NICKEL-CATALYZED BOLYLATION OF ARYL HALIDES WITH 4,4,6-TRIMETHYL-1,3,2-DIOXABORINANE

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Supporting Information

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General Considerations.

All experiments were carried out under a nitrogen atmosphere using oven-dried (120 °C) glassware. NMR spectra were recorded on a JEOL JNM-A500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz). Chemical shifts of ^{1}H NMR and ^{13}C NMR signals reported δ ppm referenced to the solvent or an internal $SiMe_4$. Mass spectra were obtained at an ionization potential of 70 eV with a Shimadzu GC/MS QP-5000 spectrometer. GLC analyses were carried out with a Shimadzu GC-14B equipped with a glass column (OV-17 on Chromosorb W, 2 m) and with a capillary column (DB-1, 0.53 mmI.D., 30 m). GLC yields were determined using suitable hydrocarbons as internal standards.

Materials.

Toluene was distilled from sodium benzophenone ketyl before use. Aryl halides **2**, Et_3N and DPPF were purchased from commercial sources, and used without purification. 4,4,6-Trimethyl-1,3,2-dioxaborinane (**1a**),[1] $NiCl_2$(dppp),[2] and (4-EtO_2C-C_6H_4)NiBr(PPh_3)$_2$[3] were prepared by the literature method.

Nickel-Catalyzed Borylation. General Procedure.

In a glove box, $NiCl_2$(dppp) (6.8 mg, 25 μmol) and DPPF (13.9 mg, 50 μmol) were placed in a screw-capped vial containing a stir bar, and dissolved in 1 mL of toluene. After being stirred for 30 min at room temperature, Et_3N (104 μL, 0.75 mmol), aryl halide **2** (0.250 mmol), and **1a** (50 μL, 0.375 mmol) were successively added. The vial was sealed with a cap and removed from the glove box. The reaction mixture was then stirred at 100 °C for 18 h. The resulting mixture was allowed to cool to room temperature, diluted with Et_2O, washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by Kugelrohr distillation to give the desired 2-aryl-4,4,6-trimethyl-1,3,2-dioxaborinane **3**. **3a**,[1] **3b**,[1] **3c**,[1] **3e**,[4] **3f**,[5] **3g**,[5] **3h**[6] and **3i**[1] were identified by comparison of their ^{1}H NMR spectra with those of authentic samples.

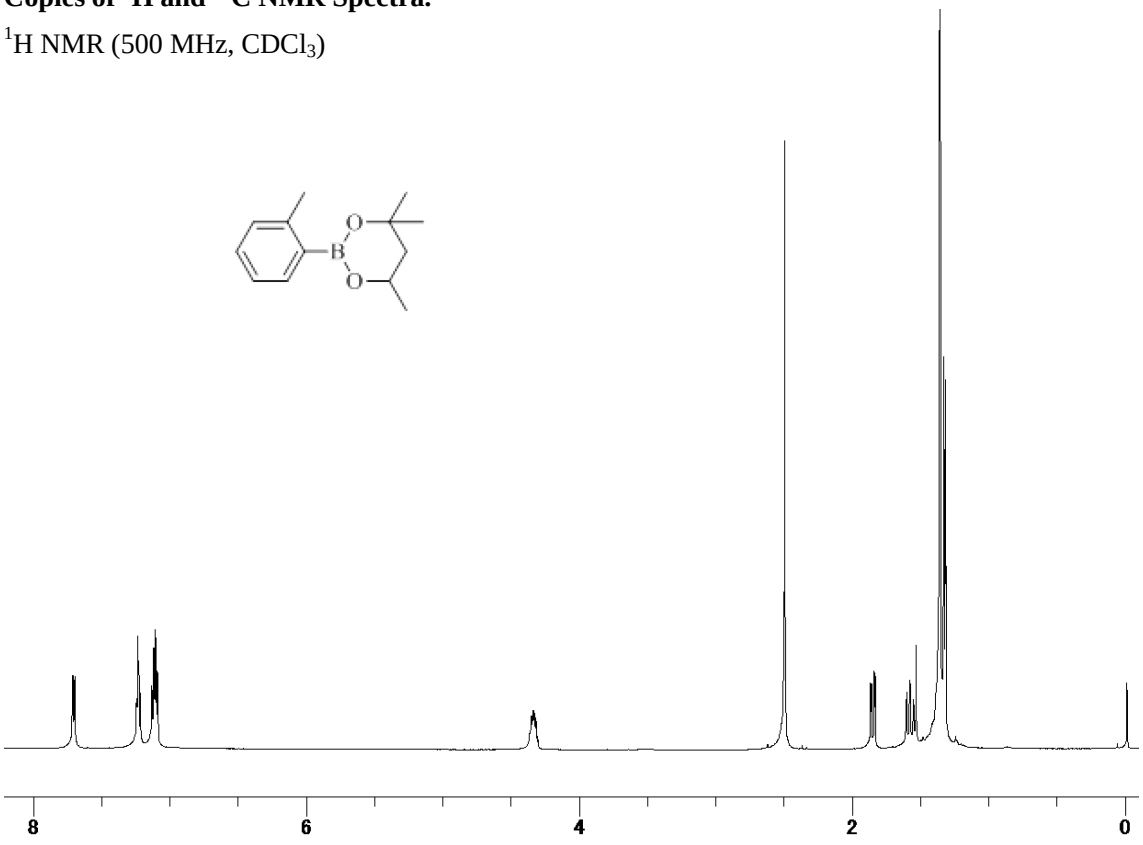
3k: ^{1}H NMR ($CDCl_3$): δ1.34 (d, *J* = 6.4 Hz, 3H), 1.37 (s, 3H), 1.38 (s, 3H), 1.59 (dd, *J* = 14.1, 11.6 Hz, 1H), 1.86 (dd, *J* = 13.8, 2.9 Hz, 1H), 2.51 (s, 3H), 4.35 (br s, 1H), 7.12 (dd, *J* = 13.4, 7.2 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.25 (s, 1H), 7.72 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 22.39, 23.25, 28.22, 31.34, 45.93, 65.02, 71.07, 124.59, 129.72, 129.87, 134.66, 143.78. EI-MS: *m/z* (%) = 218 (22, [M^+]), 161 (20), 147 (100).

Reaction of ArNiBr(PPh_3)$_2$ with 4,4,6-Trimethyl-1,3,2-dioxaborinane.

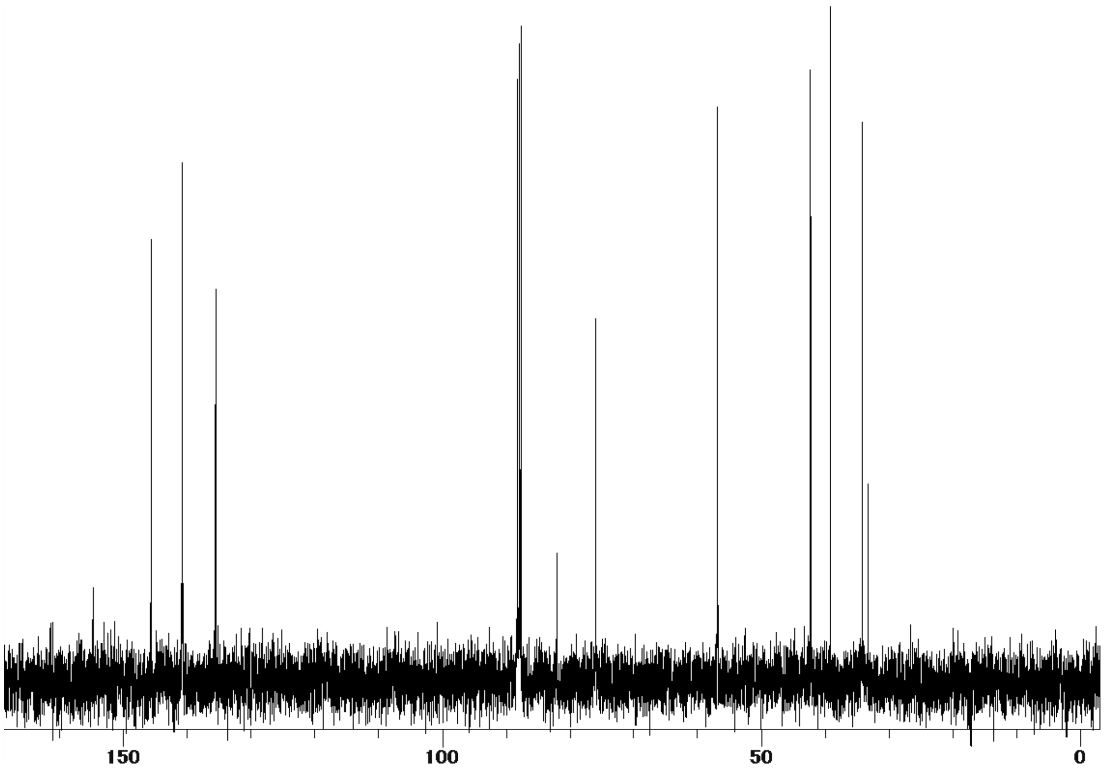
(4-EtO_2C-C_6H_4)NiBr(PPh_3)$_2$ (12.4mg, 0.015 mmol) and DPPP (6.3 mg, 0.015 mmol) were placed in a vial, and dissolved in 1 mL of toluene. After being stirred for 10 min at room temperature, **1a** (40 μL, 0.3 mmol) was added. The reaction mixture was then stirred at 100 °C for 2 h. The resulting mixture was diluted with toluene and washed with brine. The GC analysis of the organic layer indicated the formation of the desired arylboronate **3a** in 66% yield.

Copies of ^{1}H and ^{13}C NMR Spectra.

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



Computational Details.

All calculations were performed using Gaussian 09 program suite.[7] Geometries were optimized with the DFT method using the B3LYP functional in combination with a basis set (termed BS-I) employing LANL2DZ on Ni, Br and P, and 6-31G(d,p) on other atoms. Polarization functions were added for Ni (ζ(f) = 3.130), Br (ζ(d) = 0.434) and P (ζ(d) = 0.364).[8] Frequency calculations were performed with structures characterized as minima or transition states based on the observed number of imaginary frequencies, and thermodynamic corrections at 298 K and 1 atm were also calculated at the same level of theory. Single point energy calculations on optimized geometries were performed with B3LYP using a larger basis set (termed BS-II) and the CPCM solvation model (toluene). In BS-II, the Wachters+f basis set was used for Ni,[9] whereas the same basis sets as those of BS-I were employed for Br and P. For the other atoms, 6-311G(d,p) basis sets were used. Discussion of the reaction energetics in the manuscript is based on CPCM/B3LYP/BS-II//B3LYP/BS-I.

Reaction Pathway with Calculated Relative Free Energies.

The results are summarized in Figure S1. The red line represents the pathway, which is shown in Figure 1. The transition state $\mathbf{TS_{S4–S5}}$ from **7**, in which the hydride is pointing toward the aryl ligand, would account for the undesirable dehalogenation (blue line), but the activation barrier is higher than the formation of transition state $\mathbf{TS_{8–9}}$.

Marder and Lin proposed that tertiary amines assist the formation of the cationic palladium $[L_2Pd(Ar)]^+$ species.[9] The green line is represents the similar charge-separated pathway for the nickel-catalyzed borylation. We have adopted NMe_3 as a tertiary amine. Our calculations indicate that the reaction is extremely endothermic.

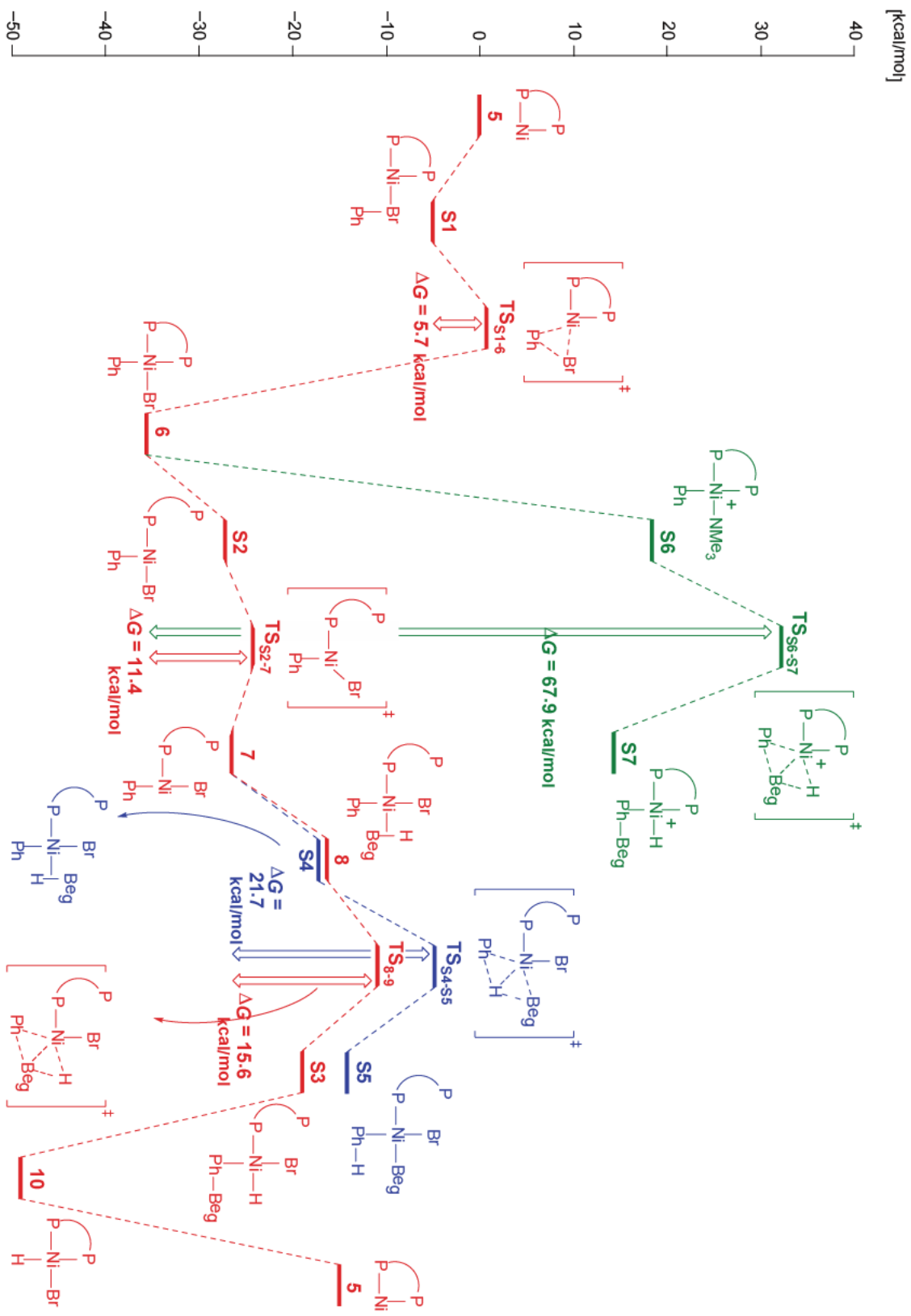


Figure S1 Schematic illustration reaction pathways with calculated relative free energies (kcal/mol) for species involved in the reaction.

Geometries and Cartesian Coordinates.

5

E = -1641.66605454 a.u.

C	1.315679	1.673541	-0.288115
C	-0.000032	2.152559	0.360975
C	-1.315723	1.673508	-0.288131
P	-1.794551	-0.121672	0.090298
Ni	0.000016	-1.223837	-0.060068
P	1.794554	-0.121630	0.090302
H	3.039830	-0.138031	-0.628508
H	2.411714	0.083480	1.368636
H	-2.411602	0.083426	1.368687
H	-3.039892	-0.138077	-0.628403
H	-2.137218	2.326490	0.025186
H	-1.242723	1.753012	-1.379167
H	2.137154	2.326544	0.025211
H	1.242688	1.753046	-1.379152
H	-0.000045	3.249469	0.309426
H	-0.000036	1.907176	1.431375

S1

E = -1886.56975420 a.u.

C	-1.225073	1.294867	-0.786049
C	-1.513151	0.251576	0.164238
C	-1.853596	0.601486	1.512239
C	-1.830870	1.916739	1.910909
C	-1.542490	2.957731	0.982447
C	-1.271122	2.653522	-0.329264
Ni	0.421351	0.216943	-0.232978
Br	-2.287767	-1.447034	-0.524311
P	2.219595	0.999141	-1.256510
C	3.827629	0.830199	-0.286433
C	4.077903	-0.584980	0.272061
C	3.181328	-1.013327	1.451567
P	1.396131	-1.370885	0.964997
H	2.389706	2.343979	-1.716247
H	2.641480	0.384724	-2.477512
H	1.587005	-2.661298	0.380469
H	0.919054	-1.856354	2.223396
H	3.607524	-1.896081	1.937518
H	3.151411	-0.215458	2.203227
H	4.665198	1.130771	-0.923005
H	3.775379	1.550984	0.538343
H	5.119027	-0.623840	0.616695
H	4.007775	-1.323627	-0.538421
H	-2.124791	-0.186354	2.207856
H	-2.060037	2.165203	2.943660
H	-1.576152	3.993003	1.309188
H	-1.120382	3.447966	-1.056303
H	-1.318378	1.101376	-1.851160

TS_{S1-6}

E = -1886.56003542 a.u.

136.0566*i* cm^{-1}

C	-3.631654	0.322968	1.154064
P	-2.041036	-0.646460	1.442077
Ni	-0.296846	-0.032482	0.188243
P	-1.364440	1.010932	-1.474553
C	-3.114631	1.590191	-1.070375
C	-3.975343	0.544425	-0.332863
H	-2.072538	-0.675440	2.872482
H	-2.550590	-1.969031	1.266260
H	-1.656928	0.289456	-2.675840
H	-0.908536	2.191529	-2.143821
H	-3.615333	1.894274	-1.994395
H	-3.013037	2.488915	-0.450341
H	-4.458270	-0.189957	1.654662
H	-3.504983	1.290999	1.653362
H	-5.018970	0.879918	-0.382786
H	-3.947162	-0.413004	-0.871197
C	1.582311	0.220881	-0.012326
Br	1.322054	-1.884151	-0.496050
C	2.255394	1.033623	-0.952246
C	2.893763	2.178587	-0.506810
C	2.917870	2.509896	0.864686
C	2.325701	1.665140	1.791233
C	1.688877	0.476909	1.373699
H	2.228627	0.779178	-2.006596
H	3.374341	2.834501	-1.228193
H	3.432873	3.407256	1.194154
H	2.397237	1.881730	2.854089
H	1.381585	-0.263415	2.103091

6

E = -1886.61980709 a.u.

C	2.203810	-0.841037	1.207736
C	1.553652	-0.600258	-0.010933
C	2.263644	-0.813525	-1.201607
C	3.594273	-1.241243	-1.174047
C	4.233952	-1.472086	0.045813
C	3.534751	-1.270926	1.236774
Ni	-0.254081	0.054933	-0.049945
P	-2.404175	0.828940	0.005525
C	-3.849078	-0.361119	-0.193359
C	-3.604959	-1.736011	0.460310
C	-2.558239	-2.611800	-0.257329
P	-0.778654	-2.059915	-0.018857
H	1.788559	-0.628852	-2.162604
H	4.132114	-1.390070	-2.107467
H	5.268105	-1.804949	0.067270
H	4.024850	-1.442847	2.192222

H	1.682599	-0.675716	2.148127
H	-2.771781	1.871077	-0.881881
H	-2.739591	1.466233	1.229224
Br	0.453594	2.319488	0.019223
H	-0.443349	-2.704562	1.202520
H	-0.098492	-2.928381	-0.910970
H	-2.637613	-3.649977	0.079388
H	-2.749822	-2.610622	-1.336909
H	-4.754813	0.095991	0.215124
H	-4.013795	-0.489662	-1.269728
H	-4.554718	-2.283909	0.461579
H	-3.333087	-1.610980	1.517422

S2

E = -1886.59849087 a.u.

C	2.402084	-1.212879	1.174902
C	1.913495	-0.684520	-0.023939
C	2.414531	-1.130313	-1.250905
C	3.422917	-2.100225	-1.272975
C	3.920686	-2.627023	-0.079719
C	3.410698	-2.182309	1.141389
Ni	0.688031	0.730040	0.016113
P	-6.415167	-2.233289	0.035146
C	-5.145879	-0.824539	-0.026976
C	-3.705691	-1.359906	-0.038858
C	-2.668631	-0.225921	-0.008898
P	-0.888376	-0.787554	-0.023682
H	2.043672	-0.718490	-2.185420
H	3.819620	-2.438251	-2.226752
H	4.703214	-3.380010	-0.101347
H	3.797641	-2.584550	2.074013
H	2.021192	-0.865898	2.131474
H	-7.569638	-1.425007	-0.214302
H	-6.299387	-2.626548	-1.337748
Br	1.713336	2.756009	0.067892
H	-0.865289	-1.743969	1.026257
H	-0.865289	-1.685999	-1.123685
H	-2.790008	0.442465	-0.869168
H	-2.790408	0.394647	0.886482
H	-5.322020	-0.177933	-0.891731
H	-5.308949	-0.217881	0.871546
H	-3.547379	-1.973764	-0.934753
H	-3.551520	-2.022549	0.821897

TS$_{S2–7}$

E = -1886.59714996 a.u.

35.8405*i* cm^{-1}

C	0.620312	1.884708	-1.155318
C	0.864668	1.333851	0.109360
C	1.033504	2.171129	1.218287
C	0.996921	3.560066	1.052235
C	0.768338	4.112046	-0.209468
C	0.579843	3.274478	-1.311042
Ni	1.234538	-0.498399	0.223150
P	-6.432585	-0.416076	-0.007671
C	-4.694767	-0.295515	-0.758614
C	-3.604524	-0.565322	0.290190
C	-2.193843	-0.385249	-0.291419
P	-0.807377	-0.705476	0.908379
H	1.213606	1.754130	2.205905
H	1.146047	4.207504	1.912337
H	0.735157	5.190539	-0.333959
H	0.406696	3.699343	-2.296332
H	0.488782	1.243022	-2.022836
H	-7.150097	-0.367852	-1.245128
H	-6.490395	-1.846155	0.058320
Br	3.158087	-1.591011	-0.341584
H	-1.188629	0.067236	2.036885
H	-1.137417	-2.000104	1.402315
H	-2.026715	-1.060729	-1.138291
H	-2.042320	0.633500	-0.663038
H	-4.587679	-0.977451	-1.607432
H	-4.592273	0.725067	-1.145678
H	-3.713599	-1.585118	0.680608
H	-3.739645	0.110676	1.143644

7

E = -1886.59934228 a.u.

C	-1.001170	2.184529	1.193910
C	-1.186511	1.573840	-0.057949
C	-1.486677	2.374555	-1.170660
C	-1.657081	3.754319	-1.022882
C	-1.498623	4.349894	0.230766
C	-1.170288	3.565434	1.338628
Ni	-1.394807	-0.292756	-0.078149
P	6.206753	-0.037928	-0.098772
C	4.489155	0.013605	0.704948
C	3.374853	-0.232288	-0.324383
C	1.978057	-0.100070	0.302656
P	0.572527	-0.416803	-0.871926
H	-1.607306	1.925545	-2.154307
H	-1.909931	4.363637	-1.886737
H	-1.622729	5.423323	0.342440
H	-1.042644	4.026500	2.314628
H	-0.744627	1.586189	2.066286
H	6.957888	-0.036373	1.119519
H	6.287288	-1.461728	-0.236328
Br	-2.227536	-2.416211	0.244535
H	0.882344	0.423263	-1.973031
H	0.910875	-1.677085	-1.430917
H	1.847041	-0.806340	1.130052
H	1.814960	0.903816	0.708607
H	4.419361	-0.707709	1.524456
H	4.378202	1.013769	1.140066
H	3.489224	-1.234249	-0.757076
H	3.476052	0.479047	-1.153517

8

E = -2141.27491548 a.u.

C	1.710530	1.921471	-1.410923
C	1.393387	1.306548	-0.188755
C	1.736246	1.971895	1.000113
C	2.395247	3.205812	0.968787
C	2.712135	3.799959	-0.254856
C	2.368874	3.154585	-1.445028
Ni	0.573638	-0.440738	-0.184860
P	-6.924669	1.317235	0.267916
C	-5.465904	0.106406	0.238369
C	-4.118475	0.841196	0.154511
C	-2.940807	-0.140313	0.061733
P	-1.278168	0.681154	-0.049517
H	1.499825	1.522248	1.961960
H	2.654340	3.704417	1.899801
H	3.217792	4.761323	-0.280993
H	2.611769	3.610819	-2.401427
H	1.454792	1.434770	-2.349908
H	-7.933624	0.355536	0.594111
H	-6.774766	1.734343	1.630764
Br	-0.461507	-2.585357	-0.266060
H	-1.463065	1.603833	-1.112767
H	-1.318730	1.599731	1.032780
H	-2.896268	-0.808356	0.927536
H	-3.019342	-0.792124	-0.813737
H	-5.488296	-0.553712	1.110307
H	-5.600027	-0.523467	-0.648697
H	-3.995595	1.483742	1.036263
H	-4.118526	1.508953	-0.716512
B	3.010848	-0.912411	0.066025
O	3.290612	-0.900828	1.398214
O	4.044806	-0.593464	-0.756729
C	5.185677	-0.335400	0.088089
C	4.623788	-0.365425	1.532624
H	5.614761	0.633291	-0.180381
H	4.549729	0.635835	1.969175
H	1.989454	-1.381865	-0.392339
H	5.199111	-1.007388	2.204600
H	5.932953	-1.115688	-0.089859

$TS_{8–9}$

E = -2141.26981178 a.u.

132.0010*i* cm^{-1}

C	-0.401639	-2.090822	-0.871923
C	-0.791436	-1.295673	0.222249
C	-0.565282	-1.798728	1.519056
C	0.029683	-3.045798	1.715207
C	0.408832	-3.820688	0.614654
C	0.186677	-3.343334	-0.679224
Ni	-0.968412	0.673347	0.109792
B	-2.681026	-0.598645	-0.098610
O	-3.522123	-1.260999	0.784042
C	-4.509280	-1.944894	-0.000352
C	-3.977612	-1.871379	-1.448230
O	-3.036921	-0.789132	-1.428324
P	1.230720	1.057888	-0.012444
C	2.522781	-0.280759	-0.124845
C	3.970358	0.233299	-0.142015
C	4.989387	-0.911572	-0.252448
P	6.766710	-0.260575	-0.372708
Br	-1.238478	3.024613	0.140766
H	-0.877643	-1.218971	2.384082
H	0.188788	-3.417910	2.723813
H	0.864688	-4.795306	0.765836
H	0.469424	-3.947051	-1.537797
H	-0.591886	-1.737128	-1.881342
H	1.602234	1.920438	-1.073763
H	1.705510	1.831032	1.076928
H	-4.617511	-2.972352	0.360991
H	-5.471697	-1.430998	0.113121
H	-4.757730	-1.660423	-2.184972
H	-3.458694	-2.794761	-1.738686
H	-2.501959	0.637464	0.254473
H	2.349395	-0.956226	0.720110
H	2.299683	-0.859154	-1.027687
H	4.106369	0.928440	-0.980247
H	4.164264	0.811067	0.770827
H	4.882922	-1.602442	0.589292
H	4.804891	-1.485065	-1.168571
H	7.419470	-1.520735	-0.183547
H	6.908353	0.104991	1.005496

S3

E = -2141.28118912 a.u.

C	1.628617	1.627900	-1.329904
C	2.220172	1.441914	-0.051901
C	1.829654	2.325905	0.992753
C	0.948548	3.369754	0.757715
C	0.383941	3.545502	-0.519289
C	0.705178	2.672843	-1.549409
Ni	0.744644	-0.203974	-0.292758
P	-7.015434	0.278611	0.390977
C	-5.363028	-0.097083	-0.458236
C	-4.166464	0.318740	0.411884
C	-2.827732	0.097304	-0.305575
P	-1.298532	0.547851	0.667449
H	2.271156	2.194560	1.976275
H	0.690800	4.054918	1.560348
H	-0.304509	4.366988	-0.696872
H	0.278729	2.810222	-2.538799
H	1.985994	1.044845	-2.173219
H	-7.845736	-0.451138	-0.519193
H	-6.974905	-0.798038	1.335553
Br	-0.039561	-2.408733	-0.202089
H	-1.624265	1.882609	1.053207
H	-1.580991	-0.076796	1.912581
H	-2.693183	-0.953066	-0.582977

H	-2.783612	0.678420	-1.234998
H	-5.292875	-1.155880	-0.723979
H	-5.358639	0.473660	-1.394751
H	-4.174414	-0.257245	1.346024
H	-4.267776	1.373428	0.698071
B	3.409744	0.447332	0.169867
O	3.748232	-0.018629	1.416453
O	4.281140	0.068331	-0.820801
C	5.173639	-0.903773	-0.251134
C	4.954294	-0.789921	1.277758
H	6.199033	-0.673856	-0.554700
H	5.771559	-0.259607	1.780318
H	1.832261	-0.923315	-0.884355
H	4.817738	-1.761631	1.759809
H	4.906135	-1.894885	-0.634014

10

E = -1655.51533780 a.u.

Ni	-0.195819	-0.565206	-0.015975
Br	-2.431611	0.121191	0.002229
P	0.635387	1.564479	0.029125
C	2.476963	1.815013	-0.252992
H	0.080595	2.553668	-0.823745
H	0.455620	2.244880	1.264569
H	2.637613	1.815569	-1.337527
H	2.774114	2.801384	0.113875
C	3.348825	0.721887	0.400436
H	4.391934	1.057793	0.364025
H	3.104459	0.630456	1.467606
C	3.281534	-0.661336	-0.279857
H	3.369943	-0.547365	-1.366634
H	4.120909	-1.283276	0.045631
P	1.692143	-1.610632	0.039227
H	1.986731	-2.232813	1.284281
H	1.885257	-2.741424	-0.798072
H	-0.690131	-1.925377	0.017016

S4

E = -2141.27613905 a.u.

C	-1.526195	2.549174	1.116872
C	-1.097852	2.038707	-0.117494
C	-1.096263	2.885135	-1.235580
C	-1.537424	4.208394	-1.127985
C	-1.971620	4.704389	0.102729
C	-1.964685	3.872835	1.224873
Ni	-0.708867	0.169491	-0.284620
P	6.944286	-0.015676	0.554385
C	5.257669	-0.796306	0.178761
C	4.127338	0.244298	0.218756
C	2.751034	-0.399504	-0.004460
P	1.335282	0.804193	0.017567
H	-0.758814	2.517121	-2.202590
H	-1.539117	4.850158	-2.005581
H	-2.309388	5.733506	0.187978
H	-2.300869	4.253207	2.186332
H	-1.535459	1.912914	1.999103
H	7.738146	-1.149720	0.189661
H	7.128309	0.617183	-0.718087
Br	-0.259534	-2.177683	-0.494039
H	1.547139	1.505162	1.233872
H	1.775562	1.808706	-0.883660
H	2.694803	-0.919835	-0.965902
H	2.524599	-1.153046	0.756358
H	5.271497	-1.309814	-0.787028
H	5.087504	-1.558143	0.948464
H	4.305729	1.009161	-0.548528
H	4.143187	0.766427	1.184070
B	-2.990974	-0.789938	-0.077957
O	-3.073749	-0.837202	1.281345
O	-3.807133	-1.639624	-0.751975
C	-4.502947	-2.420437	0.240858
C	-3.881501	-1.991872	1.596003
H	-4.352147	-3.481503	0.025967
H	-3.229625	-2.763789	2.016090
H	-2.408526	0.094976	-0.674776
H	-4.629273	-1.708879	2.341702
H	-5.572226	-2.193193	0.175807

TS$_{S4–S5}$

E = -2141.25592662 a.u.

822.4629*i* cm^{-1}

C	0.854860	3.572473	1.195282
C	0.097990	2.398076	1.197945
C	-0.251592	1.781449	-0.012699
C	0.104558	2.392452	-1.224309
C	0.861203	3.566957	-1.222809
C	1.242944	4.154792	-0.014050
Ni	-0.837738	-0.125660	-0.007417
P	6.969871	-0.959894	-0.067384
B	-2.828968	0.344711	0.014329
O	-3.543861	0.465821	1.176329
C	-4.928356	0.627801	0.810638
C	-4.958374	0.426560	-0.724550
O	-3.575633	0.475362	-1.126534
P	1.246833	-1.052275	-0.010963
H	-1.564024	1.199564	-0.011431
H	-0.206827	1.951079	-2.167303
H	1.143814	4.027972	-2.165469
H	1.824270	5.072409	-0.014627
H	1.132380	4.037804	2.137343
H	-0.219194	1.961146	2.141100
H	-5.512487	1.209170	-1.250502
H	-5.369564	-0.549061	-1.005269
H	-5.530219	-0.112225	1.345408
H	-5.254529	1.630011	1.111017
C	5.366712	0.048442	0.025214
H	6.952606	-1.433732	1.284826
H	7.863852	0.115193	0.241486

H	5.360568	0.689959	0.911625
H	5.361264	0.706876	-0.851611
C	4.123273	-0.854347	0.005602
H	4.137644	-1.519062	0.878920
C	2.818397	-0.045000	0.002563
H	4.155053	-1.506016	-0.876640
H	2.768604	0.617224	-0.869535
H	2.758038	0.608290	0.880708
H	1.494181	-1.948764	-1.085441
H	1.486237	-1.963339	1.052901
Br	-1.850236	-2.265612	-0.003214

S5

E = -2141.27613905 a.u.

C	1.733200	2.002981	0.993440
C	2.097809	2.140197	-0.368038
C	1.433014	3.098276	-1.171594
C	0.453919	3.912908	-0.626211
C	0.090542	3.776505	0.728408
C	0.710579	2.826721	1.524514
Ni	0.922508	0.272307	-0.138862
P	-6.825215	-0.720631	0.198982
C	-5.045567	-0.719035	0.851658
C	-4.089787	0.021022	-0.097595
C	-2.635739	-0.027863	0.390922
P	-1.371186	0.825821	-0.693121
H	1.726147	3.213480	-2.210864
H	-0.034329	4.662677	-1.242141
H	-0.674428	4.423094	1.148897
H	0.447339	2.734152	2.574161
H	2.328754	1.399433	1.670158
H	-7.444513	-1.220508	1.389599
H	-7.129846	0.641720	0.524432
Br	0.473462	-2.006951	-0.546953
H	-1.758382	0.319752	-1.966067
H	-1.995080	2.104099	-0.828171
H	-2.544062	0.425868	1.385588
H	-2.285660	-1.061151	0.484893
H	-5.001186	-0.287444	1.856333
H	-4.743146	-1.769422	0.936411
H	-4.408731	1.066471	-0.200689
H	-4.153013	-0.420937	-1.099735
B	2.566699	-0.702748	0.235977
O	3.596202	-0.832246	-0.676399
O	2.939892	-1.066961	1.515807
C	4.229131	-1.700339	1.430574
C	4.748450	-1.341708	0.019197
H	4.101597	-2.781105	1.561049
H	5.143195	-2.207979	-0.519969
H	2.976146	1.638619	-0.760224
H	4.872381	-1.325985	2.232810
H	5.523247	-0.565564	0.042549

S6

E = -2047.77020209 a.u.

C	4.117072	-1.559999	0.033197
C	3.446931	-1.290718	1.226788
C	2.134192	-0.802633	1.201015
C	1.486954	-0.558274	-0.019468
C	2.159197	-0.864976	-1.213672
C	3.468978	-1.351783	-1.187574
Ni	-0.243513	0.302567	-0.076582
N	0.614108	2.232834	0.014931
P	-0.783190	-1.839366	0.009429
C	-2.539770	-2.447926	-0.212962
C	-3.618460	-1.600259	0.478812
C	-3.881100	-0.251028	-0.210346
P	-2.494028	0.994887	-0.035882
H	1.673250	-0.716976	-2.176082
H	3.980408	-1.573465	-2.120114
H	5.132538	-1.943386	0.052452
H	3.937965	-1.465472	2.179982
H	1.626794	-0.618932	2.146123
H	-2.942722	2.003822	-0.928187
H	-2.853559	1.642414	1.179079
H	-0.433056	-2.393747	1.265715
H	-0.077681	-2.709096	-0.853547
H	-2.561330	-3.477034	0.158895
H	-2.729320	-2.493975	-1.291562
H	-4.792699	0.209976	0.177904
H	-4.031070	-0.402722	-1.285213
H	-4.554848	-2.168517	0.465639
H	-3.375409	-1.453249	1.539342
C	-0.302556	3.304486	-0.455523
C	0.922412	2.478508	1.449672
C	1.871189	2.366684	-0.773992
H	2.252643	3.392545	-0.691690
H	2.621727	1.672785	-0.405686
H	1.669459	2.145514	-1.823775
H	1.342228	3.483964	1.586760
H	0.008424	2.395846	2.042999
H	1.646413	1.741834	1.796298
H	0.196938	4.280533	-0.407827
H	-0.600894	3.114745	-1.488369
H	-1.187664	3.355471	0.180798

$TS_{S6–S7}$

E = -2127.89258595 a.u.

168.3418*i* cm^{-1}

C	-2.611236	2.280491	1.041760
C	-1.670910	1.247218	1.052989
C	-1.129965	0.767789	-0.153765
C	-1.535566	1.351868	-1.367462
C	-2.469698	2.388060	-1.373263
C	-3.006077	2.854119	-0.168933
Ni	0.520370	-0.296257	-0.258107
B	-1.386717	-1.336893	-0.178124

O	-1.442096	-1.828408	1.105634
C	-2.805887	-2.276762	1.300749
C	-3.383823	-2.388122	-0.129790
O	-2.469642	-1.631669	-0.957273
P	2.377027	-1.593504	-0.438031
C	4.056264	-0.779504	-0.437866
C	4.218535	0.326764	0.622670
C	3.442912	1.624814	0.327759
P	1.592199	1.488611	0.528288
H	-1.148947	0.981550	-2.313687
H	-2.786310	2.824383	-2.315894
H	-3.736293	3.657576	-0.175996
H	-3.034904	2.634911	1.976957
H	-1.384777	0.791236	1.996670
H	2.454504	-2.482058	-1.539756
H	2.475235	-2.528766	0.624646
H	-4.383804	-1.957438	-0.219334
H	-3.407694	-3.419327	-0.495801
H	-2.792123	-3.226972	1.838424
H	-3.334435	-1.531129	1.904280
H	-0.261698	-1.501931	-0.833934
H	1.403120	1.630858	1.927013
H	1.123983	2.746677	0.081915
H	3.785481	2.429574	0.984656
H	3.626584	1.951326	-0.702192
H	4.805339	-1.561866	-0.289569
H	4.211052	-0.370880	-1.442753
H	5.282385	0.582763	0.668434
H	3.963251	-0.055788	1.619297

S7

E = -2127.90950299 a.u.

B	-2.447646	-0.352390	0.198744
Ni	0.403711	-0.162850	-0.475489
H	-0.434386	-1.198566	-1.052011
C	-1.558235	0.925757	-0.017432
P	2.116353	1.048059	0.535940
H	3.098024	1.701176	-0.257642
C	3.136774	-0.121840	1.581744
H	1.841748	2.097274	1.446548
P	1.647263	-1.918799	-0.748471
H	1.556994	-2.564879	-2.004112
C	3.484675	-1.642202	-0.575831
O	-3.162275	-0.946522	-0.800587
O	-2.620910	-0.913160	1.434133
C	-3.855773	-2.075453	-0.225751
C	-3.629324	-1.941153	1.301934
H	1.351740	-3.006400	0.112353
H	-3.263689	-2.861413	1.763978
H	-4.528265	-1.614894	1.833616
H	-3.426955	-2.995437	-0.636312
H	-4.910122	-2.025275	-0.507289
C	-1.356118	1.822888	1.063597
C	-1.131830	1.337610	-1.309759
C	-0.526691	2.594244	-1.500829
C	-0.807145	3.084064	0.857034
C	-0.385167	3.468915	-0.424915
H	-1.378364	0.724145	-2.172041
H	-0.220722	2.897818	-2.497368
H	-1.691908	1.529617	2.053815
H	-0.708560	3.776028	1.688349
H	0.039650	4.456004	-0.581754
H	2.400356	-0.628737	2.215740
C	3.988852	-1.156231	0.802003
H	3.785386	0.449962	2.249161
H	3.717232	-0.905603	-1.353951
H	4.001845	-2.565299	-0.853248
H	4.131255	-2.022355	1.455892
H	4.985875	-0.736168	0.635577

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