Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The mechanism of Thiophene oxidation on Metal-free Two-dimensional Hexagonal Boron Nitride

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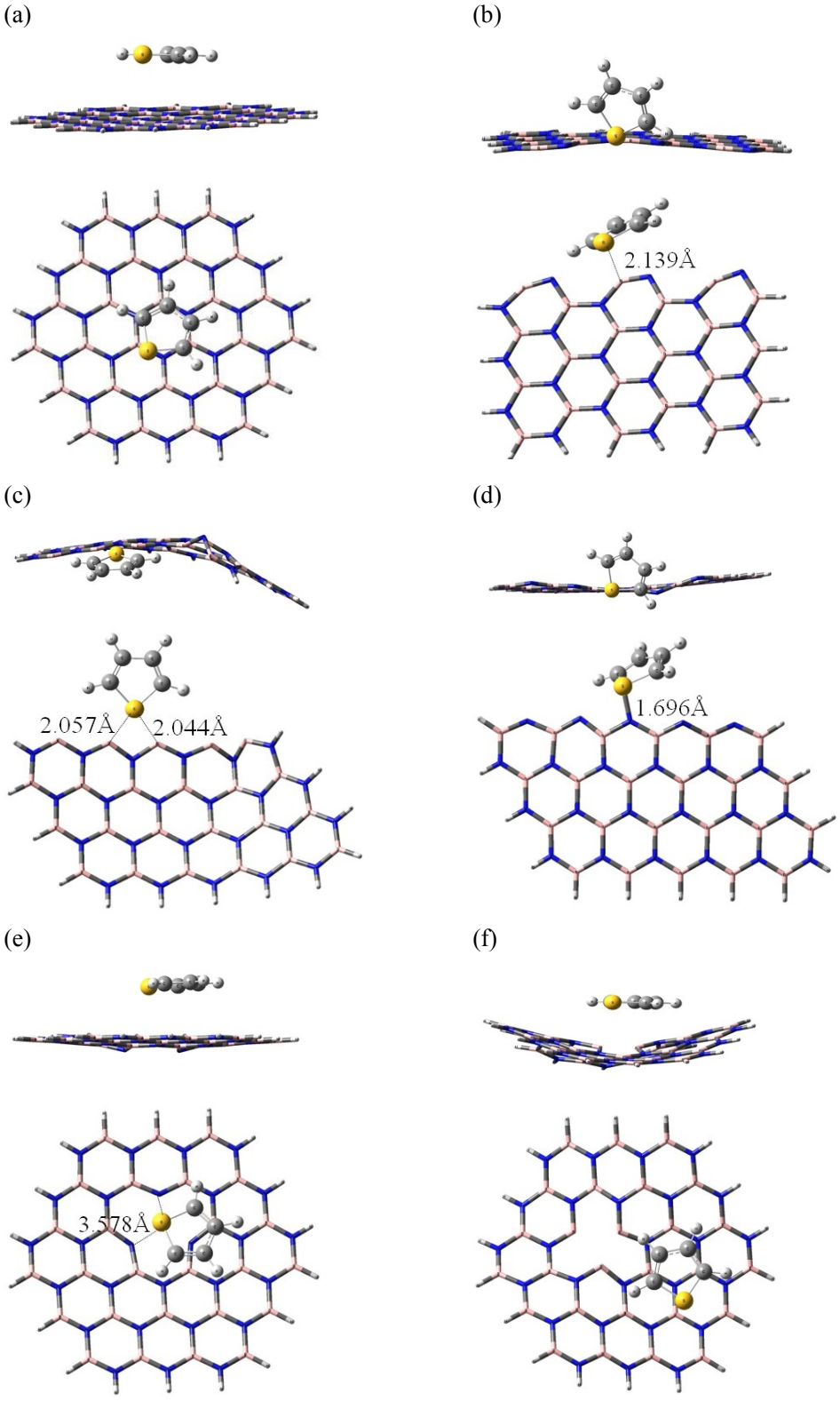

FIGURE S1 Thiophene (C_4H_4S) adsorption on perfect h-BN, armchair, zig-B, zig-N, B-vacancy, N-vacancy models.(a) perfect h-BN-C_4H_4S; (b)arm-C_4H_4S; (c)zig-B-C_4H_4S; (d) zig-N-C_4H_4S; (e) B-vacancy-C_4H_4S; (f) N-vacancy-C_4H_4S;

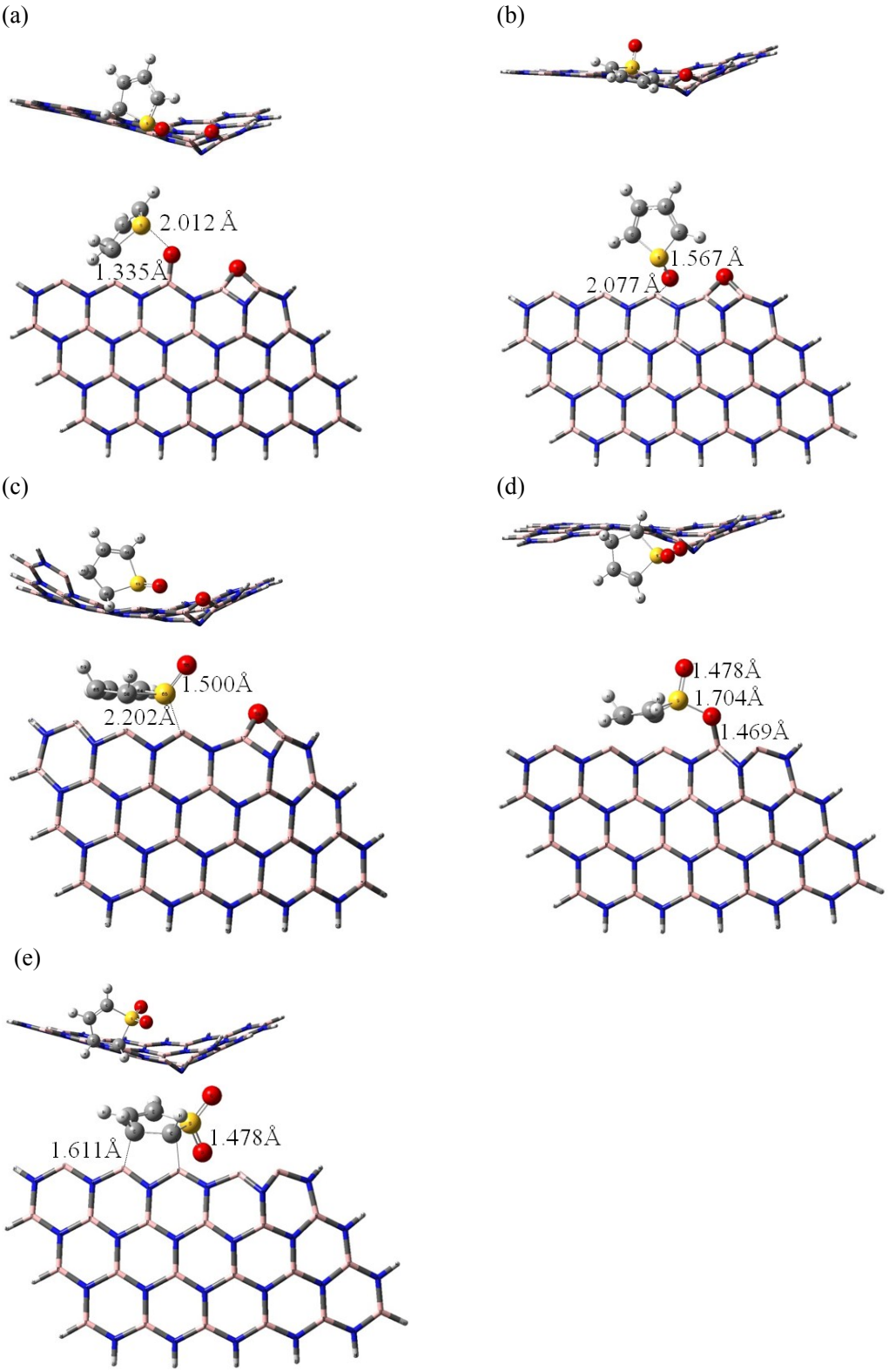

FIGURE S2 The oxidation of thiophene on zig-B models. (a) OO/C_4H_4S co-adsorption; (b)TS1-zig-B; (c)IM1-zig-B; (d) TS2-zig-B; (e) FS-zig-B

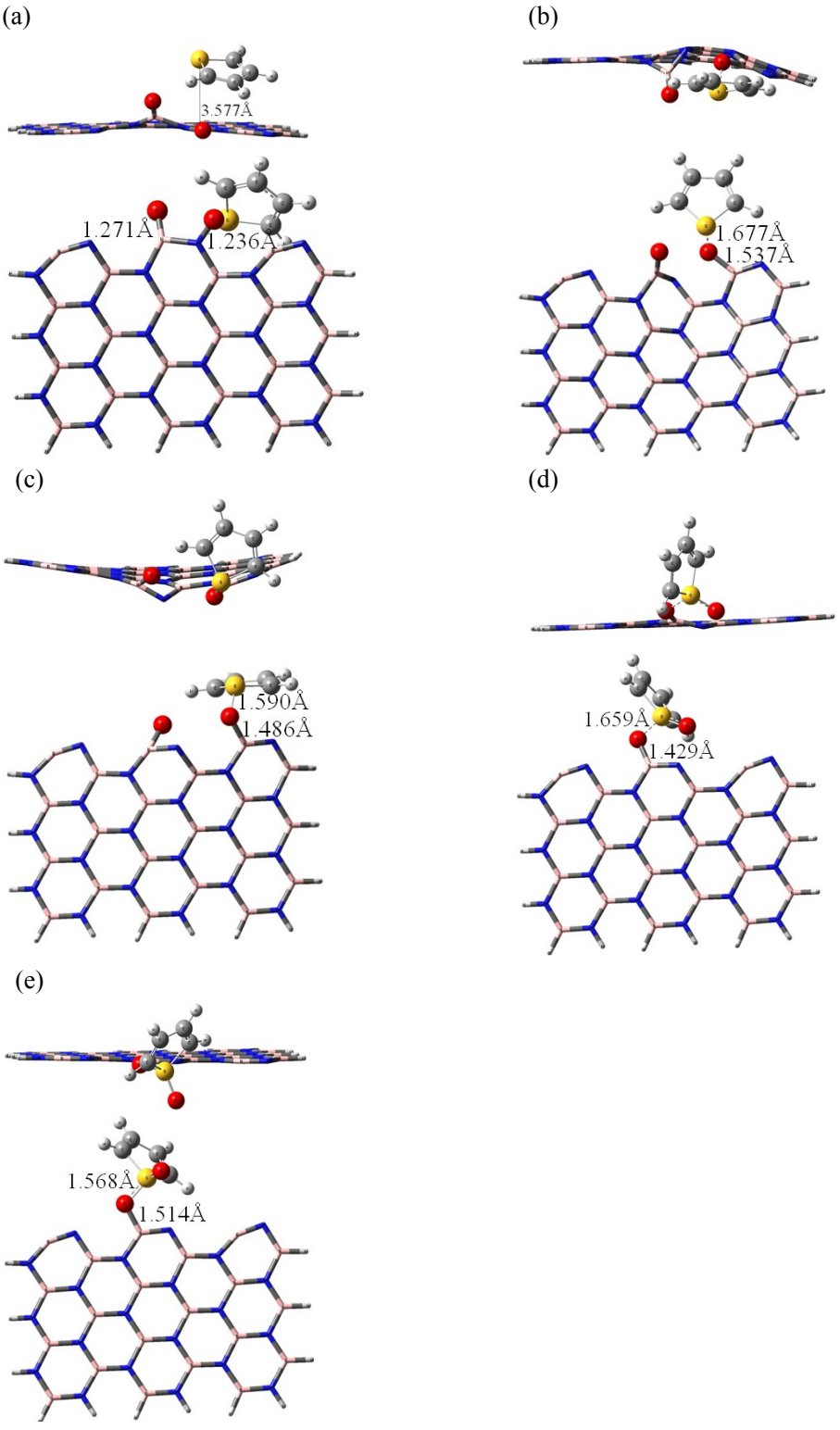

FIGURE S3 The oxidation of thiophene on armchair models.(a) OO/C_4H_4S co-adsorption; (b)TS1-arm; (c)IM1-arm; (d) TS2-arm; (e) FS-arm

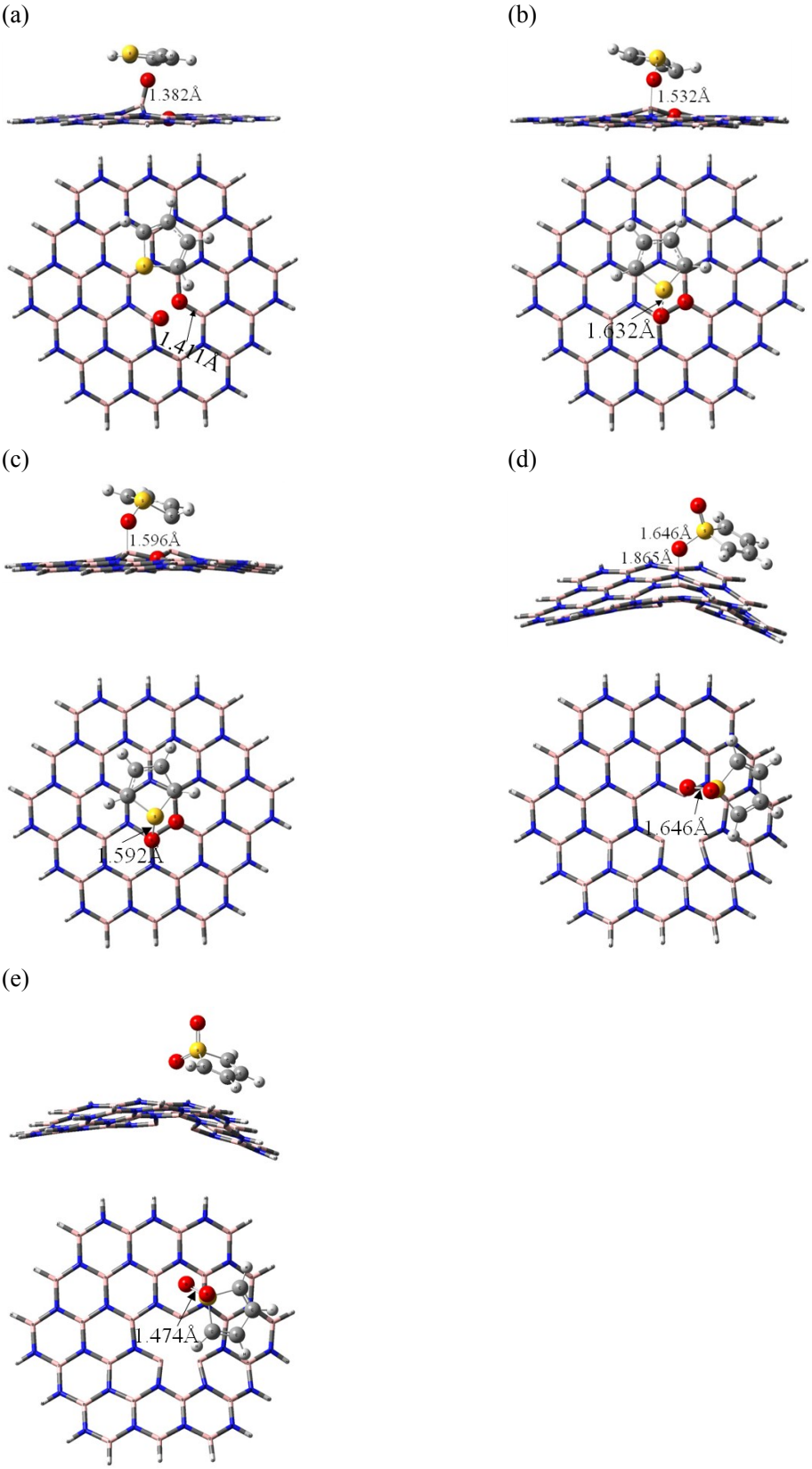

FIGURE S4 The oxidation of thiophene on N-vacancy models.(a) OO/C_4H_4S co-adsorption; (b)TS1- N-vacancy; (c)IM1-N-vacancy; (d) TS2-N-vacancy; (e) FS-N-vacancy

Table S1. The Electronic Energies (E_{elec}), Enthalpies (H_{298}), Gibbs Free Energies (G_{298}) (All in a.u.) of all species in the process of Thiophene (TH) oxidation on the edge sites.

species	E_{elec}	H_{298}	G_{298}	ΔH_{298}	ΔG_{298}
O_2	-150.3646757	-150.3575887	-150.38087		
Thiophene(TH)	-553.0696341	-552.9977261	-553.02999		
zig-B	-1841.38816	-1840.966526	-1841.0593		
2O-zig-B	-1992.211342	-1991.776248	-1991.8678	-283.719	-268.363
O_2-zig-B	-1992.043858	-1991.609428	-1991.7024	-179.037	-164.568
TH-zig-B	-2394.499474	-2394.003282	-2394.1058	-24.492	-10.3815
2O-TH- zig-B	-2545.2809	-2544.772365	-2544.8777	-282.708	-255.754
TS1-zig-B	-2545.063461	-2544.558438	-2544.6647	-148.467	-122.096
IM1-zig-B	-2545.223394	-2544.714633	-2544.8163	-246.481	-217.22
TS2-zig_B	-2545.072766	-2544.566621	-2544.6674	-153.602	-123.764
FS-zig-B	-2545.088175	-2544.578966	-2544.683	-161.349	-133.543
zig-N	-1841.297632	-1840.888720	-1840.9833		
2O-zig_N	-1991.748461	-1991.326596	-1991.4256	-50.3809	-38.5479
O_2-zig-N	-1991.693744	-1991.274590	-1991.3743	-17.7465	-6.376
TH-zig_N	-2394.418015	-2393.933549	-2394.0395	-29.5575	-16.445
2O-TH-zig-N	-2544.916424	-2544.418826	-2544.5259	-109.683	-82.6373
TS1-zig-N	-2544.769035	-2544.277822	-2544.3915	-21.2013	1.692143
IM1-zig-N	-2544.909155	-2544.412331	-2544.5196	-105.608	-78.6824
TS2-zig-N	-2544.903189	-2544.407159	-2544.5123	-102.362	-74.1244
FS-zig-N	-2544.972614	-2544.473852	-2544.5805	-144.213	-116.951
armchair	-1681.422603	-1681.040501	-1681.1289		
2O-armchair	-1831.857263	-1831.465501	-1831.5596	-42.3011	-31.2255
O_2-armchair	-1831.798076	-1831.407337	-1831.5031	-5.80277	4.210404
TH-armchair	-2234.512312	-2234.056281	-2234.1583	-11.3289	0.363454
2O-TH-armchair	-2384.953394	-2384.487844	-2384.5964	-57.7484	-35.5396
TS1-armchair	-2384.90218	-2384.439207	-2384.5405	-27.2282	-0.43976
IM1-armchair	-2384.927831	-2384.462768	-2384.5677	-42.0127	-17.5279
TS2-armchair	-2384.857649	-2384.394192	-2384.4994	1.019076	25.37337
FS-armchair	-2384.924079	-2384.457812	-2384.5647	-38.9028	-15.6046

Table S2. The Electronic Energies (E_{elec}), Enthalpies (H_{298}), Gibbs Free Energies (G_{298}) (All in a.u.) of all species in the process of thiophene (TH) oxidation on the B- and N- vacancy sites.

species	E_{elec}	H_{298}	G_{298}	ΔH_{298}	ΔG_{298}
B-vacancy	-2138.562525	-2138.048758	-2138.1492		
2O-B-vacancy	-2288.994012	-2288.467753	-2288.5717	-38.5333	-26.15
O_2-B-vacancy	-2288.902583	-2288.377384	-2288.4848	18.17407	28.40813
TH-B-vacancy	-2691.652461	-2691.062978	-2691.1852	-10.3505	-3.81808
2O-TH-B-vacancy	-2842.059213	-2841.459685	-2841.5796	-34.8978	-12.2654
TS1-B-vacancy	-2842.0331976	-2841.435822	-2841.552	-19.923	5.060052
IM1-B-vacancy	-2842.0874	-2841.486227	-2841.6083	-51.5531	-30.3131
TS2-B-vacancy	-2841.985871	-2841.389559	-2841.5095	9.107115	31.72258
FS-B-vacancy	-2842.012181	-2841.412647	-2841.5373	-5.38096	14.25195
N-vacancy	-2108.737487	-2108.222227	-2108.3231		
2O-N-vacancy	-2259.46381	-2258.934694	-2259.0396	-222.689	-210.61
TH-N-vacancy	-2661.848426	-2661.257047	-2661.3744	-23.2769	-13.3942
2O-TH-N-vacancy	-2812.558888	-2811.955833	-2812.0758	-237.382	-214.499
TS1-N-vacancy	-2812.510197	-2811.909289	-2812.0211	-208.175	-180.212
IM1-N-vacancy	-2812.513203	-2811.911202	-2812.0233	-209.375	-181.575
TS2-N-vacancy	-2812.233749	-2811.634766	-2811.7524	-35.9085	-11.5517
FS-N-vacancy	-2812.238104	-2811.636984	-2811.7576	-37.3006	-14.8559

The optimized geometries of the crucial structure reported in the paper

TS1-zig-N

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	5.050304	-5.352263	-0.131331
2	1	0	2.889125	-6.686025	-0.090350
3	1	0	-6.565043	3.612996	-0.141908
4	1	0	-4.424970	5.003816	-0.282100
5	5	0	-1.436533	0.295433	0.023559
6	5	0	0.782286	-0.872839	0.071775
7	5	0	-1.339763	-2.208412	0.042899
8	7	0	-2.114903	-0.982230	0.036399
9	7	0	0.008025	0.362160	0.044571
10	7	0	0.101856	-2.154490	0.047267
11	5	0	0.725176	1.636310	0.031849
12	5	0	0.872773	-3.383913	0.024474
13	5	0	-3.560846	-1.042475	0.033744
14	5	0	-1.563328	2.797761	-0.041762
15	5	0	2.910739	0.461753	0.207906
16	5	0	2.999445	-2.060124	0.049661
17	5	0	-1.251894	-4.716256	0.028168
18	5	0	-3.459420	-3.549714	0.055260
19	5	0	-3.683588	1.460122	-0.020061
20	5	0	-5.792344	0.105684	-0.000198
21	5	0	-3.820639	3.985094	-0.144424
22	5	0	-5.921291	2.609642	-0.091989
23	7	0	-2.435117	3.904963	-0.015217
24	7	0	-4.481159	2.681547	-0.080943
25	7	0	-6.578222	1.328792	-0.044386
26	7	0	-0.106276	2.861016	-0.081383
27	7	0	-2.231706	1.514071	-0.005463
28	7	0	-4.346058	0.175611	0.009276
29	7	0	-6.455921	-1.186654	0.031540
30	7	0	2.122753	1.629572	0.104049
31	7	0	-4.233464	-2.330891	0.051779
32	5	0	-5.673840	-2.397329	0.056166
33	5	0	5.135542	-0.711848	0.060771
34	7	0	4.313511	0.374230	0.448534
35	7	0	2.224687	-0.836565	0.110228
36	7	0	-2.020983	-3.493081	0.043839
37	7	0	4.450306	-2.017542	0.013483

38	7	0	2.317003	-3.336779	0.008240
39	7	0	0.184255	-4.667537	0.010061
40	5	0	5.230403	-3.243443	-0.063690
41	5	0	3.087983	-4.567001	-0.044137
42	5	0	0.952598	-5.895330	-0.029379
43	7	0	4.520088	-4.491010	-0.080907
44	7	0	2.371341	-5.816914	-0.059651
45	1	0	-8.685871	2.247872	-0.085701
46	1	0	-9.648666	-0.081615	-0.010512
47	1	0	8.552279	-1.814943	-0.012843
48	1	0	7.227007	-4.008414	-0.109163
49	5	0	-8.023478	1.254821	-0.048930
50	5	0	-7.900587	-1.254153	0.029282
51	7	0	-8.638088	-0.032222	-0.008317
52	7	0	6.516468	-0.782437	-0.274537
53	7	0	6.673120	-3.160792	-0.101440
54	5	0	7.362481	-1.898006	-0.109374
55	8	0	0.428022	4.039842	-0.267262
56	8	0	3.025350	3.076550	0.595993
57	1	0	-8.464083	-2.306608	0.057315
58	1	0	-6.220791	-3.457112	0.077747
59	1	0	-4.015399	-4.604662	0.065248
60	1	0	-1.814715	-5.768506	0.026666
61	1	0	0.403866	-6.956837	-0.039074
62	1	0	1.708494	6.038219	0.298220
63	6	0	2.765845	5.848021	0.189407
64	6	0	3.836304	6.618541	0.502490
65	16	0	3.275254	4.313873	-0.524544
66	6	0	5.110009	5.988719	0.204404
67	1	0	3.752132	7.606102	0.943864
68	6	0	4.976152	4.752346	-0.335855
69	1	0	6.067273	6.456025	0.409369
70	1	0	5.738168	4.044466	-0.632264

TS2-zig-N

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-5.599497	4.474704	0.412399
2	1	0	-3.586189	6.120805	0.383243
3	1	0	6.774417	-3.185185	0.364412
4	1	0	4.739995	-4.755269	0.293087

5	5	0	1.456611	-0.311836	-0.345491
6	5	0	-0.824678	0.669722	-0.459844
7	5	0	1.130535	2.183001	-0.236595
8	7	0	2.006007	1.029367	-0.255556
9	7	0	0.036976	-0.484370	-0.545633
10	7	0	-0.298208	2.000058	-0.305261
11	5	0	-0.518836	-1.831830	-0.606785
12	5	0	-1.205475	3.116993	-0.134908
13	5	0	3.431125	1.208911	-0.116377
14	5	0	1.713222	-2.818976	-0.128365
15	5	0	-2.762053	-0.823345	-0.539274
16	5	0	-3.164720	1.561829	-0.176240
17	5	0	0.769606	4.655643	-0.016353
18	5	0	3.103077	3.704484	-0.049402
19	5	0	3.744031	-1.286699	-0.029895
20	5	0	5.730657	0.244179	0.094940
21	5	0	4.056886	-3.778539	0.230452
22	5	0	6.053061	-2.241535	0.246808
23	7	0	2.664061	-3.800312	0.250566
24	7	0	4.630540	-2.432192	0.146591
25	7	0	6.608548	-0.909319	0.209560
26	7	0	0.329475	-2.945287	-0.424760
27	7	0	2.316443	-1.468013	-0.202230
28	7	0	4.302178	0.055028	-0.032570
29	7	0	6.283578	1.590971	0.110304
30	7	0	-1.941079	-1.965339	-0.751537
31	7	0	3.981212	2.555923	-0.049624
32	5	0	5.409757	2.736172	0.047204
33	5	0	-5.057108	-0.134176	-0.028388
34	7	0	-4.131078	-1.180383	-0.355876
35	7	0	-2.251041	0.489733	-0.443963
36	7	0	1.671314	3.526213	-0.113703
37	7	0	-4.575075	1.261001	-0.012243
38	7	0	-2.638394	2.898822	-0.066837
39	7	0	-0.662312	4.458823	-0.003659
40	5	0	-5.494336	2.370765	0.204512
41	5	0	-3.551187	4.001447	0.148851
42	5	0	-1.576409	5.570874	0.175238
43	7	0	-4.957321	3.706715	0.257992
44	7	0	-2.980737	5.321359	0.245372
45	1	0	8.777471	-1.648900	0.400677
46	1	0	9.546494	0.751408	0.368167
47	1	0	-8.587825	0.495485	0.266947
48	1	0	-7.572246	2.842402	0.424322

49	5	0	8.037609	-0.715573	0.309659
50	5	0	7.714619	1.775894	0.210627
51	7	0	8.545887	0.618907	0.298523
52	7	0	-6.417489	-0.257090	0.379119
53	7	0	-6.907776	2.083415	0.333403
54	5	0	-7.417234	0.738881	0.308309
55	8	0	-0.518256	-4.218760	0.193121
56	8	0	-2.766629	-5.790839	-0.533021
57	1	0	8.190834	2.871319	0.220572
58	1	0	5.869324	3.836793	0.079921
59	1	0	3.562904	4.803192	0.017101
60	1	0	1.215182	5.759368	0.072098
61	1	0	-1.161435	6.687389	0.271174
62	1	0	-3.237316	-4.537108	2.488552
63	6	0	-3.347738	-4.061882	1.521467
64	6	0	-4.245428	-3.158935	1.133506
65	16	0	-2.225307	-4.575333	0.153641
66	6	0	-4.180485	-2.651799	-0.297482
67	1	0	-5.015715	-2.758787	1.790053
68	6	0	-2.790109	-3.118298	-0.866045
69	1	0	-5.013731	-3.057900	-0.880490
70	1	0	-2.839842	-3.531755	-1.879215
