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Baylis–Hillman reaction based flexible strategy for the synthesis of gabosine I, gabosine G, *epi*-gabosine I and carba L-pentose

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ABSTRACT

A combination of diastereoselective Baylis–Hillman reaction and RCM reaction set is used as the flexible strategy for the ready access to cyclohexenoid and cyclopentenoid skeletons.

Gabosines belong to a family of unusual, C7 skeleton containing hydroxylated cyclohexenones that may be classified as pseudo or carbasugars since they show structural similarities to carbohydrates and are considered being derived from secondary metabolism (Fig. 1). They were isolated from *Streptomyces* strains[1] and display interesting biological activities such as antibiotic, anticancer, and DNA binding properties. So far three syntheses have been reported for gabosine I **1**. The first total synthesis of gabosine I was achieved by Lubineau and Billault[2] from tetra-*O*-benzyl-D-glucose using intramolecular Nozaki–Hiyama–Kishi reaction. The second synthesis of gabosine I **1** and gabosine G **3** was achieved by Shing[3] using one-pot TPAP oxidation–K_2CO_3-mediated intramolecular Horner–Wadsworth–Emmons (HWE) olefination as the key step. More recently, Shing[4] described yet another synthesis of gabosine I.

RCM has been extensively used for the synthesis of carbasugars.[5a–d] Interestingly, non-RCM based approaches are equally important synthetic strategies for such targets.[5e–h] Herein an alternate way of accessing the requisite RCM precursor via diastereoselective Baylis–Hillman reaction is conceived. Incidentally, Baylis–Hillman reaction offers a multifunctional adducts as products constituting a β-hydroxy acrylate moiety.[6a–c] These BH-adducts, endowed with an olefinic moiety, were earlier transformed by us[6d] into higher-carbon sugars wherein the olefin was assumed to be a masked ketone that was generated through ozonolysis of the adduct. The ketone on subsequent reduction afforded stereochemically diverse hydroxyl groups eventually leading to the corresponding polyols. In order to expand the synthetic horizon of BH-adducts and find newer uses of olefinic functionality, we embarked on a program of using the hydroxyl group either as its acrylate derivative in the metathesis reaction[6e] or involving the olefin directly in the metathesis reaction resulting in diverse products in each case.[6f] Taking this inspiration further, herein we report the total synthesis of gabosine I **1**, *epi*-gabosine I **2**, gabosine G **3**, and carba-L-furanose **4** wherein the highly functionalized Baylis–Hillman adduct **7** was identified as a common intermediate suitable for accessing all the products. Thus the diastereomeric mixture of adduct **7** was conceived as a common substrate for accessing three cyclitols (**1**, **3** and an epimer **2**) besides an important cyclopentitol derivative **4** using the metathesis reaction as the second key reaction.

The diastereoselective Baylis–Hillman reaction of chiral aldehyde derived from threitol **5**, with ethyl acrylate in DMSO as the solvent and DABCO as the base resulted in **7** (85%) as a chromatographically inseparable isomeric mixture. We[7a,b] and other researchers[7c,d] have shown that polar solvents like DMSO, DMF etc., not only help in stabilizing the Zwitterionic intermediate but also enhance the pK_a of the reaction medium and help in faster reaction rates. Of all the bases[8] tested, DABCO was found to be better suited when used in combination with DMSO as solvent. These reaction conditions are suitable for less reactive aldehydes. For a chiral aldehyde the stereochemical outcome could be predicted invoking a Felkin–Ahn model[9] and normally an *anti* product is the major isomer. Since the aldehyde precursor possesses an

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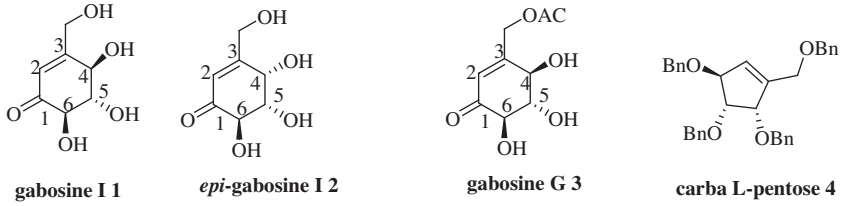
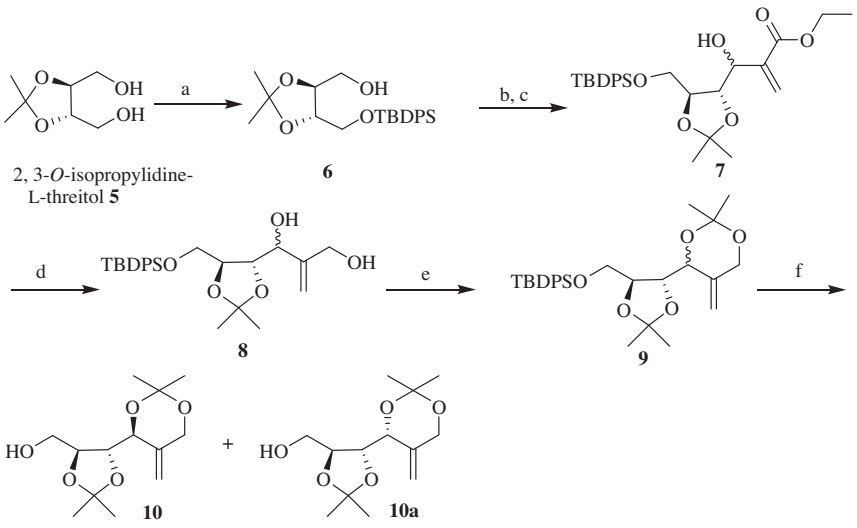
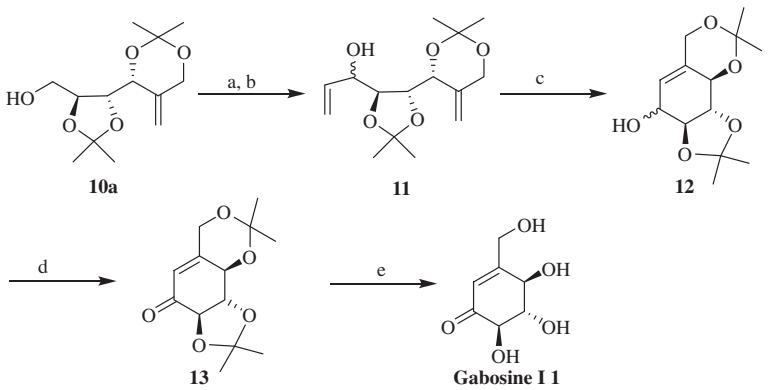


Figure 1. Various cyclitols synthesized.



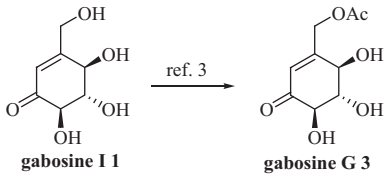
Scheme 1. Reagents and conditions: (a) TBDPS-Cl, imidazole, CH_2Cl_2, 12 h, 79%; (b) $(COCl)_2$, dry DMSO, dry CH_2Cl_2, Et_3N, −78 °C; (c) Ethyl acrylate, DABCO, DMSO, 24 h, 30% de; (d) DIBAL-H,CH_2Cl_2, −20 °C, 3 h, 91%; (e) 2,2-DMP, PTSA, CH_2Cl_2, 0 °C, 12 h, 94%; (f) TBAF, THF, 5 h.



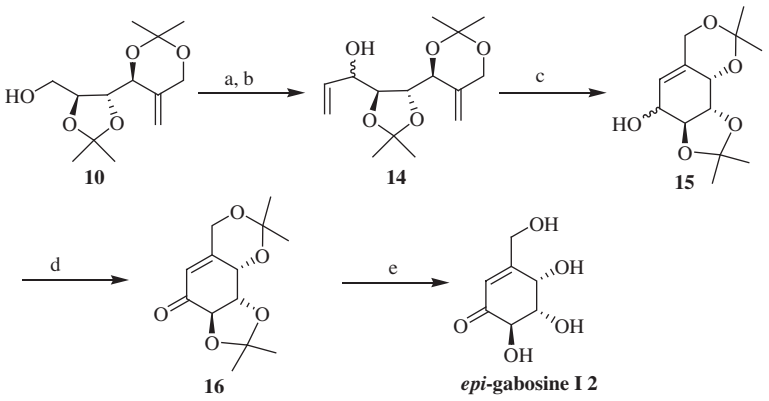
Scheme 2. Reagents and conditions: (a) $(COCl)_2$, dry DMSO, dry CH_2Cl_2, Et_3N, −78 °C; (b) vinylMgBr, THF, −20 °C, 0.33 h, 87%; (c) G-II catalyst, toluene, reflux, 5 h, 83%; (d) DMP, CH_2Cl_2, 0 °C, 2 h, 96%; (e) TFA, CH_2Cl_2, 0 °C, 2 h.

adjacent stereogenic carbon, the newly created center bears an *anti*-relationship (major isomer) to the existing one. Thus the newly created stereogenic center of the major isomer in **7** was assigned as '*S*' and the minor isomer as '*R*' based on our previous observation.[10] The major isomer on further transformations afforded bis-olefin which on ring-closing metathesis (RCM) followed by oxidation and deprotection gave *epi*-gabosine I **2**. The same set of reactions when applied for minor isomer gave gabosine I **1** (Scheme 2). The chirality could be enriched or reversed by adopting the '*double asymmetric induction*' protocol.[10] However, herein we proceeded with the isomeric mixture (**7**) since two targets could be obtained.

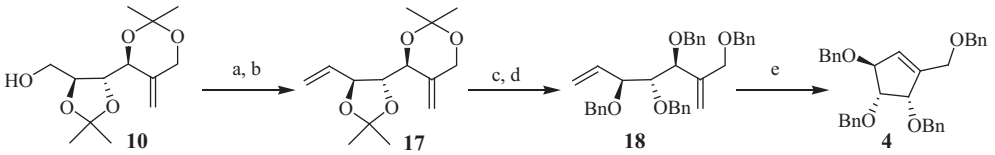
Accordingly, selective TBDPS protection of 2,3-*O*-isopropylidine-L-threitol **5** (TBDPS-Cl/imidazole/CH_2Cl_2) gave the mono silylated 2,3-*O*-isopropylidine-L-threitol **6** (79%, Scheme 1). Primary alcohol **6** on oxidation under Swern conditions furnished the corresponding aldehyde (96%), Baylis–Hillman reaction of



Scheme 3. Gabosine I can be converted to gabosine G using known procedure.



Scheme 4. Reagents and conditions: (a) $(COCl)_2$, dry DMSO, dry CH_2Cl_2, Et_3N, −78 °C; (b) vinylMgBr, THF, −20 °C, 0.2 h, 87%; (c) G-II catalyst, toluene, reflux, 5 h, 83%; (d) DMP, CH_2Cl_2, 0 °C, 2 h, 96%; (e) TFA, CH_2Cl_2, 0 °C, 2 h.



Scheme 5. Reagents and conditions: (a) $(COCl)_2$, dry DMSO, dry CH_2Cl_2, Et_3N, −78 °C; (b) CH_3^+ PPh_3I^-, KO^{t}Bu, THF, 0 °C, 8 h; (c) TFA, CH_2Cl_2, 0 °C, 2 h; (d) NaH, Bn–Br, THF, 12 h, 0 °C; (e) HG-II catalyst, toluene, reflux, 5 h, 86%.

aldehyde and ethyl acrylate in the presence of DABCO in DMSO at room temperature gave BH-adduct **7** (85%, 30% de) as an inseparable mixture of compounds. The de was evaluated using ^{1}H NMR wherein the differential integral values of olefinic protons appearing at δ 6.30 ppm (s, 0.35H) and at δ 6.27 ppm (s, 0.65H) gave the ratio of isomers, while the absolute stereochemistry of major isomer was assigned as '*S*' based on our previous observation.[10] Next, reduction of the ester group in **7** {DIBAL-H/CH_2Cl_2/−20 °C/3 h} furnished the allyl alcohol **8** (91%). The ensuing 1,3 diol moiety in **8** was protected as its acetonide (2,2-DMP/PTSA/CH_2Cl_2) to afford **9** (94%). TBDPS deprotection of **9** with TBAF afforded two separable isomers **10** and **10a** (57.8% and 31.2% respectively, overall 89%). The two isomers on further transformations independently, gave gabosine I and *epi*-gabosine I.

Initially, the minor isomer **10a** was taken up for the rest of the synthetic sequence (Scheme 2). Accordingly, the primary alcohol of **10a** on oxidation under Swern conditions followed by vinylation {vinylMgBr/THF/−20 °C/0.33 h} afforded the allyl alcohol **11** (87%, Scheme 2) as a 1:1 mixture. No effort was made to separate the isomers since the carbon bearing the newly created hydroxyl group later manifests into a ketone functionality. The bis-olefin on ring-closing metathesis[11] (Grubbs II catalyst/toluene/110 °C) afforded substituted cyclohexene derivative **12** (83%). Subsequently, **12** on oxidation[12] {DMP/CH_2Cl_2/0 °C} furnished diacetonide **13** (89%). Finally acetonide deprotection {TFA in CH_2Cl_2/0 °C} gave gabosine I **1** (95%). Compound **1** was characterized from its spectral data. Thus, ^{1}H NMR spectrum revealed the lone olefinic proton appeared at δ 6.15 ppm as a doublet (J = 1.8 Hz), the allylic proton appeared at δ 4.95 ppm as a doublet (J = 4.5 Hz) and the characteristic methine next to ketone functionality resonated at δ 4.33 as a doublet (J = 13.5 Hz). Thus the physical and spectroscopic data of synthetic **1** are consistent with the reported values.[2,3] Literature inspired[3] conversion of **1** gave **3** (Scheme 3).

Similarly, the major adduct **10** on oxidation under Swern conditions followed by vinylation (vinylMgBr/THF/−20 °C/20 min) afforded the allyl alcohol **14** (87%) as a 1:1 isomeric mixture (Scheme 4). Here too no efforts were made to separate the isomers because of its transformation into a ketone functionality. The bis-olefin on Grubbs catalyst assisted[11] ring-closing metathesis (Grubbs II catalyst/toluene/110 °C) afforded cyclohexene ring **15** (83%). Compound **15** on oxidation (DMP/CH_2Cl_2/0 °C) gave the diacetonide derivative **16** (96%). Finally, acetonide deprotection (TFA in CH_2Cl_2/0 °C) furnished *epi*-gabosine I **2** (95%). Compound **2** was thoroughly characterized from its spectral data. HRMS spectrum of **2** displayed the $[M+Na]^+$ at 197.0435, calculated gave 197.0425 for the molecular formula $C_7H_{10}O_5Na$ as an additional support.

Alternative use of **10** was envisioned (Scheme 5). Accordingly, primary alcohol **10** on Swern oxidation followed by Wittig olefination ($CH_3^+PPh_3I^-$/KO^{t}Bu/THF/0 °C/8 h) afforded the bis-olefin **17** (81%), deprotection of acetonide group (TFA/CH_2Cl_2/0 °C) gave tetrol that was protected as its benzyl ether (BnBr/NaH/THF/0 °C) to furnish the tetra benzyl protected bis-olefin **18** (73% over two steps). Hoveyda–Grubbs catalyzed ring-closing metathesis[13] (HG-II/toluene/reflux/5 h) of bis-olefin **18** afforded the carba-L-sugar **4** (86%). Interestingly **4** constitute an important synthetic precursor to access carbanucleosides and the strategy disclosed herein offers its practical approach.[14] Thus a rare and non-natural carba-L-sugar was synthesized herein.

In conclusion, we demonstrated the synthesis of gabosine I, *epi*-gabosine I and gabosine G from the common intermediate derived from diastereoselective Baylis–Hillman reaction.[15] Alongside, the synthesis of cyclopentenoid derivative, accessed through this protocol demonstrated the versatility and generality of the strategy.[15] The protocol described herein is general and amenable for the synthesis of similar cylcitols.

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References and notes

1. Bach, G.; Breiding-Mack, S.; Grabley, S.; Hammann, P.; Hutter, K.; Thiericker, R.; Uhr, H.; Wink, J.; Zeeck, A. *Liebigs Ann. Chem.* **1993**, *3*, 241–250.
2. Lubineau, A.; Billault, I. *J. Org. Chem.* **1998**, *63*, 5668–5671.

3. Shing, T. K. M.; Cheng, H. M. *J. Org. Chem.* **2007**, *72*, 6610–6613.
4. Shing, T. K. M.; Chen, Y.; Ng, W. L. *Synlett* **2011**, 1318–1320.
5. (a) Callam, C. S.; Lowory, T. L. *Org. Lett.* **2000**, *2*, 167–169; (b) Callam, C. S.; Lowory, T. L. *J. Org. Chem.* **2001**, *66*, 8961–8972; (c) Banerjee, S.; Nayyek, A.; Sinha, S.; Bhoumik, T.; Ghosh, S. *J. Mol. Catal. A: Chem.* **2006**, *254*, 85–92; (d) Yang, Y.-X.; Li, Z.; Feng, H.-J.; Chen, G.-R.; Li, Y.-C. *Tetrahedron Lett.* **2010**, *51*, 3848–3851; (e) Carpintero, M.; Mayoralas, A. F.; Jaramillo, C. *J. Org. Chem.* **1997**, *62*, 1916–1917; (f) Mehta, G.; Mohal, N. *Tetrahedron Lett.* **1998**, *39*, 3285–3286; (g) Mehta, G.; Talukdar, P.; Mohal, N. *Tetrahedron Lett.* **2001**, *42*, 7663–7666; (h) Boyd, D. R.; Sharma, N. D.; Acarc, C. A.; Malone, J. F.; O'dowd, C. R.; Allen, C. C. R.; Stevenson, P. J. *Org. Lett.* **2010**, *12*, 2206–2209.
6. (a) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811–892; (b) Radha Krishna, P.; Rachna, S.; Reddy, P. S. *Synlett* **2008**, 2897–2912; (c) Basavaiah, D.; Reddy, B. S.; Badsara, S. S. *Chem. Rev* **2010**, *110*, 5447–5674; (d) Radha Krishna, P.; Reddy, P. V. N.; Shreeshailam, A.; Uday Kiran, M.; Jagdeesh, B. *Tetrahedron Lett.* **2007**, *48*, 6466–6470; (e) Radha Krishna, P.; Narasingam, M.; Kannan, V. *Tetrahedron Lett.* **2004**, *45*, 4773–4775; (f) Radha Krishna, P.; Narasingam, M. *J. Comb. Chem.* **2007**, *9*, 62–69.
7. (a) Radha Krsihna, P.; Manjuvani, A.; Kannan, V.; Sharma, G. V. M. *Tetrahedron Lett.* **2004**, *45*, 1183–1185; (b) Radha Krsihna, P.; Manjuvani, A.; Raja Sekhar, E. *ARKIVOC* **2005**, *iii*, 99–109; (c) Yu, C. Z.; Liu, B.; Hu, L. Q. *J. Org. Chem.* **2001**, *66*, 5413–5418; (d) Price, K. E.; Broadwater, S. J.; Jung, H. M.; McQuade, D. T. *Org. Lett.* **2005**, *7*, 147–150.
8. (a) Iwabuchi, Y.; Nakatani, M.; Yokoyama, N.; Hatakeyama, S. *J. Am. Chem. Soc.* **1999**, *121*, 10219–10220; (b) Aggarwal, V. K.; Dean, D. K.; Mereu, A.; Williams, R. *J. Org. Chem.* **2002**, *67*, 510–514; (c) Faltin, C.; Fleming, E. M.; Connon, S. J. *J. Org. Chem.* **2004**, *69*, 6496–6599; (d) Radha Krishna, P.; Raja Sekhar, E.; Kannan, V. *Synthesis* **2004**, 857–860; (e) Radha Krishna, P.; Kannan, V.; Narasimha Reddy, P. V. *Adv. Synth. Cat.* **2004**, *346*, 603–606.
9. Roush, W. R.; Adam, M.; Walts, A. E.; Harris, D. *J. Am. Chem. Soc.* **1986**, *108*, 3422–3434.
10. Radha Krishna, P.; Sachwani, R.; Kannan, V. *Chem. Commun.* **2004**, 2580–2581.
11. Schol, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956.
12. Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155–4156.
13. Radha Krishna, P.; Kadiyala, R. R. *Tetrahedron Lett.* **2010**, *51*, 4981–4983.
14. (a) Gillaizeau, I.; Charamon, S.; Agrofogli, L. A. *Tetrahedron Lett.* **2001**, *42*, 8817–8819; (b) Yoshida, N.; Kamikubo, T.; Ogasawara, K. *Tetrahedron Lett.* **1998**, *39*, 4677–4678; (c) Ono, M.; Nishimura, K.; Tsubouchi, H.; Nagaoka, Y.; Tomioka, K. *J. Org. Chem.* **2001**, *66*, 8199–8203.
15. *Spectral data for selected compounds*: **Compound 10**: Pale yellow syrup. $[\alpha]_D^{25}$ +34.6 (*c* 0.8, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 5.23 (s, 1H), 5.02 (s, 1H), 4.35–4.32 (m, 2H), 4.23 (d, 1H, *J* = 13.3 Hz), 4.12–4.07 (m, 1H), 3.94–4.00 (m, 1H), 3.82–3.78 (dd, 1H, *J* = 11.4, 4.4 Hz), 3.75–3.66 (m, 1H), 1.42 (d, 6H, *J* = 4.4 Hz), 1.37 (d, 6H, *J* = 9.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.1, 110.0, 109.4, 80.3, 77.8, 72.5, 66.3, 63.4, 29.4, 27.4; ESIMS: 281 $(M+Na)^+$, HRMS *m*/*z*: Calcd for $C_{13}H_{22}O_5Na$: 281.1364, Found: 281.1368. **Compound 10a**: Pale yellow syrup. $[\alpha]_D^{25}$ −66.9 (*c* 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ; 5.13 (s, 1H), 5.02 (s, 1H), 4.50 (br s, 1H), 4.33 (d, 1H, *J* = 12.1 Hz) 4.23–4.14 (m, 3H), 3.81 (d, 1H, *J* = 11.5 Hz), 3.67 (m, 1H), 1.43–1.35 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.2, 109.5, 109.1, 99.9, 77.8, 76.5, 69.1, 64.4, 62.4, 27.1, 26.6; ESIMS: 281 $(M+Na)^+$, HRMS *m*/*z*: Calcd for $C_{13}H_{22}O_5Na$: 281.1365, Found: 281.1367. **Compound 13**: Colorless syrup $[\alpha]_D^{25}$ −33.1 (*c* 0.44, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 5.83 (s, 1H), 4.80 (d, 1H, *J* = 8.0 Hz), 4.60–4.44 (2d, 2H), 4.16 (d, 1H, *J* = 10.6 Hz), 3.99 (dd, 1H, *J* = 10.2, 8.4 Hz), 1.59 (s, 3H), 1.51 (s, 6H), 1.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.2, 156.7, 121.5, 112.3, 102.9, 76.4, 74.7, 65.3, 64.6, 28.5, 26.4, 22.8 cm^{-1}. ESIMS: *m*/*z* 277 $(M+Na)^+$. Anal. Calcd for $C_{13}H_{18}O_5$ (254.115): C, 61.40; H, 7.14. Found: C, 61.22, H, 6.98. **Compound 1**: Solid mp 99–101 °C. $[\alpha]_D^{25}$ −57.5 (*c* 0.3, MeOH). ^1H NMR (300 MHz, CD_3OD): δ 6.15 (d, 1H, *J* = 1.8 Hz), 4.51 (d, 1H, *J* = 18.5 Hz, H-4), 4.39–4.29 (m, 2H, H-5), 4.03 (d, 1H, *J* = 10.5 Hz, H-6), 3.58 (dd, 1H, *J* = 10.5, 8.6 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.5, 168.1, 121.3, 79.5, 78.1, 73.7, 62.1. IR (neat): 3435, 1742, 1621 cm^{-1}. HRMS *m*/*z*: Calcd for: $C_7H_{10}O_5Na$: 197.0425. Found: 197.0429. **Compound 16**: Colorless syrup. $[\alpha]_D^{25}$ +33.1 (*c* 0.44, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 5.86 (d, 1H, *J* = 1.5 Hz), 4.95 (d, 1H, *J* = 4.5 Hz), 4.70–4.62 (m, 2H), 4.33 (d, 1H, *J* = 13.5 Hz), 3.95 (dd, 1H, *J* = 10.5, 5.2 Hz), 1.64 (s, 3H), 1.51 (d, 6H, *J* = 3.0 Hz), 1.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.7, 152.7, 121.6, 112.7, 101.9, 74.7, 65.3, 64.6, 60.4, 29.6, 27.7, 26.4, 21.7. IR (neat): 1735, 1620 cm^{-1}. ESIMS: *m*/*z* 277 $(M+Na)^+$. Anal. Calcd for $C_{13}H_{18}O_5$ (254.115): C, 61.40; H, 7.14. Found: C, 60.87, H, 7.33. **Compound 2**: Solid mp 118–119 °C. $[\alpha]_D^{25}$ +76.5 (*c* 0.5, MeOH); ^1H NMR (300 MHz, CD_3OD): δ 6.12 (s, 1H), 4.41 (d, 1H, *J* = 18 Hz, H-4), 4.34 (d, 1H, *J* = 10.2 Hz, H-6), 4.27–4.23 (m, 2H, H-5), 3.70 (dd, 1H, *J* = 10.2, 3.8 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.1, 164.2, 122.9, 74.8, 74.2, 68.2, 63.3. IR(neat): 3435, 1742, 1621 cm^{-1}. HRMS *m*/*z*: Calcd for: $C_7H_{10}O_5Na$: 197.0425. Found: 197.0435. **Compound 17**: Colorless syrup. $[\alpha]_D^{25}$ +31.9 (*c* 0.8, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 5.81–5.95 (m, 1H), 5.28–5.39 (m, 1H), 5.12 (br s, 2H), 4.92 (s, 1H), 4.46–4.32 (m, 1H), 4.22 (br s, 1H), 4.13–4.03 (m, 1H), 3.92–3.90 (s, 1H), 3.61–3.55 (m, 1H), 1.48–1.32 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.0, 136.6, 135.6, 118.8, 109.4, 108.17, 80.5, 77.8, 68.9, 64.25, 27.1, 26.3. ESIMS: *m*/*z* 277 $(M+Na)^+$. Anal. Calcd for $C_{14}H_{22}O_4$ (254.150): C, 66.12; H, 8.72. Found: C, 65.96, H, 8.34. **Compound 4**: Colorless syrup. $[\alpha]_D^{25}$+80.5 (*c* 0.65, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.35–7.11 (m, 20H), 5.99 (s, 1H), 4.83–4.76 (m, 1H), 4.72–4.55 (m, 7H), 4.49 (d, 2H, *J* = 12.0 Hz), 4.15–4.05 (m, 2H), 4.02 (t, 1H, *J* = 5.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.3, 138.5, 138.4, 138.3, 138.1, 130.3, 128.5, 128.4, 128.3, 128.0, 128.1, 127.8, 127.7, 127.7, 127.6, 86.4, 84.4, 72.7, 72.3, 71.9, 71.5, 67.2. ESIMS: *m*/*z* 529 $(M+Na)^+$. Anal. Calcd for $C_{13}H_{34}O_4$ (506.245): C, 80.60; H, 6.76. Found: C, 80.42, H. 6.23.