

Mechanistic Insights into the Cobalt Catalyzed O-arylation Reaction Employing L-Valine Ligand: A DFT Study

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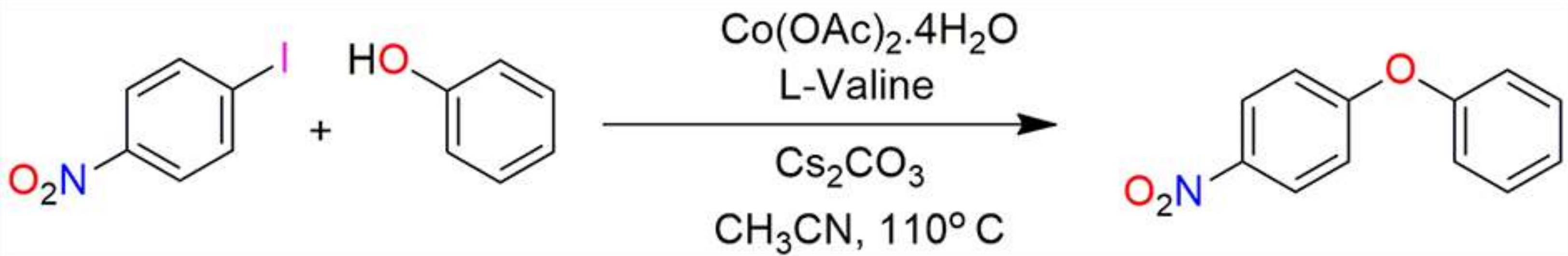
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Abstract

In the present work, we report the first theoretical investigation into the mechanism of cobalt catalyzed C-O cross-coupling reaction of phenols and electron-deficient aryl iodides using the amino acid L-valine as ligand with the aid of the Density Functional Theory method. The substituent effect on the substrates was explored to garner the role of functional groups in controlling the feasibility of the reaction..

Introduction

Transition metals are widely used as catalysts in cross-coupling reaction. Cobalt-valine complex has proved to be an efficient catalyst for C-O cross coupling reaction of aryl halides with phenols¹ (**Scheme 1**).



Scheme 1. Reaction conditions for O-arylation of phenols using electron-deficient aryl iodides

Methodology

All molecular geometries were optimized without any structural constraints with Density Functional Level of Theory (DFT) using Becke3LYP functional. The D3 version of Grimme's dispersion² was added to enhance the accuracy . The C, H, N, O, and Cl atoms were described by a 6-31+G(d) basis set. I and Co atoms were described using LANL2DZ basis set. Single point calculations were performed on the gas phase optimized geometries with a Conductor-like Polarizable Continuum Model (CPCM) solvation model. Acetonitrile was the solvent used in our O-arylation studies ($\epsilon = 35.69$). The single point Gibbs free energy values, corrected after incorporating the solvation correction is used to study reaction energetics.

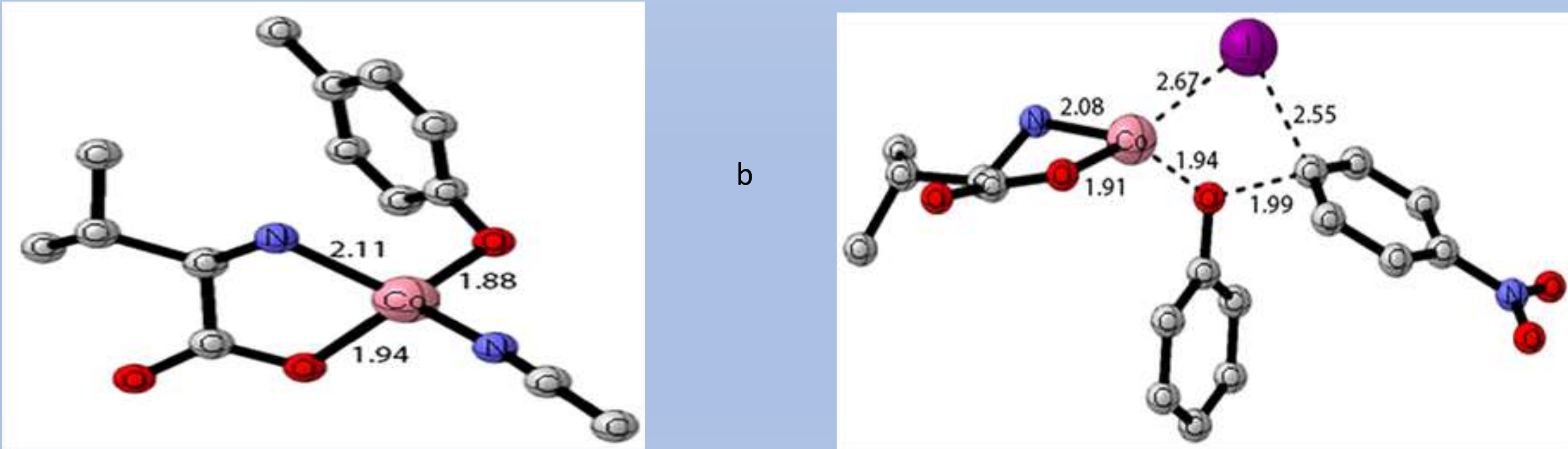
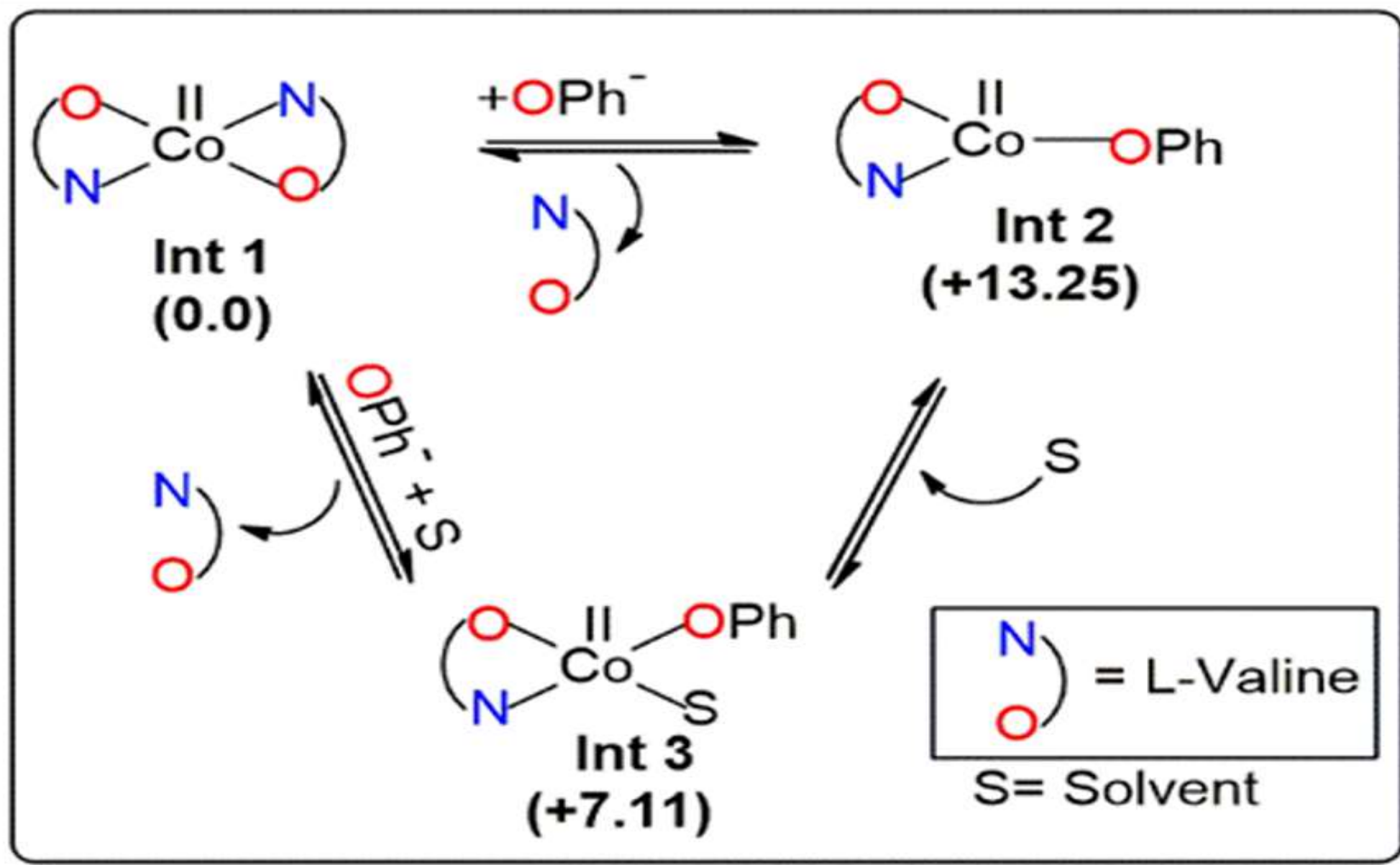


Fig. 1. Optimized geometries of the active catalyst (a) and transition state (b) involved in the reaction. (The bond lengths are given in Å).

Results and Discussion

- Previous experimental study confirms the absence of radical intermediates using radical scavengers¹.
- Absence of reducing agents in the system.

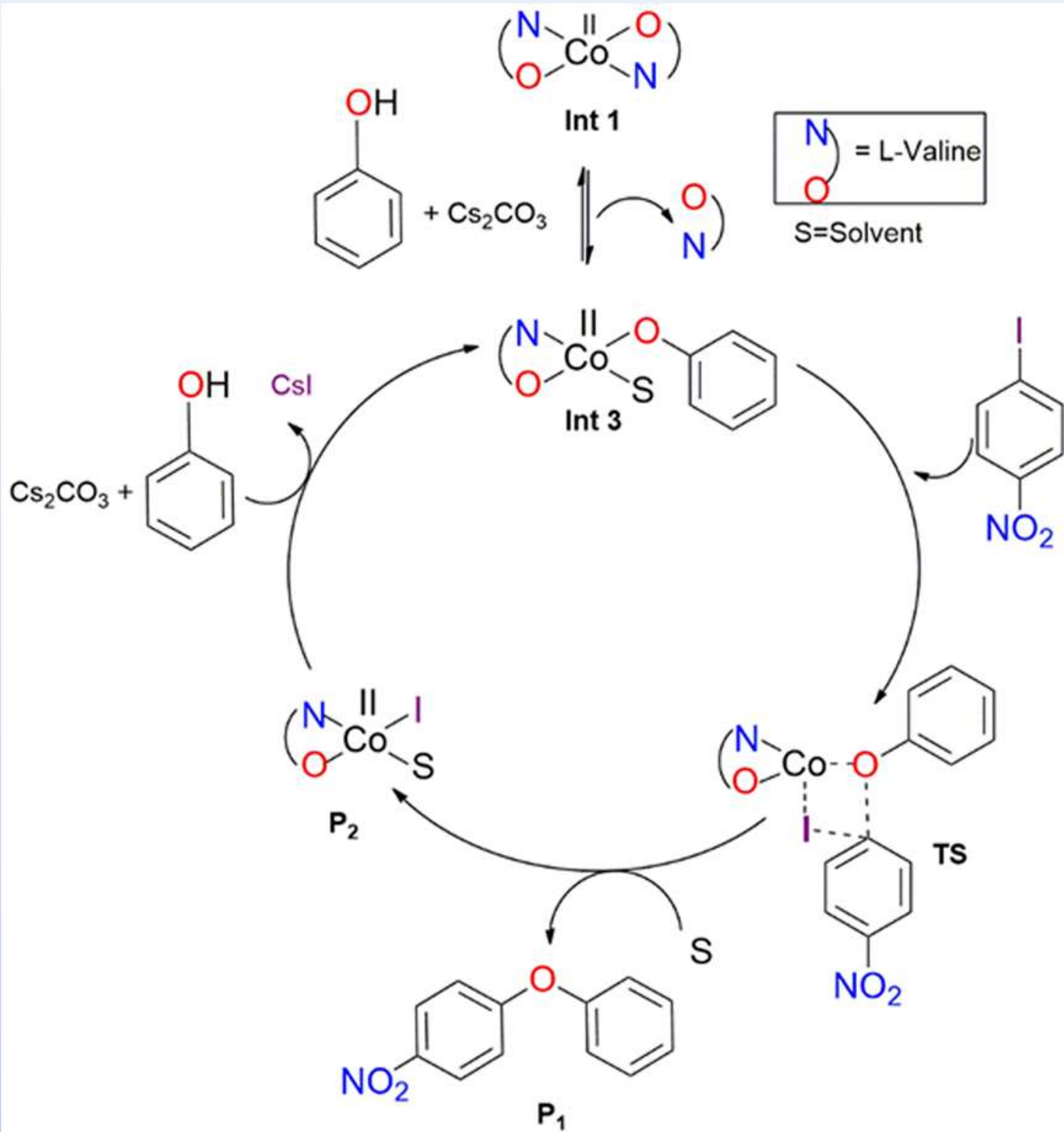
- Plausible mechanism : σ bond metathesis.
- Equilibrium between different cobalt-valine complexes in solution (**Scheme 2**).
- Active catalytic species : Tetrahedral, L-valine ligated cobalt (II) phenoxide complex (**Int 3**) in quartet state (**Fig. 1a**)
- Tetrahedral, L-valine ligated cobalt (II) phenoxide complex (**Int 3**) in quartet state (**Fig. 1a**) .
- Proposed catalytic cycle for the reaction (**Scheme 3**).
- Simultaneous breaking of carbon - iodine bond in aryl halide and formation of carbon-oxygen bond occurs through a cyclic four-membered transition state (**Fig. 1b**).
- Activation barrier (at 130^o C): 37.28 kcal/mol (**Fig. 2**) .
- FMO analysis : Electron withdrawing groups on substrates decreases the FMO energies.
- The electron-deficient groups on aryl iodides - lowers LUMO energy - increases interaction between FMOs of the substrates - lowers the activation barrier (**Table 1**) .
- Hammett correlation studies of LUMO of aryl halide vs σ_{para} were also conducted (**Fig. 3**)



Scheme 2. Equilibrium between different Cobalt complexes formed in solution (values in parenthesis gives the Gibbs free energy changes in (kcal/mol).

Table 1. Effect of functional groups on the activation barrier.

Substituent on Phenol	Substituent on ArI	LUMO of aryl iodide (eV)	HOMO of Phenoxide complex (eV)	Co- $E_{LUMO}-E_{HOMO}$ (eV)	$\Delta G^\ddagger$ (kcal/mol)
H	CH ₃	-0.0398	-0.2137	0.174	41.23
H	H	-0.0411	-0.2137	0.173	38.85
H	CN	-0.0703	-0.2137	0.143	38.84
H	NO ₂	-0.1159	-0.2137	0.0978	37.28
CH ₃	NO ₂	-0.1159	-0.2073	0.0914	36.29
Cl	NO ₂	-0.1159	-0.2154	0.0995	37.47
CN	NO ₂	-0.1159	-0.2277	0.1118	40.78



Scheme 3. Catalytic cycle for the σ -bond metathesis mechanism of the Co (II) catalyzed O-arylation reaction.

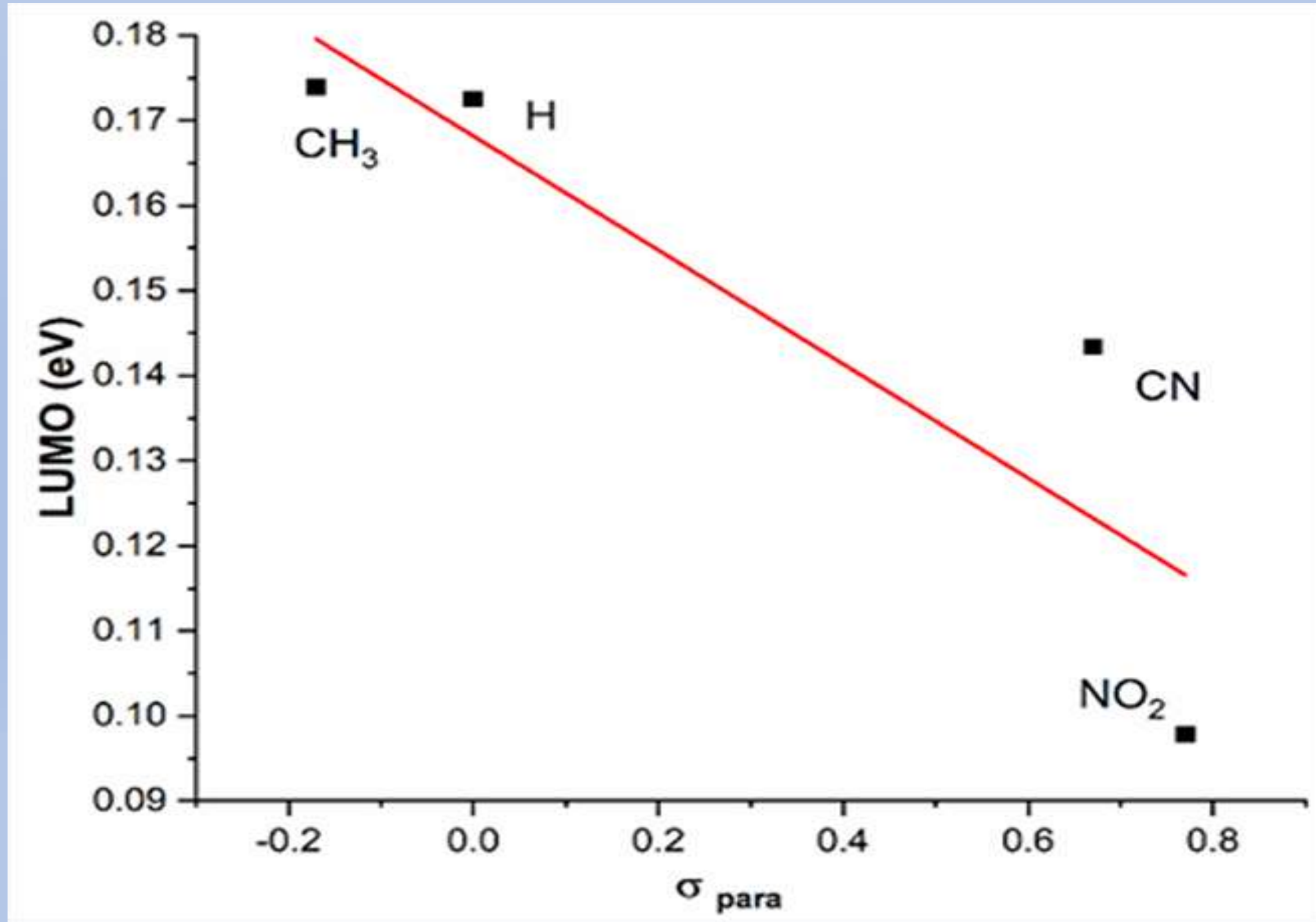


Fig. 3. The Hammett correlation study of LUMO vs σ_{para} for the para substituted aryl iodides

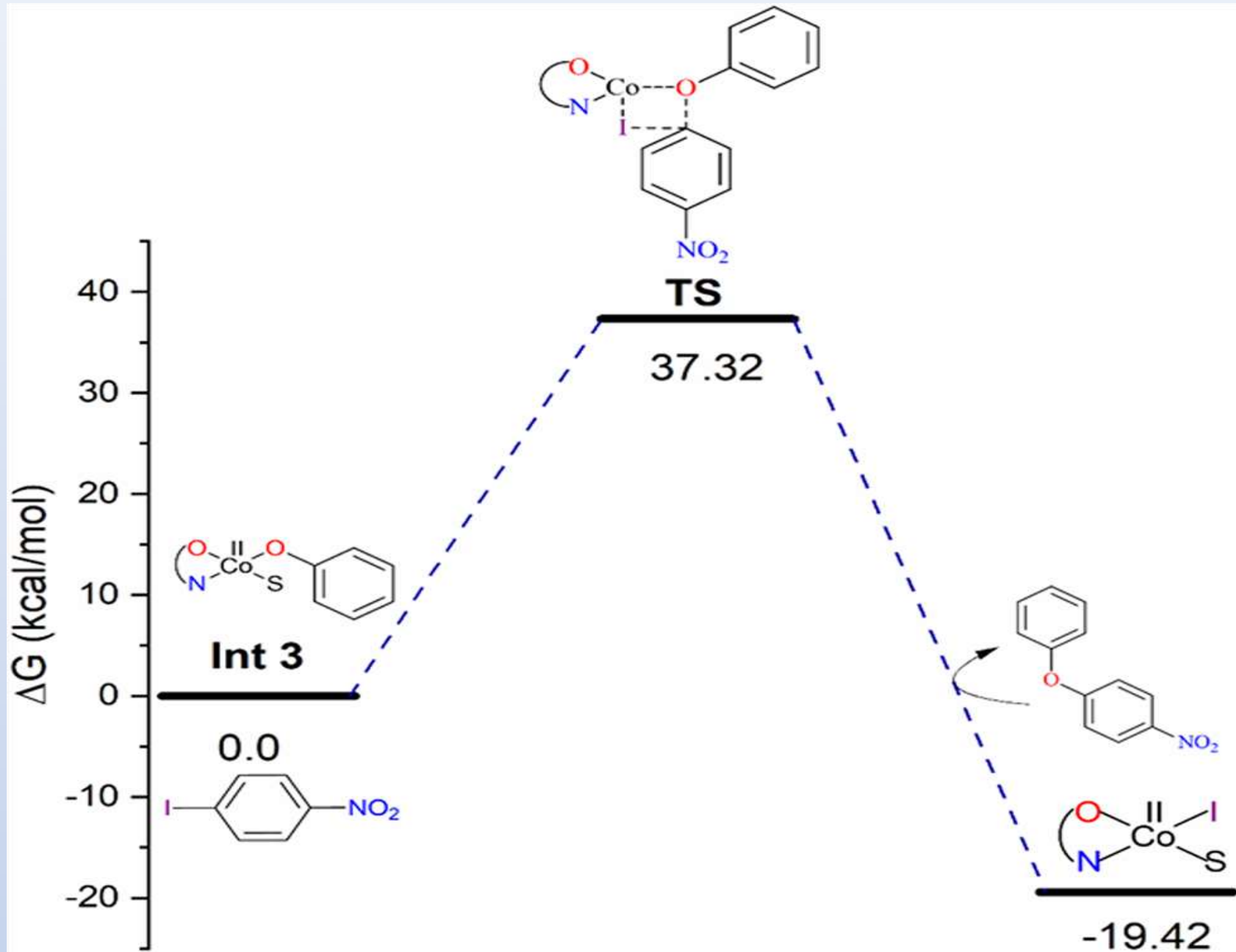


Fig. 2. The free energy profile (kcal/mol) for the catalytic cycle of the cobalt-catalyzed O-arylation reaction calculated at DFT/B3LYP/-D3 method for the model system.

Conclusions

- Cobalt (II) catalyzed C-O cross coupling reaction using L-valine ligand proceeds through a σ - bond metathesis mechanism.
- The electron - withdrawing groups at the para - position of aryl iodides lowers the activation barrier by lowering the LUMO energy of aryl iodide.

References

- 1.S.M. Ujwaldev, S. Saranya, N. Ann, H. Gopinathan, Novel cobalt - valine catalyzed O - arylation of phenols with electron deficient aryl iodides, Monatshefte Für Chemie - Chemical Monthly. 150 (2019) 339–346.
2. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, Journal of Chemical Physics. 132 (2010).

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