

Supplementary Information for:

Advanced kinetic calculations with multi-path variational transition state theory for reactions between dimethylamine and nitrogen dioxide in atmospheric and combustion temperature range

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Table S1. Forward and reverse activation energies ($\Delta E_{\ddagger}^{\rightarrow}$ and $\Delta E_{\ddagger}^{\leftarrow}$, in kcal mol⁻¹) and reaction energies (ΔE , in kcal mol⁻¹) at 0 K without ZPE corrections for H-abstraction reactions from DMA by NO₂ at the N-site, as calculated by various quantum chemical methods based on the lowest-energy-structures optimized by the BH&HLYP/cc-pVTZ method.

Table S2. Forward and reverse activation energies ($\Delta E_{\ddagger}^{\rightarrow}$ and $\Delta E_{\ddagger}^{\leftarrow}$, in kcal mol⁻¹) and reaction energies (ΔE , in kcal mol⁻¹) at 0 K without ZPE corrections for H-abstraction reactions from DMA by NO₂ at the C-site, as calculated by various quantum chemical methods based on the lowest-energy-structures optimized by the BH&HLYP/cc-pVTZ method.

Table S3. Mean unsigned deviations (MUD, in kcal mol⁻¹) of various combinations from CCSD(T)-F12/jun-cc-pVTZ.

Table S4. Relative energies (in kcal mol⁻¹) of the involved species for the reactions between DMA and NO₂ at the M08-HX/ma-TZVP level of theory.

Table S5. Optimized geometries and frequencies of involved species with the lowest energies for DMA + NO₂ reactions at the M08-HX/ma-TZVP level of theory. Multi-structural conformers are also shown with the energies relative to their ground-state structures. The T1 values of the involved species with the lowest-energy-structures for the H-abstraction reactions are also provided

Figure S1. Seven highest vibrational frequencies of general TSs along the reaction coordinate for (a) R1a and (b) R1c.

Table S1. Forward and reverse activation energies ($\Delta E_{\ddagger}^{\#}$ and $\Delta E_{\ddagger}^{\#}$, in kcal mol⁻¹) and reaction energies (ΔE , in kcal mol⁻¹) at 0 K without ZPE corrections for H-abstraction reactions from DMA by NO₂ at the N-site, as calculated by various quantum chemical methods based on the lowest-energy-structures optimized by the BH&HLYP/cc-pVTZ method.

Method	Basis set	R1a			R1b			R1c		
		$\Delta E_{\ddagger}^{\#}$	$\Delta E_{\ddagger}^{\#}$	ΔE	$\Delta E_{\ddagger}^{\#}$	$\Delta E_{\ddagger}^{\#}$	ΔE	$\Delta E_{\ddagger}^{\#}$	$\Delta E_{\ddagger}^{\#}$	ΔE
BH&HLYP	cc-pVTZ	21.9	0.1	21.8	13.4	0.1	13.3	20.7	7.1	13.6
	MG3S	21.1	0.2	20.9	13.1	-0.5	13.6	19.4	6.0	13.4
	ma-TZVP	21.6	0.4	21.2	13.7	-0.2	13.9	19.8	6.0	13.8
	jun-cc-pVTZ	21.5	0.6	20.9	13.2	0.0	13.2	19.4	6.4	13.0
	jul-cc-pVTZ	21.5	0.5	21.0	13.3	0.1	13.2	19.4	6.4	13.0
	maug-cc-pVTZ	21.6	0.5	21.1	13.3	0.0	13.3	19.5	6.4	13.1
	aug-cc-pVTZ	21.5	0.6	20.9	13.2	0.1	13.1	19.3	6.4	12.9
M06-2X	cc-pVTZ	19.0	-5.7	24.7	11.4	-4.3	15.7	18.8	2.7	16.1
	MG3S	18.8	-5.6	24.4	11.7	-4.5	16.2	18.5	2.3	16.2
	ma-TZVP	19.6	-5.1	24.7	12.5	-4.1	16.6	19.0	2.3	16.7
	jun-cc-pVTZ	18.9	-5.2	24.1	11.4	-4.2	15.6	18.1	2.5	15.6
	jul-cc-pVTZ	19.0	-5.1	24.1	11.4	-4.2	15.6	18.0	2.4	15.6
	maug-cc-pVTZ	19.0	-5.3	24.3	11.5	-4.2	15.7	18.2	2.5	15.7
	aug-cc-pVTZ	18.9	-5.2	24.1	11.3	-4.2	15.5	17.9	2.4	15.5
M06-2X-D3	cc-pVTZ	18.9	-5.9	24.8	11.3	-4.4	15.7	18.7	2.6	16.1
	MG3S	18.7	-5.7	24.4	11.5	-4.8	16.3	18.3	2.1	16.2
	ma-TZVP	19.5	-5.2	24.7	12.4	-4.3	16.7	18.9	2.2	16.7
	jun-cc-pVTZ	18.8	-5.3	24.1	11.3	-4.3	15.6	17.9	2.3	15.6
	jul-cc-pVTZ	18.8	-5.5	24.4	11.3	-4.3	15.6	17.9	2.3	15.6
	maug-cc-pVTZ	18.9	-5.4	24.3	11.4	-4.3	15.7	18.1	2.4	15.7
	aug-cc-pVTZ	18.7	-5.4	24.1	11.2	-4.3	15.5	17.8	2.3	15.5
M08-HX	cc-pVTZ	20.5	-3.4	23.9	12.4	-3.5	15.9	19.5	3.0	16.5
	MG3S	19.7	-3.5	23.2	12.0	-4.3	16.3	18.5	2.1	16.4
	ma-TZVP	20.8	-3.0	23.8	13.5	-3.4	16.9	19.7	2.8	16.9
	jun-cc-pVTZ	20.4	-3.1	23.5	12.6	-3.4	16.0	18.8	2.7	16.1
	jul-cc-pVTZ	20.4	-3.1	23.5	12.6	-3.4	16.0	18.8	2.7	16.1
	maug-cc-pVTZ	20.5	-3.1	23.6	12.7	-3.4	16.1	19.0	2.9	16.1
	aug-cc-pVTZ	20.3	-3.1	23.4	12.5	-3.5	16.0	18.7	2.7	16.0
ω B97X-D	cc-pVTZ	18.1	-6.8	24.9	11.6	-7.0	18.6	18.1	-0.6	18.7
	MG3S	17.5	-6.5	24.0	11.2	-7.5	18.7	17.2	-1.1	18.3
	ma-TZVP	18.4	-6.2	24.6	12.5	-6.9	19.4	18.2	-0.8	19.0
	jun-cc-pVTZ	18.2	-6.2	24.4	11.9	-6.6	18.5	17.7	-0.5	18.2
	jul-cc-pVTZ	18.2	-6.2	24.4	11.9	-6.6	18.5	17.6	-0.6	18.2
	maug-cc-pVTZ	18.2	-6.3	24.5	11.8	-6.7	18.5	17.6	-0.5	18.1
	aug-cc-pVTZ	18.1	-6.2	24.3	11.8	-6.7	18.5	17.6	-0.5	18.1
B3LYP	cc-pVTZ	15.2	-8.5	23.7	9.0	-8.7	17.7	14.0	-3.7	17.7
	MG3S	15.1	-7.9	23.0	9.4	-8.6	18.0	13.8	-3.6	17.4
	ma-TZVP	15.5	-7.8	23.3	10.0	-8.5	18.5	14.2	-3.7	17.9
	jun-cc-pVTZ	15.5	-7.6	23.1	9.6	-8.0	17.6	13.9	-3.2	17.1
	jul-cc-pVTZ	15.5	-7.6	23.1	9.6	-8.0	17.6	13.8	-3.2	17.0
	maug-cc-pVTZ	15.5	-7.7	23.2	9.7	-8.1	17.8	13.9	-3.2	17.1
	aug-cc-pVTZ	15.4	-7.6	23.0	9.5	-8.1	17.6	13.8	-3.2	17.0

PW6B95	cc-pVTZ	17.7	-7.1	24.8	11.1	-7.5	18.6	16.5	-2.4	18.9
	MG3S	17.3	-6.8	24.1	11.2	-7.6	18.8	16.1	-2.4	18.5
	ma-TZVP	17.9	-6.5	24.4	11.9	-7.4	19.3	16.5	-2.5	19.0
	jun-cc-pVTZ	17.8	-6.4	24.2	11.5	-7.0	18.5	16.2	-2.0	18.2
	jul-cc-pVTZ	17.8	-6.4	24.2	11.5	-7.0	18.5	16.1	-2.1	18.2
	maug-cc-pVTZ	17.8	-6.5	24.3	11.6	-7.0	18.6	16.3	-2.0	18.3
	aug-cc-pVTZ	17.7	-6.5	24.2	11.4	-7.0	18.4	16.1	-2.0	18.1
M05-2X	cc-pVTZ	19.6	-4.0	23.6	11.1	-4.9	16.0	18.7	2.3	16.4
	MG3S	19.3	-3.9	23.2	11.3	-5.2	16.5	18.2	1.7	16.5
	ma-TZVP	19.9	-3.8	23.7	12.1	-5.0	17.1	18.7	1.6	17.1
	jun-cc-pVTZ	19.4	-3.5	22.9	11.0	-4.9	15.9	17.8	1.9	15.9
	jul-cc-pVTZ	19.4	-3.6	23.0	11.1	-4.8	15.9	17.7	1.8	15.9
	maug-cc-pVTZ	19.5	-3.6	23.1	11.2	-4.8	16.0	17.9	1.9	16.0
	aug-cc-pVTZ	19.3	-3.6	22.9	11.0	-4.9	15.9	17.6	1.8	15.8
MN15-L	cc-pVTZ	14.6	-8.3	22.9	8.0	-6.6	14.6	14.2	-1.1	15.3
	MG3S	14.5	-7.5	22.0	8.3	-6.4	14.7	14.2	-0.6	14.8
	ma-TZVP	15.2	-7.5	22.7	8.8	-6.2	15.0	14.4	-0.8	15.2
	jun-cc-pVTZ	14.8	-7.6	22.4	8.4	-6.2	14.6	14.0	-0.7	14.7
	jul-cc-pVTZ	14.6	-7.8	22.4	8.3	-6.3	14.6	13.8	-0.9	14.7
	maug-cc-pVTZ	14.9	-7.6	22.5	8.6	-6.1	14.7	14.1	-0.7	14.8
	aug-cc-pVTZ	14.5	-7.8	22.3	8.1	-6.5	14.6	13.7	-1.0	14.7
CCSD(T)-F12	cc-pVDZ-F12	21.5	-3.1	24.6	14.1	-3.0	17.1	21.3	4.6	16.7
	jun-cc-pVTZ	21.1	-3.3	24.4	13.6	-3.4	17.0	20.9	4.2	16.7
	DLPNO-CCSD(T)/CBS(T-Q) ^a	25.5	1.3	24.2	16.7	0.0	16.7	23.6	7.3	16.3
T1 values for TSs			0.039		0.031		0.030			

^a: derived with the two-point exponential scheme $[E(x) = E_{\text{CBS}} + \frac{B}{(x+1)^4}]$.

Table S2. Forward and reverse activation energies ($\Delta E_{\ddagger}^{\#}$ and $\Delta E_{\ddagger}^{\#}$, in kcal mol⁻¹) and reaction energies (ΔE , in kcal mol⁻¹) at 0 K without ZPE corrections for H-abstraction reactions from DMA by NO₂ at the C-site, as calculated by various quantum chemical methods based on the lowest-energy-structures optimized by the BH&HLYP/cc-pVTZ method.

Method	Basis set	R2a			R2b			R2c		
		$\Delta E_{\ddagger}^{\#}$	$\Delta E_{\ddagger}^{\#}$	ΔE	$\Delta E_{\ddagger}^{\#}$	$\Delta E_{\ddagger}^{\#}$	ΔE	$\Delta E_{\ddagger}^{\#}$	$\Delta E_{\ddagger}^{\#}$	ΔE
BH&HLYP	cc-pVTZ	19.9	-1.6	21.5	18.2	5.0	13.2	23.6	10.1	13.5
	MG3S	19.2	-1.3	20.5	18.2	5.1	13.1	23.1	10.1	13.0
	ma-TZVP	19.8	-1.2	21.0	18.8	5.0	13.8	23.5	9.8	13.7
	jun-cc-pVTZ	19.6	-1.0	20.6	18.4	5.6	12.8	23.1	10.5	12.6
	jul-cc-pVTZ	19.6	-1.0	20.6	18.4	5.6	12.8	23.1	10.5	12.6
	maug-cc-pVTZ	19.6	-1.1	20.7	18.4	5.5	12.9	23.1	10.4	12.7
	aug-cc-pVTZ	19.5	-1.0	20.5	18.3	5.6	12.7	23.0	10.5	12.5
M06-2X	cc-pVTZ	15.8	-6.7	22.5	13.6	0.2	13.4	19.0	5.1	13.9
	MG3S	15.3	-6.4	21.7	14.0	0.4	13.6	18.7	5.1	13.6
	ma-TZVP	16.0	-6.2	22.2	14.7	0.5	14.2	19.3	5.1	14.2
	jun-cc-pVTZ	15.4	-6.3	21.7	13.9	0.7	13.2	18.4	5.2	13.2
	jul-cc-pVTZ	15.4	-6.3	21.7	13.9	0.8	13.1	18.4	5.3	13.1
	maug-cc-pVTZ	15.5	-6.3	21.8	13.8	0.6	13.2	18.5	5.4	13.1
	aug-cc-pVTZ	15.3	-6.3	21.6	13.8	0.8	13.0	18.3	5.3	13.0
M06-2X-D3	cc-pVTZ	15.6	-6.9	22.5	13.5	0.1	13.4	18.8	4.9	13.9
	MG3S	15.1	-6.6	21.7	13.8	0.2	13.6	18.6	5.0	13.6
	ma-TZVP	15.9	-6.3	22.2	14.6	0.4	14.2	19.2	5.0	14.2
	jun-cc-pVTZ	15.3	-6.4	21.7	13.7	0.5	13.2	18.3	5.1	13.2
	jul-cc-pVTZ	15.3	-6.6	21.9	13.7	0.6	13.1	18.3	5.2	13.1
	maug-cc-pVTZ	15.4	-6.4	21.8	13.7	0.5	13.2	18.4	5.3	13.1
	aug-cc-pVTZ	15.2	-6.4	21.6	13.6	0.6	13.0	18.2	5.2	13.0
M08-HX	cc-pVTZ	15.9	-5.1	21.0	14.6	1.6	13.0	19.5	6.0	13.5
	MG3S	14.8	-4.8	19.6	14.3	1.6	12.7	18.6	5.8	12.8
	ma-TZVP	16.1	-4.3	20.4	15.7	2.2	13.5	19.9	6.3	13.6
	jun-cc-pVTZ	15.7	-4.4	20.1	14.9	2.3	12.6	19.0	6.3	12.7
	jul-cc-pVTZ	15.7	-4.5	20.2	15.0	2.4	12.6	19.0	6.3	12.7
	maug-cc-pVTZ	15.8	-4.4	20.2	14.9	2.2	12.7	19.1	6.4	12.7
	aug-cc-pVTZ	15.6	-4.4	20.0	14.9	2.3	12.6	18.9	6.3	12.6
ω B97X-D	cc-pVTZ	15.5	-7.6	23.1	14.3	-2.5	16.8	19.3	2.4	16.9
	MG3S	14.5	-7.3	21.8	14.0	-2.5	16.5	18.4	2.3	16.1
	ma-TZVP	15.6	-7.1	22.7	15.2	-2.3	17.5	19.4	2.3	17.1
	jun-cc-pVTZ	15.3	-7.0	22.3	14.7	-1.8	16.5	18.9	2.7	16.2
	jul-cc-pVTZ	15.3	-7.0	22.3	14.7	-1.8	16.5	18.9	2.8	16.1
	maug-cc-pVTZ	15.4	-7.0	22.4	14.7	-1.9	16.6	19.0	2.8	16.2
	aug-cc-pVTZ	15.3	-6.9	22.2	14.7	-1.7	16.4	18.8	2.8	16.0
B3LYP	cc-pVTZ	14.6	-7.5	22.1	11.8	-4.2	16.0	17.1	1.0	16.1
	MG3S	14.1	-6.9	21.0	12.1	-3.8	15.9	16.8	1.4	15.4
	ma-TZVP	14.6	-6.9	21.5	12.6	-4.1	16.7	17.2	1.1	16.1
	jun-cc-pVTZ	14.5	-6.6	21.1	12.3	-3.4	15.7	16.8	1.7	15.1
	jul-cc-pVTZ	14.6	-6.5	21.1	12.3	-3.3	15.6	16.8	1.8	15.0
	maug-cc-pVTZ	14.6	-6.6	21.2	12.3	-3.5	15.8	16.9	1.8	15.1
	aug-cc-pVTZ	14.5	-6.5	21.0	12.2	-3.4	15.6	16.7	1.7	15.0

PW6B95	cc-pVTZ	15.8	-7.3	23.1	13.6	-3.2	16.8	18.6	1.5	17.1
	MG3S	15.1	-6.8	21.9	13.7	-3.0	16.7	18.2	1.8	16.4
	ma-TZVP	15.8	-6.7	22.5	14.4	-3.0	17.4	18.7	1.6	17.1
	jun-cc-pVTZ	15.6	-6.5	22.1	14.0	-2.4	16.4	18.3	2.2	16.1
	jul-cc-pVTZ	15.6	-6.5	22.1	14.0	-2.4	16.4	18.3	2.3	16.0
	maug-cc-pVTZ	15.7	-6.5	22.2	14.0	-2.5	16.5	18.3	2.1	16.2
	aug-cc-pVTZ	15.5	-6.5	22.0	13.9	-2.4	16.3	18.2	2.2	16.0
M05-2X	cc-pVTZ	15.3	-5.9	21.2	13.8	0.1	13.7	19.4	5.3	14.1
	MG3S	14.8	-5.7	20.5	14.1	0.3	13.8	19.1	5.3	13.8
	ma-TZVP	15.5	-5.7	21.2	14.9	0.3	14.6	19.8	5.2	14.6
	jun-cc-pVTZ	15.0	-5.5	20.5	14.0	0.6	13.4	18.8	5.4	13.4
	jul-cc-pVTZ	15.0	-5.4	20.4	14.0	0.6	13.4	18.7	5.4	13.3
	maug-cc-pVTZ	15.1	-5.5	20.6	14.0	0.5	13.5	18.9	5.5	13.4
	aug-cc-pVTZ	14.9	-5.4	20.3	13.9	0.6	13.3	18.6	5.3	13.3
MN15-L	cc-pVTZ	14.9	-9.4	24.3	11.4	-4.6	16.0	16.6	-0.1	16.7
	MG3S	14.2	-8.7	22.9	11.6	-4.0	15.6	16.4	0.7	15.7
	ma-TZVP	15.6	-8.5	24.1	12.5	-4.0	16.5	17.0	0.3	16.7
	jun-cc-pVTZ	14.6	-8.5	23.1	11.8	-3.5	15.3	16.3	0.7	15.4
	jul-cc-pVTZ	14.5	-8.7	23.2	11.7	-3.7	15.4	16.3	0.8	15.5
	maug-cc-pVTZ	14.7	-8.5	23.2	11.8	-3.7	15.5	16.4	0.9	15.5
	aug-cc-pVTZ	14.3	-8.7	23.0	11.6	-3.7	15.3	16.1	0.7	15.4
CCSD(T)-F12	cc-pVDZ-F12	18.6	-4.1	22.7	17.6	2.4	15.2	22.3	7.5	14.8
	jun-cc-pVTZ	18.4	-3.9	22.3	17.6	2.7	14.9	23.0	8.5	14.5
	DLPNO-CCSD(T)/CBS(T-Q) ^a	19.9	-1.8	21.7	19.5	5.3	14.2	26.4	12.5	13.9
T1 values for TSs			0.020		0.027		0.044			

^a: derived with the two-point exponential scheme $[E(x) = E_{\text{CBS}} + \frac{B}{(x+1)^4}]$.

Table S3. Mean unsigned deviations (MUD, in kcal mol⁻¹) of various combinations from CCSD(T)-F12/jun-cc-pVTZ.

MUD	BH&HLYP	M06-2X	M06-2X-D3	M08-HX	ω B97X-D	B3LYP	PW6B95	M05-2X	MN15-L
cc-pVTZ	1.8 (3.8)	1.9 (4.1)	2.0 (4.2)	1.4 (3.5)	3.0 (6.1)	4.1 (7.9)	3.4 (7.0)	1.9 (3.8)	4.5 (8.6)
MG3S	1.9 (3.5)	2.0 (4.3)	2.0 (4.4)	1.8 (4.4)	3.1 (6.2)	4.1 (7.8)	3.4 (6.7)	2.0 (4.0)	4.2 (7.9)
ma-TZVP	1.8 (3.8)	1.5 (3.7)	1.6 (3.8)	1.1 (3.1)	2.9 (6.2)	4.1 (8.0)	3.3 (6.9)	1.6 (3.4)	4.1 (8.2)
jun-cc-pVTZ	2.1 (3.9)	2.1 (4.6)	2.1 (4.7)	1.5 (4.1)	2.7 (5.7)	3.8 (7.4)	3.0 (6.3)	2.1 (4.3)	4.1 (7.7)
jul-cc-pVTZ	2.1 (3.9)	2.1 (4.6)	2.1 (4.8)	1.5 (4.0)	2.7 (5.7)	3.8 (7.4)	3.0 (6.3)	2.1 (4.3)	4.2 (7.7)
maug-cc-pVTZ	2.1 (3.8)	2.0 (4.6)	2.1 (4.7)	1.4 (3.9)	2.7 (5.7)	3.8 (7.4)	3.0 (6.3)	2.0 (4.2)	4.1 (7.6)
aug-cc-pVTZ	2.2 (3.9)	2.1 (4.7)	2.2 (4.9)	1.6 (4.2)	2.7 (5.7)	3.8 (7.4)	3.1 (6.3)	2.1 (4.4)	4.3 (7.8)
CCSD(T)-F12/cc-pVDZ-F12: 0.3 (1.0)									
DLPNO-CCSD(T)/CBS(T-Q): 2.4 (4.6)									

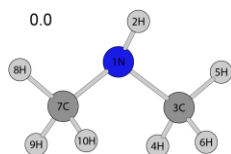
Values in parentheses are the maximum deviations. Single-point energy calculations are carried out based on the ground-state structures optimized by BH&HLYP/cc-pVTZ.

Table S4. Relative energies (in kcal mol⁻¹) of the involved species for the reactions between DMA and NO₂ at the M08-HX/ma-TZVP level of theory.

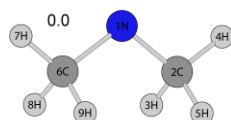
Reactions	Species	Relative energy	Literature data	BSSE	Reactions	Species	Relative energy
Reactants	DMA + NO ₂	0.0			Reactants	DMA + NO ₂	0.0
R1a	RC1a	-0.8		0.11	R3a	RC3a	-0.4
	TS1a	17.7				TS3a	53.6
	PC1a	12.4				PC3a	16.9
	CH ₃ NCH ₃ + HNO ₂	22.5				CH ₃ NH + CH ₃ NO ₂	19.7
R1b	RC1b	-3.0		0.24	R3b	RC3b (- RC3a)	-0.4
	TS1b	10.7	<u>10.7</u>			TS3b	57.2
	PC1b	5.3	<u>6.9</u>			PC3b	19.9
	CH ₃ NCH ₃ + <i>cis</i> -HONO	14.8	<u>16.1</u>			CH ₃ NH + <i>cis</i> -CH ₃ ONO	22.5
R1c	RC1c (- RC1b)*	-3.0			R3c	RC3c (- RC3a)	
	TS1c	17.4				TS3c	64.7
	PC1c	5.0				PC3c	21.7
	CH ₃ NCH ₃ + <i>trans</i> -HONO	14.9				CH ₃ NH + <i>trans</i> -CH ₃ ONO	23.7
R2a	RC2a (- RC1a)	-0.8			R4a	RC4a (- RC1b)	-3.0
	TS2a	13.8				TS4a	49.5
	PC2a	11.8				PC4a	25.4
	CH ₃ NHCH ₂ + HNO ₂	10.1				CH ₃ + CH ₃ NHNO ₂	27.2
R2b	RC2b	-0.6		0.12	R4b	RC4b (- RC1b)	-3.0
	TS2b	13.2				TS4b	70.9
	PC2b	5.6				PC4b	51.0
	CH ₃ NHCH ₂ + <i>cis</i> -HONO	14.4				CH ₃ + <i>cis</i> -CH ₃ NHONO	51.9
R2c	RC2c (- RC1a)	-0.8			R4c	RC4c (- RC1b)	-3.0
	TS2c	17.8				TS4c	73.6
	PC2c	5.3				PC4c	50.8
	CH ₃ NHCH ₂ + <i>trans</i> -HONO	14.5				CH ₃ + <i>trans</i> -CH ₃ NHONO	51.6
					R5	RC5 (-RC1b)	-3.0
						TS5	38.6
						Product-5	10.6

*: The symbol means that RCs have the same structures.

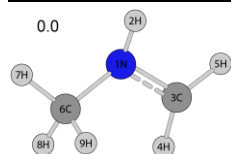
Table S5. Optimized geometries and frequencies of involved species with the lowest energies for DMA + NO₂ reactions at the M08-HX/ma-TZVP level of theory. Multi-structural conformers are also shown with the energies relative to their ground-state structures. The T1 values of the involved species with the lowest-energy-structures for the H-abstraction reactions are also provided



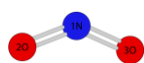
Geometry – Dimethylamine – C _s				Frequency (cm ⁻¹)					
N	0.031312	0.591082	0.000000	233.81	270.86	385.85	769.52	966.23	1031.20
H	-0.763860	1.216921	0.000000	1097.24	1186.45	1201.06	1266.19	1428.58	1456.54
C	0.026340	-0.218306	1.201868	1464.20	1475.98	1483.69	1504.92	1506.24	2951.88
H	0.962743	-0.786363	1.257905	2953.11	3059.12	3061.99	3116.99	3117.07	3572.07
H	-0.027784	0.421469	2.087744	T1 value: 0.009					
H	-0.805220	-0.945591	1.242653						
C	0.026340	-0.218306	-1.201868						
H	-0.027784	0.421469	-2.087744						
H	0.962743	-0.786363	-1.257905						
H	-0.805220	-0.945591	-1.242653						



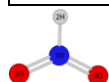
Geometry – CH ₃ NCH ₃ – C _{2v}				Frequency (cm ⁻¹)					
N	0.000066	0.641663	0.000000	102.96	164.18	436.44	936.31	949.03	1010.87
C	0.000009	-0.165643	1.182709	1028.22	1206.19	1232.09	1385.69	1405.47	1449.33
H	0.883372	-0.826696	1.207852	1459.72	1477.07	1479.58	2955.63	2962.83	3011.05
H	0.000274	0.458901	2.079675	3015.42	3117.42	3118.17	T1 value: 0.014		
H	-0.883756	-0.826156	1.208050						
C	0.000009	-0.165643	-1.182709						
H	0.000274	0.458901	-2.079675						
H	0.883372	-0.826696	-1.207852						
H	-0.883756	-0.826156	-1.208050						



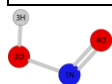
Geometry – CH ₃ NHCH ₂ – C ₁				Frequency (cm ⁻¹)					
N	0.092419	0.479615	-0.126718	195.31	325.64	389.93	574.30	624.27	986.05
H	0.117274	1.426561	0.217539	1039.37	1135.08	1254.70	1314.67	1436.16	1464.70
C	1.243815	-0.246856	0.072780	1472.33	1491.09	1540.57	2989.83	3075.66	3128.97
H	1.218676	-1.291046	-0.216039	3171.63	3290.01	3634.09	T1 value: 0.016		
H	2.184296	0.288091	0.054187						
C	-1.179396	-0.185722	0.032116						
H	-1.989840	0.475733	-0.285365						
H	-1.198118	-1.074371	-0.608451						
H	-1.367570	-0.510489	1.067384						



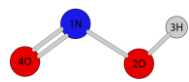
Geometry – NO ₂ – C _{2v}				Frequency (cm ⁻¹)		
N	0.000000	-0.000000	0.311667	789.59	1479.00	1797.08
O	0.000000	1.087744	-0.136446	T1 value: 0.023		
O	-0.000000	-1.087744	-0.136446			



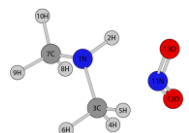
Geometry – HNO ₂ – C _{2v}				Frequency (cm ⁻¹)					
N	-0.000020	0.301890	0.000000	819.14	1106.73	1479.01	1531.67	1737.63	3216.59
H	0.000192	1.346071	0.000000	T1 value: 0.019					
O	-0.000005	-0.221939	1.080957						
O	-0.000005	-0.221939	-1.080957						



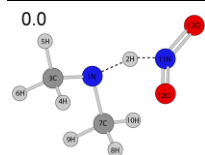
Geometry – <i>cis</i> -HONO – C _s				Frequency (cm ⁻¹)					
N	-0.157152	-0.515722	0.000175	697.61	708.88	991.55	1384.38	1787.71	3705.25
O	1.063105	0.066540	-0.000206	T1 value: 0.020					
H	0.916487	1.029112	-0.000420						
O	-1.042265	0.251447	-0.000120						



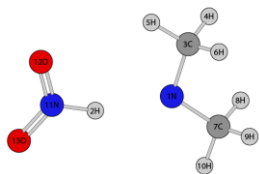
Geometry – <i>trans</i> -HONO – C _s				Frequency (cm ⁻¹)					
N	0.160174	0.476065	0.000001	578.0839	708.36	916.12	1346.99	1847.60	3873.25
O	-1.010251	-0.254285	-0.000001	T1 value:					
H	-1.703937	0.414566	0.000006						
O	1.090453	-0.216616	-0.000036						



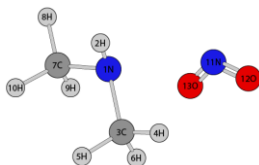
Geometry – RC1a – C _s				Frequency (cm ⁻¹)					
N	1.84545600	0.00030700	-0.46457200	18.03	39.19	48.45	82.38	91.65	124.90
H	1.22607300	0.00342900	-1.26495300	237.30	271.82	391.21	778.02	790.12	967.38
C	1.63854400	-1.20125100	0.31458200	1031.47	1095.69	1180.16	1203.61	1266.06	1427.15
H	0.65398800	-1.23461700	0.82103600	1454.77	1462.49	1475.45	1476.53	1479.84	1501.95
H	1.73112900	-2.08662100	-0.32105100	1508.47	1799.25	2931.78	2936.09	3058.35	3060.72
H	2.40571200	-1.26603300	1.09548500	3120.80	3120.91	3577.74	T1 value: 0.017		
C	1.64173900	1.19802200	0.32135100						
H	0.65721800	1.23117500	0.82785900						
H	2.40904800	1.25635400	1.10262000						
H	1.73676500	2.08669200	-0.30930200						
N	-1.64344800	0.00282600	0.08739100						
O	-2.67272200	-0.00441400	0.65429300						
O	-1.31673800	0.00529700	-1.04517000						



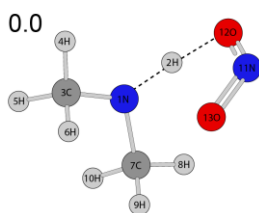
Geometry – TS1a – C _s				Frequency (cm ⁻¹)					
N	-1.162187	0.092244	-0.568393	-1819.16	T1 value: 0.039				
H	0.094637	0.113156	-0.534186	37.03					
C	-1.674793	1.169846	0.232030	391.51					
H	-1.348320	1.051645	1.280265	1030.14					
H	-1.316387	2.130397	-0.145476	1426.97					
H	-2.772577	1.155805	0.224352	1632.88					
C	-1.625361	-1.197723	-0.136969	3137.75					
H	-1.297038	-1.390899	0.899486	3138.57					
H	-2.722835	-1.226673	-0.146668						
H	-1.230750	-1.982454	-0.786664						
N	1.246027	0.048796	0.031781						
O	1.211733	-0.138313	1.226444						
O	2.232664	0.174455	-0.642340						



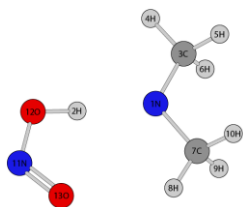
Geometry – PC1a – C ₁				Frequency (cm ⁻¹)					
N	1.24864400	-0.14562800	-0.00102700	6.73	33.24	64.38	86.48	124.43	147.81
H	-0.58534900	-0.36823500	0.00005800	153.15	284.93	444.46	808.43	957.83	963.45
C	1.66477500	1.22626200	-0.00094800	1011.57	1027.40	1219.08	1234.05	1239.84	1385.56
H	2.28565100	1.43928500	-0.88640400	1405.43	1450.33	1455.08	1456.60	1478.37	1481.32
H	0.79749400	1.89063500	0.00218300	1600.44	1713.59	2946.90	2971.99	2979.73	3028.93
H	2.29185500	1.43822100	0.88038100	3034.33	3130.59	3134.68			
C	2.34700800	-1.06321500	0.00087200						
H	2.99373500	-0.89349900	-0.87525600	T1 value: 0.017					
H	2.97783800	-0.90564500	0.89084500						
H	1.99421800	-2.09668700	-0.00861600						
N	-1.61726400	-0.12043600	0.00015500						
O	-1.85884900	1.06507000	0.00163500						
O	-2.42187600	-1.01755800	-0.00121300						



Geometry – RC1b – C ₁				Frequency (cm ⁻¹)					
N	-1.15353000	0.24335300	-0.52156400	45.88	97.17	114.04	125.79	159.51	193.57
H	-1.56805300	0.66007400	-1.34509400	235.81	276.48	388.79	775.38	790.74	962.82
C	-1.10039200	1.20683400	0.56107400	1032.82	1097.13	1190.11	1196.51	1264.75	1427.55
H	-0.59058500	2.11685200	0.23085100	1453.74	1460.67	1470.15	1473.78	1481.91	1503.99
H	-2.09376700	1.47980000	0.95726900	1508.32	1785.37	2973.88	2976.67	3061.60	3073.55
H	-0.52186400	0.77998300	1.39130800	3123.69	3127.00	3574.58			
C	-1.86332700	-0.96474100	-0.14815600						
H	-1.93473200	-1.63989100	-1.00586200	T1 value: 0.017					
H	-1.29909400	-1.48069900	0.63837300						
H	-2.88037100	-0.77425700	0.23684800						
N	1.51844300	-0.30253600	-0.28133200						
O	1.92490100	0.80042900	-0.33784700						
O	1.33964800	-1.07294600	0.59273000						

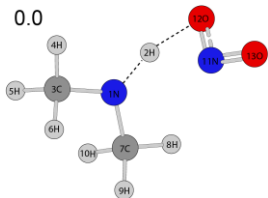


Geometry – TS1b – C _s				Frequency (cm ⁻¹)					
N	-0.958765	-0.000048	-0.471980	-778.93					
H	0.153145	0.000111	-0.862803	45.05	80.28	118.14	122.47	165.52	235.82
C	-1.495620	1.219699	0.050132	291.87	354.16	570.17	887.55	978.01	1026.59
H	-0.952039	2.072608	-0.360496	1043.25	1048.88	1231.00	1231.63	1337.96	1393.70
H	-2.558572	1.293762	-0.220111	1407.06	1441.34	1458.17	1462.71	1487.31	1506.90
H	-1.424138	1.235436	1.146264	1581.84	1593.76	3005.66	3009.09	3070.80	3072.66
C	-1.495331	-1.219974	0.050007	3150.00	3150.20				
H	-0.951642	-2.072721	-0.360814						
H	-1.423721	-1.235867	1.146129	T1 value: 0.031					
H	-2.558302	-1.294187	-0.220121						
N	1.921286	0.000318	0.224693						
O	1.471576	0.000306	-0.958786						
O	1.085957	0.000151	1.101281						

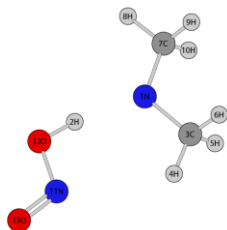


Geometry – PC1b – C ₁				Frequency (cm ⁻¹)					
N	1.17693800	-0.09418600	0.00040300	22.39	88.10	93.68	104.32	125.03	164.17
H	-0.51365200	-0.71976400	0.00071800	196.06	233.77	448.07	764.10	934.15	958.87
C	2.38247900	-0.86593000	-0.00074300	1009.04	1021.24	1028.57	1094.46	1220.86	1240.52
H	2.16150300	-1.93568900	-0.00161000	1384.05	1404.52	1449.35	1456.26	1477.47	1480.12
H	2.99554100	-0.62345500	-0.88389300	1511.60	1738.04	2972.98	2978.80	3029.50	3034.98
H	2.99586900	-0.62510400	0.88266100	3129.53	3141.19				
C	1.41404400	1.31736300	0.00057100	3176.82					
H	0.46791300	1.86256000	0.00108200						
H	2.00614900	1.60752200	0.88382200						
H	2.00558900	1.60799200	-0.88287100						
N	-2.34868800	-0.19262300	-0.00014800						
O	-1.41952000	-1.14258800	0.00077700						
O	-1.91745400	0.90821300	-0.00086000						
				T1 value: 0.017					

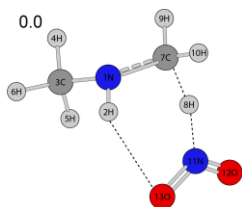
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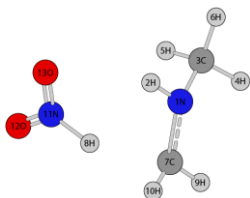
Geometry – TS1c – C _s				Frequency (cm ⁻¹)					
N	-1.103131	0.000006	0.219450	-1444.69					
H	-0.133514	-0.000098	0.809384	26.85	63.16	99.79	120.21	135.54	213.73
C	-1.715302	-1.227384	-0.169048	316.79	353.90	632.49	836.00	980.50	1033.69
H	-1.102186	-2.068104	0.159052	1041.12	1055.39	1222.12	1242.64	1348.04	1398.52
H	-2.722170	-1.307483	0.269919	1409.98	1441.52	1452.08	1461.24	1480.96	1595.97
H	-1.830874	-1.262174	-1.261556	1597.33	1670.29	2989.97	2992.53	3054.75	3056.07
C	-1.715522	1.227528	-0.168283	3153.84	3154.15				
H	-1.102366	2.068146	0.160004						
H	-1.831512	1.262812	-1.260730						
H	-2.722233	1.307353	0.271100						
N	1.409821	-0.000127	-0.237397						
O	1.230390	-0.000041	1.018938						
O	2.522841	-0.000124	-0.662972						
				T1 value: 0.030					



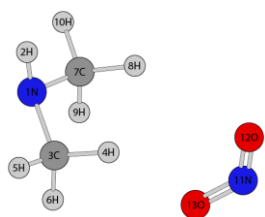
Geometry – PC1c – C ₁				Frequency (cm ⁻¹)					
N	1.36345700	-0.10022500	0.00221900	13.25	71.39	81.62	93.55	124.69	140.81
H	-0.31356600	-0.74745100	0.01061700	196.87	218.49	447.85	769.79	897.01	959.26
C	1.50360600	1.32544000	0.00533400	997.53	1010.55	1025.41	1029.83	1221.77	1241.08
H	0.52308400	1.80694100	0.00056700	1384.56	1405.43	1451.58	1456.94	1478.19	1482.40
H	2.06711900	1.65350200	0.89398800	1535.11	1812.17	2974.05	2979.88	3031.39	3036.77
H	2.07980000	1.65886500	-0.87299500	3133.02	3133.87	3347.25			
C	2.61914700	-0.78648100	-0.00812800						
H	2.47333700	-1.86884900	-0.00186600						
H	3.20330300	-0.50661100	-0.89982500						
H	3.22437200	-0.49826900	0.86663600						
N	-1.86177700	0.26767600	-0.00723900						
O	-1.28173700	-0.94635700	0.01382600						
O	-3.03147800	0.20835200	-0.00697800						
				T1 value: 0.017					



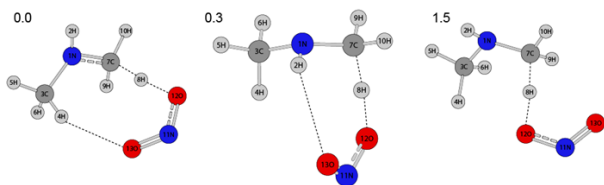
Geometry – TS2a – C ₁				Frequency (cm ⁻¹)					
N	1.698369	0.207486	-0.463549	-1625.20					
H	1.503048	-0.210880	-1.362596	44.43	106.04	119.19	167.04	255.79	268.45
C	1.999899	-0.742217	0.583780	396.61	453.14	547.09	697.51	842.13	991.40
H	2.420059	-0.207798	1.441628	1053.83	1092.20	1136.20	1258.09	1306.81	1350.37
H	1.102961	-1.288833	0.912271	1429.99	1444.38	1464.37	1473.63	1484.53	1528.42
H	2.738417	-1.464611	0.229104	1540.53	1679.51	3005.24	3084.22	3094.15	3143.61
C	0.915205	1.300698	-0.148928	3183.94	3617.26				
H	-0.335917	0.797745	0.055640	T1 value: 0.020					
H	1.182469	1.773498	0.798770						
H	0.771657	2.001035	-0.972896						
N	-1.342445	-0.060625	-0.004403						
O	-2.363326	0.122249	0.594737						
O	-1.070491	-1.006235	-0.705073						



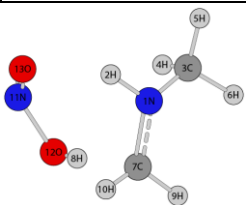
Geometry – PC2a – C ₁				Frequency (cm ⁻¹)					
N	1.68121400	0.06391500	-0.42838500	29.92	77.04	105.36	135.30	151.45	204.88
H	1.31064100	-0.26806000	-1.30706500	229.42	404.88	436.23	668.72	771.48	813.13
C	1.84292300	-0.95473000	0.58300600	990.13	1046.36	1133.44	1190.22	1255.46	1330.55
H	2.46287800	-0.55857700	1.39353000	1435.89	1456.56	1469.36	1474.63	1482.37	1547.79
H	0.88180900	-1.28230600	1.00923500	1556.39	1716.59	2801.29	2994.81	3086.96	3138.94
H	2.34586300	-1.82602500	0.15733300	3139.17	3253.78	3626.92			
C	1.29582300	1.32540700	-0.05832600	T1 value: 0.018					
H	-0.63769200	0.76062300	0.19859800						
H	1.66350200	1.67847700	0.90090300						
H	1.16490900	2.04939300	-0.85611200						
N	-1.45213600	0.09842100	0.00340100						
O	-2.44168700	0.21097900	0.67555200						
O	-1.26180500	-0.70022200	-0.88425300						



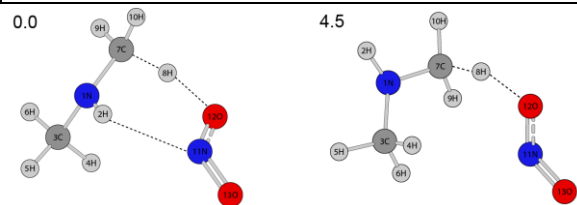
Geometry – RC2b – C _s				Frequency (cm ⁻¹)					
N	2.22042600	0.01530800	-0.12671200	29.11	44.55	64.06	75.70	92.14	92.95
H	2.63401700	0.03617400	-1.05001700	253.64	285.57	395.45	778.82	784.74	967.45
C	1.44911500	-1.19882000	0.04553900	1031.44	1098.32	1187.16	1200.30	1266.41	1426.97
H	0.54568000	-1.23910500	-0.59255300	1454.86	1462.20	1474.26	1476.91	1481.51	1502.88
H	2.06745000	-2.07467900	-0.17253200	1506.67	1795.00	2942.36	2944.89	3060.00	3063.83
H	1.11825500	-1.27071100	1.08845700	3116.46	3118.32	3575.52			
C	1.41585100	1.20114300	0.08436600	T1 value: 0.017					
H	0.51141000	1.23593100	-0.55278000						
H	1.08454300	1.23069300	1.12927700						
H	2.00868700	2.10074000	-0.10610400						
N	-2.16428000	0.02546000	0.07075800						
O	-1.90901300	0.00561100	-1.07866200						
O	-1.53509500	-0.04540600	1.06222400						



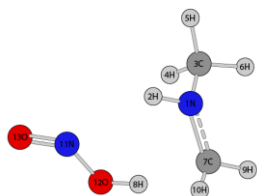
Geometry – TS2b – C ₁				Frequency (cm ⁻¹)						
N	1.772492	0.377627	-0.323686	-994.25						
H	1.926136	0.629024	-1.288303	35.51	101.27	129.42	148.11	195.85	275.20	
C	1.887414	-1.025300	-0.011461	416.44	490.52	506.86	642.98	892.26	989.30	
H	0.966052	-1.572392	-0.259607	1059.73	1091.36	1132.91	1259.30	1295.48	1309.79	
H	2.732305	-1.456237	-0.553610	1368.55	1436.35	1441.81	1454.13	1469.63	1483.79	
H	2.062495	-1.140173	1.062975	1538.44	1587.22	3011.16	3066.87	3093.03	3142.81	
C	0.885895	1.168429	0.381019	3160.88	3639.38					
H	-0.327617	0.953996	0.046733							
H	0.880815	0.942073	1.450807							
H	0.994785	2.235043	0.167781							
N	-2.061254	-0.303267	-0.055812							
O	-1.655343	0.869935	-0.275515							
O	-1.265538	-1.115229	0.325241							
				T1 value: 0.027						



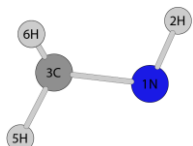
Geometry – PC2b – C ₁				Frequency (cm ⁻¹)						
N	1.59695500	-0.09179500	-0.49895800	30.29	69.85	114.11	124.14	159.28	168.33	
H	1.14910600	-0.50980300	-1.30139000	209.89	403.83	418.41	668.84	742.31	752.02	
C	1.68250900	-0.95705300	0.65547300	875.74	989.34	1043.28	1060.56	1135.38	1255.29	
H	0.70624300	-1.10116300	1.14523900	1329.70	1431.51	1436.85	1468.20	1474.99	1483.34	
H	2.07511300	-1.93357300	0.36263800	1550.81	1741.14	2992.91	3086.88	3140.21	3140.55	
H	2.36811800	-0.51304400	1.38429900	3257.65	3282.81	3624.58				
C	1.33260600	1.23948300	-0.31266800							
H	-0.63124100	0.96065600	0.31710000							
H	1.77009000	1.69851600	0.56944300							
H	1.20964200	1.84543300	-1.20376400							
N	-2.07090100	-0.26967500	0.08891200							
O	-1.51504000	0.76135700	0.72646200							
O	-1.41247800	-0.71277200	-0.78397100							
				T1 value: 0.018						



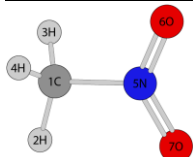
Geometry – TS2c – C ₁				Frequency (cm ⁻¹)						
N	-1.493586	0.070838	-0.584978	-853.94						
H	-0.926730	0.404047	-1.354148	86.09	97.42	148.13	180.87	210.53	309.55	
C	-1.813393	1.058734	0.418096	411.52	477.81	601.20	720.05	813.09	988.53	
H	-0.967650	1.219856	1.102574	1055.21	1099.71	1149.15	1249.27	1292.41	1356.76	
H	-2.067330	2.006502	-0.060497	1364.46	1433.32	1456.42	1473.13	1480.94	1530.97	
H	-2.672052	0.713255	1.002258	1606.04	1640.78	3009.70	3071.18	3098.04	3152.85	
C	-1.232758	-1.228105	-0.178162	3162.35	3608.13					
H	-0.124872	-1.208326	0.345993							
H	-1.933323	-1.573438	0.587316							
H	-1.132229	-1.925121	-1.013388							
N	1.284635	0.197079	-0.181520							
O	1.208317	-0.754517	0.652304							
O	2.299478	0.829954	-0.210581							
				T1 value: 0.044						



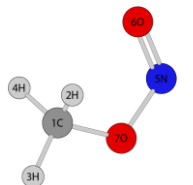
Geometry – PC2c – C ₁				Frequency (cm ⁻¹)					
N	1.61864000	-0.13022600	-0.56733300	35.39	71.52	104.87	134.21	142.99	178.84
H	1.03581000	-0.34397000	-1.36310200	210.28	396.04	416.85	647.68	748.39	753.13
C	1.71019300	-1.18063700	0.42070800	828.99	986.39	990.81	1046.59	1136.85	1256.16
H	0.79904800	-1.26185700	1.03365800	1330.63	1437.88	1442.82	1468.40	1475.30	1487.38
H	1.89005400	-2.13953300	-0.07079300	1553.72	1817.35	2996.93	3086.73	3140.66	3142.33
H	2.55320000	-0.97118000	1.08706500	3257.42	3450.61	3628.84			
C	1.61532200	1.17797400	-0.16166200						
H	-0.32098000	1.07259000	0.54324100	T1 value: 0.018					
H	2.21707400	1.41230000	0.71160000						
H	1.51102500	1.93118500	-0.93525900						
N	-1.50386300	-0.06783400	-0.32616200						
O	-1.23313200	0.74892900	0.71878700						
O	-2.57208800	-0.53607200	-0.25706500						



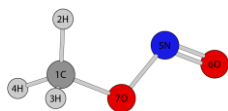
Geometry – CH ₃ NH – C ₅				Frequency (cm ⁻¹)					
N	0.79861500	-0.15307000	0.00001400	208.86	950.56	1000.78	1077.34	1328.09	1387.49
H	1.21641900	0.78145700	-0.00008100	1468.38	1473.53	2971.99	3023.71	3112.92	3434.82
C	-0.62558200	0.01321000	0.00001400						
H	-0.96288400	0.58438100	-0.88068200						
H	-1.12744100	-0.95820700	0.00003700						
H	-0.96290800	0.58460100	0.88054400						



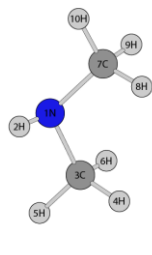
Geometry – CH ₃ NO ₂ – C ₁				Frequency (cm ⁻¹)					
C	-1.31389800	-0.03690900	-0.00047300	11.72	484.83	643.97	687.19	973.65	1110.24
H	-1.62911900	-1.07632300	-0.05120100	1141.46	1398.94	1449.11	1461.08	1506.91	1706.52
H	-1.64999700	0.54270400	-0.86049900	3093.37	3192.34	3223.53			
H	-1.64302800	0.44780700	0.91947800						
N	0.17493900	0.00000100	-0.00144300						
O	0.68679900	1.09255500	0.00027700						
O	0.76082100	-1.05414800	0.00036800						



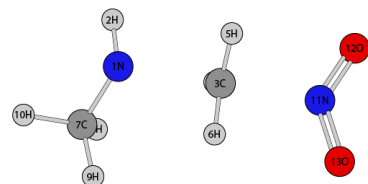
Geometry – <i>cis</i> -CH ₃ ONO – C ₅				Frequency (cm ⁻¹)					
C	1.27706100	0.40895400	0.00002400	223.59	370.61	381.18	773.98	917.01	1072.65
H	1.09589300	1.01831100	-0.89102100	1166.05	1202.84	1442.71	1467.71	1482.72	1759.21
H	2.29588800	0.02260400	0.00088800	3048.06	3126.32	3176.18			
H	1.09465300	1.01910600	0.89025200						
N	-0.89111500	-0.50811900	0.00005400						
O	-1.18332200	0.62671900	-0.00002600						
O	0.44444700	-0.74633300	-0.00005300						



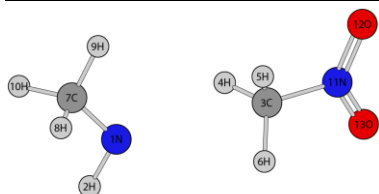
Geometry – <i>trans</i> -CH ₃ ONO – C _s				Frequency (cm ⁻¹)					
C	-1.62035900	0.13053600	-0.00028900	102.34	224.01	395.55	666.29	907.70	1124.36
H	-1.49197200	1.21738500	0.00154500	1175.38	1214.12	1454.69	1474.28	1498.89	1825.01
H	-2.16890400	-0.18017700	0.89299100	3043.17	3135.60	3138.11			
H	-2.16715600	-0.17734200	-0.89568100						
N	0.66446000	0.42804300	0.00051800						
O	1.71017800	-0.07861200	-0.00045200						
O	-0.34780700	-0.50131100	0.00035800						



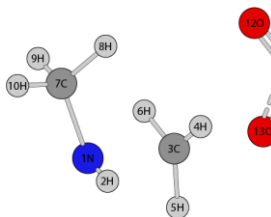
Geometry – RC3a – C ₁				Frequency (cm ⁻¹)					
N	-2.22314100	-0.39867400	-0.08380200	27.69	66.18	76.37	82.89	95.15	110.08
H	-2.84143000	-0.69180200	0.66175000	265.68	289.60	392.36	770.66	788.59	966.57
C	-1.00910300	-1.18683100	-0.06103000	1030.57	1099.86	1187.55	1202.08	1263.90	1424.99
H	-0.36169300	-0.97917700	0.81222300	1451.65	1462.83	1475.09	1479.57	1481.57	1503.17
H	-1.24823400	-2.25429400	-0.06778700	1509.18	1797.04	2944.50	2955.38	3049.66	3062.83
H	-0.42583700	-0.97414600	-0.96685900	3115.58	3118.36	3576.92			
C	-1.95155300	1.02111800	0.02238700						
H	-1.34811900	1.29020200	0.90844000						
H	-1.39276200	1.34867100	-0.86282500						
H	-2.88960600	1.58318200	0.05261600						
N	2.05211200	0.25305500	-0.25851500						
O	2.31299800	-0.81080600	0.17104000						
O	1.37060400	1.14717800	0.09027500						



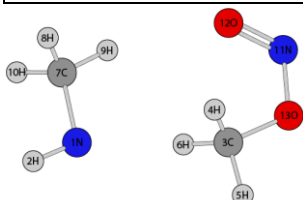
Geometry – TS3a – C ₁				Frequency (cm ⁻¹)					
N	-2.12758200	0.57362600	0.38556500	-1230.47					
H	-2.23175800	1.43272100	-0.15900700	25.89	119.94	134.65	160.39	218.37	253.75
C	-0.23377500	0.26249600	0.26318000	308.27	445.56	536.08	767.34	810.70	1006.98
H	-0.34427400	0.28453000	-0.81834500	1037.03	1073.57	1142.12	1183.02	1193.21	1338.52
H	-0.02511100	1.18027300	0.79852400	1354.48	1359.64	1405.12	1422.48	1458.60	1486.97
H	-0.34321200	-0.67164600	0.80013400	1714.09	2983.80	3046.99	3079.37	3104.79	3256.76
C	-2.79645900	-0.49447300	-0.31790200	3290.51	3461.91				
H	-2.52726400	-0.58311800	-1.38182200						
H	-2.59208700	-1.45005400	0.17616700						
H	-3.88138100	-0.31805700	-0.27365800						
N	1.60670600	-0.04924600	-0.00748300						
O	2.25109400	0.90850200	-0.31216600						
O	1.97048400	-1.17768200	0.12963700						



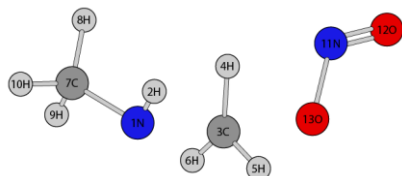
Geometry – PC3a – C ₁				Frequency (cm ⁻¹)					
N	2.63069400	-0.55669500	0.00484300	11.35	21.69	42.12	50.31	65.39	70.71
H	3.07821600	-1.47702800	0.00389600	104.88	290.96	490.95	637.30	690.90	951.28
C	-0.42989500	-0.15956200	-0.06633500	973.27	1005.90	1081.61	1102.70	1133.93	1330.81
H	-0.07292300	-0.20913900	0.96321800	1376.54	1388.04	1443.19	1449.06	1466.02	1475.64
H	0.01440400	0.69255000	-0.57465300	1511.81	1698.56	2981.98	3034.33	3105.33	3122.22
H	-0.23485300	-1.10164900	-0.57267900	3205.17	3236.98	3452.43			
C	3.66864800	0.43227800	0.01798600						
H	4.32834600	0.32874300	-0.85885300						
H	3.24493000	1.44011500	0.02193400						
H	4.31732700	0.31754400	0.90158800						
N	-1.90292700	0.04559500	-0.00822200						
O	-2.30278500	1.18481900	0.01493900						
O	-2.59750700	-0.94103600	0.03872300						



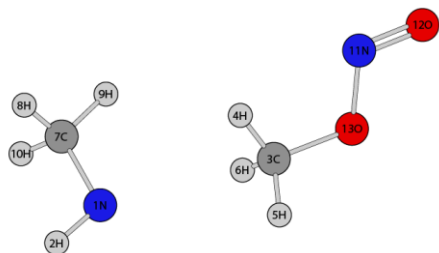
Geometry – TS3b – C ₁				Frequency (cm ⁻¹)					
N	-2.08479200	-0.61385200	0.11821300	-1112.17					
H	-2.26367600	-0.79853300	1.10780700	69.62	77.42	159.37	207.05	232.94	267.71
C	-0.20277200	-0.83648100	-0.06871500	325.63	388.41	445.15	742.43	850.33	1011.86
H	-0.14309400	-0.24497100	0.84285500	1027.46	1060.75	1122.88	1200.03	1210.66	1249.28
H	-0.22345300	-1.91689200	-0.03612700	1328.18	1335.48	1372.33	1406.49	1462.35	1478.28
H	-0.23433600	-0.33438500	-1.02796100	1591.10	2973.84	3051.47	3078.88	3109.81	3256.63
C	-2.38062200	0.77079200	-0.15075800	3306.94	3465.57				
H	-1.75035000	1.46707500	0.42771600						
H	-2.23355300	0.98178200	-1.21461500						
H	-3.42605300	0.98562600	0.11016900						
N	2.18483700	0.26092500	0.00051800						
O	1.48130900	1.21784400	0.13340200						
O	1.65301300	-0.87722900	-0.09891600						



Geometry – PC3b – C ₁				Frequency (cm ⁻¹)					
N	2.56055500	0.66669500	-0.00139200	53.11	59.60	72.19	96.98	112.37	148.42
H	3.55529100	0.90610300	-0.00110400	265.36	288.98	382.87	388.44	788.79	926.76
C	-0.50614800	1.11361400	0.00071400	952.89	1003.61	1072.31	1076.39	1156.84	1197.32
H	-0.00189400	0.72327800	0.88924300	1324.79	1387.49	1426.66	1460.64	1465.94	1473.07
H	-0.48692000	2.20244400	0.00046700	1488.57	1739.90	2969.91	3022.91	3058.60	3113.70
H	-0.00054400	0.72296900	-0.88685600	3142.23	3188.97	3455.30			
C	2.45220800	-0.76356900	0.00079700						
H	2.94964800	-1.19974400	0.88272900						
H	1.40235000	-1.07413500	-0.00044600						
H	2.95278400	-1.20306700	-0.87760100						
N	-2.16156500	-0.55776800	-0.00032400						
O	-1.21547200	-1.25517400	-0.00046500						
O	-1.88952900	0.76259900	0.00002900						



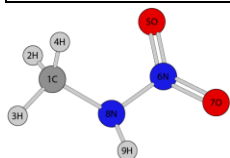
Geometry – TS3c – C ₁				Frequency (cm ⁻¹)						
N	2.22938800	-0.42196200	-0.38215000	-984.09						
H	2.27389700	-0.32478800	-1.39834800	43.78	115.01	138.90	163.64	204.37	216.13	
C	0.50764400	-0.68717100	0.06140200	316.20	413.00	418.05	697.90	795.40	1008.37	
H	0.29528500	0.23700000	-0.48583200	1015.75	1061.00	1078.18	1231.33	1234.51	1254.37	
H	0.39163400	-1.64629900	-0.42360000	1325.40	1343.21	1386.23	1408.81	1456.35	1482.91	
H	0.67595200	-0.67177300	1.13049100	1688.60	2998.53	3020.02	3065.00	3122.27	3230.29	
C	2.79386400	0.74355400	0.24634600	3301.28	3483.51					
H	2.33600600	1.68660200	-0.08661500							
H	2.69177900	0.66345800	1.33251100							
H	3.86204400	0.79663300	-0.00502600							
N	-1.84991100	0.39990100	-0.23076200							
O	-3.02457100	0.51418600	-0.09184500							
O	-1.34942700	-0.62977500	0.38938500							



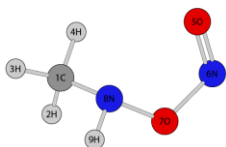
Geometry – PC3c – C ₁				Frequency (cm ⁻¹)						
N	2.88708300	-0.51753000	-0.26065800	19.31	42.51	78.33	81.80	94.16	114.18	
H	3.79270100	-0.90308600	-0.53957300	135.33	234.95	302.45	405.69	678.45	925.84	
C	-0.11318800	-0.72213800	0.05933100	949.26	1004.02	1077.66	1115.14	1164.58	1211.35	
H	0.18990400	0.07510700	-0.62493600	1325.19	1386.36	1432.89	1462.68	1466.42	1477.94	
H	0.12622100	-1.69123500	-0.38124700	1488.86	1812.36	2972.19	3026.11	3053.75	3103.79	
H	0.41690900	-0.61573200	1.00965500	3143.78	3161.93	3460.11				
C	3.09711000	0.83426800	0.16695900							
H	3.53160000	1.44614400	-0.64037600							
H	2.15338000	1.29107500	0.48179700							
H	3.81031300	0.88417300	1.00571500							
N	-2.05450200	0.47724000	-0.24808600							
O	-3.20086800	0.54808400	-0.05163400							
O	-1.51821000	-0.65773400	0.28818800							



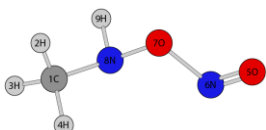
Geometry – CH ₃ – D _{3h}				Frequency (cm ⁻¹)						
C	0.00028000	0.00002300	-0.00000300	517.33	1404.11	1405.63	3134.22	3310.25	3319.21	
H	-0.43157400	-0.99058800	0.00000700							
H	1.07360600	0.12231500	0.00000700							
H	-0.64371400	0.86813500	0.00000700							



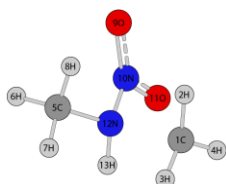
Geometry – CH ₃ NHNO ₂ – C ₁				Frequency (cm ⁻¹)						
C	-1.78947900	0.01925400	0.08368100	148.37	188.27	316.34	536.00	607.89	765.86	
H	-1.93391300	0.82414200	-0.63861800	834.82	983.01	1143.40	1157.60	1214.24	1408.84	
H	-2.59067600	-0.71274500	-0.03469100	1438.79	1457.35	1479.84	1505.20	1710.47	3040.08	
H	-1.81840100	0.44179700	1.09510500	3131.84	3165.53	3643.31				
O	0.50846800	1.25249500	-0.02682300							
N	0.60530800	0.04838500	-0.02251100							
O	1.62479200	-0.59504200	0.08345600							
N	-0.54554800	-0.66547200	-0.19383500							
H	-0.40453500	-1.60873900	0.13748000							



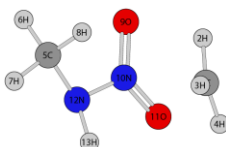
Geometry – <i>cis</i> -CH ₃ NHONO – C ₁				Frequency (cm ⁻¹)					
C	1.64787800	0.51534200	0.27522800	99.40	225.90	277.67	397.48	500.37	642.96
H	2.01710700	-0.02654200	1.15565100	808.99	934.69	1002.62	1091.33	1163.86	1230.36
H	2.49496400	0.84263100	-0.33444000	1430.40	1465.58	1485.47	1509.53	1812.39	3025.69
H	1.09799400	1.40267800	0.59917400	3113.69	3143.04	3562.59			
O	-1.36758800	0.83362600	-0.23198600						
N	-1.39435900	-0.20763700	0.27691900						
O	-0.19829900	-0.91920800	0.22350400						
N	0.78525100	-0.29660800	-0.57240200						
H	1.29352100	-1.09645400	-0.93551200						



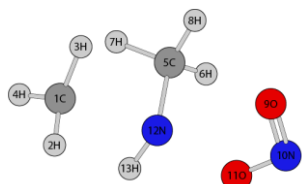
Geometry – <i>trans</i> -CH ₃ NHONO – C ₁				Frequency (cm ⁻¹)					
C	-2.00629600	-0.46688400	-0.02544400	92.35	187.86	214.38	385.56	452.90	624.94
H	-2.16439900	-0.72719700	1.02951900	792.31	946.56	1015.86	1130.33	1174.84	1225.96
H	-2.94178100	-0.09411400	-0.45260400	1431.43	1464.10	1488.71	1517.96	1842.41	3022.96
H	-1.70916100	-1.36318500	-0.57585400	3110.84	3142.50	3531.47			
O	2.17806300	-0.26701300	0.08934700						
N	1.20081500	0.04566500	-0.44792900						
O	0.16117400	0.17905000	0.48017800						
N	-0.99760300	0.56402000	-0.21658000						
H	-1.28326400	1.42170600	0.24696800						



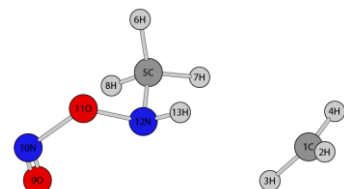
Geometry – TS4a – C ₁				Frequency (cm ⁻¹)					
C	-1.39464800	-1.35183400	0.48484900	-799.99					
H	-1.36296100	-0.93207400	1.48564700	86.34	101.52	170.07	186.68	281.53	327.93
H	-2.36869300	-1.37476100	0.00531200	553.84	611.08	633.50	739.00	748.90	887.13
H	-0.74527700	-2.20298200	0.30576900	1000.88	1017.11	1144.24	1152.23	1202.89	1319.43
C	-1.19467500	1.26131200	-0.30813400	1390.54	1408.10	1424.71	1434.59	1461.10	1491.48
H	-0.69679700	2.09422400	-0.81086800	1611.86	3069.22	3096.80	3160.28	3182.22	3257.83
H	-2.18964600	1.09663500	-0.72572500	3258.83	3559.94				
H	-1.26102900	1.47052800	0.75954600						
O	1.08734100	0.79154000	0.93082700						
N	0.87315500	0.08450000	-0.05861300						
O	1.59915300	-0.79664300	-0.53813200						
N	-0.43166100	0.02929400	-0.48438700						
H	-0.42206800	-0.36418500	-1.42053300						



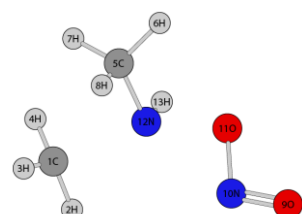
Geometry – PC4a – C ₁				Frequency (cm ⁻¹)					
C	-2.42143400	0.57135500	0.15900800	51.25	85.36	88.04	124.91	152.68	167.95
H	-1.94044000	0.33681900	1.10074200	185.50	212.90	321.96	534.42	591.47	609.67
H	-2.89006100	1.53581100	0.01706000	767.07	833.40	982.78	1139.75	1159.67	1213.23
H	-2.52743000	-0.20147900	-0.59098300	1398.81	1401.53	1413.65	1441.99	1457.31	1477.06
C	0.97541900	1.60958100	-0.00606900	1499.75	1705.75	3040.78	3118.82	3133.09	3168.31
H	1.84465500	1.50328000	0.64442000	3294.35	3304.78	3632.66			
H	1.17671100	2.38535500	-0.74736200						
H	0.10463600	1.89084600	0.59887500						
O	0.66964700	-0.68776900	1.18657600						
N	0.40962900	-0.71570900	0.00623500						
O	-0.10307900	-1.63171900	-0.59677900						
N	0.75886300	0.37650100	-0.73291300						
H	0.19602300	0.39411900	-1.57201400						



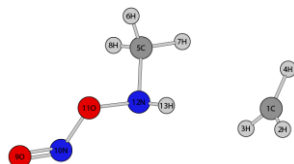
Geometry – TS4b – C ₁				Frequency (cm ⁻¹)					
C	-2.28911600	-0.92070400	-0.12940900	-969.40					
H	-2.11127800	-1.71561600	-0.84287700	75.34	121.38	155.67	183.40	214.25	304.97
H	-2.13801700	-1.16250600	0.91598500	373.66	387.36	455.94	567.14	620.00	883.73
H	-3.08048300	-0.21439600	-0.36376500	914.50	962.04	1002.63	1044.65	1131.04	1252.51
C	-0.71883600	1.20146600	0.68726800	1343.60	1408.09	1417.32	1421.77	1473.21	1492.48
H	-0.10779200	2.09321000	0.52098900	1701.92	3048.80	3106.26	3131.76	3147.76	3267.19
H	-1.76897900	1.50009700	0.75285900	3287.63	3526.12				
H	-0.42312700	0.72259600	1.62331700						
O	1.41168700	-0.85631800	0.76733500						
N	1.85515200	-0.27533500	-0.15902100						
O	1.01959700	0.45036500	-0.85730400						
N	-0.55182500	0.23140300	-0.40698100						
H	-0.89616700	0.64719500	-1.27189300						



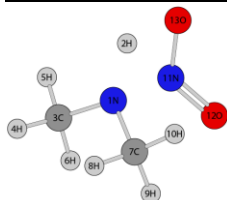
Geometry – PC4b – C ₁				Frequency (cm ⁻¹)					
C	-3.42514400	-0.63201700	0.19468200	17.55	61.14	89.98	98.27	112.61	119.21
H	-3.69350500	-1.34403000	-0.57415200	208.78	219.99	282.38	404.74	502.58	583.31
H	-2.63689600	-0.86816700	0.89813300	656.35	814.25	943.90	1004.06	1090.62	1164.48
H	-4.01064000	0.26927500	0.31609200	1231.54	1406.25	1410.09	1426.38	1464.99	1481.38
C	-0.43506800	1.39208800	0.12179000	1506.19	1809.84	3023.97	3111.27	3123.15	3140.97
H	-0.33390000	2.04562800	-0.75435300	3303.32	3304.82	3545.28			
H	-1.44697100	1.48377400	0.52794600						
H	0.27670700	1.70119200	0.89158100						
O	1.90419900	-0.39656200	0.97325400						
N	2.08013600	-0.43276600	-0.17290300						
O	0.96164100	-0.15108700	-0.94814800						
N	-0.22163200	-0.01426600	-0.19271300						
H	-0.92978000	-0.33768300	-0.84562000						



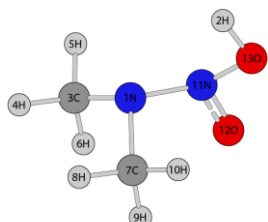
Geometry – TS4c – C ₁				Frequency (cm ⁻¹)						
C	-2.33402400	-1.16404400	0.09055200	-986.66						
H	-1.93082300	-2.12127500	-0.21730700	21.82	119.34	149.17	159.58	182.82	271.16	
H	-2.42069400	-1.00312200	1.15932700	376.74	396.80	412.83	601.19	651.22	782.34	
H	-3.12665000	-0.74833700	-0.52644900	951.38	984.21	1006.22	1057.43	1136.18	1254.63	
C	-1.20317300	1.32199600	0.31411900	1339.02	1411.09	1420.92	1425.74	1473.91	1486.17	
H	-0.70100400	2.18945100	-0.12256000	1766.40	3049.17	3098.04	3138.75	3141.04	3255.95	
H	-2.28322500	1.42461100	0.17915100	3279.58	3528.82					
H	-0.98202600	1.27606000	1.38382800							
O	2.67293900	-0.32491900	0.18072200							
N	1.51087500	-0.47057900	0.25947700							
O	0.85240600	0.41370200	-0.51026100							
N	-0.73764500	0.07408200	-0.30843200							
H	-0.94776500	0.10011900	-1.30502300							



Geometry – PC4c – C ₁				Frequency (cm ⁻¹)						
C	3.49580700	-0.92483900	-0.05015400	38.66	44.73	82.38	92.42	98.27	103.29	
H	3.55822800	-1.78215000	0.60637200	191.76	206.43	232.50	391.74	455.45	579.43	
H	2.83595000	-0.94889200	-0.90796100	629.34	807.93	965.73	1015.29	1131.09	1177.81	
H	4.16418800	-0.08759500	0.09864800	1231.58	1405.07	1408.47	1429.94	1466.31	1489.97	
C	0.81285100	1.50277400	-0.09629300	1517.54	1839.46	3021.58	3108.23	3123.21	3140.08	
H	0.70266100	2.02250700	0.86465900	3300.66	3307.96	3523.86				
H	1.86832200	1.49716900	-0.38507000							
H	0.24411400	2.03659800	-0.86209100							
O	-2.86473400	-0.50985300	0.00689100							
N	-1.79118200	-0.45886200	-0.42660600							
O	-0.91455400	0.08344000	0.51734300							
N	0.37150000	0.11740100	-0.05011700							
H	0.94666400	-0.40371300	0.60731600							



Geometry – TS5 – C ₁				Frequency (cm ⁻¹)						
C	0.58913200	0.14637100	-0.31904200	-1657.38						
H	-0.16946800	0.65714800	-1.17072400	95.52	191.37	217.13	265.98	286.98	350.97	
H	1.52887900	0.91729300	0.48139000	468.34	651.96	701.40	730.08	984.30	1044.23	
H	2.50346200	0.92361900	-0.01463200	1072.33	1097.97	1204.90	1214.98	1270.06	1386.69	
C	1.15930600	1.93992500	0.58062300	1418.67	1441.98	1461.19	1469.45	1480.00	1491.26	
H	1.62874000	0.46473800	1.47504300	1507.69	2195.63	3039.93	3044.55	3126.61	3132.15	
H	0.95711000	-1.25141800	-0.49161000	3156.03	3157.46					
H	1.94401600	-1.30501000	-0.95840100							
O	0.97303200	-1.74812800	0.48528000							
N	0.21345600	-1.73772900	-1.12729500							
O	-0.83867600	0.23926900	0.28453200							
N	-1.25831200	-0.67341400	0.97292900							
H	-1.41939700	0.68725200	-0.84380500							



Geometry – Product-5 – C ₁				Frequency (cm ⁻¹)					
C	-0.56197700	0.22897100	-0.43835100	94.67	221.91	248.84	287.87	296.44	337.62
H	1.45338700	0.64895700	-1.45377200	374.00	522.50	609.67	668.15	790.30	952.73
H	-1.58657500	-0.80716600	-0.42481000	1045.40	1075.84	1105.18	1196.91	1241.05	1269.33
H	-2.52937300	-0.34767400	-0.73161200	1320.48	1415.66	1440.66	1461.72	1475.99	1481.91
C	-1.32214600	-1.58991200	-1.13977800	1499.85	1546.98	3014.51	3016.48	3113.20	3113.86
H	-1.70535700	-1.25128100	0.57402600	3150.78	3152.07	3845.65			
H	-0.85005700	1.28031500	0.53994200						
H	-1.75968400	1.79635800	0.22315800						
O	-0.99342600	0.86155000	1.54654100						
N	-0.02207400	1.99313300	0.55626600						
O	0.68108400	-0.38652500	-0.10440700						
N	0.85760800	-0.89735600	0.99932900						
H	1.72548100	0.41646200	-0.55761900						

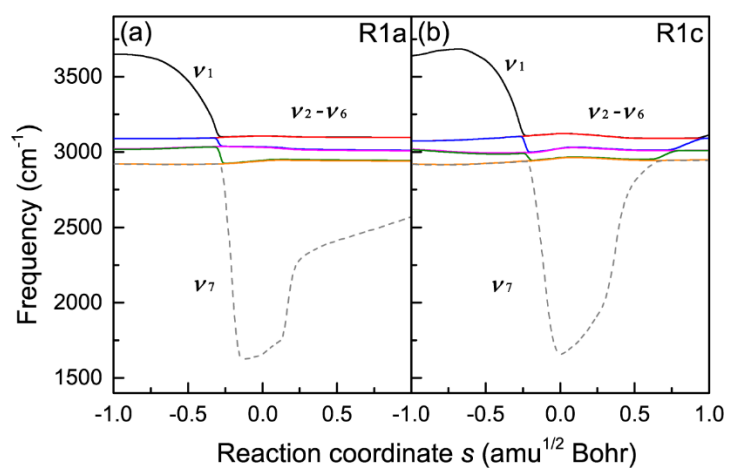


Figure S1. Seven highest vibrational frequencies of general TSs along the reaction coordinate for (a) R1a and (b) R1c.