EurJOC
European Journal of Organic Chemistry

Research Article
doi.org/10.1002/ejoc.202300177

Chemistry Europe
European Chemical Societies Publishing

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Synthesis of Aryl- and Alkyl-Containing 3-Methylene-5-hydroxy Esters via a Barbier Allylation Reaction

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The formation of C–C bonds via the allylation of carbonyl compounds has been widely applied in total syntheses. Amongst the many possible strategies, the Barbier-type allylation in aqueous media has received only moderate attention over the last decades despite its mild reaction conditions. In this study, we investigated the indium (In^0) and zinc (Zn^0) mediated Barbier allylation reaction to efficiently synthesize base-labile 3-methylene-5-hydroxy containing building blocks for natural product total synthesis. As model study we selected the allylation of lipidic undecanal with ethyl 3-(bromomethyl)but-3-enoate in the presence of either Zn^0 or In^0 and investigated the effects of additives on yields and selectivities. We then applied the optimized reaction conditions to sterically demanding allyl bromides and functionalized aromatic aldehydes yielding eleven new homoallylic alcohols, one of which was further transformed via oxidation and reduction sequences.

Introduction

Addition of allylic organometallic reagents to a carbonyl compound represents one of the most important ways of creating new carbon-carbon bonds with functionalities which can subsequently participate in a number of synthetically useful transformations like dihydroxylation, epoxidation, hydroboration, hydrogenation, hydration, olefin metathesis, ozonolysis, or cycloaddition.[1,2] The development of stereoselective allylation reactions has been an attractive and growing research field for the past two decades with many remarkable achievements in terms of stereoselectivity and efficiency,[3] as well as their implementation in the synthesis of numerous natural products. However, finding a matching efficient protocol for a given synthetic problem is not always straightforward as the basic character of organometallic reagents, their high sensitivity to moisture and reactivity remains a major synthetic challenge.

Driven by the goal to synthesize functionalized lipids of microbial origin for biological testing, we recently investigated the synthesis of chiral aliphatic *syn*- and *anti*-β,δ-dihydroxy esters using a combination of Ti-BINOL catalyzed asymmetric Mukaiyama aldol reaction of Chan's diene with various aldehydes and diastereoselective reduction.[4] This time, we investigated a synthetic approach towards the 3-methylene-5-hydroxy core motif as building block for the synthesis of complex microbial natural products (Figure 1A). The motif still represents a challenging synthetic target as basic conditions often cause the isomerization of the exo-methylene moiety to the more stable conjugated double bond system.

Amongst the different reported allylation reactions, the Barbier allylation mediated by zero-valent metals (indium or zinc) has emerged as an useful method for preparation of homoallylic alcohols under mild conditions (Figure 1B).[5] Barbier reactions are often performed using the cheaper metal Zn^0, which require harsher reaction conditions due to the relative high ionization energy of Zn^0 (9.39 eV) and necessity to remove the oxide layers prior to reaction. In contrast, the more expensive In^0 has been much appreciated as an alternative metal as it rarely forms oxide layers (lower first ionization potential (5.8 eV)) and tends to form less basic but reactive, nontoxic, water-tolerant organometallic species *in situ*.[6]

The use of indium In^0-mediated Barbier allylation reaction in water was first reported by Li and Chan in 1991 for the synthesis of sialic acids.[7] In 1996, Paquette and co-workers reported that In^0-mediated allylation of carbonyl compounds possessing a hydroxyl group proceed with high diastereoselectivity.[8] Similarly, the addition of allyl indium reagents to pro-chiral aldehydes or imines was reported to proceeded in protic solvents under substrate control with good to excellent yields and selectivities.[9] Despite these effective methods, only few reports discussed the use of sterically more

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202300177

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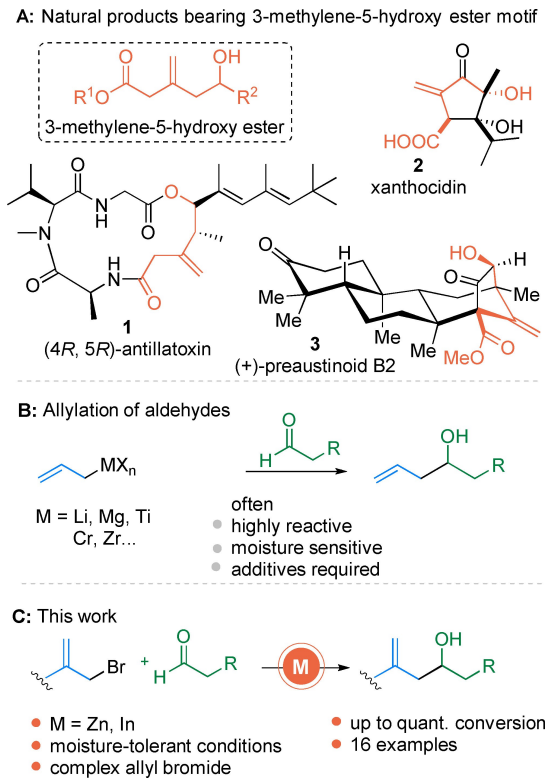


Figure 1. (A) Examples of natural products containing 3-methylene-5-hydroxy ester motif. **(B)** General scheme for allylation reaction using different moisture-sensitive metallorganyls. **(C)** Overview of reaction applied in this study.

demanding allyl halide reagents for allylation reactions until today. In this study, we investigated the applicability of substituted 3-methylene containing alkyl halides and long-chain aliphatic aldehydes in a Barbier-type allylation reaction to synthesize base-labile 3-methylene-5-hydroxy ester derivatives preferentially under aqueous reaction conditions (Figure 1C).

Results and Discussion

First, commercially available allyl bromide **4** was reacted with undecanal **5a** in the presence of either Zn^0 dust or In^0 using previously reported Barbier reaction conditions (Figure 2), which yielded homoallylic alcohol **6a** in 92%.

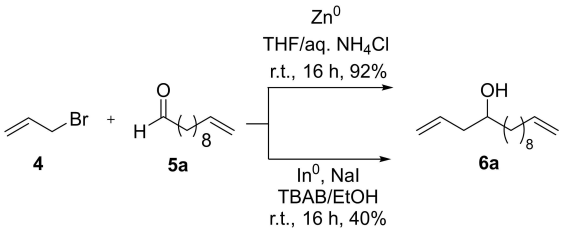


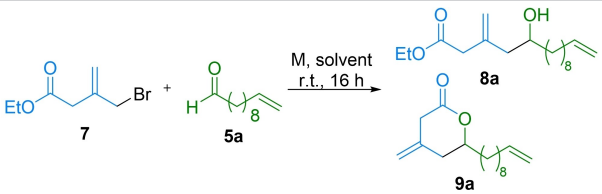
Figure 2. Comparison of Zn^0- and In^0-mediated Barbier allylation reaction of linear unsubstituted substrates.

We then investigated the application of other allyl bromides such as substituted 3-methylene-bromide[10] **7** with a focus on using aqueous reaction conditions.

Reaction of **7** with undecanal **5a** in the presence of Zn^0 yielded the functionalized 3-methylene-5-hydroxy ester **8a** in 36% (Table 1, entry 2). Performing the same reaction in a sonication bath yielded product **8a** in 51% and lactone **9a** (Table 2, see below) in 12% after 4 h. Extension of the reaction time to 6 h led to almost complete conversion yielding 61% of product **8a** and 38% of lactone **9a** (Table S1, entry 1,2). Further elongation of the reaction time (>10 h) however, cause the decomposition of materials (Table S1, entry 3–5). We then compared the reaction using either Zn^0 or In^0 in the presence of different biphasic aqueous systems. When the Barbier allylation was performed in the presence of THF and sat. aq. NH_4Cl solution (Table 1, entry 1–2), transformation with Zn^0 afforded almost 3-fold higher yields compared to the reaction performed with In^0 (13% vs 36%).

The exchange of the organic solvent to ethanol, THF, toluene or DCM (entry 3–10), in combination with either solid NH_4Cl or sat. aq. solution, resulted only in low yields (<30%). When DMF was used as solvent and NH_4Cl salt as additive (entry 11–12), the homoallylic alcohol **8a** was formed in only minor amounts using either one of the metals (16% and 12%). Using either water or saturated aq. NH_4Cl solution as solvent,

Table 1. Screening of reaction conditions (solvent and ammonium source).



Entry	M	Solvent	Ammonium source	Yield 8a [%]
1	In	THF, water[a] (1:1)	NH_4Cl	13[c]
2	Zn	THF, water[a] (1:1)	NH_4Cl	36[c]
3	In	ethanol, water[a] (1:1)	NH_4Cl	28[c]
4	Zn	ethanol, water[a] (1:1)	NH_4Cl	27[c]
5	In	THF, hexane (8.75:1.25)	NH_4Cl (s)[b]	–
6	Zn	THF, hexane (8.75:1.25)	NH_4Cl (s)[b]	20[c]
7	In	toluene, water[a] (1:1)	NH_4Cl	12[c]
8	Zn	toluene, water[a] (1:1)	NH_4Cl	–
9	In	DCM, water[a] (1:1)	NH_4Cl	16[c]
10	Zn	DCM, water[a] (1:1)	NH_4Cl	–
11	In	DMF	NH_4Cl (s)[b]	16[c]
12	Zn	DMF	NH_4Cl (s)[b]	12[c]
13	In	water	–	30[c]
14	Zn	water	–	11[c]
15	In	water[a]	NH_4Cl	37[c]
16	Zn	water[a]	NH_4Cl	–
17	In	water	NH_4HCO_2	38[c]
18	In	water	TBAB[d]	66[e]
19	In	water	TBAI[d]	93[e]
20	In	water	TBAB + NaI[f]	93
21	Zn	water, THF	TBAB[d]	61[g]

[a] NH_4Cl used as a saturated aqueous solution; [b] 10 mol% of solid NH_4Cl. [c] formation of minor amounts of lactone **9a** observed by TLC; [d] saturated aq. solution; [e] lactone **9a** isolated in 7%; [f] 10 mol%; [g] lactone **9a** isolated in 38%.

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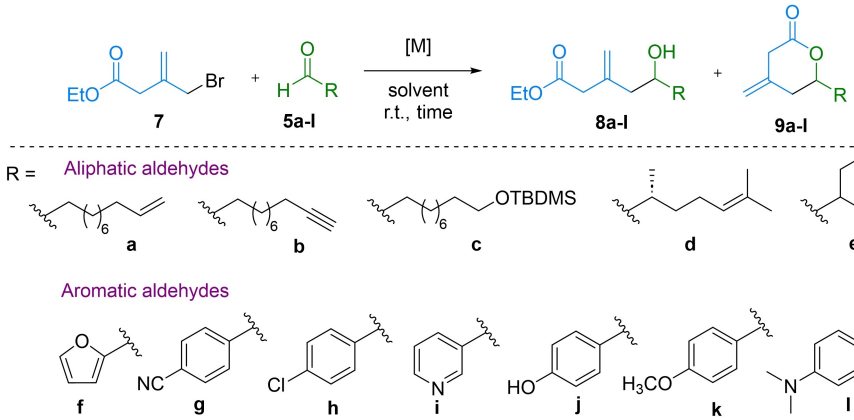
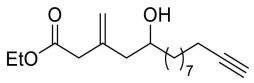
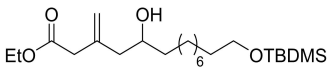
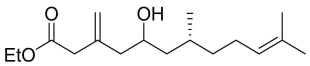
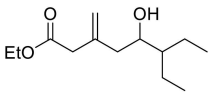
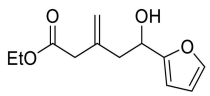
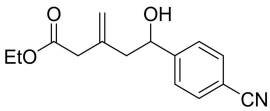
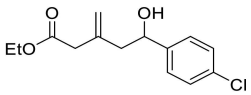
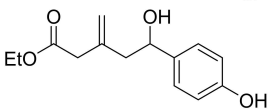
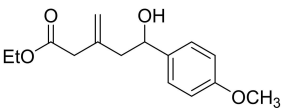
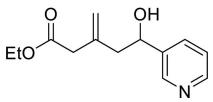
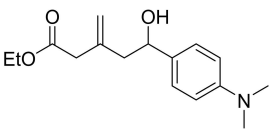
Table 2. Expanding scope of optimized reaction conditions for different aldehydes.



Entry	Aldehyde	M	Additive/Solvent	Time [h]	Yield 8a–l [%]	Structure of product
1	**5b**	In	TBAI[a]	16	29 (**8b**)	
2	**5b**	In	TBAB[a]	16	79 (**8b**)	
3	**5b**	Zn	TBAB/THF	6	54 (**8b**)	
4	**5c**	In	TBAB[a]	16	57 (**8c**)	
5	**5c**	Zn	TBAB/THF	6	60 (**8c**)	
6	**5d**	In	TBAB[a]	16	64 (**8d**)[d]	
7	**5d**	Zn	TBAB/THF	6	51 (**8d**)	
8	**5e**	In	TBAB/EtOH	16	99 (**8e**)	
9	**5f**	In	TBAB/EtOH	6	99 (**8f**)[13]	
10	**5g**	In	TBAB/EtOH	16	Quant. (**8g**)	
11	**5h**	In	TBAB/EtOH	6	99 (**8h**)	
12	**5j**	In	TBAB/EtOH/NaI	16	Quant. (**8j**)	
13	**5k**	In	TBAB/EtOH	16	99 (**8k**)	
14	**5i**	In	TBAB[a]	16	28 (**8i**)	
15	**5i**	In	TBAB/EtOH	16	–	
16	**5l**	In	TBAB[a]	16	12 (**8l**)	

[a] As a saturated aqueous solution; [b] **9a** isolated in 7% yield: [c] **9a** isolated in 38% yield; [d] *dr* 50:50.

the In^0-mediated reaction afforded around 30–40% yield, while Zn^0 yielded significantly less product (entry 13–16).

As NH_4Cl had a beneficial effect on the In^0-mediated allylation, we then tested the effects of different ammonium additives.[11] Replacing NH_4Cl by ammonium formate afforded

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comparable overall yields including lactone **9a** (entry 17). Similar to previous reports, the use of sat. aq. tetrabutylammonium bromide (TBAB) was beneficial to the reaction outcome yielding **8a** in 66% (entry 18). Replacement of TBAB with TBAI, resulted in almost complete conversion (93% yield, entry 19). Identical yields were observed when a sat. aq. TBAB solution together with NaI (10 mol%) were employed to catalyse *in situ* TBAI formation by ion exchange (entry 20). In comparison, the reaction with Zn^0 and TBAB resulted in formation of homoallylic alcohol in 61% (entry 21). These findings supported the hypothesis, that tetrabutylammonium salts are also more beneficial for the conversion of sterically complex allyl halide and aldehydes likely due to a better way of complexation and electron transfer.

Using improved reaction conditions, the effect of prolonged reaction times and elevated temperatures was analyzed. As observed for reactions using sonication, increased reaction times of 48 h or 72 h decreased the yield of ester **8a** (75% or 30% respectively) and caused increasing formation of lactone **9a** (56%), instead (Table S2, entry 2–3). Lactone formation became even more facile when the reaction temperature was elevated to 40 °C (Table S2, entry 4) resulting in a ratio 1:4 (20% vs 80%). Increasing the reaction temperature to 60 °C for 16 h resulted exclusively in the formation of lactone **9a** (Table S2, entry 5). Therefore, the best conditions for the formation of allyl ester **8a** showing minimal side reactions were 16 h reaction time at room temperature.

Substrate scope

We then expanded the reaction scope to aldehydes carrying different functionalities. For comparison, we first converted commercially available allyl bromide **4** with two different aldehydes (Figure 3) yielding products **6b** and **6m** in 78% and 83% yield, respectively.

The substrate scope was then expanded to aliphatic branched (**5d**, **5e**) and unbranched aldehydes carrying an alkyne moiety (**5b**), protected alcohol (**5c**), aromatic moieties carrying electron withdrawing substituents (**5g**, **5h**) or electron donating substituents (**5j**, **5k**, **5l**) and finally to heterocyclic furfural **5f** and picolinaldehyde **5i** (Table 2). When undec-10-yn-1-al **5b** was transformed using In^0, the reaction in a sat. aq. solution of TBAI resulted in only 29% yield (Table 2, entry 1),

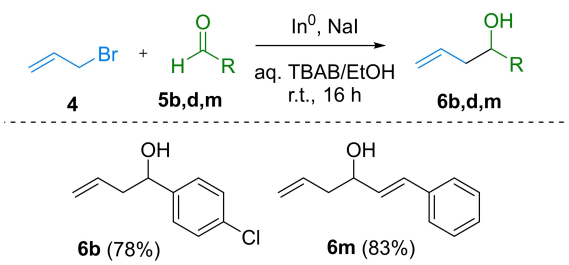

Figure 3. Barbier allylation with allyl bromide **4** and various aldehydes using optimized conditions.

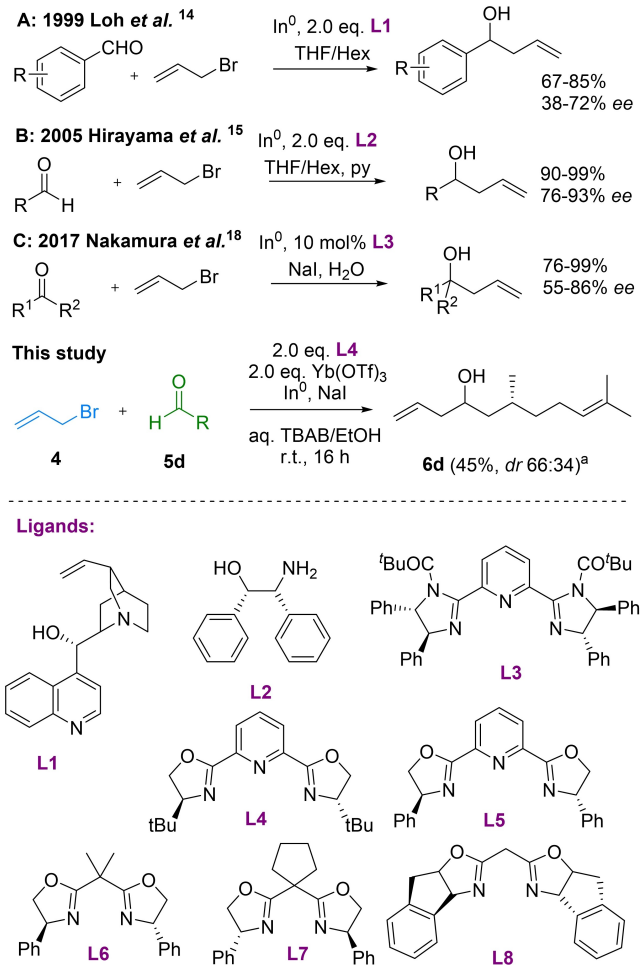

Figure 4. Literature examples of In^0-mediated Barbier allylation employing various chiral promotors; [a] diastereomeric ratio (*dr*) was determined by chiral HPLC analysis using Lux® 5 µm Amylose-1 column (2% *i*-PrOH in heptane).

while the use of TBAB afforded 79% isolated yield of product **5b** (entry 2). In comparison, reaction with Zn^0 yielded 54% (entry 3). To our delight, application of protected alcohol **5c** generated product **8c** in nearly same quantities in case of both metals (entries 4–5). When **7** was transformed with (*R*)-citronellal **5d** product **8d** was obtained in 64% (In^0) and 51% (Zn^0), respectively, similar to the transformation with allyl bromide. Reaction with 2-ethylbutanal **5e** using In^0 resulted in quantitative formation of **8e** (entry 8). Next, the allylation of aromatic aldehydes was examined and again, nearly quantitative transformation was observed (entry 9–13). These results indicate that aromatic *p*-substituted aldehydes with electron withdrawing (EWG) as well as donating (EDG) groups and heterocycles are well tolerated. In contrast, allylation of nitrogen-containing aromatic aldehydes (**5i**, **5l**) led to formation of only minor quantities of product or did not proceed at all (entry 14–16). Here, we hypothesize that *in situ* generated allylindium species may form complexes with substrates **5i** and **5l**, which thereby reduced the overall reactivity of organometallic species. This hypothesis is supported by findings of Yasuda et al. who

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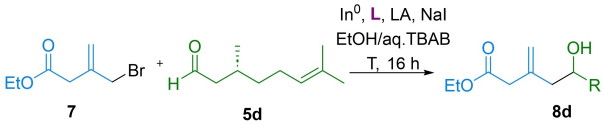
demonstrated the formation of allylindium dibromide and diallylindium bromide by complexing these highly reactive species with different pyridine ligands.[12]

Many enantioselective allylation procedures make use of Lewis acids to activate the carbonyl moiety towards nucleophilic attack and an electron-rich chiral ligand, which simultaneously cause chiral induction and increase nucleophilicity of organometallic species by coordination. In 1999, Loh et al. employed (+)-cinchonine **L1** and (−)-cinchonidine alkaloids as chiral ligands in the allylation reaction of different aldehydes with either allyl bromide or prenyl bromide (Figure 4A).[14] They demonstrated excellent yields (up to 99%) and enantioselectivities (up to 90% *ee*) using aromatic aldehydes, but reactions with aliphatic and α,β-unsaturated aldehydes only led to moderate selectivities (41–59% *ee*). In 2005, Hirayama et al. established an allylation protocol using pyridine and commercially available (*1S,2R*)-(+)-2-amino-1,2,diphenylethanol ligand **L2** (Figure 4B).[15] The transformation of mainly aromatic aldehydes and allyl bromide in the presence of In^0 led to high yields (up to 99%) and moderate to high enantioselectivities (76–93% *ee*). Similar studies were performed by Haddad et al. on the allylation of prochiral ketones.[16,17] In 2017, Nakamura et al. reported the enantioselective In^0-mediated Barbier allylation of aromatic aldehydes and ketones using bis(imidazoline)catalyst **L3** (Figure 3C) with excellent yields (up to 99%) and moderate to high enantioselectivities (55–86% *ee*).[18] Despite this progress, examples of the use of structurally diverse allyl bromides still remain sparse.

As a moderate degree of substrate control for the allylation reaction of citronellal **5d** with either allyl bromide or substrate **7** was observed, we questioned if a higher diastereoselectivity could be achieved by a catalyst-controlled reaction. In this study, we tested the effects of Lewis-acidic lanthanide triflates ($Ce(OTf)_3$ and $Yb(OTf)_3$), known to tolerate aqueous conditions,[19,20] and five different chiral bisoxazoline (BOX and PyBOX) commercially available ligands **L4-8** on the transformation of allyl bromide **7** with aldehyde **5d** (Table 3).[21] To increase solubility of Lewis acid and ligands, a 1:1 mixture of saturated aq. TBAB solution and ethanol was used as solvent.

When **7** was treated with a mixture of **L4** (20 mol%) and $Yb(OTf)_3$ (20 mol%), the reaction proceeded smoothly in 87% yield (Table 3, entry 2); but without any signs of stereoselectivity. We then increased the amount of Lewis acid and **L4** to 2.0 equivalents,[15–17] which caused a drop in yield and stereoselectivity (*dr* 14%) (entry 3 and 4). An exchange of ligand **L4** to **L5** resulted in the loss of stereoselectivity (entries 6, 8), while the use of ligands **L6**, **L7** and **L8** abolished reactivity completely (entry 7-10). Our preliminary results suggest that PyBOX ligands (such as **L4** and **L5**) might be suitable for the transformation of sterically demanding substrates as aldehyde **5**, but a careful and intensive evaluation of match or miss-match ligand/substrate pairs will be required to achieve higher yields and selectivities.

Table 3. Screening of different ligands using optimized conditions for sterically complex allyl bromide **7** and (*R*)-citronellal **5d**.



7 5d 8d

Entry	L	LA	Temperature [T]/°C	Yield/ [%]	*dr*[c]/ [%]
1	–	–	r.t.	64	50:50
2	L4[a]	$Yb(OTf)_3$[a]	r.t.	87	50:50
3	L4[b]	$Yb(OTf)_3$[b]	r.t.	47	57:43
4	L4[b]	$Ce(OTf)_3$[b]	r.t.	33	56:44
5	L4[b]	$Ce(OTf)_3$[b]	0	42	59:41
6	L5[b]	$Ce(OTf)_3$[b]	0	67	53:47
7	L8[a]	$Ce(OTf)_3$[b]	r.t.	81	55:45
8	L5[b]	$Ce(OTf)_3$[b]	r.t.	83	50:50
9	L6[b]	$Ce(OTf)_3$[b]	r.t.	–	–
10	L7[b]	$Ce(OTf)_3$[b]	r.t.	–	–
11	L8[b]	$Ce(OTf)_3$[b]	r.t.	–	–

[a] Catalytic amount (20 mol%); [b] stoichiometric amount (2.0 equiv.); [c] determined by chiral HPLC analysis using Lux® 5 µm Amylose-1 column (2% *i*-PrOH in heptane).

To finally demonstrate the applicability of synthesized substrates, compound **8d** was subjected to different synthetic transformations (Figure 5). Catalytic hydrogenation of homoallylic alcohol **8d** using palladium on carbon, for example, yielded product **10** in 41%. Dess-Martin oxidation resulted in the formation of ketone **11** in satisfying 75% yield. Acid and base labile character or substrate **8d** was apparent after the use of saponification conditions led to the formation of lactone **12** in nearly quantitative yield (99%). Protection of homoallylic alcohol **8d** with MOM group was achieved in excellent 94% yield and its subsequent Weinreb amide formation was accomplished in 78% yield to give **13**.

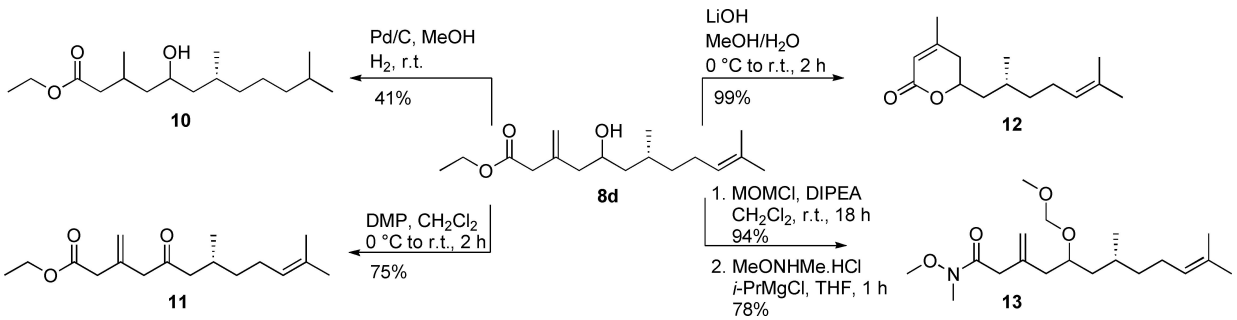


Figure 5. Selected further transformations of homoallylic alcohol **8d** prepared using optimized conditions.

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doi.org/10.1002/ejoc.202300177

Conclusion

In our quest to synthesize building blocks for natural product total synthesis, we optimized reaction conditions for In^0- and Zn^0-mediated Barbier allylation reactions in aqueous media in the presence of tetrabutylammonium salts. Reactions conditions were employed in the transformation of sterically complex allyl bromides and branched aliphatic aldehydes, including allyl bromide **7**, a yet unreported compound for this transformation, and various aldehydes with varying stereoelectronic properties. The obtained substrates carrying the 3-methylene-5-hydroxy core motif and their corresponding lactones represent valuable building blocks and can undergo series of modifications such as hydrogenation, hydrolysis, reduction, aminolysis or Michael addition. Our synthetic study and newly generated substrates provide a solid foundation for further endeavors to develop and optimize stereoselective reaction conditions towards more complex allyl halides and non-aromatic aldehydes.

Experimental Section

experimental procedures/data are provided in the Supporting Information free of charge.

Acknowledgements

We are grateful for financial support from the Leibniz Association. CB greatly acknowledges funding from the European Union's Horizon 2020 research and innovation program (ERC Grant number: 802736, MORPHEUS). We are deeply thankful for funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation, Grant BE4799/2-1, EXSPHINGO). We would like to thank Mrs. Heike Heinecke (Leibniz – HKI) for a measurement of NMR spectra. We also acknowledge funding from the German Exchange Service (DAAD) for Walid K. Al-Jammal. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: synthetic methods · allyl bromide · Barbier reaction · C–C bond formation · natural products

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Manuscript received: February 23, 2023
Revised manuscript received: March 22, 2023
Accepted manuscript online: April 7, 2023