Supporting Information

Theoretical study on the gas phase reaction of acrylonitrile with hydroxyl radical

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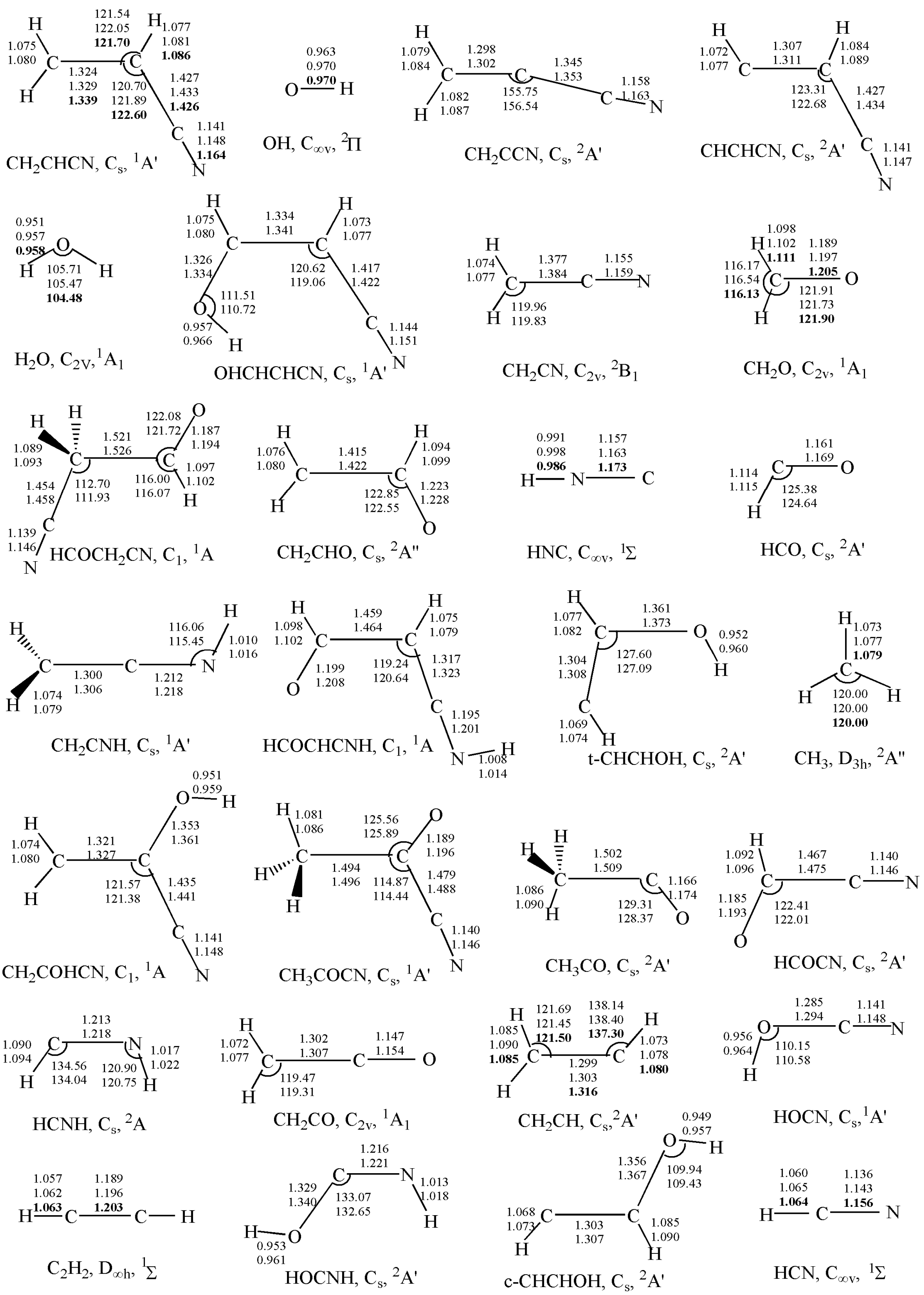
Fig. S1 Optimized geometries (length in Å and angle in degree) (a) for reactants and products, (b) for other intermediates and transition states. The geometries of 1-TS11 and 1-TS13 are obtained by BHandHLYP with 6-31+G(d,p) basis set. The experimental data are in bold.

(a)



(b)

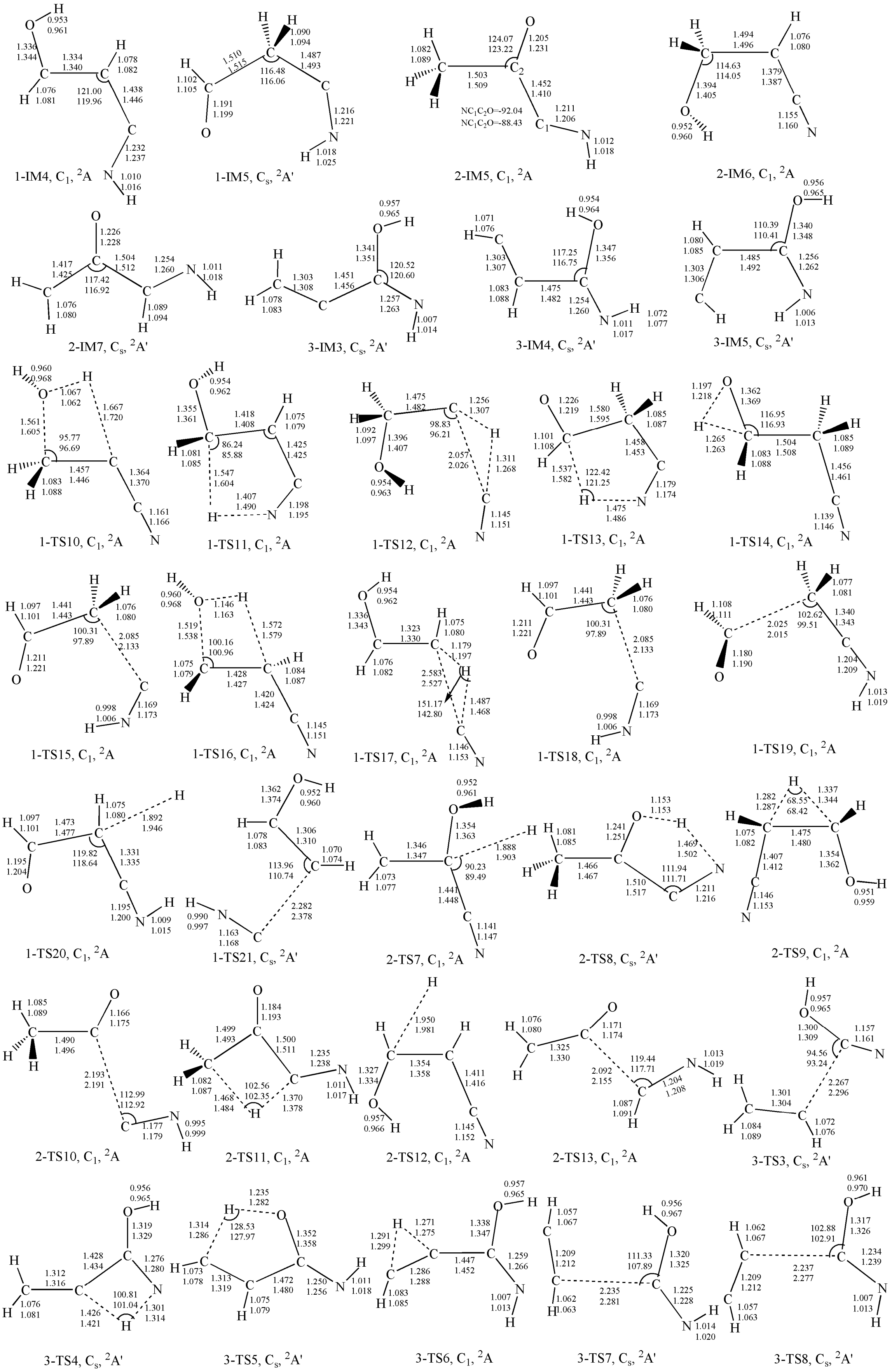
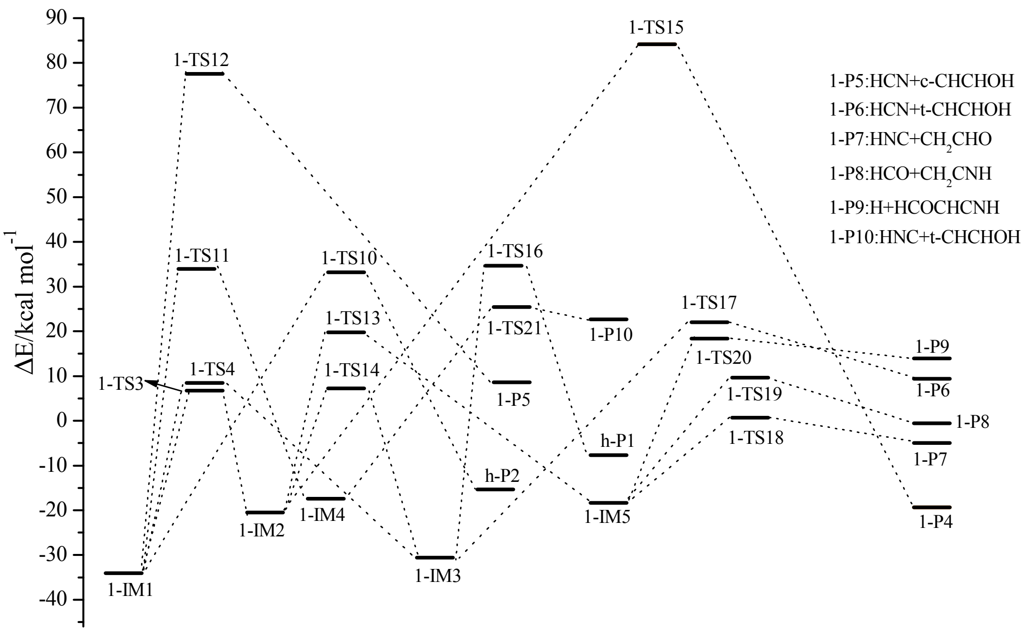
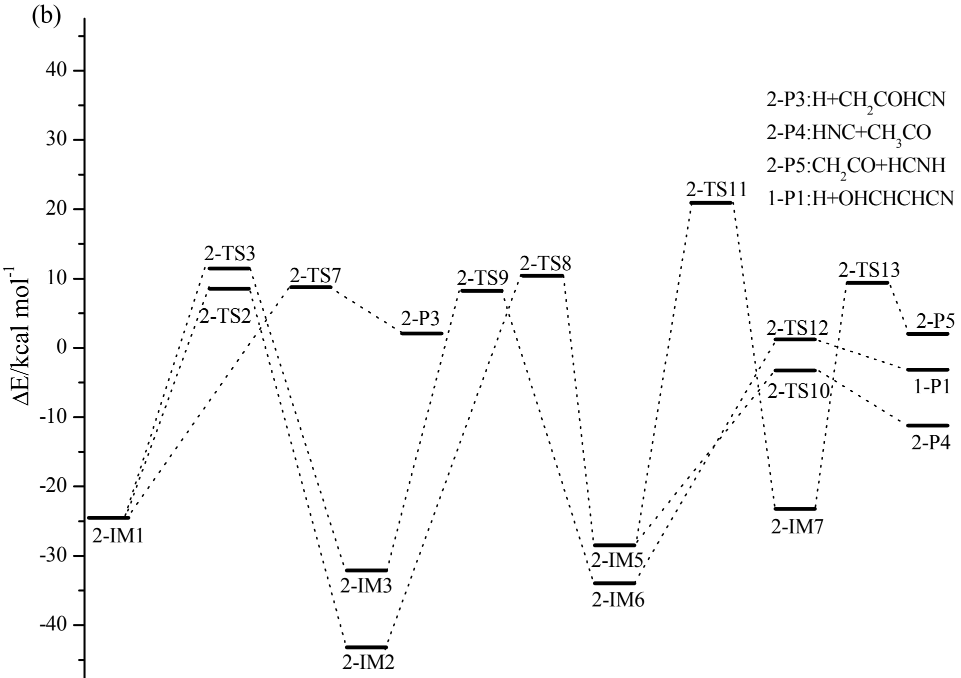

1-IM4, C_1, ^2A
1-IM5, C_s, $^2A'$
2-IM5, C_1, ^2A
2-IM6, C_1, ^2A
2-IM7, C_s, $^2A'$
3-IM3, C_s, $^2A'$
3-IM4, C_s, $^2A'$
3-IM5, C_s, $^2A'$
1-TS10, C_1, ^2A
1-TS11, C_1, ^2A
1-TS12, C_1, ^2A
1-TS13, C_1, ^2A
1-TS14, C_1, ^2A
1-TS15, C_1, ^2A
1-TS16, C_1, ^2A
1-TS17, C_1, ^2A
1-TS18, C_1, ^2A
1-TS19, C_1, ^2A
1-TS20, C_1, ^2A
1-TS21, C_s, $^2A'$
2-TS7, C_1, ^2A
2-TS8, C_s, $^2A'$
2-TS9, C_1, ^2A
2-TS10, C_1, ^2A
2-TS11, C_1, ^2A
2-TS12, C_1, ^2A
2-TS13, C_1, ^2A
3-TS3, C_s, $^2A'$
3-TS4, C_s, $^2A'$
3-TS5, C_s, $^2A'$
3-TS6, C_1, ^2A
3-TS7, C_s, $^2A'$
3-TS8, C_s, $^2A'$

Fig. S2 Other reaction pathways from (a) 1-IM1, (b) 2-IM1, and (c) 3-IM1 at the BMC-CCSD//BHandHLYP/6-311++G(d,p) level

(a)




(b)
ΔE/kcal mol-1
2-P3:H+CH2COHCN
2-P4:HNC+CH3CO
2-P5:CH2CO+HCNH
1-P1:H+OHCHCHCN
2-IM1
2-TS3
2-TS2
2-TS7
2-P3
2-TS9
2-TS8
2-TS11
2-TS12
2-TS10
2-TS13
2-P5
1-P1
2-P4
2-IM7
2-IM5
2-IM6
2-IM3
2-IM2

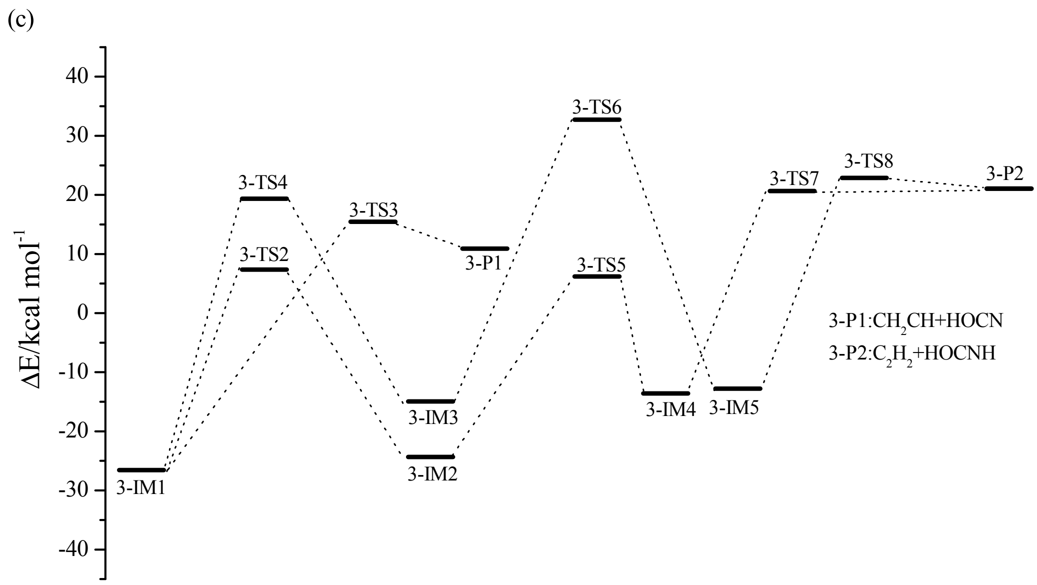

(c)
ΔE/kcal mol-1
3-IM1
3-TS4
3-TS2
3-TS3
3-P1
3-TS6
3-TS5
3-IM3
3-IM2
3-IM4
3-IM5
3-TS7
3-TS8
3-P2
3-P1:CH2CH+HOCN
3-P2:C2H2+HOCNH

Table S1 Relative Energies(ΔE), Reaction Enthalpies(ΔH), Gibbs Free Energies(ΔG), and Entropies(ΔS) for various species in the OH + CH_2=CHCN reaction

species	ΔE^a	ΔE^b	ΔH^c	ΔH^d	ΔG^e	ΔS^f	ΔS^g
R:CH_2=CHCN+OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-P1:H+OHCHCHCN	6.18	-3.37	6.03	-3.51	-0.53	-9.15	-9.67
1-P2:CH_2CN+CH_2O	-16.35	-17.07	-16.34	-17.09	-19.85	3.83	3.69
1-P3:H+HCOCH_2CN	4.12	-3.22	4.23	-3.12	-2.21	-7.13	-7.09
1-P4:HCN+CH_2CHO	-16.51	-18.27	-16.79	-18.59	-18.37	2.20	1.98
1-P5:HCN+c-CHCHOH	16.70	12.94	16.69	12.84	11.35	3.72	2.98
1-P6:HCN+t-CHCHOH	15.70	11.39	15.55	11.24	8.64	2.86	2.83
1-P7: HNC+CH_2CHO	-3.96	-5.33	-4.08	-5.47	-5.56	3.35	3.66
1-P8:HCO+CH_2CNH	3.58	0.41	3.56	0.37	-2.01	5.62	5.42
1-P9:H+HCOCHCNH	20.15	12.42	20.11	12.39	16.71	-8.77	-8.92
1-P10:HNC+t-CHCHOH	28.25	24.33	28.25	24.36	21.45	3.62	3.66
h-P1:H_2O+CHCHCN	0.22	-3.54	0.59	-3.25	-8.48	2.46	3.44
h-P2:H_2O+CH_2CCN	-8.30	-11.54	-7.74	-10.98	-15.99	2.81	4.66
2-P1:CH_3+HCOCN	-3.28	-4.03	-2.93	-3.73	-8.52	2.24	6.41
2-P2:H+CH_3COCN	3.76	-3.35	3.93	-3.18	-3.08	-7.87	-7.40
2-P3:H+CH_2COHCN	13.09	4.21	13.26	4.23	4.92	-8.05	-8.98
2-P4: HNC+CH_3CO	-7.81	-10.83	-7.64	-10.62	-12.84	4.91	6.41
2-P5:CH_2CO+HCNH	6.80	3.52	6.78	3.48	0.85	4.67	4.47
3-P1:CH_2CH+HOCN	18.12	14.95	18.08	14.90	9.08	5.92	5.67
3-P2:C_2H_2+HOCNH	28.31	23.45	28.23	23.36	20.54	1.84	1.50
CR1	-1.01	-2.44	-0.81	-2.60	2.98	-15.57	-22.72
1-IM1	-30.19	-35.34	-31.28	-36.38	-26.19	-31.14	-29.86
1-IM2	-21.58	-23.88	-22.86	-25.18	-11.78	-33.10	-33.13
1-IM3	-25.22	-31.12	-26.31	-32.24	-22.06	-31.96	-32.29
1-IM4	-12.11	-18.67	-13.26	-19.86	-8.65	-32.24	-32.76
1-IM5	-13.39	-18.48	-14.57	-19.65	-9.94	-32.12	-31.74

2-IM1	-18.78	-23.42	-19.70	-24.16	-16.44	-31.06	-25.68
2-IM2	-38.12	-43.86	-39.11	-44.83	-34.79	-31.18	-31.21
2-IM3	-26.84	-33.04	-27.95	-34.14	-23.82	-31.75	-31.77
2-IM4	-18.43	-20.77	-19.66	-22.07	-9.23	-33.14	-33.62
2-IM5	-24.23	-29.29	-25.15	-30.25	-19.62	-29.07	-30.10
2-IM6	-29.77	-35.06	-30.81	-36.15	-25.56	-30.66	-31.24
2-IM7	-20.89	-23.84	-22.24	-25.19	-14.38	-33.26	-33.33
3-IM1	-23.50	-27.48	-24.91	-28.89	-17.68	-34.40	-34.48
3-IM2	-23.10	-25.09	-24.38	-26.42	-15.43	-33.31	-33.74
3-IM3	-9.34	-14.92	-10.59	-16.14	-6.62	-32.73	-32.35
3-IM4	-6.83	-13.11	-8.19	-14.47	-4.82	-34.28	-34.36
3-IM5	-6.67	-12.86	-8.02	-14.21	-4.52	-32.45	-32.49
1-TS1	1.01	-1.54	0.15	-2.45	6.73	-29.45	-29.95
1-TS2	12.07	6.40	10.97	5.30	11.97	-33.00	-33.02
1-TS3	13.91	6.61	12.32	5.02	16.31	-35.17	-35.20
1-TS4	16.34	7.75	15.18	6.63	16.90	-32.83	-32.48
1-TS5	-2.21	-7.35	-3.31	-8.47	1.05	-31.01	-31.36
1-TS6	9.01	4.42	7.93	3.37	8.64	-31.85	-31.72
1-TS7	11.99	5.92	10.89	4.84	12.32	-32.97	-32.86
1-TS8	12.86	8.80	11.96	7.93	17.76	-29.94	-29.72
1-TS9	21.54	—	20.40	—	—	-31.43	—
1-TS10	39.62	31.32	38.31	30.12	41.41	-33.13	-32.05
1-TS11	82.16	71.56	80.67	70.20	42.35	-35.42	-34.27
1-TS12	84.77	77.15	84.11	76.37	86.89	-28.50	-29.75
1-TS13	66.60	20.97	65.14	19.46	28.99	-34.46	-35.06
1-TS14	14.44	5.97	13.14	4.68	19.82	-32.99	-32.85
1-TS15	86.97	84.11	86.07	83.19	96.39	-29.48	-29.68
1-TS16	43.22	32.26	41.84	30.88	43.35	-34.21	-34.20
1-TS17	33.32	25.80	32.79	25.26	34.70	-25.79	-25.83
1-TS18	5.51	-1.37	4.65	-2.31	9.37	-29.85	-30.96

1-TS19	15.84	8.06	14.86	7.04	17.89	-29.93	-30.35
1-TS20	24.00	18.72	22.91	17.67	26.87	-32.43	-32.16
1-TS21	32.64	25.49	32.33	25.18	32.34	-24.71	-24.46
2-TS1	4.97	1.16	3.97	0.21	8.87	-31.29	-30.85
2-TS2	17.20	8.82	15.94	7.61	17.17	-33.76	-33.47
2-TS3	20.68	11.22	19.89	10.23	19.59	-27.52	-30.55
2-TS4	16.32	8.19	14.74	6.63	17.31	-35.54	-35.43
2-TS5	3.00	-3.35	2.13	-4.09	4.00	-30.13	-27.88
2-TS6	11.22	6.61	10.13	5.60	9.99	-32.50	-31.83
2-TS7	19.34	13.43	18.17	12.25	17.55	-33.41	-33.59
2-TS8	19.44	9.96	18.09	8.66	18.79	-33.29	-32.97
2-TS9	16.18	7.76	14.87	6.45	16.94	-33.54	-33.64
2-TS10	0.96	-5.52	0.74	-5.63	3.22	-22.74	-22.23
2-TS11	29.02	22.01	27.66	20.62	29.76	-33.83	-34.14
2-TS12	9.97	3.70	8.78	2.53	9.64	-33.14	-33.06
2-TS13	17.59	9.16	16.71	8.35	17.37	-29.78	-29.41
3-TS1	6.29	3.13	5.32	2.24	9.30	-30.62	-28.68
3-TS2	16.52	8.94	14.95	7.37	16.41	-35.19	-35.21
3-TS3	25.26	17.69	24.65	17.23	22.24	-27.77	-25.44
3-TS4	29.75	22.05	28.26	20.57	28.52	-35.01	-34.98
3-TS5	15.58	7.50	13.70	5.64	15.79	-37.76	-37.75
3-TS6	41.22	32.72	40.11	31.68	40.60	-32.29	-31.64
3-TS7	30.89	22.68	30.23	22.10	27.66	-27.56	-26.22
3-TS8	33.19	24.59	32.52	23.93	30.38	-28.40	-28.17
h-TS1	11.58	6.09	10.86	5.29	12.05	-28.32	-29.34
h-TS2	9.83	5.59	9.17	4.84	11.23	-27.78	-28.46

Except ΔS, the energies are given in kcal/mol. ΔS is given in cal $mol^{-1}K^{-1}$. [a]BHandHLYP/6-311++G(d,p);[b]M05-2X/6-311++G(d,p);[c]BHandHLYP/6-311++G(d,p);[d]M05-2X/6-311++G(d,p); [e]BMC-CCSD//M05-2X; [f]BMC-CCSD//BHandHLYP; [g]BMC-CCSD//M05-2X.

Table S2 The moment of inertia (I_a, I_b and I_c), rotational symmetry number, and optical isomers number of the major species.

species	I_a, I_b, I_c (amu bohr^2)	$N_{rotational\ symmetry}$	$N_{optical\ isomers}$
CH_2=CHCN	35.06430, 358.37170, 393.43599	1	1
OH	0.00000, 3.14106, 3.14106	1	1
OHCHCHCN	133.43620, 479.70426, 613.14046	1	1
CH_2CN	6.22732, 172.76173, 178.98905	2	1
CH_2O	6.24984, 45.26714, 51.51699	2	1
$HCOCH_2CN$	65.99964, 693.54258, 735.16211	1	1
CH_2CCN	9.24535, 404.29671, 413.54206	1	1
CHCHCN	26.88727, 351.20175, 378.08903	1	1
H_2O	2.10612, 4.13283, 6.23894	2	1
HCN	0.00000, 39.47944, 39.47944	1	1
CH_2CHO	26.46461, 154.96262, 181.42723	1	1
CH_3	6.21535, 6.21535, 12.43071	6	1
HCOCN	26.01984, 354.12103, 380.14087	1	1
CH_3COCN	174.31300, 427.27655, 590.56403	1	1
CR1	199.26208, 788.88597, 928.64920	1	1
1-IM1	66.19537, 765.30966, 781.14651	1	1
1-IM2	65.14201, 740.25202, 783.50335	1	1
1-IM3	59.79830, 758.00906, 801.84974	1	1
2-IM1	192.05053, 434.45896, 584.11564	1	1
2-IM2	186.15571, 442.98593, 618.04491	1	1
2-IM3	134.51797, 582.06221, 659.01650	1	1
2-IM4	188.18104, 443.89373, 586.86790	1	1
3-IM1	166.33665, 392.99720, 559.33385	1	1
3-IM2	154.49832, 418.57302, 572.28719	1	1
1-TS1	161.82507, 667.78341, 761.36676	1	1
1-TS2	55.53482, 763.79125, 794.02637	1	1

1-TS3	103.78997, 624.99686, 642.14278	1	1
1-TS4	57.66140, 773.27460, 799.14553	1	1
1-TS5	93.07888, 749.79156, 818.59525	1	1
1-TS6	73.57553, 716.57638, 759.96671	1	1
1-TS7	58.53305, 756.00671, 791.86439	1	1
1-TS8	63.16001, 746.06937, 788.13540	1	1
1-TS9	163.18925, 540.62970, 675.51110	1	1
2-TS1	232.06736, 460.55287, 629.85507	1	1
2-TS2	185.02172, 439.81651, 610.86100	1	1
2-TS3	206.00448, 526.78960, 681.22082	1	1
2-TS4	153.11066, 476.02232, 570.47867	1	1
2-TS5	251.30210, 444.88315, 641.52183	1	1
2-TS6	189.03212, 443.64769, 594.97229	1	1
3-TS1	211.31126, 404.46421, 615.77546	1	1
3-TS2	189.78707, 508.43298, 698.22004	1	1
h-TS1	266.30909, 517.09646, 783.40555	1	1
h-TS2	275.98873, 564.15802, 835.24066	1	1

Table S3 The Z-matrix (Cartesian coordinates) of the major species.

Species	Coordinates(Atom, X, Y, Z)			
CR1	C	-0.442955	1.315239	-0.220768
	H	-1.373942	1.732733	0.117047
	H	-0.043592	1.666370	-1.156319
	C	0.181645	0.395609	0.500827
	H	-0.221477	0.046745	1.435732
	C	1.413421	-0.195859	0.090184
	N	2.394445	-0.687040	-0.225652
	O	-2.492892	-0.792380	-0.044028
	H	-2.091630	-1.387460	-0.686131
1-IM1	C	0.991566	-0.458476	0.282737
	H	0.710342	-1.383537	-0.215859
	H	1.236792	-0.706650	1.312763
	C	-0.147255	0.508328	0.261866
	H	0.046459	1.539562	0.502308
	C	-1.446672	0.121451	0.000233
	N	-2.527590	-0.215735	-0.226241
	O	2.159847	0.097285	-0.261624
	H	2.034923	0.254663	-1.191550
1-IM2	C	0.949031	-0.544212	0.000000
	H	0.775063	-1.186110	0.868254
	H	0.775063	-1.186110	-0.868254
	C	0.000000	0.657418	0.000000
	H	0.186828	1.270698	-0.875637
	C	-1.395163	0.242888	0.000000
	N	-2.477019	-0.114969	0.000000
	O	2.261518	-0.187620	0.000000
	H	0.186828	1.270698	0.875637
1-IM3	C	-0.935705	-0.479288	-0.030383
	H	-0.765612	-1.437595	0.424974
	H	-0.007325	1.118819	1.067456
	C	0.085006	0.606652	0.106006
	H	-0.053733	1.365096	-0.664258
	C	1.444596	0.096868	-0.004624
	N	2.507580	-0.304551	-0.083167
	O	-2.239216	-0.119302	-0.021860
	H	-2.376051	0.694556	-0.497115
2-IM1	C	-1.086521	1.208708	-0.140969
	H	-2.158823	1.254191	-0.082076
	H	-0.525343	2.067108	-0.458691
	C	-0.415315	-0.016379	0.373653
	H	-0.524040	-0.075932	1.455505

	C	1.032445	0.015072	0.092353
	N	2.147184	0.045510	-0.139816
	O	-1.000818	-1.202025	-0.103720
	H	-0.999192	-1.192143	-1.056488
2-IM2	C	-1.255900	1.116243	0.000000
	H	-1.301558	1.756766	0.877962
	H	-2.116294	0.459910	0.000000
	C	0.000000	0.334228	0.000000
	H	-1.301558	1.756766	-0.877962
	C	0.063237	-1.048011	0.000000
	N	0.129497	-2.201276	0.000000
	O	1.132940	1.064325	0.000000
	H	1.905384	0.506126	0.000000
2-IM3	C	-0.112347	0.895044	-0.219243
	H	-0.350363	1.863831	0.208553
	H	0.056840	1.035744	-1.283051
	C	1.119559	0.349860	0.415871
	H	1.213113	0.332810	1.489923
	C	-1.280364	0.025369	-0.048892
	N	-2.180814	-0.655909	0.107516
	O	1.698308	-0.651005	-0.283941
	H	2.398562	-1.054617	0.217075
2-IM4	C	1.202712	-1.049088	-0.119955
	H	2.239310	-0.912252	0.160477
	H	0.814885	-1.949426	0.341854
	C	0.389496	0.161707	0.353680
	H	0.515168	0.256601	1.434906
	C	-1.051220	-0.018072	0.077276
	N	-2.160234	-0.169908	-0.132711
	O	0.896983	1.296913	-0.209767
	H	1.130486	-1.148155	-1.196125
3-IM1	C	-0.318212	-1.841882	0.000000
	H	-0.959636	-2.705664	0.000000
	H	0.744614	-2.006736	0.000000
	C	-0.827348	-0.621645	0.000000
	H	-1.888818	-0.447520	0.000000
	C	0.000000	0.588221	0.000000
	N	-0.494186	1.741511	0.000000
	O	1.331353	0.375746	0.000000
	H	1.785682	1.215220	0.000000
3-IM2	C	1.930427	0.054282	0.025538
	H	2.886447	-0.439107	0.014078
	H	1.918502	1.130076	0.072615
	C	0.800330	-0.631626	-0.020031

	H	0.784668	-1.706692	-0.064420
	C	-0.511935	0.042510	0.003693
	N	-1.609736	-0.792728	-0.015974
	O	-0.652752	1.251620	-0.029467
	H	-2.412384	-0.239136	0.270080
1-TS1	C	-0.861759	0.858411	-0.417881
	H	-0.771896	0.588919	-1.453531
	H	-1.706890	1.453483	-0.131294
	C	0.158815	0.671575	0.446409
	H	0.091661	1.005276	1.467171
	C	1.348852	-0.008997	0.081743
	N	2.311008	-0.560801	-0.196350
	O	-2.036835	-0.840909	0.077591
	H	-1.370702	-1.520739	0.209747
1-TS2	C	-0.912871	-0.349049	-0.107884
	H	-0.736326	-1.346285	-0.467753
	H	-0.792922	-1.205225	1.635627
	C	0.099443	0.525183	0.086430
	H	-0.089662	1.549428	0.360824
	C	1.447688	0.116730	-0.005702
	N	2.544695	-0.198141	-0.078072
	O	-2.206294	-0.029123	-0.124228
	H	-2.349167	0.864866	0.174563
1-TS3	C	1.137251	0.558039	-0.388152
	H	0.838911	0.606747	-1.427516
	H	1.784479	1.384554	-0.124386
	C	0.023282	0.293458	0.580359
	H	0.083947	0.769216	1.545549
	C	-1.286675	0.019463	0.097145
	N	-2.335469	-0.214475	-0.292135
	O	1.710414	-0.704833	-0.049435
	H	0.714478	-0.846288	0.710660
1-TS4	C	-0.993562	-0.438792	0.196159
	H	-0.777612	-1.491447	0.154727
	H	-0.408865	0.096450	1.271966
	C	0.128153	0.524011	0.197431
	H	-0.110047	1.570356	0.124401
	C	1.455271	0.113318	-0.033576
	N	2.534443	-0.241013	-0.187439
	O	-2.226798	-0.033623	-0.186421
	H	-2.169362	0.589494	-0.907739
1-TS5	C	1.010627	-0.912697	0.000000
	H	0.550855	-1.268586	0.924178
	H	0.550855	-1.268586	-0.924178

	C	0.000000	0.875436	0.000000
	H	0.385826	1.294504	-0.912215
	C	-1.363163	0.511929	0.000000
	N	-2.455401	0.165827	0.000000
	O	2.178708	-0.507579	0.000000
	H	0.385826	1.294504	0.912215
1-TS6	C	-1.056559	-0.311054	-0.219855
	H	-0.793159	-1.159315	-0.862599
	H	-0.621196	-1.498073	1.132377
	C	0.051036	0.703258	0.041590
	H	-0.129614	1.199996	0.987818
	C	1.382016	0.120267	0.015804
	N	2.414766	-0.359573	-0.012264
	O	-2.199996	-0.069642	0.067986
	H	-0.018386	1.456709	-0.740867
1-TS7	C	-0.929533	-0.405892	0.094291
	H	-0.742961	-1.397932	0.463252
	H	0.108313	1.583556	1.457167
	C	0.065239	0.479040	-0.125616
	H	-0.124297	1.417803	-0.617446
	C	1.422009	0.055942	-0.059157
	N	2.513618	-0.275520	-0.016708
	O	-2.225397	-0.149058	-0.038073
	H	-2.379493	0.743136	-0.338537
1-TS8	C	0.970603	-0.430215	0.035182
	H	0.674260	-1.434530	0.338818
	H	0.060303	1.258810	-0.893076
	C	-0.091113	0.640372	-0.013697
	H	0.046783	1.287906	0.853523
	C	-1.444287	0.108701	-0.001412
	N	-2.495578	-0.329124	0.009626
	O	2.137633	-0.153039	-0.175805
	H	2.975417	0.502848	0.919360
1-TS9	C	-1.354634	0.241487	-0.221348
	H	-2.174939	0.536720	-0.861162
	H	0.005025	1.122492	1.191650
	C	-0.383233	1.154766	0.192624
	H	-0.240354	2.065329	-0.362043
	C	1.230575	-0.450691	0.055368
	N	2.296640	-0.056352	-0.166348
	O	-1.293738	-0.986086	0.094775
	H	-0.272553	-1.114763	0.277922
2-TS1	C	1.019395	-1.242198	-0.223139
	H	1.987171	-1.543673	0.132417

	H	0.683053	-1.614913	-1.174272
	C	0.282496	-0.344147	0.486577
	H	0.545130	-0.099414	1.498702
	C	-1.072087	-0.062619	0.114944
	N	-2.155249	0.143348	-0.176743
	O	1.175255	1.353789	-0.059372
	H	1.090518	1.318037	-1.014969
2-TS2	C	1.216000	-1.158494	-0.062690
	H	2.267807	-0.983997	-0.171605
	H	0.767812	-2.104872	-0.291774
	C	0.366009	0.025871	0.121342
	H	0.785883	-0.647963	1.109954
	C	-1.045633	-0.063475	-0.005526
	N	-2.189170	-0.118686	-0.044702
	O	0.969852	1.227524	-0.125203
	H	0.525618	1.924033	0.349206
2-TS3	C	-1.021936	1.207898	-0.104883
	H	-1.349757	1.325311	-1.121260
	H	-0.818192	2.073664	0.493714
	C	-0.845209	-0.027240	0.424225
	H	-0.518963	-0.156922	1.442366
	C	1.384961	0.432484	-0.159092
	N	2.250824	-0.307535	0.014023
	O	-1.170598	-1.109224	-0.253125
	H	-0.810968	-1.894366	0.150518
2-TS4	C	-1.211718	0.960576	-0.126623
	H	-1.971982	1.381266	0.509236
	H	-0.825988	1.567290	-0.928357
	C	-0.306636	-0.070011	0.471560
	H	-0.383755	-0.188581	1.545873
	C	1.102626	0.017750	0.093708
	N	2.204446	0.102380	-0.182404
	O	-1.006019	-1.093810	-0.225391
	H	-1.706877	-0.176046	-0.678663
2-TS5	C	-1.387507	1.271447	-0.094620
	H	-2.366911	0.915881	0.170059
	H	-0.910635	1.977426	0.563490
	C	-0.255299	-0.554486	0.409156
	H	-0.552238	-0.397773	1.445344
	C	1.063440	0.002000	0.079671
	N	2.095455	0.431136	-0.144593
	O	-0.777017	-1.393806	-0.298900
	H	-1.146071	1.323201	-1.140786
2-TS6	C	1.247623	-1.048246	-0.061594

	H	2.270362	-0.819964	0.207212
	H	0.857713	-1.847020	0.557228
	C	0.413650	0.199643	0.040018
	H	0.387378	0.246320	1.837364
	C	-1.048402	-0.021695	0.001113
	N	-2.169440	-0.218132	-0.057591
	O	0.846858	1.318491	-0.122278
	H	1.218543	-1.378551	-1.097666
3-TS1	C	-1.133561	-1.444430	0.000000
	H	-2.055829	-1.998089	0.000000
	H	-0.208941	-1.989322	0.000000
	C	-1.159257	-0.123459	0.000000
	H	-2.086877	0.423632	0.000000
	C	0.000000	0.728302	0.000000
	N	0.544366	1.759854	0.000000
	O	1.507186	-0.481983	0.000000
	H	2.240503	0.138188	0.000000
3-TS2	C	0.081101	-2.068126	0.000000
	H	-0.245759	-3.101267	0.000000
	H	1.144512	-1.890894	0.000000
	C	-0.782173	-1.095446	0.000000
	H	-1.849986	-1.003913	0.000000
	C	0.000000	1.032805	0.000000
	N	-0.950700	1.692540	0.000000
	O	1.251914	0.682921	0.000000
	H	1.797243	1.469524	0.000000
h-TS1	C	-1.206945	0.714883	0.000000
	H	-2.147953	1.236585	0.000000
	H	-1.367948	-0.566752	0.000000
	C	0.000000	1.238158	0.000000
	H	0.145935	2.307871	0.000000
	C	1.177812	0.434789	0.000000
	N	2.116639	-0.214333	0.000000
	O	-1.356923	-1.734763	0.000000
	H	-0.416325	-1.926246	0.000000
h-TS2	C	-0.291059	1.711051	0.028207
	H	-1.302002	2.079196	0.012138
	H	0.509334	2.431522	0.089919
	C	-0.045690	0.420614	-0.033621
	H	-1.050800	-0.327657	-0.162064
	C	1.185098	-0.259547	-0.014414
	N	2.157962	-0.861064	0.006701
	O	-2.055976	-0.990383	-0.076402
	H	-1.904556	-1.465265	0.743282

Table S4 The harmonic vibrational frequencies of the major species.

Species	Frequencies(cm^{-1})
CH_2=CHCN	250(*242*),[a] 368(*362*), 605(*570*), 743(*683*), 909(*869*), 1043(*954*), 1055(*972*), 1148(*1096*), 1365(*1282*), 1494(*1416*), 1749(*1615*), 2460(*2239*), 3243(*3042*), 3273(*3078*), 3340(*3125*)
OH	3880(*3737*)
OHCHCHCN	147, 310, 461, 533, 652, 772, 773, 990, 1044, 1157, 1284, 1411, 1476, 1746, 2437, 3301, 3320, 3918
CH_2CN	404, 450, 688, 1072, 1077, 1493, 2205, 3251, 3363
CH_2O	1261(*1167*), 1308(*1249*), 1585(*1500*), 1906(*1746*), 3005(*2782*), 3075(*2843*)
HCOCH_2CN	56, 191, 381, 491, 552, 757, 998, 1074, 1094, 1272, 1349, 1465, 1491, 1918, 2482, 3055, 3128, 3200
CH_2CCN	135, 279, 464, 616, 895, 986, 1004, 1478, 1847, 2182, 3170, 3260
CHCHCN	253, 388, 585, 735, 814, 906, 1039, 1303, 1706, 2461, 3178, 3348
H_2O	1651(*1595*), 3983(*3657*), 4087(*3756*)
HCN	816(*712*), 816(*712*), 2303(*2089*), 3548(*3312*)
CH_2CHO	476, 523, 788, 1013, 1015, 1192, 1444, 1524, 1579, 3075, 3232, 3350
CH_3	525(*606*), 1451(*1396*), 1451(*1396*), 3189(*3004*), 3373(*3160*), 3373(*3160*)
HCOCN	247, 326, 653, 959, 1051, 1459, 1896, 2464, 3114
CH_3COCN	130, 193, 274, 453, 620, 634, 747, 1027, 1090, 1247, 1452, 1512, 1516, 1902, 2459, 3122, 3186, 3240
CR1	8, 36, 99, 154, 249, 257, 377, 606, 744, 909, 1041, 1053, 1148, 1365, 1494, 1740, 2457, 3244, 3279, 3344, 3884
1-IM1	55, 199, 347, 412, 438, 571, 621, 918, 1080, 1124, 1151, 1228, 1366, 1436, 1480, 1544, 2213, 3111, 3149, 3277, 3997
1-IM2	107, 173, 404, 421, 553, 561, 881, 987, 1067, 1119, 1199, 1337, 1349, 1440, 1466, 1524, 2475, 3055, 3081, 3149, 3194
1-IM3	94, 178, 359, 399, 409, 551, 630, 964, 991, 1069, 1222, 1274, 1290, 1404, 1489, 1514, 2482, 3060, 3113, 3294, 3985
2-IM1	113, 205, 252, 357, 417, 530, 610, 645, 836, 1004, 1120, 1178, 1273, 1380, 1456, 1496, 2473, 3113, 3239, 3364, 3980

2-IM2	104, 202, 266, 374, 400, 463, 650, 774, 1048, 1055, 1201, 1403, 1455, 1479, 1517, 1552, 2248, 3104, 3154, 3221, 3985
2-IM3	89, 202, 362, 387, 400, 565, 686, 917, 948, 1054, 1239, 1266, 1353, 1375, 1499, 1506, 2464, 3139, 3185, 3243, 4015
2-IM4	200, 223, 250, 303, 536, 617, 817, 920, 1005, 1083, 1167, 1270, 1393, 1455, 1532, 1548, 2473, 3075, 3138, 3222, 3231
3-IM1	130, 280, 424, 484, 508, 588, 807, 869, 1042, 1058, 1077, 1260, 1362, 1371, 1493, 1726, 1786, 3241, 3287, 3336, 3965
3-IM2	110, 259, 282, 480, 509, 627, 798, 850, 1064, 1067, 1108, 1158, 1301, 1371, 1487, 1628, 1753, 3236, 3282, 3331, 3563
1-TS1	313*i*,[b] 97, 151, 229, 250, 447, 602, 707, 768, 911, 997, 1029, 1146, 1329, 1474, 1623, 2415, 3265, 3280, 3368, 3903
1-TS2	807*i*, 176, 189, 400, 439, 467, 482, 550, 589, 818, 1048, 1072, 1192, 1305, 1353, 1434, 1674, 2428, 3263, 3306, 3976
1-TS3	2346*i*, 146, 231, 437, 571, 656, 836, 917, 1015, 1135, 1149, 1160, 1215, 1360, 1395, 1579, 1976, 2421, 3161, 3223, 3258
1-TS4	1982*i*, 140, 197, 272, 419, 471, 564, 738, 772, 1029, 1145, 1243, 1267, 1332, 1400, 1486, 2205, 2389, 3275, 3284, 3918
1-TS5	634*i*, 78, 143, 297, 401, 508, 599, 773, 906, 1029, 1108, 1159, 1274, 1474, 1500, 1627, 2358, 3045, 3129, 3236, 3335
1-TS6	872*i*, 92, 180, 389, 424, 462, 493, 558, 807, 1000, 1060, 1091, 1267, 1350, 1442, 1496, 1754, 2480, 3051, 3133, 3199
1-TS7	777*i*, 189, 195, 334, 409, 468, 523, 568, 582, 916, 999, 1062, 1194, 1313, 1360, 1432, 1701, 2456, 3263, 3310, 3969
1-TS8	1462*i*, 58, 168, 216, 382, 476, 550, 601, 752, 1001, 1045, 1083, 1263, 1352, 1443, 1487, 1696, 2483, 3104, 3125, 3174
1-TS9	498*i*, 103, 148, 243, 365, 538, 704, 927, 954, 1008, 1071, 1211, 1313, 1378, 1524, 1667, 2209, 2343, 3237, 3257, 3362
2-TS1	475*i*, 159, 196, 238, 277, 451, 600, 652, 831, 898, 934, 1037, 1143, 1308, 1472, 1599, 2464, 3244, 3299,

	3353, 3912
2-TS2	2067*i*, 196, 289, 367, 399, 422, 591, 628, 710, 791, 997, 1208, 1288, 1365, 1426, 1478, 2219, 2392, 3259, 3395, 3984
2-TS3	237*i*, 52, 76, 243, 311, 446, 504, 700, 920, 1017, 1029, 1214, 1349, 1387, 1500, 1685, 2273, 3262, 3281, 3379, 3985
2-TS4	2286*i*, 211, 242, 399, 557, 593, 740, 863, 1015, 1030, 1110, 1138, 1176, 1306, 1427, 1481, 2003, 2478, 3178, 3214, 3333
2-TS5	392*i*, 126, 143, 256, 283, 454, 575, 591, 652, 906, 963, 1031, 1428, 1460, 1472, 1603, 2458, 3122, 3173, 3345, 3356
2-TS6	1016*i*, 181, 196, 288, 434, 470, 511, 637, 643, 755, 1033, 1080, 1232, 1454, 1518, 1523, 1707, 2458, 3122, 3199, 3240
3-TS1	556*i*, 76, 202, 259, 361, 400, 513, 749, 865, 898, 1038, 1065, 1128, 1368, 1485, 1753, 2169, 3252, 3273, 3359, 3911
3-TS2	504*i*, 63, 180, 218, 278, 283, 376, 561, 819, 907, 987, 1096, 1120, 1287, 1431, 1697, 2285, 3161, 3268, 3343, 3924
h-TS1	2156*i*, 84, 160, 200, 271, 403, 559, 639, 699, 819, 868, 951, 979, 1142, 1337, 1511, 1730, 2459, 3234, 3298, 3914
h-TS2	2084*i*, 95, 136, 208, 237, 402, 498, 615, 714, 775, 924, 1035, 1067, 1169, 1361, 1475, 1754, 2414, 3220, 3320, 3925

[a]experimental data from ref. 49; [b]*i* stands for imaginary frequency

Note S1: Other unimportant channels from 1-IM1, 2-IM1 and 3-IM1

1-IM2 can convert to 1-IM3 through 1-TS14 with a barrier of 27.75 kcal/mol. Apparently, the transition between 1-IM2 and 1-IM3 is not easy. 1-P8 (HCO+CH_2CNH) and 1-P9 (H+HCOCHCNH) can be generated by paths of 1-IM2→1-TS13→1-IM5→1-TS19→1-P8 and 1-IM2→1-TS13→1-IM5→1-TS20→1-P9, respectively. 1-IM1 can undergo 1,4 H-shift via 1-TS11 with a barrier of 68.07 kcal/mol to generate 1-IM4.

Starting from 2-IM1, 2-IM2 and 2-IM3, there are less important paths:

2-IM1→2-TS7→2-P3 (H+CH_2COHCN)

2-IM2→2-TS8→2-IM5→2-TS11→2-IM7→2-TS13→2-P5 (CH_2CO+HCNH)

2-IM3→2-TS9→2-IM6→2-TS12→1-P1 (H+ OHCHCHCN)

Starting from 3-IM1, the product channels of 3-P1 (CH_2CH+HOCN) and 3-P2 (C_2H_2+HOCNH) are found as follows:

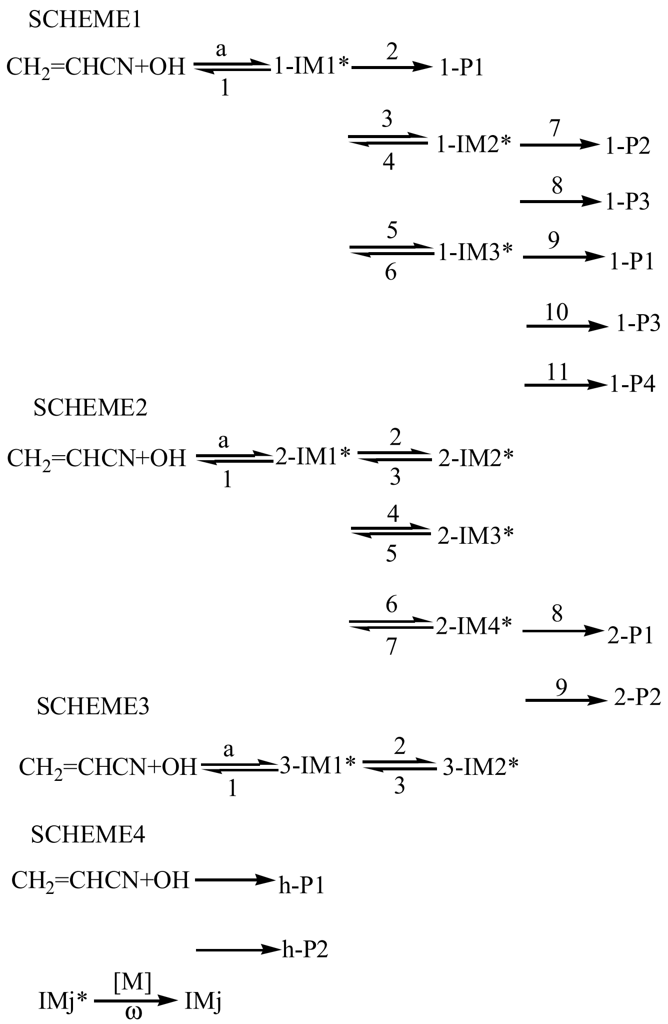
3-IM1→3-TS3 →3-P1 (CH_2CH+HOCN)

3-IM1→3-TS2→3-IM2→3-TS5→3-IM4→3-TS7→3-P2 (C_2H_2+HOCNH)

3-IM1→3-TS4→3-IM3→3-TS6→3-IM5→3-TS8→3-P2 (C_2H_2+HOCNH)

Note S2: Multichannel RRKM treatment for the OH+CH_2=CHCN reaction

The reaction schemes employed in the calculation is as follows:



Where "*" represents the vibrational excitation of intermediate (IMj). Steady-state approximation for energized intermediate (IMj*) leads to the following expressions:

For Scheme 1:

$$k_{1-P1}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{k_2(E)}{X_4}+\frac{k_5(E)k_9(E)}{X_3X_4}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (1)$$

$$k_{1-P2}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{k_7(E)k_3(E)}{X_2X_4}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (2)$$

$$k_{1-P3}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{k_3(E)k_8(E)}{X_2X_4}+\frac{k_5(E)k_{10}(E)}{X_3X_4}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq}$$

(3)

$$k_{1-P4}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{k_5(E)k_{11}(E)}{X_3X_4}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (4)$$

$$k_{1-IM1}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{\omega}{X_4}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (5)$$

$$k_{1-IM2}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{\omega k_3(E)}{X_2X_4}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (6)$$

$$k_{1-IM3}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{\omega k_5(E)}{X_3X_4}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (7)$$

With the following definition:

$X_1=k_1(E)+k_2(E)+k_3(E)+k_5(E)+\omega$

$X_2=k_4(E)+k_7(E)+k_8(E)+\omega$

$X_3=k_6(E)+k_9(E)+k_{10}(E)+k_{11}(E)+\omega$

$X_4=X_1-k_3(E)*k_4(E)/X_2-k_5(E)*k_6(E)/X_3$

For Scheme 2:

$$k_{2-P1}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{k_8(E)k_2(E)}{X_1X_5}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (8)$$

$$k_{2-P2}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{k_9(E)k_2(E)}{X_1X_5}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (9)$$

$$k_{2-IM1}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{\omega}{X_5}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (10)$$

$$k_{2-IM2}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{\omega k_2(E)}{X_1X_5}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (11)$$

$$k_{2-IM3}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{\omega k_4(E)}{X_2X_5}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (12)$$

$$k_{2-IM4}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{\omega k_6(E)}{X_3X_5}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (13)$$

With the following definition:

$X_1=k_3(E)+k_8(E)+k_9(E)+\omega$

$X_2=k_5(E)+\omega$

$X_3=k_7(E)+\omega$

$X_4=k_2(E)+k_4(E)+k_6(E)+\omega$

$X_5=X_4-k_2(E)*k_3(E)/X_1-k_4(E)*k_5(E)/X_2-k_6(E)*k_7(E)/X_3$

For Scheme 3:

$$k_{3-IM1}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{\omega}{X_3}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (14)$$

$$k_{3-IM2}(T,P)=\frac{\alpha_a}{h}\frac{Q_t^{\neq}Q_r^{\neq}}{Q_{CH_2=CHCN}Q_{OH}}e^{-E_a/RT}\times\int_0^{\infty}\frac{X_2\omega}{X_3}N_a(E^{\neq})e^{-E^{\neq}/RT}dE^{\neq} \quad (15)$$

With the following definition:

$X_1=k_1(E)+k_2(E)+\omega$

$X_2=k_2(E)/(k_3(E)+\omega)$

$X_3=X_1-k_3(E)*X_2$

The microcannonical rate constants are calculated using RRKM theory as follows:

$$k_i(E)=\alpha_i C_i N_i(E_i^{\neq})/h\rho_j(E_j) \quad (16)$$

In the above equations, α_a is statistical factor for the reaction path a, and α_i is the statistical factor (degeneracy) for the ith reaction path; E_a is the energy barrier for the reaction step a. Q_{OH} and $Q_{CH_2=CHCN}$ are the total partition function of OH and CH_2=CHCN, respectively; $Q_t^{\neq}$ and $Q_r^{\neq}$ are the translational and rotational partition functions of entrance transition state; $N_a(E^{\neq})$ is the number of state for the association transition state with excess energy $E^{\neq}$ above the association barrier. $k_i(E)$ is the energy-specific rate constant for the *i*th channel, and C_i is the ratio of the overall rotational partition function of TS_i and IM_j; $N_i(E_i^{\neq})$ is the number of states at the energy above the barrier height for transition state *i*; $\rho_j(E_j)$ is the density of states at energy E_j of intermediate *j*. The density of states and the number of states are calculated using the extended Beyer-Swinehart algorithm. Where $\omega=\beta_c Z_{LJ}[M]$, and β_c is the collision efficiency, which is calculated using Troe's weak collision approximation with the energy transfer parameter $-\langle \Delta E \rangle$. Z_{LJ} is Lennard-Jones collision frequency, and [M] is the concentration of the bath gas M.