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Co-solvent Promoted O-Benzylation with Silver(I) Oxide: Synthesis of 1'-Benzylated Sucrose Derivatives, Mechanistic Studies and Scope Investigation

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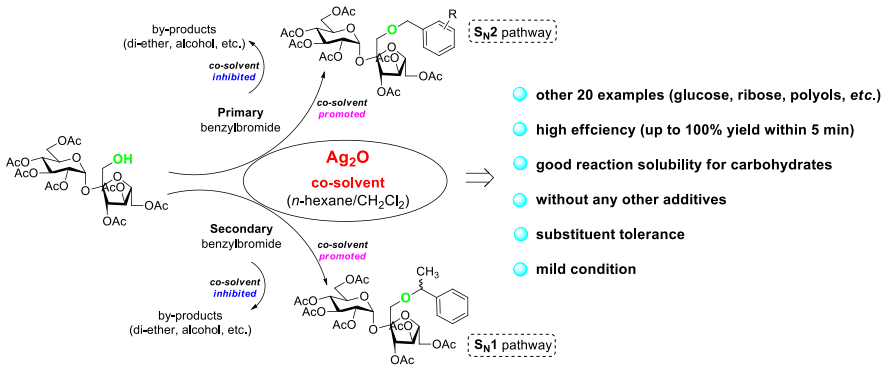


ABSTRACT

A co-solvent promoted O-benzylation strategy with Ag_2O was developed. The co-solvent consisting of CH_2Cl_2 and *n*-hexane can not only improve the reaction solubility for carbohydrates but also increase the benzylation efficiency. The formations of by-products are greatly inhibited in the developed method. This method is simple, mild, and highly effective. By which, numerous 1'-benzylated sucrose derivatives were prepared including a photoreactive (trifluoromethyl)phenyldiazirine-based sucrose.

The mechanisms of benzylation with primary and secondary benzyl bromides were also elaborated. Furthermore, the application scope with alcohols, glucose and ribose derivatives were investigated.

INTRODUCTION

Benzylation of hydroxyl groups has emerged as an important topic in synthetic chemistry and carbohydrate field. The generated benzyl ether and its variants are important hydroxyl-protecting groups because of its inherent stability, easy installation, compatibility with many reaction conditions and numerous deprotection methods.[1] Traditionally, sodium hydride (NaH)[2] and silver (I) oxide (Ag_2O)[3] are widely used as the reagents to mediate the O-benzylation of carbohydrates. Despite the high efficiency of NaH in the benzylation process, its strong alkaline condition, substrate limitation and tedious post-processing are major barriers to its wide application. Alternatively, Ag_2O-mediated O-benzylation strategy has been used as an indispensable strategy due to its mild condition, easy post-processing and low environmental impact. Nonetheless, many reports suffered the excess use of reagents, preparation of fresh Ag_2O, poor solubility of the substrate, low reaction yields or long reaction time.[3d-e] Furthermore, the reaction mechanisms still remain ambiguous. In view of the great importance of Ag_2O-mediated O-benzylation in carbohydrates field and synthetic chemistry, more efficient improvements deserve to be carried out eagerly.

Sucrose, consisting of three primary hydroxyls and five secondary hydroxyls, serves as an important starting platform for the preparation of surfactants, macrocyclic derivatives, functional materials, food additives and pharmaceutical compounds.[4] It is also the major form of transported carbon in a lot of plant species and is transported through cell membranes in many tissue types.[5] To study sucrose carrier protein and the physiology of sucrose transport, modifications of 1'-postion of

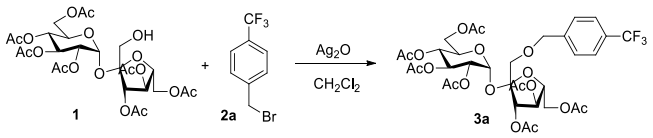
sucrose to construct nonnatural sucrose analogues are the widely used strategies.[6] Meanwhile, sucralose, fructooligosaccharides (1-kestose, nystose and 1-*β*-fructofuranosylnystose) and the Achyranthes bidentata B1 polysaccharides[7], isolated from a traditional Chinese herbal medicine *Achyranthes bidentata* Blume, could all be regarded as the 1'-substituted sucrose, indicating that the 1'-position is tolerable for numerous modification. However, it has been reported that the more sterically hindered 1'-hydroxyl of sucrose present the lowest reactivity among the primary hydroxyls in many reactions[8], which bring many trouble for the modification of 1'-position of sucrose. Herein, we developed a co-solvent promoted O-benzylation strategy, which can not only improve the reaction solubility but also increase the benzylation efficiency for 1'-sucrose. Furthermore, we comprehensively elaborated the benzylation mechanisms for the first time and prepared a 3-(trifluoromethyl)-3-phenyldiazirine (TPD)[9] coupled sucrose derivative based on aforementioned strategy, which can be used as useful photoreactive component to study sucrose and its derivatives in photoaffinity labelling[10]. Furthermore, many substrates including alcohols, glucose and ribose derivatives were subjected into the reaction to further expand its application scope.

RESULTS AND DISCUSSION

Initially, we would like to prepare the 1'-OH-heptaacetylsucrose **1** as a precursor for subsequent benzylation. To conveniently obtain compound **1**, we averted the tedious strategy by protection and deprotection[11] and chose a more efficient enzymatic method[12] involving the hydrolysis of commercially available octaacetylsucrose in the presence of Alcalase®. Next, sucrose **1**[13] was reacted with *p*-(trifluoromethyl)benzyl bromide **2a** with Ag_2O in CH_2Cl_2 which is the commonly used solvent in carbohydrates field (Table 1). Temperature optimization indicated that 60 °C is ideal for the reaction

(Table 1, entries 1-4), and 2 equiv of **2a** and 3 equiv of Ag_2O were selected as the optimial reagents ratio (Table 1, entries 5-6). Any additive failed to improve the reaction yield (Table 1, entries 7-8) but the N_2 atmosphere made contribution to the reaction yield although only 23% yield was obtained (Table 1, entry 9). Reagent amount screening showed that excess reagents (Table 1, entries 10-13) are required to obtain the satisfactory yield. Despite of the good yield, this is not an effective strategy for wide application especially for the benzylation with precious benzyl bromides. Based on the significant solvent effect on nucleophilic substitution, we carried out the optimization of reaction solvents (Table 2). Although there is no universal polarity scale for the sixteen solvents tested in this study, we select dipole moment (μ) and dielectric constant (ε) as general indicator of solvent polarity.[14] Benzylation of **1** was evidently sensitive to solvent polarity. High-polarity solvents such as MeCN, DMF and acetone failed to afford desired product (Table 2, entries 1-3). With low-polarity solvents such as EtOAc and $CHCl_3$ (Table 2, entries 6 and 7), **3a** was obtained in 19% and 39%, respectively. No desired product was obtained when THF or 1,4-dioxane was used as the solvent (Table 2, entries 5 and 12). The desired products were obtained in moderate yield in other solvents (Table 2, entries 8-11 and 13). Interestingly, when cylcohexane, *n*-hexane and *n*-pentane were used as the solvents (Table 2, entries 14-16), the reaction yield drastically increased although these solvents are not widely used in carbohydrates field because of their low solubility. These results indicated that benzylation correlated more closely with the solvent's dielectric constant (ε) than dipole moment (μ).

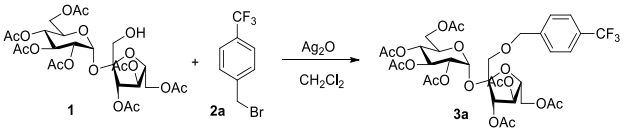
Table 1. O-Benzylation of 1'-Sucrose with 2a in the Presence of Ag_2O[a]



entry	**2a** (equiv)	Ag_2O (equiv)	temp (ºC)	time (h)	yield **3a** (%)[b]
1	2	2	rt	144	8
2	2	2	40	70	14
3	2	2	60	24	17
4	2	2	80	16	15
5	2	3	60	24	21
6	2	4	60	18	17
7[c]	2	3	60	24	trace
8[d]	2	3	60	24	0
9[e]	2	3	60	24	23
10[e]	4	6	60	24	38
11[e]	6	9	60	24	53
12[e]	8	12	60	24	69
13[e]	10	15	60	24	82

[a]Reaction conditions: **1** (0.1 mmol), **2a**, Ag_2O, CH_2Cl_2 (1 mL), MS 4Å (200 mg) in a sealed tube under dark. [b]Isolated yield. [c]KI (0.01 equiv) was added. [d]*n*-Bu_4NI (0.01 equiv) was added. [e]Under N_2.

Table 2. Solvent Optimization[a]



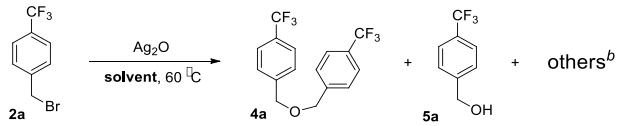
entry	solvent	μ[b]	ε[c]	time (h)	yield **3a** (%)[d]
1	MeCN	3.2	37.5	24	0
2	DMF	3.8	36.7	24	0
3	acetone	2.9	20.6	24	0
4	CH_2Cl_2	1.8	9.1	24	23
5	THF	1.8	7.6	24	0
6	EtOAc	1.7	6.0	24	19
7	$CHCl_3$	1.1	4.8	24	39
8	Et_2O	1.3	4.3	12	56
9	isopropyl ether	1.2	3.9	12	59
10	toluene	0.4	2.4	20	47
11	benzene	0	2.3	16	50
12	1,4-dioxane	0.4	2.2	24	0

13	CCl_4	0	2.2	16	62
14	cyclohexane	0.3	2.0	16	76
15	*n*-hexane	0	1.9	16	79
16	*n*-pentane	0	1.8	16	78

[a]**1** (0.1 mmol), **2a** (2.0 equiv), Ag_2O (3.0 equiv), solvent (1 mL), MS 4Å (200 mg), in a sealed tube at 60 °C under N_2. [b]Dipole moment (debye). [c]Dielectric constant (F/m). [d]Isolated yield.

For the solvents that failed to afford desired product (Table 2, entries 1-3, 5 and 12), we found that sucrose **1** still remained but benzyl bromide **2a** consumed completely.[15] To clearly elucidate the derivation of **2a** and the factors affecting benzylation of **1**, we carried out a series of control experiments of which **2a** was alone reacted with Ag_2O in various solvents (Table 3). These results indicated that in non-polar solvent such as *n*-hexane, the formation of di-benzyl ether and benzyl alcohol (by-products for benzylation of **1**) were greatly inhibited. Furthermore, the inertness of *n*-hexane toward **2a** also contributed to the benzylation of **1**.

Table 3. Derivation of 2a with Ag_2O in Different Solvents[a]



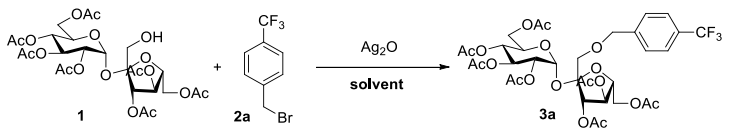
entry	solvent	time (h)	**4a**/**5a**/others (%)[c]	**4a**/**5a**/others (%)[d]
1	MeCN	15	10/62/28	10/57/33
2	DMF	4	-[e]	-[e]
3	acetone	6	4/22/74	4/24/72
4	THF	8	2/20/78	2/12/86
5	1,4-dioxane	18	27/60/13	24/57/19
6	CH_2Cl_2	13	86/4/10	84/4/12
7	EtOAc	20	63/8/29	58/12/30
8	$CHCl_3$	20	40/4/56	47/6/47
9	Et_2O	16	83/7/10	76/8/16
10	isopropyl ether	18	83/3/14	78/5/17

11	toluene	24	61/2/37	60/3/37
12	benzene	24	71/1/28	79/2/19
13	CCl_4	32	90/1/9	82/2/16
14	cyclohexane	30	99/0/1	95/0/5
15	*n*-hexane	32	98/0/2	93/0/7
16	*n*-pentane	32	98/0/2	96/0/4

[a]Reaction conditions: **2a** (0.2 mmol), Ag_2O (1.0 equiv), solvent (0.5 mL), MS 4Å (100 mg), in a sealed tube at 60 ºC under N_2. [b]Others: unidentified products. [c]Ratios were determined by ^{1}H-NMR for reaction mixtures. [d]Ratios were determined by ^{19}F-NMR for reaction mixtures. [e]Complicated mixtures, ratios were not successfully determined.

Despite that *n*-hexane was the most effective solvent for the benzylation of **1** in present work, the low solubility for carbohydrates severely limit its wide application. Co-solvents consisting of two or more solvents have been utilized as a useful strategy in organic synthesis. Thus, we assumed that the combination of *n*-hexane with other high-polarity solvent might improve the reaction solubility. Initially, additive solvents were examined divided by their miscibility with *n*-hexane (Table 4, entries 1-7). Obviously, hexane-immiscible solvents failed to afford **3a** (Table 4, entries 1-2) but hexane-miscible solvents worked well (Table 4, entries 3-6). Composition screening revealed that the combination of *n*-hexane and CH_2Cl_2 provided a dramatic increase of the reaction yield and reactants were highly soluble in it (Table 4, entry 7). Co-solvent comprising cyclohexane and CH_2Cl_2 also provided high benzylating efficiency (Table 4, entry 8). Tuning of the ratio of *n*-hexane and CH_2Cl_2 revealed 4:1 as the optimal volume ratio (Table 4, entry 9).

Table 4. Co-solvent Promoted O-Benzylation of 1 with Ag_2O[a]

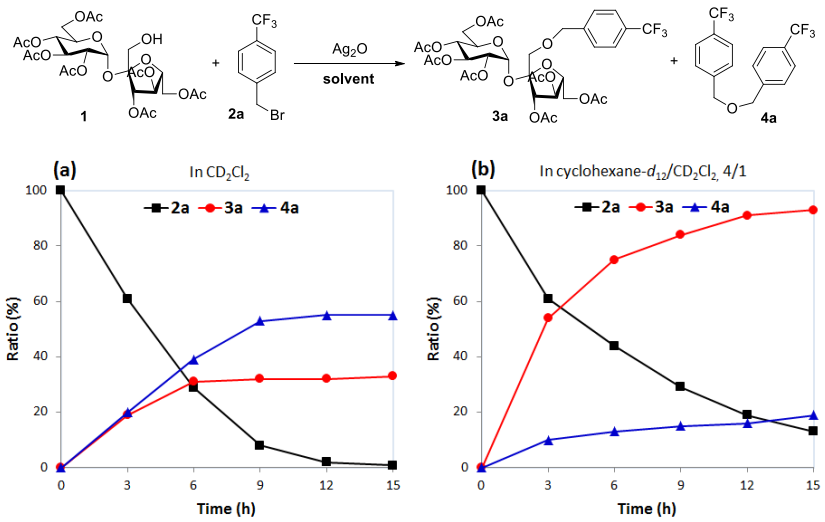


entry	solvent (volume ratio)	time (h)	yield **3a** (%)[b]
1	*n*-hexane/MeCN (4/1)	24	0
2	*n*-hexane/DMF (4/1)	24	0
3	*n*-hexane/THF (4/1)	24	trace
4	*n*-hexane/acetone (4/1)	24	35
5	*n*-hexane/EtOAc (4/1)	20	79
6	*n*-hexane/$CHCl_3$ (4/1)	20	76
7	***n*-hexane/CH_2Cl_2 (4/1)**	**15**	**91**
8	cyclohexane/CH_2Cl_2 (4/1)	15	90
9	*n*-hexane/CH_2Cl_2 (2/1)	15	79

[a]**1** (0.1 mmol), **2a** (2.0 equiv), Ag_2O (3.0 equiv), solvent (1 mL), MS 4Å (200 mg), in a sealed tube at 60 °C under N_2. [b]Isolated yield.

To highlight the efficiency of co-solvent in the benzylation of **1**, we carried out a kinetic investigation of benzylation process in CD_2Cl_2 and deuterated co-solvent (cyclohexane-d_{12}[16] and CD_2Cl_2), respectively (Figure 1). As can be seen in the kinetic curve plot, when the reaction was carried out in CD_2Cl_2 (Figure 1, a), benzyl bromide **2a** consumed rapidly along with the formation of desired product **3a** and the major by-product **4a**. Evidently, **4a** was generated prior to the desired product **3a**, and benzyl bromide **2a** was completely consumed within 15 h. While, when the reaction was carried out in deuterated co-solvent (Figure 1, b), formation of the desired product **3a** drastically increased and the generation of by-product **4a** was significantly inhibited. Meanwhile, 13% of benzyl bromide **2a** remained in the reaction mixture after 15 h.

Figure 1. Kinetic investigation of O-benzylation of **1** in CD_2Cl_2 and deuterated co-solvent[a]

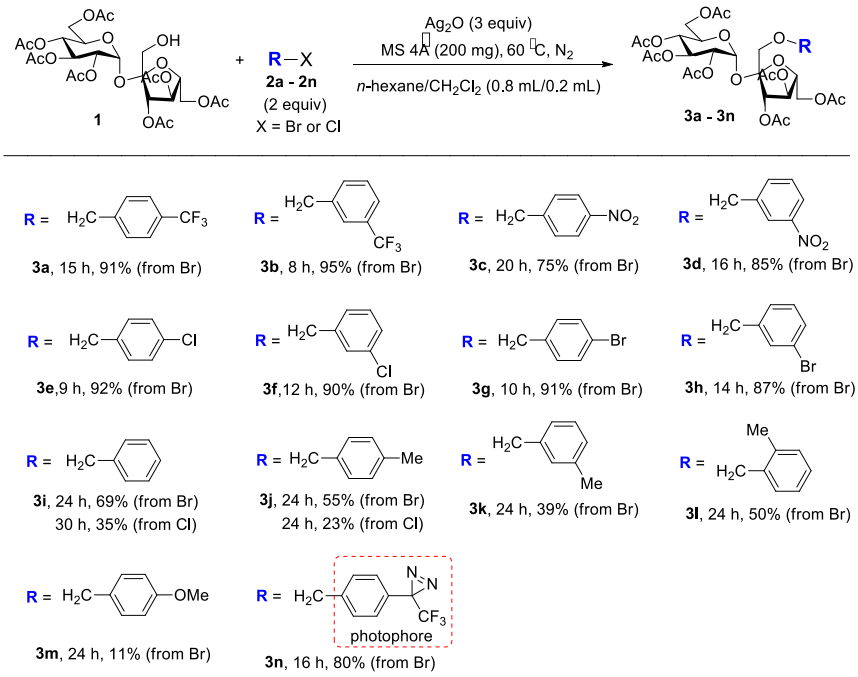


[a]**1** (0.1 mmol), **2a** (2.0 equiv), Ag_2O (3.0 equiv), solvent (a: CD_2Cl_2 1 mL, b: cyclohexane-d_{12}/CD_2Cl_2 = 0.8 mL/0.2 mL), MS 4Å (200 mg), in a sealed tube at 60 °C under N_2. Ratio was determined by ^{1}H-NMR. (For detail, see Supporting Information).

With the optimal condition in hand, we proceeded to investigate the co-solvent promoted O-benzylation of **1** with other benzyl halides (Table 5). Primary benzyl bromides bearing electron-deficient groups could give good yields as compared with that substituted with electron-rich groups, indicating that the electronic nature of the aryl ring is crucial for the reaction. For benzyl bromides that were substituted with electron-deficient groups such as -CF_3 and -NO_2 which are kinds of *meta*-directors in electrophilic aromatic substitution, *meta*-substituted benzyl bromides (**3b** and **3d**) showed slight priority to react with **1** compared with *para*-substituted ones (**3a** and **3c**). Opposite results were obtained when the substituent was changed to -Cl and -Br, kinds of *ortho*/*para*-directors in electrophilic aromatic substitution (**3e** and **3f**, **3g** and **3h**). As for methyl substitution, the *para*- and *ortho*-substituted benzyl bromide (**3j** and **3l**) afforded the desired products in higher yield than that of *meta*-substitution (**3k**). Compared with benzyl bromides, benzyl chlorides showed lower reactivity in the benzylation of **1** (**3i** and **3j**). Strong electron-rich substituent gave only a low yield of desired

product (**3m**). Satisfactorily, *p*-TPD benzyl bromide[17] could readily react with **1** giving a photoreactive 1'-sucrose derivative in 80% yield (**3n**).

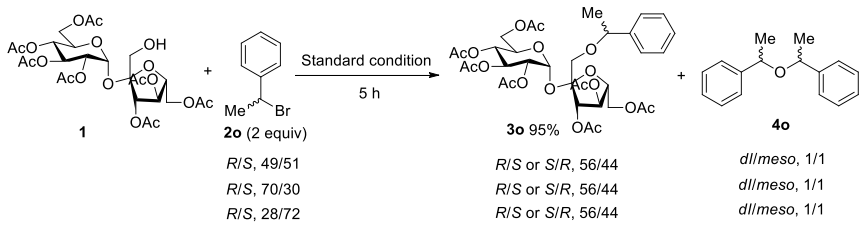
Table 5. Co-solvent Promoted O-benzylation of 1 with Other Benzyl Halides[a]



[a]**1** (0.1 mmol), isolated yield.

In addition, to gain more insight into the stereochemistry of the reaction, we carried out the benzylation of **1** with secondary benzyl bromide **2o** as shown in Scheme 1. Interestingly, the reaction smoothly furnished **3o** in excellent yield (95%) within 5 h. By using different enantioenriched **2o**, the reactions readily afford to **3o** in the same enantiomer ratio. Furthermore, di-benzyl ether **4o** was detected with a *dl*- and *meso*-mixture in the ratio of 1/1. These results indicated that a planar benzyl intermediate should be involved during the reaction.

Scheme 1. O-Benzylation of 1 with Secondary Benzyl Bromide 2o



Finally, all 1'-benzylated sucrose derivatives were subjected to deacetylation in methanolic ammonia (Scheme 2). The corresponding desired products were obtained in good yields (up to 99%). Furthermore, the photoreactivity of **6n** in CH_3OH were tested under the UV irradiation (Figure 2). The half-life ($t_{1/2}$) was calculated as 1.1 min indicating its good photoreactivity for the investigation of sucrose in photoaffinity labeling. To clearly confirm the photoreactive product, we performed the photoreaction of **6n** in CH_3OH and CD_3OD respectively and analyzed the reaction mixtures by ESI-HRMS (For detail, see Supporting Information).

Scheme 2. Deacylation of 1'-Benzylated Sucroses

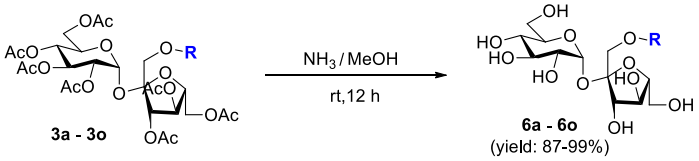
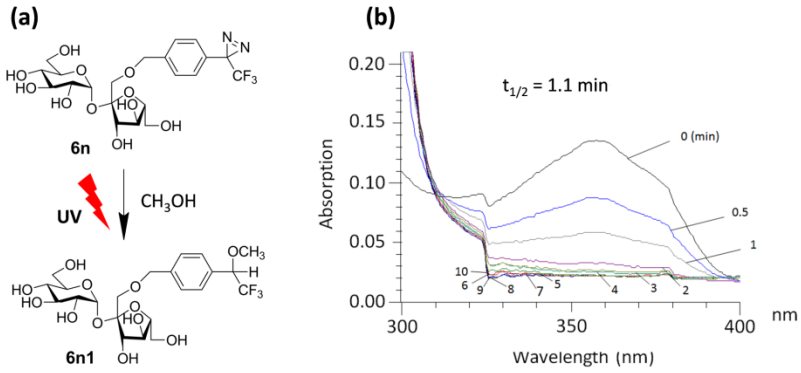
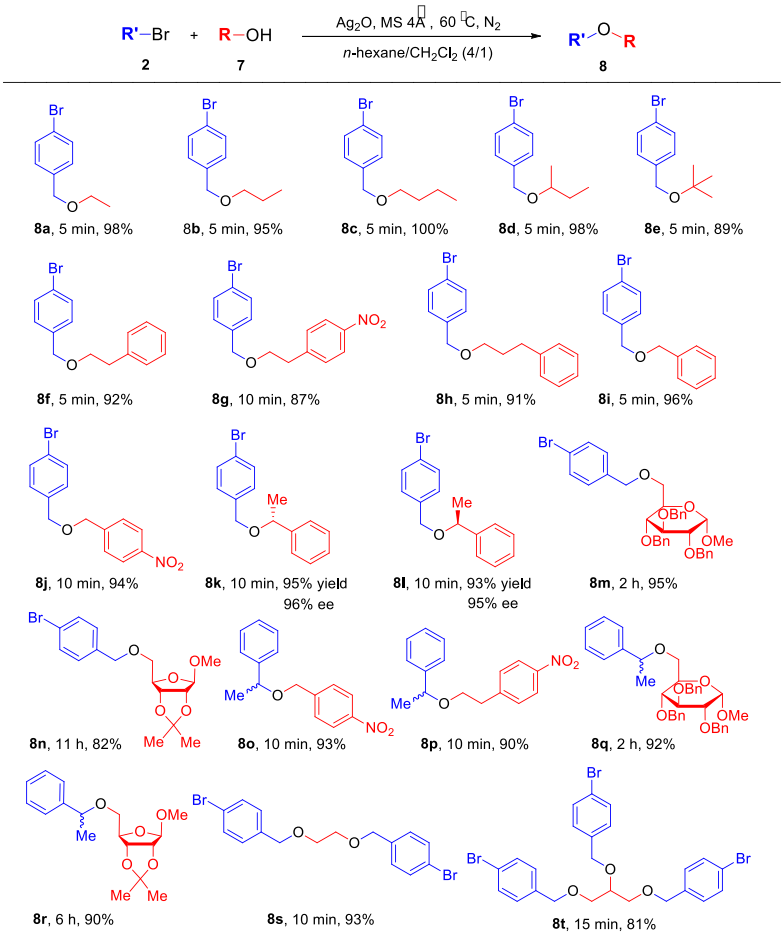


Figure 2. (a) UV irradiation of **6n** in CH_3OH (b) UV-vis spectrum of **6n** in CH_3OH with a time window of 0-10 min.



To further expand the application scope of the co-solvent promoted O-benzylation strategy, many substrates were tested as shown in Table 6. In consideration of the high benzylation efficiency and the lower price, we chose 4-bromobenzyl bromide **2g** as the benzylation reagent to perform the initial study. As expected, both of the aliphatic and aromatic alcohols can be benzylated to afford desired products in excellent yields with short time (**8a**-**8j**). When enantioenriched secondary benzyl alcohols were used, the chiral purity of the desired products can be well remained (**8k** and **8l**). Notably, other carbohydrates such as glucose and ribose derivatives were also subjected into the developed strategy and the reactions readily furnished corresponding products in good yields which indicating the good application potentiality of the co-solvent promoted O-benzylation strategy (**8m** and **8n**). Secondary benzyl bromide **2o** also worked well in this study (**8o**-**8r**). Furthermore, O-benzylation with polyols were examined and the multi-benzylated products can be obtained in good isolated yields (**8s** and **8t**).

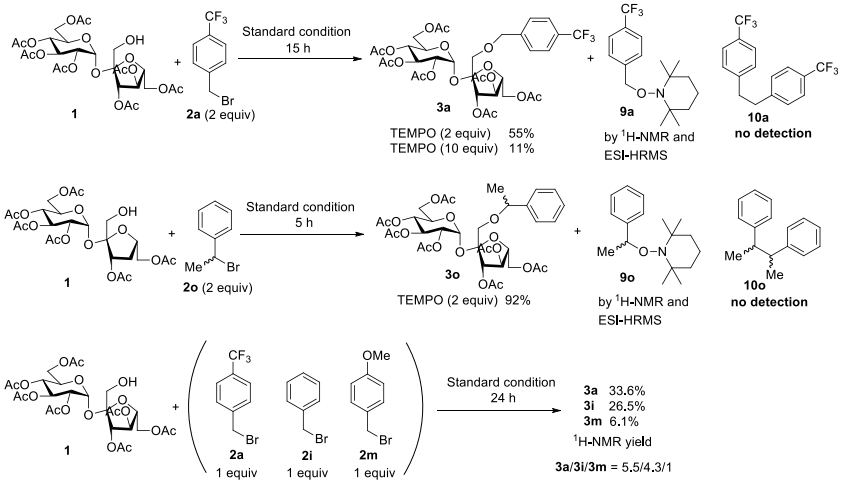
Table 6. Scope Investigation



To explore the benzylation mechanism, several control experiments have been carried out (Scheme 3). The benzylation of **1** were conducted under the standard conditions in the presence of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as a radical scavenger[18]. In the presence of 2 equiv of TEMPO, the benzylation yield with **2a** dropped to 55%, and the corresponding benzyl-TEMPO adduct **9a** can be detected by ^{1}H-NMR and ESI-HRMS. Although formation of **9a** may indicate a radical process, 10 equiv of TEMPO did not completely inhibit the reaction and no bibenzyl derivative **10a** (product derived from radical pathway[19]) was detected in these reactions. Besides, a control

experiment of which **2a** was directly treated with TEMPO readily afford to **9a** in 76% yield. A competition experiment indicated that benzylation of **1** with primary benzyl bromide bearing strong electron-rich substituent (**2m**) proceeded much more slowly than for the other two substrates (**2a** and **2i**). On the basis of above mentioned results, we proposed that a S_N2 pathway is more reliable for benzylation of **1** with primary benzyl bromides. Furthermore, addition of 2 equiv of TEMPO had no significant effect on the benzylation of **1** with secondary benzyl bromide **2o** although TEMPO adduct **9o** was also detectable indicating a S_N1 pathway may involve in the benzylation with secondary benzyl bromide.

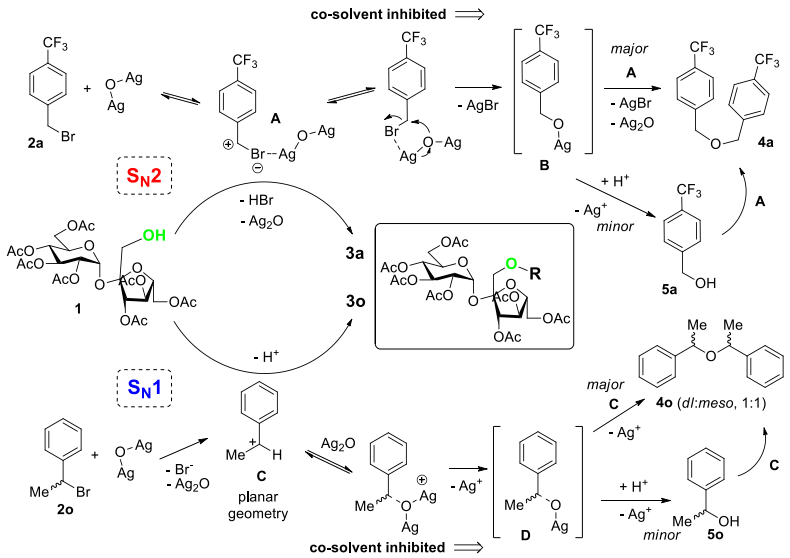
Scheme 3. Control Experiments



Based on the result presented above, we outline the plausible benzylation mechanism (Scheme 4). Initially, bromine of **2a** is abstracted by Ag_2O to form a long-chain intermediate **A**, which is further attacked by 1'-hydroxyl of **1** giving desired product **3a**. Meanwhile, intermediate **A** can convert to silver-alkoxy[20] intermediate **B** via self-cyclization following with the formation of **4a** and **5a**. Furthermore, benzylation of **1** with secondary benzyl bromide **2o** involve a halogenophilic attack by

Ag_2O, removal of bromine forming a planar benzylic carbocation **C**, the subsequent attack towards two sides of **C** by **1** forming racemic products **3o**. Meanwhile, di-benzyl ether **4o** and alcohol **5o** are also formed during the process.

Scheme 4. Mechanistic Hypothesis



CONCLUSIONS

In conclusion, we presented a comprehensive investigation of solvent effect on the O-benzylation with Ag_2O and developed a co-solvent promoted strategy that can not only improve the reaction solubility but also increase the reaction yield. The co-solvent strategy could significantly inhibit the formation of di-benzyl ether and alcohol which were major by-products in Ag_2O-mediated benzylation reaction. The benzylation yield can reach to 95% in the co-solvent promoted system despite of the relatively low reactivity of 1'-hydroxyl of sucrose. Furthermore, benzylation mechanisms with primary and secondary benzyl bromide were well elaborated for the first time. Involving which strategy, we

successfully prepared photoreactive 1'-sucrose derivative which acts as a promising reagent to investigate sucrose in photoaffinity labeling. The developed co-solvent promoted O-benzylation strategy are successfully applied for the other substrates such as commonly used alcohols, glucose and ribose derivatives that indicating its potential utility in both of carbohydrate field and synthetic chemistry. Additional studies on the expansion of its scope and preparation of glycosides are currently underway.

EXPERIMENTAL SECTION

General Remarks. Chemical reagents and solvents were purchased and used without further purification (Commercial available Ag_2O was directly used without any treatment). Column chromatography was performed using silica gel (200-400 mesh). HR-ESI mass spectra were recorded with a UPLC ESI-TOF mass spectrometer.

Synthesis of 1'-OH-heptaacetylsucrose 1. To the solution of octaacetyl sucrose (1.00 g, 1.47 mmol) in 0.1 M phosphate buffer (50 mL, pH 7) containing a mixture of DMF and H_2O (10 mL, DMF:H_2O=1:3), Alcalase® 2.4 L (2 mL) was added. The mixture was incubated at 37 °C for 24 h. The mixture was extracted with ethyl acetate, concentrated under reduced pressure, then subjected to column chromatography on silica gel (EtOAc:*n*-hexane, 10:1) to afford 1'-OH-heptaacetylsucrose **1** (0.25 g, 27.4%).

Co-solvent Promoted O-Benzylation of 1'-Sucrose in the Present of Ag_2O. To a solution of 1'-OH-heptaacetylsucrose **1** (0.1 mmol, 64 mg) in co-solvent (*n*-hexane/CH_2Cl_2, 0.8 mL/0.2 mL) in a glass sealed tube, benzyl bromide **2** (2.0 equiv), Ag_2O (3.0 equiv) and molecular sieves 4Å (200 mg) were added, respectively. The reaction mixture was stirred at 60 °C under dark in the presence of N_2.

After the reaction was finished, the mixture was filtered by celite (or centrifugation) and concentrated, and the residue was purified through silica gel column chromatography (EtOAc:Hexane=3:2) to afford corresponding 1'-benzylated sucrose derivative.

Preparation of Enantioenriched (*R*)-1-(1-bromoethyl)benzene (*R*)-2o and (*S*)-1-(1-bromoethyl)benzene (*S*)-2o. To a stirred solution of (*S*)-1-phenyl ethanol or (*R*)-1-phenyl ethanol (1.0 g, 8.2 mmol) in anhydrous hexane (30 mL) at 0 °C, PBr_3 (0.5 equiv) was added dropwise. The reaction was monorted by TLC analysis. After reaction for 15 min, the reaction mixture was slowly poured into 50 mL ice-water. The organic phase was washed with saturated $NaHCO_3$ solution (30 mL×2), 1 M HCl (30 mL), and brine (30 mL×3), respectively, dried with anhydrous $MgSO_4$, and concentrated by evaporation. A: yield: 93%, $[\alpha]_D$ = +41 (*c* 1, $CHCl_3$); ratio: (*R*)-**2o**/(*S*)-**2o** = 70/30 (by HPLC), Daicel Chiralpak AY-H, *i*-PrOH-hexane 0/100, flow rate 0.2 mL/min, t_R: 23.80 min (*R*)-**2o** and 25.09 min (*S*)-**2o**, 210 nm detection. B: yield: 93%, $[\alpha]_D$ = -41 (*c* 1, $CHCl_3$); ratio: (*S*)-**2o**/(*R*)-**2o** = 72/28 (by HPLC), Daicel Chiralpak AY-H, *i*-PrOH-hexane 0/100, flow rate 0.2 mL/min, t_R: 23.88 min (*R*)-**2o** and 25.19 min (*S*)-**2o**, 210 nm detection. C: For commercial available (1-bromoethyl)benzene: $[\alpha]_D$ = 0 (*c* 1, $CHCl_3$); ratio: (*R*)-**2o**/(*S*)-**2o** = 49/51 (by HPLC), Daicel Chiralpak AY-H, *i*-PrOH-hexane 0/100, flow rate 0.2 mL/min, t_R: 23.85 min (*R*)-**2o** and 25.16 min (*S*)-**2o**, 210 nm detection.

Deacylation of 1'-Benzylated Sucrose Derivatives. To a solution of 1'-benzylated sucrose derivative **3** (0.2 mmol) in methanol (4 mL), NH_3 gas was bubbled. Then the mixture was stirred at room temperature for 12 h. After removal of the solvent under vacuo, the residue was purified through silica gel column chromatography (EtOAc:MeOH=5:1) to afford 1'-benzylated sucrose.

Co-solvent Promoted O-Benzylation of Alcohols, Glucose and Ribose Derivatives in the Present of Ag_2O. To a solution of **7** (0.3 mmol) in co-solvent (*n*-hexane/CH_2Cl_2, 4/1) in a glass sealed tube, benzyl bromide (2.0 equiv for **8a**-**8r**, 4.0 equiv for **8s**, 6.0 equiv for **8t**), Ag_2O (3.0 equiv for **8a**-**8r**, 6.0 equiv for **8s**, 9.0 equiv for **8t**) and molecular sieves 4Å were added, respectively. The reaction mixture was stirred at 60 °C under dark in the presence of N_2. After the reaction was finished, the mixture was filtered by celite (or centrifugation) and concentrated, and the residue was purified through silica gel column chromatography (CH_2Cl_2:Hexane=1:1 for **8a**-**8l**, **8o**-**8p**; EtOAc:hexane=1:2 for **8m**-**8n**, **8q**-**8t**) to afford corresponding products.

*1'-OH-heptaacetylsucrose (**1**).*[12] Colorless oil (0.25 g, 27.4%): $[\alpha]_D$ +50 (*c* 0.2 $CHCl_3$) (lit[12a].: +43, *c* 2.0 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.67 (d, J = 3.7 Hz, 1H), 5.49 – 5.42 (m, 3H), 5.09 (t, J = 9.7 Hz, 1H), 4.93 (dd, J = 10.4, 3.7 Hz, 1H), 4.33 – 4.11 (m, 6H), 3.71 (d, J = 12.6 Hz, 1H), 3.59 (d, J = 12.6 Hz, 1H), 2.19 (s, 3H), 2.12 (s, 3H), 2.09 (s, 6H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.82, 170.78, 170.6, 170.3, 170.1(2C), 169.6, 105.2, 89.8, 78.7, 76.4, 74.7, 70.1, 69.7, 68.4, 68.2, 63.6, 63.5, 61.7, 20.5 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{26}H_{36}O_{18}Na$ 659.1799, found 659.1822.

*1'-[p-(trifluoromethyl)benzyl]heptaacetylsucrose (**3a**).* Colorless oil (72.3 mg, 91%): $[\alpha]_D$ +55 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 5.71 – 5.69 (m, 2H), 5.48 – 5.39 (m, 2H), 5.08 (t, J = 9.7 Hz, 1H), 4.86 (dd, J = 10.3, 3.8 Hz, 1H), 4.65 (s, 2H), 4.32 – 4.12 (m, 6H), 3.64 (d, J = 10.5 Hz, 1H), 3.44 (d, J = 10.5 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.5, 170.4, 170.0, 169.8, 169.6, 169.4, 141.6, 129.8 (q, J = 32.1 Hz), 127.5, 125.2 (d, J = 3.5 Hz), 124.0 (q, J =

272.5 Hz), 104.1, 89.4, 78.3, 75.4, 74.3, 72.5, 70.1, 70.0, 69.5, 68.1, 68.0, 63.1, 61.4, 20.2 and 20.0 (7C); ^{19}F-NMR (470 MHz, $CDCl_3$): δ = -62.53 ppm; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{34}H_{41}F_3O_{18}Na$ 817.2143, found 817.2161.

*1'-[m-(trifluoromethyl)benzyl]heptaacetylsucrose (**3b**).* Colorless oil (75.4 mg, 95%): $[\alpha]_D$ +52 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.62 – 7.49 (m, 4H), 5.72 – 5.69 (m, 2H), 5.48 – 5.40 (m, 2H), 5.08 (t, *J* = 8.9 Hz, 1H), 4.86 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.65 (s, 2H), 4.31 – 4.11 (m, 6H), 3.66 (d, *J* = 10.5 Hz, 1H), 3.46 (d, *J* = 10.5 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.3, 170.10, 170.06, 169.9, 169.7, 138.7, 130.91 (q, *J* = 32.5 Hz), 130.86, 129.0, 124.7 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 271.7 Hz), 104.3, 89.6, 78.5, 75.6, 74.4, 72.9, 70.5, 70.2, 69.7, 68.3, 68.2, 63.4, 61.6, 20.5 and 20.4 and 20.3 (7C); ^{19}F-NMR (470 MHz, $CDCl_3$): δ = -62.64 ppm; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{34}H_{41}F_3O_{18}Na$ 817.2143, found 817.2166.

*1'-(p-nitrobenzyl)heptaacetylsucrose (**3c**).* Colorless oil (57.8 mg, 75%): $[\alpha]_D$ +54 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 5.72 – 5.69 (m, 2H), 5.49 – 5.41 (m, 2H), 5.09 (t, *J* = 9.7 Hz, 1H), 4.86 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.70 (s, 2H), 4.33 – 4.13 (m, 6H), 3.70 (d, *J* = 10.5 Hz, 1H), 3.49 (d, *J* = 10.5 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.3, 170.02 (2C), 169.95, 169.6, 147.7, 145.1, 127.9, 123.8, 104.3, 89.6, 78.5, 75.6, 74.4, 72.4, 70.9, 70.3, 69.7, 68.3, 68.2, 63.3, 61.6, 20.51 and 20.46 and 20.39 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{33}H_{41}NO_{20}Na$ 794.2120, found 794.2119.

*1'-(m-nitrolbenzyl)heptaacetylsucrose (**3d**).* Colorless oil (65.6 mg, 85%): $[\alpha]_D$ +60 (*c* 1 $CHCl_3$);

^{1}H NMR (270 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.17 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 8.1 Hz, 1H), 5.72 – 5.69 (m, 2H), 5.48 – 5.41 (m, 2H), 5.08 (t, J = 9.7 Hz, 1H), 4.86 (dd, J = 10.4, 3.7 Hz, 1H), 4.70 (s, 2H), 4.34 – 4.12 (m, 6H), 3.70 (d, J = 10.4 Hz, 1H), 3.50 (d, J = 10.4 Hz, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.3, 170.08, 170.06, 170.0, 169.7, 148.6, 139.9, 133.4, 129.6, 122.9, 122.3, 104.2, 89.6, 78.5, 75.6, 74.4, 72.4, 70.9, 70.2, 69.7, 68.3, 68.2, 63.3, 61.6, 20.5 and 20.4 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{33}H_{41}NO_{20}Na$ 794.2120, found 794.2135.

*1'-(p-chlorobenzyl)heptaacetylsucrose (**3e**).* Colorless oil (70.1 mg, 92%): $[\alpha]_D$ +54 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.33 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 5.69 – 5.67 (m, 2H), 5.48 – 5.38 (m, 2H), 5.08 (t, J = 9.7 Hz, 1H), 4.86 (dd, J = 10.4, 3.7 Hz, 1H), 4.55 (s, 2H), 4.32 – 4.11 (m, 6H), 3.60 (d, J = 10.5 Hz, 1H), 3.41 (d, J = 10.5 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.6, 170.2, 170.1 (2C), 169.8, 169.6, 136.0, 133.7, 129.1, 128.7, 104.4, 89.6, 78.4, 75.6, 74.5, 72.8, 70.2, 70.0, 69.7, 68.2 (2C), 63.4, 61.6, 20.5 and 20.4 and 20.3 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{33}H_{41}Cl^{35}O_{18}Na$ 783.1879, found 783.1882 or calcd for $C_{33}H_{41}Cl^{37}O_{18}Na$ 785.1850, found 785.1863.

*1'-(m-chlorobenzyl)heptaacetylsucrose (**3f**).* Colorless oil (68.6 mg, 90%): $[\alpha]_D$ +56 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.30 – 7.20 (m, 3H), 5.71 – 5.68 (m, 2H), 5.47 – 5.39 (m, 2H), 5.08 (t, J = 9.6 Hz, 1H), 4.86 (dd, J = 10.4, 3.8 Hz, 1H), 4.56 (s, 2H), 4.31 – 4.11 (m, 6H), 3.62 (d, J = 10.5 Hz, 1H), 3.43 (d, J = 10.5 Hz, 1H), 2.14 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.2, 170.1 (2C), 169.9, 169.7, 139.7, 134.5, 129.8, 128.1, 127.7, 125.7, 104.4, 89.6, 78.5, 75.6, 74.5, 72.8, 70.2 (2C),

69.7, 68.2 (2C), 63.4, 61.6, 20.51 and 20.47 and 20.3 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{33}H_{41}Cl^{35}O_{18}Na$ 783.1879, found 783.1899 or calcd for $C_{33}H_{41}Cl^{37}O_{18}Na$ 785.1850, found 785.1870.

*1'-(p-bromobenzyl)heptaacetylsucrose (**3g**).* Colorless oil (73.4 mg, 91%): $[\alpha]_D$ +56 (*c* 1 $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 5.69 – 5.67 (m, 2H), 5.47 – 5.38 (m, 2H), 5.08 (t, *J* = 9.6 Hz, 1H), 4.86 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.53 (s, 2H), 4.31 – 4.11 (m, 6H), 3.60 (d, *J* = 10.6 Hz, 1H), 3.40 (d, *J* = 10.6 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.3, 170.1 (2C), 169.9, 169.7, 136.6, 131.7, 129.5, 121.9, 104.4, 89.6, 78.5, 75.6, 74.5, 72.9, 70.2, 70.0, 69.7, 68.2 (2C), 63.4, 61.6, 20.5 and 20.3 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{33}H_{41}Br^{79}O_{18}Na$ 827.1374, found 827.1390 or calcd for $C_{33}H_{41}Br^{81}O_{18}Na$ 829.1353, found 829.1377.

*1'-(m-bromobenzyl)heptaacetylsucrose (**3h**).* Colorless oil (70.1 mg, 87%): $[\alpha]_D$ +55 (*c* 1 $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.43 (dt, *J* = 7.2, 1.8 Hz, 1H), 7.29 – 7.20 (m, 2H), 5.71 – 5.68 (m, 2H), 5.47 – 5.39 (m, 2H), 5.08 (t, *J* = 9.6 Hz, 1H), 4.86 (dd, *J* = 10.4, 3.8 Hz, 1H), 4.56 (s, 2H), 4.32 – 4.11 (m, 6H), 3.62 (d, *J* = 10.5 Hz, 1H), 3.42 (d, *J* = 10.5 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.2, 170.1 (2C), 169.9, 169.6, 137.0, 131.0, 130.6, 130.1, 126.2, 122.6, 104.4, 89.6, 78.5, 75.6, 74.5, 72.8, 70.22, 70.15, 69.7, 68.2 (2C), 63.4, 61.6, 20.50 and 20.47 and 20.3 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{33}H_{41}Br^{79}O_{18}Na$ 827.1374, found 827.1400 or calcd for $C_{33}H_{41}Br^{81}O_{18}Na$ 829.1353, found 829.1381.

*1'-benzylheptaacetylsucrose (**3i**).*[21] Colorless oil (50.1 mg, 69%): $[\alpha]_D$ +56 (*c* 1 $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 5H), 5.72 – 5.68 (m, 2H), 5.47 – 5.38 (m, 2H), 5.07 (t, *J* = 9.7 Hz,

1H), 4.86 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.59 (s, 2H), 4.32 – 4.10 (m, 6H), 3.60 (d, *J* = 10.6 Hz, 1H), 3.41 (d, *J* = 10.6 Hz, 1H), 2.11 (s, 6H), 2.08 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.2, 170.1 (2C), 169.9, 169.7, 137.6, 128.5, 127.9, 127.8, 104.5, 89.6, 78.3, 75.6, 74.6, 73.6, 70.2, 69.8 (2C), 68.24, 68.18, 63.5, 61.7, 20.52 and 20.46 and 20.2 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{33}H_{42}O_{18}Na$ 749.2269, found 749.2257.

1'-(p-methylbenzyl)heptaacetylsucrose ***(3j)***. Colorless oil (40.7 mg, 55%): $[\alpha]_D$ +51 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.71 – 5.67 (m, 2H), 5.47 – 5.37 (m, 2H), 5.07 (t, *J* = 9.6 Hz, 1H), 4.86 (dd, *J* = 10.4, 3.8 Hz, 1H), 4.54 (s, 2H), 4.31 – 4.10 (m, 6H), 3.56 (d, *J* = 10.6 Hz, 1H), 3.39 (d, *J* = 10.6 Hz, 1H), 2.34 (s, 3H), 2.11 (s, 6H), 2.08 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.9, 170.7, 170.3, 170.2 (2C), 169.9, 169.7, 137.7, 134.5, 129.2, 128.0, 104.6, 89.6, 78.4, 75.6, 74.6, 73.5, 70.2, 69.8, 69.6, 68.3, 68.2, 63.5, 61.7, 21.0, 20.54 and 20.48 and 20.3 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{34}H_{44}O_{18}Na$ 763.2425, found 763.2428.

1'-(m-methylbenzyl)heptaacetylsucrose ***(3k)***. Colorless oil (28.9 mg, 39%): $[\alpha]_D$ +56 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 1H), 7.14 – 7.09 (m, 3H), 5.73 – 5.68 (m, 2H), 5.47 – 5.38 (m, 2H), 5.07 (t, *J* = 9.7 Hz, 1H), 4.86 (dd, *J* = 10.4, 3.7 Hz, 1H), 4.55 (s, 2H), 4.31 – 4.10 (m, 6H), 3.58 (d, *J* = 10.6 Hz, 1H), 3.40 (d, *J* = 10.6 Hz, 1H), 2.35 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.3, 170.2, 170.1, 169.8, 169.7, 138.2, 137.5, 128.7, 128.6, 128.4, 124.9, 104.5, 89.6, 78.4, 75.6, 74.6, 73.7, 70.1, 69.8, 69.7, 68.23, 68.15, 63.5, 61.7, 21.2, 20.51 and 20.46 and 20.3 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{34}H_{44}O_{18}Na$ 763.2425, found 763.2452.

*1'-(o-methylbenzyl)heptaacetylsucrose (**3l**).* Colorless oil (37.0 mg, 50%): $[\alpha]_D$ +55 (*c* 1 $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 1H), 7.22 – 7.17 (m, 3H), 5.69 – 5.66 (m, 2H), 5.48 – 5.36 (m, 2H), 5.07 (t, *J* = 9.7 Hz, 1H), 4.86 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.58 (dd, *J* = 20.0, 12.0 Hz, 2H), 4.31 – 4.10 (m, 6H), 3.63 (d, *J* = 10.5 Hz, 1H), 3.43 (d, *J* = 10.5 Hz, 1H), 2.33 (s, 3H), 2.11 (s, 6H), 2.09 (s, 3H), 2.03 (s, 3H), 2.01 (s, 6H), 1.96 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.3, 170.2 (2C), 169.8, 169.7, 136.9, 135.4, 130.4, 128.8, 128.1, 125.8, 104.6, 89.7, 78.5, 75.7, 74.7, 72.0, 70.2, 70.0, 69.8, 68.3, 68.2, 63.5, 61.7, 20.5 and 20.4 and 20.3 (7C), 18.60; HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{34}H_{44}O_{18}Na$ 763.2425, found 763.2441.

*1'-(p-methoxylbenzyl)heptaacetylsucrose (**3m**).* Colorless oil (8.3 mg, 11%): $[\alpha]_D$ +56 (*c* 1 $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.71 – 5.67 (m, 2H), 5.47 – 5.37 (m, 2H), 5.07 (t, *J* = 9.5 Hz, 1H), 4.86 (dd, *J* = 10.3, 3.8 Hz, 1H), 4.51 (s, 2H), 4.31 – 4.10 (m, 6H), 3.81 (s, 3H), 3.55 (d, *J* = 10.6 Hz, 1H), 3.38 (d, *J* = 10.6 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.03 (s, 6H), 2.01 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8, 170.7, 170.3, 170.2 (2C), 169.9, 169.7, 159.5, 129.5, 113.9, 104.6, 89.6, 78.4, 75.6, 74.6, 73.3, 70.2, 69.8, 69.4, 68.3, 68.2, 63.5, 61.7, 55.2, 20.6 and 20.5 and 20.4 (7C); HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{34}H_{44}O_{19}Na$ 779.2374, found 779.2380.

*1'-[p-(trifluorodiazirinyl)benzyl]heptaacetylsucrose (**3n**).* Colorless oil (66.7 mg, 80%): $[\alpha]_D$ +53 (*c* 1 $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 5.70 – 5.68 (m, 2H), 5.47 – 5.39 (m, 2H), 5.08 (t, *J* = 9.3 Hz, 1H), 4.86 (dd, *J* = 9.9, 4.1 Hz, 1H), 4.60 (s, 2H), 4.32 – 4.11 (m, 6H), 3.60 (d, *J* = 10.5 Hz, 1H), 3.41 (d, *J* = 10.5 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.7, 170.6, 170.2,

170.0 (2C), 169.8, 169.6, 139.4, 128.6, 128.0, 126.6, 122.1 (q, J = 275.3 Hz), 104.3, 89.5, 78.4, 75.5, 74.4, 72.7, 70.1 (2C), 69.7, 68.2, 68.1, 63.3, 61.6, 28.2 (q, J = 39.9 Hz), 20.5 and 20.4 and 20.2 (7C); ^{19}F-NMR (470 MHz, $CDCl_3$): δ = -65.28 ppm; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{35}H_{41}N_2O_{18}F_3Na$ 857.2204, found 857.2191.

*1'-((1-methyl)benzyl)heptaacetylsucrose (**3o**).* Colorless oil (70.3 mg, 95%, mixture of (*R*)- and (*S*)-isomers): $[\alpha]_D$ +54 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 5H), 5.76 – 5.63 (m, 2H), 5.46 – 5.29 (m, 2H), 5.10 – 5.01 (m, 1H), 4.84 (dd, J = 10.3, 3.8 Hz, 1H), 4.50 – 4.41 (m, 1H), 4.33 – 4.05 (m, 6H), 3.49 – 3.42 (m, 1H), 3.27 – 3.17 (m, 1H), 2.18 – 1.86 (m, 21H), 1.46 – 1.43 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.8 – 169. 7 (7C), 143.1 and 142.8, 128.64 and 128.59, 127.9 and 127.8, 126.3, 104.8 and 104.7, 89.8 and 89.5, 79.3, 79.2 and 79.0, 78.3, 75.7 and 75.5, 75.2 and 74.7, 70.2 and 70.1, 69.8 and 69.7, 68.3 and 68.20, 68.15 and 68.1, 63.54 and 63.48, 61.6, 23.9 and 23.7, 20.6 – 20.2 (7C); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{34}H_{44}O_{18}Na$ 763.2425, found 763.2443.

*1'-[p-(trifluoromethyl)benzyl]sucrose (**6a**).* White solid (96.0 mg, 96%): mp 90–92 °C; $[\alpha]_D$ +57 (*c* 1 CH_3OH); ^{1}H NMR (270 MHz, CD_3OD) δ 7.66 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 5.41 (d, J = 3.8 Hz, 1H), 4.76 (d, J = 12.5 Hz, 1H), 4.69 (d, J = 12.5 Hz, 1H), 4.27 (d, J = 8.5 Hz, 1H), 4.11 – 4.03 (m, 1H), 3.86 – 3.61 (m, 9H), 3.41 (dd, J = 6.4, 3.3 Hz, 1H), 3.37 (s, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 144.3, 130.8 (q, J = 31.9 Hz), 129.0 (d, J = 2.0 Hz), 126.3 (d, J = 2.6 Hz), 125.8 (q, J = 272.1 Hz), 105.2, 94.0, 83.5, 78.6, 75.3, 74.7, 74.3, 73.7, 73.1, 71.4 (2C), 63.3, 62.2; ^{19}F-NMR (470 MHz, CD_3OD): δ = -64.00 ppm. HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{20}H_{27}F_3O_{11}Na$ 523.1403, found 523.1423.

*1'-[m-(trifluoromethyl)benzyl]sucrose (**6b**)*. White solid (93.0 mg, 93%): mp 91–93 °C; $[\alpha]_D$ +55 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 7.61 – 7.44 (m, 4H), 5.32 (d, *J* = 3.8 Hz, 1H), 4.67 (d, *J* = 12.5 Hz, 1H), 4.60 (d, *J* = 12.5 Hz, 1H), 4.17 (d, *J* = 8.6 Hz, 1H), 4.05 – 3.95 (m, 1H), 3.77 – 3.62 (m, 7H), 3.57 (t, *J* = 10.7 Hz, 2H), 3.33 (dd, *J* = 6.2, 3.5 Hz, 1H), 3.29 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 141.2, 132.4, 131.8 (q, *J* = 32.0 Hz), 130.3, 125.8 (q, *J* = 271.4 Hz), 125.4 (q, *J* = 3.8 Hz), 125.2 (q, *J* = 3.8 Hz), 105.2, 94.0, 83.5, 78.6, 75.3, 74.7, 74.3, 73.8, 73.1, 71.4 (2C), 63.3, 62.2; ^{19}F-NMR (470 MHz, CD_3OD): δ = -64.08 ppm. HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{20}H_{27}F_3O_{11}Na$ 523.1403, found 523.1395.

*1'-(p-nitrobenzyl)sucrose (**6c**)*. White solid (85.9 mg, 90%): mp 93–95 °C; $[\alpha]_D$ +53 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 8.26 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 5.42 (d, *J* = 3.7 Hz, 1H), 4.83 (d, *J* = 13.3 Hz, 1H), 4.75 (d, *J* = 13.3 Hz, 1H), 4.27 (d, *J* = 8.5 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.87 – 3.64 (m, 9H), 3.41 (dd, *J* = 8.6, 4.8 Hz, 1H), 3.37 (s, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 149.0, 147.7, 129.3, 124.6, 105.3, 94.1, 83.7, 78.7, 75.4, 74.8, 74.4, 73.4, 73.2, 71.6, 71.5, 63.4, 62.3; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{19}H_{27}NO_{13}Na$ 500.1380, found 500.1382.

*1'-(m-nitrobenzyl)sucrose (**6d**)*. White solid (85.9 mg, 90%): mp 91–93 °C; $[\alpha]_D$ +53 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 8.26 (s, 1H), 8.16 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 5.39 (d, *J* = 3.8 Hz, 1H), 4.77 (d, *J* = 13.0 Hz, 1H), 4.71 (d, *J* = 13.0 Hz, 1H), 4.23 (d, *J* = 8.5 Hz, 1H), 4.07 – 4.01 (m, 1H), 3.85 – 3.60 (m, 9H), 3.38 (dd, *J* = 6.6, 3.1 Hz, 1H), 3.34 (d, *J* = 3.3 Hz, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 150.0, 142.4, 134.9, 130.8, 123.6, 123.3, 105.3, 94.1, 83.6, 78.7, 75.3, 74.7, 74.4, 73.4, 73.2, 71.5 (2C), 63.3, 62.3; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{19}H_{27}NO_{13}Na$ 500.1380, found 500.1382.

1'-(p-chlorobenzyl)sucrose ***(6e)***. White solid (88.7 mg, 95%): mp 90–92 °C; $[\alpha]_D$ +55 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 7.38 – 7.25 (m, 4H), 5.37 (d, *J* = 3.8 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.20 (d, *J* = 8.5 Hz, 1H), 4.05 – 3.99 (m, 1H), 3.82 – 3.55 (m, 9H), 3.37 (dd, *J* = 5.8, 4.0 Hz, 1H), 3.34 (s, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 138.6, 134.6, 130.5, 129.6, 105.3, 94.1, 83.6, 78.8, 75.4, 74.8, 74.4, 73.8, 73.3, 71.5, 71.2, 63.4, 62.3; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{19}H_{27}Cl^{35}O_{11}Na$ 489.1140, found 489.1116 or calcd for $C_{19}H_{27}Cl^{37}O_{11}Na$ 491.1110, found 491.1086.

1'-(m-chlorobenzyl)sucrose ***(6f)***. White solid (81.3 mg, 87%): mp 90–92 °C; $[\alpha]_D$ +59 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 7.39 (s, 1H), 7.33 – 7.26 (m, 3H), 5.38 (d, *J* = 3.8 Hz, 1H), 4.64 (d, *J* = 12.2 Hz, 1H), 4.57 (d, *J* = 12.2 Hz, 1H), 4.22 (d, *J* = 8.5 Hz, 1H), 4.11 – 4.00 (m, 1H), 3.83 – 3.56 (m, 9H), 3.38 (dd, *J* = 6.3, 3.4 Hz, 1H), 3.34 (s, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 142.2, 135.5, 131.1, 128.84, 128.76, 127.1, 105.3, 94.1, 83.6, 78.7, 75.4, 74.8, 74.4, 73.8, 73.2, 71.5, 71.3, 63.4, 62.3; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{19}H_{27}Cl^{35}O_{11}Na$ 489.1140, found 489.1158 or calcd for $C_{19}H_{27}Cl^{37}O_{11}Na$ 491.1110, found 491.1137.

1'-(p-bromobenzyl)sucrose ***(6g)***. White solid (101.2 mg, 99%): mp 89–91 °C; $[\alpha]_D$ +59 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.37 (d, *J* = 3.7 Hz, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.54 (d, *J* = 12.2 Hz, 1H), 4.20 (d, *J* = 8.5 Hz, 1H), 4.05 – 3.99 (m, 1H), 3.82 – 3.55 (m, 9H), 3.38 (dd, *J* = 5.8, 4.0 Hz, 1H), 3.34 (s, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 139.1, 132.7, 130.8, 122.5, 105.3, 94.1, 83.6, 78.8, 75.4, 74.8, 74.4, 73.8, 73.3, 71.5, 71.2, 63.4, 62.3; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{19}H_{27}Br^{79}O_{11}Na$ 533.0634, found 533.0652 or calcd for $C_{19}H_{27}Br^{81}O_{11}Na$ 535.0614, found 535.0634.

1'-(m-bromobenzyl)sucrose ***(6h)***. White solid (92.0 mg, 90%): mp 90–92 °C; $[\alpha]_D$ +52 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 7.55 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 5.37 (d, *J* = 3.8 Hz, 1H), 4.63 (d, *J* = 12.3 Hz, 1H), 4.56 (d, *J* = 12.3 Hz, 1H), 4.22 (d, *J* = 8.5 Hz, 1H), 4.11 – 4.00 (m, 1H), 3.83 – 3.55 (m, 9H), 3.38 (dd, *J* = 6.2, 3.6 Hz, 1H), 3.34 (s, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 142.5, 131.9, 131.8, 131.4, 127.6, 123.5, 105.3, 94.1, 83.6, 78.7, 75.4, 74.8, 74.4, 73.8, 73.3, 71.5, 71.3, 63.4, 62.3; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{19}H_{27}Br^{79}O_{11}Na$ 533.0634, found 533.0663 or calcd for $C_{19}H_{27}Br^{81}O_{11}Na$ 535.0614, found 535.0632.

1'- benzylsucrose ***(6i)***.[21] White solid (78.7 mg, 91%): mp 78–80 °C; $[\alpha]_D$ +57 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 7.39 – 7.25 (m, 5H), 5.38 (d, *J* = 3.8 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 8.5 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.83 – 3.56 (m, 9H), 3.38 (dd, *J* = 5.8, 3.9 Hz, 1H), 3.35 (s, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 139.6, 129.6, 129.0, 128.9, 105.3, 94.1, 83.6, 78.8, 75.4, 74.8, 74.7, 74.4, 73.3, 71.5, 71.2, 63.3, 62.3; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{19}H_{28}O_{11}Na$ 455.1529, found 455.1538.

1'-(p-methylbenzyl)sucrose ***(6j)***. White solid (79.5 mg, 89%): mp 85–87 °C; $[\alpha]_D$ +58 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 7.25 (d, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 5.38 (d, *J* = 3.7 Hz, 1H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.21 (d, *J* = 8.5 Hz, 1H), 4.08 – 4.00 (m, 1H), 3.83 – 3.54 (m, 9H), 3.39 (t, *J* = 4.8 Hz, 1H), 3.35 (brs, 1H), 2.33 (s, 3H); ^{13}C NMR (68 MHz, CD_3OD) δ 138.7, 136.5, 130.1, 129.2, 105.3, 94.0, 83.5, 78.8, 75.4, 74.7, 74.6, 74.3, 73.2, 71.4, 71.0, 63.3, 62.2, 21.1; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{20}H_{30}O_{11}Na$ 469.1686, found 469.1693.

1'-(m-methylbenzyl)sucrose ***(6k)***. White solid (83.0 mg, 93%): mp 86–88 °C; $[\alpha]_D$ +57 (*c* 1 CH_3OH); ^1H NMR (270 MHz, CD_3OD) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.17 (s, 1H), 7.14 (d, *J* = 7.5 Hz,

1H), 7.08 (d, *J* = 7.5 Hz, 1H), 5.38 (d, *J* = 3.8 Hz, 1H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.21 (d, *J* = 8.5 Hz, 1H), 4.06 – 4.00 (m, 1H), 3.83 – 3.54 (m, 9H), 3.38 (dd, *J* = 5.8, 3.9 Hz, 1H), 3.35 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (68 MHz, CD_3OD) δ 139.5, 139.3, 129.7, 129.53, 129.45, 126.1, 105.3, 94.1, 83.5, 78.8, 75.4, 74.8 (2C), 74.4, 73.3, 71.4, 71.1, 63.3, 62.3, 21.4; HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{20}H_{30}O_{11}Na$ 469.1686, found 469.1678.

1'-(o-methylbenzyl)sucrose ***(6l)***. White solid (81.2 mg, 91%): mp 83–85 °C; $[\alpha]_D$ +58 (*c* 0.2 CH_3OH); ^{1}H NMR (270 MHz, CD_3OD) δ 7.33 – 7.30 (m, 1H), 7.18 – 7.10 (m, 3H), 5.38 (d, *J* = 3.8 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.21 (d, *J* = 8.5 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.83 – 3.56 (m, 9H), 3.38 (dd, *J* = 6.1, 3.8 Hz, 1H), 3.34 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (68 MHz, CD_3OD) δ 138.2, 137.4, 131.3, 130.0, 129.1, 126.9, 105.4, 94.1, 83.6, 78.7, 75.5, 74.8, 74.4, 73.3, 73.1, 71.5, 71.1, 63.3, 62.3, 18.9; HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{20}H_{30}O_{11}Na$ 469.1686, found 469.1698.

1'-(p-methoxylbenzyl)sucrose ***(6m)***. White solid (83.2 mg, 90%): mp 83–85 °C; $[\alpha]_D$ +59 (*c* 1 CH_3OH); ^{1}H NMR (270 MHz, CD_3OD) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.37 (d, *J* = 3.8 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 4.18 (d, *J* = 8.5 Hz, 1H), 4.06 – 3.96 (m, 1H), 3.85 – 3.52 (m, 9H), 3.78 (s, 3H), 3.37 (t, *J* = 4.6 Hz, 1H), 3.34 (s, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 161.1, 131.5, 130.8, 114.9, 105.3, 94.1, 83.6, 78.9, 75.5, 74.8, 74.41, 74.40, 73.3, 71.5, 70.9, 63.4, 62.3, 55.7; HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{20}H_{30}O_{12}Na$ 485.1635, found 485.1645.

1'-[p-(trifluorodiazirinyl)benzyl]sucrose ***(6n)***. White solid (98.3 mg, 91%): mp 73–75 °C; $[\alpha]_D$ +50 (*c* 1 CH_3OH); ^{1}H NMR (270 MHz, CD_3OD) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H),

5.39 (d, J = 3.9 Hz, 1H), 4.70 (d, J = 12.7 Hz, 1H), 4.63 (d, J = 12.7 Hz, 1H), 4.23 (d, J = 8.5 Hz, 1H), 4.09 – 3.97 (m, 1H), 3.84 – 3.57 (m, 9H), 3.39 (dd, J = 5.7, 2.6 Hz, 1H), 3.35 (s, 1H); ^{13}C NMR (68 MHz, CD_3OD) δ 142.2, 129.4, 129.3, 127.7, 123.8 (q, J = 273.7 Hz), 105.2, 94.1, 83.6, 78.7, 75.4, 74.7, 74.4, 73.7, 73.2, 71.4, 71.3, 63.3, 62.3, 29.4 (q, J = 40.5 Hz); ^{19}F-NMR (470 MHz, CD_3OD): δ = -67.15 ppm. HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{21}H_{27}N_2O_{11}F_3Na$ 563.1465, found 563.1488.

*1'-((1-methyl)benzyl)sucrose (**6o**).* White solid (87.5 mg, 98%, mixture of (*R*)- and (*S*)-isomers): mp 60–62 °C; $[\alpha]_D$ +53 (*c* 1 CH_3OH); ^{1}H NMR (270 MHz, CD_3OD) δ 7.37 – 7.21 (m, 5H), 5.33 (d, J = 3.8 Hz, 0.5H) and 5.30 (d, J = 3.8 Hz, 0.5H), 4.63 – 4.48 (m, 1H), 4.27 (d, J = 8.5 Hz, 0.5H) and 4.15 (d, J = 8.5 Hz, 0.5H), 4.01 (t, J = 7.9 Hz, 1H), 3.81 – 3.49 (m, 9H), 3.43 – 3.33 (m, 2H), 1.44 – 1.40 (m, 3H); ^{13}C NMR (68 MHz, CD_3OD) δ 145.1 and 145.0, 129.68 and 129.65, 128.7, 127.5 and 127.4, 105.6 and 105.1, 94.03 and 93.96, 83.7 and 83.6, 80.3 and 80.2, 79.2 and 78.6, 75.5 and 75.4, 74.9 and 74.7, 74.4 and 74.3, 73.3 and 73.2, 71.4, 70.1 and 69.2, 63.4 and 63.2, 62.2, 24.4 and 24.2; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{20}H_{30}O_{11}Na$ 469.1686, found 469.1687.

*1-bromo-4-(ethoxymethyl)benzene (**8a**).*[22] Colorless oil (63.2 mg, 98%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.45 (s, 2H), 3.53 (q, J = 7.0 Hz, 2H), 1.24 (t, J = 7.0 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.8, 131.6, 129.4, 121.4, 71.9, 65.9, 15.1; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_9H_{10}BrO$ 214.9895, found 214.9910.

*1-bromo-4-(propoxymethyl)benzene (**8b**).*[23] Colorless oil (65.3 mg, 95%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.45 (s, 2H), 3.42 (t, J = 6.7 Hz, 2H), 1.70 – 1.59 (m, 2H), 0.94 (t, J = 6.7 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.9, 131.5, 129.3, 121.4, 72.2, 72.0, 22.8, 10.5; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{10}H_{12}BrO$ 229.0051, found 229.0046.

*1-bromo-4-(butoxymethyl)benzene (**8c**).*[24] Colorless oil (72.9 mg, 100%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 4.44 (s, 2H), 3.46 (t, J = 6.5 Hz, 2H), 1.65 – 1.54 (m, 2H), 1.46 – 1.35 (m, 2H), 0.92 (t, J = 6.5 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.9, 131.5, 129.3, 121.3, 72.1, 70.3, 31.7, 19.2, 13.8; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{11}H_{14}BrO$ 243.0208, found 243.0189.

*1-bromo-4-(sec-butoxymethyl)benzene (**8d**).* Colorless oil (71.4 mg, 98%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 4.46 (q, J = 12.1 Hz, 2H), 3.49 – 3.38 (m, 1H), 1.66 – 1.43 (m, 2H), 1.18 (d, J = 6.2 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 138.4, 131.5, 129.3, 121.2, 76.4, 69.5, 29.1, 19.0, 9.7; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{11}H_{14}BrO$ 243.0208, found 243.0182.

*1-bromo-4-(tert-butoxymethyl)benzene (**8e**).*[24] White solid (64.9 mg, 89%): mp 45–47 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.39 (s, 2H), 1.28 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 139.1, 131.4, 129.1, 120.9, 73.6, 63.4, 27.6; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{11}H_{14}BrO$ 243.0208, found 243.0191.

*1-bromo-4-(phenethoxymethyl)benzene (**8f**).* Colorless oil (80.3 mg, 92%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43 (d, J = 8.3 Hz, 2H), 7.28 – 7.13 (m, 7H), 4.46 (s, 2H), 3.67 (t, J = 8.3 Hz, 2H), 2.91 (t, J = 8.3 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 139.0, 137.6, 131.5, 129.3, 129.0, 128.5, 126.3, 121.4, 72.1, 71.3, 36.3; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{15}H_{14}BrO$ 291.0208, found 291.0219.

*1-bromo-4-((4-nitrophenethoxy)methyl)benzene (**8g**).* white solid (87.7 mg, 87%): mp 93–95 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.14 (d, J = 7.2 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.13 (d, J = 7.1 Hz, 2H), 4.45 (s, 2H), 3.72 (t, J = 6.5 Hz, 2H), 3.01 (t, J = 6.2 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ

147.2, 146.8, 137.1, 131.6, 129.8, 129.2, 123.6, 121.6, 72.3, 70.1, 36.1; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{15}H_{15}BrNO_3$ 336.0235, found 336.0218.

*1-bromo-4-((3-phenylpropoxy)methyl)benzene (**8h**).*[25] Colorless oil (83.3 mg, 91%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.30 – 7.16 (m, 7H), 4.44 (s, 2H), 3.47 (t, J = 6.3 Hz, 2H), 2.71 (t, J = 7.5 Hz, 2H), 1.98 – 1.88 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.0, 137.8, 131.6, 129.4, 128.6, 128.4, 125.9, 121.4, 72.1, 69.6, 32.3, 31.2; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{16}H_{16}BrO$ 305.0364, found 305.0386.

*1-((benzyloxy)methyl)-4-bromobenzene (**8i**).*[26] Colorless oil (79.8 mg, 96%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.36 – 7.30 (m, 5H), 7.24 (d, J = 8.4 Hz, 2H), 4.55 (s, 2H), 4.50 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 138.1, 137.4, 131.6, 129.5, 128.5, 127.9, 121.5, 72.2, 71.3; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{14}H_{12}BrO$ 277.0051, found 277.0061.

*1-bromo-4-(((4-nitrobenzyl)oxy)methyl)benzene (**8j**).* Pale yellow oil (90.8 mg, 94%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.22 (d, J = 8.8 Hz, 2H), 7.54 – 7.49 (m, 4H), 7.25 (d, J = 8.8 Hz, 2H), 4.64 (s, 2H), 4.57 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 147.6, 145.7, 136.7, 131.8, 129.5, 127.9, 123.8, 122.0, 72.0, 70.9; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{14}H_{13}BrNO_3$ 322.0079, found 322.0084.

*(R)-1-bromo-4-((1-phenylethoxy)methyl)benzene (**8k**).*[27] Colorless oil (82.9 mg, 95%): $[\alpha]_D$ +78 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3 Hz, 2H), 7.37 – 7.28 (m, 5H), 7.18 (d, J = 8.3 Hz, 2H), 4.48 (q, J = 6.5 Hz, 1H), 4.38 (d, J = 12.2 Hz, 1H), 4.25 (d, J = 12.2 Hz, 1H), 1.48 (d, J = 6.5 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.6, 137.8, 131.5, 129.4, 128.6, 127.7, 126.4, 121.4, 69.5, 24.0; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{15}H_{14}BrO$ 291.0208, found 291.0197; HPLC (Chiralcel OJ column, *n*-hexane:*i*-PrOH = 85:15, 0.5 mL/min, 210 nm), t_R (major) = 19.45 min, t_R

(minor) = 15.08 min; ee = 96%

*(S)-1-bromo-4-((1-phenylethoxy)methyl)benzene (**8l**).*[27] Colorless oil (81.2 mg, 93%): $[\alpha]_D$ -78 (*c* 1 $CHCl_3$); ^1H NMR, ^{13}C NMR and HRMS-ESI are identical with **8k**. HPLC (Chiralcel OJ column, *n*-hexane:*i*-PrOH = 85:15, 0.5 mL/min, 210 nm), t_R (major) = 14.99 min, t_R (minor) = 19.45 min; ee = 95%

*(2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-(((4-bromobenzyl)oxy)methyl)-6-methoxytetrahydro-2H-pyran (**8m**).*[28] Colorless oil (180.4 mg, 95%): $[\alpha]_D$ +23 (*c* 1 $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.34 – 7.12 (m, 17H), 4.98 (d, J = 10.9 Hz, 1H), 4.87 – 4.38 (m, 8H), 3.98 (t, J = 9.2 Hz, 1H), 3.77 – 3.62 (m, 4H), 3.55 (dd, J = 9.6, 3.6 Hz, 1H) 3.37 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 138.9, 138.32, 138.26, 137.1, 131.6, 129.5, 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 127.7, 121.6, 98.2, 82.1, 79.9, 77.7, 75.8, 75.0, 73.4, 72.6, 70.0, 68.7, 55.1; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{35}H_{37}BrO_6Na$ 657.1651, found 657.1677.

*(3aR,4R,6R,6aR)-4-(((4-bromobenzyl)oxy)methyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (**8n**).* Colorless oil (91.8 mg, 82%): $[\alpha]_D$ -45 (*c* 1 $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 4.96 (s, 1H), 4.67 (d, J = 5.9 Hz, 1H), 4.57 (d, J = 5.9 Hz, 1H), 4.50 (s, 2H), 4.39 – 4.33 (m, 1H), 3.54 – 3.41 (m, 2H), 3.29 (s, 3H), 1.48 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.2, 131.6, 129.3, 121.6, 112.5, 109.4, 85.1, 82.1, 72.5, 71.2, 54.8, 26.4, 24.9; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{16}H_{21}BrO_5Na$ 397.0450, found 397.0432.

*1-nitro-4-((1-phenylethoxy)methyl)benzene (**8o**).* Colorless oil (71.7 mg, 93%, mixture of (*R*)- and (*S*)-isomers): ^1H NMR (270 MHz, $CDCl_3$) δ 8.19 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H),

7.38 – 7.31 (m, 5H), 4.56 – 4.40 (m, 3H), 1.53 (d, J = 6.5 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 147.4, 146.5, 143.1, 128.7, 127.9, 127.8, 126.3, 123.6, 78.2, 69.1, 23.9; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{15}H_{15}NO_3Na$ 280.0950, found 280.0970.

*1-nitro-4-(2-(1-phenylethoxy)ethyl)benzene (**8p**).* Colorless oil (73.2 mg, 90%, mixture of (*R*)- and (*S*)-isomers): ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.13 (d, J = 8.7 Hz, 2H), 7.36 – 7.19 (m, 7H), 4.37 (q, J = 6.5 Hz, 1H), 3.55 (t, J = 6.5 Hz, 2H), 2.95 (t, J = 6.5 Hz, 2H), 1.40 (d, J = 6.5 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 147.5, 146.7, 143.6, 129.9, 128.5, 127.6, 126.2, 123.5, 78.4, 68.3, 36.3, 23.8; HRMS-ESI (m/z) $[M + K]^+$ calcd for $C_{16}H_{17}NO_3K$ 310.0846, found 310.0832.

*(2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-methoxy-6-((1-phenylethoxy)methyl)tetrahydro-2H-pyran (**8q**).*[29] Colorless oil (156.8 mg, 92%, mixture of (*R*)- and (*S*)-isomers): $[\alpha]_D$ +18 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.34 – 7.17 (m, 20H), 4.98 (d, J = 10.8 Hz, 1H), 4.90 – 4.77 (m, 3H), 4.69 – 4.55 (m, 3H), 4.32 (q, J = 6.5 Hz, 1H), 3.98 (t, J = 9.5 Hz, 1H), 3.71 – 3.51 (m, 4H), 3.44 (dd, J = 10.6, 4.1 Hz, 1H), 3.35 (s, 3H), 1.42 (d, J = 6.5 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.7, 138.9, 138.5, 138.4, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 126.3, 98.1, 82.3, 79.9, 79.0, 77.8, 75.7, 75.0, 73.3, 70.2, 67.4, 55.0, 24.0; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{36}H_{40}O_6Na$ 591.2723, found 591.2728.

*(3aR,4R,6R,6aR)-4-methoxy-2,2-dimethyl-6-((1-phenylethoxy)methyl)tetrahydrofuro[3,4-d][1,3]dioxole (**8r**).* Colorless oil (83.2 mg, 90%, mixture of (*R*)- and (*S*)-isomers): $[\alpha]_D$ -43 (*c* 1 $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 5H), 4.93 (d, J = 3.6 Hz, 1H), 4.72 – 4.55 (m, 1H), 4.43 – 4.28 (m, 2H), 3.40 – 3.30 (m, 2H), 3.28 – 3.22 (m, 3H), 1.48 – 1.43 (m, 6H), 1.33 – 1.31 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.7 and 143.6, 128.5, 127.6, 126.3, 126.2, 112.4, 109.3, 85.5

and 85.4, 85.2, 82.3 and 82.1, 78.6 and 78.4, 69.6 and 69.5, 54.7 and 54.6, 26.4, 25.0, 24.0 and 23.9; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{17}H_{24}O_5Na$ 331.1521, found 331.1519.

*1,2-bis((4-bromobenzyl)oxy)ethane (**8s**).*[30] White solid (111.6 mg, 93%): mp 49–51 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 4H), 7.22 (d, J = 8.3 Hz, 4H), 4.52 (s, 4H), 3.64 (s, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.4, 131.6, 129.4, 121.5, 72.5, 69.6; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{16}H_{16}Br_2O_2Na$ 422.9394, found 422.9382.

*tri-O-(4-bromobenzyl)glycerol (**8t**).* Colorless oil (145.6 mg, 81%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 6H), 7.25 – 7.15 (m, 6H), 4.62 (s, 2H), 4.47 (s, 4H), 3.80 – 3.72 (m, 1H), 3.59 (d, J = 4.6 Hz, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.7, 137.3, 131.6, 131.5, 129.4, 129.3, 121.6, 121.5, 72.6, 71.5, 70.3; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{24}H_{23}Br_3O_3Na$ 620.9075, found 620.9046.

*bis(4-(trifluoromethyl)benzyl)ether (**4a**).*[26] Colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 4H), 7.48 (d, J = 8.0 Hz, 4H), 4.63 (s, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.1, 130.1 (q, J = 32.2 Hz), 127.7, 125.5 (q, J = 3.7 Hz), 124.2 (q, J = 271.9 Hz), 71.6; ^{19}F-NMR (470 MHz, $CDCl_3$): δ = -62.52 ppm; HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{16}H_{13}OF_6$ 335.0871, found 335.0894.

UV-vis Analysis of 6n in CH_3OH and CD_3OD. A methanolic solution (1 mM, 1 mL) of compound **6n** in a quartz cuvette was irradiated under 100 W black-light at a distance 1 cm from the surface of light source. The half-life ($t_{1/2}$) was calculated from the decrements of the absorbance around 356 nm.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H- and ^{13}C-NMR spectra, ^{1}H-NMR for different 1'-hydrogens of **1**, Kinetic investigation of benzylation for **1** in different solvents, Mass spectra of **6n** and corresponding photolysis products, HPLC chromatogram of **8k** and **8l**.

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Notes

The authors declare no competing financial interest.

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