Supporting Information

Rhodium-catalyzed ene-cycloisomerization of allylic-sulfide-tethered alkylidenecyclopropanes: DFT analysis of origins of regio- and diastereo-selectivities

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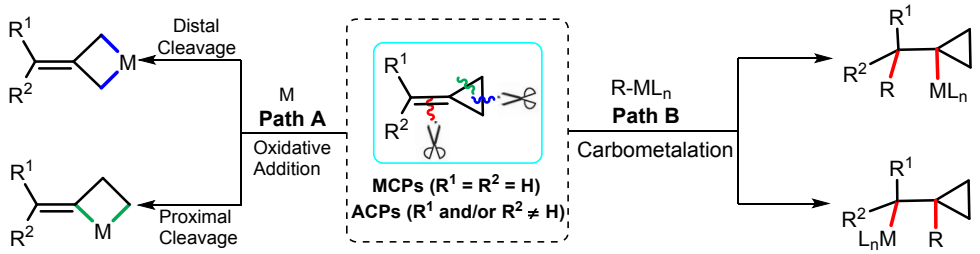
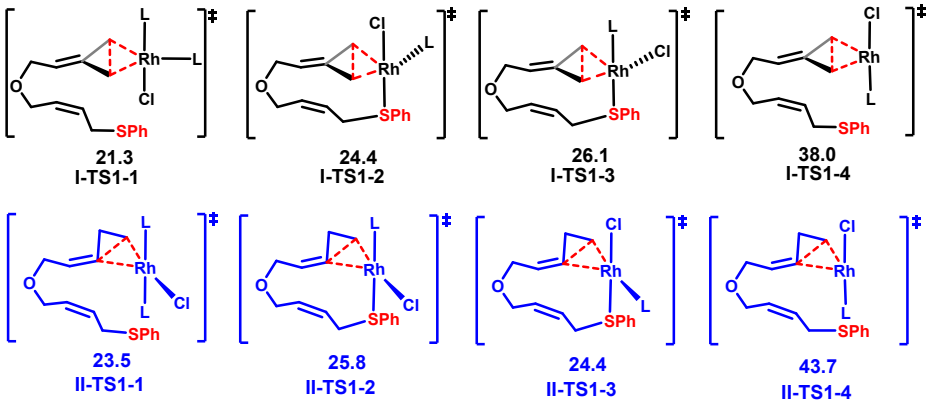
Section 1. Transition-metal-catalyzed reaction pathways for MCPs and ACPs

When the cyclopropane ring of a MCP or an ACP reacts with a transition-metal catalyst M, either the proximal or distal C–C σ bond of the three-membered ring moiety can be activated (Scheme S1, path A). When the exo-methylene moiety of a MCP or an ACP reacts with an organic transition-metal complex R–MLn, the exo-methylene moiety of the MCP or ACP can be activated first, and two different regioisomers can be formed (Scheme S1, path B).



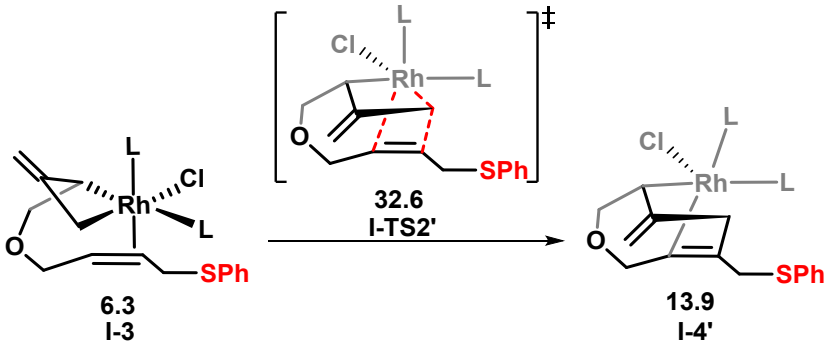
Scheme S1 Transition-metal-catalyzed reaction pathways for MCPs and ACPs.

Section 2. Other possible isomers of proximal and distal ring opening of ACP



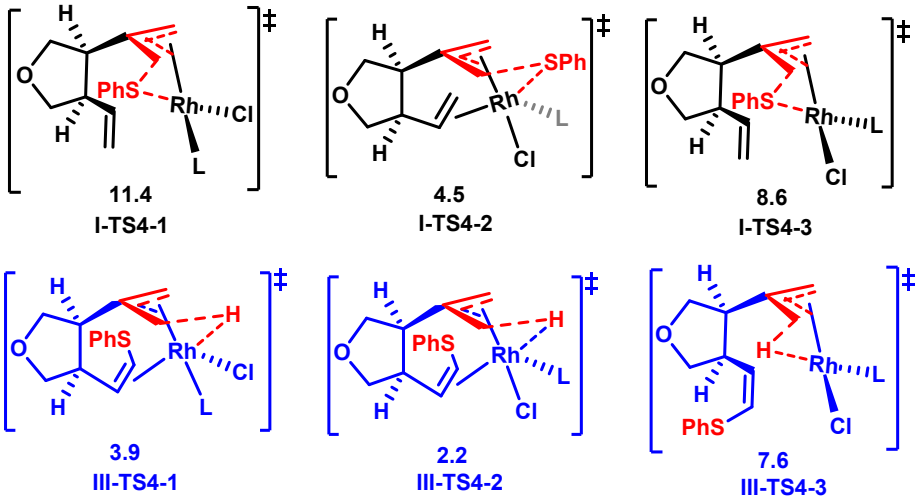
Scheme S2 Isomers of proximal and distal ring opening of ACP. Values shown are relative free energies in kcal/mol.

Section 3. Other possible alkene insertion mode from I-3



Scheme S3 Other possible alkene insertion mode from **I-3**. Values shown are relative free energies in kcal/mol.

Section 4. Isomers of I-TS4 and III-TS4



Scheme S4 Isomers of **I-TS4** and **III-TS4**. Values shown are relative free energies in kcal/mol.

Section 5. Two-step process from IV-4

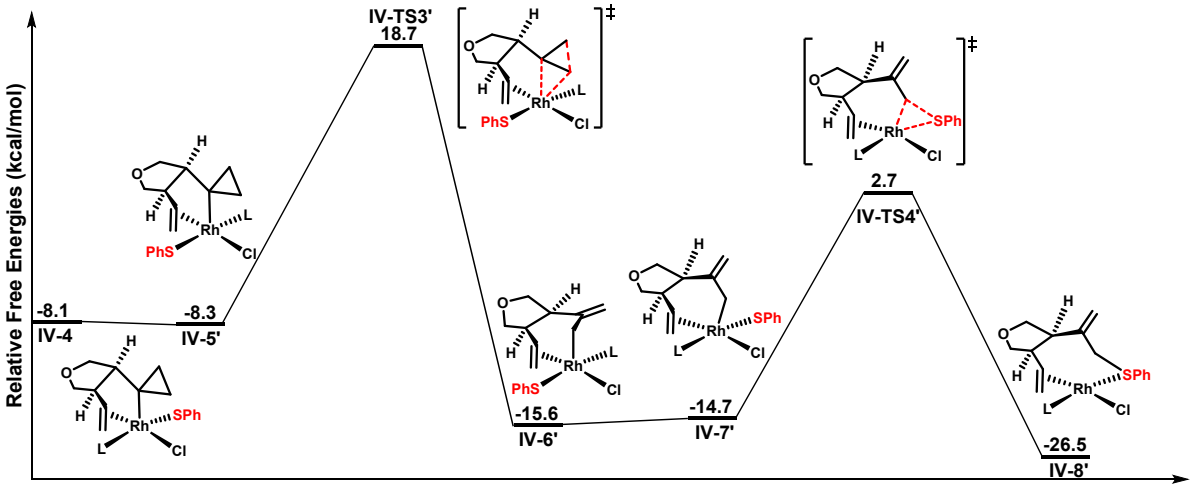
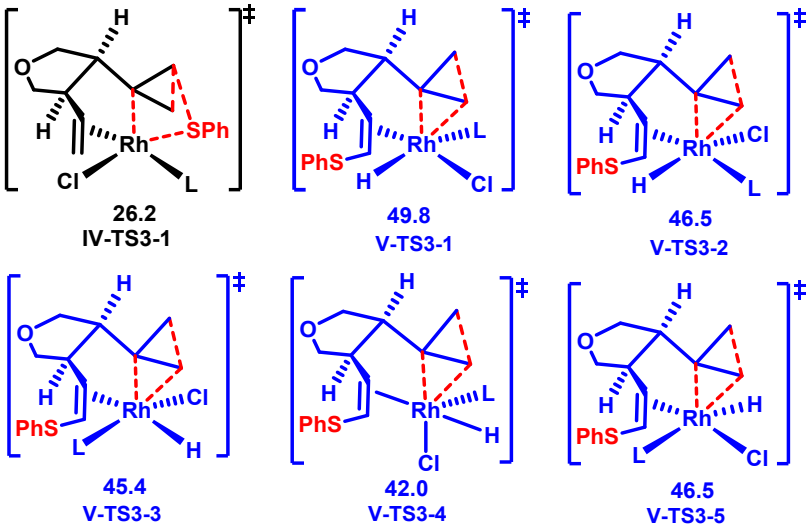


Fig. S1. Calculated free-energy profiles for two-step process from **IV-4**. Values shown are relative free energies in kcal/mol.

Section 6. Isomers of IV-TS3 and V-TS3



Scheme S5 Isomers of **IV-TS3** and **V-TS3**. Values shown are relative free energies in kcal/mol.

Section 7. Formation of diastereomeric 2-RS in path B

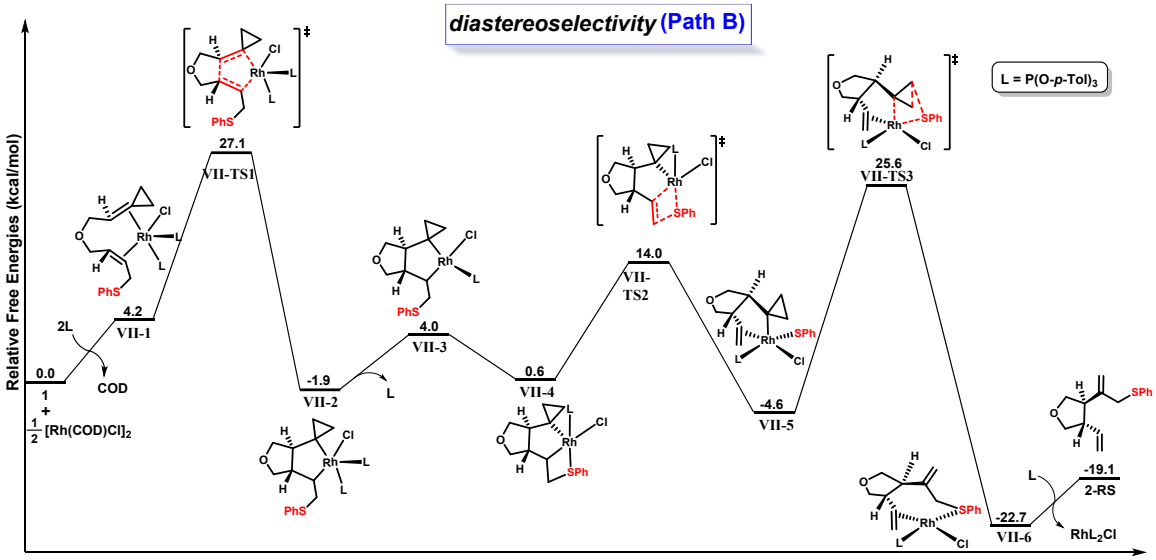
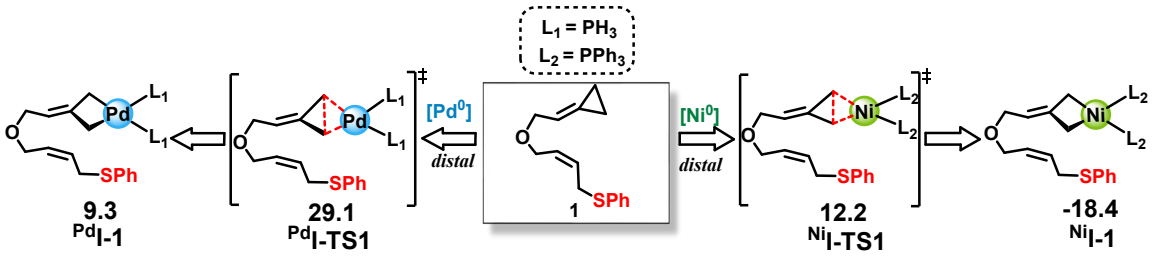


Fig. S2. Calculated free-energy profiles for formation of diastereomer **2-RS** in path B.

Section 8. Ring opening of ACP through distal C–C cleavage with the Pd(0) and Ni(0) catalysts



Scheme S6 Distal C–C cleavage with the Pd(0) and Ni(0) systems. Values shown are relative free energies in kcal/mol.

Section 9. Ring opening of ACP with the Pd(0) and Ni(0) catalysts using ligand P(O-*p*-Tol)$_3$

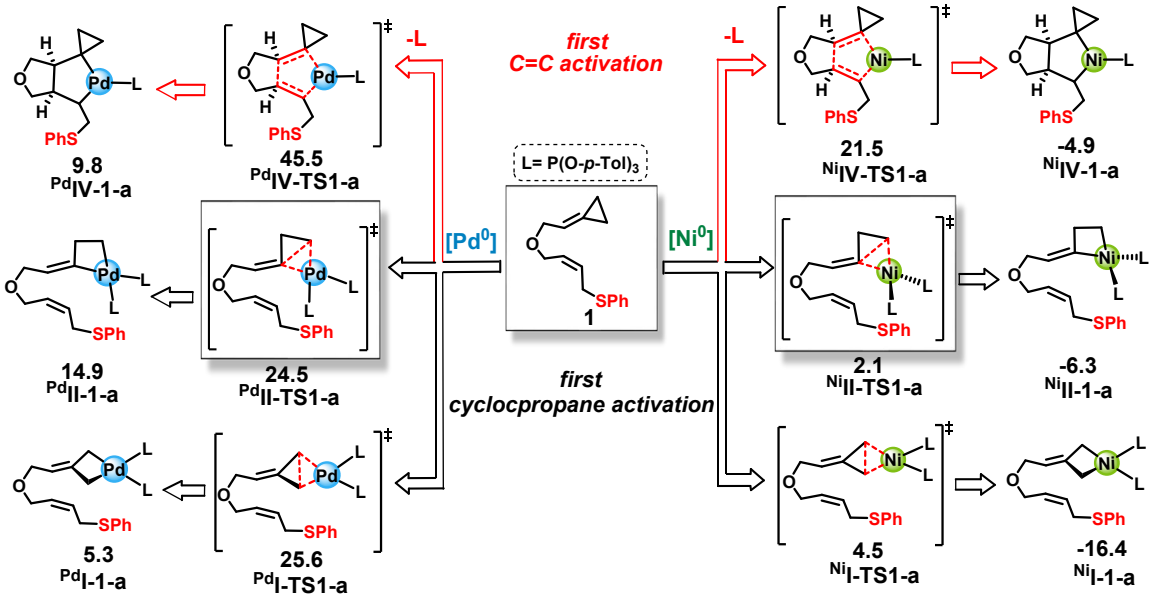
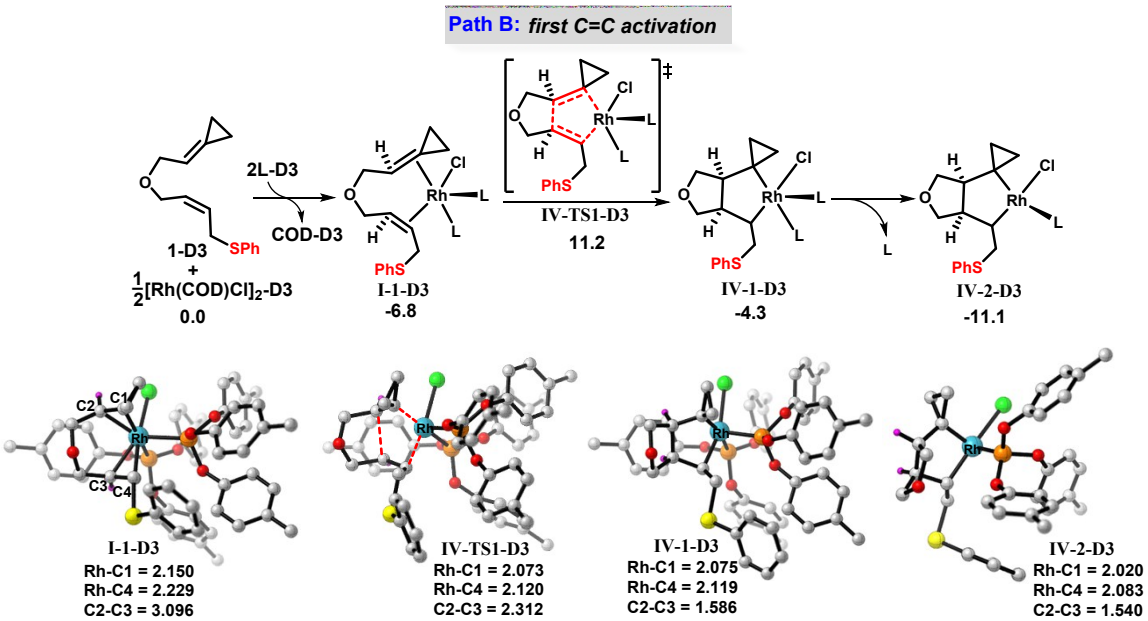


Fig. S3. Comparison of two divergent pathways for Pd(0) and Ni(0) systems using ligand P(O-*p*-Tol)$_3$. Values shown are relative free energies in kcal/mol.

Section 10. DFT with D3 dispersion correction



Scheme S7 Intermediates and transition states optimized with the dispersion corrections in Scheme 2. Interatomic distances are in angstroms, and energies are in kcal/mol.

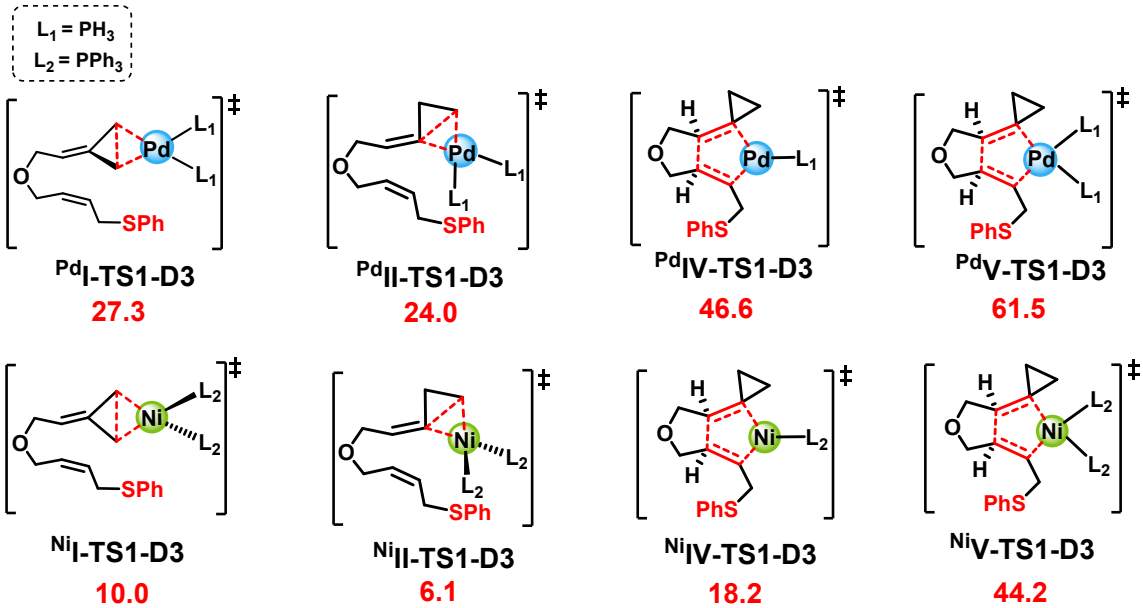


Fig. S4. Key transition states optimized with the dispersion corrections for Ni and Pd cases. Values shown are relative free energies in kcal/mol.

Section 11. Other possible pathway from I-4 to 2-RR

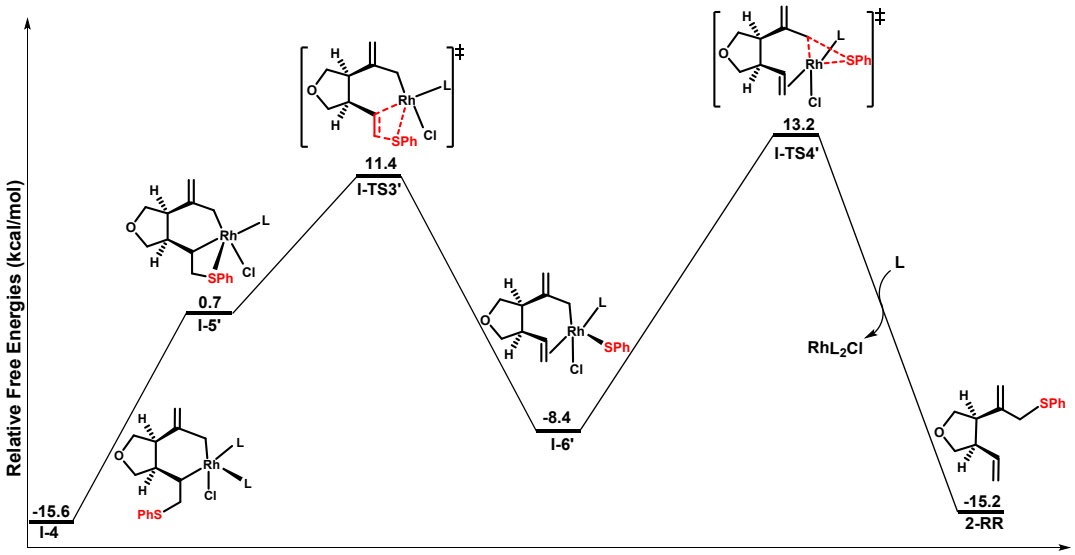


Fig. S5. Calculated free-energy profiles for other pathway starting from **I-4**. Values shown are relative free energies in kcal/mol.

Section 12. 3D structures of key species labeled in Figs. 1, 2 and 6

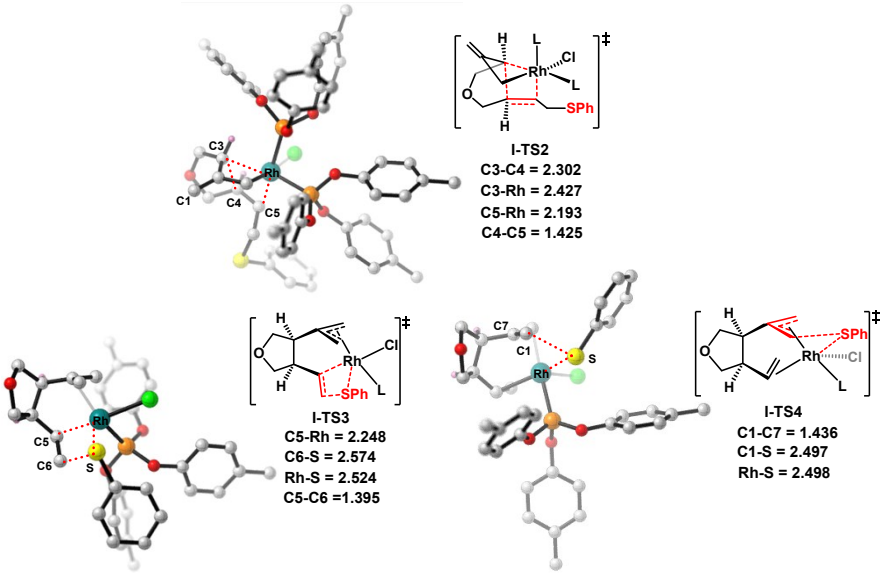


Fig. S6. Optimized structures of key species labeled in Figs. 1 and 2. Key bond lengths are given in Å.

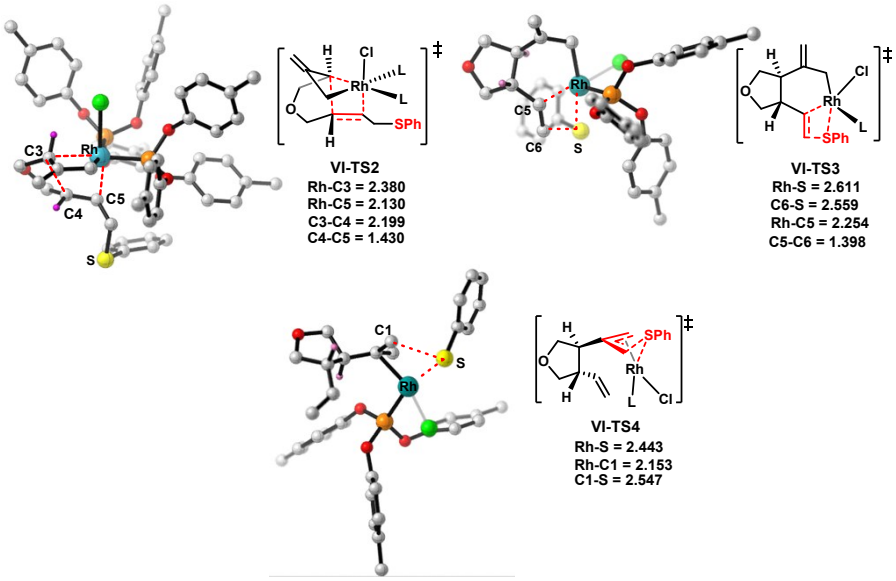


Fig. S7. Optimized structures of key species labeled in Fig. 6. Key bond lengths are given in Å.

Section 13. RDG analysis

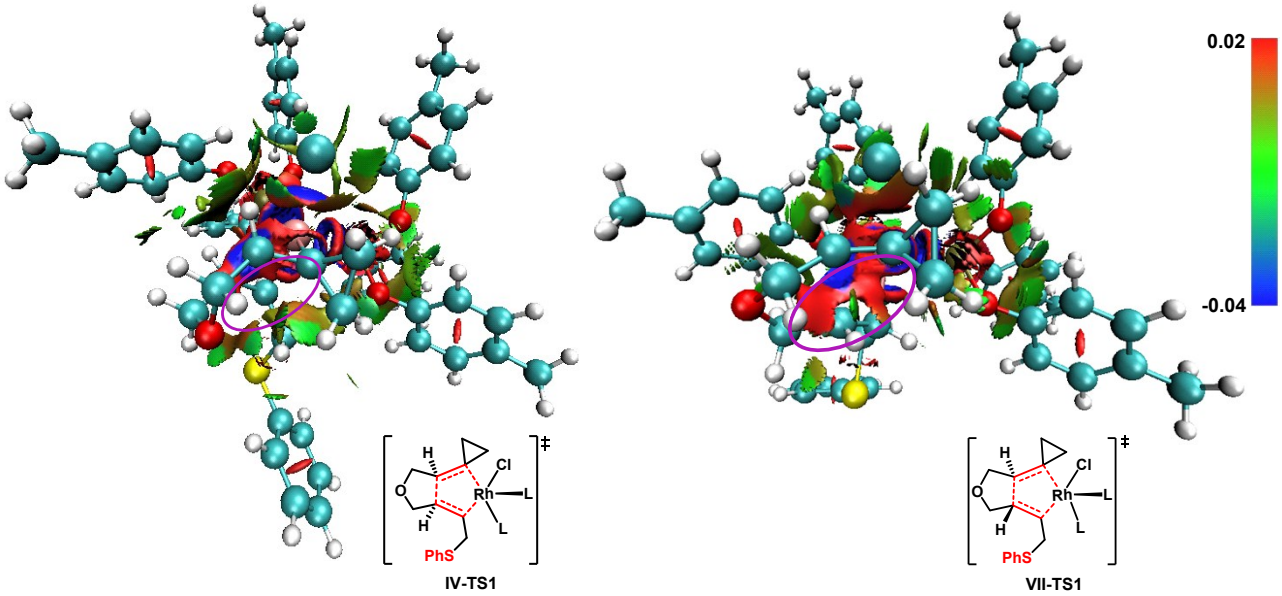
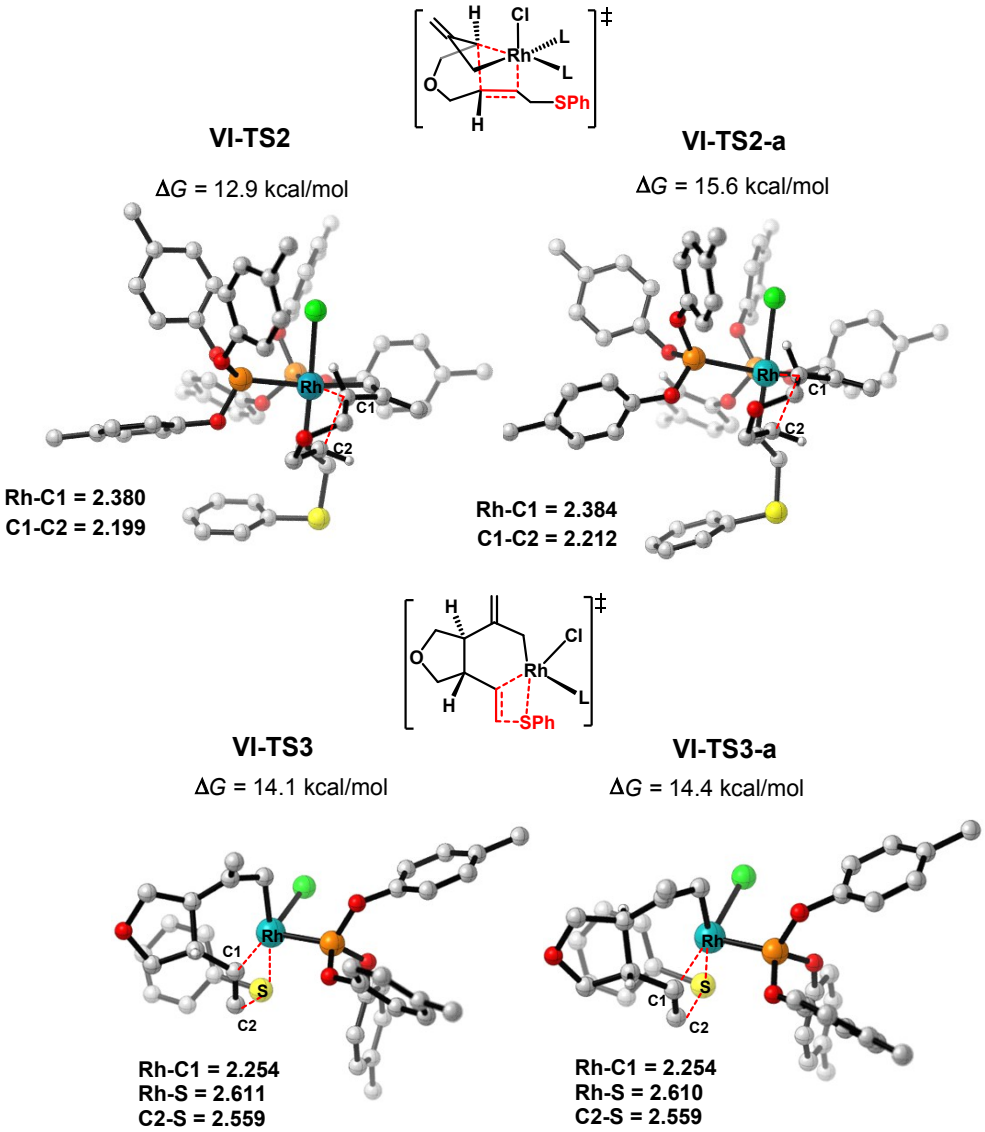


Fig. S8. RDG analysis of **IV-TS1** and **VII-TS1**. The RDG isosurface map were performed with Multiwfn 3.6[1] and VMD 1.9[2] software packages.

The analysis of RDG isosurface for **VII-TS1** demonstrates that there is a significant

steric repulsion (red surface).

Section 14. Conformers of VI-TS2 and VI-TS3



Scheme S8 Conformers of **VI-TS2** and **VI-TS3**. Interatomic distances are in angstroms, and energies are in kcal/mol.

Section 15. Table of energy values

Table S1 Energies (in Hartree) for all TS and intermediates.

Geometry	E_0	E	$H_{373.15}$	$G_{373.15}$	$E_{(sol,M06)}$
1	-1055.637697	-1055.637697	-1055.610138	-1055.708430	-1055.201576
$[Rh(COD)Cl]_2$	-1763.555431	-1763.522618	-1763.521437	-1763.626762	-1765.245048
COD	-311.917101	-311.905650	-311.904468	-311.959144	-311.7268187
L	-1379.872794	-1379.836080	-1379.834898	-1379.957007	-1379.224797
I-1	-4385.208837	-4385.101018	-4385.099836	-4385.387181	-4384.544593
I-TS1	-4385.203859	-4385.095139	-4385.093957	-4385.394547	-4384.513911
I-2	-4385.237653	-4385.130368	-4385.129186	-4385.420817	-4384.53044
I-3	-4385.208545	-4385.100369	-4385.099187	-4385.387831	-4384.536859
I-TS2	-4385.164151	-4385.099218	-4385.098273	-4385.274456	-4384.525732
I-4	-4385.240558	-4385.133424	-4385.132242	-4385.425179	-4384.571787
I-5	-3005.392960	-3005.325518	-3005.324337	-3005.516000	-3005.358529
I-6	-3005.387134	-3005.319870	-3005.318688	-3005.507323	-3005.35876
I-TS3	-3005.359454	-3005.292158	-3005.290977	-3005.479310	-3005.331403
I-7	-3005.370129	-3005.301851	-3005.300669	-3005.495054	-3005.343453
I-8	-3005.376031	-3005.307419	-3005.306237	-3005.501284	-3005.348662
I-TS4	-3005.344133	-3005.276548	-3005.275367	-3005.466649	-3005.318682
I-9	-3005.380974	-3005.313395	-3005.312213	-3005.504673	-3005.357809
RhL_2Cl	-3329.569412	-3329.488139	-3329.486958	-3329.721843	-3329.315269
II-TS1	-4385.197472	-4385.089396	-4385.088214	-4385.379584	-4384.512032
II-2	-4385.232976	-4385.125010	-4385.123828	-4385.413517	-4384.529874
III-TS3	-3005.351298	-3005.284060	-3005.282878	-3005.474328	-3005.320943
III-7	-3005.354414	-3005.286652	-3005.285470	-3005.478596	-3005.321915
III-8	-3005.372449	-3005.305068	-3005.303886	-3005.496759	-3005.32848
III-TS4	-3005.357561	-3005.289300	-3005.288118	-3005.484474	-3005.326561
III-9	-3005.368315	-3005.301620	-3005.300438	-3005.491612	-3005.331592
IV-TS1	-4385.185964	-4385.079342	-4385.078160	-4385.365069	-4384.517044
IV-1	-4385.215936	-4385.109499	-4385.108317	-4385.391952	-4384.542865
IV-2	-3005.365414	-3005.298013	-3005.296832	-3005.489137	-3005.329512
IV-3	-3005.359457	-3005.292067	-3005.290886	-3005.481943	-3005.329457
IV-TS2	-3005.338607	-3005.272617	-3005.271435	-3005.457177	-3005.306054
IV-4	-3005.358229	-3005.290254	-3005.289073	-3005.481238	-3005.335047
IV-TS3	-3005.320000	-3005.251563	-3005.250381	-3005.444463	-3005.294757
IV-5	-3005.394455	-3005.326482	-3005.325300	-3005.518438	-3005.364282
V-TS2	-3005.323076	-3005.256245	-3005.255063	-3005.444630	-3005.29372
V-3	-3005.331679	-3005.263827	-3005.262645	-3005.456456	-3005.297545

V-4	-3005.341172	-3005.273197	-3005.272015	-3005.466802	-3005.306159
V-TS3	-3005.289799	-3005.221594	-3005.220412	-3005.415662	-3005.256980
V-5	-3005.363623	-3005.295552	-3005.294370	-3005.488689	-3005.316655
V-6	-3005.350559	-3005.282634	-3005.281453	-3005.473798	-3005.306204
V-TS4	-3005.346656	-3005.278893	-3005.277712	-3005.472137	-3005.314024
V-7	-3005.397984	-3005.330182	-3005.329001	-3005.522645	-3005.362646
VI-3	-4385.210753	-4385.102529	-4385.101347	-4385.394910	-4384.549037
VI-TS2	-4385.405105	-4385.301816	-4385.300635	-4385.569931	-4384.526443
VI-4	-4385.244248	-4385.137465	-4385.136283	-4385.421811	-4384.564518
VI-5	-3005.384402	-3005.317956	-3005.316775	-3005.505948	-3005.346915
VI-6	-3005.363953	-3005.296651	-3005.295469	-3005.484430	-3005.324459
VI-TS3	-3005.338826	-3005.271390	-3005.270209	-3005.459681	-3005.299640
VI-7	-3005.345888	-3005.277977	-3005.276796	-3005.465629	-3005.308690
VI-8	-3005.371465	-3005.301979	-3005.300798	-3005.499180	-3005.340637
VI-TS4	-3005.355339	-3005.286937	-3005.285756	-3005.479147	-3005.320825
VI-9	-3005.397296	-3005.328379	-3005.327198	-3005.525978	-3005.370654
VII-1	-4385.201377	-4385.093295	-4385.092114	-4385.383589	-4384.540304
VII-TS1	-4385.170731	-4385.063898	-4385.062716	-4385.348040	-4384.503725
VII-2	-4385.219432	-4385.112856	-4385.111674	-4385.396121	-4384.550129
VII-3	-3005.353683	-3005.286030	-3005.284848	-3005.477451	-3005.315719
VII-4	-3005.352419	-3005.285122	-3005.283941	-3005.472768	-3005.321136
VII-TS2	-3005.332644	-3005.266540	-3005.265358	-3005.451403	-3005.29991
VII-5	-3005.351924	-3005.283760	-3005.282578	-3005.477525	-3005.329493
VII-TS3	-3005.307062	-3005.238304	-3005.237122	-3005.433499	-3005.281349
VII-6	-3005.392686	-3005.324882	-3005.323700	-3005.515300	-3005.358297
2-RR	-4385.272666	-4385.165932	-4385.164751	-4385.468300	-4384.571183
2-RS	-4385.276819	-4385.168116	-4385.166935	-4385.476384	-4384.577450
3	-4385.283424	-4385.178250	-4385.177068	-4385.473422	-4384.574996
$Pd(PH_3)_2$	-813.083325	-813.073901	-813.072719	-813.125614	-814.2625607
$Ni(PPh_3)_2$	-2241.756617	-2241.704621	-2241.703439	-2241.858174	-3579.755105
^{Pd}I-TS1	-1868.690403	-1868.651373	-1868.650191	-1868.781074	-1869.417828
^{Pd}I-1	-1868.727270	-1868.688887	-1868.687706	-1868.815728	-1869.449238
^{Pd}II-TS1	-1868.686667	-1868.647977	-1868.646795	-1868.777339	-1869.418677
^{Pd}II-1	-1868.713886	-1868.675449	-1868.674267	-1868.803359	-1869.436206
^{Pd}IV-TS1	-1525.502058	-1525.470723	-1525.469541	-1525.577342	-1526.257767
^{Pd}IV-1	-1525.567909	-1525.536419	-1525.535237	-1525.642444	-1526.321066
^{Ni}I-TS1	-3297.375160	-3297.295839	-3297.294658	-3297.516292	-4634.937218
^{Ni}I-1	-3297.417771	-3297.336199	-3297.335018	-3297.559117	-4634.986029
^{Ni}II-TS1	-3297.370779	-3297.288964	-3297.287782	-3297.516119	-4634.953506
^{Ni}II-1	-3297.393569	-3297.311600	-3297.310418	-3297.536398	-4634.966359

^{Ni}IV-TS1	-2261.144484	-2261.092676	-2261.091494	-2261.245574	-3599.215314
^{Ni}IV-1	-2261.188759	-2261.135598	-2261.134416	-2261.292651	-3599.258899
I-TS1-1	-4385.212305	-4385.107098	-4385.105917	-4385.394298	-4384.513024
I-TS1-2	-3005.311028	-3005.242330	-3005.241148	-3005.436015	-3005.283262
I-TS1-3	-3005.314367	-3005.245900	-3005.244718	-3005.438312	-3005.280495
I-TS1-4	-3005.309103	-3005.239834	-3005.238653	-3005.443508	-3005.261670
II-TS1-1	-4385.193109	-4385.084650	-4385.083468	-4385.377312	-4384.509454
II-TS1-2	-3005.308020	-3005.240376	-3005.239194	-3005.431006	-3005.281079
II-TS1-3	-3005.304790	-3005.236320	-3005.235138	-3005.427984	-3005.283286
II-TS1-4	-3005.301508	-3005.232498	-3005.231316	-3005.431006	-3005.252479
I-TS2′	-4385.169555	-4385.062264	-4385.061082	-4385.349155	-4384.495018
I-4′	-4385.206766	-4385.100189	-4385.099007	-4385.383784	-4384.524773
I-TS4-1	-3005.338233	-3005.269674	-3005.268492	-3005.461480	-3005.304061
I-TS4-2	-3005.346673	-3005.279469	-3005.278287	-3005.466296	-3005.315028
I-TS4-3	-3005.340908	-3005.272596	-3005.271414	-3005.464472	-3005.30845
III-TS4-1	-3005.340738	-3005.273253	-3005.272071	-3005.462525	-3005.31596
III-TS4-2	-3005.348055	-3005.281263	-3005.280081	-3005.470362	-3005.318619
III-TS4-3	-3005.347765	-3005.280843	-3005.279662	-3005.470645	-3005.310093
I-5′	-3005.362547	-3005.294813	-3005.293632	-3005.486248	-3005.321001
I-TS3′	-3005.346931	-3005.280459	-3005.279277	-3005.466755	-3005.304061
I-6′	-3005.371530	-3005.303014	-3005.301832	-3005.494736	-3005.335583
I-TS4′	-3005.333168	-3005.265249	-3005.264067	-3005.455675	-3005.301197
IV-TS3-1	-3005.307171	-3005.238597	-3005.237415	-3005.429701	-3005.280358
V-TS3-1	-3005.271204	-3005.202844	-3005.201662	-3005.396890	-3005.242796
V-TS3-2	-3005.282543	-3005.213946	-3005.212764	-3005.410053	-3005.248044
V-TS3-3	-3005.282731	-3005.214281	-3005.213099	-3005.409137	-3005.249818
V-TS3-4	-3005.346730	-3005.278912	-3005.277731	-3005.473201	-3005.315013
V-TS3-5	-3005.282199	-3005.214009	-3005.212827	-3005.406548	-3005.247984
IV-5′	-3005.360410	-3005.293714	-3005.292532	-3005.480537	-3005.335367
IV-TS3′	-3005.317022	-3005.248706	-3005.247525	-3005.441811	-3005.292397
IV-6′	-3005.383785	-3005.315833	-3005.314652	-3005.503717	-3005.347070
IV-7′	-3005.381811	-3005.313730	-3005.312548	-3005.504053	-3005.345603
IV-TS4′	-3005.348235	-3005.280451	-3005.279270	-3005.471056	-3005.317846
IV-8′	-3005.394455	-3005.326482	-3005.325300	-3005.518438	-3005.364282
PdL_2	-2886.559246	-2886.480230	-2886.479048	-2886.709851	-2886.458314
^{Pd}I-TS1-a	-3942.168132	-3942.063136	-3942.061955	-3942.351825	-3941.619082
^{Pd}I-1-a	-3942.196165	-3942.089695	-3942.088514	-3942.381172	-3941.651422
^{Pd}II-TS1-a	-3942.158251	-3942.052568	-3942.051387	-3942.342979	-3941.620907
^{Pd}II-1-a	-3942.177444	-3942.070871	-3942.069690	-3942.362316	-3941.636163
^{Pd}IV-TS1-a	-2562.240667	-2562.175091	-2562.173910	-2562.367813	-2562.362649

^{Pd}IV-1-a	-2562.303968	-2562.238375	-2562.237193	-2562.428897	-2562.419538
NiL_2	-2929.079129	-2929.003615	-2929.002434	-2929.223318	-4266.770904
^{Ni}I-TS1-a	-3984.708505	-3984.602920	-3984.601739	-3984.892530	-5321.965328
^{Ni}I-1-a	-3984.739320	-3984.633330	-3984.632148	-3984.921788	-5321.998687
^{Ni}II-TS1-a	-3984.703091	-3984.597925	-3984.596743	-3984.886469	-5321.969193
^{Ni}II-1-a	-3984.719060	-3984.612736	-3984.611555	-3984.903226	-5321.982535
^{Ni}IV-TS1-a	-2604.796749	-2604.732646	-2604.731464	-2604.919906	-3942.713467
^{Ni}IV-1-a	-2604.840817	-2604.775323	-2604.774141	-2604.965678	-3942.755556
$Pd(PH_3)_2$-D3	-813.087952	-813.077521	-813.076339	-813.132189	-814.2631772
PH_3-D3	-343.141734	-343.137979	-343.136798	-343.169163	-343.1344263
$Ni(PPh_3)_2$-D3	-2241.841240	-2241.787252	-2241.786071	-2241.947717	-3579.762161
PPh_3-D3	-1036.223112	-1036.198774	-1036.197593	-1036.285742	-1035.718672
1-D3	-1055.645532	-1055.619751	-1055.618569	-1055.709415	-1055.199924
$[Rh(COD)Cl]_2$ -D3	-1763.613321	-1763.580613	-1763.579431	-1763.684594	-1765.24547
COD-D3	-311.932603	-311.921204	-311.920022	-311.974563	-311.7266213
L-D3	-1379.892062	-1379.855771	-1379.854589	-1379.973325	-1379.223275
I-1-D3	-4385.415080	-4385.308933	-4385.307751	-4385.582280	-4384.553395
IV-TS1-D3	-4385.392624	-4385.287821	-4385.286639	-4385.558026	-4384.524693
IV-1-D3	-4385.421350	-4385.316833	-4385.315651	-4385.586093	-4384.549471
IV-2-D3	-3005.488803	-3005.422304	-3005.421123	-3005.610668	-3005.337035
^{Pd}I-TS1-D3	-1868.730089	-1868.691198	-1868.690017	-1868.821768	-1869.419521
^{Pd}II-TS1-D3	-1868.735041	-1868.696941	-1868.695759	-1868.819548	-1869.4248
^{Pd}IV-TS1-D3	-1525.549261	-1525.518484	-1525.517302	-1525.620960	-1526.254456
^{Pd}V-TS1-D3	-1868.683800	-1868.647655	-1868.646473	-1868.762114	-1869.365094
^{Ni}I-TS1-D3	-3297.519500	-3297.438076	-3297.436894	-3297.661528	-4634.946119
^{Ni}II-TS1-D3	-3297.474268	-3297.393878	-3297.392696	-3297.607556	-4634.952307
^{Ni}IV-TS1-D3	-2261.242954	-2261.190665	-2261.189483	-2261.342631	-3599.214332
^{Ni}V-TS1-D3	-3297.477940	-3297.398221	-3297.397039	-3297.607198	-4634.89168
VI-TS2-a	-4385.197831	-4385.091838	-4385.090657	-4385.373305	-4384.522047
VI-TS3-a	-3005.338795	-3005.271395	-3005.270213	-3005.459230	-3005.299228

E_0 = Sum of electronic and zero-point Energies by B3LYP in solvent

E = Sum of electronic and thermal Energies by B3LYP in solvent

$H_{373.15}$ = Sum of electronic and thermal Enthalpies by B3LYP in solvent

$G_{373.15}$ = Sum of electronic and thermal Free Energies by B3LYP in solvent

$E_{(sol, M06)}$ = Single point energies calculated by M06 in solvent

Section 16. Calculated imaginary frequencies of all transition states species

Table S2. Calculated imaginary frequencies of all transition states species for substrate

Species	Frequency
I-TS1	-90.17
I-TS2	-231.90
I-TS3	-215.39
I-TS4	-259.97
II-TS1	-316.28
III-TS3	-552.77
III-TS4	-832.92
IV-TS1	-240.15
IV-TS2	-236.71
IV-TS3	-478.71
V-TS2	-518.30
V-TS3	-538.78
V-TS4	-730.61
VI-TS2	-256.62
VI-TS3	-192.47
VI-TS4	-185.77
VII-TS1	-290.13
VII-TS2	-225.8
VII-TS3	-499.08
^{Pd}I-TS1	-320.47
^{Pd}II-TS1	-311.34
^{Pd}IV-TS1	-293.22
^{Ni}I-TS1	-313.52
^{Ni}II-TS1	-142.67
^{Ni}IV-TS1	-270.81
I-TS1-1	-250.15
I-TS1-2	-276.67
I-TS1-3	-35.38
I-TS1-4	-107.11
II-TS1-1	-175.67
II-TS1-2	-195.63
II-TS1-3	-318.52
II-TS1-4	-215.40

I-TS2′	-405.37
I-TS4-1	-246.83
I-TS4-2	-260.61
I-TS4-3	-186.83
III-TS4-1	-735.57
III-TS4-2	-822.38
III-TS4-3	-1025.26
I-TS3′	-247.47
I-TS4′	-252.55
IV-TS3-1	-488.99
V-TS3-1	-567.80
V-TS3-2	-469.38
V-TS3-3	-469.14
V-TS3-4	-444.07
V-TS3-5	-541.48
IV-TS3′	-513.94
IV-TS4′	-230.47
^{Pd}I-TS1-a	-307.86
^{Pd}II-TS1-a	-316.79
^{Pd}IV-TS1-a	-267.79
^{Ni}I-TS1-a	-315.91
^{Ni}II-TS1-a	-278.50
^{Ni}IV-TS1-a	-294.45
IV-TS1-D3	-236.61
^{Pd}I-TS1-D3	-319.35
^{Pd}II-TS1-D3	-293.84
^{Pd}IV-TS1-D3	-287.81
^{Pd}V-TS1-D3	-634.78
^{Ni}I-TS1-D3	-312.08
^{Ni}II-TS1-D3	-40.63
^{Ni}IV-TS1-D3	-265.84
^{Ni}V-TS1-D3	-509.03
VI-TS2-a	-241.46
VI-TS3-a	-192.35

Section 17. References

1 T. Lu and F. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer, *J. Comput. Chem*., 2012, **33**, 580.

2 E. R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcíá, A. J. Cohen and W. Yang, Revealing Noncovalent Interactions, *J. Am. Chem. Soc.,* 2010, **132**, 6498.