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Supplement of

Chlorine radical-initiated atmospheric oxidation of imines: implications for structural influence on the nitrosamine formation

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Content

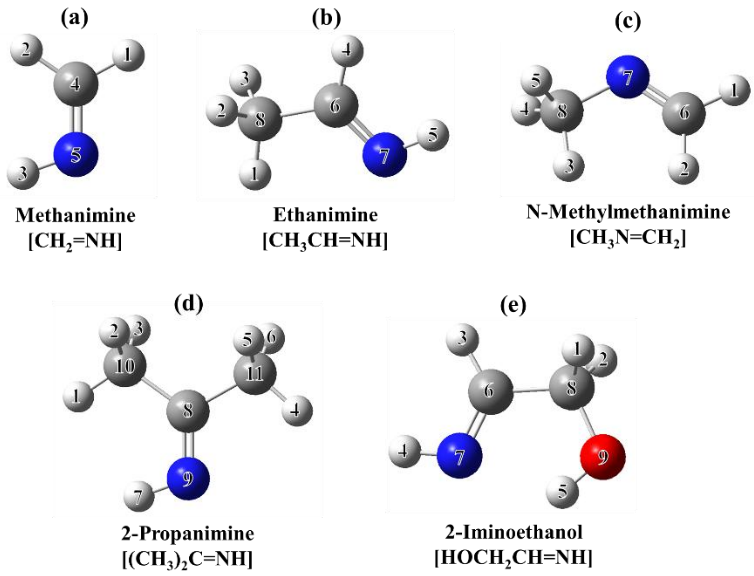


Figure S1. Global minimum of five typical imines obtained at CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p) level. The white, red, blue, and gray spheres represent H, O, N, and C atoms, respectively.

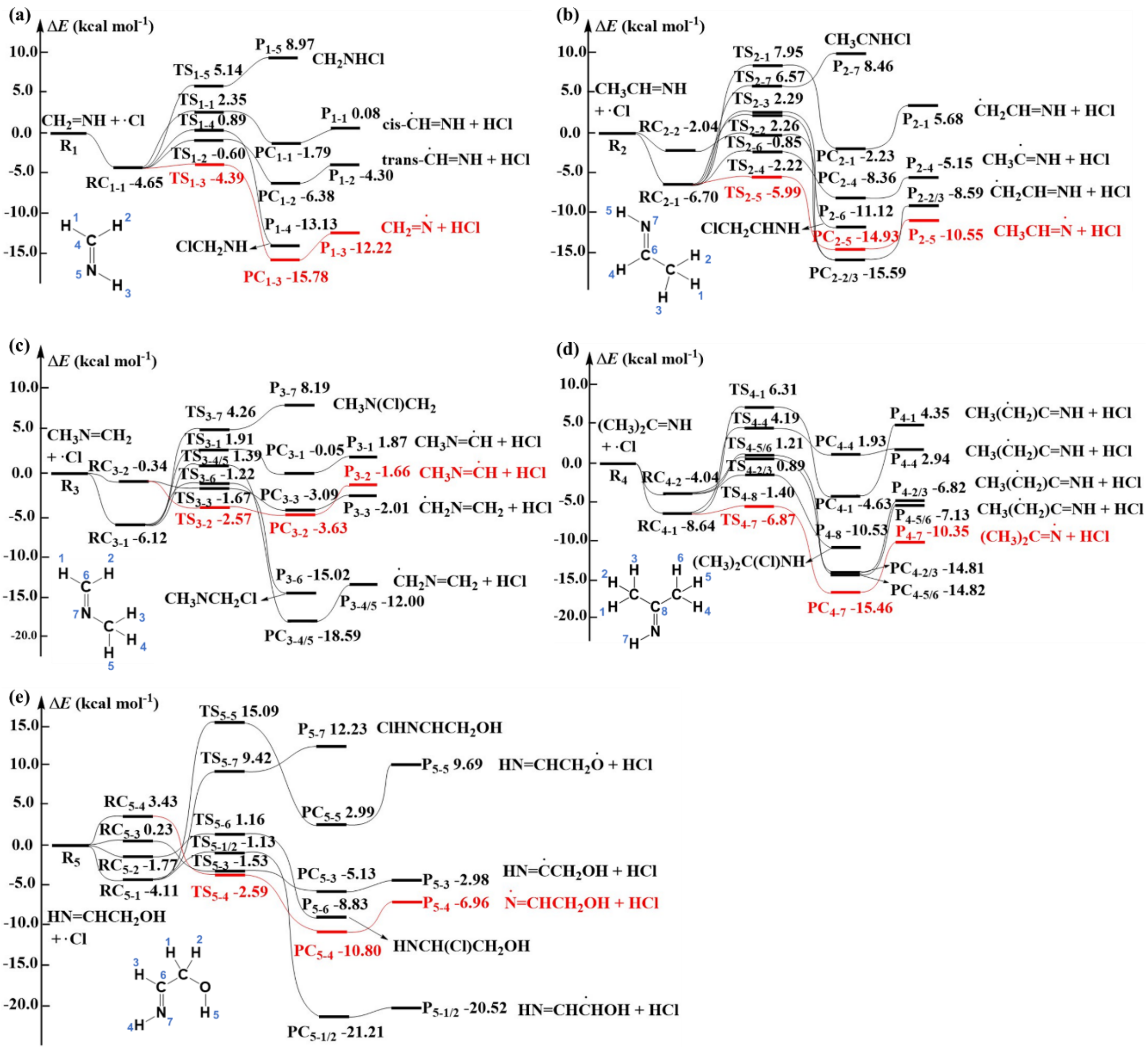


Figure S2. ZPE-corrected potential energy surface for the reaction of **(a)** CH_2=NH, **(b)** CH_3CH=NH, **(c)** $CH_3N=CH_2$, **(d)** $(CH_3)_2C$=NH, and **(e)** HN=$CHCH_2OH$ with ·Cl calculated at the CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p) level of theory. R_n, RC_{n-m}, PC_{n-m}, TS_{n-m}, and P_{n-m} represent R, RC, PC, TS, and P, respectively. n denotes different imines, m denotes different species.

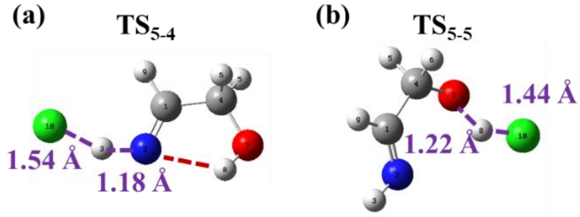


Figure S3. Optimized geometries of TSs for $TS_{5\text{-}4}$ **(a)** and $TS_{5\text{-}5}$ **(b)** in the ·Cl + $HN{=}CHCH_2OH$ reactions. The dashed red line in **(a)** indicates the intramolecular hydrogen bond. The distances are in Å.

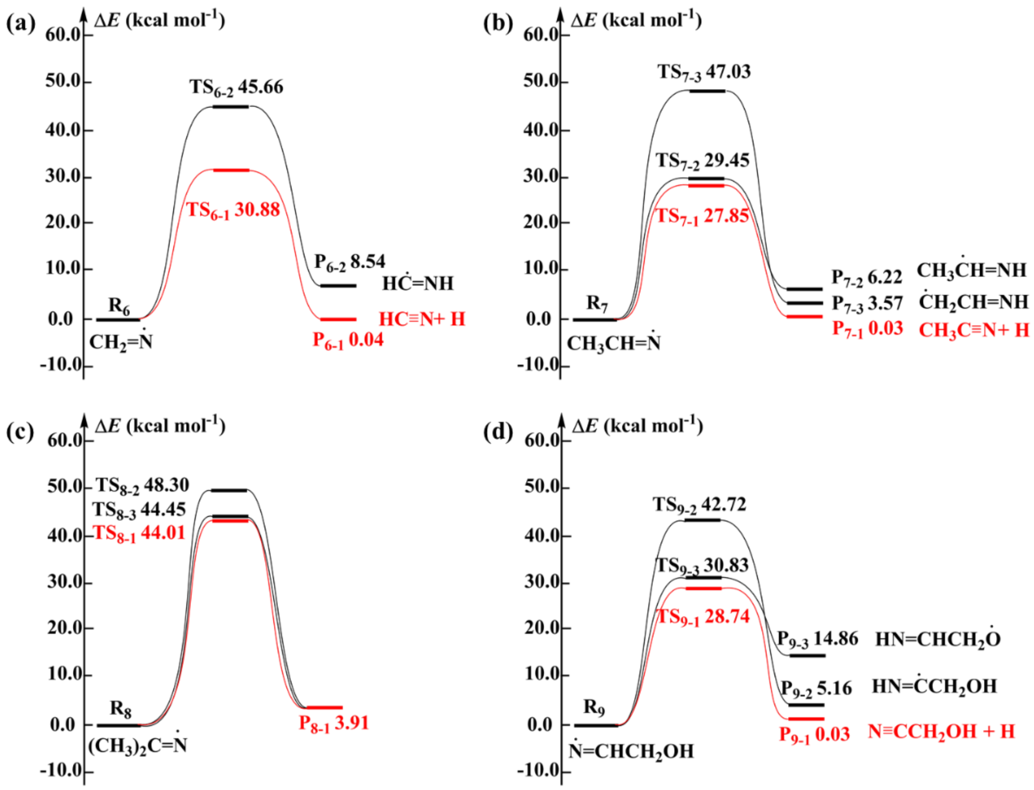


Figure S4. ZPE-corrected potential energy surfaces for the isomerization and dissociation of **(a)** CH_2=N·, **(b)** CH_3CH=N·, **(c)** $(CH_3)_2$C=N·, and **(d)** ·N=CHCH_2OH at CCSD(T)/6-311+G(2df,2p)//M06-2X/6-31+G(d,p) level.

Table S1. Polarizabilities (α) and the first ionization potentials (I) used in the long-range transition state theory (LRTST).

Species	**α/a_0^3**	**I/(eV)**
CH_2=NH	21.21*	9.52*
·CH=NH (P_{1-1})	20.86*	6.64*
·CH=NH (P_{1-2})	22.04*	6.83*
CH_2=N· (P_{1-3})	19.30*	7.17*
CH_3CH=NH	33.69*	9.42*
·CH_2CH=NH (P_{2-1})	29.58*	7.46*
·CH_2CH=NH ($P_{2-2/3}$)	35.90*	9.01*
·CH_3C=NH (P_{2-4})	33.75*	6.11*
CH_3CH=N· (P_{2-5})	31.05*	6.82*
CH_3N=CH_2	34.01*	9.07*
CH_3N=CH· (P_{3-1})	35.32*	5.89*
CH_3N=CH· (P_{3-2})	36.69*	6.02*
·CH_2N=CH_2 (P_{3-3})	34.04*	6.28*
·CH_2N=CH_2 ($P_{3-4/5}$)	36.60*	6.71*
$(CH_3)_2$C=NH	45.41*	9.07*
·(CH_3)(CH_2)=NH (P_{4-1})	41.16*	6.95*
·(CH_3)(CH_2)=NH ($P_{4-2/3}$)	47.00*	8.69*
·(CH_3)(CH_2)=NH (P_{4-4})	41.17*	7.01*
·(CH_3)(CH_2)=NH ($P_{4-5/6}$)	47.09*	8.91*
(CH_3)(CH_2)=N· (P_{4-7})	42.32*	6.13*
HN=CHCH_2OH	37.71*	8.99*
·HN=CHCHOH ($P_{5-1/2}$)	41.70*	7.51*
·HN=CCH_2OH (P_{5-3})	37.61*	6.48*
·N=CHCH_2OH (P_{5-4})	35.25*	6.78*
HN=CHCHO· (P_{5-5})	34.61*	7.40*
·Cl	14.71#	12.97#
HCl	16.97#	12.74#

* α and I were calculated at CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p) level of theory, respectively

#Obtained from the NIST database

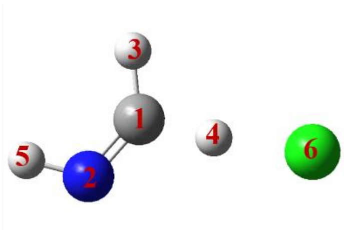
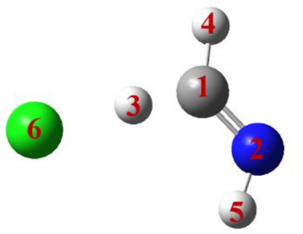
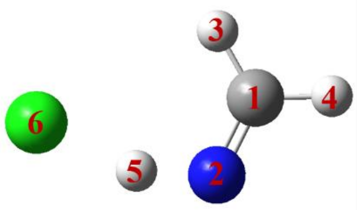
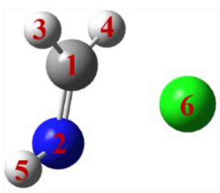
Table S2. Lennard-Jones parameters of the intermediates for various reactions used in the MultiWell simulations.

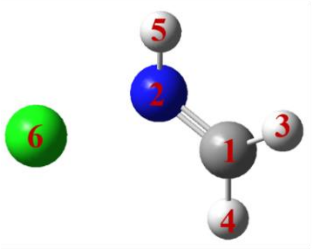
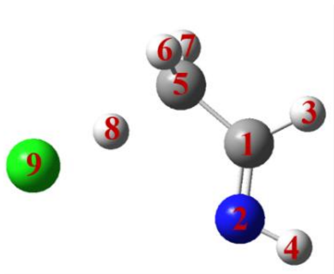
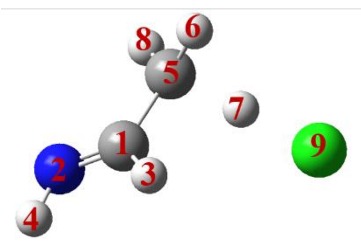
Reactions	σ/(Å)	ε/(K)
CH_2=NH + ·Cl	4.8	408
CH_3CH=NH + ·Cl	5.3	445
CH_3N=CH_2 + ·Cl	5.3	427
$(CH_3)_2C$=NH + ·Cl	5.7	473
HN=$CHCH_2OH$ + ·Cl	5.0	557
CH_2=N· + O_2	4.5	326
CH_3CH=N· + O_2	5.1	453
$(CH_3)_2C$=N· + O_2	5.6	480
·N=$CHCH_2OH$ + O_2	5.2	570
CH_2=N· + NO	4.6	429
CH_3CH=N· + NO	5.2	526
$(CH_3)_2C$=N· + NO	5.6	514
·N=$CHCH_2OH$ + NO	5.3	603

Table S3. Calculated E_a and ΔE values (in kcal mol^{-1}) of TS_{3-1} for the ·Cl + $CH_3N{=}CH_2$ reaction at the CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p) and CCSD(T)/6-311+g(2df,2p)//MP2/6-31+G(d,p) methods.

Methods	$\boldsymbol{E_a}$	$\boldsymbol{\Delta E}$
CCSD(T)/aug-cc-pVTZ //MP2/6-31+g(3df,2p)	1.91	1.87
CCSD(T)/6-311+g(2df,2p) //MP2/6-31+G(d,p)	2.77	2.74

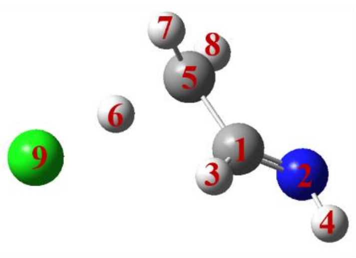
Table S4. NBO charge (*e*) distribution for all TSs of the reactions of five imines and ·Cl.

Species	Number	Cites	Charge
TS_{1-1} 	1	C	0.097
	2	N	-0.671
	3	H1	0.198
	4	H2	0.140
	5	H3	0.404
	6	Cl	-0.168
TS_{1-2} 	1	C	0.045
	2	N	-0.670
	3	H1	0.144
	4	H2	0.214
	5	H3	0.399
	6	Cl	-0.131
TS_{1-3} 	1	C	-0.060
	2	N	-0.321
	3	H1	0.245
	4	H2	0.225
	5	H3	0.340
	6	Cl	-0.428
TS_{1-4} 	1	C	-0.096
	2	N	-0.571
	3	H1	0.210
	4	H2	0.223

	5	H3	0.371
	6	Cl	-0.137
TS_{1-5}	1	C	-0.108
	2	N	-0.625
	3	H1	0.189
	4	H2	0.200
	5	H3	0.427
	6	Cl	-0.083
TS_{2-1}	1	C1	0.100
	2	N	-0.665
	3	H1	0.187
	4	H2	0.382
	5	C2	-0.442
	6	H3	0.243
	7	H4	0.243
	8	H5	0.222
	9	Cl	-0.271
TS_{2-2}	1	C1	0.087
	2	N	-0.628
	3	H1	0.189
	4	H2	0.379
	5	C2	-0.469
	6	H3	0.246
	7	H4	0.220

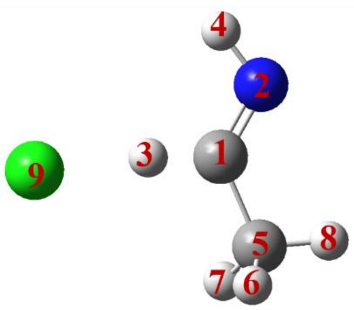
8	H5	0.254
9	Cl	-0.278

$TS_{2\text{-}3}$



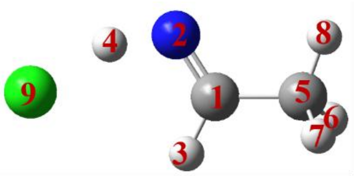
1	C1	0.087
2	N	-0.629
3	H1	0.189
4	H2	0.379
5	C2	-0.469
6	H3	0.220
7	H4	0.246
8	H5	0.254
9	Cl	-0.278

$TS_{2\text{-}4}$

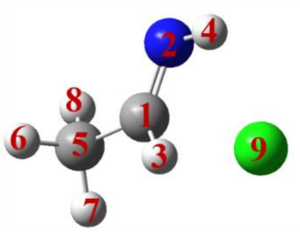
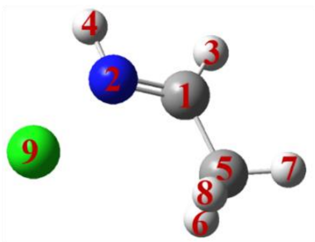


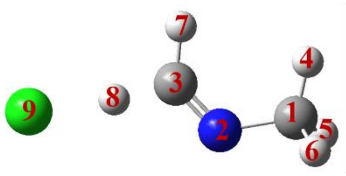
1	C1	0.210
2	N	-0.702
3	H1	0.140
4	H2	0.387
5	C2	-0.708
6	H3	0.241
7	H4	0.246
8	H5	0.250
9	Cl	-0.064

$TS_{2\text{-}5}$



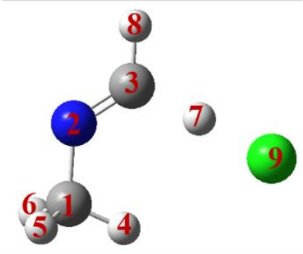
1	C1	0.143
2	N	-0.345
3	H1	0.250
4	H2	0.347

	5	C2	-0.705
	6	H3	0.254
	7	H4	0.254
	8	H5	0.249
	9	Cl	-0.447
$TS_{2\text{-}6}$	1	C1	0.116
	2	N	-0.575
	3	H1	0.221
	4	H2	0.376
	5	C2	-0.698
	6	H3	0.247
	7	H4	0.239
	8	H5	0.253
	9	Cl	-0.179
$TS_{2\text{-}7}$	1	C1	0.076
	2	N	-0.648
	3	H1	0.193
	4	H2	0.428
	5	C2	-0.715
	6	H3	0.240
	7	H4	0.235
	8	H5	0.243
	9	Cl	-0.051
$TS_{3\text{-}1}$	1	C1	-0.438



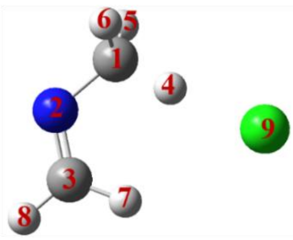
2	N	-0.479
3	C2	0.072
4	H1	0.193
5	H2	0.234
6	H3	0.234
7	H4	0.186
8	H5	0.142
9	Cl	-0.144

$TS_{3\text{-}2}$

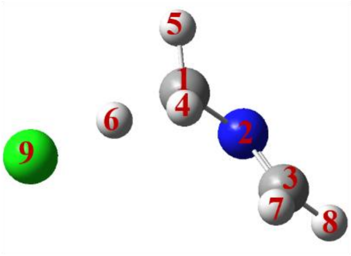
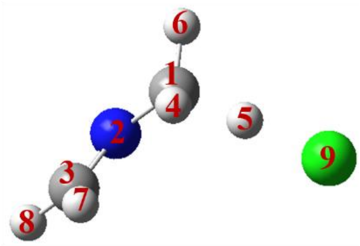


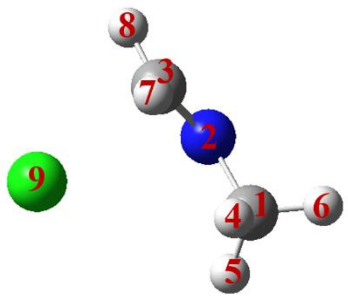
1	C1	-0.445
2	N	-0.451
3	C2	0.105
4	H1	0.225
5	H2	0.235
6	H3	0.235
7	H4	0.183
8	H5	0.230
9	Cl	-0.318

$TS_{3\text{-}3}$



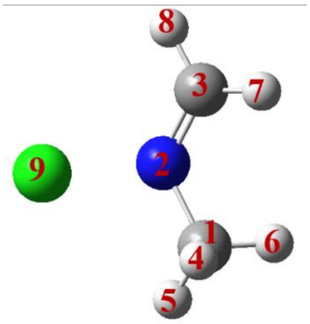
1	C1	-0.387
2	N	-0.492
3	C2	-0.045
4	H1	0.137
5	H2	0.232
6	H3	0.232
7	H4	0.177

	8	H5	0.202
	9	Cl	-0.056
TS_{3-4}	1	C1	-0.267
	2	N	-0.492
	3	C2	-0.012
	4	H1	0.206
	5	H2	0.245
	6	H3	0.203
	7	H4	0.163
	8	H5	0.201
	9	Cl	-0.246
TS_{3-5}	1	C1	-0.267
	2	N	-0.492
	3	C2	-0.012
	4	H1	0.206
	5	H2	0.203
	6	H3	0.245
	7	H4	0.163
	8	H5	0.201
	9	Cl	-0.246
TS_{3-6}	1	C1	-0.462
	2	N	-0.399
	3	C2	-0.089
	4	H1	0.192



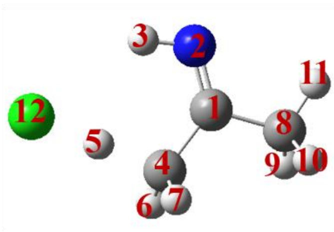
5	H2	0.238
6	H3	0.230
7	H4	0.198
8	H5	0.230
9	Cl	-0.140

TS_{3-7}



1	C1	-0.425
2	N	-0.448
3	C2	-0.110
4	H1	0.221
5	H2	0.239
6	H3	0.225
7	H4	0.183
8	H5	0.208
9	Cl	-0.094

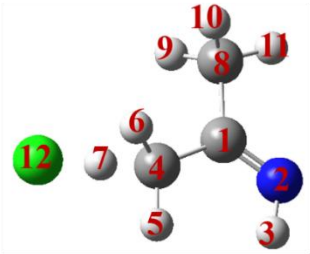
TS_{4-1}



1	C1	0.268
2	N	-0.681
3	H1	0.384
4	C2	-0.438
5	H2	0.221
6	H3	0.246
7	H4	0.246
8	C3	-0.686
9	H5	0.233
10	H6	0.257

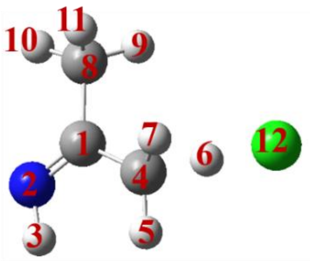
11	H7	0.233
12	Cl	-0.283

TS$_{4-2}$

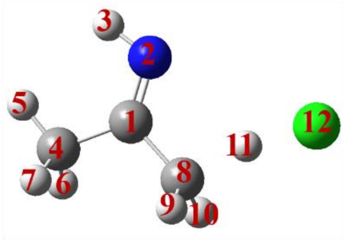
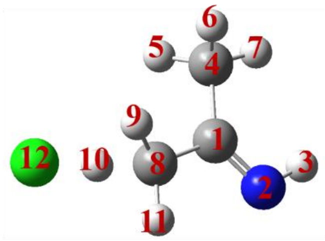


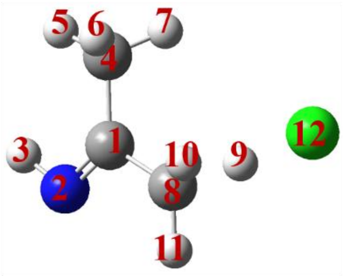
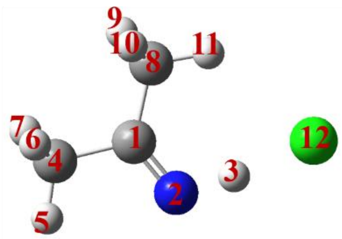
1	C1	0.259
2	N	-0.630
3	H1	0.366
4	C2	-0.465
5	H2	0.239
6	H3	0.249
7	H4	0.221
8	C3	-0.691
9	H5	0.247
10	H6	0.232
11	H7	0.251
12	Cl	-0.278

TS$_{4-3}$



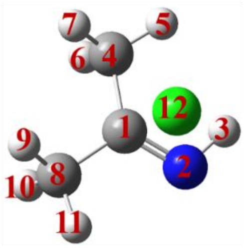
1	C1	0.259
2	N	-0.630
3	H1	0.366
4	C2	-0.465
5	H2	0.239
6	H3	0.221
7	H4	0.249
8	C3	-0.691
9	H5	0.247
10	H6	0.251

	11	H7	0.232
	12	Cl	-0.278
$TS_{4\text{-}4}$ 	1	C1	0.271
	2	N	-0.675
	3	H1	0.371
	4	C2	-0.698
	5	H2	0.237
	6	H3	0.242
	7	H4	0.242
	8	C3	-0.426
	9	H5	0.241
	10	H6	0.241
	11	H7	0.227
	12	Cl	-0.272
$TS_{4\text{-}5}$ 	1	C1	0.257
	2	N	-0.637
	3	H1	0.369
	4	C2	-0.703
	5	H2	0.232
	6	H3	0.256
	7	H4	0.239
	8	C3	-0.448
	9	H5	0.241
	10	H6	0.222

	11	H7	0.257
	12	Cl	-0.285
$TS_{4\text{-}6}$ 	1	C1	0.257
	2	N	-0.637
	3	H1	0.369
	4	C2	-0.703
	5	H2	0.232
	6	H3	0.239
	7	H4	0.256
	8	C3	-0.448
	9	H5	0.222
	10	H6	0.241
	11	H7	0.257
	12	Cl	-0.285
$TS_{4\text{-}7}$ 	1	C1	0.328
	2	N	-0.359
	3	H1	0.344
	4	C2	-0.683
	5	H2	0.251
	6	H3	0.248
	7	H4	0.248
	8	C3	-0.701
	9	H5	0.250
	10	H6	0.250

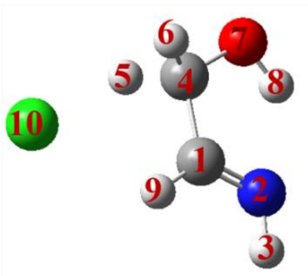
11	H7	0.281
12	Cl	-0.456

TS$_{4\text{-}8}$



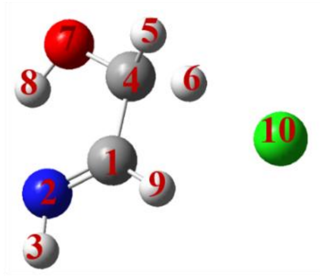
1	C1	0.311
2	N	-0.562
3	H1	0.367
4	C2	-0.691
5	H2	0.242
6	H3	0.239
7	H4	0.253
8	C3	-0.682
9	H5	0.244
10	H6	0.236
11	H7	0.259
12	Cl	-0.216

TS$_{5\text{-}1}$



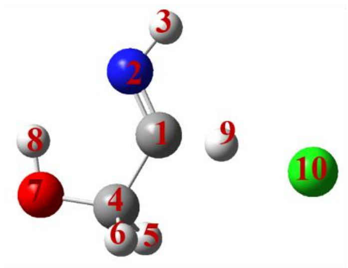
1	C1	0.147
2	N	-0.744
3	H1	0.394
4	C2	-0.051
5	H2	0.167
6	H3	0.223
7	O	-0.808
8	H4	0.542
9	H5	0.199
10	Cl	-0.069

TS_{5-2}



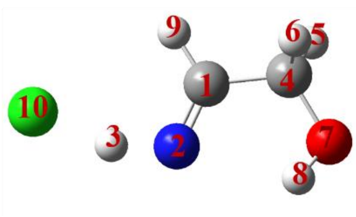
1	C1	0.147
2	N	-0.744
3	H1	0.394
4	C2	-0.051
5	H2	0.223
6	H3	0.167
7	O	-0.808
8	H4	0.542
9	H5	0.199
10	Cl	-0.069

TS_{5-3}

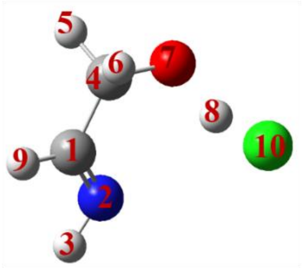
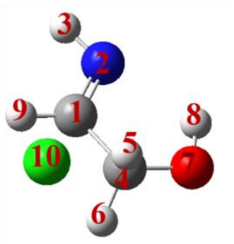


1	C1	0.225
2	N	-0.732
3	H1	0.405
4	C2	-0.106
5	H2	0.218
6	H3	0.218
7	O	-0.817
8	H4	0.532
9	H5	0.129
10	Cl	-0.071

TS_{5-4}



1	C1	0.108
2	N	-0.351
3	H1	0.339
4	C2	-0.101

	5	H2	0.236
	6	H3	0.218
	7	O	-0.796
	8	H4	0.517
	9	H5	0.254
	10	Cl	-0.423
$TS_{5\text{-}5}$ 	1	C1	0.116
	2	N	-0.682
	3	H1	0.388
	4	C2	-0.184
	5	H2	0.247
	6	H3	0.258
	7	O	-0.303
	8	H4	0.398
	9	H5	0.192
	10	Cl	-0.430
$TS_{5\text{-}6}$ 	1	C1	0.082
	2	N	-0.603
	3	H1	0.390
	4	C2	-0.093
	5	H2	0.204
	6	H3	0.229
	7	O	-0.815
	8	H4	0.530

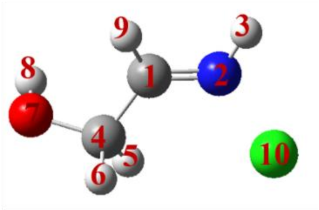
	9	H5	0.235
	10	Cl	-0.159
TS_{5-7} 	1	C1	0.053
	2	N	-0.634
	3	H1	0.431
	4	C2	-0.115
	5	H2	0.208
	6	H3	0.224
	7	O	-0.807
	8	H4	0.503
	9	H5	0.200
	10	Cl	-0.062

Table S5. Calculated E_a values (in kcal mol^{-1}) for the CH_2=N + O_2, CH_3CHN + O_2, and $HOCH_2$CHN + O_2 reactions at the CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p), CCSD(T)/6-311+G(2df,2p)//M06-2X/6-31+G(d,p) and CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ methods.

Methods	**TS_{10-1}**	**TS_{11-1}**	**TS_{13-1}**
CCSD(T)/aug-cc-pVTZ //MP2/6-31+g(3df,2p)	6.10	5.04	5.03
CCSD(T)/6-311+G(2df,2p) //M06-2X/6-31+G(d,p)	12.25	10.86	10.89
CCSD(T)/aug-cc-pVTZ //MP2/aug-cc-pVTZ	5.83	4.84	4.87

Table S6. Calculated E_a values (in kcal mol^{-1}) for the CH_2=N + NO, CH_3CHN + NO, $(CH_3)_2$C=N· + NO and $HOCH_2$CHN + NO reactions at the CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p), CCSD(T)/6-311+G(2df,2p)//M06-2X/6-31+G(d,p) and CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ methods.

Methods	**TS_{14-2}**	**TS_{15-2}**	**TS_{16-2}**	**TS_{17-2}**
CCSD(T)/aug-cc-pVTZ //MP2/6-31+g(3df,2p)	6.79	5.29	3.81	4.89
CCSD(T)/6-311+G(2df,2p) //M06-2X/6-31+G(d,p)	14.05	12.31	9.62	11.59
CCSD(T)/aug-cc-pVTZ //MP2/aug-cc-pVTZ	6.59	5.10	3.77	4.74

Table S7. Calculated energies of NO-adducts (in kcal mol^{-1}) for the CH_2=N + NO, CH_3CHN + NO, $(CH_3)_2$C=N· + NO and $HOCH_2$CHN + NO reactions at the CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p) and CCSD(T)/6-311+G(2df,2p)//M06-2X/6-31+G(d,p) methods.

Methods	**IM_{14-1}**	**IM_{15-1}**	**IM_{16-1}**	**IM_{17-1}**
CCSD(T)/aug-cc-pVTZ //MP2/6-31+g(3df,2p)	-26.21	-27.51	-28.02	-30.95
CCSD(T)/6-311+G(2df,2p) //M06-2X/6-31+G(d,p)	-20.58	-23.99	-23.17	-25.71