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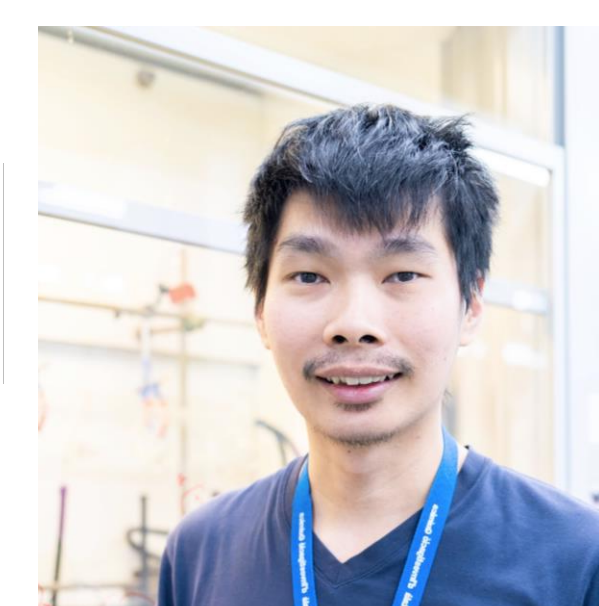


EXCELENCIA SEVERO OCHOA

# Regiodivergent Single Carbon Insertion of C(sp<sup>2</sup>)-C(sp<sup>2</sup>) Bonds

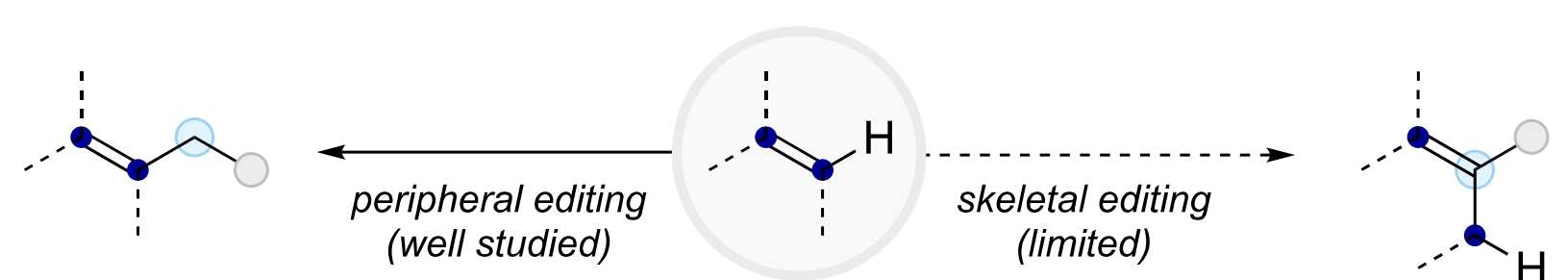
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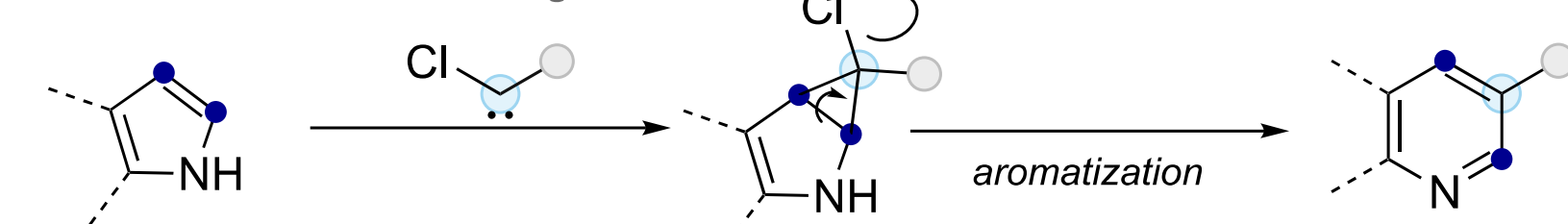
## Introduction & Optimization

A C(sp<sup>2</sup>)-C(sp<sup>2</sup>) single carbon insertion

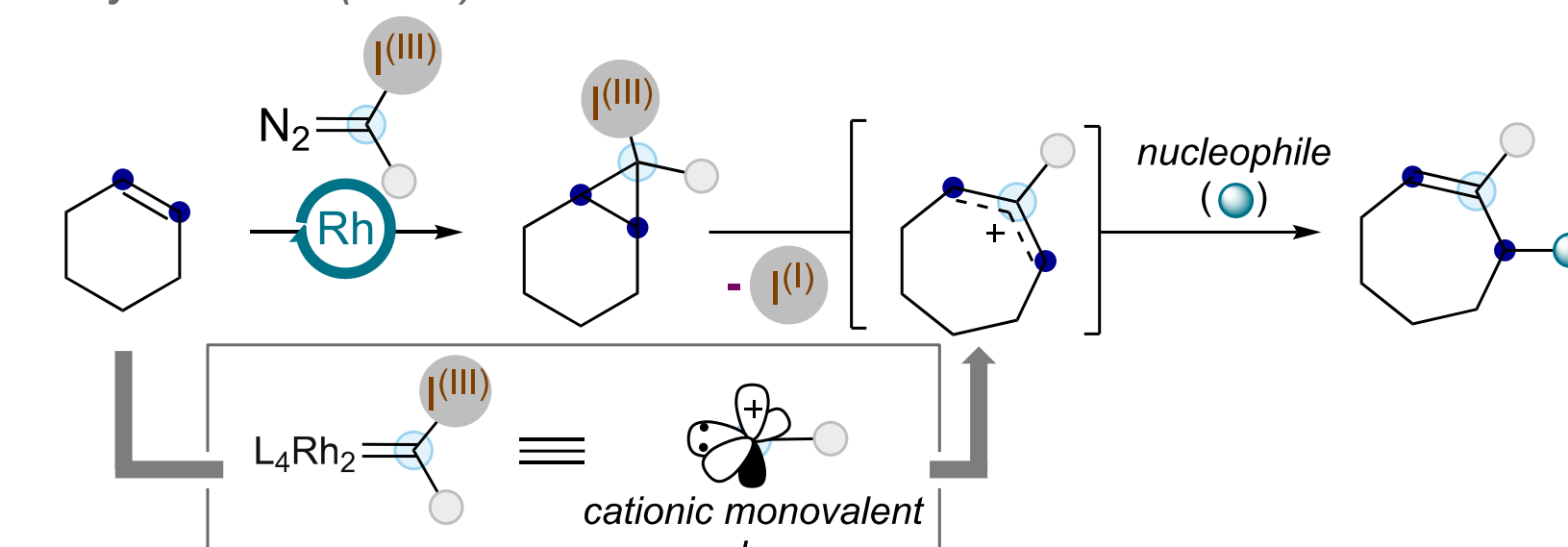


### B State-of-the-art

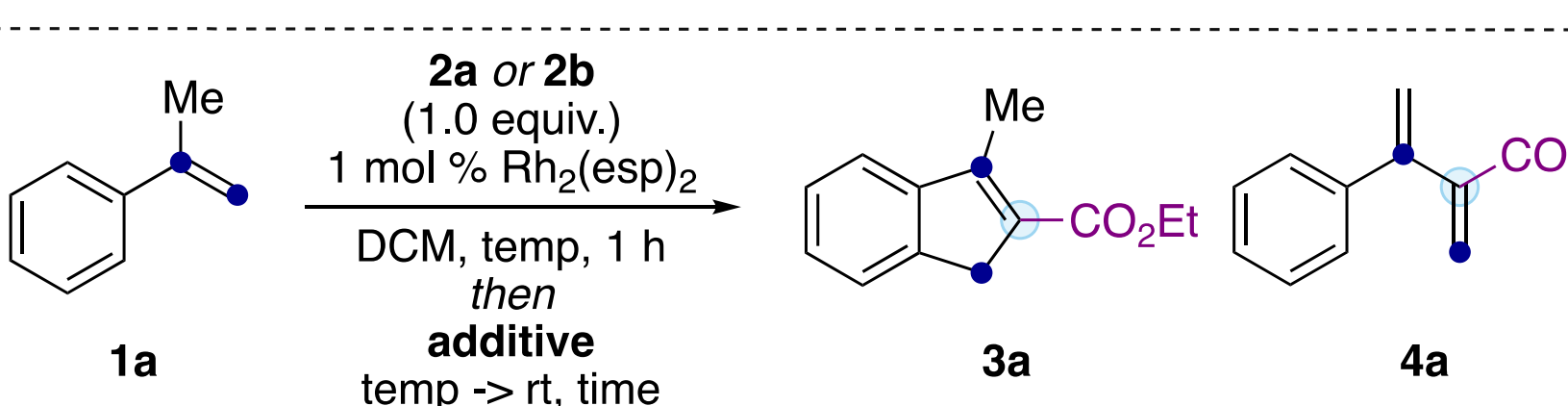
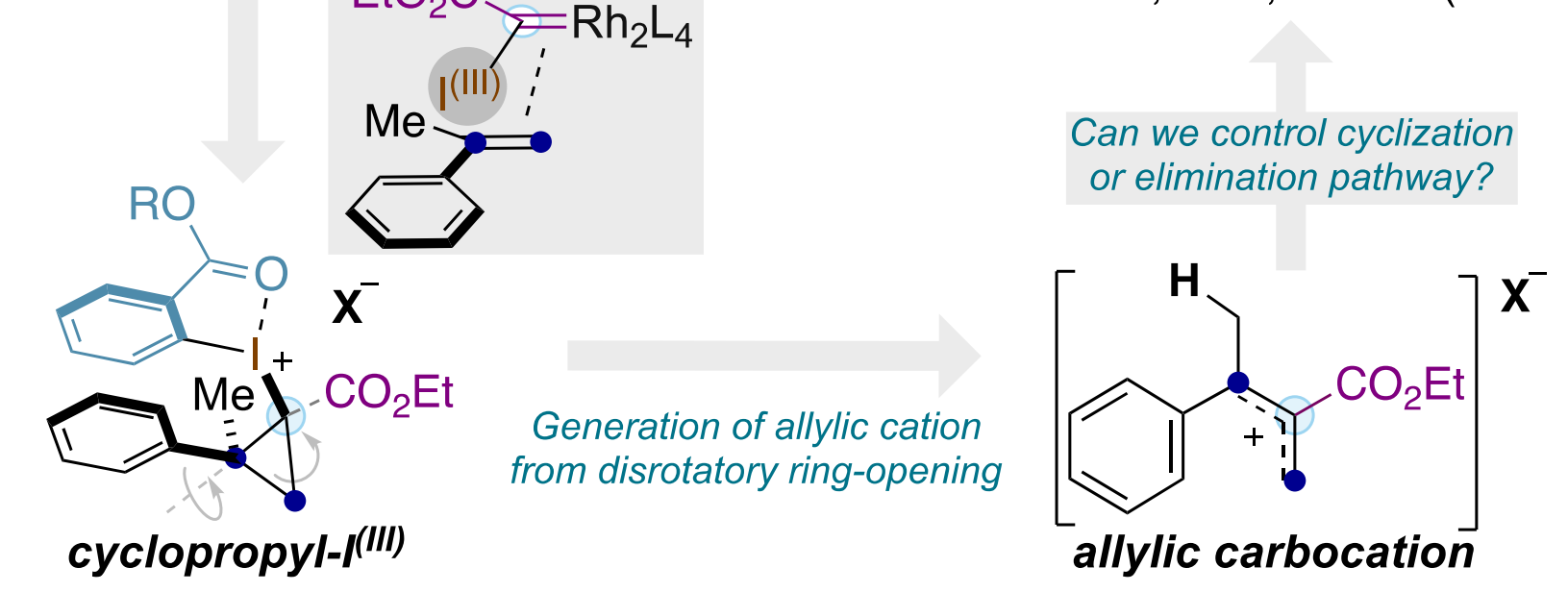
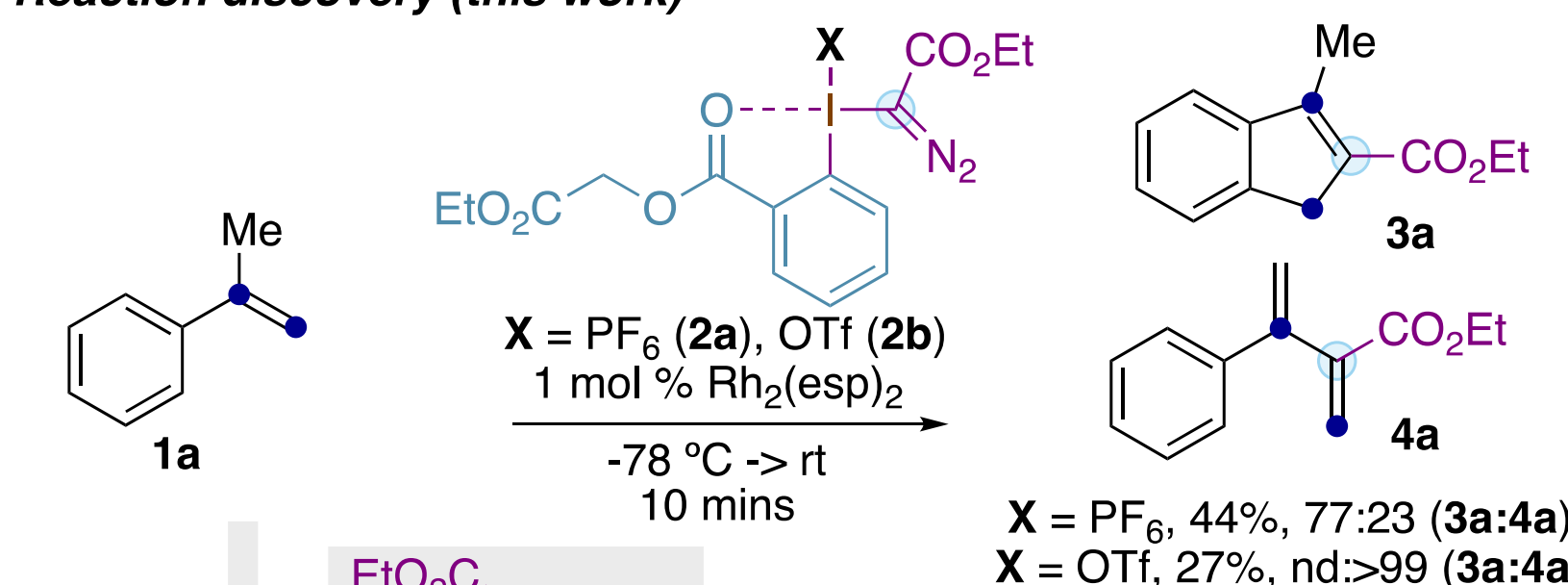
■ Ciamician-Dennstedt rearrangement



■ Carbyne transfer (Suero)

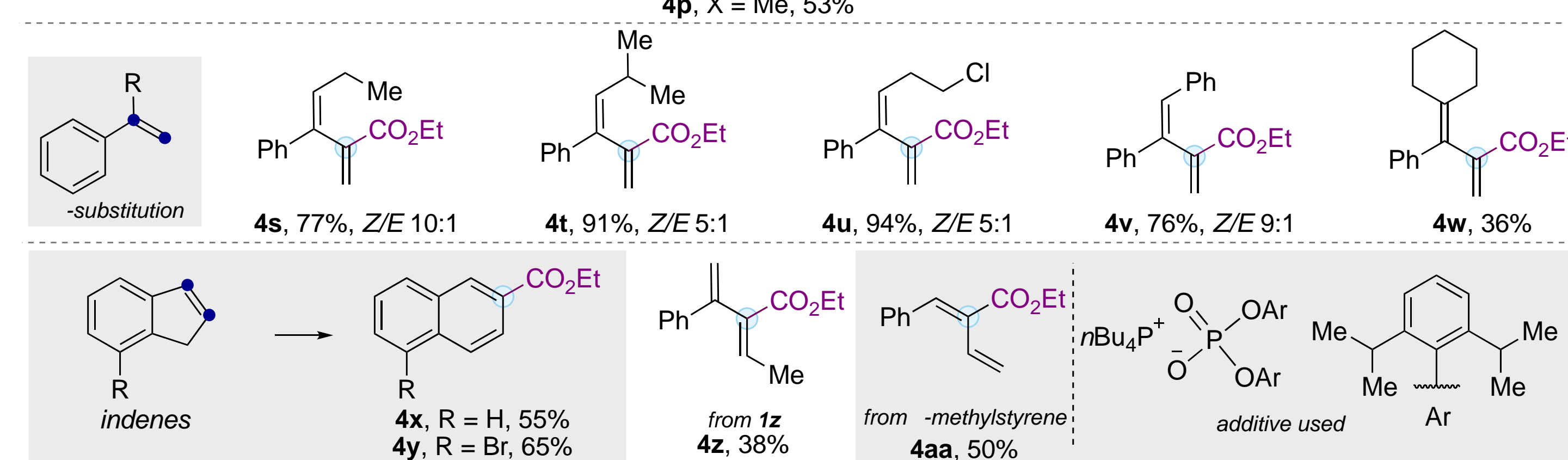
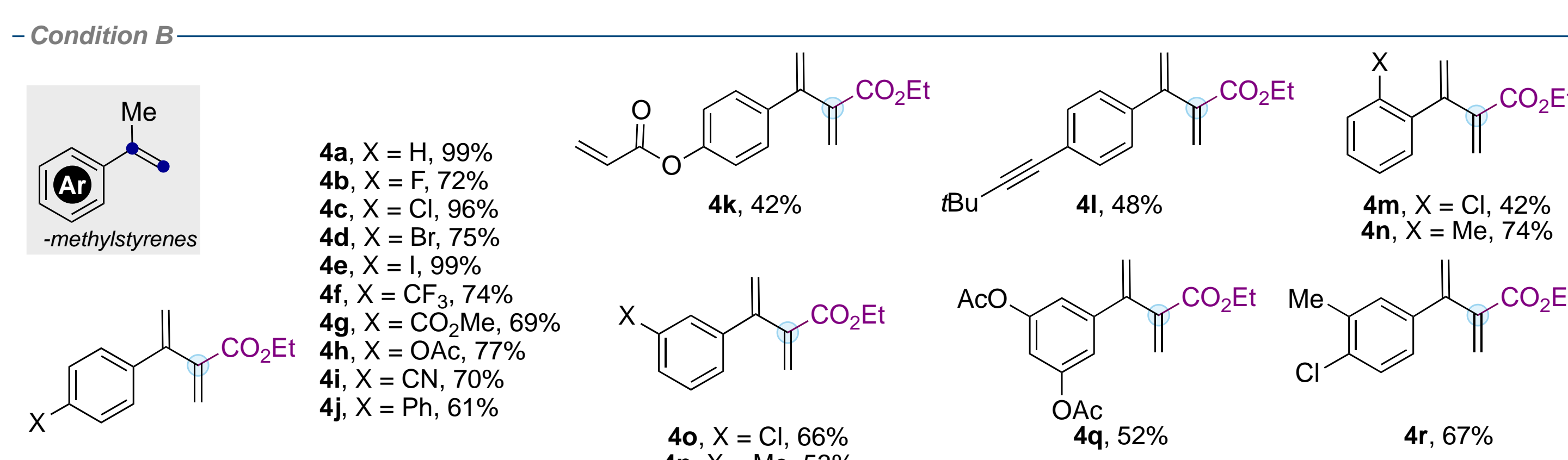
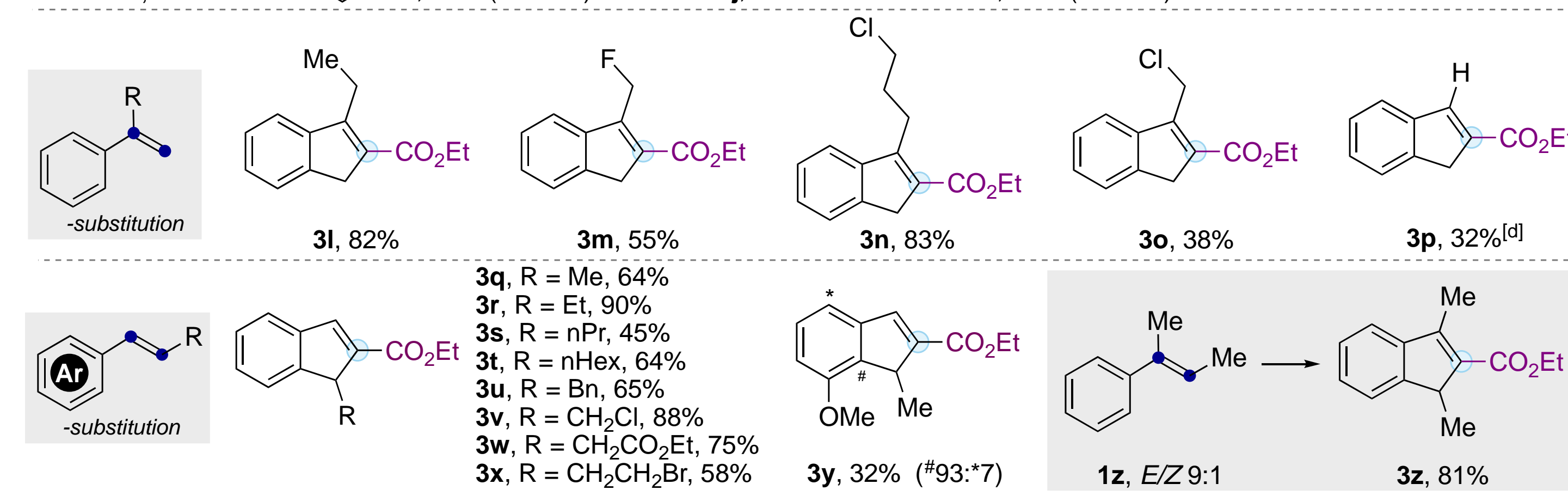
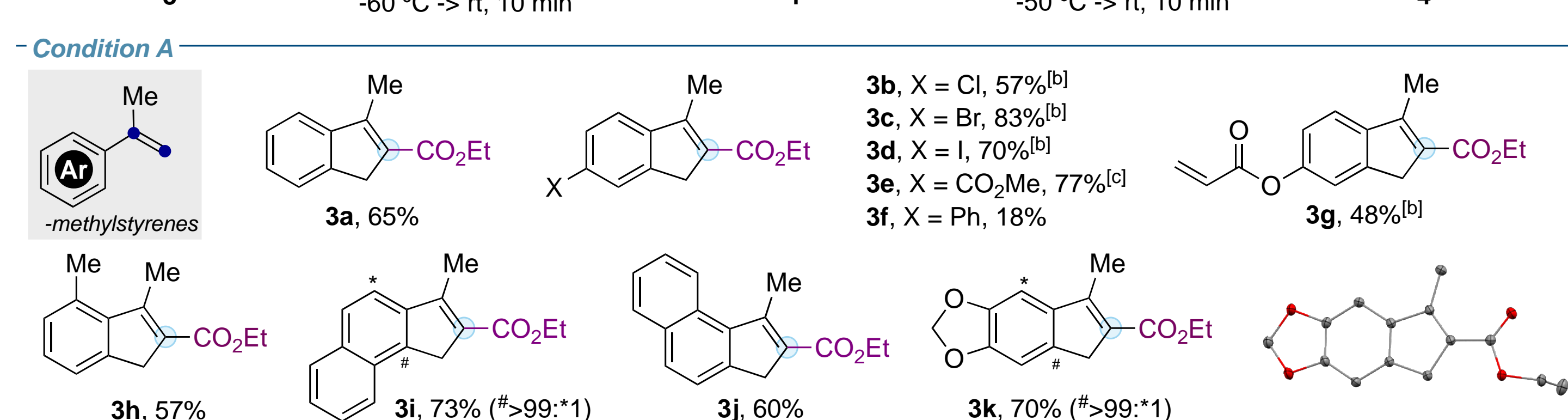
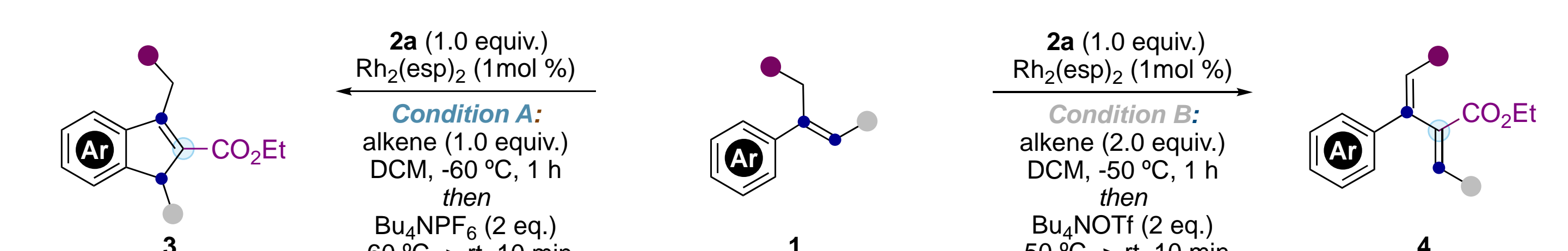


### C Reaction discovery (this work)

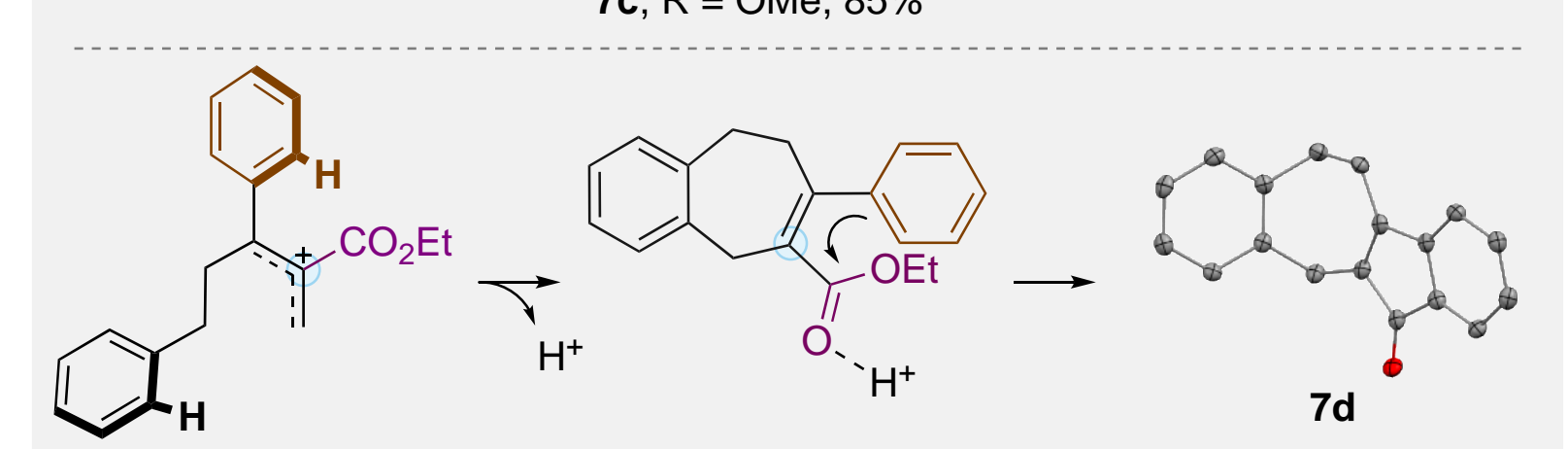
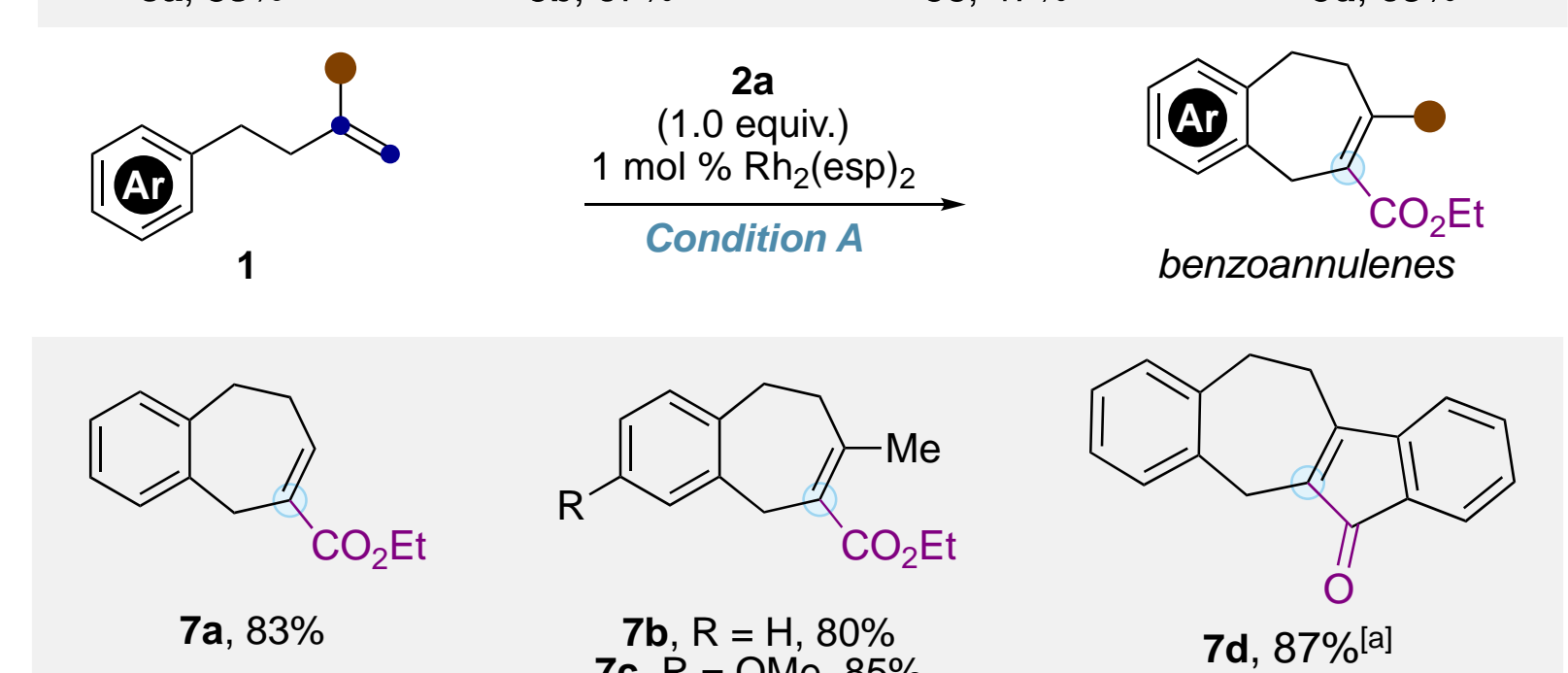
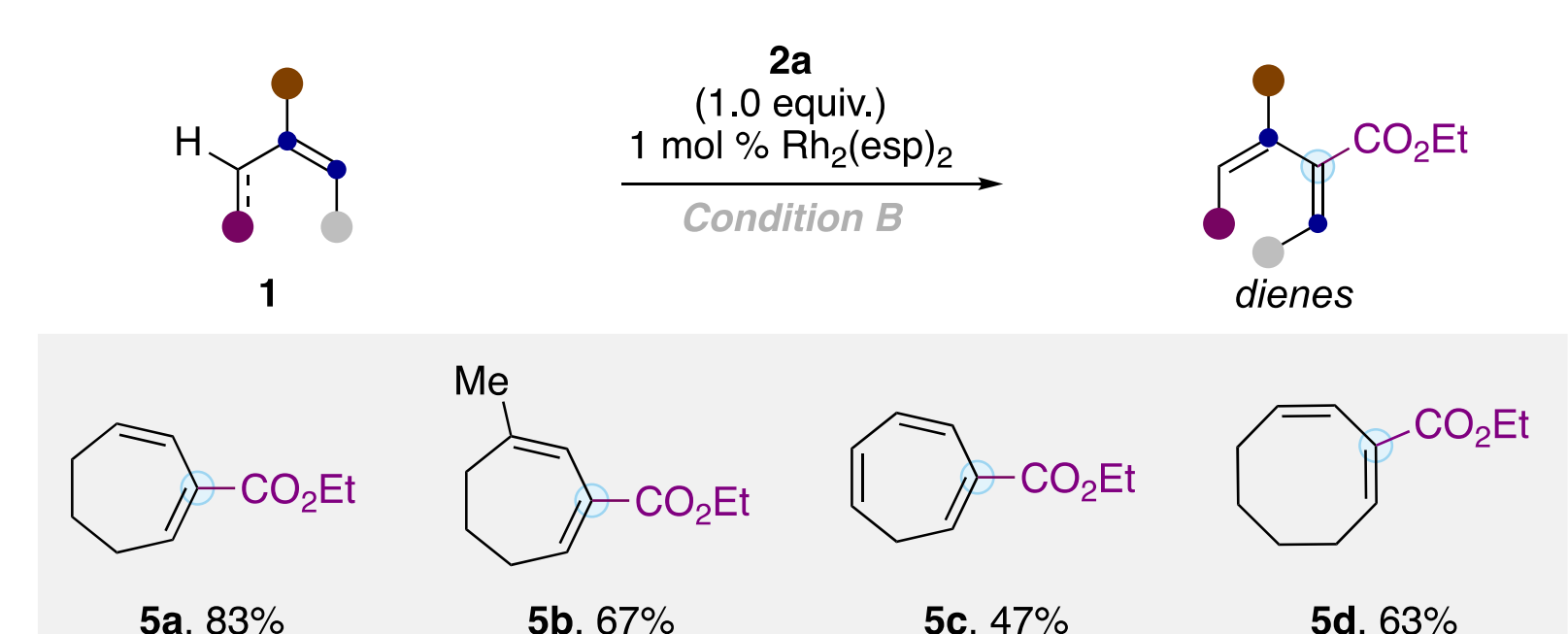


entry	1a	2a or 2b	temp	additive	time	3a:4a	yield <sup>b</sup> (3a)
1	1 equiv.	2a	-60 °C	-	10 mins	77:23	34%
2	1 equiv.	2a	-60 °C	-	1 h	>99:1	54%
3	1 equiv.	2a	-60 °C	TBAPF <sub>6</sub> (20 mol %)	1 h	>99:1	64%
4	1 equiv.	2a	-60 °C	TBAPF <sub>6</sub> (1 equiv.)	1 h	>99:1	72%
5	1 equiv.	2b	-60 °C	TBAPF <sub>6</sub> (1 equiv.)	1 h	>99:1	30%
6	1 equiv.	2a	-60 °C	TBAPF <sub>6</sub> (2 equiv.)	1 h	>99:1	75%
7	1 equiv.	2a	-60 °C	TBAPF <sub>6</sub> (2 equiv.)	10 mins	>99:1	75%
8	1 equiv.	2a	-60 °C	TBAOTf (2 equiv.)	10 mins	1:>99	46%
9	2 equiv.	2a	-60 °C	TBAOTf (2 equiv.)	10 mins	1:>99	58%
10	2 equiv.	2a	-50 °C	TBAOTf (2 equiv.)	10 mins	1:>99	99%

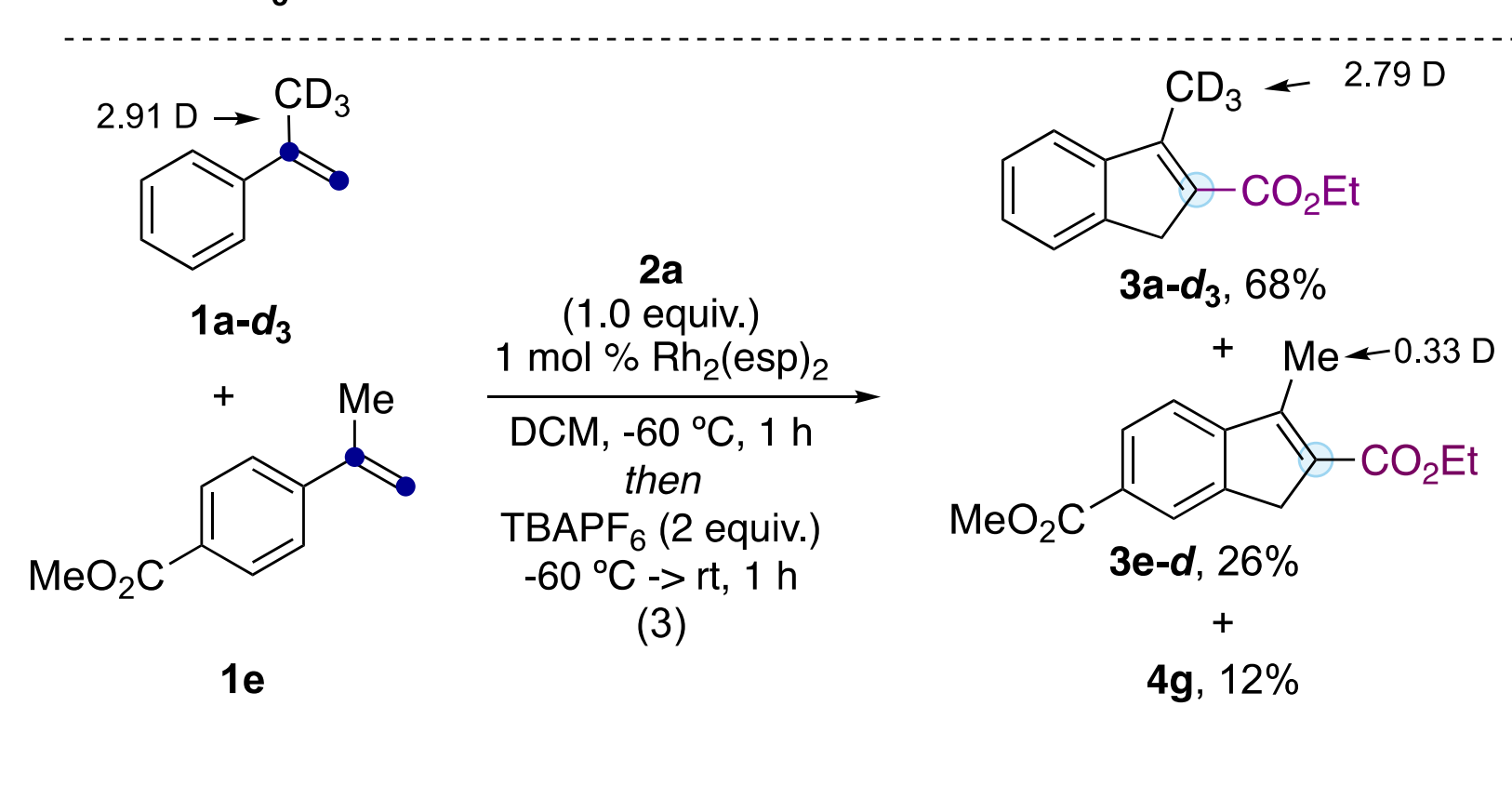
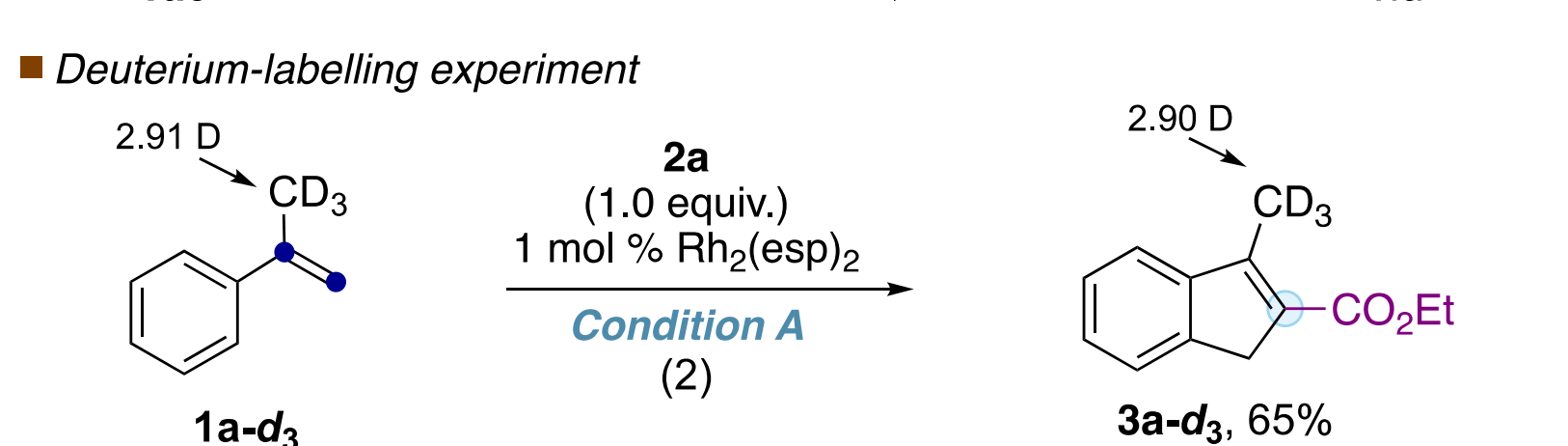
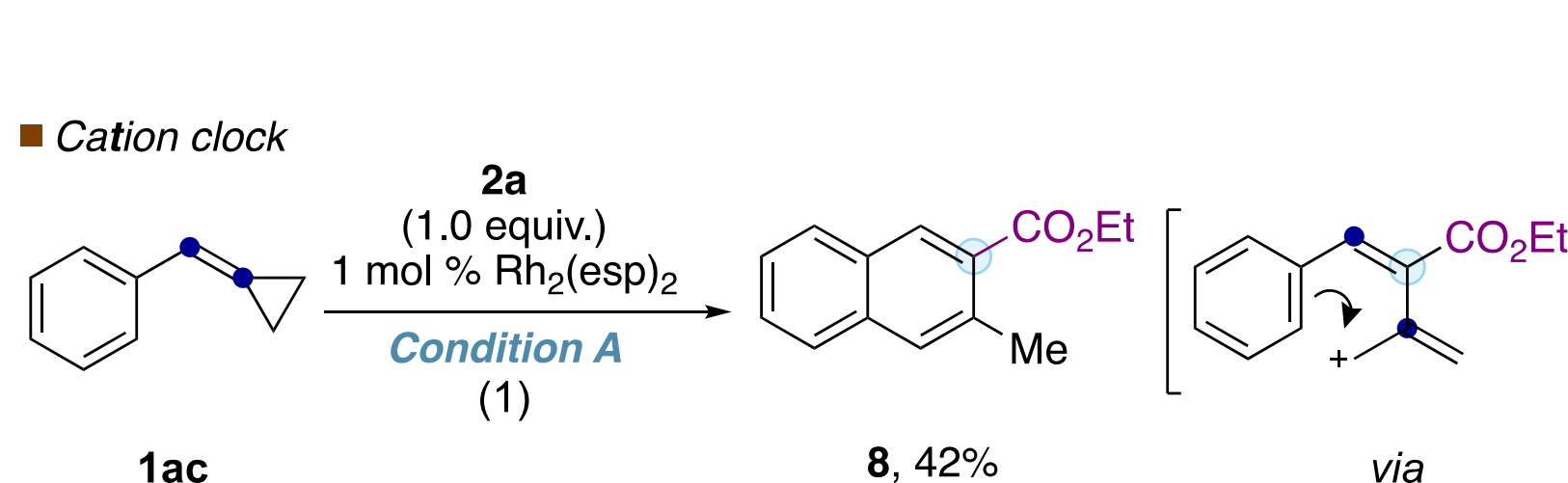
## Scope



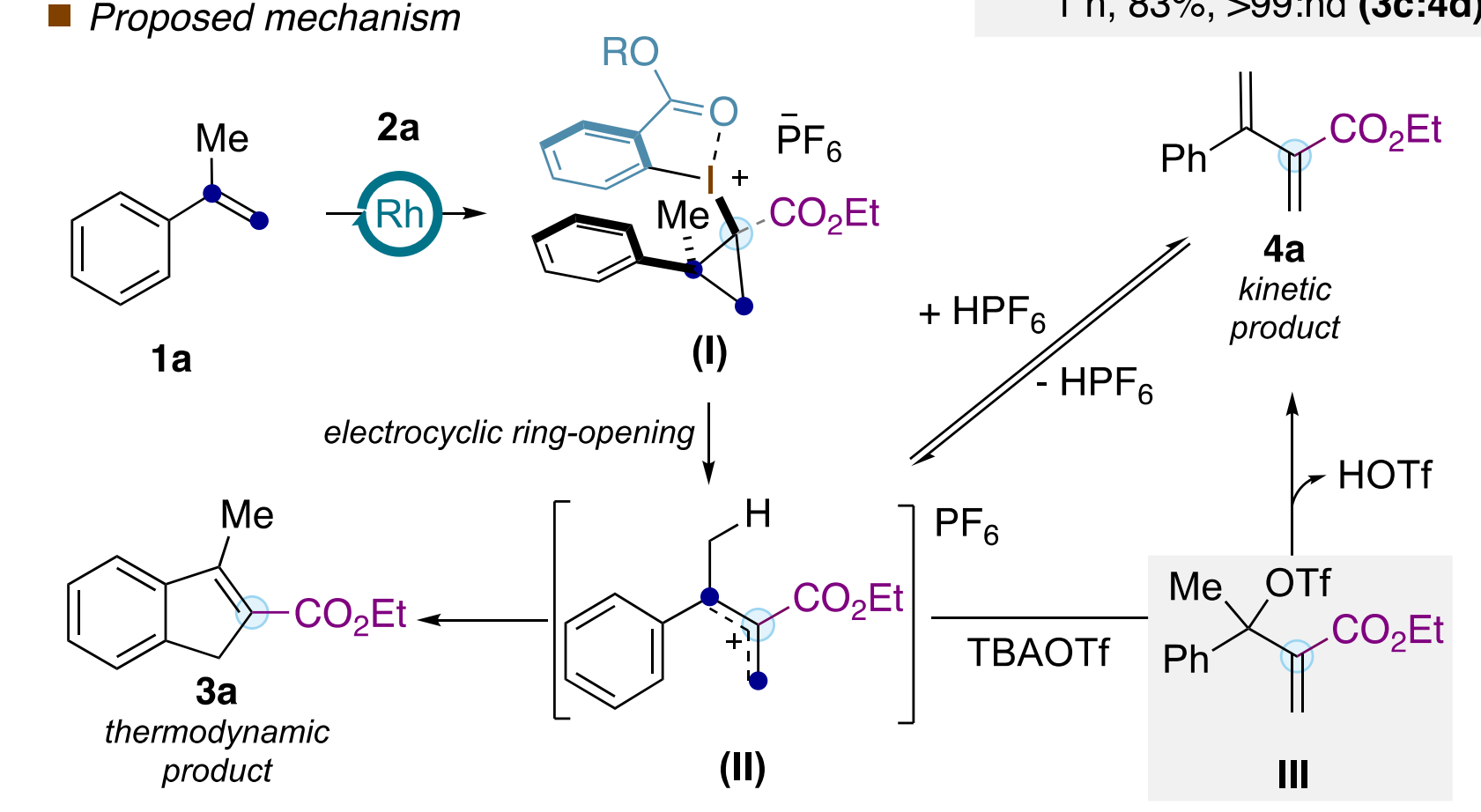
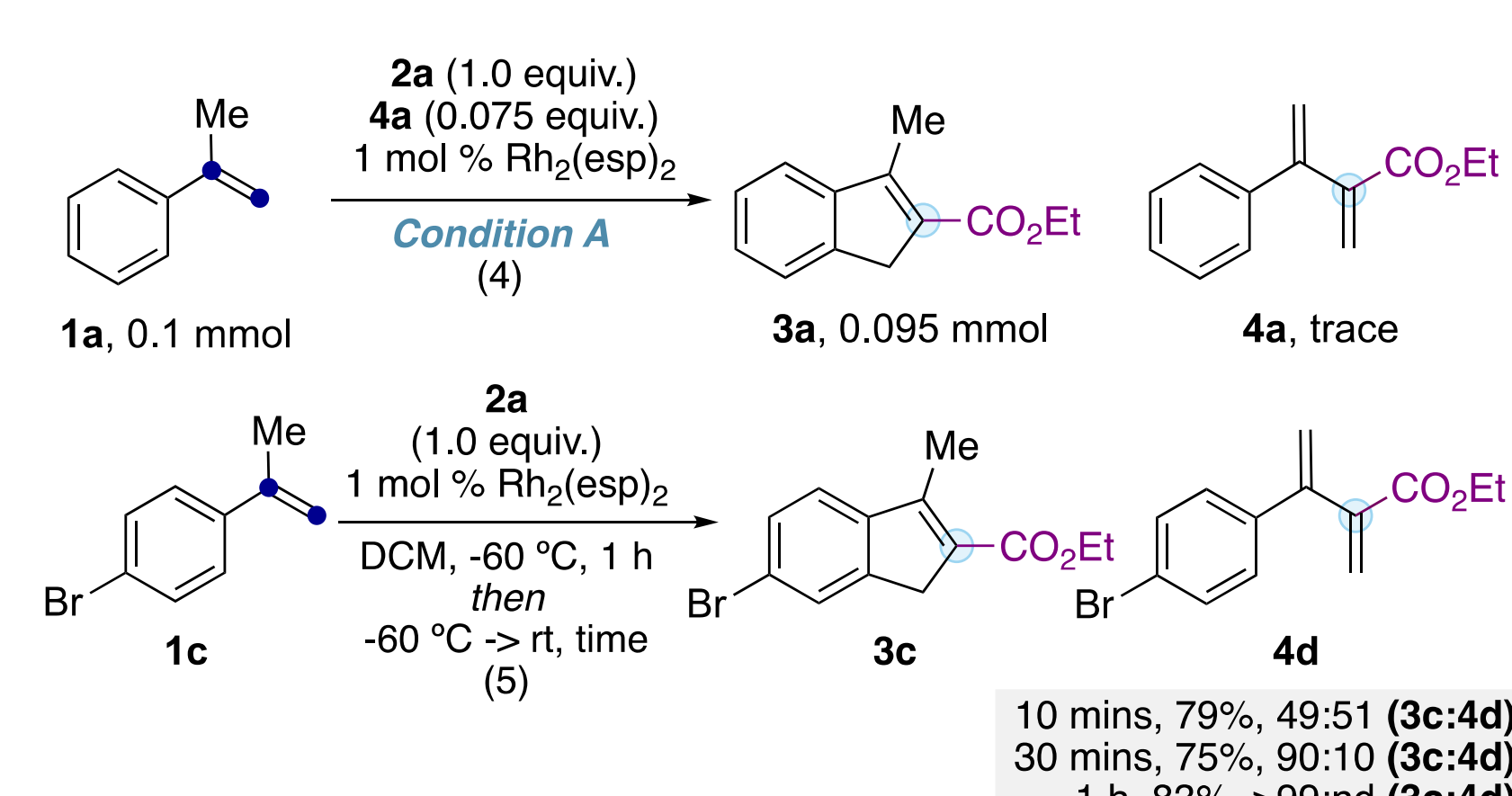
## Dienes and Benzoannulenes



## Reaction mechanism



## Dienes as reaction intermediate



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