Supporting Information for:

Product Branching in the Low Temperature Reaction of CN with Propyne by Chirped-Pulse Microwave Spectroscopy in Uniform Supersonic Flows

Chamara Abeysekera,[1] Baptiste Joalland,[1] Nuwandi Ariyasingha,[1] Lindsay N. Zack,[1] Ian R. Sims,[2] Robert W. Field,[3] Arthur G. Suits,[1,]*

[1] Department of Chemistry, Wayne State University, 5101 Cass Avenue, Detroit, MI 48202, USA
[2] Institut de Physique de Rennes, UMR CNRS-UR1 6251, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042, Rennes Cedex, France
[3] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

This document contains the energies, structures, and vibrational frequencies of the different minima and transition states of the complex-mediated pathways in the CN + C_3H_4 potential energy surface, along with the RRKM unimolecular reaction rates used to determine the branching ratios presented in the accompanying paper. All optimizations were performed at the CBS-QB3 level of theory with the Gaussian 09 package. The reaction rates take into account semiclassical tunneling correction using the Eckart method.

In addition, we includeplots of the raw time sequences and the integrated kinetic traces for the spectra.

Summary of Contents

Figure S19-S23 Time sequence plots and integrated kinetic traces for all species studied.

Secondary Reactions

We have considered the possibility that primary products of the CN + CH_3CCH reaction go on to react further. We have excluded closed shell products which would not react with the reactant propyne (which is in large excess). Of the three potential radical products, H atoms react roughly two to three orders of magnitude more slowly than CN with propyne at room temperature.[1,2] and even more slowly at lower temperatures, and so their further reaction can be discounted. This is also the case for methyl radicals which have been shown to react only very slowly with propyne at elevated temperatures, probably in an addition reaction.[3] Propargyl radicals are not thought to be reactive with propyne at room temperature and below.[4] We conclude therefore that interference from secondary products is unlikely in this study.

1. Carty, D.; Le Page, V.; Sims, I. R.; Smith, I. W. M., Chem Phys Lett 2001, 344, 310-316.

2. Whytock, D. A.; Payne, W. A.; Stief, L. J. J. Chem. Phys. 1976, 65, 191-195.

3. Getty, R. R.; Kerr, J. A.; Trotman-Dickenson, A. F. Journal of the Chemical Society A -Inorganic Physical Theoretical 1967, 1360.

4. Faravelli, T.; Goldaniga, A.; Zappella, L.; Ranzi, E.; Dagaut, P.; Cathonnet, M. Proceedings of the Combustion Institute 2000, 28, 2601-2608.

Theoretical Results

Table S1: C2 cplx 1, E(0K) = -209.092847 Ha Minimum **1**

XYZ coordinates (Angstroem)

C	-0.823786	1.456095	-0.000083
C	-0.425543	0.199379	0.000353
C	-1.357843	-0.994254	-0.000087
H	-0.380322	2.440161	-0.000322
H	-2.395087	-0.660705	-0.000373
H	-1.181989	-1.613870	0.883086
H	-1.181461	-1.613722	-0.883264
C	0.988525	-0.070887	0.000074
N	2.121535	-0.299123	-0.000095

Frequencies (cm^{-1})

166.1209	190.1237	294.3287
364.5887	553.7417	572.9435
724.2122	762.8417	839.5232
1029.5753	1055.1991	1186.8646
1407.2281	1480.8037	1482.0166
1653.1261	2322.8406	3037.2923
3096.4922	3133.6071	3253.1272

Table S2: C2 cplx 2, E(0K) = -209.092086 Ha Minimum **2**

XYZ coordinates (Angstroem)

C	-0.933862	1.397310	0.000037
C	-0.400303	0.192469	-0.000359
C	-1.208421	-1.097928	0.000043
H	-1.925505	1.824454	0.000305
H	-2.276769	-0.881931	0.000187
H	-0.966691	-1.692994	0.884488
H	-0.966984	-1.693304	-0.884268
C	1.029934	0.048894	0.000213
N	2.173124	-0.114385	-0.000045

Frequencies (cm^{-1})

167.0163	196.0891	287.3634
357.0909	579.9489	585.5788
712.8065	744.6216	843.9148
1019.3212	1038.0765	1181.5278
1401.1972	1478.2728	1482.5014
1657.8141	2336.9014	3035.4546
3098.0297	3128.6186	3247.7541

Table S3: C1 cplx 1, E(0K) = -209.099132 Ha Minimum **3**

XYZ coordinates (Angstroem)

C	-0.186202	0.976833	-0.000004
C	1.076432	0.590265	-0.000001
C	1.890977	-0.624440	0.000001
H	-0.454829	2.030352	0.000019
H	1.256685	-1.522624	-0.000048
H	2.536818	-0.660039	0.882765
H	2.536891	-0.659996	-0.882711
C	-1.269596	0.040094	0.000000
N	-2.135033	-0.726315	0.000001

Frequencies (cm^{-1})

119.0126	125.6511	312.3650
345.4311	480.1501	625.8963
788.6632	879.9003	992.9117
1039.0338	1055.9300	1294.0229
1394.0949	1449.3504	1460.2084
1716.8929	2325.0790	2981.3343
3059.2614	3080.7328	3131.8799

Table S4: C1 cplx 2, E(0K) = -209.099913 Ha Minimum **4**

XYZ coordinates (Angstroem)

C	0.148977	0.530175	-0.000098
C	-0.912755	-0.252247	-0.000001
C	-2.371844	-0.156235	-0.000005
H	0.037768	1.618842	-0.000049
H	-2.700028	0.893866	-0.000301
H	-2.795366	-0.645956	0.882342
H	-2.795381	-0.646451	-0.882068
C	1.491181	0.044103	0.000284
N	2.588522	-0.316439	-0.000143

Frequencies (cm^{-1})

151.3891	152.6848	205.6766
337.7896	465.4218	547.0275
781.2936	890.8911	1039.1499
1039.8720	1060.1615	1279.7360
1397.2662	1447.7749	1464.9537
1732.9942	2340.1858	2974.0875
3044.3038	3056.8166	3079.9099

Table S5: Hmig C1 cplx, E(0K) = -209.104106 Ha Minimum **5**

XYZ coordinates (Angstroem)

C	-0.184107	0.028451	0.000001
C	1.037220	0.495944	0.000002
C	2.296237	-0.327782	-0.000001
H	1.173069	1.582029	-0.000006
H	2.078817	-1.395396	0.000015
H	2.901609	-0.088811	0.880312
H	2.901589	-0.088833	-0.880333
C	-1.520568	-0.025054	0.000000
N	-2.689682	-0.148335	-0.000001

Frequencies (cm^{-1})

75.7165	145.0247	212.0534
408.2470	457.4282	542.2634
750.8947	781.7734	1031.8175
1054.3033	1094.5517	1313.2260
1403.5920	1480.9592	1484.4224
1822.0260	2102.4464	3024.6753
3045.8579	3074.4343	3130.1101

Table S6: cyclic cplx, E(0K) = -209.057833 Ha

XYZ coordinates (Angstroem)

C	-0.241635	1.226989	0.000006
C	0.524046	0.158220	-0.000014
C	1.858989	-0.471263	-0.000004
H	-0.326516	2.303615	0.000001
H	2.652374	0.278842	-0.000515
H	1.968754	-1.111964	-0.879290
H	1.969113	-1.111096	0.879876
C	-0.932199	-0.059574	-0.000002
N	-1.931275	-0.783662	0.000002

Frequencies (cm^{-1})

125.1358	217.4201	273.4962
466.8658	540.2685	637.7450
770.1509	834.9581	948.5357
1026.5571	1045.0247	1124.1797
1402.1426	1471.4677	1475.4393
1646.1066	1847.3388	3032.7149
3092.8301	3111.9193	3228.8988

Table S7: TS1, E(0K) = -209.086203 Ha

XYZ coordinates (Angstroem)

C	-0.915994	1.395492	-0.000003
C	-0.421597	0.185500	-0.000003
C	-1.244758	-1.096605	0.000002
H	-1.347331	2.369577	0.000023
H	-2.308903	-0.863366	0.000031
H	-1.008429	-1.695147	0.883854
H	-1.008473	-1.695127	-0.883876
C	1.012423	0.009745	-0.000006
N	2.156098	-0.154391	0.000005

Frequencies (cm^{-1})

-693.5174	157.2089	193.2332
287.7105	381.6658	568.2614
590.6715	657.6227	757.6497
1006.5866	1037.6367	1136.8026
1398.5119	1479.3148	1480.2342
1657.5327	2325.4082	3034.2813
3095.5787	3134.0949	3430.8721

Table S8: TS2a, E(0K) = -209.054160 Ha

XYZ coordinates (Angstroem)

C	-0.222927	1.143033	0.000009
C	0.605545	0.132988	-0.000030
C	1.950358	-0.454328	0.000004
H	-0.296660	2.225276	0.000021
H	2.725952	0.320486	-0.000334
H	2.084764	-1.089740	-0.879966
H	2.084943	-1.089134	0.880387
C	-1.096466	0.015394	-0.000011
N	-2.002580	-0.769916	0.000008

Frequencies (cm^{-1})

-643.7619	121.6364	190.1193
249.2026	431.5677	497.1890
762.7353	863.7365	925.6304
1042.2331	1042.5503	1135.8555
1396.6239	1461.1201	1466.6856
1792.7890	1910.3111	3006.5083
3077.4532	3089.4812	3158.0532

Table S9: TS2b, E(0K) = -209.053514 Ha

XYZ coordinates (Angstroem)

C	-0.092305	1.338424	0.000025
C	0.486569	0.168664	0.000006
C	1.783491	-0.561591	-0.000008
H	-0.032568	2.416133	-0.000119
H	2.616944	0.142136	-0.000224
H	1.853641	-1.203348	-0.881903
H	1.853838	-1.203025	0.882109
C	-0.904149	-0.179269	0.000017
N	-1.990498	-0.678467	-0.000014

Frequencies (cm^{-1})

-693.0590	131.6562	237.5815
262.4844	444.8605	533.7826
686.8723	746.0676	771.7350
974.9039	1044.3276	1170.7505
1402.3082	1473.8765	1480.8162
1745.6345	1941.9274	3038.6412
3099.8690	3125.0753	3242.2234

Table S10: TS3, E(0K) = -209.091281 Ha

XYZ coordinates (Angstroem)

C	-0.219522	0.784123	-0.000002
C	0.965373	0.230061	-0.000015
C	2.270177	-0.392085	0.000001
H	-0.353942	1.871034	0.000036
H	2.394684	-1.028746	-0.883648
H	2.394915	-1.028039	0.884124
H	3.091815	0.339581	-0.000396
C	-1.439849	0.025152	-0.000013
N	-2.426363	-0.576762	0.000008

Frequencies (cm^{-1})

-260.6381	24.1620	190.7992
309.7329	398.3587	544.2226
777.2891	841.0796	980.6567
1008.4971	1023.4951	1297.1753
1402.1960	1444.3842	1463.5327
1810.9939	2326.9312	2961.5360
3018.1972	3025.9344	3059.6687

Table S11: TS4, E(0K) = -209.025541 Ha

XYZ coordinates (Angstroem)

C	-0.213014	0.476824	-0.000011
C	1.080438	0.435918	-0.000032
C	2.298780	-0.407537	0.000007
H	0.418421	1.579869	0.000100
H	2.025294	-1.469860	-0.000282
H	2.909396	-0.198754	0.881971
H	2.909765	-0.198359	-0.881605
C	-1.492992	-0.044424	-0.000004
N	-2.614593	-0.353941	0.000008

Frequencies (cm^{-1})

-2120.7924	104.7178	132.6588
233.4553	301.4980	367.5025
531.9388	557.2652	708.0209
1024.7037	1025.2681	1061.2061
1389.1937	1460.0039	1469.2127
1925.8534	2260.5062	2318.7590
3002.6226	3081.8777	3098.3683

Table S12: TS5a, E(0K) = -209.043654 Ha

XYZ coordinates (Angstroem)

C	0.322630	0.585020	0.000004
C	-0.818702	1.011712	0.000012
C	-2.477377	-0.757711	0.000002
H	-1.627194	1.704856	0.000022
H	-1.806605	-1.605053	-0.000008
H	-2.960460	-0.488838	-0.930357
H	-2.960454	-0.488856	0.930369
C	1.533567	-0.038313	-0.000006
N	2.570573	-0.560909	-0.000014

Frequencies (cm^{-1})

-361.8872	49.9734	88.1213
246.1877	286.0633	415.7077
446.0882	530.1917	567.1750
676.3678	687.6092	801.9725
909.9393	1408.8916	1416.7160
2074.3339	2310.3344	3095.6435
3262.6556	3273.2585	3430.6733

Table S13: TS5b, E(0K) = -209.037740

XYZ coordinates (Angstroem)

C	1.175537	-1.445221	0.000001
C	0.294464	-0.590880	0.000003
C	1.124632	1.559507	-0.000001
H	2.094296	-1.983101	0.000000
H	2.187783	1.359366	0.000305
H	0.679931	1.901360	0.925785
H	0.680414	1.901110	-0.926111
C	-1.035732	-0.207357	0.000002
N	-2.142262	0.132139	-0.000001

Frequencies (cm^{-1})

-483.5199	61.7801	148.2981
252.1317	260.3252	486.0613
489.4080	530.7576	546.0952
571.2507	710.0046	861.5394
913.6938	1414.4248	1417.2161
1990.9261	2344.6161	3092.2103
3259.6224	3261.2658	3443.6866

Table S14: TS6a, E(0K) = -209.038847 Ha

XYZ coordinates (Angstroem)

C	0.223132	-0.039201	-0.000017
C	-0.989142	0.057579	0.000065
C	-2.430502	-0.162783	0.000129
H	-1.141469	2.079786	0.000274
H	-2.638711	-1.236334	0.000033
H	-2.892436	0.283337	-0.883769
H	-2.892330	0.283157	0.884173
C	1.586327	-0.037829	-0.000099
N	2.746579	-0.045220	-0.000169

Frequencies (cm^{-1})

-637.6042	138.5622	143.5684
170.3946	373.0976	410.0666
431.6909	558.3889	561.3711
681.4646	1040.0460	1055.5093
1174.5938	1411.3800	1467.4838
1472.1661	2217.1255	2347.6628
3033.6744	3100.2877	3102.4913

Table S15: TS6b, E(0K) = -208.999758

XYZ coordinates (Angstroem)

C	0.147911	-0.300090	-0.319243
C	1.243623	-0.956308	-0.028398
C	1.446024	0.823701	0.037215
H	1.510594	-1.570895	0.835983
H	0.744593	1.558343	0.454356
H	1.904422	1.167592	-0.880659
H	2.185572	0.683949	0.837927
C	-1.189144	-0.072854	-0.023107
N	-2.319381	0.170616	0.107657

Frequencies (cm^{-1})

-760.0358	73.0368	146.7634
167.6616	323.1890	367.6534
477.6617	555.8097	561.1147
699.2882	1034.4174	1047.5922
1174.0559	1409.0451	1462.2693
1465.8191	2200.7155	2366.9940
3018.6657	3078.2487	3092.2636

Table S16: TS7a, E(0K) = -209.035993 Ha

XYZ coordinates (Angstroem)

C	-0.181494	0.709281	0.000033
C	0.961058	0.066593	0.000024
C	2.138841	-0.498874	0.000020
H	-0.196569	1.797323	0.000087
H	3.539971	1.080217	0.000127
H	2.607146	-0.811248	-0.927945
H	2.607108	-0.811341	0.927974
C	-1.446578	0.048861	-0.000026
N	-2.484088	-0.458588	-0.000079

Frequencies (cm^{-1})

-473.5601	130.9426	176.4194
256.0706	362.6500	402.3114
410.0297	614.7055	680.4814
879.4802	908.0063	942.6248
1003.0314	1125.2371	1341.6974
1453.2108	2008.2984	2342.3740
3123.0002	3127.2015	3202.6180

Table S17: TS7b, E(0K) = -209.035599 Ha

XYZ coordinates (Angstroem)

C	-0.204970	-0.821889	0.000003
C	1.001390	-0.308395	0.000005
C	2.183882	0.248648	0.000007
H	-0.345015	-1.900360	0.000008
H	1.886686	2.315418	-0.000004
H	2.721806	0.413923	-0.928019
H	2.721799	0.413932	0.928035
C	-1.388198	-0.022628	-0.000005
N	-2.362556	0.597525	-0.000012

Frequencies (cm^{-1})

-515.7902	124.5304	208.5662
276.7048	342.9260	407.7656
418.9700	611.7780	689.5265
876.0490	910.2964	944.7199
1004.5587	1124.8580	1339.1478
1452.6398	2005.4015	2341.2691
3123.7950	3132.7960	3202.7704

Table S18: Unimolecular reaction rates (s^{-1}) with the five low-energy complexes numeroted from 1 to 5 (see Tables S1-5) and the three exit channels numeroted from 6 to 8 as the energy increases.

k (1 => 2) = .774146E+13
k (2 => 1) = .888271E+13
k (1 => 6) = .579485E+10
k (2 => 3) = .181510E+11
k (3 => 2) = .371402E+10
k (2 => 6) = .662817E+10
k (3 => 4) = .363129E+13
k (4 => 3) = .402967E+13
k (3 => 7) = .547689E+09
k (3 => 8) = .109960E+09
k (4 => 5) = .717695E+07
k (5 => 4) = .611148E+06
k (4 => 7) = .607496E+09
k (4 => 8) = .120707E+09
k (5 => 6) = .172761E+10
k (5 => 7) = .520853E+08

Figure S19. Time series and integrated kinetic traces for HCN product.

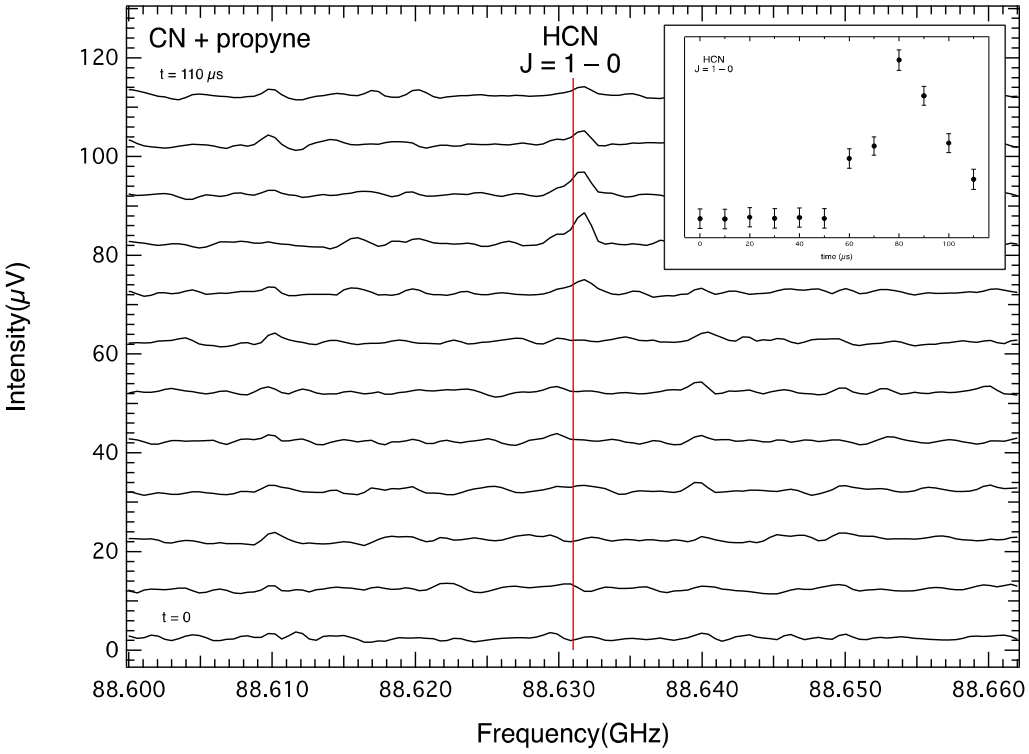

Figure S20. Time series and integrated kinetic traces for HCCCN product.

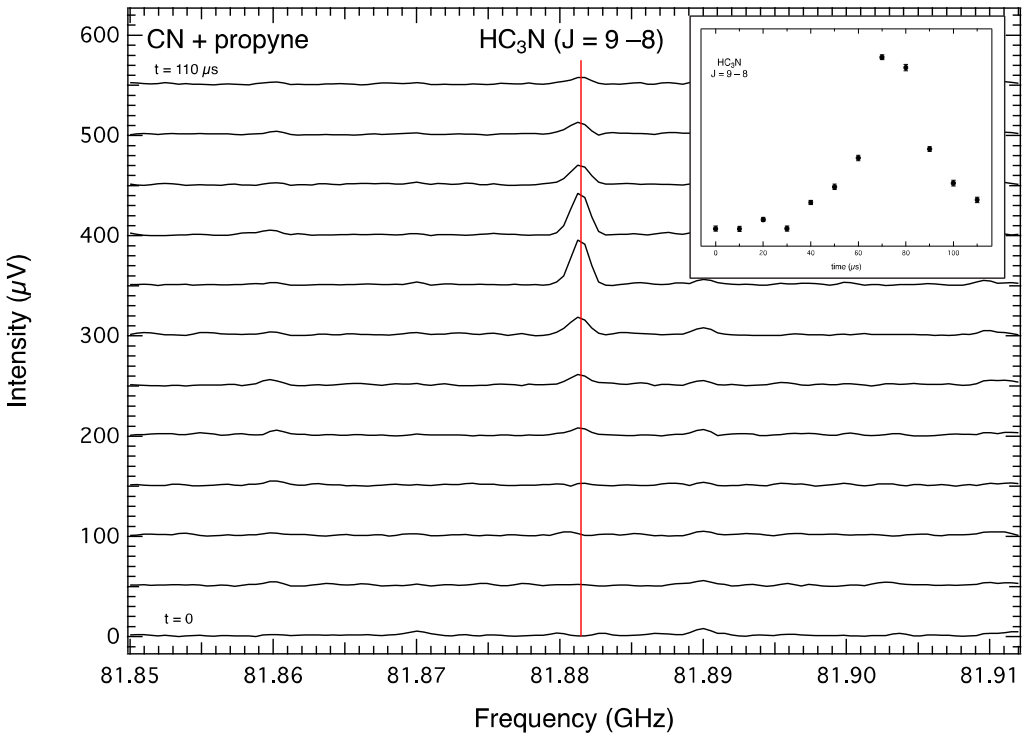

Figure S21. Time series and integrated kinetic traces for CH3CCCN product on $J_K(20_0$-$19_0)$ transition.

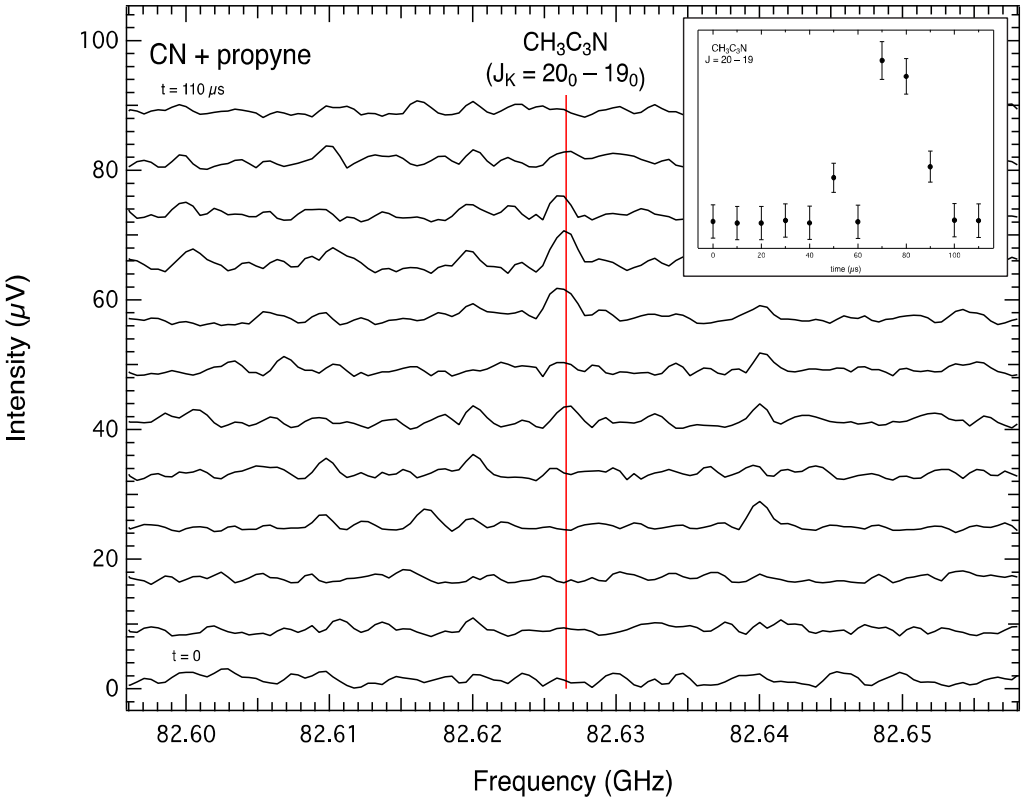

Figure S22. Time series and integrated kinetic traces for CH3CCCN product on $J_K(21_0$-$20_0)$ transition.