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ARTICLE

Efficient synthesis of oligosaccharyl 1,2-*O*-orthoesters from *n*-pentenyl glycosides and application to the pentaarabinofuranoside of mycobacterial cell surface

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Complex oligosaccharide syntheses employ the use of more than one glycosyl donor and hence, methods for the interconversion of glycosyl donors are highly valuable for the overall synthesis plan. Herein, *n*-pentenyl glycosides are efficiently converted to glycosyl 1,2-*O*-orthoesters in the presence of both acid and base sensitive functional groups. Identified protocol was found to be suitable for the synthesis of trisaccharyl and tetrasaccharyl 1,2-*O*-orthoester as well. Furthermore, an iterative synthesis of pentaarabinofuranoside present in the *Mycobacterium tuberculosis* cell surface was accomplished using this method.

Introduction

Molecular glycobiology studies require pure and structurally defined glycoconjugates or oligosaccharides which are available in Nature as micro and heterogeneous forms.[1] Oligosaccharide synthesis is still a challenging task even after development of many elegant strategies.[2] Oligosaccharides are often synthesized from reducing end to the non-reducing end or from the non-reducing end to the reducing end while employing the synthesis in a convergent or linear fashion. Each oligosaccharide is unique and hence its synthesis requires optimization of glycosyl donor/acceptors and sometimes strategies as well.[3,4] Often, oligosaccharides are synthesized with an alkyl group at the reducing end.[5a,b] The alkyl group is chosen in such a way that it does not get affected during the course of the entire synthesis. Recent developments in the field of glycoconjugate chemistry have led to a renewed interest in the use of glycosyl 1,2-*O*-orthoesters[5c-f] with long shelf-life as glycosyl donors. Current methods are suitable for the synthesis of 1,2-orthoesters of the easily accessible saccharides.[5] However, far too little attention has been paid to the synthesis of 1,2-orthoester of an oligosaccharide with multiple protecting groups.

Traditionally, 1,2-orthoesters are synthesized from corresponding 2-*O*-acylated glycosyl halides by the treatment of an alcohol under basic conditions.[6] Hence, oligosaccharyl 1,2-*O*-orthoester synthesis would require: (i) an acyl group at the *C*-2 position of the sugar at the reducing end, (ii) a halide at the reducing end of the oligosaccharide. Routinely employed conditions for the synthesis of glycosyl bromides[7] such as HBr/AcOH[7a,c] or AcBr/MeOH[7c] are found to be more suitable for monosaccharides and disaccharides. Further, these conditions would not be really encouraging for oligosaccharyl bromide synthesis as they lead to the cleavage of the acid sensitive functional groups and/or interglycosidic bonds.

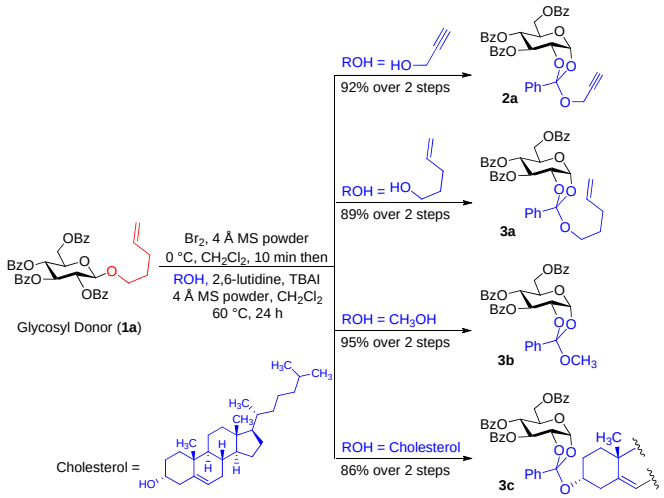
However, a rarely exploited but highly useful method for the synthesis of glycosyl halides is the conversion of *n*-pentenyl glycosides in the presence of molecular bromine.[8] The conversion of *n*-pentenyl glycosides to glycosyl bromide would then assist its conversion to corresponding alkyl 1,2-orthoesters in basic conditions. In particular, we got interested in conversion of *n*-pentenyl glycosides into propargyl 1,2-orthoesters as this switching would be beneficial: (i) for increased reactivity and yield; (ii) as the glycosidation becomes catalytic; (iii) since the leaving group becomes traceless; (iv) affords 1,2-*trans* stereoselectivity; (v) for facilitated purification; (vii) for orthogonal activation with glycosyl donors, and (viii) for the convergent synthesis of oligosaccharides.

Results and Discussion

Mindful of these advantages, conversion of *n*-pentenyl glycosides into propargyl 1,2-orthoesters was considered first. Easily accessible *n*-pentenyl 2,3,4,6-tetra-*O*-benzoyl β-D-glucopyranoside (**1a**)[9] was treated with molecular bromine in the presence of 4 Å molecular sieves at 0 ºC in CH_2Cl_2 for 10 min to observe complete conversion of compound **1a** into anomeric bromide.[8] The resulting glucosyl bromide was quickly concentrated *in vacuo* and redissolved in CH_2Cl_2, treated with propargyl alcohol, 2,6-lutidine, TBAI in the presence of 4 Å MS powder at 60 ºC for 24 h to obtain propargyl 1,2-orthoester **2a**[6] in 92% yield over two steps (Scheme 1).[10]

Similarly, changing the nucleophile from propargyl alcohol to 4-penten-1-ol afforded *n*-pentenyl orthoester **3a**[6] in 89% yield under aforementioned conditions (Scheme 1). In this endeavor, less reactive *n*-pentenyl glucoside was converted into a more reactive and stable *n*-pentenyl or propargyl 1,2-orthoesters in very high yield. In addition, the methodology has been gauged by preparing methyl and cholesterol 1,2-*O*-orthoesters **3b** and **3c** in 95% and 86% yields respectively using methanol and cholesterol.[10]

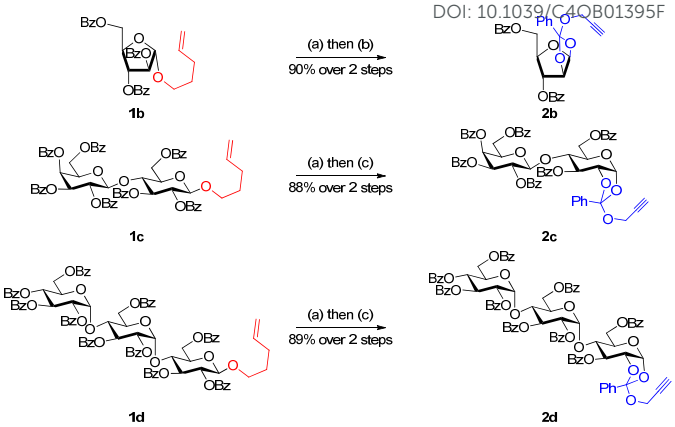
Scheme 1. Conversion *n*-pentenyl glucoside into glucosyl 1,2-orthoesters



The protocol was found to be appropriate for furanosides as well. For example, the *n*-pentenyl 2,3,5-tri-*O*-benzoyl α-D-arabinofuranoside **1b**[11a] was successfully converted into propargyl 1,2-orthobenzoate (**2b**) at room temperature in 90% yield over two steps. Similarly, per-*O*-benzoyl derivatives of *n*-pentenyl lactoside **1c**[7b] and maltotrioside **1d** were subjected to the above delineated reaction conditions with only deviation being the reaction was needed to be conducted at 60 ºC to obtain corresponding propargyl 1,2-orthobenzoates **2c**[6] and **2d** in 88% and 89% yield respectively (Scheme 2).[10] Conversion of a less reactive glycosyl donor to a more reactive and stable glycosyl donor will be an interesting strategy for the synthesis of oligosaccharides.[12] In this regard, mycobacterial arabinan synthesis has been considered in order to illustrate the benefits of converting *n*-pentenyl glycosides to 1,2-orthoesters.

Mycobacterium tuberculosis (Mtb) is the etiological agent for the tuberculosis which kills more than ~2 million lives annually.[13] Two main oligosaccharides (arabinogalactan and lipoarabinomanan) are identified on the cell surface of Mtb in which arabinose and galactose exists in furanoside form.[14a] Ethambutol, a frontline drug, was proven to act by inhibiting the arabinan biosynthesis.[14b] As a result, arabinan synthesis has been a subject of intense investigation[15] and herein, the utility of *n*-pentenyl furanoside conversion into propargyl 1,2-orthoester strategy to synthesize a pentasaccharide in an iterative fashion was demonstrated.

Scheme 2. Synthesis of propargyl 1,2-orthobenzoates from *n*-pentenyl furanosides, disaccharides and trisaccharides

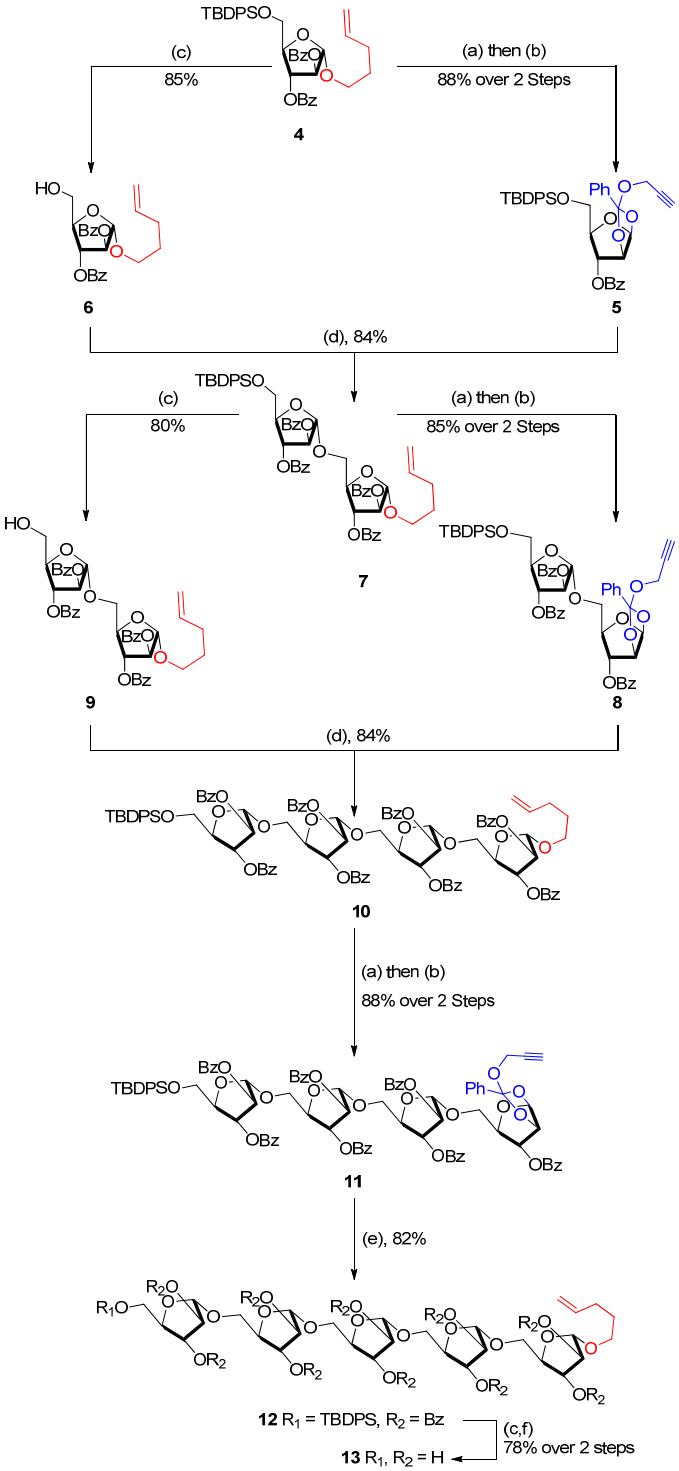


Reagents. (a) Br_2, 4 Å MS powder, 0 ºC, CH_2Cl_2, 10 min; (b) propargyl alcohol, 2,6-lutidine, TBAI, 4 Å MS powder, 25 ºC, CH_2Cl_2, 5 h; (c) propargyl alcohol, 2,6-lutidine, TBAI, 4 Å MS powder, 60 ºC, CH_2Cl_2, 24 h.

Accordingly, our investigation started with the successful conversion of easily accessible *n*-pentenyl furanoside **4** to the orthoester **5** in 88% under above identified reaction conditions. The glycosyl acceptor **6** was synthesized from compound **4** by deprotection of the *C*-5-silyl ether Scheme 3. Iterative conversion of *n*-pentenyl glycosides to propargyl 1,2-orthoesters for the synthesis of pentaarabinan of mycobacterial cell wall using HF.Py to yield compound **6** in 85% yields at room temperature for 4 h. 1,2-*Trans* diastereoselective gold(III)-catalyzed glycosidation between the orthoester **5** and aglycon **6** afforded the disaccharide **7** in 1 h. In continuation, propargyl 1,2-orthoester **8** in very good yield was obtained and the deprotection of the silyl ether of compound **7** resulted in the glycosyl acceptor **9**. The furanosylation between glycosyl donor **8** and the glycosyl acceptor **9** under gold(III)-catalyzed glycosidation conditions afforded the tetrasaccharide **10**. Tetrasaccharide **10** was again successfully converted to the 1,2-orthoester **11** under aforementioned mild conditions in 88% yield.

It is gratifying to note that the current method enabled synthesis of 1,2-orthoester of oligosaccharides (**2d** and **11**) as well in a facile manner without affecting any functionality on the glycan. The formation of tetrasaccharide 1,2-orthoester **11** was confirmed on the NMR spectral analysis. In the ^{1}H NMR spectrum of tetrasaccharide **11,** anomeric proton of the furanoside at the reducing end was noticed at δ 6.35 (d, *J* 4.3 Hz) ppm and acetylenic methine was found at δ 2.36 ppm. In the ^{13}C NMR spectrum, the presence of alkyne was confirmed based on the resonances at δ 52.0, 73.7 and 79.3 ppm along with quaternary carbon of 1,2-orthoester at δ 122.5 ppm which confirmed the successful formation of tetrasaccharyl 1,2-orthoester **11**. Further orthoester **11** was treated with one molar equivalent of glycosyl acceptor **6** to afford the pentaarabinan **12** in the presence of 7 mol% of $AuCl_3$; however, the conversion was found to be slow and less yielding (50%).

Scheme 2. Synthesis of Pentaarabinofuranoside of mycobacterium cell surface



Reagents. (a) Br_2, 4 Å MS powder, 0 ºC, CH_2Cl_2, 10 min; (b) propargyl alcohol, 2,6-lutidine, TBAI, 4 Å MS powder, 25 ºC, CH_2Cl_2, 10 h; (c) HF.Py, 4: 1 THF-Py, 0 ºC-25 ºC, 4 h, (d) 7 mol% $AuCl_3$, 4 Å MS powder, 25 ºC, CH_2Cl_2, 1 h; (e) 7 mol% each of $AuCl_3$ and AgOTf, 4 Å MS powder, 25 ºC, CH_2Cl_2, 2 h; (f) NaOMe, MeOH, 24 h, 25 ºC.

Addition of 7 mol% each of $AuCl_3$ and AgOTf was found to be highly beneficial for the successful synthesis of pentasaccharide **12** (Scheme 3).[16a] Gold trichloride upon reaction with silver triflate is known to form gold(III) triflate which in turn was found to be better in gold-catalyzed reactions.[16] Pentasaccharide **12** displayed five singlets for the five anomeric protons around δ 5.16-5.59 ppm as in the ^{1}H NMR spectrum, five anomeric carbons were identified at δ 105.6, 105.7, 105.8, 105.9 and 105.9 ppm in the ^{13}C NMR spectrum and gave very good mass spectral matching (m/z calcd. for $C_{116}H_{108}NaO_{31}Si$: 2047.6542, found: 2047.6522). Silyl ether deprotection of **12** was carried out using HF.Py and global deprotection of benzoates was performed under Zemplén conditions to obtain fully deprotected pentaarabinan (**13**) as *n*-pentenyl glycoside.[10]

Conclusions

In conclusion, a facile protocol for the synthesis of 1,2-orthoesters from *n*-pentenyl glycosides has been found. Identified method is shown to be compatible for pyranosides, furanosides and oligosaccharides as well. Furthermore, the utility of the methodology is shown by the successful synthesis of pentaarabinofuranoside present in the cell surface of *Mycobacterium tuberculosis* in an iterative fashion.

Experimental section

General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Unless otherwise reported all reactions were performed under argon atmosphere. Removal of solvent *in vacuo* refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. $AuCl_3$ and AgOTf were purchased from multinational commercial vendors. 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. Optical rotations were measured on a digital polarimeter. 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 mass analyzer. Low resolution mass spectroscopy (LRMS) was performed on UPLC-MS.

General procedure for the synthesis of 1,2-*O*-orthoesters from *n*-pentenyl glycosides: Pent-4-enyl pyranoside (**1a**) (1.00 g, 1.5 mmol) in anhydrous CH_2Cl_2 (10 mL) containing 4 Å molecular sieves powder (0.50 g) and cooled to 0 °C. Bromine (0.078 mL, 1.5 mmol) in CH_2Cl_2 (1 mL) was added drop-wise to the reaction mixture and was stirred at 0 °C for 10 min. The reaction mixture was concentrated under reduced pressure to afford 2,3,4,6-tetra-*O*-benzoyl glucopyranosyl bromide as a solid along with 4 Å molecular sieves powder which was immediately used in the next step without any additional purification.

The crude pyranosyl bromide prepared vide supra was redissolved in 10 mL anhydrous CH_2Cl_2 and propargyl alcohol (0.13 mL, 2.3 mmol) and 2,6-lutidine (0.35 mL, 3.0 mmol) were added. Catalytic amount of tetra *n*-butyl ammonium iodide was added to the reaction and stirred for 24 h at 60 °C. After completion of reaction (judged by TLC), the reaction mixture was filtered through a bed of celite and the filtrate was diluted with CH_2Cl_2 (100 mL) and water (100 mL) and the aqueous layer was extracted with CH_2Cl_2 (2x50 mL) and the organic extract was washed with saturated oxalic acid solution, saturated sodium bicarbonate solution. The organic phase was collected, dried over sodium sulphate and concentrated *in vacuo*. The crude residue of orthoester was purified by silica gel column chromatography (EtOAc:Petroleum ether 20:80) to obtain **2a** (0.88 g, 92% over two steps) as a white solid.

Similar procedure was applied for the synthesis of **3a**,[6] **3b**,[18] **3c**,[18] **2a**,[6,7b] **2b**,[11a] **2c**,[6] **2d**, **5**, **7**, and **11**.

General procedure for deprotection of *O*-silyl ethers: To a solution of *O*-TBDPS protected saccharide **4** (1.50 g, 2.26 mmol) in 20 mL of THF:Py (10:2) was added HF.Py (2 mL) at 0 °C and the reaction mixture was stirred for 4 h at room temperature. The reaction mixture was treated with sat solution of aq. sodium bicarbonate and the compound was extracted with EtOAc (2 x 50 mL) from the aqueous layer. The EtOAc layer was dried over anhydrous sodium sulphate and concentrated *in vacuo* to obtain a crude residue which was purified by flash silica gel column chromatography (EtOAc:pet ether, 25:75) to give required saccharide **6** (0.82 g, 85%) as a yellow gum.

Similar procedure was applied for the synthesis of **9**.

General procedure for gold(III) catalyzed 1,2-trans furanosylation: To a CH_2Cl_2 solution (25 mL) containing glycosyl donor **5** (1.19 g, 1.88 mmol) and glycosyl acceptor **6** (0.80 g, 1.88 mmol) with 4 Å molecular sieves powder (1.00 g) was added a catalytic amount of $AuCl_3$ (40 mg, 0.13 mmol) [for compound **12**: Silver triflate (7 mol%) as an additive] and stirred at room temperature. After 2 h at room temperature, the reaction mixture was neutralized by the addition of Et_3N and filtered through celite and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography using ethyl acetate-petroleum ether to obtain 1,2-*trans* glycoside as a fluffy solid **7** (1.58 g, 84%).

Similar procedure was applied for the synthesis of **10**, **12**.

Deprotection under Zemplén conditions: Silyl ether of **12** (100 mg, 0.049 mmol) was carried out under aforementioned conditions using HF.Py which was directly used in the next step for the saponification of benzoates. The residue was redissolved in methanol and sodium methoxide (0.049 mmol, freshly prepared) and stirred at 25 °C. After 24 h, the reaction mixture was treated with Amberlite IR-120 and filtered. The filtrate was concentrated and diluted with a solution containing 1:1 mixture of water-ethyl acetate and the compound **13** in aqueous layer was washed with ethyl acetate (10 mL) and was concentrated *in vacuo*. The crude was purified by reverse phase C18-silica gel column chromatography using acetonitrile:water as mobile phase to get fully deprotected **13** as a colourless fluffy solid (29 mg, 78% over two steps).

Pent-4-enyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-α-D-glucopyranosyl)-α-D-glucopyranoside (1d): This compound is prepared by the known procedure[8,9] using maltotriose (0.50 g, 0.99 mmol) as the starting material, Yield: (1.10 g, 68% over two steps); $[\alpha]_D^{25}$ +76.0 (*c* 0.8 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3065, 2927, 1725, 1594, 1451, 1265, 1098, 706; ^1H NMR (399.78, $CDCl_3$): δ 1.58 (2 H, dt, *J* 16.2, 7.9), 1.92 (2 H, quintet, *J* 6.7), 3.48 (1 H, dt, *J* 9.6, 6.7), 3.85 (1 H, dt, *J* 9.7, 6.2), 4.05 (1 H, ddd, *J* 9.4, 4.5, 2.0), 4.22 (1 H, d, *J* 9.5), 4.33 – 4.50 (6 H, m), 4.60 (1 H, dd, *J* 12.4, 2.8), 4.66 (1 H, dd, *J* 12.2, 4.8), 4.72 (1 H, d, *J* 7.5), 4.56 – 4.82 (1 H, m), 4.77 – 4.83 (1 H, m), 4.98 (1 H, dd, *J* 12.0, 1.8), 5.08 (1 H, dd, *J* 10.0, 3.9), 5.22 – 5.29 (2 H, m), 5.50 – 5.72 (4 H, m), 5.74 (1 H, d, *J* 3.9), 5.92 (1 H, dd, *J* 9.7, 8.5), 6.09 (1 H, t, *J* 10.1), 7.06 – 7.63 (30 H, m), 7.51 – 7.63 (6 H, m), 7.69 – 7.76 (4 H, m), 7.79 – 7.89 (4 H, m), 7.91 – 7.98 (2 H, m), 8.02 – 8.08 (2 H, m), 8.14 – 8.21 (2 H, m,); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.5, 29.7, 62.2, 63.0, 63.2, 69.0, 69.1, 69.1, 70.0, 70.0, 70.7, 70.8, 71.7, 72.3, 72.8, 73.6, 73.7, 75.0, 96.4, 96.7, 100.5, 114.8, 127.8-129.9 (50C), 132.9 (4C), 133.0 (2C), 133.1, 133.2, 133.3 (2C), 137.7, 164.7, 164.9, 165.0, 165.1, 165.3, 165.5(2C), 165.7, 165.8, 166.1; HRMS (ESI) : m/z calcd for $[C_{93}H_{80}O_{26}+Na]^+$: 1636.4869; Found: 1636.4886.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,6-tri-O-benzoyl-4-O-(2,3,4,6-tetra-O-benzoyl-α-D-glucopyra-nosyl)-α-D-glucopyranosyl)-β-D-(prop-2-yn-1-yl)-1,2-orthobenzoate (2d): This compound is prepared using the above mentioned general procedure using **1d** (1.00 g, 0.62 mmol) as the starting material, Yield: (0.873 g, 89%); $[\alpha]_D^{25}$ +89.0 (*c* 1.2 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3301, 3065, 2970, 2114, 1728, 1640, 1451, 1267, 1101, 707; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.18 (1 H, d, *J* 1.9), 2.91 – 3.01 (1 H, m), 3.11 – 3.19 (1 H, m), 3.89 (1 H, d, *J* 7.8), 4.09 – 4.17 (2 H, m), 4.22 – 4.59 (7 H, m), 4.78 (2 H, q, *J* 8.4), 5.07 (1 H, dd, *J* 10.3, 3.9), 5.22 (1 H, dd, *J* 10.6, 3.9), 5.32 – 5.39 (1 H, m), 5.65 (1 H, t, *J* 9.8), 5.83 (1 H, d, *J* 3.7), 5.94 (1 H, d, *J* 5.2), 6.01 – 6.19 (3 H, m), 6.79 – 7.57 (32 H, m), 7.55 – 8.11 (18 H, m); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 51.8, 62.3, 63.3, 63.6, 67.5, 67.9, 68.9, 69.1, 69.2, 69.8, 70.8, 71.0, 71.7, 72.4, 72.9, 73.0, 73.7, 78.9, 94.0, 97.0, 97.6, 121.3, 126.7-130.2 (50C), 132.8, 133.0, 133.0, 133.1, 133.2, 133.2, 133.2, 133.3, 133.6, 133.6, 164.7, 164.8, 165.0, 165.5, 165.7, 165.7, 165.9, 166.0, 166.1; HRMS (ESI) : m/z calcd for $[C_{91}H_{74}O_{26}+Na]^+$: 1605.4366; Found: 1605.4384.

(Pent-4-enyl) 2,3-di-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranoside (4): This compound is prepared using the known procedure[10,15] using arabinose (4.00 g, 26.64 mmol) as the starting material, Yield: (5.67 g, 32% over three steps); $[\alpha]_D^{25}$+11.0 (*c* 1.4 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3070, 2927, 1725, 1594, 1268, 1109, 700; ^1H NMR (399.78, $CDCl_3$): δ 1.05 (9 H, s), 1.66 – 1.90 (2 H, m), 2.18 (2 H, dt, *J* 13.1, 6.8), 3.53 (1 H, dt, *J* 9.5, 6.2), 3.78 (1 H, dt, *J* 9.5, 6.7), 4.01 (2 H, dABq, *J* 11.1, 5.0), 4.37 (1 H, q, *J* 4.8), 4.93 – 5.10 (2 H, m), 5.21 (1 H, s), 5.21 (1 H, s), 5.45 (1 H, d, *J* 1.4), 5.84 (1 H, ddt, *J*

16.9, 10.1, 6.7), 7.14 – 7.83 (16 H, m), 7.94 – 8.23 (4 H, m); ^{13}C NMR (100.53, $CDCl_3$): δ 19.3, 26.7, 26.7, 26.7, 28.7, 30.3, 63.6, 66.6, 77.4, 82.3, 82.9, 105.7, 114.9, 127.6, 127.6, 127.7, 128.3, 128.3, 128.4, 129.2, 129.5, 129.6, 129.6, 129.6, 129.8, 129.9, 129.9, 129.9, 133.1, 133.2, 133.3, 133.3, 134.8, 135.6, 135.6, 135.6, 135.6, 138.1, 165.4, 165.5; HRMS (ESI) : m/z calcd for $[C_{40}H_{44}O_7Si+Na]^+$: 687.2754; Found: 687.2750.

3-*O*-Benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-*O*-orthobenzoate (5): This compound is prepared using the above mentioned general procedure using **4** (1.5 g, 2.26 mmol) as the starting material, Yield: (1.26 g, 88%); $[\alpha]_D^{25}$ –20.0 (*c* 1.2, $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3293, 3066, 2939, 1727, 1595, 1453, 1266, 1106, 704; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 0.99 (9 H, s), 2.37 (1 H, t, *J* 2.2), 3.63 (2 H, dd, *J* 7.5, 4.1), 3.84 – 4.02 (2 H, m), 4.46 (1 H, t, *J* 7.5), 5.09 (1 H, d, *J* 4.3), 5.67 (1 H, s), 6.33 (1 H, d, *J* 4.3), 6.97 – 7.86 (18 H, m), 8.09 (2 H, d, *J* 7.9); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.1, 26.7, 26.7, 26.7, 51.9, 63.4, 73.7, 77.5, 79.3, 85.0, 87.2, 106.5, 122.4, 126.3, 126.3, 127.5, 127.6, 127.6, 127.6, 128.2, 128.3, 128.4, 128.4, 129.2, 129.6, 129.6, 129.6, 129.8, 129.8, 133.1, 133.1, 133.4, 134.2, 135.3, 135.4, 135.4, 135.4, 165.1; HRMS (ESI) : m/z calcd for $[C_{38}H_{38}O_7Si+Na]^+$: 657.2284; Found: 657.2281.

(Pent-4-enyl) 2,3-di-*O*-benzoyl-α-D-arabinofuranoside (6): This compound is prepared using the above mentioned general procedure using **4** (1.5 g, 2.26 mmol) as the starting material, Yield: (0.818 g, 85%); $[\alpha]_D^{25}$ –32.8 (*c* 1.0 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3512, 3071, 2931, 1723, 1601, 1451, 1265, 1176, 710; ^{1}H NMR (399.78, $CDCl_3$): δ 1.60 – 1.94 (2 H, m), 2.08 – 2.31 (2 H, m), 2.43 (1 H, br s), 3.54 (1 H, dt, *J* 9.5, 6.2), 3.79 (1 H, dt, *J* 9.5, 6.6), 3.99 (2 H, d, *J* 11.7), 4.32 (1 H, q, *J* 4.1), 4.89 – 5.08 (2 H, m), 5.23 (1 H, s), 5.40 – 5.48 (1 H, m), 5.53 (1 H, d, *J* 1.3), 5.82 (1 H, ddt, *J* 16.9, 10.2, 6.6), 7.24 – 7.77 (6 H, m), 7.79 – 8.35 (4 H, m); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.2, 62.3, 66.7, 77.8, 81.7, 83.6, 105.5, 114.9, 128.4, 128.4, 128.5, 128.5, 129.0, 129.1, 129.7, 129.8, 129.9, 129.9, 133.5, 133.5, 138.0, 165.3, 166.1; HRMS (ESI) : m/z calcd for $[C_{24}H_{26}O_7+Na]^+$: 449.1576; Found: 449.1573.

(Pent-4-enyl)-2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benozyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (7): This compound is prepared using the above mentioned general procedure using **5** (1.19 g, 1.88 mmol) and **6** (0.80 g, 1.88 mmol) as the starting material, Yield: (1.58 g, 84%); $[\alpha]_D^{25}$ –12.4 (*c* 1.0 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3070, 2927, 1727, 1594, 1451, 1268, 1115, 715; ^{1}H NMR (399.78 MHz, $CDCl_3$): 1.02 (9 H, s), 1.68 – 1.80 (2 H, m), 2.12 – 2.23 (2 H, m), 3.52 (1 H, dt, *J* 9.0, 5.9), 3.79 (1 H, dt, *J* 9.2, 6.5), 3.93 (1 H, dd, *J* 11.2, 2.5), 3.99 (1 H, d, *J* 4.4), 4.20 (1 H, dt, *J* 11.1, 6.5), 4.33 (1 H, d, *J* 2.3), 4.48 (1 H, d, *J* 3.9), 4.51 (1 H, dd, *J* 10.5, 5.9), 4.92 – 5.06 (2 H, m), 5.22 (1 H, s), 5.38 (1 H, s), 5.51 (1 H, s), 5.58 (1 H, s), 5.63 (1 H, s), 5.64 (1 H, s), 5.81 (1 H, ddt, *J* 16.8, 10.1, 6.5), 7.14 – 7.80 (22 H, m), 7.87 – 8.19 (8 H, m); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.2, 26.7, 26.7, 26.7, 28.7, 30.3, 63.3, 66.1, 66.6, 77.4, 77.5, 81.7, 81.8, 82.1, 83.2, 105.6, 105.9, 114.9, 127.5-133.3 (30C), 135.6, 135.6, 135.6, 135.7, 135.9, 135.9, 138.1, 165.2, 165.4, 165.5, 165.6; HRMS (ESI) : m/z calcd for $[C_{59}H_{60}O_{31}Si+Na]^+$: 1027.3701; Found: 1027.3711.

3-*O*-Benzoyl-5-*O*-(2,3-di-*O*-benozyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-*O*-orthobenzoate (8): This compound is prepared using the above mentioned general procedure using **7** (0.80 g, 0.80 mmol) as the starting material, Yield: (0.66 g, 85%); $[\alpha]_D^{25}$ –18.9 (*c* 1.2 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3434, 3070, 2931, 1721, 1588, 1264, 1107, 706; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.01 (9 H, s), 2.37 (1 H, t, *J* 2.5), 3.51 (1 H, dd, *J* 10.4, 7.5), 3.72 – 3.80 (1 H, m), 3.90 – 3.96 (1 H, m), 3.96 – 4.02 (1 H, m), 4.26 (1 H, q, *J* 4.4), 4.34 (1 H, d, *J* 2.2), 4.44 – 4.56 (1 H, m), 4.61 (1 H, t, *J* 7.4), 5.05 (1 H, s), 5.12 (1 H, d, *J* 4.3), 5.34 – 5.45 (1 H, m), 5.50 – 5.68 (2 H, m), 6.36 (1 H, d, *J* 4.3), 7.10 – 7.75 (24 H, m), 7.86 – 8.22 (6 H, m); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.3, 26.8, 26.8, 26.8, 52.0, 63.2, 66.8, 73.8, 77.2, 77.9, 79.4, 82.2, 83.2, 85.0, 85.4, 105.9, 106.8, 122.6, 126.5, 126.5, 127.7, 127.7, 127.7, 127.7, 127.8, 128.0, 128.0, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 129.7, 129.7, 129.9, 129.9, 130.0, 130.0, 130.0, 130.0, 130.0, 133.2, 133.3, 133.5, 133.6, 135.6, 135.7, 135.7, 135.7, 135.7, 136.0, 165.3, 165.4, 165.7; HRMS (ESI) : m/z calcd for $[C_{57}H_{54}O_{13}Si+Na]^+$: 997.3231; Found: 997.3238.

(Pent-4-enyl)-2,3-di-O-benzoyl-5-O-(2,3-di-O-benozyl-α-D-arabinofuranosyl)-α-D-ara-binofuranoside (9): This compound is prepared using the above mentioned general procedure using **7** (0.70 g, 0.70 mmol) as the starting material, Yield: (0.43 g, 80%); $[\alpha]_D^{25}$ –19.0 (*c* 1.0 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3422, 3070, 2928, 1724, 1598, 1451, 1264, 1110, 712; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.40 – 1.90 (2 H, m), 2.07 – 2.34 (2 H, m), 2.39 (1 H, br s), 3.51 (1 H, dt, *J* 9.5, 6.1), 3.77 (1 H, dt, *J* 9.5, 6.6), 3.96 (2 H, dd, *J* 11.2, 2.9), 4.02 (1 H, dd, *J* 12.1, 3.5), 4.20 (1 H, dd, *J* 11.2, 4.6), 4.44 (1 H, td, *J* 4.6, 3.0), 4.51 (1 H, q, *J* 4.0), 4.88 – 5.08 (2 H, m), 5.22 (1 H, s), 5.42 (1 H, s), 5.43 – 5.45 (1 H, m), 5.51 (1 H, d, *J* 1.2), 5.62 (1 H, d, *J* 5.0), 5.66 (1 H, d, *J* 1.3), 5.82 (1 H, ddt, *J* 16.9, 10.2, 6.7), 7.04 – 7.73 (12 H, m), 7.75 – 8.30 (8 H, m); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.2, 62.2, 66.1, 66.6, 77.3, 77.7, 81.6, 81.7, 81.8, 83.6, 105.5, 105.7, 114.9, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.9, 129.0, 129.0, 129.2, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.8, 133.3, 133.4, 133.4, 133.5, 138.0, 165.1, 165.4, 165.7, 166.1; HRMS (ESI) : m/z calcd for $[C_{43}H_{42}O_{13}+Na]^+$: 789.2523; Found: 789.2520.

Pent-4-enyl-2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabino-furanoside (10) : This compound is prepared using the above mentioned general procedure using **9** (0.42 g, 0.55 mmol) and **8** (0.53 g, 0.55 mmol) as the starting material, Yield: (0.78 g, 84%); $[\alpha]_D^{25}$ +2.4 (*c* 1.2 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3068, 2933, 1724, 1599, 1452, 1266, 1109, 708; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 0.99 (9 H, s), 1.79 – 1.65 (2 H, m), 2.21 – 2.09 (2 H, m), 3.50 (1 H, dt, *J* 9.5, 6.2),3.76 (1 H, dt, *J* 9.5, 6.6), 3.98 – 3.85 (5 H, m), 4.17 (3 H, ddd, *J* 14.7, 7.9, 3.2), 4.42 (1 H, dd, *J* 7.6, 4.5), 4.47 (1 H, q, *J* 4.5), 4.64 – 4.56 (2 H, m), 5.04 – 4.90 (2 H, m),

5.21 (1 H, s), 5.35 (1 H, s), 5.39 (1 H, s), 5.40 (1 H, s), 5.48 (1 H, t, *J* 2.1), 5.53 (1 H, t, *J* 4.0), 5.65 – 5.59 (6 H, m), 5.80 (1 H, ddt, *J* 16.9, 10.2, 6.7), 7.59 – 7.19 (30 H, m), 7.67 (4 H, m), δ 8.06 – 7.86 (16 H, m); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.4, 26.9, 26.9, 26.9, 28.9, 30.4, 60.6, 63.4, 65.8, 65.9, 66.0, 66.8, 66.8, 77.3, 77.4, 81.7, 81.7, 81.9, 81.9, 82.1, 82.1, 82.3, 83.2, 105.7, 105.9, 106.0, 106.0, 115.0, 127.8-130.1 (50C), 133.2, 133.3, 133.3, 133.3, 133.5, 133.5, 133.5, 133.5, 135.8, 135.8, 138.2, 165.3, 165.3, 165.4, 165.6, 165.6, 165.7, 165.7, 165.8; HRMS (ESI): m/z calcd for $[C_{97}H_{92}O_{25}Si+Na]^+$: 1708.5628; Found: 1708.5620.

3-*O*-Benzoyl-5-*O*-(2,3-di-*O*-benozyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-*O*-orthobenzoate (11): This compound is prepared using the above mentioned general procedure using **10** (0.70 g, 0.42 mmol) as the starting material, Yield: (0.61 g, 88%); $[\alpha]_D^{25}$ –2.1 (*c* 1.0 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3302, 3071, 2927, 2105, 1725, 1596, 1454, 1265, 1107, 708; ^{1}H NMR 399.78 MHz, $CDCl_3$): δ 1.00 (9 H, s), 2.36 (1 H, t, *J* 2.5), 3.51 (1 H, dd, *J* 10.3, 7.2), 3.67 (1 H, dd, *J* 11.2, 2.7), 3.78 (1 H, dd, *J* 10.3, 7.7), 3.88 (1 H, dd, *J* 9.5, 2.5), 3.92 (2 H, dd, *J* 5.2, 2.4), 3.96 (2 H, d, *J* 4.5), 4.07 (1 H, dd, *J* 11.2, 4.0), 4.17 (1 H, dd, *J* 11.3, 4.1), 4.28 (1 H, dd, *J* 7.4, 3.9), 4.49 (1 H, q, *J* 4.6), 4.58-4.62 (2 H, m), 5.56 (1 H, d, *J* 1.3), 5.61-5.63 (3 H, m), 5.11 (1 H, d, *J* = 4.3 Hz), 5.30 (1 H, s), 5.45 (1 H, *J* 1.2), 5.52 (1 H, s), 5.06 (1 H, s), 5.38 (1 H, s), 5.60 (1 H, s), 6.35 (1 H, d, *J* 4.3), 7.21-7.70 (36 H, m), 7.87-8.05 (14 H, m); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.2, 26.7 (3C), 52.0, 63.3, 65.5, 65.7, 66.4, 76.7, 77.2, 77.3, 77.7, 81.4, 81.5, 82.0, 82.1, 82.1, 82.1, 83.1, 84.8, 85.3, 105.4, 105.8, 105.9, 106.7, 122.5, 126.4 (2C), 127.6-135.6 (59C), 165.0, 165.1, 165.2 (2C), 165.4, 165.6 (2C); HRMS (ESI): m/z calcd for $[C_{95}H_{86}O_{25}Si+Na]^+$: 1678.5159; Found: 1678.5206.

Pent-4-enyl-2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (12): This compound is prepared using the above mentioned general procedure using **11** (0.50 g, 0.30 mmol) and **6** (0.13 g, 0.30 mmol) as the starting material, Yield: (0.50 g, 82%); $[\alpha]_D^{25}$ +5.7 (*c* 1.0 in $CHCl_3$); IR(cm^{-1}, $CHCl_3$): 3070, 2927, 1727, 1591, 1451, 1268, 1113, 714; ^{1}H NMR (399.78, $CDCl_3$): δ 0.95 (9 H, s), 1.69 (2 H, dd, *J* 12.7, 6.3), 2.12 (2 H, dt, *J* 11.5, 6.9), 3.46 (1 H, dt, *J* 9.4, 6.2), 3.72 (1 H, dt, *J* 9.3, 6.6), 3.79 – 3.99 (6 H, m), 4.05 – 4.23 (4 H, m), 4.38 (1 H, q, *J* 4.4), 4.43 (1 H, q, *J* 4.5), 4.48 – 4.61 (3 H, m), 4.81 – 5.04 (2 H, m), 5.16 (1 H, s), 5.32 (1 H, s), 5.34 (2 H, s), 5.35 (1 H, s), 5.46 (1 H, s), 5.51 (1 H, s), 5.53 – 5.64 (8 H, m), 5.77 (1 H, ddt, *J* 16.9, 10.2, 6.7), 7.12 – 7.57 (36 H, m), 7.64 (4 H, ddd, *J* 7.6, 3.7, 1.3), 7.79 – 8.08 (20 H, m); ^{13}C NMR (100.53, $CDCl_3$): δ 19.2, 26.7, 26.7, 26.7, 28.7, 30.3, 63.3, 65.7, 65.7, 65.8, 65.9, 66.6, 77.1, 77.2, 77.2, 77.3, 81.4, 81.5, 81.5, 81.7, 81.7, 81.8, 82.0, 82.0, 82.0, 82.0, 82.1, 83.1, 105.6, 105.7, 105.8, 105.9, 114.9, 126.2-129.9 (56C), 133.0, 133.1, 133.1, 133.1, 133.1, 133.2, 133.2, 133.3, 133.3, 133.3, 133.4, 133.4, 135.6, 135.6, 135.6, 135.6, 138.1, 165.1, 165.1, 165.1, 165.1, 165.4, 165.4, 165.5, 165.5, 165.6, 165.6; HRMS (ESI) : m/z calcd for $[C_{116}H_{108}O_{31}Si+Na]^+$: 2047.6542; Found: 2047.6532.

Pent-4-enyl [5-O-(5-O-(5-O-(5-O-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl]-α-D-arabinofuranoside (13):

This compound is prepared using the known procedure[15] using (0.1 g, 0.049 mmol) as the starting material, Yield: (29 mg, 78% over two steps); $[\alpha]^{20}_D$ +77.5 (*c* 1.7 in H_2O); IR(cm^{-1}, KBr): 3295, 2922, 2848, 1640, 1402, 1069, 1035; ^{1}H NMR (399.78 MHz, D_2O): ^{1}H NMR (399.78 MHz, D_2O): δ 1.70 (2 H, quintet, *J* 6.8), 2.13 (2 H, q, *J* 7.0), 3.71 (1 H, dd, *J* 12.3, 5.8), 3.81 (2 H, s), 3.87 (1 H, td, *J* 10.9, 10.2, 4.7), 3.95 (1 H, dd, *J* 5.9, 3.2), 3.65 – 4.25 (22 H, m), 5.01 (1 H, s), 4.99 – 5.13 (2 H, m), 5.08 (4 H, s), 5.89 (1 H, ddt, *J* 13.4, 10.2, 6.7);^{13}C NMR (100.53 MHz, $CDCl_3$): δ 27.8, 29.5, 61.1, 61.1, 66.7, 66.8, 66.9, 67.8, 76.4, 76.5, 76.5, 76.7, 76.7, 80.7, 80.8, 80.8, 80.9, 80.9, 81.7, 82.3, 82.3, 83.9, 83.9, 107.2, 107.4, 107.4, 107.5, 107.5, 114.8, 138.7; HRMS (ESI) : m/z calcd for $[C_{30}H_{50}O_{21}+Na]^+$: 769.2742; Found: 769.2731.

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Notes and references

†Electronic Supplementary Information (ESI) available: Copies of ^{1}H, ^{13}C and DEPT NMR spectra for all new compounds. See DOI: 10.1039/b000000x/

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