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Iridium-Catalyzed Regio- and Enantioselective Allylic Substitution of Silyl Dienolates Derived from Dioxinones

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Abstract

We report Ir-catalyzed, regio- and enantioselective allylic substitution reactions of unstabilized silyl dienolates derived from dioxinones. Asymmetric allylic substitution of a variety of allylic trichloroethyl carbonates with these silyl dienolates gave γ-allylated products selectively in 60–84% yield and 90–98% ee.

Keywords

Ir-catalyzed asymmetric allylic substitution; Silyl dienolates; Dioxinones; γ-Selective asymmetric alkylation

The alkylation of 1,3-dicarbonyl compounds (e.g. **A**) is a classic reaction in organic chemistry. Because the α-position contains the most acidic proton, electrophiles add to this site in the presence of a base to give product **B**. This fundamental reactivity has been translated to one of the most commonly studied reactions of organometallic catalysis for organic synthesis – asymmetric allylic substitution of soft, stabilized, anionic carbon nucleophiles.[1,2]

Alkylations of β-keto esters **D** to form the isomeric γ-alkylated products **E** are also classic reactions in organic chemistry.[3] These reactions occur in the presence of a base that is strong enough to doubly deprotonate the dicarbonyl compounds; electrophiles then add to the most nucleophilic γ-position with high regioselectivity. Despite the value of the γ-alkylation reaction, catalytic asymmetric allylations of 1,3-dicarbonyl compounds **D** at the γ-position have not been reported. The products **F** in Figure 1 of such allylations are highly versatile synthetic intermediates [4] because they contain three functional groups: an alkene, an ester, and a ketone carbonyl group.

Silyl dienolates (**2**) are synthetically equivalent to β-keto ester dianions.[5a–c] After the formation of a new carbon-carbon bond at the γ-position, the dioxinone moiety in the product (e.g. **3**) can be induced to extrude acetone to generate an acyl ketene intermediate. This intermediate can then be trapped with alcohols to give β-keto esters. As shown by Sato,

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Carreira and Evans, silyl dienolates **2** undergo enantioselective aldol reactions with aldehydes to provide γ-addition products with high regioselectivity;[5d–h] however, these reagents have not undergone catalytic enantioselective reactions with alkyl or allyl electrophiles.

Here, were port Ir-catalyzed enantioselective allylic substitution reactions [6–9] of silyl dienolates **2** derived from dioxinones with trichloroethyl (Troc) allylic carbonates that occur in good yields with high γ-selectivities, enantioselectivities, and branched-to-linear selectivities (Figure 1). This reaction sets the stereogenic center at the electrophilic carbon atom and is the equivalent of γ-selective, asymmetric alkylations of β-keto esters; the dioxinone moiety in these products can be transformed to a variety of functional groups, while preserving the enantiomeric excess of the product. The key to achieving highly enantioselective and γ-selective alkylations is the combination of a dioxinone as an equivalent of the β-keto ester, a Troc ester of the allylic alcohol as the electrophile, and a chiral, nonracemic phosphoramidite ligand on iridium.

We began our studies on the allylic substitution reaction with silyl dienolate **2a** under the conditions we have developed for the asymmetric allylation with α,β-unsaturated ketones.[9i] Although Mayr and co-workers have determined that the π-nucleophilicity at the α-position of dienolates **2** is much weaker than that at the γ-position,[10] there are cases in which the nucleophilic addition occurred at the α position selectively.[11] Therefore, to identify an appropriate allylic electrophile for the reaction, several cinnamyl alcohol derivatives were synthesized and asymmetric allylic substitution reactions of these derivatives with dienolate **2a** were examined.

As shown in Table 1, treatment of the cinnamyl acetate (1 equiv) and silyl dienolate **2a** (2 equiv) with 2 mol % $[Ir(cod)Cl]_2$ and 4 mol % (S_a,S_c,S_c)-**L** in the presence of KF(1 equiv) and 18-crown-6 (1 equiv) at 50 °C for 24 h provided a 2:1 mixture of γ-substituted product **3a** and α-substituted product **4a** in 53% and 28% yield, respectively (entry 1, Table 1). When the cinnamyl acetate was replaced with the cinnamyl benzoate, a 1:1 mixture of **3a** (36% yield) and **4a** was obtained (entry 2, Table 1). Because prolonged heating (24 h) was required for the full conversion of these cinnamyl esters, further investigation of the reaction was conducted with more reactive cinnamyl phosphates and carbonates as the electrophile. When the ethyl cinnamyl phosphate was employed in the reaction, the consumption of the starting phosphate was complete in 12 h at 50 °C. But no improvement of the regioselectivity was achieved (entry 3, Table 1). The allylation reaction of the *t*-butyl cinnamyl carbonate with **2a** also gave a 1:1 mixture of **3a** (41% yield) and **4a** (entry 4, Table 1). However, when the methyl cinnamyl carbonate was utilized, a 6:1 mixture of **3a** and **4a** was obtained with **3a** as the major isomer in 62% yield and 96% ee (entry 5, Table 1). Finally, the allylic substitution of the trichloroethyl cinnamyl carbonate with silyl dienolate **2a** provided a 10:1 mixture of **3a** and **4a** (entry 6, Table 1). γ-Allylated product **3a** was obtained in 74% yield and 97% ee after purification.

Table 2 summarizes the scope of allylic carbonate **1** that undergoes the asymmetricallylation with silyl dienolate **2a** under the developed conditions. In general, allylic substitution of a variety of substituted cinnamyl carbonates with **2a** gave the allylation products **3a–i** in good

yields with high enantioselectivities and γ–selectivities, although in cases of **3d** and **3f**, moderate γ/α–selectivities were observed. Alkenyl- and alkyl-substituted allylic carbonates also reacted to provide the allylated products **3j–k** in 63–69% yield with 9–12:1 γ–selectivity. Allylation of the allylic carbonate containing a heterocyclic indolyl group gave product **3l** in 71% yield with excellent γ–selectivity. In all cases, the allylated products were obtained with ≥90% ee and >20:1 branched-to-linear selectivities.

Allylic substitution reactions with silyl dienolate **2b** were examined next. With a methyl substituent at the α-position in **2b**, we anticipated that the asymmetric allylation of allylic esters with **2b** should proceed with high γ-selectivity. Indeed, when the reaction was performed with the cinnamyl acetate and silyl dienolate **2b** under standard conditions, γ–substituted product **5a** was obtained in 60% yield with >20:1 γ–selectivity. However, a significant amount of linear product **6a** (21%) was also isolated (entry 1, Table 3). Because high branched-to-linear selectivities (>20:1) were observed in the allylic substitution reactions with silyl dienolate **2a** (Tables 1 and 2), we expected that reactions with dienolate **2b** should proceed with comparable b/l selectivities. The unexpected low branched-to-linear selectivity presumably resulted from the steric interaction because nucleophile **2b** is sterically more hindered than **2a**.

To address the low branched-to-linear selectivity issue, allylation reactions of a variety of cinnamyl alcohol derivatives with silyl dienolate **2b** were explored. The reaction of the cinnamyl benzoate with **2b** only gave a 2:1 mixture of **5a** (54% yield) and **6a** (entry 2, Table 3). The branched-to-linear selectivity decreased to 1:1 in the reaction of the ethyl cinnamyl phosphate with **2b** (entry 3, Table 3). The reaction of the *t*-butyl cinnamyl carbonate with **2b** provided a 2.5:1 mixture of **5a** (56% yield) and **6a** (entry 4, Table 3). The b/l selectivity was improved to 4:1 when the methyl cinnamyl carbonate was utilized (entry 5, Table 1). Finally, with the trichloroethyl cinnamyl carbonate, again, as the electrophile, the allylic substitution with **2b** provided **5a** in 81% yield, 90% ee and a 15:1 branched to linear selectivity (entry 6, Table 3).

Table 4 summarizes the results of the asymmetric allylation of silyl dienolate **2b** with allylic carbonates **1**. A wide range of allylic troc ester sreadily participated in the reaction to give allylated products in good yields with high enantioselectivities and branched-to-linear selectivities. Allylation of **2b** with substituted cinnamyl carbonates afforded products **5a–g** in 66–81% yield with 90–98% ee and 12–16:1 branched-to-linear product ratios. Reactions of alkenyl- and alkyl-substituted allylic carbonates gave products **5h–i** in 60–78% yields with 90–92% ee and 18–20:1 branched selectivities. The allylic carbonate with an indolyl group also reacted to provide product **5j** in 84% yield with 90% ee and an excellent branched selectivity. In all cases, detectable amounts of α-allylated products were not formed from these reactions. The absolute configuration of allylation product **5j** was determined by single crystal X-ray diffraction.

A series of experiments evaluating the influence of the ligand and leaving group on the regioselectivity of the reaction is shown in Scheme 1. No allylation reaction of cinnamyl carbonate **1a** with silyl dienolate **2a** or **2b** was observed in the absence of $[Ir(cod)Cl]_2$ and (S_a,S_C,S_C)-**L** (panel a, Scheme 1). However, $[Ir(cod)Cl]_2$ does catalyze the allylic

substitution of **1a** with dienolate **2a** or **2b** without the added phosphoramidite ligand. As shown in panel b of Scheme 1, the allylation of carbonate **1a** with silyl dienolate **2a** at 50 °C for 12 h gave a 2:1 mixture (±)-**3a** and **4a** in 55% combined yield in the presence of 2 mol % $[Ir(cod)Cl]_2$, KF (1 equiv) and 18-crown-6 (1 equiv). Under the identical reaction conditions, the reaction of **1a** with **2b** gave a 1:1 mixture of (±)-**5a** and **6a**. However, the same reactions conducted with the catalyst generated from [Ir(cod) Cl_2 and the phosphoramidite ligand (S_a,S_C,S_C)-**L** occurred with much higher regioselectivity (in the case of **2a**) and branched-to-linear selectivity (in the case of **2b**) (panel c, Scheme 1). These data show that the identity of the leaving group of the allylic electrophile alone does not control the site selectivities of these reactions. Instead, the combination of the phosphoramidite ligand **L** and the leaving group of the allylic electrophile is crucial to obtaining high regioselectivity at the nucleophiles and high branched to linear selectivity at the electrophile.

The dioxinone moiety is a useful precursor to a variety of functional groups.[12] To demonstrate the synthetic utility of our asymmetric allylations of dioxinones, a number of transformations of compound **3a** were conducted. As illustrated in Scheme 2, treatment of **3a** with K_2CO_3 and MeOH at ambient temperature gave β-keto ester **7** in 95% yield. The reaction of **3a** with butanol at 120 °C for 2 h gave butyl ester **8** in 78% yield. Likewise, treatment of **3a** with benzyl amine under the same reaction conditions produced β-keto amide **9** in 76% yield.

In addition to serving as a masked β-keto ester, the dioxinone moiety in **3a** can be utilized for the synthesis of heterocycles, such as tetramic acids. These heterocyclic compounds are important pharmacophores in agrochemicals as well as pharmaceutical agents.[13] Treatment of **3a** with *N*-benzyl-glycine ethyl ester at 130 °C for 2 h provided the corresponding amide, which underwent subsequent Dieckmann cyclization under basic conditions to give tetramic acid **10** in 71% yield (two steps). The reaction of compound **3a** with phenyl isocyanate at 130 °C afforded 1,3-oxazin-2,4-dione **11** in 78% yield.

In conclusion, we have developed an Ir-catalyzed γ-selective asymmetric allylation of silyl dienolates derived from dioxinones. By utilizing the silyl dienolate as the synthetic equivalent of the β-keto ester dianion, the inherent α-selectivity of β-keto esters was inverted to the γ-selectivity. Under the developed reaction conditions, asymmetric allylic substitution of a variety of allylic trichloroethyl carbonates with silyl dienolates gave γ-allylated products in 60–84% yield and 90–98% ee with high γ-selectivity and branched-to-linear selectivity. The control experiments revealed that the nature of the leaving group of allylic electrophiles in combination with the added chiral phosphoramidite ligand is key to the high regioselectivity and branched-to-linear selectivity of the reaction. Further studies of silyl dienolates are currently underway in this laboratory.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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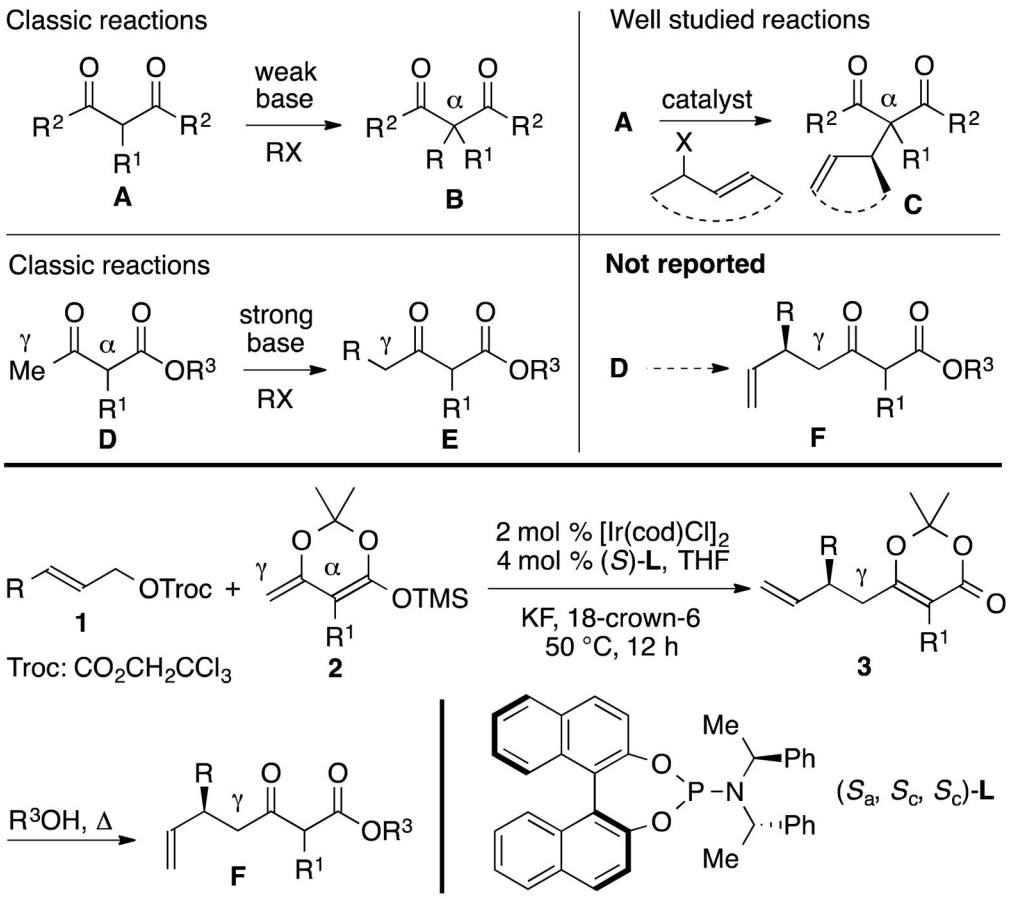
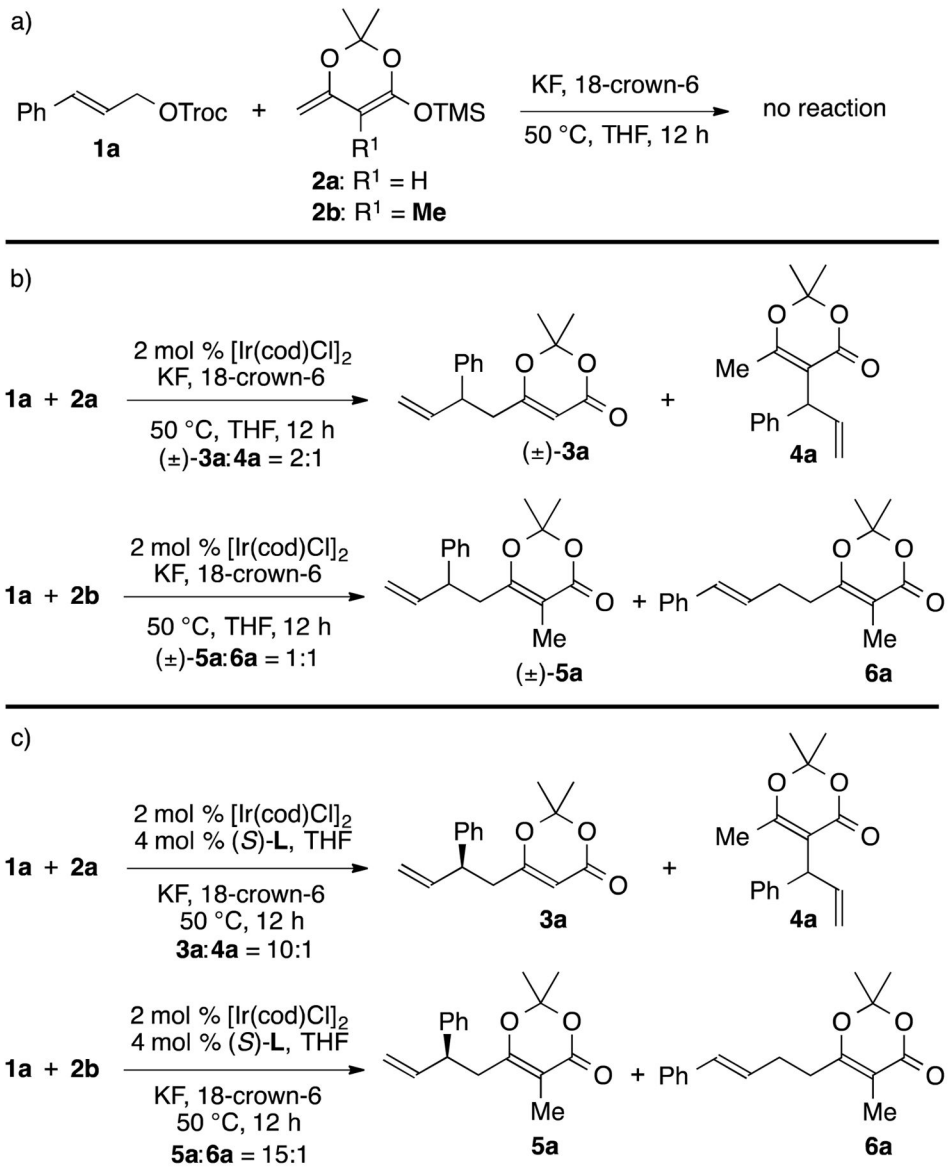
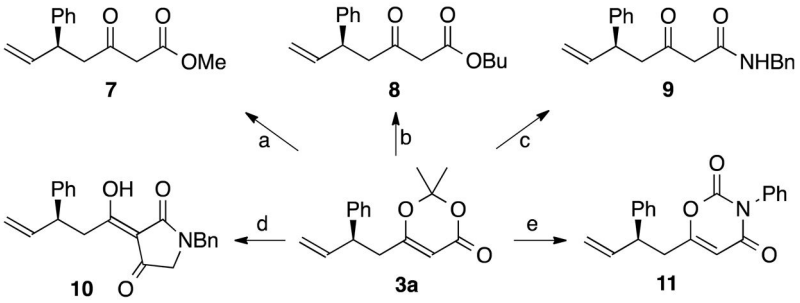


Figure 1.
Ir-catalyzed Regio- and Enantioselective Allylic Substitution with Silyl Dienolates



Scheme 1.
Comparison of the Results of Control Experiments

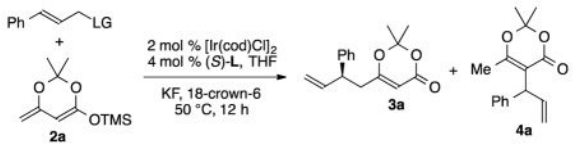


Scheme 2.

Derivatization of **3a**: (a) K_2CO_3, MeOH, rt, 95**%**. (b) BuOH, toluene, 120 °C, 2 h, 78%. (c) $BnNH_2$, toluene, 120 °C, 2 h, 76%. (d) i, *N*-Benzyl-glycine ethyl ester, toluene, 130 °C, ii, KO*t*-Bu, THF, rt, 71% over two steps. (e) phenyl isocyanate, 130 °C, 4 h, 78%.

Table 1

Evaluation of the Allylic Electrophile for the Ir-Catalyzed Asymmetric Allylic Substitution with Silyl Dienolate **2a**.[a]



entry	LG	γ:α (3a:4a)[b]	yield (3a)[c]	% ee (3a)[d]
1	OCOMe[e]	2:1	53%	N.D.
2	OCOPh[e]	1:1	36%	N.D.
3	$OP(O)(OEt)_2$	1:1	38%	N.D.
4	OCO_2t-Bu	1:1	41%	N.D.
5	OCO_2Me	6:1	62%	96%
6	$OCO_2CH_2CCl_3$	10:1	74%	97%

[a]Reaction conditions: cinnamyl ester (0.2 mmol, 1.0 equiv), silyl dienolate **2a** (0.4 mmol, 2.0 equiv), $[Ir(cod)Cl]_2$ (2 mol %), (S_a,S_C,S_C)-**L** (4 mol %), KF (1.0 equiv), 18-crown-6 (1.0 equiv), THF (0.4 mL), 50 °C, 12 h.

[b]Ratios of γ to α-substitution (**3a:4a**) were determined by ^{1}H NMR analysis of the crude reaction mixtures.

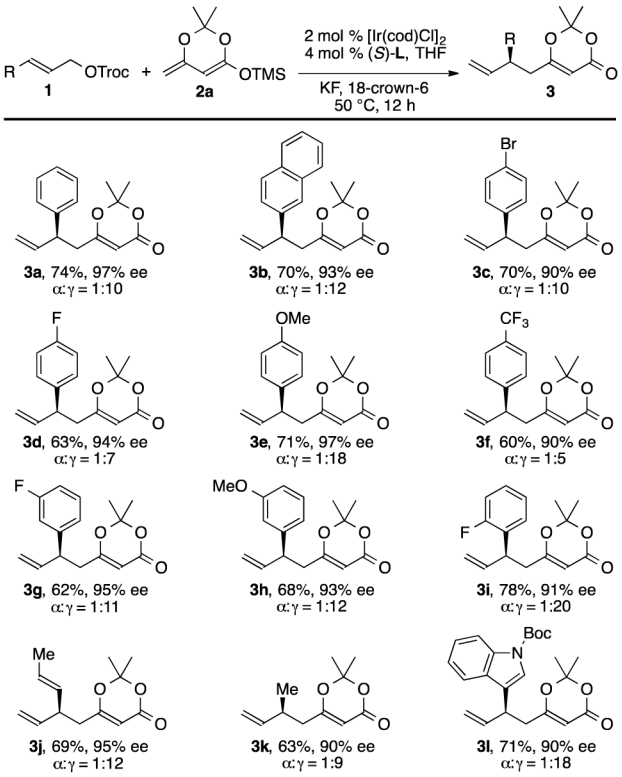
[c]Yields of isolated products were listed.

[d]The ee was determined by chiral HPLC analysis. N.D. = Not determined.

[e]Reactions were carried out at 50 °C for 24 h.

Table 2

Scope of the Ir-catalyzed Asymmetric Allylic Substitution of Trichloroethyl Allylic Carbonates **1** with Silyl Dienolate **2a**.[a–e]



[a]Reaction conditions: allylic carbonate **1** (0.2 mmol, 1.0 equiv), silyl dienolate **2a** (0.4 mmol, 2.0 equiv), $[Ir(cod)Cl]_2$ (2 mol%), (S_a,S_C,S_C)-**L** (4 mol%), KF (1.0 equiv), 18-crown-6 (1.0 equiv), THF (0.4 mL), 50 °C, 12 h.

[b]The ee was determined by chiral HPLC analysis.

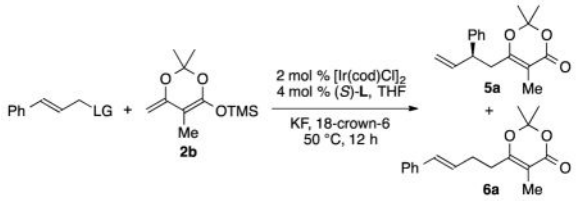
[c]Ratios of γ to α-substitution were determined by ^{1}H NMR analysis of the crude reaction mixtures.

[d]Yields of isolated products were listed (the average of at least two runs).

[e]OTroc: $OCO_2CH_2CCl_3$.

Table 3

Evaluation of the Allylic Electrophile for the Ir-Catalyzed Asymmetric Allylic Substitution with Dienolate **2b**.[a]



entry	LG	b:l (5a:6a)[b]	yield (5a)[c]	% ee (5a)[d]
1	OCOMe[e]	2:5:1	60%	N.D.
2	OCOPh[e]	2:1	54%	N.D.
3	$OP(O)(OEt)_2$	1:1	41%	N.D.
4	OCO_2t-Bu	2:5:1	56%	N.D.
5	OCO_2Me	4:1	67%	N.D.
6	$OCO_2CH_2CCl_3$	15:1	81%	90%

[a] Reaction conditions: cinnamyl ester (0.2 mmol, 1.0 equiv), silyl dienolate **2b** (0.4 mmol, 2.0 equiv), $[Ir(cod)Cl]_2$ (2 mol%), (S_a,S_C,S_C)-**L** (4 mol %), KF (1.0 equiv), 18-crown-6 (1.0 equiv), THF (0.4 mL), 50 °C, 12 h.

[b] Branched to linear ratios (**5a:6a**) were determined by ^{1}H NMR analysis of the crude reaction mixtures.

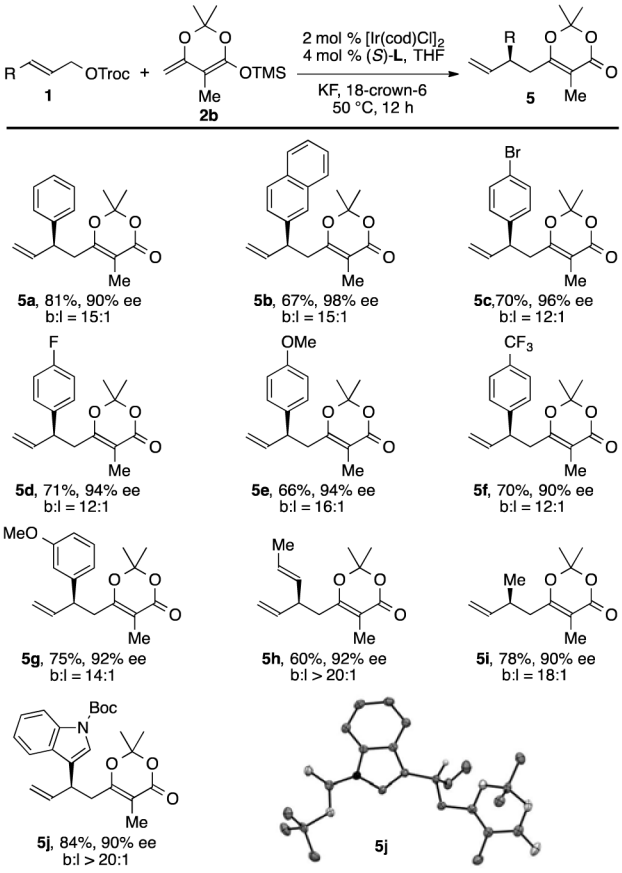
[c] Yields of isolated products were listed.

[d] The ee was determined by chiral HPLC analysis. N.D. = Not determined.

[e] Reactions were carried out at 50 °C for 24 h.

Table 4

Scope of the Ir-Catalyzed Asymmetric Allylic Substitution of Trichloroethyl Allylic Carbonates **1** with Silyl Dienolate **2b**.



[a] Reaction conditions: allylic carbonate **1** (0.2 mmol, 1.0 equiv), silyl dienolate **2b** (0.4 mmol, 2.0 equiv), $[Ir(cod)Cl]_2$ (2 mol%), (S_a,S_C,S_C)-**L** (4 mol%), KF (1.0 equiv), 18-crown-6 (1.0 equiv), THF (0.4 mL), 50 °C, 12 h.

[b] The ee was determined by chiral HPLC analysis.

[c] Branched to linear ratios (b:l) were determined by ^{1}H NMR analysis of the crude reaction mixtures.

[d] Yields of isolated products were listed (the average of at least two runs).

[e] OTroc: $OCO_2CH_2CCl_3$.