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

Tsuyoshi Shinozuka*

Cite This: ACS Omega 2021, 6, 8447−8455

ACCESS

Metrics & More

Article Recommendations

Supporting Information

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(PPh3)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 Et3SiH 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.2b 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 alkytones.2b Conversely, a decarboxylative cross-coupling reaction was reported to be catalyzed by Pd0/Brettphos,4d and decarbonylation of the Mizoroki−Heck-type reaction in the presence of (PhCH2)2Bu3NCl has been described.4z Thus, the selectivity of the palladium-catalyzed cross-coupling of acyl halides remains incompletely understood, and further investigations are needed.

Aroyl C-glycosides are naturally occurring compounds, and many synthetic analogues have been reported to possess a variety of biological activities.5 The palladium-catalyzed aroylation 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 reported8,9 We found that the selectivity of the palladium-catalyzed aroylation and arylation of 1-tributylstannyl glycal 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-glucal synthesis as 10 mol % PdCl2[1,2-bis(diphenylphosphino)ethane (dppe)], 2 equiv of Na2CO3, 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 % PdCl2(dppe), which resulted in almost no reaction (entry 1). When Na2CO3 was omitted, trace amounts of aroyl C-glucal 3a and aryl C-glucal 4a were observed.
However, the reaction remained sluggish, and a large amount of the starting D-glucal 1a was not consumed. The use of PdCl₂(CH₃CN)₂ has been reported to be effective for aroyl C-glycal synthesis, and it increased the yield 3a (20%, entry 3). As Table 1.

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

| entry | Y | equiv | catalyst (10 mol %) | additives (equiv) | yield of 3 (%)b | yield of 4 (%)b | reaction time (h) |
|-------|---|-------|---------------------|-----------------|----------------|----------------|-------------------|
| 1     | 2a| H     | 1.2 PdCl₂(dppe)     | Na₂CO₃ (3 equiv) | 0              | 0              | 30                |
| 2     | 2a| H     | 1.2 PdCl₂(dppe)     | none            | <1             | <1             | 30                |
| 3     | 2a| H     | 1.2 PdCl₂(CH₃CN)₂   | Na₂CO₃ (3 equiv) | 20 (3a)        | <1             | 7                 |
| 4     | 2a| H     | 3 PdCl₂(CH₃CN)₂     | none            | 70 (3a)        | <1             | 1.5               |
| 5     | 2b| CO₂Me| 3 PdCl₂(CH₃CN)₂     | none            | 22 (3b)        | <1             | 5.5               |
| 6     | 2c| CN    | 3 PdCl₂(CH₃CN)₂     | none            | 24 (3c)        | 13 (4c)        | 1                 |
| 7     | 2c| CO₂Me| 3 PdCl₂(CH₃CN)₂     | none            | 21 (3b)        | <1             | 5                 |
| 8     | 2c| CO₂Me| 3 PdCl₂(dppe)      | none            | 15 (3b)        | 2 (4b)         | 25                |
| 9     | 2c| CO₂Me| 3 PdCl₂(PPhCN)₂    | none            | 12 (3b)        | 3 (4b)         | 25                |
| 10    | 2c| CO₂Me| 3 PdCl₂            | none            | 17 (3b)        | 0 (4b)         | 25                |
| 11    | 2c| CO₂Me| 3 Pd(OAc)₂         | none            | 57 (3b)        | <1             | 0.5               |
| 12    | 2c| CO₂Me| 3 Pd(OAc)₂         | CuI (2 equiv)   | 44 (3b)        | 6 (4b)         | 1.5               |
| 13    | 2c| CO₂Me| 3 Pd(TFA)₂         | none            | 19 (3b)        | <1             | 3                 |
| 14    | 2c| CO₂Me| 3 [PdCl₂(allyl)]₂ | none            | 12 (3b)        | 3 (4b)         | 5                 |
| 15    | 2c| CO₂Me| 3 Pd(dbu)₂         | none            | <1             | 0              | 29.5              |
| 16    | 2c| CO₂Me| 3 Pd(acac)₂        | none            | 44 (3b)        | <1             | 3                 |
| 17    | 2c| CO₂Me| 3 PdCl₂(cod)       | none            | 20 (3b)        | <1             | 3                 |
| 18    | 2c| CO₂Me| 3 PdCl₂(nbdi)      | none            | 26 (3b)        | <1             | 6.5               |
| 19    | 2c| CO₂Me| 3 Pd(TMEDA)₂       | none            | 24 (3b)        | 0              | 29                |
| 20    | 2c| CO₂Me| 3 Pd(EDA)₂         | none            | 28 (3b)        | 0              | 30.5              |
| 21    | 2c| CO₂Me| 3 PdCl₂(2,2′-bipyridine) | none          | 36 (3b)        | <1             | 7.5               |
| 22    | 2c| CO₂Me| 3 Pd(PPh₃)₂        | none            | <1             | 71 (4b)        | 4.5               |
| 23    | 2c| CO₂Me| 3 PdCl₂(PPh₃)₂     | none            | 4 (3b)         | 38 (4b)        | 3                 |
| 24    | 2c| CO₂Me| 3 Pd(AsPh₃)₂       | none            | 12 (3b)        | 8 (4b)         | 4.5               |
|       | 2b| CO₂Me| 3 PdCl₂(2,2′-bipyridine) | none          | 36 (3b)        | <1             | 7.5               |
|       | 2b| CO₂Me| 3 Pd(OAc)₂         | CuI (2 equiv)   | 44 (3b)        | 6 (4b)         | 1.5               |
|       | 2b| CO₂Me| 3 Pd(TFA)₂         | none            | 19 (3b)        | <1             | 3                 |
|       | 2b| CO₂Me| 3 [PdCl₂(allyl)]₂ | none            | 12 (3b)        | 3 (4b)         | 5                 |
|       | 2b| CO₂Me| 3 Pd(dbu)₂         | none            | <1             | 0              | 29.5              |
|       | 2b| CO₂Me| 3 Pd(acac)₂        | none            | 44 (3b)        | <1             | 3                 |
|       | 2b| CO₂Me| 3 PdCl₂(cod)       | none            | 20 (3b)        | <1             | 3                 |
|       | 2b| CO₂Me| 3 PdCl₂(nbdi)      | none            | 26 (3b)        | <1             | 6.5               |
|       | 2b| CO₂Me| 3 Pd(TMEDA)₂       | none            | 24 (3b)        | 0              | 29                |
|       | 2b| CO₂Me| 3 Pd(EDA)₂         | none            | 28 (3b)        | 0              | 30.5              |
|       | 2b| CO₂Me| 3 PdCl₂(2,2′-bipyridine) | none          | 36 (3b)        | <1             | 7.5               |
|       | 2b| CO₂Me| 3 Pd(PPh₃)₂        | none            | <1             | 71 (4b)        | 4.5               |
|       | 2b| CO₂Me| 3 PdCl₂(PPh₃)₂     | none            | 4 (3b)         | 38 (4b)        | 3                 |
|       | 2b| CO₂Me| 3 Pd(AsPh₃)₂       | none            | 12 (3b)        | 8 (4b)         | 4.5               |

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

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

| entry | Y | equiv | catalyst (10 mol %) | additives (equiv) | yield of aroyl C-glycal (%)b | yield of aryl C-glycal (%)b | reaction time (h) |
|-------|---|-------|---------------------|-----------------|-----------------------------|-----------------------------|-------------------|
| 1a    | 2a| H     | 1.2 PdCl₂(dppe)     | Na₂CO₃ (3 equiv) | 89 (3a)                     | <1 (4a)                     | 1                 |
| 2b    | 2c| 4-CO₂Me| 1.2 PdCl₂(dppe)     | none            | 57 (3b)                     | <1 (4b)                     | 0.5               |
| 2c    | 2a| 4-CN  | 1.2 PdCl₂(dppe)     | none            | 48 (3c)                     | 22 (4c)                     | 4                 |
| 2d    | 2a| 4-Me  | 1.2 PdCl₂(dppe)     | none            | 54 (3d)                     | 0 (4d)                      | 1                 |
| 2b    | 2a| 4-CN  | 1.2 PdCl₂(dppe)     | none            | 82 (5a)                     | 0 (6a)                      | 1                 |
|       | 2a| 4-Me  | 1.2 PdCl₂(dppe)     | none            | 74 (5b)                     | 0 (6b)                      | 1                 |
|       | 2a| 4-CN  | 1.2 PdCl₂(dppe)     | none            | 62 (5c)                     | <1 (6c)                     | 1                 |
|       | 2a| 4-Me  | 1.2 PdCl₂(dppe)     | none            | 88 (5d)                     | 0 (6d)                      | 0.5               |

**The reaction was performed using 1c (0.10 mmol), 2 (0.30 mmol), and Pd catalyst (0.010 mmol %) in refluxing toluene (5 mL). bIsolated yield. cProduct was isolated with an inseparable impurity.
this reaction remained sluggish with several byproducts, further optimization was required. When Na₂CO₃ 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 PdCl₂(PPh₃)₂ led to comparable results as PdCl₂(CH₃CN)₂ (Table 1, entry 7). The use of bidentate phosphine ligands, such as PdCl₂(dppp) or PdCl₂[1,1′-bis(diphenylphosphino)ferrocene (dppf)], did not improve the yield even after 25 h (entries 8 and 9). When PdCl₂ was employed, aroyl C-D-glucal 3b was isolated at 17% yield (entry 10). The use of PdCl₂ was reported for synthesizing aromatic ketone from acyl chlorides and arylboronic acid. The counterion 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 PdCl₂ required a longer time than 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). 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(PPh₃)₄ provided aroyl C-D-glucal 4b selectively (71% yield) with a trace amount of aroyl adduct 3b (entry 22). It is interesting to note that Pd(PPh₃)₄ was reported to catalyze the synthesis of ketone from acid chloride and boronic acids. The use of PdCl₂(PPh₃)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(PPh₃)₄ produces aroyl 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 benzyloxy chloride (2a) was reacted, aroyl adduct 3a was obtained at 89% yield, which is better than that catalyzed by PdCl₂(CH₃CN)₂ (Table 1, entry 4). 4-Toluoyl adduct 3d was also formed in a selective manner. When 4-cyanobenzyloxy 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 methoxy carbonyl or cyano group, it remains unclear why such diminished selectivity was observed. Similar high selectivity was observed when 1-tributylstannyl β-galactal 1b was reacted with aroyl chlorides 2a and 2b 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(PPh₃)₄ was used as a catalyst, an unsubstituted aroyl 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. 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. When the reaction of 1-tributylstannyl β-galactal 1b and 2b was catalyzed by Pd(PPh₃)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(PPh₃)₄. In fact, the reaction of 1b catalyzed by Pd(PPh₃)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(PPh₃)₄ resulted in the

---

**Table 3. Reactions of 6-Deoxy-1-l-fucal 1c or L-fucal 1d and Aroyl Chlorides 2a–d**

| Entry | Aroyl Chloride | Pd(OAc)₂ Yield (%) | Reaction Time (h) | Product | Pd(PPh₃)₄ Yield (%) | Reaction Time (h) |
|-------|----------------|---------------------|-------------------|---------|---------------------|-------------------|
| 1c    | 2a H           | 75 (7a)             | 1                 | 12, 53' (7a) | 36', 18' (8a)       | 4'                |
| 2b    | 4-CO₂Me        | 76 (7b)             | 1                 | <1, <1' (7b) | 34, 19' (8b)       | 2'                |
| 2c    | 4-CN           | 49 (7c)             | 8' (8c)           | 4, 6' (7c) | 32', 84' (8c)      | 8'                |
| 2d    | 4-Me           | 81 (7d)             | 1                 | 39 (7d)    | <1 (8d)            | 6'                |
| 1d    | 2a H           | 84 (9a)             | 0 (10a)           | 38 (9a)   | 410 (10a)          | 5'                |
| 2b    | 4-CO₂Me        | 90 (9b)             | 1 (10b)           | 44 (9b)   | 21 (10b)           | 8'                |
| 2c    | 4-CN           | 57 (9c)             | 1 (10c)           | 58 (9c)   | 19 (10c)           | 7'                |
| 2d    | 4-Me           | 91 (9d)             | 0 (10d)           | 55 (9d)   | 0 (10d)            | 4.5'              |

Notes: The reaction was performed using 1b (0.10 mmol), 2 (0.30 mmol), and Pd catalyst (0.01 mmol) in refluxing toluene (5 mL) unless otherwise noticed. Isolated yield. The palladium catalyst was used at 0.020 mmol. A small amount of the adduct decomposed after several days. Product was isolated with inseparable impurities.
formulation of aryl C-\-galactal 6d. This was an unexpected result because other stannylic glycals 1a, 1c, and 1d provided aryl 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 aryl 6-deoxy-C-\-glycals 7a–7d and aryl C-\-fucals 9a–9d was observed when Pd(OAc)2 was employed as a catalyst for all aryl 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 aryl C-\-glycals 7 and 9. The selectivity was lower in the reaction between 1c and 2c than the reactions of 1a with 2a, 2b, or 2d. However, the selectivity was better than that of the reaction of 1a with 2c (Table 2). As reported previously, 1-fucal analogues tend to exhibit instability, and a small amount of aryl adduct 9a decomposed after several days of standing at room temperature, as confirmed by the 1H 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(PPh3)4 was utilized in this reaction. Although aryl 6-deoxy-C-\-glycals 8a–8c were formed preferentially when 2a–2c were used in reactions catalyzed by Pd(PPh3)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(PPh3)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(PPh3)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 1H NMR spectra (see the Supporting Information). The reaction of 1c with 2c catalyzed by Pd(PPh3)4 was messy, and the adduct 8a contained an inseparable impurity. The reaction of 1-tributylstannyl-L-\-fucal 1d catalyzed by Pd(PPh3)4 lost selectivity when 2b and 2c were used. In these reactions, the formation of aryl adducts 9b and 9c was preferred.

Again, when an electron-releasing 4-toluoyl chloride (2d) was reacted in the presence of Pd(PPh3)4 only aryl 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(PPh3)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 aryl 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.

An electron-releasing group at the 4-position of aryl chloride is an important factor for selective arylation. This could be explained by the stronger Ar−C=O bond with the four-electron-releasing group.

## CONCLUSIONS

In conclusion, the selectivity of the palladium-catalyzed arylation and arylation of 1-tributylstannyl glycals 1a–1d with aryl chlorides 2a–2d was investigated. The reaction catalyzed by Pd(OAc)2 provided aryl C-\-glycals selectively with high yields for all 1-tributylstannyl glycals (1a–1d) examined. Although aryl C-\-glycals 4a–4c were selectively obtained with the reaction of four-electron-withdrawing or unsubstituted aryl chlorides (2a–2c) with 1-tributylstannyl L-glucal 1a catalyzed by Pd(PPh3)4, the selectivity was diminished or lost when the reaction was performed with other 1-ributylstannyl glycals (1b–1d). When the reaction was performed with electron-releasing 2d, the selective formation of aryl 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(PPh3)4. Thus, further research on selective arylation is required.

## EXPERIMENTAL SECTION

All reactions were performed in glass flasks under N2. 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. 1H and 13C 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 (δ) 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 Quadrupole-ToF MS and an Acquity UHPLC system.

### General Procedure of Palladium-Catalyzed Coupling Reactions

To a solution of 1-tributylstannyl glucal 1 (0.10 mmol) in toluene (5 mL) was added palladium catalyst (0.01 mmol), followed by aryl 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]-o-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, CHCl3); \( 1^H \) NMR (400 MHz, CDCl3): \( \delta 7.98 \) (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); \( 1^3C \) NMR (100 MHz, CDCl3): \( \delta 190.7 \) (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), 18.1 (Me), 18.0 (Me), 12.5 (CH), 12.3 (CH), 12.0 (CH); HRMS (FAB) \( m/z \): [M + Na]+ caddl for C31H24O7Si3Na, 741.4742; found, 741.4728.

#### 2,6-Anhydro-3-deoxy-1-[4-(methoxycarbonyl)phenyl]-4,5,7-tris-O-[tri(propan-2-\-yl)silyl]-o-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, CHCl3); \( 1^H \) NMR (400 MHz, CDCl3): \( \delta 8.06 \) (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
and Pd(OAc)₂ (2.0 mg, 0.010 mmol) to provide 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. The spectral characteristics were in agreement with the previously reported data.³ ¹H NMR (400 MHz, CDCl₃): δ 8.45 (2H, d, J = 7.8 Hz), 8.22 (2H, d, J = 7.8 Hz), 8.11 – 7.97 (2H, m), 5.90 – 5.60 (1H, m), 5.72 – 5.80 (1H, m), 3.95 (3H, s), 1.12 – 1.01 (63H, m). ¹³C NMR (100 MHz, CDCl₃): δ 189.7 (C), 166.4 (C), 149.3 (C), 140.3 (C), 133.3 (C), 129.7 (C), 129.2 (CH), 110.9 (CH), 81.4 (CH), 60.7 (CH), 51.2 (Me), 18.2 (Me), 18.0 (Me), 12.6 (CH), 12.0 (CH); HRMS (FAB) m/z: [M + H]⁺ calcd for C₅₈H₈₄O₃Si₇, 874.6491; found, 874.6490.

2,4-Anhydro-1-[(4-cyanophenyl)l]yl)-3-deoxy-4,5,7-tris-O-[(trisopropyl)l]yl]-α-arabino-hept-2-ene (4a). The reaction was performed with 1a (90 mg, 0.10 mmol), 2a (35 µL, 0.30 mmol), and Pd(OAc)₂ (2.0 mg, 0.010 mmol) to provide 4a. The spectral characteristics were in agreement with the previously reported data.³ ¹H NMR (400 MHz, CDCl₃): δ 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). ¹³C NMR (100 MHz, CDCl₃): δ 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 (CH₂), 18.2 (Me), 18.1 (Me), 18.0 (Me), 12.6 (CH), 12.5 (CH), 12.1 (CH); HRMS (FAB) m/z: [M + K]⁺ calcd for C₄₉H₇₅O₃Si₂K, 729.4532; found, 729.4521.

1,5-Anhydro-2-deoxy-1-[(4-methoxybenzyl)phenyl]l]yl)-3,4,6-tris-O-[(trisopropyl)l]yl]-α-arabino-hex-1-enitol (4b). The reaction was performed with 1a (90 mg, 0.10 mmol), 2b (60 mg, 0.30 mmol), and Pd(PPh₃)₄ (12 mg, 0.010 mmol) to provide 4b. The reaction was performed with 1a (90 mg, 0.10 mmol), 2b (60 mg, 0.30 mmol), and Pd(PPh₃)₄ (12 mg, 0.010 mmol) to provide 4b. The spectral characteristics were in agreement with the previously reported data.

https://doi.org/10.1021/acsomega.1c00218
ACS Omega 2021, 6, 8447–8455
(6.4 mg, 88%). [α]D$^23$ = −35.7 (c = 1.1, CHCl$_3$); $^1$H 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 (6H, 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 + Na$^+$] ccalcd for C$_{13}$H$_{21}$O$_2$Si$_2$Na, 608.5107; found, 608.5094.

2.6-Anhydro-3,7-dideoxy-1-[4-(methoxycarbonyl)phenyl]-4,5-bis-O-[tri(propan-2-yl)silyl]-l-arabino-hept-2-ene (7a). The reaction was performed with 1c (73 mg, 0.10 mmol), 2b (60 mg, 0.03 mmol), and Pd(OAc)$_2$ (2.0 mg, 0.010 mmol) to provide 7a (45.6 mg, 76%). [α]D$^25$ = 35.9 (c = 0.4, CHCl$_3$); $^1$H 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, t, J = 1.4, 7.1 Hz, H-3), 4.23 (1H, dt, J = 2.1, 5.2 Hz, H-7), 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$^+$] ccalcd for C$_{32}$H$_{57}$O$_4$Si$_2$Na, 627.3513; found, 627.3506.

2.6-Anhydro-1-[4-cyanophenyl]-2,6-dideoxy-1-phenyl-3,7-dideoxy-4-[4-methylphenyl]-4,5-bis-O-[tri(propan-2-yl)silyl]-l-arabino-hept-2-ene (7c). The reaction was performed with 1c (73 mg, 0.10 mmol), 2c (50 mg, 0.03 mmol), and Pd(OAc)$_2$ (2.0 mg, 0.010 mmol) to provide 7c (281 mg, 49%) and 8c (44 mg, 8%). [α]D$^25$ = 56.3 (c = 1.5, CHCl$_3$); $^1$H 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, t, J = 1.9, 7.1 Hz, H-6), 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 (C), 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 + Na$^+$] ccalcd for C$_{35}$H$_{59}$O$_4$Si$_2$Na, 635.3554; found, 635.3551.

2.6-Anhydro-3,7-dideoxy-l-1,4-methylphenyl)-4,5-bis-O-[tri(propan-2-yl)silyl]-l-arabino-hept-2-ene (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) to provide 7d (45.3 mg, 81%; 21.9 mg, 39%, respectively). [α]D$^25$ = 38.8 (c = 1.4, CDCl$_3$); $^1$H 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, t, J = 1.9, 7.2 Hz, H-5), 4.23 (1H, dt, J = 2.1, 5.6 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$^+$] ccalcd for C$_{32}$H$_{57}$O$_4$Si$_2$, 581.3759; found, 581.3768.

1.5-Anhydro-2,6-dideoxy-1-phenyl-3,4-bis-O-[tri(propan-2-yl)silyl]-l-arabino-hept-1-ene (8a). The reaction was performed with 1c (73 mg, 0.10 mmol), 2a (35 μL, 0.30 mmol), and Pd(PPh$_3$)$_2$ (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. [α]D$^25$ = 28.3 (c = 0.8, CHCl$_3$); $^1$H 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, t, J = 2.0, 7.1 Hz, H-3), 4.25−4.21 (1H, 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), 14.8 (Me), 13.8 (CH), 12.7 (CH), 12.6 (CH).
The reaction was performed with 1c (73 mg, 0.10 mmol), 2b (60 mg, 0.30 mmol), and Pd(OAc)$_2$ (12 mg, 0.06 mmol) to provide 8b (19.7 mg, 34%). [α]$^2$D = 29.3 (c = 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 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, 1H, q, 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$_3$): δ 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]$^+$ cadd for C$_{32}$H$_{56}$O$_4$Si$_2$, 577.3745; found, 577.3759.

The reaction was performed with 1c (73 mg, 0.10 mmol), 2c (50 mg, 0.30 mmol), and Pd(PPh$_3$)$_4$ (12 mg, 0.06 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 $^1$H NMR spectra (see the Supporting Information). [α]$^2$D = 44.2 (c = 0.3, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 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, q, 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$_3$): δ 148.0 (C), 140.7 (C), 132.0 (CH), 125.6 (CH), 119.0 (C), 111.5 (C), 99.7 (CH), 77.5 (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]$^+$ cadd for C$_{32}$H$_{57}$O$_5$Si$_2$, 544.3642; found, 544.3647.

The reaction was performed with 1d (73 mg, 0.10 mmol), 2a (35 μL, 0.30 mmol), and Pd(OAc)$_2$ (20 mg, 0.06 mmol) to provide 9a (45.7 mg, 84%). A small amount of the adduct 9a was decomposed after several days, as confirmed by the $^1$H NMR spectra (see the Supporting Information). [α]$^2$D = 64.0 (c = 0.7, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.87 (2H, d, J = 3.6 Hz), 7.65 (2H, d, J = 3.6 Hz), 6.62 (1H, m), 4.58 (1H, m), 4.48 (1H, m), 4.15 (1H, m), 3.10 (1H, d, J = 7.2 Hz), 1.33–1.37 (50H, m); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 190.9 (C), 149.7 (C), 136.7 (C), 123.5 (CH), 129.7 (CH), 120.8 (CH), 112.8 (CH), 75.1 (CH), 70.3 (CH), 63.8 (CH), 18.4 (Me), 18.1 (Me), 14.1 (Me), 13.2 (Me), 12.6 (CH); HRMS (FAB) m/z: [M + Na]$^+$ cadd for C$_{45}$H$_{64}$O$_{10}$S$_2$Na, 569.3458; found, 569.3469.

The reaction was performed with 1d (73 mg, 0.10 mmol), 2b (60 mg, 0.30 mmol), and Pd(OAc)$_2$ (2 mg, 0.010 mmol) to provide 9b (53.9 mg, 90%). [α]$^2$D = 70.9 (c = 1.4, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 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), 1.13–1.17 (54H, m); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 190.2 (C), 166.4 (C), 149.6 (C), 140.5 (C), 133.2 (CH), 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]$^+$ cadd for C$_{45}$H$_{64}$O$_{10}$S$_2$Na, 627.3513; found, 627.3486.

The reaction was performed with 1d (73 mg, 0.10 mmol), 2c (50 mg, 0.30 mmol), and Pd(PPh$_3$)$_4$ (12 mg, 0.06 mmol) to provide 10c (10.0 mg, 19%) and 9c (33.0 mg, 58%). [α]$^2$D = 74.0 (c = 0.4, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.65 (2H, d, J = 9.5 Hz).
1H NMR spectra and 13C NMR 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)

AUTHOR INFORMATION

Corresponding Author
Tsuosyo Shinozuka – R&D Planning & Management Department, R&D Division, Daiichi Sankyo Co., Ltd., Tokyo 140-8710, Japan; orcid.org/0000-0002-7785-6080; Phone: +81-70-1440-2862; Email: sinozu.xf6@gmail.com, shinozuka.tsuoyo.s@daiichisankyo.co.jp; Fax: +81-3-5436-8561

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.1c00218

Notes
The author declares no competing financial interest.

ACKNOWLEDGMENTS
The author would like to thank Dr. Susumu Satoh for supporting this research.

ABBREVIATIONS
TIPS, trisopropylsilyl; dppf, 1,1′-bis(diphenylphosphino)-ferrocene; dpe, 1,2-bis(diphenylphosphino)ethane

REFERENCES
(1) Review on ketone synthesis by cross-coupling of acyl halide, See: (a) Blanetti, M.; Rosso, H.; Prandi, C.; Degastino, A.; Venturello, P. Suzuki-miyaura cross-coupling in acylation reactions, scope and recent developments. Molecules 2013, 18, 1188–1213. (b) Dieter, R. K. Reaction of Acyl Chlorides with Organometallic Reagents: A Banquet Table of Metals for Ketone Synthesis. Tetrahedron 1999, 55, 4177–4236.
(2) Examples of ketone synthesis by cross-coupling of acyl halide, See: (a) Higashi, S.; Uno, S.; Ohsuga, Y.; Noumi, M.; Saito, R. Palladium-catalyzed cross-coupling of acryl chlorides with aryl stannanes in the presence of triethylsilane: Efficient access to aromatic ketones. Tetrahedron Lett. 2020, 61, 152466. (b) Atoke, S.; Masuno, H.; Sonoda, M.; Suzuki, Y.; Shinohara, H.; Shibata, S.; Ogawa, A. Pd-catalyzed coupling reaction of acid chlorides with terminal alkynes using 1-(2- pyridylethynyl)-2-(2-thienylbenzyl) benzene ligand. Tetra- hedron Lett. 2012, 53, 1764–1767. (c) Lerebours, R.; Camacho-Soto, A.; Wolf, C. Palladium-Catalyzed Chemoselective Cross-Coupling of Acyl Chlorides and Organostannanes. J. Org. Chem. 2005, 70, 8601–8604. (d) Wang, Y.; Burton, D. J. Copper(I)-Only Catalyzed Reactions of (E)-2,3-Difluoro-3-stannylacryl Esters with Acid Chlorides and Mechanistic Studies of the “Copper Effect” in Stille Coupling Reactions. Org. Lett. 2006, 8, 1109–1111. (e) Bandgar, B. P.; Patil, A. V. A rapid, solvent-free, ligandless and mild method for preparing aromatic ketones from acyl chlorides and arylboronic acids via a Suzuki–Miyaura type of coupling reaction. Tetrahedron Lett. 2005, 46, 7627–7630. (f) Urawa, Y.; Ogura, K. A convenient method for preparing aromatic ketones from acyl chlorides and arylboronic acids via Suzuki–Miyaura type coupling reaction. Tetrahedron Lett. 2003, 44, 271–273. (g) Kubo, K.; Ohyama, S.-i.; Shimizu, T.; Takami, A.; Murooka, H.; Nishitoba, T.; Kato, S.; Yagi, M.; Kobayashi, Y.; Inuma, N.; Itoe, T.; Nakamura, K.; Iijima, H.; Osawa, T.; Izawa, T. Synthesis and Structure–Activity Relationship for New Series of 4-Phenoyquinoline Derivatives as Specific Inhibitors of Platelet-Derived Growth Factor Receptor Tyrosine Kinase. Bioorg. Med. Chem. 2003, 11, 5117–5133. (h) Haddach, M.; McCarthy, J. R. New Method for the Synthesis of Ketones: The Palladium-Catalyzed Cross-Coupling of Acyl Chlorides with Arylboronic Acids. Tetrahedron Lett. 1999, 40, 3109–3112. (i) Jousseaux, B.; Kwon, H.; Verlha, J.-B.; Denat, F.; Dubac, J. 3(or 5)-Formyl-2-furan (or pyrrole)carboxylic acids and 3(or 4)-Formyl-2-furan (or pyrrole)carboxamides via Alkoxycarbonylation or Carbomethylation of Stannylated Formyl Heterocycles. Synlett 1993, 1993, 117–118. (j) Miletin, D.; Stille, J. K. Mild, Selective, General Method of Ketone Synthesis from Acid Chlorides and Organotin Compounds Catalyzed by Palladium. J. Org. Chem. 1979, 44, 1613–1618.
(3) Review on decarbonylative cross-coupling, See: (a) Ogigawa, Y.; Sakai, N. Acyl Fluorides in Late-Transition-Metal Catalysis. Angew. Chem., Int. Ed. 2020, 59, 574–594. (b) Guo, L.; Rueping, M. Transition-Metal-Catalyzed Decarbonylative Coupling Reactions: Concepts, Classifications, and Applications. Chem. Eur. J. 2018, 24, 7794–7809. (c) Gooden, L. J.; Rodríguez, N.; Gooßen, K. Carboxylic Acids as Substrates in Homogeneous Catalysis. Angew. Chem., Int. Ed. 2008, 47, 3100–3120.
(4) Examples of decarbonylative cross-coupling, See: (a) Liu, C.; Ji, C.-L.; Qin, Z.-X.; Hong, X.; Szostak, M. Synthesis of Biaryl via Decarbonylative Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling of Carboxylic Acids. Science 2019, 369, 749–759. (b) Malapit, C. A.; Ichishi, N.; Sanford, M. S. Pd-Catalyzed Decarbonylative Cross-Couplings of Aroyl Chlorides. Org. Lett. 2017, 19, 4412–4415. (c) Shi, S.; Meng, G.; Szostak, M. Synthesis of Biaryl through Nickel-Catalyzed Suzuki–Miyaura Coupling of Amidines by Carbon–Nitrogen Bond Cleavage. Angew. Chem., Int. Ed. 2016, 55, 6959–6963. (d) Muto, K.; Yamaguchi, J.; Musaev, D. G.; Itami, K. Decarbonylative organoboron cross-coupling of esters by nickel catalysis. Nat. Commun. 2015, 6, 7508. (e) LaBerge, N. A.; Love, J. Nickel-Catalyzed Decarbonylative Coupling of Aroyl Esters and Arylboronic Acids. Eur. J. Org. Chem. 2015, 2015, 5568–5553. (f) Correa, A.; Cornellia, J.; Martin, R. Nickel-Catalyzed Decarbonylative C–H Coupling Reactions: A Strive for Preparing Bis(hetero)aryl Backbone. Angew. Chem., Int. Ed. 2013, 52, 1878–1880. (g) Amaike, K.; Muto, K.; Yamaguchi, J.; Itami, K. Decarbonylative C–H Coupling of Azoles and Aroyl Esters: Unprecedented Nickel Catalysis and Application to the Synthesis of Muscoride A. J. Am. Chem. Soc. 2012, 134, 13573–13576. (h) Zhao, X.; Yu, Z. Rhodium-Catalyzed Regioselective C-H Functionalization via Decarbonylation of Acid Chlorides and C-H Bond Activation under Phosphine-Free Conditions. J. Am. Chem. Soc. 2008, 130, 8136–8137. (i) Sugihara, T.; Satoh, T.; Miura, M. Mizoroki–Heck type arylation of alkenes using acyl chlorides under base-free conditions. Tetrahedron Lett. 2005, 46, 8269–8271. (j) Blaser, H.-U.; Spencer, A. The palladium-catalysed arylation of activated alkenes with aryl chlorides. J. Organomet. Chem. 1982, 233, 267–274.
(5) (a) Kitamura, K.; Ando, Y.; Matsumoto, T.; Suzuki, K. Total Synthesis of Aryl C-Glycoside Natural Products: Strategies and Tactics. Chem. Rev. 2018, 118, 1495–1598. (b) Bühlig, T.; Griffith, B. R.; Thorson, J. S. Structure, activity, synthesis and biosynthesis of aryl-C-glycosides. Nat. Prod. Rep. 2005, 22, 742–760.
(6) (a) Bächle, F.; Siemens, N.; Ziegler, T. Glycoconjugated Pthalaloycanines as Photosensitizers for PDT—Overcoming Aggregation in Solution. Eur. J. Org. Chem. 2019, 2019, 7089–7116. (b) Bayer, M.; Bächle, F.; Ziegler, T. Synthesis and Pd-catalyzed coupling of 1-C-stannylated glycals. J. Carbohydr. Chem. 2018, 37, 347–369. (c) Choutka, J.; Pohl, R.; Parkan, K. MOP and EE Protecting Groups
in Synthesis of α- or β-Naphthyl-C-Glycosides from Glycals. ACS Omega 2018, 3, 7875−7887. (d) Khatri, H. R.; Nguyen, H.; Dunaway, J. K.; Zhu, J. Total Synthesis of Antitumor Antibiotic Derhodinosylurdamycin A. Chem. Eur J. 2015, 21, 13553−13557. (e) Hartung, J.; Wright, B. J. D.; Danishefsky, S. J. Studies Toward the Total Synthesis of Pluraflavin A. Chem.—Eur J. 2014, 20, 8731−8736. (f) Wurst, J. M.; Liu, G.; Tan, D. S. Hydrogen-Bonding Catalysis and Inhibition by Simple Solvents in the Stereoselective Kinetic Epoxide-Opening Spirocyclization of Glycal Epoxides to Form Spiroketalts. J. Org. Chem. 2011, 76, 7916−7925. (g) Liu, G.; Wurst, J. M.; Tan, D. S. Stereoselective Synthesis of Benzannulated Spiroketalts: Influence of the Aromatic Ring on Reactivity and Conformation. Org. Lett. 2009, 11, 3670−3673. (h) Molianen, S. B.; Tan, D. S. Enantioselective synthesis of erythro-4-deoxyglycals as scaffolds for target- and diversity-oriented synthesis: new insights into glycal reactivity. Org. Biomol. Chem. 2005, 3, 798−803. (i) Dubbuka, S. R.; Steunenberg, P.; Vogel, P. Aryl and arylmethyl C-glycosides through desulfinitive Stille and carboxylative Stille cross-coupling of tinglycals and sulfonyl chlorides. Synlett 2004, 35, 1235−1238. (j) Friesen, R. W.; Loo, R. W.; Sturino, C. F. The preparation of C-aryl glucals via palladium-catalyzed cross-coupling methods. Can. J. Chem. 1994, 72, 1262−1272. (k) Dubois, E.; Beau, J.-M. Papulacandins and chaetiacandin: a stereoselective route to their basic skeleton by a palladium-mediated arylation of 4,6-O-benzylidenen-3-0-tert-butylmethylsilyl-1-tributylstannyln-d-glucal. Carbohydr. Res. 1992, 223, 157−167. (l) Friesen, R. W.; Sturino, C. F. The preparation of C-glycals. The palladium-catalyzed coupling of 3,4,6-tri-O-(tert-butylmethylsilyl)-1-(tributylstannyl)-d-glucal and aryl bromides. J. Org. Chem. 1990, 55, 2572−2574. (m) Dubois, E.; Beau, J.-M. Arylation of 1-tributylstannyl glucals catalyzed by palladium: A synthetic route to the basic skeleton of the papulacandins and chaetiacandin. Tetrahedron Lett. 1990, 31, 5165−5168. (n) Friesen, R. W.; Sturino, C. F. Stereoselective oxidative spiroketalization of a C-arylglucal derived from palladium-catalyzed coupling. Synthesis of the C-arylglycoside spiroketal nucleus of the papulacandins. J. Org. Chem. 1990, 55, 5808−5810.

(7) Shinozuka, T. Synthesis of Benzyl 2-Deoxy-C-Glycosides. ACS Omega 2020, 5, 33196−33205.

(8) (a) Dubois, E.; Beau, J.-M. Synthesis of C-glycopyranosyl compounds by a palladium-catalyzed coupling reaction of 1-tributylstannyl-d-glucals with organic halides. Carbohydr. Res. 1992, 228, 103−120. (b) Dubois, E.; Beau, J.-M. Formation of C-glycosides by a palladium-catalysed coupling reaction of tributylstannyln glyxals with organic halides. J. Chem. Soc., Chem. Commun. 1990, 1191−1192.

(9) Alternatives approach to acyl C-glycal synthesis, See: Vedachalam, S.; Tan, S. M.; Cai, S.; Liu, X.-W. N-Heterocyclic Carbene Catalyzed C-Glycosylation: A Concise Approach from Stetter Reaction. Org. Lett. 2012, 14, 174−177.

(10) The Control of decarboxylation of acid fluorides by the catalytic system was reported, See: Blanchard, N.; Bizet, V. Acid Fluorides in Transition-Metal Catalysis: A Good Balance between Stability and Reactivity. Angew. Chem., Int. Ed. 2019, 58, 6814−6817.

(11) Espinet, P.; Echavarren, A. M. The Mechanisms of the Stille Reaction. Angew. Chem., Int. Ed. 2004, 43, 4704−4734.

(12) (a) Sakamoto, S.; Kawanishi, E.; Nomura, S.; Ishikawa, T. Aryl-β-C-glicosidation using glucal boronate: application to the synthesis of tri-O-methylnorbergenin. Tetrahedron 2012, 68, 5744−5753. (b) Friesen, R. W.; Loo, R. W. Preparation of C-aryl glucals via the palladium catalyzed coupling of metalated aromatics with 1-iodo-3,4,6-tri-O-(triisopropylsilyl)-d-glucal. J. Org. Chem. 1991, 56, 4821−4823.

(13) Basolo, F.; Pearson, R. G. The trans effect in Metal Complexes. Prog. Inorg. Chem. 1962, 4, 381−453.

(14) In the rhodium-catalyzed decarboxylation of aldehydes, it was reported the reaction is accelerated by electron-withdrawing aldehyde substituents, See: Fristrup, P.; Kreis, M.; Palmelund, A.; Norby, P.-O.; Madsen, R. The Mechanism for the Rhodium-Catalysed Decarboxylation of Aldehydes: A Combined Experimental and Theoretical Study. J. Am. Chem. Soc. 2008, 130, 5206−5215.