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Supporting Information

A Photoionization Reflectron Time-of-Flight Mass Spectrometric Study on the Detection of Ethynamine ($HCCNH_2$) and 2H-Azirine (c-H_2CCHN)

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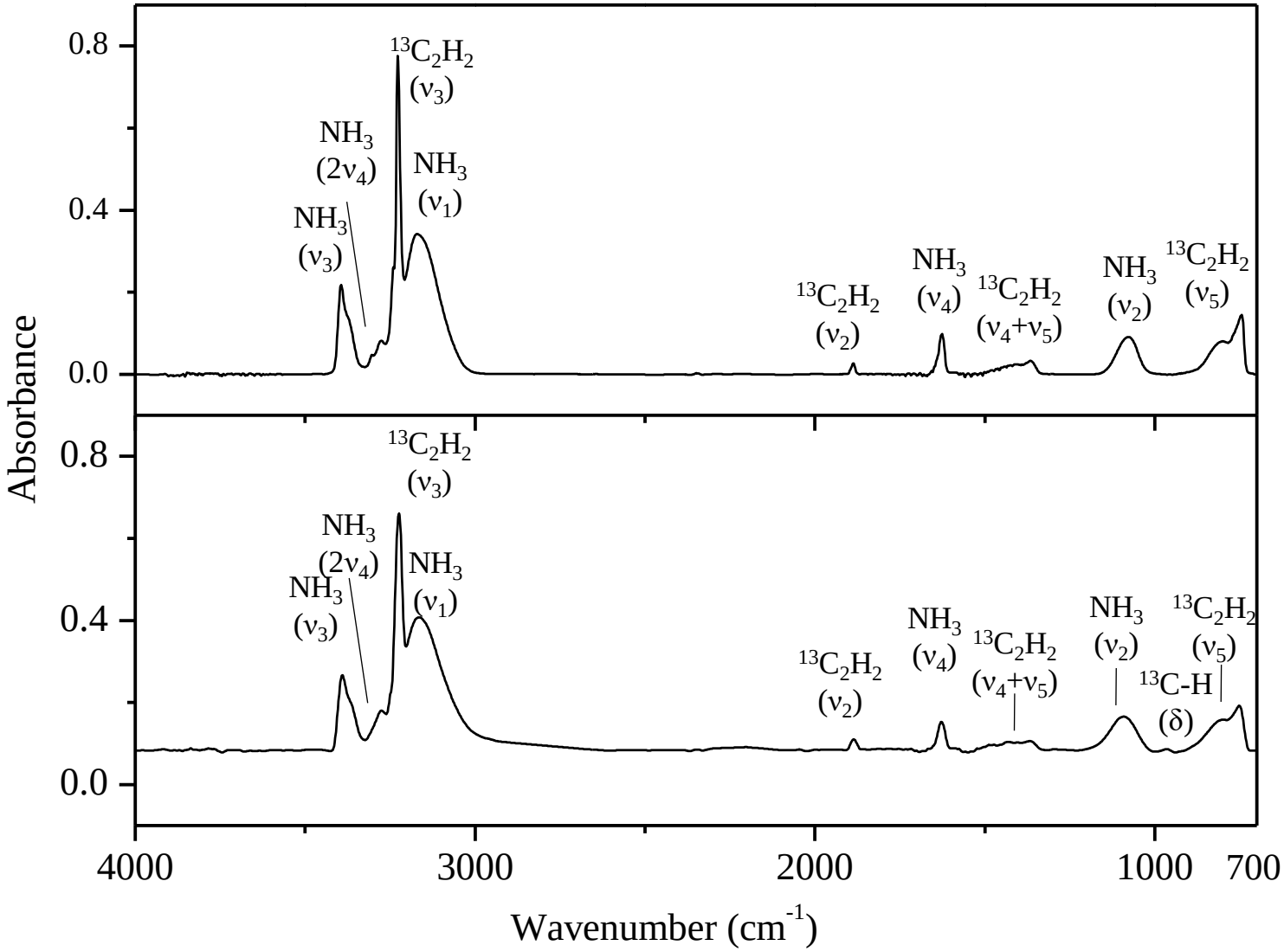

Figure S1: Infrared spectra for $^{13}C_2H_2$:NH_3 ice before (top) and after (bottom) electron irradiation of 100 nA for 60 minutes. Newly obtained peaks after electron irradiation are shown in Table S5.

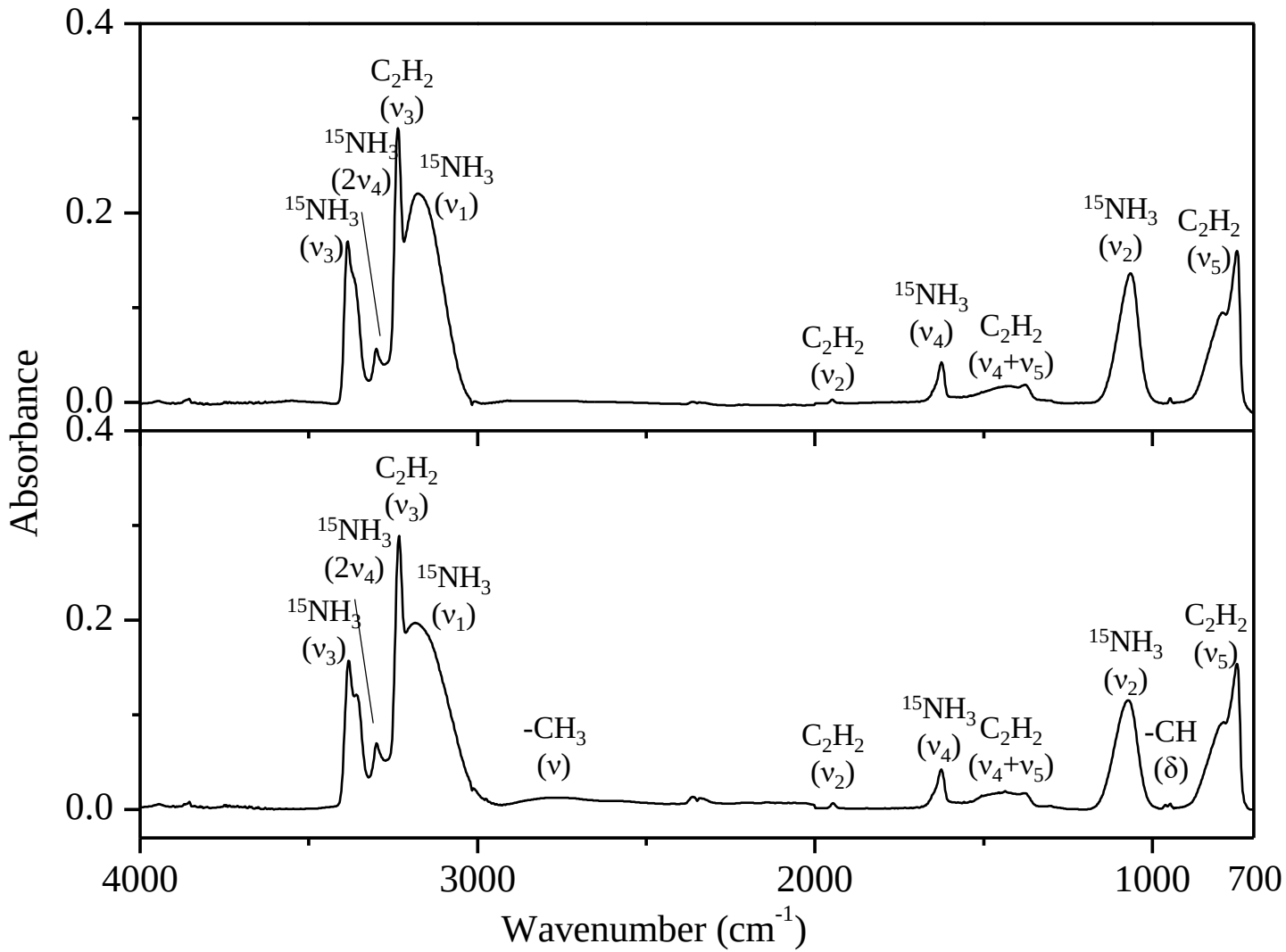

Figure S2: Infrared spectra for C_2H_2:$^{15}NH_3$ ice before (top) and after (bottom) electron irradiation of 100 nA for 60 minutes. Newly obtained peaks after electron irradiation are shown in Table S6.

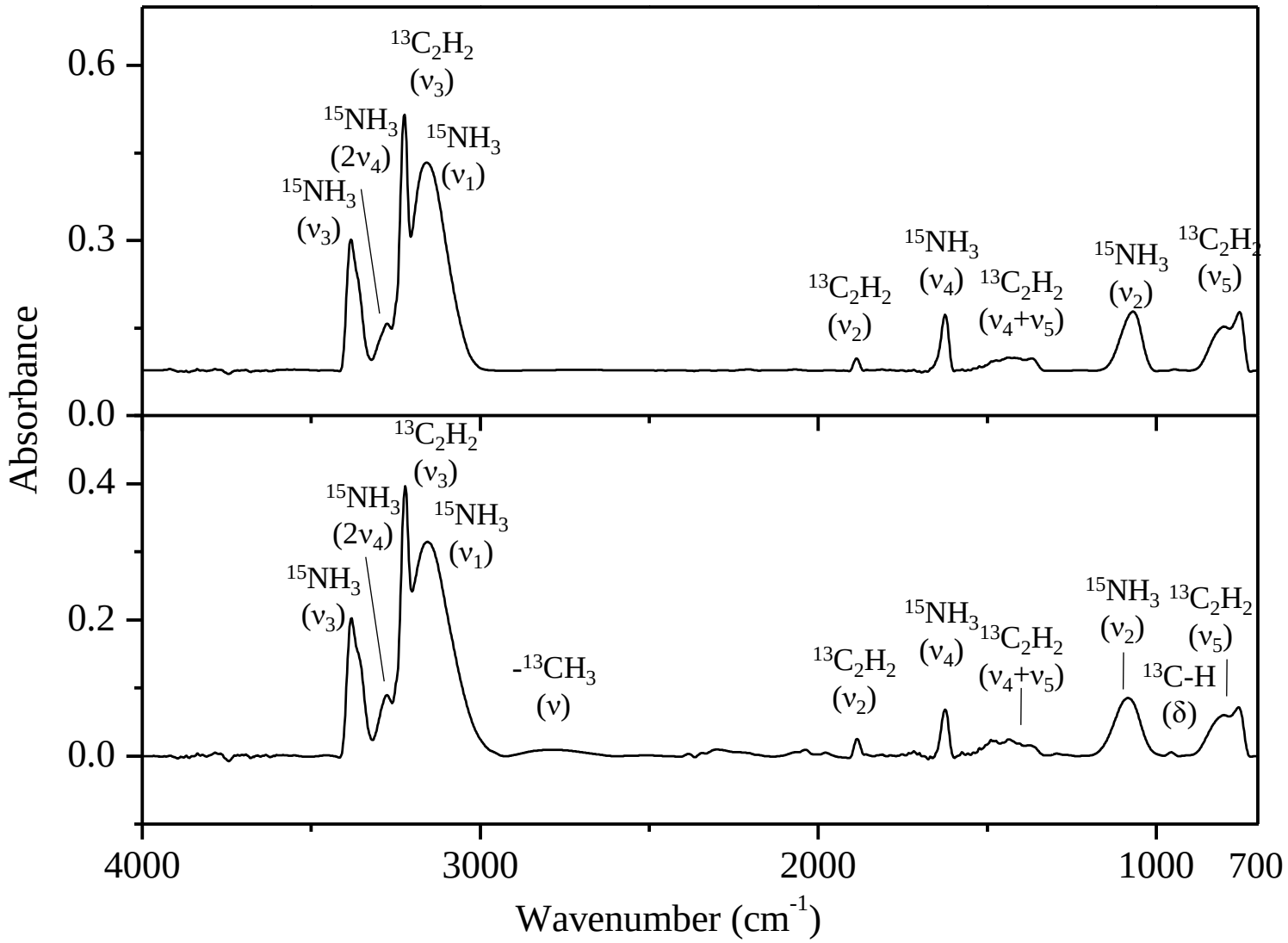

Figure S3: Infrared spectra for $^{13}C_2H_2$:$^{15}NH_3$ ice before (top) and after (bottom) electron irradiation of 100 nA for 60 minutes. Newly obtained peaks after electron irradiation are shown in Table S7.

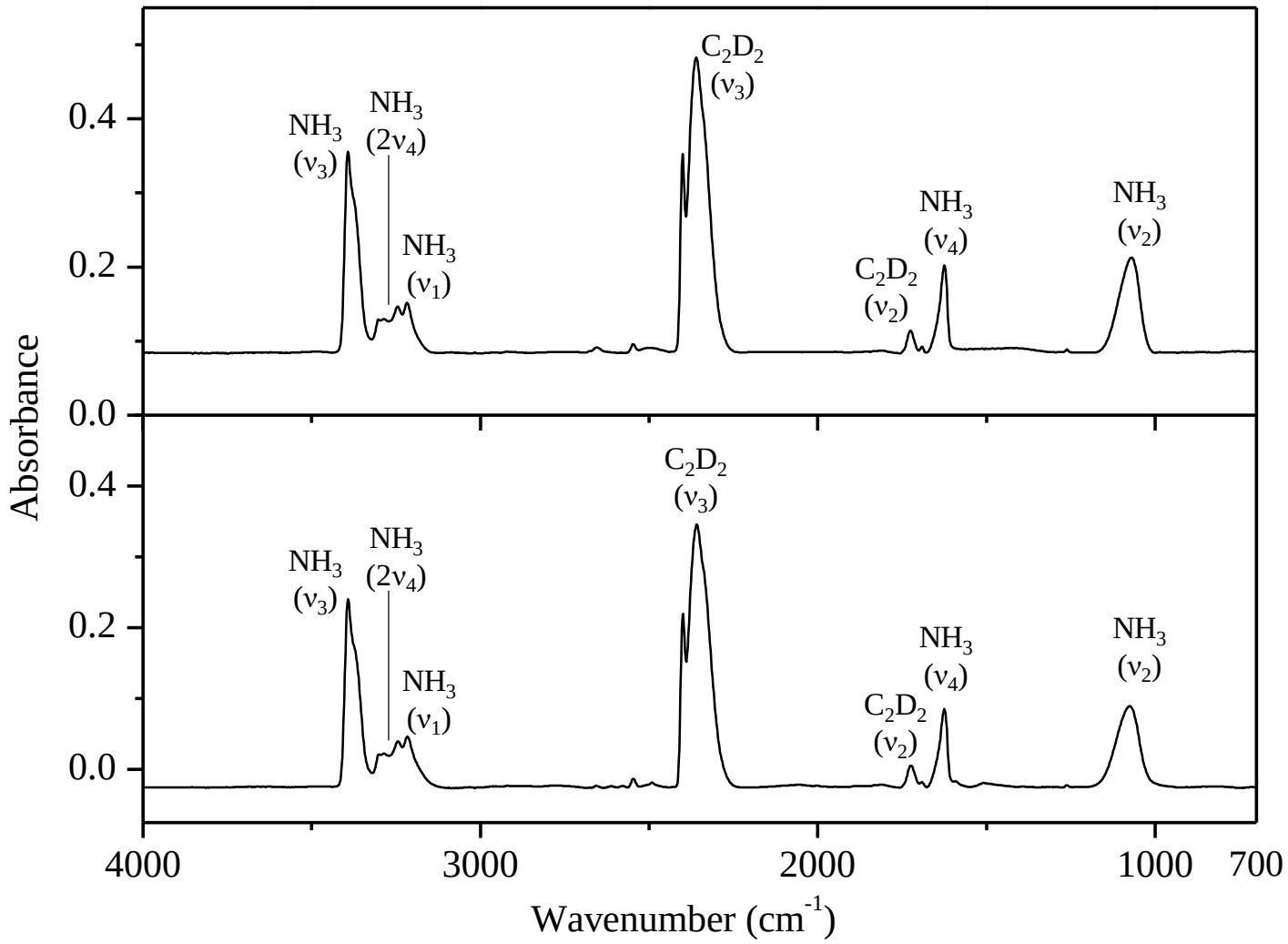

Figure S4: Infrared spectra for C_2D_2:NH_3 ice before (top) and after (bottom) electron irradiation of 100 nA for 60 minutes. Newly obtained peaks after electron irradiation are shown in Table S8.

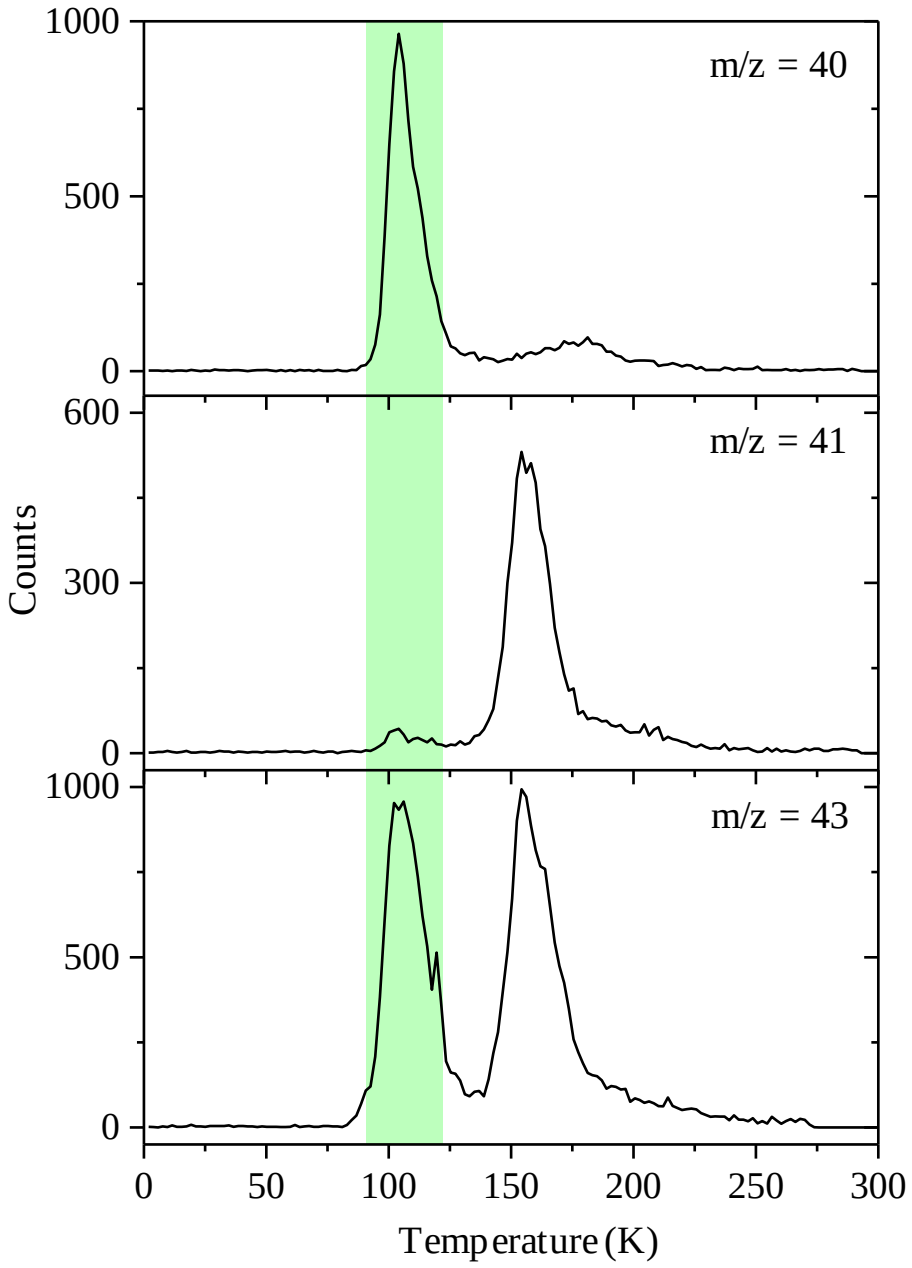

Figure S5: Temperature-programmed desorption profiles at m/z = 40 (top, C_2H_2:NH_3 ice), m/z = 41 (center, C_2H_2:NH_3 ice) and m/z = 43 (bottom, $^{13}C_2H_2$:NH_3 ice) confirming the assignment of C_3H_4 in Figure 6. The center panel shows $^{13}C^{12}C_2H_4$ with natural isotopic abundance in the C_2H_2:NH_3 ice.

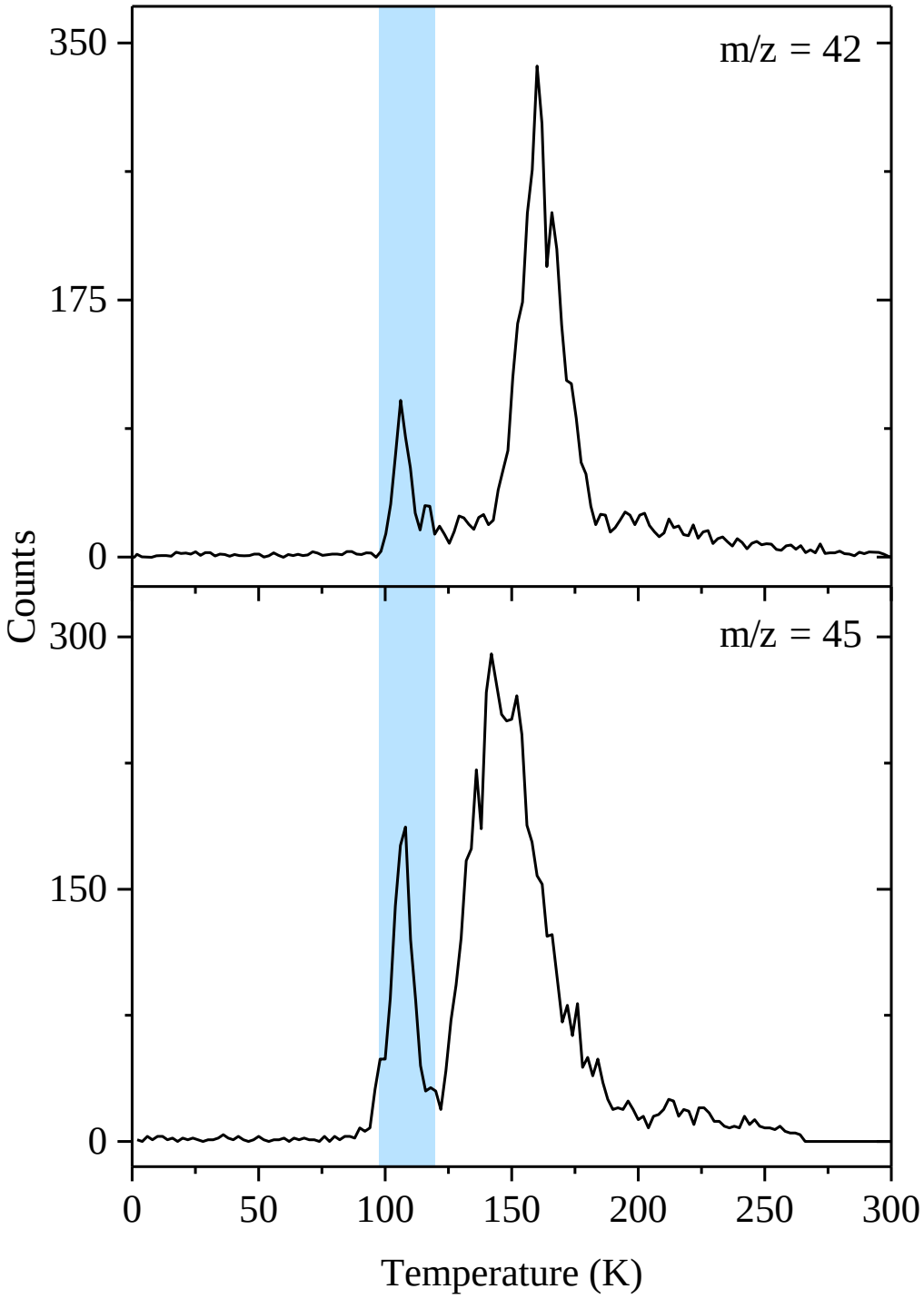

Figure S6: Temperature-programmed desorption profiles at m/z = 42 (top, C_2H_2:NH_3 ice) and m/z = 45 (bottom, $^{13}C_2H_2$:NH_3 ice) confirming the assignment of C_3H_6 in Figure 6.

Table S1: Description of different ices with composition, ratio, thickness, irradiation current and time, dose per C_2H_2 and NH_3 molecule and used photon energy.

Ice Number	Ice Composition	Ice Ratio	Ice Thickness (nm)	Current (nA)	Irradiation Time (s)	Dose (eV C_2H_2 molecule^{-1})	Dose (eV NH_3 molecule^{-1})	Photon Energy (eV)
I	C_2H_2/NH_3	1:1.1 ± 0.2	1000 ± 100	100 ± 10	3600 ± 10	5.0 ± 0.8	3.5 ± 0.6	10.49
II	C_2H_2/NH_3	1:1.2 ± 0.1	1000 ± 100	100 ± 10	3600 ± 10	5.0 ± 1.0	3.5 ± 0.6	9.80
III	C_2H_2/NH_3	1:1.0 ± 0.2	1000 ± 100	100 ± 10	3600 ± 10	5.0 ± 0.8	3.5 ± 0.6	8.81
IV	$^{13}C_2H_2/NH_3$	1:1.1 ± 0.2	1000 ± 100	100 ± 10	3600 ± 10	5.0 ± 0.8	3.5 ± 0.8	10.49
V	$C_2H_2/^{15}NH_3$	1:1.1 ± 0.2	1000 ± 100	100 ± 10	3600 ± 10	5.0 ± 0.8	3.5 ± 0.8	10.49
VI	$^{13}C_2H_2/^{15}NH_3$	1:1.1 ± 0.1	1000 ± 100	100 ± 10	3600 ± 10	5.0 ± 0.8	3.5 ± 0.6	10.49
VII	C_2D_2/NH_3	1:1.1 ± 0.2	1000 ± 100	100 ± 10	3600 ± 10	5.0 ± 1.0	3.5 ± 0.6	10.49
VII	C_2D_2/NH_3	1:1.1 ± 0.2	1000 ± 100	10 ± 1	300 ± 10	0.042 ± 0.007	0.029 ± 0.005	9.81

Table S2: Data applied to calculate the average irradiation dose per molecule.

Initial kinetic energy of the electrons, E_{init} (keV)	5
Density of ice (gm cm^{-3})	0.74 ± 0.02
Thickness of ice (nm)	1000 ± 100
Average penetration depth, l_{ave} (nm)	350 ± 30
Maximum penetration depth, l_{max} (nm)	700 ± 50
Average kinetic energy of backscattered electrons, E_{bs} (keV)	1.1 ± 0.2
Average kinetic energy of transmitted electrons, E_{trans} (keV)	0
Irradiated area, A (cm^2)	1.0 ± 0.1

Table S3: Parameters used to generate VUV photons.

YAG 1 wavelength (nm)	Dye 1 wavelength (nm)	Dye 1	YAG 2 wavelength (nm)	Dye 2 wavelength (nm)	Dye 2	Gas, pressure (Torr)	VUV energy (eV)
-	-	-	355	-	-	Xe, 1.3×10^{-4}	10.49
532	606.948	Rh 610/ Rh 640 mix	355	505	Coumarin 503	Kr, 8.0×10^{-5}	9.80
355	445.132	Coumarin 450	532	-	-	Xe, 1.4×10^{-4}	8.81

Table S4: Assignments of infrared absorptions of C_2H_2:NH_3 ice at 5 K before and after electron irradiation.

Assignments	Positions (cm^{-1})	References
Before irradiation at 5 K		
C_2H_2 (ν_5)	746	[1]
NH_3 (ν_2)	1077	[2]
C_2H_2 ($\nu_4+\nu_5$)	1389	[1]
NH_3 (ν_4)	1627	[2]
C_2H_2 (ν_2) C_2H_2 ($2\nu_4+\nu_5$)	1950	[1,3-5]
NH_3 (ν_1)	3187	[2]
C_2H_2 (ν_3)	3239	[1]
NH_3 ($2\nu_4$)	3303	[2]
NH_3 (ν_3)	3394	[2]
New Peaks after irradiation at 5 K		
δ(C=CH)	962	[1]
$\delta(CH_2)$	1277	[1]
$\nu(C=C)_{aromatic}$	1440	[1]
$\nu(C=C)$ aromatic $\delta(NH_2)_{R\text{-}NH_2}$	1594	[1]
ν(CCN)	2054	[6]
ν(C≡C)	2110	[1]
ν(CH)	2801, 2973	[1]

Table S5: Assignments of infrared absorptions of $^{13}C_2H_2$:NH_3 ice at 5 K before and after electron irradiation.

Assignments	Positions (cm^{-1})	References
Before irradiation at 5 K		
$^{13}C_2H_2$ (ν_5)	745	[1]
NH_3 (ν_2)	1075	[2]
$^{13}C_2H_2$ ($\nu_4+\nu_5$)	1371	[1]
NH_3 (ν_4)	1628	[2]
$^{13}C_2H_2$ (ν_2)	1887	[1]
NH_3 (ν_1)	3175	[2]
$^{13}C_2H_2$ (ν_3)	3231	[1]
NH_3 ($2\nu_4$)	3295	[2]
NH_3 (ν_3)	3397	[2]
New peaks after irradiation at 5 K		
$\delta(^{13}CH)$	952	[1]

Table S6: Assignments of infrared absorptions of C_2H_2:$^{15}NH_3$ ice at 5 K before and after electron irradiation.

Assignments	Positions (cm^{-1})	References
Before irradiation at 5 K		
C_2H_2 (ν_5)	750	[1]
$^{15}NH_3$ (ν_2)	1070	[2]
C_2H_2 ($\nu_4+\nu_5$)	1374	[1]
$^{15}NH_3$ (ν_4)	1626	[2]
C_2H_2 (ν_2)	1890	[1]
$^{15}NH_3$ (ν_1)	3160	[2]
C_2H_2 (ν_3)	3236	[1]
$^{15}NH_3$ ($2\nu_4$)	3300	[2]
$^{15}NH_3$ (ν_3)	3384	[2]
New peaks after irradiation at 5 K		
δ(CH)	962	[1]
ν(CH)	2819	[1]

Table S7: Assignments of infrared absorptions of $^{13}C_2H_2$:$^{15}NH_3$ ice at 5 K before and after electron irradiation.

Assignments	Positions (cm^{-1})	References
Before irradiation at 5 K		
$^{13}C_2H_2$ (ν_5)	756	[1]
$^{15}NH_3$ (ν_2)	1074	[2]
$^{13}C_2H_2$ ($\nu_4+\nu_5$)	1371	[1]
$^{15}NH_3$ (ν_4)	1627	[2]
$^{13}C_2H_2$ (ν_2)	1887	[1]
$^{15}NH_3$ (ν_1)	3156	[2]
$^{13}C_2H_2$ (ν_3)	3228	[1]
$^{15}NH_3$ ($2\nu_4$)	3294	[2]
$^{15}NH_3$ (ν_3)	3387	[2]
New Peaks after irradiation at 5 K		
$\delta(^{13}CH)$	961	[1]
$\nu(^{13}CH_3)$	2825	[1]

Table S8: Assignments of infrared absorptions of C_2D_2:NH_3 ice at 5 K before and after electron irradiation.

Assignments	Positions (cm^{-1})	References
Before irradiation at 5 K		
NH_3 (ν_2)	1074	[2]
NH_3 (ν_4)	1627	[2]
C_2D_2 (ν_2)	1727	[1]
C_2D_2 (ν_3)	2360	[1]
NH_3 (ν_1)	3218	[2]
NH_3 ($2\nu_4$)	3302	[2]
NH_3 (ν_3)	3392	[2]
New Peaks after irradiation at 5 K		
$\nu(CD_3)$	2809	[1]

Table S9: Calculated adiabatic ionization energies (IE) and relative energies (E_{rel}) of C_2H_3N isomers with average deviations calculated from the error limits. Combined error limits are used to obtain the corrected calculated ionization energies and 0.03 eV was subtracted to correct for the electric field effect.

Name	Computed IE (eV)	Experimental IE (eV)	Experimental error limits (eV)	Computed IE – experimental IE (max) (eV)	Computed IE – experimental IE (min) (eV)	Corrected IE after error analysis (eV)	Corrected IE with electric field effect (eV)
Acetonitrile	12.20	12.20 ± 0.01	12.19 - 12.21	–0.01	+0.01	12.18 - 12.25	12.15 - 12.22
Methyl Isocyanide	11.25	11.24 ± 0.01	11.23 - 11.25	+0.0	+0.02	11.23 - 11.30	11.20 - 11.27
Ketenimine	8.73	-	-	-	-	8.71 - 8.78	8.68 - 8.75
Ethynylamine	8.90	-	-	-	-	8.88 - 8.95	8.85 - 8.92
2H-Azirine	10.02	10.05 ± 0.03	10.02 - 10.08	–0.06	+0.0	10.00 - 10.07	9.97 - 10.04
1H-Azirine	8.33	-	-	-	-	8.31 - 8.38	8.28 - 8.35
				Average –0.02 ± 0.03	Average +0.01 ± 0.01		
				Error limits –0.05 - +0.01	Error limits +0.0 - +0.02		
				Combined error limits –0.05 - +0.02			

Table S10: Molecular coordinates and harmonic frequencies from quantum chemical calculations.

C_2H_2, acetylene

H 0.0000 0.0000 -1.66908303
C 0.0000 0.0000 -0.60510471
C 0.0000 0.0000 0.60510471
H 0.0000 0.0000 1.66908303
Wavenumbers [cm-1] 593.08 593.08 748.31 748.31 1994.58
Wavenumbers [cm-1] 3393.94 3502.00

CCH, ethynyl radical

C 0.0000000000 0.0000000000 -0.6750625630
C 0.0000000000 0.0000000000 0.5403745176
H 0.0000000000 0.0000000000 1.6049944574
Wavenumbers [cm-1] 278.68 278.68 2004.20 3444.14

NH, imidogen

N 0.0000 0.0000 0.0000
H 0.0000 0.0000 1.03668664
Wavenumbers [cm-1] 3317.28

NH_2, amino radical

N 0.0000000000 0.0000000000 -0.0806070955
H 0.0000000000 0.8033459298 0.5600727250
H 0.0000000000 -0.8033459298 0.5600727250
Wavenumbers [cm-1] 1539.34 3359.58 3453.36

C_2H_3N, 1H-azirine (6)

N -0.0806076258 0.0000000000 -0.8878302726
C 0.0116959326 -0.6417622321 0.4942210338
C 0.0116959326 0.6417622321 0.4942210338
H -0.0131455220 -1.6269428525 0.9180257742
H -0.0131455220 1.6269428525 0.9180257742
H 0.8676974175 0.0000000000 -1.2770950580
Wavenumbers [cm-1] 537.43 560.32 713.75 879.55 972.92
Wavenumbers [cm-1] 1058.26 1145.50 1366.18 1724.65 3288.93
Wavenumbers [cm-1] 3338.32 3351.37

C_2H_3N, 2H-azirine (3)

H 0.0000000000 1.4535830288 -1.1215274672
C 0.0000000000 0.6073958417 -0.4496674329
C 0.0000000000 0.0384991239 0.8894397266
N 0.0000000000 -0.6530257799 -0.5054401431
H -0.9228189527 -0.0378160990 1.4524058114
H 0.9228189527 -0.0378160990 1.4524058114
Wavenumbers [cm-1] 699.70 772.34 987.35 996.12 1039.38
Wavenumbers [cm-1] 1106.95 1265.33 1510.90 1684.83 3115.43
Wavenumbers [cm-1] 3207.87 3226.36

$HCCNH_2$, ethynamine (4)

NH2CCH CCSD(T)/AVTZ ENERGY=-132.46823705

H	-0.8315632832	0.3579402605	-1.6260192838
N	0.0000000000	-0.0515210672	-1.2229212807
C	0.0000000000	-0.0170034916	0.1425472155
C	0.0000000000	0.0136146471	1.3537592695
H	0.0000000000	0.0404576969	2.4156339309
H	0.8315632832	0.3579402605	-1.6260192838

Wavenumbers [cm-1] 332.84 380.23 494.83 651.71 684.03
Wavenumbers [cm-1] 1054.41 1214.31 1648.28 2195.58 3467.63
Wavenumbers [cm-1] 3538.94 3629.52

CH_2CNH, ketenimine (5)

H	-0.8066589280	0.0000000000	-1.7445645132
N	0.0810974039	0.0000000000	-1.2432770524
C	-0.0262057255	0.0000000000	-0.0149436361
C	-0.0006162401	0.0000000000	1.3021840973
H	-0.0003395930	-0.9364819812	1.8411710348
H	-0.0003395930	0.9364819812	1.8411710348

Wavenumbers [cm-1] 403.53 458.64 705.78 904.08 998.00
Wavenumbers [cm-1] 1046.33 1133.09 1438.30 2072.79 3173.44
Wavenumbers [cm-1] 3268.71 3477.95

t-$HCCHNH_2$ radical (7)

C	-0.0030675689	0.3953267209	-0.1283769754
N	0.0592287489	-0.1602566416	1.1634599115
H	-0.4764157623	0.3618109741	1.8426482803
H	-0.1991831810	-1.1378202522	1.1828963210
C	-0.0141150447	-0.2670138529	-1.2755531509
H	0.0253365116	-0.0122241309	-2.3210084247
H	0.0319528658	1.4861924577	-0.1426269316

Wavenumbers [cm-1] 331.91 461.86 560.84 712.29 797.53
Wavenumbers [cm-1] 811.48 1078.32 1218.22 1311.72 1640.72
Wavenumbers [cm-1] 1674.94 3083.72 3277.97 3534.50 3637.35

CH_2CHNH radical (8)

C	0.0000000000	0.1900867886	-1.2277827760
C	0.0000000000	-0.4383020219	0.0279446524
N	0.0000000000	0.2834542834	1.1313532513
H	0.0000000000	-0.3352857413	1.9444865308
H	0.0000000000	-1.5302999581	0.0528119819
H	0.0000000000	1.2714121321	-1.2786520669
H	0.0000000000	-0.3869820030	-2.1426100566

Wavenumbers [cm-1] 479.79 506.89 678.01 805.22 989.46
Wavenumbers [cm-1] 1038.32 1094.39 1231.99 1353.18 1452.47
Wavenumbers [cm-1] 1503.15 3078.61 3155.68 3266.32 3445.56

c-CH_2CHNH radical (9)

C	-0.0055477348	-0.0572990621	-0.8596634138
N	-0.0944996825	-0.6176742926	0.5338288192
C	0.0977429342	0.7716719713	0.3433662737
H	-0.5115079719	1.5550833072	0.7733464144
H	0.7519551896	-1.1110388102	0.8068619601
H	0.9035965606	-0.2345015713	-1.4250742130
H	-0.9294752891	-0.1388586568	-1.4210182142

Wavenumbers [cm-1]	714.98	764.03	865.30	908.97	995.23
Wavenumbers [cm-1]	1080.21	1106.33	1140.26	1198.29	1309.42
Wavenumbers [cm-1]	1509.41	3110.00	3193.18	3202.07	3483.53

Intermediate in formation of 1H-azirine from C_2H_2 + NH (*)

C	-0.757935	0.403808	0.016135
C	-0.187052	-0.732547	0.016089
H	-0.254796	-1.805979	0.030571
H	-1.236250	1.355987	0.015725
N	0.843419	0.281376	-0.145028
H	1.257033	0.452790	0.775557

Wavenumbers [cm-1]	356.92	579.79	752.87	820.36	942.25	1097.94
Wavenumbers [cm-1]	1124.95	1366.50	1769.61	3249.74	3326.00	3396.11

TS C_2H_2+NH_2 → 7

C	-0.0001682446	0.5974114034	-0.5653284454
N	-0.0000043480	-0.0923336201	1.5237504597
H	-0.8034826225	-0.7231024220	1.4230050044
H	0.8037022077	-0.7227690493	1.4230484091
C	0.0003483687	-0.3910953557	-1.2832429280
H	-0.0021848199	-1.3271086290	-1.7915293197
H	-0.0001207726	1.5975403592	-0.2008272441

TS 7 → 8

C	-0.128774	0.387026	0.000000
N	-1.145368	-0.373136	0.000000
H	-2.006789	0.173176	0.000000
H	-0.224911	1.483378	0.000000
C	1.246067	-0.130209	0.000000
H	1.772518	-0.292805	0.929992
H	1.772518	-0.292805	-0.929992

TS 7 → 4

C	-0.0111240548	0.0766060510	-0.1390895621
N	0.0608770646	-0.0911466866	1.2183307961
H	-0.2623821402	0.7148987351	1.7351404556
H	-0.4008271432	-0.9362039533	1.5277359929
C	0.0013012115	-0.1095646961	-1.3477876272
H	-0.0150019652	-0.0940506497	-2.4109807699
H	-0.0507057612	1.9747111692	-0.0640631103

TS 8 → 9

H	-1.6284666830	0.4165723585	-0.1755034248
C	-0.6950011894	-0.1213898334	-0.0615708335
C	0.2356739285	0.0197283167	1.0145112079
H	0.5077954937	0.9950711858	1.4050285411
H	0.8128225880	-0.8346268579	1.3522250774
N	0.3490464477	0.0989217124	-0.9296508295
H	0.9308924836	-0.7402310362	-1.0185882626

TS 8 → 5

H	-0.9327625946	-0.0363755070	-1.6523222838
N	0.0063583343	0.0027461249	-1.2543790269
C	0.0107442067	-0.0015052501	-0.0200120791
C	-0.0904238767	-0.0011416771	1.3042003512
H	-0.0993226474	0.9391361795	1.8373687634
H	-0.0137367484	-0.9331088046	1.8461908246
H	1.9069578066	0.0237287846	0.0971883761

TS 9 → 3

C	0.0180994931	-0.0647526135	-0.8964457947
N	-0.1537491691	-0.5388253409	0.5677850419
C	0.0400597565	0.7156814149	0.3267288634
H	0.2325409206	1.6294111546	0.8655851752
H	1.1326627739	-1.4261897073	0.9109018358
H	0.9519319941	-0.3587775311	-1.3675598653
H	-0.8736293881	-0.1134489470	-1.5101084512

TS 9 → 6

C	-0.1914679792	-0.4470445704	-0.6185695434
N	-0.0773635508	-0.1812080799	0.8829730955
C	0.0815358169	0.7668326249	-0.2850051754
H	0.2176090191	1.8194723445	-0.4447287432
H	0.8630098209	-0.4780250108	1.1626194446
H	1.8687083541	-1.4096067597	-0.9637467398
H	-0.5642613681	-1.2244245677	-1.2569152662

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