

SUPPORTING INFORMATION**Mechanism of Cobalt-Porphyrin–Catalyzed Aziridination**

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Figure S1. Optimized TSs for aziridination of 2-methyl-1-butene, (*Z*)-2-butene, and (*E*)-2-butene.

Figure S2. Optimized geometries for aziridination of isobutene.

Coordinates for all optimized structures.

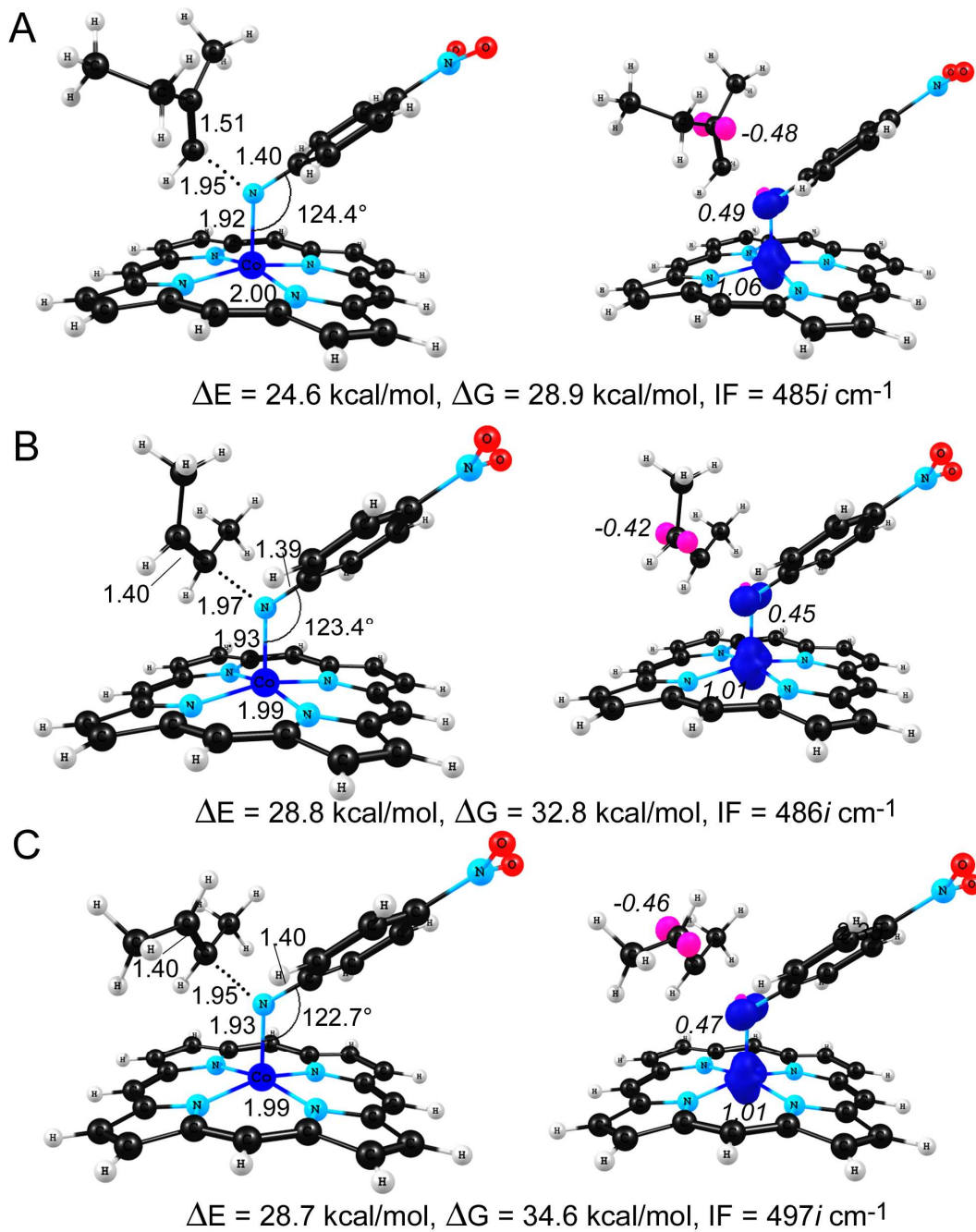


Figure S1. Optimized TS structures (left), spin density profiles (right), computed energies and imaginary frequencies (IF) for Co-porphyrin–nitrene mediated aziridination of 2-methyl-1-butene (A), (Z)-2-butene (B), and (E)-2-butene (C).

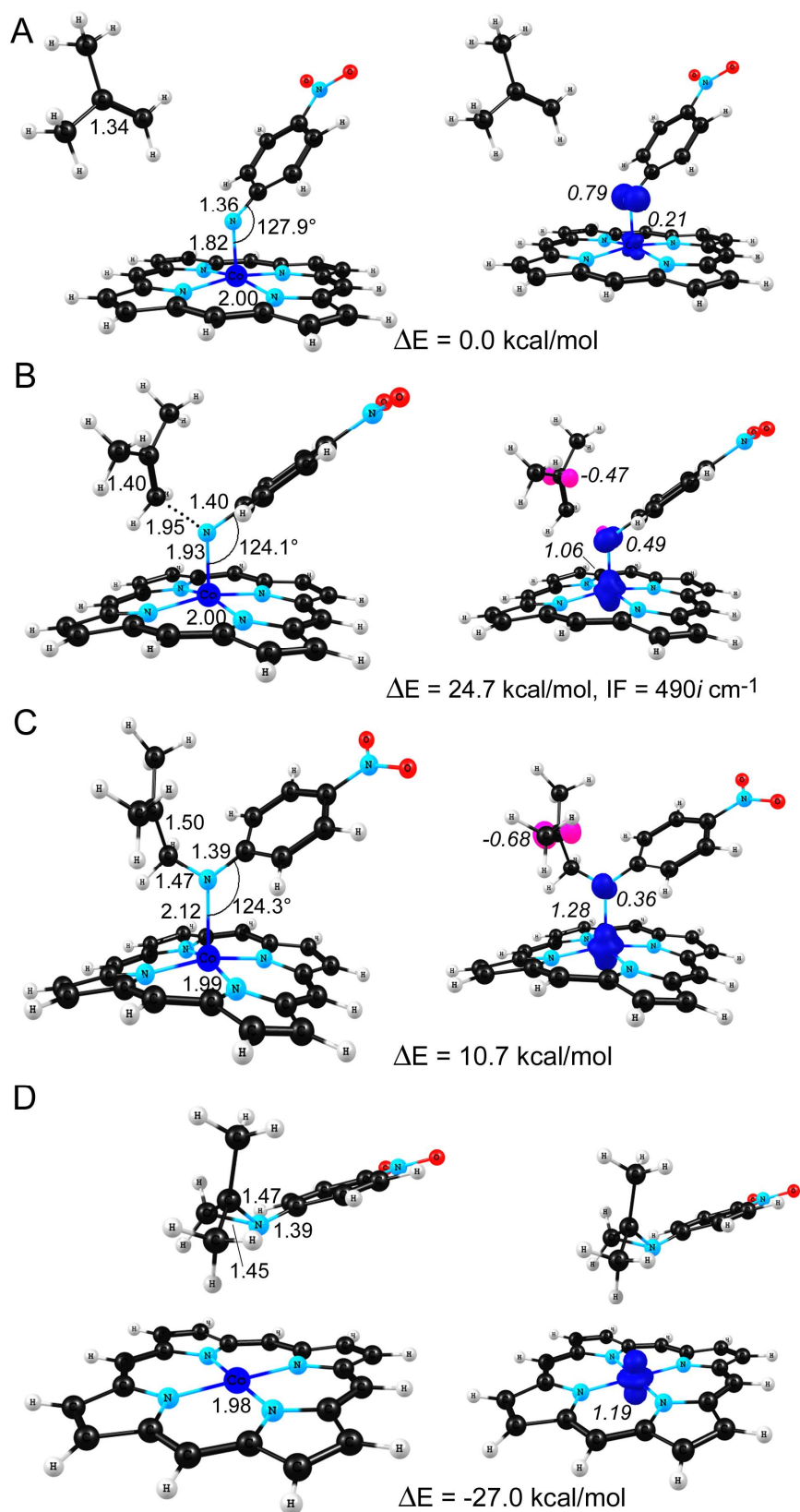


Figure S2. Optimized structures (left) and spin density profiles (right) for Co-porphyrin–nitrene mediated aziridination of isobutene: (A) reactants, (B) TS, (C) intermediate, and (D) products.

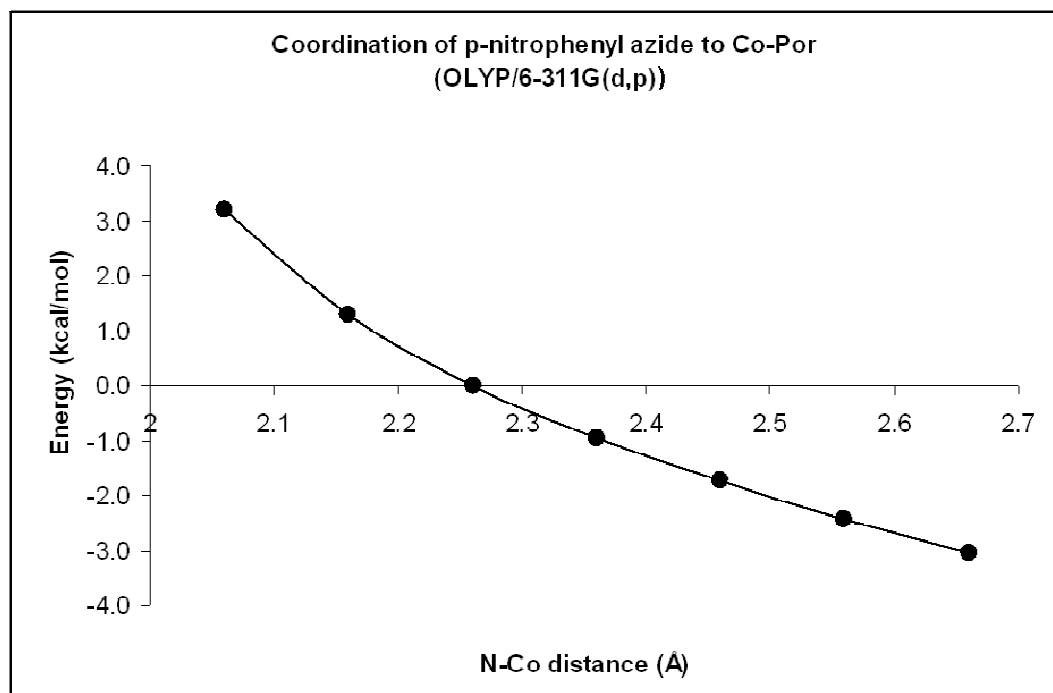
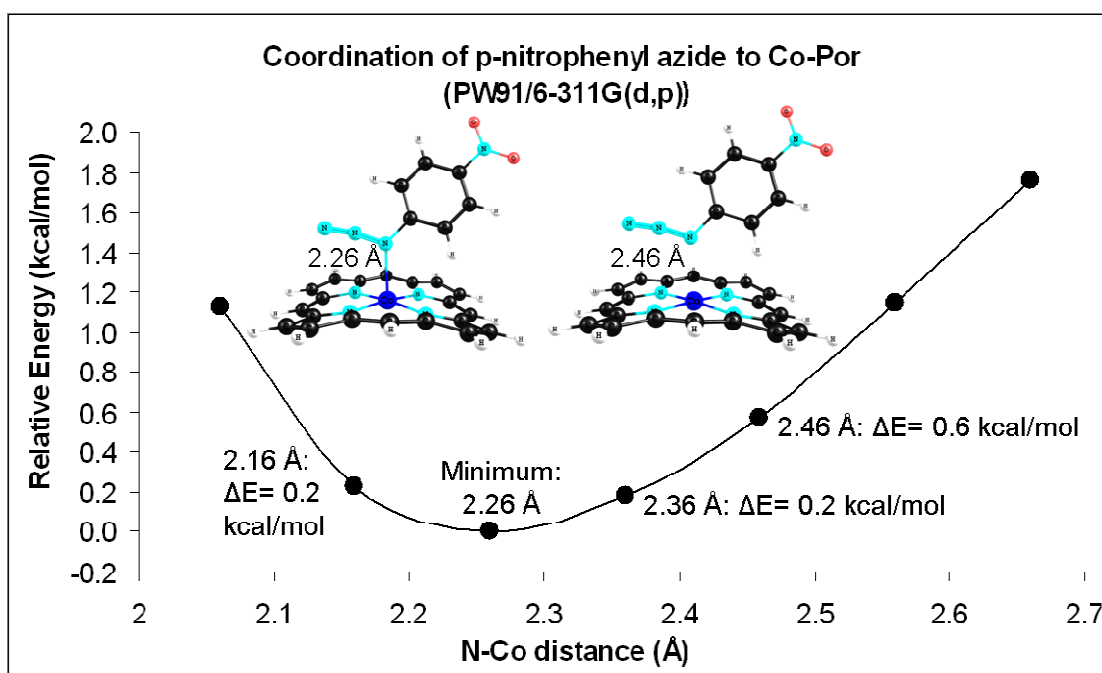


Figure S3. Potential energy surfaces for binding of azide to Co-Por employing PW91 (top) or OLYP (bottom).

Coordinates for optimized geometries

A. Nitrene formation from Co-porphyrin and *p*-nitrophenyl azide:

Reactants, Co-porphyrin and *p*-nitrophenyl azide

Co	-1.692306	0.603150	0.081381
C	-3.183391	-1.406761	-3.358568
C	-2.430314	-0.382433	-2.681063
C	-3.357816	-1.615673	-1.125556
C	-3.774279	-2.163115	-2.391218
C	-1.754318	0.639539	-3.331251
C	-1.141013	1.702161	-2.684298
C	-0.443991	3.081916	-1.130682
C	-0.147923	3.700402	-2.397382
C	-0.565397	2.834413	-3.363340
C	-0.094149	3.623274	0.097924
C	-0.266034	2.974743	1.312409
C	-0.745476	1.462692	2.825000
C	-0.066898	2.532977	3.509289
C	0.215705	3.481019	2.571814
C	-1.272583	0.347593	3.459727
C	-2.043321	-0.616784	2.827062
C	-3.186717	-1.718458	1.317248
C	-3.427386	-2.372662	2.577852
C	-2.702915	-1.697676	3.514038
C	-3.690600	-2.164569	0.104180
C	2.374585	-1.546296	-0.201579
C	3.392613	-2.518509	-0.266119
C	4.727324	-2.128685	-0.234575
C	5.045508	-0.770773	-0.138205
C	4.045205	0.204855	-0.072593
C	2.711593	-0.183064	-0.104527
O	6.712659	0.843825	-0.007776
O	7.321483	-1.245548	-0.170687
N	0.995003	-1.836252	-0.227319
N	0.613727	-3.010641	-0.311964
N	0.101494	-4.031448	-0.387189
N	-2.535678	-0.519057	-1.309210
N	-1.058832	1.855942	-1.312332
N	6.469909	-0.359016	-0.102869
N	-2.338797	-0.637720	1.476441
N	-0.859325	1.735319	1.473734
H	-4.423127	-3.023764	-2.506708
H	-3.253289	-1.509945	-4.435421
H	0.143470	2.549253	4.572575
H	-2.623845	-1.891378	4.577691
H	-4.060325	-3.242771	2.709594
H	-0.510589	2.944690	-4.440341
H	0.382363	4.599518	0.105927
H	-1.747282	0.633286	-4.417469
H	-4.348584	-3.028719	0.113826
H	-1.112798	0.248897	4.529632
H	0.714366	4.434590	2.702919
H	0.329679	4.666420	-2.515071
H	3.145032	-3.574557	-0.340723
H	5.525982	-2.861379	-0.283432
H	4.321522	1.250975	0.003300
H	1.915968	0.552985	-0.054421

TS, Co-porphyrin and *p*-nitrophenyl azide

Co	-1.102538	0.103702	0.472492
C	2.082157	-1.310844	-1.556349
C	1.367739	-0.147342	-1.172333
C	2.116810	1.016272	-0.867202
C	3.503897	1.012581	-0.922933
C	4.178538	-0.150972	-1.308914
C	3.468013	-1.310788	-1.636551
C	-0.974146	-2.867174	1.022171
C	-1.702526	-4.095438	0.834886
C	-2.914018	-3.755734	0.306908
C	-2.905014	-2.326437	0.129047
C	0.241150	-2.769922	1.688869
C	0.800428	-1.568685	2.103576
C	1.060212	0.566736	2.538376
C	2.031365	-0.141398	3.333991
C	1.888574	-1.465123	3.043424
C	0.943040	1.949168	2.495317
C	0.101576	2.636293	1.629297
C	-1.323650	3.077297	0.014472
C	-0.763554	4.336268	0.431702
C	0.099751	4.065286	1.454185
C	-2.359423	2.946368	-0.902272
C	-3.083335	1.775703	-1.087654
C	-3.851643	-0.258502	-0.794232
C	-4.844884	0.455299	-1.556774
C	-4.353158	1.708906	-1.767846
C	-3.931407	-1.604987	-0.468695
N	-0.033289	-0.066142	-1.135280
N	-0.560705	-0.943677	-2.401542
N	-1.563860	-1.058252	-2.922812
N	5.652955	-0.153213	-1.377203
N	-1.713772	-1.790923	0.575310
N	0.309898	-0.317457	1.787709
N	-0.781847	2.041230	0.749895
N	-2.777169	0.561354	-0.509481
O	6.209520	-1.189420	-1.748170
O	6.243827	0.881075	-1.057168
H	-5.784362	0.033040	-1.894377
H	-4.814091	2.534307	-2.298159
H	2.438163	-2.307866	3.446528
H	-1.337493	-5.078589	1.109058
H	-3.741662	-4.404925	0.045100
H	-1.030995	5.299808	0.013221
H	1.591991	2.533126	3.141709
H	-2.699004	3.841598	-1.415305
H	-4.828411	-2.144761	-0.758079
H	0.727555	-3.690583	1.998223
H	2.731466	0.328569	4.015022
H	0.695614	4.759312	2.035896
H	1.531492	-2.217349	-1.786720
H	4.011704	-2.201836	-1.933341
H	4.073062	1.908102	-0.696058
H	1.592293	1.927402	-0.610278

Products: Co-porphyrin–nitrene and N₂

Co	-0.989515	-0.781840	0.106393
C	-3.009378	1.477198	3.115059
C	-2.002002	0.566179	2.630237
C	-3.339891	0.974759	0.944586
C	-3.855167	1.713250	2.072443
C	-1.001624	0.007639	3.413951
C	-0.175899	-1.025474	2.990517
C	0.658797	-2.667237	1.790550
C	1.133200	-2.852323	3.136537
C	0.640404	-1.816145	3.874090
C	1.020015	-3.465178	0.713390
C	0.698208	-3.179285	-0.606480

C	-0.068482	-2.164525	-2.399818
C	0.763943	-3.246801	-2.855405
C	1.214301	-3.895263	-1.743120
C	-0.856232	-1.385690	-3.237086
C	-1.874647	-0.557119	-2.786272
C	-3.280360	0.479562	-1.463717
C	-3.735414	0.706771	-2.814182
C	-2.847221	0.081764	-3.637916
C	-3.859982	1.055442	-0.340688
C	1.368064	0.854786	-0.178221
C	1.760907	2.230789	-0.409165
C	3.086308	2.609472	-0.462108
C	4.091532	1.640587	-0.289735
C	3.759674	0.294182	-0.063792
C	2.434466	-0.093382	-0.007690
N	0.042352	0.686817	-0.165714
N	-1.554463	4.990919	-0.503138
N	-2.654192	4.966732	-0.385811
N	-2.223945	0.255341	1.307403
N	-0.144904	-1.543644	1.708496
N	-0.091561	-2.119066	-1.017450
N	-2.156886	-0.316323	-1.460030
N	5.504350	2.040398	-0.348161
O	6.359582	1.162326	-0.190693
O	5.756852	3.232486	-0.551800
H	-4.740991	2.337536	2.049161
H	-3.062335	1.858905	4.128245
H	0.940487	-3.491724	-3.896411
H	-2.851007	0.029250	-4.720613
H	-4.614784	1.281818	-3.080935
H	0.777463	-1.615422	4.930379
H	1.646604	-4.330813	0.908277
H	-0.923672	0.328244	4.448804
H	-4.746523	1.665648	-0.487655
H	-0.732814	-1.507510	-4.309327
H	1.848622	-4.772077	-1.683104
H	1.769517	-3.668333	3.459079
H	0.966920	2.960255	-0.538796
H	3.368845	3.642858	-0.635324
H	4.559484	-0.428310	0.064730
H	2.193231	-1.131095	0.165868

B. Co-porphyrin-nitrene-mediated aziridination of isobutene:

Reactants: Co-porphyrin-nitrene and isobutene

Co	0.362526	-1.529193	0.087454
C	3.146035	-1.334988	-1.162057
C	4.520155	-1.031550	-0.844507
C	4.575984	-0.847016	0.504212
C	3.236607	-1.043922	1.002395
C	2.681121	-1.574836	-2.446375
C	1.364936	-1.874328	-2.765158
C	-0.787019	-2.267111	-2.631963
C	-0.431865	-2.381127	-4.022623
C	0.906917	-2.138503	-4.104778
C	-2.070160	-2.448771	-2.138716
C	-2.407999	-2.383366	-0.796193
C	-2.295712	-2.196278	1.384221
C	-3.656660	-2.543932	1.067341
C	-3.727392	-2.656200	-0.288103
C	-1.828610	-2.007560	2.675349
C	-0.516412	-1.694147	2.995576
C	1.612624	-1.195872	2.837310
C	1.283836	-1.175541	4.239036
C	-0.038539	-1.491134	4.338307
C	-1.022549	0.967074	-0.123413
C	-1.572038	1.514378	1.077043
C	-2.628503	2.410126	1.038442

C	-3.177547	2.781604	-0.197184
C	-2.667610	2.265969	-1.397038
C	-1.610632	1.370560	-1.362339
C	2.884592	-0.953107	2.340644
C	2.283435	4.031226	-0.033371
C	3.408586	4.743429	-0.200407
C	3.426051	6.250504	-0.107152
C	4.735841	4.085997	-0.495420
N	-1.531767	-2.098350	0.235313
N	0.321386	-1.968568	-1.864571
N	2.372374	-1.357219	-0.022973
N	0.503768	-1.523760	2.080150
N	0.141283	0.264623	-0.114957
N	-4.306025	3.730008	-0.235225
O	-4.732264	4.160235	0.839979
O	-4.761382	4.038151	-1.339959
H	5.479046	4.331913	0.277449
H	5.435686	-0.609481	1.120213
H	5.324166	-0.976376	-1.569454
H	-4.441841	-2.687504	1.800524
H	-0.647109	-1.585165	5.230307
H	1.988834	-0.958869	5.033328
H	1.541924	-2.140545	-4.983223
H	-2.858906	-2.680695	-2.848483
H	3.398160	-1.528611	-3.261034
H	3.663572	-0.697802	3.053273
H	-2.537717	-2.115582	3.490979
H	-4.582582	-2.912891	-0.902449
H	-1.126235	-2.624559	-4.818536
H	-1.196110	0.977190	-2.285360
H	-3.111493	2.576348	-2.337537
H	-3.042114	2.831465	1.949155
H	-1.130072	1.233333	2.027312
H	1.330865	4.514891	0.177332
H	2.270635	2.945274	-0.103134
H	4.648273	2.996697	-0.550433
H	5.151562	4.445037	-1.448446
H	3.777059	6.701110	-1.047122
H	2.434842	6.657981	0.114808
H	4.118534	6.591360	0.676474

TS: Co-porphyrin–nitrene and isobutene

Co	1.161032	0.355310	0.642351
C	-2.055240	-1.381289	-0.221615
C	-1.330748	-0.293865	-0.774606
C	-2.078996	0.769301	-1.346095
C	-3.468015	0.758273	-1.348730
C	-4.146248	-0.329213	-0.785477
C	-3.444913	-1.401982	-0.223785
C	2.019402	2.817251	-0.935479
C	3.047461	3.313394	-1.816468
C	4.004832	2.345114	-1.884304
C	3.545709	1.250509	-1.065201
C	0.926416	3.564445	-0.515959
C	0.039413	3.167478	0.476576
C	-0.933015	2.029573	2.078991
C	-1.568402	3.322600	2.045026
C	-0.973234	4.024959	1.040155
C	-1.287853	1.011445	2.952272
C	-0.710532	-0.250760	2.962813
C	0.533707	-1.986211	2.463306
C	-0.355996	-2.402234	3.518470
C	-1.119605	-1.319161	3.838769
C	1.535755	-2.788010	1.932260
C	2.516151	-2.340286	1.056512
C	3.769937	-1.030778	-0.175912
C	4.461231	-2.292372	-0.075578
C	3.673358	-3.112214	0.677095
C	4.234241	0.054724	-0.907588

C	0.761573	-0.837949	-2.532443
C	0.029176	-1.848570	-3.170396
C	0.261818	-3.295206	-2.844610
C	-1.084436	-1.541398	-4.127755
O	-6.188791	-1.316172	-0.275914
O	-6.209411	0.615626	-1.291379
N	0.065080	-0.283403	-0.797457
N	2.327743	1.549102	-0.491342
N	0.051299	1.944040	1.115078
N	0.303372	-0.667864	2.124968
N	2.578255	-1.071875	0.519446
N	-5.625002	-0.344458	-0.784280
H	5.424065	-2.506694	-0.525325
H	3.859652	-4.136346	0.980106
H	-1.173959	5.039123	0.713911
H	3.037609	4.288359	-2.290534
H	4.940700	2.356917	-2.431362
H	-0.365148	-3.390627	3.963834
H	-2.082567	1.210747	3.665301
H	1.604391	-3.812227	2.288048
H	5.192206	-0.046737	-1.409744
H	0.801518	4.558513	-0.936275
H	-2.364780	3.636174	2.710046
H	-1.891499	-1.235604	4.595150
H	-1.503370	-2.209120	0.211018
H	-3.996914	-2.233279	0.203089
H	-4.038137	1.576635	-1.776619
H	-1.545794	1.610794	-1.777733
H	0.726458	0.161300	-2.962585
H	1.720331	-1.107317	-2.105973
H	0.408348	-3.888417	-3.760378
H	1.132957	-3.440400	-2.199439
H	-0.609942	-3.740193	-2.336609
H	-2.062476	-1.862720	-3.735580
H	-1.152521	-0.474530	-4.359820
H	-0.946310	-2.087572	-5.074029

Intermediate: Co-porphyrin-nitrene and isobutene

Co	1.158228	0.173746	-0.697068
C	-2.072348	0.861418	0.717366
C	-1.413073	-0.368045	0.989592
C	-2.247388	-1.501211	1.231876
C	-3.630550	-1.410374	1.184729
C	-4.238193	-0.176313	0.916980
C	-3.455148	0.961970	0.686745
C	1.096289	-2.730780	-1.593691
C	1.852407	-3.957588	-1.553912
C	3.042536	-3.666619	-0.953637
C	2.995436	-2.271102	-0.595826
C	-0.116813	-2.582440	-2.255760
C	-0.716416	-1.357137	-2.518432
C	-1.046789	0.803340	-2.696831
C	-2.005888	0.164528	-3.563501
C	-1.815985	-1.178732	-3.434823
C	-0.955010	2.176327	-2.511496
C	-0.100215	2.791195	-1.605615
C	1.379449	3.117350	-0.017995
C	0.810146	4.405098	-0.326292
C	-0.092384	4.205678	-1.329561
C	2.451562	2.926407	0.844679
C	3.166012	1.738834	0.947104
C	3.899170	-0.292678	0.552471
C	4.895405	0.358610	1.365368
C	4.430354	1.613718	1.627616
C	3.990149	-1.607862	0.111795
C	0.608762	-1.306645	1.945503
C	0.267369	-0.845076	3.333609
C	0.565796	0.550486	3.764786
C	-0.539436	-1.706986	4.241029

N	-5.704856	-0.078757	0.876885
N	2.837067	0.559137	0.309680
N	0.802074	2.132362	-0.793545
N	-0.266781	-0.137837	-2.056016
N	1.799191	-1.708213	-0.992223
N	-0.025647	-0.424787	0.958659
O	-6.203321	1.017019	0.601052
O	-6.358034	-1.098734	1.120230
H	5.826014	-0.097144	1.684063
H	4.905255	2.403506	2.198736
H	-2.342905	-1.985554	-3.931300
H	1.518391	-4.903021	-1.966340
H	3.881238	-4.326232	-0.761850
H	1.097875	5.337048	0.147035
H	-1.624006	2.810450	-3.086200
H	2.817762	3.787480	1.396782
H	4.887343	-2.164694	0.367402
H	-0.570271	-3.470317	-2.687317
H	-2.728292	0.689048	-4.178192
H	-0.707056	4.937904	-1.840611
H	-1.466993	1.744660	0.560584
H	-3.943583	1.912131	0.496060
H	-4.255132	-2.283924	1.342804
H	-1.800190	-2.473566	1.412123
H	0.341597	-2.365868	1.809912
H	1.690968	-1.245678	1.795198
H	1.059180	0.547964	4.749790
H	1.195385	1.082010	3.050815
H	-0.357326	1.141278	3.898016
H	-1.622414	-1.554350	4.075090
H	-0.349798	-2.775110	4.074337
H	-0.352951	-1.470980	5.296309

Products: Co-porphyrin and aziridine product

Co	-1.892440	0.062117	-0.803157
C	-5.438021	0.025784	1.555453
C	-4.411693	-0.583891	0.750305
C	-3.922002	1.548070	0.888701
C	-5.125047	1.348685	1.654340
C	-4.342999	-1.942885	0.480786
C	-3.299851	-2.550867	-0.201796
C	-1.416001	-2.889711	-1.268757
C	-1.993688	-4.186466	-1.026033
C	-3.173136	-3.974857	-0.376657
C	-0.244491	-2.683896	-1.982389
C	0.248768	-1.434077	-2.325384
C	0.468641	0.730379	-2.572764
C	1.523749	0.117121	-3.338629
C	1.396526	-1.228455	-3.171799
C	0.312823	2.100612	-2.429172
C	-0.626616	2.694299	-1.598860
C	-2.239591	2.999212	-0.147411
C	-1.702269	4.301104	-0.448955
C	-0.709043	4.112728	-1.363095
C	2.715432	0.053568	1.490141
C	3.397994	-1.178016	1.344178
C	4.664957	-1.224327	0.779765
C	5.271478	-0.041311	0.338072
C	4.611630	1.186794	0.460489
C	3.347049	1.233529	1.033586
C	-3.326085	2.784567	0.688089
C	0.833727	1.091834	2.825141
C	0.886606	-0.348998	3.269205
C	1.852666	-0.711122	4.385700
C	-0.376918	-1.190807	3.203373
N	6.612841	-0.091678	-0.269387
N	1.407847	0.078974	1.959398
N	-1.570039	2.013913	-0.851082
N	-0.316126	-0.227061	-1.957327

N	-2.218842	-1.888083	-0.754806
N	-3.483279	0.356433	0.339410
O	7.164366	-1.192077	-0.356208
O	7.108840	0.969015	-0.658802
H	-5.658237	2.132692	2.179957
H	-6.277096	-0.505513	1.990056
H	2.267970	0.661159	-3.908668
H	-0.076109	4.853964	-1.837588
H	-2.061253	5.230290	-0.021162
H	-3.896619	-4.704849	-0.031868
H	0.297246	-3.557479	-2.333466
H	-5.138437	-2.576781	0.862253
H	-3.766893	3.647024	1.180004
H	0.998320	2.749359	-2.966793
H	2.008676	-2.022324	-3.584051
H	-1.549667	-5.126218	-1.334097
H	2.915725	-2.097916	1.662994
H	5.194665	-2.164658	0.668023
H	5.100307	2.088547	0.106353
H	2.828941	2.185057	1.117623
H	1.513322	1.791161	3.316236
H	-0.106582	1.527231	2.487438
H	-0.964904	-1.073796	4.122088
H	-0.998821	-0.899283	2.353631
H	-0.131950	-2.254598	3.092843
H	2.172083	-1.757645	4.313551
H	2.747996	-0.082723	4.376758
H	1.357158	-0.584463	5.355999

C. Co-porphyrin–nitrene-mediated aziridination of other alkenes:

TS: Co-porphyrin-nitrene and 2-methyl-1-butene

Co	-1.076708	-0.852313	0.422580
C	-3.876099	1.930050	2.088544
C	-2.650529	1.170660	2.070636
C	-3.808191	0.538744	0.319688
C	-4.603353	1.525016	1.008684
C	-1.694972	1.211924	3.077515
C	-0.618240	0.339670	3.172748
C	0.776405	-1.309239	2.791453
C	1.112394	-0.774251	4.086315
C	0.254627	0.260287	4.317025
C	1.458340	-2.351472	2.178680
C	1.176491	-2.834696	0.909166
C	0.275809	-3.116617	-1.069932
C	1.365196	-4.055852	-0.971100
C	1.916238	-3.890119	0.264140
C	-0.592672	-3.049654	-2.151721
C	-1.751964	-2.285359	-2.180728
C	-3.405223	-0.983748	-1.568299
C	-3.783596	-1.568249	-2.831164
C	-2.748419	-2.366024	-3.219624
C	1.331088	0.580967	-0.474110
C	2.027824	1.265927	0.554778
C	3.413830	1.369274	0.546071
C	4.138894	0.788839	-0.500723
C	3.487627	0.112233	-1.539026
C	2.102059	0.016601	-1.525013
C	-4.189822	-0.079963	-0.863678
C	-0.858277	1.813823	-1.687496
C	-0.183397	3.040106	-1.766927
C	0.883392	3.292639	-2.791973
C	-0.465729	4.135277	-0.766282
C	-1.399550	5.247734	-1.295861
N	-0.285617	-0.622262	2.240437
N	0.173381	-2.366755	0.084158
N	-0.062313	0.503275	-0.480515
N	-2.158209	-1.427476	-1.180793

N	5.613796	0.893445	-0.511764
N	-2.612610	0.330652	0.977656
O	6.218765	0.379578	-1.455456
O	6.154484	1.488251	0.423371
H	-5.588770	1.851784	0.696575
H	-4.144053	2.652978	2.850748
H	1.643539	-4.760976	-1.746040
H	-2.664892	-2.978979	-4.109932
H	-4.723280	-1.384557	-3.339598
H	0.190565	0.903479	5.187418
H	2.279376	-2.808420	2.723475
H	-1.842994	1.920576	3.887656
H	-5.160224	0.177839	-1.278385
H	-0.391781	-3.696825	-3.000970
H	2.746289	-4.424404	0.711739
H	1.903859	-1.151993	4.723399
H	1.457296	1.718019	1.359213
H	3.945023	1.891488	1.335414
H	4.075676	-0.328738	-2.337557
H	1.589834	-0.508671	-2.325328
H	-0.829187	1.158975	-2.556462
H	-1.795861	1.791290	-1.144756
H	-0.915506	3.701376	0.134617
H	0.481140	4.599987	-0.450180
H	1.877475	3.390979	-2.327474
H	0.941409	2.493644	-3.537143
H	0.707471	4.238041	-3.326546
H	-1.552750	6.017298	-0.528726
H	-0.983892	5.741041	-2.181977
H	-2.380734	4.841261	-1.567128

TS: Co-porphyrin-nitrene and (Z)-2-butene

Co	-1.131088	0.233281	-0.668435
C	2.064798	1.001149	1.127408
C	1.337154	-0.193513	0.870823
C	2.092084	-1.376688	0.645252
C	3.480046	-1.371679	0.680913
C	4.158154	-0.172878	0.932788
C	3.454152	1.016371	1.151822
C	-2.680242	2.401023	0.810541
C	-3.887692	2.637657	1.562832
C	-4.606569	1.480349	1.522759
C	-3.824097	0.532497	0.768206
C	-1.748685	3.385937	0.510440
C	-0.698313	3.225309	-0.383957
C	0.672054	2.373338	-1.868792
C	0.991666	3.774252	-1.766629
C	0.148672	4.301187	-0.833000
C	1.349516	1.476712	-2.683915
C	1.079353	0.117891	-2.751297
C	0.191609	-1.857978	-2.418211
C	1.263351	-2.038477	-3.366336
C	1.806965	-0.808403	-3.582660
C	-0.671611	-2.872202	-2.025655
C	-1.816795	-2.676474	-1.264700
C	-2.806872	-3.694219	-1.017680
C	-3.824474	-3.092644	-0.337314
C	-3.441336	-1.715425	-0.151764
C	-4.207655	-0.781159	0.534118
C	-0.794325	-0.827627	2.585087
C	-0.412081	0.250252	3.572763
C	-0.380234	-2.159804	2.723537
C	0.730946	-2.680365	3.574280
N	-0.055571	-0.171256	0.886454
N	-2.641550	1.104265	0.342170
N	-0.367568	2.047167	-1.022667
N	0.093971	-0.534914	-2.037589
N	-2.209168	-1.470567	-0.722359
N	5.635173	-0.163528	0.965104

O	6.220965	-1.233566	0.782584
O	6.198636	0.913829	1.172622
H	-0.924525	-2.901893	2.140061
H	-4.755171	-3.526948	0.009800
H	-2.732314	-4.723289	-1.350612
H	0.079571	5.326311	-0.487069
H	-4.151841	3.581469	2.026297
H	-5.579275	1.272944	1.954210
H	1.534034	-2.986111	-3.817889
H	2.154778	1.863778	-3.301532
H	-0.478928	-3.873089	-2.401839
H	-5.166642	-1.105598	0.928173
H	-1.897934	4.371870	0.941768
H	1.763773	4.274207	-2.340143
H	2.622838	-0.535369	-4.241901
H	1.562662	-2.298509	0.430717
H	4.051154	-2.278057	0.506731
H	4.002802	1.931887	1.348487
H	1.514494	1.918071	1.307973
H	-1.794548	-0.713852	2.183578
H	-0.702069	1.235574	3.199782
H	-0.942353	0.080933	4.521163
H	0.658721	0.269322	3.794429
H	1.331031	-3.434273	3.046790
H	1.405558	-1.900444	3.936962
H	0.322503	-3.194135	4.462450

TS: Co-porphyrin-nitrene and (*E*)-2-butene

Co	1.067186	0.247728	0.663591
C	2.545313	-3.736035	1.223702
C	1.583716	-2.673105	1.371888
C	3.312034	-1.815502	0.333876
C	3.628118	-3.197988	0.592363
C	0.381036	-2.799584	2.055348
C	-0.451896	-1.736247	2.375558
C	-1.229693	0.293999	2.652520
C	-2.050767	-0.577601	3.455645
C	-1.577100	-1.841116	3.271588
C	-1.406003	1.667289	2.571100
C	-0.642897	2.512080	1.776519
C	0.385446	0.601321	-3.507472
C	0.819670	3.257280	0.321792
C	0.023785	4.387820	0.727155
C	-0.875594	3.927241	1.643654
C	1.905579	3.340837	-0.540237
C	2.789943	2.299447	-0.787538
C	3.832497	0.376869	-0.650966
C	4.693015	1.263127	-1.395630
C	4.037461	2.453917	-1.494596
C	-1.355129	-0.195226	-0.927236
C	-2.070037	-1.422652	-0.884211
C	-3.456225	-1.459693	-0.956419
C	-4.172722	-0.261410	-1.062221
C	-3.507914	0.968746	-1.099492
C	-2.119598	0.997072	-1.037996
C	4.147747	-0.941057	-0.349669
C	0.754670	-0.611546	-2.680911
C	0.252049	-1.865925	-3.055165
C	0.858567	-3.186124	-2.719280
N	-5.647486	-0.297058	-1.135141
N	0.039099	-0.138547	-0.925512
N	2.662702	1.017808	-0.293754
N	0.401632	2.111769	0.968827
N	2.060176	-1.502549	0.821170
N	-0.257788	-0.426145	1.986404
O	-6.197570	-1.401043	-1.121430
O	-6.245567	0.779388	-1.205360
H	-0.686359	-1.892688	-3.612046
H	4.560589	-3.679780	0.320799

H	2.407479	-4.749454	1.583302
H	0.162450	5.400926	0.367000
H	4.369806	3.370705	-1.968284
H	5.671546	0.996102	-1.778299
H	-1.926468	-2.765550	3.717015
H	-2.207533	2.109676	3.155566
H	0.116574	-3.781416	2.437966
H	5.110622	-1.318931	-0.682014
H	2.124580	4.307597	-0.984850
H	-1.633893	4.481741	2.184496
H	-2.875873	-0.247785	4.076299
H	-1.513650	-2.346858	-0.775399
H	-3.997130	-2.400102	-0.923593
H	-4.084612	1.883732	-1.188815
H	-1.600847	1.947439	-1.085814
H	1.775058	-0.605391	-2.309270
H	1.051461	-3.762496	-3.638677
H	1.800782	-3.088207	-2.175091
H	0.184188	-3.816026	-2.116970
H	0.604448	1.532096	-2.978681
H	0.972560	0.597525	-4.436902
H	-0.673460	0.597386	-3.786351

D. Co-porphyrin–nitrene-mediated amination of 2-methyl-1-butene:

Reactants: Co-porphyrin–nitrene and 2-methyl-1-butene:

Co	-0.364880	-1.590569	0.097124
C	-1.012427	2.001330	1.062899
C	-0.813057	1.227707	-0.122474
C	-1.358707	1.735693	-1.341621
C	-2.046350	2.938462	-1.373585
C	-2.220677	3.668078	-0.189185
C	-1.701230	3.203247	1.027368
C	-0.959816	-1.397437	3.076582
C	-0.316339	-1.379989	4.364531
C	1.010363	-1.598589	4.140989
C	1.173029	-1.751062	2.718202
C	-2.319209	-1.204507	2.882752
C	-2.946907	-1.243770	1.647648
C	-3.334243	-1.450122	-0.499110
C	-4.609127	-1.229586	0.132894
C	-4.368269	-1.100181	1.467076
C	-3.173285	-1.653111	-1.860528
C	-1.956798	-1.907116	-2.475596
C	0.183253	-2.230653	-2.823462
C	-0.465878	-2.328628	-4.105096
C	-1.797128	-2.130533	-3.888757
C	1.547440	-2.396093	-2.636327
C	2.182548	-2.362817	-1.404006
C	3.596856	-2.577214	-1.218070
C	3.834161	-2.467400	0.118968
C	2.563650	-2.184838	0.740952
C	2.392159	-1.996763	2.104189
C	3.331829	2.967311	-0.237686
C	4.646584	3.156488	-0.434735
C	5.575970	1.992201	-0.728714
C	6.512808	1.607502	0.432864
C	5.266934	4.533619	-0.384207
N	0.040078	0.168822	-0.123213
N	-0.042959	-1.637217	2.072299
N	-2.315061	-1.457313	0.435930
N	-0.740319	-1.981077	-1.825876
N	1.556683	-2.140081	-0.197614
N	-2.959124	4.944050	-0.223613
O	-3.397111	5.325929	-1.312199
O	-3.091783	5.560293	0.837279
H	4.772935	-2.571244	0.650874

H	4.299563	-2.791178	-2.015198
H	-5.076928	-0.933672	2.270031
H	-0.828112	-1.226094	5.307574
H	1.816333	-1.662612	4.862934
H	0.044270	-2.534212	-5.039115
H	-4.060973	-1.621324	-2.485601
H	2.157530	-2.581865	-3.515657
H	3.272082	-2.057442	2.738214
H	-2.936450	-1.025719	3.758448
H	-5.557192	-1.191346	-0.390916
H	-2.608495	-2.137640	-4.607426
H	-1.203849	1.171656	-2.255684
H	-2.455269	3.328188	-2.300330
H	-1.848761	3.794215	1.925675
H	-0.592108	1.639732	1.996049
H	2.662503	3.799461	-0.023854
H	2.876657	1.979536	-0.283379
H	4.974769	1.117163	-1.002445
H	6.190052	2.236366	-1.609746
H	5.757139	4.778397	-1.337912
H	4.519236	5.306438	-0.180214
H	6.042579	4.604904	0.390427
H	7.142911	0.753749	0.152806
H	7.181997	2.428219	0.715770
H	5.936564	1.324251	1.321785

TS1: Co-porphyrin–nitrene mediated H-abstraction from 2-methyl-1-butene

Co	0.857352	0.750094	0.656185
C	1.494030	-1.320091	2.795053
C	2.538532	-2.189870	3.272088
C	3.642823	-1.927102	2.515355
C	3.259526	-0.920705	1.557854
C	0.233185	-1.223460	3.369853
C	-0.693272	-0.238354	3.055653
C	-1.594327	1.587871	2.242081
C	-2.440131	1.155342	3.326194
C	-1.890974	0.010100	3.819047
C	-1.828542	2.720429	1.476058
C	-1.055793	3.105774	0.388986
C	0.439656	3.098528	-1.217868
C	-0.444285	4.205178	-1.477193
C	-1.362626	4.221219	-0.467699
C	1.561863	2.802111	-1.981223
C	2.529431	1.876761	-1.615934
C	3.699180	0.453689	-0.431026
C	4.547361	0.886967	-1.514329
C	3.813085	1.756415	-2.263022
C	-1.361282	-0.676278	-0.617920
C	-2.155634	0.265876	-1.327939
C	-3.520291	0.081748	-1.499765
C	-4.135948	-1.060744	-0.973583
C	-3.389088	-2.017495	-0.276030
C	-2.025689	-1.824445	-0.100384
C	4.087360	-0.452297	0.546011
C	0.843266	-2.791197	-1.617420
C	1.351420	-3.769402	-0.579842
C	1.675015	-2.430685	-2.769899
C	0.974885	-1.720920	-3.911152
C	3.005316	-2.700636	-2.847164
N	0.016225	-0.513576	-0.518297
N	-0.532447	0.721010	2.076503
N	0.058379	2.432177	-0.070282
N	-5.586463	-1.258370	-1.155859
N	2.463554	1.059307	-0.507595
N	1.945953	-0.544842	1.747772
O	-6.216940	-0.376382	-1.745006
O	-6.086972	-2.293498	-0.708088
H	4.629670	-2.370648	2.583701
H	2.433776	-2.888270	4.094591

H	-0.349114	4.887750	-2.314083
H	4.110629	2.301946	-3.151269
H	5.569873	0.560596	-1.665423
H	-2.234191	-0.602036	4.645148
H	-2.693292	3.329377	1.723499
H	-0.008205	-1.904775	4.180840
H	5.101159	-0.839843	0.502028
H	1.739747	3.398749	-2.871360
H	-2.182555	4.912583	-0.310440
H	-3.333223	1.673521	3.655683
H	-1.452913	-2.550909	0.466729
H	-3.890818	-2.890540	0.128947
H	-4.117616	0.801286	-2.050496
H	-1.671988	1.132498	-1.762073
H	3.584104	-2.418539	-3.723896
H	3.544517	-3.208386	-2.053065
H	0.557826	-1.560966	-0.977789
H	-0.193167	-2.989631	-1.909237
H	0.541332	-0.772384	-3.573611
H	1.662089	-1.506686	-4.735342
H	0.148770	-2.328451	-4.304464
H	0.622595	-3.909436	0.224972
H	1.529219	-4.758013	-1.031334
H	2.289828	-3.448191	-0.119224

Intermediate: H-abstraction from 2-methyl-1-butene

Co	-0.098840	-1.531601	0.354960
C	0.890321	2.467319	0.168917
C	1.012229	1.145700	-0.361773
C	2.215883	0.838350	-1.059632
C	3.208323	1.786061	-1.234670
C	3.040664	3.082856	-0.721350
C	1.873438	3.424137	-0.024177
C	-1.942723	-2.200702	-1.955257
C	-3.332152	-2.223329	-2.339118
C	-4.051583	-1.915935	-1.223406
C	-3.096669	-1.674983	-0.170552
C	-0.897612	-2.553558	-2.796970
C	0.414672	-2.720143	-2.379485
C	2.196764	-2.877665	-1.111764
C	2.548549	-3.436103	-2.392072
C	1.447733	-3.316011	-3.187438
C	3.081878	-2.724514	-0.054577
C	2.777005	-2.069443	1.129570
C	1.722593	-0.939591	2.684607
C	3.085401	-1.081396	3.127789
C	3.734502	-1.803413	2.172167
C	0.714474	-0.370118	3.447247
C	-0.631688	-0.420575	3.114981
C	-2.511200	-0.871326	2.073915
C	-2.866192	-0.301115	3.347420
C	-1.698514	-0.004445	3.986655
C	-3.432429	-1.231223	1.100091
C	-3.473391	3.957469	-0.318603
C	-4.060206	3.102863	-1.269295
C	-5.312849	2.528122	-1.103986
C	-4.066799	4.363543	0.995431
C	-3.259886	2.782146	-2.523658
N	-0.045580	0.277126	-0.313909
N	-1.807990	-1.874226	-0.622178
N	0.882245	-2.449395	-1.107509
N	1.539989	-1.542459	1.453122
N	-1.135672	-0.956079	1.943133
N	4.097486	4.084450	-0.906548
O	3.910502	5.215166	-0.443653
O	5.117114	3.742688	-1.515546
H	-3.882706	-0.149541	3.691849
H	-1.557734	0.433285	4.968209

H	1.322812	-3.625450	-4.218752
H	-3.694442	-2.466918	-3.331289
H	-5.126834	-1.840594	-1.110361
H	3.472431	-0.696333	4.064046
H	4.093412	-3.100032	-0.180036
H	0.987497	0.075864	4.399251
H	-4.486445	-1.110193	1.332599
H	-1.135582	-2.794343	-3.829139
H	3.518315	-3.853318	-2.637988
H	4.769023	-2.126165	2.155037
H	-0.006546	2.729303	0.727922
H	1.769363	4.427736	0.375588
H	4.118234	1.548994	-1.776356
H	2.342461	-0.152403	-1.476627
H	-5.737568	1.881304	-1.867444
H	-5.918454	2.701935	-0.218992
H	-0.803607	0.728830	0.194305
H	-2.480936	4.346488	-0.546013
H	-2.516241	1.999311	-2.325533
H	-3.906990	2.425753	-3.331504
H	-2.718273	3.661820	-2.889159
H	-3.557470	5.244649	1.401039
H	-5.135717	4.601561	0.919049
H	-3.976853	3.565079	1.751157

TS2: Co-porphyrin–nitrene mediated amination of 2-methyl-1-butene

Co	-1.262247	0.714138	0.526673
C	2.191602	0.172449	-1.743227
C	1.401797	-0.367885	-0.685449
C	2.100649	-0.938874	0.414542
C	3.485714	-0.954741	0.463454
C	4.224791	-0.403917	-0.592987
C	3.577862	0.156130	-1.702366
C	-3.202641	-1.576105	1.039834
C	-4.365084	-2.232996	0.496070
C	-4.726517	-1.531023	-0.615180
C	-3.777682	-0.453761	-0.749441
C	-2.565581	-1.970816	2.208068
C	-1.509843	-1.289385	2.796222
C	0.017749	0.215809	3.239434
C	0.004188	-0.699424	4.352947
C	-0.941475	-1.640174	4.073843
C	0.853921	1.319628	3.153127
C	0.871744	2.210612	2.090139
C	0.432406	3.212034	0.193496
C	1.479684	3.971374	0.829550
C	1.747638	3.352763	2.012835
C	-0.153358	3.566306	-1.013192
C	-1.234948	2.910008	-1.584465
C	-2.901218	1.524178	-1.917779
C	-2.946864	2.492163	-2.984254
C	-1.906896	3.350241	-2.780206
C	-3.804604	0.479356	-1.776913
C	-0.482442	-2.636681	-2.059837
C	0.442909	-3.574635	-1.517629
C	1.622683	-3.891507	-2.143073
C	-0.427638	-2.087343	-3.448299
C	0.075149	-4.239332	-0.205119
N	0.023311	-0.391808	-0.727559
N	-2.846080	-0.487054	0.270272
N	-0.907218	-0.156325	2.282691
N	0.067253	2.129198	0.970371
N	-1.845955	1.784666	-1.062541
N	5.696938	-0.417298	-0.539386
O	6.312650	0.062439	-1.495846
O	6.232648	-0.908182	0.458429
H	-3.690495	2.506232	-3.773082
H	-1.620704	4.216913	-3.365318
H	-1.252837	-2.486031	4.676333

H	-4.841995	-3.104778	0.929700
H	-5.559787	-1.707690	-1.285907
H	1.930201	4.866764	0.416861
H	1.539978	1.500280	3.975856
H	0.231137	4.445363	-1.522694
H	-4.595030	0.393130	-2.517600
H	-2.948714	-2.848479	2.721230
H	0.635671	-0.613282	5.229894
H	2.466910	3.630774	2.774582
H	1.691170	0.632752	-2.593144
H	4.172484	0.579141	-2.505586
H	4.012927	-1.389244	1.306480
H	1.528524	-1.366831	1.229240
H	2.311193	-4.612812	-1.709908
H	1.924642	-3.439844	-3.082943
H	-0.256189	0.009389	-1.621312
H	-1.421698	-2.515365	-1.530331
H	-0.793414	-4.898532	-0.333961
H	0.900213	-4.842287	0.185408
H	-0.195263	-3.493519	0.547831
H	-1.141009	-1.269120	-3.583593
H	0.569576	-1.734158	-3.735055
H	-0.699106	-2.870912	-4.175632

Products: Co-porphyrin and aminated 2-methyl-1-butene

Co	2.320705	0.642875	0.143988
C	-4.213033	-1.637946	-0.189151
C	-3.335674	-0.539777	0.002460
C	-3.915072	0.751298	0.149176
C	-5.286424	0.935081	0.111355
C	-6.131661	-0.168480	-0.073688
C	-5.588326	-1.449137	-0.225306
C	-1.125863	-1.856662	0.124112
C	-1.197435	-2.736301	-1.132028
C	-1.361736	-4.067488	-1.083005
C	-1.283701	-2.575563	1.476321
C	-0.984595	-2.016679	-2.442428
C	0.571302	2.694418	1.535898
C	-0.264479	3.837303	1.276032
C	-0.261265	4.027093	-0.074225
C	0.587106	3.007790	-0.634024
C	0.793017	2.168566	2.799829
C	1.553657	1.037137	3.052013
C	1.732850	0.466190	4.361782
C	2.503497	-0.646026	4.202084
C	2.803353	-0.744022	2.797147
C	4.157233	-1.338119	-1.227766
C	4.967338	-2.501214	-0.973749
C	4.830279	-2.792638	0.349799
C	3.947198	-1.798876	0.903300
C	3.600465	-1.734584	2.244009
C	0.878141	2.899315	-1.985515
C	1.749330	1.964731	-2.523254
C	3.193085	0.331830	-2.740604
C	3.000996	0.892347	-4.053136
C	2.096371	1.902000	-3.919482
C	4.016046	-0.752118	-2.476164
N	3.529487	-0.909598	-0.071503
N	2.423190	0.995034	-1.801274
N	1.092686	2.184396	0.358120
N	-7.585673	0.021637	-0.110778
N	-1.965541	-0.648956	0.024426
N	2.213987	0.290331	2.091478
O	-8.021502	1.170606	0.020159
O	-8.296063	-0.976374	-0.270938
H	2.852405	-1.342049	4.956266
H	1.312777	0.873676	5.274159
H	3.496057	0.541211	-4.951225

H	5.554040	-3.018863	-1.723892
H	5.284024	-3.597419	0.916708
H	-0.780792	4.409114	2.038599
H	0.412313	3.608685	-2.663422
H	0.325938	2.665427	3.645286
H	4.001497	-2.494051	2.909007
H	4.568415	-1.184385	-3.305495
H	1.695277	2.557680	-4.683724
H	-0.771386	4.789535	-0.651682
H	-3.265167	1.612757	0.294958
H	-5.721171	1.922579	0.226510
H	-6.257157	-2.290838	-0.373562
H	-3.815376	-2.635746	-0.326653
H	-1.350957	-4.663861	-1.993344
H	-1.508971	-4.612014	-0.155034
H	-1.479629	0.212188	0.224384
H	-0.104786	-1.445031	0.112869
H	-0.037527	-1.460463	-2.436938
H	-0.960453	-2.720176	-3.279737
H	-1.777324	-1.283778	-2.633226
H	-1.158405	-1.851705	2.287915
H	-2.265309	-3.043780	1.591392
H	-0.515787	-3.346905	1.594400