Table S1. Moments of Inertia (I_a, I_b, I_c, in amu) and harmonic vibrational frequencies (in cm^{-1}) of various species through the H + CH_3CN reaction at the B3LYP/6-311++G(2d,2p) level.

Species	I_a, I_b, I_c	Frequencies [a]
CH_3CN	11.3, 194.8, 194.8	379[2] (*362*), 924 (*920*), 1064[2] (*1041*), 1418 (*1389*), 1481[2] (*1454*), 2352 (*2268*), 3056 (*2954*), 3122[2] (*3009*)
H_2	0.99	4420 (*4401*)
CN	31.2	2147 (*2069*)
CH_3	6.3, 6.3, 12.5	537 (*606*), 1410[2] (*1403*), 3114 (*3004*), 3290[2] (*3161*)
CH_4	11.4, 11.4, 11.4	1345[3] (*1306*), 1564[2] (*1534*), 3036 (*2917*), 3136[3] (*3019*)
HCN	40.1	751[2] (*712*) , 2192 (*2097*), 3443 (*3311*)
HNC	39.4	413[2] (*464*), 2098 (*2024*), 3803 (*3653*)
CH_2CN	6.3, 174.4, 180.7	384, 428, 678 (*664*), 1037, 1054, 1452, 2118, 3167, 3270
CH_2CNH	8.8, 185.4, 189.1	424, 481, 714(*690*), 899(*872*), 1004(*1000*), 1039, 1162(*1124*), 1443, 2102(*2044*), 3168, 3253, 3484
CH_3CHN	31.4, 173.3, 193.6	186, 434, 747, 905, 1051, 1070, 1250, 1392, 1480, 1485, 1721, 2959, 3043, 3098, 3141
cis-CH_3CNH	31.4, 173.3, 193.6	161, 407, 645, 891, 938, 1040, 1059, 1388, 1462, 1474, 1885, 2984, 3086, 3109, 3241
trans-CH_3CNH	21.4, 191.2, 201.5	150, 438, 667, 899, 978, 1043, 1168, 1387, 1465, 1471, 1816, 3014, 3094, 3106, 3455
CH_2CHNH	30.5, 162.5, 193.1	487, 496, 682, 832, 991, 1072, 1140, 1232, 1380, 1457, 1502, 3106, 3140, 3242, 3412
CH_2CNH_2	19.8, 187.8, 201.7	234, 393, 522, 665, 849, 989, 1081, 1190, 1428, 1645, 1703, 3069, 3198, 3540, 3636
TS1	27.0, 209.1, 224.4	1427i,[b] 271, 370, 482, 553, 957, 1017, 1066, 1261, 1279, 1409, 1450, 2304, 3105, 3178
TS2	26.2, 194.2, 209.2	779i, 164, 411, 463, 530, 913, 1058, 1070, 1414, 1478, 1482, 2231, 3058, 3128, 3132
TS3	40.6, 246.5, 274.7	459i, 56,[c] 272, 482, 529, 736, 743, 887, 1415, 1428, 2016, 3099, 3255, 3275, 3339
TS4	19.0, 209.6, 217.3	918i, 96,[c] 266, 408, 545, 916, 1053, 1064, 1413, 1475, 1475, 2227, 3037, 3101, 3122
TS5	22.0, 192.4, 203.4	996i, 124, 401, 447, 857, 975, 1041, 1370, 1465, 1470, 1902, 2999, 3092, 3107, 3857
TS6	34.7, 286.8, 309.1	323i, 28,[c] 203, 391, 411, 466, 490, 751, 1412, 1422, 2004, 3109, 3270, 3285, 3747

(*Continued*)

TS7	32.6, 286.2, 306.4	354i, 23,[c] 205, 269, 427, 452, 480, 755, 1413, 1420, 1996, 3109, 3271, 3283, 3791
TS8	22.8, 191.9, 203.5	2083i, 167, 362, 434, 864, 1003, 1042, 1376, 1462, 1471, 1778, 2480, 3018, 3105, 3121
TS9	43.1, 133.0, 163.9	2136i, 456, 741, 834, 890, 1049, 1074, 1166, 1256, 1412, 1629, 1897, 3100, 3146, 3203
TS10	20.4, 186.3, 198.5	1775i, 369, 509, 743, 836, 992, 1041, 1102, 1201, 1454, 1743, 2031, 3038, 3218, 3377
TS11	27.1, 162.3, 177.6	2359i, 182, 656, 755, 852, 929, 1026, 1072, 1253, 1423, 1533, 1701, 3097, 3165, 3434
TS12	18.9, 192.6, 205.1	2057i, 296, 411, 681, 846, 949, 1089, 1114, 1138, 1424, 1689, 2275, 3097, 3222, 3430
TS13	23.2, 189.9, 200.6	776i, 123, 445, 547, 565, 723, 887, 1012, 1049, 1130, 1438, 2009, 3165, 3257, 3511
TS14	17.0, 202.1, 212.4	777i, 316, 335, 461, 557, 740, 900, 994, 1095, 1143, 1439, 2040, 3148, 3233, 3508
TS15	12.7, 271.2, 271.2	1237i, 123[2], 602[2], 638, 1289[2], 1371[2], 1404, 2238, 3025, 3192[2]

[a] The value in square bracket stands for degeneracy. The experimental vibrational frequencies are listed by *Italics* in brackets. [b] i represents imaginary frequency. [c] These low-frequency vibrational motions have been substituted by free internal rotors around the suitable axes in the RRKM-TST calculation. The corresponding internal rotational moments of inertia (in amu) are: 10.2 (TS3); 11.2 (TS4); 10.4 (TS6); 10.3 (TS7).

Note S1. Rate constant expressions for the C-addition path (mechanism II) and the N-addition path (mechanism III):

Mechanism II:

$$\mathrm{H{+}CH_3CN} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{CH_3CHN^*} \xrightarrow{3} \mathrm{CH_3{+}HCN}$$

$$\xrightarrow{w} \mathrm{CH_3CHN}$$

$$k_{HCN} = \frac{l_1}{h}\frac{Q^{\neq}_{TR,1}}{Q_H Q_{CH_3CN}} e^{-E_1/RT} \int_0^{\infty} \frac{k_3 W(E)}{k_2 + k_3 + w} e^{-E/RT} dE$$

$$k_{II} = \frac{l_1}{h}\frac{Q^{\neq}_{TR,1}}{Q_H Q_{CH_3CN}} e^{-E_1/RT} \int_0^{\infty} \frac{(k_3 + w) W(E)}{k_2 + k_3 + w} e^{-E/RT} dE$$

Mechanism III:

$$\mathrm{H{+}CH_3CN} \underset{2}{\overset{1}{\rightleftharpoons}} cis\text{-}\mathrm{CH_3CNH^*} \underset{4}{\overset{3}{\rightleftharpoons}} trans\text{-}\mathrm{CH_3CNH^*} \xrightarrow{6} \mathrm{CH_3{+}HNC}$$

$$\xrightarrow{w_2} trans\text{-}\mathrm{CH_3CHN}$$

$$\xrightarrow{5} \mathrm{CH_3{+}HNC}$$

$$\xrightarrow{w_1} cis\text{-}\mathrm{CH_3CNH}$$

$$k_{HNC} = \frac{l_1}{h}\frac{Q^{\neq}_{TR,1}}{Q_H Q_{CH_3CN}} e^{-E_1/RT} \int_0^{\infty} \frac{X_2 k_5 + k_3 k_6}{X_1 X_2 - k_3 k_4} W(E) e^{-E/RT} dE$$

$$k_{III} = \frac{l_1}{h}\frac{Q^{\neq}_{TR,1}}{Q_H Q_{CH_3CN}} e^{-E_1/RT} \int_0^{\infty} \frac{X_2 (k_5 + w_1) + k_3 (k_6 + w_2)}{X_1 X_2 - k_3 k_4} W(E) e^{-E/RT} dE$$

$$X_1 = k_2 + k_3 + k_5 + w_1$$

$$X_2 = k_4 + k_6 + w_2$$

$$k_i(E) = l_i C_i W_i(E_i^{\neq})/N_j(E_j)$$

$$w_j = \beta_c Z_{LJ} [M]$$

In the above equations, l_i is the statistical factor for the ith reaction path; E_1 is the energy barrier for the step 1; Q_H and Q_{CH3CN} are the total partition functions of H and CH_3CN, respectively. $Q^{\neq}_{TR,1}$ is the translational and rotational partition functions of the transition state for the step 1; $k_i(E)$ is the energy specific rate constant for the ith channel; C_i is the ratio of the overall rotational partition function of the transition state for the ith channel and the jth intermediate. $W(E)$ is the sum of states of the transition state for the step 1 with excess energy E above the association barrier; $W_i(E_i^{\neq})$ has the similar meaning but for the ith channel; $N_j(E_j)$ is the density of state for the jth intermediate with excess energy E_j; w_j is the effective collision frequency for the jth intermediate; β_c is the collision efficiency which is calculated by Troe's weak-collision approximation; Z_{LJ} is the Lennard-Jones collision frequency; [M] is the concentration of the bath gas M; h is the Planck's constant; R is the gas constant; and T is the temperature.