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A new route to 2-*C*- and 4-*C*-branched sugars by palladium–indium bromide-mediated carbonyl allylation

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Palladium-catalysed carbonyl allylations can be effectively applied to the regio- and diastereoselective synthesis of 2-*C*- and 4-*C*-branched sugars from allylic esters or carbonates *via* the formation of π-allylpalladium(II) intermediates and their reductive transmetalation with indium(I) bromide.

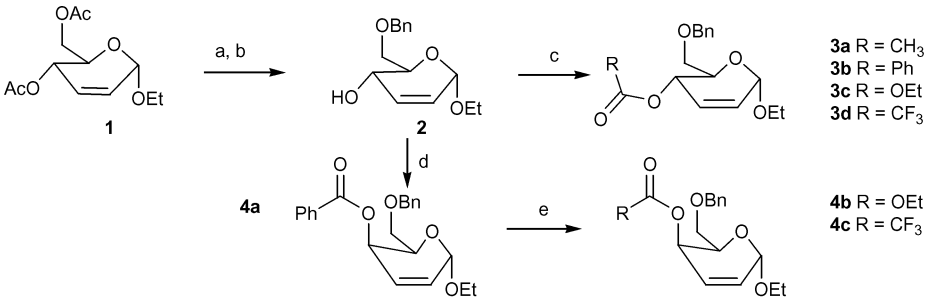
Introduction

The allylation reaction has received a great deal of attention as an important C–C bond forming reaction. In particular indium has emerged as the reagent of choice to mediate the reaction between an allyl halide and a carbonyl compound because of its environmentally benign properties allied with a high degree of chemo-, regio- and diastereoselectivity especially in aqueous media.[1] This methodology has been widely studied from a mechanistic point of view[2] and also for various synthetic applications.[3] For example, we recently reported the synthesis of *C*-branched sugars and *C*-disaccharides under indium promoted Barbier-type allylations in aqueous media.[4] In particular, starting with 4-bromo-2-enopyranosides, we could access different 2-*C*-branched sugars and 4-*C*-branched sugars as well as *C*-disaccharides.[4a,b] The preparation of the allylic indium reagent was also reported by reductive transmetalation of π-allylpalladium(II) complexes obtained from a large variety of allylic substrates with indium salts in various solvents.[5] This umpolung methodology was successfully extended to vinyloxiranes,[6] vinylaziridines,[7] *N*-acylnitroso Diels–Alder cycloadducts,[8] or π-allylpalladium species obtained from aryl iodides and allenes in the presence of palladium.[9] The higher availability of usable allylic acetates prompted us to examine the use of this methodology for preparing *C*-branched sugars in organic solvents as well as in aqueous media. Indeed, this avoids the preparation of bromide derivatives that are less accessible than hydroxyl groups naturally present in sugars.

Results and discussion

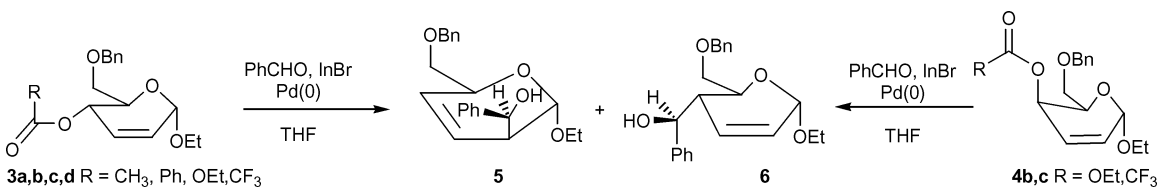
We started our investigation by studying the reactivity of compounds **3a–d**, which were readily available from **1**[10] (Scheme 1). After deacetylation (NaOMe/MeOH) and selective benzylation at O-6, the allylic alcohol **2**[11] was obtained in 85% yield in two steps. Adequate protection of the hydroxyl group under standard conditions furnished **3a–d** in nearly quantitative yields.

We then tested the allylation reaction of benzaldehyde with these substrates using indium(I) bromide and palladium(0) in anhydrous THF as the solvent (Scheme 2). As shown in Table 1, the yield in allylation compounds is dependant on the nature of the leaving group. Indeed, when the reaction was carried out with **3a** or **3b**, which possess an acetate or a benzoate leaving group, poor yields of coupling adducts were obtained even with heating and a high catalyst loading (20 mol% of $Pd(PPh_3)_4$) (entries 1 and 2). The yields of coupling products were greatly increased when carbonate or trifluoroacetate were used as leaving groups.



a) MeONa/MeOH b) i) Bu_2SnO, toluene, ii) nBu_4NBr, BnBr (**2**, 85% for 2 steps) c) Ac_2O, pyridine (**3a**, 100%) or PhCOCl, pyridine, DMAP (**3b**, 94%) or $ClCO_2Et$, pyridine, DMAP, CH_2Cl_2 (**3c**, 90%) or $(CF_3CO)_2O$, 2,6-lutidine, CH_2Cl_2 (**3d**, 92%). d) PPh_3, DEAD, $PhCO_2H$, THF **(4a**, 88%). e) i) MeONa/ MeOH ii) $ClCO_2Et$, pyridine, DMAP, CH_2Cl_2(**4b**, 89%) or $(CF_3CO)_2O$, 2,6-lutidine, CH_2Cl_2(**4c**, 80%).

Scheme 1 Reagents and conditions for synthesis of compounds **3a–d** and **4b** and **4c**.



Scheme 2 Palladium-catalysed carbonyl allylation of allylic substrates with benzaldehyde.

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Table 1 Palladium-catalysed allylation of benzaldehyde with indium bromide and allylic substrates **3a–d** and **4b** and **4c** under various conditions

Entry[a]	**3** or **4**	Pd(0) (mol%)	Conditions	Yield[b] (%)	**5**/**6**[c]
1	**3a**	$Pd(PPh_3)_4$ (20)	60 °C, 36 h	8	100/0
2	**3b**	$Pd(PPh_3)_4$ (20)	60 °C, 48 h	31	100/0
3	**3c**	$Pd(PPh_3)_4$ (20)	r.t., 18 h	96	37/63
4	**3c**	$Pd(PPh_3)_4$ (10)	r.t., 12 h	80	36/64
5	**3c**	$Pd(OAc)_2$ (10) $3PPh_3$	r.t., 12 h	82	44/56
6[e]	**3c**	$Pd(PPh_3)_4$ (10)	r.t., 12 h	82	99/1
7[d]	**3c**	$Pd(PPh_3)_4$ (10)	r.t., 6 h	65	66/34
8	**3d**	$Pd(PPh_3)_4$ (20)	r.t., 3 h	93	100/0
9	**3d**	$Pd(PPh_3)_4$ (10)	r.t., 3 h	77	100/0
10	**3d**	$Pd(OAc)_2$ (10) $3PPh_3$	r.t., 3 h	90	100/0
11	**3d**	$Pd(OAc)_2$ (5) $3PPh_3$	r.t., 3 h	86	100/0
12	**3d**	$Pd(OAc)_2$ (2) $5PPh_3$	r.t., 12 h	76	100/0
13	**4b**	$Pd(PPh_3)_4$ (20)	r.t., 6 h	95	50/50
14[e]	**4b**	$Pd(PPh_3)_4$ (10)	r.t., 12 h	40	0/100
15	**4c**	$Pd(PPh_3)_4$ (10)	r.t., 4 h	51	0/100

[a] The reactions were carried out in a Barbier-type manner with InBr/allylic substrate/PhCHO (2/2/1) in THF (unless specified). [b] Isolated yield following chromatography. [c] Determined by ^1H NMR spectroscopy. [d] THF/H_2O (2/1). [e] 2 equivalents of LiCl were added.

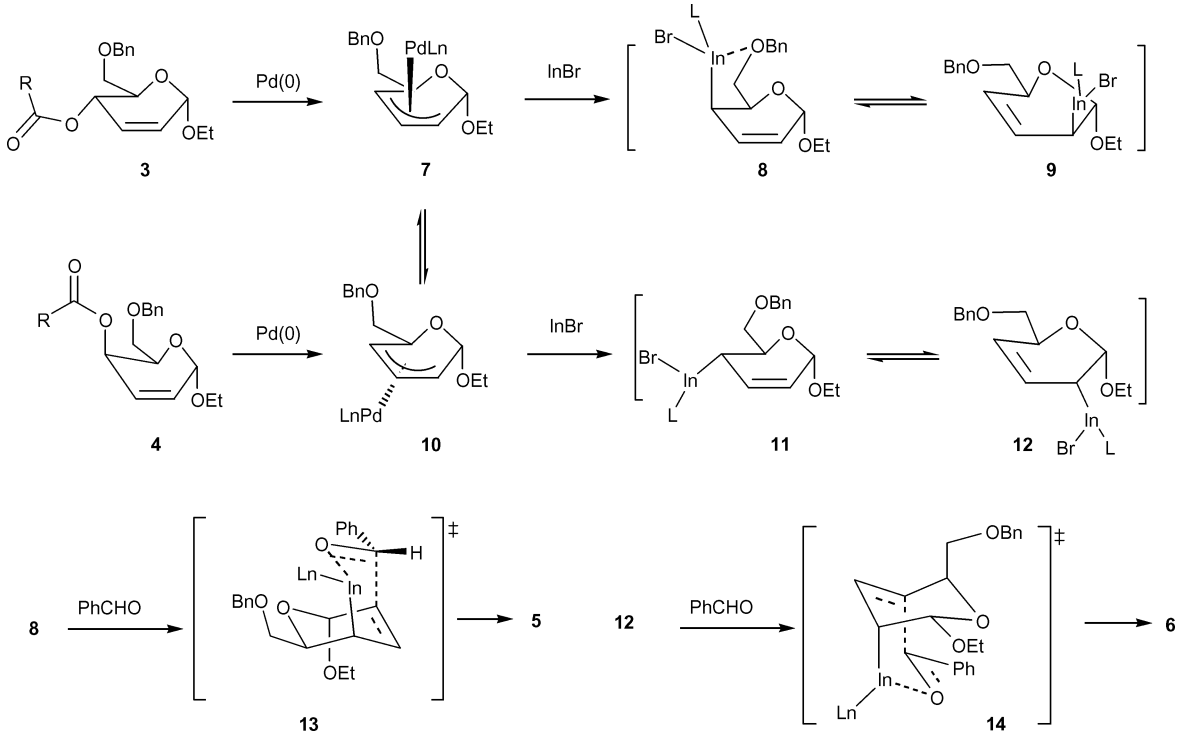
Indeed, with the carbonate **3c** (R = OEt), the reaction was carried out at room temperature with 20 mol% of $Pd(PPh_3)_4$ and led to a mixture of regioisomers **5** and **6** in a 37/63 ratio and 96% yield (entry 3). The reaction was highly stereoselective since for each regioisomer, a single stereoisomer was observed. The yields were slightly decreased using 10 mol% of catalyst (entries 4 and 5). For the trifluoroacetate **3d**, the 2-*C*-axial diastereoisomer **5** was the sole product obtained in high yield even with only 2 mol% of catalyst (entries 8–12). In this case, it was found that $Pd(OAc)_2$ used in combination with PPh_3 gave better results than $Pd(PPh_3)_4$ contrary to what was observed with the carbonate **3c** (entries 9 and 10 *versus* 4 and 5).

The reaction was also carried out with **3c** in aqueous media using a mixture of THF/H_2O (2/1) to produce compounds **5** and **6** in a 66/34 ratio and 65% yield (entry 7). This decreasing yield was due to the competitive hydrolysis of the carbonate compound leading back to compound **2**. Using these aqueous conditions, the trifluoroacetate **3d** was found to be too labile and no coupling adduct was obtained. We also tried the $Pd(OAc)_2$–TPPTS catalyst that was described recently by our group to favourably affect the generation of π-allylpalladium species and their aqueous transmetalation with indium salts.[5c] However, this system was found to be ineffective with these two substrates.

The allylation reaction with compounds **4b** and **4c** with the leaving group in the axial position was also tested. They were readily synthesized from **2** by a Mitsunobu reaction giving **4a**[11] in 83% yield. After removal of the benzoate group (MeONa/MeOH), the corresponding alcohol was protected to give **4b** or **4c** in high yields (Scheme 1).

The carbonate **4b** (R = OEt) was then submitted to similar conditions involving Pd(0)/InBr and provided the same coupling adducts **5** and **6** in a 50/50 ratio and 95% yield (entry 13). On the other hand, the reaction with the trifluoroacetate **4c** ($R = CF_3$) led to the 4-*C*-equatorial adduct **6** as the sole product but in a modest 51% yield due to a partial degradation of the starting material (entry 15).

Inspection of the regio- and stereochemistry for these 2-*C*- and 4-*C*-branched sugars derived from allylindium reactions has led to a postulated mechanism depicted in Scheme 3. In the catalytic process, Pd(0) complexes may react with alkenes **3** or **4** to form



Scheme 3 Rationalisation of the formation of **5** and **6**.

π-allyl species with inversion of configuration of the carbon bearing the leaving group.[12] The resulting π-allylpalladium(II) complexes **7** or **10** are then reductively transmetalated with indium(I) salts to give allylindium(III) species, which react with benzaldehyde. As was recently confirmed by our group, InBr approaches from the same face as the palladium leading to a reductive transmetalation with retention of configuration.[5c]

Starting from the trifluoroacetate **3d** (R = CF_3), the two possible allylindium(III) regioisomers **8** and **9** can be formed. However, the allylindium species **8** is probably preferred because of a possible chelation operating between the indium and the oxygen on the C-6 position of the sugar moiety. Then, the reaction of the allylindium **8** and benzaldehyde led to the formation of compound **5** probably through the currently accepted six-membered cyclic transition state **13** between the carbonyl compound and the allylindium.[1–4] In this transition state, the preferential equatorial position of the phenyl group of benzaldehyde affords **5** as a single diastereoisomer with C-7 (*S*) configuration.[13]

In opposition, when starting from the carbonate **3c** (R = OEt), we observed, along with the expected **5**, the formation of compound **6**. This derivative must result from intermediate **12**, which reacts with benzaldehyde through a six-membered-ring transition state **14**, which requires the inversion of the pyranosidic ring leading to indium in the axial position. In this transition state, the phenyl group is still preferentially in an equatorial position, which led to the 4-*C*-equatorial adduct **6** as a single diasteroisomer with C-7 (*S*) configuration.[13] The intermediate allylindium species **12** can probably result from an isomerisation of the π-allylpalladium(II) complex **7** to **10** by Pd(0).[14] After reductive transmetalation of **10** with indium(I) salts, a mixture of **11** and **12** can be obtained. However, **12** is probably favored by stabilisation of the anionic charge in the C-2 position due to the neighbouring electrophilic anomeric centre in the absence of a possible chelation between the indium and the oxygen on the C-6 position of intermediate **11**.

In order to verify our hypothesis that inversion occurs at the π-allylpalladium stage and not at the allylindium one (equilibration between **9** and **12**), we synthesised 2-bromo-4-enopyranoside **20** with the bromide atom in an axial C-2 position. This compound was prepared by selective protection of **15**[15] by a benzoate group at the O-2 position[16] then the cleavage of the 4,6-*O*-benzylidene group with $NaBH_3CN$ and HCl affords the 6-*O*-benzyl derivative **17**. Treated with PPh_3, CHI_3 and imidazole in refluxing toluene,[16] this later led to the allylic benzoate **18** in 84% yield. After removal of the 2-O protecting group and treatment of the resulting alcohol **19** with PPh_3 and CBr_4 in CH_2Cl_2, the desired allylic bromide **20** was obtained. This was then submitted to a Barbier-type allylation reaction with benzaldehyde and indium bromide in THF (Scheme 4). In this case, the reaction does not proceed at room temperature but at 60 °C. After 36 hours, the only coupling adduct was **5**, which was obtained in a poor yield of 35%. Considering that the exchange Br/In takes place with retention of stereochemistry and that the alkylation occurs at the γ position, one can deduce that **5** comes from **8** after a stereospecific 1,3 indium migration of **9**. This result provides strong evidence in favour of the assertion that the allylindium(III) species **9** do not epimerise to **12** under the reaction conditions.

In order to increase regioselectivity with the carbonate **3c**, the InBr/Pd(0)-mediated carbonyl allylation was carried out in the presence of 2 equivalents of LiCl, which is known for having an influence on the reactivity and selectivity of Pd-catalysed allylic substitution reactions (Table 1, entry 6).[17] In this case, the chloride anion has a beneficial effect on the regiochemistry and the coupling adducts **5** and **6** were obtained in a 99/1 ratio and 82% yield.

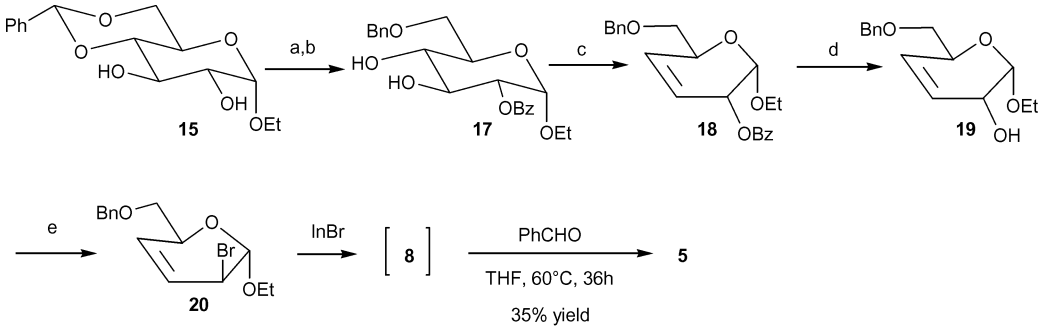
In the case of the axial derivatives, starting from the trifluoroacetate **4c**, the resulting π-allylpalladium(II) complex **10** is reductively transmetalated with indium(I) salts to give preferentially the allylindium(III) species **12**, which allylates benzaldehyde and gives **6** as the sole coupling product. For this substrate, the allylation step is less favorable since a change in the conformation of the sugar moiety is needed so that the reaction occurs. However, with the carbonate **4b** (R = OEt), isomerisation of the π-allylpalladium(II) complex **10** takes place leading to a mixture of **5** and **6**. In this case, the regioselectivity can also be controlled by the addition of lithium chloride[17] in the reaction mixture furnishing only **6** but in a modest 40% yield (Table 1, entry 14).

In conclusion, the above results show that 2-*C*- and 4-*C*-branched sugars are effectively obtainable from readily available allylic esters or carbonates *via* the formation of π-allylpalladium(II) intermediates and their reductive transmetalation with indium(I) bromide. Work is currently in progress in our laboratory to extend this methodology to pyranosides that contain allylic esters or carbonates in other positions.

Experimental

General

All moisture-sensitive reactions requiring anhydrous conditions were conducted in oven-dried apparatus under an atmosphere of argon. If necessary, solvents were dried and distilled prior to use. External reaction temperatures are reported unless stated otherwise. Reactions were monitored on silica gel 60 F_{254}. Detection was performed using UV light and/or 5% sulfuric acid in ethanol, followed by heating. Flash chromatographies were performed on silica gel 6–35 μm. $[a]_D$ Values (in deg cm^3 g^{-1} dm^{-1}) were measured on an Electronic Digital Jasco DIP-370 Polarimeter. IR spectra were recorded as thin films unless stated otherwise. NMR spectra were recorded in $CDCl_3$ unless stated otherwise with Bruker AC 200, 250 or Bruker AM 400 spectrometers. ^1H NMR chemical shifts are reported relative to $CHCl_3$ (δ_H 7.26), ^{13}C NMR chemical shifts are reported



a) i) Bu_2SnO, MeOH. ii) PhCOCl, NEt_3, dioxane (**16**, 90%). b) $NaBH_3CN$, HCl/Et_2O, THF, 4Å MS (**17**, 87%). c) PPh_3, CHI_3, imidazole, toluene (**18**, 84%). d) MeONa/MeOH (**19**) . e)PPh_3, CBr_4, CH_2Cl_2 (**20**, 61% from **18**).

Scheme 4 Reagents and conditions for the synthesis of compound **20**. Barbier-type allylation of **20** with benzaldehyde and InBr.

relative to $CDCl_3$ (δ_C [central line of three] 77.0). Coupling constants (J) are given in Hz. Mass spectra were recorded in positive mode on a Finnigan MAT 95 S spectrometer using electrospray ionization. Elemental analyses were performed at the Service Central de Microanalyses du CNRS (Gif-sur-Yvette, France).

Ethyl 6-*O*-benzyl-2,3-dideoxyhex-2-enopyranoside 2

To a solution of **1** (10 g, 38.8 mmol) in MeOH (300 mL) at room temperature was added sodium methanolate (105 mg, 1.94 mmol). After 2 hours, the solvent was removed under reduced pressure and the crude residue was dissolved in toluene (150 mL). Bu_2SnO (10.6 g, 42.6 mmol) was added and the reaction mixture was refluxed while water was continuously removed by means of a Dean Stark trap. After 4 h, nBu$_4$NBr (14.1 g, 43.8 mmol) and BnBr were added and the reaction was then allowed to warm at 115 °C for 18 hours. The temperature of the reaction was cooled to room temperature before addition of ethyl acetate (200 mL) and water (100 mL). The two phases were separated and the organic one was washed with a saturated aqueous solution of $NaHCO_3$ (100 mL) and then with brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 8/2) gave allylic alcohol **2** as a colourless oil (8.7 g g, 85%). Data consistent with the literature.[11]

Ethyl 4-*O*-acetyl-6-*O*-benzyl 2,3-dideoxyhex-2-enopyranoside 3a

Compound **2** (0.95 g, 3.6 mmol) was dissolved in pyridine (2 mL) and acetic anhydride (0.7 mL, 7.2 mmol) was added. After 12 hours at room temperature, solvents were co-evaporated with toluene and the residue was purified by flash chromatography (SiO_2, petroleum ether (40–65 °C)/AcOEt = 85/15) to afford **3a** (1.1 g, 100%) as a colourless oil (Found: C, 66.55; H, 7.09; O, 25.95. $C_{17}H_{22}O_5$ requires C, 66.65; H, 7.24; O, 26.11%); $[a]_D^{25}$ − 122.4 (c 0.5 in $CHCl_3$); υ_{max}/cm^{-1} 2976, 2896, 1741, 1455, 1372, 1234, 1103, 1045, 907, 738, 699; δ_H (250 MHz, $CDCl_3$) 7.50–7.25 (5H, m), 5.90 (1H, dd, J 3, 12), 5.83 (1H, dt, J 2, 12), 5.44 (1H, dd, J 2, 10), 5.15–5.05 (1H, m), 4.67 (1H, d, J 12), 4.51 (1H, d, J 12), 4.15–4.05 (1H, m), 3.87 (1H, dq, J 7, 10), 3.7–3.5 (3H, m), 1.97 (3H, s), 1.25 (3H, t J 7); δ_C (62.5 MHz, $CDCl_3$) 170.0, 152.0, 129.0, 128.0, 127.6, 127.4, 127.3, 93.9, 73.0, 68.3, 67.6, 65.3, 63.8, 20.6, 15.0; MS (EI) 329 ([M + Na]$^+$, 100%); HRMS (EI high resolution): m/z 329.136310. $C_{17}H_{22}NaO_5$ requires 329.136493.

Ethyl 4-*O*-benzoyl-6-*O*-benzyl-2,3-dideoxyhex-2-enopyranoside 3b

Compound **2** (0.66 g, 2.5 mmol) was dissolved in pyridine (2.8 mL). DMAP (15 mg, 0.12 mmol) and benzoyl choride ((0.6 mL, 5 mmol) were added and the reaction mixture was stirred 4 hours at room temperature. Solvents were co-evaporated with toluene and the residue was diluted with ethyl acetate (20 mL). The organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 10 mL) and then with brine (10 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 9/1) gave allylic benzoate **3b** (0.87 g, 94%) as a colourless oil (Found: C, 71.81; H, 6.55; O, 21.6. $C_{22}H_{24}O_5$ requires C, 71.72; H, 6.57; O, 21.71%); $[a]_D^{25}$ 178 (c 0.6 in $CHCl_3$); υ_{max}/cm^{-1} 3062, 3031, 2975, 2895, 1721, 1496, 1316, 1267, 1108, 1050, 1026, 736, 713; δ_H (200 MHz, $CDCl_3$) 7.97 (2H, d, J 8), 7.60–7.10 (8H, m), 6.03 (1H, d, J 12), 5.88 (1H, dt, J 2, 12), 5.70 (1H, dd, J 2, 9), 5.16–5.09 (1H, m), 4.64 (1H, d, J 12), 4.53 (1H, d, J 12), 4.32–4.20 (1H, m), 3.98 (1H, dq, J 7, 9), 3.7–3.5 (3H, m), 1.29 (3H, t J 6); δ_C (62.5 MHz, $CDCl_3$) 165.7, 152.6, 137.8, 133.1, 129.6, 129.4, 128.2, 128.1, 127.9, 127.4, 127.3, 94.2, 73.2, 68.7, 68.1, 65.9, 64.1, 15.2; MS (EI) 391 ([M + Na]$^+$, 100%); HRMS (EI high resolution): m/z 391.152240. $C_{22}H_{24}NaO_5$ requires 391.152143.

Ethyl 6-*O*-benzyl-4-*O*-(ethylcarbonate)-2,3-dideoxyhex-2-enopyranoside 3c

Compound **2** (0.66 g, 2.5 mmol) was dissolved in CH_2Cl_2. Pyridine (1.4 mL, 12.5 mmol), DMAP (15 mg, 0.12 mmol) and $ClCO_2Et$ (0.66 mL, 6.8 mmol) were added successively at 0 °C. After 12 hours at room temperature, solvents were co-evaporated with toluene and the residue was diluted with ethyl acetate (20 mL) and H_2O (10 mL). The aqueous phase was extracted with ethyl acetate (3 × 15 mL) and the combined organic phases were washed with a saturated aqueous solution of $NaHCO_3$ (2 × 10 mL) and then with brine (10 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 85/15) gave allylic carbonate **3c** (0.8 g, 95%) as a colourless oil (Found: C, 64.29; H, 7.11; O, 28.51. $C_{18}H_{24}O_6$ requires C, 64.27; H, 7.19; O, 28.54%); $[a]_D^{25}$ 102 (c 0.7 in $CHCl_3$); υ_{max}/cm^{-1} 3032, 2979, 2902, 1747, 1525, 1450, 1373, 1257, 1103, 1050, 1015; δ_H (250 MHz, $CDCl_3$) 7.40–7.20 (5H, m), 5.97 (1H, d, J 10), 5.84 (1H, td, J 2, 10), 5.32 (1H, dd, J 2, 9), 5.12–5.04 (1H, m), 4.68 (1H, d, J 12), 4.53 (1H, d, J 12), 4.21 (1H, dd, J 2, 7), 4.14 (1H, dd, J 2, 7), 4.07 (1H, td, J 3, 9), 3.85 (1H, qd, J 7, 10), 3.7–3.43 (3H, m), 1.33–1.18 (6H, m); δ_C (62.5 MHz, $CDCl_3$) 154.8, 138.4, 129.2, 128.7, 128.6, 128.0, 127.9, 94.6, 73.7, 69.3, 69.1, 68.1, 64.6, 64.5, 15.7, 14.5; MS (EI) 359 ([M + Na]$^+$, 100%); HRMS (EI high resolution): m/z 359.1472. $C_{18}H_{24}NaO_6$ requires 359.1465.

Ethyl 6-*O*-benzyl-4-*O*-trifluoroacetyl-2,3-dideoxyhex-2-enopyranoside 3d

To a solution of **2** (0.66 g, 2.5 mmol) in CH_2Cl_2 (10 mL) was added successively at 0 °C 2,6-lutidine (0.3 mL, 2.6 mmol), DMAP (30 mg, 0.25 mmol) and trifluoroacetic anhydride (0.4 mL, 2.6 mmol). After 3 hours at room temperature, H_2O (15 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with a saturated aqueous solution of K_2HPO_4 (2 × 15 mL) and then with brine (15 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 85/15) gave allylic trifluoroacetate **3d** (0.83 g, 92%) as a colourless oil (Found: C, 57.05; H, 5.38. $C_{17}H_{19}F_3O_5$ requires C, 56.67; H, 5.31; F, 15.82; O, 22.20.%); $[a]_D^{25}$ 90 (c 0.5 in $CHCl_3$); υ_{max}/cm^{-1} 2978, 2899, 1787, 1454, 1372, 1223, 1160, 1109, 1050, 1018, 734; δ_H (250 MHz, $CDCl_3$) 7.45–7.20 (5H, m), 6.0–5.91 (1H, m), 5.89 (1H, d, J 11), 5.69 (1H, d, J 10), 5.13–5.08 (1H, m), 4.69 (1H, d, J 12), 4.48 (1H, d, J 12), 4.16 (1H, dt, J 3, 9), 3.86 (1H, dq, J 7, 10), 3.68–3.52 (3H, m), 1.26 (3H, t, J 7); δ_C (62.5 MHz, $CDCl_3$) 150.0, 137.3, 129.6, 128.4, 127.8, 126.7, 94.1, 73.5, 69.3, 67.8, 67.0, 64.5, 15.2; MS (EI) 287 (100%); 383 ([M + Na]$^+$, 40%).

Ethyl 4-*O*-benzoyl-6-*O*-benzyl-2,3-dideoxyhex-2-enopyranoside 4a

To a solution of **2** (1.3 g, 4.9 mmol) in anhydrous THF (12 mL) were added triphenylphosphine (2.3 g, 8.8 mmol), benzoic acid (1.1 g, 9 mmol) and DIAD (1.8 mL, 9.1 mmol). The reaction mixture was stirred for 2 hours at room temperature and EtOAc (30 mL) was added to the residue. The organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (3 × 15 mL) and then with brine (15 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 95/5) gave the allylic benzoate **4a** as a colourless oil (1.5 g, 83%). Data consistent with the literature.[11]

Ethyl 6-*O*-benzyl-4-*O*-(ethylcarbonate)-2,3-dideoxyhex-2-enopyranoside 4b

To a solution of **4a** (0.87 g, 2.36 mmol) in MeOH (10 mL) at room temperature was added sodium methanolate (6 mg, 0.118 mmol). After 12 hours at room temperature, the solvent was removed under reduced pressure and the crude residue was dissolved in CH_2Cl_2 (15 mL). Pyridine (1.4 mL, 12.5 mmol), DMAP (30 mg, 0.25 mmol) and $ClCO_2Et$ (1.3 mL, 13.8 mmol) were added successively at 0 °C. After 2 hours at room temperature, H_2O (20 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with a saturated aqueous solution of $NaHCO_3$ (15 mL) and then with brine (10 mL), dried over $MgSO_4$, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 95/5 to 9/1) gave allylic carbonate **4b** (0.7 g, 89%) as a colourless oil (Found: C, 63.63; H, 7.03; O, 29.25. $C_{18}H_{24}O_6$ requires C, 64.27; H, 7.19; O, 28.54%; $[\alpha]_D^{25}$ −146 (*c* 0.4 in $CHCl_3$); υ_{max}/cm^{-1} 2978, 2876, 1742, 1455, 1372, 1259, 1101, 1050, 1009, 739; δ_H (250 MHz, $CDCl_3$) 7.40–7.20 (5H, m), 6.19 (1H, dd, *J* 5, 10), 6.05 (1H, dd, *J* 3, 10), 5.08 (1H, d, *J* 2), 4.90 (1H, dd, *J* 2, 5), 4.62 (1H, d, *J* 12), 4.54 (1H, d, *J* 12), 4.38 (1H, td, *J* 2, 7), 4.2 (1H, dd, *J* 1, 7), 4.14 (1H, dd, *J* 1, 7), 3.86 (1H, dq, *J* 7, 9), 3.71 (2H, d, *J* 7), 3.56 (1H, dq, *J* 7, 9), 1.28 (3H, t, *J* 7, CH_2CH_3), 1.23 (3H, t, *J* 7); δ_C (62.5 MHz, $CDCl_3$) 154.6, 138.0, 131.1, 128.7, 128.6, 128.0, 124.7, 93.5, 73.2, 68.6, 67.4, 65.8, 64.0, 63.6, 15.1, 14.0; MS (EI) 359 ([M + Na]$^+$, 100%); HRMS (EI high resolution): *m/z* 359.147820. $C_{18}H_{24}NaO_6$ requires 359.147058.

Ethyl 6-*O*-benzyl-4-*O*-trifluoroacetyl-2,3-dideoxyhex-2-enopyranoside 4c

To a solution of **4a** (1.5 g, 4.08 mmol) in MeOH (20 mL) at room temperature was added sodium methanolate (11 mg, 0.2 mmol). After 12 hours at room temperature, the solvent was removed under reduced pressure and the crude residue was purified by flash chromatography (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 8/2 to 7/3) to afford allylic alcohol as a colourless oil (0.88 g, 81%). The latter (0.88 g, 3.3 mmol) was dissolved in CH_2Cl_2 (15 mL) and 2,6-lutidine (0.42 mL, 3.63 mmol), DMAP (40 mg, 0.33 mmol) and trifluoroacetic anhydride (0.5 mL, 3.63 mmol) were added successively at 0 °C. After 3 hours at room temperature, H_2O (15 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with a saturated aqueous solution of K_2HPO_4 (2 × 15 mL) and then with brine (15 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 9/1) gave allylic trifluoroacetate **4c** (1.18 g, 99%) as a colourless oil (Found: C, 56.39; H, 5.28. $C_{17}H_{19}F_3O_5$ requires C, 56.67; H, 5.31; F, 15.82; O, 22.20%); $[\alpha]_D^{25}$ −171 (*c* 0.9 in $CHCl_3$); υ_{max}/cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.50–7.20 (5H, m), 6.15–6.10 (2H, m), 5.24–5.18 (1H, m), 5.09–5.05 (1H, m), 4.55–4.35 (3H, m), 3.82 (1H, dq, *J* 7, 9), 3.71–3.47 (3H, m), 1.22 (3H, t, *J* 7), 1.23 (3H, t, *J* 7); δ_C (62.5 MHz, $CDCl_3$) 154.0, 137.5, 132.9, 128.4, 127.8, 127.6, 122.9, 93.4, 73.5, 67.9, 67.1, 66.6, 64.1, 15.1; MS (EI) 287 (100%); 383 ([M + Na]$^+$, 80%).

General procedure for palladium–indium bromide mediated carbonyl allylation

To a solution of **3a–d** or **4b, c** (0.5 mmol) in dry THF (1.5 mL) was added Pd^0 under argon at room temperature. The reaction mixture was stirred for 5 min before addition of benzaldehyde (26 μL, 0.25 mmol) and indium bromide (97 mg, 0.5 mmol). After completion of the reaction, the solvents were evaporated under reduced pressure and the crude residue was purified by flash chromatography (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 9/1 to 8/2) to afford to **5** and/or **6** as a colourless oil.[13]

Ethyl 6-*O*-benzyl-2-*C*-[(*S*)-1-phenyl-1-hydroxymethyl]-3,4-dideoxy-α-D-*threo*-hex-3-enopyranoside 5. R*f* = 0.27 (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 9/1); Found: C, 74.36; H, 7.49; O, 18.31. $C_{22}H_{26}O_4$ requires C, 74.55; H, 7.39; O, 18.06%); $[\alpha]_D^{25}$ 66 (*c* 0.6 in $CHCl_3$); υ_{max}/cm^{-1} 3446, 3062, 3031, 2974, 2863, 1495, 1454, 1363, 1311, 1186, 1116, 1066, 1022, 920, 845, 766, 734, 700; δ_H (250 MHz, $CDCl_3$) 7.50–7.20 (10H, m, Ph), 5.80 (1H, dt, *J* 1, 12, H-3), 5.48 (1H, dt, *J* 2, 12, H-4), 5.11 (1H, bs, H-1), 4.69 (1H, d, *J* 7, H-7), 4.64 (2H, s, CH_2Ph), 4.42–4.32 (1H, m, H-5), 3.82 (1H, dq, *J* 7, 10, CH_2CH_3), 3.61 (2H, dd, *J* 1, 4, H-6 and H-6′), 3.53 (1H, dq, *J* 7, 10, CH_2CH_3), 2.95–2.75 (1H, bs, O*H*), 2.55–2.45 (1H, m, H-2), 1.20 (3H, t *J* 7, CH_2CH_3); δ_C (62.5 MHz, $CDCl_3$) 142.4, 137.9, 128.2, 128.1, 127.7, 127.6, 127.5, 127.4, 124.3, 96.7, 74.7, 73.2, 71.9, 67.6, 63.3, 46.0, 15.0; MS (EI) 377 ([M + Na]$^+$, 100%); HRMS (EI high resolution): *m/z* 377.172879. $C_{22}H_{26}NaO_4$ requires 377.173120.

Ethyl 6-*O*-benzyl-4-*C*-[(*S*)-1-phenyl-1-hydroxymethyl]-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside 6. R*f* = 0.24 (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 9/1); Found: C, 73.87; H, 7.56; O, 17.99. $C_{22}H_{26}O_4$ requires C, 74.55; H, 7.39; O, 18.06%); $[\alpha]_D^{25}$ 3.6 (*c* 0.3 in $CHCl_3$); υ_{max}/cm^{-1} 3450, 3087, 3032, 2976, 2927, 2876, 1495, 1453, 1266, 1089, 1050, 1012, 737, 702; δ_H (250 MHz, $CDCl_3$) 7.50–7.20 (10H, m, Ph), 5.75 (1H, dt, *J* 3, 10, H-3), 5.51 (1H, dd, *J* 2, 10, H-2), 4.97 (1H, bs, H-1), 4.61 (1H, d, *J* 12, CH_2Ph), 4.53 (1H, dd, *J* 3, 8, H-7), 4.51 (1H, d, *J* 12, CH_2Ph), 4.04 (1H, td, *J* 4, 8, H-5), 3.90–3.74 (2H, m, H-6 and CH_2CH_3), 3.68 (1H, dd, *J* 4, 10, H-6′), 3.52 (1H, qd, *J* 7, 10, CH_2CH_3), 3.14 (1H, d, *J* 3, O*H*), 2.82 (1H, m, H-4), 1.22 (3H, t, *J* 7); δ_C (62.5 MHz, $CDCl_3$) 142.6, 138.2, 130.4, 128.9, 128.8, 128.3, 128.2, 128.1, 127.3, 127.2, 94.0, 75.9, 73.8, 72.8, 69.6, 63.9, 44.4, 15.8; MS (EI) 377 ([M + Na]$^+$, 100%); HRMS (EI high resolution): *m/z* 377.17225. $C_{22}H_{26}NaO_4$ requires 377.1723.

Ethyl 4,6-benzylidene-2-*O*-benzoyl-α-D-glucopyranoside 16

To a solution of **15** (1.5 g, 5.1 mmol) in dry MeOH (20 mL) was added Bu_2SnO (1.24 g, 5 mmol) and the reaction mixture was refluxed for 1 hour after which the solution became completely clear. The solvents were removed under reduced pressure and the crude residue was diluted in dry dioxane (37.5 mL). NEt_3 (0.8 mL, 5.5 mmol) and benzoyl chloride (0.64 mL, 5.5 mmol) were then added and the reaction mixture was stirred for 1 hour at room temperature. The reaction mixture was filtered over Celite and the solvents were evaporated under reduced pressure. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 85/15 to 8/2) gave **16** (1. 8 g, 90%) as a colourless oil (Found: C, 66.13; H, 6.15; O, 27.84. $C_{22}H_{24}O_7$ requires C, 65.99; H, 6.04; O, 27.84%); $[\alpha]_D^{25}$ 10.7 (*c* 0.6 in $CHCl_3$); υ_{max}/cm^{-1} 3450, 3066, 3038, 2977, 2927, 2870, 1720, 1630, 1524, 1453, 1380, 1334, 1277, 1097, 1031, 988, 758, 710; δ_H (250 MHz, $CDCl_3$) 8.13 (2H, d, *J* 7), 7.65–7.35 (8H, m), 5.59 (1H, s), 5.22 (1H, d, *J* 4), 5.05 (1H, dd, *J* 4, 9), 4.45–4.30 (2H, m), 3.97 (1H, dd, *J* 4, 9), 3.82–3.75 (2H, m), 3.64 (1H, t, *J* 9), 3.51 (1H, qd, *J* 7,10), 2.90–2.75 (1H, bs), 2.70–2.62 (1H, bs), 1.22 (3H, t *J* 7); δ_C (62.5 MHz, $CDCl_3$) 166.2, 137.0, 133.2, 129.8, 129.2, 128.3, 128.2, 126.3, 126.2, 101.9, 96.4, 81.4, 74.0, 68.8, 68.7, 63.9, 62.1, 14.9; MS (EI) 423 ([M + Na]$^+$, 100%).

Ethyl 6-*O*-benzyl-2-*O*-benzoyl-α-D-glucopyranoside 17

To a solution of **16** (2.38 g, 5.95 mmol) in dry THF (60 mL) was added powdered molecular sieves (4 Å, 3.2 g), orange methyl and $NaBH_3CN$ (3.2 g, 50.8 mmol). After 15 min at room temperature, the yellow solution was cooled to 0 °C and a saturated solution of HCl in ether was added until the solution turned to pink. The reaction mixture was then added to a cold saturated aqueous solution of $NaHCO_3$ (100 mL) and the aqueous phase was extracted with Et_2O (3 × 100 mL). The

combined organic layers were washed with H_2O (3 × 10 mL) and then with brine (100 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 6/4) gave compound **17** (2.1 g, 87%) as a white solid (Found: C, 65.51; H, 6.53; O, 27.62. $C_{22}H_{26}O_7$ requires C, 65.66; H, 6.51; O, 27.83%); $[\alpha]_D^{25}$ − 109 (*c* 0.5 in $CHCl_3$); υ_{max}/cm^{-1} 3484, 3351, 3089, 3066, 3037, 2983, 2864, 1712, 1603, 1584, 1496, 1452, 1316, 1288, 1158, 1115, 1046, 705; δ_H (250 MHz, $CDCl_3$) 8.08 (2H, d, *J* 7), 7.65–7.25 (8H, m), 5.15 (1H, d, *J* 3), 4.94 (1H, dd, *J* 3, 10), 4.66 (1H, d, *J* 12), 4.47 (1H, d, *J* 12), 4.22–4.10 (1H, m), 3.92–3.65 (5H, m), 3.49 (1H, dd, *J* 7, 10), 3.00–2.92 (1H, bs), 2.70–2.62 (1H, bs), 1.19 (3H, t *J* 7); δ_C (62.5 MHz, $CDCl_3$) 166.4, 137.8, 133.1, 129.8, 129.6, 128.3, 128.2, 127.6, 95.8, 73.7, 73.5, 71.7, 71.6, 69.8, 69.5, 63.6, 14.9; MS (EI) 425 ([M + Na]$^+$, 100%).

Ethyl 2-*O*-benzoyl-6-*O*-benzyl-3,4-dideoxyhex-3-enopyranoside 18

To a solution of **17** (0.125 g, 0.31 mmol) in toluene (10 mL) was added successively PPh_3 (0.33 g, 1.3 mmol), imidazole (43 mg, 0.635 mmol) and CHI_3 (0.244 g, 0.62 mmol) and the reaction mixture was allowed to warm to reflux for 45 min. The solution was cooled and diluted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 20 mL), dried over Na_2SO_4, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 9/1) gave compound **18** (95 mg, 84%) as a colourless oil (Found: C, 71.99; H, 6.66; O, 21.82. $C_{22}H_{24}O_5$ requires C, 71.72; H, 6.57; O, 21.71%); $[\alpha]_D^{25}$ − 31 (*c* 0.3 in $CHCl_3$); υ_{max}/cm^{-1} 3063, 3031, 2975, 2863, 1718, 1452, 1319, 1267, 1099, 714; δ_H (250 MHz, $CDCl_3$) 8.08 (2H, d, *J* 7), 7.55–7.20 (8H, m), 5.99 (1H, dt, *J* 2, 10), 5.87 (1H, d, *J* 10), 5.62–5.55 (1H, m), 5.39 (1H, d, *J* 4), 4.65 (2H, s), 4.52–4.42 (1H, m), 3.87 (1H, dq, *J* 7, 10), 3.72–3.51 (3H, m), 1.22 (3H, t *J* 7); δ_C (62.5 MHz, $CDCl_3$) 165.7, 137.6, 132.8, 129.4, 129.2, 128.1, 128.0, 127.3, 123.1, 94.3, 73.1, 71.6, 67.4, 66.9, 63.8, 14.8; MS (EI) 391 ([M + Na]$^+$, 100%); HRMS (EI high resolution): *m/z* 391.15215. $C_{22}H_{24}NaO_5$ requires 391.152143.

Ethyl 6-*O*-benzyl-2-bromo-3,4-dideoxyhex-3-enopyranoside 20

To a solution of **18** (0.86 g, 2.3 mmol) in MeOH (10 mL) was added sodium methanolate (6 mg, 0.115 mmol). After 2 days at room temperature, the solvent was removed under reduced pressure and the crude residue was diluted in ethyl acetate. The organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (20 mL), brine (20 mL) then dried over Na_2SO_4, filtered and concentrated. The crude residue was diluted in CH_2Cl_2 (10 mL) and PPh_3 (0.9 g, 3.45 mmol) and CBr_4 (0.84 g, 2.5 mmol) were successively added at −10 °C. After 2 hours at 0 °C then 12 hours at room temperature, a saturated aqueous solution of $NaHCO_3$ (10 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated. Flash chromatography of the crude residue (SiO_2, petroleum ether (40–65 °C)/ethyl acetate = 95/5) afforded compound **20** (0.46 g mg, 61% for two steps) as a colorless oil. $[\alpha]_D^{25}$ 232 (*c* 0.4 in $CHCl_3$); υ_{max}/cm^{-1} 3030, 2976, 2865, 1496, 1363, 1335, 1187, 1112, 1062, 761; δ_H (400 MHz, $CDCl_3$) 7.45–7.20 (5H, m), 6.01 (1H, dd, *J* 5, 10), 5.88 (1H, dd, *J* 2, 10), 5.19 (1H, s), 4.62 (2H, s), 4.54–4.48 (1H, m), 3.83 (1H, dq, *J* 7, 10), 3.69 (1H, dd, *J* 6, 10), 3.61 (1H, dq, *J* 7, 10), 3.58 (1H, dd, *J* 6, 10), 1.21 (3H, t *J* 7); δ_C (62.5 MHz, $CDCl_3$) 138.0, 129.4, 129.4, 128.3, 127.7, 127.6, 124.5, 99.2, 73.5, 71.7, 67.4, 64.1, 42.7, 15.0; MS (EI) 349 ([M + Na]$^+$, 98%), 351 ([M + Na]$^+$, 100%); HRMS (EI high resolution): *m/z* 349.04132. $C_{15}H_{19}NaBrO_3$ requires 349.041537.

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