

Supporting Information

Mechanistic Insights into Ni–Al Co-Catalyzed Alkyne Carbophosphination

Enabled by C–P Bond Activation

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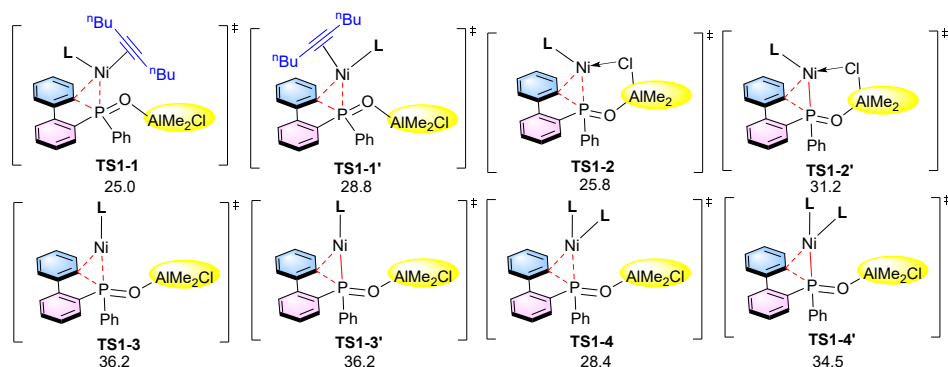
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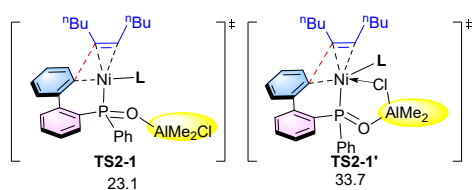
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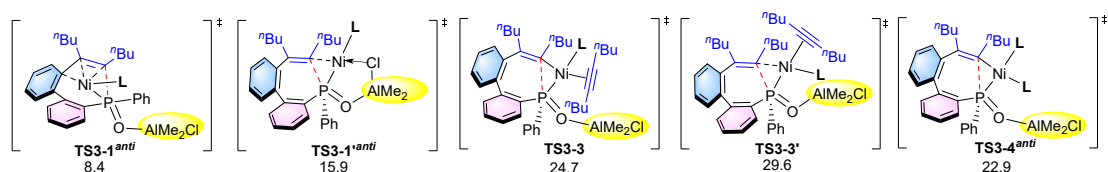
Section 1. Other Possible Isomers



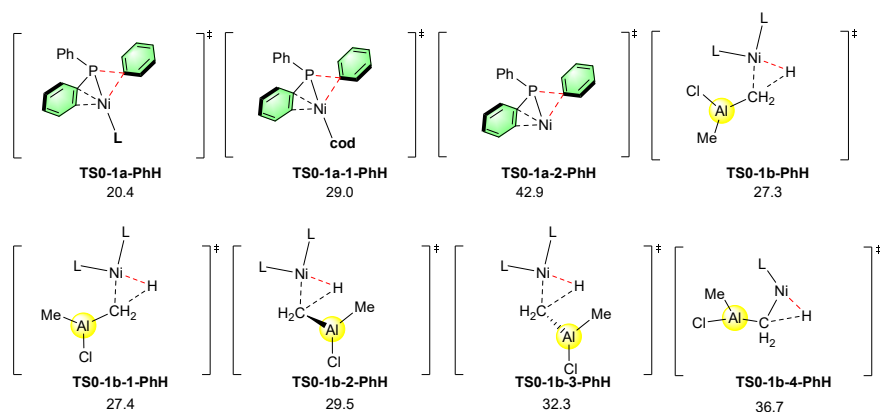
Scheme S1 Relative free energies (in kcal/mol) of other possible isomers of TS1-1.



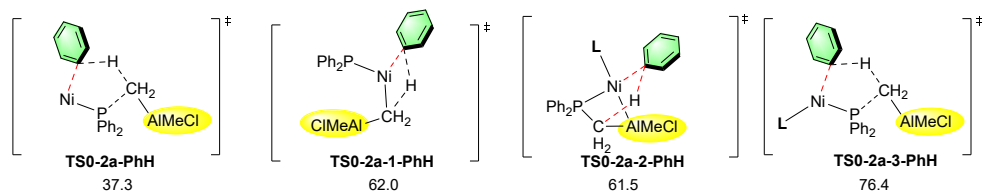
Scheme S2 Relative free energies (in kcal/mol) of other possible isomers of TS2-1.



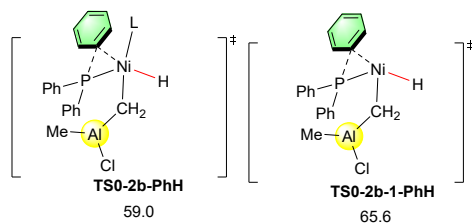
Scheme S3 Relative free energies (in kcal/mol) of other possible isomers of TS3-1^{anti} and TS3-3^{anti}.



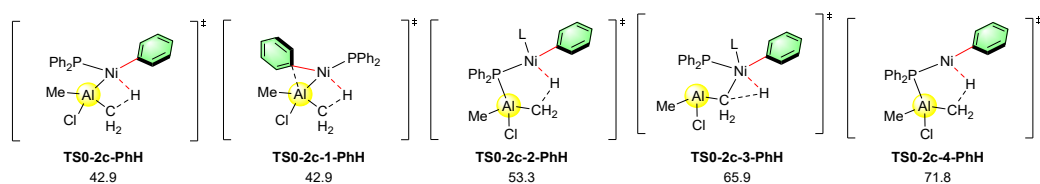
Scheme S4 Relative free energies (in kcal/mol) of other possible isomers of TS0-1a-PhH and TS0-1b-PhH.



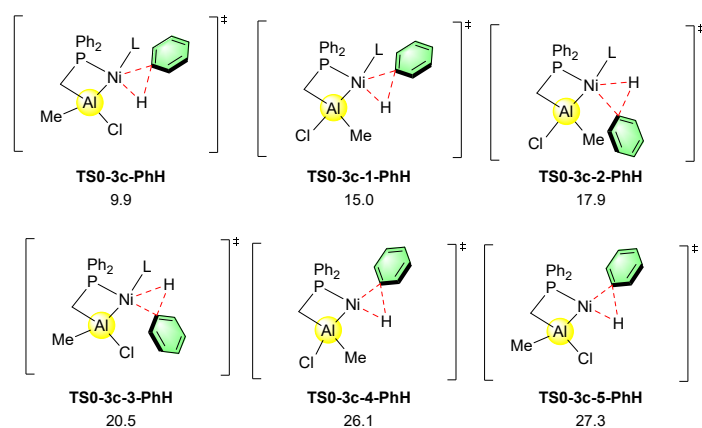
Scheme S5 Relative free energies (in kcal/mol) of other possible isomers of **TS0-2a-PhH**.



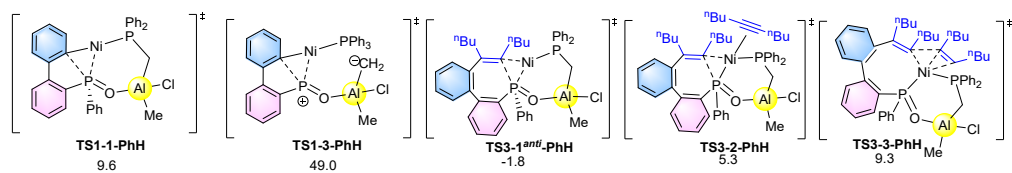
Scheme S6 Relative free energies (in kcal/mol) of other possible isomers of **TS0-2b-PhH**.



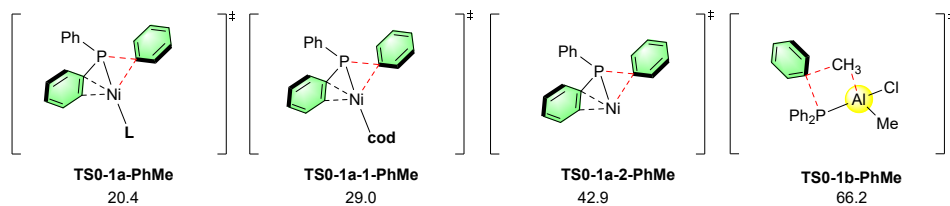
Scheme S7 Relative free energies (in kcal/mol) of other possible isomers of **TS0-2c-PhH**.



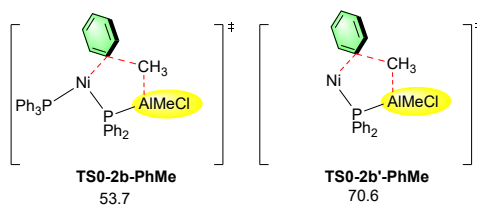
Scheme S8 Relative free energies (in kcal/mol) of other possible isomers of **TS0-3c-PhH**.



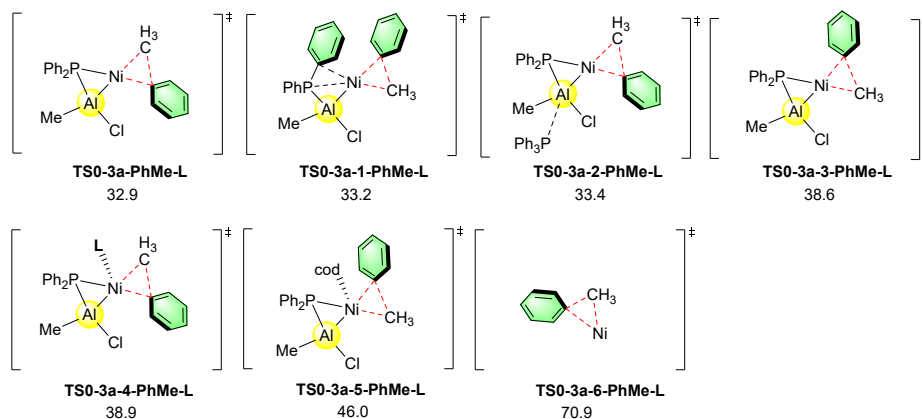
Scheme S9 Relative free energies (in kcal/mol) of other possible isomers of **TS1-1-PhH** and **TS3-1-PhH^{anti}**.



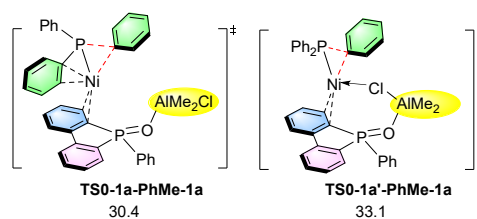
Scheme S10 Relative free energies (in kcal/mol) of other possible isomers of **TS0-1a-PhMe-L**.



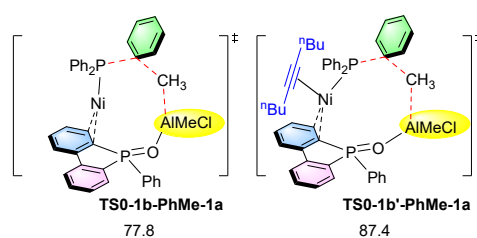
Scheme S11 Relative free energies (in kcal/mol) of other possible isomers of **TS0-2b-PhMe-L**.



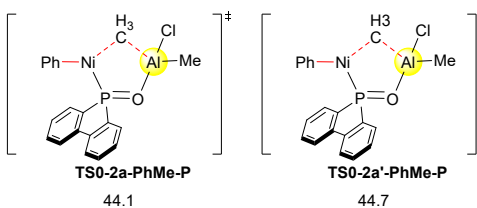
Scheme S12 Relative free energies (in kcal/mol) of other possible isomers of **TS0-3a-PhMe-L**.



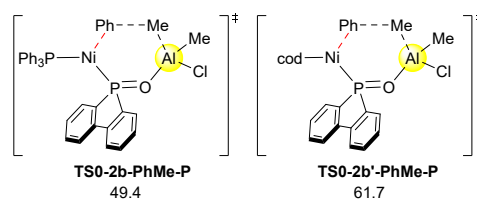
Scheme S13 Relative free energies (in kcal/mol) of other possible isomers of **TS0-1a-PhMe-1a**.



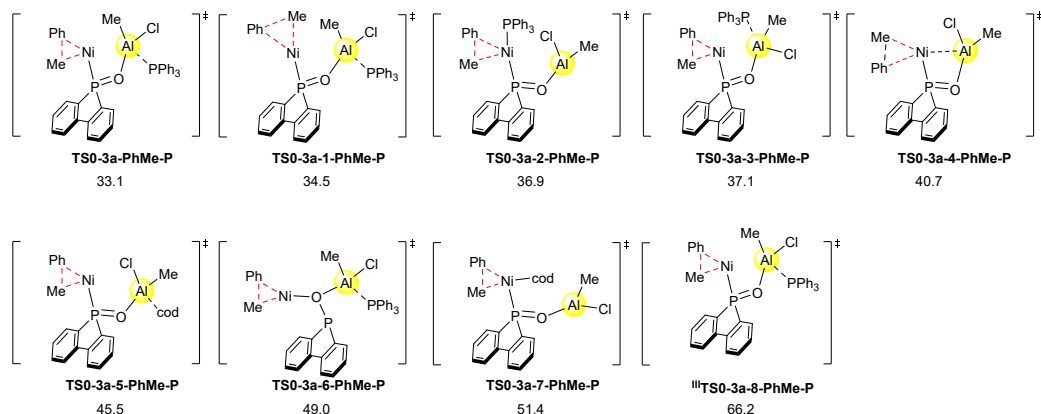
Scheme S14 Relative free energies (in kcal/mol) of other possible isomers of **TS0-1b-PhMe-1a**.



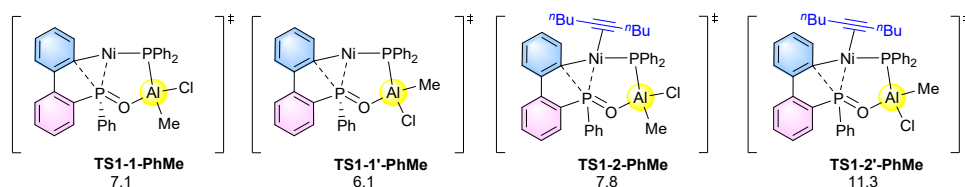
Scheme S15 Relative free energies (in kcal/mol) of other possible isomers of **TS0-2a-PhMe**.



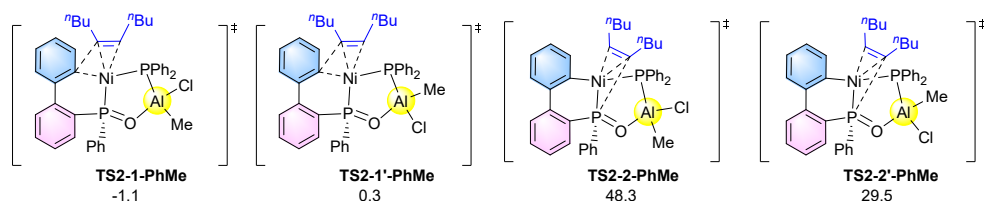
Scheme S16 Relative free energies (in kcal/mol) of other possible isomers of **TS0-2b-PhMe**.



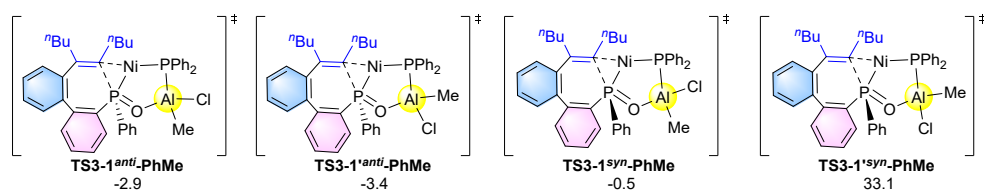
Scheme S17 Relative free energies (in kcal/mol) of other possible isomers of **TS0-3a-PhMe**.



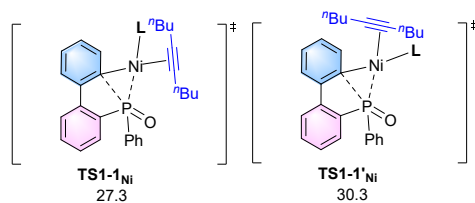
Scheme S18 Relative free energies (in kcal/mol) of other possible isomers of **TS1-1-PhMe**.



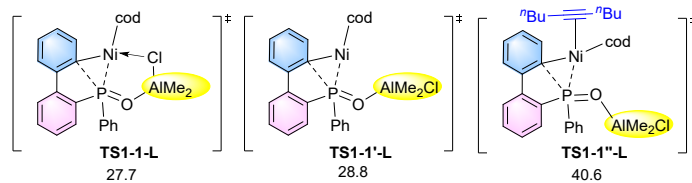
Scheme S19 Relative free energies (in kcal/mol) of other possible isomers of **TS2-1-PhMe**.



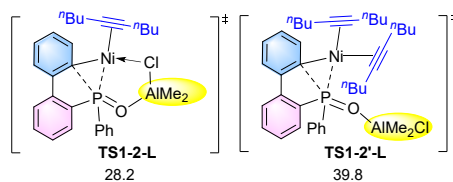
Scheme S20 Relative free energies (in kcal/mol) of other possible isomers of **TS3-1^{anti}-PhMe**.



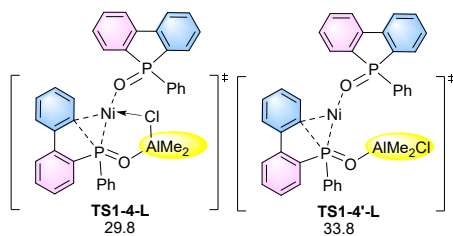
Scheme S21 Relative free energies (in kcal/mol) of other possible isomers of **TS1-1_{Ni}**.



Scheme S22 Relative free energies (in kcal/mol) of other possible isomers of **TS1-1-L**.



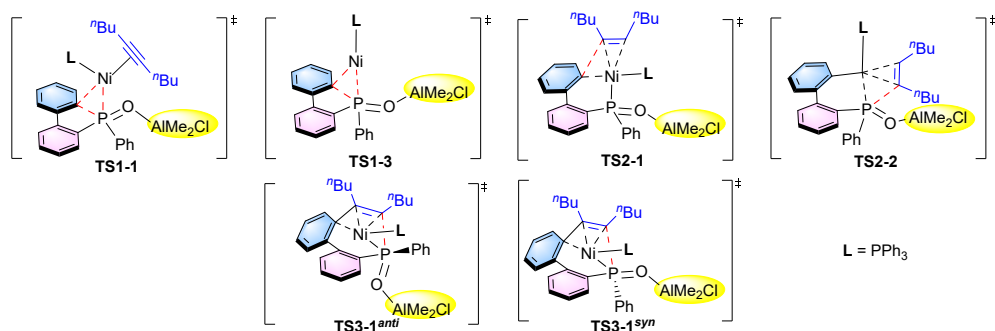
Scheme S23 Relative free energies (in kcal/mol) of other possible isomers of **TS1-2-L**.



Scheme S24 Relative free energies (in kcal/mol) of other possible isomers of **TS1-4-L**.

Section 2. Optimization with M06, M06L and WB97XD Methods

Table S1. Relative free energies (in kcal/mol) for the important transition states with M06, M06L, and WB97XD methods.



Species	$\Delta\Delta G$ (B3LYP)	$\Delta\Delta G$ (M06)	$\Delta\Delta G$ (M06L)	$\Delta\Delta G$ (WB97XD)	$\Delta\Delta G$ (B3LYP/BS1 ^a)
TS1-1	0.0	0.0	0.0	0.0	0.0
TS1-3	11.2	6.0	4.0	9.5	6.0
TS2-1	0.0	0.0	0.0	0.0	0.0
TS2-2	27.2	25.4	30.3	26.5	28.6
TS3-1 ^{anti}	0.0	0.0	0.0	0.0	0.0
TS3-1 ^{syn}	10.8	10.6	12.6	10.8	7.3

^aBS1 = 6-31G**/LANL2DZ

Section 3. Alternative Pathways and Mechanistic Analysis for Model

A

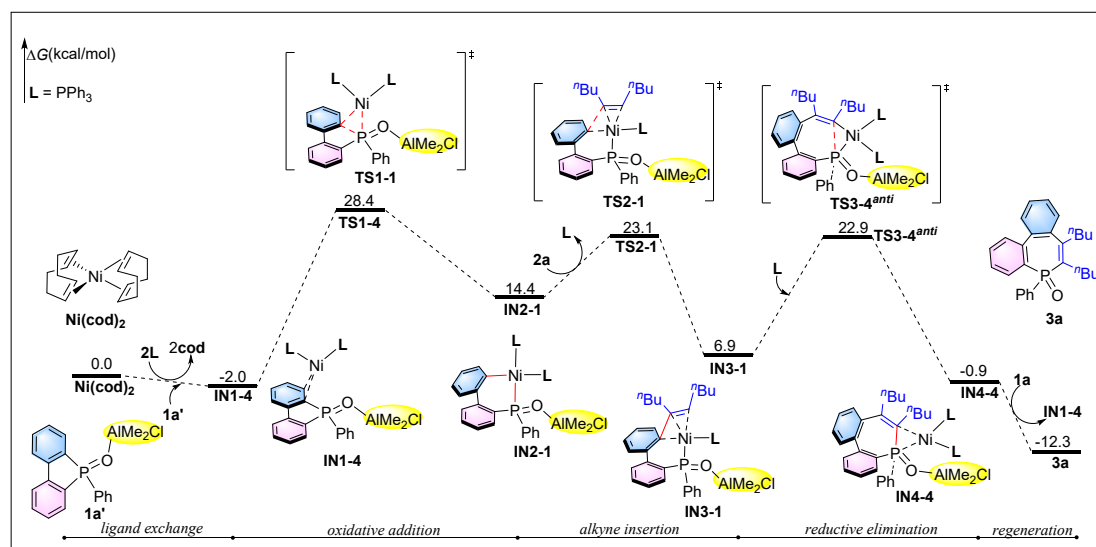


Fig. S1 Calculated energy profile for Model A with two coordinated phosphine ligands.

Relative free energies are given in kcal/mol.

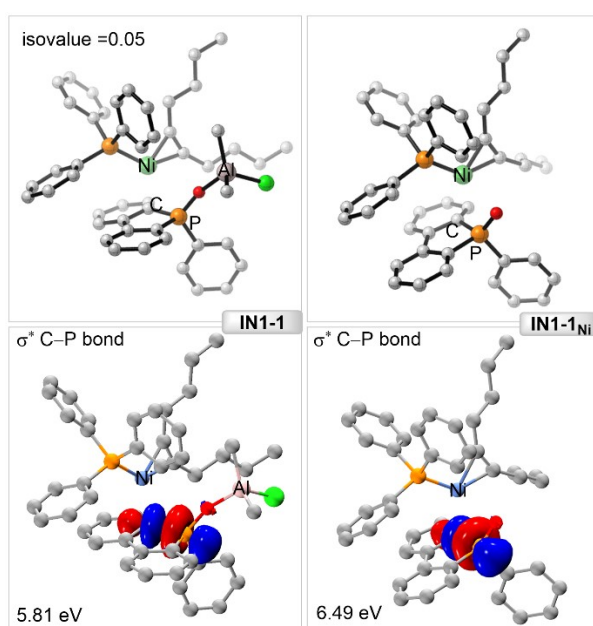


Fig. S2 Optimized structures and key NBO orbital energy values for **IN1-1** and **IN1-1_{Ni}**.

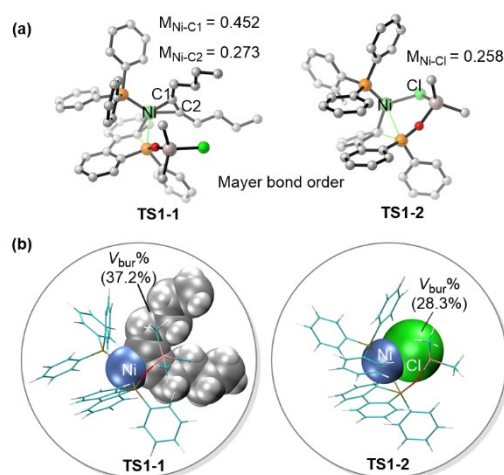


Fig. S3 (a) Mayer bond order and (b) percent buried volumes for **2a** and the Cl atom in TS1-1 and TS1-2.

Section 4. Coordination and transformation pathway of substrate **1a** with **AlMe₂Cl**

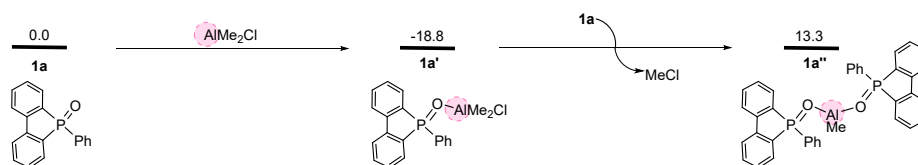


Fig. S4 Coordination and transformation pathway of substrate **1a** with **AlMe₂Cl**. Values shown are relative free energies in kcal/mol.

Section 5. Alternative Pathways for Model B

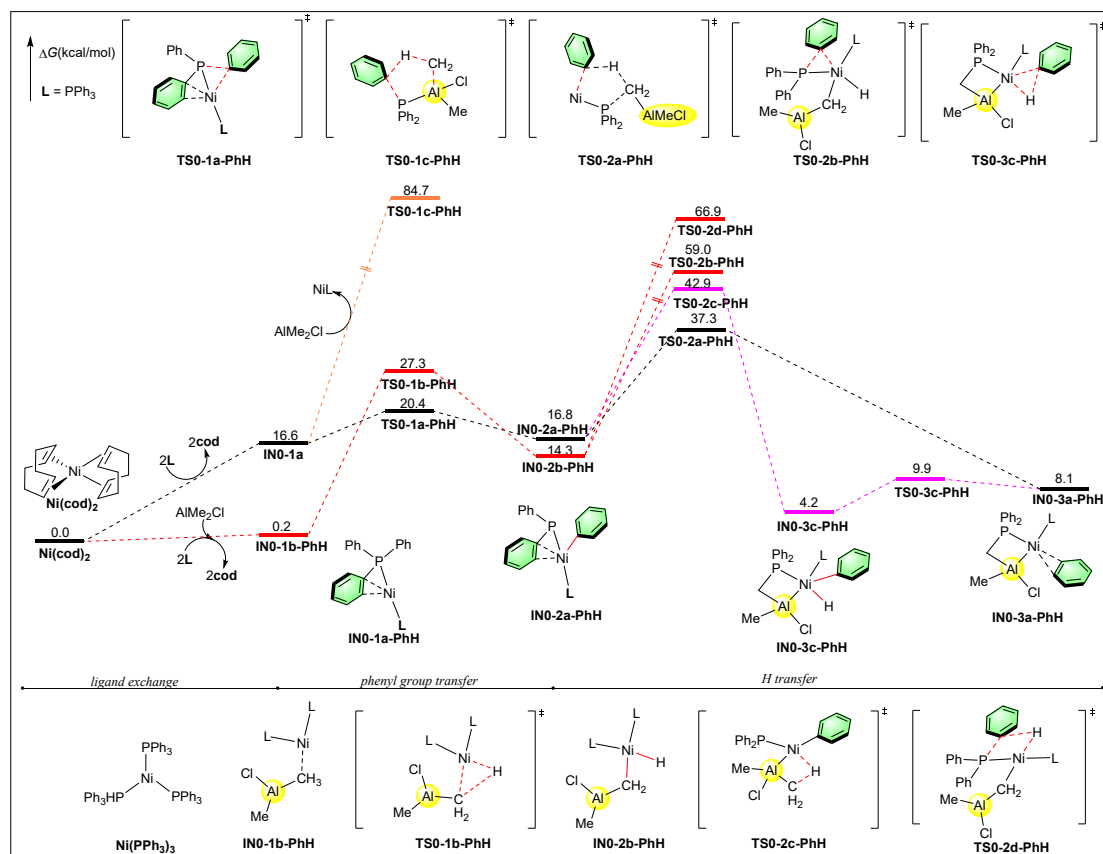


Fig. S5 Calculated energy profiles for the formation of **IN0-3a-PhH** involving benzene dissociation in Model B. Relative Free energies are given in kcal/mol.

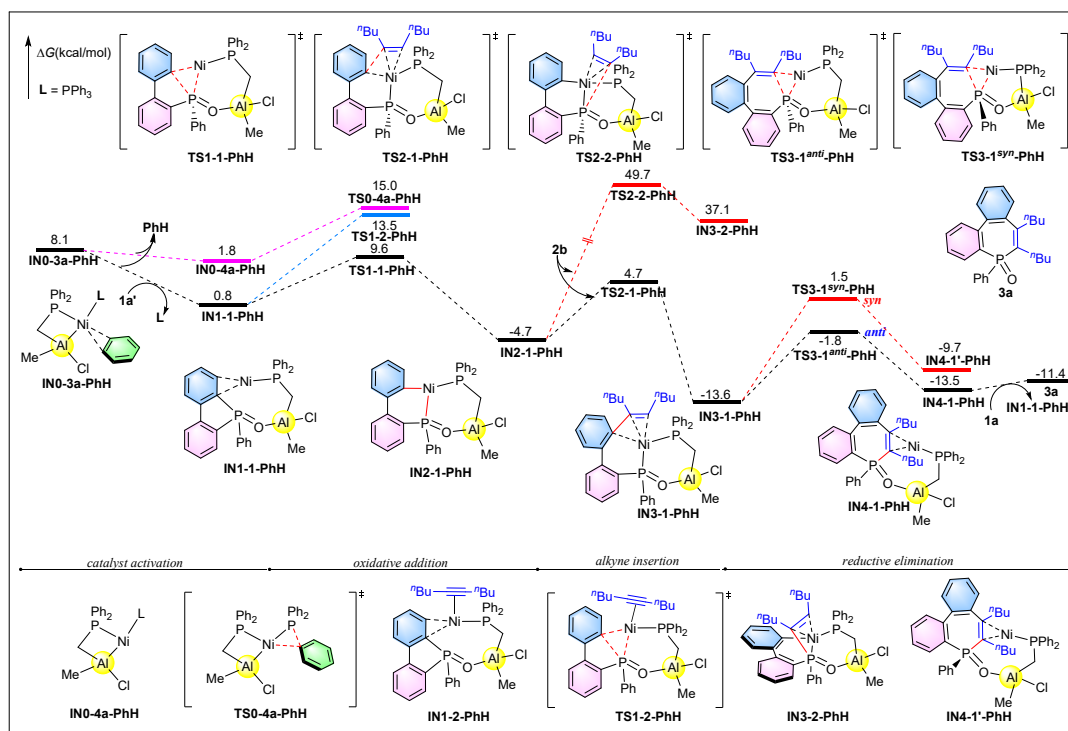


Fig. S6 Calculated energy profiles for the transformation from **IN0-3a-PhH** to **3a** involving benzene dissociation in Model B. Relative Free energies are given in kcal/mol.

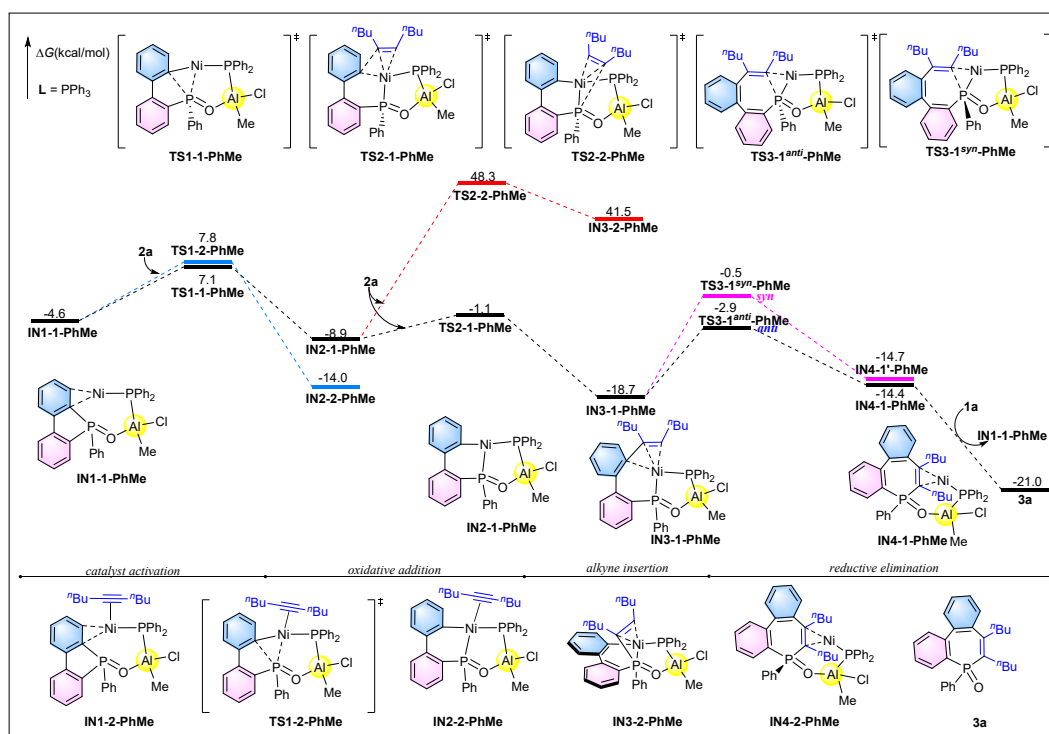


Fig. S7 Calculated energy profiles for the transformation from **IN1-1-PhMe** to **3a** in

Model B. Relative Free energies are given in kcal/mol.

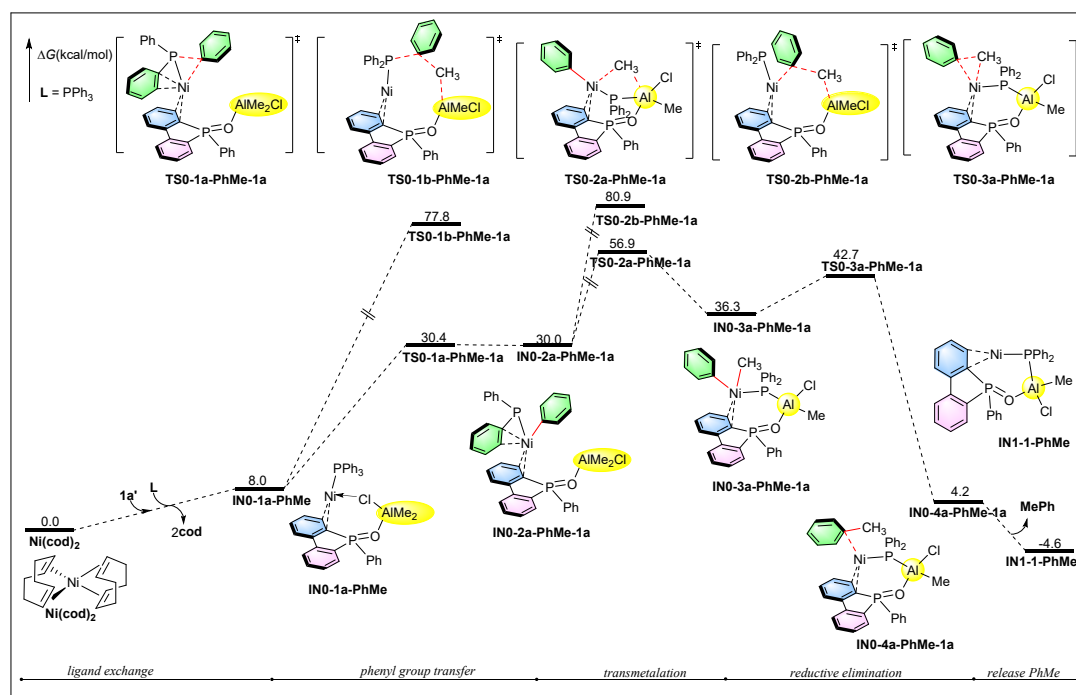


Fig. S8 Calculated energy profiles for the formation of **IN1-1-PhMe** via alternative pathways assisted by **1a** in Model B. Relative Free energies are given in kcal/mol.

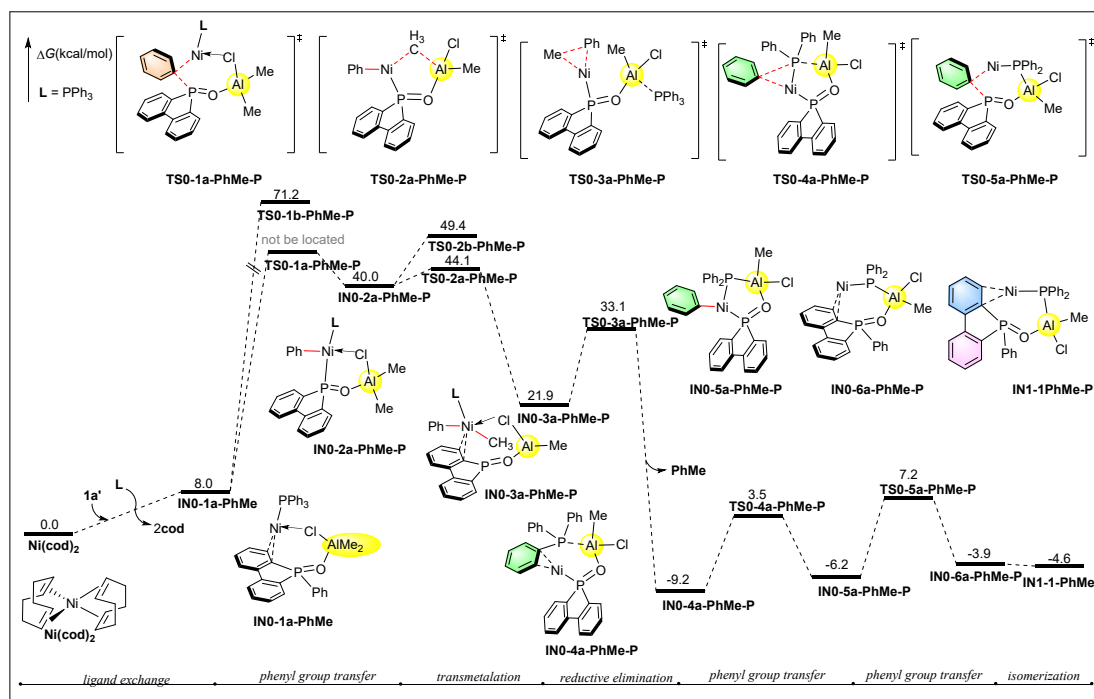


Fig. S9 Calculated energy profiles for the formation of **IN1-1-PhMe** via alternative pathways involving phenyl migration from **1a** in Model B. Relative free energies are

given in kcal/mol.

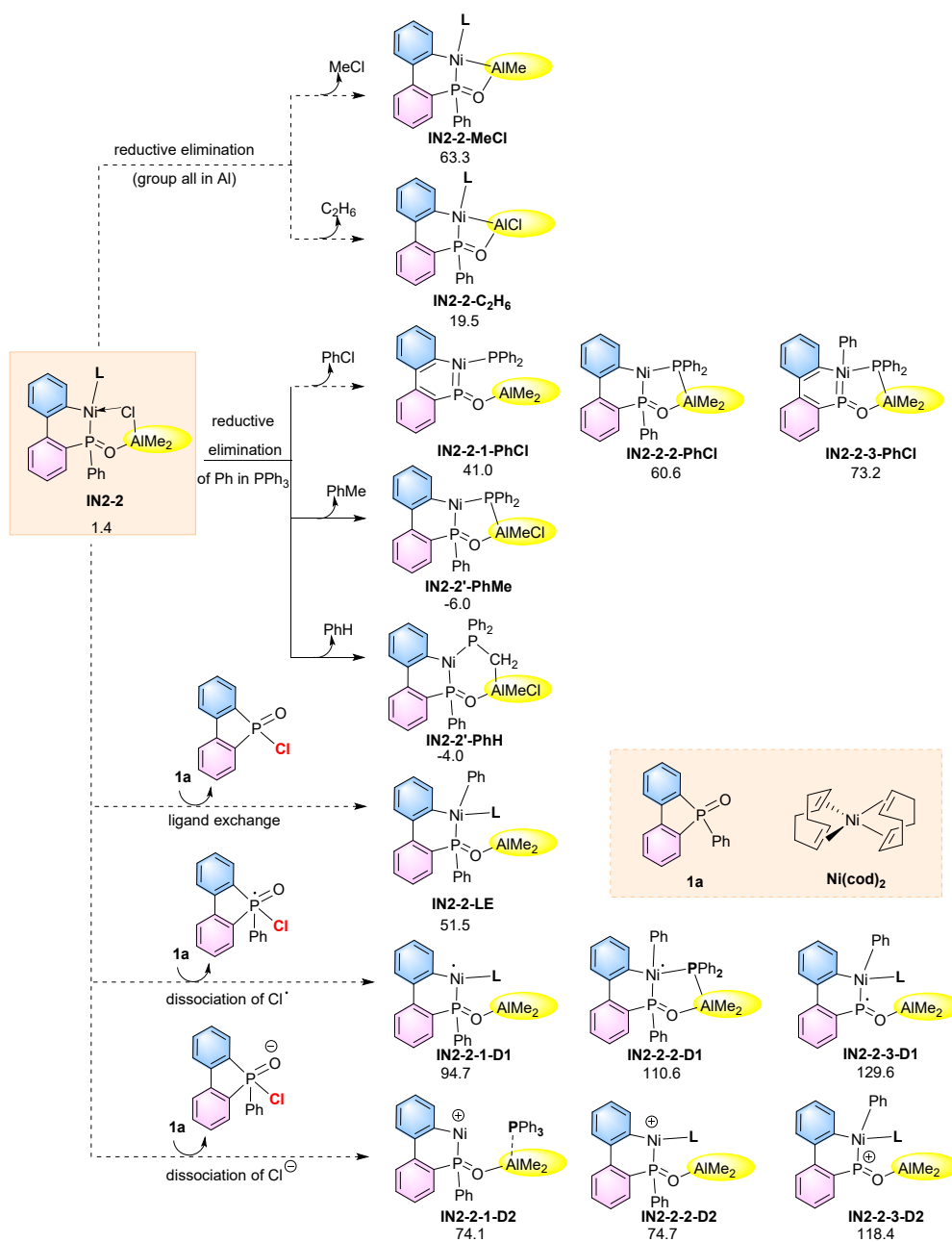


Fig. S10 Calculated energy profiles of higher-energy alternative pathways in Model B.

Relative free energies are given in kcal/mol.

Section 6. Alternative Pathways Without AlMe₂Cl Participation

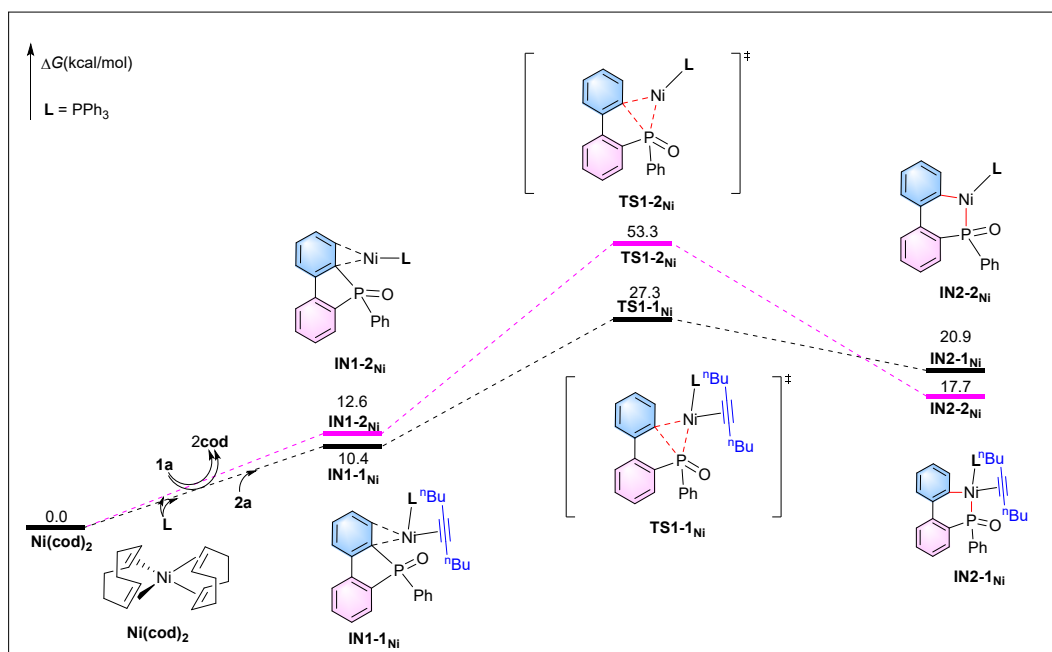


Fig. S11 Calculated energy profiles of higher-energy alternative pathways without AlMe₂Cl participation. Relative free energies are given in kcal/mol.

Section 7. Alternative Pathways in the Absence of Nickel Catalyst

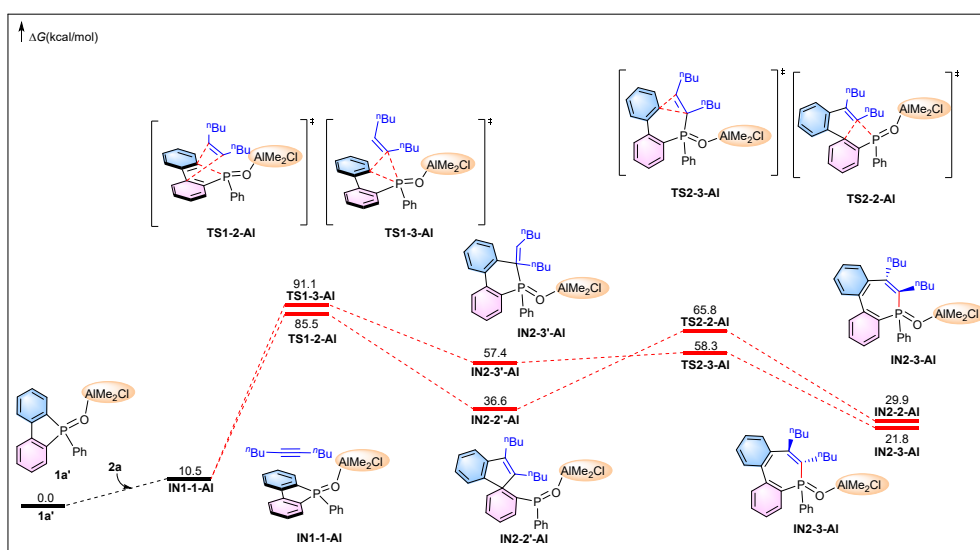


Fig. S12 Calculated energy profiles of higher-energy alternative pathways in the

absence of Ni catalyst. Relative free energies are given in kcal/mol.

Section 8. Alternative Pathways in the Absence of the PPh₃ Ligand

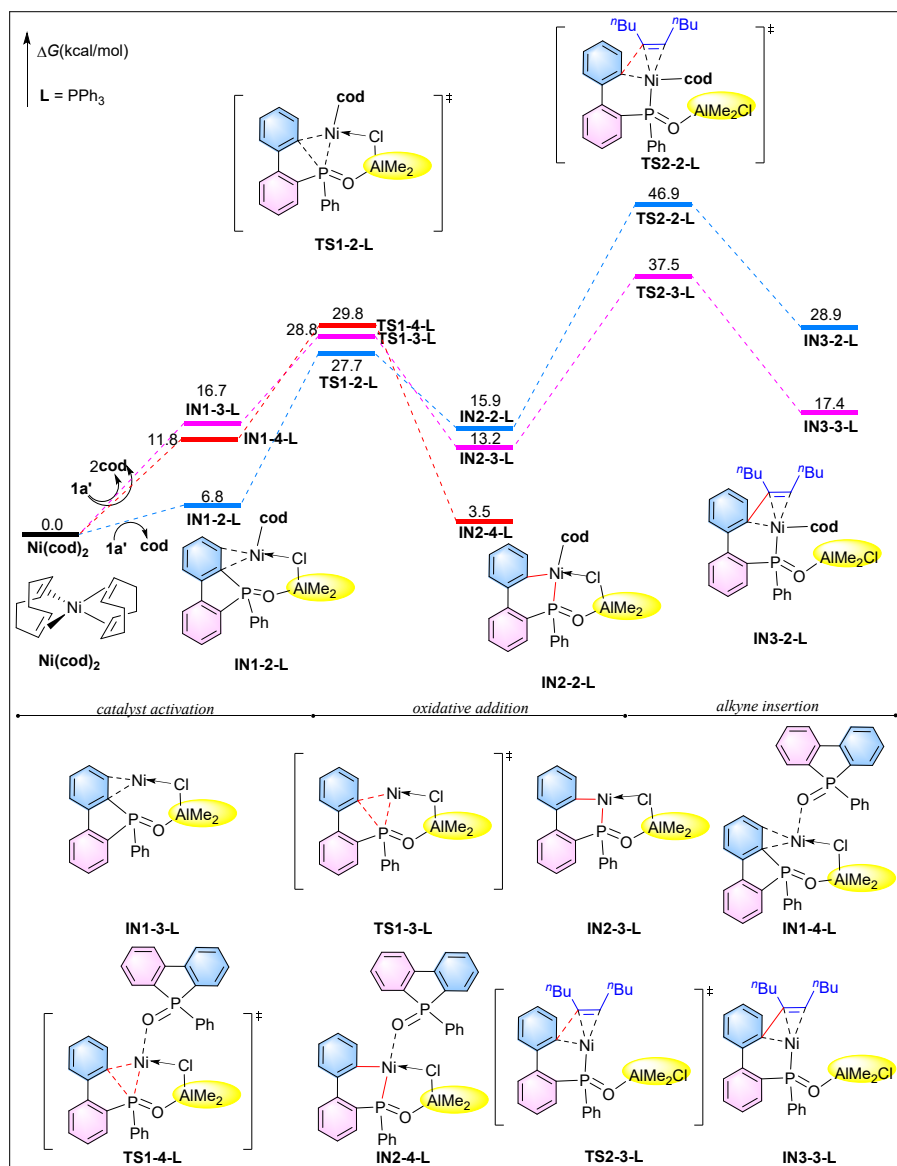


Fig. S13 Calculated energy profiles of higher-energy alternative pathways in the absence of the PPh₃ ligand. Relative free energies are given in kcal/mol.

Section 9. Energies (in Hartree) of all TSs and Intermediates

Geometry	E_0	E	$H_{298.15}$	$G_{298.15}$	$E_{(sol,M06)}$
Ni(cod)₂	-2131.536173	-2131.519893	-2131.518949	-2131.577514	-2132.156406
cod	-311.645243	-311.637838	-311.636893	-311.676681	-311.8977125
PPh₃	-1035.472751	-1035.456934	-1035.45599	-1035.519022	-1036.004315
1a	-1109.485011	-1109.469674	-1109.46873	-1109.528719	-1110.086175
1a'	-1891.786	-1891.762116	-1891.761172	-1891.840819	-1892.645516
1a''	-2921.544905	-2921.50885	-2921.507906	-2921.616325	-2922.900929
2a	-391.342588	-391.329466	-391.328522	-391.385081	-391.6914264
IN1-1	-4826.883495	-4826.827091	-4826.826147	-4826.977781	-4828.714927
TS1-1	-4826.860776	-4826.804768	-4826.803824	-4826.954218	-4828.691882
IN2-1	-4826.886542	-4826.829707	-4826.828763	-4826.982175	-4828.706647
IN1-2	-4435.495124	-4435.452885	-4435.451941	-4435.57146	-4436.994728
TS1-2	-4435.475637	-4435.433705	-4435.43276	-4435.551741	-4436.970825
IN2-2	-4435.522138	-4435.479615	-4435.478671	-4435.601023	-4437.008284
IN1-3	-4435.482914	-4435.440249	-4435.439305	-4435.561331	-4436.992117
TS1-3	-4435.445249	-4435.402622	-4435.401678	-4435.523972	-4436.950509
IN2-3	-4435.489427	-4435.446614	-4435.445669	-4435.569001	-4436.98533
IN1-4	-5471.035752	-5470.976399	-5470.975455	-5471.132729	-5473.048441
TS1-4	-5470.99624	-5470.937263	-5470.936319	-5471.091781	-5473.00117
TS2-1	-4826.874949	-4826.819105	-4826.818161	-4826.968085	-4828.695456
IN3-1	-4826.903522	-4826.847745	-4826.846801	-4826.995698	-4828.724045
TS2-2	-4826.827879	-4826.771994	-4826.771049	-4826.921307	-4828.651452
IN3-2	-4826.864433	-4826.808235	-4826.807291	-4826.959715	-4828.688886
TS3-1^{anti}	-4826.888635	-4826.833109	-4826.832165	-4826.982629	-4828.719019
IN4-1	-4826.911059	-4826.855316	-4826.854372	-4827.004733	-4828.744343
TS3-1^{syn}	-4826.871572	-4826.816696	-4826.815752	-4826.963819	-4828.704802
IN4-1'	-4826.892275	-4826.836802	-4826.835858	-4826.987304	-4828.727643
TS3-2	-5218.250104	-5218.180369	-5218.179425	-5218.360431	-5220.413225
IN4-2	-5218.291827	-5218.222022	-5218.221078	-5218.403691	-5220.457894
TS3-3	-5218.256202	-5218.187771	-5218.186827	-5218.361805	-5220.407885
IN4-3	-5218.273762	-5218.205728	-5218.204784	-5218.377937	-5220.421956
3a	-2283.192957	-2283.155935	-2283.154991	-2283.265	-2284.386784
TS1-1'	-4826.854913	-4826.798674	-4826.79773	-4826.949808	-4828.684361
TS1-2'	-4435.470372	-4435.428151	-4435.427206	-4435.547023	-4436.961699
TS1-3'	-4435.445249	-4435.402622	-4435.401678	-4435.523972	-4436.950509
TS1-4'	-5470.982675	-5470.923048	-5470.922104	-5471.080944	-5472.988002
TS2-1'	-4826.866874	-4826.81169	-4826.810746	-4826.957106	-4828.682768
TS3-1'^{anti}	-4826.884379	-4826.829467	-4826.828523	-4826.976145	-4828.711087
TS3-4^{anti}	-5862.396186	-5862.324816	-5862.323871	-5862.504896	-5864.737613

IN4-4	-5862.438178	-5862.366879	-5862.365934	-5862.546446	-5864.778239
TS3-3'	-5218.245349	-5218.176152	-5218.175208	-5218.353382	-5220.408563
IN0-1a	-3579.164445	-3579.129911	-3579.128966	-3579.232753	-3580.343704
TS0-1a-PhH	-3579.156611	-3579.122373	-3579.121428	-3579.225283	-3580.336492
IN0-2a-PhH	-3579.169421	-3579.134647	-3579.133702	-3579.239692	-3580.342176
IN0-1b-PhH	-4361.453336	-4361.410405	-4361.409461	-4361.533462	-4362.900452
TS0-1b-PhH	-4361.417788	-4361.375992	-4361.375048	-4361.494854	-4362.857831
IN0-2b-PhH	-4361.438746	-4361.396489	-4361.395544	-4361.517125	-4362.877956
TS0-1c-PhH	-1817.609144	-1817.585206	-1817.584262	-1817.665222	-1818.393611
TS0-2a-PhH	-3325.882929	-3325.857488	-3325.856544	-3325.940216	-3326.805324
IN0-3a-PhH	-4361.440919	-4361.398168	-4361.397224	-4361.520804	-4362.88724
TS0-2b-PhH	-4361.373066	-4361.331112	-4361.330168	-4361.45155	-4362.804986
TS0-2c-PhH	-3325.872419	-3325.846723	-3325.845779	-3325.932125	-3326.79434
IN0-3c-PhH	-4361.455486	-4361.413205	-4361.41226	-4361.53389	-4362.893843
TS0-3c-PhH	-4361.442386	-4361.400094	-4361.39915	-4361.521421	-4362.881757
TS0-2d-PhH	-4361.354416	-4361.311994	-4361.31105	-4361.433963	-4362.788597
IN0-4a-PhH	-4129.420152	-4129.383081	-4129.382137	-4129.495767	-4130.725201
PhH	-231.989321	-231.984955	-231.984011	-232.016779	-232.1484322
TS0-4a-PhH	-4129.406199	-4129.36948	-4129.368536	-4129.479578	-4130.705163
IN1-1-PhH	-4203.479064	-4203.442747	-4203.441803	-4203.55132	-4204.838378
TS1-1-PhH	-4203.466104	-4203.430373	-4203.429429	-4203.537591	-4204.824734
IN2-1-PhH	-4203.5069	-4203.470716	-4203.469772	-4203.577146	-4204.849935
TS1-2-PhH	-4594.852778	-4594.802553	-4594.801609	-4594.941	-4596.537605
TS2-1-PhH	-4594.889892	-4594.841118	-4594.840174	-4594.973439	-4596.559109
IN3-1-PhH	-4594.921459	-4594.872543	-4594.871599	-4595.004939	-4596.589895
TS2-2-PhH	-4594.810612	-4594.76114	-4594.760196	-4594.897183	-4596.482156
IN3-2-PhH	-4594.832741	-4594.783398	-4594.782454	-4594.917267	-4596.506801
TS3-1^{anti}-PhH	-4594.887291	-4594.838742	-4594.837798	-4594.972142	-4596.56899
IN4-1-PhH	-4594.901966	-4594.853157	-4594.852213	-4594.986841	-4596.589108
TS3-1^{syn}-PhH	-4594.876371	-4594.827865	-4594.826921	-4594.962096	-4596.563178
IN4-1'-PhH	-4594.897371	-4594.848947	-4594.848002	-4594.981025	-4596.584871
TS0-1a-1-PhH	-2855.311796	-2855.286155	-2855.285211	-2855.367528	-2856.21423
TS0-1a-2-PhH	-2543.602986	-2543.585955	-2543.585011	-2543.649301	-2544.269978
TS0-1b-1-PhH	-4361.415156	-4361.372804	-4361.37186	-4361.493546	-4362.854933
TS0-1b-2-PhH	-4361.411293	-4361.368868	-4361.367924	-4361.490463	-4362.850381
TS0-1b-3-PhH	-4361.403633	-4361.36061	-4361.359666	-4361.485902	-4362.841335
TS0-1b-4-PhH	-3325.880474	-3325.854567	-3325.853622	-3325.940721	-3326.803269
TS0-2a-1-PhH	-3325.850713	-3325.825395	-3325.824451	-3325.907912	-3326.767228
TS0-2a-2-PhH	-4361.359363	-4361.316979	-4361.316035	-4361.438107	-4362.799332
TS0-2a-3-PhH	-4361.328025	-4361.285383	-4361.284439	-4361.407537	-4362.772982
TS0-2b-1-PhH	-3325.844323	-3325.819042	-3325.818098	-3325.902528	-3326.75988
TS0-2c-1-PhH	-3325.84215	-3325.816654	-3325.815709	-3325.900497	-3326.76627
TS0-2c-2-PhH	-4361.383675	-4361.341111	-4361.340166	-4361.462717	-4362.811646

TS0-2c-3-PhH	-4361.363096	-4361.320674	-4361.31973	-4361.442989	-4362.790562
TS0-2c-4-PhH	-3325.839266	-3325.813245	-3325.812301	-3325.89903	-3326.74688
TS0-3c-1-PhH	-4361.433249	-4361.39169	-4361.390745	-4361.511286	-4362.87797
TS0-3c-2-PhH	-4361.432529	-4361.390616	-4361.389672	-4361.510946	-4362.870796
TS0-3c-3-PhH	-4361.426527	-4361.384658	-4361.383714	-4361.504442	-4362.867983
TS0-3c-4-PhH	-3325.888732	-3325.863492	-3325.862548	-3325.948956	-3326.821877
TS0-3c-5-PhH	-3325.891816	-3325.866271	-3325.865327	-3325.951835	-3326.819353
TS1-3-PhH	-4203.418153	-4203.382162	-4203.381218	-4203.488418	-4204.762481
TS3-2-PhH	-4986.263976	-4986.201577	-4986.200632	-4986.364273	-4988.279401
TS3-3-PhH	-4986.274361	-4986.212785	-4986.211841	-4986.371768	-4988.277768
TS0-1a-PhMe	-3579.156611	-3579.122373	-3579.121428	-3579.225283	-3580.336492
IN0-2a-PhMe	-3579.169421	-3579.134647	-3579.133702	-3579.239692	-3580.342176
TS0-1b-PhMe	-1817.613036	-1817.589354	-1817.58841	-1817.667797	-1818.414189
IN0-3a-PhMe-L	-3325.902964	-3325.87663	-3325.875686	-3325.962741	-3326.82293
TS0-2b-PhMe	-4361.383609	-4361.341404	-4361.34046	-4361.461085	-4362.816087
TS0-3a-PhMe-L	-3325.885451	-3325.859753	-3325.858809	-3325.943891	-3326.815544
IN0-4a-PhMe-L	-3325.932388	-3325.906376	-3325.905432	-3325.99158	-3326.865001
TS0-1a-1-PhMe	-2855.311796	-2855.286155	-2855.285211	-2855.367528	-2856.21423
TS0-1a-2-PhMe	-2543.602986	-2543.585955	-2543.585011	-2543.649301	-2544.269978
TS0-1a-CH4	-3579.131786	-3579.096909	-3579.095965	-3579.203838	-3580.310584
IN0-2a-CH4	-3579.154865	-3579.120141	-3579.119197	-3579.224674	-3580.330875
TS0-2a-CH4	-4361.386406	-4361.343409	-4361.342465	-4361.467157	-4362.82455
IN0-4a-CH4	-4361.43794	-4361.393253	-4361.392309	-4361.52049	-4362.88151
IN1-1-CH4	-4395.03591	-4394.996318	-4394.995374	-4395.111359	-4396.496289
TS0-2b'-PhMe	-3325.831413	-3325.8058	-3325.804856	-3325.889811	-3326.754537
TS0-3a-1-PhMe-L	-3325.888166	-3325.862575	-3325.861631	-3325.945258	-3326.816244
TS0-3a-2-PhMe-L	-4361.404094	-4361.361468	-4361.360524	-4361.483148	-4362.847287
TS0-3a-3-PhMe-L	-3325.883442	-3325.85768	-3325.856735	-3325.942235	-3326.805891
TS0-3a-4-PhMe-L	-4361.404944	-4361.362408	-4361.361464	-4361.483027	-4362.840196
TS0-3a-5-PhMe-L	-3637.550615	-3637.515776	-3637.514832	-3637.620735	-3638.713962
TS0-3a-6-PhMe-L	-1779.319464	-1779.311938	-1779.310993	-1779.352186	-1779.659752
TS0-1a-PhMe-1a	-4435.490064	-4435.44707	-4435.446126	-4435.570161	-4436.996583
IN0-2a-PhMe-1a	-4435.459082	-4435.41667	-4435.415726	-4435.536523	-4436.960479
TS0-1b-PhMe-1a	-4435.464207	-4435.421086	-4435.420142	-4435.543654	-4436.960022
TS0-2a-PhMe-1a	-4435.378318	-4435.336524	-4435.33558	-4435.454306	-4436.886845
IN0-3a-PhMe-1a	-4435.429356	-4435.387975	-4435.387031	-4435.504755	-4436.922434
TS0-2b-PhMe-1a	-4435.461982	-4435.419314	-4435.41837	-4435.541262	-4436.95201
TS0-3a-PhMe-1a	-4435.382193	-4435.339766	-4435.338821	-4435.460089	-4436.878696
IN0-4a-PhMe-1a	-4435.447632	-4435.405423	-4435.404479	-4435.525835	-4436.941478
TS0-1a'-PhMe-1a	-4435.509056	-4435.46643	-4435.465486	-4435.588961	-4437.003274
TS0-1b'-PhMe-1a	-4435.460731	-4435.418536	-4435.417592	-4435.537726	-4436.957364
IN0-1a-PhMe	-4435.495939	-4435.453477	-4435.452532	-4435.574632	-4436.996876
IN0-2a-PhMe-P	-3399.932069	-3399.906687	-3399.905742	-3399.989608	-3400.912787

TS0-1b-PhMe-P	-1891.669973	-1891.646935	-1891.645991	-1891.722759	-1892.53111
TS0-2a-PhMe-P	-3399.937858	-3399.913126	-3399.912182	-3399.993513	-3400.909698
IN0-3a-PhMe-P	-4435.481286	-4435.438195	-4435.437251	-4435.562014	-4436.972326
TS0-2b-PhMe-P	-4435.446672	-4435.404974	-4435.40403	-4435.522619	-4436.933709
TS0-3a-PhMe-P	-4435.458164	-4435.41558	-4435.414636	-4435.538701	-4436.953988
IN0-4a-PhMe-P	-4164.240126	-4164.205476	-4164.204532	-4164.308357	-4165.557124
TS0-4a-PhMe-P	-4164.216838	-4164.182381	-4164.181436	-4164.285162	-4165.536258
IN0-5a-PhMe-P	-4164.241639	-4164.206294	-4164.20535	-4164.313667	-4165.548148
TS0-5a-PhMe-P	-4164.208361	-4164.173613	-4164.172669	-4164.27854	-4165.527841
IN0-6a-PhMe-P	-4164.22403	-4164.189071	-4164.188127	-4164.29349	-4165.5471
TS0-2a'-PhMe-P	-3399.938956	-3399.914613	-3399.913669	-3399.992471	-3400.91135
TS0-2b'-PhMe-P	-3711.594198	-3711.561149	-3711.560205	-3711.657231	-3712.805533
TS0-3a-1-PhMe-P	-4435.459362	-4435.416978	-4435.416033	-4435.538683	-4436.953621
TS0-3a-2-PhMe-P	-4435.455344	-4435.413144	-4435.4122	-4435.535105	-4436.949906
TS0-3a-3-PhMe-P	-4435.462349	-4435.420292	-4435.419348	-4435.540609	-4436.950462
TS0-3a-4-PhMe-P	-3399.934536	-3399.90958	-3399.908636	-3399.99104	-3400.914628
TS0-3a-5-PhMe-P	-3711.601867	-3711.567769	-3711.566825	-3711.67022	-3712.824936
TS0-3a-6-PhMe-P	-4435.446067	-4435.403894	-4435.40295	-4435.52419	-4436.932291
TS0-3a-7-PhMe-P	-3711.599633	-3711.566128	-3711.565184	-3711.665953	-3712.818305
TS0-3a-8-PhMe-P	-4435.415033	-4435.371855	-4435.370911	-4435.495934	-4436.899247
TS1-1-PhMe	-4164.210022	-4164.175612	-4164.174668	-4164.27912	-4165.529319
IN2-1-PhMe	-4164.247397	-4164.212302	-4164.211358	-4164.319669	-4165.552689
TS1-2-PhMe	-4555.605617	-4555.55721	-4555.556266	-4555.690083	-4557.249193
IN2-2-PhMe	-4555.649744	-4555.600986	-4555.600042	-4555.734416	-4557.285439
TS2-1-PhMe	-4555.630434	-4555.582425	-4555.581481	-4555.715896	-4557.263481
IN3-1-PhMe	-4555.660746	-4555.612748	-4555.611804	-4555.746583	-4557.293936
TS2-2-PhMe	-4555.554077	-4555.505844	-4555.504899	-4555.638917	-4557.184043
IN3-2-PhMe	-4555.567324	-4555.519212	-4555.518268	-4555.650671	-4557.198605
TS3-1 ^{anti} -PhMe	-4555.627559	-4555.580072	-4555.579128	-4555.711753	-4557.269149
IN4-1-PhMe	-4555.641357	-4555.593778	-4555.592834	-4555.72604	-4557.288577
TS3-1 ^{syn} -PhMe	-4555.621	-4555.573742	-4555.572798	-4555.70484	-4557.266388
IN4-1'-PhMe	-4555.640387	-4555.592616	-4555.591671	-4555.726379	-4557.287862
TS1-1'-PhMe	-4164.211593	-4164.17708	-4164.176136	-4164.281278	-4165.529952
TS1-2'-PhMe	-4555.604232	-4555.556733	-4555.555789	-4555.68696	-4557.247509
TS2-1'-PhMe	-4555.627462	-4555.579536	-4555.578592	-4555.712312	-4557.261898
TS2-2'-PhMe	-4555.552449	-4555.504226	-4555.503281	-4555.637922	-4557.183463
TS3-1' ^{anti} -PhMe	-4555.627166	-4555.579485	-4555.578541	-4555.712501	-4557.268461
TS3-1' ^{syn} -PhMe	-4555.61987	-4555.57288	-4555.571935	-4555.702433	-4557.265946
IN2-2-MeCl	-3935.480909	-3935.442055	-3935.441111	-3935.556251	-3936.801454
IN2-2-C ₂ H ₆	-4355.764039	-4355.726347	-4355.725403	-4355.838314	-4357.176477
IN2-2-1-PhCl	-3743.952421	-3743.916339	-3743.915395	-3744.024746	-3745.172481
IN2-2-2-PhCl	-3743.920681	-3743.884733	-3743.883789	-3743.990522	-3745.143738
IN2-2-3-PhCl	-3743.914512	-3743.878279	-3743.877335	-3743.98446	-3745.122191

IN2-2-LE	-4206.758046	-4206.711932	-4206.710988	-4206.838481	-4208.259858
IN2-2-1-D1	-3975.33946	-3975.298178	-3975.297234	-3975.417132	-3976.706627
IN2-2-2-D1	-3975.332368	-3975.290988	-3975.290044	-3975.409329	-3976.681266
IN2-2-3-D1	-3975.295904	-3975.253736	-3975.252792	-3975.375307	-3976.647224
IN2-2-1-D2	-3975.175014	-3975.134078	-3975.133134	-3975.250764	-3976.569728
IN2-2-2-D2	-3975.170273	-3975.128991	-3975.128047	-3975.248657	-3976.565508
IN2-2-3-D2	-3975.115215	-3975.073524	-3975.07258	-3975.191881	-3976.496009
IN1-1 _{Ni}	-4044.573608	-4044.525199	-4044.524255	-4044.661372	-4046.150215
TS1-1 _{Ni}	-4044.552637	-4044.504613	-4044.503668	-4044.639101	-4046.123647
IN2-1 _{Ni}	-4044.573402	-4044.524713	-4044.523769	-4044.660816	-4046.133465
IN1-2 _{Ni}	-3653.175273	-3653.140306	-3653.139362	-3653.247301	-3654.424676
TS1-2 _{Ni}	-3653.119042	-3653.084201	-3653.083257	-3653.189567	-3654.359252
IN2-2 _{Ni}	-3653.186215	-3653.151578	-3653.150633	-3653.257067	-3654.419046
TS2-1 _{Ni}	-4044.556482	-4044.508911	-4044.507967	-4044.640791	-4046.118739
IN3-1 _{Ni}	-4044.58807	-4044.540168	-4044.539224	-4044.673401	-4046.14731
TS3-1 ^{anti} _{Ni}	-4044.579195	-4044.531929	-4044.530985	-4044.663227	-4046.149268
IN4-1 _{Ni}	-4044.600039	-4044.552782	-4044.551838	-4044.683944	-4046.172598
TS1-1' _{Ni}	-4044.554523	-4044.507192	-4044.506248	-4044.636778	-4046.124424
IN1-1-Al	-2283.150369	-2283.111936	-2283.110992	-2283.223274	-2284.346965
TS1-1 ^{anti} -Al	-2283.032386	-2282.995256	-2282.994311	-2283.103742	-2284.237643
IN2-1-Al	-2283.194168	-2283.157164	-2283.15622	-2283.266543	-2284.387059
TS1-1 ^{syn} -Al	-2283.032386	-2282.995256	-2282.994311	-2283.103742	-2284.23309
IN2-1'-Al	-2283.174564	-2283.137825	-2283.136881	-2283.245345	-2284.369657
TS1-2-Al	-2283.044165	-2283.006677	-2283.005733	-2283.115069	-2284.226566
IN2-2'-Al	-2283.117345	-2283.079861	-2283.078917	-2283.190074	-2284.306591
TS2-2-Al	-2283.072745	-2283.03641	-2283.035465	-2283.140881	-2284.26278
IN2-2-Al	-2283.130363	-2283.093763	-2283.092819	-2283.199547	-2284.322267
TS1-3-Al	-2283.020308	-2282.983016	-2282.982071	-2283.091205	-2284.218385
IN2-3'-Al	-2283.072548	-2283.035292	-2283.034348	-2283.143542	-2284.272966
TS2-3-Al	-2283.069056	-2283.032477	-2283.031533	-2283.139764	-2284.273054
IN2-3-Al	-2283.135852	-2283.098785	-2283.097841	-2283.207754	-2284.33191
IN1-1-L	-3791.36122	-3791.321671	-3791.320727	-3791.436773	-3792.679407
TS1-1-L	-3791.33859	-3791.299197	-3791.298253	-3791.413938	-3792.650516
IN2-1-L	-3791.373096	-3791.333107	-3791.332163	-3791.449429	-3792.68065
IN1-2-L	-3711.672505	-3711.639131	-3711.638187	-3711.736228	-3712.89312
TS1-2-L	-3711.646	-3711.61332	-3711.612375	-3711.708	-3712.861889
IN2-2-L	-3711.646	-3711.61332	-3711.612375	-3711.708	-3712.861889
IN1-3-L	-3399.955535	-3399.929738	-3399.928794	-3400.013629	-3400.949999
TS1-3-L	-3399.936542	-3399.911101	-3399.910156	-3399.994228	-3400.929614
IN2-3-L	-3399.981413	-3399.955717	-3399.954773	-3400.039824	-3400.956347
IN1-4-L	-4509.500446	-4509.457746	-4509.456802	-4509.580993	-4511.066539
TS1-4-L	-4509.485778	-4509.44413	-4509.443185	-4509.562351	-4511.042666
IN2-4-L	-4509.539331	-4509.497089	-4509.496145	-4509.617832	-4511.084082

TS2-1-L	-3791.348793	-3791.309733	-3791.308789	-3791.423464	-3792.653289
IN3-1-L	-3791.391286	-3791.352673	-3791.351729	-3791.464476	-3792.696986
TS2-2-L	-4103.003984	-4102.956824	-4102.95588	-4103.084784	-4104.548784
IN3-2-L	-4103.033733	-4102.986709	-4102.985765	-4103.114286	-4104.579616
TS2-3-L	-4182.713205	-4182.660117	-4182.659173	-4182.803656	-4184.357731
IN3-3-L	-4182.734928	-4182.681797	-4182.680853	-4182.825947	-4184.375517
TS3-1^{anti}-L	-3791.353507	-3791.315112	-3791.314168	-3791.426234	-3792.667632
IN4-1-L	-3791.369688	-3791.331267	-3791.330323	-3791.441842	-3792.690105
TS1-1'-L	-3711.631174	-3711.59765	-3711.596706	-3711.696049	-3712.854865
TS1-1''-L	-4103.003228	-4102.95583	-4102.954886	-4103.083844	-4104.558559
TS1-2'-L	-4182.704208	-4182.650571	-4182.649627	-4182.797581	-4184.350414
TS1-4'-L	-4509.475906	-4509.434441	-4509.433497	-4509.552066	-4511.036856

E_0 = Sum of electronic and zero-point energies calculated by B3LYP-D3

E = Sum of electronic and thermal energies calculated by B3LYP-D3

$H_{298.15}$ = Sum of electronic and thermal enthalpies calculated by B3LYP-D3

$G_{298.15}$ = Sum of electronic and thermal free energies calculated by B3LYP-D3

$E_{(\text{sol}, \text{M06})}$ = Single point energies calculated by B3LYP-D3 in solvent

Section 10. Calculated Imaginary Frequencies of All Transition States

Species

Species	Frequency
TS1-1	-139.22
TS1-2	-154.65
TS1-3	-180.66
TS1-4	-138.50
TS2-1	-224.05
TS2-2	-171.46
TS3-1^{anti}	-134.95
TS3-1^{syn}	-107.97
TS3-2	-146.07
TS3-3	-312.28
TS1-1'	-80.75
TS1-2'	-107.06
TS1-3'	-242.13
TS1-4'	-144.56
TS2-1'	-189.01
TS3-1'^{anti}	-102.08
TS3-4^{anti}	-148.46
TS3-2'	-142.87
TS0-1a-PhH	-137.79
TS0-1b-PhH	-135.1
TS0-1c-PhH	-235.22
TS0-2a-PhH	-1125.35
TS0-2b-PhH	-82.2
TS0-2c-PhH	-1139.75
TS0-3c-PhH	-726.09
TS0-2d-PhH	-210.14
TS0-4a-PhH	-126.62
TS1-1-PhH	-98.14
TS1-2-PhH	-148.29
TS2-1-PhH	-194.03
TS2-2-PhH	-341.47
TS3-1^{anti}-PhH	-109.65
TS3-1^{syn}-PhH	-118.44
TS0-1a-1-PhH	-116.01
TS0-1a-2-PhH	-168.41
TS0-1b-1-PhH	-818.36

TS0-1b-2-PhH	-685.08
TS0-1b-3-PhH	-802.06
TS0-1b-4-PhH	-486.38
TS0-2a-1-PhH	-1044.05
TS0-2a-2-PhH	-1530.27
TS0-2a-3-PhH	-802.21
TS0-2b-1-PhH	-122.1
TS0-2c-1-PhH	-896.27
TS0-2c-2-PhH	-594.87
TS0-2c-3-PhH	-152.81
TS0-2c-4-PhH	-274.69
TS0-3c-1-PhH	-19.63
TS0-3c-2-PhH	-529.67
TS0-3c-3-PhH	-91.9
TS0-3c-4-PhH	-518.34
TS0-3c-5-PhH	-470.37
TS1-3-PhH	-73.93
TS3-2-PhH	-77.34
TS3-3-PhH	-77.50
TS0-1a-PhMe	-137.79
TS0-1b-PhMe	-648.74
TS0-2b-PhMe	-659.07
TS0-3a-PhMe-L	-366.43
TS0-1a-1-PhMe	-116.01
TS0-1a-2-PhMe	-168.41
TS0-1a-CH4	-813.38
TS0-2a-CH4	-606.46
TS0-2b'-PhMe	-589.46
TS0-3a-1-PhMe-L	-390.96
TS0-3a-2-PhMe-L	-414.89
TS0-3a-3-PhMe-L	-344.11
TS0-3a-4-PhMe-L	-347.49
TS0-3a-5-PhMe-L	-374.52
TS0-3a-6-PhMe-L	-508.84
TS0-1a-PhMe-1a	-135.24
TS0-1b-PhMe-1a	-453.69
TS0-2a-PhMe-1a	-153.15
TS0-2b-PhMe-1a	-556.07
TS0-3a-PhMe-1a	-332.25
TS0-1a'-PhMe-1a	-154.88
TS0-1b'-PhMe-1a	-636.89
TS0-1b-PhMe-P	-592.2
TS0-2a-PhMe-P	-41.78

TS0-2b-PhMe-P	-425.18
TS0-3a-PhMe-P	-408.38
TS0-4a-PhMe-P	-124.92
TS0-5a-PhMe-P	-125.64
TS0-2a'-PhMe-P	-37.41
TS0-2b'-PhMe-P	-341.07
TS0-3a-1-PhMe-P	-395.89
TS0-3a-2-PhMe-P	-411.44
TS0-3a-3-PhMe-P	-342.32
TS0-3a-4-PhMe-P	-336.84
TS0-3a-5-PhMe-P	-397.03
TS0-3a-6-PhMe-P	-450.74
TS0-3a-7-PhMe-P	-371.34
TS0-3a-8-PhMe-P	-471.85
TS1-1-PhMe-P	-133.45
TS1-2-PhMe-P	-93.57
TS2-1-PhMe-P	-238.67
TS2-2-PhMe-P	-342.31
TS3-1^{anti}-PhMe-P	-129.11
TS3-2-PhMe-P	-87.48
TS1-1'-PhMe-P	-150.45
TS1-2'-PhMe-P	-119.08
TS2-1'-PhMe-P	-255.35
TS2-2'-PhMe-P	-352.65
TS3-1^{anti}-PhMe-P	-128.61
TS3-2'-PhMe-P	-60.22
TS1-1_{Ni}	-154.94
TS1-2_{Ni}	-160.08
TS2-1_{Ni}	-261.8
TS3-1^{anti}_{Ni}	-124.63
TS1-2'_{Ni}	-140.74
TS1-1^{anti}-Al	-367.81
TS1-1^{syn}-Al	-283.47
TS1-2-Al	-253.36
TS2-2-Al	-388.42
TS1-3-Al	-407.69
TS2-3-Al	-58.09
TS1-1-L	-82.74
TS1-2-L	-57.65
TS1-3-L	-129.74
TS1-4-L	-54.07
TS2-1-L	-306.91
TS2-2-L	-232.55

TS2-3-L	-284.51
TS3-1-L	-149.37
TS1-1'-L	-187.69
TS1-1''-L	-124.07
TS1-2'-L	-138.32
TS1-4'-L	-56.25