

# **Zn(II) byproduct enhances the Cu-catalyzed cross-coupling of bromozinc-difluorophosphonate with iodobenzoates: A DFT study**

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## **Supporting Information**

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The supplemental file geometries.xyz contains the computed Cartesian coordinates of all of the molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, <http://www.ccdc.cam.ac.uk/pages/Home.aspx>) for visualization and analysis.

## Detailed procedure to obtain the Gibbs free energy values

The computed Gibbs free energies were corrected to use a standard state corresponding to species in solution with a standard concentration of 1 M. The final Gibbs free energies at a given temperature, computed on the basis of the rigid rotor/harmonic oscillator approach to statistical mechanics, are obtained with the following formula:

$$\Delta G_T^\circ = E_{BS2} + H_{corr,BS1} - TS_{BS1} + RT \ln(C^\circ/C^{1atm})$$

where  $E_{BS2}$  is the electronic energy, including the solvent and dispersion terms, obtained with the large basis sets (BS2).  $H_{corr,BS1}$  is the thermal correction to the enthalpy and contains the zero-point energy plus the vibrational, rotational and translational energies;  $TS_{BS1}$  accounts for the entropic correction. Both these terms are obtained with the small basis sets (BS1). Gibbs free energies as output by Gaussian, which refer to an ideal gas ( $p = 1$  atm) standard state, were corrected to use a standard state corresponding to species in solution with a standard concentration of 1 M. This was performed by adding an extra term to the Gaussian computed Gibbs free energy of each species; this correction is computed as  $RT \ln(C^\circ/C^{1atm})$ , where  $C^\circ$  is the standard reference state concentration (1 M), and  $C^{1atm}$  is the concentration of an ideal gas under the standard  $p = 1$  atm conditions ( $C^{1atm} = 1/V_m = P/RT = 0.0365$  M for an ideal gas at 333.15 K and 1 atm). Numerically, this corrective term equals to 2.2 kcal mol<sup>-1</sup> per molecule at 333.15 K.

**Table S1.** Computed energy terms (in Hartrees) for all the species. The final  $G_T^\circ$  values are computed with the formula shown above. The value of the term  $RT \ln(C^\circ/C^{1atm})$  is equal to 0.00349 Hartrees at 333.15.

Species	$E_{BS2}$	$H_{corr,BS1}$	$T\Delta S_{BS1}$	$G_{333.15K}^\circ$
<b>I1</b>	-1065.0684	0.1883	0.0645	-1064.9411
[ZnBrCF <sub>2</sub> P(O)(OEt) <sub>2</sub> (1,4-dioxane) <sub>2</sub> ]	-2223.2863	0.4440	0.1080	-2222.9468
<b>I2</b>	-2980.5966	0.5016	0.1317	-2980.2232
<b>TMTS</b>	-2980.5716	0.5004	0.1282	-2980.1958
<b>I3</b>	-2980.6021	0.5015	0.1329	-2980.2301
[ZnBrI(1,4-dioxane) <sub>2</sub> ]	-1555.5877	0.2713	0.0780	-1555.3909
<b>I4</b>	-1732.7628	0.3604	0.0942	-1732.4931
Methyl 2-I-benzoate ( <b>S</b> )	-755.4676	0.1449	0.0552	-755.3744
<b>I5</b>	-2488.2495	0.5071	0.1278	-2487.8668
<b>OATS</b>	-2488.2319	0.5056	0.1227	-2487.8455
<b>I6</b>	-2488.2631	0.5079	0.1223	-2487.8740
<b>RETS</b>	-2488.2435	0.5069	0.1203	-2487.8535
<b>P1</b>	-1423.2299	0.3192	0.0861	-1422.9933
1,4-dioxane	-307.7703	0.1295	0.0385	-307.6758
<b>I7</b>	-3736.0894	0.6478	0.1655	-3735.6036
<b>OATS2</b>	-3736.0648	0.6470	0.1578	-3735.5721
<b>I8</b>	-3736.1025	0.6497	0.1575	-3735.6069
<b>RETS2</b>	-3736.0819	0.6483	0.1557	-3735.5858
<b>P2</b>	-2671.0603	0.4605	0.1237	-2670.7200
<b>I9</b>	-3428.3116	0.5163	0.1461	-3427.9379
<b>OATS3</b>	-3428.2821	0.5148	0.1411	-3427.9050
<b>I10</b>	-3428.3080	0.5172	0.1400	-3427.9273
<b>RETS3</b>	-3428.2778	0.5158	0.1396	-3427.8981
<b>P3</b>	-2363.2786	0.3285	0.1035	-2363.0501
Methyl 4-I-benzoate ( <b>S2</b> )	-755.4764	0.1451	0.0553	-755.3831
<b>I7b</b>	-3736.0952	0.6482	0.1680	-3735.6115
<b>I9b</b>	-3428.3173	0.5167	0.1459	-3427.9430
<b>OATS3b</b>	-3428.2917	0.5151	0.1395	-3427.9126
<b>I10b</b>	-3428.2998	0.5168	0.1431	-3427.9226

<b>RETS3b</b>	-3428.2771	0.5158	0.1420	-3427.8998
<b>P3b</b>	-2363.2771	0.3288	0.1060	-2363.0508
1-((2-iodophenyl)diazenyl)piperidine ( <b>S3</b> )	-887.7992	0.2546	0.0646	-887.6057
<b>I7c</b>	-3868.4202	0.7578	0.1715	-3867.8304
<b>OATS2c</b>	-3868.3962	0.7569	0.1663	-3867.8022
<b>I8c</b>	-3868.4286	0.7592	0.1640	-3867.8299
<b>RETS2c</b>	-3868.4076	0.7579	0.1637	-3867.8099
<b>P2c</b>	-2803.3918	0.5704	0.1326	-2802.9506
<b>I9c</b>	-3560.6458	0.6263	0.1537	-3560.1697
<b>OATS3c</b>	-3560.6242	0.6246	0.1484	-3560.1445
<b>I10c</b>	-3560.6392	0.6274	0.1470	-3560.1554
<b>RETS3c</b>	-3560.6091	0.6255	0.1496	-3560.1297
<b>P3c</b>	-2495.6116	0.4385	0.1107	-2495.2803
2-(2-I-phenyl)pyridine ( <b>S4</b> )	-774.6829	0.1710	0.0557	-774.5641
<b>I7d</b>	-3755.3152	0.6745	0.1624	-3754.7996
<b>OATS2d</b>	-3755.2865	0.6731	0.1598	-3754.7696
<b>I8d</b>	-3755.3116	0.6758	0.1581	-3754.7904
<b>RETS2d</b>	-3755.2955	0.6745	0.1581	-3754.7757
<b>P2d</b>	-2690.2758	0.4874	0.1221	-2689.9071
<b>I9d</b>	-3447.5389	0.5431	0.1463	-3447.1386
<b>OATS3d</b>	-3447.5128	0.5416	0.1402	-3447.1079
<b>I10d</b>	-3447.5335	0.5435	0.1421	-3447.1286
<b>RETS3d</b>	-3447.5075	0.5425	0.1404	-3447.1019
<b>P3d</b>	-2382.5078	0.3551	0.1022	-2382.2515