Comprehensive thermochemical benchmark set of realistic closed-shell metal organic reactions

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Statistical measure for a set $\{x_1, \dots, x_n\}$ of data points with references $\{r_1, \dots, r_n\}$ are

- Mean deviation (MD): $MD = \frac{1}{n}\sum_i \ (x_i - r_i)$
- Mean absolute deviation (MAD): $MAD = \frac{1}{n}\sum_i \ |x_i - r_i|$
- Root mean square deviation (RMSD): $RMSD = \sqrt{\frac{1}{n}\sum_i \ |x_i - r_i|^2}$
- Maximum absolute deviation (MAXADEV): $MAXADEV = \ \max\{|x_i - r_i|\}$

Reactions of the MOR41 set:

All geometries can be found as *.xyz coordinates in the structure archive file.

The MOR41 set consists of the following reactions in the given stoichiometry.

Table S 1: All 41 Reaction of the MOR41 set. The reference energies are given in [kcal/mol]. The molecules are named according to their name in the structure archive file.

Reaction					**Reference [kcal/mol]**
1.	-1 x ED01	-1 x CO	1 x PR01		-43.1
2.	-1 x ED02	-1 x CO	1 x PR02		-46.6
3.	-1 x ED03	-1 x CO	1 x PR03		-27.6
4.	-1 x ED04	-1 x CO	1 x PR04		-62.5
5.	-1 x ED05	-1 x CO	1 x PR05		3.7
6.	-1 x ED01	-1 x H2	1 x PR06		-23.2
7.	-1 x ED07	-1 x H2	1 x PR07		-16.2
8.	-1 x ED08	-1 x H2	1 x PR08		-17.2
9.	-1 x ED09	-1 x H2	1 x PR09		-18.7
10.	-1 x ED10	-1 x C3H8	1 x PR10		-22.6
11.	-1 x ED11	-1 x C2H6	1 x PR11		27.0
12.	-1 x ED01	-1 x C2H4	1 x PR12		-29.8
13.	-1 x ED13	-1 x C2H4	1 x PR13		-43.2
14.	-1 x ED14	-1 x COD	1 x PR14		-52.0
15.	-1 x ED15	-1 x CO2	1 x PR15		-4.1
16.	-1 x ED16a	-1 x ED16b	1 x PR16		-39.8
17.	-1 x ED17	-1 x MeOH	1 x PR17		-16.1
18.	-1 x ED18	-1 x MeI	1 x PR18		-34.2
19.	-1 x ED18	-1 x AcI	1 x PR19		-40.1
20.	-1 x ED18	-1 x AcCl	1 x PR20		-30.2
21.	-1 x ED21	-1 x MeI	1 x PR21		-15.1
22.	-1 x ED22	-1 x I2	1 x PR22		-35.9
23.	-1 x ED18	-1 x I2	1 x PR23		-55.0
24.	-1 x ED24	-1 x PCy3	1 x PR24		-41.6
25.	-1 x ED25	-1 x PCy3	1 x PR25		-45.9
26.	-1 x ED26	-2 x PMe3	1 x PR26	1 x COD	-36.4
27.	-1 x ED26	-1 x ED27	1 x PR27	1 x COD	-21.8
28.	-1 x ED26	-1 x ED28	1 x PR28	1 x COD	-36.3
29.	-1 x ED29	-1 x ED28	1 x PR29	1 x COD	-28.3
30.	-1 x ED29	-1 x ED30	1 x PR30	1 x COD	-14.0
31.	-1 x ED29	-1 x ED31	1 x PR31	1 x COD	-29.9
32.	-1 x ED32	-1 x COD	1 x PR32	2 x C2H4	-1.8
33.	-1 x ED33	-1 x PhOH	1 x PR33	1 x C2H4	-10.7
34.	-1 x ED33	-1 x PhSH	1 x PR34	1 x C2H4	-25.6
35.	-1 x ED33	-1 x PhSeH	1 x PR35	1 x C2H4	-30.9
36.	-1 x ED36	-1 x I2	1 x PR36	1 x C2H4	-39.8
37.	-1 x ED37	-3 x MeCN	1 x PR37	1 x Bz	-14.0
38.	-1 x ED37	-3 x PMe3	1 x PR38	1 x Bz	-64.4
39.	-2 x ED39	1 x PR39			-63.9
40.	-1 x ED40a	-1 x ED40b	1 x PR40		-65.8
41.	-1 x ED41	1 x PR41			-3.2

Calculated energies for all reactions and tested methods:

Pure GGA functionals

Table S 2: Calculated reaction energies for pure GGA functionals. All values are given in [kcal/mol] D3(BJ): D3 applied with Becke-Johnson damping. All calculations were performed with the def2-QZVPP basis set.

Reaction	B97-D	B97-D3(BJ)	BLYP	BLYP-D3(BJ)	BLYP-NL	BP86	BP86-D3(BJ)	LC-BLYP	MPWLYP	MPWLYP-D3(BJ)
1	-34.4	-40.7	-35.8	-41.6	-43.8	-42.0	-46.8	-44.8	-37.5	-40.6
2	-37.1	-42.8	-37.6	-42.8	-45.5	-45.4	-49.6	-49.7	-39.2	-41.9
3	-20.9	-25.2	-21.8	-25.8	-28.3	-27.9	-31.2	-30.0	-23.2	-25.3
4	-62.4	-68.9	-62.1	-67.6	-69.9	-70.0	-74.3	-68.2	-64.0	-66.8
5	3.5	-2.2	2.3	-2.9	-4.4	-1.8	-6.1	1.6	0.5	-2.3
6	-11.8	-13.6	-13.3	-14.2	-18.2	-17.6	-18.2	-24.8	-14.8	-15.5
7	-7.7	-10.0	-9.5	-9.7	-14.4	-12.9	-12.3	-19.1	-11.0	-11.3
8	-3.2	-10.0	-4.4	-10.0	-10.3	-9.4	-14.0	-20.4	-5.8	-9.2
9	-18.4	-7.9	-20.7	-9.4	-12.9	-21.2	-10.0	-27.0	-20.8	-13.0
10	-6.0	-18.9	-8.7	-20.6	-23.2	-15.8	-26.2	-20.6	-10.9	-18.1
11	39.7	24.6	37.2	22.7	22.7	33.6	20.8	32.6	34.7	26.2
12	-13.7	-22.0	-15.0	-22.2	-27.5	-23.0	-28.9	-28.7	-17.2	-21.4
13	-28.1	-38.5	-29.0	-38.4	-41.8	-37.4	-45.4	-43.0	-31.1	-36.4
14	-24.3	-41.3	-26.8	-43.1	-49.2	-38.9	-53.5	-48.3	-29.9	-40.0
15	5.7	3.3	2.3	0.8	-1.6	3.4	2.3	-10.0	0.5	-0.4
16	-3.4	-37.8	-8.0	-39.9	-40.1	-17.5	-46.2	-36.7	-12.9	-33.2
17	1.5	-6.3	-3.4	-8.9	-17.9	-6.3	-10.8	-19.9	-6.2	-10.2
18	-8.4	-28.9	-10.0	-31.1	-29.3	-18.0	-37.2	-29.3	-12.9	-24.5
19	-9.3	-33.1	-10.9	-35.4	-33.4	-19.5	-41.8	-34.7	-14.2	-27.9
20	-4.0	-25.7	-7.1	-28.3	-27.3	-13.2	-32.0	-27.3	-10.4	-22.4
21	5.0	-15.4	2.0	-17.8	-17.4	-4.7	-22.2	-11.6	-1.5	-12.5
22	-12.2	-30.2	-11.5	-32.1	-30.4	-20.4	-40.5	-23.4	-13.7	-25.4
23	-24.4	-47.2	-24.7	-49.9	-46.3	-34.2	-57.7	-46.5	-27.6	-40.9
24	2.4	-39.8	-0.3	-41.5	-37.9	-10.0	-48.4	-32.4	-5.6	-32.3
25	4.5	-44.8	1.4	-46.5	-42.9	-9.8	-54.2	-35.2	-4.9	-36.3
26	-27.8	-42.0	-26.3	-41.3	-31.7	-25.5	-40.0	-35.3	-28.6	-38.0
27	-27.8	-26.7	-24.0	-25.3	-17.2	-21.4	-24.0	-21.6	-23.5	-24.7
28	-36.6	-41.2	-33.4	-40.1	-31.2	-32.0	-39.3	-35.5	-33.5	-37.7
29	-28.8	-32.3	-26.8	-31.6	-24.2	-25.4	-30.5	-27.3	-26.7	-29.7
30	-20.1	-24.0	-19.9	-25.7	-17.0	-17.0	-23.4	-11.3	-19.5	-23.0
31	-31.8	-32.0	-30.0	-31.9	-23.9	-26.4	-29.2	-27.8	-29.4	-30.8
32	-1.1	1.0	0.1	0.9	0.1	-0.1	0.1	2.4	1.5	2.0
33	-13.7	-15.9	-15.5	-18.4	-16.0	-8.6	-12.2	-12.9	-15.7	-18.6
34	-22.4	-28.8	-22.5	-30.2	-25.5	-20.4	-28.3	-21.9	-22.6	-27.7
35	-26.2	-33.0	-25.8	-34.7	-29.5	-24.3	-33.4	-25.7	-26.0	-31.4
36	-32.6	-37.9	-31.9	-39.8	-35.0	-30.4	-38.6	-30.2	-32.1	-35.8
37	-26.8	-34.6	-31.6	-38.2	-33.2	-26.7	-32.4	-23.6	-34.2	-38.2
38	-37.0	-78.8	-37.9	-79.9	-63.0	-43.8	-82.4	-57.1	-43.3	-68.2
39	-40.2	-50.2	-42.0	-52.8	-55.7	-49.1	-58.8	-63.4	-44.1	-49.6
40	-52.2	-61.8	-55.6	-65.8	-66.9	-60.7	-70.0	-67.0	-57.8	-63.4
41	-16.6	-9.0	-13.4	-6.6	-3.4	-6.9	-1.6	-2.4	-12.8	-9.73

Reaction	PBE	PBE-D3(BJ)	PBE-NL	REVPBE	REVPBE-D3(BJ)	REVPBE-NL	RPBE	RPBE-D3(BJ)	RPBE-NL
1	-44.0	-46.7	-48.1	-38.0	-44.1	-47.2	-37.3	-49.1	-45.4
2	-47.5	-49.9	-51.4	-41.6	-47.0	-50.5	-40.6	-51.6	-48.6
3	-29.5	-31.3	-32.8	-24.3	-28.4	-31.6	-23.5	-31.8	-30.1
4	-72.4	-75.0	-76.3	-66.3	-72.4	-75.0	-65.6	-76.5	-73.4
5	-4.5	-7.0	-8.1	0.0	-5.4	-7.3	0.2	-8.6	-6.5
6	-19.0	-19.7	-21.4	-14.1	-15.5	-19.8	-13.5	-11.6	-18.6
7	-14.3	-14.7	-16.7	-9.6	-11.3	-15.2	-9.3	-4.3	-14.2
8	-10.8	-13.8	-13.9	-6.0	-12.4	-12.9	-5.5	-13.7	-11.7
9	-20.7	-14.6	-15.5	-19.8	-9.2	-11.6	-19.5	-10.0	-11.8
10	-17.9	-24.1	-25.9	-11.0	-23.5	-27.2	-10.6	-28.3	-25.2
11	31.6	24.4	23.4	37.3	22.5	21.3	37.2	18.0	22.6
12	-25.9	-29.5	-32.4	-19.0	-26.9	-33.0	-18.3	-26.1	-30.9
13	-40.1	-44.8	-46.8	-33.0	-43.0	-47.4	-32.2	-49.0	-45.2
14	-43.2	-51.7	-55.8	-33.3	-49.9	-58.1	-32.4	-55.8	-54.8
15	2.6	1.8	0.6	6.2	4.1	2.0	5.9	3.8	2.1
16	-22.2	-39.3	-41.2	-7.9	-41.2	-43.1	-7.2	-42.9	-39.4
17	-8.4	-11.9	-16.6	-0.9	-8.0	-17.0	-0.7	-2.3	-15.3
18	-21.5	-31.2	-32.3	-12.8	-33.1	-34.3	-12.3	-44.9	-31.8
19	-23.4	-34.9	-36.2	-13.8	-37.4	-38.7	-13.4	-48.9	-36.0
20	-16.5	-26.8	-28.0	-7.8	-28.9	-30.0	-7.6	-38.3	-27.8
21	-9.0	-18.2	-19.9	0.7	-19.1	-20.7	0.8	-28.2	-18.6
22	-23.4	-32.7	-34.3	-17.1	-35.4	-37.8	-16.6	-49.0	-35.5
23	-37.7	-48.7	-49.9	-28.7	-51.6	-52.7	-28.0	-65.8	-49.8
24	-15.4	-37.7	-38.4	-1.0	-42.4	-41.9	-0.7	-48.8	-38.2
25	-16.1	-42.1	-42.9	1.3	-47.1	-46.8	1.4	-52.3	-42.6
26	-27.5	-35.1	-31.0	-23.6	-37.8	-29.1	-24.5	-42.0	-29.5
27	-21.5	-22.1	-18.1	-24.6	-24.2	-16.5	-25.2	-30.1	-18.1
28	-32.3	-35.5	-31.6	-33.2	-38.3	-30.4	-33.6	-44.3	-31.2
29	-25.2	-27.4	-24.0	-26.0	-29.8	-22.8	-26.2	-35.5	-23.4
30	-16.6	-19.2	-15.6	-19.3	-23.7	-15.7	-20.0	-28.7	-16.9
31	-25.7	-26.6	-22.9	-28.5	-29.1	-21.3	-28.9	-36.3	-22.6
32	1.0	1.5	0.6	-1.7	0.0	-1.7	-1.4	-0.4	-1.5
33	-6.8	-8.9	-8.0	-7.7	-10.1	-7.7	-8.3	-5.4	-8.5
34	-19.5	-23.5	-21.9	-19.3	-26.0	-22.4	-19.4	-27.1	-22.4
35	-23.5	-27.8	-26.3	-23.1	-30.4	-26.9	-23.1	-34.2	-26.8
36	-29.9	-32.8	-32.1	-30.2	-36.0	-33.5	-30.5	-41.4	-33.6
37	-26.4	-29.8	-27.5	-20.8	-28.1	-22.3	-21.0	-31.1	-22.4
38	-49.8	-70.4	-64.6	-37.9	-79.0	-65.2	-38.7	-99.9	-63.7
39	-50.5	-55.2	-57.8	-42.9	-52.8	-58.2	-41.9	-68.8	-55.7
40	-63.4	-68.2	-69.5	-56.9	-66.4	-69.4	-56.6	-79.5	-67.8
41	-6.4	-3.6	-1.3	-11.4	-4.3	0.2	-12.9	2.6	-2.5

meta-GGA functionals

Table S 3: Calculated reaction energies for meta-GGA functionals. All values are given in [kcal/mol] D3(BJ): D3 applied with Becke-Johnson damping, D3(0): D3 applied with zero-damping. All calculations were performed with the def2-QZVPP basis set.

Reaction	M06L	M06L-D3(0)	SCAN	SCAN-D3(BJ)	TPSS	TPSS -D3(BJ)	TPSS -NL
1	-40.6	-41.1	-45.5	-46.2	-42.8	-46.4	-48.7
2	-44.9	-45.2	-51.8	-52.4	-46.5	-49.7	-52.3
3	-26.9	-27.2	-33.3	-33.7	-29.0	-31.4	-33.7
4	-64.6	-65.0	-76.0	-76.7	-68.0	-71.3	-73.6
5	-2.4	-2.8	-3.9	-4.5	-1.8	-5.1	-6.8
6	-18.0	-18.3	-20.2	-20.5	-17.5	-18.2	-21.0
7	-16.7	-16.9	-16.2	-16.4	-13.2	-13.4	-16.7
8	-7.2	-8.0	-16.0	-17.0	-9.9	-13.6	-14.3
9	-8.5	-6.4	-19.0	-16.4	-19.0	-10.6	-12.3
10	-12.0	-14.0	-24.1	-26.3	-16.2	-24.3	-27.3
11	31.8	29.9	23.6	21.3	30.7	21.1	19.5
12	-24.1	-25.0	-30.0	-31.1	-24.7	-29.4	-34.0
13	-39.2	-40.1	-46.7	-48.0	-39.3	-45.3	-48.8
14	-48.0	-51.2	-52.2	-55.6	-41.2	-52.3	-58.4
15	5.6	5.4	-3.9	-4.2	2.2	1.2	-0.6
16	-38.2	-44.6	-34.4	-41.2	-21.3	-43.5	-46.5
17	-17.1	-18.8	-15.3	-16.8	-10.9	-15.2	-22.1
18	-23.4	-25.1	-30.1	-32.8	-22.1	-35.4	-36.9
19	-27.1	-29.4	-34.8	-38.2	-24.2	-39.9	-41.6
20	-23.0	-25.2	-28.1	-31.2	-18.1	-31.8	-33.7
21	-12.3	-14.0	-16.2	-18.8	-6.9	-19.5	-21.8
22	-20.3	-22.1	-33.2	-35.9	-25.9	-39.2	-40.5
23	-39.6	-40.8	-47.4	-50.1	-39.3	-54.8	-55.9
24	-33.2	-42.2	-28.7	-38.0	-13.6	-42.7	-43.5
25	-37.4	-47.7	-31.6	-42.5	-13.3	-47.4	-48.4
26	-32.3	-34.3	-32.9	-35.6	-23.2	-33.6	-27.4
27	-22.0	-22.4	-21.3	-21.7	-19.8	-21.0	-14.6
28	-33.3	-34.2	-34.5	-35.6	-29.8	-34.5	-28.3
29	-25.4	-25.9	-27.3	-28.0	-22.9	-26.2	-21.0
30	-11.8	-12.6	-14.0	-14.9	-13.2	-17.2	-11.3
31	-23.2	-24.4	-26.0	-26.7	-24.6	-26.0	-20.2
32	1.5	1.5	1.4	1.5	-0.8	-0.3	-1.1
33	-11.0	-12.9	-10.2	-11.6	-10.5	-13.4	-11.3
34	-20.9	-22.6	-21.7	-23.5	-21.6	-27.0	-24.2
35	-22.4	-24.0	-25.6	-27.3	-25.4	-31.4	-28.6
36	-29.8	-29.5	-32.7	-33.1	-34.1	-38.7	-36.8
37	-25.7	-26.6	-26.9	-28.2	-26.2	-30.6	-27.4
38	-55.9	-60.6	-61.5	-68.3	-44.1	-72.0	-63.5
39	-55.4	-56.0	-58.6	-59.8	-52.9	-59.4	-63.2
40	-64.4	-65.6	-66.7	-68.1	-62.1	-68.6	-70.5
41	-4.9	-5.0	-3.8	-3.3	-4.3	-0.6	2.6

Hybrid functionals

Table S 4: Calculated reaction energies for hybrid functionals. All values are given in [kcal/mol] D3(BJ): D3 applied with Becke-Johnson damping, D3(0): D3 applied with zero-damping. All calculations were performed with the def2-QZVPP basis set.

Reaction	B1B95	B1B95-D3(BJ)	B3LYP	B3LYP-D3(BJ)	B3LYP-NL	B3PW91	B3PW91-D3(BJ)	B3PW91-NL	BHLYP	BHLYP-D3(BJ)	camB3LYP	camB3LYP-D3(BJ)
1	-39.8	-43.9	-36.2	-41.0	-42.0	-39.6	-44.7	-46.6	-33.1	-37.1	-37.5	-40.1
2	-41.6	-45.2	-38.0	-42.3	-43.6	-42.7	-47.2	-49.5	-34.4	-37.9	-40.5	-42.7
3	-21.2	-24.0	-19.7	-23.0	-24.4	-23.1	-26.6	-28.7	-14.3	-17.0	-21.4	-23.1
4	-61.1	-64.6	-62.1	-66.6	-67.2	-66.3	-70.8	-72.8	-60.3	-63.8	-62.0	-64.3
5	3.9	0.3	4.4	0.1	-0.7	1.8	-2.7	-3.8	7.5	4.1	5.3	3.0
6	-18.5	-18.4	-15.3	-16.0	-18.9	-17.3	-18.0	-21.5	-15.6	-15.8	-18.3	-18.6
7	-15.1	-13.4	-11.3	-11.3	-15.0	-12.7	-12.7	-16.9	-12.4	-11.7	-13.9	-13.4
8	-9.7	-13.1	-7.2	-11.8	-11.8	-9.9	-14.8	-15.2	-9.4	-12.9	-12.3	-14.9
9	-15.0	-6.4	-21.0	-11.5	-14.4	-21.0	-10.2	-13.9	-20.2	-12.5	-23.2	-16.0
10	-10.7	-18.9	-6.5	-16.5	-18.4	-10.2	-20.9	-23.0	-1.5	-9.5	-9.4	-15.5
11	38.5	28.3	40.1	28.0	28.3	39.2	26.2	26.4	47.3	37.6	40.2	32.9
12	-24.7	-29.1	-17.0	-22.9	-26.3	-21.7	-28.0	-32.5	-15.6	-20.1	-19.8	-23.1
13	-37.1	-43.6	-30.1	-37.9	-40.4	-35.7	-44.0	-46.8	-29.0	-35.3	-33.7	-38.0
14	-41.4	-53.2	-30.2	-43.9	-47.0	-36.8	-51.6	-56.3	-29.1	-40.2	-35.0	-43.8
15	-0.8	-1.4	-2.9	-4.2	-6.2	-0.5	-1.8	-3.7	-15.8	-16.6	-8.4	-9.1
16	-25.8	-47.6	-13.7	-40.5	-39.3	-16.6	-45.6	-45.0	-17.8	-38.9	-21.6	-39.0
17	-8.9	-11.3	-5.5	-10.1	-16.5	-4.5	-9.5	-17.2	-7.6	-10.7	-10.5	-13.3
18	-22.4	-39.6	-14.1	-31.9	-29.2	-18.1	-37.0	-35.1	-17.2	-32.2	-19.4	-30.0
19	-26.1	-45.7	-16.8	-37.4	-34.3	-20.8	-42.7	-40.5	-22.2	-39.4	-23.7	-36.2
20	-17.8	-33.5	-11.2	-28.9	-26.9	-13.0	-31.9	-30.7	-14.9	-29.4	-17.0	-27.5
21	-7.4	-22.4	-0.2	-16.7	-15.6	-2.9	-20.4	-19.8	-1.9	-15.3	-3.3	-13.0
22	-20.9	-38.9	-13.5	-30.8	-28.0	-18.7	-37.6	-35.4	-11.9	-26.6	-15.1	-26.8
23	-40.0	-61.8	-30.8	-52.0	-47.4	-35.6	-58.1	-54.6	-35.5	-53.6	-36.5	-49.3
24	-23.2	-53.3	-9.4	-44.2	-39.4	-12.0	-50.1	-45.4	-17.7	-45.8	-18.5	-42.3
25	-23.3	-57.6	-8.2	-48.6	-43.8	-10.9	-55.2	-50.3	-17.0	-49.3	-18.6	-46.3
26	-26.6	-38.3	-31.2	-43.8	-35.4	-28.4	-42.4	-33.0	-37.9	-48.1	-34.4	-43.1
27	-21.6	-24.4	-26.2	-27.5	-21.1	-25.0	-26.8	-19.0	-30.4	-31.9	-26.3	-28.3
28	-32.4	-39.1	-36.8	-42.6	-35.2	-35.7	-42.2	-33.8	-41.9	-47.0	-38.2	-42.7
29	-24.6	-29.5	-28.8	-33.0	-26.9	-27.8	-32.4	-25.5	-31.7	-35.5	-29.4	-32.5
30	-8.4	-14.4	-16.7	-21.7	-14.6	-14.3	-20.0	-11.8	-13.2	-17.6	-13.8	-17.7
31	-25.0	-28.3	-31.5	-33.3	-27.2	-29.4	-31.5	-24.2	-35.0	-37.0	-31.9	-34.0
32	-2.8	-3.2	0.3	0.8	0.2	-1.0	-0.4	-1.1	0.4	0.6	0.8	0.8
33	-6.6	-8.8	-15.5	-18.0	-15.8	-8.0	-11.3	-8.6	-17.8	-19.7	-15.4	-18.2
34	-20.8	-27.4	-24.1	-30.7	-26.3	-21.2	-28.6	-24.0	-26.8	-32.3	-23.9	-28.9
35	-25.8	-34.2	-27.7	-35.3	-30.6	-25.5	-33.9	-28.9	-31.0	-37.7	-27.8	-33.4
36	-32.7	-41.5	-34.2	-40.9	-36.2	-32.0	-39.2	-34.8	-37.1	-43.4	-33.2	-37.7
37	-13.2	-17.6	-28.1	-33.7	-28.9	-20.4	-26.3	-21.7	-23.2	-27.5	-23.5	-26.9
38	-43.9	-76.3	-43.6	-78.9	-63.3	-44.1	-82.2	-66.1	-47.3	-76.2	-48.1	-70.5
39	-56.0	-65.7	-47.6	-56.7	-58.4	-51.1	-60.6	-62.9	-53.4	-61.6	-54.6	-59.8
40	-62.3	-71.2	-58.6	-67.2	-66.9	-60.5	-69.6	-70.2	-60.6	-68.2	-61.1	-66.3
41	-5.4	0.5	-12.3	-6.6	-4.4	-7.7	-2.1	-1.1	-11.2	-6.5	-9.0	-6.6

Reaction	M06	M06-D3(0)	M06-2X	M06-2X-D3(0)	mPW1B95	mPW1B95-D3(BJ)	PBE0	PBE0-D3(BJ)	PBE0-NL
1	-41.3	-41.7	-34.5	-34.6	-40.8	-42.8	-42.1	-44.7	-45.8
2	-40.2	-40.5	-31.4	-31.5	-42.5	-44.2	-45.2	-47.4	-48.8
3	-21.2	-21.5	-10.7	-10.8	-21.8	-23.2	-24.7	-26.4	-27.6
4	-58.2	-58.6	-52.8	-52.9	-62.2	-64.0	-69.0	-71.4	-72.4
5	1.3	0.9	4.2	4.1	2.9	1.2	-0.1	-2.4	-3.3
6	-19.7	-20.1	-16.6	-16.7	-19.7	-19.8	-19.8	-20.3	-21.9
7	-15.5	-15.6	-12.5	-12.6	-16.4	-15.5	-15.2	-15.3	-17.4
8	-2.9	-3.7	-6.6	-7.1	-11.1	-13.0	-12.7	-15.4	-15.6
9	-8.2	-6.1	-7.0	-6.4	-15.0	-9.3	-21.0	-14.5	-16.2
10	-8.7	-10.6	-7.4	-8.2	-11.8	-16.5	-13.3	-19.3	-20.6
11	36.5	34.7	38.7	38.1	37.4	31.7	37.1	30.0	29.6
12	-26.2	-27.1	-24.0	-24.2	-26.3	-28.6	-25.6	-29.0	-31.4
13	-38.2	-39.1	-33.4	-33.7	-38.6	-41.9	-39.3	-43.7	-45.4
14	-47.6	-50.8	-43.6	-45.1	-43.7	-50.7	-42.4	-50.8	-53.8
15	6.3	6.1	-17.4	-17.5	-3.1	-3.5	-3.7	-4.4	-5.4
16	-35.1	-41.4	-33.0	-35.9	-29.9	-43.3	-24.0	-40.8	-41.3
17	-12.3	-14.1	-12.4	-13.1	-11.2	-13.0	-8.2	-11.4	-15.5
18	-21.8	-23.4	-24.9	-25.4	-24.9	-34.0	-23.3	-33.0	-33.0
19	-25.8	-28.0	-31.1	-31.8	-29.2	-39.8	-26.8	-38.3	-38.3
20	-19.4	-21.6	-22.2	-22.9	-20.6	-29.0	-18.1	-28.1	-28.4
21	-6.1	-7.7	-12.4	-12.9	-10.2	-18.2	-8.2	-17.3	-18.1
22	-12.3	-14.2	-13.8	-14.3	-22.5	-32.8	-22.5	-32.3	-32.4
23	-39.1	-40.4	-42.0	-42.4	-42.8	-54.3	-41.2	-52.4	-52.2
24	-33.6	-42.6	-31.6	-36.1	-28.1	-47.0	-20.7	-43.0	-41.6
25	-38.1	-48.5	-36.6	-41.5	-29.0	-50.7	-21.2	-47.3	-45.8
26	-34.0	-35.9	-36.1	-36.9	-28.8	-35.9	-31.4	-39.2	-34.6
27	-19.4	-19.8	-21.4	-21.6	-21.5	-23.6	-24.4	-25.5	-21.4
28	-33.3	-34.2	-35.2	-35.5	-32.9	-37.0	-36.0	-39.7	-35.4
29	-23.9	-24.4	-26.1	-26.2	-24.7	-27.6	-27.5	-30.0	-26.6
30	-9.5	-10.3	-10.0	-10.4	-7.6	-11.3	-13.1	-16.1	-12.3
31	-23.6	-24.8	-24.7	-25.4	-24.6	-26.9	-28.4	-29.6	-25.9
32	1.1	1.2	1.7	1.6	-1.8	-2.1	0.4	0.7	0.1
33	-7.6	-9.5	-13.0	-13.9	-6.8	-9.1	-6.6	-9.0	-7.7
34	-21.1	-22.8	-23.3	-24.1	-21.1	-25.4	-20.9	-25.2	-23.1
35	-23.9	-25.4	-28.6	-29.4	-26.2	-31.3	-25.4	-30.0	-27.9
36	-28.4	-28.2	-34.5	-34.3	-33.1	-37.8	-32.0	-35.3	-34.0
37	-21.2	-22.0	-18.3	-18.7	-14.6	-17.2	-20.2	-23.4	-21.2
38	-57.8	-62.6	-54.6	-56.4	-48.4	-66.8	-51.5	-72.2	-65.0
39	-59.1	-59.7	-57.7	-57.9	-58.2	-62.9	-54.8	-59.6	-61.4
40	-64.2	-65.4	-70.7	-71.0	-64.2	-68.8	-64.5	-69.2	-69.9
41	-4.4	-4.5	-8.5	-8.6	-2.1	-0.2	-6.0	-3.4	-1.4

Reaction	PW6B95	PW6B95-D3(BJ)	PW6B95-NL	TPSS0	TPSS0-D3(BJ)	TPSS0-NL	TPSSh	TPSSh-D3(BJ)	TPSSh-NL	ωB97X-V	ωB97X-D3(BJ)
1	-39.6	-41.4	-42.0	-40.9	-44.6	-46.0	-42.1	-45.5	-47.7	-39.9	-38.8
2	-41.0	-42.5	-43.3	-44.3	-47.5	-49.3	-45.7	-48.6	-51.1	-43.9	-42.3
3	-21.0	-22.2	-22.9	-24.1	-26.6	-28.2	-26.9	-29.2	-31.4	-23.6	-22.4
4	-60.9	-62.4	-63.1	-65.8	-69.2	-70.6	-66.8	-70.0	-72.1	-63.9	-62.4
5	3.2	1.6	1.0	2.1	-1.2	-2.2	-0.1	-3.2	-4.8	3.7	3.8
6	-18.7	-18.8	-20.0	-18.6	-19.1	-21.6	-18.0	-18.7	-21.3	-19.6	-18.9
7	-15.6	-15.0	-17.0	-14.4	-14.4	-17.5	-13.7	-13.8	-17.1	-15.7	-14.1
8	-9.7	-11.4	-11.6	-12.2	-15.9	-16.2	-10.9	-14.4	-15.1	-16.4	-14.3
9	-14.5	-9.6	-10.8	-19.9	-12.2	-13.9	-19.4	-11.0	-13.1	-16.2	-15.5
10	-10.8	-14.9	-15.8	-11.8	-19.7	-21.6	-14.5	-22.3	-25.0	-17.7	-14.2
11	37.0	32.1	31.8	36.7	27.3	26.7	32.9	23.6	22.3	33.5	35.9
12	-24.7	-26.8	-28.6	-24.2	-28.8	-32.4	-24.6	-29.1	-33.4	-26.7	-23.9
13	-37.0	-39.9	-41.0	-38.3	-44.4	-46.7	-38.9	-44.7	-48.0	-40.4	-37.8
14	-41.5	-47.7	-49.5	-40.2	-51.0	-55.3	-40.8	-51.7	-57.1	-49.1	-46.4
15	-2.8	-3.1	-4.0	-4.3	-5.3	-6.7	0.0	-0.9	-2.6	-8.3	-4.7
16	-28.6	-40.5	-41.1	-22.9	-44.1	-45.5	-21.9	-43.7	-46.0	-40.3	-38.6
17	-11.0	-12.7	-16.1	-10.1	-13.8	-19.9	-10.5	-14.5	-21.1	-17.5	-14.3
18	-23.5	-31.1	-30.3	-23.6	-37.2	-36.8	-22.7	-35.7	-36.8	-31.5	-26.1
19	-27.6	-36.5	-35.6	-27.3	-43.1	-42.7	-25.4	-40.7	-41.9	-38.4	-32.4
20	-19.7	-26.9	-26.9	-19.2	-32.9	-33.0	-18.5	-31.8	-33.3	-29.1	-24.1
21	-9.4	-16.2	-16.3	-6.6	-19.2	-19.8	-6.7	-18.9	-20.9	-12.7	-8.5
22	-21.0	-29.5	-28.1	-24.3	-37.6	-37.5	-25.3	-38.6	-39.3	-27.6	-22.4
23	-41.0	-50.4	-48.7	-42.3	-58.3	-57.1	-40.5	-55.7	-56.3	-51.1	-44.1
24	-26.5	-43.3	-42.0	-19.1	-46.9	-45.9	-15.8	-44.6	-44.4	-42.9	-41.5
25	-27.4	-46.7	-45.5	-18.9	-51.2	-50.4	-15.5	-49.2	-49.1	-47.1	-45.3
26	-29.7	-35.8	-32.1	-28.3	-38.2	-32.0	-25.2	-35.6	-29.2	-37.9	-40.9
27	-22.1	-23.7	-20.2	-23.4	-24.5	-18.9	-21.3	-22.8	-16.4	-24.1	-28.5
28	-33.3	-36.7	-33.1	-34.2	-38.8	-33.0	-31.6	-36.4	-30.2	-38.4	-41.3
29	-25.2	-27.5	-24.6	-25.8	-29.1	-24.2	-24.1	-27.5	-22.4	-28.6	-31.6
30	-8.6	-11.6	-8.4	-10.7	-14.5	-9.1	-12.2	-16.3	-10.4	-14.3	-17.0
31	-25.4	-27.2	-24.0	-27.6	-29.0	-23.8	-25.9	-27.5	-21.7	-29.1	-33.1
32	-1.3	-1.5	-1.7	-1.0	-0.5	-1.2	-0.9	-0.5	-1.2	-1.0	0.6
33	-8.8	-10.9	-10.0	-9.8	-12.1	-10.7	-10.1	-13.2	-11.0	-13.7	-15.7
34	-21.8	-25.6	-23.7	-22.7	-27.9	-25.2	-22.0	-27.6	-24.6	-25.5	-26.6
35	-26.8	-31.1	-28.9	-27.0	-33.0	-30.0	-26.0	-32.1	-29.1	-30.0	-30.4
36	-33.6	-37.2	-35.2	-35.4	-40.3	-37.8	-34.6	-39.2	-37.2	-35.6	-33.6
37	-17.0	-19.3	-17.8	-20.0	-24.3	-21.1	-23.6	-27.8	-24.7	-13.1	-16.2
38	-48.7	-64.4	-58.4	-46.8	-74.2	-64.1	-45.1	-72.6	-63.7	-62.6	-62.6
39	-56.6	-60.6	-61.1	-56.3	-63.2	-65.3	-54.3	-60.6	-64.0	-61.5	-57.8
40	-63.1	-67.0	-66.8	-63.3	-70.0	-70.6	-62.5	-68.8	-70.5	-66.8	-64.7
41	-3.8	-2.5	-0.9	-4.5	-0.3	2.2	-4.4	-1.0	2.8	-3.6	-7.5

Double-hybrid functionals

Table S 5: Calculated reaction energies for double hybrid functionals. All values are given in [kcal/mol]. D3(BJ): D3 applied with Becke-Johnson damping. All calculations were performed with the def2-QZVPP basis set.

Reaction	B2GPPLYP	B2GPPLYP-D3(BJ)	B2PLYP	B2PLYP-D3(BJ)	B2PLYP-NL	DOD-BLYP-D3(BJ)	DOD-PBEB95-D3(BJ)	DOD-PBEPBE-D3(BJ)	DOD-PBEP86-D3(BJ)	DOD-SVWN-D3(BJ)
1	-46.6	-48.8	-44.4	-46.8	-46.6	-44.2	-45.8	-47.4	-47.4	-48.1
2	-51.8	-53.7	-49.7	-51.8	-52.3	-47.9	-50.0	-52.7	-52.3	-53.1
3	-37.8	-39.3	-35.5	-37.1	-36.6	-32.9	-33.1	-36.6	-36.6	-37.2
4	-56.9	-58.6	-60.0	-62.2	-62.9	-55.0	-58.5	-61.0	-59.9	-59.4
5	5.9	4.1	4.0	1.9	1.3	5.8	3.8	2.3	3.0	3.9
6	-21.9	-21.6	-20.2	-20.3	-21.2	-15.9	-20.6	-20.4	-20.3	-22.1
7	-14.1	-12.5	-13.2	-12.8	-14.7	-8.3	-14.0	-12.6	-12.6	-14.0
8	-9.9	-11.4	-8.8	-11.0	-10.5	-10.7	-12.4	-13.5	-13.3	-14.1
9	-15.6	-11.6	-16.2	-11.0	-11.6	-10.8	-10.0	-11.9	-12.7	-14.8
10	-17.6	-21.6	-15.6	-20.7	-20.7	-20.8	-21.0	-23.4	-23.8	-24.0
11	28.3	23.6	30.2	24.0	25.0	22.8	25.0	22.4	21.8	22.4
12	-31.8	-33.8	-28.9	-31.7	-32.7	-26.5	-32.4	-32.9	-32.2	-33.1
13	-43.6	-46.9	-40.6	-44.6	-44.8	-42.8	-45.3	-47.1	-46.9	-47.2
14	-47.8	-53.6	-45.2	-52.3	-52.8	-48.7	-54.7	-56.0	-54.8	-54.2
15	11.7	11.5	10.4	9.8	6.8	7.7	6.2	8.1	7.7	7.2
16	-30.7	-40.6	-26.8	-40.5	-40.8	-39.3	-43.7	-43.4	-43.2	-42.4
17	-11.9	-12.5	-10.4	-12.5	-16.4	-8.1	-13.2	-11.4	-12.0	-13.0
18	-26.4	-35.8	-23.5	-33.0	-30.5	-34.0	-35.7	-37.2	-36.4	-35.6
19	-31.2	-41.5	-27.7	-38.6	-36.2	-39.7	-42.0	-43.2	-42.3	-41.4
20	-22.0	-29.9	-19.6	-28.8	-27.6	-30.6	-31.2	-32.0	-32.0	-30.9
21	-8.1	-16.1	-6.7	-15.2	-14.3	-15.7	-18.4	-18.8	-18.5	-17.3
22	-32.4	-42.6	-28.7	-38.3	-34.7	-38.7	-38.6	-41.9	-40.7	-39.8
23	-46.8	-58.4	-42.9	-54.5	-50.0	-55.0	-56.9	-59.0	-57.7	-56.8
24	-28.5	-42.9	-23.5	-41.9	-41.0	-43.4	-46.3	-46.5	-45.7	-43.8
25	-32.2	-48.4	-26.0	-47.1	-46.5	-48.6	-51.6	-52.1	-51.6	-49.4
26	-31.2	-37.2	-30.3	-37.1	-33.6	-39.8	-35.1	-37.3	-37.8	-36.4
27	-20.7	-22.8	-21.2	-22.4	-19.3	-26.0	-21.2	-22.8	-22.6	-21.4
28	-34.2	-38.1	-34.0	-37.4	-34.0	-40.8	-35.7	-38.0	-37.8	-36.6
29	-27.8	-31.0	-27.7	-30.2	-27.4	-33.4	-28.0	-30.4	-30.4	-29.3
30	-13.3	-16.9	-14.7	-17.7	-14.4	-21.7	-13.5	-17.3	-17.7	-16.1
31	-29.7	-32.3	-29.9	-31.4	-28.3	-35.9	-28.4	-31.3	-31.5	-30.3
32	-1.7	-2.0	-1.3	-1.3	-1.5	-1.8	-2.6	-2.0	-1.2	-1.2
33	-5.6	-6.2	-7.9	-9.4	-9.6	-10.7	-6.4	-6.0	-7.0	-6.7
34	-19.9	-23.2	-20.8	-24.5	-23.1	-26.4	-23.4	-23.9	-23.9	-23.2
35	-25.2	-29.8	-25.7	-30.1	-27.8	-32.3	-29.5	-30.1	-29.8	-28.9
36	-39.6	-44.8	-38.6	-42.7	-39.2	-43.8	-41.3	-42.2	-41.9	-41.3
37	-19.6	-21.4	-21.8	-24.6	-23.7	-22.0	-14.4	-17.4	-19.6	-19.5
38	-58.3	-75.2	-54.9	-73.6	-66.3	-79.1	-70.5	-76.8	-77.0	-72.8
39	-59.8	-65.9	-56.6	-61.7	-61.6	-64.5	-65.6	-65.8	-66.1	-66.2
40	-61.6	-67.1	-60.1	-64.8	-63.9	-67.2	-67.4	-68.3	-68.4	-67.9
41	-5.2	-2.5	-6.7	-3.9	3.5	-3.9	-0.5	-1.4	-1.7	-1.6

Reaction	DSD-BLYP-D3(BJ)	DSD-PBEB95-D3(BJ)	DSD-PBEPBE-D3(BJ)	DSD-PBEP86-D3(BJ)	DSD-SVWN-D3(BJ)	MPW2PLYP	MPW2PLYP-D3(BJ)
1	-50.5	-46.9	-49.4	-50.7	-52.6	-44.1	-45.5
2	-55.4	-51.6	-55.0	-56.2	-58.1	-48.9	-50.1
3	-41.8	-35.1	-40.0	-41.9	-43.6	-33.9	-34.8
4	-56.4	-58.0	-59.1	-57.9	-57.8	-60.6	-61.9
5	4.7	4.1	3.2	4.0	4.2	4.0	2.7
6	-22.1	-21.7	-22.1	-23.2	-24.8	-20.6	-20.9
7	-13.0	-14.7	-13.4	-14.4	-15.4	-14.0	-14.0
8	-11.7	-12.3	-13.2	-13.2	-14.3	-9.8	-11.3
9	-11.6	-10.3	-12.0	-12.9	-13.6	-16.6	-12.9
10	-24.0	-21.5	-24.6	-25.4	-27.0	-15.2	-18.6
11	20.5	24.6	21.0	20.4	19.2	30.9	27.0
12	-35.3	-33.9	-35.4	-36.5	-38.4	-28.7	-30.6
13	-49.0	-46.3	-48.9	-49.8	-51.8	-40.7	-43.1
14	-55.3	-55.3	-57.1	-56.9	-58.5	-45.1	-49.9
15	14.5	8.6	12.2	13.6	13.7	6.3	6.0
16	-42.2	-43.2	-43.3	-42.9	-45.3	-28.7	-38.3
17	-13.0	-13.7	-12.2	-13.6	-14.8	-11.7	-13.5
18	-35.3	-35.3	-36.8	-36.0	-37.6	-24.7	-30.0
19	-40.9	-41.4	-42.7	-41.7	-43.5	-29.3	-35.6
20	-30.5	-30.5	-31.2	-30.7	-32.1	-21.0	-26.6
21	-15.8	-17.5	-17.6	-16.7	-17.6	-8.0	-13.0
22	-42.7	-39.3	-43.3	-43.0	-44.9	-28.3	-33.7
23	-57.0	-56.6	-58.9	-57.8	-59.7	-44.1	-50.2
24	-43.8	-45.2	-45.5	-44.0	-46.4	-26.3	-39.1
25	-51.4	-50.6	-51.5	-50.4	-53.4	-28.9	-43.9
26	-35.7	-33.9	-35.5	-34.8	-35.0	-32.5	-36.9
27	-21.0	-20.3	-21.2	-20.0	-19.4	-22.0	-22.7
28	-36.4	-34.8	-36.5	-35.4	-35.2	-35.1	-37.1
29	-30.0	-27.3	-29.3	-28.7	-28.6	-28.2	-29.6
30	-16.0	-12.7	-16.1	-15.3	-14.3	-14.0	-15.7
31	-31.2	-27.7	-30.1	-29.4	-29.0	-30.2	-31.1
32	-1.9	-2.8	-2.4	-1.8	-1.7	-0.5	-0.4
33	-4.2	-5.0	-3.7	-3.0	-2.1	-8.9	-10.4
34	-21.5	-22.2	-22.1	-20.9	-20.5	-21.6	-24.0
35	-27.6	-28.3	-28.3	-26.9	-26.6	-26.4	-29.1
36	-42.5	-41.1	-42.1	-41.5	-41.5	-38.7	-40.5
37	-20.6	-13.8	-16.4	-17.8	-18.5	-22.8	-24.7
38	-75.4	-68.9	-75.0	-73.6	-75.0	-57.2	-68.7
39	-66.3	-65.5	-65.9	-66.4	-68.4	-57.8	-60.4
40	-66.7	-66.8	-67.4	-67.3	-68.4	-61.4	-64.1
41	-1.6	-0.4	-1.1	-1.0	0.2	-6.7	-5.3

Reaction	PBE0-2	PBE0-DH	PBE0-DH-D3(BJ)	PBE0-DH-NL	PWPB95	PWPB95-D3(BJ)	PWRB95
1	-53.3	-44.7	-47.1	-47.0	-42.4	-43.9	-41.0
2	-59.0	-49.6	-51.7	-52.1	-46.4	-47.6	-42.5
3	-44.8	-30.4	-32.1	-32.0	-30.0	-30.0	-23.6
4	-55.9	-68.3	-70.5	-70.8	-60.2	-61.5	-62.5
5	5.3	0.7	-1.4	-1.7	3.5	2.2	2.1
6	-26.4	-21.7	-21.9	-22.9	-20.2	-20.1	-19.6
7	-17.0	-16.0	-15.6	-17.4	-15.5	-14.5	-16.3
8	-13.9	-13.9	-16.1	-15.7	-10.6	-11.9	-12.0
9	-14.9	-18.3	-13.1	-14.2	-13.9	-9.9	-12.1
10	-24.3	-15.0	-20.0	-20.1	-15.4	-18.7	-17.6
11	23.2	35.6	29.5	30.4	31.8	27.8	28.7
12	-40.3	-30.2	-33.0	-34.1	-29.0	-30.5	-28.8
13	-52.4	-42.9	-46.8	-47.1	-40.6	-43.0	-41.2
14	-57.7	-48.8	-55.9	-56.6	-48.0	-53.0	-51.0
15	14.2	-1.1	-1.6	-3.4	3.3	3.1	-2.7
16	-39.7	-30.2	-43.9	-43.6	-32.4	-41.6	-40.7
17	-14.5	-10.8	-12.8	-16.4	-12.2	-13.1	-14.9
18	-34.3	-28.0	-37.5	-35.0	-27.0	-34.2	-29.6
19	-39.8	-33.0	-43.9	-41.4	-31.8	-40.0	-35.0
20	-27.8	-22.7	-31.9	-30.4	-23.0	-29.2	-26.6
21	-13.1	-10.7	-19.3	-18.1	-11.4	-17.5	-15.5
22	-42.7	-29.0	-38.7	-35.7	-28.1	-36.3	-27.8
23	-56.5	-48.0	-59.6	-55.5	-46.2	-55.3	-47.4
24	-39.2	-28.9	-47.3	-45.5	-30.5	-44.0	-40.4
25	-45.1	-30.8	-51.9	-50.3	-32.7	-48.0	-44.3
26	-30.7	-32.6	-39.4	-35.4	-28.8	-34.1	-30.2
27	-18.2	-23.4	-24.5	-21.4	-19.5	-21.3	-17.7
28	-33.1	-36.3	-39.8	-36.1	-31.9	-35.3	-31.0
29	-26.6	-28.0	-30.5	-27.6	-24.9	-27.3	-23.3
30	-10.0	-11.2	-14.2	-11.0	-9.9	-12.9	-9.1
31	-27.0	-28.8	-30.3	-27.2	-25.6	-27.7	-19.1
32	-2.6	-0.8	-0.7	-1.0	-2.4	-2.8	-2.3
33	2.8	-4.6	-6.1	-6.0	-6.8	-8.2	-9.2
34	-16.7	-20.9	-24.6	-23.0	-21.1	-24.3	-22.6
35	-22.8	-26.0	-30.4	-28.1	-26.5	-30.5	-27.4
36	-39.3	-35.6	-39.7	-36.8	-37.0	-41.2	-34.3
37	-12.4	-16.2	-19.0	-17.5	-14.0	-15.7	-14.9
38	-65.4	-56.8	-75.5	-67.4	-52.8	-66.6	-58.5
39	-66.6	-60.1	-65.1	-64.8	-59.6	-63.6	-60.2
40	-66.0	-65.4	-70.1	-69.1	-62.8	-66.6	-65.2
41	0.2	-3.4	-0.6	0.2	-2.3	-0.8	3.4

Low-cost and wavefunction methods:

Table S 6: Calculated reaction energies for low-cost (composite) and wavefunction methods. All values are given in [kcal/mol]. All calculations were performed with the def2-QZVPP basis set unless denoted otherwise.

Reaction	B97-3c	PBEh-3c	PBE-D3(-BJ)/ def2-TZVP	PBE0-D3(-BJ)/ def2-SVP	B3LYP/ def2-SVP	B3LYP-D3(-BJ)/ def2-SVP	MP2	SCS-MP2	SOS-MP2	RPA
1	-45.2	-47.5	-50.0	-49.6	-41.1	-45.9	-59.8	-50.6	-46.0	-35.8
2	-48.7	-50.5	-53.0	-52.6	-43.2	-47.4	-62.6	-53.1	-48.4	-37.3
3	-30.3	-30.6	-33.5	-33.2	-26.6	-29.9	-54.7	-42.9	-37.0	-21.5
4	-76.0	-75.9	-78.8	-76.7	-67.5	-71.9	-30.6	-31.9	-32.5	-59.4
5	-5.5	-4.2	-9.5	-6.3	0.4	-3.9	10.1	11.7	12.6	6.1
6	-13.7	-15.6	-20.2	-22.4	-17.5	-18.2	-28.9	-23.9	-21.3	-16.7
7	-8.0	-12.7	-15.1	-15.9	-12.5	-12.5	-16.7	-13.8	-12.3	-13.9
8	-11.6	-4.4	-17.5	-14.7	-7.0	-11.6	-9.2	-7.6	-6.8	-11.7
9	-10.2	-11.8	-8.2	-19.1	-26.2	-16.6	-10.2	-12.8	-14.2	-12.5
10	-18.0	-8.7	-30.1	-21.4	-10.0	-20.0	-31.3	-23.5	-19.5	-17.7
11	24.9	41.7	17.3	30.5	40.4	28.3	8.8	16.9	21.0	27.0
12	-25.6	-28.9	-33.7	-32.8	-21.4	-27.3	-46.0	-35.8	-30.8	-25.7
13	-41.6	-39.6	-49.0	-45.5	-32.8	-40.7	-59.8	-49.7	-44.6	-38.1
14	-52.0	-54.8	-61.5	-64.9	-45.0	-58.8	-57.9	-48.0	-43.1	-48.9
15	0.8	-16.4	1.3	-6.4	-5.8	-7.1	20.4	11.0	6.2	-5.5
16	-37.8	-36.6	-57.1	-47.0	-20.6	-47.4	-43.9	-34.9	-30.4	-38.3
17	-8.0	-14.9	-16.3	-17.7	-12.3	-16.9	-16.2	-12.4	-10.4	-13.2
18	-35.1	-32.1	-41.8	-36.1	-17.0	-34.8	-32.8	-26.5	-23.4	-27.7
19	-40.0	-39.0	-47.5	-42.7	-20.8	-41.4	-37.4	-31.4	-28.4	-34.1
20	-30.7	-29.0	-38.0	-33.7	-16.2	-33.9	-26.2	-21.6	-19.3	-26.2
21	-21.7	-16.2	-27.7	-23.9	-7.2	-23.7	-9.6	-6.5	-5.0	-12.2
22	-39.5	-27.3	-43.7	-31.9	-12.2	-29.5	-45.3	-34.6	-29.3	-26.2
23	-57.3	-52.4	-60.8	-56.0	-33.6	-54.8	-52.3	-45.3	-41.9	-45.0
24	-41.8	-45.1	-61.0	-52.8	-18.3	-53.2	-44.7	-35.4	-30.8	-37.8
25	-44.3	-48.0	-69.3	-56.0	-16.0	-56.4	-56.2	-44.0	-37.9	-42.0
26	-38.5	-43.1	-42.8	-38.0	-28.8	-41.4	-28.6	-29.9	-30.6	-29.6
27	-23.2	-26.5	-22.4	-20.5	-19.9	-21.2	-13.6	-17.6	-19.6	-16.0
28	-38.8	-42.9	-38.8	-37.2	-33.0	-38.8	-30.0	-32.4	-33.7	-30.2
29	-28.6	-31.2	-29.6	-26.1	-23.5	-27.6	-25.3	-26.5	-27.0	-22.8
30	-17.9	-15.4	-22.0	-15.4	-15.4	-20.3	-10.6	-12.6	-13.6	-12.3
31	-28.5	-29.7	-27.5	-23.9	-25.0	-27.0	-24.9	-29.9	-31.4	-25.2
32	-0.2	-2.2	1.9	0.8	0.9	1.5	-4.1	-3.8	-3.6	-3.8
33	-15.2	-12.6	-12.3	-13.9	-19.2	-21.8	11.3	2.4	-2.0	-11.9
34	-31.9	-30.4	-28.2	-29.5	-26.9	-33.5	-10.3	-14.9	-17.2	-23.7
35	-36.1	-32.0	-32.7	-31.7	-28.2	-35.8	-15.4	-19.6	-21.7	-28.0
36	-43.1	-39.7	-36.1	-37.4	-34.2	-40.9	-36.1	-37.2	-37.8	-35.5
37	-31.6	-27.4	-33.7	-31.1	-35.2	-40.7	-12.8	-12.5	-12.3	-9.8
38	-80.3	-72.9	-92.1	-78.6	-47.8	-83.0	-71.9	-62.8	-58.3	-58.2
39	-55.2	-66.9	-59.6	-64.9	-52.9	-62.0	-68.7	-63.4	-60.8	-57.0
40	-66.4	-71.2	-73.6	-75.4	-65.6	-74.2	-63.9	-60.8	-59.3	-61.8
41	-5.4	-4.5	-0.9	-0.4	-9.0	-3.4	-0.7	5.6	7.9	4.0

Frozen-core approximation used in correlated calculations:

All correlated calculations (except for the canonical CCSD(T)/aug-cc-pwCVTZ[1] calculations, for which only the two 1s electrons of the manganese atom were frozen) including the RPA and the MP2 part of the double hybrid functional calculations were performed with the frozen-core approximation, i.e., only valence (and the eight 2s and 2p sub-valence electrons for 3d transition metals) electrons are correlated. The number of core electrons was chosen according to the ORCA 4.0.0[2] default setting (see the manual ORCA manual for details). For calculations performed with TURBOMOLE, the number of core electrons was adapted if necessary for consistency to the ORCA 4.0.0 default settings. The following number of core electrons not treated by ECPs was frozen in the calculation of the respective molecule:

Table S 7: Number of frozen-core electrons for each molecule of the MOR41 test set. The molecules are named according to their name in the structure archive file.

AcCl	16	ED28	32	PR11	38
AcI	14	ED29	20	PR12	34
Bz	12	ED30	64	PR13	18
C2H4	4	ED31	72	PR14	68
C2H6	4	ED32	22	PR15	28
C3H8	6	ED33	68	PR16	76
CO2	6	ED36	24	PR17	60
CO	4	ED37	24	PR18	56
COD	16	ED39	18	PR19	60
ED01	30	ED40a	16	PR20	62
ED02	26	ED40b	24	PR21	50
ED03	22	ED41	80	PR22	68
ED04	28	H2	0	PR23	62
ED05	2	I2	16	PR24	126
ED07	68	MeCN	6	PR25	126
ED08	106	MeI	10	PR26	62
ED09	102	MeOH	4	PR27	60
ED10	24	PCy3	46	PR28	62
ED11	34	PhOH	14	PR29	36
ED13	14	PhSeH	30	PR30	68
ED14	52	PhSH	22	PR31	76
ED15	22	PMe3	16	PR32	30
ED16a	50	PR01	34	PR33	78
ED16b	26	PR02	30	PR34	86
ED17	56	PR03	26	PR35	94
ED18	46	PR04	32	PR36	36
ED21	40	PR05	2	PR37	30
ED22	52	PR06	30	PR38	60
ED24	80	PR07	68	PR39	36
ED25	80	PR08	106	PR40	40
ED26	46	PR09	102	PR41	80
ED27	30	PR10	30		

Investigation of the local error in the DLPNO-CCSD(T) calculations

Table S 8: Estimation of the local error due to the approximations employed in the DLPNO implementation[3,4] of CCSD(T) as evaluated in comparison to the respective canonical CCSD(T)/def2-SVP result for nine representative reactions of the MOR41 test set. All values are given in kcal/mol.

Reaction	ΔE (CCSD(T)) def2-SVP	ΔE (DLPNO-CCSD(T)) (*TightPNO* settings)	local error
1	-50.55	-49.42	1.13
5	2.68	5.33	2.65
6	-25.87	-25.96	-0.09
18	-33.40	-33.12	0.28
21	-20.50	-20.19	-0.31
26	-26.11	-27.11	-1.00
37	-13.11	-13.55	0.44
39	-71.55	-71.05	0.50
40	-71.16	-70.87	0.30

An important accuracy check for the DLPNO-CCSD(T)/*TightPNO* reference values is the estimation of the local error stemming from the additional approximations in DLPNO-CCSD(T) compared to CCSD(T). The latter is well known for yielding reaction energies with chemical accuracy, provided that only single-reference molecules are involved and the basis set limit is approximately reached. For the estimation of the local error (defined as the difference between the respective DLPNO-CCSD(T) and CCSD(T) reaction energy), the small def2-SVP basis set (with the corresponding auxiliary basis set for the DLPNO-CCSD(T) calculations) was applied to compare the reaction energy of nine representative reactions of the MOR41 test set (different reaction motifs, including also a few larger molecules). Due to the huge computational demands of the canonical CCSD(T) calculations, the larger basis def2-TZVPP basis could not be used to this end but the local error is expected to be roughly the same for larger and smaller basis sets.[5] In order to check this assumption, the same set of nine reactions was re-calculated with canonical CCSD(T) and DLPNO-CCSD(T)/*TightPNO* using the def2-TZVP basis (def2-TZVP/C auxiliary basis set for the DLPNO calculations). Compared to the local error for the small def2-SVP basis set (MD = 0.39 kcal/mol, MAD = 0.67 kcal/mol), the local error obtained with the def2-TZVP is slightly larger (MD = 0.57 kcal/mol, MAD = 0.85 kcal/mol). However, this 0.2 kcal/mol difference on average small enough to conclude, that the local error for the large def2-QZVPP basis set is expected to be still below 1 kcal/mol on average and hence, the 2 kcal/mol uncertainty estimation of the reference values is realistic, also keeping further error source as, e.g., remaining basis set incompleteness and superposition errors in mind.

Table S 9: Estimation of the local error due to the approximations employed in the DLPNO implementation[3,4] of CCSD(T) as evaluated in comparison to the respective canonical CCSD(T)/def2-TZVP result for nine representative reactions of the MOR41 test set. All values are given in kcal/mol.

Reaction	ΔE (CCSD(T)) def2-TZVP	ΔE (DLPNO-CCSD(T)) (*TightPNO* settings)	local error
1	-43.54	-41.82	1.72
5	4.72	7.60	2.88
6	-20.14	-20.16	-0.02
18	-34.03	-33.45	0.58
21	-13.86	-13.34	0.52
26	-31.29	-31.87	-0.58
37	-11.79	-12.59	-0.80
39	-59.85	-58.74	1.11
40	-65.74	-65.47	0.27

Only for reaction (5), a significantly larger local error is observed which is probably due to the error arising from the semi-local approximation in the perturbative triples excitations for the product of reaction (5). Hence, the reaction energy for reaction (5) was calculated using canonical CCSD(T), which could be applied together with a large triple-zeta basis including core-valence correlation but the def2-QZVPP basis used in the CBS extrapolation of the DLPNO-CCSD(T) reaction energies was computationally too demanding for canonical CCSD(T) calculations.

Investigation of the BSSE in the DLPNO-CCSD(T) calculations

Although a CBS extrapolation based on the def2-TZVPP and def2-QZVPP basis sets should be reasonably close to the basis set limit for reaction energies, the remaining basis set incompleteness error (BSIE) and basis set superposition error (BSSE) should be estimated in order to give a reasonable estimation for the uncertainty of the calculated reference reaction energies. While the BSIE could only be estimated by comparing to results with even larger basis sets which are computationally not feasible for the MOR41 test set, the intermolecular part of the BSSE can be estimated, at least for reactions of the type A + B → C under the assumption, that the standard counterpoise correction (CP) scheme proposed by Boys and Bernardi[6] is also valid for reactions where a covalent bond is formed between molecule A and B (as it is the case for the reactions included in the MOR41 test set) which is certainly debatable. Hence, the estimation of the BSSE as deviation between the CP corrected and non-corrected reaction energies for two example reactions of the MOR41 test set as presented in Tab. S 10 can only provide a rough estimate for the remaining BSSE of the MOR41 reference values. Reaction (1) suffers much more from the BSSE while for reaction (6), already the def2-TZVPP value has shows a BSSE well below 1 kcal/mol. However, at the estimated CBS the BSSE for reaction (1) is clearly smaller than for the def2-TZVPP basis set. Keeping in mind that the local error is on average of the same size but opposite direction, one may benefit from error cancellation if the reference values are not counterpoise corrected (which would anyway only be possible for a few reactions in an approximate form), at least for some of the reactions considered in the MOR41 test set. Together with the results from the investigation of the local error, the 2 kcal/mol uncertainty in the reference reaction energies seem to be a decent estimate and even if the error would be slightly larger for a few reactions, this will not significantly change the statistics of the benchmark study on the MOR41 test set, since the majority of the reaction energies should be more accurate than 2 kcal/mol.

Table S 10: DLPNO-CCSD(T)/TightPNO reaction energies with and without the Boys-Bernardi counterpoise correction for reaction (1) and (6) of the MOR41 test set. All values are given in kcal/mol.

	basis set	ΔE w/o CP correction	ΔE CP corrected	deviation
reaction (1)	def2-TZVPP	-41.8	-39.4	2.4
	def2-QZVPP	-42.4	-40.8	1.6
	CBS(TQ)	-43.1	-42.0	1.1
reaction (6)	def2-TZVPP	-21.9	-21.1	0.8
	def2-QZVPP	-22.6	-21.9	0.7
	CBS(TQ)	-23.2	-22.6	0.6

Comparison to back-corrected experimental reaction energies

Table S 11: Comparison of experimental values to calculated reference values for six selected reactions. The experimental $\Delta H_{exptl.}$ were back-corrected to $\Delta E_{"explt."}$. All values are given in kcal/mol.

Reaction	$\Delta H_{exptl.}$	ΔH->ΔE	$\Delta E_{"explt."}$	ΔE_{ref}	ΔE_{ref} - $\Delta E_{"explt."}$
1	-37.0 ± 5.0[7]	1.8 ± 0.5	-38.8 ± 5.5	-43.1 ± 2.0	-4.3
2	-41.0 ± 3.1[8]	1.8 ± 0.5	-42.8 ± 3.6	-46.6 ± 2.0	-3.8
3	-24.8 ± 1.9[9]	1.5 ± 0.5	-26.3 ± 2.4	-27.6 ± 2.0	0.9
5	4.8 ± 2.5[10]	3.0 ± 0.5	1.8 ± 3.0	3.7 ± 2.0	1.9
12	-25.1 ± 1.0[11]	1.9 ± 0.5	-27.0 ± 1.5	-29.8 ± 2.0	-2.8
21	-12.2 ± 0.7[12]	2.1 ± 0.5	-14.3 ± 1.2	-15.1 ± 2.0	-0.7

A comparison of the calculated reference reaction energies to back-corrected experimental reaction energies was carried out for six exemplary reactions, for which experimental determined reaction enthalpies with their respective uncertainty are available in the literature. The experimental reaction enthalpies were back-corrected to "experimental" reaction energies, since the scope of MOR41 test set is to benchmark calculated gas-phase reaction energies at 0 K. To this end, harmonic frequencies were calculated at the TPSS-D3(BJ)/def2-TZVP level of theory and the thermostatistical corrections from enthalpy to energy were obtained with the coupled rigid-rotor-harmonic-oscillator approximation[13] for each molecule in the gas phase at 298.15 K. The vibrational frequencies were used unscaled. All calculations were performed using TURBOMOLE 7.0.2 with the numerical quadrature grid m5. The 0.5 kcal/mol uncertainty of the ΔH->ΔE back-correction is a conservative estimation since the value of this correction itself does not exceed 3 kcal/mol for the six investigated reactions. For the reactions (1), (3), (5), and (21), the deviation of calculated reference reaction energy from the back-corrected experimental reaction energy is smaller than the uncertainty of the latter. Even for reaction (2) and (12), ΔE_{ref} is within the error bar of the respective back-corrected experimental reaction energy, at least if the estimated 2 kcal/mol uncertainty is taken into account. Hence, we trust that the accuracy of the non-relativistic DLPNO-CCSD(T)/*TightPNO*/CBS reference values without core-valence and higher order correlation contributions is sufficient to reliably benchmark the performance of more approximate methods for the thermochemistry of transition metal reaction of realistic size.

DFT-D3 parameters for DSD- and DOD-DHDFs

For the calculation of the dispersion corrected DSD- and DOD-type DHDFs, the following D3(BJ) damping parameters were applied (the parameters s_8 and a_1 were kept zero):[14]

Table S 12: s_6 and a_2 values used for the calculation of the D3(BJ) dispersion correction for DSD- and DOD-DHDFs.

Reaction	s_6	a_2
DSD-SVWN	0.46	5.60
DSD-PBEP86	0.48	5.60
DSD-PBEB95	0.61	6.20
DSD-PBE	0.78	6.10
DSD-BLYP	0.57	5.40
DOD-SVWN	0.57	5.60
DOD-PBEP86	0.72	5.40
DOD-PBEB95	0.71	6.00
DOD-PBE	0.91	5.90
DOD-BLYP	0.96	5.10

Comparison of the performance for first row and second/third row transition metal complexes

The MOR41 test set was divided into two subsets, containing reactions involving 3d-transition metals and 4d+5d transition metals, respectively, which were analyzed separately and discussed at the end of the "Benchmark study on MOR41" section of the paper.

Table S 13: MAD of the best performing DFA/wavefunction method of each class and the average MAD for each class of dispersion corrected DFAs and MP2-based wavefunction methods for two subsets of the MOR41 test set (3d and 4d/5d). All values are given in kcal/mol.

Functional	3d metals	4d + 5d metals
SCAN-D3(BJ)	4.7	2.7
ωB97X-V	2.6	2.1
PWPB95-D3(BJ)	1.9	1.8
RPA	4.7	4.4
PWRB95	1.9	4.0
Ø (meta-)GGA	5.0	4.6
Ø Hybrid	3.7	3.7
Ø DHDF	4.6	2.9
Ø MP2-based	10.7	5.8

Investigation of the ground-state multiplicities

As an additional evidence for the statement that all molecules of the MOR41 test set have a closed-shell electronic structure, we calculated also higher (triplet and quintet) multiplicities and evaluated the vertical energy splitting w.r.t. the singlet multiplicity. These calculations were performed with the PBE-D3(BJ)/def2-QZVP level of theory using the original TPSS-D3(BJ)/def2-TZVP singlet geometries.

Table S 14: Singlet-triplet and singlet-quintet energy differences and their corresponding expectation value of S^2 for the triplet and quintet state of all molecules in the MOR41 test set. All values are evaluated at the PBE-D3(BJ)/def2-QZVP (ORCA 4.0.0 default settings) level of theory. All energies are given in kcal/mol.

	ΔE(T-S)	*<S²> (T)*	*ΔE(5-S)*	*<S²> (5)*
AcCl	107.1	2.00	265.1	6.01
AcI	95.3	2.01	201.3	6.01
Bz	101.0	2.03	191.6	6.01
C2H4	103.5	2.01	307.5	6.00
C2H6	204.1	2.00	426.3	6.00
C3H8	184.8	2.00	405.3	6.00
CO	136.4	2.01	300.3	6.01
CO2	179.1	2.00	364.1	6.00
COD	98.1	2.01	196.3	6.01
ED01	28.6	2.01	108.0	6.02
ED02	22.4	2.01	95.0	6.03
ED03	57.1	2.01	161.9	6.00
ED04	35.6	2.03	102.2	6.01
ED05	98.4	2.02	191.5	6.04
ED07	42.2	2.01	110.9	6.01
ED08	66.6	2.00	150.1	6.01
ED09	39.2	2.00	119.9	6.01

	ΔE(T-S)	*<S²> (T)*	*ΔE(5-S)*	*<S²> (5)*
ED10	8.9	2.00	103.5	6.01
ED11	49.0	2.00	121.2	6.01
ED13	20.5	2.00	124.9	6.01
ED14	32.9	2.01	121.7	6.02
ED15	70.7	2.01	158.2	6.01
ED16a	55.3	2.00	144.7	6.02
ED16b	95.6	2.01	197.5	6.01
ED17	43.0	2.01	114.3	6.01
ED18	69.6	2.00	174.2	6.01
ED21	69.7	2.00	155.4	6.01
ED22	60.6	2.00	149.1	6.00
ED24	36.6	2.02	81.1	6.02
ED25	41.4	2.01	85.3	6.01
ED26	53.2	2.01	120.4	6.01
ED27	110.6	2.00	220.9	6.01
ED28	113.3	2.00	222.7	6.01
ED29	78.5	2.00	192.4	6.01
ED30	92.4	2.01	183.4	6.01
ED31	71.1	2.01	156.4	6.01
ED32	62.2	2.00	134.8	6.00
ED33	73.2	2.00	172.0	6.01
ED36	53.6	2.01	133.1	6.01
ED37	66.8	2.01	140.4	6.01
ED39	44.0	2.01	125.6	6.01
ED40a	26.8	2.01	99.7	6.01
ED40b	113.5	2.00	261.6	6.01
ED41	45.7	2.01	96.6	6.01
H2	234.0	2.00		
I2	37.1	2.00	189.2	6.00
MeCN	153.3	2.01	303.2	6.01
MeI	98.0	2.00	258.6	6.00
MeOH	147.2	2.00	373.4	6.00
PCy3	109.2	2.00	252.2	6.00
PhOH	93.4	2.02	186.2	6.01
PhSeH	87.8	2.01	178.7	6.01
PhSH	87.5	2.01	178.4	6.01
PMe3	116.4	2.00	285.2	6.00
PR01	86.6	2.00	175.4	6.01
PR02	83.1	2.02	165.8	6.03
PR03	92.3	2.01	184.9	6.01
PR04	55.3	2.01	112.8	6.02
PR05	63.4	2.00	156.6	6.01
PR06	69.3	2.01	156.0	6.01
PR07	65.3	2.01	137.5	6.01
PR08	80.9	2.00	170.1	6.01
PR09	61.8	2.00	136.1	6.01
PR10	77.6	2.00	156.9	6.01
PR11	56.1	2.00	139.8	6.01
PR12	72.3	2.01	157.5	6.02
PR13	73.0	2.00	161.7	6.00
PR14	54.3	2.01	128.0	6.01
PR15	47.3	2.01	143.0	6.01
PR16	80.4	2.00	167.0	6.01

	ΔE(T-S)	<S²> (T)	ΔE(5-S)	<S²> (5)
PR17	49.4	2.01	135.1	6.01
PR18	81.6	2.00	171.4	6.01
PR19	75.8	2.00	164.3	6.01
PR20	79.4	2.01	172.8	6.01
PR21	47.5	2.00	114.5	6.01
PR22	49.0	2.00	118.0	6.01
PR23	52.3	2.00	135.3	6.01
PR24	30.6	2.01	74.9	6.02
PR25	33.0	2.01	80.3	6.02
PR26	59.0	2.01	124.6	6.01
PR27	54.5	2.01	126.3	6.01
PR28	56.8	2.01	128.2	6.01
PR29	90.8	2.00	207.8	6.01
PR30	80.8	2.00	171.6	6.01
PR31	75.2	2.00	162.0	6.01
PR32	67.4	2.01	139.5	6.01
PR33	73.4	2.01	157.5	6.01
PR34	70.5	2.01	159.7	6.01
PR35	69.2	2.01	156.9	6.01
PR36	36.1	2.01	94.3	6.01
PR37	65.3	2.00	133.3	6.01
PR38	77.3	2.00	157.0	6.01
PR39	64.6	2.01	139.1	6.01
PR40	64.6	2.01	136.6	6.01
PR41	33.1	2.02	90.6	6.01

The four molecules with the smallest PBE/def2-QZVP vertical triplet-singlet energy differences were re-calculated with the double hybrid functional B2GPPLYP-D3(BJ), which is known to be yield accurate singlet-triplet splitting energies, to double check whether the singlet state is clearly the lowest in energy. The def2-TZVP basis was employed in these calculations and the geometries were re-optimized separately for the singlet and triplet state using PBE0-D3(BJ)/def2-TZVP, i.e. the *Δ*E(T-S) values presented in Tab. S 15 correspond to non-vertical singlet-triplet splitting energies. They are even larger (> 10 kcal/mol) than the vertical PBE/def2-QZVP singlet-triplet-splitting energies and hence, spin-state mixing should not an issue for the molecules in considered in the MOR41 test set. Thus, single-reference DLPNO-CCSD(T)/*TightPNO*/CBS calculations are a reliable choice to obtain accurate reference values.

Table S 15: Non-vertical singlet-triplet energy differences calculated at the B2GPPLYP-D3(BJ)/def2-TZVP level of theory for four selected molecules of the MOR41 test set. All energies are given in kcal/mol.

	ΔE(T-S)
ED01	30.2
ED02	21.5
ED10	12.8
ED40a	26.4

Dependence of the functional performance on the system size

As a first attempt to investigate the functional performance on the system size, we have chosen the five smallest ((2), (3), (4), (13), (40)) and five largest ((8), (9), (16), (24), (25)) reactions according to the number of electrons in the product, but the average MADs of 4.1 kcal/mol and 4.3 kcal/mol over all dispersion corrected DFAs are not significantly different.

However, as there is no well-defined measure for the "size" of a whole reaction, we have used the change in dispersion energy as a second attempt to quantify the size of the chemical reaction. To this end, B3LYP is a good choice since it is a rather repulsive functional and hence larger absolute values of the D3(BJ) energy are obtained compared to other DFAs. The deviation of the B3LYP-D3(BJ)/def2-QZVPP reaction energies form the reference values was plotted against the differences in the dispersion energy obtained from the same calculation for the respective reaction but no correlation between both could be obtained. Even for the reactions (16), (24), (25), and (38) with large (> 25 kcal/mol) relative contribution of the dispersion energy, the deviation of the respective B3LYP-D3(BJ) reaction energy from the reference value varies strongly between -0.7 kcal/mol (reaction 16) and -14.5 kcal/mol (reaction 38).

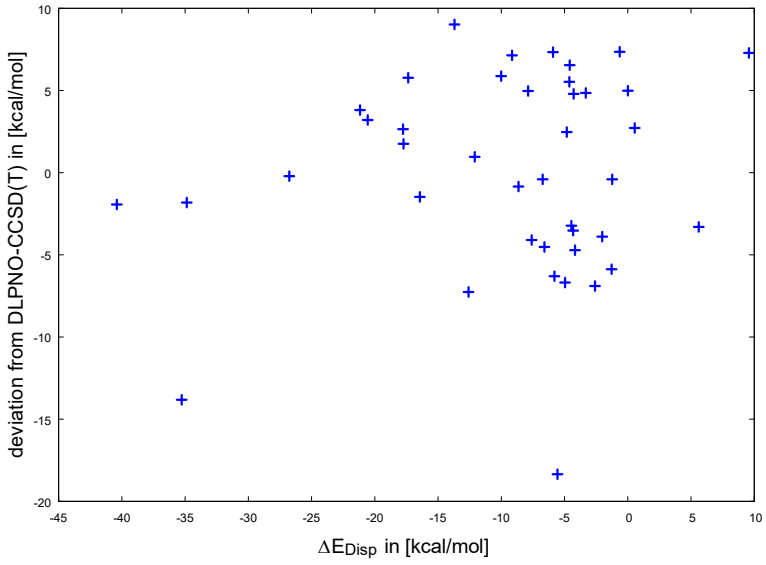

Figure S1: Deviation of ΔE(B3LYP-D3(BJ)/def2-QZVPP) from the reference reaction energy vs. the relative contribution of the dispersion energy ΔE_{Disp} obtained from the same calculation of the respective reaction from the MOR41 test set.

Related to this investigation is the question whether diffuse functions are mandatory for an accurate reference calculation since they may contribute significantly to the long-range part of the correlation energy. However, as can be concluded form Fig. S1, the accuracy of a particular DFA for the MOR41 benchmark does not correlate with a large dispersion interaction contribution to the respective reaction thus showing that the semi-diffuse basis functions included in the def2-TZVPP and def2-QZVPP basis sets are sufficient to accurately describe long-range dispersion interactions with the DLPNO-CCSD(T)/*TightPNO* method for the molecules contained in MOR41. Moreover, the CBS(def2-TZVPP/def2-QZVPP) reaction energies are closer to the basis set limit and suffer less from BSSE than respective aug-cc-pVTZ calculations (aug-cc-pVQZ calculations are not computationally feasible for the large molecules of the MOR41 test set and may have linear dependencies even for the smaller systems).

Investigation of the fractional occupation number weighted density

As an additional check for static correlation the fractional occupation number weighted density (FOD)[15,16]was calculated at the PBE/def2-TZVP (T_{el} = 5000 K) level of theory for all molecules of the MOR41 test set. Only for one molecules (ED40a: [$Ti(CH_3)_2CH_3$]), a larger integrated FOD value per electron of N_{FOD}/N_{el} = 0.03 was obtained but the corresponding FOD plot shown in Fig. S2 shows only rather localized FOD around the Ti atom and the carbene C atom. According to the rules of thumb given in Ref. 17 and 18, this is no indication of significant static correlation effects. Since all other molecules of the MOR41 test set have N_{FOD}/N_{el} values of at most half of the value obtained for ED40a, it can be concluded, that single-reference CCSD(T) should be a reliable and accurate electronic structure method for calculating reference reaction energies for this test set.

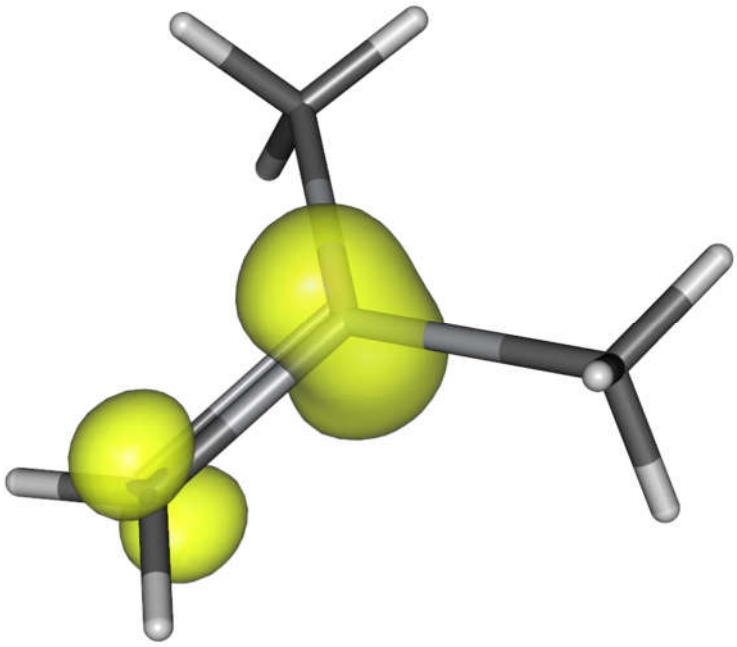

Figure S2: FOD for ED40a of the MOR41 test set obtained with PBE/def2-TZVP and T_{el} = 5000 K (ORCA 4.0.0 default settings). The FOD is depicted in yellow at a surface contour cut-off value of σ =0.005 e/Bohr^3.

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