Supporting Information

Mapping the molecular mechanism of zinc catalyzed Suzuki-Miyaura coupling reaction: A computational study

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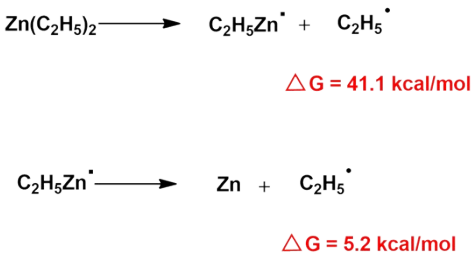
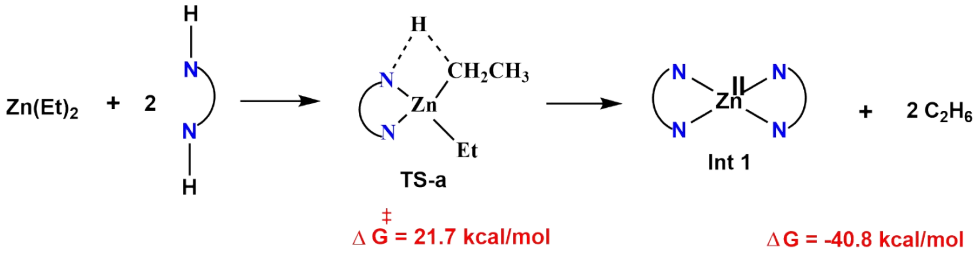
Reference

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.

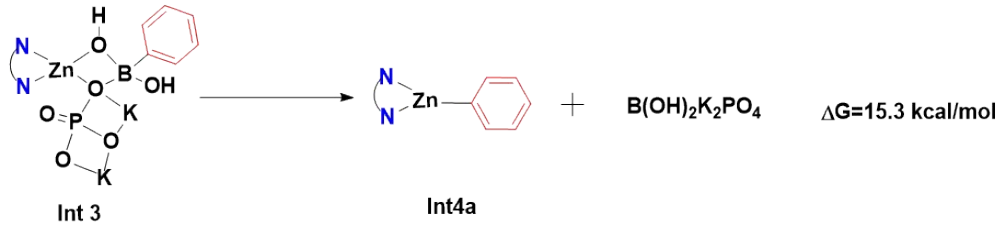
Thermal Decomposition of Diethyl Zinc



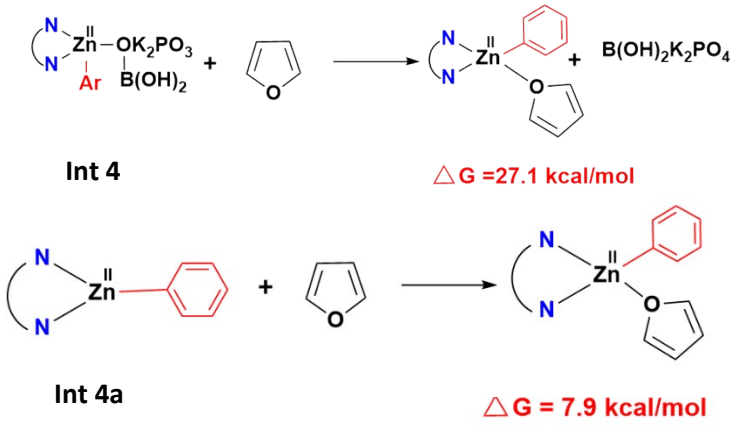
Scheme S.1: Free energy change accompanying the thermal decomposition of diethyl zinc.



Scheme S.2: Formation of Int 1 from diethyl zinc via TS-a



Scheme S3 Free energy changes accompanying formation of conventional transmetalation intermediate (**Int 4a**).



Scheme S4 Free energy changes accompanying the coordination by THF on **Int4 and Int4a**

Single Electron Transfer Mechanism

The Single Electron Transfer (SET) mechanism refers to a process in organic chemistry in which a single electron is transferred from a donor species to an acceptor, generating reactive radical intermediates. Distinct from conventional reactions involving electron pair transfer, SET operates through the transfer of electrons, facilitating a variety of radical-based transformations. This mechanism plays a key role in numerous organic reactions, particularly those mediated by transition metals where it enables bond formation or cleavage via radical intermediates. We computed the activation barrier for the SET mechanism using the Marcus-Hush Model (Outer Sphere Mechanism) and the Saveant model.

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

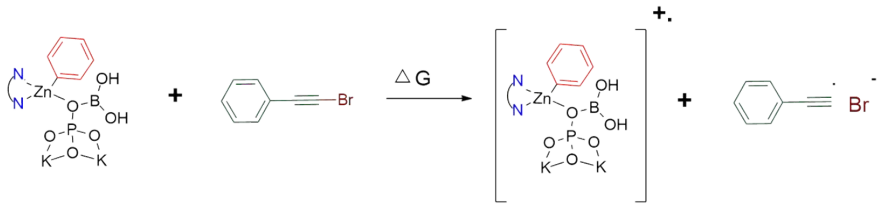
$\lambda_i \approx 0$.

The solvent reorganization energy λ_0 can be calculated with:

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

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

where a_1 and a_2 are the radii of the reactant molecules ($a1$= 4.31 A°, $a2$= 5.48 A°) and R = $a_1 + a_2$.
ΔG_r is the reaction energy.
ε_{op} is the optical dielectric constant (ε_{op} =1.97), and ε is the static dielectric constant (ε=7.42).



Int 4 **Int 5**

Scheme S5 Free energy changes accompanying the SET mechanism for Zn-catalyzed SMC.

$\Delta G^{\#} = \frac{\lambda}{4}\left[1 + \frac{\Delta G_r}{\lambda}\right]^2$ = 25.9 kcal/mol [**ΔGr = 23.7 kcal/mol**]

B) Estimation of the Activation barrier by Savéant's model

In Savéant's model, the intrinsic barrier $\Delta G^{\ddagger}_0$ includes contribution from bond dissociation free energy (BDFE).

$$\Delta G^{\ddagger}_0 = \frac{\lambda}{4} = \frac{\lambda i + \lambda + BDFE}{4}$$

λ_0 and λ_i are the same as in the Marcus-Hush theory. Thus, $\lambda = \lambda_0 + \lambda_i + BDFE = 0 + 12.93 + 69.80 = 82.73$ kcal/mol, $\Delta G^{\ddagger}_0 = 18.93$ kcal/mol.

$$\Delta G^{\#} = \frac{\lambda}{4}\left[1 + \frac{\Delta G_r}{\lambda}\right]^2$$ = 38.42 kcal/mol

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

(A) 1- bromophenyl acetylene

E sol = -320.961248 a.u

G sol = -320.895543 a.u

6	0.053487000	0.000123000	-0.000226000
6	-1.376772000	0.000058000	-0.000196000
6	-2.089526000	1.216824000	-0.000141000
6	-2.089395000	-1.216773000	-0.000123000
6	-3.485162000	1.211502000	-0.000063000
1	-1.543761000	2.155781000	-0.000163000
6	-3.485047000	-1.211603000	-0.000051000
1	-1.543555000	-2.155685000	-0.000152000
6	-4.186841000	-0.000093000	-0.000029000
1	-4.025562000	2.154241000	-0.000037000
1	-4.025317000	-2.154416000	-0.000014000
1	-5.273434000	-0.000128000	0.000055000
6	1.266813000	0.000162000	-0.000161000
35	3.107608000	-0.000028000	0.000179000

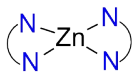
(B) Aryl Boronic Acid

E sol = -408.295078 a.u

G sol = -408.202858 a.u

5	3.101556000	-1.985498000	-6.352310000
6	3.848957000	-3.332586000	-6.675472000
6	3.710198000	-3.961707000	-7.929232000
6	4.681963000	-3.952760000	-5.722483000
6	4.367992000	-5.160567000	-8.219209000
1	3.065083000	-3.524988000	-8.689555000
6	5.353166000	-5.145333000	-6.007768000
1	4.829804000	-3.493078000	-4.746882000
6	5.194387000	-5.753567000	-7.258034000
1	4.236546000	-5.631116000	-9.190252000
1	5.998047000	-5.598121000	-5.258986000
1	5.711310000	-6.683226000	-7.481952000
8	2.732241000	-1.618536000	-5.080547000
8	2.758742000	-1.067964000	-7.316173000
1	2.896969000	-2.298383000	-4.411453000
1	3.090138000	-1.283512000	-8.199727000

(C). Int1



E sol = -602.745086 a.u

G sol = -602.478493 a.u

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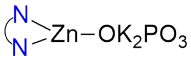
7	1.452783000	1.529230000	-0.397530000
1	1.519791000	2.247927000	0.324915000
6	2.781507000	-0.100381000	0.877219000
1	3.758362000	-0.618315000	0.896800000
1	2.780395000	0.594996000	1.734372000
6	2.716995000	0.759032000	-0.406856000
1	3.592044000	1.422694000	-0.502340000
1	2.691210000	0.106150000	-1.287643000
6	1.911396000	-2.267868000	0.281469000
1	2.829086000	-2.783341000	0.628271000
1	1.072817000	-2.959112000	0.437600000
1	2.021790000	-2.150781000	-0.819701000
6	1.135964000	2.180620000	-1.676252000
1	0.204423000	2.745620000	-1.573700000
1	1.932004000	2.860510000	-2.015411000
1	0.992531000	1.412254000	-2.442887000
7	-1.063531000	-0.705333000	-1.427525000
7	-1.780066000	0.720295000	0.944194000
1	-0.531788000	-0.538036000	-2.278972000
6	-2.237374000	0.204494000	-1.407140000
1	-3.012490000	-0.137560000	-2.110462000
1	-1.881097000	1.186835000	-1.736536000
6	-2.811466000	0.336104000	0.009674000
1	-3.633215000	1.080997000	-0.040127000
1	-3.309026000	-0.621845000	0.290618000
6	-2.283316000	0.799366000	2.296791000
1	-1.473508000	1.065286000	2.988914000
1	-3.077173000	1.567449000	2.411098000
1	-2.727139000	-0.154318000	2.663900000
6	-1.424183000	-2.134408000	-1.373789000
1	-2.147742000	-2.409860000	-2.155435000
1	-0.518643000	-2.734842000	-1.490750000
1	-1.860502000	-2.361952000	-0.397115000

(D). Int2



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G sol = -1032.967096 a.u

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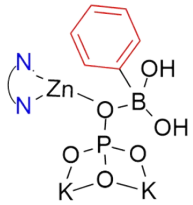
6	3.202056000	-0.528319000	1.367605000
1	3.978442000	-1.225735000	1.732697000
1	3.104930000	0.259444000	2.134250000
6	3.728623000	0.148831000	0.079637000
7	2.734608000	1.148987000	-0.373713000
1	4.718383000	0.608693000	0.231072000
1	3.821423000	-0.598013000	-0.717573000
1	2.761129000	1.944832000	0.265366000
6	2.071683000	-2.539029000	0.661289000
1	1.083217000	-2.999621000	0.527553000
1	2.582487000	-2.599648000	-0.323914000
1	2.647038000	-3.192526000	1.347100000
6	2.948185000	1.636815000	-1.745974000
1	2.812446000	0.804022000	-2.442938000
1	2.201032000	2.402070000	-1.975707000
1	3.954037000	2.058163000	-1.891075000
8	-1.951777000	1.902058000	-1.852266000
15	-1.611988000	0.835273000	-0.800728000
8	-2.857801000	0.131562000	-0.168779000
8	-0.627225000	-0.309258000	-1.384691000
8	-0.699860000	1.424041000	0.397803000
19	-2.255363000	-2.457224000	-1.006319000
19	-2.410073000	0.939820000	2.462123000

(E) Int 3a



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G sol = -1441.191441 a.u

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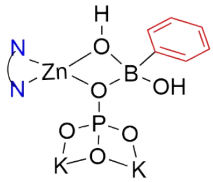
1	-1.329725000	-2.616403000	-0.224560000
8	-0.208762000	-0.265293000	-0.856916000
8	-2.497291000	-0.772308000	-1.569619000
1	-2.076183000	-1.491599000	-2.085693000
6	-2.126621000	0.561947000	0.588659000
6	-2.317270000	0.396862000	1.974619000
6	-2.286831000	1.869421000	0.081662000
6	-2.640083000	1.470707000	2.811899000
1	-2.212813000	-0.598413000	2.399914000
6	-2.602286000	2.957057000	0.908198000
1	-2.168685000	2.042898000	-0.986400000

6	-2.778962000	2.759188000	2.281644000
1	-2.778055000	1.306095000	3.878641000
1	-2.715674000	3.951362000	0.481291000
1	-3.022967000	3.597049000	2.930427000
30	0.703911000	1.290028000	0.044508000
7	1.764250000	1.227914000	1.721911000
6	3.137872000	1.558862000	1.375825000
6	1.356145000	1.832458000	2.974529000
6	3.494313000	1.028168000	-0.025538000
1	3.855938000	1.112189000	2.091105000
1	3.325611000	2.654890000	1.411218000
1	0.302153000	1.605368000	3.174611000
1	1.950203000	1.453253000	3.830392000
1	1.464560000	2.938522000	2.990229000
7	2.549377000	1.532054000	-1.053250000
1	4.529922000	1.293632000	-0.284684000
1	3.397685000	-0.062306000	-0.031329000
1	2.450822000	0.853052000	-1.823060000
6	2.872849000	2.866555000	-1.577274000
1	3.883838000	2.902763000	-2.009514000
1	2.146231000	3.133563000	-2.350953000
1	2.810588000	3.609567000	-0.776136000
15	0.752658000	-1.377563000	-1.776774000
8	1.420886000	-0.443260000	-2.817170000
8	1.722865000	-1.996770000	-0.759783000
8	-0.308996000	-2.330117000	-2.370690000
19	0.988831000	-1.769548000	1.852253000
19	-0.980845000	0.722371000	-3.652062000

(F) Int3



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G sol = -1441.182883 a.u

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6	-3.993384000	0.667821000	-0.212032000
1	-4.947283000	0.996921000	-0.649105000
1	-3.630864000	1.468694000	0.440446000
6	-4.193817000	-0.607633000	0.621680000
1	-4.907556000	-0.368467000	1.434782000
1	-4.701169000	-1.375996000	-0.004983000

6	-3.081660000	-2.285703000	1.932457000
1	-2.103241000	-2.641784000	2.281169000
1	-3.711737000	-2.120808000	2.829895000
1	-3.555370000	-3.122144000	1.373536000
6	-3.513141000	0.147963000	-2.592011000
1	-4.196204000	0.925567000	-2.965989000
1	-2.687606000	0.028395000	-3.300166000
1	-4.060893000	-0.798817000	-2.539481000
5	0.956125000	-0.771369000	-1.285012000
8	-0.039557000	-1.936640000	-1.400313000
1	0.307245000	-2.752017000	-1.009817000
30	-1.603526000	-0.962651000	-0.357597000
8	1.200720000	-0.234465000	-2.599097000
1	1.367801000	0.724968000	-2.464579000
6	2.281464000	-1.250893000	-0.471092000
6	3.543660000	-1.330366000	-1.087919000
6	2.218606000	-1.581076000	0.898109000
6	4.693218000	-1.705074000	-0.377242000
1	3.620884000	-1.075101000	-2.142841000
6	3.354729000	-1.962316000	1.621274000
1	1.259759000	-1.512515000	1.410381000
6	4.601724000	-2.021708000	0.983541000
1	5.656544000	-1.749523000	-0.881936000
1	3.274126000	-2.205437000	2.679110000
1	5.489617000	-2.312015000	1.540752000
8	0.131095000	0.189087000	-0.436309000
15	0.354976000	1.853115000	-0.246884000
8	0.925905000	2.016315000	1.186104000
8	1.378918000	2.237349000	-1.342917000
8	-1.068907000	2.425796000	-0.397374000
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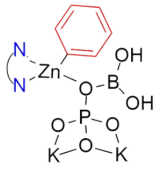
19	-1.312229000	1.164649000	2.590456000

(G) Int4



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G sol = -1441.198354 a.u

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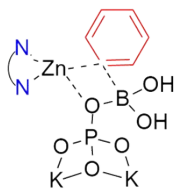
6	-0.951347000	-2.775973000	-0.277366000
1	-1.343377000	-3.748209000	-0.636860000
1	-1.793531000	-2.066488000	-0.316385000
6	-0.565115000	-2.939483000	1.213610000
7	-0.094757000	-1.644334000	1.743721000
1	-1.411810000	-3.331832000	1.803795000
1	0.260596000	-3.656194000	1.304171000
1	-0.892077000	-0.997134000	1.819214000
6	1.036509000	-3.335054000	-1.512422000
1	1.832246000	-2.922834000	-2.148203000
1	1.546985000	-3.850360000	-0.670174000
1	0.530447000	-4.133115000	-2.095465000
6	0.577069000	-1.741150000	3.044120000
1	1.499338000	-2.323291000	2.938580000
1	0.843667000	-0.736355000	3.387011000
1	-0.051926000	-2.221387000	3.810688000
6	2.926954000	0.037090000	0.095379000
6	4.083876000	-0.701482000	-0.241594000
6	3.151375000	1.368004000	0.513778000
6	5.376194000	-0.158742000	-0.171563000
1	3.979709000	-1.736222000	-0.571447000
6	4.434417000	1.930162000	0.592829000
1	2.300812000	1.992463000	0.787266000
6	5.555604000	1.165033000	0.248388000
1	6.240288000	-0.764292000	-0.442204000
1	4.560637000	2.961026000	0.921306000
1	6.554070000	1.593762000	0.306498000
5	-1.088441000	3.662713000	0.036084000
8	-1.508049000	4.964330000	0.232608000
1	-0.802796000	5.596637000	0.026825000
8	0.181913000	3.410449000	-0.411258000
1	0.283103000	2.422406000	-0.470991000
8	-2.015776000	2.683005000	0.314931000
15	-1.855984000	1.026850000	0.143528000
8	-2.851299000	0.603290000	-0.947387000
8	-0.365118000	0.834601000	-0.314798000
8	-2.155372000	0.423840000	1.522753000
19	-1.113244000	-0.364562000	-2.948105000
19	-4.429373000	-0.999026000	0.806843000

(H) TS 1

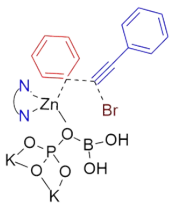


E sol = -1441.400227 a.u

G sol = -1441.162009 a.u

5	-0.987165000	-2.067828000	0.068452000
8	-0.717345000	-2.557527000	1.393284000
1	-1.541347000	-2.784769000	1.846768000
8	0.250858000	-2.016509000	-0.675231000
8	-2.142541000	-2.548942000	-0.561975000
1	-1.891341000	-2.742357000	-1.502912000
6	-1.416559000	-0.069981000	0.344844000
6	-2.255063000	0.224210000	1.441278000
6	-1.645103000	0.673768000	-0.837239000
6	-3.287618000	1.167155000	1.360322000
1	-2.109617000	-0.317619000	2.375871000
6	-2.666299000	1.623475000	-0.938160000
1	-1.002836000	0.481187000	-1.696159000
6	-3.497274000	1.866310000	0.164629000
1	-3.927521000	1.358647000	2.219649000
1	-2.819014000	2.174140000	-1.864930000
1	-4.299774000	2.597200000	0.093624000
30	0.745174000	-0.217447000	0.603751000
7	2.485633000	-0.680932000	1.476123000
6	3.522083000	0.099503000	0.820819000
6	2.660056000	-0.693623000	2.915067000
6	3.254225000	0.192348000	-0.690163000
1	4.524339000	-0.353873000	0.957157000
1	3.603663000	1.128510000	1.239017000
1	1.843832000	-1.254292000	3.389376000
1	3.611725000	-1.177249000	3.216853000
1	2.673066000	0.319741000	3.373487000
7	1.905897000	0.740393000	-0.969757000
1	4.032288000	0.793932000	-1.184150000
1	3.277456000	-0.814022000	-1.121904000
1	1.544117000	0.318696000	-1.840600000
6	1.850463000	2.206661000	-1.029875000
1	2.515840000	2.613565000	-1.806503000
1	0.822396000	2.516757000	-1.241706000
1	2.143309000	2.632528000	-0.064593000
15	0.532959000	-2.296115000	-2.331456000
8	0.736054000	-0.892654000	-2.955459000
8	1.775742000	-3.192222000	-2.306923000
8	-0.781506000	-2.948251000	-2.842624000
19	2.253076000	-3.566372000	0.519989000
19	-1.638375000	-0.832503000	-4.425873000

(I) TS 2



E sol = -1762.375290 a.u

G sol = -1762.050582 a.u

6	2.449547000	0.108483000	0.165320000
6	3.435818000	0.951717000	-0.394984000
6	2.767862000	-0.488566000	1.411464000
6	4.660041000	1.194758000	0.243892000
1	3.245341000	1.430756000	-1.352708000
6	3.993117000	-0.272638000	2.050422000
1	2.035395000	-1.132790000	1.889839000
6	4.946416000	0.579234000	1.470225000
1	5.392066000	1.856401000	-0.215923000
1	4.206570000	-0.762069000	2.998999000
1	5.895246000	0.762577000	1.968886000
6	0.500326000	1.104096000	0.309502000
6	-0.195811000	0.931765000	1.333998000
6	-0.494575000	0.288776000	2.571267000
6	-0.742038000	1.045716000	3.740526000
6	-0.561405000	-1.122933000	2.662583000
6	-1.035796000	0.414342000	4.950112000
1	-0.702088000	2.130332000	3.686166000
6	-0.871924000	-1.744728000	3.871120000
1	-0.339023000	-1.712465000	1.780082000
6	-1.110443000	-0.982821000	5.023079000
1	-1.216025000	1.015513000	5.838030000
1	-0.914514000	-2.830434000	3.917127000
1	-1.348833000	-1.470840000	5.964416000
35	0.401140000	2.230777000	-1.261626000
7	0.582339000	-3.057914000	-0.293935000
6	-0.848711000	-3.227752000	-0.458659000
6	1.154768000	-3.852609000	0.766516000
6	-1.548723000	-1.901532000	-0.822798000
1	-1.333807000	-3.586905000	0.469251000
1	-1.111643000	-3.987508000	-1.229693000
1	2.226182000	-3.631453000	0.860919000
1	0.700626000	-3.671452000	1.764564000
1	1.067238000	-4.952100000	0.610926000
7	-0.786668000	-1.119640000	-1.823988000
1	-2.575282000	-2.093107000	-1.173414000
1	-1.606014000	-1.272794000	0.069339000
1	-1.090107000	-0.150114000	-1.765876000
6	-0.962404000	-1.584221000	-3.212960000
1	-2.025764000	-1.654368000	-3.486484000
1	-0.460276000	-0.883538000	-3.884819000
1	-0.479904000	-2.553566000	-3.342800000
30	1.296273000	-1.335396000	-1.065261000
1	1.726180000	-2.801691000	-5.884993000
8	2.208497000	-2.356570000	-6.636750000
5	3.402960000	-1.905881000	-6.139747000
8	4.310651000	-1.276115000	-6.968923000
8	3.786830000	-2.044895000	-4.822363000

1	3.980708000	-1.225052000	-7.878867000
15	2.851052000	-2.671221000	-3.584426000
8	3.748260000	-3.656302000	-2.820990000
8	2.507724000	-1.415287000	-2.727904000
8	1.625601000	-3.334924000	-4.250624000
19	5.115661000	-2.189970000	-1.017305000
19	1.404446000	-5.286457000	-2.262784000

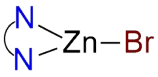
(J) Product 1

E sol = -539.491492 a.u

G sol = -539.339116 a.u

6	0.609066000	-0.000019000	0.000004000
6	2.035686000	-0.000010000	0.000003000
6	2.752335000	1.216483000	0.000048000
6	2.752357000	-1.216491000	-0.000064000
6	4.147516000	1.211352000	0.000051000
1	2.206914000	2.155817000	0.000076000
6	4.147537000	-1.211334000	-0.000056000
1	2.206954000	-2.155834000	-0.000115000
6	4.850165000	0.000015000	0.000007000
1	4.687650000	2.154393000	0.000092000
1	4.687688000	-2.154366000	-0.000108000
1	5.936792000	0.000026000	0.000013000
6	-0.609066000	-0.000026000	0.000005000
6	-2.035690000	-0.000007000	-0.000006000
6	-2.752354000	-1.216490000	0.000067000
6	-2.752335000	1.216485000	-0.000042000
6	-4.147536000	-1.211334000	0.000054000
1	-2.206951000	-2.155833000	0.000148000
6	-4.147515000	1.211351000	-0.000055000
1	-2.206915000	2.155819000	-0.000070000
6	-4.850166000	0.000014000	-0.000020000
1	-4.687681000	-2.154370000	0.000098000
1	-4.687650000	2.154393000	-0.000077000
1	-5.936792000	0.000024000	-0.000043000

(K) Product 2



E sol = -347.422510 a.u

G sol = -347.303776 a.u

30	0.041851000	-0.218910000	-0.245982000
7	-1.545536000	-1.412934000	-0.323336000
7	-1.336463000	1.512208000	-0.257423000
1	-1.458432000	1.816919000	-1.225109000
6	-2.682729000	-0.529662000	-0.570210000
1	-3.634925000	-1.008570000	-0.287892000
1	-2.749763000	-0.309996000	-1.649232000
6	-2.582778000	0.823628000	0.170620000
1	-3.462499000	1.459553000	-0.009167000
1	-2.498918000	0.647288000	1.249412000
6	-1.764599000	-2.282257000	0.830046000
1	-2.608082000	-2.976457000	0.658229000
1	-0.869481000	-2.892163000	1.005857000
1	-1.982249000	-1.750442000	1.779350000
6	-0.983754000	2.685381000	0.563977000
1	-0.091617000	3.160603000	0.146905000
1	-1.800222000	3.419444000	0.605370000
1	-0.756818000	2.351400000	1.580546000
35	2.540418000	-0.063649000	0.046397000

(L) $B(OH)_2K_2PO_4$

E sol = -875.549430 a.u

G sol = -875.540224 a.u

5	-1.747289000	-1.483253000	-0.284489000
8	-2.456430000	-0.356657000	-0.680437000
1	-3.308002000	-0.599692000	-1.075168000
8	-2.353911000	-2.708271000	-0.525704000
1	-1.800085000	-3.440360000	-0.213591000
8	-0.529542000	-1.429320000	0.300087000
15	0.426186000	-0.064611000	0.741355000
8	0.694897000	0.668496000	-0.600164000
8	-0.456511000	0.741626000	1.707068000
8	1.684051000	-0.720508000	1.330794000
19	-1.539037000	2.364420000	-0.301379000
19	3.370158000	-0.108496000	-0.786109000

(M) ArB(OH)2K2PO4-

E sol = -1107.299658 a.u

G sol = -1107.206812 a.u

5	3.379939000	-2.359765000	-5.407248000
8	4.120757000	-2.190428000	-4.150932000
15	3.986729000	-2.703281000	-2.575486000
8	5.242227000	-2.131927000	-1.882425000
8	2.647126000	-2.079834000	-2.052283000
8	3.906289000	-4.256669000	-2.588533000
19	2.277831000	0.038359000	-3.758489000
19	1.233137000	-4.341852000	-3.104898000
6	3.971072000	-3.579333000	-6.334172000
6	3.940011000	-3.525491000	-7.742015000
6	4.480887000	-4.762640000	-5.758831000
6	4.392165000	-4.585066000	-8.542461000
1	3.558637000	-2.625496000	-8.223147000
6	4.936350000	-5.828950000	-6.544990000
1	4.515182000	-4.831085000	-4.672711000
6	4.893544000	-5.746961000	-7.943998000
1	4.357198000	-4.503824000	-9.628166000
1	5.328742000	-6.726696000	-6.068364000
1	5.250012000	-6.572936000	-8.556728000
8	1.913258000	-2.582881000	-5.134800000
8	3.428077000	-1.050422000	-6.156188000
1	1.473105000	-2.666311000	-5.993802000
1	4.343906000	-0.867433000	-6.413124000

(N) Potassium DMEDA

E sol = - 296.718960a.u

G sol = -296.602513 a.u

7	0.037209000	-1.240786000	0.669072000
6	-0.559831000	-1.940280000	-0.482699000
1	-0.865749000	-2.967516000	-0.200869000
1	0.219167000	-2.037345000	-1.253597000
6	-1.770958000	-1.207830000	-1.074032000
7	-1.483002000	0.091734000	-1.595117000
1	-2.195827000	-1.907867000	-1.845801000
1	-2.567346000	-1.198255000	-0.271059000
6	-2.664589000	0.611184000	-2.223958000
1	-3.543145000	0.729969000	-1.530801000
1	-2.478830000	1.608328000	-2.655888000
1	-3.061879000	-0.025968000	-3.061636000
6	1.059997000	-2.043297000	1.342994000
1	1.905281000	-2.199611000	0.661119000
1	1.431088000	-1.510087000	2.225731000
1	0.700479000	-3.039485000	1.662350000
1	-0.711259000	-1.036759000	1.332597000
19	0.776374000	1.300785000	-0.607962000

(O) $K_3PO_4ArB(OH)_2$

E sol = -1135.427552 a.u

G sol = -1135.337953 a.u

5	3.355476000	-2.406252000	-5.362591000
8	4.141565000	-2.260623000	-4.118217000
15	3.985161000	-2.757706000	-2.532235000
8	5.368738000	-2.385211000	-1.940496000
8	2.792718000	-1.943730000	-1.947110000
8	3.697826000	-4.281561000	-2.541419000
19	2.328979000	0.077979000	-3.727208000
19	1.007745000	-4.111621000	-2.828351000
6	3.975325000	-3.606245000	-6.298274000
6	4.149252000	-3.483091000	-7.690488000
6	4.356043000	-4.837789000	-5.720622000
6	4.683423000	-4.519091000	-8.472026000
1	3.862246000	-2.552015000	-8.177662000
6	4.889581000	-5.880673000	-6.487618000
1	4.234099000	-4.959647000	-4.644962000
6	5.058260000	-5.725832000	-7.871179000
1	4.807777000	-4.384475000	-9.545414000
1	5.176795000	-6.816205000	-6.009255000
1	5.475738000	-6.533004000	-8.469682000
8	1.914314000	-2.641806000	-5.034417000
8	3.382246000	-1.087914000	-6.087540000
1	1.428940000	-2.711362000	-5.869866000
1	4.275592000	-0.907234000	-6.414361000
19	6.893586000	-2.628471000	-4.208347000

(P) K_2PO_4-

E sol = -698.948315 a.u

G sol = -698.970413 a.u

8	4.309055000	-1.865066000	-4.090490000
15	3.173328000	-2.756596000	-3.459240000
8	3.834634000	-3.964649000	-2.654797000
8	2.363179000	-1.898460000	-2.388128000
8	2.174784000	-3.333805000	-4.530911000
19	5.119922000	-1.631155000	-1.370016000
19	1.024182000	-4.540246000	-2.200176000

(Q) CH_3CH_2-

E sol = -79.240064 a.u

G sol = -79.204339 a.u

6	0.838126000	0.000000000	-0.155839000
1	1.265606000	0.882524000	0.361028000
6	-0.694372000	0.000000000	0.014712000
1	-1.084022000	0.000000000	1.060844000
1	-1.154857000	0.877789000	-0.468071000
1	-1.154857000	-0.877789000	-0.468070000
1	1.265606000	-0.882524000	0.361028000

(R) CH_3CH_3

E sol = -79.834171 a.u

G sol = -79.782528 a.u

6	0.767205000	0.000001000	0.000001000
1	1.164414000	-0.775557000	0.666567000
1	1.164390000	0.965081000	0.338313000
6	-0.767205000	-0.000001000	-0.000001000
1	-1.164390000	-0.965075000	-0.338331000
1	-1.164322000	0.189504000	1.004958000
1	-1.164414000	0.775570000	-0.666552000
1	1.164322000	-0.189523000	-1.004954000

(S) Zn(Et)

E sol = -144.789215 a.u

G sol = -144.755091 a.u

30	0.958220000	-0.071837000	0.000001000
6	-1.104238000	0.721670000	0.000002000
1	-1.200739000	1.355232000	0.892034000
1	-1.200516000	1.355177000	-0.892113000
6	-2.103790000	-0.436860000	-0.000001000
1	-1.970638000	-1.079220000	0.881510000
1	-3.156206000	-0.105239000	-0.000343000
1	-1.970336000	-1.079696000	-0.881134000

(T) $Zn(Et)_2$

E sol = -224.041769 a.u

G sol = -223.948673 a.u

30	0.000001000	0.380216000	0.000188000
6	-2.045499000	0.339462000	0.331437000
1	-2.242082000	0.412130000	1.412971000
1	-2.504981000	1.234241000	-0.117900000
6	2.045313000	0.339189000	-0.332186000
1	2.241404000	0.410946000	-1.413861000
1	2.504905000	1.234420000	0.116152000
6	2.714634000	-0.928378000	0.234643000
1	2.295573000	-1.839417000	-0.214832000
1	3.804013000	-0.959469000	0.064463000
1	2.559098000	-1.014441000	1.319134000
6	-2.714466000	-0.928654000	-0.234555000
1	-2.295521000	-1.839241000	0.215939000
1	-3.803917000	-0.959682000	-0.064828000
1	-2.558429000	-1.015689000	-1.318897000

(U) DMEDA

E sol = -269.152760 a.u

G sol = -269.017418 a.u

6	-0.662335000	-0.375564000	0.070014000
1	-0.721254000	-1.159895000	-0.698178000
1	-0.687777000	-0.885915000	1.050890000
6	0.662336000	0.375565000	-0.070012000
1	0.721255000	1.159894000	0.698180000
1	0.687777000	0.885917000	-1.050887000
7	1.802449000	-0.523674000	0.123508000
1	1.758196000	-1.264142000	-0.575958000
7	-1.802449000	0.523675000	-0.123509000
1	-1.758195000	1.264145000	0.575954000
6	-3.089806000	-0.164075000	-0.002184000
1	-3.209690000	-0.711621000	0.950841000
1	-3.904000000	0.563252000	-0.088101000
1	-3.193440000	-0.887532000	-0.819827000
6	3.089806000	0.164075000	0.002187000
1	3.904000000	-0.563252000	0.088101000
1	3.209690000	0.711626000	-0.950835000
1	3.193440000	0.887529000	0.819833000

(V) DMEDA-

E sol = -268.596993 a.u

G sol = -268.478228 a.u

6	-0.650109000	-0.404615000	0.007508000
1	-0.718841000	-1.141724000	-0.804864000
1	-0.701790000	-0.972224000	0.957457000
6	0.704222000	0.310403000	-0.066250000
1	0.664695000	1.167844000	0.673120000
1	0.749210000	0.832291000	-1.063596000
7	1.802995000	-0.572275000	0.161325000
7	-1.783696000	0.523046000	-0.128350000
1	-1.691573000	1.246337000	0.584291000
6	-3.078668000	-0.135983000	0.032038000
1	-3.172335000	-0.706062000	0.976784000
1	-3.882958000	0.608267000	-0.001820000
1	-3.234789000	-0.840011000	-0.795089000
6	3.025026000	0.164020000	0.039034000
1	3.901100000	-0.485416000	0.201371000
1	3.179245000	0.651966000	-0.966590000
1	3.130072000	1.018285000	0.769606000

(W) Ethane radical

E sol = -79.163254 a.u

G sol = -79.128144 a.u

6	-0.010715000	0.796630000	0.000000000
1	0.064123000	1.354196000	0.929530000
1	0.064123000	1.354196000	-0.929530000
6	-0.010715000	-0.695762000	0.000000000
1	1.015608000	-1.106779000	0.000000000
1	-0.507638000	-1.103410000	0.889651000
1	-0.507638000	-1.103410000	-0.889651000

(X) K_3PO_4

E sol = -727.077957 a.u

G sol = -727.103858 a.u

8	3.808830000	-2.173226000	-4.162351000
15	3.244776000	-2.882486000	-2.862296000
8	4.458389000	-3.282626000	-1.921522000
8	2.302783000	-1.870447000	-2.084356000
8	2.425462000	-4.178964000	-3.213916000
19	2.134717000	-0.024396000	-4.074255000
19	2.231808000	-4.242750000	-0.298551000
19	6.437761000	-2.748352000	-3.688403000

(Y) CH3CH2K

E sol = -107.351985 a.u

G sol = -107.321858 a.u

6	1.347074000	0.818430000	-0.000003000
1	1.731151000	1.372999000	-0.879170000
6	1.959794000	-0.600290000	0.000000000
1	1.637637000	-1.183691000	0.879365000
1	1.637679000	-1.183677000	-0.879389000
1	3.072419000	-0.661855000	0.000027000
1	1.731108000	1.372984000	0.879192000
19	-1.560590000	-0.053979000	0.000000000

(Z) K^+

E sol = -28.080071 a.u

G sol = -28.095247 a.u

19	6.510830000	-2.102234000	-4.690408000

(A') KBr

E sol = -41.446294 a.u

G sol = -41.471418 a.u

35	0.000000000	0.000000000	1.157668000
19	0.000000000	0.000000000	-2.132546000

(B') Zn

E sol = -65.602821 a.u

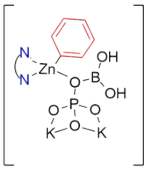
G sol = -65.618698 a.u

30	0.000000000	0.000000000	0.000000000

SET

(I) Int6

+.



Charge = 1

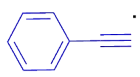
Multiplicity = Doublet

E sol = -1441.279059 a.u

G sol = -1441.045725 a.u

30	-1.033434000	-0.841175000	-0.513174000
7	0.015334000	-2.368338000	0.740655000
6	0.887766000	-3.213388000	-0.037851000
1	0.907117000	-4.236622000	0.367992000
1	1.909226000	-2.807859000	0.050385000
6	0.459296000	-3.214003000	-1.507818000
7	0.278838000	-1.821373000	-1.964515000
1	1.207017000	-3.745578000	-2.113501000
1	-0.499064000	-3.734519000	-1.621078000
1	1.163805000	-1.317507000	-1.803097000
6	0.307882000	-2.290450000	2.146526000
1	-0.590594000	-1.989135000	2.694499000
1	0.707676000	-3.227756000	2.557288000
1	1.064672000	-1.498188000	2.288040000
6	-0.110343000	-1.718840000	-3.381371000
1	-1.088493000	-2.188670000	-3.524727000
1	-0.188780000	-0.662302000	-3.652244000
1	0.617679000	-2.206662000	-4.044695000
6	-2.938885000	-0.186071000	-0.106823000
6	-3.968279000	-1.008564000	0.399543000
6	-3.247629000	1.185836000	-0.241377000
6	-5.227729000	-0.501547000	0.752068000
1	-3.788631000	-2.076313000	0.526980000
6	-4.501062000	1.711039000	0.105940000
1	-2.492590000	1.869999000	-0.629973000
6	-5.497563000	0.864639000	0.606473000
1	-5.996277000	-1.168116000	1.139772000
1	-4.701181000	2.774368000	-0.015001000
1	-6.472334000	1.263865000	0.877857000
5	1.613900000	3.013922000	-1.350883000
8	2.324473000	4.084382000	-1.848848000
1	1.769221000	4.660003000	-2.396686000
8	0.284058000	2.865889000	-1.653504000
1	-0.039324000	2.055157000	-1.184828000
8	2.318037000	2.144713000	-0.544235000
15	1.812803000	0.702962000	0.126273000
8	2.166771000	0.774269000	1.614456000
8	0.248361000	0.728175000	-0.088591000
8	2.507350000	-0.417309000	-0.653870000
19	-0.568221000	1.712230000	2.416869000
19	4.485063000	-0.871590000	1.387892000

(II)



Charge = 0

Multiplicity = Doublet

E sol = -307.713368 a.u

G sol = -307.646957 a.u

6	-2.073488000	0.000000000	0.000086000
6	-0.679735000	0.000000000	-0.000037000
6	0.045438000	-1.232651000	-0.000003000
6	0.045438000	1.232651000	0.000009000
6	1.430604000	-1.223930000	0.000053000
1	-0.508870000	-2.165544000	-0.000027000
6	1.430604000	1.223930000	0.000064000
1	-0.508869000	2.165544000	-0.000007000
6	2.124986000	0.000000000	0.000084000
1	1.981736000	-2.159275000	0.000074000
1	1.981735000	2.159276000	0.000092000
1	3.211270000	-0.000001000	0.000130000
6	-3.350014000	0.000000000	-0.000127000

(III)

-

Br

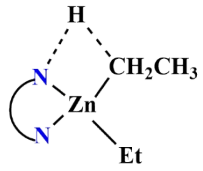
Charge = -1

Multiplicity = Singlet

E sol = -13.333812 a.u

G sol = -13.349988 a.u

35	0.000000000	0.000000000	0.000000000



TS a

E sol : -493.176719

G sol : -492.930904

30	-0.515862000	0.732158000	0.709882000
7	0.356617000	0.757349000	-1.378338000
7	1.448068000	-0.058366000	1.114311000
1	-0.312151000	0.391300000	-2.053606000
6	1.526315000	-0.155518000	-1.330542000
1	2.176359000	-0.007423000	-2.205808000
1	1.134061000	-1.176025000	-1.363668000

6	2.332124000	0.030150000	-0.036726000
1	3.118477000	-0.746772000	-0.015551000
1	2.860211000	1.000833000	-0.051534000
6	2.131900000	0.042389000	2.391717000
1	1.404691000	-0.089042000	3.202036000
1	2.917542000	-0.725904000	2.510649000
1	2.612102000	1.027018000	2.526990000
6	0.704808000	2.138823000	-1.763027000
1	1.267779000	2.176890000	-2.706944000
1	-0.212763000	2.723551000	-1.863467000
1	1.311458000	2.592532000	-0.974076000
1	0.587459000	-0.972684000	1.023698000
6	-0.638137000	-1.844987000	0.908677000
6	-0.955379000	-2.349388000	2.328020000
1	-0.146472000	-2.642562000	0.322860000
1	-1.585079000	-1.651399000	0.368943000
1	-1.561993000	-3.271036000	2.367847000
1	-0.030843000	-2.556607000	2.887955000
1	-1.500747000	-1.586116000	2.902934000
6	-2.007627000	2.045962000	1.311876000
6	-2.299849000	3.156132000	0.284528000
1	-1.724976000	2.496343000	2.275932000
1	-2.926188000	1.470680000	1.506944000
1	-3.113043000	3.833186000	0.596171000
1	-1.414485000	3.781601000	0.106792000
1	-2.589323000	2.737041000	-0.689370000

Int 4a

30	-0.713411000	0.732568000	0.783653000
7	-0.357733000	-1.221587000	1.023259000
6	-0.421845000	-1.846901000	-0.291781000
1	-0.493932000	-2.946665000	-0.217540000
1	0.508999000	-1.633555000	-0.845357000
6	-1.596667000	-1.337771000	-1.156289000
7	-1.451221000	0.124066000	-1.341098000
1	-1.653760000	-1.860954000	-2.125001000
1	-2.541457000	-1.505546000	-0.625316000
1	-0.669892000	0.292374000	-1.976187000
6	-1.180411000	-1.920999000	2.001728000
1	-1.127633000	-1.402058000	2.967960000
1	-2.257499000	-1.996867000	1.739805000
1	-0.829143000	-2.958401000	2.167272000
6	-2.650079000	0.784423000	-1.878938000
1	-3.459401000	0.703618000	-1.145942000
1	-2.437087000	1.845231000	-2.040944000
1	-2.990642000	0.338628000	-2.825861000
6	-0.816201000	2.741955000	1.211472000
6	0.177549000	3.434856000	1.936806000
6	-1.926544000	3.507705000	0.792035000
6	0.076483000	4.803652000	2.226905000

1	1.057715000	2.897828000	2.290421000
6	-2.046962000	4.875773000	1.076428000
1	-2.727311000	3.028103000	0.229337000
6	-1.040643000	5.529778000	1.796940000
1	0.864820000	5.302483000	2.788293000
1	-2.921428000	5.429579000	0.738559000
1	-1.126400000	6.590728000	2.021749000

Justification for Chosen Methodology

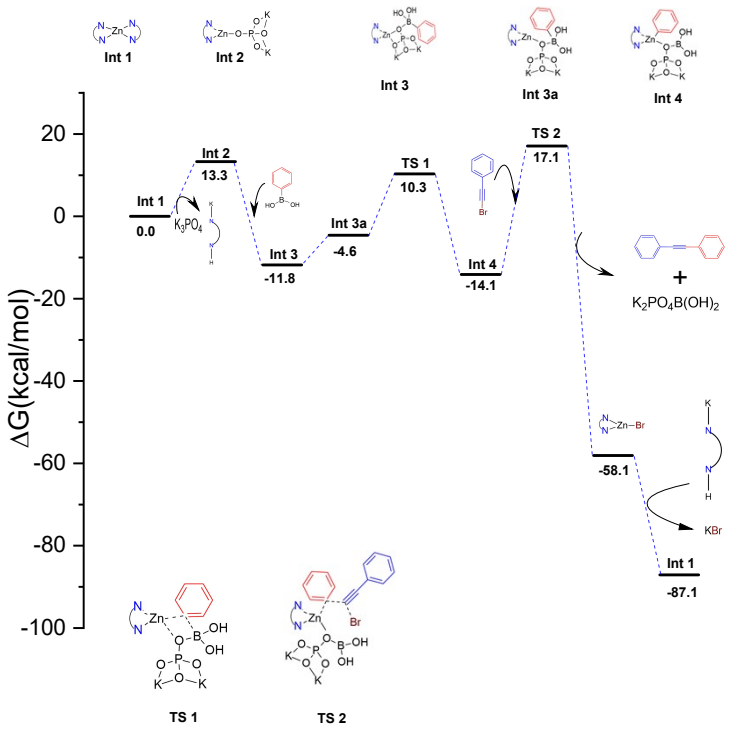


Fig S1: Free energy profile (kcal/mol) for the catalytic mechanism of Zn catalyzed SMC reaction involving the initial trans-metalation step calculated by the DFT/m06l method. Def2SVP basis set for K, Br and Zn, C, H, B, O, P. Solvation = CPCM/THF solvent.

We optimized the structures in the current basis set with the B3LYP functional and in a higher basis set with M06L. It was observed that geometric parameters, such as bond length and bond angle, were similar to experimental values in both cases. However, in calculating energetics, B3LYP showed better accuracy, while M06L tended to slightly underestimate energy values. The energy span calculated using the B3LYP functional (27.2 kcal/mol) closely aligns with the experimental temperature requirement of 80°C. In contrast, the energy span obtained with the M06 functional with def2svp basis set is 31.2 kcal/mol, (Fig S1) suggesting that for estimating the energetics, the lower basis set could be more suitable for accurately modeling the system considered in our study.

Table S1: Comparison between the experimental and theoretical Zn–N bond lengths

Method	**Zn-N_1**	**Zn-N_2**	**Bond Angle N_1-Zn-N_2**
Experimental [ref]	2.2	2.2	80.7
B3LYP	2.3	2.3	83.9
M06l	2.2	2.2	84.4

Ref: *A. Johansson, M. Håkansson and S. Jagner, Chem. – A Eur. J., 2005, 11, 5311–5318.*