

# **A Mountaineering Strategy to Excited States: Highly-Accurate Energies and Benchmarks for Medium Size Molecules Supporting Information**

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## S1 Basis set and frozen-core effects

### S1.1 Cyanoacetylene, cyanogen, and diacetylene

Table S1: CC3 vertical transition energies of cyanoacetylene, cyanogen, and diacetylene using various atomic basis sets. FC stands for frozen core. All values are in eV.

	6-31+G(d) FC	<i>aug-cc-pVDZ</i> FC	<i>aug-cc-pVTZ</i> FC	<i>aug-cc-pVQZ</i> FC	<i>aug-cc-pVQZ</i> Full	d- <i>aug-cc-pVQZ</i> FC	<i>aug-cc-pV5Z</i> FC
Cyanoacetylene							
$^1\Sigma^-$	6.02	5.92	5.80	5.79	5.79	5.79	5.79
$^1\Delta$	6.29	6.17	6.08	6.06	6.07	6.06	6.07
$^3\Sigma^+$	4.44	4.43	4.45	4.46	4.46	4.46	4.47
$^3\Delta$	5.35	5.28	5.22	5.22	5.21	5.22	5.22
$^1A''[F]$	3.70	3.60	3.54	3.54	3.54		
Cyanogen							
$^1\Sigma_u^-$	6.62	6.52	6.39	6.38	6.38	6.38	6.38
$^1\Delta_u$	6.88	6.77	6.66	6.64	6.65	6.64	6.64
$^3\Sigma_u^+$	4.92	4.89	4.90	4.91	4.91	4.91	4.92
$^1\Sigma_u^-[F]$	5.27	5.19	5.06	5.05	5.05	5.05	5.04
Diacetylene							
$^1\Sigma_u^-$	5.57	5.44	5.34	5.33	5.34	5.33	5.33
$^1\Delta_u$	5.83	5.69	5.61	5.60	5.60	5.60	5.60
$^3\Sigma_u^+$	4.07	4.06	4.08	4.10	4.09	4.10	4.09
$^3\Delta_u$	4.93	4.86	4.80	4.80	4.80	4.80	4.80

## S1.2 Cyclopropenone, cyclopropenethione, and methylenecyclopropene

Table S2: CC3 vertical transition energies of cyclopropenone, cyclopropenethione, and methylenecyclopropene using various atomic basis sets. FC stands for frozen core. All values are in eV.

	6-31+G(d) FC	<i>aug-cc-pVDZ</i> FC	<i>aug-cc-pVTZ</i> FC	<i>aug-cc-pVQZ</i> FC	d- <i>aug-cc-pVQZ</i> Full	<i>aug-cc-pV5Z</i> FC
Cyclopropenone						
$^1B_1(n \rightarrow \pi^*)$	4.32	4.22	4.21	4.23	4.22	4.23
$^1A_2(n \rightarrow \pi^*)$	5.68	5.59	5.57	5.58	5.57	5.58
$^1B_2(n \rightarrow 3s)$	6.39	6.21	6.32	6.37	6.38	6.38
$^1B_2(\pi \rightarrow \pi^*)$	6.70	6.56	6.54	6.56	6.56	6.56
$^1B_2(n \rightarrow 3p)$	6.92	6.88	6.96	6.99	7.00	6.99
$^1A_1(n \rightarrow 3p)$	7.00	6.88	7.00	7.05	7.06	7.06
$^1A_1(\pi \rightarrow \pi^*)$	8.51	8.32	8.28	8.28	8.28	8.26
$^3B_1(n \rightarrow \pi^*)$	4.02	3.90	3.91	3.93	3.92	3.94
$^3B_2(\pi \rightarrow \pi^*)$	4.92	4.90	4.89	4.91	4.90	4.92
$^3A_2(n \rightarrow \pi^*)$	5.48	5.38	5.37	5.39	5.37	5.39
$^3A_1(\pi \rightarrow \pi^*)$	6.89	6.79	6.83	6.84	6.83	6.85
Cyclopropenethione						
$^1A_2(n \rightarrow \pi^*)$	3.46	3.47	3.43	3.44	3.42	3.44
$^1B_1(n \rightarrow \pi^*)$	3.45	3.42	3.43	3.45	3.43	3.45
$^1B_2(\pi \rightarrow \pi^*)$	4.67	4.66	4.64	4.66	4.64	4.66
$^1B_2(n \rightarrow 3s)$	5.26	5.23	5.34	5.39	5.39	5.38
$^1A_1(\pi \rightarrow \pi^*)$	5.53	5.52	5.49	5.49	5.48	5.49
$^1B_2(n \rightarrow 3p)$	5.83	5.86	5.93	5.95	5.95	5.91
$^3A_2(n \rightarrow \pi^*)$	3.33	3.34	3.31	3.31	3.29	3.31
$^3B_1(n \rightarrow \pi^*)$	3.34	3.30	3.31	3.34	3.32	3.34
$^3B_2(\pi \rightarrow \pi^*)$	4.01	4.03	4.02	4.04	4.03	4.04
$^3A_1(\pi \rightarrow \pi^*)$	4.06	4.09	4.03	4.04	4.02	4.04
Methylenecyclopropene						
$^1B_2(\pi \rightarrow \pi^*)$	4.38	4.32	4.31	4.31	4.31	4.32
$^1B_1(\pi \rightarrow 3s)$	5.65	5.35	5.44	5.47	5.48	5.46
$^1A_2(\pi \rightarrow 3p)$	5.97	5.86	5.95	5.98	5.99	5.97
$^1A_1(\pi \rightarrow \pi^*)$	6.17	6.15	6.13	6.09	6.10	5.98
$^3B_2(\pi \rightarrow \pi^*)$	3.50	3.49	3.50	3.50	3.50	3.51
$^3A_1(\pi \rightarrow \pi^*)$	4.74	4.74	4.74	4.75	4.74	4.75

### S1.3 Acrolein, butadiene, and glyoxal

Table S3: CC3 vertical transition energies of acrolein, butadiene, and glyoxal using various atomic basis sets. FC stands for frozen core.  
All values are in eV.

	6-31+G(d) FC	aug-cc-pVDZ FC	aug-cc-pVTZ FC	aug-cc-pVQZ Full	d-aug-cc-pVQZ FC	aug-cc-pV5Z FC
Acrolein						
$^1A''(n \rightarrow \pi^*)$	3.83	3.77	3.74	3.75	3.74	
$^1A'(\pi \rightarrow \pi^*)$	6.83	6.67	6.65	6.65	6.65	
$^1A''(n \rightarrow \pi^*)$	6.94	6.75	6.75	6.77	6.76	
$^1A'(n \rightarrow 3s)$	7.22	6.99	7.07	7.11	7.11	
$^3A''(n \rightarrow \pi^*)$	3.55	3.47	3.46	3.47	3.46	
$^3A'(\pi \rightarrow \pi^*)$	3.94	3.95	3.94	3.95	3.94	
$^3A'(\pi \rightarrow \pi^*)$	6.25	6.22	6.19	6.20	6.19	
$^3A''(n \rightarrow \pi^*)$	6.81	6.60	6.61	6.63	6.62	
Butadiene						
$^1B_u(\pi \rightarrow \pi^*)$	6.41	6.25	6.22	6.21	6.22	
$^1B_g(\pi \rightarrow 3s)$	6.53	6.26	6.33	6.35	6.36	
$^1A_g(\pi \rightarrow \pi^*)$	6.73	6.68	6.67	6.67	6.67	
$^1A_u(\pi \rightarrow 3p)$	6.87	6.57	6.64	6.66	6.67	
$^1A_u(\pi \rightarrow 3p)$	6.93	6.73	6.80	6.82	6.83	
$^1B_u(\pi \rightarrow 3p)$	7.98	7.86	7.68	7.54	7.55	
$^3B_u(\pi \rightarrow \pi^*)$	3.35	3.36	3.36	3.37	3.36	
$^3A_g(\pi \rightarrow \pi^*)$	5.22	5.21	5.20	5.21	5.20	
$^3B_g(\pi \rightarrow 3s)$	6.46	6.20	6.28	6.30	6.31	
Glyoxal						
$^1A_u(n \rightarrow \pi^*)$	2.94	2.90	2.88	2.87	2.88	
$^1B_g(n \rightarrow \pi^*)$	4.34	4.30	4.27	4.27	4.27	
$^1A_g(n, n \rightarrow \pi^*, \pi^*)$	6.74	6.70	6.76	6.74	6.76	
$^1B_g(n \rightarrow \pi^*)$	6.81	6.59	6.58	6.59	6.58	
$^1B_u(n \rightarrow 3p)$	7.72	7.55	7.67	7.72	7.73	
$^3A_u(n \rightarrow \pi^*)$	2.55	2.49	2.49	2.49	2.49	
$^3B_g(n \rightarrow \pi^*)$	3.97	3.91	3.90	3.91	3.91	
$^3B_u(\pi \rightarrow \pi^*)$	5.22	5.20	5.17	5.18	5.18	
$^3A_g(\pi \rightarrow \pi^*)$	6.35	6.34	6.30	6.31	6.31	

## S1.4 Acetone, cyanoformaldehyde, isobutene, propynal, thioacetone, and thiopropynal

Table S4: CC3 vertical transition energies of acetone, cyanoformaldehyde, isobutene, propynal, thioacetone, and thiopropynal using various atomic basis sets. FC stands for frozen core. All values are in eV.

	6-31+G(d) FC	<i>aug-cc-pVDZ</i> FC	<i>aug-cc-pVTZ</i> FC	<i>aug-cc-pVQZ</i> FC	<i>d-aug-cc-pVQZ</i> Full	<i>d-aug-cc-pVQZ</i> FC
Acetone						
$^1A_2(n \rightarrow \pi^*)$	4.55	4.50	4.48	4.49	4.48	
$^1B_2(n \rightarrow 3s)$	6.65	6.31	6.43	6.48	6.49	
$^1A_2(n \rightarrow 3p)$	7.83	7.37	7.45	7.48	7.49	
$^1A_1(n \rightarrow 3p)$	7.81	7.39	7.48	7.52	7.53	
$^1B_2(n \rightarrow 3p)$	7.87	7.56	7.59	7.60	7.61	
$^3A_2(n \rightarrow \pi^*)$	4.21	4.16	4.15	4.17	4.16	
$^3A_1(\pi \rightarrow \pi^*)$	6.32	6.31	6.28	6.30	6.28	
Cyanoformaldehyde						
$^1A''(n \rightarrow \pi^*)$	3.91	3.86	3.83	3.84	3.83	3.84
$^1A''(\pi \rightarrow \pi^*)$	6.64	6.51	6.42	6.41	6.41	6.41
$^3A''(n \rightarrow \pi^*)$	3.53	3.47	3.46	3.47	3.46	3.47
$^3A'(\pi \rightarrow \pi^*)$	5.07	5.03	5.01	5.02	5.01	5.02
Isobutene						
$^1B_1(\pi \rightarrow 3s)$	6.77	6.39	6.45	6.47	6.49	
$^1A_1(\pi \rightarrow 3p)$	7.16	7.00	7.00	6.99	7.00	
$^3A_1(\pi \rightarrow \pi^*)$	4.52	4.54	4.53	4.54	4.54	
Propynal						
$^1A''(n \rightarrow \pi^*)$	3.90	3.85	3.82	3.83	3.82	3.83
$^1A''(\pi \rightarrow \pi^*)$	5.69	5.59	5.51	5.50	5.50	5.50
$^3A''(n \rightarrow \pi^*)$	3.56	3.50	3.49	3.50	3.49	3.50
$^3A'(\pi \rightarrow \pi^*)$	4.46	4.40	4.43	4.44	4.43	4.44
Thioacetone						
$^1A_2(n \rightarrow \pi^*)$	2.58	2.59	2.55	2.56		
$^1B_2(n \rightarrow 4s)$	5.65	5.44	5.55	5.60		
$^1A_1(\pi \rightarrow \pi^*)$	6.09	5.97	5.90	5.88	5.87	
$^1B_2(n \rightarrow 4p)$	6.59	6.45	6.51	6.52		
$^1A_1(n \rightarrow 4p)$	6.95	6.54	6.61	6.64	6.64	
$^3A_2(n \rightarrow \pi^*)$	2.36	2.36	2.34	2.35		
$^3A_1(\pi \rightarrow \pi^*)$	3.45	3.51	3.46	3.47	3.46	
Thiopropynal						
$^1A''(n \rightarrow \pi^*)$	2.09	2.09	2.05	2.06	2.04	
$^3A''(n \rightarrow \pi^*)$	1.84	1.83	1.81	1.82	1.81	

## S1.5 Cyclopentadiene, furan, imidazole, pyrrole, and thiophene

Table S5: CC3 vertical transition energies of furan and pyrrole using various atomic basis sets. FC stands for frozen core. All values are in eV.

	6-31+G(d) FC	<i>aug-cc-pVDZ</i> FC	<i>aug-cc-pVTZ</i> FC	<i>aug-cc-pVQZ</i> FC	<i>aug-cc-pVQZ</i> Full
Furan					
$^1A_2(\pi \rightarrow 3s)$	6.26	6.00	6.08	6.10	6.12
$^1B_2(\pi \rightarrow \pi^*)$	6.50	6.37	6.34	6.34	6.34
$^1A_1(\pi \rightarrow \pi^*)$	6.71	6.62	6.58	6.58	6.58
$^1B_1(\pi \rightarrow 3p)$	6.76	6.55	6.63	6.65	6.67
$^1A_2(\pi \rightarrow 3p)$	6.97	6.73	6.80	6.82	6.83
$^1B_2(\pi \rightarrow 3p)$	7.53	7.39	7.23	7.13	7.14
$^3B_2(\pi \rightarrow \pi^*)$	4.28	4.25	4.22	4.22	4.22
$^3A_1(\pi \rightarrow \pi^*)$	5.56	5.51	5.48	5.49	5.48
$^3A_2(\pi \rightarrow 3s)$	6.18	5.94	6.02	6.05	6.07
$^3B_1(\pi \rightarrow 3p)$	6.69	6.51	6.59	6.61	6.63
Pyrrole					
$^1A_2(\pi \rightarrow 3s)$	5.25	5.15	5.24	5.27	5.28
$^1B_1(\pi \rightarrow 3p)$	5.99	5.89	5.98	6.01	6.02
$^1A_2(\pi \rightarrow 3p)$	6.27	5.94	6.01	6.03	6.05
$^1B_2(\pi \rightarrow \pi^*)$	6.33	6.28	6.25	6.22	6.23
$^1A_1(\pi \rightarrow \pi^*)$	6.43	6.35	6.32	6.31	6.31
$^1B_2(\pi \rightarrow 3p)$	7.20	7.00	6.83	6.74	6.75
$^3B_2(\pi \rightarrow \pi^*)$	4.59	4.56	4.53	4.53	4.52
$^3A_2(\pi \rightarrow 3s)$	5.22	5.12	5.21	5.24	5.26
$^3A_1(\pi \rightarrow \pi^*)$	5.54	5.49	5.46	5.47	5.46
$^3B_1(\pi \rightarrow 3p)$	5.91	5.82	5.92	5.95	5.97

Table S6: CC3 vertical transition energies of cyclopentadiene, imidazole, and thiophene using various atomic basis sets. FC stands for frozen core. All values are in eV.

	6-31+G(d) FC	<i>aug-cc-pVDZ</i> FC	<i>aug-cc-pVTZ</i> FC	<i>aug-cc-pVQZ</i> FC
Cyclopentadiene				
$^1B_2(\pi \rightarrow \pi^*)$	5.79	5.59	5.54	5.53
$^1A_2(\pi \rightarrow 3s)$	6.08	5.70	5.77	5.79
$^1B_1(\pi \rightarrow 3p)$	6.57	6.34	6.40	6.42
$^1A_2(\pi \rightarrow 3p)$	6.67	6.39	6.45	6.46
$^1B_2(\pi \rightarrow 3p)$	7.06	6.55	6.56	6.55
$^1A_1(\pi \rightarrow \pi^*)$	6.67	6.59	6.57	6.57
$^3B_2(\pi \rightarrow \pi^*)$	3.33	3.32	3.32	3.32
$^3A_1(\pi \rightarrow \pi^*)$	5.16	5.14	5.12	5.13
$^3A_2(\pi \rightarrow 3s)$	6.01	5.65	5.73	5.75
$^3B_1(\pi \rightarrow 3p)$	6.51	6.30	6.36	6.38
Imidazole				
$^1A''(\pi \rightarrow 3s)$	5.77	5.60	5.71	5.73
$^1A'(\pi \rightarrow \pi^*)$	6.51	6.43	6.41	6.41
$^1A''(n \rightarrow \pi^*)$	6.66	6.42	6.50	6.53
$^1A'(\pi \rightarrow 3p)$	7.04	6.93	6.87	6.86
$^3A'(\pi \rightarrow \pi^*)$	4.83	4.78	4.75	4.76
$^3A''(\pi \rightarrow 3s)$	5.72	5.57	5.67	5.70
$^3A'(\pi \rightarrow \pi^*)$	5.88	5.78	5.74	5.75
$^3A''(n \rightarrow \pi^*)$	6.48	6.37	6.33	6.33
Thiophene				
$^1A_1(\pi \rightarrow \pi^*)$	5.79	5.70	5.65	5.64
$^1B_2(\pi \rightarrow \pi^*)$	6.23	6.05	5.96	5.94
$^1A_2(\pi \rightarrow 3s)$	6.26	6.07	6.14	6.16
$^1B_1(\pi \rightarrow 3p)$	6.18	6.19	6.14	6.11
$^1A_2(\pi \rightarrow 3p)$	6.32	6.33	6.25	6.22
$^1B_1(\pi \rightarrow 3s)$	6.62	6.42	6.50	6.53
$^1B_2(\pi \rightarrow 3p)$	7.45	7.45	7.29	7.18
$^1A_1(\pi \rightarrow \pi^*)$	7.50	7.41	7.35	7.33
$^3B_2(\pi \rightarrow \pi^*)$	3.95	3.96	3.94	3.93
$^3A_1(\pi \rightarrow \pi^*)$	4.90	4.82	4.77	4.77
$^3B_1(\pi \rightarrow 3p)$	6.00	6.01	5.95	5.92
$^3A_2(\pi \rightarrow 3s)$	6.20	6.01	6.09	5.99

## S1.6 Benzene, pyrazine, and tetrazazine

Table S7: CC3 vertical transition energies of benzene using various atomic basis sets. FC stands for frozen core. All values are in eV.

	6-31+G(d) FC	<i>aug-cc-pVDZ</i> FC	<i>aug-cc-pVTZ</i> FC	<i>aug-cc-pVQZ</i> FC
Benzene				
$^1B_{2u}(\pi \rightarrow \pi^*)$	5.13	5.11	5.09	5.09
$^1B_{1u}(\pi \rightarrow \pi^*)$	6.68	6.50	6.44	6.43
$^1E_{1g}(\pi \rightarrow 3s)$	6.75	6.46	6.52	6.54
$^1A_{2u}(\pi \rightarrow 3p)$	7.24	7.02	7.08	7.10
$^1E_{2u}(\pi \rightarrow 3p)$	7.34	7.09	7.15	7.16
$^3B_{1u}(\pi \rightarrow \pi^*)$	4.18	4.19	4.18	4.19
$^3E_{1u}(\pi \rightarrow \pi^*)$	4.95	4.89	4.86	4.87
$^3B_{2u}(\pi \rightarrow \pi^*)$	6.06	5.86	5.81	5.81

Table S8: CC3 vertical transition energies of pyrazine and tetrazine using various atomic basis sets. FC stands for frozen core. All values are in eV.

	6-31+G(d)	<i>aug-cc-pVDZ</i>	<i>aug-cc-pVTZ</i>	<i>aug-cc-pVQZ</i>	
	FC	FC	FC	FC	Full
Pyrazine					
$^1B_{3u}(n \rightarrow \pi^*)$	4.28	4.19	4.14	4.14	4.13
$^1A_u(n \rightarrow \pi^*)$	5.08	4.98	4.97	4.98	4.97
$^1B_{2u}(\pi \rightarrow \pi^*)$	5.10	5.07	5.03	5.02	5.02
$^1B_{2g}(n \rightarrow \pi^*)$	5.86	5.78	5.71	5.71	
$^1A_g(n \rightarrow 3s)$	6.74	6.54	6.66	6.70	6.71
$^1B_{1g}(n \rightarrow \pi^*)$	6.87	6.75	6.73	6.73	
$^1B_{1u}(\pi \rightarrow \pi^*)$	7.10	6.92	6.86	6.85	6.85
$^1B_{1g}(\pi \rightarrow 3s)$	7.36	7.13	7.20	7.23	
$^1B_{2u}(n \rightarrow 3p)$	7.39	7.14	7.25	7.29	7.30
$^1B_{1u}(n \rightarrow 3p)$	7.56	7.38	7.45	7.48	7.49
$^1B_{1u}(\pi \rightarrow \pi^*)$	8.19	7.99	7.94	7.93	7.93
$^3B_{3u}(n \rightarrow \pi^*)$	3.68	3.60	3.59	3.59	3.59
$^3B_{1u}(\pi \rightarrow \pi^*)$	4.39	4.40	4.39	4.40	4.39
$^3B_{2u}(\pi \rightarrow \pi^*)$	4.56	4.46	4.40	4.40	4.40
$^3A_u(n \rightarrow \pi^*)$	5.05	4.93	4.93	4.94	
$^3B_{2g}(n \rightarrow \pi^*)$	5.18	5.11	5.08	5.09	5.07
$^3B_{1u}(\pi \rightarrow \pi^*)$	5.38	5.32	5.29	5.29	5.28
Tetrazine					
$^1B_{3u}(n \rightarrow \pi^*)$	2.53	2.49	2.46	2.45	2.45
$^1A_u(n \rightarrow \pi^*)$	3.75	3.69	3.67	3.68	3.67
$^1A_g(n, n \rightarrow \pi^*, \pi^*)$	6.22	6.22	6.21	6.19	6.17
$^1B_{1g}(n \rightarrow \pi^*)$	5.01	4.97	4.91	4.90	4.88
$^1B_{2u}(\pi \rightarrow \pi^*)$	5.29	5.27	5.23	5.22	5.21
$^1B_{2g}(n \rightarrow \pi^*)$	5.56	5.53	5.46	5.46	5.45
$^1A_u(n \rightarrow \pi^*)$	5.61	5.59	5.52	5.52	5.50
$^1B_{3g}(n, n \rightarrow \pi^*, \pi^*)$	7.64	7.62	7.62	7.60	7.58
$^1B_{2g}(n \rightarrow \pi^*)$	6.24	6.17	6.13	6.13	6.10
$^1B_{1g}(n \rightarrow \pi^*)$	7.04	6.98	6.92	6.92	6.91
$^3B_{3u}(n \rightarrow \pi^*)$	1.87	1.86	1.85	1.86	1.85
$^3A_u(n \rightarrow \pi^*)$	3.48	3.43	3.44	3.45	3.43
$^3B_{1g}(n \rightarrow \pi^*)$	4.25	4.23	4.20	4.21	4.18
$^3B_{1u}(\pi \rightarrow \pi^*)$	4.54	4.54	4.54	4.54	4.53
$^3B_{2u}(\pi \rightarrow \pi^*)$	4.65	4.58	4.52	4.52	4.51
$^3B_{2g}(n \rightarrow \pi^*)$	5.11	5.09	5.05	5.05	5.04
$^3A_u(n \rightarrow \pi^*)$	5.17	5.15	5.11	5.11	5.10
$^3B_{3g}(n, n \rightarrow \pi^*, \pi^*)$	7.35	7.33	7.35	7.34	7.32
$^3B_{1u}(\pi \rightarrow \pi^*)$	5.51	5.46	5.42	5.43	5.42

### S1.6.1 Pyridazine, pyridine, pyrimidine and triazine

Table S9: CC3 vertical transition energies of pyridazine and pyridine using various atomic basis sets. FC stands for frozen core. All values are in eV.

	6-31+G(d) FC	<i>aug-cc-pVDZ</i> FC	<i>aug-cc-pVTZ</i> FC	<i>aug-cc-pVQZ</i> FC
Pyridazine				
$^1B_1(n \rightarrow \pi^*)$	3.95	3.86	3.83	3.83
$^1A_2(n \rightarrow \pi^*)$	4.49	4.39	4.37	4.38
$^1A_1(\pi \rightarrow \pi^*)$	5.36	5.33	5.29	5.29
$^1A_2(n \rightarrow \pi^*)$	5.88	5.80	5.74	5.74
$^1B_2(n \rightarrow 3s)$	6.26	6.06	6.17	6.21
$^1B_1(n \rightarrow \pi^*)$	6.51	6.41	6.37	6.37
$^1B_2(\pi \rightarrow \pi^*)$	6.96	6.79	6.74	6.73
$^3B_1(n \rightarrow \pi^*)$	3.27	3.20	3.19	3.20
$^3A_2(n \rightarrow \pi^*)$	4.19	4.11	4.11	4.12
$^3B_2(\pi \rightarrow \pi^*)$	4.39	4.39	4.38	4.39
$^3A_1(\pi \rightarrow \pi^*)$	4.93	4.87	4.83	4.82
Pyridine				
$^1B_1(n \rightarrow \pi^*)$	5.12	5.01	4.96	4.96
$^1B_2(\pi \rightarrow \pi^*)$	5.23	5.21	5.17	5.17
$^1A_2(n \rightarrow \pi^*)$	5.55	5.41	5.40	5.41
$^1A_1(\pi \rightarrow \pi^*)$	6.84	6.64	6.63	6.62
$^1A_1(n \rightarrow 3s)$	6.92	6.71	6.76	6.80
$^1A_2(\pi \rightarrow 3s)$	6.98	6.74	6.81	6.83
$^1B_2(\pi \rightarrow \pi^*)$	7.50	7.40	7.38	7.40
$^1B_1(\pi \rightarrow 3p)$	7.54	7.32	7.38	7.40
$^1A_1(\pi \rightarrow \pi^*)$	7.56	7.34	7.39	7.40
$^3A_1(\pi \rightarrow \pi^*)$	4.33	4.34	4.33	4.34
$^3B_1(n \rightarrow \pi^*)$	4.57	4.47	4.46	4.47
$^3B_2(\pi \rightarrow \pi^*)$	4.92	4.83	4.79	4.79
$^3A_1(\pi \rightarrow \pi^*)$	5.14	5.08	5.05	5.05
$^3A_2(n \rightarrow \pi^*)$	5.51	5.37	5.35	5.37
$^3B_2(\pi \rightarrow \pi^*)$	6.46	6.30	6.25	6.25

Table S10: CC3 vertical transition energies of pyrimidine and triazine using various atomic basis sets. FC stands for frozen core. All values are in eV.

	6-31+G(d) FC	<i>aug-cc-pVDZ</i> FC	<i>aug-cc-pVTZ</i> FC	<i>aug-cc-pVQZ</i> FC
Pyrimidine				
$^1B_1(n \rightarrow \pi^*)$	4.58	4.48	4.44	4.45
$^1A_2(n \rightarrow \pi^*)$	4.99	4.89	4.86	4.87
$^1B_2(\pi \rightarrow \pi^*)$	5.47	5.44	5.41	5.40
$^1A_2(n \rightarrow \pi^*)$	6.07	5.98	5.93	5.93
$^1B_1(n \rightarrow \pi^*)$	6.39	6.29	6.26	6.27
$^1B_2(n \rightarrow 3s)$	6.81	6.61	6.72	6.76
$^1A_1(\pi \rightarrow \pi^*)$	7.08	6.93	6.87	6.86
$^3B_1(n \rightarrow \pi^*)$	4.20	4.12	4.10	4.11
$^3A_1(\pi \rightarrow \pi^*)$	4.55	4.56	4.55	4.56
$^3A_2(n \rightarrow \pi^*)$	4.77	4.67	4.66	4.67
$^3B_2(\pi \rightarrow \pi^*)$	5.08	5.00	4.96	4.96
Triazine				
$^1A''_1(n \rightarrow \pi^*)$	4.85	4.76	4.73	4.74
$^1A''_2(n \rightarrow \pi^*)$	4.84	4.78	4.74	4.74
$^1E''(n \rightarrow \pi^*)$	4.89	4.82	4.78	4.79
$^1A'_2(\pi \rightarrow \pi^*)$	5.84	5.81	5.78	5.78
$^1A'_1(\pi \rightarrow \pi^*)$	7.45	7.31	7.24	7.23
$^1E'(n \rightarrow 3s)$	7.44	7.24	7.35	7.39
$^1E''(n \rightarrow \pi^*)$	7.89	7.82	7.79	7.78
$^1E'(\pi \rightarrow \pi^*)$	8.12	7.97	7.92	7.92
$^3A''_2(n \rightarrow \pi^*)$	4.40	4.35	4.33	4.34
$^3E''(n \rightarrow \pi^*)$	4.59	4.52	4.51	4.51
$^3A''_1(n \rightarrow \pi^*)$	4.87	4.78	4.75	4.76
$^3A'_1(\pi \rightarrow \pi^*)$	4.88	4.88	4.88	4.89
$^3E'(\pi \rightarrow \pi^*)$	5.70	5.64	5.61	5.61
$^3A'_2(\pi \rightarrow \pi^*)$	6.85	6.69	6.63	6.62

## S2 Multiconfigurational results

### S2.1 Basis set effects

Table S11: Vertical transition energies of cyanoacetylene, cyanogen, and diacetylene using various atomic basis sets and multi-reference methods. All values are in eV and have been obtained within the FC approximation. The CASPT2 calculations are performed with a level shift of 0.3 and a IPEA of 0.25. Pop, AVDZ, AVTZ, and AVQZ respectively stand for 6-31+G(d), *aug-cc-pVDZ*, *aug-cc-pVTZ*, and *aug-cc-pVQZ*.

	CASPT2(8,8)				PC-NEVPT2(8,8)				SC-NEVPT2(8,8)			
	Pop	AVDZ	AVTZ	AVQZ	Pop	AVDZ	AVTZ	AVQZ	Pop	AVDZ	AVTZ	AVQZ
Cyanoacetylene												
$^1\Sigma^-$	6.00	5.86			5.93	5.78			5.98	5.83		
$^1\Delta$	6.26	6.13			6.22	6.10			6.27	6.14		
$^3\Sigma^+$	4.47	4.45			4.46	4.45			4.51	4.49		
$^3\Delta$	5.30	5.21			5.28	5.19			5.31	5.23		
Cyanogen												
$^1\Sigma_u^-$	6.63	6.56	6.40	6.37	6.56	6.49	6.32	6.29	6.61	6.54	6.37	6.34
$^1\Delta_u$	6.93	6.84	6.70	6.66	6.91	6.81	6.66	6.63	6.95	6.86	6.71	6.68
$^3\Sigma_u^+$	4.91	4.89	4.86	4.86	4.92	4.91	4.88	4.89	4.96	4.95	4.92	4.93
$^1\Sigma_u^-$ [F]		5.23	5.07			5.14	4.97			5.17	5.01	
Diacetylene												
$^1\Sigma_u^-$		5.56	5.43			5.47	5.33			5.53	5.39	
$^1\Delta_u$		5.80	5.68			5.73	5.61			5.78	5.67	
$^3\Sigma_u^+$		4.12	4.11			4.09	4.08			4.14	4.13	
$^3\Delta_u$		4.89	4.81			4.86	4.78			4.90	4.82	

## S2.2 Active Spaces

In the following tables, NEVPT2 vertical transition energies are provided using different sizes of active space. The composition of the active space is specified in terms of number of active orbitals per irreducible representation only for the NEVPT2 result chosen in the article (Tables 1–4). Similarly, the state-averaging procedure and the CASSCF vertical transition energies given correspond to the underlying reference calculation for the final NEVPT2 values of the article. Note that, in all these calculations, the ground state is always included in the state averaging procedure. In addition, we chose carefully the states to be averaged in the case of non-abelian point groups in order to describe correctly the degeneracy of doubly-degenerate states (e.g.,  $\Delta$  states of cyanoacetylene, cyanogen and diacetylene, and  $E$  states of benzene and triazine).

Table S12: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of acetone.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1A_2(V; n \rightarrow \pi^*)$	(2,3,1,0)	(1,0,0,2)	4.77 <sup>b</sup>	4.57 <sup>a</sup> , 4.48 <sup>b</sup>
$^1B_2(R; n \rightarrow 3s)$	(4,2,1,0)	(1,0,2,0)	5.50 <sup>c</sup>	6.81 <sup>c</sup>
$^1A_2(R; n \rightarrow 3p)$	(2,3,1,0)	(1,0,0,2)	7.46 <sup>b</sup>	7.65 <sup>b</sup>
$^1A_1(R; n \rightarrow 3p)$	(2,2,2,0)	(2,0,0,0)	7.03 <sup>d</sup>	7.75 <sup>d</sup>
$^1B_2(R; n \rightarrow 3p)$	(4,2,1,0)	(1,0,2,0)	6.44 <sup>c</sup>	7.91 <sup>c</sup>
$^3A_2(V; n \rightarrow \pi^*)$	(2,2,1,0)	(1,0,0,1)	4.47 <sup>a</sup>	4.20 <sup>a</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(2,2,0,0)	(2,0,0,0)	6.22 <sup>e</sup>	6.28 <sup>e</sup>

<sup>a</sup>Using reference (6e,5o) active space including valence  $\pi$ ,  $n_O$ ,  $\sigma_{CO}$  and  $\sigma_{CO}^*$  orbitals. <sup>b</sup>Using reference (6e,6o) active space including valence  $\pi$ ,  $n_O$ ,  $\sigma_{CO}$ ,  $\sigma_{CO}^*$  and  $3p_x$  orbitals. <sup>c</sup>Using reference (6e,7o) active space including valence  $\pi$ ,  $n_O$ ,  $\sigma_{CO}$ ,  $\sigma_{CO}^*$ ,  $3s$  and  $3p_z$  orbitals. <sup>d</sup>Using reference (6e,6o) active space including valence  $\pi$ ,  $n_O$ ,  $\sigma_{CO}$ ,  $\sigma_{CO}^*$  and  $3p_y$  orbitals. <sup>e</sup>Using reference (4e,4o) active space including valence  $\pi$ ,  $\sigma_{CO}$  and  $\sigma_{CO}^*$  orbitals.

Table S13: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of acrolein.

State	Active space ( $a'$ , $a''$ )	State average ( $A'$ , $A''$ )	CASSCF	NEVPT2
$^1A''(\text{V}; n \rightarrow \pi^*)$	(8,4)	(1,3)	4.02 <sup>a</sup>	3.76 <sup>a</sup> , 3.73 <sup>b</sup>
$^1A'(\text{V}; \pi \rightarrow \pi^*)$	(8,4)	(4,0)	8.24 <sup>a</sup>	6.67 <sup>a</sup>
$^1A''(\text{V}; n \rightarrow \pi^*)$	(8,4)	(1,3)	7.63 <sup>a</sup>	7.16 <sup>a,c</sup> , 7.57 <sup>b,c</sup>
$^1A'(\text{R}; n \rightarrow 3s)$	(8,4)	(4,0)	6.98 <sup>a</sup>	7.05 <sup>a</sup>
$^3A''(\text{V}; n \rightarrow \pi^*)$	(8,4)	(1,3)	3.86 <sup>a</sup>	3.46 <sup>a</sup> , 3.44 <sup>b</sup>
$^3A'(\text{V}; \pi \rightarrow \pi^*)$	(8,4)	(4,0)	4.31 <sup>a</sup>	3.95 <sup>a</sup>
$^3A'(\text{V}; \pi \rightarrow \pi^*)$	(8,4)	(4,0)	6.76 <sup>a</sup>	6.23 <sup>a</sup>
$^3A''(\text{V}; n \rightarrow \pi^*)$	(8,4)	(1,3)	7.47 <sup>a</sup>	6.83 <sup>a,d</sup> , 7.06 <sup>b,d</sup>

<sup>a</sup>Using reference (12e,12o) active space including valence  $\pi$ ,  $\sigma_{\text{CC}}$ ,  $\sigma_{\text{CO}}$ ,  $\sigma_{\text{CC}}^*$ ,  $\sigma_{\text{CO}}^*$ ,  $n_{\text{O}}$  and 3s orbitals. <sup>b</sup>Using reference (12e,13o) active space including valence  $\pi$ ,  $\sigma_{\text{CC}}$ ,  $\sigma_{\text{CO}}$ ,  $\sigma_{\text{CC}}^*$ ,  $\sigma_{\text{CO}}^*$ ,  $n_{\text{O}}$ , 3s and 3p<sub>z</sub> orbitals.

<sup>c</sup>Substantial Rydberg and doubly-excited character. <sup>d</sup>Substantial doubly-excited character.

Table S14: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of benzene.

State	Active space ( $a_g$ , $b_{3u}$ , $b_{2u}$ , $b_{1g}$ , $b_{1u}$ , $b_{2g}$ , $b_{3g}$ , $a_u$ )	State average ( $A_g$ , $B_{3u}$ , $B_{2u}$ , $B_{1g}$ , $B_{1u}$ , $B_{2g}$ , $B_{3g}$ , $A_u$ )	CASSCF	NEVPT2
$^1B_{2u}(\text{V}; \pi \rightarrow \pi^*)$	(0,0,0,0,2,1,2,1)	(1,1,0,0,0,0,0,0)	4.98 <sup>a</sup>	5.32 <sup>a</sup> , 5.32 <sup>b</sup>
$^1B_{1u}(\text{V}; \pi \rightarrow \pi^*)$	(0,0,0,0,4,1,2,2)	(1,1,2,0,0,0,0,0)	7.27 <sup>b</sup>	6.01 <sup>a</sup> , 6.43 <sup>b</sup>
$^1E_{1g}(\text{R}; \pi \rightarrow 3s)$	(1,0,0,0,2,1,2,1)	(1,0,0,0,0,1,1,0)	5.90 <sup>c</sup>	6.75 <sup>c</sup>
$^1A_{2u}(\text{R}; \pi \rightarrow 3p)$	(0,1,1,0,2,1,2,1)	(1,0,0,0,2,0,0,1)	6.14 <sup>d</sup>	7.40 <sup>d</sup>
$^1E_{2u}(\text{R}; \pi \rightarrow 3p)$	(0,1,1,0,2,1,2,1)	(1,0,0,0,2,0,0,1)	6.21 <sup>d</sup>	7.45 <sup>d</sup>
$^3B_{1u}(\text{V}; \pi \rightarrow \pi^*)$	(0,0,0,0,4,1,2,2)	(1,0,1,0,0,0,0,0)	3.85 <sup>b</sup>	4.44 <sup>a</sup> , 4.32 <sup>b</sup>
$^3E_{1u}(\text{V}; \pi \rightarrow \pi^*)$	(0,0,0,0,4,1,2,2)	(1,1,1,0,0,0,0,0)	4.85 <sup>b</sup>	4.99 <sup>a</sup> , 4.92 <sup>b</sup>
$^3B_{2u}(\text{V}; \pi \rightarrow \pi^*)$	(0,0,0,0,4,1,2,2)	(1,1,0,0,0,0,0,0)	6.75 <sup>b</sup>	5.30 <sup>a</sup> , 5.51 <sup>b</sup>

<sup>a</sup>Using reference (6e,6o) active space including valence  $\pi$  orbitals. <sup>b</sup>Using reference (6e,9o) active space including valence  $\pi$  and three 3p<sub>z</sub> orbitals. <sup>c</sup>Using reference (6e,7o) active space including valence  $\pi$  and 3s orbitals. <sup>d</sup>Using reference (6e,8o) active space including valence  $\pi$ , 3p<sub>x</sub> and 3p<sub>y</sub> orbitals.

Table S15: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of butadiene.

State	Active space ( $a_g, a_u, b_u, b_g$ )	State average ( $A_g, A_u, B_u, B_g$ )	CASSCF	NEVPT2
$^1B_u(V; \pi \rightarrow \pi^*)$	(0,4,0,4)	(1,0,2,0)	6.65 <sup>c</sup>	6.04 <sup>a</sup> , 6.73 <sup>b</sup> , 6.68 <sup>c</sup>
$^1B_g(R; \pi \rightarrow 3s)$	(4,2,3,2)	(1,0,0,1)	5.94 <sup>d</sup>	6.44 <sup>d</sup>
$^1A_g(V; \pi \rightarrow \pi^*)$	(3,2,3,2)	(2,0,0,0)	6.99 <sup>a</sup>	6.70 <sup>a</sup>
$^1A_u(R; \pi \rightarrow 3p)$	(3,2,5,2)	(1,2,0,0)	5.95 <sup>e</sup>	6.84 <sup>e</sup>
$^1A_u(R; \pi \rightarrow 3p)$	(3,2,5,2)	(1,2,0,0)	6.12 <sup>e</sup>	7.01 <sup>e</sup>
$^1B_u(R; \pi \rightarrow 3p)$	(0,4,0,4)	(1,0,2,0)	7.93 <sup>c</sup>	6.99 <sup>b</sup> , 7.45 <sup>c</sup>
$^3B_u(V; \pi \rightarrow \pi^*)$	(3,2,3,2)	(1,0,1,0)	3.55 <sup>a</sup>	3.40 <sup>a</sup>
$^3A_g(V; \pi \rightarrow \pi^*)$	(3,2,3,2)	(2,0,0,0)	5.52 <sup>a</sup>	5.30 <sup>a</sup>
$^3B_g(R; \pi \rightarrow 3s)$	(4,2,3,2)	(1,0,0,1)	5.89 <sup>d</sup>	6.38 <sup>d</sup>

<sup>a</sup>Using reference (10e,10o) active space including valence  $\pi$ ,  $\sigma_{CC}$  and  $\sigma_{CC}^*$  orbitals. <sup>b</sup>Using reference (10e,11o) active space including valence  $\pi$ ,  $\sigma_{CC}$ ,  $\sigma_{CC}^*$  and  $3p_z$  orbitals. <sup>c</sup>Using reference (4e,8o) active space including valence  $\pi$  and four  $3p_z$ . <sup>d</sup>Using reference (10e,11o) active space including valence  $\pi$ ,  $\sigma_{CC}$ ,  $\sigma_{CC}^*$  and  $3s$  orbitals. <sup>e</sup>Using reference (10e,12o) active space including valence  $\pi$ ,  $\sigma_{CC}$ ,  $\sigma_{CC}^*$ ,  $3p_x$  and  $3p_y$  orbitals.

Table S16: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of cyanoacetylene.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF <sup>a</sup>	NEVPT2 <sup>a</sup>
$^1\Sigma^-(V; \pi \rightarrow \pi^*)$	(0,4,4,0)	(1,0,0,1)	6.54	5.78
$^1\Delta(V; \pi \rightarrow \pi^*)$	(0,4,4,0)	(2,0,0,1)	6.80	6.10
$^3\Sigma^+(V; \pi \rightarrow \pi^*)$	(0,4,4,0)	(2,0,0,0)	4.86	4.45
$^3\Delta(V; \pi \rightarrow \pi^*)$	(0,4,4,0)	(2,0,0,1)	5.64	5.19
$^1A''[F](V; \pi \rightarrow \pi^*)$	( $a':4, a'':4$ )	( $A':1, A'':2$ )	4.30	3.50

<sup>a</sup>All calculations using a full valence  $\pi$  active space of (8e,8o).

Table S17: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of cyanoformaldehyde.

State	Active space ( $a', a''$ )	State average ( $A', A''$ )	CASSCF	NEVPT2
$^1A''(V; n \rightarrow \pi^*)$	(3,4)	(1,2)	4.02 <sup>a</sup>	3.98 <sup>a</sup>
$^1A''(V; \pi \rightarrow \pi^*)$	(3,4)	(1,2)	7.61 <sup>a</sup>	6.44 <sup>a</sup>
$^3A''(V; n \rightarrow \pi^*)$	(3,4)	(1,1)	3.52 <sup>a</sup>	3.58 <sup>a</sup>
$^3A'(V; \pi \rightarrow \pi^*)$	(2,4)	(2,0)	4.98 <sup>b</sup>	5.35 <sup>b</sup>

<sup>a</sup> Using reference (8e,7o) active space including valence  $\pi$  and  $n_O$  orbitals. <sup>b</sup> Using reference (6e,6o) active space including valence  $\pi$  orbitals.

Table S18: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of cyanogen.

State	Active space ( $a_g, b_{3u}, b_{2u}, b_{1g},$ $b_{1u}, b_{2g}, b_{3g}, a_u$ )	State average ( $A_g, B_{3u}, B_{2u}, B_{1g},$ $B_{1u}, B_{2g}, B_{3g}, A_u$ )	CASSCF <sup>a</sup>	NEVPT2 <sup>a</sup>
$^1\Sigma_u^-$ (V; $\pi \rightarrow \pi^*$ )	(0,2,2,0,0,2,2,0)	(1,0,0,0,0,0,1)	7.14	6.32
$^1\Delta_u$ (V; $\pi \rightarrow \pi^*$ )	(0,2,2,0,0,2,2,0)	(1,0,0,0,1,0,0,1)	7.46	6.66
$^3\Sigma_u^+$ (V; $\pi \rightarrow \pi^*$ )	(0,2,2,0,0,2,2,0)	(1,0,0,0,1,0,0,0)	5.28	4.88
$^1\Sigma_u^-$ [F](V; $\pi \rightarrow \pi^*$ )	(0,2,2,0,0,2,2,0)	(1,0,0,0,0,0,1)	5.68	4.97

<sup>a</sup>All calculations using a full valence  $\pi$  active space of (8e,8o).

Table S19: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of cyclopentadiene.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1B_2$ (V; $\pi \rightarrow \pi^*$ )	(0,4,0,2)	(1,0,2,0)	6.71 <sup>c</sup>	4.96 <sup>a</sup> ,4.92 <sup>b</sup> ,5.65 <sup>c</sup>
$^1A_2$ (R; $\pi \rightarrow 3s$ )	(2,2,0,2)	(1,0,0,2)	5.21 <sup>d</sup>	5.92 <sup>d</sup>
$^1B_1$ (R; $\pi \rightarrow 3p$ )	(0,2,1,2)	(1,1,0,0)	6.08 <sup>e</sup>	6.42 <sup>e</sup>
$^1A_2$ (R; $\pi \rightarrow 3p$ )	(2,2,0,2)	(1,0,0,2)	5.78 <sup>d</sup>	6.59 <sup>d</sup>
$^1B_2$ (R; $\pi \rightarrow 3p$ )	(0,4,0,2)	(1,0,2,0)	6.16 <sup>c</sup>	6.58 <sup>b</sup> ,6.60 <sup>c</sup>
$^1A_1$ (V; $\pi \rightarrow \pi^*$ )	(0,2,0,2)	(3,0,0,0)	6.49 <sup>a,f</sup>	6.75 <sup>a,f</sup>
$^3B_2$ (V; $\pi \rightarrow \pi^*$ )	(0,2,0,2)	(1,0,1,0)	3.26 <sup>a</sup>	3.41 <sup>a</sup>
$^3A_1$ (V; $\pi \rightarrow \pi^*$ )	(0,2,0,2)	(3,0,0,0)	4.92 <sup>a</sup>	5.30 <sup>a</sup>
$^3A_2$ (R; $\pi \rightarrow 3s$ )	(1,2,0,2)	(1,0,0,1)	5.53 <sup>g</sup>	5.73 <sup>g</sup>
$^3B_1$ (R; $\pi \rightarrow 3p$ )	(0,2,1,2)	(1,1,0,0)	6.05 <sup>e</sup>	6.40 <sup>e</sup>

<sup>a</sup>Using reference (4e,4o) active space including valence  $\pi$  orbitals. <sup>b</sup>Using reference (4e,5o) active space including valence  $\pi$  and  $3p_x$  orbitals. <sup>c</sup>Using reference (4e,6o) active space including valence  $\pi$  and two  $3p_x$  orbitals. <sup>d</sup>Using reference (4e,6o) active space including valence  $\pi$ ,  $3s$  and  $3p_z$  orbitals. <sup>e</sup>Using reference (4e,5o) active space including valence  $\pi$  and  $3p_y$  orbitals. <sup>f</sup>Strong double-excitation character. <sup>g</sup>Using reference (4e,5o) active space including valence  $\pi$  and  $3s$  orbitals.

Table S20: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of cyclopropenone.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF <sup>a</sup>	NEVPT2 <sup>a</sup>
$^1B_1(V; n \rightarrow \pi^*)$	(2,3,1,1)	(1,3,0,0)	4.92	4.04
$^1A_2(V; n \rightarrow \pi^*)$	(0,4,2,1)	(1,0,0,3)	5.64	5.85
$^1B_2(R; n \rightarrow 3s)$	(2,3,1,1)	(1,0,3,0)	5.68	6.51
$^1B_2(V; \pi \rightarrow \pi^*)$	(2,3,1,1)	(1,0,3,0)	6.40	6.82
$^1B_2(R; n \rightarrow 3p)$	(2,3,1,1)	(1,0,3,0)	6.35	7.07
$^1A_1(R; n \rightarrow 3p)$	(0,4,2,1)	(4,0,0,0)	6.84	7.28
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,4,2,1)	(4,0,0,0)	10.42	8.19
$^3B_1(V; n \rightarrow \pi^*)$	(2,3,1,1)	(1,3,0,0)	4.72	3.51
$^3B_2(V; \pi \rightarrow \pi^*)$	(2,3,1,1)	(1,0,3,0)	4.39	5.10
$^3A_2(V; n \rightarrow \pi^*)$	(0,4,2,1)	(1,0,0,3)	5.40	5.60
$^3A_1(V; \pi \rightarrow \pi^*)$	(0,4,2,1)	(4,0,0,0)	6.59	7.16

<sup>a</sup>All calculations using reference (6e,7o) active space.

Table S21: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of cyclopropenethione.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1A_2(V; n \rightarrow \pi^*)$	(0,3,1,1)	(1,0,0,1)	3.44 <sup>a</sup>	3.52 <sup>a</sup>
$^1B_1(V; n \rightarrow \pi^*)$	(0,3,1,1)	(1,1,0,0)	3.57 <sup>a</sup>	3.50 <sup>a</sup>
$^1B_2(V; \pi \rightarrow \pi^*)$	(2,3,1,1)	(1,0,3,0)	4.51 <sup>b</sup>	4.77 <sup>b</sup>
$^1B_2(R; n \rightarrow 3s)$	(2,3,1,1)	(1,0,3,0)	4.59 <sup>b</sup>	5.35 <sup>b</sup>
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,3,0,1)	(2,0,0,0)	6.46 <sup>c</sup>	5.54 <sup>c</sup>
$^1B_2(R; n \rightarrow 3p)$	(2,3,1,1)	(1,0,3,0)	5.27 <sup>b</sup>	5.99 <sup>b</sup>
$^3A_2(V; n \rightarrow \pi^*)$	(0,3,1,1)	(1,0,0,1)	3.26 <sup>a</sup>	3.38 <sup>a</sup>
$^3B_1(V; n \rightarrow \pi^*)$	(0,3,1,1)	(1,1,0,0)	3.51 <sup>a</sup>	3.40 <sup>a</sup>
$^3B_2(V; \pi \rightarrow \pi^*)$	(2,3,1,1)	(1,0,3,0)	3.80 <sup>b</sup>	4.21 <sup>c</sup> ,4.17 <sup>b</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(0,3,0,1)	(2,0,0,0)	3.83 <sup>c</sup>	4.13 <sup>c</sup>

<sup>a</sup>Using reference (6e,5o) active space. <sup>b</sup>Using reference (6e,7o) active space. <sup>c</sup>Using reference (4e,4o) active space.

Table S22: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of diacetylene.

State	Active space ( $a_g, b_{3u}, b_{2u}, b_{1g},$ $b_{1u}, b_{2g}, b_{3g}, a_u$ )	State average ( $A_g, B_{3u}, B_{2u}, B_{1g},$ $B_{1u}, B_{2g}, B_{3g}, A_u$ )	CASSCF <sup>a</sup>	NEVPT2 <sup>a</sup>
$^1\Sigma_u^-$ (V; $\pi \rightarrow \pi^*$ )	(0,2,2,0,0,2,2,0)	(1,0,0,0,0,0,1)	6.13	5.33
$^1\Delta_u$ (V; $\pi \rightarrow \pi^*$ )	(0,2,2,0,0,2,2,0)	(1,0,0,0,1,0,0,1)	6.39	5.61
$^3\Sigma_u^+$ (V; $\pi \rightarrow \pi^*$ )	(0,2,2,0,0,2,2,0)	(1,0,0,0,1,0,0,0)	4.54	4.08
$^3\Delta_u$ (V; $\pi \rightarrow \pi^*$ )	(0,2,2,0,0,2,2,0)	(1,0,0,0,1,0,0,1)	5.28	4.78

<sup>a</sup>All calculations using a full valence  $\pi$  active space of (8e,8o).

Table S23: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of furan.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1A_2$ (R; $\pi \rightarrow 3s$ )	(2,3,0,2)	(1,0,0,2)	5.26 <sup>a</sup>	6.28 <sup>a</sup>
$^1B_2$ (V; $\pi \rightarrow \pi^*$ )	(0,4,0,2)	(1,0,2,0)	7.78 <sup>c</sup>	5.92 <sup>b</sup> , 6.20 <sup>c,d</sup>
$^1A_1$ (V; $\pi \rightarrow \pi^*$ )	(0,3,0,2)	(3,0,0,0)	6.73 <sup>b,e</sup>	6.77 <sup>b,e</sup>
$^1B_1$ (R; $\pi \rightarrow 3p$ )	(0,3,1,2)	(1,1,0,0)	6.07 <sup>f</sup>	6.71 <sup>f</sup>
$^1A_2$ (R; $\pi \rightarrow 3p$ )	(2,3,0,2)	(1,0,0,2)	5.87 <sup>a</sup>	6.99 <sup>a</sup>
$^1B_2$ (R; $\pi \rightarrow 3p$ )	(0,4,0,2)	(1,0,2,0)	6.54 <sup>c</sup>	7.01 <sup>c,d</sup>
$^3B_2$ (V; $\pi \rightarrow \pi^*$ )	(0,3,0,2)	(1,0,1,0)	3.94 <sup>b</sup>	4.42 <sup>b</sup>
$^3A_1$ (V; $\pi \rightarrow \pi^*$ )	(0,3,0,2)	(3,0,0,0)	5.41 <sup>b</sup>	5.60 <sup>b</sup>
$^3A_2$ (R; $\pi \rightarrow 3s$ )	(1,3,0,2)	(1,0,0,1)	5.57 <sup>g</sup>	6.08 <sup>g</sup>
$^3B_1$ (R; $\pi \rightarrow 3p$ )	(0,3,1,2)	(1,1,0,0)	6.04 <sup>f</sup>	6.68 <sup>f</sup>

<sup>a</sup>Using reference (6e,7o) active space including valence  $\pi$ , 3s and 3p<sub>z</sub> orbitals. <sup>b</sup>Using reference (6e,5o) active space including valence  $\pi$  orbitals. <sup>c</sup>Using reference (6e,6o) active space including valence  $\pi$  and 3p<sub>x</sub> orbitals.

<sup>d</sup>Increasing the  $\pi$  3p<sub>x</sub> active space leads to strong mixing in the zeroth-order wavefunction requiring

QD-NEVPT2 (see Pastore et al., Chem. Phys. Lett. 2006, 426, 445–451). <sup>e</sup>Strong double-excitation

character. <sup>f</sup>Using reference (6e,6o) active space including valence  $\pi$  and 3p<sub>y</sub> orbitals. <sup>g</sup>Using reference (6e,6o) active space including valence  $\pi$  and 3s orbitals.

Table S24: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of glyoxal.

State	Active space ( $a_g, a_u, b_u, b_g$ )	State average ( $A_g, A_u, B_u, B_g$ )	CASSCF	NEVPT2
$^1A_u(V; n \rightarrow \pi^*)$	(4,2,4,2)	(1,1,0,0)	3.42 <sup>a</sup>	2.90 <sup>a</sup>
$^1B_g(V; n \rightarrow \pi^*)$	(4,2,4,3)	(1,0,0,2)	4.68 <sup>b</sup>	4.31 <sup>a</sup> , 4.30 <sup>b</sup>
$^1A_g(V; n, n \rightarrow \pi^*, \pi^*)$	(4,2,4,2)	(2,0,0,0)	5.92 <sup>a</sup>	5.52 <sup>a</sup>
$^1B_g(V; n \rightarrow \pi^*)$	(4,2,4,3)	(1,0,0,2)	7.35 <sup>b</sup>	6.91 <sup>a,c</sup> , 6.64 <sup>b,c</sup>
$^1B_u(R; n \rightarrow 3p)$	(4,2,5,2)	(1,0,1,0)	7.04 <sup>d</sup>	7.84 <sup>d</sup>
$^3A_u(V; n \rightarrow \pi^*)$	(4,2,4,2)	(1,1,0,0)	3.06 <sup>a</sup>	2.49 <sup>a</sup>
$^3B_g(V; n \rightarrow \pi^*)$	(4,2,4,2)	(1,0,0,1)	4.61 <sup>a</sup>	3.99 <sup>a</sup>
$^3B_u(V; \pi \rightarrow \pi^*)$	(4,2,4,2)	(1,0,1,0)	5.46 <sup>a</sup>	5.17 <sup>a</sup>
$^3A_g(V; \pi \rightarrow \pi^*)$	(4,2,4,2)	(2,0,0,0)	6.69 <sup>a</sup>	6.33 <sup>a</sup>

<sup>a</sup>Using reference (14e,12o) active space including valence  $\pi$ , two  $n_O$ ,  $\sigma_{CC}$ ,  $\sigma_{CO}$ ,  $\sigma_{CC}^*$  and  $\sigma_{CO}^*$  orbitals.

<sup>b</sup>Using reference (14e,13o) active space including valence  $\pi$ , two  $n_O$ ,  $\sigma_{CC}$ ,  $\sigma_{CO}$ ,  $\sigma_{CC}^*$ ,  $\sigma_{CO}^*$  and  $3p_z$  orbitals.

<sup>c</sup>Non-negligible doubly-excited and Rydberg character. <sup>d</sup>Using reference (14e,13o) active space including valence  $\pi$ , two  $n_O$ ,  $\sigma_{CC}$ ,  $\sigma_{CO}$ ,  $\sigma_{CC}^*$ ,  $\sigma_{CO}^*$  and  $3p_x$  orbitals.

Table S25: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of imidazole.

State	Active space ( $a', a''$ )	State average ( $A', A''$ )	CASSCF	NEVPT2
$^1A''(R; \pi \rightarrow 3s)$	(2,5)	(1,3)	5.04 <sup>b</sup>	5.97 <sup>a</sup> , 5.93 <sup>b</sup>
$^1A'(V; \pi \rightarrow \pi^*)$	(0,9)	(3,0)	6.18 <sup>e</sup>	6.86 <sup>c</sup> , 6.81 <sup>d</sup> , 6.73 <sup>e</sup>
$^1A''(V; n \rightarrow \pi^*)$	(2,5)	(1,3)	7.13 <sup>b</sup>	6.97 <sup>f</sup> , 6.96 <sup>b</sup>
$^1A'(R; \pi \rightarrow 3p)$	(0,9)	(3,0)	6.73 <sup>e</sup>	7.08 <sup>d</sup> , 7.00 <sup>e</sup>
$^3A'(V; \pi \rightarrow \pi^*)$	(0,9)	(3,0)	4.55 <sup>e</sup>	4.98 <sup>c</sup> , 4.86 <sup>e</sup>
$^3A''(R; \pi \rightarrow 3s)$	(2,5)	(1,3)	5.03 <sup>b</sup>	5.93 <sup>a</sup> , 5.91 <sup>b</sup>
$^3A'(V; \pi \rightarrow \pi^*)$	(0,9)	(3,0)	5.69 <sup>e</sup>	6.09 <sup>c</sup> , 5.91 <sup>e</sup>
$^3A''(V; n \rightarrow \pi^*)$	(2,5)	(1,3)	6.58 <sup>b</sup>	6.49 <sup>f</sup> , 6.48 <sup>b</sup>

<sup>a</sup>Using reference (6e,6o) active space including valence  $\pi$  and  $3s$  orbitals. <sup>b</sup>Using reference (8e,7o) active space including valence  $\pi$ ,  $n_N$  and  $3s$  orbitals. <sup>c</sup>Using reference (6e,5o) active space including valence  $\pi$  orbitals.

<sup>d</sup>Using reference (6e,6o) active space including valence  $\pi$  and one  $3p_z$  orbitals. <sup>e</sup>Using reference (6e,9o) active space including valence  $\pi$  and four  $3p_z$  orbitals. <sup>f</sup>Using reference (8e,6o) active space including valence  $\pi$  and  $n_N$  orbitals.

Table S26: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of isobutene.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1B_1(R; \pi \rightarrow 3s)$	(3,2,0,0)	(1,1,0,0)	6.12 <sup>a</sup>	6.63 <sup>a</sup>
$^1A_1(R; \pi \rightarrow 3p)$	(2,3,0,0)	(2,0,0,0)	6.90 <sup>b</sup>	7.20 <sup>b</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(2,2,0,0)	(2,0,0,0)	4.66 <sup>c</sup>	4.61 <sup>c</sup>

<sup>a</sup>Using reference (4e,5o) active space including valence  $\pi$ ,  $\sigma_{CC}$ ,  $\sigma_{CC}^*$  and  $3s$  orbitals. <sup>b</sup>Using reference (4e,5o) active space including valence  $\pi$ ,  $\sigma_{CC}$ ,  $\sigma_{CC}^*$  and  $3p_x$  orbitals. <sup>c</sup>Using reference (4e,4o) active space including valence  $\pi$ ,  $\sigma_{CC}$  and  $\sigma_{CC}^*$  orbitals.

Table S27: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of methylenecyclopropene.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1B_2(V; \pi \rightarrow \pi^*)$	(0,3,0,1)	(1,0,1,0)	4.47 <sup>a</sup>	4.37 <sup>a</sup>
$^1B_1(R; \pi \rightarrow 3s)$	(1,3,0,1)	(1,1,0,0)	4.92 <sup>c</sup>	5.51 <sup>b</sup> , 5.49 <sup>c</sup>
$^1A_2(R; \pi \rightarrow 3p)$	(0,3,1,1)	(1,0,0,1)	5.37 <sup>c</sup>	6.00 <sup>c</sup>
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,6,0,1)	(5,0,0,0)	5.37 <sup>e</sup>	6.33 <sup>d</sup> , 6.36 <sup>e</sup>
$^3B_2(V; \pi \rightarrow \pi^*)$	(0,3,0,1)	(1,0,1,0)	3.44 <sup>a</sup>	3.66 <sup>a</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(0,5,0,1)	(4,0,0,0)	4.60 <sup>d</sup>	4.87 <sup>d</sup>

<sup>a</sup>Using reference (4e,4o) active space. <sup>b</sup>Using reference (6e,6o) active space. <sup>c</sup>Using reference (4e,5o) active space. <sup>d</sup>Using reference (4e,6o) active space. <sup>e</sup>Using reference (4e,7o) active space.

Table S28: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of propynal.

State	Active space ( $a', a''$ )	State average ( $A', A''$ )	CASSCF	NEVPT2
$^1A''(V; n \rightarrow \pi^*)$	(3,4)	(1,2)	4.00 <sup>a</sup>	3.95 <sup>a</sup>
$^1A''(V; \pi \rightarrow \pi^*)$	(3,4)	(1,2)	6.62 <sup>a</sup>	5.50 <sup>a</sup>
$^3A''(V; n \rightarrow \pi^*)$	(3,4)	(1,1)	3.52 <sup>a</sup>	3.59 <sup>a</sup>
$^3A'(V; \pi \rightarrow \pi^*)$	(2,4)	(2,0)	4.69 <sup>b</sup>	4.63 <sup>b</sup>

<sup>a</sup>Using reference (8e,7o) active space including valence  $\pi$  and  $n_O$  orbitals. <sup>b</sup>Using reference (6e,6o) active space including valence  $\pi$  orbitals.

Table S29: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of pyrazine.

State	Active space ( $a_g, b_{3u}, b_{2u}, b_{1g},$ $b_{1u}, b_{2g}, b_{3g}, a_u$ )	State average ( $A_g, B_{3u}, B_{2u}, B_{1g},$ $B_{1u}, B_{2g}, B_{3g}, A_u$ )	CASSCF	NEVPT2
$^1B_{3u}(V; n \rightarrow \pi^*)$	(1,2,0,1,1,2,0,1)	(1,1,0,0,0,0,0,0)	4.76 <sup>a</sup>	4.17 <sup>a</sup>
$^1A_u(V; n \rightarrow \pi^*)$	(1,2,0,1,1,2,0,1)	(1,0,0,0,0,0,0,1)	5.90 <sup>a</sup>	4.77 <sup>a</sup>
$^1B_{2u}(V; \pi \rightarrow \pi^*)$	(0,2,0,1,0,2,0,1)	(1,0,1,0,0,0,0,0)	4.97 <sup>b</sup>	5.32 <sup>b</sup> , 5.37 <sup>c</sup>
$^1B_{2g}(V; n \rightarrow \pi^*)$	(1,2,0,1,1,2,0,1)	(1,0,0,0,0,1,0,0)	5.80 <sup>a</sup>	5.88 <sup>a</sup>
$^1A_g(R; n \rightarrow 3s)$	(2,2,0,1,1,2,0,1)	(2,0,0,0,0,0,0,0)	6.69 <sup>d</sup>	6.70 <sup>d</sup>
$^1B_{1g}(V; n \rightarrow \pi^*)$	(1,2,0,1,1,2,0,1)	(1,0,0,1,0,0,0,0)	7.16 <sup>a</sup>	6.75 <sup>a</sup>
$^1B_{1u}(V; \pi \rightarrow \pi^*)$	(0,4,0,1,0,2,0,2)	(1,0,0,0,3,0,0,0)	8.04 <sup>f</sup>	6.38 <sup>b</sup> , 6.31 <sup>e</sup> , 6.81 <sup>f</sup>
$^1B_{1g}(R; \pi \rightarrow 3s)$	(1,2,0,1,0,2,0,1)	(1,0,0,1,0,0,0,0)	6.73 <sup>g</sup>	7.33 <sup>g</sup>
$^1B_{2u}(R; n \rightarrow 3p)$	(1,2,1,1,1,2,0,1)	(1,0,2,0,0,0,0,0)	7.49 <sup>c</sup>	7.25 <sup>c</sup>
$^1B_{1u}(R; n \rightarrow 3p)$	(1,2,0,1,2,2,0,1)	(1,0,0,0,3,0,0,0)	7.83 <sup>e</sup>	7.42 <sup>e</sup>
$^1B_{1u}(V; \pi \rightarrow \pi^*)$	(0,4,0,1,0,2,0,2)	(1,0,0,0,3,0,0,0)	9.65 <sup>f</sup>	7.29 <sup>b</sup> , 6.96 <sup>e</sup> , 8.25 <sup>f</sup>
$^3B_{3u}(V; n \rightarrow \pi^*)$	(1,2,0,1,1,2,0,1)	(1,1,0,0,0,0,0,0)	4.16 <sup>a</sup>	3.56 <sup>a</sup>
$^3B_{1u}(V; \pi \rightarrow \pi^*)$	(0,4,0,1,0,2,0,2)	(1,0,0,0,2,0,0,0)	3.98 <sup>f</sup>	4.68 <sup>b</sup> , 4.57 <sup>f</sup>
$^3B_{2u}(V; \pi \rightarrow \pi^*)$	(0,2,0,1,0,2,0,1)	(1,0,1,0,0,0,0,0)	4.62 <sup>b</sup>	4.42 <sup>b</sup>
$^3A_u(V; n \rightarrow \pi^*)$	(1,2,0,1,1,2,0,1)	(1,0,0,0,0,0,0,1)	5.85 <sup>a</sup>	4.75 <sup>a</sup>
$^3B_{2g}(V; n \rightarrow \pi^*)$	(1,2,0,1,1,2,0,1)	(1,0,0,0,0,1,0,0)	5.25 <sup>a</sup>	5.21 <sup>a</sup>
$^3B_{1u}(V; \pi \rightarrow \pi^*)$	(0,4,0,1,0,2,0,2)	(1,0,0,0,2,0,0,0)	5.15 <sup>f</sup>	5.43 <sup>b</sup> , 5.35 <sup>f</sup>

<sup>a</sup>Using reference (10e,8o) active space including valence  $\pi$  and  $n_N$  orbitals. <sup>b</sup>Using reference (6e,6o) active space including valence  $\pi$  orbitals. <sup>c</sup>Using reference (10e,9o) active space including valence  $\pi$ ,  $n_N$  and  $3p_y$  orbitals. <sup>d</sup>Using reference (10e,9o) active space including valence  $\pi$ ,  $n_N$  and  $3s$  orbitals. <sup>e</sup>Using reference (10e,9o) active space including valence  $\pi$ ,  $n_N$  and  $3p_z$  orbitals. <sup>f</sup>Using reference (6e,9o) active space including valence  $\pi$  and three  $3p_x$  orbitals. <sup>g</sup>Using reference (6e,7o) active space including valence  $\pi$  and  $3s$  orbitals.

Table S30: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of pyridazine.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1B_1(V; n \rightarrow \pi^*)$	(1,3,1,3)	(1,1,0,0)	4.29 <sup>a</sup>	3.80 <sup>a</sup>
$^1A_2(V; n \rightarrow \pi^*)$	(1,3,1,3)	(1,0,0,1)	4.83 <sup>a</sup>	4.40 <sup>a</sup>
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,3,0,3)	(2,0,0,0)	5.12 <sup>b</sup>	5.58 <sup>b</sup>
$^1A_2(V; n \rightarrow \pi^*)$	(1,3,1,3)	(1,0,0,2)	6.26 <sup>a</sup>	5.88 <sup>a</sup>
$^1B_2(R; n \rightarrow 3s)$	(2,3,1,3)	(1,0,1,0)	5.99 <sup>c</sup>	6.21 <sup>c</sup>
$^1B_1(V; n \rightarrow \pi^*)$	(1,3,1,3)	(1,2,0,0)	7.16 <sup>a</sup>	6.64 <sup>a</sup>
$^1B_2(V; \pi \rightarrow \pi^*)$	(0,6,0,6)	(1,0,3,0)	7.58 <sup>e</sup>	7.82 <sup>b</sup> , 7.19 <sup>d</sup> , 7.10 <sup>e</sup>
$^3B_1(V; n \rightarrow \pi^*)$	(1,3,1,3)	(1,1,0,0)	3.60 <sup>a</sup>	3.13 <sup>a</sup>
$^3A_2(V; n \rightarrow \pi^*)$	(1,3,1,3)	(1,0,0,1)	4.49 <sup>a</sup>	4.14 <sup>a</sup>
$^3B_2(V; \pi \rightarrow \pi^*)$	(0,6,0,6)	(1,0,1,0)	4.06 <sup>e</sup>	4.65 <sup>b</sup> , 4.55 <sup>d</sup> , 4.49 <sup>e</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(0,3,0,3)	(2,0,0,0)	4.93 <sup>b</sup>	4.94 <sup>b</sup>

<sup>a</sup>Using reference (10e,8o) active space including valence  $\pi$  and  $n_N$  orbitals. <sup>b</sup>Using reference (6e,6o) active space including valence  $\pi$  orbitals. <sup>c</sup>Using reference (10e,9o) active space including valence  $\pi$ ,  $n_N$  and  $3s$  orbitals. <sup>d</sup>Using reference (6e,9o) active space including valence  $\pi$ ,  $n_N$  and three  $3p_x$  orbitals. <sup>e</sup>Using reference (6e,12o) active space including valence  $\pi$ ,  $n_N$  and six  $3p_x$  orbitals.

Table S31: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of pyridine.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1B_1(V; n \rightarrow \pi^*)$	(1,4,1,2)	(1,2,0,0)	5.43 <sup>b</sup>	5.17 <sup>a</sup> ,5.15 <sup>b</sup>
$^1B_2(V; \pi \rightarrow \pi^*)$	(0,7,0,3)	(1,0,2,0)	5.03 <sup>d</sup>	5.44 <sup>c</sup> ,5.31 <sup>d</sup>
$^1A_2(V; n \rightarrow \pi^*)$	(2,4,0,2)	(1,0,0,2)	6.30 <sup>e</sup>	5.32 <sup>a</sup> ,5.29 <sup>e</sup>
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,4,0,2)	(2,0,0,0)	7.90 <sup>c</sup>	6.69 <sup>c</sup>
$^1A_1(R; n \rightarrow 3s)$	(2,4,0,2)	(2,0,0,0)	6.40 <sup>e</sup>	6.99 <sup>e</sup>
$^1A_2(R; \pi \rightarrow 3s)$	(2,4,0,2)	(1,0,0,2)	6.60 <sup>e</sup>	6.96 <sup>f</sup> ,6.86 <sup>e</sup>
$^1B_2(V; \pi \rightarrow \pi^*)$	(0,7,0,3)	(1,0,2,0)	7.45 <sup>d</sup>	8.61 <sup>a</sup> ,7.83 <sup>d</sup>
$^1B_1(R; \pi \rightarrow 3p)$	(1,4,1,2)	(1,2,0,0)	7.12 <sup>b</sup>	7.57 <sup>g</sup> ,7.45 <sup>b</sup>
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,4,0,2)	(4,0,0,0)	9.49 <sup>c</sup>	6.97 <sup>c</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(0,4,0,2)	(2,0,0,0)	3.98 <sup>c</sup>	4.60 <sup>c</sup>
$^3B_1(V; n \rightarrow \pi^*)$	(1,4,0,2)	(1,1,0,0)	4.65 <sup>a</sup>	4.58 <sup>a</sup>
$^3B_2(V; \pi \rightarrow \pi^*)$	(0,7,0,3)	(1,0,2,0)	4.83 <sup>d</sup>	4.90 <sup>c</sup> ,4.88 <sup>d</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(0,4,0,2)	(3,0,0,0)	5.11 <sup>c</sup>	5.19 <sup>c</sup>
$^3A_2(V; n \rightarrow \pi^*)$	(1,4,0,2)	(1,0,0,1)	5.94 <sup>a</sup>	5.33 <sup>a</sup>
$^3B_2(V; \pi \rightarrow \pi^*)$	(0,7,0,3)	(1,0,2,0)	6.93 <sup>d</sup>	7.00 <sup>c</sup> ,6.29 <sup>d</sup>

<sup>a</sup>Using reference (8e,7o) active space including valence  $\pi$  and  $n_N$  orbitals. <sup>b</sup>Using reference (8e,8o) active space including valence  $\pi$ ,  $n_N$  and  $3p_y$  orbitals. <sup>c</sup>Using reference (6e,6o) active space including valence  $\pi$  orbitals. <sup>d</sup>Using reference (6e,10o) active space including valence  $\pi$  and four  $3p_x$  orbitals. <sup>e</sup>Using reference (8e,8o) active space including valence  $\pi$ ,  $n_N$  and  $3s$  orbitals. <sup>f</sup>Using reference (6e,8o) active space including valence  $\pi$  and  $3s$  orbitals. <sup>g</sup>Using reference (6e,7o) active space including valence  $\pi$  and  $3p_y$  orbitals.

Table S32: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of pyrimidine.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1B_1(V; n \rightarrow \pi^*)$	(1,4,1,2)	(1,1,0,0)	4.85 <sup>a</sup>	4.55 <sup>a</sup>
$^1A_2(V; n \rightarrow \pi^*)$	(1,4,1,2)	(1,0,0,1)	5.52 <sup>a</sup>	4.84 <sup>a</sup>
$^1B_2(V; \pi \rightarrow \pi^*)$	(0,7,0,4)	(1,0,1,0)	5.23 <sup>e</sup>	5.71 <sup>b</sup> , 5.57 <sup>d</sup> , 5.53 <sup>e</sup>
$^1A_2(V; n \rightarrow \pi^*)$	(1,4,1,2)	(1,0,0,2)	6.70 <sup>a</sup>	6.02 <sup>a</sup>
$^1B_1(V; n \rightarrow \pi^*)$	(1,4,1,2)	(1,2,0,0)	7.20 <sup>a</sup>	6.40 <sup>a</sup>
$^1B_2(R; n \rightarrow 3s)$	(2,4,1,2)	(1,0,2,0)	6.86 <sup>c</sup>	6.77 <sup>c</sup>
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,7,0,4)	(2,0,0,0)	7.62 <sup>e</sup>	7.47 <sup>b</sup> , 7.11 <sup>e</sup>
$^3B_1(V; n \rightarrow \pi^*)$	(1,4,1,2)	(1,1,0,0)	4.45 <sup>a</sup>	4.17 <sup>a</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(0,7,0,4)	(2,0,0,0)	4.25 <sup>e</sup>	4.84 <sup>b</sup> , 4.67 <sup>e</sup>
$^3A_2(V; n \rightarrow \pi^*)$	(1,4,1,2)	(1,0,0,1)	5.20 <sup>a</sup>	4.72 <sup>a</sup>
$^3B_2(V; \pi \rightarrow \pi^*)$	(0,7,0,4)	(1,0,1,0)	5.00 <sup>e</sup>	5.08 <sup>b</sup> , 5.01 <sup>e</sup>

<sup>a</sup>Using reference (10e,8o) active space including valence  $\pi$  and  $n_N$  orbitals. <sup>b</sup>Using reference (6e,6o) active space including valence  $\pi$  orbitals. <sup>c</sup>Using reference (10e,9o) active space including valence  $\pi$ ,  $n_N$  and  $3s$  orbitals. <sup>d</sup>Using reference (6e,9o) active space including valence  $\pi$  and three  $3p_x$  orbitals. <sup>e</sup>Using reference (6e,11o) active space including valence  $\pi$  and five  $3p_x$  orbitals.

Table S33: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of pyrrole.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1A_2(R; \pi \rightarrow 3s)$	(1,3,0,2)	(1,0,0,1)	4.49 <sup>a</sup>	5.51 <sup>a</sup>
$^1B_1(R; \pi \rightarrow 3p)$	(0,3,1,2)	(1,1,0,0)	5.22 <sup>b</sup>	6.32 <sup>b</sup>
$^1A_2(R; \pi \rightarrow 3p)$	(2,3,0,2)	(1,0,0,2)	4.89 <sup>c</sup>	6.44 <sup>c</sup>
$^1B_2(V; (\pi \rightarrow \pi^*)$	(0,4,0,2)	(1,0,2,0)	7.73 <sup>e</sup>	6.48 <sup>e,f</sup>
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,3,0,2)	(3,0,0,0)	6.47 <sup>d</sup>	6.53 <sup>d</sup>
$^1B_2(R; \pi \rightarrow 3p)$	(0,4,0,2)	(1,0,2,0)	5.82 <sup>e</sup>	6.50 <sup>d</sup> , 6.62 <sup>e,f</sup>
$^3B_2(V; \pi \rightarrow \pi^*)$	(0,3,0,2)	(1,0,1,0)	4.24 <sup>d</sup>	4.74 <sup>d</sup>
$^3A_2(R; \pi \rightarrow 3s)$	(1,3,0,2)	(1,0,0,1)	4.47 <sup>a</sup>	5.49 <sup>a</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(0,3,0,2)	(3,0,0,0)	5.52 <sup>d</sup>	5.56 <sup>d</sup>
$^3B_1(R; \pi \rightarrow 3p)$	(0,3,1,2)	(1,1,0,0)	5.18 <sup>b</sup>	6.28 <sup>b</sup>

<sup>a</sup>Using reference (6e,6o) active space including valence  $\pi$  and  $3s$  orbitals. <sup>b</sup>Using reference (6e,6o) active space including valence  $\pi$  and  $3p_y$  orbitals. <sup>c</sup>Using reference (6e,7o) active space including valence  $\pi$ ,  $3s$  and  $3p_z$  orbitals. <sup>d</sup>Using reference (6e,5o) active space including valence  $\pi$  orbitals. <sup>e</sup>Using reference (6e,6o) active space including valence  $\pi$  and  $3p_x$  orbitals. <sup>f</sup>Increasing the  $\pi$   $3p_x$  active space leads to strong mixing in the zeroth-order wavefunction requiring a multi-state treatment (see Roos et al., J. Chem. Phys. 2002, 116, 7526–7536).

Table S34: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of tetrazine.

State	Active space ( $a_g, b_{3u}, b_{2u}, b_{1g},$ $b_{1u}, b_{2g}, b_{3g}, a_u$ )	State average ( $A_g, B_{3u}, B_{2u}, B_{1g},$ $B_{1u}, B_{2g}, B_{3g}, A_u$ )	CASSCF	NEVPT2
$^1B_{3u}(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,1,0,0,0,0,0,0)	2.99 <sup>a</sup>	2.35 <sup>a</sup>
$^1A_u(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,0,0,0,0,1)	4.37 <sup>a</sup>	3.58 <sup>a</sup>
$^1A_g(V; n, n \rightarrow \pi^*, \pi^*)$	(1,2,1,1,1,2,1,1)	(2,0,0,0,0,0,0,0)	5.42 <sup>a</sup>	4.61 <sup>a</sup>
$^1B_{1g}(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,1,0,0,0,0)	5.41 <sup>a</sup>	4.95 <sup>a</sup>
$^1B_{2u}(V; \pi \rightarrow \pi^*)$	(0,2,0,1,0,2,0,1)	(1,0,1,0,0,0,0,0)	5.04 <sup>b</sup>	5.56 <sup>b</sup>
$^1B_{2g}(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,0,0,1,0,0)	5.43 <sup>a</sup>	5.63 <sup>a</sup>
$^1A_u(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,0,0,0,0,2)	6.37 <sup>a</sup>	5.62 <sup>a</sup>
$^1B_{3g}(V; n, n \rightarrow \pi^*, \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,0,0,0,1,0)	6.59 <sup>a</sup>	6.15 <sup>a</sup>
$^1B_{2g}(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,0,0,2,0,0)	6.79 <sup>a</sup>	6.13 <sup>a</sup>
$^1B_{1g}(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,2,0,0,0,0)	7.18 <sup>a</sup>	6.76 <sup>a</sup>
$^3B_{3u}(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,1,0,0,0,0,0,0)	2.38 <sup>a</sup>	1.73 <sup>a</sup>
$^3A_u(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,0,0,0,0,1)	4.06 <sup>a</sup>	3.36 <sup>a</sup>
$^3B_{1g}(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,1,0,0,0,0)	4.66 <sup>a</sup>	4.24 <sup>a</sup>
$^3B_{1u}(V; \pi \rightarrow \pi^*)$	(0,4,0,1,0,2,0,2)	(1,0,0,0,2,0,0,0)	3.90 <sup>c</sup>	4.80 <sup>b</sup> , 4.70 <sup>a</sup>
$^3B_{2u}(V; \pi \rightarrow \pi^*)$	(0,2,0,1,0,2,0,1)	(1,0,1,0,0,0,0,0)	4.68 <sup>b</sup>	4.58 <sup>b</sup>
$^3B_{2g}(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,0,0,1,0,0)	5.17 <sup>a</sup>	5.27 <sup>a</sup>
$^3A_u(V; n \rightarrow \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,0,0,0,0,2)	6.12 <sup>a</sup>	5.13 <sup>a</sup>
$^3B_{3g}(V; n, n \rightarrow \pi^*, \pi^*)$	(1,2,1,1,1,2,1,1)	(1,0,0,0,0,0,1,0)	6.56 <sup>a</sup>	5.51 <sup>a</sup>
$^3B_{1u}(V; \pi \rightarrow \pi^*)$	(0,4,0,1,0,2,0,2)	(1,0,0,0,2,0,0,0)	5.32 <sup>c</sup>	5.64 <sup>b</sup> , 5.56 <sup>c</sup>

<sup>a</sup>Using reference (14e,10o) active space including valence  $\pi$  and  $n_N$  orbitals. <sup>b</sup>Using reference (6e,6o) active space including valence  $\pi$  orbitals. <sup>c</sup>Using reference (6e,9o) active space including valence  $\pi$  and three  $3p_x$  orbitals.

Table S35: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of thioacetone.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1A_2(V; n \rightarrow \pi^*)$	(2,2,1,0)	(1,0,0,1)	2.72 <sup>a</sup>	2.55 <sup>a</sup>
$^1B_2(R; n \rightarrow 4s)$	(4,2,1,0)	(1,0,2,0)	4.80 <sup>b</sup>	5.72 <sup>b</sup>
$^1A_1(V; \pi \rightarrow \pi^*)$	(2,2,2,0)	(3,0,0,0)	6.94 <sup>d</sup>	6.09 <sup>c</sup> , 6.24 <sup>d</sup>
$^1B_2(R; n \rightarrow 4p)$	(4,2,1,0)	(1,0,2,0)	5.57 <sup>b</sup>	6.62 <sup>b</sup>
$^1A_1(R; n \rightarrow 4p)$	(2,2,2,0)	(3,0,0,0)	6.24 <sup>d</sup>	6.52 <sup>d</sup>
$^3A_2(V; n \rightarrow \pi^*)$	(2,2,1,0)	(1,0,0,1)	2.52 <sup>a</sup>	2.32 <sup>a</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(2,2,0,0)	(2,0,0,0)	3.52 <sup>c</sup>	3.48 <sup>c</sup>

<sup>a</sup>Using reference (6e,5o) active space including valence  $\pi$ ,  $n_O$ ,  $\sigma_{CO}$  and  $\sigma_{CO}^*$  orbitals. <sup>b</sup>Using reference (6e,7o) active space including valence  $\pi$ ,  $n_O$ ,  $\sigma_{CO}$ ,  $\sigma_{CO}^*$ , 4s and  $4p_z$  orbitals. <sup>c</sup>Using reference (4e,4o) active space including valence  $\pi$ ,  $\sigma_{CO}$  and  $\sigma_{CO}^*$  orbitals. <sup>d</sup>Using reference (6e,6o) active space including valence  $\pi$ ,  $n_O$ ,  $\sigma_{CO}$ ,  $\sigma_{CO}^*$  and  $4p_y$  orbitals.

Table S36: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of thiophene.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,3,0,2)	(3,0,0,0)	6.11 <sup>a</sup>	5.84 <sup>a</sup>
$^1B_2(V; \pi \rightarrow \pi^*)$	(0,5,0,2)	(1,0,2,0)	6.94 <sup>c</sup>	5.64 <sup>a</sup> , 5.54 <sup>b</sup> , 6.10 <sup>c</sup>
$^1A_2(R; \pi \rightarrow 3s)$	(1,3,0,2)	(1,0,0,1)	5.70 <sup>d</sup>	6.20 <sup>d</sup>
$^1B_1(R; \pi \rightarrow 3p)$	(0,3,1,2)	(1,1,0,0)	6.02 <sup>e</sup>	6.19 <sup>e</sup>
$^1A_2(R; \pi \rightarrow 3p)$	(0,3,1,2)	(1,0,0,1)	6.05 <sup>e</sup>	6.40 <sup>e</sup> , 6.52 <sup>f</sup>
$^1B_1(R; \pi \rightarrow 3s)$	(1,3,1,2)	(1,2,0,0)	5.78 <sup>f</sup>	6.73 <sup>d</sup> , 6.71 <sup>f</sup>
$^1B_2(R; \pi \rightarrow 3p)$	(0,5,0,2)	(1,0,2,0)	6.80 <sup>c</sup>	7.42 <sup>b</sup> , 7.25 <sup>c</sup>
$^1A_1(V; \pi \rightarrow \pi^*)$	(0,3,0,2)	(3,0,0,0)	8.29 <sup>a,g</sup>	7.39 <sup>a,g</sup>
$^3B_2(V; \pi \rightarrow \pi^*)$	(0,3,0,2)	(1,0,1,0)	3.68 <sup>a</sup>	4.13 <sup>a</sup>
$^3A_1(V; \pi \rightarrow \pi^*)$	(0,3,0,2)	(3,0,0,0)	4.97 <sup>a</sup>	4.84 <sup>a</sup>
$^3B_1(R; \pi \rightarrow 3p)$	(0,3,1,2)	(1,1,0,0)	5.86 <sup>e</sup>	5.98 <sup>e</sup>
$^3A_2(R; \pi \rightarrow 3s)$	(1,3,0,2)	(1,0,0,1)	5.65 <sup>d</sup>	6.14 <sup>d</sup>

<sup>a</sup>Using reference (6e,5o) active space including valence  $\pi$  orbitals. <sup>b</sup>Using reference (6e,6o) active space including valence  $\pi$  and  $3p_x$  orbitals. <sup>c</sup>Using reference (6e,7o) active space including valence  $\pi$  and two  $3p_x$  orbitals. <sup>d</sup>Using reference (6e,6o) active space including valence  $\pi$  and  $3s$  orbitals. <sup>e</sup>Using reference (6e,6o) active space including valence  $\pi$  and  $3p_y$  orbitals. <sup>f</sup>Using reference (6e,7o) active space including valence  $\pi$ ,  $3s$  and  $3p_y$  orbitals. <sup>g</sup>Strong double-excitation character.

Table S37: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of thiopropynal.

State	Active space ( $a', a''$ )	State average ( $A', A''$ )	CASSCF <sup>a</sup>	NEVPT2 <sup>a</sup>
$^1A''(V; n \rightarrow \pi^*)$	(3,4)	(1,1)	2.06	2.05
$^3A''(V; n \rightarrow \pi^*)$	(3,4)	(1,1)	1.85	1.81

<sup>a</sup>All calculations using reference (8e,7o) active space including valence  $\pi$  and  $n_O$  orbitals.

Table S38: NEVPT2/aug-cc-pVTZ vertical transition energies (in eV) of triazine.

State	Active space ( $a_1, b_1, b_2, a_2$ )	State average ( $A_1, B_1, B_2, A_2$ )	CASSCF	NEVPT2
$^1A''_1(V; n \rightarrow \pi^*)$	(2,4,1,2)	(1,2,0,2)	5.88 <sup>a</sup>	4.61 <sup>a</sup>
$^1A''_2(V; n \rightarrow \pi^*)$	(2,4,1,2)	(1,1,0,0)	5.14 <sup>a</sup>	4.89 <sup>a</sup>
$^1E''(V; n \rightarrow \pi^*)$	(2,4,1,2)	(1,2,0,2)	5.51 <sup>a</sup>	4.88 <sup>a</sup>
$^1A'_2(V; \pi \rightarrow \pi^*)$	(0,6,0,3)	(1,0,1,0)	5.55 <sup>d</sup>	6.10 <sup>b</sup> , 6.15 <sup>c</sup> , 5.95 <sup>d</sup>
$^1A'_1(V; \pi \rightarrow \pi^*)$	(0,6,0,3)	(2,0,0,0)	8.20 <sup>d</sup>	7.06 <sup>b</sup> , 7.30 <sup>d</sup>
$^1E'(R; n \rightarrow 3s)$	(3,4,1,2)	(2,0,2,0)	6.15 <sup>c</sup>	7.45 <sup>c</sup>
$^1E''(V; n \rightarrow \pi^*)$	(2,4,1,2)	(1,1,0,1)	8.26 <sup>a</sup>	7.98 <sup>a</sup>
$^1E'(V; \pi \rightarrow \pi^*)$	(0,6,0,3)	(4,0,3,0)	10.03 <sup>d</sup>	7.74 <sup>b</sup> , 8.34 <sup>d</sup>
$^3A''_2(V; n \rightarrow \pi^*)$	(2,4,1,2)	(1,1,0,0)	4.74 <sup>a</sup>	4.51 <sup>a</sup>
$^3E''(V; n \rightarrow \pi^*)$	(2,4,1,2)	(1,2,0,2)	5.14 <sup>a</sup>	4.61 <sup>a</sup>
$^3A''_1(V; n \rightarrow \pi^*)$	(2,4,1,2)	(1,2,0,2)	5.88 <sup>a</sup>	4.71 <sup>a</sup>
$^3A'_1(V; \pi \rightarrow \pi^*)$	(0,6,0,3)	(2,0,0,0)	4.46 <sup>d</sup>	5.20 <sup>b</sup> , 5.05 <sup>d</sup>
$^3E'(V; \pi \rightarrow \pi^*)$	(0,6,0,3)	(3,0,1,0)	5.57 <sup>d</sup>	5.83 <sup>b</sup> , 5.73 <sup>d</sup>
$^3A'_2(V; (\pi \rightarrow \pi^*))$	(0,6,0,3)	(1,0,1,0)	7.70 <sup>d</sup>	5.83 <sup>b</sup> , 6.36 <sup>d</sup>

<sup>a</sup>Using reference (12e,9o) active space including valence  $\pi$  and  $n_N$  orbitals. <sup>b</sup>Using reference (6e,6o) active space including valence  $\pi$  orbitals. <sup>c</sup>Using reference (12e,10o) active space including valence  $\pi$ ,  $n_N$  and  $3s$  orbitals. <sup>d</sup>Using reference (6e,9o) active space including valence  $\pi$  and three  $3p_x$  orbitals.

### **S3 Selected CI results**

Table S39: Vertical excitations (in eV) for various states of the studied molecules computed with an extrapolated SCI method (exFCI). The number of determinants  $N_{\text{det}}$  of the largest SCI wave functions and their corresponding excitation energies are also reported. The extrapolation error is estimated as the difference in excitation energy between the largest SCI wave function and its corresponding extrapolated value.

Molecule	Transition	6-31+G(d)				aug-cc-pVDZ	
		$N_{\text{det}}$	SCI	exFCI	$N_{\text{det}}$	SCI	exFCI
Acetone	$^1A_2(V; n \rightarrow \pi^*)$	26526782	4.55	4.60 ± 0.05			
	$^3A_2(V; n \rightarrow \pi^*)$	26553941	4.22	4.18 ± 0.04			
Acrolein	$^1A''(V; n \rightarrow \pi^*)$	23273572	3.84	3.85 ± 0.01			
	$^3A''(V; n \rightarrow \pi^*)$	26531491	3.59	3.60 ± 0.01	15827189	3.58	3.51 ± 0.07
Butadiene	$^3A'(V; \pi \rightarrow \pi^*)$	37480261	4.01	3.98 ± 0.03	15827189	4.05	3.96 ± 0.09
	$^1B_u(V; \pi \rightarrow \pi^*)$	20552493	6.43	6.41 ± 0.02			
Cyanocetylene	$^1A_u(R; \pi \rightarrow 3p)$	20552493	6.96	6.95 ± 0.01	12521242	6.72	6.72 ± 0.00
	$^3B_u(V; \pi \rightarrow \pi^*)$	49847526	3.40	3.37 ± 0.03			
Cyanoformaldehyde	$^3A_g(V; \pi \rightarrow \pi^*)$				17235280	6.29	6.21 ± 0.08
	$^3B_g(V; \pi \rightarrow 3s)$	49847526	6.43	6.40 ± 0.03			
Cyanoformaldehyde	$^1\Sigma^-(V; \pi \rightarrow \pi^*)$	21269249	6.01	6.02 ± 0.01	11023351	5.93	5.84 ± 0.09
	$^1\Delta(V; \pi \rightarrow \pi^*)$	21269249	6.29	6.28 ± 0.01	11023351	6.19	6.14 ± 0.05
Cyanoformaldehyde	$^3\Sigma^+(V; \pi \rightarrow \pi^*)$	18198954	4.48	4.45 ± 0.03	25646703	4.47	4.41 ± 0.06
	$^3\Delta(V; \pi \rightarrow \pi^*)$	18198954	5.35	5.32 ± 0.03	25646703	5.28	5.20 ± 0.08
Cyanoformaldehyde	$^1A''[F](V; \pi \rightarrow \pi^*)$	104485975	3.70	3.67 ± 0.03	62248690	3.61	3.50 ± 0.02
	$^1A''(V; n \rightarrow \pi^*)$	17778047	3.94	3.92 ± 0.02	19020785	3.93	3.98 ± 0.05
	$^1A''(V; \pi \rightarrow \pi^*)$	17778047	6.67	6.60 ± 0.07	19020785	6.57	6.58 ± 0.01

Continued on next page

Molecule	Transition	6-31+G(d)				aug-cc-pVQZ	
		$N_{\text{det}}$	SCI	exFCI	$N_{\text{det}}$	SCI	exFCI
Cyanogen	$3A''(\text{V}; n \rightarrow \pi^*)$	21 011 221	3.54	$3.48 \pm 0.06$	48 532 729	3.51	$3.52 \pm 0.01$
	$3A'(\text{V}; \pi \rightarrow \pi^*)$				48 532 729	5.10	$5.07 \pm 0.03$
	$1\Sigma_u^- (\text{V}; \pi \rightarrow \pi^*)$	12 1991 55	6.61	$6.58 \pm 0.03$	20 9495 13	6.52	$6.44 \pm 0.08$
	$1\Delta_u (\text{V}; \pi \rightarrow \pi^*)$	12 1991 55	6.89	$6.87 \pm 0.02$	20 9495 13	6.78	$6.74 \pm 0.04$
	$3\Sigma_u^+ (\text{V}; \pi \rightarrow \pi^*)$	34 1277 36	4.97	$4.91 \pm 0.06$	25 7606 68	4.94	$4.87 \pm 0.07$
	$1\Sigma_u^- [\text{F}] (\text{V}; \pi \rightarrow \pi^*)$	21 4163 04	5.36	$5.31 \pm 0.05$	28 8841 38	5.17	$5.26 \pm 0.09$
	$1B_1(\text{V}; n \rightarrow \pi^*)$	48 8976 96	4.40	$4.38 \pm 0.02$			
Cyclopropenone	$1A_2(\text{V}; n \rightarrow \pi^*)$	24 5411 16	5.70	$5.64 \pm 0.06$			
	$3B_1(\text{V}; n \rightarrow \pi^*)$	24 008 328	4.07	$4.00 \pm 0.07$			
	$3B_2(\text{V}; \pi \rightarrow \pi^*)$	48 311 362	4.95	$4.95 \pm 0.00$			
	$1A_2(\text{V}; n \rightarrow \pi^*)$	39 385 657	3.46	$3.45 \pm 0.01$			
	$1B_1(\text{V}; n \rightarrow \pi^*)$	39 385 657	3.50	$3.44 \pm 0.05$			
	$1B_2(\text{V}; \pi \rightarrow \pi^*)$	39 385 657	4.68	$4.59 \pm 0.09$			
	$3A_2(\text{V}; n \rightarrow \pi^*)$	23 904 962	3.32	$3.29 \pm 0.03$			
Diacetylene	$3B_2(\text{V}; \pi \rightarrow \pi^*)$	23 904 962	4.06	$4.03 \pm 0.03$			
	$1\Sigma_u^- (\text{V}; \pi \rightarrow \pi^*)$	18 955 451	5.58	$5.52 \pm 0.06$	19 192 556	5.45	$5.47 \pm 0.02$
	$1\Delta_u (\text{V}; \pi \rightarrow \pi^*)$	18 955 451	5.85	$5.84 \pm 0.01$	19 192 556	5.45	$5.69 \pm 0.02$
	$3\Sigma_u^+ (\text{V}; \pi \rightarrow \pi^*)$	13 777 757	4.11	$4.04 \pm 0.07$	26 668 471	4.11	$4.07 \pm 0.04$
	$3\Delta_u (\text{V}; \pi \rightarrow \pi^*)$	13 777 757	4.93	$4.94 \pm 0.01$	26 668 471	4.87	$4.85 \pm 0.02$
	$1A_u (\text{V}; n \rightarrow \pi^*)$	51 656 090	2.96	$2.93 \pm 0.03$	34 125 394	2.94	$2.93 \pm 0.01$
	$1B_g(\text{V}; n \rightarrow \pi^*)$	24 394 242	4.34	$4.28 \pm 0.06$			

Molecule	Transition	6-31+G(d)				aug-cc-pVDZ	
		$N_{\text{det}}$	SCI	exFCI	$N_{\text{det}}$	SCI	exFCI
Isobutene	$3A_u(\text{V}; n \rightarrow \pi^*)$	47 693 908	2.58	2.54 ± 0.04			
	$1B_1(\text{R}; \pi \rightarrow 3s)$	28 095 377	6.86	6.78 ± 0.08			
	$1A_1(\text{R}; \pi \rightarrow 3p)$	59 728 169	7.22	7.16 ± 0.02			
	$3A_1\text{V}; (\pi \rightarrow \pi^*)$	32 440 621	4.54	4.56 ± 0.02			
	$1B_2(\text{V}; \pi \rightarrow \pi^*)$	51 918 524	4.35	4.32 ± 0.03			
	$1A_2(\text{R}; \pi \rightarrow 3p)$	25 146 911	6.02	5.92 ± 0.10			
Methylenecyclopropene	$1A_1(\text{V}; \pi \rightarrow \pi^*)$	31 721 213	6.21	6.20 ± 0.01			
	$3B_2(\text{V}; \pi \rightarrow \pi^*)$	24 379 551	3.50	3.44 ± 0.06	43 090 114	3.49	3.45 ± 0.04
	$3A_1(\text{V}; \pi \rightarrow \pi^*)$	24 379 551	4.77	4.67 ± 0.10	43 090 114	4.77	4.79 ± 0.02
	$1A''(\text{V}; n \rightarrow \pi^*)$	48 945 252	3.90	3.84 ± 0.06	28 249 344	3.92	3.89 ± 0.03
	$1A''(\text{V}; \pi \rightarrow \pi^*)$	26 554 616	5.72	5.64 ± 0.08	28 249 344	5.72	5.63 ± 0.09
	$3A''(\text{V}; n \rightarrow \pi^*)$	23 182 284	3.58	3.54 ± 0.04			
Propynal	$3A'(\text{V}; \pi \rightarrow \pi^*)$	39 375 360	4.52	4.44 ± 0.08			
	$1A_2(\text{V}; n \rightarrow \pi^*)$	26 515 070	2.56	2.61 ± 0.05			
	$3A_2(\text{V}; n \rightarrow \pi^*)$	63 669 401	2.36	2.36 ± 0.00			
	$1A''(\text{V}; n \rightarrow \pi^*)$	15 782 429	2.07	2.08 ± 0.01			

## **S4 Benchmarks**

### **S4.1 Raw data**

Table S40: Comparisons between the TBE(FC) / *aug-cc-pVTZ* benchmark (see Table 11) and the results obtained with various computational approaches using the same basis set.

Compound	State	TBE	CIS(D)	CC2	CCSD	STEOM	CC(3)	CCSDT-3	CC3	ADC(2)
Acetone	$A_2(V; n \rightarrow \pi^*)$	4.47	4.51	4.55	4.54	4.40	4.48	4.49	4.48	4.37
	${}^1B_2(R; n \rightarrow 3s)$	6.46	5.91	5.91	6.59	6.62	6.46	6.50	6.43	5.87
	${}^1A_2(R; n \rightarrow 3p)$	7.47	6.83	6.84	7.57	7.47	7.51	7.45	7.45	6.81
	${}^1A_1(R; n \rightarrow 3p)$	7.51	7.04	6.89	7.63	7.68	7.52	7.55	7.48	6.85
	${}^1B_2(R; n \rightarrow 3p)$	7.62	6.93	7.02	7.72	7.61	7.65	7.59	7.59	6.99
	${}^3A_2(V; n \rightarrow \pi^*)$	4.13	4.15	4.16	4.15	4.05			4.15	4.00
	${}^3A_1(V; \pi \rightarrow \pi^*)$	6.25	6.50	6.50	6.19	6.05			6.28	6.37
	${}^1A''(V; n \rightarrow \pi^*)$	3.78	3.89	3.85	3.91	3.85	3.80	3.78	3.74	3.68
	${}^1A'(V; \pi \rightarrow \pi^*)$	6.69	6.88	6.80	6.87	6.69	6.71	6.65	6.74	
Acrolein	${}^1A''(V; n \rightarrow \pi^*)$	6.72	7.76	6.68	7.27	6.98	6.94	6.89	6.75	6.59
	${}^1A'(R; n \rightarrow 3s)$	7.08	6.92	6.40	7.24	7.25	7.12	7.15	7.07	6.35
	${}^3A''(V; n \rightarrow \pi^*)$	3.51	3.56	3.49	3.55	3.48			3.46	3.33
	${}^3A'(V; \pi \rightarrow \pi^*)$	3.94	4.14	4.06	3.88	3.72			3.94	4.05
	${}^3A'(V; \pi \rightarrow \pi^*)$	6.18	6.42	6.37	6.14	6.00			6.19	6.31
	${}^3A''(V; \pi \rightarrow \pi^*)$	6.54	6.55	7.09					6.61	6.47
Benzene	${}^1B_{2u}(V; \pi \rightarrow \pi^*)$	5.06	5.32	5.26	5.20	5.01	5.14	5.11	5.09	5.27
	${}^1B_{1u}(V; \pi \rightarrow \pi^*)$	6.45	6.61	6.48	6.50	6.51	6.47	6.45	6.44	6.45
	${}^1E_{1g}(R; \pi \rightarrow 3s)$	6.52	6.57	6.47	6.58	6.65	6.54	6.54	6.52	6.52
	${}^1A_{2u}(R; \pi \rightarrow 3p)$	7.08	7.08	7.00	7.12	7.17	7.10	7.09	7.08	7.06
	${}^1E_{2u}(R; \pi \rightarrow 3p)$	7.15	7.14	7.06	7.20	7.20	7.17	7.16	7.15	7.12
	${}^3B_{1u}(V; \pi \rightarrow \pi^*)$	4.16	4.47	4.37	4.00				4.18	4.37
	${}^3E_{1u}(V; \pi \rightarrow \pi^*)$	4.85	5.12	5.08	4.93	4.88			4.86	5.07
	${}^3B_{2u}(V; \pi \rightarrow \pi^*)$	5.81	5.95	5.89	5.77	5.78			5.81	5.87
	${}^1B_u(V; \pi \rightarrow \pi^*)$	6.22	6.24	6.16	6.35	6.33	6.24	6.22	6.12	
	${}^1B_g(R; \pi \rightarrow 3s)$	6.33	6.34	6.26	6.40	6.38	6.33	6.34	6.33	6.31
	${}^1A_g(V; \pi \rightarrow \pi^*)$	6.50	7.35	7.09	7.12	6.86	6.76	6.67	6.67	7.14
	${}^1A_u(R; \pi \rightarrow 3p)$	6.64	6.65	6.57	6.71	6.69	6.65	6.66	6.64	6.63
	${}^1A_u(R; \pi \rightarrow 3p)$	6.80	6.78	6.70	6.87	6.92	6.80	6.81	6.80	6.76
	${}^1B_u(R; \pi \rightarrow 3p)$	7.68	7.71	7.63	7.76	7.68			7.68	7.48
	${}^3B_u(V; \pi \rightarrow \pi^*)$	3.36	3.55	3.45	3.29	3.17			3.36	3.46
	${}^3A_g(V; \pi \rightarrow \pi^*)$	5.20	5.33	5.30	5.17	5.03			5.20	5.27
	${}^3B_g(R; \pi \rightarrow 3s)$	6.29	6.31	6.21	6.33	6.42			6.28	6.27
	${}^1\Sigma^-(V; \pi \rightarrow \pi^*)$	5.80	6.14	6.03	5.88	5.87	5.84	5.81	5.80	5.99
Cyanoacetylene										Continued on next page

Compound	State	TBE	CIS(D)	CC2	CCSD	STEOM	CC(3)	CCSDT-3	CC3	ADC(2)
Cyanoformaldehyde	$^1\Delta(V; \pi \rightarrow \pi^*)$	6.07	6.41	6.30	6.15	6.20	6.11	6.09	6.08	6.25
	$^3\Sigma^+(V; \pi \rightarrow \pi^*)$	4.44	4.89	4.80	4.38	4.35			4.45	4.77
	$^3\Delta(V; \pi \rightarrow \pi^*)$	5.21	5.60	5.50	5.24	5.22			5.22	5.46
	$^3\Delta(V; \pi \rightarrow \pi^*)$	3.54	3.83	3.79	3.58	3.52	3.58	3.54	3.54	3.63
	$^1A''[F](V; \pi \rightarrow \pi^*)$	3.81	3.98	3.97	3.94	3.80	3.87	3.86	3.83	3.83
	$^1A''(V; n \rightarrow \pi^*)$	6.46	7.10	6.74	6.67	6.56	6.50	6.47	6.42	6.73
	$^3A''(V; n \rightarrow \pi^*)$	3.44	3.54	3.51	3.49	3.42			3.46	3.37
	$^3A'(V; \pi \rightarrow \pi^*)$	5.01	5.43	5.34	4.97	4.89			5.01	5.27
	$^1\Sigma_u^-(V; \pi \rightarrow \pi^*)$	6.39	6.85	6.72	6.50	6.46	6.44	6.40	6.39	6.67
	$^1\Delta_u(V; \pi \rightarrow \pi^*)$	6.66	7.15	7.02	6.78	6.80	6.72	6.68	6.66	6.95
Cyanogen	$^3\Sigma_u^+(V; \pi \rightarrow \pi^*)$	4.91	5.44	5.35	4.84	4.81			4.90	5.31
	$^1\Sigma_u^-[F](V; \pi \rightarrow \pi^*)$	5.05	5.61	5.48	5.13	5.07	5.14	5.06	5.06	5.39
	$^1B_2(V; \pi \rightarrow \pi^*)$	5.56	5.62	5.52	5.67	5.59	5.53	5.56	5.54	5.49
	$^1A_2(R; \pi \rightarrow 3s)$	5.78	5.75	5.66	5.83	5.80	5.78	5.78	5.77	5.71
	$^1B_1(R; \pi \rightarrow 3p)$	6.41	6.33	6.26	6.45	6.44	6.41	6.40	6.40	6.31
	$^1A_2(R; \pi \rightarrow 3p)$	6.46	6.37	6.30	6.50	6.60	6.46	6.46	6.45	6.35
	$^1B_2(R; \pi \rightarrow 3p)$	6.56	6.50	6.42	6.61	6.65	6.57	6.56	6.56	6.48
	$^1A_1(V; \pi \rightarrow \pi^*)$	6.52	7.63	6.86	6.96	6.71	6.66	6.57	6.57	6.91
	$^3B_2(V; \pi \rightarrow \pi^*)$	3.31	3.52	3.42	3.24	3.11			3.32	3.42
	$^3A_1(V; \pi \rightarrow \pi^*)$	5.11	5.30	5.36	5.09	4.79			5.12	5.23
Cyclopentadiene	$^3A_2(R; \pi \rightarrow 3s)$	5.73	5.73	5.62	5.78	5.86			5.73	5.67
	$^3B_1(R; \pi \rightarrow 3p)$	6.36	6.31	6.22	6.40	6.47			6.36	6.27
	$^1B_1(V; n \rightarrow \pi^*)$	4.26	4.27	4.01	4.53	4.18	4.28	4.31	4.21	3.88
	$^1A_2(V; n \rightarrow \pi^*)$	5.55	5.65	5.65	5.40		5.59	5.59	5.57	5.47
	$^1B_2(R; n \rightarrow 3s)$	6.34	6.32	5.84	6.44	6.36	6.35	6.38	6.32	5.79
	$^1B_2(V; \pi \rightarrow \pi^*)$	6.54	6.60	6.46	6.82	6.59	6.61	6.54	6.33	
	$^1B_2(R; n \rightarrow 3p)$	6.98	6.48	6.56	7.09	7.07	6.98		6.96	6.43
	$^1A_1(R; n \rightarrow 3p)$	7.02	6.54	6.47	7.12		7.02	7.06	7.00	6.41
	$^1A_1(V; \pi \rightarrow \pi^*)$	8.28	8.22	8.28	8.35	8.19	8.29		8.28	8.10
	$^3B_1(V; n \rightarrow \pi^*)$	3.93	4.15	3.73	4.18	4.13			3.91	3.62
Cyclopropenone	$^3B_2(V; \pi \rightarrow \pi^*)$	4.88	5.26	4.99	4.91	4.88			4.89	4.90
	$^3A_2(V; n \rightarrow \pi^*)$	5.35	5.96	5.45	5.40	5.01			5.37	5.28
	$^3A_1(V; \pi \rightarrow \pi^*)$	6.79	6.97	7.02	6.76	6.39			6.83	6.84
	$^1A_2(V; n \rightarrow \pi^*)$	3.41	3.45	3.53	3.51	3.34	3.43	3.46	3.43	3.38
	$^1B_1(V; n \rightarrow \pi^*)$	3.45	3.56	3.50	3.84	3.51	3.56	3.43	3.43	3.37
	$^1B_2(V; \pi \rightarrow \pi^*)$	4.60	5.06	4.91	4.98	4.69	4.73	4.64	4.72	
	$^1B_2(R; n \rightarrow 3s)$	5.34	5.24	5.22	5.41	5.45	5.38	5.38	5.34	5.17
	$^1A_1(V; \pi \rightarrow \pi^*)$	5.46	5.47	5.59	5.55	5.48	5.52	5.49	5.36	
	$^1B_2(R; n \rightarrow 3p)$	5.92	5.93	5.82	6.03	6.05	5.93	5.97	5.93	5.77

Continued on next page

Compound	State	TBE	CIS(D)	CC2	CCSD	STEOM	CC(3)	CCSDT-3	CC3	ADC(2)
Diacetylene	$^3A_2(V; n \rightarrow \pi^*)$	3.28	3.34	3.37	3.34	3.23	3.30	3.23	3.23	3.23
	$^3B_1(V; n \rightarrow \pi^*)$	3.32	3.55	3.38	3.69	3.55	3.31	3.26	3.31	3.26
	$^3B_2(V; \pi \rightarrow \pi^*)$	4.01	4.62	4.24	4.16	4.05	4.02	4.12	4.02	4.12
	$^3A_1(V; \pi \rightarrow \pi^*)$	4.01	4.12	4.16	3.97	3.87	4.03	4.04	4.03	4.04
	$^1\Sigma_u^-(V; \pi \rightarrow \pi^*)$	5.33	5.62	5.51	5.41	5.37	5.35	5.34	5.49	5.49
	$^1\Delta_u(V; \pi \rightarrow \pi^*)$	5.61	5.86	5.76	5.67	5.64	5.62	5.61	5.72	5.72
	$^3\Sigma_u^+(V; \pi \rightarrow \pi^*)$	4.10	4.48	4.39	4.01	4.05	4.08	4.37	4.37	4.37
	$^3\Delta_u(V; \pi \rightarrow \pi^*)$	4.78	5.14	5.03	4.82	4.87	4.80	5.01	5.01	5.01
	$^1A_2(R; \pi \rightarrow 3s)$	6.09	6.16	6.06	6.17	6.15	6.10	6.09	6.08	6.12
	$^1B_2(V; \pi \rightarrow \pi^*)$	6.37	6.59	6.45	6.51	6.45	6.38	6.37	6.34	6.47
Furan	$^1A_1(V; \pi \rightarrow \pi^*)$	6.56	7.01	6.77	6.85	6.68	6.65	6.58	6.76	6.76
	$^1B_1(R; \pi \rightarrow 3p)$	6.64	6.67	6.59	6.71	6.70	6.64	6.63	6.64	6.64
	$^1A_2(R; \pi \rightarrow 3p)$	6.81	6.84	6.75	6.89	6.93	6.82	6.81	6.80	6.82
	$^1B_2(R; \pi \rightarrow 3p)$	7.24	7.34	7.25	7.32	7.35	7.25	7.23	7.29	7.29
	$^3B_2(V; \pi \rightarrow \pi^*)$	4.20	4.51	4.43	4.15	4.17	4.22	4.41	4.41	4.41
	$^3A_1(V; \pi \rightarrow \pi^*)$	5.46	5.69	5.66	5.47	5.61	5.48	5.59	5.59	5.59
	$^3A_2(R; \pi \rightarrow 3s)$	6.02	6.13	6.01	6.11	6.20	6.02	6.08	6.08	6.08
	$^3B_1(R; \pi \rightarrow 3p)$	6.59	6.64	6.55	6.66	6.73	6.59	6.61	6.61	6.61
	$^1A_u(V; n \rightarrow \pi^*)$	2.88	3.01	2.91	3.01	2.86	2.92	2.88	2.83	2.83
	$^1A_g(V; n \rightarrow \pi^*, \pi^*)$	4.24	4.46	4.44	4.42	4.32	4.30	4.27	4.27	4.27
Glyoxal	$^1A_g(V; n \rightarrow \pi^*)$	5.61	6.57	7.01	6.51	7.12	6.75	6.73	6.58	6.50
	$^1B_g(V; n \rightarrow \pi^*)$	7.71	7.25	7.16	7.84	7.94	7.71	7.74	7.67	7.18
	$^1B_u(R; n \rightarrow 3p)$	2.49	2.59	2.47	2.56	2.44	2.44	2.49	2.39	2.39
	$^3A_u(V; n \rightarrow \pi^*)$	3.89	4.00	3.96	3.96	3.88	3.90	3.82	3.82	3.82
	$^3B_g(V; n \rightarrow \pi^*)$	5.15	5.47	5.42	5.10	4.92	5.17	5.33	5.33	5.33
	$^3B_u(V; \pi \rightarrow \pi^*)$	6.30	6.54	6.56	6.23	6.13	6.30	6.45	6.45	6.45
	$^3A_g(V; \pi \rightarrow \pi^*)$	5.71	5.81	5.69	5.80	5.91	5.73	5.72	5.71	5.75
	$^1A''(R; \pi \rightarrow 3s)$	6.41	6.73	6.51	6.59	6.76	6.47	6.46	6.41	6.50
	$^1A'(V; \pi \rightarrow \pi^*)$	6.50	6.52	6.47	6.58	6.66	6.53	6.51	6.50	6.51
	$^1A'(R; \pi \rightarrow 3p)$	6.83	7.40	6.41	7.02	6.92	6.93	6.91	6.87	6.87
Imidazole	$^3A'(V; \pi \rightarrow \pi^*)$	4.73	5.04	4.94	4.68	4.66	4.75	4.92	4.92	4.92
	$^3A''(R; \pi \rightarrow 3s)$	5.66	5.80	5.66	5.77	5.87	5.67	5.72	5.72	5.72
	$^3A'(V; \pi \rightarrow \pi^*)$	5.74	6.06	5.94	5.77	5.60	5.74	5.93	5.93	5.93
	$^3A''(V; n \rightarrow \pi^*)$	6.31	6.47	6.36	6.40	6.28	6.33	6.31	6.31	6.31
	$^1B_1(R; \pi \rightarrow 3s)$	6.46	6.46	6.37	6.54	6.59	6.46	6.45	6.43	6.43
	$^1A_1(R; \pi \rightarrow 3p)$	7.01	7.01	6.95	7.09	7.11	7.01	7.00	7.00	6.97
	$^3A_1(V; (\pi \rightarrow \pi^*))$	4.53	4.68	4.62	4.48	4.22	4.53	4.62	4.62	4.62
	$^1B_2(V; \pi \rightarrow \pi^*)$	4.28	4.72	4.51	4.58	4.76	4.35	4.38	4.31	4.46
	Methylenecyclopropene									

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Compound	State	TBE	CIS(D)	CC2	CCSD	STEOM	CC(3)	CCSDT-3	CC3	ADC(2)
Propynal	$^1B_1(\text{R}; \pi \rightarrow 3s)$	5.44	5.43	5.35	5.48	5.45	5.44	5.45	5.44	5.38
	$^1A_2(\text{R}; \pi \rightarrow 3p)$	5.96	5.94	5.85	6.00	6.01	5.96	5.97	5.95	5.87
	$^1A_1(\text{V}; \pi \rightarrow \pi^*)$	6.12	6.14	6.09	6.18	6.21	6.12	6.14	6.13	6.09
	$^3B_2(\text{V}; \pi \rightarrow \pi^*)$	3.49	3.94	3.64	3.57	3.67			3.50	3.61
	$^3A_1(\text{V}; \pi \rightarrow \pi^*)$	4.74	4.86	4.81	4.69	4.78			4.74	4.80
	$^1A''(\text{V}; n \rightarrow \pi^*)$	3.80	3.95	3.96	3.84	3.82	3.86	3.85	3.82	3.78
	$^1A''(\text{V}; \pi \rightarrow \pi^*)$	5.54	5.95	5.71	5.69	5.72	5.57	5.55	5.51	5.73
	$^3A''(\text{V}; n \rightarrow \pi^*)$	3.47	3.55	3.53	3.53	3.40			3.49	3.38
	$^3A'(\text{V}; \pi \rightarrow \pi^*)$	4.47	4.81	4.71	4.40	4.38			4.43	4.67
	$^1B_{3u}(\text{V}; n \rightarrow \pi^*)$	4.15	4.37	4.14	4.32	4.10			4.14	4.17
Pyrazine	$^1A_u(\text{V}; n \rightarrow \pi^*)$	4.98	4.91	4.86	5.23	5.04			4.97	4.88
	$^1B_{2u}(\text{V}; \pi \rightarrow \pi^*)$	5.02	5.26	5.14	5.15	4.83	5.09	5.06	5.03	5.17
	$^1B_{2g}(\text{V}; n \rightarrow \pi^*)$	5.71	6.22	5.86	6.00	5.71	5.84	5.80	5.71	5.87
	$^1A_g(\text{R}; n \rightarrow 3s)$	6.65	6.20	6.20	6.83	6.86	6.71	6.74	6.66	6.30
	$^1B_{1g}(\text{V}; n \rightarrow \pi^*)$	6.74	7.31	6.67	7.14	7.33	6.85	6.87	6.73	6.67
	$^1B_{1u}(\text{V}; \pi \rightarrow \pi^*)$	6.88	7.13	6.89	6.96	6.90	6.88	6.86	6.86	6.88
	$^1B_{1g}(\text{R}; \pi \rightarrow 3s)$	7.21	7.31	7.21	7.26	7.22	7.22	7.21	7.20	7.27
	$^1B_{2u}(\text{R}; n \rightarrow 3p)$	7.24	7.30	6.74	7.44	7.49	7.31	7.35	7.25	
	$^1B_{1u}(\text{R}; n \rightarrow 3p)$	7.44	7.19	7.03	7.60	7.50	7.52	7.45		
	$^1B_{1u}(\text{V}; \pi \rightarrow \pi^*)$	7.98	7.85	7.87	8.20	8.20	7.98	8.02	7.94	
Pyridazine	$^3B_{3u}(\text{V}; n \rightarrow \pi^*)$	3.59	3.84	3.60	3.70	3.48			3.59	3.62
	$^3B_{1u}(\text{V}; \pi \rightarrow \pi^*)$	4.35	4.76	4.60	4.19	3.93			4.39	4.57
	$^3B_{2u}(\text{V}; \pi \rightarrow \pi^*)$	4.39	4.67	4.57	4.40	4.32			4.40	4.59
	$^3A_u(\text{V}; n \rightarrow \pi^*)$	4.93	4.93	4.82	5.16	4.97			4.93	4.84
	$^3B_{2g}(\text{V}; n \rightarrow \pi^*)$	5.08	5.41	5.17	5.21	4.89			5.08	
	$^3B_{1u}(\text{V}; \pi \rightarrow \pi^*)$	5.28	5.59	5.59	5.35	5.21			5.29	
	$^1B_1(\text{V}; n \rightarrow \pi^*)$	3.83	4.12	3.78	4.03	3.76	3.91	3.89	3.83	3.79
	$^1A_2(\text{V}; n \rightarrow \pi^*)$	4.37	4.84	4.26	4.65	4.44	4.46	4.47	4.37	4.27
	$^1A_1(\text{V}; \pi \rightarrow \pi^*)$	5.26	5.51	5.43	5.43	5.36	5.32	5.29	5.29	5.44
	$^1A_2(\text{V}; n \rightarrow \pi^*)$	5.72	5.62	5.79	6.01	5.76	5.84	5.82	5.74	5.81
Pyridine	$^1B_2(\text{R}; n \rightarrow 3s)$	6.17	5.83	5.59	6.42	6.45	6.27	6.31	6.17	5.69
	$^1B_1(\text{V}; n \rightarrow \pi^*)$	6.37	6.39	6.33	6.67	6.47	6.46	6.47	6.37	6.35
	$^1B_2(\text{V}; \pi \rightarrow \pi^*)$	6.75	6.86	6.88	6.88	6.81	6.77	6.74	6.85	
	$^3B_1(\text{V}; n \rightarrow \pi^*)$	3.19	3.50	3.18	3.30	3.06			3.19	3.19
	$^3A_2(\text{V}; n \rightarrow \pi^*)$	4.11	4.64	4.01	4.31	4.13			4.11	4.02
	$^3B_2(\text{V}; \pi \rightarrow \pi^*)$	4.34	4.75	4.61	4.17	3.89			4.38	4.60
	$^3A_1(\text{V}; \pi \rightarrow \pi^*)$	4.82	5.18	5.07	4.86	4.78			4.83	5.06
Pyridine	$^1B_1(\text{V}; n \rightarrow \pi^*)$	4.95	5.22	4.99	5.17	4.94	5.04	5.03	4.96	4.98
	$^1B_2(\text{V}; \pi \rightarrow \pi^*)$	5.14	5.40	5.32	5.29	5.03	5.23	5.20	5.17	5.33

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Compound	State	TBE	CIS(D)	CC2	CCSD	STEOM	CC(3)	CCSDT-3	CC3	ADC(2)
Pyrimidine	$^1A_2(V; n \rightarrow \pi^*)$	5.40	5.33	5.28	5.64	5.45	5.46	5.48	5.40	5.27
	$^1A_1(V; \pi \rightarrow \pi^*)$	6.62	6.84	6.24	6.96	6.98	6.67	6.65	6.63	6.31
	$^1A_1(R; n \rightarrow 3s)$	6.76	6.38	6.68	6.71	6.83	6.86	6.76	6.76	6.65
	$^1A_2(R; \pi \rightarrow 3s)$	6.82	6.88	6.79	6.87	6.94	6.83	6.83	6.81	6.83
	$^1B_2(V; \pi \rightarrow \pi^*)$	7.40	7.56	7.37	7.55	7.40	7.40	7.40	7.38	6.87
	$^1B_1(R; \pi \rightarrow 3p)$	7.38	7.42	7.34	7.43	7.49	7.40	7.40	7.38	7.38
	$^1A_1(V; \pi \rightarrow \pi^*)$	7.39	7.56	7.45	7.59	7.44	7.47	7.47	7.39	7.48
	$^3A_1(V; \pi \rightarrow \pi^*)$	4.30	4.66	4.53	4.15	3.93	4.33	4.33	4.53	
	$^3B_1(V; n \rightarrow \pi^*)$	4.46	4.72	4.48	4.59	4.41	4.46	4.46	4.47	
	$^3B_2(V; \pi \rightarrow \pi^*)$	4.79	5.08	4.98	4.83	4.78	4.79	4.79	4.98	
Pyrrole	$^3A_1(V; \pi \rightarrow \pi^*)$	5.04	5.33	5.29	5.11	5.03	5.05	5.05	5.28	
	$^3A_2(V; n \rightarrow \pi^*)$	5.36	5.36	5.24	5.58	5.39	5.35	5.35	5.23	
	$^3B_2(V; \pi \rightarrow \pi^*)$	6.24	6.40	6.39	6.26	6.25	6.25	6.25	6.35	
	$^1A_1(V; n \rightarrow \pi^*)$	4.44	4.57	4.41	4.66	4.36	4.51	4.44	4.37	
	$^1A_2(V; n \rightarrow \pi^*)$	4.85	4.97	4.77	5.07	4.81	4.94	4.86	4.73	
	$^1B_2(V; \pi \rightarrow \pi^*)$	5.38	5.58	5.54	5.53	5.15	5.47	5.44	5.41	5.52
	$^1A_2(V; n \rightarrow \pi^*)$	5.92	6.06	5.96	6.20	5.91	6.03	6.02	5.93	5.93
	$^1B_1(V; n \rightarrow \pi^*)$	6.26	7.22	6.25	6.54	6.26	6.34	6.36	6.26	6.22
	$^1B_2(R; n \rightarrow 3s)$	6.70	6.23	6.20	6.88	6.90	6.77	6.81	6.72	6.25
	$^1A_1(V; \pi \rightarrow \pi^*)$	6.88	7.07	6.84	6.97	6.91	6.89	6.87	6.83	
Tetrazine	$^3A_1(V; n \rightarrow \pi^*)$	4.09	4.31	4.07	4.25	4.02	4.10	4.05		
	$^3A_1(V; \pi \rightarrow \pi^*)$	4.51	4.91	4.77	4.39	4.11	4.55	4.76		
	$^3A_2(V; n \rightarrow \pi^*)$	4.66	5.01	4.60	4.83	4.63	4.66	4.58		
	$^3B_2(V; \pi \rightarrow \pi^*)$	4.96	5.23	5.17	4.99	4.88	4.96	5.14		
	$^1A_2(R; \pi \rightarrow 3s)$	5.24	5.34	5.23	5.34	5.36	5.26	5.24	5.30	
	$^1B_1(R; \pi \rightarrow 3p)$	6.00	6.04	5.91	6.04	6.08	6.00	5.98	5.94	
	$^1A_2(R; \pi \rightarrow 3p)$	6.00	6.04	5.96	6.09	6.15	6.04	6.03	6.01	
	$^1B_2(V; (\pi \rightarrow \pi^*)$	6.26	6.62	6.30	6.35	6.44	6.28	6.27	6.25	
	$^1A_1(V; \pi \rightarrow \pi^*)$	6.30	6.64	6.47	6.51	6.39	6.36	6.32	6.47	
	$^1B_2(R; \pi \rightarrow 3p)$	6.83	7.00	6.89	6.93	6.85	6.83	6.91		
$B_{3u}$	$^3B_2(V; \pi \rightarrow \pi^*)$	4.51	4.81	4.72	4.45	4.15	4.53	4.71		
	$^3A_2(R; \pi \rightarrow 3s)$	5.21	5.33	5.20	5.30	5.41	5.21	5.27		
	$^3A_1(V; \pi \rightarrow \pi^*)$	5.45	5.70	5.66	5.49	5.12	5.46	5.62		
	$^3B_1(R; \pi \rightarrow 3p)$	5.91	6.01	5.86	5.97	6.06	5.92	5.89		
	$^1B_{3u}(V; n \rightarrow \pi^*)$	2.47	2.67	2.38	2.64	2.36	2.52	2.46		
	$^1A_u(V; n \rightarrow \pi^*)$	3.69	3.93	3.53	3.96	3.73	3.78	3.67		
	$^1A_g(V; n \rightarrow \pi^*, \pi^*)$	4.93	5.58	5.02	4.90	5.09	6.77	6.21		
$B_{2u}$	$^1B_{1g}(V; n \rightarrow \pi^*)$	5.21	5.40	5.31	5.37	4.92	5.31	5.26	5.23	
	$^1B_{2u}(V; \pi \rightarrow \pi^*)$									Continued on next page

Compound	State	TBE	CIS(D)	CC2	CCSD	STEOM	CC(3)	CCSDT-3	CC3	ADC(2)
	$^1B_{2g}(\text{V}; n \rightarrow \pi^*)$	5.45	6.09	5.64	5.84	5.49	5.64	5.57	5.46	5.68
	$^1A_u(\text{V}; n \rightarrow \pi^*)$	5.53	5.64	5.56	5.77	5.50	5.63		5.52	5.59
	$^1B_{3g}(\text{V}; n \rightarrow \pi^*, \pi^*)$	6.15	6.12	6.08	6.18	6.66	6.34	6.32	6.13	6.21
	$^1B_{2g}(\text{V}; n \rightarrow \pi^*)$	6.91	6.39	6.95	7.32	7.04	7.05		6.92	6.97
	$^1B_{1g}(\text{V}; n \rightarrow \pi^*)$	1.85	2.13	1.81	1.96	1.70			1.85	1.85
	$^3B_{3u}(\text{V}; n \rightarrow \pi^*)$	3.45	4.00	3.31	3.66	3.47			3.44	3.35
	$^3A_u(\text{V}; n \rightarrow \pi^*)$	4.20	4.46	4.27	4.31	3.96			4.20	4.27
	$^3B_{1g}(\text{V}; n \rightarrow \pi^*)$	4.49	4.96	4.81	4.27	3.90			4.54	4.80
	$^3B_{2u}(\text{V}; \pi \rightarrow \pi^*)$	4.52	4.87	4.77	4.53	4.43			4.52	4.76
	$^3B_{2g}(\text{V}; n \rightarrow \pi^*)$	5.04	5.47	5.15	5.23	4.91			5.05	5.16
	$^3A_u(\text{V}; n \rightarrow \pi^*)$	5.11	5.74	5.13	5.28	5.04			5.11	5.16
	$^3B_{3g}(\text{V}; n \rightarrow \pi^*, \pi^*)$	5.51							7.35	
Thioacetone	$^3B_{1u}(\text{V}; \pi \rightarrow \pi^*)$	5.42	5.74	5.70	5.52	5.43			5.42	5.67
	$^1A_2(\text{V}; n \rightarrow \pi^*)$	2.53	2.55	2.63	2.63	2.47			2.55	2.47
	$^1B_2(\text{R}; n \rightarrow 4s)$	5.56	5.59	5.50	5.67	5.72			5.61	5.55
	$^1A_1(\text{V}; \pi \rightarrow \pi^*)$	5.88	6.01	6.09	6.01	5.90			5.93	5.90
	$^1B_2(\text{R}; n \rightarrow 4p)$	6.51	6.54	6.44	6.59	6.62			6.54	6.43
	$^1A_1(\text{R}; n \rightarrow 4p)$	6.61	6.52	6.53	6.71	6.76			6.66	6.48
	$^3A_2(\text{V}; n \rightarrow \pi^*)$	2.33	2.30	2.33	2.35	2.25			2.34	2.20
	$^3A_1(\text{V}; \pi \rightarrow \pi^*)$	3.45	3.60	3.59	3.66	3.22			3.46	3.52
	$^1A_1(\text{V}; \pi \rightarrow \pi^*)$	5.64	5.77	5.75	5.78	5.69			5.65	5.72
	$^1B_2(\text{V}; \pi \rightarrow \pi^*)$	5.98	6.24	6.07	6.12	6.00			5.99	6.07
Thiophene	$^1A_2(\text{R}; \pi \rightarrow 3s)$	6.14	6.18	6.07	6.22	6.18			6.15	6.15
	$^1B_1(\text{R}; \pi \rightarrow 3p)$	6.14	6.44	6.15	6.31	6.23			6.18	6.14
	$^1A_2(\text{R}; \pi \rightarrow 3p)$	6.21	6.42	6.35	6.32	6.16			6.28	6.25
	$^1B_1(\text{R}; \pi \rightarrow 3s)$	6.49	6.49	6.48	6.56	6.52			6.52	6.50
	$^1B_2(\text{R}; \pi \rightarrow 3p)$	7.29	7.37	7.26	7.38	7.35			7.31	7.34
	$^1A_1(\text{V}; \pi \rightarrow \pi^*)$	7.31	7.68	7.48	7.57	7.46			7.42	7.35
	$^3B_2(\text{V}; \pi \rightarrow \pi^*)$	3.92	4.22	4.12	3.85	3.70			3.94	4.11
	$^3A_1(\text{V}; \pi \rightarrow \pi^*)$	4.76	5.02	4.91	4.77	4.71			4.77	4.86
	$^3B_1(\text{R}; \pi \rightarrow 3p)$	5.93	6.28	6.00	6.12	6.16			5.95	6.09
	$^3A_2(\text{R}; \pi \rightarrow 3s)$	6.08	6.17	6.03	6.16	6.24			6.09	6.11
Thiopropynal	$^1A''(\text{V}; n \rightarrow \pi^*)$	2.03	2.14	2.20	2.15	2.06	2.07	2.08	2.05	2.08
	$^3A''(\text{V}; n \rightarrow \pi^*)$	1.80	1.83	1.84	1.83	1.79			1.81	1.74
	$^1A_1''(\text{V}; n \rightarrow \pi^*)$	4.72	4.59	4.64	4.92	4.62	4.77	4.80	4.73	4.58
	$^1A_2''(\text{V}; n \rightarrow \pi^*)$	4.75	4.86	4.75	4.99	4.76			4.82	4.74
	$^1E''(\text{V}; n \rightarrow \pi^*)$	4.78	4.84	4.72	4.99	4.74			4.86	4.69
	$^1A'_2(\text{V}; \pi \rightarrow \pi^*)$	5.75	5.83	5.89	5.91	5.45			4.78	4.66
									5.78	5.83
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Compound	State	TBE	CIS(D)	CC2	CCSD	STEOM	CC(3)	CCSDT-3	CC3	ADC(2)
$^1A_1'$ (V; $\pi \rightarrow \pi^*$ )	7.24	7.39	7.32	7.34	7.28	7.27	7.24	7.18		
$^1E'$ (R; $n \rightarrow 3s$ )	7.32	7.83	6.87	7.45	7.37	7.41	7.35	6.89		
$^1E''$ (V; $n \rightarrow \pi^*$ )	7.78		7.71	8.13	7.96		7.79			
$^1E'$ (V; $\pi \rightarrow \pi^*$ )	7.94	7.84	7.63	8.14		7.95		7.65		
$^3A_2''$ (V; $n \rightarrow \pi^*$ )	4.33	4.52	4.32	4.51	4.32		4.33	4.29		
$^3E''$ (V; $n \rightarrow \pi^*$ )	4.51	4.71	4.46	4.67	4.47		4.51	4.42		
$^3A_1''$ (V; $n \rightarrow \pi^*$ )	4.73	4.65	4.65	4.91	4.43		4.75	4.59		
$^3A_1'$ (V; $\pi \rightarrow \pi^*$ )	4.85	5.27	5.12	4.74	4.69		4.88	5.10		
$^3E'$ (V; $\pi \rightarrow \pi^*$ )	5.59	5.91	5.88	5.70	5.61		5.61	5.82		
$^3A_2'$ (V; $(\pi \rightarrow \pi^*)$ )	6.62	6.71	6.76	6.59	6.60		6.63	6.63		

## S4.2 Statistical analysis

Table S41: MSE (in eV) obtained for various subsets of transition energies.

Method	Singlet	Triplet	Valence	Rydberg	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
CIS(D)	0.10	0.24	0.24	-0.05	0.19	0.28
ADC(2)	-0.04	0.07	0.06	-0.13	-0.04	0.14
CC2	-0.03	0.11	0.10	-0.17	0.01	0.17
STEOM-CCSD	0.06	-0.06	-0.04	0.12	-0.02	-0.06
CCSD	0.15	0.05	0.12	0.09	0.19	0.07
CCSDR(3)	0.05		0.07	0.02	0.08	0.06
CCSDT-3	0.05		0.06	0.03	0.08	0.04
CC3	0.00	0.01	0.01	0.00	0.00	0.01
NEVPT2	0.10	0.08	0.08	0.12	0.05	0.11

## S5 Geometries

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

### S5.1 Acetone

C	0.00000000	0.00000000	0.18807702
C	0.00000000	2.42007545	-1.31764698
C	0.00000000	-2.42007545	-1.31764698
O	0.00000000	0.00000000	2.48269094
H	0.00000000	4.03690733	-0.05185132
H	0.00000000	-4.03690733	-0.05185132
H	1.66061256	2.48420530	-2.53995285
H	-1.66061256	2.48420530	-2.53995285
H	1.66061256	-2.48420530	-2.53995285
H	-1.66061256	-2.48420530	-2.53995285

### S5.2 Acrolein

C	-1.11645072	-0.68348783	0.00000000
C	1.20647847	0.83714564	0.00000000
C	3.46831059	-0.28872636	0.00000000
O	-3.23666415	0.19187203	0.00000000
H	-0.80613858	-2.74747338	0.00000000
H	0.98699813	2.86613511	0.00000000
H	5.20930864	0.77443560	0.00000000
H	3.60951559	-2.33000749	0.00000000

### S5.3 Benzene

C	0.00000000	2.63144965	0.00000000
C	-2.27890225	1.31572483	0.00000000
C	-2.27890225	-1.31572483	0.00000000
C	0.00000000	-2.63144965	0.00000000
C	2.27890225	-1.31572483	0.00000000
C	2.27890225	1.31572483	0.00000000
H	-4.04725813	2.33668557	0.00000000
H	-4.04725813	-2.33668557	0.00000000
H	-0.00000000	-4.67337115	0.00000000
H	4.04725813	-2.33668557	0.00000000
H	4.04725813	2.33668557	0.00000000
H	0.00000000	4.67337115	0.00000000

### S5.4 Butadiene

C	1.14656244	0.00000000	0.75468820
C	-1.14656244	0.00000000	-0.75468820
C	3.48132647	0.00000000	-0.22482805
C	-3.48132647	0.00000000	0.22482805
H	0.90770978	0.00000000	2.78883925
H	-0.90770978	0.00000000	-2.78883925
H	3.77525814	0.00000000	-2.24895470
H	-3.77525814	0.00000000	2.24895470
H	5.13664967	0.00000000	0.96861890
H	-5.13664967	0.00000000	-0.96861890

### S5.5 Cyanoacetylene

C	0.00000000	0.00000000	-3.59120182
C	0.00000000	0.00000000	-1.30693904
C	0.00000000	0.00000000	1.28880240
N	0.00000000	0.00000000	3.48692211
H	0.00000000	0.00000000	-5.59619886

Lowest excited state

C	1.99411175	0.00000000	2.81781077
C	-0.07304269	0.00000000	1.33125774
C	-0.63630126	0.00000000	-1.14556678
N	-1.39755756	0.00000000	-3.26154643
H	1.90749857	0.00000000	4.87279180

## S5.6 Cyanoformaldehyde

C	-0.91561483	0.00000000	-1.22522833
C	-0.01092219	0.00000000	1.39523175
N	0.64170259	0.00000000	3.48820325
O	0.50833684	0.00000000	-3.00337867
H	-2.97202213	0.00000000	-1.42565674

## S5.7 Cyanogen

Ground state

C	0.00000000	0.00000000	1.30401924
C	0.00000000	0.00000000	-1.30401924
N	0.00000000	0.00000000	3.49784121
N	0.00000000	0.00000000	-3.49784121

Lowest excited state

C	0.00000000	0.00000000	1.22784115
C	0.00000000	0.00000000	-1.22784115
N	0.00000000	0.00000000	3.56462559
N	0.00000000	0.00000000	-3.56462559

## S5.8 Cyclopentadiene

C	0.00000000	0.00000000	-2.33113051
C	0.00000000	2.22209092	-0.56871188
C	0.00000000	-2.22209092	-0.56871188
C	0.00000000	1.38514451	1.83772922
C	0.00000000	-1.38514451	1.83772922
H	1.66130504	0.00000000	-3.56414299
H	-1.66130504	0.00000000	-3.56414299
H	0.00000000	4.16550405	-1.18116624
H	0.00000000	-4.16550405	-1.18116624
H	0.00000000	2.54514584	3.51352303
H	0.00000000	-2.54514584	3.51352303

## S5.9 Cyclopropenone

C	0.00000000	1.27491826	-1.86930519
C	0.00000000	-1.27491826	-1.86930519
C	0.00000000	0.00000000	0.51814554
O	0.00000000	0.00000000	2.79326776
H	0.00000000	2.92791371	-3.05679837
H	0.00000000	-2.92791371	-3.05679837

## S5.10 Cyclopropenethione

C	0.00000000	1.26230744	-2.86571925
C	0.00000000	-1.26230744	-2.86571925
C	0.00000000	0.00000000	-0.49233236
S	0.00000000	0.00000000	2.57821680
H	0.00000000	2.97773331	-3.95114059
H	0.00000000	-2.97773331	-3.95114059

## S5.11 Diacetylene

C	0.00000000	0.00000000	1.29447700
C	0.00000000	0.00000000	-1.29447700
C	0.00000000	0.00000000	3.58448429
C	0.00000000	0.00000000	-3.58448429
H	0.00000000	0.00000000	5.58943003
H	0.00000000	0.00000000	-5.58943003

## S5.12 Furan

C	0.00000000	2.06365826	-0.60051250
C	0.00000000	-2.06365826	-0.60051250
C	0.00000000	1.35348578	1.86336416
C	0.00000000	-1.35348578	1.86336416
O	0.00000000	0.00000000	-2.13945332
H	0.00000000	3.86337287	-1.53765695
H	0.00000000	-3.86337287	-1.53765695
H	0.00000000	2.59168789	3.47168051
H	0.00000000	-2.59168789	3.47168051

## S5.13 Glyoxal

C	1.21360282	0.75840215	0.00000000
C	-1.21360282	-0.75840215	0.00000000
O	3.25581408	-0.26453186	0.00000000
O	-3.25581408	0.26453186	0.00000000
H	0.96135276	2.81883243	0.00000000
H	-0.96135276	-2.81883243	0.00000000

### S5.14 Imidazole

C	0.41662795	2.06006259	0.00000000
C	-1.52618386	-1.62343163	0.00000000
C	1.04160471	-1.93007427	0.00000000
N	-1.90345764	0.94914956	0.00000000
N	2.24215443	0.38083431	0.00000000
H	0.65501634	4.07748278	0.00000000
H	-3.57500545	1.84103166	0.00000000
H	-3.06363894	-2.94559167	0.00000000
H	2.08673940	-3.67001102	0.00000000

### S5.15 Isobutene

C	0.00000000	0.00000000	2.70790758
C	0.00000000	0.00000000	0.18431282
C	0.00000000	2.39894572	-1.32482735
C	0.00000000	-2.39894572	-1.32482735
H	0.00000000	1.74848405	3.76691310
H	0.00000000	-1.74848405	3.76691310
H	0.00000000	4.05897160	-0.10582007
H	0.00000000	-4.05897160	-0.10582007
H	1.66026992	2.48337908	-2.55086178
H	-1.66026992	2.48337908	-2.55086178
H	1.66026992	-2.48337908	-2.55086178
H	-1.66026992	-2.48337908	-2.55086178

### S5.16 Methylenecyclopropene

C	0.00000000	0.00000000	0.53512883
C	0.00000000	0.00000000	3.04739824
C	0.00000000	1.25042956	-1.88571561
C	0.00000000	-1.25042956	-1.88571561
H	0.00000000	2.96887531	-2.96270271
H	0.00000000	-2.96887531	-2.96270271
H	0.00000000	1.75335023	4.08608382
H	0.00000000	-1.75335023	4.08608382

## S5.17 Propynal

C	-0.78051115	0.00000000	-1.38900384
C	-0.17873562	0.00000000	1.27825868
C	0.23763714	0.00000000	3.52644798
O	0.80143996	0.00000000	-3.04628328
H	-2.80713069	0.00000000	-1.82768750
H	0.64026209	0.00000000	5.48853193

## S5.18 Pyrazine

C	0.00000000	2.13188686	1.31510863
C	0.00000000	-2.13188686	1.31510863
C	0.00000000	2.13188686	-1.31510863
C	0.00000000	-2.13188686	-1.31510863
N	0.00000000	0.00000000	2.66620111
N	0.00000000	0.00000000	-2.66620111
H	0.00000000	3.88751412	2.35234226
H	0.00000000	-3.88751412	2.35234226
H	0.00000000	3.88751412	-2.35234226
H	0.00000000	-3.88751412	-2.35234226

## S5.19 Pyridazine

C	0.00000000	1.30150855	-2.31552865
C	0.00000000	-1.30150855	-2.31552865
C	0.00000000	2.49271907	0.03513416
C	0.00000000	-2.49271907	0.03513416
N	0.00000000	1.26228251	2.23104685
N	0.00000000	-1.26228251	2.23104685
H	0.00000000	4.52804172	0.19299731
H	0.00000000	-4.52804172	0.19299731
H	0.00000000	2.39011496	-4.03967703
H	0.00000000	-2.39011496	-4.03967703

## S5.20 Pyridine

C	0.00000000	0.00000000	-2.66451139
C	0.00000000	2.25494985	-1.32069889
C	0.00000000	-2.25494985	-1.32069889
C	0.00000000	2.15398594	1.30669632
C	0.00000000	-2.15398594	1.30669632
N	0.00000000	0.00000000	2.62778932
H	0.00000000	0.00000000	-4.70641516
H	0.00000000	4.05768507	-2.27625442
H	0.00000000	-4.05768507	-2.27625442
H	0.00000000	3.88059079	2.40341581
H	0.00000000	-3.88059079	2.40341581

## S5.21 Pyrimidine

C	0.00000000	0.00000000	2.41518350
C	0.00000000	-0.00000000	-2.60410885
C	0.00000000	2.23272561	-1.22869402
C	0.00000000	-2.23272561	-1.22869402
N	0.00000000	2.26214196	1.29619742
N	0.00000000	-2.26214196	1.29619742
H	0.00000000	0.00000000	4.45780256
H	0.00000000	0.00000000	-4.64120942
H	0.00000000	4.05149341	-2.16351748
H	0.00000000	-4.05149341	-2.16351748

## S5.22 Pyrrole

C	0.00000000	2.11924634	0.62676569
C	0.00000000	-2.11924634	0.62676569
C	0.00000000	1.34568862	-1.85506908
C	0.00000000	-1.34568862	-1.85506908
N	0.00000000	0.00000000	2.10934391
H	0.00000000	0.00000000	4.00257355
H	0.00000000	3.97648410	1.44830201
H	0.00000000	-3.97648410	1.44830201
H	0.00000000	2.56726559	-3.47837232
H	0.00000000	-2.56726559	-3.47837232

### S5.23 Tetrazine

C	0.00000000	0.00000000	2.38208164
C	0.00000000	0.00000000	-2.38208164
N	2.25673244	0.00000000	1.24973261
N	-2.25673244	0.00000000	1.24973261
N	2.25673244	0.00000000	-1.24973261
N	-2.25673244	0.00000000	-1.24973261
H	0.00000000	0.00000000	4.41850901
H	0.00000000	0.00000000	-4.41850901

### S5.24 Thioacetone

C	0.00000000	0.00000000	0.68476030
C	0.00000000	2.38541696	2.20685096
C	0.00000000	-2.38541696	2.20685096
S	0.00000000	0.00000000	-2.39920303
H	0.00000000	4.04609254	1.00090614
H	0.00000000	-4.04609254	1.00090614
H	1.65894780	2.42602225	3.43712000
H	-1.65894780	2.42602225	3.43712000
H	1.65894780	-2.42602225	3.43712000
H	-1.65894780	-2.42602225	3.43712000

### S5.25 Thiophene

C	0.00000000	2.33342542	-0.09858421
C	0.00000000	-2.33342542	-0.09858421
C	0.00000000	1.34371718	-2.48297725
C	0.00000000	-1.34371718	-2.48297725
S	0.00000000	0.00000000	2.17250692
H	0.00000000	4.29028016	0.44577296
H	0.00000000	-4.29028016	0.44577296
H	0.00000000	2.48760051	-4.16768392
H	0.00000000	-2.48760051	-4.16768392

## S5.26 Thiopropynal

C	-0.00382924	0.00000000	-1.25249909
C	-2.27832423	0.00000000	0.15152736
C	-4.26309583	0.00000000	1.29548793
S	2.81920288	0.00000000	-0.00828974
H	-0.23056990	0.00000000	-3.28862183
H	-5.97712967	0.00000000	2.33206931

## S5.27 Triazine

C	0.00000000	-2.11414732	-1.22060353
C	0.00000000	0.00000000	2.44120705
C	0.00000000	2.11414732	-1.22060353
N	0.00000000	-2.24624733	1.29687150
N	0.00000000	2.24624733	1.29687150
N	0.00000000	0.00000000	-2.59374300
H	0.00000000	3.88296710	-2.24183210
H	0.00000000	-3.88296710	-2.24183210
H	0.00000000	0.00000000	4.48366420