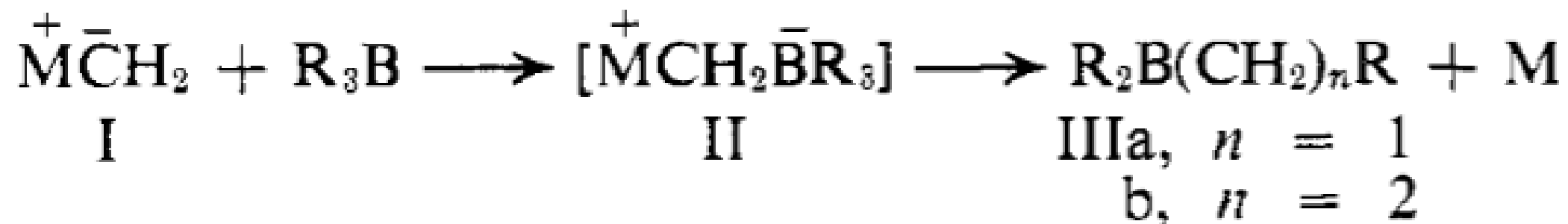




Ylide-borane reaction

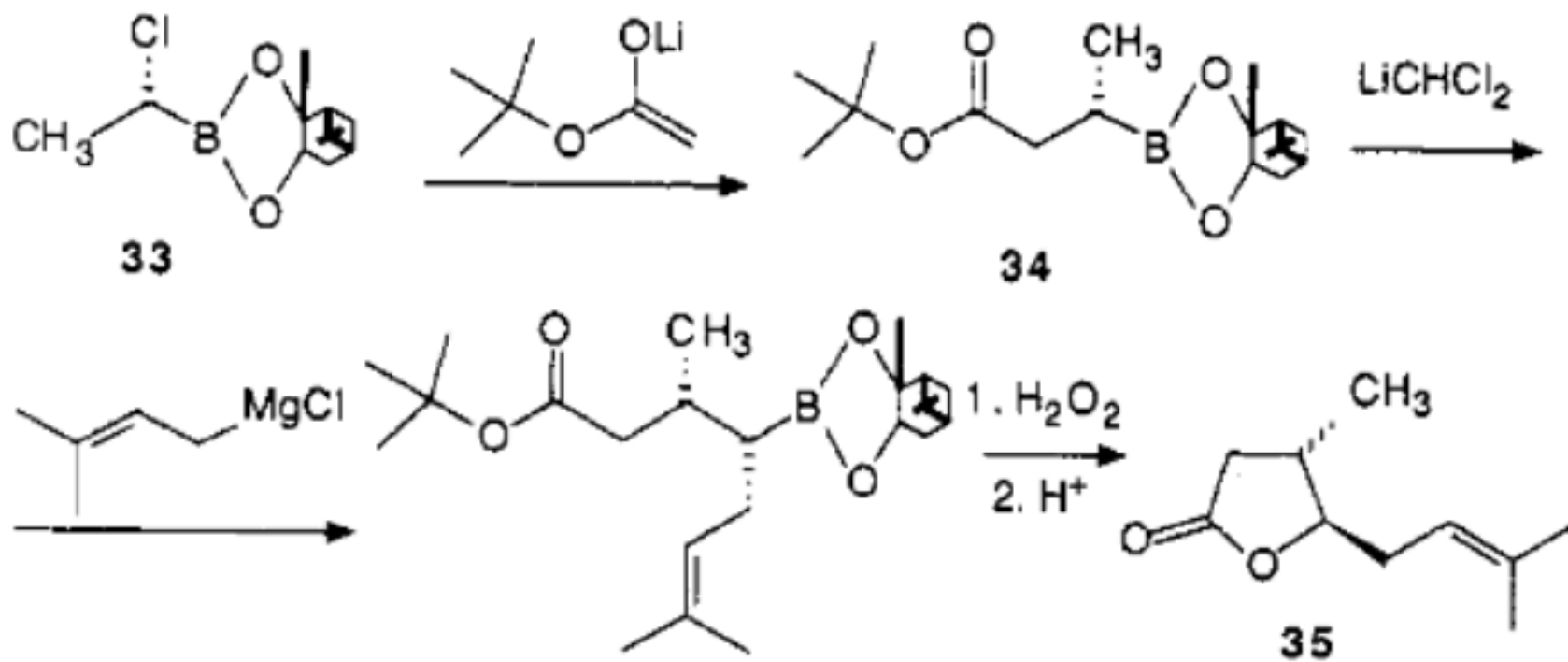


汇报人：王振洋

日期：2024. 11. 23

潘赛勇组

J. Am. Chem. Soc. 1967, 89, 25, 6804-6805





Synthesis and Applications of Chiral Organoboranes Generated from Sulfonium Ylides

Varinder K. Aggarwal, Guang Yu Fang, and Andreas T. Schmidt

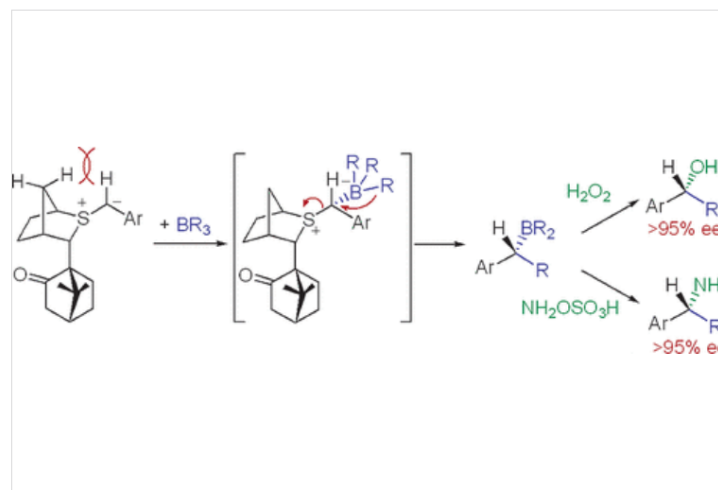
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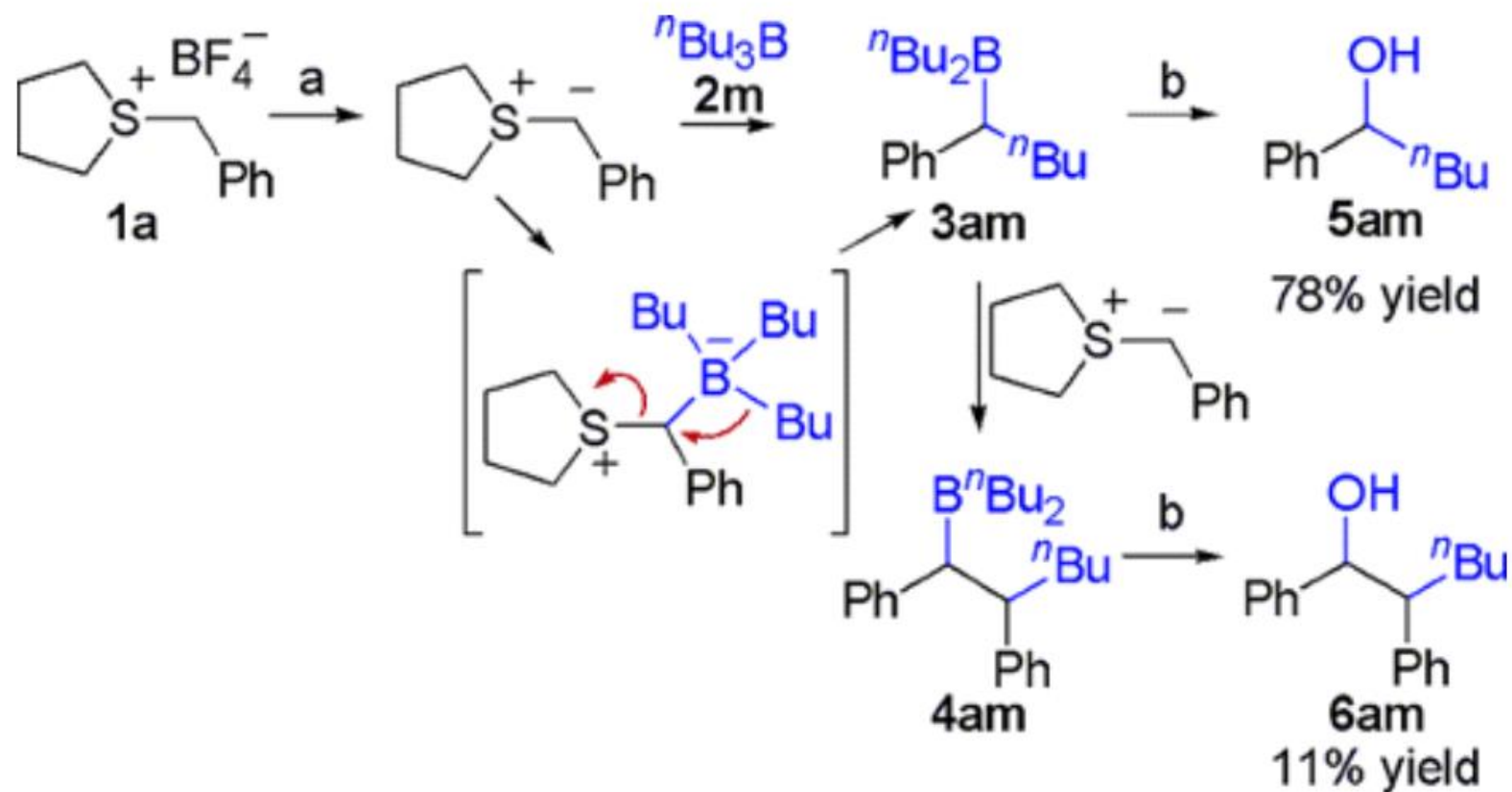
Supporting Information (1)

Abstract

The reactions of aryl-stabilized sulfonium ylides with trialkyl/triarylboranes have been investigated. Clean monohomologation of the boranes with only a small amount of the higher homologation products (<10%) was observed. The homologation products were isolated as the alcohols (treatment with $\text{H}_2\text{O}_2/\text{NaOH}$) and amines (treatment with $\text{NH}_2\text{OSO}_3\text{H}$). Although the reactions were conveniently conducted at 5°C , the ylide reaction with tributylborane was very fast even at -78°C (complete after 15 min). Use of chiral sulfides rendered the reactions asymmetric, and high enantioselectivity (>95% ee) was observed in all cases. The ylide-borane reaction was applied to short syntheses of the anti-inflammatory agents neobenodine and cetirizine, both of which contain a chiral diarylmethylalkoxy and diarylmethylamino moiety, respectively.

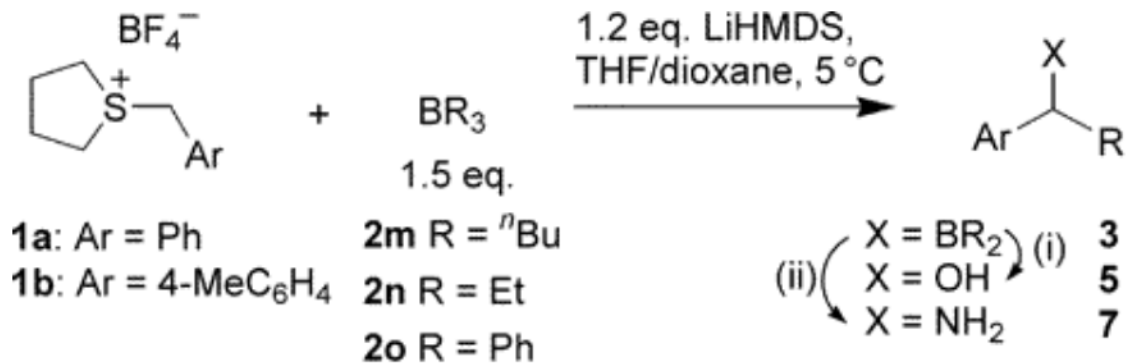


如何克服 homologation reactions?
using substituted ylides



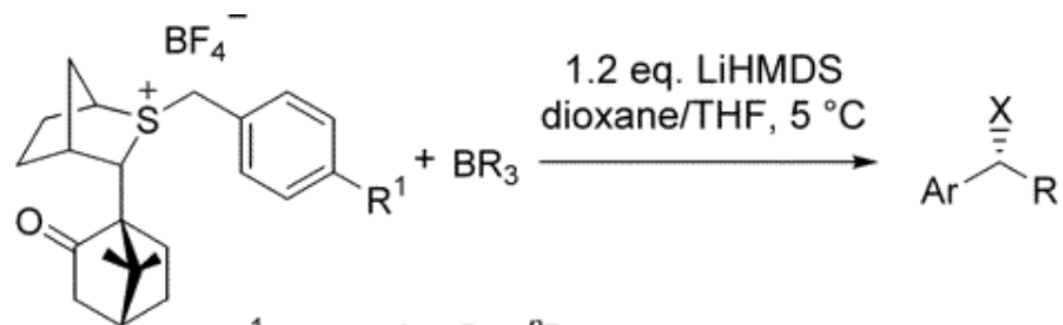
Scheme 1. Reaction of Sulfonium Salt **1a** with Tributylborane **2m**^a

^a Conditions: (a) 1.2 equiv LiHMDS, THF/dioxane, -78 °C; (b) H₂O₂/NaOH.



(i) H₂O₂, NaOH, (ii) NH₂OSO₃H

entry	R	Ar	X	compound/yield (%) ^a
1	ⁿ Bu	Ph	OH	5am/78
2	ⁿ Bu	Ph	NH ₂	7am/74
3	Et	Ph	OH	5an/76
4	Et	Ph	NH ₂	7an/77
5	Ph	4-MeC ₆ H ₄	OH	5bo/87
6	Ph	4-MeC ₆ H ₄	NH ₂	7bo/17

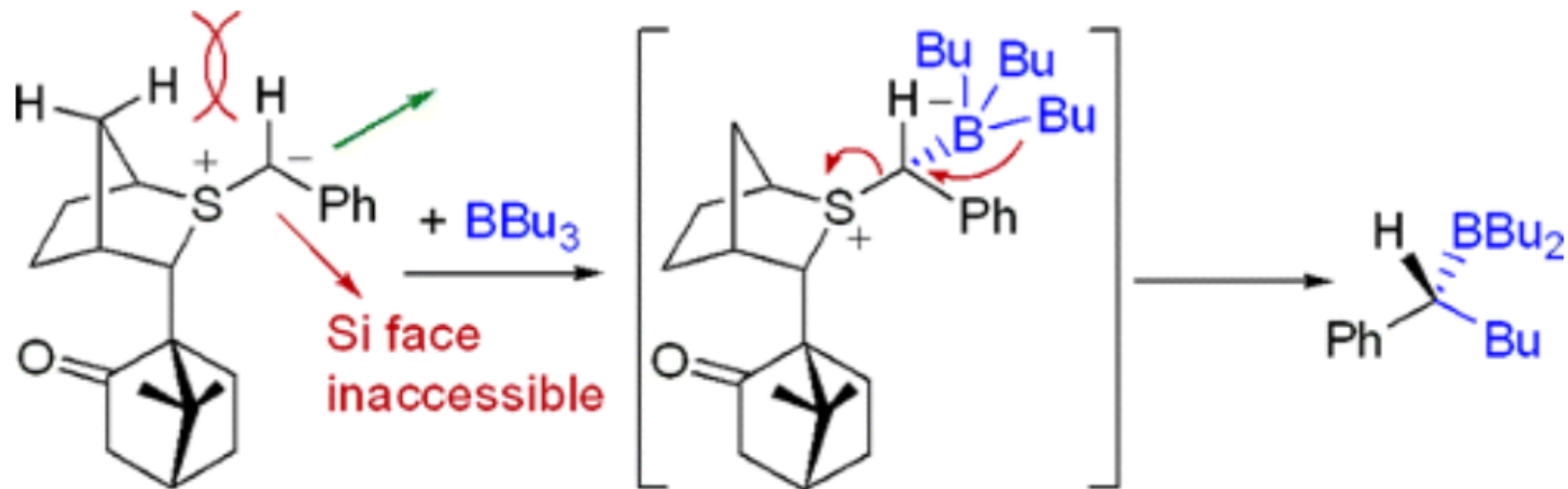


9a $R^1 = \text{H}$; **2m** $R = {}^n\text{Bu}$
9b $R^1 = \text{Me}$ **2n** $R = \text{Et}$
9c $R^1 = \text{Cl}$ **2o** $R = \text{Ph}$

(ii) $\left(\begin{array}{l} X = \text{BR}_2 \\ X = \text{OH} \\ X = \text{NH}_2 \end{array} \right) \xrightarrow{\text{(i)}} \begin{array}{l} \mathbf{11} \\ \mathbf{12} \\ \mathbf{13} \end{array}$

(i) $\text{H}_2\text{O}_2, \text{NaOH}$, (ii) $\text{NH}_2\text{OSO}_3\text{H}$

entry	R	Ar	X	product	yield ^b /ee ^c (%)
1	ⁿ Bu	Ph	OH	12am	70/95
2	ⁿ Bu	Ph	NH ₂	13am	72/97 ^d
3	Et	Ph	OH	12an	73/96
4	Et	Ph	NH ₂	13an	68/97 ^d
5	Ph	4-MeC ₆ H ₄	OH	12bo	87/95
6	Ph	4-ClC ₆ H ₄	NH ₂	13co	68/96 ^d



Scheme 4. Control of Enantioselectivity



Transition-Metal-Free Suzuki-Type Cross-Coupling Reaction of Benzyl Halides and Boronic Acids via 1,2-Metalate Shift [Click to copy article link](#)

Zhiqi He, Feifei Song, Huan Sun, and Yong Huang

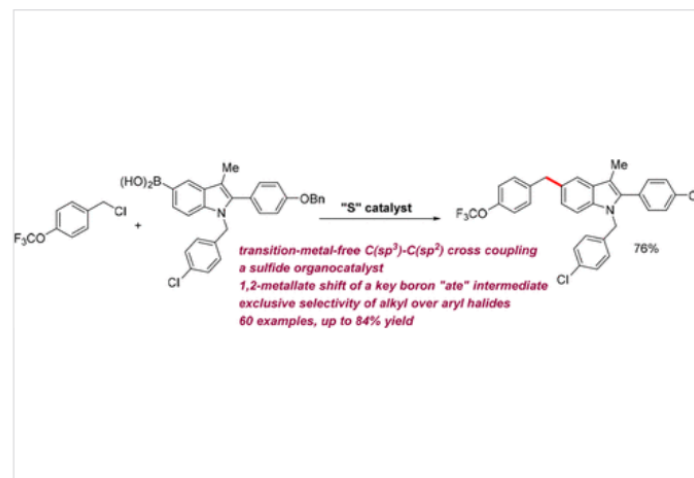
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Supporting Information (1)

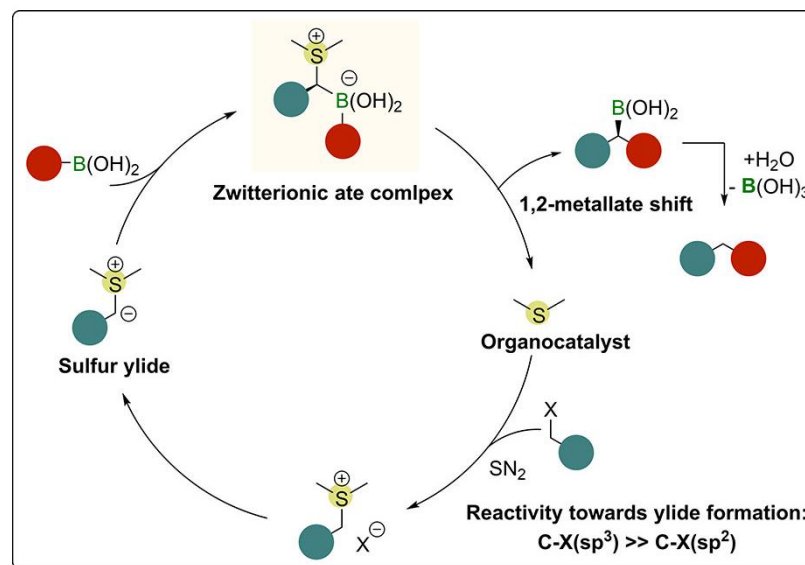
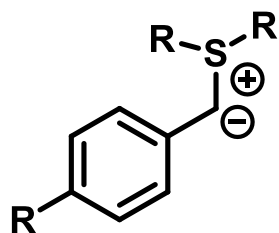
Abstract

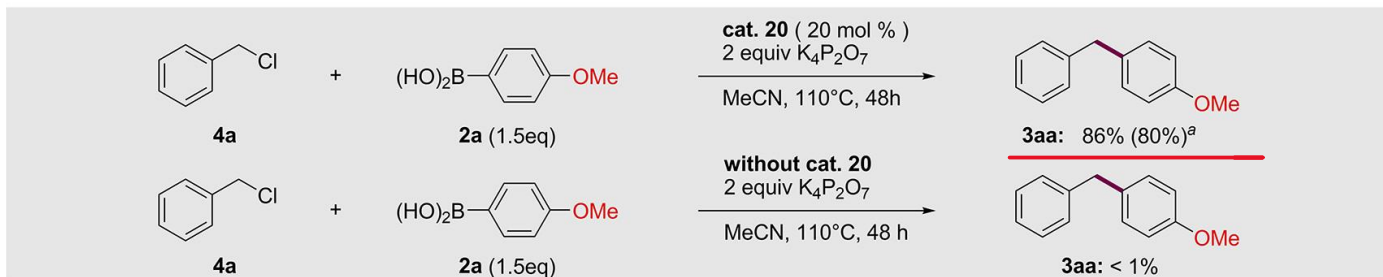
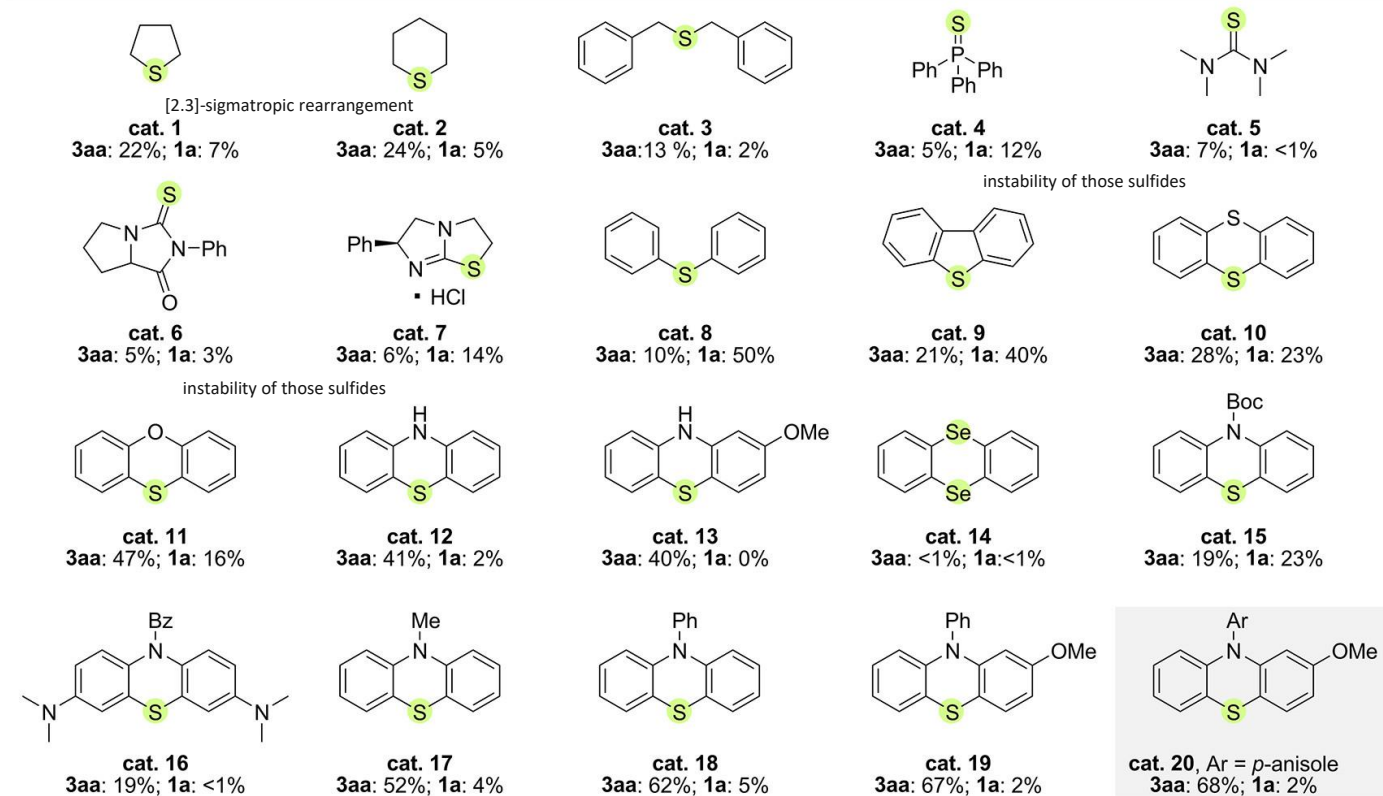
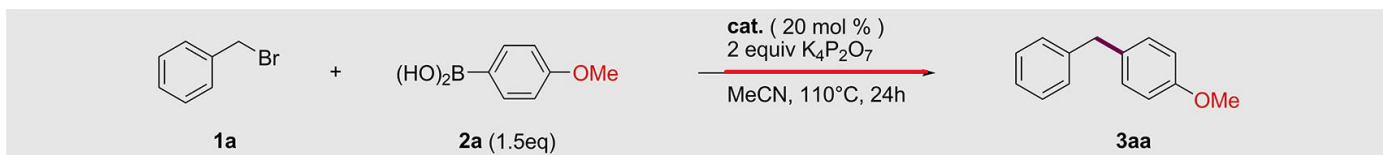
Cross-coupling of organoboron compounds with electrophiles (Suzuki–Miyaura reaction) has greatly advanced C–C bond formation and has been well received in medicinal chemistry. During the past 50 years, transition metals have played a central role throughout the catalytic cycle of this important transformation. In this process, chemoselectivity among multiple carbon–halogen bonds is a common challenge. In particular, selective oxidative addition of transition metals to alkyl halides rather than aryl halides is difficult due to unfavorable transition states and bond strengths. We describe a new approach that uses a single organic sulfide catalyst to activate both $C(sp^3)$ halides and arylboronic acids via a zwitterionic boron “ate” intermediate. This “ate” species undergoes a 1,2-metalate shift to afford Suzuki coupling products using benzyl chlorides and arylboronic acids. Various diaryl methane analogues can be prepared, including those with complex and biologically active motifs. The reactions proceed under transition-metal-free conditions, and $C(sp^2)$ halides, including aryl bromides and iodides, are unaffected. The orthogonal chemoselectivity is demonstrated in the streamlined synthesis of highly functionalized diaryl methane scaffolds using multi-halogenated substrates. Preliminary mechanistic experiments suggest both the sulfonium salt and the sulfur ylide are involved in the reaction, with the formation of sulfonium salt being the slowest step in the overall catalytic cycle.



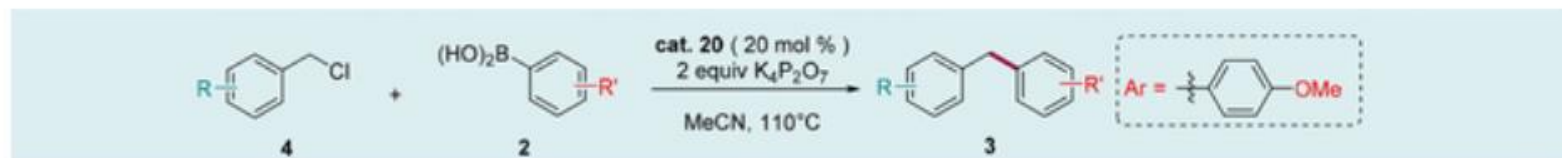


c) Proposed Sulfide-catalyzed Cross-coupling

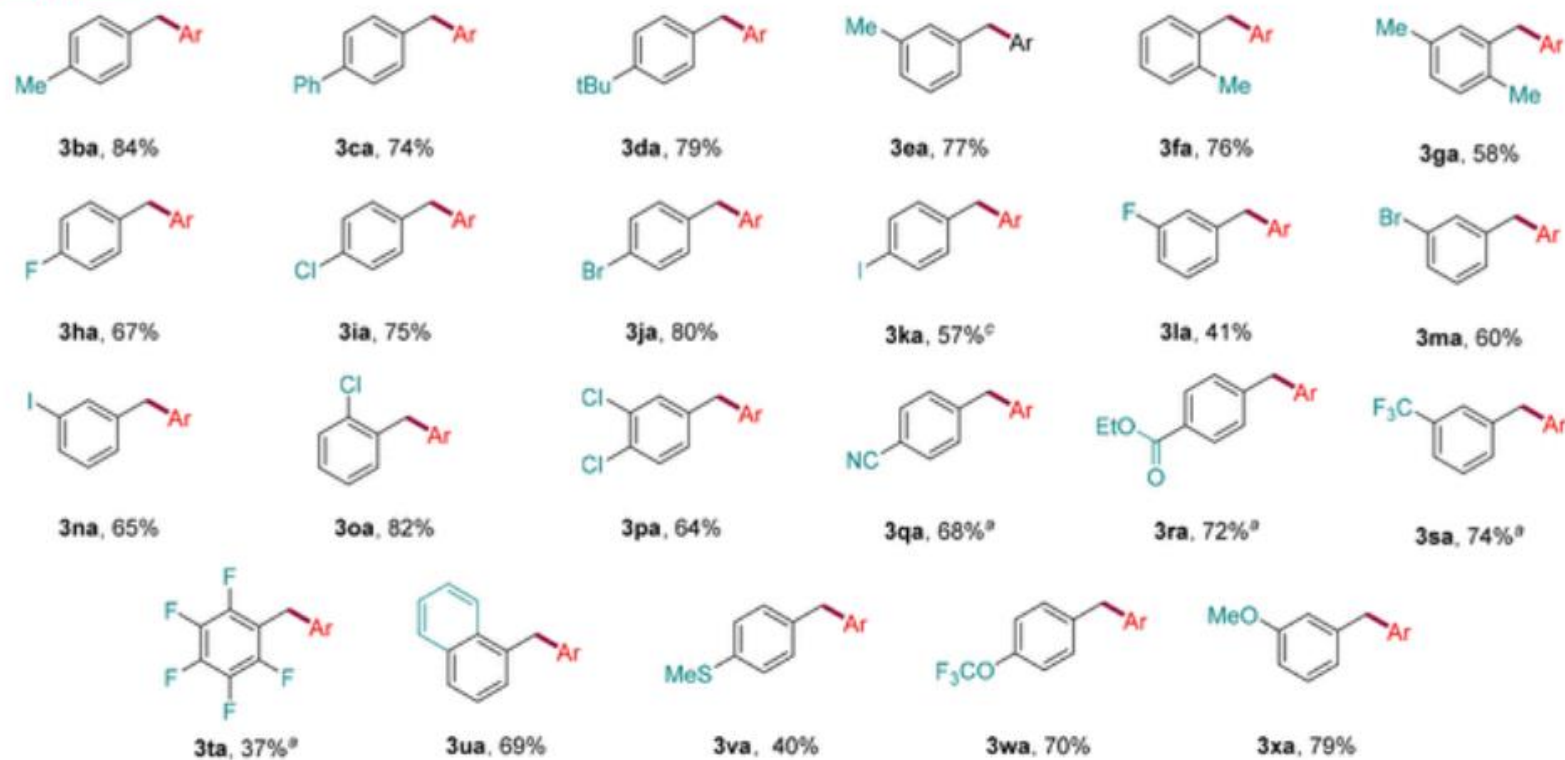




$\text{K}_4\text{P}_2\text{O}_7$ exhibits the best overall balance of activity and basicity

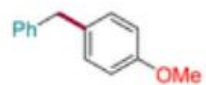


benzyl chlorids

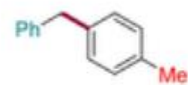




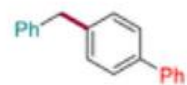
boronic acids



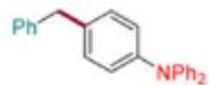
3aa, 80%



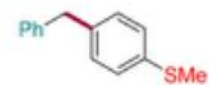
3ab, (44%)^b



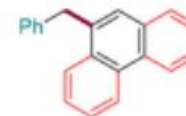
3ac, 50%^b



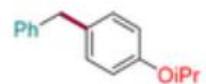
3ad, 81%



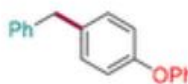
3ae, 53%



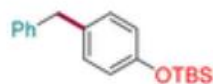
3af, 84%



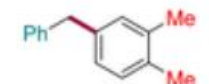
3ag, 81%^c



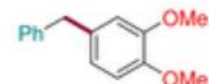
3ah, 52%^c



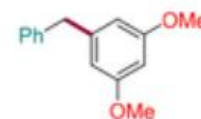
3ai, 72%^c



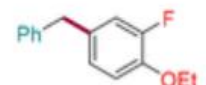
3aj, (47%)^{b,c,d}



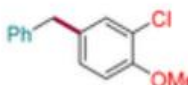
3ak, 54%^{b,c}



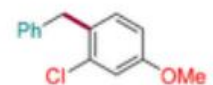
3al, 58%^{b,c}



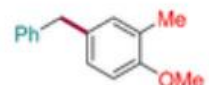
3am, 61%



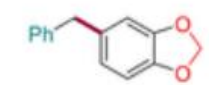
3an, 79%



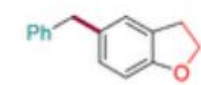
3ao, 52%



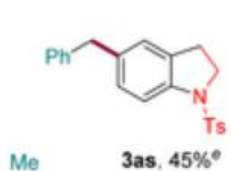
3ap, 73%^b



3aq, 44%



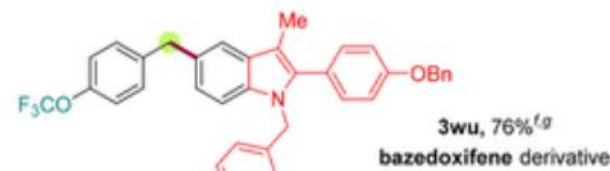
3ar, 72%



3as, 45%^e

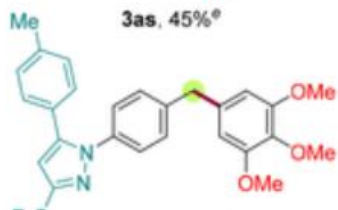


3at, 57%^{f,g}



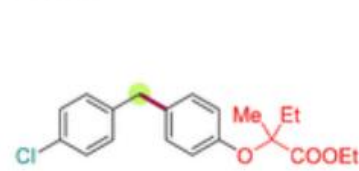
3wu, 76%^{f,g}

basedoxifene derivative

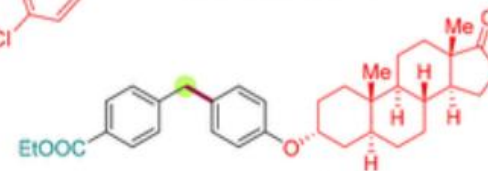


3yv, 52%^f

celecoxib derivative



beclobrate, 51%^o

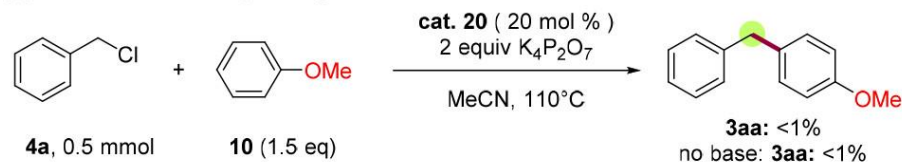


3rw, 65%^{f,g}

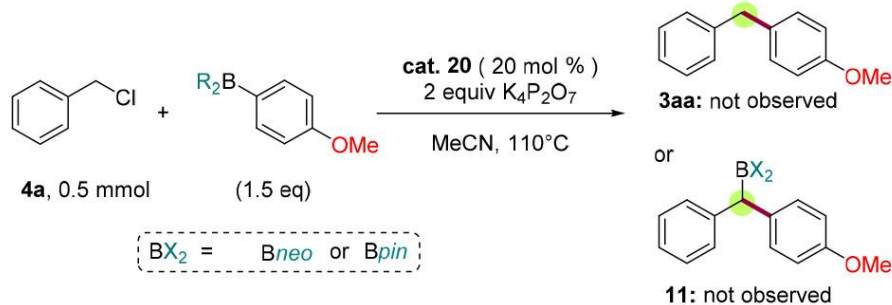
androsterone derivative

Mechanistic experiments

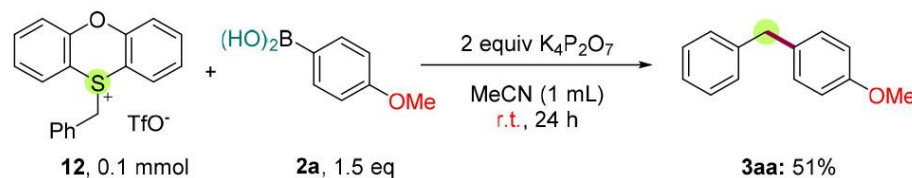
(a) The Friedel-Crafts pathway



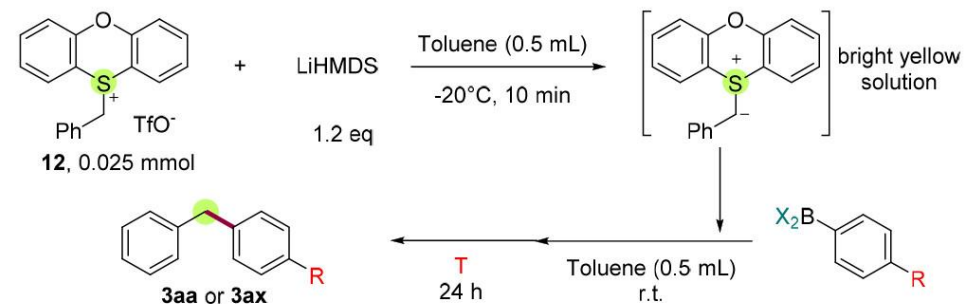
(b) The reactions using boronic esters



(c) Cross-coupling using sulfonium salts

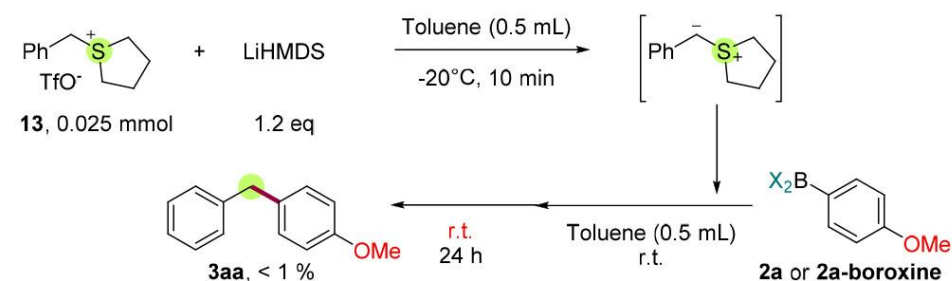


(d) *In situ* sulfide ylide formation and subsequent cross-coupling for cat. 11



entry	X	R	T	yield
1	boronic acid	-OMe	r.t.	55%
2	boroxine	-OMe	r.t.	27%
3	boroxine	-COOEt	r.t.	trace
4	boroxine	-COOEt	60 °C	23%

(e) *In situ* sulfide ylide formation and subsequent cross-coupling for cat. 1



better nucleophile
 poor leaving group
 disfavor the 1,2-metalate shift

A Thioether-Catalyzed Cross-Coupling Reaction of Allyl Halides and Arylboronic Acids

Jingwei Xu, Zhiqi He, Jiwei Zhang, Jian Chen✉, Yong Huang✉

First published: 30 August 2022 | <https://doi.org/10.1002/anie.202211408> | Citations: 5

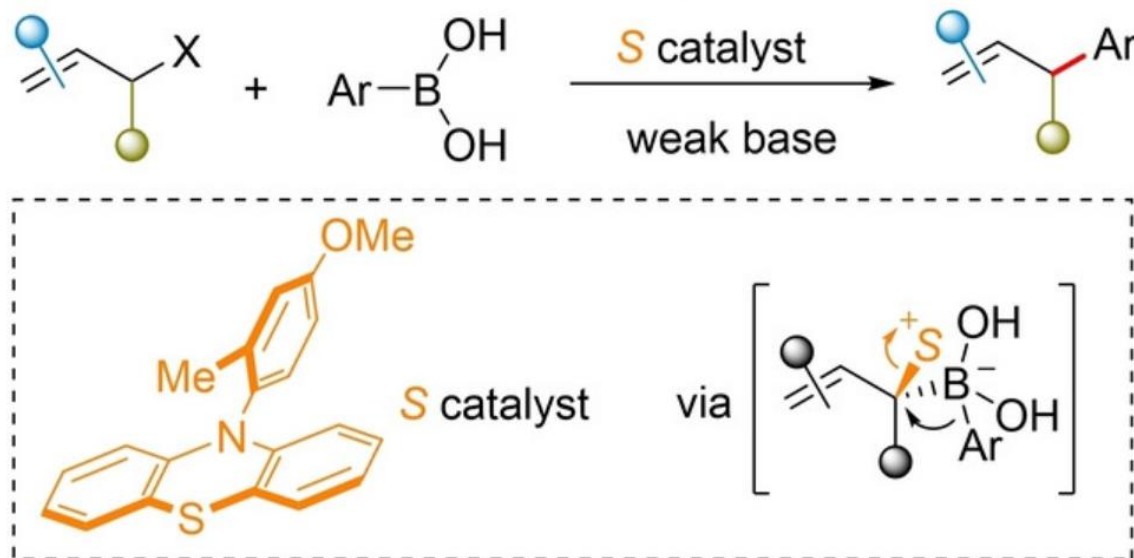
find full-text with SFX

SECTIONS

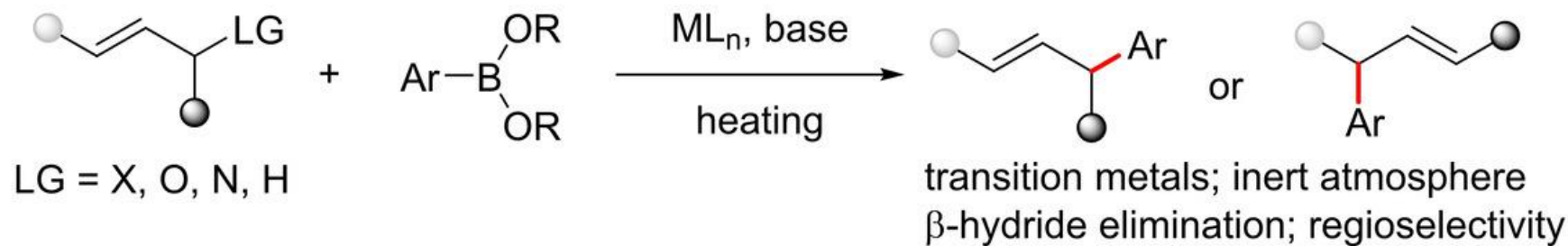


Graphical Abstract

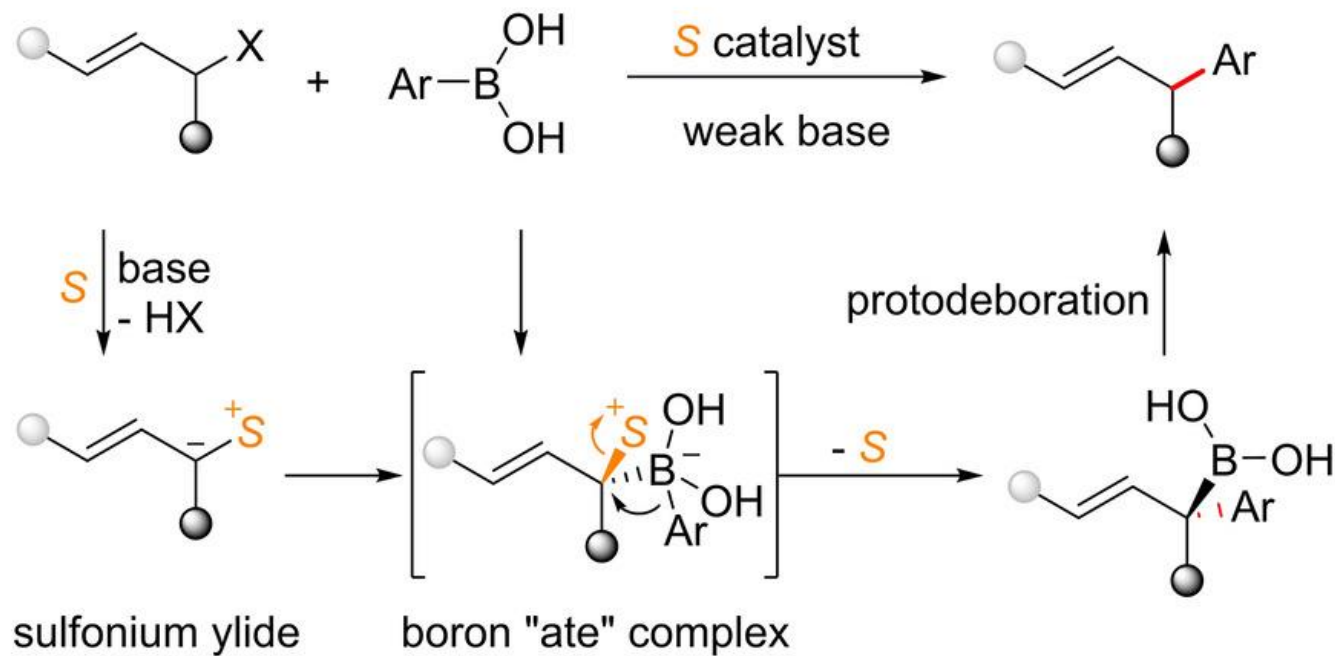
An organocatalytic cross-coupling of allyl bromides and arylboronic acids was developed using a designer thioether catalyst. Preliminary mechanistic studies suggested the involvement of a key sulfoxonium ylide that binds to the arylboronic acid and triggers 1,2-aryl migration.



A) Transition-metal-catalyzed allylation of arylboronic acids



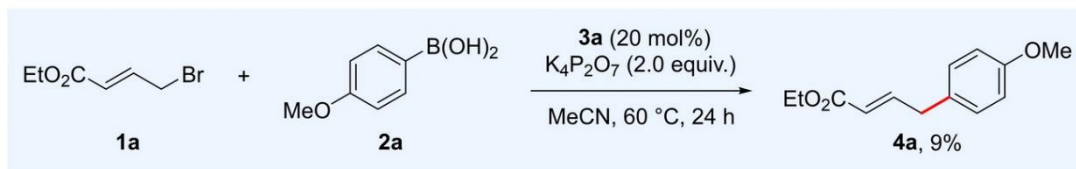
B) Sulfide-catalyzed allylation of arylboronic acids (*this work*)



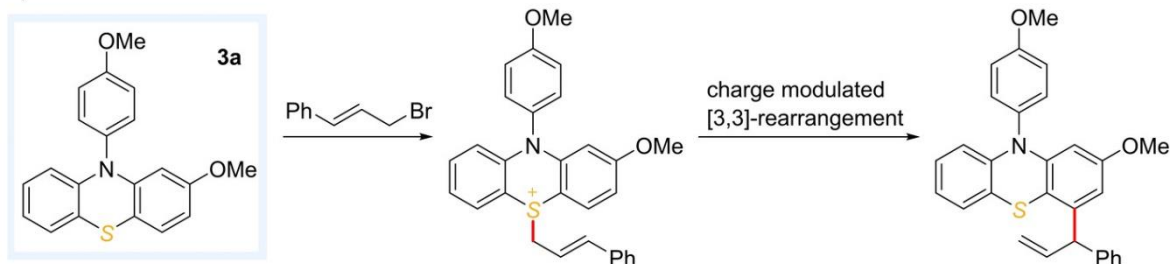
organocatalysis
no β -hydride elimination
mild conditions
no interference by C_{sp^2} -X



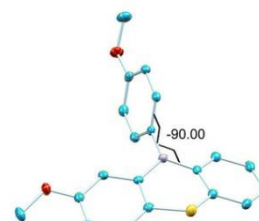
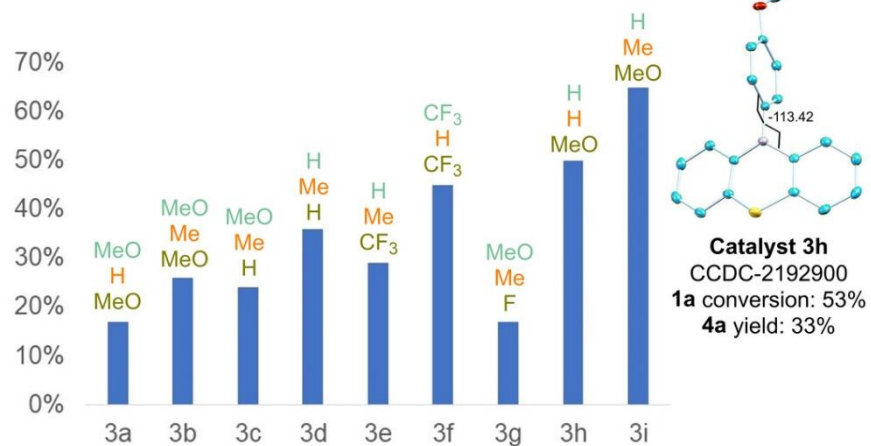
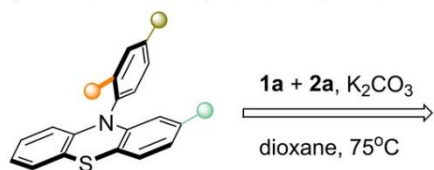
A) Initial allyl-aryl cross-coupling using sulfide cat. **3a**



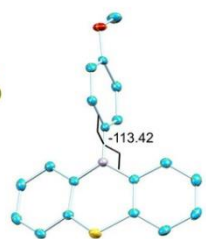
B) Deactivation of cat. **3a**



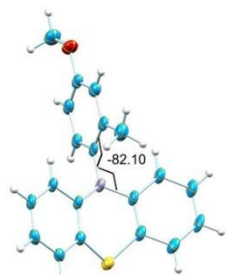
C) Structure-reactivity relationship of cat. **3**



Catalyst 3a
CCDC-2192889
1a conversion: 81%
4a yield: 6%



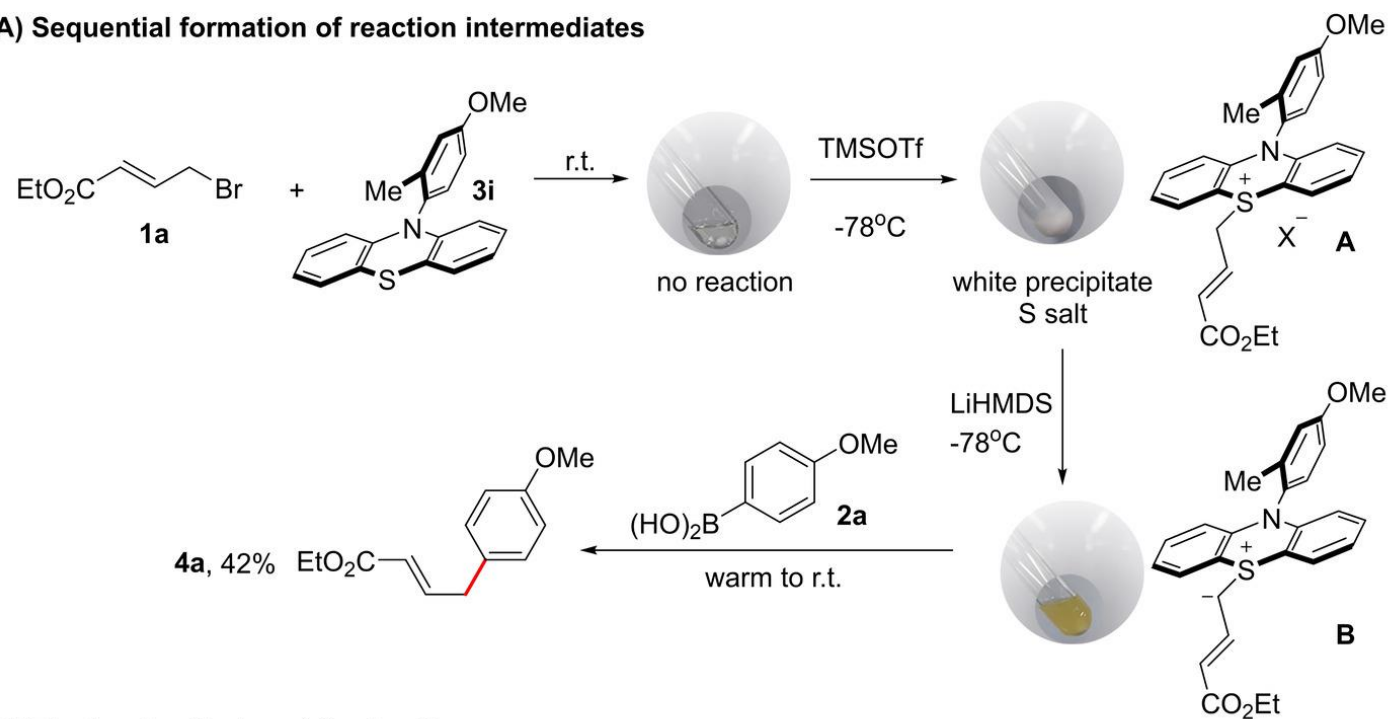
Catalyst 3h
CCDC-2192900
1a conversion: 53%
4a yield: 33%



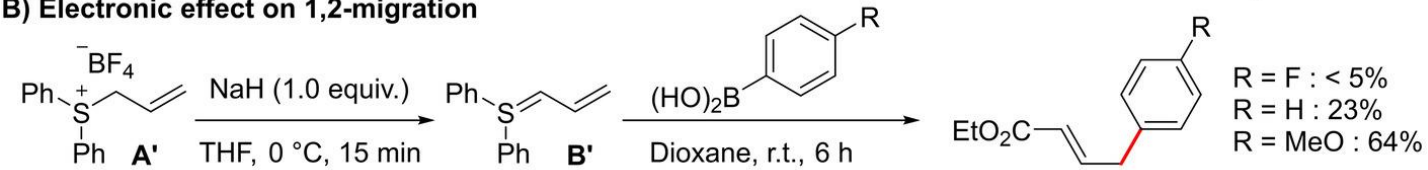
Catalyst 3i
CCDC-2192901
1a conversion: 62%
4a yield: 51%

solvent and base did not result
electronic and topological modification

A) Sequential formation of reaction intermediates



B) Electronic effect on 1,2-migration



C) Alternative synthesis of catalyst 3i under strict transition-metal-free conditions

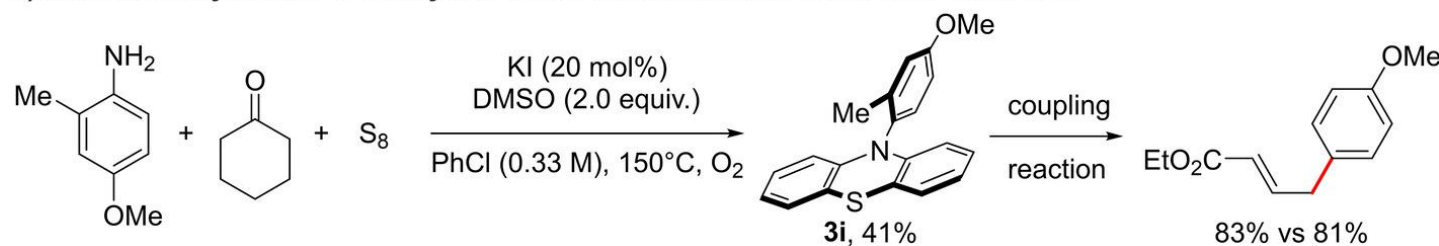
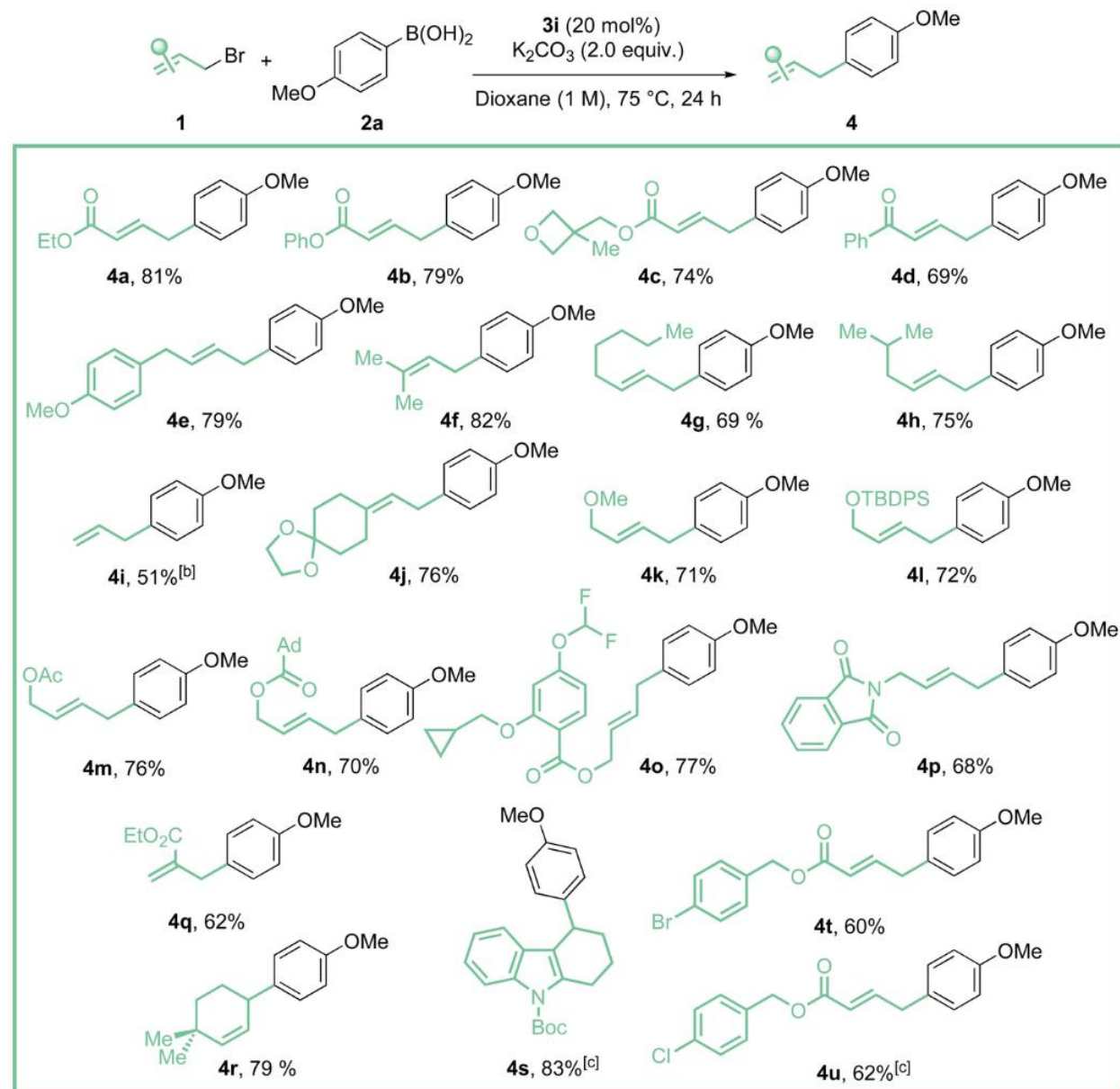


Table 1. Generality with respect to the allyl bromide.^[a]



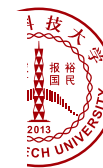
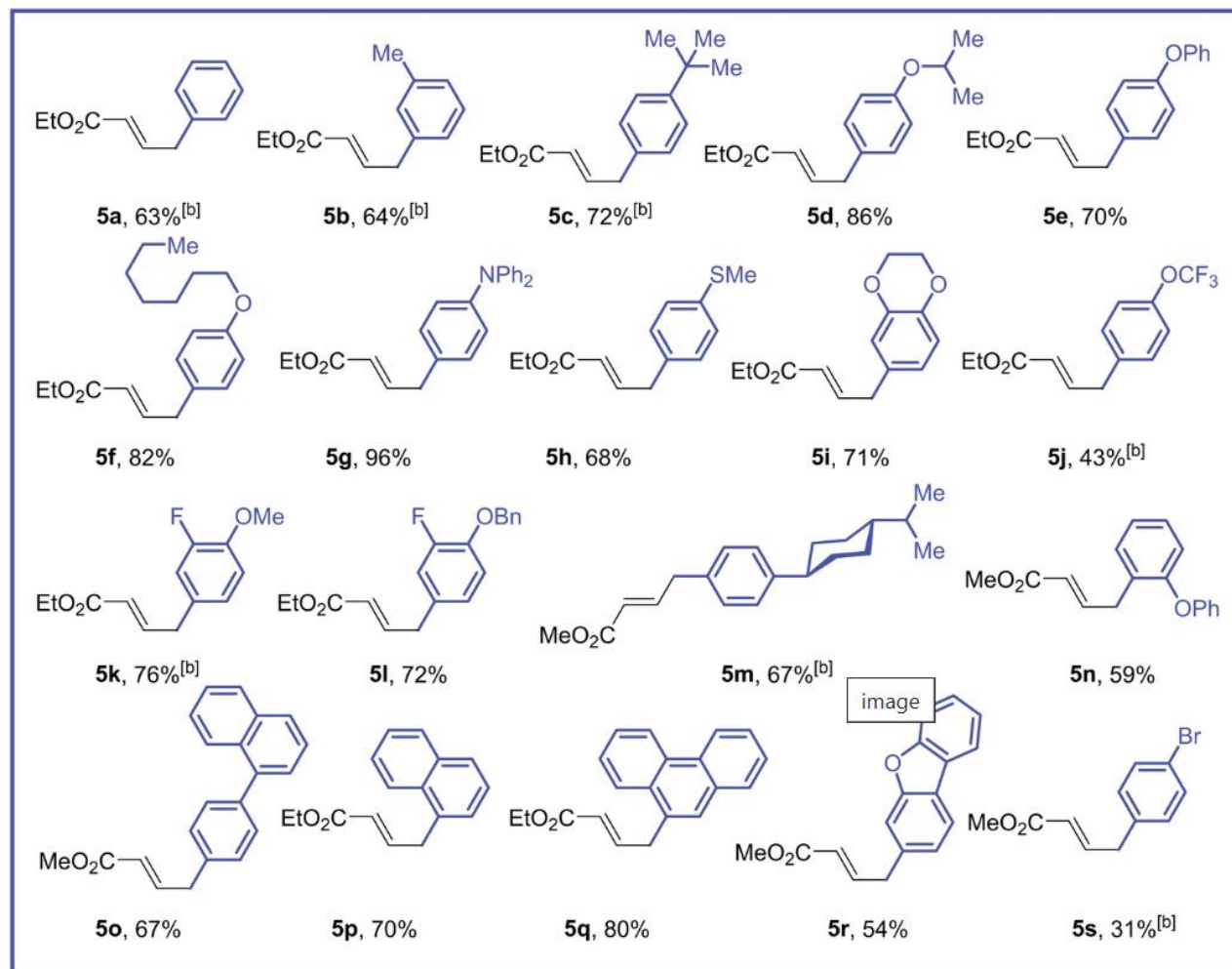
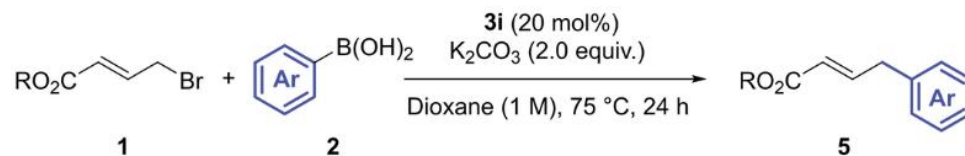
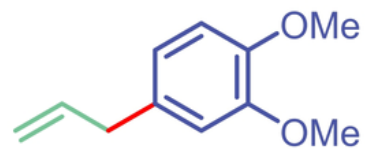
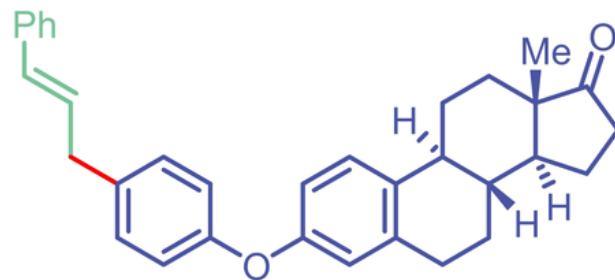


Table 2. Scope of the reaction with respect to the arylboronic acid.^[a]

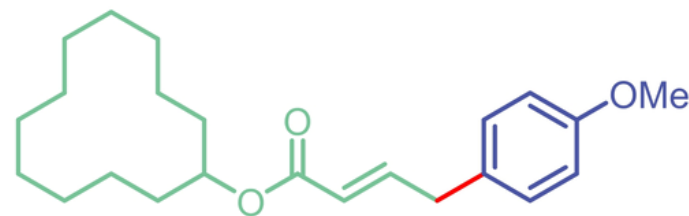




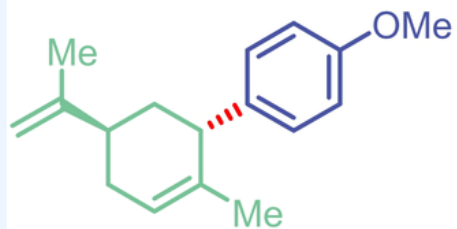
mythyl eugenol **6a**, 55%^[b]



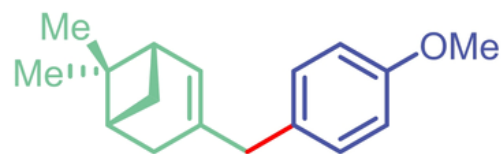
estrone derivative **6b**, 69%



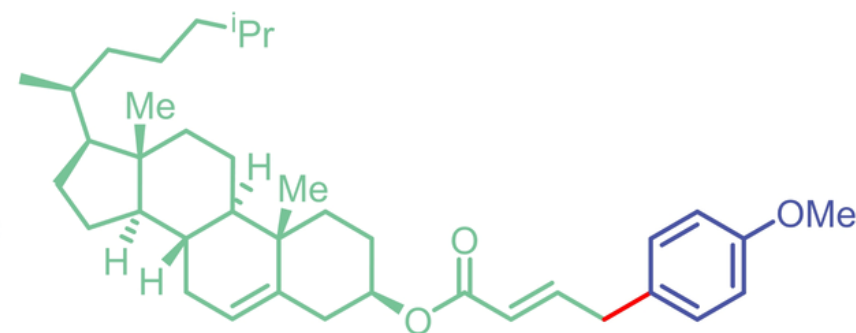
cyclododecanol derivative **6c**, 63%



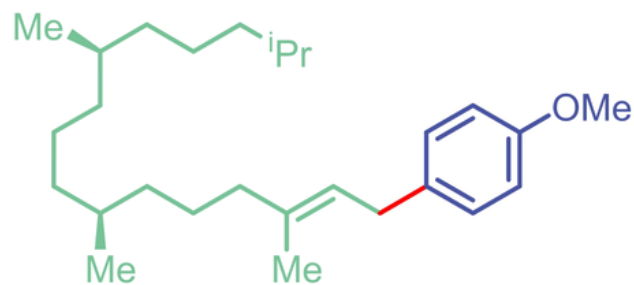
carvone derivative **6d**, 81%



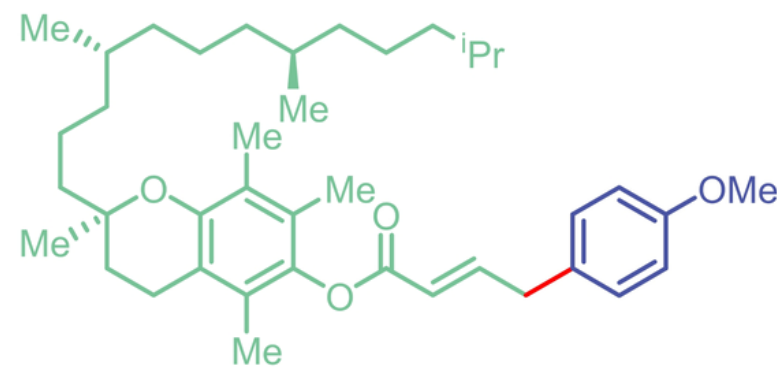
myrtenal derivative **6e**, 70%



cholesterol derivative **6f**, 78%



phytol derivative **6g**, 77%



vitamin E derivative **6h**, 81%



上海科技大学
ShanghaiTech University

感谢聆听

