Supporting Information:

Mechanisms and dynamics of halophilic reaction between CH_2CN^- and CCl_4

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Table S1: Electronic energies (kcal/mol) of stationary points on the PES relative to the reactants for the reactions of CH_2CN^- with CCl_4 at the B3LYP/6-311++G** level of theory using spherical and Cartesian basis sets

	Spherical basis	Cartesian basis
Reactant	0	0
int1	-13.19	-13.09
ts1	-5.95	-5.85
HP	-20.71	-20.54
ts2	11.71	12.12
int3	-35.67	-35.39
ts3	-30.35	-30.05
int4	-34.14	-33.81
EP	-18.36	-18.23
int5	-4.47	-4.21
ts4	4.38	4.79
int6	-59.34	-58.97
S_N2 prdt	-56.78	-56.47

Table S2: Energies (kcal/mol) of stationary points on the PES relative to the reactants for the reaction of CCl_4 with CH_2CN^- using different methods with 6-311++G** basis set including zero-point energies

	halophilic pathway				H/Cl exchange pathway					S_N2 pathway			
theory	**int1**	**ts1**	**int2**	**HP**	**ts2**	**int3**	**ts3**	**int4**	**EP**	**int5**	**ts4**	**int6**	**S_N2**
B3LYP	-12.52	-6.11	-25.49	-19.11	12.07	-33.67	-30.93	-32.02	-16.27	-4.31	5.43	-55.02	-52.58
MP2	-9.14	-6.97	-18.46	-9.47	12.49*	-30.16	-30.44	-31.91	-11.53	-4.48	8.27	-62.95	-57.57
B971	-13.58	-7.20	-27.39	-19.74	12.09	-35.68	-33.87	-33.96	-16.22	-6.12	4.45	-57.01	-53.14
OLYP	-14.79	-3.46*	-25.35	-20.02	6.31	-32.31	-30.95	-30.62	-16.39	-9.97	4.50	-45.96	-47.84
BHandH	-12.67	-8.21	-21.51	-10.04	27.01	-32.07	-32.65	-34.55	-13.82	-9.48	6.57	-65.29	-58.53
OPBE	-12.82	-4.94*	-23.50	-16.05	12.87	-30.41	-31.28	-30.42	-15.54	-7.41	7.93	-49.40	-47.42
BHandHLYP	-8.65	-4.92	-23.11	-18.04	28.72	-33.53	-29.52	-32.82	-17.40	-1.44*	14.07	-61.01	-58.37
ωB97XD	-9.44	-5.96	-23.07	-16.70	23.87	-34.24	-32.45	-33.89	-15.64	-5.59	10.42	-61.06	-56.92
M06-2X	-10.44	-7.34	-24.14	-16.79	22.03	-34.30	-31.87	-33.29	-14.90	-7.97*	5.80	-62.15	-56.19
CAM-B3LYP	-9.22	-5.19	-21.59	-15.62	25.17	-31.80	-29.62	-31.76	-15.67	-2.08	11.80	-58.66	-55.64

* Energies correspond to structures obtained by constrained optimization. See text for details.

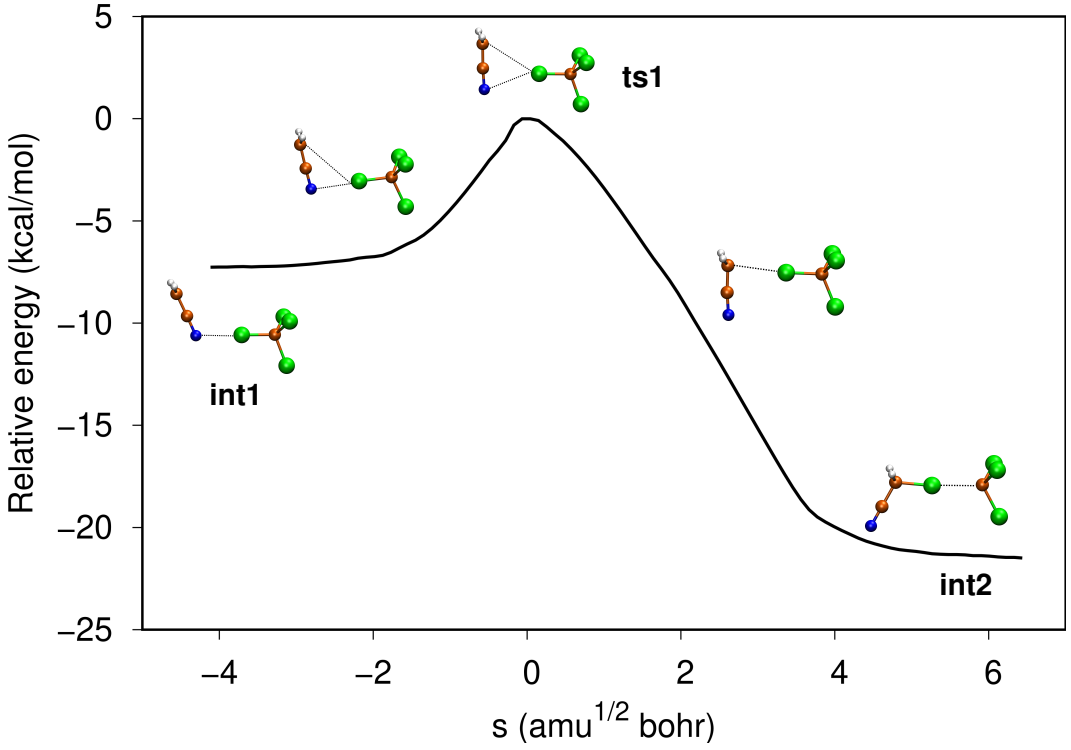

Figure S1: IRC from **ts1** connecting **int1** and **int2** via **ts1**.

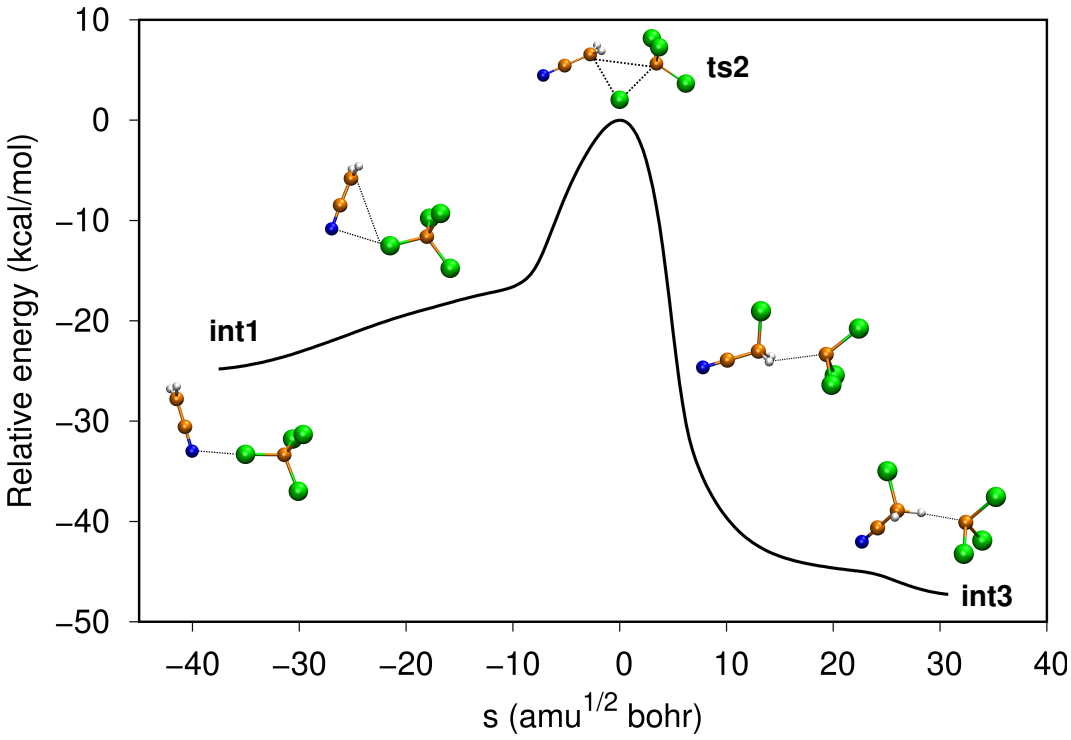

Figure S2: IRC from **ts2** connecting the **int1** and **int3** via **ts2**.

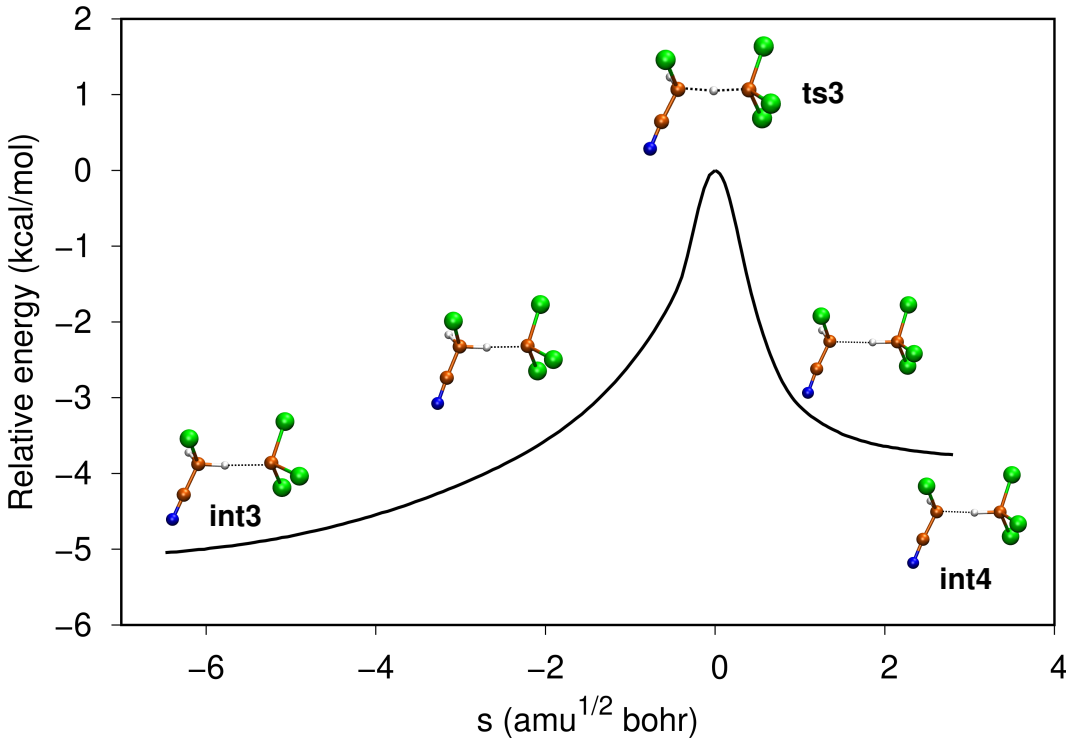

Figure S3: IRC from **ts3** connecting the **int3** and **int4** via **ts3**.

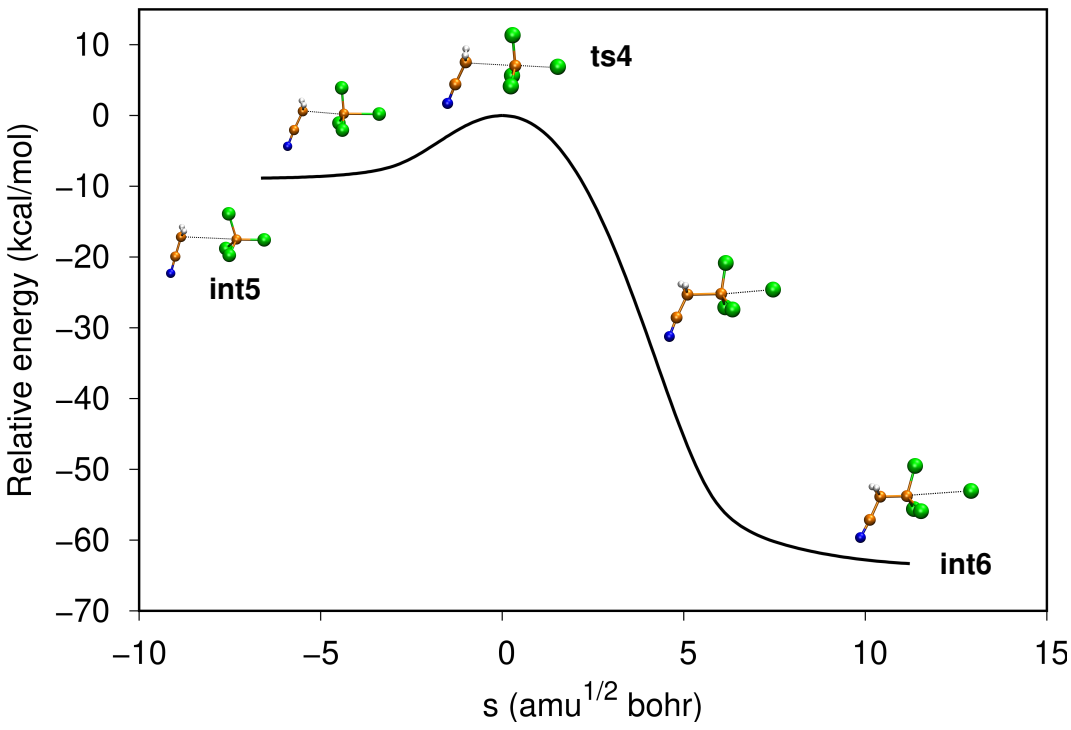

Figure S4: IRC from **ts4** connecting the **int5** and **int6** via **ts4**.

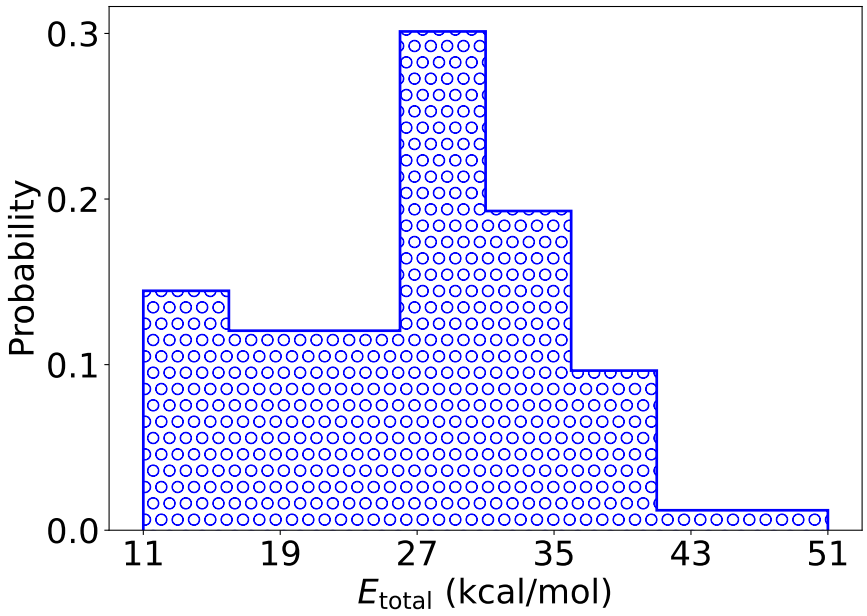

Figure S5: Distribution of total energy of non-reactive bimolecular AIMD trajectories.

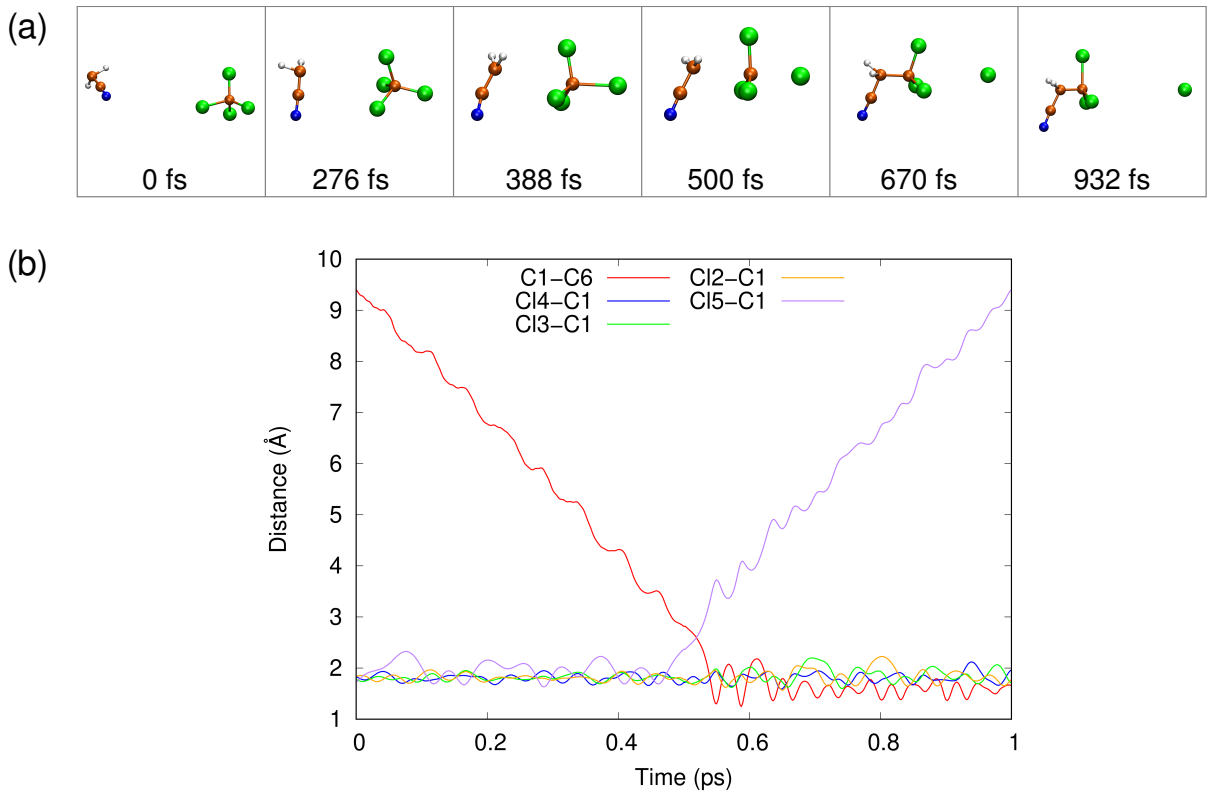

Figure S6: (a) Snapshots of a representative S_N2 trajectory initiated from **ts4**. The 500 fs frame corresponds the initial coordinates used in the computation of the trajectory in the forward and reverse directions. (b) Plot of important bond lengths as a function of integration time for the same representative trajectory.

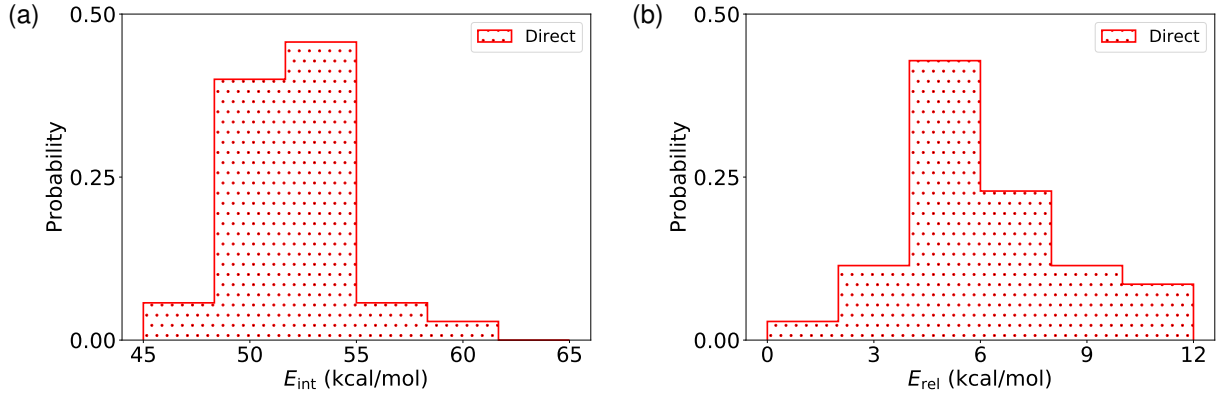

Figure S7: Distribution of (a) internal and (b) relative translational energies for S_N2 products.

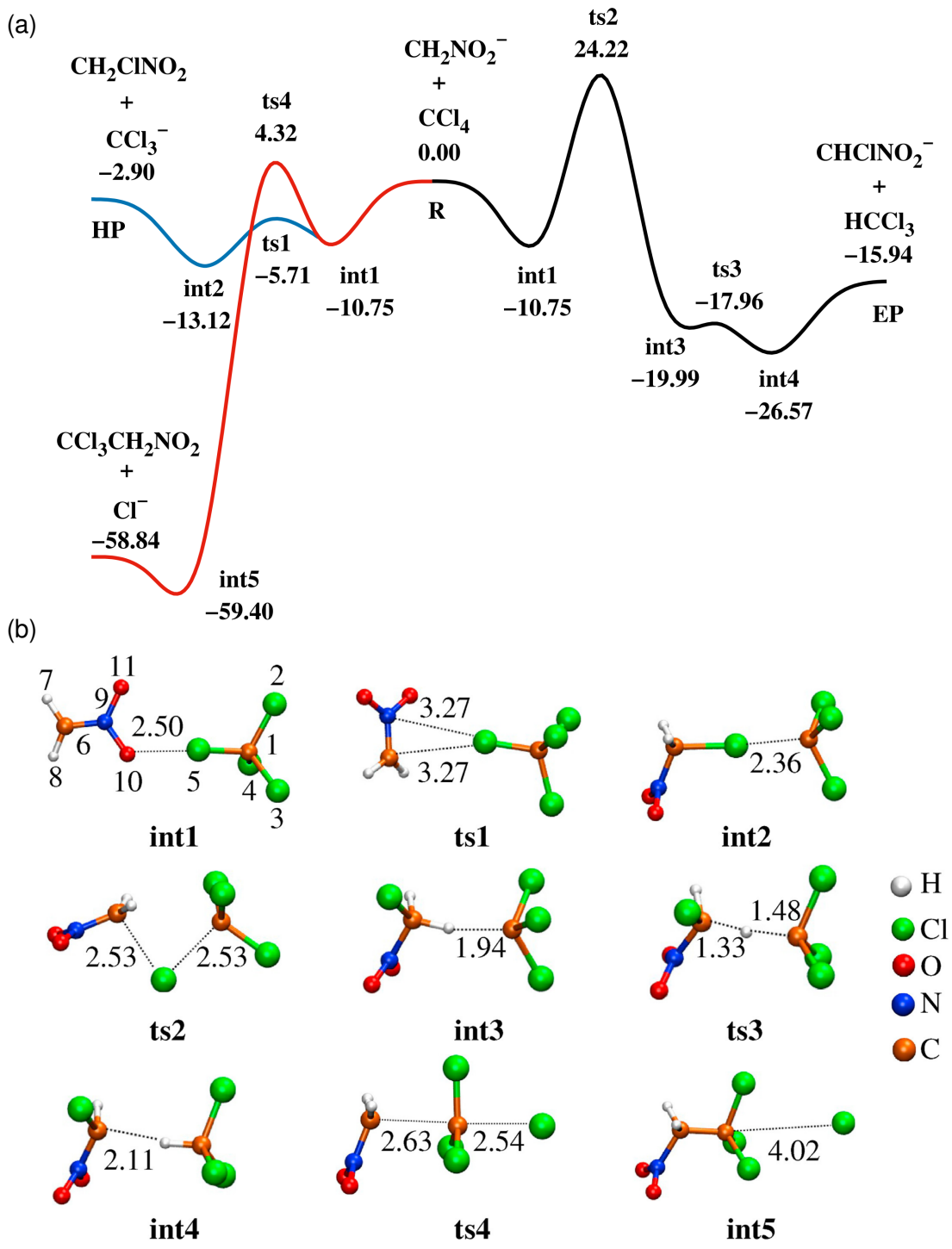

Figure S8: (a) Potential energy profiles depicting halophilic (S_N2@Cl) path (blue), S_N2 path (red), and direct H/Cl exchange path (black) for the reaction of $CH_2NO_2^-$ with CCl_4 obtained at B3LYP/6-311++G** level of theory. The energies are in kcal/mol and do not include zero-point energy. (b) Stationary point structures on the PES for the $CH_2NO_2^-$ + CCl_4 reaction obtained at the B3LYP/6-311++G** level of theory. The atom indices used to define different internal coordinates are indicated in **int1**. Important inter-atomic distances are given in Å units.[S1]

Coordinates of stationary points on the PES at B3LYP/6-311++G level of theory.**

Coordinates are in Å units and energies are in atomic units.

CCl_4
Electronic energy = −1878.98312214 A.U.
Sum of electronic and zero-point energy = −1878.973908 A.U.

C	−0.000000	−0.000000	0.000000
Cl	0.000000	0.000000	1.791417
Cl	1.688964	0.000000	−0.597139
Cl	−0.844482	−1.462686	−0.597139
Cl	−0.844483	1.462686	−0.597139

CH_2CN^-
Electronic energy = −132.191862617 A.U.
Sum of electronic and zero-point energy = −132.161856 A.U.

C	0.092919	0.186639	0.064375
H	−0.052479	−0.097751	1.100173
H	1.021123	−0.105228	−0.413273
C	−0.646250	1.227301	−0.465119
N	−1.298095	2.096404	−0.931821

int1
Electronic energy = −2011.19601274 A.U.
Sum of electronic and zero-point energy = −2011.155708 A.U.

C	−3.859012	0.244967	0.000518
C	−4.752631	−0.781639	−0.002646
N	−3.095422	1.155680	0.003397
H	−5.102285	−1.202838	−0.935718
H	−5.103260	−1.207821	0.927795
Cl	−0.663764	0.462057	0.001374
C	1.098059	−0.027167	−0.000458
Cl	1.633936	−0.549872	1.664174
Cl	1.392706	−1.413247	−1.146687
Cl	2.163885	1.365999	−0.518878

ts1
Electronic energy = −2011.18446001 A.U.
Sum of electronic and zero-point energy = −2011.145498 A.U.

C	3.824932	0.184041	−0.080543
C	3.985327	−1.079117	0.446527
N	3.630509	1.261056	−0.529923
H	4.186157	−1.200691	1.503667
H	4.177951	−1.917215	−0.211644
Cl	0.702946	0.097915	−0.060813
C	−1.033390	−0.021136	−0.010630
Cl	−1.717054	−0.317051	−1.665920
Cl	−1.569602	−1.384794	1.061205
Cl	−1.782325	1.512667	0.641232

int2
Electronic energy = −2011.21873626 A.U.
Sum of electronic and zero-point energy = −2011.176381 A.U.

C	0.063908	−0.277755	0.072060
H	0.001057	−0.214227	1.157357
H	1.100920	−0.184843	−0.247036
C	−0.489279	−1.529867	−0.387342
Cl	−0.848291	1.245456	−0.610447
N	−0.933295	−2.532352	−0.755932
C	−1.944476	3.410964	−1.423164
Cl	−2.438261	4.522511	0.006946
Cl	−0.781911	4.440272	−2.477180
Cl	−3.492431	3.191862	−2.447451

CCl_3^-
Electronic energy = −592.405461790 A.U.
Sum of electronic and zero-point energy = −592.368565 A.U.

C	−0.085269	0.148050	−0.060292
Cl	0.011376	−0.019738	1.866940
Cl	1.763963	−0.019736	−0.611593
Cl	−0.865108	−1.537449	−0.611726

CH_2ClCN
Electronic energy = −1418.80253165 A.U.
Sum of electronic and zero-point energy = −1418.797661 A.U.

C	0.001357	−0.165815	1.544867
C	0.007946	−0.097741	0.092903
N	0.013163	−0.016806	−1.056542
H	−0.890252	0.319601	1.938907
H	0.889382	0.319551	1.946980
Cl	−0.001386	−1.874335	2.139063

ts2
Electronic energy = −2011.15631863 A.U.
Sum of electronic and zero-point energy = −2011.116532 A.U.

C	−2.200159	−0.783813	0.000006
H	−1.727411	−1.055390	−0.930362
H	−1.727416	−1.055376	0.930381
C	−3.509429	−0.339707	−0.000001
N	−4.610487	0.055731	−0.000007
Cl	−0.891565	1.595288	0.000001
C	1.063164	−0.039116	−0.000001
Cl	2.457961	1.078200	−0.000010
Cl	1.087592	−1.080959	1.483559
Cl	1.087586	−1.080973	−1.483551

int3
Electronic energy = −2011.23182401 A.U.
Sum of electronic and zero-point energy = −2011.189416 A.U.

C	2.728839	1.235338	0.034813
C	1.972342	0.059966	-0.347457
H	1.893305	-0.004123	-1.431146
Cl	2.825630	-1.451317	0.213132
H	0.939266	0.057497	0.073908
N	3.321249	2.181167	0.330691
C	-1.125735	0.018685	0.131229
Cl	-2.074815	-1.509425	0.696447
Cl	-2.076839	1.475374	0.858554
Cl	-1.469964	0.120442	-1.760470

ts3
Electronic energy = −2011.22335336 A.U.
Sum of electronic and zero-point energy = −2011.185062 A.U.

C	2.481070	1.222723	-0.155560
C	1.743846	0.085011	-0.594573
H	1.789349	-0.018791	-1.677693
Cl	2.472527	-1.465584	0.089841
N	3.006973	2.188369	0.222718
H	0.376022	0.084960	-0.233182
C	-0.998792	0.035724	-0.003849
Cl	-1.457911	-0.059015	1.766593
Cl	-1.768277	1.554794	-0.705964
Cl	-1.750512	-1.409341	-0.863662

int4
Electronic energy = −2011.22939640 A.U.
Sum of electronic and zero-point energy = −2011.186788 A.U.

C	-1.891706	0.110889	0.644900
C	-2.596228	1.235820	0.173029
H	-1.976504	-0.010976	1.722786
Cl	-2.583534	-1.461532	-0.082280
H	0.027198	0.086008	0.192570
N	-3.084554	2.214868	-0.241025
C	1.140263	0.038995	0.008821
Cl	1.802447	-1.416478	0.845775
Cl	1.458231	-0.061989	-1.758586
Cl	1.889086	1.531513	0.691418

$CHClCN^-$
Electronic energy = −591.824537615 A.U.
Sum of electronic and zero-point energy = −591.801772 A.U.

C	-0.010539	0.096672	1.409385
Cl	0.175495	-0.201061	-0.429158
C	1.216719	0.050827	2.071265
N	2.202738	-0.062398	2.702456
H	-0.541786	1.038850	1.502713

$CHCl_3$
Electronic energy = −1419.37969876 A.U.
Sum of electronic and zero-point energy = −1419.359926 A.U.

C	0.012713	-0.022020	0.008989
Cl	-0.870162	-1.443886	-0.615301
Cl	-0.018270	0.031646	1.794226
Cl	1.685522	0.031652	-0.615302
H	-0.497486	0.861663	-0.351773

int5
Electronic energy = −2011.18232593 A.U.
Sum of electronic and zero-point energy = −2011.142632 A.U.

C	-0.177606	0.294723	0.872013
Cl	-0.984397	-1.264132	0.456437
Cl	-0.973306	1.681271	-0.008870
Cl	1.580114	0.218950	0.474849
C	0.004918	0.031127	-2.820077
C	0.630104	-1.038920	-3.423052
N	1.169045	-1.961545	-3.922259
Cl	-0.357359	0.582940	2.685772
H	-1.060647	0.011612	-2.643387
H	0.549284	0.944741	-2.630289

ts4
Electronic energy = −2011.16800000 A.U.
Sum of electronic and zero-point energy = −2011.127116 A.U.

C	0.440956	0.081514	0.000000
Cl	-0.008482	-0.682498	-1.497136
Cl	0.789720	1.795336	-0.000003
Cl	-0.008480	-0.682494	1.497138
Cl	2.710292	-0.633355	0.000000
C	-2.157070	1.046886	0.000000
C	-3.068101	-0.000392	0.000000
H	-2.007562	1.591478	0.923498
H	-2.007562	1.591478	-0.923498
N	-3.784492	-0.928546	0.000000

int6
Electronic energy = −2011.26955395 A.U.
Sum of electronic and zero-point energy = −2011.223440 A.U.

C	-0.070249	0.128400	-0.566578
Cl	-0.929403	-1.325950	0.026594
Cl	-0.933473	1.611109	-0.045220
Cl	1.612085	0.147070	0.045420
C	-0.064246	0.137751	-2.108536
C	0.599359	-0.999083	-2.743838
N	1.105534	-1.865161	-3.311375
Cl	-0.330878	0.526833	3.437988
H	-1.101872	0.169306	-2.448508
H	0.427875	1.055933	-2.437176

Cl_3CCH_2CN
Electronic energy = −1550.96173641 A.U.
Sum of electronic and zero-point energy = −1550.915834 A.U.

C	0.328138	0.000029	0.068339
Cl	0.171856	1.467516	-0.951403
C	-0.741626	0.000259	1.174780
C	-2.115840	-0.000140	0.681851
N	-3.212651	-0.000447	0.330711
Cl	1.940293	0.000581	0.874656
Cl	0.172328	-1.468249	-0.950336
H	-0.585616	0.884656	1.797126
H	-0.585331	-0.883634	1.797769

References

(S1) Mitra, S.; Dutta, S. S.; Sharma, N.; Lourderaj, U. *Int. J. Mass Spectrom.* **2021**, *459*, 116470.