Electronic Supplementary Material (ESI) for Dalton Transactions

Experimental and Computational Studies on the Formation of Cyanate from Early Metal Terminal Nitrido Ligands and Carbon Monoxide

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Supplementary Information

Contents

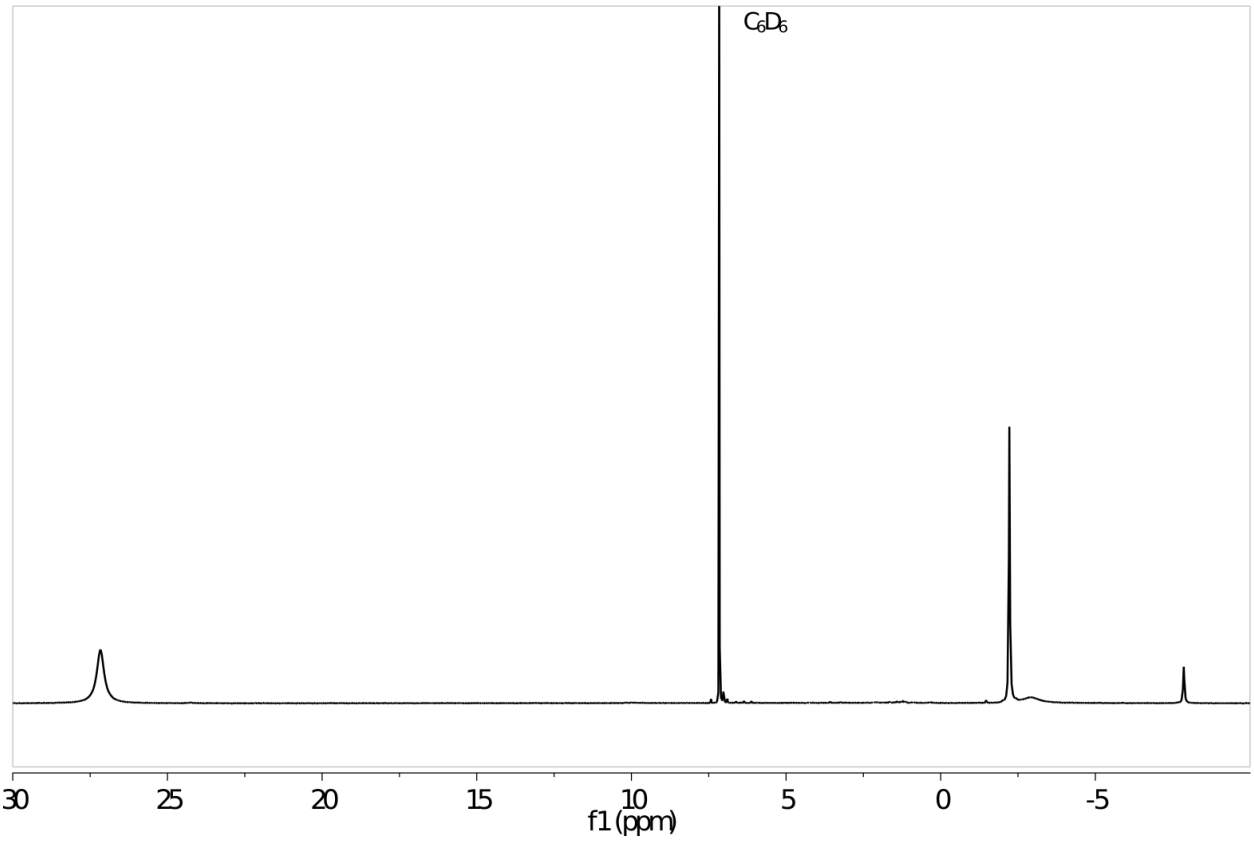

Figure S1. ^{1}H NMR spectrum of **5** in C_6D_6.

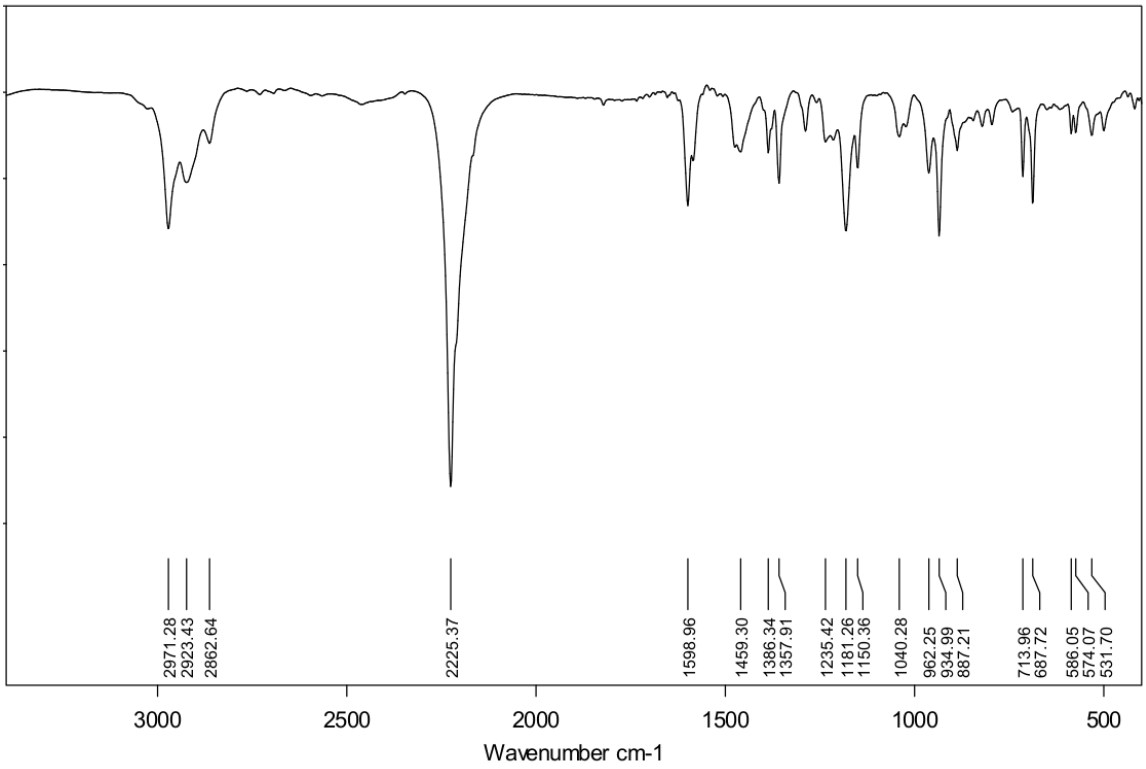

Figure S2. Transmission IR spectrum of **5** in pressed KBr.

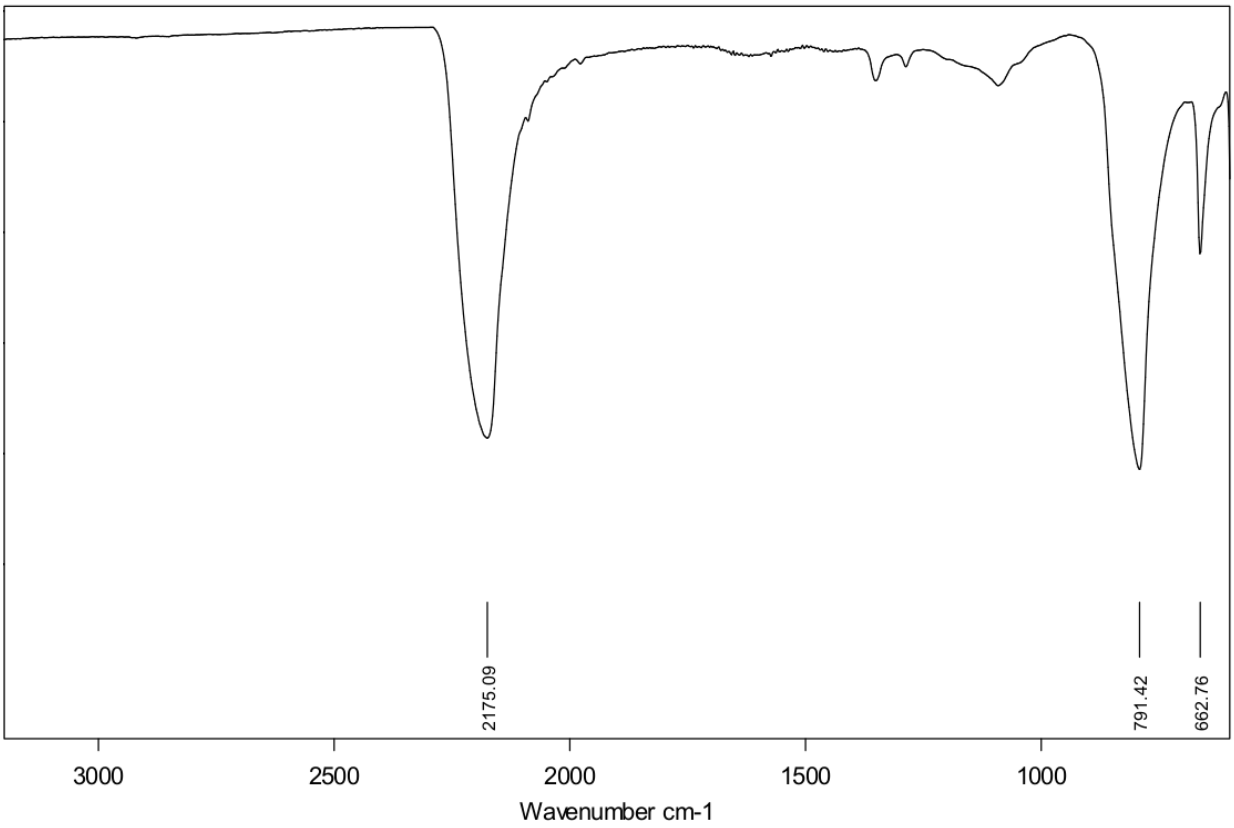

Figure S3. Diamond ATR-IR spectrum of neat AgOCN from KC_8 reduction of **5**.

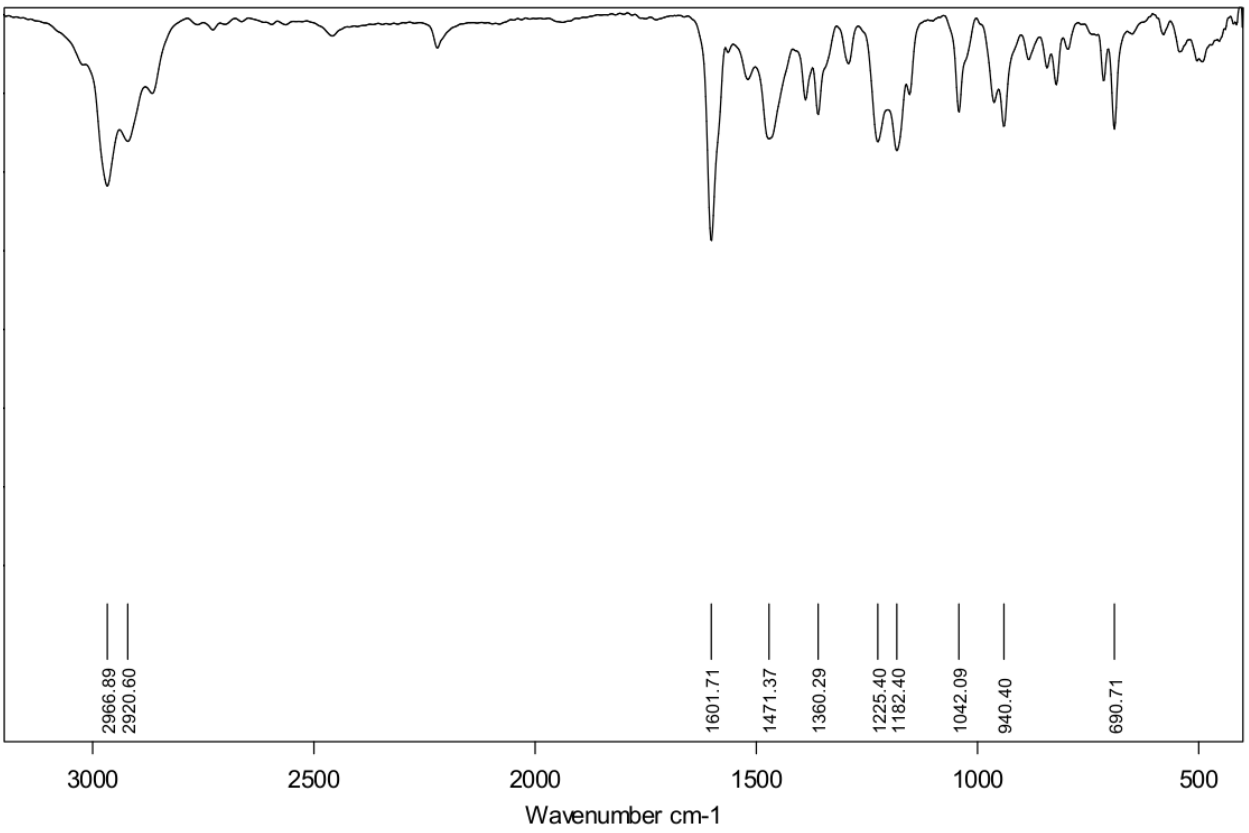

Figure S4. Transmission IR spectrum of **2** in pressed KBr from KC_8 reduction of **5**.

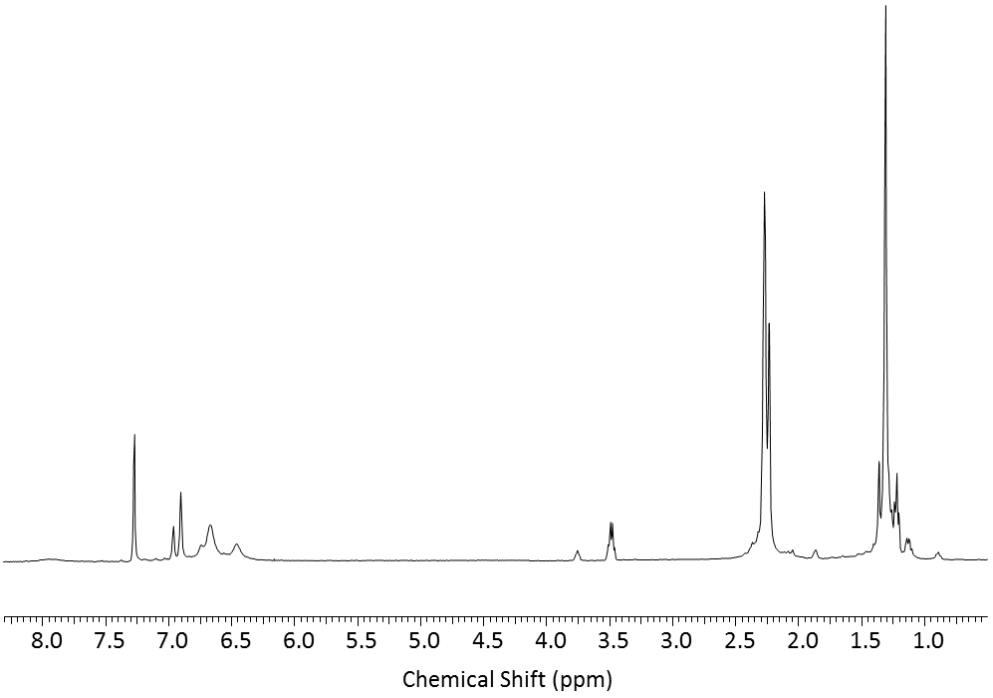

Figure S5. ^{1}H NMR spectrum of **[7][OTf]$_2$** in C_6D_6.

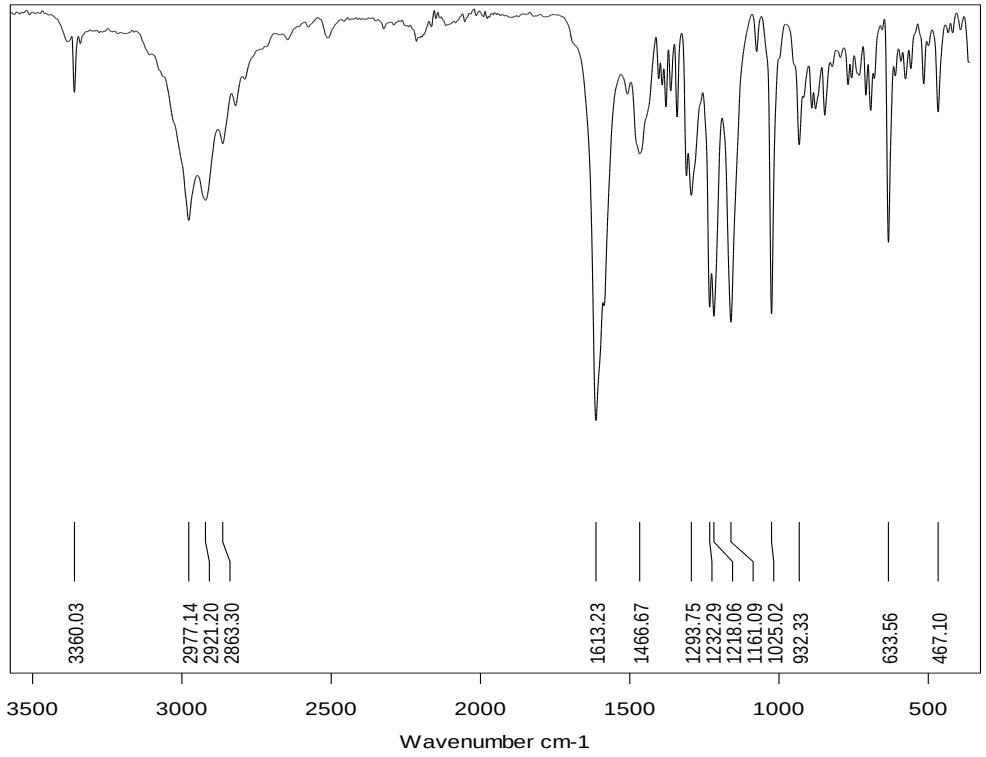

Figure S6. Mid-IR transmission spectrum of **[7][OTf]$_2$** in KBr.

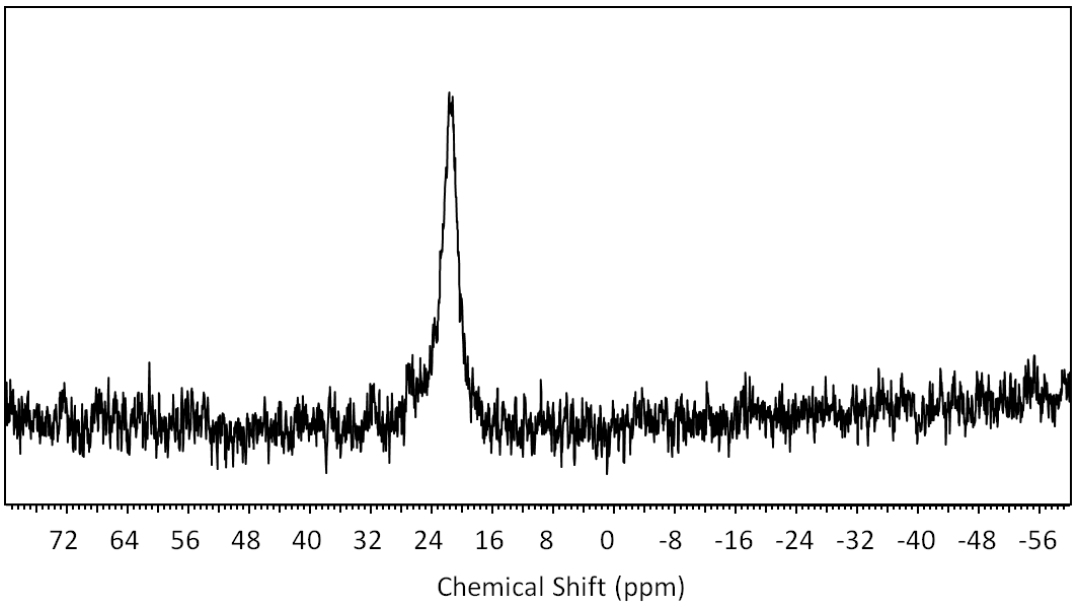

Figure S7. ^{19}F NMR spectrum of **8** in C_6D_6.

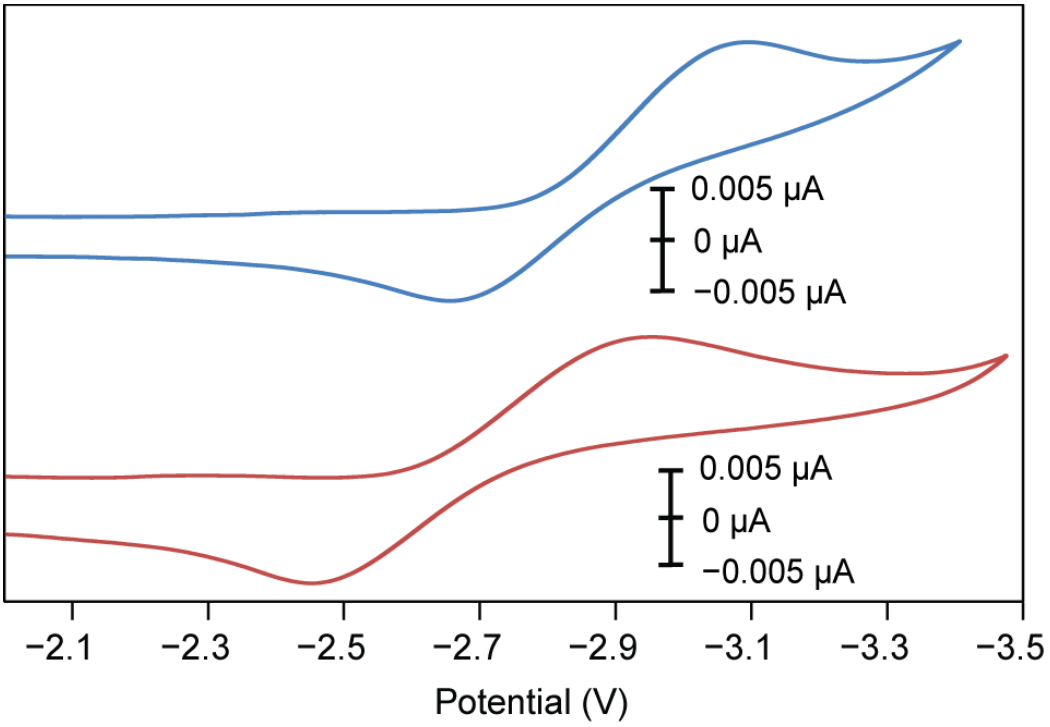

Figure S8. Cyclic voltammograms of **1** (blue) and **9** (red) in 0.1 M $[Bu_4N][B(C_6F_5)_4]$ in THF referenced to Fc/Fc^+ with a scan rate of 300 mV/sec..

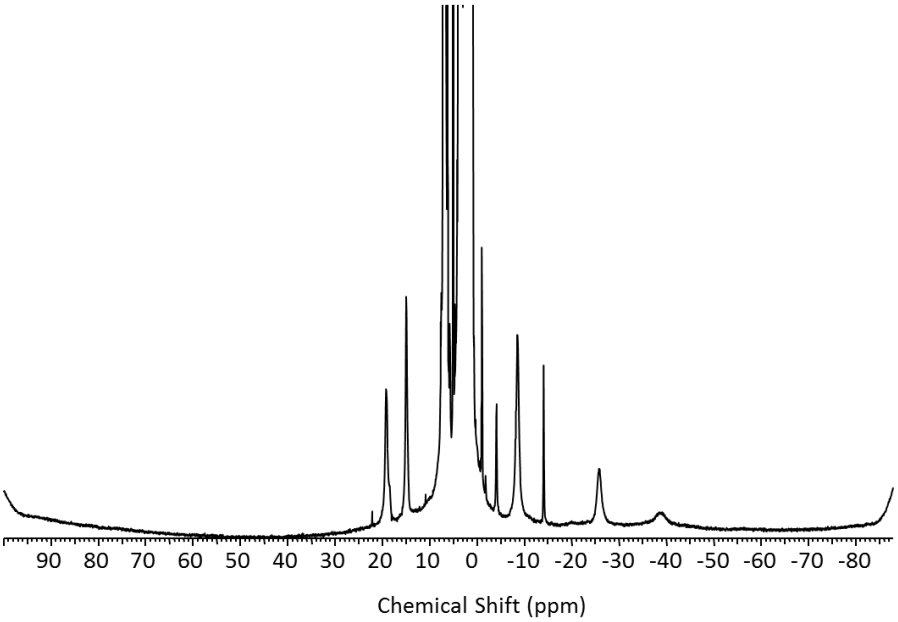

Figure S9. ^{1}H NMR spectrum of paramagnetic region of **10** in C_6D_6.

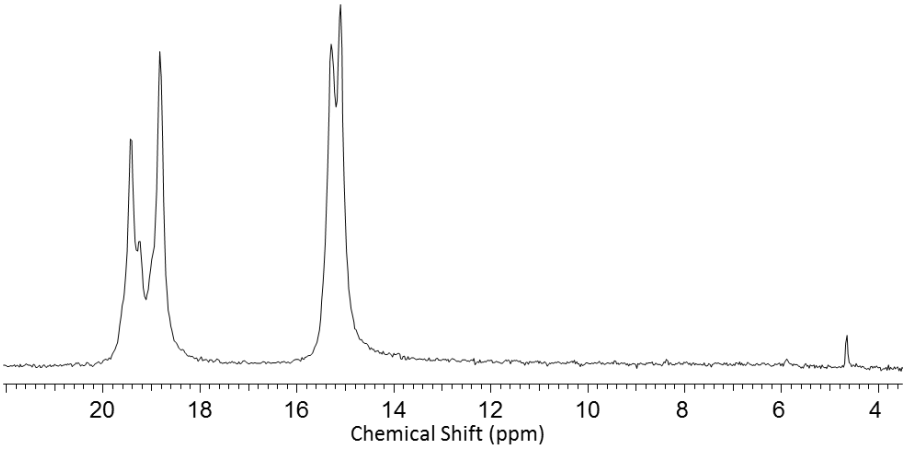

Figure S10. ^{2}H NMR spectrum of **10** in THF.

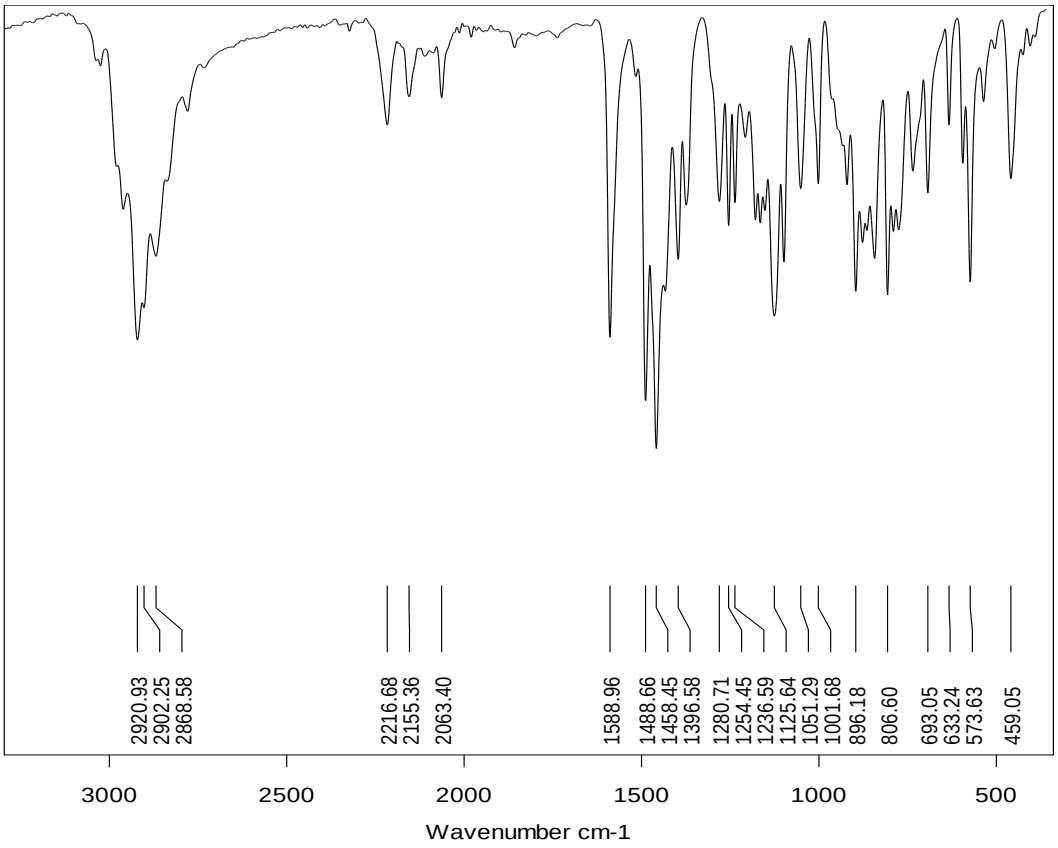

Figure S11. Diamond ATR-FTIR spectrum of **10**.

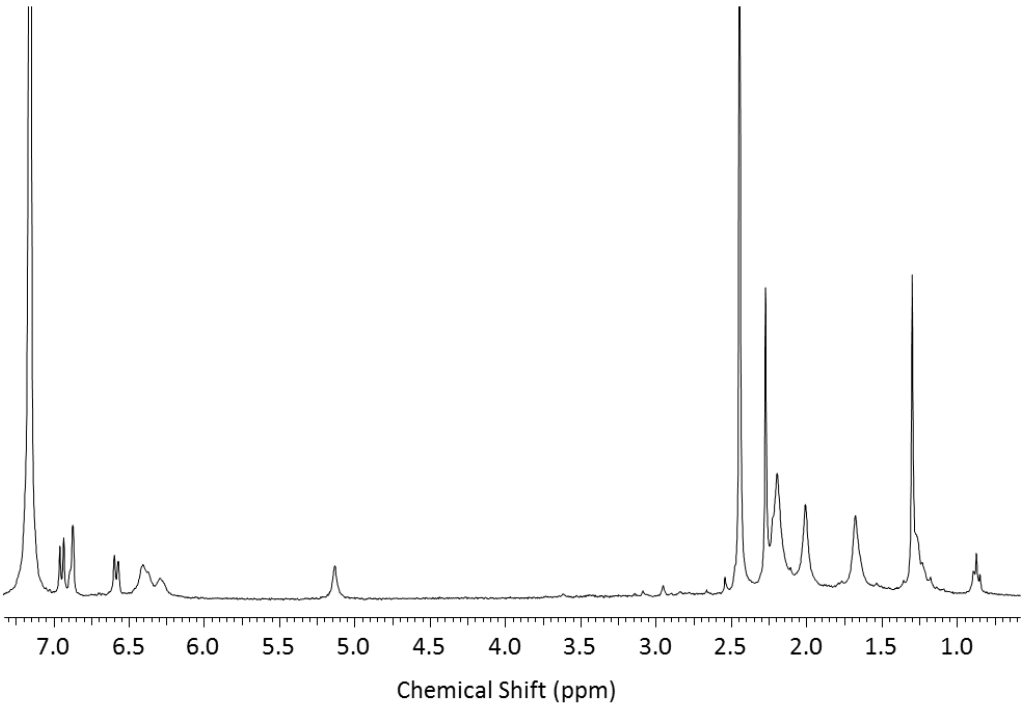

Figure S12. ^{1}H NMR spectrum of **11** in C_6D_6.

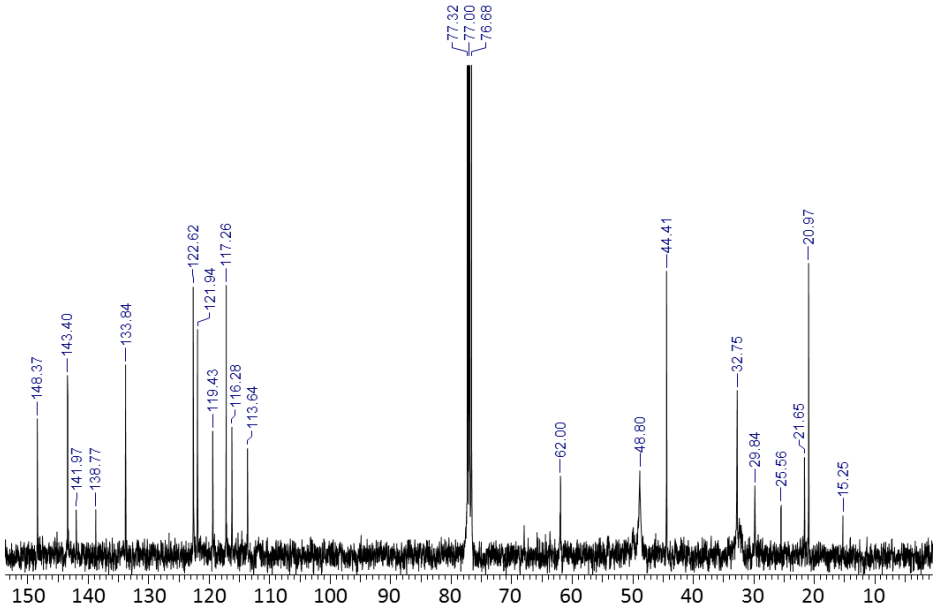

Figure S13. ^{13}C NMR spectrum of **11** in $CDCl_3$.

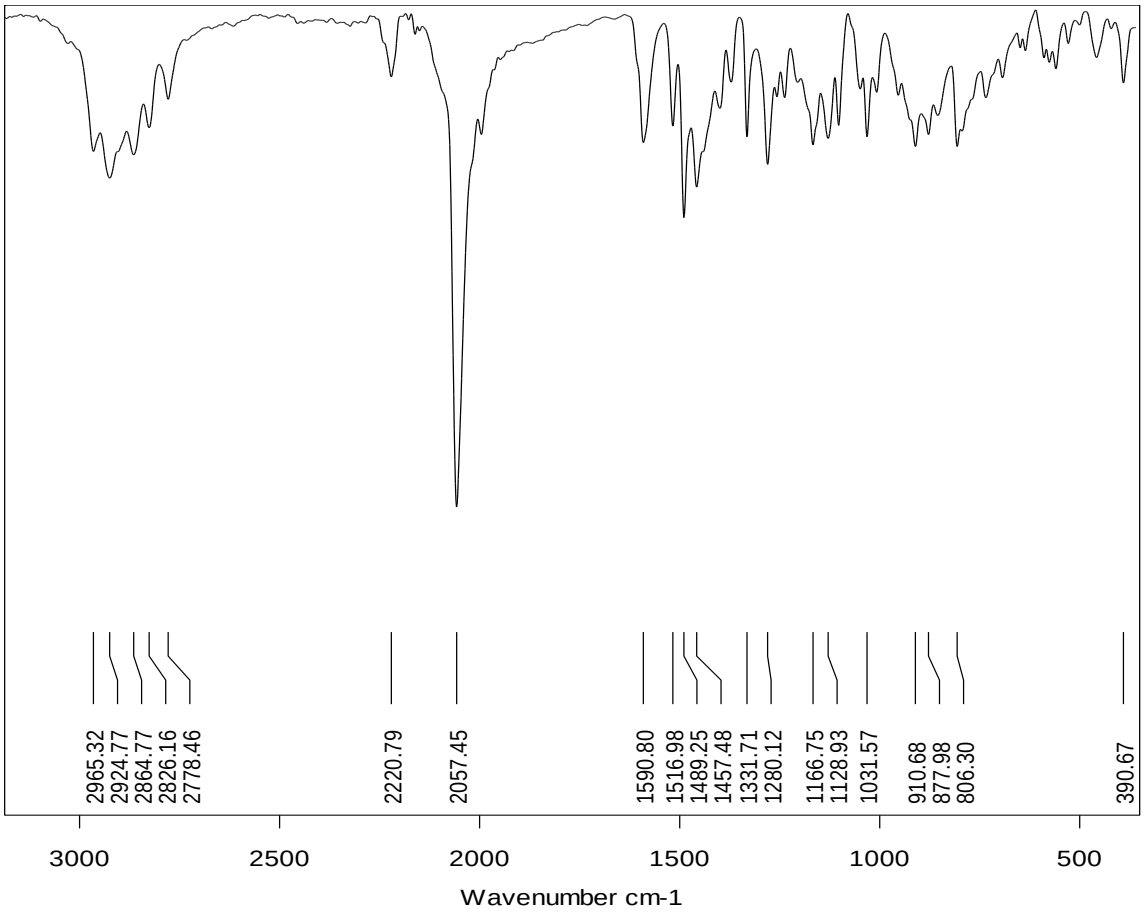

Figure S14. Diamond ATR-FTIR spectrum of **11**.

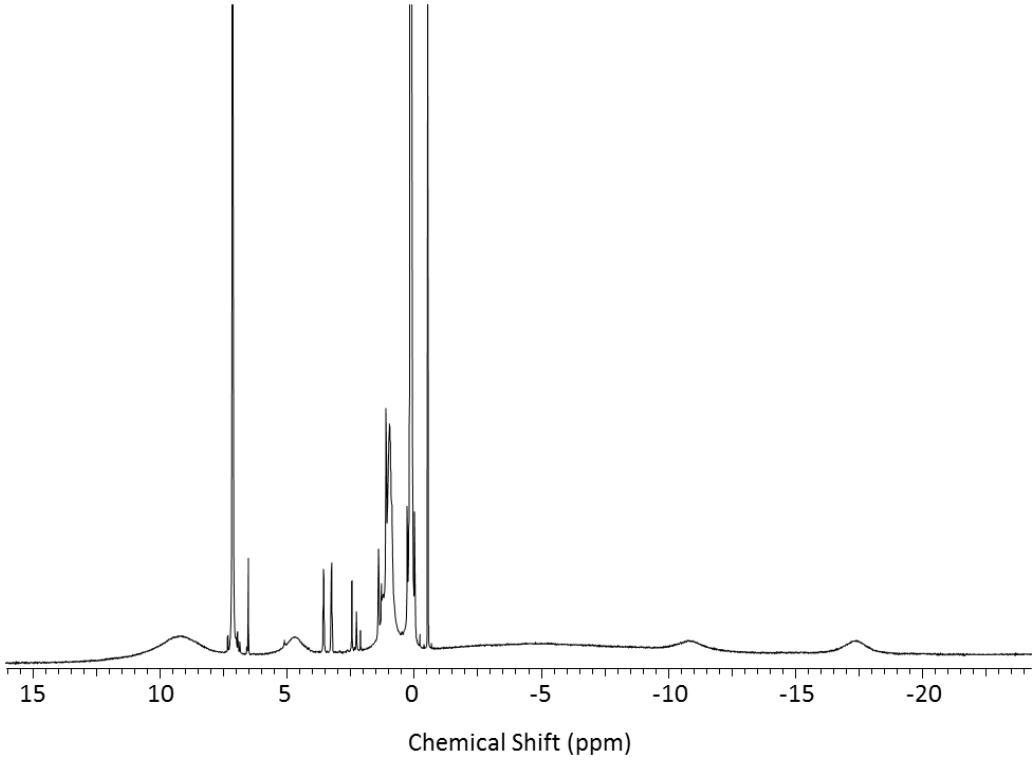

Figure S15. ^{1}H NMR spectrum of **12** in C_6D_6 containing HMDSO for Evans' method.

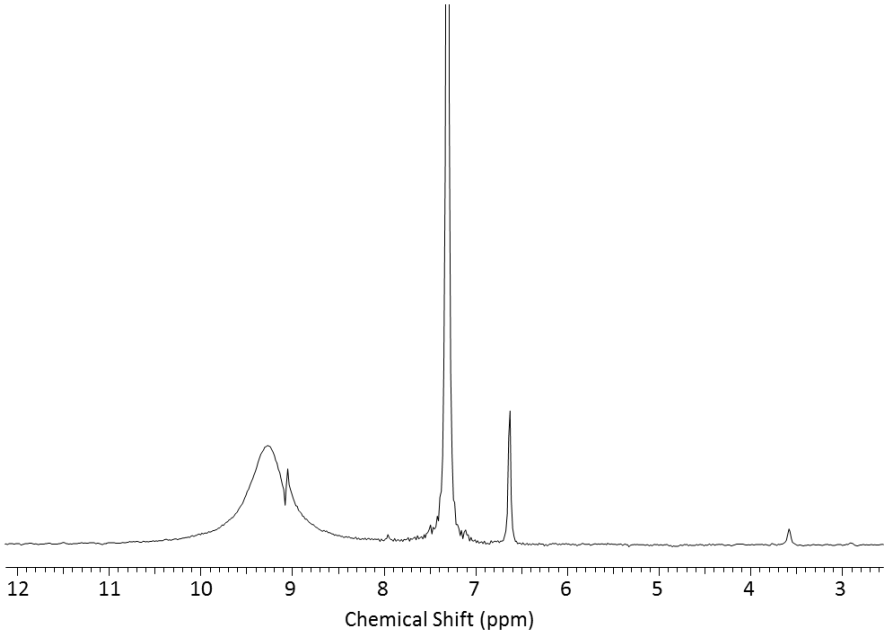

Figure S16. ^{2}H NMR spectrum of **12** in THF containing C_6D_6 for Evans' method.

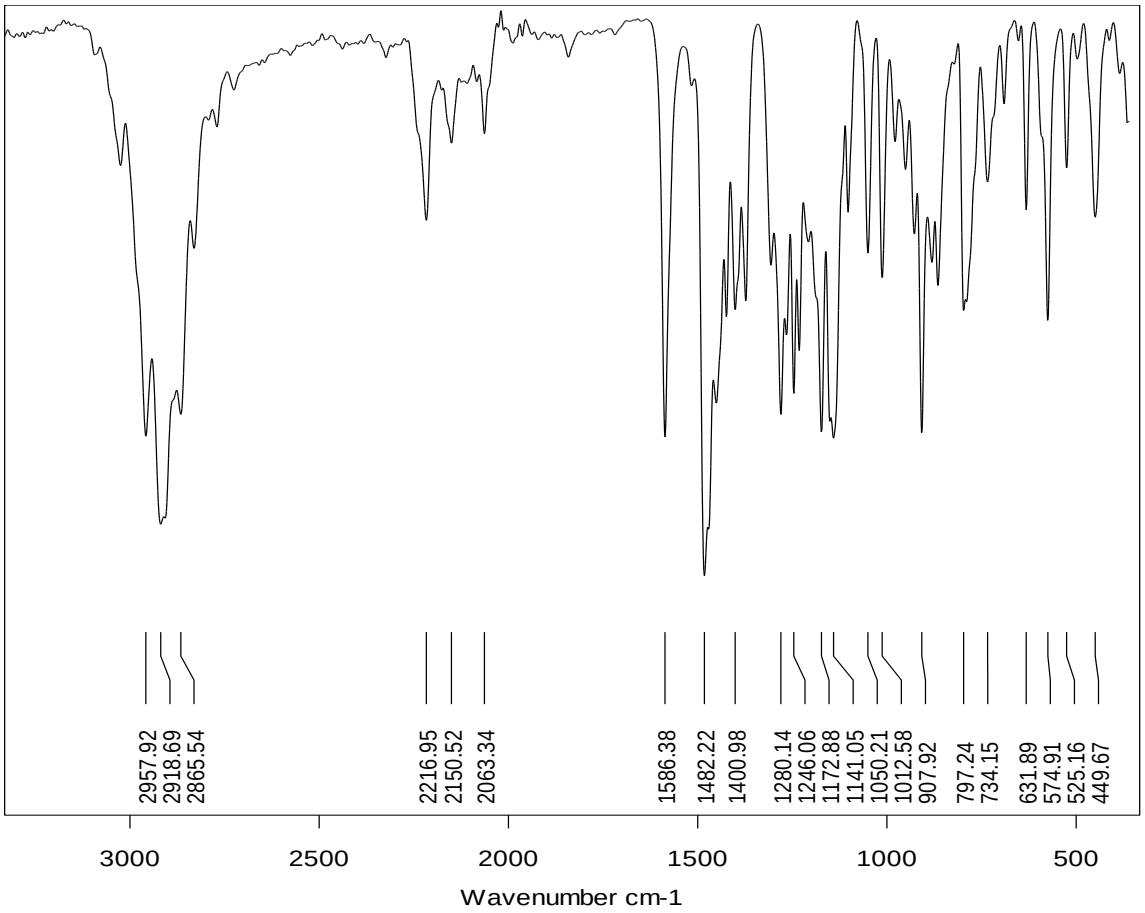

Figure S17. Diamond ATR-FTIR spectrum of **12**.

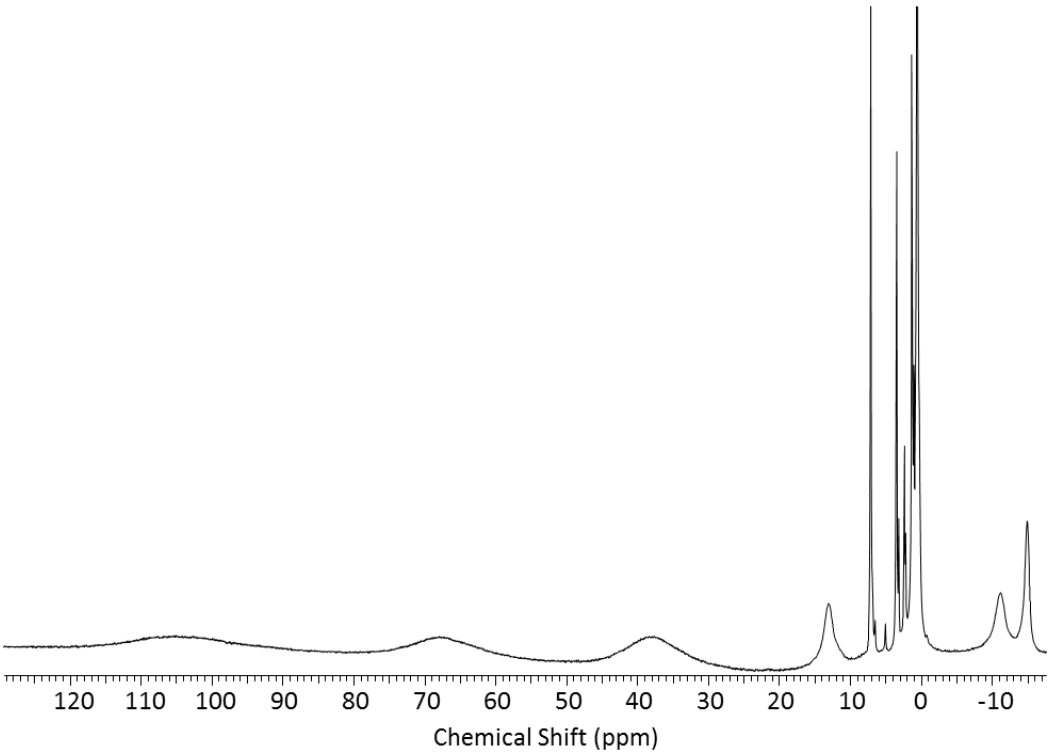

Figure S18. ^{1}H NMR spectrum of **13** in C_6D_6.

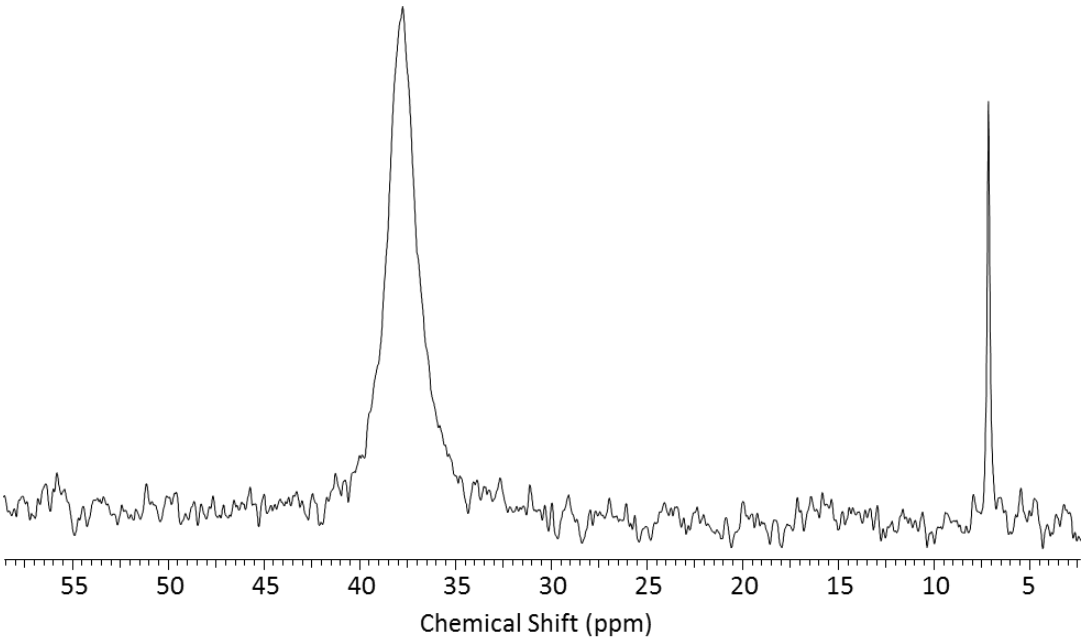

Figure S19. ^{2}H NMR spectrum of **13** in C_6H_6.

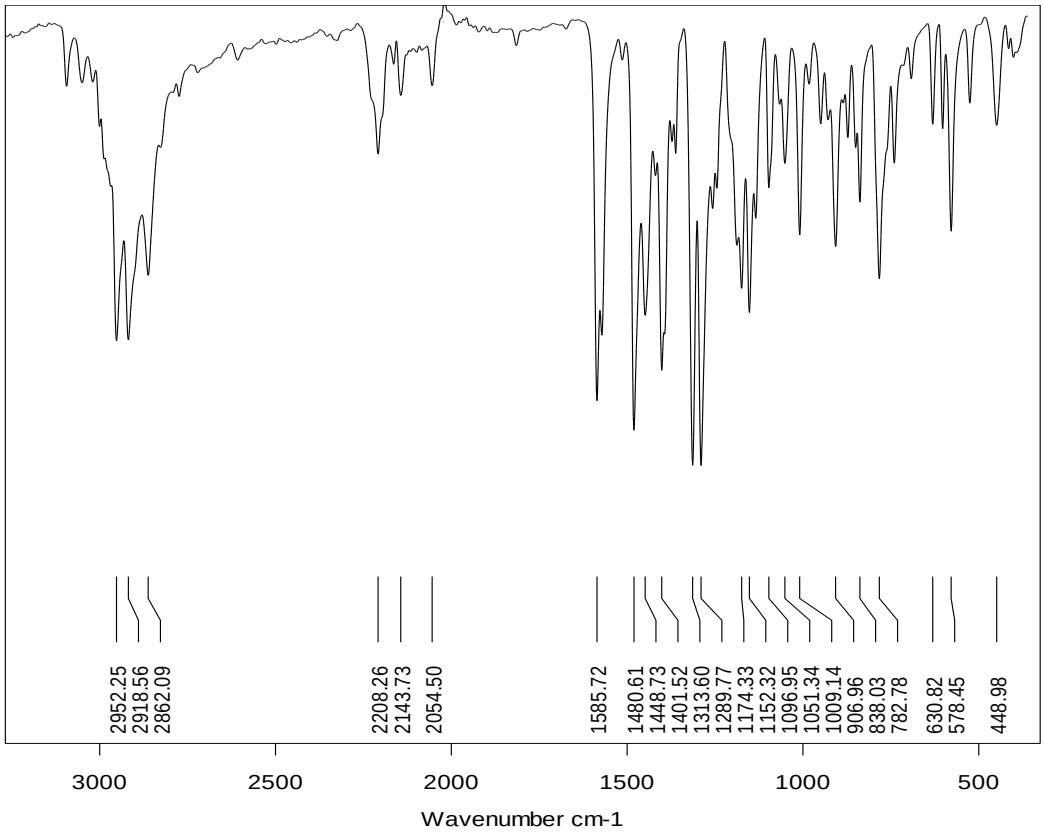

Figure S20. Diamond ATR-FTIR spectrum of **13**.

Table S1. Crystal data and refinement parameters for α-**5**, β-**5**, **7** and **10**.

Compound	α-**5**	β-**5**	**7**	**10**
Empirical formula	$C_{37}H_{54}MoN_4O$	$C_{37}H_{54}MoN_4O$	$C_{86}H_{132}Mo_2N_8O_7$	$C_{26}H_{42}Cl_2MoN_4$
CCDC No.	961017	961016	961022	961020
Temperature (K)	100	173	100	100
Crystal System	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.274(2)	11.9028(8)	11.8143(6)	9.5016(8)
b (Å)	11.269(2)	10.6135(8)	11.9134(6)	10.2855(9)
c (Å)	28.865(4)	29.811(2)	16.8751(9)	15.796(1)
α (°)	90	90	79.050(1)	91.198(2)
β (°)	95.380(2)	93.675(1)	86.767(1)	105.138(1)
γ (°)	90	90	65.461(1)	115.939(1)
Volume (Å^3)	3650.7(9)	3758.3(5)	2120.6(2)	1323.7(2)
Z, ρ (g/cm^3)	4, 1.213	4, 1.178	1, 1.238	2, 1.449
μ (mm^{-1})	0.39	0.38	0.35	0.72
θ (°)	1.42 − 30.51	1.37 − 27.76	1.23 − 29.13	1.35 – 27.10
limiting indices	$-16 \le h \le 16$	$-15 \le h \le 15$	$-16 \le h \le 16$	$-12 \le h \le 12$
	$-16 \le k \le 16$	$-13 \le k \le 13$	$-15 \le k \le 16$	$-13 \le k \le 13$
	$-41 \le l \le 40$	$-38 \le l \le 39$	$-23 \le l \le 23$	$-20 \le l \le 19$
refl collec./unique	91196 / 11074	72770 / 8837	45521/11340	25509 / 5835
R(int)	0.08	0.06	0.03	0.056
no. of parameters	403	394	522	310
$R1^a/wR2^a$ ($I > 2\sigma(I)$)	0.0920 / 0.1939	0.0395 / 0.0888	0.0361 / 0.0908	0.0371 / 0.0833
$R1^a/wR2^a$ for all data	0.1354 / 0.2147	0.0623 / 0.0994	0.0419 / 0.0958	0.0510 / 0.0909
goodness-of-fit on F^2	1.280	1.09	1.06	1.04
larg diff peak/hole (e·Å^{-3})	1.441 / −1.130	0.386 / −0.325	0.973 / −0.896	0.501 / −0.652

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

Table S2. Crystal data and refinement parameters for **11**, **12**, **13** and **14**.

Compound	**11**	**12**	**13**	**14**
Empirical formula	$C_{26}H_{42}MoN_8$	$C_{26}H_{42}ClN_4V$	$C_{39}H_{66}ClN_6V_{1.5}$	$C_{62}H_{96}MoN_9V$
CCDC No.	961021	961018	961019	961023
Temperature (K)	100	100	100	100
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	9.3180(6)	9.328(2)	17.631(2)	10.491(1)
b (Å)	18.593(1)	33.209(6)	9.686(1)	10.876(2)
c (Å)	16.049(1)	17.787(4)	24.542(3)	28.605(4)
α (°)	90.00	90.00	90.00	88.905(4)
β (°)	101.961(1)	103.715(3)	103.421(2)	85.552(4)
γ (°)	90.00	90.00	90.00	68.327(3)
Volume ($Å^3$)	2720.1(3)	5353(2)	4076.8(8)	3023.7(7)
Z, ρ (g/cm^3)	4, 1.374	8, 1.233	4, 1.191	2, 1.224
μ (mm^{-1})	0.512	0.49	0.45	0.41
θ (°)	1.70 − 30.52	1.23 – 28.70	1.19 – 30.49	0.71 – 24.78
limiting indices	$-13 \le h \le 13$	$-11 \le h \le 12$	$-25 \le h \le 25$	$-12 \le h \le 12$
	$-26 \le k \le 26$	$-44 \le k \le 44$	$-13 \le k \le 13$	$-12 \le k \le 12$
	$-22 \le l \le 22$	$-24 \le l \le 24$	$-34 \le l \le 33$	$0 \le l \le 33$
refl collec./unique	76191 / 8311	100488 / 13814	24332/12330	N/A / 10542
R(int)	0.05	0.11	0.02	N/A
no. of parameters	328	601	612	841
$R1^a/wR2^a$ ($I > 2\sigma(I)$)	0.0280 / 0.0998	0.0801 / 0.1632	0.0432 / 0.1096	0.0551 / 0.1175
$R1^a/wR2^a$ for all data	0.0364 / 0.135	0.1283 / 0.1842	0.0618 / 0.1280	0.0722 / 0.1258
goodness-of-fit on F^2	0.918	1.11	0.795	1.141
larg diff peak/hole ($e \cdot Å^{-3}$)	0.763 / −0.723	0.776 / −0.713	0.403 / −0.361	0.684 / −0.714

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

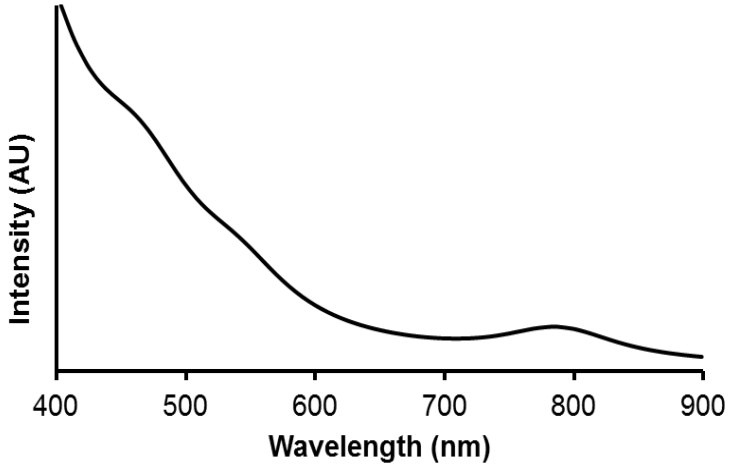

Figure S21. DFT modeled UV/VIS absorption spectrum of **5** with a Laurentian broadening of 50 applied to first 100 roots.

Table S3. Cartesian coordinates for DFT optimized $(CH_3)_4Si$.

Atom	x	y	z
H	0.3087	1.378474	-2.08742
H	-1.22362	1.786446	-1.29435
H	-0.46064	-1.69981	-1.80306
H	-1.95762	-1.2663	-0.95362
C	-0.16959	1.535615	-1.10998
H	2.309418	-0.71203	-0.71787
C	-0.88691	-1.47317	-0.81562
H	0.306768	2.412778	-0.64943
Si	-0.00036	-0.00018	-0.00295
H	-0.80284	-2.38165	-0.20258
C	1.838505	-0.4205	0.232329
H	2.39781	0.439324	0.627967
H	1.973852	-1.25141	0.939716
C	-0.78527	0.357198	1.690935
H	-1.84843	0.618676	1.594502
H	-0.28093	1.192999	2.196354
H	-0.71885	-0.51646	2.35506

Table S4. Cartesian coordinates for DFT optimized **5** (S = 1).

Atom	x	y	z
C	-2.77181	0.681616	-1.41797
C	0.266801	-1.88295	2.044737
C	0.174317	-3.2391	1.670872
C	1.108402	-4.16973	2.117506
C	2.176679	-3.76528	2.92559
C	2.291337	-2.42365	3.289517
C	1.344241	-1.49247	2.859864
C	-2.03121	-0.89604	2.312056
C	-3.04036	-1.79414	1.57786
C	-1.88113	-1.37437	3.764455
C	-2.54609	0.548161	2.334498
C	2.236694	-1.01468	-1.33229
C	2.960938	-1.81132	-0.4277
C	4.350433	-1.71142	-0.33924
C	5.047265	-0.82417	-1.15965
C	4.340939	-0.02689	-2.06695
C	2.953267	-0.11012	-2.14222
C	0.234325	-1.89248	-2.57608
C	-1.05037	-2.58844	-2.11093
C	-0.08342	-0.94148	-3.74136
C	1.219388	-2.97257	-3.05011
C	1.568289	1.847909	1.389653
C	1.093595	2.263442	2.650519
C	1.936999	2.294257	3.757675
C	3.269149	1.882485	3.641545
C	3.748359	1.451891	2.404517
C	2.910186	1.439969	1.288175
C	0.421795	3.145066	-0.4353
C	-0.86928	3.759061	0.129972
C	1.587528	4.125816	-0.23428
C	0.259018	2.897234	-1.9397
N	-1.71648	0.44013	-0.88944
N	-0.69527	-0.91605	1.61394
N	0.813248	-1.12993	-1.41114
N	0.722386	1.829364	0.236396
O	-3.81672	0.924294	-1.94294
Mo	0.000000	0.00000	0.000000
H	-0.64562	-3.55222	1.026422
H	1.010375	-5.21618	1.825143

H	2.910585	-4.49474	3.269481
H	3.116696	-2.09522	3.922373
H	1.415246	-0.45307	3.176331
H	-3.15488	-1.47651	0.535065
H	-4.02543	-1.74156	2.063288
H	-2.72027	-2.84399	1.588436
H	-1.15658	-0.75835	4.313061
H	-1.55569	-2.42013	3.824396
H	-2.85086	-1.29424	4.273546
H	-1.84022	1.198135	2.866449
H	-3.51354	0.592752	2.853064
H	-2.68648	0.944599	1.324219
H	2.423037	-2.53104	0.187406
H	4.888991	-2.34146	0.36983
H	6.133629	-0.75311	-1.09769
H	4.875842	0.672128	-2.71148
H	2.402953	0.524956	-2.83501
H	-0.83392	-3.27874	-1.28618
H	-1.48478	-3.16568	-2.93854
H	-1.80143	-1.86896	-1.771
H	0.827942	-0.46601	-4.12669
H	-0.77702	-0.15551	-3.42143
H	-0.54806	-1.49218	-4.57189
H	2.150407	-2.54236	-3.43873
H	0.755169	-3.55446	-3.8577
H	1.474641	-3.66374	-2.2363
H	0.05185	2.565441	2.746842
H	1.551364	2.630551	4.721228
H	3.926439	1.901408	4.511443
H	4.785706	1.131706	2.299056
H	3.296593	1.137596	0.316154
H	-1.71244	3.070051	0.004273
H	-1.11046	4.695816	-0.39284
H	-0.76559	3.991707	1.197629
H	2.528174	3.709435	-0.61786
H	1.733428	4.385073	0.821446
H	1.376903	5.053684	-0.78261
H	1.177267	2.466974	-2.35874
H	0.056464	3.845683	-2.45574
H	-0.57009	2.214609	-2.15043

Table S5. Cartesian coordinates for DFT optimized CO.

Atom	x	y	Z
C	0.000	0.000	-0.568397
O	0.000	0.000	0.568397

Table S6. Cartesian coordinates for DFT optimized **1-mod** (S = 0) constrained to have the same coordination geometry as **1**.

Atom	x	y	z
Mo	-0.00907	0.001629	0.019748
N	1.630391	0.001017	0.017324
N	-0.42638	1.936439	0.006396
N	-0.43127	-0.95002	-1.66456
N	-0.41841	-0.98035	1.688929
C	0.475713	-1.74195	-2.47711
C	-1.80738	-1.05548	-2.12731
H	0.408945	-1.45584	-3.54349
H	1.506482	-1.59817	-2.14068
H	0.233811	-2.8191	-2.41055
H	-2.48579	-0.45073	-1.50639
H	-2.17246	-2.09919	-2.10285
H	-1.91016	-0.69286	-3.16664
C	0.485431	3.02653	-0.29361
C	-1.80408	2.393018	0.115946
H	0.254499	3.479519	-1.27587
H	1.51575	2.660034	-0.31711
H	0.412336	3.829196	0.463696
H	-2.15713	2.865888	-0.81954
H	-2.48456	1.558597	0.344813
H	-1.91846	3.135658	0.926643
C	0.496734	-1.28389	2.775148
C	-1.79258	-1.33013	2.018105
H	0.25966	-0.68688	3.67526
H	0.435924	-2.35028	3.061936
H	1.524503	-1.06144	2.473763
H	-1.89348	-2.41184	2.222555
H	-2.15436	-0.78767	2.911354
H	-2.47444	-1.09433	1.186604

Table S7. Cartesian coordinates for DFT optimized **5-mod** (S = 1), constrained to have the same coordination geometry as **5**.

Atom	x	y	z
Mo	-0.00228	0.002636	0.002714
N	1.958494	0.001478	0.003244
N	-0.41541	1.920208	0.004283
N	-0.41782	-0.95255	-1.65938
N	-0.41106	-0.95824	1.663431
C	0.455101	-1.75977	-2.49462
C	-1.76306	-0.82707	-2.19505
H	0.515848	-1.3535	-3.52162
H	1.465746	-1.7806	-2.07404
H	0.091957	-2.80168	-2.57002
H	-2.37354	-0.14959	-1.5739
H	-2.28706	-1.80034	-2.23076
H	-1.75737	-0.40612	-3.21736
C	0.458591	3.046228	-0.27734
C	-1.75807	2.323561	0.388491
H	0.0925	3.636226	-1.13809
H	1.467373	2.691361	-0.51226
H	0.525065	3.729346	0.590104
H	-2.28513	2.843116	-0.43333
H	-2.3688	1.447802	0.666365
H	-1.74642	2.997335	1.265054
C	0.464533	-1.27718	2.778197
C	-1.75453	-1.48917	1.824358
H	0.102328	-0.82301	3.719278
H	0.527816	-2.36969	2.939104
H	1.474229	-0.90045	2.584788
H	-1.74518	-2.58501	1.970553
H	-2.27875	-1.03527	2.685882
H	-2.36687	-1.29155	0.928018
C	3.163986	0.015062	0.022974
O	4.35758	0.026245	0.039321

Table S8. Cartesian coordinates for DFT optimized intermediate in reaction of CO with **1-mod** on path to **5-mod** (S = 0) where CO binds to metal.

Atom	x	y	z
N	1.834463	-0.46383	-0.6231
Mo	0.250807	-0.03506	-0.43495
N	-0.42732	-0.92334	1.285953
N	-0.64257	-1.22883	-1.75207
N	0.082294	1.720767	-1.42613
C	0.354763	-1.77145	2.16289
C	-1.69145	-0.5469	1.882794
C	0.027453	-2.01879	-2.76584
C	-2.07998	-1.39682	-1.80279
C	1.160996	2.625782	-1.76572
C	-1.2181	2.304993	-1.68403
H	1.316561	-2.01539	1.702351
H	0.5451	-1.29149	3.144381
H	-0.17826	-2.71912	2.367548
H	-1.5594	-0.00843	2.843612
H	-2.27174	0.111294	1.217823
H	-2.31807	-1.43354	2.092625
H	-0.25099	-3.08723	-2.69015
H	1.113144	-1.9336	-2.65969
H	-0.24742	-1.68391	-3.78465
H	-2.3671	-2.45623	-1.66136
H	-2.58313	-0.81848	-1.01474
H	-2.50006	-1.07184	-2.77377
H	2.130171	2.144133	-1.60586
H	1.096942	2.927714	-2.82831
H	1.130928	3.558365	-1.16627
H	-1.39298	3.231015	-1.10135
H	-1.3282	2.570362	-2.75307
H	-2.02904	1.602156	-1.44372
C	0.756345	1.33885	1.25004
O	0.778497	1.964513	2.211408

Table S9. Cartesian coordinates for DFT optimized **1**

Atom	x	y	z
H	-1.68157	-1.3873	-4.89829
H	-0.04948	-1.78734	-4.3206
H	-1.49501	0.900894	-4.11882
C	-1.11056	-1.76502	-4.03985
H	-1.43483	-2.79465	-3.84777
H	4.299629	-0.64182	-3.64674
H	0.138364	0.616446	-3.47107
C	-0.93237	0.580982	-3.23083
H	-3.44356	-0.47493	-3.30404
C	-1.34917	-0.84194	-2.83458
H	2.464035	0.665526	-2.61326
C	4.075573	-0.76691	-2.58629
H	-1.13372	1.293494	-2.42459
C	-2.84015	-0.84772	-2.46389
H	5.600557	-2.26903	-2.27448
H	1.852485	-2.4031	-2.25527
H	-3.19147	-1.85996	-2.22653
C	3.04926	-0.0241	-2.00662
H	2.433571	-4.81017	-2.12735
C	1.110154	-3.12538	-1.92089
C	4.802182	-1.68238	-1.81881
H	2.150284	2.735907	-1.84146
C	1.427484	-4.48353	-1.86107
N	-0.49915	-1.28068	-1.66239
H	-3.02001	-0.19874	-1.59829
C	-0.1743	-2.67248	-1.58264
C	0.466083	-5.41779	-1.47569
H	0.712057	-6.47953	-1.43855
C	-1.12877	-3.62286	-1.17181
C	-0.81703	-4.98021	-1.13338
H	-2.11942	-3.28099	-0.87535
H	0.5269	2.854522	-1.1103
C	1.600484	2.9765	-0.92255
H	-1.5754	-5.69934	-0.82025
C	2.744327	-0.15584	-0.63814
H	1.790607	4.033955	-0.68906
H	4.146011	2.013706	-0.39842
C	4.493854	-1.83921	-0.46756
N	-1.14328	0.984539	-0.00129

N	1.717669	0.632446	-0.02678
Mo	-0.06152	-0.26952	0.000638
C	3.480299	-1.07975	0.119573
H	5.049986	-2.55213	0.142558
C	2.042486	2.084415	0.247782
C	3.550437	2.25572	0.48981
H	3.753723	3.301395	0.756293
H	-2.96101	-0.27887	1.033602
H	0.300978	-3.72878	1.083752
H	-2.9732	-2.05779	1.125054
H	3.895782	1.620982	1.316434
H	3.266418	-1.17937	1.182088
H	0.215828	2.467316	1.383998
C	1.300833	2.516361	1.520064
C	-2.9342	-1.13373	1.716851
N	-0.4642	-1.24288	1.695223
C	0.95395	-3.2512	1.811885
H	2.248808	-4.96032	1.998452
H	1.56767	3.551667	1.77377
C	0.663927	-1.94329	2.229655
C	2.043185	-3.94552	2.341495
H	-3.8309	-1.0936	2.350698
H	1.577889	1.873141	2.365448
H	-1.57213	1.064029	2.688115
C	-1.67441	-1.10747	2.593109
H	-1.76735	-3.24865	3.0383
C	1.505972	-1.34878	3.189108
C	2.856	-3.35405	3.308494
C	-1.63155	0.213112	3.37744
H	1.311024	-0.32293	3.498665
H	3.700878	-3.90056	3.728855
C	-1.74646	-2.28966	3.572399
C	2.579572	-2.05074	3.732791
H	-2.54112	0.325914	3.984729
H	-0.77144	0.248279	4.058444
H	-2.66856	-2.20934	4.16308
H	-0.90086	-2.30569	4.27036
H	3.213382	-1.57253	4.481123

Table S10. Cartesian coordinates for DFT optimized **9** (S = 0).

Atom	x	y	z
C	-0.4418	-1.62866	1.724096
C	-0.48329	-2.99223	1.367153
C	0.431817	-3.90828	1.886958
C	1.423356	-3.44368	2.749333
C	1.517016	-2.10348	3.107462
C	0.579665	-1.20409	2.591892
C	-2.79077	-0.7491	1.879282
C	-3.73247	-1.67601	1.090528
C	-2.67989	-1.23915	3.334455
C	-3.37318	0.673064	1.894496
C	1.49486	-0.90541	-1.67484
C	2.185317	-1.76265	-0.80014
C	3.580096	-1.74374	-0.71307
C	4.287291	-0.85719	-1.5176
C	3.644818	0.012963	-2.39669
C	2.250954	-0.00666	-2.45532
C	-0.5116	-1.64845	-2.99545
C	-1.83178	-2.32525	-2.59372
C	-0.78265	-0.63264	-4.11907
C	0.453619	-2.73634	-3.5002
C	0.900737	2.02769	0.946605
C	0.468413	2.423845	2.229229
C	1.354382	2.499179	3.304402
C	2.68495	2.138561	3.098613
C	3.148638	1.719304	1.85682
C	2.250731	1.669226	0.786854
C	-0.37088	3.343245	-0.77691
C	-1.66487	3.889817	-0.14805
C	0.771265	4.356046	-0.57691
C	-0.58311	3.150927	-2.28703
N	-2.29961	0.59014	-1.19238
N	-1.41683	-0.69978	1.232057
N	0.065468	-0.95718	-1.77212
N	0.000394	2.001219	-0.16887
Mo	-0.863122	0.221087	-0.45262
H	-1.24925	-3.33357	0.670572
H	0.393473	-4.96579	1.621167
H	2.306988	-1.7739	3.783432
H	0.616718	-0.15652	2.889661

H	-3.81689	-1.33882	0.048858
H	-4.73877	-1.66836	1.537259
H	-3.37431	-2.71535	1.099033
H	-2.00196	-0.60298	3.921554
H	-2.32195	-2.27505	3.402589
H	-3.67385	-1.19719	3.8027
H	-2.70519	1.358867	2.435419
H	-4.34897	0.672765	2.403171
H	-3.5192	1.054723	0.877237
H	1.617229	-2.47442	-0.20176
H	4.1151	-2.41032	-0.03541
H	4.231428	0.700857	-3.00756
H	1.730646	0.686951	-3.11636
H	-1.66671	-3.04091	-1.77546
H	-2.24663	-2.87538	-3.45175
H	-2.57526	-1.58755	-2.27012
H	0.147354	-0.16313	-4.47044
H	-1.4653	0.152606	-3.7677
H	-1.24884	-1.13173	-4.98269
H	1.404151	-2.32024	-3.85957
H	-0.01602	-3.2705	-4.33885
H	0.676713	-3.47106	-2.7132
H	-0.58151	2.676046	2.379297
H	1.02336	2.816295	4.29456
H	4.196474	1.443617	1.731017
H	2.605255	1.377288	-0.20138
H	-2.48654	3.173318	-0.28005
H	-1.9541	4.836698	-0.62979
H	-1.53784	4.090119	0.925387
H	1.714331	3.986427	-1.00465
H	0.944189	4.590225	0.481854
H	0.511535	5.293799	-1.08902
H	0.323223	2.741478	-2.75621
H	-0.80619	4.119131	-2.76013
H	-1.42029	2.47231	-2.48846
F	3.553577	2.197445	4.147615
F	2.327555	-4.3307	3.253084
F	5.648354	-0.83382	-1.44417

Table S11. Cartesian coordinates for DFT optimized OCN–Mo(N[R]Ar_F)$_3$ (S = 1).

Atom	x	y	z
C	-3.41815	0.854454	-1.7522
C	-0.36875	-1.71601	1.722139
C	-0.44867	-3.07397	1.343431
C	0.473954	-4.01231	1.803395
C	1.512226	-3.57971	2.628421
C	1.642776	-2.24928	3.011266
C	0.698086	-1.32587	2.555515
C	-2.67685	-0.74148	1.985439
C	-3.67897	-1.64522	1.243947
C	-2.52853	-1.22458	3.439375
C	-3.19928	0.702274	2.010308
C	1.598957	-0.85662	-1.66286
C	2.324056	-1.66979	-0.76971
C	3.716577	-1.5947	-0.68124
C	4.388294	-0.69551	-1.50228
C	3.71341	0.129778	-2.40186
C	2.322813	0.054232	-2.4631
C	-0.40259	-1.72871	-2.91989
C	-1.69117	-2.42676	-2.46108
C	-0.71513	-0.76995	-4.08322
C	0.585394	-2.80881	-3.39627
C	0.938317	2.014933	1.054921
C	0.468416	2.421644	2.322966
C	1.314581	2.472296	3.429551
C	2.643542	2.078231	3.273325
C	3.145562	1.651174	2.048999
C	2.287553	1.624552	0.946272
C	-0.21643	3.322034	-0.76292
C	-1.50839	3.932243	-0.18927
C	0.950624	4.304902	-0.55921
C	-0.38243	3.080624	-2.27037
N	-2.36215	0.608821	-1.22205
N	-1.3347	-0.75263	1.285553
N	0.173385	-0.96664	-1.74542
N	0.085849	1.997328	-0.09594
O	-4.46287	1.101121	-2.27893
Mo	-0.64279	0.166054	-0.33288
H	-1.25662	-3.39119	0.684145
H	0.405523	-5.06472	1.523918

H	2.463823	-1.94739	3.662672
H	0.762422	-0.28617	2.876483
H	-3.79284	-1.3245	0.200536
H	-4.66751	-1.60195	1.72694
H	-3.35174	-2.69479	1.251972
H	-1.80696	-0.60826	3.994734
H	-2.20247	-2.27179	3.49931
H	-3.50149	-1.14736	3.94629
H	-2.49969	1.354176	2.551766
H	-4.17221	0.741808	2.522249
H	-3.33337	1.102612	0.999074
H	1.783823	-2.39541	-0.16155
H	4.2774	-2.2297	0.005762
H	4.275745	0.823141	-3.02908
H	1.777293	0.704286	-3.1475
H	-1.4769	-3.12864	-1.6432
H	-2.12884	-2.99487	-3.2954
H	-2.44072	-1.70741	-2.11298
H	0.199108	-0.29022	-4.46149
H	-1.41251	0.014577	-3.76303
H	-1.17412	-1.31676	-4.92158
H	1.517367	-2.37821	-3.78664
H	0.120792	-3.39065	-4.20589
H	0.842087	-3.50369	-2.58388
H	-0.57726	2.709862	2.430796
H	0.95718	2.800204	4.406882
H	4.192005	1.35613	1.961751
H	2.673245	1.329357	-0.02956
H	-2.35288	3.243059	-0.31707
H	-1.75225	4.874035	-0.70516
H	-1.4019	4.158909	0.881247
H	1.893703	3.892401	-0.9456
H	1.097531	4.564149	0.497982
H	0.738069	5.235294	-1.10579
H	0.539633	2.660485	-2.69593
H	-0.59479	4.030877	-2.78251
H	-1.20752	2.391105	-2.48204
F	3.472215	2.117071	4.354058
F	2.422498	-4.49076	3.072972
F	5.746564	-0.6173	-1.42981

Table S12. Cartesian coordinates for DFT optimized **4** (S = 0).

Atom	x	y	z
V	2.563164	3.623794	4.982403
N	2.121533	5.611502	5.00128
N	3.630051	3.702657	6.712449
N	1.363325	2.227196	4.471119
N	3.715391	3.58036	3.918513
C	3.218202	7.82958	4.842709
H	3.833273	7.887974	3.931679
H	3.682459	8.478713	5.593825
H	2.226863	8.219118	4.59495
C	3.169482	6.39145	5.304527
C	4.286325	5.928994	6.031032
H	5.090406	6.657612	6.133165
C	4.470073	4.745889	6.778323
C	5.697346	4.683958	7.656662
H	5.539264	4.06261	8.543629
H	6.014959	5.684286	7.969978
H	6.525334	4.23299	7.089567
C	0.885444	6.1712	4.526013
C	-0.03358	6.718147	5.458982
C	-1.25549	7.205014	4.980695
H	-1.97044	7.633328	5.684542
C	-1.57667	7.159528	3.627796
H	-2.53694	7.54091	3.277937
C	-0.66064	6.632606	2.724204
H	-0.90783	6.612684	1.662125
C	0.58209	6.13837	3.141431
C	0.268547	6.823883	6.948543
H	1.201533	6.277897	7.140738
C	0.488667	8.286126	7.372303
H	1.290616	8.76464	6.796728
H	0.757957	8.341015	8.43681
H	-0.42452	8.880785	7.227809
C	-0.82706	6.18352	7.812113
H	-0.55289	6.241877	8.874747
H	-0.97909	5.128694	7.553661
H	-1.78937	6.701493	7.697926
C	1.565241	5.641161	2.090403
H	2.442299	5.228458	2.605804
C	0.976133	4.51364	1.23128

H	0.642875	3.668817	1.845743
H	1.73615	4.133932	0.53535
H	0.121017	4.858734	0.632182
C	2.049686	6.798765	1.201289
H	2.492397	7.611152	1.792928
H	1.224975	7.227816	0.614053
H	2.811348	6.440689	0.494857
C	3.73855	2.603635	7.635315
C	2.973361	2.632045	8.830529
C	3.079944	1.548469	9.709155
H	2.504225	1.550883	10.6342
C	3.89751	0.458373	9.422591
H	3.961003	-0.37701	10.12127
C	4.627117	0.439013	8.240437
H	5.261493	-0.41967	8.016706
C	4.571284	1.500177	7.326766
C	2.069454	3.809412	9.175654
H	1.730885	4.242124	8.222274
C	2.829589	4.908578	9.938272
H	3.661666	5.319363	9.355505
H	3.237171	4.516014	10.881
H	2.153911	5.740203	10.18483
C	0.822966	3.402197	9.97066
H	0.140662	4.257439	10.05831
H	1.072202	3.087066	10.99365
H	0.28013	2.585677	9.479835
C	5.400476	1.416177	6.052422
H	5.270824	2.351752	5.493028
C	6.898154	1.241684	6.349951
H	7.280549	2.02515	7.017516
H	7.474621	1.280957	5.415309
H	7.108992	0.272914	6.824759
C	4.90114	0.283452	5.142276
H	3.844431	0.41352	4.880183
H	5.015376	-0.69898	5.622891
H	5.473639	0.268616	4.204729
C	1.319236	1.279886	3.416292
C	2.364645	1.198198	2.475312
H	3.208757	1.879271	2.577057
C	2.316821	0.279889	1.435167
H	3.147274	0.248466	0.725409
C	1.237482	-0.6041	1.270609

C	0.200116	-0.51624	2.202564
H	-0.66321	-1.17919	2.109393
C	0.230852	0.400012	3.254712
H	-0.60527	0.43143	3.950934
C	1.211926	-1.60535	0.147087
H	0.229969	-2.08807	0.063106
H	1.957865	-2.40094	0.296989
H	1.438259	-1.13471	-0.82037
C	0.291933	2.152038	5.422694
C	-0.84452	2.963355	5.291345
C	-1.90051	2.851918	6.196375
H	-2.77827	3.489118	6.070887
C	-1.86289	1.929799	7.250253
C	-0.72146	1.121946	7.373776
H	-0.66606	0.390487	8.183031
C	0.341845	1.23031	6.481922
C	-2.99502	1.825283	8.236353
H	-3.93237	2.21087	7.816142
H	-2.78271	2.405416	9.147793
H	-3.16386	0.786404	8.54892
H	-0.90232	3.667049	4.460267
H	1.216733	0.586955	6.582489

Table S13. Cartesian coordinates for DFT optimized OCN–V(nacnac)(N[*p*-tol]$_2$) (S = 1).

Atom	x	y	z
V	-0.18912	0.187635	-0.31593
N	-0.74783	1.209769	-1.82848
N	-1.12119	0.647018	1.370969
N	-1.11705	-1.54409	-0.55247
N	1.742186	0.116472	-0.09267
O	-0.92388	2.588855	-3.77976
C	-0.82272	1.906857	-2.80882
C	-1.8131	-0.24783	2.108411
C	-2.03985	-1.56962	1.689612
H	-2.56878	-2.19364	2.408781
C	-1.77066	-2.17429	0.455313
C	-2.39857	0.129377	3.449348
H	-1.85675	-0.38023	4.258312
H	-3.44466	-0.19695	3.511144
H	-2.35575	1.20535	3.637905

C	-2.21287	-3.60781	0.283309
H	-2.9668	-3.87735	1.030282
H	-1.35284	-4.28066	0.41546
H	-2.61568	-3.80518	-0.71545
C	2.34134	1.168572	-0.8494
C	2.038662	2.505926	-0.54471
H	1.409859	2.730575	0.317362
C	2.513702	3.54659	-1.34278
H	2.242055	4.573644	-1.0912
C	3.335493	3.300717	-2.44741
C	3.653285	1.963503	-2.73533
H	4.279022	1.737315	-3.60143
C	3.163141	0.916171	-1.96343
H	3.405342	-0.11254	-2.22584
C	3.874977	4.425448	-3.28863
H	3.231151	5.312141	-3.23417
H	3.960542	4.133472	-4.3434
H	4.878953	4.729027	-2.95407
C	2.52858	-0.7796	0.637422
C	3.939949	-0.74253	0.65528
H	4.466189	0.015257	0.077475
C	4.670725	-1.65347	1.412612
H	5.761556	-1.59099	1.394736
C	4.053024	-2.64131	2.192445
C	2.651856	-2.66513	2.188394
H	2.126379	-3.40759	2.793703
C	1.904857	-1.75887	1.441704
H	0.81468	-1.80527	1.493673
C	4.858732	-3.60648	3.020815
H	4.242964	-4.44588	3.368837
H	5.283958	-3.12145	3.91309
H	5.701792	-4.02366	2.452485
C	-0.9677	2.012008	1.82372
C	-1.84986	2.999848	1.310521
C	-1.66778	4.326995	1.715012
H	-2.33436	5.097295	1.327581
C	-0.65514	4.684385	2.599579
H	-0.52974	5.725958	2.898121
C	0.193288	3.705362	3.103163
H	0.979692	3.988766	3.803712
C	0.060946	2.358615	2.739126
C	-3.00784	2.652807	0.38495

H	-2.78035	1.68437	-0.07839
C	-3.19625	3.665801	-0.75169
H	-3.57462	4.630993	-0.38614
H	-3.93129	3.285913	-1.47372
H	-2.26081	3.850175	-1.293
C	-4.31659	2.496017	1.178864
H	-4.23808	1.723514	1.953918
H	-5.14083	2.216779	0.507212
H	-4.58998	3.439422	1.673003
C	1.00547	1.342795	3.370233
H	0.816305	0.365284	2.907992
C	2.48377	1.684593	3.130035
H	2.710366	1.806532	2.066102
H	3.122269	0.878391	3.515083
H	2.770341	2.611625	3.646853
C	0.7573	1.212315	4.883881
H	1.012782	2.145687	5.405107
H	1.387105	0.415399	5.303279
H	-0.2879	0.980109	5.119773
C	-1.2242	-2.10637	-1.88597
C	-0.2284	-2.96778	-2.40161
C	-0.40876	-3.50225	-3.68477
H	0.35227	-4.16931	-4.09205
C	-1.53184	-3.20421	-4.44503
H	-1.6528	-3.63318	-5.44053
C	-2.50044	-2.34824	-3.92891
H	-3.37633	-2.10991	-4.53267
C	-2.37325	-1.77991	-2.65747
C	1.024666	-3.34458	-1.62889
H	1.00602	-2.81105	-0.67105
C	2.291486	-2.90238	-2.37541
H	2.442145	-3.4889	-3.29294
H	3.177675	-3.03701	-1.74042
H	2.230097	-1.84644	-2.6628
C	1.09499	-4.84886	-1.32372
H	0.208449	-5.20335	-0.78204
H	1.978218	-5.06888	-0.70828
H	1.175016	-5.44136	-2.24619
C	-3.47807	-0.86261	-2.1443
H	-3.06621	-0.2912	-1.30271
C	-3.9441	0.151321	-3.19878
H	-3.1048	0.697438	-3.64395

H	-4.62071	0.884891	-2.73837
H	-4.50346	-0.3304	-4.01305
C	-4.686	-1.66069	-1.62384
H	-5.12098	-2.27814	-2.42306
H	-5.46888	-0.97694	-1.26534
H	-4.41923	-2.32474	-0.79319

Table S14. Cartesian coordinates for DFT optimized **4-mod** (S = 0).

Atom	x	y	z
N	-0.15357	0.433786	-0.01647
V	1.357591	0.01808	-0.01408
N	2.274103	1.636578	0.012407
N	1.754267	-1.24895	-1.54585
N	1.749684	-1.23359	1.53171
C	3.732866	1.593452	0.021568
C	1.754153	2.990724	0.03533
H	4.095354	0.555765	0.005429
H	4.145552	2.08109	0.923465
H	4.158337	2.113477	-0.85582
H	0.660855	2.960931	0.027145
H	2.104528	3.569542	-0.83936
H	2.091327	3.53313	0.938233
C	2.015741	-2.50508	1.262867
C	2.01555	-2.51869	-1.26268
C	2.139847	-3.11093	0.003196
C	1.623126	-0.81509	2.922569
C	1.619132	-0.84756	-2.9409
H	1.825124	-1.64963	3.612241
H	2.329739	-0.00353	3.146466
H	0.60924	-0.43705	3.114207
H	1.828084	-1.6875	-3.62181
H	2.316293	-0.03108	-3.17596
H	0.60052	-0.48261	-3.13357
H	2.153615	-3.18997	-2.12254
H	2.361913	-4.1761	0.008995
H	2.158433	-3.16588	2.130097

Table S15. Cartesian coordinates for DFT optimized product of CO and **4-mod** (S = 1).

Atom	x	y	z
N	0.016268	0.284554	-0.01246
V	1.909837	0.038647	0.015338
N	2.643934	1.765993	0.027162
N	2.095033	-1.23096	-1.49061
N	2.052539	-1.26114	1.500926
C	4.073282	2.028884	0.031721
C	1.849322	2.98446	0.039521
H	4.642172	1.085618	0.024478
H	4.386841	2.597362	0.92787
H	4.389066	2.612227	-0.85402
H	0.781848	2.743339	0.035636
H	2.066837	3.612956	-0.84456
H	2.065331	3.595672	0.936085
C	1.728729	-2.53411	1.241229
C	1.762567	-2.50821	-1.26604
C	1.497062	-3.09403	-0.0216
C	2.613894	-0.96375	2.817678
C	2.693063	-0.90618	-2.7844
H	3.706782	-1.09011	2.816657
H	2.392305	0.073581	3.096846
H	2.194508	-1.62635	3.591844
H	3.786184	-1.02636	-2.75258
H	2.473469	0.134877	-3.0507
H	2.301335	-1.55733	-3.58238
H	1.71577	-3.1653	-2.14493
H	1.183631	-4.13641	-0.0367
H	1.660201	-3.20979	2.104465
C	-1.16866	0.056852	-0.01034
O	-2.34433	-0.1362	-0.01092

Table S16. Cartesian coordinates for DFT optimized intermediate product on reaction pathway of CO + **4-mod** (S = 0).

Atom	x	y	z
N	0.01543	0.010759	-0.01689
V	1.598879	0.009613	-0.00079
N	2.113668	1.84468	0.002337
N	1.947494	-2.00876	-0.46754
N	1.923493	-0.46701	1.983727

C	3.510641	2.152852	-0.23139
C	1.262853	3.014925	0.014328
H	4.116664	1.221149	-0.28968
H	3.931279	2.77408	0.597491
H	3.663884	2.725889	-1.18069
H	0.211939	2.70905	0.175716
H	1.334224	3.58921	-0.94461
H	1.566711	3.715209	0.831635
C	1.506482	-1.62531	2.476244
C	1.521756	-2.9448	0.372154
C	1.183908	-2.77055	1.726709
C	2.453566	0.525745	2.904404
C	2.491563	-2.45192	-1.7418
H	2.368855	0.185668	3.9624
H	3.529675	0.726849	2.699572
H	1.911906	1.489573	2.793452
H	2.519249	-3.56363	-1.81211
H	3.530375	-2.08012	-1.88326
H	1.886002	-2.06647	-2.59305
H	1.475263	-3.98405	-0.01924
H	0.817602	-3.65003	2.272935
H	1.453678	-1.7153	3.582735
C	1.440839	0.410391	-2.03146
O	1.142282	0.843408	-3.05717

Table S17. Cartesian coordinates for DFT optimized **11** (S = 0).

Atom	x	y	z
Mo	-1.29294	0.650365	-0.67555
N	-2.91871	0.371914	-0.6648
N	-1.39225	2.560232	-1.47753
N	-2.35678	3.178113	-1.87131
N	-3.22504	3.82462	-2.27792
N	-1.07035	1.175771	1.281618
C	0.204541	0.890463	1.826164
C	1.378824	1.193444	1.081572
C	2.626603	0.809123	1.574533
H	3.525081	1.043643	1.005062
C	2.754012	0.136417	2.790804
H	3.744609	-0.15074	3.14788
C	1.621681	-0.16673	3.548844

C	0.37032	0.206185	3.04447
H	-0.51637	-0.09789	3.59753
N	1.220856	1.905989	-0.15833
C	2.340916	1.785456	-1.09388
H	3.245681	2.323802	-0.75139
H	2.039503	2.224245	-2.05279
H	2.594583	0.733751	-1.25623
C	0.949768	3.33547	0.096562
H	0.080955	3.436958	0.751502
H	0.718606	3.835694	-0.84901
H	1.822294	3.821201	0.570892
C	1.725918	-0.88638	4.868174
H	2.722476	-1.3234	5.007874
H	0.98877	-1.69774	4.947007
H	1.544128	-0.20447	5.712456
C	-2.13723	1.748988	2.195142
C	-1.52456	2.530452	3.374727
H	-1.03582	1.900032	4.122716
H	-2.32825	3.079708	3.881975
H	-0.78752	3.264814	3.023503
C	-3.07901	0.650211	2.714381
H	-3.58423	0.156178	1.876079
H	-3.85078	1.094964	3.358483
H	-2.5523	-0.11181	3.302297
C	-2.9836	2.762777	1.403717
H	-2.35728	3.565225	0.99455
H	-3.72289	3.217798	2.076329
H	-3.52674	2.288624	0.581883
N	-0.41626	-1.23366	-0.68335
C	0.636207	-1.26764	-1.6118
C	0.431316	-0.56965	-2.83034
C	1.420937	-0.53219	-3.80647
H	1.263436	0.01357	-4.73521
C	2.636907	-1.19011	-3.60603
H	3.406936	-1.14412	-4.37732
C	2.872943	-1.89596	-2.42179
C	1.873692	-1.91782	-1.44177
H	2.080916	-2.41862	-0.49954
N	-0.8665	0.098093	-2.96147
C	-1.90235	-0.87705	-3.41056
H	-1.6614	-1.24983	-4.41883
H	-2.87696	-0.37927	-3.4193

H	-1.94197	-1.7121	-2.71041
C	-0.8494	1.216052	-3.92673
H	-0.09659	1.955191	-3.64248
H	-1.82958	1.700117	-3.92702
H	-0.65139	0.854408	-4.948
C	4.174124	-2.62013	-2.19442
H	4.485239	-2.57066	-1.14268
H	4.98108	-2.2014	-2.80866
H	4.084493	-3.68558	-2.45488
C	-0.82918	-2.52615	-0.02027
C	-2.27182	-2.39389	0.474392
H	-2.36242	-1.61283	1.235747
H	-2.58826	-3.34611	0.920846
H	-2.95974	-2.14538	-0.34106
C	0.053248	-2.83657	1.208364
H	1.063719	-3.16153	0.93697
H	-0.40251	-3.65313	1.787069
H	0.139742	-1.95761	1.853908
C	-0.77242	-3.71468	-0.99673
H	-1.47756	-3.58604	-1.82864
H	-1.05399	-4.63285	-0.46415
H	0.227858	-3.86838	-1.41738

Table S18. Cartesian coordinates for DFT optimized $OCN(N_3)Mo(N[R]Ar_{MeL})_2$ (S = 1).

Atom	x	y	z
Mo	-1.05822	0.760248	-0.61784
N	-2.98965	0.244665	-0.87384
N	-1.56675	2.619648	-1.32775
N	-2.56375	3.145809	-1.76628
N	-3.46359	3.71812	-2.21655
N	-1.1193	1.170727	1.36693
C	0.117349	0.867144	1.968211
C	1.282556	1.085982	1.189069
C	2.540269	0.766776	1.682379
H	3.429829	0.941508	1.079208
C	2.682104	0.201604	2.953755
H	3.676363	-0.05621	3.320828
C	1.558603	-0.03813	3.746889
C	0.294156	0.288645	3.238703
H	-0.57936	0.038856	3.836005

N	1.058869	1.709611	-0.11698
C	2.181808	1.511177	-1.05777
H	3.076011	2.066304	-0.73173
H	1.888815	1.894986	-2.03956
H	2.428095	0.45197	-1.15072
C	0.908682	3.183598	0.088334
H	0.083435	3.375932	0.776035
H	0.675787	3.660106	-0.86784
H	1.842263	3.593533	0.502949
C	1.684735	-0.64836	5.118251
H	2.692359	-1.04673	5.288555
H	0.968718	-1.46915	5.262676
H	1.485055	0.094074	5.905214
C	-2.23622	1.720007	2.228187
C	-1.68625	2.604983	3.365836
H	-1.15499	2.05434	4.147001
H	-2.528	3.123418	3.842964
H	-1.00437	3.370585	2.972033
C	-3.11337	0.591663	2.799515
H	-3.61221	0.045217	1.990895
H	-3.89344	1.021837	3.443255
H	-2.54651	-0.12943	3.400146
C	-3.13745	2.628732	1.379908
H	-2.5717	3.47476	0.972668
H	-3.9385	3.028089	2.015559
H	-3.60343	2.089128	0.552513
N	-0.30195	-1.17949	-0.72255
C	0.670535	-1.2828	-1.73295
C	0.48978	-0.5003	-2.90414
C	1.437536	-0.50467	-3.92266
H	1.290035	0.102942	-4.81391
C	2.594693	-1.27856	-3.82009
H	3.331751	-1.25937	-4.62407
C	2.803932	-2.07637	-2.69131
C	1.845622	-2.0631	-1.67181
H	2.047346	-2.64827	-0.77984
N	-0.74284	0.282004	-2.96624
C	-1.83694	-0.58644	-3.48798
H	-1.59374	-0.92115	-4.50904
H	-2.77375	-0.02271	-3.49713
H	-1.95636	-1.45428	-2.83679
C	-0.64674	1.462082	-3.84953

H	0.150274	2.131385	-3.5125
H	-1.59256	2.00737	-3.81626
H	-0.46368	1.170684	-4.89547
C	4.029839	-2.9434	-2.56905
H	4.348743	-3.05024	-1.52412
H	4.871584	-2.53461	-3.14227
H	3.836282	-3.95638	-2.95344
C	-0.68352	-2.45032	0.00804
C	-2.0799	-2.28606	0.613639
H	-2.12997	-1.40279	1.255897
H	-2.31424	-3.16894	1.223159
H	-2.84684	-2.19067	-0.16011
C	0.278195	-2.73535	1.182607
H	1.3042	-2.95459	0.87019
H	-0.08355	-3.61046	1.741375
H	0.311664	-1.88146	1.866845
C	-0.74106	-3.66266	-0.93959
H	-1.44152	-3.47835	-1.76533
H	-1.10649	-4.53629	-0.38325
H	0.229817	-3.92668	-1.37156
C	-4.14651	-0.05098	-1.00909
O	-5.29517	-0.35675	-1.1408

Table S19. Cartesian coordinates for constrained H-atom only DFT optimization of **12** starting from crystal structure coordinates (S = 1).

Atom	x	y	z
V	-1.02066	-0.09805	1.256501
Cl	-2.57278	-0.19793	2.972415
N	-0.9788	2.165767	1.528407
N	-1.42065	0.559274	-0.51735
N	0.852707	-0.63044	1.234581
N	-1.12415	-2.35001	1.130828
C	1.648657	-0.0369	3.441495
H	0.75941	0.596187	3.515838
H	2.45159	0.435767	4.025472
H	1.400765	-0.98841	3.930336
C	0.944108	-1.56451	0.18808
C	-0.10225	-2.52824	0.121178
C	-0.49541	1.599735	-0.76138
C	3.103779	-1.41101	2.039348

H	2.632666	-2.35559	2.342465
H	3.881223	-1.17197	2.778526
H	3.601407	-1.57838	1.078895
C	2.758791	0.976188	1.438265
H	3.107509	0.812234	0.411261
H	3.635103	1.251991	2.044598
H	2.082377	1.834581	1.404562
C	1.911804	-1.59368	-0.80603
H	2.678766	-0.82054	-0.82683
C	-0.66556	-2.93827	2.412752
H	-0.56546	-4.03039	2.310061
H	-1.39451	-2.70309	3.195561
H	0.298984	-2.50981	2.687142
C	-3.70121	-0.16831	-0.83239
H	-3.5092	-0.90528	-0.04805
H	-4.43602	-0.59529	-1.52997
H	-4.16612	0.698454	-0.34523
C	-0.09789	-3.49328	-0.85518
H	-0.89019	-4.24156	-0.89615
C	-0.26246	2.478137	0.313346
C	0.611926	3.545157	0.178145
H	0.77029	4.24598	0.9974
C	1.160548	2.824369	-2.06169
C	0.250754	1.776624	-1.92297
H	0.1483	1.056998	-2.73397
C	-2.42339	0.241132	-1.56914
C	1.905847	-2.56133	-1.81699
C	-0.39605	2.735005	2.753332
H	0.674272	2.528444	2.808753
H	-0.90104	2.281013	3.613433
H	-0.54238	3.827119	2.801483
C	1.304578	3.71341	-1.01631
H	2.001686	4.548648	-1.11109
C	-2.37692	2.700093	1.442776
H	-2.34607	3.799291	1.383484
H	-2.93478	2.382655	2.328152
H	-2.86447	2.298427	0.55364
C	0.891909	-3.51043	-1.8217
H	0.869494	-4.27466	-2.60057
C	2.081956	-0.26272	2.003653
C	-2.79289	1.472021	-2.40698
H	-3.04995	2.326926	-1.76779

H	-3.67425	1.234754	-3.01903
H	-1.99538	1.790776	-3.08622
C	2.957163	-2.53623	-2.89064
H	2.81213	-3.34851	-3.61374
H	3.968322	-2.6402	-2.47063
H	2.94065	-1.58751	-3.44738
C	-1.96448	-0.8863	-2.48535
H	-1.06509	-0.61196	-3.05014
H	-2.74961	-1.13817	-3.21388
H	-1.71699	-1.79004	-1.92073
C	2.000603	2.958827	-3.29412
H	2.401365	3.974921	-3.39885
H	1.433767	2.723952	-4.2055
H	2.860789	2.27173	-3.26834
C	-2.40685	-3.02639	0.792767
H	-2.71894	-2.77039	-0.22159
H	-3.16443	-2.6897	1.508254
H	-2.3088	-4.12113	0.866709

Table S20. Cartesian coordinates for H-atom only DFT optimization of **13** starting from crystal structure coordinates(S = 1.5).

Atom	x	y	z
C	2.423317	-1.21416	0.784679
C	3.124541	-0.0742	0.301948
C	4.487892	-0.11045	0.055062
H	4.999862	0.784967	-0.3014
C	5.223196	-1.27457	0.246765
H	6.292001	-1.28668	0.02834
C	4.587569	-2.40745	0.721258
C	3.214722	-2.3771	0.977049
H	2.756911	-3.29315	1.334011
C	5.360604	-3.67868	0.998841
H	6.262119	-3.74508	0.376035
H	4.750488	-4.57167	0.810538
H	5.686068	-3.72159	2.049383
C	0.279653	-2.13426	1.651437
C	0.803705	-2.47732	3.059743
H	1.811781	-2.90292	3.062512
H	0.133952	-3.20014	3.546633
H	0.827323	-1.56784	3.676047

C	0.147024	-3.38896	0.774143
H	-0.31593	-3.12558	-0.18563
H	-0.49765	-4.1321	1.26528
H	1.1022	-3.87421	0.552806
C	-1.13274	-1.57111	1.84524
H	-1.1118	-0.69389	2.505821
H	-1.78665	-2.32321	2.309866
H	-1.59055	-1.2786	0.888958
C	2.722571	1.996943	-0.97457
H	3.736268	2.418413	-0.87628
H	2.012173	2.825737	-1.07129
H	2.68186	1.384404	-1.88031
C	2.598855	1.944321	1.440205
H	2.297083	1.342103	2.303624
H	2.026905	2.879728	1.428197
H	3.669535	2.191302	1.536131
C	-2.4747	1.086968	-0.82165
C	-2.374	1.962376	0.295174
C	-3.47848	2.598284	0.826497
H	-3.36476	3.277619	1.672383
C	-4.74533	2.399397	0.290632
H	-5.60694	2.907366	0.72653
C	-4.89751	1.572199	-0.80316
C	-3.78334	0.929588	-1.35009
H	-3.94787	0.296325	-2.21571
C	-6.25511	1.358324	-1.43167
H	-6.72149	0.427749	-1.07344
H	-6.18466	1.284329	-2.52491
H	-6.94132	2.180068	-1.19005
C	-1.22341	-0.26949	-2.50054
C	0.250527	-0.67176	-2.65658
H	0.590603	-1.29906	-1.81962
H	0.888824	0.221029	-2.70946
H	0.39962	-1.24481	-3.58326
C	-2.04903	-1.56915	-2.46953
H	-3.12849	-1.40419	-2.41079
H	-1.76043	-2.17512	-1.60127
H	-1.85504	-2.16333	-3.37435
C	-1.58835	0.605744	-3.70785
H	-1.46362	0.043386	-4.64433
H	-0.92531	1.481148	-3.74613
H	-2.61946	0.973471	-3.67381

C	-0.54611	3.492249	0.165184
H	-0.56351	3.376886	-0.92373
H	0.475674	3.721201	0.489966
H	-1.19992	4.335837	0.444371
C	-0.96739	2.366272	2.273053
H	-1.47815	3.278545	2.621073
H	0.078124	2.413648	2.594988
H	-1.44448	1.495437	2.730716
N	1.071268	-1.06472	1.002056
N	2.345	1.167037	0.197769
N	-1.30045	0.49325	-1.23751
N	-1.01547	2.229447	0.789984
V	0.219638	0.543412	0.10801