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Dimethyltin Dichloride Catalyzed Regioselective Alkylation of *cis*-1,2-Diols at Room Temperature

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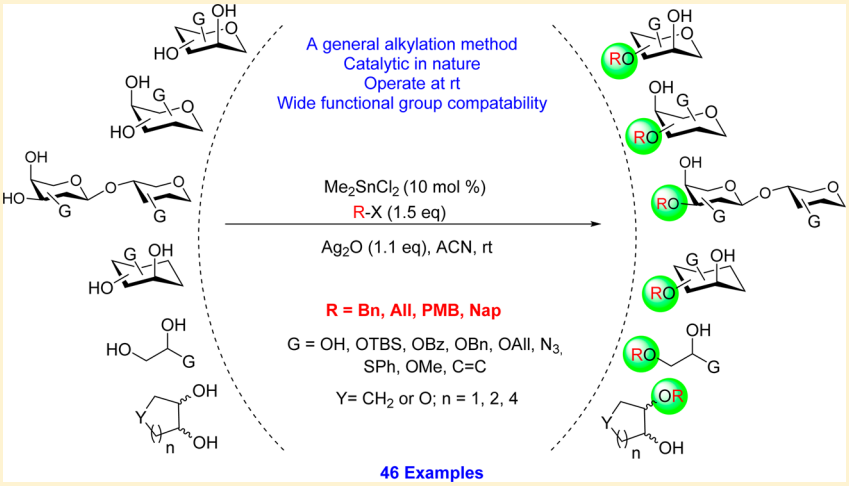
Supporting Information



ABSTRACT: Here, we have developed a mild and general method for the regioselective installation of benzyl, allyl, *para*-methoxybenzyl and naphthyl groups on *cis*-1,2-diols. The optimized method operates at room temperature using dimethyltin dichloride as catalyst and silver oxide as an additive. The present method works well with both sugars (such as mono- and disaccharides) and nonsugars (such as inositols, propan-1,2-diol, 1,2-cycloalkanediols and anhydroerythritol) and also provides comparatively better functional group compatibility.

INTRODUCTION

Regioselective protection of sugars with orthogonal protecting groups plays a key role in the successful synthesis of oligosaccharides and complex glyco-conjugates.[1] In this direction, benzyl ethers and its variants, which represent an important orthogonal protecting group, are frequently used in the carbohydrate chemistry because of following advantages such as easy installation, stability, compatibility with many reaction conditions and smooth removal under milder conditions.[2] Considering the differential reactivity of equatorial and axial hydroxyl groups of sugars, many approaches have been developed for the regioselective installation of benzyl and its variants.[3,4] Among those, most commonly used are tin-mediated[5] and transition-metal (Ni, Cu, Hg) mediated[6] as well as through selective reductive opening of benzylidene ring.[2b−e] Most of these methods involve stoichiometric amount of catalysts and heating, which limits their compatibility with many sensitive functional groups containing molecules. In the past decade, catalytic-controlled regioselective methods were developed, where diarylborinic acid[4f] and modified tin-based conditions were employed.[7] In further refinement, dimethyltin dichloride has been used for regioselective acylation[8a−c] and glycosylation[8d] at room temperature; however, there is no report regarding its use in the alkylation at room temperature. In this endeavor, we envisioned that the same could be explored for the alkylation in the presence of suitable additive. Considering our interest in carbohydrate chemistry[9] and importance of mild alkylation methods, we have successfully developed a room-temperature, regioselective method for the alkylation of the *cis*-1,2-diols using dimethyltin dichloride as catalyst and silver oxide as an additive. The present method successfully used for the installation of benzyl group and its variants such as allyl, *p*-methoxybenzyl and naphthyl to a wide range of monosaccharides, disaccharides, cyclitols (inositol) and *cis*-1,2-diol containing alicyclic and cyclic systems with good to excellent yields.

RESULTS AND DISCUSSION

To start with, *cis*-1,2-diol containing manno-glycoside **1a** and benzyl bromide were selected as substrates and silver oxide (Ag_2O) as an additive. Silver oxide is well reported for the

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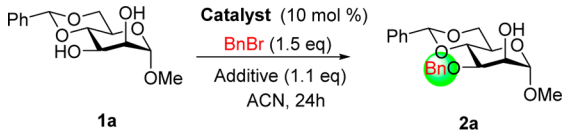
activation of alkyl bromide[10] and hence selected in the present case. In the first experiment, manno-glycoside **1a** was treated with benzyl bromide in the presence of dibutyltin oxide (Bu_2SnO) and additive silver oxide (Ag_2O) at room temperature, the 3-*O*-benzylated product **2a** was formed in a very minor (<10%) quantity (Table 1, entry a). The addition of base did not show any improvement (Table 1, entry b). Surprisingly, when dimethyltin dichloride was used, corresponding benzylated product **2a** was observed in 94% yield (Table 1, entry c). In the further refinement, the addition of base did not show any improvement (Table 1, entry d). In the absence of Ag_2O, no product formation was observed (Table 1, entry e). In the absence of dimethyltin dichloride, **2a** was formed in a very low yield (Table 1, entry f). The best conditions for the regioselective alkylation of *cis*-1,2-diols involves dimethyltin dichloride (10 mol %) as catalyst and Ag_2O (1.1 equiv) as additive at room temperature (Table 1, entry c).

Table 1. Optimization Studies

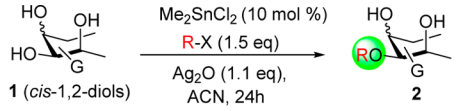


entry	catalyst	additive	base	**2a** yield (%)
a	Bu_2SnO	Ag_2O	–	<10[a]
b	Bu_2SnO	Ag_2O	TEA	<10[a]
c	Me_2SnCl_2	Ag_2O	–	94[b]
d	Me_2SnCl_2	Ag_2O	TEA	93[b]
e	Me_2SnCl_2	–	–	–
f	–	Ag_2O	–	10[a]

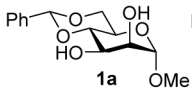
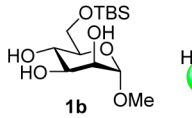
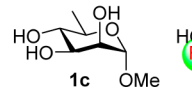
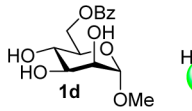
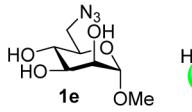
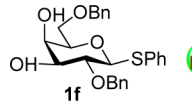
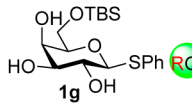
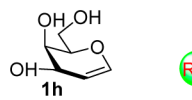
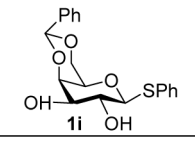
[a]Yields were determined by ^{1}H NMR. [b]Isolated yields.

With the optimized conditions in hand, the further investigation was conducted with benzyl and its other variants and *cis*-1,2-diol containing sugars (Table 2). When the reaction with benzyl variants such as allyl (All) bromide, *p*-methoxybenzyl (PMB) chloride and 2-naphthylmethyl (Nap) bromide was tried, coupling underwent smoothly and furnished corresponding 3-*O*-substitued products **2b**, **2c** and **2d** in a yield of 92, 97 and 95% respectively. Further, the suitability of present optimized conditions toward the tolerance of base sensitive functional groups such as silyl and benzoyl as well as heat sensitive group such as azido has also been investigated. 6-*O*-TBS-mannoglycoside **1b** when reacted with benzyl and its variants (allyl, PMB and naphthyl halides), regioselective corresponding 3-*O*-substitued products **2e**, **2f**, **2g** and **2h** were obtained in an excellent yield of 85, 81, 87 and 79%, respectively. Similarly, 1,2-*cis*-diols containing sugar such as rhamnoside **1c** also reacted with benzyl, allyl, PMB and naphthyl halides and gave 3-*O*-substituted products **2i**, **2j**, **2k** and **2l** in a yields of 97, 96, 98 and 98%, respectively. The benzoyl- and azido-substituted mannoglycosides **1d** and **1e** also underwent alkylation and gave 3-*O*-substituted products **2m**–**s** in good to excellent yields (74–84%). Next, we studied the differentially protected *β*-galactosides, where 3,4-dihydroxy-*β*-glactoside **1f**, when explored under optimized conditions, it also reacted smoothly with benzyl, allyl and naphthyl halides and gave corresponding 3-*O*-substituted products **2t**, **2u** and **2v** in a yield of 89, 91 and 92% respectively. 6-*O*-TBS protected *β*-galactoside **1g** also reacted smoothly with all the selected halides and furnished respective 3-*O*-substituted products **2w**, **2x**, **2y** and **2z** in a yield of 84, 81, 78 and 89% respectively. The sugar with free primary hydroxy group such as galactal **1h** was also investigated, which delivered a mixture of products. Notably, when the same reaction was performed with 2.5 equiv of benzyl bromide, dibenzylated product **2a′** was obtained in a yield of 80%. *trans*-1,2-Diol containing sugar **1i** when treated under optimized conditions, 3-*O*-benzyl galactoside **2b′** was formed with 42% yield along with an unseparable 2-*O*-benzyl substituted galactoside.

Table 2. Regioselective Alkylation of *cis*-1,2-Diol Containing Monosaccharides[d]



X = Br for Bn, Allyl, and Nap groups and X = Cl for PMB group

Entry	Substrate	Product	Yields[a]
1		**2b** (R = All)	92
2		**2c** (R = PMB)	97
3		**2d** (R = Nap)	95
4		**2e** (R = Bn)	85
5		**2f** (R = All)	81
6		**2g** (R = PMB)	87
7		**2h** (R = Nap)	79
8		**2i** (R = Bn)	97
9		**2j** (R = All)	96
10		**2k** (R = PMB)	98
11		**2l** (R = Nap)	98
12		**2m** (R = Bn)	74[b]
13		**2n** (R = All)	81[b]
14		**2o** (R = Nap)	70[b]
15		**2p** (R = Bn)	85
16		**2q** (R = All)	91
17		**2r** (R = PMB)	70
18		**2s** (R = Nap)	84
19		**2t** (R = Bn)	89
20		**2u** (R = All)	91
21		**2v** (R = Nap)	92
22		**2w** (R = Bn)	84
23		**2x** (R = All)	81
24		**2y** (R = PMB)	78
25		**2z** (R = Nap)	89
26		**2a'** (R = Bn)	80[c]
27		**2b'** (R = Bn)	42

[a]Isolated yield. [b]1.0 equiv of BnBr and 2.0 equiv of Ag_2O were employed. [c]2.5 equiv of BnBr and 2.2 equiv of Ag_2O were employed. [d]Reaction performed in 0.2–1.0 mmol scale.

To further expand the scope of optimized conditions, we investigated *cis*-1,2-diols containing disaccharides and non-sugars such as cyclitols (inositol derivatives) and all the results are summarized in Table 3. Under optimized conditions, the disaccharide **3a** underwent selective benzylation at *O*-3′ with

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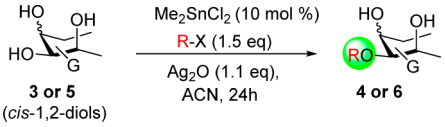
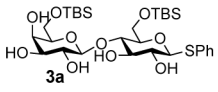
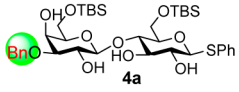
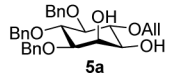
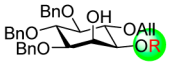
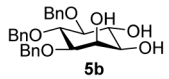
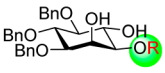
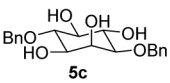
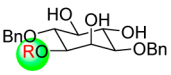
Table 3. Regioselective Alkylation of *cis*-1,2-Diol Containing Disaccharide and Cyclitols[c]



X = Br for Bn, Allyl, and Nap groups and X = Cl for PMB group.

Entry	Substrate	Product	Yield (%)[a]
1	 3a	 4a	62[b]
2 3 4 5	 5a		**6a** (R = Bn) 94 **6b** (R = All) 84 **6c** (R = PMB) 88 **6d** (R = Nap) 87
6 7 8 9	 5b		**6e** (R = Bn) 87 **6f** (R = All) 90 **6g** (R = PMB) 89 **6h** (R = Nap) 83
10 11 12 13	 5c		**6i** (R = Bn) 60[b] **6j** (R = All) 70[b] **6k** (R = PMB) 66[b] **6l** (R = Nap) 64[b]

[a]Isolated yield. [b]Reaction carried out for 36 h. [c]Reaction performed on 0.2−1.0 mmol scale.

62% of yield of product **4a**. Cyclitol such as dihydroxy-L-*myo*-inositol **5a** when treated with benzyl, allyl, PMB and naphthyl halides, corresponding 1-*O*-substituted products **6a**, **6b**, **6c** and **6d** were obtained in a yield of 94, 84, 88 and 87%, respectively. Trihydroxy-L-*myo*-inositol **5b** also worked successfully with benzyl, allyl, PMB and naphthyl halides and furnished regioselectively corresponding 1-*O*-substituted products **6e**, **6f**, **6g** and **6h** in a yield of 87, 90, 89 and 83%, respectively. Similarly, 1,4-di-*O*-benzyl-*myo*-inositol **5c** when tried, 5-*O*-substituted products **6i**, **6j**, **6k** and **6l** were obtained in a yield of 60, 70, 66 and 64%, respectively.

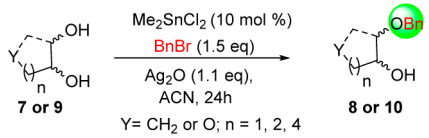
In further exploration, *cis*-1,2-diol containing alicyclic and cyclic systems were also investigated under optimized conditions (Table 4). Alicyclic diol, propan-1,2-diol having primary and secondary hydroxyl groups, underwent selectively benzylation at primary hydroxyl and delivered 75% of 1-*O*-benzyl-2-propanol **8a**. Six, five and eight membered cycloalkane-1,2-diols **9a**, **9b** and **9c** were selectively monobenzylated and furnished corresponding products **10a**, **10b** and **10c** in an excellent yield of 96, 91, 97% respectively. Furan-3,4-diol such as 1,4-anhydroerythritol when attempted, provided regioselective monobenzylated product **10d** in an excellent yield of 98%.

The literature precedents[10−12] and the present results suggested that the observed high regioselectivity could be explained by the following facts: first, complexation of tin catalyst increases the reactivity of hydroxy groups by increasing their nucleophilicity;[10] second, among the secondary alcohol, it is well-known that the equatorial OH groups are comparatively more reactive than axial partners and primary are more reactive than secondary;[11] third, activation of alkyl halide with silver[12] makes it workable at room temperature.

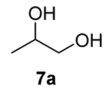
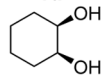
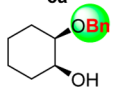
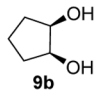
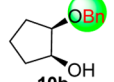
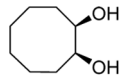
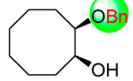
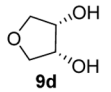
CONCLUSION

In conclusion, we have developed a mild, general and catalytic method for the regioselective alkylation of sugars and

Table 4. Regioselective Alkylation of Alicyclic and Cyclic-Diols[b]



Y= CH_2 or O; n = 1, 2, 4

Entry	Substrate	Product	Yield (%)[a]
1	 7a	 8a	75
2	 9a	 10a	96
3	 9b	 10b	91
4	 9c	 10c	97
5	 9d	 10d	98

[a]Isolated yield. [b]Reaction performed on 0.2−1.0 mmol scale.

nonsugars bearing *cis*-1,2-diol system using dimethyltin dichloride as catalyst and silver oxide as an additive at room-temperature. The operational simplicity and avoidance of high temperature are the attractive features of the present method, which finds applications in the preparation of complex molecules.

EXPERIMENTAL SECTION

General Information. Freshly dried acetonitrile by standard method of solvent purification was used for all reactions. NMR measurements (^{1}H, and ^{13}C) were recorded in $CDCl_3$ using 400/500 MHz spectrometer fitted with pulse-field gradient probe, and tetramethylsilane (TMS) or residual resonance of deuterated solvent were used as internal reference. Spectral features are tabulated in the following order: chemical shift (δ, ppm); multiplicity (brs-broad singlet, s-singlet, d-doublet, dd-double doublet, t-triplet, q-quartet, m-complex multiplet); coupling constants (J, Hz); number of protons. Mass spectra were recorded on MALDI-TOF/TOF mass spectrophotometer using 2,5-dihydroxy benzoic acid/α-cyano-4-hydroxy cinnamic acid as matrix in acetonitrile:water containing 0.01% TFA. HRMS were recorded on HRMS-6540-UHD machine. Optical rotations were measured on a digital polarimeter. Analytical TLC was performed on silica gel 60 F_{254} plates, and compounds were visualized by spraying and charring with phosphomolybdic acid or 20% H_2SO_4 in MeOH as developing reagent. Column chromatography was carried out with flash silica gel (230−400 mesh).

General Procedure. The *cis*-1,2-diol substrate **1**, **3**, **5**, **7**, **9** (0.2 to 1.0 mmol, 1 equiv), dimethyltin dichloride (10 mol %) and Ag_2O (1.1 equiv) were weighed into a 10 mL round-bottom flask and dissolved in dry acetonitrile (2 to 7 mL see below). Alkyl halide (1.5 equiv) was then added, the reaction flask was capped with a septum and purged with nitrogen. The mixture was stirred vigorously for 24 h at room temperature. The resulting mixture was diluted with CH_2Cl_2, filtered through Celite and concentrated to dryness. The resulting crude material was purified by chromatography on flash silica gel (230−400).

*Methyl-4,6-O-benzylidene-3-O-benzyl-α-D-mannopyranoside (**2a**).*[7a,13] Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside **1a**[14] (100

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mg, 0.354 mmol), benzyl bromide (63 μL, 0.532 mmol), dimethyltin dichloride (7.7 mg, 10 mol %) and Ag_2O (90.1 mg, 0.390 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (124.0 mg, 94%); R_f = 0.35 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +43.2 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.52 (m, 2H), 7.48−7.27 (m, 8H), 5.65 (s, 1H), 4.89 (d, *J* = 11.9 Hz, 1H), 4.78 (d, *J* = 15.2 Hz 1H), 4.73 (d, *J* = 2.4 Hz, 1H), 4.32 (dd, *J* = 9.2, 3.7 Hz, 1H), 4.17−4.08 (m, 2H), 3.98−3.79 (m, 3H), 3.41 (s, 3H) 2.08 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 137.6, 128.9, 128.5, 128.2, 127.9, 127.8, 126.1, 101.6, 101.1, 78.8, 75.6, 73.0, 69.9, 68.9, 63.2, 54.9; HRMS-MALDI (*m*/*z*) calcd for $C_{21}H_{24}O_6$ $[M + Na]^+$ 395.1465, found 395.1463.

*Methyl-4,6-O-benzylidene-3-O-allyl-α-D-mannopyranoside (**2b**).*[6d,15] Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside **1a** (100 mg, 0.354 mmol), allyl bromide (46 μL, 0.532 mmol), dimethyltin dichloride (7.7 mg, 10 mol %) and Ag_2O (90.1 mg, 0.390 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (105.0 mg, 92%); R_f = 0.35 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +45.3 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.49 (m, 2H), 7.47−7.32 (m, 3H), 5.99−5.89 (m, 1H), 5.61 (s, 1H), 5.33 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.22 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.80 (d, *J* = 0.7 Hz, 1H), 4.41−4.27 (m, 2H), 4.27−4.16 (m, 1H), 4.06 (dd, *J* = 15.9, 6.3 Hz, 2H), 3.92−3.76 (m, 3H), 3.42 (s, 3H), 2.66 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 134.5, 128.9, 128.2, 126.1, 117.4, 101.6, 101.1, 78.8, 75.1, 71.9, 69.9, 68.9, 63.2, 55.0; HRMS-MALDI (*m*/*z*) calcd for $C_{17}H_{22}O_6$ $[M + Na]^+$ 345.1309, found 345.1326.

*Methyl-4,6-O-benzylidene-3-O-(p-methoxybenzyl)-α-D-mannopyranoside (**2c**).*[16] Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside **1a** (100 mg, 0.354 mmol), *p*-methoxybenzyl chloride (72 μL, 0.532 mmol), dimethyltin dichloride (7.7 mg, 10 mol %) and Ag_2O (90.1 mg, 0.390 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (138.0 mg, 97%); R_f = 0.32 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +41.2 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.45 (m, 2H), 7.40−7.32 (m, 3H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 5.59 (s, 1H), 4.76 (d, *J* = 11.4 Hz, 1H), 4.69 (s, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.32−4.22 (m, 1H), 4.07 (t, *J* = 9.2 Hz, 1H), 3.94 (d, *J* = 1.9 Hz, 1H), 3.90−3.73 (m, 3H), 3.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 137.6, 130.1, 129.6, 128.9, 128.2, 126.1, 113.9, 101.6, 101.2, 78.9, 75.4, 72.8, 69.9, 68.9, 63.3, 55.3, 54.9; HRMS-MALDI (*m*/*z*) calcd for $C_{22}H_{26}O_7$ $[M + Na]^+$ 425.1571, found 425.1598.

*Methyl-4,6-O-benzylidene-3-O-(2-methylnaphthalenyl)-α-D-mannopyranoside (**2d**).* Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside **1a** (100 mg, 0.354 mmol), 2-(bromomethyl)naphthalene (117 mg, 0.532 mmol), dimethyltin dichloride (7.7 mg, 10 mol %) and Ag_2O (90.1 mg, 0.390 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (142.0 mg, 95%); R_f = 0.35 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +36.9 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.67 (m, 4H), 7.55−7.32 (m, 8H), 5.61 (s, 1H), 4.95 (d, *J* = 12.1 Hz, 1H), 4.87 (d, *J* = 13.0 Hz, 1H), 4.70 (s, 1H), 4.32−4.22 (m, 1H), 4.12 (t, *J* = 9.3 Hz, 1H), 4.02 (d, *J* = 2.0 Hz, 1H), 3.99−3.89 (m, 1H), 3.90−3.74 (m, 2H), 3.30 (s, 3H), 2.94 (brs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 135.4, 133.3, 133.1, 129.0, 128.3, 128.0, 127.7, 126.6, 126.2, 126.0, 125.8, 101.7, 101.1, 78.8, 75.6, 72.9, 69.8, 68.9, 63.3, 54.9; HRMS-MALDI (*m*/*z*) calcd for $C_{25}H_{26}O_6$ $[M + Na]^+$ 445.1622, found 445.1635.

*Methyl-6-O-(tert-butyldimethylsilyl)-3-O-benzyl-α-D-mannopyranoside(**2e**).*[4f] Methyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside **1b**[17] (100 mg, 0.324 mmol), benzyl bromide (58 μL, 0.487 mmol), dimethyltin dichloride (7.1 mg, 10 mol %) and Ag_2O (82.5 mg, 0.357 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (109 mg, 85%); R_f = 0.40 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +34.6 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.29 (m, 5H), 4.73 (s, 1H), 4.69 (d, *J* = 8.9 Hz, 2H), 3.97 (s, 1H), 3.89 (t, *J* = 7.3 Hz, 3H), 3.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.60 (dd, *J* = 9.8, 2.1 Hz, 1H), 3.36 (s, 3H), 0.91 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 128.6, 128.5, 128.0, 127.9, 127.5, 126.9, 100.4, 79.5, 72.1, 71.1, 68.8, 67.8, 65.1, 64.5, 54.8, 25.9, 18.3, −5.4; MALDI TOF MS calcd for $C_{20}H_{34}O_6Si$ $[M + Na]^+$ 421.2017, found 421.2021.

*Methyl-6-O-(tert-butyldimethylsilyl)-3-O-allyl-α-D-mannopyranoside (**2f**).* Methyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside **1b** (100 mg, 0.324 mmol), allyl bromide (42.0 μL, 0.487 mmol), dimethyltin dichloride (7.1 mg, 10 mol %) and Ag_2O (82.5 mg, 0.357 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (91 mg, 81%); R_f = 0.40 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +33.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99−5.90 (m, 1H), 5.31 (d, *J* = 17.2 Hz, 1H), 5.21 (d, *J* = 10.3 Hz, 1H), 4.73 (s, 1H), 4.02−4.28 (m, *J* = 12.3 Hz, 2H), 3.96 (s, 1H), 3.92−3.77 (m, 3H), 3.64−3.54 (m, 2H), 3.36 (s, 3H), 0.89 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 117.8, 100.4, 78.9, 70.8, 70.8, 68.9, 67.7, 64.7, 54.8, 25.8, 18.2, −5.5; HRMS-MALDI (*m*/*z*) calcd for $C_{16}H_{32}O_6Si$ $[M + Na]^+$ 371.1860, found 371.1842.

*Methyl-6-O-(tert-butyldimethylsilyl)-3-O-(p-methoxybenzyl)-α-D-Mannopyranoside (**2g**).* Methyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside **1b** (100 mg, 0.324 mmol), *p*-methoxybenzyl chloride (66.0 μL, 0.487 mmol), dimethyltin dichloride (7.1 mg, 10 mol %) and Ag_2O (82.5 mg, 0.357 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (120 mg, 87%); R_f = 0.38 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +19.8 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 6.1 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 4.74 (s, 1H), 4.63 (d, *J* = 5.0 Hz, 2H), 3.95 (d, *J* = 1.3 Hz, 1H), 3.88 (d, *J* = 5.2 Hz, 3H), 3.80 (d, *J* = 12.2 Hz, 3H), 3.64 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.60 (dd, *J* = 9.9, 5.1 Hz, 1H), 3.37 (s, 3H), 0.91 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 130.1, 129.6, 128.6, 114.0, 100.4, 79.1, 71.7, 70.9, 68.9, 67.8, 64.6, 55.2, 54.8, 25.9, 18.3, −5.4; HRMS-MALDI (*m*/*z*) calcd for $C_{21}H_{36}O_7Si$ $[M + Na]^+$ 451.2123, found 451.2124.

*Methyl-6-O-(tert-butyldimethylsilyl)-3-O-(2-methylnaphthalenyl)-α-D-mannopyranoside (**2h**).*[4f] Methyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside **1b** (100 mg, 0.324 mmol), 2-(bromomethyl)naphthalene (107.5 mg, 0.487 mmol), dimethyltin dichloride (7.1 mg, 10 mol %) and Ag_2O (82.5 mg, 0.357 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (114 mg, 79%); R_f = 0.40 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +31.9 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 12.2 Hz, 4H), 7.47 (dd, *J* = 11.5, 7.0 Hz, 3H), 4.85 (s, 2H), 4.72 (s, 1H), 3.99 (d, *J* = 1.3 Hz, 1H), 3.95−3.83 (m, 3H), 3.73 (dd, *J* = 8.9, 2.1 Hz, 1H), 3.64−3.54 (m, 1H), 3.34 (s, 3H), 0.90 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4, 133.3, 133.1, 128.4, 127.9, 127.7, 126.8, 126.2, 126.1, 125.7, 100.4, 79.4, 72.2, 70.9, 69.2, 67.9, 64.7, 54.8, 25.9, 18.3, −5.4; HRMS-MALDI (*m*/*z*) calcd for $C_{24}H_{36}O_6Si$ $[M + Na]^+$ 471.2173, found 471.2154.

*Methyl-3-O-benzyl-α-D-rhamnopyranoside (**2i**).*[4f] Methyl-α-D-rhamnopyranoside **1c**[18] (100 mg, 0.561 mmol), benzyl bromide (102.0 μL, 0.843 mmol), dimethyltin dichloride (12.3 mg, 10 mol %) and Ag_2O (142.7 mg, 0.618 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (146.0 mg, 97%); R_f = 0.37 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +15.8 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 5H), 4.73 (d, *J* = 8.8 Hz, 2H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.03 (d, *J* = 0.9 Hz, 1H), 3.74−3.53 (m, 3H), 3.38 (s, 3H), 1.34 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 128.7,

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128.2, 128.0, 100.4, 79.8, 71.7, 71.5, 67.8, 67.7, 54.8, 17.6; HRMS (m/z) calcd for $C_{14}H_{21}O_5$ $[M + H]^+$ 269.1384, found 269.1375.

*Methyl-3-O-allyl-α-D-rhamnopyranoside (**2j**).* Methyl-α-D-rhamnopyranoside **1c** (100 mg, 0.561 mmol), allyl bromide (72.0 μL, 0.843 mmol), dimethyltin dichloride (12.3 mg, 10 mol %) and Ag_2O (142.7 mg, 0.618 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (117 mg, 96%); R_f = 0.55 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +41.6 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07−5.82 (m, 1H), 5.35 (d, J = 11.2 Hz, 1H), 5.24 (d, J = 10.1 Hz, 1H), 4.72 (s, 1H), 4.20 (dd, J = 12.5, 5.5 Hz, 1H), 4.08 (dd, J = 11.9, 5.6 Hz, 1H), 4.01 (s, 1H), 3.73−3.61 (m, 1H), 3.56 (dd, J = 15.0, 5.6 Hz, 2H), 3.39 (s, 3H), 1.34 (d, J = 5.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 118.0, 100.4, 79.37, 71.3, 70.6, 67.8, 67.7, 54.8, 17.6; HRMS (m/z) calcd for $C_{10}H_{19}O_5$ $[M + H]^+$ 219.1227, found 219.1231.

*Methyl-3-O-(p-methoxybenzyl)-α-D-rhamnopyranoside (**2k**).*[19] Methyl-α-D-rhamnopyranoside **1c** (100 mg, 0.561 mmol), *p*-methyoxybenzyl chloride (111.3 μL, 0.843 mmol), dimethyltin dichloride (12.3 mg, 10 mol %) and Ag_2O (142.7 mg, 0.618 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (164.0 mg, 98%); R_f = 0.55 (hexane/EtOAc, 30:70); $[\alpha]_D$ = +11.8 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 4.72 (s, 1H), 4.65 (d, J = 11.3 Hz, 1H), 4.53 (d, J = 14.4 Hz, 1H), 4.01 (s, 1H), 3.81 (s, 3H), 3.70−3.59 (m, 2H), 3.54 (t, J = 9.2 Hz, 1H), 3.38 (s, 3H), 1.33 (d, J = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 129.8, 129.6, 114.1, 100.4, 79.5, 71.5, 71.3, 67.7, 67.6, 55.3, 54.8, 17.6; HRMS m/z calcd for $C_{15}H_{23}O_6$ $[M + H]^+$ 299.1489, found 299.1513.

*Methyl-3-O-(2-methylnaphthalenyl)-α-D-rhamnopyranoside (**2l**).*[4f] Methyl-α-D-rhamnopyranoside **1c** (100 mg, 0.561 mmol), 2-(bromomethyl)naphthalene (186 mg, 0.843 mmol), dimethyltin dichloride (12.3 mg, 10 mol %) and Ag_2O (142.7 mg, 0.618 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (175.0 mg, 98%); R_f = 0.57 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +17.3 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.70 (m, 4H), 7.45−7.37 (m, 3H), 4.76 (d, J = 11.7 Hz, 1H), 4.69−4.58 (m, 2H), 3.96 (s, 1H), 3.64−3.44 (m, 3H), 3.26 (s, 3H), 1.23 (d, J = 5.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 133.3, 133.1, 128.6, 127.9, 127.8, 126.9, 126.4, 126.2, 125.7, 100.4, 79.8, 71.8, 71.6, 67.8, 67.7, 54.8, 17.7; HRMS (m/z) calcd for $C_{18}H_{23}O_5$ $[M + H]^+$ 319.1540, found 319.1561.

*Methyl-6-O-benzoyl-3-O-benzyl-α-D-mannopyranoside (**2m**).* Methyl-6-*O*-benzoyl-α-D-mannopyranoside **1d** (100 mg, 0.336 mmol), benzyl bromide (41 μL, 0.336 mmol), dimethyltin dichloride (7.3 mg, 10 mol %) and Ag_2O (155.1 mg, 0.671 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 60:40) afforded the title compound as a colorless oil (96.3 mg, 74%); R_f = 0.52 (hexane/EtOAc, 50:50); $[\alpha]_D$ = +26.8 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13−8.01 (m, 2H), 7.53 (t, J = 10.6 Hz, 1H), 7.47−7.28 (m, 7H), 4.78 (s, 1H), 4.69 (d, J = 11.5 Hz, 1H), 4.67−4.60 (m, 2H), 4.57 (d, J = 12.1 Hz, 1H), 4.04−4.00 (m, 1H), 3.90−3.83 (m, 2H), 3.75−3.67 (m, 1H), 3.38 (s, 3H), 2.98 (brs, 1H), 2.66 (brs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 137.7, 133.2, 129.8, 128.7, 128.4, 128.2, 128.0, 100.5, 79.5, 72.1, 70.2, 67.8, 66.4, 64.2, 54.1; HRMS-MALDI (m/z) calcd for $C_{21}H_{24}O_7$ $[M + Na]^+$ 411.1414, found 411.1429.

*Methyl-6-O-benzoyl-3-O-Allyl-α-D-mannopyranoside (**2n**).* Methyl-6-*O*-benzoyl-α-D-mannopyranoside **1d** (100 mg, 0.336 mmol), allyl bromide (28 μL, 0.336 mmol), dimethyltin dichloride (7.3 mg, 10 mol %) and Ag_2O (155.1 mg, 0.671 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 60:40) afforded the title compound as a colorless syrup (91.8 mg, 81%); R_f = 0.52 (hexane/EtOAc, 50:50); $[\alpha]_D$ = +51.0 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.7 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 6.0−5.9 (m, 1H), 5.33 (d, J = 17.1 Hz, 1H), 5.23 (d, J = 10.4 Hz, 1H), 4.81 (s, 1H), 4.68 (dd, J = 12.0, 4.6 Hz, 1H), 4.58 (d, J = 12.2 Hz, 1H), 4.20 (dd, J = 12.5, 5.6 Hz, 1H), 4.12 (dd, J = 12.5, 5.8 Hz, 1H), 4.03 (s, 1H), 3.92−3.82 (m, 2H), 3.63 (dd, J = 8.2, 3.0 Hz, 1H), 3.40 (s, 3H), 2.95 (s, 1H), 2.53 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 134.2, 133.4, 133.2, 129.9, 129.8, 128.4, 118.2, 100.5, 79.0, 70.9, 70.2, 67.8, 66.4, 64.1, 55.0; HRMS-MALDI (m/z) calcd for $C_{17}H_{22}O_7$ $[M + Na]^+$ 361.1258, found 361.1275.

*Methyl-6-O-benzoyl-3-O-(2-methylnaphthalenyl)-α-D-mannopyranoside (**2o**).* Methyl-6-*O*-benzoyl-α-D-mannopyranoside **1d** (100 mg, 0.336 mmol), 2-(bromomethyl)naphthalene (74 mg, 0.336 mmol), dimethyltin dichloride (7.3 mg, 10 mol %) and Ag_2O (155.1 mg, 0.671 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 60:40) afforded the title compound as a colorless syrup (102.6 mg, 70%); R_f = 0.52 (hexane/EtOAc, 50:50); $[\alpha]_D$ = +30.8 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.2 Hz, 2H), 7.85−7.81 (m, 4H), 7.54 (t, J = 7.4 Hz, 1H), 7.52−7.34 (m, 5H), 4.87 (d, J = 11.7 Hz, 1H), 4.80 (d, J = 9.3 Hz, 2H), 4.68 (dd, J = 12.0, 4.6 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.06 (s, 1H), 3.97−3.81 (m, 2H), 3.76 (dd, J = 8.4, 2.8 Hz, 1H), 3.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 135.1, 133.2, 133.2, 133.1, 129.8, 128.6, 128.4, 128.0, 127.8, 126.9, 126.4, 126.2, 125.7, 100.5, 79.4, 72.2, 70.9, 67.9, 66.5, 64.1, 55.0; HRMS-MALDI (m/z) calcd for $C_{25}H_{26}O_7$ $[M + Na]^+$ 461.1571, found 461.1585.

*Methyl-6-azido-6-deoxy-3-O-benzyl-α-D-mannopyranoside (**2p**).* Methyl-6-azido-6-deoxy-α-D-mannopyranoside **1e**[20] (200 mg, 0.913 mmol), benzyl bromide (162 μL, 1.37 mmol), dimethyltin dichloride (20 mg, 10 mol %) and Ag_2O (232.1 mg, 1.00 mmol) were stirred in acetonitrile (4 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless syrup (240.7 mg, 85%); R_f = 0.55 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +5.6 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.29 (m, 5H), 4.77 (d, J = 12.0 Hz, 1H), 4.64 (d, J = 11.3 Hz, 1H), 4.54 (d, J = 11.5 Hz, 1H), 3.99 (s, 1H), 3.80−3.67 (m, 2H), 3.62 (dd, J = 8.7, 3.1 Hz, 1H), 3.51−3.43 (m, 2H), 3.37 (d, J = 10.1 Hz, 3H), 2.64 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5, 128.8, 128.6, 128.4, 128.1, 100.4, 79.6, 71.8, 71.3, 67.5, 67.0, 55.1, 51.5; HRMS-MALDI (m/z) calcd for $C_{14}H_{19}N_3O_5$ $[M + Na]^+$ 332.1217, found 332.1212.

*Methyl-6-azido-6-deoxy-3-O-allyl-α-D-mannopyranoside (**2q**).* Methyl-6-azido-6-deoxy-α-D-mannopyranoside **1e** (200 mg, 0.913 mmol), allyl bromide (115 μL, 1.37 mmol), dimethyltin dichloride (20 mg, 10 mol %) and Ag_2O (232.1 mg, 1.00 mmol) were stirred in acetonitrile (4 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless syrup (215.2 mg, 91%); R_f = 0.48 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +26.6 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98−5.90 (m, 1H), 5.34 (dd, J = 17.2, 1.1 Hz, 1H), 5.26 (d, J = 10.3 Hz, 1H), 4.79 (s, 1H), 4.20 (dd, J = 12.5, 5.7 Hz, 1H), 4.11−4.04 (m, 1H), 4.02 (s, 1H), 3.82−3.72 (m, 2H), 3.57 (dd, J = 8.6, 3.0 Hz, 1H), 3.55−3.49 (m, 2H), 3.42 (s, 3H), 2.75 (s, 1H), 2.68 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.0, 118.4, 100.4, 79.3, 71.2, 70.6, 67.5, 67.0, 55.2, 51.5; HRMS (m/z) calcd for $C_{10}H_{18}N_3O_5$ $[M + H]^+$ 260.1241, found 260.1249.

*Methyl-6-azido-6-deoxy-3-O-(p-methoxybenzyl)-α-D-mannopyranoside (**2r**).* Methyl-6-azido-6-deoxy-α-D-mannopyranoside **1e** (200 mg, 0.913 mmol), *p*-methoxybenzyl chloride (185 μL, 1.37 mmol), dimethyltin dichloride (20 mg, 10 mol %) and Ag_2O (232.1 mg, 1.00 mmol) were stirred in acetonitrile (4 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless syrup (216.7 mg, 70%); R_f = 0.54 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +2.3 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 4.76 (d, J = 1.1 Hz, 1H), 4.62 (d, J = 11.3 Hz, 1H), 4.48 (d, J = 11.3 Hz, 1H), 3.98 (d, J = 1.2 Hz, 1H), 3.81 (s, 3H), 3.72 (t, J = 10.4 Hz, 2H), 3.61 (dd, J = 8.7, 3.0 Hz, 1H),

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3.54−3.44 (m, 2H), 3.40 (s, 3H), 2.57 (s, 1H), 2.49 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 129.7, 129.5, 114.1, 100.4, 79.3, 71.4, 71.2, 67.5, 67.0, 55.3, 55.1, 51.5; HRMS-MALDI (m/z) calcd for $C_{15}H_{21}N_3O_6$ [M + Na]$^+$ 362.1323, found 362.1335.

*Methyl-6-azido-6-deoxy-3-O-(2-methylnaphthalenyl)-α-D-mannopyranoside (**2s**).* Methyl-6-azido-6-deoxy-α-D-mannopyranoside **1e** (200 mg, 0.913 mmol), 2-(bromomethyl)naphthalene (302 mg, 1.37 mmol), dimethyltin dichloride (20 mg, 10 mol %) and Ag_2O (232.1 mg, 1.00 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless syrup (278.0 mg, 84%); R_f = 0.55 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +8.2 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.74 (m, 4H), 7.51−7.41 (m, 3H), 4.80 (d, J = 11.8 Hz, 1H), 4.74 (d, J = 0.7 Hz, 1H), 4.66 (d, J = 11.7 Hz, 1H), 4.00 (d, J = 1.2 Hz, 1H), 3.78 (t, J = 9.4 Hz, 1H), 3.73−3.62 (m, 2H), 3.51−3.43 (m, 2H), 3.35 (s, 3H), 2.69 (brs, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.9, 133.2, 133.1, 128.7, 128.0, 127.8, 127.0, 126.5, 126.3, 125.6, 100.5, 79.6, 71.9, 71.3, 67.6, 67.1, 55.1, 51.5; HRMS-MALDI (m/z) calcd for $C_{18}H_{21}N_3O_5$ [M + Na]$^+$ 382.1373, found 382.1395.

*Phenyl-2,3,6-tri-O-benzyl-1-thio-β-D-galactopyranoside (**2t**).*[21] Phenyl-2,6-di-*O*-benzyl-1-thio-β-D-galactopyranoside **1f**[22] (120 mg, 0.265 mmol), benzyl bromide (48 μL, 0.398 mmol), dimethyltin dichloride (5.8 mg, 10 mol %) and Ag_2O (67.4 mg, 0.292 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (128.0 mg, 89%); R_f = 0.35 (hexane/EtOAc, 70:30); $[\alpha]_D$ = −4.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 5.4 Hz, 2H), 7.30−6.99 (m, 18H), 4.65 (d, J = 10.3 Hz, 1H), 4.57 (d, J = 10.1 Hz, 1H), 4.52 (d, J = 6.0 Hz, 1H), 4.47 (d, J = 11.0 Hz, 2H), 4.39 (s, 2H), 3.92 (d, J = 2.2 Hz, 1H), 3.67−3.55 (m, 3H), 3.46−3.35 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 138.0, 137.7, 134.0, 131.8, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.85, 127.82, 127.4, 87.8, 82.6, 77.1, 77.1, 75.8, 73.8, 72.2, 69.5, 67.0; HRMS-MALDI (m/z) calcd for $C_{33}H_{34}O_5S$ [M + Na]$^+$ 565.2019, found 565.2005.

*Phenyl-3-O-allyl-2,6-di-O-benzyl-1-thio-β-D-galactopyranoside (**2u**).* Phenyl-2,6-di-*O*-benzyl-1-thio-β-D-galactopyranoside **1f** (120 mg, 0.265 mmol), allyl bromide (33 μL, 0.398 mmol), dimethyltin dichloride (5.8 mg, 10 mol %) and Ag_2O (67.4 mg, 0.292 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (118.0 mg, 91%); R_f = 0.35 (hexane/EtOAc, 70:30); $[\alpha]_D$ = −9.2 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.46 (m, 2H), 7.35 (d, J = 7.3 Hz, 2H) 7.29−7.13 (m, 12H), 5.89−5.80 (m, 1H), 5.23 (d, J = 17.2 Hz, 1H), 5.12 (d, J = 10.4 Hz, 1H), 4.73 (d, J = 10.3 Hz, 1H), 4.65 (d, J = 10.2 Hz, 1H), 4.56 (d, J = 9.8 Hz, 1H), 4.50 (s, 2H), 4.16−4.06 (m, 2H), 4.03 (d, J = 2.8 Hz, 1H), 3.77−3.67 (m, 2H), 3.63 (t, J = 9.4 Hz, 1H), 3.54 (t, J = 5.7 Hz, 1H), 3.41 (dd, J = 8.9, 3.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.9, 134.4, 134.0, 131.8, 129.0, 128.4, 128.39, 128.3, 127.8, 127.8, 127.4, 117.7, 87.7, 82.4, 77.0, 75.8, 73.8, 71.2, 69.5, 67.1; HRMS-MALDI (m/z) calcd for $C_{29}H_{32}O_5S$ [M + Na]$^+$ 515.1863, found 515.1877.

*Phenyl-3-O-(2-methylnaphthalenyl)-2,6-di-O-benzyl-1-thio-β-D-galactopyranoside (**2v**).* Phenyl-2,6-di-*O*-benzyl-1-thio-β-D-galactopyranoside **1f** (120 mg, 0.265 mmol), 2-(bromomethyl)naphthalene (88 mg, 0.398 mmol), dimethyltin dichloride (5.8 mg, 10 mol %) and Ag_2O (67.4 mg, 0.292 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (144.6 mg, 92%); R_f = 0.36 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +7.6 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.75 (m, 4H), 7.62 (dd, J = 5.0, 1.8 Hz, 2H), 7.55−7.43 (m, 5H), 7.40−7.23 (m, 11H), 4.98−4.79 (m, 4H), 4.69 (d, J = 9.7 Hz, 1H), 4.60 (s, 2H), 4.18 (s, 1H), 3.83 (t, J = 4.9 Hz, 3H), 3.72−3.58 (m, 2H), 2.67 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 138.0, 135.1, 134.0, 133.3, 133.1, 131.8, 128.9, 128.5, 128.4, 128.3, 127.9, 127.9, 127.8, 127.7, 127.4, 126.8, 126.3, 126.1, 125.8, 87.8, 82.5, 77.1, 75.8, 73.8, 72.2, 69.5, 67.1; MALDI TOF MS calcd for $C_{37}H_{36}O_5S$ [M + Na]$^+$ 615.2176, found 615.2190.

*Phenyl-6-O-(tert-butyldimethylsilyl)-3-O-benzyl-1-thio-β-D-galactopyranoside (**2w**).*[7b] Phenyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside **1g**[17] (120 mg, 0.311 mmol), benzyl bromide (55 μL, 0.466 mmol), dimethyltin dichloride (6.8 mg, 10 mol %) and Ag_2O (78.4 mg, 0.342 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc,70:30) afforded the title compound as a colorless oil (124.3 mg, 84%); R_f = 0.35 (hexane/EtOAc, 70:30); $[\alpha]_D$ = −32.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 4.9 Hz, 2H), 7.46−7.19 (m, 8H), 4.82−4.67 (m, 2H), 4.51 (d, J = 9.7 Hz, 1H), 4.07 (s, 1H), 3.99−3.74 (m, 3H), 3.53−3.34 (m, 2H), 2.62 (brs, 1H), 2.47 (brs, 1H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 132.5, 132.3, 128.9, 128.6, 128.1, 127.9, 127.8, 88.7, 81.7, 78.6, 72.1, 69.0, 66.6, 62.7, 25.9, 18.3, −5.3, −5.4; HRMS-MALDI (m/z) calcd for $C_{25}H_{36}O_5Ssi$ [M + Na]$^+$ 499.1945, found 499.1943.

*Phenyl-6-O-(tert-butyldimethylsilyl)-3-O-allyl-1-thio-β-D-galactopyranoside (**2x**).* Phenyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside **1g** (120 mg, 0.311 mmol), allyl bromide (40 μL, 0.466 mmol), dimethyltin dichloride (6.8 mg, 10 mol %) and Ag_2O (78.4 mg, 0.342 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (109.0 mg, 81%); R_f = 0.35 (hexane/EtOAc, 70:30); $[\alpha]_D$ = −3.3 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.49 (m, 2H), 7.28 (t, J = 6.0 Hz, 3H), 6.03−5.90 (m, 1H), 5.32 (d, J = 16.1 Hz, 1H), 5.22 (d, J = 10.3 Hz, 1H), 4.53 (d, J = 9.7 Hz, 1H), 4.29−4.15 (m, 2H), 4.12 (d, J = 2.4 Hz, 1H), 3.96−3.86 (m, 2H), 3.79 (t, J = 9.3 Hz, 1H), 3.51 (t, J = 5.5 Hz, 1H), 3.39 (dd, J = 8.9, 2.9 Hz, 1H), 2.65 (brs, 1H), 2.48 (brs, 1H), 0.91 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 132.4, 128.9, 127.8, 117.9, 88.7, 81.5, 78.5, 70.9, 68.7, 66.5, 62.8, 25.9, 18.3, −5.4, −5.5; HRMS-MALDI (m/z) calcd for $C_{21}H_{34}O_5SSi$ [M + Na]$^+$ 449.1788, found 449.1770.

*Phenyl-6-O-(tert-butyldimethylsilyl)-3-O-(p-methoxybenzyl)-1-thio-β-D-galactopyranoside (**2y**).* Phenyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside **1g** (120 mg, 0.311 mmol), *p*-methoxybenzyl chloride (61 μL, 0.466 mmol), dimethyltin dichloride (6.8 mg, 10 mol %) and Ag_2O (78.4 mg, 0.342 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (122.0 mg, 78%); R_f = 0.35 (hexane/EtOAc, 70:30); $[\alpha]_D$ = −11.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.49 (m, 2H), 7.36−7.21 (m, 5H), 6.86 (t, J = 12.5 Hz, 2H), 4.74−4.61 (m, 2H), 4.52 (d, J = 8.7 Hz, 1H), 4.06 (d, J = 2.4 Hz, 1H), 3.94−3.85 (m, 2H), 3.84−3.76 (m, 4H), 3.47 (t, J = 5.6 Hz, 1H), 3.41 (dd, J = 8.9, 2.9 Hz, 1H), 2.61 (brs, 1H), 2.46 (brs, 1H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 132.3, 129.8, 129.6, 128.9, 127.8, 114.0, 88.8, 81.4, 78.6, 71.7, 68.8, 66.6, 62.6, 55.3, 25.9, 18.3, −5.4, −5.5; HRMS-MALDI (m/z) calcd for $C_{26}H_{38}O_6SSi$ [M + Na]$^+$ 529.2015, found 529.2015.

*Phenyl-6-O-(tert-butyldimethylsilyl)-3-O-(2-methylnaphthalenyl)-1-thio-β-D-galactopyranoside (**2z**).* Phenyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside **1g** (120 mg, 0.311 mmol), 2-(bromomethyl)naphthalene (103 mg, 0.466 mmol), dimethyltin dichloride (6.8 mg, 10 mol %) and Ag_2O (78.4 mg, 0.342 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (145.0 mg, 89%); R_f = 0.35 (hexane/EtOAc, 70:30); $[\alpha]_D$ = −32.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.78 (m, 4H), 7.55−7.46 (m, 5H), 7.28 (d, J = 5.2 Hz, 3H), 4.97−4.87 (m, 2H), 4.50 (d, J = 9.6 Hz, 1H), 4.10 (s, 1H), 3.92−3.82 (m, 3H), 3.51−3.42 (m, 2H), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2 133.2, 133.1, 132.5, 132.4, 128.9, 128.5, 127.9, 127.8, 127.8, 126.9, 126.3, 126.1, 125.7, 88.7, 81.6, 78.5, 72.2, 69.0, 66.8, 62.7, 25.9,

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18.3, −5.4, −5.5; HRMS-MALDI (m/z) calcd for $C_{29}H_{38}O_5SSi$ [M + Na]$^+$ 549.2101, found 549.2105.

*3,6-Di-O-(benzyl)-D-galactal (**2a′**).*[4f] D-Galactal (45 mg, 0.308 mmol), benzyl bromide **1h** (76 μL, 0.647 mmol), dimethyltin dichloride (6.7 mg, 10 mol %) and Ag_2O (149.0 mg, 0.647 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 90:10) afforded the title compound as a colorless oil (80.4 mg, 80%); $[\alpha]_D$ = +10.5 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.25 (m, 10H), 6.42 (d, J = 4.8 Hz, 1H), 4.79 (d, J = 5.2 Hz, 1H), 4.63−4.54 (m, 4H), 4.20−4.16 (m, 1H), 4.07 (d, J = 4.1 Hz, 1H), 4.00 (t, J = 6.1 Hz, 1H), 3.81−3.74 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 136.7, 136.6, 127.5, 127.4, 127.0, 126.9, 126.8, 98.4, 74.3, 72.6, 69.6, 69.4, 68.2, 61.9; HRMS-MALDI (m/z) calcd for $C_{20}H_{22}O_4$ [M + Na]$^+$ 349.1410, found 349.1431.

*Phenyl-4,6-O-benzylidene-3-O-benzyl-1-thio-β-D-galactopyranoside (**2b′**).*[6a,23] Phenyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside **1i**[24] (100 mg, 0.277 mmol), benzyl bromide (50 μL, 0.417 mmol), dimethyltin dichloride (6.0 mg, 10 mol %) and Ag_2O (70 mg, 0.306 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (51.7 mg, 42%); R_f = 0.32 (hexane/EtOAc, 70:30); R_f = 0.32 (hexane/EtOAc, 30:70); $[\alpha]_D$ = +15.6 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.3 Hz, 2H), 7.38−7.09 (m, 13H), 5.35 (s, 1H), 4.71−4.58 (m, 2H), 4.44 (d, J = 9.4 Hz, 1H), 4.27 (d, J = 12.3 Hz, 1H), 4.06 (d, J = 2.1 Hz, 1H), 3.90−3.84 (m, 2H), 3.43 (dd, J = 9.1, 2.7 Hz, 1H), 3.36 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 137.9, 133.7, 129.1, 128.9, 128.5, 128.1, 128.0, 127.9, 126.5, 101.1, 87.1, 80.3, 73.3, 71.7, 70.1, 69.4, 67.2; HRMS-MALDI (m/z) calcd for $C_{26}H_{26}O_5S$ [M + Na]$^+$ 473.1393, found 473.1376.

*Phenyl-6,6′-di-O-(tert-butyldimethylsilyl)-3′-O-benzyl-1-S-β-D-lactoside (**4a**).* Phenyl-6,6′-di-*O*-(*tert*-butyldimethylsilyl)-1-*S*-α-D-Lactoside **3a** (200 mg, 0.301 mmol), benzyl bromide (55 μL, 0.452 mmol), dimethyltin dichloride (6.6 mg, 10 mol %) and Ag_2O (76.6 mg, 0.332 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (140.8 mg, 62%); $[\alpha]_D$ = +4.3 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 4.1 Hz, 2H), 7.43−7.26 (m, 8H), 4.76 (s, 2H), 4.52 (d, J = 9.7 Hz, 1H), 4.34 (d, J = 7.8 Hz, 1H), 4.04−3.91 (m, 3H), 3.91−3.78 (m, 3H), 3.66 (t, J = 8.7 Hz, 1H), 3.56 (t, J = 9.2 Hz, 1H), 3.52−3.46 (m, 1H), 3.45−3.31 (m, 3H), 2.95 (brs, 1H), 2.67 (brs, 1H), 2.57 (brs, 1H), 0.93 (s, 9H), 0.89 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.07 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 133.1, 131.9, 128.8, 128.6, 128.1, 128.0, 127.9, 103.9, 87.1, 80.5, 80.2, 78.9, 76.2, 75.1, 72.2, 71.6, 70.7, 65.9, 62.6, 61.6, 25.9, 25.9, 18.3, 18.3, −5.1, −5.2, −5.4, −5.4; HRMS-MALDI (m/z) calcd for $C_{37}H_{60}O_{10}SSi_2$ [M + Na]$^+$ 775.3338, found 775.3337.

*6-O-Allyl-1,3,4,5-tetra-O-benzyl-L-myo-inositol (**6a**).* 6-*O*-Allyl-3,4,5-tri-*O*-benzyl-L-*myo*-inositol **5a**[25] (200 mg, 0.408 mmol), benzyl bromide (72 μL, 0.612 mmol), dimethyltin dichloride (8.9 mg, 10 mol %) and Ag_2O (103 mg, 0.449 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (222.5 mg, 94%); $[\alpha]_D$ = +9.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.24 (m, 20H), 6.03−5.93 (m, 1H), 5.27 (dd, J = 17.2, 1.4 Hz, 1H), 5.15 (d, J = 10.4 Hz, 1H), 4.91−4.80 (m, 4H), 4.70 (d, J = 5.7 Hz, 4H), 4.36 (qd, J = 12.2, 5.7 Hz, 2H), 4.19 (s, 1H), 3.95 (t, J = 9.5 Hz, 1H), 3.85 (t, J = 9.5 Hz, 1H), 3.44−3.28 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.7, 138.1, 138.0, 135.3, 128.5, 128.4, 128.0, 127.9, 127.8, 127.6, 127.5, 116.6, 83.2, 81.1, 80.9, 79.8, 79.6, 76.0, 75.9, 74.6, 72.8, 72.7, 67.7; MALDI TOF MS calcd for $C_{37}H_{40}O_6$ [M + Na]$^+$ 603.2717, found 603.2714.

*1,6-Di-O-allyl-3,4,5-tri-O-benzyl-L-myo-inositol (**6b**).* 6-*O*-Allyl-3,4,5-tri-*O*-benzyl-L-*myo*-inositol **5a** (200 mg, 0.408 mmol), allyl bromide (53 μL, 0.612 mmol), dimethyltin dichloride (8.9 mg, 10 mol %) and Ag_2O (103 mg, 0.379 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (181.7 mg, 84%); $[\alpha]_D$ = +15.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.12 (m, 15H), 5.99−5.77 (m, 2H), 5.31−5.16 (m, 2H), 5.15−5.03 (m, 2H), 4.85−4.72 (m, 4H), 4.64 (d, J = 12.1 Hz, 2H), 4.32−4.18 (m, 2H), 4.15−4.08 (m, 3H), 3.87 (t, J = 9.5 Hz, 1H), 3.72 (t, J = 9.5 Hz, 1H), 3.36−3.28 (m, 2H), 3.16 (dd, J = 9.6, 2.7 Hz, 1H), 2.38 (brs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.0, 135.3, 134.7, 129.8, 129.0, 128.5, 128.3, 128.0, 127.9, 127.8, 127.6, 117.3, 116.6, 83.1, 81.1, 80.8, 79.9, 79.4, 75.9, 74.6, 72.8, 71.9, 67.8; HRMS-MALDI (m/z) calcd for $C_{33}H_{38}O_6$ [M + Na]$^+$ 553.2561, found 553.2565.

*6-O-Allyl-3,4,5-tri-O-benzyl-1-O-(p-methoxybenzyl)-L-myo-inositol (**6c**).*[25] 6-*O*-Allyl-3,4,5-tri-*O*-benzyl-L-*myo*-inositol **5a** (200 mg, 0.408 mmol), *p*-methoxybenzyl chloride (83 μL, 0.612 mmol), dimethyltin dichloride (8.9 mg, 10 mol %) and Ag_2O (103 mg, 0.379 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (219.6 mg, 88%); R_f = 0.32 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +8.6 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.27 (m, 17H), 6.92 (d, J = 8.3 Hz, 2H), 6.08−5.95 (m, 1H), 5.37−5.28 (m, 1H), 5.20 (d, J = 10.3 Hz, 1H), 4.94−4.82 (m, 4H), 4.77−4.59 (m, 4H), 4.39 (qd, J = 12.1, 5.8 Hz, 2H), 4.19 (s, 1H), 3.98 (t, J = 9.5 Hz, 1H), 3.97−3.84 (m, 4H), 3.41 (dd, J = 16.9, 8.2 Hz, 2H), 3.36−3.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 138.9, 138.8, 138.0, 135.41, 130.2, 129.5, 128.5, 128.3, 128.0, 127.9, 127.8, 127.6, 127.5, 116.5, 113.9, 83.2, 81.1, 80.9, 79.8, 79.3, 76.0, 75.9, 74.7, 72.7, 72.5, 67.7, 55.3; HRMS-MALDI (m/z) calcd for $C_{38}H_{42}O_7$ [M + Na]$^+$ 633.2823, found 633.2824.

*6-O-Allyl-3,4,5-tri-O-benzyl-1-O-(2-methylnaphthalenyl)-L-myo-inositol (**6d**).* 6-*O*-Allyl-3,4,5-tri-*O*-benzyl-L-*myo*-inositol **5a** (200 mg, 0.408 mmol), 2-(bromomethyl)naphthalene (135 mg, 0.612 mmol), dimethyltin dichloride (8.9 mg, 10 mol %) and Ag_2O (103 mg, 0.379 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (223.7 mg, 87%); R_f = 0.32 (hexane/EtOAc, 70:30); $[\alpha]_D$ = +2.5 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.74 (m, 4H), 7.54−7.43 (m, 3H), 7.29 (dd, J = 21.2, 13.8 Hz, 15 H), 6.07−5.98 (m, 1H), 5.30 (d, J = 18.0 Hz, 1H), 5.18 (d, J = 10.3 Hz, 1H), 4.89−4.81 (m, 6H), 4.68 (s, 2H), 4.43 (dd, J = 12.1, 5.6 Hz, 1H), 4.36 (dd, J = 12.2, 5.6 Hz, 1H), 4.19 (s, 1H), 3.95 (t, J = 9.5 Hz, 1H), 3.88 (t, J = 9.5 Hz, 1H), 3.45−3.33 (m, 3H), 2.51 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.7, 137.9, 135.5, 1354, 133.3, 133.1, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 126.6, 126.2, 126.0, 125.8, 116.6, 83.2, 81.1, 81.0, 79.8, 79.5, 76.0, 75.9, 74.6, 72.9, 72.7, 67.8; HRMS-MALDI (m/z) calcd for $C_{41}H_{42}O_6$ [M + Na]$^+$ 653.2874, found 653.2865.

*1,3,4,5-Tetra-O-benzyl-L-myo-inositol (**6e**).* 3,4,5-Tri-*O*-benzyl-L-*myo*-inositol **5b**[26] (100 mg, 0.222 mmol), benzyl bromide (39 μL, 0.333 mmol), dimethyltin dichloride (4.8 mg, 10 mol %) and Ag_2O (56 mg, 0.244 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (104.4 mg, 87%); R_f = 0.58 (hexane/EtOAc, 50:50); $[\alpha]_D$ = +8.2 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.30 (m, 20H), 4.98 (dd, J = 10.6, 3.7 Hz, 2H), 4.95−4.86 (m, 2H), 4.82−4.70 (m, 4H), 4.28 (s, 1H), 4.15 (t, J = 9.3 Hz, 1H), 4.05 (t, J = 9.2 Hz, 1H), 3.47 (d, J = 9.5 Hz, 1H), 3.40 (dd, J = 23.8, 14.8 Hz, 1H), 3.30 (d, J = 9.5 Hz, 1H), 2.59 (brs, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 138.0, 137.8, 128.7, 128.6, 128.5, 128.5, 128.1, 128.02, 127.99, 127.9, 127.7, 82.9, 80.9, 80.0, 79.2, 75.9, 75.5, 72.7, 72.5, 72.4, 67.1; HRMS-MALDI (m/z) calcd for $C_{34}H_{36}O_6$ [M + Na]$^+$ 563.2404, found 563.2407.

*1-O-Allyl-3,4,5-tri-O-benzyl-L-myo-inositol (**6f**).* 3,4,5-Tri-*O*-benzyl-L-*myo*-inositol **5b** (100 mg, 0.222 mmol), allyl bromide (29 μL, 0.333 mmol), dimethyltin dichloride (4.8 mg, 10 mol %) and Ag_2O (56 mg, 0.244 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the

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title compound as a colorless oil (98.0 mg, 90%); R_f = 0.58 (hexane/EtOAc, 50:50); $[\alpha]_D$ = +11.4 (c 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.51−7.26 (m, 15H), 5.99−5.91 (m, 1H), 5.31 (d, J = 17.2 Hz, 1H), 5.21 (t, J = 13.8 Hz, 1H), 4.95−4.84 (m, 4H), 4.81−4.70 (m, 2H), 4.33−4.19 (m, 2H), 4.18−4.10 (m, 1H), 4.10−3.90 (m, 2H), 3.46 (d, J = 9.5 Hz, 1H), 3.38 (t, J = 9.2 Hz, 1H), 3.19 (d, J = 9.5 Hz, 1H), 2.49 (brs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 137.9, 134.5, 128.5, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 118.0, 82.9, 81.0, 80.0, 78.9, 75.9, 75.5, 72.8, 72.2, 71.3, 66.9; HRMS-MALDI (m/z) calcd for $C_{30}H_{34}O_6$ $[M + Na]^+$ 513.2448, found 513.2453.

1-O-(p-Methoxybenzyl)-3,4,5-tri-O-benzyl-L-myo-inositol (**6g**). 3,4,5-Tri-*O*-benzyl-L-*myo*-inositol **5b** (100 mg, 0.222 mmol), *p*-methoxybenzyl chloride (45 μL, 0.333 mmol), dimethyltin dichloride (4.8 mg, 10 mol %) and Ag_2O (56 mg, 0.244 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (112.7 mg, 89%); R_f = 0.56 (hexane/EtOAc, 50:50); $[\alpha]_D$ = +9.4 (c 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44−7.23 (m, 17H), 6.90 (d, J = 4.8 Hz, 2H), 4.97−4.80 (m, 4H), 4.80−4.58 (m, 4H), 4.23 (s, 1H), 4.06 (t, J = 12.5 Hz, 1H), 3.98 (t, J = 9.4 Hz, 1H), 3.81 (s, 3H), 3.42 (d, J = 9.6 Hz, 1H), 3.35 (dd, J = 12.4, 6.2 Hz, 1H), 3.22 (d, J = 9.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 138.7, 137.9, 129.8, 129.6, 128.5, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 114.0, 82.9, 80.9, 80.0, 78.7, 75.9, 75.5, 72.7, 72.4, 72.0, 67.0, 55.3; HRMS-MALDI (m/z) calcd for $C_{35}H_{38}O_7$ $[M + Na]^+$ 593.2510, found 593.2512.

1-O-(2-Methylnaphthalenyl)-3,4,5-tri-O-benzyl-L-myo-inositol (**6h**). 3,4,5-Tri-*O*-benzyl-L-*myo*-inositol **5b** (100 mg, 0.222 mmol), 2-(bromomethyl)naphthalene (74 mg, 0.333 mmol), dimethyltin dichloride (4.8 mg, 10 mol %) and Ag_2O (56 mg, 0.244 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 70:30) afforded the title compound as a colorless oil (108.8 mg, 83%); R_f = 0.58 (hexane/EtOAc, 50:50); $[\alpha]_D$ = +1.3 (c 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (t, J = 7.1 Hz, 3H), 7.44−7.39 (m, 3H), 7.27−7.16 (m, 16H), 4.86−4.72 (m, 6H), 4.61 (s, 2H), 4.16 (s, 1H), 4.03 (t, J = 9.4 Hz, 1H), 3.90 (t, J = 9.3 Hz, 1H), 3.31 (d, J = 8.9 Hz, 1H), 3.26 (t, J = 9.3 Hz, 1H), 3.20 (d, J = 9.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 137.8, 135.2, 133.2, 133.1, 128.5, 128.4, 128.0, 127.9, 127.9, 127.8, 127.7, 126.8, 126.3, 126.2, 125.8, 82.9, 80.9, 79.9, 78.9, 75.9, 75.5, 72.7, 72.5, 72.5, 67.2; HRMS-MALDI (m/z) calcd for $C_{38}H_{38}O_6$ $[M + Na]^+$ 613.2551, found 613.2556.

1,3,6-Tri-O-benzyl-D/L-myo-inositol (**6i**). 3,6-Di-*O*-benzyl-D/L-*myo*-inositol **5c**[27] (80 mg, 0.222 mmol), benzyl bromide (41 μL, 0.333 mmol), dimethyltin dichloride (4.8 mg, 10 mol %) and Ag_2O (56 mg, 0.244 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 36 h. Column chromatographic purification (hexane/EtOAc, 60:40) afforded the title compound as a colorless oil (60.0 mg, 60%); R_f = 0.29 (hexane/EtOAc, 50:50); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45−7.28 (m, 15H), 4.97 (d, J = 11.2 Hz, 1H), 4.81 (d, J = 11.2 Hz, 1H), 4.75−4.66 (m, 4H), 4.25 (t, J = 2.4 Hz, 1H), 3.99 (t, J = 9.4 Hz, 1H), 3.85 (t, J = 9.4 Hz, 1H), 3.49−3.39 (m, 2H), 3.24 (dd, J = 9.5, 2.5 Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 137.8, 137.7, 128.6, 128.5, 128.5, 128.1, 128.0, 127.97, 127.94, 127.78, 80.5, 79.7, 79.0, 75.5, 74.3, 72.5, 72.3, 71.9, 67.0; HRMS-MALDI (m/z) calcd for $C_{27}H_{30}O_6$ $[M + Na]^+$ 473.1935, found 473.1952.

1-O-Allyl-3,6-di-O-benzyl-D/L-myo-inositol (**6j**). 3,6-Di-*O*-benzyl-D/L-*myo*-inositol **5c** (80 mg, 0.222 mmol), allyl bromide (28 μL, 0.333 mmol), dimethyltin dichloride (4.8 mg, 10 mol %) and Ag_2O (56 mg, 0.244 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 36 h. Column chromatographic purification (hexane/EtOAc, 60:40) afforded the title compound as a colorless oil (62.2 mg, 70%); R_f = 0.29 (hexane/EtOAc, 50:50); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.28 (m, 10H), 5.96−5.87 (m, 1H), 5.29 (d, J = 17.2 Hz, 1H), 5.19 (d, J = 10.4 Hz, 1H), 4.93 (d, J = 11.2 Hz, 1H), 4.71 (dd, J = 23.8, 11.5 Hz, 3H), 4.24 (s, 1H), 4.22−4.08 (m, 2H), 3.95 (t, J = 9.4 Hz, 1H), 3.77 (t, J = 9.4 Hz, 1H), 3.40 (t, J = 9.3 Hz, 1H), 3.31−3.24 (m, 2.2 Hz, 2H), 2.84 (brs, 2H), 2.55 (brs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 137.7, 134.5, 128.6, 128.5, 128.1, 128.1, 128.0, 127.8, 117.7, 80.3, 79.6, 79.1, 75.5, 74.1, 72.3, 71.9, 71.6, 67.01; HRMS-MALDI (m/z) calcd for $C_{23}H_{28}O_6$ $[M + Na]^+$ 423.1778, found 423.1748.

1-O-(p-Methoxybenzyl)-3,6-di-O-benzyl-D/L-myo-inositol (**6k**). 3,6-Di-*O*-benzyl-D/L-*myo*-inositol **5c** (80 mg, 0.222 mmol), *p*-methoxybenzyl chloride (45 μL, 0.333 mmol), dimethyltin dichloride (4.8 mg, 10 mol %) and Ag_2O (56 mg, 0.244 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 36 h. Column chromatographic purification (hexane/EtOAc, 60:40) afforded the title compound as a colorless oil (70.4 mg, 66%); R_f = 0.29 (hexane/EtOAc, 50:50); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.17 (m, 12H), 6.79 (d, J = 8.5 Hz, 2H), 4.87 (d, J = 11.2 Hz, 1H), 4.72−4.52 (m, 5H), 4.13 (s, 1H), 3.88 (t, J = 9.4 Hz, 1H), 3.76−3.70 (m, 4H), 3.32 (t, J = 9.8 Hz, 2H), 3.15 (dd, J = 9.5, 2.2 Hz, 1H), 2.38 (brs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 138.7, 137.7, 129.8, 129.6, 128.6, 128.5, 128.1, 128.0, 127.8, 113.9, 80.4, 79.4, 79.0, 75.5, 74.2, 72.2, 72.1, 71.9, 66.9, 55.3; HRMS-MALDI (m/z) calcd for $C_{28}H_{32}O_7$ $[M + Na]^+$ 503.2040, found 503.2061.

1-O-(2-Methylnaphthalenyl)-3,6-di-O-benzyl-D/L-myo-inositol (**6l**). 3,6-Di-*O*-benzyl-D/L-*myo*-inositol **5c** (80 mg, 0.222 mmol), *p*-methoxybenzyl chloride (73 mg, 0.333 mmol), dimethyltin dichloride (4.8 mg, 10 mol %) and Ag_2O (56 mg, 0.244 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 36 h. Column chromatographic purification (hexane/EtOAc, 60:40) afforded the title compound as a colorless syrup (71.1 mg, 64%); R_f = 0.29 (hexane/EtOAc, 50:50); ^1H NMR (500 MHz, $CDCl_3$) δ 7.88−7.73 (m, 4H), 7.49−7.44 (m, 3H), 7.39−7.26 (m, 10H), 4.98 (d, J = 11.2 Hz, 1H), 4.88−4.78 (m, 3H), 4.65 (dd, J = 32.1, 11.7 Hz, 2H), 4.22 (s, 1H), 3.96 (t, J = 9.4 Hz, 1H), 3.85 (t, J = 9.4 Hz, 1H), 3.41 (dd, J = 16.9, 8.1 Hz, 2H), 3.19 (d, J = 7.8 Hz, 1H), 2.88 (brs, 2H), 2.62 (brs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 137.6, 135.2, 133.2, 133.1, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 126.8, 126.3, 126.1, 125.9, 80.5, 79.6, 79.0, 75.6, 74.2, 72.6, 72.3, 72.0, 67.0; MALDI TOF MS calcd for $C_{31}H_{32}O_6$ $[M + Na]^+$ 523.2091, found 523.2093.

1-O-Benzyl-2-propanol (**8a**).[4i] Propane-1,2-diol **7a** (30 mg, 0.39 mmol), benzyl bromide (70 μL, 0.59 mmol), dimethyltin dichloride (8.6 mg, 10 mol %) and Ag_2O (100.3 mg, 0.43 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 90:10) afforded the title compound as a colorless oil (118.0 mg, 75%); R_f = 0.35 (hexane/EtOAc, 90:10); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44−7.20 (m, 5H), 4.62−4.46 (m, 2H), 4.03−3.87 (m, 1H), 3.49−3.38 (m, 1H), 3.29−3.17 (m, 1H), 1.09 (dd, J = 16.4, 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 128.5, 127.8, 127.8, 75.8, 73.3, 66.5, 18.6; HRMS (m/z) calcd for $C_{10}H_{13}O_2$ $[M-H]^-$ 165.0921, found 165.0922.

cis-2-(Benzyloxy)cyclohexanol (**10a**).[4i] *cis*-1,2-Cyclohexandiol **9a** (30 mg, 0.26 mmol), benzyl bromide (46 μL, 0.39 mmol), dimethyltin dichloride (5.6 mg, 10 mol %) and Ag_2O (65.1 mg, 0.28 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (51.1 mg, 96%); R_f = 0.65 (hexane/EtOAc, 80:20); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.15 (m, 5H), 4.55 (d, J = 11.8 Hz, 1H), 4.44 (d, J = 11.8 Hz, 1H), 3.83−3.75 (m, 1H), 3.48−3.39 (m, 1H), 1.80−1.70 (m, 2H), 1.60−1.40 (m, 4H), 1.29−1.14 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 128.5, 127.7, 127.6, 78.2, 70.2, 68.8, 30.4, 26.5, 22.1, 21.2; HRMS (m/z) calcd for $C_{13}H_{19}O_2$ $[M + H]^+$ 207.1380, found 207.1386.

cis-2-(Benzyloxy)cyclopentanol (**10b**).[4i] *cis*-1,2-Cyclopentanediol **9b** (30 mg, 0.29 mmol), benzyl bromide (52 μL, 0.44 mmol), dimethyltin dichloride (6.4 mg, 10 mol %) and Ag_2O (74.1 mg, 0.32 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (51.3 mg, 91%); R_f = 0.60 (hexane/EtOAc, 80:20); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42−7.32 (m, 5H), 4.62 (d, J = 11.8 Hz, 1H), 4.55 (d, J = 11.8 Hz, 1H), 4.13−4.09 (m, 1H), 3.89−3.79 (m, 1H), 2.53 (s,

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1H), 1.91−1.72 (m, 5H), 1.55−1.46 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 128.5, 127.8, 127.7, 81.4, 72.2, 71.57, 31.1, 27.9, 19.7; HRMS (m/z) calcd for $C_{12}H_{17}O_2$ $[M + H]^+$ 193.1223, found 193.1228.

*cis-2-(Benzyloxy)cyclooctanol (**10c**).*[4i] *cis*-1,2-Cyclooctanediol **9c** (30 mg, 0.21 mmol), benzyl bromide (37 μL, 0.31 mmol), dimethyltin dichloride (4.6 mg, 10 mol %) and Ag_2O (52.5 mg, 0.23 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (47.2 mg, 97%); R_f = 0.69 (hexane/EtOAc, 80:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.21 (m, 5H), 4.63 (d, J = 11.8 Hz, 1H), 4.52 (d, J = 11.7 Hz, 1H), 3.98−3.92 (m, 1H), 3.70−3.52 (m, 1H), 2.07−1.91 (m, 1H), 1.90−1.33 (m, 11H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 128.4, 127.7, 127.6, 80.9, 71.5, 70.8, 29.4, 26.8, 26.6, 25.5, 25.5, 22.5; HRMS (m/z) calcd for $C_{15}H_{23}O_2$ $[M + H]^+$ 235.1693, found 235.1693.

*(3R,4S)-4-(Benzyloxy)tetrahydrofuran-3-ol (**10d**).* (3*R*,4*S*)-Tetrahydrofurandiol **9d** (30 mg, 0.29 mmol), benzyl bromide 51 μL, 0.43 mmol), dimethyltin dichloride (6.4 mg, 10 mol %) and Ag_2O (74.1 mg, 0.32 mmol) were stirred in acetonitrile (3 mL) under nitrogen atmosphere at room temperature for 24 h. Column chromatographic purification (hexane/EtOAc, 80:20) afforded the title compound as a colorless oil (10.1 mg, 98%); R_f = 0.50 (hexane/EtOAc, 80:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.21 (m, 5H), 4.53 (s, 2H), 4.21−4.16 (m, 1H), 4.02−3.95 (m, 1H), 3.85−3.78 (m, 2H), 3.74−3.64 (m, 2H), 2.86 (s, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 137.2, 128.6, 128.2, 127.9, 78.3, 73.4, 72.6, 70.4, 70.0; HRMS (m/z) calcd for $C_{11}H_{15}O_3$ $[M + H]^+$ 195.1016, found 195.1015.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01898.

Copies of ^{1}H and ^{13}C NMR. (PDF)

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Notes

The authors declare no competing financial interest.

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