TABLE SM-1: Ab Initio Total Energies (a.u.)

	MP2/ cc-pVDZ	SVWN5/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2
CCl_4	-1876.536607	-1872.634109	-1878.902011	-1878.897022
$CHCl_3$	-1417.496763	-1414.509842	-1419.314574	-1419.315195
CH_2Cl_2	-958.452581	-956.379224	-959.719644	-959.725350
CH_3Cl	-499.406600	-498.245976	-500.120307	-500.130327
CH_4	-40.361566	-40.114710	-40.520473	-40.533604
CCl_3OH	-1492.548145	-1489.246334	-1494.555802	-1494.558605
$CHCl_2OH$	-1033.499902	-1031.113025	-1034.959541	-1034.967790
CH_2ClOH	-574.443606	-572.969067	-575.351673	-575.365300
CH_3OH	-115.391869	-114.830242	-115.747263	-115.764602
CCl_3SH	-1815.150117	-1811.335380	-1817.497586	-1817.496449
$CHCl_2SH$	-1356.107398	-1353.207994	-1357.907091	-1357.911625
CH_2ClSH	-897.059253	-895.072661	-898.307574	-898.317268
CH_3SH	-438.014735	-436.942538	-438.710937	-438.724070
CCl_3NO_3	-1696.529692	-1692.328488	-1699.070431	-1699.054470
$CHCl_2NO_3$	-1237.488883	-1234.205498	-1239.483627	-1239.475243
CH_2ClNO_3	-778.438606	-776.069592	-779.882889	-779.881303
CH_3NO_3	-319.392999	-317.938575	-320.285180	-320.288055
$CCl_3(HCO_3)$	-1680.658500	-1676.492477	-1683.156160	-1683.168297
$CHCl_2(HCO_3)$	-1221.623880	-1218.372752	-1223.574551	-1223.592138
$CH_2Cl(HCO_3)$	-762.577482	-760.239504	-763.977097	-763.999623
$CH_3(HCO_3)$	-303.528458	-302.103416	-304.375441	-304.402536
$CCl_3(H_2PO_4)$	-2059.219069	-2054.233133	-2062.325982	-2062.352315
$CHCl_2(H_2PO_4)$	-1600.181335	-1596.111162	-1602.740681	-1602.772916
$CH_2Cl(H_2PO_4)$	-1141.134112	-1137.978076	-1143.143336	-1143.180485
$CH_3(H_2PO_4)$	-682.079792	-679.836239	-683.537699	-683.579515
$CCl_3(HSO_3)$	-2040.243162	-2035.503330	-2043.194766	-2043.193515
$CHCl_2(HSO_3)$	-1581.202853	-1577.381136	-1583.604581	-1583.610277
$CH_2Cl(HSO_3)$	-1122.152528	-1119.243568	-1124.005653	-1124.016533
$CH_3(HSO_3)$	-663.099393	-661.10406	-664.39976	-664.415861
$CCl_3(HSO_4)$	-2115.26214	-2110.208191	-2118.402934	-2118.403728
$CHCl_2(HSO_4)$	-1656.221318	-1652.082936	-1658.814176	-1658.821227
$CH_2Cl(HSO_4)$	-1197.179463	-1193.955737	-1199.223017	-1199.235829
$CH_3(HSO_4)$	-738.135588	-735.816416	-739.615916	-739.632951
CCl_3F	-1516.529908	-1513.178025	-1518.576241	-1518.580856
$CHCl_2F$	-1057.486343	-1055.048515	-1058.983606	-1058.993622
CH_2ClF	-598.436770	-596.911211	-599.382281	-599.397447
CH_3F	-139.383318	-138.769772	-139.775167	-139.794870

Table SM-2: Enthaply Corrections (a.u.) from ab initio calculations.

	MP2/ cc-pVDZ	SVWN5/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2
CCl_4	0.016362	0.015912	0.015583	0.015854
$CHCl_3$	0.025664	0.024784	0.024696	0.025221
CH_2Cl_2	0.034352	0.033086	0.033214	0.033911
CH_3Cl	0.042270	0.040651	0.040971	0.041770
CH_4	0.049252	0.047309	0.047720	0.048627
CCl_3OH	0.030368	0.029453	0.029188	0.029804
$CHCl_2OH$	0.039625	0.038208	0.038135	0.039036
CH_2ClOH	0.047158	0.045314	0.045419	0.046534
CH_3OH	0.056302	0.054099	0.054379	0.055586
CCl_3SH	0.025829	0.024893	0.024688	0.025158
$CHCl_2SH$	0.034972	0.033615	0.033603	0.034353
CH_2ClSH	0.043428	0.041705	0.041903	0.042791
CH_3SH	0.051287	0.049305	0.049701	0.050647
CCl_3NO_3	0.034027	0.033528	0.032544	0.033373
$CHCl_2NO_3$	0.043740	0.042608	0.041832	0.043078
CH_2ClNO_3	0.052822	0.050946	0.050426	0.051921
CH_3NO_3	0.061118	0.058826	0.058459	0.060083
$CCl_3(HCO_3)$	0.047661	0.046556	0.045728	0.046936
$CHCl_2(HCO_3)$	0.056561	0.055755	0.055214	0.056717
$CH_2Cl(HCO_3)$	0.066464	0.064262	0.063934	0.065611
$CH_3(HCO_3)$	0.074686	0.072135	0.072033	0.073784
$CCl_3(H_2PO_4)$	0.059681	0.058497	0.057866	0.059247
$CHCl_2(H_2PO_4)$	0.069342	0.067467	0.067172	0.068830
$CH_2Cl(H_2PO_4)$	0.078293	0.075946	0.075875	0.077738
$CH_3(H_2PO_4)$	0.086425	0.083985	0.083961	0.085934
$CCl_3(HSO_3)$	0.042231	0.041326	0.040673	0.041665
$CHCl_2(HSO_3)$	0.051803	0.050013	0.049736	0.051180
$CH_2Cl(HSO_3)$	0.060651	0.058637	0.058418	0.060050
$CH_3(HSO_3)$	0.068728	0.066412	0.066330	0.068080
$CCl_3(HSO_4)$	0.048567	0.047511	0.046611	0.047869
$CHCl_2(HSO_4)$	0.058110	0.056460	0.055801	0.057377
$CH_2Cl(HSO_4)$	0.067158	0.065092	0.064644	0.066430
$CH_3(HSO_4)$	0.075456	0.072904	0.072689	0.074561
CCl_3F	0.017613	0.017228	0.016832	0.017174
$CHCl_2F$	0.027032	0.026073	0.025924	0.026538
CH_2ClF	0.035845	0.034371	0.034431	0.035252
CH_3F	0.043730	0.041891	0.042132	0.043083

Table SM-3: Zero point energy corrections (a.u.) from ab initio vibrational calculations.

	MP2/ cc-pVDZ	SVWN5/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2
CCl_4	0.009904	0.009310	0.008866	0.009238
$CHCl_3$	0.020338	0.019356	0.019201	0.019792
CH_2Cl_2	0.029885	0.028562	0.028654	0. 029885
CH_3Cl	0.038327	0.036679	0.036989	0.037803
CH_4	0.045439	0.043483	0.043902	0.044815
CCl_3OH	0.023935	0.022790	0.022444	0.023168
$CHCl_2OH$	0.034159	0.032569	0.032454	0.033419
CH_2ClOH	0.042885	0.040992	0.041070	0.042217
CH_3OH	0.052076	0.049781	0.050065	0.051277
CCl_3SH	0.018802	0.017661	0.017382	0.017962
$CHCl_2SH$	0.029036	0.027499	0.027438	0.028293
CH_2ClSH	0.038204	0.036335	0.036367	0.037415
CH_3SH	0.046779	0.044736	0.045139	0.046094
CCl_3NO_3	0.024718	0.024412	0.023042	0.024237
$CHCl_2NO_3$	0.035856	0.034680	0.033593	0.035147
CH_2ClNO_3	0.046024	0.044051	0.043326	0.045022
CH_3NO_3	0.055293	0.052899	0.052385	0.054152
$CCl_3(HCO_3)$	0.038614	0.037340	0.036303	0.037703
$CHCl_2(HCO_3)$	0.049465	0.047652	0.046962	0.048593
$CH_2Cl(HCO_3)$	0.059593	0.057269	0.056831	0.058618
$CH_3(HCO_3)$	0.068546	0.065785	0.065647	0.067502
$CCl_3(H_2PO_4)$	0.047937	0.046514	0.045716	0.047401
$CHCl_2(H_2PO_4)$	0.058956	0.057161	0.056390	0.058214
$CH_2Cl(H_2PO_4)$	0.069044	0.066793	0.066301	0.068309
$CH_3(H_2PO_4)$	0.077816	0.075397	0.075231	0.077346
$CCl_3(HSO_3)$	0.031801	0.030691	0.029720	0.031040
$CHCl_2(HSO_3)$	0.042871	0.041160	0.040339	0.042057
$CH_2Cl(HSO_3)$	0.052649	0.050459	0.050060	0.051950
$CH_3(HSO_3)$	0.061533	0.059121	0.058797	0.060772
$CCl_3(HSO_4)$	0.037827	0.036578	0.035375	0.036959
$CHCl_2(HSO_4)$	0.048643	0.046803	0.045885	0.047751
$CH_2Cl(HSO_4)$	0.058728	0.056551	0.055899	0.057934
$CH_3(HSO_4)$	0.067855	0.065148	0.064772	0.066839
CCl_3F	0.011573	0.011068	0.010571	0.011009
$CHCl_2F$	0.022027	0.020982	0.020773	0.021451
CH_2ClF	0.031587	0.030064	0.030095	0.030950
CH_3F	0.039881	0.038023	0.038260	0.039223

TABLE SM-4: Calculated enthalpy changes (kcal/mol) for the isodesmic reactions in the gas phase: $CCl_xH_yN + CH_4 \rightarrow Cl_xH_{y+1} + CH_3N$. The ab initio energy values used to determine these enthalpy changes are given by Tables SM-3 and SM-4.

	$\Delta H_{isodesmic}$(298.15K, 1 bar)			
	MP2/ cc-pVDZ	**LDA/ DZVP2**	**BP91/ DZVP2**	**B3LYP/ DZVP2**
CCl_3OH	14.70	14.48	10.42	9.28
$CHCl_2OH$	11.79	12.51	9.32	8.33
CH_2ClOH	5.56	6.08	4.26	3.87
CCl_3SH	1.29	-0.25	-3.43	-4.47
$CHCl_2SH$	1.92	1.51	-0.89	-1.64
CH_2ClSH	0.23	-0.13	-1.35	-1.59
$CCl_3(NO_3)$	3.14	-1.53	-3.74	-7.45
$CHCl_2(NO_3)$	4.61	2.76	0.87	-1.42
$CH_2Cl(NO_3)$	1.18	0.61	-0.53	-1.36
$CCl_3(HCO_3)$	-1.08	-1.89	-6.34	-7.77
$CHCl_2(HCO_3)$	4.79	4.38	1.41	0.13
$CH_2Cl(HCO_3)$	3.28	3.79	1.99	1.05
$CCl_3(HSO_3)$	7.20	4.20	2.22	0.58
$CHCl_2(HSO_3)$	9.08	9.25	4.86	3.05
$CH_2Cl(HSO_3)$	5.77	5.87	4.53	3.21
$CCl_3(HSO_4)$	-3.35	-0.31	-2.53	-4.72
$CHCl_2(HSO_4)$	-1.78	2.65	0.92	-0.63
$CH_2Cl(HSO_4)$	0.10	5.78	5.37	4.66
$CCl_3(H_2PO_4)$	4.54	2.96	-1.72	-3.46
$CHCl_2(H_2PO_4)$	7.98	7.97	3.82	2.54
$CH_2Cl(H_2PO_4)$	6.54	7.50	4.48	3.51
CCl_3F	8.74	9.58	5.80	4.33
CCl_2HF	8.66	9.93	6.88	5.54
$CClH_2F$	5.84	6.92	5.17	4.28
CH_3F				

TABLE SM-5: Gas-phase standard Gibbs free energies (kcal/mol) of formation (ΔG_f(298K)). The experimental and ab initio values used to determine these Gibbs free energies can be found in Tables 2-3. The isodesmic exchange reactions are: $CCl_xH_yN + CH_4 \rightarrow Cl_xH_{y+1} + CH_3N$.

	ΔG°_f(298.15K) (isodesmic formulation)				ΔG°_f (298.15K)
	MP2/ cc-pVDZ	LDA/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2	Exp
CCl_3OH	-55.14	-55.20	-51.25	-49.98	
$CHCl_2OH$	-51.61	-52.21	-50.51	-49.46	
CH_2ClOH	-43.73	-43.71	-42.98	-42.56	
CH_3OH					-38.71
CCl_3SH	-5.17	-3.88	-0.79	+0.38	
$CHCl_2SH$	-5.16	-4.98	-2.64	-1.76	
CH_2ClSH	-2/60	-2.51	-1.96	-1.12	
CH_3SH					-2.22
$CCl_3(NO_3)$	-13.48	-8.33	-6.79	-2.54	
$CHCl_2(NO_3)$	-14.03	-12.39	-11.64	-8.26	
$CH_2Cl(NO_3)$	-9.90	-8.90	-8.15	-6.95	
$CH_3(NO_3)$					-9.77
$CCl_3(HCO_3)$	-125.72	-125.15	-121.06	-119.38	
$CHCl_2(HCO_3)$	-129.90	-131.35	-128.64	-127.35	
$CH_2Cl(HCO_3)$	-128.53	-129.22	-127.58	-126.51	
$CH_3(HCO_3)$					
$CCl_3(HSO_3)$	-105.07	-102.36	-101.05	-97.70	
$CHCl_2(HSO_3)$	-105.44	-105.27	-101.92	-99.72	
$CH_2Cl(HSO_3)$	-101.37	-101.71	-100.64	-98.95	
$CH_3(HSO_3)$					
$CCl_3(HSO_4)$	-134.12	-137.38	-135.67	-133.07	
$CHCl_2(HSO_4)$	-134.74	-139.41	-134.61	-136.23	
$CH_2Cl(HSO_4)$	-136.01	-141.61	-141.57	-140.53	
$CH_3(HSO_4)$					
$CCl_3(H_2PO_4)$	-236.22	-235.09	-230.65	-228.53	
$CHCl_2(H_2PO_4)$	-238.76	-238.44	-235.38	-233.89	
$CH_2Cl(H_2PO_4)$	-236.04	-236.71	-234.49	-233.38	
$CH_3(H_2PO_4)$					
CCl_3F	-60.94	-61.92	-58.27	-56.67	-58.54
CCl_2HF	-60.82	-62.17	-59.21	-57.80	-59.71
$CClH_2F$	-56.85	-57.97	-56.27	-55.34	-56.20
CH_3F					-50.28