after the first PCET step, in the presence of **TFAH (Q=0, S=1/2)**. Structure preceding the second protonation and reduction of the complex in the two-proton mechanism.

C	7.03877373919353	16.06959695899485	8.01575559084074
C	7.27672339881403	17.43774322242829	7.79727481379413
C	8.36909838483915	18.05171926424016	8.42719810804481
C	9.19961067790982	17.32531796776824	9.27904995823386
C	8.94986439722509	15.96407699004166	9.52541770595230
C	7.86227265623787	15.34864008678979	8.87557473740959
N	6.49249874949577	18.22483776087220	6.91671245698697
C	5.17106351769885	18.15783835649286	6.64307907050673
S	4.49845747624720	19.21806719907596	5.45053708857752
Ni	2.41765278944188	18.67867815205766	5.76741961538597
N	2.96692729822634	17.52104468069932	7.16246978868793
N	4.37165432086369	17.28532087875918	7.28948008207046
S	9.91754741788330	14.94950765816129	10.60079657604419
C	11.19553906722373	16.07010779761741	11.23085794121498
N	0.83532772941904	17.72176899260523	5.87994624190335
C	0.88399990067955	16.59604680178168	6.65639802581037
C	2.14365374123839	16.38111055441675	7.22424676962609
C	2.62158924017685	15.13420490315255	7.88592982328464
N	-0.32630158333453	18.07270670461471	5.29291340857553
C	-0.19499283888706	19.17992852196013	4.57156662931352
S	1.32108802054092	20.08444612983080	4.50555474858070
N	-1.23488160338768	19.68111730911362	3.83992432148559
C	-2.54571771099425	19.22298767486331	3.63938684425688
C	-3.08782823786681	18.06660327575883	4.22525194405661
C	-4.40975125623020	17.69639865870323	3.95986352659078
C	-5.22166140547912	18.46306610907695	3.11076926089913
C	-4.67368609443135	19.62350651016974	2.52503486840951
C	-3.36259828120493	19.99523438833188	2.78453371133883
S	-6.90442219687851	18.08309487480841	2.71253721598399
C	-7.23650213493156	16.55201231244090	3.62414281684766
C	-0.32589664495585	15.73353719465634	6.82788811627908
O	2.45075833934749	18.95851419987906	9.29032060751635
C	3.18807080438890	18.50303771201161	10.27190909370156
C	2.87233382444331	19.25458531340491	11.60304941267771
F	1.60923180567322	18.97214008430472	12.01496363519574
O	4.02155742476079	17.60873840904210	10.24089463514471
F	3.72146014006734	18.88875141064709	12.58209241955066
F	2.96614927806438	20.59789012914269	11.44581087093651
H	-1.01123176303118	20.54315417648721	3.34585021151530
H	6.97328041567402	19.00316840324072	6.46716346387638
H	10.03751407191435	17.83476972961307	9.75251413121423
H	-2.95536146874297	20.89641241504579	2.32047456323314
H	-5.28147731140881	20.23936240219761	1.85916851548174
H	-4.79665429681011	16.79368194478291	4.43143349843196
H	8.56894124077646	19.11024537194999	8.25079995599045
H	-2.47393270481383	17.46087772858795	4.88728144822871
H	-1.13809265100127	16.29864780300197	7.31048614616980
H	-0.10341268118104	14.85671446039675	7.44566577201165
H	-0.70668619117686	15.39386103833589	5.85322487152782
H	6.23839097101767	15.55001385750260	7.48976497385397
H	1.83998556861147	14.36774338487053	7.89893491305041
H	2.94260898894228	15.31694149542176	8.92425315112036
H	3.48980978837458	14.72066552937699	7.34573796165302
H	7.66388262710453	14.28672914798574	9.03257191840549
H	-8.27668366613193	16.29758303146908	3.38597712540221
H	-7.14063588349490	16.70326221573105	4.70679798199173
H	-6.58046331492179	15.73863052834085	3.28998476875624
H	11.82520514103691	16.45341496509138	10.41872840948096
H	11.80672692520207	15.45473290791216	11.90223414804513
H	10.75391384838464	16.89649803487405	11.80077563655172
H	2.63413482646132	18.39763056629399	8.38361329666055
H	4.65230336769582	16.98567271277395	8.23489365563129

Table S17. Cartesian coordinates of **$NiSCH_3(H_2)$**, after first PCET step, followed by a proton transfer, in the presence of **TFA^- (Q=0, S=1/2)**. Structure preceding the second reduction.

C	-3.31805762506296	19.86927061078166	2.54747677356215
C	-2.51964365336413	19.15337919205912	3.46600408316025
C	-3.07282752119259	18.03852076813179	4.11768865721013
C	-4.39053531374384	17.65470137675067	3.85602463071284
C	-5.18637230874776	18.36636952115226	2.94479658168891
C	-4.62543001985834	19.48407286202014	2.29154122513902
N	-1.21289583183790	19.62722137728685	3.66255078166460
C	-0.18736219986319	19.17522786806217	4.43754070954598
S	1.31978617179503	20.09445309334963	4.38607421457553
Ni	2.37288270279000	18.79694018247089	5.76641118907833
N	0.82588758363159	17.80470042224516	5.84011421252486
N	-0.31382538253229	18.08875562157042	5.19553551904102
S	-6.86200627714134	17.96532401448584	2.54754877109952
C	-7.22038225253226	16.51125738061713	3.56864032886072
S	4.43095368214023	19.41600798131935	5.49860974345338
C	5.11276663381469	18.36296550636364	6.69296932454026
N	4.34118575894760	17.49148731418153	7.38705408088372
N	2.92029105321524	17.71047024844250	7.24939513595168
C	2.10362029303163	16.49777264874064	7.26529580246051
C	2.58264549388981	15.31441785963152	8.02585321464439
N	6.43394221568856	18.41300637368858	6.93053227108386
C	7.20685847061019	17.57619729502583	7.79049915001976
C	7.07303676901753	16.17917725451073	7.76981570404696
C	7.86906828377633	15.39505058961639	8.59744922637990
C	8.82469787301227	15.98426709606393	9.45042823953986
C	8.96256614476459	17.38241968501367	9.45151418273935
C	8.15386690106255	18.16996460561248	8.63088819801068
S	9.78074782779533	14.88697331430919	10.45209030608824
C	10.89284294166941	15.98522080527509	11.37008106641480
C	0.90066188509133	16.66175998045914	6.60944417636360
C	-0.26225516744761	15.72325852820868	6.66277234690353
O	2.63915941563497	18.97197155495150	9.62144200511468
C	3.48774546702919	18.43856160584179	10.38913599489774
O	4.37243006027063	17.58690671228582	10.13320890309561
C	3.40030075411667	18.94205376346507	11.87136852106329
F	3.65470977606342	20.27992524288781	11.94205624445542
F	2.15436989959006	18.74247082255134	12.38473190818615
F	4.27743751699631	18.32405684952531	12.69754225056807
H	-0.98972236987568	20.46782826177266	3.13173172612354
H	6.92845797526714	19.17446990550890	6.46693470935801
H	9.69228424064360	17.87217261805562	10.09452931522844
H	-2.89985852082117	20.73670370075578	2.03201523637143
H	-5.22057301866565	20.05552675395133	1.57655799098392
H	-4.78812800594964	16.78596471311035	4.37943783292901
H	8.26243105101067	19.25578964786823	8.64358934934574
H	-2.47333407742612	17.47502236467525	4.82818028313518
H	-1.14062470134681	16.23080742099352	7.08810413218822
H	-0.03588423249738	14.84626604397147	7.27773798066565
H	-0.53758953569417	15.39139331344301	5.65147500450941
H	6.36060845672557	15.70250797203234	7.09677068958199
H	1.85611205373262	14.49678193480519	7.97583515337260
H	2.76498142384511	15.55686873458935	9.08567253824766
H	3.53533019945107	14.94549790302861	7.61238172880891
H	7.75871822947307	14.30938955400445	8.57037666633128
H	-8.25932822974690	16.24768943689649	3.33513942356825
H	-7.13850072518821	16.74491435515403	4.63747707326818
H	-6.56674145979709	15.66987076411541	3.30683626107405
H	11.55228004899900	16.54112952406541	10.69207174542460
H	11.49793059003075	15.31798063016707	11.99620842987517
H	10.33118638276872	16.67338194279754	12.01385391473972
H	2.67205978941688	18.29559653560358	8.12897712758572
H	4.57918841352367	17.35159703967908	8.41016801251397

Table S18. Cartesian coordinates of **$NiSCH_3(H_2)$** after two proton and electron transfers, in the presence of **TFA^- (Q=-1, S=0)**.

C	6.81435900410516	16.13151027611386	8.18275969164605
C	7.15101013346904	17.45949556116828	7.86655064683919
C	8.38298529138554	17.97080279995797	8.30288290820418
C	9.26005045129241	17.18555457958461	9.05021876345006
C	8.92040627827274	15.86405705752505	9.38409201945334
C	7.68791684405733	15.35181362547359	8.93452780127313
N	6.34236827057650	18.30367727040415	7.06798331727958
C	5.00842541360348	18.29361687334862	6.82811218593370
S	4.37284170643237	19.32014686925396	5.60172221992889
Ni	2.27408571071430	18.81111731978860	5.87894817288298
N	2.78225272159530	17.75624437543946	7.40814407999797
N	4.20108569529883	17.48388707003440	7.56249387377511
S	9.94129249494031	14.77652917169163	10.33613781424844
C	11.41070523272300	15.76991899238610	10.71067076407168
N	0.74238402102725	17.76056632223832	5.88633391468933
C	0.73724095997837	16.75395179061847	6.84076706832985
C	1.90214504248289	16.59702632969332	7.55105071567760
C	2.31883512581799	15.47685014743761	8.44599622282407
N	-0.46555978032280	18.16787228616499	5.37336296662908
C	-0.35577895216987	19.26281648302090	4.66432635660742
S	1.15978924758734	20.19197927086684	4.61742735515147
N	-1.40086815390752	19.77756861950909	3.91069139325451
C	-2.63538353006116	19.22879097733311	3.56426347025751
C	-3.09397087420000	17.96856548090764	3.99233672054998
C	-4.35016425578116	17.49653905849438	3.59264634085687
C	-5.18374132561306	18.25985447782439	2.76439857920362
C	-4.72507300443780	19.52409988108560	2.33829185674014
C	-3.48048934064012	19.99756923900301	2.72948495961399
S	-6.79340430878332	17.75733515354698	2.20468547738594
C	-7.01523054626629	16.11461428227505	2.93866947275376
C	-0.48559099313855	15.89778859095111	6.99723206568742
O	2.67337296927479	19.24053612740652	9.79496906778110
C	3.51109376421058	18.69308002164378	10.55671869480899
C	3.49312217571661	19.25462073698109	12.02330515989108
F	2.25958985543606	19.11300204780821	12.58853103100389
O	4.34444990381499	17.78277352308656	10.31971192600628
F	4.37920330610033	18.64394809915080	12.84873365248545
F	3.78780041177653	20.58741289258001	12.03898914340671
H	-1.21135322964995	20.69537506608890	3.51723309017774
H	6.84096676908046	19.04507148452839	6.57770467495472
H	10.20634384915060	17.61892199929233	9.37110493885863
H	-3.14557611802132	20.97924508109465	2.38542317269650
H	-5.35125831514506	20.14277721625624	1.69148031890131
H	-4.66763689322144	16.51550591417718	3.94605773774653
H	8.65913390057729	18.99722202450091	8.05317685960712
H	-2.46238883529085	17.36686690239113	4.64255471840092
H	-1.32425269276913	16.48908817408338	7.39480503561889
H	-0.30043807405519	15.06053717589909	7.67992508965547
H	-0.80996181963465	15.49856512348255	6.02513483794981
H	5.88282447882292	15.69310580561125	7.82876897819057
H	1.55640619071779	14.68887493308481	8.45561604129973
H	2.48575527477677	15.80027521261326	9.48723198014951
H	3.26016434997361	15.01378077382282	8.10084331881330
H	7.40941319265710	14.32220113189073	9.16790943216961
H	-8.00555546775218	15.78087387665135	2.60462659969652
H	-7.00166997821026	16.16096650666197	4.03506437754541
H	-6.25631258174443	15.40908526583497	2.57708028648144
H	11.93715187702946	16.06485910966096	9.79440648021217
H	12.05743307014390	15.10983162674652	11.30190890074786
H	11.15347074627419	16.65299610427779	11.30867324793544
H	2.57847349346209	18.43351638331953	8.20000563706663
H	4.43604484645987	17.40726342623104	8.58998137454379

Table S19. Cartesian coordinates of **NiCN** in neutral form, in the presence of **TFAH (Q=0, S=0).**

C	8.89776247041981	17.39577367003433	8.03222760746534
C	7.63021858367457	16.88919860502049	7.67104204397366
C	7.36000652807411	15.51594788038446	7.83007661492555
C	8.34264711424099	14.67449976101156	8.33878417491560
C	9.60734393640781	15.18028218660589	8.69743883125188
C	9.87618355699519	16.55639707325896	8.53876355568713
N	6.71333515456349	17.81911978401819	7.17042995067686
C	5.43322226255571	17.68150337561404	6.72100233888989
S	4.65552254118839	19.18238406759812	6.18485899522950
Ni	2.79184325461158	18.20903574053765	5.65052325152852
N	3.56981285818277	16.60983882191563	6.21441905202033
N	4.83567853622981	16.50219559005861	6.69790270349769
C	10.60807574752207	14.30883758834051	9.21607109537410
N	11.42851602922674	13.59458649434731	9.64071494875913
S	1.59514685750873	19.88896387393091	4.98592811531235
C	0.18783388082351	18.91286395058265	4.59206064360926
N	0.15674616878380	17.58809389978063	4.72359182244220
N	1.32159181598699	17.11793597214506	5.28248412352508
C	1.46469658542877	15.84546300792170	5.60486643887730
C	0.39595017687627	14.81439991273246	5.48390025473535
N	-0.88743795299970	19.59225618872529	4.10666837835624
C	-2.22828437874291	19.21416992726307	3.94005618882868
C	-2.79752157070957	18.07063257597989	4.53007426467820
C	-4.14618764235917	17.79438804883609	4.34192536682311
C	-4.94993920505214	18.65076759054585	3.56422844969229
C	-4.38097287067380	19.80309443326726	2.98362580470884
C	-3.03584445524804	20.07913990766171	3.17330208755697
C	-6.33114958590026	18.35744347777616	3.37067657711680
N	-7.46274316678430	18.11755576890848	3.21279619300061
C	2.79699371534131	15.54144552093455	6.12800899096221
C	3.24343095044928	14.17978656341401	6.53664724342783
O	-0.70286486097517	16.14483635370618	2.66220458405363
C	-0.28930767248933	16.60242334416998	1.49753532868937
O	0.35385526406074	17.60723598150786	1.26577537989415
C	-0.74256440089026	15.64207523543055	0.35136678773074
F	-0.18616971527718	14.41292060846532	0.50545837678226
F	-2.09076890166381	15.48888236873594	0.34459635840760
F	-0.37107617239465	16.11914747378808	-0.85166102162439
H	7.06392123861978	18.77575741731808	7.13109493940813
H	-0.68682554190773	20.56035852164209	3.85775382136583
H	-4.99704065974303	20.47358803119679	2.38523408961717
H	9.10688912872044	18.45969707041862	7.90862238603652
H	10.85129313148736	16.95743567004473	8.81376896917709
H	8.13082056274486	13.61244060561773	8.46142096908907
H	-2.59533683479156	20.97092107133772	2.72437469701547
H	6.38576317406998	15.12172826178903	7.55514222167663
H	4.27048172142645	13.99827579783543	6.19322989792014
H	2.58257818924013	13.40733027533374	6.12912445443889
H	3.24660905329559	14.08814045527688	7.63516205559796
H	-2.19290256205343	17.40993746513841	5.14610834678802
H	0.39609874791540	14.16595932056558	6.37058959875230
H	0.57090249285689	14.16918760980968	4.60803456511082
H	-0.59022496324556	15.27845718782174	5.38295161369779
H	-4.58560360999109	16.91144052575013	4.80533903280566
H	-0.38504570563658	16.75362208814810	3.45749143972064

Table S20. Cartesian coordinates of **NiCN(H)** after first PCET step in the presence of **TFA^- (Q=-1, S=1/2)**.

C	8.85519210882626	17.44906785637180	8.34162804472465
C	7.62738441138818	16.93853255643355	7.85259626722824
C	7.38055792309788	15.54921517437917	7.93774782421545
C	8.33519302176088	14.70792868741355	8.49411575253307
C	9.55699646165104	15.21881114279718	8.97976107266006
C	9.80420285871400	16.60902057275869	8.89514604074703
N	6.73722700731872	17.85440307812418	7.31343515887698
C	5.47904550996826	17.69614169813725	6.76594232231634
S	4.69602537416516	19.19215172054728	6.21654946117502
Ni	2.87890533253908	18.20221155152453	5.56295545837662
N	3.66058231246606	16.61055882751764	6.11873508799386
N	4.90627721293362	16.51836656064930	6.66104297265843
C	10.52758801543488	14.34837324284275	9.54602536562280
N	11.32659252330317	13.63275592803002	10.01170054806786
S	1.63259693914216	19.87411987017341	4.95759698069974
C	0.30465843753035	18.91255739785410	4.38775024688291
N	0.35820098069322	17.57621442726844	4.46679160570416
N	1.50213362529893	17.07687111670762	5.03904984807363
C	1.65038456015819	15.76373151509937	5.34054801170053
C	0.56746830503763	14.76214627346744	5.10257808825182
N	-0.77642740770657	19.54407264824476	3.82211151082315
C	-2.12872429149650	19.20247483210306	3.82149585802461
C	-2.66579395763856	18.14250539095053	4.58052430059929
C	-4.03007327980405	17.89264781867211	4.55811099289431
C	-4.89407816030887	18.68695949065636	3.77502756848499
C	-4.35679161942166	19.75240739311246	3.01915953431827
C	-2.99526910666677	20.00390471325056	3.04511674267208
C	-6.29094954805689	18.42093126982870	3.75095105800062
N	-7.43937667058646	18.20376883880459	3.73232344786437
C	2.91812711232650	15.49467295925716	5.92938736335820
C	3.43614200436855	14.14935203636917	6.32520958551729
O	-0.88393402750513	16.18404824048848	2.60478073242726
C	-0.58633234433770	16.49370348220040	1.40848101309715
O	0.19911462365666	17.34862656449792	0.97204493970265
C	-1.35813353147796	15.61412047592440	0.35722787650961
F	-1.03180716568084	14.29307579095803	0.48445662622191
F	-2.70992149093315	15.70540377989917	0.51757636382170
F	-1.08948351645221	15.96323347100533	-0.92630859347705
H	7.06082453248173	18.82004043266963	7.32094742095081
H	-0.56865653789520	20.47743622947060	3.46999474780853
H	-5.01561999463254	20.37544809115181	2.41486639657052
H	9.05122722263174	18.52113611266206	8.27886863031499
H	10.74396228367354	17.01760784305920	9.26662550760694
H	8.13703844569879	13.63753959736712	8.55601422380169
H	-2.58324931974401	20.82847196210842	2.46079256175341
H	6.44084211230041	15.15056879898149	7.56419408116430
H	4.36590884183626	13.91387071873646	5.78406786330815
H	2.70550186309828	13.36180257200769	6.11154979447001
H	3.67825150056280	14.12053340583282	7.39898887793750
H	-2.02077799638731	17.52328178201361	5.19989932825381
H	0.81643600660133	13.79866763955815	5.55940922558491
H	0.38424182588265	14.60016472180746	4.02946178798672
H	-0.38263499211957	15.11113457715874	5.53832527797481
H	-4.43850816336365	17.07730630328613	5.15518438841217
H	-0.18387717433123	16.97216481780830	3.72247780673113

Table S21. Cartesian coordinates of **NiCN(H)** after the first PCET and a second reduction, in the presence of **TFA^- (Q=-2, S=0)**.

C	-2.58329658608708	18.13750310838179	4.66588309338957
C	-2.10232737521201	19.17478802414040	3.83245681728707
C	-3.03861611920583	19.96330774520689	3.11807735644212
C	-4.39674376218354	19.72630375187745	3.22674775959362
C	-4.87596167722854	18.68623072142823	4.05929139473179
C	-3.94422895583435	17.90375951480124	4.77887471609952
N	-0.75921589300839	19.47113667796456	3.69127208255831
C	0.33331951682715	18.87034654239830	4.31899162090505
S	1.55547375302662	19.83461429406298	5.06583408397257
Ni	2.95937486051608	18.21385629567701	5.43927910972465
N	1.70284453557884	17.04356155612068	4.69809171033293
N	0.49086890377153	17.54041574364528	4.26349049246658
C	-6.26779347021660	18.43603952356582	4.17227481875412
N	-7.41671191462467	18.23228078986659	4.26752182707498
N	3.68267702372617	16.63164163105118	6.13354181020585
C	3.01017962545936	15.47812236890102	5.77552426182678
C	1.80789090815419	15.72291668554157	5.11156844162350
C	0.70012155810718	14.74223891957828	4.88004584543420
N	4.96823386856945	16.52492296551029	6.59038738421024
C	5.58695057436914	17.68014311073176	6.61867271092959
S	4.87878713180472	19.14850796515990	5.92443556484039
N	6.84691490124463	17.83548373940789	7.20447322716453
C	7.65205413206617	16.96115380963187	7.89471440689073
C	7.31556923152208	15.60564439333034	8.15096652268409
C	8.18765339949960	14.79199199837798	8.85798844312153
C	9.42425282600845	15.28449696038497	9.33548839994345
C	9.76394302993649	16.63799472111958	9.07742841232354
C	8.89803955001621	17.45192238186203	8.37448052867223
C	10.30727029165209	14.44335541116209	10.05667937035236
C	3.58747947619757	14.13191263708747	6.09391448303631
O	-0.94297126811376	16.16550092412392	2.37719721733681
C	-0.73102169664887	16.44285398143951	1.16243853839897
C	-1.68707903277990	15.65347805183027	0.19017067887413
F	-2.99910695154011	15.95876020785588	0.42025874275406
O	0.09047086656775	17.21574994542656	0.63603622757421
F	-1.45295404782611	15.90907375105184	-1.12437084514140
F	-1.56425917325032	14.30114522266567	0.35274380036880
H	7.22292340568268	18.77520514739753	7.09500331409893
H	-0.55412101821237	20.37822655590126	3.27410201617872
H	-5.10295944423580	20.34259620697735	2.66971262734407
H	9.16907630254120	18.49228388916699	8.18219849602396
H	10.71333180866452	17.03569716495233	9.43737693082955
H	7.91570821856191	13.75293716228095	9.04902127216611
H	-2.67666268629741	20.76727428229231	2.47417971071788
H	6.36713509706007	15.22155710798228	7.78211605515205
H	4.51603575791568	13.94889751461805	5.52772085307349
H	2.88069020092381	13.33019549763108	5.84674673056072
H	3.85070421011214	14.04743116981597	7.16029090271611
H	-1.88466598493570	17.52133799188219	5.22935350972834
H	0.96461533952101	13.75297743093891	5.27186829329326
H	0.44466697102338	14.63340412054673	3.81409518539457
H	-0.22559064057128	15.06505824863203	5.39019266829396
H	-4.30172938891504	17.10743008989638	5.43250796385888
H	-0.07556428536965	16.97245074645752	3.55789109301782
N	11.03804709566945	13.74857560026106	10.65342932079381

Table S22. Cartesian coordinates of **$NiSCH_3(H)$** after the first PCET step, in the presence of **TFAH (Q=0, S=1/2)**. Structure preceding the second protonation and reduction of the complex in the two-proton mechanism.

C	7.08744614859345	16.11150148469348	7.87785438891056
C	7.29447999178503	17.50361452376998	7.73255799771043
C	8.34321197245627	18.12257901228522	8.44580014227929
C	9.15659970139868	17.36322427029641	9.27778048546669
C	8.94847967310037	15.97656068553803	9.42133394498758
C	7.89868337164353	15.35697533924933	8.70733560065063
N	6.42553303280044	18.17447478028247	6.87751335711799
C	6.34216579062047	19.49426243412828	6.50361579875529
S	5.06788548973939	19.89680115598494	5.35735311944311
Ni	5.62432596607284	22.00171502713616	5.21573303848600
N	6.95533334916620	21.61673056379642	6.44702385813847
N	7.17782869359994	20.40200754979027	6.98776252975245
C	9.78659843371941	15.20893637640359	10.27761874408949
N	10.47482555598253	14.57881470871962	10.98092745004895
S	4.57006138721757	22.69670871686484	3.45175660664986
C	4.96083180007492	24.36948575745145	3.62468108082346
N	5.80340330724507	24.76790506503028	4.59606930404079
N	6.09751704216130	23.79149563229658	5.59236716198328
C	7.36357227038076	23.86902898304844	6.18660527957680
C	8.15442099444365	25.13049485132015	6.14242527996070
N	4.38351680520799	25.26740247583416	2.78289380001689
C	4.62905541833128	26.63623399993281	2.58801985549086
C	5.85072674554699	27.25692228410382	2.90807636497006
C	6.02296373202451	28.61486443694195	2.66416452621896
C	4.98424646748302	29.37243441940310	2.09121816584800
C	3.76845363952923	28.74391345460532	1.74936408400244
C	3.59655459407198	27.39084579919122	1.99584451909307
C	5.16414922080898	30.76532519248768	1.84748544037543
N	5.31095680629433	31.90590377708241	1.64736084204846
C	7.73371917364223	22.67343319488250	6.82049161535105
C	8.84601364184566	22.50001385167262	7.80396130102054
O	4.33419755535393	24.45003656142008	7.48503922837039
C	4.22563048407022	25.75877400728842	7.46027598408069
O	4.77550626423246	26.54553566699609	6.70481078875162
C	3.25282098148006	26.25604015944507	8.57412607182742
F	2.02363855597601	25.70466475081276	8.42121954798838
F	3.71540744186281	25.91150568481005	9.80149294304981
F	3.12017363964978	27.59437126160811	8.53581584317540
H	5.71850548473077	17.58270487136490	6.44396061298406
H	3.62790679245121	24.87536484184063	2.22110527138799
H	2.96338569267591	29.32307291776653	1.29818280512362
H	6.27713402951355	15.62947658818114	7.32755753002453
H	7.72798540049304	14.28558363729271	8.81059191172751
H	9.96504165933954	17.84677940672493	9.82634815993359
H	2.65477837724336	26.90493100312653	1.73703386134136
H	8.50735666498483	19.19145437250569	8.33964619037157
H	8.45424936629213	22.14524655389598	8.76944174773390
H	9.37456196150778	23.44406617742408	7.97386623210224
H	9.56700843684720	21.74704337347139	7.45241731073236
H	6.68808039065072	26.68323539816518	3.30035016753133
H	9.10967756521692	25.01850113709455	6.66508598658325
H	7.60947517407080	25.97409089505669	6.59660158544326
H	8.37023369063356	25.40789898731949	5.09723958193272
H	6.97295948298477	29.09022797683189	2.90619572120095
H	5.01720011883193	24.12397181314083	6.74793191188060
H	5.68586357191870	25.71687415219269	4.98417732141383

Table S23. Cartesian coordinates of **NiCN(H_2)**, after first PCET step, followed by a proton transfer, in the presence of **TFA^- (Q=0, S=1/2)**. Structure preceding the second reduction.

C	7.22044164518833	16.01364048822708	7.72807116208618
C	7.38764514534350	17.41461028131371	7.63820985669627
C	8.41194997371157	18.03851718339570	8.37969579120559
C	9.24341632646868	17.27288960307571	9.18800884211197
C	9.07544393790405	15.87666911569089	9.27732986398055
C	8.04966859066408	15.25269867969107	8.53424159457175
N	6.50128536437125	18.09034989348932	6.80063022905825
C	6.37078255235648	19.41644091309195	6.48575170837473
S	5.10101968103194	19.83375912220674	5.34233929131181
Ni	5.54328209909727	21.95330239612322	5.34644287848135
N	6.88236961003108	21.55922602462747	6.54377260236152
N	7.16647843251243	20.33929549696453	7.01680151008430
C	9.93184503784590	15.10203769767212	10.11023372086009
N	10.63447865560741	14.46665536796904	10.79369824193512
S	4.47654758777012	22.64792696806650	3.60100314301432
C	4.86540903803411	24.32228849821890	3.78595577192733
N	5.62824887017145	24.76732459627006	4.80665102295298
N	5.90984286696050	23.77465246368679	5.81806933583224
C	7.25489793411531	23.83968223951866	6.38891373679937
C	7.96154818841380	25.14502701310069	6.42583662332042
N	4.36986516388324	25.19092873046379	2.87494900972959
C	4.63801900492475	26.55555186744646	2.64406217245048
C	5.81442710052806	27.19784290217765	3.06619505813599
C	6.01603539153499	28.53871853453579	2.76017923895100
C	5.05060871772597	29.25494600033788	2.02742273003062
C	3.87883551717391	28.60383120634366	1.59188269942584
C	3.67878280615875	27.26598714631658	1.89799786100768
C	5.26179604662297	30.63138558744188	1.71987916673496
N	5.43481298032821	31.75757358741155	1.46740301379507
C	7.66832313496479	22.62956914698040	6.91198826704144
C	8.85896867344597	22.41419252671394	7.78941378898497
O	4.17153766217432	24.80570870754963	7.60105816658782
C	4.13750243823739	26.04337948830791	7.36414945398610
O	4.68129023108425	26.69221878226819	6.43420813310950
C	3.29589137779833	26.86734214872474	8.39708855106326
F	2.01667552537010	26.40580734435519	8.46035796189680
F	3.82780266651548	26.75636118645904	9.64649123910130
F	3.23392873477299	28.18642623254178	8.10149556632725
H	5.82186834064392	17.48923157933231	6.33614211673211
H	3.68060444042776	24.77831432771695	2.24608837955887
H	3.13083014404888	29.15115305857585	1.01931187704572
H	6.42820315855018	15.52912004922739	7.15436236420704
H	7.91081408784011	14.17365543037203	8.59606108920972
H	10.03402891182066	17.75900407616058	9.75955630642165
H	2.77196005317660	26.76028879254311	1.56323008508412
H	8.54620684241514	19.11475332066652	8.31646528310826
H	8.54560778244120	21.98950265723859	8.75429054551220
H	9.38784300992308	23.35380655947898	7.97803017207810
H	9.55347114163708	21.69749052688570	7.32804301921284
H	6.58840309156724	26.65542710639011	3.60418819412342
H	8.93240948044522	25.05072249493552	6.92281411587454
H	7.37116205718254	25.91332254361203	6.95139672366393
H	8.14033392898101	25.51826786908686	5.40423556690341
H	6.93188971577837	29.03372207136129	3.08142564325048
H	5.19871721590788	24.01861623034990	6.60310009149478
H	5.33456288636946	25.68012813729011	5.28616642119302

Table S24. Cartesian coordinates of **NiCN(H_2)** after two proton and electron transfers, in the presence of **TFA^- (Q=-1, S=0)**.

C	7.14054754913166	16.00279549813478	7.90571973860227
C	7.35336327607139	17.39165646767806	7.70263244777120
C	8.53833100646517	17.97903949865718	8.20979815396773
C	9.46759797216264	17.20042356969594	8.88557333190811
C	9.25271414784385	15.81958864206678	9.08482742930313
C	8.06704984510329	15.23116026881814	8.58103328574713
N	6.37891759307440	18.08864340962185	7.01981200141969
C	6.28996191004185	19.43085452311393	6.65483355730202
S	4.94362462893449	19.84749221383467	5.57888625857588
Ni	5.50769940878907	21.93902285905653	5.37663205770105
N	6.96021610429651	21.53747010646584	6.45818440968657
N	7.13961920282690	20.33188171984389	7.07696116713849
C	10.20882238338845	15.03324249364920	9.77977983243590
N	10.99691836468153	14.38443527783764	10.35184851212295
S	4.44015926104577	22.67214421798169	3.63607871437135
C	4.84104481162481	24.32928116677845	3.81950151161931
N	5.63386862834644	24.76578798364998	4.82845801887012
N	5.90631023990798	23.76314168346843	5.84390608330717
C	7.21459890080070	23.85876902770107	6.49068893873841
C	7.85854301552109	25.19816958480371	6.62414161788789
N	4.32276027584864	25.22785944767344	2.93269455373607
C	4.64577906988125	26.56361760028218	2.65808741180076
C	5.83348185205654	27.19040643712295	3.08263492992713
C	6.08525788466971	28.51028340785532	2.72989488131698
C	5.16219485761366	29.23197637598400	1.94738600605117
C	3.97886151149268	28.59919289341473	1.51081322059348
C	3.72840199813914	27.28281990441654	1.86267471486546
C	5.42457725100723	30.58643544682748	1.59430979490252
N	5.63937628091373	31.69734802826541	1.30471622109677
C	7.64019747447318	22.64036705247182	6.95651651786821
C	8.78367831683307	22.43143945978447	7.90451254618656
O	4.00814858002900	24.86255884099690	7.58222189148264
C	4.01465179049286	26.09581568550133	7.33921571394519
O	4.60859425729637	26.73563961831400	6.43276340994663
C	3.13391352692888	26.94351452088079	8.32338412538721
F	1.81977979813816	26.58950070459833	8.22198464187396
F	3.50458339496005	26.73626999447505	9.61851868910353
F	3.20428761882750	28.27832201348545	8.09830384561093
H	5.58557757950159	17.53077712400554	6.71173887007243
H	3.59570858161219	24.83245040411815	2.33700447952377
H	3.26136777957150	29.14669619198117	0.90024206764076
H	6.22917010222738	15.54107763431816	7.51999809147801
H	7.88600131016424	14.16603774218007	8.72699648320200
H	10.37735944714166	17.66311771431214	9.26992896661152
H	2.81220921853147	26.79534295619809	1.52552077309711
H	8.70517520287110	19.04387948268818	8.06616978834247
H	8.42534182174320	22.00693016121750	8.85422816749300
H	9.29773831377191	23.37465724267924	8.12093268488004
H	9.50998836843018	21.71795516840330	7.48870657298781
H	6.57510271635822	26.64740362434537	3.66384955154459
H	8.82648801508522	25.11145293622335	7.13148436305378
H	7.24011210604875	25.91391515425571	7.19115334231294
H	8.04731807706055	25.65173385045206	5.63527634854282
H	7.00943022483927	28.98733704977286	3.05529619937398
H	5.15959633502449	23.95955798509277	6.57592106002800
H	5.34021981035762	25.67337193254811	5.29913200564350

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