Supporting Information for

Chlorine Radical-Initiated Atmospheric Oxidation of Imines: Implications for Structural Influence on the Nitrosamine Formation

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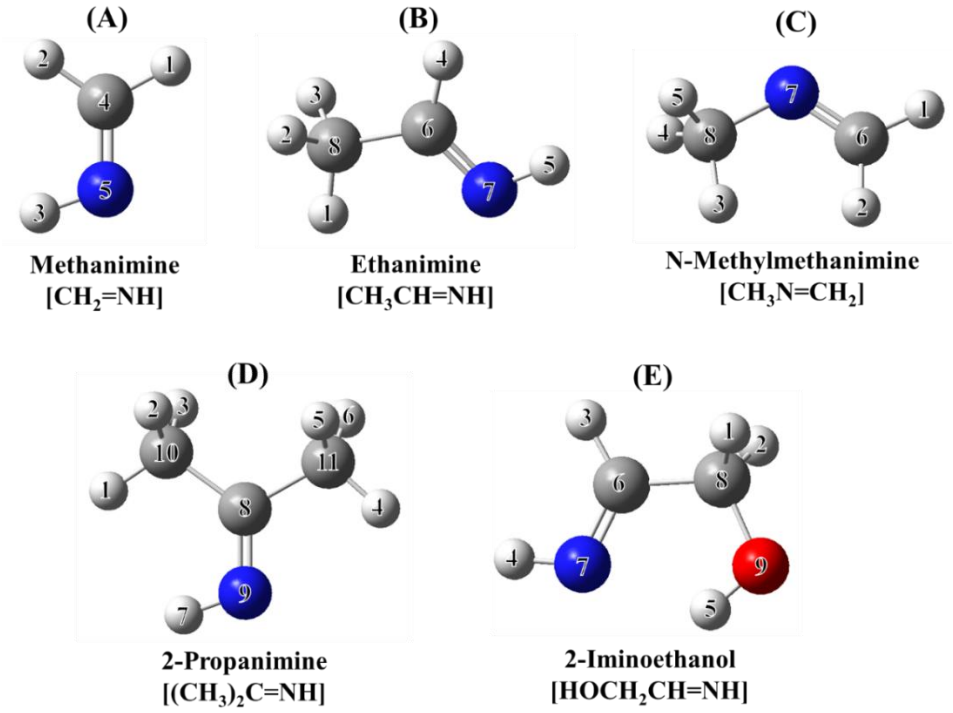


Figure S1. Global minimum of five typical imines obtained at CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p) level. The white, red, blue, and gray spheres represent H, O, N, and C atoms, respectively.

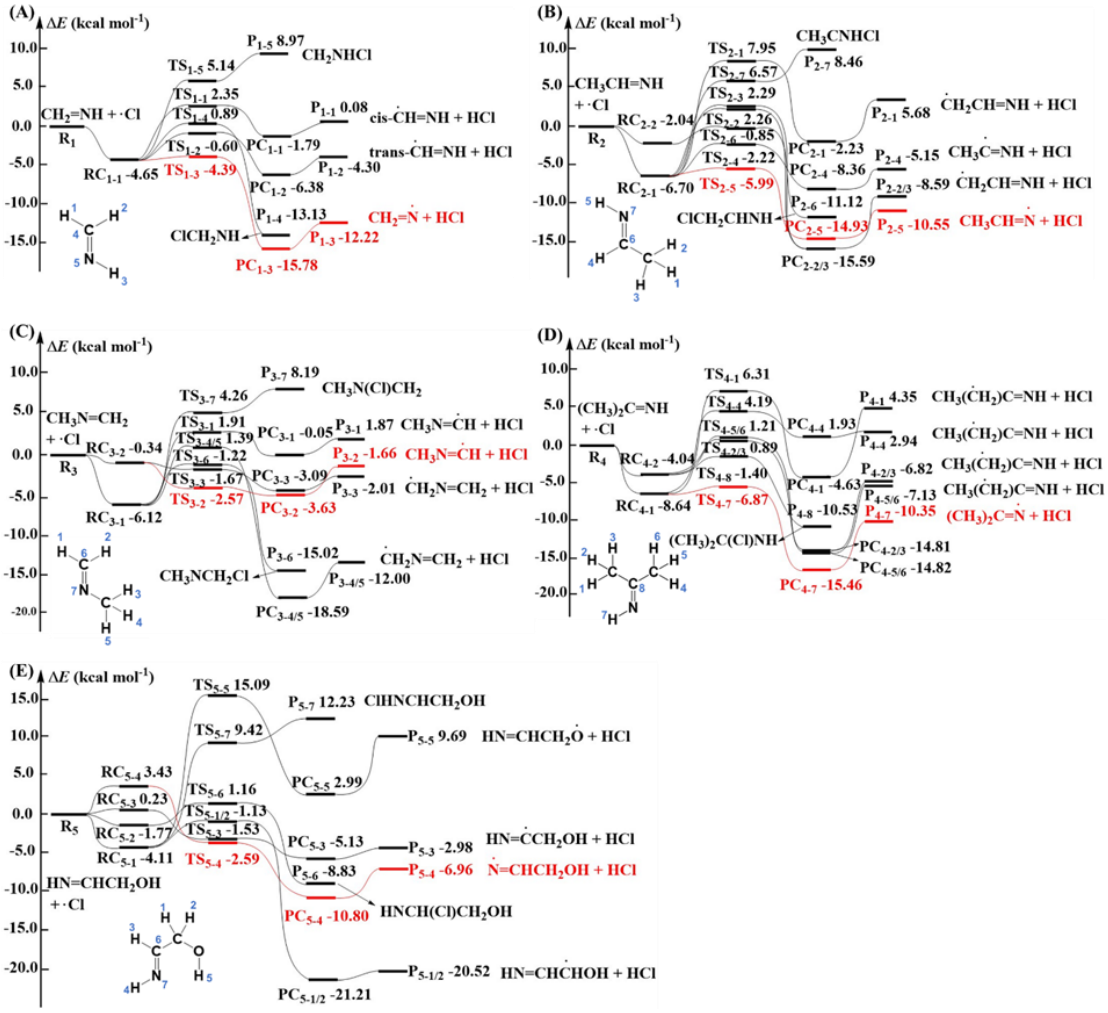


Figure S2. ZPE-corrected potential energy surface for the reaction of (A) CH_2=NH, (B) CH_3CH=NH, (C) CH_3N=CH_2, (D) $(CH_3)_2C$=NH, and (E) HN=$CHCH_2OH$ with ·Cl calculated at the CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p) level of theory. $IM_{n\text{-}m}$, $TS_{n\text{-}m}$, and $P_{n\text{-}m}$ represent IM, TS, and P, respectively. n denotes different imines radicals, m denotes different species.

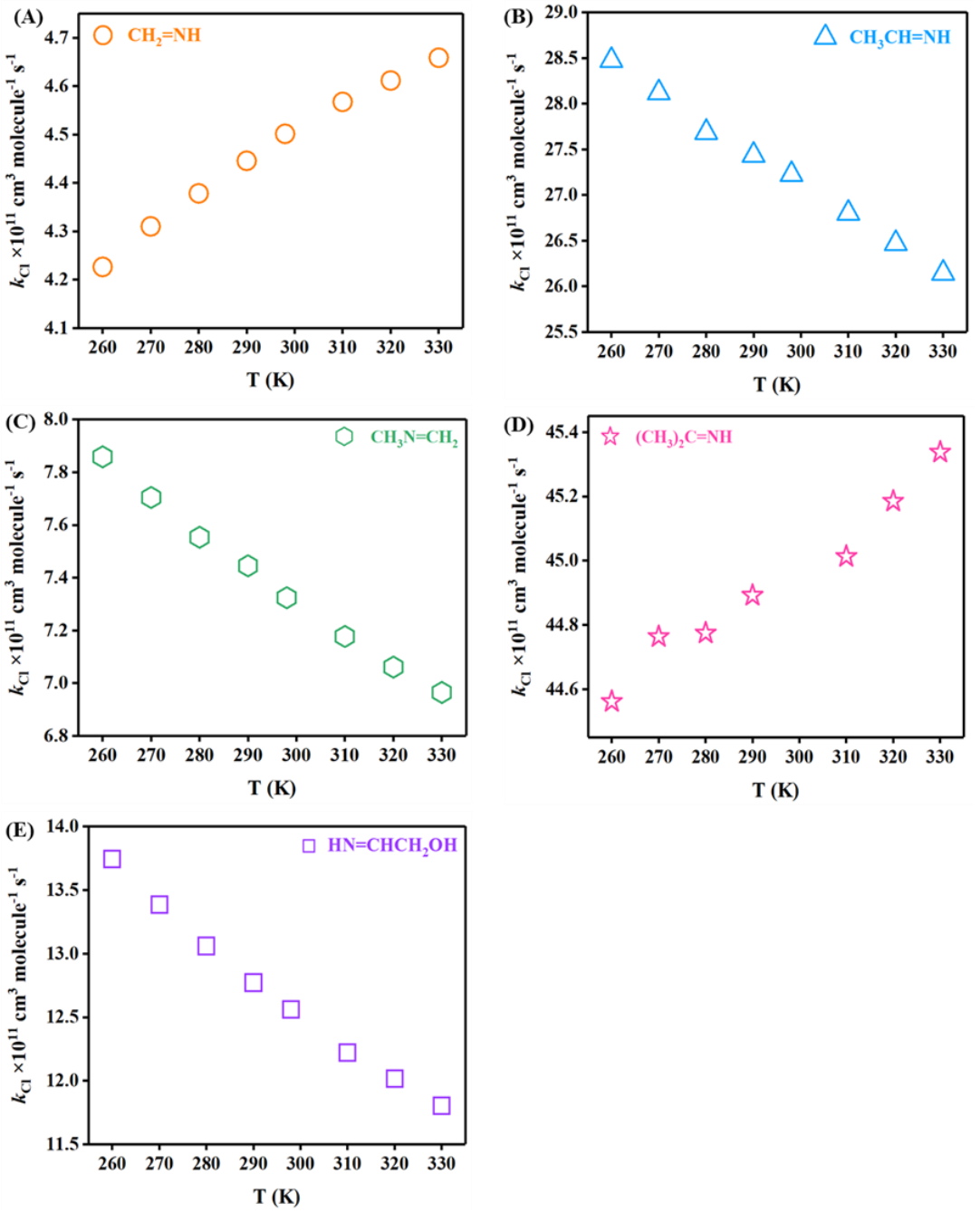


Figure S3. Reaction rate constants (k_{Cl}) for the reactions of (A) CH_2=NH, (B) CH_3CH=NH, (C) CH_3N=CH_2, (D) $(CH_3)_2C$=NH, and (E) HN=$CHCH_2OH$ initiated by ·Cl in the temperature range of 260 - 300 K.

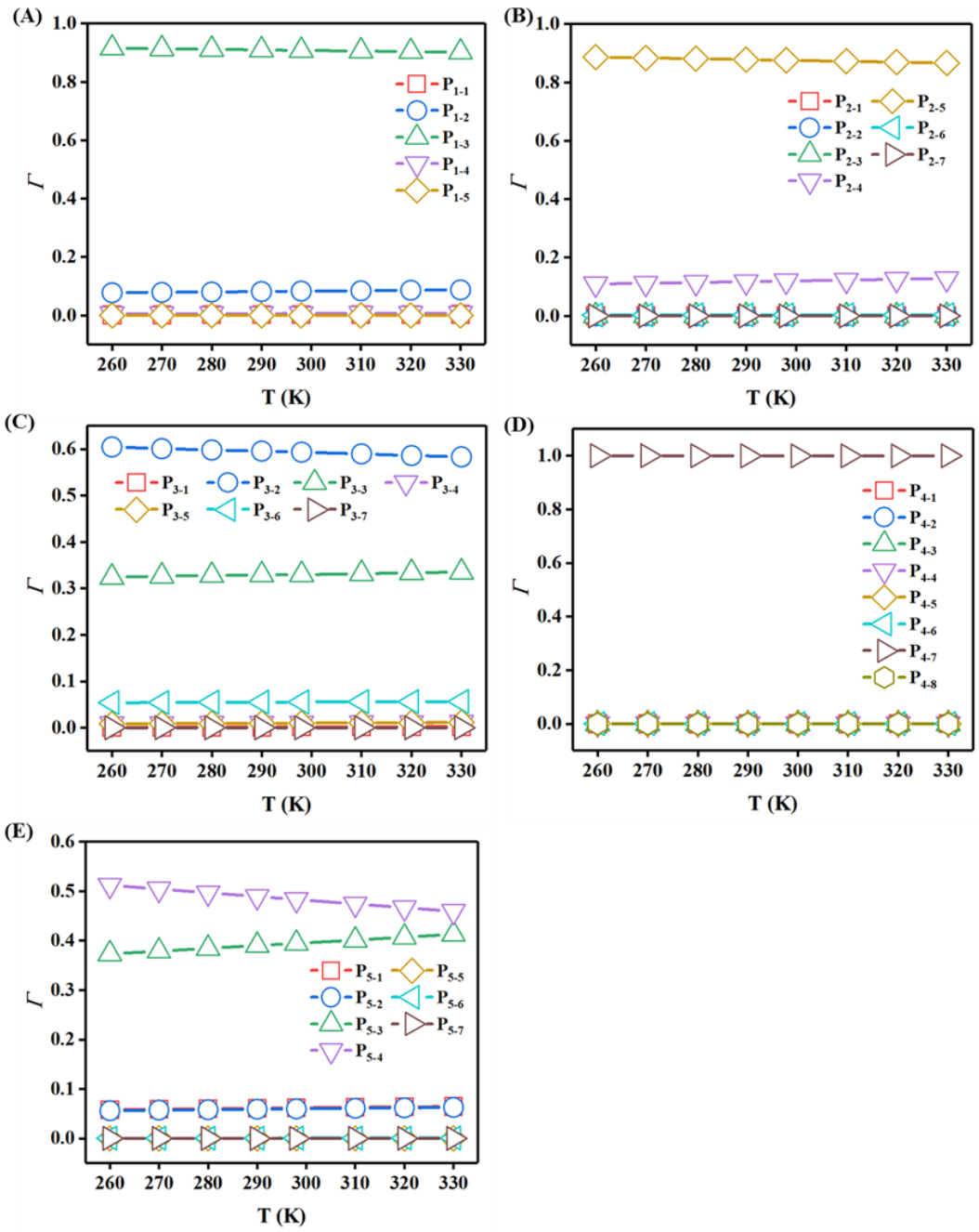


Figure S4. Branching ratios (Γ) for the formation of products for the reactions of (A) CH_2=NH, (B) CH_3CH=NH, (C) CH_3N=CH_2, (D) $(CH_3)_2C$=NH, and (E) HN=$CHCH_2OH$ initiated by ·Cl in the temperature range of 260 - 300 K.

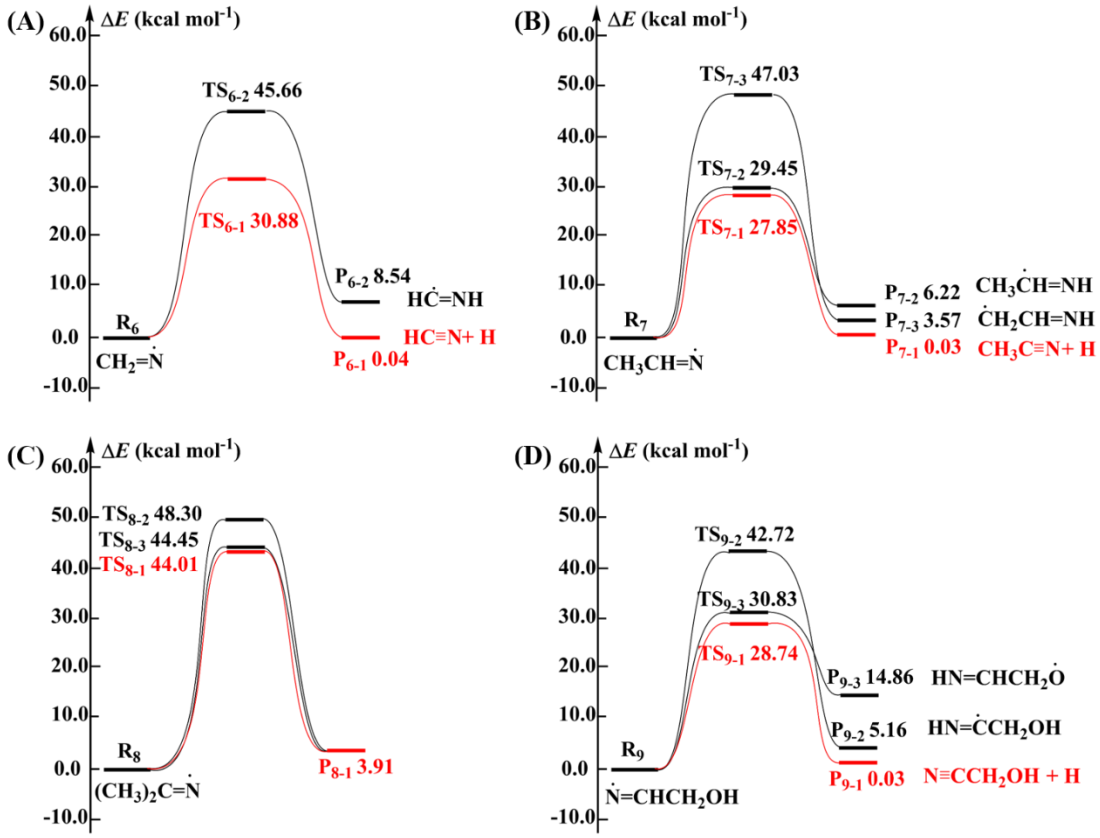


Figure S5. ZPE-corrected potential energy surfaces for the isomerization and dissociation of (A) CH_2=N·, (B) CH_3CH=N·, (C) $(CH_3)_2C$=N·, and (D) ·N=$CHCH_2OH$ at CCSD(T)/6-311+G(2df,2p)//M06-2X/6-31+G(d,p) level.

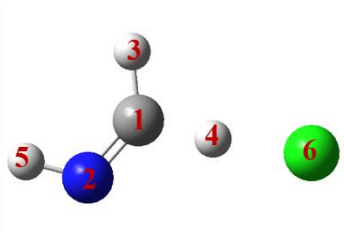
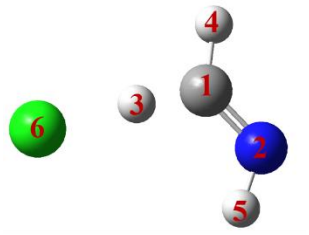
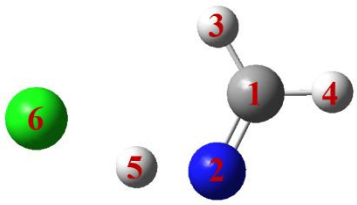
Table S1. Lennard-Jones parameters of the intermediates for various reactions used in the MultiWell or MESMER simulations.

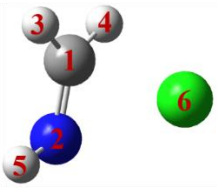
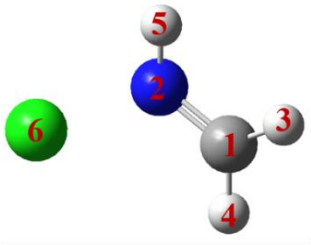
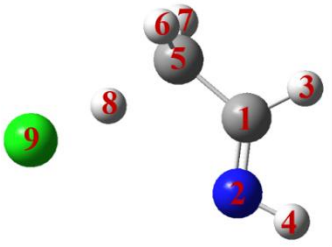
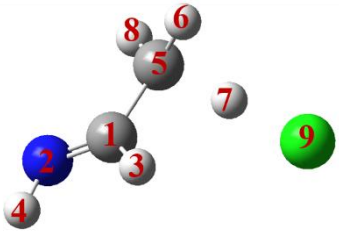
Reactions	σ/(Å)	ε/(K)
CH_2=NH + ·Cl	4.8	408
CH_3CH=NH + ·Cl	5.3	445
CH_3N=CH_2 + ·Cl	5.3	427
$(CH_3)_2C$=NH + ·Cl	5.7	473
HN=$CHCH_2OH$ + ·Cl	5.0	557
CH_2=N· + O_2	4.5	326
CH_3CH=N· + O_2	5.1	453
$(CH_3)_2C$=N· + O_2	5.6	480
·N=$CHCH_2OH$ + O_2	5.2	570
CH_2=N· + NO	4.6	429
CH_3CH=N· + NO	5.2	526
$(CH_3)_2C$=N·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

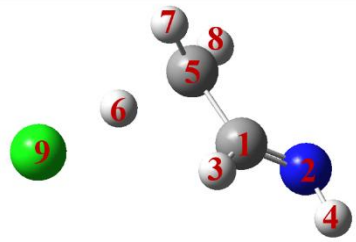
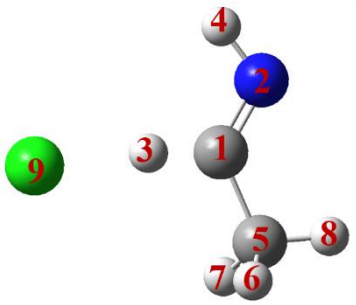
Table S2. Calculated E_a and ΔE values (in kcal mol^{-1}) of $TS_{3\text{-}1}$ for the ·Cl + $CH_3N{=}CH_2$ reaction at the CCSD(T)/aug-cc-pVTZ//MP2/6-31+G(3df,2p) and CCSD(T)/6-311+g(2df,2p)//MP2/6-31+G(d,p) methods.

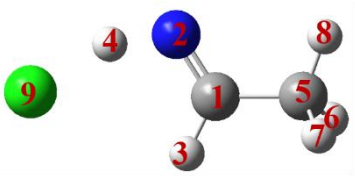
Methods	E_a	ΔE
CCSD(T)/aug-cc-pVTZ //MP2/6-31+g(3df,2p)	1.91	1.87
CCSD(T)/6-311+g(2df,2p) //MP2/6-31+G(d,p)	2.77	2.74

Table S3. NBO charge distribution for all TSs of the reactions of five imines and ·Cl.

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

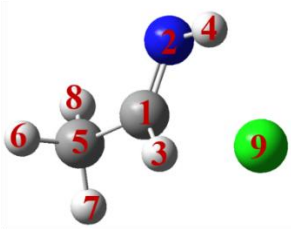
	4	H2 site	0.223
	5	H3 site	0.371
	6	Cl site	-0.137
TS_{1-5}	1	C site	-0.108
	2	N site	-0.625
	3	H1 site	0.189
	4	H2 site	0.200
	5	H3 site	0.427
	6	Cl site	-0.083
TS_{2-1}	1	C1 site	0.100
	2	N site	-0.665
	3	H1 site	0.187
	4	H2 site	0.382
	5	C2 site	-0.442
	6	H3 site	0.243
	7	H4 site	0.243
	8	H5 site	0.222
	9	Cl site	-0.271
TS_{2-2}	1	C1 site	0.087
	2	N site	-0.628
	3	H1 site	0.189
	4	H2 site	0.379
	5	C2 site	-0.469
	6	H3 site	0.246

	7	H4 site	0.220
	8	H5 site	0.254
	9	Cl site	-0.278
TS_{2-3} 	1	C1 site	0.087
	2	N site	-0.629
	3	H1 site	0.189
	4	H2 site	0.379
	5	C2 site	-0.469
	6	H3 site	0.220
	7	H4 site	0.246
	8	H5 site	0.254
	9	Cl site	-0.278
TS_{2-4} 	1	C1 site	0.210
	2	N site	-0.702
	3	H1 site	0.140
	4	H2 site	0.387
	5	C2 site	-0.708
	6	H3 site	0.241
	7	H4 site	0.246
	8	H5 site	0.250
	9	Cl site	-0.064
TS_{2-5}	1	C1 site	0.143
	2	N site	-0.345
	3	H1 site	0.250



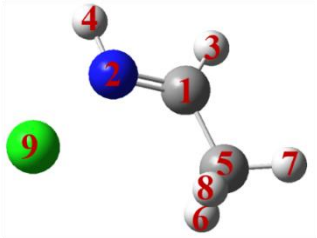
4	H2 site	0.347
5	C2 site	-0.705
6	H3 site	0.254
7	H4 site	0.254
8	H5 site	0.249
9	Cl site	-0.447

$TS_{2\text{-}6}$

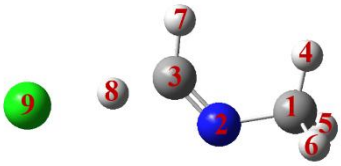
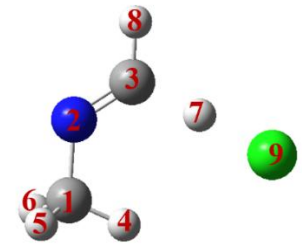
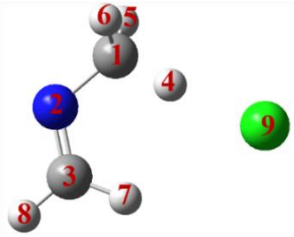


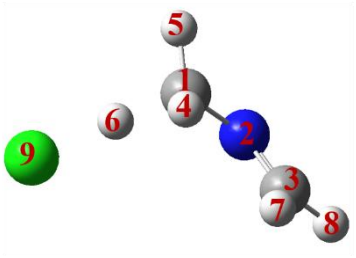
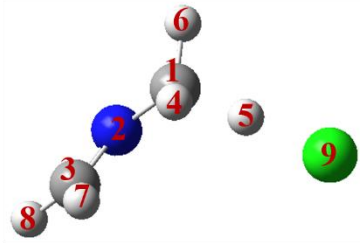
1	C1 site	0.116
2	N site	-0.575
3	H1 site	0.221
4	H2 site	0.376
5	C2 site	-0.698
6	H3 site	0.247
7	H4 site	0.239
8	H5 site	0.253
9	Cl site	-0.179

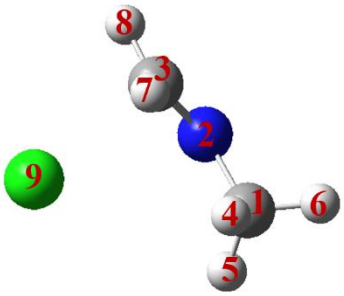
$TS_{2\text{-}7}$



1	C1 site	0.076
2	N site	-0.648
3	H1 site	0.193
4	H2 site	0.428
5	C2 site	-0.715
6	H3 site	0.240
7	H4 site	0.235
8	H5 site	0.243
9	Cl site	-0.051

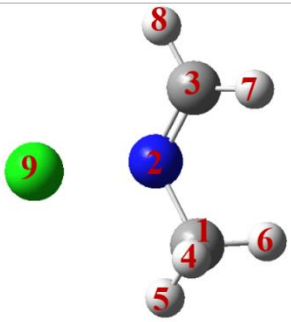
TS_{3-1} 	1	C1 site	-0.438
	2	N site	-0.479
	3	C2 site	0.072
	4	H1 site	0.193
	5	H2 site	0.234
	6	H3 site	0.234
	7	H4 site	0.186
	8	H5 site	0.142
	9	Cl site	-0.144
TS_{3-2} 	1	C1 site	-0.445
	2	N site	-0.451
	3	C2 site	0.105
	4	H1 site	0.225
	5	H2 site	0.235
	6	H3 site	0.235
	7	H4 site	0.183
	8	H5 site	0.230
	9	Cl site	-0.318
TS_{3-3} 	1	C1 site	-0.387
	2	N site	-0.492
	3	C2 site	-0.045
	4	H1 site	0.137
	5	H2 site	0.232
	6	H3 site	0.232

	7	H4 site	0.177
	8	H5 site	0.202
	9	Cl site	-0.056
TS_{3-4} 	1	C1 site	-0.267
	2	N site	-0.492
	3	C2 site	-0.012
	4	H1 site	0.206
	5	H2 site	0.245
	6	H3 site	0.203
	7	H4 site	0.163
	8	H5 site	0.201
	9	Cl site	-0.246
TS_{3-5} 	1	C1 site	-0.267
	2	N site	-0.492
	3	C2 site	-0.012
	4	H1 site	0.206
	5	H2 site	0.203
	6	H3 site	0.245
	7	H4 site	0.163
	8	H5 site	0.201
	9	Cl site	-0.246
TS_{3-6}	1	C1 site	-0.462
	2	N site	-0.399
	3	C2 site	-0.089



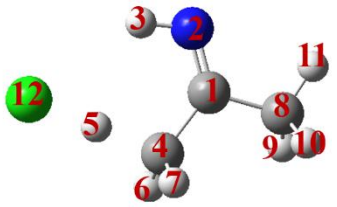
4	H1 site	0.192
5	H2 site	0.238
6	H3 site	0.230
7	H4 site	0.198
8	H5 site	0.230
9	Cl site	-0.140

$TS_{3\text{-}7}$

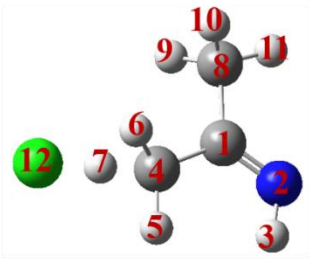
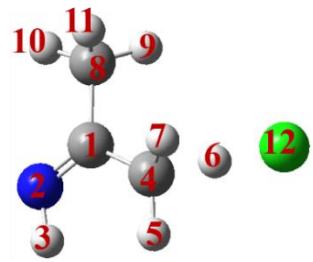


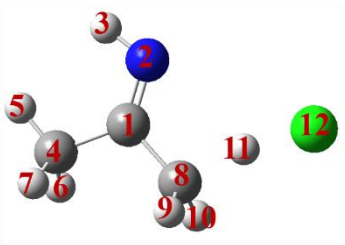
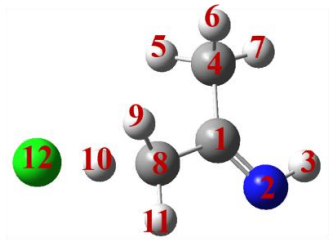
1	C1 site	-0.425
2	N site	-0.448
3	C2 site	-0.110
4	H1 site	0.221
5	H2 site	0.239
6	H3 site	0.225
7	H4 site	0.183
8	H5 site	0.208
9	Cl site	-0.094

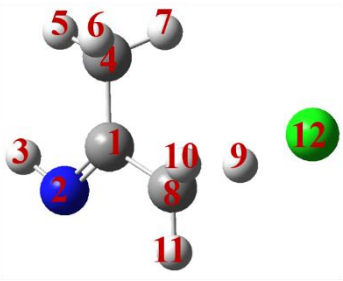
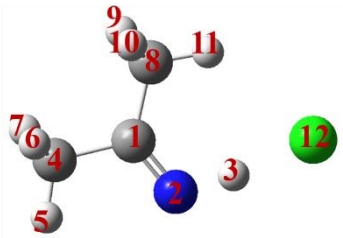
$TS_{4\text{-}1}$

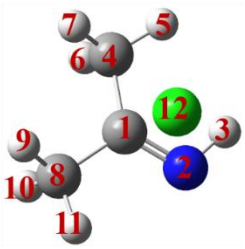
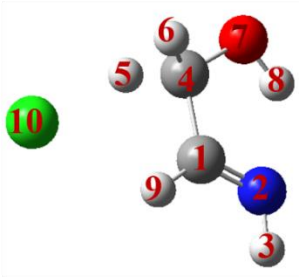


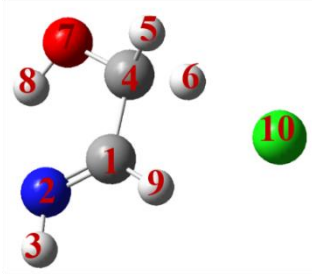
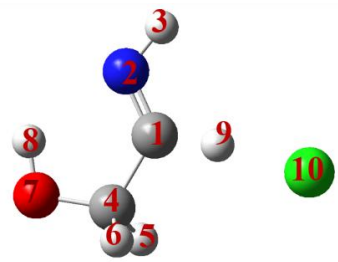
1	C1 site	0.268
2	N site	-0.681
3	H1 site	0.384
4	C2 site	-0.438
5	H2 site	0.221
6	H3 site	0.246
7	H4 site	0.246
8	C3 site	-0.686
9	H5 site	0.233

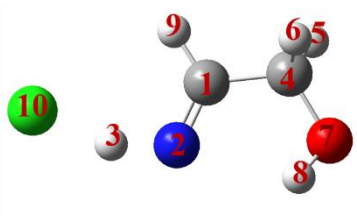
	10	H6 site	0.257
	11	H7 site	0.233
	12	Cl site	-0.283
TS_{4-2} 	1	C1 site	0.259
	2	N site	-0.630
	3	H1 site	0.366
	4	C2 site	-0.465
	5	H2 site	0.239
	6	H3 site	0.249
	7	H4 site	0.221
	8	C3 site	-0.691
	9	H5 site	0.247
	10	H6 site	0.232
	11	H7 site	0.251
	12	Cl site	-0.278
TS_{4-3} 	1	C1 site	0.259
	2	N site	-0.630
	3	H1 site	0.366
	4	C2 site	-0.465
	5	H2 site	0.239
	6	H3 site	0.221
	7	H4 site	0.249
	8	C3 site	-0.691
	9	H5 site	0.247

	10	H6 site	0.251
	11	H7 site	0.232
	12	Cl site	-0.278
TS_{4-4} 	1	C1 site	0.271
	2	N site	-0.675
	3	H1 site	0.371
	4	C2 site	-0.698
	5	H2 site	0.237
	6	H3 site	0.242
	7	H4 site	0.242
	8	C3 site	-0.426
	9	H5 site	0.241
	10	H6 site	0.241
	11	H7 site	0.227
	12	Cl site	-0.272
TS_{4-5} 	1	C1 site	0.257
	2	N site	-0.637
	3	H1 site	0.369
	4	C2 site	-0.703
	5	H2 site	0.232
	6	H3 site	0.256
	7	H4 site	0.239
	8	C3 site	-0.448
	9	H5 site	0.241

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

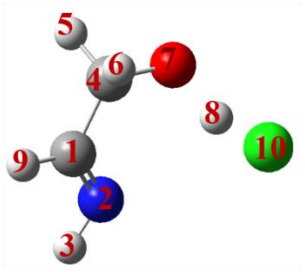
	10	H6 site	0.250
	11	H7 site	0.281
	12	Cl site	-0.456
TS_{4-8} 	1	C1 site	0.311
	2	N site	-0.562
	3	H1 site	0.367
	4	C2 site	-0.691
	5	H2 site	0.242
	6	H3 site	0.239
	7	H4 site	0.253
	8	C3 site	-0.682
	9	H5 site	0.244
	10	H6 site	0.236
	11	H7 site	0.259
	12	Cl site	-0.216
TS_{5-1} 	1	C1 site	0.147
	2	N site	-0.744
	3	H1 site	0.394
	4	C2 site	-0.051
	5	H2 site	0.167
	6	H3 site	0.223
	7	O site	-0.808
	8	H4 site	0.542
	9	H5 site	0.199

	10	Cl site	-0.069
TS_{5-2} 	1	C1 site	0.147
	2	N site	-0.744
	3	H1 site	0.394
	4	C2 site	-0.051
	5	H2 site	0.223
	6	H3 site	0.167
	7	O site	-0.808
	8	H4 site	0.542
	9	H5 site	0.199
	10	Cl site	-0.069
TS_{5-3} 	1	C1 site	0.225
	2	N site	-0.732
	3	H1 site	0.405
	4	C2 site	-0.106
	5	H2 site	0.218
	6	H3 site	0.218
	7	O site	-0.817
	8	H4 site	0.532
	9	H5 site	0.129
	10	Cl site	-0.071
TS_{5-4}	1	C1 site	0.108
	2	N site	-0.351
	3	H1 site	0.339



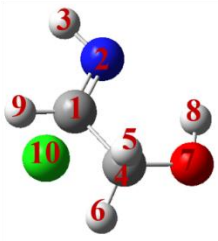
4	C2 site	-0.101
5	H2 site	0.236
6	H3 site	0.218
7	O site	-0.796
8	H4 site	0.517
9	H5 site	0.254
10	Cl site	-0.423

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



1	C1 site	0.116
2	N site	-0.682
3	H1 site	0.388
4	C2 site	-0.184
5	H2 site	0.247
6	H3 site	0.258
7	O site	-0.303
8	H4 site	0.398
9	H5 site	0.192
10	Cl site	-0.430

$TS_{5\text{-}6}$



1	C1 site	0.082
2	N site	-0.603
3	H1 site	0.390
4	C2 site	-0.093
5	H2 site	0.204
6	H3 site	0.229
7	O site	-0.815

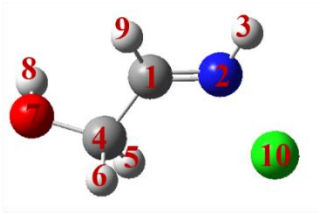
	8	H4 site	0.530
	9	H5 site	0.235
	10	Cl site	-0.159
$TS_{5\text{-}7}$ 	1	C1 site	0.053
	2	N site	-0.634
	3	H1 site	0.431
	4	C2 site	-0.115
	5	H2 site	0.208
	6	H3 site	0.224
	7	O site	-0.807
	8	H4 site	0.503
	9	H5 site	0.200
	10	Cl site	-0.062

Table S4. Calculated E_a values (in kcal mol^{-1}) for the CH_2=N + O_2, CH_3CHN + O_2, $(CH_3)_2C$=N· + O_2 and $HOCH_2CHN$ + 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_{12-1}	TS_{13-1}	$TS_{12-1'}$	TS_{12-2}
CCSD(T)/aug-cc-pVTZ //MP2/6-31+g(3df,2p)	6.10	5.04	43.19	5.03	4.79	31.80
CCSD(T)/6-311+G(2df,2p) //M06-2X/6-31+G(d,p)	12.25	10.86	49.05	10.89	7.01	31.89
CCSD(T)/aug-cc-pVTZ //MP2/aug-cc-pVTZ	5.83	4.84	42.98	4.87	4.61	31.72

Table S5. Calculated E_a values (in kcal mol^{-1}) for the CH_2=N + NO, CH_3CHN + NO, $(CH_3)_2C$=N· + NO and $HOCH_2CHN$ + 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 S6. Calculated energies of NO-adducts (in kcal mol^{-1}) for the CH_2=N + NO, CH_3CHN + NO, $(CH_3)_2C$=N· + NO and $HOCH_2CHN$ + 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	$IM_{14\text{-}1}$	$IM_{15\text{-}1}$	$IM_{16\text{-}1}$	$IM_{17\text{-}1}$
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