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# Investigation of the Selectivity of the Palladium-Catalyzed Aroylation and Arylation of Stannyl Glycals with Aroyl Chlorides

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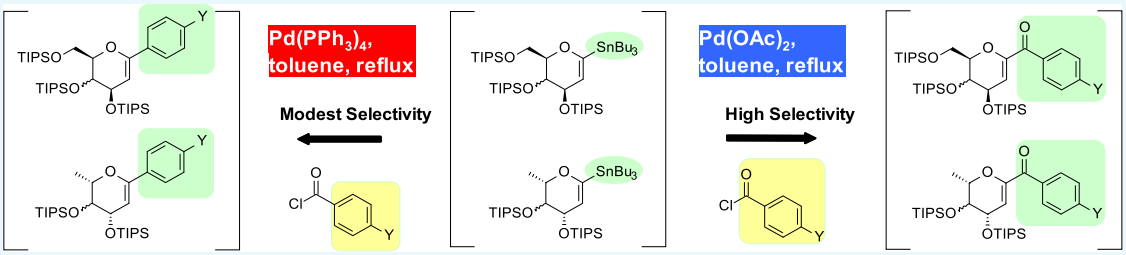


**ABSTRACT:** The selectivity of the palladium-catalyzed aroylation and arylation of 1-tributylstannyl glycals with aroyl chlorides was investigated. The selectivity was controlled by the palladium catalyst, and high selectivity was achieved *via* ligand modification of the palladium catalyst. The reaction catalyzed by $Pd(OAc)_2$ provided aroyl *C*-glycals with high selectivity, whereas the reaction catalyzed by $Pd(PPh_3)_4$ produced aryl *C*-glycals with diminished selectivity. The scope and limitation of the selectivity in this reaction are discussed.

## INTRODUCTION

The palladium-catalyzed cross-coupling of acyl halides is a useful reaction for the preparation of carbonyl compounds.[1,2] The intermediate of this reaction, acylpalladium complex, leads to the desired carbonyl compound, whereas a decarbonylated compound is obtained if decarbonylation of the intermediate occurs.[3,4] In the Stille reaction of aroyl chlorides, it was reported that the addition of $Et_3SiH$ was effective for aromatic ketone synthesis,[2a] and the use of *bis*(di-*tert*-butylchlorophosphine)-palladium(II) dichloride was beneficial for preparing a variety of diarylketones.[2c] 1-(2-Pyridylethynyl)-2-(2-thienylethynyl)-benzene was also reported as an efficacious ligand in the palladium-catalyzed Heck reaction of acid chlorides for synthesizing alkynones.[2b] Conversely, a decarbonylative cross-coupling reaction was reported to be catalyzed by $Pd^0$/Brettphos,[4b] and decarbonylation of the Mizoroki−Heck-type reaction in the presence of $(PhCH_2)Bu_3NCl$ has been described.[4i,j] Thus, the selectivity of the palladium-catalyzed cross-coupling of acyl halides remains incompletely understood, and further investigations are needed.

Aryl *C*-glycosides are naturally occurring compounds, and many synthetic analogues have been reported to possess a variety of biological activities.[5] The palladium-catalyzed arylation of 1-tributylstannyl glycal is a useful reaction for obtaining aryl *C*-glycoside analogues, and it has been used for natural product synthesis.[6] In the course of research dedicated to expanding the synthetic utility of glycals,[7] a novel type of aroyl *C*-glycoside that is expected to display a variety of biological activities was designed. To investigate the biological roles of aroyl *C*-glycoside, the elaboration of its synthetic method was required because only limited examples have been reported.[8,9] We found that the selectivity of the palladium-catalyzed aroylation and arylation of 1-tributylstannyl glycals **1** was influenced by the palladium catalyst. In this study, we demonstrated that aroyl *C*-glycals can be obtained in a selective manner by modifying the ligand of the catalyst, whereas the selectivity for synthesizing aryl *C*-glycals was diminished.[10]

## RESULTS AND DISCUSSION

The study was initiated by optimizing the reaction of triisopropylsilyl (TIPS)-protected 1-tributylstannyl D-glucal **1a** with aroyl chloride **2** to obtain aroyl *C*-glucal **3**, as presented in Table 1 (0.10 mmol scale). As reported previously,[7] we optimized the cross-coupling reaction condition for benzyl *C*-glycal synthesis as 10 mol % $PdCl_2$[1,2-*bis*(diphenylphosphino)-ethane (dppe)], 2 equiv of $Na_2CO_3$, and 3 equiv of benzyl bromide in refluxing toluene. To elaborate the synthetic utility of this reaction condition, 1.2 equiv of benzoyl chloride (**2a**) was reacted with 1-tributylstannyl D-glucal **1a** in refluxing toluene in the presence of 10 mol % $PdCl_2$(dppe), which resulted in almost no reaction (entry 1). When $Na_2CO_3$ was omitted, trace amounts of aroyl *C*-glucal **3a** and aryl *C*-glucal **4a** were observed

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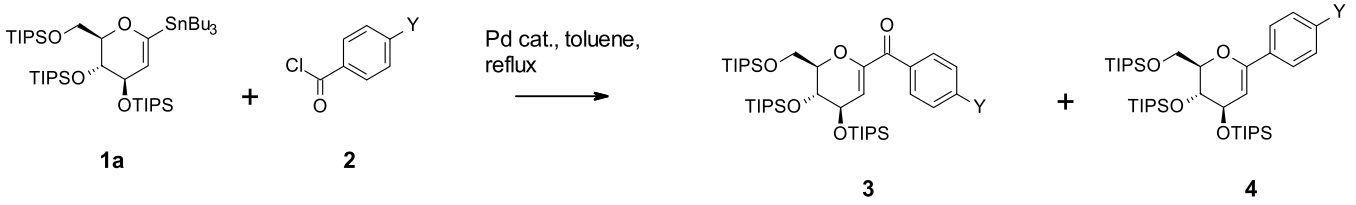
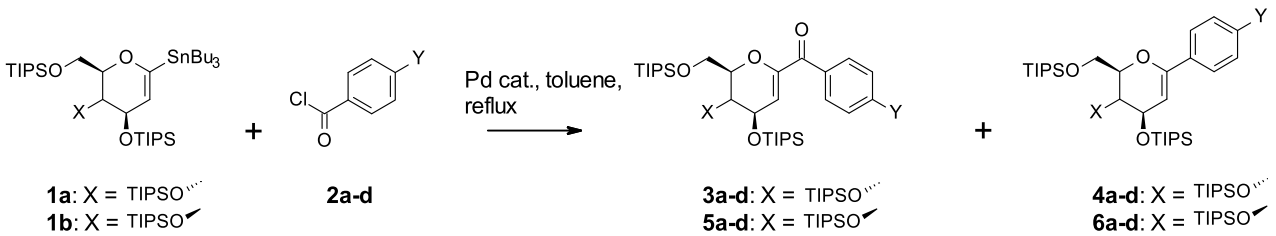
**Table 1. Influence of Palladium Catalysts on the Selectivity of 3 and 4**[a]




| entry | 2 | Y | equiv | catalyst (10 mol %) | additives (equiv) | yield of 3 (%)[b] | yield of 4 (%)[b] | reaction time (h) |
|---|---|---|---|---|---|---|---|---|
| 1 | **2a** | H | 1.2 | $PdCl_2$(dppe) | $Na_2CO_3$ (3 equiv) | 0 | 0 | 30 |
| 2 | **2a** | H | 1.2 | $PdCl_2$(dppe) | none | <1 | <1 | 30 |
| 3 | **2a** | H | 1.2 | $PdCl_2(CH_3CN)_2$ | $Na_2CO_3$ (3 equiv) | 20 (**3a**) | <1 | 7 |
| 4 | **2a** | H | 3 | $PdCl_2(CH_3CN)_2$ | none | 70 (**3a**) | <1 | 1.5 |
| 5 | **2b** | $CO_2Me$ | 3 | $PdCl_2(CH_3CN)_2$ | none | 22 (**3b**) | <1 | 5.5 |
| 6 | **2c** | CN | 3 | $PdCl_2(CH_3CN)_2$ | none | 24 (**3c**) | 13 (**4c**) | 1 |
| 7 | **2b** | $CO_2Me$ | 3 | $PdCl_2(PhCN)_2$ | none | 21 (**3b**) | <1 | 5 |
| 8 | **2b** | $CO_2Me$ | 3 | $PdCl_2$(dppe) | none | 15 (**3b**) | 2 (**4b**) | 25 |
| 9 | **2b** | $CO_2Me$ | 3 | $PdCl_2$(dppf) | none | 12 (**3b**) | 3 (**4b**) | 25 |
| 10 | **2b** | $CO_2Me$ | 3 | $PdCl_2$ | none | 17 (**3b**) | 0 (**4b**) | 25 |
| 11 | **2b** | $CO_2Me$ | 3 | $Pd(OAc)_2$ | none | 57 (**3b**) | <1 | 0.5 |
| 12 | **2b** | $CO_2Me$ | 3 | $Pd(OAc)_2$ | CuI (2 equiv) | 44 (**3b**) | 6 (**4b**) | 1.5 |
| 13 | **2b** | $CO_2Me$ | 3 | $Pd(TFA)_2$ | none | 19 (**3b**) | <1 | 3 |
| 14 | **2b** | $CO_2Me$ | 3 | $[PdCl_2(allyl)_2]_2$ | none | 12 (**3b**) | 3 (**4b**) | 5 |
| 15 | **2b** | $CO_2Me$ | 3 | $Pd_2(dba)_3$ | none | <1 | 0 | 29.5 |
| 16 | **2b** | $CO_2Me$ | 3 | $Pd(acac)_2$ | none | 44 (**3b**) | <1 | 3 |
| 17 | **2b** | $CO_2Me$ | 3 | $PdCl_2$(cod) | none | 20 (**3b**) | <1 | 3 |
| 18 | **2b** | $CO_2Me$ | 3 | $PdCl_2$(nbd) | none | 26 (**3b**) | <1 | 6.5 |
| 19 | **2b** | $CO_2Me$ | 3 | $Pd_2(TMEDA)_2$ | none | 24 (**3b**) | 0 | 29 |
| 20 | **2b** | $CO_2Me$ | 3 | $Pd_2(EDA)_2$ | none | 28 (**3b**) | 0 | 30.5 |
| 21 | **2b** | $CO_2Me$ | 3 | $PdCl_2$(2,2′-bipyridine) | none | 36 (**3b**) | 0 | 30.5 |
| 22 | **2b** | $CO_2Me$ | 3 | $Pd(PPh_3)_4$ | none | <1 | 71 (**4b**) | 7.5 |
| 23 | **2b** | $CO_2Me$ | 3 | $PdCl_2(PPh_3)_2$ | none | 4 (**3b**) | 38 (**4b**) | 3 |
| 24 | **2b** | $CO_2Me$ | 3 | $Pd(AsPh_3)_4$ | none | 12 (**3b**) | 8 (**4b**) | 4.5 |

[a]The reaction was performed using **1a** (0.10 mmol), **2** (0.30 mmol), and Pd catalyst (0.010 mmol) in toluene (5 mL) under reflux. [b]Isolated yield.

**Table 2. Reactions of 1-Tributylstannyl D-Glucal 1a or D-Galactal 1b with Aroyl Chlorides 2a−d**[a]




| | | | $Pd(OAc)_2$ | | | $Pd(PPh_3)_4$ | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | Y | yield of aroyl *C*-glycal (%)[b] | yield of aryl *C*-glycal (%)[b] | reaction time (h) | yield of aroyl *C*-glycal (%)[b] | yield of aryl *C*-glycal (%)[b] | reaction time (h) |
| **1a** | **2a** | H | 89 (**3a**) | <1 (**4a**) | 1 | 0 (**3a**) | 67 (**4a**) | 11 |
| | **2b** | 4-$CO_2Me$ | 57 (**3b**) | <1 (**4b**) | 0.5 | <1 (**3b**) | 71 (**4b**) | 7.5 |
| | **2c** | 4-CN | 48 (**3c**) | 22 (**4c**) | 4 | <1 (**3c**) | 56 (**4c**) | 34 |
| | **2d** | 4-Me | 54 (**3d**) | 0 (**4d**) | 1 | 30 (**3d**) | <1 (**4d**) | 7 |
| **1b** | **2a** | H | 82 (**5a**) | 0 (**6a**) | 1 | 25 (**5a**) | 50[c] (**6a**) | 4.5 |
| | **2b** | 4-$CO_2Me$ | 74 (**5b**) | 0 (**6b**) | 1 | 25 (**5b**) | <1 (**6b**) | 4.5 |
| | **2c** | 4-CN | 62 (**5c**) | <1 (**6c**) | 1 | 46 (**5c**) | 16[c] (**6c**) | 28 |
| | **2d** | 4-Me | 88 (**5d**) | 0 (**6d**) | 0.5 | 27 (**5d**) | 30[c] (**6d**) | 25 |

[a]The reaction was performed using **1c** (0.10 mmol), **2** (0.30 mmol), and Pd catalyst (0.010 mmol %) in refluxing toluene (5 mL). [b]Isolated yield. [c]Product was isolated with an inseparable impurity.

(entry 2). However, the reaction remained sluggish, and a large amount of the starting D-glucal **1a** was not consumed. The use of $PdCl_2(CH_3CN)_2$ has been reported to be effective for aroyl *C*-glucal synthesis,[8] and it increased the yield **3a** (20%, entry 3). As



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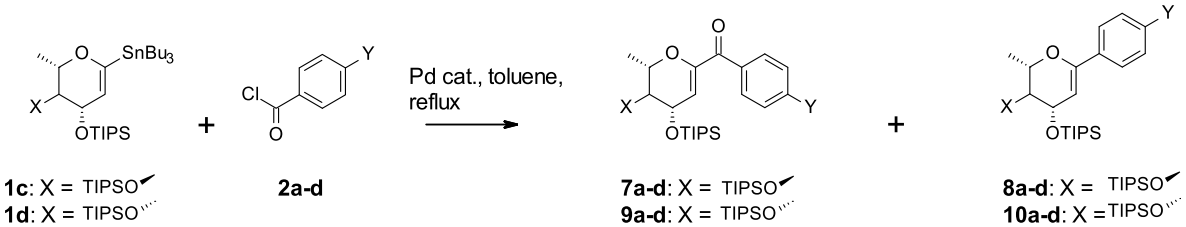
**Table 3. Reactions of 6-Deoxy-L-glucal 1c or L-fucal 1d and Aroyl Chlorides 2a−d[a]**




| | | | $Pd(OAc)_2$ | | | $Pd(PPh_3)_4$ | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | Y | yield of aroyl *C*-glycal (%)[b] | yield of aryl *C*-glycal (%)[b] | reaction time (h) | yield of aroyl *C*-glycal (%)[b] | yield of aryl *C*-glycal (%)[b] | reaction time (h) |
| **1c** | **2a** | H | 75 (**7a**) | 0 (**8a**) | 1 | 12, 53[c] (**7a**) | 36[e], 18[c,e] (**8a**) | 4, 5[c] |
| | **2b** | 4-$CO_2$Me | 76 (**7b**) | <1 (**8b**) | 2 | <1, <1[c] (**7b**) | 34, 19[c] (**8b**) | 2, 4[c] |
| | **2c** | 4-CN | 49 (**7c**) | 8[d] (**8c**) | 2 | 4, 6[c] (**7c**) | 32[d], 84[c,d] (**8c**) | 8, 4.5[c] |
| | **2d** | 4-Me | 81 (**7d**) | 0 (**8d**) | 1 | 39 (**7d**) | <1 (**8d**) | 6 |
| **1d** | **2a** | H | 84 (**9a**)[d] | 0 (**10a**) | 0.5 | 38 (**9a**)[d] | 49 (**10a**)[d] | 5 |
| | **2b** | 4-$CO_2$Me | 90 (**9b**) | <1 (**10b**) | 2 | 44 (**9b**) | 21 (**10b**) | 8 |
| | **2c** | 4-CN | 57 (**9c**) | <1 (**10c**) | 1 | 58 (**9c**) | 19 (**10c**) | 7 |
| | **2d** | 4-Me | 91 (**9d**) | 0 (**10d**) | 1 | 55 (**9d**) | 0 (**10d**) | 4.5 |

[a]The reaction was performed using **1b** (0.10 mmol), **2** (0.30 mmol), and Pd catalyst (0.010 mmol) in refluxing toluene (5 mL) unless otherwise noticed. [b]Isolated yield. [c]The palladium catalyst was used at 0.020 mmol. [d]A small amount of the adduct decomposed after several days. [e]Product was isolated with an inseparable impurity.

this reaction remained sluggish with several byproducts, further optimization was required. When $Na_2CO_3$ was omitted and the amount of **2** was increased (3 equiv), the reaction proceeded smoothly, and the desired aroyl adduct **3a** was obtained at 70% yield (entry 4). As 4-substituted aroyl chlorides **2b** and **2c** under this reaction led to poor results (entries 5 and 6), the effects of the palladium catalyst were examined in the reaction with aroyl chloride **2b**. The use of $PdCl_2(PhCN)_2$ led to comparable results as $PdCl_2(CH_3CN)_2$ (entry 7). The use of bidentate phosphine ligands, such as $PdCl_2$(dppe) or $PdCl_2$[1,1′-*bis*(diphenylphosphino)ferrocene (dppf)], did not improve the yield even after 25 h (entries 8 and 9). When $PdCl_2$ was employed, aroyl *C*-D-glucal **3b** was isolated at 17% yield (entry 10). The use of $PdCl_2$ was reported for synthesizing aromatic ketone from acyl chlorides and arylboronic acid.[2e] The counter ion of the palladium catalyst is critical because the use of $Pd(OAc)_2$ improved the yield of **3b** (57%) with trace amounts of **4b** (entry 11). The reaction with $PdCl_2$ required a longer time than that with $Pd(OAc)_2$, which completed within less than 1 h. The reaction catalyzed by $Pd(OAc)_2$ at a scale of 1.0 mmol was performed to confirm the reproducibility of the reaction with a similar yield of **3b** (66%), and a trace amount of **4b** was observed in this reaction. The addition of CuI was not beneficial for the reaction (entry 12).[11] This result led us to examine $Pd(TFA)_2$, which resulted in obtaining **3b** at diminished yield (entry 13). Among the olefin ligands examined, $Pd(acac)_2$ provided the best yield, which was comparable to that of $Pd(OAc)_2$ (entries 11 and 16). The nitrogen ligand also provided **3b** selectively in modest yields (entries 19−21). The monodentate phosphine ligand gave the opposite result. The use of $Pd(PPh_3)_4$ provided aryl *C*-D-glucal **4b** selectively (71% yield) with a trace amount of aroyl adduct **3b** (entry 22). It is interesting to note that $Pd(PPh_3)_4$ was reported to catalyze the synthesis of ketone from acid chloride and boronic acids.[2h] The use of $PdCl_2(PPh_3)_2$ diminished the yield of **4b**. The arsine ligand led to diminished selectivity.

As the use of $Pd(OAc)_2$ provides aroyl *C*-D-glucal **3b** and $Pd(PPh_3)_4$ produces aryl *C*-D-glucal **4b** in a selective manner, the influence of 4-substituents of aroyl chloride on selectivity was investigated, as presented in Table 2. When benzoyl chloride (**2a**) was reacted, aroyl adduct **3a** was obtained at 89% yield, which is better than that catalyzed by $PdCl_2(CH_3CN)_2$ (Table 1, entry 4). 4-Toluoyl adduct **3d** was also formed in a selective manner. When 4-cyanobenzoyl chloride (**2c**) was reacted with $Pd(OAc)_2$, the selectivity was diminished, and aroyl *C*-D-glucal **3c** and aryl *C*-D-glucal **4c** were isolated at yields of 48 and 22%, respectively. Because there are no significant differences in the electrostatic nature of the aromatic ring substituted with the methoxycarbonyl or cyano group, it remains unclear why such diminished selectivity was observed. Similar high selectivity was observed when 1-tributylstannyl D-galactal **1b** was reacted with aroyl chlorides **2** catalyzed by $Pd(OAc)_2$ (Table 2). In particular, the benzoyl and 4-toluoyl adducts **5a** and **5d** were obtained with greater than 80% yield. Thus, it is clear that the reaction catalyzed by $Pd(OAc)_2$ proceeded selectively and required less than 1 h to complete, excluding the reaction of **1a** and **2c**.

When $Pd(PPh_3)_4$ was used as a catalyst, an unsubstituted aryl *C*-D-glucal (**4a**) and its analogue with an electron-withdrawing substituent (**4c**) were selectively formed. These reactions required longer times to complete. The reactions with benzoyl chloride (**2a**) resulted in high selectivity with both catalysts. Compounds **4a** and **4c** have been reported, and both compounds exhibited identical spectra, as previously reported.[6j,12] Aroyl chloride with an electron-donating substituent exhibited the opposite selectivity. 4-Toluoyl *C*-D-glucal **3d** was isolated selectively regardless of the palladium catalyst used. It was reported that electron-rich aryl esters primarily formed ketone in nickel-catalyzed coupling of aryl esters and arylboronic acid.[4e] When the reaction of 1-tributylstannyl D-galactal **1b** and **2b** was catalyzed by $Pd(PPh_3)_4$, only a trace amount of aryl *C*-D-galactal **6b** was formed, and the corresponding aroyl adduct **5b** was isolated at 25% yield. Furthermore, selectivity was lost when **2a** and **2c** were catalyzed by $Pd(PPh_3)_4$. In fact, the reaction of **1b** catalyzed by $Pd(PPh_3)_4$ was not clean, and aryl *C*-D-galactals **6a**, **6c**, and **6d** contained inseparable impurities. The reaction of 4-toluoyl chloride (**2d**) catalyzed by $Pd(PPh_3)_4$ resulted in the



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formation of aryl *C*-D-galactal **6d**. This was an unexpected result because other stannyl glycals **1a**, **1c**, and **1d** provided aroyl *C*-glycals **3d**, **7d**, and **9d** selectively (Tables 2 and 3; *vide infra*).

The selectivity with 6-deoxy-1-tributylstannyl-L-glucal **1c** and 1-tributylstannyl-L-fucal **1d** was then investigated under the same reaction condition, as described in Table 3. The selective formation of aroyl 6-deoxy-*C*-L-glucals **7a**−**7d** and aroyl *C*-L-fucals **9a**−**9d** was observed when $Pd(OAc)_2$ was employed as a catalyst for all aroyl chlorides (**2a**−**2d**) examined. These reactions completed in less than 2 h. The use of **2c** led to adducts **7c** and **9c** with lower yields than those of the aroyl *C*-glycals **7** and **9**. The selectivity was lower in the reaction between **1c** and **2c** than the reactions of **1c** with **2a**, **2b**, or **2d**. However, the selectivity was better than that of the reaction of **1a** with **2c** (Table 2). As reported previously, L-fucal analogues tend to exhibit instability,[7] and a small amount of aroyl adduct **9a** decomposed after several days of standing at room temperature, as confirmed by the $^1$H NMR spectra (see the Supporting Information). As the corresponding aryl analogue **10a** also displayed instability, the selectivity of adducts **9a** and **10a** cannot be discussed.

The selectivity was diminished when $Pd(PPh_3)_4$ was utilized in this reaction. Although aryl 6-deoxy-*C*-L-glucals **8a**−**8c** were formed preferably when **2a**−**2c** were used in reactions catalyzed by $Pd(PPh_3)_4$, the isolated yields and selectivity were lower than those of **4a**−**4c** (Table 2). **8a**, **8b**, and **8c** were isolated with yields of 36, 34, and 32%, respectively. The amount of the palladium catalyst was revealed to affect the yield of the reaction. When 20 mol % $Pd(PPh_3)_4$ was used, **8b** was obtained at lower yield, whereas the yield of **8c** was greatly improved to 84%. Conversely, the use of 20 mol % $Pd(PPh_3)_4$ reversed the selectivity for **7a** and **8a**. Compound **8c** displayed instability, and a small amount of **8c** decomposed after several days at room temperature, which was confirmed by the $^1$H NMR spectra (see the Supporting Information). The reaction of **1c** with **2c** catalyzed by $Pd(PPh_3)_4$ was messy, and the adduct **8a** contained an inseparable impurity. The reaction of 1-tributylstannyl-L-fucal **1d** catalyzed by $Pd(PPh_3)_4$ lost selectivity when **2b** and **2c** were used. In these reactions, the formation of aroyl adducts **9b** and **9c** was preferred.

Again, when an electron-releasing 4-toluoyl chloride (**2d**) was reacted in the presence of $Pd(PPh_3)_4$, only aroyl *C*-glycal **7d** or **9d** was isolated with a modest yield.

The high selectivity associated with the use of $Pd(OAc)_2$ and diminished selectivity with $Pd(PPh_3)_4$ could be explained by the rates of transmetallation and decarbonylation of acylpalladium complexes. It appears that under ligand-free conditions, such as the use of $Pd(OAc)_2$, transmetallation proceeds preferably to provide aroyl adducts, whereas decarbonylation is accelerated when a sterically bulkier ligand, such as triphenylphosphine, was used as the palladium ligand. The higher trans effect of phosphine also accelerated decarbonylation by promoting the creation of the vacant site necessary for decarbonylation.[13]

An electron-releasing group at the 4-position of aroyl chloride is an important factor for selective aroylation. This could be explained by the stronger Ar−CO bond with the four-electron-releasing group.[14]

## CONCLUSIONS

In conclusion, the selectivity of the palladium-catalyzed aroylation and arylation of 1-tributylstannyl glycals **1a**−**1d** with aroyl chlorides **2a**−**2d** was investigated. The reaction catalyzed by $Pd(OAc)_2$ provided aroyl *C*-glycals selectively with high yields for all 1-tributylstannyl glycals (**1a**−**1d**) examined. Although aryl *C*-D-glucals **4a**−**4c** were selectively obtained with the reaction of four-electron-withdrawing or unsubstituted aroyl chlorides (**2a**−**2c**) with 1-tributylstannyl D-glucal **1a** catalyzed by $Pd(PPh_3)_4$, the selectivity was diminished or lost when the reaction was performed with other 1-tributylstannyl glycals (**1b**−**1d**). When the reaction was performed with electron-releasing **2d**, the selective formation of aroyl adducts was observed regardless of the catalyst used. However, the selectivity was lost when the reaction of **2d** and stannyl D-galactal **1c** was catalyzed by $Pd(PPh_3)_4$. Thus, further research on selective arylation is required.

## EXPERIMENTAL SECTION

All reactions were performed in glass flasks under $N_2$. Starting reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Chromatographic elution was conducted under continuous monitoring by thin-layer chromatography using silica gel 60F254 (Merck & Co., Inc.) as the stationary phase and the elution solvent used in column chromatography as the mobile phase. A UV detector was used for detection. Silica gel SK-85 (230−400 mesh) or silica gel SK-34 (70−230 mesh), both of which were manufactured by Merck & Co., Inc., was used as the column-packing silica gel. $^1$H and $^{13}$C NMR spectra were obtained on Varian Unity 400 MHz or JEOL JNM-GSX400 MHz spectrometers. Spectra were recorded in the indicated solvent at ambient temperature, and chemical shifts were reported in ppm ($\delta$) relative to the solvent peak. Resonance patterns are represented by the following notations: br (broad signal), s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). HRMS was conducted using an LC−MS system consisting of a Waters Xevo Quadropole-ToF MS and an Acquity UHPLC system.

**General Procedure of Palladium-Catalyzed Coupling Reactions.** To a solution of 1-tributylstannyl glycal **1**[7] (0.10 mmol) in toluene (5 mL) was added palladium catalyst (0.01 mmol), followed by aroyl chloride **2** (0.30 mmol). The reaction mixture was stirred at reflux for the times indicated in Tables 2 and 3. The solution was concentrated under reduced pressure. Column chromatography afforded the coupled product.

*2,6-Anhydro-3-deoxy-1-phenyl-4,5,7-tris-O-[tri(propan-2-yl)silyl]-D-arabino-hept-2-enose (**3a**).* The reaction was performed with **1a** (90 mg, 0.10 mmol), **2a** (35 $\mu$L, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **3a** (64.4 mg, 89%). $[\alpha]D^{23} = -7.4$ (c = 0.2, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.98 (1H, dd, $J$ = 1.1, 7.9 Hz), 7.53 (1H, t, $J$ = 7.4 Hz), 7.40 (2H, t, $J$ = 7.6 Hz), 5.82 (1H, dd, $J$ = 2.0, 5.0 Hz, H-2), 5.42−4.48 (1H, m), 4.19−4.17 (2H, m), 4.11 (1H, dd, $J$ = 7.9, 11.5 Hz, H-6), 3.90 (1H, dd, $J$ = 4.4, 11.6 Hz), 1.08 (63H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 190.7 (C), 149.3 (C), 136.5 (C), 132.5 (CH), 130.1 (CH), 127.9 (CH), 107.6 (CH), 81.8 (CH), 69.5 (CH), 65.8 (CH), 61.5 ($CH_2$), 18.1 (Me), 18.0 (Me), 12.5 (CH), 12.3 (CH), 12.0 (CH); HRMS (FAB) $m/z$: $[M + Na]^+$ cacld for $C_{40}H_{74}O_5Si_3Na$, 741.4742; found, 741.4728.

*2,6-Anhydro-3-deoxy-1-[4-(methoxycarbonyl)phenyl]-4,5,7-tris-O-[tri(propan-2-yl)silyl]-D-arabino-hept-2-enose (**3b**).* The reaction was performed with **1a** (90 mg, 0.10 mmol), **2b** (60 mg, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **3b** (39.7 mg, 57%). $[\alpha]D^{23} = -6.5$ (c = 0.7, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.06 (2H, d, $J$ = 8.6 Hz), 8.01 (2H, d, $J$ = 8.2 Hz), 5.88 (1H, dd, $J$ = 1.4, 5.2 Hz, H-2), 5.42−4.48


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(2H, m), 4.19−4.16 (1H, m), 4.11 (1H, dd, $J$ = 8.0, 11.3 Hz, H-6), 3.95 (3H, s), 3.88 (1H, dd, $J$ = 4.3, 11.7 Hz, H-6), 1.08−1.08 (63H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 190.2(C), 166.5(C), 148.9 (C), 140.2 (C), 133.2 (C), 129.8 (CH), 129.1 (CH), 108.2 (CH), 81.9 (CH), 69.4 (CH), 65.6 (CH), 61.4 ($CH_2$), 52.4 (Me), 18.1 (Me), 17.9 (Me), 12.4 (CH), 12.3 (CH), 12.0 (CH); HRMS (FAB) $m/z$: $[M + Na]^+$ cacld for $C_{42}H_{76}O_7Si_3Na$, 799.4797; found, 799.4785.

*2,6-Anhydro-1-(4-cyanophenyl)-3-deoxy-4,5,7-tris-O-[tri(propan-2-yl)silyl]-D-arabino-hept-2-enose (**3c**).* The reaction was performed with **1a** (90 mg, 0.10 mmol), **2c** (50 mg, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **3c** (35.4 mg, 48%) and **4c** (15.5 mg, 22%). $[\alpha]D^{23}$ = −7.1 (c = 0.6, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.09 (2H, d, $J$ = 8.2 Hz), 7.69 (2H, d, $J$ = 7.7 Hz), 5.95 (1H, dd, $J$ = 1.5, 5.8 Hz, H-2), 5.41−4.48 (1H, m), 4.18−4.16 (1H, m), 4.14−4.11 (2H, m), 3.82 (1H, dd, $J$ = 3.5, 11.7 Hz, H-6), 1.08−1.08 (63H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 189.0 (C), 148.4 (C), 139.9 (C), 131.7 (CH), 130.4 (CH), 118.2 (C), 115.7 (C), 108.3 (CH), 82.2 (CH), 69.5 (CH), 65.5 (CH), 61.3 ($CH_2$), 18.1 (Me), 18.0 (Me), 17.9 (Me), 12.4 (CH), 12.3 (CH), 11.9 (CH); HRMS (FAB) $m/z$: $[M + Na]^+$ cacld for $C_{41}H_{73}O_5NSi_3Na$, 766.4694; found, 766.4690.

*2,6-Anhydro-3-deoxy-1-(4-methylphenyl)-4,5,7-tris-O-[tri(propan-2-yl)silyl]-D-arabino-hept-2-enose (**3d**).* The reaction was performed with **1a** (90 mg, 0.10 mmol), **2d** (40 $\mu$L, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) or $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **3d** (39.7 mg, 54%; 22.2 mg, 30%). $[\alpha]D^{23}$ = −9.5 (c = 0.2, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.91 (2H, d, $J$ = 8.2 Hz), 7.20 (2H, d, $J$ = 8.2 Hz), 5.79 (1H, dd, $J$ = 2.7, 4.0 Hz, H-2), 5.41−4.47 (1H, m), 4.19−4.17 (2H, m), 4.10 (1H, dd, $J$ = 8.0 Hz, 11.6, H-6), 3.91 (1H, dd, $J$ = 4.6, 11.6 Hz, H-6), 2.40 (3H, s), 1.08−1.08 (63H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 190.4 (C), 149.6 (C), 143.3 (C), 133.9 (C), 130.3 (CH), 128.7 (CH), 106.9 (CH), 81.7 (CH), 69.5 (CH), 65.8 (CH), 61.5 ($CH_2$), 21.7 (Me), 18.2 (Me), 18.1 (Me), 18.0 (Me), 12.5 (CH), 12.3 (CH), 12.0 (CH); HRMS (FAB) $m/z$: $[M + Na]^+$ cacld. for $C_{41}H_{76}O_5Si_3Na$, 755.4898; found, 755.4896.

*1,5-Anhydro-2-deoxy-1-phenyl-3,4,6-tris-O-[tri(propan-2-yl)silyl]-D-arabino-hex-1-enitol (**4a**).* The reaction was performed with **1a** (90 mg, 0.10 mmol), **2a** (35 $\mu$L, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **4a** (46.5 mg, 67%). The spectral characteristics were in agreement with the previously reported data.[12] $[\alpha]D^{23}$ = −11.4 (c = 0.3, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.65−7.61 (2H, m), 7.49−7.27 (3H, m), 5.35 (1H, dd, $J$ = 1.2, 5.7 Hz, H-2), 4.46 (1H, dt, $J$ = 2.1, 7.8 Hz), 4.19−4.14 (1H, m), 4.13 (1H, m), 4.11 (1H, dd, $J$ = 7.8, 11.3 Hz, H-6), 3.90 (1H, dd, $J$ = 4.3, 11.1 Hz), 1.08−1.08 (63H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 150.3 (C), 136.3 (C), 128.2 (CH), 127.9 (CH), 125.4 (CH), 96.7 (CH), 81.3 (CH), 70.1 (CH), 66.8 (CH), 62.0 ($CH_2$), 18.2 (Me), 18.1 (Me), 18.0 (Me), 12.6 (CH), 12.5 (CH), 12.1 (CH); HRMS (FAB) $m/z$: $[M + K]^+$ cacld for $C_{39}H_{74}O_4Si_3K$, 729.4532; found, 729.4521.

*1,5-Anhydro-2-deoxy-1-[4-(methoxycarbonyl)phenyl]-3,4,6-tris-O-[tri(propan-2-yl)silyl]-D-arabino-hex-1-enitol (**4b**).* The reaction was performed with **1a** (90 mg, 0.10 mmol), **2b** (60 mg, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **4b** (53.2 mg, 71%). $[\alpha]D^{23}$ = −6.8 (c = 1.1, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.00 (2H, d, $J$ = 8.6 Hz), 7.70 (2H, d, $J$ = 8.4 Hz), 5.47 (1H, dd, $J$ = 1.3, 5.2 Hz, H-2), 4.50−4.48 (1H, m), 4.19−4.17 (1H, m), 4.15−4.10 (2H, m), 3.92 (3H, s), 3.86 (1H, dd, $J$ = 3.7, 11.2 Hz, H-6), 1.08−1.08 (63H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 167.0 (C), 149.3 (C), 140.6 (C), 129.7 (C), 129.4 (CH), 125.2 (CH), 98.7 (CH), 81.5 (CH), 70.0 (CH), 66.5 (CH), 61.9 ($CH_2$), 52.1 (Me), 18.2 (Me), 18.1 (Me), 18.0 (Me), 12.6 (CH), 12.4 (CH), 12.0 (CH); HRMS (FAB) $m/z$: $[M + H]^+$ cacld for $C_{41}H_{77}O_6Si_3$, 749.5028; found, 749.5012.

*1,5-Anhydro-1-(4-cyanophenyl)-2-deoxy-3,4,6-tris-O-[tri(propan-2-yl)silyl]-D-arabino-hex-1-enitol (**4c**).* The reaction was performed with **1a** (90 mg, 0.10 mmol), **2c** (50 mg, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **4c** (39.9 mg, 56%). The spectral characteristics were in agreement with the previously reported data.[6j] $[\alpha]D^{23}$ = −9.5 (c = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.61 (2H, d, $J$ = 8.4 Hz), 7.03 (2H, d, $J$ = 8.5 Hz), 5.48 (1H, dd, $J$ = 1.0, 5.0 Hz, H-2), 4.51−4.47 (1H, m), 4.18−4.16 (1H, m), 4.14−4.09 (2H, m), 3.84 (1H, dd, $J$ = 3.7, 11.6 Hz, H-6), 1.08−1.08 (63H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.5 (C), 140.5 (C), 131.9 (CH), 125.7 (CH), 119.0 (C), 111.6 (C), 99.5 (CH), 81.7 (CH), 69.9 (CH), 66.3 (CH), 61.7 ($CH_2$), 18.1 (Me), 18.0 (Me), 12.5 (CH), 12.4 (CH), 12.0 (CH); HRMS (FAB) $m/z$: $[M + H]^+$ cacld for $C_{40}H_{74}O_4NSi_3$, 716.4926; found, 716.4925.

*2,6-Anhydro-3-deoxy-1-phenyl-4,5,7-tris-O-[tri(propan-2-yl)silyl]-D-lyxo-hept-2-enose (**5a**).* The reaction was performed with **1b** (90 mg, 0.10 mmol), **2a** (35 $\mu$L, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **5a** (58.7 mg, 82%). $[\alpha]D^{23}$ = −32.6 (c = 3.2, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.10−7.82 (2H, m), 7.53 (1H, t, $J$ = 7.3 Hz), 7.40 (2H, t, $J$ = 7.8 Hz), 6.00−5.41 (1H, m), 4.67−3.75 (5H, m), 1.12−1.01 (63H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 190.3 (C), 149.6 (C), 136.5 (C), 132.6 (CH), 130.0 (CH), 128.0 (CH), 110.1 (CH), 81.4 (CH), 70.1 (CH), 64.2 (CH), 60.4 ($CH_2$), 18.9 (Me), 18.0 (Me), 12.6 (CH), 12.0 (CH); HRMS (FAB) $m/z$: $[M - H]^-$ cacld for $C_{40}H_{73}O_5Si_3$, 717.4766; found, 717.4757.

*2,6-Anhydro-3-deoxy-1-[4-(methoxycarbonyl)phenyl]-4,5,7-tris-O-[tri(propan-2-yl)silyl]-D-lyxo-hept-2-enose (**5b**).* The reaction was performed with **1b** (90 mg, 0.10 mmol), **2b** (60 mg, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **5b** (49.8 mg, 74%). $[\alpha]D^{23}$ = −35.0 (c = 0.2, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.06 (2H, d, $J$ = 8.2 Hz), 8.11−7.97 (2H, m), 5.90−5.60 (1H, m), 5.72−3.98 (5H, m), 3.95 (3H, s), 1.12−1.01 (63H, m), $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 189.7 (C), 166.4 (C), 149.3 (C), 140.3 (C), 133.3 (C), 129.7 (CH), 129.2 (CH), 110.9 (CH), 81.4 (CH), 70.0 (CH), 64.3 (CH), 61.0 ($CH_2$), 52.4 (Me), 18.2 (Me), 18.0 (Me), 12.6 (CH), 12.0 (CH); HRMS (FAB) $m/z$: $M^{+\bullet}$ cacld for $C_{42}H_{76}O_7Si_3$, 776.4899; found, 776.4905.

*2,6-Anhydro-1-(4-cyanophenyl)-3-deoxy-4,5,7-tris-O-[tri(propan-2-yl)silyl]-D-lyxo-hept-2-enose (**5c**).* The reaction was performed with **1b** (90 mg, 0.10 mmol), **2c** (50 mg, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **5c** (46.1 mg, 62%). $[\alpha]D^{23}$ = −30.7 (c = 1.7, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.23−7.91 (2H, m), 7.69 (2H, d, $J$ = 8.4 Hz), 6.19−5.41 (1H, m), 4.85−3.63 (5H, m), 1.12−1.01 (63H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 188.6 (C), 148.5 (C), 139.8 (C), 131.8 (CH), 130.4 (CH), 118.2 (C), 115.8 (C), 111.5 (CH), 80.8 (CH), 70.1 (CH), 64.2 (CH), 60.2 ($CH_2$), 18.3 (Me), 18.2 (Me), 18.0 (Me), 12.6 (CH), 12.0 (CH); HRMS (FAB) $m/z$: $M^{+\bullet}$ cacld for $C_{41}H_{73}O_5NSi_3$, 743.4797; found, 743.4790.

*2,6-Anhydro-3-deoxy-1-(4-methylphenyl)-4,5,7-tris-O-[tri(propan-2-yl)silyl]-D-lyxo-hept-2-enose (**5d**).* The reaction was performed with **1b** (90 mg, 0.10 mmol), **2d** (40 $\mu$L, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **5d**



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(64.2 mg, 88%). $[\alpha]D^{23}$ = −35.7 (c = 1.1, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.99−7.82 (2H, m), 7.20 (2H, d, J = 8.0 Hz), 5.95−5.35 (1H, m), 4.85−3.65 (5H, m), 2.40 (3H, s), 1.11−1.03 (63H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 189.9 (C), 150.0 (C), 143.5 (C), 133.8 (C), 130.2 (CH), 128.7 (CH), 109.7 (CH), 81.3 (CH), 70.0 (CH), 64.4 (CH), 60.5 ($CH_2$), 21.7 (Me), 18.2 (Me), 18.0 (Me), 12.6 (CH), 12.0 (CH); HRMS (FAB) *m/z*: $M^{+\bullet}$ cacld for $C_{41}H_{76}O_5Si_3$, 732.5001; found, 732.5006.

*1,5-Anhydro-2-deoxy-1-phenyl-3,4,6-tris-O-[tri(propan-2-yl)silyl]-D-lyxo-hex-1-enitol (**6a**).* The reaction was performed with **1b** (90 mg, 0.10 mmol), **2a** (35 μL, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **6a** (34.2 mg, 50%) and **5a** (17.9 mg, 25%). Compound **6a** was isolated with an inseparable impurity. $[\alpha]D^{23}$ = −23.3 (c = 1.7, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.62−7.59 (2H, m), 7.33−7.28 (3H, m), 5.39−5.26 (1H, m), 4.52−4.35 (2H, m), 4.31 (1H, t, J = 4.0 Hz), 4.28−4.10 (2H, m), 1.11−1.00 (63H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 150.3 (C), 135.4 (C), 128.5 (CH), 128.0 (CH), 125.4 (CH), 98.7 (CH), 80.9 (CH), 76.7 (CH), 70.2 (CH), 70.0 ($CH_2$), 18.3 (Me), 18.0 (Me), 12.7 (CH), 12.1 (CH); HRMS (FAB) *m/z*: $[M - H]^-$ cacld for $C_{39}H_{73}O_4Si_3$, 689.4817; found, 689.4797.

*1,5-Anhydro-1-(4-cyanophenyl)-2-deoxy-3,4,6-tris-O-[tri(propan-2-yl)silyl]-D-lyxo-hex-1-enitol (**6c**).* The reaction was performed with **1b** (90 mg, 0.10 mmol), **2c** (50 mg, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **6c** (11.1 mg, 16%) and **5c** (34.1 mg, 46%). Compound **6c** was isolated with an inseparable impurity. $[\alpha]D^{23}$ = −22.1 (c = 0.4, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.69 (2H, d, J = 8.5 Hz), 7.60 (2H, d, J = 8.3 Hz), 5.54−5.37 (1H, m), 4.55−4.34 (2H, m), 4.31 (1H, d, J = 3.7 Hz), 4.26−4.08 (2H, m), 1.10−1.03 (63H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 148.6 (C), 139.6 (C), 133.9 (CH), 125.7 (CH), 118.9 (C), 112.0 (C), 101.8 (CH), 80.9 (CH), 70.0 (CH), 60.9 (CH), 60.8 ($CH_2$), 18.2 (Me), 17.9 (Me), 12.7 (CH), 12.0 (CH); HRMS (FAB) *m/z*: $[M + H]^+$ cacld for $C_{40}H_{74}O_4NSi_3$, 716.4926; found, 716.4935.

*1,5-Anhydro-2-deoxy-1-(4-methylphenyl)-3,4,6-tris-O-[tri(propan-2-yl)silyl]-D-lyxo-hex-1-enitol (**6d**).* The reaction was performed with **1b** (90 mg, 0.10 mmol), **2d** (40 μL, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **6d** (21.2 mg, 30%) and **5d** (19.8 mg, 27%). Compound **6d** was isolated with an inseparable impurity. $[\alpha]D^{23}$ = −27.2 (c = 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.49 (2H, d, J = 8.1 Hz), 7.11 (2H, d, J = 8.1 Hz), 5.39−5.20 (1H, m), 4.50−4.34 (2H, m), 4.33−4.28 (1H, m), 4.28−4.18 (1H, m), 4.15−4.12 (1H, m), 2.34 (3H, s), 1.11−1.00 (63H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 150.3 (C), 142.8 (C), 132.6 (C), 128.7 (CH), 128.0 (CH), 98.7 (CH), 81.0 (CH), 70.2 (CH), 65.2 (CH), 61.0 ($CH_2$), 21.2 (Me), 18.3 (Me), 18.2 (Me), 18.0 (Me), 12.7 (CH), 12.1 (CH); HRMS (FAB) *m/z*: $[M + H]^+$ cacld for $C_{40}H_{77}O_4Si_3$, 705.5130; found, 705.5094.

*2,6-Anhydro-3,7-dideoxy-1-phenyl-4,5-bis-O-[tri(propan-2-yl)silyl]-L-arabino-hept-2-enose (**7a**).* The reaction was performed with **1c** (73 mg, 0.10 mmol), **2a** (35 μL, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **7a** (40.8 mg, 75%). $[\alpha]D^{23}$ = 39.7 (c = 0.7, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.89 (2H, dd, J = 1.1, 7.9 Hz), 7.54 (1H, t, J = 7.7 Hz), 7.42 (2H, t, J = 7.9 Hz), 5.76 (1H, dd, J = 1.4, 5.1 Hz, H-2), 4.56 (1H, tq, J = 1.8, 6.9 Hz, H-5), 4.23 (1H, dt, J = 2.1, 5.2 Hz, H-3), 4.01 (1H, dd, J = 2.0, 3.7 Hz, H-4), 1.45 (3H, d, J = 6.8 Hz), 1.07−1.07 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 191.5 (C), 148.7 (C), 136.8 (C), 132.5 (CH), 129.8 (CH), 128.0 (CH), 108.6 (CH), 75.8 (CH), 72.7 (CH), 66.5 (CH), 18.1 (Me), 15.7 (Me), 12.5 (CH), 12.4 (CH); HRMS (FAB) *m/z*: $[M + Na]^+$ cacld for $C_{31}H_{54}O_4Si_2Na$, 569.3458; found, 569.3488.

*2,6-Anhydro-3,7-dideoxy-1-[4-(methoxycarbonyl)phenyl]-4,5-bis-O-[tri(propan-2-yl)silyl]-L-arabino-hept-2-enose (**7b**).* The reaction was performed with **1c** (73 mg, 0.10 mmol), **2b** (60 mg, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **7b** (45.6 mg, 76%). $[\alpha]D^{23}$ = 35.9 (c = 0.4, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.08 (2H, d, J = 8.5 Hz), 7.92 (2H, d, J = 8.3 Hz), 5.80 (1H, dd, J = 1.4, 5.2 Hz, H-2), 4.56 (1H, tq, J = 1.4, 7.1 Hz, H-5), 4.23 (1H, dt, J = 2.1, 5.2 Hz, H-3), 4.02 (1H, dd, J = 2.0, 3.6 Hz, H-4), 3.95 (3H, s), 1.44 (3H, d, J = 7.2 Hz), 1.07−1.07 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 190.9 (C), 166.4 (C), 148.3 (C), 140.4 (C), 133.2 (C), 129.6 (CH), 129.2 (CH), 109.4 (CH), 75.9 (CH), 72.5 (CH), 66.4 (CH), 52.4 (Me), 18.1 (Me), 15.6 (Me), 12.5 (CH), 12.4 (CH); HRMS (FAB) *m/z*: Found $[M + Na]^+$ cacld for $C_{33}H_{56}O_6Si_2Na$, 627.3513; found, 627.3506.

*2,6-Anhydro-1-(4-cyanophenyl)-3,7-dideoxy-4,5-bis-O-[tri(propan-2-yl)silyl]-L-arabino-hept-2-enose (**7c**).* The reaction was performed with **1c** (73 mg, 0.10 mmol), **2c** (50 mg, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **7c** (28.1 mg, 49%) and **8c** (4.4 mg, 8%). $[\alpha]D^{23}$ = 56.3 (c = 1.5, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.97 (2H, d, J = 8.5 Hz), 7.71 (2H, d, J = 8.5 Hz), 5.84 (1H, dd, J = 1.4, 5.2 Hz, H-2), 4.55 (1H, tq, J = 1.9, 7.1 Hz, H-5), 4.23 (1H, dt, J = 1.7, 5.6 Hz, H-3), 4.02 (1H, d, J = 1.8 Hz, H-4), 1.43 (3H, d, J = 7.2 Hz), 1.08−1.08 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 189.8 (C), 148.1 (C), 140.2 (C), 131.8 (CH), 130.1 (CH), 118.1 (C), 115.7 (C), 109.2 (CH), 76.1 (CH), 72.4 (CH), 66.2 (CH), 18.1 (Me), 18.0 (Me), 15.6 (Me), 12.5 (CH), 12.4 (CH); HRMS (FAB) *m/z*: $[M + H]^+$ cacld for $C_{32}H_{54}O_4NSi_2$, 572.3591; found, 72.3588.

*2,6-Anhydro-3,7-dideoxy-1-(4-methylphenyl)-4,5-bis-O-[tri(propan-2-yl)silyl]-L-arabino-hept-2-enose (**7d**).* The reaction was performed with **1c** (73 mg, 0.10 mmol), **2d** (40 μL, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) or $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **7d** (45.3 mg, 81%; 21.9 mg, 39%, respectively). $[\alpha]D^{23}$ = 38.8 (c = 1.4, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.82 (2H, d, J = 8.1 Hz), 7.22 (2H, d, J = 8.0 Hz), 5.74 (1H, dd, J = 1.4, 5.2 Hz, H-2), 4.55 (1H, tq, J = 1.9, 7.2 Hz, H-5), 4.23 (1H, dt, J = 2.1, 4.5 Hz, H-3), 4.01 (1H, dd, J = 2.0, 3.7 Hz, H-4), 2.41 (3H, s), 1.44 (3H, d, J = 7.1 Hz), 1.09−1.07 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 191.1 (C), 148.9 (C), 143.3 (C), 134.0 (C), 130.0 (CH), 128.7 (CH), 107.8 (CH), 75.8 (CH), 72.7 (CH), 66.5 (CH), 21.7 (Me), 18.1 (Me), 15.7 (Me), 12.5 (CH), 12.4 (CH); HRMS (FAB) *m/z*: $[M + H]^+$ cacld for $C_{32}H_{57}O_4Si_2$, 561.3795; found, 561.3768.

*1,5-Anhydro-2,6-dideoxy-1-phenyl-3,4-bis-O-[tri(propan-2-yl)silyl]-L-arabino-hex-1-enitol (**8a**).* The reaction was performed with **1c** (73 mg, 0.10 mmol), **2a** (35 μL, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **8a** (18.4 mg, 36%) and **7a** (6.7 mg, 12%). Compound **8a** was isolated with an inseparable impurity. $[\alpha]D^{23}$ = 28.3 (c = 0.8, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.60 (2H, d, J = 6.7 Hz), 7.34−7.29 (3H, m), 5.36 (1H, dd, J = 1.2, 5.1 Hz, H-2), 4.49 (1H, tq, J = 2.0, 7.1 Hz, H-5), 4.25−4.21 (1H, m, H-3), 3.99 (1H, d, J = 1.5 Hz, H-4), 1.44 (3H, d, J = 7.2 Hz), 1.06−1.06 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 149.7 (C), 136.6 (C), 128.1 (CH), 128.0 (CH), 125.3 (CH), 97.0 (CH), 75.2 (CH), 73.3 (CH), 67.6 (CH), 18.2 (Me), 18.0 (Me), 16.1 (Me),


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12.6 (CH), 12.3 (CH); HRMS (FAB) $m/z$: $[M + H]^+$ cacld for $C_{30}H_{55}O_3Si_2$, 519.3690; found, 519.3655.

*1,5-Anhydro-2,6-dideoxy-1-[4-(methoxycarbonyl)phenyl]-3,4-bis-O-[tri(propan-2-yl)silyl]-L-arabino-hex-1-enitol (**8b**).* The reaction was performed with **1c** (73 mg, 0.10 mmol), **2b** (60 mg, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **8b** (19.7 mg, 34%). $[\alpha]D^{23}$ = 29.3 (c = 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.00 (2H, d, $J$ = 8.6 Hz), 7.66 (2H, d, $J$ = 8.3 Hz), 5.48 (1H, dd, $J$ = 1.3, 5.1 Hz, H-2), 4.51 (1H, tq, $J$ = 2.0, 7.0 Hz, H-5), 4.24 (1H, dt, $J$ = 2.0, 5.2 Hz, H-3), 4.01 (1H, d, $J$ = 1.5 Hz, H-4), 3.91 (3H, s), 1.44 (3H, d, $J$ = 7.2 Hz), 1.07 (42H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 166.9 (C), 148.8 (C), 140.8 (C), 129.6 (C), 129.5 (CH), 125.0 (CH), 98.9 (CH), 75.4 (CH), 73.1 (CH), 67.3 (CH), 52.1 (Me), 18.2 (Me), 18.1 (Me), 16.0 (Me), 12.6 (CH), 12.5 (CH); HRMS (FAB) $m/z$: $[M + H]^+$ cacld for $C_{32}H_{57}O_5Si_2$, 577.3745; found, 577.3759.

*1,5-Anhydro-1-(4-cyanophenyl)-2,6-dideoxy-3,4-bis-O-[tri(propan-2-yl)silyl]-L-arabino-hex-1-enitol (**8c**).* The reaction was performed with **1c** (73 mg, 0.10 mmol), **2c** (50 mg, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **8c** (17.4 mg, 32%) and **7c** (2.1 mg, 4%). A small amount of the adduct **8c** decomposed after several days, as confirmed by the $^1H$ NMR spectra (see the Supporting Information). $[\alpha]D^{23}$ = 44.2 (c = 0.3, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.70 (2H, d, $J$ = 8.5 Hz), 7.62 (2H, d, $J$ = 8.4 Hz), 5.49 (1H, d, $J$ = 4.7 Hz, H-2), 4.52 (1H, tq, $J$ = 1.6, 7.0 Hz, H-5), 4.23 (1H, dt, $J$ = 2.1, 5.2 Hz, H-3), 4.01 (1H, d, $J$ = 1.7 Hz, H-4), 1.43 (3H, d, $J$ = 7.0 Hz), 1.09−1.09 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 148.0 (C), 140.7 (C), 132.0 (CH), 125.6 (CH), 119.0 (C), 111.5 (C), 99.7 (CH), 75.5 (CH), 72.9 (CH), 67.1 (CH), 18.1 (Me), 18.0 (Me), 15.9 (Me), 12.5 (CH); HRMS (FAB) $m/z$: $[M + H]^+$ cacld for $C_{31}H_{54}O_3NSi_2$, 544.3642; found, 544.3647.

*2,6-Anhydro-3,7-dideoxy-1-phenyl-4,5-bis-O-[tri(propan-2-yl)silyl]-L-lyxo-hept-2-enose (**9a**).* The reaction was performed with **1d** (73 mg, 0.10 mmol), **2a** (35 $\mu$L, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **9a** (45.7 mg, 84%). A small amount of the adduct **9a** was decomposed after several days, as confirmed by the $^1H$ NMR spectra (see the Supporting Information). $[\alpha]D^{23}$ = 64.0 (c = 0.7, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (400 MHz) 7.87 (2H, d, $J$ = 7.1 Hz), 7.53 (1H, t, $J$ = 7.3 Hz), 7.41 (2H, t, $J$ = 7.5 Hz), 5.61 (1H, m), 4.62 (1H, m), 4.53 (1H, m), 4.09 (1H, m), 1.51 (3H, d, $J$ = 6.6 Hz), 1.13−1.07 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 190.9 (C), 149.7 (C), 136.7 (C), 132.5 (CH), 129.7 (CH), 128.0 (CH), 112.8 (CH), 75.1 (CH), 70.3 (CH), 63.8 (CH), 18.4 (Me), 18.1 (Me), 14.1 (Me), 13.2 (CH), 12.6 (CH); HRMS (FAB) $m/z$: $[M + Na]^+$ cacld for $C_{31}H_{54}O_4Si_2Na$, 569.3458; found, 569.3469.

*2,6-Anhydro-3,7-dideoxy-1-[4-(methoxycarbonyl)phenyl]-4,5-bis-O-[tri(propan-2-yl)silyl]-L-lyxo-hept-2-enose (**9b**).* The reaction was performed with **1d** (73 mg, 0.10 mmol), **2b** (60 mg, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **9b** (53.9 mg, 90%). $[\alpha]D^{23}$ = 70.9 (c = 1.4, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.07 (2H, d, $J$ = 8.3 Hz), 7.89 (2H, d, $J$ = 8.5 Hz), 5.63 (1H, m), 4.64 (1H, m), 4.33 (1H, m), 4.13 (1H, m), 4.09 (3H, s), 1.49 (3H, d, $J$ = 6.6 Hz), 1.13−1.07 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 190.2 (C), 166.4 (C), 149.6 (C), 140.5 (C), 133.2 (C), 129.5 (CH), 129.2 (CH), 113.9 (CH), 75.3 (CH), 70.2 (CH), 67.7 (CH), 52.4 (Me), 18.4 (Me), 18.3 (Me), 18.2 (Me), 18.1 (Me), 14.1 (Me), 13.3 (CH), 12.6 (CH); HRMS (FAB) $m/z$: $[M + Na]^+$ cacld for $C_{33}H_{56}O_6Si_2Na$, 627.3513; found, 627.3486.

*2,6-Anhydro-1-(4-cyanophenyl)-3,7-dideoxy-4,5-bis-O-[tri(propan-2-yl)silyl]-L-lyxo-hept-2-enose (**9c**).* The reaction was performed with **1d** (73 mg, 0.10 mmol), **2c** (50 mg, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) to provide **9c** (32.4 mg, 57%). $[\alpha]D^{23}$ = 68.3 (c = 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.95 (2H, d, $J$ = 8.5 Hz), 7.71 (2H, d, $J$ = 8.4 Hz), 5.64 (1H, m), 4.65 (1H, m), 4.30 (1H, m), 4.08 (1H, m), 1.48 (3H, d, $J$ = 6.6 Hz), 1.13−1.07 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 189.0 (C), 149.5 (C), 140.2 (C), 131.8 (CH), 130.0 (CH), 118.1 (C), 115.7 (C), 113.9 (CH), 75.4 (CH), 70.1 (CH), 68.0 (CH), 18.3 (Me), 18.2 (Me), 16.1 (Me), 13.4 (CH), 12.6 (CH); HRMS (FAB) $m/z$: $[M + H]^+$ cacld for $C_{32}H_{54}O_4NSi_2$, 572.3591; found, 572.3622.

*2,6-Anhydro-3,7-dideoxy-1-(4-methylphenyl)-4,5-bis-O-[tri(propan-2-yl)silyl]-L-lyxo-hept-2-enose (**9d**).* The reaction was performed with **1d** (73 mg, 0.10 mmol), **2d** (40 $\mu$L, 0.30 mmol), and $Pd(OAc)_2$ (2.0 mg, 0.010 mmol) or $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **9d** (50.8 mg, 91%, 31.1 mg; 55%, respectively). $[\alpha]D^{23}$ = 79.2 (c = 1.8, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.81 (2H, d, $J$ = 8.2 Hz), 7.21 (2H, d, $J$ = 8.1 Hz), 5.59 (1H, m), 4.62 (1H, m), 4.34 (1H, m), 4.09 (1H, m), 2.41 (3H, s), 1.51 (3H, d, $J$ = 6.6 Hz), 1.23−1.08 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 190.5 (C), 149.9 (C), 143.4 (C), 133.9 (C), 130.0 (CH), 128.7 (CH), 111.7 (CH), 75.0 (CH), 70.3 (CH), 67.5 (CH), 21.7 (Me), 18.4 (Me), 18.2 (Me), 15.7 (Me), 13.2 (CH), 12.7 (CH); HRMS (FAB) $m/z$: $M^{+\bullet}$ cacld for $C_{32}H_{56}O_4Si_2$, 560.3717; found, 560.3696.

*1,5-Anhydro-2,6-dideoxy-1-phenyl-3,4-bis-O-[tri(propan-2-yl)silyl]-L-lyxo-hex-1-enitol (**10a**).* The reaction was performed with **1d** (73 mg, 0.10 mmol), **2a** (35 $\mu$L, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **10a** (25.6 mg, 49%) and **9a** (20.8 mg, 38%). A small amount of the adduct **10a** was decomposed after several days, as confirmed by the $^1H$ NMR spectra (see the Supporting Information). $[\alpha]D^{23}$ = 57.4 (c = 0.8, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.56 (2H, dd, $J$ = 1.5, 8.1 Hz), 7.35−7.28 (3H, m), 5.28 (1H, d, $J$ = 4.23 Hz), 4.56 (1H, t, $J$ = 3.5 Hz), 4.40−4.38 (1H, m), 4.15 (1H, t, $J$ = 3.7 Hz), 1.50 (3H, d, $J$ = 6.7 Hz), 1.13−1.07 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 150.2 (C), 135.8 (C), 128.3 (CH), 128.1 (CH), 125.2 (CH), 98.8 (CH), 74.2 (CH), 70.7 (CH), 66.6 (CH), 18.3 (Me), 18.2 (Me), 14.9 (Me), 12.9 (CH), 12.8 (CH); HRMS (FAB) $m/z$: $[M + Na]^+$ cacld for $C_{30}H_{54}O_3Si_2Na$, 541.3509; found, 541.3499.

*1,5-Anhydro-2,6-dideoxy-1-[4-(methoxycarbonyl)phenyl]-3,4-bis-O-[tri(propan-2-yl)silyl]-L-lyxo-hex-1-enitol (**10b**).* The reaction was performed with **1d** (73 mg, 0.10 mmol), **2b** (60 mg, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **10b** (12.0 mg, 21%) and **9b** (26.5 mg, 44%). $[\alpha]D^{23}$ = 57.3 (c = 0.4, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.99 (2H, d, $J$ = 8.6 Hz), 7.62 (2H, d, $J$ = 8.5 Hz), 5.38 (1H, d, $J$ = 3.6 Hz), 4.58 (1H, m), 4.39 (1H, m), 4.14 (1H, t, $J$ = 3.6 Hz), 3.91 (3H, s), 1.50 (3H, d, $J$ = 6.7 Hz), 1.13−1.07 (42H, m); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 166.9 (C), 149.4 (C), 140.0 (C), 129.6 (C), 129.5 (CH), 124.9 (CH), 100.9 (CH), 74.4 (CH), 70.6 (CH), 66.9 (CH), 52.1 (Me), 18.3 (Me), 18.2 (Me), 13.0 (Me), 12.8 (CH); HRMS (FAB) $m/z$: $[M + H]^+$ cacld for $C_{32}H_{57}O_5Si_2$, 577.3745; found, 577.3741.

*1,5-Anhydro-1-(4-cyanophenyl)-2,6-dideoxy-3,4-bis-O-[tri(propan-2-yl)silyl]-L-lyxo-hex-1-enitol (**10c**).* The reaction was performed with **1d** (73 mg, 0.10 mmol), **2c** (50 mg, 0.30 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) to provide **10c** (10.0 mg, 19%) and **9c** (33.0 mg, 58%). $[\alpha]D^{23}$ = 74.0 (c = 0.4, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.65(2H, d, $J$ = 9.5


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Hz), 7.61 (2H, d, $J$ = 8.5 Hz), 5.37 (1H, m), 4.59 (1H, m), 4.37 (1H, m), 4.12 (1H, t, $J$ = 3.3 Hz), 1.49 (3H, d, $J$ = 6.8 Hz), 1.11−1.08 (42H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.7 (C), 139.9 (C), 132.0 (CH), 125.5 (CH), 118.9 (C), 111.5 (C), 101.9 (CH), 74.5 (CH), 70.5 (CH), 66.9 (CH), 18.3 (Me), 18.2 (Me), 15.4 (Me), 13.1 (CH), 12.8 (CH); HRMS (FAB) $m/z$: $[M + H]^+$ cacld for $C_{31}H_{54}O_3NSi_2$, 544.3642; found, = 544.3614.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00218.

$^1$HNMR spectra and $^{13}$CNMR spectra of compounds **3a**, **3b**, **3c**, **3d**, **4a**, **4b**, **4c**, **5a**, **5b**, **5c**, **5d**, **6b**, **6c**, **6d**, **7a**, **7b**, **7c**, **7d**, **8a**, **8b**, **8c**, **9a**, **9b**, **9c**, **9d**, **10a**, **10b**, and **10c** (PDF)

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### Notes

The author declares no competing financial interest.

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## ■ ABBREVIATIONS

TIPS, triisopropylsilyl; dppf, 1,1′-*bis*(diphenylphosphino)-ferrocene; dppe, 1,2-*bis*(diphenylphosphino)ethane

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