Supplementary data

A Detailed Theoretical Investigation to Unravel the Molecular Mechanism of Ligand-free Copper-Catalyzed Suzuki Cross-Coupling Reaction

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Reference

Gaussian 09, Revision *D.01*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

I. Cartesian coordinates for Model System

(A) EtOH-Cu-I

E sol= -1806.8064411 a.u

G sol= -1806.842709 a.u

O	-2.386943	-0.539516	-0.022751
Cu	-0.459830	-0.259287	0.009496
I	1.970132	0.101624	-0.011745
H	-2.701523	-1.294784	0.505781
C	-3.283689	0.603669	0.175702
C	-4.713037	0.229004	-0.166760
H	-2.891015	1.371926	-0.492502
H	-3.181416	0.946653	1.210142

H	-5.358841	1.106008	-0.043897
H	-4.787484	-0.117591	-1.202762
H	-5.085748	-0.558861	0.498700

(B) Aryl Boronic acid

E sol = -408.297741 a.u

G sol = -408.206027 a.u

B	1.740805	-0.000002	-0.000011
O	2.388581	-1.214183	0.021811
H	3.357328	-1.178067	0.026781
O	2.388573	1.214185	-0.021805
H	3.357320	1.178078	-0.026737
C	0.174365	0.000004	-0.000014
C	-0.551925	-1.207209	-0.010313
C	-0.551929	1.207212	0.010311
C	-1.949962	-1.211611	-0.011490
H	-0.012880	-2.151166	-0.018371
C	-1.949965	1.211607	0.011494
H	-0.012884	2.151169	0.018375
C	-2.651847	-0.000003	0.000001
H	-2.491704	-2.154303	-0.021154
H	-2.491710	2.154297	0.021174
H	-3.739148	-0.000003	0.000010

(C) $K_2PO_4^-$

E solv = -698.972636 a.u

G solv= -698.994904 a.u

O	1.847561	-0.495133	1.567719
O	-0.148839	-0.857293	-0.036401
P	0.597093	0.193631	0.897843
O	1.091891	1.370017	-0.053773
O	-0.410630	0.764323	1.965923
K	-1.675868	1.497654	-0.854241
K	2.502136	-0.905791	-1.330147

(D) I^-

Gsol = - 11.586795a.u

E sol= - 11.569947a.u

I	0.00000000	0.00000000	0.00000000

(E) Br^-

Gsol = - 13.360540 a.u

E sol= -13.344365 a.u

Br	0.00000000	0.00000000	0.00000000

(F) **Int 1**

E sol= - -2494.326971 a.u

G sol = -2494.279891 a.u

O	2.921213	-0.895675	-0.750000
O	1.298583	0.746416	-1.959685
P	1.497056	-0.261083	-0.781689
O	1.171944	0.446238	0.589053
O	0.437452	-1.486792	-0.970854
K	-0.061460	2.672923	-0.473843
K	3.528539	-0.174346	1.880338
Cu	-1.260499	-1.180489	-0.376291
O	-3.042006	-0.902416	0.289560
C	-3.410348	0.453268	0.710237
C	-4.760491	0.452486	1.401713
H	-3.396503	1.103564	-0.170287
H	-2.605916	0.752439	1.384111
H	-5.000351	1.469747	1.731888
H	-5.554581	0.124132	0.720332
H	-4.750118	-0.205483	2.276908
H	-3.740864	-1.263610	-0.284873

(G) **Int 2**

E sol= -2902.659407a.u

G sol = - 2902.494463a.u

O	-2.705088	0.897781	0.683268
O	-0.631536	-0.048404	-0.492656
P	-2.084020	0.803770	-0.742301
O	-1.642361	2.164073	-1.302954
O	-2.890385	-0.119548	-1.685997
K	-4.235239	-1.741320	0.247750
K	-1.546394	3.400199	1.283408
Cu	1.070635	0.708861	-0.223946
O	2.914600	1.156074	0.139985
H	3.291488	0.387070	0.616934
C	3.786897	1.479666	-0.991769
C	5.186634	1.809332	-0.507767

H	3.779909	0.631418	-1.683847
H	3.304995	2.333111	-1.471696
H	5.168836	2.652406	0.190897
H	5.643524	0.945904	-0.009421
H	5.816714	2.077309	-1.363664
C	0.904464	-1.906014	0.294107
C	1.793964	-2.264455	-0.740748
C	1.465666	-1.700471	1.570991
C	3.173934	-2.369032	-0.529277
H	1.390465	-2.430834	-1.737023
C	2.845195	-1.801002	1.801156
H	0.802798	-1.427629	2.388835
C	3.707980	-2.125859	0.744190
H	3.835418	-2.628148	-1.353211
H	3.248416	-1.622869	2.795914
H	4.779952	-2.196167	0.912617
O	-1.494632	-1.599313	1.212216
O	-1.197572	-2.363951	-1.101404
H	-1.854547	-1.805119	-1.564496
H	-1.836275	-0.699110	1.388878
B	-0.664273	-1.555252	-0.007753

(H) **TS 1**

G sol= - 2902.470878a.u

E sol= -2902.636725a.u

O	1.918741	0.830333	-1.455474
O	1.189498	0.158162	0.915515
P	2.209449	1.199058	0.031172
O	1.710037	2.608002	0.400501
O	3.636453	0.853798	0.500769
K	3.965247	-1.694002	1.449046
K	0.037290	3.028307	-1.797690
Cu	-1.037112	0.345605	0.605755
O	-1.639776	2.194600	0.933934
H	-2.605532	2.302885	0.978427
C	-1.013866	2.907309	2.055793
C	-1.390971	4.377124	2.036995
H	-1.323719	2.417537	2.985267
H	0.052949	2.755945	1.884984
H	-1.061724	4.854486	1.107838
H	-2.474202	4.517431	2.141443
H	-0.904280	4.887026	2.876985
C	-0.999424	-1.457353	-0.201550
C	-1.800209	-2.444016	0.419601
C	-1.144586	-1.335795	-1.608002
C	-2.670261	-3.270877	-0.303910
H	-1.726058	-2.576405	1.497828

C	-2.013798	-2.145634	-2.344902
H	-0.532762	-0.603553	-2.132502
C	-2.779098	-3.122318	-1.691545
H	-3.262140	-4.026277	0.209753
H	-2.094029	-2.024908	-3.423752
H	-3.450759	-3.761943	-2.259887
O	1.676786	-1.738444	-0.542322
O	0.930306	-2.049004	1.717976
H	0.734746	-2.966690	1.477437
H	1.802856	-0.988353	-1.174833
B	0.931154	-1.219050	0.549769

(I) **CuI**

G sol = -1651.818034 a.u

E sol = -1651.793089 a.u

Cu	0.000000	0.000000	-1.593592
I	0.000000	0.000000	0.871965

(I) **Ethanol**

G sol = -154.997951 a.u

E sol = -155.052541 a.u

O	-1.246809	-0.257881	-0.111071
C	-0.074979	0.560788	0.047628
H	-0.122615	1.285922	-0.770709
H	-0.131829	1.118510	0.993834
C	1.218294	-0.244733	-0.021391
H	1.287652	-0.785181	-0.972470
H	1.269724	-0.974756	0.796613
H	2.086547	0.420568	0.065160
H	-1.274903	-0.898343	0.618713

(J) **Int 3**

E sol = -2027.084622 a.u

G sol = -2026.953351a.u

Cu	-0.622755	-0.070248	-0.286197
O	-2.569392	-0.178755	-0.478495
C	-3.418394	0.368470	0.581397
C	-4.856008	-0.088662	0.414753
H	-3.328217	1.459543	0.570131

H	-2.974587	-0.011064	1.503388
H	-5.461513	0.304075	1.239817
H	-5.284384	0.283383	-0.523688
H	-4.920537	-1.181813	0.423981
H	-2.909798	0.104107	-1.346090
C	1.261500	-0.018201	-0.072737
C	2.031344	-1.196376	0.082252
C	1.985427	1.198385	-0.051496
C	3.423607	-1.168534	0.247540
H	1.532616	-2.164467	0.074661
C	3.377431	1.241815	0.113047
H	1.450139	2.139810	-0.165934
C	4.104528	0.054819	0.263897
H	3.976134	-2.099606	0.363776
H	3.894064	2.200299	0.123774
H	5.184509	0.082664	0.391936

(K) **Species C**

G sol = - 320.895928 a.u

E sol = - 320.961648 a.u

C	-3.485625	-1.211729	0.000164
C	-2.090102	-1.216955	0.000096
C	-1.376876	0.000002	0.000063
C	-2.090106	1.216957	0.000099
C	-3.485629	1.211726	0.000167
C	-4.187388	-0.000003	0.000200
H	-4.025826	-2.154594	0.000189
H	-1.544390	-2.156072	0.000068
H	-1.544397	2.156075	0.000073
H	-4.025834	2.154588	0.000194
H	-5.273955	-0.000005	0.000252
C	0.053649	0.000004	-0.000008
C	1.267191	0.000006	-0.000067
Br	3.108106	-0.000001	-0.000144

(L) **Species D**

G sol = -539.339639 a.u

E sol = -539.492110 a.u

C	4.147912	-1.211679	0.000000
C	2.752720	-1.216838	0.000000
C	2.035881	0.000019	0.000001
C	2.752762	1.216851	0.000001

C	4.147954	1.211643	0.000001
C	4.850531	-0.000030	0.000001
H	4.687978	-2.154760	0.000000
H	2.207391	-2.156339	0.000000
H	2.207467	2.156372	0.000001
H	4.688052	2.154706	0.000002
H	5.937118	-0.000049	0.000001
C	-2.752720	-1.216838	-0.000001
C	-4.147912	-1.211679	-0.000001
C	-4.850531	-0.000030	-0.000001
C	-4.147954	1.211643	0.000000
C	-2.752762	1.216851	0.000000
C	-2.035881	0.000019	-0.000001
H	-2.207391	-2.156339	-0.000001
H	-4.687978	-2.154760	-0.000002
H	-5.937118	-0.000049	-0.000001
H	-4.688052	2.154706	0.000000
H	-2.207467	2.156372	0.000000
C	0.609156	0.000045	0.000000
C	-0.609156	0.000045	0.000000

(M) **$B(OH)_2K_2PO_4$**

E sol = -875.560114 a.u

G sol = -875.551471 a.u

B	1.732576	1.499907	-0.294658
O	-1.679384	0.724923	1.357404
O	0.522402	1.441377	0.309436
P	-0.420042	0.072051	0.763638
O	-0.687095	-0.675406	-0.566999
O	0.468720	-0.715582	1.741373
O	2.456358	0.373602	-0.655728
H	3.297621	0.609778	-1.076188
O	2.308677	2.728422	-0.585318
H	1.739928	3.460904	-0.301924
K	1.574736	-2.371017	-0.319641
K	-3.391432	0.072613	-0.806912

(N) **Ph $B(OH)_2K_2PO_4$**

E sol = -1107.328026 a.u

G sol = -1107.234191 a.u

B	-0.222025	0.016437	0.893625
O	2.617883	-0.090758	1.477643
O	0.736149	0.007924	-0.274068
P	2.390386	0.001054	-0.065670
O	2.881104	-1.258609	-0.830382
O	2.886062	1.341255	-0.674287
O	-0.012020	1.263707	1.696172
H	0.907392	1.194425	2.016216
O	0.007299	-1.201483	1.727251
H	0.950497	-1.126373	1.982410
K	0.520012	2.843588	-0.711924
K	0.553845	-2.845556	-0.656417
C	-1.751502	0.002826	0.328631
C	-2.063525	-0.049992	-1.043268
C	-2.843212	0.038185	1.219874
C	-3.386891	-0.067872	-1.508216
H	-1.246715	-0.077034	-1.762148
C	-4.170756	0.021577	0.775007
H	-2.646518	0.079425	2.289937
C	-4.449182	-0.031800	-0.597908
H	-3.588520	-0.109853	-2.577373
H	-4.988187	0.050244	1.493631
H	-5.478322	-0.045285	-0.950626

(O) **Int 4**

E sol = -2348.069837 a.u

G sol = -2347.849674 a.u

C	-0.640622	4.683861	0.129397
C	-1.097928	3.377946	-0.050866
C	-0.218087	2.289215	0.127210
C	1.118983	2.534121	0.485291
C	1.568523	3.843467	0.664483
C	0.692755	4.921250	0.488016
H	-1.324613	5.516738	-0.010640
H	-2.131150	3.191957	-0.330194
H	1.789592	1.690627	0.608204
H	2.604221	4.022534	0.940994
H	1.046054	5.939606	0.626190
C	-0.728663	0.949330	-0.048640
C	-1.615336	0.054708	-0.198828
Br	-3.492969	-0.280374	-0.237615
Cu	0.109058	-0.807260	-0.250272
O	-0.125889	-2.818199	-0.504630
C	-1.268830	-3.505497	0.084717
H	-2.134193	-3.081475	-0.427610
H	-1.191336	-4.567250	-0.170588
C	-1.345804	-3.281865	1.585324

H	-1.415103	-2.210070	1.805027
H	-2.235006	-3.777539	1.992141
H	-0.462035	-3.687765	2.091093
H	0.701656	-3.261364	-0.244765
C	2.065761	-0.819561	-0.192790
C	2.728543	-1.592002	0.785892
C	2.888319	-0.179848	-1.144748
C	4.125386	-1.725714	0.816994
H	2.144930	-2.099033	1.555360
C	4.284071	-0.306900	-1.132048
H	2.429781	0.441069	-1.913668
C	4.909636	-1.082525	-0.146891
H	4.598370	-2.328080	1.590908
H	4.884108	0.200133	-1.886026
H	5.992826	-1.180803	-0.130032

(P) **TS 2**

E sol = -2348.034885 a.u

G sol = -2347.818744 a.u

Cu	0.481684	-0.939126	-0.351322
O	-1.079107	-1.894770	-1.156344
C	-2.378576	-1.828695	-0.480109
H	-2.468210	-0.784198	-0.181379
H	-2.328633	-2.450609	0.419271
C	2.253958	-0.319726	-0.016547
C	2.742239	0.795561	-0.709082
C	3.111342	-1.081244	0.788948
C	4.110010	1.099414	-0.661178
H	2.063899	1.421700	-1.282084
C	4.477805	-0.777428	0.832285
H	2.719874	-1.907059	1.378502
C	4.977110	0.312077	0.106014
H	4.492900	1.954617	-1.213444
H	5.147327	-1.381646	1.440212
H	6.035394	0.556272	0.152133
C	-0.008787	0.052736	1.204710
C	-0.174422	-0.101883	2.415627
C	-0.360935	-0.306233	3.807604
C	0.548536	0.239037	4.745368
C	-1.458270	-1.058764	4.290446
C	0.357432	0.042669	6.113258
H	1.397013	0.816094	4.388301
C	-1.633474	-1.255990	5.660117
H	-2.163263	-1.483370	3.581013
C	-0.730738	-0.706197	6.580154
H	1.063860	0.473419	6.818544
H	-2.481114	-1.838850	6.011955
H	-0.873400	-0.859548	7.646383

Br	-0.841208	1.742845	-0.144576
C	-3.492957	-2.254233	-1.416420
H	-3.371088	-3.296724	-1.733977
H	-4.454964	-2.170486	-0.897426
H	-3.519347	-1.614628	-2.304934
H	-0.907520	-2.810901	-1.438229

(Q) **Int 4'**

E sol = -2348.069163 a.u

G sol = -2347.849781 a.u

C	0.481684	-0.939126	-0.351322
C	-1.079107	-1.894770	-1.156344
C	-2.378576	-1.828695	-0.480109
C	-2.468210	-0.784198	-0.181379
C	-2.328633	-2.450609	0.419271
C	2.253958	-0.319726	-0.016547
H	2.742239	0.795561	-0.709082
H	3.111342	-1.081244	0.788948
H	4.110010	1.099414	-0.661178
H	2.063899	1.421700	-1.282084
H	4.477805	-0.777428	0.832285
C	2.719874	-1.907059	1.378502
C	4.977110	0.312077	0.106014
Br	4.492900	1.954617	-1.213444
Cu	5.147327	-1.381646	1.440212
O	6.035394	0.556272	0.152133
C	-0.008787	0.052736	1.204710
H	-0.174422	-0.101883	2.415627
H	-0.360935	-0.306233	3.807604
C	0.548536	0.239037	4.745368
H	-1.458270	-1.058764	4.290446
H	0.357432	0.042669	6.113258
H	1.397013	0.816094	4.388301
H	-1.633474	-1.255990	5.660117
C	-2.163263	-1.483370	3.581013
C	-0.730738	-0.706197	6.580154
C	1.063860	0.473419	6.818544
C	-2.481114	-1.838850	6.011955
H	-0.873400	-0.859548	7.646383
C	-0.841208	1.742845	-0.144576
H	-3.492957	-2.254233	-1.416420
C	-3.371088	-3.296724	-1.733977
H	-4.454964	-2.170486	-0.897426
H	-3.519347	-1.614628	-2.304934
H	-0.907520	-2.810901	-1.438229

(R) **TS 2'**

E sol = **-2348.036015**

G sol = **-2347.817849**

C	-1.460886	0.755682	0.144505
C	5.034377	0.862547	0.509279
C	5.578149	0.293198	-0.650464
C	4.753107	-0.401842	-1.545394
C	3.390597	-0.532480	-1.287518
C	2.832142	0.038625	-0.118495
H	3.673389	0.741202	0.778510
H	5.673987	1.402021	1.202143
H	6.640201	0.392126	-0.856779
H	5.175150	-0.842385	-2.444290
H	2.746718	-1.069788	-1.977211
C	3.245226	1.182651	1.673510
C	1.453512	-0.097040	0.159729
Br	0.235742	-0.140092	0.381477
Cu	-1.079225	-1.482157	1.330174
O	-0.497880	2.649279	-0.282664
C	-0.758135	3.692124	0.695841
H	-0.246010	4.604707	0.370123
H	-1.836058	3.852729	0.639242
C	-0.333116	3.276111	2.096115
H	-0.866276	2.368220	2.403597
H	0.744049	3.076618	2.140904
H	-0.565814	4.073857	2.811292
H	0.460122	2.472530	-0.312866
C	-3.355255	1.212512	-0.032468
C	-3.805064	2.321803	-0.783265
C	-4.360524	0.434402	0.582217
C	-5.164946	2.636198	-0.919876
H	-3.073113	2.958326	-1.280048
C	-5.725376	0.734535	0.461994
H	-4.071215	-0.435894	1.173283
C	-6.133057	1.841221	-0.293241
H	-5.469891	3.498518	-1.510984
H	-6.468540	0.108656	0.953951
H	-7.189746	2.080553	-0.392372

(S) **Int 6**

E sol = - 2660.269728a.u

G sol = - 2660.205489a.u

O	-1.641901	0.865341	-0.618790
O	-3.159768	-1.032002	-1.621458
P	-2.319456	-0.592240	-0.404411
O	-3.156602	-0.571950	0.905239
O	-0.977849	-1.466776	-0.240783
K	-5.574666	-1.429237	-0.194920

K	-2.511780	2.014804	1.811889
Cu	0.148083	0.129474	-0.353057
C	2.077727	-0.064840	-0.107023
C	2.896022	-1.228465	0.126685
C	4.288039	-1.088722	0.304444
C	2.312953	-2.509124	0.178172
C	5.078260	-2.216824	0.528763
H	4.737663	-0.100514	0.265858
C	3.112428	-3.631664	0.400648
H	1.238063	-2.597430	0.043010
C	4.494378	-3.489772	0.576268
H	6.150447	-2.103631	0.665794
H	2.657554	-4.617990	0.437680
H	5.114186	-4.365411	0.749662
C	1.747015	1.143543	-0.282726
Br	2.276858	2.969896	-0.409276

(T) **TS4**

E sol = -2660.236019 a.u

G sol = -2660.172795 a.u

C	4.926967	0.487993	0.880620
C	5.579839	0.331154	-0.350397
C	4.837720	0.083418	-1.513882
C	3.449584	-0.003026	-1.455111
C	2.779295	0.144299	-0.214082
C	3.540383	0.392307	0.956406
H	5.503311	0.681694	1.780887
H	6.662583	0.403109	-0.402931
H	5.344779	-0.037238	-2.467047
H	2.868358	-0.187444	-2.353508
H	3.029278	0.509010	1.907245
C	1.377480	0.031601	-0.145749
C	0.133549	0.000336	-0.111220
Br	-1.191957	-1.593747	0.273640
O	-3.068865	2.023069	0.040969
Cu	-1.383648	1.097563	-0.128915
O	-1.759312	1.781249	-2.045028
P	-3.216708	2.278152	-1.558832
O	-3.467941	3.760075	-1.877402
O	-4.294070	1.300760	-2.114370
K	-5.051762	-0.010110	0.282500
K	-2.495632	-0.526769	-3.446785

(U) **Int 8**

E sol = - 2660.274885a.u

G solv = -2660.211825a.u

O	-1.986037	0.610964	-0.681657
O	-3.023847	-1.668890	-1.490238
P	-2.342223	-0.937926	-0.339384
O	-3.083745	-1.007691	1.002266
O	-0.773200	-1.367077	-0.190119
K	-5.316737	-2.519664	0.108023
K	-2.961092	1.820485	1.761459
Cu	-0.142867	0.382982	-0.427775
Br	0.325660	2.718536	-0.550482
C	1.653062	-0.056061	-0.187833
C	2.819277	-0.390616	-0.031059
C	4.184579	-0.784551	0.146808
C	5.195694	0.185474	0.316714
C	4.544997	-2.149126	0.154575
C	6.526216	-0.201126	0.487750
H	4.927533	1.238268	0.312369
C	5.877727	-2.528507	0.324194
H	3.773258	-2.902732	0.025303
C	6.873084	-1.557823	0.491488
H	7.293678	0.557603	0.617438
H	6.139763	-3.583425	0.326381
H	7.909726	-1.856080	0.623616

(V) **TS 5**

E sol = -3068.574247 a.u

G sol = -3068.396230 a.u

Cu	0.481684	-0.939126	-0.351322
O	-1.079107	-1.894770	-1.156344
C	-2.378576	-1.828695	-0.480109
H	-2.468210	-0.784198	-0.181379
H	-2.328633	-2.450609	0.419271
C	2.253958	-0.319726	-0.016547
C	2.742239	0.795561	-0.709082
C	3.111342	-1.081244	0.788948
C	4.110010	1.099414	-0.661178
H	2.063899	1.421700	-1.282084
C	4.477805	-0.777428	0.832285
H	2.719874	-1.907059	1.378502
C	4.977110	0.312077	0.106014
H	4.492900	1.954617	-1.213444
H	5.147327	-1.381646	1.440212
H	6.035394	0.556272	0.152133

C	-0.008787	0.052736	1.204710
C	-0.174422	-0.101883	2.415627
C	-0.360935	-0.306233	3.807604
C	0.548536	0.239037	4.745368
C	-1.458270	-1.058764	4.290446
C	0.357432	0.042669	6.113258
H	1.397013	0.816094	4.388301
C	-1.633474	-1.255990	5.660117
H	-2.163263	-1.483370	3.581013
C	-0.730738	-0.706197	6.580154
H	1.063860	0.473419	6.818544
H	-2.481114	-1.838850	6.011955
H	-0.873400	-0.859548	7.646383
Br	-0.841208	1.742845	-0.144576
C	-3.492957	-2.254233	-1.416420
H	-3.371088	-3.296724	-1.733977
H	-4.454964	-2.170486	-0.897426
H	-3.519347	-1.614628	-2.304934
H	-0.907520	-2.810901	-1.438229

(W) **Int 9**

E sol = -2127.878860 a.u

G sol = -2127.744933 a.u

C	4.403054	-0.293201	-1.452713
C	3.090384	0.175066	-1.419782
C	2.522047	0.583497	-0.195896
C	3.282720	0.513241	0.988684
C	4.594112	0.040998	0.943295
C	5.155819	-0.365232	-0.273419
H	4.837360	-0.608929	-2.396944
H	2.494112	0.217478	-2.326077
H	2.837946	0.819556	1.930418
H	5.176518	-0.014759	1.858499
H	6.175665	-0.738244	-0.302588
C	1.163719	1.037519	-0.147369
C	0.043150	1.579835	-0.065299
Br	-1.021886	3.122950	0.047799
I	-2.937326	-0.894853	-0.273035
Cu	-0.412220	-0.310308	-0.213151
O	0.340446	-2.213668	-0.392422
C	1.461309	-2.682101	0.417482
C	1.231630	-2.416820	1.895181
H	2.324474	-2.132900	0.040097
H	1.604513	-3.746305	0.206841
H	2.109029	-2.731144	2.472259
H	1.071570	-1.346219	2.069493
H	0.357473	-2.964631	2.264366
H	-0.411898	-2.824482	-0.294546

(X) **TS 4'**

E sol = -2127.836376a.u

G sol = -2127.704623a.u

Br	0.350632	-2.323428	-0.047363
O	0.834409	2.056433	-0.270456
H	1.733390	2.411749	-0.136223
Cu	0.877331	0.026924	-0.057210
I	3.493079	0.070570	0.052886
C	-3.624255	-0.139225	0.002013
C	-4.356024	-0.042404	-1.205997
C	-4.316991	-0.130952	1.236745
C	-5.744777	0.054016	-1.173134
H	-3.824028	-0.045227	-2.152455
C	-5.705906	-0.033603	1.255345
H	-3.754966	-0.202557	2.162935
C	-6.422564	0.058995	0.054030
H	-6.301931	0.126545	-2.102774
H	-6.232898	-0.029429	2.205189
H	-7.506039	0.135977	0.074236
C	-2.213973	-0.255047	-0.023272
C	-0.981105	-0.237942	-0.036437
C	-0.142567	2.898821	0.415688
C	-0.173691	4.284232	-0.205112
H	0.110238	2.926782	1.480780
H	-1.089384	2.373464	0.291454
H	-0.934643	4.890681	0.300223
H	0.791899	4.791761	-0.095457
H	-0.423689	4.226427	-1.269642

(Y) **Int 10**

E sol = -2127.836962 a.u

G sol = -2127.706181 a.u

Cu	-0.816890	0.038675	-0.058347
Br	-0.414316	-2.290857	0.062252
C	1.059518	0.025593	-0.017130
C	2.285461	-0.088804	-0.029925
C	3.704431	-0.051810	-0.030620
C	4.421858	-0.140970	1.185696
C	4.417065	0.063272	-1.247526
C	5.814712	-0.118774	1.178362
H	3.875911	-0.227990	2.120250
C	5.809931	0.084127	-1.242045
H	3.867412	0.134875	-2.181217
C	6.512155	-0.005989	-0.032258
H	6.359351	-0.189256	2.115692
H	6.350922	0.172174	-2.180004

H	7.598436	0.012775	-0.032806
O	-0.913398	2.034026	-0.322976
I	-3.435364	-0.024128	-0.025516
C	-0.173378	2.935927	0.566315
H	-0.605896	2.860008	1.568942
H	0.837371	2.529529	0.581442
H	-1.851128	2.307269	-0.351609
C	-0.217435	4.352045	0.022833
H	-1.243901	4.735303	-0.011446
H	0.212056	4.396153	-0.983237
H	0.365918	5.006488	0.681196

(Z) **TS 5**

E sol = -3068.574247 a.u

G sol = -3068.396230 a.u

O	1.539146	1.172701	-1.115600
O	1.291864	-0.566628	0.833263
P	1.441601	1.143824	0.409016
O	0.048203	1.566599	0.973354
O	2.648561	1.582844	1.218626
K	3.424209	-1.366896	2.399188
K	-2.346425	2.745238	0.528198
C	-0.758096	-1.650731	-0.207536
C	-1.505351	-2.807774	0.148621
C	-1.349153	-0.732407	-1.124273
C	-2.724597	-3.088907	-0.458661
H	-1.081072	-3.487781	0.880617
C	-2.569423	-1.007029	-1.725569
H	-0.808076	0.177558	-1.367594
C	-3.257725	-2.184980	-1.389100
H	-3.272550	-3.990950	-0.201144
H	-2.999375	-0.311822	-2.441362
H	-4.221769	-2.391942	-1.846669
O	1.593296	-1.562245	-1.408088
O	1.429158	-2.911731	0.575995
H	1.671564	-3.602647	-0.057365
H	1.600316	-0.603005	-1.626563
B	1.019413	-1.720106	-0.119345
Cu	-0.468529	-0.503102	1.539826
Br	0.134800	-0.686245	3.956279
C	-2.268823	-0.404930	1.927866
C	-3.476536	-0.290753	2.072705
C	-4.894849	-0.127784	2.165052
C	-5.675495	-0.087495	0.989469
C	-5.535831	-0.000234	3.414977
C	-7.059261	0.077035	1.066463
H	-5.184811	-0.188249	0.025554
C	-6.920772	0.162201	3.483647
H	-4.941000	-0.029390	4.323496

C	-7.687085	0.202172	2.312139
H	-7.648792	0.106309	0.153777
H	-7.402866	0.258069	4.453020
H	-8.764780	0.329459	2.369435

(AA) **Int 7**

E sol = -3068.602849a.u

G sol = -3068.422923a.u

O	-3.278908	0.085940	1.152987
O	-1.326608	-0.728254	-0.384357
P	-2.730660	0.193403	-0.279034
O	-2.032975	1.603432	-0.526393
O	-3.667286	-0.242081	-1.405008
K	-2.769656	-2.787970	-2.187399
K	-2.562503	2.757486	2.015069
Cu	-0.193316	0.899728	-0.645513
C	0.080332	-1.698244	1.564497
C	1.096025	-2.598036	1.938394
C	0.024549	-0.485284	2.277745
C	2.015429	-2.303941	2.953088
H	1.180912	-3.547841	1.412851
C	0.934518	-0.171728	3.292931
H	-0.757183	0.226007	2.027201
C	1.940978	-1.084162	3.634728
H	2.796788	-3.019120	3.203180
H	0.862634	0.781225	3.814294
H	2.657481	-0.845888	4.417777
O	-2.261749	-2.618447	0.875233
O	-0.479380	-3.027295	-0.583530
H	0.442795	-2.829872	-0.801927
B	-0.996123	-2.068272	0.395559
H	-2.756771	-1.902012	1.316834
C	1.374378	1.969689	-0.798907
C	1.780949	0.782708	-0.853065
C	2.562331	-0.424053	-0.878714
C	2.274558	-1.437844	-1.814084
C	3.611624	-0.602857	0.041194
C	3.033502	-2.607818	-1.831018
H	1.458437	-1.295506	-2.516800
C	4.363399	-1.778042	0.018725
H	3.817310	0.169762	0.775309
C	4.078090	-2.781735	-0.913071
H	2.808466	-3.385112	-2.556097
H	5.166341	-1.914258	0.737730
H	4.662925	-3.697288	-0.922987
Br	1.710539	3.826543	-0.900902

(BB) **TS 3**

E sol= -3068.570103 a.u

G sol =-3068.390491 a.u

O	-2.609345	-1.908999	1.675794
O	-1.843136	-0.547661	-0.391826
P	-2.849711	-0.515237	1.046468
O	-2.241472	0.639126	1.852380
O	-4.241093	-0.266508	0.449869
K	-3.390511	0.943892	-2.154874
K	-0.395603	-0.358559	3.557751
C	0.534609	-1.969681	-0.655784
C	1.426773	-2.212716	-1.721944
C	0.792639	-2.663978	0.549185
C	2.505505	-3.097564	-1.606179
H	1.264357	-1.696745	-2.666989
C	1.869888	-3.544161	0.689281
H	0.103123	-2.531824	1.381209
C	2.732795	-3.761507	-0.394332
H	3.173062	-3.263292	-2.449424
H	2.039195	-4.061390	1.631647
H	3.573558	-4.444096	-0.294411
O	-2.010091	-2.972940	-0.738707
O	-1.470421	-1.454159	-2.534013
H	-1.334275	-2.256525	-3.058165
H	-2.234553	-2.886477	0.222947
B	-1.464713	-1.746800	-1.137966
Cu	0.044403	0.015012	-0.330365
C	1.533293	1.300875	-0.136574
C	0.416685	1.884091	-0.168049
Br	-0.653440	3.435061	-0.109463
C	2.966849	1.149306	-0.073658
C	3.783195	2.282540	-0.271680
C	3.561734	-0.095031	0.199443
C	5.171333	2.164066	-0.198085
H	3.323567	3.243643	-0.483879
C	4.951281	-0.203852	0.272849
H	2.930708	-0.964018	0.345489
C	5.759390	0.921789	0.074658
H	5.794640	3.040553	-0.353678
H	5.402351	-1.170018	0.482451
H	6.841028	0.832995	0.129964

(CC) **Int 4**

E sol = -2348.069837

G sol = -2347.849674

C	-0.640621	4.683861	0.129397
C	-1.097927	3.377946	-0.050866
C	-0.218086	2.289215	0.127210
C	1.118984	2.534121	0.485291
C	1.568524	3.843467	0.664483
C	0.692756	4.921250	0.488016
H	-1.324612	5.516738	-0.010640
H	-2.131149	3.191958	-0.330194
H	1.789592	1.690627	0.608204
H	2.604222	4.022533	0.940994
H	1.046056	5.939606	0.626190
C	-0.728663	0.949330	-0.048640
C	-1.615336	0.054709	-0.198828
Br	-3.492969	-0.280373	-0.237615
Cu	0.109058	-0.807260	-0.250272
O	-0.125890	-2.818199	-0.504630
C	-1.268831	-3.505497	0.084717
H	-2.134194	-3.081474	-0.427610
H	-1.191337	-4.567250	-0.170588
C	-1.345805	-3.281865	1.585324
H	-1.415104	-2.210070	1.805027
H	-2.235007	-3.777538	1.992141
H	-0.462036	-3.687765	2.091093
H	0.701655	-3.261364	-0.244765
C	2.065761	-0.819561	-0.192790
C	2.728543	-1.592003	0.785892
C	2.888319	-0.179849	-1.144748
C	4.125386	-1.725715	0.816994
H	2.144929	-2.099033	1.555360
C	4.284071	-0.306901	-1.132048
H	2.429781	0.441068	-1.913668
C	4.909636	-1.082526	-0.146891
H	4.598369	-2.328081	1.590908
H	4.884108	0.200132	-1.886026
H	5.992826	-1.180804	-0.130032

(DD) **Int 5**

E sol = -2348.073669

G sol = -2347.856279

Cu	-0.65073	-0.19711	-0.06316
Br	-1.05284	-2.51784	-0.06668
C	-2.58011	-0.17039	-0.01619
C	-3.19116	-0.09035	1.22946
C	-3.24222	0.08577	-1.21091
C	-4.52191	0.35151	1.28046
H	-2.65435	-0.34033	2.13954
C	-4.57304	0.52409	-1.14093

H	-2.74185	-0.01845	-2.16895
C	-5.20778	0.6579	0.09987
H	-5.0153	0.44559	2.24438
H	-5.10625	0.75647	-2.05917
H	-6.24097	0.99084	0.14518
C	1.29818	-0.14993	-0.03378
C	2.52406	-0.04415	-0.0125
C	3.95172	0.07135	0.01148
C	4.67393	0.33077	-1.1739
C	4.66745	-0.07064	1.2204
C	6.06532	0.44257	-1.14776
H	4.13422	0.44231	-2.11024
C	6.05887	0.04301	1.23932
H	4.12293	-0.27016	2.13918
C	6.76431	0.29977	0.05721
H	6.60502	0.64158	-2.07017
H	6.59365	-0.06939	2.17905
H	7.84738	0.38729	0.0748
O	-0.63614	1.81862	-0.27594
C	-1.50886	2.77584	0.40382
C	-1.15756	4.19195	-0.01667
H	-1.41312	2.62799	1.484
H	-2.51711	2.50096	0.09684
H	-1.8466	4.8932	0.4682
H	-0.13757	4.45809	0.28513
H	-1.24784	4.30844	-1.10174
H	0.3002	2.0428	-0.10938

(EE) **C_A**

E sol = -91.157327

G sol = -91.142111

C	-0.845625	1.158004	-0.024415
C	-1.797814	0.247505	-0.183883
Br	-2.679821	-0.644063	1.327785
H	-0.399686	1.612302	-0.906767
H	-0.485181	1.476360	0.948900
H	-2.190331	-0.102396	-1.131325

(FF) **Int 7A**

O	1.904670	-0.987185	1.991210
O	1.154945	-0.418666	-0.444566
P	1.218742	-1.596545	0.753337
O	-0.349353	-1.730250	0.973992
O	1.881686	-2.838521	0.157633
K	3.555960	-1.835732	-1.893780
K	-0.429979	-0.743480	3.646717
Cu	-0.850091	-0.235694	-0.239245

E sol = -2838.788888

G sol = - 2838.659878

C	1.314123	2.114138	-0.182387
C	1.057805	3.214345	-1.018733
C	0.757907	2.164450	1.113289
C	0.263301	4.294465	-0.605534
H	1.473491	3.227873	-2.025135
C	-0.036298	3.231551	1.543140
H	0.946483	1.331264	1.786335
C	-0.295157	4.303556	0.677220
H	0.074201	5.122507	-1.286014
H	-0.460182	3.227490	2.545699
H	-0.920253	5.133115	0.999572
O	3.377669	0.521822	0.070834
O	2.510526	0.803008	-2.084898
H	1.732328	0.991381	-2.628747
B	2.149402	0.794146	-0.664504
H	3.132777	0.192098	0.958652
C	-2.722661	0.407102	-0.372741
C	-1.932181	1.158058	-1.221076
Br	-3.929548	-1.010288	-1.058412
H	-3.053583	0.744367	0.605913
H	-1.554824	2.122460	-0.880499
H	-1.887611	0.957460	-2.289267

(GG) **Int 6A**

E sol = -2430.457351

G sol = -2430.444060

O	-3.216102	0.836474	0.125817
O	-1.392405	-0.844491	0.980790
P	-2.061844	-0.101744	-0.296257
O	-0.793354	0.788484	-0.766425
O	-2.446477	-1.160753	-1.354753
K	-1.379079	-3.446016	-0.097832
K	-1.853603	3.301160	-0.112344
Cu	0.329521	0.055880	0.686821
C	2.197693	0.624424	0.862550
C	1.909680	-0.294180	1.866252
Br	3.278908	0.093916	-0.726181
H	2.281683	1.695515	1.025719
H	1.689089	0.075033	2.868260
H	2.202422	-1.338860	1.785532

(HH) **Int 4A**

E sol = -2118.256335

G sol = -2118.087014

C	-0.791281	-2.144380	0.243826
C	-1.727445	-1.223654	0.671062
Br	-3.070141	-0.490958	-0.596814
Cu	0.108049	-0.340272	0.460739
O	-0.194912	1.566152	1.312913
C	-1.222605	2.474519	0.828629
H	-2.159746	1.942206	0.999464
H	-1.209428	3.374604	1.452911
C	-1.031847	2.800071	-0.643762
H	-1.024886	1.878451	-1.236380
H	-1.852720	3.434576	-0.998409
H	-0.089080	3.333615	-0.811442
H	0.665812	2.020298	1.309096
C	2.019200	-0.261137	0.017481
C	2.602669	0.918985	-0.500660
C	2.910161	-1.341194	0.218580
C	3.970401	1.024694	-0.795523
H	1.972005	1.787213	-0.696568
C	4.280944	-1.255396	-0.064310
H	2.523160	-2.282871	0.608434
C	4.818595	-0.066643	-0.574486
H	4.372519	1.954123	-1.196185
H	4.929070	-2.113151	0.109958
H	5.880718	0.006390	-0.798456
H	-0.308037	-2.791087	0.976560
H	-0.719562	-2.452113	-0.796304
H	-2.071738	-1.125249	1.696061

(II) **TS 2A**

E sol = -2430.457351

G sol = -2430.444060

Cu	0.220811	-0.010569	0.112885
Br	0.705130	1.819056	1.727863
C	-1.375392	-0.246568	2.687483
H	-2.149533	0.477667	2.456885
H	-1.634270	-1.085334	3.332212
C	-0.142156	-0.188626	2.179723
H	0.698397	-0.809833	2.477643
C	-0.884121	-1.297042	-0.839617
C	-0.730450	-1.480445	-2.232579
C	-1.886434	-2.060681	-0.214579

C	-1.534791	-2.370863	-2.959219
H	0.027373	-0.914838	-2.772277
C	-2.696767	-2.958706	-0.924193
H	-2.043437	-1.949117	0.858607
C	-2.521811	-3.117676	-2.304403
H	-1.390501	-2.482027	-4.032751
H	-3.461071	-3.533260	-0.403069
H	-3.145206	-3.813569	-2.861642
O	2.249975	0.205822	-0.717800
H	2.611768	1.108436	-0.728761
C	2.758507	-0.548408	-1.844249
H	2.249746	-1.512384	-1.775942
H	2.445981	-0.060484	-2.775872
C	4.269605	-0.707215	-1.779567
H	4.566873	-1.202416	-0.848595
H	4.617748	-1.313879	-2.624319
H	4.771124	0.266896	-1.833499

(JJ) **TS 3A**

E sol = - 2838.755251

G sol = -2838.628118

O	0.826855	1.794396	2.384720
O	0.093230	1.267862	-0.024466
P	1.374668	1.960349	0.941984
O	2.569293	1.051158	0.637665
O	1.454329	3.399712	0.416683
K	0.391890	3.267838	-2.205719
K	1.966948	-0.863357	2.604470
C	-2.221118	-0.376686	0.127786
C	-3.361685	-0.461418	-0.699222
C	-2.288380	-1.080182	1.352673
C	-4.503303	-1.185007	-0.332309
H	-3.356765	0.067812	-1.650814
C	-3.415333	-1.815078	1.736085
H	-1.442917	-1.031962	2.037571
C	-4.531668	-1.867886	0.890126
H	-5.367077	-1.218981	-0.993864
H	-3.430099	-2.340040	2.689483
H	-5.414627	-2.431555	1.183011
O	-1.709302	1.992212	1.466043
O	-1.901052	2.187663	-0.931118
H	-2.806245	2.473928	-0.741547
H	-0.927865	1.898760	2.069502
B	-1.318859	1.546090	0.200811
Cu	-0.357131	-0.540281	-0.727649
C	-0.323207	-2.151349	-1.928225
C	0.950699	-1.621585	-1.842646

Br	2.340736	-2.539040	-0.768300
H	1.404603	-0.983654	-2.594991
H	-0.956110	-1.876048	-2.772493
H	-0.618365	-3.033404	-1.365483

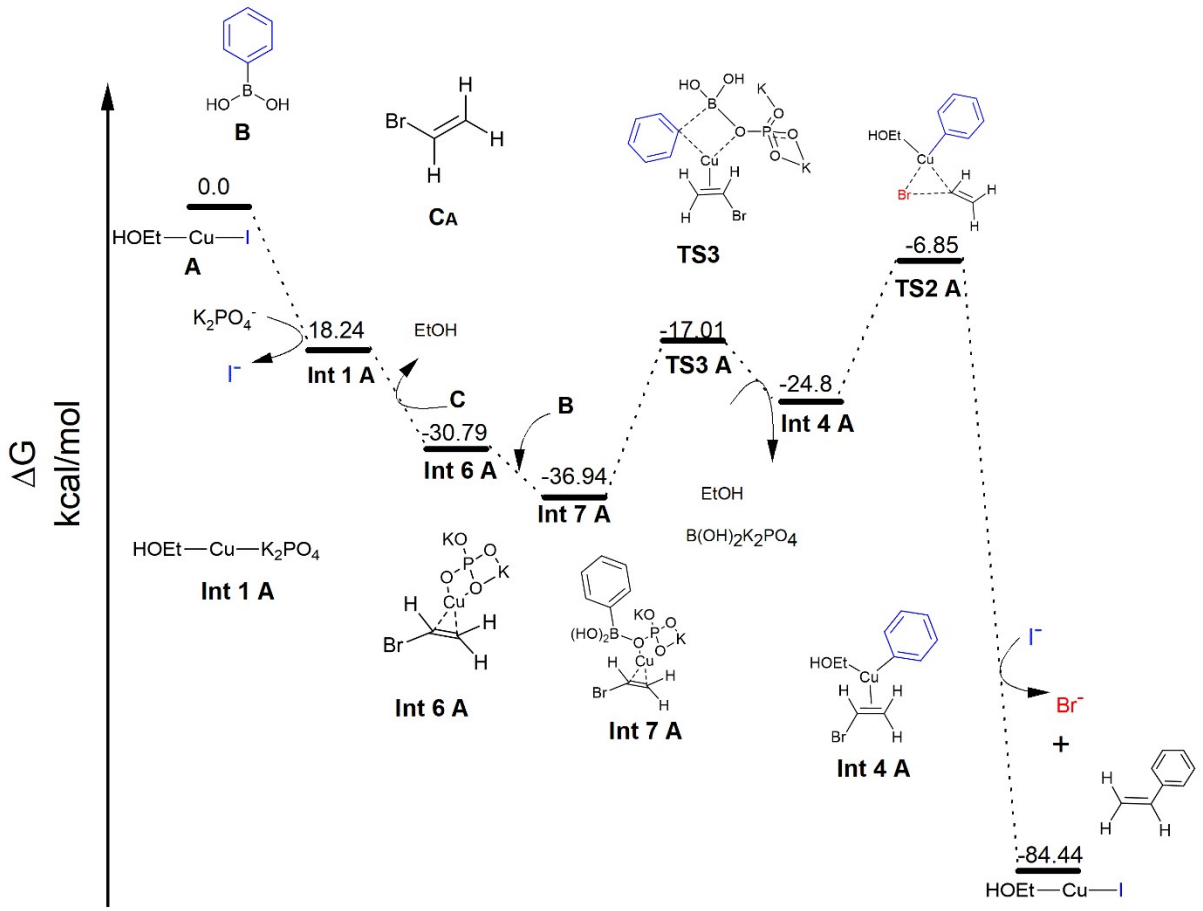

Fig. S.1. The free energy profile (kcal/mol) for Mechanism 2b elucidating the role of vinyl halide substrate as a pseudo-ligand in the ligand-free copper catalyzed Suzuki cross-coupling reaction calculated at DFT/B3LYP/-D3 method. LANL2DZ basis set for K, Br & I; 6-31+G (d) for C, H, N, O, P, Cu and B. Solvation = CPCM/ ethanol solvent.