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Synthesis of enantiopure, densely functionalized carbocycles from vinyl nitro-modified carbohydrates

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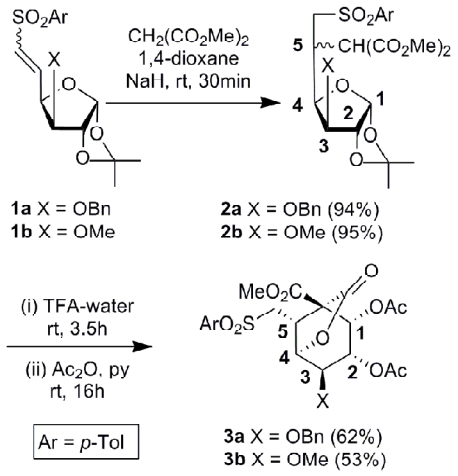
A powerful, flexible, and stereoselective general strategy for the construction of chirally pure six-membered carbocycles from easily available vinyl nitro-modified hexofuranosides is described. By using a Michael addition reaction followed by ring opening and ring closure, densely functionalized carbasugars decorated with multiple chiral centers are obtained in good overall yields.

Keywords: Nitrovinyl carbohydrates, 1,3-dicarbonyl compounds, Michael addition, enantioselectivity, carbocycles.

Introduction

The importance of six-membered carbocycles in natural products and pharmaceuticals led to outstanding development in the area of synthetic strategies for the designing of these structures[1]. In the last decade, particular emphasis has been devoted to the preparation of polyfunctionalized carbocycles from sugars[2] because many natural products and other biologically active molecules contain polyhydroxylated carbocyclic rings[1,2]. The general process includes the protection of furanosides or pyranosides, functionalization, ring opening and finally cyclization to form the carbocyclic rings. A wide variety of synthetic strategies is available for the preparation of densely functionalized carbocycles from carbohydrates[2].

Exploration of strategies for cyclitol synthesis and their biological evaluation continues to be an important area of research. Recently, domino and/or multicomponent reactions have largely been used for the synthesis of large libraries of these heterocyclic molecules by using β-dicarbonyls as an efficient partner[3]. As part of our research on the synthesis of enantiomerically pure non-carbohydrate compounds from vinyl sulfone-modified carbohydrates[4], we established a strategy for the functionalization of the C-5 position via Michael addition of nucleophiles to vinyl sulfone-modified hexofuranosides[5a-b]. This general approach led to the preparation of cyclitols and other heterocycles[5]. Thus, the vinyl sulfone-modified hexofuranosides **1a-b** were reacted with dimethylmalonate to afford a mixture of Michael adducts **2a-b** in excellent yields. Acid mediated removal of the isopropylidene group exposed the CHO (C1) group to intramolecular attack by the active methyne carbon of **2** resulting into the formation of six-membered carbocycles which underwent an additional attack of the free C4-OH at one of the malonate carbonyl carbons resulting into bicyclic compounds; the products were isolated as their acetyl derivatives **3a-b**[5b] (Scheme 1).



Scheme 1. Polyhydroxylated cyclohexanes from vinyl sulfone-modified carbohydrates.

We opined that the above synthetic approach to cyclohexane synthesis might be considered as a general strategy and deserved to be studied further using other functionalities, such as the vinyl nitro group. In general, nitro olefins are versatile compounds in organic synthesis due to their ready availability and the ease of transformation into a wide variety of functionalities[6]. Interestingly, in the recent past, enantiomerically pure cyclohexane compounds functionalized with CH_2NO_2 group, e.g. **A**[7a], **B**[7b], **C**[7c], **D**[7d] etc. (Fig. 1) have been identified as useful starting materials for the synthesis of biologically important compounds.

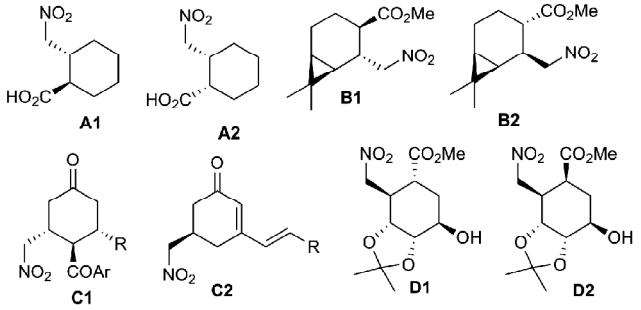
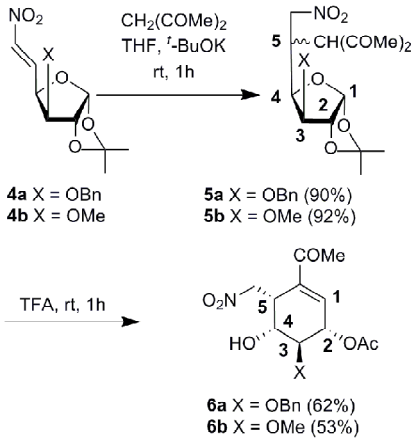


Fig. 1. Selected cyclohexanes[7] functionalized with CH_2NO_2 group.

Results and discussion

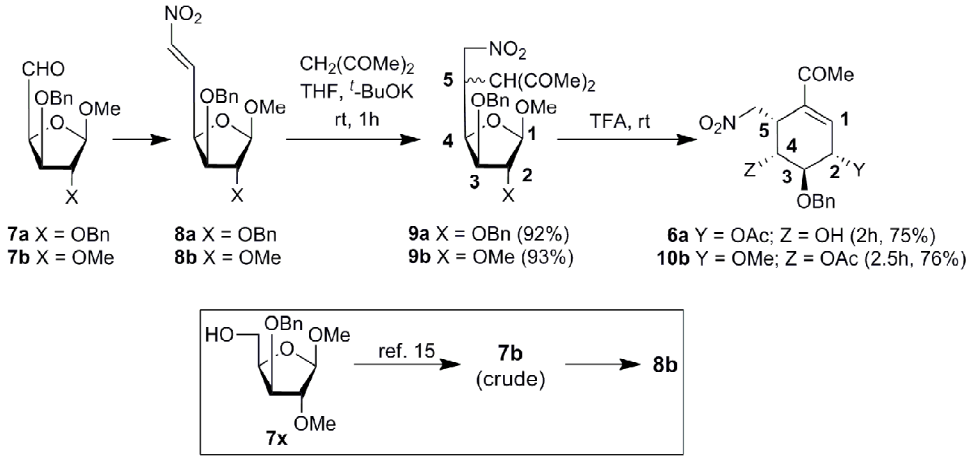
Nitrosugars have been identified as a special class of compounds for the generation of a wide ranging compounds[8]. Vinyl nitro-modified hexofuranosides were utilized in the past for the synthesis of carbocycles initiated by the Michael addition of 1,3-dithiane[9], bromonaphthalene[10], naphthaquinone[11], Rh(III) catalyzed benzamide[12] or NHC-catalyzed dual Stetter cascade cyclization reactions[13]. However, as far as our knowledge goes in the literature, there is no report on the addition of 1,3-dicarbonyl compounds to vinyl nitro-modified carbohydrates **4** or **8** leading to the synthesis of cyclohexitols. The potassium salt of acetylacetone was therefore reacted with **4a**[9b] and **4b**[13] in THF to afford a mixture of addition compounds consisting of a major β-L-ido isomer **5a** and **5b** respectively, each contaminated with a minute amount of α-D-glucoisomer (Scheme 2). The isomeric nature of **5a** and **5b** was decided on the basis of the addition pattern of nucleophiles to **1a** and **1b** reported earlier[5a-b] and only major peaks are reported in the Experimental section. Compounds **5a-b** on treatment with TFA afforded enantiopure cyclohexene derivatives **6a-b** respectively in high yields



Scheme 2. Synthesis of cyclohexenes from vinyl nitro-modified hexofuranosides.

(Scheme 2); the isomeric product was lost during work-up and purification. Notably, in each case, a cyclohexene derivative **6** was formed instead of the expected bicyclic derivative **3** obtained from the vinyl sulfone-modified carbohydrate.

The smooth synthesis of **6a-b** prompted us to extend this strategy and also identify the reaction mechanism. Thus, we synthesized vinyl nitro-modified carbohydrate **8a** from easily the available sugar aldehyde **7a**[14] following a literature procedure[9b] in high yield (Scheme 3). The aldehyde **7b** was obtained via the oxidation[15] of methyl-2-*O*-methyl-3-*O*-(phenylmethyl)-β-D-xylofuranoside **E**[16] (Scheme 3); the crude aldehyde was directly converted to the vinyl nitro-modified carbohydrate **8b**. The potassium salt of acetylacetone was reacted with **8a-b** in THF to afford a mixture of compounds consisting of a major isomer **9a-b** respectively contaminated with a minute amount of diastereomers of addition compounds in excellent yields. Compound **9a** on treatment with TFA surprisingly afforded enantiopure cyclohexene derivative **6a** whereas **9b** under similar conditions produced the expected **10b** (Scheme 3). In this case also the isomeric product was lost during work-up and purification. All cyclohexenes have shown characteristic peaks at δ 6.57–6.85 ppm in ^{1}H NMR spectra which are due to the olefinic protons. Compounds **6a**, **6b** and **10b** have comparable spectral patterns. Moreover, configuration of **6a** was unambiguously confirmed from X-ray analysis of its single crystal (Fig. 2).



7a X = OBn
7b X = OMe

8a X = OBn
8b X = OMe

9a X = OBn (92%)
9b X = OMe (93%)

6a Y = OAc; Z = OH (2h, 75%)
10b Y = OMe; Z = OAc (2.5h, 76%)

Scheme 3. Synthesis of cyclohexenes from vinyl nitro-modified hexofuranosides.

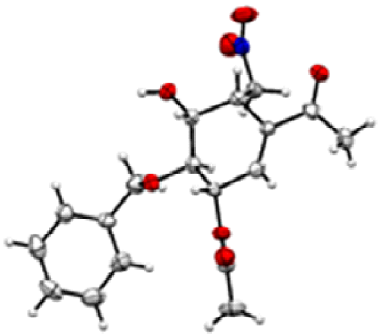
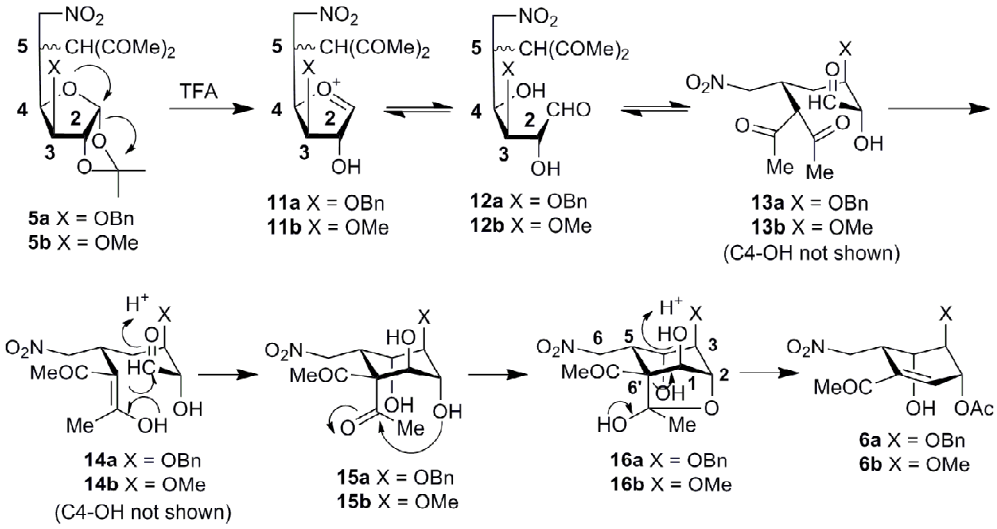


Fig. 2. ORTEP diagram of **6a** (CCDC 905009).

The most plausible mechanism of formation of cyclohexenes **6a-b** is delineated in Scheme 4. Thus, after the deprotection of **5a-b**, the oxocarbonium ion **11** opens up to form **12** which reorients itself in the chair form **13**; one of the β-dicarbonyl groups of **13** undergo keto-enol tautomerisation to form **14**. The methylidene carbon of **14** intramolecularly attacks the free CHO group (C-1) to afford **15**. The free hydroxyl group at C-2 of **15** then intramolecularly attacks the carbonyl carbon of keto group of dicarbonyl derivative to afford the hemiketal **16**. The -O-C2-C1-C6′-C(Me)O⁻- ring of **16** eventually collapses with the formation of the acetylated



5a X = OBn
5b X = OMe

11a X = OBn
11b X = OMe

12a X = OBn
12b X = OMe

13a X = OBn
13b X = OMe
(C4-OH not shown)

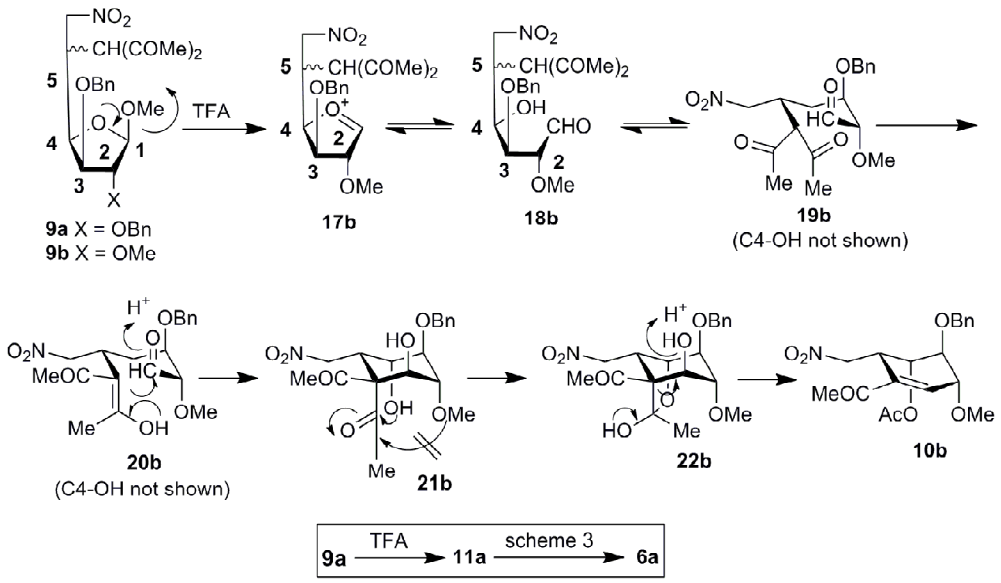
14a X = OBn
14b X = OMe
(C4-OH not shown)

15a X = OBn
15b X = OMe

16a X = OBn
16b X = OMe

6a X = OBn
6b X = OMe

Scheme 4. Plausible mechanism for the formation of **6a-b**.



Scheme 5. Plausible mechanism for the formation of **10b**.

cyclohexenes **6a-b** (Scheme 4). The mechanism was further supported by the formation of cyclohexene **10b**. In this case the C-2 hyroxyl group was protected with a methyl group. Therefore, after the demethylation of **9b**, the intermediates went through the similar reorientation as proposed in Scheme 5 (**9b**→**17b**→**18b**→**19b**→**20b**→**21b**). The intermediate **21b** (which is equivalent to **15b**) underwent an intramolecular attack by the C-4 hydroxyl group (instead of C-2 hydroxyl group) which resulted in the formation of **10b** (Scheme 5). In the case of **9a**, however the C-2 benzyl underwent deprotection in acidic medium to generate **6a** via intermediates **11a** to **16a** (Scheme 4).

In conclusion, we have developed an efficient and stereoselective general strategy for the construction of enantiomerically pure and densely functionalized cyclohexenes from easily accessible vinyl nitro-modified carbohydrates precursors. The nature of the electron deficient double bond dictated the product structure as was evident from the structural differences between bicyclic products obtained from the vinyl sulfone-modified carbohydrates and cyclohexenes generated from vinyl sulfone-modified precursors. This study establishes a new and simple strategy to carry out such transformations under mild conditions to obtain carbocycles with predictable stereoselectivity. Further studies on the application of this strategy to access six-membered carbasugars are currently underway.

Experimental

General methods: All reactions were conducted under N_2 atmosphere. Melting points were determined in open-end capillary tubes and are uncorrected. Carbohydrates and other fine chemicals were obtained from commercial suppliers and are used without purification. Solvents were dried and distilled following the standard procedures. TLC was carried out on pre-coated plates (Merck silica gel 60, f_{254}) and the spots were visualized with UV light or by charring the plate dipped in 5% H_2SO_4-MeOH solution. Column chromatography was performed on silica gel (230–400 mesh). ^1H and ^{13}C NMR for most of the compounds were recorded at 200/400 and 50/100 MHz respectively using either $CDCl_3$ as the solvent unless stated otherwise. DEPT experiments have been carried out to identify the methylene carbons. Optical rotations were recorded at 589 nm. High Resolution Mass Spectra were recorded on an Electrospray-Ionisation Mass Spectrometer.

*Compound **8a**:* Following the reported procedure[9b], sugar aldehyde **7a** (0.4 g, 1.17 mmol) was converted to the corresponding vinyl nitro analogs **8a** (0.38 g, 85%); colorless jelly; $[\alpha]_D^{30}$: –75.6 (*c* 0.56, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 3.40 (s, 3H), 3.46 (d, 1H, *J* 3.6 Hz), 4.00 (bs, 1H), 4.09–4.14 (m, 1H), 4.45 (m, 1H), 4.51 (d, 1H, *J* 3.0 Hz), 4.55–4.62 (m, 1H), 4.82–4.87 (m, 1H), 4.94 (s, 1H), 7.09–7.16 (m, 1H), 7.23–7.26 (m, 1H), 7.30 (s, 10H); ^{13}C NMR: δ 56.2, 72.3 (CH_2), 72.6 (CH_2),

77.5, 82.2, 86.1, 108.7, 127.9, 128.1, 128.2, 128.3, 128.6, 128.7, 137.2, 137.4, 138.9, 140.6; HRMS [ES, (M + Na)$^+$] Calcd. for $C_{21}H_{23}NO_6Na$ 408.1391, Obsd. 408.1423.

*Compound **8b**:* Partially protected methyl xyloside **E**[15] (0.4 g, 1.51 mmol) was oxidized[16] to the aldehyde **7b**. Following a literature procedure[9b], the crude aldehyde **7b** was converted to the corresponding vinyl nitro analogue **8b** (0.4 g, 86%); colorless jelly; $[\alpha]_D^{30}$: –85.2 (*c* 0.84, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.36 (s, 3H), 3.46 (s, 3H), 3.79 (m, 1H), 4.06–4.11 (m, 1H), 4.51 (d, 1H, *J* 10.4 Hz), 4.68 (d, 1H, *J* 12.2 Hz), 4.82–4.91 (m, 2H), 7.12–7.19 (m, 1H), 7.26–7.29 (m, 1H), 7.33 (s, 5H); ^{13}C NMR: δ 56.1, 57.9, 72.5 (CH_2), 77.4, 81.7, 87.9, 108.2, 128.0, 128.2, 128.6, 137.1, 138.8, 140.4; HRMS [ES, (M + Na)$^+$] Calcd. for $C_{15}H_{19}NO_6Na$ 332.1060, Obsd. 332.1110.

*General procedure for the synthesis of **5a**, **5b**, **9a**, and **9b**:* To a suspension of *tert*-BuOK (1.2 eqv.) in dry THF (2 mL) at ambient temperature was added acetylacetone (1.6 eqv.) and the resulting solution was stirred for 30 min at that temperature under nitrogen. A solution of vinyl nitro-modified carbohydrates **4a**, **4b**, **8a** and **8b** (1 eqv.) in dry THF (1 mL) was added dropwise to the reaction mixture. The resulting solution was then stirred for 1 h. After completion of reaction (TLC) and usual workup, the resulting residue was purified by column chromatography over silica gel (EtOAc/petroleum ether) to get the pure **5a**, **5b**, **9a** and **9b** in 9:1 diasteromeric ratio.

*Compound **5a**:* Following the general procedure, acetylacetone (0.16 mL, 1.50 mmol) was reacted with **4a** (0.3 g, 0.94 mmol) in presence of *tert*-BuOK (0.13 g, 1.13 mmol) for 1 h to yield **5a** (0.33 g, 90%); colorless jelly; $[\alpha]_D^{30}$: +57.3 (*c* 0.85, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.25 (s, 3H), 1.39 (s, 3H), 2.15 (s, 3H), 2.22 (s, 3H), 3.32–3.36 (m, 1H), 3.90 (d, 1H, *J* 2.8 Hz), 4.13–4.23 (m, 1H), 4.24 (d, 1H, *J* 5.6 Hz), 4.35–4.39 (m, 2H), 4.44–4.49 (m, 1H), 4.54–4.60 (m, 2H), 5.79 (d, 1H, *J* 3.6 Hz), 7.25–7.33 (m, 5H); ^{13}C NMR: δ 26.2, 26.6, 29.9, 31.0, 36.0, 65.4, 71.6 (CH_2), 74.2 (CH_2), 79.1, 81.0, 81.6, 104.3, 111.9, 128.2, 128.6, 136.6, 203.1, 203.5; HRMS [ES, (M + H)$^+$] Calcd. for $C_{21}H_{28}NO_8$ 422.1795, Obsd. 422.1815.

*Compound **5b**:* Following the general procedure, acetylacetone (0.20 mL, 1.96 mmol) was reacted with **4b** (0.3 g, 1.23 mmol) in presence of *tert*-BuOK (0.17 g, 1.48 mmol) for 1 h to yield **5b** (0.35 g, 92%); colorless jelly; $[\alpha]_D^{30}$: +60.5 (*c* 0.88, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 3H), 1.39 (s, 3H), 2.19 (s, 3H), 2.35 (s, 3H), 3.27 (s, 3H), 3.35–3.38 (m, 1H), 3.67 (d, 1H, *J* 3.2 Hz), 4.13 (dd, 1H, *J* 3.2, 9.6 Hz), 4.29 (d, 1H, *J* 5.0 Hz), 4.42 (dd, 1H, *J* 2.6, 13.8 Hz), 4.54–4.66 (m, 2H), 5.78 (d, 1H, *J* 2.8 Hz); ^{13}C NMR: δ 26.2, 26.7, 30.0, 31.1, 36.4, 57.0, 65.7, 74.6 (CH_2), 79.6, 81.0, 83.2, 104.5, 112.0, 203.7, 203.9; HRMS [ES, (M + H)$^+$] Calcd. for $C_{15}H_{24}NO_8$ 346.1488, Obsd. 346.1501.

*Compound **9a**:* Following the general procedure, acetylacetone (0.13 g, 1.25 mmol) was reacted with **8a** (0.3 g, 0.78 mmol) in presence of *tert*-BuOK (0.11 g, 0.94 mmol) for 1 h to yield mixture of inseparable diasteromers **9a** (0.33 g, 92%). This mixture was directly taken for next step.

*Compound **9b**:* Following the general procedure, acetylacetone (0.13 g, 1.25 mmol) was reacted with **8b** (0.3 g, 0.78 mmol) in presence of *tert*-BuOK (0.11 g, 0.94 mmol) for 1 h to yield **9b** (0.34 g, 93%); colorless jelly; $[\alpha]_D^{30}$: –88.5 (*c* 1.35, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H), 2.29 (s, 3H), 3.41 (s, 3H), 3.44 (s, 1H), 3.46 (s, 3H), 3.49–3.51 (m, 1H), 3.80 (s, 1H), 3.88 (d, 1H, *J* 4.8 Hz), 4.08–4.15 (m, 1H), 4.26 (d, 1H, *J* 6.0 Hz), 4.39–4.45 (m, 2H), 4.51 (d, 1H, *J* 5.0 Hz), 4.77 (s, 1H), 7.34–7.39 (m, 5H); ^{13}C NMR: δ 29.7, 30.8, 37.1, 56.5, 57.7, 66.3, 71.7 (CH_2), 74.5 (CH_2), 79.8, 79.9, 87.5, 108.5, 128.3, 128.5, 128.6, 128.7, 136.7, 203.4, 203.5; HRMS [ES, (M + Na)$^+$] Calcd. for $C_{20}H_{27}NO_8Na$ 432.1609, Obsd. 432.1634.

*General procedure for the synthesis of **6a**, **10b** and **6b**:* Compounds **5a**, **5b**, **9a** and **9b** were treated with TFA for 2–2.5 h at ambient temperature. After completion of the reaction (TLC), the reaction mixture was poured into satd. aqueous $NaHCO_3$ (30 mL). The reaction mixture was partitioned between aqueous $NaHCO_3$ and EtOAc (3×20 mL). Organic extracts were pooled together, dried over anhydrous Na_2SO_4 and filtered. The filtrate was purified by column chromatography over silica gel to get the pure product.

*Compound **6a**:* Following the general procedure, in 2 h, **5a** (0.25 g, 0.69 mmol) was converted to a solid crystalline **6a** (0.19 g, 82%); interestingly, under similar reaction conditions **9a** was afforded **6a**. m.p. 126°C; $[\alpha]_D^{30}$: +41.2 (*c* 1.65, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 3H), 2.32 (s, 3H), 3.62–3.71 (m, 1H), 3.86–3.93 (m, 2H), 4.50–4.54 (m, 2H), 4.71 (d, 2H, *J* 2.0 Hz), 5.47–5.52 (m, 1H), 6.57 (d, 1H, *J* 2.80 Hz), 7.29–7.36 (m, 5H); ^{13}C NMR: δ 21.0, 25.7, 37.4, 69.3, 73.2 (CH_2), 73.6, 74.8 (CH_2), 127.9, 128.2, 128.7, 137.5, 137.8,

137.9, 170.3, 197.2; HRMS [ES, (M + Na)$^+$] Calcd. for $C_{18}H_{21}NO_7Na$ 386.1185, Obsd. 386.1216.

*Compound **10b.*** Following the general procedure, in 2.5 h, **9b** (0.25 g, 0.80 mmol) was converted to a solid crystalline **10b** (0.20 g, 86%); m.p. 120°C; $[\alpha]_D^{30}$: +67.1 (*c* 0.56, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 3H), 2.39 (s, 3H), 3.46 (s, 3H), 3.48 (s, 1H), 3.71–3.77 (m, 1H), 4.01–4.05 (m, 1H), 4.50 (dd, 1H, *J* 3.4, 13.4 Hz), 4.72–4.84 (m, 3H), 5.37 (dd, 1H, *J* 6.0, 7.2 Hz), 6.85 (s, 1H), 7.28–7.39 (m, 5H); ^{13}C NMR: δ 20.9, 25.8, 38.9, 58.5, 69.7, 74.1 (CH_2), 74.3 (CH_2), 77.9, 78.7, 127.9, 128.0, 128.5, 135.8, 137.7, 140.2, 170.3, 197.8; HRMS [ES, (M + H)$^+$] Calcd. for $C_{19}H_{24}NO_7$ 378.1593, Obsd. 378.1553.

*Compound **6b**:* Following the general procedure, in 2.5 h, **5b** (0.25 g, 0.66 mmol) was converted to a solid crystalline **6b** (0.19 g, 76%); m.p. 105°C; $[\alpha]_D^{30}$: +3.31 (*c* 0.82, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 3H), 2.34 (s, 3H), 3.04 (s, 1H), 3.40–3.45 (m, 1H), 3.54 (s, 3H), 3.84–3.88 (m, 1H), 3.97 (s, 1H), 4.47–4.61 (m, 2H), 5.44 (d, 1H, *J* 7.2 Hz), 6.59 (d, 1H, *J* 2.4 Hz); ^{13}C NMR: δ 21.3, 25.9, 37.3, 60.4, 69.3, 73.4 (CH_2), 73.8, 79.4, 137.9, 138.0, 170.5, 197.4; HRMS [ES, (M + Na)$^+$] Calcd. for $C_{12}H_{17}NO_7Na$ 310.0921, Obsd. 310.0903.

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