Synthetic Methods

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Enantioselective Iridium-Catalyzed Vinylogous Reformatsky-Aldol Reaction from the Alcohol Oxidation Level: Linear Regioselectivity by Way of Carbon-Bound Enolates**

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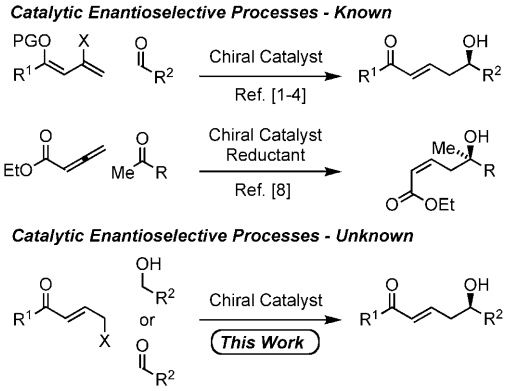
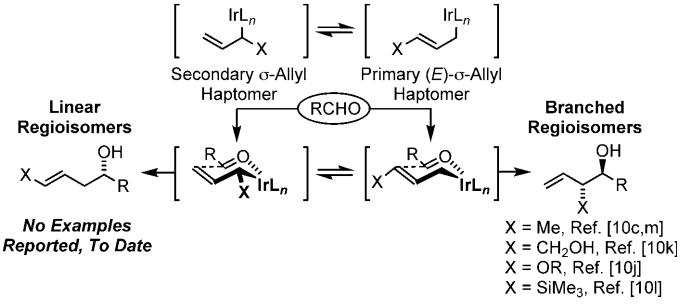
Vinylogues[1] of the aldol reaction represent an important class of carbonyl addition processes.[2] The vast majority of enantioselective vinylogous aldol additions employ dienolates and dienol ethers derived from β-ketoesters[3] in combination with chiral Lewis acids,[3a–k] chiral Lewis bases,[3k–m] or chiral hydrogen-bond donors.[3n] Dienolates and dienol ethers derived from simple α,β-unsaturated carbonyl compounds[3k–m,4] and 2-siloxy furans[5] also participate in enantioselective vinylogous aldol additions. While excellent regio- and enantioselectivities have been obtained in certain cases, the formation and tractability of the requisite dienol ethers pose a barrier to their use. Additionally, chiral Lewis acid catalyzed reactions of silyl dienol ethers often suffer from competing racemic silyl cation catalyzed background reactions, thus requiring slow addition of the dienol ether, cryogenic conditions, and high catalyst loadings. Vinylogous direct aldol additions of unmodified unsaturated carbonyl compounds potentially address these limitations,[6] however, to date, such transformations are restricted to the use of 2-(5*H*)-furanones or nitriles as aldol donors.[6,7]

In a significant departure from prior art, Kanai, Shibasaki, and co-workers devised a reductive vinylogous aldol reaction of allenic esters mediated by pinacolborane.[8] A related reductive process, the vinylogous Reformatsky reaction, could potentially deliver identical products, however, enantioselective variants are unknown.[9] Herein, under the conditions of C–C bond-forming transfer hydrogenation,[10,11] we report the first examples of enantioselective vinylogous Reformatsky-type additions, and establish catalytic conditions wherein asymmetric carbonyl addition occurs with equal facility from the alcohol or aldehyde oxidation level (Scheme 1).

In recent work, our research group has found that chiral *ortho*-cyclometalated iridium C,O-benzoates catalyze carbonyl allylation,[10a,b,e–h] crotylation,[10c,f] *tert*-prenylation,[10d,f] and a host of related carbonyl allylation processes. For such "C–C bond-forming transfer hydrogenations"[10,11] secondary alcohol dehydrogenation triggers reductive generation of allyliridium nucleophiles, which, in the presence of exogenous aldehyde, deliver products of carbonyl allylation. Of greater significance, primary alcohol dehydrogenation can simultaneously generate aldehyde–allyliridium pairs, thus enabling carbonyl addition from the alcohol oxidation level. For all reactions that occur by way of substituted π-allyl iridium intermediates, complete branched regioselectivities are accompanied by good to complete levels of *anti*-diastereoselectivity, thus suggesting carbonyl addition occurs with allylic inversion from the primary (*E*)-σ-allyl haptomer. To date, the formation of linear carbonyl addition products from substituted allyliridium nucleophiles has proven elusive (Scheme 2).



Scheme 1. Catalytic enantioselective vinylogous aldol reactions. PG = protecting group.



Scheme 2. Carbonyl addition by way of primary σ-ally haptomers typically generates branched products as *anti*-diastereomers.

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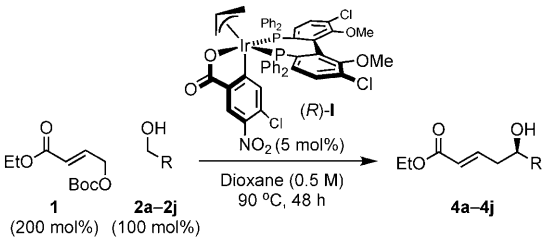
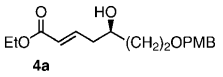
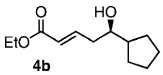
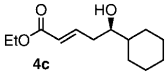
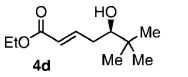
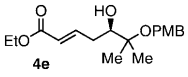
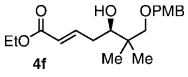
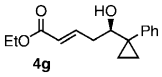
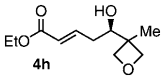
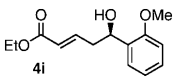
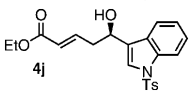
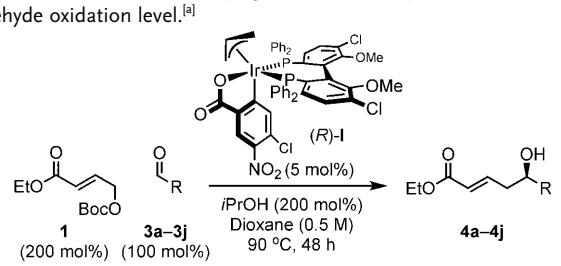
Table 1: Enantioselective vinylogous Reformatsky reaction from the alcohol oxidation level.[a]

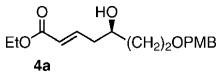
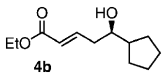
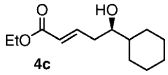
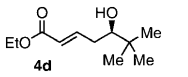
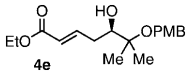
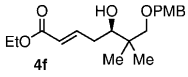
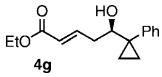
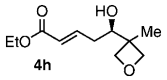
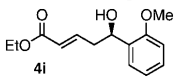
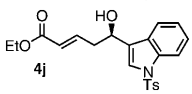


Entry	Product	Yield [%]	*ee* [%]	γ/α
1	 **4a**	87	88	1:2
2	 **4b**	74	94	5:1
3	 **4c**	77	95	5:1
4	 **4d**	59	96	≥20:1
5	 **4e**	88	96	≥20:1
6	 **4f**	75	99	≥20:1
7	 **4g**	70	97	≥20:1
8	 **4h**	61	90	≥20:1[b]
9	 **4i**	80	86	≥20:1
10	 **4j**	80	95	5:1

[a] Yields are of isolated product. Enantiomeric excess was determined by HPLC on a chiral stationary phase. See the Supporting Information for further details. [b] 24 h. Boc = *tert*-butoxycarbonyl, PMB = *para*-methoxybenzyl, Ts = 4-toluenesulfonyl.

Table 2: Enantioselective vinylogous Reformatsky reaction from the aldehyde oxidation level.[a]



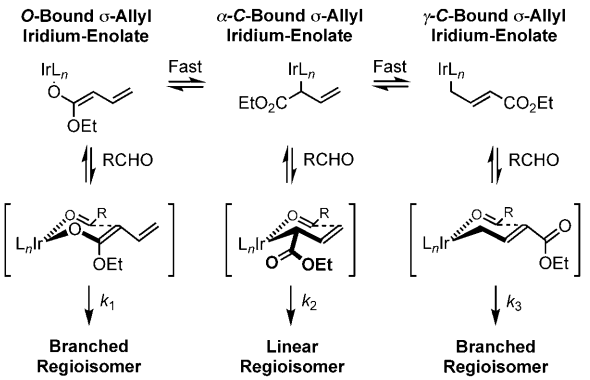
Entry	Product	Yield [%]	*ee* [%]	γ/α
1	 **4a**	65	83	1:2[b]
2	 **4b**	80	98	6:1
3	 **4c**	88	92	6:1
4	 **4d**	85	96	≥20:1
5	 **4e**	70	99	≥20:1
6	 **4f**	83	99	≥20:1
7	 **4g**	60	93	≥20:1
8	 **4h**	58	93	≥20:1
9	 **4i**	80	94	≥20:1
10	 **4j**	94	96	5:1

[a] As described in Table 1.

It was reasoned that linear carbonyl addition products might be availed upon stabilization of the secondary σ-allyl haptomer through introduction of a carbonyl moiety, in which case the secondary σ-allyl haptomer is equivalent to an η^1-C-bound iridium enolate.[12] The veracity of this analysis is borne out by the following experiments. Upon exposure of the γ-acyloxy crotonate **1** to primary alcohol **2a** in the presence of the chiral *ortho*-cyclometalated iridium C,O-benzoate complex modified by (*R*)-Cl,MeO-biphep, (2,2′-bis(diphenylphosphino)-5,5′-dichloro-6,6′-dimethoxy-1,1′-biphenyl), designated (*R*)-**I**, the products of carbonyl addition were obtained in a combined 87% yield as a 1:2 mixture of linear (88% *ee*) and branched regioisomers, thus favoring formation of the branched adduct, which appeared as a roughly equimolar mixture of diastereomers (Table 1, entry 1). Catalytic C–C coupling of cyclopentanemethanol **2b** or cyclohexanemethanol **2c** under identical conditions revealed an increased proportion of the linear regioisomer (approximately 5:1 r.r. in each case), again accompanied by high levels of enantioselectivity (94% *ee* and 95% *ee*, respectively; Table 1, entries 2 and 3). Primary neopentyl alcohols **2d**–**2h** delivered products of C–C coupling with complete linear regioselectivity and exceptional enantioselectivity (Table 1, entries 4–8). In all cases, roughly equivalent yields and selectivities are observed when the C–C coupling was performed using aldehydes **3a**–**3h** (Table 2, entries 1–8). Finally, benzylic alcohols **2i** and **2j** and the corresponding aldehydes **3i** and **3j** engage in C–C coupling to furnish adducts **4i** and **4j** (Table 1, entries 9 and 10 and Table 2, entries 9 and 10, respectively). A detailed description of the assignment of absolute stereochemistry is provided in the Supporting Information.

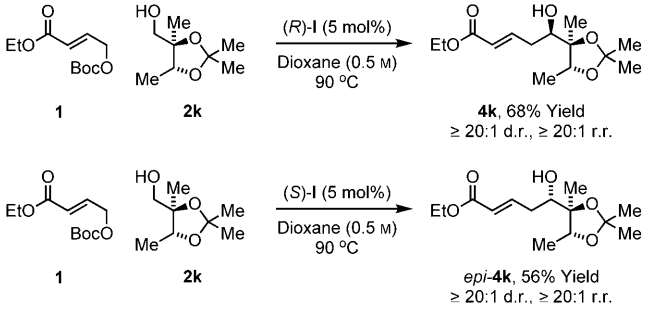
Linear regioselectivity in response to increased steric demand of the aldehyde suggests a Curtin–Hammett scenario wherein carbonyl addition occurs selectively from an equilibrating mixture of primary and secondary σ-allyl hapto-

mers.[13,14] Beyond electronic effects, it is likely that carbonyl addition from the α-C-bound iridium enolate to form the less-substituted C–C bond is favored owing to the absence of gauche interactions in the transition state. For sterically demanding aldehydes, such gauche interactions would be accentuated, thus increasing the preference for the linear regioisomer (Scheme 3).



Scheme 3. Partitioning of branched and linear regioisomers.

To further explore the scope of the vinylogous Reformatsky–aldol addition, catalyst-directed diastereoselectivity was explored in the coupling of allylic carbonate **1** to α-chiral alcohol **2k** (Scheme 4).[15] Under standard conditions employing (*R*)-**I** as the precatalyst, the linear adduct **4k** was isolated as a single regio- and stereoisomer. Using the enantiomeric precatalyst (*S*)-**I**, the linear adduct *epi*-**4k** was isolated as a single regio- and stereoisomer. Thus, complete levels of catalyst-directed diastereoselectivity are observed.[16] In contrast, using the analogous achiral iridium complex modified by biphep, (2,2′-bis(diphenylphosphino)biphenyl), diastereomers **4k** and *epi*-**4k** were produced in 58% yield in a 1:1.5 ratio, respectively, along with a 9% yield of the branched regioisomer. It should be noted that although bibhep is considered an achiral ligand, metal complexes of biphep adopt chiral racemic conformations that would attenuate substrate bias.



Scheme 4. Catalyst-directed diastereoselectivity in vinylogous Reformatsky–aldol addition from the alcohol oxidation level.

In summary, a catalytic enantioselective vinylogous Reformatsky-type addition has been described in which asymmetric carbonyl addition occurs with equal facility from the alcohol or aldehyde oxidation level. Good to excellent levels of regioselectivity and uniformly high levels of enantioselectivity are observed across a range of alcohols **2a**–**2i** and aldehydes **3a**–**3i**. Furthermore, as demonstrated in the case of α-chiral alcohol **2k**, exceptional levels of catalyst-directed diastereoselectivity may be achieved. Insight into the structure-interaction features of the catalytic system vis-à-vis partitioning of linear and branched adducts suggests a Curtin–Hammett scenario, wherein carbonyl addition occurs selectively from an equilibrating mixture of primary and secondary σ-allyl haptomers.[13,14] The collective data are consistent with carbonyl addition from the secondary α-C-bound iridium enolate to form the less-substituted C–C bond owing to the absence of gauche interactions in the transition state. Notably, in reactions conducted from the alcohol oxidation level, the only stoichiometric by-products formed are carbon dioxide and *tert*-butanol. Future studies will focus on the development of related C–C bond-forming processes that combine oxidation/construction event and thus bypass discrete alcohol oxidation and stoichiometric organometallic reagents while gaining access to more tractable synthetic intermediates in the form of alcohols.

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Keywords: aldol reaction · allylation · homogeneous catalysis · iridium · transfer hydrogenation

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