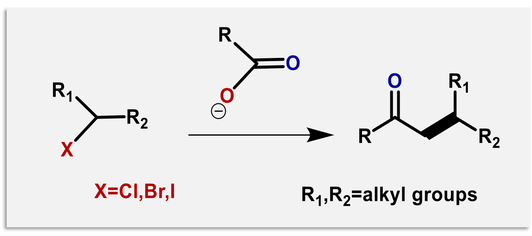
Computational Insights into Manganese Catalyzed Vinyl Cyclopropane Ring Expansion Cascade

Prativa Behera and Dr. Lisa Roy

Institute of Chemical Technology Mumbai - IOC Odisha Campus Bhubaneswar, 751013, India

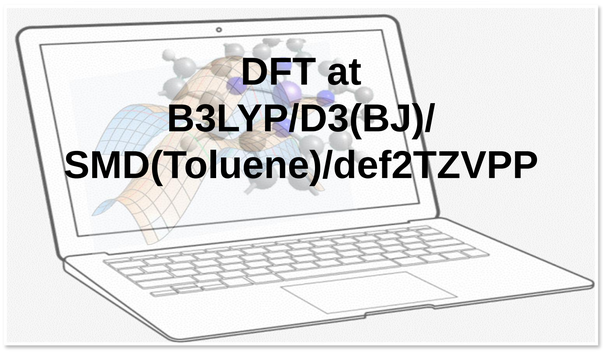
E-mail: che22pr.behera@stuiocb.ictmumbai.edu.in

Traditional Approach

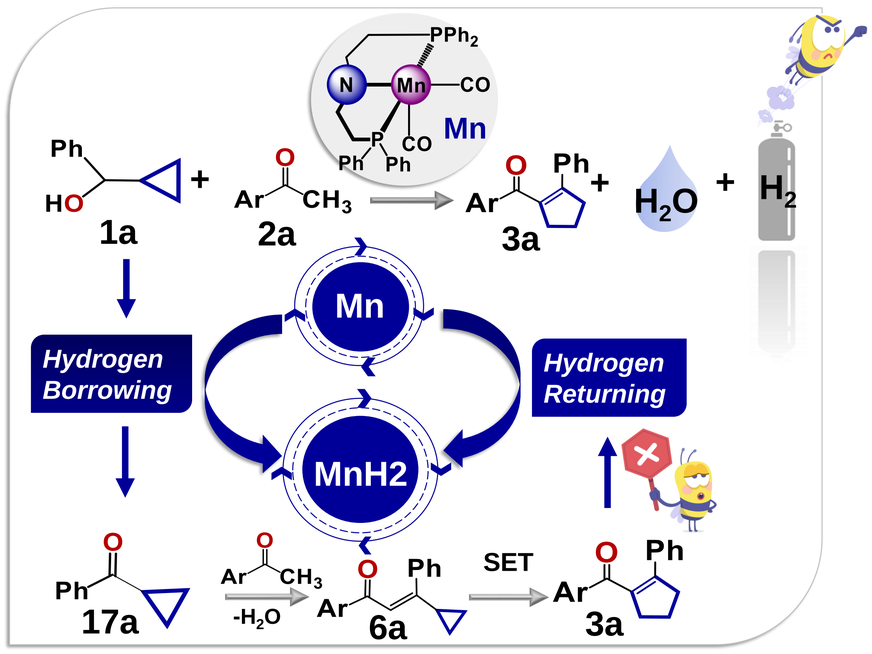


- ✓Toxic alkyl halides as electrophiles
- ✓Slow reaction with secondary halides
- ✓Stochiometric waste

Methodology



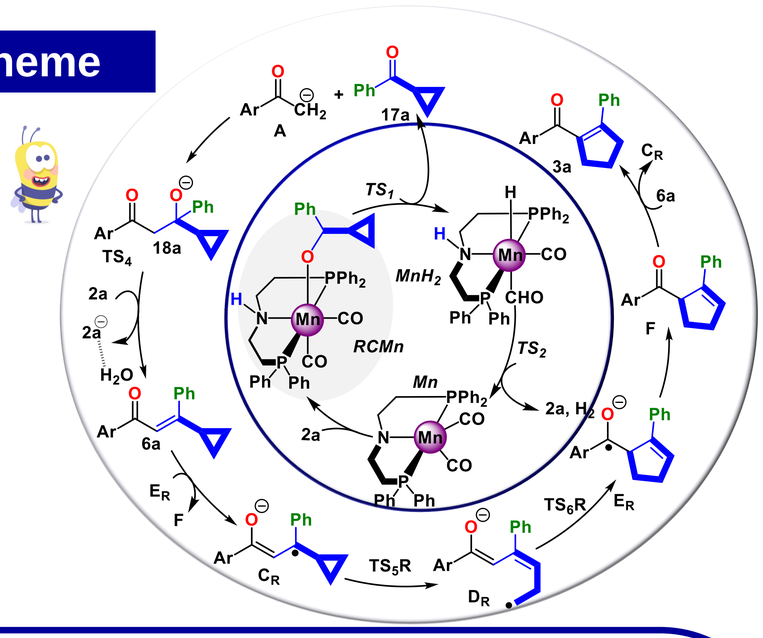
Introduction



Hydrogen borrowing Catalysis

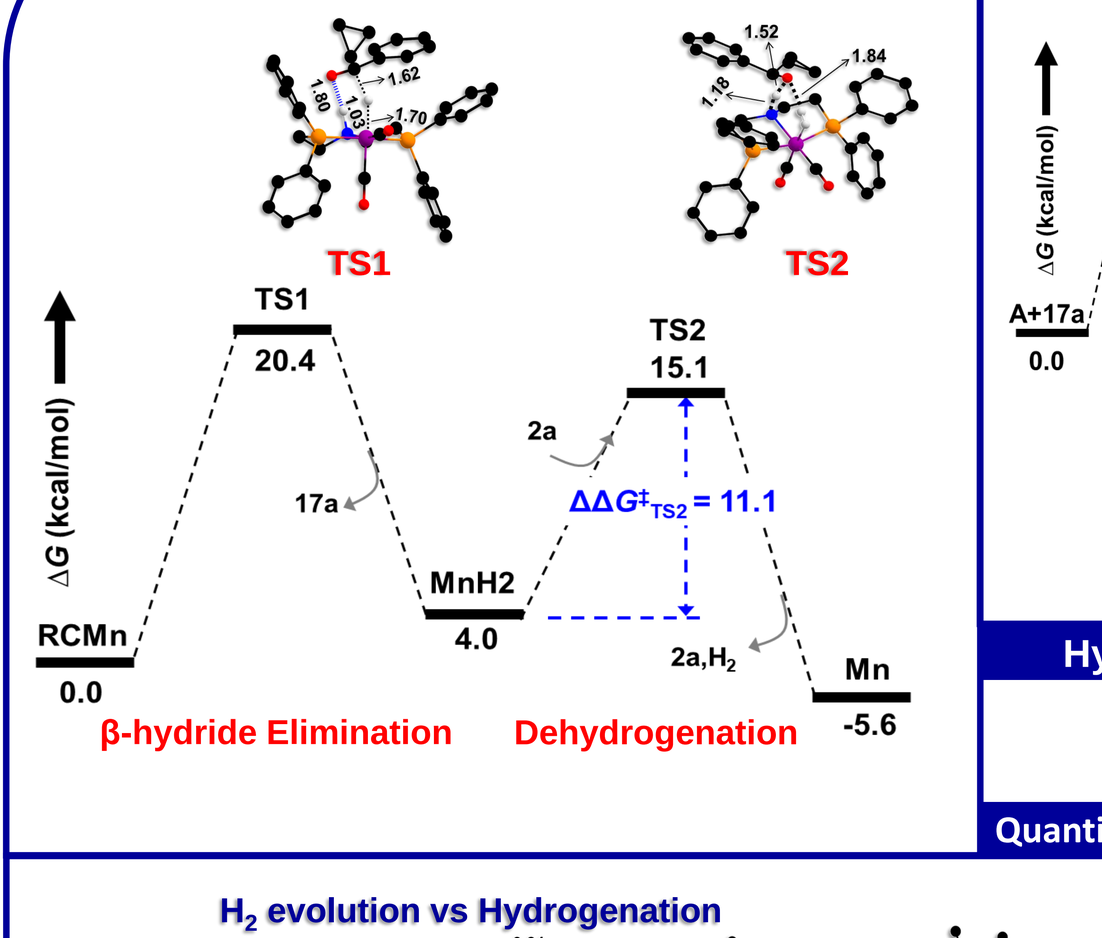
- ✓3d transition metal catalysis
- ✓Hydrogen borrowing
- ✓Interrupted hydrogen returning
- ✓Water and hydrogen gas as by product

Scheme

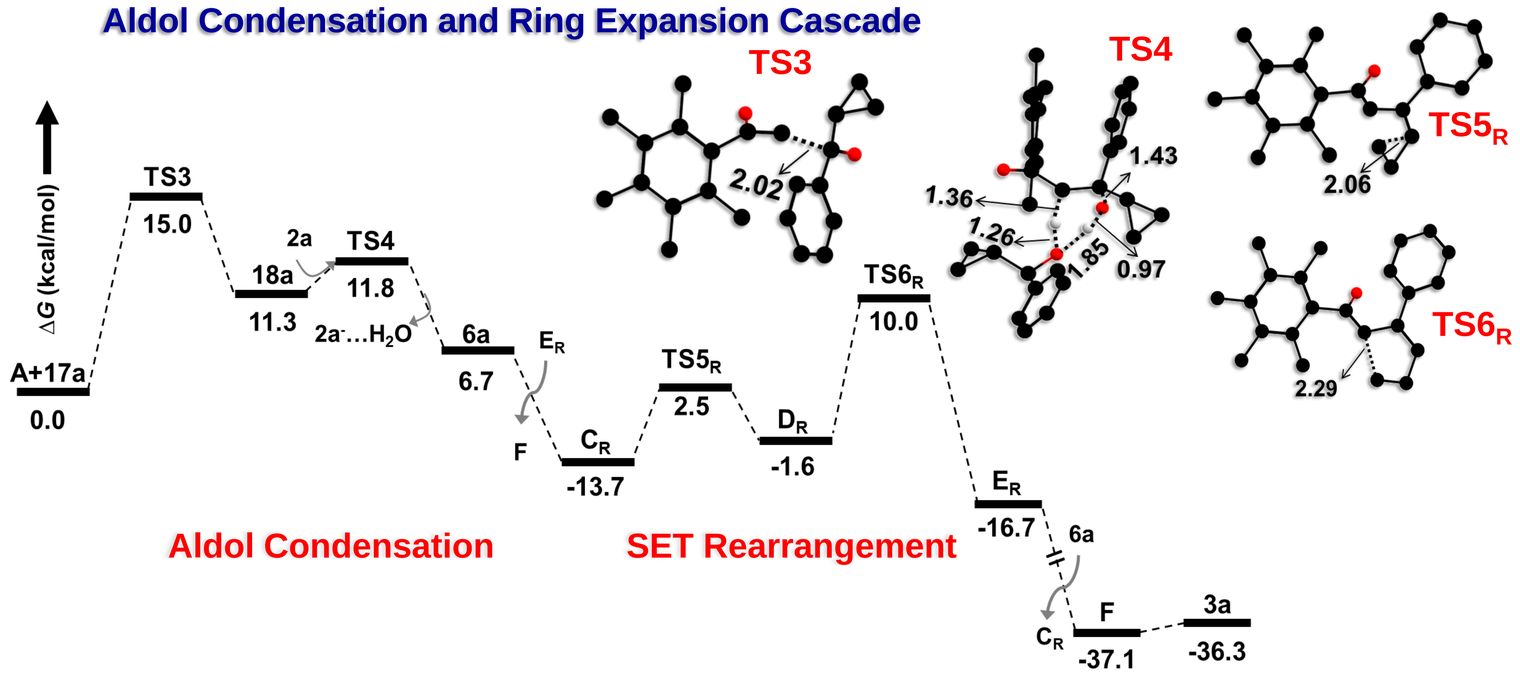


Results and Discussion

Metal Assisted Alcohol Dehydrogenation



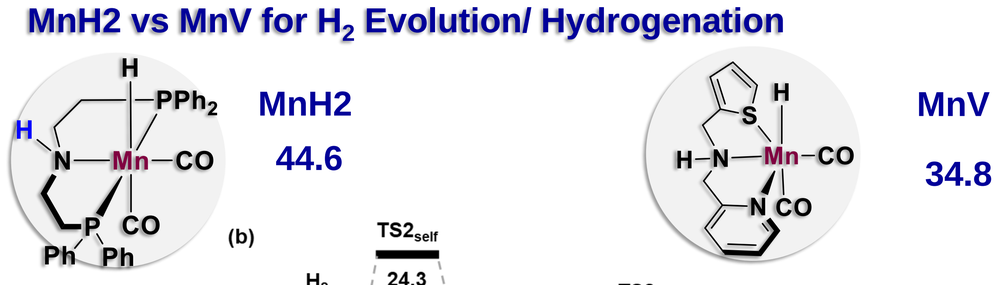
Aldol Condensation and Ring Expansion Cascade



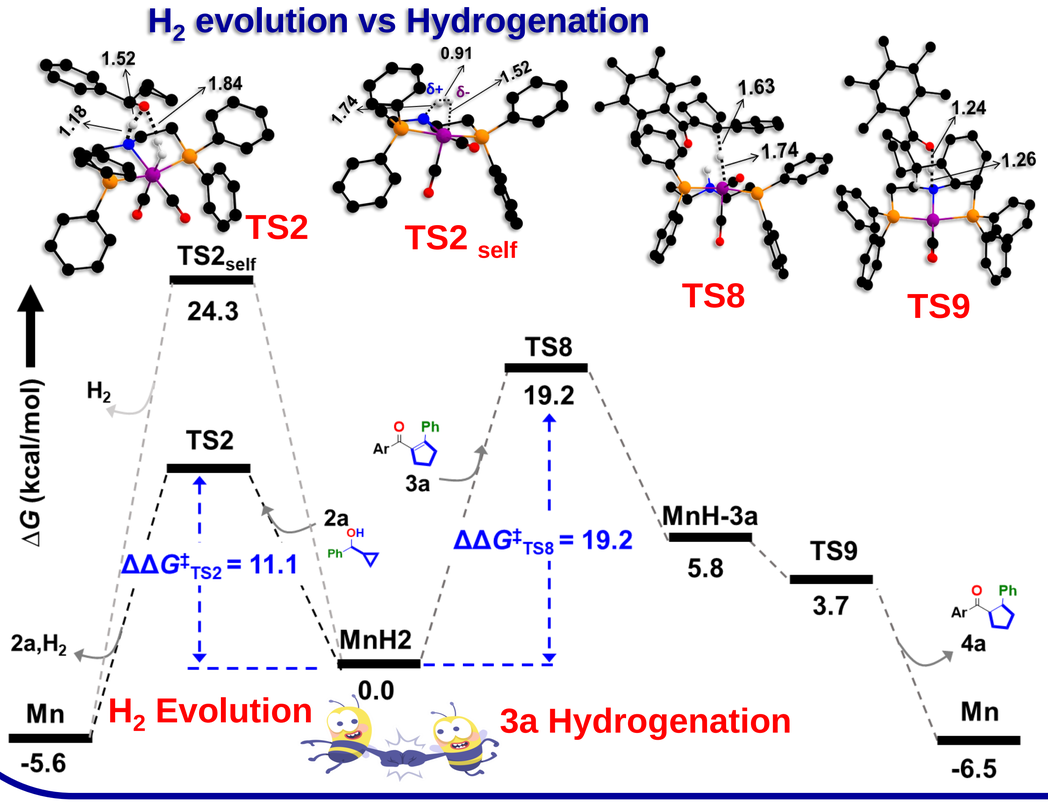
Hydricity ΔG°H M-H

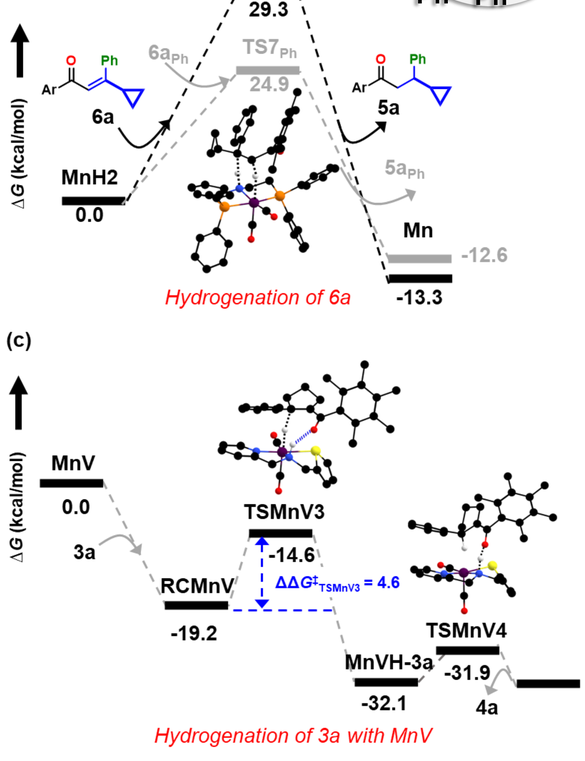
Quantifies M-H Bond Strength

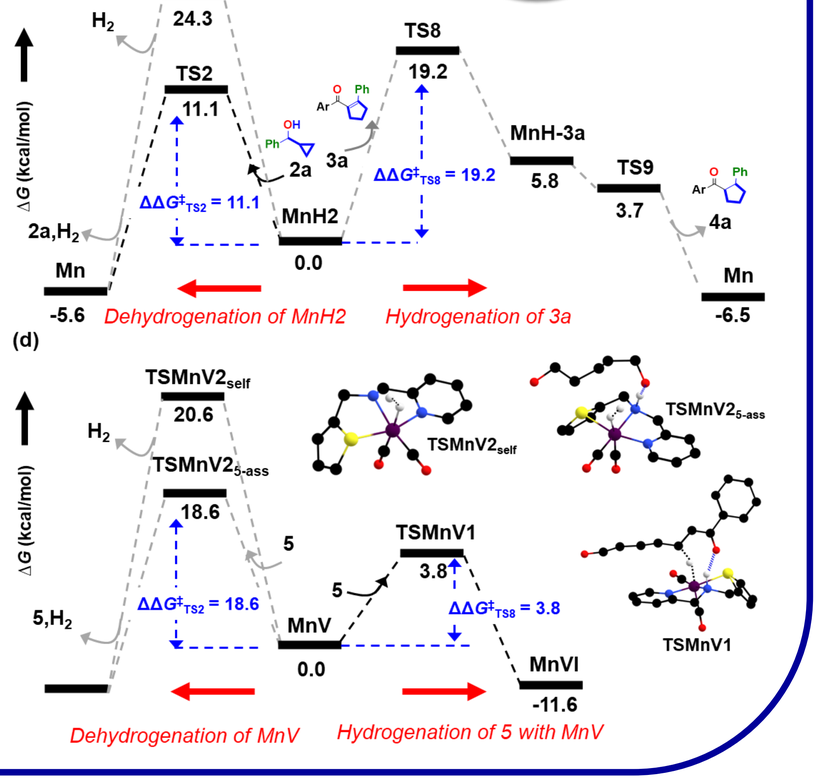
MnH2 vs MnV for H_2 Evolution/ Hydrogenation



H_2 evolution vs Hydrogenation







Conclusion

- ✓Mn catalysed aceptorless alcohol dehydrogenation
- ✓Aldol condensation & SET mediated vinyl cyclopropane ring expansion cascade
- ✓Active participation of alcohol in dehydrogenation of metal hydride and aldol condensation
- ✓Alcohol mediation is more favourable than conventional base mediated aldol condensation
- ✓Evolution of H_2 gas with regeneration of active catalyst
- ✓Unsaturated product.

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References

[1] Wübbolt, S.; Cheong, C. B.; Frost, J. R.; Christensen, K. E.; and Donohoe, T. J. A., Angew. Chem. Int. Ed. Engl. 2020, 59, 11339-11344.
[2] Luque-Urrutia, J. A.; Solà, M.; Milstein, D.; and Poater, J. Am. Chem. Soc. 2019, 141, 2398-2403.
[3] Roy, L.; Paul, A., Chem. Commun 2015, 51, 10532-10535.
[4] Jana, A.; Das, K.; Kundu, A.; Thorve, P. R.; Adhikari, D.; and Maji, B., ACS. Catal 2020, 10, 2615-2626.
[5] Sarkar, K.; Behera, P.; Roy, L; and Maji, B., Manuscript in preparation.