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Synthesis of Vinyl Chromanes from Propargyl Silanes via Tandem Electrophilic Activation – 1,2-Silyl Shift – Friedel–Crafts Cyclization

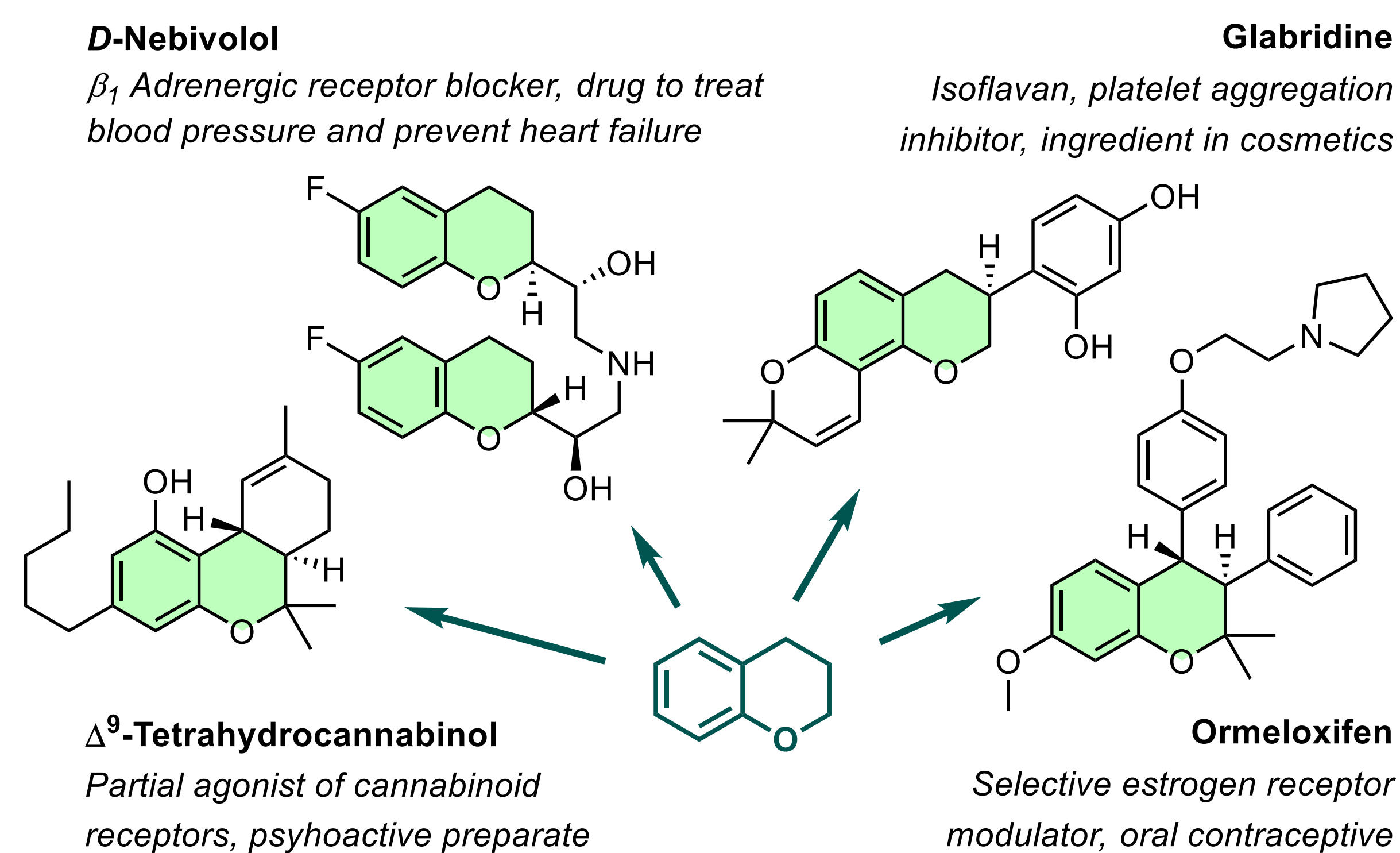
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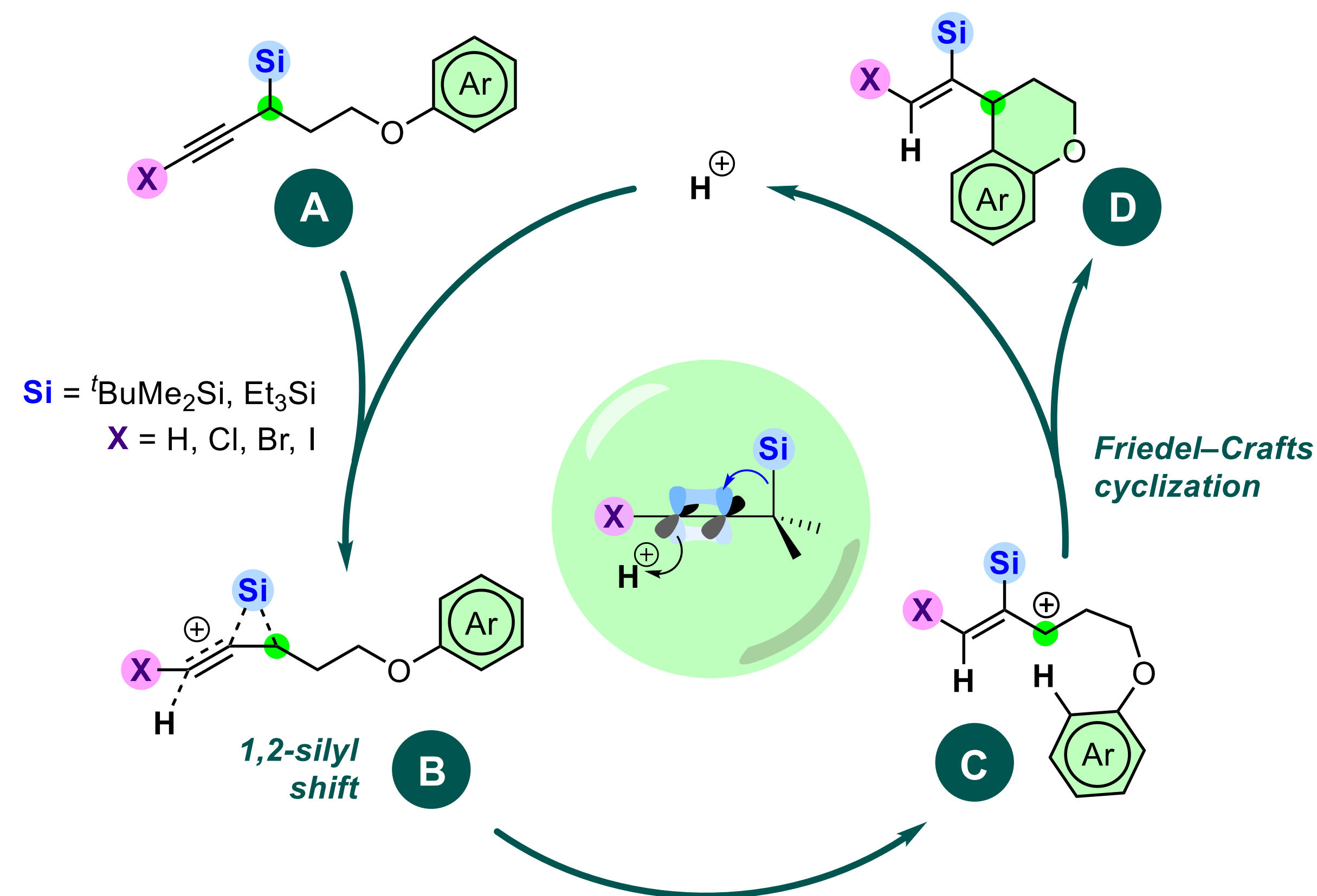
24th Tetrahedron
Symposium



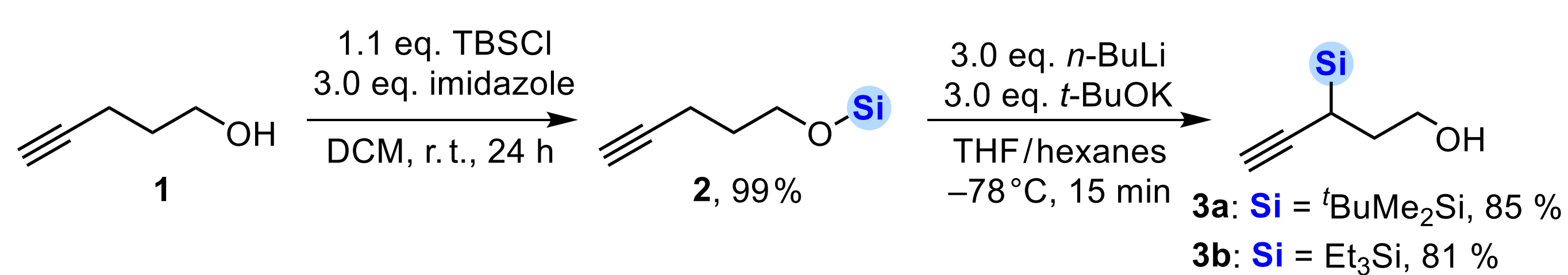
Chromane abundance



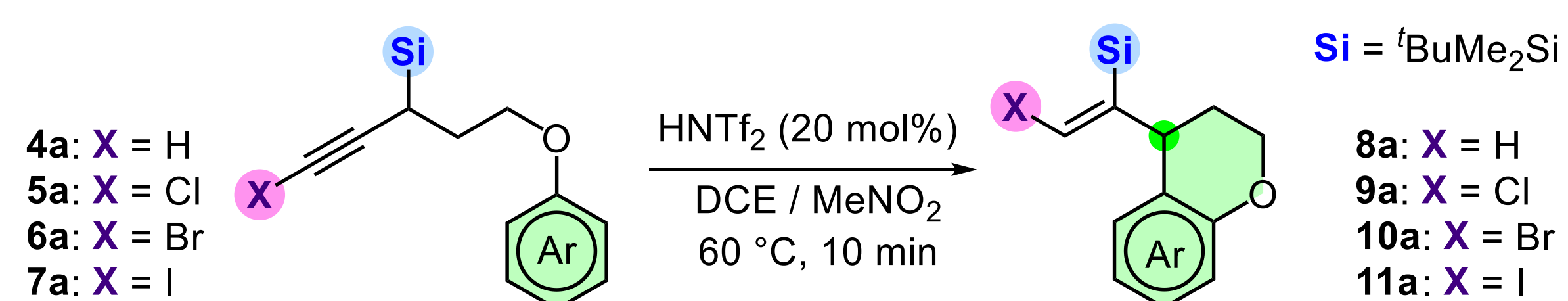
Proposed cyclization mechanism



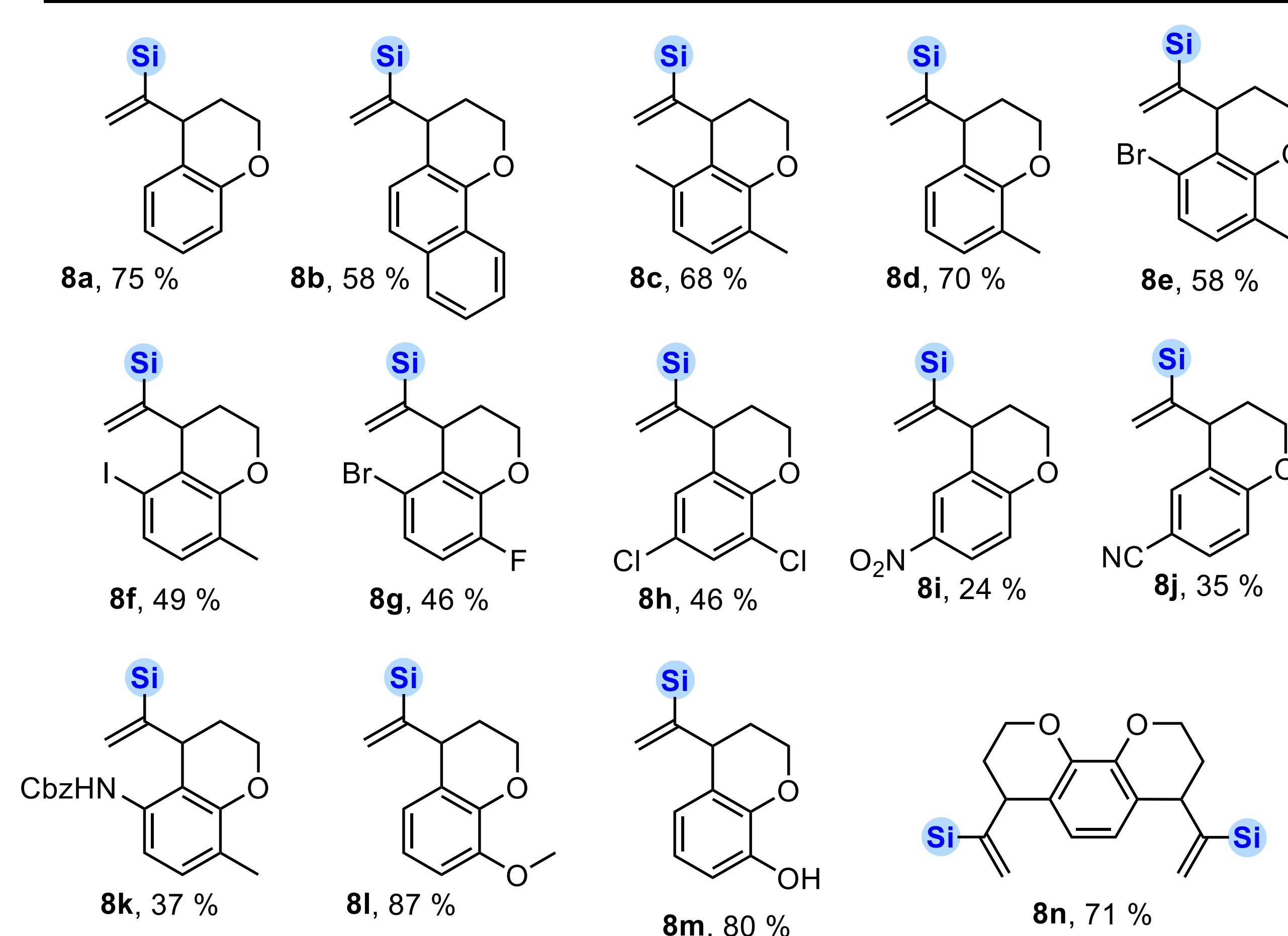
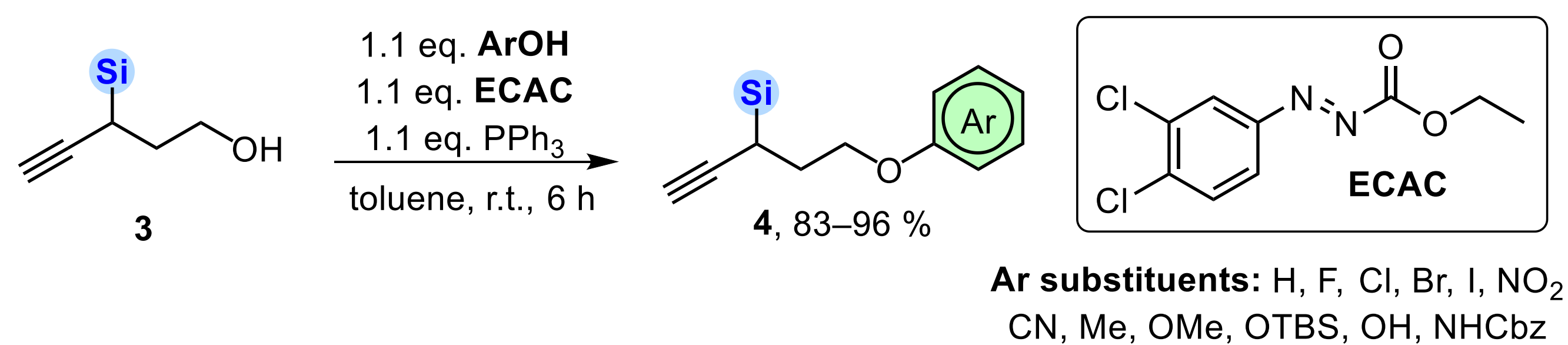
Retro-Brook rearrangement



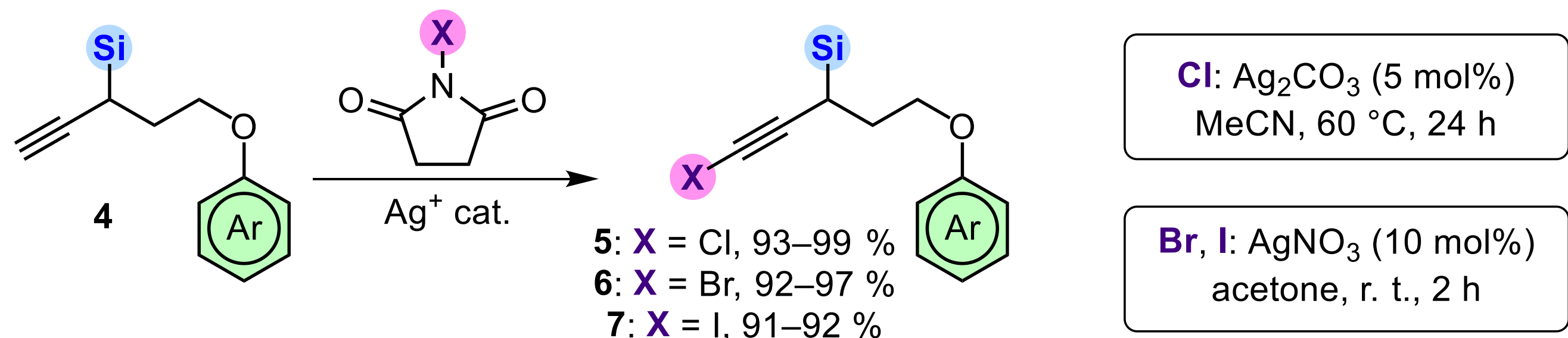
Product scope



Modified Mitsunobu reaction



Haloalkyne synthesis

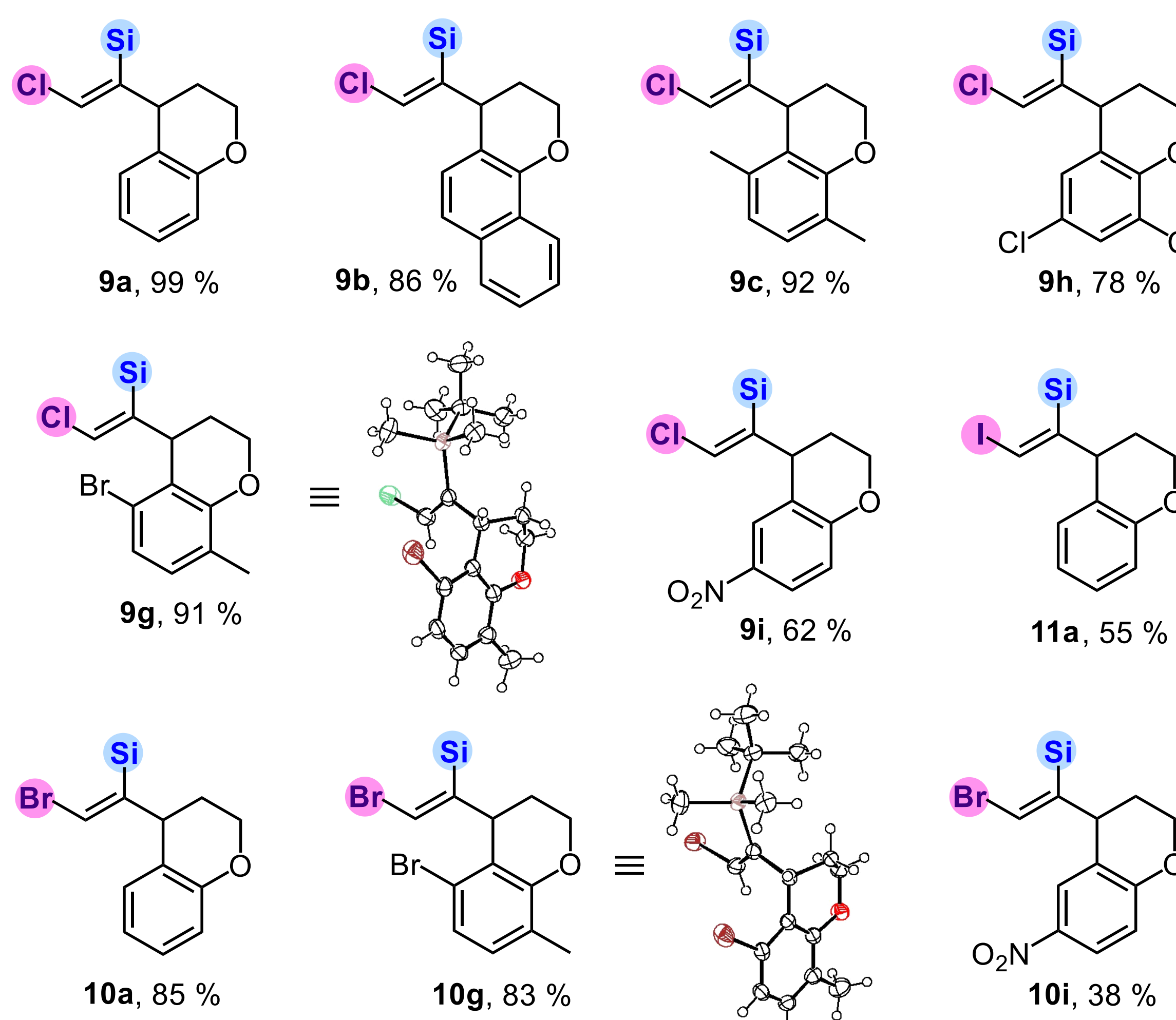


Selected optimization examples

4a → 8a

Entry No.	Acid (mol%)	Solvent	Temperature	NMR yield, %
1	HNTf ₂ (20)	MeCN, TFA, PhH, PhMe, THF	r. t.	< 20
2	HNTf ₂ (20)	DCE, DCM, CHCl ₃ , PhCF ₃	r. t.	57–68
3	HNTf ₂ (20)	MeNO ₂	r. t.	70
4	HOTf (20)	DCM, CHCl ₃	r. t.	51–56
5	HN(SO ₂ CF ₂) ₂ CF ₂ (20)	DCM, CHCl ₃	r. t.	< 5
6	HNTf ₂ (5)	MeNO ₂	r. t.	64
7	HNTf ₂ (10)	MeNO ₂	r. t.	68
8	HNTf ₂ (20–100)	MeNO ₂	r. t.	70
9	HNTf ₂ (20)	MeNO ₂	5 °C	21
10	HNTf ₂ (20)	MeNO ₂	40 °C	72
11	HNTf ₂ (20)	DCE, MeNO ₂	60 °C	80–85

I H Br Cl



Acknowledgments

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