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Zinc Amide Catalyzed Regioselective Allenylation and Propargylation of Ketones with Allenyl Boronate

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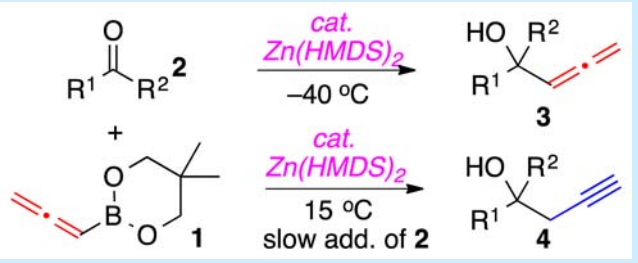
Supporting Information

ABSTRACT: Zinc amide catalyzed, regioselective allenylation and propargylation of ketones with allenyl boronate is reported. Tertiary allenyl and homopropargyl alcohols were obtained, respectively, in high selectivities, from the same starting materials, simply by changing the reaction conditions. The substrate scope was wide. Mechanistic studies suggest that the reactions are controlled under kinetic and thermodynamic conditions.



Allenylation and propargylation of ketones afford tertiary allenyl and homopropargyl alcohols. These compounds are common motifs in biologically active natural products as well as essential synthetic units,[1] but they cannot be prepared by the reduction (hydrogenation) of carbonyl compounds. Therefore, the carbon−carbon bond formation with ketones is crucial; however, control of reactivity and selectivity is difficult due to the sterically hindered nature of ketones compared with aldehydes. The conventional synthetic approaches utilize stoichiometric amounts of allenyl and propargyl metal species, which react with ketones via γ-addition to afford propargylation and allenylation products, respectively.[1b,2] For catalytic approaches,[3−6] allenyl and propargyl boronates have been used as starting materials. In the presence of catalytic amounts of mediators, allenyl and propargyl boronates react with ketones via γ-addition to afford propargylation and allenylation products, respectively.[3a,4b−h,5c] In these reactions, however, different starting materials (allenyl and propargyl species) must be prepared, which sometimes requires tedious labor. The problem might be solved if both tertiary allenyl and homopropargyl alcohols could be prepared from the same readily available starting materials.[2b,3]

Recently, Fandrick et al. reported interesting examples of regioselective allenylation and propargylation reactions, starting from the same propargyl or allenyl boronate.[5a,b] The trimethylsilyl-substituted propargyl boronate reacted with ketones to afford both tertiary allenyl and homopropargyl alcohols, stereoselectively, by simply changing the ligands of Cu. However, the selectivity was somehow dependent on the structure of the substituted propargyl boronates. Furthermore, there was no example of the successful synthesis of both these tertiary alcohols achieved when using nonsubstituted propargyl boronate. They also reported regioselective allenylation and propargylation reactions using diethylzinc; however, just one example of both allenylation and propargylation for an aldehyde from the same starting material was reported with high catalyst loading.[6b,c] Therefore, simple and practical methods for the preparation of both tertiary allenyl and homopropargyl alcohols, starting from the same starting materials, are desired.

We have recently reported that $Zn[N(SiMe_3)_2]_2$ [$Zn(HMDS)_2$] is a highly reactive catalyst for allylation reactions of ketones and related compounds with allylboronate.[7] The transmetalation of allylboronate with $Zn(HMDS)_2$ proceeds very smoothly to afford allylzinc amide species. Considering this observation,[8] we were of the opinion that the zinc amide might also participate in smooth exchange with allenyl boronate, to afford an active nucleophilic propargylzinc amide species.[9] And we also assumed that the propargylzinc amide species could isomerize to the corresponding allenylzinc species under thermodynamic conditions.[3b,6b,c]

Here, we report on zinc amide-catalyzed, highly regioselective, allenylation and propargylation of ketones from allenyl boronate, by controlling isomerization, between propargylzinc and allenylzinc species, to afford tertiary allenyl and homopropargyl alcohols, respectively. This type of general catalytic allenylation and propargylation method has not been reported previously.

We first investigated the $Zn(HMDS)_2$-catalyzed allenylation reaction of allenyl boronate **1a** or **1b** with acetophenone (**2a**). Using allenylboronic acid 2,2-dimethyl-1,3-propanediol ester (**1b**), the reaction proceeded in pentane at −20 °C in the presence of 0.2 mol % of $Zn(HMDS)_2$ and afforded the desired allenyl alcohol **3a** in high yield with good regioselectivity, whereas pinacol allenyl boronate (**1a**) gave low yield and reverse regioselectivity (Table 1, entries 1 and 2). The regioselectivity was improved when using toluene as a solvent, but the yield was rather low (entry 3). To improve the selectivity, the reaction was conducted at −40 °C using 2.0 mol % of $Zn(HMDS)_2$, and the allenyl alcohol **3a** was obtained in

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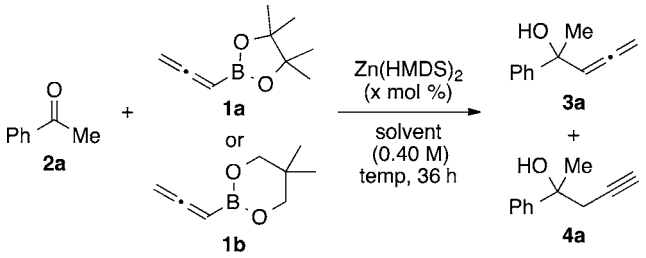
Table 1. Optimization of Reaction Conditions[a]



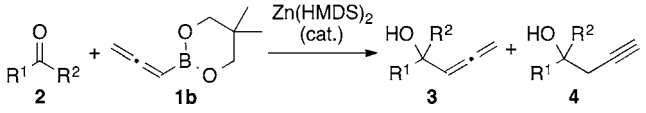
entry	1	x	solvent	temp (°C)	yield[b] (%)	3a:4a[c]
1	**1a**	0.2	pentane	−20	13[d]	13:87
2	**1b**	0.2	pentane	−20	85	75:25
3	**1b**	0.2	toluene	−20	53	87:13
4	**1b**	2.0	toluene	−40	91	96:4
5[e]	**1b**	2.0	toluene	−40	13	95:5
6[f]	**1b**	2.0	toluene	−40	22	94:6
7[g]	**1b**	2.0	toluene	−40	<5[d]	
8	**1b**	0.1	THF	20	80	29:71
9[h]	**1b**	0.3	THF	15	80	6:94

[a]The reaction of **2a** (0.40 mmol) with **1b** (0.44 mmol) was performed in a solvent (0.40 M) in the presence of $Zn(HMDS)_2$ unless otherwise noted. [b]Isolated yields of **3a** and **4a** after silica gel column chromatography. [c]Determined by ^1H NMR analysis. [d]Determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as the internal standard. [e]Et_2Zn (2.0 mol %) used instead of $Zn(HMDS)_2$. [f]Zn species prepared from Et_2Zn (2.0 mol %) and EtOH (1 equiv to **2a**) used instead of $Zn(HMDS)_2$. [g]$Zn(O^tBu)_2$ used instead of $Zn(HMDS)_2$; $Zn(O^tBu)_2$ prepared in situ from 2 mol % of $ZnCl_2$ and 4 mol % of KO^tBu. The reaction of **2a** (0.80 mmol) with **1b** (0.88 mmol) was performed in toluene (0.40 M). [h]The reaction of **2a** (0.40 mmol) with **1b** (0.60 mmol) was performed in THF (0.4 M) for 36 h in the presence of $Zn(HMDS)_2$ (0.30 mol %). **2a** was slowly added to the reaction over 12 h.

91% yield with 96:4 selectivity (entry 4). The reactivity of $Zn(HMDS)_2$ was remarkable compared with other zinc catalysts, such as Et_2Zn (without or with EtOH) and $Zn(O^tBu)_2$, as previously reported (entries 5−7).[7] We then investigated the regioselective propargylation reaction. Judging from the reaction mechanism, isomerization of propargylzinc species kinetically formed to allenylzinc species may be required under thermodynamic conditions. As expected, when the reaction was conducted in THF at 20 °C, homopropargyl alcohol **4a** was obtained as the major product (entry 8). Under the same reaction conditions, no reaction occurred without $Zn(HMDS)_2$. After optimization of the reaction conditions, it was found that lower catalyst loading and higher reaction temperature (15 °C) improved the regioselectivity (entry 9). It was revealed that both allenyl and homopropargyl alcohols were obtained, respectively, from the same allenyl boronate only by changing the reaction conditions.

Next, we investigated substrate generality of the regioselective allenylation and propargylation of ketones with allenyl boronate **1b** by using $Zn(HMDS)_2$ (Table 2). In general, when the reactions were conducted at −40 °C, the allenylation proceeded smoothly in >90% conversion after 36 h, with high regioselectivities (Table 2, conditions A). Electron-rich aromatic methyl ketones had lower selectivities than electron-deficient aromatic methyl ketones, but the reactions at −60 °C could improve the selectivities (entries 1A−6A). Regarding aliphatic ketones, the reactions at −40 °C had high reactivities and selectivities (entries 7A−9A). Phenyl aliphatic ketones also

Table 2. Zinc Amide Catalyzed Allenylation and Propargylation[a]



			yield[b] (%) (3:4)[c]	
entry	R^1, R^2 (**2**)	**3** + **4**	cond A	cond B
1	4-$MeOC_6H_4$, Me (**2b**)	**3b** + **4b**	75[d] (92:8)	64[h,i] (4:96)
2	4-BrC_6H_4, Me (**2c**)	**3c** + **4c**	93 (98:2)	90 (6:94)
3	4-$O_2NC_6H_4$, Me (**2d**)	**3d** + **4d**	70[d] (>99:1)	95 (9:91)
4	2-MeC_6H_4, Me (**2e**)	**3e** + **4e**	66[d] (96:4)	86 (9:91)
5	2-thiophenyl, Me (**2f**)	**3f** + **4f**	90 (94:6)	91[h] (10:90)
6	1-naphthyl, Me (**2g**)	**3g** + **4g**	71[d] (94:6)	79 (4:96)
7	$PhCH_2CH_2$, Me (**2h**)	**3h** + **4h**	86 (92:8)	83[h] (10:90)
8	$CH_3(CH_2)_3$, Me (**2i**)	**3i** + **4i**	82 (92:8)	65[h] (7:93)
9	-$(CH_2)_5$- (**2j**)	**3j** + **4j**	80 (90:10)	69 (9:91)
10	Ph, Et (**2k**)	**3k** + **4k**	88 (88:12)	78[j] (6:94)
11	Ph, ^{i}Bu (**2l**)	**3l** + **4l**	94 (95:5)	84[j] (8:92)
12	Ph, Ph (**2m**)	**3m** + **4m**	92 (96:4)	94[j] (20:80)
13	Ph, CO_2Me (**2n**)	**3n** + **4n**	61[d] (94:6)	89[j] (9:91)
14	4-MeC_6H_4, H (**2o**)	**3o** + **4o**	90[e,f] (96:4)	91 (12:88)
15	4-$MeOC_6H_4$,H (**2p**)	**3p** + **4p**	79 (80:20)	93 (10:90)
16	4-$O_2NC_6H_4$, H (**2q**)	**3q** + **4q**	86[d,g] (93:7)	89 (40:60)
17	2-naphthyl, H (**2r**)	**3r** + **4r**	93[d] (92:8)	80 (8:92)
18	2-furyl, H (**2s**)	**3s** + **4s**	78[d] (97:3)	77 (8:92)
19	$PhCH_2CH_2$, H (**2t**)	**3t** + **4t**	89[d] (96:4)	83 (13:87)

[a]Conditions A: The reaction of **2** (0.40 mmol) with **1b** (0.44 mmol) was performed in toluene (0.40 M) at −40 °C for 36 h in the presence of $Zn(HMDS)_2$ (0.0080 mmol, 2 mol %) unless otherwise noted. Conditions B: The reaction of **2** (0.40 mmol) with **1b** (0.60 mmol) was performed in THF (0.4 M) at 15 °C for 36 h in the presence of $Zn(HMDS)_2$ (0.0012 mmol, 0.3 mol %) unless otherwise noted. **2** was slowly added into the reaction system over 12 h. [b]Isolated yield (%) of **3** and **4** in total. [c]Determined by ^1H NMR analysis. [d]At −60 °C. [e]The reaction was conducted at −40 °C for 18 h. [f]Without catalyst, 6% conversion was observed at −40 °C for 18 h. [g]Slow addition of **2n** within 2 h. [h]at 25 °C. [i]0.1 mol % of $Zn(HMDS)_2$ was used. [j]2.0 mol % of $Zn(HMDS)_2$ was used.

gave good to high regioselectivities (entries 10A and 11A). It is noteworthy that sterically hindered benzophenone (**2m**) and phenyl glyoxylate (**2n**) were tolerated under the reaction conditions (entries 12A and 13A).

Furthermore, we could extend the substrate scope to aldehydes. The reactions of aldehydes with **1b** afforded the corresponding allenyl alcohols as major products (entries 14A−19A). Although 4-methoxybenzaldehyde (**2p**) afforded the allenyl alcohol with lower regioselectivity, the reactions at −60 °C and slow addition of the aldehyde could improve the selectivities, and the allenylation of various aldehydes proceeded smoothly to afford the desired allenyl alcohols in high yields with high regioselectivities.

Substrate generality for the propargylation of ketones was also investigated (Table 2, conditions B). While aromatic methyl ketones bearing electron-rich or electron-withdrawing substituents successfully reacted with **1b** to afford the desired propargyl alcohols **4** in high yields (entries 1B−6B), aliphatic ketones also afforded the propargylation products with slightly lower yields (entries 7B−9B). The reactions of phenyl ethyl ketone **2k** and phenyl isobutyl ketone **2l** afforded the desired products in good to high yields with high regioselectivities (entries 10B and 11B), but lower regioselectivity was observed

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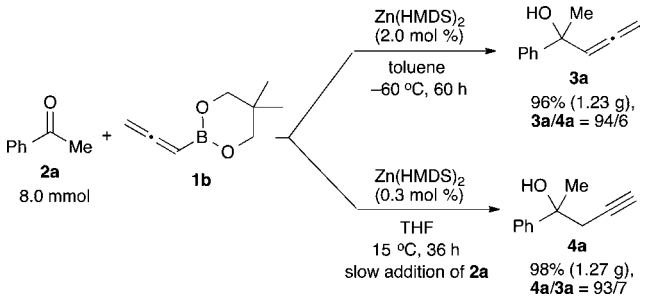
when benzophenone **2m** was employed (entry 12B). In the reaction of phenyl ethoxycarbonyl ketone **2n** with **1b**, high yield and high regioselectivity were observed (entry 13B). Regioselective propargylation of aldehydes was also possible, and high yields and moderate to high selectivities were obtained (entries 14B–19B).

These results showed that both allenyl and propargyl alcohol products could be obtained from the allenyl boronate **1b** using $Zn(HMDS)_2$, simply by changing the reaction conditions. Experiments on a gram scale were also successful (Scheme 1).

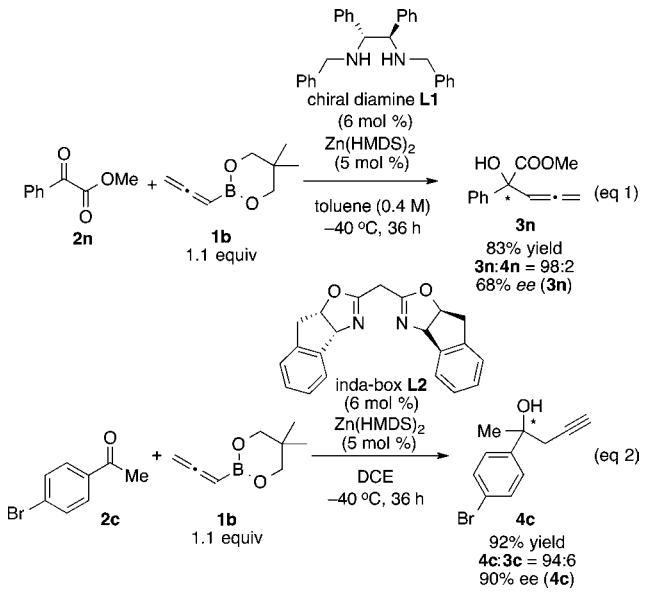
Scheme 1. Catalytic Allenylation and Propargylation in Gram Scale



To our knowledge, this is the first example of general highly regioselective allenyl and propargylation reactions of ketones from allenyl boronate using the same catalyst system with wide substrate scope.

A preliminary trial of catalytic asymmetric variants of the allenylation and propargylation of ketones was conducted.[10] A chiral zinc amide complex prepared from $Zn(HMDS)_2$ and chiral diamine **L1** or Inda-box ligand **L2** worked well to promote the asymmetric reactions. The desired allenylation reaction proceeded in 83% yield with excellent allenyl selectivity (98:2) and moderate enantioselectivity (68% ee) in the presence of the chiral zinc catalyst (5 mol %) from $Zn(HMDS)_2$ and **L1** (Scheme 2, eq 1). On the other hand, the desired propargylation reaction also proceeded in 92% yield

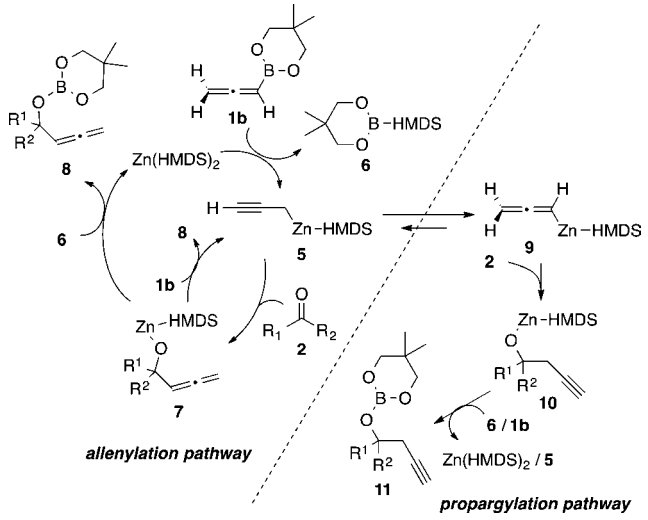
Scheme 2. Asymmetric Allenylation and Propargylation with $Zn(HMDS)_2$ and Chiral Ligands



with excellent propargyl selectivity (94:6) and high enantioselectivity (90% ee) in the presence of a chiral zinc catalyst (5 mol %) prepared from $Zn(HMDS)_2$ and **L2** (Scheme 2, eq 2).

A proposed reaction mechanism is shown in Scheme 3. The first step is transmetalation of **1b** with $Zn(HMDS)_2$ to form

Scheme 3. Proposed Catalytic Cycle for the Zinc Amide-Catalyzed Allenylation and Propargylation Reactions



propargyl zinc species **5**. Under the kinetic control conditions, **5** smoothly reacts with carbonyl compound **2** to afford the corresponding zinc alkoxide species **7**. After the boronate-to-zinc exchange reaction with boron amide **6** or direct reaction of **7** with **1b**, the boronate complex of allenyl alcohol **8** is released to regenerate $Zn(HMDS)_2$ or **5**.[7b] On the other hand, under the thermodynamic conditions, the propargylzinc species **5** smoothly formed isomerizes to form a more stable allenylzinc species **9**. The isomerization occurred even in toluene (Scheme S1) but is smoother in THF. It further reacts with **2** to form the corresponding zinc alkoxide species **10**. A low concentration of **2** suppresses the undesired addition reaction of **5** to **2** before the isomerization. After the boronate-to-zinc exchange reaction or direct reaction with **1b**, boronate complex **11** is released, accompanied by the regeneration of $Zn(HMDS)_2$ or formation of **5**. The smooth isomerization under thermodynamic conditions could be achieved as a result of the high reactivity of allenyl- and propargylzinc amide species. Our detailed mechanistic studies also supported this hypothesis (Schemes S2 and S3).[10] It was also confirmed that transmetalation of **1b** with $Zn(HMDS)_2$ was clearly faster than with $ZnEt_2$ (Scheme S4).[10] We conducted DFT calculations of stabilities of the propargylzinc and the allenylzinc amide species, which also supported that the allenylzinc amide species was more stable than the propargylzinc amide species, and that activation energies of the transition states of the allenylation and propargylation were appropriate for the regioselective reactions under similar reaction conditions (Figure S1).[11]

In conclusion, we have developed the highly regioselective allenylation and propargylation of ketones with allenyl boronate using $Zn(HMDS)_2$ as a catalyst. The desired reactions proceeded at low catalyst loading, and the tertiary allenyl and homopropargyl alcohols were selectively obtained in moderate to high yields, with wide substrate scope. By using chiral ligands for $Zn(HMDS)_2$, catalytic asymmetric allenylation and propargylation reactions were possible. Mechanistic studies

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indicated that the first transmetalation of allenyl boronate with zinc amide occurred to form propargylzinc species under kinetic conditions, to afford the allenylation products, and that the propargylzinc species isomerized to form allenylzinc species under thermodynamic conditions to afford the propargylation products. High reactivity of the zinc amide species is key for the smooth transmetalation and isomerization. Further investigations into developing asymmetric allenylation and propargylation reactions of ketones are currently in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03045.

Supporting studies, general experimental procedures, analytical data of the products, DFT calculations, and spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(11) See the Supporting Information.

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