Electronic supplementary information for:

Application of statistical learning and mechanistic modelling towards mapping the substrate electronic space in a Cu-catalyzed Suzuki-Miyaura coupling

Francisco A. Gómez-Mudarra,[a,b] Gabriel Aullón,[a,b] Jesús Jover*[,a,b]

[a] *Secció de Química Inorgànica, Departament de Química Inorgànica I Orgànica, Universitat de Barcelona, Martí i Franquès 1-11, 08028, Barcelona, Spain.* [b] *Institut de Química Teòrica i Computacional (IQTC-UB), Universitat de Barcelona, Martí i Franquès 1-11, 08028, Barcelona, Spain.* * *Correspondence to Jesús Jover (jjovermo@ub.edu)*

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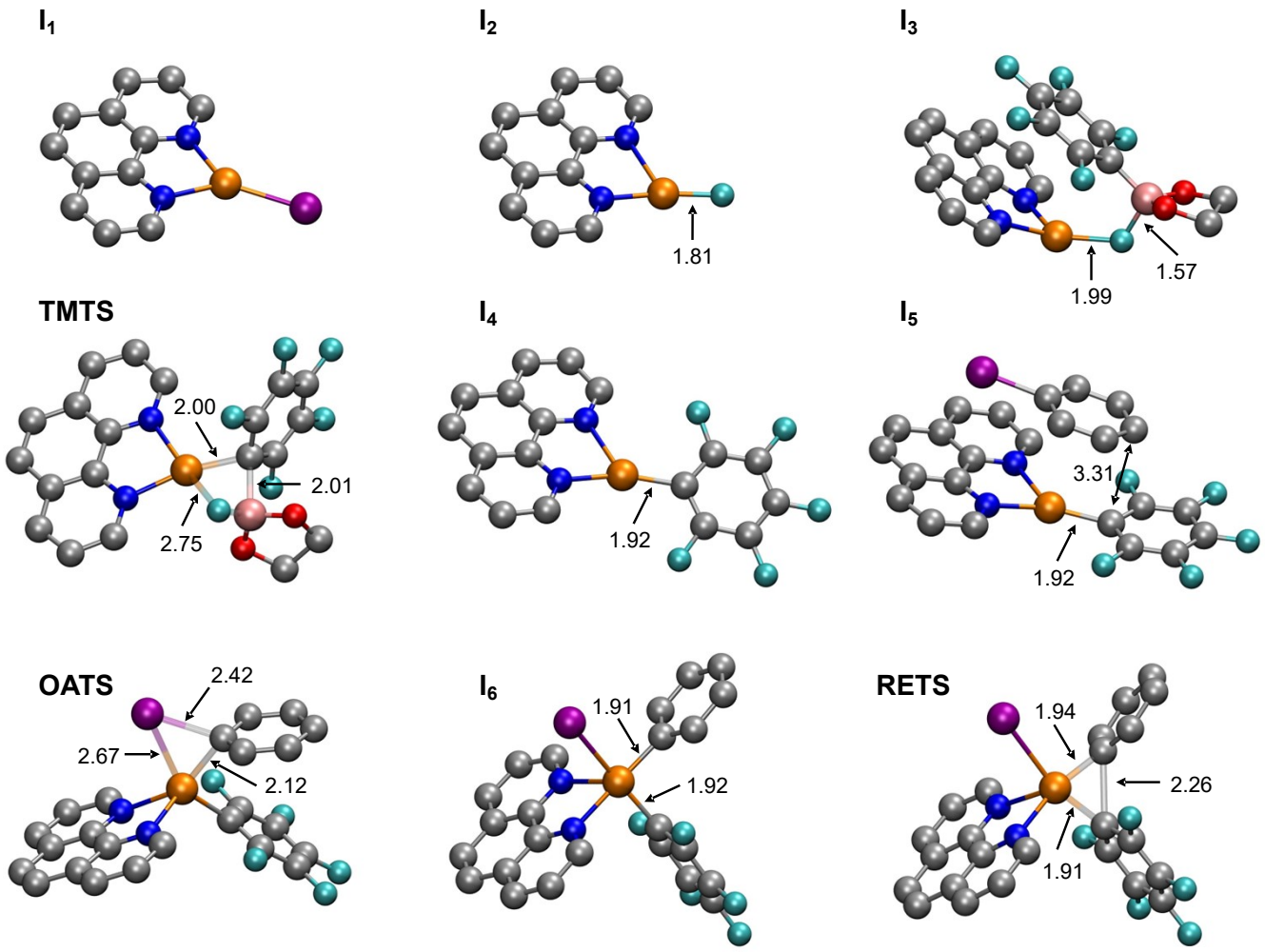


Figure S1. Optimized 3D geometries of the species formed along the lowest energy pathway in the Suzuki-Miyaura coupling between PhI and C_6F_5Bpin. All distances are given in angstroms. Color code: B = pink, C = gray, N = blue, O = red, F = cyan, Cu = orange, I = purple, for clarity all H atoms have been omitted.

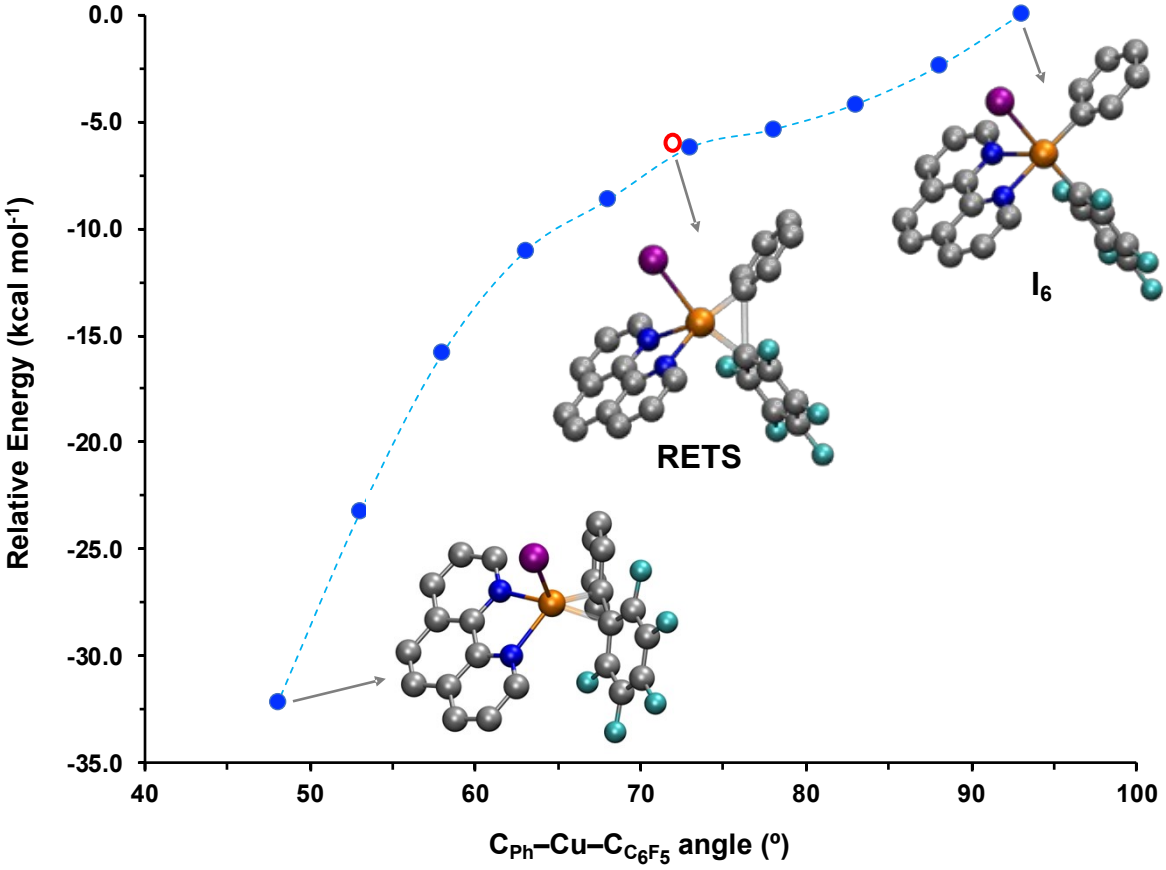


Figure S2. Relaxed potential energy surface scan of the C_{Ph}–Cu–C_{C6F5} angle from intermediate $\mathbf{I_6}$.The initial ($\mathbf{I_6}$) and final structures have been added. The red dot indicates the location of the characterized reductive elimination transition state (**RETS**) by independent DFT calculations. structure Color code: C = gray, N = blue, F = cyan, Cu = orange, I = purple, for clarity all H atoms have been omitted.

Electronic structure analysis of intermediate I_6.

The DFT computed frontier molecular orbitals of species I_6 show that the main contributions to the HOMO, HOMO-1 and HOMO-2 are ligand-based orbitals instead of doubly occupied copper-centered d-orbitals (Figure S2). This seems to indicate that I_6 adopts an inverted ligand field arrangement. Doubly occupied d-orbitals (showing some ligand delocalization) can be found at lower energies in orbitals HOMO-12 to HOMO-16.

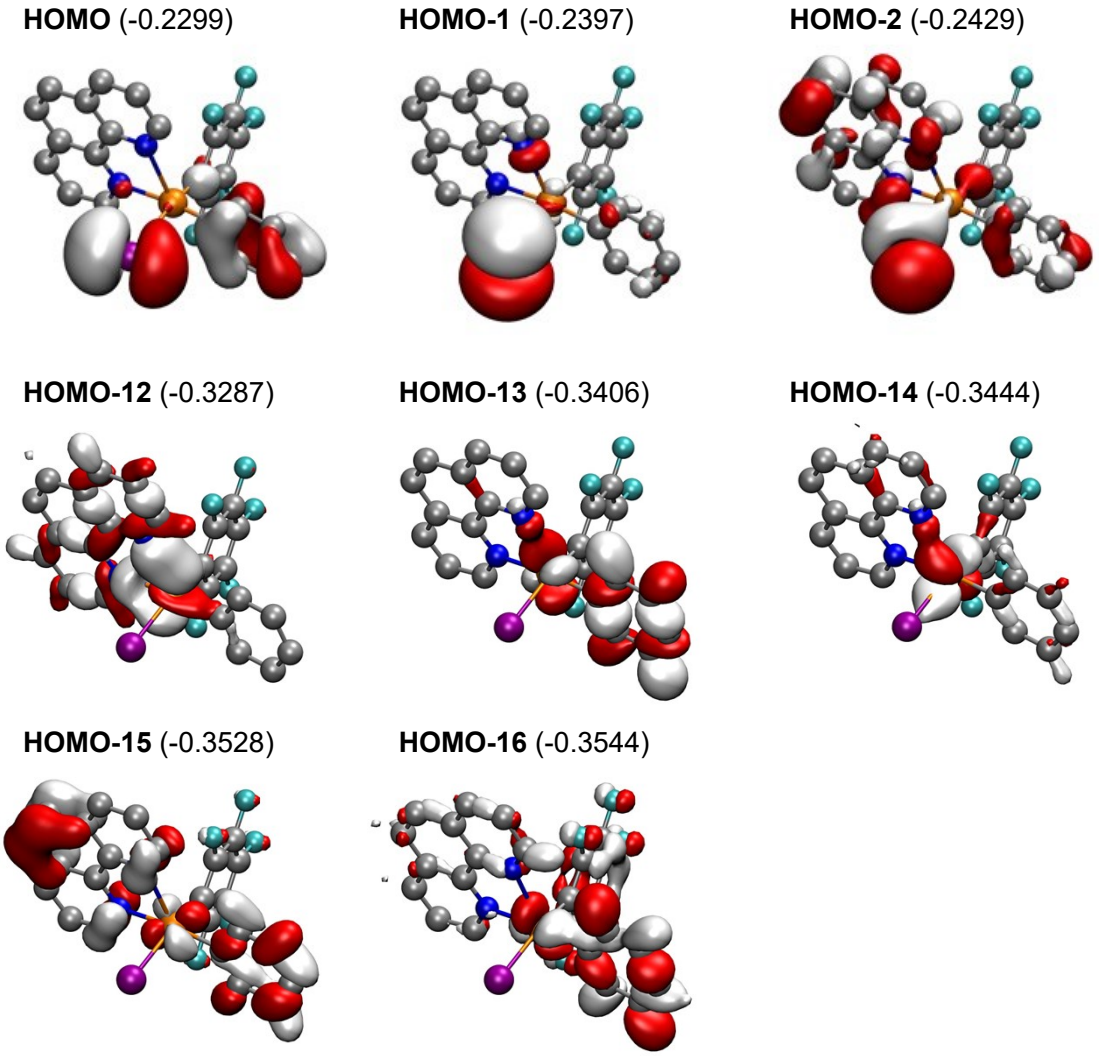


Figure S3. DFT computed frontier molecular orbitals of intermediate I_6 and their energies (in Hartrees). Color code: C = gray, N = blue, F = cyan, Cu = orange, I = purple, for clarity all H atoms have been omitted.

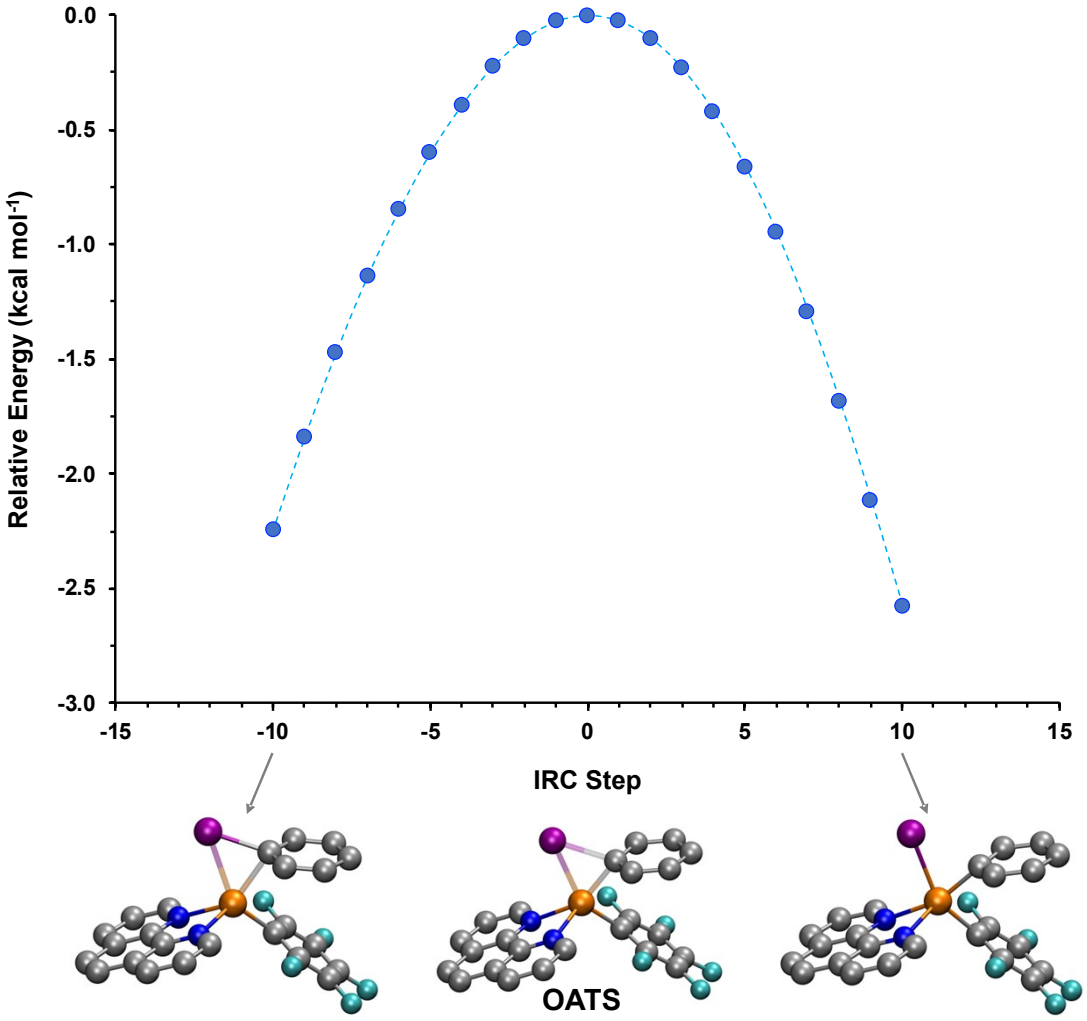
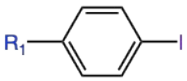
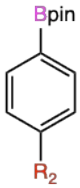


Figure S4. IRC path for the oxidative addition transition state; step 0 corresponds to the oxidative addition transition state (**OATS**) described in the main text. Color code: C = gray, N = blue, F = cyan, Cu = orange, I = purple, for clarity all H atoms have been omitted.





R_2 / R_1	NMe_2	NH_2	OH	OMe	tBu	Me	H	F	Cl	COMe	CF_3	CN	NO_2
NMe_2	t	p		t		p	p	p	t		t		p
NH_2			t		p		t			t		p	t
OH		t	p			t		t		p		t	
OMe	p			p	t		t		t		p	t	p
tBu	t					t		p		t	t		
Me	p	t	p	t			p	t	p	t			p
H	p		t			t	p		p		t		t
F	p				t	p	p	t		p		t	t
Cl	t	p			p		t		t		t		
COMe		t		t	p		t					p	t
CF_3	p	t	p			t	p	t	t	p			p
CN	t	p		t	t			t	p			p	
NO_2	t		t	p	t		p			t	p		p
C_6F_5	p		t	p		p	t	p			p	t	t

Figure S5. Substrate pairs included in the QSPR modeling: t = training set, p = prediction set.

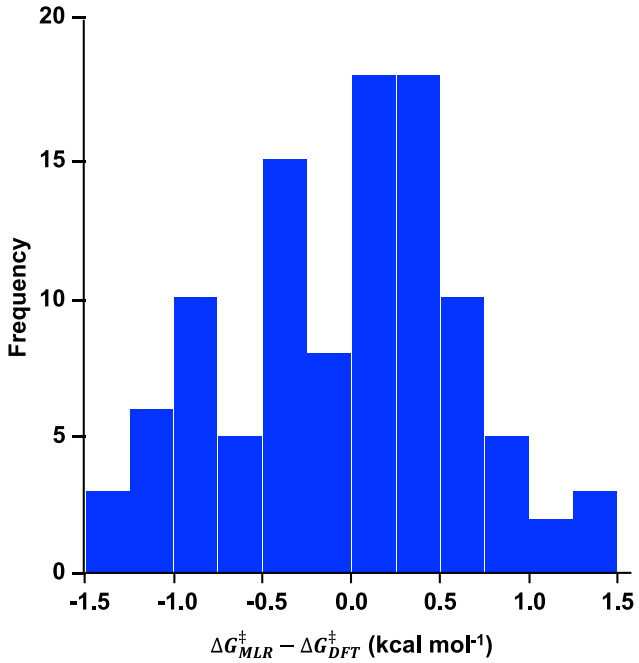


Figure S6. Distribution of errors ($\Delta G^{\ddagger}_{MLR} - \Delta G^{\ddagger}_{DFT}$) for all the substrate pairs in the dataset.

Gibbs Energy Calculation

Final Gibbs energies are computed as:

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

When T = 130°C, $RT\ln(C^\circ/C^{1atm})$ = 0.0045 Hartree. The E_{BS2}, $H_{corr,BS1}$ and S_{BS1} terms for the different species can be found in tables S1, S2 and S3.

Table S1. Energy terms (E_{BS2}, $H_{corr,BS1}$, TS_{BS1} and $G°$, in Hartrees), for all Cu-based species involved in the catalytic cycles (for species R_2-C_6H_4Bpin R_1-C_6H_4I).

R_2	R_1	Species	E_{BS2}	$H_{corr,BS1}$	TS_{BS1}	$G°$
-	-	**I1**	-1065.0864	0.1883	0.0782	-1064.9718
-	-	**I2**	-869.1283	0.1889	0.0727	-869.0077
C_6F_5	-	**I3**	-1851.2796	0.3244	0.1208	-1851.0715
	-	**TMTS**	-1851.2668	0.3232	0.1208	-1851.0599
	-	**I4**	-1497.2514	0.2442	0.1008	-1497.1035
	p-H	**I5**	-2024.7939	0.3430	0.1319	-2024.5783
	p-H	**OATS**	-2024.7601	0.3415	0.1255	-2024.5397
	p-H	**I6**	-2024.7818	0.3427	0.1256	-2024.5590
	p-H	**RETS**	-2024.7801	0.3418	0.1219	-2024.5544
	p-H	**OATS_*trans***	-2024.7561	0.3042	0.1277	-2024.5378
	p-H	**I6_*trans***	-2024.7733	0.3422	0.1238	-2024.5492
	p-H	**I4_cation**	-1497.0970	0.2441	0.1007	-1496.9479
	p-NMe_2	**I5**	-2158.8126	0.4213	0.1410	-2158.5278
	p-NMe_2	**OATS**	-2158.7745	0.4196	0.1354	-2158.4859
	p-OMe	**I5**	-2139.3585	0.3788	0.1364	-2139.1116
	p-OMe	**OATS**	-2139.3209	0.3769	0.1316	-2139.0711
	p-Me	**I5**	-2064.1275	0.3710	0.1291	-2063.8812
	p-Me	**OATS**	-2064.0910	0.3709	0.1316	-2063.8473
	p-F	**I5**	-2124.0612	0.3357	0.1344	-2123.8553
	p-F	**OATS**	-2124.0287	0.3341	0.1288	-2123.8190
	p-CF_3	**I5**	-2361.9512	0.3516	0.1387	-2361.7338
	p-CF_3	**OATS**	-2361.9168	0.3497	0.1383	-2361.7009
	p-NO_2	**I5**	-2229.3675	0.3484	0.1392	-2229.1539
	p-NO_2	**OATS**	-2229.3368	0.3466	0.1341	-2229.1197
p-NMe_2	-	**I3**	-1488.9778	0.4389	0.1212	-1488.6556
	-	**TMTS**	-1488.9517	0.4379	0.1231	-1488.6325

	-	**I4**	-1134.9253	0.3587	0.1009	-1134.6631
	p-NMe_2	**I5**	-1796.4874	0.5355	0.1401	-1796.0875
	p-NMe_2	**OATS**	-1796.4470	0.5337	0.1376	-1796.0465
	p-OMe	**I5**	-1777.0312	0.4932	0.1362	-1776.6698
	p-OMe	**OATS**	-1776.9946	0.4912	0.1339	-1776.6328
	p-Me	**I5**	-1701.8004	0.4869	0.1350	-1701.4440
	p-Me	**OATS**	-1701.7631	0.4852	0.1326	-1701.4061
	p-H	**I5**	-1662.4664	0.4575	0.1299	-1662.1343
	p-H	**OATS**	-1662.4325	0.4558	0.1265	-1662.0987
	p-F	**I5**	-1761.7363	0.4501	0.1333	-1761.4150
	p-F	**OATS**	-1761.7012	0.4484	0.1298	-1761.3781
	p-CF_3	**I5**	-1999.6225	0.4658	0.1419	-1999.2941
	p-CF_3	**OATS**	-1999.5897	0.4639	0.1393	-1999.2606
	p-NO_2	**I5**	-1867.0412	0.4627	0.1368	-1866.7109
	p-NO_2	**OATS**	-1867.0102	0.4608	0.1344	-1866.6793
p-OMe	-	**I3**	-1469.5216	0.3962	0.1156	-1469.2366
	-	**TMTS**	-1469.5003	0.3954	0.1156	-1469.2160
	-	**I4**	-1115.4747	0.3163	0.0965	-1115.2505
	p-NMe_2	**I5**	-1777.0369	0.4932	0.1353	-1776.6745
	p-NMe_2	**OATS**	-1776.9966	0.4914	0.1344	-1776.6353
	p-H	**I5**	-1643.0160	0.4152	0.1246	-1642.7209
	p-H	**OATS**	-1642.9821	0.4133	0.1202	-1642.6845
	p-NO_2	**I5**	-1847.5891	0.4203	0.1325	-1847.2967
	p-NO_2	**OATS**	-1847.5612	0.4183	0.1288	-1847.2673
p-Me	-	**I3**	-1394.2919	0.3905	0.1134	-1394.0104
	-	**TMTS**	-1394.2678	0.3894	0.1140	-1393.9880
	-	**I4**	-1040.2427	0.3102	0.0946	-1040.0227
	p-NMe_2	**I5**	-1701.8048	0.4870	0.1338	-1701.4471
	p-NMe_2	**OATS**	-1701.7650	0.4852	0.1328	-1701.4081
	p-H	**I5**	-1567.7840	0.4092	0.1225	-1567.4929
	p-H	**OATS**	-1567.7505	0.4073	0.1192	-1567.4579
	p-NO_2	**I5**	-1772.3584	0.4143	0.1306	-1772.0702
	p-NO_2	**OATS**	-1772.3304	0.4123	0.1273	-1772.0409
p-H	-	**I3**	-1354.9605	0.3611	0.1069	-1354.7017
	-	**TMTS**	-1354.9374	0.3600	0.1074	-1354.6804

	-	**I4**	-1000.9129	0.2808	0.0891	-1000.7166
	p-NMe_2	**I5**	-1662.4750	0.4576	0.1285	-1662.1414
	p-NMe_2	**OATS**	-1662.4353	0.4558	0.1263	-1662.1012
	p-H	**I5**	-1528.4542	0.3798	0.1167	-1528.1867
	p-H	**OATS**	-1528.4208	0.3779	0.1128	-1528.1512
	p-NO_2	**I5**	-1733.0270	0.3850	0.1242	-1732.7618
	p-NO_2	**OATS**	-1733.0008	0.3830	0.1202	-1732.7335
p-F	-	**I3**	-1454.2317	0.3537	0.1110	-1453.9846
	-	**TMTS**	-1454.2088	0.3526	0.1103	-1453.9621
	-	**I4**	-1100.1843	0.2734	0.0918	-1099.9982
	p-NMe_2	**I5**	-1761.7466	0.4502	0.1320	-1761.4239
	p-NMe_2	**OATS**	-1761.7069	0.4485	0.1290	-1761.3830
	p-H	**I5**	-1627.7257	0.3724	0.1202	-1627.4691
	p-H	**OATS**	-1627.6923	0.3705	0.1155	-1627.4328
	p-NO_2	**I5**	-1832.3001	0.3775	0.1256	-1832.0437
	p-NO_2	**OATS**	-1832.2717	0.3757	0.1233	-1832.0149
p-CF_3	-	**I3**	-1692.1197	0.3693	0.1174	-1691.8634
	-	**TMTS**	-1692.0959	0.3681	0.1204	-1691.8437
	-	**I4**	-1338.0717	0.2890	0.1044	-1337.8827
	p-NMe_2	**I5**	-1999.6343	0.4659	0.1419	-1999.3059
	p-NMe_2	**OATS**	-1999.5950	0.4641	0.1393	-1999.2657
	p-H	**I5**	-1865.6135	0.3880	0.1305	-1865.3515
	p-H	**OATS**	-1865.5803	0.3862	0.1258	-1865.3154
	p-NO_2	**I5**	-2070.1860	0.3932	0.1351	-2069.9235
	p-NO_2	**OATS**	-2070.1599	0.3912	0.1330	-2069.8972
p-NO_2	-	**I3**	-1559.5386	0.3663	0.1159	-1559.2837
	-	**TMTS**	-1559.5164	0.3651	0.1161	-1559.2630
	-	**I4**	-1205.4926	0.2860	0.0978	-1205.2999
	p-NMe_2	**I5**	-1867.0549	0.4630	0.1359	-1866.7234
	p-NMe_2	**OATS**	-1867.0146	0.4613	0.1348	-1866.6837
	p-H	**I5**	-1733.0341	0.3850	0.1261	-1732.7707
	p-H	**OATS**	-1733.0006	0.3832	0.1206	-1732.7335
	p-NO_2	**I5**	-1937.6088	0.3902	0.1311	-1937.3452
	p-NO_2	**OATS**	-1937.5797	0.3883	0.1286	-1937.3155

Table S2. Energy terms (E_{BS2}, $H_{corr,BS1}$, TS_{BS1} and $G°$, in Hartrees), for all reactants and products involved in the catalytic cycles.

Species	E_{BS2}	$H_{corr,BS1}$	TS_{BS1}	$G°$
p-NMe_2-C_6H_4Bpin	-619.8463	0.2501	0.0763	-619.6680
p-NH_2-C_6H_4Bpin	-541.2149	0.1903	0.0655	-541.0856
p-HO-C_6H_4Bpin	-561.0833	0.1775	0.0650	-560.9664
p-MeO-C_6H_4Bpin	-600.3928	0.2078	0.0695	-600.2502
p-tBu-C_6H_4Bpin	-643.1416	0.2910	0.0781	-642.9242
p-Me-C_6H_4Bpin	-525.1597	0.2017	0.0681	-525.0217
PhBpin	-485.8284	0.1723	0.0619	-485.7135
p-F-C_6H_4Bpin	-585.0987	0.1649	0.0647	-584.9941
p-Cl-C_6H_4Bpin	-945.4550	0.1639	0.0666	-945.3533
p-MeCO-C_6H_4Bpin	-638.5310	0.2134	0.0738	-638.3869
p-CF_3-C_6H_4Bpin	-822.9828	0.1805	0.0761	-822.8739
p-NC-C_6H_4Bpin	-578.1010	0.1728	0.0683	-577.9921
p-NO_2-C_6H_4Bpin	-690.3992	0.1775	0.0714	-690.2888
C_6F_5Bpin	-982.1350	0.1356	0.0764	-982.0713
m-NMe_2-C_6H_4Bpin	-619.8433	0.2500	0.0753	-619.6642
m-NH_2-C_6H_4Bpin	-541.2123	0.1903	0.0660	-541.0835
m-HO-C_6H_4Bpin	-561.0816	0.1774	0.0653	-560.9650
m-OMe-C_6H_4Bpin	-600.3911	0.2077	0.0699	-600.2489
m-tBu-C_6H_4Bpin	-643.1412	0.2910	0.0783	-642.9241
m-Me-C_6H_4Bpin	-525.1591	0.2016	0.0701	-525.0231
m-F-C_6H_4Bpin	-585.0981	0.1648	0.0649	-584.9937
m-Cl-C_6H_4Bpin	-945.4548	0.1639	0.0667	-945.3532
m-MeCO-C_6H_4Bpin	-638.5314	0.2135	0.0732	-638.3867
m-CF_3-C_6H_4Bpin	-822.9833	0.1805	0.0754	-822.8738
m-NC-C_6H_4Bpin	-578.1015	0.1728	0.0682	-577.9925
m-NO_2-C_6H_4Bpin	-690.4000	0.1774	0.0712	-690.2893
m,*m*'-$(NMe_2)_2$-C_6H_3Bpin	-753.8574	0.3278	0.0885	-753.6137
m,*m*'-$(OMe)_2$-C_6H_3Bpin	-714.9537	0.2431	0.0777	-714.7838
m,*m*'-Me_2-C_6H_3Bpin	-564.4898	0.2310	0.0752	-564.3296
m,*m*'-F_2-C_6H_3Bpin	-684.3660	0.1574	0.0678	-684.2721
m,*m*'-$(CF_3)_2$-C_6H_3Bpin	-1160.1355	0.1887	0.0882	-1160.0306
m,*m*'-$(NO_2)_2$-C_6H_3Bpin	-894.9650	0.1824	0.0805	-894.8586

p-NMe_2-C_6H_4I	-661.5398	0.1753	0.0661	-661.4261
p-NH_2-C_6H_4I	-582.9086	0.1155	0.0563	-582.8449
p-HO-C_6H_4I	-602.7772	0.1026	0.0557	-602.7258
p-MeO-C_6H_4I	-642.0868	0.1329	0.0603	-642.0098
p-tBu-C_6H_4I	-684.8373	0.2162	0.0682	-684.6848
p-Me-C_6H_4I	-566.8552	0.1268	0.0589	-566.7829
PhI	-527.5244	0.0975	0.0522	-527.4746
C_6H_5I monoanion	-527.6278	0.0929	0.0531	-527.5822
p-F-C_6H_4I	-626.7928	0.0900	0.0550	-626.7534
p-Cl-C_6H_4I	-987.1496	0.0890	0.0567	-987.1129
p-MeCO-C_6H_4I	-680.2271	0.1385	0.0640	-680.1482
p-CF_3-C_6H_4I	-864.6782	0.1056	0.0658	-864.6340
p-NC-C_6H_4I	-619.7965	0.0979	0.0581	-619.7523
p-NO_2-C_6H_4I	-732.0948	0.1025	0.0639	-732.0517
m-NMe_2-C_6H_4I	-661.5401	0.1752	0.0657	-661.4261
m-NH_2-C_6H_4I	-582.9088	0.1154	0.0562	-582.8451
m-HO-C_6H_4I	-602.7774	0.1026	0.0556	-602.7260
m-MeO-C_6H_4I	-642.0870	0.1328	0.0602	-642.0099
m-tBu-C_6H_4I	-684.8376	0.2162	0.0683	-684.6853
m-Me-C_6H_4I	-566.8554	0.1268	0.0584	-566.7825
m-F-C_6H_4I	-626.7928	0.0900	0.0550	-626.7534
m-Cl-C_6H_4I	-987.1495	0.0890	0.0568	-987.1128
m-MeCO-C_6H_4I	-680.2268	0.1386	0.0637	-680.1474
m-CF_3-C_6H_5I	-864.6777	0.1056	0.0659	-864.6336
m-NC-C_6H_4I	-619.7956	0.0978	0.0582	-619.7515
m-NO_2-C_6H_4I	-732.0937	0.1025	0.0614	-732.0481
m,*m*'-$(NMe_2)_2C_6H_3I$	-795.5549	0.2530	0.0791	-795.3765
m,*m*'-$(MeO)_2C_6H_3I$	-756.6495	0.1682	0.0682	-756.5451
m,*m*'-$Me_2C_6H_3I$	-606.1863	0.1562	0.0651	-606.0908
m,*m*'-$F_2C_6H_3I$	-726.0595	0.0825	0.0578	-726.0304
m,*m*'-$(CF_3)_2C_6H_3I$	-1201.8286	0.1138	0.0787	-1201.7891
p-$NMe_2C_6H_4$-C_6F_5	-1093.7718	0.2334	0.0883	-1093.6222
p-$OMeC_6H_4$-C_6F_5	-1074.3180	0.1910	0.0820	-1074.2046
p-MeC_6H_4-C_6F_5	-999.0856	0.1849	0.0807	-998.9769
Ph-C_6F_5	-959.7544	0.1556	0.0739	-959.6682

p-F-C_6H_4-C_6F_5	-1059.0235	0.1481	0.0769	-1058.9479
p-CF_3-C_6H_4-C_6F_5	-1296.9079	0.1638	0.0881	-1296.8278
p-NO_2-C_6H_4-C_6F_5	-1164.3242	0.1607	0.0830	-1164.2420
m-Me-C_6H_4-C_6F_5	-999.0853	0.1849	0.0811	-998.9770
p-$NMe_2C_6H_4$-C_6H_4-*p*-NMe_2	-731.4805	0.3478	0.0872	-731.2154
p-$NMe_2C_6H_4$-C_6H_4-*p*-OMe	-712.0283	0.3054	0.0821	-711.8005
p-$NMe_2C_6H_4$-C_6H_4-*p*-Me	-636.7966	0.2994	0.0814	-636.5741
p-$NMe_2C_6H_4$-Ph	-597.4661	0.2700	0.0739	-597.2655
p-$NMe_2C_6H_4$-C_6H_4-*p*-F	-696.7355	0.2626	0.0768	-696.5453
p-$NMe_2C_6H_4$-C_6H_4-*p*-CF_3	-934.6222	0.2783	0.0881	-934.4275
p-$NMe_2C_6H_4$-C_6H_4-*p*-NO_2	-802.0413	0.2753	0.0841	-801.8457
p-$MeOC_6H_4$-Ph	-578.0134	0.2278	0.0677	-577.8489
p-$MeOC_6H_4$-C_6H_4-*p*-NO_2	-782.5869	0.2329	0.0771	-782.4266
p-MeC_6H_4-Ph	-502.7814	0.2217	0.0669	-502.6222
p-MeC_6H_4-C_6H_4-*p*-NO_2	-707.3544	0.2268	0.0763	-707.1993
Ph-Ph	-463.4507	0.1924	0.0598	-463.3136
p-FC_6H_4-Ph	-562.7201	0.1849	0.0627	-562.5934
p-FC_6H_4-C_6H_4-*p*-NO_2	-767.2924	0.1900	0.0719	-767.1698
p-$CF_3C_6H_4$-Ph	-800.6058	0.2006	0.0734	-800.4741
p-$CF_3C_6H_4$-C_6H_4-*p*-NO_2	-1005.1774	0.2058	0.0825	-1005.0497
p-$NO_2C_6H_4$-Ph	-668.0232	0.1975	0.0689	-667.8901
p-$NO_2C_6H_4$-C_6H_4-*p*-NO_2	-872.5940	0.2026	0.0785	-872.4654
m,*m*'-$Me_2C_6H_3$-Ph	-542.1119	0.2511	0.0727	-541.9292

Table S3. Energy terms (E_{BS2}, $H_{corr,BS1}$, TS_{BS1} and $G°$, in Hartrees), for oxidative addition (**OATS**) transition states computed for different substrate pairs (for species R_2-C_6H_4Bpin R_1-C_6H_4I).

R_2	R_1	E_{BS2}	$H_{corr,BS1}$	TS_{BS1}	$G°$
p-NMe_2	*p*-Cl	-2122.0594	0.4475	0.1305	-2121.7380
p-NMe_2	*m*-tBu	-1819.7470	0.5745	0.1424	-1819.3104
p-NMe_2	*m*-CF_3	-1999.5890	0.4642	0.1376	-1999.2578
p-NH_2	*p*-OH	-1659.0544	0.4013	0.1198	-1658.7685
p-NH_2	*p*-H	-1583.8021	0.3961	0.1164	-1583.5181
p-NH_2	*p*-COMe	-1736.5061	0.4373	0.1277	-1736.1921
p-NH_2	*p*-NO_2	-1788.3820	0.4012	0.1243	-1788.1006
p-NH_2	*m*,*m*'-OMe	-1812.9293	0.4670	0.1332	-1812.5911
p-OH	*p*-NH_2	-1659.0565	0.4012	0.1207	-1658.7715
p-OH	*p*-Me	-1643.0040	0.4125	0.1220	-1642.7090
p-OH	*p*-F	-1702.9420	0.3756	0.1190	-1702.6809
p-OH	*p*-CN	-1695.9505	0.3837	0.1203	-1695.6826
p-OH	*m*-NH_2	-1659.0577	0.4012	0.1197	-1658.7717
p-OMe	*p*-OMe	-1757.5442	0.4488	0.1287	-1757.2197
p-OMe	*p*-tBu	-1800.2959	0.5320	0.1369	-1799.8964
p-OMe	*p*-Cl	-2102.6090	0.4049	0.1268	-2102.3264
p-OMe	*p*-CF_3	-1980.1393	0.4215	0.1327	-1979.8460
p-OMe	*p*-CN	-1735.2593	0.4138	0.1265	-1734.9675
p-OMe	*m*-OMe	-1757.5460	0.4489	0.1283	-1757.2209
p-OMe	*m*-NO_2	-1847.5549	0.4185	0.1303	-1847.2622
p-tBu	*p*-NMe_2	-1819.7471	0.5744	0.1420	-1819.3103
p-tBu	*p*-Me	-1725.0631	0.5259	0.1358	-1724.6685
p-tBu	*p*-COMe	-1838.4397	0.5377	0.1397	-1838.0371
p-tBu	*p*-CF_3	-2022.8882	0.5035	0.1420	-2022.5222
p-tBu	*m*-CF_3	-2022.8881	0.5048	0.1422	-2022.5210
p-Me	*p*-NH_2	-1623.1336	0.4254	0.1232	-1622.8269
p-Me	*p*-OMe	-1682.3125	0.4428	0.1263	-1681.9915
p-Me	*p*-F	-1667.0192	0.3999	0.1222	-1666.7370
p-Me	*p*-COMe	-1720.4576	0.4484	0.1304	-1720.1351
p-Me	*m*-Me	-1607.0819	0.4366	0.1254	-1606.7662
p-Me	*m*-Cl	-2027.3780	0.3989	0.1240	-2027.0986

p-Me	*m*,*m*'-CF_3	-2242.0605	0.4235	0.1412	-2241.7738
p-H	*p*-OH	-1603.6730	0.3831	0.1157	-1603.4010
p-H	*p*-Me	-1567.7512	0.4072	0.1201	-1567.4597
p-H	*p*-CF_3	-1865.5776	0.3861	0.1257	-1865.3127
p-H	*m*,*m*'-F	-1726.9578	0.3627	0.1196	-1726.7102
p-F	*p*-tBu	-1785.0059	0.4892	0.1314	-1784.6436
p-F	*p*-Me	-1667.0229	0.3998	0.1223	-1666.7409
p-F	*p*-pF	-1726.9607	0.3630	0.1193	-1726.7125
p-F	*p*-CN	-1719.9691	0.3710	0.1209	-1719.7146
p-F	*m*-Me	-1667.0235	0.3998	0.1231	-1666.7424
p-Cl	*p*-NMe_2	-2122.0648	0.4474	0.1309	-2121.7439
p-Cl	*p*-H	-1988.0498	0.3694	0.1183	-1987.7942
p-Cl	*p*-Cl	-2447.6767	0.3613	0.1204	-2447.4313
p-Cl	*p*-CF_3	-2325.2069	0.3777	0.1302	-2324.9549
p-Cl	*m*-NMe_2	-2122.0658	0.4474	0.1308	-2121.7448
p-COMe	*p*-NH_2	-1736.5101	0.4371	0.1281	-1736.1966
p-COMe	*p*-OMe	-1795.6896	0.4545	0.1323	-1795.3629
p-COMe	*p*-H	-1681.1275	0.4190	0.1245	-1680.8285
p-COMe	*p*-NO_2	-1885.7078	0.4241	0.1311	-1885.4103
p-COMe	*m*-NO_2	-1885.7004	0.4242	0.1327	-1885.4045
p-CF_3	*p*-NH_2	-1920.9634	0.4043	0.1299	-1920.6846
p-CF_3	*p*-Me	-1904.9108	0.4154	0.1322	-1904.6231
p-CF_3	*p*-F	-1964.8487	0.3787	0.1290	-1964.5945
p-CF_3	*p*-Cl	-2325.2068	0.3777	0.1306	-2324.9552
p-CF_3	*m*-F	-1964.8499	0.3787	0.1287	-1964.5955
p-CF_3	*m*,*m*'-Me	-1944.2428	0.4449	0.1382	-1943.9317
p-CN	*p*-NMe_2	-1754.7149	0.4563	0.1322	-1754.3863
p-CN	*p*-OMe	-1735.2619	0.4138	0.1271	-1734.9707
p-CN	*p*-tBu	-1778.0138	0.4971	0.1337	-1777.6459
p-CN	*p*-F	-1719.9685	0.3711	0.1213	-1719.7143
p-CN	*m*-F	-1719.9697	0.3711	0.1202	-1719.7144
p-NO_2	*p*-OH	-1808.2527	0.3884	0.1242	-1807.9840
p-NO_2	*p*-OMe	-1847.5623	0.4186	0.1302	-1847.2694
p-NO_2	*p*-tBu	-1890.3144	0.5019	0.1367	-1889.9448
p-NO_2	*p*-COMe	-1885.7071	0.4244	0.1326	-1885.4109

p-NO_2	*p*-CF_3	-2070.1572	0.3914	0.1347	-2069.8960
p-NO_2	*m*-OMe	-1847.5643	0.4187	0.1294	-1847.2706
p-NO_2	*m*-COMe	-1885.7049	0.4244	0.1319	-1885.4079
p-NO_2	*m*,*m*'-NMe_2	-2001.0326	0.5386	0.1470	-2000.6365
C_6F_5	*p*-OH	-2100.0126	0.3467	0.1290	-2099.7904
C_6F_5	*p*-CN	-2117.0360	0.3420	0.1307	-2116.8202
m-NMe_2	*p*-Me	-1701.7656	0.4852	0.1306	-1701.4066
m-NH_2	*p*-H	-1583.8036	0.3959	0.1171	-1583.5203
m-NH_2	*m*-OH	-1659.0578	0.4012	0.1199	-1658.7720
m-NH_2	*m*-CN	-1676.0774	0.3964	0.1226	-1675.7990
m-OH	*p*-Cl	-2063.3015	0.3746	0.1210	-2063.0434
m-OH	*m*-NMe_2	-1737.6902	0.4607	0.1287	-1737.3537
m-OMe	*p*-F	-1742.2528	0.4058	0.1238	-1741.9662
m-OMe	*m*-COMe	-1795.6886	0.4544	0.1322	-1795.3619
m-OMe	*m*-NO_2	-1847.5565	0.4185	0.1301	-1847.2636
m-tBu	*p*-OMe	-1800.2974	0.5323	0.1355	-1799.8961
m-Me	*p*-CF_3	-1904.9080	0.4154	0.1324	-1904.6205
m-Me	*p*-CN	-1660.0288	0.4077	0.1232	-1659.7398
m-Me	*m*-OH	-1643.0050	0.4124	0.1230	-1642.7111
m-Me	*m*-OMe	-1682.3150	0.4427	0.1272	-1681.9950
m-F	*p*-OMe	-1742.2564	0.4060	0.1234	-1741.9694
m-F	*p*-Cl	-2087.3210	0.3621	0.1201	-2087.0745
m-F	*m*-Me	-1667.0258	0.3998	0.1209	-1666.7424
m-Cl	*p*-tBu	-2145.3657	0.4882	0.1323	-2145.0054
m-Cl	*p*-F	-2087.3209	0.3622	0.1200	-2087.0743
m-Cl	*p*-H	-1988.0522	0.3695	0.1176	-1987.7958
m-Cl	*m*-$CF3_3$	-2325.2083	0.3778	0.1291	-2324.9551
m-COMe	*p*-COMe	-1833.8337	0.4603	0.1343	-1833.5032
m-COMe	*m*-$CF3_3$	-2018.2848	0.4278	0.1334	-2017.9861
m-CF_3	*p*-NH_2	-1920.9643	0.4042	0.1277	-1920.6832
m-CF_3	*p*-NO_2	-2070.1600	0.3912	0.1342	-2069.8985
m-CF_3	*m*-Me	-1904.9118	0.4155	0.1315	-1904.6234
m-CN	*p*-NMe_2	-1754.7150	0.4563	0.1318	-1754.3861
m-CN	*m*-NH_2	-1676.0844	0.3965	0.1229	-1675.8063
m-CN	*m*-tBu	-1778.0149	0.4973	0.1336	-1777.6467

m-NO_2	*p*-Me	-1772.3306	0.4126	0.1277	-1772.0412
m-NO_2	*m*-OH	-1808.2539	0.3885	0.1241	-1807.9850
m-NO_2	*m*-CF_3	-2070.1558	0.3916	0.1331	-2069.8929
m-NO_2	*m*-NO_2	-1937.5733	0.3885	0.1303	-1937.3107
m,*m*'-OMe	*p*-H	-1757.5468	0.4487	0.1291	-1757.2227
m,*m*'-Me	*p*-H	-1607.0813	0.4367	0.1254	-1606.7655
m,*m*'-F	*p*-OMe	-1841.5282	0.3985	0.1260	-1841.2512
m,*m*'-CF_3	*p*-NO_2	-2407.3180	0.3995	0.1458	-2407.0597
m,*m*'-NO_2	*p*-NMe_2	-2071.5892	0.4663	0.1428	-2071.2613
p-CF3	*p*-COMe	-2018.2872	0.4273	0.1374	-2017.9928
p-CF3	*p*-OH	-1940.8324	0.3914	0.1291	-1940.5657
p-CN	*p*-CN	-1712.9769	0.3790	0.1229	-1712.7163
p-CN	*p*-pCl	-2080.3268	0.3701	0.1216	-2080.0737
p-CN	*p*-NH_2	-1676.0833	0.3966	0.1220	-1675.8043
p-COMe	*p*-CN	-1773.4044	0.4197	0.1282	-1773.1084
p-COMe	*p*-tBu	-1838.4412	0.5378	0.1395	-1838.0384
p-Cl	*p*-NH_2	-2043.4332	0.3877	0.1212	-2043.1623
p-Cl	*p*-tBu	-2145.3638	0.4882	0.1329	-2145.0040
p-F	*p*-pCOMe	-1780.3961	0.4116	0.1272	-1780.1073
p-H	*p*-Cl	-1988.0475	0.3695	0.1174	-1987.7910
p-Me	*p*-Cl	-2027.3773	0.3989	0.1245	-2027.0985
p-Me	*p*-OH	-1643.0027	0.4125	0.1229	-1642.7086
p-NH_2	*m*-CN	-1676.0758	0.3966	0.1220	-1675.7968
p-NH_2	*m*-tBu	-1741.1167	0.5147	0.1316	-1740.7291
p-NH_2	*p*-CN	-1676.0794	0.3966	0.1215	-1675.7998
p-NH_2	*p*-tBu	-1741.1156	0.5148	0.1327	-1740.7291
p-NMe_2	*p*-NH_2	-1717.8156	0.4738	0.1306	-1717.4679
p-OH	*p*-COMe	-1756.3805	0.4244	0.1259	-1756.0776
p-OH	*p*-OH	-1678.9256	0.3883	0.1197	-1678.6525
p-tBu	*p*-F	-1785.0023	0.4891	0.1323	-1784.6410
p-NMe_2	*p*-Cl	-2122.0594	0.4475	0.1305	-2121.7380
p-NMe_2	*m*-tBu	-1819.7470	0.5745	0.1424	-1819.3104
p-NMe_2	*m*-CF_3	-1999.5890	0.4642	0.1376	-1999.2578
p-NH_2	*p*-OH	-1659.0544	0.4013	0.1198	-1658.7685
p-NH_2	*p*-H	-1583.8021	0.3961	0.1164	-1583.5181

p-NH_2	*p*-COMe	-1736.5061	0.4373	0.1277	-1736.1921
p-NH_2	*p*-NO_2	-1788.3820	0.4012	0.1243	-1788.1006
p-NH_2	*m*,*m*'-OMe	-1812.9293	0.4670	0.1332	-1812.5911
p-OH	*p*-NH_2	-1659.0565	0.4012	0.1207	-1658.7715
p-OH	*p*-Me	-1643.0040	0.4125	0.1220	-1642.7090
p-OH	*p*-F	-1702.9420	0.3756	0.1190	-1702.6809
p-OH	*p*-CN	-1695.9505	0.3837	0.1203	-1695.6826
p-OH	*m*-NH_2	-1659.0577	0.4012	0.1197	-1658.7717
p-OMe	*p*-OMe	-1757.5442	0.4488	0.1287	-1757.2197
p-OMe	*p*-tBu	-1800.2959	0.5320	0.1369	-1799.8964
p-OMe	*p*-Cl	-2102.6090	0.4049	0.1268	-2102.3264
p-OMe	*p*-CF_3	-1980.1393	0.4215	0.1327	-1979.8460
p-OMe	*p*-CN	-1735.2593	0.4138	0.1265	-1734.9675
p-OMe	*m*-OMe	-1757.5460	0.4489	0.1283	-1757.2209
p-OMe	*m*-NO_2	-1847.5549	0.4185	0.1303	-1847.2622
p-tBu	*p*-NMe_2	-1819.7471	0.5744	0.1420	-1819.3103
p-tBu	*p*-Me	-1725.0631	0.5259	0.1358	-1724.6685
p-tBu	*p*-COMe	-1838.4397	0.5377	0.1397	-1838.0371
p-tBu	*p*-CF_3	-2022.8882	0.5035	0.1420	-2022.5222
p-tBu	*m*-CF_3	-2022.8881	0.5048	0.1422	-2022.5210
p-Me	*p*-NH2	-1623.1336	0.4254	0.1232	-1622.8269
p-Me	*p*-OMe	-1682.3125	0.4428	0.1263	-1681.9915
p-Me	*p*-F	-1667.0192	0.3999	0.1222	-1666.7370
p-Me	*p*-COMe	-1720.4576	0.4484	0.1304	-1720.1351
p-Me	*m*-Me	-1607.0819	0.4366	0.1254	-1606.7662
p-Me	*m*-Cl	-2027.3780	0.3989	0.1240	-2027.0986
p-Me	*m*,*m*'-CF_3	-2242.0605	0.4235	0.1412	-2241.7738
p-H	*p*-OH	-1603.6730	0.3831	0.1157	-1603.4010
p-H	*p*-Me	-1567.7512	0.4072	0.1201	-1567.4597
p-H	*p*-CF_3	-1865.5776	0.3861	0.1257	-1865.3127
p-H	*m*,*m*'-F	-1726.9578	0.3627	0.1196	-1726.7102
p-F	*p*-tBu	-1785.0059	0.4892	0.1314	-1784.6436
p-F	*p*-Me	-1667.0229	0.3998	0.1223	-1666.7409
p-F	*p*-F	-1726.9607	0.3630	0.1193	-1726.7125
p-F	*p*-CN	-1719.9691	0.3710	0.1209	-1719.7146

p-F	*m*-Me	-1667.0235	0.3998	0.1231	-1666.7424
p-Cl	*p*-NMe_2	-2122.0648	0.4474	0.1309	-2121.7439
p-Cl	*p*-H	-1988.0498	0.3694	0.1183	-1987.7942
p-Cl	*p*-Cl	-2447.6767	0.3613	0.1204	-2447.4313
p-Cl	*p*-CF_3	-2325.2069	0.3777	0.1302	-2324.9549
p-Cl	*m*-NMe_2	-2122.0658	0.4474	0.1308	-2121.7448

Table S4. Computed C_{ipso} atomic CM5, NBO and Mulliken charges, and electrostatic potentials (EP) for different functional groups in R_1-C_6H_4I compounds.

R_1	CM5(C) / q_C	NBO(C)	Mulliken(C)	EP(C)
p-NMe_2	0.0274	-0.2259	0.1107	-14.7555
p-NH_2	0.0329	-0.2170	0.1972	-14.7464
p-OH	0.0390	-0.2060	0.2157	-14.7327
p-OMe	0.0406	-0.2068	0.1504	-14.7373
p-tBu	0.0494	-0.1815	0.0889	-14.7360
p-Me	0.0496	-0.1831	-0.0646	-14.7344
p-H	0.0562	-0.1737	0.1233	-14.7275
p-F	0.0572	-0.1895	0.1759	-14.7156
p-Cl	0.0600	-0.1782	-0.1245	-14.7118
p-COMe	0.0704	-0.1526	-0.0236	-14.7084
p-CF_3	0.0710	-0.1580	-0.1013	-14.7008
p-CN	0.0773	-0.1510	-0.0001	-14.6889
p-NO_2	0.0827	-0.1450	0.3157	-14.6826
m-NMe_2	0.0524	-0.1461	-0.5108	-14.7445
m-NH_2	0.0522	-0.1507	0.0424	-14.7365
m-OH	0.0582	-0.1550	0.0474	-14.7276
m-OMe	0.0560	-0.1569	0.0186	-14.7324
m-tBu	0.0481	-0.1624	-0.4847	-14.7333
m-Me	0.0542	-0.1626	0.1380	-14.7318
m-F	0.0643	-0.1623	0.0764	-14.7110
m-Cl	0.0641	-0.1603	-0.3572	-14.7098
m-COMe	0.0656	-0.1739	-0.4886	-14.7168
m-CF_3	0.0665	-0.1714	-0.3463	-14.7028
m-CN	0.0688	-0.1761	0.1392	-14.6925
m-NO_2	0.0718	-0.1741	-0.0132	-14.6882
C_6F_5	0.0449	-0.2785	1.2286	-14.6658
m,*m*'-Me	0.0528	-0.1518	0.0838	-14.7365
m,*m*'-F	0.0721	-0.1518	0.0486	-14.6947
m,*m*'-CF_3	0.0767	-0.1683	-0.5206	-14.6791
m,*m*'-OMe	0.0550	-0.1415	-0.1759	-14.7375
m,*m*'-NMe_2	0.0429	-0.1238	-0.9780	-14.7580

Table S5. Computed boron atomic CM5, NBO and Mulliken charges, and electrostatic potentials (EP) for different functional groups in R_2-C_6H_4Bpin compounds.

R_2	CM5(B) / q_B	NBO(B)	Mulliken(B)	EP(B)
p-NMe_2	0.3698	1.0817	0.7094	-11.4576
p-NH_2	0.3732	1.0840	0.7004	-11.4508
p-OH	0.3777	1.0874	0.6988	-11.4397
p-OMe	0.3788	1.0870	0.7017	-11.4430
p-tBu	0.3814	1.0888	0.7192	-11.4413
p-Me	0.3821	1.0888	0.6996	-11.4407
p-H	0.3851	1.0905	0.7164	-11.4360
p-F	0.3863	1.0899	0.7028	-11.4278
p-Cl	0.3884	1.0899	0.7083	-11.4249
p-COMe	0.3908	1.0886	0.6970	-11.4233
p-CF_3	0.3925	1.0902	0.6984	-11.4178
p-CN	0.3944	1.0887	0.6981	-11.4104
p-NO_2	0.3971	1.0889	0.7149	-11.4062
m-NMe_2	0.3821	1.0943	0.7277	-11.4464
m-NH_2	0.3834	1.0927	0.7238	-11.4419
m-OH	0.3867	1.0922	0.7182	-11.4377
m-OMe	0.3861	1.0925	0.7171	-11.4402
m-tBu	0.3833	1.0923	0.7125	-11.4392
m-Me	0.3821	1.0913	0.6974	-11.4387
m-F	0.3902	1.0912	0.7169	-11.4258
m-Cl	0.3911	1.0919	0.7179	-11.4241
m-COMe	0.3893	1.0914	0.7053	-11.4303
m-CF_3	0.3919	1.0917	0.6902	-11.4195
m-CN	0.3938	1.0922	0.6825	-11.4121
m-NO_2	0.3955	1.0917	0.7313	-11.4102
C_6F_5	0.4050	1.0886	0.6500	-11.3923
m,*m*'-Me	0.3828	1.0917	0.6728	-11.4419
m,*m*'-F	0.3952	1.0922	0.7171	-11.4157
m,*m*'-CF_3	0.3984	1.0930	0.6890	-11.4037
m,*m*'-NO_2	0.4049	1.0923	0.7369	-11.3865
m,*m*'-OMe	0.3866	1.0948	0.7179	-11.4450
m,*m*'-NMe_2	0.3795	1.0981	0.7391	-11.4550

Table S6. Computed DFT overall Gibbs energy barriers ($^{\Delta G_{DFT}^{\ddagger}}$, in kcal mol^{-1}) for all the substrate pairs, including q_C and q_B values (R_1 and R_2 are the substituents on the phenyl iodide and the aryl boronate ester, respectively).

R_1	R_2	qC	qB	$\Delta G_{DFT}^{\ddagger}$
p-NMe_2	*p*-NMe_2	0.02737	0.36979	39.27
p-NH_2	*p*-NMe_2	0.03294	0.36979	37.63
p-OMe	*p*-NMe_2	0.04059	0.36979	37.66
p-Me	*p*-NMe_2	0.04959	0.36979	37.49
p-H	*p*-NMe_2	0.05624	0.36979	36.98
p-F	*p*-NMe_2	0.05716	0.36979	36.55
p-Cl	*p*-NMe_2	0.05999	0.36979	36.31
p-CF_3	*p*-NMe_2	0.07097	0.36979	35.33
p-NO_2	*p*-NMe_2	0.08273	0.36979	34.72
m-tBu	*p*-NMe_2	0.04812	0.36979	36.28
m-CF_3	*p*-NMe_2	0.06650	0.36979	36.83
p-OH	*p*-NH_2	0.03900	0.37318	36.32
p-tBu	*p*-NH_2	0.04943	0.37318	35.36
p-H	*p*-NH_2	0.05624	0.37318	35.88
p-COMe	*p*-NH_2	0.07036	0.37318	35.59
p-CN	*p*-NH_2	0.07729	0.37318	33.34
p-NO_2	*p*-NH_2	0.08273	0.37318	32.40
m-CN	*p*-NH_2	0.06881	0.37318	34.71
m-tBu	*p*-NH_2	0.04812	0.37318	35.64
m,*m*'-OMe	*p*-NH_2	0.05500	0.37318	34.27
p-NH_2	*p*-OH	0.03294	0.37769	34.35
p-OH	*p*-OH	0.03900	0.37769	34.26
p-Me	*p*-OH	0.04959	0.37769	34.61
p-F	*p*-OH	0.05716	0.37769	33.75
p-COMe	*p*-OH	0.07036	0.37769	32.62
p-CN	*p*-OH	0.07729	0.37769	31.99
m-NH_2	*p*-OH	0.05225	0.37769	34.36
p-NMe_2	*p*-OMe	0.02737	0.37877	35.10
p-OMe	*p*-OMe	0.04059	0.37877	34.71
p-tBu	*p*-OMe	0.04943	0.37877	33.59
p-H	*p*-OMe	0.05624	0.37877	34.67

p-Cl	*p*-OMe	0.05999	0.37877	32.38
p-CF_3	*p*-OMe	0.07097	0.37877	33.30
p-CN	*p*-OMe	0.07729	0.37877	31.33
p-NO_2	*p*-OMe	0.08273	0.37877	31.10
m-OMe	*p*-OMe	0.05605	0.37877	34.02
m-NO_2	*p*-OMe	0.07185	0.37877	31.98
p-NMe_2	*p*-tBu	0.02737	0.38138	34.47
p-Me	*p*-tBu	0.04959	0.38138	33.62
p-F	*p*-tBu	0.05716	0.38138	32.33
p-COMe	*p*-tBu	0.07036	0.38138	31.54
p-CF_3	*p*-tBu	0.07097	0.38138	31.98
m-CF_3	*p*-tBu	0.06650	0.38138	32.46
p-NMe_2	*p*-Me	0.02737	0.38206	34.30
p-NH_2	*p*-Me	0.03294	0.38206	34.31
p-OH	*p*-Me	0.03900	0.38206	33.77
p-OMe	*p*-Me	0.04059	0.38206	34.55
p-H	*p*-Me	0.05624	0.38206	33.55
p-F	*p*-Me	0.05716	0.38206	33.27
p-Cl	*p*-Me	0.05999	0.38206	32.08
p-COMe	*p*-Me	0.07036	0.38206	31.23
p-NO_2	*p*-Me	0.08273	0.38206	29.77
m-Me	*p*-Me	0.05419	0.38206	33.48
m-Cl	*p*-Me	0.06407	0.38206	31.95
m,*m*'-CF_3	*p*-Me	0.07672	0.38206	32.65
p-NMe_2	*p*-H	0.02737	0.38507	33.50
p-OH	*p*-H	0.03900	0.38507	33.42
p-Me	*p*-H	0.04959	0.38507	32.43
p-H	*p*-H	0.05624	0.38507	32.64
p-Cl	*p*-H	0.05999	0.38507	31.66
p-CF_3	*p*-H	0.07097	0.38507	31.22
p-NO_2	*p*-H	0.08273	0.38507	29.31
m,*m*'-F	*p*-H	0.07206	0.38507	30.53
p-NMe_2	*p*-F	0.02737	0.38626	32.69
p-tBu	*p*-F	0.04943	0.38626	31.51
p-Me	*p*-F	0.04959	0.38626	32.02

p-H	*p*-F	0.05624	0.38626	31.92
p-F	*p*-F	0.05716	0.38626	31.30
p-COMe	*p*-F	0.07036	0.38626	31.36
p-CN	*p*-F	0.07729	0.38626	29.34
p-NO_2	*p*-F	0.08273	0.38626	28.78
m-Me	*p*-F	0.05419	0.38626	30.82
p-NMe_2	*p*-Cl	0.02737	0.38843	31.66
p-NH_2	*p*-Cl	0.03294	0.38843	31.94
p-tBu	*p*-Cl	0.04943	0.38843	30.80
p-H	*p*-Cl	0.05624	0.38843	30.55
p-Cl	*p*-Cl	0.05999	0.38843	31.32
p-CF_3	*p*-Cl	0.07097	0.38843	29.67
m-NMe_2	*p*-Cl	0.05236	0.38843	31.12
p-NH_2	*p*-COMe	0.03294	0.39082	31.54
p-OMe	*p*-COMe	0.04059	0.39082	30.65
p-tBu	*p*-COMe	0.04943	0.39082	30.32
p-H	*p*-COMe	0.05624	0.39082	30.13
p-CN	*p*-COMe	0.07729	0.39082	28.72
p-NO_2	*p*-COMe	0.08273	0.39082	27.16
m-NO_2	*p*-COMe	0.07185	0.39082	28.57
p-NMe_2	*p*-CF_3	0.02737	0.39253	30.92
p-NH_2	*p*-CF_3	0.03294	0.39253	30.86
p-OH	*p*-CF_3	0.03900	0.39253	30.74
p-Me	*p*-CF_3	0.04959	0.39253	30.54
p-H	*p*-CF_3	0.05624	0.39253	30.18
p-F	*p*-CF_3	0.05716	0.39253	29.97
p-Cl	*p*-CF_3	0.05999	0.39253	29.23
p-COMe	*p*-CF_3	0.07036	0.39253	27.77
p-NO_2	*p*-CF_3	0.08273	0.39253	27.21
m-F	*p*-CF_3	0.06428	0.39253	29.39
m,*m*'-Me	*p*-CF_3	0.05278	0.39253	30.10
p-NMe_2	*p*-CN	0.02737	0.39440	29.34
p-NH_2	*p*-CN	0.03294	0.39440	29.89
p-OMe	*p*-CN	0.04059	0.39440	28.94
p-tBu	*p*-CN	0.04943	0.39440	28.86

p-F	*p*-CN	0.05716	0.39440	28.95
p-Cl	*p*-CN	0.05999	0.39440	28.98
p-CN	*p*-CN	0.07729	0.39440	27.00
m-F	*p*-CN	0.06428	0.39440	28.91
p-NMe_2	*p*-NO_2	0.02737	0.39706	28.90
p-OH	*p*-NO_2	0.03900	0.39706	28.55
p-OMe	*p*-NO_2	0.04059	0.39706	27.72
p-tBu	*p*-NO_2	0.04943	0.39706	27.48
p-H	*p*-NO_2	0.05624	0.39706	28.17
p-COMe	*p*-NO_2	0.07036	0.39706	25.77
p-CF_3	*p*-NO_2	0.07097	0.39706	26.13
p-NO_2	*p*-NO_2	0.08273	0.39706	25.05
m-OMe	*p*-NO_2	0.05605	0.39706	27.04
m-COMe	*p*-NO_2	0.06556	0.39706	27.16
m,*m*'-NMe_2	*p*-NO_2	0.04294	0.39706	27.46
p-NMe_2	C_6F_5	0.02737	0.40505	27.37
p-OH	C_6F_5	0.03900	0.40505	24.38
p-OMe	C_6F_5	0.04059	0.40505	26.47
p-Me	C_6F_5	0.04959	0.40505	24.52
p-H	C_6F_5	0.05624	0.40505	24.25
p-F	C_6F_5	0.05716	0.40505	23.74
p-CF_3	C_6F_5	0.07097	0.40505	22.90
p-CN	C_6F_5	0.07729	0.40505	22.33
p-NO_2	C_6F_5	0.08273	0.40505	22.24
p-Me	*m*-NMe_2	0.04959	0.37952	34.81
p-H	*m*-NH_2	0.05624	0.38342	33.15
m-OH	*m*-NH_2	0.05818	0.38342	32.94
m-CN	*m*-NH_2	0.06881	0.38342	32.01
p-Cl	*m*-OH	0.05999	0.38673	31.06
m-NMe_2	*m*-OH	0.05236	0.38673	32.91
p-F	*m*-OMe	0.05716	0.38611	32.00
m-COMe	*m*-OMe	0.06556	0.38611	31.03
m-NO_2	*m*-OMe	0.07185	0.38611	30.36
p-OMe	*m*-tBu	0.04059	0.38331	33.15
p-CF_3	*m*-Me	0.07097	0.38413	32.36

p-CN	*m*-Me	0.07729	0.38413	31.75
m-OH	*m*-Me	0.05818	0.38413	33.24
m-OMe	*m*-Me	0.05605	0.38413	33.32
p-OMe	*m*-F	0.04059	0.39015	30.83
p-Cl	*m*-F	0.05999	0.39015	29.52
m-Me	*m*-F	0.05419	0.39015	30.58
p-tBu	*m*-Cl	0.04943	0.39113	29.93
p-F	*m*-Cl	0.05716	0.39113	29.69
p-H	*m*-Cl	0.05624	0.39113	29.56
m-CF_3	*m*-Cl	0.06650	0.39113	29.28
p-COMe	*m*-COMe	0.07036	0.38931	29.24
m-CF_3	*m*-COMe	0.06650	0.38931	30.84
p-NH_2	*m*-CF_3	0.03294	0.39193	31.62
p-NO_2	*m*-CF_3	0.08273	0.39193	26.33
m-Me	*m*-CF_3	0.05419	0.39193	30.03
p-NMe_2	*m*-CN	0.02737	0.39381	29.78
m-NH_2	*m*-CN	0.05225	0.39381	29.03
m-tBu	*m*-CN	0.04812	0.39381	28.91
p-Me	*m*-NO_2	0.04959	0.39551	28.84
m-OH	*m*-NO_2	0.05818	0.39551	28.38
m-CF_3	*m*-NO_2	0.06650	0.39551	28.20
m-NO_2	*m*-NO_2	0.07185	0.39551	26.17
p-H	*m*,*m*'-OMe	0.05624	0.38660	31.82
p-H	*m*,*m*'-Me	0.05624	0.38277	33.71
p-OMe	*m*,*m*'-F	0.04059	0.39523	28.68
p-NO_2	*m*,*m*'-CF_3	0.08273	0.39836	23.55
p-NMe_2	*m*,*m*'-NO_2	0.02737	0.40492	26.75

Table S7. Gibbs energy barriers obtained with DFT ($^{\Delta G^{\ddagger}_{DFT}}$), with multi linear regression ($\Delta G^{\ddagger}_{MLR}$) and residual errors (all of them in kcal mol^{-1}) for the substrate pairs employed to construct equation 2. Sets: t = training set, p = prediction set (for species R_2-C_6H_4Bpin R_1-C_6H_4I).

R_1	R_2	Set	$\Delta G^{\ddagger}_{DFT}$	$\Delta G^{\ddagger}_{MLR}$	Error
p-NMe_2	*p*-NMe_2	t	39.27	38.92	-0.35
p-OMe	*p*-NMe_2	t	37.66	37.95	0.30
p-Cl	*p*-NMe_2	t	36.31	36.53	0.22
p-CF_3	*p*-NMe_2	t	35.33	35.73	0.40
p-OH	*p*-NH_2	t	36.32	36.88	0.56
p-H	*p*-NH_2	t	35.88	35.62	-0.26
p-COMe	*p*-NH_2	t	35.59	34.59	-1.00
p-NO_2	*p*-NH_2	t	32.40	33.69	1.28
p-NH_2	*p*-OH	t	34.35	35.75	1.40
p-Me	*p*-OH	t	34.61	34.53	-0.08
p-F	*p*-OH	t	33.75	33.98	0.23
p-CN	*p*-OH	t	31.99	32.51	0.51
p-tBu	*p*-OMe	t	33.59	34.16	0.57
p-H	*p*-OMe	t	34.67	33.66	-1.01
p-Cl	*p*-OMe	t	32.38	33.39	1.01
p-CN	*p*-OMe	t	31.33	32.13	0.79
p-NMe_2	*p*-tBu	t	34.47	34.86	0.39
p-Me	*p*-tBu	t	33.62	33.24	-0.38
p-COMe	*p*-tBu	t	31.54	31.72	0.19
p-CF_3	*p*-tBu	t	31.98	31.68	-0.31
p-NH_2	*p*-Me	t	34.31	34.22	-0.09
p-OMe	*p*-Me	t	34.55	33.66	-0.89
p-F	*p*-Me	t	33.27	32.45	-0.82
p-COMe	*p*-Me	t	31.23	31.49	0.25
p-OH	*p*-H	t	33.42	32.72	-0.70
p-Me	*p*-H	t	32.43	31.95	-0.48
p-CF_3	*p*-H	t	31.22	30.39	-0.84
p-NO_2	*p*-H	t	29.31	29.53	0.22
p-tBu	*p*-F	t	31.51	31.54	0.03
p-F	*p*-F	t	31.30	30.98	-0.32

p-CN	*p*-F	t	29.34	29.51	0.17
p-NO_2	*p*-F	t	28.78	29.11	0.33
p-NMe_2	*p*-Cl	t	31.66	32.39	0.73
p-H	*p*-Cl	t	30.55	30.29	-0.27
p-Cl	*p*-Cl	t	31.32	30.01	-1.30
p-CF_3	*p*-Cl	t	29.67	29.21	-0.46
p-NH_2	*p*-COMe	t	31.54	31.15	-0.39
p-OMe	*p*-COMe	t	30.65	30.59	-0.06
p-H	*p*-COMe	t	30.13	29.45	-0.68
p-NO_2	*p*-COMe	t	27.16	27.52	0.36
p-NH_2	*p*-CF_3	t	30.86	30.56	-0.30
p-Me	*p*-CF_3	t	30.54	29.34	-1.20
p-F	*p*-CF_3	t	29.97	28.79	-1.19
p-Cl	*p*-CF_3	t	29.23	28.58	-0.65
p-NMe_2	*p*-CN	t	29.34	30.31	0.97
p-OMe	*p*-CN	t	28.94	29.34	0.40
p-tBu	*p*-CN	t	28.86	28.70	-0.16
p-F	*p*-CN	t	28.95	28.13	-0.82
p-NMe_2	*p*-NO_2	t	28.90	29.38	0.47
p-OH	*p*-NO_2	t	28.55	28.53	-0.03
p-tBu	*p*-NO_2	t	27.48	27.77	0.28
p-COMe	*p*-NO_2	t	25.77	26.24	0.46
p-OH	C_6F_5	t	24.38	25.73	1.35
p-H	C_6F_5	t	24.25	24.48	0.22
p-CN	C_6F_5	t	22.33	22.94	0.61
p-NO_2	C_6F_5	t	22.24	22.54	0.30
p-NH_2	*p*-NMe_2	p	37.63	38.51	0.88
p-Me	*p*-NMe_2	p	37.49	37.29	-0.19
p-H	*p*-NMe_2	p	36.98	36.81	-0.17
p-F	*p*-NMe_2	p	36.55	36.74	0.19
p-NO_2	*p*-NMe_2	p	34.72	34.87	0.15
p-tBu	*p*-NH_2	p	35.36	36.12	0.76
p-CN	*p*-NH_2	p	33.34	34.08	0.75
p-OH	*p*-OH	p	34.26	35.30	1.05
p-COMe	*p*-OH	p	32.62	33.01	0.40

p-NMe_2	*p*-OMe	p	35.10	35.77	0.68
p-OMe	*p*-OMe	p	34.71	34.81	0.10
p-CF_3	*p*-OMe	p	33.30	32.59	-0.71
p-NO_2	*p*-OMe	p	31.10	31.73	0.63
p-F	*p*-tBu	p	32.33	32.69	0.35
p-NMe_2	*p*-Me	p	34.30	34.63	0.33
p-OH	*p*-Me	p	33.77	33.78	0.01
p-H	*p*-Me	p	33.55	32.52	-1.03
p-Cl	*p*-Me	p	32.08	32.24	0.16
p-NO_2	*p*-Me	p	29.77	30.58	0.81
p-NMe_2	-	p	33.50	33.57	0.07
p-H	-	p	32.64	31.46	-1.18
p-Cl	-	p	31.66	31.19	-0.47
p-NMe_2	*p*-F	p	32.69	33.15	0.46
p-Me	*p*-F	p	32.02	31.53	-0.49
p-H	*p*-F	p	31.92	31.05	-0.88
p-COMe	*p*-F	p	31.36	30.01	-1.35
p-tBu	*p*-Cl	p	30.80	30.78	-0.01
p-NH_2	*p*-Cl	p	31.94	31.99	0.04
p-tBu	*p*-COMe	p	30.32	29.95	-0.37
p-CN	*p*-COMe	p	28.72	27.91	-0.81
p-NMe_2	*p*-CF_3	p	30.92	30.96	0.04
p-OH	*p*-CF_3	p	30.74	30.11	-0.63
p-H	*p*-CF_3	p	30.18	28.85	-1.32
p-COMe	*p*-CF_3	p	27.77	27.82	0.05
p-NO_2	*p*-CF_3	p	27.21	26.92	-0.29
p-NH_2	*p*-CN	p	29.89	29.90	0.01
p-Cl	*p*-CN	p	28.98	27.93	-1.06
p-CN	*p*-CN	p	27.00	26.66	-0.34
p-OMe	*p*-NO_2	p	27.72	28.41	0.69
p-H	*p*-NO_2	p	28.17	27.27	-0.91
p-CF_3	*p*-NO_2	p	26.13	26.19	0.06
p-NO_2	*p*-NO_2	p	25.05	25.33	0.28
p-NMe_2	C_6F_5	p	27.37	26.58	-0.79
p-OMe	C_6F_5	p	26.47	25.62	-0.85

p-Me	C_6F_5	p	24.52	24.96	0.44
p-F	C_6F_5	p	23.74	24.41	0.66
p-CF_3	C_6F_5	p	22.90	23.40	0.50

Table S8. Gibbs energy barriers obtained with DFT ($\Delta G_{DFT}^{\ddagger}$), predicted with equation 2 ($\Delta G_{MLR}^{\ddagger}$) and residual errors (all of them in kcal mol^{-1}) for reactions that include at least one *meta*-substituted substrate (for species R_2-C_6H_4Bpin R_1-C_6H_4I).

R_1	R_2	$\Delta G_{DFT}^{\ddagger}$	$\Delta G_{MLR}^{\ddagger}$	Error
m-tBu	*p*-NMe_2	36.28	37.40	1.13
m-CF_3	*p*-NMe_2	36.83	36.06	-0.77
m-CN	*p*-NH_2	34.71	34.70	0.00
m-tBu	*p*-NH_2	35.64	36.22	0.57
m-NH_2	*p*-OH	34.36	34.34	-0.02
m-OMe	*p*-OMe	34.02	33.68	-0.34
m-NO_2	*p*-OMe	31.98	32.52	0.54
m-CF_3	*p*-tBu	32.46	32.00	-0.45
m-Me	*p*-Me	33.48	32.67	-0.81
m-Cl	*p*-Me	31.95	31.94	0.00
m-Me	*p*-F	30.82	31.19	0.37
m-NMe_2	*p*-Cl	31.12	30.57	-0.55
m-NO_2	*p*-COMe	28.57	28.31	-0.26
m-F	*p*-CF_3	29.39	28.27	-1.12
m-F	*p*-CN	28.91	27.61	-1.30
m-OMe	*p*-NO_2	27.04	27.28	0.24
m-COMe	*p*-NO_2	27.16	26.59	-0.57
p-Me	*m*-NMe_2	34.81	33.89	-0.92
p-H	*m*-NH_2	33.15	32.04	-1.11
p-Cl	*m*-OH	31.06	30.61	-0.46
p-F	*m*-OMe	32.00	31.03	-0.97
p-OMe	*m*-tBu	33.15	33.22	0.07
p-CF_3	*m*-Me	32.36	31.41	-0.94
p-CN	*m*-Me	31.75	30.95	-0.80
p-OMe	*m*-F	30.83	30.83	0.00
p-Cl	*m*-F	29.52	29.41	-0.11
p-tBu	*m*-Cl	29.93	29.84	-0.08
p-F	*m*-Cl	29.69	29.28	-0.41
p-COMe	*m*-COMe	29.24	28.95	-0.30
p-NH_2	*m*-CF_3	31.62	30.76	-0.85

p-NO_2	*m*-CF_3	26.33	27.13	0.79
p-NMe_2	*m*-CN	29.78	30.52	0.74
p-Me	*m*-NO_2	28.84	28.30	-0.55
m-OH	*m*-NH_2	32.94	31.90	-1.05
m-CN	*m*-NH_2	32.01	31.12	-0.89
m-NMe_2	*m*-OH	32.91	31.16	-1.75
m-COMe	*m*-OMe	31.03	30.42	-0.61
m-NO_2	*m*-OMe	30.36	29.96	-0.40
m-OH	*m*-Me	33.24	32.35	-0.90
m-OMe	*m*-Me	33.32	32.50	-0.81
m-Me	*m*-F	30.58	29.83	-0.74
p-H	*m*-Cl	29.56	29.34	-0.21
m-CF_3	*m*-Cl	29.28	28.59	-0.69
m-CF_3	*m*-COMe	30.84	29.23	-1.61
m-Me	*m*-CF_3	30.03	29.21	-0.82
m-NH_2	*m*-CN	29.03	28.70	-0.33
m-tBu	*m*-CN	28.91	29.00	0.09
m-OH	*m*-NO_2	28.38	27.67	-0.72
m-CF_3	*m*-NO_2	28.20	27.06	-1.14
m-NO_2	*m*-NO_2	26.17	26.67	0.50

Table S9. Gibbs energy barriers obtained with DFT ($^{\Delta G^{\ddagger}_{DFT}}$), predicted with equation 2 ($\Delta G^{\ddagger}_{MLR}$) and residual errors (all of them in kcal mol^{-1}) for reactions that include a doubly *meta*-substituted substrate (R_1 and R_2 are the substituents on the phenyl iodide and the aryl boronate ester, respectively).

R_1	**R_2**	$\Delta G^{\ddagger}_{DFT}$	$\Delta G^{\ddagger}_{MLR}$	**Error**
m,*m*'-OMe	*p*-NH_2	34.27	35.71	1.44
m,*m*'-CF_3	*p*-Me	32.65	31.02	-1.63
m,*m*'-F	*p*-H	30.53	30.31	-0.22
m,*m*'-Me	*p*-CF_3	30.10	29.11	-1.00
m,*m*'-NMe_2	*p*-NO_2	27.46	28.24	0.78
p-H	*m*,*m*'-OMe	31.82	30.93	-0.89
p-H	*m*,*m*'-Me	33.71	32.27	-1.45
p-OMe	*m*,*m*'-F	28.68	29.05	0.37
p-NO_2	*m*,*m*'-CF_3	23.55	24.88	1.33
p-NMe_2	*m*,*m*'-NO_2	26.75	26.63	-0.12

Cartesian coordinates

This section includes only the optimized geometries (in xyz format) for the compounds involved in the pathway described in Scheme 2 *i.e.* the Suzuki-Miyaura coupling between PhI and C_6F_5Bpin catalyzed by [CuI(phen)].

The computed structures for all the compounds described in the main text, in the shape of Gaussian16 input and output files, have been uploaded to the ioChem-BD database, and can be retrieved in the following link: https://doi.org/10.19061/iochem-bd-1-256 (alternatively, the folder tree version can be accessed: https://iochem-bd.iciq.es/browse/handle/100/42601).

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24
I1
 Cu -8.772374  -0.107254   0.281793
 C  -8.381787  -4.522231   0.088949
 C  -7.009989  -4.662467   0.006847
 C  -6.191285  -3.510000   0.001116
 C  -6.836747  -2.251348   0.081828
 C  -8.932570  -3.229245   0.165777
 C  -4.758917  -3.566527  -0.080585
 C  -6.043999  -1.042997   0.079421
 C  -4.632623  -1.134294  -0.004742
 C  -4.010911  -2.426279  -0.083562
 C  -3.900940   0.075457  -0.005173
 H  -2.816777   0.043831  -0.068784
 C  -4.575429   1.278315   0.074959
 C  -5.980425   1.269527   0.156935
 H  -4.284640  -4.542023  -0.139997
 H  -9.038756  -5.385553   0.095567
 H  -6.549741  -5.644788  -0.053196
 H -10.006285  -3.081885   0.231979
 H  -2.927341  -2.473139  -0.145465
 H  -4.044893   2.224554   0.076383
 N  -6.695633   0.147704   0.159545
 N  -8.187933  -2.127116   0.162817
 I -10.922215   1.258791   0.431362
 H  -6.542344   2.196161   0.222122

2
CsF
 Cs  0.762903  -2.050453   0.000000
 F  -2.088764  -2.050453   0.000000

24
I2
 Cu -8.622683   0.304117   0.300268
 C  -8.375257  -4.558861   0.066044
 C  -7.001318  -4.680204   0.006908
 C  -6.197805  -3.516869   0.005585
 C  -6.861723  -2.261920   0.068759
 C  -8.936587  -3.267278   0.124360
 C  -4.765935  -3.569644  -0.056479
 C  -6.073683  -1.044940   0.069867
 C  -4.658416  -1.137282   0.000224
 C  -4.027397  -2.425346  -0.060256
 C  -3.910826   0.060916  -0.004088
 H  -2.826768   0.012304  -0.056349
 C  -4.568599   1.272757   0.057670
 C  -5.969329   1.280704   0.129337
 H  -4.285104  -4.542882  -0.100925
 H  -9.020996  -5.431080   0.067934
 H  -6.524989  -5.655787  -0.039114
 H -10.015548  -3.136731   0.170667
 H  -2.942777  -2.462021  -0.108189
 H  -4.029272   2.213697   0.055094
 N  -6.706657   0.164429   0.137618
 N  -8.210227  -2.158389   0.126532
 H  -6.516831   2.214602   0.183220
 F -10.377845   0.707300   0.464386

2
CsI
 Cs  1.309364  -2.050453   0.000000
 I  -3.385224  -2.050453   0.000000

20
C6F5-PhBpin
 B  -1.241019   0.659722   0.053741
 C  -1.366711  -0.753227   0.719646
 C  -1.757825  -1.884080  -0.006283
 C  -1.094206  -0.961653   2.076546
 C  -1.872509  -3.145478   0.569335
 C  -1.202903  -2.209144   2.682650
 C  -1.592998  -3.306444   1.922338
 O  -1.784323   0.953172  -1.166148
 O  -0.579215   1.699603   0.645479
 C  -1.395755   2.307461  -1.495934
 C  -0.745651   2.856644  -0.207350
 F  -1.700035  -4.511669   2.490223
 F  -2.246044  -4.203544  -0.165605
 F  -2.034542  -1.794017  -1.317536
 F  -0.720096   0.059442   2.864719
 F  -0.936212  -2.362908   3.988235
 H  -2.283930   2.869681  -1.796580
 H  -0.694944   2.272033  -2.336697
 H   0.232378   3.311726  -0.385554
 H  -1.385913   3.579217   0.309635

44
I3
 Cu -8.485569   0.341611  -0.722471
 C  -9.252337  -3.948414  -1.663920
 C  -8.281537  -4.531823  -0.873527
 C  -7.340554  -3.713714  -0.207737
 C  -7.448498  -2.312864  -0.392925
 C  -9.280903  -2.546670  -1.786070
 C  -6.323700  -4.237745   0.659402
 C  -6.542783  -1.431554   0.311015
 C  -5.558050  -1.981754   1.167969
 C  -5.467199  -3.406646   1.318196
 C  -4.723839  -1.080627   1.867928
 H  -3.962192  -1.469284   2.538112
 C  -4.895031   0.279125   1.696605
 C  -5.906192   0.736529   0.833261
 H  -6.262010  -5.314557   0.788909
 H  -9.994299  -4.547256  -2.181481
 H  -8.234952  -5.609849  -0.746937
 H -10.036624  -2.055091  -2.391296
 H  -4.706948  -3.805954   1.983520
 H  -4.275716   0.997908   2.222516
 N  -6.707772  -0.088117   0.161082
 N  -8.408956  -1.751241  -1.173333
 H   -6.080040   1.797620   0.687629
 F -10.142551   1.427329  -0.500591
 B -11.033151   1.196704   0.777484
 O -11.015124   2.400506   1.554983
 O -12.370384   0.971960   0.305881
 C -12.169041   3.138159   1.164824
 C -13.176195   2.055822   0.754541
 C -10.312161  -0.079970   1.510299
 C -10.662804  -1.403362   1.240589
 C  -9.232555   0.071755   2.382773
 C -10.012475  -2.500623   1.799469
 C  -8.548669  -0.995672   2.956459
 C  -8.946842  -2.295050   2.666763
 F -11.625373  -1.690745   0.336660
 F -10.369859  -3.755854   1.470462
 F  -8.279488  -3.339675   3.180781
 F  -7.474951  -0.786959   3.741014
 F  -8.732195   1.300302   2.646530
 H -13.789063   1.739502   1.614840
 H -13.855203   2.386984  -0.041869
 H -11.938363   3.801533   0.314481
 H -12.517535   3.760657   1.998047

44
TMTS
 Cu  1.553429   2.889564   3.418889
 B   2.926080   0.799369   4.385726
 F   1.942740   0.962372   5.351996
 C   3.476342   2.673045   3.913513
 C   4.310762   2.802513   2.798351
 C   3.834800   3.486529   4.993794
 C   5.416517   3.643259   2.745300
 C   4.926785   4.344106   4.996072
 C   5.726349   4.420218   3.857611
 O   2.547267   0.123239   3.198854
 O   4.157732   0.290722   4.866407
 C   3.622707  -0.740883   2.823727
 H   3.872963  -0.599039   1.766687
 H   3.319460  -1.786949   2.971936
 C   4.786683  -0.349763   3.759393
 H   5.480073   0.346723   3.263466
 H   5.362459  -1.213506   4.109167
 F   4.053878   2.087547   1.671022
 F   6.181011   3.731589   1.639956
 F   6.784758   5.243630   3.831386
 F   5.220810   5.110281   6.064140
 F   3.086802   3.467735   6.127201
 C  -0.287665   4.925409   2.393790
 C   1.772342   5.968723   2.515084
 C  -0.916078   6.090331   1.889303
 C  -1.066321   3.725528   2.601306
 C   1.241053   7.173749   2.015374
 H   2.824622   5.880950   2.773805
 C  -0.104017   7.233407   1.703390
 C  -2.321194   6.063110   1.595202
 C  -2.451119   3.733901   2.305818
 H   1.889351   8.033667   1.883419
 H  -0.548367   8.146416   1.316778
 C  -3.057363   4.932620   1.796889
 H  -2.785624   6.965996   1.208810
 C  -3.173033   2.539775   2.533401
 C  -1.135594   1.511644   3.287259
 H  -4.120737   4.916124   1.575389
 H  -4.237699   2.510198   2.318868
 C  -2.515194   1.429199   3.025937
 H  -0.584108   0.661092   3.674318
 H  -3.039905   0.498534   3.213832
 N  -0.429839   2.621699   3.080982
 N   1.032751   4.881990   2.698346

10
F-Bpin
 B  -1.244623   0.675229   0.046537
 O  -2.253778   1.223199  -0.690194
 O  -0.115571   1.431131   0.169874
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C	-1.732058	2.460089	-1.231070
C	-0.406771	2.697419	-0.467529
F	-1.354966	-0.527118	0.612014
H	-2.460297	3.259515	-1.072283
H	-1.573217	2.329780	-2.306895
H	0.419941	2.967066	-1.129722
H	-0.506841	3.463177	0.309133

34
I4

Cu	-9.283560	1.373190	0.544571
C	-9.549974	-2.893339	0.333821
C	-8.234010	-3.312172	0.322881
C	-7.197656	-2.352294	0.360122
C	-7.567230	-0.984520	0.409932
C	-9.825921	-1.516403	0.381558
C	-5.807320	-2.711501	0.349887
C	-6.536412	0.028849	0.454468
C	-5.173197	-0.363140	0.439985
C	-4.834686	-1.756906	0.387082
C	-4.203499	0.665463	0.478752
H	-3.148610	0.405023	0.468064
C	-4.612008	1.984040	0.527508
C	-5.992383	2.269080	0.539112
H	-5.550422	-3.766302	0.310849
H	-10.370869	-3.601932	0.307229
H	-7.982360	-4.368465	0.286378
H	-10.847447	-1.151779	0.391942
H	-3.784032	-2.033394	0.377603
H	-3.893746	2.797075	0.555411
N	-6.924347	1.325577	0.506473
N	-8.870580	-0.586054	0.418299
H	-6.351415	3.293891	0.571457
C	-11.510626	3.128918	1.240726
C	-10.230256	3.040175	0.706750
C	-9.676099	4.264139	0.349547
C	-10.318378	5.490225	0.499117
C	-11.599790	5.516274	1.040825
C	-12.206641	4.321796	1.416869
F	-12.166913	1.995145	1.630202
F	-13.449146	4.345703	1.942017
F	-12.246320	6.685268	1.198190
F	-9.729484	6.646854	0.131272
F	-8.422344	4.315286	-0.196199

12
PhI

C	-0.507283	-0.386369	0.000731
C	0.891218	-0.396323	0.001253
C	1.573382	0.822347	0.000714
C	0.891315	2.041099	-0.000305
C	-0.507161	2.031274	-0.000814
C	-1.207606	0.822473	-0.000304
H	-1.044595	-1.331014	0.001144
H	1.432475	-1.336444	0.002048
H	1.432687	2.981154	-0.000716
H	-1.044427	2.975945	-0.001615
H	-2.294005	0.822544	-0.000715
I	3.716390	0.822291	0.001427

46
I5

Cu	-0.985698	3.774020	5.704650
C	0.783462	0.648365	4.381753
C	0.349643	1.235289	3.191062
C	0.887272	2.453385	2.763689
C	1.864357	3.071922	3.547662
C	2.297746	2.508510	4.750516
C	1.751019	1.287564	5.159677
H	0.351026	-0.290465	4.714878
H	-0.420693	0.755869	2.593494
H	0.546839	2.908756	1.839902
H	3.048212	3.003441	5.357902
H	2.080947	0.845054	6.095760
C	-1.717201	2.036431	6.086185
C	-2.473038	1.307551	5.176896
C	-1.348250	1.322959	7.219583
C	-2.827724	-0.027968	5.342052
C	-1.668949	-0.012431	7.446990
C	-2.420137	-0.694205	6.494036
F	-1.269378	-0.658573	8.562525
F	-0.583330	1.921197	8.183356
F	-2.879043	1.882986	4.003311
F	-3.549943	-0.689228	4.413293
F	-2.753579	-1.983328	6.687087
C	-0.648613	6.160589	3.861698
C	-2.070548	4.778790	2.683948
C	0.144494	6.380201	5.050041
C	-0.622641	7.122049	2.820211
C	-2.110074	5.669923	1.593129
H	-2.623249	3.844533	2.661714
C	0.928248	7.555247	5.160869
C	0.178330	8.304180	2.966369
C	-1.386936	6.845210	1.663973
H	-2.702799	5.423671	0.718129
C	1.712699	7.712202	6.324907
C	0.920488	8.513192	4.091303
C	0.892124	5.591837	7.098094
H	0.182798	9.028324	2.156321
H	-1.391346	7.557089	0.842922
C	1.697099	6.727022	7.293751
H	2.325477	8.601954	6.440373
H	1.528810	9.406991	4.197480
H	0.855516	4.796373	7.835171
H	2.291840	6.811597	8.196961
N	-1.366294	5.014342	3.784015
N	0.135793	5.419888	6.013577
I	2.740713	4.904226	2.875604

46
OATS

Cu	-1.031138	0.101979	-0.161607
C	-3.873923	-0.187724	-1.338622
C	-4.051780	1.424027	0.303771
C	-3.060929	-1.174254	-2.016316
C	-5.231250	-0.025888	-1.721276
C	-5.406062	1.659565	-0.002356
H	-3.562003	1.970227	1.104199
C	-3.632610	-1.959893	-3.050370
C	-5.773196	-0.829990	-2.780002
C	-5.994534	0.935992	-1.021233
H	-5.964381	2.399795	0.561344
C	-2.804582	-2.921325	-3.673020
C	-5.005804	-1.758597	-3.418237
C	-1.017757	-2.244266	-2.218638
H	-6.813301	-0.683073	-3.057685
H	-7.036195	1.089743	-1.289654
C	-1.496185	-3.068023	-3.253874
H	-3.209483	-3.537240	-4.471374
H	-5.420019	-2.368377	-4.216323
H	-0.000418	-2.335013	-1.851526
H	-0.836230	-3.801153	-3.705719
N	-3.304658	0.540128	-0.346033
N	-1.769967	-1.322906	-1.626218
C	0.187136	1.749828	0.387601
C	1.507130	1.390901	0.688338
C	-0.542573	2.618369	1.205047
C	2.055763	1.821110	1.896278
C	0.024728	3.034072	2.413534
C	-0.580569	-0.975298	1.467297
C	-1.174772	-0.791292	2.703748
C	0.467993	-1.878651	1.452204
C	-0.769078	-1.444737	3.865292
C	0.922591	-2.566031	2.573547
C	0.290007	-2.344809	3.794177
I	-0.305533	1.917372	-1.979025
F	-2.209371	0.093646	2.841734
F	-1.374600	-1.226125	5.051733
F	0.703223	-2.994179	4.898681
F	1.953954	-3.434431	2.508632
F	1.152110	-2.107206	0.284957
H	2.066089	0.743163	0.022358
H	3.066165	1.516889	2.157758
H	-0.548699	3.680436	3.073266
H	-1.540650	2.931723	0.923415
C	1.316292	2.632622	2.766653
H	1.753757	2.965953	3.703394

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I6

Cu	0.601672	3.340797	3.286817
C	3.905421	1.717626	6.187700
C	3.573818	1.016378	5.026043
C	2.545415	1.477365	4.192469
C	1.890837	2.660393	4.522841
C	2.176172	3.351398	5.699687
C	3.202452	2.879001	6.526186
C	-1.016597	3.851777	0.811940
C	-1.536286	5.229098	2.613749
C	-0.212605	2.785674	0.260163
C	-1.990753	4.489307	-0.001368
C	-2.513043	5.914199	1.876601
H	-1.335473	5.481189	3.648069
C	-0.417920	2.395696	-1.090143
C	-2.174363	4.058107	-1.357864
C	-2.742383	5.541033	0.566562
H	-3.069552	6.718202	2.345591
C	0.399148	1.361021	-1.598851
C	-1.419229	3.051969	-1.881006
C	1.473247	1.245206	0.545991
H	-2.929129	4.559004	-1.957287
H	-3.492637	6.045110	-0.036065
C	1.349633	0.784786	-0.780070
H	0.270940	1.036333	-2.627806
H	-1.557416	2.730450	-2.909467
H	2.217196	0.810093	1.207230
H	1.998083	-0.008474	-1.137384
C	-0.809658	2.439469	4.232269
C	-1.273449	1.175847	3.902709
C	-1.456825	3.107816	5.260183
C	-2.380875	0.611327	4.533794
C	-2.565811	2.577490	5.912252
C	-3.028509	1.317172	5.543066
N	-0.814044	4.234979	2.099328
N	0.718646	2.208402	1.055917
I	2.448170	5.104750	2.391672
F	-1.019115	4.328946	5.663227
F	-3.184704	3.255514	6.892676
F	-4.095199	0.785835	6.158027
F	-2.824687	-0.607587	4.184347
F	-0.664689	0.438258	2.948033
H	1.626571	4.249142	5.961766
H	3.446689	3.421067	7.436527
H	4.699536	1.354411	6.834572
H	4.102814	0.102847	4.765379
H	2.268869	0.918493	3.306068

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RETS

Cu	0.765228	3.430863	3.140810
C	3.729910	1.736171	6.308774
C	3.430127	0.992185	5.164461
C	2.401740	1.398252	4.306363
C	1.712050	2.575341	4.596552
C	1.965924	3.309824	5.756640
C	2.994571	2.889154	6.604719
C	-0.773677	3.969191	0.633232
C	-1.377291	5.343291	2.407337
C	0.051608	2.896262	0.125757
C	-1.713416	4.595781	-0.225832
C	-2.330530	6.016812	1.627138
H	-1.222245	5.598649	3.449418
C	-0.090353	2.494282	-1.228497
C	-1.832766	4.156003	-1.587260
C	-2.497691	5.642230	0.307930
H	-2.916943	6.814643	2.069714
C	0.745588	1.450233	-1.685668
C	-1.052819	3.147506	-2.069195
C	1.712566	1.346911	0.510966
H	-2.560255	4.650549	-2.224578
H	-3.224965	6.140156	-0.327265
C	1.651892	0.876171	-0.815629
H	0.666342	1.114861	-2.716125
H	-1.143851	2.819468	-3.100898
H	2.417164	0.916804	1.217358
H	2.311647	0.075689	-1.134015
C	-0.501430	2.418021	4.151041
C	-0.904245	1.141208	3.772238
C	-1.307218	3.087599	5.066621
C	-2.072987	0.561724	4.259337
C	-2.479856	2.537199	5.571285
C	-2.864829	1.263128	5.163206
N	-0.622765	4.357086	1.926508
N	0.937860	2.319456	0.970017
I	2.835009	5.086192	2.425499
F	-0.969771	4.328735	5.490615

F	-3.242851	3.220020	6.438599
F	-3.992845	0.716814	5.636205
F	-2.442693	-0.666066	3.862859
F	-0.171161	0.412683	2.905484
H	1.392113	4.199933	5.984358
H	3.216668	3.465678	7.499077
H	4.524939	1.412831	6.975021
H	3.988274	0.087787	4.935979
H	2.149895	0.811548	3.432333

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Ph-C6F5

C	0.615194	1.459501	0.566705
C	1.890477	1.384034	0.000177
C	2.463617	2.524932	-0.568074
C	1.767969	3.734067	-0.571456
C	0.485762	3.818442	-0.002498
C	-0.083573	2.666833	0.567192
H	0.159919	0.576685	1.007329
H	2.433849	0.443014	0.001407
H	3.456220	2.476476	-1.007580
H	2.222531	4.616729	-1.009131
H	-1.075942	2.715606	1.003062
C	-0.256484	5.103975	-0.003201
C	-0.934749	5.569527	1.130838
C	-0.320228	5.923454	-1.137735
C	-1.635759	6.770473	1.141310
C	-1.012847	7.129283	-1.150665
C	-1.675083	7.556651	-0.005027
F	0.286378	5.550292	-2.279050
F	-1.053682	7.875741	-2.263913
F	-2.344655	8.715288	-0.005425
F	-2.262916	7.179540	2.253831
F	-0.913615	4.859614	2.273364

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OATS_trans

Cu	-0.511208	0.034298	-0.350384
C	-3.225395	-0.532590	-1.566048
C	-3.384757	1.242066	-0.087875
C	-2.403850	-1.544695	-2.192798
C	-4.601938	-0.446055	-1.898962
C	-4.755639	1.407152	-0.357913
H	-2.870531	1.878446	0.624701
C	-2.991417	-2.440223	-3.123681
C	-5.160900	-1.367559	-2.847864
C	-5.363876	0.561757	-1.265737
H	-5.311980	2.189532	0.147498
C	-2.148431	-3.412865	-3.708127
C	-4.388602	-2.326130	-3.434261
C	-0.323651	-2.517122	-2.427784
H	-6.217433	-1.283147	-3.086601
H	-6.420616	0.658191	-1.499354
C	-0.811926	-3.453542	-3.359521
H	-2.561951	-4.116578	-4.425458
H	-4.816694	-3.022404	-4.150118
H	0.722023	-2.514109	-2.132122
H	-0.138197	-4.187407	-3.789646
N	-2.645859	0.308547	-0.674597
N	-1.090995	-1.593294	-1.865387
C	-0.117865	1.533797	-1.647207
C	-0.386412	2.724692	-0.965236
C	-0.452580	1.357087	-2.993037
C	-1.111249	3.723396	-1.626474
C	-1.167925	2.368082	-3.636150
C	-0.581936	-0.833015	1.472426
C	-0.981746	-0.085069	2.567175
C	-0.285651	-2.156316	1.753428
C	-1.094555	-0.585043	3.861345
C	-0.377806	-2.722479	3.023134
C	-0.789130	-1.924464	4.086644
I	2.005690	0.426395	-0.893614
F	-1.282502	1.244855	2.407388
F	-1.485874	0.190076	4.894543
F	-0.887291	-2.443013	5.324698
F	-0.078455	-4.019699	3.245117
F	0.133457	-2.990914	0.754740
H	-0.070482	2.856548	0.064455
H	-1.354780	4.641845	-1.098449
H	-1.465618	2.232379	-4.672905
H	-0.200824	0.436992	-3.507751
C	-1.504055	3.546152	-2.955075
H	-2.055602	4.329287	-3.467624

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I6_trans

Cu	0.685776	3.318797	3.167842
C	-0.859958	3.910017	0.783494
C	-1.243501	5.428738	2.510296
C	-0.174504	2.732539	0.304587
C	-1.774198	4.583898	-0.066485
C	-2.163351	6.148368	1.732776
H	-1.011421	5.716316	3.528292
C	-0.423018	2.270255	-1.013326
C	-1.999301	4.085801	-1.394468
C	-2.426997	5.727602	0.443006
H	-2.650521	7.019398	2.156977
C	0.275570	1.114884	-1.432130
C	-1.351134	2.976173	-1.849769
C	1.322684	1.032142	0.730216
H	-2.702746	4.618500	-2.027816
H	-3.132342	6.262788	-0.186245
C	1.150556	0.494241	-0.560575
H	0.115658	0.729013	-2.435135
H	-1.525963	2.604917	-2.855614
H	1.999100	0.570978	1.445456
H	1.701677	-0.393780	-0.852258
C	-0.803605	2.373162	4.115085
C	-1.327404	1.118281	3.852343
C	-1.410037	3.071790	5.147553
C	-2.400314	0.578609	4.560663
C	-2.482635	2.582507	5.886580
C	-2.983304	1.319564	5.583527
N	-0.616495	4.351735	2.044296
N	0.681879	2.114457	1.144891
F	-0.943048	4.308945	5.499461
F	-3.038766	3.299541	6.881621
F	-4.019178	0.817818	6.277249
F	-2.880560	-0.646408	4.272148
F	-0.795531	0.331667	2.880278
C	2.051742	4.588586	2.557554
C	2.889759	4.396446	1.462755
C	2.049987	5.793060	3.260603
C	3.731018	5.441883	1.055084
H	2.897321	3.452725	0.927792
C	2.892804	6.833106	2.847894
H	1.398411	5.930191	4.120821
C	3.732874	6.657909	1.743791
H	4.384802	5.297650	0.197852
H	2.890776	7.774225	3.393017
H	4.388149	7.464193	1.424622
I	2.492920	2.278171	4.651284

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I4_cation

Cu	-9.545494	1.036437	0.515385
C	-9.389375	-3.232761	-0.183348
C	-8.030066	-3.467131	-0.084152
C	-7.151865	-2.391412	0.184739
C	-7.733435	-1.114934	0.338269
C	-9.880886	-1.925782	-0.012862
C	-5.726624	-2.522984	0.311211
C	-6.905401	0.021834	0.611408
C	-5.507579	-0.130056	0.734355
C	-4.938496	-1.439462	0.576128
C	-4.758714	1.037805	1.010878
H	-3.679919	0.968620	1.116069
C	-5.407356	2.251754	1.145433
C	-6.806301	2.309407	1.005018
H	-5.289174	-3.509732	0.192673
H	-10.085461	-4.038243	-0.388673
H	-7.627292	-4.468027	-0.209625
H	-10.940372	-1.702455	-0.080948
H	-3.862372	-1.547783	0.673048
H	-4.859068	3.162809	1.358310
N	-7.525139	1.222697	0.745536
N	-9.073083	-0.899394	0.240707
H	-7.354916	3.239489	1.104086
C	-10.683207	3.411670	1.825870
C	-10.109345	2.896850	0.674434
C	-9.913356	3.789561	-0.367890
C	-10.269481	5.133070	-0.292594
C	-10.850284	5.609426	0.880221
C	-11.061125	4.745804	1.952190
F	-10.892410	2.602563	2.896520
F	-11.621588	5.212289	3.082057
F	-11.208606	6.898297	0.976119
F	-10.067975	5.971685	-1.324203
F	-9.341913	3.361858	-1.523669

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PhI_anion

C	-0.634290	-0.393159	0.000712
C	0.771843	-0.404349	0.000828
C	1.404889	0.822395	0.000102
C	0.771920	2.049180	-0.000737
C	-0.634215	2.038073	-0.000838
C	-1.327408	0.822478	-0.000099
H	-1.180344	-1.333918	0.001319
H	1.321335	-1.342601	0.001548
H	1.321468	2.987399	-0.001228
H	-1.180213	2.978864	-0.001443
H	-2.414286	0.822511	-0.000126
I	5.111690	0.822103	0.002810