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Iridium-Catalyzed Regioselective and Enantioselective Allylation of Trimethylsiloxyfuran

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Supporting Information

ABSTRACT: We report the regio- and enantioselective allylation of an ester enolate, trimethylsiloxyfuran. This enolate reacts at the 3-position with linear aromatic allylic carbonates or aliphatic allylic benzoates to form the branched substitution products in the presence of a metallacyclic iridium catalyst. This process provides access to synthetically important 3-substituted butenolides in enantioenriched form. Stoichiometric reactions of the allyliridium intermediate suggest that the trimethylsiloxyfuran is activated by the carboxylate leaving group.

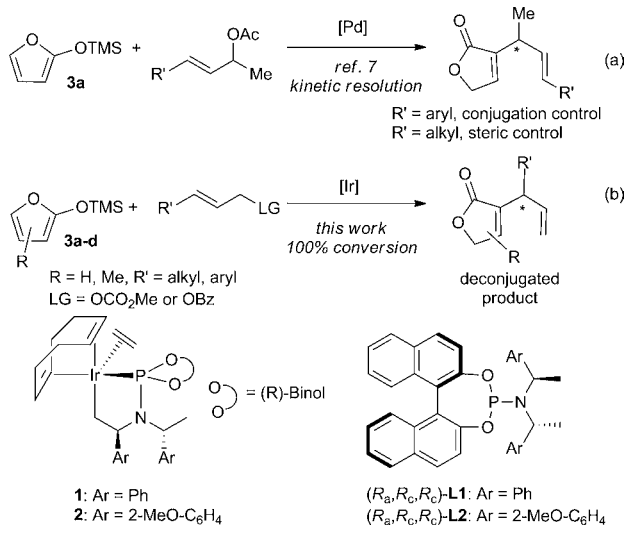
Asymmetric allylic substitution catalyzed by metallacyclic iridium phosphoramidite complexes **1** and **2**[1] forms enantioenriched materials from readily available allylic esters and a variety of heteroatom[2] and carbon[3] nucleophiles. However, the carbon nucleophiles that undergo this process are mainly stabilized enolates.[3a−h] Reactions of unstabilized enolates[3i−k] have been limited to those derived from methyl ketones. Enolates of esters that undergo iridium-catalyzed allylic substitutions possess a second electron-withdrawing group (EWG) to stabilize the enolate.

Trimethylsiloxyfuran **3a** is an important ester enolate because it can be used to construct butenolides, a motif found in over 13 000 natural products.[4] High diastereo- and enantioselectivity has been achieved by the addition of **3a** to carbonyl acceptors with Lewis acid or organic catalysts.[4a,5] These reactions occurred at C-5 of **3a**. Regioselective reactions at C-3 of **3a** to form enantioenriched, 3-substituted butenolides are rare.[6]

One set of palladium-catalyzed kinetic resolutions of methyl-substituted allylic acetate with trimethylsiloxyfuran does occur at C-3 of nucleophile **3a** (Scheme 1a).[7] In this case, the regioselectivity at the electrophile was controlled by the properties of the substrate: attack at the less hindered end of the allyl unit led to the conjugated product.[8,9] This origin of the regioselectivity restricts the scope of electrophiles that give one major product. Moreover, the reactions were limited to the unsubstituted trimethylsiloxyfuran. Asymmetric reactions with catalysts based on other metals could provide complementary selectivities to these palladium-catalyzed reactions. However, asymmetric allylic substitutions catalyzed by complexes of other metals with ester enolates lacking a second EWG have not been reported.

We report an iridium-catalyzed allylic substitution between trimethylsiloxyfuran and prochiral electrophiles to form enantioenriched 3-substituted butenolides with high regioselectivity for the more hindered product (Scheme 1b), including formation of the deconjugated product from reactions of cinnamyl carbonates. The process furnishes 3-substituted butenolides containing an easily functionalized terminal double bond and various aryl and alkyl groups at the stereogenic center. In addition to providing useful butenolides, this process begins to address the challenge of conducting allylic substitution with ester enolates.

Scheme 1. Pd- and Ir-Catalyzed Allylic Substitution with Trimethylsiloxyfuran



Our initial studies focused on the reaction of trimethylsiloxyfuran **3a** with cinnamyl carbonate **4a**. Table 1 summarizes the effect of several parameters on this reaction. Reactions catalyzed by complexes **1** and **2** with CsF to activate the silyl enolate formed the 3-allylated product **5a** regioselectively.[10,11] The reaction with catalyst **2** occurred in higher yield than the reaction with catalyst **1** (entries 1 and 2). Further assessment of fluoride activators showed that reactions conducted with ZnF_2 gave the desired product **5a** in a high 85% isolated yield with 99% ee (entry 3). The reactions with soluble fluoride salts such as tetrabutylammonium fluoride (TBAF) and tetrabutylammonium triphenyldifluorosilicate (TBAT) gave only trace amounts of the desired product (entries 4 and 5). To our surprise, this reaction also proceeded to completion without any additives, although higher catalyst loadings were needed in this case

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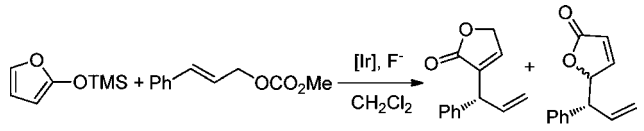
Table 1. Effect of the Catalyst and Fluoride Source on the Ir-Catalyzed Allylic Substitution of Trimethylsiloxyfuran[a]



3a 4a 5a 6a

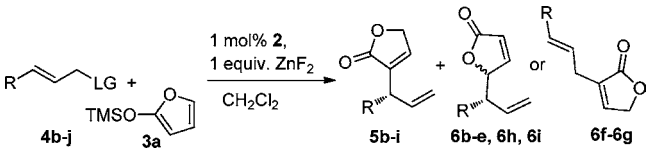
entry	cat.[b]	fluoride	yield (%)[c]	5a:6a[d]	ee (%)[e]
1	**1**	CsF	13	–	–
2	**2**	CsF	32	20:1	99
3	**2**	ZnF_2	87 (85)	20:1	99
4[f]	**2**	TBAF	trace	–	–
5	**2**	TBAT	trace	–	–
6	**2**	none	40	20:1	99
7[g]	**2**	none	89	20:1	99

[a]See the Supporting Information (SI) for experimental details. [b]1 mol % Ir catalyst was used, unless otherwise noted. [c]Determined by ^{1}H NMR analysis with mesitylene as the internal standard. The value in parentheses corresponds to the isolated yield. [d]Determined by ^{1}H NMR analysis of the crude reaction mixtures. [e]Determined by chiral HPLC analysis. [f]1-Phenylallyl alcohol was formed in 69% yield. [g]2 mol % Ir catalyst was used.

(entries 6 and 7). This final observation is consistent with the studies of stoichiometric reactions of catalytic intermediates in the absence of additives described later in this paper.

The scope of the Ir-catalyzed asymmetric allylation of trimethylsiloxyfuran in the presence of ZnF_2 is summarized in Table 2. The reaction of electron-rich 4-methoxycinnamyl

Table 2. Ir-Catalyzed Allylic Substitution of Trimethylsiloxyfuran 3a[a]



4b-j 3a 5b-i 6b-e, 6h, 6i 6f-6g

entry	R (4)	LG	yield (%)[b]	5/6[c]	ee (%)[d]
1	4-MeOC_6H_4 (**4b**)	OCO_2Me	**5b**, 70	20:1	98
2	4-FC_6H_4 (**4c**)	OCO_2Me	**5c**, 83	20:1	95
3	4-ClC_6H_4 (**4d**)	OCO_2Me	**5d**, 78	20:1	97
4[e]	3-FC_6H_4 (**4e**)	OCO_2Me	**5e**, 91	20:1	97
5[f]	*n*-propyl (**4f**)	OCO_2Me	**5f**, 18	10:1	99
6[fg]	*n*-propyl (**4g**)	OBz	**5f**, 80	10:1	96
7[fg]	methyl (**4h**)	OBz	**5g**, 71	10:1	97
8[g]	cyclohexyl (**4i**)	OBz	**5h**, 60	8:1	94
9	1-propenyl (**4j**)	OCO_2Me	**5i**, 90	1:1	–
10[h]	1-propenyl (**4j**)	OCO_2Me	**5i**, 83	3:1	99

[a]See the SI for experimental details. [b]Isolated yields. [c]Determined by ^{1}H NMR analysis of the crude reaction mixtures. [d]Determined by chiral HPLC analysis. [e]2 mol % Ir catalyst **2** was used. [f]The products **6** are 3-substituted linear products. [g]The reaction was conducted with 3 mol % Ir catalyst **2** at 50 °C. [h]2 mol % $[(dbcot)IrCl]_2$ was used.

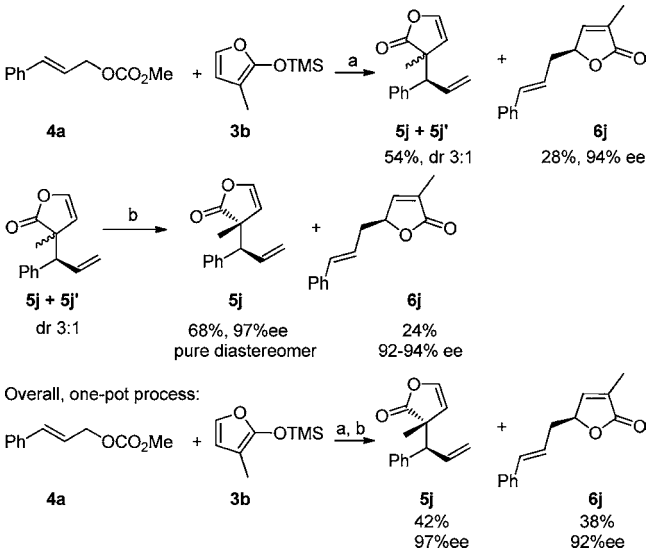
carbonate **4b** afforded the desired substitution product in good yield with exceptional enantioselectivity and high regioselectivity. The reactions of electron-poor substrates **4c–e** furnished the corresponding products in high yields with excellent regio- and enantioselectivities, although 3-substituted cinnamyl carbonate **4e** required a 2 mol % catalyst loading for full conversion.

Reactions of aliphatic allylic electrophiles occurred with some changes to the reaction conditions. Propyl-substituted allylic carbonate **4f** gave only an 18% yield of branched product **5f** with a 10:1 ratio of **5f** to the linear product **6f** (Table 2, entry 5). However, the reaction of the corresponding aliphatic allylic benzoate **4g** gave the branched allylation product **5f** in good yield and regioselectivity (10:1) with high enantioselectivity (entry 6) in the presence of 3 mol % catalyst **2** at 50 °C.

These conditions were suitable for a range of aliphatic benzoates. For example, crotyl substrate **4h** reacted to give the substitution product in 71% yield with excellent enantioselectivity (Table 2, entry 7). Furthermore, the branched product formed selectively, even when the aliphatic substituent was branched at the carbon adjacent to the allyl unit (entry 8). The allylic substitution of dienyl benzoate **4j** with catalyst **2** yielded the product as a 1:1 mixture of constitutional isomers (entry 9) but occurred with moderate regioselectivity and high enantioselectivity when dibenzo[*a*,*e*]cyclooctatetraene (DBCOT) was used as the supporting ligand instead of cyclooctadiene (COD) (entry 10).[2d]

The reactions of 3-, 4-, and 5-methyl-substituted trimethylsiloxyfurans **3b–d** revealed the effect of furanyl substituents on the catalytic process. The reaction of **3b** gave two products (Scheme 2). The 5-substituted linear product **6j** was isolated in

Scheme 2. Ir-Catalyzed Allylic Substitution with 3-Methyl-Substituted Trimethylsiloxyfuran[a]



[a](a) 2 mol % (*S*,*S*,*S*)-**2**, ZnF_2, CH_2Cl_2, 12 h; (b) 40 °C, CH_2Cl_2, 1 h.

28% yield with 94% ee, and the 3-substituted product was obtained as an inseparable mixture of diastereomers **5j** and **5j′**. Heating the mixture of diastereomers in dichloromethane at 40 °C for 1 h led to a single diastereomer **5j** containing adjacent quaternary and tertiary stereogenic centers along with linear product **6j**, which formed by a Cope rearrangement of one of the diastereomers.[12] Thus, the 3-substituted product **5j** was ultimately isolated as a single diastereomer in 97% ee by a one-pot process involving asymmetric allylation and Cope rearrangement (Scheme 2 bottom).[13]

The reaction of **3c** with **4a** in the presence of the catalyst (*S*,*S*,*S*)-**2** also gave products from allylic substitution (Scheme 3). The reaction of **3c** produced the 3-substituted product (consisting of the double-bond isomers **5k** and **5k′**) in 47%

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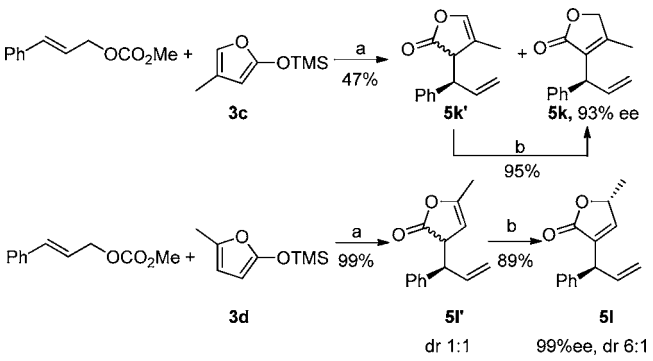
Scheme 3. Ir-Catalyzed Allylic Substitution with 4- and 5-Methyl-Substituted Trimethylsiloxyfurans[a]

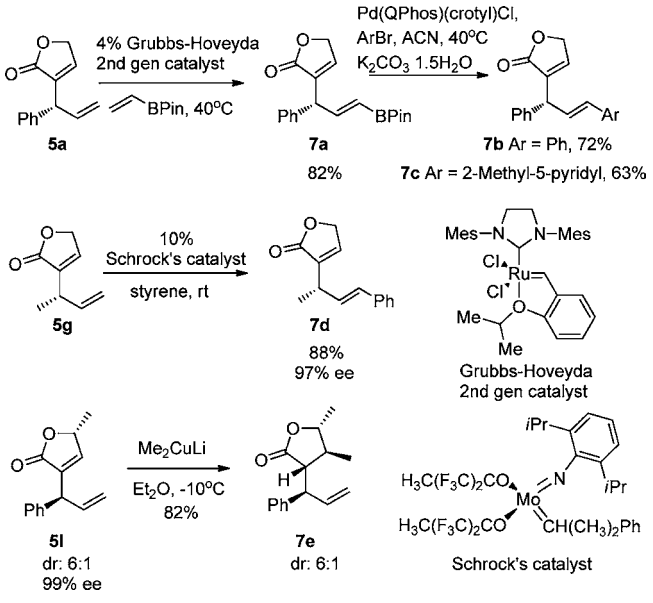


[a](a) 2 mol % (*S,S,S*)-**2**, ZnF_2, CH_2Cl_2, 12 h; (b) 20 mol % *O*-desmethylquinine, CH_2Cl_2, 12 h.

yield and the undesired 5-substituted product in 38% yield. We were able to convert isomer **5k′** to isomer **5k** with a catalytic amount of *O*-desmethylquinine under mild conditions.[14] Thus, the overall process furnished the 3-substituted product **5k** in 45% yield with 93% ee. Likewise, the reaction of **3d** gave disubstituted butenolides **5l** in an overall 88% yield with 6:1 diastereoselectivity and 99% ee after isomerization of the diastereomeric mixture of **5l′** to isomer **5l** in the presence of *O*-desmethylquinine.[14]

The products of these substitutions contained two double bonds that underwent further functionalizations (Scheme 4). For example, the terminal double bond of **5a** underwent cross-metathesis with vinyl boronate[15] in the presence of the Grubbs–Hoveyda second-generation catalyst.[16] The resulting vinyl boronate **7a** underwent Suzuki–Miyaura coupling with bromobenzene or 5-bromo-2-methylpyridine to yield **7b** or **7c** in the presence of Pd(Qphos)(crotyl)Cl. Compound **5g** was converted to **7d** by a cross-metathesis with styrene catalyzed by Schrock's catalyst.[17] In addition, the electron-deficient double bond in **5l** served as a site for conjugate additions.[18] Me_2CuLi reacted with **5l** to furnish product **7e** containing four contiguous stereogenic centers.

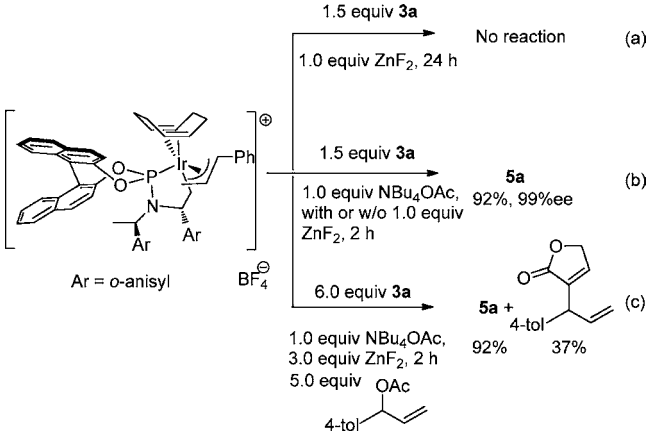
Scheme 4. Derivatization of the Butenolide Products[a]



[a]See the SI for experimental details. All yields reported here are isolated yields. Diastereomeric ratios were determined from ^{1}H NMR spectra of the crude reaction mixtures; ee was determined by chiral HPLC analysis.

Stoichiometric reactions were conducted with the Ir–allyl complex[19] to gain insight into the mode of addition and the effect of additives on this addition step. The isolated Ir–allyl complex did not react with 1.5 equiv of trimethylsiloxyfuran in the presence of ZnF_2 alone (Scheme 5a).[20] However, the

Scheme 5. Stoichiometric Reactions of the Cinnamyl Iridium Intermediate with Trimethylsiloxyfuran



iridium complex reacted immediately in the presence of 1.0 equiv of NBu_4OAc with or without ZnF_2 to form the product **5a** in 92% yield with 99% ee and the same absolute configuration as the product of the catalytic reaction (Scheme 5b). This observation suggests that the carbonate or benzoate generated in situ in the catalytic reaction activates the siloxyfuran. The *R* absolute configuration of the product of this stoichiometric reaction implies that nucleophilic attack occurs at the face anti to the iridium fragment.

To determine whether the acetate anion activated the trimethylsiloxyfuran directly or reacted with the Ir–allyl complex to release an allylic acetate that reacted in a subsequent catalytic process, the reaction of the Ir–allyl complex with trimethylsiloxyfuran **3a** was conducted in the presence of 5.0 equiv of *p*-tolyl allylic acetate (Scheme 5c). If the acetate anion were to lead to the release of the free allylic acetate, little product from the allyl group on iridium would be observed in the presence of excess tolyl-substituted allylic acetate. In the event, the reaction of the Ir–allyl complex in the presence of excess of tolyl-substituted acetate formed phenyl-substituted product **5a** in 92% yield (the *p*-tolyl product formed in only 37% yield based on *p*-tolyl allylic acetate). This yield of phenyl-substituted product **5a** was the same as that formed in the absence of *p*-tolyl allylic acetate, and the yield of **5a** was much higher than that of *p*-tolyl-substituted product. These observations suggest that the trimethylsiloxyfuran reacts directly with the Ir–allyl complex when activated by a carboxylate, not by initial release of an allylic ester.

In summary, we have reported an iridium-catalyzed asymmetric allylic substitution reaction with a silyl ketene acetal. The reactions between a variety of aromatic and aliphatic allylic carbonates or benzoates and trimethylsiloxyfuran proceeded smoothly to furnish 3-substituted butenolides with

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excellent regio- and enantioselectivity. Moreover, methyl-substituted trimethylsiloxyfurans react regioselectively to form enantioenriched products. These allylation products can be converted to an array of organic building blocks by reactions at one or the other of the alkene units of the product. Stoichiometric reactions of the Ir–allyl intermediate implied that the reaction proceeds by anti attack on the coordinated allyl ligand, as reported previously for iridium-catalyzed allylic substitution with carbon and heteroatom nucleophiles,[19a] but that the siloxyfuran is activated by coordination of the carboxylate leaving group. Further studies to expand the scope of the reaction to encompass additional silyl ketene acetals are underway in this laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(9) Consistent with this origin of the regioselectivity, we found that the palladium-catalyzed reaction of cinnamyl acetate with **3a** failed to deliver the desired product **5a**. Instead, a mixture of 3-cinnamyl-2-furanone and **6a** formed in a combined 30% yield. See the SI for details.

(10) The regioselectivity of reaction at the butenolide is distinct from that of several processes forming products from attack at C-5. The selectivities of reactions at C-5 have been rationalized by initial [4 + 2] cycloadditions with an alkene or carbonyl group. In our case, the siloxyfuran activated by an anionic group more likely reacts as an enolate, which tends to react with electrophiles at C-3.

(11) For a proposed [4 + 2] mechanism to rationalize C-5 selectivity, see: (a) Cho, C.-W.; Krische, M. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 6689. (b) Brown, D. W.; Campbell, M. M.; Taylor, A. P.; Zhang, X.-a. *Tetrahedron Lett.* **1987**, *28*, 985. For a computational study, see: (c) López, C. S.; Álvarez, R.; Vaz, B.; Faza, O. N.; de Lera, Á. R. *J. Org. Chem.* **2005**, *70*, 3654. For a C-3 aldol reaction of lithium enolate, see ref 11b.

(12) For a similar aza-Cope rearrangement, see: Kawatsura, M.; Tsuji, H.; Uchida, K.; Itoh, T. *Tetrahedron* **2011**, *67*, 7686.

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(17) Compound **7d** was determined to have an *S* configuration by comparison of the optical rotation of this material to a literature value in ref 7.

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(20) To understand the effect of ZnF_2, ^{19}F NMR experiments were conducted. The ^{19}F NMR spectrum of the catalytic reaction (Table 1, entry 3) contained a peak at −156.9 ppm, which matches the ^{19}F NMR resonance of TMSF. The same species was found in the mixture of ZnF_2 and TMSOAc but not in the mixture of ZnF_2 and trimethylsiloxyfuran. These observations suggest that ZnF_2 promotes the allylic substitution reaction by reacting with the trimethylsilyl carbonate formed in the reaction to release the carbonate, which then activates the trimethylsiloxyfuran.