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

Electronic Supporting Information: An isomeric reaction benchmark set to test if the performance of state of the art density functionals can be regarded as independent of the external potential

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Table 1: Reference isomerization energies (ref) based on RI-SCS-MP2(pFC)/cc-p(wC)V5Z computations with CCSD(T)(pFC)/cc-p(wC)TZ corrrections for higher correlation contributions in comarison to energies including relativistic corrections (RC) based on ZORA-PW6B95/def2-QZVPP results. Relativistic corrections only are also given. All values in kcal mol^{-1}.

rct	ref	ref + RC	RC
C.01	5.90	5.97	0.07
C.04	17.69	17.69	−0.01
C.05	3.76	3.77	0.01
C.06	18.89	18.83	−0.06
C.07	45.14	45.19	0.05
C.08	1.34	1.34	0.00
C.10	−9.09	−9.18	−0.09
N.01	16.64	16.64	0.00
N.02	17.88	17.96	0.08
N.03	−20.93	−20.80	0.13
N.04	12.30	12.29	−0.01
N.05	−12.00	−12.02	−0.02
N.06	32.03	31.96	−0.07
N.07	57.14	57.15	0.01
N.08	−14.16	−14.24	−0.08
N.09	−31.78	−31.93	−0.15
O.01	15.75	15.75	0.00
O.02	25.21	25.27	0.06
O.03	−63.68	−63.58	0.10
O.04	9.89	9.88	−0.01
O.05	−12.35	−12.37	−0.02
O.06	27.40	27.34	−0.06
O.07	58.80	58.84	0.04
O.08	19.64	19.77	0.13
O.09	−11.53	−11.59	−0.06
F.01	26.93	26.99	0.06
F.02	0.96	0.97	0.01
F.03	−2.68	−2.68	0.00
Si.01	6.44	6.52	0.08
Si.02	−10.06	−9.94	0.12
Si.03	−3.88	−3.77	0.11

Si.04	28.21	28.21	0.00
Si.05	33.42	33.41	−0.01
Si.06	21.48	21.43	−0.05
Si.07	28.87	28.84	−0.03
Si.08	21.99	21.99	0.00
Si.09	−4.50	−4.46	0.04
Si.10	153.72	153.39	−0.33
P.01	−4.94	−4.97	−0.03
P.02	−1.74	−1.67	0.07
P.03	22.95	23.22	0.27
P.04	26.14	26.13	−0.01
P.05	10.77	10.72	−0.05
P.06	6.61	6.23	−0.38
P.07	35.33	35.29	−0.04
P.08	−3.87	−3.97	−0.10
P.09	17.87	17.60	−0.27
P.10	33.15	32.80	−0.35
S.01	−2.59	−2.64	−0.05
S.02	−0.92	−0.88	0.04
S.03	6.57	6.66	0.09
S.04	19.77	19.77	0.00
S.05	−1.16	−1.19	−0.03
S.06	35.45	35.38	−0.07
S.07	47.08	47.06	−0.02
S.08	11.87	12.02	0.15
S.09	−3.02	−3.09	−0.07
S.10	−15.19	−16.26	−1.07
Cl.01	−3.29	−3.11	0.18
Cl.02	0.56	0.56	0.00
Cl.03	−1.64	−1.63	0.01
Ge.01	8.02	8.22	0.20
Ge.02	−7.38	−6.48	0.90
Ge.03	14.23	15.47	1.24
Ge.04	26.73	26.58	−0.15
Ge.05	24.62	23.93	−0.69
Ge.06	19.65	19.62	−0.03
Ge.07	30.69	30.37	−0.32
Ge.08	19.07	18.59	−0.48

Ge.09	−2.32	−2.23	0.09
Ge.10	93.48	88.99	−4.49
As.01	−7.86	−8.23	−0.37
As.02	−5.71	−5.54	0.17
As.03	38.69	40.11	1.42
As.04	27.23	27.09	−0.14
As.05	9.75	9.28	−0.47
As.06	−4.78	−6.59	−1.81
As.07	33.03	32.78	−0.25
As.08	−4.18	−4.71	−0.53
As.09	−3.11	−3.85	−0.74
As.10	−2.91	−6.02	−3.11
Se.01	−6.77	−7.13	−0.36
Se.02	−5.13	−5.13	0.00
Se.03	15.99	16.23	0.24
Se.04	20.83	20.75	−0.08
Se.05	0.04	−0.17	−0.21
Se.06	32.84	32.68	−0.16
Se.07	43.35	43.15	−0.20
Se.08	10.72	10.98	0.26
Se.09	−2.86	−3.19	−0.33
Se.10	−68.86	−76.50	−7.64
Br.01	−6.26	−5.62	0.64
Br.02	0.06	0.04	−0.02
Br.03	−1.63	−1.61	0.02

Table 2: Reference isomerization energies based on RI-SCS-MP2(pFC)/cc-p(wC)V5Z computations with CCSD(T)(pFC)/cc-p(wC)TZ corrrections for higher correlation contributions in comarison to RI-MP2(pFC)/cc-p(wC)V5Z with equal corrections (MP2+CC). Deviations are also given. All values in kcal mol^{-1}.

rct	reference	MP2+CC	deviation
C.01	5.90	5.88	−0.02
C.04	17.69	17.70	0.01
C.05	3.76	3.81	0.05
C.06	18.89	18.88	−0.01
C.07	45.14	45.09	−0.05
C.08	1.34	1.29	−0.05
C.10	−9.09	−9.09	0.00
N.01	16.64	16.60	−0.04
N.02	17.88	17.81	−0.07
N.03	−20.93	−20.84	0.09
N.04	12.30	12.32	0.02
N.05	−12.00	−11.92	0.08
N.06	32.03	32.05	0.02
N.07	57.14	57.09	−0.05
N.08	−14.16	−14.18	−0.02
N.09	−31.78	−31.70	0.08
O.01	15.75	15.66	−0.09
O.02	25.21	25.10	−0.11
O.03	−63.68	−63.51	0.17
O.04	9.89	9.95	0.06
O.05	−12.35	−12.31	0.04
O.06	27.40	27.43	0.03
O.07	58.80	58.70	−0.10
O.08	19.64	19.51	−0.13
O.09	−11.53	−11.50	0.03
F.01	26.93	26.83	−0.10
F.02	0.96	0.98	0.02
F.03	−2.68	−2.68	0.00
Si.01	6.44	6.41	−0.03
Si.02	−10.06	−10.04	0.02
Si.03	−3.88	−3.91	−0.03
Si.04	28.21	28.20	−0.01
Si.05	33.42	33.31	−0.11

Si.06	21.48	21.45	−0.03
Si.07	28.87	28.77	−0.10
Si.08	21.99	21.92	−0.07
Si.09	−4.50	−4.45	0.05
Si.10	153.72	153.45	−0.27
P.01	−4.94	−4.99	−0.05
P.02	−1.74	−1.78	−0.04
P.03	22.95	22.91	−0.04
P.04	26.14	26.14	0.00
P.05	10.77	10.74	−0.03
P.06	6.61	6.65	0.04
P.07	35.33	35.25	−0.08
P.08	−3.87	−3.92	−0.05
P.09	17.87	17.78	−0.09
P.10	33.15	32.98	−0.17
S.01	−2.59	−2.60	−0.01
S.02	−0.92	−0.99	−0.07
S.03	6.57	6.61	0.04
S.04	19.77	19.78	0.01
S.05	−1.16	−1.18	−0.02
S.06	35.45	35.46	0.01
S.07	47.08	47.02	−0.06
S.08	11.87	11.77	−0.10
S.09	−3.02	−2.97	0.05
S.10	−15.19	−15.03	0.16
Cl.01	−3.29	−3.16	0.13
Cl.02	0.56	0.61	0.05
Cl.03	−1.64	−1.58	0.06
Ge.01	8.02	7.98	−0.04
Ge.02	−7.38	−7.39	−0.01
Ge.03	14.23	14.20	−0.03
Ge.04	26.73	26.74	0.01
Ge.05	24.62	24.58	−0.04
Ge.06	19.65	19.64	−0.01
Ge.07	30.69	30.57	−0.12
Ge.08	19.07	19.01	−0.06
Ge.09	−2.32	−2.29	0.03
Ge.10	93.48	93.37	−0.11

As.01	−7.86	−7.91	−0.05
As.02	−5.71	−5.75	−0.04
As.03	38.69	38.65	−0.04
As.04	27.23	27.25	0.02
As.05	9.75	9.74	−0.01
As.06	−4.78	−4.72	0.06
As.07	33.03	32.93	−0.10
As.08	−4.18	−4.21	−0.03
As.09	−3.11	−3.10	0.01
As.10	−2.91	−3.02	−0.11
Se.01	−6.77	−6.78	−0.01
Se.02	−5.13	−5.21	−0.08
Se.03	15.99	16.04	0.05
Se.04	20.83	20.85	0.02
Se.05	0.04	0.02	−0.02
Se.06	32.84	32.88	0.04
Se.07	43.35	43.29	−0.06
Se.08	10.72	10.64	−0.08
Se.09	−2.86	−2.81	0.05
Se.10	−68.86	−68.56	0.30
Br.01	−6.26	−6.09	0.17
Br.02	0.06	0.12	0.06
Br.03	−1.63	−1.57	0.06

Table 3: Comparison of between cc-pVTZ and cc-p(wC)VTZ results at the HF and CCSD(T) level of theory. In the latter case, only a partial Frozen Core treatment is applied with cc-p(wC)VTZ. Given are the isomerization energies for all reactions containing 2nd and higher row atoms. Further, the deviation at the HF level (Δ(HF) = E(HF/cc-pVTZ) - E(HF/cc-p(wC)VTZ) and the additional deviation from the coupled cluster treatment ($\Delta\Delta$(CC) = Δ(CC) - Δ(HF)) are given.

rct	HF/ cc-p(wC)VTZ	HF/ cc-pVTZ	Δ(HF)	CCSD(T)/ cc-p(wC)VTZ	CCSD(T)/ cc-pVTZ	$\Delta\Delta$(CC)
Si.01	13.70	13.84	0.14	6.91	7.27	0.22
Si.02	−11.28	−11.02	0.26	−9.62	−9.27	0.09
Si.03	−16.22	−14.53	1.69	−4.40	−2.99	−0.28
Si.04	26.31	26.22	−0.09	27.79	27.48	−0.22
Si.05	29.07	28.53	−0.54	32.33	31.31	−0.48
Si.06	14.60	14.45	−0.15	21.06	20.56	−0.35
Si.07	42.48	42.65	0.17	29.27	29.78	0.34
Si.08	30.40	30.30	−0.10	21.88	21.91	0.13
Si.09	−13.49	−13.35	0.14	−3.77	−3.67	−0.04
Si.10	149.78	144.49	−5.29	149.16	143.13	−0.74
P.01	0.59	0.38	−0.21	−4.84	−4.87	0.18
P.02	−0.64	−0.73	−0.09	−1.42	−1.47	0.04
P.03	13.35	14.61	1.26	21.85	22.91	−0.20
P.04	24.57	24.59	0.02	25.66	25.62	−0.06
P.05	8.82	8.55	−0.27	9.68	9.24	−0.17
P.06	−7.66	−8.04	−0.38	5.17	4.30	−0.49
P.07	47.81	47.82	0.01	35.76	35.88	0.11
P.08	0.99	0.84	−0.15	−4.18	−4.15	0.18
P.09	18.03	18.07	0.04	16.68	16.87	0.15
P.10	30.36	26.03	−4.33	31.65	27.00	−0.32
S.01	0.47	0.16	−0.31	−2.51	−2.67	0.15
S.02	0.92	0.81	−0.11	−0.48	−0.55	0.04
S.03	5.10	4.84	−0.26	5.28	4.84	−0.18
S.04	18.53	18.55	0.02	19.19	19.11	−0.10
S.05	−1.59	−1.69	−0.10	−1.67	−1.84	−0.07
S.06	26.84	26.46	−0.38	34.64	34.06	−0.20
S.07	59.13	58.89	−0.24	47.58	47.42	0.08
S.08	14.74	14.69	−0.05	12.33	12.27	−0.01
S.09	−2.54	−2.81	−0.27	−3.15	−3.29	0.13
S.10	−10.93	−27.88	−16.95	−16.34	−34.78	−1.49
Cl.01	−9.11	−9.22	−0.11	−3.35	−3.56	−0.10

Cl.02	−0.24	−0.28	−0.04	0.36	0.30	−0.02
Cl.03	−2.95	−3.01	−0.06	−1.66	−1.73	−0.01
Ge.01	16.46	16.48	0.02	8.46	9.47	0.99
Ge.02	−9.03	−9.13	−0.10	−7.03	−7.83	−0.70
Ge.03	3.71	4.11	0.40	13.16	8.54	−5.02
Ge.04	24.39	24.40	0.01	26.37	26.05	−0.33
Ge.05	20.68	20.71	0.03	23.76	23.55	−0.24
Ge.06	11.83	11.82	−0.01	19.39	19.53	0.15
Ge.07	44.59	44.54	−0.05	31.09	31.90	0.86
Ge.08	29.03	29.09	0.06	18.96	20.78	1.76
Ge.09	−9.99	−10.01	−0.02	−1.53	−1.59	−0.04
Ge.10	90.67	88.38	−2.29	89.02	87.34	0.61
As.01	−1.39	−1.44	−0.05	−7.65	−6.69	1.01
As.02	−5.33	−5.36	−0.03	−5.44	−5.48	−0.01
As.03	29.70	30.11	0.41	37.37	33.70	−4.08
As.04	25.13	25.16	0.03	26.86	26.65	−0.24
As.05	7.67	7.66	−0.01	9.00	8.58	−0.41
As.06	−20.02	−20.00	0.02	−6.11	−5.32	0.77
As.07	46.15	46.08	−0.07	33.37	33.81	0.51
As.08	1.96	1.90	−0.06	−4.37	−3.28	1.15
As.09	−7.16	−7.27	−0.11	−2.98	−1.66	1.43
As.10	−7.54	−7.83	−0.29	−4.09	−2.33	2.05
Se.01	−3.04	−3.13	−0.09	−6.62	−5.88	0.83
Se.02	−4.27	−4.30	−0.03	−4.75	−4.83	−0.05
Se.03	15.63	15.68	0.05	14.77	13.59	−1.23
Se.04	18.83	18.88	0.05	20.36	20.15	−0.26
Se.05	−0.56	−0.56	0.00	−0.36	−0.66	−0.30
Se.06	22.86	22.90	0.04	32.25	32.52	0.23
Se.07	56.26	56.14	−0.12	43.67	44.02	0.47
Se.08	13.52	13.52	0.00	11.09	10.96	−0.13
Se.09	−1.10	−1.18	−0.08	−2.92	−2.09	0.91
Se.10	−71.67	−74.03	−2.36	−69.68	−68.25	3.79
Br.01	−13.08	−13.11	−0.03	−6.35	−6.61	−0.23
Br.02	−1.11	−1.13	−0.02	−0.16	−0.23	−0.05
Br.03	−3.38	−3.40	−0.02	−1.72	−1.78	−0.04

Table 4: Reference isomerization energies based on RI-SCS-MP2(pFC)/cc-p(wC)V5Z computations with CCSD(T)(pFC)/cc-p(wC)TZ corrrections for higher correlation contributions in comarison to RI-SCS-MP2(pFC) results at the complete basis set limit with equal corrections (SCSMP2/CBS+CC). For the extrapolation results from SCSMP2/cc-p(wC)VQZ and SCSMP2/cc-p(wC)V5Z are used as explained elsewhere.[**?**] Deviations are also given. All values in kcal mol^{-1}.

rct	reference	SCSMP2/CBS+CC	deviation
C.01	5.90	5.77	−0.13
C.04	17.69	17.71	0.02
C.05	3.76	3.74	−0.02
C.06	18.89	19.03	0.14
C.07	45.14	44.97	−0.17
C.08	1.34	1.43	0.09
C.10	−9.09	−8.92	0.17
N.01	16.64	16.61	−0.03
N.02	17.88	17.68	−0.20
N.03	−20.93	−21.24	−0.31
N.04	12.30	12.29	−0.01
N.05	−12.00	−12.10	−0.10
N.06	32.03	32.06	0.03
N.07	57.14	57.04	−0.10
N.08	−14.16	−13.97	0.19
N.09	−31.78	−31.46	0.32
O.01	15.75	15.69	−0.06
O.02	25.21	25.02	−0.19
O.03	−63.68	−63.94	−0.26
O.04	9.89	9.86	−0.03
O.05	−12.35	−12.45	−0.10
O.06	27.40	27.42	0.02
O.07	58.80	58.63	−0.17
O.08	19.64	19.49	−0.15
O.09	−11.53	−11.47	0.06
F.01	26.93	26.78	−0.15
F.02	0.96	0.94	−0.02
F.03	−2.68	−2.74	−0.06
Si.01	6.44	6.12	−0.32
Si.02	−10.06	−10.31	−0.25
Si.03	−3.88	−3.52	0.36
Si.04	28.21	28.40	0.19

Si.05	33.42	33.88	0.46
Si.06	21.48	21.76	0.28
Si.07	28.87	28.49	−0.38
Si.08	21.99	21.96	−0.03
Si.09	−4.50	−4.67	−0.17
Si.10	153.72	154.62	0.90
P.01	−4.94	−5.14	−0.20
P.02	−1.74	−1.95	−0.21
P.03	22.95	23.40	0.45
P.04	26.14	26.31	0.17
P.05	10.77	11.14	0.37
P.06	6.61	7.05	0.44
P.07	35.33	34.98	−0.35
P.08	−3.87	−3.83	0.04
P.09	17.87	18.37	0.50
P.10	33.15	33.57	0.42
S.01	−2.59	−2.81	−0.22
S.02	−0.92	−1.10	−0.18
S.03	6.57	7.07	0.50
S.04	19.77	19.97	0.20
S.05	−1.16	−0.96	0.20
S.06	35.45	35.84	0.39
S.07	47.08	46.68	−0.40
S.08	11.87	11.73	−0.14
S.09	−3.02	−3.10	−0.08
S.10	−15.19	−14.45	0.74
Cl.01	−3.29	−3.23	0.06
Cl.02	0.56	0.61	0.05
Cl.03	−1.64	−1.62	0.02
Ge.01	8.02	7.73	−0.29
Ge.02	−7.38	−7.56	−0.18
Ge.03	14.23	14.73	0.50
Ge.04	26.73	26.88	0.15
Ge.05	24.62	25.00	0.38
Ge.06	19.65	19.89	0.24
Ge.07	30.69	30.30	−0.39
Ge.08	19.07	19.02	−0.05
Ge.09	−2.32	−2.48	−0.16

Ge.10	93.48	94.52	1.04
As.01	−7.86	−8.06	−0.20
As.02	−5.71	−5.87	−0.16
As.03	38.69	39.28	0.59
As.04	27.23	27.38	0.15
As.05	9.75	10.07	0.32
As.06	−4.78	−4.38	0.40
As.07	33.03	32.66	−0.37
As.08	−4.18	−4.17	0.01
As.09	−3.11	−3.11	0.00
As.10	−2.91	−2.57	0.34
Se.01	−6.77	−7.01	−0.24
Se.02	−5.13	−5.28	−0.15
Se.03	15.99	16.49	0.50
Se.04	20.83	21.04	0.21
Se.05	0.04	0.22	0.18
Se.06	32.84	33.18	0.34
Se.07	43.35	42.93	−0.42
Se.08	10.72	10.59	−0.13
Se.09	−2.86	−3.00	−0.14
Se.10	−68.86	−68.35	0.51
Br.01	−6.26	−6.18	0.08
Br.02	0.06	0.11	0.05
Br.03	−1.63	−1.62	0.01

Table 5: Study of higher order effects on reference results for a representative subset. The methods are: CCSD(T)(pFC)/cc-p(wC)VQZ (CC/QZ), CCSD(T)(pFC)/CBS(T,Q) (CC/CBS), HF/cc-p(wC)V5Z + correlation energy from CC/CBS, HF/cc-p(wC)V5Z + correlation energy from SCS-MP2(pFC)/CBS(T,Q) (MP2/CBS) + correction of higher order correlation effects from CCSD(T)(pFC)/cc-p(wC)VTZ – SCS-MP2(pFC)/cc-p(wC)VTZ (ΔCC). All values in kcal mol^{-1}.

rct	ref	CC/QZ	CC/CBS	HF/5Z+ CC/CBS	HF/5Z+ MP2/CBS+ΔCC	MP2/QZ+ ΔCC
C.01	5.9	5.8	5.8	5.8	6.0	6.0
N.01	16.6	16.5	16.6	16.8	16.8	16.5
N.02	17.9	18.0	17.8	17.7	17.9	18.1
N.03	−20.9	−20.4	−21.1	−21.3	−21.3	−20.4
O.01	15.7	15.6	15.7	15.8	15.9	15.7
O.02	25.2	25.4	25.2	25.1	25.2	25.5
O.03	−63.7	−63.0	−63.6	−63.9	−64.2	−63.2
F.01	26.9	27.5	27.2	27.0	26.7	27.3
F.02	1.0	0.8	0.8	1.0	1.0	0.8
F.03	−2.7	−2.6	−2.7	−2.7	−2.7	−2.6
Si.01	6.4	6.6	6.2	6.2	6.5	6.7
Si.02	−10.1	−10.0	−10.3	−10.3	−10.1	−9.9
Si.03	−3.9	−4.2	−3.8	−3.8	−3.8	−4.2
P.01	−4.9	−4.8	−5.0	−4.9	−4.9	−4.8
P.02	−1.7	−1.7	−2.0	−2.0	−1.8	−1.6
P.03	22.9	22.3	22.6	22.7	23.0	22.5
S.01	−2.6	−2.5	−2.6	−2.5	−2.5	−2.4
S.02	−0.9	−0.9	−1.2	−1.2	−1.0	−0.8
S.03	6.6	6.2	6.8	6.8	6.6	6.1
Cl.01	−3.3	−3.4	−3.4	−3.4	−3.4	−3.4
Cl.02	0.6	0.5	0.6	0.6	0.6	0.5
Cl.03	−1.6	−1.6	−1.6	−1.6	−1.6	−1.6
Ge.01	8.0	8.2	7.9	7.9	8.1	8.3
Ge.02	−7.4	−7.4	−7.7	−7.6	−7.4	−7.2
Ge.03	14.2	13.7	14.1	14.2	14.2	13.7
As.01	−7.9	−7.7	−7.9	−7.8	−7.8	−7.7
As.02	−5.7	−5.7	−5.9	−5.9	−5.7	−5.6
As.03	38.7	37.8	38.2	38.2	38.7	38.1
Se.01	−6.8	−6.6	−6.7	−6.7	−6.7	−6.6
Se.02	−5.1	−5.1	−5.4	−5.4	−5.2	−5.0
Se.03	16.0	15.5	16.1	16.1	16.0	15.5

Br.01	−6.3	−6.3	−6.2	−6.2	−6.4	−6.3
Br.02	0.1	0.0	0.1	0.2	0.1	0.0
Br.03	−1.6	−1.6	−1.6	−1.6	−1.6	−1.6

1.1 Discussion of Reference Data Generation

The tables shown so far in the Supporting Information should help to judge the quality of the reference data used for the analysis in the main text (see also the disscussion there). First, the effect of including relativistic effects is shown. For the heavier elements, these effects cannot be negeleted for comparison to experiment but they should be quite invariant to the general electron structure method used and therefore can be skipped for just a method comparison. Next, the sensitivity with respect to the lower correlation method for estimating larger basis sets effects is studied. The difference between SCS-MP2 and MP2 is negligible. It never exceeds 0.3 kcal mol^{-1} and is less than 0.1 kcal mol^{-1} on average. Table 3 gives the difference between a frozen-core and a partial frozen-core treatment (with an appropriate basis set). Here, the latter treatment can be essential for heavier elements at the HF as well as at the post-HF level. Further, the effect of a still incomplete basis set is investigated in the next table by comparing the reference data with those from a basis set exptrapolation with SCS-MP2 and higher order corrections. The effects are well within the expected error range. Finally, the effect of estimating higher order effects itself is examined. As this requires Coupled-Cluster computations with larger basis sets, this only done for a subset. Different approaches are tested of which the data based on HF/cc-p(wC)V5Z plus correlation energies based on CCSD(T) and a basis set extrapolation from cc-p(wC)VTZ and cc-p(wC)VQZ should be the most accurate. The absolute deviations with respect to the reference data are 0.1 kcal mol^{-1} on average with a maximum deviation of 0.5 kcal mol^{-1}. The table includes also two data sets which allow to check the quality of higher order corrections directly. One can compare HF/cc-p(wC)V5Z plus correlation energies based on SCS-MP2 and a basis set extrapolation from cc-p(wC)VTZ and cc-p(wC)VQZ plus a correlation energy correction at the triple-ζ-level with the aforementioned data. The absolute deviation between those two approaches is 0.1 kcal mol^{-1} with a maximum of 0.4 kcal mol^{-1}. The table also includes SCS-MP2/cc-p(wC)VQZ with a correlation energy correction at the triple-ζ-level which can be compared to pure CCSD(T)/cc-p(wC)VQZ results. The mean absolute deviation is 0.1 kcal mol^{-1} again, with a maximum of just 0.2 kcal mol^{-1}.

2 Complete List of Results for all Methods in the Test Set

Table 6: Reference isomerization energies based on RI-SCS-MP2(pFC)/cc-p(wC)V5Z computations with CCSD(T)(pFC)/cc-p(wC)TZ corrrections for higher correlation contributions in comarison to SCS-MP2(pFC)/cc-p(wC)V5Z and various density functionals (same basis set) applied in the test set. Deviations are given in parentheses. All values in kcal mol^{-1}.

rct	ref.	oTPSS-D3		M11-L		B3-LYP-D3		PBE0-D3		PW6B95-D3	
C.01	5.9	3.6	(−2.3)	5.5	(−0.4)	7.4	(1.5)	1.9	(−4.0)	3.3	(−2.6)
C.04	17.7	15.3	(−2.4)	17.5	(−0.2)	16.8	(−0.9)	17.3	(−0.4)	16.5	(−1.2)
C.05	3.8	2.4	(1.4)	3.1	(−0.7)	2.4	(−1.4)	2.6	(−1.2)	2.6	(−1.2)
C.06	18.9	15.5	(−3.4)	17.7	(−1.2)	12.7	(−6.2)	21.0	(2.1)	17.9	(−1.0)
C.07	45.1	50.7	(5.5)	49.0	(3.9)	56.6	(11.4)	49.0	(3.9)	49.3	(4.2)
C.08	1.3	−1.5	(−2.9)	−2.1	(−3.4)	−1.8	(−3.2)	−1.6	(−2.9)	−1.4	(−2.7)
C.10	−9.1	−8.6	(0.5)	−10.2	(−1.1)	−8.6	(0.5)	−8.5	(0.6)	−8.4	(0.7)
N.01	16.6	17.0	(0.4)	16.7	(0.0)	19.8	(3.2)	15.1	(−1.6)	15.8	(−0.9)
N.02	17.9	16.5	(−1.4)	18.2	(0.3)	19.6	(1.7)	14.4	(−3.4)	15.4	(−2.5)
N.03	−20.9	−24.5	(−3.5)	−21.6	(−0.7)	−22.3	(−1.4)	−23.8	(−2.9)	−22.7	(−1.8)
N.04	12.3	10.0	(−2.3)	12.4	(0.1)	11.9	(−0.4)	11.9	(−0.4)	11.4	(−0.9)
N.05	−12.0	−12.4	(−0.4)	−11.1	(0.9)	−11.3	(0.7)	−12.0	(0.0)	−11.2	(0.8)
N.06	32.0	28.1	(−4.0)	31.1	(−1.0)	25.8	(−6.3)	34.3	(2.3)	31.7	(−0.4)
N.07	57.1	65.2	(8.1)	61.7	(4.6)	69.7	(12.6)	63.1	(6.0)	62.8	(5.7)
N.08	−14.2	−18.2	(−4.0)	−20.0	(−5.9)	−16.9	(−2.8)	−16.6	(−2.4)	−16.5	(−2.4)
N.09	−31.8	−40.2	(−8.5)	−36.4	(−4.6)	−43.5	(−11.7)	−34.5	(−2.7)	−35.0	(−3.2)
O.01	15.8	14.2	(−1.5)	16.2	(0.4)	17.1	(1.4)	13.3	(−2.4)	13.7	(−2.1)
O.02	25.2	24.0	(−1.2)	27.0	(1.8)	26.8	(1.6)	22.8	(−2.4)	23.1	(−2.2)
O.03	−63.7	−60.5	(3.2)	−63.3	(0.4)	−59.3	(4.4)	−62.3	(1.4)	−61.2	(2.5)
O.04	9.9	8.0	(−1.9)	10.3	(0.5)	10.4	(0.5)	9.5	(−0.4)	9.7	(−0.2)
O.05	−12.4	−11.8	(0.5)	−11.8	(0.5)	−10.8	(1.6)	−12.0	(0.3)	−11.1	(1.3)
O.06	27.4	24.6	(−2.8)	27.2	(−0.2)	22.3	(−5.1)	29.9	(2.5)	27.8	(0.4)
O.07	58.8	65.5	(6.7)	63.6	(4.8)	69.4	(10.6)	64.0	(5.2)	63.1	(4.3)
O.08	19.6	24.8	(5.2)	24.4	(4.8)	23.4	(3.8)	19.4	(−0.3)	20.6	(0.9)
O.09	−11.5	−12.2	(−0.7)	−11.9	(−0.4)	−12.5	(−1.0)	−11.8	(−0.2)	−11.6	(0.0)
F.01	26.9	24.9	(−2.0)	33.7	(6.8)	23.9	(−3.0)	26.8	(−0.2)	25.6	(−1.3)
F.02	1.0	1.1	(0.1)	1.4	(0.4)	0.9	(−0.1)	1.0	(0.1)	1.0	(0.0)
F.03	−2.7	−3.0	(−0.4)	−2.4	(0.3)	−3.1	(−0.4)	−2.9	(−0.2)	−2.8	(−0.2)
Si.01	6.4	4.7	(−1.8)	9.6	(3.1)	8.6	(2.1)	2.3	(−4.1)	4.3	(−2.1)
Si.02	−10.1	−11.4	(−1.3)	−7.4	(2.7)	−8.7	(1.3)	−12.9	(−2.9)	−12.3	(−2.3)
Si.03	−3.9	−1.4	(2.5)	−11.1	(−7.3)	−6.1	(−2.2)	1.0	(4.8)	−2.5	(1.4)

rct	ref.	oTPSS-D3		M11-L		B3-LYP-D3		PBE0-D3		PW6B95-D3	
Si.04	28.2	26.2	(−2.0)	25.3	(−3.0)	26.8	(−1.4)	28.0	(−0.2)	27.1	(−1.1)
Si.05	33.4	35.4	(2.0)	25.2	(−8.3)	31.3	(−2.1)	32.4	(−1.0)	32.6	(−0.8)
Si.06	21.5	17.2	(−4.2)	15.9	(−5.6)	14.3	(−7.2)	22.6	(1.1)	19.9	(−1.6)
Si.07	28.9	32.7	(3.8)	35.9	(7.0)	39.6	(10.7)	30.3	(1.4)	30.8	(1.9)
Si.08	22.0	19.7	(−2.3)	20.1	(−1.9)	20.1	(−1.9)	18.3	(−3.7)	19.9	(−2.1)
Si.09	−4.5	−7.5	(−3.0)	−5.4	(−0.9)	−9.3	(−4.8)	−10.5	(−6.0)	−10.0	(−5.5)
Si.10	153.7	149.7	(−4.0)	140.8	(−12.9)	149.5	(−4.2)	146.7	(−7.1)	150.1	(−3.6)
P.01	−4.9	−5.8	(−0.9)	−2.7	(2.3)	−2.2	(2.8)	−7.9	(−2.9)	−6.6	(−1.7)
P.02	−1.7	−3.5	(−1.8)	0.2	(1.9)	−0.1	(1.6)	−5.2	(−3.4)	−4.4	(−2.7)
P.03	23.0	20.8	(−2.1)	16.5	(−6.5)	19.4	(−3.5)	22.1	(−0.8)	21.3	(−1.6)
P.04	26.1	23.7	(−2.4)	23.7	(−2.4)	24.7	(−1.5)	25.6	(−0.6)	24.9	(−1.3)
P.05	10.8	10.9	(0.1)	6.4	(−4.4)	9.6	(−1.2)	10.3	(−0.5)	10.6	(−0.1)
P.06	6.6	6.0	(−0.6)	6.6	(−0.1)	−0.3	(−7.0)	10.1	(3.5)	6.7	(0.1)
P.07	35.3	41.6	(6.3)	43.0	(7.7)	47.4	(12.1)	39.1	(3.8)	39.1	(3.8)
P.08	−3.9	−6.0	(−2.1)	−7.2	(−3.4)	−5.8	(−1.9)	−6.4	(−2.5)	−5.6	(−1.8)
P.09	17.9	13.0	(−4.9)	9.8	(−8.1)	9.8	(−8.1)	16.8	(−1.1)	16.1	(−1.8)
P.10	33.2	35.6	(2.4)	37.0	(3.9)	31.0	(−2.2)	32.9	(−0.2)	31.3	(−1.8)
S.01	−2.6	−2.7	(−0.1)	−0.6	(2.0)	0.4	(2.9)	−4.7	(−2.1)	−4.1	(−1.5)
S.02	−0.9	−2.2	(−1.3)	1.8	(2.7)	1.2	(2.1)	−4.0	(−3.1)	−3.4	(−2.5)
S.03	6.6	9.0	(2.5)	5.7	(−0.9)	8.4	(1.8)	8.4	(1.8)	9.0	(2.5)
S.04	19.8	17.0	(−2.8)	17.9	(−1.9)	18.3	(−1.4)	19.1	(−0.7)	18.6	(−1.2)
S.05	−1.2	−0.8	(0.3)	−2.5	(−1.4)	−1.1	(0.1)	−0.9	(0.3)	−0.6	(0.6)
S.06	35.5	31.5	(−3.9)	33.3	(−2.1)	28.1	(−7.3)	37.2	(1.8)	34.4	(−1.0)
S.07	47.1	55.1	(8.0)	55.7	(8.6)	59.7	(12.6)	52.5	(5.5)	52.1	(5.1)
S.08	11.9	17.9	(6.0)	16.9	(5.0)	16.5	(4.6)	11.6	(−0.3)	13.1	(1.2)
S.09	−3.0	−2.6	(0.4)	−4.2	(−1.2)	−3.0	(0.0)	−2.6	(0.4)	−2.4	(0.7)
S.10	−15.2	−7.1	(8.1)	−1.3	(13.9)	−13.9	(1.3)	−12.3	(2.9)	−11.8	(3.4)
Cl.01	−3.3	−3.7	(−0.4)	−0.4	(2.9)	−4.7	(−1.4)	−3.9	(−0.6)	−3.9	(−0.6)
Cl.02	0.6	0.3	(−0.3)	1.0	(0.5)	0.2	(−0.4)	0.5	(−0.1)	0.6	(0.0)
Cl.03	−1.6	−2.4	(−0.7)	−1.4	(0.2)	−2.5	(−0.8)	−2.0	(−0.4)	−1.8	(−0.1)
Ge.01	8.0	7.2	(−0.8)	11.2	(3.2)	10.6	(2.6)	5.0	(−3.1)	6.6	(−1.4)
Ge.02	−7.4	−8.8	(−1.4)	−5.3	(2.1)	−6.0	(1.4)	−10.2	(−2.8)	−9.8	(−2.4)
Ge.03	14.2	12.8	(−1.4)	2.9	(−11.4)	13.1	(−1.2)	16.5	(2.3)	14.6	(0.4)
Ge.04	26.7	24.1	(−2.7)	22.4	(−4.3)	25.0	(−1.8)	25.8	(−1.0)	24.9	(−1.8)
Ge.05	24.6	25.2	(0.6)	12.5	(−12.1)	21.6	(−3.0)	22.1	(−2.5)	22.6	(−2.0)
Ge.06	19.7	15.0	(−4.6)	13.5	(−6.1)	12.2	(−7.5)	20.0	(0.4)	17.3	(−2.3)

rct	ref.	oTPSS-D3		M11-L		B3-LYP-D3		PBE0-D3		PW6B95-D3	
Ge.07	30.7	34.9	(4.2)	38.4	(7.7)	40.9	(10.2)	32.8	(2.1)	33.1	(2.4)
Ge.08	19.1	17.8	(−1.3)	17.5	(−1.6)	17.6	(−1.5)	16.3	(−2.8)	17.8	(−1.3)
Ge.09	−2.3	−5.4	(−3.1)	−4.1	(−1.8)	−6.1	(−3.8)	−8.2	(−5.9)	−7.6	(−5.2)
Ge.10	93.5	92.2	(−1.3)	74.3	(−19.2)	89.0	(−4.4)	87.0	(−6.5)	89.4	(−4.1)
As.01	−7.9	−7.8	(0.0)	−5.5	(2.4)	−5.4	(2.5)	−10.2	(−2.3)	−9.2	(−1.3)
As.02	−5.7	−7.2	(−1.5)	−4.0	(1.8)	−4.8	(1.0)	−9.0	(−3.3)	−8.6	(−2.9)
As.03	38.7	34.1	(−4.6)	26.8	(−11.9)	36.0	(−2.7)	37.4	(−1.3)	37.1	(−1.6)
As.04	27.2	24.3	(−2.9)	23.3	(−4.0)	25.5	(−1.7)	26.1	(−1.2)	25.5	(−1.8)
As.05	9.8	9.7	(−0.1)	2.6	(−7.2)	8.1	(−1.7)	8.2	(−1.6)	8.9	(−0.9)
As.06	−4.8	−7.8	(−3.0)	−7.0	(−2.2)	−13.2	(−8.5)	−2.5	(2.3)	−6.2	(−1.4)
As.07	33.0	39.1	(6.0)	41.8	(8.8)	44.3	(11.3)	36.9	(3.8)	36.6	(3.6)
As.08	−4.2	−5.5	(−1.3)	−7.1	(−2.9)	−5.8	(−1.6)	−6.3	(−2.1)	−5.5	(−1.3)
As.09	−3.1	−6.8	(−3.7)	−5.3	(−2.2)	−7.9	(−4.8)	−6.6	(−3.5)	−6.0	(−2.9)
As.10	−2.9	−1.1	(1.8)	−7.6	(−4.7)	−7.0	(−4.1)	−4.0	(−1.1)	−6.2	(−3.3)
Se.01	−6.8	−5.5	(1.3)	−3.6	(3.2)	−3.9	(2.8)	−8.3	(−1.5)	−7.7	(−1.0)
Se.02	−5.1	−6.0	(−0.8)	−2.0	(3.1)	−3.6	(1.5)	−8.0	(−2.8)	−7.7	(−2.5)
Se.03	16.0	17.6	(1.6)	10.9	(−5.1)	17.5	(1.6)	17.1	(1.1)	18.0	(2.0)
Se.04	20.8	17.5	(−3.3)	16.9	(−3.9)	19.0	(−1.8)	19.5	(−1.3)	19.2	(−1.7)
Se.05	0.0	0.1	(0.1)	−3.2	(−3.2)	−0.2	(−0.3)	−0.3	(−0.4)	0.1	(0.1)
Se.06	32.8	28.3	(−4.6)	28.4	(−4.4)	25.1	(−7.8)	33.7	(0.9)	31.0	(−1.9)
Se.07	43.4	51.2	(7.9)	53.5	(10.1)	55.3	(12.0)	48.8	(5.5)	48.2	(4.8)
Se.08	10.7	16.6	(5.9)	15.5	(4.8)	15.3	(4.6)	10.3	(−0.4)	11.8	(1.0)
Se.09	−2.9	−1.5	(1.3)	−3.8	(−0.9)	−2.5	(0.4)	−2.3	(0.6)	−1.8	(1.1)
Se.10	−68.9	−55.7	(13.2)	−72.0	(−3.2)	−67.8	(1.0)	−69.7	(−0.9)	−68.9	(0.0)
Br.01	−6.3	−6.6	(−0.3)	−4.5	(1.8)	−7.8	(−1.5)	−7.1	(−0.8)	−6.8	(−0.6)
Br.02	0.1	−0.4	(−0.5)	0.4	(0.3)	−0.6	(−0.7)	−0.1	(−0.2)	0.0	(−0.1)
Br.03	−1.6	−2.3	(−0.6)	−1.7	(0.0)	−2.5	(−0.9)	−2.1	(−0.5)	−1.8	(−0.1)

Table 7: Reference isomerization energies based on RI-SCS-MP2(pFC)/cc-p(wC)V5Z computations with CCSD(T)(pFC)/cc-p(wC)TZ corrrections for higher correlation contributions in comarison to SCS-MP2(pFC)/cc-p(wC)V5Z and various density functionals (same basis set) applied in the test set. Deviations are given in parentheses. All values in kcal mol^{-1}.

rct	ref.	SCS-MP2		B2GP-PLYP-D3		M06-2X		M11		ωB97X-D	
C.01	5.9	4.9	(−1.0)	5.7	(−0.2)	2.1	(−3.8)	1.4	(−4.5)	2.3	(−3.6)
C.04	17.7	17.5	(−0.2)	17.7	(0.0)	17.0	(−0.7)	17.4	(−0.3)	16.8	(−0.9)
C.05	3.8	3.7	(0.0)	3.3	(−0.4)	3.5	(−0.3)	3.3	(−0.5)	3.2	(−0.5)
C.06	18.9	19.9	(1.0)	17.7	(−1.2)	18.4	(−0.5)	20.0	(1.2)	21.8	(2.9)
C.07	45.1	45.7	(0.5)	51.8	(6.7)	50.2	(5.1)	49.9	(4.7)	48.9	(3.8)
C.08	1.3	4.2	(2.8)	1.6	(0.3)	0.6	(−0.7)	0.3	(−1.0)	−0.3	(−1.6)
C.10	−9.1	−9.9	(−0.8)	−9.3	(−0.2)	−7.7	(1.4)	−8.5	(0.6)	−9.8	(−0.7)
N.01	16.6	15.7	(−0.9)	17.8	(1.1)	14.4	(−2.3)	14.6	(−2.0)	14.8	(−1.8)
N.02	17.9	17.1	(−0.8)	17.9	(0.1)	13.9	(−3.9)	13.7	(−4.2)	15.1	(−2.8)
N.03	−20.9	−21.0	(0.0)	−22.6	(−1.7)	−23.2	(−2.3)	−23.4	(−2.5)	−21.6	(−0.7)
N.04	12.3	12.1	(−0.3)	12.4	(0.1)	12.1	(−0.3)	12.2	(−0.1)	11.4	(−0.9)
N.05	−12.0	−11.7	(0.3)	−11.5	(0.5)	−10.5	(1.5)	−11.1	(0.9)	−11.7	(0.3)
N.06	32.0	34.3	(2.3)	31.9	(−0.2)	33.0	(1.0)	35.7	(3.6)	35.7	(3.7)
N.07	57.1	58.0	(0.8)	64.9	(7.8)	63.1	(6.0)	63.5	(6.3)	62.1	(4.9)
N.08	−14.2	−12.6	(1.6)	−14.4	(−0.3)	−14.2	(0.0)	−14.5	(−0.3)	−15.6	(−1.4)
N.09	−31.8	−31.6	(0.2)	−36.4	(−4.6)	−33.2	(−1.5)	−31.5	(0.3)	−35.4	(−3.6)
O.01	15.8	14.4	(−1.3)	15.8	(0.1)	13.5	(−2.3)	13.3	(−2.5)	13.4	(−2.3)
O.02	25.2	25.0	(−0.2)	25.9	(0.7)	21.6	(−3.6)	22.3	(−2.9)	23.9	(−1.3)
O.03	−63.7	−64.8	(−1.1)	−63.4	(0.2)	−63.7	(0.0)	−64.4	(−0.7)	−62.4	(1.3)
O.04	9.9	9.7	(−0.2)	10.3	(0.4)	10.1	(0.2)	9.9	(0.0)	9.1	(−0.8)
O.05	−12.4	−12.2	(0.1)	−11.8	(0.6)	−10.9	(1.5)	−11.6	(0.7)	−11.9	(0.4)
O.06	27.4	29.1	(1.7)	27.4	(0.0)	28.5	(1.1)	30.8	(3.4)	31.3	(3.9)
O.07	58.8	59.8	(1.0)	65.7	(6.9)	63.7	(4.9)	64.0	(5.2)	62.8	(4.0)
O.08	19.6	20.3	(0.6)	21.4	(1.8)	19.0	(−0.6)	21.2	(1.5)	20.8	(1.2)
O.09	−11.5	−12.0	(−0.5)	−12.2	(−0.7)	−10.6	(1.0)	−11.8	(−0.3)	−13.2	(−1.7)
F.01	26.9	26.3	(−0.6)	26.2	(−0.7)	27.0	(0.1)	26.7	(−0.3)	26.9	(−0.1)
F.02	1.0	1.1	(0.1)	1.0	(0.1)	0.8	(−0.2)	0.8	(−0.2)	0.9	(−0.1)
F.03	−2.7	−2.7	(0.0)	−2.9	(−0.2)	−2.7	(0.0)	−2.6	(0.0)	0.0	(2.7)
Si.01	6.4	6.6	(0.1)	6.7	(0.2)	3.5	(−2.9)	2.5	(−4.0)	3.6	(−2.8)
Si.02	−10.1	−10.9	(−0.8)	−10.4	(−0.3)	−13.2	(−3.1)	−15.2	(−5.1)	−13.8	(−3.8)
Si.03	−3.9	−7.6	(−3.7)	−5.8	(−1.9)	−3.3	(0.6)	−4.6	(−0.7)	−3.6	(0.3)
Si.04	28.2	27.6	(−0.6)	28.2	(0.0)	28.2	(0.0)	29.0	(0.7)	27.2	(−1.0)

rct	ref.	SCS-MP2		B2GP-PLYP-D3		M06-2X		M11		ωB97X-D	
Si.05	33.4	32.7	(−0.7)	32.7	(−0.7)	34.0	(0.6)	36.8	(3.3)	32.8	(−0.6)
Si.06	21.5	21.9	(0.4)	19.6	(−1.9)	21.0	(−0.5)	22.9	(1.4)	23.0	(1.5)
Si.07	28.9	29.5	(0.6)	34.4	(5.5)	31.2	(2.4)	31.2	(2.3)	31.6	(2.7)
Si.08	22.0	26.3	(4.3)	23.4	(1.4)	22.1	(0.1)	22.9	(0.9)	21.6	(−0.4)
Si.09	−4.5	−6.5	(−2.0)	−7.3	(−2.8)	−11.5	(−7.0)	−13.0	(−8.5)	−12.7	(−8.2)
Si.10	153.7	156.4	(2.6)	155.1	(1.4)	155.1	(1.4)	159.7	(6.0)	147.2	(−6.5)
P.01	−4.9	−5.9	(−0.9)	−4.8	(0.2)	−7.8	(−2.9)	−8.0	(−3.1)	−7.0	(−2.1)
P.02	−1.7	−2.9	(−1.1)	−2.0	(−0.2)	−5.5	(−3.7)	−6.3	(−4.5)	−5.2	(−3.5)
P.03	23.0	22.8	(−0.1)	21.8	(−1.2)	22.5	(−0.4)	20.8	(−2.1)	20.2	(−2.8)
P.04	26.1	26.0	(−0.2)	26.2	(0.0)	25.8	(−0.3)	26.2	(0.0)	24.9	(−1.3)
P.05	10.8	11.2	(0.4)	10.8	(0.0)	11.1	(0.3)	11.6	(0.8)	10.5	(−0.3)
P.06	6.6	9.6	(3.0)	7.1	(0.5)	7.3	(0.7)	9.1	(2.5)	8.9	(2.3)
P.07	35.3	35.5	(0.2)	41.7	(6.4)	39.8	(4.4)	39.7	(4.4)	39.5	(4.2)
P.08	−3.9	−0.7	(3.2)	−3.1	(0.8)	−3.8	(0.1)	−3.3	(0.6)	−4.0	(−0.1)
P.09	17.9	18.1	(0.2)	15.0	(−2.9)	17.0	(−0.9)	21.2	(3.3)	18.3	(0.4)
P.10	33.2	34.6	(1.4)	33.7	(0.5)	28.6	(−4.5)	30.5	(−2.7)	33.4	(0.2)
S.01	−2.6	−4.1	(−1.5)	−2.5	(0.1)	−5.2	(−2.6)	−6.4	(−3.8)	−4.3	(−1.7)
S.02	−0.9	−2.3	(−1.4)	−0.9	(0.0)	−4.6	(−3.7)	−5.6	(−4.7)	−3.6	(−2.6)
S.03	6.6	7.0	(0.4)	7.7	(1.1)	8.3	(1.7)	8.2	(1.7)	7.2	(0.6)
S.04	19.8	19.9	(0.1)	19.7	(−0.1)	19.4	(−0.3)	19.9	(0.1)	18.3	(−1.4)
S.05	−1.2	−0.9	(0.3)	−1.0	(0.2)	−0.5	(0.7)	−0.3	(0.9)	−1.0	(0.2)
S.06	35.5	38.4	(2.9)	35.6	(0.1)	35.3	(−0.1)	37.3	(1.8)	37.6	(2.2)
S.07	47.1	47.4	(0.3)	54.3	(7.2)	52.5	(5.4)	51.7	(4.6)	51.9	(4.9)
S.08	11.9	12.4	(0.5)	13.8	(1.9)	11.0	(−0.9)	12.5	(0.6)	12.5	(0.6)
S.09	−3.0	−2.7	(0.3)	−3.2	(−0.2)	−2.5	(0.5)	−2.7	(0.3)	−2.9	(0.1)
S.10	−15.2	−10.6	(4.6)	−11.4	(3.8)	−19.5	(−4.3)	−19.3	(−4.1)	−11.3	(3.9)
Cl.01	−3.3	−2.9	(0.4)	−3.6	(−0.3)	−3.9	(−0.6)	−4.1	(−0.8)	−4.1	(−0.8)
Cl.02	0.6	0.7	(0.1)	0.6	(0.0)	0.7	(0.1)	0.7	(0.1)	0.6	(0.0)
Cl.03	−1.6	−1.5	(0.1)	−1.9	(−0.2)	−1.6	(0.1)	−1.5	(0.1)	−2.0	(−0.4)
Ge.01	8.0	7.6	(−0.4)	8.3	(0.3)	6.3	(−1.8)	5.9	(−2.1)	6.6	(−1.4)
Ge.02	−7.4	−8.0	(−0.6)	−7.6	(−0.2)	−11.4	(−4.0)	−12.9	(−5.6)	−10.7	(−3.3)
Ge.03	14.2	13.1	(−1.2)	14.0	(−0.3)	13.7	(−0.6)	12.7	(−1.5)	11.8	(−2.4)
Ge.04	26.7	26.4	(−0.3)	26.5	(−0.2)	27.0	(0.3)	26.6	(−0.1)	24.9	(−1.8)
Ge.05	24.6	24.9	(0.3)	23.6	(−1.1)	27.2	(2.6)	25.7	(1.0)	22.1	(−2.5)
Ge.06	19.7	20.4	(0.7)	17.7	(−1.9)	19.1	(−0.6)	20.1	(0.5)	20.2	(0.5)
Ge.07	30.7	30.9	(0.2)	36.0	(5.3)	32.4	(1.8)	34.1	(3.4)	34.5	(3.8)

rct	ref.	SCS-MP2		B2GP-PLYP-D3		M06-2X		M11		ωB97X-D	
Ge.08	19.1	22.7	(3.6)	20.4	(1.3)	21.6	(2.5)	22.2	(3.1)	19.7	(0.6)
Ge.09	−2.3	−2.9	(−0.6)	−3.8	(−1.5)	−11.0	(−8.6)	−10.2	(−7.8)	−10.1	(−7.8)
Ge.10	93.5	96.3	(2.9)	93.9	(0.4)	102.	(8.7)	97.4	(3.9)	87.5	(−5.9)
As.01	−7.9	−9.3	(−1.4)	−8.1	(−0.2)	−9.7	(−1.9)	−11.2	(−3.3)	−8.6	(−0.8)
As.02	−5.7	−7.0	(−1.3)	−6.3	(−0.5)	−10.0	(−4.3)	−11.3	(−5.6)	−8.4	(−2.7)
As.03	38.7	40.0	(1.3)	38.7	(0.1)	37.7	(−1.0)	37.2	(−1.5)	34.4	(−4.3)
As.04	27.2	27.3	(0.0)	27.2	(−0.1)	27.2	(0.0)	27.1	(−0.1)	25.2	(−2.1)
As.05	9.8	10.5	(0.7)	9.5	(−0.3)	11.1	(1.4)	10.0	(0.2)	8.3	(−1.5)
As.06	−4.8	−1.7	(3.0)	−4.9	(−0.1)	−3.7	(1.1)	−3.5	(1.2)	−4.4	(0.4)
As.07	33.0	32.9	(−0.1)	38.9	(5.9)	37.1	(4.1)	37.8	(4.8)	37.6	(4.6)
As.08	−4.2	−1.5	(2.7)	−3.6	(0.5)	−2.4	(1.7)	−3.3	(0.8)	−3.7	(0.5)
As.09	−3.1	−3.1	(0.0)	−5.1	(−2.0)	−3.2	(−0.1)	−1.0	(2.1)	−4.8	(−1.7)
As.10	−2.9	−2.6	(0.3)	−4.0	(−1.1)	−5.7	(−2.7)	−9.3	(−6.4)	−3.9	(−1.0)
Se.01	−6.8	−8.6	(−1.8)	−6.9	(−0.2)	−8.7	(−1.9)	−10.2	(−3.4)	−7.4	(−0.6)
Se.02	−5.1	−6.8	(−1.7)	−5.4	(−0.2)	−9.2	(−4.0)	−10.3	(−5.2)	−7.3	(−2.2)
Se.03	16.0	16.7	(0.7)	17.0	(1.0)	18.2	(2.2)	17.5	(1.5)	15.7	(−0.3)
Se.04	20.8	21.1	(0.2)	20.6	(−0.2)	20.5	(−0.4)	20.6	(−0.3)	18.6	(−2.2)
Se.05	0.0	0.5	(0.4)	0.0	(0.0)	0.8	(0.7)	0.4	(0.4)	−0.4	(−0.4)
Se.06	32.8	35.7	(2.9)	32.6	(−0.2)	32.2	(−0.6)	33.9	(1.0)	33.8	(0.9)
Se.07	43.4	43.4	(0.0)	50.1	(6.7)	48.8	(5.5)	48.6	(5.2)	48.6	(5.3)
Se.08	10.7	11.3	(0.5)	12.6	(1.8)	9.8	(−0.9)	11.4	(0.7)	11.3	(0.6)
Se.09	−2.9	−2.5	(0.4)	−3.2	(−0.3)	−1.6	(1.3)	−2.3	(0.6)	−2.0	(0.8)
Se.10	−68.9	−66.1	(2.7)	−67.0	(1.9)	−71.3	(−2.4)	−83.5	(−14.6)	−67.1	(1.7)
Br.01	−6.3	−5.2	(1.1)	−6.4	(−0.1)	−7.3	(−1.0)	−7.4	(−1.2)	−7.3	(−1.1)
Br.02	0.1	0.2	(0.1)	0.0	(−0.1)	0.2	(0.1)	0.2	(0.2)	0.0	(0.0)
Br.03	−1.6	−1.4	(0.2)	−1.8	(−0.2)	−1.6	(0.0)	−1.6	(0.0)	−2.0	(−0.4)

Table 8: Reference isomerization energies based on RI-SCS-MP2(pFC)/cc-p(wC)V5Z computations with CCSD(T)(pFC)/cc-p(wC)TZ corrrections for higher correlation contributions in comarison to density functionals with and without dispersion correction (same basis set). Deviations are given in parentheses. The mean deviation ($\overline{x}$), the mean absolute deviation ($\overline{|x|}$), the median of the absolute deviation($\widetilde{|x|}$), the maximum ($x_{\max}$) and minimum deviation ($x_{\min}$) are given at the end. All values in kcal mol^{-1}.

		B2GP-PLYP				B3LYP				PBE0			
		with D3		without		with D3		without		with D3		without	
rct	ref.												
C.01	5.9	5.7	(−0.2)	5.7	(−0.2)	7.4	(1.5)	7.4	(1.5)	1.9	(−4.0)	1.9	(−4.0)
C.04	17.7	17.7	(0.0)	17.7	(0.0)	16.8	(−0.9)	16.8	(−0.9)	17.3	(−0.4)	17.3	(−0.4)
C.05	3.8	3.3	(−0.4)	2.7	(−1.0)	2.4	(−1.4)	0.8	(−3.0)	2.6	(−1.2)	1.6	(−2.2)
C.06	18.9	17.7	(−1.2)	17.5	(−1.4)	12.7	(−6.2)	12.0	(−6.9)	21.0	(2.1)	20.5	(1.6)
C.07	45.1	51.8	(6.7)	52.1	(6.9)	56.6	(11.4)	57.3	(12.1)	49.0	(3.9)	49.4	(4.3)
C.08	1.3	1.6	(0.3)	1.6	(0.2)	−1.8	(−3.2)	−1.9	(−3.2)	−1.6	(−2.9)	−1.6	(−2.9)
C.10	−9.1	−9.3	(−0.2)	−9.1	(0.0)	−8.6	(0.5)	−8.2	(0.9)	−8.5	(0.6)	−8.3	(0.8)
N.01	16.6	17.8	(1.1)	17.7	(1.1)	19.8	(3.2)	19.7	(3.0)	15.1	(−1.6)	15.0	(−1.7)
N.02	17.9	17.9	(0.1)	17.8	(0.0)	19.6	(1.7)	19.3	(1.4)	14.4	(−3.4)	14.3	(−3.6)
N.03	−20.9	−22.6	(−1.7)	−22.4	(−1.5)	−22.3	(−1.4)	−21.8	(−0.9)	−23.8	(−2.9)	−23.5	(−2.6)
N.04	12.3	12.4	(0.1)	12.4	(0.1)	11.9	(−0.4)	12.1	(−0.2)	11.9	(−0.4)	12.0	(−0.3)
N.05	−12.0	−11.5	(0.5)	−11.6	(0.4)	−11.3	(0.7)	−11.3	(0.7)	−12.0	(0.0)	−12.0	(0.0)
N.06	32.0	31.9	(−0.2)	31.8	(−0.2)	25.8	(−6.3)	25.4	(−6.6)	34.3	(2.3)	34.1	(2.0)
N.07	57.1	64.9	(7.8)	65.1	(7.9)	69.7	(12.6)	70.1	(13.0)	63.1	(6.0)	63.3	(6.2)
N.08	−14.2	−14.4	(−0.3)	−14.4	(−0.3)	−16.9	(−2.8)	−16.9	(−2.8)	−16.6	(−2.4)	−16.6	(−2.4)
N.09	−31.8	−36.4	(−4.6)	−35.9	(−4.1)	−43.5	(−11.7)	−42.3	(−10.6)	−34.5	(−2.7)	−33.9	(−2.1)
O.01	15.8	15.8	(0.1)	15.9	(0.1)	17.1	(1.4)	17.1	(1.4)	13.3	(−2.4)	13.3	(−2.4)
O.02	25.2	25.9	(0.7)	25.9	(0.7)	26.8	(1.6)	26.7	(1.5)	22.8	(−2.4)	22.7	(−2.5)
O.03	−63.7	−63.4	(0.2)	−63.2	(0.5)	−59.3	(4.4)	−58.8	(4.9)	−62.3	(1.4)	−62.0	(1.7)
O.04	9.9	10.3	(0.4)	10.4	(0.5)	10.4	(0.5)	10.6	(0.8)	9.5	(−0.4)	9.7	(−0.2)
O.05	−12.4	−11.8	(0.6)	−11.8	(0.6)	−10.8	(1.6)	−10.8	(1.6)	−12.0	(0.3)	−12.0	(0.3)
O.06	27.4	27.4	(0.0)	27.5	(0.1)	22.3	(−5.1)	22.4	(−5.0)	29.9	(2.5)	29.9	(2.5)
O.07	58.8	65.7	(6.9)	65.8	(7.0)	69.4	(10.6)	69.6	(10.8)	64.0	(5.2)	64.1	(5.3)
O.08	19.6	21.4	(1.8)	21.6	(1.9)	23.4	(3.8)	23.9	(4.2)	19.4	(−0.3)	19.7	(0.0)
O.09	−11.5	−12.2	(−0.7)	−12.0	(−0.5)	−12.5	(−1.0)	−12.0	(−0.5)	−11.8	(−0.2)	−11.5	(0.1)
F.01	26.9	26.2	(−0.7)	26.4	(−0.5)	23.9	(−3.0)	24.3	(−2.7)	26.8	(−0.2)	26.9	(0.0)
F.02	1.0	1.0	(0.1)	1.0	(0.1)	0.9	(−0.1)	0.9	(0.0)	1.0	(0.1)	1.1	(0.1)
F.03	−2.7	−2.9	(−0.2)	−2.9	(−0.2)	−3.1	(−0.4)	−3.1	(−0.4)	−2.9	(−0.2)	−2.8	(−0.1)
Si.01	6.4	6.7	(0.2)	6.6	(0.1)	8.6	(2.1)	8.3	(1.9)	2.3	(−4.1)	2.2	(−4.3)
Si.02	−10.1	−10.4	(−0.3)	−10.4	(−0.4)	−8.7	(1.3)	−8.8	(1.2)	−12.9	(−2.9)	−13.0	(−2.9)
Si.03	−3.9	−5.8	(−1.9)	−5.4	(−1.5)	−6.1	(−2.2)	−5.0	(−1.1)	1.0	(4.8)	1.6	(5.4)
Si.04	28.2	28.2	(0.0)	28.3	(0.1)	26.8	(−1.4)	27.0	(−1.3)	28.0	(−0.2)	28.0	(−0.2)

		B2GP-PLYP				B3LYP				PBE0			
rct	ref.	with D3		without		with D3		without		with D3		without	
Si.05	33.4	32.7	(−0.7)	33.4	(−0.1)	31.3	(−2.1)	32.4	(−1.0)	32.4	(−1.0)	32.9	(−0.6)
Si.06	21.5	19.6	(−1.9)	19.6	(−1.9)	14.3	(−7.2)	14.0	(−7.4)	22.6	(1.1)	22.3	(0.9)
Si.07	28.9	34.4	(5.5)	34.5	(5.7)	39.6	(10.7)	40.0	(11.1)	30.3	(1.4)	30.5	(1.7)
Si.08	22.0	23.4	(1.4)	23.3	(1.4)	20.1	(−1.9)	19.9	(−2.1)	18.3	(−3.7)	18.1	(−3.9)
Si.09	−4.5	−7.3	(−2.8)	−7.3	(−2.8)	−9.3	(−4.8)	−9.4	(−4.9)	−10.5	(−6.0)	−10.6	(−6.1)
Si.10	153.7	155.1	(1.4)	155.2	(1.5)	149.5	(−4.2)	149.8	(−3.9)	146.7	(−7.1)	146.8	(−6.9)
P.01	−4.9	−4.8	(0.2)	−4.9	(0.1)	−2.2	(2.8)	−2.5	(2.5)	−7.9	(−2.9)	−8.1	(−3.1)
P.02	−1.7	−2.0	(−0.2)	−2.1	(−0.4)	−0.1	(1.6)	−0.4	(1.3)	−5.2	(−3.4)	−5.3	(−3.6)
P.03	23.0	21.8	(−1.2)	22.1	(−0.8)	19.4	(−3.5)	20.4	(−2.5)	22.1	(−0.8)	22.8	(−0.2)
P.04	26.1	26.2	(0.0)	26.2	(0.1)	24.7	(−1.5)	24.8	(−1.4)	25.6	(−0.6)	25.6	(−0.5)
P.05	10.8	10.8	(0.0)	11.1	(0.3)	9.6	(−1.2)	10.3	(−0.5)	10.3	(−0.5)	10.6	(−0.1)
P.06	6.6	7.1	(0.5)	7.1	(0.5)	−0.3	(−7.0)	−0.3	(−6.9)	10.1	(3.5)	10.1	(3.5)
P.07	35.3	41.7	(6.4)	41.7	(6.4)	47.4	(12.1)	47.5	(12.2)	39.1	(3.8)	39.1	(3.8)
P.08	−3.9	−3.1	(0.8)	−3.1	(0.7)	−5.8	(−1.9)	−5.8	(−2.0)	−6.4	(−2.5)	−6.4	(−2.5)
P.09	17.9	15.0	(−2.9)	15.7	(−2.2)	9.8	(−8.1)	11.3	(−6.6)	16.8	(−1.1)	17.5	(−0.3)
P.10	33.2	33.7	(0.5)	33.4	(0.3)	31.0	(−2.2)	30.1	(−3.1)	32.9	(−0.2)	32.3	(−0.8)
S.01	−2.6	−2.5	(0.1)	−2.5	(0.1)	0.4	(2.9)	0.2	(2.8)	−4.7	(−2.1)	−4.9	(−2.3)
S.02	−0.9	−0.9	(0.0)	−1.0	(−0.1)	1.2	(2.1)	0.9	(1.8)	−4.0	(−3.1)	−4.2	(−3.3)
S.03	6.6	7.7	(1.1)	7.9	(1.4)	8.4	(1.8)	8.9	(2.3)	8.4	(1.8)	8.6	(2.1)
S.04	19.8	19.7	(−0.1)	19.9	(0.2)	18.3	(−1.4)	18.8	(−0.9)	19.1	(−0.7)	19.4	(−0.4)
S.05	−1.2	−1.0	(0.2)	−0.8	(0.4)	−1.1	(0.1)	−0.6	(0.5)	−0.9	(0.3)	−0.7	(0.5)
S.06	35.5	35.6	(0.1)	35.5	(0.1)	28.1	(−7.3)	27.9	(−7.6)	37.2	(1.8)	37.1	(1.6)
S.07	47.1	54.3	(7.2)	54.2	(7.1)	59.7	(12.6)	59.6	(12.5)	52.5	(5.5)	52.5	(5.4)
S.08	11.9	13.8	(1.9)	14.0	(2.1)	16.5	(4.6)	17.1	(5.2)	11.6	(−0.3)	11.9	(0.0)
S.09	−3.0	−3.2	(−0.2)	−3.0	(0.0)	−3.0	(0.0)	−2.5	(0.6)	−2.6	(0.4)	−2.3	(0.7)
S.10	−15.2	−11.4	(3.8)	−10.6	(4.6)	−13.9	(1.3)	−11.9	(3.3)	−12.3	(2.9)	−11.3	(3.9)
Cl.01	−3.3	−3.6	(−0.3)	−3.6	(−0.3)	−4.7	(−1.4)	−4.6	(−1.4)	−3.9	(−0.6)	−3.8	(−0.6)
Cl.02	0.6	0.6	(0.0)	0.6	(0.1)	0.2	(−0.4)	0.3	(−0.3)	0.5	(−0.1)	0.6	(0.0)
Cl.03	−1.6	−1.9	(−0.2)	−1.8	(−0.2)	−2.5	(−0.8)	−2.4	(−0.7)	−2.0	(−0.4)	−2.0	(−0.3)
Ge.01	8.0	8.3	(0.3)	8.2	(0.2)	10.6	(2.6)	10.4	(2.3)	5.0	(−3.1)	4.8	(−3.2)
Ge.02	−7.4	−7.6	(−0.2)	−7.7	(−0.3)	−6.0	(1.4)	−6.2	(1.2)	−10.2	(−2.8)	−10.3	(−2.9)
Ge.03	14.2	14.0	(−0.3)	14.3	(0.1)	13.1	(−1.2)	14.0	(−0.2)	16.5	(2.3)	17.1	(2.9)
Ge.04	26.7	26.5	(−0.2)	26.6	(−0.1)	25.0	(−1.8)	25.2	(−1.5)	25.8	(−1.0)	25.9	(−0.9)
Ge.05	24.6	23.6	(−1.1)	24.3	(−0.3)	21.6	(−3.0)	23.0	(−1.6)	22.1	(−2.5)	22.7	(−1.9)
Ge.06	19.7	17.7	(−1.9)	17.7	(−2.0)	12.2	(−7.5)	11.9	(−7.8)	20.0	(0.4)	19.8	(0.1)
Ge.07	30.7	36.0	(5.3)	36.1	(5.4)	40.9	(10.2)	41.1	(10.4)	32.8	(2.1)	33.0	(2.3)
Ge.08	19.1	20.4	(1.3)	20.3	(1.2)	17.6	(−1.5)	17.3	(−1.7)	16.3	(−2.8)	16.2	(−2.9)
Ge.09	−2.3	−3.8	(−1.5)	−3.9	(−1.5)	−6.1	(−3.8)	−6.2	(−3.9)	−8.2	(−5.9)	−8.2	(−5.9)
Ge.10	93.5	93.9	(0.4)	94.1	(0.6)	89.0	(−4.4)	89.7	(−3.8)	87.0	(−6.5)	87.4	(−6.1)

		B2GP-PLYP				B3LYP				PBE0			
rct	ref.	with D3		without		with D3		without		with D3		without	
As.01	−7.9	−8.1	(−0.2)	−8.2	(−0.3)	−5.4	(2.5)	−5.8	(2.1)	−10.2	(−2.3)	−10.4	(−2.5)
As.02	−5.7	−6.3	(−0.6)	−6.4	(−0.7)	−4.8	(1.0)	−5.1	(0.6)	−9.0	(−3.3)	−9.2	(−3.5)
As.03	38.7	38.7	(0.1)	39.1	(0.4)	36.0	(−2.7)	37.1	(−1.6)	37.4	(−1.3)	38.1	(−0.6)
As.04	27.2	27.2	(−0.1)	27.3	(0.0)	25.5	(−1.7)	25.7	(−1.5)	26.1	(−1.2)	26.1	(−1.1)
As.05	9.8	9.5	(−0.3)	9.9	(0.2)	8.1	(−1.7)	9.1	(−0.7)	8.2	(−1.6)	8.7	(−1.0)
As.06	−4.8	−4.9	(−0.1)	−4.9	(−0.1)	−13.2	(−8.5)	−13.2	(−8.4)	−2.5	(2.3)	−2.5	(2.3)
As.07	33.0	38.9	(5.9)	39.0	(5.9)	44.3	(11.3)	44.4	(11.4)	36.9	(3.8)	36.9	(3.9)
As.08	−4.2	−3.6	(0.6)	−3.7	(0.5)	−5.8	(−1.6)	−6.0	(−1.8)	−6.3	(−2.1)	−6.4	(−2.2)
As.09	−3.1	−5.1	(−2.0)	−4.9	(−1.8)	−7.9	(−4.8)	−7.4	(−4.3)	−6.6	(−3.5)	−6.3	(−3.2)
As.10	−2.9	−4.0	(−1.1)	−4.1	(−1.2)	−7.0	(−4.1)	−7.4	(−4.5)	−4.0	(−1.1)	−4.4	(−1.5)
Se.01	−6.8	−6.9	(−0.2)	−7.0	(−0.2)	−3.9	(2.8)	−4.2	(2.6)	−8.3	(−1.5)	−8.4	(−1.7)
Se.02	−5.1	−5.4	(−0.2)	−5.5	(−0.4)	−3.6	(1.5)	−4.0	(1.2)	−8.0	(−2.8)	−8.2	(−3.0)
Se.03	16.0	17.0	(1.0)	17.3	(1.3)	17.5	(1.6)	18.2	(2.2)	17.1	(1.1)	17.4	(1.4)
Se.04	20.8	20.6	(−0.2)	20.9	(0.1)	19.0	(−1.8)	19.6	(−1.2)	19.5	(−1.3)	19.8	(−1.0)
Se.05	0.0	0.0	(0.0)	0.3	(0.2)	−0.2	(−0.3)	0.3	(0.3)	−0.3	(−0.4)	0.0	(0.0)
Se.06	32.8	32.6	(−0.2)	32.5	(−0.3)	25.1	(−7.8)	24.7	(−8.2)	33.7	(0.9)	33.5	(0.6)
Se.07	43.4	50.1	(6.7)	50.0	(6.7)	55.3	(12.0)	55.2	(11.9)	48.8	(5.5)	48.7	(5.3)
Se.08	10.7	12.6	(1.8)	12.8	(2.1)	15.3	(4.6)	16.0	(5.3)	10.3	(−0.4)	10.7	(0.0)
Se.09	−2.9	−3.2	(−0.3)	−3.0	(−0.1)	−2.5	(0.4)	−1.9	(0.9)	−2.3	(0.6)	−2.0	(0.9)
Se.10	−68.9	−67.0	(1.9)	−66.6	(2.3)	−67.8	(1.0)	−66.9	(2.0)	−69.7	(−0.9)	−69.2	(−0.4)
Br.01	−6.3	−6.4	(−0.1)	−6.3	(−0.1)	−7.8	(−1.5)	−7.7	(−1.4)	−7.1	(−0.8)	−7.0	(−0.7)
Br.02	0.1	0.0	(−0.1)	0.0	(0.0)	−0.6	(−0.7)	−0.5	(−0.5)	−0.1	(−0.2)	−0.1	(−0.1)
Br.03	−1.6	−1.8	(−0.2)	−1.9	(−0.2)	−2.5	(−0.9)	−2.5	(−0.9)	−2.1	(−0.5)	−2.1	(−0.4)
$\overline{X}$			0.5		0.6		0.0		0.2		−0.5		−0.5
$\overline{\lvert X\rvert}$			1.3		1.3		3.5		3.5		2.0		2.0
$\widetilde{\lvert X\rvert}$			0.4		0.4		2.0		2.0		1.7		1.7
$x_{\max}$			7.8		7.9		12.6		13.0		6.0		6.2
$x_{\min}$			−4.6		−4.1		−11.7		−10.6		−7.1		−6.9

Table 9: Reference isomerization energies based on RI-SCS-MP2(pFC)/cc-p(wC)V5Z computations with CCSD(T)(pFC)/cc-p(wC)TZ corrrections for higher correlation contributions in comarison to density functionals with and without dispersion correction (same basis set). Deviations are given in parentheses. The mean deviation ($\overline{x}$), the mean absolute deviation ($\overline{|x|}$), the median of the absolute deviation($\widetilde{|x|}$), the maximum ($x_{\max}$) and minimum deviation ($x_{\min}$) are given at the end. All values in kcal mol^{-1}.

		PW6B95				oTPSS				ωB97X-D			
rct	ref.	with D3		without		with D3		without		with D3		without	
C.01	5.9	3.3	(−2.6)	3.3	(−2.6)	3.6	(−2.3)	3.5	(−2.4)	2.3	(−3.6)	2.2	(−3.7)
C.04	17.7	16.5	(−1.2)	16.5	(−1.2)	15.3	(−2.4)	15.2	(−2.5)	16.8	(−0.9)	16.8	(−0.9)
C.05	3.8	2.5	(−1.2)	1.8	(−1.9)	2.4	(−1.4)	0.7	(−3.1)	3.2	(−0.5)	2.6	(−1.2)
C.06	18.9	17.9	(−1.0)	17.6	(−1.3)	15.5	(−3.4)	14.4	(−4.5)	21.8	(2.9)	21.1	(2.2)
C.07	45.1	49.3	(4.1)	49.6	(4.4)	50.7	(5.5)	51.6	(6.5)	48.9	(3.8)	49.2	(4.0)
C.08	1.3	−1.4	(−2.7)	−1.4	(−2.7)	−1.5	(−2.9)	−1.5	(−2.9)	−0.3	(−1.6)	−0.3	(−1.6)
C.10	−9.1	−8.4	(0.7)	−8.2	(0.9)	−8.6	(0.5)	−8.1	(1.0)	−9.8	(−0.7)	−9.6	(−0.5)
N.01	16.6	15.8	(−0.9)	15.7	(−1.0)	17.0	(0.4)	16.8	(0.2)	14.8	(−1.8)	14.7	(−1.9)
N.02	17.9	15.4	(−2.5)	15.3	(−2.6)	16.5	(−1.4)	16.2	(−1.7)	15.1	(−2.8)	14.9	(−3.0)
N.03	−20.9	−22.7	(−1.8)	−22.5	(−1.6)	−24.5	(−3.5)	−23.9	(−3.0)	−21.6	(−0.7)	−21.5	(−0.5)
N.04	12.3	11.4	(−0.9)	11.5	(−0.8)	10.0	(−2.3)	10.0	(−2.3)	11.4	(−0.9)	11.3	(−1.0)
N.05	−12.0	−11.2	(0.8)	−11.2	(0.8)	−12.4	(−0.4)	−12.4	(−0.4)	−11.7	(0.3)	−11.7	(0.3)
N.06	32.0	31.7	(−0.4)	31.6	(−0.4)	28.1	(−4.0)	27.4	(−4.6)	35.7	(3.7)	35.2	(3.2)
N.07	57.1	62.8	(5.7)	63.0	(5.8)	65.2	(8.1)	65.9	(8.7)	62.1	(4.9)	62.2	(5.1)
N.08	−14.2	−16.5	(−2.4)	−16.5	(−2.4)	−18.2	(−4.0)	−18.2	(−4.0)	−15.6	(−1.4)	−15.6	(−1.4)
N.09	−31.8	−35.0	(−3.2)	−34.3	(−2.6)	−40.2	(−8.5)	−39.2	(−7.4)	−35.4	(−3.6)	−35.2	(−3.4)
O.01	15.8	13.6	(−2.1)	13.7	(−2.1)	14.2	(−1.5)	14.2	(−1.5)	13.4	(−2.3)	13.3	(−2.4)
O.02	25.2	23.1	(−2.1)	23.0	(−2.2)	24.0	(−1.2)	23.9	(−1.3)	23.9	(−1.3)	23.7	(−1.5)
O.03	−63.7	−61.2	(2.5)	−61.0	(2.7)	−60.5	(3.2)	−59.9	(3.8)	−62.4	(1.3)	−62.3	(1.4)
O.04	9.9	9.7	(−0.2)	9.8	(−0.1)	8.0	(−1.9)	8.2	(−1.7)	9.1	(−0.8)	9.2	(−0.7)
O.05	−12.4	−11.1	(1.3)	−11.1	(1.3)	−11.8	(0.5)	−11.7	(0.6)	−11.9	(0.4)	−11.8	(0.5)
O.06	27.4	27.8	(0.4)	27.9	(0.5)	24.6	(−2.8)	24.5	(−2.9)	31.3	(3.9)	31.0	(3.6)
O.07	58.8	63.1	(4.3)	63.2	(4.4)	65.5	(6.7)	65.8	(7.0)	62.8	(4.0)	62.9	(4.1)
O.08	19.6	20.6	(0.9)	20.8	(1.1)	24.8	(5.2)	25.4	(5.7)	20.8	(1.2)	21.1	(1.4)
O.09	−11.5	−11.6	(0.0)	−11.3	(0.2)	−12.2	(−0.7)	−11.6	(−0.1)	−13.2	(−1.7)	−13.1	(−1.6)
F.01	26.9	25.6	(−1.3)	25.8	(−1.1)	24.9	(−2.0)	25.2	(−1.7)	26.9	(−0.1)	26.8	(−0.1)
F.02	1.0	1.0	(0.0)	1.0	(0.0)	1.1	(0.1)	1.2	(0.2)	0.9	(−0.1)	1.0	(0.0)
F.03	−2.7	−2.8	(−0.2)	−2.8	(−0.1)	−3.0	(−0.4)	−2.9	(−0.3)	−3.0	(−0.3)	−2.9	(−0.3)
Si.01	6.4	4.3	(−2.1)	4.2	(−2.2)	4.7	(−1.8)	4.4	(−2.0)	3.6	(−2.8)	3.5	(−2.9)
Si.02	−10.1	−12.3	(−2.3)	−12.4	(−2.3)	−11.4	(−1.3)	−11.5	(−1.4)	−13.8	(−3.8)	−13.9	(−3.8)
Si.03	−3.9	−2.5	(1.4)	−2.0	(1.9)	−1.4	(2.5)	−0.3	(3.6)	−3.6	(0.3)	−3.2	(0.6)
Si.04	28.2	27.1	(−1.1)	27.2	(−1.0)	26.2	(−2.0)	26.3	(−1.9)	27.2	(−1.0)	27.2	(−1.0)

		PW6B95				oTPSS				ωB97X-D			
rct	ref.	with D3		without		with D3		without		with D3		without	
Si.05	33.4	32.6	(−0.8)	33.2	(−0.2)	35.4	(2.0)	36.4	(3.0)	32.8	(−0.6)	32.5	(−1.0)
Si.06	21.5	19.9	(−1.6)	19.8	(−1.7)	17.2	(−4.2)	16.8	(−4.7)	23.0	(1.5)	22.6	(1.1)
Si.07	28.9	30.8	(1.9)	30.9	(2.0)	32.7	(3.8)	33.2	(4.3)	31.6	(2.7)	31.8	(2.9)
Si.08	22.0	19.9	(−2.1)	19.8	(−2.2)	19.7	(−2.3)	19.5	(−2.5)	21.6	(−0.4)	21.6	(−0.4)
Si.09	−4.5	−10.0	(−5.5)	−10.0	(−5.5)	−7.5	(−3.0)	−7.6	(−3.1)	−12.7	(−8.2)	−12.8	(−8.3)
Si.10	153.7	150.1	(−3.6)	150.2	(−3.5)	149.7	(−4.0)	150.0	(−3.8)	147.2	(−6.5)	147.2	(−6.5)
P.01	−4.9	−6.6	(−1.7)	−6.8	(−1.8)	−5.8	(−0.9)	−6.1	(−1.2)	−7.0	(−2.1)	−7.1	(−2.2)
P.02	−1.7	−4.4	(−2.6)	−4.5	(−2.8)	−3.5	(−1.8)	−3.9	(−2.1)	−5.2	(−3.5)	−5.3	(−3.6)
P.03	23.0	21.3	(−1.6)	21.8	(−1.2)	20.8	(−2.1)	21.9	(−1.0)	20.2	(−2.8)	20.6	(−2.3)
P.04	26.1	24.9	(−1.3)	24.9	(−1.2)	23.7	(−2.4)	23.8	(−2.4)	24.9	(−1.3)	24.9	(−1.3)
P.05	10.8	10.6	(−0.1)	11.0	(0.2)	10.9	(0.1)	11.6	(0.9)	10.5	(−0.3)	10.5	(−0.2)
P.06	6.6	6.7	(0.1)	6.8	(0.1)	6.0	(−0.6)	5.9	(−0.7)	8.9	(2.3)	8.8	(2.1)
P.07	35.3	39.1	(3.8)	39.1	(3.8)	41.6	(6.3)	41.9	(6.6)	39.5	(4.2)	39.5	(4.2)
P.08	−3.9	−5.6	(−1.8)	−5.7	(−1.8)	−6.0	(−2.1)	−6.0	(−2.1)	−4.0	(−0.1)	−4.0	(−0.1)
P.09	17.9	16.1	(−1.8)	16.8	(−1.0)	13.0	(−4.9)	14.5	(−3.4)	18.3	(0.4)	18.8	(0.9)
P.10	33.2	31.3	(−1.8)	31.0	(−2.2)	35.6	(2.4)	34.3	(1.2)	33.4	(0.2)	32.8	(−0.4)
S.01	−2.6	−4.0	(−1.5)	−4.1	(−1.5)	−2.7	(−0.1)	−3.0	(−0.4)	−4.3	(−1.7)	−4.5	(−1.9)
S.02	−0.9	−3.4	(−2.5)	−3.5	(−2.6)	−2.2	(−1.3)	−2.6	(−1.7)	−3.6	(−2.6)	−3.8	(−2.8)
S.03	6.6	9.0	(2.4)	9.3	(2.7)	9.0	(2.5)	9.5	(2.9)	7.2	(0.6)	7.2	(0.6)
S.04	19.8	18.6	(−1.2)	18.9	(−0.9)	17.0	(−2.8)	17.4	(−2.3)	18.3	(−1.4)	18.4	(−1.4)
S.05	−1.2	−0.6	(0.5)	−0.4	(0.8)	−0.8	(0.3)	−0.4	(0.8)	−1.0	(0.2)	−0.9	(0.2)
S.06	35.5	34.4	(−1.0)	34.4	(−1.1)	31.5	(−3.9)	31.1	(−4.4)	37.6	(2.2)	37.3	(1.9)
S.07	47.1	52.1	(5.0)	52.0	(5.0)	55.1	(8.0)	55.2	(8.1)	51.9	(4.9)	51.9	(4.9)
S.08	11.9	13.0	(1.2)	13.3	(1.4)	17.9	(6.0)	18.6	(6.7)	12.5	(0.6)	12.7	(0.9)
S.09	−3.0	−2.4	(0.7)	−2.1	(0.9)	−2.6	(0.4)	−2.1	(0.9)	−2.9	(0.1)	−2.8	(0.3)
S.10	−15.2	−11.8	(3.4)	−10.9	(4.3)	−7.1	(8.1)	−5.1	(10.1)	−11.3	(3.9)	−11.0	(4.2)
Cl.01	−3.3	−3.9	(−0.6)	−3.8	(−0.5)	−3.7	(−0.4)	−3.7	(−0.4)	−4.1	(−0.8)	−4.2	(−0.9)
Cl.02	0.6	0.6	(0.0)	0.6	(0.1)	0.3	(−0.3)	0.5	(−0.1)	0.6	(0.0)	0.7	(0.1)
Cl.03	−1.6	−1.8	(−0.1)	−1.8	(−0.1)	−2.4	(−0.7)	−2.2	(−0.6)	−2.0	(−0.4)	−1.9	(−0.3)
Ge.01	8.0	6.6	(−1.4)	6.5	(−1.5)	7.2	(−0.8)	6.9	(−1.1)	6.6	(−1.4)	6.5	(−1.5)
Ge.02	−7.4	−9.8	(−2.4)	−9.9	(−2.5)	−8.8	(−1.4)	−8.9	(−1.5)	−10.7	(−3.3)	−10.7	(−3.4)
Ge.03	14.2	14.6	(0.4)	15.1	(0.9)	12.8	(−1.4)	13.9	(−0.3)	11.8	(−2.4)	12.3	(−2.0)
Ge.04	26.7	24.9	(−1.8)	25.1	(−1.7)	24.1	(−2.7)	24.3	(−2.5)	24.9	(−1.8)	24.9	(−1.8)
Ge.05	24.6	22.6	(−2.0)	23.4	(−1.2)	25.2	(0.6)	26.7	(2.0)	22.1	(−2.5)	22.0	(−2.6)
Ge.06	19.7	17.3	(−2.3)	17.2	(−2.4)	15.0	(−4.6)	14.6	(−5.1)	20.2	(0.5)	19.8	(0.2)
Ge.07	30.7	33.0	(2.4)	33.1	(2.4)	34.9	(4.2)	35.3	(4.7)	34.5	(3.8)	34.7	(4.0)
Ge.08	19.1	17.8	(−1.3)	17.7	(−1.4)	17.8	(−1.3)	17.5	(−1.6)	19.7	(0.6)	19.6	(0.6)
Ge.09	−2.3	−7.6	(−5.2)	−7.6	(−5.3)	−5.4	(−3.1)	−5.5	(−3.2)	−10.1	(−7.8)	−10.1	(−7.8)
Ge.10	93.5	89.4	(−4.1)	89.7	(−3.8)	92.2	(−1.3)	92.8	(−0.7)	87.5	(−5.9)	87.6	(−5.9)

		PW6B95				oTPSS				ωB97X-D			
rct	ref.	with D3		without		with D3		without		with D3		without	
As.01	−7.9	−9.2	(−1.3)	−9.3	(−1.5)	−7.8	(0.0)	−8.2	(−0.3)	−8.6	(−0.8)	−8.8	(−0.9)
As.02	−5.7	−8.6	(−2.9)	−8.7	(−3.0)	−7.2	(−1.5)	−7.6	(−1.9)	−8.4	(−2.7)	−8.5	(−2.8)
As.03	38.7	37.1	(−1.6)	37.5	(−1.2)	34.1	(−4.6)	35.3	(−3.4)	34.4	(−4.3)	34.9	(−3.8)
As.04	27.2	25.5	(−1.8)	25.6	(−1.7)	24.3	(−2.9)	24.4	(−2.8)	25.2	(−2.1)	25.2	(−2.0)
As.05	9.8	8.9	(−0.9)	9.3	(−0.4)	9.7	(−0.1)	10.7	(1.0)	8.3	(−1.5)	8.4	(−1.4)
As.06	−4.8	−6.2	(−1.4)	−6.2	(−1.4)	−7.8	(−3.0)	−7.8	(−3.0)	−4.4	(0.4)	−4.5	(0.2)
As.07	33.0	36.6	(3.6)	36.6	(3.6)	39.1	(6.0)	39.3	(6.2)	37.6	(4.6)	37.6	(4.5)
As.08	−4.2	−5.5	(−1.3)	−5.6	(−1.4)	−5.5	(−1.3)	−5.6	(−1.4)	−3.7	(0.5)	−3.7	(0.5)
As.09	−3.1	−6.0	(−2.9)	−5.8	(−2.7)	−6.8	(−3.7)	−6.1	(−3.0)	−4.8	(−1.7)	−4.5	(−1.4)
As.10	−2.9	−6.2	(−3.3)	−6.3	(−3.3)	−1.1	(1.8)	−1.7	(1.2)	−3.9	(−1.0)	−4.4	(−1.5)
Se.01	−6.8	−7.7	(−1.0)	−7.8	(−1.1)	−5.5	(1.3)	−5.8	(1.0)	−7.4	(−0.6)	−7.5	(−0.8)
Se.02	−5.1	−7.7	(−2.5)	−7.8	(−2.7)	−6.0	(−0.8)	−6.4	(−1.3)	−7.3	(−2.2)	−7.5	(−2.4)
Se.03	16.0	18.0	(2.0)	18.3	(2.3)	17.6	(1.6)	18.3	(2.3)	15.7	(−0.3)	15.7	(−0.3)
Se.04	20.8	19.2	(−1.7)	19.5	(−1.4)	17.5	(−3.3)	18.1	(−2.8)	18.6	(−2.2)	18.7	(−2.1)
Se.05	0.0	0.1	(0.1)	0.4	(0.3)	0.1	(0.1)	0.7	(0.7)	−0.4	(−0.4)	−0.3	(−0.3)
Se.06	32.8	31.0	(−1.9)	30.8	(−2.0)	28.3	(−4.6)	27.7	(−5.2)	33.8	(0.9)	33.4	(0.6)
Se.07	43.4	48.2	(4.8)	48.1	(4.7)	51.2	(7.9)	51.3	(7.9)	48.6	(5.3)	48.6	(5.3)
Se.08	10.7	11.7	(1.0)	12.1	(1.3)	16.6	(5.9)	17.5	(6.7)	11.3	(0.6)	11.6	(0.9)
Se.09	−2.9	−1.8	(1.0)	−1.6	(1.3)	−1.5	(1.3)	−1.0	(1.9)	−2.0	(0.8)	−1.9	(1.0)
Se.10	−68.9	−68.9	(0.0)	−68.5	(0.4)	−55.7	(13.2)	−54.7	(14.2)	−67.1	(1.7)	−67.0	(1.9)
Br.01	−6.3	−6.8	(−0.6)	−6.7	(−0.5)	−6.6	(−0.3)	−6.5	(−0.2)	−7.3	(−1.1)	−7.3	(−1.1)
Br.02	0.1	0.0	(−0.1)	0.0	(−0.1)	−0.4	(−0.5)	−0.2	(−0.3)	0.0	(0.0)	0.2	(0.1)
Br.03	−1.6	−1.8	(−0.1)	−1.8	(−0.2)	−2.3	(−0.6)	−2.2	(−0.6)	−2.0	(−0.4)	−1.9	(−0.3)
$\overline{X}$			−0.6		−0.5		−0.2		0.0		−0.4		−0.5
$\overline{\lvert X\rvert}$			1.8		1.8		2.7		2.8		1.9		2.0
$\widetilde{\lvert X\rvert}$			1.6		1.5		2.1		2.2		1.4		1.4
$x_{\max}$			5.7		5.8		13.2		14.2		5.3		5.3
$x_{\min}$			−5.5		−5.5		−8.5		−7.4		−8.2		−8.3

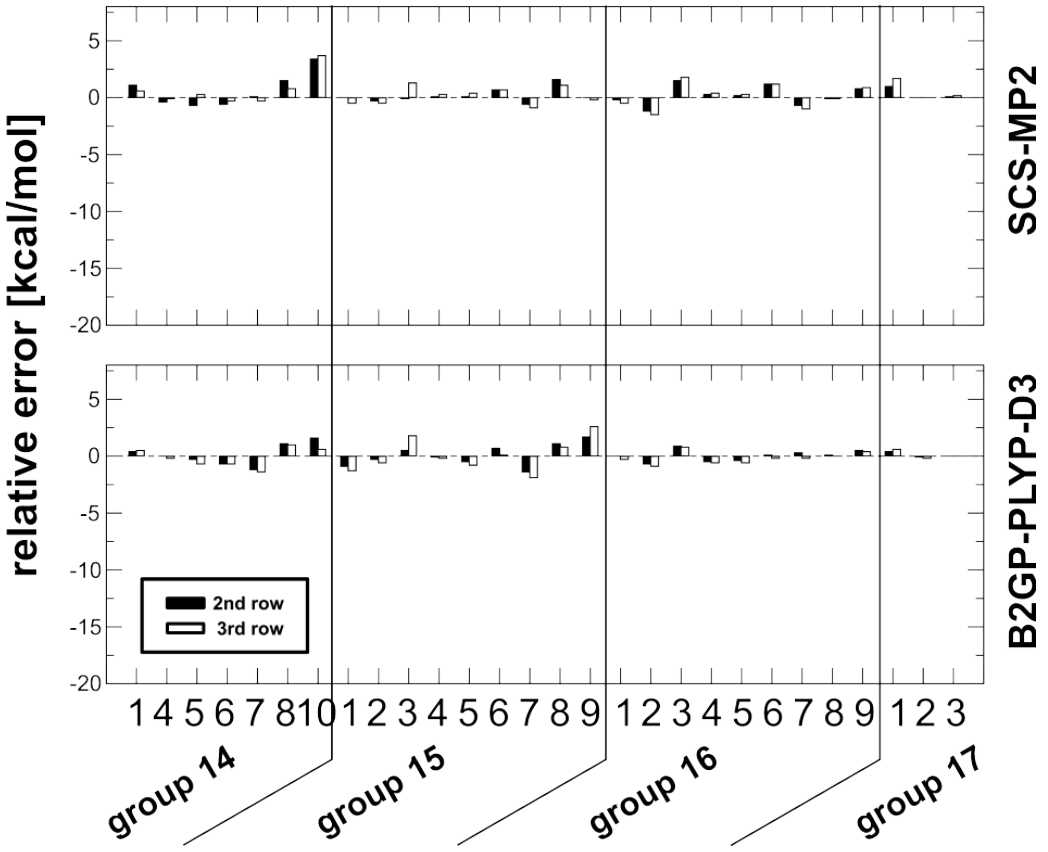

Figure 1: Relative change in deviations with respect to first row results for a given isomerization reaction set plotted for SCS-MP2 and B2GP-PLYP-D3.

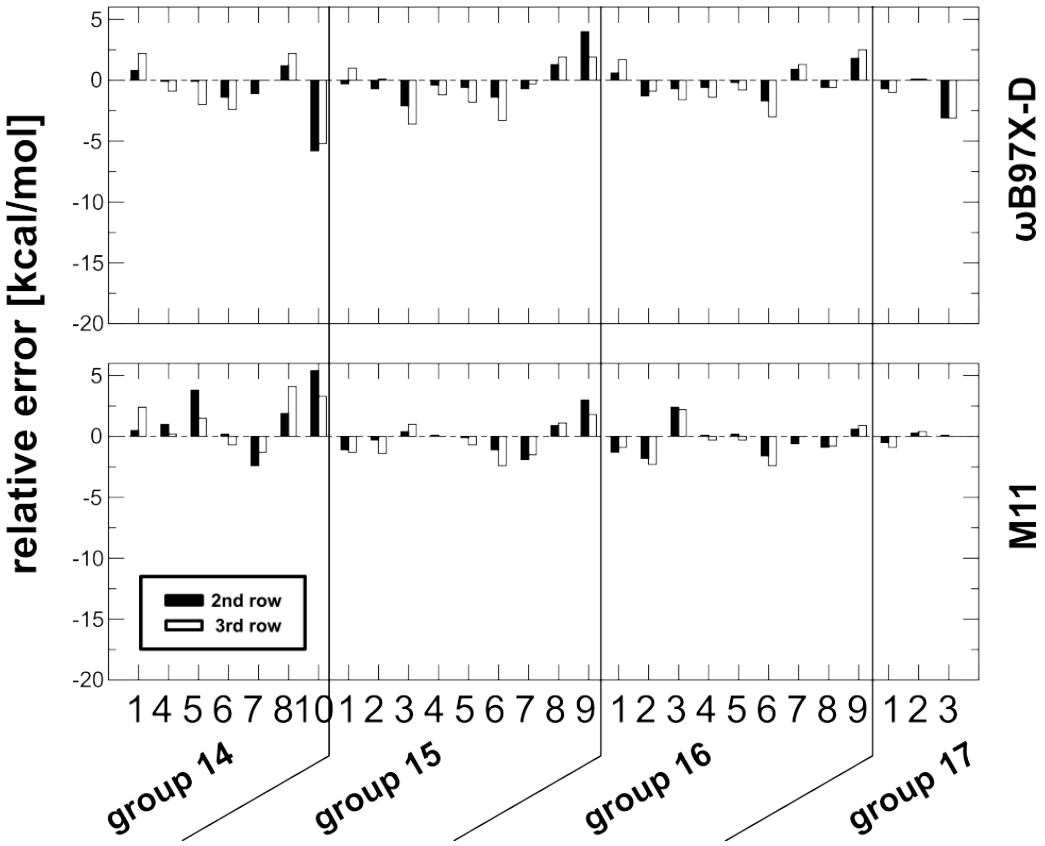

Figure 2: Relative change in deviations with respect to first row results for a given isomerization reaction set plotted for ωB97X-D and M11.

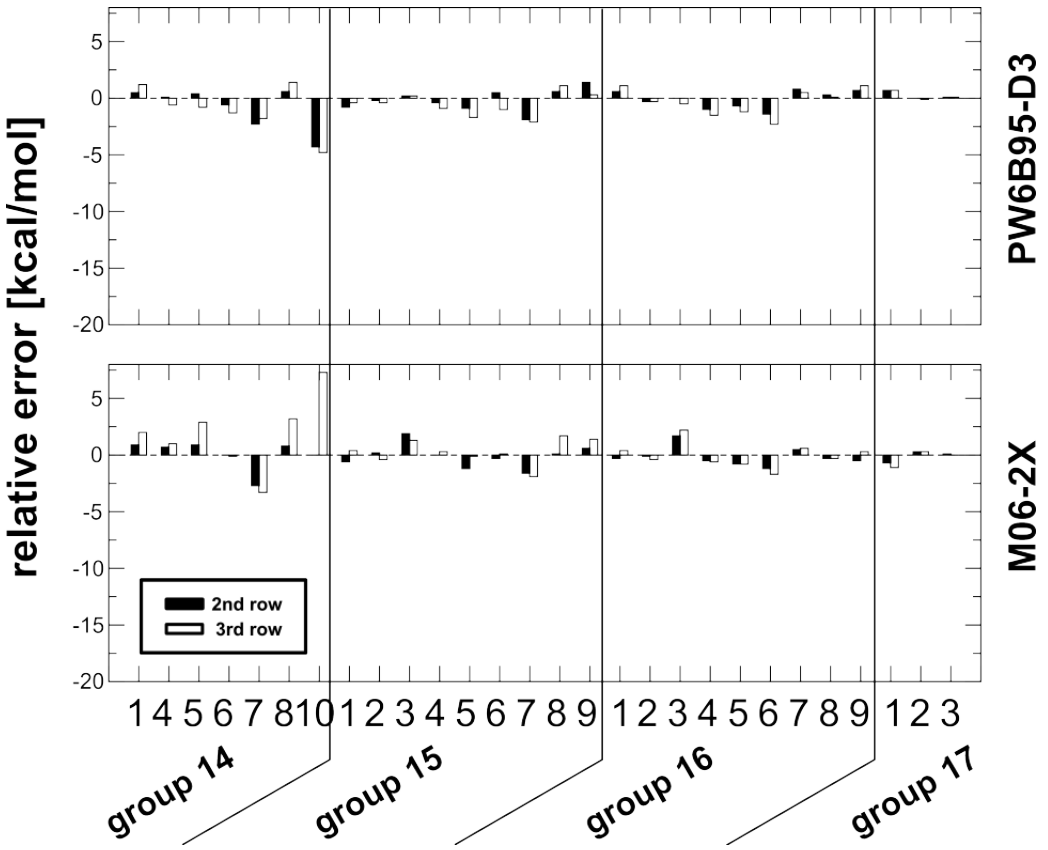

Figure 3: Relative change in deviations with respect to first row results for a given isomerization reaction set plotted for PW6B95-D3 and M06-2X.

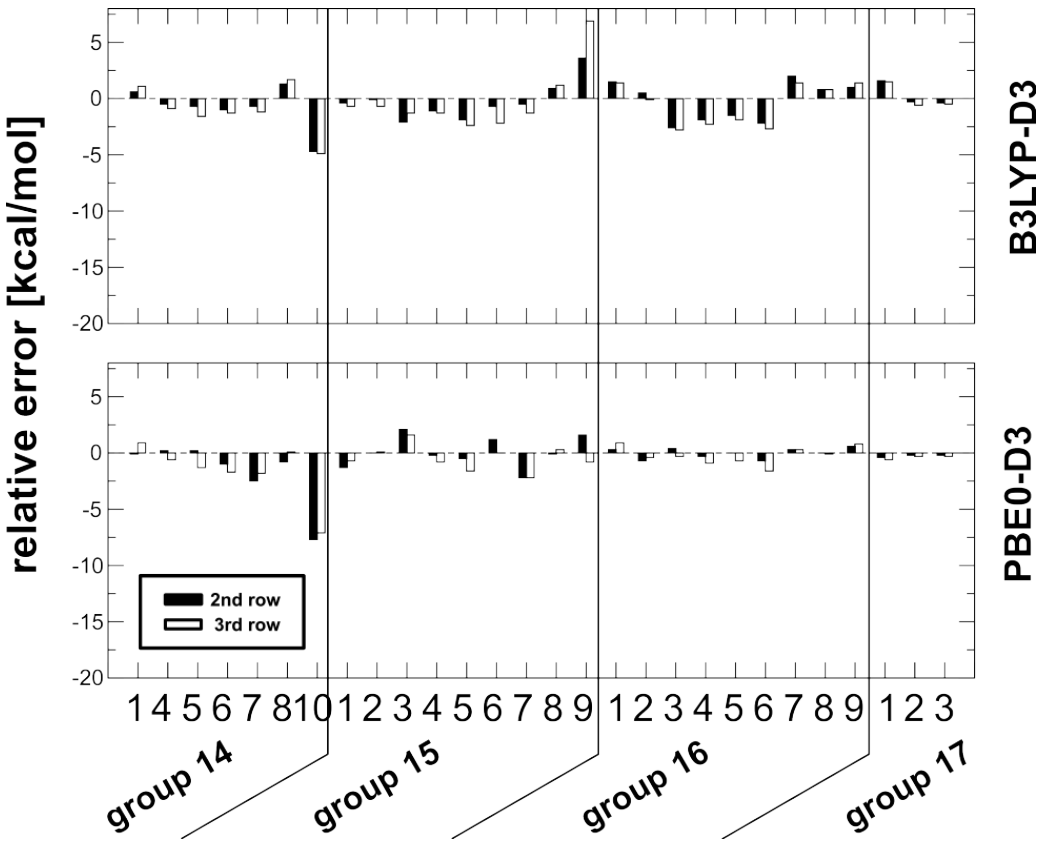

Figure 4: Relative change in deviations with respect to first row results for a given isomerization reaction set plotted for B3LYP-D3 and PBE0-D3.

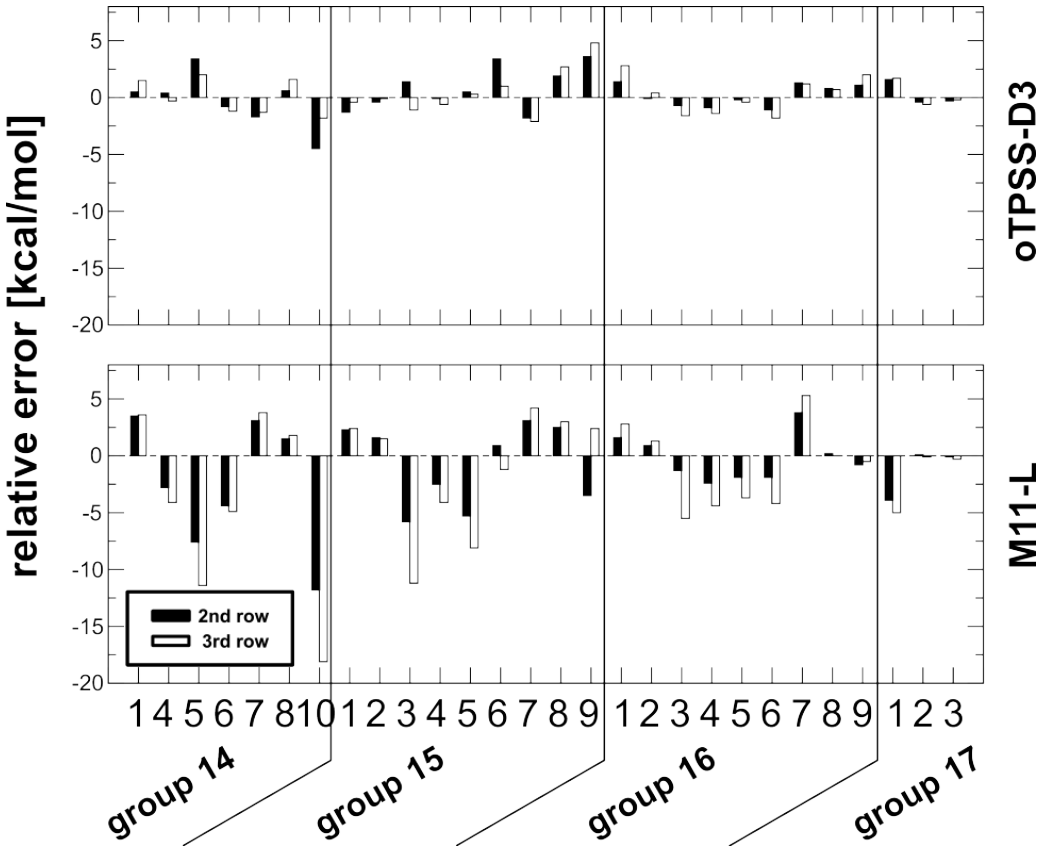

Figure 5: Relative change in deviations with respect to first row results for a given isomerization reaction set plotted for oTPSS-D3 and M11-L.