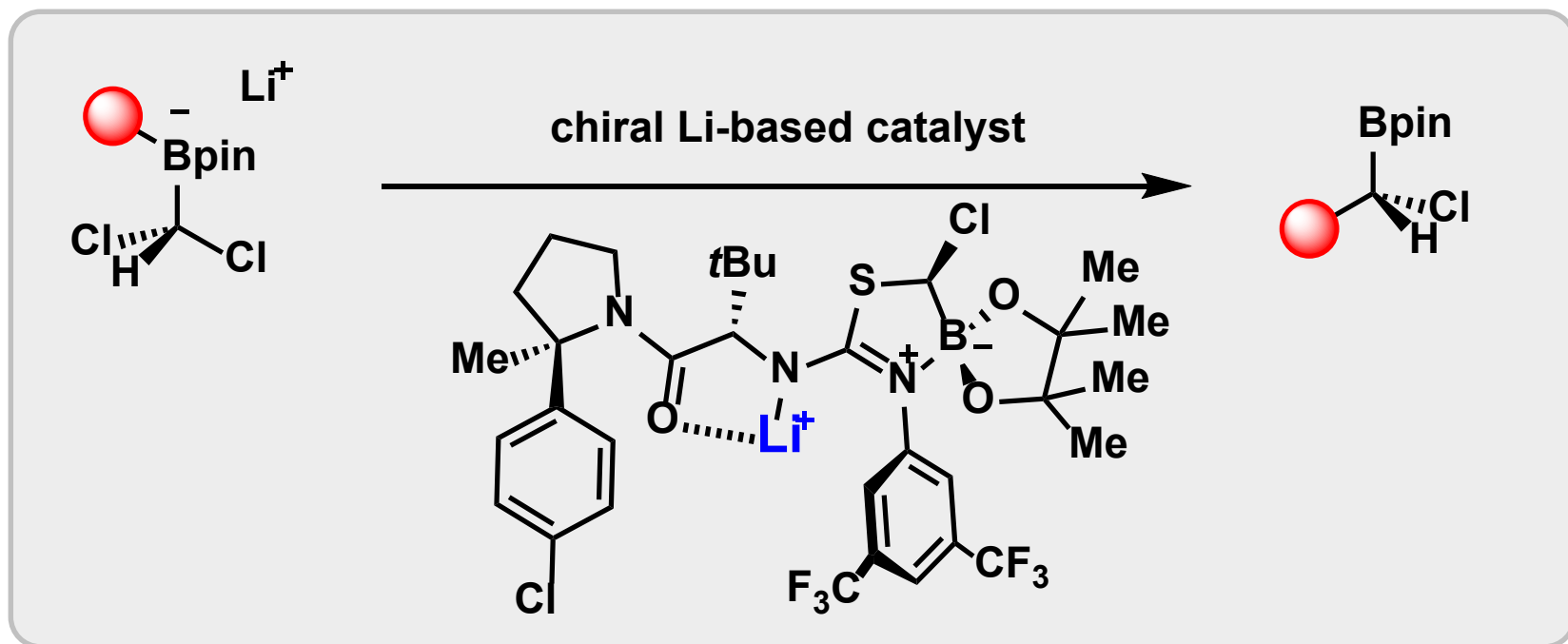


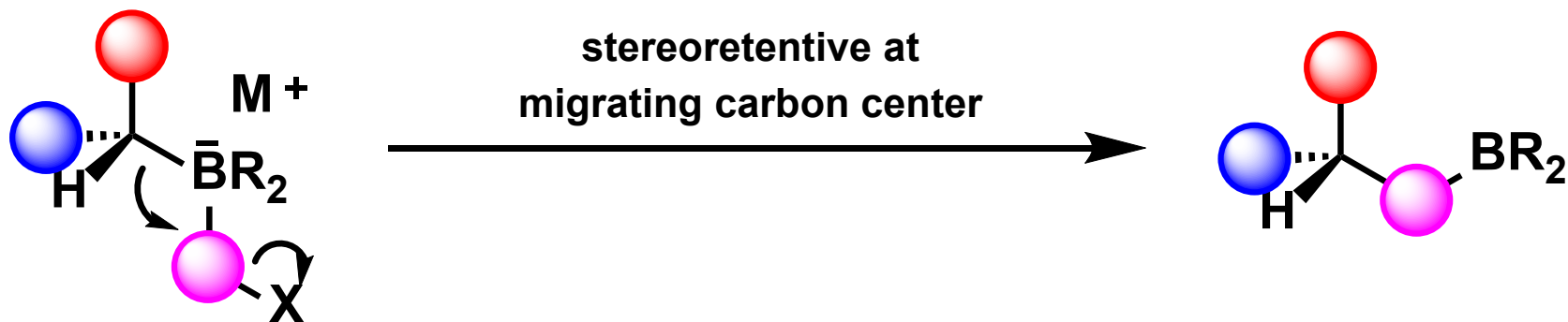
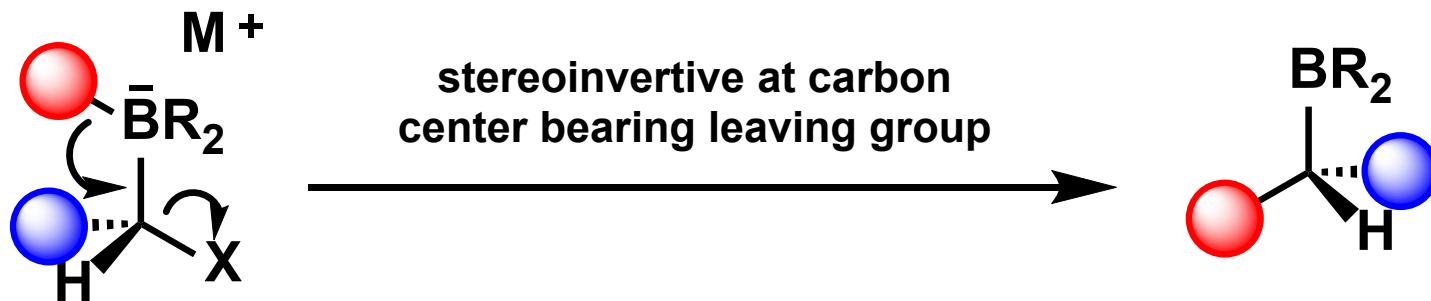
Enantioselective catalytic 1,2-boronaterearrangements



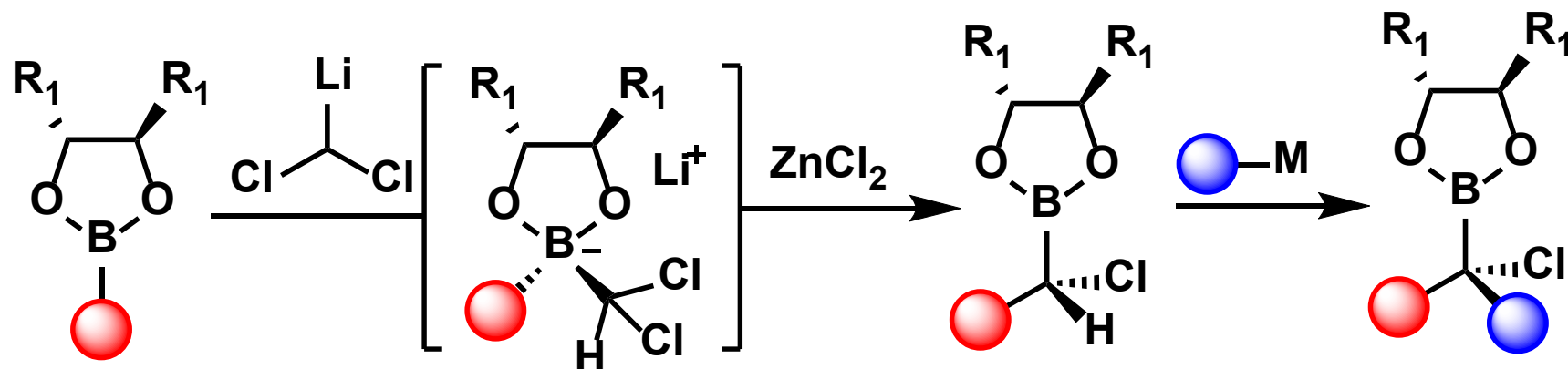
Chao Yang

15-01-2022

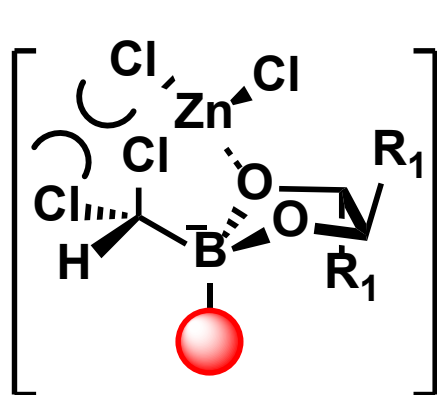
Stereochemical outcomes of 1,2-boronate rearrangements



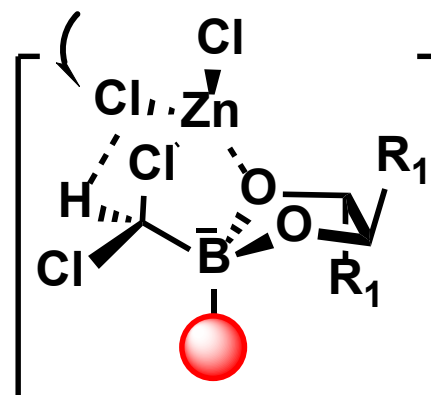
Diastereoselective Matteson homologation



attractive interaction



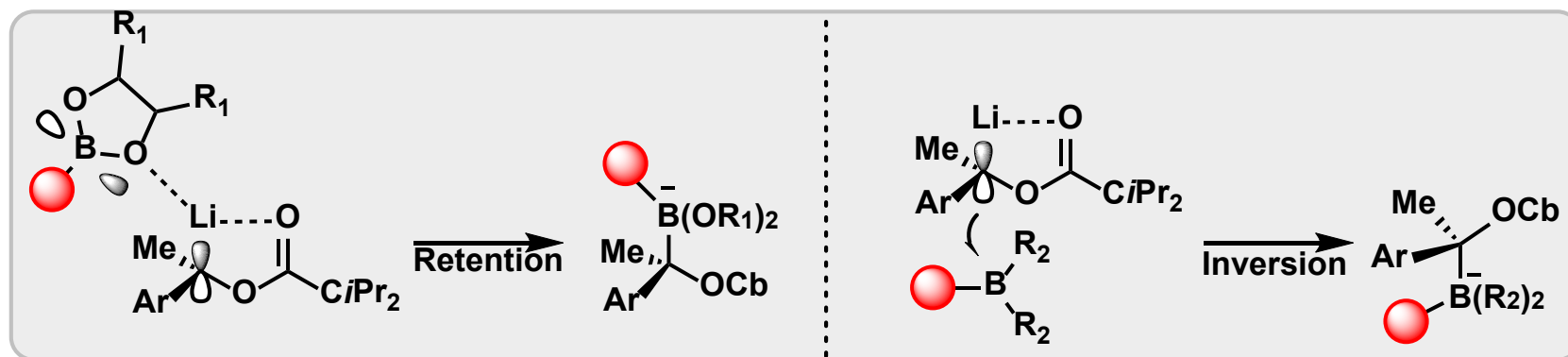
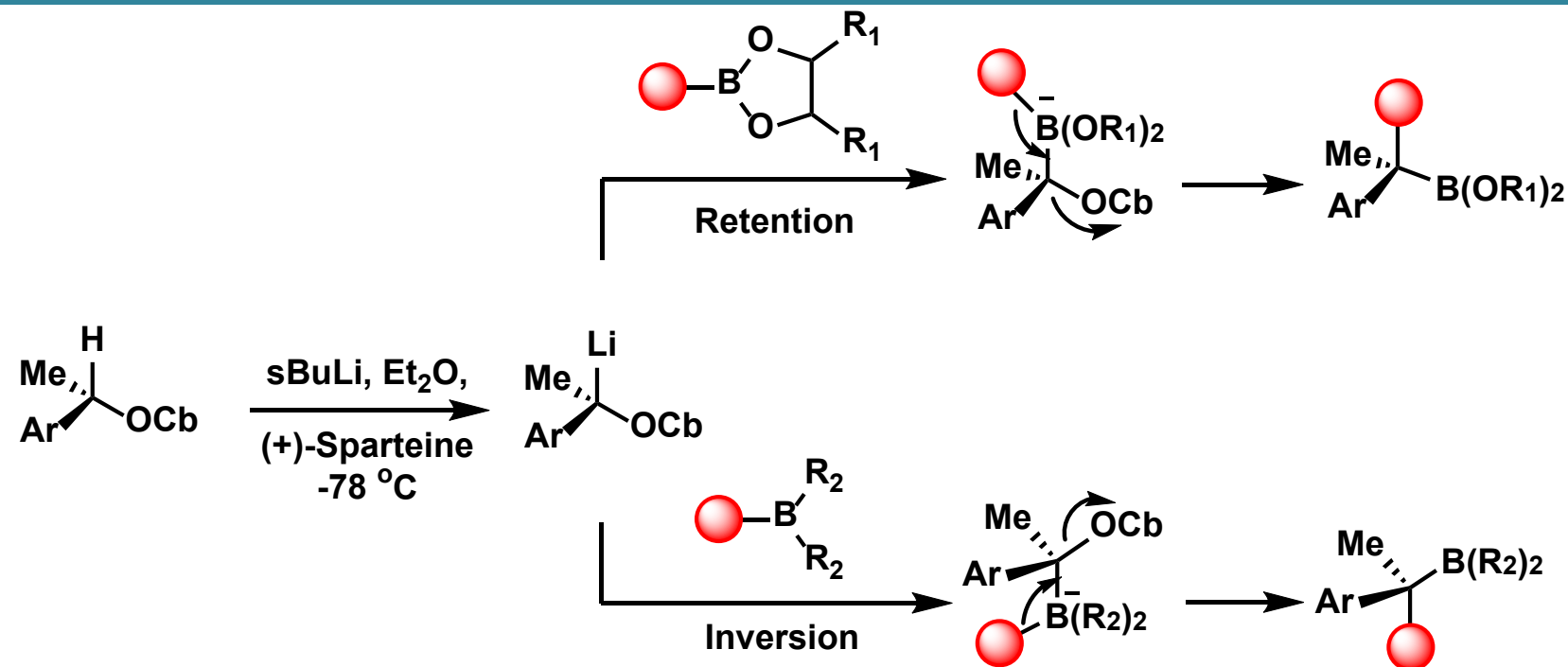
disfavoured TS



favoured TS

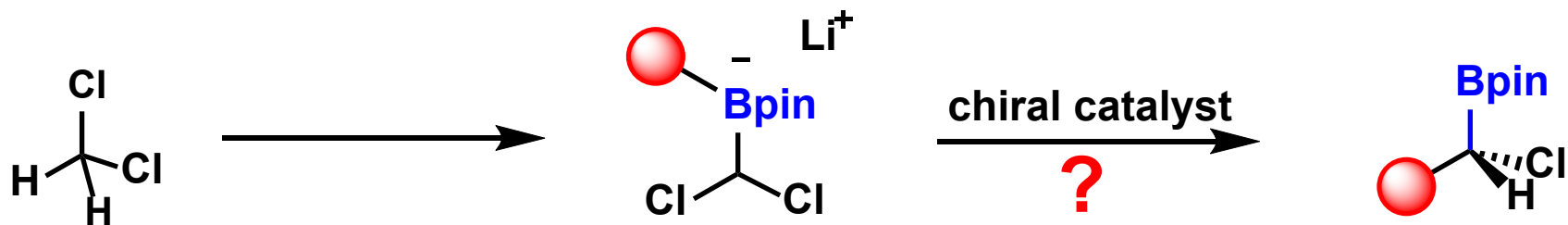
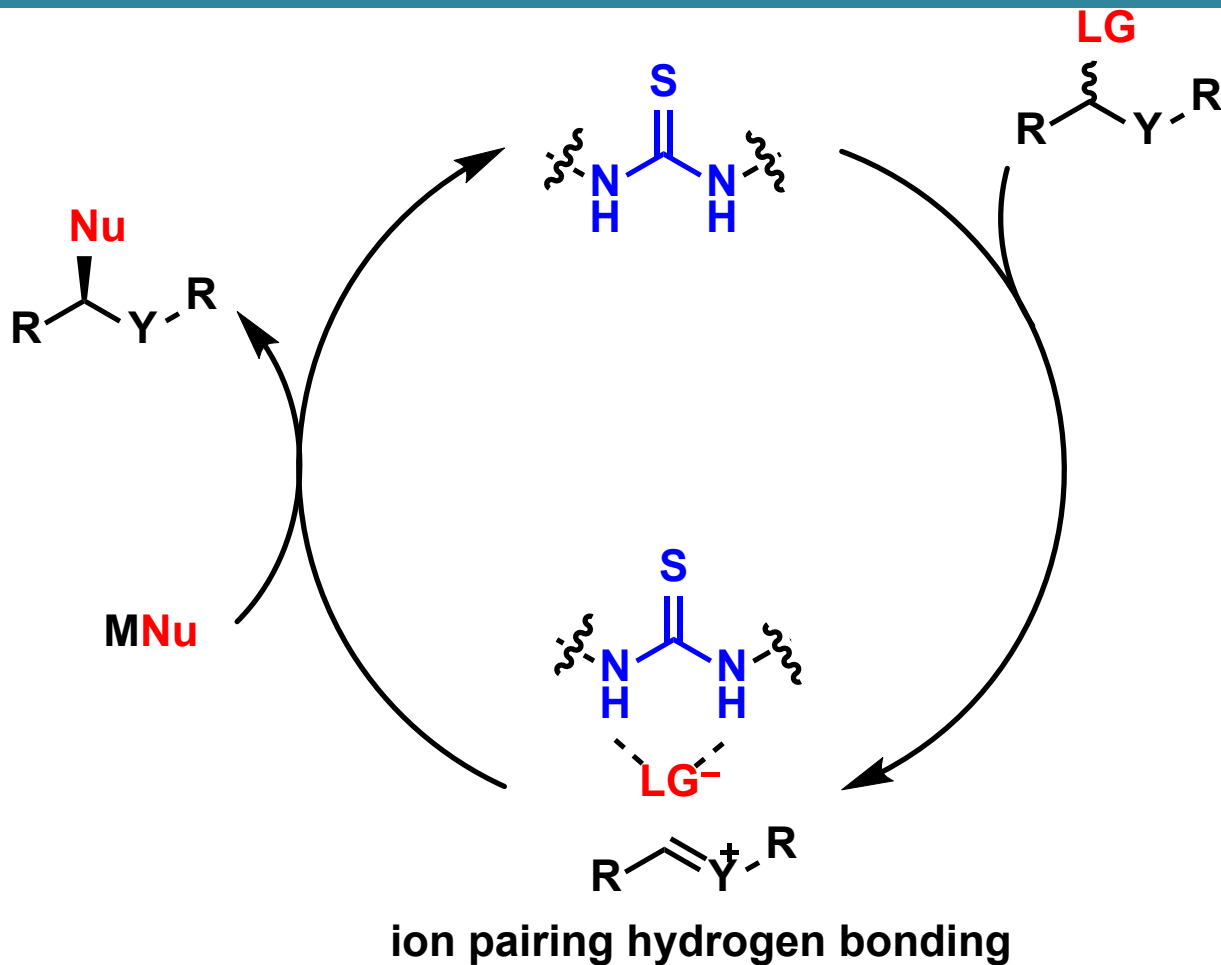
using a chiral diol auxiliary on boron

Lithiation–borylation and Rationalization



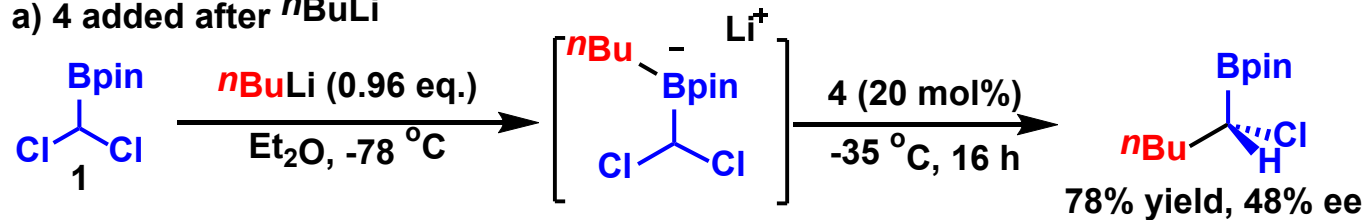
using stoichiometric chiral sparteine

Hydrogen bonding for anion-binding catalysis

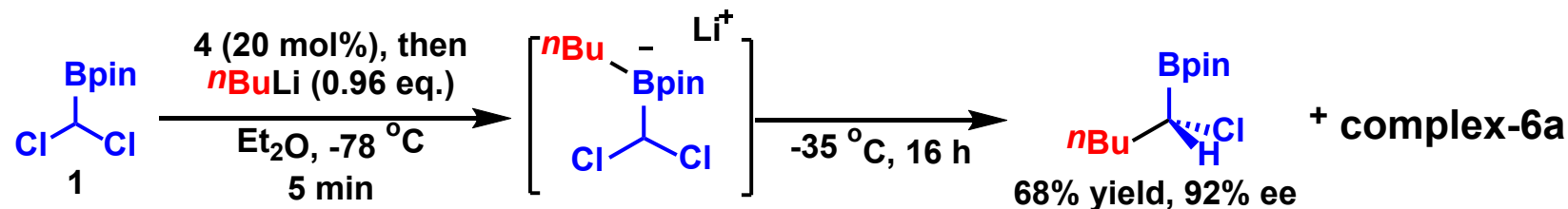


Reaction optimization

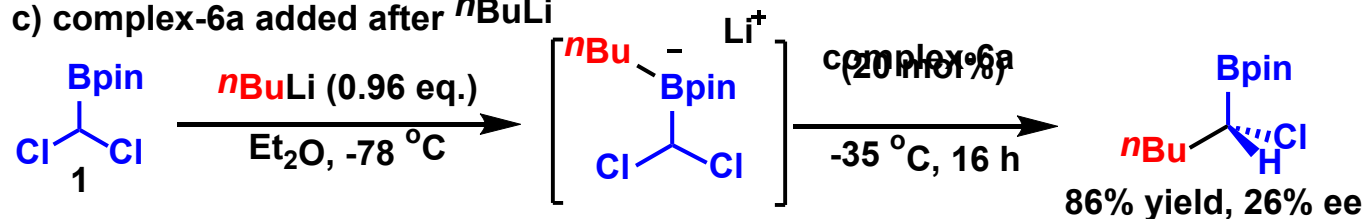
a) 4 added after $n\text{BuLi}$



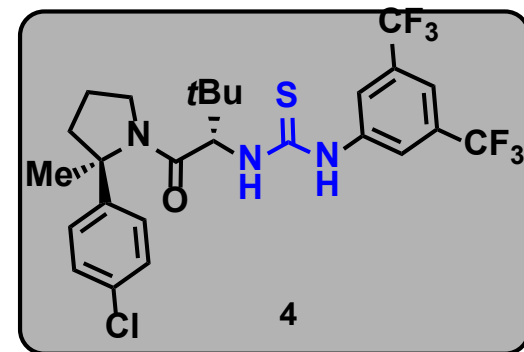
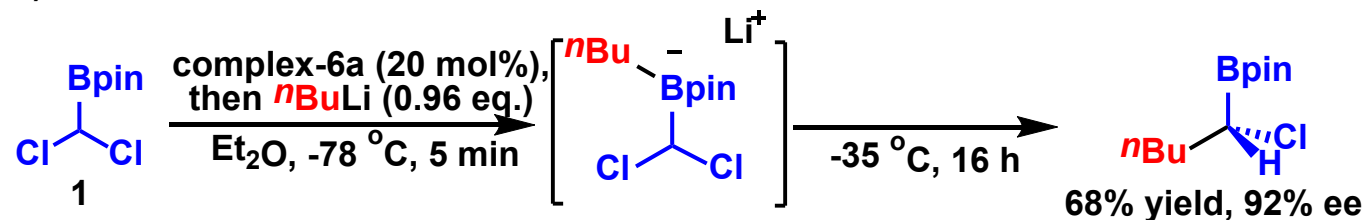
b) 4 added before $n\text{BuLi}$



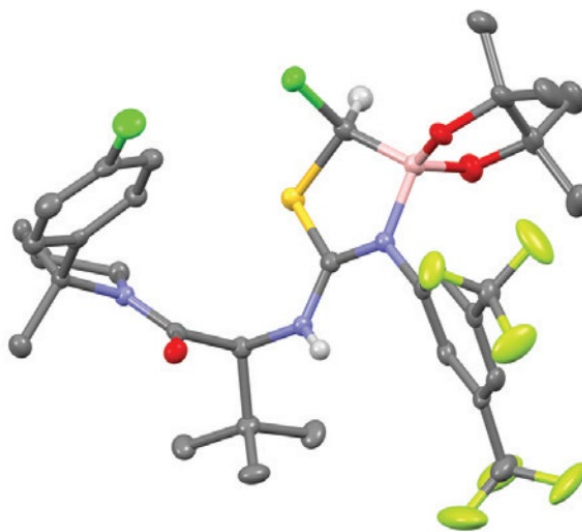
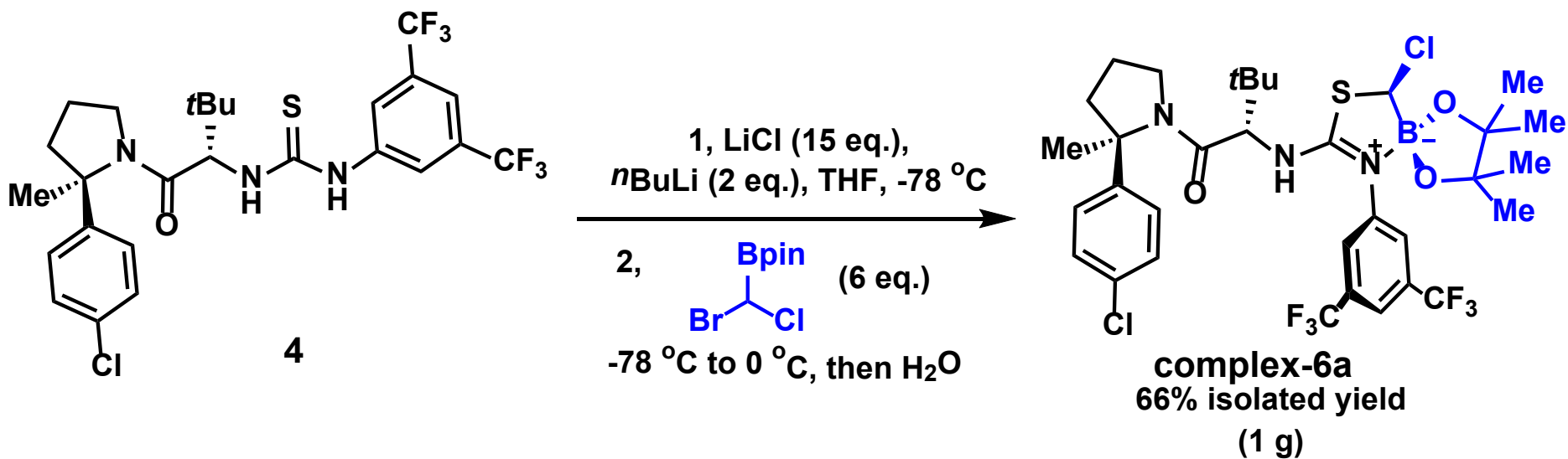
c) complex-6a added after $n\text{BuLi}$



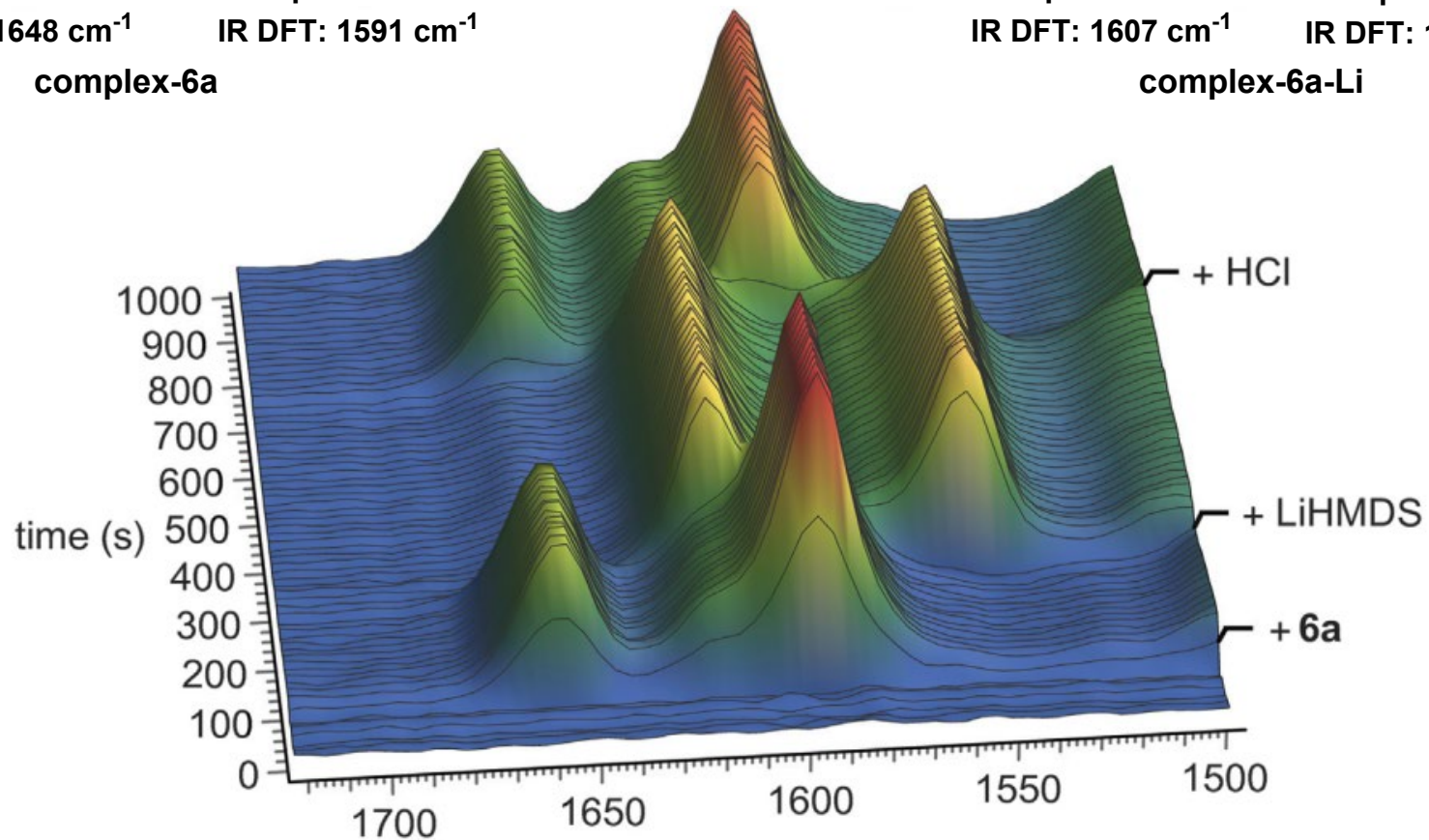
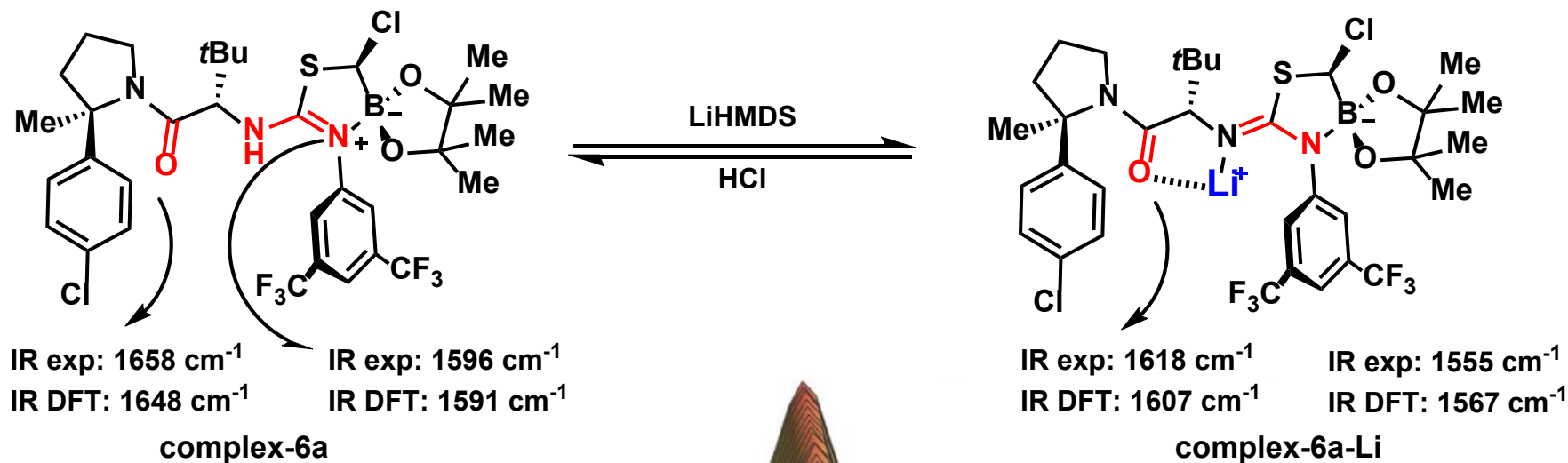
d) 4 added before $n\text{BuLi}$



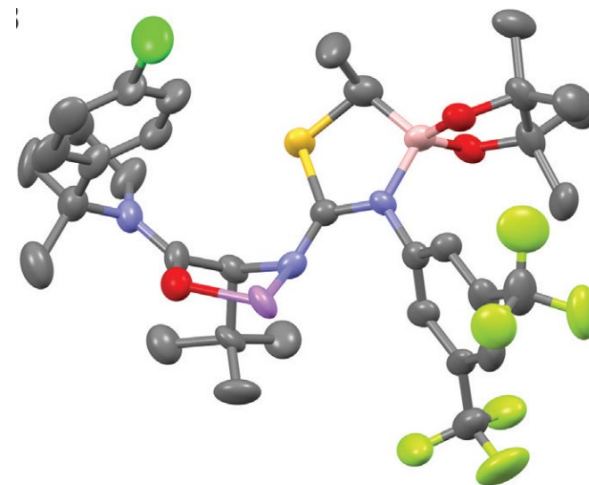
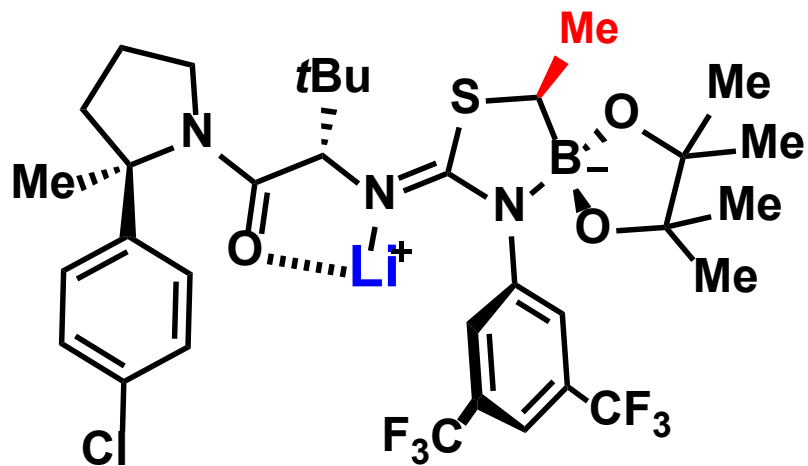
Discovery of isothium-boronate precatalyst complex-6a



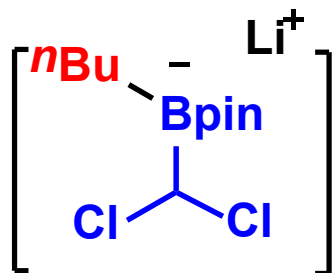
Discovery of isothium-boronate catalyst complex-6a-Li



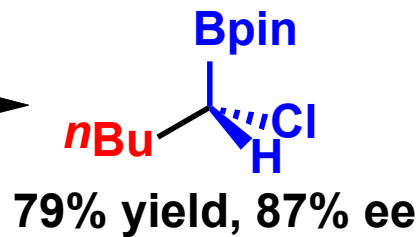
X-ray structure of complex-6b-Li



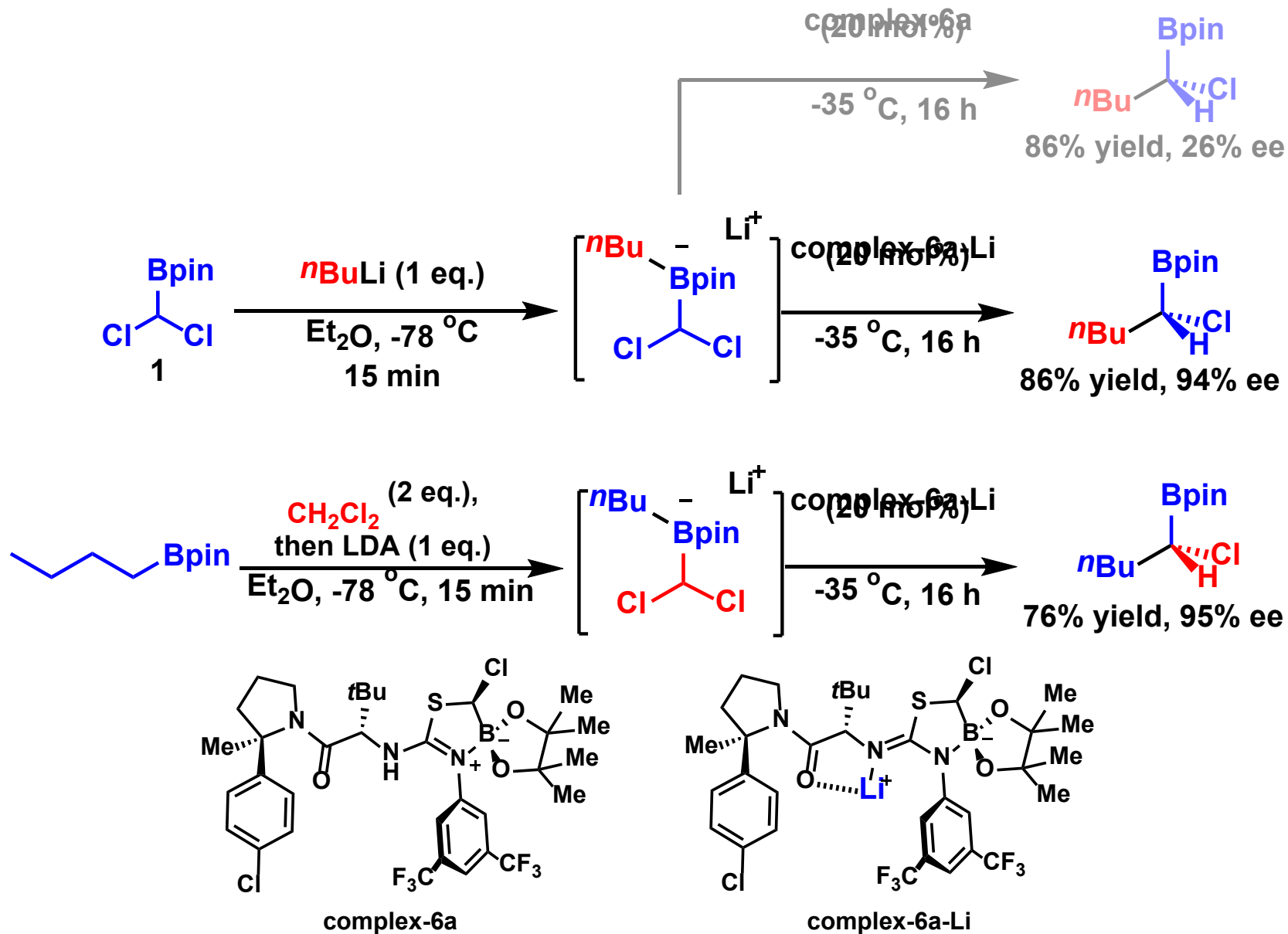
complex-6b-Li



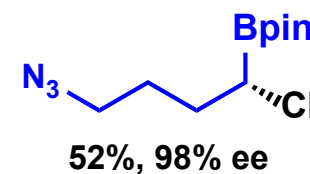
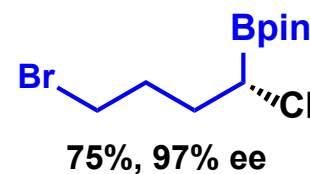
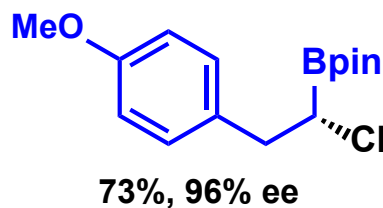
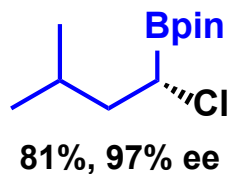
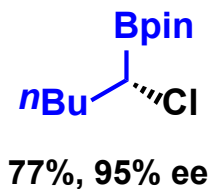
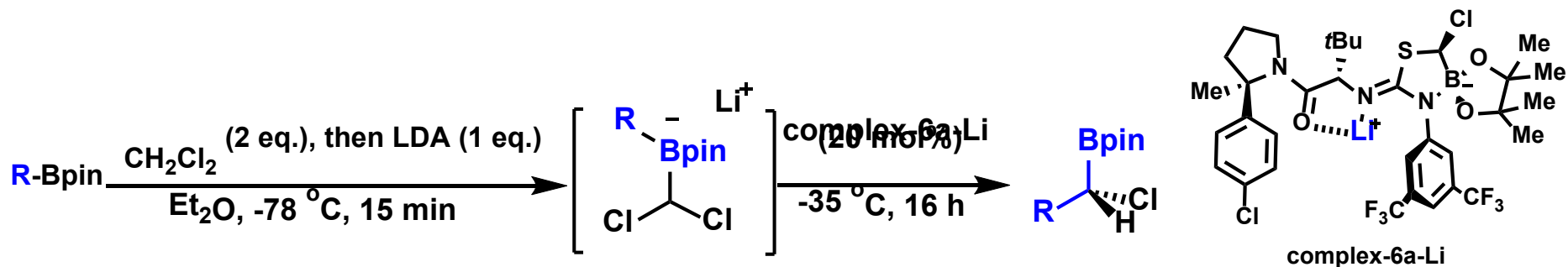
-35 °C, 20 h



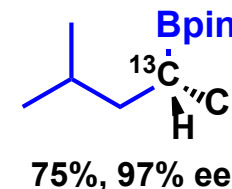
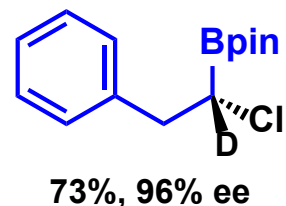
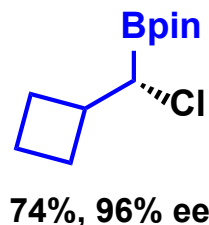
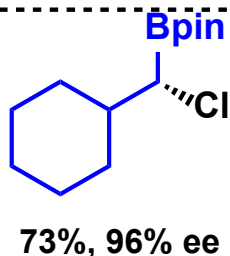
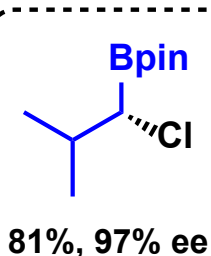
Complex-6a-Li catalyzed reaction



Scope of rearrangement catalyzed by complex-6a-Li



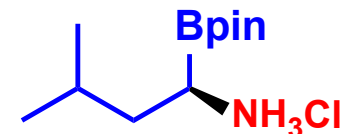
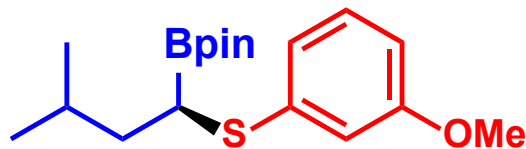
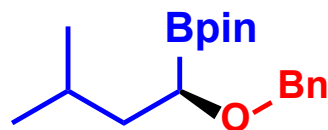
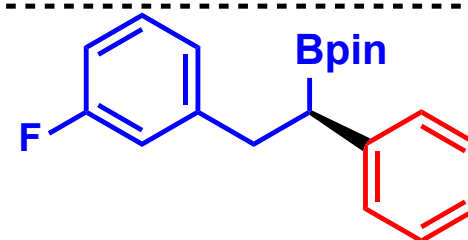
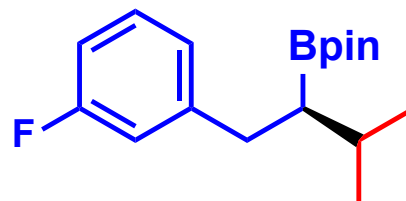
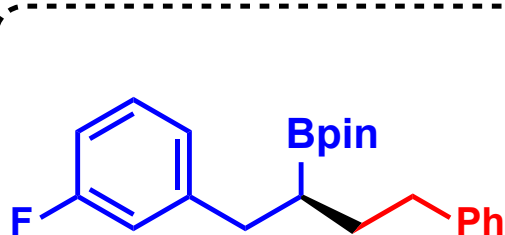
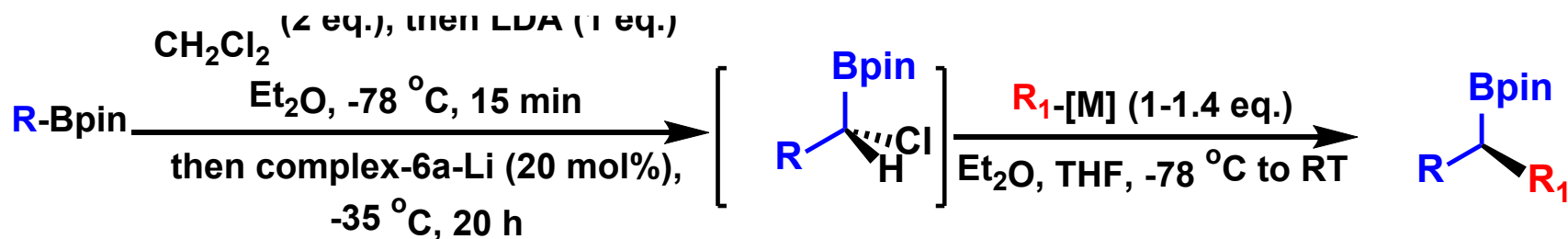
1° boronic esters



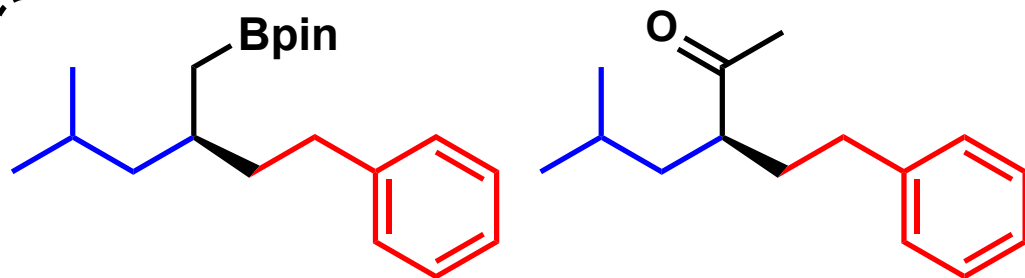
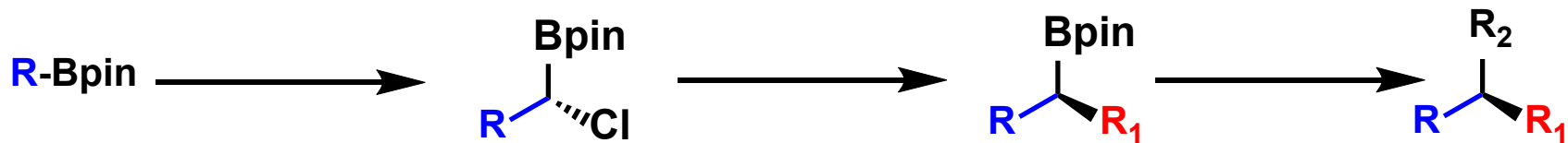
2° boronic esters

isotopically labeled DCM

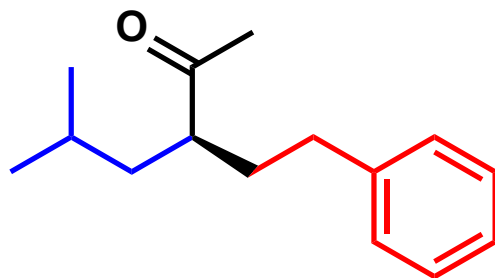
C-Cl bond elaborations of rearrangement product



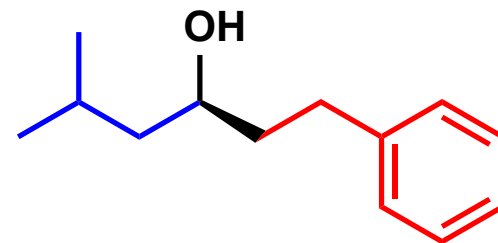
C-B elaborations of secondary boronic ester product



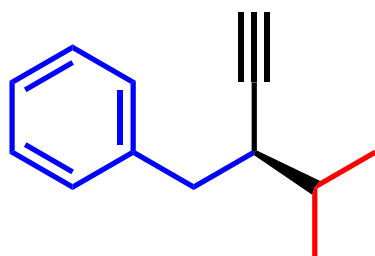
72%, 96% ee



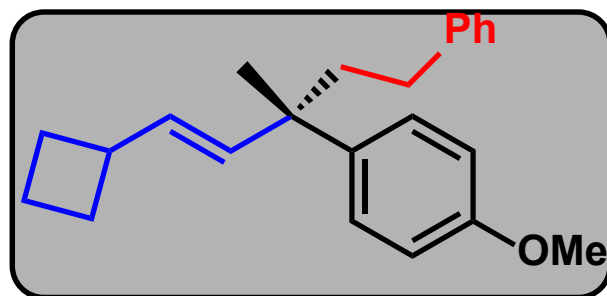
51%, 96% ee



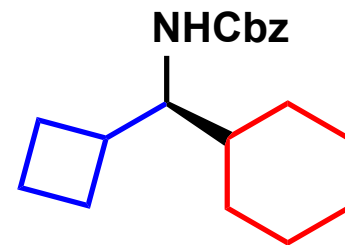
90%, 97% ee



60%, 96% ee

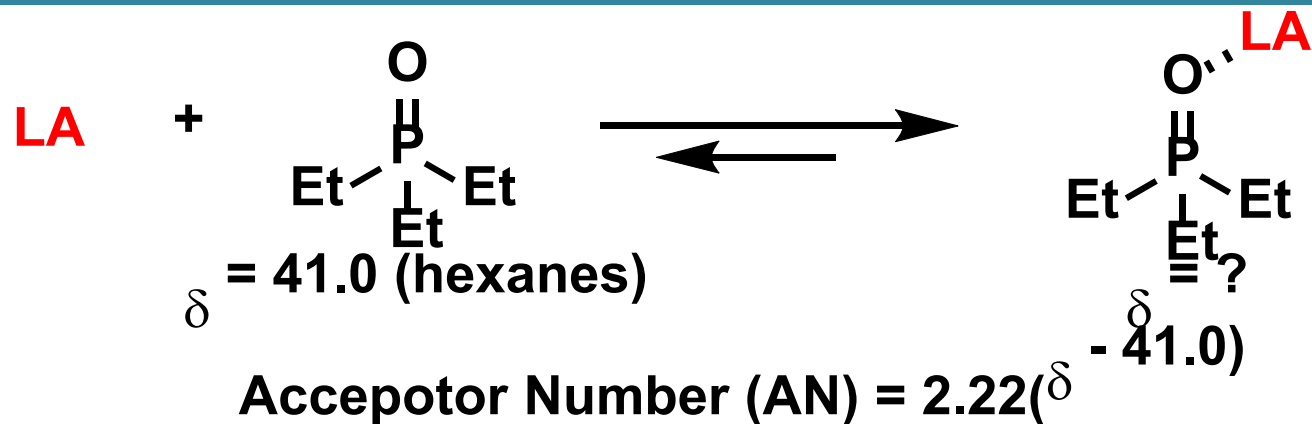


82%, 94% ee



58%, 96% ee

Gutmann-Beckett analysis



LA	AN (Et ₂ O)
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6a-Li	37
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LiHMDS	33
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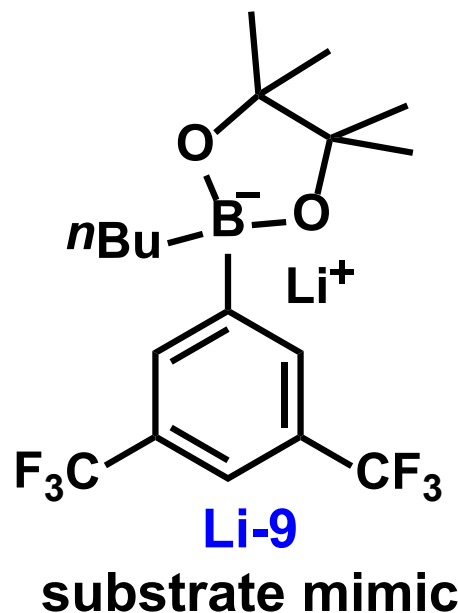
LiNTf ₂	36
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Li-9	38
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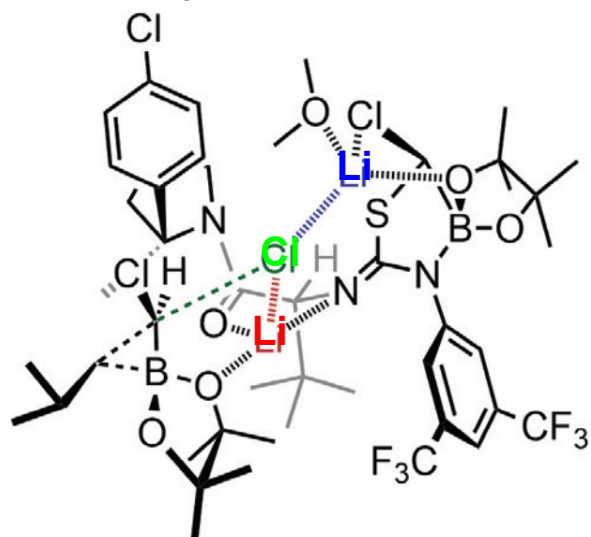
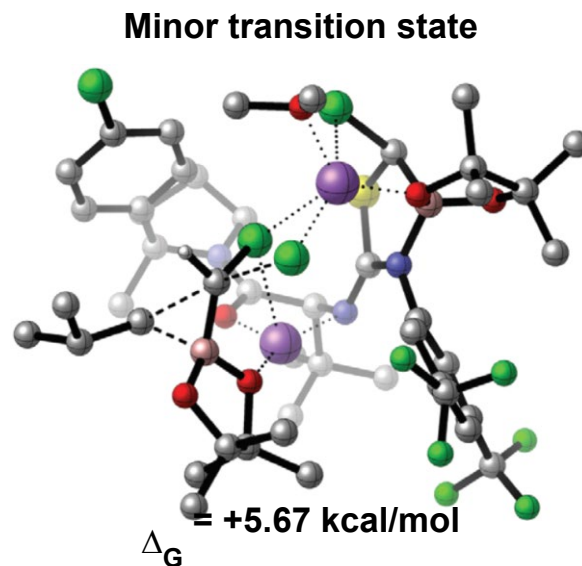
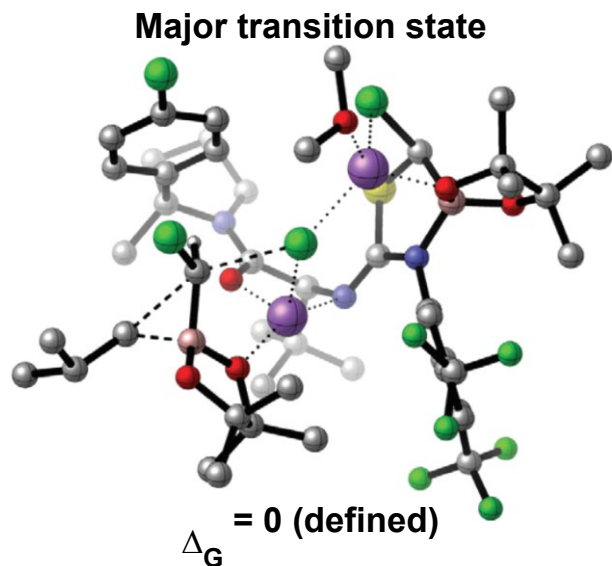
LiBAR _F	40
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SnCl ₄	59
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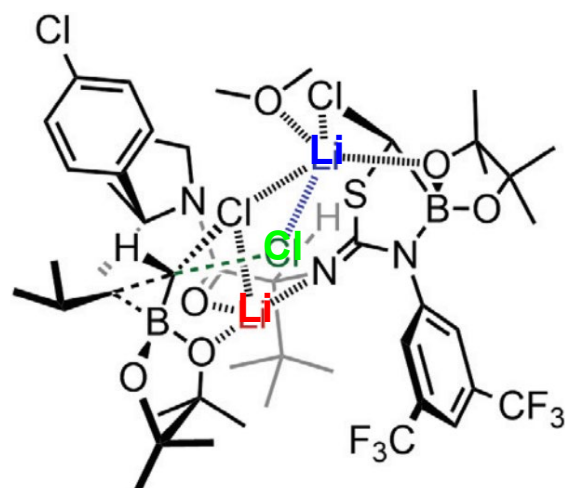
TiCl ₄	70
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Mechanistic analysis and computational study



catalyst Li ... Cl = 2.41 Å
substrate Li ... Cl = 2.30 Å



catalyst Li ... Cl = 4.81 Å
substrate Li ... Cl = 2.29 Å