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On the accuracy of orbital based multi-level approaches for closed-shell transition metal chemistry

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Table S1 Comparison of different local coupled cluster methods and different optimization schemes/thresholds for pair criteria in the case of LCCSD(T0) for the reaction 36 in MOR41 set.

Local Coupled Cluster		ΔE [kcal/mol]
LCCSD(T0)	rclose,rweak	
	3,5	−20.48
IBBA	4,6	−19.90
	5,7	−21.55
Pipek–Mezey	3,5	−43.03
PNO-CCSD(T)-F12		−39.22
DLPNO-CCSD(T_0)		−40.52

Notes and references

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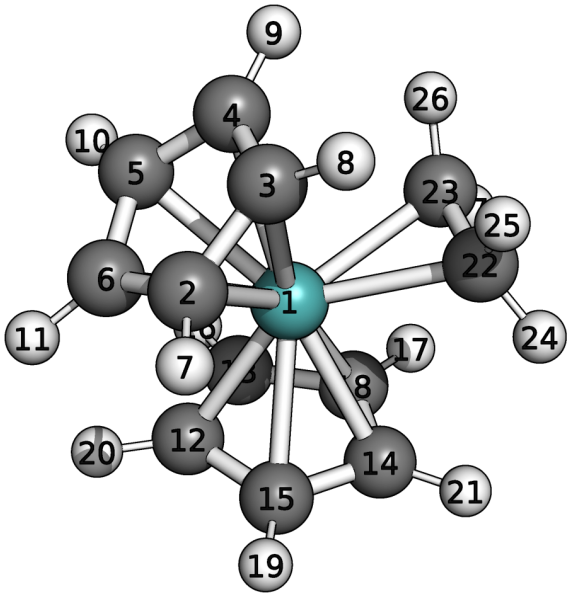

Fig. S1 Enumeration of the atoms in the reactant complex of reaction 36 from the MOR41 set.

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Table S2 Comparison of orbital domains of one of the aromatic systems obtained after IBO and Pipek-Mezey localization for reactant complex of reaction 36 from the MOR41 set. See Figure S1 for the enumeration of the atoms.

IBO localization				Pipek-Mezey localization			
Orb.	Atom	Charge	Total	Orb.	Atom	Charge	Total
36.1	5C	0.98		57.1	5C	0.98	
	4C	0.98	1.95		4C	0.98	1.96
38.1	2C	0.98		48.1	3C	0.98	
	3C	0.98			2C	0.98	1.96
	1Mo	0.03	1.98				
42.1	6C	0.98		55.1	6C	0.98	
	5C	0.97	1.96		5C	0.97	1.96
43.1	6C	0.98		49.1	6C	0.98	
	2C	0.97	1.96		2C	0.97	1.96
44.1	4C	0.99		51.1	3C	0.98	
	3C	0.99	1.97		4C	0.98	
					1Mo	0.03	1.98
63.1	5C	1.03		54.1	4C	0.84	
	6C	0.39			5C	0.75	
	4C	0.28			1Mo	0.25	
	1Mo	0.26	1.96		2C	0.07	
					3C	0.05	1.96
64.1	2C	1.03		50.1	6C	1.02	
	6C	0.42			1Mo	0.36	
	1Mo	0.26			2C	0.30	
	3C	0.25	1.95		5C	0.22	
					4C	0.04	1.94
68.1	3C	0.70		46.1	3C	0.91	
	4C	0.66			2C	0.64	
	1Mo	0.42			1Mo	0.26	
	6C	0.17	1.95		4C	0.09	
					5C	0.06	1.96

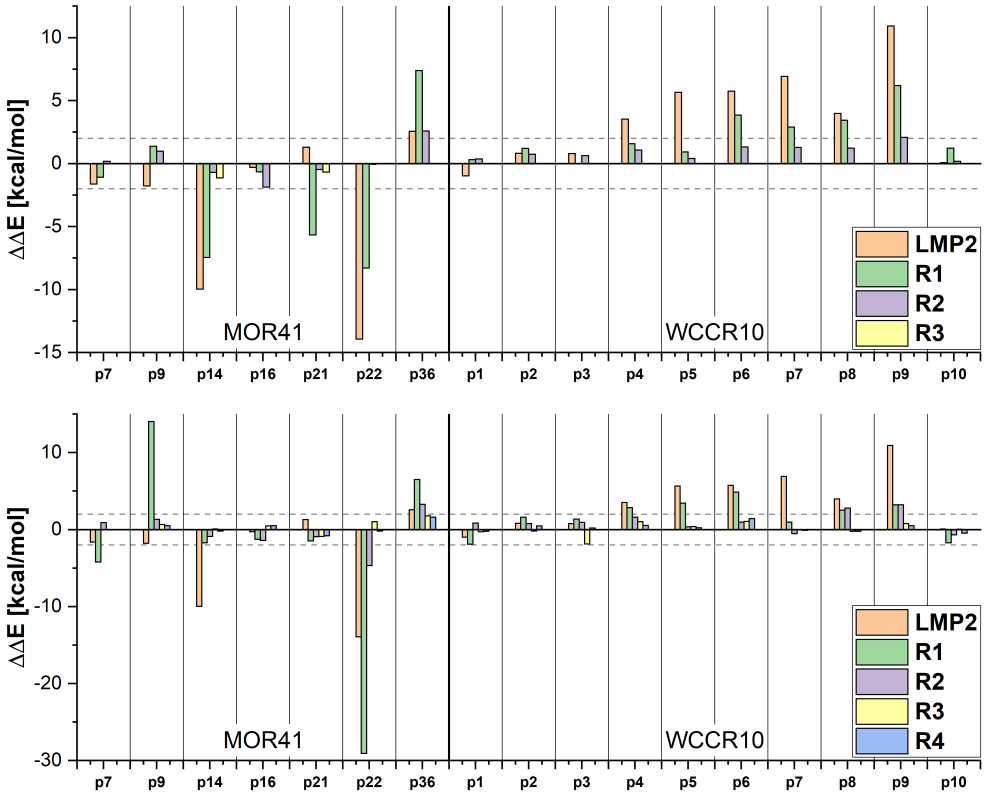

Fig. S2 Errors in the relative energies $\Delta\Delta E$ of LMP2 and LCCSD(T0):LMP2 calculations with three different manual region selections (upper panel) and four DOS region selections (lower panel) compared to LCCSD(T0) on the examples of the MOR41 and WCCR10 test sets.

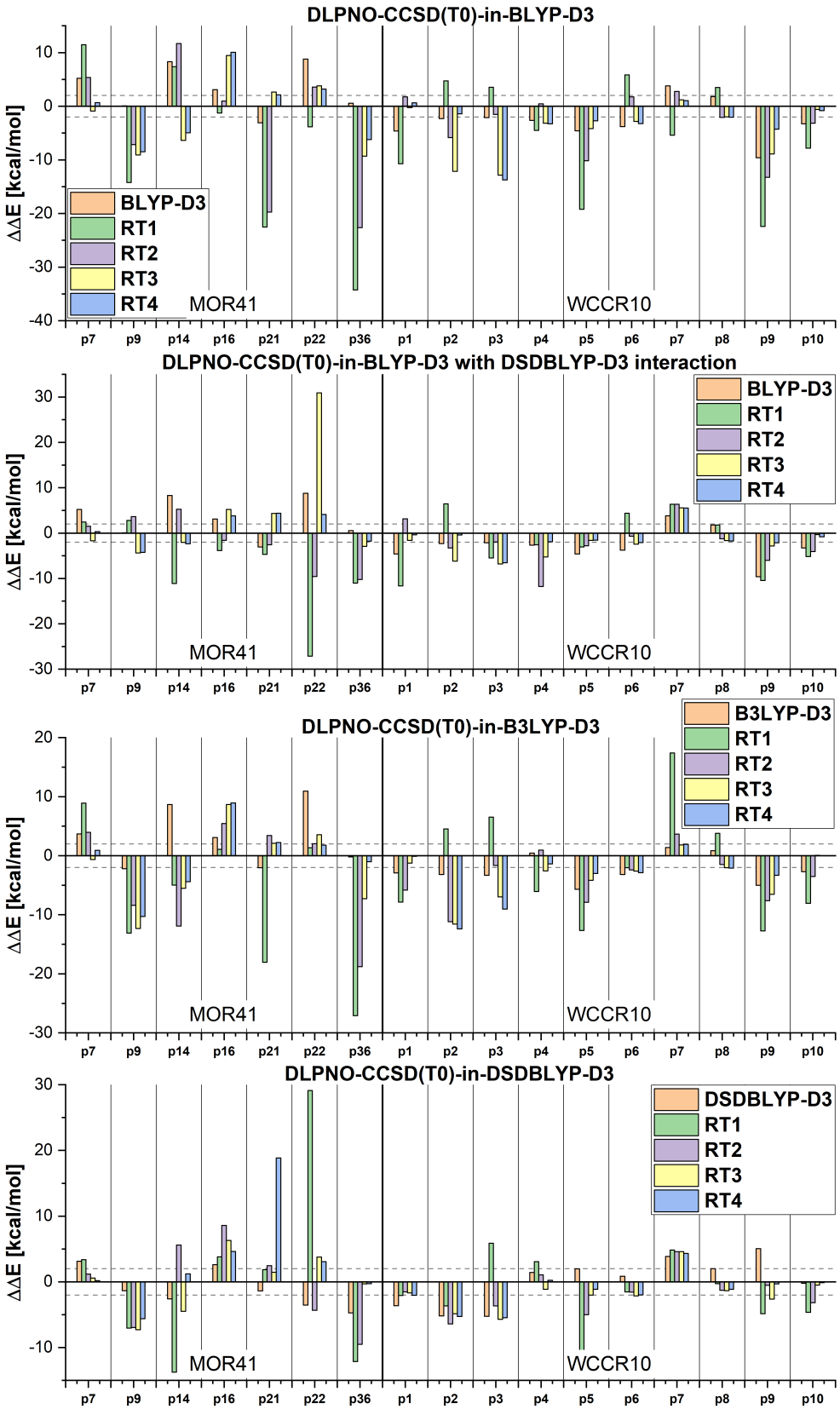

Fig. S3 Errors in the relative energies $\Delta\Delta E$ of different DFT functionals and DLPNO-CCSD(T_0)-in-DFT calculations with four different region selections compared to DLPNO-CCSD(T_0) for the MOR41 and WCCR10 test sets.

Table S3 Orbitals included in high level region in R3 but not in RT2 and vice versa for reaction 24 in MOBH35.

Reactant orbitals

R3		RT2	
Orb.	Atoms	Orb.	Atoms
51.1	73 O - 71 C	66.1	3 C - 1 C
52.1	18 O - 17 C	69.1	4 C - 2 C
56.1	6 N - 1 C	78.1	77 C - 80 H
72.1	17 C - 74 RE	92.1	12 C - 14 H
107.1	12 C - 16 P	93.1	12 C - 13 H
124.1	46 C - 16 P	97.1	3 C - 8 H
134.1	59 C - 16 P	108.1	47 C 51 H
138.1	33 C - 15 P	122.1	22 C - 29 H
139.1	16 P - 74 RE	151.1	79 C - 77 C - 83 C - 78 C

Transition state orbitals

R3		RT2	
Orb.	Atoms	Orb.	Atoms
51.1	18 O - 17 C	65.1	4 C - 3 C
52.1	73 O - 72 C	66.1	2 C - 1 C
56.1	6 N - 1 C	67.1	2 C - 3 C
72.1	17 C - 74 RE	87.1	77 C - 80 H
97.1	49 C - 58 H	91.1	3 C - 7 H
107.1	12 C - 16 P	92.1	12 C - 14 H
131.1	59 C - 16 P	93.1	12 C - 13 H
136.1	46 C - 16 P	115.1	22 C - 29 H
139.1	33 C - 15 P	117.1	47 C - 51 H
140.1	16 P - 74 RE	151.1	79 C - 77 C - 83 C - 78 C

Product orbitals

R3		RT2	
Orb.	Atoms	Orb.	Atoms
51.1	18 O - 17 C	58.1	2 C - 1 C
52.1	73 O - 72 C	60.	4 C - 3 C
55.1	6 N - 1 C	84.1	3 C - 7 H
71.1	17 C - 74 RE	88.1	2 C - 8 H
87.1	4 C - 9 H	90.1	12 C - 14 H
122.1	12 C - 16 P	91.1	12 C - 13 H
130.1	59 C - 16 P	92.1	77 C - 80 H
132.1	33 C - 15 P	135.1	22 C - 29 H
137.1	46 C - 16 P	138.1	47 C - 51 H
140.1	16 P - 74 RE	153.1	79 C - 83 C - 77 C - 78 C

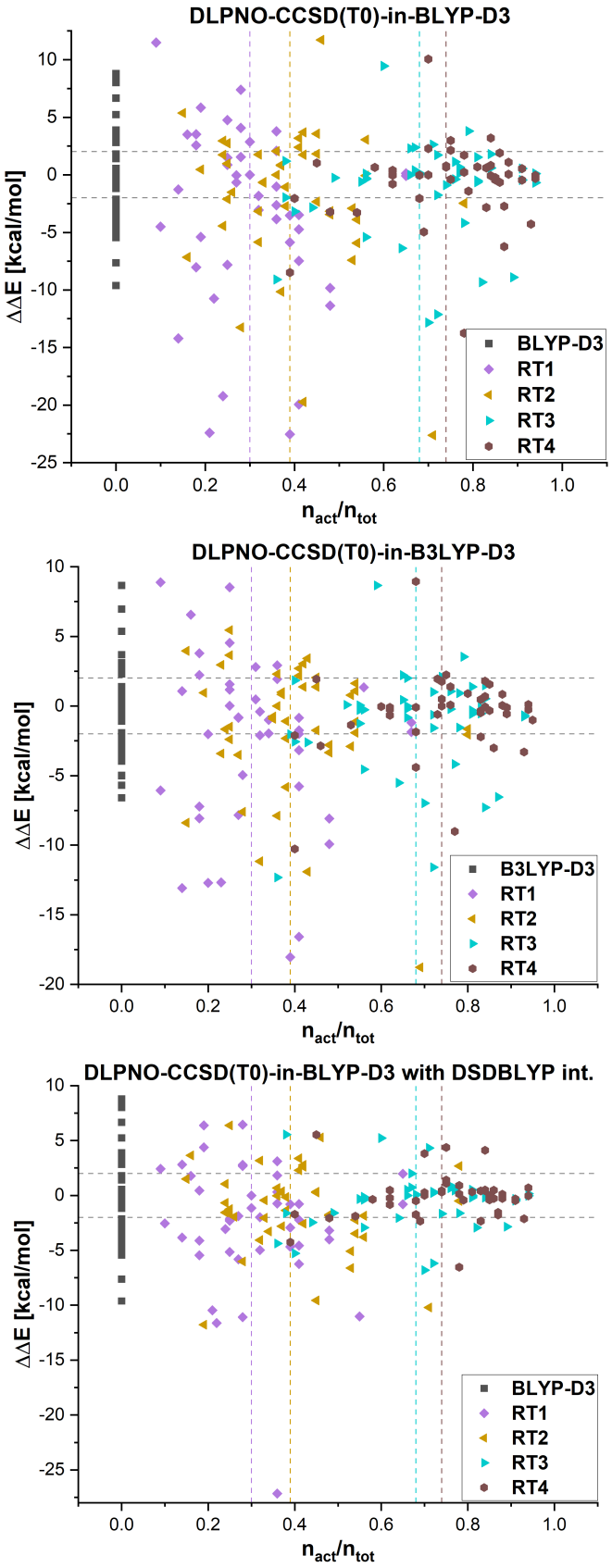

Fig. S4 Errors in the relative energies $\Delta\Delta E$ plotted against the ratio of valence orbitals correlated in the active region $n_{\mathrm{act}}/n_{\mathrm{tot}}$ in the DLPNO-CCSD(T_0)-in-DFT schemes for all systems. Vertical lines represent the average ratio of correlated orbitals for the corresponding region selection.

Table S4 Summary of DFT, LMP2 and local coupled cluster results for MOBH35 systems. Absolute errors (AE) (mean AE, max AE and min AE) and standard deviation (SD) are calculated based on DLPNO-CCSD(T_0) reference energy in the case of DFT and based on LCCSD(T0) in the case of LMP2.

MOBH35	BLYP	B3LYP	DSDBLYP	LMP2	LCCSD(T0)	DLPNO-CCSD(T_0)	DLPNO-CCSD(T)[a]
ts1	22.8	25.5	26.1	25.1	28.4	27.5	26.0
p1	8.3	8.9	11.8	14.4	12.0	12.6	10.6
ts6	13.2	15.0	15.5	16.6	17.5	16.1	15.8
p6	−0.4	1.6	1.0	6.0	5.4	0.5	1.5
ts7	21.1	24.7	25.1	20.5	25.1	28.7	27.9
p7	7.9	8.6	7.6	7.0	7.1	10.5	9.5
ts11	30.8	36.1	35.9	36.8	34.9	36.3	34.8
p11	−58.0	−57.8	−53.8	−50.2	−57.2	−55.5	−54.8
ts14	7.2	9.2	9.7	10.9	11.6	10.2	10.3
p14	−5.6	−4.4	−4.6	−2.1	−2.1	−4.4	−4.1
ts21	11.1	11.4	8.6	5.6	7.5	8.3	9.2
p21	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ts22	12.9	14.9	13.9	13.1	18.5	15.6	14.3
p22	−8.4	−11.2	−11.8	−10.9	−10.7	−12.3	−14.8
ts24	2.9	3.9	2.4	3.3	3.9	2.8	2.9
p24	−5.7	−8.4	−11.8	−10.5	−10.9	−13.8	−14.1
ts29	10.3	12.3	13.8	15.6	16.9	14.7	15.0
p29	−12.6	−13.9	−15.6	−16.1	−15.8	−16.2	−15.9
ts30	11.8	11.3	11.3	10.6	12.3	11.4	9.9
p30	−6.2	−8.2	−6.6	−4.6	−6.5	−6.0	−7.3
ts31	4.7	5.9	3.4	0.0	3.2	3.2	3.3
p31	−5.4	−5.1	−9.5	−12.6	−10.6	−12.1	−10.1
ts34	27.7	27.7	31.4	33.9	31.2	32.7	29.2
p34	24.2	22.8	28.8	35.2	29.2	29.4	26.2
ts35	12.4	14.6	16.2	18.7	16.3	17.2	18.3
p35	16.1	18.0	18.0	18.0	15.2	18.5	19.7
mean AE	3.3	2.3	1.0	2.1			
SD	3.9	3.0	1.3	2.9			
max AE	8.0	7.0	3.6	6.9			
min AE	0.0	0.0	0.0	0.0			

[a] DLPNO-CCSD(T)/CBSW1+Δ(T)/TZVP taken from Ref. 1. For detailed description of the approach they used see Ref. 2

Table S5 Summary of DFT, LMP2 and local coupled cluster results for MOR41 systems. Absolute errors (AE) (mean AE, max AE and min AE) and standard deviation (SD) are calculated based on DLPNO-CCSD(T_0) reference energy in the case of DFT and based on LCCSD(T0) in the case of LMP2.

MOR41	BLYP	B3LYP	DSDBLYP	LMP2	LCCSD(T0)	DLPNO-CCSD(T_0)	DLPNO-CCSD(T)[a]
p7	−9.2	−10.8	−11.3	−12.7	−11.0	−14.5	−16.2
p9	−9.8	−12.0	−11.2	−16.3	−14.5	−9.8	−18.7
p14	−43.8	−43.4	−54.6	−54.5	−44.5	−52.1	−52.0
p16	−39.6	−39.6	−40.0	−30.2	−29.9	−42.7	−39.8
p21	−18.0	−17.0	−16.3	−15.1	−16.3	−14.9	−15.1
p22	−33.7	−31.5	−46.0	−36.0	−22.1	−42.5	−35.9
p36	−40.0	−40.7	−45.2	−17.9	−20.5	−40.5	−39.8
mean AE	4.2	4.4	2.8	4.5			
SD	4.4	5.1	3.0	6.2			
max AE	8.8	10.9	4.7	13.9			
min AE	0.1	0.2	1.3	0.3			

[a] DLPNO-CCSD(T)/TightPNO/CBS(def2-TZVPP/def2-QZVPP) taken from Ref. 3

Table S6 Summary of DFT, LMP2 and local coupled cluster results for WCCR10 systems. Absolute errors (AE) (mean AE, max AE and min AE) and standard deviation (SD) are calculated based on DLPNO-CCSD(T_0) reference energy in the case of DFT and based on LCCSD(T0) in the case of LMP2.

WCCR10	BLYP	B3LYP	DSDBLYP	LMP2	LCCSD(T0)	DLPNO-CCSD(T_0)	DLPNO-CCSD(T)[a]
p1	25.5	27.2	26.4	23.5	24.5	30.1	25.6
p2	69.4	68.5	66.5	55.2	54.4	71.7	63.4
p3	69.9	68.7	66.8	56.3	55.5	72.0	63.0
p4	50.8	53.9	54.9	51.1	47.6	53.4	52.7
p5	48.6	47.5	55.2	48.4	42.7	53.2	45.1
p6	63.8	64.4	68.4	72.2	66.5	67.5	67.4
p7	62.9	60.4	62.9	63.7	56.8	59.1	59.7
p8	50.9	49.9	51.1	52.6	48.7	49.1	50.1
p9	32.5	37.1	47.2	45.4	34.5	42.1	35.9
p10	21.8	22.3	24.8	25.5	25.5	25.0	23.7
mean AE	3.9	2.9	2.9	3.9			
SD	3.6	2.4	3.6	3.7			
max AE	9.6	5.7	5.2	10.9			
min AE	1.8	0.4	0.2	0.1			

[a] DLPNO-CCSD(T)/CBS taken from Ref. 4

Table S7 Reaction barriers (ts*n*) and reaction energies (p*n*) of all the systems computed at LCCSD(T0):LMP2/def2-TZVP with three different manual (R1-R3) and four different DOS (RT1-RT4) region selections and full LCCSD(T0)/def2-TZVP. Absolute errors (AE) (mean AE, max AE and min AE) and standard deviation (SD) are calculated based on LCCSD(T0).

MOBH35	R1	R2	R3	RT1	RT2	RT3	RT4	LCCSD(T0)
ts1	25.3	28.2		26.1	27.1	28.1	28.3	28.4
p1	14.6	14.1		13.4	13.3	12.6	12.4	12.0
ts6	17.5	18.3	17.1	18.0	18.0	17.7	17.8	17.5
p6	8.4	7.0	4.8	4.9	5.5	5.5	5.6	5.4
ts7	19.6	24.0	23.8	22.9	24.1	25.3	25.4	25.1
p7	6.6	8.0	7.7	7.6	7.8	7.2	7.2	7.1
ts11	42.2	38.2	35.2	38.5	37.1	35.3	35.4	34.9
p11	−50.3	−56.4	−56.5	−52.4	−55.6	−56.8	−56.8	−57.2
ts14	9.1	12.3	11.6	12.0	11.9	11.7	11.8	11.6
p14	−3.3	−0.4	−2.3	−2.6	−2.6	−2.0	−1.9	−2.1
ts21	6.5	7.3		6.4	6.1	7.5	7.4	7.5
p21	0.0	0.0		0.0	0.0	0.0	0.0	0.0
ts22	14.8	14.3	18.0	17.7	17.8	18.3	18.4	18.5
p22	−7.8	−13.5	−10.8	−10.4	−10.4	−10.7	−10.6	−10.7
ts24	2.7	2.7	4.2	−8.3	−12.4	−14.1	3.6	3.9
p24	−10.2	−12.9	−10.9	−36.8	−28.2	−29.2	−11.0	−10.9
ts29	15.4	15.5	16.8	16.8	16.7	17.1	17.1	16.9
p29	−14.0	−13.4	−16.0	−18.6	−18.7	−16.0	−15.8	−15.8
ts30	12.5	12.5		12.6	12.6	12.5	12.5	12.3
p30	−4.7	−6.3		−6.8	−6.8	−6.3	−6.3	−6.5
ts31	2.8	3.4		2.9	3.1	2.8	3.4	3.2
p31	−12.3	−11.0		−12.1	−11.0	−10.4	−10.4	−10.6
ts34	33.0	31.1		31.1	31.5	31.2	31.1	31.2
p34	33.0	28.8		29.0	29.5	29.1	29.0	29.2
ts35	15.6	16.2		16.3	15.7	16.3	16.4	16.3
p35	15.1	15.1		15.2	14.3	15.3	15.4	15.2
mean AE	2.1	1.1	0.4	2.4	2.0	1.6	0.2	
SD	2.9	1.6	0.5	5.7	4.6	4.9	0.2	
max AE	7.3	4.2	1.3	25.9	17.3	18.2	0.5	
min AE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
MOR41	R1	R2	R3	RT1	RT2	RT3	RT4	LCCSD(T0)
p7	−12.1	−10.9		−15.3	−10.1	−11.1	−11.1	−11.0
p9	−13.2	−13.5		−0.5	−13.2	−13.9	−14.0	−14.5
p14	−52.0	−45.2	−45.6	−46.2	−45.4	−44.4	−44.7	−44.5
p16	−30.6	−31.8		−31.2	−31.4	−29.5	−29.4	−29.9
p21	−22.0	−16.8	−17.0	−17.8	−17.3	−17.2	−17.2	−16.3
p22	−30.4	−22.1		−51.2	−26.8	−21.1	−22.3	−22.1
p36	−13.1	−17.9	−20.5	−14.0	−17.2	−18.7	−18.9	−20.5
mean AE	4.6	1.0	0.6	8.3	1.9	0.7	0.5	
SD	5.6	1.4	0.6	13.3	2.5	0.9	0.8	
max AE	8.3	2.6	1.1	29.1	4.7	1.8	1.6	
min AE	0.7	0.1	0.0	1.3	0.9	0.0	0.0	
MOR41	R1	R2	R3	RT1	RT2	RT3	RT4	LCCSD(T0)
p1	24.8	24.9		22.6	25.4	24.2	24.3	24.5
p2	55.6	55.2		56.0	55.2	54.2	54.9	54.4
p3	-[a]	56.2		56.9	56.5	53.7	55.7	55.5
p4	49.1	48.6		50.4	49.2	48.6	48.1	47.6
p5	43.7	43.2		46.2	43.1	43.1	43.0	42.7
p6	70.4	67.8		71.4	67.5	67.6	67.9	66.5
p7	59.7	58.0		57.7	56.2	56.8	56.7	56.8
p8	52.1	49.9		51.2	51.5	48.4	48.4	48.7
p9	40.7	36.6		37.7	37.7	35.3	35.0	34.5
p10	26.7	25.6		23.7	24.8	25.5	25.0	25.5
mean AE	2.4	0.9		2.4	1.3	0.6	0.4	
SD	1.9	0.6		2.2	1.3	0.8	0.5	
max AE	6.2	2.1		4.9	3.2	1.9	1.4	
min AE	0.0	0.2		1.0	0.3	0.0	0.1	

[a] The calculation stopped without giving any kind of error message.

Table S8 Reaction barriers (ts*n*) and reaction energies (p*n*) of all the systems computed at DLPNO-CCSD(T_0)-in-BLYP-D3 for four different DOS (RT1-RT4) region selections and full DLPNO-CCSD(T_0)/def2-TZVP. Absolute errors (AE) (mean AE, max AE and min AE) and standard deviation (SD) are calculated based on DLPNO-CCSD(T_0).

MOBH35	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
ts1	30.1	30.5	27.2	27.5	27.5
p1	4.6	8.2	7.2	10.6	12.6
ts6	11.4	16.0	15.6	15.6	16.1
p6	−3.0	3.5	1.0	1.0	0.5
ts7	28.8	26.2	28.0	28.4	28.7
p7	10.4	8.0	10.6	10.5	10.5
ts11	28.8	33.4	35.7	35.6	36.3
p11	−75.4	−62.9	−53.9	−53.5	−55.5
ts14	0.4	6.4	10.8	10.3	10.2
p14	−15.8	−10.4	−2.6	−3.3	−4.4
ts21	11.2	10.4	10.6	10.6	8.3
p21	0.0	0.0	0.0	0.0	0.0
ts22	17.7	18.0	16.8	16.4	15.6
p22	−8.5	−9.1	−12.7	−12.4	−12.3
ts24	4.4	3.6	2.9	3.4	2.8
p24	−9.7	−12.9	−13.1	−16.6	−13.8
ts29	11.2	11.5	12.9	14.3	14.7
p29	−22.1	−19.6	−14.5	−13.2	−16.2
ts30	10.7	10.7	11.0	11.4	11.4
p30	−6.0	−6.6	−5.9	−5.6	−6.0
ts31	4.7	6.9	3.6	3.5	3.2
p31	−11.2	−10.3	−9.7	−10.4	−12.1
ts34	31.7	31.6	32.8	33.4	32.7
p34	26.8	26.7	29.5	30.2	29.4
ts35	14.1	14.8	16.7	16.9	17.2
p35	16.7	20.3	17.9	18.0	18.5
mean AE	4.0	2.5	0.9	0.8	
SD	5.5	3.0	1.5	1.2	
max AE	19.9	7.4	5.4	3.0	
min AE	0.0	0.0	0.0	0.0	
MOR41	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
p7	−3.0	−9.1	−15.4	−13.8	−14.5
p9	−24.1	−17.0	−18.9	−18.3	−9.8
p14	−44.7	−40.4	−58.4	−57.0	−52.1
p16	−43.9	−41.7	−33.2	−32.6	−42.7
p21	−37.5	−34.6	−12.3	−12.8	−14.9
p22	−46.3	−38.9	−38.7	−39.3	−42.5
p36	−74.8	−63.1	−49.8	−46.7	−40.5
mean AE	13.6	10.2	5.9	5.1	
SD	16.4	13.0	7.2	6.5	
max AE	34.3	22.6	9.4	10.1	
min AE	1.3	1.0	0.9	0.7	
WCCR10	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
p1	19.3	31.8	29.8	30.7	30.1
p2	76.4	65.9	59.6	70.3	71.7
p3	75.5	70.5	59.2	58.3	72.0
p4	48.9	53.9	50.3	50.2	53.4
p5	34.0	43.1	49.0	50.5	53.2
p6	73.4	69.3	64.7	64.3	67.5
p7	53.7	61.8	60.2	60.1	59.1
p8	52.6	47.0	47.1	47.0	49.1
p9	19.7	28.9	33.2	37.9	42.1
p10	17.2	21.9	24.4	24.2	25.0
mean AE	8.8	4.3	4.8	3.3	
SD	10.0	5.3	5.0	4.2	
max AE	22.4	13.3	12.8	13.7	
min AE	3.5	0.5	0.3	0.6	

Table S9 Reaction barriers (ts*n*) and reaction energies (p*n*) of all the systems computed at DLPNO-CCSD(T_0)-in-BLYP-D3 with DSDBLYP interaction for four different DOS (RT1-RT4) region selections and full DLPNO-CCSD(T_0)/def2-TZVP. Absolute errors (AE) (mean AE, max AE and min AE) and standard deviation (SD) are calculated based on DLPNO-CCSD(T_0).

MOBH35	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
ts1	28.0	28.6	27.1	27.0	27.5
p1	8.5	11.1	9.7	10.9	12.6
ts6	15.3	14.2	15.6	15.6	16.1
p6	−1.8	−3.3	0.1	0.1	0.5
ts7	27.9	28.2	28.7	28.7	28.7
p7	12.5	13.2	10.7	11.2	10.5
ts11	31.7	31.2	36.1	36.0	36.3
p11	−61.7	−62.1	−54.9	−55.0	−55.5
ts14	7.0	8.0	10.0	10.0	10.2
p14	−8.5	−7.9	−4.1	−4.3	−4.4
ts21	7.2	9.0	8.8	8.6	8.3
p21	0.0	0.0	0.0	0.0	0.0
ts22	17.5	17.9	16.5	16.1	15.6
p22	−9.2	−8.9	−11.6	−11.9	−12.3
ts24	5.5	3.2	3.2	3.2	2.8
p24	−11.0	−13.5	−13.1	−16.1	−13.8
ts29	13.9	12.9	14.9	15.8	14.7
p29	−19.1	−18.0	−15.9	−14.8	−16.2
ts30	9.5	10.9	11.2	11.9	11.4
p30	−11.8	−8.0	−6.3	−6.2	−6.0
ts31	1.1	5.9	4.0	3.4	3.2
p31	−14.4	−9.3	−10.1	−11.2	−12.1
ts34	33.0	32.5	32.7	33.0	32.7
p34	28.7	28.0	29.5	29.8	29.4
ts35	15.2	17.4	17.2	17.1	17.2
p35	13.5	18.8	18.4	18.1	18.5
mean AE	2.5	1.9	0.5	0.5	
SD	2.6	2.5	0.8	0.8	
max AE	6.2	6.6	2.9	2.3	
min AE	0.0	0.0	0.0	0.0	
MOR41	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
p7	−12.0	−13.0	−16.1	−14.1	−14.5
p9	−7.0	−6.2	−14.2	−14.1	−9.8
p14	−63.2	−46.8	−54.1	−54.4	−52.1
p16	−46.5	−44.3	−37.4	−38.9	−42.7
p21	−19.6	−17.5	−10.6	−10.5	−14.9
p22	−69.6	−52.0	−11.6	−38.4	−42.5
p36	−51.5	−50.7	−43.5	−42.3	−40.5
mean AE	9.0	4.9	7.4	3.0	
SD	10.3	6.1	12.3	3.5	
max AE	27.2	10.2	30.9	4.4	
min AE	2.4	1.5	1.7	0.3	
WCCR10	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
p1	18.4	33.2	28.5	29.7	30.1
p2	78.1	68.4	65.5	71.3	71.7
p3	66.6	70.1	65.2	65.5	72.0
p4	50.9	41.7	48.2	51.5	53.4
p5	50.1	50.4	51.6	51.7	53.2
p6	71.9	66.9	65.1	65.5	67.5
p7	65.4	65.4	64.6	64.6	59.1
p8	50.9	47.8	47.4	47.4	49.1
p9	31.7	36.1	39.3	40.0	42.1
p10	19.9	21.0	24.7	24.2	25.0
mean AE	5.7	4.1	3.4	2.3	
SD	6.5	4.9	3.5	2.9	
max AE	11.6	11.8	6.8	6.5	
min AE	1.8	0.7	0.3	0.4	

Table S10 Reaction barriers (ts*n*) and reaction energies (p*n*) of all the systems computed at DLPNO-CCSD(T_0)-in-B3LYP-D3 for four different DOS (RT1-RT4) region selections and full DLPNO-CCSD(T_0)/def2-TZVP. Absolute errors (AE) (mean AE, max AE and min AE) and standard deviation (SD) are calculated based on DLPNO-CCSD(T_0).

MOBH35	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
ts1	29.8	30.5	27.3	27.4	27.5
p1	5.4	9.2	8.1	10.8	12.6
ts6	12.9	15.0	15.5	15.5	16.1
p6	−1.3	2.1	0.4	0.4	0.5
ts7	27.5	27.0	28.0	28.4	28.7
p7	8.6	8.5	9.7	10.6	10.5
ts11	30.5	37.1	35.7	35.9	36.3
p11	−72.0	−58.4	−54.1	−53.9	−55.5
ts14	2.1	11.3	10.8	10.3	10.2
p14	−14.4	−6.4	−3.0	−3.6	−4.4
ts21	16.8	10.6	10.3	10.1	8.3
p21	0.0	0.0	0.0	0.0	0.0
ts22	17.6	17.8	16.7	16.3	15.6
p22	−9.4	−9.6	−12.5	−12.3	−12.3
ts24	3.3	3.8	3.7	3.3	2.8
p24	−11.0	−12.9	−15.3	−16.0	−13.8
ts29	13.9	11.9	13.1	14.1	14.7
p29	−18.2	−19.5	−15.2	−14.3	−16.2
ts30	10.5	10.6	11.1	10.7	11.4
p30	−6.8	−6.9	−5.9	−6.2	−6.0
ts31	4.8	6.3	3.7	3.3	3.2
p31	−10.9	−10.7	−9.9	−10.7	−12.1
ts34	31.7	31.6	32.5	33.2	32.7
p34	27.4	27.1	28.6	29.9	29.4
ts35	15.1	15.4	16.8	16.8	17.2
p35	18.1	19.9	18.0	18.0	18.5
mean AE	3.4	1.8	0.9	0.7	
SD	4.8	2.1	1.3	1.0	
max AE	16.6	3.4	4.6	2.2	
min AE	0.0	0.0	0.0	0.0	
MOR41	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
p7	−5.6	−10.5	−15.1	−13.6	−14.5
p9	−22.9	−18.2	−22.2	−20.1	−9.8
p14	−57.0	−64.0	−57.6	−56.5	−52.1
p16	−41.6	−37.2	−34.0	−33.7	−42.7
p21	−33.0	−11.5	−12.8	−12.7	−14.9
p22	−41.1	−40.4	−38.9	−40.7	−42.5
p36	−67.6	−59.3	−47.8	−41.5	−40.5
mean AE	10.6	7.7	5.7	4.2	
SD	12.6	9.5	7.2	6.0	
max AE	27.1	18.8	12.3	10.3	
min AE	1.1	2.0	0.6	0.9	
WCCR10	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
p1	22.2	24.3	28.8	30.0	30.1
p2	76.2	60.5	60.1	59.3	71.7
p3	78.6	70.4	65.0	63.0	72.0
p4	47.4	54.4	50.9	52.1	53.4
p5	40.5	45.3	49.0	50.2	53.2
p6	65.5	65.1	64.9	64.7	67.5
p7	76.5	62.7	60.9	61.0	59.1
p8	52.9	47.6	47.0	47.0	49.1
p9	29.4	34.5	35.6	38.8	42.1
p10	17.0	21.5	25.1	25.0	25.0
mean AE	8.2	4.6	4.0	3.6	
SD	9.7	4.5	3.9	4.3	
max AE	17.4	11.2	11.6	12.4	
min AE	2.0	0.9	0.1	0.0	

Table S11 Reaction barriers (ts*n*) and reaction energies (p*n*) of all the systems computed at DLPNO-CCSD(T_0)-in-DSDBLYP-D3 for four different DOS (RT1-RT4) region selections and full DLPNO-CCSD(T_0)/def2-TZVP. Absolute errors (AE) (mean AE, max AE and min AE) and standard deviation (SD) are calculated based on DLPNO-CCSD(T_0).

MOBH35	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
ts1	31.6	28.4	27.2	27.4	27.5
p1	11.3	10.2	11.0	11.6	12.6
ts6	15.6	17.4	15.3	15.6	16.1
p6	0.3	2.3	0.2	0.2	0.5
ts7	29.6	28.1	28.7	28.8	28.7
p7	12.1	10.0	11.0	10.9	10.5
ts11	32.1	36.2	35.8	36.0	36.3
p11	−62.8	−56.6	−55.1	−55.0	−55.5
ts14	7.8	10.5	10.5	10.4	10.2
p14	−8.3	−4.9	−3.8	−4.2	−4.4
ts21	10.7	9.3	9.1	9.1	8.3
p21	0.0	0.0	0.0	0.0	0.0
ts22	17.3	16.9	16.4	16.0	15.6
p22	−11.0	−11.2	−12.0	−12.4	−12.3
ts24	3.6	3.5	3.3	2.9	2.8
p24	−12.5	−13.2	−12.2	−13.4	−13.8
ts29	14.2	13.7	13.7	14.3	14.7
p29	−16.3	−18.1	−16.9	−15.7	−16.2
ts30	10.6	10.7	10.9	10.8	11.4
p30	−7.5	−7.3	−6.7	−6.8	−6.0
ts31	3.6	4.1	3.5	3.3	3.2
p31	−11.4	−9.9	−10.4	−10.7	−12.1
ts34	32.6	31.8	32.4	32.8	32.7
p34	29.1	28.1	28.9	29.6	29.4
ts35	15.3	16.8	17.2	17.2	17.2
p35	17.8	19.8	18.5	18.4	18.5
mean AE	1.6	1.0	0.6	0.4	
SD	2.3	1.2	0.7	0.5	
max AE	7.3	2.4	1.7	1.4	
min AE	0.0	0.0	0.0	0.0	
MOR41	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
p7	−11.1	−13.3	−13.9	−14.3	−14.5
p9	−16.9	−16.8	−17.1	−15.5	−9.8
p14	−65.8	−46.5	−56.5	−50.8	−52.1
p16	−38.8	−34.1	−36.4	−38.0	−42.7
p21	−13.1	−12.5	−13.5	3.9	−14.9
p22	−13.4	−46.8	−38.7	−39.4	−42.5
p36	−52.6	−50.0	−40.8	−40.8	−40.5
mean AE	10.2	5.5	3.5	4.8	
SD	14.5	6.7	4.6	7.6	
max AE	29.1	9.5	7.3	18.8	
min AE	1.9	1.2	0.3	0.2	
WCCR10	RT1	RT2	RT3	RT4	DLPNO-CCSD(T_0)
p1	28.0	28.5	28.4	28.0	30.1
p2	68.0	65.3	66.9	66.4	71.7
p3	77.9	68.4	66.3	66.5	72.0
p4	56.5	54.5	52.3	53.7	53.4
p5	41.6	48.2	51.2	52.1	53.2
p6	66.0	66.0	65.4	65.6	67.5
p7	63.9	63.6	63.6	63.4	59.1
p8	48.8	47.8	47.7	47.9	49.1
p9	37.3	41.6	39.5	41.8	42.1
p10	20.4	21.9	24.5	24.9	25.0
mean AE	4.2	2.9	2.7	2.2	
SD	5.2	3.1	2.8	2.8	
max AE	11.6	6.4	5.7	5.5	
min AE	0.3	0.5	0.5	0.1	