A Mountaineering Strategy to Excited States: Highly-Accurate Energies and Benchmarks for Exotic Molecules and Radicals

Supporting Information

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S1 Basis set and frozen-core effects

Table S1: CC3 transition energies (in eV) determined with various basis sets. FC, SC, and full stand for frozen-core (large cores), small-core (freezing only the 1s electrons) and correlating all electrons, respectively.

		6-31+G(d) FC	*aug*-cc-pVDZ FC	*aug*-cc-pVTZ FC	*aug*-cc-pVQZ FC	*aug*-cc-pVQZ SC	*aug*-cc-pVQZ Full	*aug*-cc-pCVQZ Full	*aug*-cc-pV5Z FC
Carbonylfluoride	$^1A_2$	7.33	7.34	7.31	7.31		7.29	7.28	7.31
	$^3A_2$	7.03	7.05	7.03	7.03		7.01	7.00	7.04
CCl_2	$^1B_1$	2.71	2.69	2.61	2.60	2.59	2.57	2.57	2.59
	$^1A_2$	4.46	4.40	4.35	4.37	4.36	4.34	4.33	4.36
	$^3B_1$	1.10	1.20	1.20	1.21	1.21	1.19	1.19	1.21
	$^3A_2$	4.41	4.34	4.28	4.30	4.29	4.28	4.26	4.29
CClF	$^1A''$	3.66	3.63	3.56	3.55	3.55	3.53	3.53	3.55
CF_2	$^1B_1$	5.18	5.12	5.07	5.06		5.02	5.02	5.05
	$^3B_1$	2.71	2.71	2.76	2.77		2.75	2.75	2.77
Difluorodiazirine	$^1B_1$	3.83	3.80	3.74	3.73				
	$^1A_2$	7.13	7.11	7.02	7.00				
	$^1B_2$	8.51	8.45	8.50	8.52				
	$^3B_1$	3.09	3.06	3.03	3.03				
	$^3B_2$	5.48	5.47	5.45	5.47				
	$^3B_1$	5.86	5.83	5.81	5.82				
Formylfluoride	$^1A''$	6.09	6.03	5.99	5.99		5.98	5.97	6.00
	$^3A''$	5.72	5.65	5.62	5.63		5.62	5.61	5.64
HCCl	$^1A''$	2.05	2.02	1.97	1.96	1.96	1.95	1.94	1.96
HCF	$^1A''$	2.58	2.53	2.49	2.49		2.47	2.47	2.49
HCP	$^1\Sigma^-$	5.19	5.06	4.85	4.83	4.83	4.82	4.81	4.82
	$^1\Delta$	5.48	5.33	5.15	5.12	5.11	5.11	5.09	5.10
	$^3\Sigma^+$	3.44	3.47	3.45	3.46	3.46	3.46	3.44	3.47
	$^3\Delta$	4.40	4.35	4.22	4.21	4.21	4.20	4.20	4.20
HPO	$^1A''$	2.49	2.47	2.46	2.47	2.47	2.47	2.47	2.48
HPS	$^1A''$	1.57	1.60	1.59	1.60	1.59	1.59	1.59	1.61
HSiF	$^1A''$	3.09	3.08	3.07	3.07	3.06	3.06	3.06	3.07
$SiCl_2$	$^1B_1$	3.94	3.93	3.90	3.91	3.91	3.91	3.90	3.92
	$^3B_1$	2.39	2.45	2.48	2.49	2.52	2.52	2.52	2.50
Silylidene	$^1A_2$	2.14	2.18	2.15	2.16	2.15	2.16	2.15	2.16
	$^1B_2$	3.88	3.81	3.78	3.79	3.78	3.78	3.78	3.80

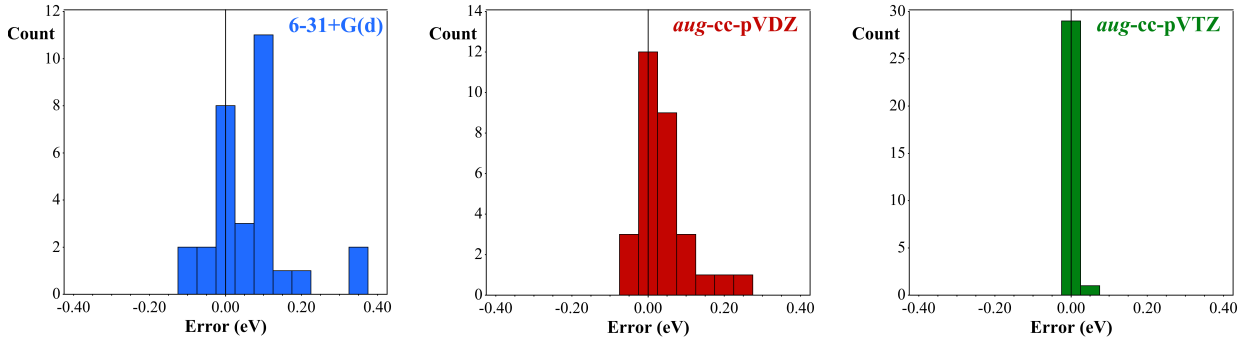

Figure S1: Histograms of the error distribution (in eV) obtained by comparing the CC3 transitions obtained with three basis set to the corresponding CC3/*aug*-cc-pVQZ values for the data listed in Table S1. Note the different Y scales.

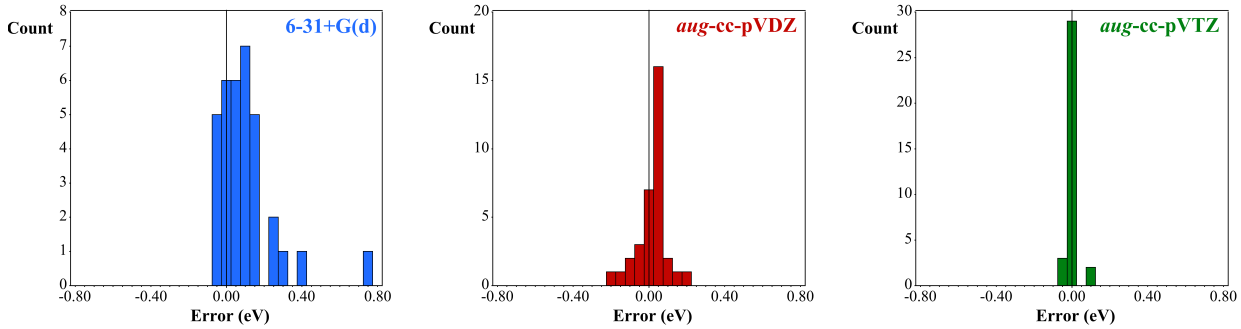

Figure S2: Histograms of the error distribution (in eV) obtained by comparing the CCSDT transitions obtained with three basis set to the corresponding CCSDT/*aug*-cc-pVQZ values for the data listed in Table 3 of the main text. Note the different Y scales.

S2 Benchmark data

Table S2: Transition energies determined with various models for the exotic set. All values are in eV and have been obtained with the *aug*-cc-pVTZ basis set applying the FC approximation.

		TBE	CIS(D)	CC2	EOM-MP2	STEOM-CCSD	CCSD	CCSDR(3)	CCSDT-3	CC3	SOS-ADC(2) [TM]	SOS-CC2 [TM]	SCS-CC2 [TM]	SOS-ADC(2) [QM]	ADC(2)	ADC(3)	ADC(2.5)
Carbonylfluoride	$^1A_2$	7.31	7.38	7.47	7.39	7.07	7.36	7.32	7.32	7.31	7.27	7.48	7.47	7.04	7.22	7.32	7.27
	$^3A_2$	7.06	7.08	7.14	7.08	6.82	7.03			7.03	7.05	7.24	7.21	6.81	6.91	7.01	6.96
CCl_2	$^1B_1$	2.59	2.59	2.58	2.36	2.35	2.61	2.59	2.61	2.61	2.58	2.67	2.64	2.44	2.46	2.41	2.44
	$^1A_2$	4.40	4.20	4.27	4.27	4.33	4.57	4.37	4.41	4.35	4.50	4.61	4.50	4.29	4.12	4.76	4.44
	$^3B_1$	1.22	1.09	1.15	0.84		1.11			1.20	1.16	1.27	1.23	1.06	0.98	0.91	0.95
	$^3A_2$	4.31	4.24	4.20	4.17	4.23	4.45			4.28	4.48	4.59	4.46	4.29	4.05	4.62	4.34
CClF	$^1A''$	3.55	3.56	3.57	3.34	3.39	3.57	3.55	3.56	3.56	3.54	3.63	3.61	3.39	3.44	3.35	3.40
CF_2	$^1B_1$	5.09	5.06	5.09	4.90	4.90	5.09	5.07	5.08	5.07	5.05	5.15	5.13	4.89	4.94	4.86	4.90
	$^3B_1$	2.77	2.63	2.70	2.47	2.61	2.69			2.76	2.74	2.84	2.79	2.64	2.54	2.48	2.51
Difluorodiazirine	$^1B_1$	3.74	3.89	3.74	3.94	3.56	3.83	3.76	3.75	3.74	3.97	3.97	3.90	3.77	3.74	3.52	3.63
	$^1A_2$	7.00	7.46	7.19	7.24		7.10	7.05	7.02	7.02	7.29	7.28	7.25	7.10	7.19	6.70	6.95
	$^1B_2$	8.52	8.53	8.29	8.90		8.69	8.55	8.55	8.50	8.95	8.82	8.65	8.77	8.42	8.50	8.46
	$^3B_1$	3.03	3.17	3.03	3.17	2.91	3.07			3.03	3.32	3.33	3.23	3.14	3.01	2.77	2.89
	$^3B_2$	5.44	5.89	5.77	5.97		5.40			5.45	5.53	5.55	5.63	5.41	5.72	5.04	5.38
	$^3B_1$	5.80	6.13	5.99	5.71	5.59	5.84			5.81	6.20	6.21	6.13	6.05	5.97	5.47	5.72
Formylfluoride	$^1A''$	5.96	6.03	6.14	6.00	5.88	6.02	5.99	6.00	5.99	5.99	6.19	6.17	5.78	5.91	5.93	5.92
	$^3A''$	5.73	5.63	5.70	5.60	5.51	5.60			5.62	5.67	5.85	5.80	5.48	5.50	5.54	5.52
HCCl	$^1A''$	1.98	1.95	1.91	1.65	1.80	1.99	1.95	1.98	1.97	2.01	2.06	2.01	1.88	1.84	1.81	1.83
HCF	$^1A''$	2.49	2.54	2.44	2.19	2.32	2.51	2.48	2.50	2.49	2.51	2.58	2.53	2.38	2.34	2.30	2.32
HCP	$^1\Sigma^-$	4.84	5.07	5.07	4.83	4.90	4.87	4.85	4.84	4.85	5.02	5.07	5.07	4.91	5.02	4.37	4.70
	$^1\Delta$	5.15	5.40	5.41	5.12	5.22	5.16	5.16	5.14	5.15	5.23	5.29	5.33	5.12	5.33	4.66	5.00
	$^3\Sigma^+$	3.47	3.74	3.73	3.55	3.41	3.36			3.45	3.37	3.38	3.50	3.30	3.69	3.10	3.40
	$^3\Delta$	4.22	4.44	4.43	4.23	4.20	4.17			4.22	4.47	4.52	4.49	4.39	4.39	3.79	4.09
HPO	$^1A''$	2.47	2.54	2.50	2.44	2.45	2.54	2.48	2.48	2.46	2.57	2.68	2.62	2.39	2.35	2.35	2.35
HPS	$^1A''$	1.59	1.68	1.68	1.39	1.55	1.67	1.59	1.60	1.59	1.74	1.79	1.75	1.60	1.62	1.39	1.51
HSiF	$^1A''$	3.05	3.16	3.14	2.78	3.02	3.12	3.07	3.08	3.07	3.22	3.24	3.21	3.12	3.11	2.88	3.00
$SiCl_2$	$^1B_1$	3.91	3.99	3.99	3.70	3.80	3.96	3.89	3.91	3.90	4.01	4.04	4.02	3.89	3.95	3.76	3.86
	$^3B_1$	2.48	2.40	2.39	2.18		2.45			2.48	2.51	2.52	2.48	2.44	2.35	2.31	2.33
Silylidene	$^1A_2$	2.11	2.39	2.37	2.09	2.21	2.29	2.16	2.17	2.15	2.35	2.35	2.35	2.24	2.37	1.87	2.12
	$^1B_2$	3.78	3.91	3.85	3.66	3.81	3.88	3.79	3.80	3.78	3.98	3.94	3.91	3.87	3.88	3.40	3.64

Table S3: Transition energies determined with various models for the radical set. All values are in eV and have been obtained with the *aug*-cc-pVTZ basis set applying the FC approximation.

		TBE	U-CCSD	RO-CCSD	U-CC3	RO-CC3
Allyl	$^2B_1$	3.39	3.70	3.48	3.48	3.44
	$^2A_1$	4.99	5.12	5.01	4.97	4.95
BeF	$^2\Pi$	4.14	4.18	4.18	4.15	4.15
	$^2\Sigma^+$	6.21	6.31	6.31	6.21	6.21
BeH	$^2\Pi$	2.49	2.51	2.51	2.50	2.50
	$^2\Pi$	6.46	6.47	6.47	6.46	6.46
BH_2	$^2B_1$	1.18	1.20	1.20	1.19	1.20
CH	$^2\Delta$	2.91	3.18	3.17	3.11	3.10
	$^2\Sigma^-$	3.29	4.58	4.39	3.61	3.55
	$^2\Sigma^+$	3.98	5.47	5.36	4.45	4.40
CH_3	$^2A_1'$	5.85	5.89	5.87	5.86	5.85
	$^2E'$	6.96	7.00	6.98	6.97	6.97
	$^2E'$	7.18	7.21	7.20	7.19	7.19
	$^2A_2''$	7.65	7.67	7.66	7.65	7.65
CN	$^2\Pi$	1.34	1.56	1.34	1.40	1.36
	$^2\Sigma^+$	3.22	3.54	3.35	3.31	3.26
CNO	$^2\Sigma^+$	1.61	2.24	2.25	1.75	1.77
	$^2\Pi$	5.49	5.68	5.60	5.52	5.51
CO^+	$^2\Pi$	3.28	3.60	3.29	3.33	3.29
	$^2\Sigma^+$	5.81	6.21	6.02	5.76	5.68
F_2BO	$^2B_1$	0.73	0.74	0.73	0.71	0.71
	$^2A_1$	2.80	2.84	2.83	2.79	2.79
F_2BS	$^2B_1$	0.51	0.51	0.49	0.48	0.48
	$^2A_1$	2.99	3.03	3.01	2.94	2.93
H_2BO	$^2B_1$	2.15	2.14	2.13	2.17	2.17
	$^2A_1$	3.49	3.53	3.51	3.52	3.52
HCO	$^2A''$	2.09	2.14	2.13	2.10	2.11
	$^2A'$	5.45	5.54	5.53	5.44	5.44
HOC	$^2A''$	0.92	0.95	0.93	0.93	0.93
H_2PO	$^2A''$	2.80	2.91	2.91	2.83	2.83
	$^2A'$	4.21	4.26	4.27	4.21	4.23
H_2PS	$^2A''$	1.16	1.18	1.14	1.16	1.15
	$^2A'$	2.72	2.79	2.77	2.75	2.75
NCO	$^2\Sigma^+$	2.89	3.04	2.94	2.94	2.86
	$^2\Pi$	4.73	5.01	5.02	4.80	4.81
NH_2	$^2A_1$	2.12	2.13	2.12	2.13	2.12
Nitromethyl	$^2B_2$	2.05	2.47	2.46	2.06	2.05
	$^2A_2$	2.38	2.71	2.71	2.47	2.46
	$^2A_1$	2.56	2.94	2.93	2.56	2.55
	$^2B_1$	5.35	5.59	5.56	5.38	5.36
NO	$^2\Sigma^+$	6.13	6.23	6.21	6.13	6.12
	$^2\Sigma^+$	7.29	7.40	7.38	7.30	7.28
OH	$^2\Sigma^+$	4.10	4.14	4.13	4.13	4.13
	$^2\Sigma^-$	8.02	7.75	7.76	7.66	7.66
PH_2	$^2A_1$	2.77	2.81	2.78	2.78	2.77
Vinyl	$^2A''$	3.26	3.51	3.35	3.34	3.30
	$^2A''$	4.69	4.91	4.80	4.76	4.73
	$^2A'$	6.20	6.38	6.32	6.22	6.24

S3 Multi-reference approaches for CON

Table S4: Vertical transition energies (eV) of CON. All calculations using a full valence active space of (15e,12o) and the *aug*-cc-pVTZ basis set. NEVPT2 calculations are performed within the partially-contracted scheme whereas CASPT2 calculations use a level shift of 0.3 a.u. and a IPEA of 0.25 a.u.

State	Active space (a_1, b_1, b_2, a_2)	State-average $(A_1, B_1, B_2, A2)$	CASSCF	NEVPT2	CASPT2	MRCI
$^4\Pi(\pi \rightarrow \pi^\star)$	(6,3,3,0)	(0,2,2,0)	3.01	2.72	2.74	2.81
$^2\Pi(\pi \rightarrow \pi^\star)$	(6,3,3,0)	(0,2,2,0)	3.94	3.52	3.55	3.62
$^2\Sigma^+(n \rightarrow \pi^\star)$	(6,3,3,0)	(1,1,1,0)	3.85	3.81	3.72	3.83
$^2\Phi(\pi \rightarrow \pi^\star)$	(6,3,3,0)	(0,2,2,0)	4.86	4.32	4.35	4.44

S4 Geometries

S4.1 Exotic compounds

Below, we provide the Cartesian coordinates of the exotic compounds investigated in this study. These are given in atomic units (bohr) and they have been obtained at the CC3(full)/*aug*-cc-pVTZ level of theory.

S4.1.1 Carbonylfluoride (F_2CO)

C	0.00000000	0.00000000	-0.30652633
O	0.00000000	0.00000000	-2.52469534
F	0.00000000	2.00254958	1.16003038
F	0.00000000	-2.00254958	1.16003038

S4.1.2 CCl_2

C	0.00000000	0.00000000	-1.60920674
Cl	0.00000000	2.65360612	0.27602958
Cl	0.00000000	-2.65360612	0.27602958

S4.1.3 CClF

C	0.29776085	0.00000000	1.47969075
F	2.16980264	0.00000000	-0.10569879
Cl	-2.46756349	0.00000000	-0.32822320

S4.1.4 CF_2

C	0.00000000	0.00000000	-1.14170749
F	0.00000000	1.94810617	0.36114458
F	0.00000000	-1.94810617	0.36114458

S4.1.5 Difluorodiazirine (CF_2N_2)

C	0.00000000	0.00000000	-0.15283028
F	0.00000000	2.06077297	-1.57706828
F	0.00000000	-2.06077297	-1.57706828
N	1.20382241	0.00000000	2.20566821
N	-1.20382241	0.00000000	2.20566821

S4.1.6 Formylfluoride (FHCO)

C	0.00536098	0.00000000	0.75320959
O	2.17369813	0.00000000	0.22287752
H	-0.83846350	0.00000000	2.62640974
F	-1.84051320	0.00000000	-0.99373750

S4.1.7 HCCl

H	-1.88068369	0.00000000	-0.14323924
Cl	2.28559426	0.00000000	-0.43261163
C	-0.40491057	0.00000000	1.32161964

S4.1.8 HCF

C	-0.13561085	0.00000000	1.20394474
F	1.85493976	0.00000000	-0.27610752
H	-1.71932891	0.00000000	-0.18206846

S4.1.9 HCP

H	0.00000000	0.00000000	-4.03090449
C	0.00000000	0.00000000	-2.01691641
P	0.00000000	0.00000000	0.91401621

S4.1.10 HPO

H	0.31668637	0.00000000	0.14072725
P	-0.80573521	0.00000000	2.65136926
O	1.43391190	0.00000000	4.38886277

S4.1.11 HPS

H	-2.56278959	0.00000000	2.36296006
P	0.09114182	0.00000000	1.82568543
S	0.07946992	0.00000000	-1.85778170

S4.1.12 HSiF

Si	-0.06438136	0.00000000	1.67253150
F	2.24990164	0.00000000	-0.33928119
H	-2.18552027	0.00000000	-0.28748154

S4.1.13 $SiCl_2$

Si	0.00000000	0.00000000	-1.78528322
Cl	0.00000000	3.04414528	0.71619419
Cl	0.00000000	-3.04414528	0.71619419

S4.1.14 Silylidene (H_2CSi)

C	0.00000000	0.00000000	-2.09539928
Si	0.00000000	0.00000000	1.14992930
H	0.00000000	1.70929524	-3.22894481
H	0.00000000	-1.70929524	-3.22894481

S4.2 Radicals

Below, we provide the Cartesian coordinates of the radical compounds investigated in this study. These are given in atomic units (bohr) and they have been obtained at the UCCSD(T)(full)/*aug*-cc-pVTZ level of theory, except when noted.

S4.2.1 Allyl (C_3H_5)

C	0.00000000	0.00000000	0.83050732
C	0.00000000	2.30981224	-0.38722841
C	0.00000000	-2.30981224	-0.38722841
H	0.00000000	0.00000000	2.87547067
H	0.00000000	4.06036949	0.65560561
H	0.00000000	-4.06036949	0.65560561
H	0.00000000	2.41059890	-2.42703281
H	0.00000000	-2.41059890	-2.42703281

S4.2.2 BeF

Be	0.00000000	0.00000000	-1.77936990
F	0.00000000	0.00000000	0.79083149

S4.2.3 BeH

Be	0.00000000	0.00000000	0.25103976
H	0.00000000	0.00000000	-2.24485003

S4.2.4 BH_2

B	0.00000000	0.00000000	0.14984923
H	0.00000000	2.01119016	-0.81846345
H	0.00000000	-2.01119016	-0.81846345

S4.2.5 CH

C	0.00000000	0.00000000	-0.16245872
H	0.00000000	0.00000000	1.93436816

S4.2.6 CH_3

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	2.03379507
H	0.00000000	1.76131924	-1.01689753
H	0.00000000	-1.76131924	-1.01689753

S4.2.7 CN

C	0.00000000	0.00000000	-1.18953886
N	0.00000000	0.00000000	1.01938091

S4.2.8 CNO

C	0.00000000	0.00000000	-2.50680714
N	0.00000000	0.00000000	-0.22402176
O	0.00000000	0.00000000	2.07682752

S4.2.9 CON

Optimized at the U-CCSDT/cc-pVTZ level.

C	0.00000000	0.00000000	-2.44062558
O	0.00000000	0.00000000	-0.20455596
N	0.00000000	0.00000000	2.32515818

S4.2.10 CO^+

C	0.00000000	0.00000000	-1.20324172
O	0.00000000	0.00000000	0.90271821

S4.2.11 F_2BO

O	0.00000000	0.00000000	2.65260017
B	0.00000000	0.00000000	0.07681654
F	0.00000000	2.16433924	-1.13888019
F	0.00000000	-2.16433924	-1.13888019

S4.2.12 F_2BS

S	0.00000000	0.00000000	2.64960984
B	0.00000000	0.00000000	-0.74406239
F	0.00000000	2.14169276	-2.01390354
F	0.00000000	-2.14169276	-2.01390354

S4.2.13 H_2BO

O	0.00000000	0.00000000	1.17360276
B	0.00000000	0.00000000	-1.27133435
H	0.00000000	1.98370787	-2.36904602
H	0.00000000	-1.98370787	-2.36904602

S4.2.14 HCO

H	0.00000000	-2.55038496	1.39798104
C	0.00000000	-1.17300976	-0.19046167
O	0.00000000	1.04073447	0.05480615

S4.2.15 HOC

H	0.00000000	1.82002973	1.50851586
O	0.00000000	0.96467865	-0.12887834
C	0.00000000	-1.43868535	0.04508983

S4.2.16 H_2PO

P	0.00000000	0.87766783	-0.10010856
O	0.00000000	-1.95912323	0.05701315
H	2.08101554	2.05955113	1.08591181
H	-2.08101554	2.05955113	1.08591181

S4.2.17 H_2PS

P	0.00000000	1.81994516	-0.10769248
S	0.00000000	-1.93707861	0.02086846
H	2.03762554	2.75934101	1.32385757
H	-2.03762554	2.75934101	1.32385757

S4.2.18 NCO

N	0.00000000	0.00000000	-2.39343558
C	0.00000000	0.00000000	-0.07238136
O	0.00000000	0.00000000	2.14968523

S4.2.19 NH_2

N	0.00000000	0.00000000	0.15111603
H	0.00000000	1.51574744	-1.04982949
H	0.00000000	-1.51574744	-1.04982949

S4.2.20 Nitromethyl (CH_2-NO_2)

C	0.00000000	0.00000000	-2.58417104
N	0.00000000	0.00000000	0.08692471
O	0.00000000	-2.06715629	1.15098225
O	0.00000000	2.06715629	1.15098225
H	0.00000000	1.81656349	-3.48616378
H	0.00000000	-1.81656349	-3.48616378

S4.2.21 NO

N	0.00000000	0.00000000	-1.15775086
O	0.00000000	0.00000000	1.01357658

S4.2.22 OH

O	0.00000000	0.00000000	-0.10864763
H	0.00000000	0.00000000	1.72431679

S4.2.23 PH_2

P	0.00000000	0.00000000	0.11427641
H	0.00000000	1.91899987	-1.75604411
H	0.00000000	-1.91899987	-1.75604411

S4.2.24 Vinyl (C_2H_3)

C	0.00000000	1.16769663	-0.04303146
C	0.00000000	-1.29945364	0.15810072
H	0.00000000	2.38429609	1.59801822
H	0.00000000	2.08759130	-1.87998309
H	0.00000000	-2.90307925	-1.08814513