SUPPORTING INFORMATION

Unveiling the molecular mechanism of Mn and Zn catalyzed Ullmann-type C-O 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.

Mechanism of Ligand-Free Manganese Catalyzed C-O Cross-Coupling Reaction

A. Estimation of the Activation barrier by Marcus Theory

According to the Marcus equation, the total reorganization energy is given as:

$$\lambda = \lambda_0 + \lambda_i \quad (1)$$

where, λ_0 is the solvent reorganization energy and λi is the inner reorganization energy, which we estimate as $\lambda_i \approx 0$.

The solvent reorganization energy λo can be calculated with:

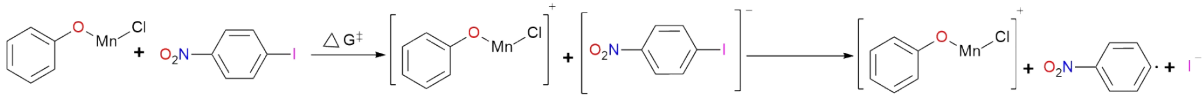
$$\lambda o = (332 kcal/mol)\left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right]\left[\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}\right] \quad (2)$$

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left[1 + \frac{\Delta G_r}{\lambda}\right]^2 \quad (3)$$

where a_1 and a_2 are the radii of the reactant molecules (a_1= 5.19 A°, a_2= 4.24 A°) and R = a_1 + a_2.

ΔG_r is the reaction energy.

ε_{op} is the optical dielectric constant (ε_{op} =1.8068), and ε is the static dielectric constant (ε = 35.68).



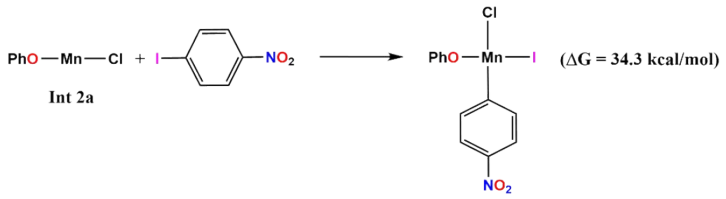
Scheme S1 *SET mechanism of Mn catalysed ligand free O-arylation.*

B. Halogen Atom Transfer Mechanism (HAT)

The activation barrier is approximated using Saveant's Model.

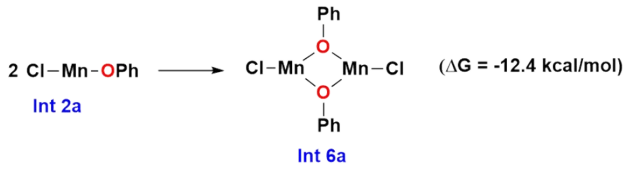
Scheme S2 *HAT mechanism of Mn catalysed ligand free O-arylation.*

C. Oxidative Addition



Scheme S3 *Oxidative Addition of Mn catalysed ligand free O-arylation reaction.*

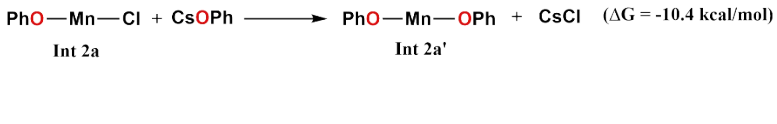
D. Binuclear Mechanism

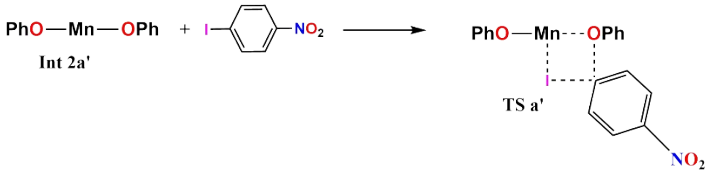


Scheme S4: Possibilities of formation of dimeric species involved in Mn-catalysed O-arylation reaction.

The spin state of the dimer **(Int 6a)** we have optimised is in 11-tet state. It is found that the formation of the dimeric species Int 6a from Int 2a proceeds via an exergonic reaction having Gibbs Free energy of formation of about -12.4 kcal/mol. Subsequently, the oxidative addition of aryl halide with Int 6a takes place and leads to the formation of the oxidative addition product **Int 6b**. However, the aforesaid reaction involves an endergonic process having a Gibbs free energy of formation of about 39.3 kcal/mol which is unfavorable under the given experimental temperature requirement of 1100C. Hence-forth, the oxidative addition product formed (Int 6b) is found to be unstable (Scheme S.4) which lead us to exclude the binuclear mechanistic in our study.

Formation of $(PhO)_2Mn$ from PhOMnCl





Electronic effect of Functional groups in controlling the feasibility of Mn (II) catalyzed O-arylation reaction

We have explored the electronic effect of different functional groups at the para-position of both reactants involved in the cross-coupling reaction under this σ- bond metathesis mechanism. Based on the experimental results, we have taken into consideration two sets of reactions for our investigation. The first set comprises studies on the reaction between unsubstituted phenol and p-substituted aryl iodides. The aryl halides with para-NO_2, -CN, -H, and -CH3 substituents were subjected to σ-bond metathesis mechanism for phenol. The transition state was characterized for each of the cross-coupling reactions. The activation barrier obtained for the reaction between phenol and aryl halide with substituents -NO2,-CN, and -H is 33.8, 35.7, and 38.7 kcal/mol respectively. From the results obtained, it seems that an increase in the electron-withdrawing nature of the substituent like -NO_2 and -CN at the para-position of aryl halide leads to a decrease in the activation barrier for the reaction. Furthermore, a similar effect in the activation barrier has been observed for the reaction between -CN and -NO_2 para-substituted aryl halides with p-Cresol and p-Chlorophenol. For the cross-coupling reactions in each of these cases, para-Cresol and p-chlorophenol were fixed as one the coupling partners Although under the experimental conditions, the unsubstituted aryl halide do not undergo the cross-coupling reaction, we have considered them in our study to rationalize the experimental

results. The reaction with the 4-Iodobenzene exhibited a very high activation barrier of 38.7 and kcal/mol The second group consists of the study of cross-coupling reactions between the para-substituted phenol with the 4-Iodonitrobenzene and 4-Iodobenzonitrile. The effect of the functional group on the phenolic moiety was studied by fixing the p-nitro aryl halide and 4-iodobenzonitrile as one of the coupling partners and varying the substituents at the para position of phenol by -H, -Cl, and -CH3 functional groups. Regarding the second set of reactions, it was discovered that the presence of an electron-donating group, like $-CH_3$, lowers the activation barrier for the O-arylation reaction, whereas the presence of an electron-withdrawing group, such as -Cl, raises the activation barrier for the O-arylation reaction (**Table S1**).

Substitution at aryl halide	Substitution at phenol	$\Delta G^{\ddagger}$ (kcal/mol)	ΔG (kcal/mol)
H	H	38.7	-19.1
NO_2	H	33.8	-21.9
NO_2	CH_3	32.8	-22.9
NO_2	Cl	34.5	-20.8
CN	H	35.7	-20.3
CN	CH_3	34.7	-20.7
CN	Cl	36.4	-19.2

Table S1: Effect of functional groups on the ligand-free Mn(II) catalyzed C-O coupling reaction. ($\Delta G^{\ddagger}$ is the activation energy and ΔG is the Gibbs free Energy)

Furthermore, to acquire more information to rationalize the effect of different substituents on the feasibility of ligand-free manganese-catalyzed C-O coupling reaction, the reaction between the active catalyst and p-substituted iodobenzene was considered. The Frontier molecular orbital theory (FMO) facilitates the analysis of the reactivity between the two molecules involved in the reaction by computing their Frontier orbital gap (HOMO-LUMO gap) A reaction having a small HOMO-LUMO gap could lead to a rise in bonding interactions amongst the species involved. The FMOs involved in the O-arylation reaction could be the HOMO of the manganese phenoxide complex and the LUMO of aryl halides. The observed results show that the inclusion of the electron-withdrawing group at the para position of the aryl halide lowers the energy of LUMO. Accordingly, the HOMO-LUMO energy gap of the concerned reactants gets reduced. However, in the case of phenolic moiety, the presence of electron donating groups decreases the HOMO-LUMO gap by increasing the HOMO energy of the manganese-phenoxide complex, thereby reducing the activation barrier for the reaction (**Table S2).**

Substituent at aryl halide	Substituent at phenol	LUMO of Ar-I (eV)	HOMO of active catalyst (eV)	LUMO-HOMO (eV)	$\Delta G^{\ddagger}$ (kcal/mol)
H	H	-1.3	-5.7	4.4	38.7
NO_2	H	-3.2	-5.7	2.5	33.8
CN	H	-1.9	-5.7	3.7	35.7
NO_2	CH_3	-3.2	-5.5	2.3	32.8
CN	CH_3	-1.9	-5.5	3.6	34.7
NO_2	Cl	-3.2	-5.7	2.5	34.5
CN	Cl	-1.9	-5.7	3.8	36.4

Table S2: Effect of functional groups on the activation barrier and energies of the FMO orbitals involved in Mn-catalyzed O-arylation reaction.

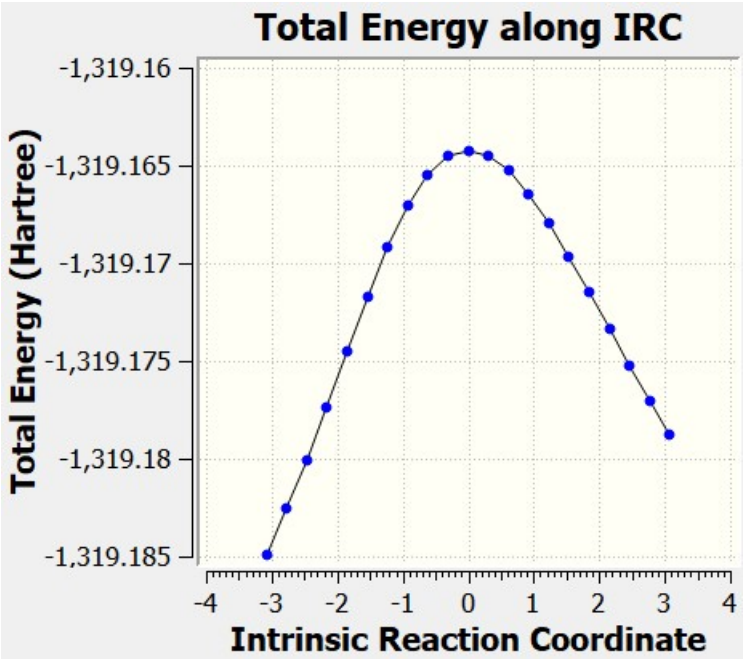


Figure S1. IRC of Ligand-Free Manganese Catalyzed O-Arylation Reaction

Cartesian coordinates and Energies(a.u) from UB3LYP-D3 method and solvation correction to free energies of Optimized geometries involved in the reaction mechanism

$MnCl_2$

E sol= -1024.951583
G sol= -1024.972821

25	-0.365513000	0.244563000	0.060338000
17	-0.426505000	2.562375000	0.323568000
17	-0.304411000	-2.073224000	-0.203213000

Phenol

E sol =-307.482686
G sol= -307.407967

8	-0.426043000	2.592763000	0.222633000
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6	-1.091284000	4.569799000	-0.991839000
6	-1.086376000	4.571658000	1.436875000
6	-1.570180000	5.884801000	-0.988314000
1	-0.906750000	4.041145000	-1.922697000

6	-1.565265000	5.886687000	1.433263000
1	-0.898089000	4.044485000	2.367824000
6	-1.807349000	6.546517000	0.222458000
1	-1.759440000	6.389597000	-1.932143000
1	-1.750659000	6.392913000	2.377093000
1	-2.179976000	7.567202000	0.222409000
1	0.544820000	2.550447000	0.221874000

Cs_2CO_3

E sol =-307.482686
G sol= -307.407967

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8	0.039241000	-0.927701000	0.012298000
8	-1.881582000	0.268023000	0.066341000
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55	2.995117000	0.209460000	0.052468000

$CsHCO_3$

E sol =-284.689437
G sol= -284.696628

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8	-0.096432000	-3.526560000	-0.132656000
8	1.289119000	-1.738046000	-0.022021000
1	0.774143000	-3.929761000	0.029045000
55	0.603667000	1.424404000	-0.530602000

PhOCs

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G sol= -327.076188

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6	-0.913226000	3.789232000	0.273507000
6	-1.093634000	4.509482000	-0.954673000
6	-1.172655000	4.538347000	1.469290000
6	-1.488106000	5.848669000	-0.976351000
1	-0.907108000	3.976800000	-1.886666000
6	-1.568777000	5.876315000	1.432520000
1	-1.046612000	4.028223000	2.423628000
6	-1.732670000	6.554156000	0.213016000
1	-1.606489000	6.352247000	-1.935583000
1	-1.751821000	6.402239000	2.369351000
1	-2.039702000	7.596868000	0.190743000
55	2.540848000	2.936204000	-0.030837000

Water

E sol =-76.429834
G sol= -76.427167

8	2.219618000	0.089206000	0.000000000
1	3.189375000	0.129575000	0.000000000
1	1.933959000	1.016816000	0.000000000

Acetonitrile

E sol =-132.768281
G sol= -132.746894

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7	1.732489000	0.154135000	-0.000408000
6	-0.890808000	0.154300000	0.000090000
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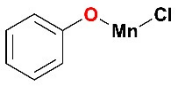
1	-1.264555000	-0.873560000	-0.035619000



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1	-3.085220000	1.456452000	-0.427090000
6	-4.361748000	-2.170911000	0.099616000
1	-2.308888000	-2.766776000	-0.245624000
6	-5.268490000	-1.106100000	0.186988000
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1	-6.317973000	-1.290164000	0.400743000
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Solvent coordinated PhOMnCl

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G sol= -1004.294027

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6	-2.415767000	-0.529369000	-0.109654000
6	-3.462502000	0.233683000	-0.679209000
6	-2.760401000	-1.737728000	0.542054000
6	-4.789446000	-0.194335000	-0.596726000
1	-3.208351000	1.163824000	-1.182201000
6	-4.091048000	-2.157512000	0.619370000
1	-1.967355000	-2.338561000	0.980792000
6	-5.119260000	-1.392295000	0.053094000
1	-5.573545000	0.414268000	-1.042912000
1	-4.325037000	-3.090745000	1.127908000
1	-6.153134000	-1.721137000	0.116418000
17	2.704489000	-0.203292000	1.260580000
7	0.661523000	-2.937422000	-0.065813000
6	0.633152000	-4.076068000	-0.273080000
6	0.593798000	-5.507182000	-0.531559000
1	1.610577000	-5.911332000	-0.525169000
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Water coordinated PhOMnCl

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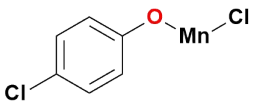

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6	-3.451939000	0.441599000	-0.278639000
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1	-3.092387000	1.456668000	-0.424161000
6	-4.360982000	-2.178191000	0.098817000
1	-2.315962000	-2.769289000	-0.243378000
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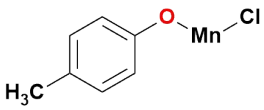

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1	-5.482022000	1.034527000	0.001091000
1	-4.695362000	-3.183249000	0.247311000
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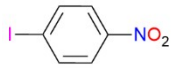
Substitued aryl halides



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6	2.119385000	-0.299672000	0.181053000
6	1.420140000	0.906024000	0.172488000
6	0.031645000	0.892552000	-0.000744000
6	-0.671061000	-0.306123000	-0.166339000
1	-0.497923000	-2.453151000	-0.284821000
1	3.194257000	-0.312914000	0.313775000
1	1.959018000	1.838009000	0.300067000
1	-1.746876000	-0.309880000	-0.300046000
53	-1.040102000	2.744901000	-0.012018000
7	2.145091000	-2.760221000	0.024073000
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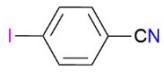

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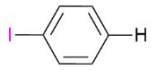
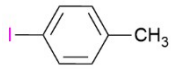
6	1.424370000	0.895541000	0.172828000
6	0.037289000	0.881841000	-0.000771000
6	-0.665770000	-0.315325000	-0.165785000
1	-0.501889000	-2.458030000	-0.285375000
1	3.199580000	-0.312333000	0.314766000
1	1.962730000	1.827850000	0.300910000
1	-1.741980000	-0.318535000	-0.299100000
53	-1.033484000	2.740360000	-0.013963000
6	2.147341000	-2.763298000	0.023212000

7	2.732740000	-3.770126000	0.029690000



E sol =-243.074748
G sol= -243.016424

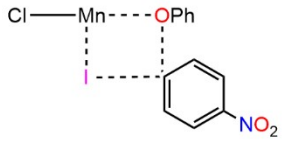
6	0.036048000	-1.508774000	-0.156091000
6	1.423917000	-1.515386000	0.016347000
6	2.109601000	-0.307492000	0.179990000
6	1.416424000	0.909310000	0.172549000
6	0.030741000	0.894253000	-0.000931000
6	-0.672609000	-0.300910000	-0.166051000
1	-0.505092000	-2.442528000	-0.284055000
1	3.188012000	-0.302933000	0.314505000
1	1.953458000	1.843396000	0.299959000
1	-1.749265000	-0.301615000	-0.300145000
53	-1.048792000	2.761399000	-0.013764000
1	1.967658000	-2.455845000	0.023100000



E sol =-282.363952
G sol= -282.281372

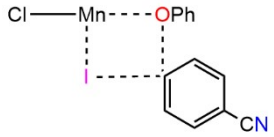
6	-0.736891000	0.365923000	-0.023037000
6	0.665536000	0.340492000	-0.016750000
6	1.346084000	1.567375000	-0.002678000
6	0.656980000	2.784547000	0.009617000
6	-0.739150000	2.775738000	0.006495000
6	-1.446372000	1.572457000	-0.010808000
1	-1.292195000	-0.569258000	-0.039579000
1	2.433797000	1.579817000	-0.003105000
1	1.209350000	3.718441000	0.018436000
1	-2.531645000	1.561920000	-0.017759000
6	1.423389000	-0.966911000	0.004519000
1	1.656719000	-1.264888000	1.035524000
1	0.839641000	-1.776177000	-0.446836000
1	2.373958000	-0.886684000	-0.534214000
53	-1.807250000	4.637800000	0.020726000

Transition states involved in the σ-bond metathesis mechanism for the various sets of reactions considered in the study.



E sol =-1319.164235
G sol= -1319.030044

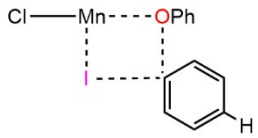
6	1.640484000	2.137334000	-1.462041000
6	1.719945000	1.581214000	-0.175940000
6	2.190050000	2.349665000	0.899214000
6	2.571131000	3.676825000	0.684218000
6	2.486324000	4.238813000	-0.596242000
6	2.015861000	3.467333000	-1.666569000
8	1.375922000	0.268627000	0.024870000
1	2.247300000	1.898151000	1.884408000
1	2.933911000	4.273304000	1.517289000
1	2.783524000	5.271323000	-0.758476000
1	1.947609000	3.898906000	-2.661747000
1	1.277897000	1.520107000	-2.279090000
6	2.875972000	-0.843309000	-0.080443000
6	3.599122000	-0.690089000	1.120327000
6	4.938286000	-0.348959000	1.061792000
6	5.560315000	-0.160431000	-0.186867000
6	4.830795000	-0.306314000	-1.381297000
6	3.490340000	-0.646277000	-1.333884000
1	3.107148000	-0.837113000	2.074559000
1	5.508512000	-0.227101000	1.975209000
1	5.319616000	-0.155980000	-2.336694000
1	2.917924000	-0.761720000	-2.246625000
25	-0.557286000	-0.391392000	-0.184524000
53	1.388476000	-2.754996000	-0.054895000
7	6.948673000	0.185292000	-0.241911000
8	7.486708000	0.348030000	-1.354670000
8	7.580898000	0.315327000	0.824655000
17	-2.762412000	0.349013000	0.144444000



E sol =-1206.895367
G sol= -1206.763507

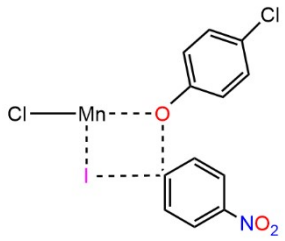
6	1.603152000	2.155486000	-1.460400000
6	1.693855000	1.595811000	-0.175008000
6	2.180638000	2.366132000	0.893353000
6	2.564854000	3.691385000	0.673930000
6	2.467643000	4.254442000	-0.605426000
6	1.981601000	3.483816000	-1.669620000
8	1.354422000	0.289537000	0.029682000
1	2.248315000	1.914628000	1.878112000
1	2.939963000	4.286257000	1.502848000
1	2.767024000	5.285780000	-0.771219000
1	1.903762000	3.915379000	-2.664240000
1	1.229317000	1.539528000	-2.273662000
6	2.925392000	-0.828791000	-0.076468000
6	3.626520000	-0.686235000	1.124122000
6	4.977060000	-0.361357000	1.065572000
6	5.614594000	-0.173183000	-0.178947000
6	4.872002000	-0.309926000	-1.370213000
6	3.520275000	-0.634711000	-1.325777000

1	3.130353000	-0.828743000	2.076796000
1	5.539463000	-0.251190000	1.988042000
1	5.353602000	-0.163497000	-2.332502000
1	2.944723000	-0.737917000	-2.238016000
25	-0.543484000	-0.426122000	-0.201456000
53	1.353143000	-2.773221000	-0.050081000
17	-2.754287000	0.311246000	0.123290000
6	7.001883000	0.157002000	-0.231190000
7	8.136155000	0.427643000	-0.272795000



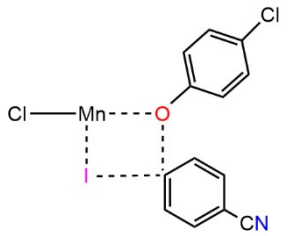
E sol =-1114.641984
G sol= -1114.505793

6	1.488343000	2.197267000	-1.448300000
6	1.655771000	1.635662000	-0.168242000
6	2.233928000	2.406944000	0.856283000
6	2.623389000	3.724182000	0.602986000
6	2.442983000	4.286751000	-0.668065000
6	1.871408000	3.518150000	-1.690757000
8	1.305496000	0.349866000	0.069984000
1	2.365982000	1.957733000	1.835894000
1	3.065955000	4.315899000	1.400626000
1	2.743196000	5.313546000	-0.858860000
1	1.728676000	3.946479000	-2.679836000
1	1.048657000	1.584484000	-2.231253000
6	2.976894000	-0.838408000	-0.078273000
6	3.625265000	-0.784448000	1.141054000
6	4.995657000	-0.483802000	1.108362000
6	5.648523000	-0.240590000	-0.105972000
6	4.929045000	-0.296395000	-1.304878000
6	3.556710000	-0.593958000	-1.308026000
1	3.105348000	-0.965401000	2.074174000
1	5.541297000	-0.436923000	2.047650000
1	5.423218000	-0.106778000	-2.254615000
1	2.986004000	-0.626385000	-2.228497000
25	-0.524312000	-0.456439000	-0.196978000
53	1.205114000	-2.773278000	-0.168727000
17	-2.745806000	0.272326000	0.123865000
1	6.708244000	-0.003183000	-0.116765000



E sol =-1778.759005
G sol= -1778.636720

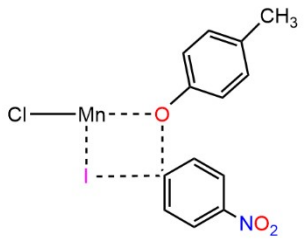
6	1.628937000	2.140295000	-1.458898000
6	1.713426000	1.580140000	-0.175312000
6	2.195171000	2.347545000	0.895123000
6	2.584239000	3.671656000	0.687049000
6	2.487975000	4.215615000	-0.596383000
6	2.008280000	3.465821000	-1.673262000
8	1.372080000	0.270295000	0.024846000
1	2.259329000	1.900888000	1.881528000
1	2.957178000	4.272330000	1.510214000
1	1.940212000	3.906483000	-2.662493000
1	1.258581000	1.531265000	-2.277875000
6	2.876220000	-0.831197000	-0.080780000
6	3.596150000	-0.680970000	1.121041000
6	4.937306000	-0.345427000	1.063819000
6	5.560218000	-0.157900000	-0.184038000
6	4.831971000	-0.299276000	-1.379290000
6	3.489589000	-0.633841000	-1.333502000
1	3.102286000	-0.827024000	2.074418000
1	5.507259000	-0.226738000	1.977800000
1	5.322188000	-0.149399000	-2.334024000
1	2.917222000	-0.746285000	-2.246644000
25	-0.562095000	-0.411130000	-0.187338000
53	1.385112000	-2.757257000	-0.059550000
7	6.951077000	0.183682000	-0.237491000
8	7.489331000	0.347245000	-1.349356000
8	7.582195000	0.308757000	0.829637000
17	-2.765633000	0.331840000	0.142074000
17	2.981417000	5.888031000	-0.862782000



E sol =-1666.490328
G sol= -1666.370277

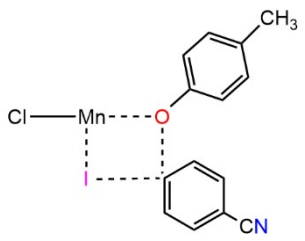
6	1.595213000	2.158059000	-1.458823000
6	1.688988000	1.593679000	-0.176162000
6	2.184836000	2.362401000	0.888877000
6	2.576363000	3.685098000	0.677960000
6	2.469089000	4.230719000	-0.603968000
6	1.976790000	3.482434000	-1.676228000
8	1.351495000	0.290019000	0.026551000
1	2.257848000	1.915090000	1.874558000
1	2.959429000	4.283961000	1.497906000
1	1.900649000	3.923863000	-2.664633000
1	1.215591000	1.550625000	-2.275015000
6	2.925110000	-0.817873000	-0.077478000
6	3.622890000	-0.676410000	1.124419000
6	4.974833000	-0.356006000	1.067353000
6	5.614090000	-0.170008000	-0.176412000
6	4.873070000	-0.304431000	-1.368755000
6	3.519985000	-0.624829000	-1.326249000
1	3.124577000	-0.817388000	2.076179000
1	5.536388000	-0.247542000	1.990489000
1	5.356368000	-0.159458000	-2.330366000
1	2.945059000	-0.726825000	-2.239017000
25	-0.549522000	-0.442485000	-0.199623000
53	1.351952000	-2.775777000	-0.053679000

17	-2.758336000	0.297751000	0.125883000
6	7.002544000	0.156587000	-0.226821000
7	8.137447000	0.424243000	-0.266881000
17	2.964713000	5.902782000	-0.874075000



E sol =-1358.484764
G sol= -1358.326716

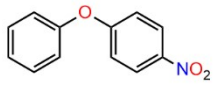
6	1.643084000	2.128751000	-1.450218000
6	1.714125000	1.569023000	-0.165742000
6	2.193226000	2.338538000	0.902674000
6	2.589210000	3.659802000	0.681812000
6	2.518162000	4.239880000	-0.595457000
6	2.034617000	3.452305000	-1.654421000
8	1.367454000	0.256510000	0.034955000
1	2.253036000	1.892525000	1.890411000
1	2.962522000	4.249129000	1.516505000
1	1.973798000	3.877956000	-2.653755000
1	1.279062000	1.517246000	-2.271135000
6	2.866506000	-0.854392000	-0.079263000
6	3.595113000	-0.700890000	1.118914000
6	4.929864000	-0.344688000	1.056452000
6	5.545101000	-0.143951000	-0.193988000
6	4.812542000	-0.295747000	-1.386119000
6	3.476418000	-0.650743000	-1.334528000
1	3.108671000	-0.855943000	2.074760000
1	5.502310000	-0.219574000	1.968050000
1	5.296017000	-0.137077000	-2.342908000
1	2.901909000	-0.768974000	-2.245640000
25	-0.562797000	-0.399394000	-0.176750000
53	1.386593000	-2.766580000	-0.051836000
7	6.927492000	0.221240000	-0.252975000
8	7.459343000	0.396406000	-1.367216000
8	7.562408000	0.356392000	0.811760000
17	-2.769107000	0.339068000	0.151272000
6	2.923790000	5.678072000	-0.824536000
1	3.414173000	5.804543000	-1.796539000
1	2.047544000	6.340393000	-0.814670000
1	3.610125000	6.029717000	-0.046752000



E sol =-1246.215758
G sol= -1246.060135

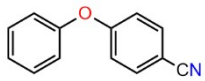
6	1.597664000	2.143604000	-1.449291000
6	1.680854000	1.580835000	-0.166464000
6	2.163139000	2.357575000	0.898496000
6	2.549856000	3.679875000	0.675424000
6	2.471902000	4.259110000	-0.603131000
6	1.980939000	3.470360000	-1.656486000
8	1.343856000	0.273457000	0.038645000
1	2.224817000	1.914287000	1.887605000
1	2.918570000	4.274204000	1.508951000
1	1.903530000	3.897217000	-2.654173000
1	1.223754000	1.533096000	-2.266820000
6	2.920047000	-0.837384000	-0.076850000
6	3.626608000	-0.689864000	1.120547000
6	4.971887000	-0.345352000	1.056958000
6	5.601308000	-0.144923000	-0.189941000
6	4.855502000	-0.291129000	-1.378179000
6	3.508908000	-0.635188000	-1.328258000
1	3.136938000	-0.840666000	2.075371000
1	5.536754000	-0.228670000	1.977164000
1	5.330874000	-0.136178000	-2.342273000
1	2.931082000	-0.744234000	-2.238429000
25	-0.549154000	-0.445197000	-0.191901000
53	1.362820000	-2.788063000	-0.047004000
17	-2.761236000	0.290074000	0.132272000
6	6.982518000	0.208292000	-0.247586000
7	8.111804000	0.498707000	-0.293682000
6	2.931187000	5.680172000	-0.838530000
1	2.696355000	6.324203000	0.016557000
1	4.019115000	5.721160000	-0.986106000
1	2.463331000	6.111118000	-1.730283000

Cross-coupled products



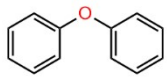
E sol =-743.063755
G sol= -742.917762

8	-0.875339000	1.034106000	0.008311000
6	-1.080631000	2.361553000	-0.386747000
6	-1.220005000	3.348186000	0.588657000
6	-1.074210000	2.665579000	-1.746828000
6	-1.361902000	4.679538000	0.184344000
1	-1.217220000	3.071464000	1.638611000
6	-1.214899000	4.001156000	-2.139237000
1	-0.960945000	1.868344000	-2.475135000
6	-1.360033000	5.007168000	-1.176889000
1	-1.471008000	5.458446000	0.933811000
1	-1.210224000	4.252437000	-3.196195000
1	-1.468270000	6.042929000	-1.486199000
6	-1.945475000	0.236936000	0.281880000
6	-1.639706000	-1.064757000	0.717897000
6	-3.280387000	0.651790000	0.143494000
6	-2.662048000	-1.950819000	1.017631000
1	-0.599701000	-1.358047000	0.814551000
6	-4.306059000	-0.237065000	0.444369000
1	-3.513454000	1.654254000	-0.194934000
6	-3.992982000	-1.529489000	0.879505000
1	-2.441109000	-2.956027000	1.355039000
1	-5.340884000	0.066328000	0.342737000
7	-5.067935000	-2.453647000	1.193265000
8	-4.774314000	-3.595267000	1.576446000
8	-6.238856000	-2.067137000	1.066379000



E sol =-630.796848
G sol= -630.653140

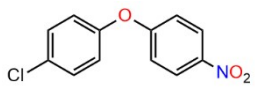
8	-1.779231000	0.957484000	-1.289654000
6	-1.488496000	2.277465000	-1.045170000
6	-1.813766000	2.931170000	0.144329000
6	-0.827719000	2.961003000	-2.076495000
6	-1.466048000	4.287828000	0.285795000
1	-2.323385000	2.410401000	0.945909000
6	-0.491036000	4.304426000	-1.918265000
1	-0.587766000	2.425551000	-2.989898000
6	-0.804885000	4.984504000	-0.738386000
1	0.020167000	4.826352000	-2.721421000
1	-0.545446000	6.029898000	-0.610800000
6	-2.447779000	0.214563000	-0.313895000
6	-1.702645000	-0.508493000	0.617400000
6	-3.841834000	0.168694000	-0.330732000
6	-2.375168000	-1.297425000	1.556789000
1	-0.618569000	-0.448687000	0.599444000
6	-4.504447000	-0.623084000	0.613155000
1	-4.388540000	0.744575000	-1.071438000
6	-3.773949000	-1.354856000	1.557044000
1	-1.804894000	-1.866408000	2.285851000
1	-5.590017000	-0.667739000	0.608300000
1	-4.292381000	-1.969408000	2.287692000
6	-1.797878000	4.965998000	1.505929000
7	-2.065923000	5.518588000	2.495467000



E sol =-538.544517
G sol= -538.396778

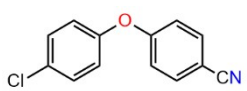
8	-1.131989000	0.888946000	-0.716920000
6	-1.209694000	2.271947000	-0.773851000
6	-1.545109000	3.044884000	0.343424000

6	-0.858268000	2.874502000	-1.984203000
6	-1.536330000	4.438540000	0.234377000
1	-1.809207000	2.562433000	1.279155000
6	-0.845842000	4.269783000	-2.078222000
1	-0.600042000	2.248122000	-2.832921000
6	-1.188161000	5.056965000	-0.972716000
1	-1.797273000	5.040961000	1.100532000
1	-0.573460000	4.739107000	-3.019817000
1	-1.182198000	6.140599000	-1.049655000
6	-2.089374000	0.166089000	-0.022526000
6	-1.645446000	-0.961800000	0.672344000
6	-3.449532000	0.491594000	-0.070244000
6	-2.575259000	-1.772568000	1.330755000
1	-0.583861000	-1.190128000	0.689005000
6	-4.368182000	-0.322855000	0.598533000
1	-3.780719000	1.366967000	-0.619819000
6	-3.938242000	-1.455410000	1.300619000
1	-2.230255000	-2.649429000	1.872194000
1	-5.424959000	-0.071373000	0.563433000
1	-4.658068000	-2.084338000	1.816877000



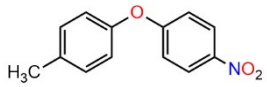
E sol =-1202.657436
G sol= -1202.523878

8	-0.873235000	1.054925000	0.070806000
6	-1.078592000	2.370063000	-0.350404000
6	-1.171026000	3.382299000	0.603282000
6	-1.121455000	2.646569000	-1.715763000
6	-1.314109000	4.706773000	0.182681000
1	-1.131635000	3.135685000	1.659480000
6	-1.264109000	3.969685000	-2.141034000
1	-1.044139000	1.836925000	-2.434419000
6	-1.360815000	4.983882000	-1.185540000
1	-1.386872000	5.509009000	0.909179000
1	-1.298447000	4.205840000	-3.199206000
6	-1.945781000	0.247560000	0.314699000
6	-1.639432000	-1.056861000	0.739828000
6	-3.279333000	0.659103000	0.160946000
6	-2.662211000	-1.951520000	1.012021000
1	-0.599612000	-1.346101000	0.849355000
6	-4.305478000	-0.238731000	0.433674000
1	-3.512912000	1.664941000	-0.167117000
6	-3.992484000	-1.534933000	0.856477000
1	-2.441820000	-2.959758000	1.340462000
1	-5.340015000	0.061387000	0.320306000
7	-5.068139000	-2.469220000	1.140250000
8	-4.774349000	-3.612063000	1.518714000
8	-6.238310000	-2.088806000	0.993178000
17	-1.540401000	6.653564000	-1.718888000



E sol =-1090.388374
G sol= -1090.257821

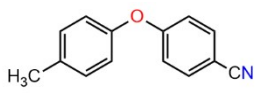
8	-1.780488000	0.957359000	-1.286009000
6	-1.488980000	2.279388000	-1.042297000
6	-1.813521000	2.933471000	0.146575000
6	-0.828920000	2.959986000	-2.075317000
6	-1.465112000	4.290253000	0.286109000
1	-2.322751000	2.414654000	0.949684000
6	-0.491623000	4.303447000	-1.918952000
1	-0.590036000	2.422980000	-2.988034000
6	-0.804467000	4.984892000	-0.739596000
1	0.019192000	4.824200000	-2.723047000
1	-0.544442000	6.030317000	-0.613610000
6	-2.447254000	0.216410000	-0.313293000
6	-1.705456000	-0.508747000	0.618666000
6	-3.840962000	0.167027000	-0.328528000
6	-2.369502000	-1.301263000	1.558312000
1	-0.621542000	-0.452759000	0.606756000
6	-4.510471000	-0.623475000	0.608799000
1	-4.393230000	0.740697000	-1.066169000
6	-3.765405000	-1.346983000	1.542865000
1	-1.808805000	-1.873701000	2.289521000
1	-5.593996000	-0.675422000	0.610686000
6	-1.795750000	4.970071000	1.505643000
7	-2.062998000	5.524087000	2.494540000
17	-4.606551000	-2.345518000	2.726658000



E sol =-782.384293

G sol= -782.21440

8	-0.870980000	1.046383000	0.073281000
6	-1.078622000	2.367428000	-0.345434000
6	-1.173332000	3.378078000	0.608666000
6	-1.129954000	2.649648000	-1.708321000
6	-1.324524000	4.699970000	0.180582000
1	-1.133216000	3.128510000	1.664793000
6	-1.281148000	3.977534000	-2.118605000
1	-1.056668000	1.841412000	-2.429917000
6	-1.379294000	5.022059000	-1.185348000
1	-1.401154000	5.491593000	0.922173000
1	-1.323616000	4.202017000	-3.181696000
6	-1.941477000	0.241087000	0.316502000
6	-1.637741000	-1.066856000	0.735882000
6	-3.276199000	0.654315000	0.168667000
6	-2.660996000	-1.960701000	1.007457000
1	-0.598151000	-1.358683000	0.841296000
6	-4.302780000	-0.242510000	0.440970000
1	-3.507473000	1.662107000	-0.154765000
6	-3.991541000	-1.541588000	0.857831000
1	-2.441344000	-2.970670000	1.331149000
1	-5.337182000	0.059858000	0.332002000
7	-5.067074000	-2.474224000	1.140955000
8	-4.774797000	-3.620485000	1.511721000
8	-6.237710000	-2.090824000	1.001607000
6	-1.506460000	6.458857000	-1.638113000
1	-0.517654000	6.928128000	-1.728933000
1	-1.993116000	6.528468000	-2.616875000
1	-2.085551000	7.053680000	-0.923379000



E sol =-670.114986
G sol= -669.947310

8	-1.774591000	0.962414000	-1.295490000
6	-1.484029000	2.281882000	-1.051495000
6	-1.811030000	2.936776000	0.137128000
6	-0.821631000	2.965413000	-2.082029000
6	-1.463561000	4.293486000	0.278338000
1	-2.321884000	2.416017000	0.937904000
6	-0.485255000	4.308959000	-1.924146000
1	-0.580188000	2.429555000	-2.994841000
6	-0.800865000	4.989811000	-0.745165000
1	0.027148000	4.830416000	-2.726871000
1	-0.541649000	6.035291000	-0.617781000
6	-2.443249000	0.220250000	-0.317735000
6	-1.704417000	-0.498798000	0.619852000
6	-3.836335000	0.171329000	-0.328218000
6	-2.379340000	-1.281242000	1.561692000
1	-0.619976000	-0.440204000	0.609864000
6	-4.495633000	-0.615493000	0.620374000
1	-4.389274000	0.744671000	-1.066550000
6	-3.781456000	-1.354194000	1.577886000
1	-1.804538000	-1.842254000	2.294798000
1	-5.582439000	-0.653951000	0.614616000
6	-1.797317000	4.972202000	1.497641000
7	-2.067076000	5.525222000	2.486505000
6	-4.502932000	-2.230121000	2.576960000
1	-4.679051000	-3.231908000	2.162543000
1	-3.919463000	-2.353830000	3.495689000
1	-5.479443000	-1.811480000	2.844135000

MnICl

E sol =-576.171894
G sol= -576.201044

25	0.637876000	-0.167680000	0.425103000
17	2.955826000	-0.454860000	0.266493000
53	-2.046863000	0.297226000	0.681871000

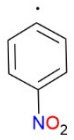
Oxidative Addition- Product

E sol =-1319.160828
G sol= -1319.029203

6	-2.482587000	0.702610000	0.212145000
6	-4.651407000	1.104940000	-0.786243000
6	-4.315377000	0.325010000	-1.920005000
6	-3.076833000	-0.268036000	-2.007065000
1	-2.780913000	-0.870508000	-2.859665000
1	-5.040389000	0.200181000	-2.718144000
1	-5.630631000	1.569771000	-0.726292000
6	0.880416000	1.319225000	0.194959000
6	1.048005000	1.974713000	1.416493000
6	0.986984000	3.368832000	1.453014000
6	0.768653000	4.062698000	0.259133000
6	0.614764000	3.411158000	-0.968520000
6	0.680217000	2.017642000	-0.997955000

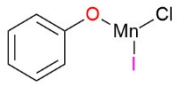
1	1.211438000	1.415277000	2.330716000
1	1.106764000	3.905851000	2.386247000
1	0.450799000	3.979941000	-1.875872000
1	0.562685000	1.494980000	-1.941673000
6	-3.727097000	1.284604000	0.272308000
6	-2.113531000	-0.095933000	-0.938958000
8	-0.965705000	-0.645194000	-1.046110000
25	0.753694000	-0.712402000	0.152891000
1	-4.007264000	1.884032000	1.132942000
1	-1.758888000	0.815023000	1.010447000
53	3.410453000	-0.817193000	-0.241903000
17	-0.183762000	-1.285051000	2.222207000
7	0.703198000	5.526664000	0.294669000
8	0.853416000	6.094357000	1.381988000
8	0.500372000	6.130502000	-0.764349000

HAT



E sol =-436.089446
G sol= -436.032229

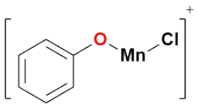
6	-0.254565000	-0.450834000	0.177708000
6	1.136107000	-0.424746000	0.015149000
6	1.859977000	0.761666000	-0.156632000
6	1.164465000	1.977925000	-0.166239000
6	-0.205092000	1.909422000	-0.002945000
6	-0.955020000	0.762595000	0.168625000
1	-0.773626000	-1.393147000	0.307473000
1	2.936303000	0.734157000	-0.278828000
1	1.694569000	2.916444000	-0.296859000
1	-2.033633000	0.778688000	0.291917000
7	1.866682000	-1.696239000	0.025325000
8	1.224997000	-2.740650000	0.181357000
8	3.093211000	-1.669745000	-0.122507000



E sol =-883.042816
G sol= -882.991281

25	0.517993000	-1.366667000	-0.202716000
8	-1.302989000	-0.334450000	-0.353871000
6	-2.545282000	-0.593287000	-0.200681000
6	-3.511240000	0.470017000	-0.367189000
6	-3.017844000	-1.918605000	0.133253000
6	-4.854934000	0.214652000	-0.203050000
1	-3.136227000	1.456606000	-0.619744000
6	-4.366449000	-2.147262000	0.291771000
1	-2.287863000	-2.713224000	0.248146000
6	-5.292850000	-1.089275000	0.127219000
1	-5.582977000	1.010439000	-0.326042000
1	-4.726075000	-3.140425000	0.542383000
1	-6.353546000	-1.282490000	0.254739000
17	1.812937000	-0.468070000	1.560436000
53	1.242287000	-3.357944000	-1.993168000

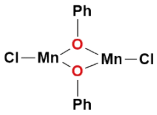
SET



E sol =-871.310353
G sol= -871.251368

25	0.472633000	-1.204927000	-0.191719000
8	-1.292694000	-0.398166000	-0.537549000
6	-2.533733000	-0.641811000	-0.321848000
6	-3.459831000	0.464307000	-0.278475000
6	-3.022109000	-1.985091000	-0.123174000
6	-4.794219000	0.230379000	-0.032964000
1	-3.062607000	1.462637000	-0.429725000
6	-4.362883000	-2.192738000	0.110454000
1	-2.311782000	-2.804535000	-0.171538000
6	-5.255035000	-1.093288000	0.162016000
1	-5.496024000	1.056903000	0.014878000
1	-4.743840000	-3.198383000	0.256730000
1	-6.309006000	-1.269485000	0.353165000
17	2.489713000	-1.796166000	0.711241000

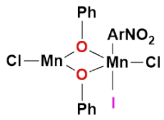
Dimer formation



E sol = -1743.262369
G sol= -1743.121746

8	1.343496000	-0.011760000	-0.054205000
25	0.031596000	1.618292000	-0.111410000
25	-0.032819000	-1.587909000	-0.019584000
8	-1.342573000	0.043134000	-0.057652000
17	0.254121000	3.957740000	-0.337680000
17	-0.260246000	-3.926484000	0.203328000
6	2.700216000	-0.058459000	-0.021207000
6	3.392582000	-1.173962000	-0.529815000
6	3.444365000	1.004816000	0.524294000
6	4.788495000	-1.224331000	-0.486356000
1	2.829995000	-1.997092000	-0.961907000
6	4.840656000	0.949961000	0.556801000
1	2.920874000	1.869309000	0.923984000
6	5.524928000	-0.163894000	0.055214000
1	5.300639000	-2.098427000	-0.881792000

1	5.394749000	1.784017000	0.981022000
1	6.610250000	-0.204764000	0.085550000
6	-2.699921000	0.073376000	-0.021581000
6	-3.381229000	1.142962000	0.590210000
6	-3.454798000	-0.966796000	-0.596020000
6	-4.778357000	1.172247000	0.615549000
1	-2.809946000	1.946599000	1.048036000
6	-4.851511000	-0.933915000	-0.558906000
1	-2.935919000	-1.796401000	-1.069494000
6	-5.525471000	0.135741000	0.043119000
1	-5.283044000	2.010806000	1.089718000
1	-5.414260000	-1.749471000	-1.007007000
1	-6.611453000	0.160678000	0.066706000



E sol = -2190.808750
G sol= -2190.591907

8	0.289303000	1.394461000	0.781234000
25	-0.725408000	2.439926000	-0.695531000
25	-0.394315000	-0.498666000	0.846810000
8	-2.084476000	0.750154000	-0.200891000
17	-0.742064000	4.313007000	-2.098828000
17	-1.339120000	-0.503739000	3.031917000
6	1.489447000	1.770110000	1.327755000
6	1.664826000	1.719026000	2.718299000
6	2.544889000	2.188435000	0.503696000
6	2.890122000	2.092427000	3.276950000
1	0.839769000	1.374968000	3.334163000
6	3.765189000	2.563133000	1.071261000
1	2.401141000	2.201439000	-0.572632000
6	3.945353000	2.516334000	2.459093000
1	3.019903000	2.051605000	4.355566000
1	4.578686000	2.883399000	0.425133000
1	4.896891000	2.804325000	2.897544000
6	-3.337667000	0.545499000	-0.390900000

6	-4.039767000	1.200260000	-1.470761000
6	-4.064328000	-0.351247000	0.481584000
6	-5.375367000	0.945381000	-1.671056000
1	-3.479878000	1.866958000	-2.118252000
6	-5.406237000	-0.575375000	0.267717000
1	-3.523090000	-0.797585000	1.307438000
6	-6.069970000	0.059896000	-0.806653000
1	-5.905615000	1.419870000	-2.490703000
1	-5.960470000	-1.237025000	0.925837000
1	-7.127064000	-0.125454000	-0.970106000
6	2.384115000	-1.535135000	0.651240000
6	3.659608000	-1.686663000	0.105308000
6	3.867979000	-1.300794000	-1.222336000
6	2.840976000	-0.772685000	-2.014908000
6	1.574081000	-0.625408000	-1.453857000
6	1.351171000	-0.998236000	-0.124063000
1	2.211137000	-1.826260000	1.683736000
1	4.474802000	-2.092309000	0.692559000
1	3.036879000	-0.481966000	-3.040089000
1	0.769433000	-0.205495000	-2.050859000
7	5.201263000	-1.453357000	-1.800583000
8	6.104777000	-1.910291000	-1.089024000
8	5.375308000	-1.118108000	-2.979080000
53	-1.374604000	-2.837953000	-0.108828000

Mechanism of Ligand-Assisted Manganese Catalyzed C-O Cross-Coupling Reaction

A. Estimation of the Activation barrier by Marcus Theory

According to the Marcus equation, the total reorganization energy is given as:

$$\lambda = \lambda_0 + \lambda_i \quad (1)$$

where, λ_0 is the solvent reorganization energy and λi is the inner reorganization energy, which we estimate as $\lambda_i \approx 0$.

The solvent reorganization energy λo can be calculated with:

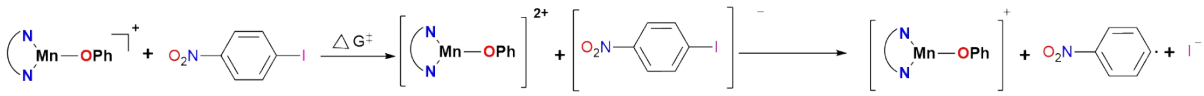
$$\lambda o = (332 kcal/mol)\left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right]\left[\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}\right] \quad (2)$$

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left[1 + \frac{\Delta G_r}{\lambda}\right]^2 \quad (3)$$

where a_1 and a_2 are the radii of the reactant molecules (a_1= 4.55 A°, a_2= 4.66 A°) and R = a_1 + a_2.

ΔG_r is the reaction energy.

ε_{op} is the optical dielectric constant (ε_{op} =1.8068), and ε is the static dielectric constant (ε=35.68).



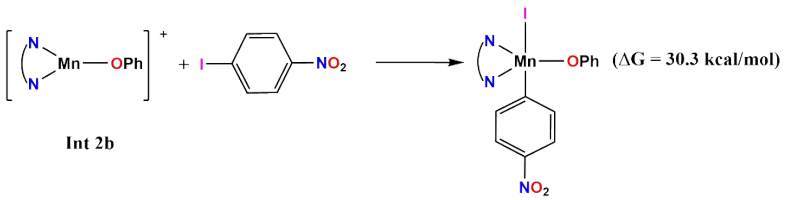
Scheme S5 *SET mechanism of Mn catalysed ligand assisted O-arylation*

B. Halogen Atom Transfer Mechanism (HAT)

The activation barrier is approximated using Saveant's Model.

Scheme S6 *HAT mechanism of Mn catalysed ligand assisted O-arylation*

C. Oxidative Addition



Scheme S7 *Oxidative addition of Mn catalysed ligand assisted O-arylation*

Cartesian coordinates and Energies(a.u) from UB3LYP-D3 method and solvation correction to free energies of Optimized geometries involved in the reaction mechanism for Ligand-assised Mn-catalyzed O-Arylation reaction

Selection of active catalyst for the ligand-assisted Mn catalyzed O-arylation reaction

In order to probe the active catalyst involved in the ligand-assisted Mn catalyzed O-arylation, we have considered differed modes of DMEDA ligand including the neutral, monoanionic, dianionic species (**Figure S1**). Among them neutral DMEDA is found to be more favourable.

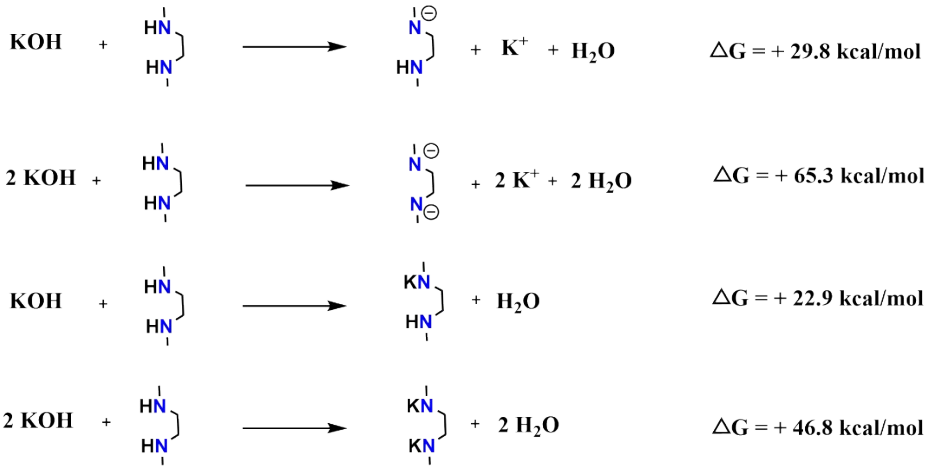


Figure S2: Formation of different modes of DMEDA.

KOH

E sol = -104.217536
G sol= -104.231776

8	0.000000000	0.000000000	-1.690094000
1	0.000000000	0.000000000	-2.659552000
19	0.000000000	0.000000000	0.851595000

PhOK

E sol = -335.300044
G sol= -335.244587

8	-0.235435000	2.737376000	0.255019000
6	-0.760018000	3.929550000	0.244294000
6	-1.041383000	4.630874000	-0.973968000
6	-1.087058000	4.633197000	1.449665000
6	-1.596909000	5.911752000	-0.978841000
1	-0.806370000	4.130681000	-1.912881000
6	-1.642132000	5.914096000	1.431023000
1	-0.887348000	4.135112000	2.397821000
6	-1.906367000	6.574858000	0.220032000
1	-1.792176000	6.402663000	-1.932010000
1	-1.872910000	6.407021000	2.375170000
1	-2.338961000	7.572245000	0.210922000
19	2.275534000	1.930408000	0.145300000

DMEDA-Neutral

E sol = -269.152402
G sol= -269.017093

6	5.061498000	-0.785375000	-0.777448000
6	5.409766000	0.421530000	-1.650086000
1	5.832541000	-1.560865000	-0.952067000
1	5.138879000	-0.505968000	0.283514000
1	6.492988000	0.619983000	-1.533389000
1	5.254517000	0.166555000	-2.708676000
7	4.604991000	1.607942000	-1.349046000
7	3.710290000	-1.301098000	-1.010635000
6	3.439214000	-2.519037000	-0.244948000
1	2.447449000	-2.904196000	-0.504652000
1	4.180957000	-3.322049000	-0.414691000
1	3.441832000	-2.283414000	0.826335000
6	5.030039000	2.779737000	-2.116650000
1	4.447543000	3.653862000	-1.806757000
1	6.104308000	3.017553000	-2.001804000
1	4.838970000	2.605340000	-3.182607000
1	4.687792000	1.814686000	-0.354081000
1	3.605212000	-1.503242000	-2.004465000

DMEDA-Monoanionic

E sol = -268.606176
G sol= -268.487389

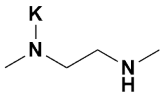
7	-1.567126000	-0.375843000	-0.457469000
7	1.484423000	-0.491747000	0.155871000
6	0.682832000	0.688789000	-0.197452000
1	1.121306000	1.604584000	0.251019000
1	0.730317000	0.814360000	-1.289167000
6	-0.784663000	0.590782000	0.241005000
1	-1.198140000	1.637593000	0.149534000
1	-0.770907000	0.426175000	1.361589000
1	1.319337000	-0.703840000	1.139844000
6	-2.907517000	-0.338554000	0.049163000
1	-3.416688000	0.663497000	-0.051434000
1	-3.553369000	-1.064081000	-0.471923000
1	-2.996134000	-0.573898000	1.148278000
6	2.915942000	-0.280404000	-0.052839000

1	3.477608000	-1.156109000	0.292036000
1	3.113421000	-0.152752000	-1.124746000
1	3.312603000	0.613920000	0.466902000

DMEDA-Dianionic

E sol = -268.049207
G sol= -267.948055

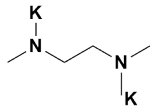
7	-1.559272000	-0.464190000	-0.379042000
7	1.559421000	-0.463774000	0.379654000
6	0.746754000	0.568516000	-0.193021000
1	1.138324000	1.596021000	0.078080000
1	0.785660000	0.571125000	-1.323051000
6	-0.746770000	0.568520000	0.192988000
1	-1.138438000	1.595808000	-0.078762000
1	-0.785627000	0.571999000	1.323041000
6	-2.911105000	-0.279913000	0.050096000
1	-3.358753000	0.720671000	-0.232040000
1	-3.581260000	-1.044999000	-0.377440000
1	-3.059868000	-0.326245000	1.169042000
6	2.911049000	-0.280000000	-0.050384000
1	3.581340000	-1.044632000	0.377706000
1	3.059112000	-0.327604000	-1.169330000
1	3.358897000	0.720858000	0.230393000



E sol = -296.903976
G sol= -296.787933

7	1.524574000	-0.248655000	-0.171001000
7	-1.464687000	-0.445379000	0.387812000
6	-0.678924000	-1.387781000	-0.426453000
1	-1.119511000	-2.404128000	-0.386001000
1	-0.740124000	-1.053182000	-1.472523000
6	0.793833000	-1.466305000	-0.004319000
1	1.229935000	-2.326082000	-0.586293000
1	0.805607000	-1.847148000	1.060354000
1	-1.338478000	-0.696863000	1.368993000
6	2.897050000	-0.478712000	0.178752000
1	3.405891000	-1.276685000	-0.431460000
1	3.498566000	0.436337000	0.051905000
1	3.053291000	-0.810883000	1.243085000

6	-2.893669000	-0.485191000	0.070628000
1	-3.443394000	0.179560000	0.746389000
1	-3.047294000	-0.127938000	-0.955262000
1	-3.333544000	-1.497713000	0.142168000
19	-0.005258000	2.062679000	-0.063720000



E sol = -324.650862
G sol= -324.553707

7	-1.368723000	0.671158000	0.386281000
7	1.368668000	-0.670931000	0.385916000
6	0.771396000	-0.016099000	1.516522000
1	1.082501000	-0.481731000	2.492995000
1	1.119211000	1.057144000	1.628263000
6	-0.771458000	0.015599000	1.516503000
1	-1.082634000	0.480599000	2.493266000
1	-1.119296000	-1.057712000	1.627578000
6	-2.792167000	0.693889000	0.557853000
1	-3.141756000	1.218233000	1.490987000
1	-3.289304000	1.199657000	-0.286295000
1	-3.267075000	-0.326931000	0.633373000
6	2.792037000	-0.694644000	0.557782000
1	3.289064000	-1.199749000	-0.286825000
1	3.267502000	0.325831000	0.634526000
1	3.141143000	-1.220229000	1.490403000
19	0.714481000	1.781663000	-1.110622000
19	-0.714366000	-1.781092000	-1.111252000

K^+

E sol = -28.272936

G sol= -28.288112

19	0.000000000	0.000000000	0.000000000

$Mn(DMEDA)_2$

E sol = -642.551889

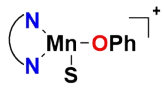
G sol= -642.251906

6	4.834886000	-0.624689000	-0.825045000
6	5.016013000	0.877938000	-1.014457000
1	5.745864000	-1.160470000	-1.120608000
1	4.639867000	-0.850978000	0.229411000
1	5.911297000	1.225502000	-0.483712000
1	5.144786000	1.109535000	-2.077713000
7	3.802476000	1.594231000	-0.545714000
7	3.660932000	-1.092131000	-1.606087000
6	3.298949000	-2.498138000	-1.308329000
1	2.472938000	-2.795563000	-1.958788000
1	4.147891000	-3.176529000	-1.460820000
1	2.968189000	-2.565950000	-0.268626000
6	3.799031000	3.027033000	-0.919733000
1	2.912214000	3.501217000	-0.492305000
1	4.698639000	3.543054000	-0.560651000
1	3.749074000	3.107629000	-2.008728000
1	3.781473000	1.537591000	0.475137000
1	3.904329000	-1.036979000	-2.597798000
25	2.038329000	0.411923000	-1.269214000
7	0.440213000	0.866049000	-2.766766000
1	0.574926000	0.261760000	-3.577600000
6	-0.861842000	0.914795000	-0.652857000
1	-1.830262000	0.660334000	-0.203419000
1	-0.730232000	1.997525000	-0.571768000
7	0.256855000	0.274253000	0.090824000
1	0.444308000	0.835378000	0.921866000
6	0.478965000	2.272176000	-3.240330000
1	1.439143000	2.451614000	-3.729829000
1	-0.336804000	2.481176000	-3.943566000
1	0.397222000	2.948607000	-2.386389000
6	-0.041370000	-1.108460000	0.538405000
1	0.804664000	-1.477650000	1.122687000
1	-0.953139000	-1.145860000	1.147637000
1	-0.165765000	-1.756612000	-0.332190000
6	-0.849126000	0.493186000	-2.122868000
1	-1.696223000	0.953369000	-2.647461000
1	-0.955741000	-0.592009000	-2.205421000

E sol = -680.408498
G sol= -680.187252

6	5.213721000	-0.868529000	-0.826036000
6	5.498292000	0.432232000	-1.573317000
1	5.939721000	-1.640075000	-1.111591000
1	5.300751000	-0.708351000	0.254456000
1	6.541456000	0.737978000	-1.422300000
1	5.343453000	0.289118000	-2.648554000
7	4.555871000	1.486370000	-1.122367000
7	3.822130000	-1.317602000	-1.099104000
6	3.406902000	-2.455382000	-0.245169000
1	2.408129000	-2.778339000	-0.548188000
1	4.104374000	-3.298580000	-0.328379000
1	3.369216000	-2.122229000	0.795268000

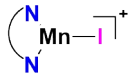
6	4.586269000	2.702789000	-1.966357000
1	3.903675000	3.442293000	-1.540180000
1	5.595699000	3.129026000	-2.030277000
1	4.240826000	2.445149000	-2.971125000
6	0.347666000	4.684041000	0.180777000
6	0.885126000	3.404582000	0.013220000
6	0.276314000	2.470199000	-0.858539000
6	-0.890470000	2.874686000	-1.548508000
6	-1.419834000	4.155376000	-1.374264000
6	-0.807982000	5.073414000	-0.509100000
1	0.836068000	5.380979000	0.858861000
1	1.780268000	3.109577000	0.558141000
1	-1.364429000	2.163233000	-2.220765000
1	-2.317726000	4.439038000	-1.919708000
1	-1.223402000	6.068602000	-0.375005000
8	0.751870000	1.234193000	-1.032465000
1	4.820854000	1.758298000	-0.172950000
1	3.782924000	-1.628915000	-2.072648000
25	2.545196000	0.492647000	-0.954571000



E sol = -813.190389
G sol= -813.930758

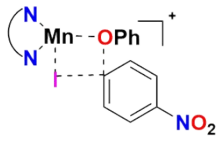
6	4.881835000	-0.574196000	-1.446341000
6	4.937252000	0.927701000	-1.710675000
1	5.438014000	-1.120026000	-2.219560000
1	5.344038000	-0.800963000	-0.478781000
1	5.976370000	1.254847000	-1.846219000
1	4.389183000	1.166252000	-2.629315000
7	4.281994000	1.659831000	-0.599128000
7	3.468248000	-1.025827000	-1.381353000
6	3.336184000	-2.422079000	-0.909298000
1	2.282893000	-2.710837000	-0.944106000
1	3.925219000	-3.116693000	-1.522357000
1	3.680125000	-2.480057000	0.126603000
6	4.046850000	3.088153000	-0.906464000
1	3.624262000	3.574597000	-0.024322000
1	4.972296000	3.600288000	-1.200740000
1	3.317809000	3.156461000	-1.717322000
6	-0.248997000	4.682105000	0.085084000
6	0.413520000	3.452516000	0.038765000
6	0.437048000	2.683614000	-1.150248000
6	-0.230416000	3.205336000	-2.284727000
6	-0.889072000	4.435438000	-2.228381000
6	-0.906736000	5.187252000	-1.044782000
1	-0.250724000	5.250643000	1.013039000
1	0.924777000	3.067317000	0.919240000
1	-0.215776000	2.623251000	-3.203446000
1	-1.392800000	4.810747000	-3.117140000
1	-1.421160000	6.143700000	-1.004483000
8	1.056019000	1.509342000	-1.228455000
1	4.892588000	1.604730000	0.218469000
1	3.081018000	-0.975758000	-2.326130000
25	2.383291000	0.533104000	-0.160236000

6	1.978696000	-1.140904000	2.717606000
6	1.750271000	-1.892982000	3.941438000
1	1.440916000	-1.211330000	4.739609000
1	0.963110000	-2.634447000	3.773428000
1	2.671693000	-2.403667000	4.237306000
7	2.157808000	-0.544644000	1.741857000



E sol = -384.974073
G sol= -384.841926

6	5.235127000	-0.831712000	-0.739892000
6	5.592270000	0.374341000	-1.604524000
1	5.952525000	-1.645093000	-0.905830000
1	5.272025000	-0.561827000	0.321471000
1	6.632002000	0.676390000	-1.428854000
1	5.491631000	0.118660000	-2.664942000
7	4.655847000	1.494164000	-1.325252000
7	3.847394000	-1.274886000	-1.038105000
6	3.366519000	-2.324482000	-0.107468000
1	2.373201000	-2.649692000	-0.425219000
1	4.045565000	-3.186017000	-0.088208000
1	3.294234000	-1.900375000	0.897287000
6	4.743265000	2.587214000	-2.321747000
1	4.075463000	3.396320000	-2.016974000
1	5.767127000	2.971551000	-2.410658000
1	4.416192000	2.207282000	-3.293079000
1	4.894409000	1.883083000	-0.410000000
1	3.841059000	-1.668082000	-1.982508000
25	2.627999000	0.589494000	-1.113042000
53	0.089619000	1.560123000	-0.722775000



E sol = -1127.968068
G sol= -1127.668428

6	5.157446000	-0.590848000	-0.629223000
6	5.459922000	0.517184000	-1.633717000
1	5.951593000	-1.347798000	-0.646113000
1	5.104452000	-0.179844000	0.385034000
1	6.457432000	0.935844000	-1.452176000
1	5.445119000	0.114428000	-2.652472000
7	4.416578000	1.572780000	-1.557243000
7	3.835905000	-1.196574000	-0.934908000
6	3.386012000	-2.159452000	0.098171000
1	2.442875000	-2.605554000	-0.226561000
1	4.128579000	-2.949949000	0.263082000
1	3.219773000	-1.621399000	1.035202000
6	4.497920000	2.546169000	-2.672362000
1	3.749725000	3.326430000	-2.514539000
1	5.494153000	3.001321000	-2.737820000

1	4.276161000	2.029147000	-3.609567000
6	-0.033990000	3.963513000	0.834818000
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6	-2.728147000	0.005503000	1.238935000
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Oxidative addition Product

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7	3.546568000	-1.389372000	2.177674000
7	2.624736000	-4.056905000	1.641235000
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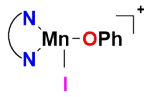
HAT



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7	4.825430000	1.401420000	-0.768701000
7	3.669838000	-1.240037000	-1.153371000
6	3.264165000	-2.479619000	-0.450565000
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1	1.900525000	3.659970000	0.107409000

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53	2.254240000	0.292615000	2.308198000

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1	4.005673000	-3.238208000	-0.149048000
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1	4.396340000	2.310354000	-3.131639000
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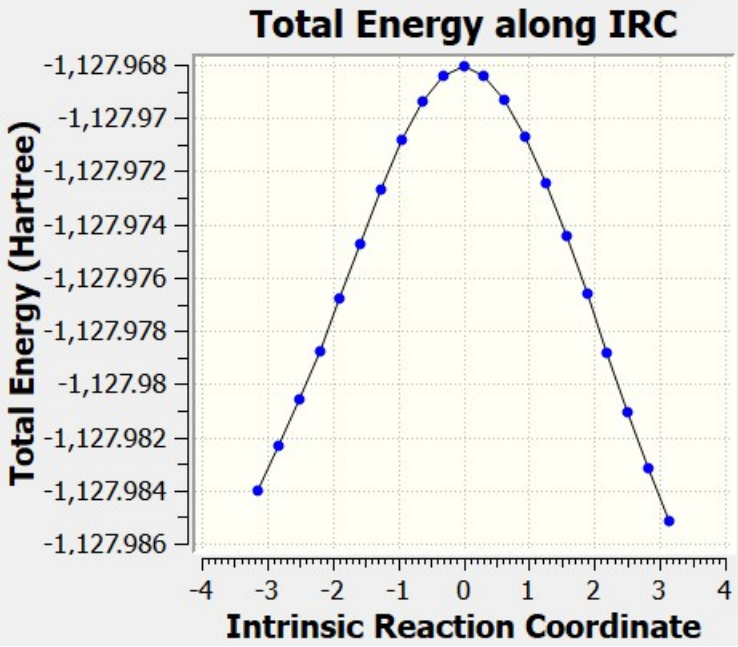


Figure S3: IRC of ligand assisted Mn-Catalyzed O-arylation reaction.

Mechanism of Ligand-Assisted Zinc Catalyzed C-O Cross-Coupling Reaction

A. Estimation of the Activation barrier by Marcus Theory

According to the Marcus equation, the total reorganization energy is given as:

$\lambda = \lambda_0 + \lambda_i$ (1)

where, λ_0 is the solvent reorganization energy and λ_i is the inner reorganization energy, which we estimate as $\lambda_i \approx 0$.

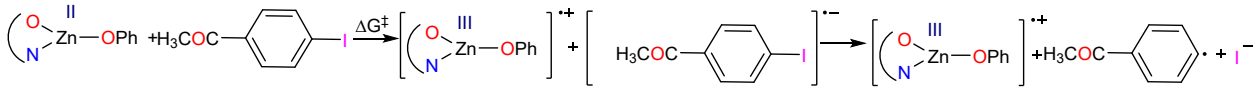
The solvent reorganization energy λ_0 can be calculated with:

$$\lambda o = (332 kcal/mol)\left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right]\left[\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}\right] \quad (2)$$

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left[1 + \frac{\Delta G_r}{\lambda}\right]^2 \quad (3)$$

where a_1 and a_2 are the radii of the reactant molecules (a_1 = 4.85 A^0, a_2 = 4.79 A^0) and R = a_1 + a_2.
ΔG_r is the reaction energy.

ε_{op} is the optical dielectric constant (ε_{op} =1.8068) and ε is the static dielectric constant (ε=35.68).



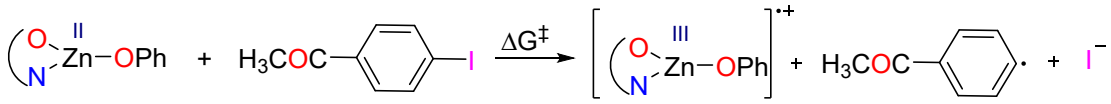
Scheme S8 *SET mechanism of Zn catalysed ligand assisted O-arylation*

B. Estimation of the Activation energy by Savéant's model

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left[1 + \frac{\Delta G_r}{\lambda}\right]^2$$

$$\frac{\lambda}{4} = (\lambda i + \lambda_0 + BDFE)/4 \qquad (4)$$

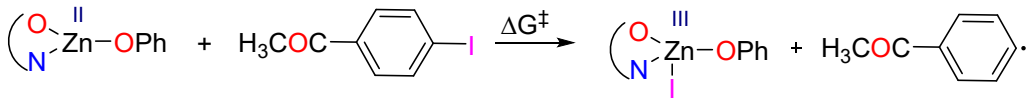
BDFE is the Bond dissociation Free Energy



Scheme S9 *SET mechanism of Zn catalysed ligand assisted O-arylation.*

BDFE = 49.12 kcal/mol

C. Halogen Atom Transfer Mechanism (HAT)



Scheme S10 *HAT mechanism of Zn catalysed ligand assisted O-arylation.*

The activation barrier is approximated using Saveant's Model

Model Reaction and Molecular Properties of Zinc-Proline Complexes

2(L-proline)$^-$ + $Zn(Et)_2$ → Zn (L-proline)$_2$+2$CH_3CH_2^-$ (S1)

Int 1c ΔG= +44.8 kcal/mol

2(L-proline) + $Zn(Et)_2$ → Zn (L-proline)$_2$+2CH_3CH_3 (S2)

Int 1 ΔG = -82.5 kcal/mol

2(L-proline) + $ZnCl_2$ → Zn (L-proline)$_2$ + 2 HCl (S3)

Int 1c ΔG = +20.8 kcal/mol

2(L-proline) + $Zn(OAc)_2$ → Zn(L-Proline)$_2$ + 2 AcOH (S4)

Int 1c ΔG = -8.7 kcal/mol

Accordingly, the L-proline ligand in our reaction system, in its zwitter ionic state, is expected to interact with the diethyl zinc. However, the experiment has shown that other Zn(II) salts such as $ZnCl_2$ or $Zn(OAc)_2$, failed to act as good catalytic sources for the model reaction. These experimental observations could be rationalised by computing

the Gibb's free energy of formation of Zn(L-Proline)$_2$ [**Int 1c**] from $ZnCl_2$ and Zn(OAc)$_2$ **(Equation S3-S4)**. For, the $ZnCl_2$ catalytic source, a significant positive Gibb's free energy of formation (20.8 kcal/mol) was observed while for Zn(OAc)$_2$, a slight negative gibbs free energy of formation (-8.7 kcal/mol) was observed. Henceforth, while comparing the equations **S2, S3** and **S4**, the formation of **Int 1c** from diethyl Zinc tends to be highly favorable over the other two salts. Thus, the diethyl zinc turns out to be the most favourable catalytic source for the formation of Zn-proline complexes in line with the experimental observation.

The coordination of L-proline ligand to the zinc (II) centre could alter its structural properties, which could be demonstrated by analysing the bonds surrounding the α- carbon of the proline ligand. It can be seen that the coordination has caused the bond lengths of the amino acid proline C 1 -C 2, C 1 -O, and C 2 -N to shift from 1.56 to 1.55 A°, 1.52 to 1.50 A°, and 1.27 to 1.31 A°, respectively (**Table S3**). Further, the coordination of the zinc ion with the proline ligand was also supported by the vibrational frequency analysis. The N-H bond's stretching vibrations in the free ligand (3249.36 and 3534.23cm^{-1}) were blue-shifted (3532.40–3540.70 cm^{-1}) in the Zn(II)-proline complex. This suggests that the deprotonation of NH_2^+ in the free proline ligand before it gets coordinated to zinc (II) metal centre.

Table S3. Variation of bond lengths between Zn and coordinated atoms of the proline ligand during the formation of Zn (Proline)$_2$ complex [a]

Species	Zn-O_{pro}	Zn-N_{pro}	C_1- C_2	C_2-N	C_1-O
Free proline	-	-	1.56	1.52	1.27
Zn(proline)$_2$	2.05	2.17	1.55	1.50	1.31

[a] All the values of bond lengths are given in A° units

3.4 Effect of Functional Groups in the Substrate Molecules on the Feasibility of the O-arylation Reaction

Further, it was gleaned from the experiment that the reported etherification reactions proceed efficiently in presence of electron-withdrawing substituents on aryl iodides. Consequently, a detailed computational study was conducted to probe the electronic effect of functional groups on aryl halide in controlling the feasibility of reaction. The electronic structure calculations were conducted by varying the functional groups at *para* position of aryl halides by -H, -CN, -NO_2, -$COCH_3$ and -CH_3 groups to reveal the experimental findings

Even though, the substrate scope of unsubstituted and *p*-methyl aryl iodides are not studied in the experiment, we have considered them in our study to account for the trends observed in the experiment. The activation barrier for each O-arylation reactions were calculated to probe the electronic effects of substituents, by characterizing the transition states involved, It was objectified that the addition of electron-withdrawing groups (-CN, -NO_2, -$COCH_3$) at the para position of the aryl iodide considerably decreased the activation barrier for σ- bond metathesis pathway (**Table S4**). Moreover, as compared to $COCH_3$ group (35.0 kcal/mol), the presence of the –NO_2 group (31.6 kcal/mol), at the para position considerably decreases the activation barrier of the reaction. This observation could account for the necessity of a lower temperature (120° C) for 4-nitroiodobenzene in the experiment. Contrastingly, when electron releasing groups –CH_3(38.1 kcal/mol), or unsubstituted aryl halide (37.7 kcal/mol) are considered, an elevation in the activation barrier for the reaction was observed. These findings vindicate the high yields observed in experiment when the reaction was performed using the para-substituted aryl iodides.

The FMO'S investigated for understanding the electronic effects of functional groups are the Highest Occupied Molecular Orbital (HOMO) of the proline ligated zinc complex **(Int 2**) and the Lowest Unoccupied Molecular Orbital

(LUMO) of the aryl halide. The energy gap between these interacting orbitals are calculated to analyze the correlation between energy gap and the electronic nature of the substituents (**Table 55**).

A considerable decrease in the HOMO-LUMO gap was seen when the the aryl iodide is substituted with a strong electron-withdrawing groups, -NO_2, CN, $COCH_3$ at the para-position in comparison to the substitution by electron-releasing groups (CH_3). The results garnered from our theoretical studies was in close agreement with the experimental findings, that the aryl iodides substituted by electron-withdrawing groups at para-position emerge as better substrates over the electron-rich aryl iodides. It is evident from **(Table S5)** that the electron-withdrawing groups at the *para* - position of aryl iodide tend to decrease the LUMO energy of aryl iodide. This leads to a decrease in the HOMO-LUMO gap of the participating species, eventually reducing the activation energy of the reaction as compared to the unsubstituted aryl iodides and electron rich aryl iodides. These theoretical results also strongly corroborate with the experimental findings.

Substituent on aryl iodide (X)	$\Delta G^{\ddagger}$	ΔG^0
CH_3	38.04	-21.00
H	37.66	-21.31
$COCH_3$	35.04	-22.28
CN	33.87	-23.06
NO_2	31.61	-23.75

Table S4. Effect of functional groups on the activation barrier of the zinc catalyzed C –O cross-coupling reaction ($\Delta G^{\ddagger}$ is the free energy of activation. ΔG^0 is the reaction-free energy)

Substituent on Arl	LUMO of aryl iodide (eV)	HOMO of Zn-Phenoxide complex (eV)	E_{LUMO}-E_{HOMO} (eV)	$\Delta G^{\ddagger}$ (kcal/mol)
CH_3	-1.13	-5.66	4.53	38.1
H	-1.14	-5.66	4.49	37.7
$COCH_3$	-2.18	-5.66	3.48	35.1
CN	-1.97	-5.66	3.69	33.9
NO_2	-3.19	-5.66	2.46	31.6

Table S5. Effect of the functional groups on the energy of the frontier molecular orbitals of the species involved in the Zn catalyzed C –O cross-coupling reaction and their correlation with activation barrier.

Effect of amino acid ligand L-valine on the feasibility of the O-arylation reaction

All the above mechanistic studies on the Zn(II) catalyzed O-arylation reaction were performed using L-proline as the ancillary ligand. We have then, explored the suitability of L-Valine ligand for the model system using 4-iodoacetophenone. Our study revealed the reaction require an activation barrier of about 35.8 kcal/mol, which could rationalise the lower yield for O-arylation reaction employing L-valine as ligand for the model system. Intriguingly, a low temperature reaction is attainable if 4-nitroiodobenzene is used as the substrate.

However, experimental observations indicate a lower yield for the above protocol. Further, several studies have reported 4-nitroiodobenzene as a suitable substrate for O-arylation reaction employing L-valine as the ancillary ligand for carbon-heteroatom cross-coupling reactions. Again, the existence of stable Zn(II)-Valine complexes are reported in literature. Henceforth, we have extended our investigation on Zn(II)-catalysed O-arylation reactions using L-Valine as the ancillary ligand for the substrate 4-nitroiodobenzene,. To our delight, computational calculations

showed L-valine to be an equally competent ligand as that of L-proline with the same activation barrier (31.6 kcal/mol), thereby manifesting as a befitting ligand for Zn catalyzed O-arylation reaction for the substrate 4-nitroiodobenzene. Nonetheless, a lower temperature (<120°C) could be sufficient enough to overcome this barrier by reducing the decomposition of 4-nitroiodobenzene at higher temperatures. The results obtained could thus aid in developing sustainable reaction protocols by employing L-Valine as the ancillary ligand for the substrate 4-nitroiodobenzene by overcoming the poor yield constraint found in the Zn(II) catalyzed O-arylation reaction. Regardless of the comparatively favorable activation barrier associated with the valine assisted protocol, the formation of the active catalyst is hindered by an unfavorable free energy of formation of +9.7kcal/mol. Consequently, proline is identified as a better ligand to valine in the zinc-catalyzed O-arylation reaction.

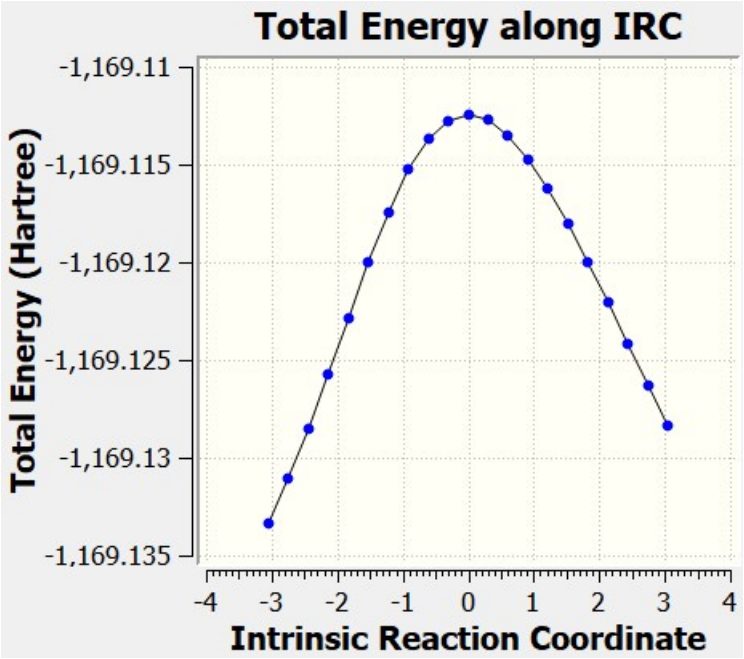


Figure S4: IRC of zinc catalyzed etherification reaction.

Cartesian coordinates and Energies (a.u) from B3LYP-D3 method and solvation correction to free energies of Optimized geometries involved in the reaction mechanism

Free Proline Ligand

E_{sol}: -401.300099

$G_{sol:}$ -401.185538

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6	4.297379000	0.674378000	0.952003000
1	2.178498000	-1.397602000	1.226199000
1	1.765374000	-0.576216000	2.745123000
6	3.905945000	-1.131929000	2.526571000
6	4.863825000	-0.679629000	1.416298000
1	4.736804000	1.501155000	1.507689000
6	4.422613000	0.932606000	-0.574311000
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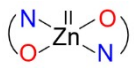
1	4.123968000	-0.612320000	3.464035000
1	4.851799000	-1.396571000	0.590637000
1	5.894182000	-0.578153000	1.754450000
8	3.339278000	0.935903000	-1.217396000
1	2.545946000	1.394266000	1.901519000
8	5.585526000	1.087453000	-0.993381000
1	2.331510000	0.709148000	0.404807000

Int 1



E_{sol}: -867.117571

$G_{sol:}$ -866.891672

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6	-2.735966000	1.124570000	4.602927000
6	-2.355804000	-1.285167000	4.691641000
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6	-2.979275000	-2.581235000	4.134689000
1	-3.278478000	1.250846000	6.721541000

1	-1.609104000	0.749443000	6.422726000
1	-4.132176000	-0.905022000	5.882045000
1	-2.733804000	-1.401459000	6.843712000
8	-3.745931000	-2.484678000	3.109624000
8	-2.721486000	-3.629747000	4.737945000
1	-1.595854000	0.006773000	3.269804000
7	-6.142959000	-0.349426000	2.214974000
6	-6.805131000	0.205238000	3.448363000
6	-6.378705000	0.598046000	1.091944000
1	-6.093945000	0.178908000	4.274924000
1	-7.661228000	-0.410931000	3.726489000
6	-7.216966000	1.644532000	3.080515000
6	-6.412953000	1.954336000	1.810330000
1	-7.342889000	0.403310000	0.613633000
6	-5.280291000	0.542526000	0.013177000
1	-7.015375000	2.348658000	3.889340000
1	-8.286983000	1.687019000	2.861075000
1	-5.390390000	2.257112000	2.063180000
1	-6.856832000	2.734549000	1.192220000
8	-4.130821000	0.092652000	0.371158000
8	-5.557026000	0.975264000	-1.111234000
1	-6.528720000	-1.261550000	1.991095000

Acetonitrile

E_{sol}: -132.801618

$G_{sol:}$ -132.780346

6	0.568422000	0.154118000	-0.000212000
7	1.722159000	0.154093000	-0.000329000
6	-0.886766000	0.154296000	0.000065000
1	-1.261347000	0.635591000	0.905063000
1	-1.261713000	0.697383000	-0.869092000
1	-1.261796000	-0.869892000	-0.035493000

Ethane

E_{sol}: -79.850410

$G_{sol:}$ -79.799148

6	-3.949686000	1.605515000	-0.021076000
1	-3.602386000	2.151613000	0.861283000
1	-3.602387000	2.151613000	-0.903437000
1	-5.043344000	1.642181000	-0.021076000
6	-3.439541000	0.162616000	-0.021076000
1	-2.345883000	0.125950000	-0.021078000
1	-3.786839000	-0.383482000	0.861284000
1	-3.786842000	-0.383483000	-0.903435000

Phenol

E_{sol}: -307.557114

G_{sol}: -307.482097

6	-1.039881000	-1.181269000	-0.039561000
6	0.351129000	-1.134622000	-0.140144000
6	1.000995000	0.102430000	-0.149132000
6	0.262677000	1.284890000	-0.057843000
6	-1.125227000	1.224985000	0.042234000
6	-1.785751000	-0.006092000	0.051951000
1	-1.538286000	-2.145194000	-0.033304000
1	0.926816000	-2.053179000	-0.210567000
1	0.784684000	2.235623000	-0.066009000
1	-1.692887000	2.147155000	0.113237000
1	-2.866657000	-0.047791000	0.129623000
8	2.363456000	0.221159000	-0.245362000
1	2.779863000	-0.648407000	-0.302675000

Phenoxide Anion

E_{sol}: -307.081891

$G_{sol:}$ -307.020058

6	-1.102852000	-1.201171000	-0.000023000
6	0.288672000	-1.209036000	-0.000061000

6	1.062873000	-0.000005000	-0.000255000
6	0.288679000	1.209031000	-0.000062000
6	-1.102844000	1.201174000	-0.000024000
6	-1.824676000	0.000003000	-0.000057000
1	-1.638037000	-2.148919000	0.000040000
1	0.828467000	-2.153821000	0.000019000
1	0.828480000	2.153812000	0.000018000
1	-1.638024000	2.148925000	0.000038000
1	-2.910137000	0.000007000	-0.000024000
8	2.353425000	-0.000009000	0.000090000

Caesium Phenoxide

E_{sol}: -326.930285

$G_{sol:}$ -326.875881

6	-0.992806000	-1.191009000	-0.099777000
6	0.388883000	-1.173896000	0.069822000
6	1.127240000	0.048998000	0.188389000
6	0.338555000	1.243495000	0.123522000
6	-1.042558000	1.210717000	-0.043771000
6	-1.732218000	-0.003195000	-0.159173000
1	-1.504355000	-2.147281000	-0.188520000
1	0.946021000	-2.107567000	0.111246000
1	0.857159000	2.196182000	0.206215000
1	-1.593728000	2.147895000	-0.087559000
1	-2.809309000	-0.022453000	-0.291355000
8	2.415649000	0.072797000	0.313255000
55	3.032094000	-0.275647000	-2.833947000

Caesium Carbonate

E_{sol}: -303.851415

G_{sol}: -303.877827

8	1.228678000	0.095010000	0.676342000

6	1.359673000	-0.398873000	-0.516017000
8	2.509447000	-0.318549000	-1.124843000
8	0.355994000	-0.964275000	-1.113170000
55	4.142042000	1.511198000	0.930434000
55	1.413468000	-0.510160000	-4.149458000

Caesium Hydrogen Carbonate

E_{sol}: -284.495813

G_{sol}: -284.503201

8	1.192221000	0.131594000	0.644157000
6	1.452170000	-0.392736000	-0.455317000
8	2.495035000	-0.322067000	-1.145952000
8	0.410339000	-1.177523000	-0.984222000
55	4.185324000	1.530956000	1.075202000
1	0.719420000	-1.531044000	-1.829315000

$ZnCl_2$

E_{sol}: -986.213420

G_{sol}: -986.237311

30	0.463236000	-1.602182000	0.091958000
17	-1.553580000	-1.565601000	-0.960555000
17	2.480053000	-1.638762000	1.144471000

HCl

E_{sol}: -460.830366

G_{sol}: -460.841773

17	-1.523992000	-1.566138000	-0.945114000
1	-0.377225000	-1.586938000	-0.346653000

$Zn(OAc)_2$

E_{sol}: -522.830553

G_{sol}: -522.768966

8	-1.257564000	-2.279485000	-0.188525000
8	2.567087000	-2.007753000	0.522362000
30	0.669505000	-2.298804000	0.144948000

6	3.224634000	-1.058395000	-0.077235000
6	-1.776181000	-3.229050000	-0.910600000
8	-1.143366000	-4.195519000	-1.347128000
8	2.737568000	-0.280485000	-0.902502000
6	4.683022000	-0.969369000	0.336121000
1	5.166102000	-1.942321000	0.222207000
1	5.213275000	-0.223861000	-0.254648000
1	4.744850000	-0.700819000	1.394156000
6	-3.254642000	-3.049200000	-1.201734000
1	-3.801656000	-2.837657000	-0.280906000
1	-3.387381000	-2.187548000	-1.862077000
1	-3.668721000	-3.933392000	-1.684091000

CH_3COOH

E_{sol}: -229.165128

G_{sol}: -229.131127

8	-1.319045000	-1.674730000	-1.030676000
6	-1.599319000	-2.996538000	-1.021471000
8	-0.735217000	-3.842246000	-0.947415000
6	-3.076076000	-3.249748000	-1.114360000
1	-3.590643000	-2.760134000	-0.284699000
1	-3.467664000	-2.820815000	-2.039533000
1	-3.273105000	-4.318959000	-1.092154000
1	-0.357404000	-1.553363000	-0.970960000

Proline Anion

E_{sol}: -400.822344

$G_{sol:}$ -400.723126

7	2.844156000	0.729803000	1.433009000
6	2.535153000	-0.630251000	1.912506000
6	4.242888000	0.703126000	0.929874000
1	2.202595000	-1.240738000	1.066200000
1	1.723328000	-0.601916000	2.643687000
6	3.858981000	-1.173973000	2.469402000

6	4.883621000	-0.625841000	1.462180000
1	4.774175000	1.567273000	1.335254000
6	4.378150000	0.755110000	-0.611392000
1	3.882543000	-2.264699000	2.550356000
1	4.035907000	-0.758270000	3.467743000
1	5.015065000	-1.337064000	0.640897000
1	5.867634000	-0.454442000	1.903227000
8	3.453521000	0.273009000	-1.313655000
1	2.817503000	1.354708000	2.232733000
8	5.466504000	1.238635000	-1.037882000

Caesium Proline

E_{sol}: -420.671369

$G_{sol:}$ -420.577368

7	2.850335000	0.765846000	1.507175000
6	2.514094000	-0.561094000	2.058614000
6	4.195099000	0.655386000	0.883587000
1	2.042226000	-1.167636000	1.277453000
1	1.799517000	-0.462301000	2.879437000
6	3.856062000	-1.183331000	2.468933000
6	4.779405000	-0.728126000	1.329043000
1	4.825435000	1.464887000	1.259555000
6	4.213446000	0.736970000	-0.658290000
1	3.817029000	-2.271103000	2.577866000
1	4.183271000	-0.759341000	3.424963000
1	4.726322000	-1.443482000	0.501785000
1	5.827215000	-0.651017000	1.625168000
8	3.198457000	0.368956000	-1.304502000
1	2.921017000	1.418226000	2.281087000
8	5.313705000	1.104917000	-1.165020000
55	5.068837000	-1.210895000	-3.557129000

Valine

E_{sol}: -402.513976

$G_{sol:}$ -402.381698

7	-1.768782000	0.728249000	0.647797000
6	-2.810614000	-0.375170000	0.649812000
1	-2.758661000	-0.856383000	1.626115000
6	-4.232700000	0.161655000	0.419584000
6	-2.358829000	-1.409992000	-0.433393000
8	-1.337500000	-1.087851000	-1.099685000
8	-3.057635000	-2.434724000	-0.518372000
1	-2.145982000	1.655929000	0.462043000
1	-1.237809000	0.777055000	1.514678000
1	-4.852866000	-0.739231000	0.412417000
6	-4.396350000	0.857049000	-0.938961000
6	-4.699627000	1.055005000	1.575838000
1	-3.811044000	1.780394000	-1.012467000
1	-4.099074000	0.207197000	-1.765412000
1	-5.441281000	1.136351000	-1.091551000
1	-4.126223000	1.986092000	1.639591000
1	-5.746579000	1.336608000	1.439053000
1	-4.610573000	0.542755000	2.537670000
1	-1.131449000	0.455055000	-0.129459000

Zn- $(Valine)_2$

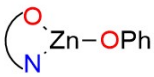
E_{sol}: -869.553114

$G_{sol:}$ -869.291407

7	1.800902000	-0.682267000	0.540950000
6	2.834002000	0.382073000	0.428469000
1	2.687312000	1.035150000	1.295268000
6	4.282587000	-0.149600000	0.467407000
6	2.559126000	1.297368000	-0.799059000
8	1.399597000	1.214519000	-1.346198000
7	-1.800978000	0.682307000	0.540440000
6	-2.833853000	-0.382099000	0.426614000

1	-2.687012000	-1.036231000	1.292597000
6	-4.282569000	0.149149000	0.466124000
6	-2.558613000	-1.295827000	-0.801992000
8	-1.398768000	-1.212542000	-1.348357000
8	-3.448235000	-2.077395000	-1.152966000
8	3.448735000	2.079606000	-1.148533000
1	-2.100141000	1.528140000	0.061586000
1	-1.660680000	0.943430000	1.510750000
1	2.100150000	-1.527816000	0.061648000
1	1.660046000	-0.944060000	1.510996000
1	4.918192000	0.738077000	0.412917000
1	-4.917923000	-0.738615000	0.410209000
6	4.614607000	-1.039241000	-0.738384000
6	4.574134000	-0.873754000	1.787227000
6	-4.614678000	1.040464000	-0.738406000
6	-4.574570000	0.871237000	1.786986000
1	-4.049432000	1.979053000	-0.729180000
1	-4.412044000	0.532765000	-1.684510000
1	-5.672929000	1.314127000	-0.726865000
1	-3.984227000	1.787890000	1.886062000
1	-5.628106000	1.158177000	1.843237000
1	-4.354395000	0.235604000	2.650185000
1	5.672691000	-1.313568000	-0.726869000
1	4.048768000	-1.977488000	-0.730839000
1	4.412640000	-0.529946000	-1.683771000
1	5.627578000	-1.161069000	1.843251000
1	4.353944000	-0.239386000	2.651353000
1	3.983508000	-1.790383000	1.884776000
30	0.000305000	0.000615000	-0.467663000

Int 2



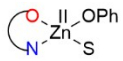
E_{sol}: -773.359050

G_{sol}: -773.172959

8	-1.537794000	-1.430962000	-0.324539000
6	-2.545166000	-0.610387000	-0.040700000
6	-2.442541000	0.455110000	0.882971000
6	-3.797858000	-0.804454000	-0.666938000
6	-3.532445000	1.279698000	1.156963000
1	-1.498360000	0.623578000	1.393921000
6	-4.881123000	0.024165000	-0.386256000
1	-3.894995000	-1.619112000	-1.378473000
6	-4.762201000	1.076748000	0.526561000
1	-3.417369000	2.088868000	1.872909000
1	-5.828654000	-0.152253000	-0.888015000
1	-5.607639000	1.721753000	0.741788000
7	1.566574000	0.520819000	-1.037778000
6	1.023089000	1.908862000	-0.822551000
6	2.913190000	0.431384000	-0.379329000
1	0.226675000	1.861526000	-0.077875000
1	0.592898000	2.284084000	-1.750943000
6	2.205571000	2.727618000	-0.301230000
6	2.993885000	1.691046000	0.504411000
1	3.692402000	0.471458000	-1.143801000
6	3.134961000	-0.856763000	0.437505000
1	1.885213000	3.583167000	0.296599000
1	2.810970000	3.100794000	-1.133120000
1	2.504550000	1.507275000	1.467004000
1	4.027249000	1.974856000	0.701439000
8	2.114303000	-1.600622000	0.685340000
1	1.673808000	0.350514000	-2.031809000
8	4.282654000	-1.078360000	0.835564000

30	0.371258000	-1.083362000	-0.194818000

Int 3



E_{sol}: -906.170187

G_{sol}: -905.945134

7	1.849012000	0.719056000	-1.078365000
6	1.338660000	2.098493000	-0.784887000
6	3.094785000	0.505461000	-0.260333000
1	0.585555000	2.027500000	0.002986000
1	0.862022000	2.508768000	-1.675130000
6	2.561394000	2.870575000	-0.293923000
6	3.292092000	1.814122000	0.541687000
1	3.933941000	0.356011000	-0.942583000
6	3.033438000	-0.732330000	0.657788000
1	2.292398000	3.759179000	0.280953000
1	3.177103000	3.186948000	-1.142191000
1	2.823298000	1.725445000	1.526615000
1	4.348569000	2.030752000	0.697089000
8	1.941312000	-1.402050000	0.690836000
1	2.098663000	0.670100000	-2.060729000
8	4.048976000	-0.985409000	1.318773000
30	0.452788000	-0.855299000	-0.631452000
8	-0.909991000	-1.857143000	-1.610157000
6	-1.929876000	-2.486037000	-1.035221000
6	-1.749849000	-3.376740000	0.047606000
6	-3.250056000	-2.277003000	-1.491924000
6	-2.833500000	-4.018102000	0.642173000
1	-0.741125000	-3.535331000	0.419141000
6	-4.328921000	-2.923301000	-0.892660000
1	-3.406238000	-1.588642000	-2.317087000
6	-4.134984000	-3.797381000	0.181336000

1	-2.661752000	-4.689266000	1.478920000
1	-5.333307000	-2.735969000	-1.262042000
1	-4.978632000	-4.292552000	0.650327000
6	-1.965268000	-0.317443000	1.454192000
7	-0.959026000	-0.087245000	0.942555000
6	-3.232719000	-0.621330000	2.084152000
1	-3.919375000	0.218351000	1.965155000
1	-3.659765000	-1.509254000	1.610707000
1	-3.085159000	-0.817071000	3.147470000

Zinc Metal

E_{sol}: -458.074640

G_{sol} : -458.090517

30	-0.349576000	0.444915000	0.000000000

Et_2Zn

E_{sol}: -224.078580

G_{sol}: -223.987448

30	-0.350929000	0.450096000	0.275264000
6	1.714000000	0.205131000	0.126226000
1	2.039810000	-0.616168000	0.779421000
1	2.218424000	1.105066000	0.504897000
6	2.156389000	-0.071136000	-1.321540000
1	1.859752000	0.741863000	-1.994007000
1	3.244261000	-0.194413000	-1.432300000
1	1.692681000	-0.981984000	-1.716991000
6	-2.416206000	0.686677000	0.106241000
1	-2.922100000	-0.189023000	0.536312000
1	-2.743881000	1.545651000	0.707962000
6	-2.853185000	0.875262000	-1.357106000
1	-2.553498000	0.023545000	-1.978344000
1	-3.940691000	0.990903000	-1.479155000
1	-2.388474000	1.761136000	-1.804694000

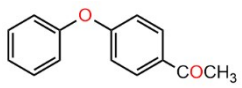
$C_2H_5^-$

E_{sol}: -79.270866

$G_{sol:}$ -79.235339

6	-3.942993000	1.643593000	-0.054633000
1	-3.615884000	2.158555000	0.868214000
1	-5.048003000	1.652046000	-0.006766000
6	-3.450419000	0.183526000	-0.015609000
1	-2.352693000	0.124328000	-0.024152000
1	-3.772171000	-0.422859000	0.858555000
1	-3.780147000	-0.381097000	-0.899494000

P_1



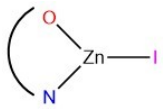
E_{sol}: -691.358323

$G_{sol:}$ -691.179227

6	-2.621266000	-0.128564000	-0.014842000
6	-1.529616000	-1.007505000	-0.077293000
6	-0.222121000	-0.542394000	-0.064966000
6	0.010859000	0.835473000	0.013196000
6	-1.061283000	1.731637000	0.074207000
6	-2.361530000	1.251163000	0.059688000
1	-1.718547000	-2.072873000	-0.136882000
1	0.606594000	-1.237061000	-0.115409000
1	-0.856731000	2.794462000	0.132286000
1	-3.174909000	1.964946000	0.107917000
6	-4.002299000	-0.682955000	-0.030156000
8	-4.196222000	-1.892034000	-0.094473000
6	-5.172782000	0.275292000	0.035268000
1	-5.156247000	0.971221000	-0.808159000
1	-6.103690000	-0.289216000	0.014496000

1	-5.137380000	0.875040000	0.949072000
8	1.259380000	1.395606000	0.028274000
6	2.383901000	0.568820000	0.018638000
6	3.015799000	0.306205000	-1.191732000
6	2.881710000	0.078315000	1.221551000
6	4.176109000	-0.468731000	-1.195032000
1	2.600461000	0.705789000	-2.110010000
6	4.041060000	-0.696931000	1.207603000
1	2.364488000	0.303654000	2.147431000
6	4.688711000	-0.971554000	0.001712000
1	4.677852000	-0.677694000	-2.133731000
1	4.438312000	-1.083058000	2.140181000
1	5.591020000	-1.573422000	-0.004663000

P_2



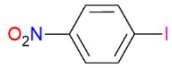
E_{sol}: -477.824369

$G_{sol:}$ -477.727586

7	-1.599847000	0.721629000	0.874563000
6	-1.640538000	2.143115000	0.366001000
6	-2.783589000	-0.014800000	0.326427000
1	-0.764128000	2.314310000	-0.260617000
1	-1.597822000	2.838870000	1.203693000
6	-2.933357000	2.247370000	-0.452234000
6	-3.170641000	0.806082000	-0.914286000
1	-3.601418000	0.005078000	1.050722000
6	-2.492414000	-1.487022000	-0.023350000
1	-2.837330000	2.951401000	-1.280764000
1	-3.762650000	2.579679000	0.178937000
1	-2.504306000	0.556176000	-1.747431000
1	-4.195083000	0.605859000	-1.226938000

8	-1.261325000	-1.831095000	-0.165506000
1	-1.637073000	0.714915000	1.888479000
8	-3.462710000	-2.232791000	-0.187857000
30	0.128242000	-0.392879000	0.264397000
53	2.720132000	0.085119000	-0.129214000

Substituted Aryl Halides



E_{sol}: -447.661701

$G_{sol:}$ -447.606155

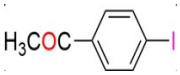
6	-0.264645000	1.216694000	0.000086000
6	0.420249000	0.000000000	0.000055000
6	-0.264645000	-1.216694000	0.000085000
6	-1.654762000	-1.218132000	0.000148000
6	-2.329991000	0.000000000	0.000184000
6	-1.654762000	1.218132000	0.000148000
1	0.270759000	2.157155000	0.000062000
1	0.270759000	-2.157155000	0.000060000
1	-2.204432000	-2.149277000	0.000172000
1	-2.204432000	2.149277000	0.000173000
53	2.547660000	0.000000000	-0.000042000
7	-3.799436000	0.000000000	0.000256000
8	-4.379452000	1.082638000	-0.000269000
8	-4.379452000	-1.082638000	-0.000268000

E_{sol}: -335.363429

$G_{sol:}$ -335.309562

6	0.636867000	1.215398000	0.000000000
6	-0.048057000	0.000000000	0.000000000
6	0.636867000	-1.215398000	0.000000000
6	2.027178000	-1.215360000	0.000000000

6	2.727135000	0.000000000	0.000000000
6	2.027178000	1.215360000	0.000000000
1	0.101185000	2.156255000	0.000000000
1	0.101185000	-2.156255000	0.000000000
1	2.565255000	-2.155787000	0.000000000
1	2.565255000	2.155787000	0.000000000
53	-2.179326000	0.000000000	0.000000000
6	4.156521000	0.000000000	0.000000000
7	5.312749000	0.000000000	0.000000000



E_{sol}: -395.788097

$G_{sol:}$ -395.698347

6	-0.203413000	1.247705000	0.000018000
6	0.458134000	0.018274000	-0.000010000
6	-0.251391000	-1.180606000	-0.000058000
6	-1.644058000	-1.145919000	-0.000058000
6	-2.331917000	0.074519000	-0.000007000
6	-1.592752000	1.266039000	-0.000001000
1	0.351813000	2.177631000	0.000047000
1	0.264501000	-2.132543000	-0.000105000
1	-2.179983000	-2.087170000	-0.000090000
1	-2.119178000	2.213124000	0.000020000
8	-4.393936000	1.233604000	-0.000052000
6	-3.827237000	0.149848000	-0.000002000
6	-4.621358000	-1.136576000	0.000081000
1	-4.385528000	-1.741312000	0.880334000
1	-5.685104000	-0.904614000	-0.000013000
1	-4.385386000	-1.741520000	-0.879986000
53	2.591968000	-0.026644000	0.000008000

E_{sol}: -243.089933

G_{sol}: -243.032091

6	-1.261384000	-1.214879000	0.000000000
6	-0.578822000	0.000000000	0.000000000
6	-1.261384000	1.214879000	0.000000000
6	-2.657628000	1.206165000	0.000000000
6	-3.357558000	0.000000000	0.000000000
6	-2.657628000	-1.206165000	0.000000000
1	-0.723481000	-2.155202000	0.000000000
1	-0.723481000	2.155202000	0.000000000
1	-3.193185000	2.149857000	0.000000000
1	-3.193185000	-2.149857000	0.000000000
53	1.564565000	0.000000000	0.000000000
1	-4.442169000	0.000000000	0.000000000

E_{sol}: -282.41829

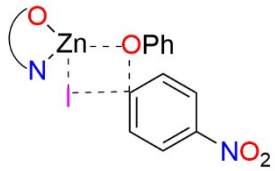
$G_{sol:}$ -282.336000

6	-0.001637000	0.864210000	-1.210645000
6	-0.000805000	0.176140000	0.000000000
6	-0.001637000	0.864210000	1.210645000
6	-0.001637000	2.259362000	1.198982000
6	0.001503000	2.980458000	0.000000000
6	-0.001637000	2.259362000	-1.198982000
1	-0.005645000	0.331459000	-2.154160000
1	-0.005645000	0.331459000	2.154160000
1	-0.005640000	2.790260000	2.146495000
1	-0.005640000	2.790260000	-2.146495000
53	-0.005697000	-1.967042000	0.000000000
6	0.034216000	4.488583000	0.000000000

1	-0.456189000	4.900732000	0.884901000
1	1.066683000	4.854383000	0.000000000
1	-0.456189000	4.900732000	-0.884901000

Transition State

TS_1



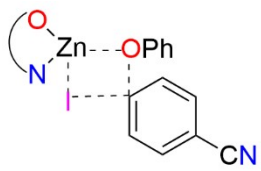
E_{sol}: -1220.992356

G_{sol}: -1220.728735

8	-0.114707000	0.842424000	-1.102579000
6	-0.882899000	1.971560000	-0.862668000
6	-1.123121000	2.403774000	0.444173000
6	-1.428396000	2.660396000	-1.946570000
6	-1.906697000	3.535143000	0.662988000
1	-0.691389000	1.852001000	1.271209000
6	-2.207534000	3.794103000	-1.720575000
1	-1.234233000	2.301803000	-2.950993000
6	-2.451102000	4.232174000	-0.417266000
1	-2.090429000	3.872328000	1.677783000
1	-2.627370000	4.333621000	-2.563106000
1	-3.059792000	5.113335000	-0.244498000
7	2.769589000	0.902017000	1.476974000
6	2.292341000	-0.125256000	2.441517000
6	4.215350000	0.599956000	1.238327000
1	1.203257000	-0.134341000	2.470234000
1	2.665499000	0.102205000	3.445555000
6	2.924588000	-1.401517000	1.895030000
6	4.321529000	-0.946563000	1.414824000
1	4.824470000	1.108064000	1.988100000

6	4.705879000	1.049438000	-0.149577000
1	2.338110000	-1.774503000	1.050241000
1	2.970550000	-2.193993000	2.642553000
1	4.603717000	-1.438065000	0.482609000
1	5.092486000	-1.178351000	2.149800000
8	3.816209000	1.221210000	-1.065605000
1	2.666300000	1.835420000	1.867093000
8	5.921803000	1.173670000	-0.314789000
53	0.222225000	-1.882008000	-2.360667000
6	-1.057666000	-0.608767000	-0.836850000
6	-0.878226000	-1.031970000	0.513046000
6	-2.386216000	-0.385394000	-1.304286000
6	-1.951808000	-1.155275000	1.357108000
1	0.118013000	-1.256831000	0.866681000
6	-3.454653000	-0.521012000	-0.453102000
1	-2.544281000	-0.093185000	-2.333830000
6	-3.256211000	-0.893982000	0.891166000
1	-1.799155000	-1.458451000	2.384755000
1	-4.458580000	-0.340608000	-0.814735000
30	1.891824000	0.965973000	-0.490271000
7	-4.361857000	-1.009639000	1.770246000
8	-5.508762000	-0.776865000	1.340125000
8	-4.163725000	-1.335624000	2.957637000

TS_2



E_{sol}: -1108.688640

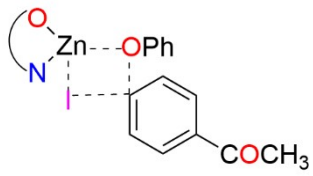
G_{sol}: -1108.428548

8	-0.279816000	0.838912000	-0.997123000
6	-0.955691000	1.986943000	-0.675454000

6	-0.961863000	2.468162000	0.639218000
6	-1.674824000	2.658527000	-1.669535000
6	-1.668521000	3.627946000	0.950411000
1	-0.405812000	1.928416000	1.397599000
6	-2.379858000	3.817599000	-1.351242000
1	-1.662210000	2.268570000	-2.680884000
6	-2.380139000	4.305208000	-0.042392000
1	-1.665685000	4.001868000	1.969073000
1	-2.930165000	4.340849000	-2.126468000
1	-2.930044000	5.207857000	0.201925000
7	2.777267000	0.524487000	1.236927000
6	2.551848000	-0.730795000	2.037926000
6	4.241358000	0.608093000	0.898834000
1	2.117965000	-1.490680000	1.384622000
1	1.845129000	-0.529401000	2.842709000
6	3.942231000	-1.160602000	2.505238000
6	4.821050000	-0.757471000	1.317339000
1	4.696613000	1.398576000	1.499442000
6	4.530656000	0.938159000	-0.578122000
1	3.990635000	-2.227165000	2.733153000
1	4.234038000	-0.606182000	3.402791000
1	4.708783000	-1.480527000	0.502631000
1	5.881437000	-0.683701000	1.556051000
8	3.540728000	0.965282000	-1.399837000
1	2.531570000	1.326212000	1.808231000
8	5.709000000	1.138257000	-0.886699000
53	0.316294000	-2.008897000	-1.939604000
6	-1.338706000	-0.658474000	-0.659502000
6	-1.301226000	-0.927593000	0.714353000
6	-2.551925000	-0.509598000	-1.340557000
6	-2.491529000	-1.062897000	1.406766000
1	-0.352583000	-1.030346000	1.223863000

6	-3.737068000	-0.652863000	-0.638449000
1	-2.562806000	-0.290831000	-2.399848000
6	-3.726275000	-0.930279000	0.741797000
1	-2.466297000	-1.271963000	2.470551000
1	-4.680209000	-0.548108000	-1.163393000
30	1.697574000	0.682497000	-0.614977000
6	-4.946423000	-1.068448000	1.456574000
7	-5.942022000	-1.178533000	2.040050000

TS_3



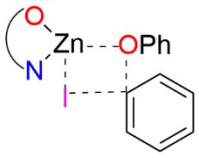
E_{sol}: -1169.112465

$G_{sol:}$ -1168.815460

8	-0.274306000	0.826229000	-1.018761000
6	-0.953692000	1.973866000	-0.710002000
6	-0.959324000	2.473775000	0.597998000
6	-1.681593000	2.627522000	-1.710184000
6	-1.673125000	3.632764000	0.895714000
1	-0.398772000	1.947189000	1.362374000
6	-2.393936000	3.785666000	-1.405480000
1	-1.670475000	2.223324000	-2.715975000
6	-2.393273000	4.291450000	-0.103484000
1	-1.669778000	4.020353000	1.909295000
1	-2.951145000	4.293797000	-2.185906000
1	-2.949172000	5.193198000	0.130454000
7	2.765948000	0.524409000	1.230540000
6	2.550569000	-0.731269000	2.031905000
6	4.232179000	0.627412000	0.906189000
1	2.149994000	-1.503740000	1.372142000
1	1.820011000	-0.542310000	2.818251000

6	3.939191000	-1.125051000	2.534070000
6	4.834146000	-0.717995000	1.359457000
1	4.665162000	1.439447000	1.494253000
6	4.531737000	0.932590000	-0.574376000
1	4.006067000	-2.187297000	2.777041000
1	4.199384000	-0.552885000	3.430335000
1	4.757744000	-1.455921000	0.554036000
1	5.886917000	-0.615371000	1.620245000
8	3.548997000	0.938528000	-1.405015000
1	2.505156000	1.323412000	1.799012000
8	5.711358000	1.136063000	-0.876054000
53	0.324574000	-2.030735000	-1.953329000
6	-1.338096000	-0.678255000	-0.659037000
6	-1.283474000	-0.940200000	0.715017000
6	-2.554295000	-0.536329000	-1.329129000
6	-2.470370000	-1.073355000	1.412086000
1	-0.328534000	-1.037914000	1.214183000
6	-3.730961000	-0.679391000	-0.607357000
1	-2.576217000	-0.322291000	-2.389356000
6	-3.720485000	-0.948224000	0.773894000
1	-2.441657000	-1.276495000	2.476786000
1	-4.667247000	-0.575334000	-1.143399000
6	-4.958093000	-1.088919000	1.567690000
8	-4.921205000	-1.324575000	2.775053000
6	-6.296231000	-0.931117000	0.871183000
1	-6.386129000	0.057310000	0.411818000
1	-6.415277000	-1.669773000	0.073540000
1	-7.097600000	-1.059994000	1.597380000
30	1.700427000	0.661907000	-0.630016000

TS_4



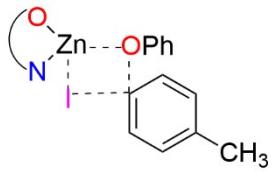
E_{sol}: -1016.409809

G_{sol}: -1016.145029

8	-0.248927000	0.894527000	-1.023895000
6	-0.918294000	2.030197000	-0.696161000
6	-0.916500000	2.516844000	0.618920000
6	-1.667688000	2.695110000	-1.676532000
6	-1.636854000	3.664730000	0.941430000
1	-0.345311000	1.983972000	1.371364000
6	-2.386970000	3.842005000	-1.347442000
1	-1.667644000	2.304161000	-2.687897000
6	-2.375785000	4.331458000	-0.038963000
1	-1.625672000	4.037242000	1.960841000
1	-2.959331000	4.354646000	-2.114118000
1	-2.937610000	5.224341000	0.214290000
7	2.778203000	0.506130000	1.230922000
6	2.563887000	-0.749833000	2.032225000
6	4.242131000	0.606507000	0.897527000
1	2.147732000	-1.517589000	1.376626000
1	1.845855000	-0.557194000	2.829165000
6	3.956096000	-1.155600000	2.515532000
6	4.840656000	-0.745610000	1.334076000
1	4.683280000	1.410998000	1.489982000
6	4.532743000	0.922390000	-0.582681000
1	4.019427000	-2.219912000	2.750312000
1	4.230130000	-0.591374000	3.412705000
1	4.750422000	-1.476956000	0.524079000
1	5.896904000	-0.651412000	1.583899000
8	3.546294000	0.924876000	-1.408115000
1	2.522391000	1.305505000	1.801052000

8	5.710106000	1.135088000	-0.888422000
53	0.370986000	-2.029326000	-1.968977000
6	-1.398124000	-0.661074000	-0.631429000
6	-1.331636000	-0.928289000	0.724834000
6	-2.580886000	-0.513553000	-1.331841000
6	-2.538494000	-1.097466000	1.408329000
1	-0.380638000	-1.015937000	1.232994000
6	-3.773308000	-0.692561000	-0.623618000
1	-2.584471000	-0.279976000	-2.388083000
6	-3.760160000	-0.984219000	0.741397000
1	-2.509546000	-1.318326000	2.470854000
1	-4.714610000	-0.599117000	-1.156358000
30	1.698524000	0.646196000	-0.622888000
1	-4.691434000	-1.116644000	1.280737000

TS_5



E_{sol}: -1055.736348

$G_{sol:}$ -1055.448342

8	-0.235195000	0.905072000	-1.032384000
6	-0.904645000	2.038830000	-0.703458000
6	-0.902664000	2.525579000	0.611900000
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1	-0.330244000	1.993359000	1.363904000
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6	4.249553000	0.603800000	0.895031000
1	2.146348000	-1.511406000	1.378439000
1	1.846809000	-0.544678000	2.827220000
6	3.955037000	-1.152375000	2.517702000
6	4.842267000	-0.749478000	1.335795000
1	4.692640000	1.407900000	1.486618000
6	4.543932000	0.915863000	-0.585323000
1	4.014063000	-2.216160000	2.755991000
1	4.230374000	-0.586312000	3.413324000
1	4.749599000	-1.482744000	0.527796000
1	5.898696000	-0.658919000	1.586218000
8	3.558995000	0.920893000	-1.412495000
1	2.530416000	1.311645000	1.792597000
8	5.722705000	1.123601000	-0.889221000
53	0.389137000	-2.027510000	-1.976948000
6	-1.395200000	-0.658415000	-0.635871000
6	-1.331131000	-0.919822000	0.719645000
6	-2.576448000	-0.508519000	-1.331840000
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1	-0.382358000	-1.003849000	1.232691000
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1	-2.585802000	-0.272360000	-2.387555000
6	-3.774426000	-0.972115000	0.749751000
1	-2.505757000	-1.296193000	2.466084000
1	-4.707194000	-0.584067000	-1.155674000
30	1.708854000	0.646975000	-0.630378000
6	-5.067638000	-1.182104000	1.500302000
1	-5.018570000	-0.763271000	2.508906000

1	-5.910790000	-0.717134000	0.984249000
1	-5.297668000	-2.248070000	1.605295000

Cross-Coupled Product

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$G_{sol:}$ -743.089381

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6	-0.032173000	0.844951000	0.011948000
6	-1.099279000	1.754556000	0.052524000
6	-2.401145000	1.291402000	0.042679000
1	-1.781187000	-2.060444000	-0.090570000
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1	-0.885526000	2.815700000	0.091696000
1	-3.232662000	1.981951000	0.074219000
8	1.211963000	1.394561000	0.024011000
6	2.336960000	0.562645000	0.013822000
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6	2.856063000	0.109197000	1.221254000
6	4.098318000	-0.515283000	-1.204917000
1	2.507696000	0.637143000	-2.122679000
6	4.013109000	-0.669664000	1.206381000
1	2.358965000	0.365368000	2.150005000
6	4.634082000	-0.982783000	-0.003968000
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1	4.428904000	-1.028342000	2.141702000
1	5.534485000	-1.587384000	-0.010793000
7	-4.004056000	-0.580330000	-0.016582000
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8 -4.922427000 0.239983000 0.018916000

E_{sol}: -630.934457

$G_{sol:}$ -630.791681

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6 -0.456914000 0.774268000 0.022430000

6 -1.546324000 1.652048000 0.086632000

6 -2.836680000 1.153100000 0.067086000

1 -2.117347000 -2.175044000 -0.148496000

1 0.180827000 -1.284697000 -0.115027000

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1 -3.679515000 1.832271000 0.117300000

8 0.777627000 1.358109000 0.044576000

6 1.919798000 0.553668000 0.022824000

6 2.539007000 0.295752000 -1.194912000

6 2.442757000 0.082035000 1.222180000

6 3.714035000 -0.456461000 -1.208897000

1 2.103359000 0.680870000 -2.109908000

6 3.617194000 -0.670044000 1.197176000

1 1.934064000 0.304242000 2.153468000

6 4.252918000 -0.940426000 -0.015895000

1 4.206794000 -0.662305000 -2.152978000

1 4.035084000 -1.041444000 2.126645000

1 5.166722000 -1.524483000 -0.030934000

6 -4.382968000 -0.751395000 -0.035443000

7 -5.461905000 -1.169892000 -0.049921000

E_{sol}: -538.657727

$G_{sol:}$ -538.511422

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6	2.263392000	-1.055618000	0.679048000
6	3.514406000	-0.442833000	0.616444000
1	2.761827000	2.122531000	-1.480328000
1	0.538418000	1.031704000	-1.384608000
1	2.100519000	-1.945105000	1.277284000
1	4.342447000	-0.862672000	1.177914000
8	0.000062000	-1.207293000	0.000430000
6	-1.199368000	-0.516367000	0.041550000
6	-2.262870000	-1.055383000	-0.679631000
6	-1.372958000	0.625398000	0.824969000
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6	-2.626498000	1.233626000	0.872723000
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6	-3.700553000	0.704946000	0.154506000
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1	-2.762759000	2.121575000	1.481199000
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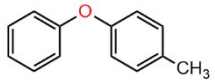
1	4.673336000	1.182726000	-0.198228000



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6	-0.701364000	0.729815000	-0.108969000
6	-1.556514000	1.114583000	0.915294000
6	-2.859944000	0.614355000	0.944133000
1	-2.767851000	-1.321765000	-1.834948000
1	-0.455420000	-0.432732000	-1.899387000
1	-1.202110000	1.800214000	1.676991000
1	-3.525042000	0.921366000	1.745536000
8	0.568696000	1.294183000	-0.163686000
6	1.677942000	0.481910000	-0.035684000
6	2.888130000	1.019461000	-0.479032000
6	1.635390000	-0.788374000	0.541658000
6	4.060252000	0.279903000	-0.344693000
1	2.894428000	2.009098000	-0.922430000
6	2.817718000	-1.519983000	0.666124000
1	0.696080000	-1.201077000	0.888773000
6	4.032246000	-0.994929000	0.226146000
1	4.998046000	0.701187000	-0.691858000
1	2.782495000	-2.507360000	1.114991000
1	4.946002000	-1.570482000	0.326218000
6	-4.718020000	-0.837650000	0.009822000
1	-5.192004000	-0.806889000	-0.975027000
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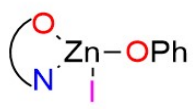
HAT



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6	-2.608510000	0.909945000	1.700945000
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6	-4.214797000	0.778013000	-0.153376000
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1	-4.479436000	1.992793000	1.616320000
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6	1.798199000	1.810480000	0.584923000
1	3.520556000	0.819711000	-0.268050000
6	2.600707000	-0.577842000	1.057066000
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1	2.165186000	3.053108000	-1.152490000
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1	2.469859000	2.400293000	1.207764000
8	1.889151000	-1.631314000	0.871356000
1	2.350621000	0.020912000	-1.966979000
8	3.356246000	-0.394255000	2.018177000
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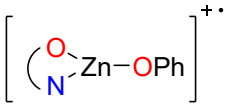
53	1.174806000	-3.140373000	-3.122410000



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6	-3.937437000	-0.858307000	-0.592445000
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1	-1.509044000	0.798768000	1.238249000
6	-5.015324000	-0.077075000	-0.261892000
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6	1.256620000	1.908182000	-0.954689000
6	3.001577000	0.336072000	-0.278234000
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6	2.412689000	2.663443000	-0.295740000
6	3.039107000	1.595535000	0.605573000
1	3.852458000	0.343486000	-0.962637000
6	3.085379000	-0.959033000	0.552007000
1	2.069946000	3.542021000	0.253822000
1	3.134753000	2.993164000	-1.048840000
1	2.426091000	1.444758000	1.500909000
1	4.053971000	1.827418000	0.926764000
8	2.009563000	-1.652064000	0.697646000

1	1.919838000	0.263157000	-2.042129000
8	4.176682000	-1.235768000	1.055213000
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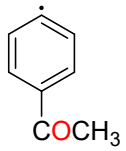

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1	-2.354634000	2.283331000	-0.000253000
1	0.112286000	2.111295000	-0.000388000
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8	2.144312000	-1.319546000	-0.000363000
6	1.630597000	-0.209341000	-0.000077000
6	2.490720000	1.034555000	0.000415000
1	2.287118000	1.650278000	0.880895000
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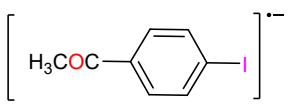

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Multiplicity : 2

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6	-1.653317000	-1.158928000	-0.000327000
6	-2.390789000	0.076460000	-0.000148000
6	-1.602170000	1.280538000	-0.000223000
1	0.340687000	2.188439000	-0.000293000
1	0.252071000	-2.143167000	-0.000518000
1	-2.182733000	-2.107741000	-0.000517000
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8	-4.464716000	1.256952000	0.000177000
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6	-4.621991000	-1.158933000	0.000341000
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1	-4.409703000	-1.782633000	-0.881608000
53	2.614632000	-0.025135000	0.000112000

I

E_{sol}: -11.571193

$G_{sol:}$ -11.588041

53	0.000000000	0.000000000	0.000000000

I·

E_{sol}: -11.364334

$G_{sol:}$ -11.381837

53	0.000000000	0.000000000	0.000000000

Justification for chosen computational methodology for both Mn and Zn catalysed cross coupling reactions

For modelling transition metal catalysis, the choice of computational methodology might depend on the nature of transition metal involved. In the present study, for the model systems involving Mn-catalysts, B3LYP functional employing SDD basis sets for Mn and Iodine atoms emerged as the suitable computational methodology. However, for Zn-catalyzed model system, B3LYP functional employing LANL2DZ for Zn and Iodine atoms emerged as the suitable one. We tried to optimize the model system for Zn-catalyzed cross-coupling reaction using SDD basis set. Howbeit, the activation barrier obtained does not concord with the experimental temperature

requirements (145^0C), as it tend to underestimate the activation barrier (29.1 kcal/mol) when SDD basis set is employed. Thus, we have used slightly different computational methodologies for the Mn and Zn catalyzed counter parts.

Basis set	LANL2DZ	SDD
Activation Barrier ($\Delta G^{\ddagger}$)	35.0 kcal/mol	29.1 kcal/mol

Table S1 : Justification for using SDD basis set for Zn atom in this study as SDD basis set tend to under-estimate the activation barrier in comparison to LANL2DZ.