Supplementary Information

Thermal Decomposition Mechanism and Kinetics of Perfluorooctanoic Acid (PFOA) and Other Perfluorinated Carboxylic Acids: A Theoretical Study

M. Yasir Khan, Jiaou Song, Milad Narimani, Gabriel da Silva*

Department of Chemical Engineering, University of Melbourne, Victoria 3010, Australia.

*Corresponding author. Email: gdasilva@unimelb.edu.au

List of Figures

List of Tables

Decomposition of PFOA

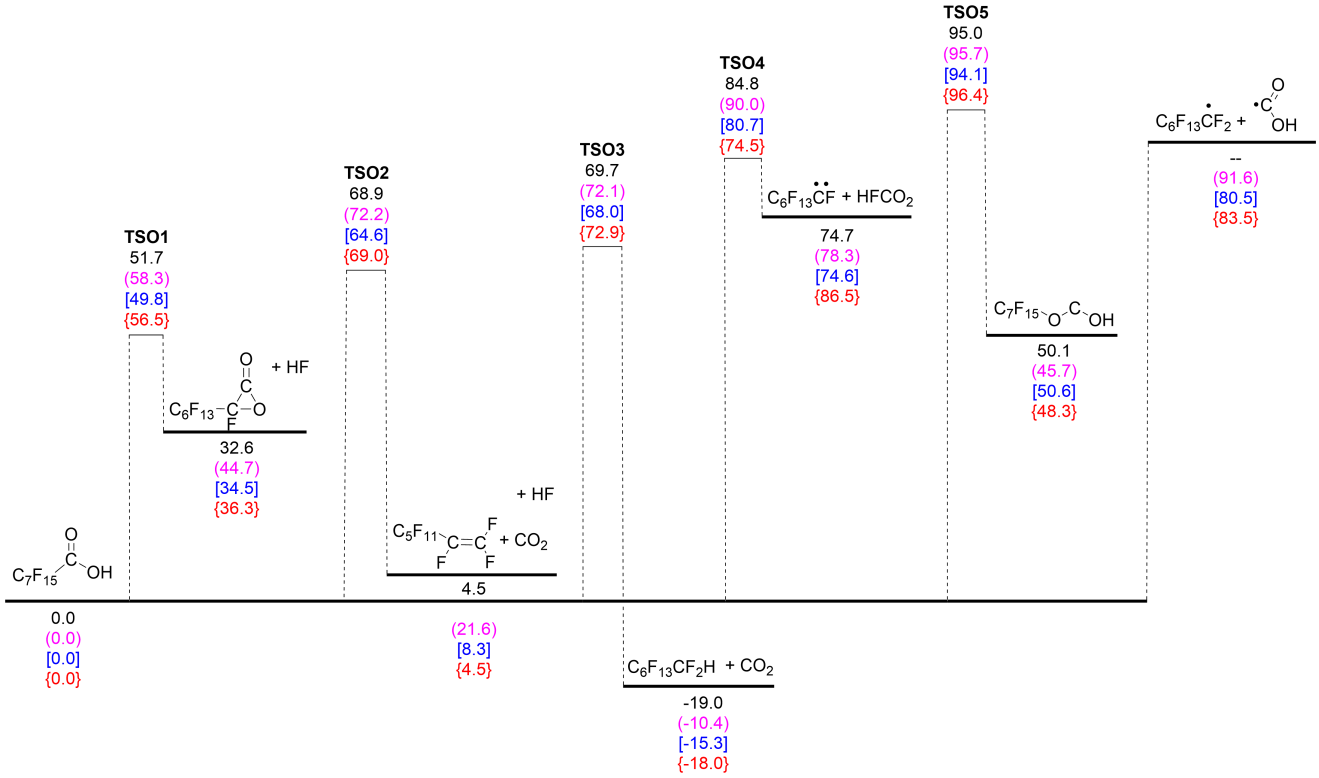


Figure S1: Potential energy diagram for thermal decomposition mechanism of PFOA. Energies are 0 K enthalpies in kcal/mol calculated at the DSD-PBEB95/def2-TZVPP, (M062X/6-31G(2df,p)), [PBE0/def2-TZVPP], and {BMK/6-31++G(2df,p)} levels of theory.

Table S1: Arrhenius expressions for the decomposition channels of PFOA presented in Fig. 1 (article), units are: s, cal, K, and mol.

Transition states	Arrhenius expression (s^{-1})
TSO1 ($C_6F_{13}CFCO_2$ + HF)	$k = 2.66 \times 10^{13}\, e^{\frac{-52605}{RT}}$
TSO2 ($C_5F_{11}CF{=}CF_2$ + CO_2 + HF)	$k = 1.83 \times 10^{14}\, e^{\frac{-70023}{RT}}$
TSO3 ($C_6F_{13}CF_2H$ + CO_2)	$k = 7.03 \times 10^{14}\, e^{\frac{-71285}{RT}}$
TSO4 ($C_6F_{13}CF$ + $HFCO_2$)	$k = 9.23 \times 10^{13}\, e^{\frac{-85966}{RT}}$
TSO5 ($C_7F_{15}OCOH$)	$k = 4.83 \times 10^{13}\, e^{\frac{-95974}{RT}}$

Table S2: Half lives of PFOA based on TSO1, TSO2, and TSO3, assuming a first order decomposition reaction.

Temperature	TSO1	TSO2	TSO3
(K)	half life (s)	half life (s)	half life (s)
300	$5.05 \times 10^{+24}$	$3.33 \times 10^{+36}$	$6.88 \times 10^{+36}$
400	$1.46 \times 10^{+15}$	$7.01 \times 10^{+23}$	$8.99 \times 10^{+23}$
500	$2.69 \times 10^{+09}$	$1.67 \times 10^{+16}$	$1.58 \times 10^{+16}$
600	$4.00 \times 10^{+05}$	$1.35 \times 10^{+11}$	$1.04 \times 10^{+11}$
700	$7.32 \times 10^{+02}$	$3.06 \times 10^{+07}$	$2.02 \times 10^{+07}$
800	$6.44 \times 10^{+00}$	$5.60 \times 10^{+04}$	$3.29 \times 10^{+04}$
900	1.62×10^{-01}	$4.13 \times 10^{+02}$	$2.21 \times 10^{+02}$
1000	8.45×10^{-03}	$8.07 \times 10^{+00}$	$4.00 \times 10^{+00}$
1200	1.00×10^{-04}	2.18×10^{-02}	9.60×10^{-03}
1400	4.19×10^{-06}	3.14×10^{-04}	1.27×10^{-04}
1600	3.86×10^{-07}	1.30×10^{-05}	4.94×10^{-06}
1800	6.01×10^{-08}	1.08×10^{-06}	3.92×10^{-07}
2000	1.35×10^{-08}	1.48×10^{-07}	5.13×10^{-08}

Decomposition of iso-PFOA

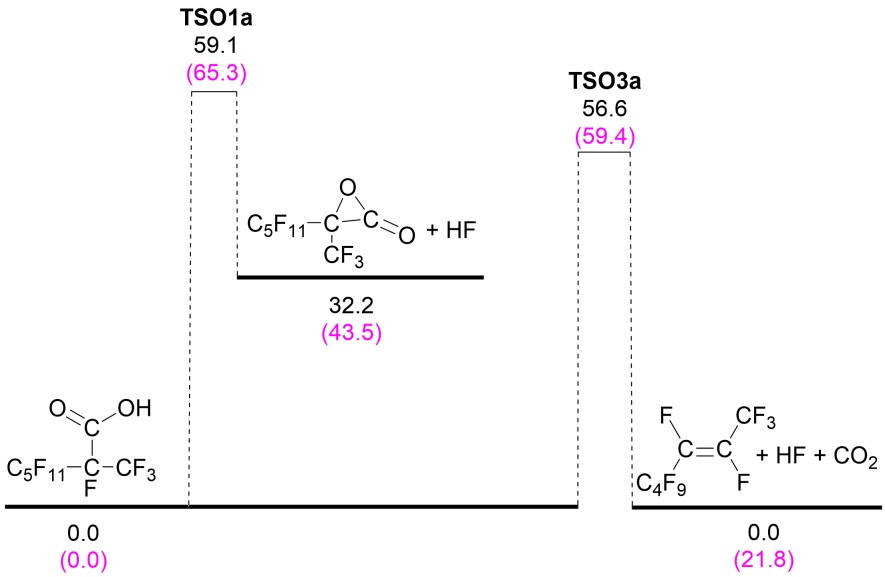


Figure S2: Potential energy diagram for thermal decomposition mechanism for 2,3,3,4,4,5,5,6,6,7,7,7-Dodecafluoro-2-(trifluoromethyl) heptanoic acid (iso-PFOA). Energies are 0 K enthalpies in kcal/mol calculated at the DSD-PBEB95/def2-TZVPP and (M062X/6-31G(2df,p)) levels of theory.

Table S3: Arrhenius expressions for the decomposition channels of iso-PFOA presented in Fig. S2, units are: s, cal, K, and mol.

Transition states	Arrhenius expression (s^{-1})
TSO1a ($C_8F_{14}O_2$ + HF)	$k = 1.15 \times 10^{13}\, e^{\frac{-59764}{RT}}$
TSO3a ($C_4F_9CF{=}CFCF_3$ + HF + CO_2)	$k = 1.38 \times 10^{14}\, e^{\frac{-57874}{RT}}$

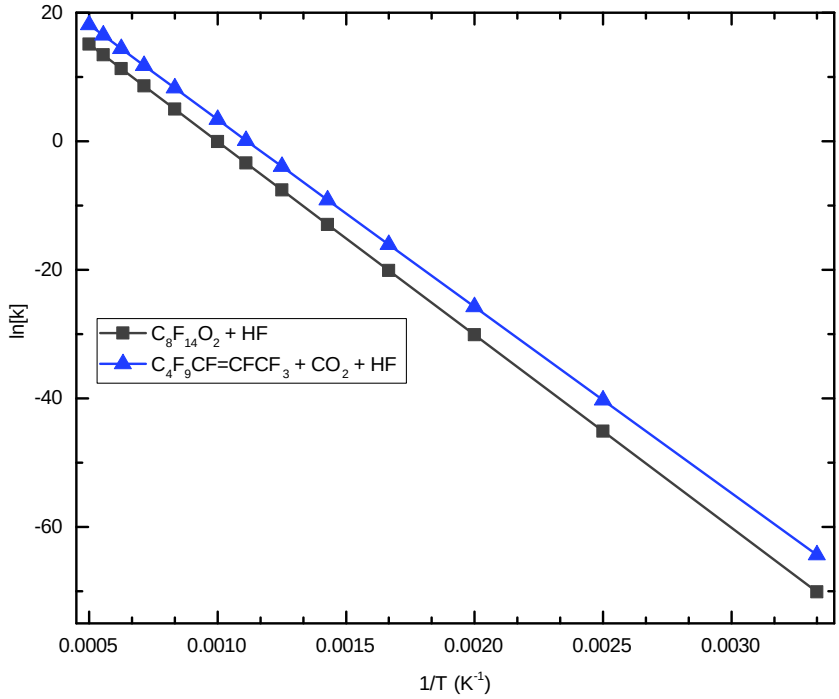


Figure S3: Arrhenius plot of the reaction rate constants, k (s^{-1}), for the thermal decomposition of iso-PFOA (see PES Fig. S2). Arrhenius expressions for $C_8F_{14}O_2$ + HF (TSO1a), and $C_4F_9CF{=}CFCF_3$ + HF + CO_2 (TSO3a) are $k = 1.15 \times 10^{13}\, e^{\frac{-59764}{RT}}$, and $k = 1.38 \times 10^{14}\, e^{\frac{-57874}{RT}}$, respectively, (units are s, cal, K, mol).

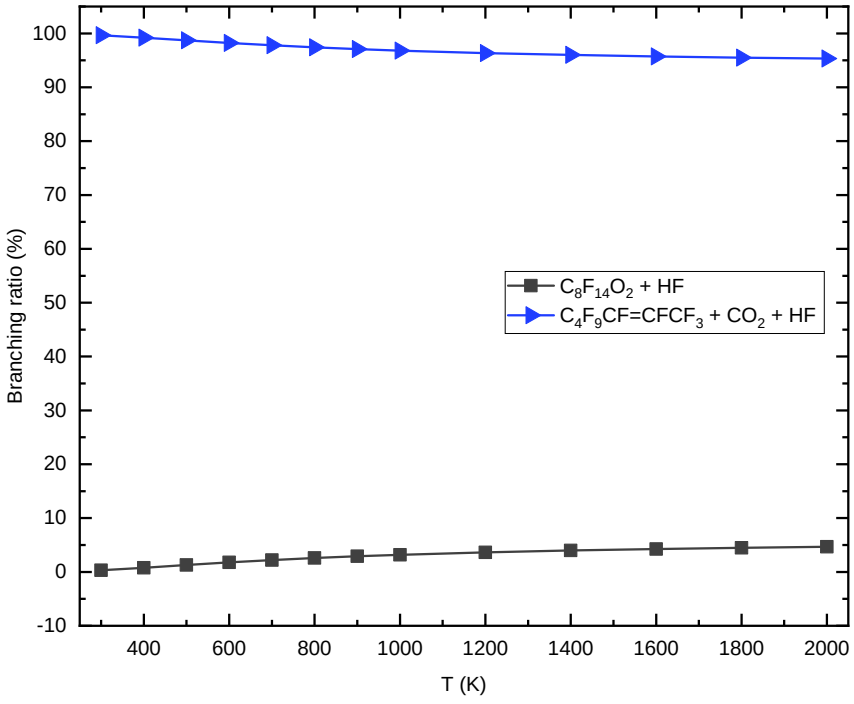


Figure S4: Branching ratio of the degradation products for the thermal decomposition of iso-PFOA (see PES Fig. S2), $C_8F_{14}O_2$ + HF (TSO1a), and $C_4F_9CF{=}CFCF_3$ + HF + CO_2 (TSO3a).

Table S4: Half lives of iso-PFOA based on the transition state TSO1a and TSO3a (assuming a first order decomposition reaction)

Temperature	TSO1a	TSO3a
(K)	half life (s)	half life (s)
300	$1.92 \times 10^{+30}$	$6.20 \times 10^{+27}$
400	$2.73 \times 10^{+19}$	$2.14 \times 10^{+17}$
500	$8.34 \times 10^{+12}$	$1.09 \times 10^{+11}$
600	$3.75 \times 10^{+08}$	$6.75 \times 10^{+06}$
700	$2.92 \times 10^{+05}$	$6.57 \times 10^{+03}$
800	$1.35 \times 10^{+03}$	$3.58 \times 10^{+01}$
900	$2.06 \times 10^{+01}$	6.17×10^{-01}
1000	7.23×10^{-01}	2.38×10^{-02}
1200	4.69×10^{-03}	1.77×10^{-04}
1400	1.27×10^{-04}	5.29×10^{-06}
1600	8.46×10^{-06}	3.77×10^{-07}
1800	1.02×10^{-06}	4.80×10^{-08}
2000	1.88×10^{-07}	9.19×10^{-09}

Arrhenius plot and branching ratio for Perfluoro-3-Hexyl-α-lactone

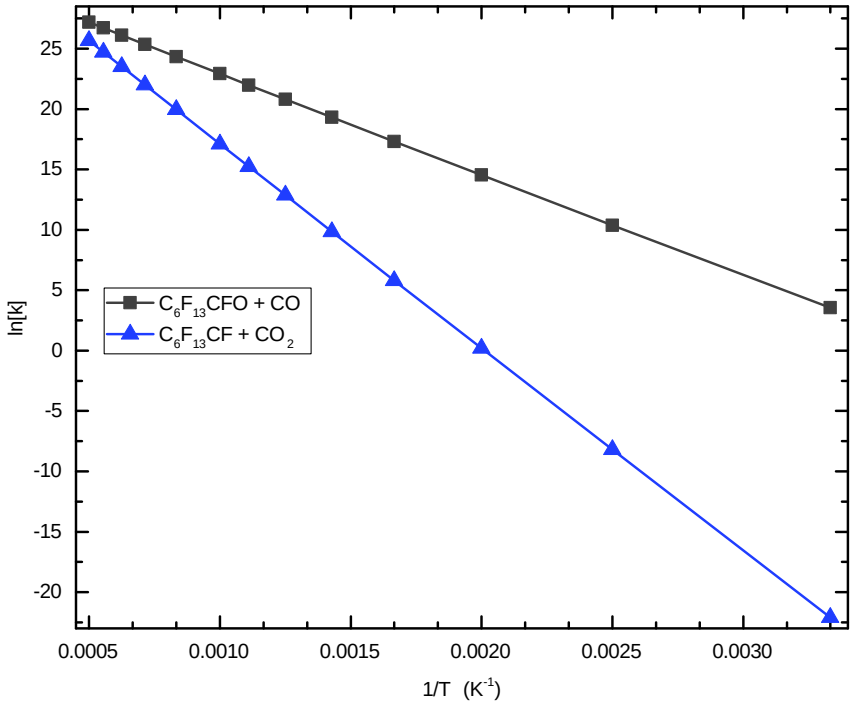


Figure S5: Arrhenius plot of the reaction rate constants, k (s^{-1}), for the thermal decomposition of Perfluoro-3-Hexyl-α-lactone (PES Fig. 6a (article)). Arrhenius expressions for $C_6F_{13}CFO$ + CO (TS1O1), and $C_6F_{13}CF$ + CO_2 (TS1O2) are $k = 3.95 \times 10^{13}\, e^{\frac{-16610}{RT}}$, and $k = 5.91 \times 10^{14}\, e^{\frac{-33528}{RT}}$, respectively, (units are s, cal, K, mol).

Table S5: Arrhenius expressions for the decomposition channels presented in Fig. 6 (article), units are: s, cal, K, and mol.

Transition states	Arrhenius expression
TS1O1 ($C_6F_{13}CFO$ + CO)	$k^{a} = 3.95 \times 10^{13}\, e^{\frac{-16610}{RT}}$
TS1O2 ($C_6F_{13}CF$ + CO_2)	$k^{a} = 5.91 \times 10^{14}\, e^{\frac{-33528}{RT}}$
TS1O3 ($C_6F_{13}COOH$ + HF)	$k^{b} = 8.68 \times 10^{-15}\, e^{\frac{-38665}{RT}}$

[a] the unit of the k is s^{-1}
[b] the unit of the k is cm^3 $molecule^{-1}$ s^{-1}

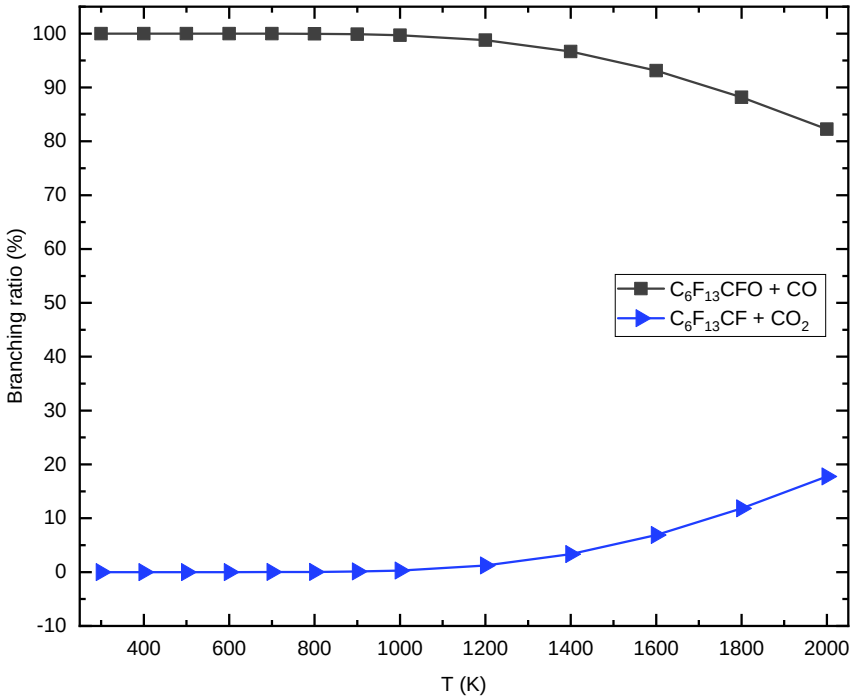


Figure S6: Branching ratio of the degradation products for the thermal decomposition of Perfluoro-3-Hexyl-α-lactone (PES Fig. 6a (article)), $C_6F_{13}CFO$ + CO (TS1O1), and $C_6F_{13}CF$ + CO_2 (TS1O2).

Table S6: Half lives of Perfluoro-3-Hexyl-α-lactone based on the transition state TS1O1 and TS1O2

Temperature	TS1O1	TS1O2
(K)	half life (s)	half life (s)
300	1.98×10^{-02}	$2.71 \times 10^{+09}$
400	2.14×10^{-05}	$2.52 \times 10^{+03}$
500	3.41×10^{-07}	5.75×10^{-01}
600	2.11×10^{-08}	2.08×10^{-03}
700	2.86×10^{-09}	3.71×10^{-05}
800	6.35×10^{-10}	1.79×10^{-06}
900	1.96×10^{-10}	1.69×10^{-07}
1000	7.64×10^{-11}	2.55×10^{-08}
1200	1.85×10^{-11}	1.49×10^{-09}
1400	6.71×10^{-12}	1.95×10^{-10}
1600	3.13×10^{-12}	4.23×10^{-11}
1800	1.73×10^{-12}	1.29×10^{-11}
2000	1.07×10^{-12}	4.97×10^{-12}

Decomposition of Perfluoroheptanoic acid

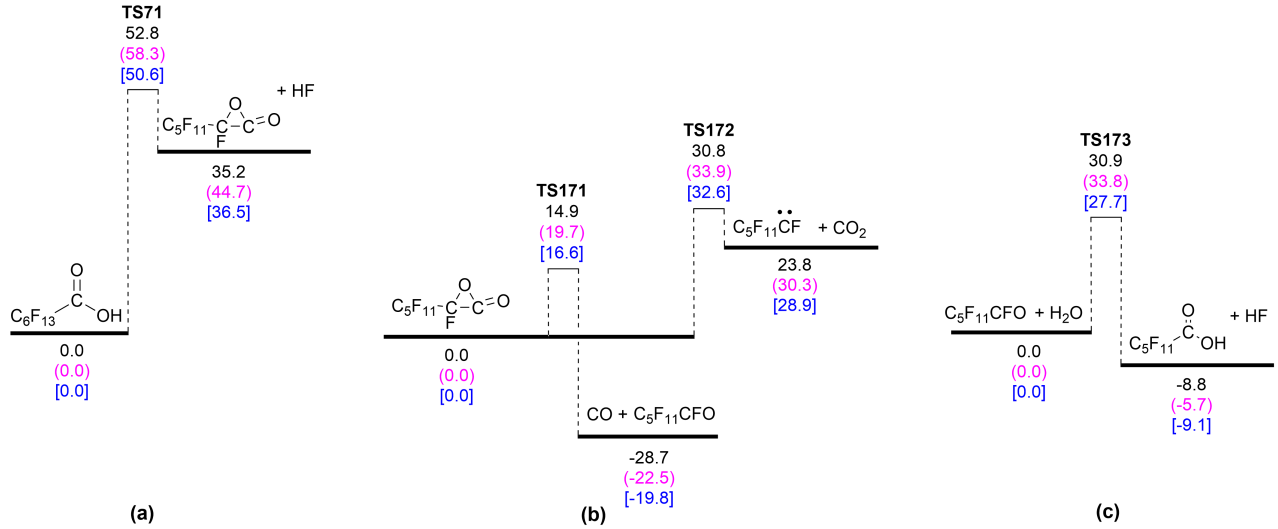


Figure S7: Potential energy diagram for thermal decomposition mechanism of (a) Perfluoroheptanoic acid, (b) Perfluoro-3-Pentyl-α-lactone, (c) hydrolysis of perfluoro-hexane aldehyde to Perfluorohexanoic acid, Energies are (0 K enthalpies, kcal/mol) calculated at the DSD-PBEB95/def2-TZVPP, (M062X/6-31G(2df,p)), [PBE0/def2-TZVPP] levels of theory.

Table S7: Arrhenius expressions for the decomposition channels presented in Fig. S7, units are: s, cal, K, and mol.

Transition states	Arrhenius expression
TS71 ($C_5F_{11}CFCO_2$ + HF)	$k^{a} = 1.98 \times 10^{13}\, e^{\frac{-53669}{RT}}$
TS171 ($C_5F_{11}CFO$ + CO)	$k^{a} = 3.29 \times 10^{13}\, e^{\frac{-15983}{RT}}$
TS172 ($C_5F_{11}CF$ + CO_2)	$k^{a} = 5.89 \times 10^{14}\, e^{\frac{-32414}{RT}}$
TS173 ($C_5F_{11}COOH$ + HF)	$k^{b} = 1.86 \times 10^{-15}\, e^{\frac{-32076}{RT}}$

[a] the unit of the k is s^{-1}
[b] the unit of the k is cm^3 $molecule^{-1}$ s^{-1}

Table S8: Half lives of Perfluoroheptanoic acid (TS71) and Perfluoro-3-Pentyl-α-lactone (TS171, and TS172) by assuming a first order decomposition reaction.

Temperature	TS71	TS171	TS172
(K)	half life (s)	half life (s)	half life (s)
300	$4.03 \times 10^{+25}$	8.30×10^{-03}	$4.19 \times 10^{+08}$
400	$7.46 \times 10^{+15}$	1.17×10^{-05}	$6.24 \times 10^{+02}$
500	$1.05 \times 10^{+10}$	2.17×10^{-07}	1.88×10^{-01}
600	$1.31 \times 10^{+06}$	1.50×10^{-08}	8.23×10^{-04}
700	$2.11 \times 10^{+03}$	2.19×10^{-09}	1.67×10^{-05}
800	$1.68 \times 10^{+01}$	5.13×10^{-10}	8.94×10^{-07}
900	3.92×10^{-01}	1.66×10^{-10}	9.12×10^{-08}
1000	1.93×10^{-02}	6.69×10^{-11}	1.46×10^{-08}
1200	2.10×10^{-04}	1.71×10^{-11}	9.35×10^{-10}
1400	8.23×10^{-06}	6.43×10^{-12}	1.31×10^{-10}
1600	7.22×10^{-07}	3.08×10^{-12}	2.98×10^{-11}
1800	1.08×10^{-07}	1.74×10^{-12}	9.45×10^{-12}
2000	2.37×10^{-08}	1.10×10^{-12}	3.76×10^{-12}

Decomposition of Perfluorohexanoic acid

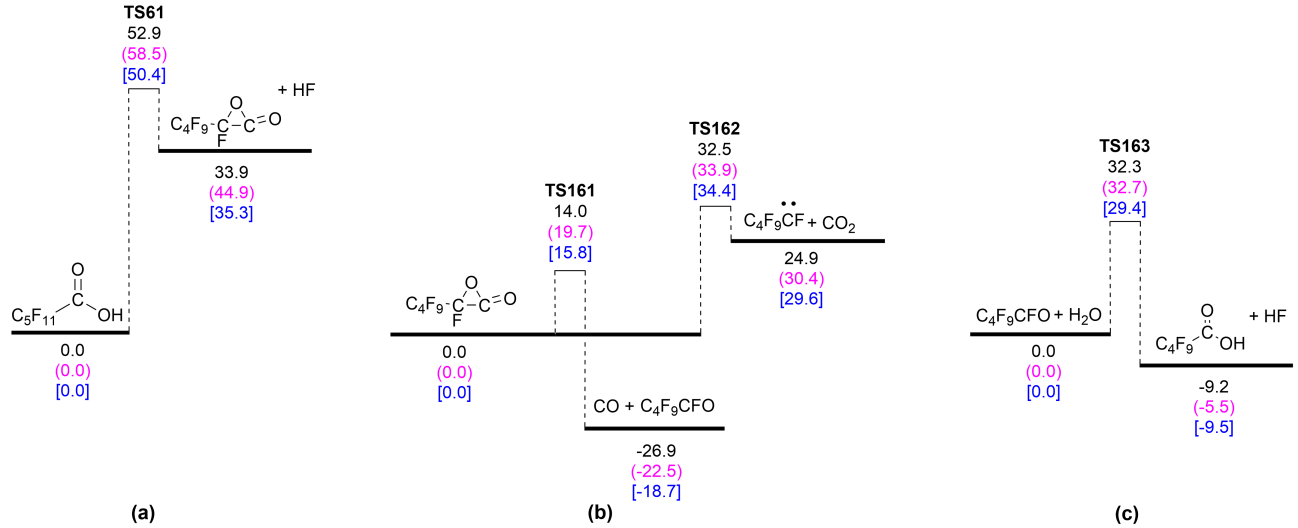


Figure S8: Potential energy diagram for thermal decomposition mechanism of (a) Perfluorohexanoic acid, (b) Perfluoro-3-Butyl-α-lactone, (c) hydrolysis of perfluoro-pentane aldehyde to Perfluoropentanoic acid, Energies are (0 K enthalpies, kcal/mol) calculated at the DSD-PBEB95/def2-TZVPP, (M062X/6-31G(2df,p)), [PBE0/def2-TZVPP] levels of theory.

Table S9: Arrhenius expressions for the decomposition channels presented in Fig. S8, units are: s, cal, K, and mol.

Transition states	Arrhenius expression
TS61 ($C_4F_9CFCO_2$ + HF)	$k^{a} = 2.80 \times 10^{13}\, e^{\frac{-53801}{RT}}$
TS161 (C_4F_9CFO + CO)	$k^{a} = 3.42 \times 10^{13}\, e^{\frac{-15108}{RT}}$
TS162 (C_4F_9CF + CO_2)	$k^{a} = 1.22 \times 10^{14}\, e^{\frac{-33980}{RT}}$
TS163 (C_4F_9COOH + HF)	$k^{b} = 3.30 \times 10^{-15}\, e^{\frac{-33509}{RT}}$

[a] the unit of the k is s^{-1}
[b] the unit of the k is cm^3 $molecule^{-1}$ s^{-1}

Table S10: Half lives of Perfluorohexanoic acid (TS61) and Perfluoro-3-Butyl-α-lactone (TS161, and TS162) by assuming a first order decomposition reaction.

Temperature	TS61	TS161	TS162
(K)	half life (s)	half life (s)	half life (s)
300	$3.56 \times 10^{+25}$	1.84×10^{-03}	$2.80 \times 10^{+10}$
400	$6.24 \times 10^{+15}$	3.73×10^{-06}	$2.16 \times 10^{+04}$
500	$8.51 \times 10^{+09}$	8.67×10^{-08}	$4.38 \times 10^{+00}$
600	$1.03 \times 10^{+06}$	6.90×10^{-09}	1.47×10^{-02}
700	$1.64 \times 10^{+03}$	1.12×10^{-09}	2.48×10^{-04}
800	$1.30 \times 10^{+01}$	2.84×10^{-10}	1.15×10^{-05}
900	2.99×10^{-01}	9.76×10^{-11}	1.05×10^{-06}
1000	1.46×10^{-02}	4.14×10^{-11}	1.55×10^{-07}
1200	1.57×10^{-04}	1.14×10^{-11}	8.70×10^{-09}
1400	6.12×10^{-06}	4.51×10^{-12}	1.11×10^{-09}
1600	5.33×10^{-07}	2.25×10^{-12}	2.36×10^{-10}
1800	7.96×10^{-08}	1.31×10^{-12}	7.07×10^{-11}
2000	1.74×10^{-08}	8.47×10^{-13}	2.70×10^{-11}

Decomposition of Perfluoropentanoic acid

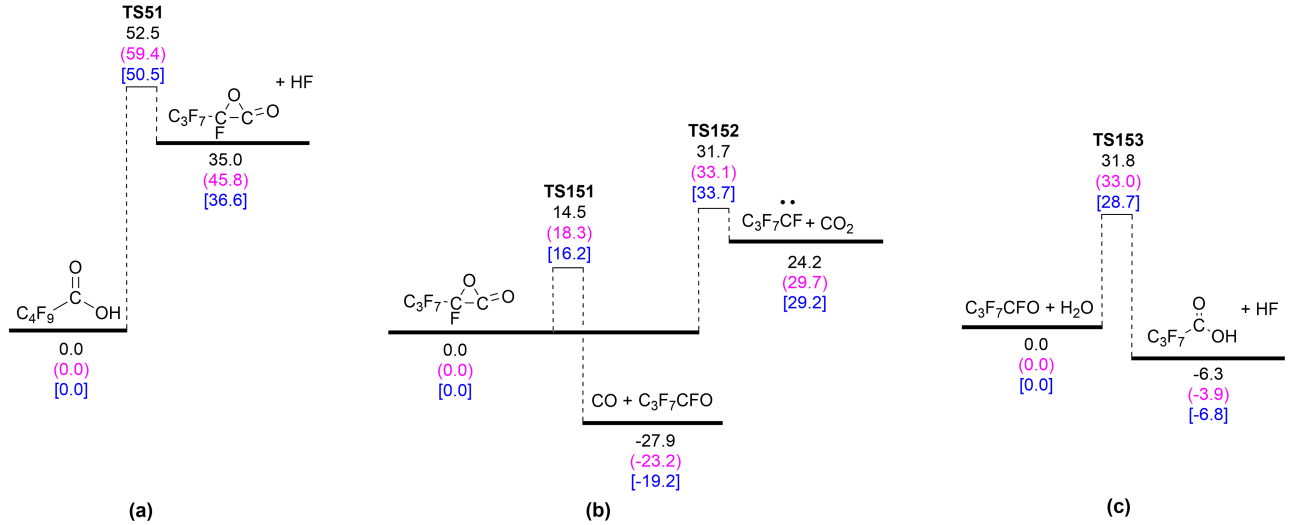


Figure S9: Potential energy diagram for thermal decomposition mechanism of (a) Perfluoropentanoic acid, (b) Perfluoro-3-Propyl-α-lactone, (c) hydrolysis of perfluoro-butane aldehyde to Perfluorobutanoic acid, Energies are (0 K enthalpies, kcal/mol) calculated at the DSD-PBEB95/def2-TZVPP, (M062X/6-31G(2df,p)), [PBE0/def2-TZVPP] levels of theory.

Table S11: Arrhenius expressions for the decomposition channels presented in Fig. S9, units are: s, cal, K, and mol.

Transition states	Arrhenius expression
TS51 ($C_3F_7CFCO_2$ + HF)	$k^{a} = 2.25 \times 10^{13}\, e^{\frac{-53400}{RT}}$
TS151 (C_3F_7CFO + CO)	$k^{a} = 2.51 \times 10^{13}\, e^{\frac{-15611}{RT}}$
TS152 (C_3F_7CF + CO_2)	$k^{a} = 9.29 \times 10^{13}\, e^{\frac{-33156}{RT}}$
TS153 (C_3F_7COOH + HF)	$k^{b} = 3.56 \times 10^{-16}\, e^{\frac{-32807}{RT}}$

[a] the unit of the k is s^{-1}
[b] the unit of the k is cm^3 $molecule^{-1}$ s^{-1}

Table S12: Half lives of Perfluoropentanoic acid (TS51) and Perfluoro-3-Propyl-α-lactone (TS151, and TS152) by assuming a first order decomposition reaction.

Temperature	TS51	TS151	TS152
(K)	half life (s)	half life (s)	half life (s)
300	$2.27 \times 10^{+25}$	5.83×10^{-03}	$9.28 \times 10^{+09}$
400	$4.70 \times 10^{+15}$	9.60×10^{-06}	$1.01 \times 10^{+04}$
500	$7.09 \times 10^{+09}$	1.96×10^{-07}	$2.51 \times 10^{+00}$
600	$9.21 \times 10^{+05}$	1.44×10^{-08}	9.70×10^{-03}
700	$1.53 \times 10^{+03}$	2.19×10^{-09}	1.81×10^{-04}
800	$1.26 \times 10^{+01}$	5.33×10^{-10}	9.04×10^{-06}
900	2.98×10^{-01}	1.76×10^{-10}	8.75×10^{-07}
1000	1.49×10^{-02}	7.27×10^{-11}	1.35×10^{-07}
1200	1.66×10^{-04}	1.92×10^{-11}	8.11×10^{-09}
1400	6.60×10^{-06}	7.38×10^{-12}	1.08×10^{-09}
1600	5.86×10^{-07}	3.60×10^{-12}	2.40×10^{-10}
1800	8.87×10^{-08}	2.06×10^{-12}	7.40×10^{-11}
2000	1.95×10^{-08}	1.31×10^{-12}	2.89×10^{-11}

Decomposition of Perfluorobutanoic acid

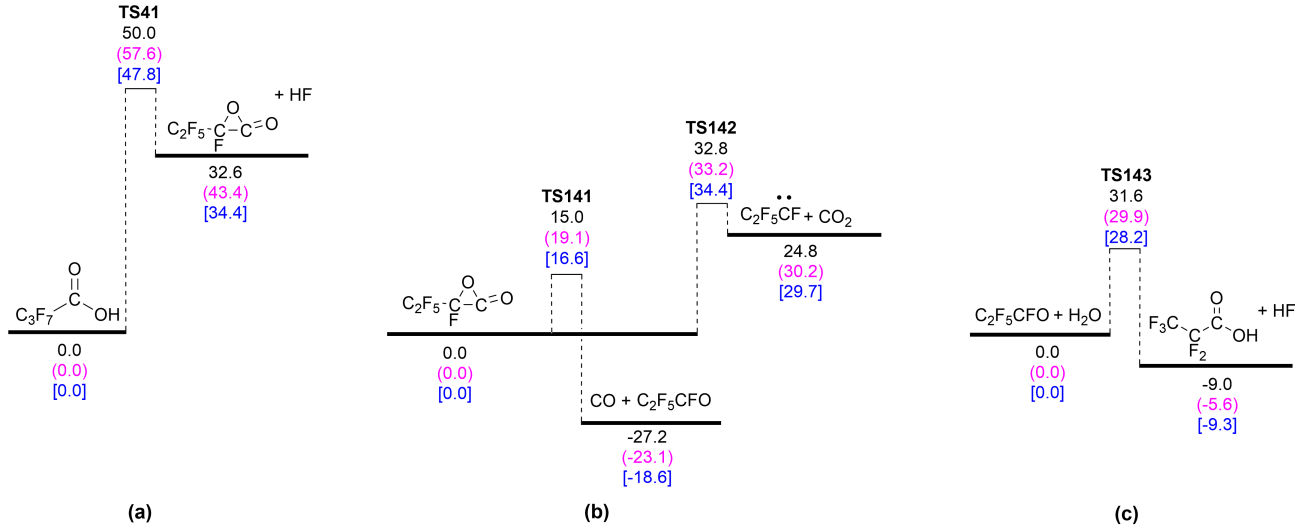


Figure S10: Potential energy diagram for thermal decomposition mechanism of (a) Perfluorobutanoic acid, (b) Perfluoro-3-Ethyl-α-lactone, (c) hydrolysis of perfluoro-propane aldehyde to Pentafluoropropionic acid, Energies are (0 K enthalpies, kcal/mol) calculated at the DSD-PBEB95/def2-TZVPP, (M062X/6-31G(2df,p)), [PBE0/def2-TZVPP] levels of theory.

Table S13: Arrhenius expressions for the decomposition channels presented in Fig. S10, units are: s, cal, K, and mol.

Transition states	Arrhenius expression
TS41 ($C_2F_5CFCO_2$ + HF)	$k^{a} = 6.93 \times 10^{13}\, e^{\frac{-50915}{RT}}$
TS141 (C_2F_5CFO + CO)	$k^{a} = 2.55 \times 10^{13}\, e^{\frac{-16064}{RT}}$
TS142 (C_2F_5CF + CO_2)	$k^{a} = 1.26 \times 10^{14}\, e^{\frac{-34221}{RT}}$
TS143 (C_2F_5COOH + HF)	$k^{b} = 1.50 \times 10^{-15}\, e^{\frac{-32785}{RT}}$

[a] the unit of the k is s^{-1}
[b] the unit of the k is cm^3 $molecule^{-1}$ s^{-1}

Table S14: Half lives of Perfluorobutanoic acid (TS41) and Perfluoro-3-Ethyl-α-lactone (TS141, and TS142) by assuming a first order decomposition reaction.

Temperature	TS41	TS141	TS142
(K)	half life (s)	half life (s)	half life (s)
300	$1.14 \times 10^{+23}$	1.23×10^{-02}	$4.09 \times 10^{+10}$
400	$6.66 \times 10^{+13}$	1.67×10^{-05}	$2.83 \times 10^{+04}$
500	$1.88 \times 10^{+08}$	3.04×10^{-07}	$5.39 \times 10^{+00}$
600	$3.70 \times 10^{+04}$	2.06×10^{-08}	1.74×10^{-02}
700	$8.29 \times 10^{+01}$	2.99×10^{-09}	2.86×10^{-04}
800	8.51×10^{-01}	6.96×10^{-10}	1.30×10^{-05}
900	2.40×10^{-02}	2.24×10^{-10}	1.17×10^{-06}
1000	1.38×10^{-03}	8.99×10^{-11}	1.69×10^{-07}
1200	1.89×10^{-05}	2.28×10^{-11}	9.32×10^{-09}
1400	8.76×10^{-07}	8.55×10^{-12}	1.17×10^{-09}
1600	8.70×10^{-08}	4.09×10^{-12}	2.47×10^{-10}
1800	1.44×10^{-08}	2.30×10^{-12}	7.33×10^{-11}
2000	3.40×10^{-09}	1.45×10^{-12}	2.78×10^{-11}

Decomposition of Pentafluoropropionic acid

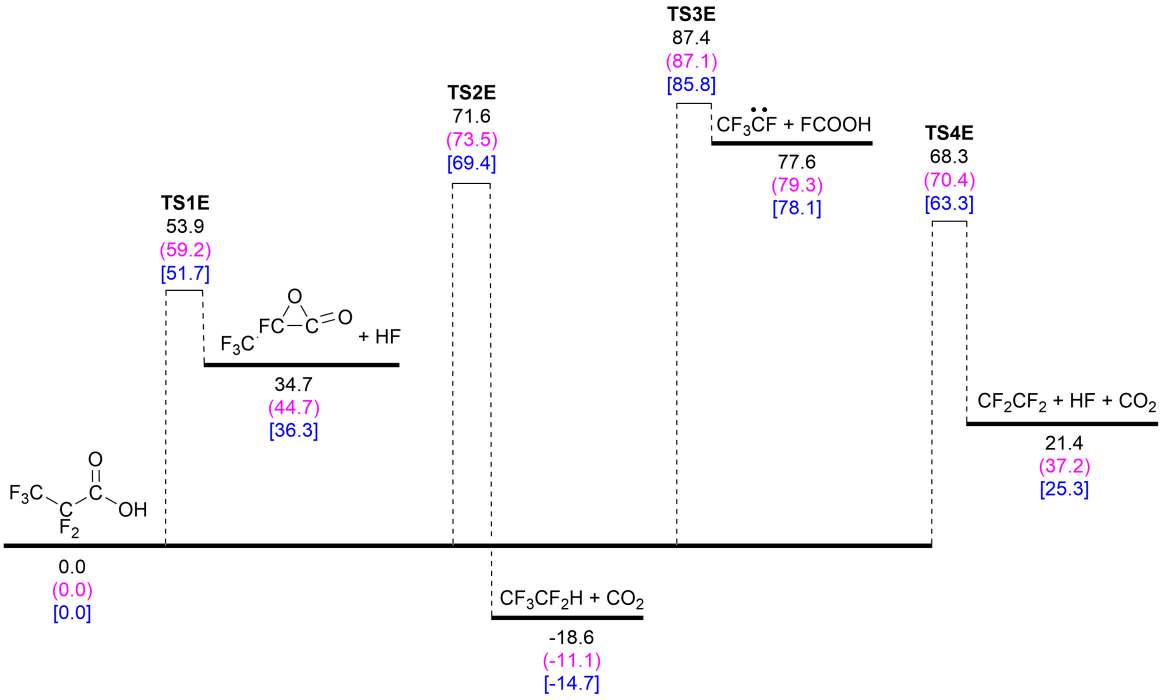


Figure S11: Potential energy diagram for thermal decomposition mechanism for Pentafluoropropionic acid. Energies are 0 K enthalpies in kcal/mol calculated at the DSD-PBEB95/def2-TZVPP, (M062X/6-31G(2df,p)), [PBE0 /def2-TZVPP] levels of theory.

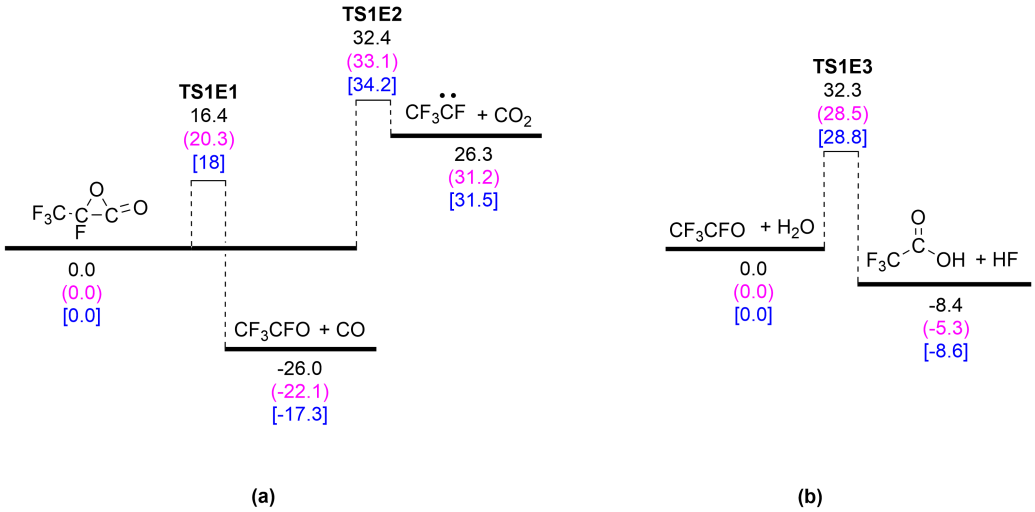
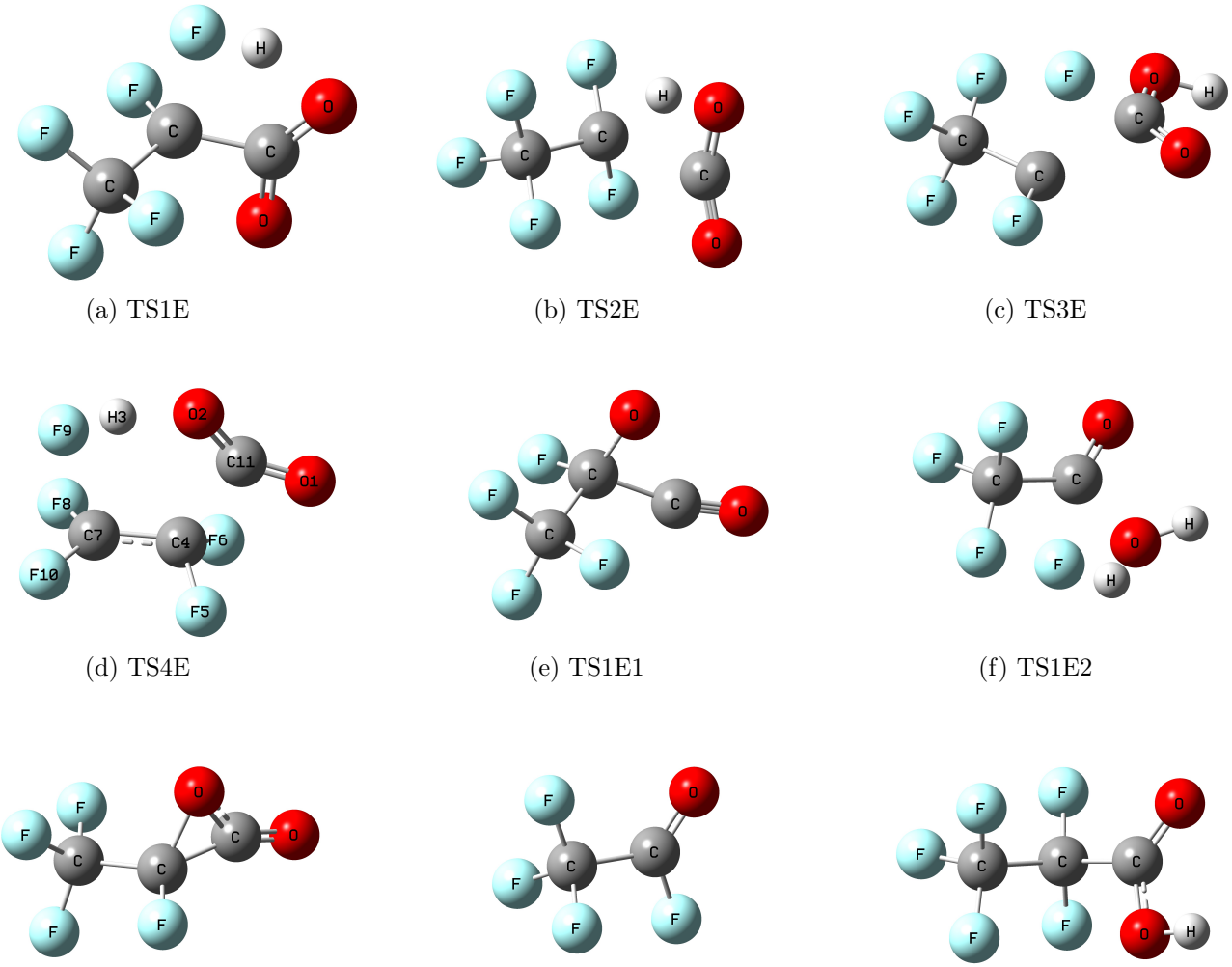


Figure S12: Potential energy diagram for thermal decomposition mechanism for (a) Perfluoro-3-Methyl-α-lactone, (b) hydrolysis of perfluoroacetyl fluoride to trifluoroacetic acid (TFA), Energies are (0 K enthalpies, kcal/mol) calculated at the DSD-PBEB95/def2-TZVPP, (M062X/6-31G(2df,p)), [PBE0/def2-TZVPP] levels of theory.



(a) TS1E (b) TS2E (c) TS3E

(d) TS4E (e) TS1E1 (f) TS1E2

(g) Perfluoro-Methyl-α-lactone (h) Perfluoroacetyl fluoride (i) PFPA

Figure S13: Optimized transition states and ground state structures reported in Figure S11 and Figure S12, Transition states (a-f) Perfluoro-Methyl-α-lactone (g), Perfluoroacetyl fluoride (h), TFA (i) at the M06-2X/6-31G(2df,p) level of theory

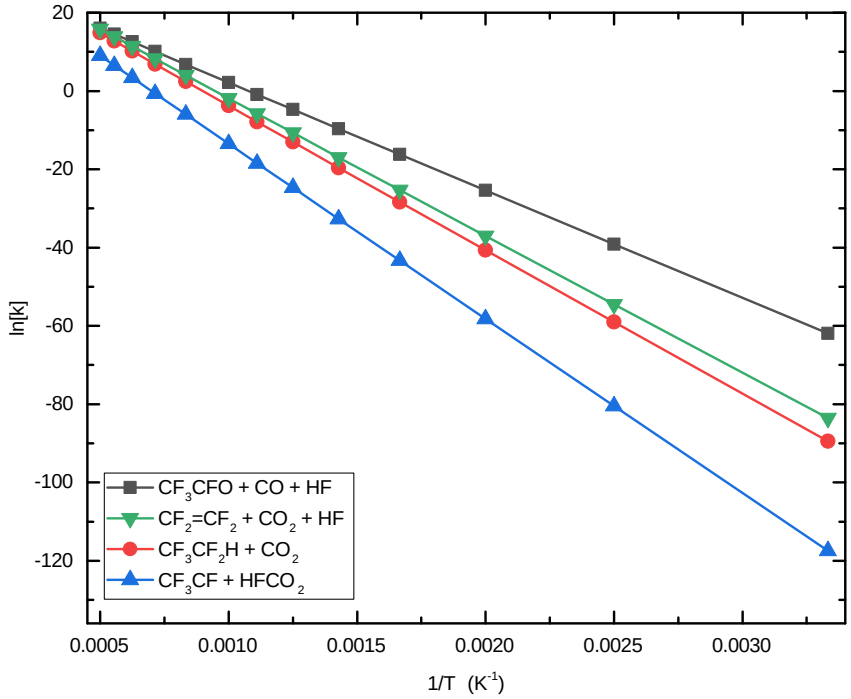


Figure S14: Arrhenius plot of the reaction rate coefficients, k (s^{-1}), for the thermal decomposition of Pentafluoropropionic acid (see PES Fig. S11). Arrhenius expressions for CF_3CFO + CO + HF (TS1E), + CF_3CF_2H + CO_2 (TS2E), CF_3CF + FCOOH (TS3E), and CF_2CF_2 + HF + CO_2 (TS4E) are $k = 8.10 \times 10^{12}\, e^{\frac{-54706}{RT}}$, $k = 2.40 \times 10^{14}\, e^{\frac{-73180}{RT}}$, $k = 3.75 \times 10^{13}\, e^{\frac{-88780}{RT}}$, and $k = 2.90 \times 10^{14}\, e^{\frac{-69763}{RT}}$ respectively (units are s, cal, K, mol).

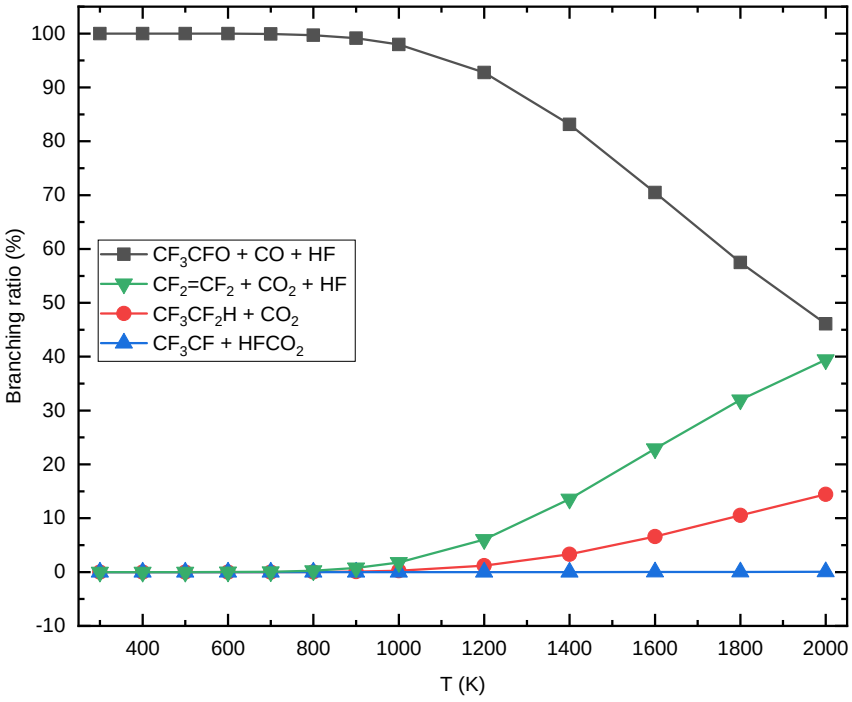


Figure S15: Branching ratio of the degradation products for the thermal decomposition of Pentafluoropropionic acid (see PES Fig. 4 in the article), CF_3CFO + CO + HF (TS1E), + CF_3CF_2H + CO_2 (TS2E), CF_3CF + FCOOH (TS3E), and CF_2CF_2 + HF + CO_2 (TS4E).

Table S15: Arrhenius expressions for the decomposition channels presented in Fig. S11, and Fig. S12, units are: s, cal, K, and mol.

Transition states	Arrhenius expression
TS1E (CF_3CFCO_2 + HF)	$k^{a} = 8.10 \times 10^{12}\, e^{\frac{-54706}{RT}}$
TS1E1 (CF_3CFO + CO)	$k^{a} = 4.81 \times 10^{13}\, e^{\frac{-17533}{RT}}$
TS1E2 (CF_3CF + CO_2)	$k^{a} = 1.72 \times 10^{14}\, e^{\frac{-33884}{RT}}$
TS1E3 (CF_3COOH + HF)	$k^{b} = 4.13 \times 10^{-15}\, e^{\frac{-33581}{RT}}$

[a] the unit of the k is s^{-1}
[b] the unit of the k is cm^3 $molecule^{-1}$ s^{-1}

Table S16: Half lives of Pentafluoropropionic acid (TS1E) and Perfluoro-Methyl-α-lactone (TS1E1, and TS1E2) by assuming a first order decomposition reaction.

Temperature	TS1E	TS1E1	TS1E2
(K)	half life (s)	half life (s)	half life (s)
300	$5.68 \times 10^{+26}$	7.63×10^{-02}	$1.70 \times 10^{+10}$
400	$6.72 \times 10^{+16}$	5.62×10^{-05}	$1.35 \times 10^{+04}$
500	$7.27 \times 10^{+10}$	7.09×10^{-07}	$2.82 \times 10^{+00}$
600	$7.59 \times 10^{+06}$	3.76×10^{-08}	9.62×10^{-03}
700	$1.08 \times 10^{+04}$	4.56×10^{-09}	1.64×10^{-04}
800	$7.90 \times 10^{+01}$	9.31×10^{-10}	7.69×10^{-06}
900	$1.71 \times 10^{+00}$	2.70×10^{-10}	7.08×10^{-07}
1000	7.98×10^{-02}	9.98×10^{-11}	1.05×10^{-07}
1200	7.95×10^{-04}	2.24×10^{-11}	5.93×10^{-09}
1400	2.94×10^{-05}	7.67×10^{-12}	7.60×10^{-10}
1600	2.46×10^{-06}	3.43×10^{-12}	1.62×10^{-10}
1800	3.56×10^{-07}	1.83×10^{-12}	4.89×10^{-11}
2000	7.56×10^{-08}	1.11×10^{-12}	1.87×10^{-11}

Decomposition of Perfluorononanoic acid (PFNA)

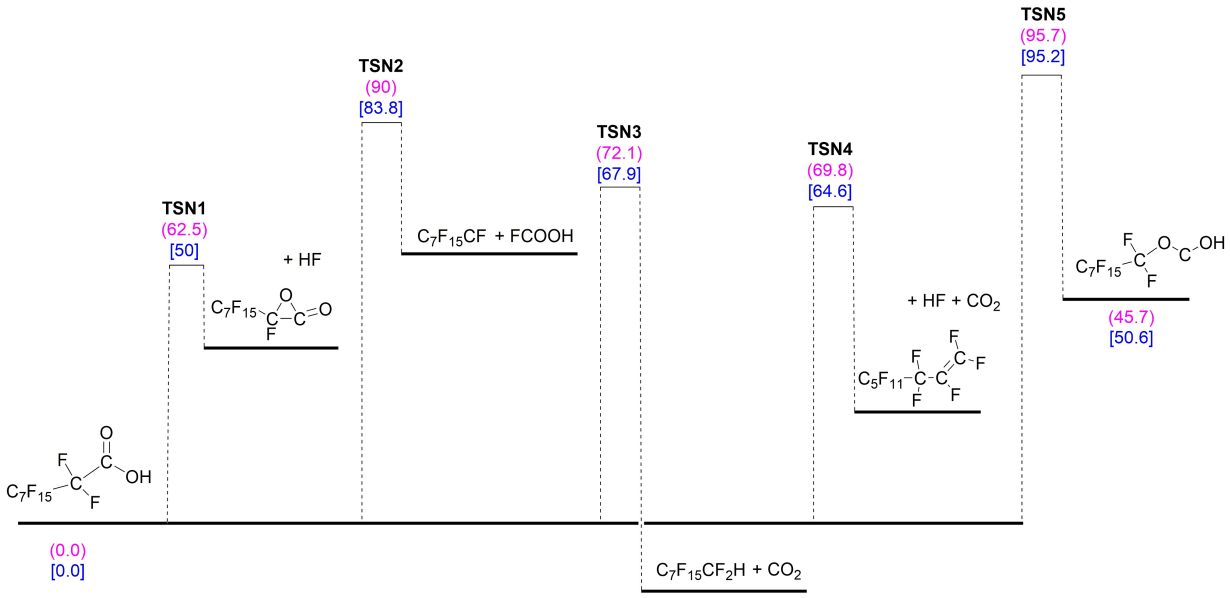


Figure S16: Potential energy diagram for thermal decomposition mechanism for Perfluorononanoic acid (PFNA). Energies are 0 K enthalpies in kcal/mol calculated at the (M062X/6-31G(2df,p)), [PBE0/def2-TZVPP] levels of theory.

Table S17: Arrhenius expressions for the decomposition of Perfluorononanoic acid presented in Fig. S16, units are: s, cal, K, and mol.

Transition states	Arrhenius expression (s^{-1})
TSN1 ($C_7F_{15}CFCO_2$ + HF)	$k = 4.37 \times 10^{13}\, e^{\frac{-63345}{RT}}$
TSN2 ($C_7F_{15}CF$ + FCOOH)	$k = 1.35 \times 10^{14}\, e^{\frac{-91199}{RT}}$
TSN3 ($C_7F_{15}CF_2H$ + CO_2)	$k = 1.24 \times 10^{15}\, e^{\frac{-73706}{RT}}$
TSN4 ($C_7F_{14}CF_2$ + HF + CO_2)	$k = 5.94 \times 10^{14}\, e^{\frac{-71120}{RT}}$
TSN5 ($C_8F_{17}OCOH$)	$k = 3.64 \times 10^{13}\, e^{\frac{-96642}{RT}}$

Table S18: Half lives of Perfluorononanoic acid based on the transition state TSN1, TSN3, and TSN4 (assuming a first order decomposition reaction)

Temperature	TSN1	TSN3	TSN4
(K)	half life (s)	half life (s)	half life (s)
300	$2.05 \times 10^{+32}$	$2.26 \times 10^{+38}$	$6.45 \times 10^{+36}$
400	$6.56 \times 10^{+20}$	$1.07 \times 10^{+25}$	$8.60 \times 10^{+23}$
500	$8.12 \times 10^{+13}$	$1.03 \times 10^{+17}$	$1.55 \times 10^{+16}$
600	$1.99 \times 10^{+09}$	$4.49 \times 10^{+11}$	$1.04 \times 10^{+11}$
700	$1.01 \times 10^{+06}$	$6.54 \times 10^{+07}$	$2.07 \times 10^{+07}$
800	$3.38 \times 10^{+03}$	$8.56 \times 10^{+04}$	$3.43 \times 10^{+04}$
900	$4.00 \times 10^{+01}$	$4.85 \times 10^{+02}$	$2.34 \times 10^{+02}$
1000	$1.15 \times 10^{+00}$	$7.67 \times 10^{+00}$	$4.30 \times 10^{+00}$
1200	5.52×10^{-03}	1.50×10^{-02}	1.06×10^{-02}
1400	1.21×10^{-04}	1.72×10^{-04}	1.43×10^{-04}
1600	6.88×10^{-06}	5.99×10^{-06}	5.65×10^{-06}
1800	7.35×10^{-07}	4.37×10^{-07}	4.54×10^{-07}
2000	1.23×10^{-07}	5.35×10^{-08}	6.02×10^{-08}

Decomposition of Trifluoroacetic acid (TFA)

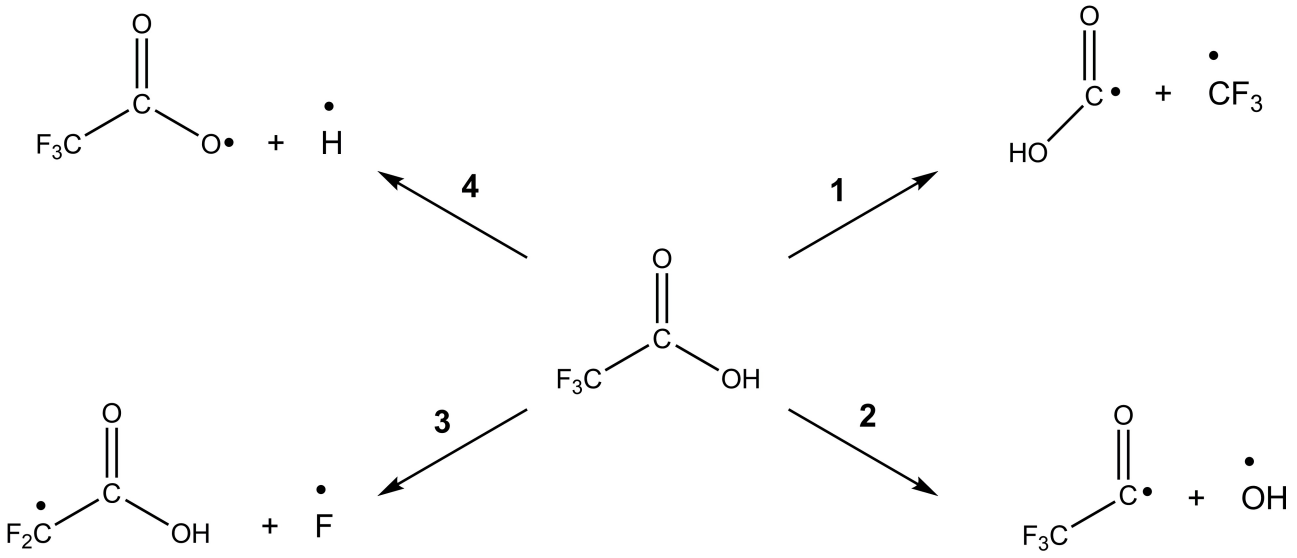
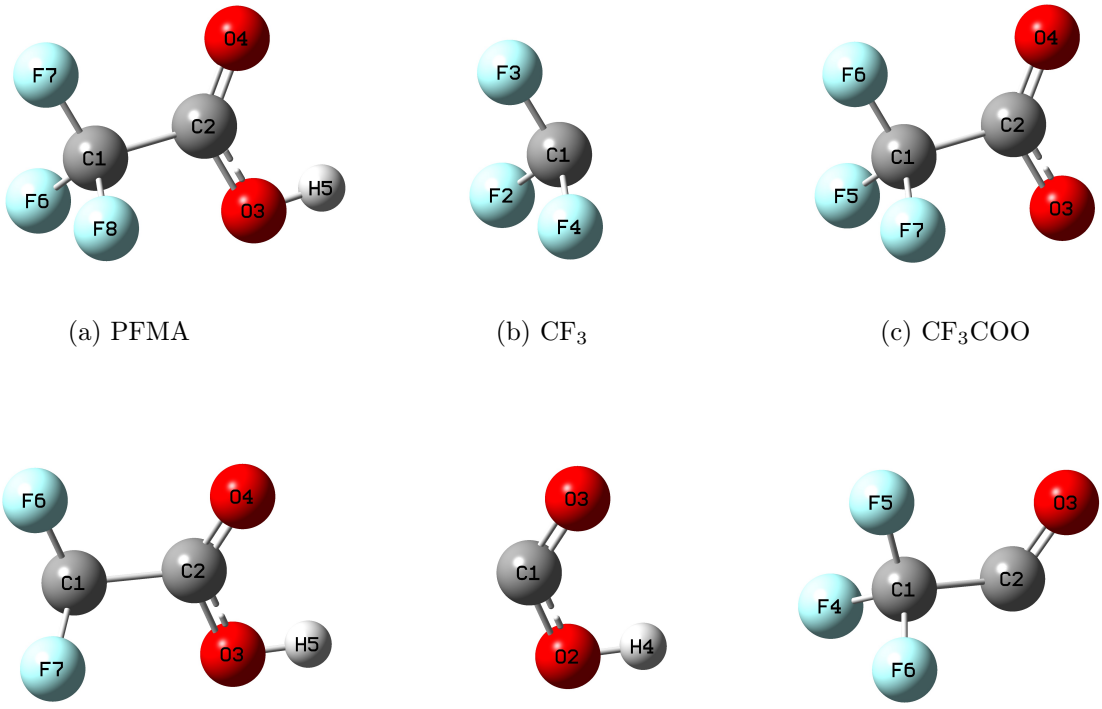


Figure S17: Formation of different radicals resulting from direct bonds dissociation of trifluoroacetic acid (TFA).

Table S19: Energies are 0 K enthalpies in kcal/mol for the different bond dissociation energies of TFA, calculated at different levels of theory with zero-point corrections.

Reactions[a]	BDE at M062X[b]	BDE at M062X[c]	BDE at PBE0[d]
1	90.6	93.6	86.1
2	110.7	114.1	107.8
3	117	121.3	111.8
4	114.4	115.1	107.4

[a] the numbers (1, 2, ...) represents different decomposition channels as per Figure S17
[b] Bond dissociation energies at M062X with 6-31++G(2df,p) basis set
[c] Bond dissociation energies at M062X with 6-31G(2df,p) basis set
[d] Bond dissociation energies at PBE0/def2-TZVPP



(a) PFMA (b) CF_3 (c) CF_3COO

(d) CF_2COOH (e) COOH (f) CF_3CO

Figure S18: Optimized (M06-2X/6-31G(2df,p)) ground state structures of the key species involve in the radical network of TFA dissociation S17

Table S20: Energies are 0 K enthalpies in kcal/mol for TFA transition states, calculated at different levels of theory with zero-point corrections.

Functional / Basis set	Transition states				
	TS1M	TS2M	TS3M	TS4M	TS5M
M062X / 6-31G(2df,p)	55.4	54.8	74.7	76.2	97.7
M062X / 6-31++G(2df,p)	53.7	54.4	73.9	75	98.1
M062X / 6-311++G(2df,p)	54.2	54.8	74.1	75.7	99.1
MP2 / 6-31G(2df,p)	51.4	54.8	73	78	98.6
G4	49.5	54.5	75	75.8	99.4
G3XK	49.7	53.8	73.8	76	99.4
PBE0/def2-TZVPP	48.4	52.4	70.6	73.2	97.7
DSD-PBEB95/def2-TZVPP	50.1	52.2	73.1	75.3	99.2

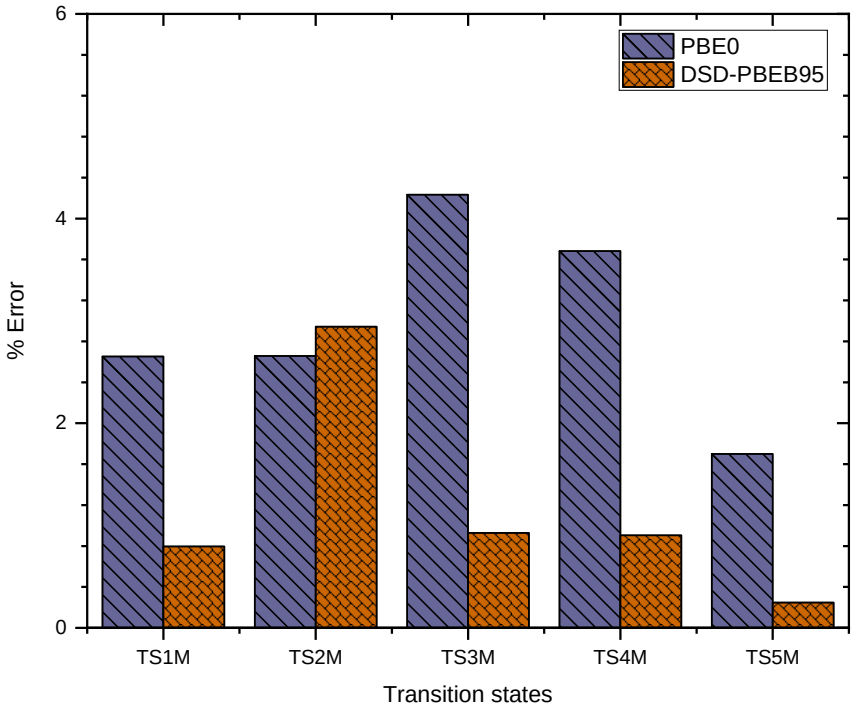


Figure S19: Comparison of the absolute percentage error (%) between DSD-PBEB95/def2-TZVPP and PBE0/def2-TZVPP for the transition states of TFA (Table S20). The percentage errors are calculated with reference to G3X-K method.

Table S21: Arrhenius expressions for the decomposition channels presented in Fig. 8 (article), and Fig. 12 (article), units are: s, cal, K, and mol.

Transition states	Arrhenius expression
TS1M ($C_2F_2O_2$ + HF)	$k^{a} = 1.24 \times 10^{13}\, e^{\frac{-51131}{RT}}$
TS2M (CF_2 + HF + CO_2)	$k^{a} = 6.62 \times 10^{14}\, e^{\frac{-54049}{RT}}$
TS1M1 (CF_2O + CO)	$k^{a} = 3.70 \times 10^{13}\, e^{\frac{-15613}{RT}}$
TS1M2 (CF_2 + CO_2)	$k^{a} = 1.52 \times 10^{14}\, e^{\frac{-20642}{RT}}$
TS1M3 (FCOOH + HF)	$k^{b} = 8.92 \times 10^{-15}\, e^{\frac{-40736}{RT}}$
TS1M4 (HF + CO_2)	$k^{a} = 2.77 \times 10^{13}\, e^{\frac{-31302}{RT}}$

[a] the unit of the k is s^{-1}
[b] the unit of the k is cm^3 $molecule^{-1}$ s^{-1}

Table S22: Half lives of TFA (TS1M, TS2M), difluoroacetolactone (TS1M1, and TS1M2), and perfluoroformic acid (TS1M4) by assuming a first order decomposition reaction.

Temperature	TS1M	TS2M	TS1M1	TS1M2	TS1M4
(K)	half life (s)	half life (s)	half life (s)	half life (s)	half life (s)
300	$9.05 \times 10^{+23}$	$2.08 \times 10^{+24}$	4.02×10^{-03}	$4.51 \times 10^{+00}$	$1.41 \times 10^{+09}$
400	$4.91 \times 10^{+14}$	$3.69 \times 10^{+14}$	6.49×10^{-06}	8.89×10^{-04}	$3.20 \times 10^{+03}$
500	$1.31 \times 10^{+09}$	$4.88 \times 10^{+08}$	1.32×10^{-07}	5.10×10^{-06}	$1.27 \times 10^{+00}$
600	$2.49 \times 10^{+05}$	$5.71 \times 10^{+04}$	9.67×10^{-09}	1.60×10^{-07}	6.79×10^{-03}
700	$5.41 \times 10^{+02}$	$8.70 \times 10^{+01}$	1.48×10^{-09}	1.34×10^{-08}	1.60×10^{-04}
800	$5.43 \times 10^{+00}$	6.64×10^{-01}	3.59×10^{-10}	2.07×10^{-09}	9.52×10^{-06}
900	1.51×10^{-01}	1.49×10^{-02}	1.19×10^{-10}	4.84×10^{-10}	1.06×10^{-06}
1000	8.56×10^{-03}	7.10×10^{-04}	4.92×10^{-11}	1.51×10^{-10}	1.81×10^{-07}
1200	1.15×10^{-04}	7.31×10^{-06}	1.30×10^{-11}	2.61×10^{-11}	1.27×10^{-08}
1400	5.26×10^{-06}	2.76×10^{-07}	5.01×10^{-12}	7.46×10^{-12}	1.89×10^{-09}
1600	5.18×10^{-07}	2.36×10^{-08}	2.45×10^{-12}	2.91×10^{-12}	4.48×10^{-10}
1800	8.52×10^{-08}	3.46×10^{-09}	1.40×10^{-12}	1.40×10^{-12}	1.46×10^{-10}
2000	2.01×10^{-08}	7.44×10^{-10}	8.96×10^{-13}	7.76×10^{-13}	5.91×10^{-11}

Input parameters for calculating Arrhenius equation

Table S23: Moments of inertia (amu Å^2) of PFOA and transition states presented in Fig. 3 (article) at M06-2X/6-31G(2df,p) level of theory.

PFOA	TSO1	TSO2	TSO3	TSO4	TSO5
1067.7519	1046.7990	1348.3833	1142.8377	1051.4440	1059.2800
3077.5722	3203.9260	2657.6037	3061.7572	3164.1531	3125.8619
3087.0123	3246.6330	2964.2908	3144.9687	3235.9781	3183.4073

Table S24: Moments of inertia (amu Å^2) of Perfluoro-3-Hexyl-α-lactone, C7-perfluorinated aldehyde, water, and transition states presented in Fig. 6 (article) at M06-2X/6-31G(2df,p) level of theory.

Perfluoro-3-Hexyl-α-lactone	TS1O1	TS1O2	C7-perfluor-aldehyde	TS1O3	H_2O
943.4444	958.5473	880.2531	924.5387	844.1324	0.6223
2903.3260	2908.9023	3379.9748	2195.4573	2925.9218	1.1529
2977.0477	2968.2873	3618.4516	2284.3431	3027.6094	1.7751

Table S25: Moments of inertia (amu Å^2) of iso-PFOA and transition states presented in Fig. S2 at M06-2X/6-31G(2df,p) level of theory.

iso-PFOA	TSO1a	TSO3a
1187.4809	1162.6853	1290.7950
2868.0111	2919.6861	2783.2586
3046.7600	3077.3826	3149.1679

Table S26: Moments of inertia (amu Å^2) of Perfluoroheptanoic acid, Perfluoro-3-Pentyl-α-lactone, C6-perfluorinated aldehyde, and transition states presented in Fig. S7 at M06-2X/6-31G(2df,p) level of theory.

Perfluoroheptanoic acid	TS71	Perfluoro-3-Pentyl-α-lactone	TS171	TS172	C6-perfluor-aldehyde	TS173
928.1958	920.8460	814.0983	829.7240	710.6124	928.1958	738.5314
2183.6417	2292.4965	2101.4722	2108.3860	2484.2529	2183.6417	1952.5680
2252.1857	2369.8054	2126.2089	2115.7658	2666.2006	2252.1857	2069.6325

Table S27: Moments of inertia (amu Å^2) of Perfluorohexanoic acid, Perfluoro-3-Butyl-α-lactone, C5-perfluorinated aldehyde, and transition states presented in Fig. S8 at M06-2X/6-31G(2df,p) level of theory.

Perfluorohexanoic acid	TS61	Perfluoro-3-Butyl-α-lactone	TS161	TS162	C5-perfluor-aldehyde	TS163
787.8833	760.5855	656.3563	657.8056	620.8723	621.5517	615.4466
1539.3858	1638.6320	1458.0615	1461.8673	1592.1628	1010.5987	1313.7153
1550.3755	1690.6116	1550.7881	1562.9094	1777.5774	1105.5279	1400.8420

Table S28: Moments of inertia (amu Å^2) of Perfluoropentanoic acid, Perfluoro-3-Propyl-α-lactone, C4-perfluorinated aldehyde, and transition states presented in Fig. S9 at M06-2X/6-31G(2df,p) level of theory.

Perfluoropentanoic acid	TS51	Perfluoro-3-Propyl-α-lactone	TS151	TS152	C4-perfluor-aldehyde	TS153
539.2549	561.0585	469.7882	461.2358	501.5964	344.4996	506.8395
1166.7417	1181.6837	1022.1265	1087.9100	1059.8475	808.9615	769.6775
1258.1485	1224.4244	1167.1474	1125.2759	1216.2579	884.4997	888.0573

Table S29: Moments of inertia (amu Å^2) of Perfluorobutanoic acid, Perfluoro-3-Ethyl-α-lactone, C3-perfluorinated aldehyde, and transition states presented in Fig. S10 at M06-2X/6-31G(2df,p) level of theory.

Perfluorobutanoic acid	TS41	Perfluoro-3-Ethyl-α-lactone	TS141	TS142	C3-perfluor-aldehyde	TS143
452.6047	464.7400	372.2819	374.5382	394.5556	245.7231	323.7817
635.0798	668.1176	555.6605	561.5900	572.8367	425.2609	494.9196
726.7646	718.6269	689.5264	675.8427	734.3221	492.5800	548.7975

Table S30: Moments of inertia (amu Å^2) of Pentafluoropropionic acid, Perfluoro-3-Methyl-α-lactone, perfluoroacetyl fluoride, and transition states TS1E, TS1E1, TS1E2, and TS1E3 at M06-2X/6-31G(2df,p) level of theory.

Pentafluoropropionic acid	TS1E	Perfluoro-3-Methyl-α-lactone	TS1E1	TS1E2	perfluoroacetyl fluoride	TS1E3
264.3090	279.2783	188.0904	199.1059	185.8845	130.2849	184.1494
428.8612	425.1791	363.6109	355.6236	412.1597	200.0109	276.2056
453.9933	479.2018	410.2399	396.7983	456.3799	242.3844	288.7638

Table S31: Moments of inertia (amu Å^2) of PFNA and transition states presented in Fig. S16 at M06-2X/6-31G(2df,p) level of theory.

PFNA	TSN1	TSN2	TSN3	TSN4	TSN5
1219.2104	1281.7428	1222.8366	1278.1915	1212.5914	1212.7660
4103.6517	4225.7978	4236.2015	4219.6915	4488.8732	4179.5513
4182.3080	4364.2917	4274.5890	4331.1406	4637.7767	4264.9656

Table S32: Moments of inertia (amu Å^2) of trifluoroacetic acid (TFA) and transition states presented in Fig. 8 (article) at M06-2X/6-31G(2df,p) level of theory.

TFA	TS1M	TS2M	TS3M	TS4M	TS5M
129.7888	169.1218	156.2471	128.0567	123.4051	104.4252
201.6972	185.3823	227.1101	244.2496	213.9509	249.2848
242.3712	269.9239	301.8061	284.3486	257.9037	263.6763

Table S33: Moments of inertia (amu Å^2) of Difluoroacetolactone, carbonyl fluoride, perfluoro-formic acid, and transition states TS1M1, TS1M2, TS1M3, and TS1M4 at M06-2X/6-31G(2df,p) level of theory.

Difluoroaceto-lactone	TS1M1	TS1M2	carbonyl-fluoride	TS1M3	perfluoro-formic acid	TS1M4
69.3763	76.0858	74.9645	42.2453	86.0556	42.1273	37.4962
165.7822	168.7328	189.6020	42.5542	100.8976	43.7945	56.0327
183.8265	179.1693	196.9133	84.7996	103.4559	85.9218	93.5289

Table S34: Vibrational frequencies (cm^{-1}) of PFOA, and transition state TSO1 and TSO2 at M06-2X/6-31G(2df,p) level of theory

PFOA			TSO1			TSO2		
C1	C2	C3	C4	C5	C6	C7	C8	C9
42.79	388.34	1286.32	44.68	388.11	1303.97	9.16	377.87	1293.27
51.76	428.95	1292.95	52.59	440.75	1311.13	38.77	390.00	1313.67
58.78	472.31	1304.85	61.39	445.09	1326.87	53.19	445.95	1320.71
68.37	494.60	1324.04	68.03	484.61	1329.17	69.51	484.63	1332.25
79.91	511.52	1333.98	83.36	497.10	1334.55	78.50	499.47	1335.51
97.55	524.79	1341.17	110.44	509.56	1355.45	91.09	530.70	1354.99
111.04	551.24	1354.09	114.82	542.06	1367.49	122.98	554.23	1372.84
138.61	568.64	1364.49	138.71	551.30	1370.41	129.80	560.42	1376.56
145.77	602.37	1370.23	144.20	602.56	1415.89	144.19	600.92	1409.39
151.30	630.39	1373.25	150.62	641.26	1423.19	158.34	607.17	1411.58
151.96	637.06	1420.69	152.59	653.46	1518.37	176.49	655.18	1565.73
171.90	652.51	1444.56	176.49	672.71	1891.85	186.78	666.48	1891.66
190.92	660.47	1944.67	186.29	678.78	2649.14	197.89	678.34	2211.73
207.42	679.74	3816.97	198.38	686.16		219.63	688.39	
228.44	683.00		210.41	741.08		232.14	721.06	
246.49	721.60		230.98	778.45		250.32	740.55	
255.38	778.75		258.35	803.29		259.99	772.92	
275.46	800.63		265.27	923.66		268.82	783.22	
279.35	925.95		276.90	981.02		280.86	915.52	
289.85	989.12		286.72	997.51		295.20	989.06	
305.09	1051.88		298.04	1051.08		308.89	1062.99	
313.99	1113.17		303.19	1121.78		320.97	1069.73	
318.44	1158.74		314.06	1178.07		323.88	1142.70	
320.32	1189.24		317.54	1213.78		332.49	1192.71	
332.45	1203.82		324.92	1251.47		342.11	1212.49	
343.67	1227.91		328.63	1256.84		346.28	1217.83	
368.56	1256.73		344.03	1275.71		349.66	1238.66	
377.42	1265.41		367.28	1282.48		363.69	1269.23	
384.43	1272.76		384.48	1294.54		373.32	1278.35	
up C2	up C3		up C5	up C6		up C8	up C9	

Table S35: Vibrational frequencies (cm^{-1}) of transition states TSO3, TSO4, and TSO5 at M06-2X/6-31G(2df,p) level of theory

TO3			TSO4			TSO5		
C1	C2	C3	C4	C5	C6	C7	C8	C9
22.58	385.27	1273.49	25.14	416.56	1294.06	33.02	440.41	1284.03
29.15	409.88	1287.65	39.81	450.16	1306.87	42.44	457.80	1294.16
46.92	458.90	1294.49	54.75	480.55	1320.51	60.73	480.19	1323.89
60.29	487.20	1326.05	68.45	494.08	1327.28	67.23	489.00	1334.28
67.05	499.69	1333.33	83.88	503.60	1332.59	68.89	502.59	1340.33
89.75	517.82	1350.06	96.16	511.41	1336.59	95.69	518.80	1346.50
106.19	551.41	1354.49	114.12	550.99	1356.71	113.12	550.96	1358.20
129.40	598.20	1364.01	130.30	577.62	1370.93	137.38	601.98	1364.77
137.65	604.53	1371.34	142.91	583.10	1382.98	143.04	637.63	1367.64
148.00	617.32	1376.13	147.89	602.98	1428.01	149.90	640.96	1420.82
153.39	628.52	1421.01	156.04	635.61	1555.93	152.55	662.64	1430.69
165.68	653.47	2027.31	169.26	655.00	1578.79	168.04	673.20	1594.33
177.08	661.47	2343.15	189.75	670.78	3868.21	189.04	674.68	3607.16
190.13	678.24		209.35	681.17		205.71	682.04	
210.79	682.36		230.23	693.51		219.61	685.16	
220.61	711.83		236.80	774.73		231.81	755.92	
233.27	778.56		249.76	779.03		257.92	777.91	
259.45	905.21		260.14	836.14		275.59	847.00	
277.63	942.97		280.84	906.69		281.16	930.61	
282.63	968.14		295.31	962.66		286.00	984.40	
287.97	1020.56		304.28	1031.27		310.71	1038.74	
303.71	1085.82		308.69	1080.07		313.22	1077.61	
315.44	1134.81		316.67	1103.22		318.26	1134.81	
318.81	1153.95		321.72	1141.21		325.12	1180.40	
321.47	1185.82		327.09	1193.01		331.70	1215.22	
332.47	1210.42		339.35	1220.38		340.88	1224.91	
346.39	1232.45		357.84	1258.64		367.53	1256.48	
369.04	1252.89		370.78	1281.13		383.79	1261.40	
379.86	1264.61		386.02	1288.29		385.08	1270.31	
up C2	up C3		up C5	up C6		up C8	up C9	

Table S36: Vibrational frequencies (cm^{-1}) of Perfluoro-3-Hexyl-α-lactone, and transition states TS1O1, and TS1O2 at M06-2X/6-31G(2df,p) level of theory

Perfluoro-3-Hexyl-α-lactone			TS1O1			TS1O2		
C1	C2	C3	C4	C5	C6	C7	C8	C9
32.45	486.26	1336.57	34.91	461.83	1348.93	13.75	415.21	1336.51
47.66	505.51	1355.43	47.45	486.20	1356.28	43.02	467.53	1343.98
56.33	521.94	1366.51	58.51	501.60	1368.67	51.84	515.36	1375.38
72.78	551.10	1369.63	70.25	515.51	1369.11	69.46	544.52	1393.24
85.72	561.25	1371.32	85.11	550.38	1423.26	79.80	553.99	1399.05
111.53	602.66	1386.12	110.41	555.67	1472.71	90.20	577.88	1426.10
123.44	603.48	1423.40	121.20	602.13	2253.32	97.55	601.38	2342.14
134.64	648.68	2119.40	135.35	635.41		116.64	612.19	
147.15	659.13		146.90	649.37		140.69	659.21	
155.33	678.36		153.13	650.72		157.02	660.76	
169.40	681.05		173.30	677.69		173.39	682.65	
185.44	712.45		188.06	682.14		190.91	697.90	
208.16	721.61		205.95	722.75		209.28	706.07	
229.20	778.76		228.87	778.22		215.42	774.58	
237.55	837.35		237.43	889.64		230.07	834.66	
259.46	919.74		256.95	955.46		235.47	887.12	
278.67	977.20		277.24	1023.25		246.74	974.95	
287.40	1050.11		280.39	1093.75		264.40	1076.04	
298.32	1119.80		291.31	1129.08		280.63	1195.72	
313.55	1175.46		309.21	1171.85		287.94	1201.65	
315.71	1197.10		313.45	1214.05		315.25	1222.15	
323.06	1220.38		315.54	1250.22		317.53	1252.22	
328.42	1259.17		324.98	1256.46		320.55	1260.10	
338.54	1263.40		338.66	1273.22		331.17	1272.67	
366.27	1277.64		366.08	1282.67		347.74	1283.44	
373.86	1286.18		375.79	1293.58		367.80	1296.93	
384.29	1299.72		384.41	1308.56		376.48	1313.52	
389.30	1326.07		386.53	1325.42		381.09	1322.81	
446.63	1333.94		433.51	1333.67		392.12	1327.63	
up C2	up C3		up C5	up C6		up C8	up C9	

Table S37: Vibrational frequencies (cm^{-1}) of C7-perfluorinated aldehyde, and transition states TS1O3, and water at M06-2X/6-31G(2df,p) level of theory

C7-perfluoro-aldehyde			TS1O3			H_2O
C1	C2	C3	C4	C5	C6	C7
47.75	542.38	1423.70	21.00	460.80	1332.60	1658.61
60.15	550.87	2011.43	40.25	492.90	1335.10	3884.24
67.33	581.81		63.89	516.28	1341.53	3990.62
78.23	602.65		74.47	523.83	1360.20	
87.80	648.79		85.27	549.21	1383.80	
121.92	652.87		105.05	572.25	1425.40	
132.99	677.62		131.05	602.64	1435.88	
152.54	681.28		153.22	625.64	1978.72	
156.58	732.65		161.73	652.86	2129.49	
162.48	779.00		185.88	665.92	3822.43	
187.00	791.29		191.11	671.10		
206.41	935.81		217.10	693.62		
233.81	1004.43		243.53	697.23		
244.31	1080.86		258.22	772.61		
264.03	1140.32		283.63	827.26		
278.77	1181.53		290.12	903.12		
287.51	1220.52		294.62	961.97		
302.39	1257.93		300.65	1012.22		
311.16	1259.20		309.02	1105.49		
316.27	1281.86		320.22	1123.06		
325.36	1290.36		322.34	1178.16		
341.27	1304.71		337.69	1195.35		
365.38	1323.93		354.72	1228.63		
377.84	1329.56		366.90	1248.72		
386.53	1334.66		374.43	1269.19		
393.83	1354.53		393.40	1277.66		
456.01	1369.91		404.11	1292.54		
488.47	1371.52		414.16	1306.23		
507.74	1376.28		436.65	1325.46		
up C2	up C3		up C5	up C6		

Table S38: Vibrational frequencies (cm^{-1}) of iso-PFOA, and transition state TSO1a and TSO3a at M06-2X/6-31G(2df,p) level of theory

PFOA			TSO1			TSO2		
C1	C2	C3	C4	C5	C6	C7	C8	C9
34.20	393.13	1291.04	32.94	407.15	1302.08	34.66	395.35	1284.79
49.65	450.21	1291.94	51.89	444.31	1308.42	45.68	434.93	1296.01
62.94	485.80	1314.33	63.83	477.32	1320.89	49.71	455.88	1302.61
71.92	504.48	1324.30	81.75	506.02	1326.24	63.35	523.14	1337.11
75.37	535.69	1326.88	95.11	519.09	1335.38	66.15	529.10	1341.64
93.76	551.44	1330.99	108.55	550.65	1350.96	81.28	544.75	1343.14
112.44	560.92	1335.03	115.06	566.11	1353.45	90.13	552.46	1376.23
126.39	564.10	1356.91	121.48	593.34	1354.67	106.64	590.43	1387.85
137.79	603.35	1369.83	138.91	604.18	1363.71	125.13	601.23	1426.50
151.51	621.37	1381.92	148.28	632.00	1436.61	151.07	615.86	1435.53
157.63	641.53	1422.71	163.02	645.11	1454.35	159.86	633.11	1537.27
171.55	648.32	1428.45	168.31	668.29	1864.88	168.77	655.11	1795.70
199.07	670.87	1945.16	185.24	680.63	2272.57	197.01	685.98	2219.54
203.73	682.29	3813.61	195.99	709.79		206.46	711.70	
219.51	699.75		206.90	748.83		213.27	724.51	
235.99	725.26		217.56	776.14		235.13	756.20	
269.04	778.98		254.54	797.96		248.00	769.80	
275.16	792.00		283.71	896.59		259.22	786.14	
284.98	903.74		289.03	992.13		289.22	881.87	
292.34	981.46		306.76	1063.60		295.59	944.22	
303.44	1068.15		314.36	1072.16		297.62	1058.78	
316.40	1081.24		325.60	1107.46		306.28	1080.70	
317.48	1150.68		329.81	1166.15		322.36	1148.60	
326.45	1190.07		335.04	1209.49		338.36	1194.24	
336.71	1206.84		352.64	1243.29		343.79	1213.36	
362.36	1240.20		366.75	1265.32		351.06	1243.26	
369.31	1259.52		371.47	1279.77		354.25	1257.63	
376.22	1266.62		374.93	1288.18		375.87	1268.91	
384.62	1273.19		395.57	1295.27		383.96	1270.63	
up C2	up C3		up C5	up C6		up C8	up C9	

Table S39: Vibrational frequencies (cm^{-1}) of Perfluoroheptanoic acid, Perfluoro-3-Pentyl-α-lactone, and transition state TS71 at M06-2X/6-31G(2df,p) level of theory

Perfluoroheptanoic acid			Perfluoro-3-Pentyl-α-lactone		TS71		
C1	C2	C3	C4	C5	C6	C7	C8
46.44	525.87	1374.44	38.74	602.84	52.49	504.99	1420.58
52.98	551.68	1423.00	58.52	604.07	60.45	538.49	1518.52
70.22	573.95	1444.51	72.09	659.40	73.30	553.87	1891.90
75.15	602.29	1944.74	78.40	663.84	77.53	602.52	2648.27
89.91	633.25	3813.97	115.10	681.56	105.98	650.42	
116.92	640.50		125.34	711.91	117.92	656.84	
132.49	653.33		129.47	721.02	134.43	678.87	
141.25	673.51		154.49	778.84	148.52	684.79	
152.74	682.04		166.89	837.83	152.61	740.84	
167.91	721.30		182.22	927.52	168.65	778.74	
190.63	778.83		214.40	998.32	185.25	803.84	
208.65	800.24		228.59	1084.04	198.80	932.28	
235.54	937.62		247.13	1162.62	216.03	992.50	
246.53	1010.04		267.05	1197.56	241.28	1001.28	
262.73	1082.58		283.49	1217.63	264.48	1087.49	
278.01	1142.95		292.79	1261.79	268.25	1166.32	
288.20	1186.59		312.71	1273.40	280.06	1209.47	
303.97	1201.96		318.97	1282.18	300.82	1252.28	
312.85	1231.15		326.86	1295.79	304.84	1270.42	
315.19	1256.70		336.59	1323.53	315.53	1283.71	
323.26	1270.89		361.28	1332.62	319.06	1294.61	
341.61	1281.59		375.81	1342.19	325.72	1297.97	
364.91	1291.60		384.78	1362.68	338.13	1311.77	
379.01	1301.29		399.02	1369.02	367.08	1323.45	
386.12	1326.38		466.34	1373.68	383.44	1332.76	
390.70	1332.86		499.76	1386.60	397.83	1335.40	
444.60	1343.84		520.32	1421.55	443.36	1362.81	
486.45	1357.59		549.04	2119.63	461.66	1375.41	
506.64	1370.49		562.65		494.16	1415.44	
up C2	up C3		up C5		up C7	up C8	

Table S40: Vibrational frequencies (cm^{-1}) of C6-perfluorinated aldehyde, and transition states TS171, TS172, and TS173 at M06-2X/6-31G(2df,p) level of theory

C6-perfluorinated aldehyde		TS171		TS172		TS173	
C1	C2	C3	C4	C5	C6	C7	C8
52.40	664.46	42.30	554.33	38.25	572.62	38.39	564.36
56.30	682.19	59.19	603.49	40.63	606.94	58.00	599.24
75.89	730.52	75.39	635.35	52.11	626.79	64.45	628.72
83.21	777.94	81.92	650.80	68.05	659.98	84.96	662.68
121.67	791.89	112.18	666.16	78.70	673.48	102.47	669.08
129.23	950.19	124.50	681.48	98.36	695.24	139.99	677.20
156.24	1032.42	133.61	721.99	117.15	706.19	150.08	697.39
158.44	1115.70	155.48	778.66	145.25	770.68	184.71	775.57
182.38	1176.21	168.74	892.31	168.98	838.76	192.51	828.60
215.86	1215.22	184.54	972.77	187.38	902.79	241.83	919.60
232.16	1259.11	213.24	1052.51	202.71	987.42	257.44	981.29
254.91	1274.52	230.02	1117.12	221.84	1174.79	268.37	1059.26
268.48	1290.18	248.43	1156.65	227.12	1199.96	285.27	1114.71
282.59	1302.18	266.09	1210.45	241.94	1227.50	291.13	1142.28
300.04	1320.20	279.81	1250.54	250.31	1254.55	303.83	1198.01
307.42	1330.15	283.66	1267.58	273.65	1263.65	310.72	1230.40
320.17	1335.84	306.13	1276.50	282.37	1276.78	324.93	1252.24
334.85	1361.04	313.66	1291.86	297.28	1300.94	338.90	1274.64
362.96	1374.66	318.00	1310.74	314.67	1308.27	343.38	1295.43
376.46	1376.59	335.30	1321.38	315.69	1327.08	368.68	1303.18
386.11	1424.45	361.58	1331.27	336.56	1334.67	377.01	1313.41
409.75	2011.77	379.58	1353.71	362.73	1340.98	393.60	1330.55
473.24		385.03	1362.94	376.14	1349.25	406.78	1343.65
501.68		394.00	1374.07	380.11	1380.47	417.43	1347.79
540.40		445.22	1421.19	398.50	1395.47	449.19	1382.58
550.96		472.51	1474.16	427.35	1436.46	484.81	1401.05
581.04		498.09	2252.96	508.51	2341.91	513.29	1421.76
603.03		512.06		538.40		517.17	1978.48
652.15		551.15		552.13		555.56	2133.87
up C2		up C4		up C6		up C8	3823.30

Table S41: Vibrational frequencies (cm^{-1}) of Perfluorohexanoic acid, Perfluoro-3-Butyl-α-lactone, and transition states TS61, and TS161 at M06-2X/6-31G(2df,p) level of theory

Perfluorohexanoic acid		Perfluoro-3-Butyl-α-lactone		TS61		TS161	
C1	C2	C3	C4	C5	C6	C7	C8
41.38	641.50	25.09	720.61	36.20	674.63	33.52	720.63
54.80	663.59	55.91	779.81	57.46	682.10	53.54	779.11
69.99	680.20	76.55	837.87	70.89	739.45	74.89	897.83
76.50	720.33	111.01	937.15	99.07	778.18	105.49	998.20
118.95	779.38	119.06	1032.14	118.41	805.37	118.90	1093.29
121.18	800.23	134.93	1136.29	130.07	944.40	136.85	1138.57
145.25	952.74	171.32	1198.55	151.09	997.21	169.29	1208.56
161.66	1037.82	177.63	1215.43	161.57	1034.70	181.73	1258.00
184.99	1119.10	214.93	1269.45	185.67	1139.20	214.69	1267.06
217.85	1183.02	233.60	1276.61	196.56	1209.40	233.28	1288.09
234.72	1199.39	241.89	1291.81	218.57	1262.41	241.97	1304.67
248.45	1226.58	276.79	1319.68	239.34	1271.87	272.11	1329.67
268.74	1270.98	296.43	1332.24	264.26	1289.69	284.56	1331.99
280.63	1273.71	310.24	1348.49	270.42	1302.45	300.99	1354.07
303.87	1289.22	321.26	1371.16	295.62	1307.77	313.95	1373.56
308.34	1303.86	327.35	1374.34	305.54	1319.80	323.43	1422.05
319.94	1320.41	360.43	1387.34	309.63	1333.31	363.56	1473.86
333.01	1329.70	373.62	1422.76	322.93	1344.90	370.84	2253.15
361.51	1349.38	382.10	2119.97	328.82	1375.03	383.05	
376.09	1364.88	417.73		362.84	1416.25	408.46	
387.29	1377.97	488.19		379.58	1422.45	455.20	
402.13	1423.09	517.79		413.16	1518.48	486.50	
463.66	1444.97	551.48		443.63	1891.48	508.44	
500.62	1944.30	562.90		483.47	2644.56	545.96	
525.11	3816.57	589.05		498.40		560.29	
551.50		619.22		537.99		601.77	
572.03		661.78		552.34		636.59	
603.05		677.44		604.10		658.48	
634.21		711.34		650.66		678.20	
up C2		up C4		up C6		up C8	

Table S42: Vibrational frequencies (cm^{-1}) of C5-perfluorinated aldehyde, and transition states TS162, and TS163 at M06-2X/6-31G(2df,p) level of theory

C5-perfluorinated aldehyde		TS162		TS163	
C1	C2	C3	C4	C5	C6
39.23	1074.51	44.52	696.81	24.95	697.43
59.44	1164.54	55.70	774.72	65.44	771.69
85.96	1211.77	61.60	842.81	85.05	833.71
107.28	1270.31	93.02	938.24	115.33	937.20
138.32	1278.67	94.69	1079.08	140.38	1001.69
156.97	1300.21	127.60	1201.65	163.82	1108.27
176.26	1320.00	169.35	1224.15	185.29	1121.71
218.33	1332.03	176.84	1256.04	221.09	1197.17
242.53	1341.43	198.17	1266.05	245.92	1236.19
248.74	1374.85	223.98	1293.42	259.35	1260.89
277.79	1378.06	225.83	1318.82	288.34	1280.43
295.78	1419.93	247.05	1329.57	298.93	1301.32
309.70	2011.32	259.62	1330.67	310.48	1329.46
326.96		282.31	1341.35	319.88	1335.79
358.88		306.24	1370.68	330.22	1339.31
376.44		316.62	1396.88	363.41	1364.12
382.06		323.31	1431.25	373.83	1428.00
432.05		346.84	2342.58	387.17	1430.83
491.43		374.32		414.26	1976.98
533.77		385.19		441.29	2136.98
556.33		398.93		465.34	3822.10
570.79		465.11		504.84	
613.59		529.47		515.34	
656.13		548.47		550.30	
678.02		579.95		578.38	
728.73		607.44		604.70	
777.40		659.46		635.36	
792.81		670.41		669.14	
969.21		676.12		674.24	
up C2		up C4		up C6	

Table S43: Vibrational frequencies (cm^{-1}) of Perfluoropentanoic acid, Perfluoro-3-Propyl-α-lactone, and transition states TS51, and TS151 at M06-2X/6-31G(2df,p) level of theory

Perfluoropentanoic acid		Perfluoro-3-Propyl-α-lactone		TS51		TS151	
C1	C2	C3	C4	C5	C6	C7	C8
34.77	923.17	20.41	1217.33	36.13	984.34	37.24	1252.36
51.91	1078.26	42.79	1271.18	61.83	1114.80	45.50	1278.09
68.64	1194.34	75.49	1281.64	69.90	1210.67	67.03	1298.69
90.78	1201.38	95.87	1309.31	105.28	1259.21	120.21	1321.31
122.77	1242.82	156.89	1330.98	138.14	1272.39	123.84	1333.28
149.74	1273.74	197.40	1339.83	156.45	1296.89	184.38	1389.19
197.34	1282.07	223.30	1366.28	172.42	1299.02	211.64	1433.94
228.77	1301.31	236.14	1392.79	208.89	1325.85	240.50	1478.36
237.25	1303.15	236.81	1442.26	243.49	1339.36	247.22	2260.86
248.70	1336.85	287.77	2118.17	246.45	1384.26	290.03	
272.08	1339.70	300.22		256.47	1406.53	293.54	
296.24	1384.13	329.31		280.78	1433.44	321.61	
296.39	1434.94	350.13		297.44	1502.45	339.59	
332.83	1448.49	361.21		325.30	1891.83	366.27	
353.63	1941.76	386.04		337.82	2629.38	381.39	
384.61	3814.41	445.64		351.26		414.62	
388.87		527.30		380.38		469.65	
420.23		535.69		392.85		518.99	
509.10		550.82		422.55		543.51	
536.34		612.25		496.87		552.73	
542.76		627.42		549.36		602.25	
556.76		672.20		590.30		627.71	
607.95		712.08		602.18		679.34	
619.37		731.33		633.78		714.09	
647.92		775.67		691.27		775.35	
688.26		826.66		758.99		919.64	
718.80		935.80		772.24		1025.13	
775.08		1114.98		806.46		1116.08	
793.19		1193.43		942.16		1202.25	
up C2		up C4		up C6		up C8	

Table S44: Vibrational frequencies (cm^{-1}) of C4-perfluorinated aldehyde, and transition states TS152, and TS153 at M06-2X/6-31G(2df,p) level of theory

C4-perfluorinated aldehyde		TS152		TS153	
C1	C2	C3	C4	C5	C6
21.47	1367.45	29.14	1258.45	50.28	1167.32
51.01	1396.00	57.68	1281.36	72.22	1240.59
92.25	1431.89	69.72	1313.81	120.20	1284.03
124.32	2008.80	75.83	1329.43	158.08	1296.94
198.69		143.18	1331.54	182.10	1311.64
201.84		171.80	1342.50	234.14	1329.32
227.70		194.93	1391.40	257.52	1358.07
251.08		216.80	1434.59	288.95	1391.32
287.52		235.82	2341.72	292.25	1429.29
310.13		240.82		319.58	1981.03
335.33		277.55		331.39	2134.10
378.54		294.83		351.88	3825.59
383.12		318.73		369.01	
423.14		346.43		387.68	
512.61		363.36		414.59	
547.94		391.91		456.82	
606.13		408.34		497.40	
619.22		515.15		514.31	
707.37		549.75		554.13	
736.77		574.29		571.24	
784.40		619.20		599.01	
794.36		660.69		650.04	
946.08		679.61		669.76	
1173.25		698.36		682.23	
1213.70		768.58		772.71	
1255.47		848.58		840.11	
1295.44		964.66		957.15	
1310.12		1197.37		1046.47	
1334.19		1216.21		1116.46	
up C2		up C4		up C6	

Table S45: Vibrational frequencies (cm^{-1}) of Perfluorobutanoic acid (C_3F_7COOH), Perfluoro-3-Ethyl-α-lactone ($C_3F_6CO_2$), C3-perfluorinated aldehyde (C_3F_6O) and transition states TS41, TS141, TS142, and TS143 at M06-2X/6-31G(2df,p) level of theory

C_3F_7COOH		$C_3F_6CO_2$	TS41		TS141	TS142	C_3F_6O	TS143
C1	C2	C3	C4	C5	C6	C7	C8	C9
52.29	1313.77	33.16	15.37	1348.74	50.44	49.19	43.12	75.54
64.60	1337.15	77.26	86.15	1406.75	78.55	61.67	82.80	92.73
87.04	1355.18	123.49	105.20	1432.53	123.02	75.28	148.64	182.58
131.38	1418.55	164.86	148.31	1507.57	165.26	163.57	205.13	214.64
179.09	1436.56	217.70	181.49	1893.42	217.39	198.58	234.95	223.44
219.03	1969.14	245.80	209.59	2640.53	245.47	216.84	268.13	263.30
246.03	3838.57	273.57	218.21		269.57	248.70	337.61	314.19
268.96		326.79	250.52		299.96	269.52	362.18	327.00
296.04		330.02	271.92		329.92	293.54	424.59	354.25
321.75		363.35	296.22		355.76	348.19	425.57	379.85
345.98		393.45	331.58		395.21	382.73	550.11	426.84
380.56		462.77	347.79		427.94	384.71	598.52	472.62
392.87		521.86	385.54		494.99	448.46	677.71	523.62
458.84		574.37	415.30		549.88	549.28	730.90	555.00
519.28		601.32	439.86		559.45	598.41	785.37	576.44
539.22		670.20	555.93		610.94	620.43	810.97	614.27
558.03		697.19	566.16		671.40	674.33	1061.78	646.45
596.76		721.64	632.80		682.76	696.33	1213.55	667.22
607.56		783.63	640.68		783.65	764.04	1267.03	769.70
665.77		835.28	750.93		977.58	863.43	1324.03	860.86
724.74		1027.49	776.08		1056.83	1102.67	1334.60	998.97
777.26		1165.77	815.85		1171.71	1214.49	1381.06	1127.77
792.69		1209.67	996.10		1276.84	1268.50	1445.90	1132.52
1005.86		1275.37	1038.28		1290.53	1313.01	2006.62	1264.08
1131.82		1300.95	1170.66		1318.85	1322.23		1286.00
1199.14		1328.43	1272.07		1339.34	1335.26		1322.84
1259.30		1361.58	1284.36		1436.85	1344.13		1329.55
1274.09		1383.63	1299.25		1478.24	1420.99		1424.59
1299.82		1436.01	1332.08		2259.65	2335.05		1456.13
up C2		2120.64	up C5					1987.29
								2172.89
								3816.65

Table S46: Vibrational frequencies (cm^{-1}) of Pentafluoropropionic acid (C_2F_5COOH), Perfluoro-3-Methyl-α-lactone ($C_2F_4CO_2$), perfluoroacetyl fluoride (C_2F_4O) and transition states TS1E, TS1E1, TS1E2, and TS1E3 at M06-2X/6-31G(2df,p) level of theory

C_2F_5COOH	$C_2F_4CO_2$	TS1E	TS1E1	TS1E2	C_2F_4O	TS1E3
21.92	52.73	59.21	47.96	67.10	48.91	60.56
61.63	129.97	116.36	123.39	73.56	225.14	201.81
141.70	204.51	134.04	215.92	171.69	236.57	225.39
215.02	254.14	166.85	240.30	202.94	391.71	321.48
248.21	336.83	244.40	299.30	251.15	434.76	339.67
287.01	371.33	268.01	374.80	271.25	525.82	381.80
357.40	425.38	284.17	409.95	374.35	607.71	471.95
375.22	543.38	329.30	457.46	437.66	710.16	497.97
382.41	553.80	395.17	526.19	548.96	789.77	567.38
497.58	597.84	450.82	570.69	574.83	846.06	592.14
545.26	698.24	507.15	616.34	662.03	1177.78	606.50
556.06	722.41	572.65	677.38	692.42	1289.92	657.07
613.14	791.63	633.34	793.20	729.20	1345.84	757.22
641.93	841.50	718.41	999.09	910.10	1410.32	890.65
689.30	1113.12	774.22	1126.73	1254.04	2021.77	1036.77
781.27	1209.81	823.79	1306.13	1304.73		1144.20
793.16	1309.39	1045.27	1324.52	1326.11		1297.85
1048.83	1328.10	1086.64	1359.95	1341.09		1331.79
1176.50	1368.53	1230.33	1502.67	1374.02		1355.38
1203.00	1433.58	1281.73	2252.32	2338.67		1462.77
1240.99	2120.79	1288.93				1999.17
1258.59		1314.49				2181.73
1265.03		1390.75				3815.72
1350.11		1477.61				
1422.18		1845.53				
1893.57		2438.45				
3788.34						

Table S47: Vibrational frequencies (cm^{-1}) of Perfluorononanoic acid (PFNA), and transition state TSN1 and TSN2 at M06-2X/6-31G(2df,p) level of theory

PFNA			TSN1			TSN2		
C1	C2	C3	C4	C5	C6	C7	C8	C9
42.75	349.13	1169.60	23.11	348.13	1194.31	18.29	342.52	1123.83
44.81	368.15	1191.53	38.40	350.79	1211.97	38.53	361.29	1153.39
57.45	377.08	1205.53	53.20	373.17	1244.08	47.05	369.58	1195.12
65.42	383.98	1227.56	78.06	393.09	1250.69	60.65	385.47	1221.84
69.12	387.98	1248.44	81.11	395.28	1271.40	72.26	402.92	1255.69
81.79	416.10	1265.93	90.21	422.49	1284.44	86.09	446.34	1267.30
103.76	458.52	1268.16	107.16	445.34	1288.65	103.70	464.02	1283.61
106.23	486.24	1280.26	108.50	454.99	1290.08	109.23	491.11	1287.03
138.76	498.88	1286.83	115.27	485.87	1301.34	132.58	494.37	1300.08
143.39	515.25	1297.35	131.62	503.67	1312.08	142.39	502.28	1307.26
149.72	525.68	1303.81	142.88	520.44	1315.87	150.27	515.59	1322.43
152.74	551.12	1323.00	156.05	550.69	1327.77	151.56	550.64	1328.89
158.08	572.63	1334.54	167.93	563.74	1333.04	163.33	577.82	1331.45
174.35	602.26	1339.71	172.00	603.07	1337.52	170.25	582.10	1336.08
193.47	629.84	1348.69	185.00	625.90	1345.85	190.99	602.61	1351.64
202.70	635.91	1359.26	206.14	645.78	1353.62	206.20	632.07	1361.63
229.89	646.97	1364.23	211.13	665.99	1376.92	229.97	652.35	1371.15
244.01	658.18	1369.07	249.89	670.24	1411.84	235.40	659.77	1383.26
250.22	671.36	1374.29	259.07	679.03	1437.86	245.80	679.26	1420.52
269.55	680.25	1420.59	265.56	704.88	1500.81	256.96	681.55	1554.67
279.91	684.63	1444.93	271.92	736.47	1894.19	272.44	691.69	1579.43
282.44	722.12	1944.64	287.67	775.67	2648.68	284.57	773.20	3870.88
291.46	778.33	3816.11	296.59	800.87		291.05	778.49	
308.40	800.81		305.46	900.24		304.79	832.11	
313.53	917.73		314.11	962.12		312.69	902.94	
314.07	974.04		326.45	995.13		316.99	948.61	
321.99	1027.31		332.71	1012.75		319.67	1007.43	
327.98	1084.87		338.89	1075.79		322.66	1068.50	
336.15	1132.11		344.15	1135.58		330.72	1083.95	
up C2	up C3		up C5	up C6		up C8	up C9	

Table S48: Vibrational frequencies (cm^{-1}) of transition states TSN3, TSN4, and TSN5 at M06-2X/6-31G(2df,p) level of theory

TN3			TSN4			TSN5		
C1	C2	C3	C4	C5	C6	C7	C8	C9
17.60	335.50	1136.02	21.52	347.63	1156.01	34.21	345.50	1152.70
22.67	351.43	1162.68	32.87	351.45	1205.24	45.73	368.61	1186.89
43.11	368.95	1194.97	37.51	367.30	1216.68	53.15	381.75	1218.33
53.48	379.80	1208.47	46.98	374.98	1224.12	59.76	386.85	1225.61
63.67	385.14	1228.24	52.64	381.56	1248.28	69.41	424.08	1249.02
67.47	394.89	1245.39	60.27	399.94	1276.23	79.40	456.52	1260.46
100.17	439.74	1267.38	76.55	439.32	1277.76	104.35	471.07	1268.90
101.15	476.71	1271.68	106.68	454.18	1290.92	106.38	483.94	1277.97
124.69	493.21	1276.37	107.02	471.00	1296.25	137.62	496.02	1286.14
143.45	502.69	1284.82	144.73	503.64	1302.37	146.83	506.48	1298.41
146.91	519.74	1300.03	147.65	526.34	1323.67	149.97	520.31	1323.13
153.97	551.35	1322.89	162.10	552.43	1331.06	154.10	551.69	1334.01
155.47	601.98	1333.78	168.44	589.01	1333.57	154.54	602.71	1337.59
170.10	614.90	1346.10	178.64	600.88	1337.10	174.31	634.64	1344.08
178.18	623.89	1353.81	211.08	611.08	1343.43	191.44	638.99	1354.54
192.29	628.66	1361.25	223.30	622.17	1352.19	203.62	658.66	1362.84
207.67	646.17	1367.03	231.90	663.28	1379.90	219.14	666.16	1363.64
219.01	660.28	1369.39	238.73	672.84	1424.65	230.45	673.05	1369.08
232.03	669.25	1377.35	256.17	685.78	1444.26	248.16	680.60	1419.12
248.86	679.34	1421.03	260.69	692.08	1575.81	272.49	683.35	1431.08
271.25	684.47	2029.09	267.21	709.77	2003.85	279.21	685.29	1594.24
281.17	715.33	2341.39	285.11	735.98	2261.65	285.31	753.54	3607.41
283.39	778.55		293.81	776.38		290.43	778.06	
290.37	903.86		299.88	791.41		312.89	846.62	
309.49	938.11		315.53	897.58		315.33	922.93	
313.09	967.69		320.79	948.90		317.22	971.00	
316.59	996.39		327.88	1020.75		320.33	1021.27	
323.88	1053.90		338.47	1034.54		330.58	1059.04	
327.02	1107.42		343.13	1109.76		336.31	1103.68	
up C2	up C3		up C5	up C6		up C8	up C9	

Table S49: Vibrational frequencies (cm^{-1}) of trifluoroacetic acid (TFA), and transition states TS1M, TS2M, TS3M, TS4M, and TS5M at M06-2X/6-31G(2df,p) level of theory

TFA	TS1M	TS2M	TS3M	TS4M	TS5M
16.85	111.33	46.58	47.77	105.09	83.37
233.73	164.05	112.69	163.38	161.67	133.35
246.38	230.90	120.62	167.98	173.93	346.23
389.89	269.27	199.21	250.36	303.37	415.08
426.29	271.52	274.70	398.77	397.81	457.42
512.49	424.04	319.73	511.83	442.50	527.98
593.67	600.81	607.96	538.70	536.36	597.51
601.63	699.04	678.27	628.86	593.48	680.89
674.53	779.71	709.95	705.26	684.24	744.58
802.03	835.59	735.00	757.82	732.05	755.87
813.28	940.26	844.61	951.27	811.12	982.62
1167.64	1149.36	1096.61	1154.51	1100.16	1127.79
1207.84	1336.32	1308.47	1183.09	1323.74	1227.31
1223.15	1445.24	1384.70	1252.44	1424.64	1351.58
1290.58	1449.93	1396.14	1373.90	1446.04	1405.36
1438.76	1878.51	2143.96	2029.19	1840.75	1582.58
1900.89	2923.57	3090.71	2316.74	3872.31	3601.95
3805.75					

Table S50: Vibrational frequencies (cm^{-1}) of Difluoroacetolactone (CF_2CO_2), carbonyl fluoride (CF_2O), perfluoro-formic acid (FCOOH), and transition states TS1M1, TS1M2, TS1M3, and TS1M4 at M06-2X/6-31G(2df,p) level of theory

CF_2CO_2	TS1M1	TS1M2	CF_2O	TS1M3	FCOOH	TS1M4
202.49	182.74	115.43	595.63	325.12	520.89	433.60
358.81	309.18	222.78	635.05	433.98	569.55	679.76
469.29	478.34	239.86	816.37	465.61	630.75	763.62
516.51	507.72	436.69	1033.34	531.77	806.77	874.63
682.18	605.13	688.38	1354.05	533.58	993.40	1061.25
702.07	617.51	723.40	2050.20	675.58	1225.59	1355.36
747.10	835.78	730.62		759.22	1383.64	2108.68
849.10	1079.72	1318.45		958.05	2034.36	2339.56
1255.31	1227.50	1361.41		1126.89	3865.97	
1346.01	1520.53	1363.32		1225.92		
1414.09	2237.20	2177.52		1433.49		
2125.09				2012.74		
				2183.03		
				3831.18		

Cartesian Coordinates (Å) at M06-2X/6-31G(2df,p) level of theory

The optimized geometries of the key species observed in Fig. 1 (article) are given in Tables S51 – Table S56.

Table S51: Cartesian coordinates (Å) of PFOA

0	1			
F		-0.93781800	-1.27558400	-1.47963800
F		0.62036900	-1.87017000	-0.08699000
F		1.39695900	-0.17064800	-1.88570500
F		-0.18151300	1.24114000	-1.39099100
F		-1.77387200	-1.93658700	0.90991700
F		-0.50810100	-0.45762800	1.86784800
F		2.17713800	1.98550600	-0.63207900
F		0.87868700	1.59808800	1.06196100
F		-3.06146800	0.14640800	1.78492300
F		-1.80253800	1.53324900	0.68013300
F		2.15326000	-0.62951700	1.64285400
F		3.51656800	1.03645400	1.35196300
F		-3.69908900	-1.03592400	-0.69994300
F		-2.73529700	0.65432300	-1.62470600
F		-4.35934600	0.96497400	-0.25683500
O		4.23947100	0.11517200	-1.04826100
O		3.49417600	-1.86444400	-0.27444800
C		-0.22007400	-0.88853500	-0.41743500
C		0.63185300	0.31153100	-0.89139900
C		-1.20307400	-0.73779900	0.76443200
C		1.58739700	1.02710100	0.08741800
C		-2.33532200	0.31067000	0.67637500
C		2.69985400	0.17210200	0.73456600
C		-3.30611000	0.21191900	-0.51992100
C		3.51947300	-0.67536300	-0.25806700
H		4.73138700	-0.45234400	-1.65855500

Table S52: Cartesian coordinates (Å) of TSO1

0	1			
F		1.16065700	1.94632800	0.44865900
F		-0.48655400	1.11204400	1.60336000
F		-1.08869100	2.01519900	-0.82144100
F		0.28496800	0.62518000	-1.75195600
F		1.81790200	0.05620900	2.13863300
F		0.40771200	-1.34233400	1.26161300
F		-2.31107200	0.01217200	-1.88729900
F		-1.01401700	-1.44989400	-0.92150600
F		2.96545000	-1.78386900	0.74643700
F		1.73760700	-1.41210800	-1.00761200
F		-2.18491000	-0.94468200	1.40468900
F		-3.68929000	-1.86298900	-0.48453400
F		4.36608600	-0.50999100	-0.98714400
F		3.82722100	0.88361800	0.56421100
F		2.85260200	0.96803200	-1.35568000
O		-4.94035400	0.10255600	0.07110500
O		-3.25792600	1.51242700	0.80453100
C		0.35190000	0.89399700	0.58304100
C		-0.50857400	0.82773900	-0.69848200
C		1.22201800	-0.31201000	1.00355900
C		-1.61029900	-0.26742600	-0.79161000
C		2.31614300	-0.84680000	0.05164000
C		-2.61171800	-0.36933200	0.36052600
C		3.36975800	0.16447200	-0.44473600
C		-3.82516000	0.49129500	0.40381700
H		-4.44920100	-1.22770000	-0.36548800

Table S53: Cartesian coordinates (Å) of TSO2

0	1			
F		1.56237900	1.89216900	0.09364700
F		0.14127500	1.85348400	1.70682200
F		-0.82931700	2.79131100	-0.49516200
F		-0.08043300	1.13176500	-1.67794300
F		1.51794700	-0.16732400	2.09272800
F		-0.21449500	-0.93705800	1.03183900
F		-2.97285500	1.66622200	-0.59001200
F		-2.13114500	0.94407100	1.46343500
F		2.07530400	-2.12837100	0.53460900
F		1.19689700	-1.18575400	-1.21349400
F		-1.31985400	-1.18188200	-1.41500300
F		-3.43402100	-0.61115500	-1.56172700
F		3.70405300	0.31998400	0.63166700
F		3.06746200	0.52061700	-1.42109400
F		4.03165900	-1.27948200	-0.76848000
O		-3.02363500	-1.17211100	1.66263000
O		-2.77886100	-2.77289400	0.04976100
C		0.48802800	1.25306900	0.57932400
C		-0.61554500	1.47609300	-0.49852600
C		0.90385900	-0.19778400	0.91349300
C		-2.01423100	0.81869400	-0.45900300
C		1.83287000	-0.96174300	-0.06702800
C		-2.31268100	-0.51319400	-0.84066000
C		3.20072100	-0.31769700	-0.41079200
C		-2.79133900	-1.74220100	0.60407400
H		-2.56383000	0.01125700	1.66909700

Table S54: Cartesian coordinates (Å) of TSO3

0	1			
F		-0.85999300	-0.99837000	-1.65233600
F		0.80715700	-1.62193500	-0.40690700
F		1.32003600	0.39585500	-1.94335100
F		-0.35606600	1.55577900	-1.18374200
F		-1.53440700	-2.09125400	0.62361900
F		-0.40379800	-0.63767500	1.77131200
F		2.02848400	2.34124800	-0.41525700
F		0.78262000	1.67558900	1.23893100
F		-3.00548700	-0.31211400	1.81830700
F		-1.92561400	1.35106200	0.92534900
F		2.18201000	-0.50504700	1.52791700
F		3.55096000	1.16213700	1.26225100
F		-3.59138600	-1.16389900	-0.80822800
F		-2.83917000	0.74145800	-1.47577600
F		-4.44281700	0.66332200	-0.05193500
O		3.96557300	-0.54803100	-1.45669000
O		3.77462500	-2.13479300	0.24466900
C		-0.14920500	-0.69308500	-0.56099100
C		0.55913400	0.64566900	-0.85848100
C		-1.09714400	-0.82884500	0.65050300
C		1.50168700	1.26466400	0.19216200
C		-2.33350500	0.09565100	0.73876800
C		2.67087400	0.36096900	0.61939100
C		-3.32553400	0.07770900	-0.44376400
C		3.73089600	-1.21041800	-0.43031200
H		3.32244800	0.18328500	-0.81887100

Table S55: Cartesian coordinates (Å) of TSO4

0	1			
F		-0.89564600	-0.45398100	1.92544900
F		0.80038200	0.79522600	1.34501300
F		1.08008000	-1.84410100	1.07954400
F		-0.42887100	-1.90218200	-0.46721600
F		-1.55572200	1.90419000	1.03915100
F		-0.39921900	1.64833700	-0.78293000
F		2.24911200	-1.74153300	-1.22005300
F		0.82212200	-0.30640000	-2.01108300
F		-3.05549100	1.56471000	-1.02619200
F		-1.99770700	-0.22228900	-1.66697600
F		2.22061600	1.52262700	-1.07315000
F		4.57732800	0.31737900	-0.62386100
F		-3.65752400	0.24289700	1.35594300
F		-2.84668700	-1.55117800	0.48056900
F		-4.47807100	-0.53282100	-0.47918400
O		3.66131500	-0.85627500	1.05869500
O		3.68388500	1.42116200	1.18995300
C		-0.22363700	0.03917700	0.89203200
C		0.45948400	-1.13016000	0.15167000
C		-1.14693800	1.01806300	0.13308600
C		1.49550000	-0.68985500	-0.92535000
C		-2.39277700	0.48519400	-0.60892400
C		2.45149500	0.43951800	-0.49750400
C		-3.37285900	-0.36699500	0.21982700
C		3.64785200	0.40601300	0.49185500
H		3.81738100	-0.69275600	1.99544600

Table S56: Cartesian coordinates (Å) of TSO5

0	1			
F		-0.93251500	-1.62202000	1.09598600
F		0.58043100	-0.28023700	1.88684900
F		1.37413700	-1.89684000	-0.04379000
F		-0.17197100	-1.17723800	-1.38325300
F		-1.83271900	0.63129300	2.03315900
F		-0.58617600	1.81240000	0.71027000
F		2.15666900	-0.30453100	-2.04218000
F		0.85485400	1.28026500	-1.37610500
F		-3.12831700	1.73198900	0.07678300
F		-1.83358300	0.86273400	-1.43712800
F		2.06998500	1.66750700	0.79682600
F		3.50933500	1.61505500	-0.72750100
F		-3.70821100	-0.89275300	0.91145800
F		-2.70163500	-1.57354300	-0.86718600
F		-4.35631800	-0.21682200	-1.02715300
O		4.77141400	-1.40092700	0.23095600
O		3.23452500	-0.19297700	1.24739500
C		-0.22932900	-0.50686400	0.85283200
C		0.64365500	-0.82749800	-0.38527700
C		-1.24408100	0.66031100	0.83276300
C		1.59387200	0.24283200	-0.96864300
C		-2.36734400	0.67738900	-0.22992700
C		2.69826300	0.81143200	-0.04310800
C		-3.30492700	-0.54714200	-0.29783500
C		3.77080500	-0.57520500	0.16148700
H		4.94130800	-1.59562600	1.17612200

The optimized geometries of the key species observed in Fig. 6 (article) are given in Tables S57 – Table S62.

Table S57: Cartesian coordinates (Å) of Perfluoro-3-Hexyl-α-lactone

0	1			
F		-0.93753100	-0.49690000	1.91197000
F		0.69236200	0.92742700	1.68705300
F		1.35051800	-1.58081300	1.35651400
F		-0.08300100	-1.84764300	-0.25206100
F		-1.65344900	1.86119700	1.04874200
F		-0.27939100	1.77262400	-0.62963700
F		2.45939600	-1.64651900	-0.96972900
F		1.17246800	-0.08254100	-1.77042200
F		-2.82471800	1.45474800	-1.22598500
F		-1.57423300	-0.25787900	-1.70480700
F		2.32699100	1.73896500	-0.23346500
F		-3.64297400	0.06538000	1.07478100
F		-2.64901500	-1.66715800	0.26687700
F		-4.18602700	-0.68849000	-0.86802100
O		5.32748200	0.11584300	-0.50556900
O		3.50793100	0.14469600	0.99773600
C		-0.15156600	0.12328800	1.02763600
C		0.71133300	-0.96728500	0.35719700
C		-1.05428500	1.04505200	0.17860300
C		1.78064600	-0.53175300	-0.67258800
C		-2.15184600	0.42158900	-0.71363100
C		2.79332500	0.50500000	-0.20574800
C		-3.18472900	-0.49741800	-0.02872200
C		4.21947900	0.22554300	-0.13668500

Table S58: Cartesian coordinates (Å) of TS1O1

0	1			
F		-1.01664000	-0.63511800	1.87990800
F		0.62195900	0.79743000	1.82514000
F		1.27732000	-1.70703300	1.33895200
F		-0.08095100	-1.82199000	-0.34863000
F		-1.69510900	1.77655800	1.16298000
F		-0.25097000	1.81479000	-0.45635000
F		2.49241400	-1.58601700	-0.95836800
F		1.25450000	0.05253900	-1.65882000
F		-2.76866900	1.55232200	-1.17980300
F		-1.50133300	-0.12171400	-1.74125300
F		2.36584700	1.72323900	-0.03086600
F		-3.68741000	-0.00303900	0.96494200
F		-2.65780900	-1.67482500	0.07817000
F		-4.14089400	-0.61022700	-1.05086700
O		5.30870100	0.15047100	-0.76303500
O		3.45513100	0.10196500	1.13518500
C		-0.19032900	0.04349500	1.07726700
C		0.69556300	-1.00470800	0.36802800
C		-1.05698400	1.02782600	0.25949500
C		1.80467300	-0.49682200	-0.57591800
C		-2.11673400	0.47979000	-0.72275900
C		2.83364700	0.46425000	0.06588200
C		-3.17839000	-0.48455600	-0.15465500
C		4.20506300	0.29876900	-0.55124200

Table S59: Cartesian coordinates (Å) of TS1O2

0	1			
F		4.04179700	1.69848700	-0.07950400
O		4.98312900	-1.81474400	-0.31405600
O		3.91091600	-0.47842300	1.25979300
C		3.47231900	0.57819200	-0.39386200
C		4.40597100	-1.06205000	0.34006500
C		1.96989000	0.77900100	-0.06138700
F		1.74939600	1.14946900	1.19959900
F		1.59190200	1.77384800	-0.88388100
C		1.13458100	-0.46236900	-0.41848400
F		1.09903700	-0.55973300	-1.74700100
F		1.73872200	-1.55562000	0.07358200
C		-0.31888400	-0.52549300	0.11909000
F		-0.28580700	-0.65774900	1.44446000
F		-0.84626100	-1.62947000	-0.42525000
C		-1.22416200	0.66260700	-0.23944600
C		-2.67267300	0.59888400	0.30880100
F		-1.27119800	0.77615200	-1.56664500
F		-0.69958500	1.77534400	0.28528900
F		-3.30541200	1.64926100	-0.21862300
F		-2.63236400	0.72750500	1.63467400
C		-3.50285000	-0.65781400	-0.01753300
F		-3.13272900	-1.66095100	0.75834600
F		-4.77572900	-0.39162600	0.21210800
F		-3.35371400	-0.99718500	-1.28597400

Table S60: Cartesian coordinates (Å) of C7-perfluorinated aldehyde

0	1			
F		0.50484200	-0.53826700	-1.92233000
F		-1.10758100	0.90332100	-1.65433600
F		-1.77012400	-1.59269200	-1.27024100
F		-0.30643400	-1.84515100	0.31562800
F		1.29268500	1.80459500	-1.14085700
F		-0.05164700	1.81447400	0.56194700
F		-2.82380900	-1.54656900	1.10391300
F		-1.50645200	0.04531900	1.77825800
F		2.49480200	1.46989500	1.13883500
F		1.22779100	-0.20843400	1.69245300
F		-2.74225300	1.77772400	0.35613900
F		3.27216600	0.00566200	-1.11607400
F		2.23925800	-1.68591300	-0.27211400
F		3.80594300	-0.72482000	0.83830100
O		-4.11437100	0.25082000	-0.44717600
C		-0.24041000	0.09927800	-1.01762300
C		-1.09546000	-0.96841400	-0.30107300
C		0.69641300	1.03773300	-0.22469500
C		-2.13800900	-0.46985600	0.72313400
C		1.79888000	0.43102900	0.67141300
C		-3.13539200	0.54173000	0.13094900
C		2.80602800	-0.52464600	-0.00015300

Table S61: Cartesian coordinates (Å) of TS1O3

0	1			
F		0.11739600	-1.21969400	1.18732900
F		-0.89911900	-1.47510700	-0.71182500
F		-1.11863600	0.88777900	1.60646400
F		-0.33046800	1.71336700	-0.23900700
F		1.67219800	-1.60273100	-0.92514400
F		0.84928100	0.12911400	-1.92810500
F		-2.83556300	1.98907400	-0.16457200
F		-2.30445400	0.49896100	-1.63859900
F		2.38701800	1.61539500	-0.70790700
F		1.65346800	0.88168300	1.20388300
F		-3.59905000	-1.46051900	-0.75554300
F		4.07881800	-0.52042200	-0.84459100
F		3.33273300	-1.21374000	1.06320300
F		4.29401400	0.70413000	0.91044000
O		-4.50674400	0.21568300	0.78962900
C		-0.18212500	-0.62448500	0.03532600
C		-1.00225800	0.68022600	0.29691200
C		1.13522000	-0.39037800	-0.73843300
C		-2.41295400	0.73462000	-0.33697500
C		2.15635100	0.52400700	0.01249200
C		-3.48874100	-0.15368200	0.34276200
C		3.50797100	-0.15720300	0.28975600
O		-2.70034100	-1.30325700	1.18944400
H		-3.04697100	-1.86268800	0.28624400
H		-3.25587400	-1.46094800	1.96591100

Table S62: Cartesian coordinates (Å) of perfluoroheptanoic acid

0	1			
F		1.25437900	1.69378500	-1.31446700
F		-0.09456100	1.82857200	0.38178800
F		-1.09492300	0.68763800	-1.76270700
F		0.52549500	-0.76580900	-1.83499500
F		2.47979800	1.61135200	0.96193800
F		1.25721700	-0.02446800	1.70755500
F		-1.76688600	-1.73922100	-1.07143500
F		-0.29164800	-1.80770900	0.51888500
F		3.84563500	-0.55830200	0.86155200
F		2.27736400	-1.68863300	-0.07293600
F		-1.45299000	0.13509200	1.82488300
F		-2.87776000	-1.39041200	1.22255400
O		-3.82631400	0.16696900	-0.72932800
O		-2.96993600	1.85189600	0.49601100
C		0.67707200	1.00275800	-0.32701900
C		-0.23561600	-0.03032900	-1.02115000
C		1.79948900	0.51526200	0.61670400
C		-1.09096500	-1.00470700	-0.18462900
C		2.81692600	-0.48850000	0.03624000
C		-2.11225700	-0.37863300	0.79131400
C		-3.01441900	0.70762700	0.17437200
H		-4.36892400	0.87883300	-1.09722300
F		3.23860500	-0.08973300	-1.15052900

The optimized geometries of the key species observed in Figure S2 are given in Tables S63 – Table S65.

Table S63: Cartesian coordinates (Å) of iso-PFOA

0	1			
F		-2.13496600	2.03055100	0.10167500
F		-0.60363100	1.49627300	-1.33860300
F		0.25664300	1.98147400	1.10051700
F		-1.10314500	0.51007100	1.94914200
F		-2.98134100	0.43671500	-1.75969000
F		-1.43065800	-1.03816100	-1.37701400
F		1.37855700	-0.20513400	1.98450500
F		0.17912500	-1.46677700	0.68848400
F		-3.99702500	-1.53186600	-0.46504800
F		-2.43627500	-1.57493700	1.00846700
F		1.16477600	-0.36371200	-1.49807700
O		3.09736900	1.58171200	0.68847300
O		2.23790500	2.02524000	-1.34436200
C		-1.31590900	1.05370600	-0.30258100
C		-0.35656900	0.80788100	0.88266600
C		-2.20001200	-0.10356200	-0.82086700
C		0.75591000	-0.26822900	0.80373500
C		-3.12876400	-0.79229500	0.20122100
C		1.78859600	-0.10227000	-0.33073000
C		2.39055000	1.31159400	-0.40676200
H		3.45365600	2.47654800	0.59243700
F		-3.78223800	0.10461100	0.91751800
C		2.92451500	-1.14853000	-0.22500000
F		3.80456300	-0.89118000	-1.18532400
F		2.44091200	-2.36263200	-0.41436900
F		3.54628600	-1.11217700	0.93721600

Table S64: Cartesian coordinates (Å) of TSO1a

0	1			
F		-1.87037200	1.38218200	1.65640800
F		-0.55561200	1.91175800	-0.00086700
F		0.44353500	0.45113000	1.97631300
F		-0.96813800	-1.13972500	1.61725200
F		-3.38989900	1.51042700	-0.24885500
F		-2.00496200	0.72672200	-1.71027700
F		0.67586300	-2.08374100	0.09561300
F		0.11281300	-0.49026000	-1.26029800
F		-4.09058600	-0.87418200	-1.16082800
F		-2.20171100	-1.73259900	-0.59442500
F		2.58927700	-0.93808100	-1.81328900
O		3.86641800	-1.84730600	-0.04363400
O		2.86736000	-0.69073400	1.70981500
C		-1.28570600	0.93148300	0.54596100
C		-0.28860300	-0.15296700	1.04277300
C		-2.43531100	0.60090600	-0.45914200
C		0.64398100	-0.76422400	-0.06659700
C		-3.08477800	-0.78364000	-0.31383600
C		2.08948700	-0.26330700	-0.07289400
C		3.11267800	-1.08998700	0.56223500
H		3.28319700	-1.48977600	-1.29014700
C		2.44075400	1.19918000	-0.37251500
F		3.73652100	1.28715800	-0.60471000
F		1.77766200	1.60594900	-1.43612300
F		2.13455900	1.96769200	0.65227000
F		-3.53433200	-0.94782800	0.91679300

Table S65: Cartesian coordinates (Å) of TSO3a

0	1			
F		2.31759800	1.86624600	-0.67439400
F		1.94480000	1.18652500	1.34626600
F		0.13478700	2.80937700	0.56896500
F		-0.08673100	1.87921400	-1.38021200
F		0.95144100	-1.20326500	0.25386900
F		1.58082100	-0.44037300	-1.69994800
F		-1.97449600	1.65827300	1.02660400
F		-0.34300000	0.35832300	2.00165400
F		3.33922100	-2.08400200	-0.67795700
F		4.12160600	-0.07951300	-0.62179100
F		-1.00141300	-0.58260800	-1.37933600
O		-1.42808100	-1.67553400	1.96229700
O		-1.72455000	-2.75625900	-0.03454000
C		1.55556200	1.06754900	0.08149400
C		0.11355200	1.64589800	-0.07874100
C		1.79301100	-0.37659400	-0.38963400
C		-1.13836600	0.88798800	0.40813100
C		3.22030700	-0.89750800	-0.11107200
C		-1.67806900	-0.22555600	-0.26921400
C		-1.58903400	-1.92947300	0.77576400
H		-0.82482000	-0.58233800	2.11046800
F		3.42103700	-1.01795500	1.18722500
C		-3.17693700	-0.14661700	-0.53122100
F		-3.52111000	0.99793800	-1.11946700
F		-3.84320000	-0.22760300	0.61678200
F		-3.54739400	-1.13362400	-1.31998800

The optimized geometries of the key species observed in Figure S7 are given in Tables S66 – Table S72.

Table S66: Cartesian coordinates (Å) of perfluoroheptanoic acid

0	1			
F		1.25437900	1.69378500	-1.31446700
F		-0.09456100	1.82857200	0.38178800
F		-1.09492300	0.68763800	-1.76270700
F		0.52549500	-0.76580900	-1.83499500
F		2.47979800	1.61135200	0.96193800
F		1.25721700	-0.02446800	1.70755500
F		-1.76688600	-1.73922100	-1.07143500
F		-0.29164800	-1.80770900	0.51888500
F		3.84563500	-0.55830200	0.86155200
F		2.27736400	-1.68863300	-0.07293600
F		-1.45299000	0.13509200	1.82488300
F		-2.87776000	-1.39041200	1.22255400
O		-3.82631400	0.16696900	-0.72932800
O		-2.96993600	1.85189600	0.49601100
C		0.67707200	1.00275800	-0.32701900
C		-0.23561600	-0.03032900	-1.02115000
C		1.79948900	0.51526200	0.61670400
C		-1.09096500	-1.00470700	-0.18462900
C		2.81692600	-0.48850000	0.03624000
C		-2.11225700	-0.37863300	0.79131400
C		-3.01441900	0.70762700	0.17437200
H		-4.36892400	0.87883300	-1.09722300
F		3.23860500	-0.08973300	-1.15052900

Table S67: Cartesian coordinates (Å) of TS71

0	1			
F		-1.56667000	2.08788800	0.36091200
F		-0.07430600	1.56316000	-1.13441700
F		0.72644600	1.66492400	1.43958200
F		-0.68046000	0.10095600	1.96113900
F		-2.55963400	0.81214100	-1.65638700
F		-1.11968500	-0.80949000	-1.50019300
F		1.90190900	-0.60770600	1.72670100
F		0.48146200	-1.64417800	0.43634400
F		-3.76981400	-1.17111500	-0.62571800
F		-2.17901300	-1.66153900	0.72850500
F		1.53081400	-0.47961500	-1.67904300
F		3.11501800	-1.96432000	-0.28056300
O		4.41033200	0.05062600	-0.29806200
O		2.74491500	1.65193100	-0.43701000
C		-0.84764900	1.09026600	-0.14951200
C		0.08003300	0.60107600	0.98152400
C		-1.82581000	0.09036400	-0.80881900
C		1.12728000	-0.50057000	0.65109000
C		-2.80011300	-0.67046300	0.11668400
C		2.05027900	-0.26116400	-0.54480800
C		3.29354600	0.54579700	-0.41233100
H		3.89202400	-1.33885800	-0.25460500
F		-3.31711200	0.14740200	1.01560700

Table S68: Cartesian coordinates (Å) of Perfluoro-3-Pentyl-α-lactone

0	1			
F		1.32939000	-0.10001000	-2.10589900
F		-0.12722700	1.33492300	-1.36302000
F		-1.00123700	-1.13634100	-1.75657000
F		0.46212600	-1.93859300	-0.36307500
F		2.40077900	1.72479500	-0.62935200
F		1.01460800	1.39630200	1.01299300
F		-2.06052500	-1.76868500	0.50142600
F		-0.62481200	-0.60185500	1.65170700
F		3.63225000	0.42364900	1.18986400
F		2.02568800	-0.96250700	1.51760400
F		-1.63621400	1.65935800	0.77028800
O		-4.76977600	0.28635100	0.64989200
O		-2.96621700	0.61052200	-0.83811400
C		0.64681600	0.29367800	-1.03032300
C		-0.28822200	-0.87380800	-0.65943800
C		1.66759500	0.81031900	0.00864900
C		-1.29185800	-0.67331200	0.49981000
C		2.64013500	-0.22633700	0.60996800
C		-2.21337500	0.53419700	0.39296000
C		-3.65920400	0.40846400	0.29285500
F		3.12702100	-1.01039100	-0.33498000

Table S69: Cartesian coordinates (Å) of TS171

0	1			
F		1.44247600	1.59992800	1.34113700
F		-0.02732700	0.11886400	1.95876400
F		-0.90834800	2.13694100	0.44299800
F		0.45913400	1.58830700	-1.15320100
F		2.46497600	-0.74587800	1.61704500
F		0.98094500	-1.69452800	0.34336500
F		-2.10703300	0.91228800	-1.50789100
F		-0.72993000	-0.76478300	-1.46007200
F		3.56278600	-1.24242800	-0.63125000
F		1.91573100	-0.50028800	-1.79021100
F		-1.68315100	-1.63622000	0.75722600
O		-4.76302000	-0.75078500	-0.42814900
O		-2.89466500	0.24500500	1.17175600
C		0.70482600	0.56567600	0.93311200
C		-0.26535500	1.12130300	-0.12882800
C		1.67593400	-0.57640300	0.55333600
C		-1.32448000	0.16443200	-0.71203400
C		2.59250800	-0.34678900	-0.66671800
C		-2.25898500	-0.49574100	0.33036200
C		-3.64786600	-0.71285700	-0.22844900
F		3.11885100	0.86430000	-0.63274800

Table S70: Cartesian coordinates (Å) of TS172

0	1			
F		3.25898400	1.95256300	-0.10326300
O		4.61261200	-1.41123000	-0.51395200
O		3.48437200	-0.26140100	1.16455400
C		2.81881800	0.77746900	-0.42424300
C		3.98968300	-0.75358400	0.19818600
C		1.32623200	0.77078300	-0.00119000
F		1.13378300	1.07191300	1.28237100
F		0.76648300	1.73246500	-0.75841600
C		0.63670400	-0.55640900	-0.35632100
F		0.61356700	-0.66496000	-1.68430900
F		1.35414700	-1.57434500	0.14245000
C		-0.79977300	-0.74510400	0.19007100
F		-0.73250900	-0.86308200	1.51586700
F		-1.25496900	-1.89097300	-0.32909100
C		-1.79423400	0.38053500	-0.15291600
C		-3.26702200	-0.01050800	0.09067900
F		-1.67223400	0.71783200	-1.43818600
F		-1.51724100	1.43511300	0.61684000
F		-3.66991600	-0.87779100	-0.81806800
F		-4.00989600	1.07808100	0.00495500
F		-3.40779100	-0.53882100	1.29435900

Table S71: Cartesian coordinates (Å) of C6-perfluorinated aldehyde

0	1			
F		-0.81962600	-0.16535600	2.14013300
F		0.51607400	1.35227900	1.32828300
F		1.53626500	-1.07204400	1.62547800
F		0.04561400	-1.93055900	0.29253300
F		-2.08878100	1.60574800	0.78556300
F		-0.77695000	1.43344800	-0.93841700
F		2.48465300	-1.55914800	-0.74151600
F		0.93182100	-0.39718300	-1.72448900
F		-3.33339700	0.29588600	-1.02485300
F		-1.66650000	-0.97990400	-1.47664600
F		1.94609200	1.79968200	-0.93292500
O		3.55444000	0.76094500	0.16099000
C		-0.22950200	0.27579300	1.03065600
C		0.74348100	-0.83052400	0.57917700
C		-1.33701400	0.76604800	0.07042300
C		1.66597100	-0.51601600	-0.61782300
C		-2.27520800	-0.30799900	-0.51716000
C		2.52475700	0.74298800	-0.40163700
F		-2.66308800	-1.14610400	0.42799800

Table S72: Cartesian coordinates (Å) of TS173

0	1			
F		0.54349900	1.20048300	-1.41084200
F		-0.35053700	1.56893700	0.53024400
F		-0.59303000	-0.98966200	-1.56384600
F		0.37662100	-1.61543900	0.27248700
F		2.23676800	1.83939600	0.51055500
F		1.55421400	0.20331900	1.75888900
F		-2.10567900	-2.03151600	0.42152600
F		-1.56079600	-0.39182000	1.72159700
F		3.03880900	-1.38133700	0.55489400
F		2.27269800	-0.77404600	-1.36228600
F		-3.03563900	1.40734900	0.78551000
O		-3.94516000	-0.44205200	-0.54717100
C		0.36344100	0.69477400	-0.19337100
C		-0.39473500	-0.66819900	-0.28738300
C		1.74066200	0.60192400	0.50259400
C		-1.74906100	-0.74560700	0.45633400
C		2.76797600	-0.34203800	-0.20670100
C		-2.92294000	0.02042900	-0.20981100
O		-2.26994200	1.13595600	-1.20309600
H		-2.58565200	1.75022900	-0.32483300
H		-2.88741800	1.19478700	-1.94582600
F		3.88549800	0.31278700	-0.45175000

The optimized geometries of the key species observed in Figure S8 are given in Tables S73 – Table S79.

Table S73: Cartesian coordinates (Å) of Perfluorohexanoic acid

0	1			
F		-2.04136000	1.60275200	0.87677000
F		-0.73708300	1.46849800	-0.85853100
F		0.53000100	1.25164900	1.42168000
F		-0.82080100	-0.30386000	2.12521200
F		-3.33823900	0.42909100	-0.98049900
F		-1.72394700	-0.88082500	-1.51363200
F		1.53147200	-1.19778100	1.53581200
F		0.01936400	-1.94981200	0.16823600
F		0.87818400	-0.40361800	-1.77230000
F		2.51195300	-1.48341200	-0.82991500
O		3.31037800	0.71859700	0.45544500
O		2.16622600	1.81476200	-1.14592500
C		-1.31842600	0.77388300	0.11815800
C		-0.22414500	0.20472600	1.04758000
C		-2.29700100	-0.23712800	-0.51522500
C		0.73525500	-0.87599500	0.51446900
C		1.63200500	-0.48468800	-0.68031800
C		2.39294600	0.84290300	-0.49861800
H		3.75556200	1.57316500	0.54557700
F		-2.70867700	-1.10848700	0.38961000

Table S74: Cartesian coordinates (Å) of TS61

0	1			
F		-2.39400700	1.53988900	-0.49271900
F		-0.89927000	0.43696100	-1.63515900
F		0.03783400	2.14446600	0.21277800
F		-1.04368900	1.10822200	1.77873100
F		-3.28720800	-0.81775800	-1.02918000
F		-1.48544600	-1.80036400	-0.39356600
F		1.58137700	0.63647400	1.65780600
F		0.26302100	-1.09000600	1.44119600
F		1.01897400	-1.35324200	-1.07799400
F		2.87612600	-1.54852600	0.70664900
O		3.85346400	0.15389600	-0.66649200
O		1.96113500	1.18675400	-1.50994600
C		-1.50272900	0.55168200	-0.44793500
C		-0.44420800	0.96859400	0.59440900
C		-2.27487000	-0.75773600	-0.18592500
C		0.74453200	-0.00012400	0.84427400
C		1.55766900	-0.45222800	-0.36915900
C		2.67066500	0.37678300	-0.90500700
H		3.55163600	-0.96775600	0.25680200
F		-2.73157900	-0.79825800	1.05043100

Table S75: Cartesian coordinates (Å) of Perfluoro-3-Butyl-α-lactone

0	1			
F		2.17138200	0.99929100	1.32436400
F		0.74387500	-0.62438000	1.59192000
F		-0.34185300	1.72887600	1.13163600
F		0.80085300	1.98853800	-0.70026900
F		3.20187600	-1.12939100	0.35208600
F		1.42253100	-1.70164100	-0.70491600
F		-1.74895300	1.40777400	-1.04594500
F		-0.37807000	-0.10278500	-1.81807900
F		-1.09690700	-1.80666300	0.08042000
O		-4.29855500	-0.59951200	-0.01447800
O		-2.33695200	-0.20053200	1.23605600
C		1.31790100	0.18831400	0.69874200
C		0.22190700	1.09364100	0.10124200
C		2.13754400	-0.67476600	-0.28273800
C		-0.90721500	0.42407200	-0.71078600
C		-1.71808700	-0.64453300	0.00764800
C		-3.15210900	-0.52584400	0.22189200
F		2.52353400	0.04427700	-1.32106500

Table S76: Cartesian coordinates (Å) of TS161

0	1			
F		-2.26799600	1.07823100	-1.15248600
F		-0.82930300	-0.48605100	-1.63605300
F		0.21348400	1.88110500	-1.02298100
F		-0.79756800	1.89799700	0.89959700
F		-3.19608900	-1.15400400	-0.32195900
F		-1.35549800	-1.76446200	0.59889200
F		1.79668500	1.35439200	1.00835100
F		0.51141900	-0.25329200	1.70418500
F		1.15109700	-1.76578500	-0.28303500
O		4.33291300	-0.57597800	0.08176600
O		2.19972300	-0.10025000	-1.42336800
C		-1.36316100	0.23716500	-0.64856900
C		-0.25252800	1.11636700	-0.03721400
C		-2.11145000	-0.72493200	0.29788900
C		0.93995200	0.39661400	0.61938500
C		1.73377400	-0.55160900	-0.30974800
C		3.19977300	-0.59566500	0.05973100
F		-2.46392500	-0.10566600	1.41037700

Table S77: Cartesian coordinates (Å) of TS162

0	1			
F		2.57812900	1.97732700	-0.14272500
O		3.98282200	-1.36444300	-0.56910700
O		2.86513100	-0.22892300	1.12616400
C		2.15260300	0.79355000	-0.45185400
C		3.36154400	-0.71580000	0.15251800
C		0.66996000	0.76077000	0.00100500
F		0.49555600	1.06810400	1.28591700
F		0.07559100	1.70468000	-0.75339300
C		-0.00431500	-0.57899100	-0.33193500
F		-0.06955800	-0.68225000	-1.65970700
F		0.74561400	-1.58613100	0.13966500
C		-1.41960900	-0.78834500	0.25045000
F		-1.32718100	-0.92181700	1.57324700
F		-1.88543800	-1.92254500	-0.27709900
C		-2.44409900	0.32155500	-0.04579300
F		-3.64357200	-0.10578100	0.30277200
F		-2.44446700	0.61735300	-1.33369300
F		-2.15579900	1.40555900	0.65359500

Table S78: Cartesian coordinates (Å) of C5-perfluorinated aldehyde

0	1			
F		1.66825400	1.28739100	1.21231500
F		0.47647200	-0.49283100	1.62436200
F		-0.92127500	1.66553000	1.06352500
F		0.09253900	1.92649800	-0.84438200
F		2.97060300	-0.70486100	0.31569300
F		1.25314900	-1.64710600	-0.56286000
F		-2.35232000	0.91863000	-1.01472100
F		-0.80128100	-0.45634800	-1.68029500
F		-1.28769000	-2.06454800	0.24836100
O		-2.85553500	-0.74386100	1.05922600
C		0.91758200	0.33320800	0.66522500
C		-0.31287400	1.03383000	0.05639900
C		1.81668100	-0.48538000	-0.28668800
C		-1.36068500	0.12561300	-0.61595600
C		-1.94709600	-0.92853500	0.33957800
F		2.03073000	0.17636200	-1.40923600

Table S79: Cartesian coordinates (Å) of TS163

0	1			
F		1.21196200	-1.06325500	1.51488600
F		0.42894500	-1.39784800	-0.48541100
F		-0.41369000	0.75750500	1.80641600
F		0.67649600	1.85093900	0.29357200
F		3.02890400	-1.20285700	-0.47832400
F		2.13255400	0.49717200	-1.44617400
F		-1.76192500	1.95523800	-0.27153400
F		-0.81896000	0.57231000	-1.64127500
F		-2.17661300	-1.48100900	-1.16502100
O		-3.48059400	0.05662100	0.23606100
C		0.97231600	-0.49151900	0.33817600
C		0.00463100	0.71956900	0.54127200
C		2.32595200	-0.10042300	-0.28412900
C		-1.23050200	0.73717000	-0.38895200
C		-2.37205500	-0.24200100	0.00068700
O		-1.72889400	-1.41114500	0.93516800
H		-1.84415400	-1.92636300	-0.04888800
H		-2.43380000	-1.63297500	1.56006400
F		2.99808400	0.69611000	0.52582900

The optimized geometries of the key species observed in Figure S9 are given in Tables S80 – Table S86.

Table S80: Cartesian coordinates (Å) of Perfluoropentanoic acid

0	1			
F		-1.65845100	-0.56235300	-1.62562500
F		-2.32724400	-1.57447100	0.17880500
O		-2.08857100	1.75730800	-0.60548800
O		-2.75699500	0.81739100	1.33025600
C		-1.62812600	-0.54183300	-0.29189800
C		-2.24279600	0.75791600	0.25871800
H		-2.44548800	2.55585000	-0.19100500
C		-0.16984300	-0.75348200	0.17534800
F		-0.18463700	-0.94052800	1.49552300
F		0.29692800	-1.85193800	-0.42411400
C		0.76644900	0.42770500	-0.13403800
F		0.60632000	0.81928500	-1.39827200
F		0.43679400	1.43421500	0.68641000
C		2.26016500	0.11378700	0.07669200
F		2.45410000	-0.42095200	1.26940700
F		2.94361000	1.24139400	-0.00947700
F		2.68757100	-0.71998600	-0.85222100

Table S81: Cartesian coordinates (Å) of TS51

0	1			
F		-1.68656600	0.09590400	1.90602700
F		-2.31958000	1.56996800	-0.11466100
O		-2.68996600	-1.56392700	0.49830100
O		-2.11286700	-0.74105200	-1.58945100
C		-1.62588200	0.50673100	-0.06123700
C		-2.25446600	-0.80731100	-0.36379000
H		-2.16999700	-0.72596200	1.60773100
C		-0.12689200	0.80563100	-0.21143400
F		0.04154400	1.46674400	-1.35334700
F		0.21783600	1.60096200	0.80178100
C		0.75717600	-0.45975800	-0.21369600
F		0.27044800	-1.33599900	0.67041600
F		0.73691600	-0.99512700	-1.42848600
C		2.22233000	-0.15269600	0.15770200
F		2.64167300	0.89144200	-0.53969800
F		2.96610900	-1.20107600	-0.13463700
F		2.32707200	0.10831700	1.44551600

Table S82: Cartesian coordinates (Å) of Perfluoro-3-Propyl-α-lactone

0	1			
F		-2.51256000	-1.47549900	-0.45847300
O		-2.72509900	1.93805000	-0.41612500
O		-2.29594600	0.20779800	1.13263000
C		-1.79360400	-0.44152300	-0.05588400
C		-2.35406500	0.90037600	-0.01403200
C		-0.31092100	-0.80565500	0.00505200
F		-0.06882800	-1.43326800	1.15941700
F		-0.03961300	-1.62927200	-1.00788700
C		0.59695900	0.42866300	-0.11097800
F		0.38857000	0.97202600	-1.31269700
F		0.25417600	1.30961900	0.83526200
C		2.10174800	0.14005200	0.03795000
F		2.36284200	-0.29740200	1.25548200
F		2.76548300	1.26203100	-0.17116400
F		2.48633700	-0.76359700	-0.84490600

Table S83: Cartesian coordinates (Å) of TS151

0	1			
F		-1.73663300	-1.16747200	-1.20487800
O		-3.07220200	1.82497800	-0.22204100
O		-2.78256200	-0.64172500	0.74862900
C		-1.79437000	-0.45809100	-0.05528800
C		-2.41629300	0.90164900	-0.23234800
C		-0.36671100	-0.40082200	0.54131100
F		-0.34999000	0.61042500	1.42491500
F		-0.13638800	-1.54641500	1.17130100
C		0.72962200	-0.15327900	-0.50678600
F		0.95846900	-1.27508600	-1.18189200
F		0.28827800	0.79688500	-1.34849200
C		2.06577400	0.32716900	0.09113800
F		1.95983100	1.56996200	0.52339300
F		2.99896500	0.27545200	-0.84136400
F		2.40968800	-0.45994900	1.09691900

Table S84: Cartesian coordinates (Å) of TS152

0	1			
F		2.31372800	1.75265900	-0.14349700
O		3.18108900	-1.77507700	-0.48371500
O		2.20746700	-0.45129600	1.16309200
C		1.71356800	0.64681400	-0.45122300
C		2.64900700	-1.02490400	0.21061200
C		0.23254100	0.85731800	-0.04562500
F		0.07286100	1.21389000	1.22995100
F		-0.18330700	1.86808400	-0.82713700
C		-0.63650900	-0.36849000	-0.36855400
F		-0.70246500	-0.48650200	-1.69482400
F		-0.07725000	-1.47534600	0.13824200
C		-2.07180800	-0.28004700	0.18165000
F		-2.06593200	-0.39337200	1.49665400
F		-2.78808500	-1.26386200	-0.33202400
F		-2.61724400	0.87632100	-0.15582800

Table S85: Cartesian coordinates (Å) of C4-perfluorinated aldehyde

0	1			
F		-3.11200600	-0.60400600	-0.00045700
O		-2.31607000	1.45102200	-0.00002300
C		-2.14262500	0.28943600	-0.00014200
C		-0.79337100	-0.44642000	0.00019500
F		-0.73284900	-1.22019200	1.08764900
F		-0.73263500	-1.22092800	-1.08672500
C		0.38846800	0.53274300	0.00001400
F		0.30658600	1.29107900	-1.09373900
F		0.30672200	1.29116700	1.09374400
C		1.77334800	-0.14219200	-0.00008200
F		1.92094100	-0.89230100	1.07720100
F		2.69715000	0.80139300	0.00016600
F		1.92093900	-0.89172100	-1.07780900

Table S86: Cartesian coordinates (Å) of TS153

0	1			
F		1.89504800	-1.23352800	0.97214800
F		0.91808500	-1.31502100	-0.94206900
F		0.53574100	0.71078900	1.65247400
F		1.33065000	1.81025500	-0.03695600
F		-1.19435100	1.98526100	0.00518300
F		-0.58562500	0.71869800	-1.63848200
F		-1.79854000	-1.38755200	-1.04078900
O		-2.79908200	0.03282600	0.69414500
C		1.56691300	-0.52767900	-0.09276400
C		0.68711200	0.70088300	0.32630400
C		-0.71541500	0.78190500	-0.31859200
C		-1.76024900	-0.23049000	0.22147400
O		-0.93392400	-1.45111900	0.92483000
H		-1.24873300	-1.90087300	-0.04707000
H		-1.48937100	-1.72818200	1.66702900
F		2.66921200	-0.10804800	-0.68154300

The optimized geometries of the key species observed in Figure S10 are given in Tables S87 – Table S93.

Table S87: Cartesian coordinates (Å) of Perfluorobutanoic acid

0	1			
F		-0.89681500	0.52482200	1.64879600
F		-1.59449500	1.67304100	-0.06808600
O		-1.62653200	-1.72301800	0.55549700
O		-2.12581600	-0.66658600	-1.34425400
C		-0.93354400	0.58228900	0.29996900
C		-1.64392100	-0.67108800	-0.26029300
H		-1.22856600	-1.48865100	1.40387400
C		0.51671900	0.73073900	-0.20188800
F		0.49228100	1.02393800	-1.49932800
F		1.09218200	1.72564900	0.47423700
C		1.36998300	-0.53512000	-0.01894200
F		1.26686500	-0.98195900	1.22899700
F		0.94095000	-1.47956900	-0.84001600
F		2.63146800	-0.26763600	-0.27870100

Table S88: Cartesian coordinates (Å) of TS41

0	1			
F		-1.27060900	0.31698600	1.79543700
F		-1.52668300	1.67320100	-0.37911900
O		-2.18385300	-1.39845300	0.39425300
O		-1.38464700	-0.72807100	-1.67470000
C		-0.93871500	0.56591100	-0.17364100
C		-1.63304600	-0.71666400	-0.46487000
H		-1.75542100	-0.50399600	1.49940100
C		0.58641800	0.72832000	-0.14740400
F		0.96458500	1.24433100	-1.31458500
F		0.87877400	1.58559600	0.82594400
C		1.35585800	-0.58491900	0.09460200
F		1.29700900	-1.35135300	-0.97416900
F		2.61344000	-0.28879700	0.35571500
F		0.83018700	-1.22881900	1.12322700

Table S89: Cartesian coordinates (Å) of Perfluoro-3-Ethyl-α-lactone

0	1			
F		1.64709600	1.73221700	0.06373600
O		2.47161200	-1.49752800	-0.63950200
O		1.45039100	-0.32872300	1.14001100
C		1.06111100	0.54661700	0.05539000
C		1.83921100	-0.67035500	-0.09942200
C		-0.43240300	0.70632500	-0.17282600
F		-0.89961200	1.65064200	0.64591800
F		-0.62162500	1.09375800	-1.43686700
C		-1.24290900	-0.57808500	0.06631300
F		-1.27652600	-0.86783100	1.35161800
F		-2.47218700	-0.40476700	-0.37521600
F		-0.68004400	-1.58368600	-0.59372100

Table S90: Cartesian coordinates (Å) of TS141

0	1			
F		1.72824800	1.62811900	0.03007200
O		2.39902200	-1.64344900	-0.53851700
O		1.31168200	-0.15752900	1.38478200
C		1.07992100	0.46719700	0.27775200
C		1.79543100	-0.70903900	-0.32227900
C		-0.36865000	0.68222500	-0.21541100
F		-0.86175100	1.76531700	0.37767400
F		-0.35217900	0.86101500	-1.54159100
C		-1.28303700	-0.51017700	0.09181100
F		-1.49920900	-0.62137500	1.38237300
F		-2.43493000	-0.36323500	-0.53496700
F		-0.69435900	-1.62244200	-0.35371300

Table S91: Cartesian coordinates (Å) of TS142

0	1			
F		1.19143900	2.05542000	0.03270400
O		2.87449400	-1.07757300	-0.68159000
O		1.53924900	-0.32685200	1.06802700
C		0.86959600	0.89280400	-0.42876200
C		2.14176000	-0.60224000	0.07146400
C		-0.62673000	0.70420000	-0.09628300
F		-1.00741400	1.35335200	1.00233500
F		-1.23588800	1.26235700	-1.15862200
C		-1.10012500	-0.76134600	0.00584000
F		-0.35888100	-1.53371900	-0.78209700
F		-1.00988400	-1.20114100	1.24476200
F		-2.35903300	-0.84350400	-0.38408900

Table S92: Cartesian coordinates (Å) of C3-perfluorinated aldehyde

0	1			
F		-2.52535100	-0.20039100	0.00018700
O		-1.32549100	1.64852300	-0.00003500
C		-1.39419800	0.47537600	0.00012700
C		-0.21901300	-0.50836900	-0.00010400
F		-0.29866200	-1.27887500	1.08709200
F		-0.29894800	-1.27839800	-1.08753700
C		1.14215500	0.19813500	0.00002800
F		1.25884900	0.94847600	1.07966600
F		2.09730900	-0.71505300	-0.00003600
F		1.25905500	0.94879300	-1.07937600

Table S93: Cartesian coordinates (Å) of TS143

0	1			
F		1.36459100	0.72002900	-1.29721500
F		2.33217800	-0.28039800	0.34106200
F		0.29893000	-1.62858400	-0.89143400
F		0.11741200	-1.28253900	1.24410000
F		-1.51861900	0.73854500	1.25857500
O		-2.29655000	-0.82542300	-0.48515800
C		1.21860400	0.31638100	-0.04677900
C		0.06840500	-0.70579900	0.04726900
C		-1.36237200	-0.18839400	-0.17640600
O		-1.25800200	1.30559400	-0.80353000
H		-1.44937900	1.51912000	0.26635400
H		-2.06276200	1.39923900	-1.33380100
F		1.00559000	1.36707400	0.72629400

The optimized geometries of the key species observed in Figure S13 are given in Tables S94 – Table S103.

Table S94: Cartesian coordinates (Å) of Pentafluoropropionic acid

0	1			
F		-0.05762300	1.75942900	-0.16288200
F		-0.07856400	0.54954700	1.64997200
F		0.94567400	-0.44033400	-1.51412500
F		1.12770000	-1.45363400	0.37886500
F		2.17531500	0.39537800	0.04825100
O		-1.68054000	-1.25681100	0.47529100
O		-2.20753100	0.42631800	-0.92511400
C		-0.14560200	0.52256700	0.31419400
C		1.06440700	-0.27089500	-0.20469900
C		-1.48307300	-0.09096000	-0.13621500
H		-2.52234000	-1.61380000	0.15816900

Table S95: Cartesian coordinates (Å) of TS1E

0	1			
O		-1.19471300	-1.73240400	0.02214100
O		-2.33647500	0.19111500	-0.58350100
H		-1.54186300	1.42335100	-0.36303200
C		-0.22051500	-0.02627400	0.51461100
F		-0.09650300	0.07300500	1.77270100
F		-0.69989900	1.85241700	-0.03854600
C		-1.46754800	-0.53462900	-0.10970800
C		1.11643600	-0.07959300	-0.23220900
F		1.85138900	0.95161200	0.12925600
F		0.88831100	-0.04569700	-1.52516000
F		1.74793800	-1.19245500	0.08594300

Table S96: Cartesian coordinates (Å) of TS2E

0	1		
O	2.24566000	-0.70632000	-0.87746300
O	2.07846900	0.12096000	1.29848700
H	1.03345400	0.57123600	0.99869800
C	-0.01928000	0.66674000	-0.14423700
F	-0.50056100	1.82517500	0.37607800
F	0.10146900	0.83050800	-1.47042100
C	1.92824400	-0.21347700	0.10848500
C	-1.07016700	-0.40627300	0.10112000
F	-1.27924100	-0.52065300	1.40946100
F	-2.22021200	-0.13668500	-0.49135600
F	-0.61915100	-1.57282300	-0.35255000

Table S97: Cartesian coordinates (Å) of TS3E

0	1		
F	-0.21252600	1.77837800	0.25919300
F	0.91783100	0.00675700	-1.14502700
F	-2.15965600	-0.01482100	1.06547500
F	-1.10707000	-1.49281300	-0.10133700
F	-1.86389100	0.28463400	-1.05011300
O	1.76798100	-1.37453600	0.35194500
O	2.58458500	0.74788200	0.22870700
C	-0.02277600	0.52551200	0.43650400
C	-1.32068200	-0.20519000	0.05041300
C	1.75662400	-0.07719400	0.04136300
H	2.52827400	-1.50476000	0.93140200

Table S98: Cartesian coordinates (Å) of TS4E

0	1			
O		2.55242300	-0.08929600	-0.14819000
O		1.23817500	1.75880500	0.10738800
H		-0.10017500	1.90799900	-0.01063500
C		0.20380100	-0.69451600	0.03634200
F		0.47636100	-1.31160000	1.19255500
F		0.49125900	-1.47457200	-1.00718800
C		-1.16401900	-0.27328700	-0.00443000
F		-1.82149400	-0.27985900	-1.08506900
F		-1.08879700	1.76621400	-0.12132100
F		-1.84823500	-0.15392200	1.05319900
C		1.60914000	0.60440000	-0.02399900

Table S99: Cartesian coordinates (Å) of Perfluoro-3-Methyl-α-lactone

0	1			
O		-1.14747700	0.21566300	1.12407900
O		-2.58521700	-0.67971000	-0.51980100
C		-0.33558000	0.48766000	-0.03971000
F		-0.17585600	1.76550800	-0.32821700
C		-1.63106600	-0.16925900	-0.06614000
C		0.99034800	-0.25035400	-0.03910300
F		1.58564500	-0.10428000	-1.20961600
F		0.78383600	-1.53474100	0.19226800
F		1.77519100	0.24063500	0.90506400

Table S100: Cartesian coordinates (Å) of TS1E1

0	1			
F		0.74320900	-1.50368500	-0.39258600
F		1.36225000	-0.29121700	1.27314700
F		-0.21144000	1.67701200	0.58147900
O		-2.57477400	-0.79165300	0.32890200
O		-0.94629600	0.57556200	-1.26880600
C		0.95588700	-0.25953200	0.01429400
C		-0.35455800	0.53965200	-0.12649000
C		-1.57466500	-0.26096200	0.27455900
F		1.88471200	0.29719800	-0.73481300

Table S101: Cartesian coordinates (Å) of TS1E2

0	1			
F		-0.10751600	1.80826900	-0.09241700
O		2.81261400	-0.35382900	-0.65576500
O		1.28092200	-0.07650100	1.07186200
C		0.15947700	0.60450300	-0.47887400
C		1.94843200	-0.16154700	0.08349400
C		-1.04497400	-0.26453300	-0.06880500
F		-1.97563600	-0.04268300	-0.99430500
F		-1.54709900	0.04092200	1.11417600
F		-0.71707100	-1.54294100	-0.08786100

Table S102: Cartesian coordinates (Å) of perfluoroacetyl fluoride

0	1			
O		1.55594800	1.15069100	0.00005000
C		0.94222200	0.15069900	-0.00002600
F		1.47685800	-1.05407600	-0.00009200
C		-0.58869700	0.02073900	-0.00005000
F		-0.97636000	-0.64629600	-1.07607800
F		-1.14321300	1.21158600	0.00113900
F		-0.97603400	-0.64834100	1.07503800

Table S103: Cartesian coordinates (Å) of TS1E3

0	1		
F	-1.44558300	-0.75606500	-0.89492300
F	-0.87572200	1.27275300	-0.47644400
F	1.25171500	0.88278000	0.95648900
O	1.00371200	-1.52391100	0.43876300
C	-0.81265500	0.03196600	-0.03747700
C	0.62849600	-0.46798800	0.09653400
O	1.43337500	0.26066600	-1.10569200
H	1.66465300	0.91375400	-0.24327000
H	2.17173700	-0.33736000	-1.29232800
F	-1.40020200	-0.04994500	1.13895500

The optimized geometries of the key species observed in Figure 8 and Figure 12 (article) are given in Tables S104 – Table S116.

Table S104: Cartesian coordinates (Å) of trifluoroacetic acid (TFA)

0	1			
F		-0.98626600	-0.67272100	-1.07545800
F		-1.17922600	1.18135800	-0.00017400
F		-0.98658100	-0.67254800	1.07546600
O		1.50576800	-1.03826600	0.00001200
O		1.48489400	1.21436700	0.00000100
C		-0.60050600	0.00010700	0.00000500
C		0.93044300	0.16146100	0.00024000
H		2.46375100	-0.90301100	-0.00008400

Table S105: Cartesian coordinates (Å) of TS1M

0	1			
F		0.91707800	-0.90766400	1.04804700
F		1.17081200	1.59335300	0.00001100
F		0.91701900	-0.90762000	-1.04809000
O		-1.29030800	1.29319900	0.00000300
O		-1.61212400	-0.99172900	0.00001600
C		0.36737800	-0.47283400	0.00000400
C		-1.04447400	0.10171500	0.00001600
H		0.23784500	1.81233400	0.00001100

Table S106: Cartesian coordinates (Å) of TS2M

0	1		
F	-1.21555100	-0.75581000	-1.03592200
F	-0.98445600	1.59270100	0.00008900
F	-1.21542500	-0.75585100	1.03591800
O	1.39683000	1.15490700	-0.00007300
O	1.87246100	-1.09117100	0.00003800
C	-0.55202400	-0.43748300	-0.00004000
C	1.31948300	-0.05056500	-0.00003800
H	-0.02019300	1.68905100	-0.00001400

Table S107: Cartesian coordinates (Å) of TS3M

0	1		
F	-0.91570600	0.72477900	-1.07530600
F	-0.91497300	0.72327300	1.07637700
F	-1.63043800	-1.00125200	-0.00050800
O	1.55711100	-1.30491800	-0.00026000
O	1.76812900	1.01699400	-0.00013800
C	-0.69680700	-0.02834600	-0.00006600
C	1.39183900	-0.07017600	-0.00004100
H	0.37794200	-1.12667400	-0.00124400

Table S108: Cartesian coordinates (Å) of TS4M

0	1		
F	-1.50520000	-1.06910300	-0.14699500
F	-1.56051200	1.00834400	-0.18985100
F	0.33869800	0.01870100	1.31248400
O	1.37090200	-1.10219100	-0.33341700
O	1.38067900	1.17549100	-0.38655200
C	-0.82351800	-0.01253500	-0.29633200
C	0.88419000	0.13627900	-0.06453200
H	2.16645700	-0.95034300	-0.85581000

Table S109: Cartesian coordinates (Å) of TS5M

0	1			
F		0.90669100	1.26561600	-0.47742900
F		1.44195200	-0.73144800	-0.71933200
F		1.03021100	-0.02905200	1.26269400
O		-2.41166700	0.34606400	-0.04465400
O		-0.68661300	-1.01001600	-0.10409500
C		0.66485500	0.05589900	0.01607200
C		-1.13541900	0.15463000	0.14283200
H		-2.80006600	-0.49760300	-0.35683100

Table S110: Cartesian coordinates (Å) of Difluoroacetolactone

0	1			
F		1.21626100	1.07255200	-0.23981800
F		1.21626000	-1.07255300	-0.23981600
O		-2.06842500	-0.00000100	-0.46934300
O		-0.30930100	0.00000100	1.11368500
C		0.48530000	0.00000000	-0.06534500
C		-0.96378000	0.00000000	-0.07432700

Table S111: Cartesian coordinates (Å) of TS1M1

0	1			
F		-1.13378200	-1.06702900	-0.35149200
F		-1.13378500	1.06702500	-0.35149800
O		2.12967900	0.00000000	-0.32762500
O		0.02802200	0.00000400	1.26086400
C		-0.47011800	0.00000000	0.08435700
C		0.99453600	0.00000100	-0.27419300

Table S112: Cartesian coordinates (Å) of TS1M2

0	1			
F		-1.33491800	-1.04023600	-0.12692200
F		-1.33483800	1.04078700	-0.12336400
O		1.96138500	0.00141900	-0.72299500
O		0.68861600	-0.00239500	1.21083000
C		-0.62206700	0.00061300	-0.33727700
C		1.09336600	-0.00013900	0.06225900

Table S113: Cartesian coordinates (Å) of carbonyl fluoride

0	1			
F		0.00000000	1.05442500	-0.62756700
F		0.00000000	-1.05442500	-0.62756700
O		0.00000000	0.00000000	1.30825300
C		0.00000000	0.00000000	0.13836300

Table S114: Cartesian coordinates (Å) of TS1M3

0	1			
F		0.60558800	0.80661500	0.90199600
F		-0.86934300	-0.92961800	0.61267000
O		1.15511600	-0.64578000	-0.70020300
C		0.37600600	-0.03274100	-0.08580700
O		-0.84747300	0.63287000	-0.85087600
H		-1.36047500	-0.11967200	-0.20232600
H		-0.98289800	1.52641700	-0.50619400

Table S115: Cartesian coordinates (Å) of perfluoro-formic acid

0	1			
F		0.17180600	1.21852700	0.00001000
O		0.95322500	-0.81579300	-0.00002300
O		-1.25351300	-0.46784600	0.00009500
C		-0.14546200	-0.07571000	-0.00010100
H		1.72882200	-0.24337600	-0.00006100

Table S116: Cartesian coordinates (Å) of TS1M4

0	1			
F		-1.03635200	-0.82456800	0.00000200
O		-0.33902400	1.16765300	0.00000200
O		1.38312600	-0.39459200	-0.00000300
C		0.36489500	0.14185400	0.00000500
H		-1.21502000	0.38550300	-0.00004200