Supplementary Information for

Ab Initio Kinetics of the C_2H_2 + NH_2 Reaction: A Revisited Study

Tam V.-T. Mai,[1,2,*] and Lam K. Huynh[3,*]

[1] Molecular Science and Nano-Materials Lab, Institute for Computational Science and Technology, SBI Building, Quang Trung Software City, Tan Chanh Hiep Ward, District 12, Ho Chi Minh City, Vietnam.
[2] University of Science, Vietnam National University – HCMC, 227 Nguyen Van Cu, Ward 4, District 5, Ho Chi Minh City, Vietnam.
[3] International University, Vietnam National University – HCMC, Quarter 6, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam.

[*]Corresponding authors.

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Table S1: The optimized geometries, electronic energies at 0 K ($E_{elec}^{0\,K}$), zero-point energy (ZPE) corrections, harmonic wavenumbers of the species involved, calculated at W1U level of theory for the title reaction.

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
C_2H_2	6	0.000000000	0.000000000	0.597916000	-77.351957	0.026986	649.9072	649.9072	764.6045
($D_{\infty h}$)	1	0.000000000	0.000000000	1.658970000			764.6045	2073.1196	3420.0894
	6	0.000000000	0.000000000	-0.597916000			3523.4533		
	1	0.000000000	0.000000000	-1.658970000			(612; 612; 730; 730; 1974; 3289; 3374)[1]		
NH_2	7	0.000000000	0.000000000	0.142608000	-55.902140	0.018950	1541.9570	3343.9041	3432.4239
(C_{2v})	1	0.000000000	0.802809000	-0.499128000			(1497.3[2]; 3219.4[2]; 3301.1[3])		
	1	0.000000000	-0.802809000	-0.499128000					
Pre-complex	7	2.362770000	-0.000099000	-0.000144000	-133.258873	0.047886	70.8076	83.2654	120.9008
(C_{2v})	1	2.995547000	0.807972000	-0.000092000			181.5667	228.4737	683.2630
	1	2.998184000	-0.806095000	-0.000026000			684.9784	857.0639	862.9835
	6	-1.011251000	-0.000315000	-0.000011000			1536.0104	2057.4018	3343.0461
	1	0.057552000	-0.000701000	-0.000181000			3363.7453	3454.6567	3491.1912
	6	-2.208834000	0.000138000	0.000178000					
	1	-3.270159000	0.000582000	0.000311000					
Post-complex	6	-1.533619000	-0.204116000	-0.000003000	-133.229403	0.052044	20.2642	140.4393	336.5477
(C_s)	1	-2.501597000	-0.645268000	0.000027000			392.7580	449.9968	586.5183
	6	-0.560415000	0.540156000	-0.000024000			646.5753	886.1141	1628.4031
	1	1.531903000	-0.662442000	-0.837082000			1630.1576	1886.0881	3429.2736
	7	1.426196000	-0.108322000	0.000004000			3494.3238	3657.1201	3660.1671
	1	2.017699000	0.709131000	-0.001786000					
	1	1.532820000	-0.659408000	0.838973000					
TS_abs	6	-1.762588000	0.139297000	-0.000046000	-133.219851	0.048511	-515.6749	82.7617	112.1709
(C_s)	1	-2.794814000	0.394488000	-0.000048000			326.7903	510.8597	633.3006
	6	-0.631585000	-0.292814000	0.000062000			653.2661	891.7770	1523.1800
	1	0.931072000	-0.626519000	0.000257000			1619.7180	2006.0464	2435.1257
	7	1.810389000	-0.004084000	0.000027000			3443.0589	3481.9539	3573.9683
	1	1.777973000	0.591237000	0.823349000					
	1	1.778080000	0.590485000	-0.823843000					
TS1	7	-1.470123000	-0.069752000	-0.000006000	-133.247578	0.049607	-434.0626	***147.2623***	263.0029
(C_s)	1	-1.404641000	-0.701606000	0.802838000			539.7978	605.0456	686.1956
	1	-1.404621000	-0.701672000	-0.802796000			739.7407	776.9018	823.3555

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
	6	0.537467000	0.601917000	-0.000002000			1547.2610	1917.5821	3382.5865
	1	0.238323000	1.622408000	-0.000005000			3393.9426	3475.5969	3476.5512
	6	1.301833000	-0.345482000	0.000002000					
	1	1.826002000	-1.269474000	0.000005000					
TS2	6	-1.336037000	0.091585000	-0.068783000	-133.225730	0.049028	-1675.4296	371.1014	417.6667
(C_1)	1	-1.922647000	0.988344000	0.124690000			***486.0595***	618.1310	627.9075
	6	-0.102434000	-0.328779000	-0.106871000			858.8672	1070.8965	1172.9764
	1	-0.903945000	-0.994528000	0.598449000			1635.9604	1785.1952	2280.7641
	7	1.172004000	0.108228000	0.080346000			3067.6441	3485.0384	3642.7115
	1	1.336761000	1.107250000	0.088908000					
	1	1.916629000	-0.435503000	-0.320547000					
TS3	6	-1.337659000	0.066812000	0.002494000	-133.246302	0.045394	-780.2215	321.6548	343.0979
(C_1)	1	-1.996672000	-0.694484000	-0.388672000			464.7865	567.4944	739.4782
	6	-0.044646000	-0.106224000	0.014161000			901.0108	991.8833	1092.2731
	1	-1.769793000	0.970765000	0.410856000			1147.2771	1434.9299	2055.3668
	7	1.183249000	-0.115821000	-0.076592000			3143.0561	3226.8609	3496.4726
	1	2.071827000	1.320631000	-0.264793000					
	1	1.705724000	-0.549698000	0.678823000					
TS4	6	-1.301134000	-0.167705000	0.028240000	-133.293482	0.053138	-638.1956	***356.0744***	430.0653
(C_1)	1	-2.242555000	-0.656938000	-0.015096000			508.4606	658.6957	853.2946
	6	-0.133531000	0.407322000	-0.006484000			1063.1637	1171.6435	1336.8879
	1	-0.063720000	1.498035000	-0.022117000			1639.3315	1679.2404	3027.4430
	7	1.131242000	-0.200462000	-0.090842000			3439.9969	3527.7282	3632.6589
	1	1.135303000	-1.180065000	0.151700000					
	1	1.860269000	0.304504000	0.390871000					
TS5	6	-1.354079000	-0.143276000	0.003108000	-133.228019	0.045686	-596.7543	***177.1261***	421.0369
(C_1)	1	-2.413744000	-0.155650000	0.029403000			457.0668	490.7359	518.1082
	6	-0.153825000	0.021516000	-0.003449000			601.6659	683.0527	1076.4382
	1	-0.125194000	1.976758000	0.065269000			1198.1999	1628.9317	2165.7274
	7	1.188547000	-0.117542000	-0.085210000			3474.4045	3534.8344	3626.5862
	1	1.547500000	-0.966630000	0.326364000					
	1	1.719030000	0.698877000	0.177479000					
TS6	6	1.137402000	-0.319040000	-0.006426000	-133.234255	0.048682	-1822.2549	115.4953	658.4294
(C_1)	1	2.158139000	0.040856000	0.111109000			793.3455	934.4426	1008.5208

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
	6	0.048918000	0.542543000	-0.015166000			1065.0947	1114.9543	1159.1477
	1	-0.039380000	1.624956000	-0.011143000			1376.4832	1414.2525	2010.2182
	7	-1.016090000	-0.267891000	-0.018183000			3110.9612	3147.7804	3459.6893
	1	-0.157772000	-1.181416000	-0.007085000					
	1	-1.966280000	0.049821000	0.163948000					
TS7	6	-1.273241000	0.303984000	0.022491000	-133.234730	0.050603	-1248.2614	318.1868	458.1802
(C_1)	1	-2.222891000	-0.142782000	-0.257094000			***534.6196***	672.3388	916.8117
	6	-0.111359000	-0.342381000	-0.149786000			1094.0254	1171.7833	1254.9531
	1	-0.825999000	-0.770118000	0.777518000			1610.0249	1636.0766	2219.6038
	7	1.155319000	0.083915000	0.053214000			3133.5027	3510.0225	3681.8710
	1	1.354018000	1.074937000	0.072177000					
	1	1.915240000	-0.519060000	-0.201333000					
TS8	6	0.070607000	0.021004000	-0.000001000	-133.248458	0.045243	-788.4878	110.1815	446.3989
(C_1)	1	-0.052100000	1.881860000	0.000052000			557.3263	574.3921	726.3712
	7	1.263305000	-0.241252000	-0.000017000			888.3457	1010.2280	1043.5216
	1	1.899139000	0.551068000	0.000002000			1133.2676	1433.6803	2023.8069
	6	-1.253126000	-0.118837000	0.000007000			3160.9322	3252.0048	3499.1308
	1	-1.797538000	-0.078555000	-0.931474000					
	1	-1.797521000	-0.078612000	0.931501000					
TS9	6	-0.052649000	0.427296000	0.000043000	-133.290056	0.051689	-1199.6210	323.3253	***436.4390***
(C_s)	1	0.001176000	1.530877000	0.000198000			507.9475	751.5753	951.2621
	7	-1.173434000	-0.164295000	-0.000159000			988.5669	1143.2130	1416.9971
	1	-2.040550000	-0.636235000	-0.000369000			1473.9770	1508.5968	2895.7541
	6	1.200203000	-0.224540000	0.000120000			3131.2863	3241.1256	3918.9029
	1	2.121291000	0.343807000	0.000319000					
	1	1.246796000	-1.304921000	-0.000018000					
TS10	6	0.111603000	-0.287227000	-0.102986000	-133.250220	0.049889	-1771.9790	401.0056	554.7502
(C_1)	1	-0.647634000	-0.936704000	0.714572000			741.2751	847.7466	1006.5520
	7	1.256810000	0.230339000	-0.041640000			1044.6290	1142.2677	1205.5827
	1	2.008622000	-0.374236000	0.272743000			1453.2916	1724.0621	2008.9236
	6	-1.223677000	0.130105000	0.000617000			3047.5441	3214.1018	3506.8341
	1	-1.986861000	-0.467127000	-0.476695000					
	1	-1.499357000	1.108430000	0.395074000					
TS11	6	0.112309000	-0.294894000	-0.107477000	-133.243531	0.049335	-1776.1339	370.7758	511.7982

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
(C_1)	1	-0.699666000	-0.927926000	0.680506000			750.4558	835.5311	989.9530
	7	1.313631000	0.008277000	0.050087000			1042.2583	1103.2175	1205.7693
	1	1.578203000	0.953201000	-0.242129000			1452.4147	1763.5047	2039.1681
	6	-1.214925000	0.158366000	-0.006832000			3029.2537	3209.4137	3352.0572
	1	-1.988235000	-0.396187000	-0.518500000					
	1	-1.470019000	1.132146000	0.415368000					
TS12 (C_s)	6	0.171508000	-0.152510000	0.000001000	-133.286575	0.045989	-928.0291	***97.1097***	269.8738
	7	1.333297000	-0.164028000	-0.000001000			410.6883	555.4406	920.8705
	1	2.128526000	1.238006000	0.000001000			1052.5186	1062.9991	1409.0026
	6	-1.263468000	0.072216000	0.000000000			1469.2808	1469.4916	2235.2719
	1	-1.477615000	1.143808000	-0.000044000			3027.3364	3092.9328	3114.0732
	1	-1.716119000	-0.375963000	-0.884062000					
	1	-1.716108000	-0.375889000	0.884105000					
IM1_trans (C_1)	6	-1.330772000	-0.113976000	0.026890000	-133.298959	0.054957	***325.2759***	448.4972	558.5426
	1	-1.809859000	-1.076335000	-0.000345000			666.0633	799.5325	888.5935
	6	-0.139313000	0.435324000	-0.008054000			1068.3332	1191.9039	1331.6107
	1	-0.057812000	1.519540000	-0.026490000			1643.1654	1670.5167	3108.3731
	7	1.108318000	-0.206754000	-0.090919000			3266.2539	3527.8031	3628.7614
	1	1.086204000	-1.189825000	0.136396000					
	1	1.843743000	0.265814000	0.413855000					
IM1_cis (C_1)	6	-1.279957000	-0.295965000	0.024317000	-133.301094	0.054880	***351.4663***	469.9626	525.4230
	1	-2.331077000	-0.079127000	-0.002184000			665.3285	789.1309	825.3711
	6	-0.147748000	0.367689000	-0.004379000			1083.0663	1215.9473	1317.0054
	1	-0.175952000	1.459223000	-0.023532000			1642.9377	1688.2999	3047.6907
	7	1.144913000	-0.152904000	-0.088975000			3285.8592	3539.9236	3642.3267
	1	1.213029000	-1.132841000	0.141550000					
	1	1.845842000	0.392733000	0.387359000					
IM2_cis (C_s)	6	0.000000000	0.413884000	0.000000000	-133.339236	0.055049	492.1578	***532.4970***	673.1736
	1	0.133548000	1.498806000	0.000000000			834.1530	1000.4143	1051.9201
	7	-1.189911000	-0.138045000	0.000000000			1111.7891	1249.1466	1353.7140
	1	-1.911790000	0.582900000	0.000000000			1462.2551	1513.9427	3039.4325
	6	1.151834000	-0.370857000	0.000000000			3150.8689	3256.2399	3442.0992
	1	2.135699000	0.074422000	0.000000000					
	1	1.060912000	-1.447977000	0.000000000					

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
IM2_trans	6	0.000000000	0.446588000	0.000000000	-133.338363	0.055021	***491.3708***	495.7911	686.5832
(C_s)	1	0.163865000	1.523480000	0.000000000			837.4915	990.8775	1077.9686
	7	-1.253587000	0.060706000	0.000000000			1143.3314	1237.4744	1380.9563
	1	-1.296837000	-0.962740000	0.000000000			1454.5994	1499.7807	3095.7540
	6	1.126453000	-0.375241000	0.000000000			3135.2269	3236.5585	3387.5603
	1	2.124527000	0.039489000	0.000000000					
	1	1.024837000	-1.453255000	0.000000000					
IM3	6	-1.276349000	0.105004000	-0.015145000	-133.310134	0.054855	***249.8432***	383.8476	489.4761
(C_1)	1	-2.145876000	-0.478551000	0.252932000			666.3011	840.3149	987.4750
	6	-0.064336000	-0.409811000	0.036637000			1080.7826	1190.5188	1426.1667
	1	-1.448970000	1.122573000	-0.364433000			1636.6704	1711.5499	3062.2008
	7	1.179934000	0.122313000	-0.048385000			3191.9137	3528.4798	3633.0798
	1	1.933787000	-0.491083000	-0.311163000					
	1	1.445631000	0.819715000	0.632405000					
IM4	6	-0.192149000	-0.402819000	-0.000026000	-133.333301	0.054909	***150.4621***	434.7220	669.2686
(C_1)	7	-1.246804000	0.237520000	-0.000002000			900.5396	975.5665	1041.8215
	1	-2.119513000	-0.287965000	0.000054000			1169.9517	1383.6194	1461.1371
	6	1.212363000	0.079857000	-0.000005000			1466.0664	1827.8587	3004.5789
	1	1.257501000	1.173048000	-0.000700000			3085.0088	3097.1824	3434.3901
	1	1.733903000	-0.304383000	0.877367000					
	1	1.734457000	-0.305567000	-0.876517000					
H	1	0.000000000	0.000000000	0.000000000	-0.499994	0.000000			
CH_2=CH=NH	6	1.247479000	0.000082000	0.014492000	-132.754859	0.043657	421.8141	486.7953	713.5278
(C_s)	1	1.793789000	-0.930924000	0.024729000			900.3438	1001.9827	1032.4863
	6	-0.058761000	-0.000453000	0.003620000			1166.2780	1439.3138	2121.7789
	1	1.792759000	0.931678000	0.026096000			3163.1084	3247.7176	3467.9683
	7	-1.271175000	0.000394000	-0.127065000					
	1	-1.820629000	-0.001287000	0.729960000					
CH≡C-NH_2	6	-1.362373000	0.000002000	0.010913000	-132.732893	0.044191	367.7640	427.0221	491.7885
(C_s)	1	-2.421718000	0.000059000	0.024433000			615.0623	699.2190	1082.6439
	6	-0.161536000	-0.000033000	-0.001886000			1202.4095	1640.4080	2244.7294
	1	1.632940000	-0.835434000	0.261981000			3483.8810	3530.1810	3612.3076
	7	1.185618000	0.000018000	-0.086099000					

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
	1	1.632905000	0.835434000	0.262120000					
CH_3CN (C_{3v})	6	0.280682000	-0.000012000	-0.000076000	-132.799170	0.045171	380.3381	380.4888	928.0983
	7	1.430292000	0.000002000	0.000035000			1062.3344	1062.4953	1414.3748
	6	-1.174159000	0.000003000	0.000017000			1475.1759	1475.4713	2367.5481
	1	-1.550379000	-0.401247000	0.940432000			3048.7785	3116.2521	3116.4719
	1	-1.550334000	1.015060000	-0.122662000			(362; 362; 920; 1041; 1041; 1385; 1448; 1448; 2267; 2954;		
	1	-1.550465000	-0.613767000	-0.817664000			3009; 3009)[1]		
C_2H ($C_{\infty v}$)	6	0.000000000	0.000000000	-0.471812000	-76.630558	0.013988	294.0731	294.0732	2095.1101
	1	0.000000000	0.000000000	-1.534690000			3456.8967		
	6	0.000000000	0.000000000	0.727593000			(371.6; 371.6; 1840.6; 3298.9)[2]		
NH_3 (C_{3v})	7	0.000000000	0.000000000	0.115415000	-56.586361	0.034252	1064.1054	1676.5984	1676.5987
	1	0.000000000	0.937940000	-0.269302000			3461.4409	3577.9857	3577.9859
	1	-0.812280000	-0.468970000	-0.269302000			(950; 1627; 1627; 3337; 3444; 3444)[1]		
	1	0.812280000	-0.468970000	-0.269302000					

[a] Frequency modes in *italic* and **bold** corresponds to the internal rotations. Frequencies in the parentheses ("( )") are taken from experimental studies.

Table S2: High-pressure rate constants for the C_2H_2 + NH_2 system calculated at W1U method[a].

No.	Reaction	$k^{\infty}(T) = A \times T^n \times \exp(-E_a/RT)$			$k^{\infty}(T)$ at 300 K [b]
		A [b]	n	E_a/R (K)	
1	C_2H_2 + NH_2 → IM1_trans (via TS1)	1.95×10^{-19}	2.40	2.34×10^{3}	6.81×10^{-17} $(6.56\times10^{-17})^4$
	(reverse reaction)	2.07×10^{10}	1.18	1.47×10^{4}	9.01×10^{-9}
2	IM1_trans → IM3 (via TS2)	3.60×10^{-18}	9.08	1.35×10^{4}	3.04×10^{-15}
	(reverse reaction)	1.03×10^{-19}	9.50	1.69×10^{4}	1.06×10^{-20}
3	IM3 → P1 (via TS3)	7.73×10^{6}	1.93	1.67×10^{4}	3.12×10^{-13}
	(reverse reaction)	1.25×10^{-16}	1.69	2.44×10^{3}	5.76×10^{-16}
4	IM1_trans → IM1_cis (via TS4)	1.87×10^{12}	0.32	1.16×10^{3}	2.42×10^{11}
	(reverse reaction)	8.98×10^{11}	0.42	1.84×10^{4}	2.14×10^{10}
5	IM1_cis → P2 (via TS5)	1.59×10^{10}	1.26	2.03×10^{4}	9.98×10^{-17}
	(reverse reaction)	2.86×10^{-14}	1.16	1.53×10^{3}	1.32×10^{-13}
6	IM1_cis → IM2_cis (via TS6)	1.20×10^{-25}	11.0	9.36×10^{3}	8.22×10^{-12}
	(reverse reaction)	5.18×10^{-25}	11.1	2.16×10^{4}	9.78×10^{-29}
7	IM3 → IM1_cis (via TS7)	6.10×10^{2}	3.07	2.01×10^{4}	2.02×10^{-19}
	(reverse reaction)	1.02×10^{4}	2.74	1.73×10^{4}	5.15×10^{-15}
8	IM2_cis → P1 (via TS8)	1.32×10^{9}	1.64	2.55×10^{4}	1.95×10^{-24}
	(reverse reaction)	2.96×10^{-16}	1.68	1.77×10^{3}	1.19×10^{-14}
9	IM2_cis → IM2_trans (via TS9)	1.73×10^{6}	2.21	1.31×10^{4}	6.53×10^{-8}
	(reverse reaction)	1.40×10^{6}	2.23	1.28×10^{4}	1.50×10^{-7}
10	IM2_cis → IM4 (via TS10)	1.70×10^{-27}	11.7	1.64×10^{4}	3.05×10^{-22}
	(reverse reaction)	1.11×10^{-29}	12.3	1.42×10^{4}	9.25×10^{-20}
11	IM2_trans → IM4 (via TS11)	1.05×10^{-30}	12.6	1.73×10^{4}	2.06×10^{-24}
	(reverse reaction)	8.45×10^{-33}	13.2	1.54×10^{4}	2.73×10^{-22}
12	IM4 → P3 (via TS12)	4.54×10^{8}	1.62	1.14×10^{4}	1.37×10^{-4}
	(reverse reaction)	2.28×10^{-15}	1.49	3.32×10^{3}	1.74×10^{-16}
13	C_2H_2 + NH_2 → P4 (via TS_abs)	1.01×10^{-17}	2.07	1.20×10^{4}	6.53×10^{-30}
	(reverse reaction)	2.00×10^{-19}	2.40	-7.43×10^{2}	2.06×10^{-12}

[a] Rate constants are valid for 250−2000 K. [b] Units of [s^{-1}] for first-order reactions and [cm^3 $molecule^{-1}$ s^{-1}] for second-order reactions. This work calculated at composite W1U method including asymmetric Eckart tunneling, HIR treatments and symmetry reactions.

Table S3: $k(T, P)\_{tot}$ (overall rate constants) for the $C_2H_2 + NH_2 \rightarrow$ products, calculated at different pressures.

T (K)	$k(T, P)\_{tot}$ (cm^3/molecule/s)					
	1 torr	100 torr	350 torr	760 torr	7600 torr	76000 torr
250	5.89E-18	8.83E-18	8.93E-18	8.95E-18	8.97E-18	8.98E-18
300	3.22E-17	6.51E-17	6.74E-17	6.80E-17	6.87E-17	6.83E-17
400	1.99E-16	7.81E-16	8.84E-16	9.26E-16	9.61E-16	9.69E-16
500	4.32E-16	3.05E-15	3.98E-15	4.41E-15	5.11E-15	5.27E-15
600	5.75E-16	6.48E-15	9.79E-15	1.16E-14	1.60E-14	1.74E-14
700	7.24E-16	9.54E-15	1.63E-14	2.10E-14	3.52E-14	4.28E-14
800	1.06E-15	1.11E-14	2.12E-14	2.94E-14	6.10E-14	8.44E-14
900	2.29E-15	1.12E-14	2.27E-14	3.31E-14	8.64E-14	1.42E-13
1000	5.25E-15	1.02E-14	1.88E-14	2.91E-14	9.87E-14	2.06E-13
1100	1.19E-14	1.32E-14	1.70E-14	2.24E-14	7.88E-14	2.43E-13
1200	2.40E-14	2.45E-14	2.52E-14	2.81E-14	5.55E-14	2.07E-13
1300	4.45E-14	4.46E-14	4.46E-14	4.68E-14	5.58E-14	1.41E-13
1400	7.80E-14	7.67E-14	7.75E-14	7.87E-14	8.28E-14	1.20E-13
1500	1.27E-13	1.27E-13	1.27E-13	1.26E-13	1.27E-13	1.45E-13
1600	1.98E-13	2.00E-13	1.97E-13	1.99E-13	1.99E-13	2.08E-13
1700	2.94E-13	2.97E-13	2.97E-13	2.98E-13	2.96E-13	3.00E-13
1800	4.32E-13	4.27E-13	4.36E-13	4.32E-13	4.31E-13	4.33E-13
1900	6.09E-13	6.03E-13	6.11E-13	6.07E-13	5.99E-13	5.98E-13
2000	8.29E-13	8.32E-13	8.27E-13	8.16E-13	8.29E-13	8.27E-13

Table S4: T1 diagnostics for the species involved in C_2H_2 + NH_2 reaction computed at CCSD(T)/cc-pVQZ based on the B3LYP/cc-pVTZ+d geometries.

No.	Species	T1 diagnostics
1	C_2H_2	0.01321782
2	NH_2	0.00896154
3	Pre-complex	0.01178331
4	Post-complex	0.04330313
5	TS_abs	**0.05380368**
6	TS1	0.03674252
7	TS2	0.02111373
8	TS3	0.02296102
9	TS4	0.03114341
10	TS5	0.02573060
11	TS6	0.02541486
12	TS7	0.02831653
13	TS8	0.03121704
14	TS9	0.03037410
15	TS10	0.02736871
16	TS11	0.02482530
17	TS12	0.02745000
18	IM1_trans	0.03240451
19	IM1_cis	0.03197558
20	IM2_cis	0.03134199
21	IM2_trans	0.03135945
22	IM3	0.03456314
23	IM4	0.02621243
24	H	0.00000000
25	CH_2=C=NH	0.01482788
26	CH≡C-NH_2	0.01249674
27	CH_3-CN	0.01257055
28	NH_3	0.00697993
29	C_2H	**0.06161988**

Table S5: Detailed kinetic submechanism in NASA format for the reaction C_2H_2 + NH_2.

```
nh2                 N   1H   2         G   300.000  2500.000 1500.000     1
3.09786197E+001-5.80869974E-0024.27200343E-005-1.38198100E-0081.66008466E-012    2
-6.65507990E+003-1.58005028E+0021.84885080E+000-9.75357607E-0041.90034679E-006    3
-1.60102836E-0094.88145238E-0135.02798167E+0033.02015340E+000                    4
c2h2                C   2H   2         G   300.000  2500.000 1500.000     1
9.09914958E+001-1.96550770E-0011.62240222E-004-5.89024426E-0087.92482452E-012    2
-2.53230506E+004-4.68031180E+0021.49205542E+0006.17451208E-003-1.23898918E-005    3
9.91993784E-009-2.73892860E-0126.39663254E+0031.49301670E+001                    4
im1_trans           C   2H   4N   1     G   300.000  2500.000 1500.000     1
2.12326681E+002-4.25689724E-0013.23666959E-004-1.08207365E-0071.34170712E-011    2
-7.18056602E+004-1.12050326E+0034.21568470E+0001.01040052E-003-4.06490110E-007    3
-1.03713068E-0097.01499713E-0138.63764954E+0032.15555483E+001                    4
im1_cis             C   2H   4N   1     G   300.000  2500.000 1500.000     1
2.88680792E+000-2.23544706E-0034.58246041E-006-2.11675610E-0092.95258311E-013    2
1.04583494E+0043.22450180E+0014.17852977E+0001.40964706E-003-2.44203743E-006    3
2.09713955E-009-7.11966468E-0138.47153553E+0032.17356057E+001                    4
im2_cis             C   2H   4N   1     G   300.000  2500.000 1500.000     1
1.55453657E+001-2.21472984E-0021.56209534E-005-4.54382529E-0094.49882929E-013    2
1.44016460E+003-4.07514276E+0013.96184233E+0002.80871421E-003-5.07290606E-006    3
3.94771170E-009-1.08873324E-0125.60444457E+0032.21980200E+001                    4
im2_trans           C   2H   4N   1     G   300.000  2500.000 1500.000     1
-1.58634849E+0014.18970296E-002-3.27527796E-0051.15150103E-008-1.52924239E-012    2
1.36623976E+0041.31747498E+0023.90340040E+0003.72985595E-003-7.59121665E-006    3
6.34523676E-009-1.86412157E-0125.66298388E+0032.23505682E+001                    4
im3                 C   2H   4N   1     G   300.000  2500.000 1500.000     1
-1.41992609E+0023.13146661E-001-2.48631899E-0048.66996243E-008-1.11927500E-011    2
6.21268314E+0048.18227507E+0023.55995748E+0005.48768887E-003-1.18900850E-005    3
1.05568099E-008-3.25400050E-0127.85617374E+0032.45127275E+001                    4
im4           C   2N   1H   4     G   300.000  2500.000 1500.000     1
1.39657640E+002-2.88226577E-0012.27859475E-004-7.91633659E-0081.01974031E-011    2
-4.42026494E+004-7.16465012E+0023.81285450E+0004.08685153E-003-8.87339942E-006    3
7.52701034E-009-2.17103803E-0126.09949328E+0032.29768582E+001                    4
ts1                 N   1H   4C   2     G   300.000  2500.000 1500.000     1
-3.26816759E+0026.83736293E-001-5.25091997E-0041.77746805E-007-2.23859819E-011    2
1.39362074E+0051.83413137E+0033.56215887E+0004.50197999E-003-9.02984309E-006    3
7.68706447E-009-2.37061069E-0121.21574142E+0042.22386396E+001                    4
ts2                 C   2H   4N   1     G   300.000  2500.000 1500.000     1
2.64724972E+002-5.52958536E-0014.35906810E-004-1.51195809E-0071.94686525E-011    2
-8.35908063E+004-1.40125415E+0035.15624801E+000-5.42109369E-0031.11801912E-005    3
-9.37138948E-0092.72502814E-0121.35293713E+0041.51770862E+001                    4
ts3                 C   2H   4N   1     G   300.000  2500.000 1500.000     1
-1.24963959E+0022.60654771E-001-1.94801255E-0046.40281181E-008-7.81757263E-012    2
6.24990694E+0047.33081929E+0024.29545875E+0004.99183563E-004-1.93476907E-006    3
2.29651098E-009-7.94965163E-0131.18638552E+0042.16575042E+001                    4
ts4                 C   2H   4N   1     G   300.000  2500.000 1500.000     1
2.37834879E+002-4.72312608E-0013.54454689E-004-1.17015144E-0071.43378629E-011    2
-8.25828739E+004-1.26620940E+0034.73755600E+000-3.64082241E-0038.47714622E-006    3
-7.67230788E-0092.35952565E-0128.82562763E+0031.68414816E+001                    4
```

ts5 C 2H 4N 1 G 300.000 2500.000 1500.000 1
2.42347452E+002-4.82325465E-0013.61620421E-004-1.19008253E-0071.45099756E-011 2
-7.95416553E+004-1.28947202E+0035.20356800E+000-4.91396232E-0038.21995130E-006 3
-5.49246485E-0091.24455050E-0121.31260448E+0041.53455687E+001 4
ts6 C 2H 4N 1 G 300.000 2500.000 1500.000 1
-5.69254379E+0019.76836905E-002-5.08972703E-0058.45857628E-0091.01725323E-013 2
4.13684434E+0043.70253157E+0026.02825523E+000-9.71024971E-0031.81297057E-005 3
-1.32980226E-0083.29173744E-0121.28041835E+0041.37416756E+001 4
ts7 C 2H 4N 1 G 300.000 2500.000 1500.000 1
8.25827310E+001-1.65729375E-0011.29439273E-004-4.42127620E-0085.57417057E-012 2
-1.61253102E+004-4.08268105E+0023.47683558E+0004.77473448E-003-1.01220445E-005 3
8.80759677E-009-2.64242717E-0121.31525924E+0042.22881930E+001 4
ts8 C 2H 4N 1 G 300.000 2500.000 1500.000 1
-3.81416577E+0028.26059702E-001-6.55384440E-0042.28457247E-007-2.95311466E-011 2
1.53879235E+0052.12126195E+0036.72179295E+000-1.41542912E-0022.83847136E-005 3
-2.35350273E-0086.82730982E-0121.14090419E+0041.12974927E+001 4
ts9 C 2H 4N 1 G 300.000 2500.000 1500.000 1
-1.21373494E+0022.49402602E-001-1.83522393E-0045.94357478E-008-7.15774414E-012 2
5.90023680E+0047.11976047E+0024.60801827E+000-3.08788925E-0038.05575554E-006 3
-7.66249266E-0092.37898280E-0128.98028961E+0031.72631747E+001 4
ts10 C 2H 4N 1 G 300.000 2500.000 1500.000 1
-1.71925353E+0023.64610761E-001-2.80434758E-0049.50853380E-008-1.19974481E-011 2
7.94183671E+0049.86653324E+0024.72665023E+000-2.82427159E-0035.99836131E-006 3
-4.83712265E-0091.26586808E-0121.18696501E+0041.92882485E+001 4
ts11 C 2H 4N 1 G 300.000 2500.000 1500.000 1
7.65164923E+001-1.30210919E-0018.54117281E-005-2.40890181E-0082.45560109E-012 2
-1.87834938E+004-3.83748282E+0025.16325064E+000-4.73670091E-0038.64684011E-006 3
-6.40541903E-0091.66896103E-0121.22678852E+0041.73279390E+001 4
ts12 C 2N 1H 4 G 300.000 2500.000 1500.000 1
1.15505364E+001-1.86777357E-0021.74725360E-005-7.24658666E-0091.11984990E-012 2
6.69737036E+003-1.91993084E+0014.41696551E+000-2.39870566E-0036.81946354E-006 3
-6.89141337E-0092.22008128E-0128.86398310E+0031.86880359E+001 4
ts_abs C 2H 4N 1 G 300.000 2500.000 1500.000 1
1.50092994E+002-2.95137747E-0012.17255464E-004-6.91139632E-0088.03383976E-012 2
-4.15780591E+004-7.77893913E+0026.24280268E+000-1.34779445E-0022.87256579E-005 3
-2.30948572E-0086.07465734E-0121.39247269E+0041.42729221E+001 4
ch2cnh C 2H 3N 1 G 300.000 2500.000 1500.000 1
1.01756086E+002-2.03546333E-0011.57350257E-004-5.36540649E-0086.81266470E-012 2
-3.23510638E+004-5.18059722E+0022.89840954E+0004.94965077E-003-8.93733895E-006 3
6.56266835E-009-1.68270982E-0125.13771018E+0032.22432816E+001 4
h H 1 G 300.000 2500.000 1500.000 1
5.81798613E-0013.04299756E-005-2.24587211E-0087.29794003E-012-8.81051484E-016 2
6.09430563E+003-7.42447376E-0035.96967320E-0018.73608570E-007-1.71249373E-009 3
1.35696245E-012-3.78262084E-0166.08821338E+003-9.13185345E-002 4
chcnh2 C 2H 3N 1 G 300.000 2500.000 1500.000 1
7.75246885E+001-1.42039118E-0011.01040731E-004-3.15205387E-0083.65731734E-012 2
-2.34045482E+004-3.90515972E+0024.48185364E+000-4.04605515E-0039.02566566E-006 3
-8.15918640E-0092.50480499E-0126.62223649E+0031.53701646E+001 4
ch3cn C 2N 1H 3 G 300.000 2500.000 1500.000 1

-2.00503496E+0024.27014473E-001-3.31316818E-0041.13098862E-007-1.43291800E-011 2
7.92214061E+0041.13511231E+0033.73182395E+0001.17428248E-0043.94579790E-007 3
-5.85039019E-0101.99849250E-0131.80241594E+0031.81938699E+001 4
c2h C 2H 1 G 300.000 2500.000 1500.000 1
1.49118181E+002-2.82686570E-0012.00931697E-004-6.26973253E-0087.24308427E-012 2
-4.47477742E+004-8.11088646E+0023.30461713E+000-8.30820627E-0031.54781327E-005 3
-1.19465191E-0083.27855817E-0121.57286776E+0042.73406806E-001 4
nh3 N 1H 3 G 300.000 2500.000 1500.000 1
-3.27504935E+0017.24546826E-002-5.52651161E-0051.84696205E-008-2.28185006E-012 2
1.18459103E+0042.00163983E+0022.31988386E+0005.53841451E-004-1.31394459E-006 3
1.18812116E-009-3.65770547E-013-1.61429889E+0037.85286751E+000 4
pre-complex N 1H 4C 2 G 300.000 2500.000 1500.000 1
-1.09004952E+0032.25749001E+000-1.72355319E-0035.77502956E-007-7.16929407E-011 2
4.30281725E+0056.02340466E+0038.05555051E+000-1.90688245E-0023.66930807E-005 3
-2.91833704E-0088.09165336E-0121.06186426E+0048.81260319E+000 4
post-complex C 2H 4N 1 G 300.000 2500.000 1500.000 1
-1.87852283E+0034.03829753E+000-3.20810817E-0031.11883563E-006-1.44603190E-010 2
7.08094642E+0051.02713971E+004-2.86110009E+0004.76944599E-002-1.01220547E-004 3
8.28521542E-008-2.28864727E-0111.45379932E+0045.59918768E+001 4

Table S6: Reaction energies, ΔE_{rxn}, barrier heights, $\Delta V^{\ddagger}$ (including ZPE corrections), calculated at W1U method between NH_2 radical with several hydrocarbons.

Addition		
Species	ΔE_{rxn} (kcal/mol)	$\Delta V^{\ddagger}$ (kcal/mol)
C_2H_2	-22.6	6.4
C_2H_4	-18.0	4.6
CH_2=CH-CH_3	-7.7	1.9
CH_2=**C**H-CH_3	-7.8	2.0
Abstraction		
C_2H_2	24.8	23.1
C_2H_4	2.8	13.7
C_2H_6	-6.6	10.6

Table S7: Comparison of the barrier height of the channels via **TS1** and **TS_abs** at 0 K (including ZPE) obtained from the different levels of theory. Units are in kcal/mol.

Reaction channel	CCSD(T)/cc-pV(T,Q)Z//			
	B3LYP	M06-2X	UCCSD	UCCSD(T)
TS1	7.0[a] 7.0[b]	7.2[a] 7.4[b]	7.5[a] 7.6[b]	7.5[a] 7.6[b]
TS_abs	24.1[a] 24.8[b]	23.7[a] 24.2[b]	24.0[a] 24.5[b]	N/A[a] 24.8[b]

[a],[b] with the optimization and frequency calculations obtained at the basis sets, cc-pVTZ+d and cc-pVDZ, respectively.

Table S8: Comparison of calculated thermodynamic properties of all structures related to the title reaction with literature data. Unit: $\Delta_f H^{298\,K}$ in kcal·mol^{-1}, $S^{298\,K}$ in cal·mol^{-1}·K^{-1} (NIST = Webbook NIST, webbook.nist.gov, ATcT = Active Thermochemical Tables[5,6][a]).

Species	Method	$\Delta_f H^{298\,K}$	$S^{298\,K}$
C_2H_2	*Ab initio*[b] ATcT NIST	54.6 54.5 (54.3 ± 0.2)[7]; 54.2[8]	47.9 48.0 48.0[8]
NH_2	*Ab initio*[b] ATcT NIST	44.3 45.1 45.5[8]	46.6 46.6 46.5[8]
Pre-complex	*Ab initio*[b]	97.1	75.8
Post-complex	*Ab initio*[b]	117.7	72.3
TS_abs	*Ab initio*[b]	121.2	70.8
TS1	*Ab initio*[b]	104.1	67.6
TS2	*Ab initio*[b]	116.9	66.2
TS3	*Ab initio*[b]	102.0	64.3
TS4	*Ab initio*[b]	77.1	65.7
TS5	*Ab initio*[b]	113.9	68.4
TS6	*Ab initio*[b]	111.4	64.2
TS7	*Ab initio*[b]	112.0	65.6
TS8	*Ab initio*[b]	100.7	65.9
TS9	*Ab initio*[b]	78.2	63.7
TS10	*Ab initio*[b]	101.9	62.1
TS11	*Ab initio*[b]	105.8	62.4
TS12	*Ab initio*[b]	77.1	66.1
IM1_trans	*Ab initio*[b]	74.8	65.5
IM1_cis	*Ab initio*[b]	73.4	65.7
IM2_cis	*Ab initio*[b]	49.2	62.4
IM2_trans	*Ab initio*[b]	49.8	62.6
IM3	*Ab initio*[b]	67.7	66.8
IM4	*Ab initio*[b]	53.2	64.3
H	*Ab initio*[b] ATcT NIST	52.1 52.1 52.1[8]	27.5 27.4 27.4[8]
CH_2=C=NH (ethenimine)	*Ab initio*[b]	44.6	59.8
CH≡C-NH_2 (ethynamine)	*Ab initio*[b]	58.9	60.8
CH_3CN (acetonitrile)	*Ab initio*[b] ATcT NIST	17.7 17.7 (17.7 ± 0.1)[9]; 15.7[10]	58.1 58.1 N/A
NH_3	*Ab initio*[b] ATcT NIST	-11.1 -10.9 -11.0[8]	46.1 46.0 46.1[8]
CH≡C	*Ab initio*[b] ATcT NIST	135.0 135.8 (133.0 ± 2.0)[11] ;114.0[8]	51.8 51.0 49.6[8]

[a] Values collected from Burcat's online database, http://garfield.chem.elte.hu/Burcat/burcat.html (access date: April 2019); [b] This work calculated at W1U level of theory; $\Delta_f H$ was calculated by atomization method.

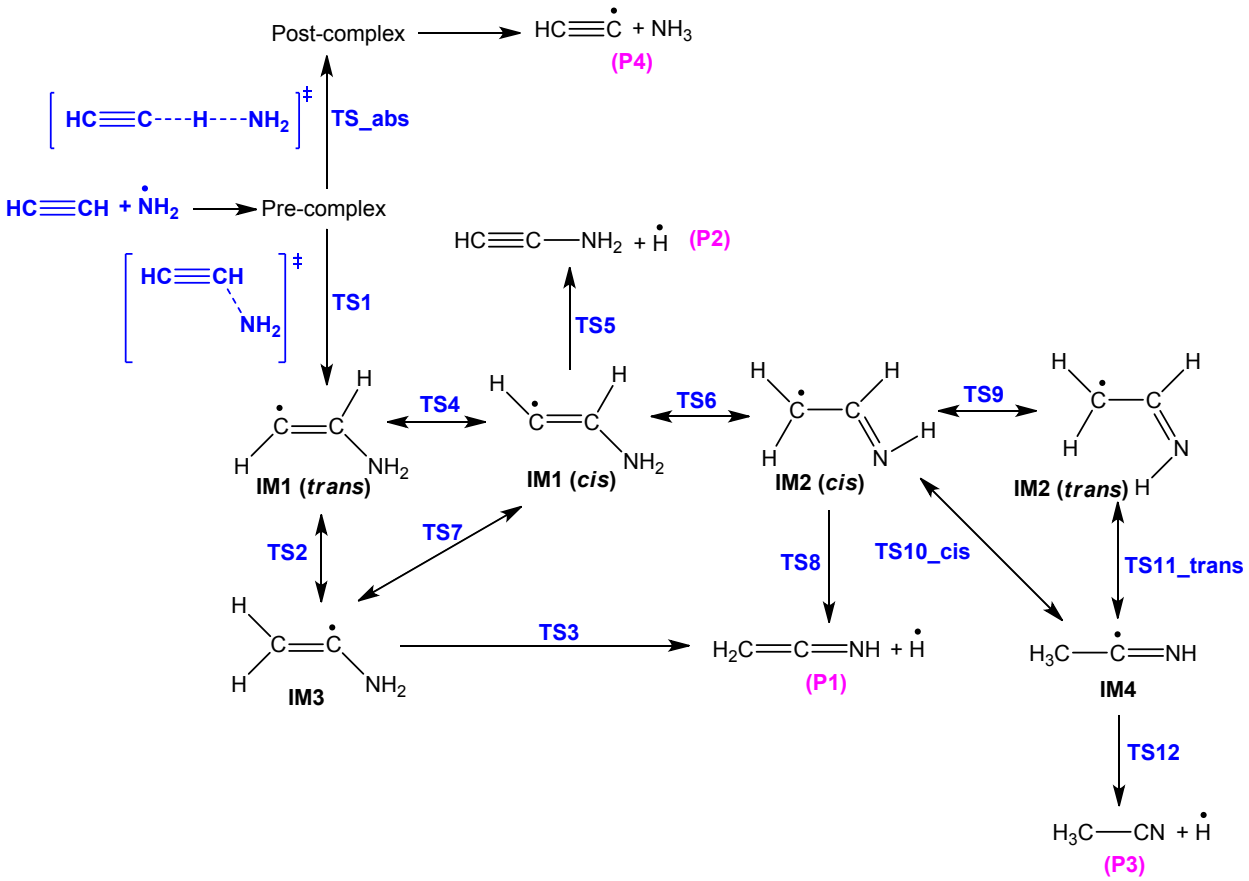
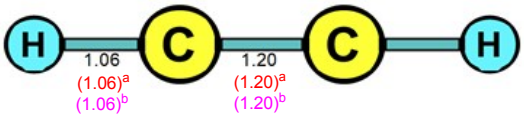
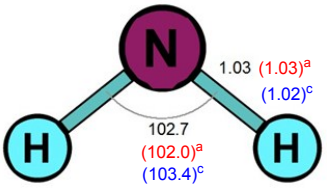


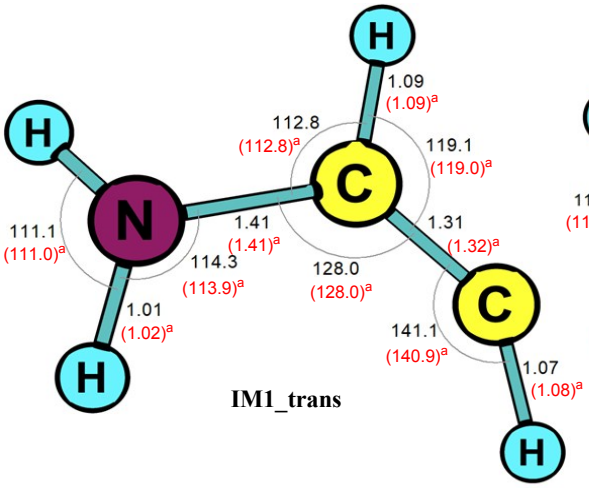
Figure S1: Reaction pathway scheme of the C_2H_2 + NH_2 reaction.



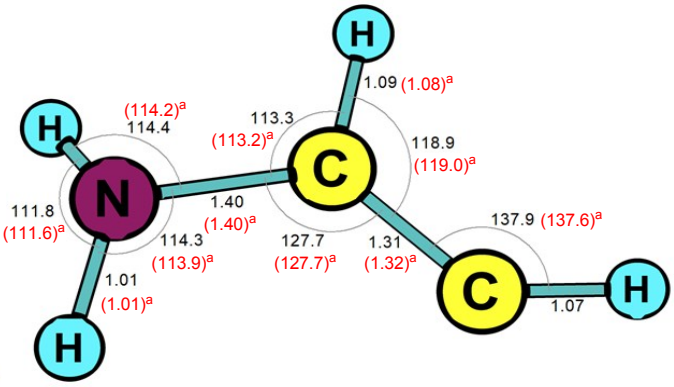
C_2H_2



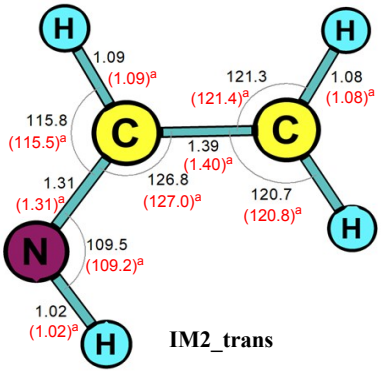
NH_2



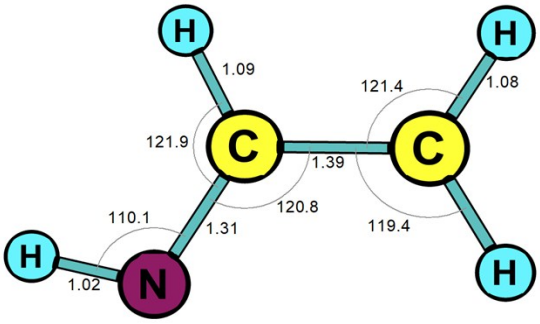
IM1_trans



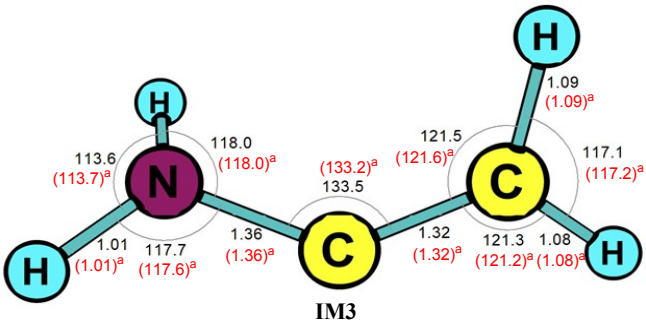
IM1_cis



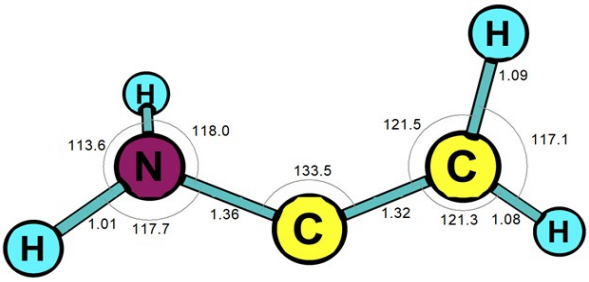
IM2_trans



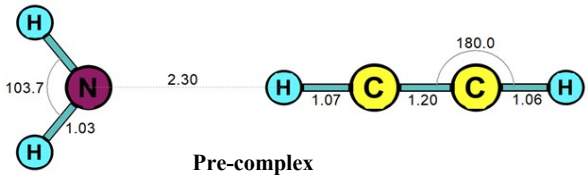
IM2_cis



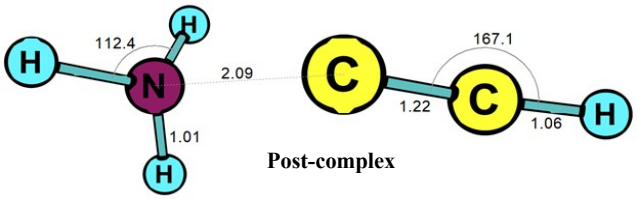
IM3



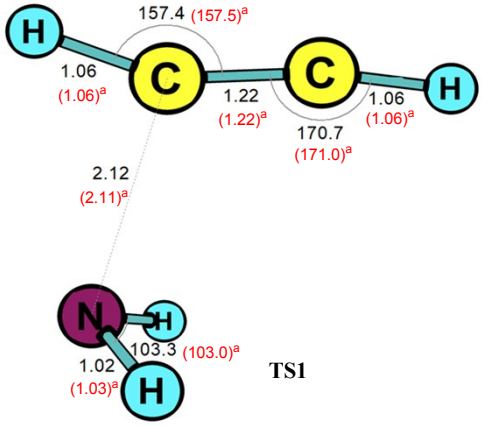
IM4



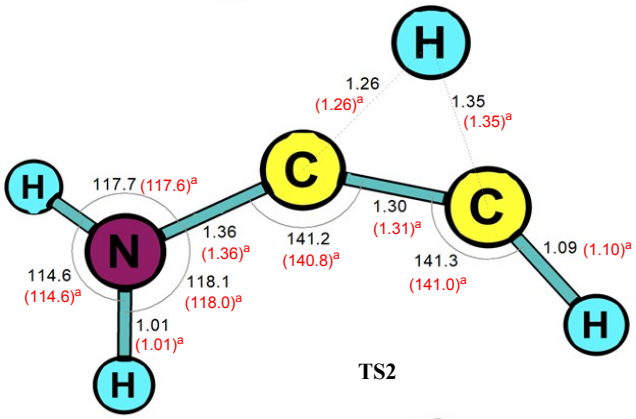
Pre-complex



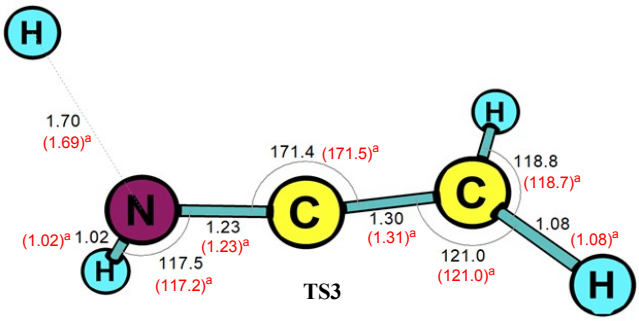
Post-complex



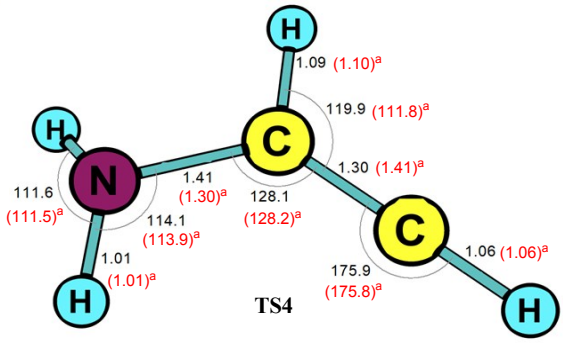
TS1



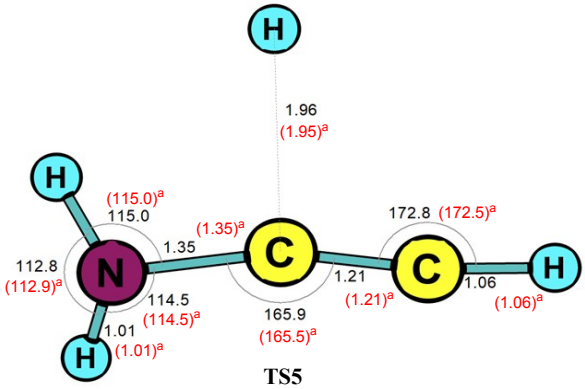
TS2



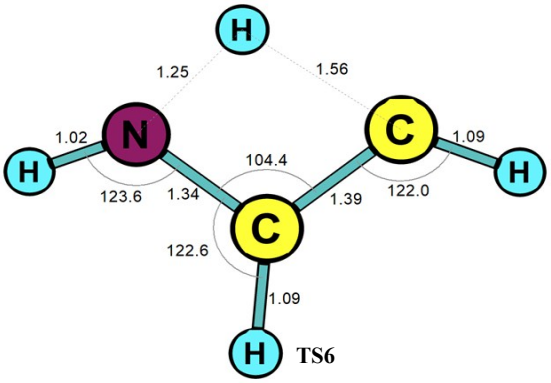
TS3



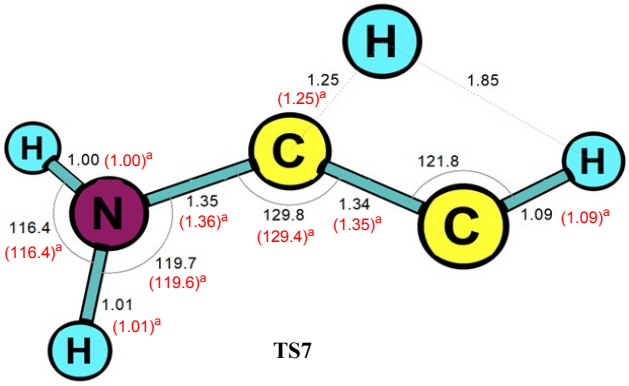
TS4



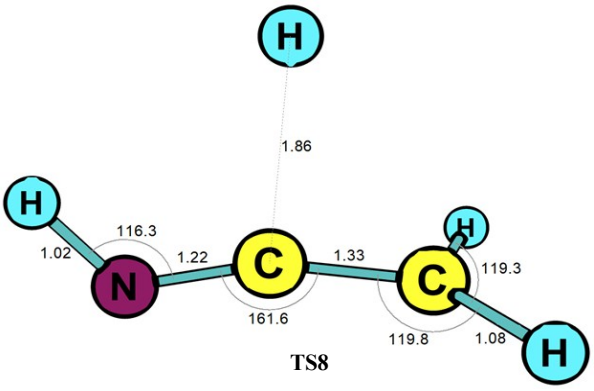
TS5



TS6



TS7



TS8

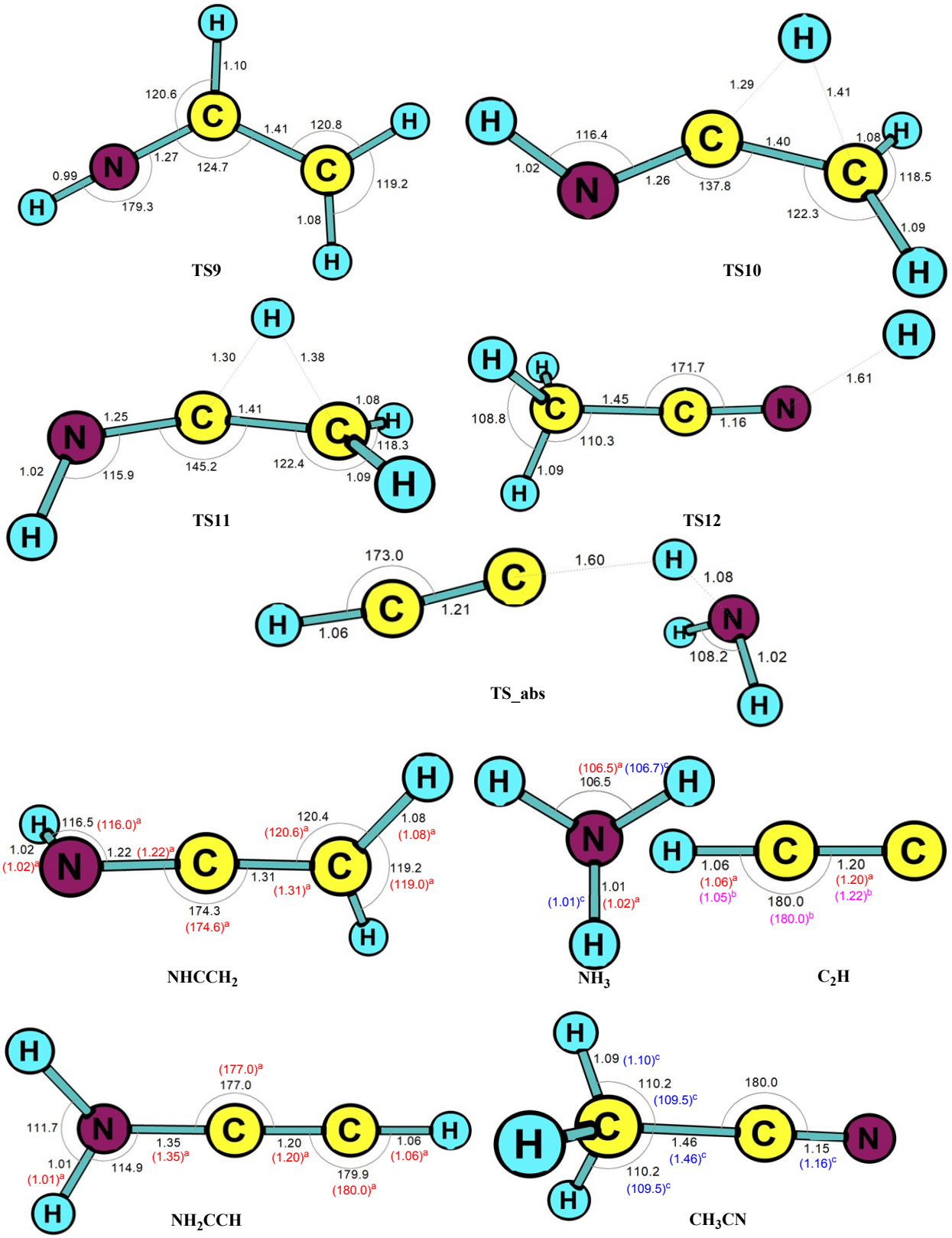


Figure S2: B3LYP/cc-pVTZ+d optimized geometries for the species involved in the C_2H_2 + NH_2 reaction. All structures were obtained for the lowest-energy conformer of a given species. Bond lengths are in Å and angles are in degree (°). [a] From the work of Moskaleva *et al.*[4]; [b] from the work of Kuchitsu[12] and [c] from the work of Herzberg[13].

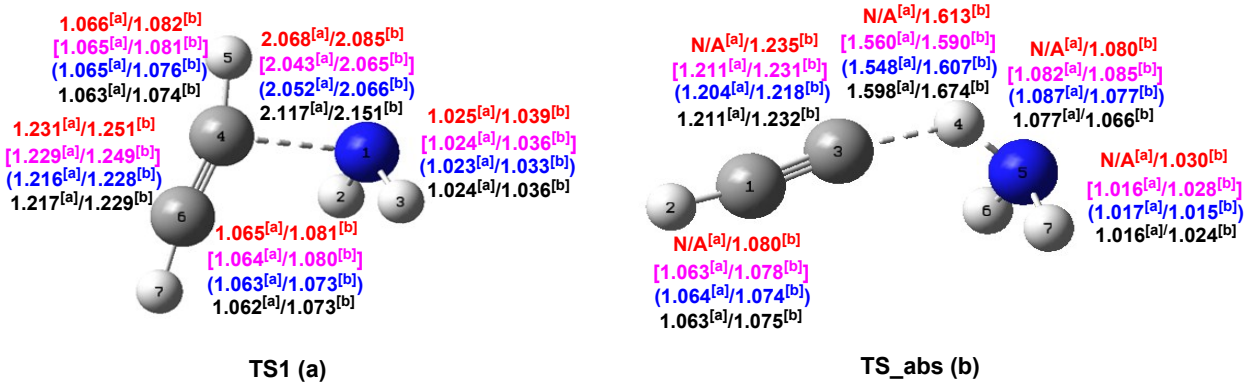
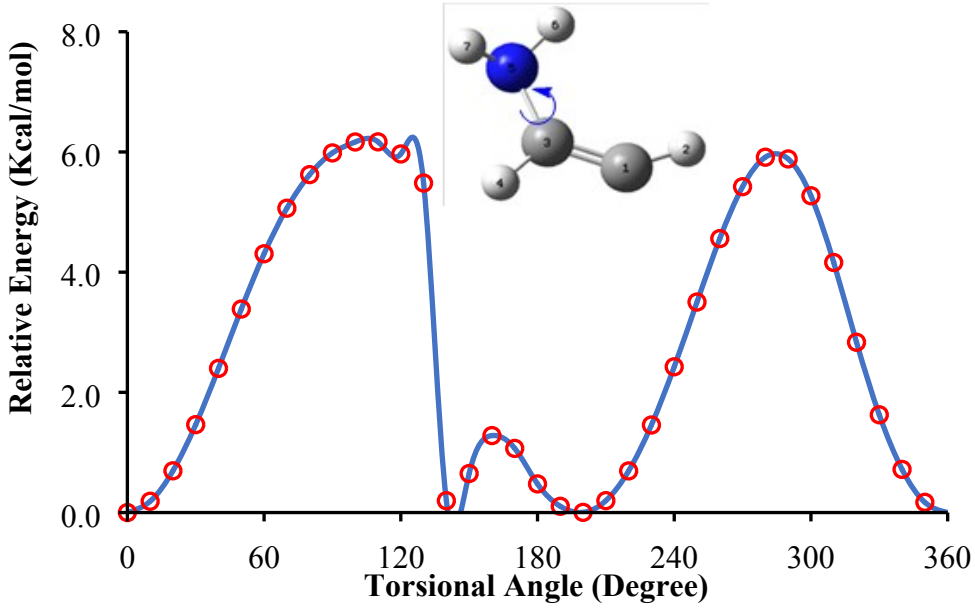
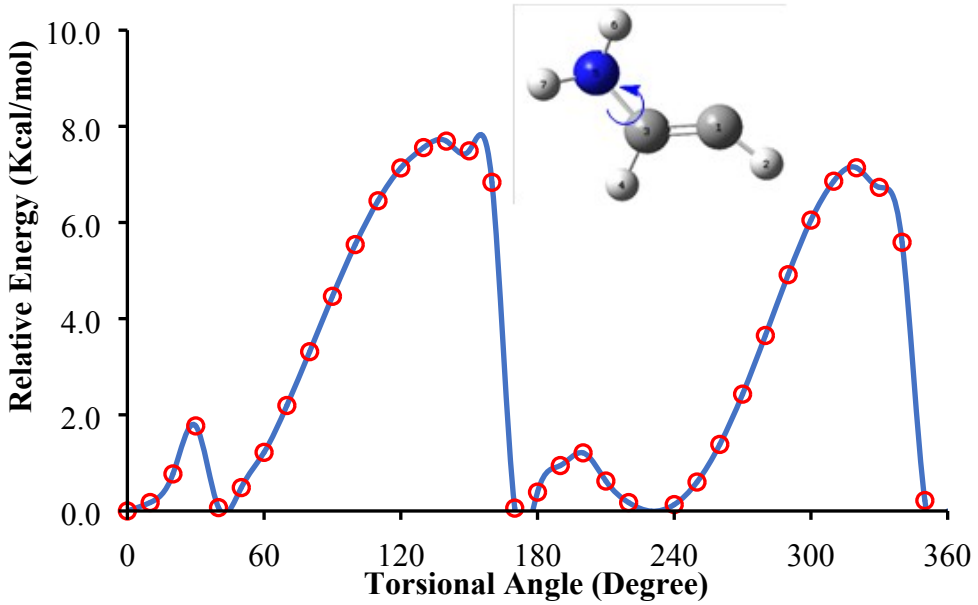
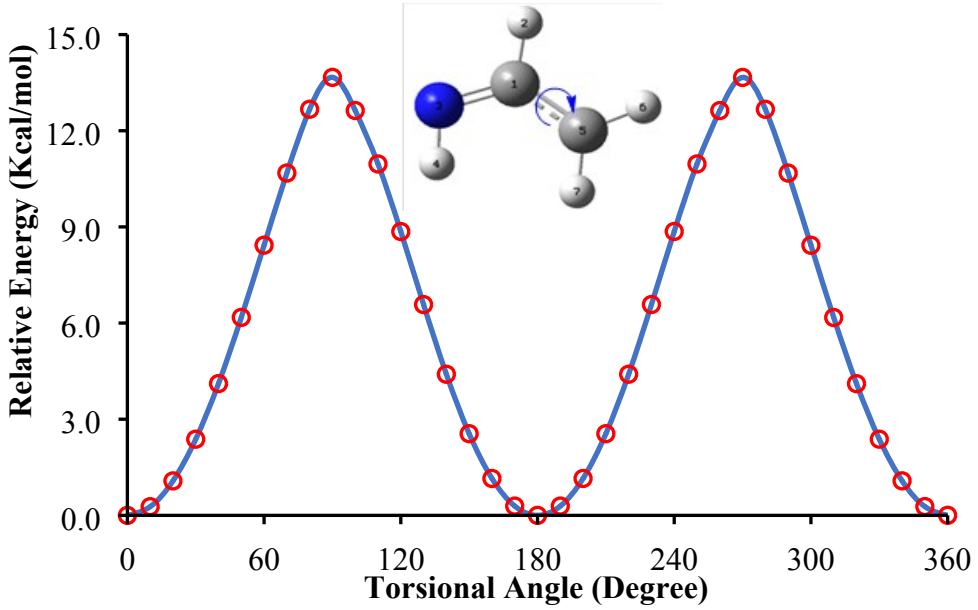
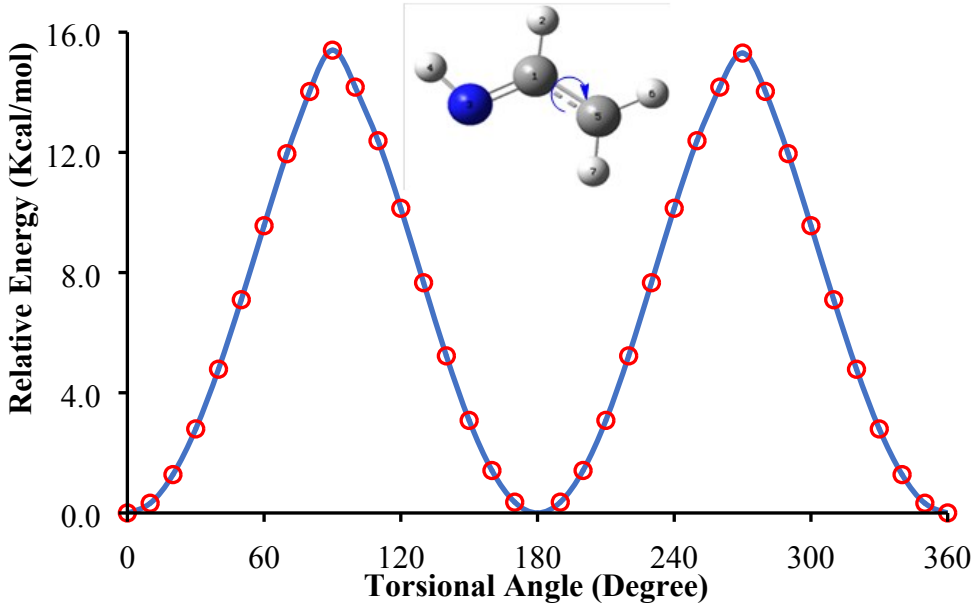
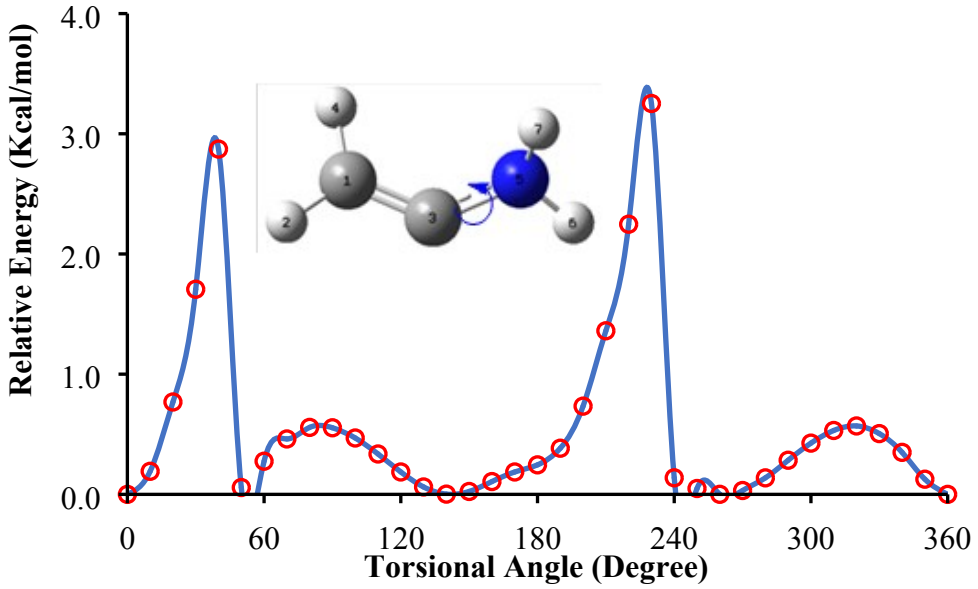
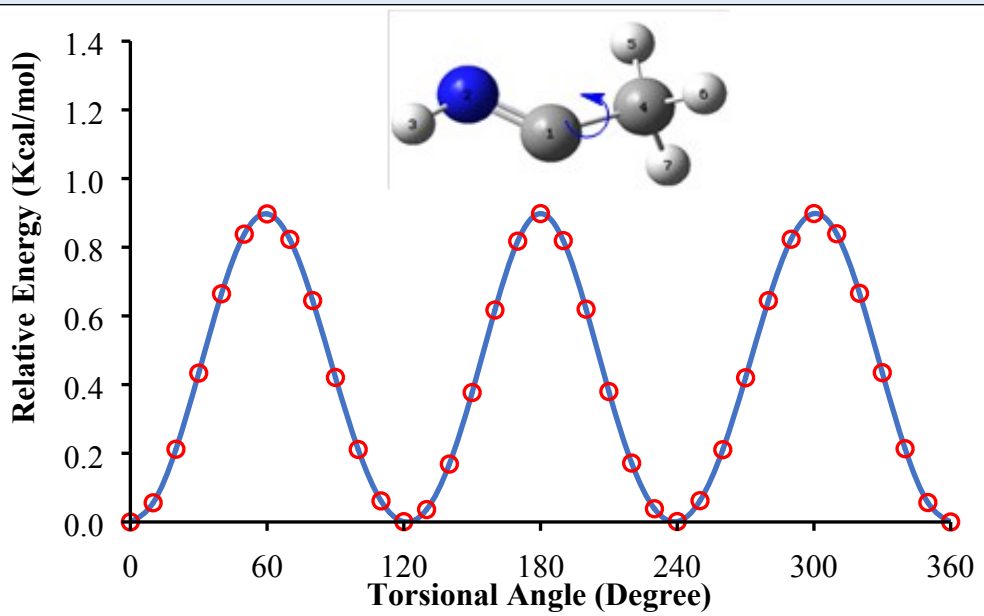
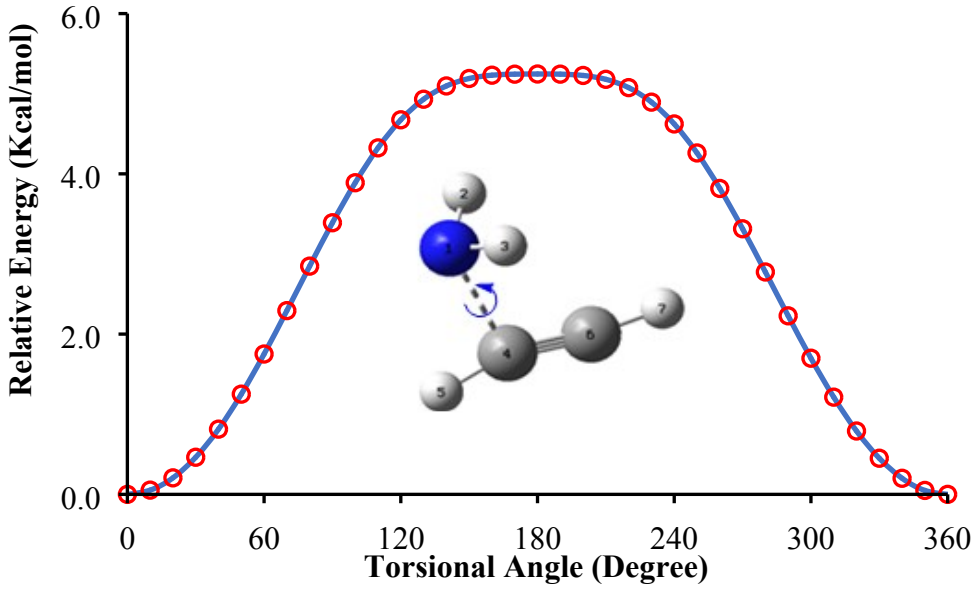


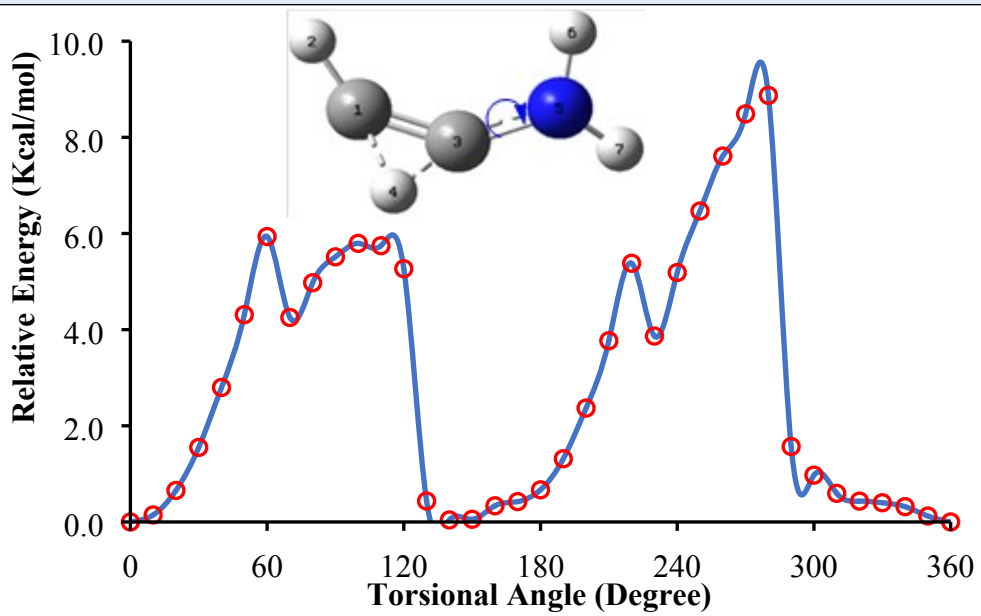
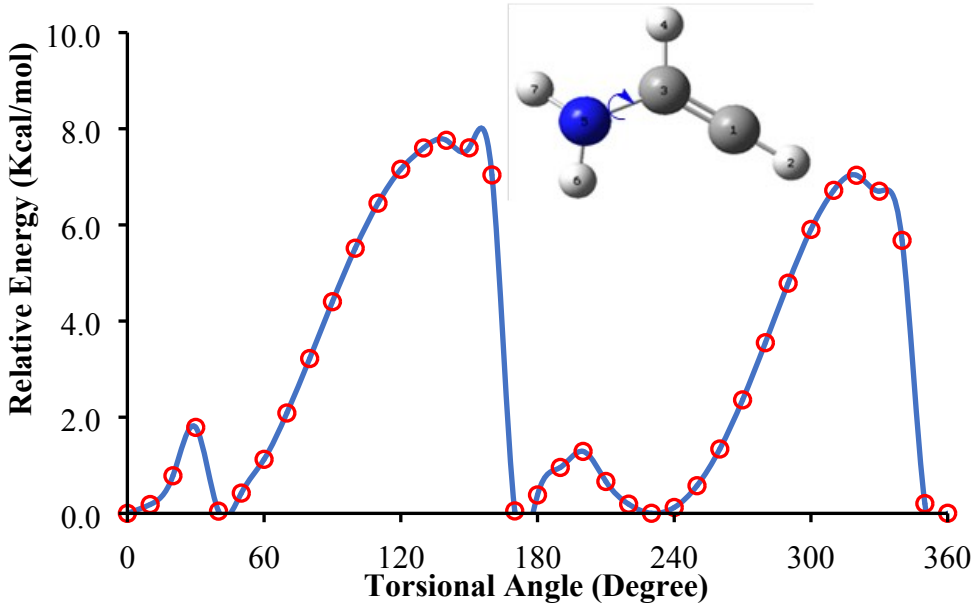
Figure S3: Geometrical parameters of **TS1** and **TS_abs,** optimized at B3LYP (black), M06-2X (blue), UCCSD (pink) and UCCSD(T) (red) with two basis sets, cc-pVTZ+d[a] and cc-pVDZ[b]. Units are in Å.

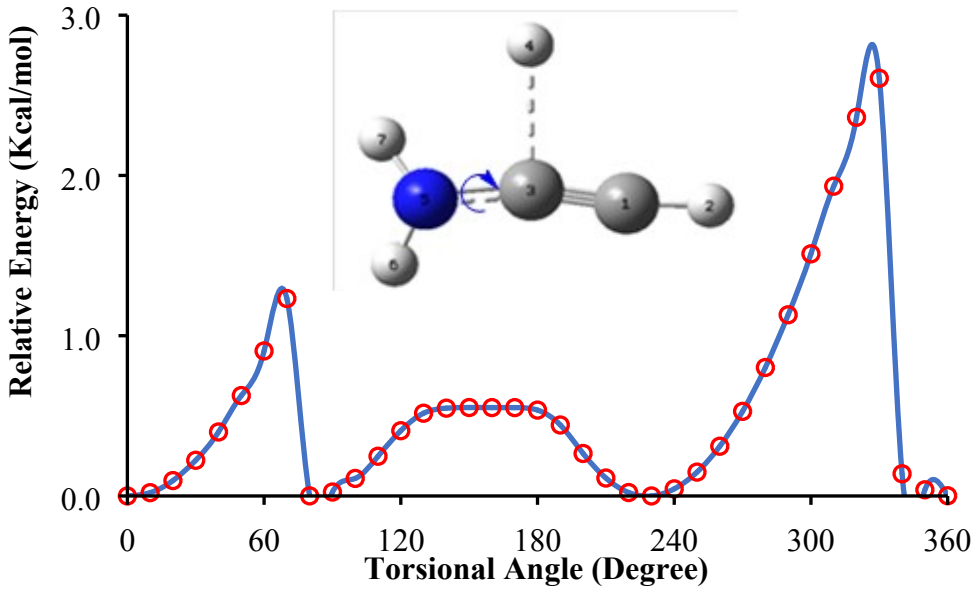
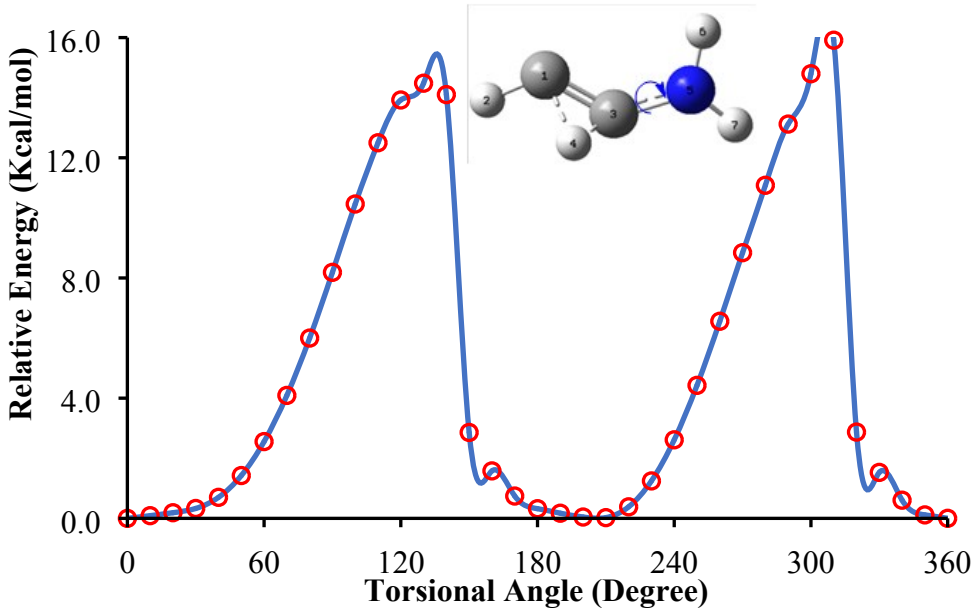
Species	Potential energy surfaces for the internal rotations
IM1_trans	

Species	Potential energy surfaces for the internal rotations
IM1_cis	
IM2_trans	

Species	Potential energy surfaces for the internal rotations
IM2_cis	
IM3	

Species	Potential energy surfaces for the internal rotations
IM4	
TS1	

Species	Potential energy surfaces for the internal rotations
TS2	
TS4	

Species	Potential energy surfaces for the internal rotations
TS5	
TS7	

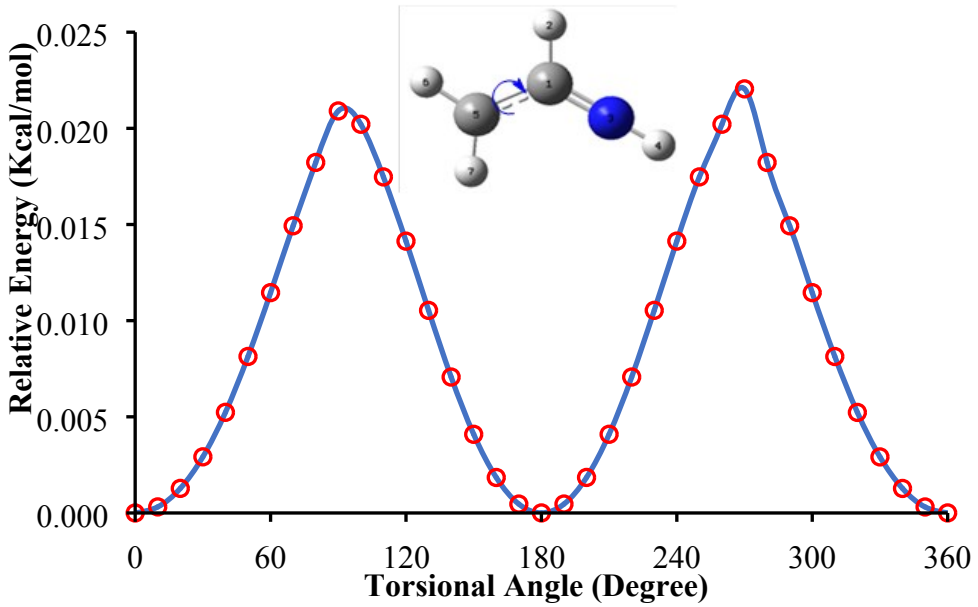
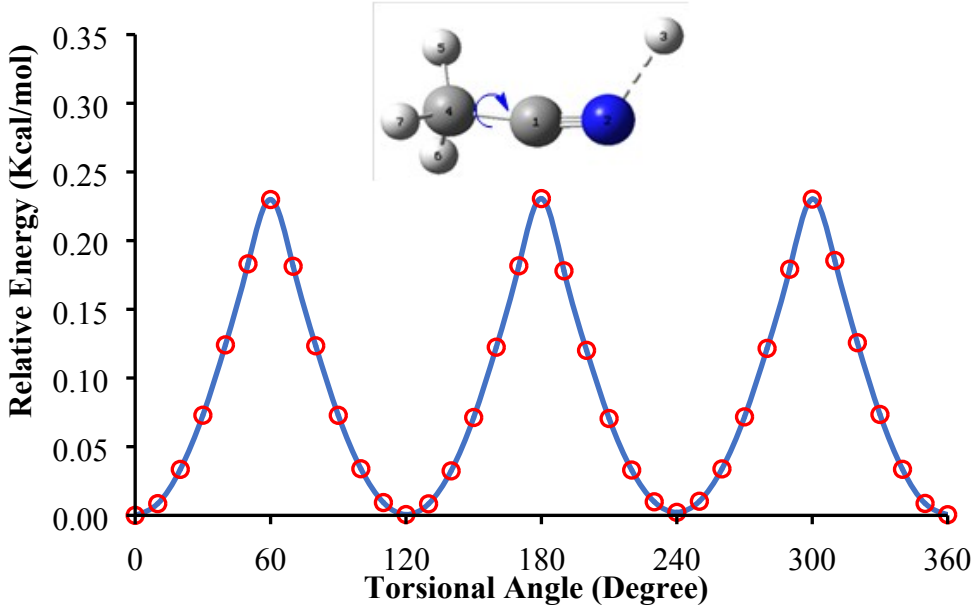
Species	Potential energy surfaces for the internal rotations
TS9	
TS12	

Figure S4: Hindrance potentials for the species involved in the $C_2H_2 + NH_2$ reaction, calculated at B3LYP/6-311G(2d,d,p) level of theory.

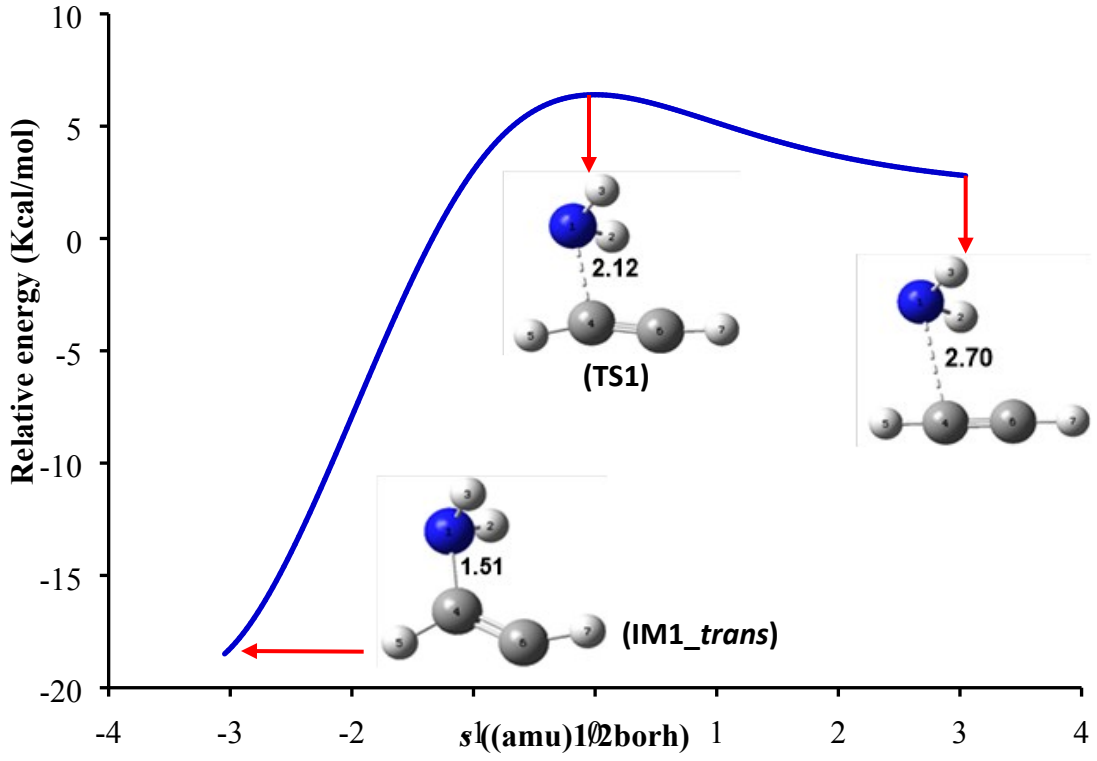
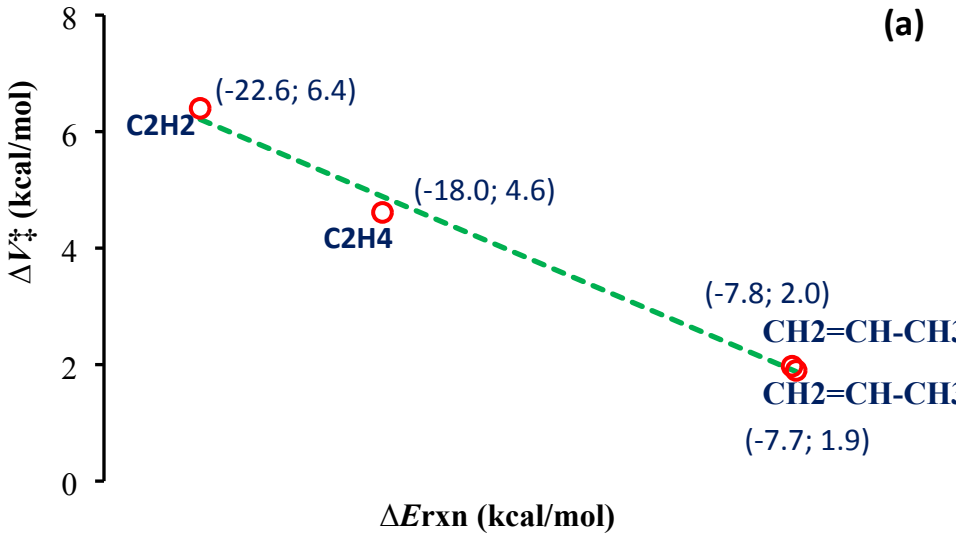


Figure S5: IRC plot for the addition of NH_2 to C_2H_2 (via TS1) calculated at B3LYP/cc-pVTZ+d level of theory. Distances are in Å.



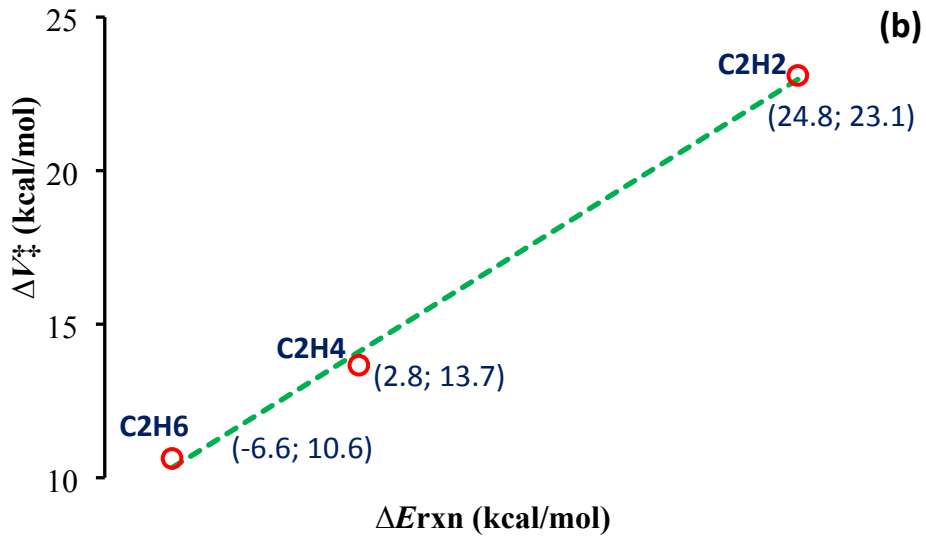


Figure S6: Linear energy relationship (LER) between reaction energy, ΔE_{rxn}, and reaction barrier heights, $\Delta V^{\ddagger}$, calculated at W1U level of theory (0 K): N-addition (**a**) and H-abstraction (**b**) reactions. Zero-point energy corrections were included. Note that there are two different sites, namely, terminal and non-terminal (denoted by the underlined carbons as in Fig. S6a) for propylene.

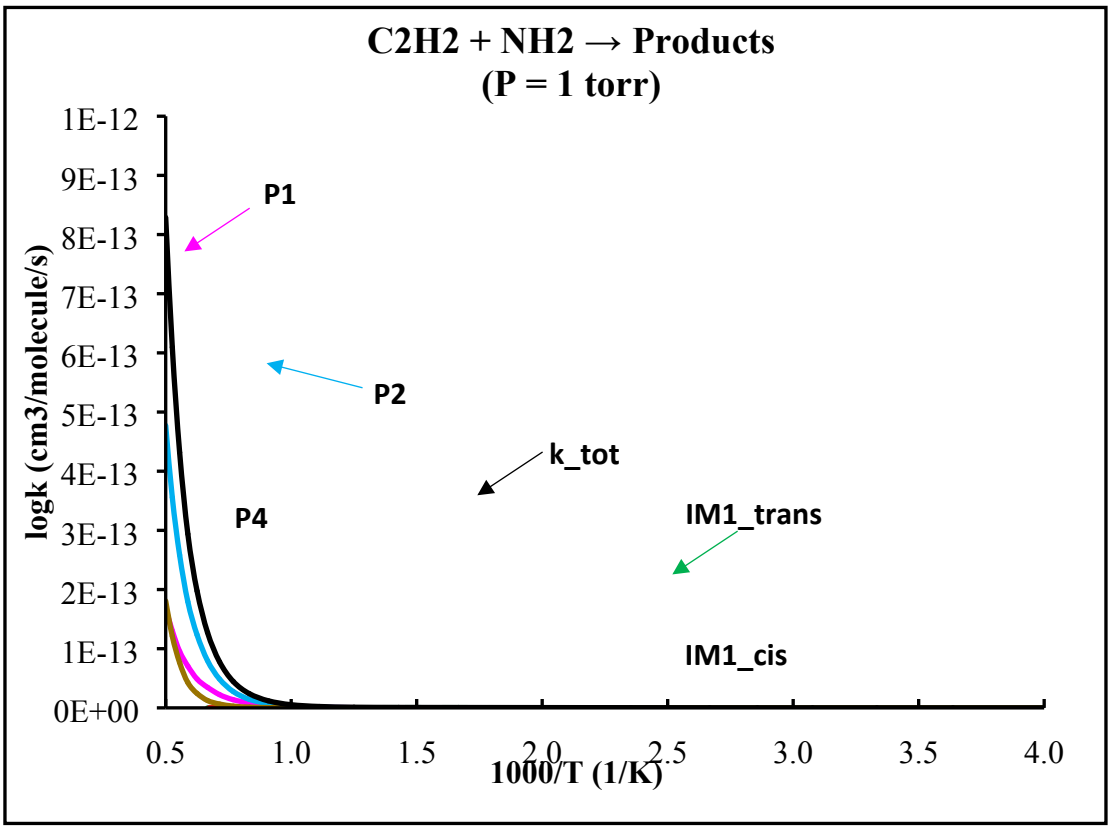
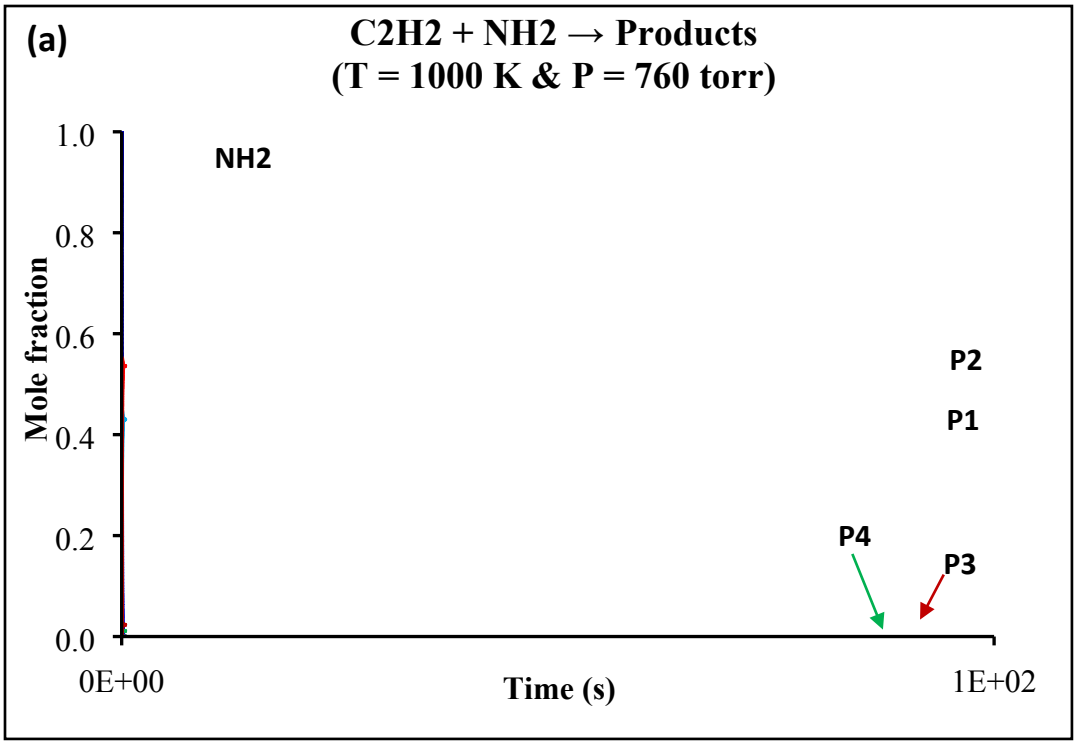
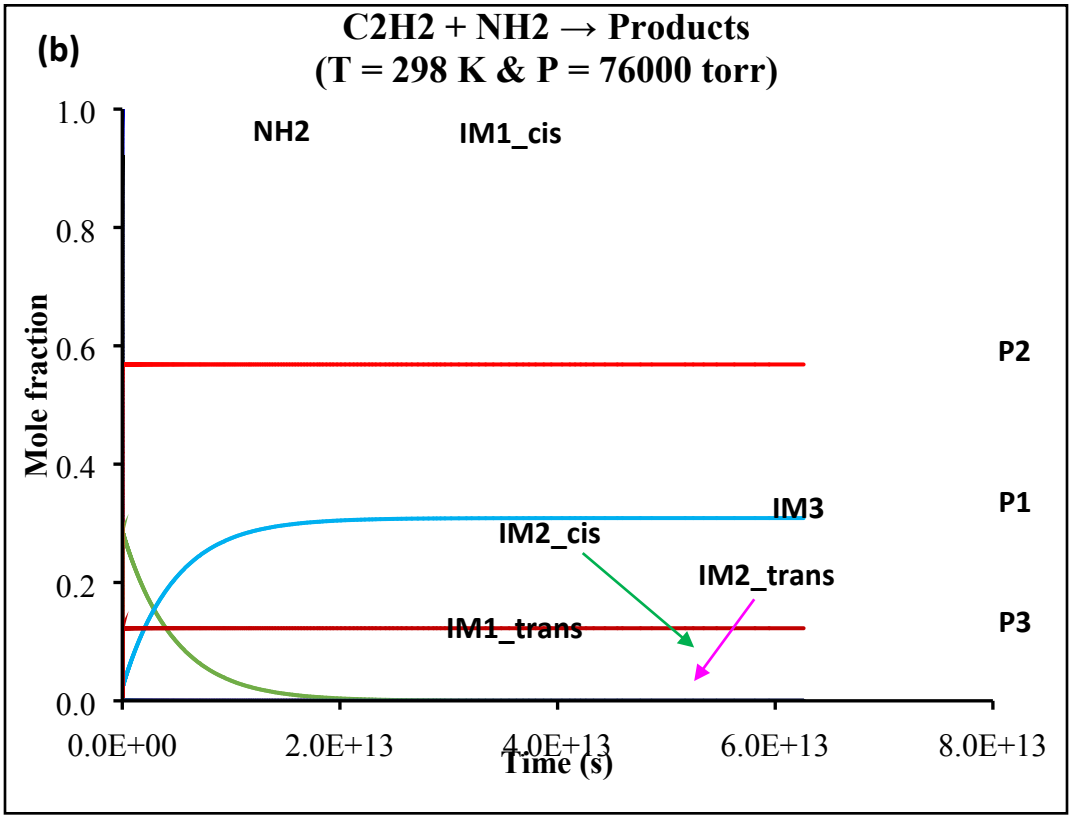


Figure S7: Calculated rate constants, $k(T, P)$, for the $C_2H_2 + NH_2 \rightarrow$ products as a function of temperature at $P = 1$ torr.


(a)
C2H2 + NH2 → Products
(T = 1000 K & P = 760 torr)
Mole fraction
1.0
0.8
0.6
0.4
0.2
0.0
NH2
P2
P1
P4
P3
0E+00
Time (s)
1E+02


(b)
C2H2 + NH2 → Products
(T = 298 K & P = 76000 torr)
Mole fraction
1.0
0.8
0.6
0.4
0.2
0.0
NH2
IM1_cis
P2
IM3
P1
IM2_cis
IM2_trans
IM1_trans
P3
0.0E+00
2.0E+13
4.0E+13
6.0E+13
8.0E+13
Time (s)

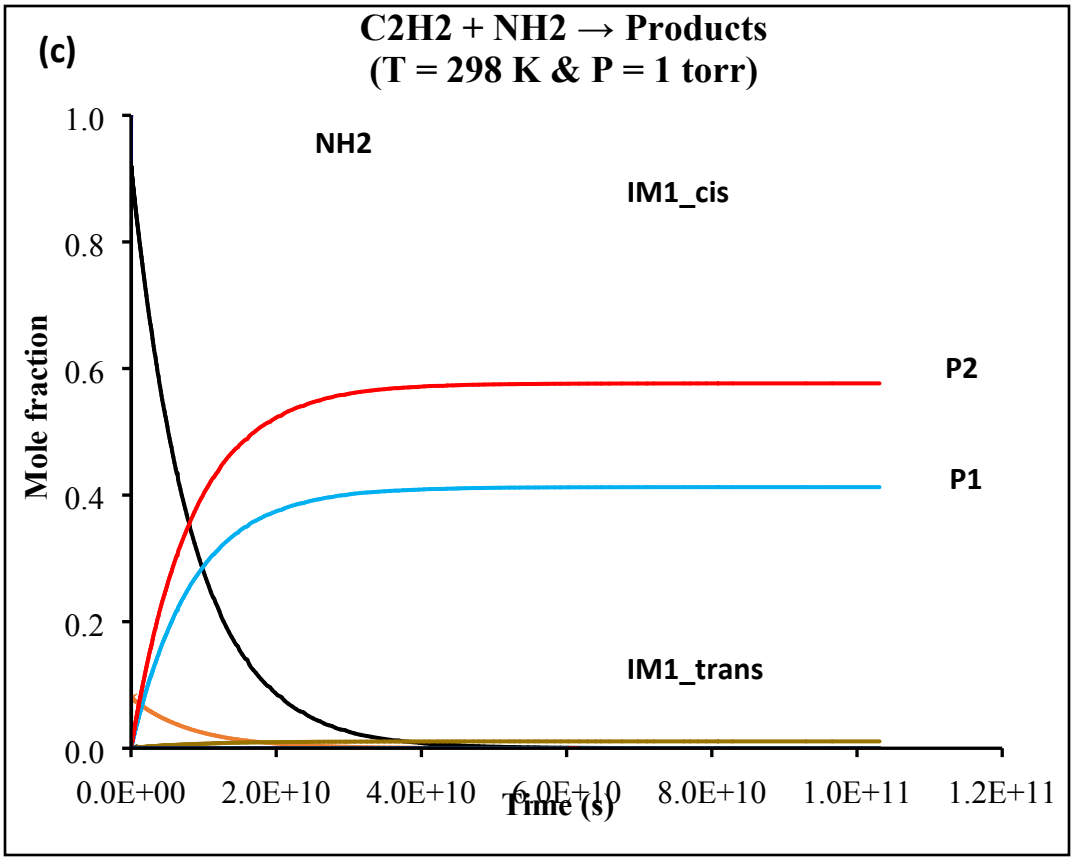


Figure S8: Time-resolved species profiles for the $C_2H_2 + NH_2 \rightarrow$ products, simulated at $T = 1000$ K and $P = 760$ torr (a); $T = 298$ K and $P = 76000$ torr (b) and $T = 298$ K and $P = 1$ torr (c) using stochastic approach: $[C_2H_2]/[N_2] = 10^{-3}$, $[C_2H_2]_0 >> [NH_2]_0$ and the numbers of trials = 10^6. The calculations were carried out using the full PES described in Figure 1 (in main text).

References

(1) T. Shimanouchi, *Tables of Molecular Vibrational Frequencies, Consolidated Volume 1, NSRDS NBS-39*,

(2) M.E. Jacox, Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules. *J. Phys. Chem.Ref. Data* **1994**, *Monograph 3*

(3) K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Co, 1979.

(4) L.V. Moskaleva, M.C. Lin, Theoretical Study of the NH_2+C_2H_2 Reaction. *J. Phys. Chem. A* **1998**, *102* (24), 4687-4693.

(5) B. Ruscic; R.E. Pinzon; G.v. Laszewski; D. Kodeboyina; A. Burcat; D. Leahy; D. Montoya, A.F. Wagner, *J. Phys.: Conf. Ser.* **2005**, *16*, 561-570.

(6) B. Ruscic; R.E. Pinzon; M.L. Morton; N.K. Srinivasan; M.C. Su; J.W. Sutherland, J.V. Michael, Active Thermochemical Tables: accurate enthalpy of formation of hydroperoxyl radical, HO_2. *J. Phys. Chem. A* **2006**, *110* (21), 6592-6601.

(7) J.A. Manion, Evaluated Enthalpies of Formation of the Stable Closed Shell C1 and C2 Chlorinated Hydrocarbons. *J. Phys. Chem. Ref. Data* **2002**, *31* (1), 123.

(8) M.W. Chase, Jr, NIST-JANAF Thermochemical Tables, Fourth Edition. *J. Phys. Chem. Ref. Data, Monograph 9* **1998**, 1-1951.

(9) X.-W. An, M. Månsson, Enthalpies of combustion and formation of acetonitrile. *J. Chem. Thermodyn.* **1983**, *15* (3), 287-293.
(10) J.H. Baldt, H.K.K. Hall, Thermochemistry of strained-ring bridgehead nitriles and esters. *J. Am. Chem. Soc.* **1971**, *93* (1), 140-145.
(11) W. Tsang, Heats of Formation of Organic Free Radicals by Kinetic Methods in Energetics of Organic Free Radicals. *Martinho Simoes, J.A.; Greenberg, A.; Liebman, J.F., eds., Blackie Academic and Professional, London* **1996**, 22-58.
(12) K. Kuchitsu(ed), *Structure of Free Polyatomic Molecules - Basic Data*, Springer, Berlin, 1998.
(13) G. Herzberg, *Electronic spectra and electronic structure of polyatomic molecules*, Van Nostrand, New York, 1966.