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# Hypervalent Iodine Mediated Synthesis of *C*-2 *Deoxy* Glycosides and Amino Acid Glycoconjugates

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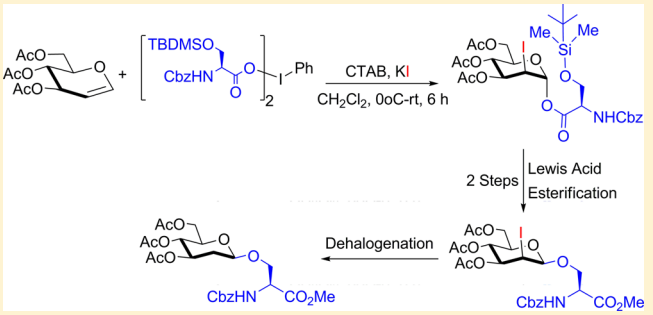
Supporting Information

**ABSTRACT:** A simple, efficient, and practical method for the synthesis of *C*-2 *deoxy*-2-iodo glycoconjugates in self-assembled structures was found using $PhI(OCOR)_2$. 2-Iodo glycoserinyl esters were intramolecularly converted into 2-iodo serinyl glycosides which upon dehalogenation gave *C*-2 *deoxy* amino acid glycoconjugates.




## INTRODUCTION

Stereo- and regioselective reactions are well sought after in organic chemistry; frequently, stereo- and regioselectivities are obtained by taking advantage of steric environments such as chiral auxiliaries, reagents, and solvents.[1] The utility of self-assembled structures for the above is a promising alternative.[2] It is desirable that the self-assembled structure (i) is stable at the temperature of the reaction; (ii) does not react with reagents; (iii) does not disassemble during the reaction; and (iv) should be accessible from simple precursors. It is known that cetylammonium bromide (CTAB) forms organic solvent-stable surfactant-assembled lipophilic nanoreactors.[3] Addition of polyvalent iodine reagents onto electron-rich $\pi$-systems was found to be suitable for the current investigation since various iodobenzene dicarboxylates react with electron-rich $\pi$-systems.[4] Earlier studies showed that indenes can be regioselectively functionalized using $PhI(OAc)_2$ in CTAB derived nano-reactors.[5]

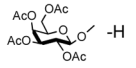
Easily available glycals possess an electron-rich $\pi$-bond, and the utility of hypervalent iodine ($I^{III}$) reagents on glycals was studied for the selective C3-*O*-oxidation, *C*-2 heteroatom substitution, and oxidative glycosidation.[6,7] In this premise, regioselective iodination of glycals has been hypothesized through surfactant-assembled structures by using CTAB and polycoordinated iodine reagents for the synthesis of 2-*deoxy*-2-iodo acetates. Notably, 2-*deoxy*-2-iodo glycopyranosyl acetates are important precursors for the synthesis of 2-*deoxy*-, 2-alkyl, and 2-amino glycosides. Biological significance and their versatility coupled with the challenge of synthesizing 2-*deoxy*-glycopyranosides[7] had attracted many researchers to develop strategies for their synthesis utilizing hypervalent iodine reagent,[7a−h] de novo,[8] and dehydrative[7i] glycosidation. 2-*Deoxy*-glycopyranosides can be accessed through moderately stable *C*-2 triflates,[9] or by the addition of electrophilic iodine in a poorly regioselective manner to the electron rich $\pi$-bond of glycals.[7] Therefore, we thought of studying the reaction of hypervalent iodination on glycals in the presence of CTAB-assembled self-assembled structures for the regioselective synthesis of 2-*deoxy*-glycosides.

## RESULTS AND DISCUSSION

To begin our investigation, a $CH_2Cl_2$ solution of per-*O*-acetyl glucal **1a** at 0 °C was added to $PhI(OAc)_2$, CTAB, and KI. The resulting turbid solution was stirred at room temperature for 6 h to observe the formation of two inseparable products **2a** and **3a** in a 95:5 ratio which were characterized by NMR and MS analysis (Scheme 1);[10] importantly, no regioisomeric mixture was noticed. The origin of selectivity is attributed to the micellar environment as postulated earlier.[5,10] The formation of compound **3a** is possible due to the halide counterion exchange between CTAB and KI which was confirmed through a control

**Scheme 1. Synthesis of *C*-2 *Deoxy* *C*-2 Iodo Anomeric Acetates in Self Assembled Structures**


**1a-1c** **2a-2c** **3a-3c**

| No. | $R_1$ | $R_2$ | $R_3$ | $R_4$ | X | % Yield | Ratio |
|---|---|---|---|---|---|---|---|
| **1a** | -OAc | -OAc | -H | $-CH_2OAc$ | I | 85 | **2a:3a** = 95:5 |
| | -OAc | -OAc | -H | $-CH_2OAc$ | Br | 71 | **2a:3a** = 0:100 |
| **1b** | -OAc | -H | -OAc | $-CH_2OAc$ | I | 80 | **2b:3b** = 94:5 |
| **1c** | -OAc |  | -H | $-CH_2OAc$ | I | 75 | **2c:3c** = 95:5 |

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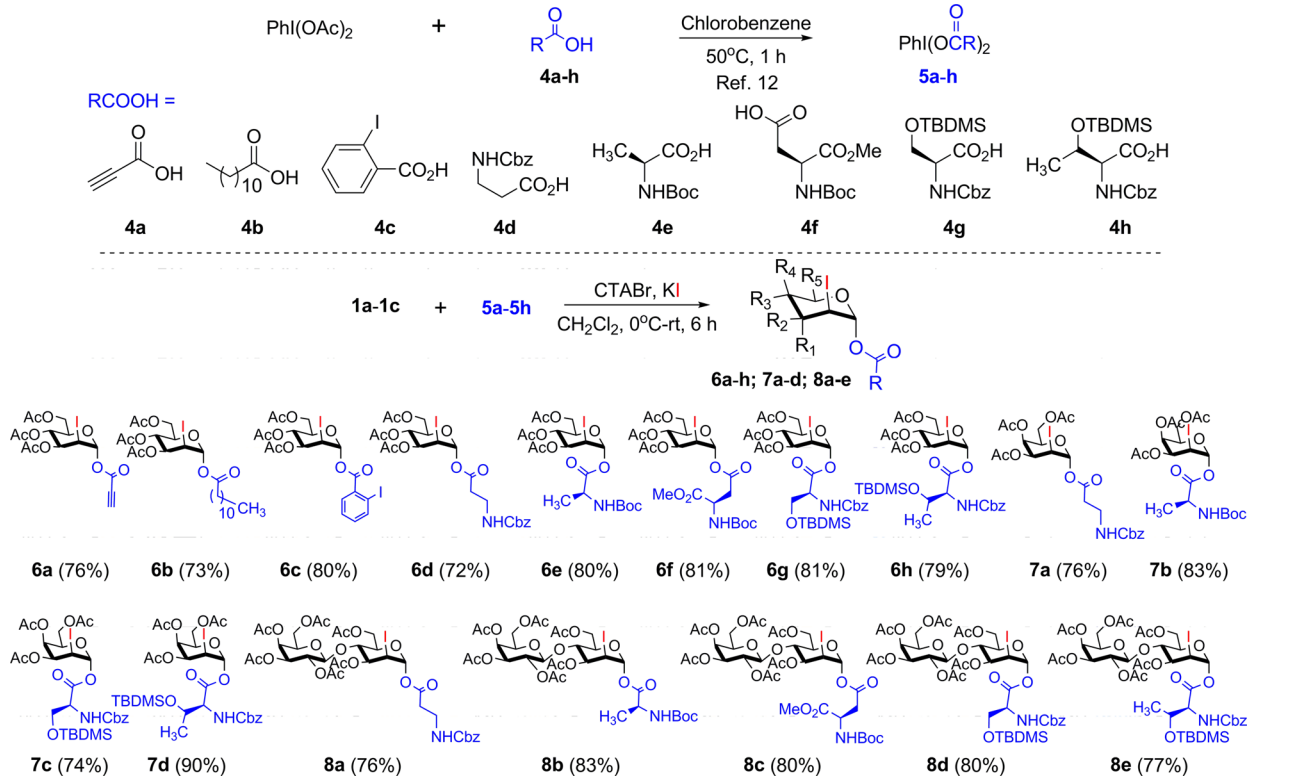
**Scheme 2. Hypervalent Iodine for the Synthesis of *C*-2 *Deoxy*-2-iodo Anomeric Esters**




experiment wherein KBr was added in place of KI to observe compound **3a** only (Scheme 1).

A regioisomeric mixture of products was noticed in the absence of CTAB. In addition, it is desirable to maintain the CTAB concentration at a critical micellar concentration (CMC) at 10 mol % for 15 mL in order to obtain self-assembled structures;[5a,10] otherwise, a regioisomeric mixture of iodoacetates is observed. Both iodo- (**2a**) and bromo- (**3a**) saccharides can be subjected to the $Bu_3SnH$/AIBN reaction to obtain corresponding 2-*deoxy* derivatives.[11] Furthermore, anomeric esters are important as they can be easily activated by the addition of Lewis acids to obtain a variety of glycosides. A similar reaction between per-*O*-acetyl galactal and $PhI(OAc)_2$ in CTAB and KI gave corresponding iodo acetate **2b** and bromo acetate **3b** with a 94:5 ratio of **2b**:**3b** (Scheme 1). Acetyl groups of the iodobenzene diacetate can be exchanged with carboxylic acids by slow evaporation of a solution of an equimolar mixture of $PhI(OAc)_2$ and carboxylic acid (**4a**–**4h**) in chlorobenzene around 50 °C over 1 h.[12] The exchange reaction worked well, and various $PhI(OCOR)_2$ compounds (**5a**–**5h**) were synthesized. Further, the generality of the regioselective halo ester glycoside synthesis was investigated with hypervalent iodine esters **5a**–**5h.**

Gratifyingly, the formation of iodo ester glycosides in very good yield along with a minor amount of bromo esters was noticed. For example, the reaction between glucal and iodoso esters **5a**–**h** gave 2-*deoxy*-glycosyl esters **6a**–**h** in very good yields (Scheme 2).[10] Similar products in good yields were noticed with galactal (**1b**) and lactal (**1c**) to give products **7a**–**d** and **8a**–**e** in good yields with selected phenyl iodosoesters (Scheme 2). Good quality crystals of compound **6e** could be obtained by slow evaporation from ethyl acetate and light petroleum (60–80 °C) and was subjected to X-ray structure determination.[10,13] The crystal structure of compound **6e** confirmed the presence of an iodo group in the manno-configuration and $\alpha$-configured ester moiety.[10,13]

Amino acid glycoconjugates are interesting since they can be easily converted to *N*-carboxy anhydrides (NCAs) for the synthesis of glycopolypeptides by ring-opening polymerization with amines in the presence of proton sponge.[14] Additionally, amino acid glycoconjugates **6g**, **6h**, **7c**, **7d**, **8d**, and **8e** are correctly positioned to undergo intramolecular glycosidation in the presence of a suitable Lewis acid. The activator not only is able to cleave the silyl ether to give **A**, but also can perform as a Lewis acid to facilitate the departure of the anomeric ester. The resulting intermediate can further be attacked by the nucleophile in an intramolecular fashion to result in acid **B** (Figure 1). Subsequently, radical deiodination should give access to 2-*deoxy* glycosides.

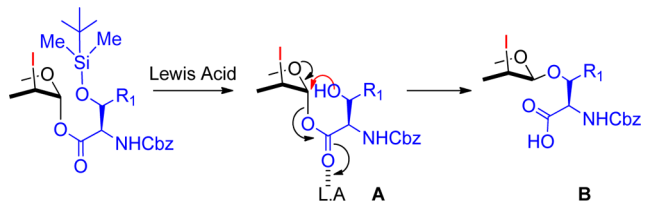



**Figure 1.** Rationale for the intramolecular aglycon delivery.

The biological significance of many natural products was found to be dependent on the presence of 2-*deoxy* glycosides.[15] However, the stereoselective synthesis of 2-*deoxy* glycosides is still a challenge due to the absence of any directing group at the *C*-2 position.[16] It is interesting to observe that NIS mediated amino acid glycoconjugate synthesis from glycals results[16a] in the 2-iodo $\alpha$-glycosides whereas the current protocol gives access to $\beta$-glycosides in a stereoselective fashion.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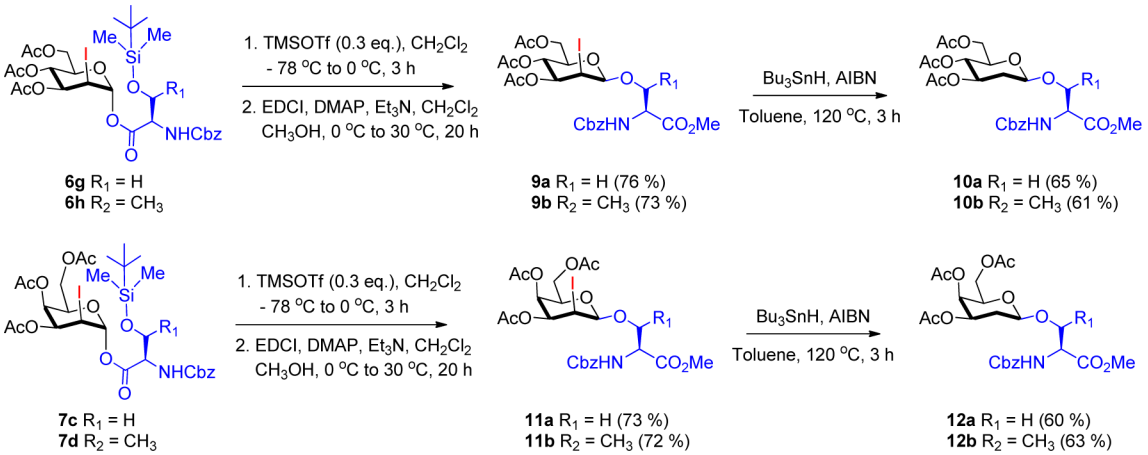
**Scheme 3. Synthesis of *C*-2 Iodo Amino Acid Glycosides**




After several experiments with amino acid glycoconjugate **6g**, a catalytic amount of TMSOTf in $CH_2Cl_2$ at −78 °C was found to be suitable for this transformation (Scheme 3). Initially, cleavage[17] of silyl ether was noticed by TLC-MS analysis that subsequently was converted to *C*-2-iodo serinyl glycoside as a carboxylic acid in a very good yield; the acid was easily purified by converting it to the corresponding methyl ester **9a** under EDCI/DMAP/MeOH conditions (Scheme 3). Similar results were also observed with the threonine derivative **6h** to obtain **9b** in good yield. In addition, galacto-derived serine and threonine anomeric esters **7c** and **7d** also underwent the intramolecular glycosidation to give *β*-galactosyl amino acid glycoconjugates **11a** and **11b**. Compounds **9a−b** and **11a−b** were successfully subjected to radical mediated deiodination[11] using $Bu_3SnH$ and AIBN in toluene at 120 °C to obtain 2-*deoxy* *β*-glycosides **10a−b** and **12a−b** which are otherwise fairly difficult to synthesize in a stereoselective manner.

## CONCLUSIONS

We have identified a practical, efficient, simple, and fully stereoselective method for the synthesis of 2-*deoxy*-2-iodo glycosides in self-assembled structures. Various 2-iodo glycosyl esters were synthesized in a stereoselective fashion. Intramolecular glycosidation of anomeric serinyl esters afforded *β*-serinyl glycosides, and the radical mediated deiodination at C-2 position resulted in 2-*deoxy* serinyl glycosides. Further investigation on the utilization of 2-*deoxy* serinyl glycosides for the synthesis of glycopolypeptides and other materials is currently underway.

## EXPERIMENTAL SECTION

**General Methods.** Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Unless otherwise reported all reactions were performed under an argon atmosphere. Removal of solvent *in vacuo* refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. Analytical thin-layer chromatography was performed on precoated silica plates ($F_{254}$, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. Optical rotations were measured on a polarimeter. IR spectra were recorded on an FT-IR spectrometer. NMR spectra were recorded on either a 400 or 500 MHz spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. High resolution mass spectroscopy (HRMS) was performed using a TOF mass analyzer. Low resolution mass spectroscopy (LRMS) was performed on UPLC-MS.

*Procedure for the Synthesis of Compounds **2a**.* A two-neck round-bottom flask containing glucal (0.272 g, 1.0 mmol), anhydrous $MgSO_4$ (0.5 g), and $CH_2Cl_2$ (15 mL) at 0 °C was added to $PhI(OCOCH_3)_2$ (0.644 g, 2.0 mmol), CTAB (0.039 g, 10 mol %), and KI (0.166 g, 1.0 mmol). The reaction mixture was stirred at 25 °C for 6 h and diluted with water and extracted with $CH_2Cl_2$ (3 × 25 mL), and the combined organic portions were washed with aq. sodium bicarbonate and brine solution (2 × 10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography using ethyl acetate and light petroleum ether (bp 60−70 °C) to obtain compound **2a** (0.389 g, 85%) as a colorless thick syrup. The same general procedure was adopted for synthesizing compounds **2a−2c**, **3a**, **6a−6h**, **7a−7d**, and **8a−8e**.

*Synthesis of Compound **9a**.* To *C*-2 *deoxy* 2-iodo amino acid glycoconjugate **6g** (0.750 g, 1.00 mmol) in $CH_2Cl_2$ (10 mL) was added 4 Å molecular sieves powder (0.5 g) at room temperature. After stirring for 30 min, the reaction mixture was cooled to −78 °C and TMSOTf (45 μL, 0.25 mmol) was added and stirred for 30 min. The reaction mixture was slowly warmed to 0 °C and stirred for 3 h, diluted with $CH_2Cl_2$, and filtered through Celite. The filtrate was subsequently neutralized with excess triethylamine and concentrated *in vacuo*, and the residue was purified by silica gel column chromatography to give 2-iodo acid which was directly used for esterification. 2-Iodo acid (0.637 g, 1.00 mmol) was redissolved in $CH_2Cl_2$ (10 mL), and MeOH (61 μL, 1.5 mmol) was added followed by cooling to 0 °C. 1-(3-(Dimethylamino)propyl)-3-ethyl carbodiimide (EDCI) (0.249 g, 1.30 mmol), $Et_3N$ (181 μL, 1.30 mmol), and DMAP (0.030 g, 0.25 mmol) were added and stirred for 20 h at 25 °C. The reaction was quenched with water and extracted with $CH_2Cl_2$ (2 × 25 mL). The combined organic layers were washed with saturated $NaHCO_3$, water, and brine, dried, and concentrated *in vacuo* to obtain a residue that was purified by silica gel column chromatography using EtOAc and light petroleum (bp 60−70 °C) to afford compound **9a** (0.485 g, 76%) as a colorless thick syrup. The same general procedure was adopted for synthesizing compounds **9b** and **11a−11b**.

**Compound 2a.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material. Yield: (0.389 g, 85%); $[\alpha]_D$ = +31.2 (*c* = 1.0, $CHCl_3$); $^1$H NMR (399.78 MHz, $CDCl_3$) *δ* 2.07 (s, 3 H), 2.11 (s, 3H), 2.12 (s, 3H), 2.17 (s, 3H), 4.11 (ddd, 1H, *J* = 7.4, 4.9 Hz), 4.16 (dd, 1H, *J* = 12.3, 4.4 Hz), 4.23 (dd, 1H, *J* = 12.3, 4.4 Hz), 4.53 (dd, 1H, *J* = 4.3, 1.5 Hz), 4.59 (dd, 1H, *J* = 9.5, 4.4 Hz), 5.46 (t, 1H, *J* = 9.6 Hz), 6.39 (s, 1H); $^{13}$C NMR (100.53 MHz, $CDCl_3$) *δ* 20.6, 20.7, 20.9, 20.9, 27.1, 61.8, 67.0, 68.6, 71.4, 94.7, 168.2, 169.3, 169.9, 170.7; IR ($CHCl_3$) *ν* 2925, 1747, 1216, 1048 cm$^{-1}$; HRMS (TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{19}INaO_9$ 480.9971, found 480.9979.

**Compound 2b.** This compound is prepared using the above-mentioned general procedure using **1b** (0.272 g, 1 mmol) as the starting material. Yield: (0.367 g, 80%); $[\alpha]_D$ = +43.2 (*c* = 1.0,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$CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.98 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 2.13 (s, 3H), 4.12 (d, 2H, $J$ = 6.6 Hz), 4.20−4.23 (m, 1H), 4.34 (td, 1H, $J$ = 6.7, 1.9 Hz), 4.83 (t, 1H), 5.35−5.39 (m, 1H), 6.44 (d, 1H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 18.8, 20.6, 20.8, 20.9, 28.9, 61.4, 64.7, 64.8, 69.0, 96.0, 168.2, 169.6, 170.0, 170.4; IR ($CHCl_3$) $\nu$ 2925, 1745, 1219, 1143 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for calcd for $C_{14}H_{19}INaO_9$ 480.9971, found 480.9979.

**Compound 2c.** This compound is prepared using the above-mentioned general procedure using **1c** (0.560 g, 1 mmol) as the starting material. Yield: (0.560 g, 75%); $[\alpha]_D$ = +17.0 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.98 (s, 3H), 2.07 (s, 9H), 2.14 (s, 3H), 2.16 (s, 3H), 2.17 (s, 3H), 3.91−3.96 (m, 1H), 4.07 (dd, 1H, $J$ = 11.1, 6.9 Hz), 4.19 (m, 4H), 4.54 (dd, 1H, $J$ = 12.1, 1.8 Hz), 4.60 (d, 1H, $J$ = 7.9 Hz), 4.71 (dd, 1 H, $J$ = 3.9, 1.6 Hz), 5.00 (dd, 1H, $J$ = 10.4, 3.5 Hz), 5.17 (dd, 1H, $J$ = 10.4, 8.0 Hz), 5.36−5.38 (m, 1H), 5.43 (dd, 1H, $J$ = 8.9, 3.9 Hz), 6.22 (d, 1H, $J$ = 1.3 Hz); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.5, 20.6 (4C), 20.8, 20.8, 22.6, 52.1, 61.1, 61.2, 66.7, 68.3, 69.1, 70.7, 70.9, 72.5, 73.4, 90.7, 101.2, 169.2, 169.4, 170.1, 170.1, 170.1, 170.1, 170.3, 170.4; IR ($CHCl_3$) $\nu$ 2930, 1746, 1221, 1053 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{26}H_{35}INaO_{17}$ 769.0817, found 769.0816.

**Compound 3a.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material. Yield: (0.292 g, 71%); $[\alpha]_D$ = +31.0 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 2.07 (s, 3H), 2.11 (s, 6H), 2.18 (s, 3H), 4.11 (ddd, 1H, $J$ = 10.0, 4.5, 2.5 Hz), 4.15 (dd, 1H, $J$ = 12.4, 2.4 Hz), 4.24 (dd, 1H, $J$ = 12.4, 4.5 Hz), 4.44 (dd, 1H, $J$ = 3.9, 1.7 Hz), 5.20 (dd, 1H, $J$ = 9.7, 4.0 Hz), 5.49 (t, 1H, $J$ = 9.8 Hz), 6.32 (d, 1H, $J$ = 1.5 Hz); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.5, 20.6, 20.7, 20.8, 47.8, 61.8, 65.5, 68.7, 71.2, 93.1, 168.0, 169.2, 170.0, 170.6; IR ($CHCl_3$) $\nu$ 2925, 1745, 1219, 1143 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{14}H_{19}BrNaO_9$ 433.0110, 435.0090, found 433.0078, 435.0087.

**Compound 6a.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material. Yield: (0.356 g, 76%); $[\alpha]_D$ = +61.0 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 2.08 (s, 3H), 2.12 (s, 3H), 2.12 (s, 3H), 3.07 (s, 1 H), 4.13−4.19 (m, 2 H), 4.24 (dd, 1H, $J$ = 12.7, 4.8 Hz), 4.59 (bs, 1H), 4.60 (d, 1H, $J$ = 6.0 Hz), 5.41 5.53 (m, 1H), 6.47 (s, 1H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.6, 20.7, 20.9, 26.2, 61.6, 66.7, 68.4, 71.8, 73.3, 77.1, 96.0, 149.7, 169.3, 169.8, 170.6; IR ($CHCl_3$) $\nu$ 3258, 2950, 1741, 1145, 1059 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{15}H_{17}INaO_9$ 490.9815, found 490.9825.

**Compound 6b.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material, Yield: (0.437 g, 73%); $[\alpha]_D$ = +25.8 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 0.82 0.92 (m, 3 H), 1.21 1.37 (m, 16 H), 1.65 (q, 2H, $J$ = 7.3 Hz), 2.07 (s, 3H), 2.11 (s, 3H), 2.11 (s, 3H), 2.40 (t, 1H, $J$ = 7.5 Hz), 4.11 (ddd, 1H, $J$ = 9.9, 4.6, 2.5 Hz), 4.15 (dd, 1H, $J$ = 12.4, 2.4 Hz), 4.22 (dd, 1H, $J$ = 12.3, 4.6 Hz), 4.53 (dd, 1H, $J$ = 4.4, 1.6 Hz), 4.58 (dd, 1H, $J$ = 9.4, 4.4 Hz), 5.45 (t, 1H, $J$ = 9.7 Hz), 6.40 (d, 1H, $J$ = 1.4 Hz); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 14.0, 20.5, 20.6, 20.7, 22.5, 24.6, 27.2, 28.8, 29.1, 29.2, 29.3, 29.4(2C), 31.8, 33.9, 61.7, 66.9, 68.6, 71.3, 94.3, 169.2, 169.7, 170.5, 170.8; IR ($CHCl_3$) $\nu$ 2932, 1745, 1132, 1045 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{24}H_{39}INaO_9$ 621.1536, found 621.1547.

**Compound 6c.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material. Yield: (0.517 g, 80%); $[\alpha]_D$ = +27.6 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 2.07 (s, 3H), 2.12 (s, 3H), 2.12 (s, 3H), 4.14 4.33 (m, 3H), 4.75 (d, 1H, $J$ = 2.1 Hz), 4.78 (d, 1H, $J$ = 4.5 Hz), 5.47−5.59 (m, 1H), 6.67 (s, 1H), 7.22 (td, 1H, $J$ = 7.6, 1.7 Hz), 7.47 (td, 1H, $J$ = 7.6, 1.1 Hz), 7.83 (dd, 1H, $J$ = 7.8, 1.6 Hz), 8.04 (dd, 1H, $J$ = 7.9, 1.0 Hz); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.6, 20.8, 20.9, 27.0, 61.8, 66.9, 68.8, 72.0, 93.9, 96.1, 128.2, 131.6, 133.4, 133.5, 141.6, 163.9, 169.3, 169.9, 170.7; IR ($CHCl_3$) $\nu$ 3013, 2931, 1746, 1551, 1441, 1121, 1033, 661 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{19}H_{20}I_2NaO_9$ 668.9094, found 668.9141.

**Compound 6d.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material. Yield: (0.447 g, 72%); $[\alpha]_D$ = +19.9 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 2.06 (s, 3H), 2.10 (s, 6H), 2.67 (t, 2H, $J$ = 5.8 Hz), 3.51 (q, 2H, $J$ = 6.0 Hz), 4.07−4.18 (m, 2H), 4.21 (dd, 1H, $J$ = 12.4, 4.4 Hz), 4.52 4.58 (m, 2H), 5.10 (s, 2H), 5.36 (t, 1H, $J$ = 6.1 Hz), 5.46 (t, 1H, $J$ = 9.4 Hz), 6.41 (s, 1H), 7.35 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.6, 20.7, 20.9, 26.9, 34.3, 36.4, 61.7, 66.8(2C), 68.6, 71.5, 94.9, 128.0−128.5 (5C), 136.2, 156.3, 169.3, 169.8, 169.9, 170.7; IR ($CHCl_3$) $\nu$ 3396, 3051, 2958, 1742, 1520, 1130, 1005 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{23}H_{28}INNaO_{11}$ 644.0605, found 644.0597.

**Compound 6e.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material. Yield: (0.470 g, 80%); mp: 131 °C; $[\alpha]_D$ = +7.80 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.45 (s, 9H), 1.46 (s, 3H), 2.08 (s, 3H), 2.11 (s, 3H), 2.12 (s, 3H), 4.16 (dd, 2H, $J$ = 14.0, 11.1 Hz), 4.24 (dd, 1H, $J$ = 12.0, 4.0 Hz), 4.31−4.40 (m, 1H), 4.51−4.60 (m, 2H), 5.02 (d, 1H, $J$ = 7.1 Hz), 5.48 (t, 1H, $J$ = 9.4 Hz), 6.40 (s, 1H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 18.1, 21.0, 20.7, 20.9, 26.7, 28.2 (3C), 49.0, 61.6, 66.7, 68.7, 71.6, 80.2, 95.5, 155.0, 169.3, 169.8, 170.7, 171.1; IR ($CHCl_3$) $\nu$ 3384, 2981, 1747, 1515, 1454, 1160, 1057, 666 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for [$C_{20}H_{30}INNaO_{11}$ 610.0761, found 610.0770.

**Compound 6f.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material. Yield: (0.550 g, 81%); $[\alpha]_D$ = +40.0 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.45 (s, 9H), 2.08 (s, 3H), 2.11 (s, 3H), 2.12 (s, 3H), 2.93−3.04 (m, 2H), 3.79 (s, 3H), 4.10−4.19 (m, 2H), 4.23 (dd, 1H, $J$ = 12.3, 4.4 Hz), 4.53 (dd, 1H, $J$ = 9.5, 4.4 Hz), 4.57−4.66 (m, 2H), 5.46 (t, 1H, $J$ = 9.7 Hz), 5.58 (d, 1H, $J$ = 8.0 Hz), 6.38 (s, 1H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.5, 20.6, 20.8, 26.8, 28.2 (3C), 36.9, 49.9, 52.8, 61.6, 66.8, 68.5, 71.6, 80.3, 95.3, 155.1, 168.4, 169.2, 169.7, 170.6, 171.0; IR ($CHCl_3$) $\nu$3374, 2977, 1745, 1510, 1438, 1162, 1056, 669 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{22}H_{32}INNaO_{13}$ 668.0816, found 668.0789

**Compound 6g.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material. Yield: (0.603 g, 81%); $[\alpha]_D$ = +8.0 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 0.03 (s, 3H), 0.04 (s, 3H), 0.85 (s, 9H), 2.05 (s, 3H), 2.09 (s, 3H), 2.11 (s, 3H), 3.88 (dd, 1H, $J$ = 10.3, 3.1 Hz), 4.08−4.11 (m, 2H), 4.11−4.14 (m, 1H), 4.23 (dd, 1H, $J$ = 12.5, 4.3 Hz), 4.46−4.49 (m, 1H), 4.50 (dd, 1H, $J$ = 4.4, 1.5 Hz), 4.58 (dd, 1H, $J$ = 9.5, 4.4 Hz), 5.15 (d, 2H, $J$ = 10.9 Hz), 5.46 (t, 1H, $J$ = 9.8 Hz), 5.58 (d, 1H, $J$ = 8.5 Hz), 6.42 (s, 1H), 7.32−7.39 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ −5.7, −5.6, 18.2, 20.6, 20.7, 20.8, 25.7 (3C), 26.6, 56.0, 62.0, 63.4, 66.8, 67.3, 68.4, 71.6, 95.6, 128.2−128.6 (5C), 136.0, 155.9, 168.1, 169.3, 170.0, 170.7; IR ($CHCl_3$) $\nu$ 3365, 2934, 1747, 1512, 1427, 1117, 1056, 668 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{29}H_{42}INNaO_{12}Si$ 774.1419, found 774.1423.

**Compound 6h.** This compound is prepared using the above-mentioned general procedure using **1a** (0.272 g, 1 mmol) as the starting material, Yield: (0.605 g, 79%); $[\alpha]_D$ = +5.4 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 0.00 (s, 3H), 0.05 (s, 3H), 0.82 (s, 9H), 1.24 (d, 3H, $J$ = 6.2 Hz), 2.03 (s, 3H), 2.09 (s, 6H), 3.98−4.14 (m, 2H), 4.22 (dd, 1H, $J$ = 12.8, 4.3 Hz), 4.31 (dd, 1H, $J$ = 9.3, 1.7 Hz), 4.40−4.62 (m, 3H), 5.16 (d, 2H, $J$ = 6.6 Hz), 5.46 (t, 2H, $J$ = 9.2 Hz), 6.39 (s, 1H), 7.29−7.41 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ −5.4, −4.4, 17.8, 20.5, 20.6, 20.7, 20.8, 25.5(3C), 26.6, 60.0, 61.4, 66.6, 67.3, 68.4, 68.5, 71.5, 95.5, 128.2−128.5 (5C), 135.9, 156.5, 168.4, 169.2, 169.6, 171.0; IR ($CHCl_3$) $\nu$ 3445, 2955, 1744, 1512, 1426, 1136, 1063, 698 $cm^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{30}H_{44}INNaO_{12}Si$ 788.1575, found 788.1581.

**Compound 7a.** This compound is prepared using the above-mentioned general procedure using **1b** (0.272 g, 1 mmol) as the starting material. Yield: (0.472 g, 76%); $[\alpha]_D$ = +41.2 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 2.01 (s, 3H), 2.08 (s, 3H), 2.18 (s, 3H), 2.51−2.69 (m, 2H), 3.48 (dt, 2H, $J$ = 13.6, 6.4 Hz), 4.16 (d, 2H, $J$ = 6.6 Hz), 4.30 (d, 1H, $J$ = 4.6 Hz), 4.38 (t, 1H, $J$ = 5.9 Hz), 4.84−4.88 (m, 1H), 5.08 (s, 2H), 5.40−5.42 (m, 2H), 6.52 (d, 1H, $J$ = 1.2 Hz), 7.31−7.37 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 18.6, 20.5, 20.7, 20.8, 34.3, 36.3, 61.4, 64.6, 64.7, 66.7, 69.0, 96.1, 128.0−


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128.4 (5C), 136.1, 156.2, 169.4, 169.7, 169.9, 170.4; IR ($CHCl_3$) $\nu$ 3383, 2951, 1745, 1519, 1427, 1130, 1059, 666 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + Na]^+$ calcd for $C_{23}H_{28}INNaO_{11}$ 644.0605, found 644.0617.

**Compound 7b.** This compound is prepared using the above-mentioned general procedure using **1b** (0.272 g, 1 mmol) as the starting material. Yield: (0.487 g, 83%); $[\alpha]_D$ = +22.4 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.42 (s, 3H), 1.44 (s, 9H), 2.05 (s, 3H), 2.09 (s, 3H), 2.19 (s, 3H), 4.12−4.25 (m, 2H), 4.31 (d, 2H, $J$ = 4.3 Hz), 4.47 (t, 1H, $J$ = 6.1 Hz), 4.86 4.91 (m, 1H), 5.20 (m, 1H, $J$ = 7.3 Hz), 5.45 (s, 1H), 6.52 (s, 1H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 17.7, 18.5, 20.5, 20.6, 20.7, 28.1 (3C), 49.0, 61.2, 64.6 (2C), 69.0, 79.9, 96.5, 154.9, 169.2, 169.7, 170.2, 170.8; IR ($CHCl_3$) $\nu$ 3372, 2980, 1748, 1515, 1427, 1166, 1060, 670 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + Na]^+$ calcd for $C_{20}H_{30}INNaO_{11}$ 610.0761, found 610.0771.

**Compound 7c.** This compound is prepared using the above-mentioned general procedure using **1b** (0.272 g, 1 mmol) as the starting material. Yield: (0.556 g, 74%); $[\alpha]_D$ = +20.6 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ −0.07 (s, 3H), −0.05 (s, 3H), 0.76 (s, 9H), 1.94 (s, 3H), 1.99 (s, 3H), 2.10 (s, 3H), 3.79 (dd, 1H, $J$ = 10.3, 3.1 Hz), 3.99 (dd, 1H, $J$ = 10.3, 2.7 Hz), 4.07 (dd, 1H, $J$ = 15.6, 6.6 Hz), 4.16 (d, 1H, $J$ = 4.9 Hz), 4.25−4.32 (m, 1H), 4.38 (dt, 1H, $J$ = 8.3, 2.8 Hz), 4.71 4.79 (m, 1H), 5.05 (d, 2H, $J$ = 4.4 Hz), 5.34 (s, 1H), 5.52 (d, 1H, $J$ = 8.4 Hz), 6.46 (s, 2H), 7.24−7.30 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ −5.7, −3.7, 18.0, 18.0, 20.5, 20.7, 20.9, 25.6 (3C), 25.7, 61.3, 63.3, 64.5, 64.6, 67.2, 69.3, 97.2, 128.2−128.5 (5C), 136.0, 155.9, 168.1, 169.3, 170.0, 170.3; IR ($CHCl_3$) $\nu$ 3367, 2953, 1748, 1513, 1464, 1130, 1058, 670 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + Na]^+$ calcd for $C_{29}H_{42}INNaO_{12}Si$ 774.1419, found 774.1425.

**Compound 7d.** This compound is prepared using the above-mentioned general procedure using **1b** (0.272 g, 1 mmol) as the starting material. Yield: (0.689 g, 90%); $[\alpha]_D$ = +29.4 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ −0.05 (s, 3H), 0.00 (s, 3H), 0.78 (s, 9H), 1.20 (d, 3H, $J$ = 6.2 Hz), 1.97 (s, 3H), 2.04 (s, 3H), 2.13 (s, 3H), 4.00−4.07 (m, 1H), 4.12 (ddd, 1H, $J$ = 11.3, 6.5, 1.4 Hz), 4.20−4.25 (m, 2H), 4.28 (t, 1H, $J$ = 6.6 Hz), 4.35−4.43 (m, 1H), 4.77 (t, 1H, $J$ = 3.5 Hz), 5.08−5.16 (m, 2H), 5.36 (s, 1H), 5.41 (d, 1H, $J$ = 8.9 Hz), 6.47 (s, 1H), 7.25−7.39 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ −5.4, −4.3, 17.8, 18.1, 20.6, 20.8, 20.9, 20.9, 25.5(3C), 60.0, 61.3, 64.5, 64.6, 67.3, 68.4, 69.3, 97.3, 128.3, 128.6, 136.0, 156.6, 168.6, 169.3, 169.9, 170.3; IR ($CHCl_3$) $\nu$ 3446, 2934, 1749, 1511, 1426, 1136, 1067, 699 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + Na]^+$ calcd for $C_{30}H_{44}INNaO_{12}Si$ 788.1575, found 788.1572.

**Compound 8a.** This compound is prepared using the above-mentioned general procedure using **1c** (0.560 g, 1 mmol) as the starting material. Yield: (0.691 g, 76%); $[\alpha]_D$ = +31.5 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.98 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.12 (s, 3H), 2.15 (s, 3H), 2.16 (s, 3H), 2.65 (t, 2H, $J$ = 5.8 Hz), 3.50 (q, 2H, $J$ = 5.9 Hz), 3.92 3.98 (m, 1H), 3.99 4.14 (m, 4H), 4.18 (dd, 1H, $J$ = 11.3, 6.8 Hz), 4.43 (dd, 1H, $J$ = 12.1, 1.7 Hz), 4.49−4.54 (m, 1H), 4.61 (d, 1H, $J$ = 8.0 Hz), 4.67 (dd, 1H, $J$ = 7.2, 4.1 Hz), 5.00 (dd, 1H, $J$ = 10.5, 3.5 Hz), 5.10 (s, 2H), 5.16 (dd, 1H, $J$ = 10.4, 7.9 Hz), 5.30 (t, 1H, $J$ = 6.0 Hz), 5.36 5.40 (m, 1H), 6.35 (d, 1H, $J$ = 2.5 Hz), 7.32 7.38 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.5, 20.6 (2C), 20.7, 20.8, 21.0, 26.9, 34.4, 36.4, 61.1, 61.7, 66.7, 66.8, 69.0, 69.4, 70.7, 70.9, 71.8, 75.4, 94.7, 101.4, 128.1−128.5 (5C), 136.3, 156.2, 169.3, 169.5, 170.0, 170.1 (2C), 170.4 (2C); IR ($CHCl_3$) $\nu$ 3378, 2929, 1747, 1516, 1461, 1133, 1076, 668 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + Na]^+$ calcd for $C_{35}H_{44}INNaO_{19}$ 932.1449, found 932.1443.

**Compound 8b.** This compound is prepared using the above-mentioned general procedure using **1c** (0.560 g, 1 mmol) as the starting material. Yield: (0.727 g, 83%); $[\alpha]_D$ = +25.8 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.44 (s, 9H), 1.98 (s, 3H), 2.03 (s, 3H), 2.08 (d, 6H, $J$ = 1.1 Hz), 2.14 (s, 3H), 2.15 (s, 3H), 2.17 (s, 3H), 3.99 (t, 1H, $J$ = 6.6 Hz), 4.05−4.13 (m, 3H), 4.14−4.21 (m, 2H), 4.29−4.36 (m, 1H), 4.43 (d, 1H, $J$ = 11.8 Hz), 4.50−4.55 (m, 1H), 4.64 (d, 1H, $J$ = 7.9 Hz), 4.68 (s, 1H), 5.02 (dd, 1H, $J$ = 0.4, 3.3 Hz), 5.15 (dd, 1H, $J$ = 10.4, 8.1 Hz), 5.23 (d, 1H, $J$ = 7.1 Hz), 5.38 (d, 1H, $J$ = 3.4 Hz), 6.35 (s, 1H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 17.7, 20.2, 20.3 (2C), 20.4, 20.5, 20.7, 26.7, 28.0 (3C), 48.9, 61.0, 61.4, 66.6, 68.8, 69.1, 70.4, 70.6, 71.6, 75.0, 80.0, 95.0, 101.1, 154.8, 169.0, 169.2, 169.7, 169.8, 170.1 (2C), 171.1; IR ($CHCl_3$) $\nu$ 3382, 2981, 1747, 1514, 1453, 1164, 1053, 666 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + Na]^+$ calcd for $C_{32}H_{46}INNaO_{19}$ 898.1606, found 898.1613.

**Compound 8c.** This compound is prepared using the above-mentioned general procedure using **1c** (0.560 g, 1 mmol) as the starting material. Yield: (0.774 g, 80%); $[\alpha]_D$ = +35.4 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.45 (s, 9H), 1.98 (s, 3H), 2.08 (s, 6H), 2.15 (s, 6H), 2.17 (s, 3H), 2.90−3.09 (m, 2H), 3.78 (s, 3H), 3.95 (t, 1H, $J$ = 6.7 Hz), 4.01−4.15 (m, 4H), 4.18 (dd, 1H, $J$ = 11.2, 6.7 Hz), 4.46 (dd, 1H, $J$ = 12.0, 1.5 Hz), 4.54 (s, 1H), 4.61 (dd, 3H, $J$ = 12.1, 7.4 Hz), 5.00 (dd, 1H, $J$ = 10.4, 3.5 Hz), 5.15 (dd, 1H, $J$ = 10.4, 7.9 Hz), 5.32 5.43 (m, 1H), 5.50 (d, 1H, $J$ = 8.1 Hz), 6.33 (d, 1H, $J$ = 2.0 Hz); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.5, 20.6, 20.6, 20.7, 20.8, 20.9, 27.0, 28.2 (3C), 36.9, 49.9, 52.9, 61.1, 61.6, 66.8, 69.0, 69.1, 70.7, 70.9, 72.0, 75.2, 80.4, 95.2, 101.4, 155.2, 168.7, 169.3, 169. 5, 170.0, 170.1, 170.4 (2C), 171.1; IR ($CHCl_3$) $\nu$ 3678, 2929, 1746, 1512, 1434, 1164, 1052, 756 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + Na]^+$ calcd for $C_{34}H_{48}INNaO_{21}$ 956.1661, found 956.1667.

**Compound 8d.** This compound is prepared using the above-mentioned general procedure using **1c** (0.560 g, 1 mmol) as the starting material. Yield: (0.832 g, 80%); $[\alpha]_D$ = +18.0 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 0.03 (s, 3H), 0.04 (s, 3H), 0.85 (s, 9H), 1.98 (s, 3H), 2.07 (s, 6H), 2.10 2.18 (m, 9H), 3.88 (dd, 1H, $J$ = 10.4, 3.1 Hz), 3.94 (t, 1H, $J$ = 6.7 Hz), 3.97 4.04 (m, 1H), 4.07 (m, 4H), 4.18 (dd, 1H, $J$ = 11.2, 6.7 Hz), 4.41 (d, 1H, $J$ = 13.6 Hz), 4.41−4.53 (m, 2H), 4.61 (d, 1H, $J$ = 7.9 Hz), 4.72 (dd, 1H, $J$ = 7.0, 4.1 Hz), 5.00 (dd, 1H, $J$ = 10.4, 3.4 Hz), 5.06−5.23 (m, 3H), 5.37 (d, 1H, $J$ = 3.2 Hz), 5.58 (d, 1H, $J$ = 8.6 Hz), 6.39 (d, 1H, $J$ = 2.4 Hz), 7.32−7.40 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ −5.6, −5.6, 18.1, 20.5, 20.6, 20.6, 20.7, 20.8, 20.9, 25.7 (3C), 26.5, 55.9, 61.1, 61.6, 63.3, 66.7, 67.2, 69.0, 69.3, 70.7, 70.9, 71.8, 75.4, 95.4, 101.4, 128.2−128.5 (5C), 136.1, 155.9, 168.3, 169.2, 169.2, 170.0, 170.1, 170.4 (2C); IR ($CHCl_3$) $\nu$ 3369, 2935, 1748, 1514, 1425, 1112, 1057, 699 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + K]^+$ calcd for $C_{41}H_{58}IKNO_{20}Si$ 1078.2003, found 1078.2015.

**Compound 8e.** This compound is prepared using the above-mentioned general procedure using **1c** (0.560 g, 1 mmol) as the starting material. Yield: (0.811 g, 77%); $[\alpha]_D$ = +13.0 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ −0.07 (s, 3H), −0.02 (s, 3H), 0.75 (s, 9H), 1.17 (d, 3H, $J$ = 6.2 Hz), 1.89 (s, 3H), 1.99 (s, 6H), 2.02 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 3.85 3.95 (m, 2H), 3.96−4.05 (m, 2H), 4.09 (dd, 2H, $J$ = 11.2, 6.8 Hz), 4.23 (dd, 1H, $J$ = 9.4, 1.6 Hz), 4.35 (m, 2H), 4.46 (dd, 1H, $J$ = 4.0, 2.2 Hz), 4.55 (d, 1H, $J$ = 7.9 Hz), 4.59 (dd, 1H, $J$ = 8.0, 4.8 Hz), 4.93 (dd, 1H, $J$ = 10.4, 3.3 Hz), 5.00−5.14 (m, 3H), 5.29 (d, 1H, $J$ = 3.3 Hz), 5.40 (d, 1H, $J$ = 9.5 Hz), 6.29 (d, 1H, $J$ = 1.9 Hz), 7.23−7.36 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ −5.5, −4.4, 17.7, 20.4, 20.4, 20.5, 20.5, 20.6, 20.7, 20.7, 25.4 (3C), 26.8, 59.8, 61.0, 61.4, 66.6, 67.2, 68.4, 68.9, 69.1, 70.5, 70.8, 71.7, 74.9, 95.2, 101.1, 128.1−128.4 (5C), 136.0, 156.4, 168.9, 169.1, 169.1, 169.9, 169.9, 170.2, 170.3; IR ($CHCl_3$) $\nu$ 3445, 2932, 1745, 1512, 1462, 1134, 1071, 698 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + K]^+$ calcd for $C_{42}H_{60}IKNO_{20}Si$ 1092.2160, found 1092.2193.

**Compound 9a.** This compound is prepared using the above-mentioned general procedure using **6g** (0.750 g, 1 mmol) as the starting material. Yield: (0.494 g, 76%); $[\alpha]_D$ = +40.7 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (399.78 MHz, $CDCl_3$) $\delta$ 2.03 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 3.80 (s, 3H), 3.92−4.01 (m, 3H), 4.12 (dd, 1H, $J$ = 12.3, 2.3 Hz), 4.18 (dd, 1H, $J$ = 12.3, 5.0 Hz), 4.48 (dd, 1H, $J$ = 4.3, 1.3 Hz), 4.54 (dt, 2H, $J$ = 9.2, 5.6 Hz), 5.14 (d, 3H, $J$ = 5.8 Hz), 5.31 (t, 1H, $J$ = 9.6 Hz), 5.82 (d, 1H, $J$ = 8.2 Hz), 7.31−7.39 (m, 5H); $^{13}C$ NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.5, 20.6, 20.8, 28.5, 52.8, 54.1, 61.9, 67.1, 68.7 (2C), 68.9, 69.6, 101.8, 128.0−128.4 (5C), 135.9, 155.7, 169.3, 169.6, 170.0, 170.5; IR ($CHCl_3$) $\nu$ 3378, 2930, 1742, 1519, 1452, 1123, 1051, 699 $cm^{-1}$; HRMS (TOF) $m/z$ $[M + Na]^+$ calcd for $C_{24}H_{30}INNaO_{12}$ 674.0710, found 674.0709.

**Compound 9b.** This compound is prepared using the above-mentioned general procedure using **6h** (0.750 g, 1 mmol) as the starting material. Yield: (0.485 g, 73%); $[\alpha]_D$ = +35.6 ($c$ = 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.31 (d, 3H, $J$ = 6.4 Hz), 2.05


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(s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 3.78 (s, 3H), 4.06 (ddd, 1H, $J$ = 9.8, 5.2, 2.4 Hz), 4.13 (dd, 1H, $J$ = 12.2, 2.3 Hz), 4.20 (dd, 1H, $J$ = 12.2, 5.3 Hz), 4.32−4.39 (m, 2H), 4.44 (dd, 1H, $J$ = 9.7, 2.3 Hz), 4.53 (dd, 1H, $J$ = 9.3, 4.3 Hz), 5.16 (d, 3H, $J$ = 9.4 Hz), 5.31 (t, 1H, $J$ = 9.6 Hz), 5.48 (d, 1H, $J$ = 9.6 Hz), 7.30−7.44 (m, 5H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 17.8, 20.6, 20.6, 20.9, 28.8, 52.7, 58.5, 62.2, 67.3, 67.5, 68.7, 69.7, 77.3, 102.6, 128.2−128.5 (5C), 135.9, 156.5, 169.4, 169.7, 170.6, 170.6; IR ($CHCl_3$) $\nu$ 3358, 2950, 1744, 1518, 1452, 1175, 1038, 643 cm$^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{25}H_{32}INNaO_{12}$ 688.0867, found 688.0861.

**Compound 10a.** This compound is prepared by the reported procedure[11] using **9a** (0.400 g, 0.6 mmol) as the starting material. Yield: (0.210 g, 65%); $[\alpha]_D$ = +48.6 ($c$ = 1.0, $CHCl_3$); $^1$H NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.73 (td, 1H, $J$ = 12.9, 3.7 Hz), 1.93 (s, 3H), 1.95 (s, 3H), 2.00 (s, 3H), 2.13 (dd, 1H, $J$ = 13.1, 5.3 Hz), 3.71 (s, 3H), 3.84 (s, 3H), 3.96 (d, 1H, $J$ = 12.2 Hz), 4.19 (dd, 1H, $J$ = 12.2, 4.7 Hz), 4.48 (d, 1H, $J$ = 8.0 Hz), 4.82−4.93 (m, 2H), 5.07 (s, 2H), 5.15 (td, 1H, $J$ = 11.0, 5.4 Hz), 5.67 (d, 1H, $J$ = 8.4 Hz), 7.24−7.33 (m, 5H); $^{13}$C NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.7 (2C), 20.9, 34.7, 52.7, 54.2, 62.1, 67.2, 68.3, 68.4, 68.7, 69.0, 97.7, 128.1−128.5 (5C), 136.0, 155.8, 169.8, 170.1, 170.3, 170.7; IR ($CHCl_3$) $\nu$ 3356, 2956, 1740, 1518, 1450, 1132, 1047, 668 cm$^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{24}H_{31}NNaO_{12}$ 548.1744, found 548.1753.

**Compound 10b.** This compound is prepared by the reported procedure[11] using **9b** (0.400 g, 0.6 mmol) as the starting material. Yield: (0.202 g, 61%); $[\alpha]_D$ = +39.8 ($c$ = 1.0, $CHCl_3$); $^1$H NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.30 (d, 3H, $J$ = 6.4 Hz), 1.77 (td, 1H, $J$ = 12.7, 3.8 Hz), 2.00 (s, 3H), 2.04 (s, 3H), 2.04 (m, 1H), 2.07 (s, 3H), 3.74 (s, 3H), 3.98−4.07 (m, 2H), 4.27 (dd, 1H, $J$ = 12.0, 4.9 Hz), 4.34 (dd, 1H, $J$ = 6.4, 2.2 Hz), 4.40 (dd, 1H, $J$ = 9.7, 2.2 Hz), 4.88−5.00 (m, 2H), 5.15 (s, 2H), 5.15−5.29 (m, 1H), 5.48 (d, 1H, $J$ = 9.8 Hz), 7.31−7.43 (m, 5H); $^{13}$C NMR (100.53 MHz, $CDCl_3$) $\delta$ 18.2, 20.6 (2C), 20.9, 35.1, 52.5, 58.5, 62.2, 67.2, 68.3, 68.5, 69.3, 76.2, 98.4, 128.1−128.4 (5C), 136.0, 156.4, 169.8, 170.1, 170.6, 170.9; IR ($CHCl_3$) $\nu$ 3361, 2955, 1742, 1516, 1453, 1128, 1051, 700 cm$^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{25}H_{33}NNaO_{12}$ 562.1900, found 562.1909.

**Compound 11a.** This compound is prepared using the above-mentioned general procedure using **7c** (0.750 g, 1 mmol) as the starting material. Yield: (0.474 g, 73%); $[\alpha]_D$ = +35.6 ($c$ = 1.0, $CHCl_3$); $^1$H NMR (399.78 MHz, $CDCl_3$) $\delta$ 2.03 (s, 3H), 2.07 (s, 3H), 2.16 (s, 3H), 3.79 (s, 3H), 3.97 (s, 2H), 4.12 (d, 1H, $J$ = 10.8 Hz), 4.20 (t, 3H, $J$ = 9.9 Hz), 4.50 4.63 (m, 1H), 4.85 (s, 1H), 5.13 (s, 2H), 5.28 (s, 1H), 5.35 (s, 1H), 5.78 (d, 1H, $J$ = 7.5 Hz), 7.29−7.40 (m, 5H); $^{13}$C NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.6, 20.7, 20.8, 20.9, 23.8, 52.8, 54.1, 61.9, 65.2, 67.1, 67.6, 68.9, 102.8, 128.0−128.5 (5C), 136.0, 155.8, 169.4, 169.9, 170.0, 170.5; IR ($CHCl_3$) $\nu$ 3361, 2953, 1744, 1517, 1429, 1119, 1053, 669 cm$^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{24}H_{30}INNaO_{12}$ 674.0710, found 674.0708.

**Compound 11b.** This compound is prepared using the above-mentioned general procedure using **7d** (0.750 g, 1 mmol) as the starting material. Yield: (0.478 g, 72%); $[\alpha]_D$ = +40.4 ($c$ = 1.0, $CHCl_3$); $^1$H NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.31 (d, 3H, $J$ = 6.4 Hz), 2.04 (s, 3H), 2.06 (s, 3H), 2.16 (s, 3H), 3.79 (s, 3H), 4.09 (d, 1H, $J$ = 5.0 Hz), 4.11−4.15 (m, 1H), 4.20 (dd, 1H, $J$ = 11.4, 7.2 Hz), 4.30−4.35 (m, 1H), 4.37 (dd, 1H, $J$ = 6.4, 2.3 Hz), 4.42 (dd, 1H, $J$ = 9.7, 2.2 Hz), 4.79−4.84 (m, 1H), 5.14 (s, 2H), 5.30 (s, 1H), 5.35 (s, 1H), 5.46 (d, 1H, $J$ = 9.7 Hz), 7.31−7.41 (m, 5H); $^{13}$C NMR (100.53 MHz, $CDCl_3$) $\delta$ 18.0, 20.6, 20.7, 20.8, 20.9, 52.7, 58.5, 62.0, 65.0, 65.3, 67.3 (2C), 77.1, 104.0, 128.1−128.5 (5C), 136.0, 156.5, 169.5, 169.9, 170.4, 170.7; IR ($CHCl_3$) $\nu$ 3359, 2951, 1745, 1518, 1452, 1174, 1038, 702 cm$^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{25}H_{32}IN\ NaO_{12}$ 688.0867, found 688.0861.

**Compound 12a.** This compound is prepared by the reported procedure[11] using **11a** (0.400 g, 0.6 mmol) as the starting material. Yield: (0.193 g, 60%); $[\alpha]_D$ = +62.6 ($c$ = 1.0, $CHCl_3$); $^1$H NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.76 (dd, 1H, $J$ = 12.9, 4.9 Hz), 1.91 (s, 3H), 1.96 (s, 3H), 2.01 (dd, 1H, $J$ = 12.8, 3.6 Hz), 2.05 (s, 3H), 3.71 (s, 3H), 3.85 (d, 2H, $J$ = 3.0 Hz), 3.99 (m, 3H), 4.44−4.54 (m, 1H), 4.90 (d, 1H, $J$ = 3.1 Hz), 5.07 (d, 2H, $J$ = 1.8 Hz), 5.12 (dt, 1H, $J$ = 12.5, 4.2 Hz), 5.24 (d, 1H, $J$ = 2.4 Hz), 5.67 (d, 1H, $J$ = 8.3 Hz), 7.23−7.33 (m, 5H); $^{13}$C NMR (100.53 MHz, $CDCl_3$) $\delta$ 20.7, 20.7, 20.8, 29.9, 52.7, 54.2, 62.4, 65.8, 66.4, 67.2 (2C), 68.4, 98.2, 128.1−128.5 (5C), 136.0, 155.9, 170.0, 170.2, 170.4, 170.5; IR ($CHCl_3$) $\nu$ 3356, 2956, 1744, 1519, 1449, 1164, 1033, 701 cm$^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{24}H_{31}N\ NaO_{12}$ 548.1744, found 548.1754.

**Compound 12b.** This compound is prepared by the reported procedure[11] using **11b** (0.400 g, 0.6 mmol) as the starting material. Yield: (0.209 g, 63%); $[\alpha]_D$ = +102.8 ($c$ = 1.0, $CHCl_3$); $^1$H NMR (399.78 MHz, $CDCl_3$) $\delta$ 1.30 (d, 3H, $J$ = 6.4 Hz), 1.70 (dd, 1H, $J$ = 12.7, 5.0 Hz), 1.98 (s, 3H), 2.04 (s, 3H), 2.04 (m, 1H), 2.12 (s, 3H), 3.75 (s, 3H), 4.07 (dd, 2H, $J$ = 6.4, 2.2 Hz), 4.18 (t, 1H, $J$ = 6.5 Hz), 4.35 (dd, 1 H, $J$ = 6.4, 2.1 Hz), 4.39 (dd, 1H, $J$ = 9.8, 2.1 Hz), 4.98 (d, 1H, $J$ = 3.2 Hz), 5.15 (s, 2H), 5.15−5.21 (m, 1H), 5.31 (d, 1H, $J$ = 2.1 Hz), 5.44 (d, 1H, $J$ = 9.7 Hz), 7.32−7.41 (m, 5H); $^{13}$C NMR (100.53 MHz, $CDCl_3$) $\delta$ 18.3, 20.6, 20.7, 20.8, 30.2, 52.5, 58.6, 62.5, 65.8, 66.5, 67.1, 67.2, 76.1, 99.1, 128.1−128.5 (5C), 136.0, 156.5, 170.1, 170.2, 170.4, 171.1; IR ($CHCl_3$) $\nu$ 3358, 2955, 1744, 1517, 1452, 1169, 1028, 701 cm$^{-1}$; HRMS (TOF) $m/z$ [M + Na]$^+$ calcd for $C_{25}H_{33}NNaO_{12}$ 562.1900, found 562.1909.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Copies of $^1$H, $^{13}$C, and DEPT NMR spectra for all compounds, crystallographic data of compound **6e**, and FE-SEM images of micelles. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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(10) See Supporting Information for spectral charts, crystallographic data for compound **6e**, and FE-SEM images of micelles.

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(13) Crystal data of compound **6e** (CCDC 978459): $C_{20}H_{29}INO_{11}$, $M$ = 586.34, monoclinic, space group $P2(1)$, $a$ = 9.1343(7), $b$ = 6.8955(5), $c$ = 20.2243(15) Å, $V$ = 1273.56(16) Å$^3$, $Z$ = 2, $D_{calcd}$ = 1.529 g cm$^{-1}$, $T$ = 173(2) K, $\mu$ = 10.370 mm$^{-1}$, $F(000)$ = 594, $\lambda$ = Cu K$\alpha$ = 1.5418 Å, reflections measured 2979, 2954 unique, observed with $I > 2\sigma(I)$, final $R_1$ = 0.0328, $wR_2$ = 0.0830. See Supporting Information for the ORTEP diagram and other details.

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