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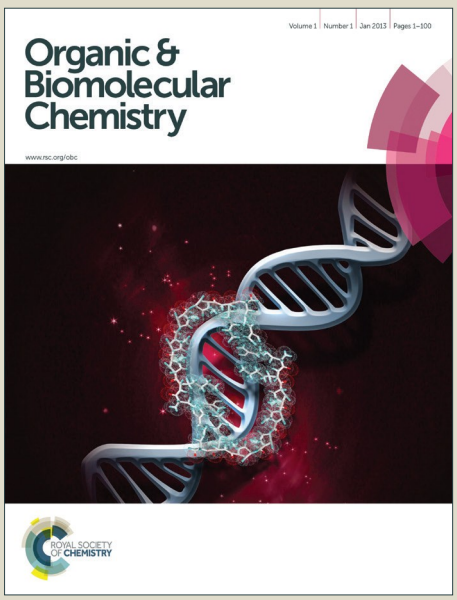

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Catalytic asymmetric formal γ-allylation of deconjugated butenolides

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A formal γ-allylation of deconjugated butenolides is reported based on a two-step sequence consisting of a catalytic diastereo- and enantioselective vinylogous nucleophilic addition to vinyl sulfones and Julia-Kocienski olefination. This highly modular approach delivers densely functionalized butenolides containing a quaternary stereogenic centre in excellent yield with high enantioselectivity.

Introduction

Structural motifs, prevalent in natural products and bioactive molecules, remain the utmost inspiration for the development of new synthetic strategies.[1] Butenolides are among such commonly encountered motifs and are present in >13,000 natural products.[2] Consequently, there has been considerable interest in efficient and economical synthesis of functionalized butenolides, especially those containing a stereogenic center. Initial works based on silyloxy furans[3] eventually made way for more direct approaches using either conjugated or deconjugated butenolides.[4] A number of catalytic asymmetric C–C bond forming transformations have been developed during the past few years, particularly using γ-substituted deconjugated butenolides as the nucleophile.[5]

Allyl group is among the most versatile substituents in organic chemistry since a diverse range of functionalities can be accessed through the modification of allylic unit. Regio- and enantioselective allylic substitution on butenolides has the potential to generate densely functionalized molecular architectures. Strategies towards this goal mostly relied on silyloxyfurans or related pre-activated starting materials.[6] In contrast, the use of unactivated butenolides for allylic alkylation remained limited. In 2010, Chen and co-workers reported the first direct asymmetric allylic alkylation of deconjugated butenolides with the help of dimeric cinchona alkaloids as the catalyst.[7] We have also developed an enantioselective umpolung addition of the same nucleophiles to allenoates through the synergistic combination of achiral Lewis base and chiral anion-binding catalysis.[8] However, both these strategies are restricted to allylic substituents bearing an electron-withdrawing functional group.

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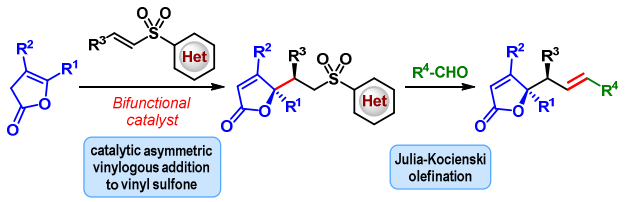
†Electronic Supplementary Information (ESI) available: Experimental details, characterization and analytical data. CCDC 1407861 (**3ba**) and 1407862 (**3af**). See DOI: 10.1039/x0xx00000x

The installation of an unfunctionalized allyl group on the unactivated butenolides constitutes a serious challenge. While contemplating possible tactics towards this objective, we became interested in the two-step allylation approach consisting of a conjugate addition to a heteroaryl vinyl sulfone and Julia-Kocienski olefination[9] (Scheme 1). This strategy has been elegantly adopted for the enantioselective formal allylic alkylation of direct carbon-centered nucleophiles such as α-branched aldehydes[10] and nitroalkanes[11] by the research groups of Cid and Ooi, respectively.[12] However, the application of this strategy for the enantioselective allylic alkylation of vinylogous nucleophiles is yet to be achieved.



Scheme 1 Two-step γ-allylation of deconjugated butenolides through catalytic asymmetric vinylogous addition to vinyl sulfones.

We realized that the successful implementation of this two-step strategy on deconjugated butenolides, in a γ-selective fashion, would not only give rise to the first asymmetric vinylogous addition to vinyl sulfones but an enantioselective γ-allylation of unactivated butenolides could also be accomplished (Scheme 1). The modular nature of this three-component approach would enable the synthesis of γ-allylic butenolides with desired substitution pattern through the choice of building blocks. More importantly, this route would allow complete regiocontrol of the allylic side chain (when $R^3 \neq R^4 \neq H$). The identification of a suitable catalyst system for the enantioselective conjugate addition would obviously be the key to the success of this strategy.

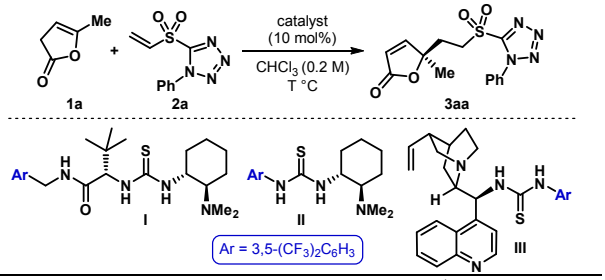
Based on our previous works with deconjugated butenolides,[5f,j,l-m] we hypothesized that tertiary amino (thio)urea based bifunctional catalysts[13] should be able to

activate both the reaction partners and at the same time, organize them for a face-selective conjugate addition. Herein, we present the successful execution of this strategy for the first catalytic enantioselective vinylogous nucleophilic addition to vinyl sulfones. Subsequent merger with Julia-Kocienski olefination for the enantioselective synthesis of γ-allylic butenolides is also described.

Results and discussion

Initially for the purpose of identifying the optimum catalyst and reaction conditions, α-angelica lactone **1a** and vinyl (1-phenyl-1*H*-tetrazol-5-yl) sulfone (vinyl PT-sulfone) **2a** were chosen as the model substrates (Table 1). The choice of **2a** was motivated by its precedence and compatibility of the expected product to the Julia-Kocienski olefination conditions.[14] We have recently reported the tertiary amino-thiourea derivative **I** as an efficient catalyst for the direct vinylogous Michael addition of deconjugated butenolides to prochiral 2,2-disubstituted cyclopentene-1,3-diones and demonstrated the importance of its secondary amide side chain for catalytic efficiency.[5f] The same catalyst was once again found to be extremely effective for this direct vinylogous addition of **1a** to vinyl sulfone **2a**. The desired γ-addition product **3aa** was

Table 1 Catalyst evaluation and reaction optimization[a]



Entry	Catalyst	Additive	*T* (°C)/ *t* (h)	Yield[b] (%)	er[c]
1	-	-	25 (24)	n.r.[d]	-
2	**I**	-	25 (0.5)	94	83:17
3	**I**	-	0 (2)	99	86:14
4	**I**	-	–40 (7.5)	99	90:10
5	**I**	5Å MS	–40 (1)	99	90:10
6	**II**	5Å MS	25 (4)	82	52:48
7	**III**	5Å MS	25 (53)	92	50:50
8	**I**	5Å MS	25 (0.1)	99	83:17

[a] Unless otherwise stated, reactions were carried out using 1.1 equiv. of **1a** and 1.0 equiv. of **2a**. [b] Isolated yield after column chromatography. [c] Enantiomeric ratio (er) was determined by HPLC analysis using a stationary phase chiral column. [d] n.r. = no reaction.

obtained exclusively in 94% yield within 30 min, albeit with moderate enantioselectivity (83:17 er), when the reaction was carried out using only 10 mol% of **I** in $CHCl_3$ at 25 °C (entry 2). The improvement in enantioselectivity was possible by lowering the reaction temperature to –40 °C (entry 4). The drop in reaction rate under these conditions can be restored by using 5Å MS without affecting the enantioselectivity (entry 5). Further efforts to improve the enantioselectivity by changing various parameters such as catalyst, reaction medium, temperature or concentration proved unsuccessful (see ESI). Nevertheless, the superiority of the catalyst **I** over the other commonly employed catalysts **II** and **III** became quite obvious (entries 6-8).

Table 2 Scope of the enantioselective vinylogous Michael addition with respect to butenolides[a]

Entry	R^1	R^2	1	t (h)	3	Yield[b] (%)	er[c]
1	Me	H	**1a**	1	**3aa**	99	90:10
2	Et	H	**1b**	1	**3ba**	82	89:11
3	*n*-Pr	H	**1c**	1	**3ca**	85	86:14
4	*i*-Pr	H	**1d**	1	**3da**	95	88:12
5	*i*-Bu	H	**1e**	1.5	**3ea**	98	85:15
6	Bn	H	**1f**	0.5	**3fa**	93	80:20
7	Ph	H	**1g**	0.2	**3ga**	99	93:7
8	4-BrC_6H_4	H	**1h**	0.2	**3ha**	80	85:15
9	4-MeC_6H_4	H	**1i**	0.2	**3ia**	87	94:6
10	4-$OMeC_6H_4$	H	**1j**	0.2	**3ja**	98	95:5
11	3,4-$Me_2C_6H_3$	H	**1k**	0.2	**3ka**	98	94:6
12	2-Naphthyl	H	**1l**	0.1	**3la**	99	92:8
13	2-Furyl	H	**1m**	0.1	**3ma**	99	85:15
14	Me	Ph	**1n**	0.5	**3na**	96	83:17
15	Me	CO_2Et	**1o**	0.1	**3oa**	99	81:19
16	-$(CH_2)_4$-		**1p**	7	**3pa**	99	83:17

[a] Reactions were carried out on a 0.084 mmol scale. [b] Isolated yield after column chromatography. [c] Determined by HPLC analysis (see ESI).

With the optimum catalyst and reaction conditions (Table 1, entry 5) in hand, we chose to explore the scope and limitations of this direct asymmetric vinylogous Michael addition for other deconjugated butenolides and vinyl sulfones. Table 2 shows the results of the reaction of various mono- and disubstituted deconjugated butenolides (**1a-p**) towards the addition to vinyl PT-sulfone **2a**. Both γ-alkyl and γ-aryl substituted butenolides displayed complete γ-selectivity and underwent facile Michael addition to produce **3** in good to excellent yield. However, the enantioselectivities of these reactions were found to be highly dependent on the nature of the substituents, with γ-aryl butenolides providing somewhat superior er (entries 7-12). β,γ-Disubstituted butenolides could also be employed and the γ-addition products were obtained

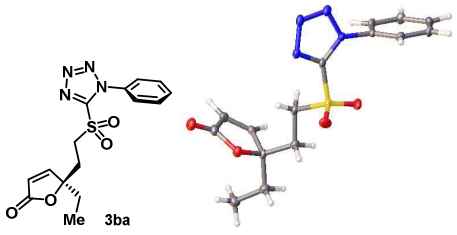
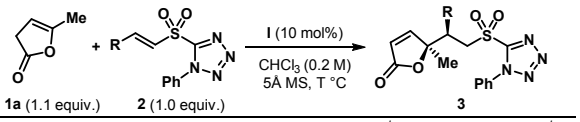


Fig. 1 Absolute configuration of **3ba** and its X-ray structure.

in excellent yield but with moderate er (entries 14-16). The absolute configuration of the Michael adduct **3ba** was found to be *R* by X-ray crystallography (Fig. 1),[15] and the stereochemistry of all other products was assigned by analogy.

Having established the applicability of various deconjugated butenolides for the addition to unsubstituted vinyl PT-sulfone (**2a**), we next investigated the utility of β-substituted vinyl sulfones (**2b-h**) with α-angelica lactone **1a** (Table 3). It must be mentioned that despite their synthetic potential, this type of substituted vinyl PT sulfones have rarely been employed in enantioselective transformations.[11] As expected, these substrates were found to be significantly less reactive compared to their unsubstituted counterpart **2a**. Consequently, higher reaction temperature and/or longer reaction time are often required to achieve useful yield of the Michael adducts. Nonetheless, in all the cases the reactions were completely diastereoselective, although the enantioselectivity once again appeared to be substrate dependent. β-Alkyl, aryl and heteroaryl substituted vinyl sulfones could be used and in almost all cases, the products were obtained in excellent yields with moderate to good enantioselectivities. The relative configuration of the products was determined through X-ray diffraction analysis of **3af** (Fig. 2).[15]

Table 3 Scope of the enantioselective vinylogous Michael addition with respect to vinyl sulfones[a]



1a (1.1 equiv.) **2** (1.0 equiv.) **3**

Entry	R	2	*T* (°C)	t (h)	3	Yield[b] (%)	dr[c]	er[d]
1	Me	**2b**	–40	96	**3ab**	93	>20:1	90:10
2	Ph	**2c**	–40	57	**3ac**	95	>20:1	93:7
3	4-MeC_6H_4	**2d**	0	96	**3ad**	31	>20:1	89:11
4	3-ClC_6H_4	**2e**	0	4	**3ae**	96	>20:1	88:12
5	4-BrC_6H_4	**2f**	0	72	**3af**	83	>20:1	84:16
6	2-Naphthyl	**2g**	0	80	**3ag**	88	>20:1	87:13
7	2-Furyl	**2h**	0	36	**3ah**	95	>20:1	87:13

[a] Reactions were carried out on a 0.084 mmol scale. [b] Isolated yield after column chromatography. [c] Determined by ^{1}H-NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis (see ESI).

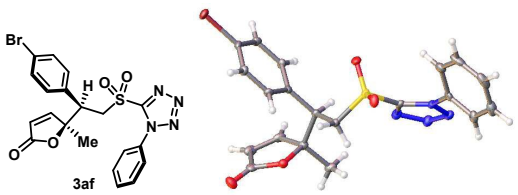
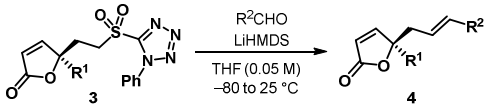


Fig. 2 X-Ray structure of **3af** with its relative configuration.

After successfully developing the catalytic asymmetric direct vinylogous Michael addition reaction, and showcasing the scope of butenolides and vinyl PT-sulfones, we focussed on transforming these adducts (**3**) to γ-allylated butenolides through Julia-Kocienski olefination.[9] Considering the densely functionalized nature of the butenolide derivatives, the selection of suitable reaction conditions was imperative for the preservation of stereochemical integrity. To our delight, using lithium hexamethyldisilazide (LiHMDS) as the base, the reaction of a number of aromatic and aliphatic aldehydes with the Michael adducts (**3aa** and **3ja**) led to the formation of γ-allyl butenolides **4**, in moderate to high yield with virtually no erosion in enantiomeric ratio (Table 4). More importantly, in all these cases the products, containing a quaternary stereogenic center, were obtained exclusively as a single diastereomer with respect to the newly formed olefin (*E*/*Z* >20:1).

Table 4 Formal γ-allylation of butenolides through Julia-Kocienski olefination of **3**

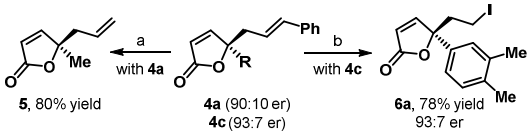


3 **4**

Entry	R^1	R^2	t (h)	4	Yield[a] (%)	*E*/*Z*[b]	er[c]
1	Me	Ph	2	**4a**	99	>20:1	90:10
2	Me	4-MeC_6H_4	2	**4b**	34	>20:1	n.d.
3	3,4-Me$_2C_6H_3$	Ph	2	**4c**	99	>20:1	93:7
4	3,4-Me$_2C_6H_3$	3-$NO_2C_6H_4$	3	**4d**	70	>20:1	n.d.
5	3,4-Me$_2C_6H_3$	*c*-Hex	2	**4e**	33	>20:1	n.d.

[a] Isolated yield after column chromatography. [b] Determined by ^{1}H-NMR analysis of the crude reaction mixture. [c] Determined by HPLC analysis (see ESI). n.d. = not determined.

As demonstration of the utility of the γ-allylated butenolides, we elaborated the products to some synthetically useful intermediates (Scheme 2). For example, ozonolysis of **4a** followed by in situ Wittig olefination afforded **5** in 80% yield. *Ent*-**5** has previously been used for the synthesis of (–)-ngaione.[16] Similarly, **4c** was converted to the γ-iodoethyl butenolide **6a** in high yield through a three-step sequence. The stereochemical integrity of the starting material was preserved throughout these transformations.



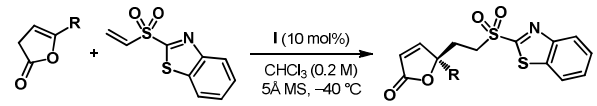
5, 80% yield **4a** (90:10 er) **4c** (93:7 er) **6a**, 78% yield 93:7 er

(a) i. O_3, CH_2Cl_2/MeOH, –78 °C, 3 min; ii. $Ph_3P{=}CH_2$, THF, –80 to 0 °C, 30 min; (b) iii. O_3, CH_2Cl_2/MeOH, –78 °C, 3 min, then $NaBH_4$, $CeCl_3$, MeOH, 0 °C, 20 min; iv. MsCl, Et_3N, CH_2Cl_2, 0 to 25 °C, 2 h; v. NaI, acetone, 60 °C, 5 h

Scheme 2 Synthetic elaboration of γ-allylated butenolides.

Intrigued by the possibility of utilizing similar class of 'two-carbon electrophiles' for the vinylogous Michael addition of deconjugated butenolides, we decided to extend our newly developed protocol to other vinyl sulfones and vinyl phenyl selenone. Given the compatibility of benzothiazol-2-yl sulfones (BT-sulfones) in Julia-Kocienski olefination,[9,17] vinyl BT-sulfone **7** was first examined under reaction conditions identical to those employed for vinyl PT-sulfone **2a**. As expected, **7** proved to be comparable to **2a**, both in terms of reactivity and enantioselectivity, and the Michael adducts (**8a-b**) were

obtained in near quantitative yield with high er (Scheme 3). Using **I** as the catalyst, these reactions proceed with the same sense of enantioinduction, as established through the conversion of **8a** to the corresponding γ-allylated butenolide **4a** (see ESI).

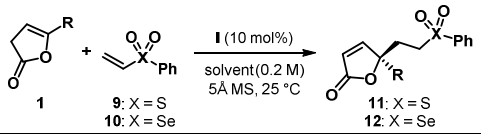


R	Time	Yield (%)	er
Me (**8a**)	3.5 h	96	95:5
4-OMeC$_6$H$_4$ (**8b**)	5 min	98	95:5

Scheme 3 Catalytic enantioselective vinylogous Michael addition of deconjugated butenolides to vinyl BT-sulfones.

Due to the structural resemblance with vinyl sulfones, vinyl selenones are expected to exhibit similar electrophilic properties and can act as Michael acceptors. Besides, the nucleofugality of arylselenonyl group renders the resulting Michael adducts vulnerable towards displacement with other nucleophiles.[18] This two-step strategy has the potential to generate products which cannot be accessed directly through conjugate addition. Irrespective of these advantages, enantioselective addition reaction to vinyl selenones remains relatively less explored compared to vinyl sulfones.[19]

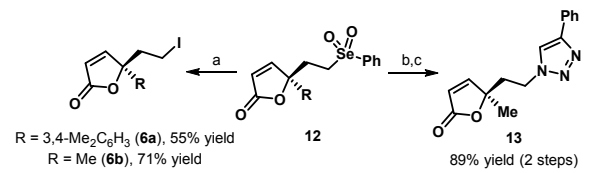
Table 5 Enantioselective vinylogous Michael addition to vinyl phenyl sulfone and selenone[a]



Entry	R	X	Solvent	t (h)		Yield[b] (%)	er[c]
1	Me (**1a**)	S	$CHCl_3$	48	**11**	<5	n.d.
2	Me (**1a**)	Se	$CHCl_3$	90	**12a**	76	92:8
3	Me (**1a**)	Se	toluene	72	**12a**	80	89:11
4	4-OMeC$_6$H$_4$ (**1j**)	Se	toluene	0.2	**12b**	79	92:8
5	3,4-Me$_2$C$_6$H$_3$ (**1k**)	Se	toluene	0.3	**12c**	92	91:9

[a] Reactions using 1.1 equiv. of **1** and 1.0 equiv. of **9** or **10**. [b] Isolated yield after column chromatography. [b] Determined by HPLC analysis (see ESI). n.d. = not determined.

In our investigation, we found a distinct reactivity difference between vinyl phenyl sulfone (**9**) and selenone (**10**). While the former turned out to be completely unreactive towards butenolide **1a** (Table 5, entry 1), the latter afforded the Michael adduct **12a** with good yield and enantioselectivity (entries 2-3). γ-Aryl substituted butenolides (**1j-k**) were expectedly more reactive and the corresponding adducts (**12b-c**) were obtained in high yield with good enantioselectivity within 10-15 min (entries 4-5).



(a) NaI, acetone, 25 °C, 10 min; (b) NaN_3, DMF, 40 °C, 30 min; (c) PhCCH, $CuSO_4$•$5H_2O$, sodium ascorbate, *t*-BuOH/H_2O, 25 °C, 20 h

Scheme 4 Synthetic transformations with vinyl selenone adducts.

The phenylselenonyl group of the resulting Michael adducts (**12**) was then subjected to displacement with different nucleophiles (Scheme 4). Using iodide as the nucleophile, the γ-iodoethyl butenolides (**6a-b**) were isolated in moderate to good yield. The absolute configuration of **6a** observed in this case was found to be the same as that obtained from **4c** (Scheme 2) and thereby established the stereochemistry of **12c** (see ESI). Displacement of the phenylselenonyl group with azide proceeded cleanly to deliver the corresponding azide, which was directly converted to the triazole derivative **13** through the Cu-catalyzed click reaction with phenylacetylene.

Conclusions

In summary, we have accomplished an asymmetric formal γ-allylation of deconjugated butenolides through the development of the first catalytic diastereo- and enantioselective vinylogous nucleophilic addition to vinyl sulfones. With the help of a bifunctional tertiary amino-thiourea derivative as catalyst, this two-step sequence provides a modular route to densely functionalized butenolides containing a quaternary stereogenic centre. The compatibility of our catalyst system for the enantioselective vinylogous addition to vinyl selenone has also been demonstrated.

Acknowledgements

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