



Introduction

Hydrogen bonding networks for the allosteric control of enzymatic reactivity are common, but rarely employed in organometallic catalysis.

A. Controlled enzyme catalysis via hydrogen bonding network gate

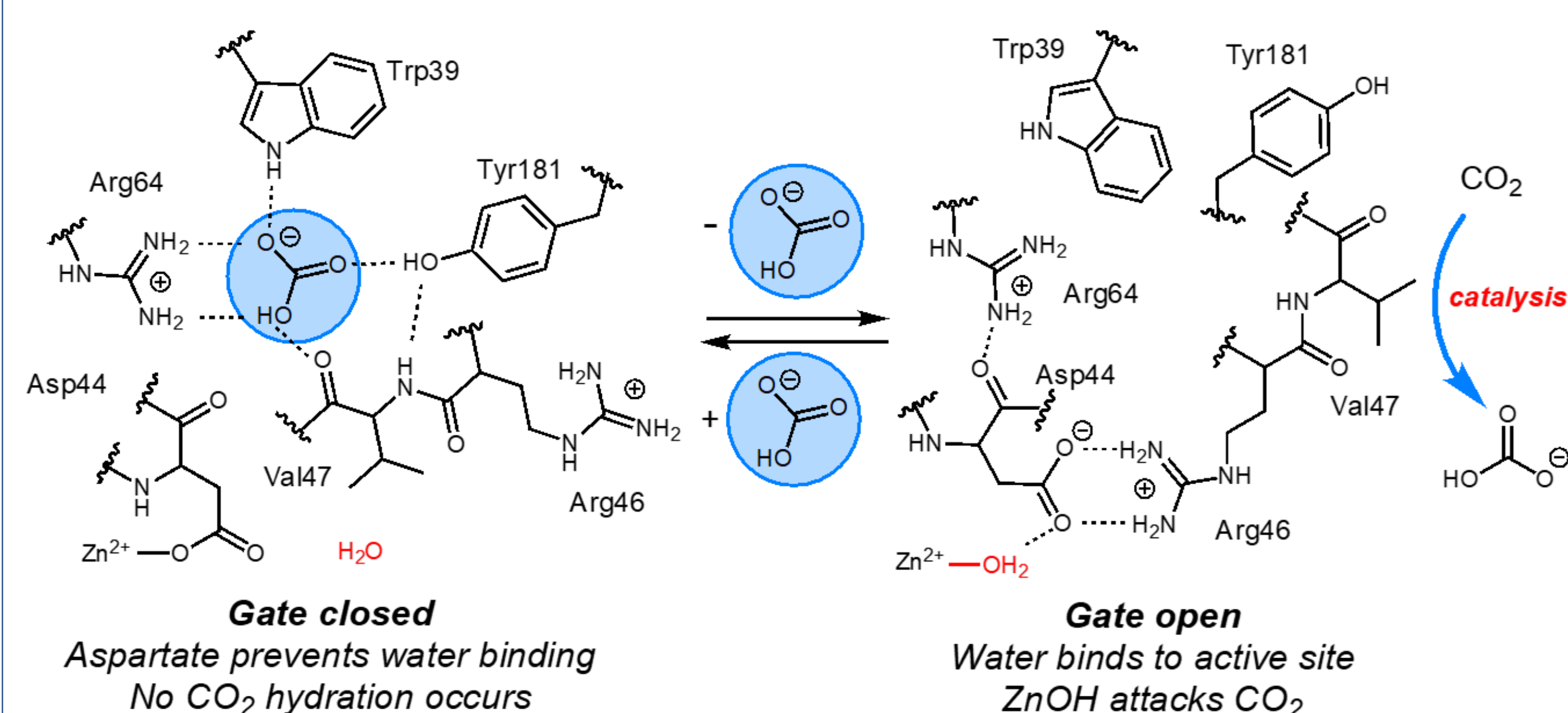


Figure 1: (A) Hydrogen bonding gate in β -carbonic anhydrase for controlled bicarbonate formation.

Synthesis: Diethyl Amino Control Complexes

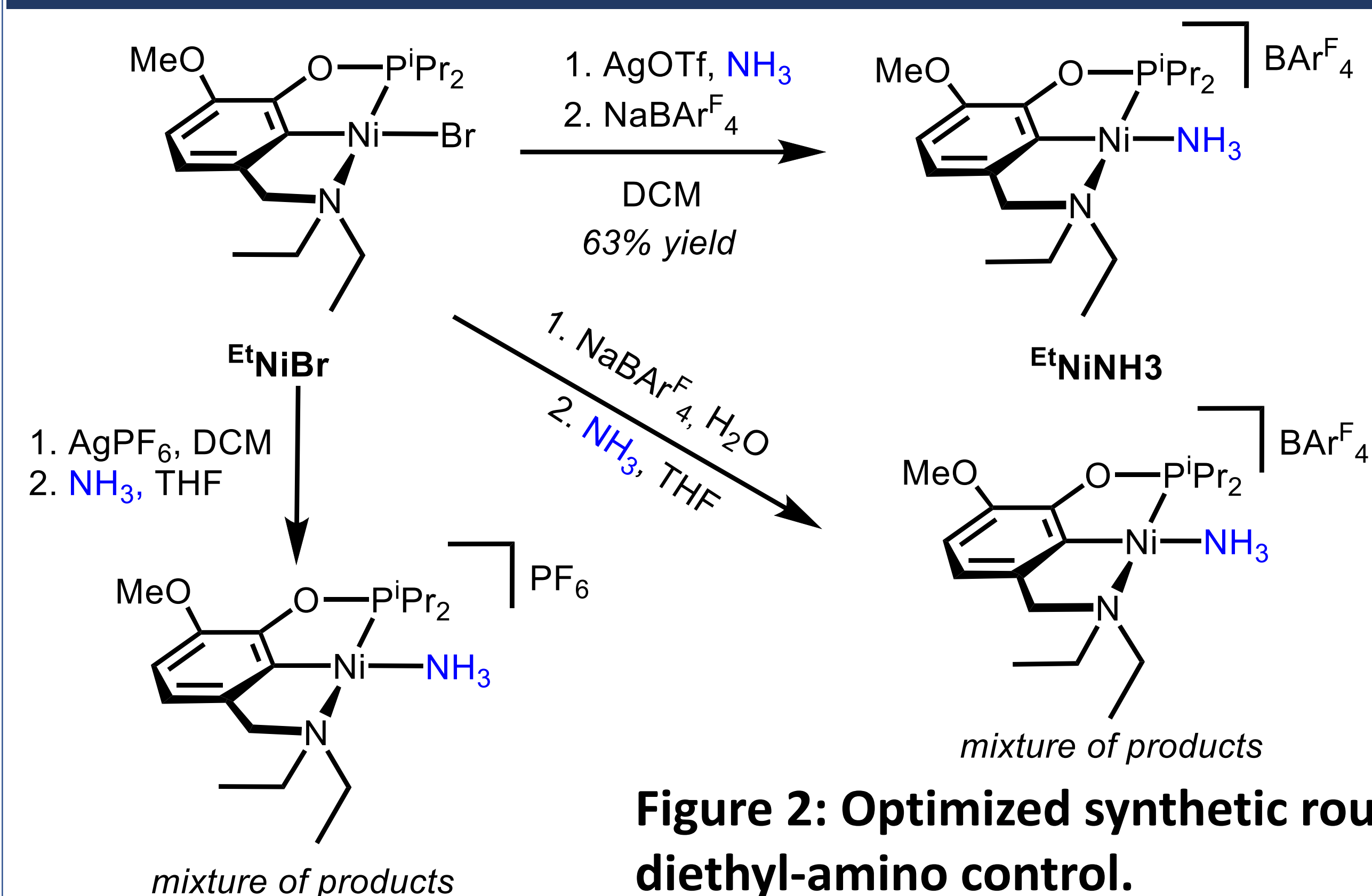
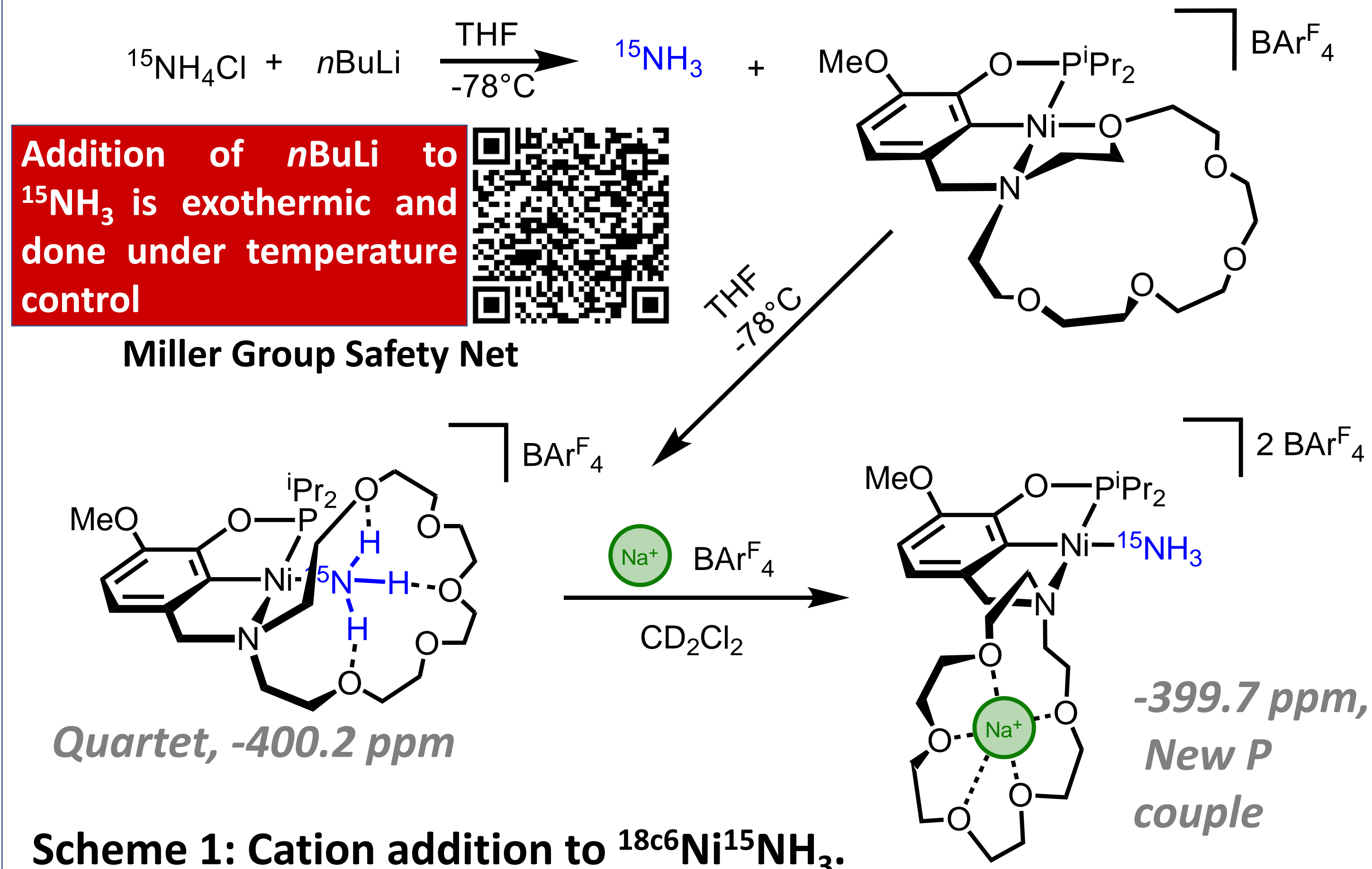


Figure 2: Optimized synthetic route to diethyl-amino control.

¹⁵NH₃ Studies & Safety Statement



Characterization of H-Bonding Networks

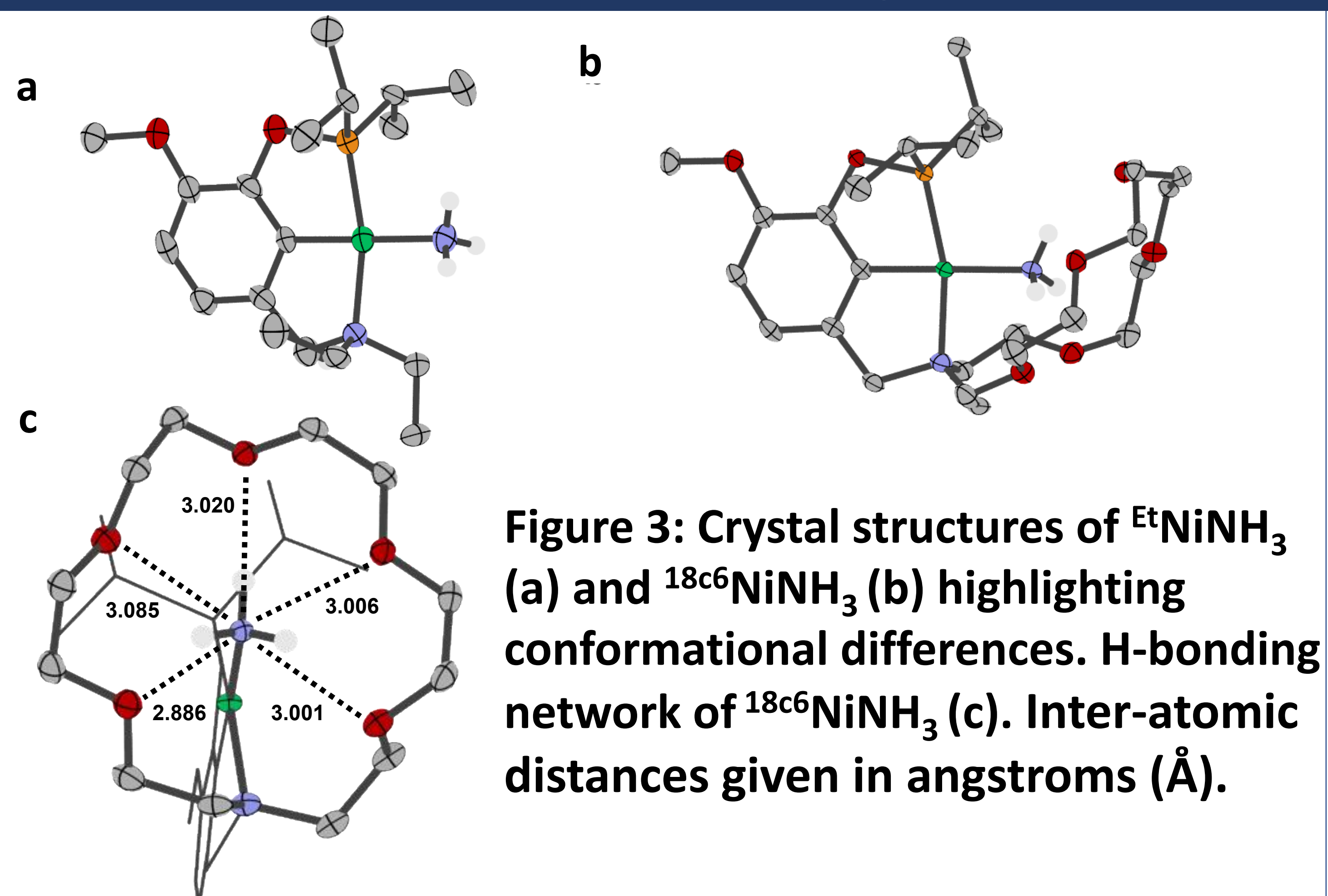
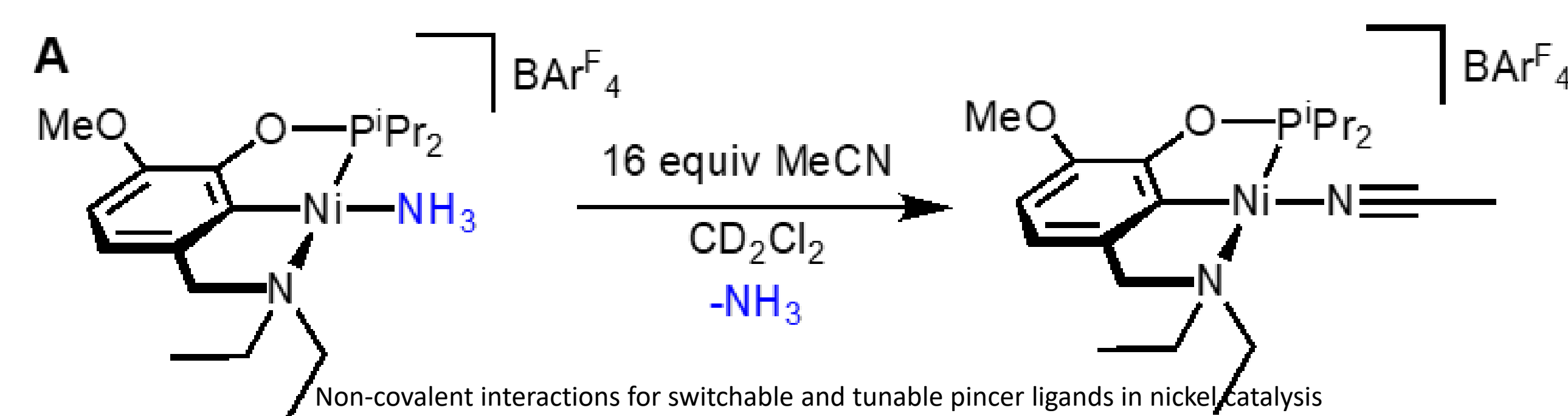
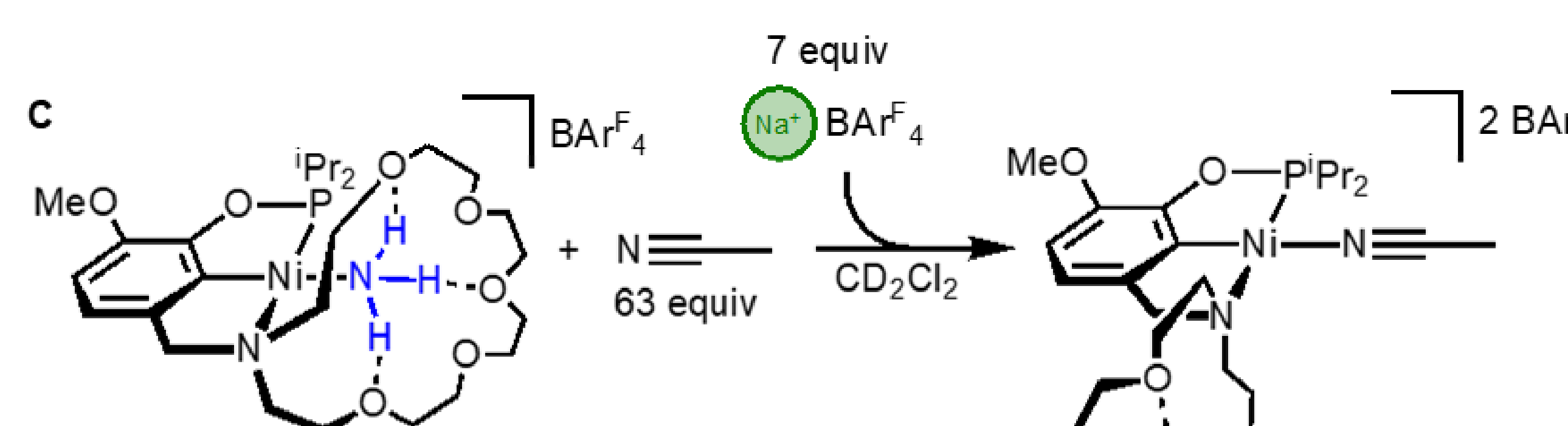
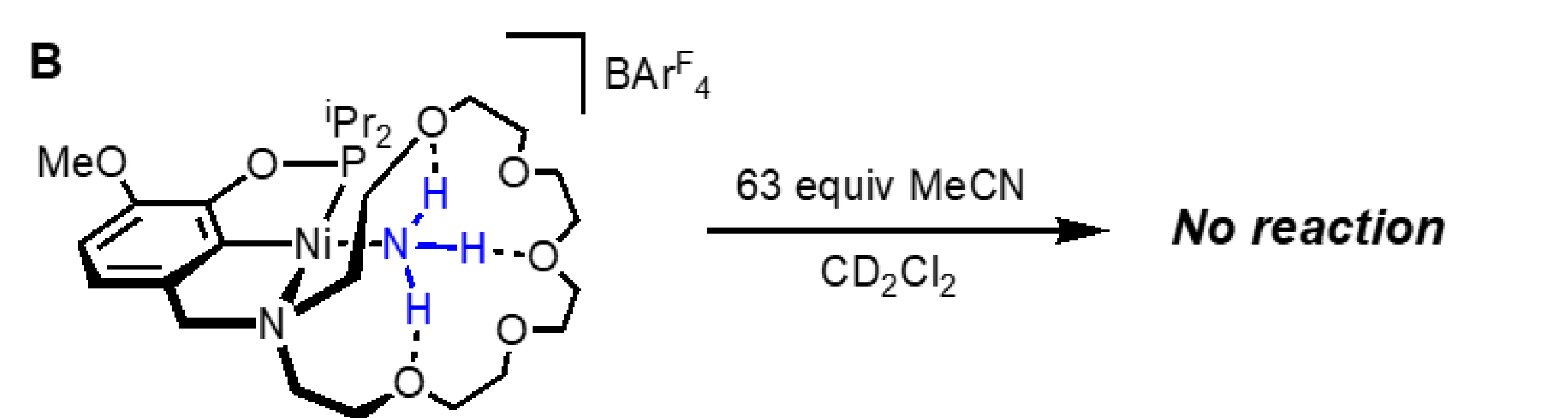


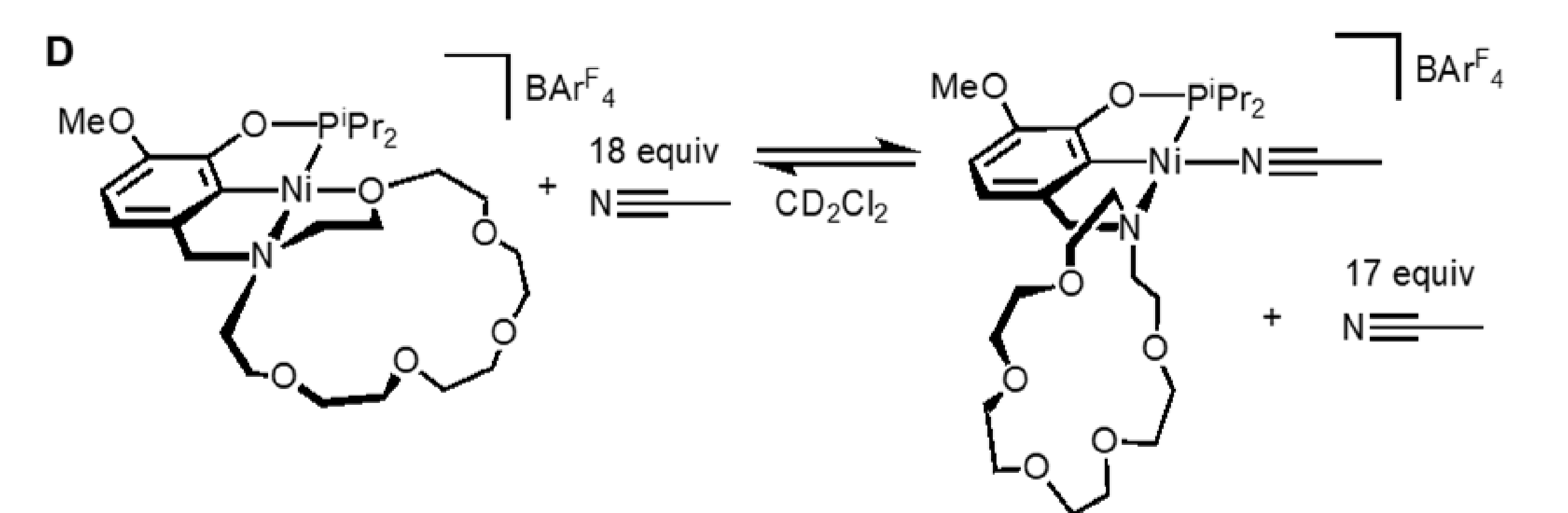
Figure 3: Crystal structures of EtNiNH_3 (a) and $^{18}\text{c}6\text{NiNH}_3$ (b) highlighting conformational differences. H-bonding network of $^{18}\text{c}6\text{NiNH}_3$ (c). Inter-atomic distances given in angstroms (\AA).



Facile substitution without supramolecular gate



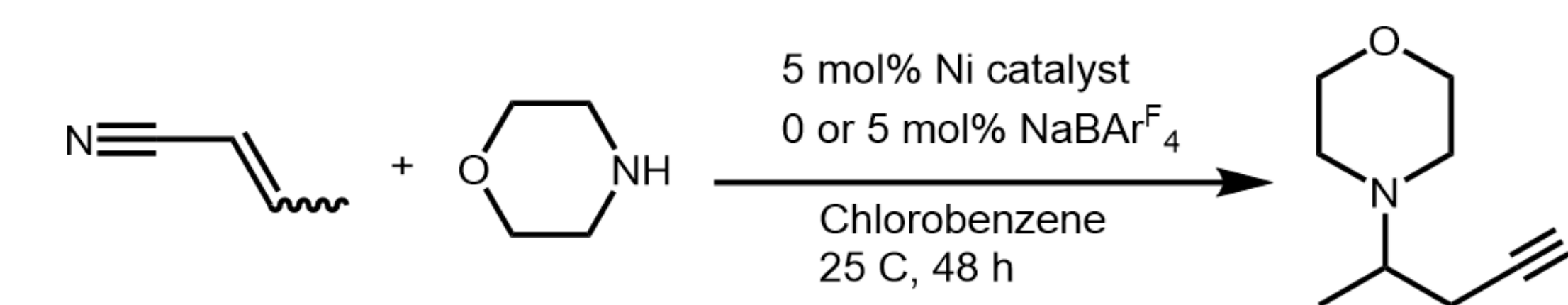
Sodium breaks H-bonding network, enables substitution



Scheme 2: Ligand substitution studies of EtNiNH_3 (a), $^{18}\text{c}6\text{NiNH}_3$ (b), $\text{Na}^+@^{18}\text{c}6\text{NiNH}_3$ (c) and $^{18}\text{c}6\text{Ni}$ (d).

Switchable Hydroamination

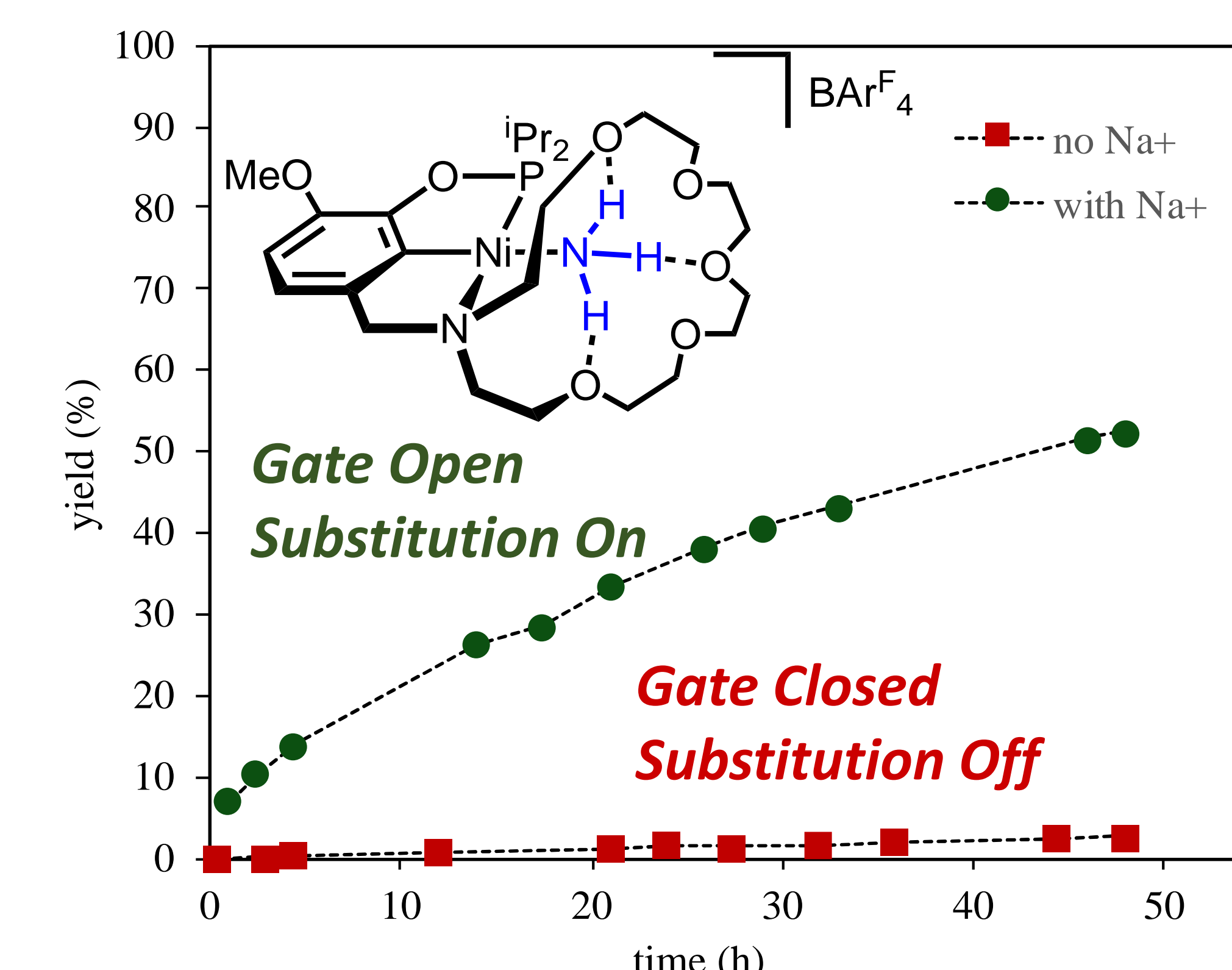
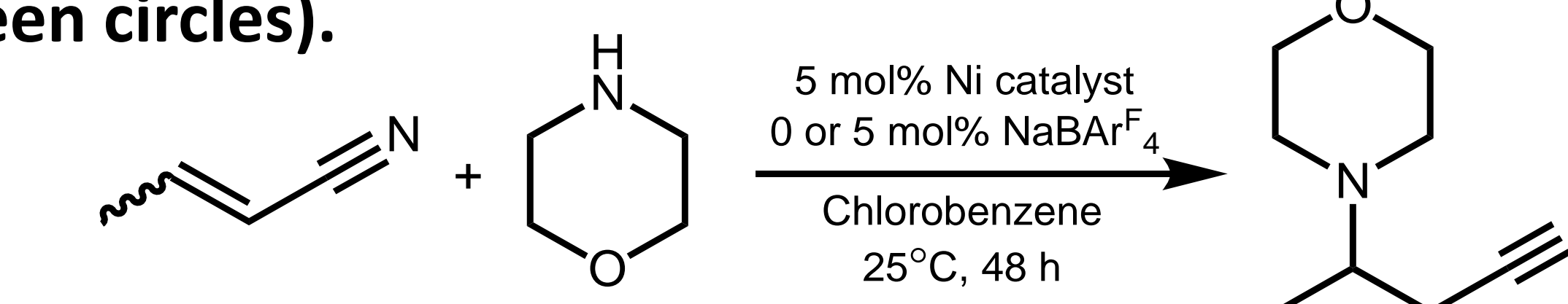
Table 1: Yields of hydroamination of crotonitrile with morpholine catalyzed by Ni complexes with and without NaBARF₄ after 48 hours.



	EtNiNH_3	$^{18}\text{c}6\text{NiNH}_3$
no Na⁺	70%	2.7%
with Na⁺	66%	53%
reactivity ratio^a	1.0	59

^aRatio of initial rates with and without NaBARF₄.

Figure 5: Hydroamination of crotonitrile with morpholine catalyzed by $^{18}\text{c}6\text{NiNH}_3$, with no salt additive (red squares) and with NaBARF₄ (green circles).



Conclusions

Pincer-crown ether nickel complexes can be regulated by two cofactors

- (1) Ammonia ligand enabling H-bonding network between primary and secondary coordination sphere
- (2) Na⁺ ion, which can break the network to form cation-dipole interactions

These interactions can be leveraged to enable switchable ligand substitution and hydroamination of crotonitrile.

Acknowledgements

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