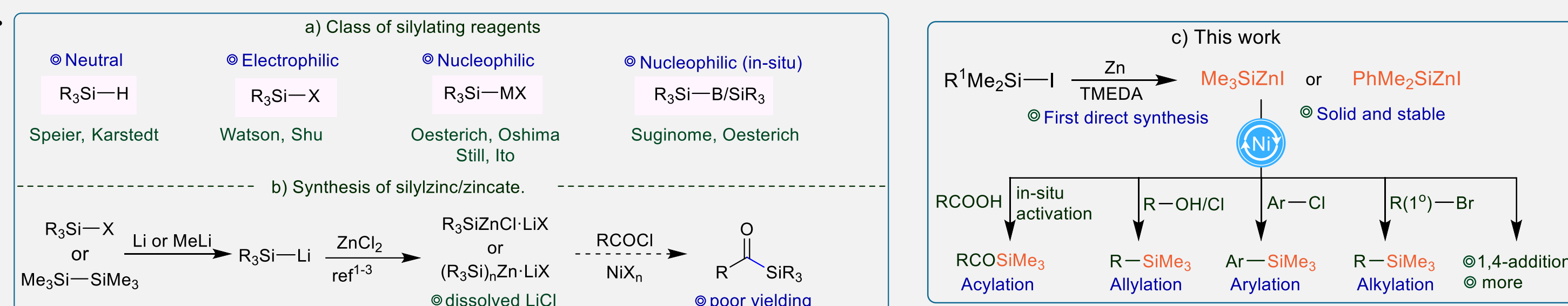
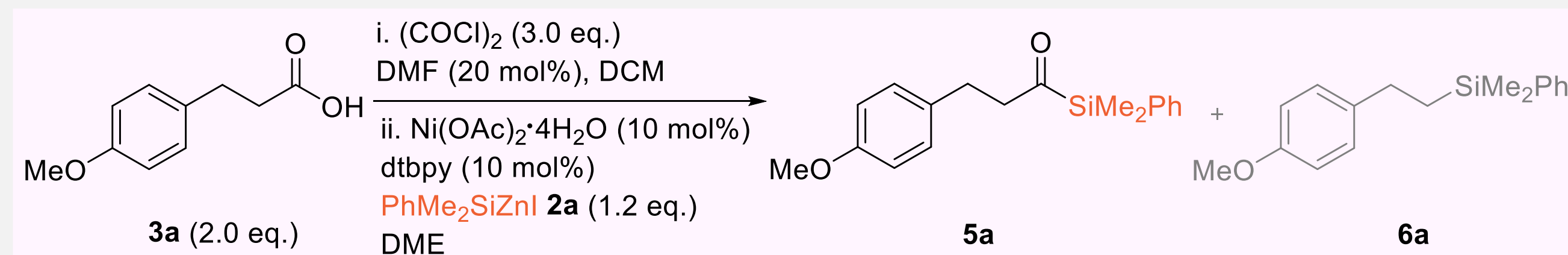


1. Introduction

The milder and more practical method for the synthesis of organosilanes is imperative due to its diverse synthetic utility. The formation of the C-Si bond was achieved by hydrosilylation, coupling of organometallic reagent to silyl halides, and coupling of silyl anions to electrophiles. The silylzinc reagents are milder and, owing to their excellent functional group tolerance and difficult to synthesize. However, the dissolved LiCl in silylzinc may have a detrimental effect. A synthetic method that can avoid the use of silyllithium was developed by the direct insertion of zinc into silyl halides.



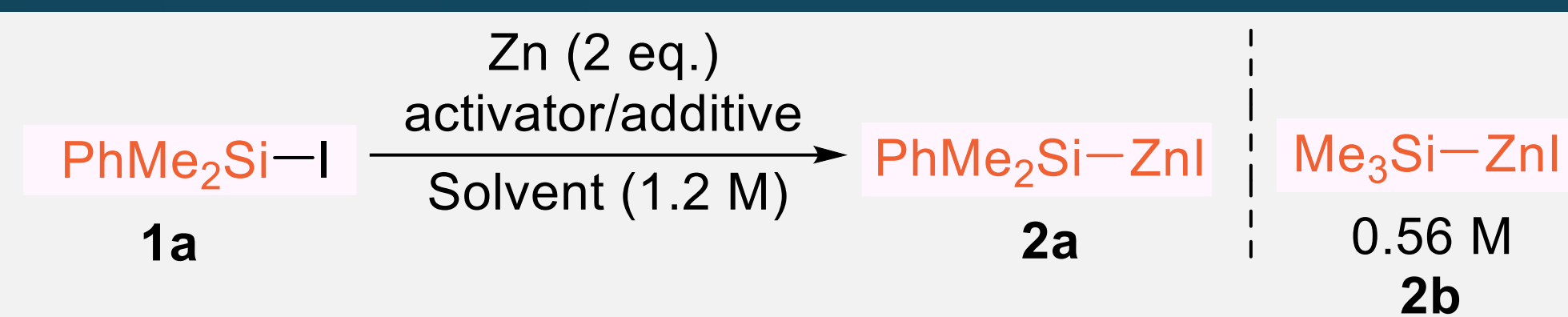
4. Optimization



Entry	Deviation from the above	Temp., time	5a ^d (%)
1	NiBr ₂ •diglyme, THF	60 °C, 4 h	92
2	NiCl ₂ , THF	60 °C, 4 h	29 ^c
3	Ni(acac) ₂ , THF	60 °C, 4 h	66
4	NiBr ₂ bpy, THF	60 °C, 4 h	21
5	THF	60 °C, 4 h	86
6	20 mol% of CuI or CuCN	60 °C, 4 h	2
7	bpy instead of dtbpy, THF	60 °C, 4 h	70 ^c
8	dppe instead of dtbpy, THF	60 °C, 4 h	10
9	Toluene	60 °C, 4 h	38
10	None	60 °C, 4 h	95
11	None	rt, 12 h	90
12	5 mol% Ni(OAc)₂•4H₂O	rt, 12 h	94 (86)^e
13	2 mol% Ni(OAc) ₂ •4H ₂ O	rt, 12 h	52
14	Ni(COD) ₂ (1.5 eq. 3a)	rt, 12 h	95 ^d
15	Without Ni(OAc) ₂ •4H ₂ O	rt, 12 h	2
16	Silylzinc from PhMe ₂ SiLi	rt, 12 h	23
17	1 eq. LiCl additive	rt, 12 h	42
18	4.2 mmol of 2a	rt, 12 h	(80)

^a Reaction conditions: 0.39 mmol of **3a**, 0.234 mmol of PhMe₂SiZnI•TMEDA **2a** (0.66 M in toluene), 0.0195 mmol of Ni(OAc)₂•4H₂O and dtbpy, 0.17 M (overall concentration). Isolated acid-chloride **4a** was used in entries 1–6 and 15–17; in situ acidchloride **4a** was used in entries 7–14 and 18. ^b Yield determined by ¹H NMR using 1,3,5-trimethoxy benzene as an internal standard. ^c Incomplete reaction; unreacted starting material was observed in the crude NMR. ^d 1.0 eq. of PhMe₂SiZnI was used. ^e Reactions were repeated at least 10 times throughout the project. DME: 1,2-dimethoxy ethane, yield in parentheses is isolated yield.

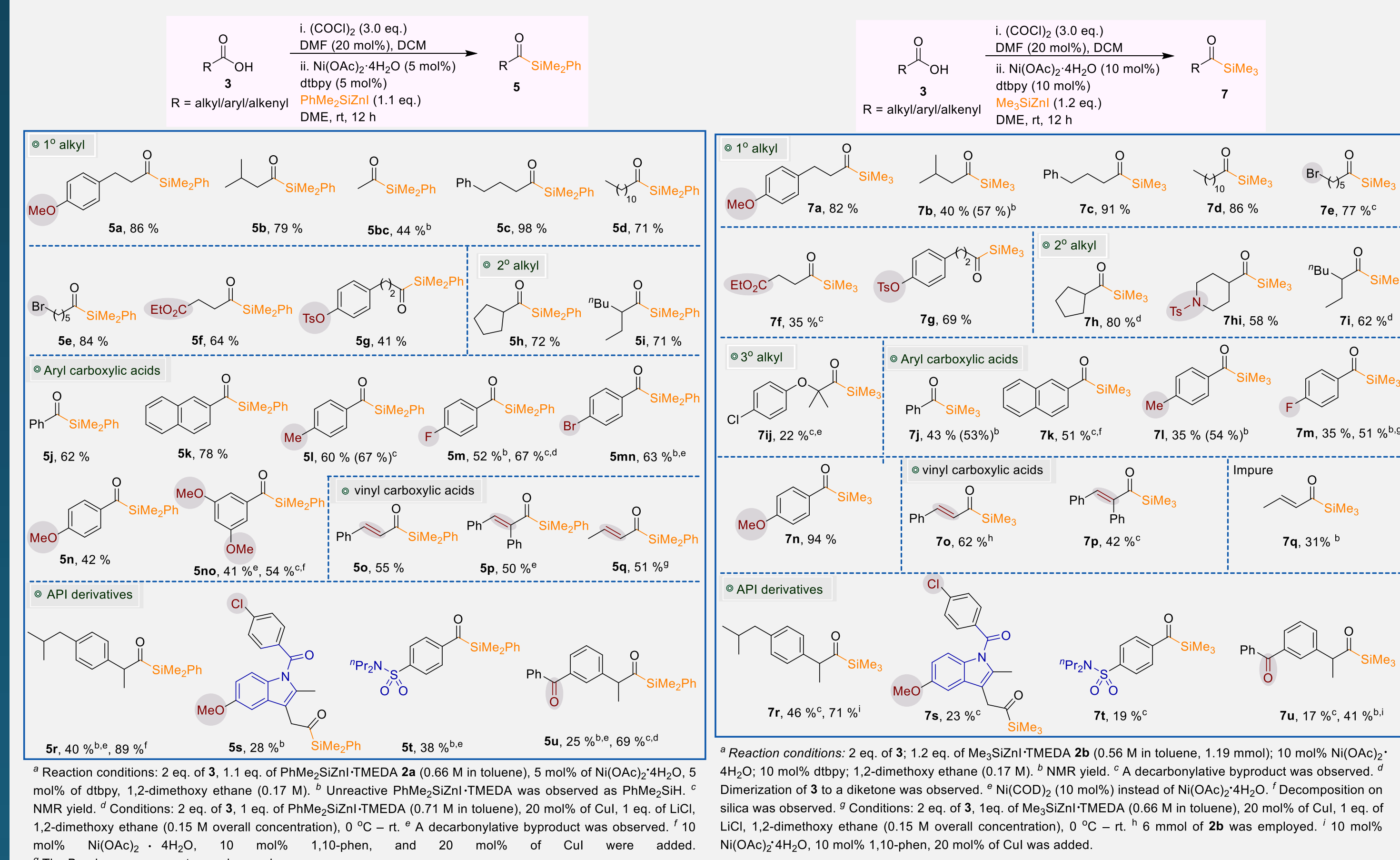
2. Synthesis of silylzinc reagents



Entry	Activator	Additive, solvent, temperature	2a (M)
1	—	THF, 60 °C	ND
2	TMSCl	THF, 60 °C/toluene, 70 °C	ND
3	Iodine	DMA, 80 °C/toluene, 70 °C	ND
4	—	LiCl, toluene, 70 °C	ND
5	DBE	LiCl, toluene, 70 °C/THF, 60 °C	ND ^a
6	Iodine	TMEDA, toluene, 66 °C, 63 h	0.21
7	Iodine	TMEDA, toluene, 70-90 °C, 63 h	0.68^b
8	Iodine	NMP/DMA, toluene, 85 °C	ND

Reaction conditions: additive/activator: Me₃SiCl (0.12 eq.), iodine (0.03/0.05 eq.), DBE (0.03 eq.), LiCl (1.0 eq.), TMEDA (1.1 eq.), NMP/DMA (1.5 eq.). ^a Me₃SiCl (1.5 mol%) was used. ^b An average of 5 isolated runs. M: molarity, DBE: 1,2-dibromoethane, NMP: N-methyl-2-pyrrolidone, DMA: dimethylacetamide. ND: not detected.

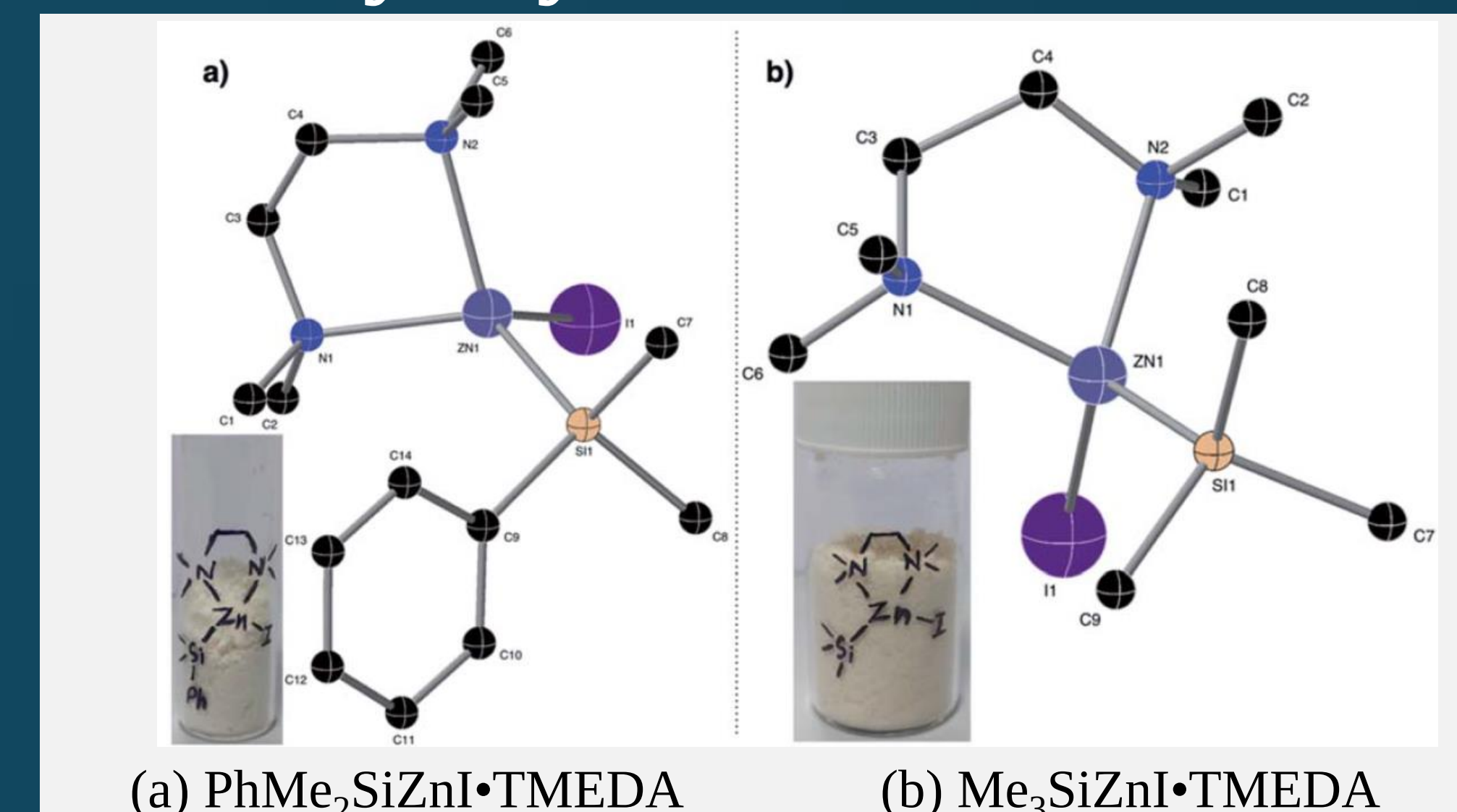
5. Substrate scope on catalysis



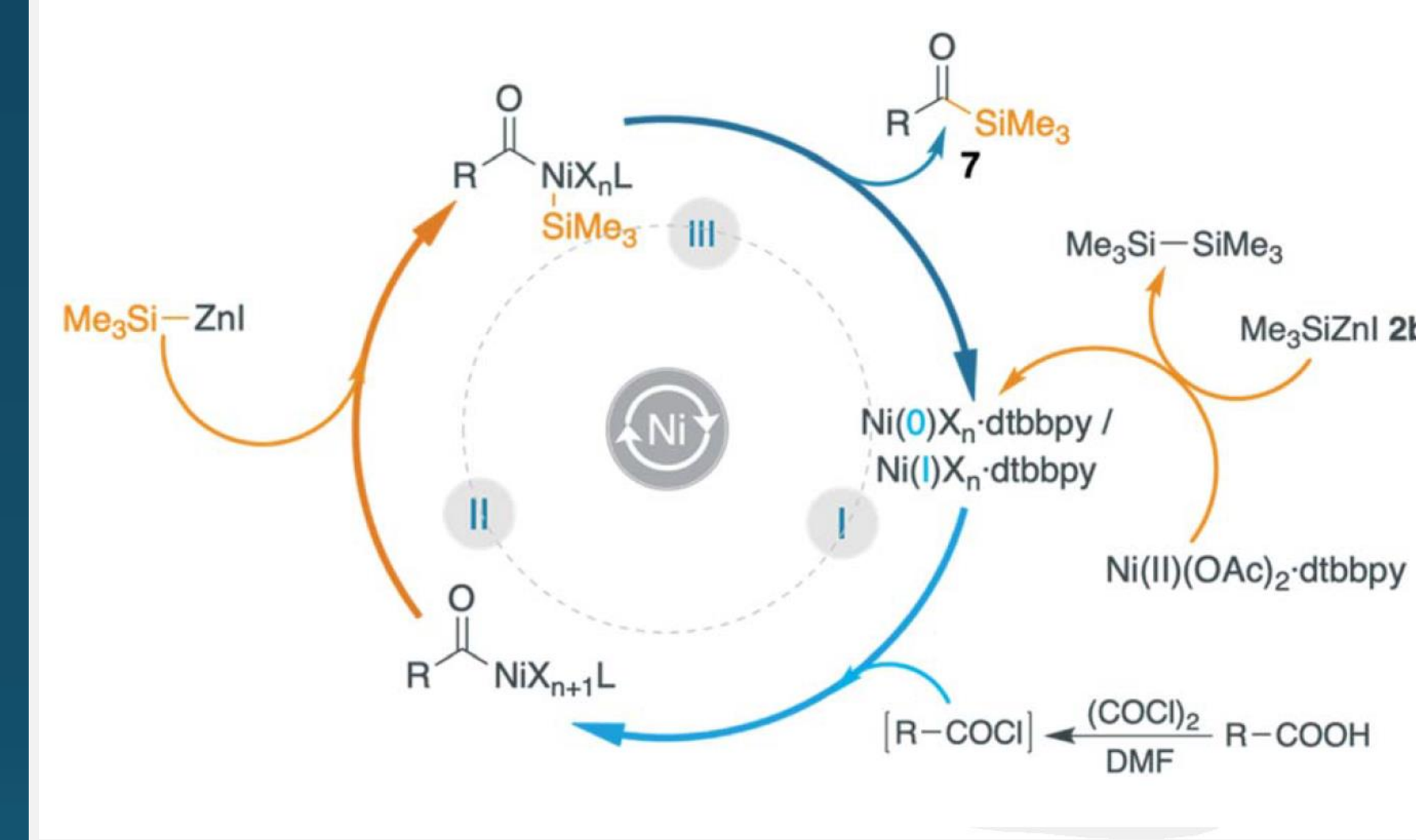
9. Acknowledgement

We acknowledge financial support from the Science and Engineering Research Board, Ramanujan Fellowship, IISER Trivandrum. CSIR (Council of Scientific and Industrial Research) for fellowship

3. X-ray crystal structures



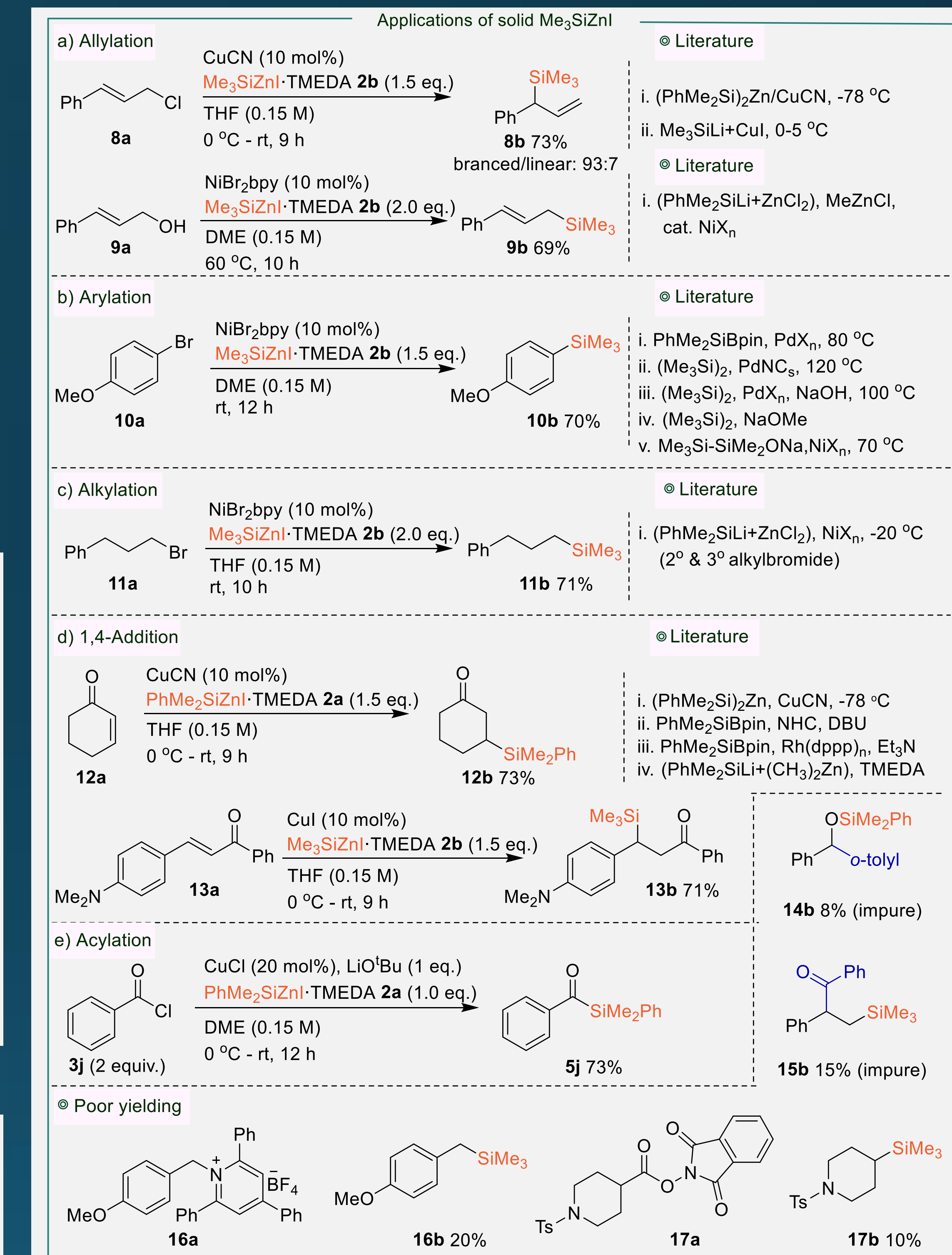
6. Mechanistic hypothesis



8. Conclusion

- For the first time, we have developed a method for direct synthesis of silylzinc reagents from silyl iodides and their structures were confirmed by single-crystal XRD
- The absence of dissolved lithium/magnesium salts in these reagents could be beneficial for various chemical processes
- We demonstrated the practical synthesis of acylsilanes from unactivated alkyl acid chlorides by nickel, copper and dual catalysis
- The general synthetic utility of these reagents is shown in a broad range of reactions.

7. Applications of solid Me_3SiZnI



10. Reference

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