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Iridium-Catalyzed Enantioselective Allylic Substitutions of Aliphatic Esters via Silyl Ketene Acetals

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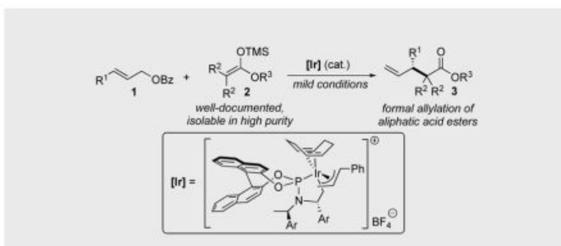
Abstract

Enantioselective allylic substitutions with enolates derived from aliphatic esters under mild conditions remain challenging. Herein we report iridium-catalyzed enantioselective allylations of silyl ketene acetals, the silicon enolates of esters, to form products containing a quaternary carbon at the nucleophile moiety and a tertiary carbon at the electrophile moiety. Under relatively neutral conditions, the allylated aliphatic esters were obtained with excellent regioselectivity and enantioselectivity. These products were readily converted to primary alcohols, carboxylic acids, amides, isocyanates, and carbamates, as well as tetrahydrofuran (THF) and γ-butyrolactone derivatives, without erosion of enantiomeric purity.

Graphical abstract



Enantioselective allylic substitutions with enolates derived from aliphatic esters under mild conditions remain challenging. Herein we report iridium-catalyzed enantioselective allylations of silyl ketene acetals, the silicon enolates of esters, to form products containing a quaternary carbon at the nucleophile moiety and a tertiary carbon at the electrophile moiety. Under relatively neutral conditions, the allylated aliphatic esters were obtained with excellent regioselectivity and enantioselectivity. These products were readily converted to primary alcohols, carboxylic acids, amides, isocyanates, and carbamates, as well as tetrahydrofuran (THF) and γ-butyrolactone derivatives, without erosion of enantiomeric purity.

Keywords

alkylation; asymmetrical catalysis; enantioselectivity; esters; iridium

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Catalytic asymmetric allylic substitutions with enolates form C–C bonds reliably with high enantioselectivity.[1] Such reactions with enolates derived from ketones and aldehydes form products bearing α-stereogenic centers[2], β-stereogenic centers[3], or both[4]. These reactions of stabilized enolates generated from carboxylic acid derivatives containing proximal electron-withdrawing groups (such as acyl, carboxyalkyl, nitro or cyano groups),[5] heteroatom functionalities[6], or aromatic substituents[7] also occur. However, analogous transformations of the unstabilized enolates derived from aliphatic esters are rare. Reported enantioselective examples are limited to palladium-catalyzed reactions of lactones or ester equivalents with symmetrical allylic electrophiles, and one recently reported example of a ruthenium-catalyzed process.[8–9]

The low acidity of the α hydrogens of the aliphatic esters and the instability of the ester-derived enolates make allylation of ester enolates challenging. Stoichiometric strong bases are required to form the enolates *in situ* without self-condensation, substrates that bear base-sensitive functionalities (for example, acetoxyl group) are not tolerated, and Claisen condensation between the ester products and the enolates can lead to side products. Finally, cyclopropanation has been shown to compete with the allylation process when palladium catalysts are used.[10]

To develop a general method for the enantioselective allylation of aliphatic esters under mild conditions, we envisioned that silyl ketene acetals, the silicon enolates of esters, could be employed as the nucleophiles because they are significantly less basic than the alkali metal enolates formed *in situ* by deprotonation. Iridium complexes **[Ir]** (Scheme 1) developed in our group could catalyze this proposed transformation because they enable enantioselective allylic substitution reactions with various nucleophiles under relatively neutral conditions, without competing formation of cyclopropanes.[11]

The allylation of silyl ketene acetals containing *gem*-dialkyl groups would be particularly valuable because the resulting enantioenriched α-allyl esters containing a quaternary α-carbon and a tertiary β-stereocenters are inaccessible by asymmetric Michael additions or asymmetric hydrogenations of the α,β-unsaturated esters. Furthermore, the enantioselective allylations of stabilized malonate-type nucleophiles followed by fragmentation (desulfonylation and decarboxylation) would not afford these highly substituted products.[12]

Herein we report enantioselective allylations of silyl ketene acetals catalyzed by a metallocyclic iridium complex (Scheme 1) to form the allylated aliphatic esters with high regio- and enantioselectivity under mild conditions. Due to the versatility of the ester functionality in organic synthesis, these products are readily transformed to primary alcohols, carboxylic acids, amides, isocyanates, carbamates, tetrahydrofuran (THF) derivatives and γ-butyrolactone derivatives without erosion of enantiomeric purity.

We began our studies on enantioselective allylic substitutions of aliphatic silyl ketene acetals by examining the reactions between cinnamyl methyl carbonate and ketene acetal **2a** in the presence of a series of metallacyclic iridium complexes containing a series of aryl substituents on the ligands (Table 1, entry 1–4). A catalytic amount of tetrabutylammonium acetate ($^{n}Bu_4NOAc$) was added to activate the silicon enolate because our previous studies demonstrated that carboxylates could activate silyl enol ethers in related iridium-catalyzed allylation reactions.[3f, 13] The reaction conducted with iridium catalyst **[Ir]-2** bearing two 2-anisyl substituents on the ligand gave the ester product **3aa** in 50% yield with >20:1 branched/linear selectivity and 98% ee. The yield was modest because side product **sp** (33%) was formed from competitive nucleophilic acyl substitution of **2a** with the carbonyl group of cinnamyl methyl carbonate. To suppress the formation of **sp**, we studied reactions of allylic esters containing the 2,2,2-trichloroethyl carbonate (OTroc) and the *t*-butyl carbonate (OBoc) groups that are more hindered than the methyl carbonate. Reaction of the 2,2,2-trichloroethyl carbonate gave **3aa** in a low yield of 16% and **sp** in 20% yield (entry 5), as well as an additional product in 54% yield from the allylation of 2,2,2-trichloroethoxide generated from oxidative addition of the carbonate and decarboxylation of the resulting anion. However, reaction of the *t*-butyl carbonate formed **3aa** as a single product in 97% yield with 98% ee (entry 6).

Further investigation of the effect of leaving groups included reactions of the ethyl phosphate, acetate, pivalate and benzoate derivatives of cinnamyl alcohol (entry 7–10). The reaction of cinnamyl benzoate **1a** (entry 10) delivered **3aa** in almost quantitative (96%) yield with excellent ee (>99%). However, a small amount of cinnamyl acetate (<5%) was observed, presumably from reaction of the allyl iridium intermediate and $^nBu_4NOAc$.[11d] This hypothesis was supported by the result of the reaction conducted with 0.5 equiv of $^nBu_4NOAc$ (entry 11), which gave **3aa** in a lower yield of 68% and cinnamyl acetate in 26% yield, which was higher than that from the reaction with 3 mol % of $^nBu_4NOAc$ in entry 10. To avoid the formation of cinnamyl acetate, tetrabutylammonium benzoate ($^nBu_4NOBz$) was used instead of $^nBu_4NOAc$ as the carboxylate additive, and this reaction occurred to afford **3aa** in quantitative yield with >99% ee (entry 12). The reaction with cinnamyl *t*-butyl carbonate occurred similarly to give **3aa** in 94% yield with 98% ee (entry 13). No reaction occurred in the absence of a carboxylate additive (entry 14) or with the TBS analog of **2a**.

Table 2 shows the scope of allyl benzoates that underwent the allylation process. The reactions with various cinnamyl benzoates bearing electron-neutral (**3aa**, **3ba**), electron-donating (**3ca**, **3da**), and electron-withdrawing (**3ea**–**3ia**) substituents on the aryl rings all afforded the corresponding products in ≥84% yield with >99% ee. Benzoate **1d** bearing a base-sensitive acetoxy substituent at the *para*-position of the phenyl ring underwent allylation cleanly to give **3da** in 87% yield with >99% ee, highlighting the mild conditions of these reactions. In general, the reactions of electron-deficient cinnamyl benzoates required a higher catalyst loading of 4 mol % (condition **B** for **3ea**–**3ga**) or 6 mol % (condition **C** for **3ha**, **3ia**), instead of 3 mol % (condition **A** for **3aa**–**3ca**), to reach full conversion of the allyl benzoate.

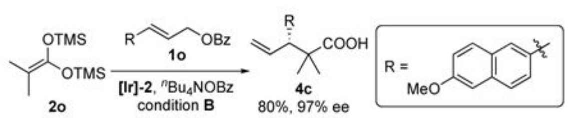
This reaction also occurred with allyl benzoates bearing heteroaryl, naphthyl, and alkenyl substituents. Allyl benzoates containing pyridyl (**1j**), furyl (**1k**), thienyl (**1l**), thiazolyl (**1m**), naphthyl (**1n**), and 6-methoxy naphthyl (**1o**) groups underwent the allylations to form products **3ja**–**3oa** in ≥83% yield with ≥98% ee. Sorbyl benzoate **1p** reacted with silyl ketene acetal **2l** to give the allylation product **3pl** in 52% yield with 98% ee.

Table 3 shows the scope of silyl ketene acetals that underwent the allylation process. Silyl ketene acetals generated from methyl (**2a**), ethyl (**2b**), isopropyl (**2c**) and phenyl (**2e**) isobutyrate reacted to form products **3aa**, **3ab**, **3cc**, and **3ce** in ≥79% yield with >99% ee. The reactivity of the silyl ketene acetal derived from *t*-butyl isobutyrate (**2d**) was lower, and **3cd** was obtained in 38% yield with 39% of **1c** unconverted. Silyl ketene acetal **2f** derived from (−)-nopol that bears a chiral hydrocarbon motif also reacted to give **3cf** in 93% yield with >20:1 dr.

In addition to the silyl ketene acetals derived from isobutyrates, *gem*-diethyl silyl ketene acetal **2g** reacted to afford **3cg** in 96% yield with >99% ee. Exocyclic *gem*-dialkyl silyl ketene acetals bearing exocyclic double bonds on 4- (**2h**), 5- (**2i**, **2n**),6- (2**j**) and 7-membered (**2k**) rings all reacted with benzoate **1c** to give products **3ch**–**3ck**, and **3cn** in ≥96 yields with ≥99% ee. Exocyclic silyl ketene acetals containing oxygen atoms or a difluoromethylene unit on the ring structure reacted similarly to give the products (**3cl**, **3cm**) in ≥93% yield with >99% ee.

To illustrate the synthetic utility of this allylation reaction, various transformations of allylation product **3oa** were conducted. For example, **3oa** was readily converted to the primary alcohol **4a** and carboxylic acid **4c** without erosion of ee after reduction and hydrolysis, respectively. The acid **4c** was further transformed into the enantioenriched amide **4e**, isocyanate **4f**, and carbamate **4g**. The terminal alkene functionality was also derivatized. An intramolecular hydroalkoxylation of the olefin moiety on alcohol **4a** occurred with silver triflate[14] as the catalyst, giving enantioenriched tetrahydrofuran derivatives **4b** and **4b′**. Although the diastereoselectivity was low (1.1:1), each diastereomer was isolated in pure form with >99% ee. Carboxylic acid **4c** underwent iodolactonization[15] to afford lactone **4d** in 84% yield as a single isomer with >99% ee.

Finally, to extend the scope of this allylation method to form α-allyl carboxylic acids directly, the silyl-protected enolate of isobutyric acid (**2o**) was tested (eq 1). The reaction between **1o** and **2o** formed carboxylic acid **4c** in 80% yield with >97% ee.



(eq 1)

In summary, we have developed enantioselective allylic substitutions with aliphatic silyl ketene acetals catalyzed by a metallacyclic iridium complex. These reactions are rare allylations of enolates derived from aliphatic esters that occur in high enantioselectivity under mild conditions. The use of silyl ketene acetals avoids the use of strong bases, leading to high functional-group tolerance; a catalytic amount of carboxylate additive (^{n}Bu$_4$NOBz) induced reactivity, presumably by activating the silyl ketene acetals. The allylated esters were obtained with excellent regio- and enantioselectivity and were readily converted to the primary alcohols, carboxylic acids, amides, isocyanates, carbamates, THF derivatives and γ-butyrolactone derivatives with preservation of enantiomeric purity. Studies to achieve the regio-, diastereo- and enantioselective allylations of unsymmetrical aliphatic acid and their derivatives are ongoing in our laboratories.[16–17]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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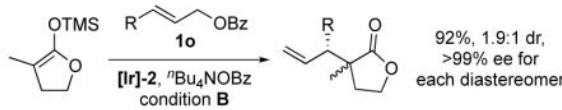
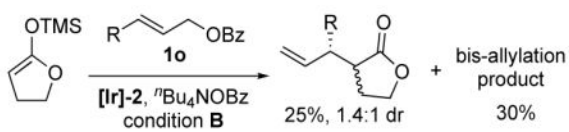
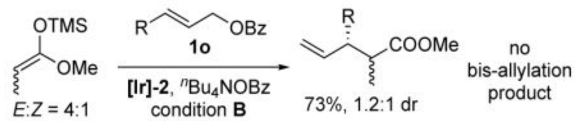
16. Preliminary results showed excellent regio- and enantioselectivity but poor diastereoselectivity for the reaction with unsymmetrical silyl ketene acetals. For example:



17. We also tested monosubstituted silyl ketene acetals for this allylaiton reaction. The reaction of **1o** with the silyl ketene acetal of γ-butyrolactone gave the product in 25% yield with 1.4:1 dr. The bis-allylation product was formed in 30% yield, which presumably resulted from the enolization of the product followed by a second allylation.



However, the reaction with the silyl ketene acetal of methyl propionate gave no bis-allylation product. This lack of reaction is presumably because acyclic esters are less acidic and less prone to enolize than lactones under the reaction condition.


OTMS
OMe
E:Z = 4:1
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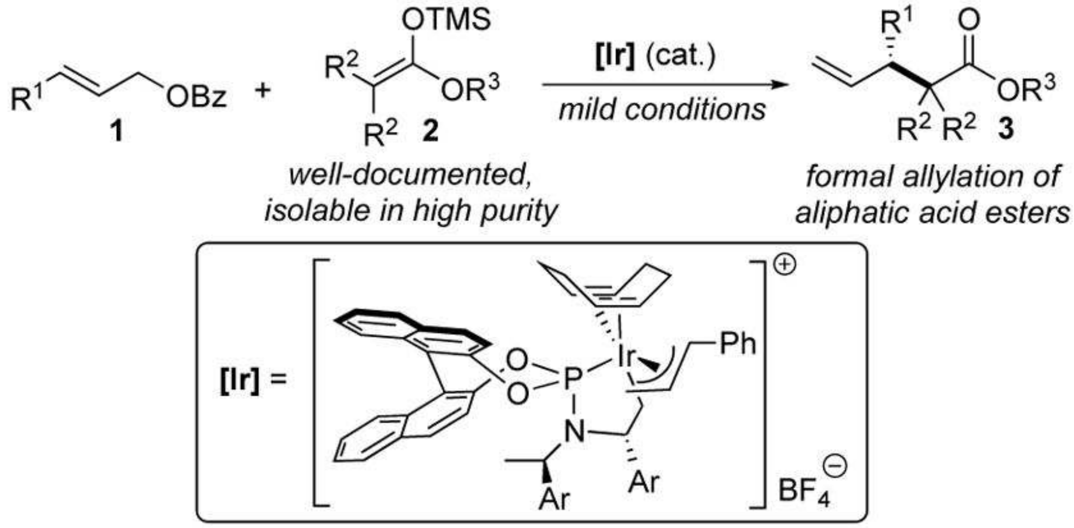
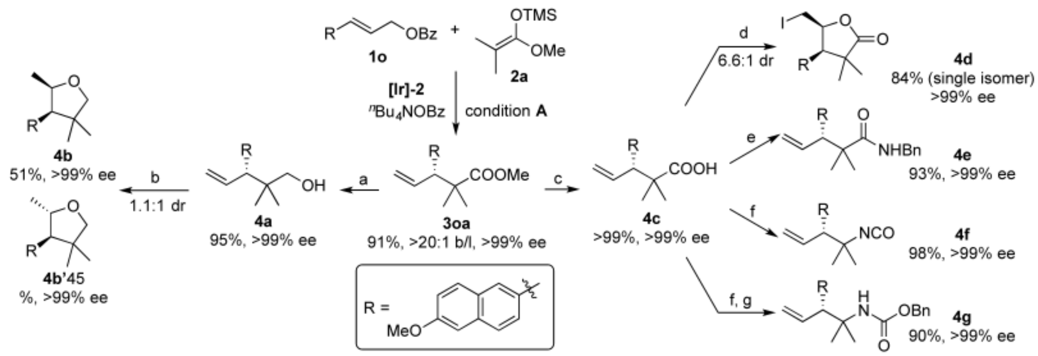


Scheme 1.

Iridium-catalyzed enantioselective allylic substitution reactions with silyl ketene acetals.

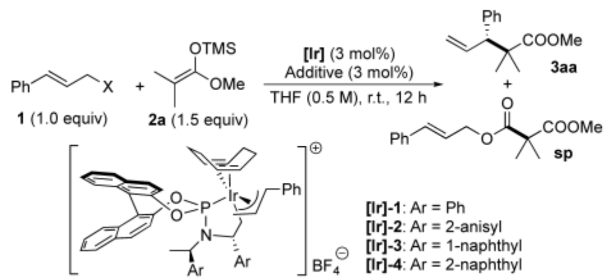


Scheme 2.

Derivatizations. Steps: a) $LiAlH_4$ (1.5 equiv), THF, 0 °C to r.t.; b) AgOTf (10 mol%), DCE, 80 °C; c) NaOH (4.0 equiv, 2 M aq), MeOH, 80 °C; d) I_2 (1.3 equiv), $NaHCO_3$ (1.4 equiv), KI (1.3 equiv), MeCN/H_2O (1:1), 0 °C to r.t.; e) $SOCl_2$ (5.0 equiv), PhH, 80 °C then $BnNH_2$ (2.0 equiv), DMAP (20 mol%), Et_3N (2.0 equiv), DCE, 80 °C; f) diphenylphosphoryl azide (1.05 equiv), Et_3N (1.7 equiv), DCE, 80 °C; g) BnOH (4.0 equiv) added to the mixture after step f, 80 °C.

Table 1

Evaluation of reaction conditions for the Ir-catalyzed allylation.[a]



Entry	X	[Ir]	Additive	b:l[b]	Yields [%][c] 3aa	sp	*ee*[%][d] 3aa
1	OCOOMe	**[Ir]-1**	^{n}Bu$_4$NOAc	19:1	17	32	n.d
2	OCOOMe	**[Ir]-2**	^{n}Bu$_4$NOAc	>20:1	50	33	98
3	OCOOMe	**[Ir]-3**	^{n}Bu$_4$NOAc	17:1	23	55	n.d.
4	OCOOMe	**[Ir]-4**	^{n}Bu$_4$NOAc	>20:1	17	33	n.d.
5	OTroc	**[Ir]-2**	^{n}Bu$_4$NOAc	>20:1	16	20	n.d.
6	OBoc	**[Ir]-2**	^{n}Bu$_4$NOAc	>20:1	97	0	98
7	OPO(OEt)$_2$	**[Ir]-2**	^{n}Bu$_4$NOAc	>20:1	23	-	n.d.
8	OAc	**[Ir]-2**	^{n}Bu$_4$NOAc	>20:1	62	-	>99
9	OPiv	**[Ir]-2**	^{n}Bu$_4$NOAc	>20:1	69	-	99
10	OBz	**[Ir]-2**	^{n}Bu$_4$NOAc	>20:1	96	-	>99
11[e]	OBz	**[Ir]-2**	^{n}Bu$_4$NOAc	>20:1	68	-	>99
12	OBz	**[Ir]-2**	^{n}Bu$_4$NOBz	>20:1	>99 (>99)	-	>99
13	OBoc	**[Ir]-2**	^{n}Bu$_4$NOBz	>20:1	96 (94)	0	98
14	OBz	**[Ir]-2**	none	-	0	-	-

[a]Reaction conditions: **1** (0.20 mmol, 1.0 equiv), **2a** (1.5 equiv), **[Ir]** (3 mol%), additive (3 mol%), THF (0.4 mL), r.t., 12 h. The absolute configuration of **3aa** was assigned by analogy.

[b]The branched/linear selectivities were determined by ^{1}H NMR analysis of the crude mixtures.

[c]Determined by ^{1}H NMR analysis of the crude mixtures with mesitylene as an internal standard. The yields within parentheses are that of the branched isomer and the linear isomer isolated.

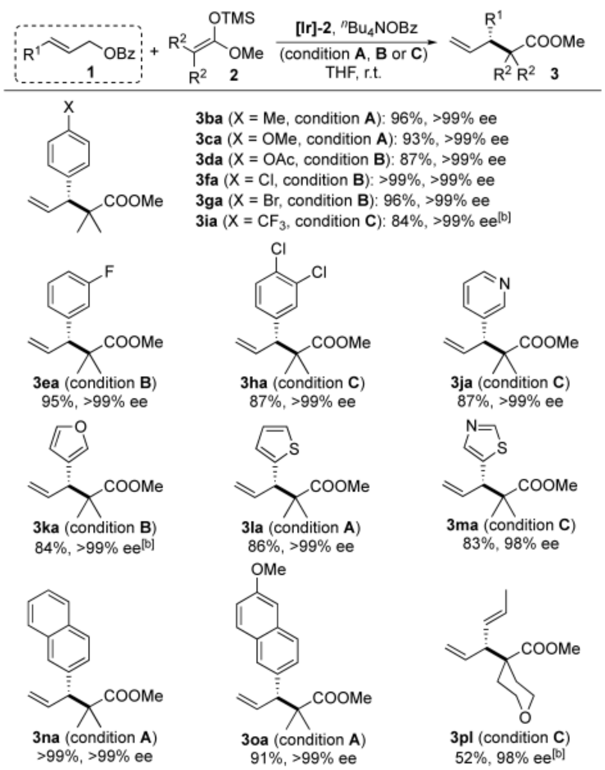
[d]Determined by chiral supercritical fluid chromatography (SFC) analysis of the branched isomer.

[e]0.5 equiv of ^{n}Bu4NOAc was added.

n.d. = not determined.

Table 2

Iridium-catalyzed allylations of silyl ketene acetals: scope of the allyl benzoates.[a]

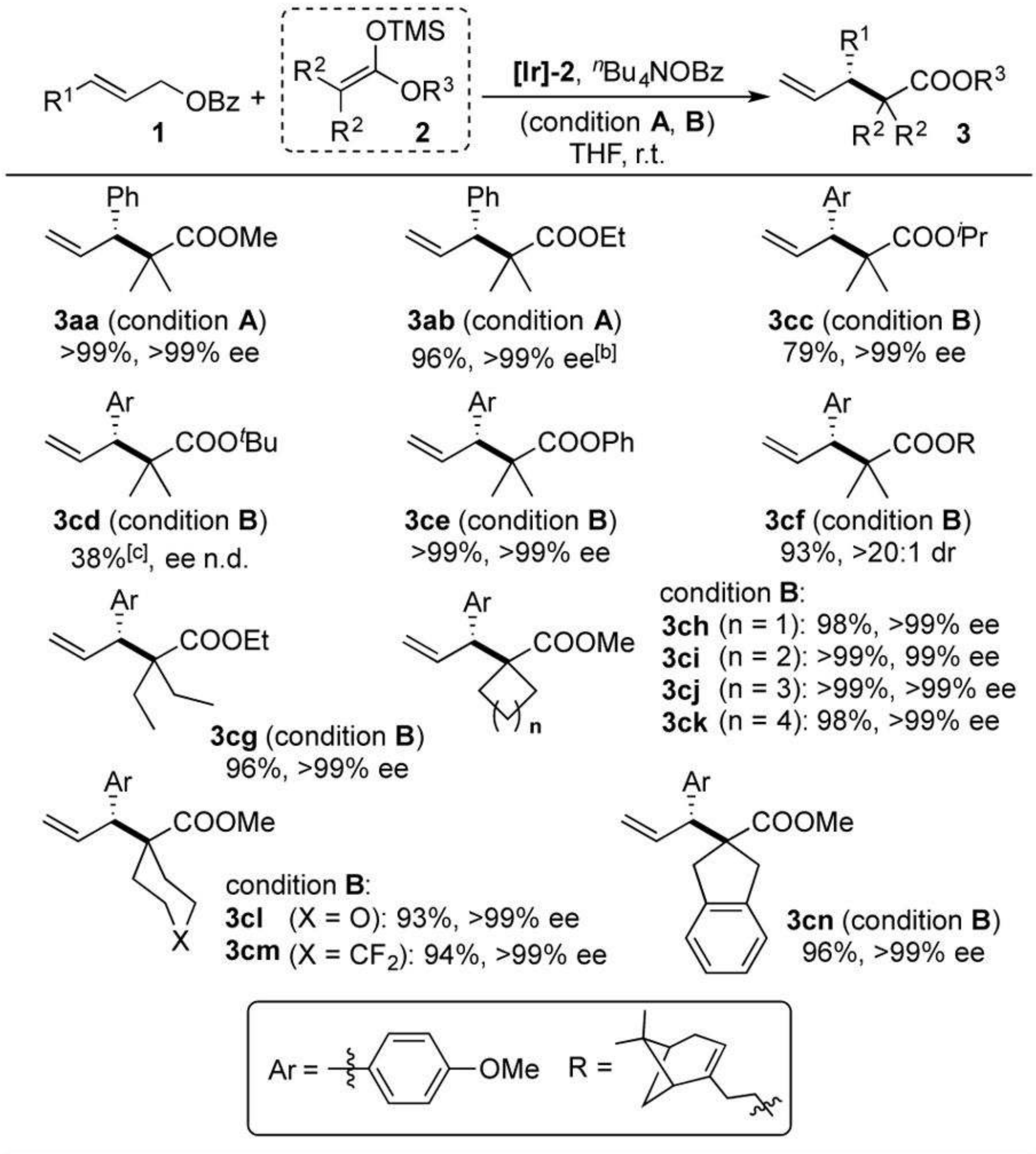


[a]Condition **A:** **[Ir]-2** (3 mol%), $^{n}Bu_4NOBz$ (3 mol%), THF (0.5 M); condition **B:** **[Ir]-2** (4 mol%), $^{n}Bu_4NOBz$ (4 mol%), THF (0.25 M); condition **C:** **[Ir]-2** (3 mol%), $^{n}Bu_4NOBz$ (3 mol%), THF (0.5 M), then another batch of **[Ir]-2** (3 mol%), $^{n}Bu_4NOBz$ (3 mol%) and THF were added after 12 h. The absolute configurations were assigned by analogy.

[b]The enantiomeric excesses were determined after further transformations of the products. See SI for details.

Table 3

Iridium-catalyzed allylations of silyl ketene acetals: scope of the silyl ketene acetals.[a]



[a]Condition **A: [Ir]-2** (3 mol%), ^{n}Bu$_4$NOBz (3 mol%), THF (0.5 M); condition **B: [Ir]-2** (4 mol%), ^{n}Bu$_4$NOBz (4 mol%), THF (0.25 M). The absolute configurations were assigned by analogy.

[b]The enantiomeric excess was determined after further transformation of the product.

[c] NMR yield.