香港中文大學
The Chinese University of Hong Kong

Journal Club

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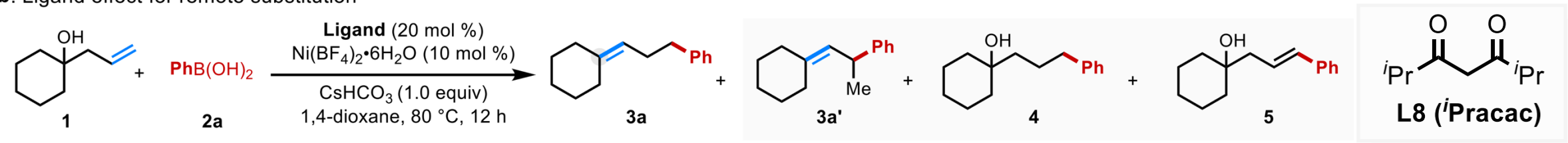
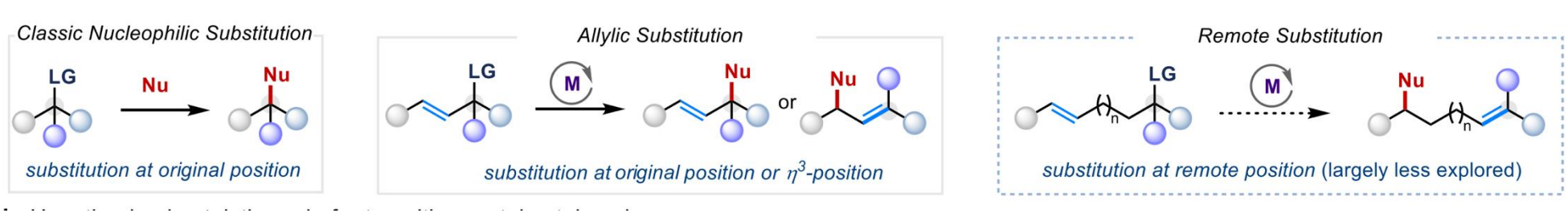
b. Ligand effect for remote substitution



- Paper suggested that remote substitution has not been explored, while classical SN_1, SN_2, allylic substitution are largely explored.
- If OH group want to be substituted, which often uses tosylate groups and halides, will decrease the yield of product.

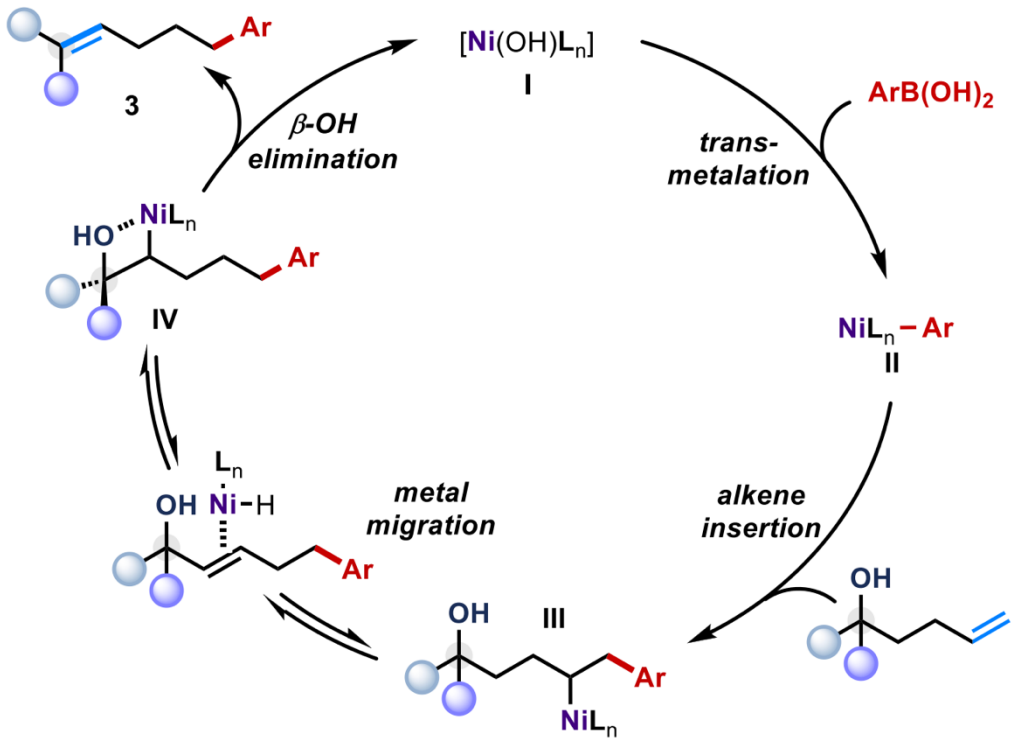


Z. K. Zhang, J. A. Lu, S. Zhang, J. X. Zhang, D. M. Wang, Y. Wu, Y. Q. Xu, Z. Y. Cao and P. Wang, *J. Am. Chem. Soc.*, 2026, **148**, 20356–20363.

Results

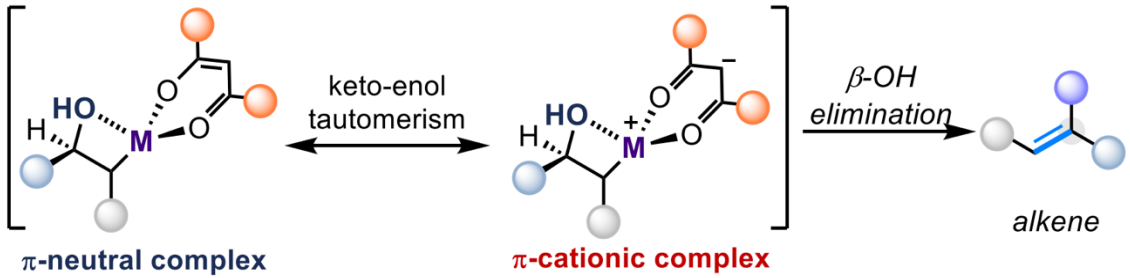
- In compound IV, we could find out that it suggests beta-OH elimination, which is normally unlikely to happen

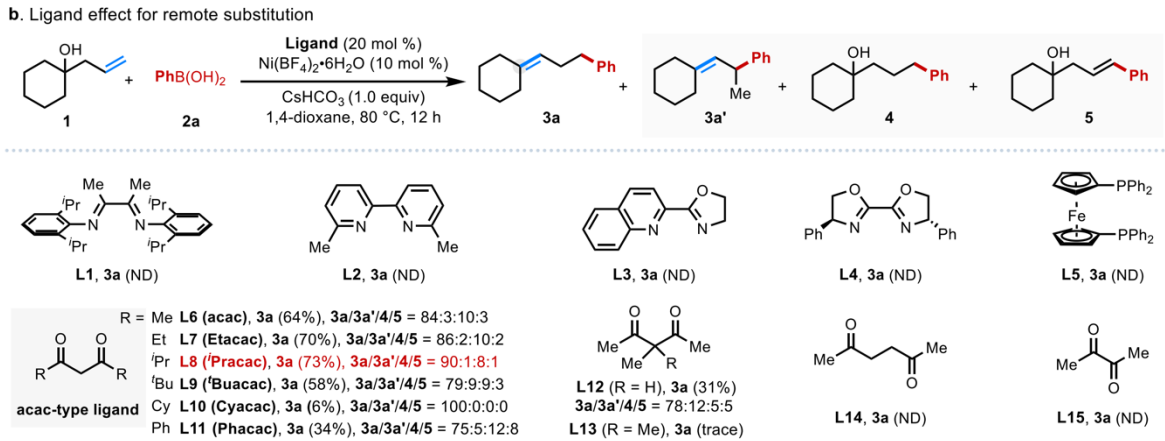
e. Proposed catalytic cycle for Ni-catalyzed remote aryl substitution

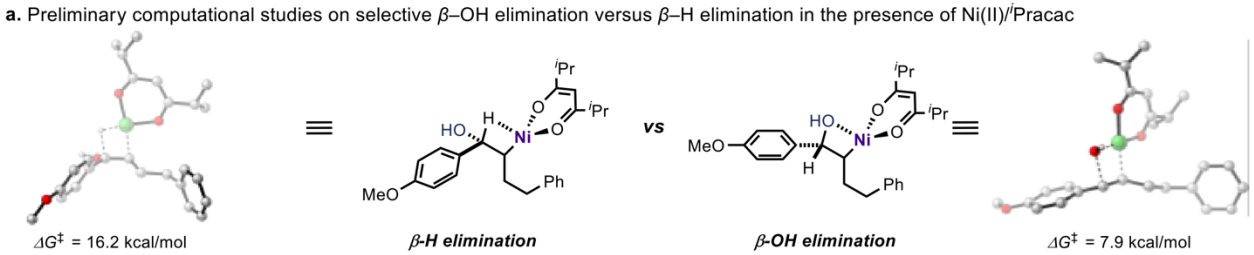


Favoring beta-OH elimination

- Ability for ketone to tautomerise
- Ligand enhance oxophilicity of metal catalyst
- Ability for ligand to make nickel more lewis acidic, favoring the Ni-O interaction
- DFT calculation has been provided below
- structure of an alcohol complexes showed a shortened Ni(II)−OH(R) bond suggesting that the β-diketone ligand could enhance the oxophilicity of the nickel metal
- Consider L12, where the enol form is more stabilised, the yield and regioselectivity decreases, suggesting the importance of rapid keto−enol tautomerism







DFT calculation

2.6.3 The Free Energy Profile for Different Pathways (kcal/mol)

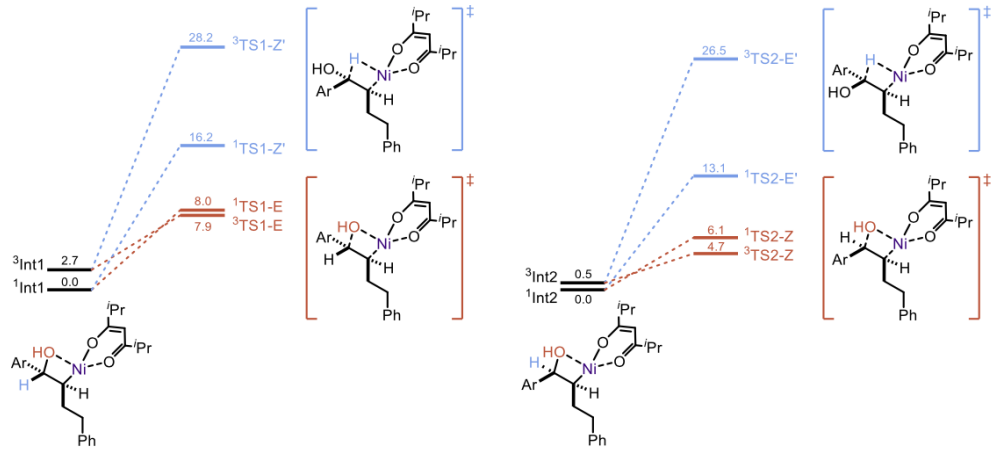


Figure S9. The free energy profile for different pathways

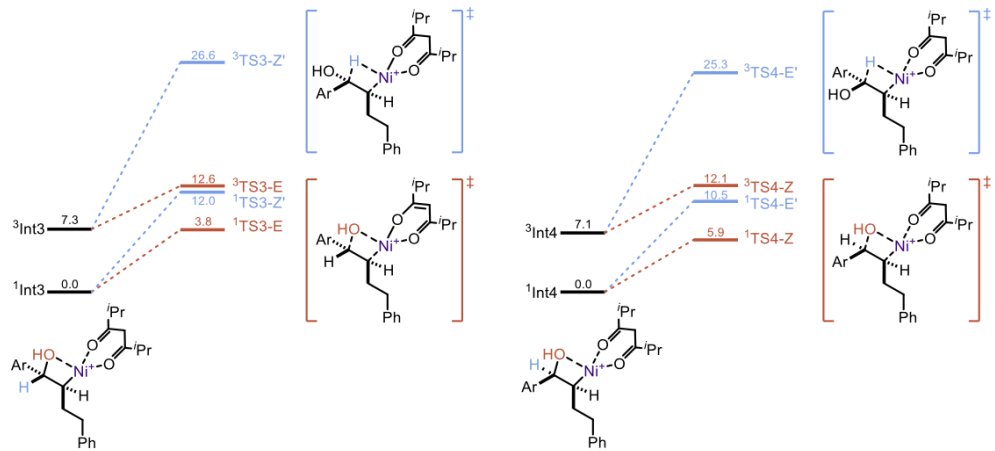
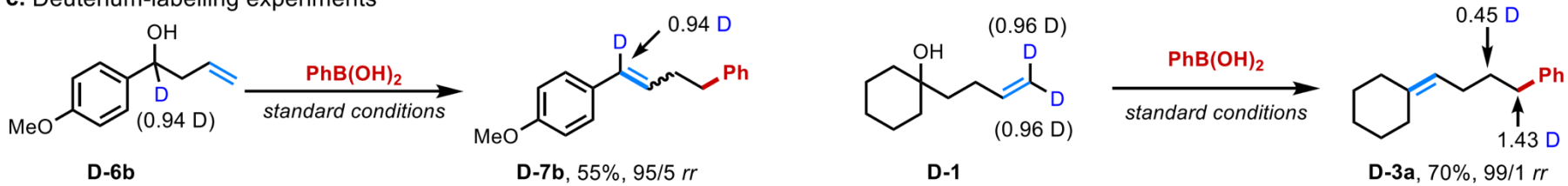


Figure S10. The free energy profile for different pathways

Evidence of chain walking

c. Deuterium-labelling experiments



D-6b

D-7b, 55%, 95/5 *rr*

D-1

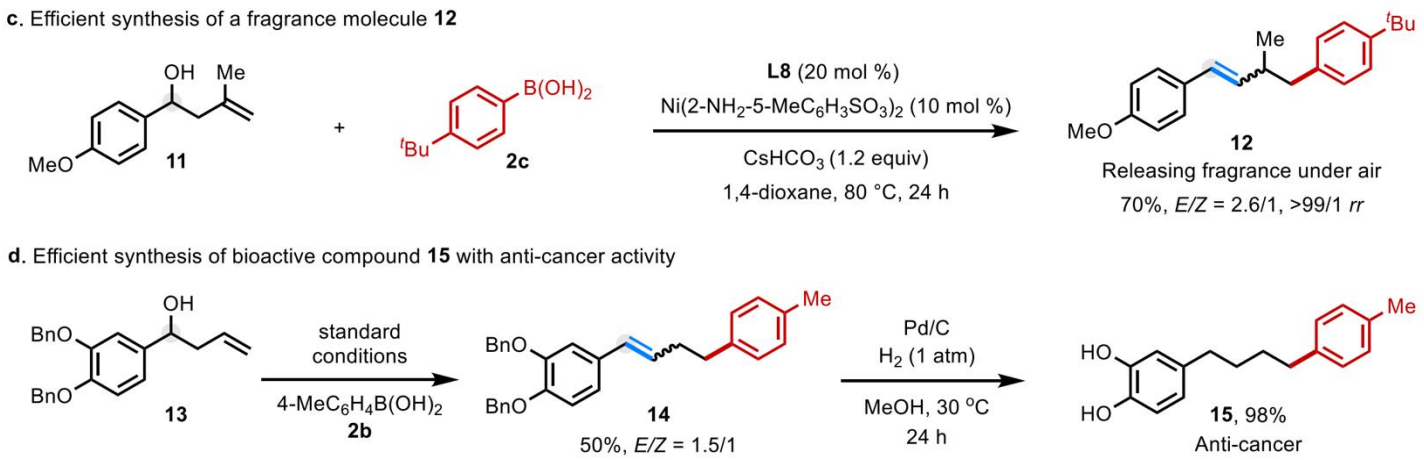
D-3a, 70%, 99/1 *rr*

Conclusion

Relies on carbo-nickelation, nickel migration, and selective β-OH elimination

Overcomes the usual preference for β-H elimination

The bulky 1,3-diketone ligand is key to enabling the desired pathway



Thank You