

## *Supporting Information*

### **Computational Study of Catalyst-Controlled Regiodivergent Pathways in Hydroboration of 1,3-Dienes: Mechanism and Origin of Regioselectivity**

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<sup>#</sup> These authors contributed equally.

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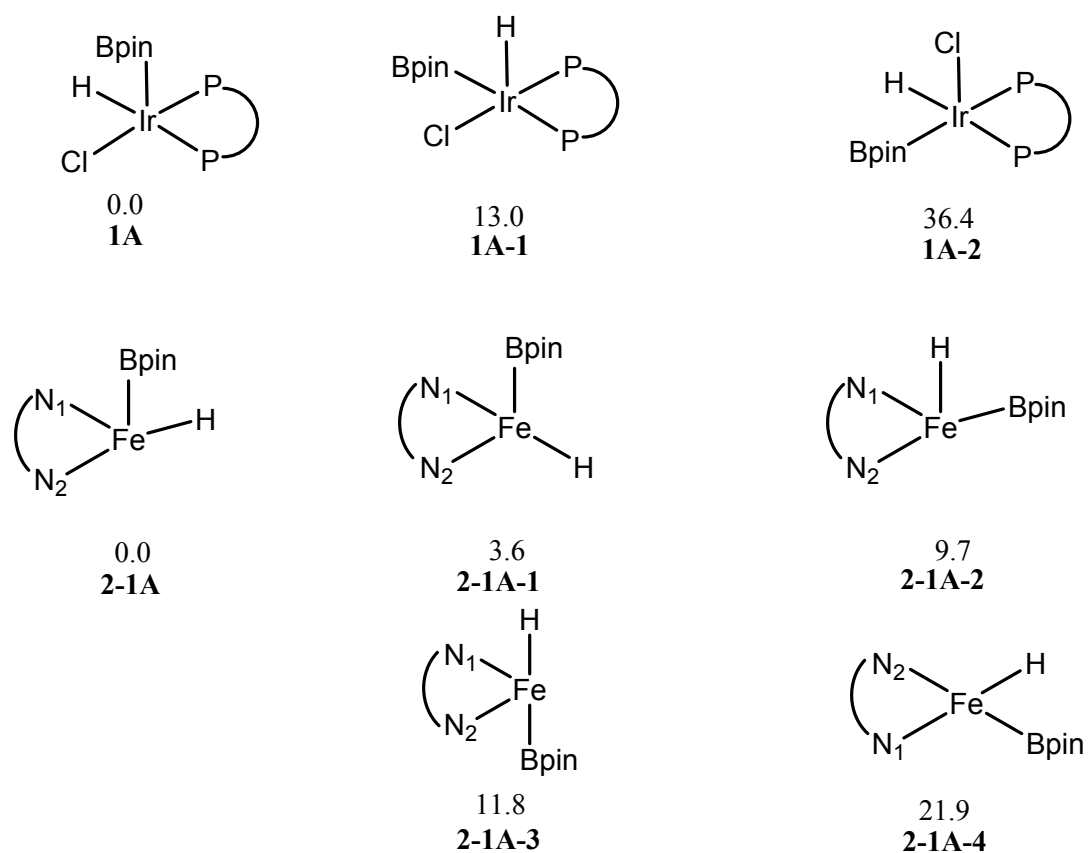
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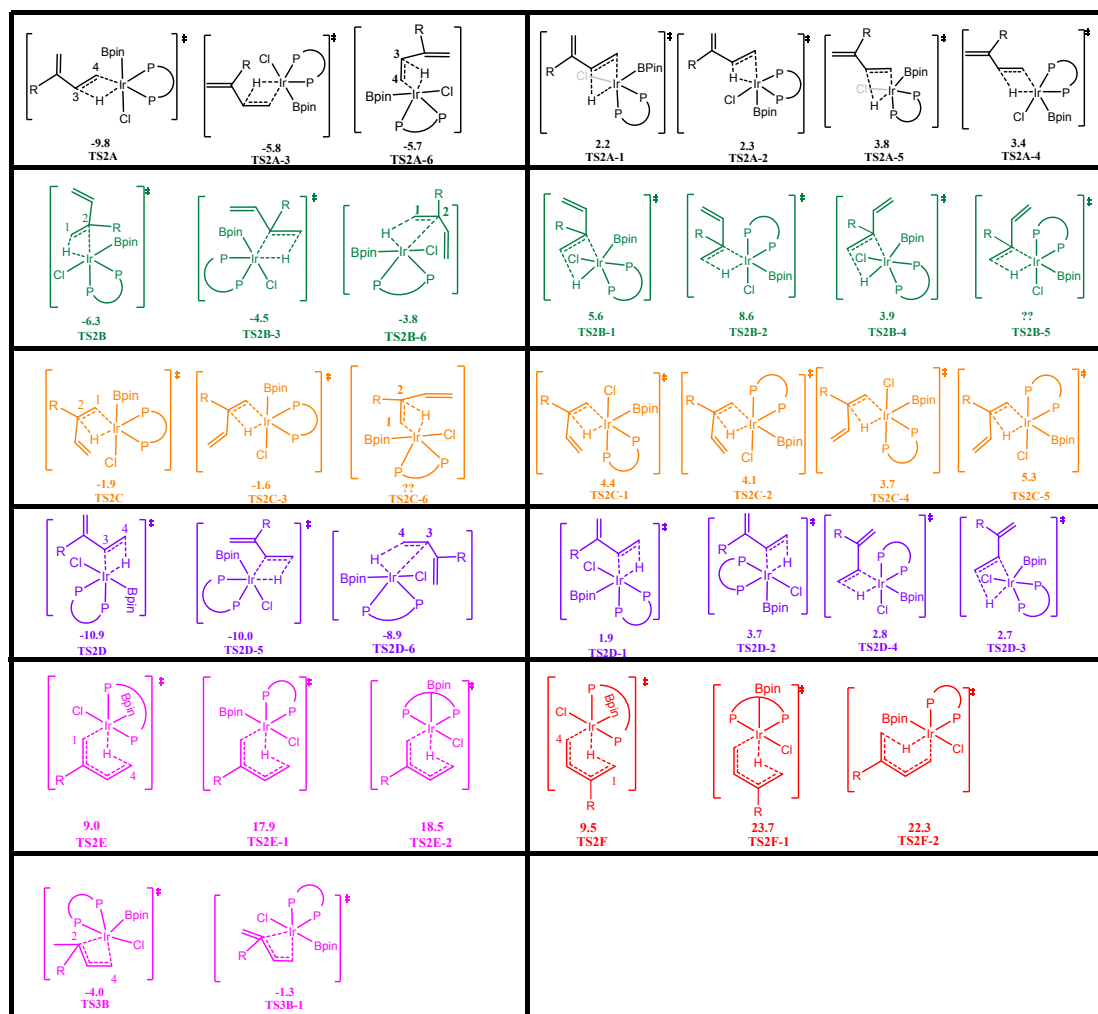
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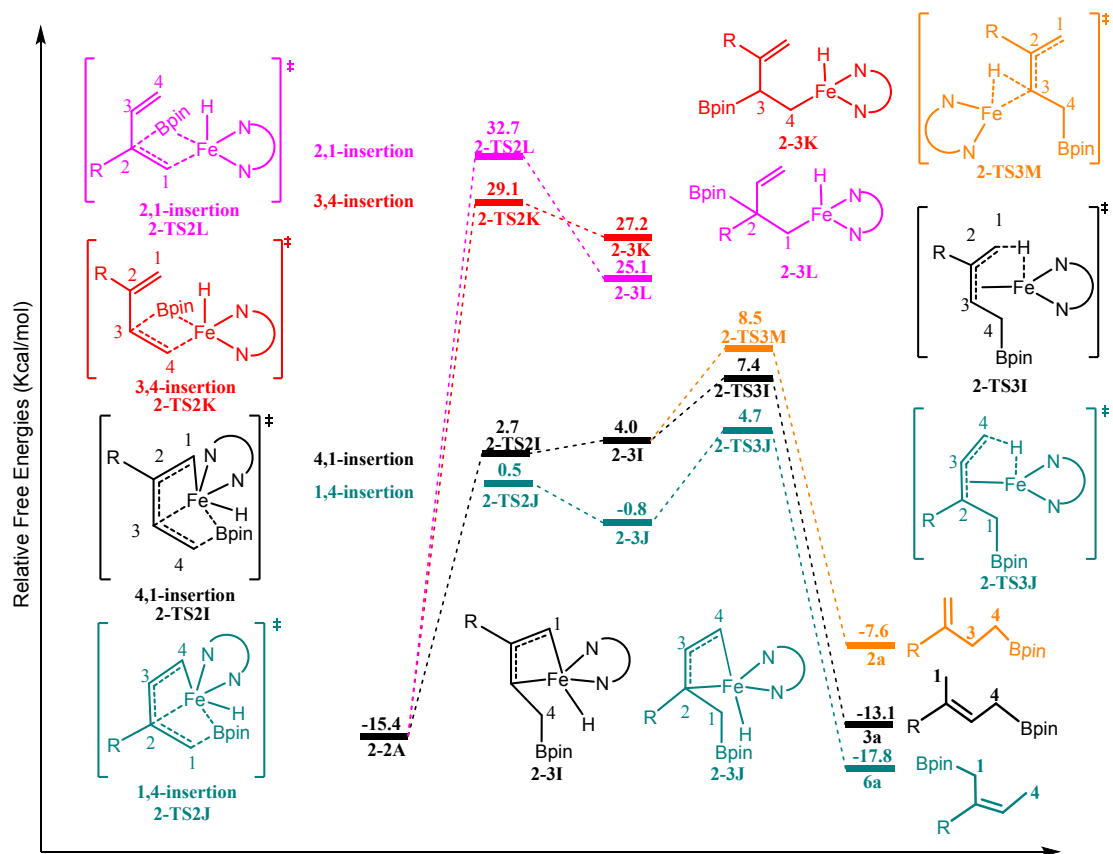
## Section 1. Other possible pathways



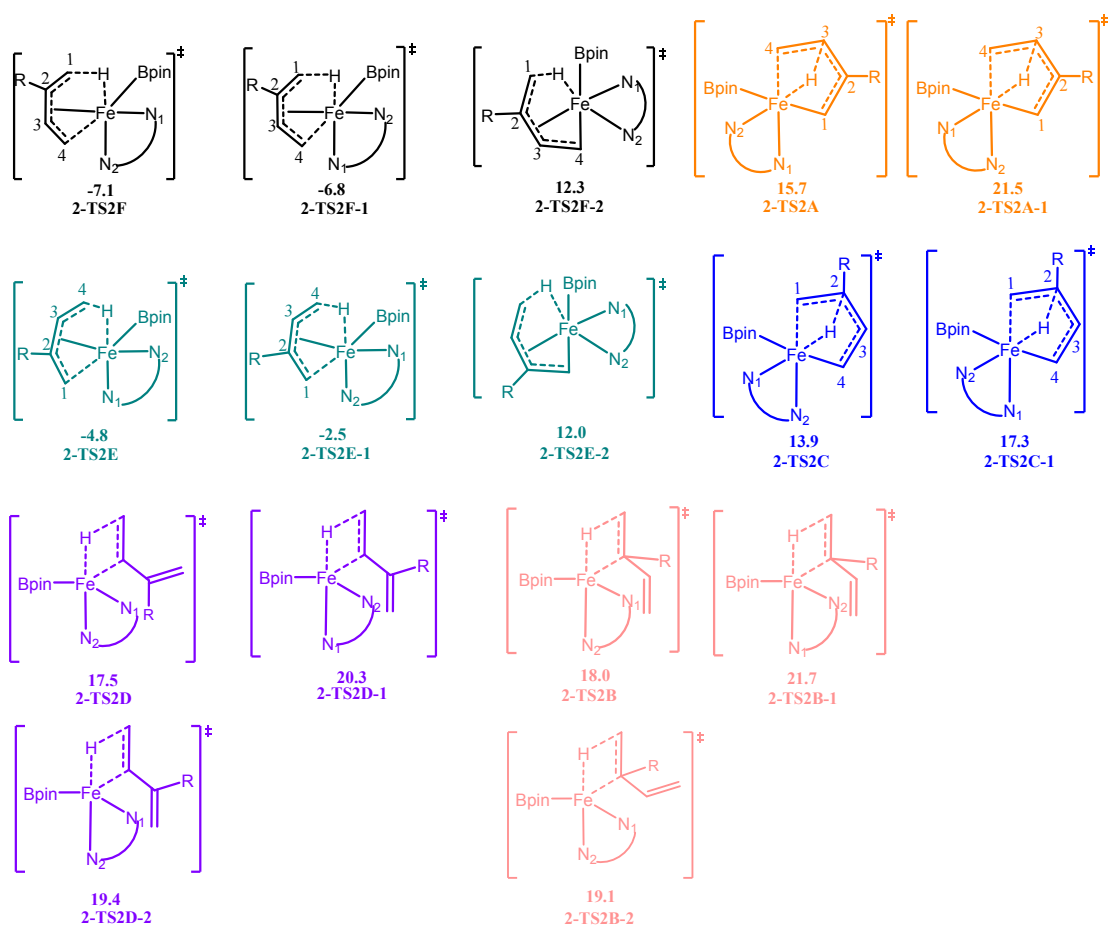
**Fig. S1** Other possible isomers of **1A** and **2-1A**. Values shown are relative free energies in kcal/mol.



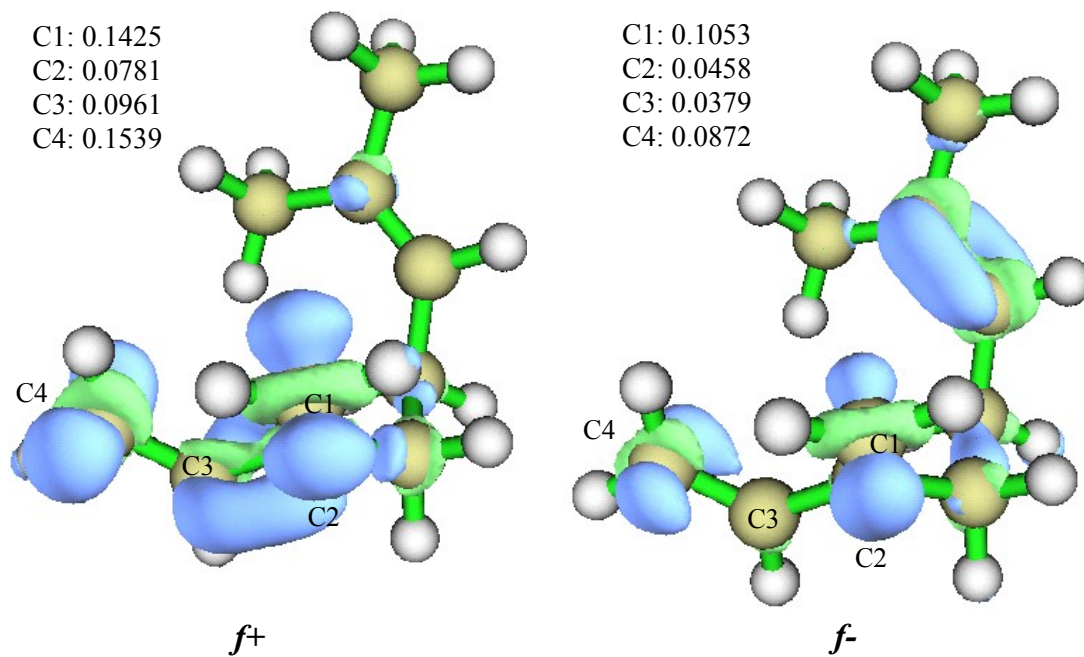
**Fig. S2** Other possible isomers of key species labeled in Fig. 1. Values shown are relative free energies in kcal/mol.



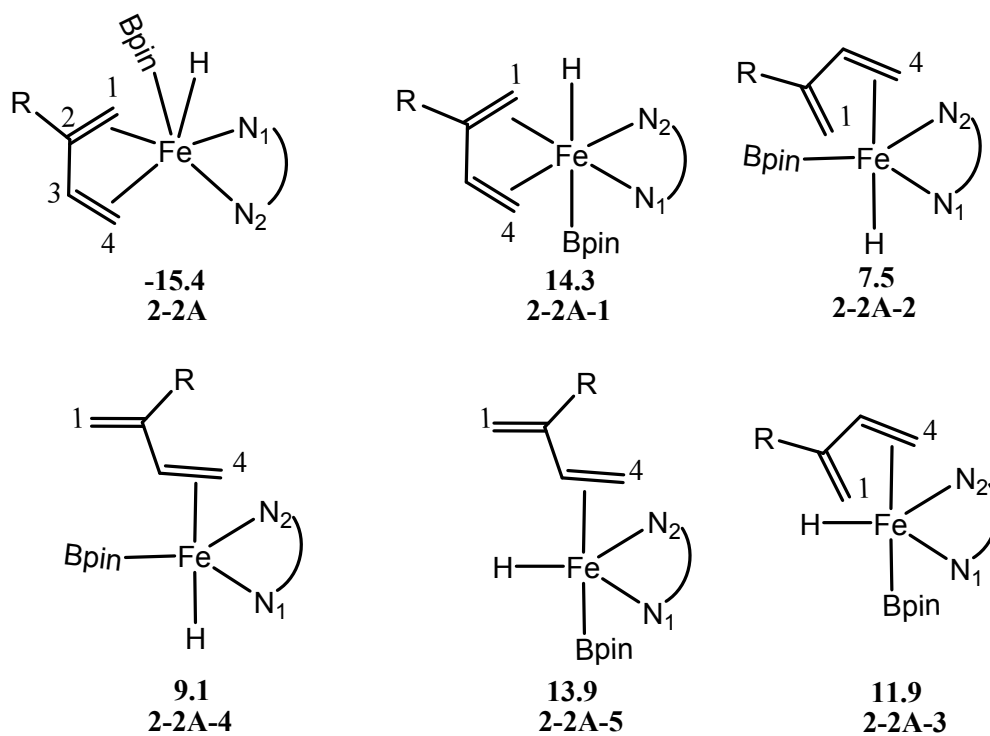
**Fig. S3** Calculated energy profiles for iron-catalyzed hydroboration of 2-substituted 1,3-dienes (boryl group migration precedes hydrogen migration). Values shown are relative free energies in kcal/mol.



**Fig. S4** Other possible isomers of key species labeled in Fig. 5. Values shown are relative free energies in kcal/mol.



**Fig. S5** The 3D representation Fukui function of **1a**.



**Fig. S6** Other possible isomers of **2-2A**. Values shown are relative free energies in kcal/mol.



**Fig. S7** Other possible conformers of key species labeled in Fig. 1 and Fig. 5. Values shown are relative free energies in kcal/mol.

## Section 2. Table of energy values.

**Table S1.** Energies (in Hartree) of All TS and Intermediates.

Geometry	$E_0$	$E$	$H_{298.15}$	$G_{298.15}$	$E_{(sol,M06)}$
1a	-390.412480	-390.400430	-390.400430	-390.450953	-390.2383936
TS2A	-3054.623701	-3054.572337	-3054.571399	-3054.713372	-3053.836983
TS2B	-3054.612420	-3054.560897	-3054.559959	-3054.701136	-3053.831454
TS2C	-3054.612146	-3054.560848	-3054.559910	-3054.699129	-3053.824453

TS2D	-3054.622855	-3054.571423	-3054.570485	-3054.711177	-3053.839468
TS2E	-3054.589106	-3054.537917	-3054.536979	-3054.677634	-3053.806948
TS2F	-3054.589125	-3054.537903	-3054.536965	-3054.677775	-3053.806191
TS3A	-3054.631216	-3054.580413	-3054.579475	-3054.720698	-3053.839268
TS3B	-3054.608081	-3054.557094	-3054.556156	-3054.693309	-3053.827723
TS3C	-3054.624226	-3054.573308	-3054.572370	-3054.713595	-3053.835378
TS3D	-3054.614842	-3054.563973	-3054.563035	-3054.701415	-3053.833102
TS4B	-3054.641825	-3054.589994	-3054.589056	-3054.733474	-3053.848305
TS4D	-3054.633124	-3054.581132	-3054.580194	-3054.725525	-3053.849418
TS3H	-3054.602921	-3054.551914	-3054.550976	-3054.689235	-3053.815016
TS3G	-3054.593967	-3054.542735	-3054.541797	-3054.680556	-3053.81228
2A	-3054.631288	-3054.579813	-3054.578875	-3054.719385	-3053.839819
3A	-3054.645482	-3054.594472	-3054.593534	-3054.734328	-3053.843348
2B	-3054.624345	-3054.572645	-3054.571707	-3054.712069	-3053.837215
3C	-3054.647726	-3054.596258	-3054.595320	-3054.738363	--3053.853902
5a-Ir	-3054.655827	-3054.603025	-3054.602087	-3054.753732	-3053.837729
3D	-3054.627779	-3054.576164	-3054.575227	-3054.715612	-3053.842861
4D	-3054.648874	-3054.596946	-3054.596008	-3054.738169	-3053.858734
5D	-3054.665675	-3054.614341	-3054.613403	-3054.754833	-3053.865868
6a-Ir	-3054.662174	-3054.610736	-3054.609798	-3054.757887	-3053.84947
6D	-3054.656779	-3054.606031	-3054.605093	-3054.743961	-3053.863246
3B	-3054.616707	-3054.565161	-3054.564223	-3054.704144	-3053.833264
4B	-3054.632822	-3054.580970	-3054.580032	-3054.723040	-3053.852273
5B	-3054.759056	-3054.614918	-3054.615855	-3054.667940	-3053.868022
6B	-3054.664015	-3054.612166	-3054.611229	-3054.753255	-3053.863387
3E	-3054.640922	-3054.583575	-3054.582583	-3054.737669	-3053.850929
3F	-3054.648020	-3054.596416	-3054.595478	-3054.737089	-3053.847749
4a-Ir	-3054.649468	-3054.597562	-3054.596624	-3054.743575	-3053.845158
3a-Ir	-3054.663089	-3054.610551	-3054.609613	-3054.758217	-3053.851481
2a-Ir	-3054.664930	-3054.613317	-3054.612380	-3054.756832	-3053.871353
7a-Ir	-3054.656765	-3054.603944	-3054.603006	-3054.754757	-3053.845083
1A	-2664.235079	-2664.196136	-2664.195198	-2664.309012	-2663.613132
TS2I	-3054.618598	-3054.567979	-3054.567041	-3054.706307	-3053.828978
TS2J	-3054.607204	-3054.556240	-3054.555303	-3054.694751	-3053.822934
TS2K	-3054.593352	-3054.542805	-3054.541867	-3054.679736	-3053.80872
TS2L	-3054.592449	-3054.541284	-3054.540347	-3054.681548	-3053.805927
TS2M	-3054.565621	-3054.514240	-3054.513302	-3054.656925	-3053.775593
TS2N	-3054.551121	-3054.500166	-3054.499228	-3054.637387	-3053.770315
3I	-3054.634135	-3054.582934	-3054.581996	-3054.723648	-3053.838000
3J	-3054.626165	-3054.575561	-3054.574623	-3054.714660	-3053.832186
3K	-3054.645436	-3054.593839	-3054.592901	-3054.737029	-3053.838258
3L	-3054.626109	-3054.574848	-3054.574848	-3054.715386	-3053.827716



3M	-3054.658083	-3054.606792	-3054.605854	-3054.750767	-3053.851227
3N	-3054.667258	-3054.616752	-3054.615814	-3054.755888	-3053.867316
Cat-Ir	-2252.519992	-2252.491986	-2252.491048	-2252.582470	-2252.016358
2-2A	-1925.572370	-1925.524116	-1925.523178	-1925.659348	-1924.845621
2-TS2F	-1925.553229	-1925.505086	-1925.504148	-1925.642370	-1924.832331
2-TS2E	-1925.552493	-1925.504542	-1925.503604	-1925.640618	-1924.834712
2-TS2D	-1925.529950	-1925.481258	-1925.480320	-1925.618846	-1924.79315
2-TS2C	-1925.520926	-1925.473481	-1925.472543	-1925.607627	-1924.799294
2-TS2B	-1925.531255	-1925.483304	-1925.483304	-1925.617725	-1924.794653
2-TS2A	-1925.522475	-1925.475035	-1925.474097	-1925.608402	-1924.796002
2-3F	-1925.569379	-1925.520944	-1925.520006	-1925.655049	-1924.834225
2-3E	-1925.570481	-1925.522591	-1925.521653	-1925.659751	-1924.836841
2-3D	-1925.559046	-1925.510424	-1925.509486	-1925.647242	-1924.824965
2-3C	-1925.532401	-1925.484338	-1925.483400	-1925.620132	-1924.794746
2-3B	-1925.558279	-1925.510007	-1925.509069	-1925.644277	-1924.824788
2-3A	1925.537087	-1925.488036	-1925.487099	-1925.626964	-1924.796582
2-TS3F	-1925.556825	-1925.508743	-1925.507805	-1925.643637	-1924.818113
2-TS3E	-1925.544867	-1925.497170	-1925.496233	-1925.629252	-1924.810113
2-TS3A	-1925.519823	-1925.471137	-1925.470200	-1925.609708	-1924.775571
2-TS3G	-1925.514660	-1925.466203	-1925.465266	-1925.602737	-1924.778999
2-TS3H	-1925.503408	-1925.455148	-1925.454210	-1925.589443	-1924.773496
3a-Fe	-2316.015103	-2315.952748	-2315.951810	-2316.133569	-2315.079565
4a-Fe	-2316.000106	-2315.938811	-2315.937873	-2316.111355	-2315.064382
6a-Fe	-2316.017155	-2315.953753	-2315.952815	-2316.139637	-2315.087045
7a-Fe	-2316.008406	-2315.948122	-2315.947184	-2316.119634	-2315.072347
2a-Fe	-2316.011040	-2315.952247	-2315.951309	-2316.123795	-2315.070831
1A-1	-2664.222033	-2664.182965	-2664.182028	-2664.297486	-2663.592464
1A-2	-2664.179036	-2664.135782	-2664.134790	-2664.259918	-2663.555102
2-1A	-1535.101218	-1535.064893	-1535.063955	-1535.174535	-1534.521886
2-1A-1	-1535.091639	-1535.055428	-1535.054490	-1535.054490	-1534.516118
2-1A-2	-1535.088477	-1535.052104	-1535.051166	-1535.161035	-1534.50638
2-1A-3	-1535.083003	-1535.046522	-1535.045584	-1535.156966	-1534.502916
2-1A-4	-1535.075218	-1535.039587	-1535.038649	-1535.147080	-1534.486945
TS2B-4	-3054.595961	-3054.544473	-3054.543535	-3054.685421	-3053.815125
TS2C-1	-3054.599708	-3054.547910	-3054.546973	-3054.689190	-3053.814361
TS2C-2	-3054.601202	-3054.549743	-3054.548805	-3054.689239	-3053.814767
TS2C-3	-3054.612859	-3054.561797	-3054.560859	-3054.699208	-3053.823928
TS2C-4	-3054.603594	-3054.552046	-3054.551109	-3054.691427	-3053.815483
TS2C-5	-3054.601103	-3054.549946	-3054.549008	-3054.687938	-3053.812871
TS2D-1	-3054.606294	-3054.555661	-3054.554723	-3054.693428	-3053.818329
TS2D-2	-3054.600166	-3054.549162	-3054.548224	-3054.687085	-3053.815829
TS2D-3	-3054.606453	-3054.555381	-3054.554443	-3054.694197	-3053.816985
TS2D-4	-3054.607389	-3054.555926	-3054.554988	-3054.696055	-3053.816884

TS2D-5	-3054.622410	-3054.571225	-3054.570288	-3054.710956	-3053.837285
TS2E-1	-3054.589787	-3054.538642	-3054.537704	-3054.677554	-3053.792773
TS-2E-2	-3054.585621	-3054.534135	-3054.533197	-3054.674689	-3053.791923
TS-2F-1	-3054.582117	-3054.530588	-3054.529650	-3054.671872	-3053.78358
2-TS2J	-1925.553367	-1925.506111	-1925.505173	-1925.636169	-1924.820267
2-TS2I	-1925.558072	-1925.510470	-1925.510470	-1925.643618	-1924.816845
2-TS2K	-1925.430365	-1925.388161	-1925.387223	-1925.505807	-1924.774713
2-TS2L	-1925.514269	-1925.466084	-1925.465146	-1925.600856	-1924.76898
2-3I	-1925.562244	-1925.513920	-1925.507341	-1925.597966	-1924.81455
2-3J	-1925.566159	-1925.517942	-1925.517004	-1925.652551	-1924.822322
2-3K	-1925.530733	-1925.482126	-1925.481188	-1925.620280	-1924.777779
2-3L	-1925.533199	-1925.484351	-1925.483413	-1925.622711	-1924.781101
2-TS3I	-1925.546710	-1925.498630	-1925.497692	-1925.634197	-1924.809297
2-TS3J	-1925.552300	-1925.504373	-1925.503436	-1925.638396	-1924.813617
2-TS3M	-1925.548877	-1925.500898	-1925.499961	-1925.636119	-1924.807536
HBpin-Fe	-411.679864	-411.670466	-411.669528	-411.712675	-411.5623539
HBpin-Ir	-411.679864	-411.670466	-411.669528	-411.712675	-411.5619787
Fe(1a)	-1513.875601	-1513.837591	-1513.836654	-1513.952151	-1513.258715
TS1	-2664.205512	-2664.167371	-2664.166433	-2664.278536	-2663.582401
Pre1	-2664.206615	-2664.167353	-2664.166415	-2664.283322	-2663.583492
TS2B-3	-3054.613103	-3054.562112	-3054.561175	-3054.698324	-3053.828534
TS2A-1	-3054.606143	-3054.554932	-3054.553994	-3054.693858	-3053.81793
TS2A-2	-3054.606199	-3054.555139	-3054.554201	-3054.693428	-3053.817704
TS2A-3	-3054.622755	-3054.571364	-3054.570426	-3054.711979	-3053.830612
TS2A-4	-3054.606551	-3054.555446	-3054.554508	-3054.693797	-3054.606551
TS2A-5	-3054.606561	-3054.555370	-3054.554432	-3054.694977	-3053.815957
TS3B-1	-3054.604298	-3054.552929	-3054.551991	-3054.691649	-3053.823379
TS2F-1	-3054.585626	-3054.534328	-3054.533391	-3054.674362	-3053.785816
TS2B-1	-3054.595819	-3054.544509	-3054.543571	-3054.682847	-3053.812455
TS2B-2	-3054.594058	-3054.542675	-3054.541737	-3054.680983	-3053.807715
2-TS2E-1	-1925.548164	-1925.500344	-1925.499406	-1925.633096	-1924.825045
2-TS2E-2	-1925.523529	-1925.475402	-1925.474464	-1925.608516	-1924.802012
2-TS2F-1	-1925.499388	-1925.452663	-1925.451726	-1925.583455	-1924.831934
2-TS2F-2	-1925.507627	-1925.460876	-1925.459939	-1925.590115	-1924.801421
2-TS2D-1	-1925.533933	-1925.486950	-1925.486012	-1925.618946	-1924.788707
2-TS2C-1	-1925.522106	-1925.475750	-1925.474812	-1925.604639	-1924.793481
2-TS2B-1	-1925.527382	-1925.479466	-1925.478528	-1925.612472	-1924.786435
2-TS2A-1	-1925.522974	-1925.474226	-1925.473288	-1925.611691	-1924.786831
2-2A-1	-1925.522694	-1925.475238	-1925.474300	-1925.606843	-1924.798216
2-2A-2	-1925.540403	-1925.491422	-1925.490485	-1925.632070	-1924.809127
2-2A-3	-1925.538156	-1925.538156	-1925.488901	-1925.627705	-1924.80205
2-2A-4	-1925.537974	-1925.489302	-1925.488364	-1925.625593	-1924.806588
2-2A-5	-1925.536582	-1925.489230	-1925.488293	-1925.621608	-1924.798981

TS2A-6	-3054.621757	-3054.571059	-3054.570121	-3054.709994	-3053.830399
TS2B-6	-3054.573314	-3054.523329	-3054.522391	-3054.659085	-3053.827349
TS2D-6	-3054.619119	-3054.567676	-3054.566738	-3054.708629	-3053.835617
2-TS2B-2	-1925.528871	-1925.480861	-1925.479924	-1925.614453	-1924.790482
2-TS2D-2	-1925.530792	-1925.483143	-1925.482205	-1925.615985	-1924.790167
TS2D-7	-3054.622522	-3054.571212	-3054.570274	-3054.710384	-3053.838665
TS2A-7	-3054.626139	-3054.575538	-3054.574601	-3054.714171	-3053.834726
TS2A-8	-3054.625858	-3054.575168	-3054.574230	-3054.574230	-3053.83593
TS2B-7	-3054.607786	-3054.556393	-3054.555455	-3054.695199	-3053.82861
TS2E-7	-3054.588376	-3054.537321	-3054.536384	-3054.675788	-3053.807035
TS2E-8	-3054.588375	-3054.537319	-3054.536382	-3054.675806	-3053.807053
TS2F-7	-3054.588308	-3054.537360	-3054.537360	-3054.675217	-3053.80546
TS2F-8	-3054.589122	-3054.537901	-3054.536964	-3054.677753	-3053.803636
2-TS2F-7	-1925.548814	-1925.500824	-1925.499886	-1925.635064	-1924.828125
2-TS2F-8	-1925.547665	-1925.499643	-1925.498705	-1925.634989	-1924.831134
2-TS2E-7	-1925.548992	-1925.500862	-1925.499924	-1925.638259	-1924.829937
2-TS2E-8	-1925.554475	-1925.507435	-1925.506497	-1925.639100	-1924.828784
2-TS2D-7	-1925.530267	-1925.484057	-1925.483119	-1925.613305	-1924.787749
2-TS2C-7	-1925.523427	-1925.475269	-1925.474331	-1925.611236	-1924.798943
2-TS2B-7	-1925.531306	-1925.484250	-1925.483312	-1925.615038	-1924.79228
2-TS2A-7	-1925.522470	-1925.475035	-1925.474097	-1925.608302	-1924.795901

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

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

$H_{298.15}$  = Sum of electronic and thermal enthalpies calculated by B3LYP in solvent

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

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

### Section 3. Calculated imaginary frequencies of all transition states species.

Species	Frequency
TS1	-23.71
TS2A	-625.18
TS3A	-238.60
TS2B	-685.07
TS3B	-157.70

TS4B	-288.38
TS2C	-612.29
TS3C	-249.30
TS2D	-652.73
TS3D	-161.19
TS4D	-241.10
TS2E	-823.80
TS2F	-837.81
TS3G	-119.40
TS3H	-272.70
TS2I	-108.08
TS2J	-109.75
TS2K	-188.12
TS2L	-191.38
TS2M	-310.06
TS2N	-493.08
2-TS2A	-743.37
2-TS2B	-882.39
2-TS2C	-522.51
2-TS2D	-881.92
2-TS2E	-1028.52
2-TS2F	-965.50
2-TS3A	-121.92
2-TS3E	-43.20
2-TS3F	-50.57
2-TS3G	-109.46
2-TS3H	-62.15
TS2A-1	-549.48
TS2A-2	-624.22
TS2A-3	-721.57
TS3B-1	-156.15
TS2B-3	-727.15
TS2B-4	-599.27
TS2C-1	-508.11
TS2C-2	-518.06
TS2C-3	-651.30
TS2C-4	-545.27
TS2C-5	-373.18
TS2D-1	-691.17
TS2D-2	-558.76
TS2D-3	-665.41
TS2D-4	-502.59
TS2D-5	-637.78

TS2E-1	-805.51
TS2E-2	-517.60
TS2F-1	-518.18
TS2F-2	-867.02
2-TS2I	-42.31
2-TS2J	-95.91
2-TS2K	-72.61
2-TS2L	-129.37
2-TS3H	-843.96
2-TS3I	-866.27
2-TS3M	-814.63
TS2A-4	-679.46
TS2A-5	-645.21
TS2B-1	-661.32
TS2B-2	-107.30
2-TS2E-1	-935.01
2-TS2E-2	-627.64
2-TS2F-1	-1007.33
2-TS2F-2	-124.66
2-TS2A-1	-696.17
2-TS2B-1	-868.38
2-TS2C-1	-544.95
2-TS2D-1	-873.34
TS2A-6	-597.01
TS2B-6	-648.51
TS2D-6	-736.44
2-TS2B-2	-909.71
2-TS2D-2	-866.25
TS2D-7	-702.18
TS2A-7	-636.49
TS2A-8	-657.08
TS2E-7	-835.38
TS2E-8	-835.24
TS2F-7	-803.24
TS2F-8	-837.61
2-TS2F-7	-999.86
2-TS2F-8	-968.86
2-TS2E-7	-1024.40
2-TS2E-8	-1019.60
2-TS2D-7	-897.93
2-TS2C-7	-531.38
2-TS2B-7	-881.19
2-TS2A-7	-743.37