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

A Noncovalent Interaction Insight onto the Concerted Metallation Deprotonation Mechanism.

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Electronic Supporting Information.

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Geometries of anag for all four systems PdOAc, PdNHAc, NiOAc, NiNHAc

PdOAc-anag

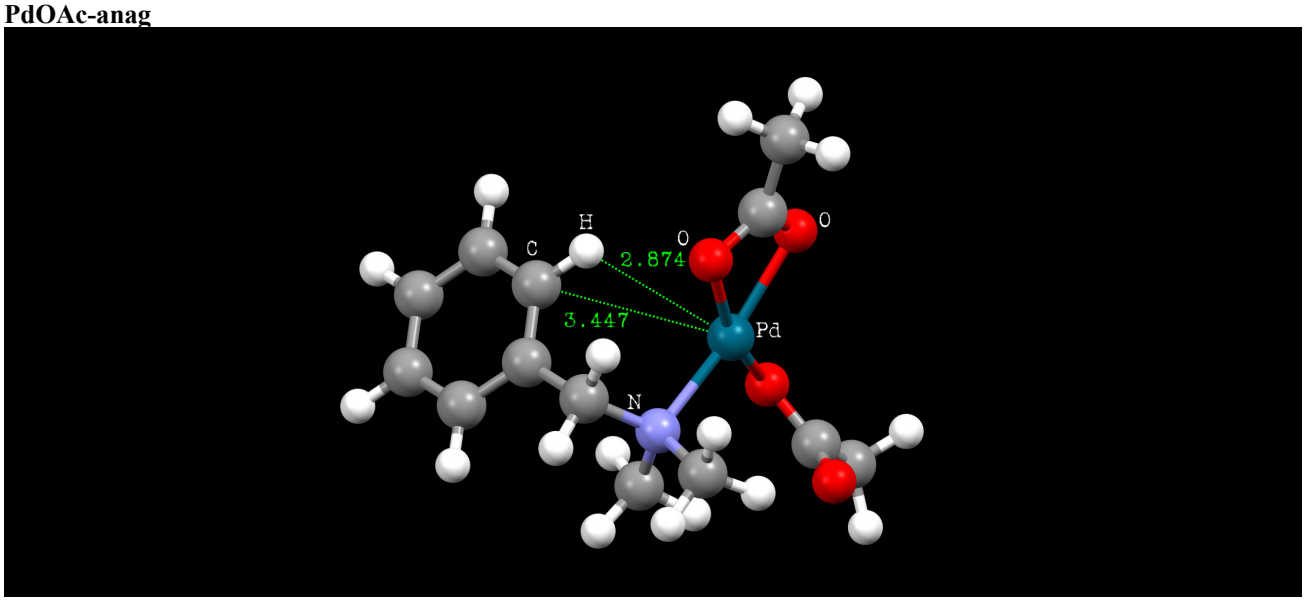

Figure S 1

PdNHAc-anag

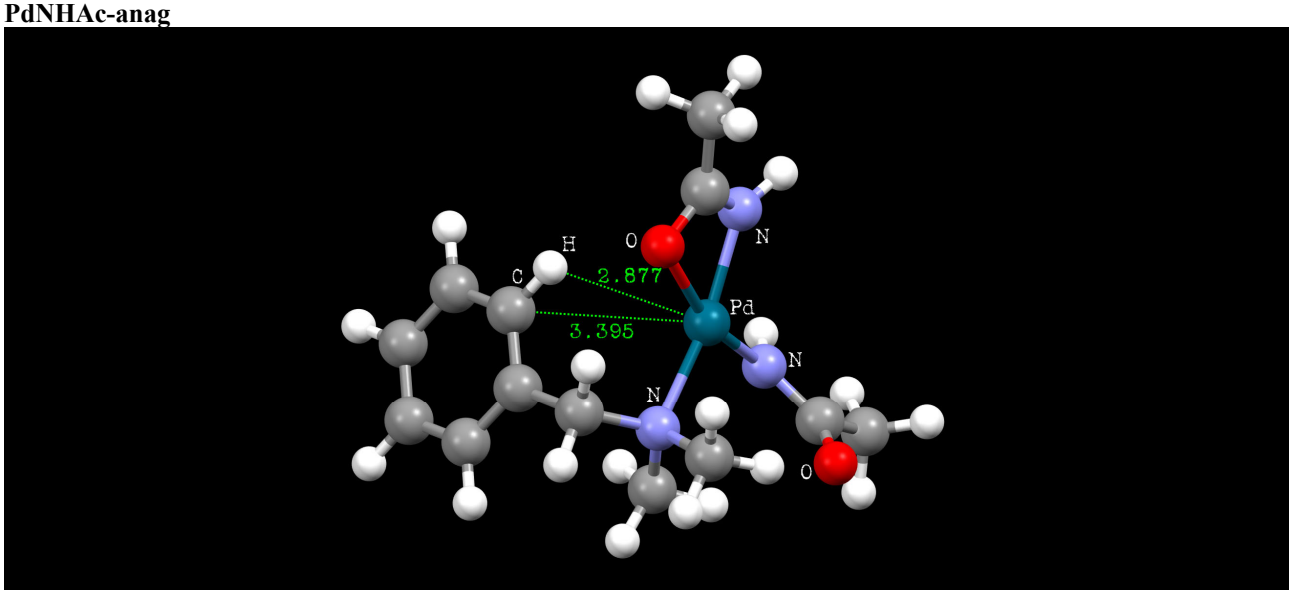

Figure S 2

NiOAc

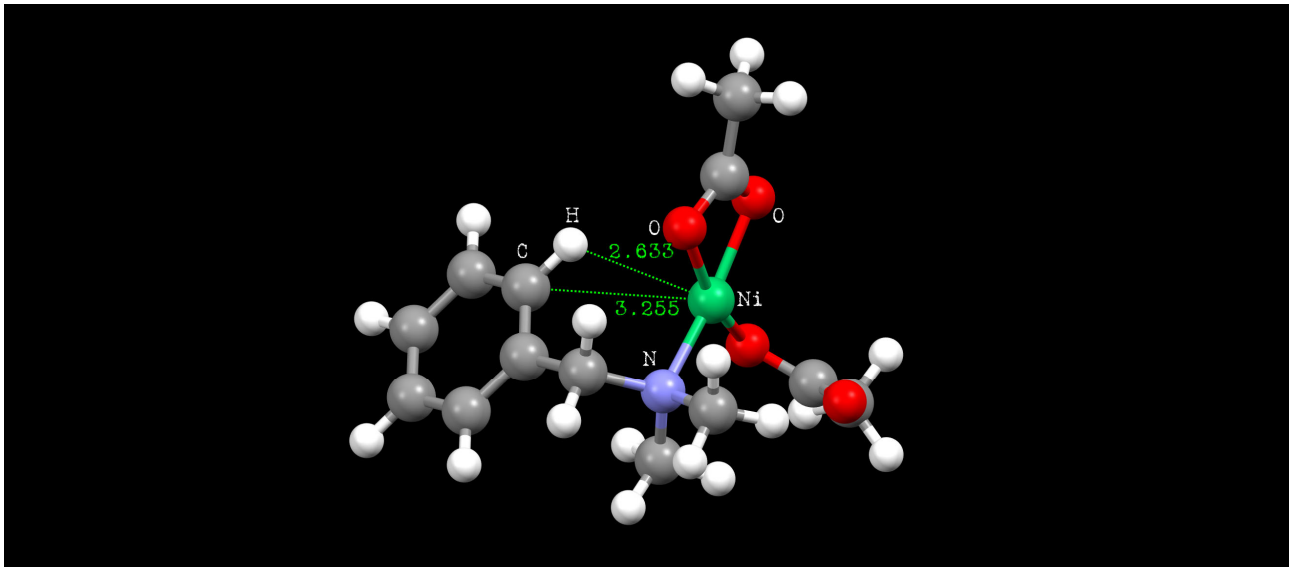

Figure S 3

NiNHAc

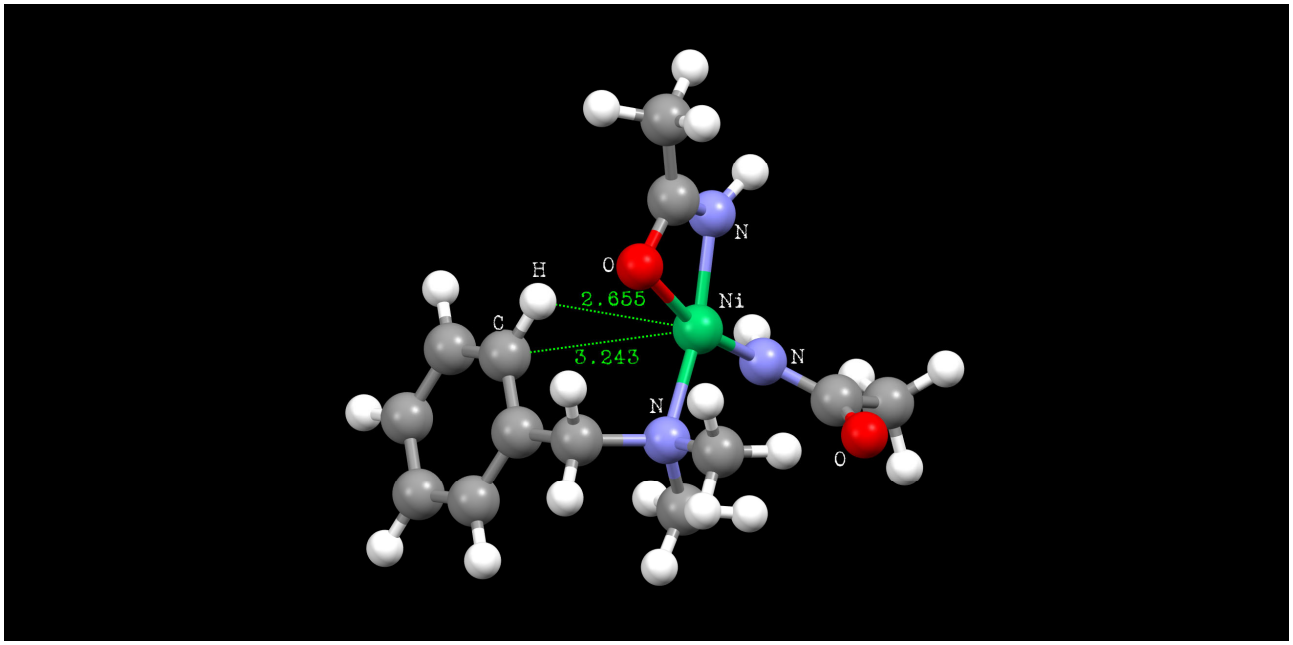

Figure S 4

High resolution Figure 1b

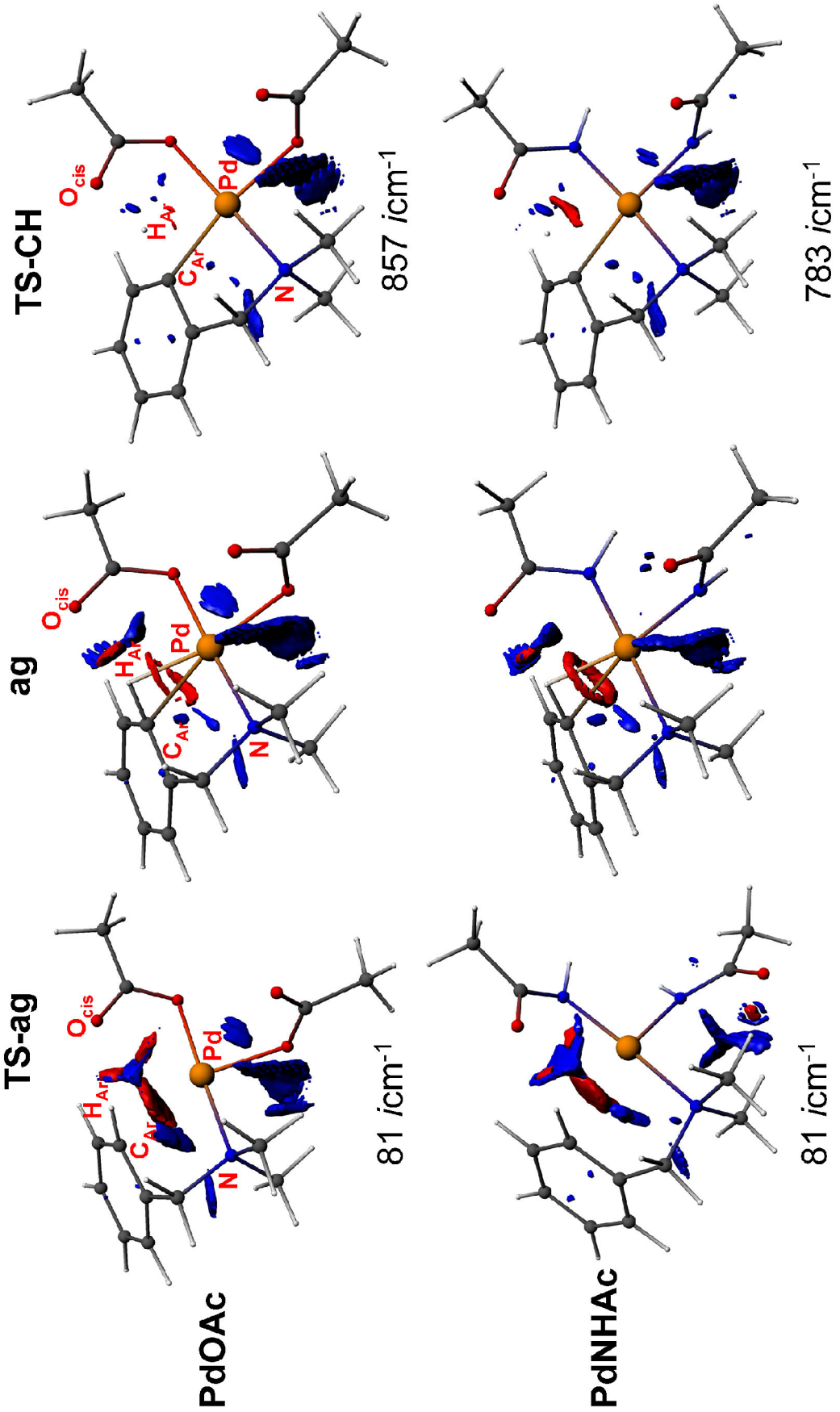

Figure S 5

High resolution Figure 2b

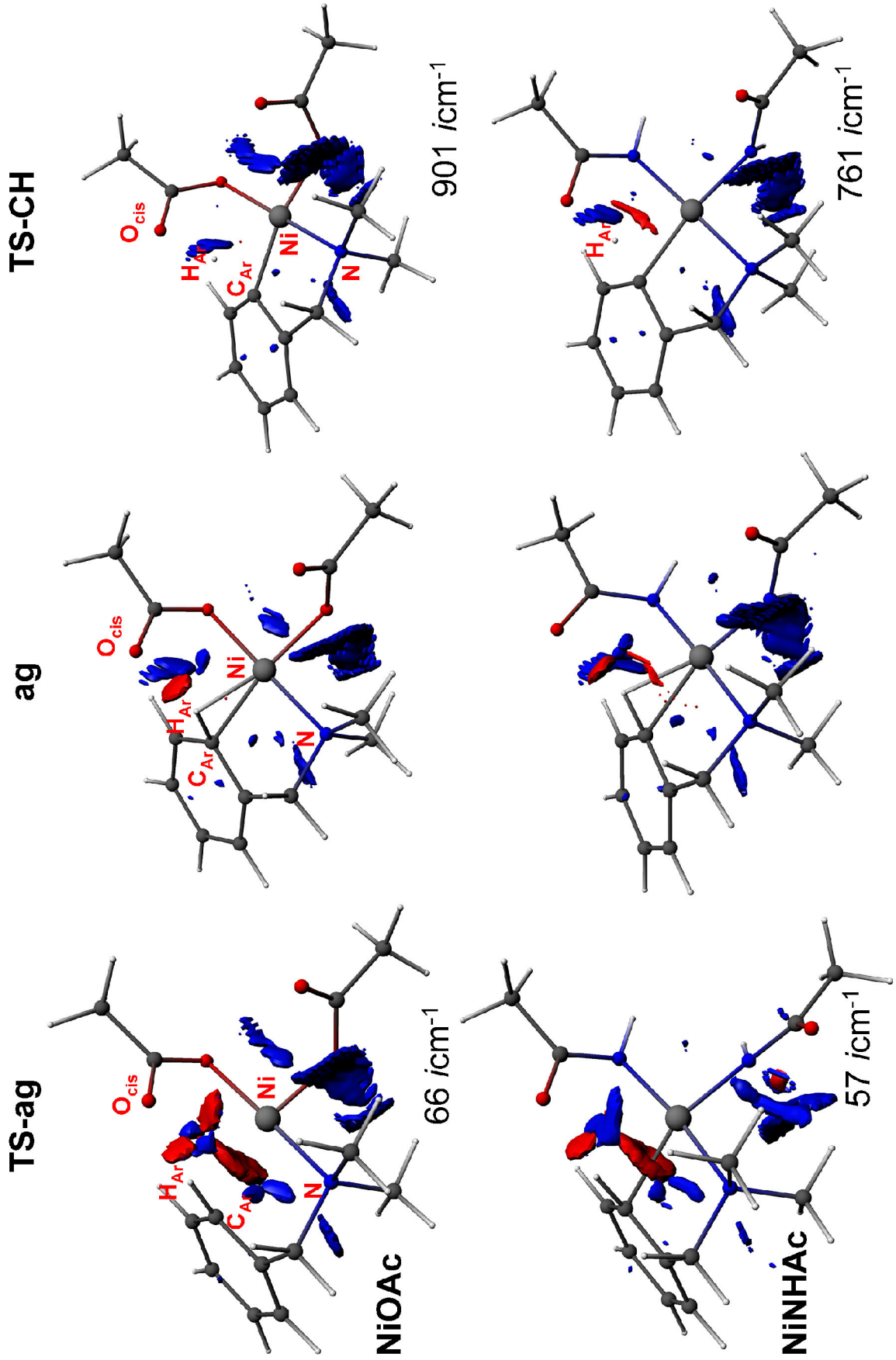

Figure S 6

Alternative representation of the IQA analysis of interactions within the metal-C_{Ar}-H_{Ar}-O_{cis} site.

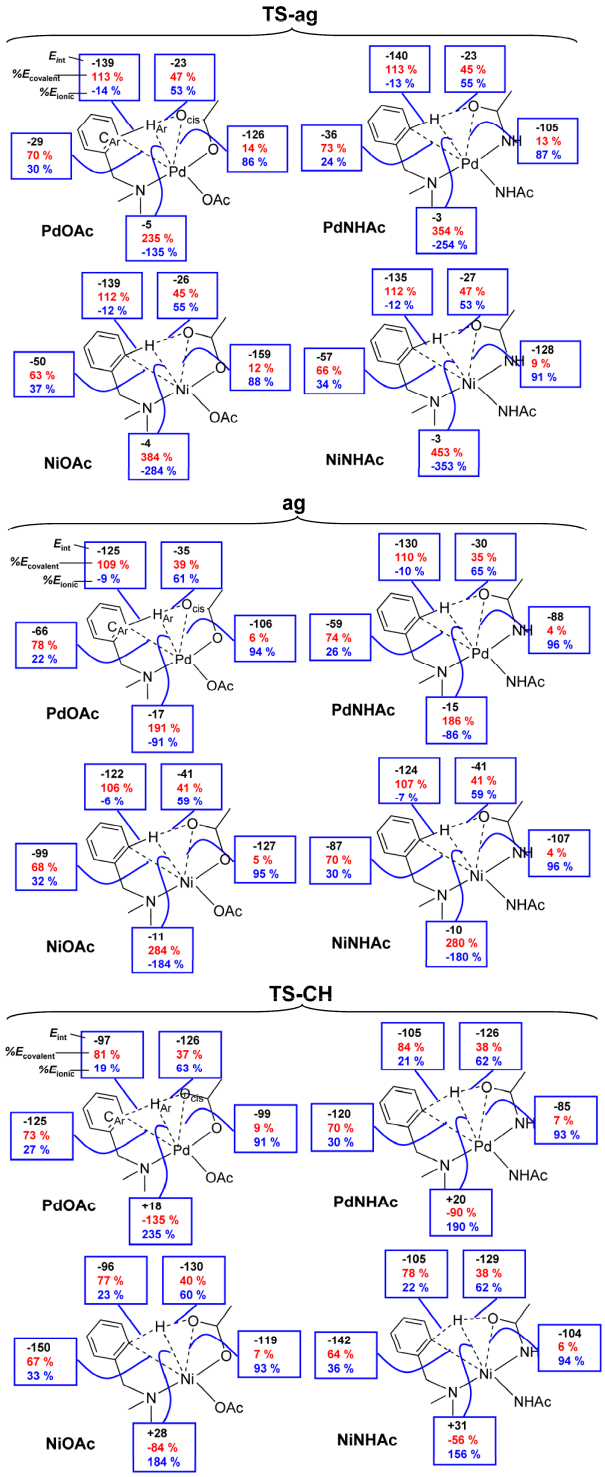

Figure S 7 IQA analysis of **TS-ag**, ag and **TS-CH** in **PdOAc**, **PdNHAc**, **NiOAc**, **NiNHAc** systems. Atom-pair interaction energies within the reactive site (black coloured, in kcal/mol) are decomposed into their covalent component (red coloured % of E_{int}) and ionic component (blue coloured % of E_{int}).

Energies of singlet state gas phase stationary geometries at the ZORA-PBE-D3(BJ)/all electron TZP level.

(geometries are provided in a separate .xyz file)

AcOH

```
Zero-Point Energy :      0.059549 a.u.
 ==================      1.620405 eV
                                          hartree              eV         kcal/mol           kJ/mol
                                   --------------------     -----------    ----------     -----------
             Bond Energy:            -1.712970779580363       -46.6123       -1074.91        -4497.40
             Zero-Point Energy:       0.059548779393052         1.6204          37.37          156.35
             Enthalpy (T=0K):        -1.653422000187311       -44.9919       -1037.54        -4341.06
```

dmba

```
Summary of Bonding Energy (energy terms are taken from the energy decomposition above)
================================================================================

  Electrostatic Energy:             -3.687517122532499       -100.3424         -2313.95         -9681.57
  Kinetic Energy:                    4.593307094356874        124.9902          2882.34         12059.73
  Coulomb (Steric+OrbInt) Energy:   -1.391224100561161        -37.8571          -873.01         -3652.66
  XC Energy:                        -4.523301729129166       -123.0853         -2838.41        -11875.93
  Dispersion Energy:                -0.023755747828824         -0.6464           -14.91           -62.37
                                   --------------------     -----------    ----------     -----------
  Total Bonding Energy:             -5.032491605694775       -136.9411         -3157.94        -13212.80
     Temp                                                       Transl     Rotat    Vibrat     Total
     ----                                                       ------     -----    ------     -----
     298.15   Entropy (cal/mole-K):                             40.615    29.653    26.081    96.349
              Internal Energy (Kcal/mole):                       0.889     0.889   127.154   128.931
              Constant Volume Heat Capacity (cal/mole-K):        2.981     2.981    32.157    38.119
```

PdOAc

$Pd_3(OAc)_6$

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-7.829931262678882	-213.0633	-4913.36	-20557.48
Kinetic Energy:	9.046314643038102	246.1627	5676.65	23751.10
Coulomb (Steric+OrbInt) Energy:	-2.642326876032584	-71.9014	-1658.09	-6937.43
XC Energy:	-8.331532061611254	-226.7125	-5228.12	-21874.43
Dispersion Energy:	-0.061969579065108	-1.6863	-38.89	-162.70
Total Bonding Energy:	-9.819445136349726	-267.2007	-6161.80	-25780.95

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	45.396	36.099	132.671	214.167
	Internal Energy (Kcal/mole):	0.889	0.889	209.809	211.586
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	107.887	113.848

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-9.819445136349719	-267.2007	-6161.80	-25780.95
Internal Energy:	0.337184227000539	9.1752	211.59	885.28
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-9.481316723335693	-257.9998	-5949.62	-24893.19
-T*S:	-0.101757423420945	-2.7690	-63.85	-267.16
Gibbs free energy:	-9.583074146756639	-260.7687	-6013.47	-25160.36

anag

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.277192885419339	-170.8111	-3939.00	-16480.77
Kinetic Energy:	7.661708004022671	208.4857	4807.79	20115.81
Coulomb (Steric+OrbInt) Energy:	-2.334830242184601	-63.5340	-1465.13	-6130.10
XC Energy:	-7.307079445588840	-198.8357	-4585.26	-19184.73
Dispersion Energy:	-0.048303068193589	-1.3144	-30.31	-126.82
Total Bonding Energy:	-8.305697637363698	-226.0095	-5211.90	-21806.61

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.528	34.118	83.499	161.145
	Internal Energy (Kcal/mole):	0.889	0.889	199.297	201.075
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	73.529	79.490

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.305697637363695	-226.0095	-5211.90	-21806.61
Internal Energy:	0.320432718913656	8.7194	201.07	841.30
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-7.984320732436553	-217.2644	-5010.24	-20962.83
-T*S:	-0.076565296680278	-2.0834	-48.05	-201.02
Gibbs free energy:	-8.060886029116832	-219.3479	-5058.28	-21163.85

TS-ag

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.277595158076167	-170.8221	-3939.25	-16481.82
Kinetic Energy:	7.724095781838685	210.1833	4846.94	20279.61
Coulomb (Steric+OrbInt) Energy:	-2.369454828711874	-64.4761	-1486.86	-6221.00
XC Energy:	-7.311909791863723	-198.9672	-4588.29	-19197.42
Dispersion Energy:	-0.049950523980705	-1.3592	-31.34	-131.15
Total Bonding Energy:	-8.284814520793784	-225.4413	-5198.80	-21751.78

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.528	33.875	80.112	157.515
	Internal Energy (Kcal/mole):	0.889	0.889	198.150	199.928
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	71.923	77.884

ag

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.331270600390512	-172.2826	-3972.93	-16622.75
Kinetic Energy:	7.587056690252467	206.4543	4760.95	19919.81
Coulomb (Steric+OrbInt) Energy:	-2.193462106942192	-59.6871	-1376.42	-5758.93
XC Energy:	-7.300580556189348	-198.6589	-4581.18	-19167.67
Dispersion Energy:	-0.049776769051990	-1.3545	-31.24	-130.69
Total Bonding Energy:	-8.288033342321576	-225.5289	-5200.82	-21760.23

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.528	33.823	78.052	155.403
	Internal Energy (Kcal/mole):	0.889	0.889	197.427	199.205
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	71.801	77.763

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.288033342321580	-225.5289	-5200.82	-21760.23
Internal Energy:	0.317452654640196	8.6383	199.20	833.47
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-7.969636501667898	-216.8648	-5001.02	-20924.28
-T*S:	-0.073836781524833	-2.0092	-46.33	-193.86
Gibbs free energy:	-8.043473283192730	-218.8740	-5047.36	-21118.14

TS-CH

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.382906191972904	-173.6877	-4005.33	-16758.32
Kinetic Energy:	7.680656910708635	209.0013	4819.69	20165.56
Coulomb (Steric+OrbInt) Energy:	-2.226531708004380	-60.5870	-1397.17	-5845.76
XC Energy:	-7.305259706776233	-198.7862	-4584.12	-19179.96
Dispersion Energy:	-0.050406949556714	-1.3716	-31.63	-132.34
Total Bonding Energy:	-8.284447645601597	-225.4313	-5198.57	-21750.81

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.528	33.743	78.467	155.738
	Internal Energy (Kcal/mole):	0.889	0.889	195.483	197.261
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	72.619	78.581

McH*

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.388562420344123	-173.8416	-4008.88	-16773.17
Kinetic Energy:	7.616292897134159	207.2499	4779.30	19996.57
Coulomb (Steric+OrbInt) Energy:	-2.174914748379308	-59.1824	-1364.78	-5710.24
XC Energy:	-7.327601691817688	-199.3942	-4598.14	-19238.62
Dispersion Energy:	-0.049182749194828	-1.3383	-30.86	-129.13
Total Bonding Energy:	-8.323968712601788	-226.5067	-5223.37	-21854.58

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.528	33.911	74.927	152.366
	Internal Energy (Kcal/mole):	0.889	0.889	197.382	199.160
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	70.695	76.656

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.323968712601788	-226.5067	-5223.37	-21854.58
Internal Energy:	0.317380833114742	8.6364	199.16	833.28
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.005643693473560	-217.8446	-5023.62	-21018.81
-T*S:	-0.072394096909469	-1.9699	-45.43	-190.07
Gibbs free energy:	-8.078037790383030	-219.8146	-5069.05	-21208.89

Mc

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-5.083513764049076	-138.3294	-3189.95	-13346.76
Kinetic Energy:	6.083550300150179	165.5418	3817.49	15972.36
Coulomb (Steric+OrbInt) Energy:	-1.778149771835714	-48.3859	-1115.81	-4668.53
XC Energy:	-5.766902538037130	-156.9254	-3618.79	-15141.00
Dispersion Energy:	-0.037743163342784	-1.0270	-23.68	-99.09
Total Bonding Energy:	-6.582758937114527	-179.1260	-4130.74	-17283.03

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	42.983	32.613	54.057	129.653
	Internal Energy (Kcal/mole):	0.889	0.889	157.013	158.790
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	54.155	60.117

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-6.582758937114536	-179.1260	-4130.74	-17283.03
Internal Energy:	0.253048186207515	6.8858	158.79	664.38
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-6.328766564893535	-172.2145	-3971.36	-16616.17
-T*S:	-0.061602090951446	-1.6763	-38.66	-161.74
Gibbs free energy:	-6.390368655844981	-173.8908	-4010.02	-16777.91

PdNHAc

anag

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.520971352314273	-177.4447	-4091.97	-17120.81
Kinetic Energy:	8.050688894468166	219.0704	5051.88	21137.08
Coulomb (Steric+OrbInt) Energy:	-2.503818346424367	-68.1324	-1571.17	-6573.77
XC Energy:	-7.655470744385613	-208.3160	-4803.88	-20099.44
Dispersion Energy:	-0.052023711963606	-1.4156	-32.65	-136.59
Total Bonding Energy:	-8.681595260619693	-236.2382	-5447.78	-22793.53

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.512	34.138	80.899	158.549
	Internal Energy (Kcal/mole):	0.889	0.889	214.379	216.156
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	76.276	82.237

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.681595260619687	-236.2382	-5447.78	-22793.53
Internal Energy:	0.344466431106843	9.3734	216.16	904.40
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.336184643499358	-226.8391	-5231.04	-21886.65
-T*S:	-0.075331600896460	-2.0499	-47.27	-197.78
Gibbs free energy:	-8.411516244395818	-228.8890	-5278.31	-22084.43

TS-ag

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.531467116000415	-177.7303	-4098.56	-17148.36
Kinetic Energy:	8.131001208299523	221.2558	5102.28	21347.94
Coulomb (Steric+OrbInt) Energy:	-2.541814647453464	-69.1663	-1595.01	-6673.53
XC Energy:	-7.667895103101756	-208.6540	-4811.68	-20132.06
Dispersion Energy:	-0.053769637302794	-1.4631	-33.74	-141.17
Total Bonding Energy:	-8.663945295558907	-235.7579	-5436.71	-22747.19

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.512	33.956	80.239	157.708
	Internal Energy (Kcal/mole):	0.889	0.889	213.331	215.108
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	74.668	80.629

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.663945295558912	-235.7579	-5436.71	-22747.19
Internal Energy:	0.342796486560694	9.3280	215.11	900.01
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.320204622984733	-226.4043	-5221.01	-21844.69
-T*S:	-0.074931958373709	-2.0390	-47.02	-196.73
Gibbs free energy:	-8.395136581358441	-228.4433	-5268.03	-22041.43

ag

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.560755743478440	-178.5272	-4116.94	-17225.26
Kinetic Energy:	7.981266074847014	217.1813	5008.32	20954.81
Coulomb (Steric+OrbInt) Energy:	-2.388778262851467	-65.0020	-1498.98	-6271.74
XC Energy:	-7.645874041401966	-208.0548	-4797.86	-20074.24
Dispersion Energy:	-0.053277465429569	-1.4498	-33.43	-139.88
Total Bonding Energy:	-8.667419438314429	-235.8525	-5438.89	-22756.31

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.512	33.962	77.590	155.064
	Internal Energy (Kcal/mole):	0.889	0.889	212.783	214.560
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	74.480	80.442

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	15.333
Entropy (cal/mole-K):	7.162
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.667419438314425	-235.8525	-5438.89	-22756.31
Internal Energy:	0.341923281840152	9.3042	214.56	897.72
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.324551970460789	-226.5226	-5223.74	-21856.11
-T*S:	-0.073675867214901	-2.0048	-46.23	-193.44
Gibbs free energy:	-8.398227837675691	-228.5274	-5269.97	-22049.54

TS-CH

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)
==

Electrostatic Energy:	-6.618126174891654	-180.0884	-4152.94	-17375.89
Kinetic Energy:	8.238046296249976	224.1686	5169.45	21628.99
Coulomb (Steric+OrbInt) Energy:	-2.552111124334914	-69.4465	-1601.47	-6700.57
XC Energy:	-7.673893174966073	-208.8173	-4815.44	-20147.80
Dispersion Energy:	-0.054067905688602	-1.4713	-33.93	-141.96
Total Bonding Energy:	-8.660152083631267	-235.6547	-5434.33	-22737.23

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.512	33.838	77.469	154.819
	Internal Energy (Kcal/mole):	0.889	0.889	210.874	212.652
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	75.048	81.010

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.660152083631262	-235.6547	-5434.33	-22737.23
Internal Energy:	0.338881708909250	9.2214	212.65	889.73
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.320326188708526	-226.4076	-5221.08	-21845.01
-T*S:	-0.073559669554342	-2.0017	-46.16	-193.13
Gibbs free energy:	-8.393885858262868	-228.4093	-5267.24	-22038.14

McH

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)
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Electrostatic Energy:	-6.593264225754165	-179.4118	-4137.34	-17310.61
Kinetic Energy:	8.024551055543853	218.3591	5035.48	21068.46
Coulomb (Steric+OrbInt) Energy:	-2.416159070255141	-65.7470	-1516.16	-6343.62
XC Energy:	-7.642449891988647	-207.9616	-4795.71	-20065.25
Dispersion Energy:	-0.053740196616966	-1.4623	-33.72	-141.09
Total Bonding Energy:	-8.681062329071066	-236.2237	-5447.45	-22792.13

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.512	33.898	72.349	149.759
	Internal Energy (Kcal/mole):	0.889	0.889	213.760	215.537
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	73.962	79.923

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	11.953
Entropy (cal/mole-K):	7.657
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.987

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.681062329071059	-236.2237	-5447.45	-22792.13
Internal Energy:	0.343480251279986	9.3466	215.54	901.81
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.336637891777587	-226.8515	-5231.32	-21887.84
-T*S:	-0.071155421631201	-1.9362	-44.65	-186.82
Gibbs free energy:	-8.407793313408789	-228.7877	-5275.97	-22074.66

Mc

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)
==

Electrostatic Energy:	-5.185824074811112	-141.1135	-3254.15	-13615.38
Kinetic Energy:	6.257678811354737	170.2801	3926.75	16429.53
Coulomb (Steric+OrbInt) Energy:	-1.864593368876115	-50.7382	-1170.05	-4895.49
XC Energy:	-5.928669015151945	-161.3273	-3720.30	-15565.72
Dispersion Energy:	-0.039315009010130	-1.0698	-24.67	-103.22
Total Bonding Energy:	-6.760722656494566	-183.9686	-4242.42	-17750.27

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	42.973	32.627	51.819	127.419
	Internal Energy (Kcal/mole):	0.889	0.889	164.473	166.250
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	55.564	61.526

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-6.760722656494560	-183.9686	-4242.42	-17750.27
Internal Energy:	0.264936718771427	7.2093	166.25	695.59
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-6.494841751709648	-176.7336	-4075.58	-17052.20
-T*S:	-0.060540795083453	-1.6474	-37.99	-158.95
Gibbs free energy:	-6.555382546793100	-178.3810	-4113.57	-17211.15

Acetamide-NH

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)
==

Electrostatic Energy:	-1.325957969766210	-36.0812	-832.05	-3481.30
Kinetic Energy:	1.719857336898261	46.7997	1079.23	4515.48
Coulomb (Steric+OrbInt) Energy:	-0.591562985817802	-16.0972	-371.21	-1553.15
XC Energy:	-1.686645063466067	-45.8959	-1058.39	-4428.29

Dispersion Energy:	-0.005178291489592	-0.1409	-3.25	-13.60
Total Bonding Energy:	-1.889486973641410	-51.4156	-1185.67	-4960.85

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	38.147	23.965	6.994	69.106
	Internal Energy (Kcal/mole):	0.889	0.889	46.203	47.980
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	9.810	15.772

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-1.889486973641410	-51.4156	-1185.67	-4960.85
Internal Energy:	0.076461189304234	2.0806	47.98	200.75
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-1.812081598323691	-49.3092	-1137.10	-4757.62
-T*S:	-0.032834456964317	-0.8935	-20.60	-86.21
Gibbs free energy:	-1.844916055288008	-50.2027	-1157.70	-4843.83

Acetamide-NH_2

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-1.333919594163826	-36.2978	-837.05	-3502.21
Kinetic Energy:	1.729179097246252	47.0534	1085.08	4539.96
Coulomb (Steric+OrbInt) Energy:	-0.591998764992073	-16.1091	-371.48	-1554.29
XC Energy:	-1.705928446853525	-46.4207	-1070.49	-4478.91
Dispersion Energy:	-0.005152232352841	-0.1402	-3.23	-13.53
Total Bonding Energy:	-1.907819941116013	-51.9144	-1197.18	-5008.98

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	38.147	23.977	11.269	73.393
	Internal Energy (Kcal/mole):	0.889	0.889	46.084	47.862
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	11.028	16.990

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-1.907819941116013	-51.9144	-1197.18	-5008.98
Internal Energy:	0.076272626869190	2.0755	47.86	200.25
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-1.830603128233338	-49.8132	-1148.72	-4806.25
-T*S:	-0.034871352494837	-0.9489	-21.88	-91.55
Gibbs free energy:	-1.865474480728174	-50.7621	-1170.60	-4897.80

NiOAc

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Summary of Bonding Energy (energy terms are taken from the energy decomposition above)
================================================================================

  Electrostatic Energy:             -6.379923249796706       -173.6065         -4003.46        -16750.49
  Kinetic Energy:                    7.641249071927135        207.9290          4794.96         20062.10
  Coulomb (Steric+OrbInt) Energy:   -2.123025944978075        -57.7705         -1332.22         -5574.00
  XC Energy:                        -7.486466951518187       -203.7171         -4697.83        -19655.72
  Dispersion Energy:                -0.046980198424488         -1.2784           -29.48          -123.35
                                   --------------------     -----------       ----------      -----------
  Total Bonding Energy:             -8.395147272790322       -228.4436         -5268.04        -22041.46
     Temp                                                      Transl     Rotat    Vibrat     Total
     ----                                                      ------     -----    ------     -----

     298.15   Entropy (cal/mole-K):                            43.101    33.855    81.711   158.667
              Internal Energy (Kcal/mole):                      0.889     0.889   199.522   201.299
              Constant Volume Heat Capacity (cal/mole-K):       2.981     2.981    72.955    78.917
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     Temp                                                      Transl     Rotat    Vibrat     Total
     ----                                                      ------     -----    ------     -----

     298.15   Entropy (cal/mole-K):                            43.101    33.855    81.711   158.667
              Internal Energy (Kcal/mole):                      0.889     0.889   199.522   201.299
              Constant Volume Heat Capacity (cal/mole-K):       2.981     2.981    72.955    78.917

     Temp                                                      Transl     Rotat    Vibrat     Total
     ----                                                      ------     -----    ------     -----

     298.15   Entropy (cal/mole-K):                            43.101    33.595    74.394   151.089
              Internal Energy (Kcal/mole):                      0.889     0.889   198.722   200.500
              Constant Volume Heat Capacity (cal/mole-K):       2.981     2.981    70.852    76.813

              Summary of energy terms
                                          hartree              eV         kcal/mol          kJ/mol
                                       --------------------     -----------       ----------      -----------
              Bond Energy:              -8.367709233633738       -227.6970         -5250.82        -21969.42
              Internal Energy:           0.319516973639480          8.6945           200.50           838.89
              pV/n = RT:                 0.000944186013486          0.0257             0.59             2.48
              Enthalpy H:               -8.047248073980771       -218.9768         -5049.72        -21128.05
              -T*S:                     -0.071787383281914         -1.9534           -45.05          -188.48
              Gibbs free energy:        -8.119035457262687       -220.9302         -5094.77        -21316.52
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Summary of Bonding Energy (energy terms are taken from the energy decomposition above)
================================================================================

  Electrostatic Energy:             -6.440677905918429       -175.2598         -4041.59        -16910.00
  Kinetic Energy:                    7.650530818315460        208.1815          4800.78         20086.47
  Coulomb (Steric+OrbInt) Energy:   -2.052644259191659        -55.8553         -1288.05         -5389.22
  XC Energy:                        -7.480655332921833       -203.5590         -4694.18        -19640.46
  Dispersion Energy:                -0.048743803903237         -1.3264           -30.59          -127.98
                                   --------------------     -----------       ----------      -----------
  Total Bonding Energy:             -8.372190483619699       -227.8189         -5253.63        -21981.18
     Temp                                                      Transl     Rotat    Vibrat     Total
     ----                                                      ------     -----    ------     -----

     298.15   Entropy (cal/mole-K):                            43.101    33.566    72.823   149.490
              Internal Energy (Kcal/mole):                      0.889     0.889   197.643   199.420
              Constant Volume Heat Capacity (cal/mole-K):       2.981     2.981    71.014    76.976

 Contributions from frequencies below 20 1/cm
 Frequency (1/cm):                                  10.654
 Entropy (cal/mole-K):                               7.885
 Internal Energy (Kcal/mole):                        0.593
 Constant Volume Heat Capacity (cal/mole-K):         1.987
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Summary of Bonding Energy (energy terms are taken from the energy decomposition above)
================================================================================

  Electrostatic Energy:             -6.483588440671703       -176.4274         -4068.51        -17022.66
  Kinetic Energy:                    7.639575987009962        207.8834          4793.91         20057.70
  Coulomb (Steric+OrbInt) Energy:   -1.993489443694870        -54.2456         -1250.93         -5233.91
  XC Energy:                        -7.481836471545610       -203.5911         -4694.92        -19643.56
  Dispersion Energy:                -0.049278667483101         -1.3409           -30.92          -129.38
                                   --------------------     -----------       ----------      -----------
  Total Bonding Energy:             -8.368617036385320       -227.7217         -5251.39        -21971.80
Summary of Bonding Energy (energy terms are taken from the energy decomposition above)
================================================================================

  Electrostatic Energy:             -6.483588440671703       -176.4274         -4068.51        -17022.66
  Kinetic Energy:                    7.639575987009962        207.8834          4793.91         20057.70
  Coulomb (Steric+OrbInt) Energy:   -1.993489443694870        -54.2456         -1250.93         -5233.91
```

XC Energy:	-7.481836471545610	-203.5911	-4694.92	-19643.56
Dispersion Energy:	-0.049278667483101	-1.3409	-30.92	-129.38
Total Bonding Energy:	-8.368617036385320	-227.7217	-5251.39	-21971.80

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Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.463772015880339	-175.8882	-4056.08	-16970.63
Kinetic Energy:	7.569800650960104	205.9848	4750.12	19874.51
Coulomb (Steric+OrbInt) Energy:	-1.960626225415197	-53.3514	-1230.31	-5147.62
XC Energy:	-7.478573015914366	-203.5023	-4692.88	-19634.99
Dispersion Energy:	-0.049208791961361	-1.3390	-30.88	-129.20
Total Bonding Energy:	-8.382379398211159	-228.0961	-5260.02	-22007.93

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.101	33.524	72.847	149.471
	Internal Energy (Kcal/mole):	0.889	0.889	198.496	200.273
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	71.314	77.275

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.382379398211144	-228.0961	-5260.02	-22007.93
Internal Energy:	0.319155810897418	8.6847	200.27	837.94
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.062279401300239	-219.3858	-5059.16	-21167.51
-T*S:	-0.071018634905051	-1.9325	-44.56	-186.46
Gibbs free energy:	-8.133298036205291	-221.3183	-5103.72	-21353.97

Mc

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-5.118105135167852	-139.2707	-3211.66	-13437.58
Kinetic Energy:	5.955072558349208	162.0458	3736.86	15635.04
Coulomb (Steric+OrbInt) Energy:	-1.553863893698669	-42.2828	-975.06	-4079.67
XC Energy:	-5.905521166762420	-160.6974	-3705.77	-15504.94
Dispersion Energy:	-0.036839588347286	-1.0025	-23.12	-96.72
Total Bonding Energy:	-6.659257225627018	-181.2076	-4178.75	-17483.88

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	42.462	32.390	51.516	126.367
	Internal Energy (Kcal/mole):	0.889	0.889	157.303	159.080
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	53.397	59.359

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-6.659257225627024	-181.2076	-4178.75	-17483.88
Internal Energy:	0.253510473708243	6.8984	159.08	665.59
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-6.404802565905294	-174.2835	-4019.07	-16815.81
-T*S:	-0.060041239265174	-1.6338	-37.68	-157.64
Gibbs free energy:	-6.464843805170469	-175.9174	-4056.75	-16973.45

NiNHAc

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Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.603164551264070	-179.6812	-4143.55	-17336.61
Kinetic Energy:	7.926801375027338	215.6992	4974.14	20811.81
Coulomb (Steric+OrbInt) Energy:	-2.216382173030333	-60.3108	-1390.80	-5819.11
XC Energy:	-7.822907020969547	-212.8721	-4908.95	-20539.04
Dispersion Energy:	-0.050655449002885	-1.3784	-31.79	-133.00
Total Bonding Energy:	-8.766307819239497	-238.5434	-5500.94	-23015.94

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.082	33.916	77.508	154.505
	Internal Energy (Kcal/mole):	0.889	0.889	214.594	216.371
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	75.548	81.510

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.766307819239490	-238.5434	-5500.94	-23015.94
Internal Energy:	0.344809651936253	9.3827	216.37	905.30
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.420553981289752	-229.1349	-5283.98	-22108.16
-T*S:	-0.073410476685001	-1.9976	-46.07	-192.74
Gibbs free energy:	-8.493964457974753	-231.1325	-5330.04	-22300.90

TS-ag

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.618890551811025	-180.1092	-4153.42	-17377.89
Kinetic Energy:	8.025771321833005	218.3923	5036.25	21071.66
Coulomb (Steric+OrbInt) Energy:	-2.262446810697277	-61.5643	-1419.71	-5940.05
XC Energy:	-7.831252521938652	-213.0992	-4914.19	-20560.95
Dispersion Energy:	-0.053067503891949	-1.4440	-33.30	-139.33
Total Bonding Energy:	-8.739886066505898	-237.8244	-5484.36	-22946.57

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.082	33.742	75.584	152.408
	Internal Energy (Kcal/mole):	0.889	0.889	213.597	215.374
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	73.528	79.490

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.739886066505898	-237.8244	-5484.36	-22946.57
Internal Energy:	0.343220828282581	9.3395	215.37	901.13
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.395721052209831	-228.4592	-5268.40	-22042.96
-T*S:	-0.072413792470265	-1.9705	-45.44	-190.12
Gibbs free energy:	-8.468134844680096	-230.4297	-5313.84	-22233.08

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Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.654608627538131	-181.0811	-4175.83	-17471.67
Kinetic Energy:	7.983345170808306	217.2379	5009.63	20960.27
Coulomb (Steric+OrbInt) Energy:	-2.206046682850911	-60.0296	-1384.32	-5791.97
XC Energy:	-7.814947049202123	-212.6555	-4903.95	-20518.14
Dispersion Energy:	-0.052286014406801	-1.4228	-32.81	-137.28
Total Bonding Energy:	-8.744543203189661	-237.9511	-5487.28	-22958.79

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.654608627538131	-181.0811	-4175.83	-17471.67
Kinetic Energy:	7.983345170808306	217.2379	5009.63	20960.27
Coulomb (Steric+OrbInt) Energy:	-2.206046682850911	-60.0296	-1384.32	-5791.97
XC Energy:	-7.814947049202123	-212.6555	-4903.95	-20518.14
Dispersion Energy:	-0.052286014406801	-1.4228	-32.81	-137.28
Total Bonding Energy:	-8.744543203189661	-237.9511	-5487.28	-22958.79

TS-CH

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.702496092709029	-182.3842	-4205.88	-17597.40
Kinetic Energy:	8.013117422015640	218.0480	5028.31	21038.44
Coulomb (Steric+OrbInt) Energy:	-2.178449131861001	-59.2786	-1367.00	-5719.52
XC Energy:	-7.821470858909673	-212.8331	-4908.05	-20535.27
Dispersion Energy:	-0.052931236705792	-1.4403	-33.21	-138.97
Total Bonding Energy:	-8.742229898169855	-237.8882	-5485.83	-22952.72

Temp		Transl	Rotat	Vibrat	Total

298.15	Entropy (cal/mole-K):	43.082	33.616	74.016	150.714
	Internal Energy (Kcal/mole):	0.889	0.889	211.144	212.922
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	74.368	80.329

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.742229898169848	-237.8882	-5485.83	-22952.72
Internal Energy:	0.339312038722489	9.2332	212.92	890.86
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.401973673433872	-228.6293	-5272.32	-22059.38
-T*S:	-0.071608932020188	-1.9486	-44.94	-188.01
Gibbs free energy:	-8.473582605454061	-230.5779	-5317.25	-22247.39

McH

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-6.672492679529544	-181.5678	-4187.05	-17518.63
Kinetic Energy:	7.919109299717633	215.4899	4969.32	20791.62
Coulomb (Steric+OrbInt) Energy:	-2.141651517333571	-58.2773	-1343.91	-5622.91
XC Energy:	-7.809132864793972	-212.4973	-4900.31	-20502.88
Dispersion Energy:	-0.052838398522390	-1.4378	-33.16	-138.73
Total Bonding Energy:	-8.757006160461845	-238.2903	-5495.10	-22991.52

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.082	33.644	78.357	155.083
	Internal Energy (Kcal/mole):	0.889	0.889	214.384	216.162
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	75.496	81.458

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-8.757006160461858	-238.2903	-5495.10	-22991.52
Internal Energy:	0.344475460543754	9.3737	216.16	904.42
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-8.411586513904616	-228.8909	-5278.35	-22084.62
-T*S:	-0.073684873011834	-2.0051	-46.24	-193.46
Gibbs free energy:	-8.485271386916450	-230.8960	-5324.59	-22278.08

Mc

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

Electrostatic Energy:	-5.259330402481648	-143.1137	-3300.28	-13808.37
Kinetic Energy:	6.165075604686471	167.7602	3868.64	16186.40
Coulomb (Steric+OrbInt) Energy:	-1.615917278616745	-43.9713	-1014.00	-4242.59
XC Energy:	-6.089486197966085	-165.7034	-3821.21	-15987.94
Dispersion Energy:	-0.037963424420575	-1.0330	-23.82	-99.67
Total Bonding Energy:	-6.837621698798582	-186.0612	-4290.67	-17952.17

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	42.450	32.372	50.075	124.898
	Internal Energy (Kcal/mole):	0.889	0.889	164.526	166.303
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	55.188	61.149

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-6.837621698798586	-186.0612	-4290.67	-17952.17
Internal Energy:	0.265021164792401	7.2116	166.30	695.81
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-6.571656347992699	-178.8239	-4123.78	-17253.88
-T*S:	-0.059342859898169	-1.6148	-37.24	-155.80
Gibbs free energy:	-6.630999207890867	-180.4387	-4161.02	-17409.69

DLPNO-CCSD(T)/ def2-TVZP computations and LED analysis

Table 1: DLPNO-CCSD(T)/def2-TVPZ energies and LED analysis for **PdOAc**. All energies in E_h.

	anag	**TS-ag**	**ag**	**TS-CH**	**McH***
E_{tot}	-988.614851	-988.588842	-988.592355	-988.584215	-988.635028
$E_{intra}^{(1)}$	-126.144213	-126.177036	-126.111932	-126.084027	-126.008614
$E_{intra}^{(2)}$	-403.006924	-402.923501	-402.687030	-402.435956	-401.847146
$E_{intra}^{(3)}$	-227.514141	-227.553801	-227.609678	-227.579818	-227.684104
$E_{intra}^{(4)}$	-227.612177	-227.603442	-227.609678	-227.693779	-227.748313
$E_{intra}^{(5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(1-2)}$	-1.204259	-1.424109	-1.806613	-2.222278	-3.360041
$E_{elstat}^{(1-2)}$	-1.074383	-1.277989	-1.601674	-1.944570	-2.926796
$E_{exch}^{(1-2)}$	-0.093690	-0.104318	-0.147488	-0.203516	-0.329903
$E_{corr}^{(1-2)}$	-0.036186	-0.041803	-0.057451	-0.074192	-0.103342
$E_{disp}^{(1-2)}$	-0.014998	-0.017009	-0.021555	-0.027265	-0.040205
$E_{inter}^{(1-3)}$	-1.382729	-1.274586	-1.219228	-1.116565	-0.916707
$E_{elstat}^{(1-3)}$	-1.239227	-1.151301	-1.102543	-1.014070	-0.838886
$E_{exch}^{(1-3)}$	-0.101804	-0.089906	-0.085427	-0.073923	-0.055947
$E_{corr}^{(1-3)}$	-0.041698	-0.033381	-0.031259	-0.028573	-0.021874
$E_{disp}^{(1-3)}$	-0.012551	-0.010029	-0.008782	-0.008198	-0.007132
$E_{inter}^{(2-3)}$	0.209086	0.237948	0.252607	0.207039	0.213207
$E_{elstat}^{(2-3)}$	0.230415	0.267575	0.288591	0.283661	0.238703
$E_{exch}^{(2-3)}$	-0.011079	-0.017306	-0.020166	-0.048417	-0.013909
$E_{corr}^{(2-3)}$	-0.010250	-0.012321	-0.015818	-0.028206	-0.011587
$E_{disp}^{(2-3)}$	-0.005122	-0.005044	-0.005829	-0.007662	-0.005507
$E_{inter}^{(1-4)}$	-1.179528	-1.199643	-1.199461	-1.093559	-0.640961
$E_{elstat}^{(1-4)}$	-1.065276	-1.080226	-1.083731	-0.994563	-0.603028
$E_{exch}^{(1-4)}$	-0.083410	-0.086649	-0.084433	-0.071809	-0.026133
$E_{corr}^{(1-4)}$	-0.030842	-0.032768	-0.031403	-0.027176	-0.011800
$E_{disp}^{(1-4)}$	-0.009324	-0.008935	-0.008971	-0.008281	-0.004978
$E_{inter}^{(2-4)}$	0.127169	0.15887705	0.183136	0.181281	0.168923
$E_{elstat}^{(2-4)}$	0.151837	0.183134	0.211126	0.211282	0.189974
$E_{exch}^{(2-4)}$	-0.011520	-0.011490	-0.014264	-0.016130	-0.011282
$E_{corr}^{(2-4)}$	-0.013148	-0.012767	-0.013726	-0.013871	-0.009768
$E_{disp}^{(2-4)}$	-0.007623	-0.006818	-0.007169	-0.007024	-0.005787
$E_{inter}^{(3-4)}$	0.186490	0.196986	0.192767	0.186535	0.136887
$E_{elstat}^{(3-4)}$	0.199482	0.208641	0.203773	0.195832	0.184751
$E_{exch}^{(3-4)}$	-0.007787	-0.005748	-0.005369	-0.004332	-0.030803
$E_{corr}^{(3-4)}$	-0.005204	-0.005907	-0.005636	-0.004965	-0.017061

$E_{disp}^{(3-4)}$	-0.001847	-0.002972	-0.002756	-0.002892	-0.004631
$E_{inter}^{(1-5)}$	0.358001	0.481465	0.566576	0.548724	0.354890
$E_{elstat}^{(1-5)}$	0.358001	0.481465	0.566576	0.548724	0.354890
$E_{exch}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(2-5)}$	-1.121058	-1.131621	-1.126940	-0.841898	-0.165151
$E_{elstat}^{(2,5)}$	-1.121058	-1.131621	-1.126940	-0.841898	-0.165151
$E_{exch}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(3-5)}$	-0.199510	-0.258280	-0.282197	-0.474643	-0.439011
$E_{elstat}^{(3-5)}$	-0.199510	-0.258280	-0.282197	-0.474643	-0.439011
$E_{exch}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(4-5)}$	-0.131060	-0.148099	-0.167589	-0.165272	-0.698884
$E_{elstat}^{(4-5)}$	-0.131060	-0.148099	-0.167589	-0.165272	-0.698884
$E_{exch}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000

Table 2: DLPNO-CCSD(T)/def2-TVPZ energies and LED analysis for **PdNHAc**. All energies in E_h.

	anag	**TS-ag**	**ag**	**TS-CH**	**McH**
E_{tot}	-948.877896	-948.854060	-948.858762	-948.849523	-948.878642
$E_{intra}^{(1)}$	-126.114543	-126.104972	-126.078147	-126.067041	-126.042010
$E_{intra}^{(2)}$	-403.087409	-403.019325	-402.891284	-402.684895	-402.320980
$E_{intra}^{(3)}$	-207.460043	-207.397682	-207.449925	-207.421048	-207.443217
$E_{intra}^{(4)}$	-207.494423	-207.480712	-207.449925	-207.585840	-207.806127
$E_{intra}^{(5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(1-2)}$	-1.105237	-1.297327	-1.551812	-1.908547	-2.704495
$E_{elstat}^{(1-2)}$	-0.990276	-1.168028	-1.387506	-1.680254	-2.357568
$E_{exch}^{(1-2)}$	-0.082145	-0.090809	-0.116460	-0.165305	-0.258780
$E_{corr}^{(1-2)}$	-0.032811	-0.038489	-0.047846	-0.062988	-0.034398
$E_{disp}^{(1-2)}$	-0.014176	-0.017036	-0.018982	-0.024674	-0.034398
$E_{inter}^{(1-3)}$	-1.597127	-1.604561	-1.563438	-1.454814	-1.133904
$E_{elstat}^{(1-3)}$	-1.422085	-1.433053	-1.394175	-1.300446	-1.019439
$E_{exch}^{(1-3)}$	-0.126121	-0.129011	-0.127039	-0.114515	-0.084031
$E_{corr}^{(1-3)}$	-0.048921	-0.043507	-0.042224	-0.039853	-0.030433
$E_{disp}^{(1-3)}$	-0.015008	-0.012769	-0.011957	-0.011473	-0.009880
$E_{inter}^{(2-3)}$	0.223528	0.254256	0.260792	0.214444	0.251121
$E_{elstat}^{(2-3)}$	0.248687	0.285921	0.297372	0.296933	0.293717
$E_{exch}^{(2-3)}$	-0.013299	-0.017758	-0.020102	-0.051737	-0.023850
$E_{corr}^{(2-3)}$	-0.011859	-0.013907	-0.016478	-0.030751	-0.018745
$E_{disp}^{(2-3)}$	-0.005818	-0.00594941	-0.006382	-0.008326	-0.007099
$E_{inter}^{(1-4)}$	-1.454294	-1.469448	-1.526635	-1.358770	-1.061295
$E_{elstat}^{(1-4)}$	-1.295144	-1.305133	-1.360382	-1.218008	-0.963711
$E_{exch}^{(1-4)}$	-0.118724	-0.122483	-0.124446	-0.104585	-0.071220
$E_{corr}^{(1-4)}$	-0.040427	-0.041831	-0.041807	-0.036176	-0.026365
$E_{disp}^{(1-4)}$	-0.012268	-0.012073	-0.118789	-0.011111	-0.008817
$E_{inter}^{(2-4)}$	0.112267	0.131714	0.184161	0.178662	0.160340
$E_{elstat}^{(2-4)}$	0.141293	0.163173	0.214352	0.211993	0.196944
$E_{exch}^{(2-4)}$	-0.138485	-0.015806	-0.015500	-0.017998	-0.020548
$E_{corr}^{(2-4)}$	-0.015178	-0.015653	-0.014692	-0.015334	-0.016055
$E_{disp}^{(2-4)}$	-0.008543	-0.008439	-0.007517	-0.007366	-0.007654
$E_{inter}^{(3-4)}$	0.205862	0.202229	0.200737	0.200496	0.168588
$E_{elstat}^{(3-4)}$	0.223765	0.220915	0.220066	0.215665	0.179882
$E_{exch}^{(3-4)}$	-0.010416	-0.010109	-0.010441	-0.007776	-0.005334
$E_{corr}^{(3-4)}$	-0.007487	-0.008577	-0.008888	-0.007393	-0.005960

$E_{disp}^{(3-4)}$	-0.002079	-0.002876	-0.003294	-0.003115	-0.002849
$E_{inter}^{(1-5)}$	0.361163	0.475508	0.553749	0.529019	0.410902
$E_{elstat}^{(1-5)}$	0.361163	0.475508	0.553749	0.529019	0.410902
$E_{exch}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(2-5)}$	-1.110780	-1.124770	-1.127063	-0.836790	-0.291471
$E_{elstat}^{(2,5)}$	-1.110780	-1.124770	-1.127063	-0.836790	-0.291471
$E_{exch}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(3-5)}$	-0.227271	-0.269837	-0.287950	-0.487638	-0.922348
$E_{elstat}^{(3-5)}$	-0.227271	-0.269837	-0.287950	-0.487638	-0.922348
$E_{exch}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(4-5)}$	-0.129589	-0.149122	-0.172465	-0.166761	-0.143746
$E_{elstat}^{(4-5)}$	-0.129589	-0.149122	-0.172465	-0.166761	-0.143746
$E_{exch}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000

Table 3: DLPNO-CCSD(T)/def2-TVPZ energies and LED analysis for **NiOAc**. All energies in E_h.

	anag	**TS-ag**	**ag**	**TS-CH**	**McH**
E_{tot}	-2370.873582	-2370.839042	-2370.832599	-2370.823087	-2370.849138
$E_{intra}^{(1)}$	-1508.527792	-1508.534666	-1508.507563	-1508.496742	-1508.483405
$E_{intra}^{(2)}$	-402.899844	-402.721913	-402.328996	-402.112114	-402.887285
$E_{intra}^{(3)}$	-227.257483	-227.439654	-227.439108	-227.412906	-227.363413
$E_{intra}^{(4)}$	-227.461677	-227.462836	-227.475519	-227.544834	-227.662716
$E_{intra}^{(5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(1-2)}$	-1.277242	-1.615421	-2.123119	-2.452593	-3.015332
$E_{elstat}^{(1-2)}$	-1.181539	-1.499446	-1.949423	-2.232483	-2.719419
$E_{exch}^{(1-2)}$	-0.068053	-0.082342	-0.124176	-0.156943	-0.208019
$E_{corr}^{(1-2)}$	-0.027650	-0.033632	-0.049520	-0.063167	-0.087895
$E_{disp}^{(1-2)}$	-0.009907	-0.011707	-0.016107	-0.020272	-0.027580
$E_{inter}^{(1-3)}$	-1.610776	-1.339738	-1.308638	-1.232025	-1.046873
$E_{elstat}^{(1-3)}$	-1.486973	-1.245081	-1.214294	-1.147129	-0.982109
$E_{exch}^{(1-3)}$	-0.086802	-0.067021	-0.066410	-0.059765	-0.046169
$E_{corr}^{(1-3)}$	-0.037001	-0.027637	-0.027934	-0.025132	-0.018595
$E_{disp}^{(1-3)}$	-0.009705	-0.007313	-0.006754	-0.006456	-0.006037
$E_{inter}^{(2-3)}$	0.213188	0.261745	0.264254	0.200665	0.246983
$E_{elstat}^{(2-3)}$	0.234044	0.289540	0.301861	0.281376	0.280793
$E_{exch}^{(2-3)}$	-0.009239	-0.014181	-0.019687	-0.049761	-0.017090
$E_{corr}^{(2-3)}$	-0.011616	-0.013614	-0.017920	-0.030950	-0.016720
$E_{disp}^{(2-3)}$	-0.006391	-0.006080	-0.007181	-0.008370	-0.007386
$E_{inter}^{(1-4)}$	-1.298534	-1.290519	-1.280998	-1.202590	-1.056076
$E_{elstat}^{(1-4)}$	-1.204843	-1.195752	-1.188792	-1.120390	-0.991063
$E_{exch}^{(1-4)}$	-0.066777	-0.066390	-0.064513	-0.057957	-0.046517
$E_{corr}^{(1-4)}$	-0.026914	-0.028377	-0.027693	-0.024242	-0.018496
$E_{disp}^{(1-4)}$	-0.006962	-0.006709	-0.006662	-0.006290	-0.005658
$E_{inter}^{(2-4)}$	0.135094	0.159010	0.180075	0.181000	0.176786
$E_{elstat}^{(2-4)}$	0.159714	0.183172	0.207264	0.208313	0.202773
$E_{exch}^{(2-4)}$	-0.010841	-0.010664	-0.012325	-0.012399	-0.011965
$E_{corr}^{(2-4)}$	-0.013779	-0.013498	-0.014865	-0.014915	-0.014021
$E_{disp}^{(2-4)}$	-0.008165	-0.007330	-0.007936	-0.007642	-0.006992
$E_{inter}^{(3-4)}$	0.201766	0.188460	0.184293	0.180086	0.170448
$E_{elstat}^{(3-4)}$	0.212262	0.02069	0.197312	0.193108	0.186368
$E_{exch}^{(3-4)}$	-0.005037	-0.005900	-0.005694	-0.005701	-0.007266
$E_{corr}^{(3-4)}$	-0.005486	-0.007709	-0.007325	-0.007322	-0.008653

$E_{disp}^{(3-4)}$	-0.002490	-0.004125	-0.003846	-0.004080	-0.005232
$E_{inter}^{(1-5)}$	0.392873	0.536944	0.618729	0.583204	0.465738
$E_{elstat}^{(1-5)}$	0.392873	0.536944	0.618729	0.583204	0.465738
$E_{exch}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(2-5)}$	-1.131060	-1.147404	-1.137099	-0.831049	-0.303739
$E_{elstat}^{(2,5)}$	-1.131060	-1.147404	-1.137099	-0.831049	-0.303739
$E_{exch}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(3-5)}$	-0.207807	-0.278367	-0.307225	-0.512079	-0.911936
$E_{elstat}^{(3-5)}$	-0.207807	-0.278367	-0.307225	-0.512079	-0.911936
$E_{exch}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(4-5)}$	-0.144289	-154683	-0.171682	-0.171110	-0.178319
$E_{elstat}^{(4-5)}$	-0.144289	-154683	-0.171682	-0.171110	-0.178319
$E_{exch}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000

Table 4: DLPNO-CCSD(T)/def2-TVPZ energies and LED analysis for **NiNHAc**. All energies in E_h.

	anag	**TS-ag**	**ag**	**TS-CH**	**McH**
E_{tot}	-2331.122911	-2331.087911	-2331.085494	-2331.076661	-2331.101760
$E_{intra}^{(1)}$	-1508.514856	-1508.514131	-1508.495393	-1508.488449	-1508.481100
$E_{intra}^{(2)}$	-402.958788	-402.751891	-402.524394	-402.524394	-402.102005
$E_{intra}^{(3)}$	-207.155827	-207.273691	-207.229759	-207.212922	-207.201967
$E_{intra}^{(4)}$	-207.341740	-207.322438	-207.331763	-207.423464	-207.600952
$E_{intra}^{(5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(1-2)}$	-1.204384	-1.577006	-1.910551	-2.191513	-1.758555
$E_{elstat}^{(1-2)}$	-1.116698	-1.465229	-1.761634	-2.002714	-2.493818
$E_{exch}^{(1-2)}$	-0.062156	-0.079097	-0.105897	-0.134277	-0.185728
$E_{corr}^{(1-2)}$	-0.025529	-0.032680	-0.043020	-0.054522	-0.185728
$E_{disp}^{(1-2)}$	-0.009511	-0.011957	-0.014735	-0.018238	-0.025155
$E_{inter}^{(1-3)}$	-1.856408	-1.640052	-1.663283	-1.584566	-1.336203
$E_{elstat}^{(1-3)}$	-1.705043	-1.507830	-1.535484	-1.457111	-1.233192
$E_{exch}^{(1-3)}$	-0.106571	-0.093556	-0.097119	-0.090264	-0.073638
$E_{corr}^{(1-3)}$	-0.044794	-0.038666	-0.040680	-0.037191	-0.029374
$E_{disp}^{(1-3)}$	-0.011689	-0.010002	-0.009461	-0.009621	-0.008154
$E_{inter}^{(2-3)}$	0.228291	0.274304	0.277036	0.213416	0.243191
$E_{elstat}^{(2-3)}$	0.251977	0.307068	0.318179	0.297731	0.288460
$E_{exch}^{(2-3)}$	-0.010615	-0.016285	-0.020969	-0.051037	-0.023530
$E_{corr}^{(2-3)}$	-0.013072	-0.016478	-0.020173	-0.033278	-0.021739
$E_{disp}^{(2-3)}$	-0.006636	-0.006983	-0.007305	-0.009548	-0.008449
$E_{inter}^{(1-4)}$	-1.540598	-1.548435	-1.552865	-1.452451	-1.244329
$E_{elstat}^{(1-4)}$	-1.415252	-1.419407	-1.426355	-1.339822	-1.156560
$E_{exch}^{(1-4)}$	-0.089399	-0.090945	-0.088853	-0.080268	-0.062809
$E_{corr}^{(1-4)}$	-0.036046	-0.038083	-0.037657	-0.033361	-0.024960
$E_{disp}^{(1-4)}$	-0.009347	-0.008893	-0.008582	-0.007859	-0.006921
$E_{inter}^{(2-4)}$	0.112331	0.130751	0.176754	0.176814	0.172406
$E_{elstat}^{(2-4)}$	0.141988	0.163573	0.206807	0.207509	0.202589
$E_{exch}^{(2-4)}$	-0.013435	-0.015364	-0.013599	-0.013975	-0.013890
$E_{corr}^{(2-4)}$	-0.016222	-0.017458	-0.016454	-0.016720	-0.016293
$E_{disp}^{(2-4)}$	-0.009337	-0.009302	-0.008218	-0.008141	-0.007870
$E_{inter}^{(3-4)}$	0.209237	0.184456	0.184435	0.184956	0.160244

$E_{elstat}^{(3-4)}$	0.224496	0.201701	0.202906	0.202653	0.178022
$E_{exch}^{(3-4)}$	-0.007267	-0.008076	-0.008556	-0.008177	-0.008471
$E_{corr}^{(3-4)}$	-0.007992	-0.009168	-0.009914	-0.009520	-0.009307
$E_{disp}^{(3-4)}$	-0.002829	-0.003610	-0.004302	-0.004439	-0.004703
$E_{inter}^{(1-5)}$	0.391475	0.540281	0.602794	0.562033	0.429188
$E_{elstat}^{(1-5)}$	0.391475	0.540281	0.602794	0.562033	0.429188
$E_{exch}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(1-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(2-5)}$	-1.123720	-1.138080	-1.122628	-0.841017	-0.310087
$E_{elstat}^{(2,5)}$	-1.123720	-1.138080	-1.122628	-0.841017	-0.310087
$E_{exch}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(2-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(3-5)}$	-0.230287	-0.297707	-0.324260	-0.513062	-0.919123
$E_{elstat}^{(3-5)}$	-0.230287	-0.297707	-0.324260	-0.513062	-0.919123
$E_{exch}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(3-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{inter}^{(4-5)}$	-0.137640	-0.154272	-0.171617	-0.168448	-0.152469
$E_{elstat}^{(4-5)}$	-0.137640	-0.154272	-0.171617	-0.168448	-0.152469
$E_{exch}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{corr}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000
$E_{disp}^{(4-5)}$	0.000000	0.000000	0.000000	0.000000	0.000000

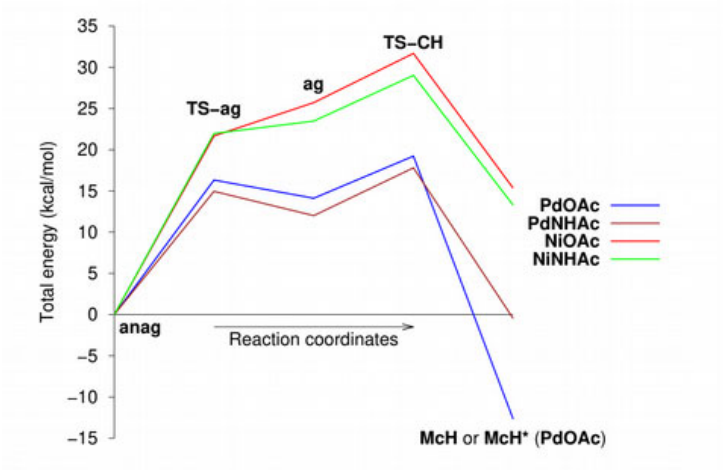

Figure S 8 Total energy profile computed at the DLPNO-CCSD(T)/def2-TZVP level of theory from the DFT-optimized geometries. All energies expressed relative to **anag**.

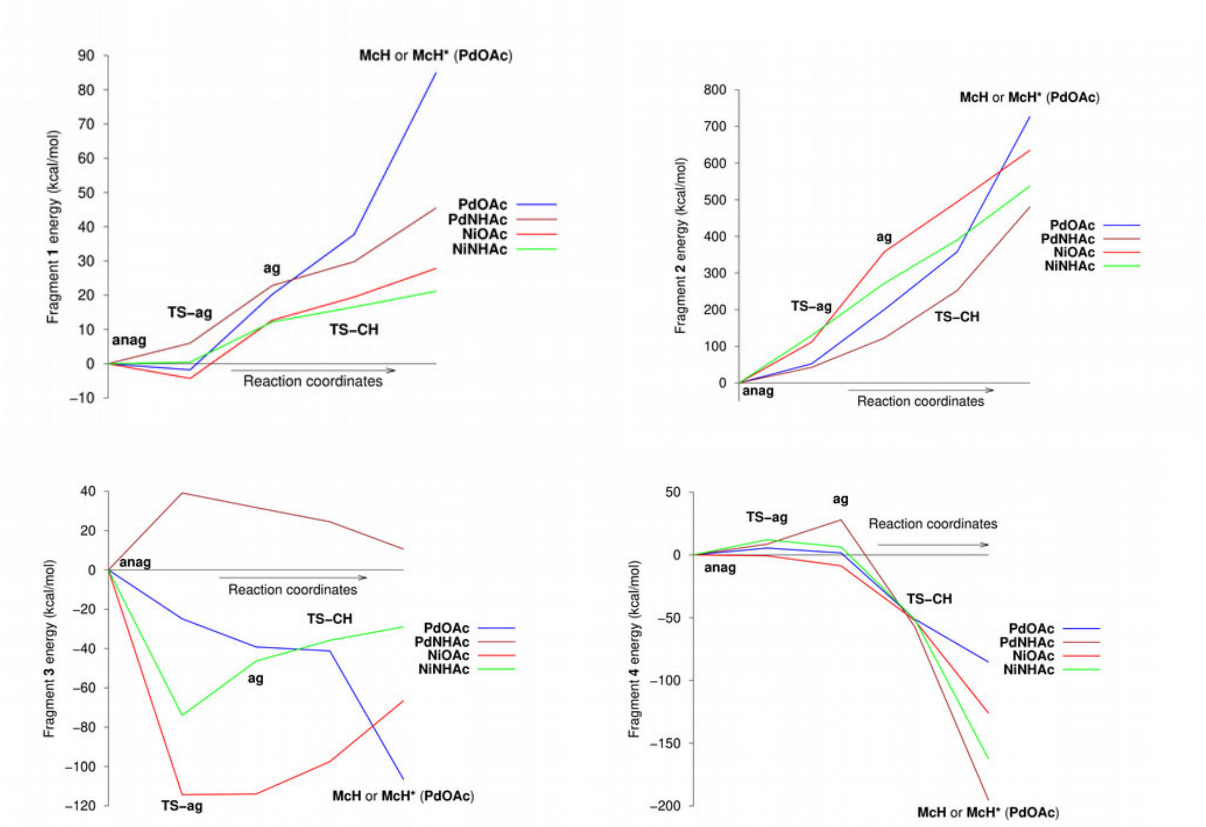

Figure S 9. Fragment energy plots along the reaction path for fragments 1 (top left), 2 (top right), 3 (bottom left) and 4 (bottom right). All energies expressed relative to **anag**.

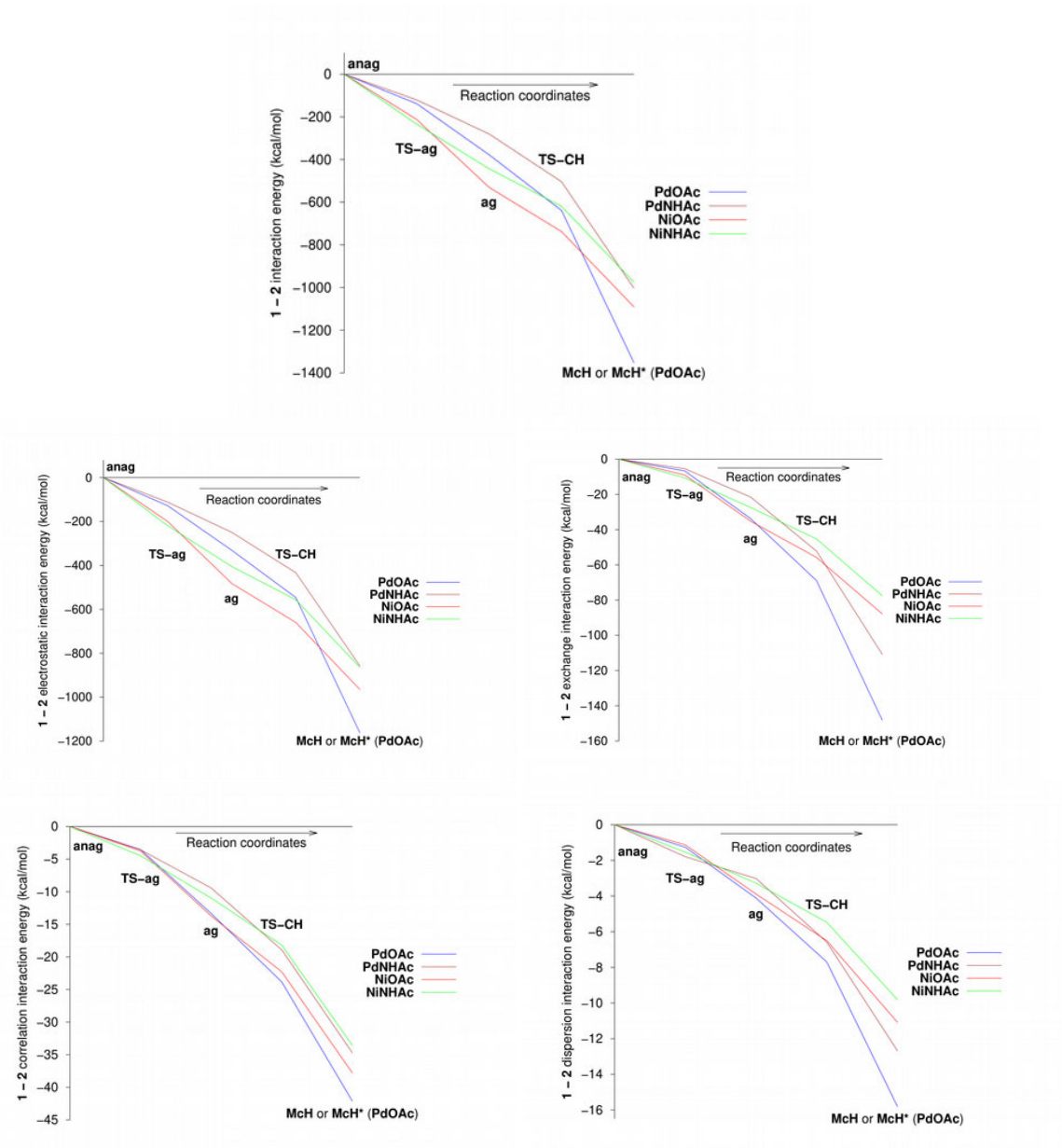

Figure S 10 Interaction energy contributions plots along the reaction path for the interaction between fragments 1 and 2. Interaction energy (top), electrostatic contribution (middle left), exchange contribution (middle right), correlation contribution (bottom left) and dispersion contribution (bottom right). All energies expressed relative to **anag**.

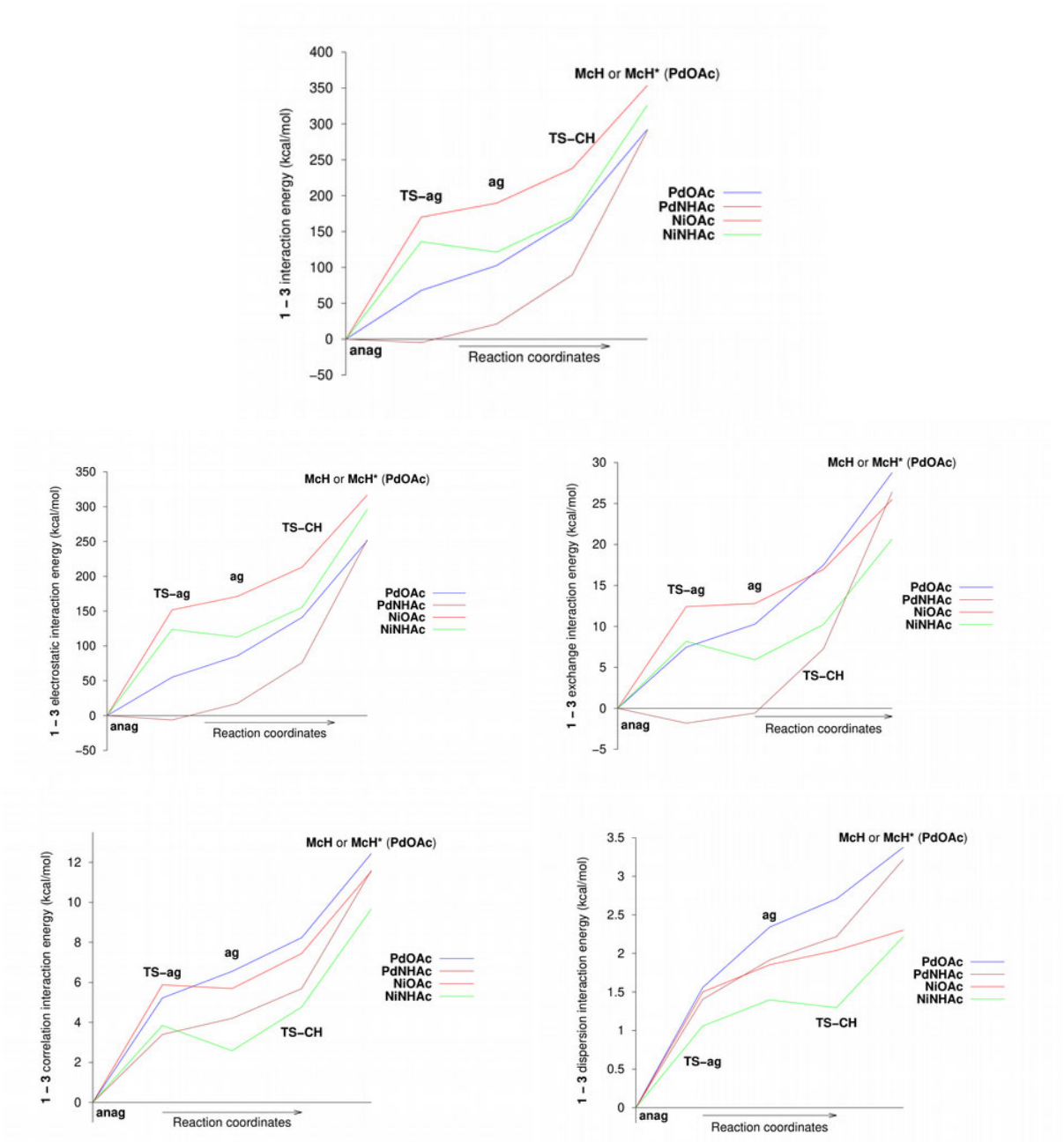

Figure S 11 Interaction energy contributions plots along the reaction path for the interaction between fragments **1** and **3**. Interaction energy (top), electrostatic contribution (middle left), exchange contribution (middle right), correlation contribution (bottom left) and dispersion contribution (bottom right). All energies expressed relative to **anag**.

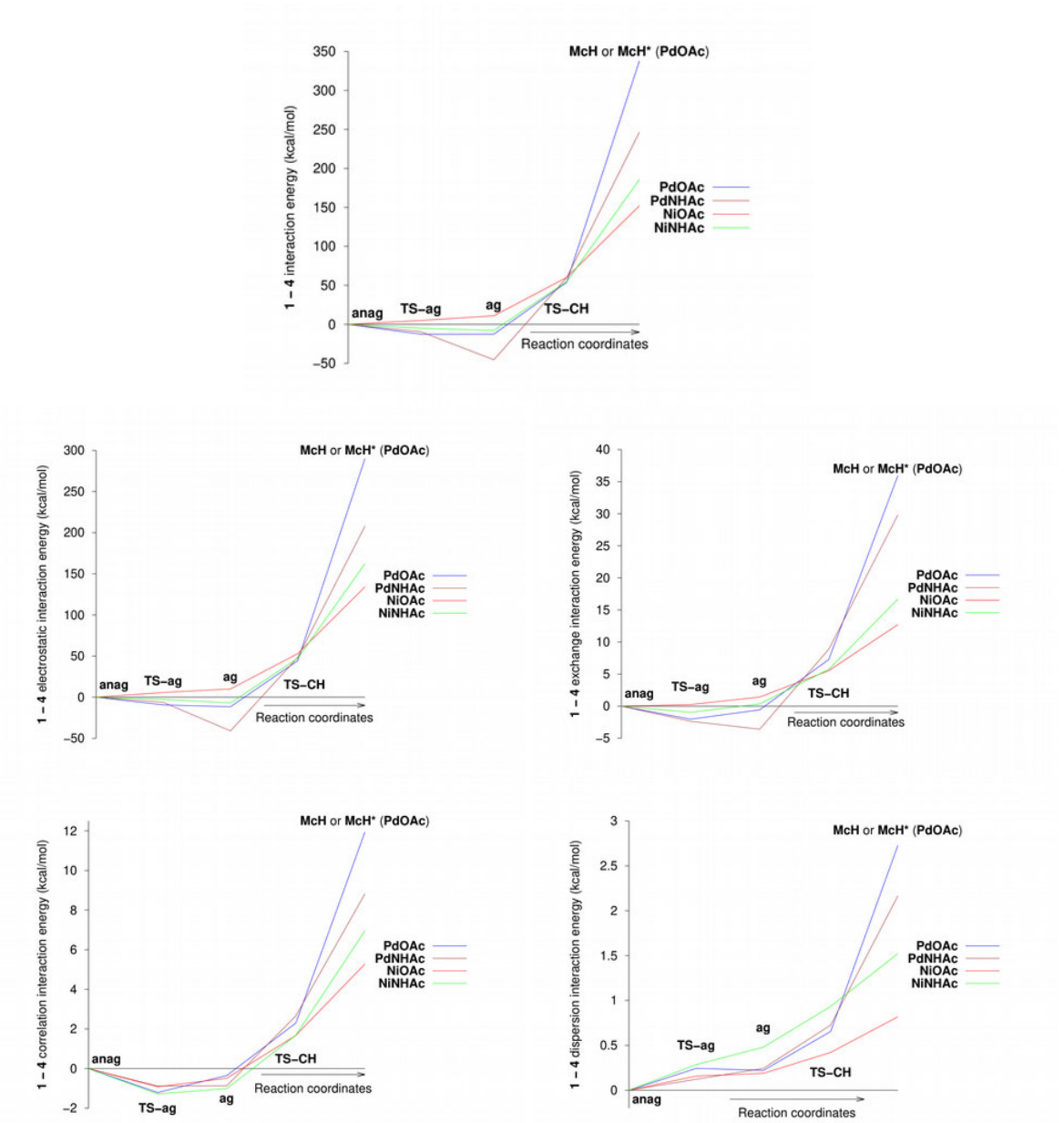

Figure S 12. Interaction energy contributions plots along the reaction path for the interaction between fragments **1** and **4**. Interaction energy (top), electrostatic contribution (middle left), exchange contribution (middle right), correlation contribution (bottom left) and dispersion contribution (bottom right). All energies expressed relative to **anag**.

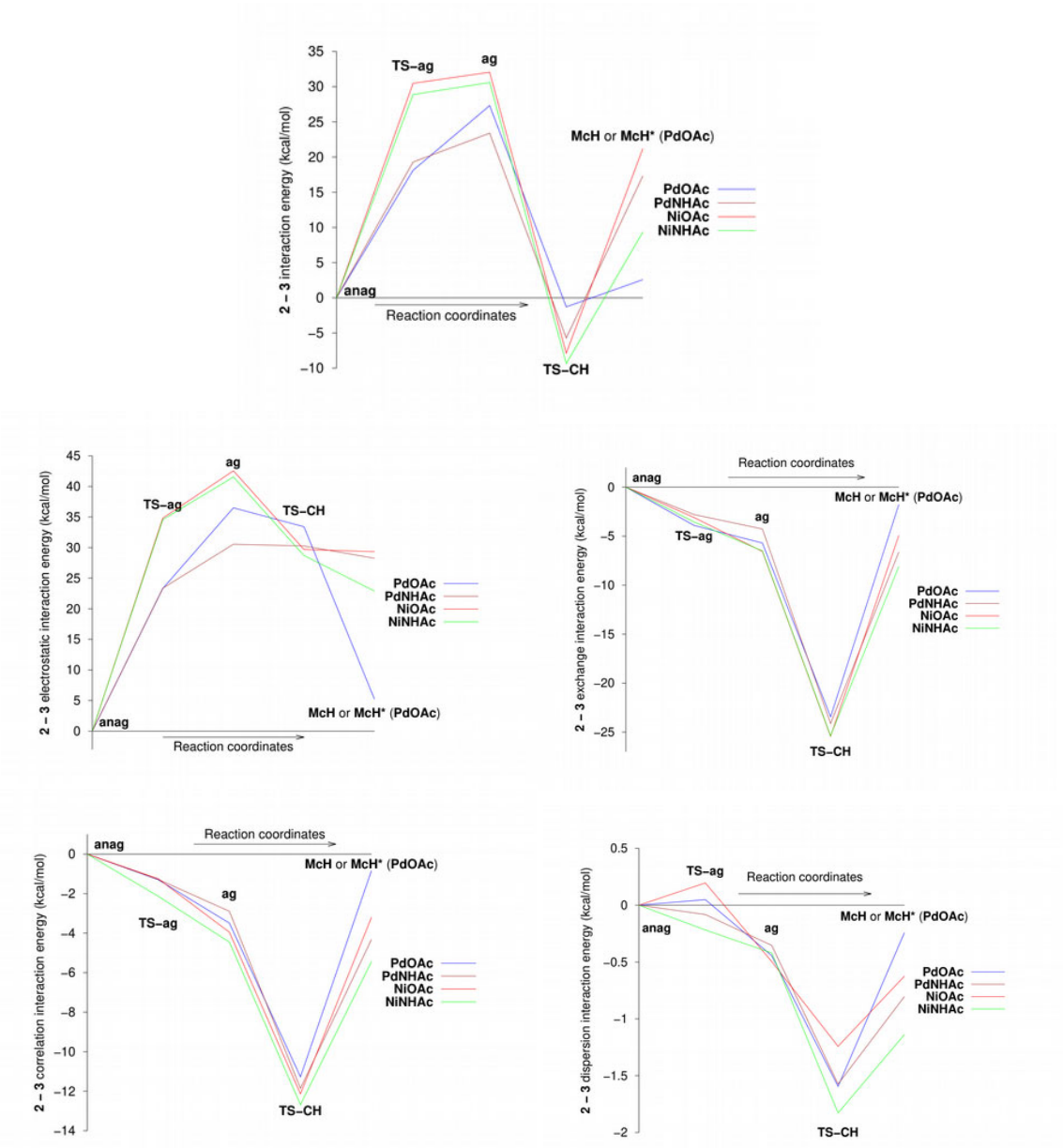

Figure S 13. Interaction energy contributions plots along the reaction path for the interaction between fragments **2** and **3**. Interaction energy (top), electrostatic contribution (middle left), exchange contribution (middle right), correlation contribution (bottom left) and dispersion contribution (bottom right). All energies expressed relative to **anag**.

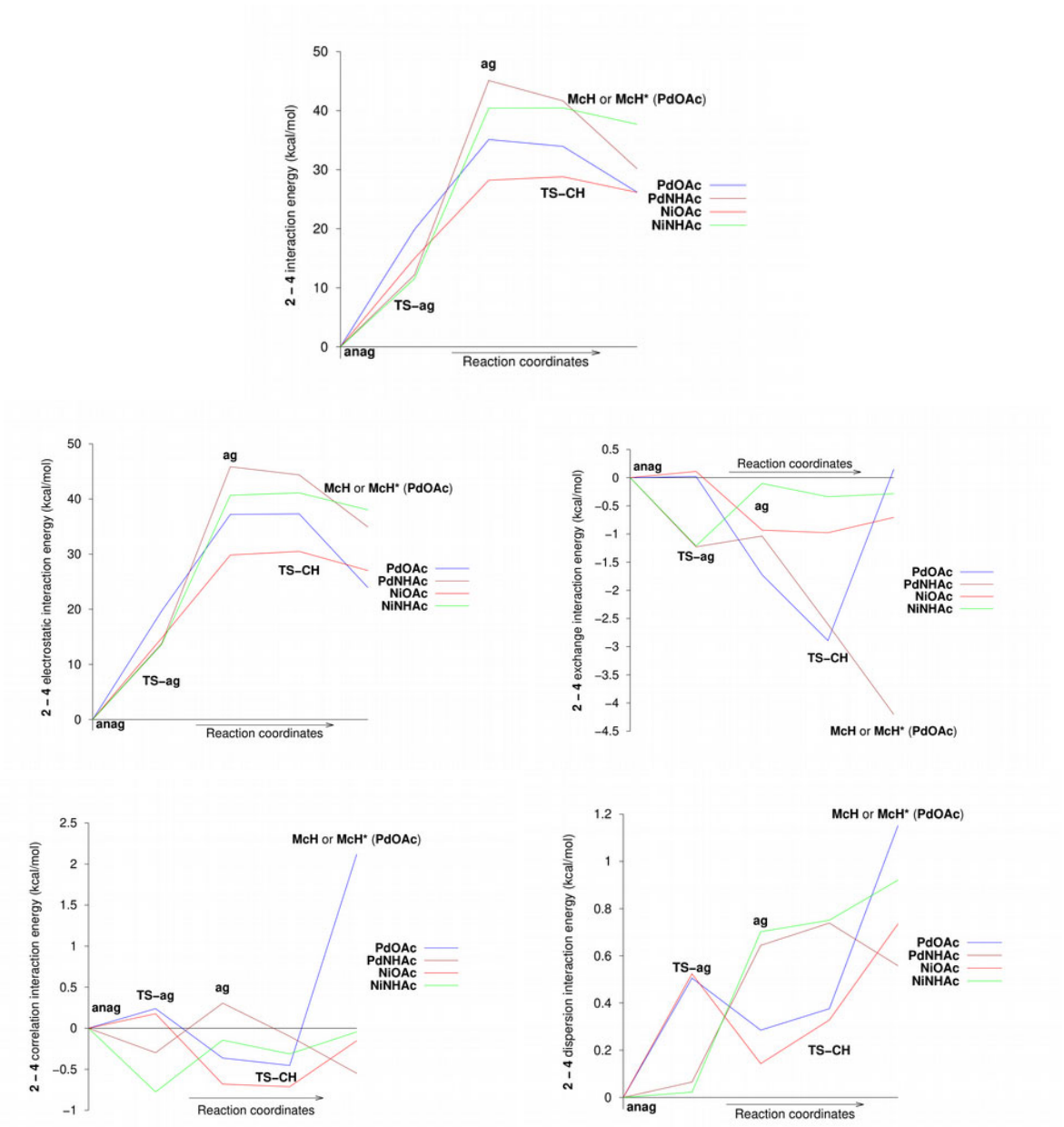

Figure S 14. Interaction energy contributions plots along the reaction path for the interaction between fragments 2 and 4. Interaction energy (top), electrostatic contribution (middle left), exchange contribution (middle right), correlation contribution (bottom left) and dispersion contribution (bottom right). All energies expressed relative to **anag**.

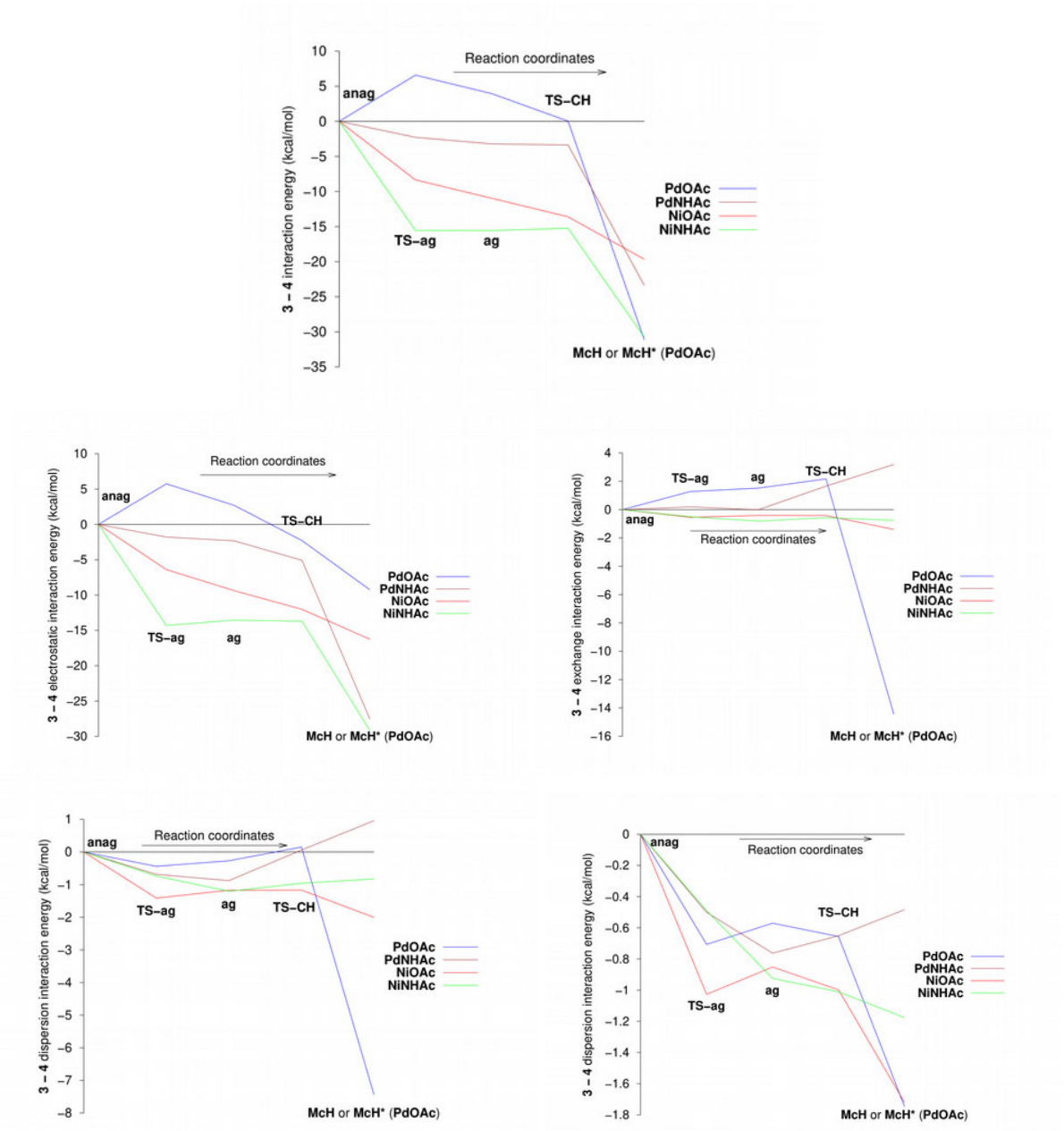

Figure S 15. Interaction energy contributions plots along the reaction path for the interaction between fragments 3 and 4. Interaction energy (top), electrostatic contribution (middle left), exchange contribution (middle right), correlation contribution (bottom left) and dispersion contribution (bottom right). All energies expressed relative to **anag**.

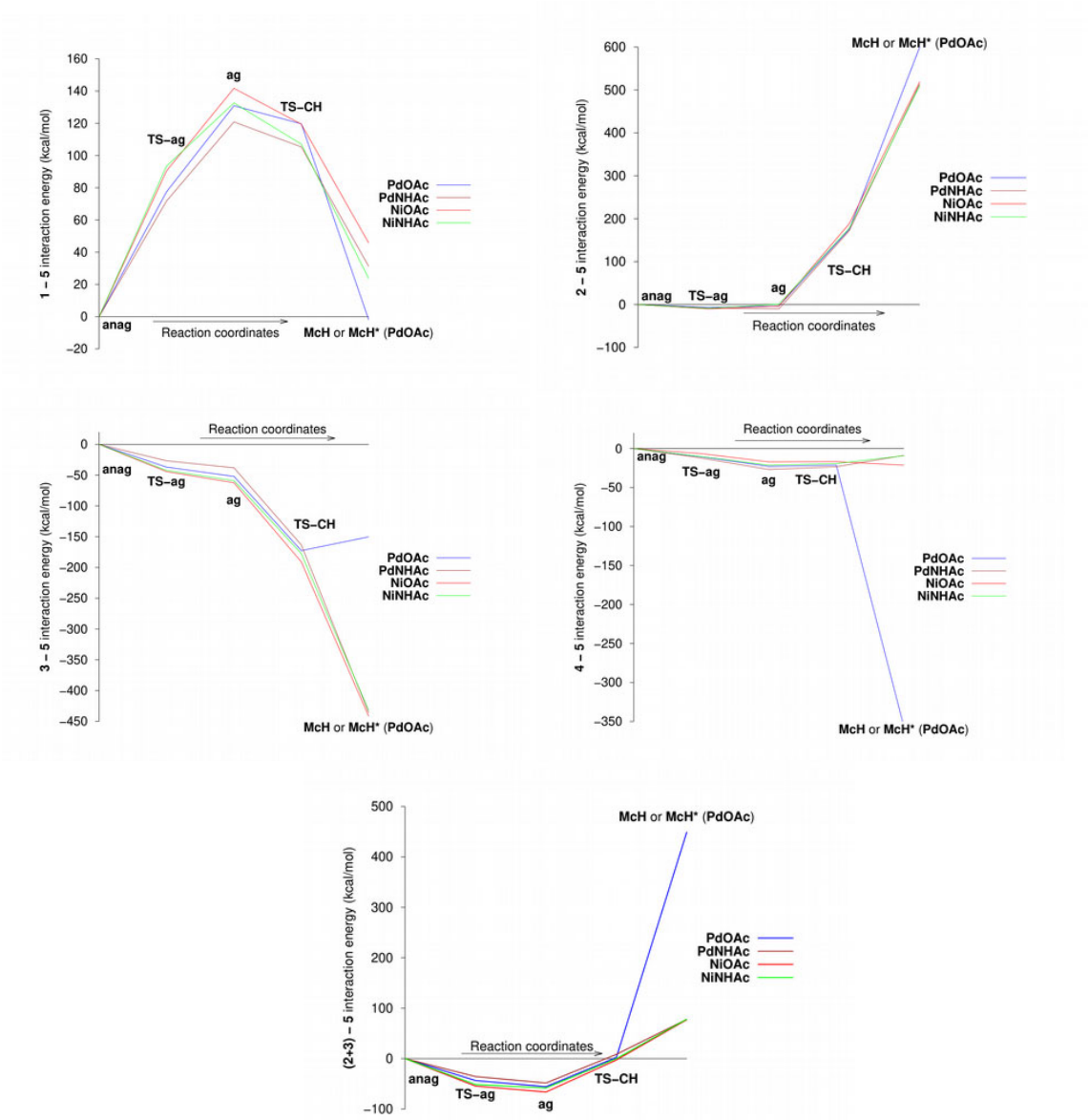

Figure S 16. Interaction energy plots along the reaction path for the interaction between fragments 1 and 5 (top left), 2 and 5 (top right), 3 and 5 (middle left), 4 and 5 (middle right), and "superfragment" 2+3 and fragment 5. All energies expressed relative to **anag**.

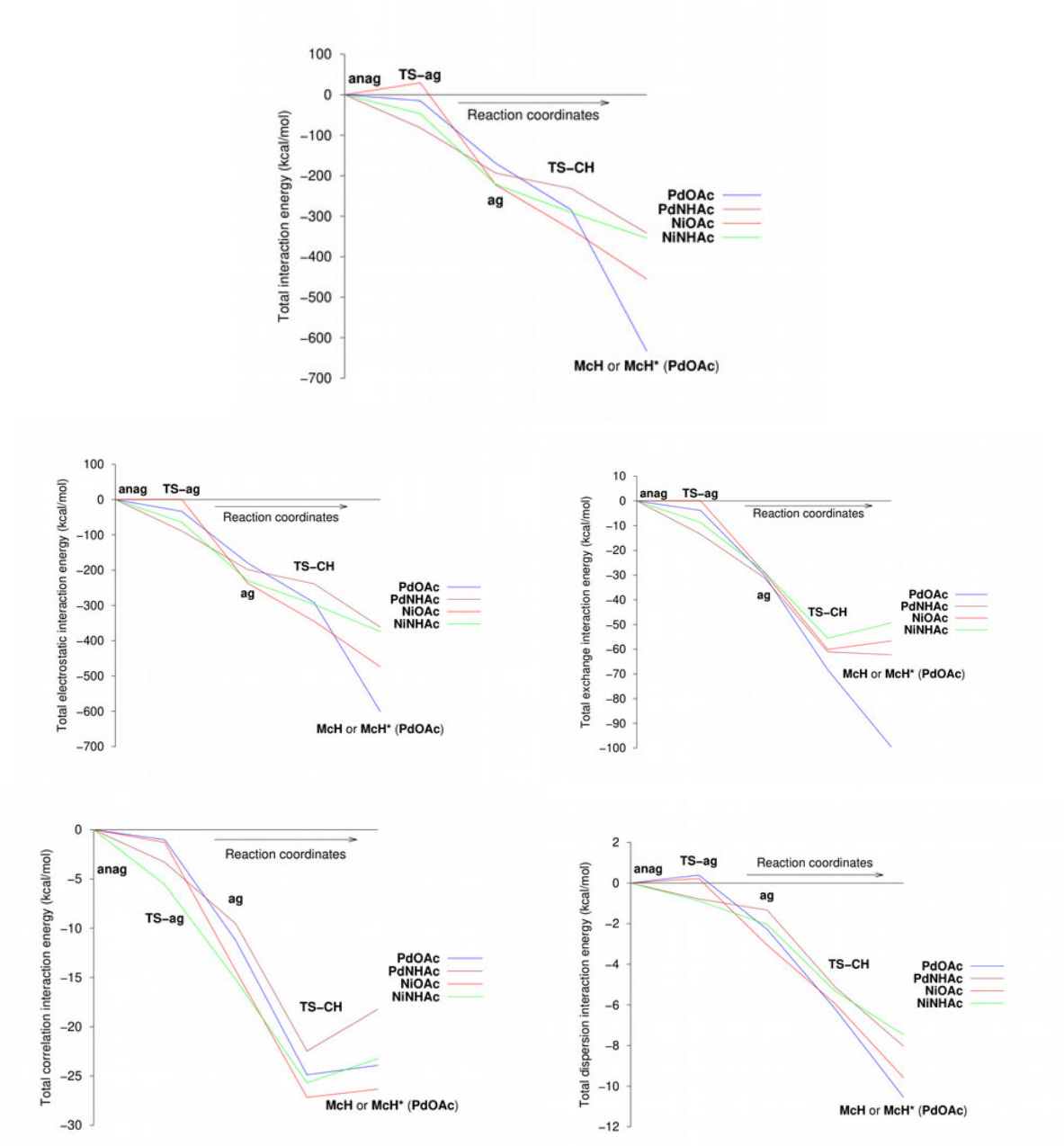

Figure S 17. Interaction energy contributions plots along the reaction path for the total interaction. Interaction energy (top), electrostatic contribution (middle left), exchange contribution (middle right), correlation contribution (bottom left) and dispersion contribution (bottom right). All energies expressed relative to **anag**.