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# Palladium-catalyzed hydroamination of *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene

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ABSTRACT

Both palladium(0) and palladium(II) methods for catalyzed hydroamination of *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene with a variety of aromatic amines have been successfully developed.



The amine functionality is one of the most ubiquitous in organic chemistry. Its importance is exemplified by the diversity of molecules that contain this functional group, which includes natural products and pharmacological agents.[1] For this reason C–N bond formation is of great interest, which is apparent from the number of methodologies that have been developed for this purpose.[2] Hydroamination, the formal addition of an N–H bond across a C=C unsaturated bond, is a highly desirable and an atom-economical process for the preparation of amine derivatives.[2d,3] Allenes constitute an important class of organic compounds with unusual chemical properties due to the cumulated double bond.[4] The catalytic hydroamination of allenes should be a straightforward method for the synthesis of allylamines. The intramolecular hydroamination of amino allenes is catalyzed by organolanthanide[5] Group 4 early transition-metal complexes,[6] and late transition-metal (Pd, Ag, Au) complexes.[2b,7] Only a small number of catalytic intermolecular hydroamination reactions of allenes have been reported.[8] We report herein on the palladium-catalyzed hydroamination of a *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) with amines in the presence of a carboxylic acid. Initially the reaction of *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) with aniline (**2**) using Yamamoto's conditions (5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$, 10 mol % $Ph_3P$, 20 mol % $CH_3COOH$ in THF at 60 °C for 24 h) was studied.[8f] Quite unexpectedly, a mixture of diallylated acetate **3** and diallylated amine **4** was obtained in 35% and 10% yields, respectively, along with trace amounts of **5** (Scheme 1). When the same reaction was carried out in the presence of trifluoroacetic acid (TFA), the mixture of desired allylic amine **5** (29%) and a minor amount (18%) of dienic amine was obtained (entry 1 in Table 1).

The reaction conditions were adjusted to find a suitable catalyst–ligand–solvent–carboxylic acid system for the desired transformation. The results are summarized in Table 1. These results suggested that both Pd(0) and Pd(II) catalysts and carboxylic acid play a dramatic part on the yields of the desired allelic amine **5**. In addition, a profound solvent effect on the reaction was observed. THF was found to be the best solvent (Table 1, entry 18).

Under the optimized reaction conditions [$Pd(OAc)_2$ was used as a catalyst, TFA as the carboxylic acid and THF as the solvent], a series of amines were tested in the reaction, and the results are summarized in Table 2.

A possible reaction pathway for Pd(0)-catalyzed hydroamination is showed in Scheme 2. The two principal mechanistic pathways to be considered for hydroamination involve either activation of the amine (part a) or palladacycle formation (path b). The oxidative addition of carboxylic acid to Pd(0) produced hydridopalladium(II) intermediate species (**I**), which on reaction with amine would give intermediate (**III**) and carboxylic acid. Species **III** would form the π-allylpalladium intermediate (**VIII**) with *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) which, after reductive elimination, would give the hydroamination product (**IX**). The formation of diallylated acetate **(VII)** and diallylated amine **(XII)** could arise by a combination of either path a or path b, intermediate (**V, X**) (Scheme 2, path a) and intermediate (**II**) (Scheme 2, path b).

On the other hand, hydroamination of *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) gave a yield of 42% allylic amine **5** using $Pd(OAc)_2$ and TFA in THF (Table 1, entry 18). The two possible mechanistic pathways to be considered for hydroamination

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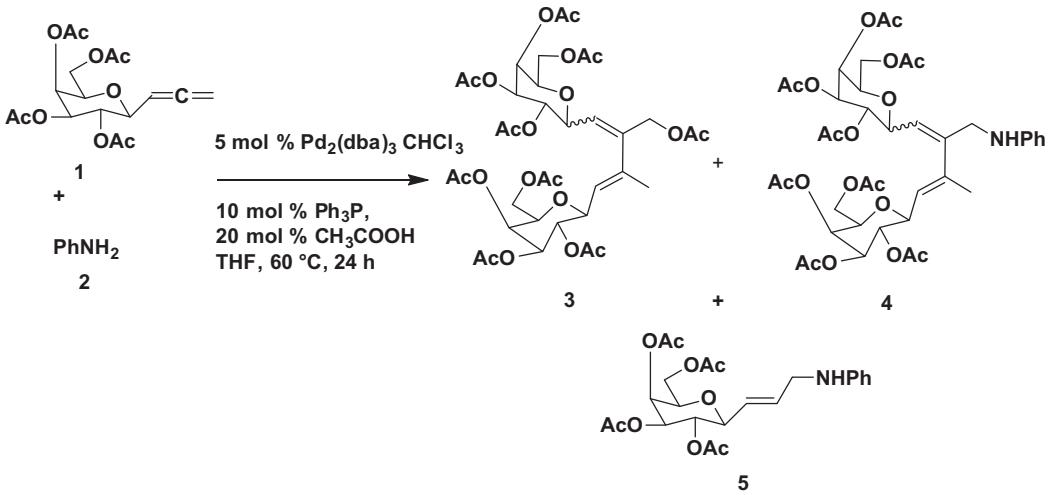



**Scheme 1.** Palladium-catalyzed hydroamination of C-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene.

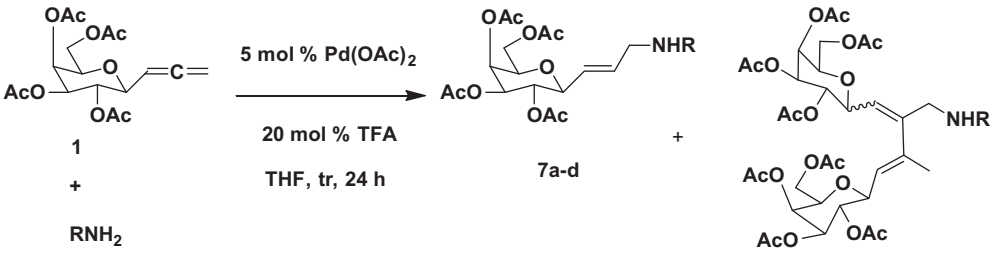
**Table 1**
Effect of reaction parameters on hydroamination of *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**)[a] with aniline[b]

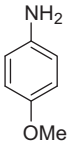
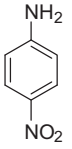
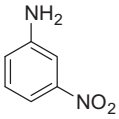
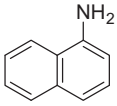
| Entry | Palladium salt and ligand (mol %) | Carboxylic acid and additive (mol %) | Solvent | Temperature (°C) | % Yield[c] | |
|---|---|---|---|---|---|---|
| | | | | | 5 | 4 |
| 1 | $Pd_2(dba)_3{\cdot}CHCl_3$ (5), $Ph_3P$ (10) | TFA (20) | THF | 60 | 29 | 18 |
| 2 | $Pd_2(dba)_3{\cdot}CHCl_3$ (5), $Ph_3P$ (10) | TFA (20) | THF | rt | 10 | 46 |
| 3 | $Pd_2(dba)_3$ (5), $Ph_3P$ (10) | TFA (20) | THF | 60 | 15 | 42 |
| 4 | $Pd_2(dba)_3$ (5), $Ph_3P$ (10) | TFA (20) | THF | rt | 13 | 42 |
| 5 | $Pd_2(dba)_3$ (5), TFP (10) | TFA (20) | THF | rt | 6 | 47 |
| 6 | $Pd_2(dba)_3$ (5), $Ph_3P$ (10) | Formic acid (20) | THF | rt | ND | 14 |
| 7 | $Pd_2(dba)_3$ (5), $Ph_3P$ (10) | Benzoic acid (20) | THF | rt | ND | 17 |
| 8 | $Pd(OAc)_2$ (5), $Ph_3P$ (20) | TFA (20) | THF | rt | 6 | 48 |
| 9 | $Pd_2(dba)_3$ (5) | TFA (20) | THF | rt | 21 | 12 |
| 10 | $Pd_2(dba)_3$ (5) | TFA (20) | THF | 60 | 23 | 12 |
| 11 | $Pd_2(dba)_3$ (10) | TFA (20) | THF | 60 | 14 | 26 |
| 12 | $Pd_2(dba)_3$ (5) | TFA (50) | THF | rt | 25 | 13 |
| 13 | $Pd_2(dba)_3$ (5) | TFA (100) | THF | rt | 22 | 10 |
| 14 | $Pd_2(dba)_3$ (5) | TFA (10) | THF | rt | 13 | 7 |
| 15 | $Pd_2(dba)_3$ (5) | TFA (5) | THF | rt | 15 | 13 |
| 16 | $Pd_2(dba)_3$ (5) | TFA (5) | DMF | rt | ND | 17 |
| 17 | $Pd_2(dba)_3$ (5) | TFA (5) | $CH_3CN$ | rt | 8 | 14 |
| 18 | $Pd(OAc)_2$ (5) | TFA (20) | THF | rt | 42 | 12 |
| 19 | $Pd(OAc)_2$ (5) | TFA (20) | THF | 60 | 32 | 9 |
| 20 | $Pd(OAc)_2$ (5) | Acetic acid (20) | THF | rt | 25 | 9 |
| 21 | $Pd(OAc)_2$ (5) | — | THF | rt | 17 | 3 |
| 22 | $Pd(OAc)_2$ (5) | — | THF | 60 | 12 | 5 |
| 23 | $Pd(OAc)_2$ (10) | TFA (20) | THF | rt | 21 | 13 |
| 24 | $Pd(OAc)_2$ (5) | TFA (20), $K_2S_2O_8$ (250) | THF | rt | 25 | 19 |
| 25 | $Pd(OAc)_2$ (5) | TFA (20), $K_2S_2O_8$ (100) | THF | rt | 17 | 12 |
| 26 | $Pd(OAc)_2$ (5) | TFA (20), LiCl (200) | THF | rt | 31 | ND |
| 27 | $Pd(OAc)_2$ (5) | LiCl (200) | THF | rt | 32 | ND |
| 28 | $Pd(OAc)_2$ (5) | TFA (50) | THF | rt | 31 | 16 |
| 29 | $Pd(OAc)_2$ (5) | TFA (20) | DCM | rt | 30 | 14 |
| 30 | $Pd(OAc)_2$ (5) | TFA (20) | $CH_3CN$ | rt | 33 | 14 |
| 31 | $Pd(OAc)_2$ (5) | TFA (20) | Toluene | rt | 24 | 15 |
| 32 | $Pd(OAc)_2$ (5) | TFA (20) | Dioxane | rt | 14 | 9 |

ND = Not detected.
[a] *C*-(Tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) was prepared according to the literature method.[9]
[b] All reactions were carried out with conditions: *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) (0.27 mmol) and aniline (0.81 mmol) in 0.5 mL of solvent for 24 h.
[c] Isolated yields.

involve either activation of the amine or activation of the allene. In the allene activation (Scheme 3, path c) the $CH_2$=C double bond of allene is activated by coordination to the palladium, and the C–N bond is formed by nucleophilic attack of amine on the coordinate allene. To liberate the product, the palladium–carbon bond in the resulting ammonioallyl complex has to be cleaved. This can be brought about either by direct protonolysis or by protonation at the palladium with subsequent C–H reductive elimination. Amine activation (Scheme 3, path d) proceeds via oxidative addition of the amine N–H bond to the coordinatively unsaturated palladium center, forming the amido hydrido complex, followed by allene coordination, insertion of the allene into the palladium–nitrogen

**Table 2**
Hydroamination of *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) with aromatic amines[a]




| Entry | Amine | Product[b] (%) | |
|---|---|---|---|
| 1 |  6a | **7a** (16) | **8a** (ND) |
| 2 |  6b | **7b** (22) | **8b** (ND) |
| 3 |  6c | **7c** (25) | **8c** (3) |
| 4 |  6d | **7d** (17) | **8d** (6) |

ND = Not detected.
[a] Reaction conditions: *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) (0.27 mmol); amine (0.81 mmol); $Pd(OAc)_2$ (5 mol %); TFA (20 mol %);THF (0.5 mL); room temperature for 24 h.
[b] Isolated yields.

bond, and finally C–H reductive elimination, liberating the product and closing the catalytic cycle.

In conclusion, we have successfully developed both Pd(0)- and Pd(II)-catalyzed methods for hydroamination of *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) with a variety of aromatic amines.

## 1. Experimental

### 1.1. General methods

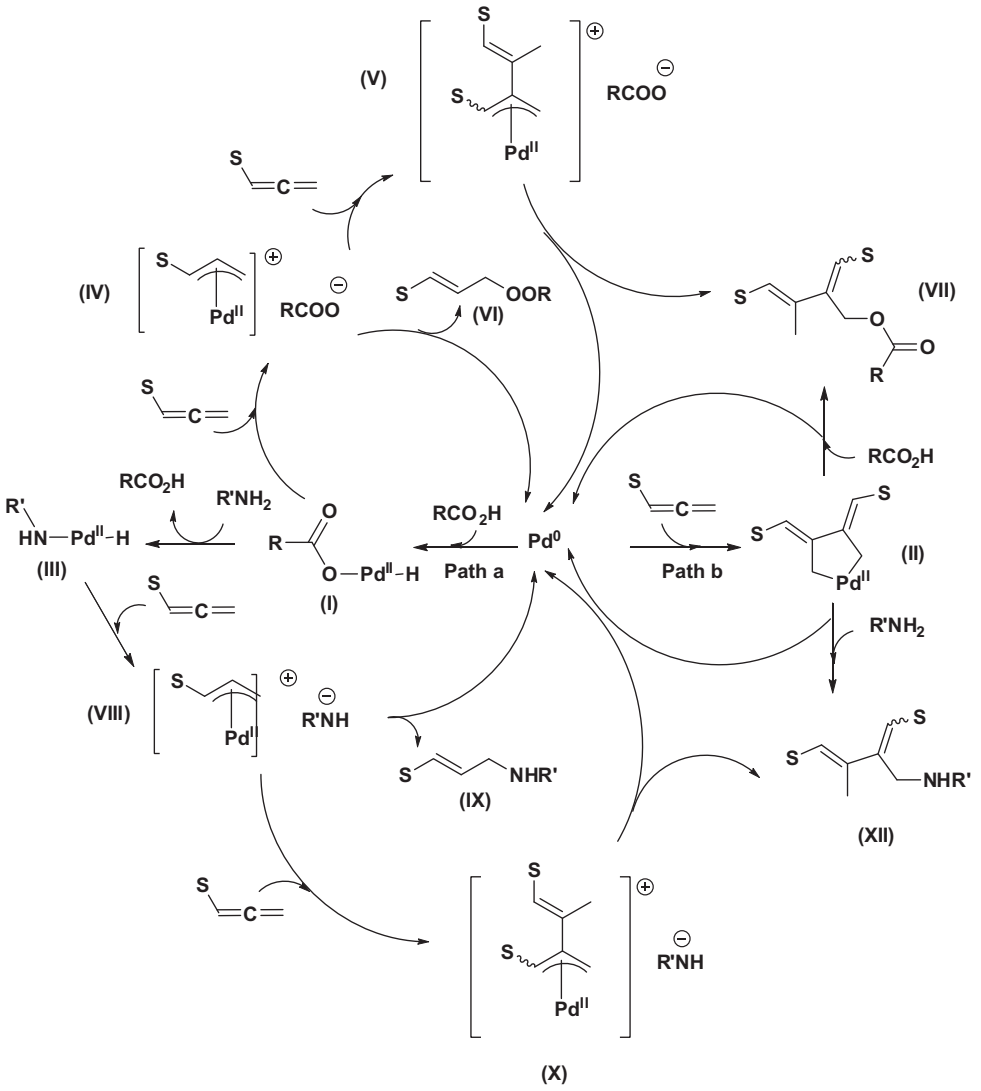
All reagents were commercially available and used without purification. Flash column chromatography was performed using Silica Gel 60 (230–400 mesh). Accurate molecular masses were recorded on a micrOTOF machine. Infrared spectra were recorded using a Perkin–Elmer FTIR spectrometer. The IR samples were prepared as thin films by evaporation of a solution of the compound in $CH_2Cl_2$ onto a germanium plate. Nuclear magnetic resonance spectra were determined at 400 MHz ($^1H$) and at 100 MHz ($^{13}C$) on Bruker spectrometers. Chemical shift values are quoted in parts per million (ppm) downfield from TMS, and coupling constants are in Hertz. Chemical shift multiplicities are reported as s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, br s = broad singlet, app. t = apparent triplet. *C*-(Tetra-*O*-acetyl-β-D-galactopyranosyl)allene [(1*S*)-2,3,4,6-(tetra-*O*-acetyl-1,5-anhydro-1-*C*-propadienyl-D-galactitol, **1**] was prepared according to the literature method.[9]

### 1.2. Typical general procedure

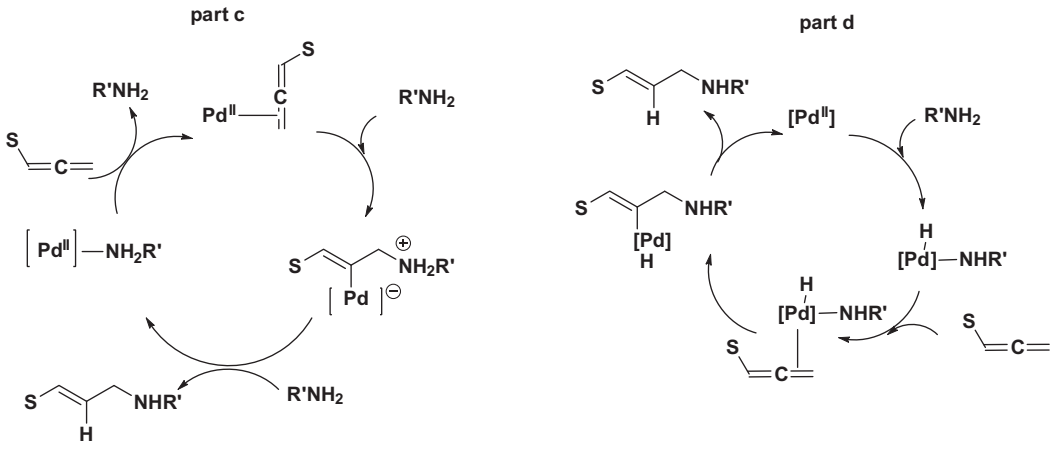
All reactions were carried out in an atmosphere of air. A reaction tube was charged with the *C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) (0.5 mmol), amines (1.5 mmol), Pd salts (catalyst, 5–10 mol %), $Ph_3P$ (ligand, 5 mol %), carboxylic acid (10–100 mol %), LiCl or LiBr (additive, 5 mol %), and solvent (1 mL/mmol). The mixture was either stirred at room temperature or heated at 60 °C for 24 h, then the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give the product.

#### 1.2.1. Data for 3

IR (film) $cm^{-1}$: 3477, 2964, 1747, 1436, 1372, 1229, 1119, 1049; $^1H$ NMR ($CDCl_3$): $\delta$ 5.92 (1H, d, *J* 6.4), 5.80 (1H, d, *J* 6.0), 5.41–5.45 (2H, m), 5.31–5.36 (2H, m), 5.24 (1H, t, *J* 2.4), 5.21 (1H, t, *J* 3.6), 5.15




**Scheme 2.** Proposed mechanistic pathways for palladium(0)-catalyzed hydroamination.




**Scheme 3.** Proposed mechanistic pathways for palladium(II)-catalyzed hydroamination.

(1H, t, *J* 6.4), 5.03–5.06 (2H, m), 4.82 (1H, d, *J* 13.2), 4.02–4.20 (6H, m), 1.90–2.20 (30H, 10 × s); $^{13}$C NMR ($CDCl_3$): $\delta$ 170.42, 170.32, 170.29, 170.15, 170.11, 170.01, 169.96, 169.82, 169.57, 145.01, 143.28, 123.86, 120.77, 69.62, 68.88, 68.76, 68.40, 68.24, 68.20, 67.98, 67.85, 67.82, 67.44, 61.67, 61.32, 59.27, 20.70, 20.66, 20.64, 20.60, 15.61; HRMS: calcd for $C_{36}H_{48}O_{20}Na$ (M+Na): *m/z* 823.2637; found: *m/z* 823.2566.

### 1.2.2. Data for 4

IR (film) cm$^{-1}$: 3440, 2361, 1747, 1637, 1372, 1226, 1023; $^1$H NMR ($CDCl_3$): $\delta$ 7.16 (2H, app. t, *J* 8 and 7.6), 6.68–6.72 (1H, m), 6.58 (2H, d, *J* 8.4), 5.83 (1H, d, *J* 6.8), 5.75 (1H, d, *J* 6.4), 5.41–5.45 (2H, m), 5.28–5.34 (2H, m), 5.21–5.26 (2H, m), 5.10–5.14 (3H, m), 5.00 (1H, app. t, *J* 6.4 and 5.6), 4.00–4.20 (6H, m), 1.80–2.10 (27H, 9 × s); $^{13}$C NMR ($CDCl_3$): $\delta$ 170.54, 170.41, 170.13, 170.09, 169.98, 169.90, 169.83, 169.81, 147.84, 144.58, 129.34, 129.24, 121.82, 120.62, 117.82, 112.75, 69.48, 69.06, 68.77, 68.36, 68.26, 68.10, 67.99, 67.91, 67.52, 61.82, 61.51, 42.14, 20.78, 20.75, 20.73, 20.67, 20.65, 15.87; HRMS: calcd for $C_{40}H_{51}NO_{18}Na$ (M+Na): *m/z* 856.3004; found: *m/z* 856.3036.

### 1.2.3. Data for 5

IR (film) cm$^{-1}$: 3418, 2361, 1746, 1633, 1604, 1507, 1371, 1226, 1051; $^1$H NMR ($CDCl_3$): $\delta$ 7.17 (2H, app. t *J* 8.4 and 7.2), 6.71 (1H, app. t *J* 8.4 and 7.2), 6.60 (2H, d, *J* 7.6), 5.98 (1H, dt, *J* 15.6 and 5.2), 5.82 (1H, q, *J* 15.6 and 5.2), 5.37 (1H, d, *J* 3.2), 5.28 (1H, dd, *J* 10.4 and 5.6), 5.10 (1H, dd, *J* 10.4 and 3.2), 4.80 (1H, t, *J* 3.2), 4.00–4.14 (3H, m), 3.84 (2H, d, *J* 5.2) 1.90–2.10 (12H, 4 × s); $^{13}$C NMR ($CDCl_3$) $\delta$: 170.52, 170.19, 170.06, 169.87, 147.64, 134.47, 129.27, 123.49, 117.87, 113.14, 72.53, 68.31, 68.29, 68.01, 61.83, 45.62, 20.73, 20.69, 20.66; HRMS: calcd for $C_{23}H_{30}NO_9$ (M+H): *m/z* 464.1921; found: *m/z* 464.1968.

### 1.2.4. Data for 7a

IR (film) cm$^{-1}$: 3442, 2362, 1747, 1638, 1515, 1372, 1231, 1023; $^1$H NMR ($CDCl_3$): $\delta$ 6.79 (2H, d, *J* 8.8), 6.60 (2H, d, *J* 8.8), 5.97 (1H, dt, *J* 15.6 and 5.2), 5.85 (1H, q, *J* 15.6 and 5.2), 5.42 (1H, d, *J* 3.2), 5.29 (1H, dd, *J* 10.4 and 5.6), 5.12 (1H, dd, *J* 10.4 and 3.2), 4.79 (1H, t, *J* 3.2), 4.00–4.10 (3H, m), 3.80 (2H, d, *J* 5.2), 1.90–2.10 (15H, 5 × s); $^{13}$C NMR ($CDCl_3$): $\delta$ 170.53, 170.23, 170.13, 170.08, 152.44, 141.82, 134.79, 123.41, 114.92, 114.57, 72.50, 68.40, 68.33, 68.04, 68.01, 61.87, 45.94, 20.72, 20.70, 20.66; HRMS: calcd for $C_{24}H_{31}NO_{10}Na$ (M+Na): *m/z* 516.1846; found: *m/z* 516.2006.

### 1.2.5. Data for 7b

IR (film) cm$^{-1}$: 3439, 2362, 1747, 1636, 1604, 1474, 1372, 1312, 1228, 1113, 1048; $^1$H NMR ($CDCl_3$): $\delta$ 8.09 (2H, d, *J* 8.8), 6.58 (2H, d, *J* 9.2), 5.96 (1H, dt, *J* 15.6 and 5.2), 5.88 (1H, q, *J* 15.6 and 5.2), 5.40 (1H, d, *J* 3.2), 5.30 (1H, dd, *J* 10.4 and 5.6), 5.10 (1H, dd, *J* 10.4 and 3.2), 4.82 (1H, t, *J* 3.2), 4.01–4.18 (3H, m), 3.95 (2H, d, *J* 5.2), 1.93–2.14 (12H, 4 × s); $^{13}$C NMR ($CDCl_3$): $\delta$ 170.64, 170.17, 170.08, 169.77, 152.98, 138.32, 132.15, 126.36, 124.85, 111.39, 72.24, 68.45, 68.23, 67.95, 67.82, 61.73, 44.89, 20.73, 20.69, 20.64; HRMS: calcd for $C_{23}H_{28}N_2O_{11}Na$ (M+Na): *m/z* 531.1591; found: *m/z* 531.1670.

### 1.2.6. Data for 7c

IR (film) cm$^{-1}$: 3398, 2926, 1748, 1622, 1532, 1351, 1228, 1050, 738; $^1$H NMR ($CDCl_3$): $\delta$ 7.55 (1H, d, *J* 7.6), 7.40 (1H, s), 7.32 (1H, t, *J* 8.4), 6.90 (1H, d, *J* 1.2), 5.99 (1H, dt, *J* 15.6 and 5.2), 5.92 (1H, q, *J* 15.6 and 5.2), 5.39 (1H, d, *J* 3.2), 5.33 (1H, dd, *J* 10.4 and 5.6), 5.11 (1H, dd, *J* 10.4 and 3.2), 4.82 (1H, t, *J* 3.2), 4.02–4.15 (3H, m), 3.93 (2H, d, *J* 5.2), 1.97–2.14 (12H, 4 × s); $^{13}$C NMR ($CDCl_3$) $\delta$: 170.61, 170.18, 170.07, 169.85, 149.44, 148.44, 132.92, 129.81, 124.40, 119.04, 112.38, 106.52, 72.39, 68.35, 68.25, 67.92, 61.73, 45.31, 20.72, 20.69, 20.66; HRMS: calcd for $C_{23}H_{28}N_2O_{11}Na$ (M+Na): *m/z* 531.1591; found: *m/z* 531.1668.

### 1.2.7. Data for 8c

IR: (film) cm$^{-1}$**:** 3736, 2362, 1744, 1540, 1370, 1225, 1023; $^1$H NMR ($CDCl_3$): $\delta$ 7.53 (1H, d, *J* 6.4), 7.41 (1H, app. t, *J* 2.4 and 2.0), 7.27 (1H, s), 6.89 (1H, d, *J* 2.0), 5.91 (1H, d, *J* 7.2), 5.40–5.46 (3H, m), 5.27–5.31 (2H, m), 5.22–5.26 (2H, m) 5.12–5.18 (4H, m), 4.01–4.15 (6H, m), 2.00–2.13 (27H, 9 × s); $^{13}$C NMR ($CDCl_3$): $\delta$ 170.61, 170.52, 170.44, 170.19, 170.05, 170.01, 169.96, 169.91, 149.44, 148.82, 144.33, 142.93, 129.74, 123.26, 118.69, 117.18, 112.09, 106.16, 70.07, 69.06, 69.02, 68.16, 67.96, 67.73, 67.59, 61.85, 61.63, 42.34, 20.80, 20.75, 20.70, 20.65, 14.12; HRMS: calcd for $C_{40}H_{50}N_2O_{20}Na$ (M+Na): *m/z* 901.2855; found: *m/z* 901.2904.

### 1.2.8. Data for 7d

IR (film) cm$^{-1}$: 3440, 2361, 1748, 1584, 1533, 1372, 1228, 1050, 773; $^1$H NMR ($CDCl_3$): $\delta$ 7.83–7.86 (1H, m), 7.77–7.82 (1H, m), 7.45–7.53 (2H, m), 7.36 (1H, d, *J* 7.6), 7.30 (1H, d, *J* 6.8), 6.61 (1H, d, *J* 7.2), 6.12 (1H, dt, *J* 15.6 and 5.2), 5.93 (1H, q, *J* 15.6 and 5.2), 5.38 (1H, d, *J* 3.2), 5.33 (1H, dd, *J* 10.4 and 5.6), 5.14 (1H, dd, *J* 10.4 and 3.2), 4.83 (1H, t, *J* 3.2), 4.07–4.15 (3H, m), 4.05 (2H, d, *J* 5.2), 1.90–2.13 (12H, 4 × s); $^{13}$C NMR ($CDCl_3$) $\delta$: 170.58, 170.20, 170.05, 169.88, 142.73, 134.34, 133.99, 128.71, 126.45, 125.79, 124.86, 123.99, 123.53, 119.84, 117.95, 105.02, 72.50, 68.39, 68.33, 68.04, 68.01, 61.87, 45.94, 20.72, 20.70, 20.66; HRMS: calcd for $C_{27}H_{31}NO_9Na$ (M+Na): *m/z* 536.1897; found: *m/z* 536.1963.

### 1.2.9. Data for 8d

IR (film) cm$^{-1}$: 3442, 2362, 2066, 1746, 1638, 1372, 1227, 1048; $^1$H NMR ($CDCl_3$): $\delta$ 7.83 (1H, d, *J* 8.8), 7.77 (1H, d, *J* 7.6), 7.35–7.46 (2H, m), 7.33 (1H, d, *J* 7.6), 7.24 (1H, d, *J* 8.4), 6.59 (1H, d, *J* 7.6), 5.94 (1H, d, *J* 7.2), 5.40–5.45 (3H, m), 5.31–5.36 (3H, m), 5.22–5.30 (2H, m), 5.16–5.21 (3H, m), 4.02–4.25 (6H, m), 1.90–2.10 (27H, 9 × s); $^{13}$C NMR ($CDCl_3$): $\delta$ 170.64, 170.56, 170.51, 170.47, 170.23, 170.20, 170.12, 170.03, 145.22, 143.30, 134.36, 134.26, 129.29, 128.99, 128.67, 128.48, 126.54, 125.84, 122.82, 120.39, 117.79, 104.13, 69.60, 69.14, 69.07, 68.56, 68.40, 68.28, 67.90, 67.86, 67.70, 61.68, 61.64, 61.14, 43.52, 20.69, 20.67, 20.63, 14.12; HRMS: calcd for $C_{44}H_{53}NO_{18}Na$ (M+Na): *m/z* 906.3160; found: *m/z* 906.3220.

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