Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for:

From Strong to Weak NF Bonds: On the Design of a New Class of Fluorinating Agents

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Table S1: The NF bond distances R(NF), local mode frequencies $\omega^a(NF)$, force constant $k^a(NF)$, bond strength order $n(NF)$, electron densities ρ_c, energy densities H_c, the energy density ratio $\frac{H_c}{\rho_c}$, NF bond dissociation energy BDE and enthalpy BDH for molecule N1-N24

#	Molecule (State), Sym.	R(NF) (Å)	$\omega^a(NF)$ (cm^{-1})	$k^a(NF)$ (mdyn/Å)	BSO n(NF)	ρ_c(NF) (e/Å^3)	H_c(NF) (h/Å^3)	$\frac{H_c}{\rho_c}$(NF) (h/e)	BDE* $\left(\frac{kcal}{mol}\right)$	BDH* $\left(\frac{kcal}{mol}\right)$	Ref.
	N-F bonds[a]										
N1	:N-F($^3\Sigma^-$), $C_{\infty v}$	1.318	1144	6.217	1.312	2.391	-3.184	-1.332	77.65	76.83	[S1]
N2	HN-F$^\bullet$($^2A''$), C_s	1.371	1035	5.088	1.148	2.107	-2.350	-1.116	74.17	71.71	[S1]
N3	FN-F$^\bullet$($^2B_1$), C_{2v}	1.347	1005	4.802	1.104	2.304	-2.670	-1.159	67.75	66.70	[S1]
N4	:C=N-F($^1\Sigma^+$), $C_{\infty v}$	1.306	1200	6.839	1.399	2.529	-3.151	-1.246	54.47	53.02	[S1]
N5	H_2N-F($^1A'$), C_s	1.427	934	4.142	1.000	1.838	-1.719	-0.935	73.10	69.27	[S1]
N6	H(F)N-F($^1A'$), C_s	1.394	923	4.047	0.985	2.055	-2.059	-1.002	68.30	65.69	[S1]
N7	F_2N-F($^1A_1$), C_{3v}	1.369	920	4.021	0.981	2.256	-2.355	-1.044	59.75	58.27	[S1]
N8	H_3C(H)N-F(^1A), C_1	1.435	911	3.946	0.968	1.800	-1.651	-0.917	73.36	70.18	[S1]
N9	H_3C(F)N-F($^1A'$), C_s	1.403	909	3.922	0.964	2.011	-1.966	-0.977	67.33	65.34	[S1]
N10	$(CH_3)_2$N-F($^1A'$), C_s	1.436	904	3.878	0.957	1.795	-1.644	-0.916	73.20	70.55	[S1]
N11	HN=N-F,cis($^1A'$), C_s	1.486	640	1.943	0.603	1.607	-1.204	-0.749	61.17	58.37	[S1]
N12	HN=N-F,tr($^1A'$), C_s	1.418	810	3.118	0.827	1.921	-1.785	-0.929	59.55	56.50	[S1]
N13	FN=N-F,cis(^1A_g), C_{2h}	1.382	902	3.868	0.955	2.099	-2.126	-1.013	21.90	20.12	[S1]
N14	FN=N-F,tr(^1A_g), C_{2h}	1.380	976	4.522	1.061	2.121	-2.202	-1.038	20.62	18.92	[S1]
N15	H_2C=N-F($^1A'$), C_s	1.412	888	3.747	0.935	1.916	-1.854	-0.968	68.82	66.10	[S1]
	Ch=NH$_{(3-n)}$F$_n$[a]										
N16	O=N(H_2)-F($^1A'$), C_s	1.660	550	1.439	0.493	1.052	-0.463	-0.440	51.11	48.67	[S2]
N17	O=N(H)(F)-F($^1A'$), C_s	1.491	582	1.608	0.531	1.654	-1.183	-0.715	54.03	51.95	[S2]
N18	O=N(F_2)-F($^1A_1$), C_{3v}	1.424	749	2.662	0.744	2.003	-1.695	-0.846	53.62	51.79	[S2]
N19	S=N(H_2)-F($^1A'$), C_s	1.771	407	0.786	0.329	0.794	-0.236	-0.297	32.72	30.84	[S2]
N20	S=N(H)(F)-F($^1A'$), C_s	1.492	308	0.452	0.227	1.631	-1.146	-0.703	34.15	32.84	[S2]
N21	S=N(F_2)-F($^1A_1$), C_{3v}	1.416	625	1.853	0.584	2.026	-1.747	-0.863	36.69	35.85	[S2]
N22	Se=N(H_2)-F($^1A'$), C_s	1.776	384	0.700	0.305	0.785	-0.227	-0.290	28.66	26.74	[S2]
N23	Se=N(H)(F)-F($^1A'$), C_s	1.448	482	1.101	0.412	1.828	-1.468	-0.803	31.76	30.46	[S2]
N24	Se=NF_2-F($^1A_1$), C_{3v}	1.392	707	2.371	0.689	2.158	-2.009	-0.931	33.23	29.14	[S2]
	Ch=NH$_{(3-n)}$F$_n$[b] (DFT)										
N16	O=N(H_2)-F($^1A'$), C_s	1.631	484	1.112	0.392	1.134	-0.495	-0.437	51.11	48.67	This work
N17	O=N(H)(F)-F($^1A'$), C_s	1.477	641	1.951	0.567	1.717	-1.194	-0.696	54.03	51.95	This work
N18	O=N(F_2)-F($^1A_1$), C_{3v}	1.416	779	2.885	0.732	2.045	-1.662	-0.813	53.62	51.79	This work
N19	S=N(H_2)-F($^1A'$), C_s	1.672	522	1.296	0.434	1.019	-0.377	-0.370	32.72	30.84	This work
N20	S=N(H)(F)-F($^1A'$), C_s	1.457	315	0.472	0.224	1.796	-1.315	-0.732	34.15	32.84	This work
N21	S=N(F_2)-F($^1A_1$), C_{3v}	1.403	687	2.239	0.620	2.102	-1.776	-0.845	36.69	35.85	This work
N22	Se=N(H_2)-F($^1A'$), C_s	1.503	367	0.639	0.273	1.557	-1.006	-0.646	28.66	26.74	This work
N23	Se=N(H)(F)-F($^1A'$), C_s	1.417	644	1.969	0.570	1.985	-1.650	-0.831	31.76	30.46	This work
N24	Se=NF_2-F($^1A_1$), C_{3v}	1.377	766	2.789	0.716	2.243	-2.064	-0.920	33.23	29.14	This work

* BDE and BDH are calculated with the G4 method. [a] Each are calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory. [b] Each are calculated at U/R-ωB97XD/aug-cc-pVTZ level of theory.

Table S2: The pyramidalization angles θ_P (degree), pyramidalization force constants ($k^a(p)$, in Dyn Å rad^2 or $k_d^a(p)$, in mDyn Å^{-1}) and frequencies $\omega^a(p)$ (cm^{-1}), calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory

#	Molecule (State), Sym.	θ_P	$k^a(p)$	$k_d^a(p)$	$\omega^a(p)$
	Cationic N-F bonds				
8	$[H_2N\text{-}F]^{\cdot+}(^2A'')$, C_s	0.0	0.548	0.445	523
9	$[H_2N\text{-}F]^{2+}(^1A')$, C_s	0.0	3.548	2.773	1249
10	$[H(F)N\text{-}F]^{\cdot+}(^2A')$, C_s	10.7	1.814	1.268	712
11	$[H(F)N\text{-}F]^{2+}(^1A_2)$, C_{2v}	0.0	4.074	2.928	1024
12	$[F_2N\text{-}F]^{\cdot+}(^2A_1)$, C_{3v}	14.8	6.270	3.822	740
13	$[F_2N\text{-}F]^{2+}(^1E)$, C_{3v}	0.0	5.705	3.825	760
14	$[CH_3C(H)N\text{-}F]^{\cdot+}(^2A)$, C_1	20.3	3.612	2.483	1221
15	$[H_3C(H)N\text{-}F]^{2+}(^1A)$, C_1	8.2	1.836	1.266	851
16	$[H_3C(F)N\text{-}F]^{\cdot+}(^2A')$, C_s	20.6	3.557	2.415	1230
17	$[H_3C(F)N\text{-}F]^{2+}(^1A')$, C_s	14.9	0.896	0.617	611
	Ch=$NF_2^{\cdot+}$, Ch = O, S, Se				
24	$[O{=}N(F)\text{-}F]^{\cdot}(^2B_2)$, C_{2v}	16.7	6.406	3.535	728
25	$[S{=}N(F)\text{-}F]^{\cdot}(^2B_2)$, C_{2v}	16.2	2.614	1.213	408
26	$[Se{=}N(F)\text{-}F]^{\cdot}(^2B_2)$, C_{2v}	19.1	1.815	0.774	322
	N-F bonds				
N5	$H_2N\text{-}F(^1A')$, C_s	25.8	3.199	2.402	1211
N6	$H(F)N\text{-}F(^1A')$, C_s	27.1	5.591	3.464	1159
N7	$F_2N\text{-}F(^1A_1)$, C_{3v}	26.4	11.010	5.872	864
N8	$H_3C(H)N\text{-}F(^1A)$, C_1	18.3	3.683	2.513	1228
N9	$H_3C(F)N\text{-}F(^1A')$, C_s	19.4	3.681	2.512	1243
N10	$(CH_3)_2N\text{-}F(^1A')$, C_s	22.6	5.028	2.400	591
	Hypervalent Fluoroamines				
N16	$O{=}N(H_2)\text{-}F(^1A')$, C_s	27.8	4.165	2.732	1522
N17	$O{=}N(H)(F)\text{-}F(^1A')$, C_s	28.2	5.746	3.220	1195
N18	$O{=}N(F_2)\text{-}F(^1A_1)$, C_{3v}	27.4	11.094	5.475	828
N19	$S{=}N(H_2)\text{-}F(^1A')$, C_s	29.1	2.642	1.654	1247
N20	$S{=}N(H)(F)\text{-}F(^1A')$, C_s	28.4	4.580	2.577	1084
N21	$S{=}N(F_2)\text{-}F(^1A_1)$, C_{3v}	28.0	9.566	4.768	770
N22	$Se{=}N(H_2)\text{-}F(^1A')$, C_s	29.0	2.478	1.550	1200
N23	$Se{=}N(H)(F)\text{-}F(^1A')$, C_s	27.2	4.381	2.576	1064
N24	$Se{=}NF_2\text{-}F(^1A_1)$, C_{3v}	27.1	8.834	4.560	757

Table S3: The pyramidalization angles θ_P (degree), pyramidalization force constants ($k^a(p)$, in Dyn Å rad^2 or $k_d^a(p)$, in mDyn Å^{-1}) and frequencies $\omega^a(p)$ (cm^{-1}), calculated at U/R-ωB97XD/aug-cc-pVTZ level of theory

#	Molecule (State), Sym.	θ_P	$k^a(p)$	$k_d^a(p)$	$\omega^a(p)$
	Ch=N$F_2^{\cdot+}$, Ch = O, S, Se				
24	[O=N(F)-F]$^{\cdot}$($^2A\prime$), C_s	16.6	6.643	3.726	746
25	[S=N(F)-F]$^{\cdot}$($^2A\prime\prime$), C_s	14.8	2.870	1.358	435
26	[Se=N(F)-F]$^{\cdot}$($^2A\prime\prime$), C_s	16.9	2.164	0.943	359
	EWG-Subst. Chalcogenides				
33	O=N($(CF_3)_2$)-F($^1A''$), C_s	24.0	8.228	3.361	701
34	S=N($(CF_3)_2$)-F($^1A''$), C_s	25.3	7.756	3.107	676
35	Se=N($(CF_3)_2$)-F($^1A''$), C_s	24.8	4.638	1.911	528
36	O=N($(NO_2)_2$)-F(^1A), C_1	26.6	5.552	2.026	523
37	S=N($(NO_2)_2$)-F(^1A), C_1	28.0	5.928	2.191	543
38	Se=N($(NO_2)_2$)-F(^1A), C_1	27.3	5.224	1.968	519
39	O=N($(CN)_2$)-F($^1A''$), C_s	26.5	5.289	2.380	591
40	S=N($(CN)_2$)-F($^1A''$), C_s	27.6	3.714	1.599	501
41	Se=N($(CN)_2$)-F($^1A''$), C_s	27.1	3.312	1.420	476
	EDG-Subst. Chalcogenides	27.4	11.094	5.475	828
42	O=N($(CH_3)_2$)-F($^1A''$), C_s	24.9	7.103	2.979	666
43	S=N($(CH_3)_2$)-F($^1A''$), C_s	24.5	4.935	2.165	561
44	Se=N($(CH_3)_2$)-F($^1A''$), C_s	22.7	6.355	2.950	655
45	O=N($(NH_2)_2$)-F(^1A), C_1	24.4	8.644	3.885	747
46	S=N($(NH_2)_2$)-F(^1A), C_1	24.3	6.837	3.306	680
47	Se=N($(NH_2)_2$)-F(^1A), C_1	23.3	7.960	3.962	746
48	O=N($(OH)_2$)-F($^1A''$), C_s	26.0	9.826	4.769	795
49	S=N($(OH)_2$)-F($^1A'$), C_s	24.5	8.019	4.146	746
50	Se=N($(OH)_2$)-F($^1A'$), C_s	23.8	8.661	4.556	785
	Hypervalent Fluoroamines				
N16	O=N(H_2)-F($^1A'$), C_s	27.7	3.917	2.599	1455
N17	O=N(H)(F)-F($^1A'$), C_s	28.0	6.315	3.581	1249
N18	O=N(F_2)-F($^1A_1$), C_{3v}	27.2	11.537	5.754	850
N19	S=N(H_2)-F($^1A'$), C_s	28.1	2.386	1.570	1143
N20	S=N(H)(F)-F($^1A'$), C_s	27.7	5.046	2.938	1137
N21	S=N(F_2)-F($^1A_1$), C_{3v}	27.7	10.176	5.169	803
30	Se=N(H_2)-F($^1A'$), C_s	24.9	2.438	1.759	1095
31	Se=N(H)(F)-F($^1A'$), C_s	26.3	4.870	2.953	1121
32	Se=NF_2-F($^1A_1$), C_{3v}	26.5	9.299	4.903	788

Table S4: The direct ionization energies (eV) from its neutral state, E_0^{ion}, or from its first ionized cationic state, E_0^{+x}

Ionization	Molecule	IE_0^{+x}
	Ionic N-F bonds[a]	
N1 → 1	[:N-F] → [:N-F]$^{\cdot+}$	12.16
N1 → 2	[:N-F] → [:N-F]$^{2+}$	35.85
N2 → 3	[HN-F] → [HN-F]$^{+}$	11.63
N3 → 4	[FN-F] → [FN-F]$^{+}$	11.51
N4 → 5	[:C=N-F] → [C=N-F]$^{\cdot+}$	12.54
N4 → 6	[:C=N-F] → [C=N-F]$^{2+}$	38.25
N5 → 8	[H_2N-F] → [H_2N-F]$^{\cdot+}$	10.43
N5 → 9	[H_2N-F] → [H_2N-F]$^{2+}$	31.91
N6 → 10	[H(F)N-F] → [H(F)N-F]$^{\cdot+}$	11.24
N6 → 11	[H(F)N-F] → [H(F)N-F]$^{2+}$	32.07
N7 → 12	[F_2N-F] → [F_2N-F]$^{\cdot+}$	12.53
N7 → 13	[F_2N-F] → [F_2N-F]$^{2+}$	33.55
N8 → 14	[H_3C(H)N-F] → [H_3C(H)N-F]$^{\cdot+}$	9.51
N8 → 15	[H_3C(H)N-F] → [H_3C(H)N-F]$^{2+}$	27.58
N9 → 16	[H_3C(F)N-F] → [H_3C(F)N-F]$^{\cdot+}$	10.37
N9 → 17	[H_3C(F)N-F] → [H_3C(F)N-F]$^{2+}$	28.87
N11 → 18	[HN=N-F, cis] → [HN=N-F]$^{2+}$	30.22
N12 → 18	[HN=N-F, tr] → [HN=N-F]$^{2+}$	30.15
N13 → 19	[FN=N-F, cis] → [FN=N-F]$^{2+}$	32.66
N14 → 19	[FN=N-F, tr] → [FN=N-F]$^{2+}$	32.61
N15 → 20	[H_2C=N-F, cis] → [H_2C=N-F]$^{2+}$	30.68
	SelectFluor, DFT[b]	
27 → 28	[(F-TEDA)]$^{\cdot+}$ → [(F-TEDA)]$^{2+}$	10.55
29 → 30	[(F-TEDA)(BF_4)]$^{\cdot}$ → [(F-TEDA)(BF_4)]$^{+}$	7.36
31 → 32	[(F-TEDA)(BF_4)$_2$]$^{\cdot-}$ → [(F-TEDA)(BF_4)$_2$]	4.34

[a] Each are calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory. [b] Each are calculated at U/R-ωB97XD/aug-cc-pVTZ level of theory.

Table S5: The electron affinities (kcal/mol) upon capture of one electron, calculated at U/R-ωB97XD/6-31++G(d,p) level of theory

Reaction	Molecule	EA
	SelectFluor	
28 → 27	$[(\text{F-TEDA})]^{2+} \rightarrow [(\text{F-TEDA})]^{\cdot+}$	-243.39
30 → 29	$[(\text{F-TEDA})(BF_4)]^{+} \rightarrow [(\text{F-TEDA})(BF_4)]^{\cdot}$	-169.66
32 → 31	$[(\text{F-TEDA})(BF_4)_2] \rightarrow [(\text{F-TEDA})(BF_4)_2]^{\cdot-}$	-100.17
	EWG-Substituted	
33	O=N$((CF_3)_2)$-F($^1A''$), C_s	-10.98
34	S=N$((CF_3)_2)$-F($^1A''$), C_s	-46.79
35	Se=N$((CF_3)_2)$-F($^1A''$), C_s	-54.93
36	O=N$((NO_2)_2)$-F(^1A), C_1	-38.77
37	S=N$((NO_2)_2)$-F(^1A), C_1	-44.34
38	Se=N$((NO_2)_2)$-F(^1A), C_1	-52.24
39	O=N$((CN)_2)$-F($^1A''$), C_s	-52.47
40	S=N$((CN)_2)$-F($^1A''$), C_s	-80.29
41	Se=N$((CN)_2)$-F($^1A''$), C_s	-84.95
	EDG-Substituted	
42	O=N$((CH_3)_2)$-F($^1A''$), C_s	47.72
43	S=N$((CH_3)_2)$-F($^1A''$), C_s	7.84
44	Se=N$((CH_3)_2)$-F($^1A''$), C_s	2.98
45	O=N$((NH_2)_2)$-F(^1A), C_1	33.05
46	S=N$((NH_2)_2)$-F(^1A), C_1	6.01
47	Se=N$((NH_2)_2)$-F(^1A), C_1	3.38
48	O=N$((OH)_2)$-F($^1A''$), C_s	12.07
49	S=N$((OH)_2)$-F($^1A'$), C_s	-12.06
50	Se=N$((OH)_2)$-F($^1A'$), C_s	-13.12

[a] Undergo the subsequent reaction: $\text{Ch=NR}_2\text{F} \xrightarrow{e^-} [\text{Ch=NR}_2]^- + \text{F}\cdot$;
[b] We use here reaction energies, thus negative (positive) EA means energy is released (needed) upon capture of one electron.

Table S6: The NF bond distance R, local mode force constants k^a, and frequencies ω^a calculated at U/R-ωB97XD/6-31++G(d,p) level of theory employing IEFPCM as model continuum solvent

#	SelectFluor	Phase	R	k^a	ω^a
27	$[(\text{F-TEDA})]^{\cdot+}$	Vacuo	1.954	1.154	493
		Water	1.991	1.023	464
		Acetonitrile	1.989	1.023	464
		DMF	1.989	1.023	464
28	$[(\text{F-TEDA})]^{2+}$	Vacuo	1.367	5.511	1077
		Water	1.371	5.341	1060
		Acetonitrile	1.370	5.346	1061
		DMF	1.370	5.346	1061

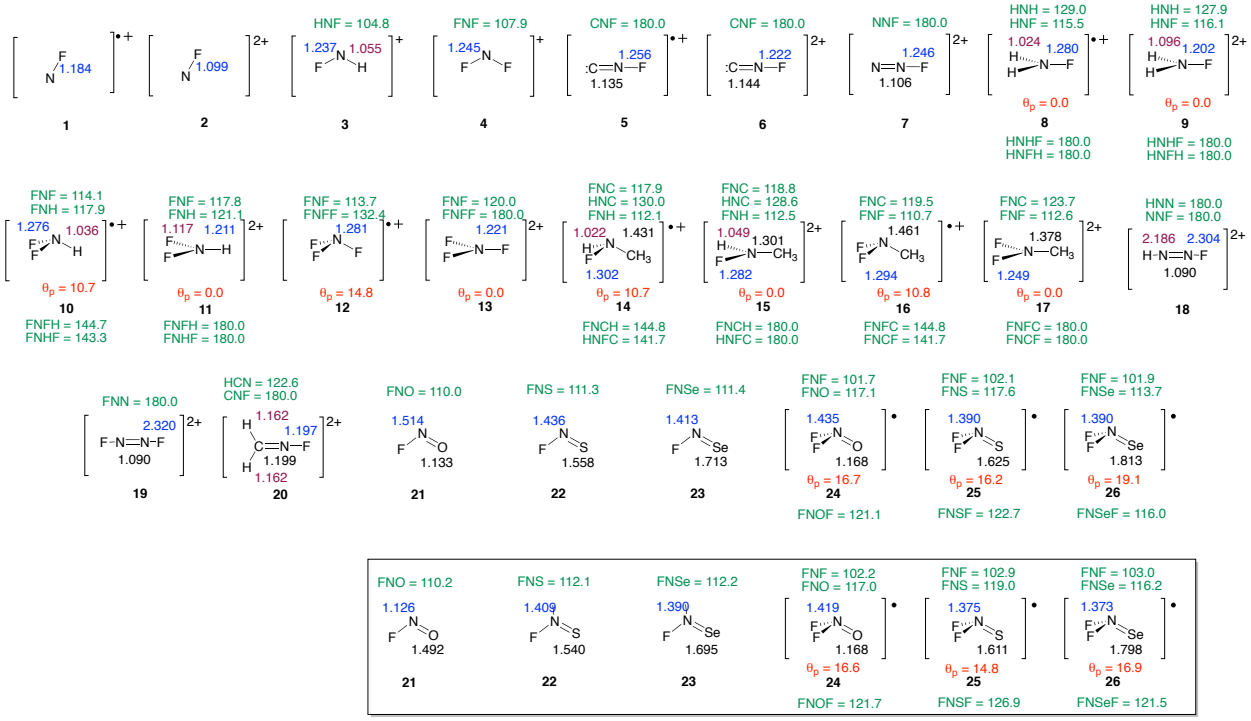


Figure S1: Optimized geometrical parameters of molecules **1**-**26**, calculated at U/R-CCSD(T)/aug-cc-pVTZ (boxed: U/R-ωB97XD) level of theory. All bond distances are in Å, and the bond angles, bond dihedrals, and pyramidalization angles (Θ_p) are in degree. The colored numbers represent the bond distances of NF (blue), NH (magenta), and N with other atoms (black).

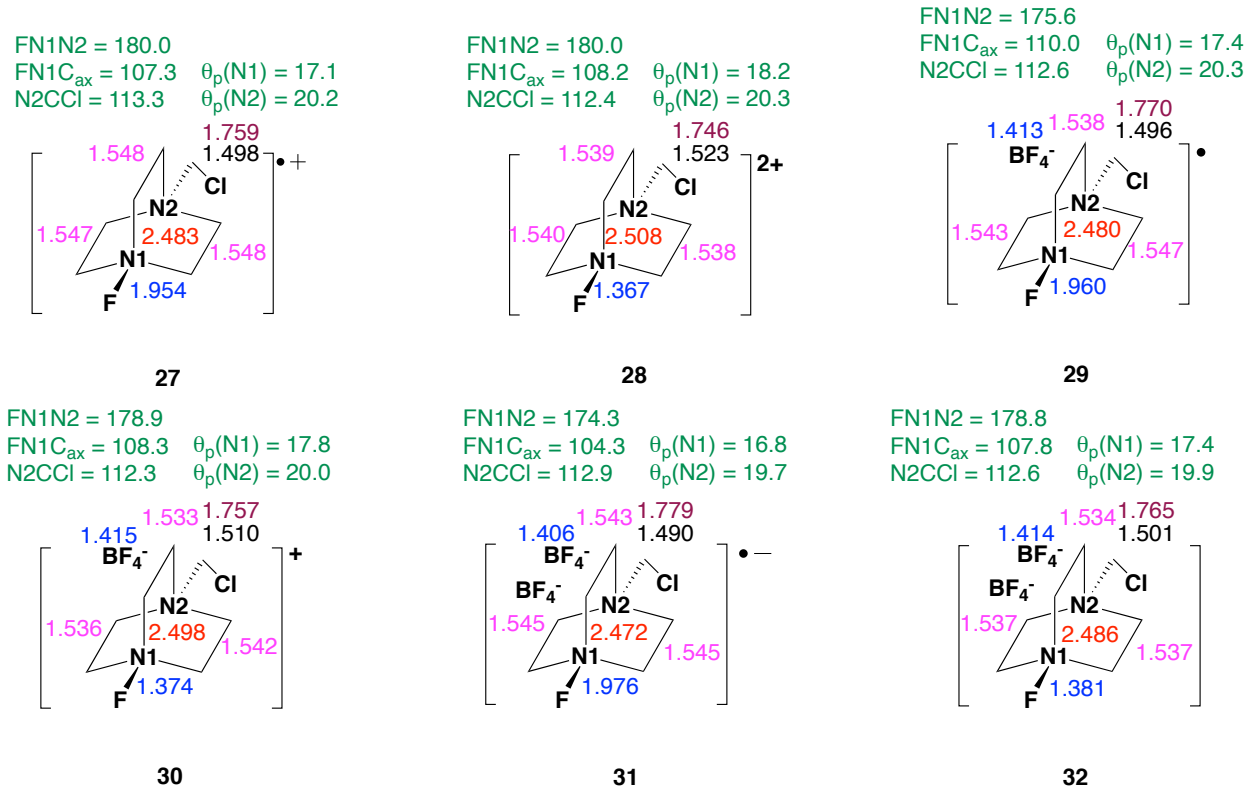


Figure S2: Optimized geometrical parameters of the SelectFluor compounds **27**-**32**, calculated at U/R-ωB97XD/aug-cc-pVTZ level of theory. All bond distances are in Å, and the bond angles, bond dihedrals, and pyramidalization angles (Θ_p) are in degree. The colored numbers represent the bond distances of NF or BF (blue), NN (red), CCl (magenta), and N2-C (black). The listed BF bond distances for tetrafluoroborate counteranions are the averaged values within the anion.

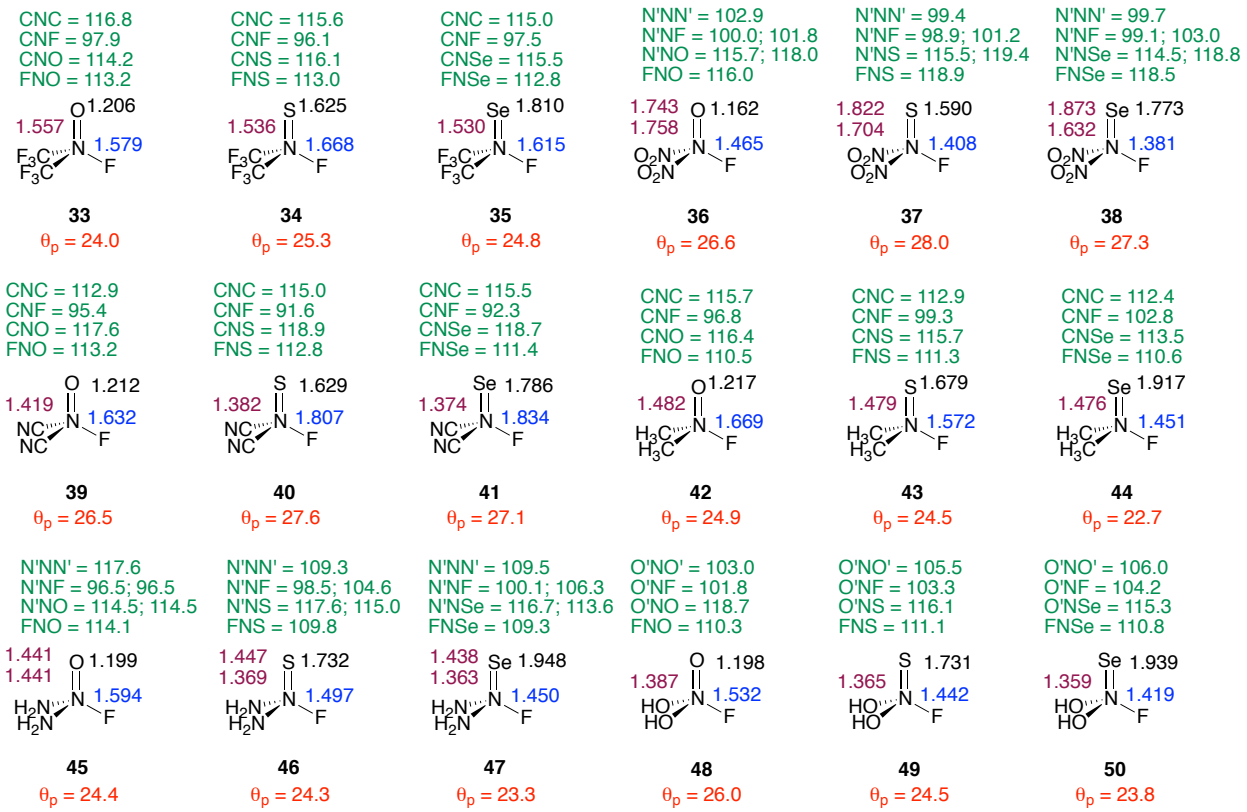


Figure S3: Optimized geometrical parameters of EWG-subsituted chalcogenides **33-41** and the EDG-subsituted chalcogenides **42-50**, calculated at U/R-ωB97XD/aug-cc-pVTZ level of theory. All bond distances are in Å, and the bond angles, bond dihedrals, and pyramidalization angles (Θ_p) are in degree. The colored numbers represent the bond distances of NF (blue), NC or NN (magenta), and N-Chalcogenides (black).

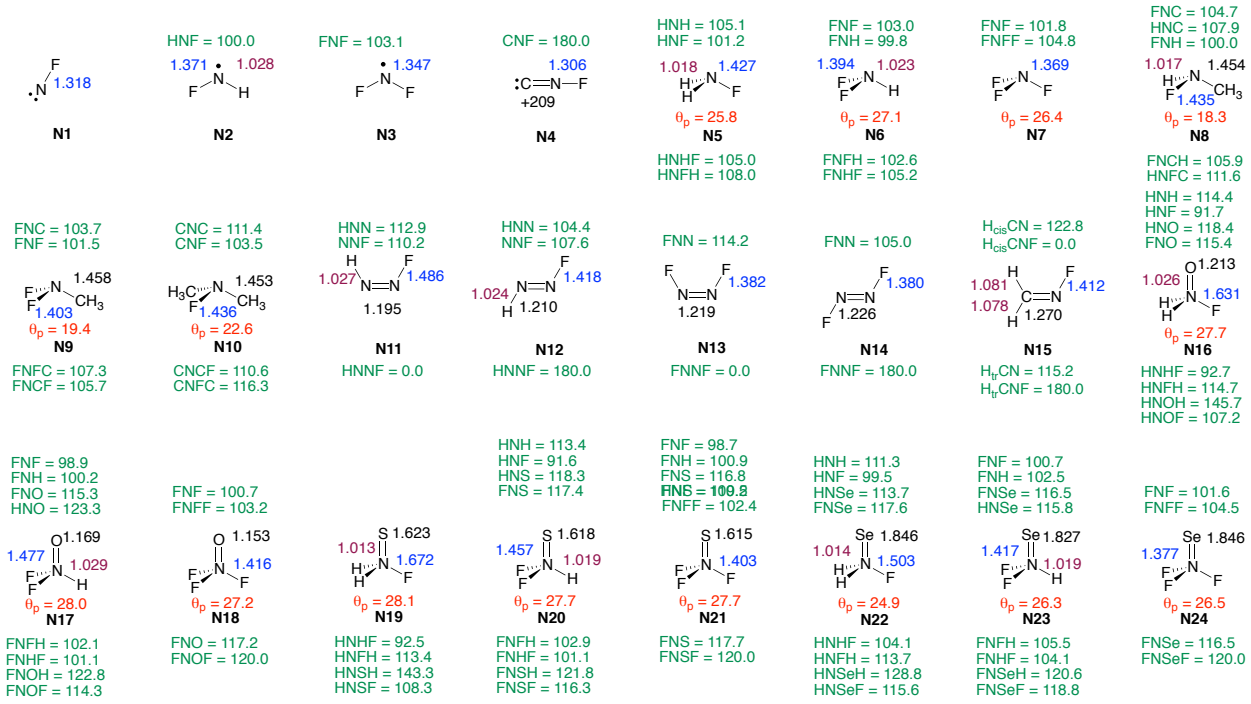


Figure S4: Optimized geometrical parameters of the chalcogenides **N1**-**N24** calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory. All bond distances are in Å, and the bond angles, bond dihedrals, and pyramidalization angles (Θ_p) are in degree. The colored numbers represent the bond distances of NF (blue), NH (magenta), and N-Chalcogenides (black).[S1,S2]

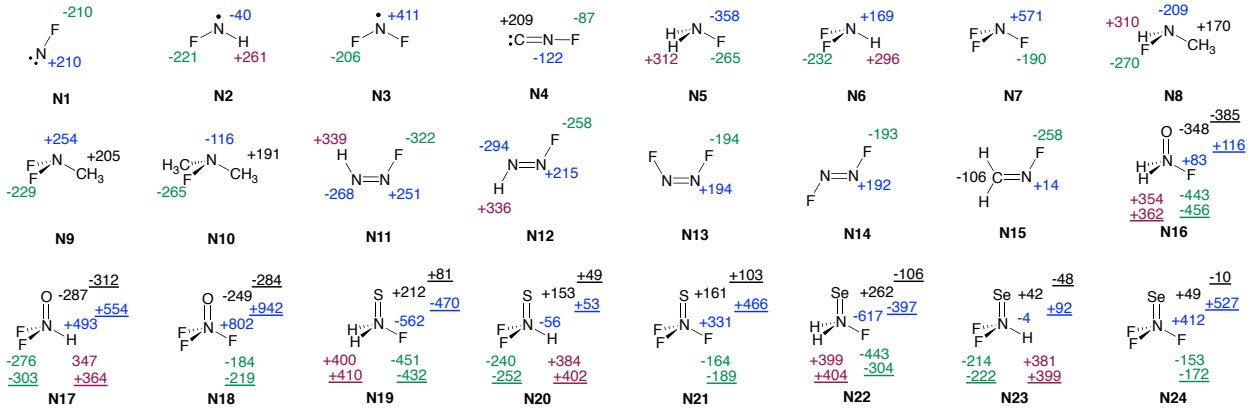


Figure S5: NBO charges of the chalcogenides **N1**-**N24**, calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory. The numbers represent the partial atomic charges on N atoms (blue), F atoms (green), and Chalcogenides (black).[S1,S2]

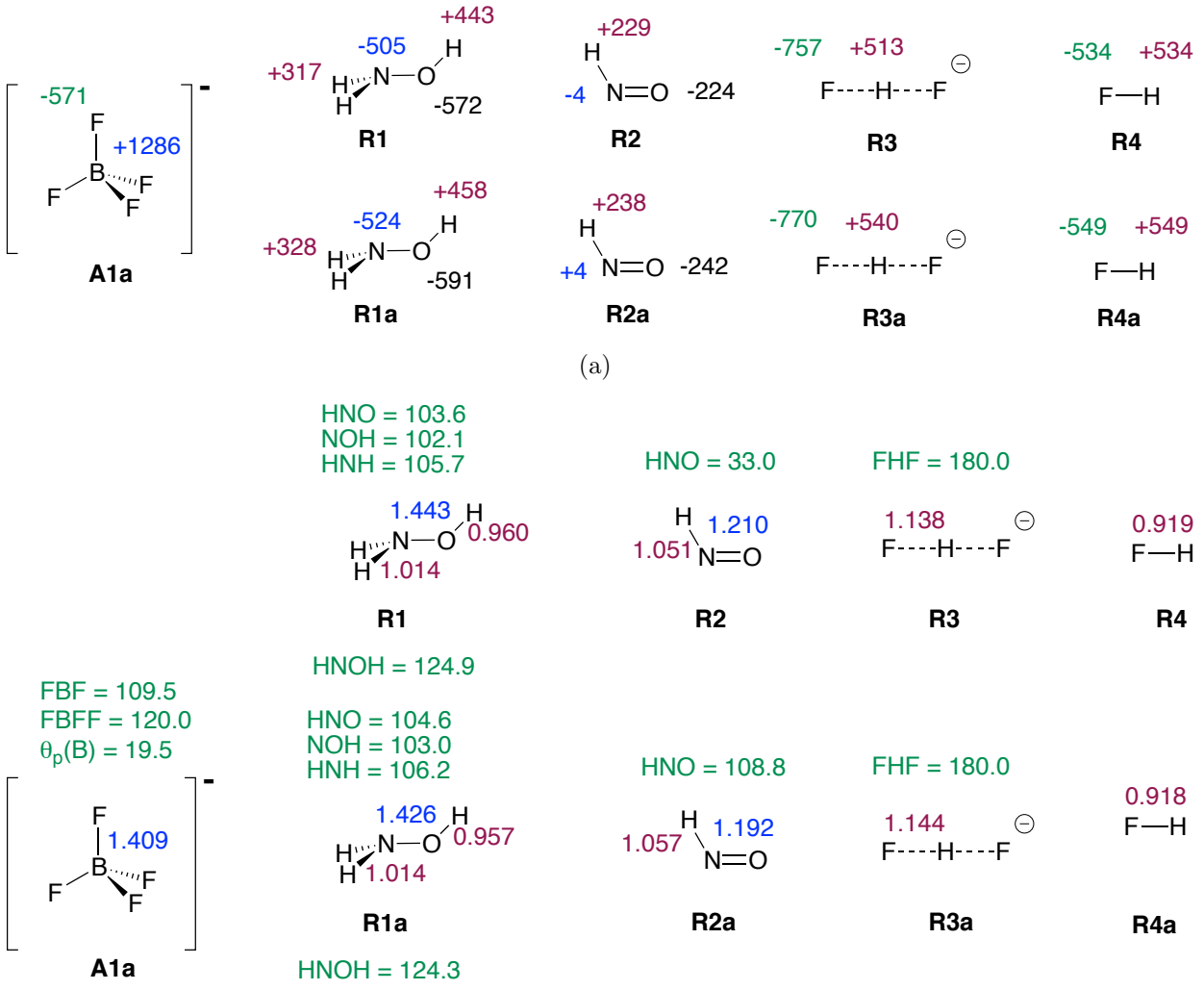
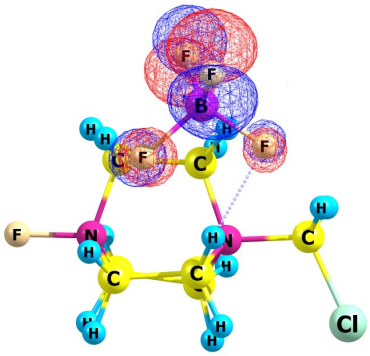
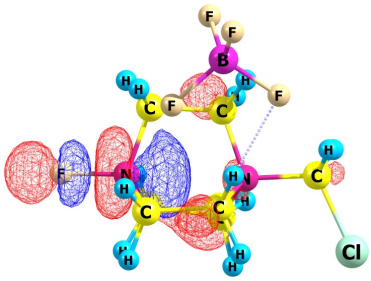


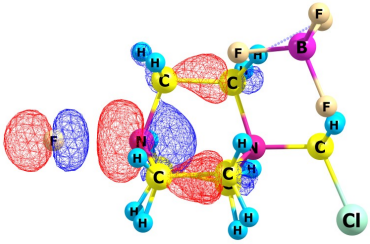
Figure S6: NBO charges (a) and optimized geometrical parameters (b) of the reference molecules **R1**-**R4** and the tetrafluoroborate anion **A1**, calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory, while molecules **R1a**-**R4a** and **A1a** were calculated at the U/R-ωB97XD/aug-cc-pVTZ level of theory. For the NBO charges, the numbers represent the partial atomic charges on N atoms (blue), F atoms (green), H atoms (magenta), and other atoms/functional groups (black). For optimized geometrical parameters, all bond distances are in Å, and the bond angles, bond dihedrals, and pyramidalization angles (Θ_p) are in degree. The colored numbers represent the bond distances of NF, NO and BF (blue), NH and OH (magenta).



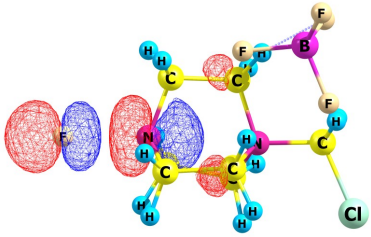
(a) HOMO, (F-TEDA)$(BF_4)^+$



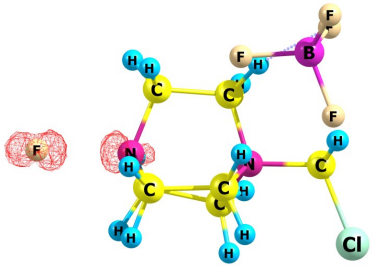
(b) LUMO, (F-TEDA)$(BF_4)^+$



(c) HOMO, (F-TEDA)$(BF_4)^{\cdot}$

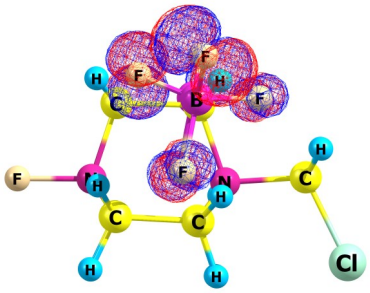


(d) LUMO, (F-TEDA)$(BF_4)^{\cdot}$

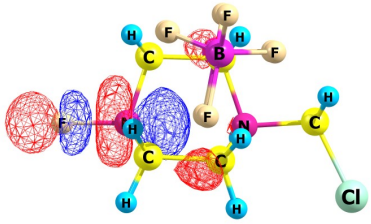


(e) Difference spin density, (F-TEDA)$(BF_4)^{\cdot}$

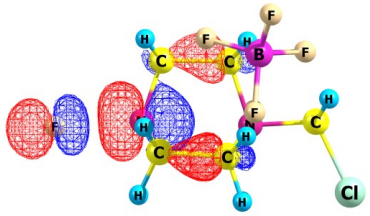
Figure S7: Frontier orbitals of F-TEDA with one tetrafluoroboro-counteranion **29-30** calculated at the ωB97XD/aug-cc-pVTZ level of theory. The difference electron spin density, red denotes positive alpha over beta spin density difference.



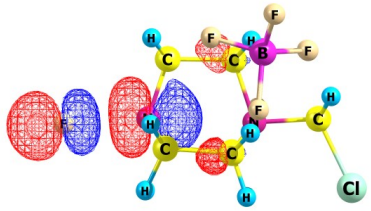
(a) HOMO, (F-TEDA)$(BF_4)_2$



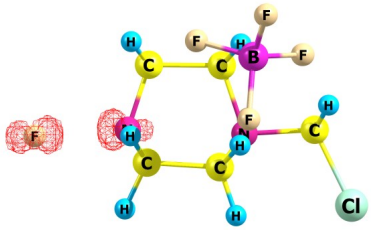
(b) LUMO, (F-TEDA)$(BF_4)_2$



(c) HOMO, (F-TEDA)$(BF_4)_2^{\cdot -}$



(d) LUMO, (F-TEDA)$(BF_4)_2^{\cdot -}$



(e) Difference spin density, (F-TEDA)$(BF_4)_2^{\cdot -}$

Figure S8: Frontier orbitals of F-TEDA with two tetrafluoroboro-counteranions **31**-**32** calculated at the ωB97XD/aug-cc-pVTZ level of theory. The difference electron spin density, red denotes positive alpha over beta spin density difference.

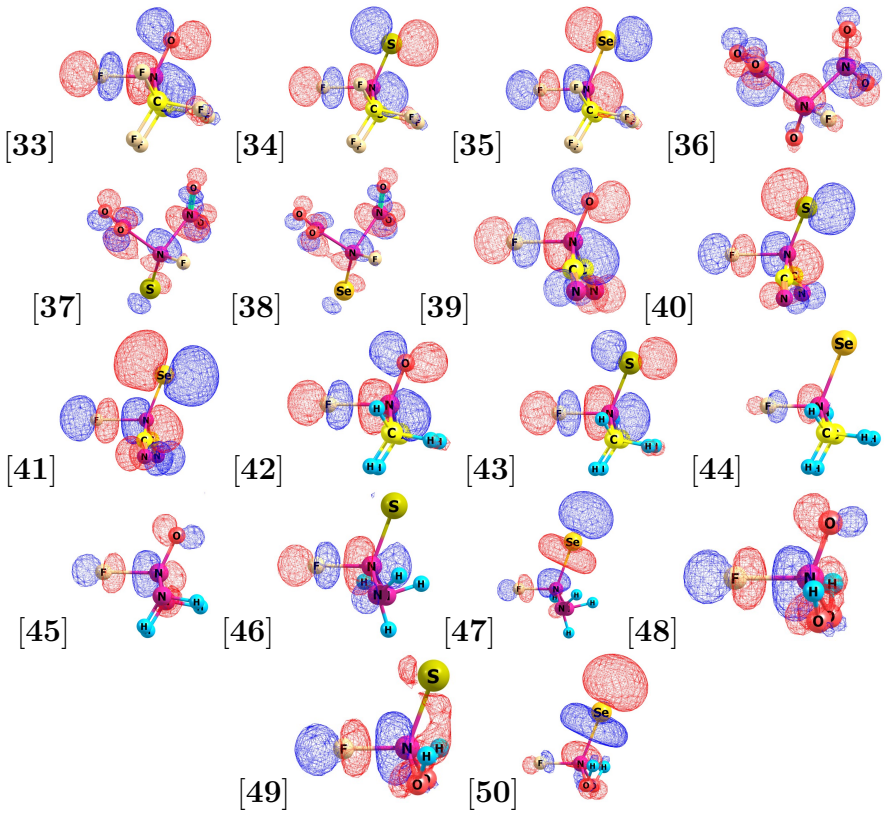


Figure S9: LUMOs of EWG- (**33-41**) and EDG-substittued (**42-50**) fluoroamine chalcogenides, calculated at the ωB97XD/aug-cc-pVTZ level of theory.

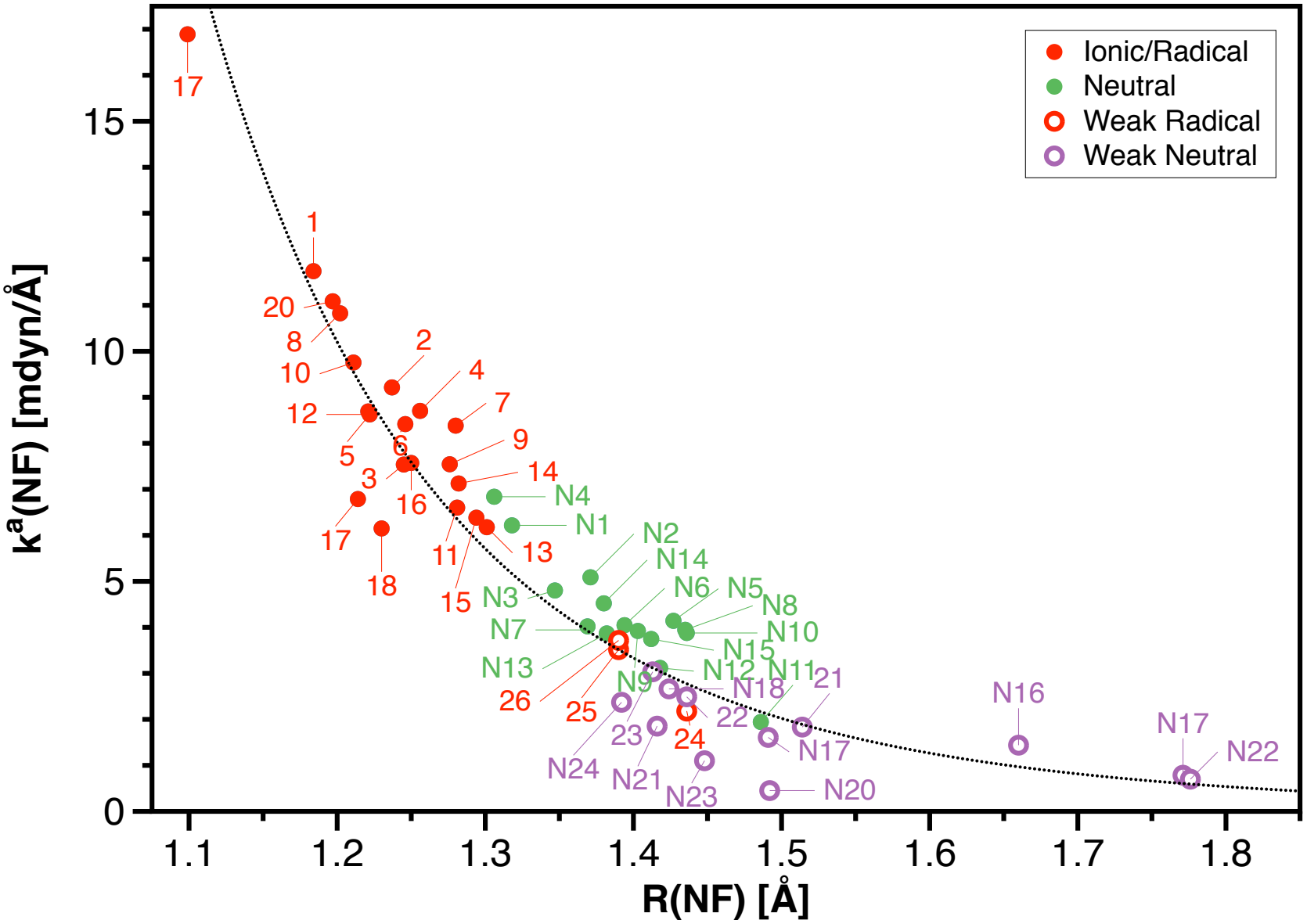


Figure S10: The Badger relationship of NF bonds within molecules **1-26** and **N1-N24** calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory.

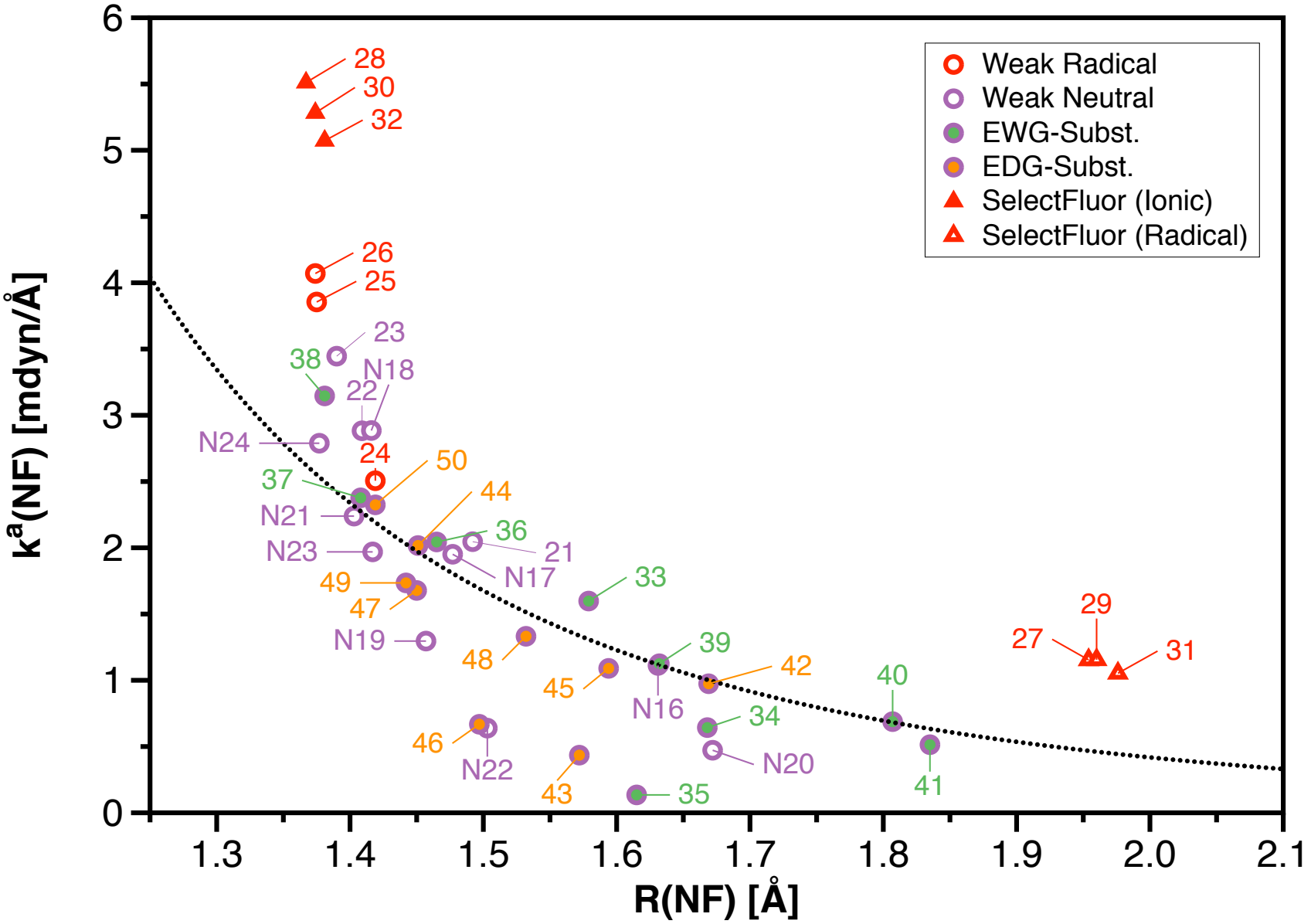


Figure S11: The Badger relationship of NF bonds within molecules **21-50** and **N16-N24** calculated at U/R-ωB97XD/aug-cc-pVTZ level of theory.

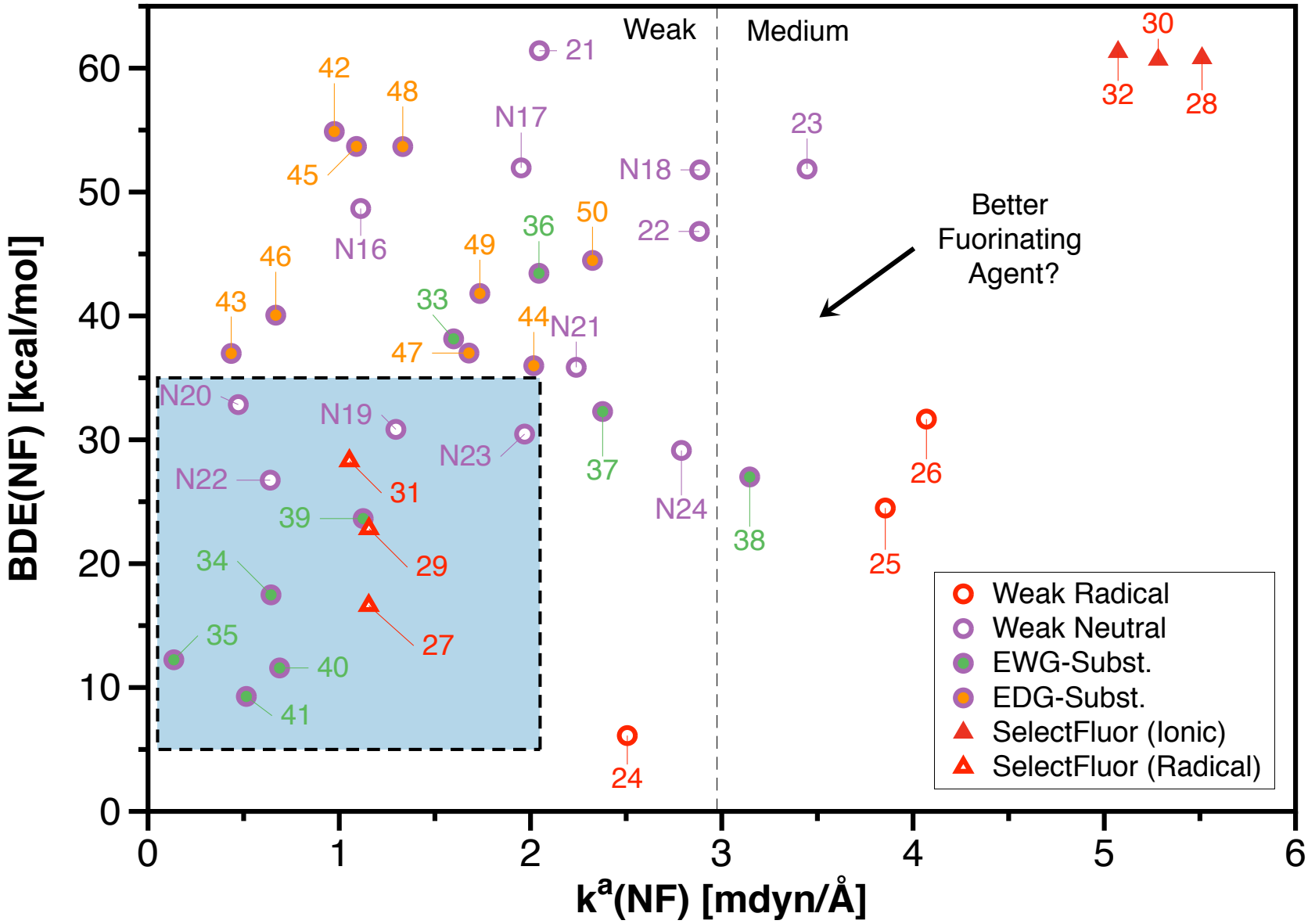


Figure S12: The NF Bond Dissociation Enthalpy BDE and the corresponding local mode force constant $k^a(NF)$ of the molecules **21-50** and and **N16-N24**, calculated at U/R-ωB97XD/aug-cc-pVTZ level of theory.

Table S7: Atomic Cartesian coordinates (in Å) of molecules 1 - 26, N1 - N24, and reference molecules R1 - R4 optimized at the U/R-CCSD(T)/aug-cc-pVTZ level of theory. Absolute energies are given in a.u.

1	[:N-F]$^{\cdot+}$($^2\Sigma^-$), $C_{\infty v}$, E = -153.84092		
N	0.000000	0.000000	0.681699
F	0.000000	0.000000	-0.502457
2	[:N-F]$^{2+}$, $C_{\infty v}$, E = -152.97011		
N	0.000000	0.000000	0.632492
F	0.000000	0.000000	-0.466188
3	[HN-F]$^+$, C_s, E = -154.48815		
N	-0.678720	-0.084109	0.000000
F	0.554779	0.013671	0.000000
H	-1.027705	0.910915	0.000000
4	[FN-F]$^+$, C_{2v}, E = -253.6119491		
N	0.000000	0.000000	0.535420
F	0.000000	-1.006645	-0.197320
F	0.000000	1.006645	-0.197320
5	[C=N-F]$^{\cdot+}$($^2\Pi$), $C_{\infty v}$, E = -191.86802		
C	0.000000	0.000000	-1.362427
N	0.000000	0.000000	-0.227568
F	0.000000	0.000000	1.028285

6 $[C{=}N\text{-}F]^{2+}$, $C_{\infty v}$, E = -190.92310

C	0.000000	0.000000	-1.354793
N	0.000000	0.000000	-0.210706
F	0.000000	0.000000	1.011035

7 $[N{=}N\text{-}F]^{+}(^{1}\Pi)$, $C_{\infty v}$, E = -208.62624

N	0.000000	0.000000	-1.280148
N	0.000000	0.000000	-0.174207
F	0.000000	0.000000	1.071956

8 $[H_2N\text{-}F]^{\cdot +}$, C_s, E = -155.18843

N	0.668866	0.000000	0.000000
H	1.110363	-0.924305	0.000000
H	1.110359	0.924307	0.000000
F	-0.610803	0.000000	0.000000

9 $[H_2N\text{-}F]^{2+}$, C_s, E = -154.39901

N	0.624663	0.000000	0.000000
H	1.105989	-0.984045	0.000000
H	1.105967	0.984057	0.000000
F	-0.577757	-0.000001	0.000000

10 $[H(F)N\text{-}F]^{\cdot +}(^{2}A')$, C_s, E = -254.25223

N	0.476758	0.062510	0.000000
F	-0.213358	-0.013302	-1.070985
F	-0.213358	-0.013302	1.070985

H	1.419730	-0.367027	0.000000

11 $[H(F)N\text{-}F]^{2+}$, C_{2v}, E = -253.48671

N	0.425934	-0.001365	0.000000
F	-0.197918	0.000323	-1.037218
F	-0.197918	0.000323	1.037218
H	1.543776	0.006793	0.000000

12 $[F_2N\text{-}F]^{\cdot+}(^2A_1)$, C_{3v}, E = -353.31179

N	0.261995	0.000000	0.000000
F	-0.064369	0.619286	-1.072634
F	-0.064369	0.619286	1.072634
F	-0.064369	-1.238571	0.000000

13 $[F_2N\text{-}F]^{2+}$, C_{3v}, E = -352.53923

N	-0.000014	0.000000	0.000000
F	0.000003	0.610606	-1.057600
F	0.000003	0.610606	1.057600
F	0.000003	-1.221211	0.000000

14 $[CH_3C(H)N\text{-}F]^{\cdot+}$, C_1, E = -194.48080

C	-1.282696	0.223582	0.000000
N	-0.026932	-0.470515	0.000000
H	-1.076533	1.289484	0.000000
H	-1.832186	-0.085628	-0.893565
H	-1.832186	-0.085628	0.893565

F	1.073262	0.224563	0.000000
H	0.156003	-1.476089	0.000000

15 $[H_3C(H)N\text{-}F]^{2+}(^1A)$, C_1, E = -193.81688

C	1.160498	0.274196	0.000007
N	0.065168	-0.427900	0.000006
H	2.061251	-0.344529	0.536305
H	1.198029	1.367572	-0.000006
H	2.061153	-0.344509	-0.536403
F	-1.060935	0.184228	-0.000003
H	-0.044185	-1.470807	-0.000005

16 $[H_3C(F)N\text{-}F]^{\cdot+}$, C_s, E = -293.55174

C	0.055298	-1.494088	0.000000
N	-0.202820	-0.056508	0.000000
H	1.142566	-1.615366	0.000000
H	-0.401764	-1.883317	-0.905968
H	-0.401764	-1.883317	0.905968
F	0.048289	0.635434	-1.064265
F	0.048289	0.635434	1.064265

17 $[H_3C(F)N\text{-}F]^{2+}(^1A')$, C_s, E = -292.8715894

C	-0.028793	-1.445927	0.000000
N	-0.011920	-0.068489	0.000000

H	1.132548	-1.685788	0.000000
H	-0.364019	-1.836893	-0.981586
H	-0.364019	-1.836893	0.981586
F	0.002757	0.624044	-1.038974
F	0.002757	0.624044	1.038974

18 $[HN{=}N\text{-}F]^{2+}(^1\Pi)$, $C_{\infty v}$, E = -208.5332103

N	0.116849	-0.000027	0.000000
N	1.206418	-0.000002	0.000000
F	-1.097503	0.000013	0.000000
H	2.302984	0.000154	0.000000

19 $[FN{=}N\text{-}F]^{2+}(^1\Pi_u)$, $D_{\infty h}$, E = -307.5288025

N	0.000000	0.000000	0.544969
N	0.000000	0.000000	-0.544969
F	0.000000	0.000000	1.774863
F	0.000000	0.000000	-1.774863

20 $[H_2C{=}N\text{-}F]^{2+}(^1B_2)$, C_{2v}, E = -192.48678

C	0.000000	0.000000	-1.298425
N	0.000000	0.000000	-0.099373
F	0.000000	0.000000	1.097445
H	0.979143	0.000000	-1.923487
H	-0.979143	0.000000	-1.923487

21 $[O{=}N\text{-}F](^2A')$, C_s, E =-552.10686

N	-0.266159	0.512252	0.000000
O	-1.074163	-0.281836	0.000000
F	1.100524	-0.140284	0.000000

22 [S=N-F]($^2A'$), C_s, E = -554.49794

N	0.339792	0.644156	0.000000
S	-1.013597	-0.127473	0.000000
F	1.455315	-0.260264	0.000000

23 [Se=N-F]($^2A'$), C_s, E = -654.19247

N	0.927363	0.675608	0.000000
Se	-0.625879	-0.046976	0.000000
F	1.949222	-0.300363	0.000000

24 [O=N(F)-F]$^{\cdot}$($^2B_2$), C_{2v}, E = -329.1091518

N	-0.207944	-0.296894	0.000000
O	-1.301412	0.112345	0.000000
F	0.624469	0.062123	1.113010
F	0.624469	0.062123	-1.113010

25 [S=N(F)-F]$^{\cdot}$($^2B_2$), C_{2v}, E = -651.7784469

N	-0.337047	-0.254575	-0.254575
S	0.048210	1.323659	1.323659
F	0.083647	-1.019962	-1.019962
F	0.083647	-1.019962	-1.019962

26 [Se=N(F)-F]$^{\cdot}$($^2B_2$), C_{2v}, E = -2654.19247

N	-0.413279	-0.863602	-0.863602
Se	0.020681	0.896447	0.896447
F	0.108810	-1.567179	-1.567179
F	0.108810	-1.567179	-1.567179

N1 NF, $C_{\infty v}$, E = -154.28771

F	0.000000	0.000000	0.559270
N	0.000000	0.000000	-0.758779

N2 NFH, C_s, E = -154.91563

N	0.757030	0.078043	0.000000
F	-0.611013	-0.008666	0.000000
H	0.999702	-0.920992	0.000000

N3 NF_2, C_{2v}, $^2B_2$, E = -254.03487

N	0.000000	0.000000	0.612141
F	0.000000	-1.055333	-0.225594
F	0.000000	1.055333	-0.225594

N4 C=NF, $C_{\infty v}$, E = -192.32890

C	0.000000	0.000000	1.415406
N	0.000000	0.000000	0.236921
F	0.000000	0.000000	-1.068642

N5 NFH_2, C_s, E = -155.57186

N	-0.082222	0.759250	0.000000
H	0.490497	0.993624	0.807740
H	0.490497	0.993624	-0.807740
F	0.008563	-0.665037	0.000000

N6 NF_2H, C_s, E = -254.66543

N	-0.610607	-0.089533	0.000000
F	0.251623	0.010313	-1.090954
F	0.251623	0.010313	1.090954
H	-1.002638	0.855181	0.000000

N7 NF_3, C_{3v}, E = -353.77212

N	0.488966	0.000000	0.000000
F	-0.120133	0.613201	-1.062095
F	-0.120133	0.613201	1.062095
F	-0.120133	-1.226402	0.000000

N8 CH_3-NFH, C_1, E = -194.83044

C	-1.218330	-0.286903	0.015995
N	-0.078160	0.608940	-0.089519
H	-1.171566	-0.934139	0.893399
H	-1.275185	-0.890077	-0.885953
H	-2.103964	0.346926	0.071235
F	1.068386	-0.248442	0.009889
H	0.003120	1.115923	0.788262

N9 CH_3-NF_2, C_s, E = -293.93275

C	-1.378180	0.136167	0.000000
N	-0.059810	-0.486760	0.000000
H	-1.285876	1.220043	0.000000
H	-1.889813	-0.217293	0.890498
H	-1.889813	-0.217293	-0.890498
F	0.591651	0.115550	1.086817
F	0.591651	0.115550	-1.086817

N10 $(CH_3)_2$-NF, C_s, E = -234.09116

N	-0.104047	0.444225	0.000000
C	-0.698165	-0.119829	1.200063
C	-0.698165	-0.119829	-1.200063
F	1.227763	-0.093390	0.000000
H	-0.228332	0.326230	2.072380
H	-0.228332	0.326230	-2.072380
H	-1.768541	0.094574	1.211153
H	-1.768541	0.094574	-1.211153
H	-0.539583	-1.199887	1.211153
H	-0.539583	-1.199887	-1.211153

N11 HN=NF, cis C_s, E = -209.64397

N	-1.138221	0.250296	0.000000
N	-0.247140	-0.545864	0.000000
F	1.063828	0.153010	0.000000
H	-0.805419	1.222339	0.000000

N12 HN=NF, tr, C_s, E = -209.64137

N	-1.072280	0.326640	0.000000
N	-0.205214	-0.517622	0.000000
F	1.044826	0.151729	0.000000
H	-1.945944	-0.206654	0.000000

N13 FN=NF, cis C_{2h}, E = -308.72897

N	0.000000	-0.609454	-0.725495
N	0.000000	0.609454	-0.725495
F	0.000000	1.176652	0.534738
F	0.000000	-1.176652	0.534738

N14 FN=NF, tr C_{2h}, E = -308.72719

N	-0.384864	0.476906	0.000000
N	0.384864	-0.476906	0.000000
F	1.645988	0.082190	0.000000
F	-1.645988	-0.082190	0.000000

N15 CH_2=NF, C_s, E = -193.61410

C	-1.146858	0.275087	0.000000
N	-0.185142	-0.553605	0.000000
F	1.026807	0.171661	0.000000
H	-0.997094	1.345316	0.000000
H	-2.131271	-0.164702	0.000000

N16 O=N(H_2)-F($^1A'$), C_s, E = -230.67087

N	-0.287152	0.475159	0.000000
O	-1.209028	-0.326349	0.000000
F	1.238556	-0.179847	0.000000
H	-0.084972	0.983830	-0.863135
H	-0.084972	0.983830	0.863135

N17 O=N(H)(F)-F($^1A'$), C_s, E = -329.78023

N	0.240322	0.321505	0.000000
O	1.311911	-0.158002	0.000000
H	0.074366	1.333938	0.000000
F	-0.642793	-0.087355	-1.129377
F	-0.642793	-0.087355	1.129377

N18 O=N(F_2)-F($^1A_1$), C_{3v}, E = -428.87494

N	0.216239	0.000000	0.000000
O	1.372836	0.000000	0.000000
F	-0.438395	0.631994	-1.094646
F	-0.438395	0.631994	1.094646
F	-0.438395	-1.263988	0.000000

N19 S=N(H_2)-F($^1A'$), C_s, E = -553.32478

N	0.231658	0.643593	0.000000
S	-1.165316	-0.174003	0.000000
F	1.732162	-0.296989	0.000000
H	0.548372	1.088120	-0.850223

H	0.548372	1.088120	0.850223

N20 S=N(H)(F)-F($^1A'$), C_s, E = -652.40695

N	0.380484	-0.198337	0.000000
S	-0.069614	1.345029	0.000000
H	1.361773	-0.460608	0.000000
F	-0.117764	-1.046451	1.121973
F	-0.117764	-1.046451	-1.121973

N21 S=N(F_2)-F($^1A_1$), C_{3v}, E = -751.49018

N	0.133392	0.000000	0.000000
S	-1.480932	0.000000	0.000000
F	0.797972	-0.625426	-1.083270
F	0.797972	-0.625426	1.083270
F	0.797972	1.250853	0.000000

N22 Se=N(H_2)-F($^1A'$), C_s, E = -2555.72656

N	0.854346	0.702742	0.000000
Se	-0.723241	-0.068922	0.000000
F	2.285746	-0.348167	0.000000
H	1.195601	1.132187	-0.846576
H	1.195601	1.132187	0.846576

N23 Se=N(H)(F)-F($^1A'$), C_s, E = -2654.80561

N	0.382820	-0.821828	0.000000
Se	-0.024465	0.923496	0.000000

H	1.365128	-1.083254	0.000000
F	-0.125835	-1.610735	1.102113
F	-0.125835	-1.610735	-1.102113

N24 Se=NF_2-F($^1A_1$), C_{3v}, E = -2753.88915

N	0.720651	0.000000	0.000000
Se	-1.092767	0.000000	0.000000
F	1.355181	-0.619382	-1.072800
F	1.355181	-0.619382	1.072800
F	1.355181	1.238763	0.000000

R1 NH_2OH, C_s, E = -131.58453

N	0.090087	-0.728962	0.000000
O	-0.075530	0.704266	0.000000
H	0.833175	1.012324	0.000000
H	-0.443075	-1.030537	0.808455
H	-0.443075	-1.030537	-0.808455

R2 HNO, C_s, E = -130.34007

N	-0.608238	-0.085137	0.000000
O	0.596800	0.019002	0.000000
H	-1.020584	0.881344	0.000000

R3 FHF^-, $D_{\infty h}$, E = -200.1986485

F	0.000000	0.000000	1.137693
F	0.000000	0.000000	-1.137693

H	0.000000	0.000000	0.000000

R4 HF, $C_{\infty v}$, E = -100.3636068

F	0.000000	0.000000	0.046303
H	0.000000	0.000000	-0.872851

Table S8: Atomic Cartesian coordinates (in Å) of molecules 36-74 at U/R-ωB97XD/6-31++G(d,p) level of theory.

21	[O=N-F]($^2A'$), C_s		
N	0.000000	0.555566	0.000000
O	1.063786	0.187280	0.000000
F	-0.945588	-0.598578	0.000000
22	[S=N-F]($^2A'$), C_s		
N	0.000000	0.721192	0.000000
S	-0.783791	-0.604317	0.000000
F	1.393406	0.513414	0.000000
23	[Se=N-F]($^2A'$), C_s		
N	0.579206	-0.915178	0.000000
Se	0.000000	0.677716	0.000000
F	-0.450493	-1.848455	0.000000
24	[O=N(F)-F]$^{\cdot}$($^2B_2$), C_{2v}		
N	0.195485	0.281271	0.000000
O	-0.610890	1.125914	0.000000
F	0.195485	-0.609789	1.104184
F	0.195485	-0.609789	-1.104184
25	[S=N(F)-F]$^{\cdot}$($^2B_2$), C_{2v}		
N	0.277238	0.000011	0.302939
S	-1.295753	-0.000007	-0.043432

F	1.043976	-1.075974	-0.079202
F	1.043956	1.075978	-0.079205

26 [Se=N(F)-F]$^{\cdot}$($^2B_2$), C_{2v}

N	0.730293	-0.474484	0.000000
Se	-0.536980	0.801341	0.000000
F	0.730293	-1.329124	1.075207
F	0.730293	-1.329124	-1.075207

27 [(F-TEDA)]$^{\cdot+}$, C_1

C	1.234661	-0.653502	-1.242307
C	-0.301208	-0.470324	-1.192642
N	-0.637007	0.397716	-0.000160
H	1.680698	-0.102516	-2.065869
H	1.499815	-1.700996	-1.353514
H	-0.829129	-1.409296	-1.058738
H	-0.692513	0.027396	-2.077022
C	-0.270488	-0.335123	1.270622
H	-0.967788	-1.158711	1.388439
H	-0.414685	0.369942	2.086874
C	-2.079211	0.803077	0.000571
H	-2.255839	1.394128	0.894291
N	1.784027	-0.155062	0.000524
C	0.190358	1.663638	-0.080724
H	-0.158989	2.335993	0.699340
C	1.680729	1.284451	0.092640

H	2.066478	1.601883	1.057500
C	1.196377	-0.810674	1.149525
H	1.259414	-1.885877	1.006465
H	1.766847	-0.553420	2.037611
Cl	-3.185168	-0.564257	0.000468
H	-2.256365	1.396061	-0.891845
H	-0.014330	2.111039	-1.050925
F	3.692815	-0.573138	0.001485
H	2.292465	1.737143	-0.682596

28 $[(\text{F-TEDA})]^{2+}$, C_1

C	1.188647	-0.913206	-1.141334
C	-0.220815	-0.312141	-1.274247
N	-0.573638	0.410204	0.000800
H	1.790379	-0.740448	-2.030240
H	1.184024	-1.975101	-0.908147
H	-0.957834	-1.092823	-1.441622
H	-0.281928	0.410827	-2.084827
C	-0.264267	-0.485148	1.174702
H	-0.762275	-1.434966	1.004360
H	-0.678862	-0.032278	2.072086
C	-2.033665	0.842390	-0.001275
H	-2.189428	1.442493	0.892099
N	1.855669	-0.212412	-0.001027
C	0.283338	1.646817	0.104135
H	0.142202	2.062475	1.099255

C	1.752587	1.270034	-0.159192
H	2.425283	1.725128	0.563541
C	1.261937	-0.644756	1.300808
H	1.549393	-1.680521	1.463475
H	1.699268	-0.022151	2.077507
Cl	-3.127097	-0.519287	-0.000408
H	-2.187944	1.437908	-0.897894
H	-0.060081	2.371110	-0.630562
F	3.180261	-0.551593	-0.002953
H	2.085317	1.512078	-1.165508

29 $[(\text{F-TEDA})(\text{BF}_4)]^{\cdot}$, C_1

N	-0.568753	0.778261	0.293537
C	-1.635448	-0.707313	-1.377454
C	-1.304266	-1.517691	0.849037
N	-2.263966	-0.988544	-0.102412
C	-0.407203	-0.350790	1.296538
C	-0.442457	0.235550	-1.114315
H	-2.377932	-0.265313	-2.037156
H	-1.838455	-1.950799	1.690367
H	0.510957	-0.280449	-1.164721
H	-1.291714	-1.639997	-1.814922
H	-0.712324	-2.288938	0.365063
H	-0.711993	0.061531	2.256928
H	-0.431006	1.090254	-1.783790
C	-1.948086	1.346348	0.470801

H	-2.109085	2.063118	-0.328065
H	-1.972521	1.872909	1.422234
C	-2.953356	0.172123	0.419261
H	-3.341526	-0.073317	1.404168
H	-3.793925	0.402741	-0.228777
C	0.514594	1.769297	0.578679
H	1.462889	1.311554	0.305275
H	0.472901	2.009718	1.635902
Cl	0.321547	3.270623	-0.339427
H	0.643301	-0.627430	1.334366
F	-3.717557	-2.274128	-0.380137
F	2.657857	0.134511	-0.869048
F	2.629269	-0.597761	1.293097
F	1.678901	-1.869118	-0.357406
B	2.784001	-1.023212	-0.052182
F	3.972697	-1.658313	-0.253046

30 $[(\text{F-TEDA})(\text{BF}_4)]^+$, C_1

N	1.110715	-0.365424	0.310391
C	0.445866	1.307763	-1.406173
C	-0.292979	1.597870	0.915539
N	0.668406	2.050807	-0.132964
C	0.153672	0.194016	1.338608
C	0.564129	-0.188949	-1.084084
H	1.190839	1.663021	-2.112984
H	-0.237660	2.308635	1.734665

H	-0.410145	-0.669225	-1.108159
H	-0.562099	1.537160	-1.742334
H	-1.286508	1.581564	0.473128
H	0.687128	0.201849	2.286215
H	1.251697	-0.681314	-1.764253
C	2.393356	0.398875	0.414317
H	3.042275	0.079095	-0.394509
H	2.868691	0.156326	1.361162
C	2.076770	1.905484	0.333284
H	2.144886	2.404286	1.295985
H	2.711165	2.415239	-0.385837
C	1.266814	-1.834565	0.623747
H	0.296302	-2.289307	0.437056
H	1.549833	-1.914541	1.669272
Cl	2.501525	-2.600287	-0.363665
H	-0.719050	-0.450974	1.401197
F	0.450062	3.386061	-0.373612
F	-1.772297	-1.652517	-0.043249
F	-2.756410	-0.038088	1.241039
F	-2.297025	0.384533	-0.953527
B	-2.782085	-0.618236	-0.040319
F	-3.984606	-1.094033	-0.406219

31 $[(\text{F-TEDA})(\text{BF}_4)_2]^{\cdot -}$, C_1

H	-1.211774	2.233558	2.218731
C	-1.206632	1.770114	1.236086

C	-1.218575	0.227660	1.329214
H	-2.065469	2.117661	0.670219
N	0.000002	2.175853	0.545821
H	-2.098232	-0.200119	0.861592
H	-1.155969	-0.120773	2.355664
N	0.000000	-0.294989	0.620853
C	1.206629	1.770112	1.236098
C	0.000009	1.730638	-0.832549
C	1.218575	0.227657	1.329215
C	-0.000002	-1.782808	0.534729
C	0.000001	0.187659	-0.821889
H	1.211757	2.233549	2.218747
H	2.065472	2.117665	0.670244
H	0.892705	2.107097	-1.321825
H	-0.892677	2.107106	-1.321836
H	2.098231	-0.200118	0.861587
H	1.155972	-0.120784	2.355662
Cl	-0.000006	-2.567477	2.131284
H	-0.906837	-2.074550	0.013276
H	0.906833	-2.074553	0.013280
H	0.898431	-0.215227	-1.278050
H	-0.898433	-0.215218	-1.278048
F	4.152330	-0.379705	0.313582
F	3.026217	0.727593	-1.342731
F	2.712886	-1.523486	-1.053577
F	4.712668	-0.742691	-1.890599

B	3.687006	-0.479759	-1.009648
F	0.000004	4.147361	0.679243
F	-2.712890	-1.523487	-1.053574
F	-4.152328	-0.379694	0.313580
F	-4.712669	-0.742687	-1.890598
F	-3.026212	0.727592	-1.342738
B	-3.687005	-0.479756	-1.009650

32 [(F-TEDA)(BF_4)$_2$], C_1

H	1.226802	-0.871531	2.785876
C	1.237496	-0.830695	1.701017
C	1.211160	0.610244	1.165509
H	2.086943	-1.375227	1.296660
N	-0.000050	-1.514920	1.230641
H	2.097518	0.807230	0.572944
H	1.142546	1.330318	1.973733
N	0.000033	0.792096	0.303303
C	-1.237509	-0.830582	1.701079
C	-0.000095	-1.648363	-0.249037
C	-1.211126	0.610323	1.165477
C	0.000084	2.129766	-0.377616
C	0.000010	-0.225067	-0.820139
H	-1.226726	-0.871358	2.785939
H	-2.087029	-1.375080	1.296825
H	-0.908565	-2.174469	-0.522756
H	0.908260	-2.174642	-0.522802

H	-2.097460	0.807291	0.572871
H	-1.142529	1.330442	1.973661
Cl	0.000134	3.473411	0.766495
H	0.904163	2.176519	-0.977877
H	-0.903990	2.176587	-0.977878
H	-0.904113	-0.050124	-1.396628
H	0.904178	-0.050222	-1.396585
F	-4.009893	-0.047990	0.428039
F	-2.842627	-1.502082	-0.884564
F	-2.854341	0.733875	-1.388328
F	-4.763292	-0.522248	-1.700138
B	-3.674455	-0.340876	-0.908998
F	-0.000096	-2.784837	1.772253
F	2.854443	0.733938	-1.388230
F	4.009913	-0.048243	0.428055
F	4.763223	-0.522413	-1.700173
F	2.842434	-1.502058	-0.884664
B	3.674421	-0.340961	-0.909003

33 O=N($(CF_3)_2$)-F($^1A''$), C_s

N	0.163653	0.579922	0.000000
O	-0.168999	1.739127	0.000000
F	1.729982	0.381972	0.000000
C	-0.146641	-0.174604	1.326684
F	0.351613	-1.382456	1.320088
F	0.351613	0.538780	2.292923

F	-1.458988	-0.229377	1.420046
C	-0.146641	-0.174604	-1.326684
F	0.351613	-1.382456	-1.320088
F	-1.458988	-0.229377	-1.420046
F	0.351613	0.538780	-2.292923

34 S=N($(CF_3)_2$)-F($^1A''$), C_s

N	-0.109798	0.412379	0.000000
S	-1.373540	1.433182	0.000000
F	1.362032	1.197355	0.000000
C	0.124168	-0.371951	1.299730
F	1.250993	-1.033810	1.264616
F	0.124168	0.473619	2.289890
F	-0.875332	-1.224827	1.423865
C	0.124168	-0.371951	-1.299730
F	1.250993	-1.033810	-1.264616
F	-0.875332	-1.224827	-1.423865
F	0.124168	0.473619	-2.289890

35 Se=N($(CF_3)_2$)-F($^1A''$), C_s

N	-0.236253	-0.013069	0.000000
Se	0.059136	-1.798722	0.000000
F	-1.806867	0.361845	0.000000
C	0.142923	0.716543	1.289912
F	-0.256068	1.964561	1.264304
F	-0.411818	0.092981	2.291343

F	1.456211	0.686509	1.398308
C	0.142923	0.716543	-1.289912
F	-0.256068	1.964561	-1.264304
F	1.456211	0.686509	-1.398308
F	-0.411818	0.092981	-2.291343

36 O=N($(NO_2)_2$)-F(^1A), C_1

N	0.068833	-0.669249	-0.172925
O	0.252371	-1.376993	-1.075563
F	-0.001016	-1.310907	1.141854
N	1.319662	0.505917	0.131248
O	0.971024	1.391335	0.830722
O	2.313076	0.228602	-0.430953
N	-1.393265	0.307325	-0.175369
O	-2.092952	0.171944	0.755156
O	-1.438203	0.933890	-1.174032

37 S=N($(NO_2)_2$)-F(^1A), C_1

N	-0.023187	0.438765	0.280134
S	-0.496636	1.866118	-0.236668
F	0.167671	0.245420	1.661718
N	-1.179656	-0.933575	-0.036062
O	-0.734618	-1.993095	0.234487
O	-2.194765	-0.535747	-0.461633
N	1.403201	-0.248261	-0.351503
O	2.251494	-0.422093	0.440323

O	1.307218	-0.407211	-1.515271

38 Se=N($(NO_2)_2$)-F(^1A), C_1

N	-0.039270	-0.130801	0.348982
Se	1.679761	-0.064935	-0.079283
F	-0.381514	-0.267318	1.680350
N	-0.998126	1.430122	-0.043216
O	-2.151628	1.340998	0.187104
O	-0.279229	2.259128	-0.444866
N	-0.991704	-1.232262	-0.388485
O	-1.427189	-2.060418	0.324548
O	-1.076272	-1.021681	-1.547848

39 O=N($(CN)_2$)-F($^1A''$), C_s

N	-0.210722	0.340739	0.000000
O	-1.015468	1.247892	0.000000
F	1.338019	0.856405	0.000000
C	-0.093976	-0.435579	1.183158
N	-0.093976	-1.060644	2.140987
C	-0.093976	-0.435579	-1.183158
N	-0.093976	-1.060644	-2.140987

40 S=N($(CN)_2$)-F($^1A''$), C_s

N	-0.070153	0.050536	0.000000
S	-0.993124	1.392956	0.000000
F	1.699396	0.416013	0.000000

C	0.041788	-0.683584	1.166036
N	0.041788	-1.298726	2.131723
C	0.041788	-0.683584	-1.166036
N	0.041788	-1.298726	-2.131723

41 Se=N($(CN)_2$)-F($^1A''$), C_s

N	0.193058	-0.351840	0.000000
Se	-0.788230	1.140725	0.000000
F	1.988390	0.026394	0.000000
C	0.290496	-1.078178	1.162097
N	0.290496	-1.687227	2.132428
C	0.290496	-1.078178	-1.162097
N	0.290496	-1.687227	-2.132428

42 O=N($(CH_3)_2$)-F($^1A''$), C_s

N	-0.219128	0.088053	0.000000
O	-0.889633	1.103814	0.000000
F	1.407908	0.461821	0.000000
C	-0.219128	-0.700514	1.254502
H	0.544197	-1.467512	1.205336
H	-0.024506	-0.000839	2.058024
H	-1.215025	-1.130207	1.350019
C	-0.219128	-0.700514	-1.254502
H	0.544197	-1.467512	-1.205336
H	-1.215025	-1.130207	-1.350019
H	-0.024506	-0.000839	-2.058024

43 S=N($(CH_3)_2$)-F($^1A''$), C_s

N	0.184523	-0.073953	0.000000
S	-1.493642	-0.012375	0.000000
F	0.807803	1.369149	0.000000
C	0.807803	-0.603304	1.232092
H	1.881343	-0.443886	1.184188
H	0.369424	-0.077089	2.071282
H	0.570607	-1.662541	1.286862
C	0.807803	-0.603304	-1.232092
H	1.881343	-0.443886	-1.184188
H	0.570607	-1.662541	-1.286862
H	0.369424	-0.077089	-2.071282

44 Se=N($(CH_3)_2$)-F($^1A''$), C_s

N	0.722580	-0.045782	0.000000
Se	-1.193048	0.031922	0.000000
F	1.288389	1.290509	0.000000
C	1.288389	-0.640978	1.226501
H	2.373648	-0.562709	1.191503
H	0.880087	-0.102516	2.073817
H	0.970968	-1.678635	1.259692
C	1.288389	-0.640978	-1.226501
H	2.373648	-0.562709	-1.191503
H	0.970968	-1.678635	-1.259692
H	0.880087	-0.102516	-2.073817

45 O=N($(NH_2)_2$)-F(^1A), C_1

N	-0.000143	-0.175604	0.127599
O	-0.000678	-0.824715	1.135929
F	0.001115	1.399947	0.366835
N	1.232287	-0.228391	-0.616556
H	1.151687	0.396055	-1.408237
H	1.325084	-1.192432	-0.916794
N	-1.232632	-0.226423	-0.616592
H	-1.150978	0.397829	-1.408320
H	-1.326995	-1.190334	-0.916761

46 S=N($(NH_2)_2$)-F(^1A), C_1

N	-0.246045	-0.069039	-0.026549
S	1.481000	0.067537	-0.018782
F	-0.810075	0.574973	1.201461
N	-0.973460	0.690711	-1.020807
H	-0.357409	0.665342	-1.828423
H	-0.956020	1.642953	-0.670918
N	-0.725229	-1.351546	0.003943
H	-1.514906	-1.451559	-0.614782
H	0.036155	-2.002973	-0.094613

47 Se=N($(NH_2)_2$)-F(^1A), C_1

N	-0.760842	-0.055478	-0.005240
Se	1.185498	0.014719	-0.011711

F	-1.258545	0.577927	1.200358
N	-1.439540	0.727986	-1.002510
H	-0.895041	0.560999	-1.844960
H	-1.260143	1.691449	-0.736598
N	-1.260854	-1.324103	-0.006239
H	-2.076256	-1.398210	-0.595365
H	-0.519923	-1.994868	-0.130193

48 O=N($(OH)_2$)-F($^1A''$), C_s

N	-0.121525	0.114530	0.000000
O	-0.459068	1.263608	0.000000
F	1.406488	0.010090	0.000000
O	-0.459068	-0.680503	1.085708
H	-0.395047	-0.056673	1.821272
O	-0.459068	-0.680503	-1.085708
H	-0.395047	-0.056673	-1.821272

49 S=N($(OH)_2$)-F($^1A'$), C_s

N	0.270949	-0.048483	0.000000
S	-1.458495	0.024706	0.000000
F	0.847129	1.273323	0.000000
O	0.847129	-0.641602	1.086396
H	0.130525	-0.625089	1.738477
O	0.847129	-0.641602	-1.086396
H	0.130525	-0.625089	-1.738477

50 Se=N($(OH)_2$)-F($^1A'$), C_s

N	0.769088	-0.052435	0.000000
Se	-1.168285	0.024730	0.000000
F	1.325471	1.252428	0.000000
O	1.325471	-0.652172	1.085056
H	0.600664	-0.655438	1.728848
O	1.325471	-0.652172	-1.085056
H	0.600664	-0.655438	-1.728848

N16 O=N(H_2)-F($^1A'$), C_s

N	0.000000	0.498324	0.000000
O	1.191490	0.271256	0.000000
F	-0.963666	-0.817866	0.000000
H	-0.429464	0.851239	0.862347
H	-0.429464	0.851239	-0.862347

N17 O=N(H)(F)-F($^1A'$), C_s

N	0.178416	0.319592	0.000000
O	-0.703709	1.087138	0.000000
H	1.169269	0.598600	0.000000
F	0.178416	-0.640714	1.122500
F	0.178416	-0.640714	-1.122500

N18 O=N(F_2)-F($^1A_1$), C_{3v}

N	0.000000	0.000000	0.196796
O	0.000000	0.000000	1.349540

F	0.000000	1.259186	-0.450885
F	1.090487	-0.629593	-0.450885
F	-1.090487	-0.629593	-0.450885

N19 S=N(H_2)-F($^1A'$), C_s

N	0.000000	0.651518	0.000000
S	0.937446	-0.673372	0.000000
F	-1.655897	0.422357	0.000000
H	-0.048029	1.206051	0.846676
H	-0.048029	1.206051	-0.846676

N20 S=N(H)(F)-F($^1A'$), C_s

N	0.422203	-0.026110	0.000000
S	-0.747035	1.091756	0.000000
H	1.397491	0.268113	0.000000
F	0.422203	-0.975191	1.104902
F	0.422203	-0.975191	-1.104902

N21 S=N(F_2)-F($^1A_1$), C_{3v}

N	0.000000	0.000000	-0.165102
S	0.000000	0.000000	1.449998
F	0.000000	1.242782	-0.816454
F	1.076281	-0.621391	-0.816454
F	-1.076281	-0.621391	-0.816454

N22 Se=N(H_2)-F($^1A'$), C_s

N	-0.493769	-0.974328	0.000000
Se	0.000000	0.804480	0.000000
F	0.603979	-2.001319	0.000000
H	-0.989713	-1.260071	0.837491
H	-0.989713	-1.260071	-0.837491

N23 Se=N(H)(F)-F($^1A'$), C_s

N	0.723846	-0.459165	0.000000
Se	-0.581738	0.819443	0.000000
H	1.682923	-0.114187	0.000000
F	0.723846	-1.362929	1.090777
F	0.723846	-1.362929	-1.090777

N24 Se=NF_2-F($^1A_1$), C_{3v}

N	0.000000	0.000000	-0.678772
Se	0.000000	0.000000	1.167476
F	0.000000	1.232045	-1.294177
F	1.066983	-0.616023	-1.294177
F	-1.066983	-0.616023	-1.294177

R1a H_2N-OH($^1A'$), C_s

N	-0.009592	0.696408	0.000000
O	-0.009592	-0.729138	0.000000
H	-0.942273	-0.944955	0.000000
H	0.543074	0.951603	0.811098
H	0.543074	0.951603	-0.811098

R2a HN=O($^1A'$), C_s

N	0.062556	0.574756	0.000000
O	0.062556	-0.617233	0.000000
H	-0.938336	0.914576	0.000000

5 H_2N-F($^1A'$), C_s

F	0.000000	0.000000	1.144378
F	0.000000	0.000000	-1.144378
H	0.000000	0.000000	0.000000

R3a F$\cdots$H$\cdots$F$^-$($^1\Sigma_g^+$), $D_{\infty h}$

F	0.000000	0.000000	0.091845
H	0.000000	0.000000	-0.826602

R4a F-H($^1\Sigma^+$), $C_{\infty v}$

N	0.671232	0.000000	-0.140055
H	0.947107	-0.810947	0.409679
H	0.947108	0.810947	0.409679
F	-0.732538	0.000000	0.017892

A1a BF_4(T_1), T_d

B	0.000000	0.000000	0.000000
F	0.813250	0.813250	0.813250
F	-0.813250	-0.813250	0.813250
F	-0.813250	0.813250	-0.813250

F	0.813250	-0.813250	-0.813250

References

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