Supplementary Materials: Hetero- and Homoleptic Magnesium Triazenides

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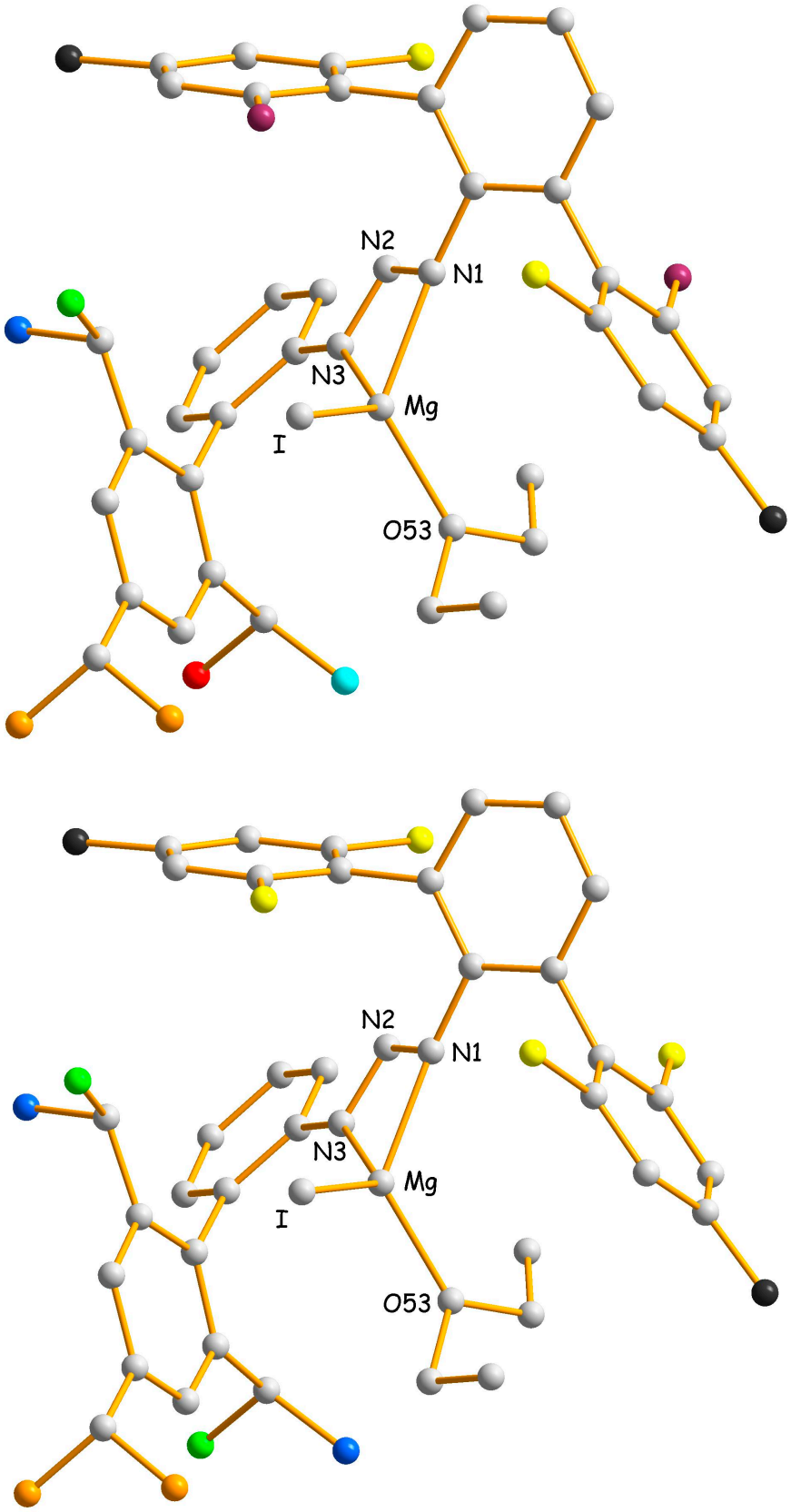
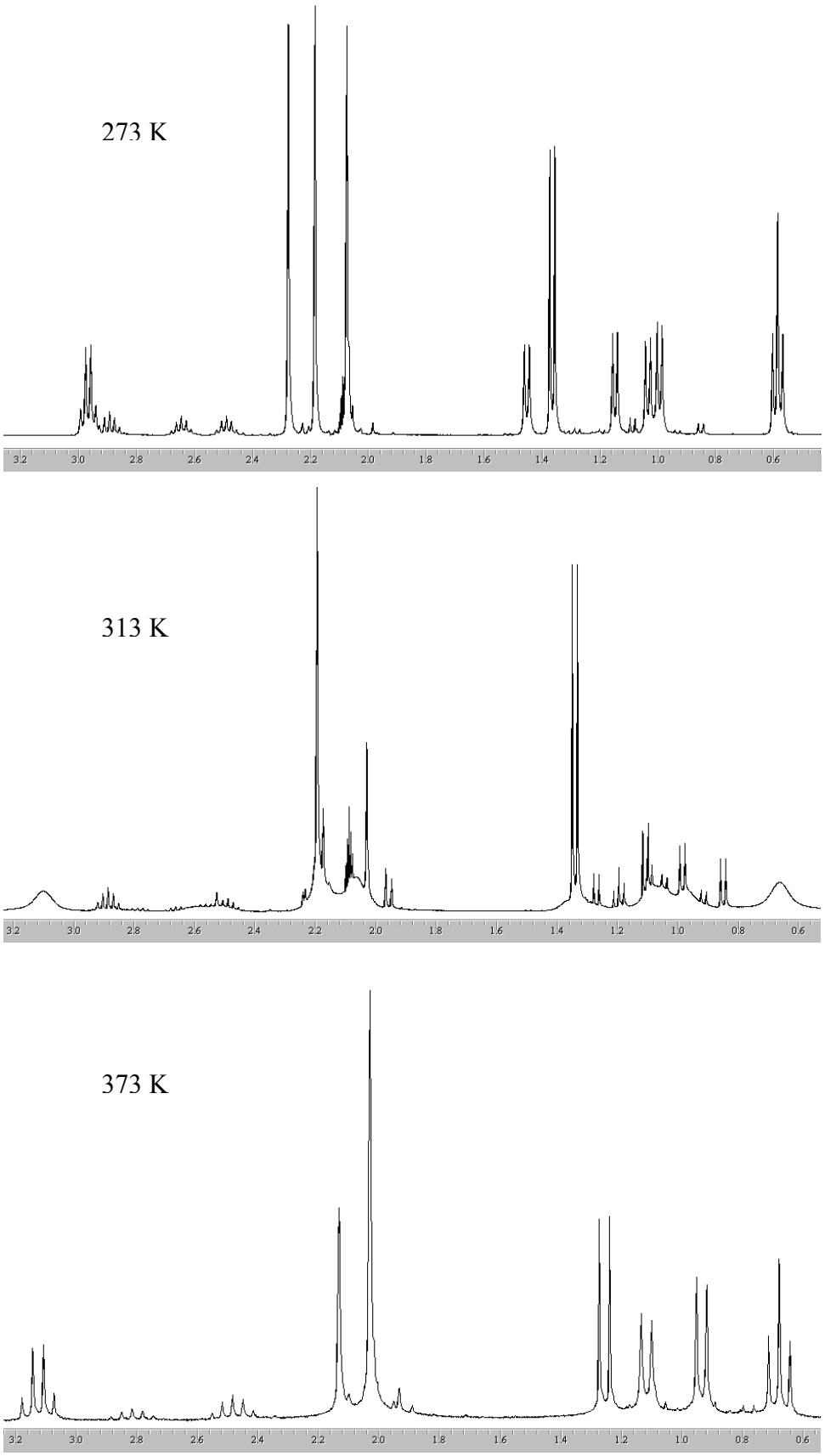


Figure S1. Molecular model of triazenide **2a** showing magnetically-equivalent methyl groups at 273 K (top) and 373 K (bottom).

Figure S2. VT ^{1}H NMR spectra for heteroleptic triazenide **2a** in [D_8]toluene.



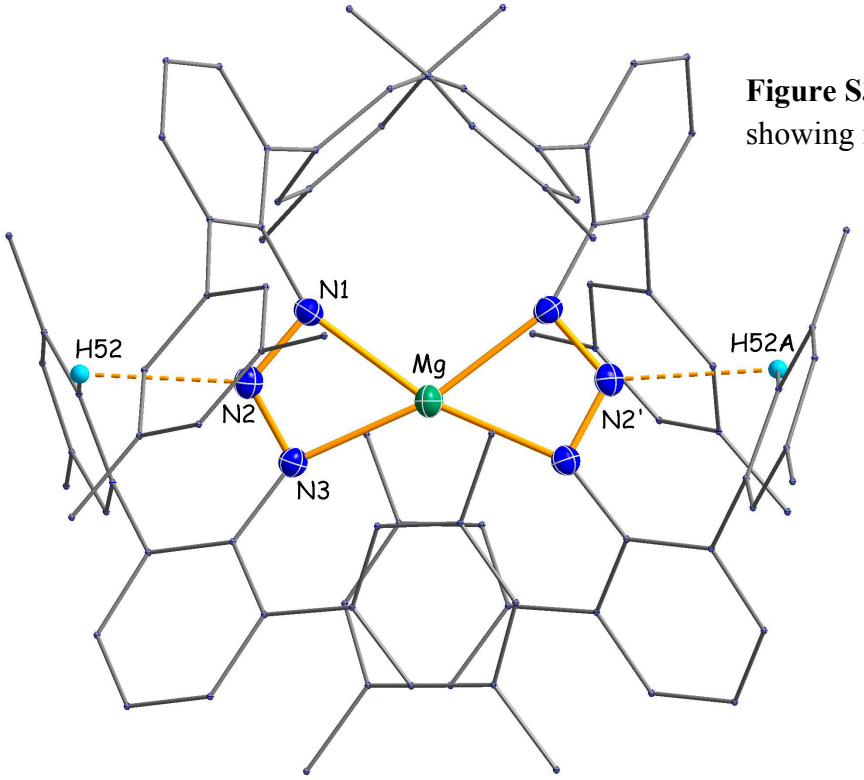


Figure S3a. Molecular structure of **4b**, showing intramolecular C–H···N contacts.

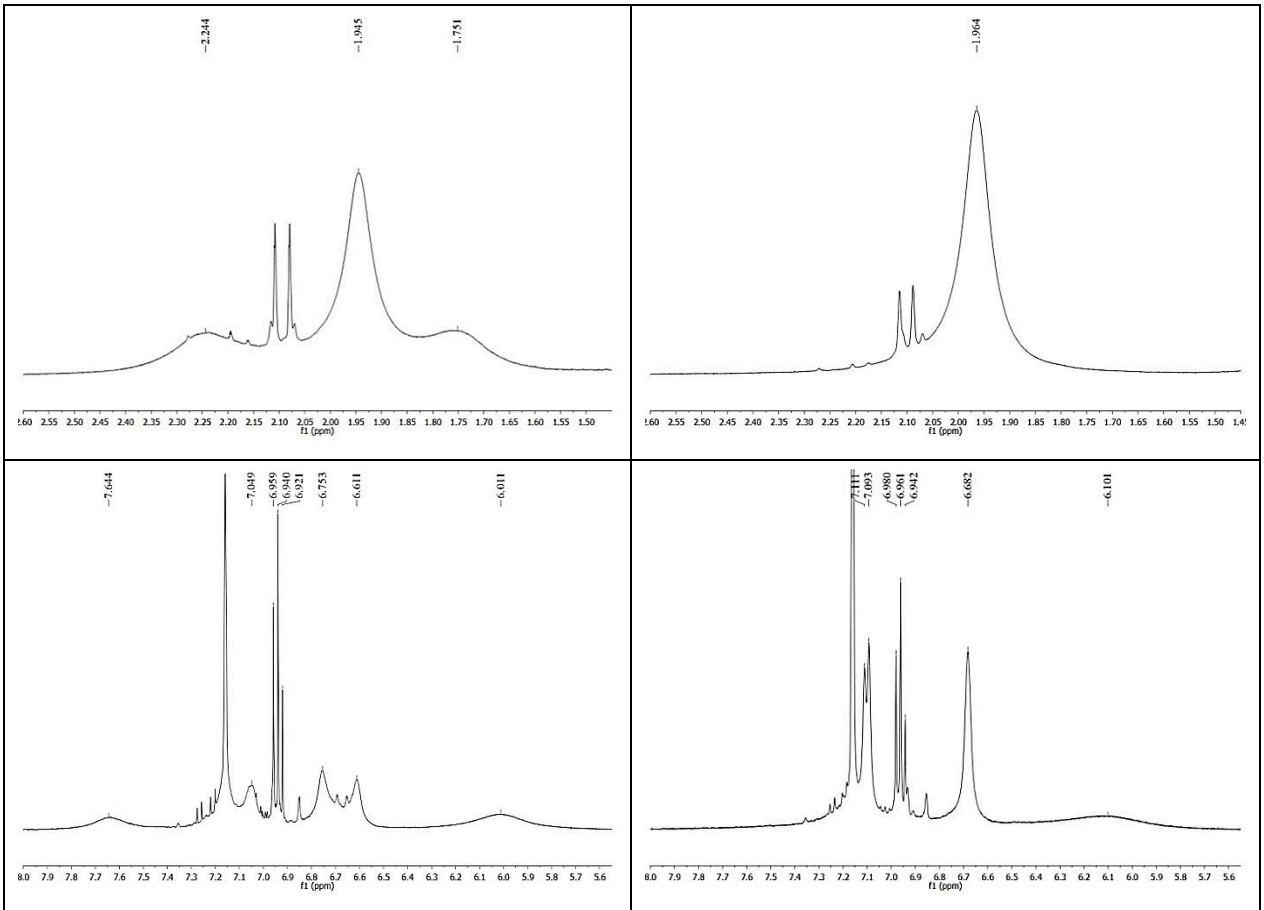


Figure S3b. VT ^{1}H NMR spectra of homoleptic triazenide **4b** at 298 K (left column) and 338 K (right column) in [D_6]benzene.

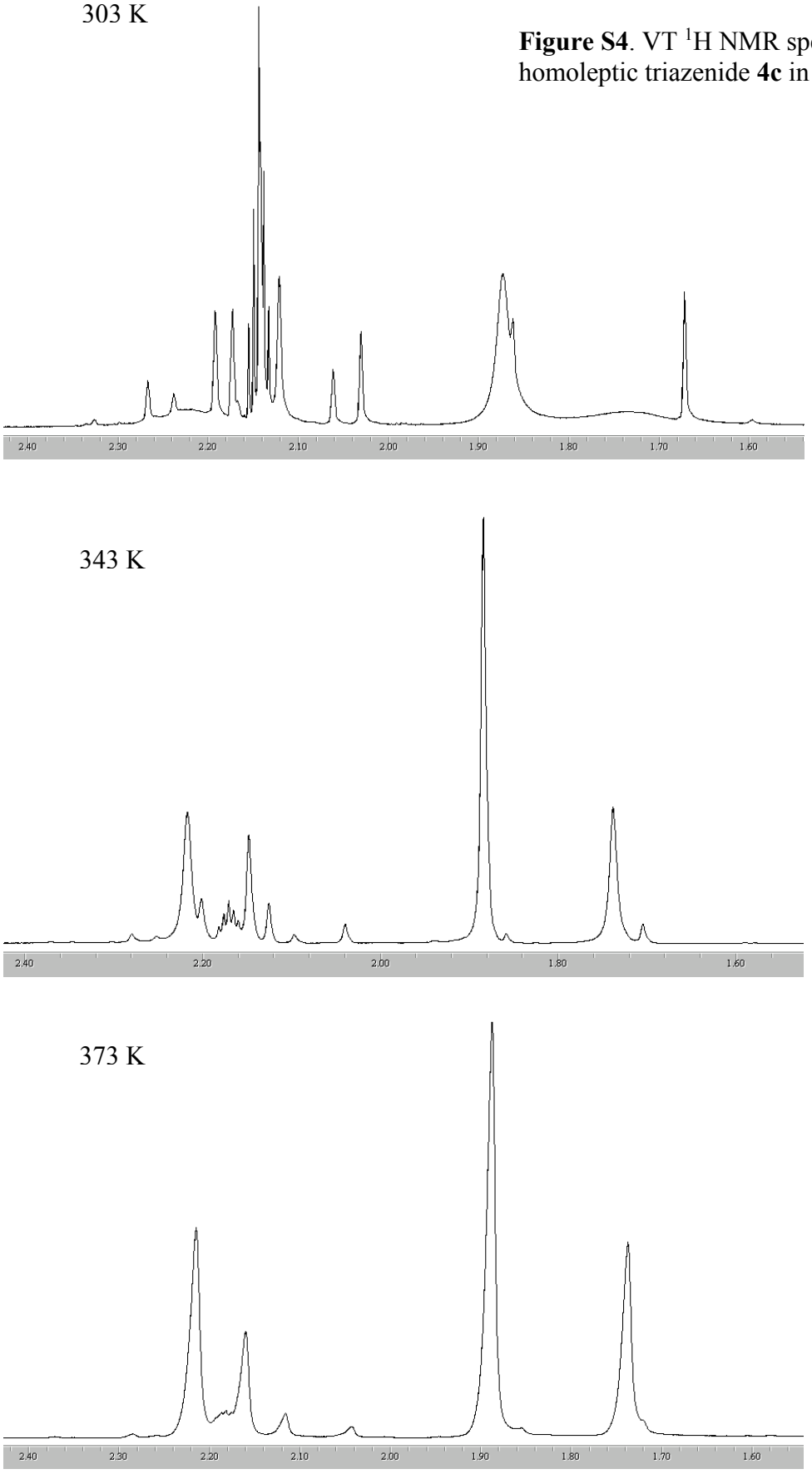


Figure S4. VT ^{1}H NMR spectra of homoleptic triazenide **4c** in [D_8]toluene.

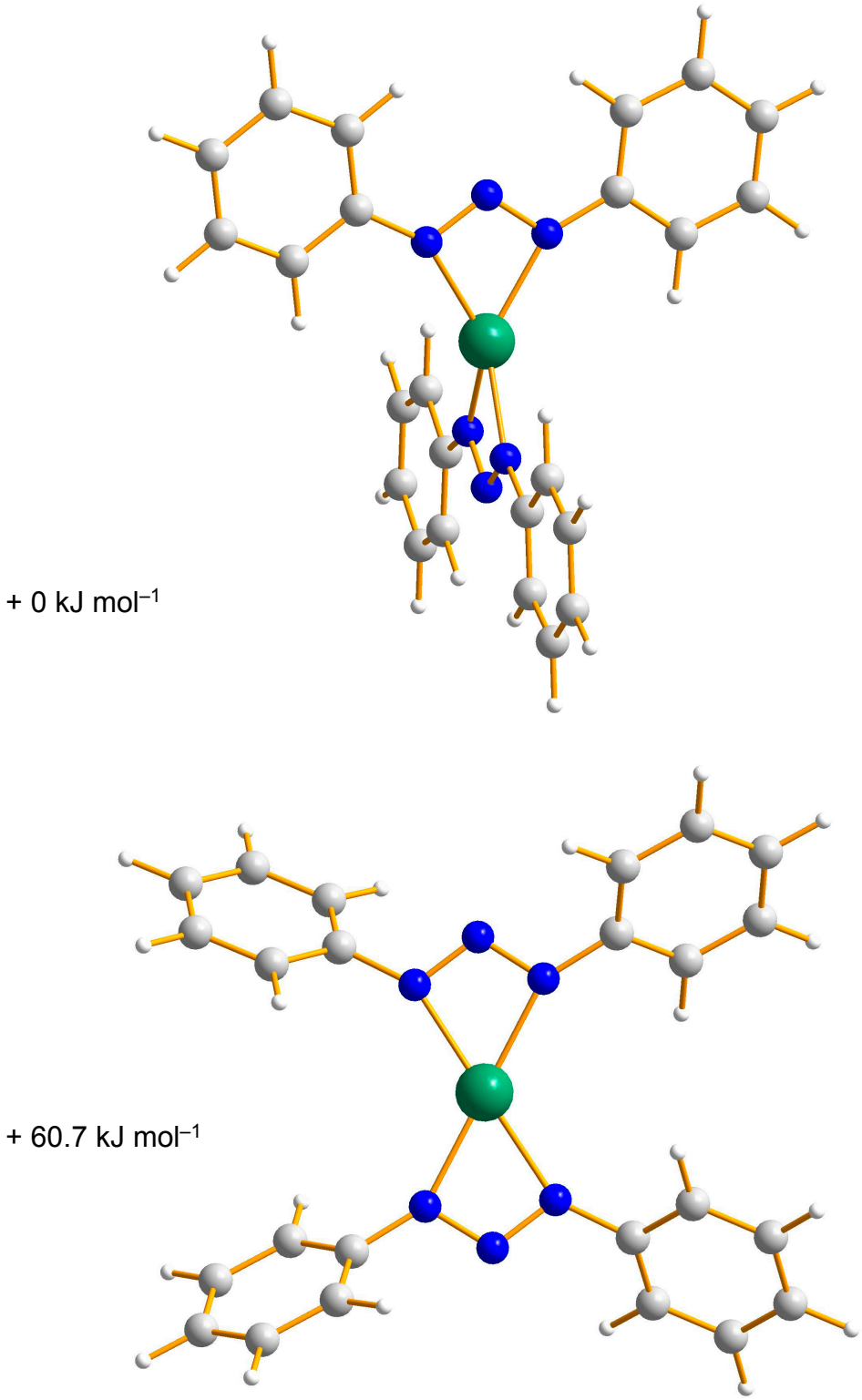


Figure S5. DFT-optimized structures of S_4-symmetric $[Mg(N_3Ph_2)_2]$ (**5**$_T$) and C_1-symmetric square planar $[Mg(N_3Ph_2)_2]$ (**5**$_{SP}$) showing ZPE-corrected relative energies.

Table S1. Coordinates for DFT-optimized $\mathbf{5_T}$ at the B3LYP/6-311+G* level of theory.

Mg	0.000000	0.000000	0.000000	N	0.000000	−1.070453	−1.802739
N	1.070453	0.000000	1.802739	N	0.000000	0.000000	−2.547070
N	0.000000	0.000000	2.547070	N	0.000000	1.070453	−1.802739
N	−1.070453	0.000000	1.802739	C	0.000000	−2.316960	−2.448803
C	2.316960	0.000000	2.448803	C	0.000000	−2.477358	−3.844183
C	2.477358	0.000000	3.844183	H	0.000000	−1.603359	−4.482795
H	1.603359	0.000000	4.482795	C	0.000000	−3.753504	−4.395097
C	3.753504	0.000000	4.395097	H	0.000000	−3.864456	−5.475040
H	3.864456	0.000000	5.475040	C	0.000000	−4.887040	−3.579493
C	4.887040	0.000000	3.579493	H	0.000000	−5.878743	−4.019123
H	5.878743	0.000000	4.019123	C	0.000000	−4.729724	−2.194629
C	4.729724	0.000000	2.194629	H	0.000000	−5.600194	−1.546443
H	5.600194	0.000000	1.546443	C	0.000000	−3.457091	−1.632397
C	3.457091	0.000000	1.632397	H	0.000000	−3.338344	−0.552949
H	3.338344	0.000000	0.552949	C	0.000000	2.316960	−2.448803
C	2.316960	0.000000	2.448803	C	0.000000	2.477358	−3.844183
C	2.477358	0.000000	3.844183	H	0.000000	1.603359	−4.482795
H	−1.603359	0.000000	4.482795	C	0.000000	3.753504	−4.395097
C	−3.753504	0.000000	4.395097	H	0.000000	3.864456	−5.475040
H	−3.864456	0.000000	5.475040	C	0.000000	4.887040	−3.579493
C	−4.887040	0.000000	3.579493	H	0.000000	5.878743	−4.019123
H	−5.878743	0.000000	4.019123	C	0.000000	4.729724	−2.194629
C	−4.729724	0.000000	2.194629	H	0.000000	5.600194	−1.546443
H	−5.600194	0.000000	1.546443	C	0.000000	3.457091	−1.632397
C	−3.457091	0.000000	1.632397	H	0.000000	3.338344	−0.552949
H	−3.338344	0.000000	0.552949				

Table S2. Coordinates for DFT-optimized $\mathbf{5_{SP}}$ at the B3LYP/6-311+G* level of theory.

Mg	−0.015128	0.000506	0.000135	N	−1.076721	1.820445	0.023562
N	−1.076542	−1.820807	−0.023707	N	−0.000874	2.555000	0.030953
N	−0.000650	−2.555680	−0.030861	N	1.055010	1.810016	0.203623
N	1.054577	−1.810862	−0.203538	C	−2.300999	2.508953	−0.171536
C	−2.300905	−2.509103	0.171428	C	−2.508289	3.344582	−1.275499
C	−2.508482	−3.344517	1.275526	H	−1.691093	3.525290	−1.965352
H	−1.691375	−3.525259	1.965479	C	−3.748412	3.946206	−1.472638
C	−3.748718	−3.945899	1.472685	H	−3.896346	4.600934	−2.325740
H	−3.896813	−4.600465	2.325887	C	−4.801269	3.696976	−0.592337
C	−4.801493	−3.696626	0.592295	H	−5.769111	4.160284	−0.753592
H	−5.769429	−4.159734	0.753569	C	−4.604959	2.839963	0.489902
C	−4.604943	−2.839832	−0.490074	H	−5.419997	2.634289	1.176476
H	−5.419896	−2.634133	−1.176747	C	−3.364237	2.242213	0.696777
C	−3.364085	−2.242375	−0.696987	H	−3.208692	1.571617	1.535483
H	−3.208350	−1.572005	−1.535842	C	2.295134	2.492167	0.253673
C	2.294989	−2.492579	−0.253592	C	3.359228	2.023781	−0.524391
C	3.358962	−2.023730	0.524351	H	3.198711	1.191082	−1.201548
H	3.198191	−1.191029	1.201448	C	4.611225	2.627673	−0.435826
C	4.611169	−2.627182	0.435769	H	5.426271	2.263087	−1.052872
H	5.426120	−2.262260	1.052743	C	4.818066	3.694002	0.438457
C	4.818351	−3.693489	−0.438462	H	5.794352	4.162516	0.507176
H	5.794806	−4.161647	−0.507211	C	3.764361	4.146739	1.232732
C	3.764766	−4.146660	−1.232650	H	3.920472	4.966383	1.927091
H	3.921138	−4.966288	−1.926970	C	2.513315	3.541255	1.155437
C	2.513495	−3.541644	−1.155301	H	1.695550	3.879118	1.782333
H	1.695804	−3.879863	−1.782102				