

Supplementary Table S1 T1 diagnostic values of key species at the CCSD(T)/cc-pVTZ level.

Species	T1 diagnostic value
HNN(CH ₃) ₂	0.01759530
H ₂ NN(CH ₃)CH ₂	0.01557973
NN(CH ₃) ₂	0.01718794
cis-HNNCH ₃	0.01262014
trans-HNNCH ₃	0.01144977
H ₂ NNCH ₂	0.00757617
CH ₂ NCH ₃	0.01110178
NN(OH) ₂	0.02252961
ONON(H)N(CH ₃) ₂	0.01863411
O ₂ NN(H)N(CH ₃) ₂	0.01510826
HO ₂ NNN(CH ₃) ₂	0.01452093
(HO) ₂ NNN(CH ₃)CH ₂	0.01705778
ONN(H)N(CH ₃) ₂ -1	0.01539487
ONN(H)N(CH ₃) ₂ -2	0.01565706
ONN(H)N(CH ₃) ₂ -3	0.01558370
HNNCH ₂	0.03380677
TS(HNN(CH ₃) ₂ = H ₂ NN(CH ₃)CH ₂)	0.01996874
TS(HNN(CH ₃) ₂ = cis-HNNCH ₃ + CH ₃)	0.03669590
TS(HNN(CH ₃) ₂ = trans-HNNCH ₃ + CH ₃)	0.03653836
TS(H ₂ NN(CH ₃)CH ₂ = H ₂ NNCH ₂ + CH ₃)	0.03334491
TS(H ₂ NN(CH ₃)CH ₂ = CH ₂ NCH ₃ + NH ₂)	0.03505883
TS(ONON(H)N(CH ₃) ₂ = NN(CH ₃) ₂ + cis-HONO)	0.02583729
PC(ONON(H)N(CH ₃) ₂ = NN(CH ₃) ₂ + cis-HONO)	0.01825213
TS(O ₂ NN(H)N(CH ₃) ₂ = HO ₂ NNN(CH ₃) ₂)	0.01638336
TS(HO ₂ NNN(CH ₃) ₂ = (HO) ₂ NNN(CH ₃)CH ₂)	0.01870449
TS((HO) ₂ NNN(CH ₃)CH ₂ = CH ₂ NCH ₃ + NN(OH) ₂)	0.02005569
PC((HO) ₂ NNN(CH ₃)CH ₂ = CH ₂ NCH ₃ + NN(OH) ₂)	0.01856303
TS(HO ₂ NNN(CH ₃) ₂ = NN(CH ₃) ₂ + trans-HONO)	0.02424603
PC(HO ₂ NNN(CH ₃) ₂ = NN(CH ₃) ₂ + trans-HONO)	0.01808546
TS(H(CH ₃)NN(CH ₃) ₂ = NN(CH ₃) ₂ + CH ₄)	0.01684441
TS(H(CH ₃)NN(CH ₃) ₂ = HNN(CH ₃)CH ₂ + CH ₄)	0.01121478
TS(ONN(H)N(CH ₃) ₂ -1 = HNN(CH ₃)CH ₂ + HNO)	0.03312092
PC(ONN(H)N(CH ₃) ₂ -1 = HNN(CH ₃)CH ₂ + HNO)	0.01685155
TS(ONN(H)N(CH ₃) ₂ -2 = NN(CH ₃) ₂ + HNO)	0.03130995
PC(ONN(H)N(CH ₃) ₂ -2 = NN(CH ₃) ₂ + HNO)	0.01670099
TS(HNN(CH ₃) ₂ + NO = HNN(CH ₃)CH ₂ + NOH)	0.02136979
TS(ONN(H)N(CH ₃) ₂ -3 = NN(CH ₃) ₂ + NOH)	0.02428854
PC(ONN(H)N(CH ₃) ₂ -3 = NN(CH ₃) ₂ + NOH)	0.01939660
TS(HNN(CH ₃) ₂ = HNN(CH ₃)CH ₂)	0.01439034
TS(HNN(CH ₃)CH ₂ = HNNCH ₂ + CH ₃)	0.02563683
TS(HNN(CH ₃) ₂ = N ₂ + C ₂ H ₆)	0.02399272