Supporting Information

Nickel-Catalyzed Selective C1−C8 Bond Cleavage of Benzocyclobutenones:

Theoretical Insights into Mechanism, Substituent Effects on Regioselectivity,

Ligand Effects on Reactivity, and Chemoselectivity

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Section 1. Optimization with M06 and PBE0 methods

Table S1. Relative Gibbs energies (in kcal/mol) for the key transition states with M06 and PBE0 methods.

1-TSa1-A **1-TSa1-B** **1-TSa2-A**

1-TSa2-C **5-TSa4** **5-TSa6**
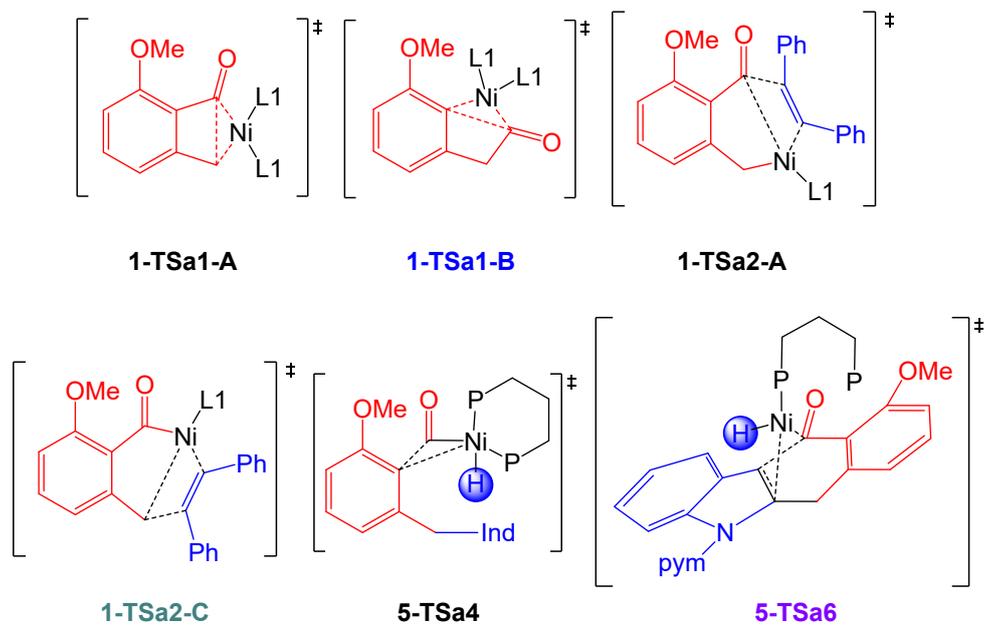
Species	$\Delta\Delta G$	Species	$\Delta\Delta G$	Species	$\Delta\Delta G$
1-TSa1-A-B3LYP-D3	0.0	1-TSa1-A-PBE0	0.0	1-TSa1-A-M06	0.0
1-TSa1-B-B3LYP-D3	2.4	1-TSa1-B-PBE0	1.8	1-TSa1-B-M06	1.9
1-TSa2-A-B3LYP-D3	0.0	1-TSa2-A-PBE0	0.0	1-TSa2-A-M06	0.0
1-TSa2-C-B3LYP-D3	5.8	1-TSa2-C-PBE0	7.4	1-TSa2-C-M06	8.9
5-TSa4-B3LYP-D3	0.0	5-TSa4-PBE0	0.0	5-TSa4-M06	0.0
5-TSa6-B3LYP-D3	21.6	5-TSa6-PBE0	19.0	5-TSa6-M06	21.6

Section 2. Other possible isomers and conformers
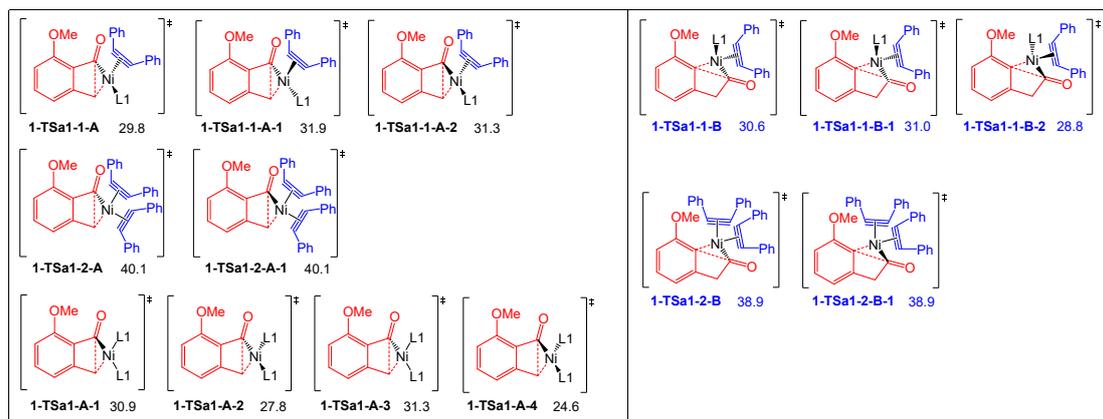
Fig. S1 Other possible isomers and conformers of oxidative addition transition states.

Values shown are relative free energies in kcal/mol.
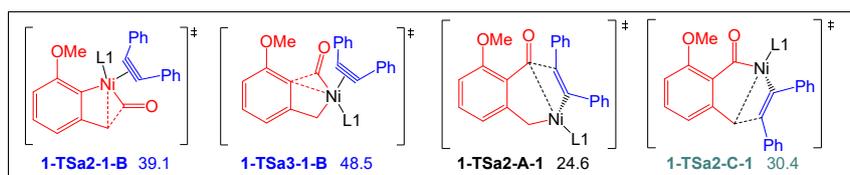
Fig. S2 Other possible coordination environment of nickel for key transition states.

Values shown are relative free energies in kcal/mol.

Section 3. The whole free-energy profiles for the formation of byproduct 4a
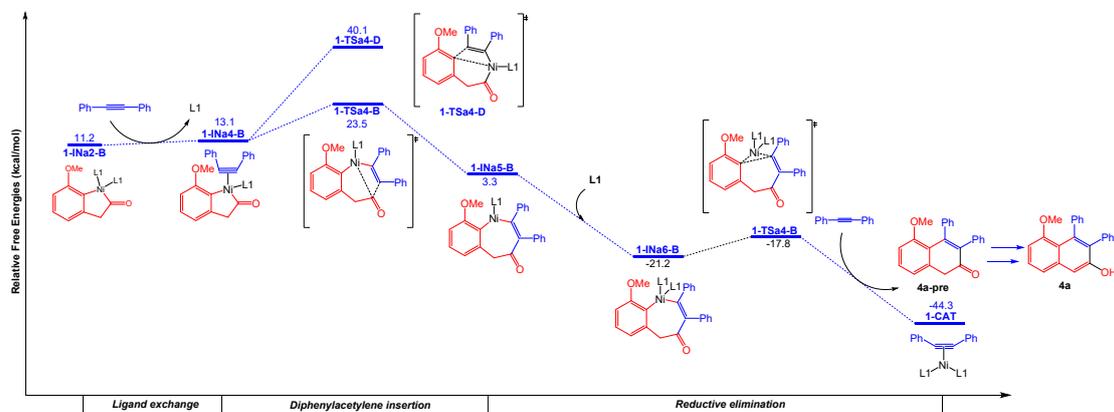
Fig. S3 Calculated free-energy profiles for the process from **1-IN2a-B** to **4a-pre**. Values shown are relative free energies in kcal/mol.

Section 4. Comparison among five substrates and four ligands
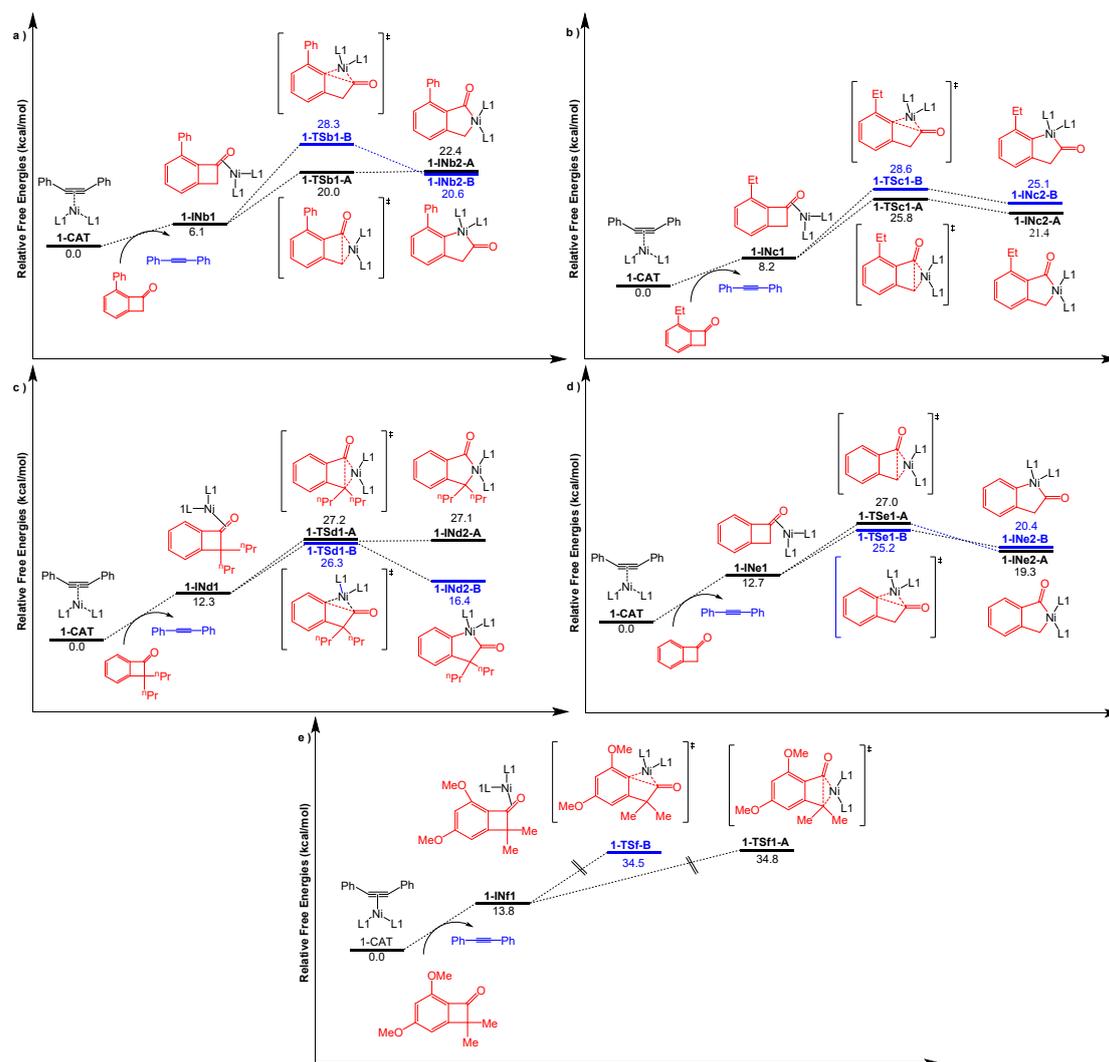
Fig. S4 Calculated energy profiles for regio-selectivity-determining steps with five substrates. Values shown are relative free energies in kcal/mol.
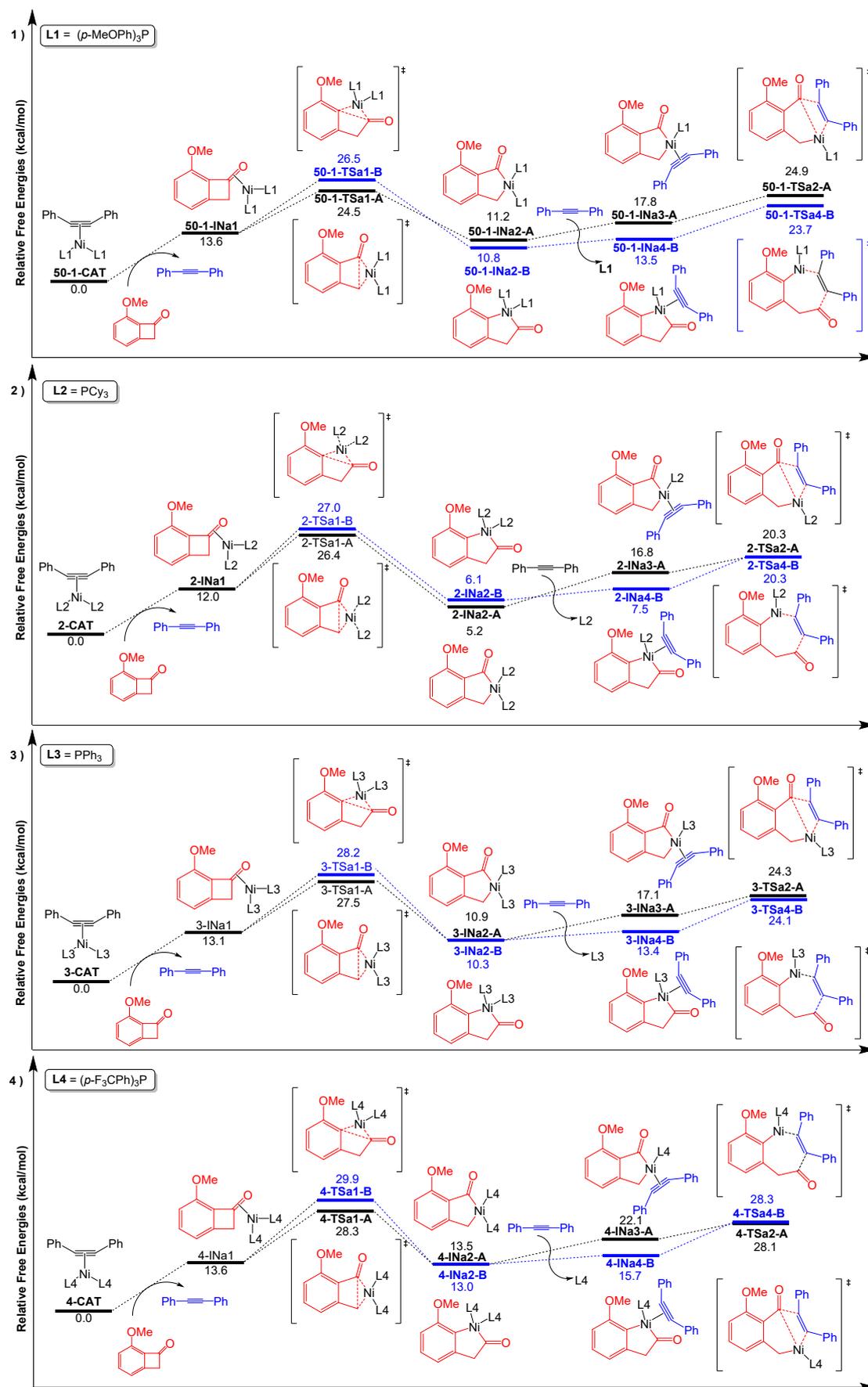
Fig. S5 Calculated energy profiles for first two steps with four ligands at 50 °C. Values

shown are relative free energies in kcal/mol.
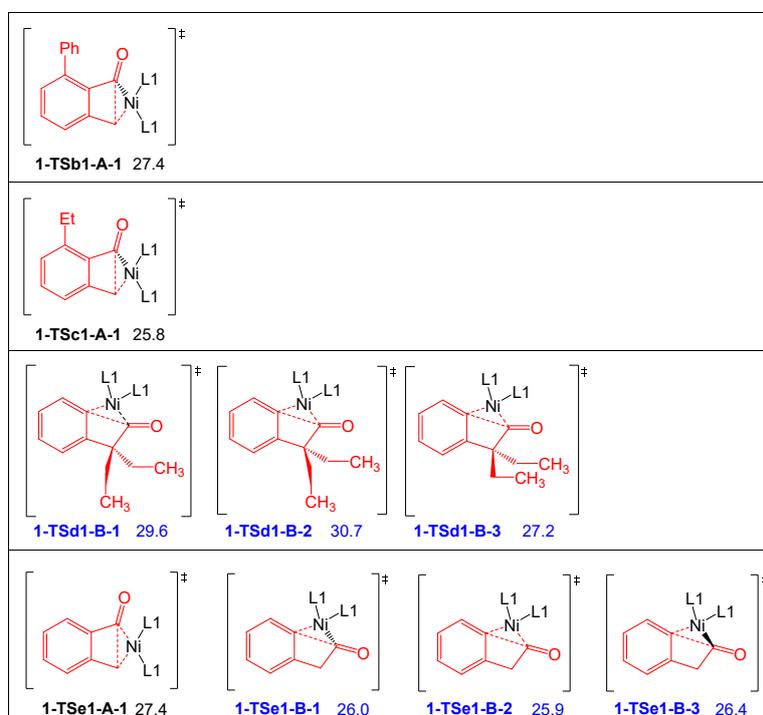
Fig. S6 Other possible isomers and conformers of oxidative addition transition state for substrates **1b-1d**. Values shown are relative free energies in kcal/mol.
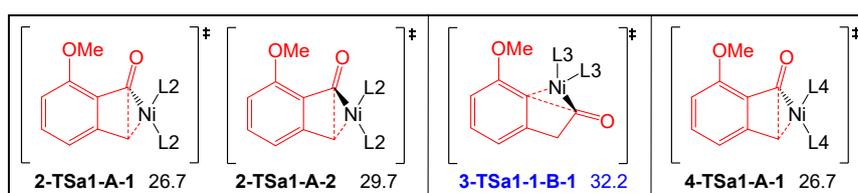
Fig. S7 Other possible isomers and conformers of oxidative addition transition state for ligands **L2-L4**. Values shown are relative free energies in kcal/mol.

1-TSe1-A
∠ C8-C1-C2-O1 = 134.8 °

1-INe1
∠ C8-C1-C2-O1 = 142.7 °

1-TSe1-B
∠ C8-C1-C2-O1 = 140.4 °
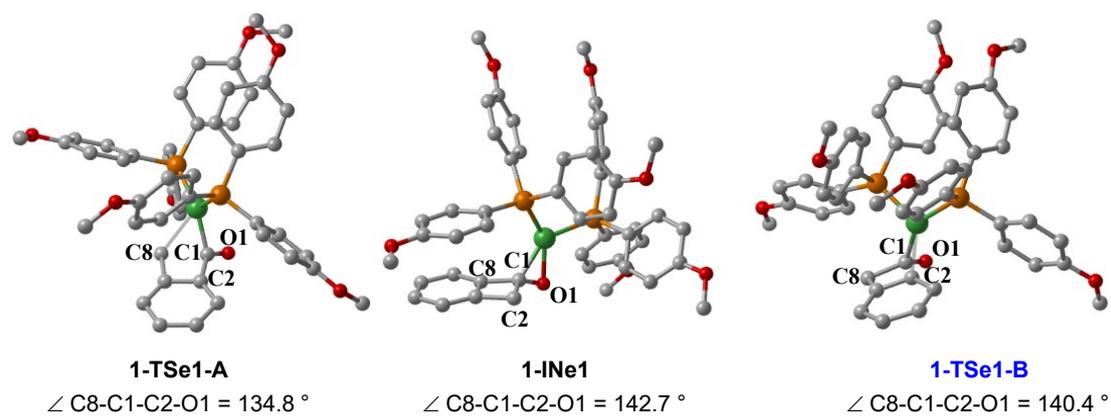
Fig. S8 Optimized structures and dihedral angle for **1-TSe1-A**, **1-INe1** and **1-TSe1-B** are shown.

| -0.72 | -0.06 | -1.64 | -0.97 | -1.89 |
| -4.01 | -3.50 | -6.60 | -4.12 | -4.90 |

Ni(L1)₂ Ni(L2)₂ **1a** (OMe) Ni(L3)₂ Ni(L4)₂
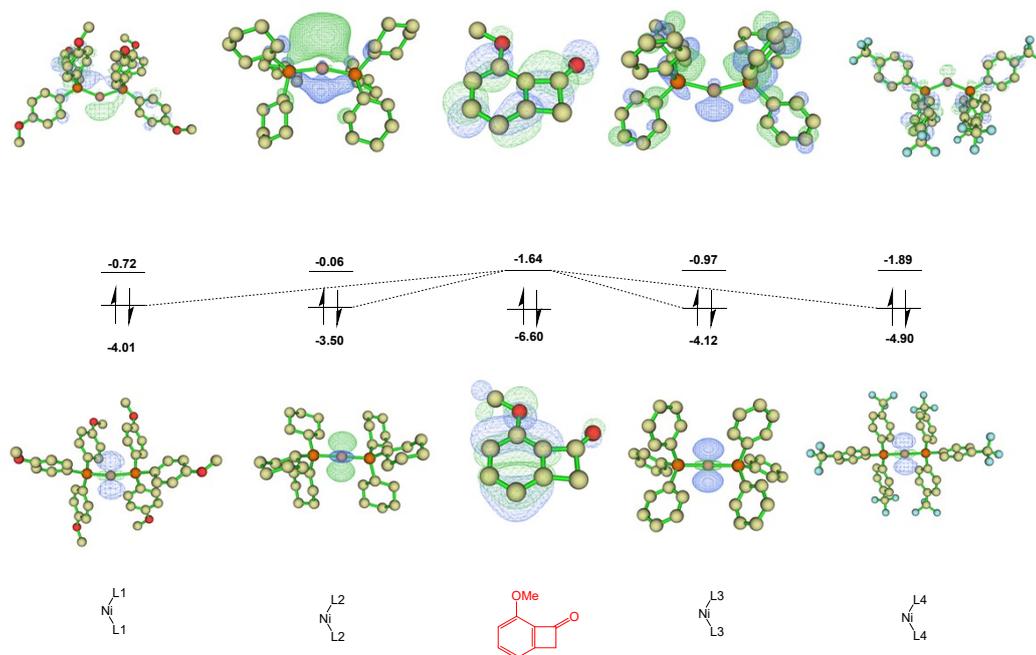
Fig. S9 Calculated frontier molecular orbitals for **1a** and Ni(Lx)₂ (x=1, 2, 3 and 4). Orbital energies are given in eV.

Section 5. Other possible pathways for the Ni-catalyzed coupling of benzocyclobutenones with indoles
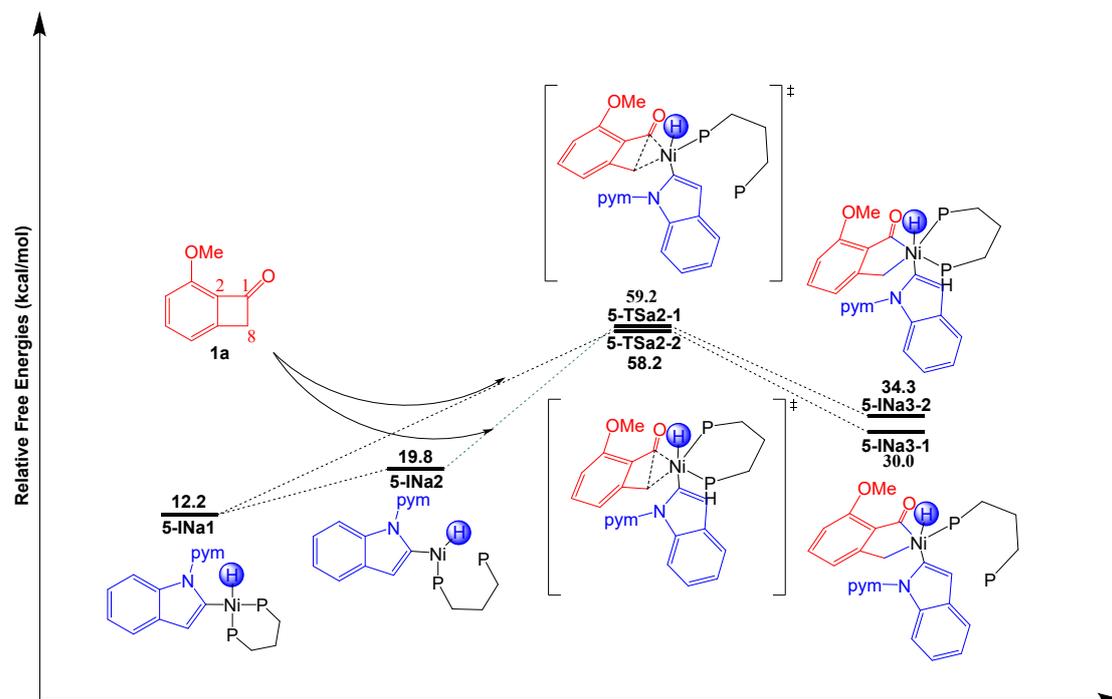
Fig. S10 Calculated free-energy profiles for oxidative addition to the C1−C8 bond of **5-INa1**. Values shown are relative free energies in kcal/mol.
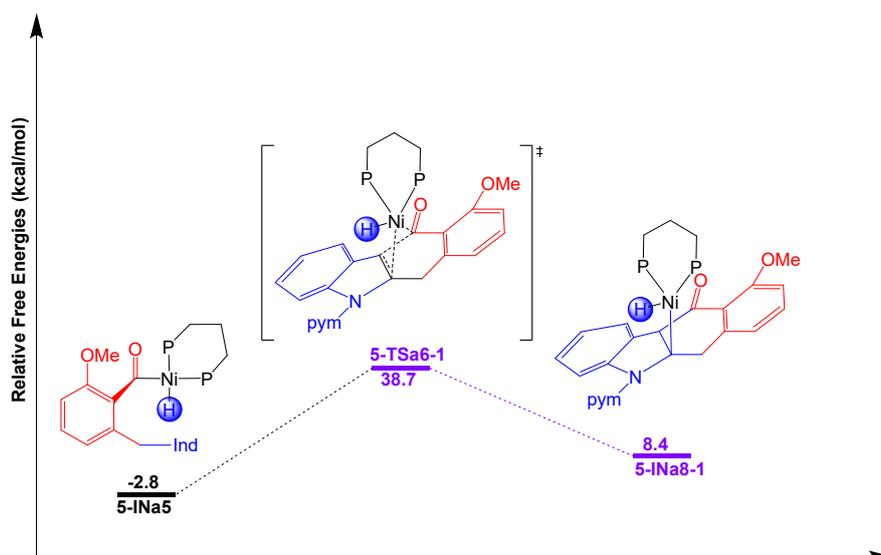
Fig. S11 Calculated free-energy profiles for bidentate cyclization process from **5-Ina5**. Values shown are relative free energies in kcal/mol.
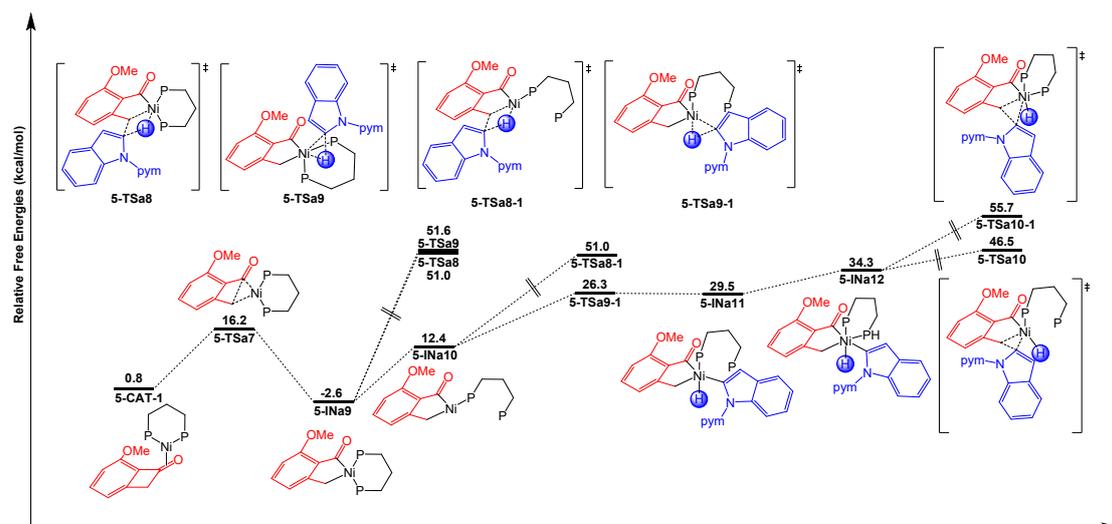
Fig. S12 Calculated free-energy profiles for the Ni-catalyzed coupling of benzocyclobutenones with indoles (C1−C8 bond cleavage precede C−H bond cleavage). Values shown are relative free energies in kcal/mol.

Section 6. Energies (in hartree) of All TSs and Intermediates

80 °C, Solvent = Toluene:

Geometry	E_0	E	$H_{353.15}$	$G_{353.15}$	$E_{(sol,M06)}$
Ni(cod)$_2$	-793.235286	-793.212270	-793.211152	-793.288386	-793.1396732
NiL$_2$	-2928.955500	-2928.886708	-2928.885590	-2929.075605	-2928.201928
1-CAT-1	-2628.007053	-2627.938624	-2627.937506	-2628.126752	-2627.1860221
NiL$_2$cod	-3240.946744	-3240.867916	-3240.866798	-3241.068770	-3240.1332592
1-CAT	-3468.428804	-3468.343947	-3468.342828	-3468.565323	-3467.4448296
1a	-498.153625	-498.141123	-498.140005	-498.196650	-411.7113978
2	-539.400534	-539.386349	-539.385231	-539.446987	-539.1605215
1-INa1	-3427.168190	-3427.086769	-3427.085650	-3427.298871	-3426.2308471
1-TSa1-A	-3427.148229	-3427.065915	-3427.064797	-3427.281382	-3426.2093251
1-TSa1-A-PBE0	-3423.608975	-3423.526448	-3423.525330	-3423.743073	-3426.2101456
1-TSa1-A-M06	-3425.151409	-3425.069208	-3425.068090	-3425.281405	-3426.2123856
1-TSa1-A-1	-3427.138150	-3427.055799	-3427.054680	-3427.269188	-3426.2012338
1-TSa1-A-2	-3427.146930	-3427.064740	-3427.063621	-3427.278118	-3426.2063363
1-TSa1-A-3	-3427.134826	-3427.052627	-3427.051508	-3427.265884	-3426.2005438
1-TSa1-A-4	-3427.148228	-3427.065914	-3427.064795	-3427.281386	-3426.2093235

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1-TSa1-1-A	-2586.730084	-2586.664635	-2586.663516	-2586.843450	-2585.9581964
1-TSa1-1-A-1	-2586.728034	-2586.662712	-2586.661594	-2586.839695	-2585.956771
1-TSa1-1-A-2	-2586.726334	-2586.660297	-2586.659178	-2586.842114	-2585.9527539
1-TSa1-2-A	-1746.311064	-1746.263342	-1746.262224	-1746.402606	-1745.7012359
1-TSa1-2-A-1	-1746.311060	-1746.263342	-1746.262223	-1746.402578	-1745.7012396
1-TSa1-B	-3427.146356	-3427.064355	-3427.063236	-3427.276658	-3426.2091941
1-TSa1-B-PBE0	-3423.603615	-3423.521293	-3423.520175	-3423.736568	-3426.2091239
1-TSa1-B-M06	-3425.149750	-3425.068027	-3425.066909	-3425.277237	-3426.2130765
1-TSa1-1-B	-2586.728230	-2586.662751	-2586.661632	-2586.840967	-2585.9579287
1-TSa1-1-B-1	-2586.732910	-2586.667888	-2586.666770	-2586.844080	-2585.9594665
1-TSa1-1-B-2	-2586.735964	-2586.670984	-2586.669865	-2586.846638	-2585.9635129
1-TSa1-2-B	-1746.312197	-1746.263222	-1746.262104	-1746.406975	-1745.700194
1-TSa1-2-B-1	-1746.312196	-1746.263222	-1746.262104	-1746.406973	-1745.7002002
1-INa2-A	-3427.177226	-3427.095535	-3427.094417	-3427.306314	-3426.2354911
1-INa2-B	-3427.183554	-3427.183554	-3427.183554	-3427.183554	-3426.2392424
1-TSa2-B	-3427.142259	-3427.059840	-3427.058721	-3427.274533	-3426.2038411
1-TSa2-1-B	-2586.718142	-2586.652025	-2586.650906	-2586.831894	-2585.9420827
1-INa3-B	-3427.156973	-3427.073192	-3427.072074	-3427.292070	-3426.2155531
1-TSa3-B	-3427.135072	-3427.052706	-3427.051588	-3427.265070	-3426.1991036
1-TSa3-1-B	-2586.702116	-2586.635795	-2586.634677	-2586.814811	-2585.9269166
1-INa3-A	-2586.750247	-2586.683283	-2586.682165	-2586.870146	-2585.9655114
1-INa4-A	-2586.758372	-2586.692563	-2586.691445	-2586.873179	-2585.9790055
1-TSa2-C	-2586.733483	-2586.668671	-2586.667552	-2586.846329	-2585.958919
1-TSa2-C-PBE0	-2583.949156	-2583.885385	-2583.884267	-2584.061126	-2585.9586883
1-TSa2-C-M06	-2585.109922	-2585.045686	-2585.044568	-2585.219456	-2585.9616118
1-TSa2-C-1	-2586.731821	-2586.667067	-2586.665949	-2586.845319	-2585.9568951
1-TSa2-A	-2586.702116	-2586.635795	-2586.634677	-2586.814811	-2585.926917
1-TSa2-A-PBE0	-2583.954412	-2583.889428	-2583.888310	-2584.069202	-2585.9669028
1-TSa2-A-M06	-2585.120069	-2585.055095	-2585.053976	-2585.232496	-2585.9708171
1-INa5-A	-2586.752840	-2586.687751	-2586.686633	-2586.866616	-2585.9782646
1-INa5-C	-2586.782784	-2586.718055	-2586.716937	-2586.896238	-2586.0012458
1-INa6-A	-3966.635904	-3966.538579	-3966.537460	-3966.779504	-3965.4729169
1-TSa4-A	-3966.614910	-3966.517867	-3966.516749	-3966.760484	-3965.4564973
1-CAT	-2628.007053	-2627.938624	-2627.937506	-2628.126752	-2627.1860221
3a-pre	-1037.647078	-1037.619126	-1037.618007	-1037.711444	-1037.2279744
1-INa4-B	-2586.764305	-2586.698614	-2586.697496	-2586.877107	-2585.9874454
1-INa5-B	-2586.784071	-2586.719244	-2586.718126	-2586.897559	-2586.0045506
1-INa6-B	-3966.649490	-3966.551865	-3966.550747	-3966.795100	-3965.4845376
1-TSa4-B	-2586.746523	-2586.681898	-2586.680780	-2586.858249	-2585.9718229
1-TSa4-B-1	-2586.744739	-2586.680401	-2586.679282	-2586.857070	-2585.9693373
1-TSa4-D	-2586.715340	-2586.650213	-2586.649094	-2586.829155	-2585.9417673
1-TSa5-B	-3966.640892	-3966.543885	-3966.542767	-3966.785451	-3965.47894
4-pre	-1037.647711	-1037.619715	-1037.618596	-1037.711333	-1037.2290201

1-CAT-1	-2628.007053	-2627.938624	-2627.937506	-2628.126752	-2627.1860221
Nicod2	-793.235286	-793.212270	-793.211152	-793.288386	-793.1396732
NicodL2	-3240.946744	-3240.867916	-3240.866798	-3241.068770	-3240.1332592
NiL2	-2928.955500	-2928.886708	-2928.885590	-2929.075605	-2928.201928
1b	-614.664372	-614.648791	-614.647673	-614.712058	-614.4042955
1-INb1	-3543.692235	-3543.607109	-3543.605991	-3543.825373	-3542.6831746
1-INb2-A	-3543.655753	-3543.571970	-3543.570852	-3543.785684	-3542.6746307
1-INb2-B	-3543.686490	-3543.613171	-3543.612147	-3543.805721	-3542.6722222
1-TSb1-A	-3543.664217	-3543.578870	-3543.577752	-3543.800173	-3542.6558668
1-TSb1-A-1	-3543.661177	-3543.576997	-3543.575879	-3543.792276	-3542.6488828
1-TSb1-B	-3543.655753	-3543.571970	-3543.570852	-3543.785684	-3542.6495454
1c	-462.228338	-462.215338	-462.214220	-462.272027	-462.0603169
1-INc1	-3391.247673	-3391.164869	-3391.163751	-3391.380712	-3390.3312749
1-INc2-A	-3391.252662	-3391.183017	-3391.181993	-3391.363908	-3390.3312999
1-INc2-B	-3391.248472	-3391.178023	-3391.177000	-3391.361377	-3390.3253233
1-TSc1-A	-3391.221070	-3391.138167	-3391.137048	-3391.354225	-3390.3010975
1-TSc1-A-1	-3391.221066	-3391.138165	-3391.137046	-3391.354210	-3390.3011016
1-TSc1-B	-3391.216259	-3391.133875	-3391.132757	-3391.347079	-3390.3004126
1d	-619.409865	-619.389361	-619.388243	-619.463611	-619.2255213
1-INd1	-3548.423014	-3548.332595	-3548.331477	-3548.566617	-3547.489804
1-INd2-A	-3548.424999	-3548.348095	-3548.347072	-3548.545955	-3547.4885935
1-INd2-B	-3548.441548	-3548.364422	-3548.363399	-3548.564057	-3547.5042672
1-TSd1-A	-3548.402040	-3548.311894	-3548.310775	-3548.542401	-3547.4680974
1-TSd1-B	-3548.402450	-3548.312773	-3548.311654	-3548.540415	-3547.4724728
1-TSd1-B-1	-3548.398314	-3548.308586	-3548.307468	-3548.538225	-3547.4654653
1-TSd1-B-2	-3548.397516	-3548.307835	-3548.306716	-3548.536765	-3547.4643431
1-TSd1-B-3	-3548.400580	-3548.310759	-3548.309640	-3548.539598	-3547.468975
1e	-383.628680	-383.619566	-383.618447	-383.667094	-383.4714218
1-INe1	-3312.643093	-3312.564162	-3312.563044	-3312.771541	-3311.7346208
1-INe2-A	-3312.655091	-3312.587757	-3312.586734	-3312.765797	-3311.741069
1-INe2-B	-3312.652613	-3312.585031	-3312.584008	-3312.764511	-3311.7387932
1-TSe1-A	-3312.622102	-3312.543129	-3312.542010	-3312.750532	-3311.7098269
1-TSe1-A-1	-3312.609086	-3312.530411	-3312.529292	-3312.736160	-3311.7021118
1-TSe1-B	-3312.623176	-3312.545359	-3312.544241	-3312.747150	-3311.7196001
1-TSe1-B-1	-3312.622655	-3312.544226	-3312.543108	-3312.749091	-3311.7148701
1-TSe1-B-2	-3312.622665	-3312.544230	-3312.543112	-3312.749158	-3311.7148816
1-TSe1-B-3	-3312.620967	-3312.542426	-3312.541308	-3312.748357	-3311.7131568
1f	-691.281283	-691.261115	-691.259997	-691.333646	-691.0553755
1-INf1	-3620.301329	-3620.212669	-3620.211550	-3620.437141	-3619.3239682
1-TSf1-A	-3620.265005	-3620.176432	-3620.175314	-3620.401287	-3619.2881991
1-TSf1-B	-3620.268910	-3620.179371	-3620.178253	-3620.407129	-3619.295825

50 °C, Solvent = Toluene:

1a-50	-498.153625	-498.143011	-498.141988	-498.191926	-497.9671672
2-50	-539.400532	-539.388616	-539.387592	-539.441848	-539.1605254
50-L1	-1379.799622	-1379.772275	-1379.771252	-1379.862957	-1379.3963482
50-1-CAT	-3468.428804	-3468.356675	-3468.355652	-3468.546990	-3467.4448296
50-1-INa1	-3427.168119	-3427.098932	-3427.097908	-3427.280973	-3426.2308607
50-1-TSa1-A	-3427.148229	-3427.078178	-3427.077155	-3427.263556	-3426.2093255
50-1-TSa1-B	-3427.146752	-3427.077254	-3427.076230	-3427.258946	-3426.2107621
50-1-INa2-A	-3427.177140	-3427.107753	-3427.106730	-3427.288282	-3426.2355996
50-1-INa2-B	-3427.183553	-3427.113862	-3427.112839	-3427.294073	-3426.2392461
50-1-INa3-A	-2586.758372	-2586.702415	-2586.701392	-2586.858181	-2585.9790055
50-1-INa4-B	-2586.764305	-2586.708465	-2586.707442	-2586.862290	-2585.9874453
50-1-TSa2-A	-2586.740194	-2586.685055	-2586.684031	-2586.837303	-2585.9683356
50-1-TSa4-B	-2586.746523	-2586.691631	-2586.690608	-2586.843608	-2585.9718229
L2	-1046.915853	-1046.893430	-1046.892407	-1046.968439	-1046.790922
2-CAT	-2802.645427	-2802.583204	-2802.582181	-2802.745134	-2802.2261803
2-INa1	-2761.393298	-2761.333737	-2761.332714	-2761.487830	-2253.3727118
2-TSa1-A	-2761.365768	-2761.305494	-2761.304470	-2761.461149	-2760.9886761
2-TSa1-A-1	-2761.365297	-2761.305144	-2761.304120	-2761.460322	-2760.9888521
2-TSa1-A-2	-2761.362002	-2761.301795	-2761.300772	-2761.456582	-2760.9846197
2-TSa1-B	-2761.365105	-2761.305060	-2761.304037	-2761.459447	-2760.9896193
2-INa2-A	-2761.400054	-2761.339199	-2761.338175	-2761.498012	-2761.0209971
2-INa2-B	-2761.403266	-2761.342361	-2761.341337	-2761.500304	-2761.0208419
2-INa3-A	-2253.871185	-2253.819005	-2253.817982	-2253.964965	-2253.3623707
2-INa4-B	-2253.879259	-2253.828133	-2253.827110	-2253.968414	-2253.3836665
2-TSa2-A	-2253.856782	-2253.806533	-2253.805510	-2253.944037	-2253.3635165
2-TSa4-B	-2253.861387	-2253.812500	-2253.811477	-2253.945804	-2253.3682417
L3	-1036.226391	-1036.207840	-1036.206816	-1036.278247	-1035.9109975
3-CAT	-2781.279073	-2781.224730	-2781.223707	-2781.375125	-2780.4696365
3-INa1	-2740.018953	-2739.966539	-2739.965516	-2740.111420	-2739.2547937
3-TSa1-A	-2739.991540	-2739.938654	-2739.937631	-2740.085461	-2739.2270994
3-TSa1-B	-2739.991632	-2739.939274	-2739.938250	-2740.083945	-2739.229291
3-TSa1-B-1	-2739.991647	-2739.939280	-2739.938257	-2740.084027	-2739.2260383
3-INa2-A	-2740.021450	-2739.968525	-2739.967502	-2740.115366	-2739.2553539
3-INa2-B	-2740.025484	-2739.972282	-2739.971259	-2740.119305	-2739.2567581
3-INa3-A	-2243.183091	-2243.136015	-2243.134992	-2243.270985	-2242.4913279
3-INa4-B	-2243.188042	-2243.141049	-2243.140026	-2243.274330	-2242.4984564
3-TSa2-A	-2243.163137	-2243.116713	-2243.115689	-2243.249920	-2242.4787012
3-TSa4-B	-2243.170448	-2243.124511	-2243.123488	-2243.255206	-2242.4829435
L4	-2047.649061	-2047.618897	-2047.617874	-2047.720782	-2047.0182001
4-CAT	-4804.133007	-4804.053525	-4804.052502	-4804.268526	-4802.6922094
4-INa1	-4762.871606	-4762.794137	-4762.793113	-4763.004469	-4761.4762784

4-TSa1-A	-4762.848329	-4762.770542	-4762.769518	-4762.980667	-4761.4503823
4-TSa1-A-1	-4762.844097	-4762.766530	-4762.765506	-4762.974381	-4761.4468299
4-TSa1-B	-4762.845279	-4762.768717	-4762.767693	-4762.975689	-4761.4506888
4-INa2-A	-4762.877084	-4762.799444	-4762.798420	-4763.006719	-4761.4784738
4-INa2-B	-4762.876556	-4762.798196	-4762.797173	-4763.010647	-4761.4744766
4-INa3-A	-3254.607878	-3254.548213	-3254.547189	-3254.715379	-3253.5985999
4-INa4-B	-3254.614626	-3254.555032	-3254.554008	-3254.722734	-3253.608086
4-TSa2-A	-3254.586896	-3254.527906	-3254.526882	-3254.694975	-3253.5863683
4-TSa4-B	-3254.595083	-3254.536570	-3254.535547	-3254.700468	-3253.5906378

140 ℃, Solvent = 1,4-dioxane:

1a-1	-498.153310	-498.136583	-498.135275	-498.206296	-497.9668201
ind	-626.923975	-626.904009	-626.902701	-626.981277	-626.6511293
5-CAT	-2523.416720	-2523.343157	-2523.341848	-2523.543933	-2522.7507199
5-INa1	-2523.401952	-2523.327938	-2523.326629	-2523.528435	-2522.727581
5-TSa1	-2523.399956	-2523.326746	-2523.325438	-2523.523943	-2522.730609
5-INa2	-2523.392981	-2523.319022	-2523.317714	-2523.523183	-2522.7134164
5-TSa2	-3021.557865	-3021.465345	-3021.464036	-3021.712533	-3020.6988549
5-TSa2-1	-3021.506482	-3021.413264	-3021.411956	-3021.659681	-3020.6460517
5-TSa2-2	-3021.507337	-3021.414312	-3021.413004	-3021.658113	-3020.6504217
5-TSa3	-3021.506078	-3021.412907	-3021.411599	-3021.661687	-3020.6409092
5-TSa3-1	-3021.462350	-3021.370012	-3021.368703	-3021.608813	-3020.6097705
5-INa3	-3021.575729	-3021.482869	-3021.481560	-3021.725093	-3020.7190002
5-INa3-1	-3021.559844	-3021.467247	-3021.465938	-3021.709116	-3020.6998347
5-INa3-2	-3021.551189	-3021.459218	-3021.457909	-3021.693908	-3020.699753
5-INa4	-3021.614262	-3021.520834	-3021.519526	-3021.767512	-3020.7512236
5-INa4-1	-3021.573204	-3021.479770	-3021.478461	-3021.724939	-3020.709399
5-INa5	-3021.611700	-3021.519596	-3021.518287	-3021.754791	-3020.760223
5-TSa4	-3021.583488	-3021.491801	-3021.490492	-3021.727172	-3020.7328028
5-TSa4-PBE0	-3018.497033	-3018.405724	-3018.404416	-3018.635492	-3020.7328028
5-TSa4-M06	-3019.794579	-3019.702888	-3019.701579	-3019.935446	-3020.7352198
5-INa6	-3021.601659	-3021.508642	-3021.507334	-3021.747811	-3020.7525879
5-INa7	-2908.242119	-2908.153540	-2908.152232	-2908.381822	-2907.4373629
5-TSa5	-2908.234639	-2908.145894	-2908.144585	-2908.375981	-2907.4286917
5-TSa6	-3021.540997	-3021.449390	-3021.448082	-3021.687765	-3020.6947882
5-TSa6-PBE0	-3018.468946	-3018.377465	-3018.376157	-3018.617796	-3020.6930125
5-TSa6-M06	-3019.761695	-3019.671295	-3019.669987	-3019.903474	-3020.6989976
5-TSa6-1	-3021.541457	-3021.451544	-3021.450236	-3021.679703	-3020.6964792
5-INa8	-3021.575696	-3021.483730	-3021.482422	-3021.723153	-3020.7215922
5-INa8-1	-3021.586774	-3021.495615	-3021.494306	-3021.731025	-3020.7419146
6a	-1011.770725	-1011.734954	-1011.733646	-1011.850360	-1011.3625462

5-CAT-1	-2394.653836	-2394.583785	-2394.582477	-2394.776058	-2394.0664386
5-TSa7	-2394.627688	-2394.557563	-2394.556254	-2394.749644	-2394.0393605
5-INa9	-2394.661722	-2394.591225	-2394.589917	-2394.783769	-2394.0711223
5-TSa8	-3021.526793	-3021.436244	-3021.434935	-3021.665557	-3020.6748974
5-TSa9	-3021.526905	-3021.435820	-3021.434511	-3021.670331	-3020.6690804
5-INa10	-2394.634563	-2394.563204	-2394.561896	-2394.766754	-2394.0361613
5-TSa8-1	-3021.507340	-3021.415812	-3021.414504	-3021.658469	-3020.6480674
5-TSa9-1	-3021.563429	-3021.471240	-3021.469931	-3021.709625	-3020.7067859
5-INa11	-3021.561136	-3021.468774	-3021.467466	-3021.706558	-3020.704447
5-INa12	-3021.551189	-3021.459218	-3021.457909	-3021.693908	-3020.699753
5-TSa10	-3021.514395	-3021.421505	-3021.420197	-3021.666705	-3020.652239
5-TSa10-1	-3021.534461	-3021.443113	-3021.441805	-3021.675652	-3020.680807

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

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

$H_{T°C}$ = Sum of electronic and thermal enthalpies calculated by B3LYP-D3 in solvent

$G_{T°C}$ = Sum of electronic and thermal free energies calculated by B3LYP-D3 in solvent

$E_{(M06)}$ = Single point energies calculated by M06-D3 in solvent

Section 7. Calculated imaginary frequencies of all transition states species

Species	Frequency
1-TSa1-A	-210.92
1-TSa1-A-1	-300.13
1-TSa1-A-2	-274.10
1-TSa1-A-3	-305.93
1-TSa1-A-4	-210.89
1-TSa1-A-PBE0	-241.61
1-TSa1-A-M06	-191.69
1-TSa1-1-A	-269.62

1-TSa1-1-A-1	-261.92
1-TSa1-1-A-2	-257.92
1-TSa1-2-A	-298.35
1-TSa1-2-A-1	-298.29
1-TSa1-B	-226.23
1-TSa1-B-PBE0	-193.31
1-TSa1-B-M06	-171.78
1-TSa1-1-B	-195.12
1-TSa1-1-B-1	-181.85
1-TSa1-1-B-2	-81.18
1-TSa1-2-B	-167.31
1-TSa1-2-B-1	-167.13
1-TSa2-A	-311.52
1-TSa2-A-1	-307.73
1-TSa2-A-PBE0	-270.34
1-TSa2-A-M06	-240.93
1-TSa2-C	-282.34
1-TSa2-C-1	-287.47
1-TSa2-C-PBE0	-269.89
1-TSa2-C-M06	-231.54
1-TSa2-B	-146.61
1-TSa2-1-B	-210.72
1-TSa3-B	-324.21
1-TSa3-1-B	-317.14
1-TSa4-A	-343.12
1-TSb1-A	-245.66
1-TSb1-A-1	-278.23
1-TSb1-B	-225.36
1-TSc1-A	-250.26
1-TSc1-A-1	-249.99
1-TSc1-B	-216.07
1-TSd1-A	-229.74
1-TSd1-B	-135.20
1-TSd1-B-1	-230.56
1-TSd1-B-2	-231.78
1-TSd1-B-3	-128.98
1-TSe1-A	-284.06
1-TSe1-A-1	-331.47
1-TSe1-B	-188.36
1-TSe1-B-1	-206.76
1-TSe1-B-2	-206.73
1-TSe1-B-3	-249.63
1-TSf1-A	-226.73

1-TSf1-B	-186.15
50-1-TSa1-A	-211.16
50-1-TSa1-B	-186.40
50-1-TSa2-A	-311.52
50-1-TSa4-B	-356.10
2-TSa1-A	-225.05
2-TSa1-A-1	-295.69
2-TSa1-A-2	-257.60
2-TSa1-B	-249.85
2-TSa2-A	-330.90
2-TSa4-B	-280.16
3-TSa1-A	-299.09
3-TSa1-B	-222.03
3-TSa1-B-1	-221.91
3-TSa2-A	-315.21
3-TSa4-B	-349.54
4-TSa1-A	-279.33
4-TSa1-A-1	-295.21
4-TSa1-B	-214.70
4-TSa2-A	-314.35
4-TSa4-B	-348.66
5-TSa1	-687.88
5-TSa2	-552.37
5-TSa2-1	-265.26
5-TSa2-2	-349.48
5-TSa3	-437.67
5-TSa3-1	-120.47
5-TSa4	-192.28
5-TSa4-PBE0	-175.16
5-TSa4-M06	-123.42
5-TSa5	-679.22
5-TSa6	-258.70
5-TSa6-PBE0	-211.76
5-TSa6-M06	-155.06
5-TSa6-1	-311.50
5-TSa7	-275.12
5-TSa8	-552.64
5-TSa9	-729.22
5-TSa8-1	-385.52
5-TSa9-1	-687.73
5-TSa10	-258.26
5-TSa10-1	-334.92