

## *Supporting Information*

### **Mechanisms and Origin of Regioselectivity for Manganese-Catalyzed**

#### **Denitrogenative Annulation and Click Reactions**

Guanghui Song, Wei Rong, Yongyin Liu, and Juan Li\*

College of Chemistry and Materials Science, Guangdong Provincial Key Laboratory of Functional Supramolecular Coordination Materials and Applications, Jinan University, Guangzhou, Guangdong 510632, P. R. China

\*Corresponding author. Email: tchjli@jnu.edu.cn

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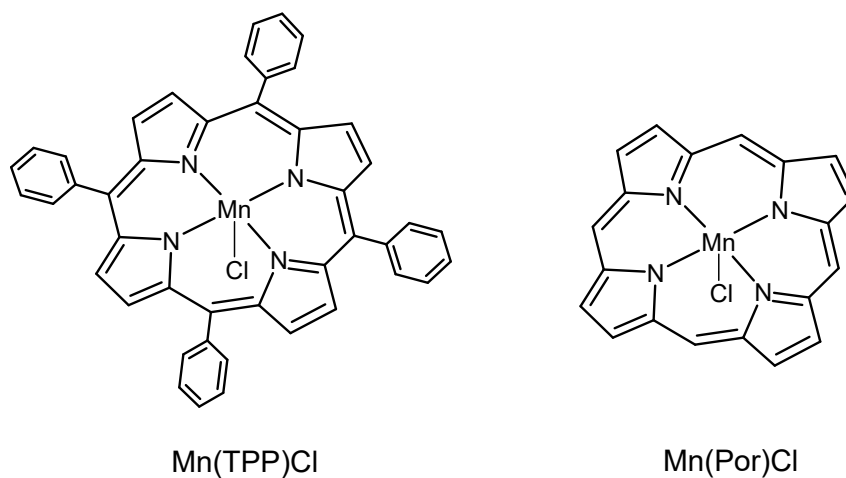
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## Section 1. Simplification of the TPP ligand

**Scheme S1** The simplification of Mn(TPP)Cl to Mn(Por)Cl.

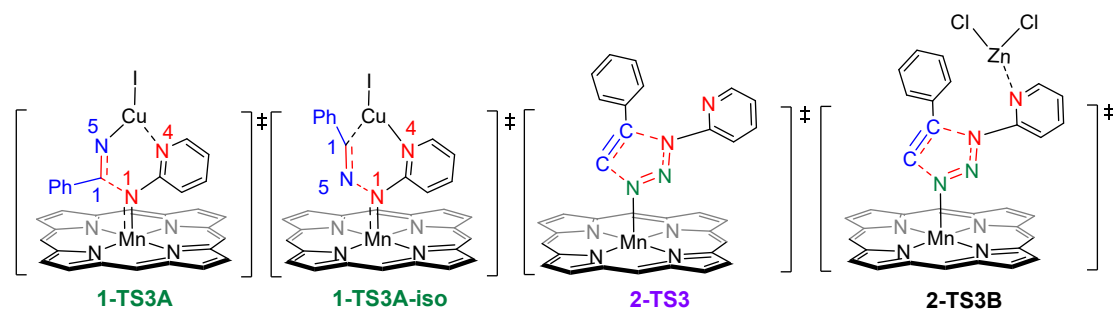


**Table S1** Relative Gibbs energies (in kcal/mol) for the regio-determining transition states with real TPP ligand.

Species	$\Delta\Delta G$
1-TS3A-TPP <sup>6</sup>	0.0
1-TS3A-TPP <sup>4</sup>	0.6
1-TS3A-iso-TPP <sup>6</sup>	16.0
1-TS3A-iso-TPP <sup>4</sup>	14.8
-----	
2-TS3B-TPP <sup>6</sup>	0.0
2-TS3B-TPP <sup>4</sup>	19.2
2-TS3-TPP <sup>6</sup>	11.6
2-TS3-TPP <sup>4</sup>	31.8

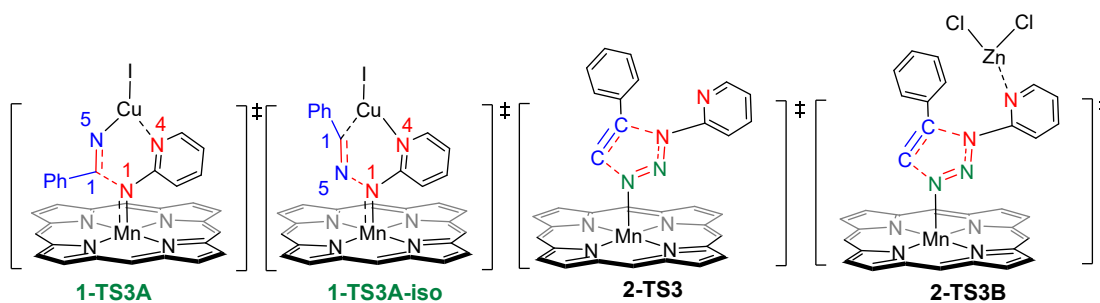
## Section 2. Optimization with B3LYP-D3, M06 and BPW91 methods

**Table S2** Relative Gibbs energies (in kcal/mol) for the regio-determining transition states with B3LYP-D3 method.



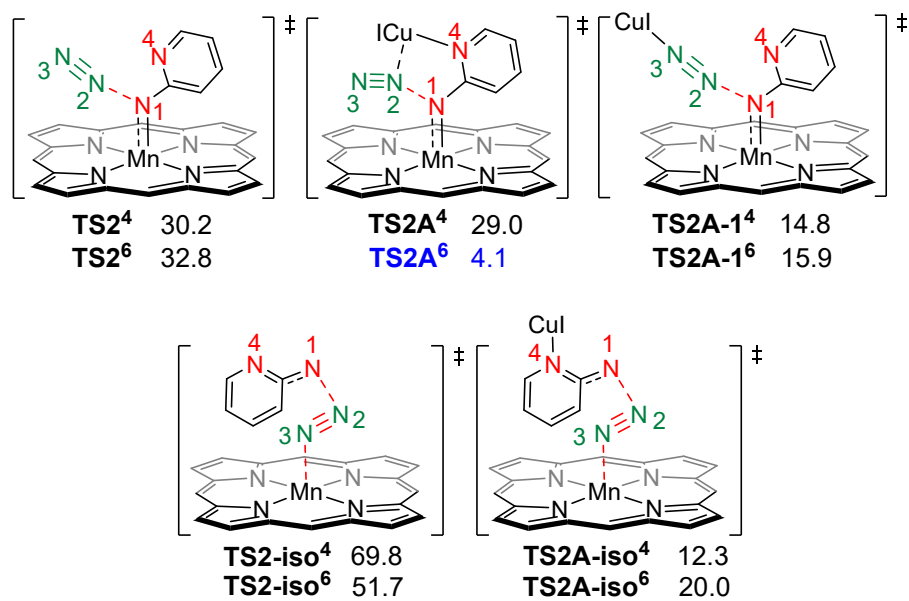
Species	$\Delta\Delta G$
1-TS3A-B3LYP-D3 <sup>4</sup>	0.0
1-TS3A-B3LYP-D3 <sup>6</sup>	0.6
1-TS3A-iso-B3LYP-D3 <sup>4</sup>	28.6
1-TS3A-iso-B3LYP-D3 <sup>6</sup>	11.8
<hr/>	
2-TS3B-B3LYP-D3 <sup>6</sup>	0.0
2-TS3B-B3LYP-D3 <sup>4</sup>	6.1
2-TS3-B3LYP-D3 <sup>6</sup>	13.4
2-TS3-B3LYP-D3 <sup>4</sup>	30.4

**Table S3** Relative Gibbs energies (in kcal/mol) for the regio-determining transition states with M06 and BPW91 methods.



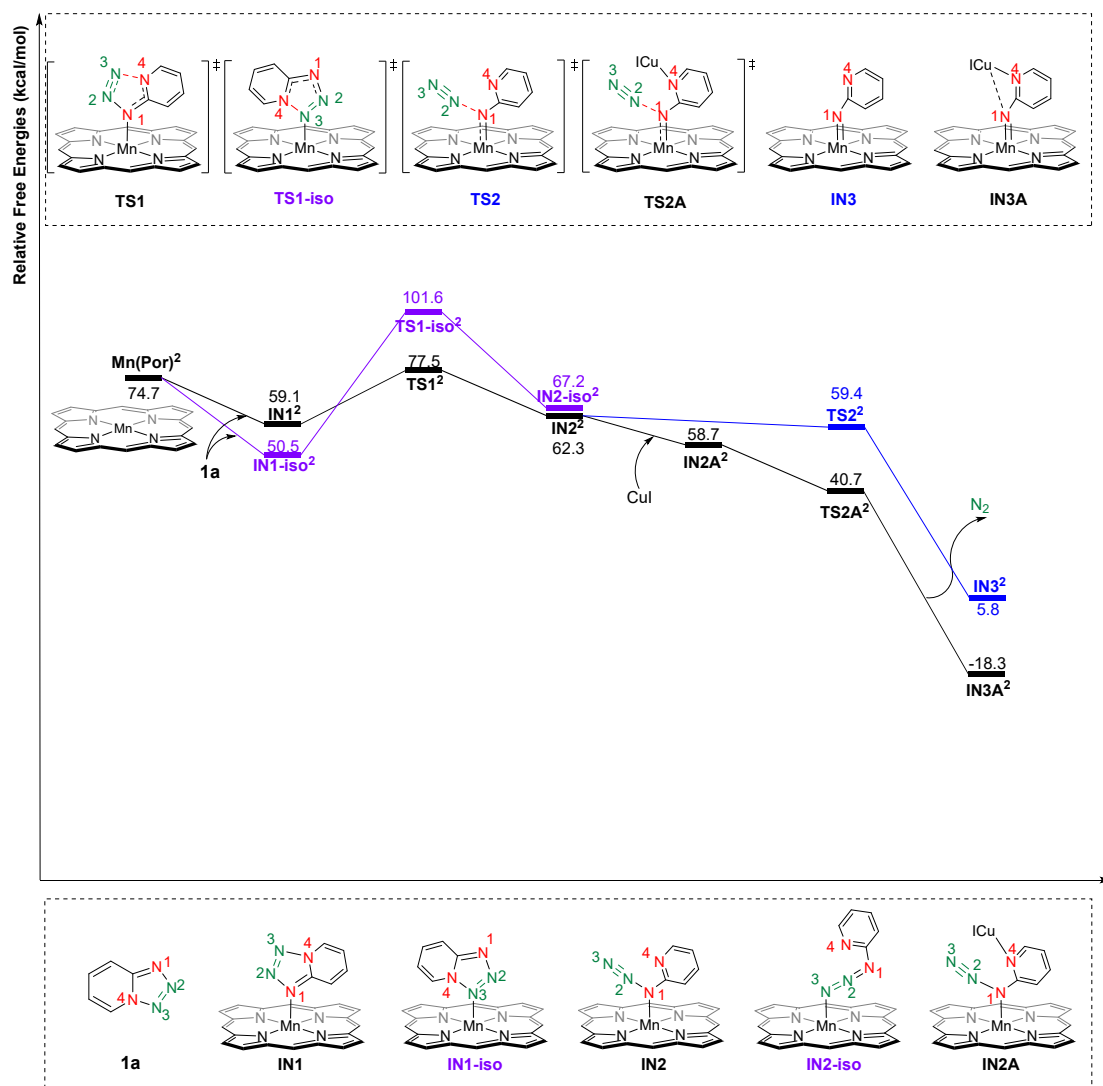
Species	$\Delta\Delta G$
1-TS3A-M06 <sup>6</sup>	0.0
1-TS3A-M06 <sup>4</sup>	29.6
1-TS3A-iso-M06 <sup>4</sup>	12.8
1-TS3A-iso-M06 <sup>6</sup>	15.6
-----	
2-TS3B-M06 <sup>6</sup>	0.0
2-TS3B-M06 <sup>4</sup>	8.5
2-TS3-M06 <sup>4</sup>	27.9
2-TS3-M06 <sup>6</sup>	14.2
-----	
1-TS3A-BPW91 <sup>6</sup>	0.0
1-TS3A-BPW91 <sup>4</sup>	11.2
1-TS3A-iso-BPW91 <sup>4</sup>	18.8
1-TS3A-iso-BPW91 <sup>6</sup>	20.4
-----	
2-TS3B-BPW91 <sup>6</sup>	0.0
2-TS3B-BPW91 <sup>4</sup>	4.9
2-TS3-BPW91 <sup>4</sup>	20.5
2-TS3-BPW91 <sup>6</sup>	4.0

### Section 3. Other possible nitrogen elimination process

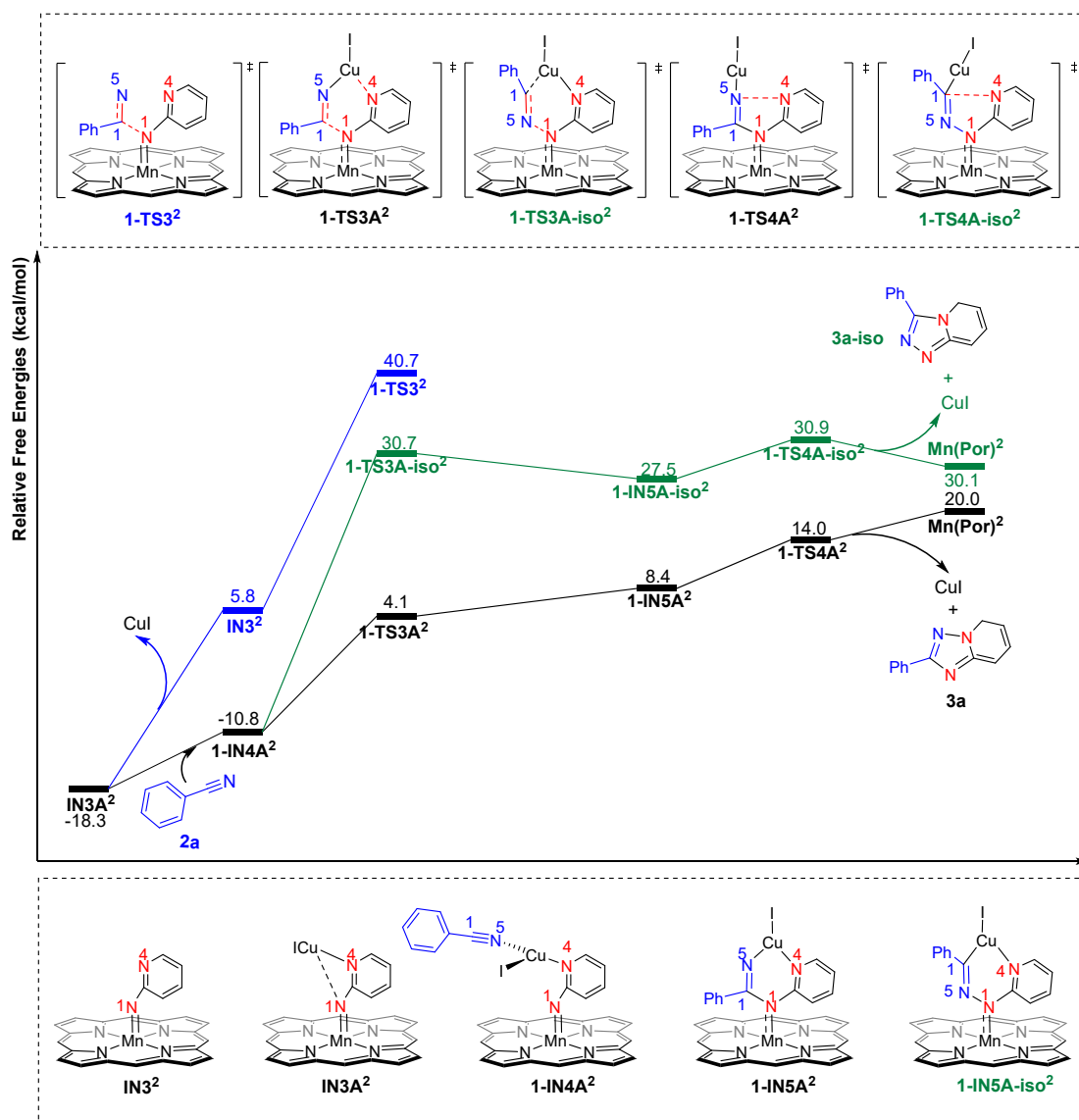


**Scheme S2** Other possible nitrogen-elimination transition state. Values shown are relative free energies in kcal/mol.

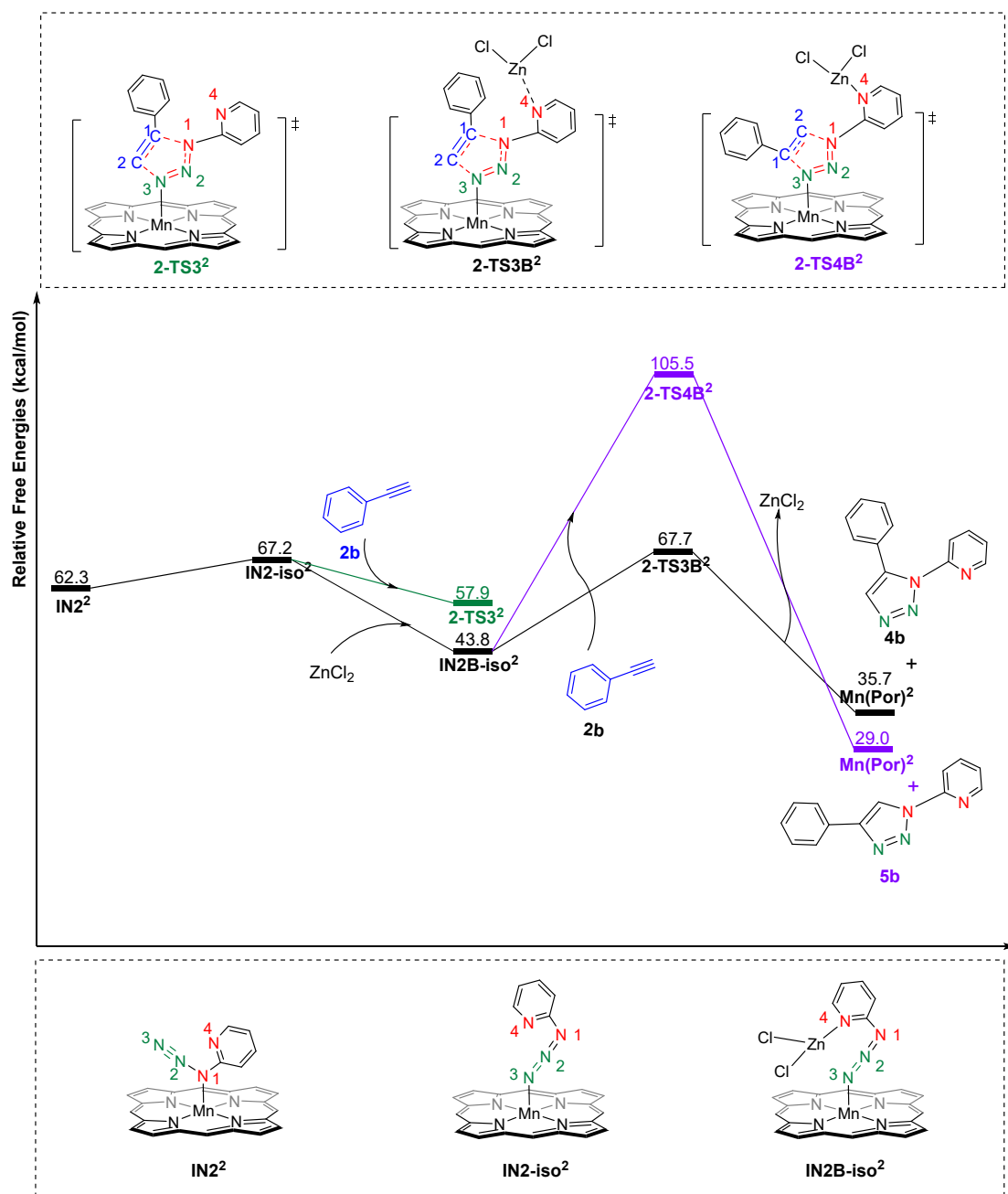
## Section 4. Mechanistic details for the doublet-state pathway



**Fig. S1** Calculated free-energy profiles for first two steps of the denitrogenative annulation along the doublet energy surface. The tetrazole ring-opening with Mn–N3 coordination is shown in purple while N<sub>2</sub> elimination without the assistance of CuI is shown in blue. The numerical values provided are relative free energies in kcal/mol.



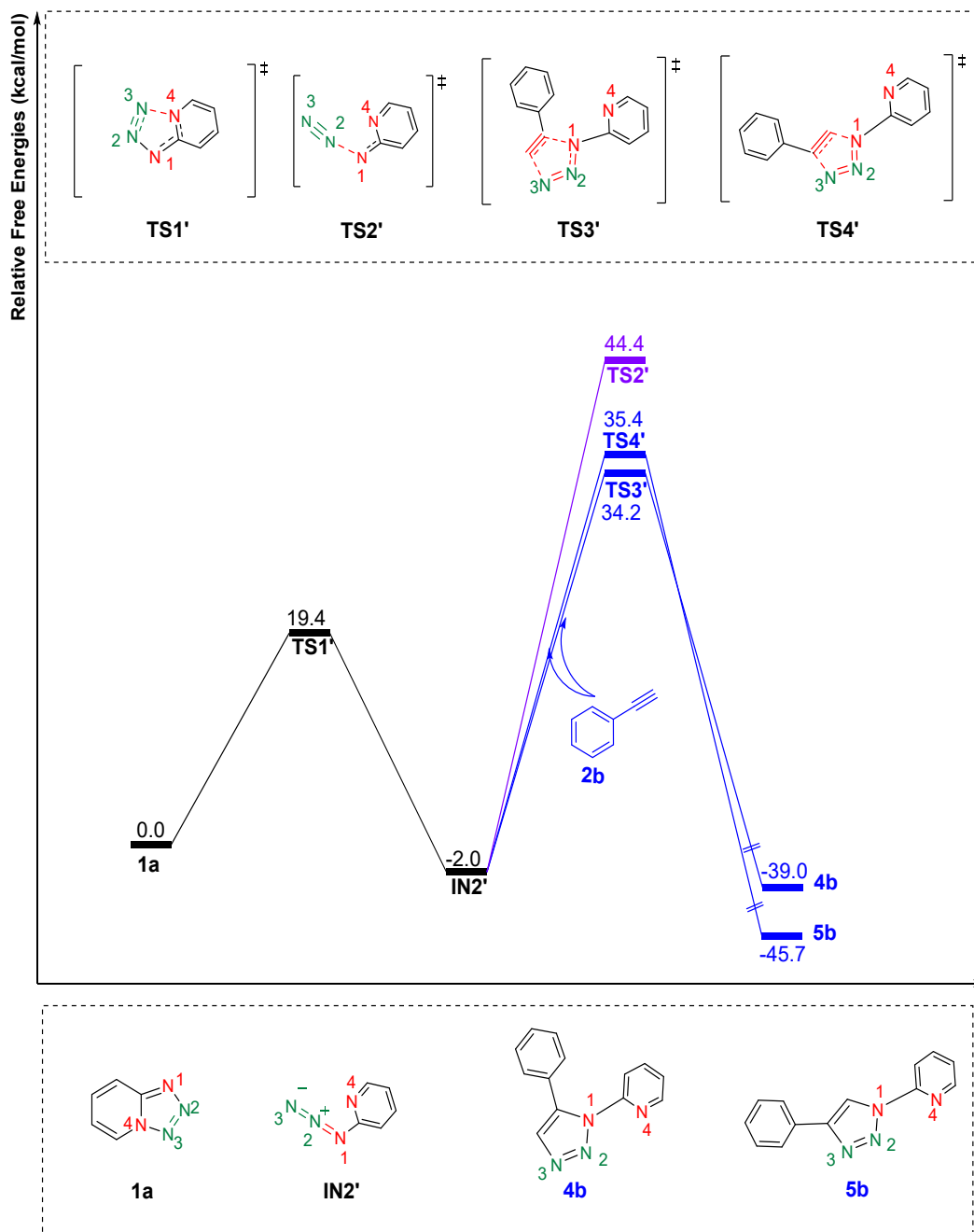
**Fig. S2** Calculated free-energy profiles for the last two steps of the denitrogenative annulation along the doublet energy surface. The pathway for the formation of regioisomer **3a-iso** is shown in green while that without the assistance of CuI is shown in blue. Numerical values are relative free energies in kcal/mol.



**Fig. S3** Calculated free energy profiles for the last two steps of the click reaction. The pathway for the formation of regioisomer **5b** is shown in purple while that without the assistance of  $\text{ZnCl}_2$  is in green. Numerical values are relative free energies in kcal/mol.

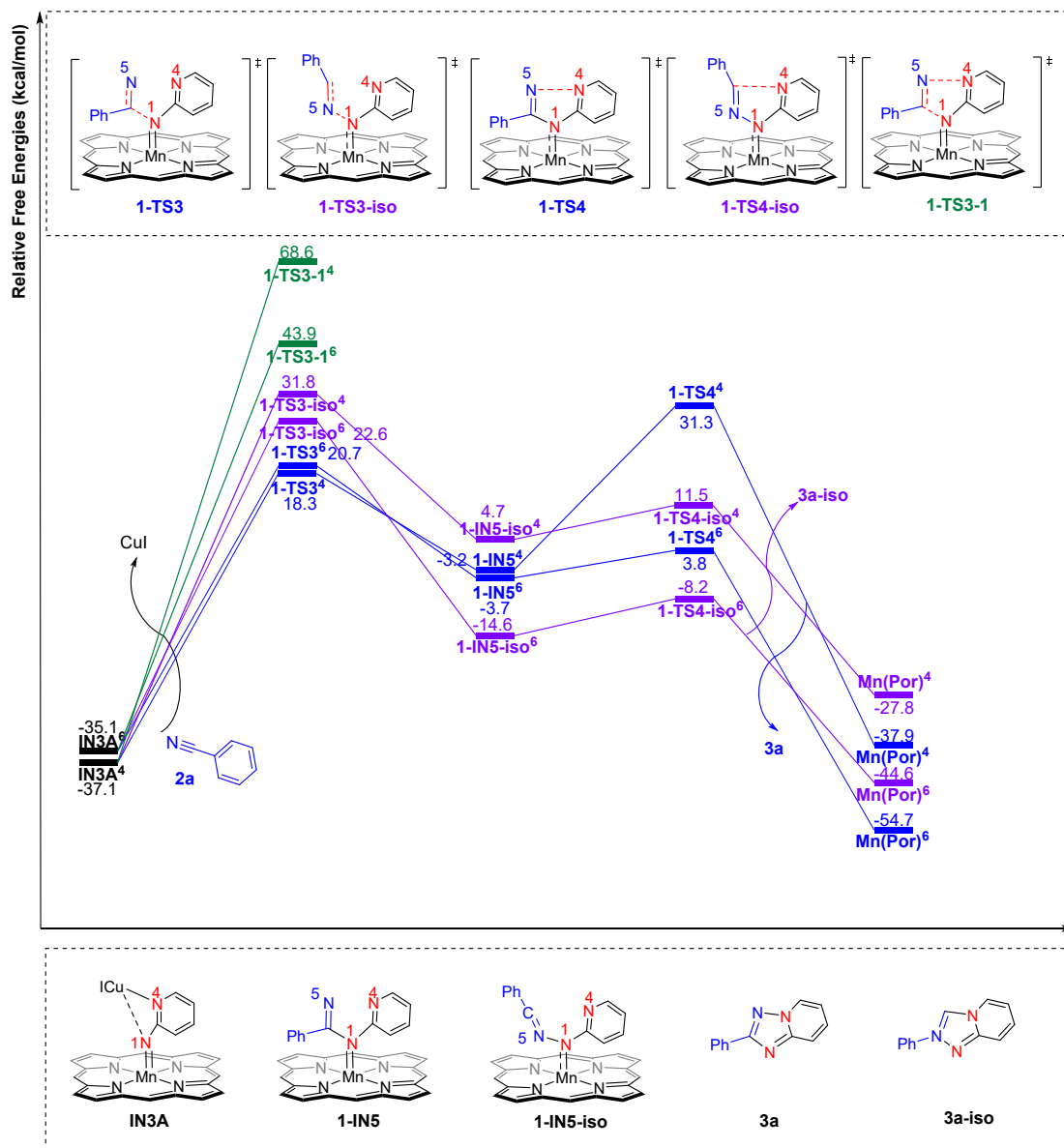
## Section 5. Pathways without the assistance of a Mn catalyst





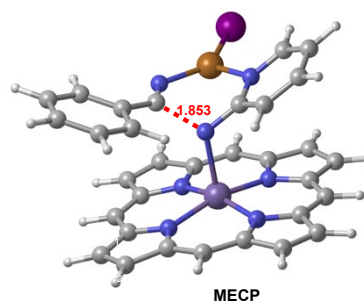
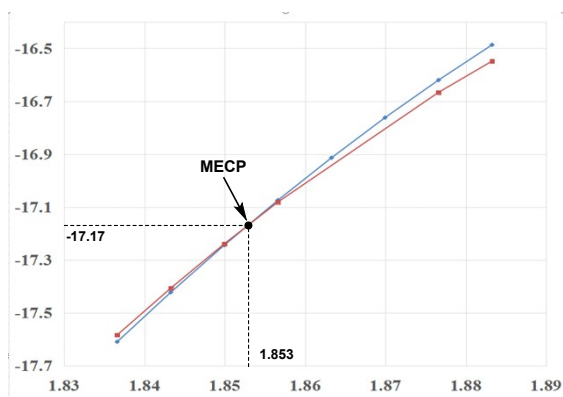
**Fig. S4** Calculated free-energy profiles for first two steps of the denitrogenative annulation and click reactions without the assistance of a Mn catalyst. The denitrogenative annulation is shown in purple while click reaction is shown in blue. The numerical values provided are relative free energies in kcal/mol.

## Section 6. Pathways without the assistance of CuI



**Fig. S5** Calculated free-energy profiles for the last two steps of the denitrogenative annulation without the assistance of CuI. The stepwise pathway for the formation of regioisomer **3a** is shown in blue while that for the formation of regioisomer **3a-iso** is shown in purple. The synergistic pathway for the formation of regioisomer **3a** is shown in green. Numerical values are relative free energies in kcal/mol.

## Section 7. Relaxed energy scans for MECF



**Fig. S6** Relaxed energy scan in the quartet (red line) and sextet (blue line) states for MECP. The structure of MECP is show. Energies are given in kcal/mol and distance in angstroms.

## Section 8. Energies (in hartree) of All TSs and Intermediate

## Solvent=benzene:

Geometry	$E_0$	$E$	$H_{373.15}$	$G_{373.15}$	$E_{(sol,M06)}$
<b>CuI</b>	-207.603212	-207.599467	-207.598285	-207.636238	-208.8312141
<b>ZnCl<sub>2</sub></b>	-986.102572	-986.098453	-986.097272	-986.134544	-1147.678568
<b>Mn(Por)<sup>2</sup></b>	-1092.064902	-1092.037791	-1092.036609	-1092.126433	-1092.2535727
<b>Mn(Por)<sup>4</sup></b>	-1092.118567	-1092.091386	-1092.090205	-1092.181133	-1092.344648
<b>Mn(Por)<sup>6</sup></b>	-1092.132870	-1092.105147	-1092.103965	-1092.196892	-1092.368084
<b>1a</b>	-411.790624	-411.781921	-411.780739	-411.830160	-411.7113978
<b>IN1<sup>2</sup></b>	-1503.890718	-1503.853810	-1503.852628	-1503.963824	-1504.0192894
<b>IN1<sup>4</sup></b>	-1503.920331	-1503.881690	-1503.880508	-1504.000530	-1504.077342
<b>IN1<sup>6</sup></b>	-1503.937695	-1503.898517	-1503.897336	-1504.018719	-1504.107253
<b>IN1-iso<sup>2</sup></b>	-1503.886219	-1503.848084	-1503.846902	-1503.962664	-1504.029473
<b>IN1-iso<sup>4</sup></b>	-1503.918491	-1503.880864	-1503.879682	-1503.996495	-1504.07341
<b>IN1-iso<sup>6</sup></b>	-1503.933256	-1503.894020	-1503.892838	-1504.015444	-1504.102596
<b>TS1<sup>2</sup></b>	-1503.853871	-1503.815478	-1503.814297	-1503.930684	-1503.983349
<b>TS1<sup>4</sup></b>	-1503.886316	-1503.848388	-1503.847206	-1503.964983	-1504.041653
<b>TS1<sup>6</sup></b>	-1503.902807	-1503.863206	-1503.862025	-1503.986147	-1504.072958
<b>TS1-iso<sup>2</sup></b>	-1503.820046	-1503.779114	-1503.777933	-1503.904944	-1503.940198
<b>TS1-iso<sup>4</sup></b>	-1503.844741	-1503.803933	-1503.802751	-1503.930147	-1504.030686
<b>TS1-iso<sup>6</sup></b>	-1503.854692	-1503.813002	-1503.811821	-1503.942594	-1504.059285
<b>TS1'</b>	-411.757413	-411.748470	-411.747288	-411.797524	-411.6772503
<b>IN2<sup>2</sup></b>	-1503.867969	-1503.829501	-1503.828319	-1503.943734	-1504.009293
<b>IN2<sup>4</sup></b>	-1503.909166	-1503.870093	-1503.868911	-1503.989574	-1504.073238
<b>IN2<sup>6</sup></b>	-1503.923198	-1503.883556	-1503.882374	-1504.005009	-1504.099278
<b>IN2-iso<sup>2</sup></b>	-1503.877150	-1503.837167	-1503.835985	-1503.961296	-1503.992554
<b>IN2-iso<sup>4</sup></b>	-1503.900526	-1503.861412	-1503.860231	-1503.982427	-1504.063213
<b>IN2-iso<sup>6</sup></b>	-1503.914404	-1503.873642	-1503.872460	-1504.000800	-1504.073238
<b>IN2A<sup>2</sup></b>	-1711.532480	-1711.532480	-1711.532480	-1711.532480	-1712.861197
<b>IN2A<sup>4</sup></b>	-1711.557310	-1711.511789	-1711.510607	-1711.651504	-1712.947112
<b>IN2A<sup>6</sup></b>	-1711.567538	-1711.521290	-1711.520109	-1711.663092	-1712.975249
<b>IN2B-iso<sup>2</sup></b>	-2490.023272	-2489.975934	-2489.974752	-2490.115807	-2651.734672
<b>IN2B-iso<sup>4</sup></b>	-2490.050122	-2490.002559	-2490.001378	-2490.143253	-2651.797619
<b>IN2B-iso<sup>6</sup></b>	-2490.052240	-2490.004035	-2490.002853	-2490.148455	-2651.788743
<b>IN2'</b>	-411.784175	-411.774022	-411.772840	-411.826215	-411.71016
<b>TS2<sup>2</sup></b>	-1503.853796	-1503.814251	-1503.813070	-1503.932122	-1504.007880
<b>TS2<sup>4</sup></b>	-1503.882401	-1503.842341	-1503.841160	-1503.962241	-1504.051994
<b>TS2<sup>6</sup></b>	-1503.875962	-1503.835591	-1503.834409	-1503.957710	-1504.045462
<b>TS2-iso<sup>4</sup></b>	-1503.844741	-1503.803933	-1503.802751	-1503.930147	-1503.982244
<b>TS2-iso<sup>6</sup></b>	-1503.854692	-1503.813002	-1503.811821	-1503.942594	-1504.006092
<b>TS2A<sup>2</sup></b>	-1711.501750	-1711.458051	-1711.456870	-1711.587341	-1712.897223
<b>TS2A<sup>4</sup></b>	-1711.524780	-1711.479465	-1711.478284	-1711.615324	-1712.910058
<b>TS2A<sup>6</sup></b>	-1711.543610	-1711.497904	-1711.496722	-1711.636226	-1712.946862

TS2A-iso <sup>4</sup>	-1711.533695	-1711.487546	-1711.486364	-1711.629154	-1712.930781
TS2A-iso <sup>6</sup>	-1711.528313	-1711.483056	-1711.481875	-1711.623117	-1712.918702
TS2A-1 <sup>4</sup>	-1711.528164	-1711.482497	-1711.481315	-1711.619789	-1712.93059
TS2A-1 <sup>6</sup>	-1711.522773	-1711.476978	-1711.475797	-1711.615656	-1712.927344
TS2'	-411.711235	-411.699925	-411.698744	-411.755962	-411.6282063
IN3 <sup>2</sup>	-1394.424301	-1394.387651	-1394.386470	-1394.500509	-1394.585169
IN3 <sup>4</sup>	-1394.420823	-1394.384148	-1394.382966	-1394.496450	-1394.601626
IN3 <sup>6</sup>	-1394.410588	-1394.373146	-1394.371964	-1394.489455	-1394.595956
IN3A <sup>2</sup>	-1602.081828	-1602.039560	-1602.038378	-1602.169675	-1603.478174
IN3A <sup>4</sup>	-1602.085049	-1602.042276	-1602.041095	-1602.173828	-1603.506438
IN3A <sup>6</sup>	-1602.077889	-1602.034975	-1602.033794	-1602.167543	-1603.501959
TS-iso <sup>4</sup>	-1503.904089	-1503.864799	-1503.863618	-1503.987820	-1504.061736
TS-iso <sup>6</sup>	-1503.916945	-1503.878355	-1503.877174	-1503.996683	-1504.086396
1-TS3 <sup>2</sup>	-1718.777011	-1718.729983	-1718.728801	-1718.865124	-1718.895305
1-TS3 <sup>4</sup>	-1718.782174	-1718.734564	-1718.733382	-1718.871252	-1718.923823
1-TS3 <sup>6</sup>	-1718.777439	-1718.729526	-1718.728344	-1718.869713	-1718.916219
1-TS3-1 <sup>4</sup>	-1718.734158	-1718.686328	-1718.685146	-1718.826499	-1718.839481
1-TS3-1 <sup>6</sup>	-1718.745835	-1718.697088	-1718.695906	-1718.839312	-1718.875156
1-TS3-iso <sup>4</sup>	-1718.770324	-1718.723498	-1718.722317	-1718.859280	-1718.901438
1-TS3-iso <sup>6</sup>	-1718.769561	-1718.721739	-1718.720558	-1718.861695	-1718.910625
1-TS3A <sup>2</sup>	-1926.449689	-1926.397198	-1926.396016	-1926.547720	-1927.8047011
1-TS3A <sup>4</sup>	-1926.457767	-1926.404169	-1926.402987	-1926.561960	-1927.833419
1-TS3A <sup>6</sup>	-1926.455336	-1926.401838	-1926.400656	-1926.559347	-1927.829639
1-TS3A-iso <sup>2</sup>	-1926.414918	-1926.362912	-1926.361730	-1926.514622	-1927.7592364
1-TS3A-iso <sup>4</sup>	-1926.412680	-1926.359392	-1926.358210	-1926.516134	-1927.792146
1-TS3A-iso <sup>6</sup>	-1926.428193	-1926.374423	-1926.373242	-1926.533811	-1927.795883
TS3'	-720.038988	-720.017863	-720.016681	-720.099012	-719.906733
1-IN4A <sup>2</sup>	-1926.482494	-1926.428420	-1926.427238	-1926.587069	-1927.8223007
1-IN4A <sup>4</sup>	-1926.480140	-1926.425612	-1926.424430	-1926.591560	-1927.833398
1-IN4A <sup>6</sup>	-1926.476115	-1926.420850	-1926.419668	-1926.589130	-1927.838406
1-TS4 <sup>4</sup>	-1718.781417	-1718.736195	-1718.736195	-1718.865108	-1718.910155
1-TS4 <sup>6</sup>	-1718.802578	-1718.802578	-1718.802578	-1718.890875	-1718.948589
1-TS4-iso <sup>4</sup>	-1718.801621	-1718.754893	-1718.753711	-1718.893521	-1718.934407
1-TS4-iso <sup>6</sup>	-1718.825606	-1718.778070	-1718.776888	-1718.919703	-1718.961327
1-TS4A <sup>2</sup>	-1926.437396	-1926.385768	-1926.384586	-1926.536214	-1927.78919
1-TS4A <sup>4</sup>	-1926.465520	-1926.413380	-1926.412198	-1926.566847	-1927.8383
1-TS4A <sup>6</sup>	-1926.470580	-1926.418272	-1926.417090	-1926.570749	-1927.841802
1-TS4A-iso <sup>2</sup>	-1926.426181	-1926.374401	-1926.373219	-1926.524643	-1927.762938
1-TS4A-iso <sup>4</sup>	-1926.451404	-1926.399245	-1926.398064	-1926.553950	-1927.804804
1-TS4A-iso <sup>6</sup>	-1926.464992	-1926.412571	-1926.411389	-1926.565777	-1927.831905
TS4'	-720.036981	-720.015810	-720.014629	-720.096594	-719.9051516
1-IN5 <sup>4</sup>	-1718.809921	-1718.762598	-1718.761416	-1718.898688	-1718.960952
1-IN5 <sup>6</sup>	-1718.810104	-1718.762807	-1718.761626	-1718.899297	-1718.961295

<b>1-IN5-iso<sup>4</sup></b>	-1718.810158	-1718.762208	-1718.761026	-1718.903920	-1718.943719
<b>1-IN5-iso<sup>6</sup></b>	-1718.832923	-1718.784410	-1718.783228	-1718.928133	-1718.971331
<b>1-IN5A<sup>2</sup></b>	-1926.460661	-1926.408462	-1926.407280	-1926.557775	-1927.8012443
<b>1-IN5A<sup>4</sup></b>	-1926.497671	-1926.445182	-1926.444000	-1926.596495	-1927.828907
<b>1-IN5A<sup>6</sup></b>	-1926.497741	-1926.445260	-1926.444078	-1926.597072	-1927.881106
<b>1-IN5A-iso<sup>2</sup></b>	-1926.434059	-1926.381987	-1926.380805	-1926.530925	-1927.771059
<b>1-IN5A-iso<sup>4</sup></b>	-1926.461034	-1926.408330	-1926.407149	-1926.560506	-1927.831771
<b>1-IN5A-iso<sup>6</sup></b>	-1926.460222	-1926.407551	-1926.406369	-1926.560156	-1927.831218
<b>2a</b>	-324.394458	-324.385269	-324.384087	-324.434476	-324.3316823
<b>2b</b>	-308.286139	-308.276270	-308.275088	-308.326495	-308.231219
<b>2-TS3<sup>2</sup></b>	-1812.142226	-1812.092354	-1812.091172	-1812.236349	-1812.226298
<b>2-TS3<sup>4</sup></b>	-1812.165357	-1812.114012	-1812.112830	-1812.269267	-1812.265247
<b>2-TS3<sup>6</sup></b>	-1812.178540	-1812.126643	-1812.125461	-1812.281735	-1812.292435
<b>2-IN3B<sup>4</sup></b>	-2798.436277	-2798.379469	-2798.378288	-2798.542493	-2960.145833
<b>2-IN3B<sup>6</sup></b>	-2798.449647	-2798.393417	-2798.392235	-2798.553716	-2960.152249
<b>2-TS3B<sup>2</sup></b>	-2798.285957	-2798.227496	-2798.226314	-2798.393774	-2959.953383
<b>2-TS3B<sup>4</sup></b>	-2798.310580	-2798.252632	-2798.251451	-2798.418617	-2960.005058
<b>2-TS3B<sup>6</sup></b>	-2798.317101	-2798.257994	-2798.256813	-2798.426703	-2960.01293
<b>2-IN4B<sup>4</sup></b>	-2798.421510	-2798.366004	-2798.364822	-2798.525789	-2960.108559
<b>2-IN4B<sup>6</sup></b>	-2798.440084	-2798.383916	-2798.382734	-2798.545119	-2960.145036
<b>2-TS4B<sup>2</sup></b>	-2798.275693	-2798.217360	-2798.216178	-2798.383483	-2959.893852
<b>2-TS4B<sup>4</sup></b>	-2798.295690	-2798.237364	-2798.236183	-2798.404208	-2959.979452
<b>2-TS4B<sup>6</sup></b>	-2798.310192	-2798.252975	-2798.251794	-2798.416963	-2960.001821
<b>3a</b>	-626.769449	-626.753325	-626.752143	-626.819230	-626.6512985
<b>3a-iso</b>	-626.747949	-626.731751	-626.730569	-626.797670	-626.6349814
<b>4b</b>	-720.163638	-720.144489	-720.143307	-720.218916	-720.0351351
<b>5b</b>	-720.175501	-720.156342	-720.155160	-720.231213	-720.0456257
<b>N<sub>2</sub></b>	-109.509598	-109.506643	-109.505462	-109.533616	-109.4847258
<b>MECP</b>	-	-	-	-	-1927.831026
<b>1-TS3A-M06<sup>4</sup></b>	-1925.313323	-1925.260516	-1925.259334	-1925.409875	-1927.7916129
<b>1-TS3A-M06<sup>6</sup></b>	-1925.310023	-1925.257287	-1925.256105	-1925.407029	-1927.8386374
<b>1-TS3A-iso-M06<sup>4</sup></b>	-1925.287731	-1925.234771	-1925.233589	-1925.386517	-1927.8163517
<b>1-TS3A-iso-M06<sup>6</sup></b>	-1925.280247	-1925.227050	-1925.225869	-1925.381131	-1927.8090197
<b>2-TS3-M06<sup>4</sup></b>	-1810.928430	-1810.878302	-1810.877120	-1811.021344	-1812.277381
<b>2-TS3-M06<sup>6</sup></b>	-1810.949066	-1810.898062	-1810.896880	-1811.043441	-1812.298737
<b>2-TS3B-M06<sup>4</sup></b>	-2796.888529	-2796.830568	-2796.829386	-2796.990472	-2960.01547
<b>2-TS3B-M06<sup>6</sup></b>	-2796.898098	-2796.839839	-2796.838657	-2797.001386	-2960.0259055
<b>1-TS3A-BPW91<sup>4</sup></b>	-1926.497900	-1926.444885	-1926.443703	-1926.595769	-1927.8141803
<b>1-TS3A-BPW91<sup>6</sup></b>	-1926.485771	-1926.430919	-1926.429738	-1926.589969	-1927.8245011
<b>1-TS3A-iso-BPW91<sup>4</sup></b>	-1926.478157	-1926.423473	-1926.422291	-1926.581532	-1927.7955984
<b>1-TS3A-iso-BPW91<sup>6</sup></b>	-1926.460489	-1926.405233	-1926.404051	-1926.567009	-1927.7889792

<b>2-TS3-BPW91<sup>4</sup></b>	-1812.092423	-1812.039636	-1812.038454	-1812.191752	-1812.265734
<b>2-TS3-BPW91<sup>6</sup></b>	-1812.085644	-1812.031826	-1812.030644	-1812.190644	-1812.284338
<b>2-TS3B-BPW91<sup>4</sup></b>	-2798.609148	-2798.550084	-2798.548903	-2798.714536	-2959.997953
<b>2-TS3B-BPW91<sup>6</sup></b>	-2798.317102	-2798.257995	-2798.256813	-2798.426705	-2960.0129432
<b>1-TS3A-B3LYP-D3<sup>4</sup></b>	-1926.568486	-1926.515371	-1926.514190	-1926.667551	-1927.838971
<b>1-TS3A-B3LYP-D3<sup>6</sup></b>	-1926.565280	-1926.512108	-1926.510926	-1926.666243	-1927.8360899
<b>1-TS3A-iso-B3LYP-D3<sup>4</sup></b>	-1926.517193	-1926.464557	-1926.463375	-1926.616798	-1927.7937557
<b>1-TS3A-iso-B3LYP-D3<sup>6</sup></b>	-1925.305314	-1925.253245	-1925.252063	-1925.400171	-1927.811979
<b>2-TS3-B3LYP-D3<sup>4</sup></b>	-1812.246671	-1812.195849	-1812.194668	-1812.343216	-1812.268758
<b>2-TS3-B3LYP-D3<sup>6</sup></b>	-1812.258138	-1812.206609	-1812.205427	-1812.356760	-1812.295898
<b>2-TS3B-B3LYP-D3<sup>4</sup></b>	-2798.409214	-2798.350955	-2798.349773	-2798.514921	-2960.011178
<b>2-TS3B-B3LYP-D3<sup>6</sup></b>	-2798.413685	-2798.355142	-2798.353960	-2798.519848	-2960.019453
<b>1-TS3A-TPP<sup>4</sup></b>	-2850.334156	-2850.250754	-2850.249572	-2850.476238	-2851.547090
<b>1-TS3A-TPP<sup>6</sup></b>	-2850.331336	-2850.247852	-2850.246670	-2850.477871	-2851.5435889
<b>1-TS3A-iso-TPP<sup>4</sup></b>	-2850.315203	-2850.231642	-2850.230461	-2850.459281	-2851.5219161
<b>1-TS3A-iso-TPP<sup>6</sup></b>	-2850.311387	-2850.227697	-2850.226515	-2850.456834	-2851.5183211
<b>2-TS3-TPP<sup>4</sup></b>	-2736.040977	-2735.960483	-2735.959301	-2736.180951	-2735.978318
<b>2-TS3-TPP<sup>6</sup></b>	-2736.053699	-2735.971551	-2735.970369	-2736.196462	-2736.005791
<b>2-TS3B-TPP<sup>4</sup></b>	-3722.182023	-3722.093153	-3722.091971	-3722.336437	-3883.6977946
<b>2-TS3B-TPP<sup>6</sup></b>	-3722.193392	-3722.103864	-3722.102682	-3722.346243	-3883.7276336

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

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

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

$G_{373.15}$  = Sum of electronic and thermal free energies calculated by B3LYP-D3 in solvent

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

## Section 9. Calculated imaginary frequencies of all transition states

species

Species	Frequency
TS1 <sup>2</sup>	-234.87
TS1 <sup>4</sup>	-263.12
TS1 <sup>6</sup>	-249.09
TS1'	-275.41
TS1-iso <sup>2</sup>	-259.33
TS1-iso <sup>4</sup>	-259.88
TS1-iso <sup>6</sup>	-246.01
TS2 <sup>2</sup>	-457.29
TS2 <sup>4</sup>	-525.61
TS2 <sup>6</sup>	-536.25
TS2-iso <sup>4</sup>	-749.47
TS2-iso <sup>6</sup>	-758.83
TS2A <sup>2</sup>	-577.23
TS2A <sup>4</sup>	-632.67
TS2A <sup>6</sup>	-495.92
TS2A-1 <sup>4</sup>	-506.99
TS2A-1 <sup>6</sup>	-508.02
TS2A-iso <sup>4</sup>	-347.17
TS2A-iso <sup>6</sup>	-414.53
TS2'	-305.75
TS-iso <sup>4</sup>	-17.02
TS-iso <sup>6</sup>	-49.95
1-TS3 <sup>2</sup>	-537.24
1-TS3 <sup>4</sup>	-421.12
1-TS3 <sup>6</sup>	-417.11
1-TS3-1 <sup>4</sup>	-388.36
1-TS3-1 <sup>6</sup>	-343.18
1-TS3-iso <sup>4</sup>	-523.88
1-TS3-iso <sup>6</sup>	-498.95
1-TS3A <sup>2</sup>	-477.12
1-TS3A <sup>4</sup>	-428.24
1-TS3A <sup>6</sup>	-419.84
1-TS3A-iso <sup>2</sup>	-444.03
1-TS3A-iso <sup>4</sup>	-519.09
1-TS3A-iso <sup>6</sup>	-550.20
TS3'	-421.33



<b>1-TS4<sup>4</sup></b>	-526.87
<b>1-TS4<sup>6</sup></b>	-701.79
<b>1-TS4-iso<sup>4</sup></b>	-158.15
<b>1-TS4-iso<sup>6</sup></b>	-145.85
<b>1-TS4A<sup>2</sup></b>	-1385.49
<b>1-TS4A<sup>4</sup></b>	-839.12
<b>1-TS4A<sup>6</sup></b>	-239.75
<b>1-TS4A-iso<sup>2</sup></b>	-32.06
<b>1-TS4A-iso<sup>4</sup></b>	-106.29
<b>1-TS4A-iso<sup>6</sup></b>	-202.45
<b>TS4'</b>	-358.02
<b>2-TS3<sup>2</sup></b>	-415.24
<b>2-TS3<sup>4</sup></b>	-410.13
<b>2-TS3<sup>6</sup></b>	-413.33
<b>2-TS3B<sup>2</sup></b>	-463.70
<b>2-TS3B<sup>4</sup></b>	-480.39
<b>2-TS3B<sup>6</sup></b>	-341.86
<b>2-TS4B<sup>2</sup></b>	-340.97
<b>2-TS4B<sup>4</sup></b>	-341.99
<b>2-TS4B<sup>6</sup></b>	-342.83
<b>1-TS3A-M06<sup>4</sup></b>	-457.07
<b>1-TS3A-M06<sup>6</sup></b>	-437.32
<b>1-TS3A-iso-M06<sup>4</sup></b>	-580.23
<b>1-TS3A-iso-M06<sup>6</sup></b>	-619.08
<b>2-TS3-M06<sup>4</sup></b>	-487.81
<b>2-TS3-M06<sup>6</sup></b>	-358.02
<b>2-TS3B-M06<sup>4</sup></b>	-565.56
<b>2-TS3B-M06<sup>6</sup></b>	-473.58
<b>1-TS3A-BPW91<sup>4</sup></b>	-268.79
<b>1-TS3A-BPW91<sup>6</sup></b>	-209.66
<b>1-TS3A-iso-BPW91<sup>4</sup></b>	-409.94
<b>1-TS3A-iso-BPW91<sup>6</sup></b>	-435.50
<b>2-TS3-BPW91<sup>4</sup></b>	-290.70
<b>2-TS3-BPW91<sup>6</sup></b>	-311.38
<b>2-TS3B-BPW91<sup>4</sup></b>	-297.09
<b>2-TS3B-BPW91<sup>6</sup></b>	-342.19
<b>1-TS3A-B3LYP-D3<sup>4</sup></b>	-402.39
<b>1-TS3A-B3LYP-D3<sup>6</sup></b>	-332.41
<b>1-TS3A-iso-B3LYP-D3<sup>4</sup></b>	-571.63
<b>1-TS3A-iso-B3LYP-D3<sup>6</sup></b>	-633.29
<b>2-TS3-B3LYP-D3<sup>4</sup></b>	-410.06
<b>2-TS3-B3LYP-D3<sup>6</sup></b>	-402.90
<b>2-TS3B-B3LYP-D3<sup>4</sup></b>	-465.64

<b>2-TS3B-B3LYP-D3<sup>6</sup></b>	-390.25
<b>1-TS3A-TPP<sup>4</sup></b>	-420.85
<b>1-TS3A-TPP<sup>6</sup></b>	-409.62
<b>1-TS3A-iso-TPP<sup>4</sup></b>	-465.21
<b>1-TS3A-iso-TPP<sup>6</sup></b>	-505.06
<b>2-TS3-TPP<sup>4</sup></b>	-407.93
<b>2-TS3-TPP<sup>6</sup></b>	-402.51
<b>2-TS3B-TPP<sup>4</sup></b>	-364.81
<b>2-TS3B-TPP<sup>6</sup></b>	-351.22