JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b00016 • Publication Date (Web): 03 May 2019

Just Accepted

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Stable Benzylic (1-Ethynylcyclohexanyl)carbonates Protect Hydroxyl Moieties by The Synergistic Action of [Au]/[Ag]-catalytic System

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Abstract:

Chemical syntheses of oligosaccharides and glycosides call utilization of many protecting groups which can be installed or deprotected without affecting other functional groups present. Benzyl ethers are routinely used in the synthesis of glycans as they can be subjected to hydrogenolysis under neutral conditions. However, installation of benzyl ethers is often carried out under strong basic conditions using benzyl halides. Many a times, strongly basic conditions will be detrimental for some of the other sensitive functionalities (e.g. esters). Later introduced reagents such as benzyl trichloroacetimidate and BnOTf are not shelf-stable and hence, a new method is highly desirable. Taking a cue from the [Au]/[Ag]-catalyzed glycosidations, we have identified a method that enables protection of hydroxyl groups as benzyl, *p*-methoxy benzyl or naphthylenemethyl ethers using easily accessible and stable carbonate reagent. A number of saccharide derived alcohols were subjected to the benzylation successfully using catalytic amount of gold-phosphite and silver triflate. Furthermore, the protocol is suitable for even protecting menthol, cholesterol, serine, disaccharide-OH and furanosyl derived alcohol easily. Often utilized Benzylidene-, silyl-, olefins, benzoates, Troc- and Fmoc-, protecting groups do not get affected during the newly

identified protocol. Regioselective protection and one-pot installation of benzyl and *p*-methoxy benzyl ethers is demonstrated.

Introduction:

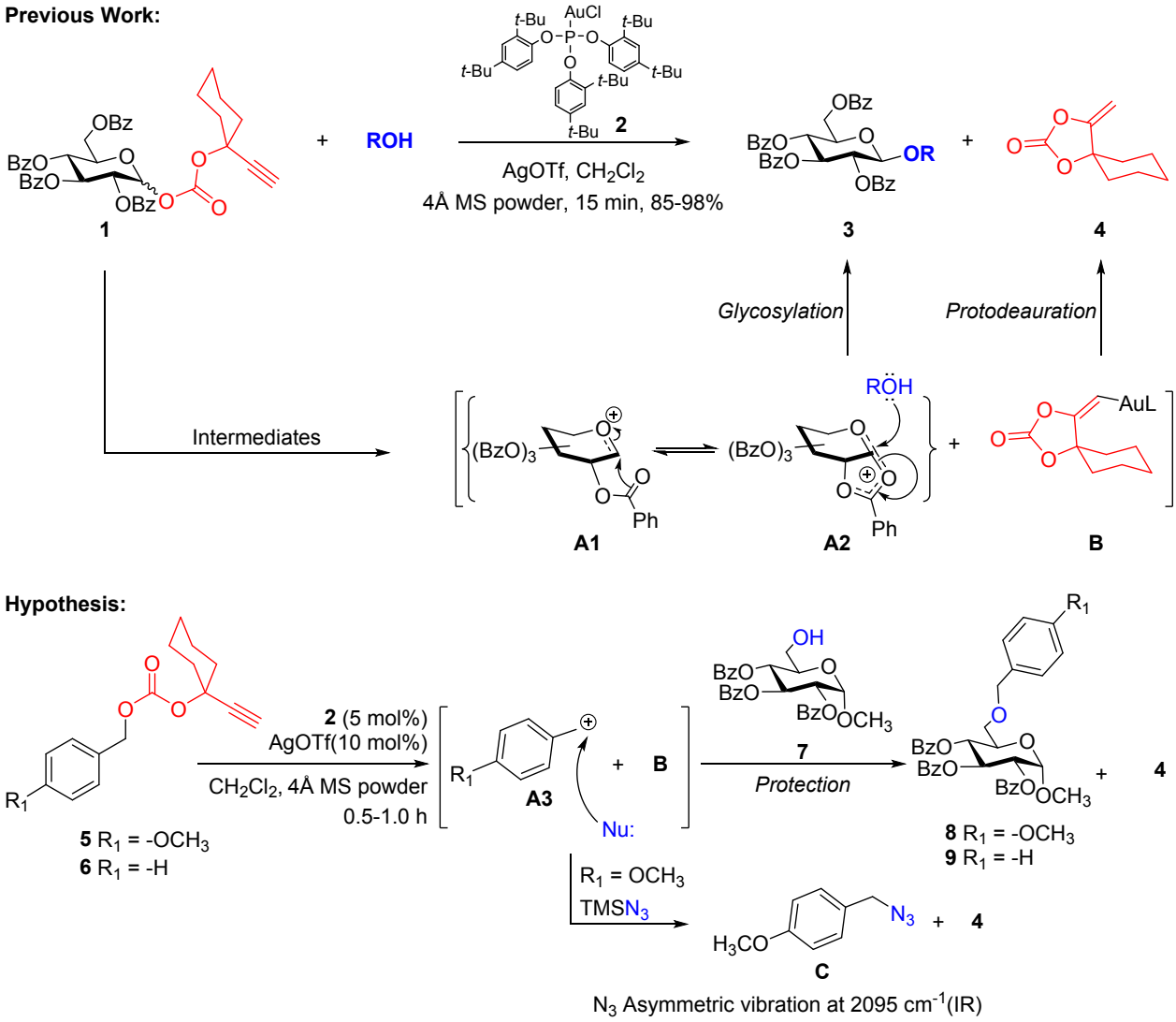
Chemical glycosidation is a condensation reaction involving a glycosyl donor and an acceptor which will be repeatedly utilized while synthesizing oligosaccharides. Chemical synthesis of oligosaccharides is still a challenging task as regioselectivity among multiple reactive alcohols is highly demanding.[1] Often, the glycosyl donor and the acceptor are protected in order to reduce undesirable competition among similarly reactive alcohols.[2] Often, glycosyl donors are prepared in a fully protected form with a leaving group at the *C*-1 position whereas the acceptor (ROH) is synthesized in such a way that a lone hydroxyl group is left for undergoing the glycosylation. Facile syntheses of large and branched oligosaccharides generally exploit protection and deprotection strategies on demand.[3,4]

Several decades of research culminated into the development of chemistry for the protection and/or deprotection of alcohols.[5] Benzylation of alcohols to afford benzyl ethers is one of the most celebrated reactions that many oligosaccharide syntheses utilize. Frequently, benzylations are conducted under NaH/DMF/benzyl halides conditions which are strongly alkaline and hence, base-labile protecting groups also get affected.[6] Later introduced BnOTf[7] permits benzylation under neutral conditions whereas benzyl trichloroacetimidates[8a-d] enable syntheses of benzyl ethers under acid catalysis using catalytic amount of TfOH. A gold-catalyzed microwave assisted synthesis of unsymmetrical ethers using alcohols as alkylating agents was recently reported by Liu *et al.*[8e] However, moisture sensitivity and instability of BnOTf and benzyl trichloroacetamidates are the major limitations of these two methods.[8]

Therefore, installation of benzylic ethers under mild catalytic conditions that provide excellent yields will be highly rewarding.

Results and Discussion

Recently, glycosyl (1-ethynylcyclohexyl)carbonates (e.g. **1**) were identified as glycosyl donors under the synergistic catalytic action of Au-phosphite (**2**) and AgOTf to afford the glycosides **3** with the extrusion of the spirocyclic carbonate **4**.[9] The reaction was postulated to undergo through the activation of alkyne by the [Au]/[Ag]-catalytic system resulting in the formation of a carbocation at the *C*-1 position extruding the Au-alkylidene **B**.[9] Thus formed carbocation is highly stabilized due to the formation of the oxocarbenium ion intermediate **A1** which will be in equilibrium with the trioxolenium ion intermediate **A2** (Scheme 1). Attack of the aglycon ROH



Scheme 1: Benzylic (1-ethynylcyclohexyl)carbonates for the synthesis of benzylic ethers

led to glycosides and the protodeauration resulted in the formation of the spirocyclic carbonate **4**. Push of electrons from the exo-cyclic oxygen is envisaged as one of the possible factors for the stabilization of the carbocation at the anomeric position. In this scenario, we hypothesized that the benzylic carbonates shall also undergo similar reaction to afford benzylic cation **A3** releasing the intermediate **B** and thus formed benzylic cation shall be available for the attack of nucleophiles. To verify our hypothesis, benzylic carbonates **5** and **6** were respectively prepared from commercially available 4-methoxy benzyl alcohol and benzyl alcohol in

excellent yields using easily accessible and stable 1-ethynylcyclohexyl (4-nitrophenyl) carbonate.[9] A model reaction was carried out between glucose-derived alcohol **7** and the carbonate **5** in the presence of 4Å MS powder, 5mol% of Au-phosphite (**2**) and 10mol% of AgOTf at 25 ^{0}C to obtain corresponding PMB-ether **8** in 95% yield and the cyclic carbonate **4**. Similar reaction with benzyl (1-ethynylcyclohexyl)carbonate **6** with alcohol **7** afforded the benzyl protected monosaccharide **9** in 84% yield. Gratifyingly, the benzoate esters were found to be intact during the reaction, the reaction was complete in 30min and most importantly, the benzylic carbonate is noticed to be very stable. Formation of the benzylic cation **A3** was established by conducting the reaction with the $TMSN_3$ instead of alcohol **7** to afford the 4-methoxy benzyl azide (**C**) and the cyclic carbonate **4**. Azide formation was confirmed by the characteristic N_3 asymmetric vibration at 2095 cm^{-1}.[10a]

A plausible mechanism can be advanced based on the literature precedence though a thorough mechanistic investigation is pending (Figure 1).[9] *p*-Methoxy benzyl carbonate **5** can be activated either by the *in situ* formed LAuOTf to give intermediate **A4** or by the sub-stoichiometric [Au,Ag] clusters to give intermediate **A5**. Intermediates **A4** and **A5** undergo 1,5-*exo*-dig cyclization giving the earlier postulated alkylidene intermediate **B** releasing the much desired benzylic carbocation **A6** that shall be attacked by the alcohol **7** to give PMB-ether **8** releasing a proton that facilitates the protodeauration to give the cyclic carbonate **4**.[10b,c] It might also be possible to obtain the product **8** by concerted bimolecular substitution reaction releasing the alkylidene **B** due to the attack of the nucleophile **7**.[10b,c]

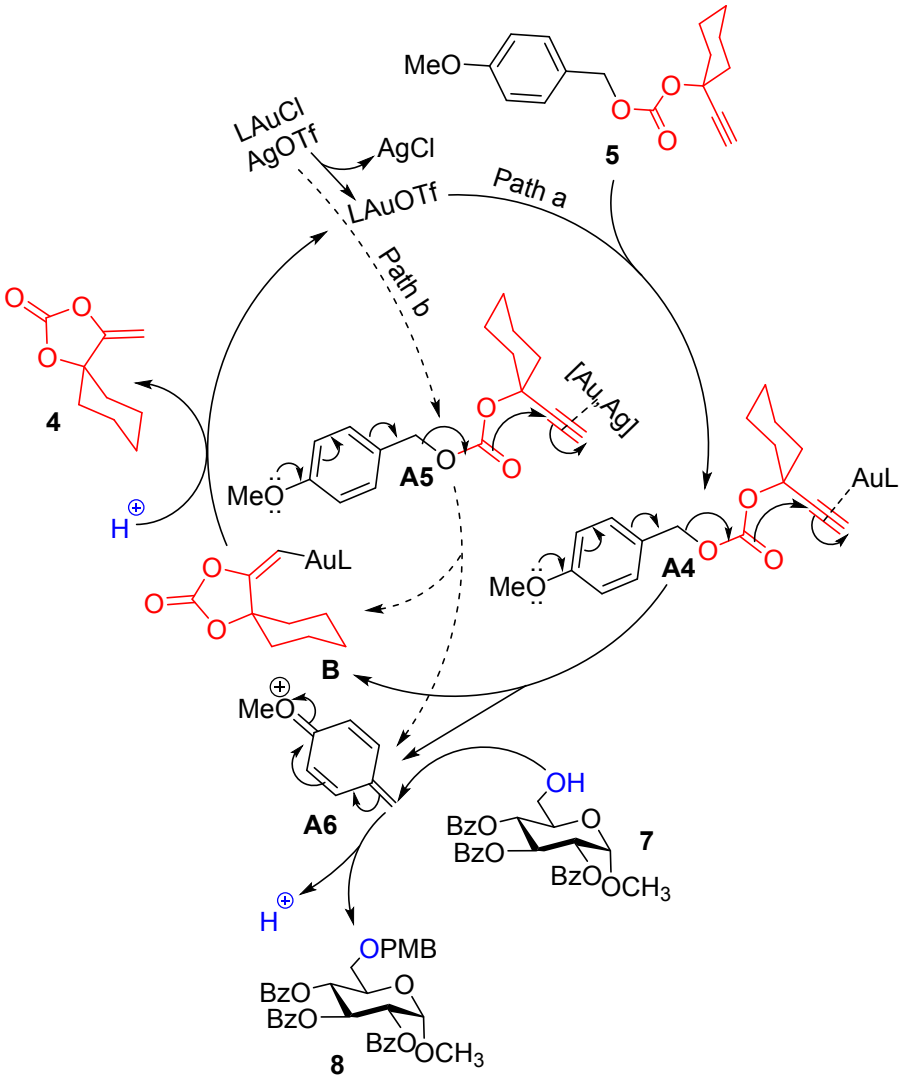


Figure 1. Plausible mechanism

Encouraged by the identification of the new benzylation protocol, we further targeted the application of this method for the synthesis of benzyl ethers to understand the substrate scope. Accordingly, it has been noticed that olefins do not get affected under these experimental conditions as evident while perform reactions on alcohols **10**,[11a] **12**,[11b] **14**[11c] to obtain corresponding PMB-ethers **11**,**13**,**15**. Noticeably, the Troc-protection on the glucosamine derivative **12** and the silyl ethers in compounds **12** and **13** were stable for these conditions. In addition, the current procedure is suitable for installation of benzyl ethers on alcohols which

are alicyclic (e.g. menthol **16**), steroidal (e.g. cholesterol **18**), amino acid (e.g. serine **20**[11d]) to afford respectively PMB-ethers **17**, **19** and **21** in very high yields (Chart 1). Furthermore, the reaction is found to be suitable for installation of PMB ethers or benzyl ethers on disaccharide (e.g. **22**[11e]), benzylidene glucoside (e.g **24**, **26**[11f]) and furanoside **28**[3] to give respective ethers **23**,**25**,**27**,**29**.

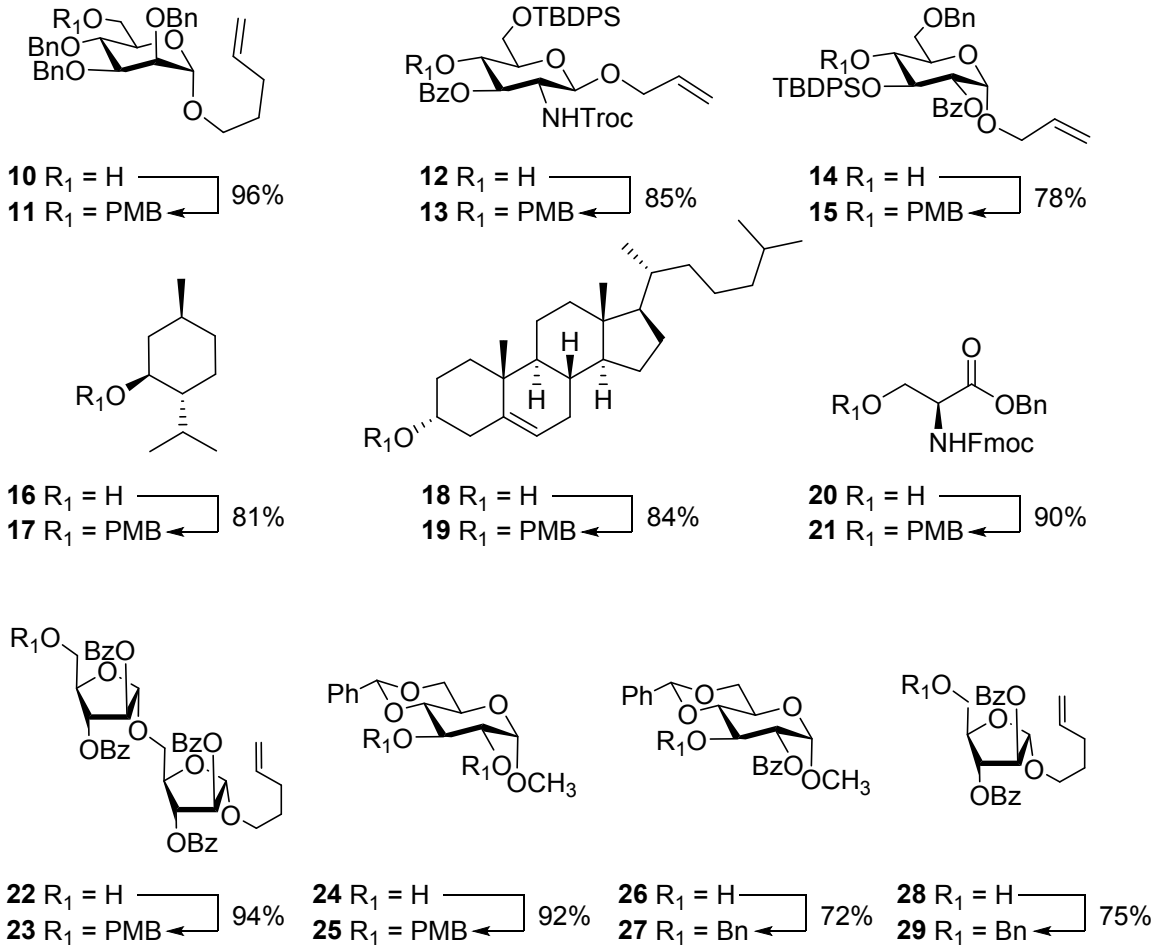
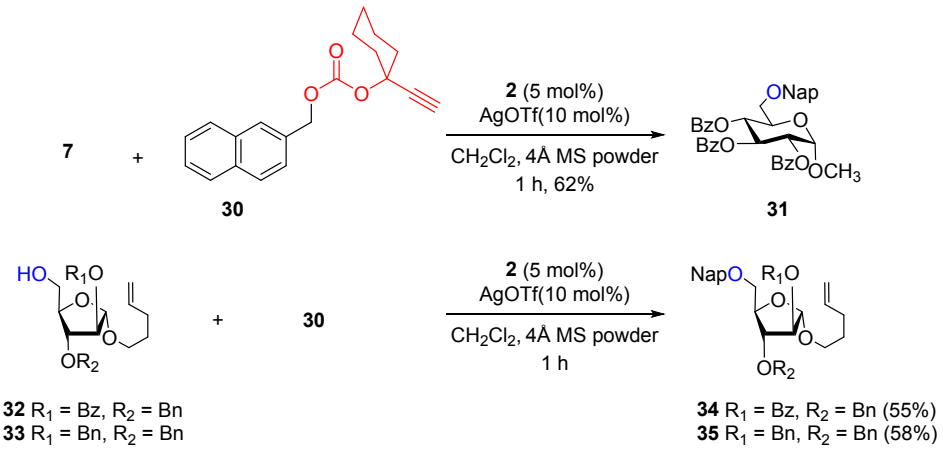


Chart 1: Substrate Scope

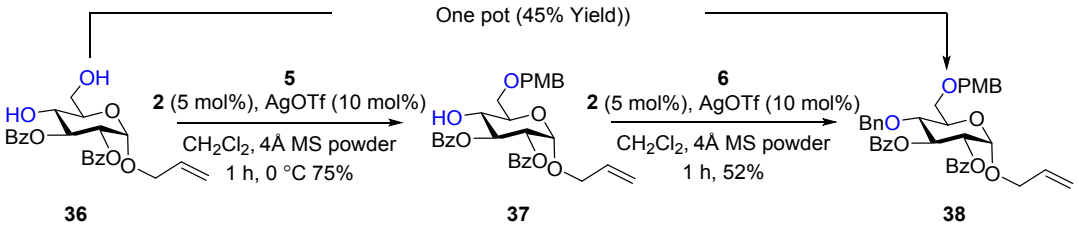
Another benzyl ether in the form of Nap-ethers gained momentum as their deprotection conditions are orthogonal to the benzyl ethers.[12] In view of this, alcohol **7** was treated with Nap-carbonate **30** in the presence of catalytic quantities of Au-phosphite (**2**) and AgOTf in CH_2Cl_2 to notice formation of Nap-ether **31** in 62% yield. Similarly, arabinofuranosyl alcohols

32[3] and **33**[3] reacted with carbonate **30** to afford desired Nap-ethers **34** and **35** in 55% and 58% yield respectively (Scheme 2).



Scheme 2: Synthesis of Nap-ethers

1^0-Alcohols are better nucleophiles than 2^0-alcohols and as a consequence, the attack of the nucleophile on the benzylic cation shall also follow the same trend. Hence, easily accessible allyl glucoside **36**[11c] possessing both primary and secondary alcohols was subjected to the benzylation conditions using PMB-carbonate **5** in the presence of catalyst **2** and AgOTf in CH_2Cl_2 to notice formation of the C6-PMB blocked glucoside **37** in 75% yield. In continuation, the PMB ether **37** was subjected to identical conditions with Bn-carbonate **6** to afford the benzyl ether **38** in 52% of isolated yield. All the reaction conditions are identical except the substrates and hence, a one pot conversion of diol **36** to compound **38** was envisioned so that the purification is minimized and overall pot-economy shall improve as a result. Accordingly, the two independent reactions are conducted one after the other in one pot without isolating the intermediate compound **37** to obtain the final compound **38** in 45% over all isolated yield (Scheme 3).



Scheme 3: PMB and Bn ethers can be introduced orthogonally and in one pot as well

To summarize, a new method for the installation of benzyl-, 4-methoxy benzyl- and Nap-ethers has been identified taking cue from the [Au]/[Ag]-catalyzed alkynyl carbonate glycosylation chemistry. These conditions are mild enough to synthesize benzyl ethers bearing olefins, silyl ethers, Troc-, Fmoc-, benzyl esters, benzoates, and benzylidenes. The mechanism was postulated to be similar to that of the alkynyl glycosyl carbonate glycosidation. One pot installation of PMB and benzyl ethers is yet another new feature of the current protocol.

Experimental Section

General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification.1-Ethynylcyclohexanol, *p*-nitrophenyl chloroformate, menthol (**16**), cholesterol (**18**), Compound **24** and all metal salts were purchased from Sigma-Aldrich. Unless otherwise reported all reactions were performed under Nitrogen atmosphere. Removal of solvent *in vacuo* refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. Analytical thin-layer chromatography was performed on pre-coated silica plates (F_{254}, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. IR spectra were recorded on a FT-IR spectrometer. NMR spectra were recorded either on a 400 or a 500 MHz with $CDCl_3$ as the solvent and TMS as the

internal standard. High resolution mass spectroscopy (HRMS) was performed using an ESI-TOF mass analyser. Low resolution mass spectroscopy (LRMS) was performed on UPLC-MS with SWADESI-TLC interface.

1-Ethynylcyclohexyl (4-methoxybenzyl) carbonate (5): DMAP (2.65 g, 21.71 mmol) was added to a CH_2Cl_2 (20 mL) solution of p-methoxybenzyl alcohol (1.77 mL, 14.48 mmol) and stirred for 30 min. 1-Ethynylcyclohexyl 4-nitrophenyl carbonate (5.03 g, 17.37 mmol) was added in three portions (3x1.7 g) in 30 min intervals. The reaction mixture was stirred for 3 h, concentrated *in vacuo* to obtain the crude residue that was purified by silica gel column chromatography using 5% ethyl acetate-hexane as mobile phase to obtain compound **5** (3.97 g, 95% yield) as a white crystalline solid.

1-Ethynylcyclohexyl (benzyl) carbonate (6): DMAP (2.03 g, 16.65 mmol) was added to a CH_2Cl_2 (15 mL) solution of benzyl alcohol (1.13 mL, 11.10 mmol) and stirred for 30 min. 1-Ethynylcyclohexyl 4-nitrophenyl carbonate (3.85 g, 13.32 mmol) was added in three portions (3x1.3 g) in 30 min intervals. The reaction mixture was stirred for 3 h, concentrated *in vacuo* to obtain the crude residue that was purified by silica gel column chromatography using 2% ethyl acetate-hexane as mobile phase to obtain compound **6** (2.7 g, 94% yield) as a white crystalline solid.

1-Ethynylcyclohexyl (napthalen-2-yl methyl) carbonate (30): DMAP (1.16 g, 16.65 mmol) was added to a CH_2Cl_2 (10 mL) solution of 2-napthalenemethanol (1.00 g, 6.32 mmol) and stirred for 30 min. 1-Ethynylcyclohexyl 4-nitrophenyl carbonate (2.19 g, 7.6 mmol) was added in three portions (3x700 mg) in 30 min intervals. The reaction mixture was stirred for 3 h, concentrated *in vacuo* to obtain the crude residue that was purified by silica gel column

chromatography using 2% ethyl acetate-hexane as mobile phase to obtain compound **30** (2.7 g, 94% yield) as a white amorphous solid.

Procedure for 1-(azidomethyl)-4-methoxybenzene synthesis (C): A solution of carbonate **5** (50 mg, 1 equiv) in CH_2Cl_2 (2 mL) was treated with excess trimethylsilyl azide (300 µL) and freshly activated 4Å molecular sieves powder, stirred for 15 min. Gold-phosphite catalyst **2** (7.62 mg, 0.05 equiv) and AgOTf (4.45 mg, 0.10 equiv) was added and stirred for 1 h. Preparative TLC was performed to avoid compound loss due to the high volatile nature of azide **C**.

General procedure of the gold-catalyzed PMB-ether preparation: To a solution of alcohol (**7,10,12,14,16,18,20,22, or 24**) (1.0 equiv) and the carbonate **5** (1.0 equiv per –OH group) in anhydrous CH_2Cl_2 (3 mL/100 mg of alcohol) was added freshly activated 4Å MS powder (30 mg/mL) and stirred for 20 minutes under nitrogen atmosphere. To the reaction mixture at 25 ^oC, gold-phosphite **2** (5 mol%) and AgOTf (10 mol%) were added and stirred for 30 minutes. At the end of the reaction as adjudged by the TLC examination, the reaction mixture was passed through a bed of celite and the filtrate was concentrated *in vacuo* to obtain a residue that was purified by silica gel column chromatography using ethyl acetate and hexane as mobile phase.

This procedure was adopted for the synthesis of compounds **8**,**11**,**13**,**15**,**17**,**19**,**21**,**23**, and **25**.

General procedure of the gold-catalyzed Benzyl ether preparation: To a solution of alcohol (**7, 26** or **28**) (1.0 equiv) and the carbonate **6** (1.2 equiv per –OH group) in anhydrous CH_2Cl_2 (3 mL/100 mg of alcohol) was added freshly activated 4Å MS powder (30 mg/mL) and stirred for 20 min under nitrogen atmosphere. To the reaction mixture at 25 ^oC, gold-phosphite

2 (5 mol%) and AgOTf (10 mol%) were added and stirred for 1 h. At the end of the reaction as adjudged by the TLC examination, the reaction mixture was passed through a bed of celite and the filtrate was concentrated *in vacuo* to obtain a residue that was purified by silica gel column chromatography using ethyl acetate and hexane as mobile phase.

This procedure was adopted for the synthesis of compounds **9**, **27** and **29**.

General procedure of the gold-catalyzed Nap-ether preparation: Alcohol (**7, 32** or **33**) (1.0 equiv) was dissolved in anhydrous CH_2Cl_2 (3 mL/ 100 mg alcohol) and freshly activated 4Å MS powder (30 mg/mL) was added and stirred for 15 min. Gold-phosphite **2** (5 mol%) and AgOTf (10 mol%) were added to the reaction mixture under nitrogen atmosphere. A solution of carbonate **30** (1.5 equiv per –OH group) in dry CH_2Cl_2 was added dropwise and slowly and stirred for 1 h at 25 ^oC. At the end of the reaction as adjudged by the TLC examination, the reaction mixture was passed through a bed of celite and the filtrate was concentrated *in vacuo* to obtain a residue that was purified by silica gel column chromatography using ethyl acetate and hexane as mobile phase.

This procedure was adopted for the synthesis of compounds **31**, **34** and **35**.

Procedure for selective primary PMB-ether protection: Alcohol (**36**) (170 mg, 0.4 mmol) was dissolved in anhydrous CH_2Cl_2 (5 mL/100 mg alcohol, to maintain the higher dilution percentage) and freshly activated 4Å MS powder was added and stirred for 20 min. Gold-phosphite **2** (10 mol%) and AgOTf (10 mol%) were added to the reaction mixture under nitrogen atmosphere. A solution of carbonate **5** (0.3 equiv, 38 mg) in 0.5 mL of dry CH_2Cl_2 was added dropwise and slowly at 0 ^oC and this process was repeated for three more times with addition of 150 mg of carbonate **5** (1.2 equiv, 0.52 mmol) in total and stirred for 30 min at

0 °C. At the end of the reaction as adjudged by the TLC examination, the reaction mixture was passed through a bed of celite and the filtrate was concentrated *in vacuo* to get a residue that was purified by silica gel column chromatography using ethyl acetate:hexane (8:92) as mobile phase to obtain compound **37** as a gum (134 mg, 75% yield).

Procedure for one-pot synthesis of PMB and Bn-ethers: Selective PMB protection was performed on alcohol **36** (120 mg) by following above delineated procedure. In the same pot, gold-phosphite **2** (5 mol%) and AgOTf (10 mol%) were added afterwards. Next, a solution of carbonate **6** (2 equiv dissolved in 1 mL of dry CH_2Cl_2) was added in a slow dropwise manner under inert atmosphere. The progress of the reaction was monitored by TLC examination, after the completion of the reaction, the mixture was passed through a bed of celite and the filtrate was concentrated *in vacuo* to obtain a residue that was purified by silica gel column chromatography using ethyl acetate and hexane as mobile phase obtaining compound **38** in an overall yield of 45% (50 mg).

Characterization Data

1-Ethynylcyclohexyl 4-methoxybenzyl carbonate (**5**): White crystalline solid, mp (^{0}C): 56-59, IR (cm^{-1}, $CHCl_3$): 3264, 2938, 2860,1746,1447,1269, 1077, 911, 730, 578; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.20 – 1.37 (ddq, J = 13.7, 9.3, 4.7 Hz, 1H), 1.45 – 1.55 (m, 1H), 1.54 – 1.73 (m, 4H), 1.77 – 1.91 (dt, J = 10.5, 4.0 Hz, 2H), 2.16 (dt, J = 10.5, 4.0 Hz, 2H), 2.62 (s, 1H), 3.77 (s, 3H), 5.07 (s, 2H), 6.83 – 6.88 (m, 2H), 7.28 – 7.33 (m, 2H); ^{13}C{^{1}H} NMR (100.67 MHz, $CDCl_3$): δ 22.6, 22.6, 25.1, 36.9, 36.9, 55.3, 69.2, 74.9, 77.6, 83.1, 114.0, 114.0, 127.5, 130.4, 130.4, 152.9, 159.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{20}O_4Na$ 311.1259; Found 311.1262.

1-Ethynylcyclohexyl benzyl carbonate (**6**): Crystalline solid, mp (^{0}C): 59-63; IR (cm^{-1}, $CHCl_3$): 3266, 2932, 2861, 1746, 1514, 1448,1231, 1077, 971, 788, 555; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.31 (ddq, J = 13.7, 9.3, 4.7 Hz, 1H), 1.46 – 1.58 (m, 1H), 1.57 – 1.74 (m, 4H), 1.86 (dt, J = 10.5, 4.0 Hz, 2H), 2.18 (dt, J = 10.5, 4.0 Hz, 2H), 2.63 (s, 1H), 5.15 (s, 2H), 6.89 – 7.75 (m, 5H); ^{13}C{^{1}H} NMR (100.67 MHz, $CDCl_3$): δ 22.6, 22.6, 25.1, 36.9, 36.9, 69.3, 75.0, 77.7, 83.1, 128.5, 128.5, 128.5, 128.6, 128.5, 135.4, 152.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{18}O_3Na$ 281.1154; Found 281.1151.

1-(azidomethyl)-4-methoxybenzene (**C**): Liquid; IR (cm^{-1}, $CHCl_3$): 2922,2851,2095 (N_3),1611,1513,1461; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 3.84 (s, 3H), 4.29 (s, 2H), 6.94 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_8H_9N_3ONa$ 186.0643; Found 186.0638.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*p*-methoxybenzyl) α-D-glucopyranoside (**8**): Eluent for purification: 15% ethyl acetate in *n*-hexane; yield 117 mg from 100 mg of compound **7** (95%); Thick syrup; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.5): +68.9^0; IR (cm^{-1}, $CHCl_3$): 2925, 2852, 1727, 1512, 1451, 1366, 1249, 1098, 1033, 754, 707 ; ^{1}H NMR (400.31 MHz, $CDCl_3$). δ 3.50 (s, 3H), 3.62 – 3.71 (m, 2H), 3.75 (s, 3H), 4.25 (ddd, *J* = 10.2, 4.5, 2.9 Hz, 1H), 4.44 – 4.58 (m, 2H), 5.26 – 5.34 (m, 2H), 5.68 (t, *J* = 9.9 Hz, 1H), 6.15 (t, *J* = 9.6 Hz, 1H), 6.74 – 6.80 (m, 2H), 7.20 – 7.26 (m, 2H), 7.27 – 7.35 (m, 2H), 7.36 – 7.48 (m, 5H), 7.50 – 7.57 (m, 2H), 7.87 – 8.03 (m, 6H);^{13}C{^{1}H} NMR (100.67 MHz, $CDCl_3$): δ 55.2, 55.6, 68.1, 68.9, 69.5, 70.7, 72.2, 73.3, 97.0, 113.7, 113.7, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 129.1, 129.2, 129.3, 129.5, 129.5, 129.7, 129.7, 129.7, 129.8, 129.8, 129.9, 129.9, 133.0, 133.2, 133.3, 159.1, 165.2, 165.8, 165.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{34}O_{10}Na$ 649.2050; Found 649.2059.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl α-D-glucopyranoside (**9**): Eluent for purification: 15% ethyl acetate in *n*-hexane; yield 150 mg from 147 mg of compound **8** (84%); Thick syrup; $[\alpha]^{25}_{D}$ ($CHCl_3$, *c* 0.5): $+37.6^0$; IR (cm^{-1}, $CHCl_3$): 3890, 3738, 2924, 2857, 1730, 1600, 1452, 1366, 1273, 1173, 1042, 917, 710 ; ^1H NMR (400.31 MHz, $CDCl_3$): δ 3.34 (s, 3H), 3.54 (t, *J* = 3.8 Hz, 2H), 4.10 (dt, *J* = 7.6, 4.5 Hz, 1H), 4.42 (dd, *J* = 12.0, 10.2 Hz, 2H), 5.08 – 5.19 (m, 2H), 5.52 (t, *J* = 9.9 Hz, 1H), 6.00 (t, *J* = 9.5 Hz, 1H), 7.02 – 7.18 (m, 7H), 7.19 – 7.30 (m, 5H), 7.35 – 7.39 (m, 2H), 7.73 – 7.78 (m, 4H), 7.84 – 7.85 (m, 2H); $^{13}C\{^1H\}$ NMR (100.67 MHz, $CDCl_3$): δ 55.7, 68.7, 69.0, 69.6, 70.7, 72.2, 73.8, 97.1, 127.7, 127.8, 127.8, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 129.2, 129.2, 129.4, 129.8, 129.8, 129.9, 129.9, 130.0, 130.0, 133.1, 133.3, 133.4, 137.7, 165.3, 165.9, 165.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{32}O_9Na$ 619.1944; Found 619.1940.

Pent-4-enyl 2,3,4-tri-*O*-benzyl-6-*O*-(*p*-methoxybenzyl) α-D-mannopyranoside (**11**): Eluent for purification: 15% ethyl acetate in *n*-hexane; yield 177 mg from 150 mg of compound **10** (96%); Syrup; $[\alpha]^{25}_{D}$ ($CHCl_3$, *c* 0.9): $+10.2^0$; IR (cm^{-1}, $CHCl_3$): 2925, 1738, 1738, 1610, 1511, 1453, 1365, 1216, 1096, 910, 818, 697; ^1H NMR (400.31 MHz, $CDCl_3$): δ 1.65 (q, *J* = 6.9 Hz, 2H), 2.09 (q, *J* = 6.7 Hz, 2H), 3.40 (dt, *J* = 9.7, 6.4 Hz, 1H), 3.68 – 3.74 (m, 2H), 3.76 – 3.82 (m, 6H), 3.93 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.99 – 4.04 (m, 1H), 4.49 (d, *J* = 3.7 Hz, 1H), 4.52 (d, *J* = 2.7 Hz, 1H), 4.63 – 4.66 (m, 3H), 4.73 – 4.80 (m, 2H), 4.89 (s, 1H), 4.90 (d, *J* = 10.6 Hz, 1H), 4.93 – 5.07 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 6.84 – 6.87 (m, 2H), 7.13 – 7.21 (m, 2H), 7.26 – 7.36 (m, 10H), 7.36 – 7.44 (m, 5H); $^{13}C\{^1H\}$ NMR (100.67 MHz, $CDCl_3$): δ 28.7, 30.4, 55.3, 67.0, 68.9, 71.9, 72.3, 72.7, 73.1, 74.9, 75.1, 75.3, 80.4, 98.0, 113.8, 113.8, 115.0, 127.7, 127.7, 127.7, 127.8, 127.8, 128.0, 128.0, 128.1, 128.1, 128.4, 128.4, 128.4, 128.5,

128.5, 128.5, 129.6, 129.6, 130.6, 138.2, 138.6, 138.6, 138.7, 159.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{40}H_{46}O_7Na$ 661.3141; Found 661.3146.

Allyl 2-*deoxy*-2-(((2,2,2-trichloroethoxy)carbonyl)amino)-3-*O*-benzoyl-4-*O*-(*p*-methoxybenzyl)-6-*O*-(*tert*-butyldiphenylsilyl) β-D-glucopyranoside (**13**): Eluent for purification: 20% ethyl acetate in *n*-hexane; yield 136 mg from 143 mg of compound **12** (85%); Yellow syrup; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): $+30.8^0$; IR (cm^{-1}, $CHCl_3$): 2933, 1738, 1516, 1367, 1216, 1105, 1036, 707; ^1H NMR(400.31 MHz, $CDCl_3$): δ 1.16 (s, 9H), 3.72 (s, 3H), 3.88 (ddd, *J* = 9.9, 3.8, 2.0 Hz, 1H), 3.93 – 4.00 (m, 3H), 4.04 (ddt, *J* = 12.8, 6.4, 1.3 Hz, 1H), 4.17 – 4.26 (m, 2H), 4.50 – 4.59 (m, 3H), 4.73 (d, *J* = 12.0 Hz, 1H), 5.02 (d, *J* = 3.6 Hz, 1H), 5.24 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.32 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.44 (d, *J* = 10.1 Hz, 1H), 5.67 (dd, *J* = 10.8, 9.1 Hz, 1H), 5.92 (dddd, *J* = 17.0, 10.4, 6.4, 5.3 Hz, 1H), 6.64 – 6.67 (m, 2H), 6.94 – 6.99 (m, 2H), 7.41 – 7.50 (m, 8H), 7.57 – 7.63 (m, 1H), 7.78 (m, 4H), 8.06 – 8.11 (m, 2H);$^{13}C\{^1H\}$ NMR (100.67 MHz, $CDCl_3$): δ 19.4, 26.9, 26.9, 26.9, 54.6, 55.1, 62.6, 68.2, 72.1, 74.1, 74.3, 74.6, 75.7, 95.3, 96.3, 113.7, 118.2, 127.6, 127.6, 127.8, 127.8, 128.4, 128.4, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.9, 129.9, 133.1, 133.2, 133.4, 133.6, 135.7, 135.7, 135.9, 135.9, 154.4, 159.2, 166.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{48}O_9NCl_3SiNa$ 878.2062 Found 878.2059.

Allyl 2-*O*-benzoyl-3-*O*-*tert*-butyldiphenylsilyl-4-O-(*p*-methoxybenzyl)-6-*O*-benzyl α-D-glucopyranoside (**15**): Eluent for purification: 15% ethyl acetate in *n*-hexane; yield 80 mg from 74 mg of compound **14** (78%); Solid, mp (^0C): 170-172; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): $+104.6^0$; IR (cm^{-1}, $CHCl_3$): 2929, 2858,1726, 1610, 1513, 1454, 1367, 1246, 1160, 1105, 927, 822, 741, 610; ^1H NMR (400.31 MHz, $CDCl_3$): δ 0.95 (s, 9H), 3.70 – 3.80 (m, 2H), 3.82 – 3.87 (m, 5H), 3.88 – 3.93 (m, 1H), 4.01 – 4.08 (m, 1H), 4.48 (d, *J* = 10.6 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.64 –

4.74 (m, 2H), 4.80 (d, *J* = 10.6 Hz, 1H), 4.97 (dt, *J* = 10.5, 1.3 Hz, 1H), 5.01 – 5.10 (m, 2H), 5.13 (dd, *J* = 3.9, 1.3 Hz, 1H), 5.64 (ddt, *J* = 16.0, 10.4, 5.2 Hz, 1H), 6.75 – 6.90 (m, 2H), 6.93 – 7.03 (m, 2H), 7.10-7.17 (m, 2H), 7.18 – 7.26 (m, 3H), 7.31 – 7.38 (m, 4H), 7.39 – 7.51 (m, 7H), 7.53-7.63 (m, 2H), 7.70-7.81 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100.67 MHz, $CDCl_3$): δ 19.6, 26.8, 26.8, 26.8, 55.3, 68.0, 68.7, 70.0, 73.5, 73.6, 73.7, 74.7, 78.9, 94.9, 113.6, 113.6, 116.5, 127.2, 127.2, 127.5, 127.5, 127.6, 127.6, 127.8, 128.0, 128.0, 128.5, 128.5, 129.0, 129.0, 129.1, 129.5, 129.7, 129.7, 129.7, 130.6, 132.4, 133.4, 133.6, 133.9, 135.3, 135.3, 136.0, 136.0, 138.0, 159.0, 165.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{47}H_{52}O_8SiNa$ 795.3329; Found 795.3332.

1-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-4-methoxybenzene (**17**): Eluent for purification: 10% ethyl acetate in *n*-hexane; yield 78 mg from 55 mg of compound **16** (81%); Liquid; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): -74.5; IR (cm^{-1}, $CHCl_3$): 3882,2951, 2922, 2865, 1739, 1612, 1513, 1456, 1369, 1246, 1040, 820, 591; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 0.70 (d, *J* = 6.9 Hz, 3H), 0.86 (s, 1H), 0.89 (s, 3H), 0.92 (s, 3H), 0.94 – 0.98 (m, 1H), 1.26 (s, 3H), 1.59 – 1.67 (m, 2H), 2.22 (d, *J* = 46.8 Hz, 2H), 3.11 – 3.18 (m, 1H), 3.79 (s, 3H), 4.33 (d, *J* = 11.1 Hz, 1H), 4.58 (d, *J* = 11.1 Hz, 1H), 6.86 (d, *J* = 6.6 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H);$^{13}C\{^{1}H\}$ NMR (100.67 MHz, $CDCl_3$): δ 16.0, 21.0, 22.4, 23.2, 25.5, 31.6, 34.6, 40.3, 48.3, 55.2, 70.0, 78.4, 113.7, 113.7, 129.3, 129.3, 131.2, 159.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{28}O_2Na$ 299.1987 Found: 299.1992.

O-(*p*-methoxybenzyl)cholesterol (**19**): Eluent for purification: 10% ethyl acetate in *n*-hexane; yield 220 mg from 200 mg of compound **18** (84%); Pale brown solid, mp (^0C): 109-111; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): -16.3^0; IR (cm^{-1}, $CHCl_3$): 2937, 2861, 1737, 1512, 1459, 1369, 1245, 1099, 1035, 818, 526; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 0.71 (s, 3H), 0.87 – 0.98 (m, 10H), 1.04 (s,

3H), 1.10-1.17 (m, 7H), 1.27 – 1.43 (m, 6H), 1.46 – 1.64 (m, 7H), 1.82 – 2.10 (m, 5H), 2.29 (ddd, *J* = 13.5, 11.0, 2.8 Hz, 1H), 2.44 (ddd, *J* = 13.3, 4.8, 2.3 Hz, 1H), 3.29 (tt, *J* = 11.2, 4.5 Hz, 1H), 3.82 (s, 3H), 4.52 (s, 2H), 5.37 (dt, *J* = 5.5, 1.9 Hz, 1H), 6.88 – 6.93 (m, 2H), 7.27 – 7.33 (m, 2H); $^{13}C\{^1H\}$ NMR (100.67 MHz, $CDCl_3$): δ 11.9, 18.8, 19.4, 21.1, 22.6, 22.9, 23.9, 24.3, 28.0, 28.3, 28.5, 31.9, 32.0, 35.8, 36.2, 36.9, 37.3, 39.2, 39.5, 39.8, 42.3, 50.2, 55.3, 56.2, 56.8, 69.6, 78.3, 113.8, 113.8, 121.5, 129.2, 129.2, 131.2, 141.0, 159.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{54}O_2Na$ 529.4022; Found 529.4023.

Benzyl *N*-(((9H-fluoren-9-yl)methoxy)carbonyl)-*O*-(*p*-methoxybenzyl)-L-serinate (**21**): Eluent for purification: 25% ethyl acetate in *n*-hexane; yield 140 mg from 105 mg of compound **20** (90%); Yellow solid; mp (^{0}C): 97-100; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): -0.1^0; IR (cm^{-1}, $CHCl_3$): 3441, 3208, 2953, 1728, 1513, 1452, 1364, 1297, 1243, 1036, 744, 528 ; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 3.76 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.82 (s, 3H), 3.97 (dt, *J* = 9.6, 2.9 Hz, 1H), 4.29 (t, *J* = 7.3 Hz, 1H), 4.46 (m, 4H), 5.18 – 5.33 (m, 2H), 5.81 – 5.93 (m, 1H), 6.90 (dd, *J* = 8.7, 2.6 Hz, 2H), 7.21 (dd, *J* = 8.6, 2.6 Hz, 2H), 7.33 – 7.41 (m, 7H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.68 (dt, *J* = 7.7, 3.9 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100.67 MHz, $CDCl_3$): δ 47.2, 54.6, 55.3, 67.3, 69.5, 73.0, 113.9, 113.9, 120.0, 120.0, 125.2, 125.3, 127.1, 127.2, 127.8, 127.8, 128.2, 128.2, 128.4, 128.4, 128.6, 128.6, 129.4, 129.4, 129.5, 135.4, 141.3, 141.3, 143.8, 144.0, 156.1, 159.4, 170.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{31}O_6NNa$ 560.2049; Found 560.2051.

4-pentenyl 2,3-di-*O*-benzoyl-5-*O*-[2,3-di-*O*-benzoyl-5-*O*-(*p*-methoxybenzyl)-α-D-arabinofuranosyl]-α-D-arabinofuranoside (**23**): Eluent for purification: 20% ethyl acetate in *n*-hexane; yield 270 mg from 250 mg of compound **22** (94%); Yellow solid; mp (^{0}C): 167-170; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): +0.4^0; IR (cm^{-1}, $CHCl_3$): 3888, 3828, 3393, 2927, 1724, 1605, 1258, 1176, 1107, 1032, 914, 711, 525 ; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.73 – 1.82 (m, 2H), 2.16 – 2.23

(m, 2H), 3.54 (dt, *J* = 9.5, 6.1 Hz, 1H), 3.78 (s, 3H), 3.79 – 3.91 (m, 3H), 3.96 (dd, *J* = 11.1, 3.1 Hz, 1H), 4.24 (dd, *J* = 11.2, 4.6 Hz, 1H), 4.49 (td, *J* = 4.7, 3.0 Hz, 1H), 4.59 – 4.66 (m, 3H), 4.98 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.23 (s, 1H), 5.45 (s, 1H), 5.50 – 5.54 (m, 2H), 5.62 (d, *J* = 1.2 Hz, 1H), 5.64 – 5.67 (m, 1H), 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 6.78 – 6.86 (m, 2H), 7.26 – 7.34 (m, 4H), 7.38 – 7.54 (m, 8H), 7.56 – 7.63 (m, 2H), 7.94 – 8.11 (m, 8H); $^{13}C\{^{1}H\}$ NMR (100.67 MHz, $CDCl_3$): δ 28.7, 30.3, 55.2, 66.2, 66.6, 69.2, 73.2, 77.7, 77.7, 81.5, 81.7, 81.8, 82.5, 105.6, 105.9, 113.7, 113.7, 114.9, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 129.0, 129.2, 129.2, 129.3, 129.3, 129.3, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 130.0, 133.1, 133.3, 133.3, 133.4, 138.1, 159.1, 165.1, 165.4, 165.6, 165.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{51}H_{50}O_{14}Na$ 909.3098; Found 909.3094.

Methyl 2,3-di-*O*-(*p*-methoxybenzyl)-4,6-*O*-benzylidene α-D-glucopyranoside (**25**): Eluent for purification: 15% ethyl acetate in *n*-hexane; yield 85 mg from 50 mg of compound **24** (92%); Thick syrup; $[\alpha]^{25}_{D}$ ($CHCl_3$, *c* 0.5): $+44.9^0$; IR (cm^{-1}, $CHCl_3$): 3070, 2890, 1682, 1533, 1450, 1265, 1216, 1090, 917, 839; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 3.38 (s, 3H), 3.51 (dd, J = 9.3, 3.7 Hz, 1H), 3.57 (t, J = 9.4 Hz, 1H), 3.69 (t, J = 10.2 Hz, 1H), 3.78 (s, 3H), 3.78 (t, J = 10.2 Hz, 1H), 3.79 (s, 3H), 4.00 (t, J = 9.3 Hz, 1H), 4.25 (dd, J = 10.0, 4.7 Hz, 1H), 4.53 (d, J = 3.7 Hz, 1H), 4.62 (d, J = 11.9 Hz, 1H), 4.72 – 4.86 (m, 3H), 5.53 (s, 1H), 6.73 – 6.99 (m, 4H), 7.20 – 7.34 (m, 4H), 7.37 (d, J = 7.0 Hz, 3H), 7.46 – 7.53 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100.67 MHz, $CDCl_3$): δ 55.2, 55.3, 55.3, 62.4, 69.1, 73.4, 75.0, 78.3, 78.7, 82.1, 99.3, 101.3, 113.7, 113.7, 113.8, 113.8, 126.1, 126.1, 128.2, 128.2, 128.9, 129.7, 129.7, 129.8, 129.8, 130.3, 130.9, 137.5, 159.2, 159.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{34}O_8Na$ 545.2151; Found 545.2147.

Methyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene α-D-glucopyranoside (**27**): Eluent for purification: 20% ethyl acetate in *n*-hexane; yield 221 mg from 250 mg of compound **26** (72%); White solid; mp (^{0}C): 135-139; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): +128.2^0; IR (cm^{-1}, $CHCl_3$): 3020, 2923, 1722, 1271, 1214, 1098, 996, 745, 668, 580 ; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 3.42 (s, 3H), 3.85 (q, *J* = 9.7, 9.2 Hz, 2H), 3.97 (td, *J* = 9.8, 4.6 Hz, 1H), 4.25 (t, *J* = 9.3 Hz, 1H), 4.38 (dd, *J* = 10.1, 4.6 Hz, 1H), 4.79 – 4.95 (m, 2H), 5.11 (d, *J* = 3.8 Hz, 1H), 5.16 (ddd, *J* = 9.5, 3.8, 0.8 Hz, 1H), 5.67 (s, 1H), 7.19 – 7.25 (m, 3H), 7.26 – 7.30 (m, 2H), 7.41 – 7.52 (m, 5H), 7.54 – 7.59 (m, 2H), 7.60 – 7.66 (m, 1H), 8.07 – 8.11 (m, 2H);^{13}C{^{1}H} NMR (100.67 MHz, $CDCl_3$): δ 55.4, 62.4, 69.0, 73.6, 74.8, 75.8, 82.3, 98.0, 101.4, 126.1, 126.1, 127.6, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 129.0, 129.7, 130.0, 130.0, 133.3, 137.4, 138.2, 166.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{28}O_7Na$ 499.1733; Found 499.1739.

4-pentenyl 2,3-di-*O*-benzoyl-5-*O*-benzyl α-D-arabinofuranoside (**29**): Eluent for purification: 15% ethyl acetate in *n*-hexane; yield 92 mg from 100 mg of compound **28** (75%); Syrup; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): -18.8^0; IR (cm^{-1}, $CHCl_3$): 2927, 1725, 1600, 1451, 1362, 1264, 1108,1067, 1029, 710; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.70 – 1.80 (m, 2H), 2.14 – 2.24 (m, 2H), 3.55 (dt, *J* = 9.5, 6.2 Hz, 1H), 3.78 – 3.85 (m, 1H), 3.85 – 3.95 (m, 2H), 4.43 – 4.50 (m, 1H), 4.67 (s, 2H), 4.97 (ddd, *J* = 10.1, 2.0, 1.1 Hz, 1H), 5.02 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.26 (s, 1H), 5.48 (d, *J* = 1.3 Hz, 1H), 5.52 (d, *J* = 4.8 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 7.24 – 7.32 (m, 3H), 7.34 – 7.42 (m, 4H), 7.42 – 7.48 (m, 2H), 7.53 – 7.61 (m, 2H), 7.97 – 8.03 (m, 2H), 8.06 – 8.10 (m, 2H); ^{13}C{^{1}H} NMR (100.67 MHz, $CDCl_3$): 28.9, 30.4, 66.8, 69.9, 73.8, 77.9, 81.9, 82.4, 105.8, 115.0, 127.7, 127.8, 127.8, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 129.3, 129.5, 130.0, 130.0, 130.0, 130.0, 133.5, 133.5, 138.1, 138.2, 165.5, 165.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{32}O_7Na$ 539.2046; Found 539.2045.

1-ethynylcyclohexyl (naphthalen-2-ylmethyl) carbonate (**30**): White amorphous solid; mp (^{0}C): 59-62; IR (cm^{-1}, $CHCl_3$): 3290, 2940, 2863, 1770, 1593, 1493, 1268, 1206, 1008, 771; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.23 – 1.40 (m, 1H), 1.49 – 1.58 (m, 1H), 1.59 – 1.75 (m, 4H), 1.82 – 1.93 (m, 2H), 2.15 – 2.24 (m, 2H), 2.64 (d, *J* = 1.4 Hz, 1H), 5.32 (s, 2H), 7.44 – 7.54 (m, 3H), 7.80 – 7.89 (m, 4H); ^{13}C{^{1}H} NMR (100.67 MHz, $CDCl_3$): 22.6, 22.7, 25.1, 36.9, 36.9, 69.5, 75.0, 77.8, 83.1, 126.0, 126.4, 126.4, 127.7, 127.8, 128.2, 128.5, 132.8, 133.3, 133.3, 152.9; HRMS (ESI-TOF) m/z: M^+ Calcd for $C_{20}H_{20}O_3$ 308.1412; Found 308.1412.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(naphthalene-2-ylmethyl) α-D-glucopyranoside (**31**): Eluent for purification: 12% ethyl acetate in *n*-hexane; yield 119 mg from 150 mg of compound **7** (62%); Syrup; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): +55.9^0; IR (cm^{-1}, $CHCl_3$): 2924, 2855, 1728, 1600, 1452, 1366, 1269, 1171, 1100, 1041, 974, 857, 756, 711; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 3.53 (s, 3H), 3.78 (t, *J* = 3.8 Hz, 2H), 4.31 (dt, *J* = 7.6, 4.5 Hz, 1H), 4.77 (dd, *J* = 12.0, 10.2 Hz, 2H), 5.32 – 5.39 (m, 2H), 5.75 (t, *J* = 9.9 Hz, 1H), 6.20 (t, *J* = 9.5 Hz, 1H), 7.31 – 7.55 (m, 12H), 7.73 – 7.80 (m, 4H), 7.90 – 7.94 (m, 4H), 8.03 – 8.04 (m, 2H); ^{13}C{^{1}H} NMR (100.67 MHz, $CDCl_3$): δ 55.6, 68.6, 68.9, 69.6, 70.7, 72.2, 73.8, 97.1, 125.8, 125.8, 126.0, 126.7, 127.7, 127.9, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 129.1, 129.1, 129.3, 129.7, 129.7, 129.7, 129.7, 130.0, 130.0, 133.0, 133.1, 133.2, 133.2, 133.4, 135.1, 165.3, 165.9, 165.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{39}H_{34}O_9Na$ 669.2101; Found 669.2097.

4-pentenyl 2-*O*-benzoyl-3-*O*-benzyl-5-*O*-naphthalene-2-ylmethyl α-D-arabinofuranoside (**34**): Eluent for purification: 15% ethyl acetate in *n*-hexane; yield 74 mg from 100 mg of compound **32** (55%); Liquid; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): +51.3^0; IR (cm^{-1}, $CHCl_3$): 3019, 2923, 2858, 1816, 1723, 1453, 1264, 1215, 1106, 816, 746, 669 ; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.69 – 1.79 (m, 2H), 2.11 – 2.21 (m, 2H), 3.51 (dt, *J* = 9.7, 6.4 Hz, 1H), 3.64 (dd, *J* = 10.7, 5.1 Hz, 1H),

3.72 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.79 (dt, *J* = 9.7, 6.6 Hz, 1H), 4.03 (d, *J* = 5.5 Hz, 1H), 4.35 (td, *J* = 5.3, 3.7 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 2H), 4.71 (q, *J* = 12.2 Hz, 1H), 4.80 (d, *J* = 12.1 Hz, 1H), 4.96 (ddd, *J* = 11.4, 2.2, 1.3 Hz, 1H), 5.04 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.18 (s, 1H), 5.38 (d, *J* = 1.4 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.19 – 7.27 (m, 3H), 7.28 – 7.33 (m, 4H), 7.38 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.44 – 7.53 (m, 3H), 7.71 – 7.76 (m, 3H), 7.79 – 7.83 (m, 1H), 7.92 – 7.97 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100.67 MHz, $CDCl_3$): δ 28.8, 30.3, 67.0, 69.5, 72.3, 73.6, 82.1, 82.1, 83.5, 106.2, 114.9, 125.8, 126.0, 126.2, 126.6, 127.8, 127.8, 128.0, 128.0, 128.0, 128.2, 128.4, 128.4, 128.5, 128.5, 129.5, 129.8, 129.8, 133.1, 133.3, 133.4, 135.5, 137.8, 138.3, 165.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{36}O_6Na$ 575.2410; Found 575.2411.

4-pentenyl 2,3-di-*O*-benzyl-5-*O*-naphthalene-2-ylmethyl α-D-arabinofuranoside (**35**): Eluent for purification: 12% ethyl acetate in *n*-hexane; yield 86 mg from 73 mg of compound **33** (58%); Liquid; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 0.5): $+39.6^0$; IR (cm^{-1}, $CHCl_3$): 2923, 2863, 1738, 1366, 1213, 1099, 909, 744, 699; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.71 – 1.79 (m, 2H), 2.14 – 2.23 (m, 2H), 3.48 (qd, *J* = 6.6, 3.3 Hz, 1H), 3.71 (tdd, *J* = 10.9, 8.4, 4.5 Hz, 2H), 3.81 (dtd, *J* = 9.8, 6.5, 3.3 Hz, 1H), 4.00 (dt, *J* = 6.9, 3.5 Hz, 1H), 4.08 (dd, *J* = 3.4, 1.5 Hz, 1H), 4.25 – 4.32 (m, 1H), 4.50 – 4.57 (m, 2H), 4.61 (dd, *J* = 11.9, 3.3 Hz, 2H), 4.78 (t, *J* = 3.6 Hz, 2H), 5.02 (dq, *J* = 10.3, 1.5 Hz, 1H), 5.05 – 5.13 (m, 2H), 5.88 (dqd, *J* = 16.9, 6.7, 3.4 Hz, 1H), 7.28 (tq, *J* = 7.5, 3.9, 3.1 Hz, 5H), 7.37 (d, *J* = 3.1 Hz, 5H), 7.51 (ddd, *J* = 8.9, 5.2, 2.3 Hz, 3H), 7.80 – 7.90 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100.67 MHz, $CDCl_3$): δ 28.8, 30.4, 67.0, 69.8, 72.0, 72.2, 73.5, 80.5, 83.6, 88.5, 106.2, 114.9, 125.9, 125.9, 126.1, 126.6, 127.7, 127.7, 127.8, 127.8, 127.9, 127.9, 127.9, 127.9, 128.2, 128.3, 128.3, 128.5, 128.5, 133.0, 133.3, 135.6, 137.6, 137.9, 138.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{38}O_5Na$ 561.2617; Found 561.2620.

Allyl 2,3,-di-*O*-benzoyl-6-*O*-(*p*-methoxybenzyl) α-D-glucopyranoside (**37**): white solid, mp (^{0}C): 153-156; $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): +140.6^0; IR (cm^{-1}, $CHCl_3$): 3497, 2922, 1725, 1609, 1513, 1453, 1275, 1103, 1037, 712, 562; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 3.23 (s, 1H), 3.75 – 3.89 (m, 5H), 3.97 – 4.11 (m, 3H), 4.27 (ddt, *J* = 13.3, 5.1, 1.6 Hz, 1H), 4.59 (q, *J* = 11.7 Hz, 2H), 5.16 (dq, *J* = 10.4, 1.4 Hz, 1H), 5.28 – 5.36 (m, 3H), 5.80 – 5.84 (m, 1H), 5.85 – 5.92 (m, 1H), 6.89 – 6.95 (m, 2H), 7.28 – 7.34 (m, 2H), 7.35 – 7.41 (m, 4H), 7.49 – 7.55 (m, 2H), 7.99 – 8.03 (m, 4H); ^{13}C{^{1}H} NMR (100.67 MHz, $CDCl_3$): δ 55.3, 68.6, 69.2, 70.5, 70.6, 71.4, 73.4, 74.1, 95.3, 113.9, 113.9, 117.6, 128.4, 128.4, 128.4, 128.4, 129.2, 129.4, 129.4, 129.8, 129.9, 129.9, 129.9, 129.9, 129.9, 133.3, 133.3, 133.5, 159.3, 166.0, 167.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{32}O_9Na$ 571.1944; Found 571.1945.

Allyl 2,3,-di-*O*-benzoyl-4-O-benzyl-6-*O*-(*p*-methoxybenzyl) α-D-glucopyranoside (**38**): Thick syrup $[\alpha]^{25}_D$ ($CHCl_3$, *c* 1.0): +164.4^0; IR (cm^{-1}, $CHCl_3$): 2966, 1725, 1615, 1508, 1480, 1134, 1037, 712, 533; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 3.70 – 3.74 (m, 1H), 3.82 (s, 3H), 3.85 (dd, *J* = 10.8, 2.7 Hz, 1H), 4.00 – 4.06 (m, 3H), 4.23 (ddt, *J* = 13.2, 5.1, 1.6 Hz, 1H), 4.44 – 4.56 (m, 3H), 4.68 (d, *J* = 11.7 Hz, 1H), 5.13 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.22 (dd, *J* = 10.2, 3.7 Hz, 1H), 5.29 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.32 (d, *J* = 3.8 Hz, 1H), 5.80 – 5.87 (m, 1H), 6.04 – 6.09 (m, 1H), 6.90 – 6.93 (m, 2H), 7.03 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.13 – 7.18 (m, 3H), 7.28 (s, 1H), 7.32 – 7.36 (m, 2H), 7.37 – 7.40 (m, 3H), 7.49 – 7.53 (m, 2H), 7.97 – 8.00 (m, 4H); ^{13}C{^{1}H} NMR (100.67 MHz, $CDCl_3$): δ 55.3, 67.7, 68.5, 70.3, 72.2, 72.8, 73.3, 74.7, 76.0, 95.3, 113.9, 113.9, 117.5, 127.7, 127.7, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 129.3, 129.7, 129.7, 129.8, 129.8, 129.9, 129.9, 133.0, 133.2, 133.5, 137.5, 139.3, 159.4, 165.7, 166.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{38}O_9Na$ 661.2414; Found 661.2412.

ASSOCIATED CONTENT

Supporting Information

Spectral charts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

SC and BM, MN acknowledges research fellowship from IISER Pune and CSIR-UGC-NET respectively. SH thanks financial assistance from DBT-New Delhi (BT/PR20820/MED/30/1875/2017). Authors thank Sandip Pasari for fruitful discussions.

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TOC Figure:

Stable Benzylic (1-Ethynylcyclohexanyl)carbonates Protect Hydroxyl Moieties by The Synergistic Action of [Au]/[Ag]-catalytic System