Supporting Information for: "Standard grids for high-precision integration of modern density functionals: SG-2 and SG-3"

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The following data can be found below:

- Table S1: Atomization energies computed for the G2 data set at the M06-2X/aug-cc-pVTZ level of theory, including both pruning errors and grid errors for SG-2 and SG-3. Pruning errors remain small (MUD = 0.09 kcal/mol for SG-2 and 0.03 kcal/mol for SG-3), albeit slightly larger than for ωB97X-V/aug-cc-pVTZ (*cf.* Table II).

- Table S2: Atomization energies computed for the G2 data set at the ωB97M-V/aug-cc-pVTZ level of theory, including both pruning errors and grid errors for SG-2 and SG-3. Pruning errors remain small (MUD = 0.09 kcal/mol for SG-2 and 0.03 kcal/mol for SG-3), albeit slightly larger than for ωB97X-V/aug-cc-pVTZ (*cf.* Table II).

- Table S3 Isomerization energies for organic reactions at the ωB97M-V/TZV(d,p) level using different integration grids. Both the pruning and grid errors are observed to be very small for SG-2 and SG-3.

- Table S4: Comparison of geometrical parameters optimized at the ωB97M-V/aug-cc-pVTZ level using various integration grids. Both the pruning and the grid errors for bond lengths and bond angles are quite small, for both SG-2 and SG-3.

- Table S5: Harmonic vibrational frequencies computed at the ωB97M-V/aug-cc-pVTZ level using SG-2 and SG-3 grids. Both pruning and grid errors are quite small.

- Table S6: Harmonic vibrational frequencies at the ωB97X-D/aug-cc-pVTZ level using SG-2 and SG-3. In this case, analytic Hessians are available in Q-Chem so we compare these analytic results to frequencies computed via finite difference of analytic gradients. Results show that there is very little difference between the two approaches, which validates other finite-difference frequencies reported in this work. Errors in ωB97X-D frequencies are comparable to those observed using M11, both of which exhibit larger errors as compared to ωB97X-V or ωB97M-V.

- Tables S8, S7 and S9: Interaction energies for the S66 data set of non-covalent dimers (using benchmark S66 geometries), computed at the ωB97X-V/, M06-2X/, and ωB97M-V/aug-cc-pVTZ levels of theory, respectively. Both pruning errors and grid errors are quite small, for all three methods and for both SG-2 and SG-3.

- Table S10: Tests of rotational invariance. Isomerization energies are computed for three different reactions upon various rigid rotations of the product and reactant species. Rotational invariance is preserved to better than 0.01 kcal/mol in each case.

- Figure S1: Potential energy curves for the "sandwich" isomer of $(C_6H_6)_2$ along the face-to-face distance coordinate, computed at the M06-2X/6-311++G(3df,3pd) level using the low-quality SG-0 and SG-1 integration grids. Very large, spurious oscillations in the potential energy curves are obtained.

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TABLE S1: Atomization energies[a] (in kcal/mol) at the M06-2X/aug-cc-pVTZ level of theory.

Molecule	Energy		Error		Energy		Error	
	SG-2	(75,302)	pruning[b]	grid[c]	SG-3	(99,590)	pruning[b]	grid[c]
BeH	678.62	678.62	0.00	−0.01	678.61	678.61	0.01	0.00
CH_2CH_2	561.22	561.05	−0.17	0.01	561.12	561.06	−0.06	0.00
CH_2O	372.04	371.98	−0.06	0.00	372.00	371.98	−0.03	0.00
CH_2singlet	179.13	179.09	−0.04	0.01	179.11	179.10	−0.01	0.00
CH_2triplet	192.48	192.35	−0.13	0.01	192.44	192.36	−0.08	0.00
CH_3CH_3	709.84	709.78	−0.06	0.03	709.82	709.81	−0.01	0.00
CH_3Cl	394.31	394.20	−0.11	0.00	394.22	394.20	−0.02	0.00
CH_3OH	512.02	511.99	−0.03	0.00	512.02	511.99	−0.02	0.00
CH_3	306.26	306.14	−0.12	0.01	306.20	306.15	−0.05	0.00
CH_3SH	472.40	472.23	−0.17	0.06	472.33	472.28	−0.05	0.00
CH_4	417.83	417.95	0.12	0.00	417.84	417.95	0.11	0.00
CH	83.19	83.19	0.00	0.01	83.20	83.20	0.00	0.00
Cl_2	58.64	58.45	−0.19	0.01	58.43	58.46	0.03	0.00
ClF	60.83	60.74	−0.09	−0.02	60.89	60.72	−0.17	0.00
ClO	62.35	62.34	−0.01	0.00	62.35	62.34	−0.01	0.00
CN	175.70	175.63	−0.07	0.03	175.66	175.66	0.00	0.00
CO_2	387.31	387.33	0.02	−0.01	387.32	387.32	0.01	0.00
CO	257.02	257.02	0.00	0.00	257.02	257.02	0.00	0.00
CS	167.28	167.24	−0.04	0.03	167.29	167.27	−0.02	0.00
F_2	32.32	32.38	0.06	−0.01	32.28	32.37	0.10	0.00
H_2O	230.62	230.65	0.03	0.00	230.65	230.66	0.01	0.00
HCCH	403.04	402.98	−0.06	0.02	403.00	402.99	−0.01	0.00
HCl	105.56	105.51	−0.05	−0.04	105.52	105.48	−0.04	0.00
HCN	309.34	309.27	−0.07	0.03	309.30	309.30	0.00	0.00
HCO	277.03	277.03	0.00	0.00	277.02	277.03	0.01	0.00
HF	139.51	139.48	−0.03	0.00	139.50	139.48	−0.02	0.00
HOCl	164.23	164.14	−0.09	0.00	164.18	164.14	−0.03	0.00
HOOH	265.96	265.99	0.03	0.01	265.97	266.00	0.03	0.00
Li_2	24.39	24.25	−0.14	0.08	24.32	24.33	0.00	0.00
LiF	137.34	137.29	−0.05	0.03	137.29	137.32	0.02	0.00
LiH	57.02	56.96	−0.06	0.03	56.99	56.99	0.00	0.00
N_2	222.65	222.53	−0.12	0.03	222.56	222.56	0.00	0.00
Na_2	19.90	19.88	−0.02	0.01	19.89	19.90	0.00	0.00
NaCl	98.30	98.26	−0.04	0.01	98.29	98.27	−0.01	0.00
NH_2NH_2	433.09	433.03	−0.06	0.04	433.04	433.07	0.03	0.00
NH_2	180.89	180.74	−0.15	0.02	180.78	180.76	−0.01	0.00
NH_3	295.48	295.44	−0.04	0.02	295.46	295.46	0.00	0.00
NH	83.18	83.06	−0.12	0.02	83.07	83.08	0.01	0.00
NO	150.50	150.53	0.03	0.02	150.55	150.55	0.00	0.00
O_2	118.15	118.17	0.02	−0.01	118.13	118.16	0.03	0.00
OH	106.45	106.44	−0.01	0.00	106.45	106.44	−0.01	0.00
P_2	117.10	117.01	−0.09	0.09	117.10	117.09	−0.01	0.00
PH_2	155.96	155.91	−0.05	0.04	155.95	155.95	0.00	0.00
PH_3	241.69	241.66	−0.03	0.04	241.68	241.70	0.02	0.00
S_2	102.59	102.35	−0.24	−0.02	102.46	102.34	−0.12	0.00
SH_2	181.23	181.14	−0.09	0.02	181.15	181.15	0.01	0.00
Si_2	74.31	74.09	−0.22	0.06	74.18	74.14	−0.03	0.00
SiH_2singlet	153.56	153.38	−0.18	0.01	153.39	153.38	−0.01	0.00
SiH_2triplet	134.21	134.04	−0.17	0.03	134.08	134.06	−0.03	0.00
SiH_3	227.24	227.02	−0.22	0.02	227.07	227.04	−0.02	0.00
SiH_3SiH_3	529.09	528.64	−0.45	0.03	528.69	528.68	−0.01	0.00
SiH_4	320.57	320.44	−0.13	0.02	320.42	320.47	0.05	0.00
SiO	188.07	187.85	−0.22	0.03	187.90	187.88	−0.02	0.00
SO_2	239.46	239.40	−0.06	−0.01	239.37	239.38	0.01	0.00
SO	121.43	121.50	0.07	−0.02	121.48	121.49	0.01	0.00
MUD[d]			0.09	0.03			0.03	0.00

[a]Using MP2/6-31G* geometries. [b]Difference between pruned and unpruned results.
[c]Difference with respect to a (250,974) grid. [d]Mean unsigned deviation.

TABLE S2: Atomization energies[a] (in kcal/mol) at the ωB97M-V/aug-cc-pVTZ level of theory.

Molecule	Energy		Error		Energy		Error	
	SG-2	(75,302)	pruning[b]	grid[c]	SG-3	(99,590)	pruning[b]	grid[c]
BeH	670.94	670.94	0.00	0.00	670.94	670.94	0.00	0.00
CH_2CH_2	562.69	562.58	−0.10	0.00	562.61	562.58	−0.03	0.00
CH_2O	373.34	373.28	−0.06	0.00	373.30	373.28	−0.03	0.00
CH_2singlet	181.19	181.15	−0.04	0.00	181.18	181.15	−0.03	0.00
CH_2triplet	190.09	190.07	−0.02	0.00	190.07	190.07	0.00	0.00
CH_3CH_3	712.00	711.92	−0.07	0.00	711.95	711.92	−0.03	0.00
CH_3Cl	395.41	395.34	−0.08	0.00	395.36	395.34	−0.02	0.00
CH_3OH	514.31	514.33	0.02	0.00	514.33	514.33	0.00	0.00
CH_3	307.89	307.88	−0.01	−0.03	307.90	307.88	−0.02	−0.03
CH_3SH	474.99	474.92	−0.07	0.00	474.94	474.92	−0.02	0.00
CH_4	419.55	419.47	−0.08	0.00	419.51	419.47	−0.04	0.00
CH	84.18	84.19	0.00	0.00	84.18	84.19	0.00	0.00
Cl_2	58.92	59.04	0.12	0.00	59.07	59.04	−0.02	0.00
ClF	62.16	62.17	0.01	0.00	62.14	62.17	0.03	0.00
ClO	64.53	64.50	−0.04	0.00	64.50	64.50	0.00	0.00
CN	174.31	174.28	−0.03	0.00	174.29	174.28	−0.01	0.00
CO_2	388.11	388.06	−0.05	0.00	388.08	388.06	−0.03	0.00
CO	258.70	258.65	−0.05	0.00	258.68	258.65	−0.02	0.00
CS	169.78	169.76	−0.02	0.00	169.79	169.76	−0.03	0.00
F_2	37.11	37.13	0.01	0.00	37.16	37.13	−0.03	0.00
H_2O	231.45	231.42	−0.03	0.00	231.44	231.42	−0.02	0.00
HCCH	402.77	402.76	−0.01	0.00	402.73	402.76	0.03	0.00
HCl	106.78	106.79	0.01	0.00	106.79	106.79	0.01	0.00
HCN	311.38	311.38	−0.01	0.00	311.36	311.38	0.01	0.00
HCO	278.82	278.77	−0.05	0.00	278.80	278.77	−0.03	0.00
HF	139.51	139.52	0.01	0.00	139.52	139.52	0.00	0.00
HOCl	165.22	165.24	0.02	0.00	165.24	165.24	0.00	0.00
HOOH	268.43	268.39	−0.05	0.00	268.42	268.39	−0.03	0.00
Li_2	23.82	23.81	0.00	0.00	23.82	23.81	−0.01	0.00
LiF	138.02	138.02	0.00	0.00	138.01	138.02	0.01	0.00
LiH	60.47	60.47	0.00	0.00	60.48	60.47	0.00	0.00
N_2	226.89	226.85	−0.04	0.00	226.85	226.85	0.00	0.00
Na_2	17.06	17.06	0.00	0.00	17.06	17.06	0.00	0.00
NaCl	97.08	97.09	0.01	0.00	97.08	97.09	0.00	0.00
NH_2NH_2	431.33	431.33	0.00	0.00	−431.33	−431.33	0.00	0.00
NH_2	181.51	181.52	0.01	0.00	−181.52	−181.52	0.00	0.00
NH_3	299.06	299.06	−0.01	0.00	299.06	299.06	0.00	0.00
NH	85.01	85.00	−0.01	0.00	84.98	85.00	0.02	0.00
NO	154.00	153.99	−0.01	0.00	154.00	153.99	0.00	0.00
O_2	120.56	120.53	−0.03	0.00	120.55	120.53	−0.02	0.00
OH	107.27	107.30	0.03	0.00	107.28	107.30	0.02	0.00
P_2	115.72	115.75	0.03	0.00	115.77	115.75	−0.02	0.00
PH_2	156.17	156.14	−0.03	0.00	156.15	156.14	−0.01	0.00
PH_3	243.57	243.55	−0.01	0.01	243.58	243.55	−0.03	0.01
S_2	102.41	102.39	−0.01	0.00	102.42	102.39	−0.03	0.00
SH_2	183.68	183.64	−0.04	0.00	183.65	183.64	−0.01	0.00
Si_2	68.08	68.08	0.00	0.00	68.09	68.08	−0.01	0.00
SiH_2singlet	154.34	154.20	−0.14	−0.01	154.21	154.20	−0.01	−0.01
SiH_2triplet	130.15	130.04	−0.10	0.00	130.06	130.04	−0.02	0.00
SiH_3	225.60	225.46	−0.14	−0.01	225.46	225.46	0.00	−0.01
SiH_3SiH_3	530.90	530.61	−0.29	−0.01	530.62	530.61	−0.01	−0.01
SiH_4	322.20	322.05	−0.15	0.00	322.07	322.05	−0.02	0.00
SiO	189.54	189.40	−0.14	0.00	189.42	189.40	−0.02	0.00
SO_2	245.05	245.02	−0.03	0.00	245.04	245.02	−0.02	0.00
SO	123.19	123.13	−0.06	0.00	123.15	123.13	−0.02	0.00
MUD[d]			0.04	0.00			0.01	0.00

[a]Using MP2/6-31G* geometries. [b]Difference between pruned and unpruned results.
[c]Difference with respect to a (250,974) grid. [d]Mean unsigned deviation.

TABLE S3: Isomerization energies (in kcal/mol) for organic reactions at the ωB97M-V/TZV(d,p) level.

Rxn.	Energy		Error		Energy		Error	
	SG-2	(75,302)	pruning[a]	grid[b]	SG-3	(99,590)	pruning[a]	grid[b]
1	−0.35	−0.34	0.01	0.02	−0.32	−0.32	0.00	0.00
2	21.61	21.60	−0.01	0.03	21.63	21.63	0.00	0.00
3	5.78	5.80	0.02	0.06	5.86	5.86	0.00	0.00
4	0.99	1.05	0.06	0.04	1.10	1.10	0.00	0.00
5	1.22	1.17	−0.05	−0.05	1.11	1.11	0.00	0.00
6	2.65	2.68	0.03	0.03	2.71	2.71	0.00	0.00
7	9.58	9.62	0.03	0.09	9.71	9.71	0.00	0.00
8	21.84	21.81	−0.03	−0.03	21.78	21.78	0.00	0.00
9	6.09	6.11	0.02	0.11	6.21	6.22	0.00	0.00
10	3.64	3.54	−0.10	−0.04	3.56	3.51	−0.05	0.00
11	0.96	1.05	0.08	0.14	1.18	1.19	0.01	0.00
13	37.87	37.73	−0.13	0.09	37.82	37.83	0.01	0.00
14	22.53	22.52	−0.02	0.01	22.52	22.52	0.00	0.00
15	7.98	7.98	0.01	−0.01	7.98	7.98	0.00	0.00
16	8.93	8.95	0.02	0.04	9.00	8.99	0.00	0.00
17	27.46	27.49	0.02	0.07	27.56	27.56	0.00	0.00
18	11.33	11.31	−0.02	−0.02	11.29	11.29	0.00	0.00
19	4.70	4.67	−0.03	0.05	4.71	4.72	0.01	0.00
20	18.56	18.58	0.02	−0.04	18.55	18.55	−0.01	0.00
21	1.18	1.16	−0.03	0.03	1.18	1.18	0.00	0.00
22	3.68	3.65	−0.03	−0.01	3.64	3.64	0.00	0.00
23	5.36	5.35	−0.01	−0.01	5.33	5.35	0.01	0.00
24	11.76	11.76	0.00	0.00	11.75	11.76	0.00	0.00
25	25.82	25.84	0.02	0.04	25.88	25.88	0.00	0.00
26	17.41	17.40	0.00	0.02	17.42	17.42	0.00	0.00
27	64.81	64.83	0.02	0.05	64.88	64.88	0.00	0.00
28	30.61	30.62	0.01	−0.01	30.61	30.61	0.00	0.00
29	13.11	13.13	0.02	0.03	13.15	13.16	0.01	0.00
30	10.32	10.31	−0.01	0.00	10.31	10.31	0.00	0.00
31	15.67	15.70	0.03	−0.03	15.67	15.67	0.00	0.00
32	6.92	6.96	0.04	0.06	7.02	7.02	0.00	0.00
33	8.78	8.79	0.00	0.04	8.82	8.83	0.01	0.00
34	7.33	7.30	−0.03	0.01	7.30	7.30	0.00	0.00
MUD[d]			0.03	0.04			0.01	0.00

[a]Difference between pruned and unpruned results. [b]Difference with respect to a (250,974) grid. [d]Mean unsigned deviation.

TABLE S4: Comparison of geometrical parameters[a] optimized at the ωB97M-V/aug-cc-pVTZ level.

Molecule	Parameter	Value		Error		Value		Error	
		SG-2	(75,302)	pruning[b]	grid[c]	SG-3	(99,590)	pruning[b]	grid[c]
H_2	r(HH)	0.74073	0.74029	−0.00044	0.00000	0.74058	0.74029	−0.00029	0.00000
Li_2	r(LiLi)	2.62504	2.62474	−0.00031	−0.00006	2.62465	2.62458	−0.00007	0.00009
N_2	r(NN)	1.08990	1.08994	0.00004	−0.00001	1.08993	1.08993	0.00000	0.00000
O_2	r(OO)	1.19868	1.19864	−0.00004	−0.00001	1.19862	1.19863	0.00000	0.00000
F_2	r(FF)	1.38170	1.38196	0.00026	0.00001	1.38190	1.38198	0.00008	−0.00001
Si_2	r(SiSi)	1.97313	1.97384	0.00071	−0.00001	1.97381	1.97381	0.00001	0.00002
P_2	r(PP)	1.88464	1.88563	−0.00001	−0.01618	1.86971	1.86958	−0.00013	−0.00013
S_2	r(SS)	1.88586	1.88563	−0.00023	0.00001	1.88586	1.88563	−0.00023	0.00001
Cl_2	r(ClCl)	1.99929	1.99982	0.00053	0.00006	1.99960	1.99987	0.00027	0.00001
SiH_2									
	r(SiH)	1.52015	1.52024	0.00009	−0.00006	1.52015	1.52015	0.00000	0.00003
	$\angle$(HSiH)	91.27604	91.27937	0.00333	−0.00383	91.27460	91.27417	−0.00043	0.00137
CH_3OH									
	$r(CH_a)$	1.08689	1.08680	−0.00009	0.00002	1.08686	1.08681	−0.00005	0.00001
	$r(CH_b)$	1.09245	1.09247	0.00002	0.00002	1.09246	1.09248	0.00002	0.00001
	r(OH)	0.95914	0.95913	−0.00001	−0.00001	0.95914	0.95912	−0.00002	0.00000
	$\angle(OCH_a)$	106.85461	106.83938	−0.01523	0.00152	106.84965	106.84074	−0.00891	0.00016
	$\angle$(COH)	108.41613	108.42132	0.00519	−0.00057	108.41589	108.42065	0.00476	0.00010
	$\angle(H_bCH_b)$	109.01194	109.04461	0.03267	−0.00073	109.02502	109.04367	0.01865	0.00021
	r(CO)	1.41980	1.41995	0.00015	0.00001	1.41987	1.41995	0.00008	0.00001
HCO									
	r(CO)	1.17061	1.17059	−0.00002	0.00001	1.17060	1.17059	−0.00001	0.00001
	r(OH)	1.12209	1.12223	0.00014	−0.00003	1.12211	1.12220	0.00009	0.00000
	$\angle$(OCH)	124.24198	124.24365	0.00167	0.00348	124.24808	124.24689	−0.00119	0.00024
NH_2NH_2									
	r(NN)	1.42977	1.43023	0.00046	−0.00001	1.42991	1.43022	0.00031	0.00000
	$r(NH_a)$	1.00962	1.00968	0.00006	−0.00001	1.00965	1.00967	0.00002	0.00000
	$r(NH_b)$	1.01260	1.01266	0.00006	−0.00002	1.01263	1.01264	0.00001	0.00000
	$\angle(NNH_b)$	112.10811	112.02791	−0.08020	−0.00118	112.07649	112.02601	−0.05048	0.00072
	$\angle(NNH_a)$	107.80480	107.74268	−0.06212	0.00225	107.78490	107.74458	−0.04032	0.00035

[a]Bond lengths in Ångstroms and bond angles in degrees. [b]Difference between pruned and unpruned results. [c]Difference with respect to a (250,974) grid.

TABLE S5: Harmonic vibrational frequencies (ν, in cm^{-1}), and differences ($\Delta\nu$) engendered by pruning and grid errors, computed at the ωB97M-V/aug-cc-pVTZ level.

Molecule	(75,302) Grid			(99,590) Grid		
	ν	Error, $\Delta\nu$		ν	Error, $\Delta\nu$	
		pruning[a]	grid[b]		pruning[a]	grid[b]
BH_3	1133.5	18.6	0.0	1151.5	0.6	0.0
	1202.5	−0.4	−0.4	1201.1	1.0	−0.4
	1203.0	−0.9	−0.4	1201.3	0.8	−0.4
	2564.9	18.0	2.2	2585.6	−2.8	2.3
	2697.6	10.4	2.3	2710.7	−2.8	2.3
	2697.8	10.2	2.3	2710.8	−2.9	2.3
Cl_2	578.3	1.2	0.8	582.3	−2.9	0.9
CO_2	679.5	−0.3	0.5	679.6	−0.4	0.4
	679.5	−0.3	0.5	679.6	−0.4	0.4
	1388.2	−0.6	0.3	1388.0	−0.4	0.4
	2411.5	−1.3	0.7	2411.0	−0.8	0.8
F_2	1107.9	−1.1	−0.5	1107.3	−0.7	−0.4
NH_2NH_2	435.0	−0.1	−2.3	433.3	1.5	−2.2
	824.1	1.8	−0.8	824.4	1.4	−0.7
	973.8	2.1	−0.7	974.4	1.4	−0.6
	1127.7	0.0	−0.1	1127.6	0.1	−0.2
	1301.1	−0.2	−0.3	1300.7	0.2	−0.2
	1328.5	0.1	0.0	1328.6	0.1	0.0
	1670.5	0.7	0.1	1670.8	0.4	0.1
	1684.4	0.3	−0.1	1684.4	0.3	−0.1
	3498.9	0.1	−1.1	3498.3	0.8	−1.2
	3507.0	0.3	−1.1	3506.5	1.0	−1.2
	3596.6	0.4	−1.5	3595.9	1.2	−1.6
	3601.0	0.4	−1.6	3600.3	1.3	−1.7
H_2O_2	392.8	−7.2	4.6	394.6	−9.1	4.7
	1011.3	−0.2	0.1	1011.4	−0.3	0.1
	1345.8	−1.1	0.2	1345.8	−1.1	0.2
	1451.2	0.4	0.2	1451.6	0.1	0.1
	3798.9	−3.0	1.7	3797.9	−2.1	1.7
	3800.0	−3.1	1.7	3799.0	−2.1	1.7
H_2	4451.2	1.5	0.0	4452.0	0.8	0.0
H_2S	1204.9	−2.0	1.5	1202.8	0.4	1.3
	2722.4	4.6	0.1	2726.9	0.2	0.0
	2734.4	5.1	−0.1	2739.1	−0.8	1.0
HCCH	691.4	0.8	0.6	690.5	1.7	0.6
	691.5	0.8	0.6	690.5	1.7	0.6
	770.5	1.0	0.6	769.5	2.1	0.6
	770.6	1.0	0.6	769.5	2.1	0.6
	2091.3	−0.3	0.3	2091.2	−0.2	0.2
	3419.3	1.5	−1.3	3418.7	2.1	−1.4
	3530.1	1.3	−1.2	3529.5	1.9	−1.3
N_2	2484.8	0.1	−0.4	2484.6	0.4	−0.5
O_2	1693.3	−0.5	0.6	1693.4	−0.5	0.5
PH_2	1129.4	−3.4	−2.0	1123.4	2.6	−2.0
	2414.4	−3.2	2.8	2414.6	−4.3	3.7
	2421.1	−2.9	2.9	2421.5	−4.1	3.7
S_2	759.2	0.9	−2.0	758.1	1.9	−1.9
SiH_2	1034.0	−4.1	−5.3	1026.3	3.6	−5.3
	2074.4	−9.6	5.2	2070.1	−5.0	4.9
	2075.2	−10.1	5.7	2070.9	−5.4	5.3
MUD[c]		2.8	1.3		1.6	1.3

[a] Difference between pruned and unpruned results.
[b] Difference with respect to a (250,974) grid.
[c] Mean unsigned deviation.

TABLE S6: Harmonic vibrational frequencies (ν, in cm^{-1}), and differences ($\Delta\nu$) engendered by pruning and grid errors, at the ωB97X-D/aug-cc-pVTZ level, comparing analytic and finite-difference results.

Molecule	Analytic Hessian						Finite Difference of Analytic Gradients					
	(75,302) Grid			(99,590) Grid			(75,302) Grid			(99,590) Grid		
	ν	Error, $\Delta\nu$		ν	Error, $\Delta\nu$		ν	Error, $\Delta\nu$		ν	Error, $\Delta\nu$	
		pruning[a]	grid[b]		pruning[a]	grid[b]		pruning[a]	grid[b]		pruning[a]	grid[b]
BH_3	1151.18	−1.96	−0.91	1149.89	−1.58	0.38	1147.69	0.06	2.60	1150.38	−0.13	−0.09
	1204.32	−0.83	−0.08	1203.82	−0.88	0.42	1204.40	−0.14	0.01	1204.70	0.28	−0.29
	1204.43	−2.15	−0.01	1204.43	−1.13	−0.01	1204.47	−0.20	-0.06	1204.79	0.26	−0.38
	2544.31	−17.08	15.49	2552.43	−11.39	7.37	2544.18	−17.77	15.64	2553.41	−9.72	6.41
	2676.60	−17.59	16.00	2684.63	−11.88	7.97	2676.57	−18.54	16.14	2686.04	−10.14	6.67
	2676.81	−18.11	15.97	2685.71	−11.45	7.07	2676.62	−18.57	16.10	2686.15	−10.09	6.57
Cl_2	586.22	3.27	0.16	587.82	−0.37	−1.44	586.22	3.27	0.16	587.82	−0.37	−1.44
CO_2	686.22	−0.08	0.19	686.26	−0.34	0.15	686.22	−0.08	0.18	686.26	0.66	0.14
	686.23	−0.08	0.19	686.27	0.66	0.15	686.22	−0.08	0.19	686.26	0.66	0.15
	1395.62	−2.49	0.45	1396.57	0.76	−0.50	1395.62	−2.49	0.45	1396.57	0.75	−0.50
	2441.00	−4.40	0.37	2442.22	1.30	−0.85	2441.01	−4.40	0.37	2442.22	1.29	−0.84
F_2	1112.02	17.52	−15.20	1091.40	−6.37	5.42	1112.01	17.51	-15.19	1091.40	−6.38	5.42
NH_2NH_2	443.95	1.06	2.63	446.31	1.92	0.27	443.93	1.06	2.62	446.30	1.92	0.25
	819.20	2.30	2.05	820.91	3.01	0.34	819.21	2.29	2.30	820.92	3.01	0.59
	969.78	1.33	2.31	971.17	1.90	0.92	969.78	1.33	2.32	971.16	1.89	0.94
	1141.33	−0.17	0.46	1142.00	0.34	−0.21	1141.33	−0.17	0.73	1142.00	0.34	0.06
	1305.85	−0.39	2.41	1307.03	0.47	1.23	1305.83	−0.40	1.11	1307.01	0.47	−0.07
	1337.09	−3.83	−0.52	1336.79	−2.73	−0.22	1337.07	−3.83	-0.16	1336.78	−2.72	0.13
	1680.82	−1.34	0.40	1681.37	−0.99	−0.15	1680.84	−1.34	0.32	1681.38	−0.99	−0.22
	1694.00	0.13	1.52	1695.21	0.74	0.31	1694.00	0.12	0.98	1695.21	0.73	−0.23
	3508.30	−2.99	0.09	3508.37	−2.06	0.02	3508.30	−3.00	1.09	3508.37	−2.07	1.02
	3516.69	−3.47	0.35	3516.93	−1.90	0.11	3516.69	−3.45	1.28	3516.92	−1.90	1.05
	3611.58	−5.75	−0.02	3611.75	−2.55	−0.19	3611.59	−5.75	1.26	3611.75	−2.55	1.10
	3616.24	−6.27	0.27	3616.44	−2.56	0.07	3616.27	−6.27	1.31	3616.47	−2.57	1.11
H_2O_2	397.28	1.11	1.47	401.15	−0.35	−2.40	397.22	1.11	1.67	401.09	−0.35	−2.20
	1025.57	7.22	−8.08	1016.35	−0.83	1.14	1025.56	7.21	-8.08	1016.35	−0.82	1.13
	1360.43	−0.27	0.65	1361.58	−0.74	−0.50	1360.36	−0.28	0.65	1361.51	−0.75	−0.50
	1468.17	0.94	0.74	1469.30	0.33	−0.39	1468.26	0.95	0.73	1469.39	0.34	−0.40
	3837.40	−3.14	2.53	3839.96	−0.29	−0.03	3837.42	−3.14	2.53	3839.98	−0.29	−0.03
	3838.80	−3.23	2.52	3841.35	−0.32	−0.03	3838.79	−3.23	2.52	3841.34	−0.32	−0.03
H_2	4438.49	−0.34	−0.01	4438.48	−0.51	0.00	4438.49	−0.35	0.00	4438.49	−0.50	0.00
H_2S	1219.51	4.26	−5.34	1211.79	2.29	2.38	1219.48	4.25	-5.33	1211.77	2.30	2.38
	2709.66	6.65	29.90	2748.10	16.01	−8.54	2709.62	6.59	29.94	2748.09	16.00	−8.53
	2721.14	5.33	31.53	2760.68	15.50	−8.01	2721.13	5.27	31.56	2760.70	15.49	−8.01
HCCH	690.45	4.36	3.06	693.77	6.25	−0.26	690.43	4.36	3.05	693.75	6.25	−0.27
	690.45	4.36	3.06	693.77	6.25	−0.26	690.46	4.37	3.06	693.79	6.27	−0.27
	777.15	4.97	2.86	780.14	6.51	−0.13	777.17	4.97	2.86	780.16	6.51	−0.13
	777.15	4.97	2.86	780.14	6.51	−0.13	777.18	4.97	2.87	780.17	6.51	−0.12
	2087.58	0.02	2.90	2089.14	−0.53	1.34	2087.59	0.02	2.89	2089.15	−0.53	1.33
	3418.57	−7.42	3.80	3421.24	−0.83	1.13	3418.59	−7.41	3.80	3421.27	−0.82	1.12
	3527.41	−6.77	3.78	3529.98	−0.88	1.21	3527.41	−6.76	3.78	3529.99	−0.87	1.20
N_2	2488.37	0.98	0.54	2489.63	1.53	−0.72	2488.37	0.97	0.55	2489.64	1.53	−0.72
O_2	1701.67	−1.71	2.06	1702.98	−0.26	0.75	1701.68	−1.71	2.05	1702.99	−0.25	0.74
PH_2	1136.66	−2.40	−4.94	1131.47	−0.41	0.25	1136.64	−2.40	-4.94	1131.46	−0.40	0.24
	2388.99	−22.50	18.21	2388.87	−31.04	18.33	2388.99	−22.48	18.20	2388.87	−31.02	18.32
	2398.12	−22.94	18.89	2399.05	−30.21	17.96	2398.18	−22.92	18.87	2399.11	−30.18	17.94
S_2	752.50	−3.50	−1.97	750.27	−2.09	0.26	752.50	−3.51	-1.96	750.27	−2.09	0.27
SiH_2	1033.32	−6.18	−2.97	1032.60	0.52	−2.25	1033.31	−6.18	-2.97	1032.59	0.52	−2.25
	2061.09	−37.16	15.16	2099.31	31.51	−23.06	2061.10	−37.15	15.16	2099.31	31.50	−23.05
	2063.95	−35.04	13.44	2099.84	30.57	−22.45	2063.96	−35.03	13.43	2099.84	30.56	−22.45
MUD[c]		6.25	5.22		5.25	2.99		6.19	5.32		5.10	2.99

[a]Difference between pruned and unpruned results. [b]Difference with respect to a (250,974) grid. [c]Mean unsigned deviation.

TABLE S7: Interaction energies (in kcal/mol) for the S66 data set computed at the M06-2X/aug-cc-pVTZ level.

Dimer	Energy		Error		Energy		Error	
	SG-2	(75,302)	pruning[a]	grid[b]	SG-3	(99,590)	pruning[a]	grid[b]
$AcNH_2$–$AcNH_2$	−16.31	−16.18	−0.13	−0.01	−16.20	−16.19	−0.01	0.00
$AcNH_2$–Uracil	−19.33	−19.07	−0.26	−0.03	−19.12	−19.10	−0.02	0.00
AcOH–AcOH	−19.98	−19.89	−0.09	0.01	−19.88	−19.88	0.00	0.00
AcOH–Uracil	−19.79	−19.72	−0.07	−0.01	−19.71	−19.73	0.02	0.00
Benzene–$AcNH_2$ (NH–π)	−4.33	−4.48	0.15	0.00	−4.33	−4.48	0.15	0.00
Benzene–AcOH (OH–π)	−5.28	−5.11	−0.17	−0.02	−5.10	−5.13	0.03	0.00
Benzene–AcOH	−4.09	−4.11	0.02	0.01	−3.95	−4.09	0.14	−0.01
Benzene–Benzene (π-stacked)	−2.65	−2.51	−0.14	−0.04	−2.48	−2.54	0.06	−0.01
Benzene–Benzene (T-shaped)	−2.75	−2.56	−0.19	−0.03	−2.59	−2.59	0.00	0.00
Benzene–Cyclopentane	−3.69	−3.52	−0.17	−0.03	−3.51	−3.55	0.04	0.00
Benzene–Ethene	−1.27	−1.44	0.17	0.00	−1.43	−1.45	0.02	0.01
Benzene–Ethyne (CH-π)	−3.07	−3.03	−0.04	0.01	−3.03	−3.02	−0.01	0.00
Benzene–$MeNH_2$ (NH-π)	−3.40	−3.46	0.06	0.02	−3.42	−3.43	0.01	−0.01
Benzene–MeOH (OH–π)	−4.77	−4.60	−0.17	0.00	−4.60	−4.61	0.01	0.01
Benzene–Neopentane	−2.73	−2.68	−0.05	−0.02	−2.68	−2.67	−0.01	−0.03
Benzene–Peptide (NH-π)	−5.55	−5.43	−0.12	0.00	−5.43	−5.45	0.02	0.02
Benzene–Pyridine (π-stacked)	−3.21	−3.15	−0.06	−0.09	−3.14	−3.21	0.07	−0.03
Benzene–Pyridine (T-shaped)	−3.08	−3.07	−0.01	−0.04	−3.04	−3.11	0.07	0.00
Benzene–Uracil (π-stacked)	−6.28	−5.97	−0.31	−0.02	−5.94	−5.98	0.04	−0.01
Cyclopentane–Cyclopentane	−2.43	−2.42	−0.01	0.01	−2.39	−2.42	0.03	0.01
Cyclopentane–Neopentane	−1.98	−2.03	0.05	0.02	−2.02	−2.00	−0.02	−0.01
Ethene–Pentane	−1.69	−1.95	0.26	−0.03	−1.86	−1.98	0.12	0.00
Ethyne–AcOH (OH-π)	−5.53	−5.45	−0.08	0.00	−5.48	−5.45	−0.03	0.00
Ethyne–H_2O (CH–O)	−2.94	−2.92	−0.02	0.02	−2.90	−2.90	0.00	0.00
Ethyne–Pentane	−1.75	−1.68	−0.07	−0.03	−1.71	−1.71	0.00	0.00
H_2O–H_2O	−5.19	−5.15	−0.04	0.02	−5.16	−5.13	−0.03	0.00
H_2O–$MeNH_2$	−7.11	−6.93	−0.18	−0.01	−7.05	−6.94	−0.11	0.00
H_2O–MeOH	−5.66	−5.73	0.07	0.00	−5.66	−5.73	0.07	0.00
H_2O–Peptide	−8.89	−8.63	−0.26	0.03	−8.71	−8.60	−0.11	0.00
H_2O–Pyridine	−6.83	−6.69	−0.14	0.00	−6.75	−6.69	−0.06	0.00
$MeNH_2$–H_2O	−7.50	−7.51	0.01	0.00	−7.51	−7.51	0.00	0.00
$MeNH_2$–$MeNH_2$	−4.11	−4.12	0.01	0.00	−4.18	−4.12	−0.06	0.00
$MeNH_2$–MeOH	−2.69	−2.79	0.10	0.00	−2.75	−2.79	0.04	0.00
$MeNH_2$–Peptide	−5.55	−5.57	0.02	0.00	−5.58	−5.57	−0.01	0.00
$MeNH_2$–Pyridine	−3.83	−3.88	0.05	−0.03	−3.87	−3.91	0.04	0.00
MeOH–H_2O	−5.11	−5.10	−0.01	0.00	−5.11	−5.10	−0.01	0.00
MeOH–$MeNH_2$	−7.45	−7.50	0.05	0.00	−7.49	−7.50	0.01	0.00
MeOH–MeOH	−5.62	−5.70	0.08	0.00	−5.63	−5.70	0.07	0.00
MeOH–Peptide	−8.51	−8.45	−0.06	−0.01	−8.47	−8.46	−0.01	0.00
MeOH–Pyridine	−7.21	−7.02	−0.19	−0.03	−7.06	−7.05	−0.01	0.00
Neopentane–Neopentane	−1.26	−1.26	0.00	0.03	−1.23	−1.23	0.00	0.00
Neopentane–Pentane	−2.06	−2.12	0.06	−0.09	−2.23	−2.21	−0.02	0.00
Pentane–$AcNH_2$	−3.53	−3.52	−0.01	−0.06	−3.56	−3.58	0.02	0.00
Pentane–AcOH	−2.27	−2.86	0.59	−0.03	−2.38	−2.89	0.51	0.00
Pentane–Pentane	−3.55	−3.56	0.01	−0.07	−3.63	−3.63	0.00	0.00
Peptide–Ethene	−2.86	−3.00	0.14	−0.03	−3.02	−3.03	0.01	0.00
Peptide–H_2O	−5.04	−5.08	0.04	−0.01	−5.10	−5.09	−0.01	0.00
Peptide–$MeNH_2$	−7.25	−7.23	−0.02	0.00	−7.25	−7.23	−0.02	0.00
Peptide–MeOH	−6.08	−6.11	0.03	−0.01	−6.08	−6.12	0.04	0.00
Peptide–Pentane	−4.05	−4.44	0.39	−0.04	−4.18	−4.48	0.30	0.00
Peptide–Peptide	−8.49	−8.55	0.06	0.01	−8.45	−8.53	0.08	−0.01
Pyridine–Ethene	−1.92	−1.85	−0.07	−0.06	−1.91	−1.91	0.00	0.00
Pyridine–Ethyne	−3.83	−3.74	−0.09	0.00	−3.76	−3.75	−0.01	0.01
Pyridine–Pyridine (CH–N)	−3.30	−3.60	0.30	0.03	−3.50	−3.57	0.07	0.00
Pyridine–Pyridine (π-stacked)	−3.47	−3.64	0.17	−0.01	−3.52	−3.66	0.14	0.01
Pyridine–Pyridine (T-shaped)	−3.38	−3.24	−0.14	0.00	−3.16	−3.24	0.08	0.00
Pyridine–Uracil (π-stacked)	−7.41	−7.02	−0.39	0.01	−6.89	−7.01	0.12	0.00
Uracil–Cyclopentane	−4.38	−3.96	−0.42	−0.01	−3.94	−3.96	0.02	−0.01
Uracil–Ethene	−3.87	−3.61	−0.26	−0.03	−3.53	−3.64	0.11	0.00
Uracil–Ethyne	−4.08	−4.05	−0.03	−0.01	−3.99	−4.07	0.08	0.01
Uracil–Uracil (Watson-Crick)	−4.47	−3.60	−0.87	0.02	−3.87	−3.58	−0.29	0.00
Uracil–Pentane	−4.95	−4.91	−0.04	−0.08	−4.89	−5.00	0.11	0.01
Uracil–Uracil (Watson-Crick)	−17.03	−16.85	−0.18	−0.01	−16.86	−16.86	0.00	0.00
Uracil–Uracil (π-stacked)	−10.98	−10.34	−0.64	−0.02	−10.32	−10.36	0.04	0.00
MUD[c]			0.11	0.02			0.03	0.00

[a]Difference between pruned and unpruned results. [b]Difference with respect to a (250,974) grid. [c]Mean unsigned deviation.

TABLE S8: Interaction energies (in kcal/mol) for the S66 data set computed at the ωB97X-V/aug-cc-pVTZ level.

Dimer	Energy		Error		Energy		Error	
	SG-2	(75,302)	pruning[a]	grid[b]	SG-3	(99,590)	pruning[a]	grid[b]
$AcNH_2$–$AcNH_2$	−16.31	−16.33	0.02	0.00	−16.33	−16.33	0.00	0.00
$AcNH_2$–Uracil	−19.28	−19.34	0.06	−0.01	−19.35	−19.34	−0.01	0.01
AcOH–AcOH	−20.10	−20.03	−0.07	0.01	−20.02	−20.03	0.01	−0.01
AcOH–Uracil	−19.89	−19.98	0.09	0.00	−19.98	−19.98	0.00	0.00
Benzene–$AcNH_2$ (NH–π)	−4.45	−4.43	−0.02	0.00	−4.43	−4.40	−0.03	0.03
Benzene–AcOH (OH–π)	−4.98	−4.97	−0.01	0.00	−4.97	−4.95	−0.02	0.02
Benzene–AcOH	−4.06	−4.01	−0.05	0.00	−4.01	−3.98	−0.03	0.03
Benzene–Benzene (π-stacked)	−2.97	−2.92	−0.05	−0.01	−2.93	−2.90	−0.03	0.03
Benzene–Benzene (T-shaped)	−2.96	−2.89	−0.07	0.00	−2.89	−2.89	0.00	0.00
Benzene–Cyclopentane	−3.74	−3.74	0.00	−0.01	−3.75	−3.74	−0.01	0.01
Benzene–Ethene	−1.41	−1.44	0.03	0.00	−1.44	−1.44	0.00	0.00
Benzene–Ethyne (CH-π)	−3.04	−3.02	−0.02	0.00	−3.02	−3.02	0.00	0.00
Benzene–$MeNH_2$ (NH-π)	−3.30	−3.30	0.00	0.00	−3.30	−3.29	−0.01	0.01
Benzene–MeOH (OH–π)	−4.35	−4.31	−0.04	−0.01	−4.32	−4.32	0.00	0.00
Benzene–Neopentane	−3.16	−3.15	−0.01	0.01	−3.14	−3.13	−0.01	0.01
Benzene–Peptide (NH-π)	−5.48	−5.45	−0.03	−0.01	−5.46	−5.45	−0.01	0.01
Benzene–Pyridine (π-stacked)	−3.51	−3.49	−0.02	−0.01	−3.50	−3.48	−0.02	0.02
Benzene–Pyridine (T-shaped)	−3.41	−3.37	−0.04	0.00	−3.37	−3.37	0.00	0.00
Benzene–Uracil (π-stacked)	−5.76	−5.83	0.07	0.00	−5.82	−5.83	0.01	−0.01
Cyclopentane–Cyclopentane	−3.08	−3.11	0.03	−0.01	−3.12	−3.09	−0.03	0.03
Cyclopentane–Neopentane	−2.62	−2.62	0.00	0.01	−2.61	−2.62	0.01	−0.01
Ethene–Pentane	−2.03	−2.03	0.00	0.00	−2.03	−2.03	0.00	0.00
Ethyne–AcOH (OH-π)	−5.20	−5.20	0.00	0.01	−5.19	−5.19	0.00	0.00
Ethyne–H_2O (CH–O)	−2.98	−2.99	0.01	0.01	−2.98	−2.98	0.00	0.00
Ethyne–Pentane	−1.85	−1.84	−0.01	0.00	−1.84	−1.84	0.00	0.00
H_2O–H_2O	−5.01	−5.00	−0.01	0.01	−4.99	−5.00	0.01	−0.01
H_2O–$MeNH_2$	−7.10	−7.08	−0.02	−0.01	−7.09	−7.10	0.01	−0.01
H_2O–MeOH	−5.60	−5.61	0.01	0.00	−5.61	−5.60	−0.01	0.01
H_2O–Peptide	−8.29	−8.29	0.00	0.01	−8.28	−8.28	0.00	0.00
H_2O–Pyridine	−7.04	−7.01	−0.03	0.00	−7.01	−7.02	0.01	−0.01
$MeNH_2$–H_2O	−7.38	−7.39	0.01	0.00	−7.39	−7.39	0.00	0.00
$MeNH_2$–$MeNH_2$	−4.01	−4.07	0.06	0.00	−4.07	−4.06	−0.01	0.01
$MeNH_2$–MeOH	−3.03	−3.04	0.01	0.00	−3.04	−3.04	0.00	0.00
$MeNH_2$–Peptide	−5.34	−5.41	0.07	0.00	−5.41	−5.39	−0.02	0.02
$MeNH_2$–Pyridine	−3.83	−3.84	0.01	−0.01	−3.85	−3.83	−0.02	0.02
MeOH–H_2O	−5.06	−5.06	0.00	0.00	−5.06	−5.06	0.00	0.00
MeOH–$MeNH_2$	−7.69	−7.67	−0.02	0.00	−7.67	−7.68	0.01	−0.01
MeOH–MeOH	−5.73	−5.75	0.02	0.00	−5.75	−5.73	−0.02	0.02
MeOH–Peptide	−8.37	−8.38	0.01	0.00	−8.38	−8.37	−0.01	0.01
MeOH–Pyridine	−7.55	−7.50	−0.05	0.00	−7.50	−7.51	0.01	−0.01
Neopentane–Neopentane	−2.00	−2.01	0.01	0.01	−2.00	−2.00	0.00	0.00
Neopentane–Pentane	−2.82	−2.82	0.00	−0.01	−2.83	−2.85	0.02	−0.02
Pentane–$AcNH_2$	−3.68	−3.69	0.01	−0.01	−3.70	−3.70	0.00	0.00
Pentane–AcOH	−3.10	−3.15	0.05	0.01	−3.14	−3.09	−0.05	0.05
Pentane–Pentane	−4.01	−4.01	0.00	−0.01	−4.02	−4.03	0.01	−0.01
Peptide–Ethene	−3.01	−3.03	0.02	0.00	−3.03	−3.03	0.00	0.00
Peptide–H_2O	−5.13	−5.14	0.01	0.01	−5.13	−5.14	0.01	−0.01
Peptide–$MeNH_2$	−7.43	−7.45	0.02	0.00	−7.44	−7.45	0.01	−0.01
Peptide–MeOH	−6.12	−6.16	0.04	0.01	−6.15	−6.14	−0.01	0.01
Peptide–Pentane	−4.43	−4.46	0.03	−0.01	−4.47	−4.44	−0.03	0.03
Peptide–Peptide	−8.64	−8.72	0.08	0.01	−8.71	−8.67	−0.04	0.04
Pyridine–Ethene	−1.85	−1.83	−0.02	−0.01	−1.84	−1.84	0.00	0.00
Pyridine–Ethyne	−4.19	−4.17	−0.02	0.00	−4.17	−4.17	0.00	0.00
Pyridine–Pyridine (CH–N)	−3.91	−3.97	0.06	0.01	−3.96	−3.96	0.00	0.00
Pyridine–Pyridine (π-stacked)	−3.93	−3.92	−0.01	0.00	−3.92	−3.91	−0.01	0.01
Pyridine–Pyridine (T-shaped)	−3.49	−3.47	−0.02	0.01	−3.46	−3.45	−0.01	0.01
Pyridine–Uracil (π-stacked)	−6.93	−6.94	0.01	0.00	−6.94	−6.91	−0.03	0.03
Uracil–Cyclopentane	−4.32	−4.33	0.01	0.00	−4.32	−4.33	0.01	−0.01
Uracil–Ethene	−3.46	−3.45	−0.01	0.00	−3.46	−3.44	−0.02	0.02
Uracil–Ethyne	−3.83	−3.86	0.03	0.00	−3.86	−3.84	−0.02	0.02
Uracil–Uracil (Watson-Crick)	−17.30	−17.36	0.06	0.00	−17.36	−17.35	−0.01	0.01
MUD			0.03	0.01			0.01	0.01

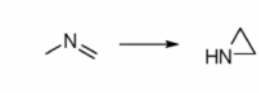
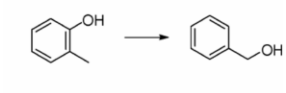
[a]Difference between pruned and unpruned results. [b]Difference with respect to a (250,974) grid. [c]Mean unsigned deviation.

TABLE S9: Interaction energies (in kcal/mol) for the S66 data set computed at the ωB97M-V/aug-cc-pVTZ level.

Dimer	Energy		Error		Energy		Error	
	SG-2	(75,302)	pruning[a]	grid[b]	SG-3	(99,590)	pruning[a]	grid[b]
$AcNH_2$–$AcNH_2$	−16.48	−16.42	0.06	0.00	−16.46	−16.42	0.04	0.00
$AcNH_2$–Uracil	−19.61	−19.44	0.17	−0.01	−19.51	−19.45	0.06	0.00
AcOH–AcOH	−19.99	−19.95	0.03	0.01	−19.93	−19.95	−0.01	0.00
AcOH–Uracil	−20.11	−20.03	0.07	0.00	−20.03	−20.03	0.00	0.00
Benzene–$AcNH_2$ (NH–π)	−4.45	−4.50	−0.05	0.00	−4.53	−4.51	0.02	0.00
Benzene–AcOH (OH–π)	−5.08	−5.09	0.00	0.00	−5.13	−5.09	0.05	0.00
Benzene–AcOH	−4.15	−4.17	−0.02	0.00	−4.19	−4.17	0.02	0.00
Benzene–Benzene (π-stacked)	−3.09	−3.16	−0.07	0.00	−3.24	−3.16	0.08	0.00
Benzene–Benzene (T-shaped)	−3.01	−3.00	0.01	0.00	−3.03	−3.01	0.02	0.00
Benzene–Cyclopentane	−3.90	−3.91	−0.01	−0.02	−3.94	−3.93	0.02	0.00
Benzene–Ethene	−1.47	−1.59	−0.12	−0.01	−1.63	−1.59	0.04	0.00
Benzene–Ethyne (CH-π)	−3.06	−3.09	−0.03	0.01	−3.09	−3.08	0.01	0.00
Benzene–$MeNH_2$ (NH-π)	−3.27	−3.43	−0.16	0.01	−3.40	−3.42	−0.03	0.00
Benzene–MeOH (OH–π)	−4.37	−4.44	−0.07	−0.01	−4.44	−4.45	−0.01	0.00
Benzene–Neopentane	−3.18	−3.24	−0.06	0.00	−3.26	−3.24	0.02	0.00
Benzene–Peptide (NH-π)	−5.65	−5.63	0.03	0.00	−5.65	−5.63	0.02	0.00
Benzene–Pyridine (π-stacked)	−3.72	−3.71	0.01	−0.03	−3.82	−3.74	0.08	0.00
Benzene–Pyridine (T-shaped)	−3.50	−3.47	0.03	−0.01	−3.47	−3.48	−0.01	0.00
Benzene–Uracil (π-stacked)	−6.22	−6.22	0.01	0.00	−6.21	−6.21	0.00	0.00
Cyclopentane–Cyclopentane	−3.20	−3.12	0.08	−0.02	−3.16	−3.14	0.02	0.00
Cyclopentane–Neopentane	−2.57	−2.61	−0.04	0.01	−2.61	−2.60	0.01	0.00
Ethene–Pentane	−1.99	−2.01	−0.02	0.00	−2.03	−2.01	0.02	−0.01
Ethyne–AcOH (OH-π)	−5.31	−5.26	0.05	0.00	−5.32	−5.26	0.06	0.00
Ethyne–H_2O (CH–O)	−2.98	−2.97	0.01	0.00	−2.97	−2.97	0.00	0.00
Ethyne–Pentane	−1.83	−1.83	0.00	0.00	−1.83	−1.83	0.00	0.00
H_2O–H_2O	−4.94	−4.99	−0.05	0.00	−4.96	−4.99	−0.04	0.00
H_2O–$MeNH_2$	−6.91	−6.99	−0.08	0.00	−6.94	−7.00	−0.06	0.00
H_2O–MeOH	−5.60	−5.60	0.00	0.00	−5.60	−5.60	0.00	0.00
H_2O–Peptide	−8.34	−8.27	0.07	0.00	−8.29	−8.27	0.02	0.00
H_2O–Pyridine	−6.88	−6.91	−0.03	0.00	−6.88	−6.91	−0.04	0.00
$MeNH_2$–H_2O	−7.30	−7.31	−0.02	0.00	−7.30	−7.31	−0.01	0.00
$MeNH_2$–$MeNH_2$	−4.05	−4.11	−0.05	0.00	−4.09	−4.10	−0.02	0.00
$MeNH_2$–MeOH	−2.97	−3.01	−0.04	0.00	−2.99	−3.01	−0.03	0.00
$MeNH_2$–Peptide	−5.54	−5.53	0.01	0.00	−5.54	−5.53	0.01	0.00
$MeNH_2$–Pyridine	−3.94	−3.96	−0.01	−0.01	−3.97	−3.97	0.00	0.01
MeOH–H_2O	−5.05	−5.08	−0.03	0.00	−5.06	−5.08	−0.02	0.00
MeOH–$MeNH_2$	−7.52	−7.58	−0.07	0.00	−7.54	−7.58	−0.04	0.00
MeOH–MeOH	−5.77	−5.77	0.00	0.00	−5.76	−5.77	0.00	0.00
MeOH–Peptide	−8.47	−8.43	0.04	0.00	−8.44	−8.44	0.00	0.00
MeOH–Pyridine	−7.46	−7.43	0.02	−0.01	−7.43	−7.44	−0.01	0.00
Neopentane–Neopentane	−1.93	−1.93	0.00	0.01	−5.38	−1.92	0.00	0.00
Neopentane–Pentane	−2.74	−2.79	−0.06	−0.02	−2.81	−2.81	0.00	0.00
Pentane–$AcNH_2$	−3.72	−3.72	0.00	0.00	−3.71	−3.72	−0.01	0.00
Pentane–AcOH	−3.22	−3.11	0.12	0.00	−3.12	−3.11	0.01	0.00
Pentane–Pentane	−3.99	−4.03	−0.03	0.01	−4.01	−4.02	−0.01	0.00
Peptide–Ethene	−2.98	−3.06	−0.08	0.00	−3.04	−3.06	−0.02	0.00
Peptide–H_2O	−5.20	−5.15	0.05	0.00	−5.15	−5.15	0.01	0.00
Peptide–$MeNH_2$	−7.45	−7.46	−0.01	0.00	−7.46	−7.46	0.00	0.00
Peptide–MeOH	−6.24	−6.21	0.03	0.00	−6.22	−6.20	0.02	0.00
Peptide–Pentane	−4.52	−4.50	0.02	−0.01	−4.50	−4.52	−0.02	0.00
Peptide–Peptide	−8.96	−8.78	0.18	0.01	−8.86	−8.78	0.08	0.00
Pyridine–Ethene	−1.95	−1.98	−0.04	−0.01	−2.00	−1.99	0.01	0.00
Pyridine–Ethyne	−4.20	−4.17	0.03	0.00	−4.18	−4.17	0.01	0.00
Pyridine–Pyridine (CH–N)	−3.90	−3.95	−0.04	0.01	−3.87	−3.93	−0.06	0.00
Pyridine–Pyridine (π-stacked)	−4.14	−4.15	−0.01	0.00	−4.17	−4.15	0.02	0.00
Pyridine–Pyridine (T-shaped)	−3.60	−3.57	0.03	0.01	−3.56	−3.55	0.00	0.00
Pyridine–Uracil (π-stacked)	−7.35	−7.28	0.07	0.00	−7.30	−7.28	0.02	0.00
Uracil–Cyclopentane	−4.56	−4.45	0.11	−0.01	−4.52	−4.46	0.06	0.00
Uracil–Ethene	−3.71	−3.61	0.10	−0.01	−3.73	−3.62	0.01	0.00
Uracil–Ethyne	−4.10	−4.03	0.07	0.00	−4.01	−4.03	−0.02	0.00
Uracil–Uracil (Watson-Crick)	−4.09	−4.07	0.02	0.00	−4.73	−4.07	0.01	0.00
Uracil–Pentane	−5.22	−5.21	0.01	−0.04	−5.63	−5.25	−0.02	0.00
Uracil–Uracil (Watson-Crick)	−17.58	−17.50	0.08	−0.02	−17.52	−17.51	0.01	0.00
Uracil–Uracil (π-stacked)	−10.85	−10.62	0.23	−0.03	−10.69	−10.65	0.04	0.00
MUD			0.05	0.01			0.02	0.00

[a]Difference between pruned and unpruned results. [b]Difference with respect to a (250,974) grid. [c]Mean unsigned deviation.

TABLE S10: Test of rotational invariance for organic isomerization reactions at the ωB97X-V/aug-cc-pVTZ level. Isomerization energies are reported for four different rotation angles θ about each of three different axes.

Reaction	Rotation Axis	Grid	ΔE / kcal mol^{-1}			
			$\theta = 0^\circ$	$\theta = 30^\circ$	$\theta = 45^\circ$	$\theta = 60^\circ$
	x	SG-2	19.87	19.87	19.87	19.87
		(75,302)	19.88	19.88	19.88	19.88
		SG-3	19.88	19.88	19.88	19.88
		(99,590)	19.88	19.88	19.88	19.88
	y	SG-2	19.87	19.87	19.87	19.87
		(75,302)	19.88	19.88	19.88	19.88
		SG-3	19.88	19.88	19.88	19.88
		(99,590)	19.88	19.88	19.88	19.88
	z	SG-2	19.87	19.87	19.87	19.87
		(75,302)	19.88	19.88	19.88	19.88
		SG-3	19.88	19.88	19.88	19.88
		(99,590)	19.88	19.88	19.88	19.88
	x	SG-2	7.68	7.69	7.69	7.69
		(75,302)	7.68	7.69	7.69	7.69
		SG-3	7.68	7.69	7.69	7.69
		(99,590)	7.68	7.68	7.68	7.68
	y	SG-2	7.68	7.69	7.69	7.69
		(75,302)	7.68	7.69	7.69	7.69
		SG-3	7.68	7.69	7.69	7.69
		(99,590)	7.68	7.68	7.68	7.68
	z	SG-2	7.68	7.69	7.69	7.69
		(75,302)	7.68	7.69	7.69	7.69
		SG-3	7.68	7.69	7.69	7.69
		(99,590)	7.68	7.68	7.68	7.68
	x	SG-2	7.22	7.22	7.22	7.22
		(75,302)	7.21	7.21	7.21	7.21
		SG-3	7.22	7.22	7.22	7.22
		(99,590)	7.21	7.21	7.21	7.21
	y	SG-2	7.22	7.22	7.22	7.22
		(75,302)	7.21	7.21	7.21	7.21
		SG-3	7.22	7.22	7.22	7.22
		(99,590)	7.21	7.21	7.21	7.21
	z	SG-2	7.22	7.22	7.22	7.22
		(75,302)	7.21	7.21	7.21	7.21
		SG-3	7.22	7.22	7.22	7.22
		(99,590)	7.21	7.21	7.21	7.21

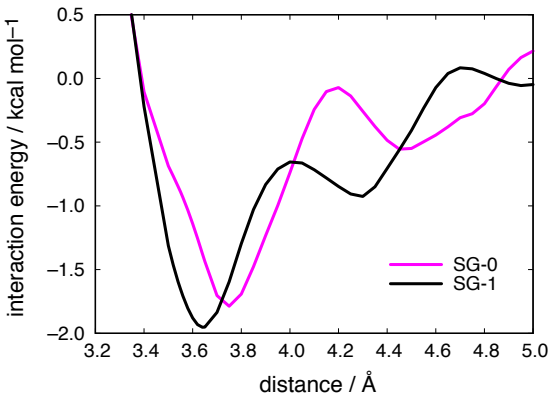


FIG. S1: Potential energy curves for the "sandwich" isomer of $(C_6H_6)_2$ along the face-to-face distance coordinate, computed at the M06-2X/6-311++G(3df,3pd) level with low-quality integration grids.