

Supplementary Table S1 T1 diagnostic values of key species at the CCSD(T)/cc-pVTZ level and zero-point energy without correction.

Species	T1 diagnostic value	ZPE (Hartree)
UDMH	0.00934234	0.110087
NHN(CH ₃) ₂	0.0175953	0.096957
cis-NH ₂ N(CH ₃)CH ₂	0.01567897	0.096339
trans-NH ₂ N(CH ₃)CH ₂	0.01557973	0.096463
NH ₂ NCH ₃	0.01776572	0.068096
N(CH ₃) ₂	0.01306291	0.077836
HNNCH ₃	0.01144977	0.056947
NN(CH ₃) ₂	0.01718794	0.085018
N(CH ₃)CH ₂	0.01110178	0.068797
TS(UDMH = N(CH ₃)CH ₂ + NH ₃)	0.01249879	0.104755
TS(UDMH = NN(CH ₃) ₂ + H ₂)	0.01595054	0.098914
TS(UDMH = HNNCH ₃ + CH ₄)	0.02937959	0.100111
TS(UDMH + NO ₂ = NHN(CH ₃) ₂ + HNO ₂)	0.0269807	0.117341
PC(UDMH + NO ₂ = NHN(CH ₃) ₂ + HNO ₂)	0.01761124	0.120939
TS(UDMH + NO ₂ = NHN(CH ₃) ₂ + trans-HONO)	0.03082276	0.118814
PC(UDMH + NO ₂ = NHN(CH ₃) ₂ + trans-HONO)	0.01814839	0.120026
TS(UDMH + NO ₂ = NHN(CH ₃) ₂ + cis-HONO)	0.03227964	0.118261
PC(UDMH + NO ₂ = NHN(CH ₃) ₂ + cis-HONO)	0.01827444	0.119696
TS(UDMH + NO ₂ = cis-NH ₂ N(CH ₃)CH ₂ + HNO ₂)	0.01888612	0.11568
PC(UDMH + NO ₂ = cis-NH ₂ N(CH ₃)CH ₂ + HNO ₂)	0.01727367	0.120317
TS(UDMH + NO ₂ = cis-NH ₂ N(CH ₃)CH ₂ + trans-HONO)	0.02585341	0.11575
PC(UDMH + NO ₂ = cis-NH ₂ N(CH ₃)CH ₂ + trans-HONO)	0.01800206	0.119311
TS(UDMH + NO ₂ = cis-NH ₂ N(CH ₃)CH ₂ + cis-HONO)	0.02710055	0.115332
PC(UDMH + NO ₂ = cis-NH ₂ N(CH ₃)CH ₂ + cis-HONO)	0.01807063	0.118865
TS(UDMH + NO ₂ = trans-NH ₂ N(CH ₃)CH ₂ + HNO ₂)	0.01875452	0.116011
PC(UDMH + NO ₂ = trans-NH ₂ N(CH ₃)CH ₂ + HNO ₂)	0.01737148	0.120614
TS(UDMH + NO ₂ = trans-NH ₂ N(CH ₃)CH ₂ + trans-HONO)	0.04247326	0.115957
PC(UDMH + NO ₂ = trans-NH ₂ N(CH ₃)CH ₂ + trans-HONO)	0.01805793	0.119248
TS(UDMH + NO ₂ = trans-NH ₂ N(CH ₃)CH ₂ + cis-HONO)	0.02522341	0.115495
PC(UDMH + NO ₂ = trans-NH ₂ N(CH ₃)CH ₂ + cis-HONO)	0.0181535	0.119258
TS(UDMH + H = NHN(CH ₃) ₂ + H ₂) (inside)	0.01998791	0.10836
TS(UDMH + H = cis-NH ₂ N(CH ₃)CH ₂ + H ₂) (inside)	0.01600436	0.107589
TS(UDMH + H = trans-NH ₂ N(CH ₃)CH ₂ + H ₂) (inside)	0.01560395	0.107658
TS(UDMH + CH ₃ = NHN(CH ₃) ₂ + CH ₄) (inside)	0.01786631	0.138719
TS(UDMH + CH ₃ = cis-NH ₂ N(CH ₃)CH ₂ + CH ₄) (inside)	0.01521917	0.138606
TS(UDMH + CH ₃ = trans-NH ₂ N(CH ₃)CH ₂ + CH ₄) (inside)	0.01485731	0.138527