TABLE 1S: Vibrational frequencies computed at the [a]B3LYP/6-31G(*d*) and [b]MP2/6-31G(*d*,*p*) levels of theory for reactants, transition structures and products involved in the H- and Cl-transfer reactions: $F_3C^{\cdot}$ + $CX_{4-n}H_n$ (*n* = 1, 2 or 3; X = Cl or F) and $F_3C^{\cdot}$ + $CCl_{4-n}H_n$ (*n* = 1, 2 or 3). Experimental values are given in italics.

Species	Frequencies (cm^{-1})																				
[c]CF_3H	487	487	681	1127	1160	1160	1404	1404	3084												
	479	479	667	1111	1158	1158	1392	1392	3084												
	508	*508*	*700*	*1137*	*1152*	*1152*	*1376*	*1376*	*3035*												
F_3C-*HCF_3	1708*i*	18	31	37	186	187	212	495	497	509	511	682	747	1038	1205	1232	1233	1241	1241	1497	1498
	2116*i*	21	29	29	184	184	215	476	476	491	491	658	722	1007	1188	1205	1205	1207	1207	1495	1495
[c]$F_3C^{\cdot}$	486	486	676	1071	1256	1256															
	477	477	669	1068	1249	1249															
	500	*500*	*701*	*1090*	*1090*	*1259*															
[c]CF_2H_2	509	1108	1109	1172	1251	1473	1538	3001	3062												
	497	1096	1115	1150	1236	1460	1546	2999	3060												
	529	*1090*	*1116*	*1176*	*1262*	*1435*	*1435*	*2949*	*3013*												
F_3C-*HCF_2H	1721*i*	15	30	57	184	189	406	491	498	529	710	1054	1142	1152	1190	1198	1226	1317	1480	1492	3023
	2154*i*	23	33	57	186	191	443	483	485	514	707	1055	1123	1139	1185	1198	1224	1312	1511	1546	3032
[d]$HF_2C^{\cdot}$	526	1000	1163	1181	1347	3059															
	514	1041	1143	1171	1338	3070															
	-	*946*	*1164*	*1173*	*1317*	-															
[c]CFH_3	1072	1182	1182	1494	1494	1502	2979	3051	3051												
	1057	1166	1166	1477	1485	1485	2976	3075	3075												
	1049	*1182*	*1182*	*1464*	*1467*	*1467*	*2965*	*3006*	*3006*												
F_3C-*$HCFH_2$	1766*i*	18	42	82	186	377	467	494	551	710	1073	1128	1184	1185	1214	1220	1433	1441	1497	3008	3102
	2193*i*	29	52	88	185	415	461	484	552	705	1073	1104	1169	1185	1203	1222	1451	1470	1534	3009	3116
[d]$H_2FC^{\cdot}$	602	1162	1182	1478	3083	3225															
	733	1151	1156	1473	3078	3228															
	-	*1163*	*1170*	-	-	-															
[c]CCl_3H	256	256	360	655	723	723	1240	1240	3142												
	263	263	367	668	783	783	1245	1245	3094												
	261	*261*	*363*	*680*	*774*	*774*	*1220*	*1220*	*3034*												
F_3C-*$HCCl_3$	1650*i*	5	47	49	156	156	172	266	266	397	493	495	630	749	756	756	1108	1223	1223	1435	1435
	1973*i*	10	54	54	157	157	176	273	273	407	482	482	643	752	817	818	1115	1211	1212	1451	1453
F_3C-*$ClCCl_2H$	407*i*	7	45	55	139	165	197	229	302	385	505	507	658	697	783	998	1063	1246	1278	1279	3152
[d]$HCl_2C^{\cdot}$	299	470	741	861	1243	3185															
	305	539	761	899	1258	3162															
	-	-	-	*902*	*1226*	-															
[c]CCl_2H_2	292	694	702	895	1138	1285	1474	3083	3148												
	299	719	763	899	1149	1291	1457	3051	3123												
	282	*717*	*758*	*898*	*1153*	*1268*	*1467*	*2999*	*3040*												
F_3C-*$HCCl_2H$	1700*i*	5	47	62	160	164	296	394	493	495	686	735	758	977	1111	1213	1217	1231	1441	1454	3109
	2048*i*	4	38	55	160	164	302	402	482	486	692	748	816	985	1118	1202	1215	1236	1450	1452	3077
F_3C-*$ClCClH_2$	431*i*	8	51	76	153	218	218	306	506	508	674	713	756	999	1069	1101	1267	1269	1428	3101	3213
	729*i*	11	52	80	171	245	247	335	498	499	669	743	782	983	1081	1138	1239	1241	1426	3063	3175
[d]$H_2ClC^{\cdot}$	136	820	993	1411	3140	3285															
	335	841	1005	1429	3125	3271															
	402	*827*	-	*1356*	-	-															
[c]$CClH_3$	707	1025	1025	1386	1481	1481	3036	3134	3134												
	747	1027	1027	1389	1466	1466	3010	3121	3121												
	731	*1017*	*1017*	*1355*	*1455*	*1455*	*2968*	*3054*	*3054*												
F_3C-*$HCClH_2$	1715*i*	6	50	88	166	371	469	494	550	709	755	1047	1059	1131	1208	1214	1421	1440	1449	3061	3160
	2080*i*	10	43	79	166	383	460	483	549	702	785	1048	1062	1139	1202	1207	1418	1435	1452	3039	3142
F_3C-*$ClCH_3$	445*i*	9	76	78	233	234	249	509	511	679	721	722	1000	1108	1258	1258	1434	1434	3065	3213	3214
	727*i*	15	81	81	250	250	283	499	499	670	777	777	983	1169	1232	1232	1431	1431	3032	3188	3188
[c]$H_3C^{\cdot}$	449	1404	1404	3078	3249	3249															
	374	1415	1415	3076	3263	3263															
	580	*1383*	*1383*	*3002*	*3184*	*3184*															

[a]Upper values correspond to the optimised frequencies at B3LYP/6-31G(*d*) level of theory. [b]Lower values correspond to the optimised frequencies at MP2/6-31G(*d*,*p*) level of theory. [c]Ref. 39. [d]Ref. 41.

TABLE 2S: Vibrational frequencies computed at the B3LYP/6-31G(*d*) level of theory for reactants, transition structures and products involved in the Cl-transfer reactions: $F_3C^{\cdot}$ + $CCl_{4-n}F_n$ (*n* = 0, 1 or 2). Experimental values are given in italics.

Species	Frequencies (cm^{-1})																			
[a]CCl_2F_2	259	307	409	419	431	641	846	1115	1214											
	261	*322*	*436*	*436*	*457*	*667*	*922*	*1099*	*1162*											
F_3C-*$ClCClF_2$	393*i*	14	46	53	145	179	195	239	258	376	415	507	509	574	665	743	1007	1133	1236	1279	1281
[b]$F_2ClC^{\cdot}$	349	398	578	734	1149	1236														
	-	-	*599*	*761*	*1148*	-														
[a]CCl_3F	239	239	340	385	385	511	793	793	1117											
	241	*241*	*349.5*	*398*	*398*	*535*	*847*	*847*	*1085*											
F_3C-*$ClCCl_2F$	388*i*	9	42	48	142	162	179	224	231	308	379	458	505	507	585	696	827	1007	1153	1284	1285
[b]$FCl_2C^{\cdot}$	275	368	451	583	865	1177														
	-	-	-	*747*	*919*	*1143*														
[a]CCl_4	214	214	309	309	309	442	730	730	730											
	218	*218*	*314*	*314*	*314*	*458*	*776*	*776*	*776*											
F_3C-*$ClCCl_3$	370*i*	1	41	43	138	154	156	209	210	291	291	379	503	505	518	685	770	772	1008	1288	1289
[a]$Cl_3C^{\cdot}$	269	270	326	472	857	858														
	240	*240*	*450*	*460*	*898*	*898*														
[a]$CClF_3$	340	340	457	551	551	773	1099	1264	1264											
	350	*350*	*474*	*560*	*560*	*782*	*1106*	*1217*	*1217*											

[a]Ref. 40. [b]Ref.41.

TABLE 3S: Partition functions (Q_T (T) translational, Q_R (T) rotational, Q_V (T) vibrational, Q_E(T) electronic, $Q_{V'}$ (T) vibrational corrected for hindered rotation, and Q_{HR} (T) hindered rotor, T = 298.15 K), hindered rotational barriers (V_o, kcal mol^{-1} T = 298.15 K) and imaginary frequencies ($\nu^{\#}$ cm^{-1}), optimised at the [a]B3LYP/6-31G(d) and [b]MP2/6-31G(d,p) levels of theory, for the species involved in H- and Cl-transfer the reactions: $F_3C^{\cdot}$ + $CX_{4-n}H_n$ (n = 1, 2 or 3; X = F or Cl) and $F_3C^{\cdot}$ + $CCl_{4-n}F_n$ (n = 0, 1 or 2).

Species	Q_T (T), 10^{-7}	Q_R (T),10^{-3}	Q_V (T)	Q_E(T)	$Q_{V'}$ (T)	Q_{HR} (T)	V_o	$\nu^{\#}$
$F_3C^{\cdot}$	2.25	11.50	1.28	2.00				
	2.25	11.50	1.30	2.00				
CF_3H	2.30	11.90	1.29	1.00				
	2.30	12.00	1.30	1.00				
F_3C-*HCF_3	6.43	512.00		2.00	335.00	41.43	2.38	1708*i*
	6.43	502.00		2.00	436.00	53.00	3.50	2116*i*
CF_2H_2	1.47	6.29	1.11	1.00				
	1.47	6.32	1.12	1.00				
F_3C-*HCF_2H	5.23	380.00		2.00	142.00	36.68	1.39	1721*i*
	5.23	354.00		2.00	126.00	48.00	3.11	2154*i*
CFH_3	0.78	0.90	1.02	1.00				
	0.78	0.90	1.02	1.00				
F_3C-*$HCFH_2$	4.10	249.00		2.00	46.50	23.54	0.81	1766*i*
	4.10	223.00		2.00	35.70	32.60	2.15	2193*i*
CCl_3H	5.03	70.20	2.69	1.00				
	5.03	67.60	2.55	1.00				
F_3C-*$HCCl_3$	10.00	1110.00		2.00	462.00	51.80	0.26	1650*i*
	10.00	1070.00		2.00	351.00	51.70	1.22	1973*i*
F_3C-*$ClCCl_2H$	10.00	1360.00		4.03	415.00	47.16	0.52	407*i*
CCl_2H_2	3.02	24.90	1.45	1.00				
	3.02	23.90	1.44	1.00				
F_3C-*$HCCl_2H$	7.43	736.00		2.00	137.00	47.76	0.25	1700*i*
	7.43	708.00		2.00	178.00	47.60	0.25	2048*i*
F_3C-*$ClCClH_2$	7.43	706.00		4.03	119.00	29.74	1.25	431*i*
	7.43	661.00		4.03	89.70	29.90	0.49	729*i*
$CClH_3$	1.39	1.77	1.05	1.00				
	1.39	1.71	1.05	1.00				
F_3C-*$HCClH_2$	5.10	366.00		2.00	41.80	30.67	0.15	1715*i*
	5.10	355.00		2.00	52.80	30.50	0.09	2080*i*
F_3C-*$ClCH_3$	5.10	275.00		4.03	437.00	11.32	0.05	445*i*
	5.10	263.00		4.03	363.00	11.20	0.13	727*i*
CCl_2F_2	5.16	91.10	2.96	1.00				
F_3C-*$ClCClF_2$	10.20	1250.00		4.03	495.00	45.84	1.90	393*i*
CCl_3F	6.22	93.00	4.26	1.00				
F_3C-*$ClCCl_2F$	11.50	1610.00		4.03	899.00	48.92	0.79	388*i*
CCl_4	7.35	33.00	6.40	1.00				
F_3C-*$ClCCl_3$	12.90	2000.00		4.03	1620.00	52.13	0.02	370*i*

[a]Upper values correspond to those optimised at the B3LYP/6-31G(d) level of theory. [b]Lower values correspond to those optimised at MP2/6-31G(d,p) level of theory.

TABLE 4S: Electronic charge distribution on reactants and transition structures, polarity variation, $\Delta p_{C\text{-}X}$ (X = H or Cl), *L* parameter and reaction enthalpies, $\Delta_r H_{298.15\,K}$ (kcal mol^{-1}) for the reactions: $F_3C^{\cdot} + CX_{4-n}H_n$ (*n* = 1, 2 or 3; X = F or Cl) and $F_3C^{\cdot} + CCl_{4-n}F_n$ (*n* = 0, 1 or 2).

Species		NPA			*L*	$\Delta_r H_{298.15\,K}$		
		q_C	q_H	q_{Cl}		B3LYP/6-31G(*d*)	MP2/6-31G(*d*,*p*)	[a]*Experimental*
CF_3H		0.97	0.16					
F_3C-*HCF_3		1.02	0.00					
$\Delta p_{C\text{-}H}$	0.21				1.000	0.00	0.00	*0.00*
CF_2H_2		0.45	0.16					
F_3C-*HCF_2H		0.52	0.10					
$\Delta p_{C\text{-}H}$	0.13				0.755	-4.73	-5.04	*-3.59*
CFH_3		-0.17	0.18					
F_3C-*$HCFH_2$		-0.28	0.11					
$\Delta p_{C\text{-}H}$	0.03				0.742	-5.07	-5.18	*-3.65*
CCl_3H		-0.34	0.28	0.02				
F_3C-*$HCCl_3$		-0.01	0.06	0.04				
$\Delta p_{C\text{-}H}$	0.55				0.595	-11.45	-11.44	*-10.54*
F_3C-*$ClCCl_2H$		-0.03	0.14	-0.09				
$\Delta p_{C\text{-}Cl}$	0.42				0.621	-14.45	-	*-8.44*
CCl_2H_2		-0.46	0.26	-0.03				
F_3C-*$HCCl_2H$		-0.02	0.05	0.01				
$\Delta p_{C\text{-}H}$	0.66				0.682	-8.46	-9.21	*-7.27*
F_3C-*$ClCClH_2$		-0.01	0.12	-0.11				
$\Delta p_{C\text{-}Cl}$	0.54				0.816	-9.17	-	*-6.07*
$CClH_3$		-0.65	0.24	-0.08				
F_3C-*$HCClH_2$		-0.03	0.04	-0.02				
$\Delta p_{C\text{-}H}$	0.82				0.819	-5.90	-6.61	*-5.90*
F_3C-*$ClCH_3$		0.01	0.23	-0.11				
$\Delta p_{C\text{-}Cl}$	0.69				1.088	-3.24	-	*-2.38*
CCl_2F_2		0.67		0.00				
F_3C-*$ClCClF_2$		0.51		-0.10				
$\Delta p_{C\text{-}Cl}$	0.07				0.846	-6.73	-	*-3.60*
CCl_3F		0.22		0.04				
F_3C-*$ClCCl_2F$		0.24		-0.08				
$\Delta p_{C\text{-}Cl}$	0.14				0.594	-13.49	-	*-13.00*
CCl_4		-0.26		0.07				
F_3C-*$ClCCl_3$		-0.05		-0.05				
$\Delta p_{C\text{-}Cl}$	0.32				0.477	-21.16	-	*-15.30*

[a]Ref. 39.