Supporting Information

Complementary Base Lowers the Barrier in SuFEx Click Chemistry for Primary Amine Nucleophiles

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Table of contents

1) Method benchmark S2
2) Alternative base catalysed TS structure S3
3) Final structures S4
4) Electronic reaction energies S5
5) Structure & output repository S5
6) Energy decomposition analysis S6
7) ADF sample input S7
8) Animated IRC S9
9) Cartesian coordinates, total energies and number of imaginary frequencies S10
10) References S19

1) Method benchmark

We benchmark the performance of several density functionals against advanced wave function-based approaches. The structures on which the benchmark was performed are not strictly identical to those reported in the main document.

Table S1. Stationary points on the SuFEx reaction path calculated with different density functionals and wave function-based methods using structures optimized by PBE-D3.

	PBE-D3	TPSS-D3[SS1]	PBE0-D3	B3LYP-D3[SS2]	M06 [SS3]	MP2 [SS4]	CCSD [SS4]	CCSD(T) [SS4]
∑(products)	1	10	-8	-5	-7	-18	-14	-14
pre-complex	-31	-28	-30	-30	-25	-28	-25	-27
TS	108	118	146	136	161	158	187	163
post-complex	-41	-29	-43	-40	-31	-49	-38	-43
MAE[b]	19.1	20.8	6.4	10.6	5.9	5.2	7.9	-
ΔE^o	-10	-1	-13	-10	-6	-22	-13	-16
$\Delta E^{\ddagger}$	139	146	176	166	186	180	211	190

[a] All calculations using def2-TZVPP basis set. Energies in kJ/mol.
[b] Mean absolute error (MAE) calculated with respect to the CCSD(T) energy of the three stationary points and the sum of products.

Within our small test set, the M06 functional agrees best with CCSD(T). PBE0-D3 is a close second and chosen over M06 as it contains fewer fit parameters.

2) Alternative base catalysed TS structure

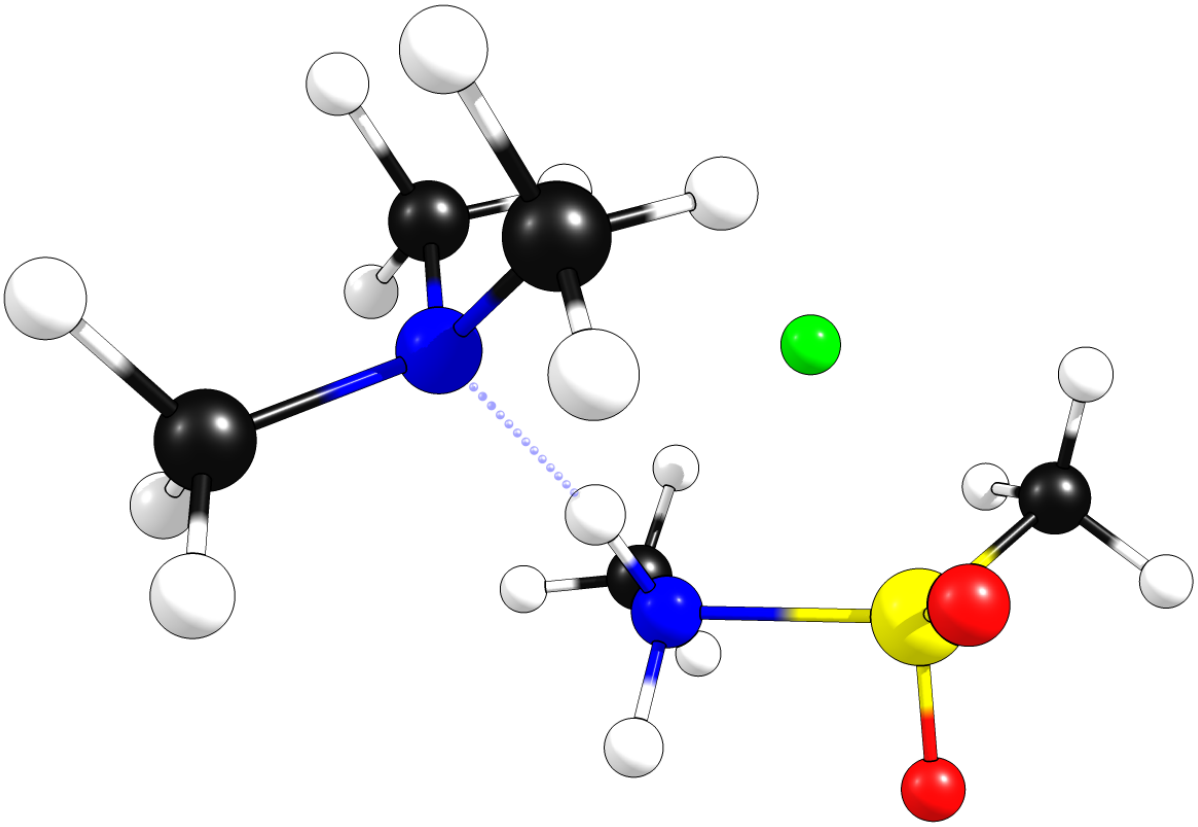


Figure S1. Alternative optimized (PBE-D3/def2-TZVPP) structure of the TS including $N(CH_3)_3$. This structure is less stable by 11 kJ/mol (ΔE) and 18 kJ/mol (ΔG) with respect to the structure given in the main manuscript.

3) Final structures

The endpoints of the reaction path calculations (IRC) are not the energetically optimal structures. Rearrangements of adducts can lead to more stable structures (lowest-energy minima). The reaction paths for these rearrangements have not been investigated, thus only thermodynamic data are given in Figure S2. Reaction energies in the main text (Table 2) are given with respect to the lowest-energy minima shown here.

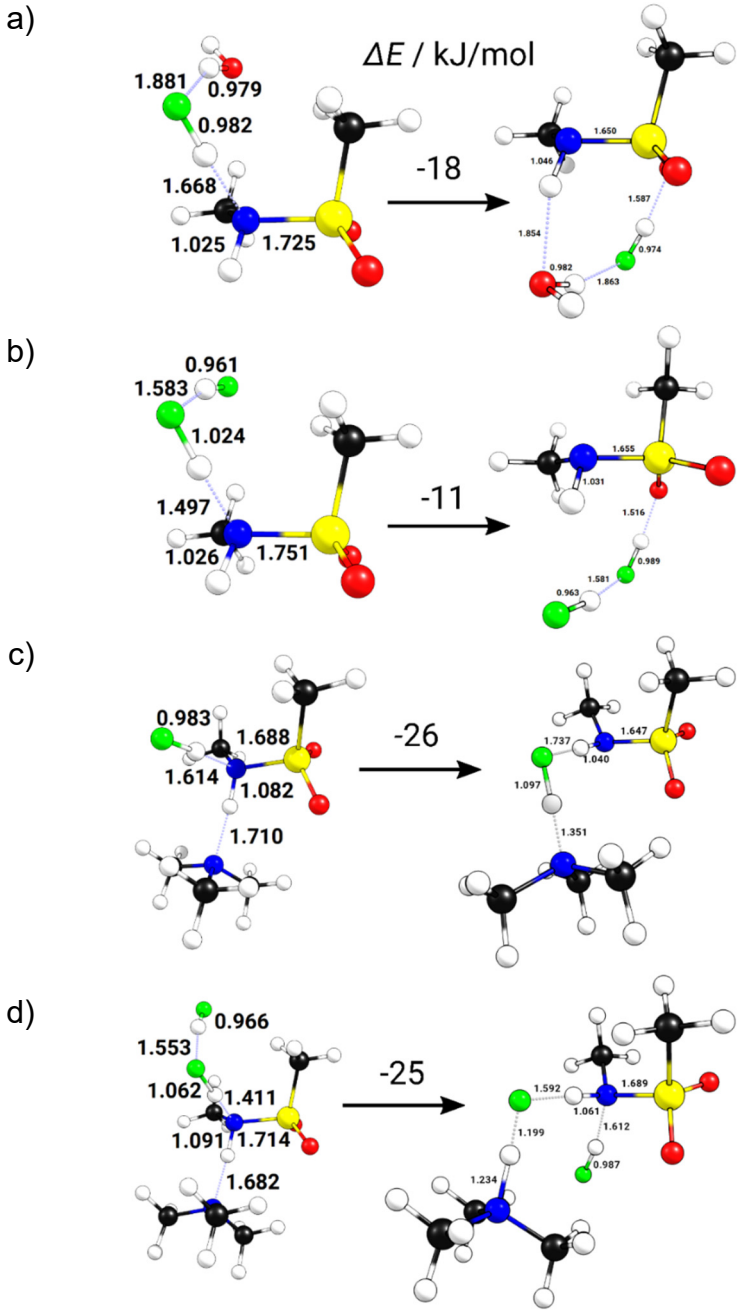


Figure S2. Optimized (PBE-D3/def2-TZVPP) structures of the IRC endpoints (left)and the most stable minima (right) found for post-complexes with additional **a)** H_2O, **b)** HF, **c)** $N(CH_3)_3$ and **d)** HF + $N(CH_3)_3$.

4) Electronic reaction energies

Table S2. Reaction energies (ΔE^0) and barriers ($\Delta E^{\ddagger}$) of the SuFEx reaction showing the influence of solvent (H_2O), side-product (HF) and base ($N(CH_3)_3$).

Solvent[a]	ΔE^o	$\Delta\Delta E^o$	$\Delta E^{\ddagger}$	$\Delta\Delta E^{\ddagger}$
in vacuo	-37	0	159	0
+H_2O (implicit)	-51	-14	145	-14
+H_2O (explicit)	-47	-10	147	-12
+HF	-12	25	169	10
+$N(CH_3)_3$	-72	-35	124	-35
+HF & $N(CH_3)_3$	-40	-3	125	-34

[a] All energies in kJ/mol at PBE0/def2-TZVPP//PBE/def2-TZVPP. Solvent correction at PBE/def2-TZVPP. Energies are given with respect to the pre- and post-complexes.

The S_N1 mechanism is not competitive due to a bond dissociation energy leading to fluorine anion of ΔE^o[+H_2O (implicit)] = 389 kJ/mol. Furthermore, a nucleophilic attack by $N(CH_3)_3$ with subsequent detachment of F^- is an endothermic process with a reaction energy of ΔE^o[+H_2O (implicit)] = 124 kJ/mol. This alternative pathway is therefore unfavorable when compared to the attack by **1**.

5) Structure & output repository

All structures computed and connected raw data can be accessed via the open-data repository NOMAD under the permanent link:

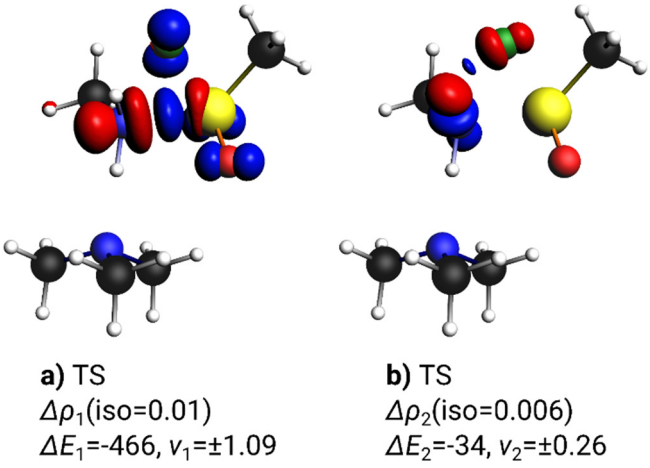
DOI: https://dx.doi.org/10.17172/NOMAD/2020.08.05-1

6) Energy decomposition analysis

Shown in Table S3 are EDA results for an alternative fragmentation scheme of **3** with a donor-acceptor picture of the S-N bond with an anionic amine fragment and a cationic sulfonyl fragment. The considerably higher orbital energy term (ΔE_{orb}) indicates that this fragmentation is a worse description of the bonding situation compared to the neutral fragmentation (electron-sharing bond) discussed in the main manuscript.

Table S3. EDA of **3** with ionic fragments.

	3	
	kJ/mol	%
ΔE_{int}	-1216	
ΔE_{Pauli}	1851	
ΔE_{elstat}	-1686	45
ΔE_{orb}	-1369	55



a) TS
$\Delta\rho_1$(iso=0.01)
ΔE_1=-466, v_1=±1.09

b) TS
$\Delta\rho_2$(iso=0.006)
ΔE_2=-34, v_2=±0.26

Figure S3. Selected deformation densities $\Delta\rho_i$ show charge flow between NOCVs of **TS** including $N(CH_3)_3$ and associated contributions to the total orbital energy (ΔE_i in kJ/mol). Eigenvalues v_i quantify the amount of transferred electron density (red: charge depletion, blue: charge accumulation). Iso-values are chosen for visual clarity. Bonding character of $\Delta\rho_i$ is a) LP(N) → p*(S) donor-acceptor bond, b) N-H---F hydrogen bond.

7) ADF sample input

```
Title Fragment-1
atoms
C       -1.09443      0.37015      1.37079
S        0.06532     -0.92532      0.96322
O        1.36096     -0.51978      1.48318
O       -0.52949     -2.20243      1.31729
H       -0.73518      1.31586      0.94975
H       -1.12288      0.43273      2.46469
H       -2.07542      0.10388      0.96595
end
symmetry NOSYM
Relativistic Scalar ZORA
SCF
 Mixing 0.2
 Iterations 300
End
 XC
  LDA LDA
  GGA PBE
  dispersion Grimme3 BJdamp
 END
 Basis
  Type TZ2P
  Core large
 End
NumericalQuality Good
UNRESTRICTED
IRREPOCCUPATIONS
   A 13 // 12
End

Title Fragment-2
atoms
C        1.11141     -0.08851     -1.37569
N        0.06724     -0.87545     -0.71265
H        2.13077     -0.40955     -1.11706
H        0.96131     -0.17303     -2.45911
H        1.00234      0.96903     -1.10396
H       -0.01551     -1.83698     -1.04366
end
symmetry NOSYM
Relativistic Scalar ZORA
SCF
 Mixing 0.2
 Iterations 300
End
 XC
  LDA LDA
  GGA PBE
  dispersion Grimme3 BJdamp
 END
 Basis
  Type TZ2P
  Core large
 End
NumericalQuality Good
UNRESTRICTED
IRREPOCCUPATIONS
   A 6 // 7
End

Title EDA-NOCV
atoms
C       -1.09443      0.37015      1.37079 f=f1
S        0.06532     -0.92532      0.96322 f=f1
O        1.36096     -0.51978      1.48318 f=f1
O       -0.52949     -2.20243      1.31729 f=f1
H       -0.73518      1.31586      0.94975 f=f1
H       -1.12288      0.43273      2.46469 f=f1
```

```
H        -2.07542       0.10388       0.96595 f=f1
C         1.11141      -0.08851      -1.37569 f=f2
N         0.06724      -0.87545      -0.71265 f=f2
H         2.13077      -0.40955      -1.11706 f=f2
H         0.96131      -0.17303      -2.45911 f=f2
H         1.00234       0.96903      -1.10396 f=f2
H        -0.01551      -1.83698      -1.04366 f=f2
end
charge 0
symmetry NOSYM
Relativistic Scalar ZORA
SCF
 Mixing 0.2
 Iterations 300
End
 XC
  LDA LDA
  GGA PBE
  dispersion Grimme3 BJdamp
 END
 Basis
  Type TZ2P
  Core large
 End
NumericalQuality Good
UNRESTRICTEDFRAGMENTS
UNRESTRICTED
fragments
f1 f1.t21
f2 f2.t21
end
ETSNOCV
End
PRINT ETSLOWDIN-Unrestricted
```

8) Animated IRC

The animated intrinsic reaction coordinate for the reaction of methylamine and sulfonylfluoride is found as animated gif in a separate file (SI.irc.gif).

9) Cartesian coordinates, total energies and number of imaginary frequencies

1

Energy = -95.77003465279 Eh, imaginary frequencies = 0

C	0.0516030	0.7048413	-0.0000000
N	0.0566021	-0.7615613	-0.0000000
H	-0.9476109	1.1815037	0.0000000
H	0.5951542	1.0679453	0.8834367
H	0.5951542	1.0679453	-0.8834367
H	-0.4470318	-1.1133916	-0.8151971
H	-0.4470318	-1.1133916	0.8151971

2

Energy = -688.0799266616 Eh, imaginary frequencies = 0

C	8.6683491	8.5879006	14.3196027
S	8.8238522	6.8426502	14.6113375
O	7.5414410	6.2004057	14.5073913
O	9.7250963	6.5958853	15.7043752
F	9.6300623	6.4661106	13.2640808
H	8.1012075	8.7378607	13.3956971
H	9.6713351	9.0214523	14.2570220
H	8.1235563	8.9959746	15.1786034

1-2

Energy = -783.854102 Eh, imaginary frequencies = 0

C	-1.208494	0.544828	2.140675
S	-0.380007	-0.103000	0.704385
O	1.043069	-0.007711	0.897141
O	-1.036987	-1.307870	0.275350
F	-0.810991	1.076336	-0.306644
H	-0.791181	1.530043	2.370834
H	-1.009470	-0.158770	2.956806
H	-2.281402	0.599283	1.931742
C	2.095733	0.266683	-2.161535
N	0.870408	-0.533561	-2.198707
H	2.665738	0.001670	-1.261708
H	2.762348	0.160456	-3.038651
H	1.828599	1.328861	-2.067045
H	1.088725	-1.529248	-2.232531
H	0.325162	-0.324208	-3.035009

TS

Energy = -783.8087896901 Eh, imaginary frequencies = 1

C	-1.2399847	0.5019112	1.9141760
S	-0.3244798	-0.5019132	0.7217433
O	1.0411018	-0.4682237	1.2390906
O	-1.0918601	-1.7269673	0.5453055
F	-1.3599833	1.1387748	-0.4781731
H	-0.7971118	1.4992398	1.9260735
H	-1.0875484	-0.0274446	2.8645997
H	-2.2818909	0.5279171	1.5956301
C	1.6040776	0.0172482	-1.4846806
N	0.2265130	-0.3850604	-1.2416100
H	2.2953680	-0.6360452	-0.9396991
H	1.8231204	-0.0277639	-2.5619706
H	1.7366690	1.0472985	-1.1369004
H	-0.0131188	-1.3217451	-1.5742280
H	-0.5320051	0.3629168	-1.3907929

3-HF

Energy = -783.8680749412 Eh, imaginary frequencies = 0

C	-0.6547039	0.7887153	1.3792012
S	0.0699190	-0.6224734	0.5716178
O	1.3970306	-0.8337002	1.1189684
O	-0.9027413	-1.6946145	0.5010035
F	-1.6016263	1.8153350	-1.5024361
H	0.0278305	1.6407573	1.2881810

H -0.7655750 0.5040836 2.4318314
H -1.6213014 1.0094036 0.9159737
C 1.4905364 0.5816704 -1.4059997
N 0.2051466 -0.0512683 -1.0500312
H 2.3498236 -0.0731302 -1.2141857
H 1.4483832 0.8508920 -2.4680988
H 1.6079591 1.5056516 -0.8278681
H 0.0004954 -0.8716159 -1.6292190
H -0.9811664 1.0809735 -1.3679584

3

Energy = -683.4558352012 Eh, imaginary frequencies = 0
C -1.0944306 0.3701538 1.3707924
S 0.0653164 -0.9253174 0.9632246
O 1.3609646 -0.5197811 1.4831754
O -0.5294902 -2.2024346 1.3172916
H -0.7351804 1.3158556 0.9497520
H -1.1228788 0.4327349 2.4646926
H -2.0754166 0.1038809 0.9659543
C 1.1114100 -0.0885077 -1.3756874
N 0.0672447 -0.8754451 -0.7126454
H 2.1307699 -0.4095533 -1.1170622
H 0.9613114 -0.1730274 -2.4591053
H 1.0023438 0.9690311 -1.1039578
H -0.0155142 -1.8369796 -1.0436648

HF

Energy = -100.3936173106 Eh, imaginary frequencies = 0
F -0.7369210 2.3513324 -0.8499349
H -0.3906690 1.4881976 -0.8542551

Precomplex benchmark

Energy = -783.8616672310 Eh, imaginary frequencies = 0
C 8.4172798 8.1182982 13.9396381
S 9.6805205 6.8878776 14.0845431
O 10.3652384 6.6788681 12.8366265
O 10.3983651 7.0427959 15.3259148
F 8.7204290 5.6001958 14.2890422
H 7.7752832 7.8553006 13.0928865
H 8.9374124 9.0648128 13.7497273
H 7.8800803 8.1449696 14.9046121
C 7.0051914 6.4384670 17.4030199
N 7.7199955 7.6814269 17.0830970
H 7.2252096 6.0185734 18.4011210
H 5.9224450 6.6139945 17.3407832
H 7.2586108 5.6763248 16.6541815
H 8.7290640 7.5224624 17.1231744
H 7.5116950 8.3976225 17.7798324

Postcomplex benchmark

Energy = -783.8654355793 Eh, imaginary frequencies = 0
C -1.3847573 0.1317828 1.4882784
S 0.1972966 -0.4894852 0.9530457
O 1.2611867 0.3492587 1.4632235
O 0.2325444 -1.9290973 1.1443379
F -0.7445286 2.3702996 -0.8498369
H -1.5044083 1.1609383 1.1316835
H -1.3582986 0.0930973 2.5834792
H -2.1721245 -0.5298264 1.1097333
C 1.3668743 -0.4050840 -1.4424320
N 0.0936900 -0.1304915 -0.7373326
H 1.6637246 -1.4612438 -1.3726393
H 1.2322023 -0.1287438 -2.4944020
H 2.1495757 0.2243142 -1.0069806
H -0.6510472 -0.7248077 -1.1172434
H -0.3830629 1.4692316 -0.8543517

1-2+H_2O

Energy = -860.2466089558 Eh, imaginary frequencies = 0
C -0.92308 0.41914 2.37017
S -0.02093 0.17772 0.86514
O 1.38204 -0.00497 1.11753

O	-0.74530	-0.72016	-0.00953
F	-0.20281	1.64731	0.24996
H	-0.44395	1.22751	2.93152
H	-0.85771	-0.52653	2.92083
H	-1.96306	0.64523	2.09907
C	2.69152	-0.45553	-2.21029
N	1.30984	-0.03358	-2.46288
H	2.86451	-0.47673	-1.12604
H	2.96965	-1.44627	-2.61881
H	3.38140	0.28728	-2.63543
H	0.65774	-0.70625	-2.05701
H	1.12249	-0.02149	-3.46616
O	-3.50656	0.23585	0.44312
H	-2.77068	-0.23323	0.00821
H	-3.77398	0.90895	-0.20047

TS+H_2O

Energy = -860.2058593847 Eh, imaginary frequencies = 1

C	-1.2138352	0.5133081	1.9036351
S	-0.4046711	-0.5446323	0.6822125
O	0.9495406	-0.6804556	1.2146411
O	-1.2715457	-1.6830113	0.4181375
F	-1.3977963	1.0559039	-0.5318598
H	-0.7435474	1.4978264	1.8578235
H	-0.9977738	0.0078983	2.8542489
H	-2.2805066	0.5531740	1.6584670
C	1.6331555	0.0907090	-1.4544274
N	0.2840021	-0.4315899	-1.2867948
H	2.3171963	-0.4406731	-0.7821464
H	1.9690323	-0.0302677	-2.4947915
H	1.6309335	1.1558968	-1.1992899
H	0.1560247	-1.3985436	-1.5929368
H	-0.4868718	0.2120557	-1.5688029
O	-3.9714773	0.4218734	0.1148322
H	-3.9255633	-0.5412967	0.0160406
H	-3.1189505	0.7283867	-0.2719648

3-HF+H_2O

Energy = -860.2644063825 Eh, imaginary frequencies = 0

C	-0.8839200	0.4974500	1.5999900
S	-0.1260300	-0.9314000	0.8561400
O	1.1933200	-1.1056400	1.4344100
O	-1.0834500	-2.0183000	0.8069900
F	-1.7943603	1.3987188	-1.3793739
H	-0.2036500	1.3513000	1.5085500
H	-1.0267900	0.2396900	2.6557800
H	-1.8370200	0.6981600	1.1007900
C	1.3105900	0.2257700	-1.1395400
N	0.0315100	-0.4198200	-0.7835500
H	2.1798000	-0.3931000	-0.8836700
H	1.2944200	0.4288000	-2.2169200
H	1.3869700	1.1861300	-0.6163700
H	-0.1433600	-1.2673100	-1.3327800
H	-1.1762900	0.6656300	-1.1666700
O	-0.0365236	3.1388469	-0.0641493
H	0.0749401	4.0491244	-0.3739740
H	-0.7588158	2.7678555	-0.6108532

Postcomplex+H_2O

Energy = -860.2699920221 Eh, imaginary frequencies = 0

C	7.9394756	8.5046288	14.0874823
S	9.0999897	7.4612966	14.9401213
O	9.0379403	6.1558631	14.2436450
O	10.3843683	8.1286720	15.0376590
F	10.1592238	4.3873945	15.7038503
H	6.9415677	8.0554599	14.1358884
H	8.2766704	8.5589445	13.0464045
H	7.9575080	9.4902373	14.5621338
C	7.3570413	6.4502531	16.6902727
N	8.4861174	7.3667195	16.4692651
H	7.0929585	6.5103468	17.7524400
H	6.4842809	6.7743697	16.1089145

H 7.5914549 5.4064213 16.4350443
H 9.3019237 7.1378709 17.0821530
H 9.7549435 5.0074364 15.0707733
O 10.8035380 6.2483551 17.7064858
H 11.5151648 6.7779780 17.3120288
H 10.7258330 5.4735725 17.1074577

H_2O
Energy = -860.2644063825 Eh, imaginary frequencies = 0
O -0.0365236 3.1388469 -0.0641493
H 0.0749401 4.0491244 -0.3739740
H -0.7588158 2.7678555 -0.6108532

1-2+HF
Energy = -884.2779825723 Eh, imaginary frequencies = 0
C -0.5958258 0.1114509 3.6488112
S -0.3843803 0.7426340 2.0030546
O 0.7784629 1.5856543 1.9351936
O -0.6113374 -0.3117352 1.0435811
F -1.6665074 1.6914371 1.9562628
H -0.5388792 0.9493275 4.3506547
H 0.2270499 -0.5923871 3.8178958
H -1.5614569 -0.4006926 3.7051219
C 1.8388498 1.2311224 -1.4439825
N 0.4199736 0.8964415 -1.6484930
H 1.9769489 1.5468439 -0.4031772
H 2.5260368 0.3956573 -1.6538575
H 2.1079501 2.0764168 -2.0896083
H 0.1322530 0.1470440 -1.0150564
H 0.2517866 0.5754769 -2.6021657
F -1.0623525 2.8655849 -0.9472542
H -0.5007522 2.1077435 -1.2619311

TS+HF
Energy = -884.2276478150 Eh, imaginary frequencies = 1
C -1.3133454 0.4366312 1.9492223
S -0.3394250 -0.4991832 0.7508587
O 1.0308061 -0.4005630 1.2335293
O -1.0632565 -1.7470628 0.5551151
F -1.1693673 1.2719986 -0.4223825
H -0.8799187 1.4349276 2.0266761
H -1.1837581 -0.1449811 2.8722807
H -2.3518463 0.4635409 1.6083262
C 1.5641364 0.0678927 -1.5225329
N 0.2301542 -0.4655162 -1.2709085
H 2.2973587 -0.4719827 -0.9136678
H 1.8229006 -0.0288135 -2.5874538
H 1.5699837 1.1264727 -1.2432806
H 0.0975237 -1.4441849 -1.5355665
H -0.5283295 0.1599870 -1.5854458
F -3.5953254 1.4241547 -0.0514110
H -2.6444156 1.4246603 -0.2612591

3-HF+HF
Energy = -884.2829952749 Eh, imaginary frequencies = 0
C -0.8845844 0.4942221 1.6452877
S -0.1586602 -0.9196493 0.8517054
O 1.1664528 -1.1385447 1.3951637
O -1.1306135 -1.9902557 0.7585009
F -1.6444640 1.4610870 -1.3578574
H -0.2545523 1.3750693 1.4729232
H -0.9215845 0.2420756 2.7115480
H -1.8897989 0.6469525 1.2398618
C 1.3203549 0.2409190 -1.1358148
N 0.0044894 -0.3537852 -0.7971891
H 2.1495664 -0.4174625 -0.8526466
H 1.3328786 0.4217295 -2.2173075
H 1.4155933 1.2063760 -0.6263198
H -0.1850992 -1.1951371 -1.3534154
H -1.0336295 0.6682507 -1.1412435
F -0.1604488 3.1126466 -0.1566600
H -0.7995002 2.6082963 -0.6677563

Postcomplex+HF

Energy = -884.2843517198 Eh, imaginary frequencies = 0

C	-0.9378910	0.7150071	1.6370515
S	-0.1762831	-0.8645731	1.3503287
O	1.1399373	-0.7821563	2.0314310
O	-1.0789709	-1.9336466	1.7149541
F	1.3955663	-3.4129648	-0.7078726
H	-0.3015330	1.5081528	1.2302675
H	-1.0242476	0.8232366	2.7239810
H	-1.9221502	0.7070298	1.1594123
C	1.1036085	-0.1311723	-0.8834624
N	-0.0013193	-0.9047860	-0.2949351
H	2.0933815	-0.4535224	-0.5306517
H	1.0499168	-0.2608706	-1.9701477
H	0.9719355	0.9356719	-0.6637665
H	0.0438486	-1.8990478	-0.5630563
H	1.9583167	-3.1840405	0.0386921
F	2.7302296	-2.5525023	1.2658090
H	2.1288542	-1.8621756	1.6407650

1-2+TMA

Energy = -958.1680364104 Eh, imaginary frequencies = 0

C	-1.1785223	1.2542235	3.3943009
S	-0.6683119	0.9408192	1.7180888
O	0.5932191	0.2476008	1.7242108
O	-1.7981705	0.4947712	0.9478292
F	-0.3752290	2.4666077	1.3106633
H	-0.3448963	1.7139794	3.9341717
H	-1.4293731	0.2796742	3.8280545
H	-2.0576240	1.9059149	3.3764781
C	1.9583377	1.5359622	-1.2152128
N	0.5477502	1.2164049	-1.4322274
H	2.3595859	0.8692493	-0.4386636
H	2.6118785	1.4481886	-2.1061687
H	2.0534484	2.5631866	-0.8331188
H	0.4546141	0.2590853	-1.7991325
H	0.1450682	1.8442047	-2.1285755
N	0.2409668	-1.8398715	-2.0042057
C	1.0584146	-2.2775037	-0.8794870
C	-1.1790432	-1.9785291	-1.7050943
C	0.5989756	-2.5446235	-3.2252214
H	0.9084226	-3.3539299	-0.6412371
H	-1.4696785	-3.0353117	-1.5136689
H	0.4271036	-3.6419176	-3.1525369
H	2.1212102	-2.1247084	-1.1137240
H	0.8132961	-1.6839415	0.0105935
H	-1.4318037	-1.3778708	-0.8219121
H	-1.7724157	-1.6101938	-2.5536317
H	0.0025634	-2.1617143	-4.0649799
H	1.6616741	-2.3806217	-3.4517597

TS+TMA

Energy = -958.1333799151 Eh, imaginary frequencies = 1

C	-1.0383741	0.3377151	1.9854745
S	-0.5851250	-0.7132275	0.5805362
O	0.7578258	-1.1544768	0.9842519
O	-1.6554909	-1.6813504	0.3742617
F	-1.5467339	1.0432625	-0.3035673
H	-0.3934741	1.2194109	1.9704772
H	-0.8318170	-0.2913821	2.8609231
H	-2.0866109	0.6127888	1.8729676
C	1.2452879	0.0943483	-1.5280639
N	-0.0825592	-0.4718187	-1.3149908
H	1.9800194	-0.4794794	-0.9508904
H	1.4997577	0.0475056	-2.5970924
H	1.2548260	1.1401301	-1.2001525
H	-0.1963287	-1.4497111	-1.7379569
H	-0.8546406	0.2105303	-1.4959112
N	-0.3320479	-3.0692240	-2.4154470
C	0.1973649	-3.9780451	-1.3946956
C	-1.7683268	-3.2825238	-2.6096075

C 0.3992534 -3.2043906 -3.6733087
H 0.1014362 -5.0387639 -1.7012572
H -1.9883609 -4.3102899 -2.9609668
H 0.3009178 -4.2200218 -4.1072297
H 1.2587958 -3.7583845 -1.2187211
H -0.3469924 -3.8232074 -0.4559049
H -2.2896352 -3.1050068 -1.6612636
H -2.1483006 -2.5725708 -3.3568917
H 0.0170817 -2.4799918 -4.4056287
H 1.4665417 -3.0054552 -3.5053942

3-HF+TMA

Energy = -958.1947460420 Eh, imaginary frequencies = 0

C -0.6537300 1.7528355 2.0602074
S 0.2608874 0.3063825 1.5565987
O 1.5146321 0.2830871 2.2920964
O -0.6360716 -0.8382549 1.5871997
F -1.4465627 1.8369173 -1.2018535
H -0.0218762 2.6380942 1.9269433
H -0.8894083 1.6142897 3.1214763
H -1.5627269 1.8228935 1.4538801
C 1.7966113 1.3291436 -0.3956462
N 0.5494470 0.6146253 -0.0776628
H 2.6811763 0.8336909 0.0258297
H 1.8820115 1.3717992 -1.4886226
H 1.7560804 2.3601854 -0.0208196
H 0.4518519 -0.3188759 -0.6151508
H -0.6983473 1.3814071 -0.7554757
N 0.1015620 -1.6800318 -1.5895383
C 0.6381487 -2.8761331 -0.9392678
C -1.3649875 -1.6986745 -1.6094085
C 0.6447178 -1.5072697 -2.9356535
H 0.3513753 -3.8026423 -1.4749795
H -1.7544037 -2.5438955 -2.2099571
H 0.3627740 -2.3409659 -3.6094670
H 1.7347085 -2.8187259 -0.9080457
H 0.2604922 -2.9267664 0.0896691
H -1.7363172 -1.7860655 -0.5811180
H -1.7374943 -0.7565087 -2.0324942
H 0.2643157 -0.5716068 -3.3672362
H 1.7412586 -1.4569815 -2.8903769

Postcomplex+TMA

Energy = -958.2037320924 Eh, imaginary frequencies = 0

C -0.7607754 -0.3342653 1.3834323
S -0.7296020 -0.4721504 -0.4046993
O 0.1295005 -1.5894253 -0.7533501
O -2.1196930 -0.4392803 -0.8442683
F -1.7311863 2.8792963 -0.0170773
H 0.2695100 -0.2946908 1.7552124
H -1.2690426 -1.2233177 1.7736576
H -1.3085288 0.5791892 1.6428419
C 1.4065048 1.0875307 -0.7749433
N -0.0331873 0.9114119 -0.9633055
H 1.9254070 0.1761801 -1.0916538
H 1.7360532 1.9155489 -1.4149723
H 1.6906059 1.3205635 0.2661742
H -0.6135356 1.7271418 -0.6817646
H -4.6357325 4.3121468 -0.4396571
H -4.8923724 2.0573501 0.3909395
C -4.4044842 3.9252009 -1.4395503
C -4.6684932 1.6556829 -0.6051959
H -5.3332547 3.8793928 -2.0335413
H -5.6138571 1.5107454 -1.1554272
H -3.6991744 4.6090610 -1.9270332
N -3.7853367 2.5970870 -1.3167128
H -2.6566895 2.7443100 -0.5896849
H -4.1488648 0.6967251 -0.5018952
C -3.3952570 2.0633715 -2.6353927
H -4.2772599 1.9470447 -3.2879246
H -2.6886507 2.7572429 -3.1072518
H -2.9065234 1.0926362 -2.4943764

TMA

Energy = -174.3028656920 Eh, imaginary frequencies = 0

N	-0.3198409	0.2028080	0.0000000
C	0.7935396	1.1370121	-0.0000000
C	-0.3193584	-0.6175753	1.1996803
C	-0.3193584	-0.6175753	-1.1996803
H	1.7855182	0.6289792	0.0000000
H	0.5911657	-1.2538421	1.2894009
H	0.5911657	-1.2538421	-1.2894009
H	0.7413716	1.7788329	-0.8905692
H	0.7413716	1.7788329	0.8905692
H	-0.3733092	0.0244888	2.0900339
H	-1.1966781	-1.2793040	1.1986526
H	-1.1966781	-1.2793040	-1.1986526
H	-0.3733092	0.0244888	-2.0900339

1-2+HF+TMA

Energy = -1058.594981171 Eh, imaginary frequencies = 0

C	-0.6962972	0.4563336	3.9861503
S	-0.7250993	0.4847401	2.2076807
O	0.6150339	0.6529420	1.7053510
O	-1.6001485	-0.5453661	1.7167894
F	-1.4759057	1.8843146	2.0322688
H	-0.1302769	1.3232437	4.3411183
H	-0.1974085	-0.4759620	4.2737039
H	-1.7279461	0.4703568	4.3514386
C	1.9785109	1.4585428	-1.4885049
N	0.7709799	0.9873408	-2.1829417
H	1.9428755	1.1139410	-0.4480339
H	2.9172929	1.1058550	-1.9472848
H	1.9915338	2.5562264	-1.4720399
H	0.7400116	-0.0524638	-2.2125621
H	0.7499606	1.3263302	-3.1454423
F	-1.3278412	1.5224798	-0.8897582
H	-0.4874260	1.3491675	-1.4328986
N	0.3153449	-1.9488898	-1.8802816
C	0.9767278	-2.2532931	-0.6144708
C	-1.1360009	-1.8748070	-1.7038557
C	0.6746484	-2.9196203	-2.9057103
H	0.6720671	-3.2424837	-0.2102860
H	-1.5589456	-2.8382129	-1.3491501
H	0.3547643	-3.9512554	-2.6432071
H	2.0664647	-2.2618909	-0.7579789
H	0.7260289	-1.4857471	0.1278519
H	-1.3863673	-1.0890195	-0.9803470
H	-1.6087422	-1.6228136	-2.6630057
H	0.1991745	-2.6479458	-3.8582935
H	1.7642688	-2.9262748	-3.0492874

TS+HF+TMA

Energy = -1058.558874895 Eh, imaginary frequencies = 1

C	-0.9580633	0.1347697	2.1222232
S	-0.5759257	-0.6345418	0.5217793
O	0.7684498	-1.1652319	0.7607470
O	-1.7554105	-1.4608366	0.2644889
F	-0.8579617	1.4446771	0.0711986
H	-0.1823268	0.8684068	2.3474084
H	-0.9357192	-0.7117304	2.8201883
H	-1.9454402	0.5933525	2.0577853
C	1.0393041	0.2376965	-1.7723692
N	-0.2280042	-0.4098174	-1.4292018
H	1.8476941	-0.2571838	-1.2224715
H	1.2202934	0.1399973	-2.8527313
H	0.9935265	1.2958411	-1.5000289
H	-0.2546041	-1.4314886	-1.7523202
H	-1.0357713	0.1157216	-1.8068320
F	-2.1032036	1.6075094	-1.9584617
H	-1.6569521	1.6693834	-1.0673358
N	-0.3200000	-3.0894287	-2.3504208
C	0.0921469	-3.9836079	-1.2652292
C	-1.7292717	-3.2957554	-2.6916508

C	0.5390071	-3.2531203	-3.5217723
H	0.0322832	-5.0483484	-1.5672742
H	-1.9222583	-4.3275419	-3.0467499
H	0.4794918	-4.2765921	-3.9438812
H	1.1246067	-3.7559363	-0.9705748
H	-0.5561966	-3.8209156	-0.3964123
H	-2.3469810	-3.0990136	-1.8067827
H	-2.0233581	-2.5959813	-3.4858127
H	0.2412675	-2.5414806	-4.3040984
H	1.5835060	-3.0555371	-3.2452942

3-HF+HF+TMA

Energy = -1058.610446129 Eh, imaginary frequencies = 0

C	-0.6584753	1.3582240	2.1908335
S	0.1570258	-0.1100887	1.6048738
O	1.4201621	-0.2610411	2.3049689
O	-0.8010854	-1.2027304	1.5648725
F	-0.2983656	3.7151746	-0.0481594
H	-0.0319331	2.2334940	1.9852820
H	-0.7918635	1.2169871	3.2694667
H	-1.6221726	1.4483581	1.6797237
C	1.7262029	0.9929645	-0.2999705
N	0.4635660	0.2666041	-0.0384622
H	2.5773443	0.5109426	0.1956521
H	1.8817979	0.9953746	-1.3859493
H	1.6378016	2.0346782	0.0317076
H	0.4242063	-0.6775486	-0.5828807
H	-0.5931429	1.0171261	-0.5969864
F	-1.3205495	1.6540716	-1.0374950
H	-0.7702224	3.0028366	-0.4979987
N	0.2251409	-2.0532942	-1.5304808
C	0.7763981	-3.1930548	-0.7932650
C	-1.2306717	-2.1655430	-1.6700318
C	0.8709507	-1.8919837	-2.8332858
H	0.6007482	-4.1496735	-1.3225189
H	-1.5178638	-3.0548985	-2.2632842
H	0.6968758	-2.7636083	-3.4943879
H	1.8590765	-3.0594462	-0.6651400
H	0.3095707	-3.2408648	0.1983479
H	-1.6828881	-2.2362672	-0.6733838
H	-1.6216066	-1.2679106	-2.1675524
H	0.4762771	-0.9963229	-3.3317399
H	1.9543034	-1.7730933	-2.6976330

Postcomplex+HF+TMA

Energy = -1058.619941395 Eh, imaginary frequencies = 0

C	-0.5477393	0.1650203	1.8389692
S	-0.9428982	-0.6635273	0.3033335
O	-0.1536314	-1.8762499	0.2026632
O	-2.3888736	-0.6955091	0.1836367
F	-1.6032896	2.6707308	-0.2198994
H	0.5402954	0.2542976	1.9317516
H	-0.9455286	-0.4605674	2.6460141
H	-1.0315256	1.1487667	1.8222932
C	1.0531695	0.4791621	-1.0871069
N	-0.4038232	0.4058122	-0.8881817
H	1.4496082	-0.5281038	-1.2517631
H	1.2370276	1.0853019	-1.9824462
H	1.5759295	0.9430258	-0.2362001
H	-1.1561555	0.1704208	-2.2939856
H	-0.8303132	1.3504671	-0.6600973
H	-4.7299626	3.4071679	0.1502184
H	-4.4490207	1.0454470	-0.4342242
C	-4.5178924	3.7050517	-0.8831047
C	-4.3030313	1.3462019	-1.4770614
H	-5.4645145	3.8140368	-1.4344183
H	-5.2717284	1.3781842	-1.9996628
H	-3.9852088	4.6632420	-0.8750542
N	-3.6631764	2.6809381	-1.5129482
H	-2.6206512	2.6489435	-0.8532740
H	-3.6419786	0.6208435	-1.9622922
C	-3.2908531	3.0568801	-2.8941847

H -4.1904126 3.1510756 -3.5218854
H -2.7595568 4.0157935 -2.8704425
H -2.6343604 2.2793027 -3.3020614
F -1.6044741 0.2114937 -3.1726157

$MeSO_2^+$
Energy = -587.9194567583 Eh, imaginary frequencies = 0
C 8.6530594 8.6264342 14.3349389
S 8.6962542 6.9135512 14.8214827
O 7.5866849 6.1297410 14.3855067
O 9.8216808 6.5333871 15.6117569
H 8.0892085 8.6747205 13.3938944
H 9.6956131 8.9656976 14.2747082
H 8.1123490 9.1385984 15.1517422

$MeSO_2^+$+TMA
Energy = -762.3381801520, imaginary frequencies = 0
C -0.7566991 -0.3103244 1.5644913
S -0.6424989 -0.8826264 -0.1147468
O 0.3429577 -1.9254645 -0.2307961
O -1.9445614 -0.9226524 -0.7272141
H 0.2448847 -0.1534248 1.9762778
H -1.2443728 -1.1482318 2.0841281
H -1.3949182 0.5770921 1.6158436
C 1.5735857 0.8479691 -0.4881612
N 0.2133674 0.6124535 -1.0494596
H 2.1310651 -0.0940076 -0.4944171
H 2.0836048 1.5873014 -1.1182357
H 1.4898397 1.2419008 0.5297135
C -0.6493109 1.8246163 -0.9608064
H -0.2239003 2.5985549 -1.6116637
H -0.6650006 2.1929187 0.0699395
H -1.6594677 1.5706575 -1.2972723
C 0.3019088 0.1291693 -2.4651944
H 0.7666326 0.9225073 -3.0624766
H -0.7064671 -0.0796143 -2.8361558
H 0.9168505 -0.7757247 -2.4972541

1-2+$(H2O)_3$
Energy = -1013.057253848, imaginary frequencies = 0
C -1.6068240 0.6198377 2.3667436
S -0.1635322 0.0398134 1.5304054
O 0.9189705 -0.2107551 2.4431912
O -0.5149102 -0.9098412 0.5021806
F 0.2243349 1.4087399 0.7463260
H -1.2918729 1.3739032 3.0955717
H -2.0289142 -0.2553265 2.8752827
H -2.3081929 1.0334651 1.6226671
C 0.9985353 0.1365811 -2.7140788
N -0.3373475 -0.4618759 -2.5745794
H 1.1302300 0.8978107 -1.9341836
H 1.8290910 -0.5842828 -2.6297716
H 1.0741309 0.6408451 -3.6863232
H -0.4235701 -0.9078522 -1.6582686
H -0.4795318 -1.1875252 -3.2779009
H -2.6651287 2.7436544 -0.1715147
O -3.3270915 2.0638058 0.1459523
O -1.4506412 3.5828530 -1.0692942
H -0.5752056 3.3925315 -0.6997696
H -4.1607216 2.5468369 0.2436961
H -1.5845793 2.8934548 -1.7894095
H -1.5773346 0.7822963 -2.6282692
H -2.8519418 1.3414017 -1.8942566
O -2.2300325 1.5507982 -2.6164670

TS+$(H2O)_3$
Energy = -1013.000779140, imaginary frequencies = 1
O 5.9975357 8.4600871 7.8918768
O 8.5406791 7.3130614 8.3551947
H 6.0515021 9.8458309 9.1895236
H 6.0068861 8.7684669 6.9740067
H 6.8361814 7.9617789 8.0056209

H	8.8061064	7.4158167	9.3027647
H	8.7915506	6.4128382	8.1008212
S	9.7728922	9.7104698	10.7311372
O	9.5686942	8.2464943	10.6785116
F	8.7948258	11.4773257	9.8106410
H	9.5854782	10.7567413	8.6184393
H	6.9782188	10.9948616	9.6915739
C	8.5284003	10.2084634	11.9372664
O	6.1687648	10.4920529	9.9177218
H	8.6872649	11.2664331	12.1476026
H	8.7395189	9.5514709	12.7913149
H	7.5385696	10.0257234	11.4945096
H	11.8469958	8.7408118	8.6086114
H	11.5731828	9.8780221	7.2517237
H	9.4786867	9.0579244	8.2948358
N	10.0452933	9.8207408	8.6929653
O	11.0582019	10.2573419	11.1245442
C	11.4567564	9.7281557	8.3352665
H	12.0162338	10.4993750	8.8735920

10) References

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