Regio- and stereo-selective synthesis of aryl 2-deoxy-*C*-glycopyranosides by palladium-catalyzed Heck coupling reactions of glycals and aryl iodides†

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The Heck coupling of aryl iodides with pyranoid glycals using a catalytic amount of $Pd(OAc)_2$ to form pyranoid aryl C-glycosides has been achieved. The reaction takes place smoothly in the presence of Ag_2CO_3 and $Cu(OAc)_2$ (or DMSO) in acetonitrile. This arylation process, which occurs in a highly regio- and stereo-selective manner, provides a simple, mild, and efficient approach to the synthesis of aryl 2-deoxy-C-glycopyranosides.

Introduction

Aryl-*C*-glycosides, due to their occurrence in biologically important natural products and their use as stable analogues of *O*-glycosides and *N*-glycosides that are resistant to enzymatic cleavage, have gained considerable attention in recent years.[1–3] In particular, the unique 2-deoxy pyranoid aryl-*C*-glycoside structure is embodied in a variety of bioactive natural products including the pluramycins (kidamycin, *etc.*), angucyclines (galtamycinone, vineomycinone B_2 methyl ester, *etc.*), and benzoisochromanequinones (medermycin, *etc.*).[3] Due to their biological importance and structural complexity, many synthetic approaches have been developed so far.[4] However, from a synthetic point of view, the highly regio- and stereo-selective formation of the aryl C-C glycosidic bond is still a predominant challenge.

The Heck reaction, a Pd-catalyzed coupling of olefins with organohalides or triflates, has become a powerful tool for C-C bond formation.[5] Pioneering work, carried out by Daves (Scheme 1, path 1)[6] and Czernecki (Scheme 1, path 2),[7] showed that the Pd (II)-mediated Heck arylation of glycals occurred to form aryl C-C glycosidic bonds by using stoichiometric Pd (II). Unfortunately, mixtures of coupling products were always obtained due to three different types of elimination approaches (Scheme 1, E-a/E-b/E-c). Except for the low yield and low regioselectivity, the use of toxic reagents such as organomercury was the other drawback of this work. More recently, Maddaford (Scheme 1, path 3)[8] and de la Figuera (Scheme 1, path 4)[9] respectively reported the Pd (II)-catalyzed Heck arylations of glycals with $ArB(OH)_2$ in the presence of a catalytic amount of $Pd(OAc)_2$, providing the carbon-Ferrier type (Scheme 1, E-a) or ring-opened products (Scheme 1, E-b). Very recently, we successfully developed a palladium (II)-catalyzed oxidative Heck-type reaction of pyranoid glycals with arylboronic acids, which underwent a Heck *syn*-β-hydride elimination to yield enol ether or ketone types of aryl *C*-glycosides in decent yields and with broad substrate scope (Scheme 1, E-c).[10] However, this approach may be hampered by the availability of arylboronic acids which are normally prepared from aryl halides. For example, *C*-nucleosides are important agents for biological research and for potential therapeutic applications, however, methods for the synthesis of pyranoid *C*-nucleosides are quite limited.[6b,11] It is not convenient to obtain pyranoid *C*-nucleosides using our oxidative Heck protocol, because the corresponding heterocyclic boronic acids are not easily prepared. Therefore, we want to investigate the possibility of the Heck arylations of pyranoid glycals with aryl halides which are more feasible materials. In fact, contrary to the well-established Pd-catalyzed Heck reaction of furanoid glycals with aryl organohalides,[11a] the Pd-catalyzed Heck reaction between pyranoid glycals and aryl halides or triflates has been less explored, and few examples were reported.[11b]

To tackle this problem, we turned our attention to the Pd-catalyzed Heck *C*-glycosylations of pyranoid glycals with aryl halides. We found that in the presence of Ag_2CO_3 and $Cu(OAc)_2$, an efficient Heck arylation occurred very smoothly between pyranoid glycals and aryl iodides using $Pd(OAc)_2$ as catalyst. The reaction only underwent a Heck *syn*-β-hydride elimination to yield the corresponding enol ether type aryl *C*-glycosides (Scheme 1, path E-c).

Results and discussion

Initially, we examined the couplings of pyranoid glycals **1a–1c** with iodobenzene (**2a**) following Daves' Heck reaction conditions (Table 1, entry 1).[11b] When **1a–1c** and **2a** were catalyzed by 40 mol% $Pd(OAc)_2$ in the presence of bases (both 0.4 eq. of n-Bu_3N and 2.0 eq. of Na_2CO_3 were added) at room temperature or 50 °C in DMF, none of the coupling products were observed, only unreacted starting materials got recovered. After intensive screening, we found that the coupling reaction between the silyl-protected glucal **1c** and iodobenzene (**2a**) occurred in the presence of 2.0 eq. of silver carbonate (Table 1, entry 4), providing the enol ether type *C*-glycoside **3a** resulted from the Heck *syn*-β-hydride elimination (Scheme 1, E-c) in 71% isolated yield, whereas the other types of elimination products were not obtained during this process. However, under the same conditions, when the acetyl- and benzyl- protected glucals **1a** and **1b** were used as the starting materials, no coupling products were formed (Table 1, entries 2 and 3). According to Daves' results,[6b] the conformational rigidity

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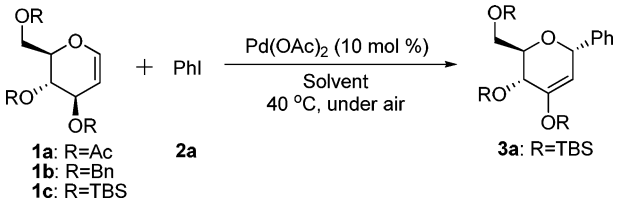
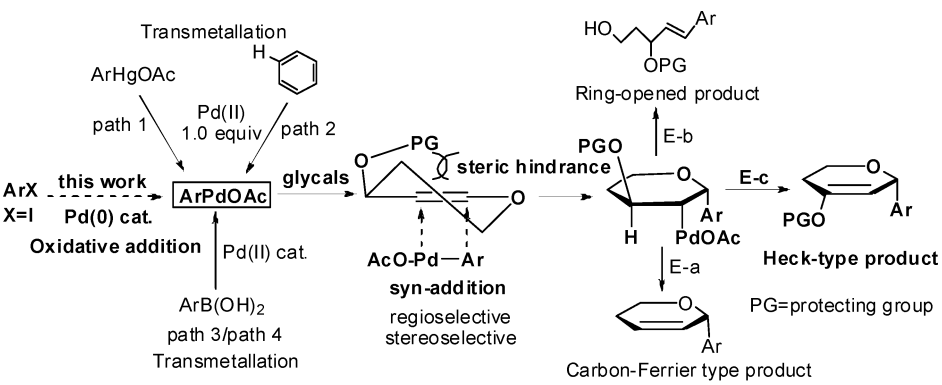
Table 1 Pd-catalyzed Heck coupling reactions of **1a–1c** with iodobenzene to form *C*-glycosides[a]



Entry	Substrate	Additives (eq.)	Solvent	*t* (h)	Yield [%][e]
1[b]	**1a–1c**	none	DMF	48	—
2	**1a**	Ag_2CO_3 (2.0)	DMF or MeCN	48	—
3	**1b**	Ag_2CO_3 (2.0)	MeCN	48	—
4	**1c**	Ag_2CO_3 (2.0)	MeCN	24	71
5	**1c**	BQ (2.0)	MeCN	24	—
6	**1c**	$Cu(OAc)_2$ (2.0)	MeCN	24	<5
7	**1c**	DMSO (4.0)	MeCN	24	<5
8	**1c**	Ag_2CO_3 (0.6)	MeCN	24	74
9	**1c**	Ag_2CO_3 (0.6), BQ (2.0)	MeCN	24	—
10	**1c**	Ag_2CO_3 (0.6), DMSO (4.0)	MeCN	15	90
11	**1c**	Ag_2CO_3 (0.6)	DMSO	24	—
12	**1c**	**Ag_2CO_3 (0.6), $Cu(OAc)_2$ (2.0)**	**MeCN**	**15/24**	**90/92**
13[c]	**1c**	Ag_2CO_3 (0.6), $Cu(OAc)_2$ (2.0)	MeCN	24	94
14[c]	**1c**	Ag_2CO_3 (0.6)	MeCN	48	72
15[c]	**1c**	Ag_2CO_3 (0.6), H_2O (4.0)	MeCN	48	73
16[d]	**1c**	Ag_2CO_3 (0.6), $Cu(OAc)_2$ (2.0)	MeCN	48	—
17[d]	**1c**	Ag_2CO_3 (0.6), DMSO (4.0)	MeCN	48	—

[a] Reaction conditions: **1a–1c** (0.1 mmol), PhI (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), and solvent (1.5 mL), 40 °C, under air. [b] 40 mol% $Pd(OAc)_2$ and Bu_3N (0.4 eq.)/Na_2CO_3 (2.0 eq.), r.t. or 50 °C. [c] The reaction was carried out under Ar. [d] PhBr (0.2 mmol) and **1c** (0.1 mmol) were used as substrates, 50 °C. [e] Isolated yield.



E-a. anti-2,3-beta-heteroatom elimination; E-b. anti-2,1-beta-heteroatom elimination;
E-c. syn-2,3-beta-hydride elimination

Scheme 1 The Heck arylations of pyranoid glycals.

and poor leaving property at *C*-3-*O*-substituent of **1c** (R = TBS, *t*-butyldimethylsilyl) may promote *syn*-β-hydride elimination of the syn-addition intermediate (the organopalladium σ-adduct), this may explain the reactivity difference between **1a–1b** and **1c**, and we chose TBS-protected pyranoid glycals as our substrates.

Subsequently, the effects of different additives on the coupling of **1c** and **2a** were checked. When *p*-benzoquinone (BQ) was used instead of silver carbonate, no coupling products were observed (Table 1, entry 5). When using $Cu(OAc)_2$ or DMSO as the additive, only a trace amount of **3a** was formed (Table 1, entries 6 and 7). It seems that silver carbonate, which might play dual roles in the reaction process (a silver source to scavenge the iodide as well as a base),[12] was crucial to the Heck coupling. Further investigation indicated that the reaction achieved a higher yield (74%) with only 0.6 eq. of Ag_2CO_3 using acetonitrile as solvent (Table 1, entry 8). However, under the same conditions but using DMSO in place of acetonitrile, no coupling reaction took place (Table 1, entry 11). Interestingly, when the combination of 0.6 eq. of Ag_2CO_3 and 2.0 eq. of $Cu(OAc)_2$ was used as the additive, coupling product **3a** was obtained in excellent isolated yield (90% for 15h and 92% for 24h, Table 1, entry 12). Another additive combination with 0.6 eq. of Ag_2CO_3 and 4.0 eq. of DMSO also gained similar results (90% yield for 15h, Table 1, entry 10). When the coupling reaction was carried out under argon atmosphere, **3a** was obtained in a little higher yield (94%) compared with the same conditions under air (Table 1, entry 13). The addition of 4.0 eq. of H_2O did not

improve the yield of **3a** (Table 1, entries 14 and 15). Although it was disclosed that silver carbonate played an important role in palladium-catalyzed Heck reactions of some organo halides,[12] it is noteworthy that the reaction efficiency can be improved by using weak oxidants ($Cu(OAc)_2$ or DMSO) as additives in this protocol. Therefore, after screening, we optimized the reaction conditions for the Heck coupling between pyranoid glycal **1c** and iodobenzene **2a**: 10 mol% $Pd(OAc)_2$, 0.6 eq. of Ag_2CO_3 in combination with 2.0 eq. of $Cu(OAc)_2$ or 4.0 eq. of DMSO, 40 °C in acetonitrile under air for 24h.

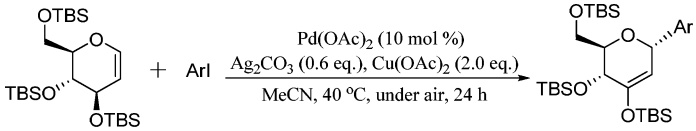
Using the optimized conditions, the coupling reaction with other substrates such as bromobenzene was examined. However, the coupling of **1c** and bromobenzene did not occur even though the reaction was performed at 50 °C for 48 h (Table 1, entries 16 and 17). This indicated that the Heck coupling reaction was only suitable for aryl iodides at this stage.

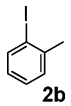
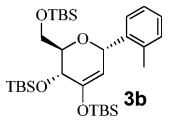
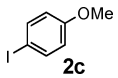
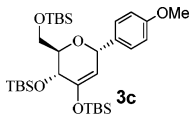
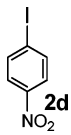
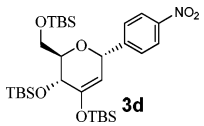
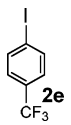
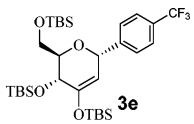
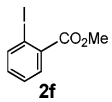
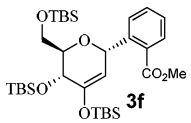
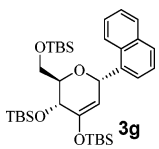
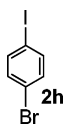
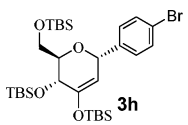
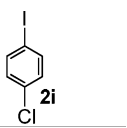
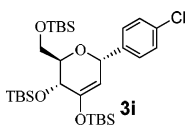
The scope of the Heck reaction of pyranoid glycal **1c** was expanded to a variety of aryl iodides (Table 2). The reaction with various aryl iodides containing electron-donating, electron-withdrawing, and sterically congested groups proceeded smoothly and efficiently (Table 2, entries 1–5), only silyl enol ether type coupling products **3** (*via* Heck syn-β-hydride elimination) were formed. In the case of electron-deficient aryl iodides such as those substituted by NO_2 (**2d**), CF_3 (**2e**), or CO_2Me (**2f**) groups, satisfactory yields (59–94%) were realized by raising the reaction temperature to 50 °C and prolonging the reaction time to 36 h (Table 2, entries 3–5). Condensed aryl iodides such as 1-iodonaphthalene (**2g**), coupled successfully with **1c** leading to **3g** in 95% isolated yield (Table 2, entry 6). It is noteworthy that the reactions with the bifunctional aryl iodides (Ar = 4-BrPh, 4-ClPh) underwent smoothly to give the regioselective coupling products **3h** and **3i** in high yields (Table 2, entries 7 and 8). The resulting compounds **3h** and **3i** can be further transformed by metal-catalyzed cross coupling reactions due to the existence of aryl halides.

Encouraged by these results, we next investigated the Heck coupling of aryl iodides with a series of pyranoid glycals (Table 3). Like the case of glucal **1c**, similar results were obtained when other glycals **1d**, **1e**, **1f** were employed, and all provided the desired single enol ether products in high isolated yields (71–98%) (Table 3, entries 1–7). For those aryl iodides with electron-withdrawing substituents, the Heck reactions achieved good yields by raising the temperature to 50 °C and prolonging the reaction time to 36 h (entries 3 and 6). Finally, we applied our protocol to the synthesis of pyranoid *C*-nucleosides: the Heck coupling of pyranoid glycal **1f** with 5-iodo-1,3-dimethyluracil **2l** proceeded well and only desired silyl enol ether *C*-nucleoside **6b** was obtained in 84% isolated yield (Table 3, entry 8). Compared with the known methods,[6b,11b] our approach to the preparation of pyranoid *C*-nucleosides is highly regioselective, more efficient, more economic, and less toxic.

In all cases, only a single anomer was obtained in each Heck coupling reaction. According to the mechanism, the configuration of the newly-introduced aryl group at the anomeric position is opposite to the C_3-*O*-substituent of the starting glycals, resulted from the syn-addition to the opposite face because of the steric hindrance (Scheme 1). The anomeric stereochemistry of the coupling product was confirmed by its ^{13}C NMR and NOESY spectra analyses.[10,13]

Table 2 Pd-catalyzed Heck reactions of **1c** with different aryl iodides[a]



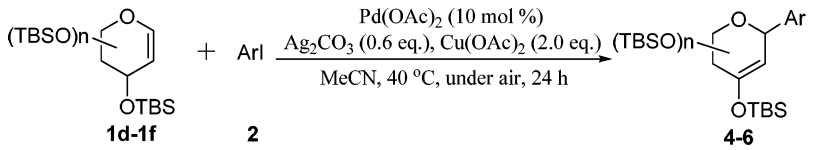
Entry	Aryl iodide	Product	Yield [%][c]
1	 **2b**	 **3b**	99
2	 **2c**	 **3c**	87
3[b]	 **2d**	 **3d**	59
4[b]	 **2e**	 **3e**	75
5[b]	 **2f**	 **3f**	94
6	 **2g**	 **3g**	95
7	 **2h**	 **3h**	82
8	 **2i**	 **3i**	92

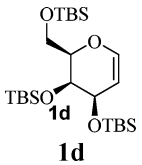
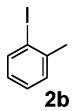
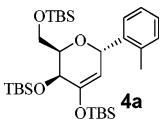
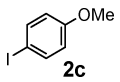
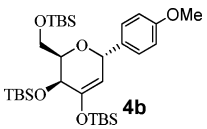
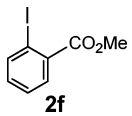
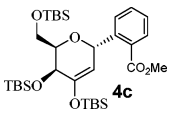
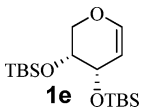
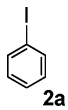
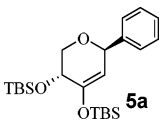
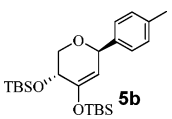
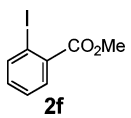
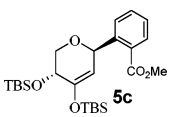
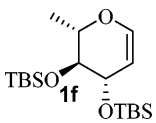
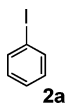
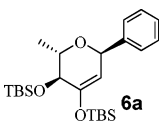
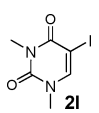
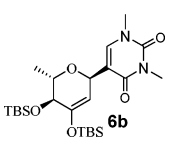
[a] Reaction conditions: **1c** (0.1 mmol), ArI (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), Ag_2CO_3 (0.06 mmol), $Cu(OAc)_2$ (0.2 mmol) in MeCN (1.5 mL), 40 °C, under air, 24 h. [b] The reaction was carried out at 50 °C for 36 h. [c] Isolated yield.

Conclusion

In summary, a simple, mild, and efficient Heck *C*-glycosylation of pyranoid glycals with various aryl iodides has been developed. No any air-sensitive phosphorous ligands were used, and the reaction was easily operated under air. Furthermore, the Heck arylation

Table 3 Pd-catalyzed Heck reactions of aryl iodides with different pyranoid glycals **1d–1f**[a]



Entry	Substrate	Aryl iodide	Product	Yield [%][c]
1	 **1d**	 **2b**	 **4a**	94
2	**1d**	 **2c**	 **4b**	78
3[b]	**1d**	 **2f**	 **4c**	81
4	 **1e**	 **2a**	 **5a**	95
5	**1e**	 **2k**	 **5b**	98
6[b]	**1e**	 **2f**	 **5c**	71
7	 **1f**	 **2a**	 **6a**	88
8	**1f**	 **2l**	 **6b**	84

[a] Reaction conditions: **1d–1f** (0.1 mmol), ArI (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), Ag_2CO_3 (0.06 mmol), $Cu(OAc)_2$ (0.2 mmol) in MeCN (1.5 mL), 40 °C, under air, 24 h. [b] The reaction was carried out at 50 °C, 36 h. [c] Isolated yield.

occurred in a regio- and stereo-selective manner, only a single enol ether coupling product (one anomer) was formed (*via* Heck syn-β-hydride elimination approach), none of the other elimination products such as ring-opened products and carbon-Ferrier type products were observed. Compared with the oxidative Heck protocol we recently disclosed,[10] the coupling reaction using aryl iodides instead of aryl boronic acids opened an alternative avenue to aryl *C*-glycosides. Since aryl halides are generally more available than aryl boronic acids, this protocol may find wide applications to the synthesis of naturally occurring 2-deoxy pyranoid aryl *C*-glycosides and pyranoid *C*-nucleosides with biological importance. Further studies on the synthetic applications and Pd-catalyzed Heck *C*-glycosylations using other organohalides or triflates are underway.

Experimental

General

All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Analytical TLC was performed using aluminium plates pre-coated with silica gel 60-F_{254} (E. Merck), with detection by fluorescence and/or by staining with acidic ceric ammonium molybdate. Column chromatography was performed by employing Silica Gel 200–300 mesh. ^{1}H-NMR spectra were recorded on a JEOL AL-300 (300 MHz), Varian INOVA-500 (500 MHz) or Advance DRX Bruker-400 spectrometers at 25 °C. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in deuterated chloroform. ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ ($\delta = 77.00$ ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High-resolution mass spectrometry was performed on a Bruker APEX IV. Elemental analyses were recorded on a Vario EL-III elemental analyzer.

Preparation of substrates

General procedure for the preparation of persilylated glycal substrates. Peracetylated glycal[14] (4.0 mmol) was dissolved in 15 mL of MeOH, 9 drops of NaOMe/MeOH solution (25–30%, w/w) were added. The reaction mixture was stirred at room temperature. The reaction was monitored by TLC (petroleum ether/ethyl acetate, 1:1). After the starting material disappeared, the reaction mixture was evaporated to dryness. The residue was dissolved in dry DMF (2 mL). Imidazole (3.0 mmol per mmol OH) was added, followed by the addition of *t*-butyldimethylsilyl chloride (2.0 mmol per mmol OH) and 4-dimethylaminopyridine (DMAP, 0.04 mmol). The resulting solution was stirred at 50 °C for 2 days. The mixture was extracted by dichloromethane (three times), and the organic layers were combined and dried over sodium sulfate, filtered, and evaporated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 120:1) to give products.

Compound 1c[15]. Colorless oil. $R_f = 0.67$ (petroleum ether/ethyl acetate, 24:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (d, 1H, $J = 6.3$ Hz), 4.69 (dd, 1H, $J = 4.8$, 6.0 Hz), 4.02–3.88 (m, 3H), 3.80–3.74 (m, 2H), 0.90, 0.89 and 0.87 (3 s, 27H), 0.1–0.005 (6 s, 18H).

Compound 1d[16]. Colorless oil. $R_f = 0.67$ (petroleum ether/ethyl acetate, 24:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (d, 1H, $J = 6.0$ Hz), 4.03 (t, 1H, $J = 3.0$ Hz), 4.11–4.02 (m, 4H), 3.89–3.82 (m, 1H), 0.91 and 0.90 (2 s, 27H), 0.098, 0.068 and 0.056 (3 s, 18H).

Compound 1e. Colorless oil. $R_f = 0.67$ (petroleum ether/ethyl acetate, 22:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (d, 1H, $J = 6.0$ Hz), 4.76 (t, 1H, $J = 5.7$ Hz), 4.04–4.02 (m, 1H), 3.94, 3.84 (m, 1H), 3.76–3.70 (m, 1H), 0.90 (s, 9H), 0.89 (s, 9H), 0.087 (s, 6H), 0.071 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.89, 102.33, 68.55, 64.65, 63.90, 25.89, 18.22, –4.15, –4.19, –4.39, –4.42, –4.86, –4.90; MS (ESI-TOF) *m/z*: $(M + Na)^+$ calcd for $(C_{17}H_{36}O_3Si_2Na^+)$ 367, found 367. Anal. Calcd for $C_{17}H_{36}O_3Si_2$: C, 59.25; H, 10.53. found: C, 58.96; H, 10.27.

Compound 1f[17]. Colorless oil. $R_f = 0.67$ (petroleum ether/ethyl acetate, 22:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (d, 1H, $J = 6.0$ Hz), 4.66 (dd, 1H, $J = 3.0$, 6.3 Hz), 4.07 (t, 1H, $J = 3.8$, Hz), 3.98–3.89 (m, 1H), 3.56 (t, 1H, $J = 6.3$ Hz), 1.32 (d, 3H, $J = 6.9$ Hz), 0.90 (s, 18H), 0.11 and 0.095 (2 s, 18H).

Heck arylation of glycals

General procedure for Heck arylation. To a mixture of the glycal (0.1 mmol) and aryl iodide (0.2 mmol) in 1.5 mL of acetonitrile was added $Pd(OAc)_2$ (0.01 mmol), Ag_2CO_3 (0.06 mmol) and $Cu(OAc)_2$ (0.2 mmol). The resulting suspension was stirred at 40 °C for 24 h under air. After the starting materials were consumed (by TLC: petroleum ether/ethyl acetate, 24/1), the reaction mixture was filtered directly and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate to give the pure product.

Compound 3a. Following the general procedure, cross-coupling afforded **3a** (92%) as a colorless oil, $R_f = 0.50$ (petroleum ether/ethyl acetate, 24/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.42 (m, 2H), 7.34–7.31 (m, 2H), 7.28–7.25 (m, 2H), 5.15 (s, 1H, H-1), 4.90 (d, 1H, $J = 3.0$ Hz, H-2), 4.07 (dd, 1H, $J = 1.5$, 3.0 Hz, H-4), 3.89–3.86 (m, 1H, H-5), 3.82–3.76 (m, 2H, H-6), 0.94 (s, 9H), 0.92 (s, 9H), 0.90 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.062 (s, 3H), 0.056 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.53 (C-3), 141.87, 128.25, 127.67, 106.07 (C-2), 79.03 (C-1), 73.36, 67.00, 62.33, 26.02, 25.91, 18.41, 18.22, 18.10, –3.91, –4.09, –4.51, –5.40; MS (ESI-TOF) *m/z*: $(M + Na)^+$ calcd for $(C_{30}H_{56}O_4Si_3Na^+)$ 587, found 587. Anal. Calcd for $C_{30}H_{56}O_4Si_3$: C, 63.95; H, 9.99. found: C, 63.77; H, 9.95.

Compound 3b. Following the general procedure, cross-coupling afforded **3b** (99%) as a colorless oil, $R_f = 0.50$ (petroleum ether/ethyl acetate, 25/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.43 (m, 1H), 7.18–7.12 (m, 3H), 5.37 (dd, 1H, $J = 1.0$, 2.5 Hz, H-1), 4.89 (d, 1H, $J = 3.0$ Hz, H-2), 4.06 (dd, 1H, $J = 1.0$, 2.5 Hz, H-4), 3.81–3.73 (m, 3H, H-5, H-6), 2.43 (s, 3H, Mε), 0.95 (s, 9H), 0.90 (s, 9H), 0.88 (s, 9H), 0.20 (s, 3H), 0.18 (s, 3H), 0.13 (s, 3H), 0.11 (s, 3H), 0.047 (s, 3H), 0.042 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.07 (C-3), 138.83, 136.97, 130.58, 128.73, 127.79, 125.62, 105.41 (C-2), 78.56 (C-1), 70.91, 66.81, 62.22, 26.08, 25.87, 19.19, 18.48, 18.23, 18.10, –3.76, –4.07, –4.56, –5.40; HRMS (ESI) *m/z*: $(M + Na)^+$ calcd for $(C_{31}H_{58}O_4Si_3Na^+)$ 601.3535, found 601.3544; $(M + K)^+$ calcd for $(C_{31}H_{58}O_4Si_3K^+)$ 617.3269, found 617.3283.

Compound 3c. Following the general procedure, cross-coupling afforded **3c** (87%) as a colorless oil, $R_f = 0.50$ (petroleum ether/ethyl acetate, 24/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, 1H, $J = 8.5$ Hz), 6.86 (d, 1H, $J = 8.5$ Hz), 5.10 (d, 1H, $J = 1.0$ Hz, H-1), 4.87 (d, 1H, $J = 3.0$ Hz, H-2), 4.06 (dd, 1H, $J = 1.5$, 3.0 Hz, H-4), 3.86–3.83 (m, 1H, H-5), 3.80–3.76 (m, 2H, H-6), 3.80 (s, 3H, MeO), 0.95 (s, 9H), 0.92 (s, 9H), 0.89 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.056 (s, 3H), 0.050 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.21, 148.50 (C-3), 134.06, 129.01, 113.60, 106.25 (C-2), 78.89 (C-1), 72.88, 67.00, 62.31, 55.24, 26.02, 25.91, 25.85, 18.40, 18.21, 18.10, –3.89, –4.16, –4.51, –5.40; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for $(C_{31}H_{59}O_5Si_3^+)$ 595.3665, found 595.3671.

Compound 3d. Following the general procedure, the reaction was carried out at 50 °C for 36 h, affording **3d** (59%) as a colorless oil, $R_f = 0.30$ (petroleum ether/ethyl acetate, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, 2H, $J = 8.7$ Hz), 7.61 (d, 2H, $J = 8.7$ Hz), 5.25 (d, 1H, $J = 1.8$ Hz, H-1), 4.83 (d, 1H, $J = 2.7$ Hz, H-2), 4.08 (d, 1H, $J = 2.1$ Hz, H-4), 3.88–3.93 (m, 1H, H-5), 3.77–3.79 (m, 2H, H-6), 0.94 (s, 9H), 0.93 (s, 9H), 0.91 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H), 0.12 (s, 6H), 0.076 (s, 3H), 0.069 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.62, 149.21, 147.38, 128.13, 123.63, 104.57 (C-2), 79.52 (C-1), 72.57, 66.94, 62.20, 25.83, 18.37, 18.20, 18.06, –4.17, –4.58, –5.42; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for ($C_{30}H_{56}NO_6Si_3^+$) 610.3410, found: 610.3423.

Compound 3e. Following the general procedure, the reaction was carried out at 50 °C for 36 h, affording **3e** (75%) as a colorless oil, $R_f = 0.50$ (petroleum ether/ethyl acetate, 25/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, 1H, $J = 8.5$ Hz), 7.55 (d, 1H, $J = 8.5$ Hz), 5.21 (d, 1H, $J = 1.5$ Hz, H-1), 4.86 (d, 1H, $J = 2.5$ Hz, H-2), 4.08 (dd, 1H, $J = 1.0$, 3.0 Hz, H-4), 3.90–3.87 (m, 1H, H-5), 3.81–3.77 (m, 2H, H-6), 0.95 (s, 9H), 0.93 (s, 9H), 0.91 (s, 9H), 0.19 (s, 3H), 0.17 (s, 3H), 0.13 (s, 6H), 0.075 (s, 3H), 0.067 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.90, 146.10, 129.83 (d, 1C, $J = 31.5$ Hz), 127.79, 125.26, 124.22 (d, 1C, $J = 269.5$ Hz, CF_3), 105.16, 79.32, 72.85, 66.98, 62.26, 57.47, 25.97, 25.85, 18.40, 18.22, 18.08, –3.94, –4.14, –4.57, –5.41; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for ($C_{31}H_{56}F_3O_4Si_3^+$) 633.3433, found 633.3434; $(M + Na)^+$ calcd for ($C_{31}H_{55}F_3O_4Si_3Na^+$) 655.3253, found 655.3254.

Compound 3f. Following the general procedure, the reaction was carried out at 50 °C for 36 h, affording **3f** (94%) as a colorless oil, $R_f = 0.30$ (petroleum ether/ethyl acetate, 25/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, 1H, $J = 7.8$ Hz), 7.80 (d, 1H, $J = 7.5$ Hz), 7.51 (t, 1H, $J = 7.8$ Hz), 7.29 (t, 1H, $J = 7.8$ Hz), 5.96 (s, 1H, H-1), 5.01 (d, 1H, $J = 2.4$ Hz, H-2), 4.10 (s, 1H, H-4), 3.97–4.01 (m, 1H, H-5), 3.89 (s, 3H), 3.78–3.80 (m, 2H, H-6), 0.95 (s, 9H), 0.92 (s, 9H), 0.90 (s, 9H), 0.065–0.16 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.88, 147.44 (C-3), 144.07, 132.28, 129.52, 129.05, 128.20, 126.96, 106.70 (C-2), 80.00 (C-1), 69.14, 67.02, 62.16, 52.04, 25.87, 18.22, 18.16, 18.06, –4.18, –4.60, –5.45; HRMS (ESI) *m/z*: $(M + Na)^+$ calcd for ($C_{32}H_{58}O_6Si_3Na^+$) 645.3433, found 645.3441; $(M + K)^+$ calcd for ($C_{32}H_{58}O_6Si_3K^+$) 661.3167, found 661.3182.

Compound 3g. Following the general procedure, cross-coupling afforded **3g** (95%) as a colorless oil, $R_f = 0.60$ (petroleum ether/ethyl acetate, 24/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (d, 1H, $J = 9.3$ Hz), 7.77–7.84 (m, 2H), 7.38–7.55 (m, 4H), 5.78 (s, 1H, H-1), 5.05 (d, 1H, $J = 2.7$ Hz, H-2), 4.16 (dd, 1H, $J = 1.2$, 2.7 Hz, H-4), 3.80–3.90 (m, 3H, H-5, H-6), 0.87–0.96 (m, 27H), 0.001–0.18 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.02 (C-3), 136.39, 134.17, 131.73, 128.91, 128.30, 126.56, 125.90, 125.52, 124.87, 105.94 (C-2), 78.90 (C-1), 72.33, 66.89, 62.06, 26.08, 25.94, 25.86, 18.48, 18.24, 18.15, –3.69, –4.08, –4.52, –5.39; HRMS (ESI) *m/z*: $(M + Na)^+$ calcd for ($C_{34}H_{58}O_4Si_3Na^+$) 637.3535, found 637.3541; $(M + K)^+$ calcd for ($C_{34}H_{58}O_4Si_3K^+$) 653.3269, found 653.3274.

Compound 3h. Following the general procedure, cross-coupling afforded **3h** (82%) as a colorless oil, $R_f = 0.50$ (petroleum ether/ethyl acetate, 24/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, 2H, $J = 8.1$ Hz), 7.30 (d, 2H, $J = 8.4$ Hz), 5.11 (s, 1H, H-1), 4.83 (d, 1H, $J = 2.7$ Hz, H-2), 4.06 (s, 1H, H-4), 3.83–3.86 (m, 1H, H-5), 3.75–3.78 (m, 2H, H-6), 0.94 (s, 9H), 0.92 (s, 9H), 0.90 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H), 0.12 (s, 6H), 0.061 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.79 (C-3), 141.08, 131.34, 129.34, 121.55, 105.47 (C-2), 79.12 (C-1), 72.76, 66.95, 62.26, 25.98, 25.85, 18.39, 18.21, 18.08, –3.93, –4.13, –4.56, –5.41; HRMS (ESI) *m/z*: $(M + Na)^+$ calcd for ($C_{30}H_{55}BrO_4Si_3Na^+$) 665.2484, found 665.2494; $(M + K)^+$ calcd for ($C_{30}H_{55}BrO_4Si_3K^+$) 681.2218, found 681.2230.

Compound 3i. Following the general procedure, cross-coupling afforded **3i** (92%) as a colorless oil, $R_f = 0.60$ (petroleum ether/ethyl acetate, 24/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, 2H, $J = 8.4$ Hz), 7.18 (d, 2H, $J = 8.4$ Hz), 5.01 (s, 1H, H-1), 4.72 (d, 1H, $J = 2.7$ Hz, H-2), 3.95 (d, 1H, $J = 2.1$ Hz, H-4), 3.72–3.74 (m, 1H, H-5), 3.64–3.66 (m, 2H, H-6), 0.83 (s, 9H), 0.80 (s, 9H), 0.78 (s, 9H), 0.065 (s, 3H), 0.043 (s, 3H), 0.005 (s, 3H), 0.000 (s, 3H), –0.052 (s, 3H), –0.058 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.78 (C-3), 140.56, 133.37, 129.00, 128.40, 105.56 (C-2), 79.13 (C-1), 72.72, 66.97, 62.26, 25.88, 18.40, 18.22, 18.09, –4.16, –4.54, –5.38; HRMS (ESI) *m/z*: $(M + Na)^+$ calcd for ($C_{30}H_{55}ClO_4Si_3Na^+$) 621.2989, found 621.2996.

Compound 4a. Following the general procedure, cross-coupling afforded **4a** (92%) as a colorless oil, $R_f = 0.30$ (petroleum ether/ethyl acetate, 25/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11–7.26 (m, 4H), 5.59 (d, 1H, $J = 3.3$ Hz, H-1), 5.05 (d, 1H, $J = 3.3$ Hz, H-2), 3.89 (d, 1H, $J = 1.8$ Hz, H-4), 3.72 (dd, 1H, $J = 5.4$, 10.2 Hz, H-6), 3.61 (dd, 1H, $J = 6.6$, 10.2 Hz, H-6), 3.49–3.53 (m, 1H, H-5), 2.48 (s, 3H), 1.00 (s, 9H), 0.92 (s, 9H), 0.77 (s, 9H), 0.27 (s, 3H), 0.26 (s, 3H), 0.15 (s, 3H), 0.14 (s, 3H), –0.070 (s, 3H), –0.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.94 (C-3), 138.33, 137.84, 130.79, 127.88, 124.88, 105.90 (C-2), 73.93 (C-1), 71.01, 67.88, 62.50, 26.10, 25.76, 19.41, 18.53, 18.44, 18.09, –3.87, –4.78, –5.48; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for ($C_{31}H_{59}O_4Si_3^+$) 579.3716, found 579.3722; $(M + Na)^+$ calcd for ($C_{31}H_{58}O_4Si_3Na^+$) 601.3535, found 601.3549.

Compound 4b. Following the general procedure, cross-coupling afforded **4b** (78%) as a colorless oil, $R_f = 0.30$ (petroleum ether/ethyl acetate, 24/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, 2H, $J = 8.7$ Hz), 6.87 (d, 2H, $J = 8.7$ Hz), 5.37 (d, 1H, $J = 3.9$ Hz, H-1), 5.17 (d, 1H, $J = 3.9$ Hz, H-2), 3.81 (s, 1H, H-4), 3.80 (s, 3H), 3.75 (dd, 1H, $J = 6.0$, 10.5 Hz, H-6), 3.67 (dd, 1H, $J = 6.6$, 10.5 Hz, H-6), 3.53 (dt, 1H, $J = 1.8$, 6.0 Hz, H-5), 0.98 (s, 9H), 0.91 (s, 9H), 0.83 (s, 9H), 0.25 (s, 3H), 0.24 (s, 3H), 0.15 (s, 3H), 0.13 (s, 3H), –0.008 (s, 3H), –0.024 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.98, 150.60 (C-3), 133.10, 128.86, 113.50, 106.08 (C-2), 73.89 (C-1), 72.91, 67.61, 62.63, 55.25, 26.02, 25.81, 18.49, 18.40, 18.16, –3.99, –4.85, –5.33; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for ($C_{31}H_{59}O_5Si_3^+$) 595.3665, found 595.3682; $(M + Na)^+$ calcd for ($C_{31}H_{58}O_5Si_3Na^+$) 617.3484, found 617.3506.

Compound 4c. Following the general procedure, the reaction was carried out at 50 °C for 36 h, affording **4c** (81%) as a colorless oil, $R_f = 0.30$ (petroleum ether/ethyl acetate, 25/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (dd, 1H, $J = 1.2$, 7.5 Hz), 7.60 (d, 1H, $J = 7.2$ Hz), 7.44 (dt, 1H, $J = 1.2$, 7.2 Hz), 7.31 (t, 1H, $J = 7.5$ Hz), 6.19 (d, 1H, $J = 3.6$ Hz, H-1), 5.11 (d, 1H, $J = 3.6$ Hz, H-2), 3.89 (s, 3H), 3.85 (d, 1H, $J = 2.1$ Hz, H-4), 3.78 (dd, 1H, $J = 6.0$, 10.5 Hz, H-6), 3.69 (dd, 1H, $J = 6.3$, 10.2 Hz, H-6), 3.59 (dt, 1H, $J = 1.8$, 6.0 Hz, H-5), 0.94 (s, 9H), 0.91 (s, 9H), 0.84 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H), 0.14 (s, 3H), 0.12 (s, 3H), 0.010

(s, 3H), –0.034 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.75, 150.55 (C-3), 141.92, 131.12, 130.44, 130.22, 127.45, 127.13, 106.08 (C-2), 75.01 (C-1), 70.30, 67.51, 62.36, 52.15, 26.01, 25.83, 18.48, 18.38, 18.19, –3.91, –4.11, –4.87, –5.40; HRMS (ESI) *m/z*: $(M + Na)^+$ calcd for ($C_{32}H_{58}O_6Si_3Na^+$) 645.3433, found: 645.3407.

Compound 5a. Following the general procedure, cross-coupling afforded **5a** (95%) as a colorless oil, $R_f = 0.50$ (petroleum ether/ethyl acetate, 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.34 (m, 5H), 5.24 (t, 1H, $J = 2.5$ Hz, H-1), 5.06 (d, 1H, $J = 2.5$ Hz, H-2), 4.19–4.17 (m, 1H, H-4), 3.96 (dd, 1H, $J = 5.0$, 11.5 Hz, H-5ε), 3.60 (dd, 1H, $J = 6.5$, 11.5 Hz, H-5α), 0.96 (s, 9H), 0.92 (s, 9H), 0.21 (s, 3H), 0.20 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.51 (C-3), 141.20, 128.40, 128.00, 127.68, 106.31 (C-2), 76.10 (C-1), 69.34, 66.23, 25.92, 18.39, 18.23, –4.04, –4.24, –4.64; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for ($C_{23}H_{41}O_3Si_2^+$) 421.2589, found 421.2605; $(M+ Na)^+$ calcd for ($C_{23}H_{40}O_3Si_2Na^+$) 443.2408, found 443.2426.

Compound 5b. Following the general procedure, cross-coupling afforded **5b** (98%) as a colorless oil, $R_f = 0.50$ (petroleum ether/ethyl acetate, 25/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, 1H, $J = 8.1$ Hz), 7.15 (d, 1H, $J = 7.8$ Hz), 5.21 (s, 1H, H-1), 4.99 (d, 1H, $J = 2.1$ Hz, H-2), 4.17 (t, 1H, $J = 6.0$ Hz, H-4), 3.95 (dd, 1H, $J = 5.1$, 11.4 Hz, H-5_c), 3.59 (dd, 1H, $J = 6.0$, 11.4 Hz, H-5_a), 2.34 (s, 3H), 0.96 (s, 9H), 0.92 (s, 9H), 0.21 (s, 6H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.40 (C-3), 138.21, 137.73, 129.06, 127.69, 106.49 (C-2), 75.89 (C-1), 69.23, 66.29, 25.93, 21.15, 18.38, 18.24, –4.00, –4.68; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for ($C_{24}H_{43}O_3Si_2^+$) 435.2745, found 435.2747; $(M + Na)^+$ calcd for ($C_{24}H_{42}O_3Si_2Na^+$) 457.2565, found 457.2566.

Compound 5c. Following the general procedure, the reaction was carried out at 50 °C for 36 h, affording **5c** (71%) as a colorless oil, $R_f = 0.30$ (petroleum ether/ethyl acetate, 24/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, 1H, $J = 1.5$, 8.0 Hz), 7.58 (d, 1H, $J = 7.5$ Hz), 7.48 (dt, 1H, $J = 1.0$, 7.5 Hz), 7.32 (dt, 1H, $J = 1.5$, 8.0 Hz), 5.98 (t, 1H, $J = 2.0$ Hz, H-1), 4.98 (d, 1H, $J = 2.5$ Hz, H-2), 4.25–4.28 (m, 1H, H-4), 4.03 (dd, 1H, $J = 5.5$, 11.5 Hz, H-5_c), 3.90 (s, 3H), 3.60 (dd, 1H, $J = 7.5$, 11.0 Hz, H-5_a), 0.93 (s, 9H), 0.91 (s, 9H), 0.16 (s, 6H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.04, 150.08 (C-3), 142.57, 131.80, 130.05, 129.23, 127.89, 127.37, 107.47 (C-2), 72.83, 69.93, 65.88, 52.18, 25.99, 25.91, 18.41, 18.22, –4.01, –4.04, –4.25, –4.67; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for ($C_{25}H_{43}O_5Si_2^+$) 479.2644, found 479.2644; $(M + Na)^+$ calcd for ($C_{25}H_{42}O_5Si_2Na^+$) 501.2463, found 501.2470.

Compound 6a. Following the general procedure, cross-coupling afforded **6a** (88%) as a colorless oil, $R_f = 0.50$ (petroleum ether/ethyl acetate, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, 2H, $J = 7.5$ Hz), 7.27–7.36 (m, 3H), 5.16 (br.s, 1H, H-1), 4.92 (d, 1H, $J = 2.7$ Hz, H-2), 3.91–3.97 (m, 1H, H-5), 3.72 (d, 1H, $J = 3.3$ Hz, H-4), 1.27 (d, 3H, $J = 6.6$ Hz), 0.95 (s, 9H), 0.92 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.67 (C-3), 141.70, 128.26, 127.84, 127.69, 106.15 (C-2), 74.01 (C-1), 72.29, 71.70, 26.08, 25.91, 18.46, 18.15, 16.85, –3.96, –4.51; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for ($C_{24}H_{43}O_3Si_2^+$) 435.2745, found 435.2752; $(M + Na)^+$ calcd for ($C_{24}H_{42}O_3Si_2Na^+$) 457.2565, found 457.2574.

Compound 6b. Following the general procedure, cross-coupling afforded **6b** (84%) as a colorless oil, $R_f = 0.30$ (petroleum ether/ethyl acetate, 3/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1H), 5.31 (s, 1H, H-1), 4.96 (s, 1H, H-2), 3.98–4.05 (m, 1H, H-5), 3.63 (s, 1H, H-4), 3.38 (s, 3H, N-CH_3), 3.36 (s, 3H, N-CH_3), 1.26 (d, 3H, $J = 6.3$ Hz), 0.94 (s, 9H), 0.92 (s, 9H), 0.18 (s, 6H), 0.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.52, 151.61, 148.41 (C-3), 141.25, 113.74, 105.06 (C-2), 75.06 (C-1), 71.51, 64.38, 37.04, 27.86, 25.85, 18.24, 18.10, 16.19, –4.12, –4.69; HRMS (ESI) *m/z*: $(M + H)^+$ calcd for ($C_{24}H_{45}N_2O_5Si_2^+$) 560.3634, found 560.3655.

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