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Lactones

Cascade Synthesis of Five-Membered Lactones using Biomass-Derived Sugars as Carbon Nucleophiles

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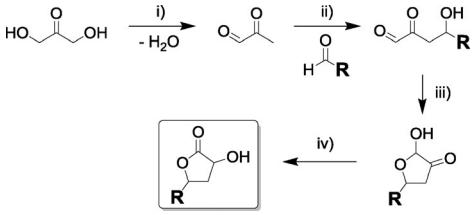
Abstract: We report the cascade synthesis of five-membered lactones from a biomass-derived triose sugar, 1,3-dihydroxyacetone, and various aldehydes. This achievement provides a new synthetic strategy to generate a wide range of valuable compounds from a single biomass-derived sugar. Among several examined Lewis acid catalysts, homogeneous tin chloride catalysts exhibited the best performance to form carbon–carbon bonds. The scope and limitations of the synthesis of five-membered lactones using aldehyde compounds are investigated. The cascade reaction led to high product selectivity as well as diastereoselectivity, and the mechanism leading to the diastereoselectivity was discussed based on isomerization experiments and density functional theory (DFT) calculations. The present results are expected to support new approaches for the efficient utilization of biomass-derived sugars.

Introduction

Carbohydrates derived from lignocellulosic materials represent the largest fraction of terrestrial biomass; various strategies for their efficient use as chemical feedstocks are currently being developed, with the aim of supplementing and ultimately replacing fossil fuels.[1] Significant advances have been reported in the development of catalysts for the conversion of these carbohydrates into key chemicals, such as degradation approaches based on dehydration of hydroxyl groups or cleavage of C–C bonds via a retro-aldol reaction.[2] However, only a limited range of products can be obtained through the above degradation process, and, therefore, a new and efficient method targeted to a wide range of compounds is required.

Five-membered lactones can be used not only as fine chemicals but also as chemical starting materials. Most of the previous reports on chemical[3] or enzymatic[4] syntheses of five-membered lactones are based on multistep processes, and, therefore, the development of a more efficient and a widely applicable approach with an inexpensive and easily available starting material is extremely significant in the field of a green and sustainable chemistry. On the other hand, we previously reported the catalytic transformation of a triose sugar (1,3-dihydroxyacetone, DHA) and formaldehyde into α-hydroxy-γ-butyrolactone (HBL), one of the most important intermediates in pharmaceutical synthesis.[5–8] Among different Lewis acid catalysts examined, tin chlorides exhibited the best performance in the above reaction. The cascade transformation involves four steps: i) isomerization and dehydration of DHA to pyruvic aldehyde (PA), ii) aldol reaction between PA and formaldehyde, iii) formation of the five-membered ring, and iv) proton transfer to form HBL (Scheme 1). Inspired by the synthesis of HBL, we set to develop a new synthetic method for preparing the valuable five-membered lactones using DHA and various aldehydes (other than formaldehyde). Here we report a cascade synthesis of five-membered lactones using biomass-derived sugars and aldehydes, along with homogeneous tin catalysts. Furthermore, the mechanism leading to the product diastereoselectivity is discussed based on isomerization experiments and DFT calculations. We also demonstrate that sequential dehydration followed by hydrogenation can be employed to prepare γ-butyrolactone derivatives.



Scheme 1. Cascade conversion of 1,3-dihydroxyacetone (DHA) and aldehydes via sequential i) isomerization and dehydration of DHA, ii) aldol reaction, iii) cyclization, and iv) 1,2-hydride shift.

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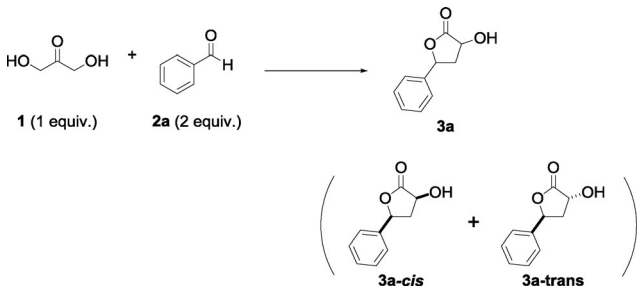
Results and Discussion

Table 1 shows the results of the C–C coupling reaction between DHA (**1**) and benzaldehyde (**2a**) catalyzed by homogeneous tin catalysts. The reactivity studies were performed in batch reactors at 160 °C using 1,4-dioxane as a solvent, **2a** as the aldehyde source, a metal/**1** ratio of 1:50, and a **1**/**2a** ratio of 1:2. As shown in Table 1, the reaction yields and selectivity of the desired coupling product **3a** were calculated based on **1** and **2a**, respectively. In order to increase the yield of the desired product, **1** was added in two batches: 0.5 equivalents of **1** were used in the first run, and the other half was added in the second run.

Table 1. Screening of catalysts with 1,3-dihydroxyacetone (DHA) (**1**) and benzaldehyde (**2a**).[a]



Entry	Catalysts	Conversion of **2a** [%][b]	Yield of **3a** [%][b,c]	Selectivity [%][d]	Diastereoselectivity [*cis*/*trans*][e]
1	$SnCl_2{\cdot}2H_2O$	11	12	55	72:28
2	$SnCl_4{\cdot}5H_2O$	22	31	70	75:25
3[f]	$SnCl_4{\cdot}5H_2O$	22	16	73	74:26
4[g]	$SnCl_4{\cdot}5H_2O$	12	17	71	68:32
5	$SnBr_2$	10	10	50	69:31
6	$SnBr_4$	2	<1	–	–
7	SnI_2	2	1	33	73:27
8	SnI_4	1	<1	–	–
9	$Sn(OAc)_2$	4	<1	–	–
10	$Sn(OTf)_2$	2	<1	–	–
11	SnO_2	2	<1	–	–
12	None	1	<1	–	–

[a] Reaction conditions: **1** (0.65 mmol), **2a** (1.3 mmol), 1,4-dioxane (4.0 mL), $SnCl_4{\cdot}5H_2O$ (0.013 mmol), Ar (4 atm), 1 h×2 batches, 160 °C. All conversions of **1** were >99%. [b] Conversion and yield were determined by ^{1}H NMR analysis. [c] Based on **1**. [d] Based on **2a**. [e] Diastereomer ratio was determined by ^{1}H NMR and GC-FID analysis. [f] **1** (1.3 mmol) was added. [g] **1** (0.65 mmol) was added in 1 step (1 h×1 batch, 160 °C).

Initially, using $SnCl_2{\cdot}2H_2O$ and $SnCl_4{\cdot}5H_2O$, the desired coupling reaction between **1** and **2a** proceeded successfully, and **3a** was obtained in 12 and 31% yields, respectively (Table 1, entries 1 and 2). As the conversion of **2a** was extremely low, the majority of this reactant was recovered unreacted. A highly selective transformation to the desired products (up to 70%) was obtained based on **2a**. Furthermore, the coupling reaction proceeded with high diastereoselectivity, and the *cis* isomer was the main product (*cis*/*trans* ratio ~75:25). On the other hand, when the reaction was performed using a **1** (1.3 mmol)/**2a** ratio of 1:1 or all the DHA was added in 1 step, the yield of **3a** based on **1** was reduced by half (Table 1, entries 3 and 4). We subsequently investigated the influence of the counter-anion of the Sn halides on the formation of each product, by conducting experiments with anhydrous $SnBr_2$, $SnBr_4$, SnI_2, and SnI_4 (Table 1, entries 5–8). The use of $SnBr_2$ gave unsatisfactory product yields, similar to those observed with $SnCl_2{\cdot}2H_2O$ (Table 1, compare entry 1), while the yield of **3a** decreased even further when $SnBr_4$ was employed (Table 1, entries 5 and 6). SnI_2 and SnI_4 exhibited even lower activity and selectivity (Table 1, entries 7 and 8). When other tin(II) or (IV) catalysts were employed, such as $Sn(OAc)_2$, $Sn(OTf)_2$, and SnO_2, the desired product **3a** was not obtained (Table 1, entries 9–11). Furthermore, we screened different metal chloride catalysts, namely, $AlCl_3$, $CrCl_3$, $FeCl_2$, $MgCl_2$, and $TiCl_4$, but they showed no activity for the present reaction. The results in Table 1 show that $SnCl_4{\cdot}5H_2O$ exhibits the best performance in the coupling reaction. However, **2a** led to a decrease in the product yields, in comparison with the yield obtained with formaldehyde.[7] This may be due not only to the steric hindrance of the benzene ring moiety, but also to the lower electrophilicity of the carbonyl carbon atom. Finally, we confirmed that the reaction does not occur in the absence of a catalyst (Table 1, entry 12).

Next, we assessed the scope and limitations of the synthesis of five-membered lactones using several other aldehydes (**2b**–**2j**) in place of **2a** (Table 2 and Figure 1). As $SnCl_4{\cdot}5H_2O$ was the most suitable homogeneous catalyst in the experiments discussed above, it was also employed as a catalyst in this part of the study. The benzaldehyde derivatives 1-naphthaldehyde (**2b**), 2-naphthaldehyde (**2c**), and 4-phenylbenzaldehyde (**2d**) led to **3b**, **3c**, and **3d**, with yields of 26%, 30%, and 31%, respectively. On the other hand, *o*-, *m*-, and *p*-substituted chlorobenzaldehyde **2f**, **2g**, **2h** led to **3f**, **3g**, and **3h**, with yields of 34%, 32%, and 31%, respectively. The use of benzaldehyde derivatives thus led to the highest selectivity in the transformation to the desired coupling products. These results show that the steric hindrance and the substituent position do not affect the reactive performance of the aldehyde source; however, the reaction carried out with anisaldehyde (**2e**) did not yield the desired product **3e**. Finally, using propionaldehyde (**2i**) and enanthaldehyde (**2j**) alkylaldehyde derivatives resulted in **3i**[9]

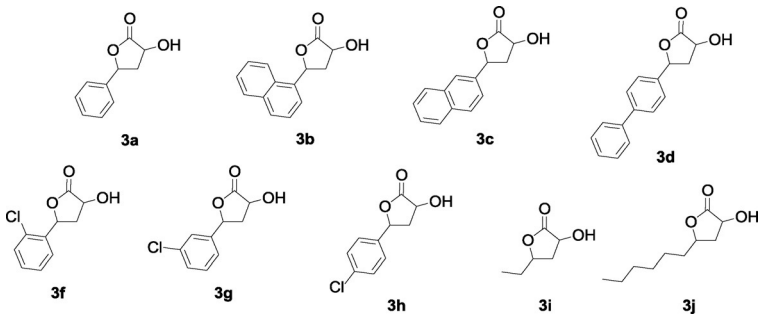
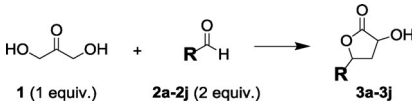


Figure 1. Five-membered lactones prepared by cascade synthesis using different aldehydes as electrophiles.

Table 2. Conversion of 1,3-dihydroxyacetone (DHA) (**1**) and various aldehydes (**2a–2j**) into five-membered lactones.[a]



1 (1 equiv.) **2a-2j** (2 equiv.) **3a-3j**

Entry	Aldehydes (R=)	Aldehydes conversion [%][b]	Products	Yield [%][b,c]	Selectivity [%][d]	Diastereoselectivity [*cis*/*trans*][e]
1	**2a** (Ph)	22	**3a**	31	70	75:25
2	**2b** (1-naphth)	18	**3b**	26	72	72:28
3	**2c** (2-naphth)	19	**3c**	30	79	78:22
4	**2d** (*p*-PhPh)	30	**3d**	31	52	75:25
5	**2e** (*p*-OMePh)	–	**3e**	<1	–	–
6	**2f** (*o*-ClPh)	29	**3f**	34	59	75:25
7	**2g** (*m*-ClPh)	32	**3g**	32	50	78:22
8	**2h** (*p*-ClPh)	28	**3h**	31	55	70:30
9	**2i** (Et)	41	**3i**	23	28	81:19
10	**2j** (*n*-Hexyl)	40	**3j**	24	30	70:30

[a] Reaction conditions: **1** (0.65 mmol), aldehyde (1.3 mmol), 1,4-dioxane (4.0 mL), $SnCl_4{\cdot}5H_2O$ (0.013 mmol), Ar (4 atm), 1 h×2 batches, 160 °C. All conversions of **1** were >99%. [b] Conversion and yield were determined by ^1H NMR analysis. [c] Based on **1**. [d] Based on aldehydes. [e] Diastereomer ratio was determined by ^1H NMR and GC-FID analysis.

and **3j** in 23% and 24% yield, respectively. Alkylaldehyde derivatives thus gave the desired coupling products in lower yields compared to benzaldehyde derivatives. The presence of electron-donating groups thus seems to decrease the electrophilicity of an aldehyde moiety. On the basis of these results, it appears that nearly all aldehydes can be employed in the present cascade reaction system, with *cis* isomers as the main products.

The mechanism controlling the observed diastereoselectivity was also examined. Initially, to investigate whether the diastereoselectivity is based on thermodynamic or kinetic control, isomerization experiments using either **3a-*cis*** or **3a-*trans*** (Scheme 2) were carried out under the same conditions as the reactions in Tables 1 and 2. **3a-*cis*** and **3a-*trans*** were easily interconverted through an α-proton abstraction under these reaction conditions. As shown in Scheme 2, when **3a-*cis*** was employed, only a small percentage was isomerized (*cis*/*trans* = 95:5), whereas the diastereomer ratio changed to *cis*/*trans* = 17:83 using **3a-*trans***. Although the reactions using either **3a-*cis*** or **3a-*trans*** were performed for a longer reaction time, a *cis*/*trans* ratio was unchanged in each case. On the other hand, as shown in entry 1 of Table 1, the coupling reaction between **1** and **2a** yielded **3a** in a *cis*/*trans* ratio of 75:25. However, the *cis*/*trans* diastereoselectivity of **3a** was 68:32 after a single run (Table 1, compare entry 4). Additionally, the *cis*-selectivity decreased when the reaction was performed for a shorter reaction time. In other words, an extension of the reaction time led to an increase in *cis*-selectivity. These results indicate that the **3a-*cis*/3a-*trans*** ratio achieved in the reactions involving **1** and **2a** under thermodynamic control. To confirm this finding, density functional theory (DFT) calculations using the Becke 3-parameter-Lee–Yang–Parr (B3LYP) hybrid functional and 6-31+G* basis set were carried out to determine the thermodynamic stability of the **3a-*cis*** and **3a-*trans*** isomers.[10] The difference in free energy (ΔG°) between **3a-*cis*** and **3a-*trans*** in 1,4-dioxane was approximately 4.67 kJ mol^{-1}, and the corresponding equilibrium constant (K = [**3a-*trans***]/[**3a-*cis***] = exp ($-\Delta G^\circ$/RT), R = 8.31 J mol^{-1} K, T = 433 K) was 0.273, that is, a *cis*/*trans* ratio of approximately 78:22 (Figure 2 and see Table S1 in the Supporting Information). These results support the experimental results in Tables 1 and 2, and show that the diastereoselectivity mechanism for the present system reflects the different thermodynamic stability of the products.

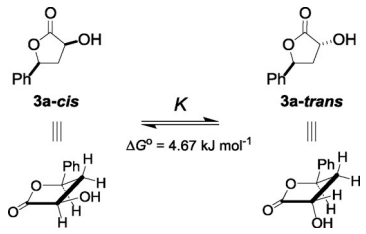
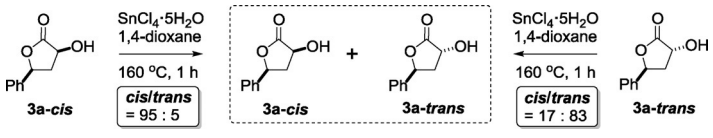
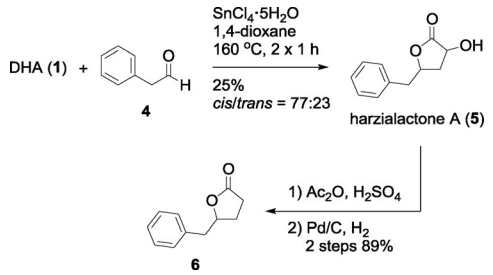


Figure 2. Relative thermodynamic stability of **3a-*cis*** and **3a-*trans*** isomers.

Finally, we demonstrated the cascade synthesis of a bioactive compound, harzialactone A (**5**), a marine metabolite isolated from the culture broth of a strain of Trichoderma harzianum OUPS-N115 by Numata and co-workers, which exhibits antitumor and cytotoxic activities against cultured P388 cells (Scheme 3).[11] The methods for preparing compound **5** reported to date have been based on either multi-step conversions or multi-component reactions.[12] Treatment of **1** and phenylacetaldehyde (**4**) with $SnCl_4{\cdot}5H_2O$ provided **5** in 25% yield (conversion of **4** = 32%, selectivity = 39%, *cis*/*trans* ratio = 77:23). These results show that the present cascade procedure is applicable to the efficient synthesis not only of important chemicals, but also of bioactive compounds. Furthermore, we performed the synthesis of γ-butyrolactone derivatives through dehydration followed by hydrogenation. The removal of hydroxyl group in α-position enhances the value of five-membered lactone derivatives. Acid treatment of the hy-



Scheme 2. Isomerization experiments using the **3a-*cis*** and **3a-*trans*** diastereomers.



Scheme 3. Scheme of dehydration followed by hydrogenation yielding γ-butyrolactone.

droxyl **5**, followed by hydrogenation catalyzed by palladium under hydrogen atmosphere yielded the desired lactone **6**[13] in two steps, with 89% yield. This result highlights the diversity of compounds that could be obtained through this synthetic approach.

Conclusions

We report a new route to the synthesis of five-membered lactones, which can be used not only as fine chemicals but also as chemical starting materials, using a biomass-derived sugar (1,3-dihydroxyacetone, DHA) as a carbon nucleophile and various aldehydes. With this achievement, we could propose a new synthetic strategy to generate a wide range of valuable compounds from a combination of a single biomass-derived triose sugar and electrophiles.

Among several examined Lewis acid catalysts, tin chlorides exhibited the best performance as homogeneous catalysts for the formation of C–C bonds between DHA and several aldehydes. The scope and limitations of the present synthesis were investigated, and we found that the present cascade reaction can be carried out with most aldehydes. Furthermore, isomerization experiments and DFT calculations showed that the observed diastereoselectivity is controlled by the different thermodynamic stability of the products. Finally, we demonstrated that sequential dehydration followed by hydrogenation can be employed to prepare γ-butyrolactone derivatives. Future work will involve the development of high-activity catalysts to increase the conversion efficiency of the aldehydes to the products.

Compared to conventional biomass conversion methods based on a dehydration of hydroxyl groups or the cleavage of C–C bonds via a retro-aldol reaction, the present method allows to obtain a greater variety of compounds with diverse structures via C–C bond formation, using a biomass-derived sugar.[14] The method reported in this study can thus provide a new possible route to the use of biomass-derived sugars.

Experimental Section

Analytical Techniques: The reaction products were identified by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) and gas chromatography-mass spectrometry (GC-MS). NMR spectra were recorded on Bruker Biospin AVANCE 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) or Bruker Biospin AVANCE 500 (500 MHz for ^{1}H, 125 MHz for ^{13}C) instruments in the solvents indicated below. Chemical shifts (ppm) were reported in parts per million (ppm), using tetramethylsilane as internal (0 ppm) reference, in $CDCl_3$ solutions. The ^{1}H NMR spectra were referenced to the $CDCl_3$ (7.26 ppm), whereas the ^{13}C NMR data were reported relative to $CDCl_3$ (77.0 ppm) as an external standard. Multiplicities are reported using the following abbreviations: *s*: singlet, *d*: doublet, *t*: triplet, *q*: quartet, *m*: multiplet, *br*: broad, *J*: coupling constant in Hz. A Shimadzu GC14B gas chromatograph equipped with a 30 m Ultra ALLOY$^+$-1 column was used for the gas chromatography with flame ionization detection (GC-FID) analysis, using the following temperature program: i) 2 min at 323 K, ii) linear ramp of 3 K min^{-1} to 373 K, iii) 5 min at 373 K, iv) linear ramp of 10 K min^{-1} to 553 K, and v) 20 min at 553 K. A Shimadzu QP2010 Plus instrument equipped with a TC-1 column was used for the GC-MS analysis. IR spectra were recorded on an FTIR 6100 spectrometer (JASCO) with a triglycine sulfate (TGS) detector. Only the strongest and/or structurally important IR peaks were reported. Electrospray ionization time-of-flight (ESI-TOF) mass spectra were measured with a Bruker micrOTOF II instrument. All reactions were monitored by thin-layer chromatography carried out on Merck silica gel plates (60F-254) with UV light, visualized by a 10% ethanolic phosphomolybdic acid or basic KMn_2O_7 solution. Wakogel C-200 silica gel was used for the column chromatography. Materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and Aldrich Inc., and used without further purification.

Synthetic procedure (Table 1, entry 2): A 50 cm^3 stainless steel autoclave equipped with a magnetic bar was charged with 1,3-dihydroxyacetone (29.3 mg, 0.33 mmol), benzaldehyde (133 mg, 1.3 mmol), 1,4-dioxane (4.0 mL), and $SnCl_4·5H_2O$ (4.6 mg, 0.013 mmol) at room temperature, then filled with argon (4 atm). After being stirred at 160 °C for 1 h under argon, the reaction mixture was cooled down to room temperature, then 1,3-dihydroxyacetone (29.3 mg, 0.33 mmol) was added to the reaction mixture, and the autoclave was filled with argon (4 atm). After being stirred at 160 °C for 1 h under argon, the reaction mixture was cooled down to room temperature, and 1,3,5-trimethylbenzene was added as an internal standard. The yield and diastereoselectivity of the desired products and the conversion rate of the aldehydes were determined at this point. Subsequently, a large amount (250 mg) of an anion exchange resin (Dowex Monosphere 550 A, OH^- form) based on a quaternary amine was added. After being stirred at the same temperature for 0.5 h, the reaction mixture was filtered through a pad of Celite and concentrated in vacuo. The residue was chromatographed on silica gel with 59:40:1 hexane:ethyl acetate:triethyl amine ratio to give the desired product.

Quantum chemical calculations: The DFT calculations were conducted at the B3LYP level theory (6–31+G* basis sets for H, C, and O) by using conductor-like polarizable continuum model (CPCM) with parameters of the Universal Force Field (UFF).[15] The geometries of **3a-*cis*** and **3-*trans*** were optimized, and the vibrational analysis was performed to confirm that they have no imaginary frequency. The Gibbs free energies (at 1 atm and 433.15 K) were compared. All calculations were performed with the Gaussian 09 program package.[10]

3a: According to the general procedure, the desired product **3a** was obtained in 31% yield (conversion of **2a** = 22%, selectivity = 70%, *cis*/*trans* = 75:25). **3a-*cis***: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.35 (m, 5H), 5.37 (dd, 1H, *J* = 5.3, 11.0 Hz), 4.69 (dd, 1H, *J* = 8.1, 11.2 Hz), 3.00 (ddd, 1H, *J* = 5.2, 8.1, 12.6 Hz), 2.25 ppm (ddd, 1H, *J* = 11.1, 11.1, 12.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.8, 137.7, 129.0, 128.9, 125.9, 77.7, 69.0, 39.6 ppm; IR (neat): $\tilde{\nu}$ = 3368, 2918,

1780, 1457, 1186, 1121, 993, 939, 763, 725, 698 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 201.0522, found 201.0517. **3a-*trans***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.44$–7.27 (m, 5H), 5.71 (dd, 1H, $J=4.2$, 7.8 Hz), 4.55 (dd, 1H, $J=7.7$, 7.7 Hz), 2.69 (ddd, 1H, $J=7.6$, 7.6, 13.2 Hz), 2.61 ppm (ddd, 1H, $J=4.2$, 7.8, 13.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=176.9$, 138.8, 128.9, 128.6, 125.0, 78.5, 67.2, 38.2 ppm; IR (neat): $\tilde{\nu}=3386$, 2926, 1775, 1456, 1182, 1122, 1007, 946, 701 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 201.0522, found 201.0519.

3b: According to the general procedure, the desired product **3b** was obtained in 26% yield (conversion of **2b** = 18%, selectivity = 72%, *cis*/*trans* = 72:28). **3b-*cis***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.95$–7.85 (m, 3H), 7.66–7.48 (m, 4H), 6.13 (dd, 1H, $J=5.3$, 10.8 Hz), 4.82 (dd, 1H, $J=8.1$, 11.0 Hz), 3.23 (ddd, 1H, $J=5.2$, 8.1, 13.0 Hz), 2.39 ppm (ddd, 1H, $J=10.9$, 10.9, 12.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=176.6$, 133.7, 133.3, 130.0, 129.4, 129.2, 126.8, 126.1, 125.5, 122.7, 122.4, 75.1, 69.0, 38.8 ppm; IR (neat): $\tilde{\nu}=3367$, 3056, 2925, 2855, 1775, 1599, 1510, 1451, 1331, 1199, 1130, 991, 927, 802, 777, 736 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 251.0679, found 251.0674. **3b-*trans***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.94$–7.80 (m, 3H), 7.62–7.42 (m, 4H), 6.39 (dd, 1H, $J=3.3$, 8.1 Hz), 4.57 (dd, 1H, $J=8.2$, 8.2 Hz), 2.87 (ddd, 1H, $J=8.3$, 8.3, 13.0 Hz), 2.75 ppm (ddd, 1H, $J=3.4$, 8.1, 12.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=177.5$, 134.3, 133.8, 129.4, 129.2, 129.1, 126.8, 126.2, 125.2, 122.4, 121.0, 76.1, 67.0, 37.2 ppm; IR (neat): $\tilde{\nu}=3423$, 3057, 2944, 1777, 1600, 1512, 1398, 1334, 1261, 1185, 1120, 1001, 942, 790, 734 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 251.0679, found 251.0674.

3c: According to the general procedure, the desired product **3c** was obtained in 30% yield (conversion of **2c** = 19%, selectivity = 79%, *cis*/*trans* = 78:22). **3c-*cis***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.92$–7.84 (m, 4H), 7.55–7.50 (m, 2H), 7.45 (dd, 1H, $J=1.6$, 8.6 Hz), 5.54 (dd, 1H, $J=5.2$, 10.9 Hz), 4.74 (dd, 1H, $J=8.1$, 11.2 Hz), 3.07 (ddd, 1H, $J=5.3$, 8.2, 12.8 Hz), 2.34 ppm (ddd, 1H, $J=11.2$, 11.2, 12.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$/MeOD): $\delta=177.4$, 135.2, 133.3, 132.9, 128.8, 127.9, 127.6, 126.5, 125.1, 122.9, 77.7, 68.6, 39.6 ppm; IR (neat): $\tilde{\nu}=3309$, 3048, 2998, 1780, 1602, 1445, 1371, 1308, 1205, 1118, 990, 935, 898, 877, 861, 822, 800, 745 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 251.0679, found 251.0674. **3c-*trans***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.91$–7.82 (m, 3H), 7.76 (br s, 1H), 7.55–7.49 (m, 2H), 7.37 (m, 1H), 5.87 (dd, 1H, $J=4.4$, 7.5 Hz), 4.59 (dd, 1H, $J=7.7$, 7.7 Hz), 2.76 (ddd, 1H, $J=7.6$, 7.6, 13.3 Hz), 2.71 ppm (ddd, 1H, $J=4.4$, 7.8, 13.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=177.0$, 136.1, 133.1, 13.0, 129.0, 128.1, 127.8, 126.8, 126.6, 123.9, 122.6, 78.6, 67.2, 38.1 ppm; IR (neat): $\tilde{\nu}=3410$, 3054, 2929, 1777, 1680, 1602, 1508, 1188, 1122, 1075, 1041, 939, 896, 861, 820, 755 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 251.0678, found 251.0679.

3d: According to the general procedure, the desired product **3d** was obtained in 31% yield (conversion of **2d** = 30%, selectivity = 52%, *cis*/*trans* = 75:25). **3d-*cis***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.65$–7.56 (m, 4H), 7.45 (t, 4H, $J=7.2$ Hz), 7.37 (t, 1H, $J=7.2$ Hz), 5.41 (dd, 1H, $J=5.3$, 11.0 Hz), 4.71 (dd, 1H, $J=8.1$, 11.2 Hz), 3.04 (ddd, 1H, $J=5.2$, 8.1, 12.6 Hz), 2.30 ppm (ddd, 1H, $J=11.2$, 11.2, 12.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$/MeOD): $\delta=177.4$, 141.8, 140.2, 136.8, 128.7, 127.5, 127.4, 127.0, 126.2, 77.2, 68.6, 39.6 ppm; IR (neat): $\tilde{\nu}=$ 3394, 2999, 2961, 2927, 1782, 1637, 1447, 1413, 1198, 1120, 994, 938, 841, 766 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 277.0835, found 277.0829. **3d-*trans***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.65$–7.56 (m, 4H), 7.45 (t, 2H, $J=7.2$ Hz), 7.40–7.34 (m, 3H), 5.76 (dd, 1H, $J=$ 4.4, 7.6 Hz), 4.58 (dd, 1H, $J=7.7$, 7.7 Hz), 2.72 (ddd, 1H, $J=7.7$, 7.7, 13.3 Hz), 2.65 ppm (ddd, 1H, $J=4.4$, 7.8, 13.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=176.9$, 141.6, 140.3, 137.7, 128.9, 127.7, 127.6, 127.1, 125.5, 78.4, 67.3, 38.2 ppm; IR (neat): $\tilde{\nu}=3421$, 2923, 1771, 1638, 1188, 1125, 1077, 1040, 1003, 945, 840, 750 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 277.0835, found 277.0838.

3f: According to the general procedure, the desired product **3f** was obtained in 34% yield (conversion of **2f** = 29%, selectivity = 59%, *cis*/*trans* = 75:25). **3f-*cis***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.50$ (dd, 1H, $J=1.6$, 7.3 Hz), 7.41–7.27 (m, 3H), 5.74 (dd, 1H, $J=5.4$, 10.6 Hz), 4.71 (dd, 1H, $J=8.4$, 11.0 Hz), 3.22 (ddd, 1H, $J=5.4$, 8.2, 12.7 Hz), 2.07 ppm (ddd, 1H, $J=11.0$, 11.0, 12.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=176.8$, 136.0, 131.4, 129.71, 129.67, 127.6, 126.2, 74.7, 68.8, 38.4 ppm; IR (neat): $\tilde{\nu}=3394$, 2939, 1782, 1576, 1446, 1322, 1187, 1015, 941, 758, 705 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 235.0132, found 235.0131. **3f-*trans***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.41$ (m, 1H), 7.32–7.28 (m, 3H), 5.94 (dd, 1H, $J=3.6$, 8.1 Hz), 4.51 (dd, 1H, $J=8.1$, 8.1 Hz), 2.78 (ddd, 1H, $J=8.2$, 8.2, 13.3 Hz), 2.57 ppm (ddd, 1H, $J=3.7$, 8.1, 13.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=177.0$, 136.8, 131.2, 130.1, 129.6, 127.3, 125.1, 76.0, 66.7, 36.9 ppm; IR (neat): $\tilde{\nu}=3420$, 2924, 1784, 1474, 1443, 1123, 1040, 754 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 235.0132, found 235.0131.

3g: According to the general procedure, the desired product **3g** was obtained in 32% yield (conversion of **2g** = 32%, selectivity = 50%, *cis*/*trans* = 78:22). **3g-*cis***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.40$–7.34 (m, 3H), 7.26 (m, 1H), 5.34 (dd, 1H, $J=5.4$, 10.9 Hz), 4.68 (dd, 1H, $J=8.1$, 11.1 Hz), 3.02 (ddd, 1H, $J=5.4$, 8.1, 12.7 Hz), 2.20 ppm (ddd, 1H, $J=11.1$, 11.1, 12.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=$ 176.3, 139.8, 134.9, 130.2, 129.1, 125.9, 123.8, 76.7, 68.8, 39.5 ppm; IR (neat): $\tilde{\nu}=3348$, 2925, 1778, 1601, 1435, 1321, 1190, 1128, 997, 950, 789 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 235.0132, found 235.0129. **3g-*trans***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.36$–7.28 (m, 3H), 7.18 (m, 1H), 5.67 (dd, 1H, $J=4.4$, 7.7 Hz), 4.52 (dd, 1H, $J=$ 7.5, 7.5 Hz), 2.71 (m, 1H), 2.56 ppm (ddd, 1H, $J=4.4$, 7.8, 12.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=176.4$, 140.9, 135.0, 130.3, 128.7, 125.2, 123.1, 77.6, 67.0, 38.1 ppm; IR (neat): $\tilde{\nu}=3379$, 2928, 1776, 1672, 1576, 1432, 1181, 1122, 1040, 959, 789 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 235.0132, found 235.0131.

3h: According to the general procedure, the desired product **3h** was obtained in 31% yield (conversion of **2h** = 28%, selectivity = 55%, *cis*/*trans* = 70:30). **3h-*cis***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.39$ (d, 2H, $J=8.6$ Hz), 7.30 (d, 2H, $J=8.6$ Hz), 5.34 (dd, 1H, $J=5.3$, 10.9 Hz), 4.68 (dd, 1H, $J=8.1$, 11.2 Hz), 3.00 (ddd, 1H, $J=5.4$, 8.2, 12.8 Hz), 2.19 ppm (ddd, 1H, $J=11.0$, 11.0, 12.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=176.5$, 136.3, 135.0, 129.1, 127.2, 76.9, 68.9, 39.5 ppm; IR (neat): $\tilde{\nu}=3357$, 2925, 1777, 1675, 1494, 1320, 1188, 1128, 1091, 1014, 937, 824, 739 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 235.0132, found 235.0131. **3h-*trans***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.40$–7.35 (m, 2H), 7.26–7.21 (m, 2H), 5.68 (dd, 1H, $J=$ 4.5, 7.2 Hz), 4.52 (dd, 1H, $J=7.5$, 7.5 Hz), 2.69 (ddd, 1H, $J=7.3$, 7.3, 13.5 Hz), 2.56 ppm (ddd, 1H, $J=4.6$, 7.6, 13.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=176.8$, 137.3, 134.5, 129.1, 126.5, 78.0, 67.2, 38.2 ppm; IR (neat): $\tilde{\nu}=3402$, 2928, 1776, 1493, 1415, 1179, 1123, 1014, 946, 832, 737, 498 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 235.0132, found 235.0133.

3i: According to the general procedure, the desired product **3i** was obtained in 23% yield (conversion of **2i** = 41%, selectivity = 28%, *cis*/*trans* = 81:19). **3i-*cis***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=4.52$ (dd, 1H, $J=8.4$, 11.1 Hz), 4.32 (m, 1H), 2.70 (ddd, 1H, $J=5.0$, 8.4, 11.1 Hz), 1.93–1.67 (m, 3H), 1.02 ppm (t, 3H, $J=7.4$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=177.2$, 78.3, 68.7, 36.6, 28.3, 9.2 ppm; IR (neat): $\tilde{\nu}=3385$, 2971, 1771, 1460, 1203, 1134, 1001, 947, 806 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 153.0522, found 153.0521. **3i-*trans***: ^1H NMR (400 MHz, $CDCl_3$): $\delta=4.58$ (m, 1H), 4.50 (dd, 1H, $J=$ 7.7, 7.7 Hz), 2.34 (ddd, 1H, $J=7.5$, 7.5, 13.3 Hz), 2.27 (ddd, 1H, $J=$ 4.2, 8.2, 12.4 Hz), 1.77–1.61 (m, 2H), 1.01 ppm (t, 3H, $J=7.4$ Hz);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.2, 79.8, 67.4, 35.1, 28.7, 9.6 ppm; IR (neat): $\tilde{\nu}$ = 3390, 2922, 1775,1462, 1189, 1127, 948 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 153.0522, found 153.0522.

3j: According to the general procedure, the desired product **3j** was obtained in 24% yield (conversion of **2j** = 40%, selectivity = 30%, *cis/trans* = 70:30). **3j-*cis***: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.52 (dd, 1H, *J* = 8.4, 11.0 Hz), 4.37 (m, 1H), 3.05 (br s, 1H), 2.68 (ddd, 1H, *J* = 5.1, 8.4, 12.6 Hz), 1.87 (ddd, 1H, *J* = 10.8, 10.8, 12.6 Hz), 1.78 (m, 1H), 1.65 (m, 1H), 1.50–1.25 (m, 8H), 0.89 ppm (t, 3H, *J* = 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.6, 77.3, 68.7, 37.1, 35.3, 31.6, 28.9, 24.9, 22.5, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 3393, 2931, 2858, 1773, 1457, 1331, 1204, 1134, 994, 904, 804, 730, 593 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 209.1148, found 209.1147. **3j-*trans***: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.63 (m, 1H), 4.49 (dd, 1H, *J* = 7.8, 7.8 Hz), 2.77 (br s, 1H), 2.34 (ddd, 1H, *J* = 7.5, 7.5, 13.3 Hz), 2.25 (ddd, 1H, *J* = 4.2, 8.2, 12.4 Hz), 1.68 (m, 1H), 1.58 (m, 1H), 1.45–1.25 (m, 8H), 0.89 ppm (t, 3H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.4, 78.8, 67.5, 35.7, 35.6, 31.6, 28.8, 25.2, 22.5, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 3401, 2930, 2858, 1777, 1458, 1189, 1123, 953, 727 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 209.1148, found 209.1148.

5: According to the general procedure, the desired product **5** was obtained in 25% yield (conversion of aldehyde **4** = 32%, selectivity = 39%, *cis/trans* = 77:23). **5-*cis***: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.21 (m, 5H), 4.58 (m, 1H), 4.49 (dd, 1H, *J* = 8.3, 11.0 Hz), 3.14 (dd, 1H, *J* = 6.5, 14.0 Hz), 2.96 (dd, 1H, *J* = 6.2, 14.0 Hz), 2.62 (ddd, 1H, *J* = 5.0, 8.3, 12.7 Hz), 1.95 ppm (ddd, 1H, *J* = 10.7, 10.7, 12.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.0, 135.4, 129.4, 128.7, 127.1, 77.3, 68.5, 41.3, 36.6 ppm; IR (neat): $\tilde{\nu}$ = 3406, 2924, 1771, 1455, 1196, 1128, 989, 700 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 215.0679, found 215.0673. **5-*trans***: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.21 (m, 5H), 4.91 (m, 1H), 3.99 (dd, 1H, *J* = 8.1, 8.1 Hz), 2.98 (m, 1H, *J* = 5.7 Hz), 2.37 (ddd, 1H, *J* = 3.7, 8.4, 12.0 Hz), 2.28 ppm (ddd, 1H, *J* = 7.9, 7.9, 13.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.3, 135.2, 129.6, 128.8, 127.2, 78.2, 67.0, 41.1, 34.4 ppm; IR (neat): $\tilde{\nu}$ = 3402, 2923, 1775, 1455, 1187, 1122, 964, 700 cm^{-1}; HRMS (ESI-TOF) $[M+Na]^+$ calcd. 215.1679, found 215.0680.

6: To a stirred solution of **5** (20.0 mg, 0.104 mmol) in Ac_2O (1.0 mL), a catalytic amount of H_2SO_4 was added at 0 °C under argon. After being stirred at the same temperature for 1 h, the reaction mixture was neutralized by amine and concentrated in vacuo. The residue was used for the next reaction without further purification.

To a stirred solution of the above residue in EtOAc (1.0 mL)/MeOH (1.0 mL), a catalytic amount of Pd/C was added at room temperature under argon. After being stirred at the same temperature for 2 h under hydrogen (1 atm), the reaction mixture was filtered through a pad of Celite and concentrated in vacuo. The residue was chromatographed on silica gel with 80:20 hexane:ethyl acetate to give **6** (16.3 mg, 0.0926 mmol, in 2 steps at 89%).

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